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Supplementary Material

Gold/Palladium Bimetallic Alloy Nanoclusters Stabilized by Chitosan as Highly Efficient and Selective Catalyst for Homocoupling of Arylboronic Acid

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1. General

The Au/Pd ratios of chitosan stabilized gold and palladium bimetallic catalyst were analyzed by ICP-AES (LEEMANLABS INC, Profile plus). UV-visible spectra of all samples were measured by JASCO V-670 spectrophotometer at 24 °C immediately and one day after the catalyst preparation. The high-resolution TEM images of all samples were recorded with a JEM-2100F at an accelerating voltage of 200 kV. Typical magnification of the images was 100,000–120,000×. Yields of biphenyl product were determined by GC 2010 (Shimadzu) with Rtx-5MS column (length 30.0 m, inner diameter 0.25 mm and film thickness 0.25 μm) for tracking the kinetic proceeds. Estimated yields of substituted biphenyl and phenol were determined by ^{1}H NMR spectra (400MHz), recorded using JEOL JMN LAMBDA 400 spectrometer with dioxane as an internal standard, $CDCl_3$ and acetone-d6 as solvent at 24 °C. Beside, the substituted biphenyl products at the end of reaction were purified by preparative thin layer chromatography with ethyl acetate in hexane as solvent. Horiba pH/DO meter, D-55 was used to measure the pH of the solutions.

2. Preparation of chitosan stabilized bimetallic Au/Pd catalyst

Chitosan stabilized bimetallic Au/Pd catalyst was prepared by co-reduction method [1] with various Au/Pd concentration (mM) ratios; 0.50/0, 0.45/0.05, 0.42/0.08, 0.40/0.10, 0.37/0.13, and 0.35/0.15. Chitosan (150 mg) was placed in a test tube ($\varnothing$ = 42 mm) and dispersed into 46.5 mL of 0.18% of acetic acid solution in MilliQ water. The solution was further added with the quantitative amount of stock 25 mM $HAuCl_4$ and 12.5 mM $PdCl_2$ to obtain the total metal concentration of 0.5 mM. The resulting solution was stirred for 30 minutes (1600 rpm) at room temperature and maintained at 6 °C before reduction and then, an aqueous solution of $NaBH_4$ (2.5 mL of 9.7 mg, 0.1 M) was rapidly added under 1600 rpm. The color of the solution immediately turned from pale yellow to dark brown, indicating the formation of small Au/Pd nanoclusters. The hydrosol of Au/Pd nanoclusters (0.5 mM) was stored in refrigerator at 5 °C and used for catalytic reactions.

3. Characterization of chitosan stabilized bimetallic Au/Pd catalyst

3.1 Inductively coupled plasma atomic emission spectroscopy (ICP-AES): The chitosan stabilized bimetallic Au/Pd hydrosol (3 mL) was dissolved in 10 mL of aqua regia. The resulting solution was adjusted to the final volume (50 mL, Milli-Q) by using volumetric flask and analyzed by ICP-AES.

3.2 UV-visible spectroscopy: UV-Visible spectra of a series of chitosan stabilized bimetallic Au/Pd hydrosol (0.5 mM) were performed at room temperature without deaerated. The sample was filled into the rectangular quartz cuvette having path length of 1 cm. Milli-Q water was used as a blank.

3.3 Transmission electron microscopy analysis (TEM): The chitosan stabilized bimetallic Au/Pd hydrosol was dropped onto the carbon coated copper grid followed by vacuum drying. The sample was then analyzed by TEM. By counting more than 300 particles, histograms were plotted.

4. Kinetics of the reaction with phenylboronic acid using a series of chitosan stabilized bimetallic Au/Pd hydrosol

Figure S1 showed the time dependent catalytic reactions of phenylboronic acid using catalyst with different Au/Pd ratios. The products in each time intervals were analyzed by GC. Hexadecane was used as internal standard for the calculation of yields.

