Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information (ESI) for

N-heterocyclic carbene palladium complex supported on ionic liquid-modified graphene oxide as an efficient and recyclable catalyst for Suzuki reaction

Siyavash Kazemi Movahed, Rahele Esmatpoursalmani and Ayoob Bazgir*

Shahid Beheshti University, Tehran, Islamic Republic of Iran.

E-mail: a_bazgir@sbu.ac.ir

TABLE OF CONTENTS

Synthesis

The graphite powder (2.5 g) was first treated with a mixture of 12.5 ml of concentrated H_2SO_4 with 2.5 g $K_2S_2O_8$ and 2.5 g P_2O_5. The mixture was kept at 80 ºC for 6 h. Subsequently, the mixture was cooled to room temperature and diluted with 500 mL de-ionized (DI) water and left overnight. The mixture was then filtered and washed with DI water to remove the residual acid. The product was dried under ambient conditions overnight. The pre-oxidized graphite was then subjected to oxidation by Hummers's method. The pretreated graphite powder was put into cold (0 ºC) concentrated H_2SO_4 (125 ml). Then $KMnO_4$ (15 g) was added gradually under stirring, and the temperature of the mixture was kept below 20 ºC by cooling. The mixture was then stirred at 35 ºC for 4 h and then diluted with DI water (250 ml). Because adding water to concentrated sulfuric acid medium releases a large amount of heat, the dilution was carried out in an ice bath to keep the temperature below 50 ºC. After adding all of the 250 mL DI water, the mixture was stirred for 2 h, and then an additional 750 mL DI water was added. Shortly thereafter, 20 ml 30% H_2O_2 was added to the mixture and the color of the mixture changed into brilliant yellow and began bubbling. The mixture was filtered and washed with 0.1 M HCl to remove metal ions, followed by 500 mL DI water to remove the acid, and then was dialyzed against DI water. The resulting GO solid was dried in air. [s1]

Preparation of IL

In a well-dried 25 mL Schlenk flask, (3-chloropropyl)trimethoxy silane (10 mmol) was added to 1-methylimidazole (10 mmol), and then the system was evacuated and purged with argon five times. After being stirred at 90 ◦C for 48 h under argon atmosphere, the resulting mixture was allowed to cool down to room temperature, was washed with dry ethyl acetate four times and dried under vacuum for 24 h at room temperature. The finally obtained ionic liquid was a kind of yellowish sticky liquids.[s2] The ^1H NMR (300 MHz) spectral data for the ionic liquid is as follows: $\delta = 0.43$ (m, 2H), 1.81(m, 2H), 3.39 (s, 9H), 3.9 (m, 2H), 4.1 (m, 2H), 7.3 (s, 1H), 7.6 (s, 1H), 10.3 (s, 1H).

Preparation of a solution of NHC-Pd in IL

In a well-dried 5 mL Schlenk flask, to a solution of IL (1 mmol) was added $Pd(OAc)_2$ (0.1 mmol) and then the system was evacuated and refilled with argon three times. The mixture was then allowed to react with stirring at 50-60 °C for 8 h and then at 100 °C for 4 under an argon atmosphere. The system was attached to the high vacuum for 2 hours to remove the by-produced acetic acid and was then allowed to cool to room temperature to afford a pale green-yellow solution of NHC-Pd in IL.[s3]

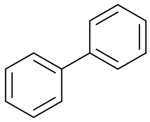
Preparation of NHC-Pd/GO-IL

The GO (0.10 g) was ultrasonically dispersed in 50 mL of ethanol. Then, solution of NHC-Pd in IL (0.10 mmol NHC-Pd in 0.90 mmol IL) was added to the GO suspension under stirring, and refluxed for 12 h. The yielded suspension was filtered and washed with ethanol for several times to get a purified NHC-Pd/GO-IL. The loading of imidazolium and imidazol-2-ylidene-Pd complex was determined to be 2.21 mmol.g^{-1} by means of the nitrogen content obtained from elementary analysis (CHN). Additionally, the loading level of the immobilized palladium was measured to be 0.22 mmol.g^{-1} by inductively coupled plasma-optical emission spectrometry (ICP-OES).

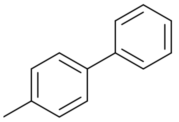
General procedure for Suzuki reaction

A mixture of NHC-Pd/GO-IL nanocomposite (0.1 mol % of Pd), K_2CO_3 (3 mmol), aryl halide (1.0 mmol), aryl boronic acid (1.3 mmol), and EtOH/H_2O (1:1) 2 mL under air was stirred for 2.5 h at 60 ºC. After completion of the reaction as indicated by TLC, the heterogeneous mixture was cooled to room temperature and filtered through a pad of celite. The filtrate was concentrated and then residue was purified by column chromatography (SiO_2, Ethyl acetate and *n*-Hexane) to yield pure product. The catalysts were recovered by simple filtration and washed extensively with acetone and deionized water and drying in the air.

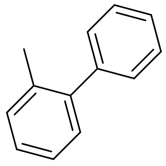
Compounds **3a**[s5], **3b**[s5], **3c**[s6], **3d**[s6], **3e**[s5], **3f**[s5] and **3g**[s7] are known compounds and were reported previously.



