Supporting Information for

Sulfur-Containing Palladacycles: Efficient Phosphine-Free Catalyst Precursors for the Suzuki Cross-Coupling Reaction at Room Temperature.

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General Methods

All reactions were carried out under an argon atmosphere in oven dried resealable Schlenk tube. 4-MeC_6H_4Br, 4-$MeOC_6H_4Br$, 1-bromonaphtalene, 2-bromonaphtalene, triethylamine, sodium acetate, dimethylacetamide, chlorobenzene, 1-chloronaphtalene, dimethyl sulfoxide and dimethylformamide were purchased from Merck. 3-$CF_3C_6H_4Br$, 2-$CF_3C_6H_4Br$, and NBu_4Br were purchased from Aldrich. 4-$CHOC_6H_4Br$, 4-$C_6H_4C_6H_4Br$, 4-$CF_3C_6H_4Br$, 2,4,dimethylbromobenzene, 4-$MeCOC_6H_4Br$, 4-$MeCOC_6H_4Cl$, 4-$MeOC_6H_4I$, 4-CNC_6H_4Cl, 4-$NO_2C_6H_4Br$, 2-Bromomesitylene, 4-$MeOC_6H_4Cl$, 4-MeC_6H_4Cl, 2-Tolylboronic acid and 4-$NO_2C_6H_4Cl$ were purchased from Across. Cesium fluoride was purchased from Fluka. Phenylboronic acid was prepared according to the previously published procedure[1]. Chemicals were used without further purification. NMR spectra were recorded on a Varian XL300 spectrometer. Infrared spectra were performed in a Bomem B-102 spectrometer. Mass spectra were obtained on a GC/MS Shimadzu QP-5050 (EI, 70eV). Gas chromatography analyses were performed on a Hewlett-Packard-5890 GC with a FID and 30 meter capillary column with a dimethylpolysiloxane stationary phase.

Typical experiment for the Suzuki coupling of aryl halide

An oven-dried resealable Schlenk flask was evacuated and back-filled with argon and charged with K_3PO_4 (424 mg, 2.0 mmol). The flask was evacuated and back-filled with argon and then were added the aryl halide (1.0 mmol) and a solution of **1** (0.67 mg, 0.002 mmol), boronic acid

(1,5 mmol) and additive N(*t*-But)$_4$Br (64.5 mg, 0.2 mmol) in 5 mL of dimethylformamide. The reaction mixture was stirred at 130°C until the starting aryl halide had been completely consumed as judged by GC analysis. The solution was then allowed to cool to room temperature, taken up in ether (20 mL) and washed with aqueous NaOH (1 M, 5 mL) and brine (2x5 mL), and then dried over $MgSO_4$. After filtration, solvent was evaporated to give the respective product.

4-Methylbiphenyl. The coupling of 4-bromotoluene with phenylboronic acid was effected using the general procedure to afford 161 mg (96% yield based on aryl bromide) of the title compound as a white solid, mp 40-41 ^oC (lit. 42-45 ^oC[2], 44-46 ^oC[3]). ^1H NMR (300 MHz, $CDCl_3$) δ 7.62-7.26 (m, 9H), 2.42 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) . δ 141.5, 138.7, 137.3, 129.8, 129.0, 127.31, 127.29, 21.4. IR (neat) ν (cm^{-1}) 3056, 3026, 1519, 1488, 1444, 1403, 1128, 822, 755, 696.GC-MS (IE, 70 eV) m/z (%): 168 (100, M^+), 167 (68), 82(43), 165 (28), 152 (23), 153 (19), 169 (13), 84 (11). The general procedure using 4-bromotoluene and 1.68 mg (0.05 mmol) of **1** at room temperature also generated the title compound (161 mg, 96% yield based on aryl bromide).

