Supporting Information

Nanoporous Palladium Catalyzed Silicon-Based One-Pot Cross-Coupling Reaction of Aryl Iodides with Organosilanes

Zhiwen Li,[†] Sha Lin,[†] Lisha Ji,[†] Zhonghua Zhang,[‡] Xiaomei Zhang,*[,†] and Yi Ding*[,†,‡]

[†] Center for Advanced Energy Materials & Technology Research (AEMT), and School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, (China). E-mail: yding@sdu.edu.cn; zhangxiaomei@sdu.edu.cn

[‡] Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials, Ministry of Education, Shandong University, Jinan 250061, (China).

Preparation of Catalyst.

$Al_{77}Pd_{23}$ (at.%) alloy was prepared by melting pure Al (99.9 wt.%) and pure Pd (99.95 wt.%) in a quartz crucible using a high frequency induction furnace in argon atmosphere. Using a single roller melt-spinning apparatus, the alloy ingots were remelted in a quartz tube by high-frequency induction heating and then rapidly solidified onto a copper roller at a circumferential speed of 18 m s^{-1}. The ribbons obtained were normally 20-50 um in thickness, 2-5 mm in width and several centimeters in length. Sodium hydroxide solution (10 wt %) was used to etch the magnesium in the Al-Pd alloy at room temperature for 6 h.

Experimental Section.

The preparation of 4-methyl-bipheny **4a** was given as a representative example. Nanoporous palladium (30 mg), THF (1.5 mL), MeOH (0.2 mL), and phenylsilane **1f** (1 mmol) were added in a micro reaction vial at room temperature. The mixture was stirred until no bubbles emerged. 1.5 mmol 4-iodotoluene and 3 mmol TBAF in 3 mL THF was added into the system without changing reaction vessel and then the reaction temperature was elevated to 80 ^{o}C. After reacting at this temperature for 6 h, the reaction mixture was concentrated by rotary evaporation and the residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (60~90 ^{o}C) (1:1) as eluent to give **4a**. The recovered catalyst was washed with THF and water and reused without further purification.

Scanning electron microscope (SEM) observation was carried out using a JEOL JSM-6700F instrument operated at an accelerating voltage of 3.0 kV.

NMR signals:

Dimethylphenylsilanol (2a): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64-7.60 (m, 2H), 7.46-7.37 (m, 3H), 3.15 (bs, 1H), 0.41 (s, 6H).

Dimethylphenylmethoxylsilane (2aa): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61-7.54 (m, 2H), 7.42-7.34 (m, 3H), 3.43 (s, 3H), 0.39 (s, 3H), 0.38 (s, 3H).

Dimethylphenylethoxylsilane (2aaa): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65-7.53 (m, 2H), 7.42-7.31 (m, 3H), 3.70-3.63 (t, J = 7.2 Hz, 2H), 1.21-1.15 (q, J = 6.9 Hz, 3H), 0.39 (s, 3H), 0.38 (s, 3H).

Diphenylsilanediols (2b): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73-7.70 (m, 4H), 7.49-7.33 (m, 6H), 2.17 (bs, 2H).

Triphenylsilanols (2c): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62-7.59 (m, 6H), 7.44-7.32 (m, 9H), 2.75-2.73 (bs, 1H).

Triethylsilanol (2d): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.65 (bs, 1H), 1.00-0.95 (t, J = 7.8 Hz, 9H), 0.59 (q, J = 7.8 Hz, 6H).

Tributylsilanol (2e): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.94 (bs, 1H), 1.37-1.30 (m, 12H), 0.92-0.87 (t, J = 6.7 Hz, 9H), 0.62-0.57 (t, J = 8.0 Hz, 6H).

Phenyltrimethoxylsilane (2f): ^{1}H NMR (400 MHz, $CDCl_3$) δ7.71-7.69 (m, 2H), 7.46-7.40 (m, 3H), 3.65 (s, 9H).

Phenyltriethoxylsilane (2ff): ^{1}H NMR (400 MHz, $CDCl_3$) δ7.70-7.66 (m, 2H), 7.40-

7.30 (m, 3H), 3.90-3.83 (q, J = 6.9 Hz, 6H), 1.25-1.20 (t, J = 7.2 Hz, 9H).

4-methyl-bipheny (4a): ^{1}H NMR (300 MHz, $CDCl_3$) δ7.53-7.49 (m, 2H), 7.44-7.41 (m, 2H), 7.40-7.32 (m, 2H), 7.28-7.22 (m, 1H), 7.19-7.15 (m, 2H), 2.33-2.32 (d, 3H).

4-methoxy-biphenyl (4b): ^{1}H NMR (300 MHz, $CDCl_3$) δ7.57-7.51 (m, 4H), 7.44-7.39 (m, 2H), 7.33-7.28 (m, 1H), 7.01-6.56 (m, 2H), 3.86 (s, 3H).

4-fluoro-bipheny (4c): ^{1}H NMR (300 MHz, $CDCl_3$) δ7.51-7.41 (m, 4H), 7.40-7.34 (m, 2H), 7.30-7.25 (m, 1H), 7.09-7.02 (m, 2H).

4-acetyl-biphenyl (4d): ^{1}H NMR (300 MHz, $CDCl_3$) δ8.06-8.02 (m, 2H), 7.71-7.67 (m, 2H), 7.65-7.61 (m, 2H), 7.51-7.38 (m, 3H), 2.64 (s, 3H).

4-nitro-biphenyl (4e): ^{1}H NMR (300 MHz, $CDCl_3$) δ8.33-8.28 (m, 2H), 7.77-7.72 (m, 2H), 7.65-7.61 (m, 2H), 7.53-7.42 (m, 3H).

4-hydroxy-bipheny (4f): ^{1}H NMR (300 MHz, $CDCl_3$) δ7.57-7.53 (m, 2H), 7.51-7.47 (m, 2H), 7.45-7.39 (m, 2H), 7.34-7.28 (m, 1H), 6.94-6.89 (m, 2H).