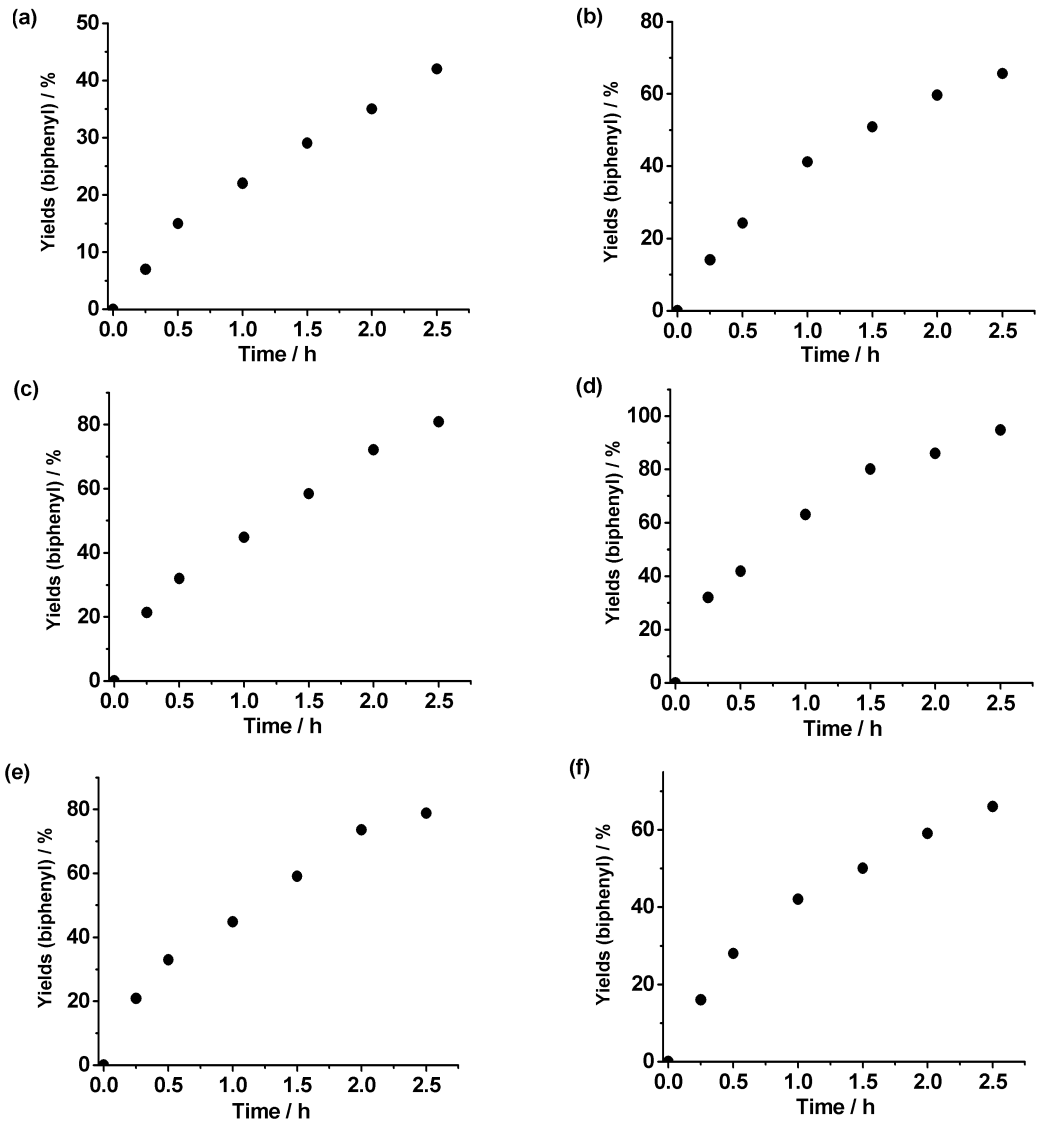

Figure S1: Plot of biphenyl yields versus reaction time intervals using catalyst with different Au/Pd ratios. (a) Au/chit, (b) $Au_{0.91}Pd_{0.09}$/chit, (c) $Au_{0.86}Pd_{0.14}$/chit, (d) $Au_{0.81}Pd_{0.19}$/chit, (e) $Au_{0.77}Pd_{0.23}$/chit, (f) $Au_{0.72}Pd_{0.28}$/chit.

Figure S2 shows the time course of conversion of phenylboronic acids by using catalyst with different Au/Pd ratios. The rate constant was estimated from the slope of –ln(1-C), where C is conversion of phenylboronic acids.

