Facile Synthesis of Palladium Nanoparticles with High Chemical Activity Using Cucurbit[6]uril as Protecting Agent

Minna Cao,[a,b] Jingxiang Ling,[a] Hongxun Yang[a] and Rong Cao*[,a]

[a] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, the Chinese Academy of Science, Fuzhou 350002, China. Fax: +86 59183796710; Tel: +86 59183796710; E-mail: rcao@fjirsm.ac.cn*
[b] *Department of Chemistry, University of Science and Technology of China, Hefei 230026, China*

Materials

CB[6] were prepared according to literatures[1]. All other reagents were commercial available and used as received, and solutions were prepared with deionized water (Milli-Q, 18.2 MΩ cm).

Instruments and characterization

The morphologies of products were studied using a JEOL-2010 transmission electron microscope (TEM) working at 200KV. The samples were prepared by placing a drop of product in ethanol onto a continuous carbon-coated copper TEM grid. Analysis of Pd content was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES), which performed on an Ultima 2 analyzer (Jobin Yvon). Fourier-transform infrared (FT-IR) spectra were taken on a Magna 750 FTIR spectrometer with samples as KBr pellets in the range of 450-4000 cm^{-1}. X-ray diffraction (XRD) patterns were recorded on a Rigaku-Dmax2500 diffractometer using CuKα radiation (λ=0.154 nm).

Preparation and Characterization of CB[6]-metal NPs

0.2 mmol of $PdCl_2$ and 0.2 mmol of CB[6] were mixed in 20 ml of water at room temperature. The mixture was stirred for half an hour to form a brown uniform suspension, and then 2 mmol of $NaBH_4$ in 20 ml of alcohol was added rapidly. As the reductant added the colour of the suspension changed to black immediately indicating the formation of Pd NPs. Stirring was kept for another 3 hours and the final products were separated by centrifugation and dried in an oven overnight at 70 °C. The other CB[6] dispersed Pd NPs were prepared using the same method with different molar ratio ranging from 6:1 to 1:2.

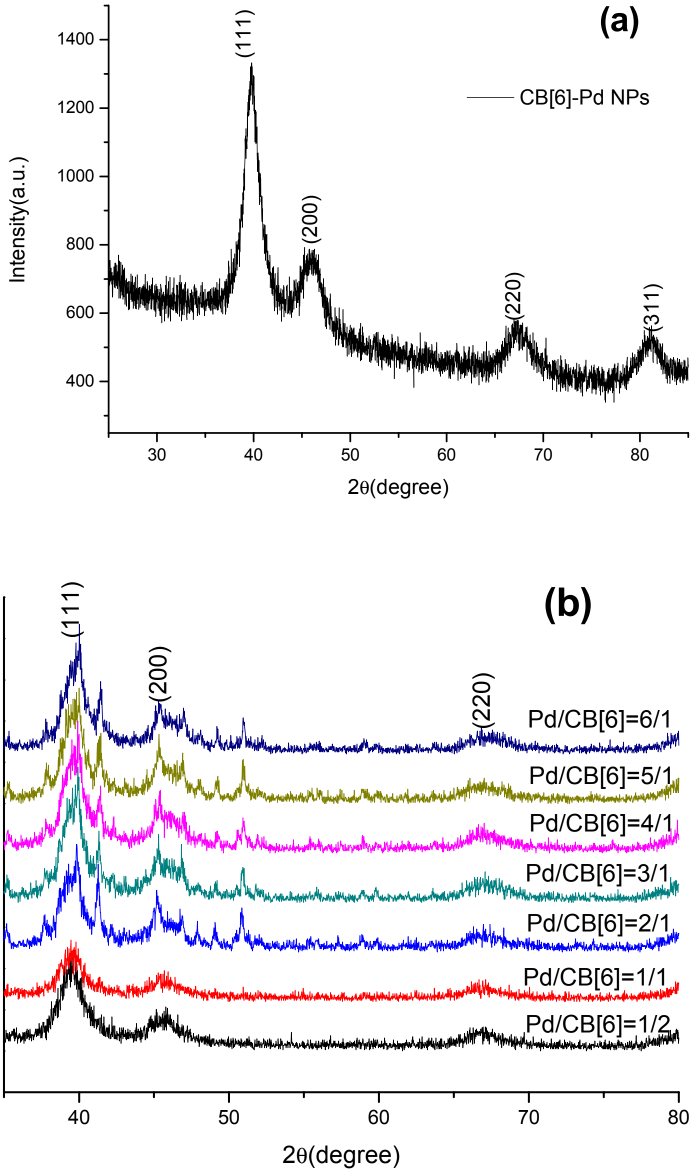


Figure S1. PXRD patterns of CB[6]-Pd NPs with the molar ratio of $PdCl_2$ to CB[6] of (a) 1:1 (b) between 1:2 and 6:1. The four main peaks correspond to (111), (200), (220) and (311) Bragg reflection of face-centered cubic (fcc) Pd.

