

# Supporting Information

## Bio-supported palladium nanoparticles as phosphine-free catalyst for Suzuki reaction in water

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## Experimental

Unless stated otherwise, all operations were performed in air with no special considerations. All chemicals and solvents were purchased from Sigma-Aldrich, and used as received.

Pd/BC nanocomposites were synthesized in the lab by following the protocol as below. The two-step preparation protocol involves a first biosynthesis of BC nanofibers (J. Z. Yang, J. W. Yu, J. Fan, D. P. Sun, W. H. Tang, X. J. Yang, *J. Hazard. Mater.*, 2011, **189**, 377) and a followed hydrothermal reaction. With the purified BC nanofibers (water content 98.4%) at hand, a typical hydrothermal reaction proceeded as follows: immersing PdCl<sub>2</sub> or Pd(NO<sub>3</sub>)<sub>2</sub> (containing 0.1 g Pd) and freshly-prepared BC nanofibers (3 g) into 50 mL DI water; degassing for 0.5 h before heating up to 140°C with vigorous stirring (1200 rpm) under N<sub>2</sub> atmosphere; adding potassium borohydride (2 g in 50 mL water) over 5 h; centrifuging and washing with water to obtain the *titled* composites.

### Instrumentation

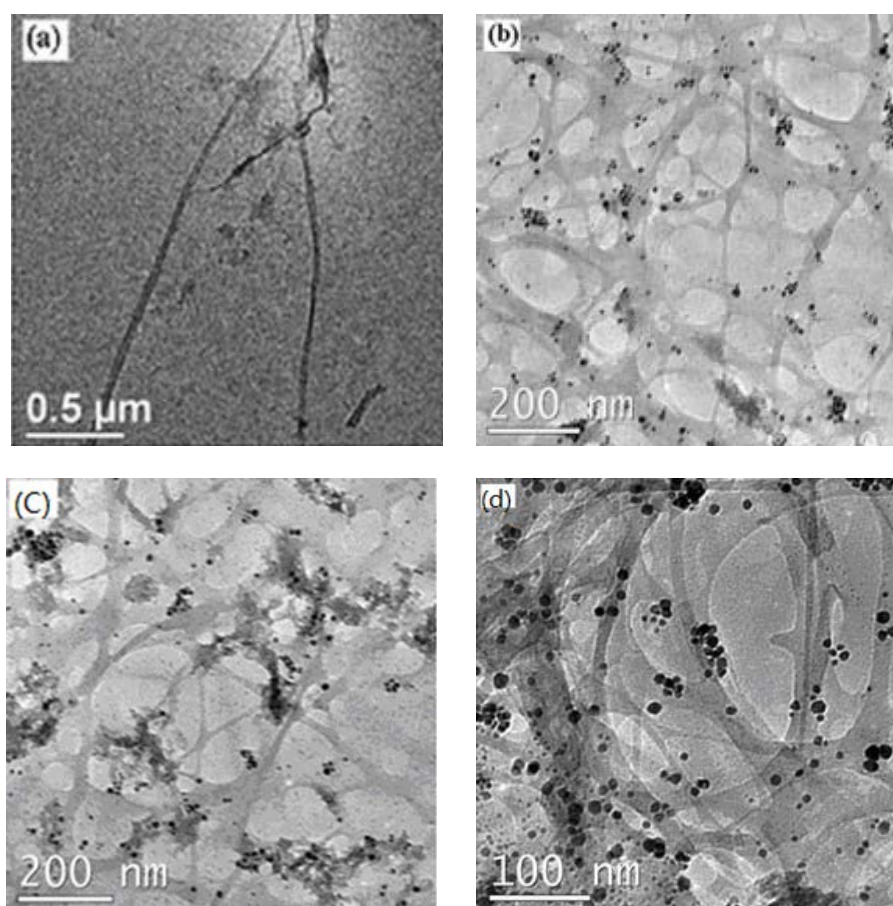
<sup>1</sup>H NMR spectra were recorded on Bruker AVANCE 500 MHz (Bio-Spin Corporation, Europe) spectrometer at room temperature in CDCl<sub>3</sub> unless otherwise specified. Chemical shifts are reported with respect to internal solvent, 7.26 ppm (<sup>1</sup>H, CDCl<sub>3</sub>). The morphology of pristine BC and Pd/BC hybrid nanofibers was investigated by means of TEM (JEM-2100). The crystallinity and the phase composition of samples were characterized by XRD (Bruker D8 ADVANCE). FT-IR spectra were obtained using a Bomem MB154S Fourier transform infrared (FTIR) spectroscopy. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI-5300 X-ray photoelectron spectrometer with an Mg K $\alpha$  excitation source (1253.6 eV). Thermogravimetric analyses (TGA) were performed on a Boyuan DTU-2C thermogravimetric analyzer from 50 to 800°C at a heating rate of 10°C/min<sup>-1</sup> in nitrogen flow.

Specific surface area of samples were obtained by BET method using BET instrument (NOVA 1000, Quanta Chrome, America).

Elemental analyses of Pd/BC catalyst before as well as after 5-cycle reactions were performed on a Perkin Elmer Optima 3300 DV ICP-AES. 5 mg of each sample was dissolved in 2.5 mL of concentrated aqua regia and the volume was adjusted to 50 mL in a volumetric flask. This solution was then used for the elemental analysis.

### ***TEM images and analysis of Pd/BC nanocomposites***

The TEM images of pristine BC nanofibers and the BC nanofiber-supported palladium nanoparticles during different hydrothermal reaction time are presented in Figure S1.



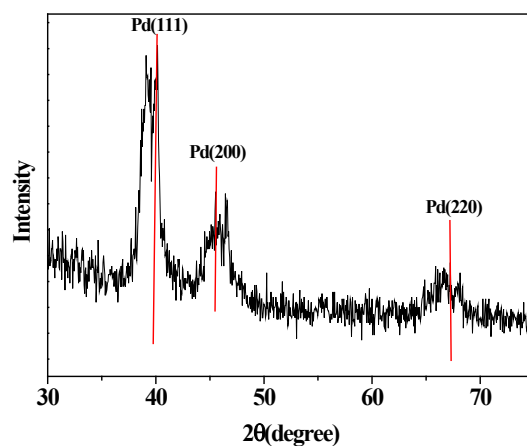
**Figure S1.** TEM images of pristine BC nanofibers (a); and catalyst after hydrothermal reaction for 1 h (b), 2 h (c), 3 h (d) during palladium growth.

The TEM image of Figure S1a shows the TEM image of BC nanofibers biosynthesized by *Acetobacter xylinum* NUST5.2, with an average diameter of about 30 nm and a length ranging from micrometers up to dozens of micrometers. TEM images of final product are shown in Figure 1d, where the deposited Pd nanocrystals

were well-dispersed on BC nanofibers with ~12 nm diameter. TEM images of the growth of Pd nanoparticles on BC nanofibers during hydrothermal reaction for 1 h, 2 h and 3 h are shown in Figure 1b, 1c and 1d, respectively. As shown in Figure 1b, the deposited Pd nanocrystals were well-dispersed on BC surface with about 20 nm diameter. The Pd obtained after 2 h reduction reaction exhibited same particle size, but the number of Pd nanocrystals witnessed a slight increase (Fig. 1c). For prolonged reaction duration (3 h), the number of Pd nanoparticles achieved a significantly increase and the diameter of Pd nanoparticles was still about 20 nm (Fig. 1d).

