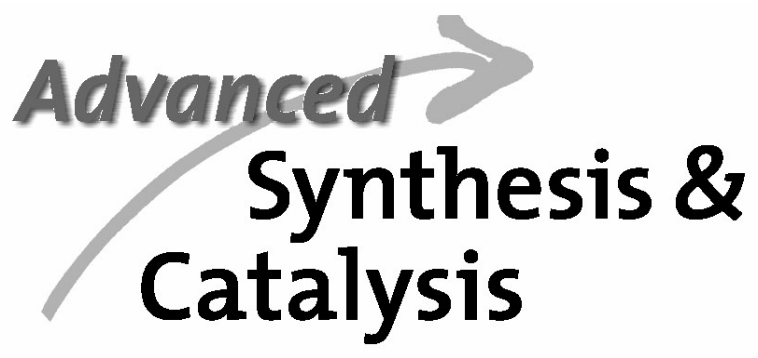

Supporting Information

Supporting information for:

Aerobic Ligand-Free Suzuki Coupling Reaction of Aryl Chlorides Catalyzed by In Situ Generated Palladium Nanoparticles at Room Temperature

Wei Han, Chun Liu* and Zilin Jin

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012 PR China

Chunliu70@yahoo.com

General Information:

All aryl chlorides and arylboronic acids were used as received (Alfa Aesar, Avocado). The PEG-400 was purchased from Acros. All other chemicals were purchased from commercial sources and used without further purification. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Varian Inova 400 spectrometer or a Bruker AVANCE? 400 spectrometer. Chemical shifts are reported in ppm relative to TMS. Mass spectra were obtained using a GCT (EI, 70 eV). Gas chromatography analyses were performed with a Tianmei 7890 Gas Chromatograph with a FID and 50-meter OV-101 column. Transmission electron microscopy (TEM) was performed on a Tecnai 20 microscope operating at 200 kV. UV-vis spectroscopy measurements (300 nm - 700 nm) were performed on a Bejing Rui-Li UV-2100 using quartz cells. All products were isolated by short chromatography on a silica gel (200-300 mesh) column using petroleum ether (60-90 °C), unless otherwise noted. Compounds described in the literature were characterized by comparison of their melting points, ^{1}HNMR, MS spectra or ^{13}C NMR spectra to reported data.

Suzuki Cross-Coupling of Aryl Chlorides with Arylboronic Acids:

General Procedure:

A mixture of aryl chloride (0.5 mmol), arylboronic acid (0.75 mmol), Pd $(OAc)_2$ (2 mol%, 2.2 mg), K_2CO_3 (1 mmol, 138 mg) and PEG-400 (4 g) was stirred at room temperature for the indicated time until complete consumption of starting material as monitored by GC. The mixture was added to brine (15 mL) and extracted four times with diethyl ether (4 ×15 mL). The solvent was concentrated *in vacuo* and the product was isolated by short chromatography on a silica gel (200-300 mesh) column.

Control experiments

In situ-formed palladium nanoparticles catalysis:

A mixture of aryl chloride (0.5 mmol), phenylboronic acid (0.75 mmol, 91.6 mg), $Pd(OAc)_2$ (1 mol%-2 mol%), K_2CO_3 (1 mmol, 138 mg) and PEG-400 (4 g) was stirred at room temperature (45 °C for 2-chloronitrobenzene). The reaction was monitored by GC and TLC. When the reaction reached

completion, the mixture was added to brine (15mL) and extracted four times with diethyl ether (4 ×15 mL), the solvent was evaporated *in vacuo* and the product isolated by short column chromatography.

Preprepared palladium nanocatalysis:

$Pd(OAc)_2$ 2 mol% (1 mol% for entries 3a and 3b in Table 3) was added into deoxygened PEG-400 (4 g) at room temperature (45 ℃ for entries 2a and 2b in Table 3) by magnetic stirring for 12 h (2 h at 45 ℃) under N_2. During the process the colour of the solution turned from light yellow to dark, indicating the generation of palladium nanoparticles. Then, the as-prepared palladium nanoparticles were used to catalyze Suzuki cross-coupling reaction under the same reactants and reactive conditions as above accordingly.

4-Trifluoromethylbiphenyl.[1] White solid: m.p.: 70-71 °C (lit.[1] m.p.: 69.0-69.3 °C); ^{1}H NMR (400 MHz, $CDCl_3$) d: 7.69 (s, 4H), 7.60 (d, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.4Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H) ppm; MS (EI): m/z : 222 [M+], 201 , 153, 152 , 151, 86.

4-Acetylbiphenyl.[1] White solid: m.p.: 121-122 ℃ (lit.[1] m.p.: 120-121 ℃); ^{1}H NMR (400 MHz, $CDCl_3$): d 8.04 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H),7.63 (d, *J* = 7.4 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 1H) ppm;[3] MS (EI): m/z (%): 196 [M+], 181 , 153, 152 , 76.

Biphenyl-2-carbonitrile.[1] Pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): d: 7.53 (d, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.34-7.31 (m, 3H), 7.05-6.98 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): d 145.58, 138.24, 133.85, 132.94, 130.19, 128.86, 128.84, 128.82, 127.66, 118.84, 111.36 ppm.

