

Supplementary Information

CuPd Nanoparticles as a Catalyst in Carbon-Carbon Cross-Coupling Reactions by Facile Oleylamine Synthesis

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Experimental

All reagents, palladium acetate trimer (45.9-48.4% purity, Alfa Aesar), copper acetate hydrate (98% purity, Aldrich), oleylamine (>50% purity, TCI), methanol (Fischer), and hexanes (Fischer) were used without any further purification.

Synthesis of CuPd nanoparticles

Copper acetate hydrate and palladium acetate trimer (0.04 grams of each) were dissolved in a 100 mL round bottom flask containing 10 mL of oleylamine. The solution was then heating to 350°C at a rate of 15°C/min under distillation conditions. The reaction was kept at 350°C for two hours before taken off heat and cooled to room temperature. The particles were rinsed and sonicated in methanol and hexanes multiple times and collected by centrifugation. The particles were dried in an oven vacuum overnight.

Characterization

The as synthesized nanoparticles were characterized using an PANalytical MPD X-Ray diffractometer (Cu K α , $\lambda=1.54$ Å) (XRD) and the data was analyzed using X'Pert Highscore. Inductively coupled plasma optical emission spectroscopy (ICP-OES) data was collected on a Varian MPX Pro. Samples were digested in aqua regia (1:3 ratio of HNO₃ and HCl) and then diluted with DI water. Transmission electron microscopy (TEM) was collected on a Zeiss Libra 120 Plus operating at 120 keV. Samples were prepped with propanol and let air dry. X-Ray photoelectron spectroscopy (XPS) was performed on a Thermo fisher Scientific ESCALAB 250 using a monochromatic Al Kr X-ray. Samples were prepared on indium foil and the data was fit using CasaXPS software.

Suzuki Cross-Coupling Reactions

Aryl halide (0.24 mmol, 1 eq.) and aryl boronic acid (0.29 mmol, 1.2 eq.) are mixed together in a 15 mL microwave tube using 4 mL of H₂O:EtOH (1:1) as solvents. To this was added potassium carbonate (0.72 mmol, 3 eq.) and CuPd nanoparticles (0.48 mg, 2.4 μmol) and the mixture was heated under microwave (250 W, 2.45 MHz) at 120°C for 10 min. The conversion % of the reaction was monitored by the GC-MS analysis. The reaction mixture was further extracted with CH₂Cl₂ (3 × 50 mL) and the organic layers were combined, dried over anhydrous MgSO₄, and filtered. The CH₂Cl₂ solvent was then evaporated under reduced pressure and the final product was purified by means of flash chromatography using hexane:ethyl acetate as eluent to give the corresponding biphenyl products.

Biphenyl (1a): Isolated Yield: 95% ¹H NMR (300 MHz, CDCl₃): δ 7.76-7.73 (m, 2H), 7.61-7.55 (m, 2H), 7.52-7.47 (m, 1H). ¹³C NMR (75.5 MHz, CDCl₃): δ 141.7, 129.2, 127.6, 127.6. GC-MS (EI, 70 eV): m/z(%) = 154 (100) [M⁺].

(4'-Methoxy-biphenyl-4-yl)-dimethyl-amine (1b): Isolated yield: 90% ¹H NMR (300 MHz, CDCl₃): δ 7.52-7.47 (t, 4H), 6.99-6.96 (d, 2H), 6.83-6.80 (d, 2H), 3.85 (s, 3H), 3.00 (s, 6H). ¹³C (75.5 MHz, CDCl₃): δ 158.5, 149.7, 134.2, 129.4, 127.56, 127.56, 114.3, 113.1, 55.5, 40.8.

4-Benzofuran-6-yl-benzonitrile (1c): Isolated yield: 88% ¹H NMR (300 MHz, DMSO-d₆): δ 8.08-8.04 (s, br, 1H), 7.98-7.76 (s, 4H), 7.77-7.60 (dd, 1H), 7.55 (s, 1H), 7.64-7.24 (m, 2H). ¹³C (75.5 MHz, DMSO-d₆): δ 167.8, 155.1, 155.04, 134.6, 132.7, 129.3, 129.07, 128.9, 127.1, 125.6, 125.04, 124.07, 122.1, 111.8, 104.2.

4'-Methylsulfanyl-biphenyl-4-carbaldehyde (1d): Isolated yield: 85% ¹H NMR (300 MHz, CDCl₃): δ 10.02 (s, 1H), 7.9-7.88 (d, 2H), 7.72-7.70 (d, 2H), 7.55-7.52 (d, 2H), 7.33-7.30 (d, 2H), 2.51 (s, 3H). ¹³C (75.5 MHz, CDCl₃): δ 192.01, 146.6, 139.7, 136.2, 135.3, 130.5, 127.8, 127.4, 126.8, 15.7.