### *XRD analysis*

The crystallographic behavior of the deposited Pd nanoparticles was further investigated by X-ray diffraction (XRD). From the XRD spectra shown in Figure S2, broad peaks are observed at  $2\theta$  values of  $40.21^\circ$ ,  $47.05^\circ$ , and  $67.81^\circ$ , which are characteristic peaks for Pd and can be assigned to the crystallographic plane of (111), (200) and (220) reflection of Pd. All of the diffraction peaks match well with those of the perfect fcc Pd crystal structure. No extra peaks are detected in this pattern, indicating clean Pd/BC composites achieved without any impurities.

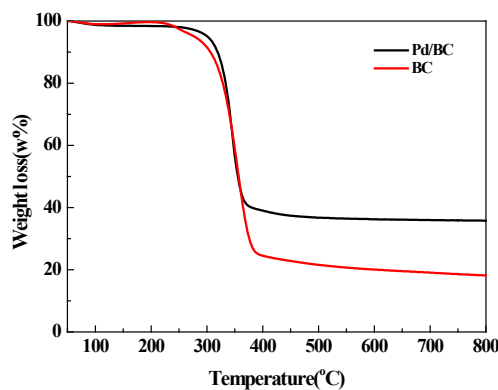


**Figure S2.** X-ray diffraction (XRD) patterns of Pd/BC catalyst.

### *TGA analysis*

Suzuki coupling usually requires heating conditions; hence, the thermal properties of the catalyst have a great impact for its catalytic activity and recyclability. The

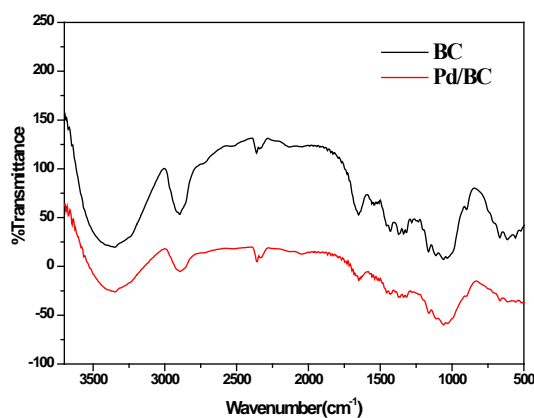
thermal stability of the pristine BC fibers and Pd/BC hybrid nanofibers was evaluated by thermogravimetric analysis (TGA) in nitrogen flow (Fig. S3). It is apparent that Pd/BC hybrid nanofibers exhibited the similar thermal stabilities as BC nanofibers, as weight loss less than 5% on heating to 300°C. Upon continuous heating up to 600°C, pure BC degrades completely, leaving only minute amounts, while 40% of the sample still remains in Pd/BC.



**Figure S3.** TGA traces of BC nanofibres and Pd/BC catalyst recorded at a heating rate of 10°C/min under nitrogen flow.

#### *Fourier infrared spectroscopic analysis (FTIR)*

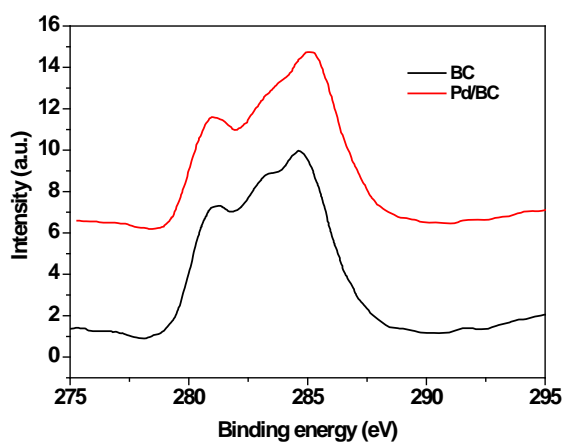
As observed from the FTIR spectra of pristine BC fibers and Pd/BC nanocomposites, we can find that no change occurred between two spectra. It indicated that Pd was deposited on the surface of BC fibers without chemical bonding and thus Pd did not change the original structure of BC fibers.



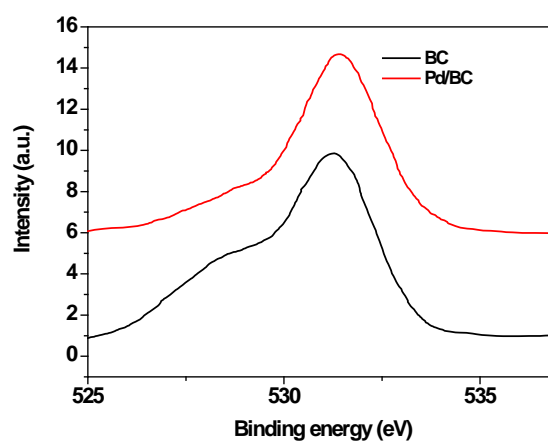
**Figure S4.** FTIR of BC nanofibers and Pd/BC catalyst.

### XPS analysis

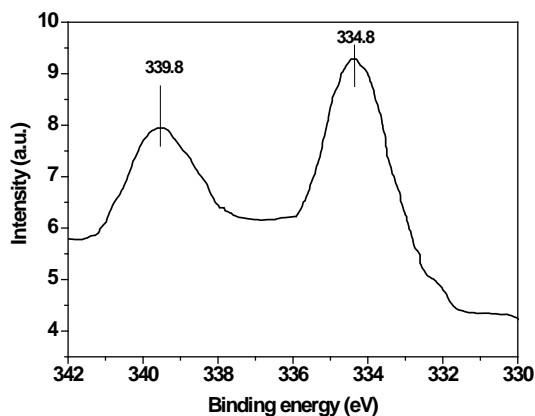
Further evidence of the high crystal quality was obtained with X-ray photoelectron spectroscopy (XPS). Figure S5 (a) and (b) showed the loaded Pd nanoparticles did not change the valence state of C and O of BC fibers, indicating that Pd was deposited on the surface of the BC nanofibers without chemical bonding. The Pd 3d spectra, characterized by spin-orbit splitting (Pd 3d<sub>5/2</sub> and Pd 3d<sub>3/2</sub> components), shows values of 334.8 and 339.8 eV, respectively. Both peaks originating from Pd agree well with the binding energies for Pd<sup>0</sup> (3d<sub>5/2</sub> 334.9 eV, 3d<sub>3/2</sub> 340.4 eV) state (D. Klemm, B. Heublein, H. P. Fink, A. Bohn, *Angew. Chem. Int. Ed.*, **2005**, *44*, 3358).



(a)



(b)



(c)

**Figure S5.** XPS analysis of the BC nanofibres and Pd/BCF catalyst: (a) the XPS analysis of C; (b) the XPS analysis of O; (c) the XPS analysis of Pd.

**General protocol for the Suzuki coupling with different arylboronic acids.** Aryl halide (1.2 equiv), arylboronic acid (1.2 equiv), base (2 equiv) and solvent (15 mL) were added to a 50 mL round bottom flask. The solution was stirred in a heated oil bath at 85°C. Pd/BC (0.05 mol%) was added into the stirring solution and the system capped with a glass septum and allowed to react for 3.5 h. or for the time indicated. The reaction mixture was cooled to room temperature prior to filtration. The Pd/BC nanocomposites were washed with ethyl acetate (3×30 mL) and then deionized water for recycling. The collected filtrate was extracted with ethyl acetate and washed with water. After drying the extract with anhydrous MgSO<sub>4</sub>, the organic solvent was removed by evaporation. The crude product was recrystallized with petroleum ether.

