

Supporting Information

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# Ullmann Homocoupling Catalyzed by Gold nanoparticles in Water and Ionic Liquid

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## **Supporting information**

**General Remarks**: All chemicals used for synthetic procedures such as aryl halides, reductants and tetraalkylammonium salts, were commercially available and were used without further purification. Reactions were monitored by GLC and GC-MS techniques by using an Agilent 5890 A gaschromatograph and an Agilent 6850/MSD 5975C instrument, respectively. Both the instruments were equipped with a capillary column HP-5MS (Agilent, 1. 30 m, i.d. 0.25 mm, s.p.t. 0.25  $\mu$ ). NMR spectra were recorded on a Varian Inova 400 MHz spectrometer. UV-vis spectra were recorded on a V-530 spectrophotometer from JASCO, and dynamic light scattering experiments were executed on Zetasizer-Nano S instrument from Malvern. TEM analyses were performed by a Tecnai 12 instrument (120 kV, Tungsten filament) by dropping proper aliquots of colloidal samples on a carbon-Cu grid. XP spectra were acquired by a Theta Probe VG Scientific spectrometer equipped with a monochromatised AlK $\alpha$  source (spot size 300  $\mu$ m). Survey and high-resolution spectra were acquired in constant analyzer energy (CAE) mode with a pass energy of 150 and 100 eV, respectively. The zeta-potential on the nanoparticle surface was measured through a Zetasizer Nano ZS90 apparatus.

Identification of known compounds was made by comparison of their spectral data with those reported in the literature (most of them are identified with the help of the NIST library).

#### **Catalyst preparation**

In general, gold nanoparticles catalysts were prepared *in situ* during catalytic test by reduction of a gold(III) source with a proper reductant. For the protocol in water, preparation procedure was similar to the our previous one adopted for palladium [21a]. For selected experiments gold nanoparticles were prepared *ex situ* according to the following literature procedure [30]: 45 mg of glucose were dissolved in 4 mL of an aqueous solution of CTAB (125 mM) and HAuCl<sub>4</sub> (50 mM). The solution was thermostated at 70°C and the reaction was triggered by increasing the pH through

the addition of 2 mL of NaOH (0.1 M) at 70°C. The relatively low temperature and pH (pH~10) avoided the formation of coloured by-products of glucose alkaline oxidative degradation, thus allowing for characterization of the gold nanoparticles through optical techniques directly in solution. Absorbance spectroscopy in the visible shows the presence of a plasmonic peak centred at 550 nm and dynamic light scattering reveals particle with an average hydrodynamic diameter of 21 nm. The surfactant cetyltrimethylammonium bromide (CTAB) was added to control the Au-NPs growth acting as capping agent. The nanoparticles are stabilised against aggregation by the products of oxidative degradation of glucose (mainly gluconate under these mild conditions) that adsorb on their surface conferring an overall negative charge (the zeta-potential was -25 mV). The gold nanoparticles have been subsequently extensively dialyzed against twice-distilled water thus obtaining a suspension of Au(0) nanoparticles without unreacted gold ions.

#### **Catalysts characterization**

At the end of the coupling reaction, the mixture was analyzed by the transmission electron microscopy (TEM) technique to ascertain both NP core morphology and size dispersion.

Colloidal Au-NPs shape was almost spherical, and nanoparticles showed an appreciable dimensional homogeneity with a mean core diameter of ca. 1 nm (aqueous colloids, fig. 1A) or 20  $\pm 6$  nm (Au-NPs in TBAA, fig. 3B). Below, are reported further TEM images of Au nanoparticles prepared in tetrabutylammonium acetate confirming those sizes an morphology.



Figure S1. TEM images of Au nanoparticles prepared in tetrabutylammonium acetate.

Surface chemical composition information of nanocolloids was obtained by means of X-ray photoelectron Spectroscopy (XPS). The analysis was performed on gold nanoparticles catalysts prepared both *in situ* and *ex situ* and most of results are presented in the text in figures 2B, 3A and 6. Below are reported the XP wide scan spectra for Au-NPs prepared *ex situ* (fig. S2) and for the post-reaction catalyst (protocol in water).