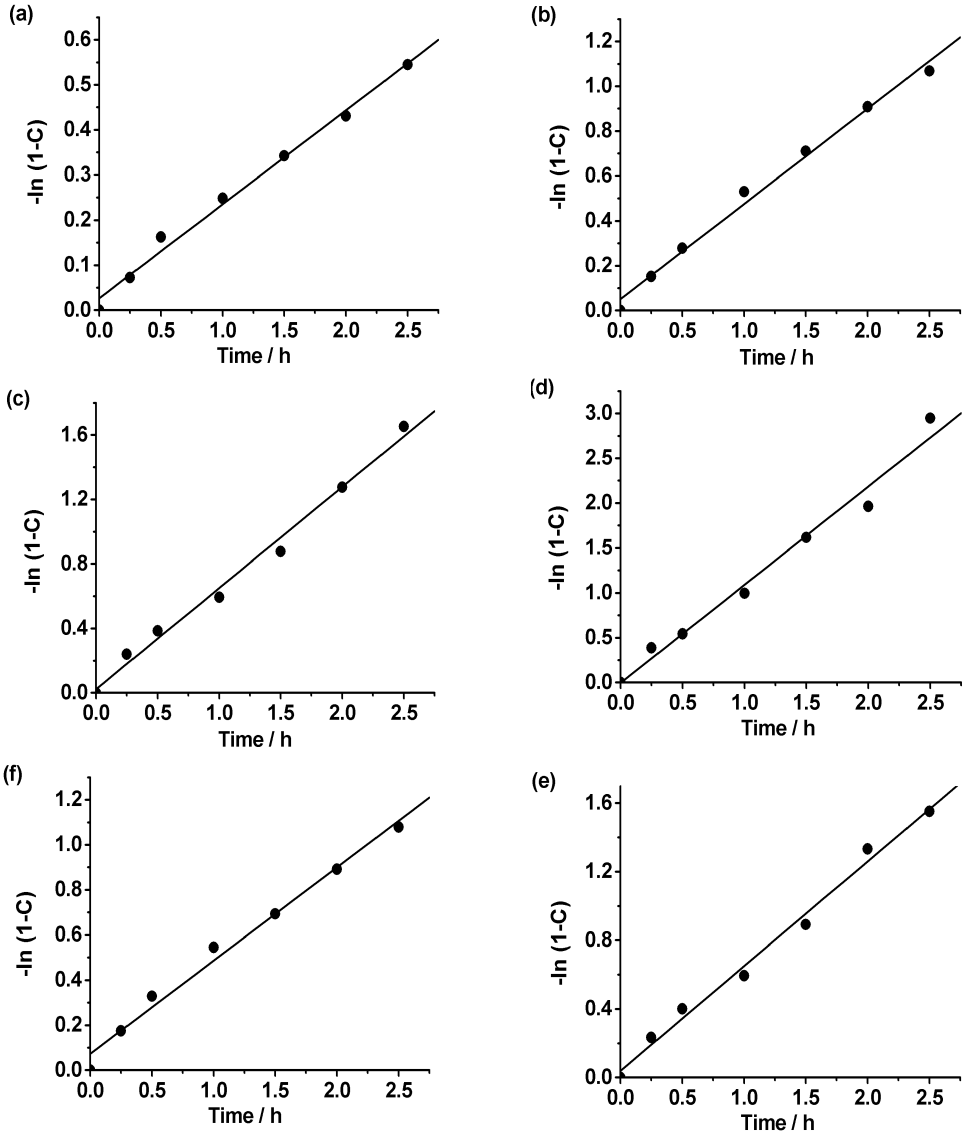

Figure S2: Plot of –ln(1-C) against the time conversion of phenylboronic acid using catalyst with different Au/Pd ratios. (a) Au/chit, (b) $Au_{0.91}Pd_{0.09}$/chit, (c) $Au_{0.86}Pd_{0.14}$/chit, (d) $Au_{0.81}Pd_{0.19}$/chit, (e) $Au_{0.77}Pd_{0.23}$/chit, (f) $Au_{0.72}Pd_{0.28}$/chit

5. Kinetics and Hammett plot analysis of the reaction with *p*-substituted arylboronic acid using $Au_{0.81}Pd_{0.19}$/chit as a catalyst

Figure S3 shows the time dependent catalytic reactions of *p*-substituted arylboronic acid using $Au_{0.81}Pd_{0.19}$/chit as a catalyst. Yields of biphenyl products were analyzed by GC. Hexadecane was used as internal standard to calculate the yields.