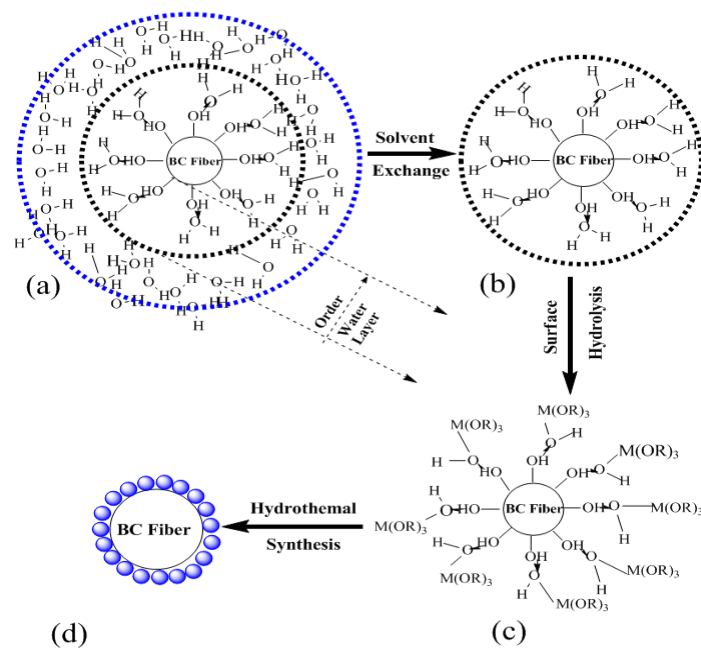
#### **Recyclability and Pd-leaching study:**

For practical applications of heterogeneous systems, the lifetime of the catalyst and its level of reusability are very important factors. To clarify this issue, we established a set of experiments for the coupling of iodobenzene with varied arylboronic acid (all entries in Table 2) using the recycled Pd/BC catalyst. After the completion of the first reaction to afford the corresponding biphenyl, the catalyst was filtered out, washed with ethyl acetate, and transferred to the reaction flask for the second-cycle reaction. A new reaction was then performed with fresh reactants under the same conditions. The Pd/BC catalyst could be used at least 5 times without any change in activity.

Pd leaching was studied by ICP-AES analysis of the catalyst before and after the five reaction cycles. The Pd concentration was found to be 5.29% before reaction and 5.26% after the reaction, which confirmed negligible Pd leaching; this is probably due to the protection from the order bound water molecules covering around BC fibers via H-bonding (Scheme S1). Also, no Pd metal was detected in the final coupling product.

Scheme S1 illustrates the entire procedure of the fabrication of Pd/BC. At the beginning, when BC was added into the PdCl<sub>2</sub> solution, the Pd<sup>2+</sup> coordinate with two adjacent C2 and C3-hydroxyl groups in the same glucose units along the BC backbone. Subsequently, when potassium borohydride solution was added into the

colloidal mixture, the  $\text{Pd}^{2+}$  was reduced to Pd. The as-prepared Pd nanoparticles were stabilized on the BC surface via coordination effect between Pd and hydroxyl groups of BC. This growth mechanism is in good agreement with the above-presented TEM photographs.



**Scheme S1.** Schematic preparation of Pd/BC catalyst.

**Coupling with palladium prepared from  $\text{Pd}(\text{NO}_3)_2$ :** iodobenzene (1.2 g, 6 mmol, 1.2 eq), phenylboronic acid (0.61 g, 5 mmol, 1 eq),  $\text{K}_2\text{CO}_3$  (1.38 g, 10 mmol, 2 eq),  $\text{H}_2\text{O}$  (15 mL), Pd/BC (0.5 g, 0.05 mol% vs phenylboronic acid), final product as a pale yellow solid (0.749 g, 97%). The catalyst was recycled to repeat the reaction twice. Yield of cycle 2 - 96%, yield of cycle 3 - 94%.

**Coupling with palladium prepared from  $\text{PdCl}_2$ :** iodobenzene (1.2 g, 6 mmol, 1.2 eq), phenylboronic acid (0.61 g, 5 mmol, 1 eq),  $\text{K}_2\text{CO}_3$  (1.38 g, 10 mmol, 2 eq),  $\text{H}_2\text{O}$  (15 mL), Pd/BC (0.5 g, 0.05 mol% vs phenylboronic acid), final product (0.755 g, 98%). The catalyst was recycled to repeat the reaction twice. Yield of cycle 2 - 97%, yield of cycle 3 - 96%.

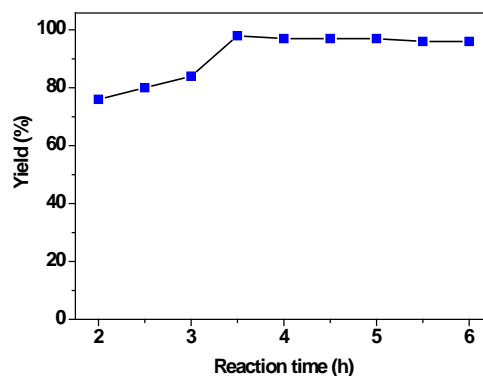
**Coupling in water:** iodobenzene (1.2 g, 6 mmol, 1.2 eq), phenylboronic acid (0.61 g, 5 mmol, 1 eq) and  $\text{K}_2\text{CO}_3$  (1.38 g, 10 mmol, 2 eq) were added to a RB flask with DI  $\text{H}_2\text{O}$  (15ml), the flask was placed in an oil bath until the temperature reached  $85^\circ\text{C}$



and the solution stirred until the base was completely dissolved. Pd/BC (0.5 g, 0.05 mol% vs phenylboronic acid) was added to the stirring solution and the system capped with a glass septum and allowed to react for 3.5 h. The reaction mixture was cooled to room temperature prior to filtration. The Pd/BC nanocomposites were washed with ethyl acetate and then deionized water for recycling. The collected filtrate was extracted with ethyl acetate and washed with water. After drying the extract with anhydrous MgSO<sub>4</sub>, the organic solvent was removed by evaporation. The crude product was recrystallized with petroleum ether to give diphenyl as a pale yellow solid (0.749 g, 97%). The catalyst was recycled to repeat the reaction twice. Yield of cycle 2 - 96%, yield of cycle 3 - 94%.

**Coupling in DMF with organic base:** iodobenzene (1.2 g, 6 mmol, 1.2 eq), phenylboronic acid (0.61 g, 5 mmol, 1 eq) and triethylamine (1.45 mL, 10 mmol, 2 eq) were added to a RB flask with DMF (15 mL). The flask was placed in an oil bath until the temperature reached 85°C and the solution stirred until the base was completely dissolved. Pd/BC (0.5 g, 0.05 mol% vs phenylboronic acid) was added to the stirring solution and the system capped with a glass septum and allowed to react for 3.5 h. The Pd/BC nanocomposites were washed with ethyl acetate and then deionized water for recycling. The collected filtrate was extracted with ethyl acetate and washed with water. After drying the extract with anhydrous MgSO<sub>4</sub>, the organic solvent was removed by evaporation. The crude product was recrystallized with petroleum ether to offer diphenyl as a pale yellow solid (0.598 g, 78%). The catalyst was recycled to repeat the reaction twice. Yield of cycle 2 - 76%, yield of cycle 3 - 73%.

**Scheme S2.** Pd/BC for cross-coupling reactions in different reaction media.



**Figure S5.** Yield varying with reaction time for aqueous coupling in Scheme S2.

### Suzuki coupling reaction of iodobenzene series

**Biphenyl:** iodobenzene (1.2 g, 6 mmol, 1.2 eq), phenylboronic acid (0.61 g, 5 mmol, 1 eq),  $K_2CO_3$  (1.38 g, 10 mmol, 2 eq),  $H_2O$  (15 mL), Pd/BC (0.5 g, 0.05 mol% vs phenylboronic acid), final product (0.755 g, 98%). The catalyst was recycled to repeat the reaction four times. Yield of cycle 2 - 97%, yield of cycle 3 - 96%, yield of cycle 4 - 92%, yield of cycle 5 - 88%.