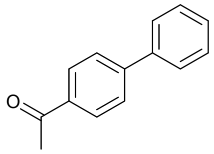
Mp. 66-68 ºC (Lit.[S5] Mp. 70-71 ºC).^{1}H-NMR ($CDCl_3$): δ 7.37 (t, 2H, *J*=7.4 Hz), 7.96-7.46 (t, 4H, *J*=7.3 Hz), 7.62 (d, 4H, *J*=7.5 Hz). MS (EI): *m/z* 154 (M^+).



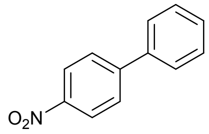
Mp. 46-47 ºC (Lit.[S5] Mp. 47-48 ºC).^{1}H-NMR ($CDCl_3$): δ 2.42 (s, 3H), 7.29-7.32 (m, 2 H), 7.36 (d, 1H, *J*=7.2 Hz), 7.45 (t, 2 H, *J*=7.5 Hz), 7.52 (d, 2H, *J*=7.5 Hz), 7.60 (d, 2 H, *J*=7.2 Hz). MS (EI): *m/z* 168 (M^+).



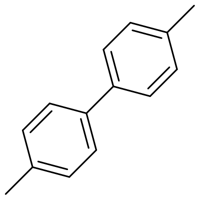
Colorless oil. ^{1}H-NMR ($CDCl_3$): δ 2.31 (s, 3H), 7.27-7.50 (m, 9 H).



Mp. 119-120 ºC (Lit.[S5] Mp. 120-121 ºC).^{1}H-NMR (DMSO-d_6): δ 2.61 (s, 3H), 7.41 (d, 1 H, *J*=6.6 Hz), 7.51 (t, 2H, *J*=7.2 Hz), 7.74 (d, 2 H, *J*=7.5 Hz), 7.83 (d, 2H, *J*=8.1 Hz), 8.04 (d, 2 H, *J*=7.8 Hz). MS (EI): *m/z* 196 (M^+).



Mp. 112-113 ºC (Lit.[S5] Mp. 114-115 ºC).^{1}H-NMR (DMSO-d_6): δ 7.47-7.5 (m, 3 H), 7.78 (d, 2H, *J*=7.2 Hz), 7.95 (d, 2 H, *J*=7.8 Hz), 7.83 (d, 2H, *J*=8.1 Hz), 8.29 (d, 2 H, *J*=7.8 Hz). MS (EI): *m/z* 199 (M^+).



Mp. 118-120 ºC (Lit.[S7] Mp. 119-120 ºC).^{1}H-NMR ($CDCl_3$): δ 2.43 (s, 6H), 7.27 (d, 4 H, *J*=7.8 Hz), 7.52 (d, 4H, *J*=8.1 Hz).MS (EI): *m/z* 182 (M^+).

Characterization

All chemicals were purchased from commercial suppliers and all solvents were purified and dried using standard procedures. IR spectra were recorded on a Bomem MB-Series FT-IR spectrophotometer. Diffraction data were collected on a STOE STADI P with scintillation detector, secondary monochromator and Cu-Ka1 radiation (λ =1. 5406 Å). XPS analysis was performed using a Gammadata-scienta ESCA 200 hemispherical analyzer equipped with an Al Ka (1486.6 eV) X-ray source. Raman spectra of GO and NHC-Pd/GO-IL nanocomposite were recorded on a Bruker SENTERR (2009) with an excitation beam wavelength at 785 nm. Scanning electron microscopy and EDX mapping characterizations of NHC-Pd/GO-IL nanocomposite were performed using an electron microscopy Philips XL-30 ESEM. Transmission Electron Microscopy characterization of NHC-Pd/GO-IL fresh and reused nanocomposites were performed using a transmission microscope Philips CM-30 with an accelerating voltage of 150 kV. HNMR spectra were recorded on a BRUKERDRX-300AVANCEspectrometer. NMR spectra were obtained in DMSO-d_6 using TMS as internal standard. Melting points of products were measured on an Elecrtothermal 9100 apparatus and are uncorrected. The concentration of palladium was estimated using Shimadzu AA-680 flame atomic absorption spectrophotometer and inductively coupled plasma optical emission spectrometer (ICP-OES) Varian Vista PRO Radial. The thermal stability of the GO and of NHC-Pd/GO-IL nanocomposite were determined using a thermogravimetric analyzer (TGA/DTA BAHR: STA 503) under air and a heating rate of 5 ºC min^{-1}. Elemental analysis of NHC-Pd/GO-IL nanocomposite was performed using an Elementar Analysensysteme GmbH VarioEL CHNS. Mass spectra were recorded on a FINNIGAN-MAT 8430 mass spectrometer operating at an ionization potential of 70 eV. Gas chromatography was performed on a Trace GC ultra from the Thermo Company equipped with FID detector and Rtx®-1 capillary column.

