Supporting Materials
for
Superparamagnetic Nanoparticle-Supported Catalysis of Suzuki Cross-Coupling Reactions

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Materials and Instrumentation. Chemicals were purchased from Acros Organics (Somerville, NJ), and Aldrich (Milwaukee, WI) and used as received without further purification. The pluronic[®] P-123 surfactant was a gift from BASF Corporation. Water was obtained from a Milli-Q reagent water system purchased from Millipore Corporation (Milford, MA). ¹H NMR and ¹³C data were obtained on a Varian VXR-300 system with an Oxford wide-bore magnet and the chemical shifts were reported in parts per million (ppm) downfield relative to tetramethylsilane using the residual proton resonance of solvents as the references (¹H NMR): CDCl₃ δ 7.27; CD₂Cl₂ δ 5.32 and (¹³C NMR): CDCl₃ δ 77.2; CD₂Cl₂ δ 54.0. TEM measurements were accomplished with a Hitachi H7100FA operating at an accelerating voltage of 75 or 100kV. Iron oxide nanoparticle specimens were deposited onto Formvar- and silicon-coated, 200 mesh copper grids (Structure Probe, Inc., West Chester, PA) and the edge of the grid touched to a filter paper to wick away most of the solvent. Images were recorded either on conventional photographic films or captured using a Gatan 789 digital camera. Magnification was calibrated using a MAG*I*CAL high resolution magnification standard accurate to 1 x 10E6 X. The permanent magnet (LifeSep[™] 50sx magnetic separator) was purchased from Dexter Magnetic Technologies (Elk Grove Village, IL).

Emulsion Polymerization Synthesis of Core/Shell Iron Oxide Nanoparticles. A solution of pluronic[®] P-123 surfactants (3 g) in deoxygenized Milli-Q water (120 mL) was vigorously stirred at ambient temperature for about 30 min. Then, 11-nm sized γ-Fe₂O₃ nanocrystals coated with oleate (20 mg)¹ in a mixture of styrene (2.25 mL, 20 mmol), 4-vinylbenzyl chloride (VBC) (0.75 mL, 5.32 mmol), and 1,4-divinylbenzene (DVB) (30 μL, 0.21 mmol) were added dropwise to the aforementioned solution. The temperature was raised to 70 °C and 2,2'-azobis(2-methylpropionitrile) (AIBN) (30 μg, 0.183 μmol) was added. After 2 h, 4-*tert*-butylcatechol (10 mg, 60 μmol) was added to quench the polymerization reaction and the mixture was gradually cooled down to room temperature. The core/shell iron oxide nanoparticles were magnetically concentrated using an external permanent magnet (LifeSep[™] 50sx magnetic separator). The collected magnetic nanoparticles were washed with toluene (4 x 30 mL), water (4 x 50 mL) and methanol (4 x 50 mL) subsequently and dried by air to give reddish powders (43 mg).

Preparation of Iron Oxide Nanoparticle Supported-Pd Catalysts. The aforementioned core/shell iron oxide nanoparticles were dissolved in toluene (45 mL) and the resulting solution was heated to reflux. Then, 1-methylimidazole (0.75 mL, 9.41 mmol) in 5 mL of toluene was added. After 16 h, the solution was cooled down to ambient temperature. Nanoparticles were concentrated magnetically by using an external permanent magnet (LifeSep[™] 50sx magnetic separator) and washed with toluene (2 x 50 mL), 0.1 M HCL (2 x 50 mL) and methanol (2 x 50 mL). Iron oxide nanoparticles were then re-dissolved in a mixture of DMF (2 mL) and 1% Na₂CO₃ solution (2 mL) followed by the addition of Pd(OAc)₂ (22 mg, 98 μmol). The temperature was raised to 50 °C. After 16 h, the mixture was cooled down to room temperature and iron oxide nanoparticles were magnetically concentrated by using the permanent magnet. The Pd-Fe₂O₃ complexes were washed with water (5 x 50 mL) and methanol (5 x 50 mL) subsequently.

General Procedures for Suzuki Cross-Coupling Reactions Catalyzed by Iron Oxide Nanoparticle Supported-Pd Catalysts. To a mixture of about 15 mg of Pd-Fe₂O₃ nanoparticles in DMF (2 mL) and 1% Na₂CO₃ solution (2 mL) were added an aryl halide reagent

(79 mmol) and an arylboronic acid (69 mmol). The temperature was raised to 50 °C. After 12 h, the mixture was cooled down to room temperature. Iron oxide nanoparticles were removed magnetically by using an external permanent magnet and air-dried for reuse in the next round of reactions. The solvents were evaporated *in vacuo* and the residues were subjected to flash chromatography purification by using 10% toluene in ethyl acetate.

2-Phenyltoluene (Entries 1, 9, and 16 of Table 1).