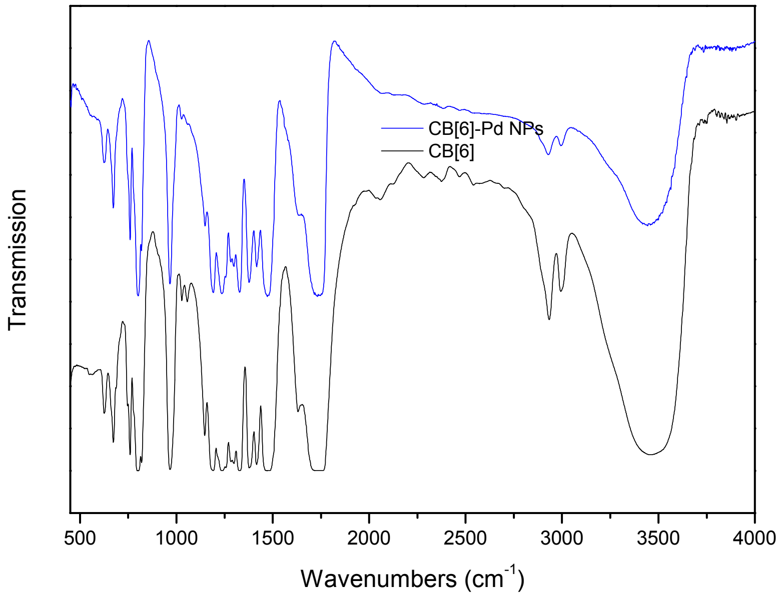


Figure S2. FT-IR spectra of CB[6] and CB[6]-Pd NPs

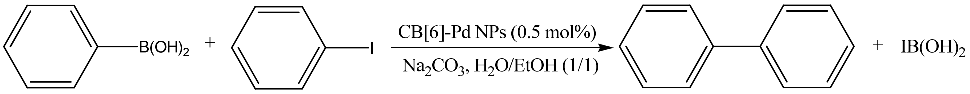
The peak around 1730 cm^{-1} is attributed to the carbonyl stretching vibration at which no changes between CB[6]-Pd NPs and CB[6] are observed, proving that there is no direct bonding between CB[6] and metal atoms.

Suzuki-Miyaura coupling reactions

The catalytic reactions were carried out in a 10 mL round bottom flask in air. Aryl halides (1 mmol, 1 equiv), sodium carbonate (3 mmol, 3 equiv), arylboronic acids (1.2 mmol, 1.2 equiv), and CB[6]-Pd NPs (5 mg, 0.5 mol%) were mixed in solvent (4 ml water and 4 ml ethanol) at reaction temperature range from 40 °C to 80 °C according to different substrates. The product was extracted with diethyl acetate (3×10 mL) and dried with Na_2SO_4. After filtration, the organic solvent was removed under reduced pressure to yield the final product. The products were quantified by GC-MS analysis with external standard method. GC-MS measurements were performed on a Varian 450-GC/240-MS. The final products were purified by chromatography on silica gel (hexane) to afford purified materials for characterization. ^{1}H NMR (400 MHz), and

^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ solutions using a Burker AVANCE 400 spectrometer. Side products are self coupling of arylboronic acid with yields less than 2 %.

