Electronic Supplementary Information

Suzuki-Miyaura cross-coupling of arenediazonium salts catalyzed by alginate/gellan-stabilized palladium nanoparticles under aerobic conditions in water.

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Experimental Section

General information

Melting points were determined with a Büchi B-545 apparatus and are uncorrected. All of the reagents and solvents are commercially available and were used as purchased, without further purification. Compounds were purified on axially compressed columns, packed with SiO_2 25-40 μm (Macherey Nagel), connected to a Gilson solvent delivery system and to a Gilson refractive index detector, and eluting with *n*-hexane/AcOEt mixtures. ^1H NMR (400.13 MHz) and ^{13}C NMR (100.6 MHz) spectra were recorded with a Brüker Avance 400 spectrometer. Infrared (IR) spectra were recorded on a JASCO FT/IR-430 spectrophotometer. Mass spectra were determined with a QP2010 Gas Chromatograph Mass spectrometer (EI ion source). Determination of Pd at mass 105 was performed by means of a sector field inductively coupled plasma mass spectrometry technique (SF-ICP-MS, Thermo-Fischer, Bremen, Germany) in medium resolution ($m/\Delta m$=3000) to avoid that interferent signals coming from molecular species, *i.e.*, $^{40}Ar^{65}Cu$, could overlap the signal of Pd at the chosen mass and overestimate the actual Pd value. Quantification of Pd was carried out through the external calibration curve. Rhodium (Rh), selected at mass 103, was used as internal standard to keep under control the instrumental drift. Single element calibrant and internal standard were prepared from 1000 mg/mL stock solutions of Pd in 10% HNO_3 and Rh in 10% HCl (High-Purity Standards, Charleston, USA) by dilution with high purity deionized water. Transmission Electron Microscopy (TEM) measurements were performed at Centro Grandi Apparecchiature - UniNetLab, University of Palermo. Ultrathin films with thickness of about 100 nm for TEM observation were prepared cutting samples with a Leica UltraMicrotome EM-UC6. The slices were mounted on 300 mesh copper grid (supplied with lacey carbon film) and then they were observed using a Jeol JEM-2100 under an accelerated voltage of 200 kV. Images were recorder by a Gatan CCD camera. For Focused Ion Beam/Scanning Electron Microscope (FIB/SEM) measurements, air-dried hydrogel beads were gold coated in an Emitech® K550 unit, and examined by a FEI Dualbeam Helios Nanolab (L.I.M.E., "Roma Tre" University, Rome, Italy). The FIB/SEM is equipped with two columns including one electron beam (SEM column) and one ion beam (FIB column), oriented at 52°, and focused on the same point of the sample. This apparatus is capable of selectively ablating (milling process) a previously marked region of the sample by using a focused ion current from a gallium source. The milling process was interrupted every few nanometers to take high resolution pictures to the cross sections by the SEM column. SEM pictures were taken with an operating voltage of 5 KV and an applied current of 43 pA. Gellan gum (Gelzan^{TM}) from *Sphingomonas elodea,* a copolymer of glucose, glucuronic acid and rhamnose residues in a 2:1:1 ratio: [→3)–β–D–glucose–(1→4)–β–D–glucuronic acid–(1→4)–β–D–glucose–(1→4)–α–L–rhamnose–(1→] and alginate sodium salt from brown algae, a copolymer of (1→4) linked β-D-mannuronic acid and α-L-guluronic acid (mannuronic/guluronic ratio 1.56), were purchased from Sigma-Aldrich.

Preparation of alginate/gellan gum beads containing Pd nanoparticles (Pd_{np}/A-G):

Palladium nanoparticles stabilized by alginate/gellan beads (Pd_{np}/**A**-**G**) were prepared dropping 10 mL of a 1% (w/v) solution of gellan gum and sodium alginate (1:1) into 100 mL of a $CaCl_2$ solution (0.24 M), at room temperature, using a syringe with a 0.7 mm diameter needle. Hydrogel beads were harden in the Ca (II) solution for 24 h, then filtered, washed with distilled water and soaked for 48 h in a 50 mL Na_2PdCl_4 aqueous solution (4.1 mM) under magnetic stirring. After this time, the gel particles were recovered by filtration, washed with distilled water and then dehydrated in a series of successive ethanol-water baths of increasing alcohol concentration (10, 30, 50, 70, 90, and 100%) for 15 min each. Reduction of palladium occurred during the dehydratation step with ethanol. Beads were then dried under supercritical CO_2 conditions (70°C and 200 mbar) and used without any further reduction or purification step.

