Electronic Supplementary Material (ESI) for Chemical Communications
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Supporting Information:

Supported Au Nanoparticles as Efficient Catalysts for Aerobic Homocoupling of Phenylboronic Acid

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Preparation of Au/MAO. (1) 30.76 g of $Mg(NO_3)_2 \cdot 6H_2O$ and 15 g $Al(NO_3)_3 \cdot 9H_2O$ were dissolved in 400 ml of water, 72 g of urea was added under stirring. After boiling for 8 h, precipitating at room temperature for 12 h, filtrating and washing with large mount of water, the sample obtained was designated as Mg-Al double hydroxide (molar ratio of Mg/Al at 3); (2) 10 g of Mg-Al double hydroxide was added into a solution of $HAuCl_4$ and stirred at room temperature for 8 h. After filtrating, washing with a large amount of water, and drying at room temperature overnight, the obtained solid was treated at 100 °C for 6 h and 400 °C for 3 h. After treating the solid sample in anhydrous solvent of toluene and EtOH with $NaBH_4$ at room temperature for 6 h to eliminate the Au^+ or Au^{3+} species, the sample designated as Au/MAO was obtained. Au loading (0.7 *wt*%) was analyzed by inductively coupled plasma spectroscopy (ICP).

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Preparation of Au/SiO_2, Au/Al_2O_3 and Au/TiO_2. As typical run, solid support of SiO_2 was added to the solution of $HAuCl_4$. After stirring at 80 ºC for 3 h (pH=9.0, adjusted by Na_2CO_3), filtrating and washing at room temperature, drying at 100 ºC for 12 h, and calcining at 400 ºC for 4 h, the sample designated as Au/SiO_2 was obtained. The Au loadings analyzed by ICP were 0.7 wt% for Au/SiO_2, 0.9 wt% for Au/Al_2O_3 and 0.7wt% for Au/TiO_2, respectively.

Poison of surface hydroxyl groups of Au/MAO by triethoxyethylsilane. (Scheme S1) 1g of Au/MAO was dried at 120 ºC under vacuum for 3 h, followed by the addition of 50 mL of anhydrous toluene containing 3g of triethoxyethylsilane. The mixtures were refluxed overnight and collected by rotary evaporation, followed by washing with a large amount of ethanol. The sample obtained was designated as poisoned-Au/MAO. These experiments were carried out in anhydrous conditions to avoid the interaction between triethoxyethylsilane and H_2O.

Sample characterization. X-ray diffraction (XRD) data were collected on a Rigaku D/MAX 2550 diffractometer with Cu KR radiation (λ=1.5418 Å). The contents of Au were determined by ICP with a Perkin-Elmer plasma 40 emission spectrometer. A FEI Titan 80-300 microscope was employed to conduct microscopy and analyses of the samples in transmission electron microscopy (TEM) modes, operating at 300 kV. IR spectra were recorded using a Bruker 66V FTIR spectrometer. XPS spectra were performed on a Thermo ESCALAB 250 with Al Kα radiation at θ=90º for the X-ray sources, the binding energies were calibrated using the C1s peak at 284.9 eV.

Catalytic tests. Aerobic coupling of henylboronic acid were performed in a 100-mL high-pressure autoclave with a magnetic stirrer (1200 rpm). The solid catalysts and substrated were both dried at 100 ºC under vacuum for 3 h before the catalytic reactions. Typically, the substrate, catalyst and solvent were mixed in the reactor. Then the reaction system was heated to a given temperature (the temperature was

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measured with a thermometer in an oil bath) and pure oxygen was introduced and kept at desired pressure. After the reaction, the product was taken out from the reaction system and analysed by gas chromatography (GC-17A and GC-14C, Shimadzu, using a flame ionization detector) with a flexible quartz capillary column coated with OV-17 and FFAP). The recyclability of the catalyst was tested by separating it from the reaction system by centrifugation, washing with large quantity of methanol and drying at 100 °C for 6 h, then the catalyst was reused in the next reaction.