2-Nitrobiphenyl.[1] Low melting pale yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): d: 7.85 (d, *J* = 8 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.50-7.49 (m, 5H), 7.33-7.31 (m, 2H) ppm; MS (EI): m/z: 199 [M+], 182,171,152,143, 127,115.

4-Nitrobiphenyl.[1] White solid: m.p.: 112-113 °C (lit.[2] m.p.: 114-114.2 °C); ^{1}H NMR (400 MHz, $CDCl_3$) d: 8.31 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* =8.8 Hz, 2H), 7.63 (d, *J* = 6.8 Hz, 2H), 7.52-7.43 (m, 3H) ppm; MS (EI): m/z: 199 [M+], 201, 200, 184, 183, 170, 169, 153, 152, 151, 141, 139, 127, 115, 102, 77.

Biphenyl- 4- carbaldehyde.[3] Low melting white solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) d: 10.04 (s, 1H), 7.94 (d, *J* = 6.8 Hz, 2H), 7.75 (d, *J* = 8.4 Hz,2H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H) ppm; MS (EI): m/z: 182 [M+], 183, 181, 154, 153, 152, 151, 128, 127, 102, 76.

4-Cyanobiphenyl.[4] White solid: m.p.: 82.5-83.5°C (lit.[5] m.p.: 86-87 °C); ^{1}H NMR (400 MHz, $CDCl_3$) d: 7.72 (m, 4H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.4Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 1H) ppm; MS (EI): m/z : 179 [M+], 180 , 178, 177 , 153, 152,151, 140, 127, 113, 99, 85, 76.

Biphenyl.[1] White solid: m.p.69-70°C (lit.[6] m.p.: 71 °C); ^{1}H NMR (400 MHz, $CDCl_3$): d: 7.59 (d, *J* = 8.4 Hz, 4H), 7.44 (t, *J* = 7.4 Hz, 4H), 7.35 (t, *J* = 7.2 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): d: 141.4, 128.9, 127.4, 127.3 ppm.

3-Methoxy-biphenyl.[7] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): d: 7.60 (d, *J* = 8.4 Hz, 2H), 7.43 (t, *J*= 6.8 Hz, 2H), 7.36 (m, 2H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.13 (s, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 3.86 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): d: 160.1, 142.9, 141.3,129.9, 128.9, 127.6, 127.4, 119.9, 113.1, 112.9, 55.5 ppm.

2-Methoxy-4'-nitrobiphenyl.[8] Low melting yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) d: 8.26 (d, *J* = 8.8 Hz, 2H), 7.70 (d, *J* =8.8Hz, 2H), 7.42 (t, *J* =7.8 , 1H), 7.34 (d, *J* = 7.6, 1H), 7.09 (t, *J* = 7.4Hz, 1H), 7.03 (d, *J* = 8.4Hz, 1H), 3.83(s, 3H) ppm; MS (EI): m/z: 229 [M+], 231, 230, 213, 199, 184, 168, 156, 139, 127, 113, 102, 84, 83.

3-Methoxy-4'-nitrobiphenyl.[9] White solid : m.p.: 86-87 °C (lit.[10] m.p.: 89-90 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) d: 8.30 (d, *J* = 6.8 Hz, 2H), 7.74 (d, *J* = 6.8Hz, 2H), 7.43 (t, *J* = 8.0, 1H), 7.21(d, *J* = 7.6Hz, 1H), 7.14(s, 1H), 7.0 (d, *J* = 8.4Hz, 1H), 3.88 (s, 3H); MS (EI): m/z: 229 [M+], 230, 213, 199, 198, 184, 183, 168, 153, 140, 139, 128, 127, 113, 89, 75, 63

4-Methoxy-4'-nitrobiphenyl.[3] Pale yellow solid: m.p.: 107-108 °C (lit.[11] m.p.: 107-108 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) d: 8.28 (d, *J* = 8.8 Hz, 2H), 7.70 (d, *J* = 8.8Hz, 2H), 7.59 (d, *J* = 8.4Hz, 2H),7.03 (d, *J* = 8.8 Hz, 2H), 3.88(s, 3H) ppm; MS (EI): m/z: 229 [M+], 230, 214, 213, 185, 183, 168, 152,140, 139, 128, 89, 63.

1-(3'-Methoxy-biphenyl-4-yl)-ethanone.[12] Low melting pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) d: 8.04 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.4Hz, 2H), 7.39 (t, *J* = 7.6Hz, 1H),7.22 (d, *J* = 7.8 Hz, 1H), 7.15 (s, 1H) 6.98 (d, *J* = 8.0, 1H), 3.88(s, 3H), 2.64 (s, 3H) ppm; MS (EI): m/z: 226 [M+], 227, 212, 211, 184, 183, 182, 158, 154, 140, 139, 113, 76.