Table S1. Reuse of CB[6]-Pd NPs as catalyst with phenylboronic acid and iodobenzene as reactants[a]



use	1st	2nd	3rd	4th	5th
yield (%)[b]	99	99	99	99	97

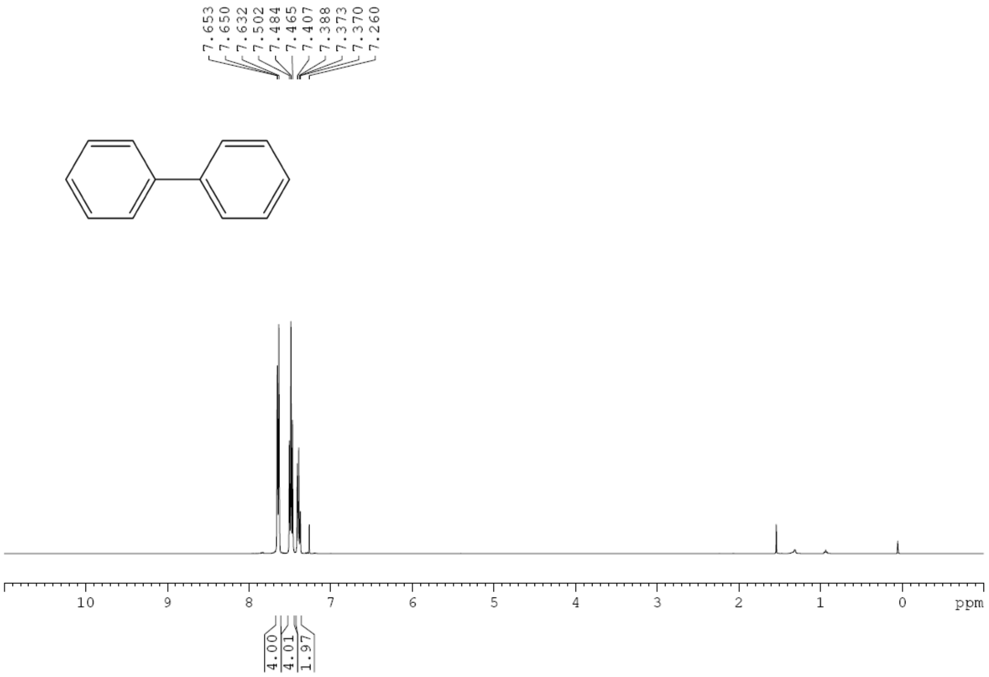
[a] Reaction conditions: Iodobenzene (1 mmol, 1 equiv.), arylboronic acid (1.2 mmol, 1.2 equiv.), Na_2CO_3 (3 mmol, 3 equiv.), CB[6]-Pd NPs (0.5 mol%), solvent: H_2O/EtOH (volume ratio: 1/1), in air. [b] Fixed reaction time of 20 minutes and fixed reaction temperature of 40 °C and the yield determined by GC-MS using external standard method.