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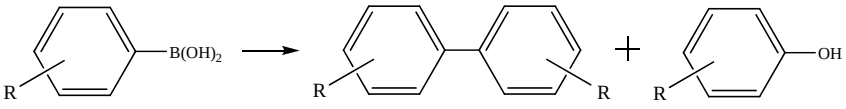
Table S1. Catalytic aerobic homocoupling of phenylboronic acid on Au/MAO using various substrates.[a]



1 **2** **3**

R	Yield (%)[b]		Conversion of **1** (%)[c]
	2	**3**	
m-Me	81.0	19.0	>99.5
m-MeO	75.9	14.1	90.0
p-Me	73.2	12.2	85.4
p-MeO	75.0	8.7	83.7
m-Cl	79.0	10.4	89.4

[a] Reaction conditions: 1 mmol of phenylboronic acid, 6 ml of MeOH solvent, 30 mg of Au catalyst, 1.5 MP of O_2, 100 ºC for 12 h, dodecane as internal standard; [b] GC yields; [c] Conversion of Ph-$B(OH)_2$ from the yield of products.

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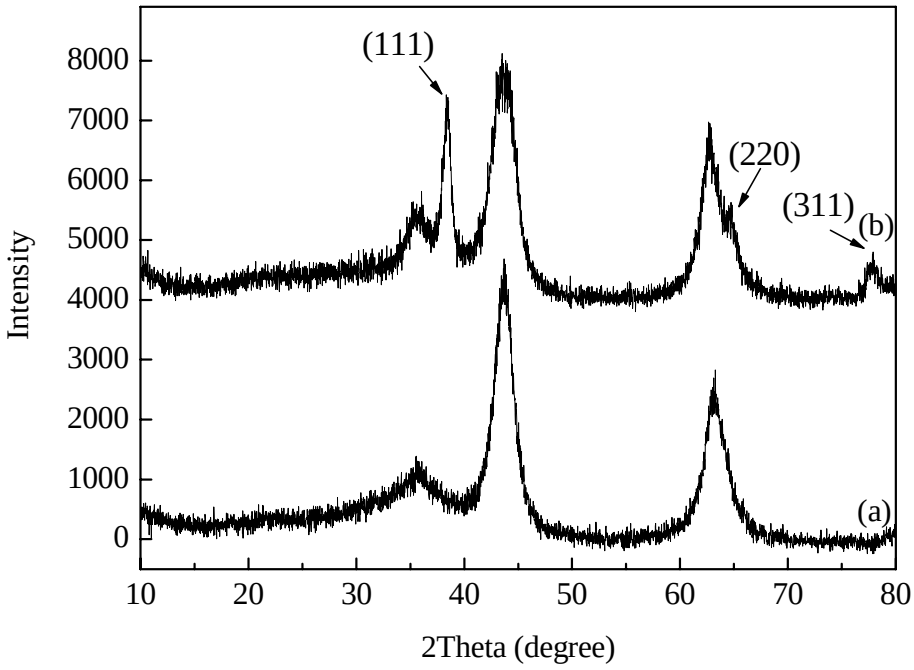

Figure S1. XRD patterns of (a) MAO and (b) Au/MAO samples.

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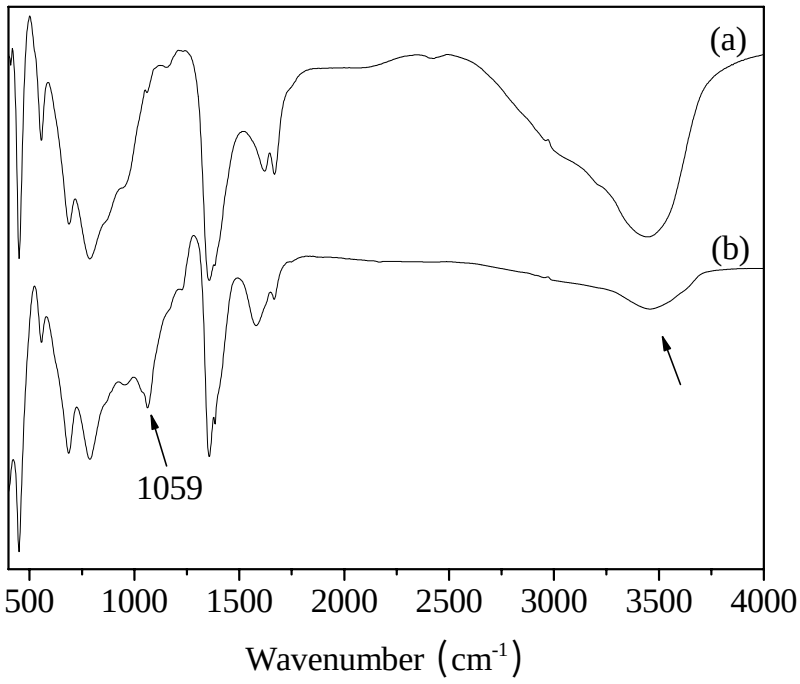