**4-Methylbiphenyl:** iodobenzene (1.2 g, 6 mmol, 1.2 eq), *p*-tolylboronic acid (0.68 g, 5 mmol, 1 eq),  $K_2CO_3$  (1.38 g, 10 mmol, 2 eq),  $H_2O$  (15 mL), Pd/BC (0.5 g, 0.05 mol% vs *p*-tolylboronic acid), final product (0.773 g, 92%). The catalyst was recycled to repeat the reaction four times. Yield of cycle 2 - 91%, yield of cycle 3 - 89%, yield of cycle 4 - 87%, yield of cycle 5 - 86%.

**Biphenyl-4-carbaldehyde:** iodobenzene (1.2 g, 6 mmol, 1.2 eq), 4-formylphenylboronic acid (0.75 g, 5 mmol, 1 eq),  $K_2CO_3$  (1.38 g, 10 mmol, 2 eq),  $H_2O$  (15mL), Pd/BC (0.5g, 0.05mol% vs 4-formylphenylboronic acid), final product (0.891 g, 95%). The catalyst was recycled to repeat the reaction four times. Yield of cycle 2 - 92%, yield of cycle 3 - 90%, yield of cycle 4 - 89%, yield of cycle 5 - 88%.

**Biphenyl-4-carbonitrile:** iodobenzene (1.2 g, 6 mmol, 1.2 eq), 4-cyanophenylboronic acid (0.74 g, 5 mmol, 1 eq),  $K_2CO_3$  (1.38 g, 10 mol, 2 eq)  $H_2O$  (15 mL), Pd/BC (0.5 g, 0.05 mol% vs 4-cyanophenylboronic acid), final product (0.788 g, 88%). The catalyst was recycled to repeat the reaction four times. Yield of cycle 2 - 85%, yield of cycle 3 - 79%, yield of cycle 4 - 69%, yield of cycle 5 - 57%.

**2-Methoxybiphenyl:** iodobenzene (1.2 g, 6 mmol, 1.2 eq), 2-methoxyphenylboronic acid (0.76 g, 5 mmol, 1 eq), K<sub>2</sub>CO<sub>3</sub> (1.38 g, 10 mmol, 2 eq), H<sub>2</sub>O (15 mL), Pd/BC (0.5g, 0.05 mol% vs 2-methoxyphenylboronic acid), final product (0.911 g, 99%). The catalyst was recycled to repeat the reaction four times. Yield of cycle 2 -97%, yield of cycle 3 - 95%, yield of cycle 4 - 94%, yield of cycle 5 - 88%.

**3-Methoxybiphenyl:** iodobenzene (1.2 g, 6 mmol, 1.2 eq), 3-methoxyphenylboronic acid (0.76 g, 5 mmol, 1 eq), K<sub>2</sub>CO<sub>3</sub> (1.38 g, 10 mmol, 2 eq), H<sub>2</sub>O (15 mL), Pd/BC (0.5 g, 0.05 mol% vs 3-methoxyphenylboronic acid), final product (0.903 g, 98%). The catalyst was recycled to repeat the reaction four times. Yield of cycle 2-98%, yield of cycle 3 - 93%, yield of cycle 4 - 89%, yield of cycle 5 - 87%.

**4-Methoxybiphenyl:** iodobenzene (1.2 g, 6 mmol, 1.2 eq), 4-methoxyphenylboronic acid (0.76 g, 5 mmol, 1 eq), K<sub>2</sub>CO<sub>3</sub> (1.38 g, 10 mmol, 2 eq), H<sub>2</sub>O (15 mL), final product (0.901 g, 98%). The catalyst was recycled to repeat the reaction four times. Yield of cycle 2 -95%, yield of cycle 3 - 93%, yield of cycle 4 - 90%, yield of cycle 5 - 86%.

### Suzuki coupling reaction of chlorobenzene series

**Biphenyl:** chlorobenzene (0.68 g, 6 mmol, 1.2 eq), phenylboronic acid (0.61 g, 5 mmol, 1 eq), K<sub>2</sub>CO<sub>3</sub> (1.38 g, 10 mmol, 2 eq), H<sub>2</sub>O (15 mL), Pd/BC (0.5 g, 0.05 mol% vs phenylboronic acid), final product (0.685 g, 89%).

**4-Methylbiphenyl:** chlorobenzene (0.68 g, 6 mmol, 1.2 eq), *p*-tolylboronic acid (0.68 g, 5 mmol, 1 eq), K<sub>2</sub>CO<sub>3</sub> (1.38 g, 10 mmol, 2 eq), H<sub>2</sub>O (15 mL), Pd/BC (0.5 g, 0.05 mol% vs *p*-tolylboronic acid), final product (0.756 g, 90%).

**Biphenyl-4-carbaldehyde:** chlorobenzene (0.68 g, 6 mmol, 1.2 eq), 4-formylphenylboronic acid (0.75 g, 5 mmol, 1 eq), K<sub>2</sub>CO<sub>3</sub> (1.38 g, 10 mmol, 2 eq), H<sub>2</sub>O (15 mL), Pd/BC (0.5 g, 0.05 mol% vs 4-formylphenylboronic acid), final product (0.837 g, 92%).

**Biphenyl-4-carbonitrile:** chlorobenzene (0.68 g, 6 mmol, 1.2 eq),

4-cyanophenylboronic acid (0.74 g, 5 mmol, 1 eq), K<sub>2</sub>CO<sub>3</sub> (1.38 g, 10 mmol, 2 eq), H<sub>2</sub>O (15 mL), Pd/BC (0.5 g, 0.05 mol% vs 4-cyanophenylboronic acid), final product (0.671 g, 75%).

**2-Methoxybiphenyl:** chlorobenzene (0.68 g, 6 mmol, 1.2 eq), 2-methoxyphenylboronic acid (0.76 g, 5 mmol, 1 eq), K<sub>2</sub>CO<sub>3</sub> (1.38 g, 10 mmol, 2 eq), H<sub>2</sub>O (15 mL), Pd/BC (0.5 g, 0.05 mol% vs 2-methoxyphenylboronic acid), final product (0.864 g, 94%).

**3-Methoxybiphenyl:** chlorobenzene (0.68 g, 6 mmol, 1.2 eq), 3-methoxyphenylboronic acid (0.76 g, 5 mmol, 1 eq), K<sub>2</sub>CO<sub>3</sub> (1.38 g, 10 mmol, 2 eq), H<sub>2</sub>O (15 mL), Pd/BC (0.5 g, 0.05 mol% vs 3-methoxyphenylboronic acid), final product (0.837 g, 91%).