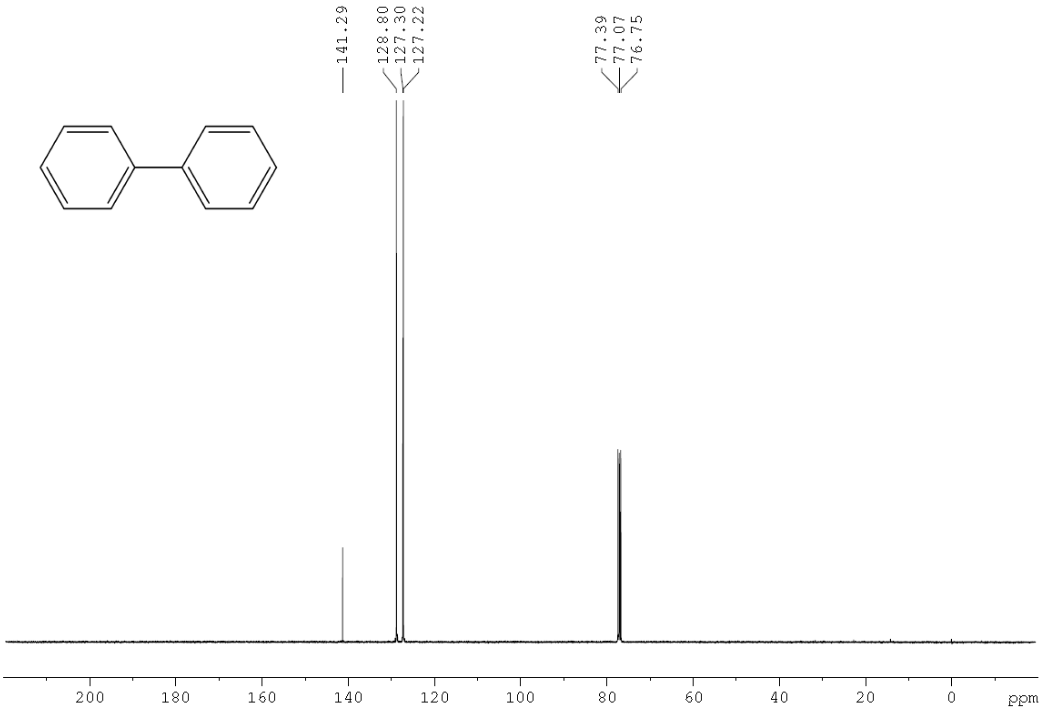
Reference

Bardelang, D.; Udachin, K. A.; Leek, D. M. Ripmeester, J. A. *CrystEngComm* **2007**, *9*, 973.