Typical procedure for the preparation of Suzuki-Miyaura cross-coupling product using 0.01 mol% of Pd_{np}/A-G:

4-Acetyldiazobenzene tetrafluoroborate (248 mg, 1 mmol), potassium 4-methoxyphenyltrifluoroborate (214 mg, 1 mmol) and Pd_{np}/**A-G** (14 mg, 0.01 mol%) in water (2 mL) were orbitally stirred for 24 h at 40 °C with a Heidolph Synthesis System. Then, after cooling, the reaction mixture was filtered out. The liquid phase was decanted, diluted with AcOEt, washed with deionized water and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by chromatography (SiO_2, 35 g, *n*-Hexane/AcOEt 96/4 v/v) to give 203,5 mg (90 % yield) of **3a:** mp: 153.7-154.3 °C; IR (KBr) 1672, 1602, 1293, 1819 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.03–8.01 (d, *J* = 8.0 Hz, 2 H), 7.67-7.65 (d, *J* = 8.0 Hz, 2 H), 7.61-7.58 (d, *J* = 8.0 Hz, 2 H), 7.03-7.01 (d, *J* = 8.0 Hz, 2H), 3.88 (s, 3H), 2.64 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 197.7, 159.9, 145.4, 135.4, 132.3, 129.0, 128.4, 126.6, 114.4, 55.4, 26.6; Anal Calcd for $C_{11}H_{10}OS$ C, 69.44; H, 5.30; found C, 69.50; H, 5.35. (Known compound, see: R. Bernini, S. Cacchi, G. Fabrizi, G. Forte, F. Petrucci, A. Prastaro, S. Niembro, A. Shafir and A. Vallribera, *Green Chem.*, 2010, **12**, 150).

Recycling procedure: The mixture was cooled at room temperature, centrifuged (3000 rpm × 20 min.) and the solution was pipetted. Then, the solid supported palladium was washed with methanol (4 × 3 mL), the resulting suspension was centrifuged and the solvent was decanted each time. The recovered solid material was dried under vacuum at 30 °C for 10 min. and reused.

3b: m.p: 97.9-98.4 °C; IR (KBr) 2923, 2360, 2341, 1673, 815 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.06–8.0 (d, *J* = 8.0 Hz, 2H), 7.68-7.66 (d, *J* = 8 Hz, 2H), 7.59-7.57 (d, *J* = 8.0 Hz, 2H), 7.47-7.45 (d, *J* = 8.0 Hz, 2H) 2.66 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 197.8, 141.2, 136.6, 135.1, 134.2, 129.4, 127.6, 29.3. Anal Calcd for $C_{14}H_{11}ClO$ C, 72.89; H, 4.81; found C, 72.85; H, 4.78

3c mp: 120.6-121.4 °C; IR (KBr) 1685, 1605, 1396, 1356, 1322, 823 cm^{-1}; ^1H NMR ($CDCl_3$) 8.09-8.07 (d, *J* = 8.0 Hz, 2H), 7.75-7.70 (m, 6H), 2.67 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 197.6, 144.2, 143.4, 136.6, 129.1, 127.6, 127.5, 125.9, 26.73. Anal Calcd for $C_{15}H_{11}F_3O$ C, 68.19; H, 4.20 found. C, 68.20; H, 4.21. (Known compound, see: B. H. Lipshutz et al. *Org. Lett.*, 2008, **10**, 4279).

3d Oil; IR (neat) 3349, 3054, 2360, 1683, 1265 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.05–8.03 (d, *J = 8.0 Hz*, 2H), 7.71-7.69 (d, *J* = 8.0 Hz, 1H),7.54-7.52 (d, *J* = 8.0 Hz, 2H), 7.42-7.38 (m, 1H), 7.34-7.32 (m, 1 H), 7.28-7.24 (m, 1 H) 2.67 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 197.7, 145.8, 141.5, 136.2, 133.3, 131.1, 129.8, 129.4, 128.1, 127.6, 122.3, 26.7; Anal Calcd for $C_{14}H_{11}BrO$ C, 61.11; H, 4.03; found C, 61.05; H, 3.98.

3e m.p.: 47.8-48.2: °C; IR (KBr) 3340, 1409, 1084 cm^{-1}; ^1H NMR ($CDCl_3$) δ, 8.03 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.62–7.65 (m, 2H), 7.46–7.49 (m, 2H), 7.36–7.42 (m, 1H), 2.64 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 198.1, 146.1, 140.2, 136.2, 129.3, 129.2, 128.6, 127.6, 127.5, 27.0; MS (m/e) 196 (M^+), 181, 152, 127, 102, 91, 76. Anal Calcd for; found. $C_{14}H_{14}O$ C, 84.81; H, 7.12; found C, 84.75; H, 7.07. (Known compound, see: G. E. Robinson and J. M. Vernon, *J. Chem. Soc. C*, 1971, 3363).