Figure S2. IR spectra of (a) Au/MAO and (b) poisoned-Au/MAO. The IR spectrum of poisoned-Au/MAO gave an additional peak at 1059 cm^{-1}, associated with the presence of Si-O bond. The intensity of the broad peak at 2700-3700 cm^{-1} assigned to the hydroxyl groups of MAO support remarkably decreased for poisoned-Au/MAO, compared with Au/MAO. These results indicate that the most of hydroxyl groups over MAO support have been successfully poisoned by triethoxyethylsilane.

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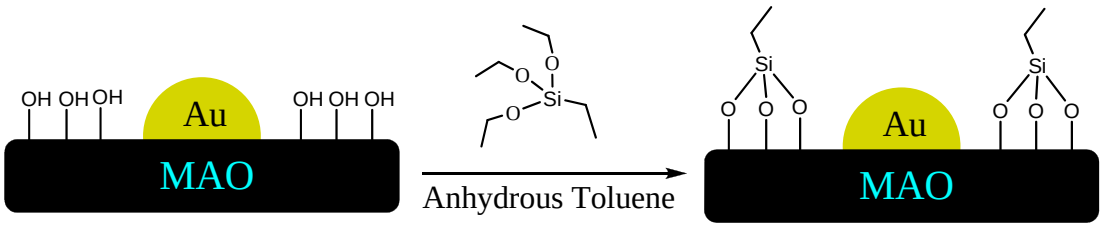

Scheme S1. The poison of the hydroxyl groups over Au/MAO with triethoxyethylsilane.

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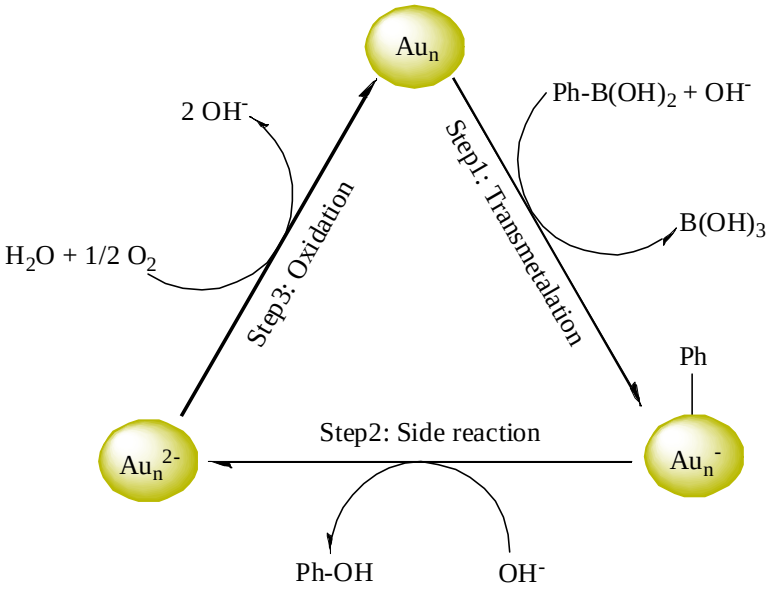

Scheme S2. The proposed mechanism for the side-reaction to form phenol in aerobic coupling of phenylboronic acid over Au/MAO catalyst.