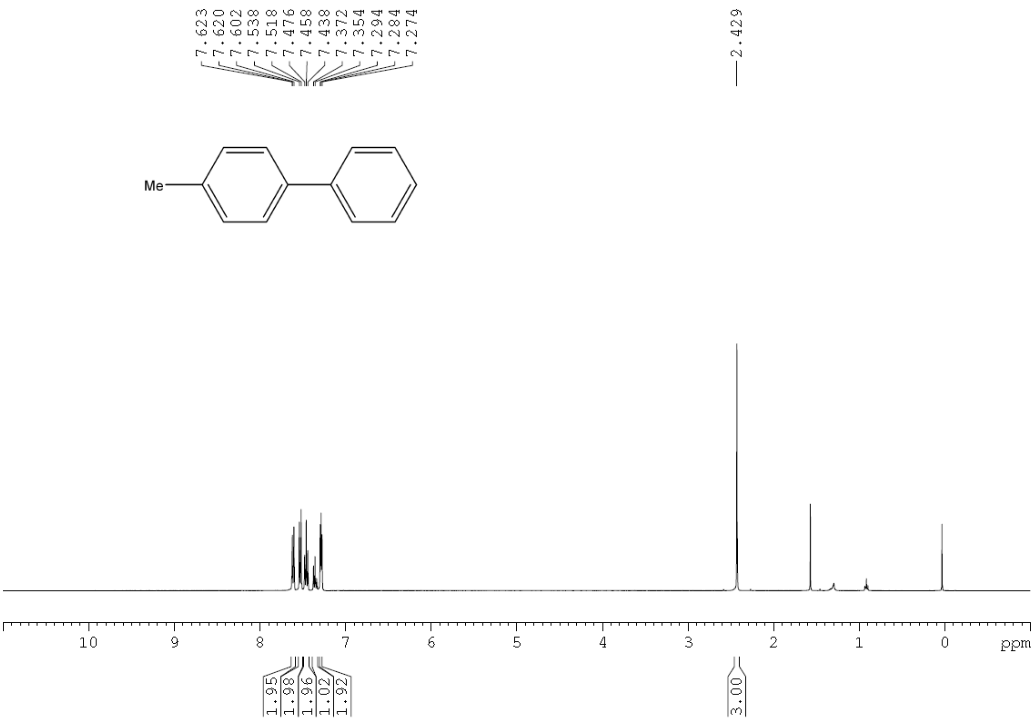
NMR Spectra

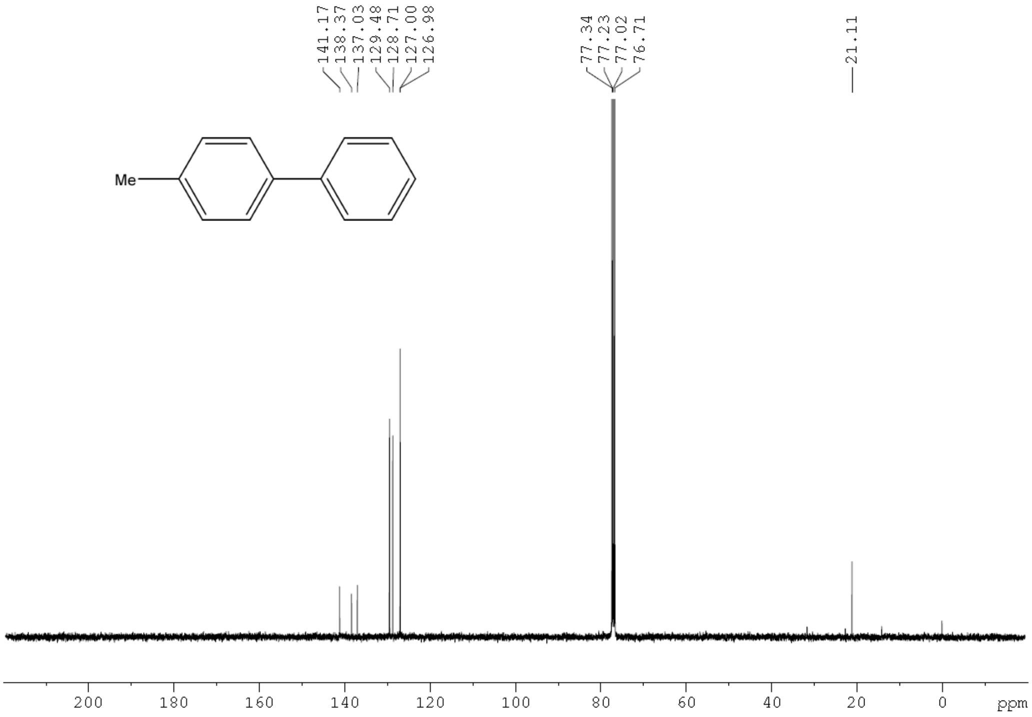
^{1}H NMR and ^{13}C NMR of Biphenyl