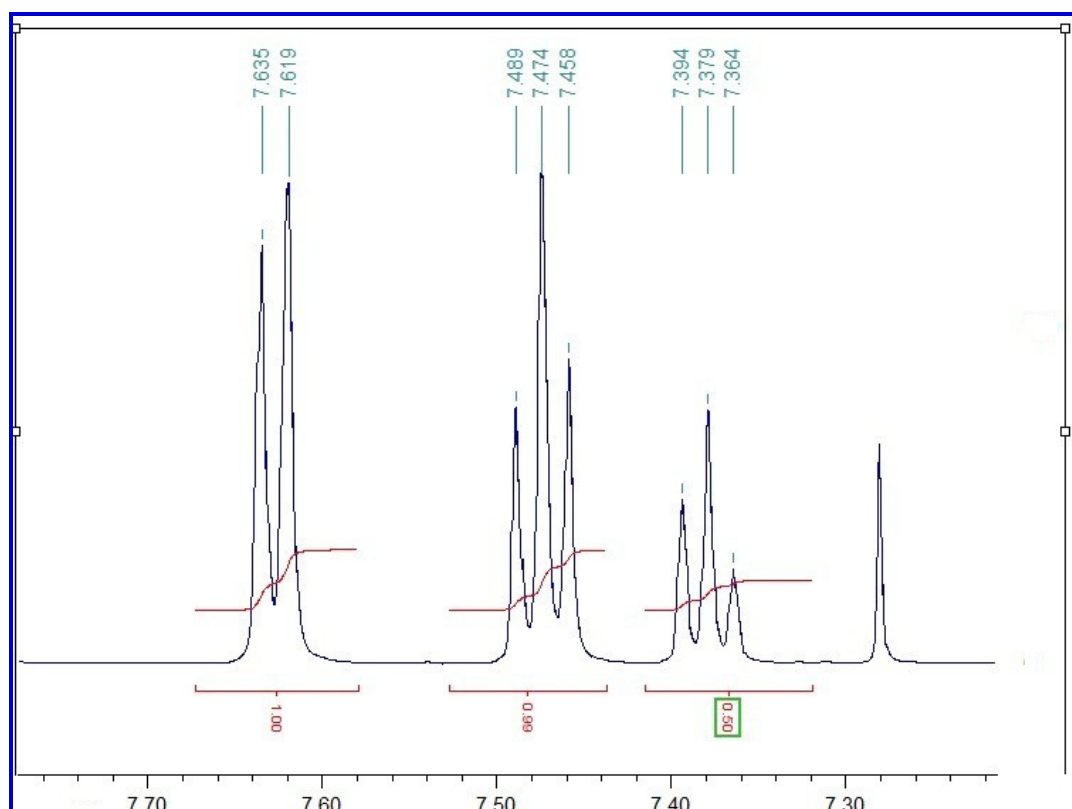
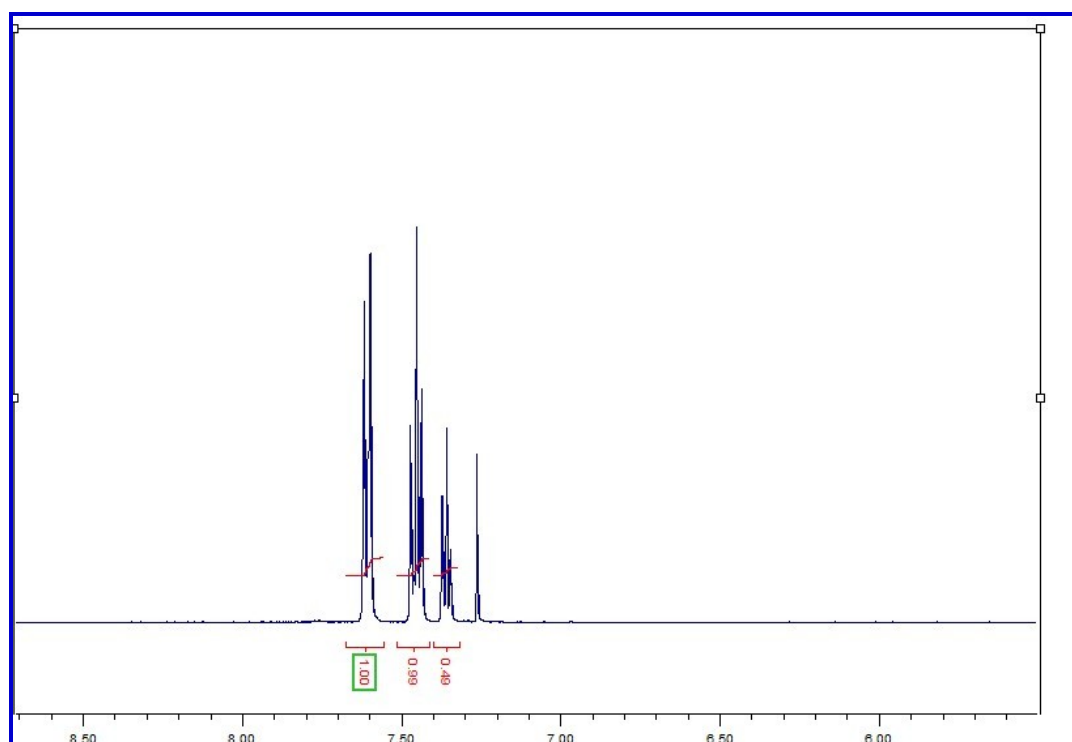
**4-Methoxybiphenyl:** chlorobenzene (0.68 g, 6 mmol, 1.2 eq), 4-methoxyphenylboronic acid (0.76g, 5 mmol, 1eq), K<sub>2</sub>CO<sub>3</sub> (1.38 g, 10 mmol, 2 eq), H<sub>2</sub>O (15 mL), Pd/BC (0.5 g, 0.05 mol% vs 4-methoxyphenylboronic acid), final product (0.828 g, 90%).