4'-ethoxy-[1,1'-biphenyl]-4-carbonitrile (1e): Isolated yield: 91% ¹H NMR (300 MHz, CDCl₃): δ 7.68-7.60 (q, 4H), 7.53-7.50 (d, 2H), 7.0-6.96 (d, 2H), 4.08-4.05 (d, 2H), 1.46-1.41 (t, 3H). ¹³C (75.5 MHz, CDCl₃): δ 159.7, 145.2, 132.7, 131.4, 128.5, 127.2, 119.2, 115.2, 110.2, 63.7, 15.03.

Heck Coupling Reaction

Iodobenzene (50 mg, 0.24 mmol) and styrene (50 mg, 0.48 mmol) are mixed together in a 15 mL microwave tube using 4 mL of H₂O:EtOH (1:1) as solvents. To this was added potassium carbonate (99 mg, 0.72 mmol), CuPd nanoparticles (0.48 mg, 2.4 μmol), and the mixture was heated under microwave (250 W, 2.45 MHz) at 150 °C for 10 min. The conversion % of the reaction was monitored by the GC-MS analysis (94%). The reaction mixture was further extracted with CH₂Cl₂ (3 × 50 mL) and the organic layers were combined, dried over anhydrous MgSO₄, and filtered. The CH₂Cl₂ solvent was then evaporated under reduced pressure and the final product was purified by means of flash chromatography using hexane:ethyl acetate as eluent to give the trans-stilbin in 90% isolated yield.

Trans-stilbin: Isolated Yield: 90% ¹H NMR (300 MHz, CDCl₃): δ 7.57-7.54 (m, 5H), 7.42-7.38 (t, 5H), 7.32-7.27 (m, 2H). ¹³C NMR (75.5 MHz, CDCl₃): δ 137.6, 128.9, 127.9, 126.8. GC-MS (EI, 70 eV): m/z(%) = 180 (100) [M⁺].

Sonogashira Coupling Reaction

Iodobenzene (50 mg, 0.24 mmol) and phenylacetylene (49 mg, 0.48 mmol) are mixed together in a 15 mL microwave tube using 4 mL of H₂O:EtOH (1:1) as solvents. To this was added potassium carbonate (99 mg, 0.72 mmol) and CuPd nanoparticles (0.48 mg, 2.4 μmol) and the mixture was heated under microwave (250 W, 2.45 MHz) at 150 °C for 10 min. The conversion % of the reaction was monitored by the GC-MS analysis (93%). The reaction mixture was further extracted with CH₂Cl₂ (3 × 50 mL) and the organic layers were combined, dried over anhydrous MgSO₄, and filtered. The CH₂Cl₂ solvent was then evaporated under reduced pressure and the final product was purified by means of flash chromatography using hexane:ethyl acetate as eluent to give the diphenylacetylene product in 91% isolated yield.

Diphenylacetylene: Isolated Yield: 91% ¹H NMR (300 MHz, CDCl₃): δ 7.54-7.50 (m, 4H), 7.32-7.29 (m, 6H), ¹³C NMR (75.5 MHz, CDCl₃): δ 131.7, 128.5, 128.2, 123.3, 89.5 GC-MS (EI, 70 eV): m/z(%) = 178 (100) [M⁺].

Procedure for Recycling the Catalyst in Suzuki Cross Coupling Reaction

Iodobenzene (50 mg, 0.24 mmol) and phenylboronic acid (35.4 mg, 0.29 mmol) are mixed together in a 15 mL microwave tube using 4 mL of H₂O:EtOH (1:1) as solvents. To this was added potassium carbonate (99 mg, 0.72 mmol) and CuPd nanoparticles (0.48 mg, 2.4 μmol) and the mixture was heated under microwave (250 W, 2.45 MHz) at 120°C for 10 min. The conversion % of the reaction was monitored by the GC-MS analysis (96%). The reaction mixture was diluted with EtOH (4 mL), the mixture was centrifuged for 5 minutes, and the solution above the catalyst was carefully decanted. The EtOH washing and centrifugation were repeated two more times to insure complete removal of the organic product from the surface of the catalyst. Upon completing this procedure, fresh reagents including iodobenzene, phenylboronic acid and potassium carbonate in a mixture of 4 mL H₂O:EtOH were added to the catalyst and the reaction mixture was heated under microwave at 120°C for 10 min for the next run. The results of the catalyst recycling experiments are summarized in Table S1.

Table S1. Recycling Experiments with CuPd Nanoparticles

Run	Conversion (%)^a
1	95
2	90
3	78
4	60

a. Conversion was determined by GC/MS based upon the consumption of the starting material.