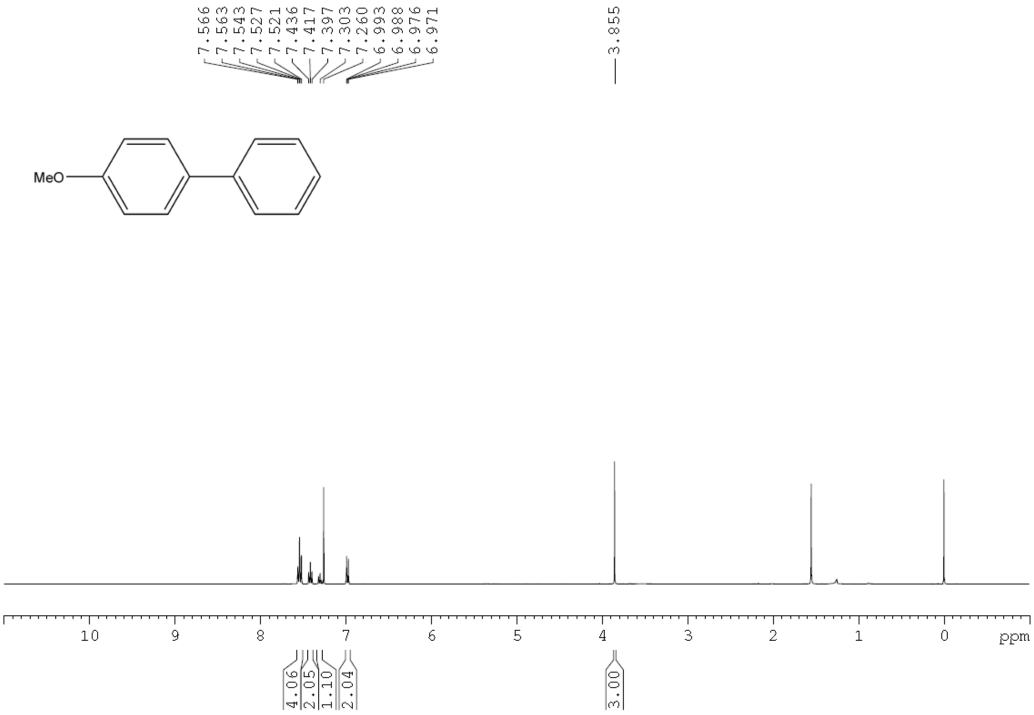


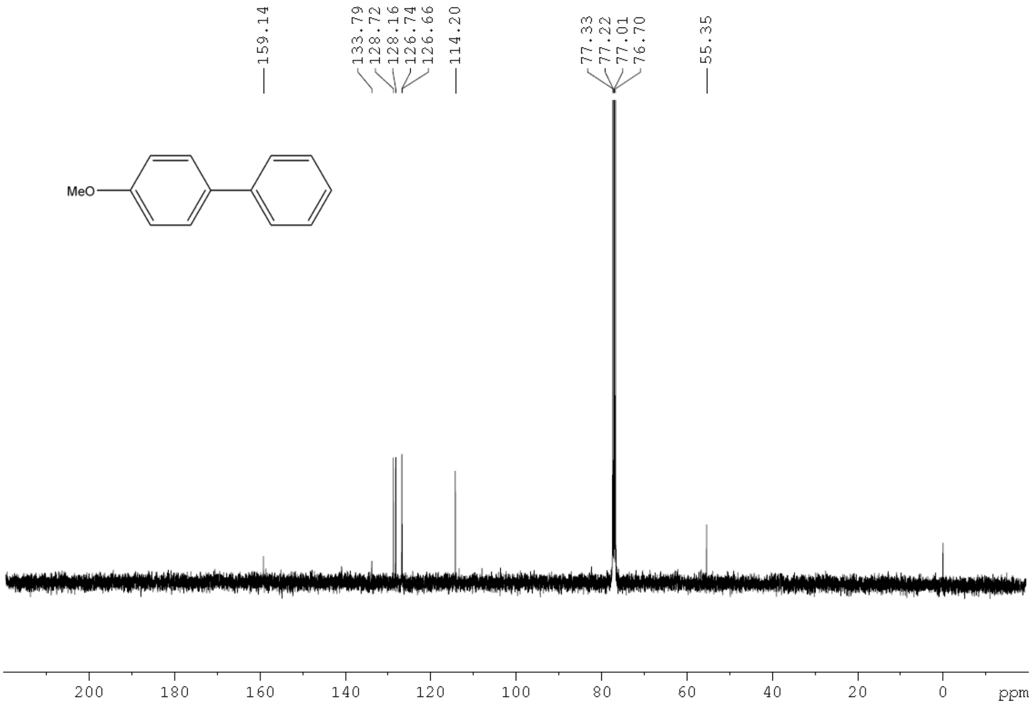
^{1}H NMR and ^{13}C NMR of 4-Methylbiphenyl