### Mechanism of Suzuki reaction

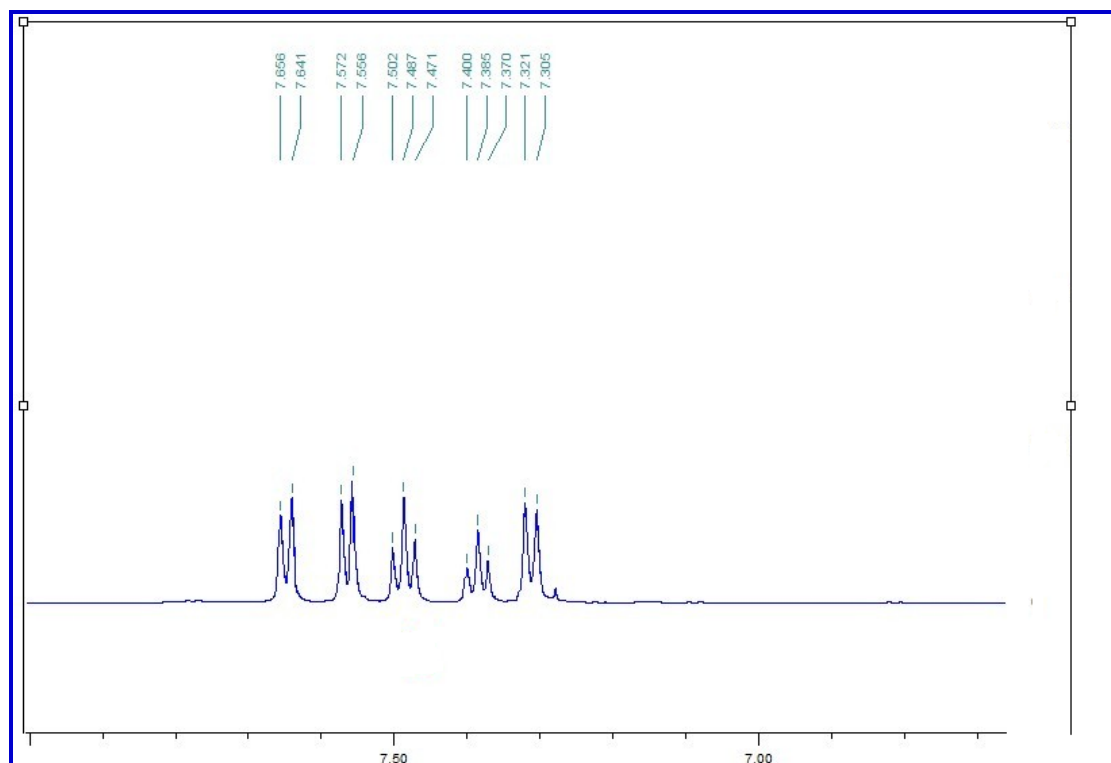
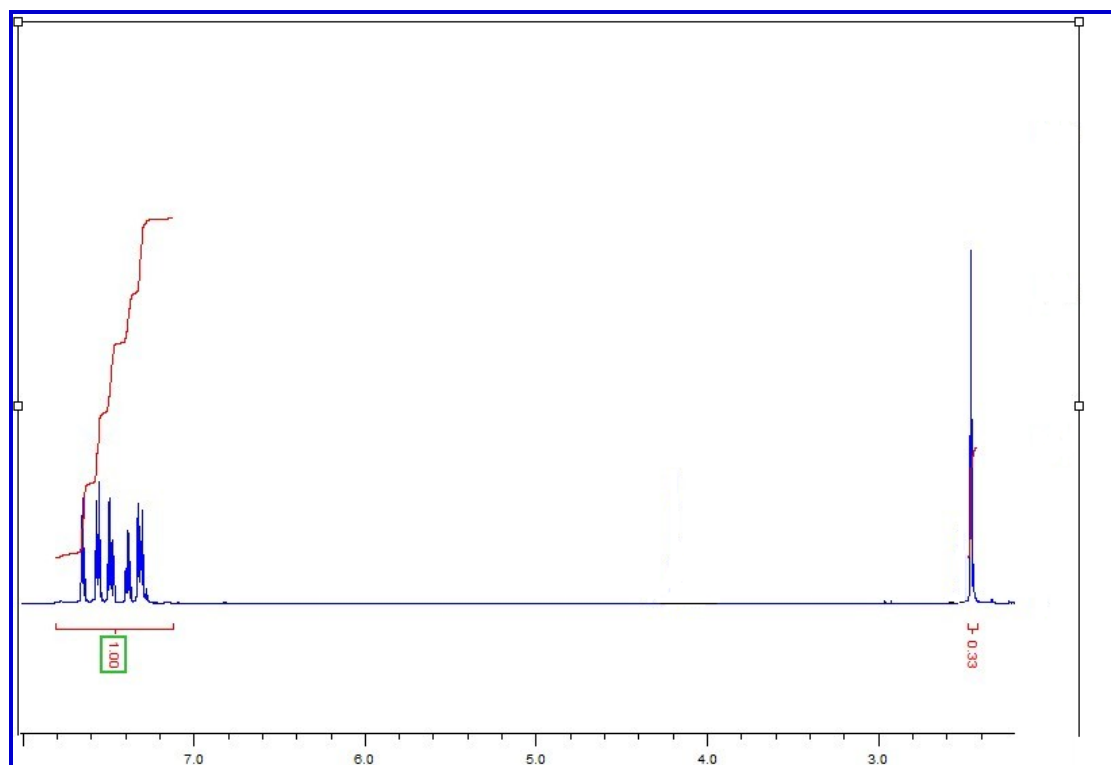
The mechanism of the Suzuki reaction is best viewed from the perspective of the palladium catalyst. The first step is the oxidative addition of palladium to the halide **2** to form the organopalladium species **3**. Reaction with base gives intermediate **4**, which via transmetalation with the boron-ate complex **6** forms the organopalladium species **8**. Reductive elimination of the desired product **9** restores the original palladium catalyst **1**.

**Scheme S3.** Schematic illustration of the mechanism of the Suzuki reaction.

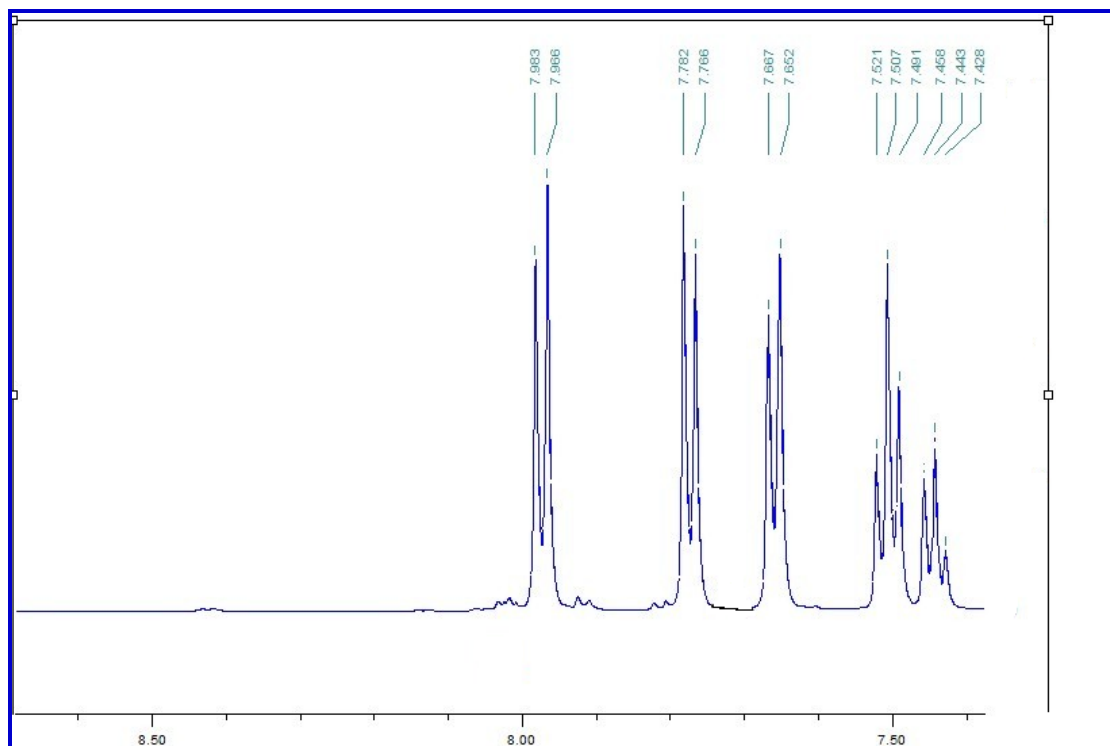
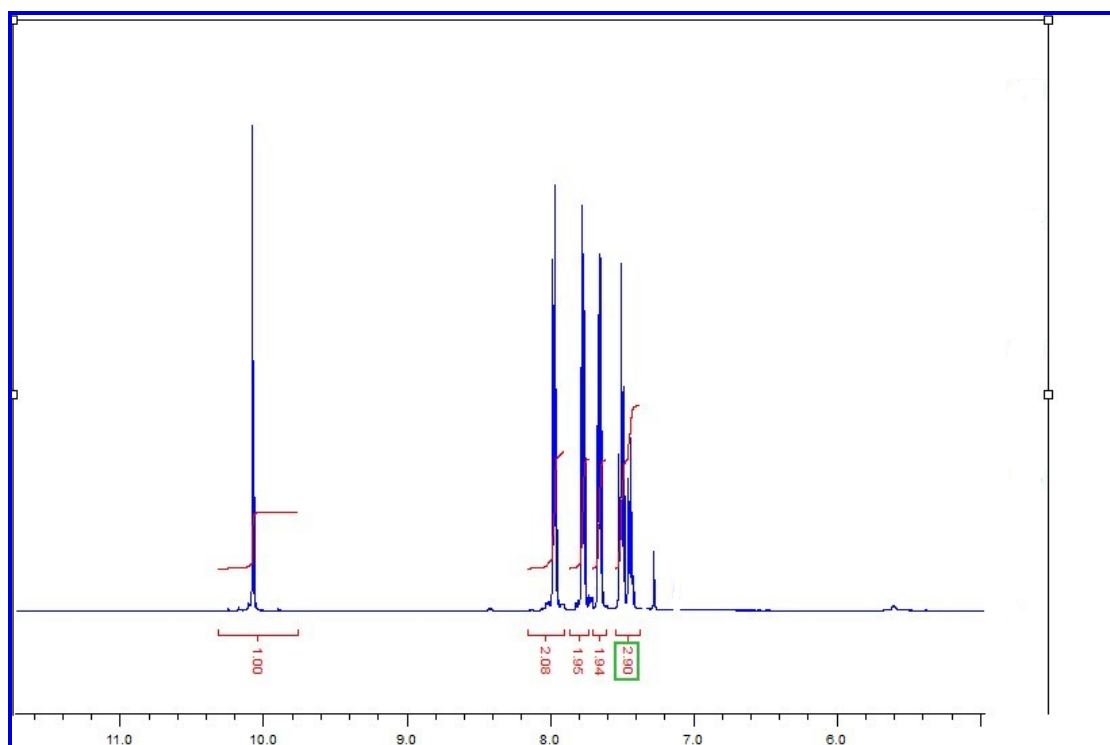
# $^1\text{H}$ NMR of biphenyl