Figure S2. Wide scan XP spectrum of Au-NPs prepared ex situ



Figure S3. Wide scan XP spectrum of the post-reaction catalyst (protocol in water).

#### **Catalytic tests**

In a 1 ml gas-tight vial, equipped with a screw cap and a magnetic bar, aryl halide (0.5 mmol), glucose (0.5 mmol), TBAOH (1.5 mL of 1M solution in water, 1.5 mmol) and gold triacetate (2mol%) were placed. In the case of the reaction in ionic liquids the TBAOH solution was replaced by 0.5 g of TBAA. For a better reproducibility of experiments, the use of a gas-tight vial having a proper capacity (leaving a very small head space) to avoid the formation of droplets of the reaction mixture on the walls of vial, is recommended. The flask was heated under air and under stirring at the reaction temperature for a maximum of 6 hours (see tables 1-2). Then, the reaction mixture was washed with HCl 5% and extracted with dichloromethane. To the organic phase a known amount of an external standard (in almost all cases biphenyl) was added and examined by glc and GC-MS, providing both conversions and products identification by comparison with spectral data reported in the literature. Isolated yields in table 3 were determined by purification of the extracted dichloromethane solutions, after evaporation of the solvent *in vacuo*, with a short pad of silica gel (eluent petroleum ether).

### **Recycling experiments**

In a typical run, at the end of the reaction, the aqueous mixture was extracted with diethyl ether (3x5mL) and the collected organic layers were evaporated under vacuum to isolate the reaction product. To the aqueous layer, containing gold nanoparticles, were added the fresh reagents *p*-iodoanisole, glucose, and TBAOH, and the reaction mixture was stirred at 90°C for the proper time. Results are collected in fig. S4.



Figure S4. Recycling experiments

List of the <sup>1</sup>H NMR signals of the reaction products:

**Biphenyl**. (Lit.<sup>1</sup>) <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.63 (m, 4H), 7.48 (m, 4H), 7.38 (m, 2H).

**4,4'-Dimethylbiphenyl**. (Lit.<sup>1</sup>) <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.49 (d, 4H, *J*= 8.4 Hz), 7.25 (d, 4H, *J*= 8.4 Hz), 2.34 (s, 6H).

**2,2'-dimethylbiphenyl**. (Lit.<sup>1</sup>) <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.27-7.20 (m, 6 H), 7.11-7.09 (m, 2 H), 2.06 (s, 6 H).

**4,4'-Dimethoxybiphenyl.** (Lit.<sup>1</sup>) <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.49 (d, J = 8.8 Hz, 4 H), 6.97 (d, J = 8.4 Hz, 4 H), 3.84 (s, 6 H).

**4,4'-dibromobiphenyl**. (Lit.<sup>2</sup>) <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  7.53 (d, J = 8.6 Hz, 4 H), 7.38 (d, J = 8.6 Hz, 4 H).

**4,4'-Difluorobiphenyl**. (Lit.<sup>3</sup>) <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  7.41 (dd like, 4H, *J*= 9.2 and 4.8 Hz), 7.12 (t like, 4H, *J*=8.2 Hz).

**4,4'-Bis(trifluoromethyl)biphenyl**. (Lit.<sup>4</sup>) <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.72 (m, 8H).

**1,1'-Binaphthyl**. (Lit.<sup>1</sup>) <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.92-7.99 (4H, m), 7.59 (m, 2H), 7.55-7.40 (m, 4H), 7.39 (m, 2H), 7.29 (2H, m).

**2,2'-Dimethoxybiphenyl**. (Lit.<sup>5</sup>) <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.22-7.35 (m, 4H), 6.94-7.04 (m, 4H), 3.76 (s, 6H).

**1,4-Diphenyl-1,3-butadiene**. (Lit.<sup>1</sup>) <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  7.44 (d, *J* = 7.4 Hz, 4 H), 7.33 (t, *J* = 7.6 Hz, 4 H), 7.26-7.22 (m, 2 H), 6.93 (m, 2 H), 6.69 (m, 2 H).

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