4-Nitrobiphenyl. The coupling of 4-bromonitrobenzene with phenylboronic acid was effected using the general procedure to afford 184 mg (92% yield based on aryl bromide) of the title compound as a yellow solid, mp 109-111.5 ^oC (lit. 102-103 ^oC[2], 114-114.5 ^oC[4]). ^1H NMR (300 MHz, $CDCl_3$) δ 8.32-8.29 (m, 2H), 7.76-7.73 (m, 2H), 7.65-7.62 (m, 2H), 7.54-7.27 (m, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 147.9, 147.3, 139.0, 129.5, 129.2, 128.0, 127.7, 124.4. IR (neat) ν (cm^{-1}) 1595, 1513, 1449, 1345, 853, 774, 740, 700.GC-MS (IE, 70 eV) m/z (%): 152 (100), 199 (95, M^+), 169 (37), 151 (30), 76 (28), 141 (27), 153 (26), 51 (26). The general procedure using 4-chloronitrobenzene and 1.68 mg (0.05 mmol) of **1** also generated the title compound (186 mg, 93% yield based on arylchloride) and the general procedure using 4-chloronitrobenzene or 4-bromobenzene and 1.68 mg (0.05 mmol) of **1** at room temperature also generated the title compound (190 mg, 95% yield based on aryl chloride; 196 mg, 98% yield based on aryl bromide).

4-Acetylbiphenyl. The coupling of 4-bromoacetophenone with phenylboronic acid was effected using the general procedure to afford 191 mg (97% yield based on aryl bromide) of the title compound as a white solid, mp 115-118 ^oC (lit. 120-121 ^oC[2], 109-110 ^oC[5]). ^1H NMR (300 MHz, $CDCl_3$) δ 8.08-8.05 (m, 2H), 7.74-7.70 (m, 2H), 7.68-7.65 (m, 2H), 7.53-7.43 (m, 3H), 2.67 (s,

3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 198.1, 146.1, 140.1, 136.1, 129.22, 129.18, 128.5, 127.54, 127.50, 26.9. IR (neat) ν (cm^{-1}) 1680, 1602, 1459, 1263, 836, 765, 720, 690.GC-MS (IE, 70 eV) m/z (%): 181 (100), 152 (54), 196 (49, M^+), 153 (40), 76 (39), 151 (15), 182 (14), 51 (12). The general procedure using 4-chloroacetophenone and 1.68 mg (0.05 mmol) of **1** also generated the title compound (180 mg, 92% yield based on aryl chloride).

4-Methoxybiphenyl. . The coupling of 4-bromoanisole with phenylboronic acid was effected using the general procedure to afford 166 mg (90% yield based on aryl bromide) of the title compound as a white solid, mp 81-83.5 ^oC (lit. 77-78.5 ^oC[2], 83-84 ^oC[3]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58-7.53 (m, 3H), 7.45-7.40 (m, 2H), 7.34-7.26 (m, 2H), 7.01-6.98 (m, 2H), 3.86 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 159.4, 141.1, 134.0, 129.0, 128.4, 127.0, 126.9, 114.5, 55.6. IR (neat) ν (cm^{-1}) 1606, 1521, 1488, 1251, 1035, 834, 760, 688. GC-MS (IE, 70 eV) m/z (%): 184 (100, M^+), 169 (55), 141 (47), 115 (34), 185 (13), 63 (11), 139 (10), 76 (10). The general procedure using 4-bromoanisole and 1.68 mg (0.05 mmol) of **1** at room temperature also generated the title compound (175 mg, 95% yield based on aryl bromide) and general procedure using 4-iodoanisole and 1.68 mg (0.05 mmol) of **1** at room temperature also generated the title compound (171 mg, 93% yield based on aryl iodide).

4-Cyanobiphenyl. The coupling of 4-chlorobenzonitrile with phenylboronic acid was effected using the general procedure to afford 161 mg (90% yield based on aryl chloride) of the title compound as a white solid, mp 89-92 ^oC (lit. 86-87 ^oC[2], 82-84 ^oC[6]). ^{1}H NMR (300 MHz, acetone-d_6) δ 7.77-7.74 (m, 4H), 7.57-7.47 (m, 5H). ^{13}C NMR (75.4 MHz, acetone-d_6) . δ 145.8, 139.1, 132.9, 129.4, 128.9, 128.0, 127.4, 118.9, 111.1. IR (neat) ν (cm^{-1}) 2226, 1605, 1484, 847, 770, 723, 697. GC-MS (IE, 70 eV) m/z (%): 179 (100, M^+), 178 (25), 76 (21), 151 (16), 180 (15), 89 (14), 51 (10), 63 (9). The general procedure using 4-chlorobenzonitrile and 1.68 mg (0.05 mmol) of **1** at room temperature also generated the title compound (165 mg, 92% yield based on aryl chloride).