IR (CH₂Cl₂ cast) 2919, 2850, 1738, 1462 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 2.40 (s, 3 H), 7.18-7.39 (m, 9 H); ¹³C NMR (CDCl₃, 300 MHz) δ 21.5, 125.3, 127.6, 128.2, 128.4, 128.5, 129.3, 129.7, 133.7, 136.5, 137.2; HREI-MS *m/z* 168.0937, Calcd. for C₁₃H₁₂ 168.0939.

3-Phenyltoluene (Entries 2, 10, and 17 of Table 1).

IR (CH₂Cl₂ cast) 2917, 2849, 1631, 1461 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 2.38 (s, 3H), 7.17-7.30 (m, 9H); ¹³C NMR (CDCl₃, 300 MHz) δ 21.5, 125.5, 128.0, 128.3, 128.8, 129.6, 129.7, 135.6, 138.9; HREI-MS *m/z* 168.0941, Calcd. for C₁₃H₁₂ 168.0939.

2-Phenylanisole (Entry 3, 12, and 18 of Table 1).

IR (CH₂Cl₂ cast) 2916, 2848, 2360, 1653, 1458 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.80, 6.83-7.20 (m, 2 H), 7.26-7.58 (m, 7H); ¹³C NMR (CDCl₃, 300 MHz) δ 56.2, 121.7, 125.6, 127.9, 128.7, 128.7, 128.9, 129.4, 136.5, 157.8; HREI-MS *m/z* 184.0886, Calcd. for C₁₃H₁₂O 184.0888.

4-Phenylanisole (Entries 4, 14 and 20 of Table 1).

IR (CH₂Cl₂ cast) 2917, 2849, 1608, 1451, 1252 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.74 (s, 3 H), 6.90-7.52 (m, 9 H); ¹³C NMR (CDCl₃, 300 MHz) δ 56.1, 115.1, 127.6, 128.0, 128.9, 129.4, 136.5, 161.0; HREI-MS *m/z* 184.0888, Calcd. for C₁₃H₁₂O 184.0888.

2-Acetylbiphenyl (Entry 5 of Table 1).

IR (CH₂Cl₂ cast) 2923, 1701, 1605, 1204 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 2.56 (s, 3 H), 7.26-7.91 (m, 9 H); ¹³C NMR (CDCl₃, 300 MHz) δ 31.1, 127.7, 127.9, 129.4, 129.7, 133.3, 134.0, 136.7, 199.8; EI-MS *m/z* 196.2, Calcd. for C₁₄H₁₂O 196.1.

3-Acetylbiphenyl (Entry 6 of Table 1).

IR (CH₂Cl₂ cast) 2923, 2852, 1689, 1681, 1453, 1234 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 2.38 (s, 3 H), 7.15-8.10 (m, 9 H); HREI-MS *m/z* 196.0885, Calcd. for C₁₄H₁₂O 196.0888.

1-Phenylnaphthalene (Entry 7 of Table 1).

IR (CH₂Cl₂ cast) 2918, 2849, 1737, 1462, 1377, 1125 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.24-7.70 (m, 12 H); HREI-MS *m/z* 204.0937, Calcd. for C₁₆H₁₂ 204.0939.

4-Cyanobiphenyl (Entry 8 of Table 1).

IR (CH₂Cl₂ cast) 2922, 2850, 2349, 1658, 1651 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.22-7.70 (m, 9 H); ¹³C NMR (CDCl₃, 300 MHz) δ 110, 116, 127.6, 127.9, 128.2, 132.8, 136.0, 137.1, 141.0; HREI-MS *m/z* 179.0733, Calcd. for C₁₃H₉N 179.0735.

4-Phenyltoluene (Entry 11 of Table 1).

IR (CH₂Cl₂ cast) 2918, 2849, 1641, 1260, 1025 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 2.41 (s, 3 H), 7.20-7.38 (m, 9 H); ¹³C NMR (CDCl₃, 300 MHz) δ 25.1, 127.6, 127.9, 128.1, 129.4, 130.0, 133.5, 136.7, 137.6; HREI-MS *m/z* 168.0939, Calcd. for C₁₃H₁₂ 168.0939.

3-Phenylanisole (Entries 13 and 19 of Table 1).

IR (CH₂Cl₂ cast) 2919, 2849, 1602, 1440, 1417, 1350 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.8 (s, 3 H), 6.8-7.50 (m, 9 H); ¹³C NMR (CDCl₃, 300 MHz) δ 60.0, 112.1, 113.2, 120.1, 125.7, 129.3, 129.8, 130.0, 136.4, 137.0, 162.1; HREI-MS *m/z* 184.0881, Calcd. for C₁₃H₁₂O 184.0888.

4-Acetylbiphenyl (Entry 15 of Table 1).

IR (CH₂Cl₂ cast) 2920, 2850, 1666, 1582, 1390, 1263 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 2.59 (s, 3 H), 7.6-7.9 (m, 9 H); HREI-MS *m/z* 196.0884, Calcd. for C₁₄H₁₂O 196.0888.

Reference:

1. Lu, J.; Fan, J.; Xu, R.; Roy, S.; Ali, N.; Gao, Y. *J. Colloid Interface Sci.* **2003**, 258, 427.