3f: m.p.: 178.2-179.4 °C; IR (KBr) 2954, 2912, 1605, 1499, 1257, 1246, 1179, 1038 cm^{-1}; ^1H NMR (CDCl3) δ, 6.95 (d, *J* = 8.0 Hz, 4H), 7.47 (d, *J* = 8.4 Hz, 4H), 3.84 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 158.7, 133.4, 127.7, 114.1, 55.3. MS *m/z* (rel. intensity): 214 (100), 199 (87), 171 (24) Anal Calcd for; $C_{14}H_{14}O_2$ C, 78.48; H, 6.59; found C, 78.46; H, 6.53 (Known compound, see: W.-J. Zhou, K.-H. Wang, J.-X. Wang, Z.-R. Gao, *Tetrahedron*, 2010, **66**, 7633).

3g: m.p.: 115.2-116.4 °C; IR (KBr) 2964, 1603, 1482, 1288, 1250, 1032 cm^{-1}; ^1H NMR (CDCl3) δ, 8.10 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 160.2, 139.3, 133.3, 133.1, 130.2, 129.5, 115.0, 56.2. Anal Calcd for; found. $C_{13}H_{11}ClO$ C, 71.40; H, 5.07; found C, 71.37; H, 5.02. (Known compound, see: W.-J. Zhou, K.-H. Wang, J.-X. Wang, Z.-R. Gao, *Tetrahedron*, 2010, **66**, 7633).

3h: mp: 73.5-73.6 °C; IR (KBr) 2923, 2853, 1607, 1586, 1500, 1287, 1245, 806 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.68 (s, 4H), 7.58-7.56 (d, *J* = 8.0 Hz, 2H), 7.04-7.01 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 159.9, 144.35, 132.2, 128.4, 126.9, 125.77, 125.73, 125.7, 125.6, 123.1, 114.5, 55.4. Anal Calcd for $C_{14}H_{11}F_3O$ C, 66.6; H, 4.4; found C, 66.7; H, 4.5.

3i: mp: 87.3-88.4°C; IR (KBr) 3032, 2904, 1603, 1596, 1483, 911, 823, 757 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.69-7.67 (d, *J* = 8.0 Hz, 2H), 7.54-7.52 (d, *J* = 8.0 Hz, 2H), 7.41 (m, 1H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 159.6, 140.8, 133.3, 130.2, 129.3, 127.9, 127.7, 114.9, 56.2; Anal Calcd for $C_{13}H_{12}O$ C, 84.75; H, 6.57; found C, 84.80; H, 6.62. (Known compound, see: W.-J. Zhou, K.-H. Wang, J.-X. Wang, Z.-R. Gao, *Tetrahedron*, 2010, **66**, 7633).

3j: mp: 114.2-115.4 °C; IR (KBr) 3047, 2988, 2227, 1709, 1608, 1277 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.15 (s, 4H), 8.15 (d, *J* = 8.6 Hz, 2H), 7.74 (m, 4H), 7.65 (d, *J* = 8.6 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 166.1, 144.5, 143.3, 132.7, 130.6, 130.3, 127.9, 127.2, 118.6, 111.8, 61.2, 14.3. MS *m/z* (rel. intensity) 251 (M, 40), 224 (11), 223 (75), 207 (18), 206 (100), 178 (23), 177 (16), 152 (6), 151 (26), 150; Anal Calcd for $C_{14}H_{11}NO$ C, 80.36; H, 5.30; found C, 80.39; H, 5.37. (Known compound, see: M. Amatore and C. Gosmini, *Angew. Chem. Int. Ed.*, 2008, **47**, 2089).

3k: mp: 124-125 °C; ^{1}H NMR ($CDCl_3$) δ 8.12-8.10 (d, *J = 8.0 Hz*, 2H), 7.86-7.84 (d, *J= 8.0 Hz*, 2H), 7.82-7.80 (d, *J* = 8.0 Hz, 2H), 7.52-7.50(d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 145.2, 139.1, 133.4, 132.9, 129.3, 129.2, 127.7, 118.7, 111.5. Anal Calcd for $C_{13}H_8ClN$ C, 73.08; H, 3.77 found C, 73.04; H, 3.73. (Known compound, see: R. Martin and S. L. Buchwald, *J. Am. Chem. Soc.*, 2007, **129**, 3844).