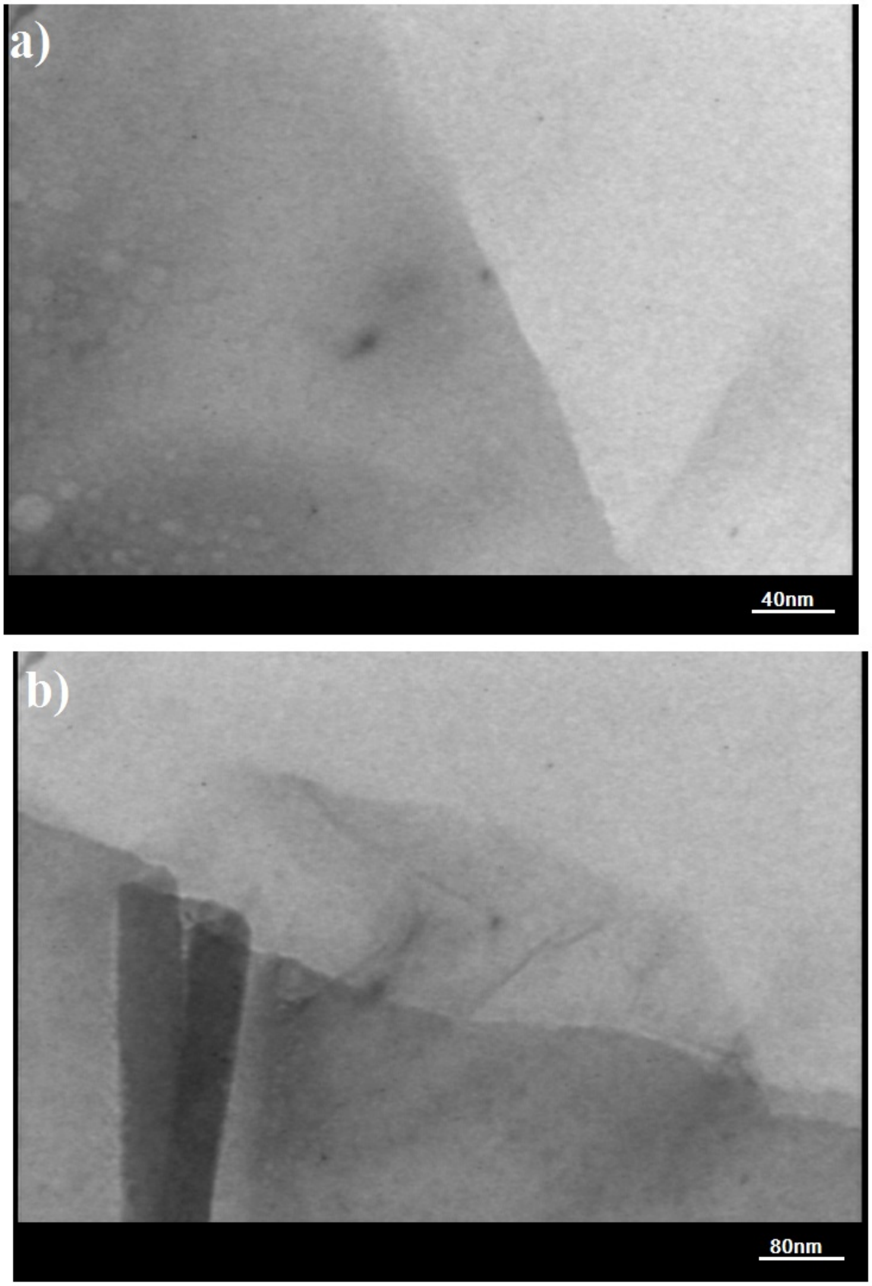


Fig. S1 TEM images for after experiments without a) boronic acid and b) all reagents (only the K_2CO_3)