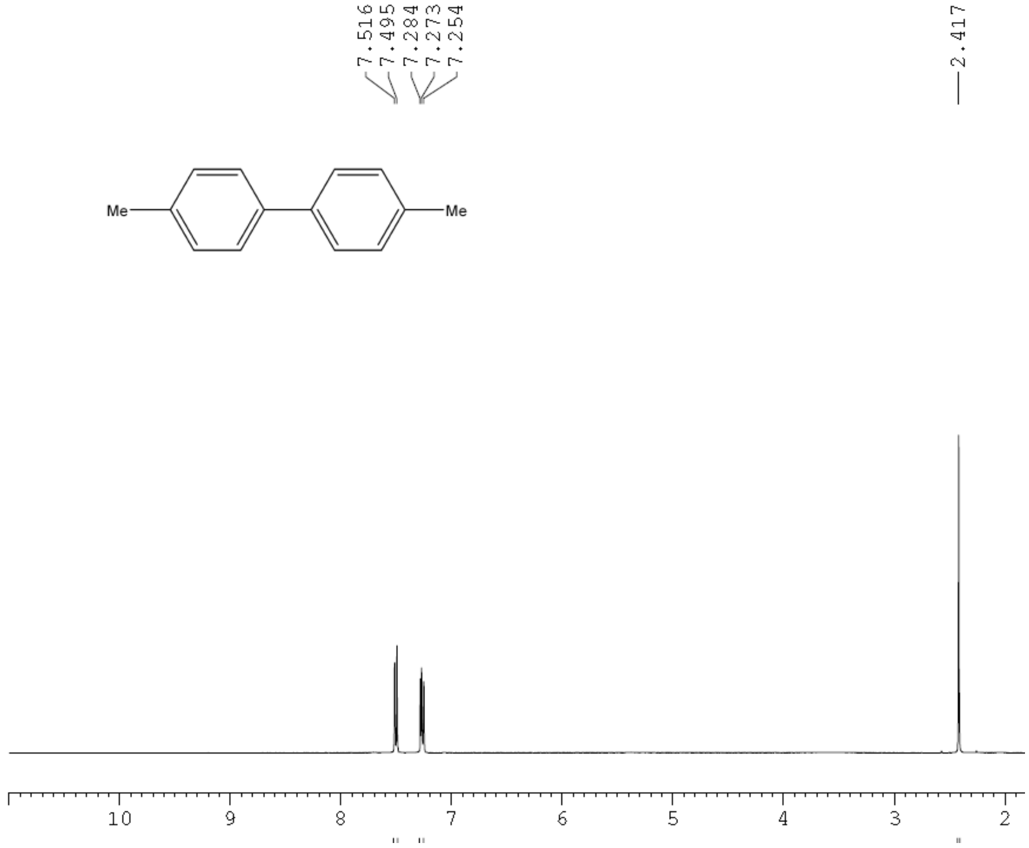


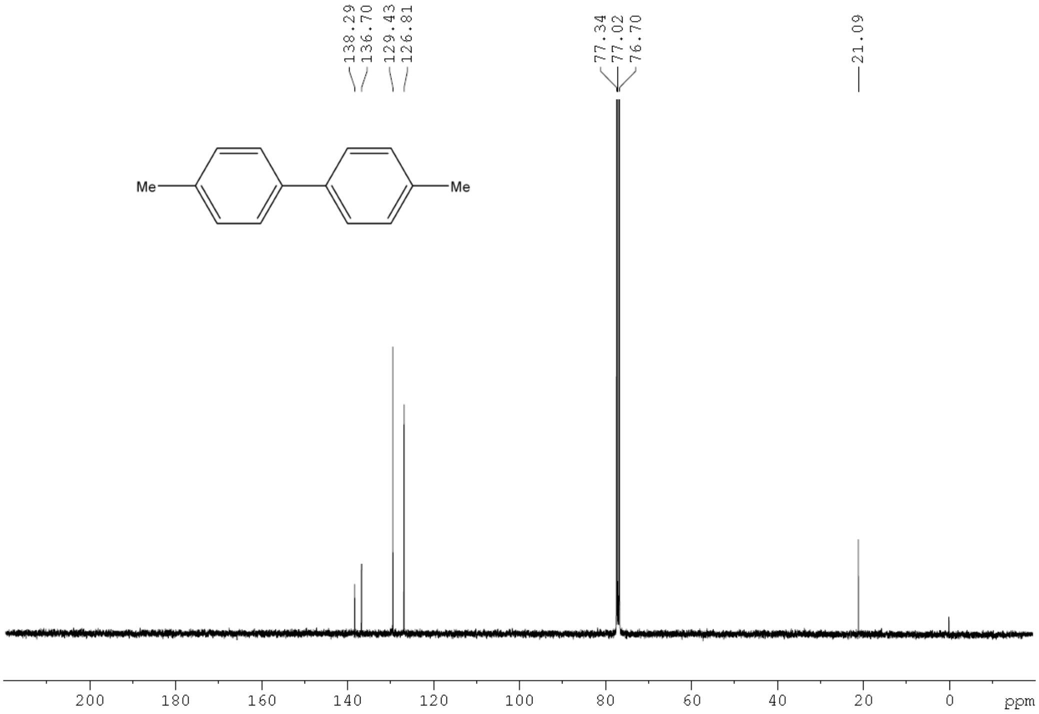
^{1}H NMR and ^{13}C NMR of 4-Methoxybiphenyl