3l: Oil; ^{1}H NMR ($CDCl_3$) δ 7.82 (m, 4H), 7.68-7.66 (d, *J = 8.0 Hz*, 2H), 7.38-7.36 (d, *J = 8.0 Hz*, 2H); ^{13}C NMR ($CDCl_3$) δ 145.2, 144.2, 132.8, 129.9, 128.4, 127.8, 125.6, 124.3, 118.8, 111.8; 247 (100) [M^+], 228(12), 197(8), 177(10) 151(8). Anal Calcd for $C_{14}H_8F_3N$ C, 68.02; H, 3.26; found C, 68.04; H, 3.28. (Known compound, see: L. Liu, Y. Zhang and B. Xin, *J. Org. Chem.*, 2006, **71**, 3994).

3m: mp: 78-79 °C; IR (KBr) 3059, 3034, 1479, 1089 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.12–8.10 (d, *J = 8.0 Hz*, 2H), 7.55-7.53 (d, *J = 8.0 Hz*, 2H), 7.43 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 140.9, 139.0, 133.2, 129.4, 129.2, 127.9, 127.6, . Anal Calcd for $C_{12}H_9Cl$ C, 76.40; H, 4.81; found C, 76.42; H, 4.84. (Known compound, see: I. Klement, M. Rottländer, C. E. Tucker, T. N. Majid and P. Knochel, *Tetrahedron*, 1996, **52**, 7201).

3n: mp: 65.5-66.8 °C; IR (KBr) 3079, 2931, 2109, 1926 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.72 (s, 4H), 7.64-7.62 (d, *J = 8.0 Hz*, 2H), 7.52-7.48 (t, J_1= *8.0 Hz*, J_2= *4.0 Hz*, 2H); 7.45-7.43 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 144.6, 139.7, 129.0, 128.7, 128.2, 127.4, 127.3, 126.1, 125.7. Anal Calcd for $C_{13}H_9F_3$ C, 70.27; H, 4.08 found C, 70.28; H, 4.09. (Known compound, see: O. Navarro et al, *J. Org. Chem.*, 2004, **69**, 3173).

3o: mp: 75.3-77.5 °C; IR (KBr) 2925, 1590, 1240 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.30 (d, *J = 9.2 Hz*, 1H), 7.43 (d, *J = 7.2 Hz*, 2H), 7.29 (d, *J = 8.0 Hz*, 2H), 6.79 (d, *J = 9.2 Hz*, 1H), 6.73 (s, 1H), 3.87 (s, 3H), 2.47 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 169.5, 147.4, 136.3, 131.4, 127.8 (q, *J = 32.9 Hz*), 124.8 (q, *J = 271.0 Hz*), 124.8 (q, *J = 3.7 Hz*), 123.6 (q, *J = 3.9 Hz*), 117.9, 115.5, 101.7, 57.0, 18.6. Anal Calcd for $C_{15}H_{13}F_3O$ C, 67.66; H, 4.92; found C, 67.77; H, 4.90.

3p: mp: 150-153 °C; IR (KBr) 2935, 1379, 808 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.58 (dd, J_1 = 6.4 Hz, J_2 = 2.0 Hz, 2H), 7.52-7.40 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 138.9, 138.5, 133.8, 132.0, 129.1, 128.5, 128.2, 121.9. Anal Calcd for $C_{12}H_8BrCl$ C, 53.87; H, 3.01; found C, 53.95; H, 3.03.

3q: wax; IR (KBr) 2931, 1465, 752 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.70 (d, *J = 8.0 Hz*, 1H), 7.47-7.20 (m, 7H); ^{13}C NMR ($CDCl_3$) δ 139.5, 133.8, 133.2, 132.6, 131.1, 131.0, 129.0, 128.2, 127.5, 122.5. Anal Calcd for $C_{12}H_8BrCl$ C, 53.87; H, 3.01; found C, 53.80; H, 2.99.

3r: oil; IR (neat) 3052, 1462, 1091, 754 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.59 (d, *J = 8.0 Hz*, 2H), 7.52-7.50 (m, 1H), 7.33-7.30 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 139.4, 138.3, 132.0, 131.3, 131.1, 130.0, 128.9, 128.5, 126.9, 121.9.
Anal Calcd for $C_{12}H_8BrCl$ C, 53.87; H, 3.01; found C, 53.76; H, 3.04.