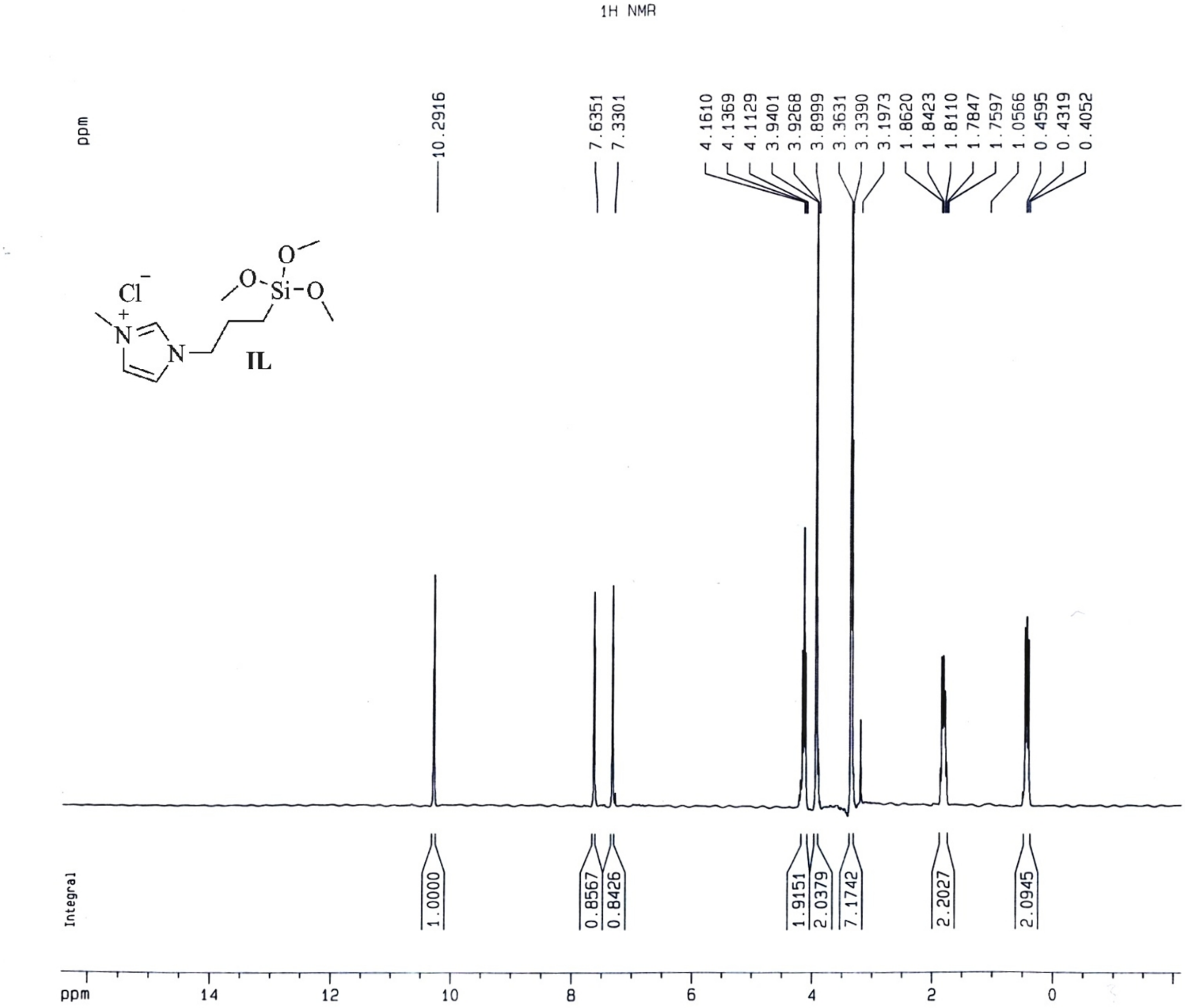


Fig. S2 ^{1}H NMR of IL

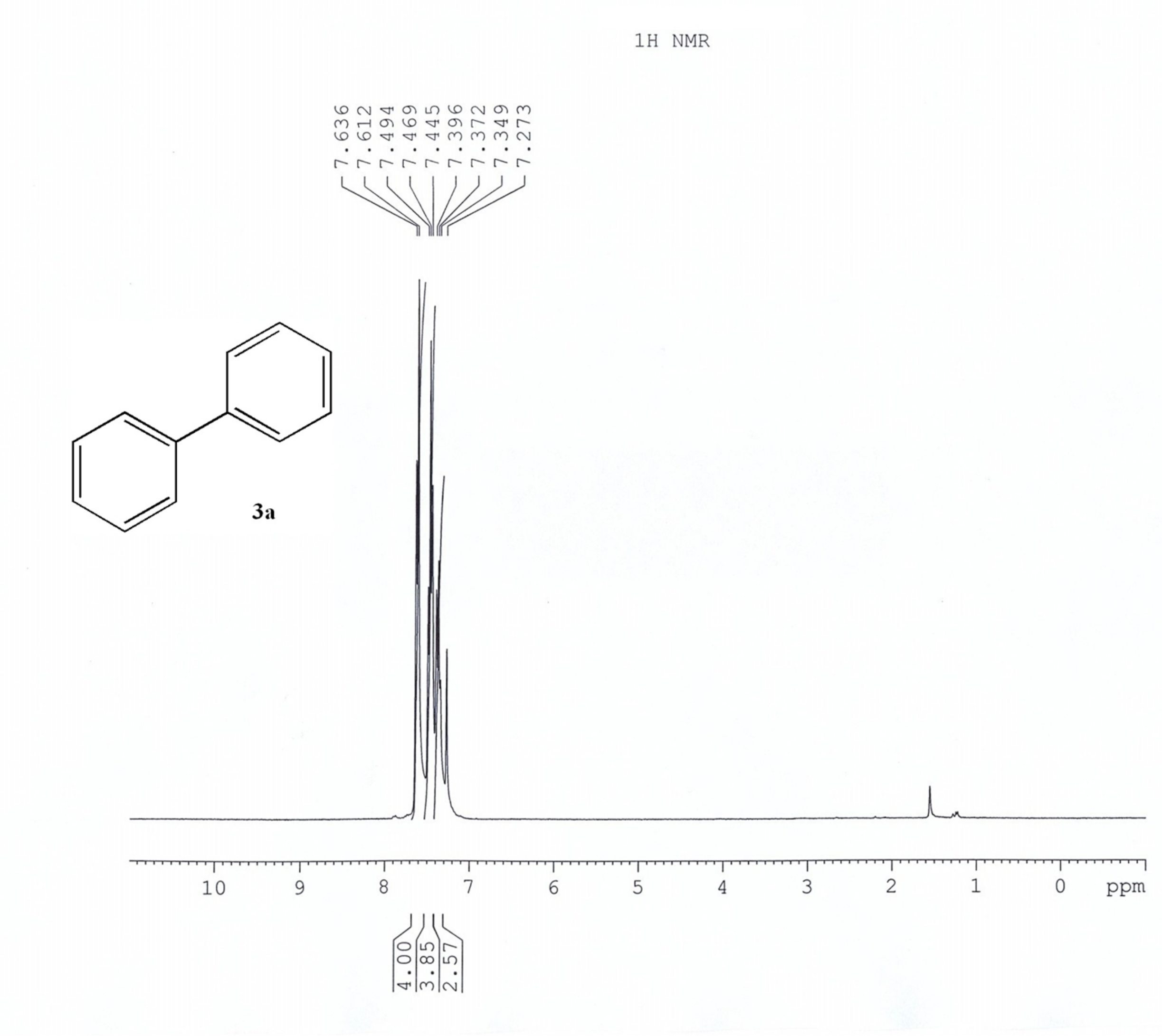


Fig. S3 ^{1}H NMR of product 3a

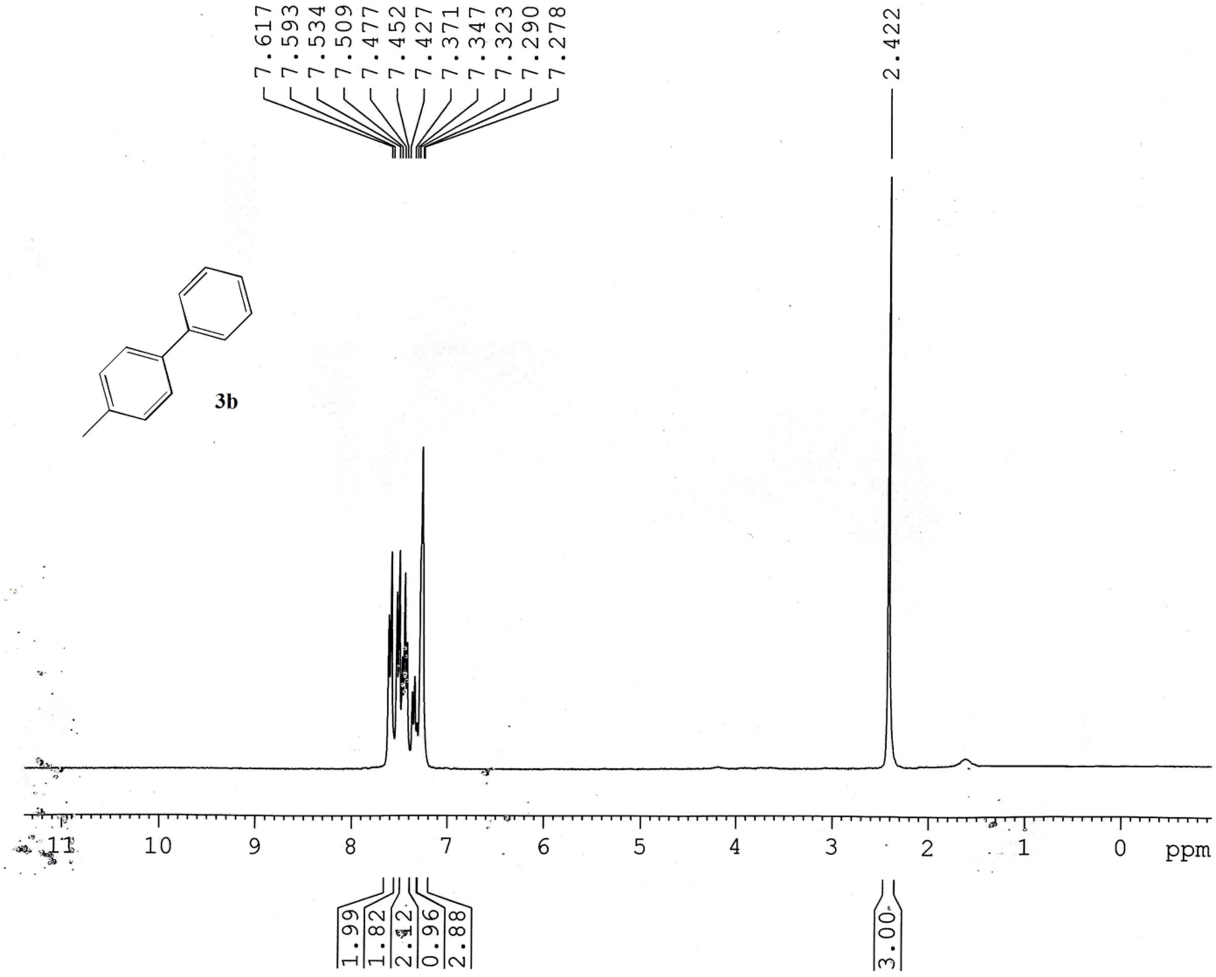


Fig. S4 ^{1}H NMR of product 3b

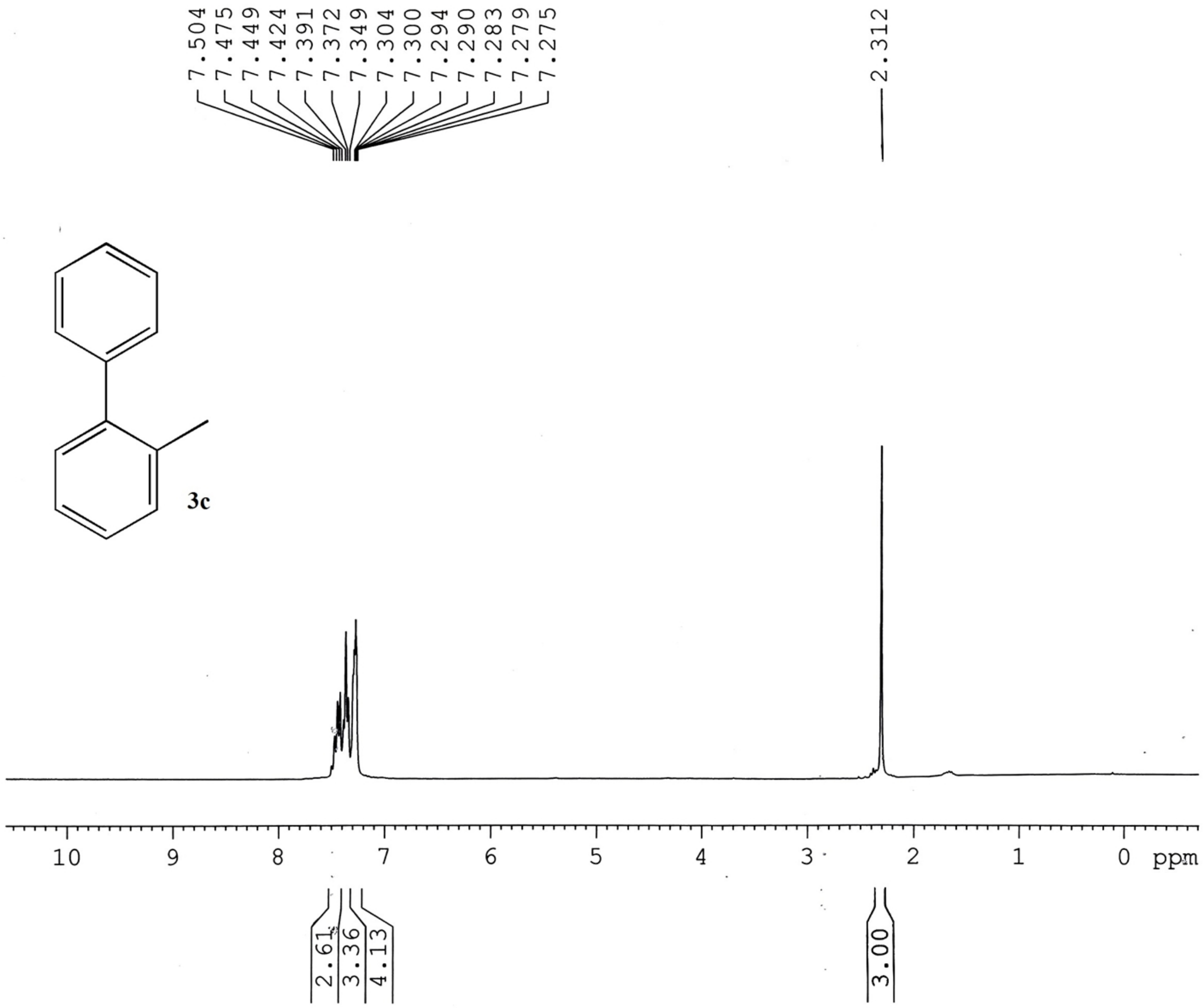