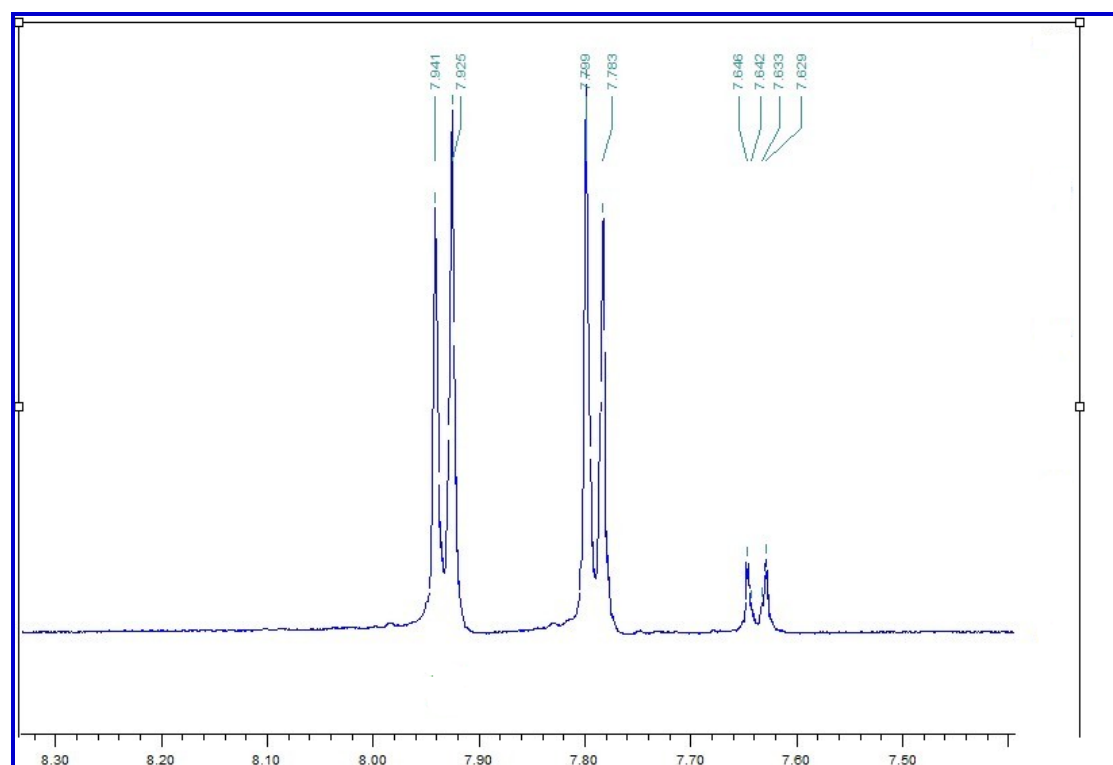
### $^1\text{H}$ NMR of 4-methylbiphenyl



### $^1\text{H}$ NMR of biphenyl-4-carbaldehyde

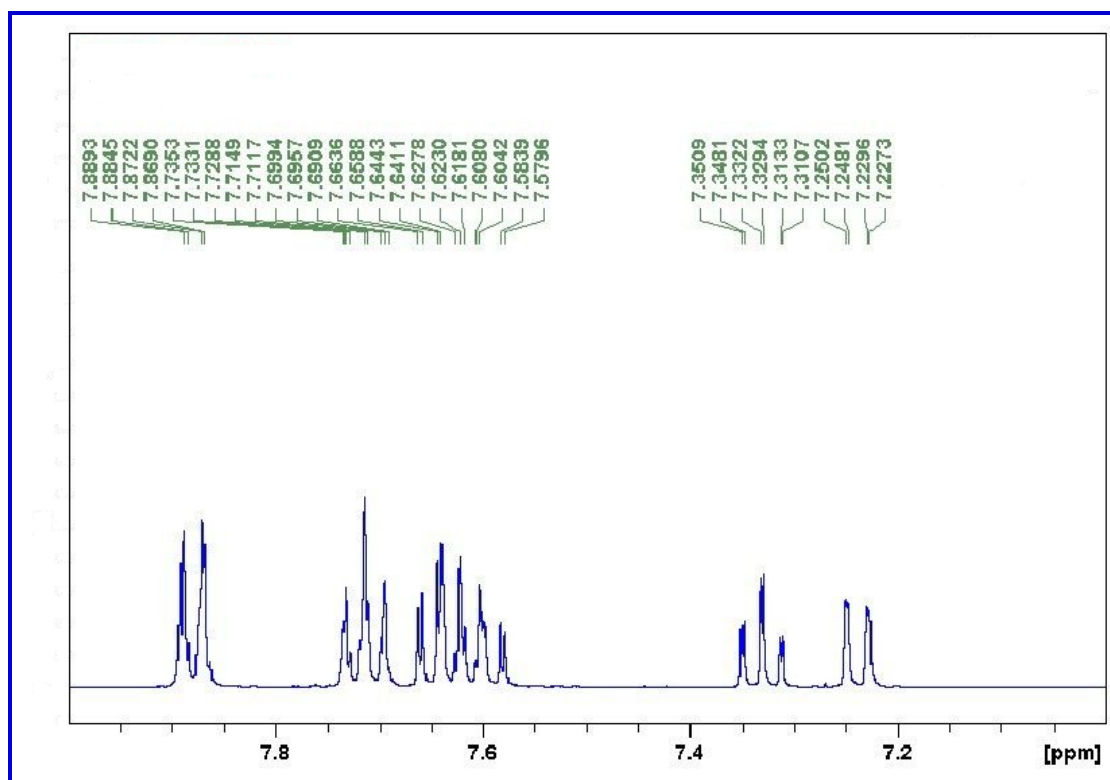
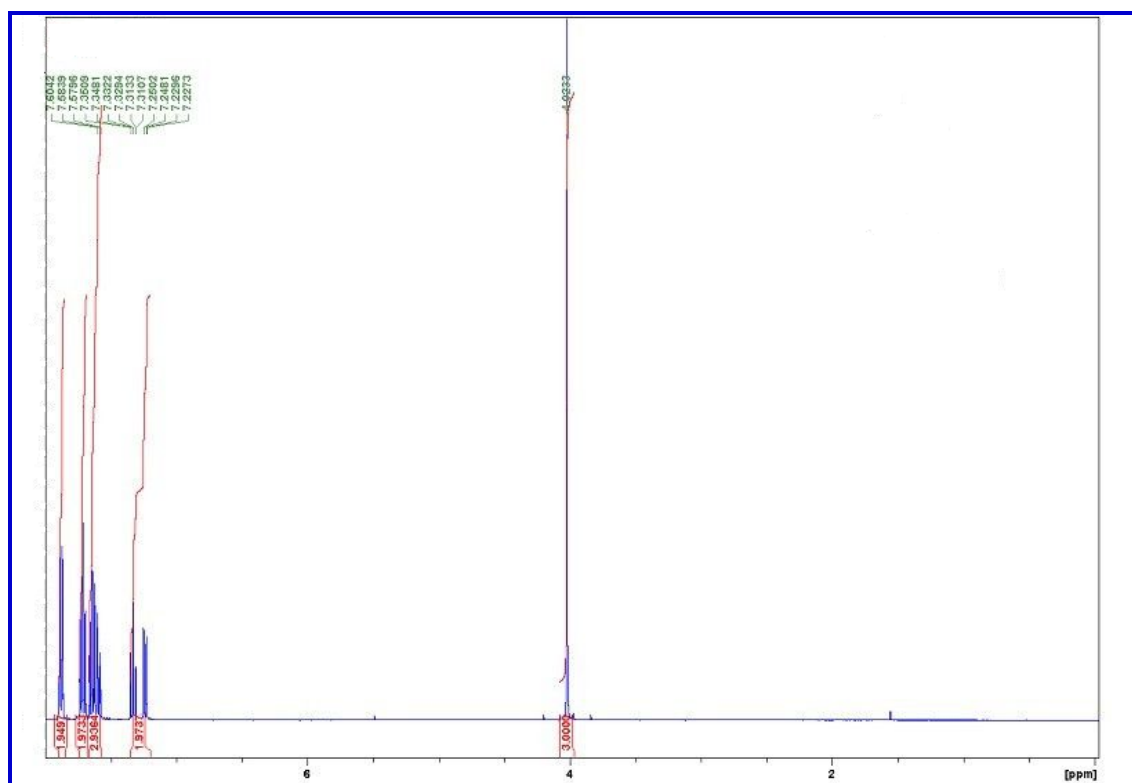