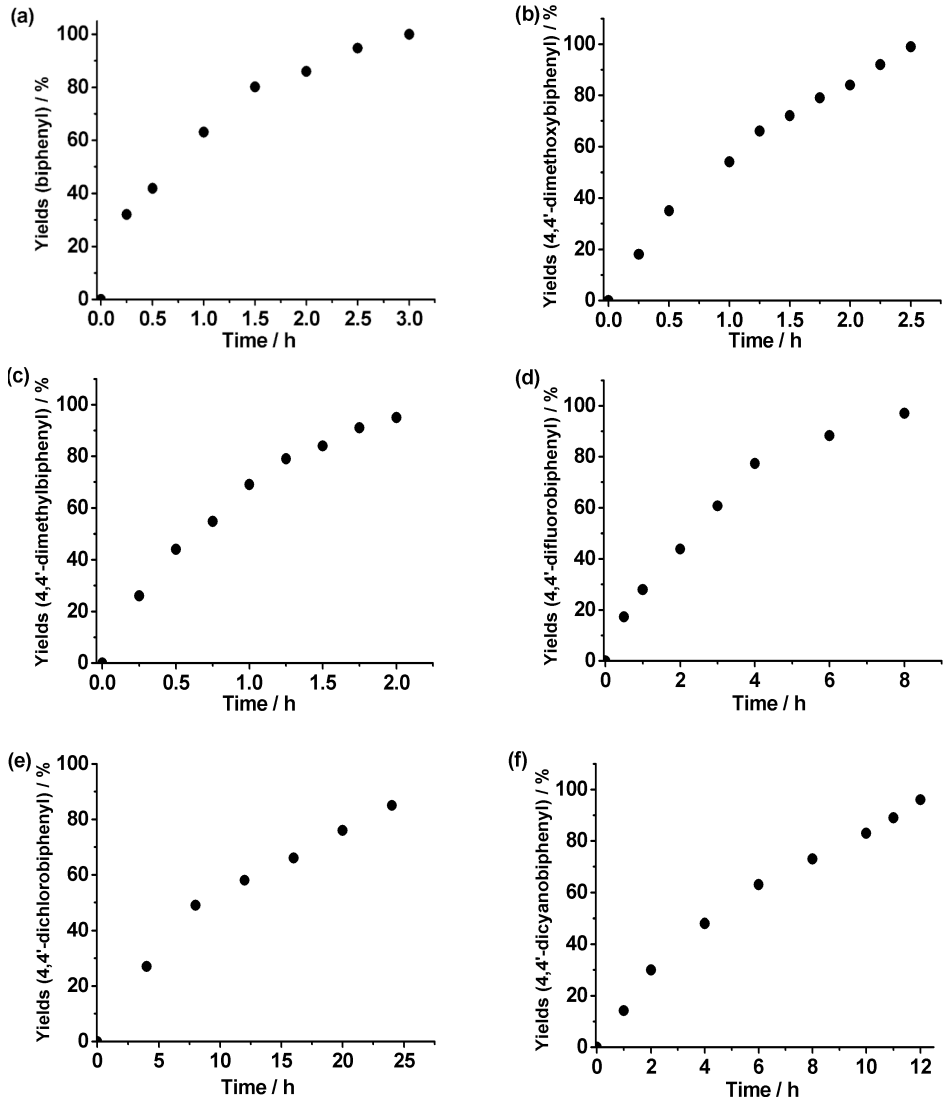

Figure S3: Plot of yield of the biphenyl products versus reaction time intervals by using $Au_{0.81}Pd_{0.19}$/chit as a catalyst. (a) phenylboronic acid, (b) *p*-methoxy phenylboronic acid, (c)

p-methyl phenylboronic acid, (d) *p*-fluoro phenylboronic acid, (e) *p*-chloro phenylboronic acid and (f) *p*-cyano phenylboronic acid.

Figure S4 shows the time course of conversion of *p*-substituted phenylboronic acids. The rate constant was estimated from the slope of –ln(1-C), where C is conversion of *p*-substituted phenylboronic acids. Hammett plots were obtained by plotting lnk/(h-1) against **σ** - or **σ** constants[2] (Figure 5, in manuscript).