Fig. S5 ^{1}H NMR of product 3c

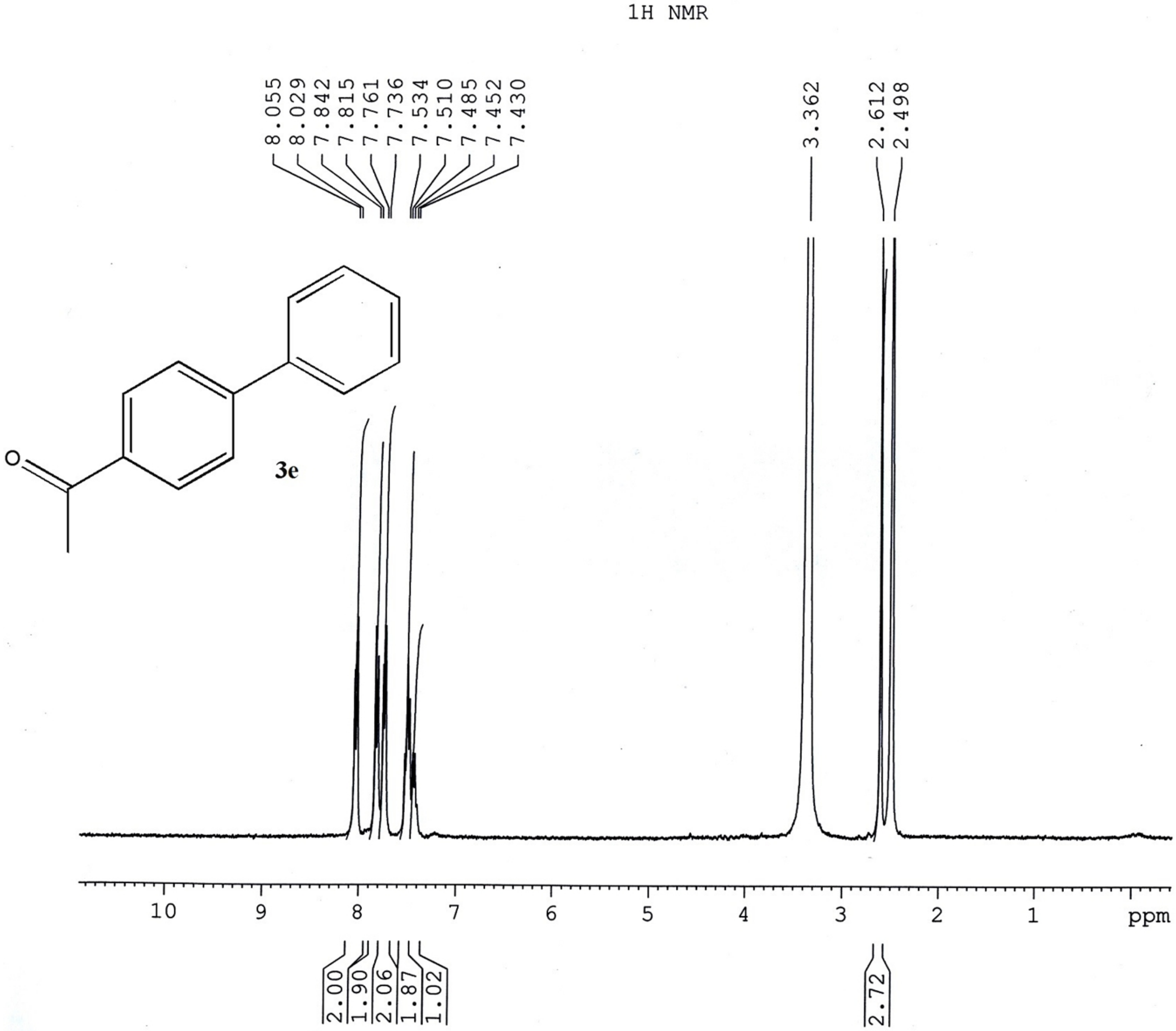


Fig. S6 ^{1}H NMR of product 3e

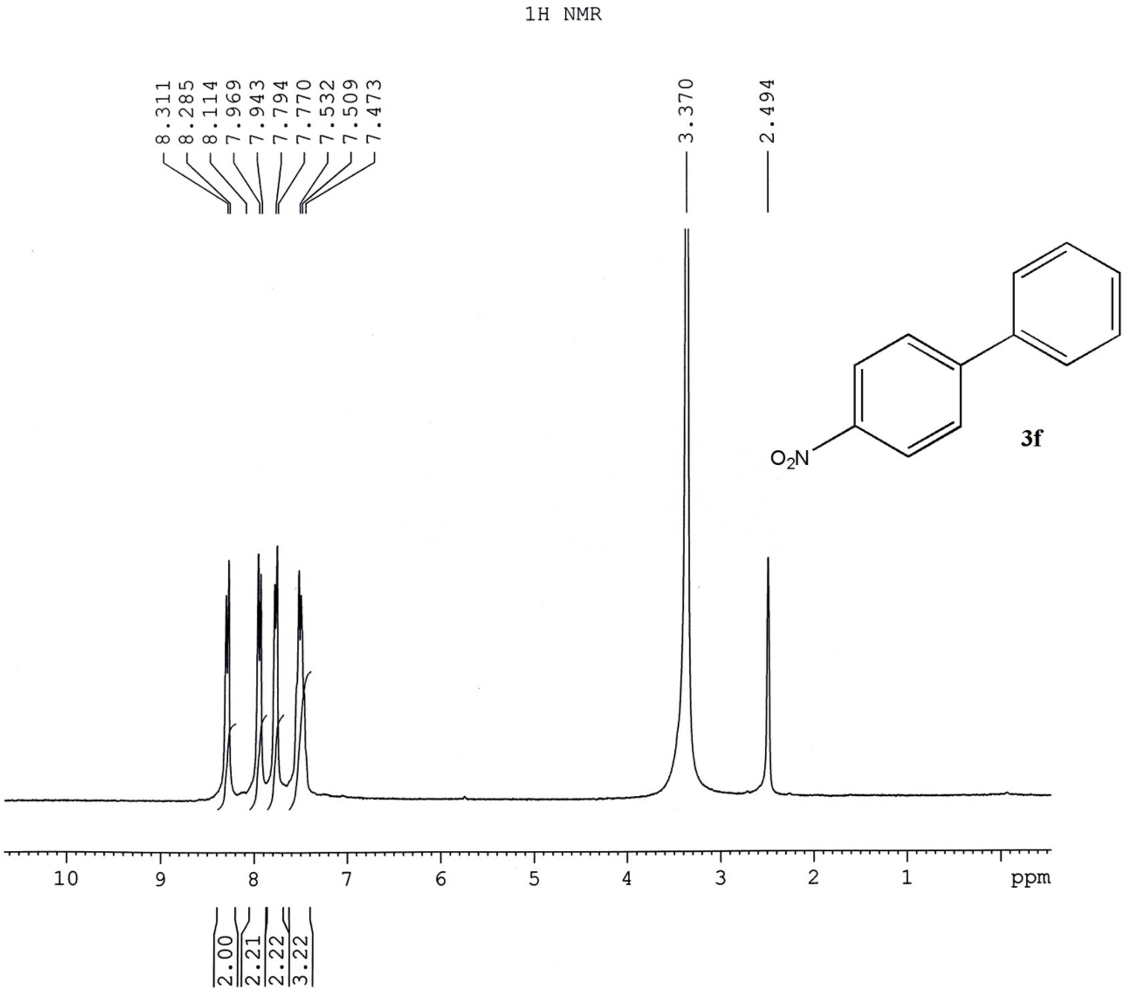


Fig. S7 ^{1}H NMR of product 3f

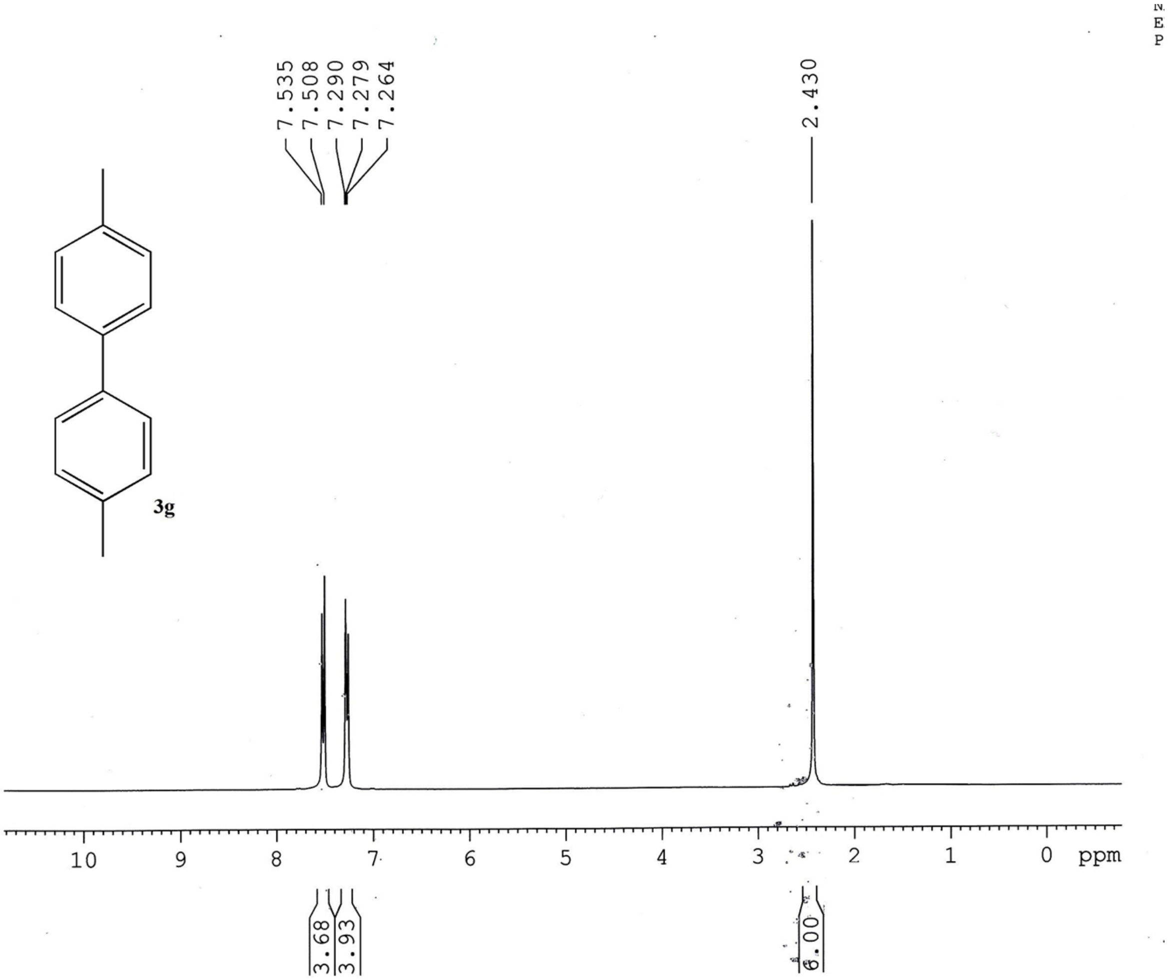


Fig. S8 ^{1}H NMR of product 3g

References

1- W.S. Hummers and R.E. Offeman *J. Am. Chem. Soc.,* 1958*,* **80**, 1339; N.I. Kovtyukhova, P.J. Olliver, B.R. Martin, T.E. Mallouk, S.A.Chizhik, E.V. Buzaneva and A.D. Gorchinsky *Chem. Mater.,* 1999, **11**, 771.

2- H. Yang, X. Han, G. Li, and Y. Wang, *Green Chem.,* 2009, **11**, 1184.

3- B. Karimi, and D. Enders, *Org. Lett.,* 2006, **8**, 1237.

4- E. Tyrrell, L. Whiteman, and N. Williams, *J. Organomet. Chem*., 2011, **696**, 3465.

5- Q. Zhang, H. Su, J. Luo and Y. Wei, *Catal. Sci. Technol.*, 2013, **3**, 235.

6- C. Diebold, J.-M. Becht, J. Lu, P. H. Toy and C. Le Drian, *Eur. J. Org. Chem.,* 2012, **2012**, 893

7- J.-B. Liu, H. Yan, H.-X. Chen, Y. Luo, J. Weng and G. Lu *Chem. Commun.*, 2013, **49**, 5268.