$^1\text{H}$  NMR of biphenyl-4-carbonitrile

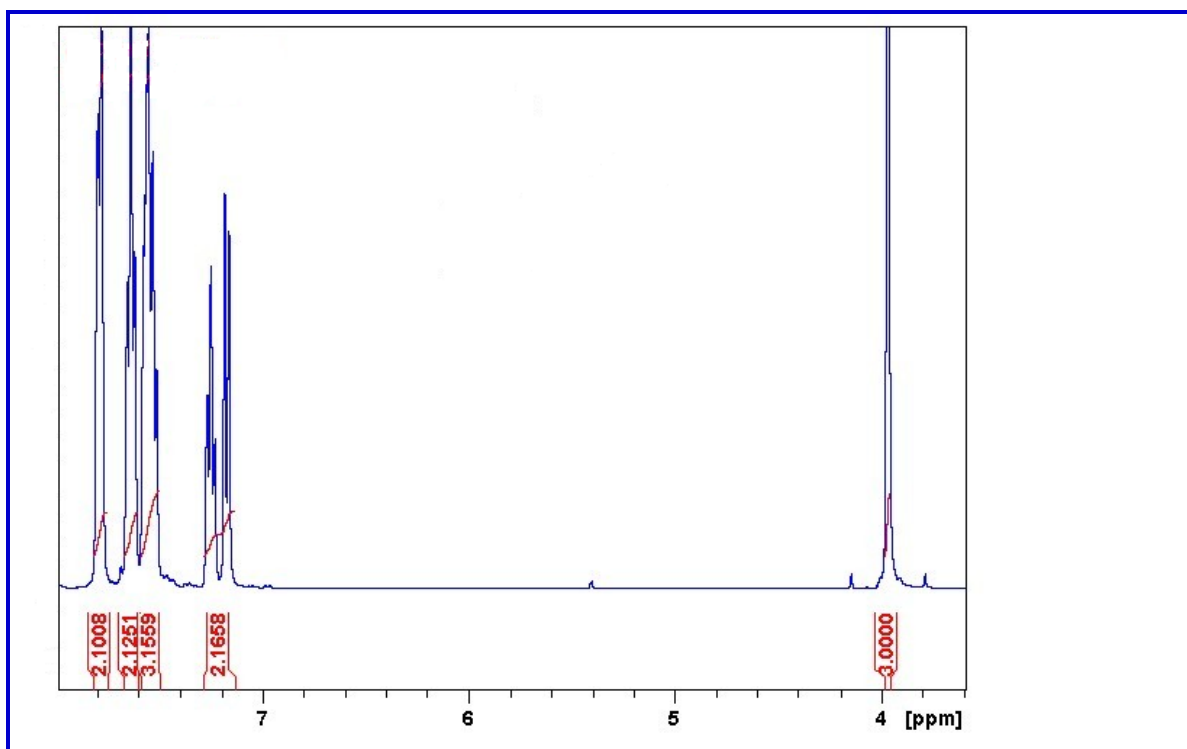
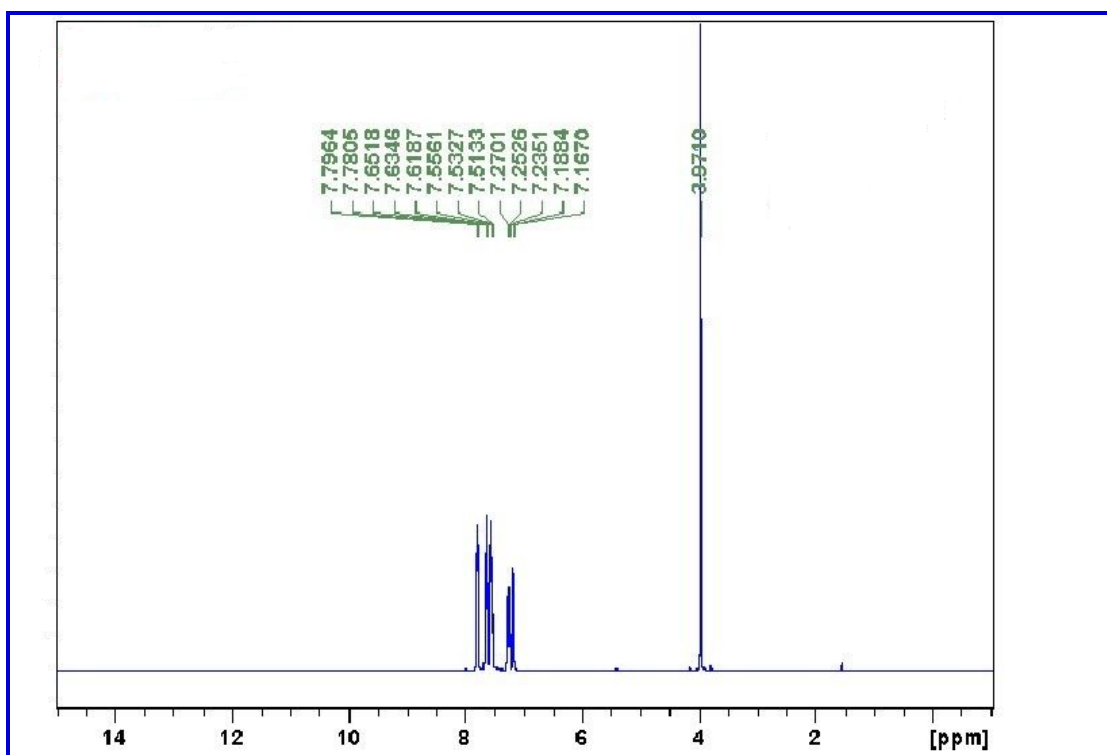




# <sup>1</sup>H NMR of 2-methoxybiphenyl



$^1\text{H}$  NMR of 3-methoxybiphenyl



### $^1\text{H}$ NMR of 4-methoxybiphenyl