3-Methoxy-4'-trifluoromethylbiphenyl.[13] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): d: 7.66 (s, 4H), 7.38 (t, *J*= 6.8 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.10 (s, 1H), 6.94 (d, *J*= 8.4 Hz, 1H), 3.84 (s, 3H) ppm; MS (EI): m/z : 252 [M+], 253, 233, 222, 209, 183, 159, 139, 63.

2-Methyl-4'-nitrobiphenyl.[8] White solid : m.p.: 101-102 °C (lit.[14] m.p.: 102-104 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) d: 8.29 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4Hz, 2H), 7.35 (m, 3H), 7.22(d, *J* = 7.2Hz, 1H), 2.27 (s, 3H) ppm; MS (EI): m/z:213 [M+], 215, 214, 197, 167, 166, 165, 152, 129, 128, 115, 89, 63.

3-Methyl-4'-nitrobiphenyl.[15] Low melting pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) d: 8.30 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 8.4Hz, 2H), 7.43 (m, 3H), 7.27(s,1H), 2.44 (s, 3H) ppm; MS (EI): m/z:213 [M+], 215, 214, 197, 183, 165, 152, 151, 128, 115, 89, 63.

4-Methyl-4'-nitrobiphenyl.[16] Pale yellow solid : m.p.: 139.5-140 °C (lit.[17] m.p.: 141-143 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) d: 8.29 (d, *J* = 8.8 Hz, 2H), 7.73 (d, *J* = 8.8Hz, 2H), 7.54(d, *J* = 8.0 Hz, 2H), 7.31(d, *J* = 7.6Hz, 2H), 2.42 (s, 3H) ppm; MS (EI): m/z:213 [M+], 215, 214, 197, 183, 165, 152, 151, 128, 115, 89, 63.

3,5-Difluoro-4'-nitrobiphenyl.[18] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) d: 8.33 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.8Hz, 2H), 7.26(s, 1H), 7.14 (s, 1H), 6.9(s, 1H) ppm; MS (EI): m/z:235 [M+], 236, 205, 188, 177, 169, 151, 143, 63.

4-Nitro-4'-trifluoromethylbiphenyl.[19] White solid: m.p.: 104-105 °C (lit.[20] m.p.: 107 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) d: 8.35 (d, *J* = 8.8 Hz, 2H), 7.76 (m, 6H) ppm; MS (EI): m/z: 267 [M+], 269, 268, 251, 153, 152, 151, 150, 126, 75, 63.

References:

1. W. Han, C. Liu, Z.-L. Jin, *Org. Lett*. **2007**, *9*, 4005-4007.
2. L. Ackermann, C. J. Gschrei, A. Althammer, M. Riederer, *Chem. Commun.* **2006**, 1419-1421.
3. N. Kataoka, Q. Shelby, J. P. Stambuli, J. F. Hartwig, *J. Org. Chem.* **2002,** *67*, 5553-5566.
4. D. Zim, V. R. Lando, J. Dupont, A. L. Monteiro, *Org. Lett.* **2001,** *3*, 3049-3051.

5. J. P. Wolfe, R. A. Singer, B. H. Yang, S. L. Buchwald, *J. Am. Chem. Soc.* **1999**, *121*, 9550-9561.
6. I. B. Berlman, H. O. Wirth, O. J. Steingraber, *J. Am. Chem. Soc.* **1968**, *90*, 566-569.
7. J.-M. Becht, A. Gissot, A. Wagner, C. Mioskowski, *Chem. Eur. J.* **2003**, *9*, 3209-3215.
8. M. J. Dai, B. Liang, C. H. Wang, J. H. Chen, Z. Yang, *Org. Lett.* **2004,** *6*, 221-224.
9. N. Arai, K. Narasaka, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1707-1714.
10. R.A. Abramovitch, O. V. Koleoso, *J.Chem.Soc.B.* **1969**, 779-785.
11. S. E. Denmark , M. H. Ober, *Org. Lett.* **2003,** *5*, 1357-1360.
12 Y. Hatanaka, K. Goda, Y. Okahara, T. Hiyama, *Tetrahedron* **1994,** *50*, 8301-8316.
13. X. Bei, H. W. Turner, W. H. Weinberg, A. S. Guram, J. L. Petersen, *J. Org. Chem.***1999**, *64*, 6797-6803.
14. S. H. Stephen, E.-B. Karam, T. Lorraine, La V. Edmond, *J. Med. Chem.* **1979**, *22*, 981-987
15. Y. Qian, A. Vogt, S.M. Sebti, A. D. Hamilton, *J. Med. Chem.* **1996**, *39*, 217-223.
16. S. P. H. Mee, V. Lee, J. E. Baldwin, *Chem. Eur. J.* **2005**, *11*, 3294-3308
17. G. E. Robinson et al., *J. Chem. Soc. B* **1971**, 1273-1282.
18. Q. P. Lin, Y. Ch. Chen, Y. Yong et al., *Synlett* **2006**, *10*, 1503-1506.
19. L. F. Liu, Y. H. Zhang, Y.G. Wang, *J. Org. Chem.* **2005,** *70*, 6122-6125.
20. C. Glende, K. Carsten, M. Klein et al, *Mutat. Res.* **2002**, *515*, 15-38.