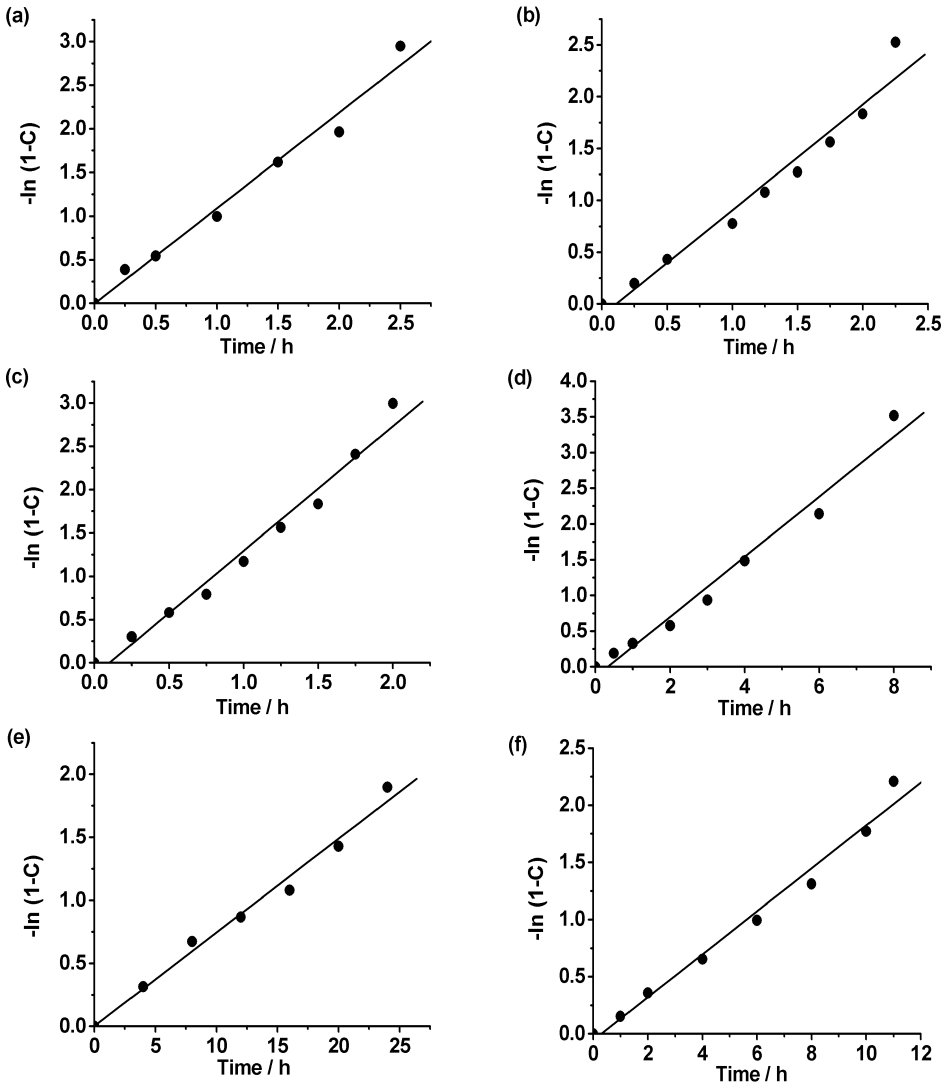

Figure S4: Plot of –ln(1-C) against the time conversion of *p*-substituted phenylboronic acids using $Au_{0.81}Pd_{0.19}$/chit as a catalyst. (a) phenylboronic acid, (b) *p*-methoxy phenylboronic acid, (c) *p*-methyl phenylboronic acid, (d) *p*-fluorophenylboronic acid, (e) *p*-chloro phenylboronic acid and (f) *p*-cyano phenylboronic acid.

References:

[1] A. Morugadoss, H. Sakurai, *J. Mol. Catal. A; Chem.* **2011**, *341*, 1. doi:10.1016/j.molcata.2011.03.019

[2] The Hammett substituent constants were taken from reported literature: C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.* **1991**, *97*, 165. doi:10.1021/cr00002a004