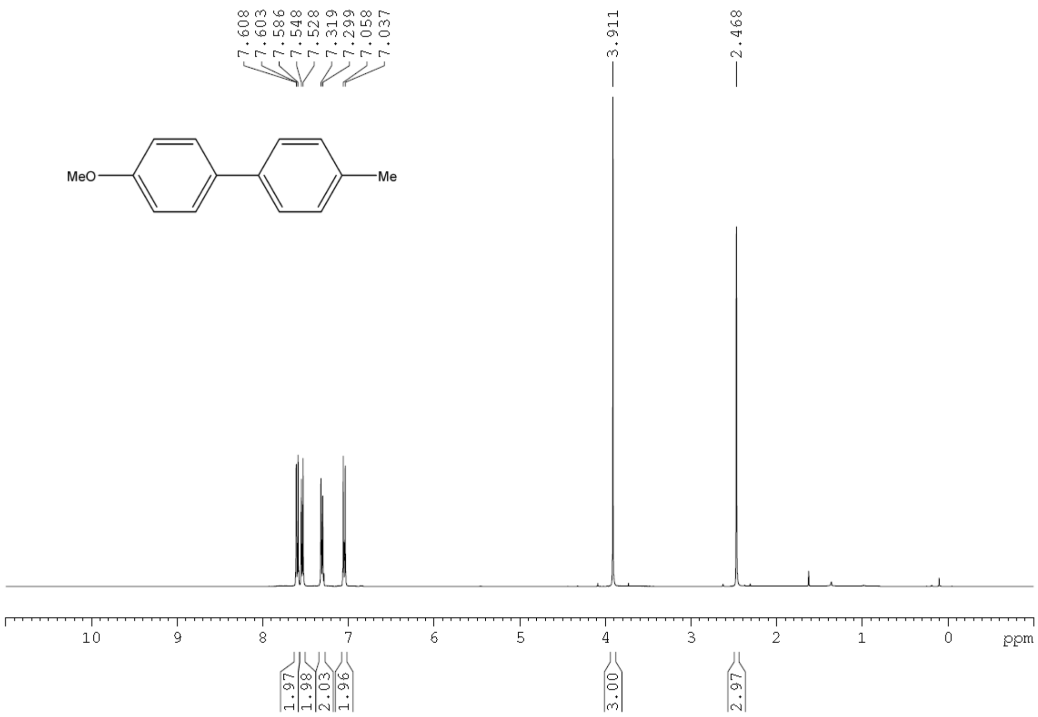


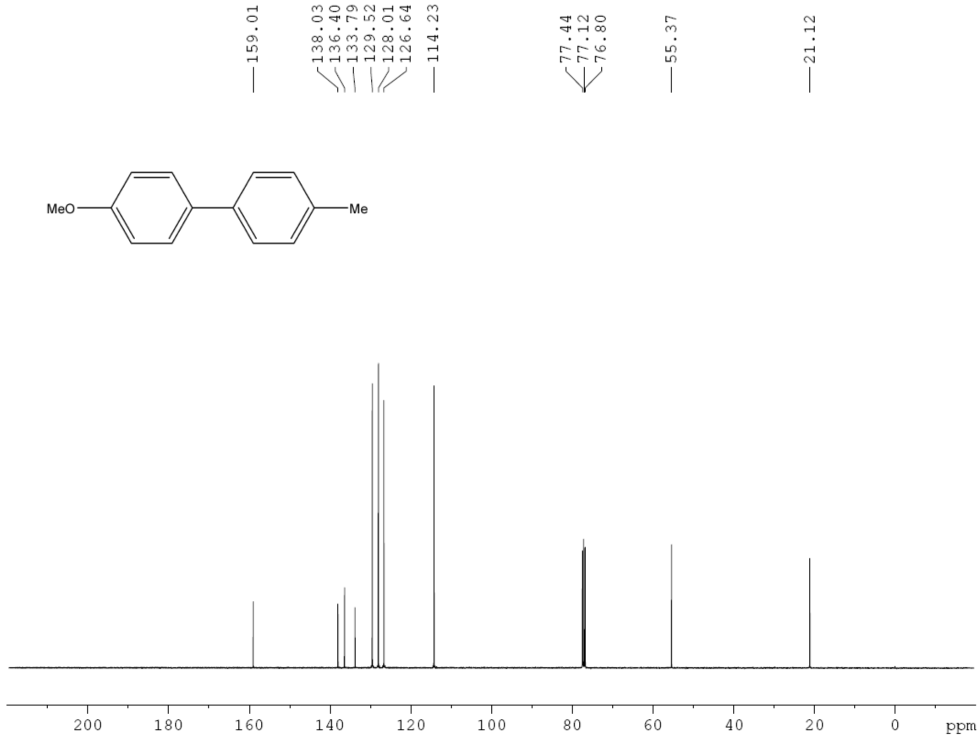
^{1}H NMR and ^{13}C NMR of 4,4’-Dimethylbiphenyl





^{1}H NMR and ^{13}C NMR of 4-Methoxy -4'-methylbiphenyl





The ^1H and ^{13}C spectra were in accordance with those described in literature.

1) Biphenyl

Z. Tang, Q. Hu, *J. Am. Chem. Soc.,* 2004, **126,** 3058

2) 4,4’-Dimethylbiphenyl

L. Wu, B. Li, Y. Huang, H. Zhou, Y. He, Q. Fan, *Org. Lett.* 2006, **8,** 3605.

3) 4-Methylbiphenyl, 4-Methoxybiphenyl and 4-Methoxy-4’-methylbiphenyl

N. Yoshikai, H. Mashima and E. Nakamura, *J. Am. Chem. Soc.,* 2005, **127,** 17978.