4-(Trifluoromethyl)biphenyl. The coupling of 4-bromotrifluoromethilbenzene with phenylboronic acid was effected using the general procedure to afford 218 mg (98% yield based on aryl bromide) of the title compound as a white solid, mp 67-67.5 ^oC. ^{1}H NMR (300 MHz,

$CDCl_3$) δ . ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 145.0, 140.1, 129.7, 129.3, 128.5, 127.7, 127.6, 126.0 (q, J=3.69 Hz). IR (neat) ν (cm^{-1}) 1614, 1404, 1326, 1071, 843, 765, 728, 690. GC-MS (IE, 70 eV) m/z (%): 222 (100, M^+), 152 (26), 153 (21), 223 (15), 201 (11), 86 (10), 203 (9), 51 (8).

3-(Trifluoromethyl)biphenyl. The coupling of 3-bromotrifluoromethilbenzene with phenylboronic acid was effected using the general procedure to afford 216 mg (97% yield based on aryl bromide) of the title compound as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.87-7.40 (m, 9H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 142.4, 140.1, 131.7, 130.7, 129.6, 129.3, 128.4, 127.5, 124.3 (q, J=3.86 Hz). IR (film) ν (cm^{-1}) 3062, 3037, 1593, 1484, 1456, 1425, 1335, 1261, 1166, 1126, 1097, 1076, 1046, 899, 805, 759, 701, 660. GC-MS (IE, 70 eV) m/z (%): 222 (100, M^+), 152 (21), 153 (18), 223 (14), 201 (12), 101 (8), 51 (8), 76 (7).

2-(Trifluoromethyl)biphenyl. The coupling of 2-bromotrifluoromethylbenzene with phenylboronic acid was effected using the general procedure to afford 206 mg (93% yield based on aryl bromide) of the title compound as a colorless oil, mp 115-118 ^oC. ^1H NMR (300 MHz, $CDCl_3$) δ 7.86-7.83 (m, 1H), 7.66-7.41 (m, 8H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 141.8, 140.2, 132.4, 131.6, 129.28, 129.26, 128.1, 127.9, 127.6, 126.3 (q, J=5.37 Hz), 122.7. IR (film) ν (cm^{-1}) 3066, 3033, 1682, 1602, 1482, 1316, 1171, 1127, 1110, 1072, 1036, 768, 749, 701, 654.GC-MS (IE, 70 eV) m/z (%): 222 (100, M^+), 201 (37), 202 (17), 152 (16), 100 (15), 51 (15), 223 (14), 183 (12).

2,4-Dimethylbiphenyl. The coupling of 2,4dimethylbromobenzene with phenylboronic acid was effected using the general procedure at room temperature to afford 171 mg (94% yield based on aryl bromide) of the title compound as a pale yellow oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.51-7.39 (m, 3H), 7.29-7.14 (m, 2H), 2,43 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 142.4, 142.0, 135.3, 132.3, 130.8, 130.5, 129.4, 128.3, 128.21, 129.19, 126.9, 21.1, 20.2. IR (neat) ν (cm^{-1}) 3026, 2922, 1601, 1488, 1442, 811, 774, 701, 631.GC-MS (IE, 70 eV) m/z (%): 167 (100), 182 (97, M^+), 165(57), 181 (35), 166 (32), 152 (23), 82 (23), 89 (22).

1-Phenylnaphthalene. The coupling of 1-bromonaphtylwith phenylboronic acid was effected using the general procedure to afford 198 mg (97% yield based on aryl bromide) of the title compound as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.93-7.86 (m, 3H), 7.57-7.43 (m, 9H

). ^{13}C NMR (75.4 MHz, $CDCl_3$) 141.2,140.7, 134.2, 132.1, 130.5, 128.7, 127.7, 127.4, 126.5, 126.2, 125.8. IR (film) ν (cm^{-1}) 3056, 1591, 1494, 1395, 801, 778, 760, 702, 616.GC-MS (IE, 70 eV) m/z (%): 203 (100), 204 (98, M^+), 101 (63), 202 (61), 205 (16), 201 (14), 88 (14), 89 (13).

2-Phenylnaphthalene. The coupling of 2-bromonaphtyl with phenylboronic acid was effected using the general procedure at room temperature to afford 198 mg (97% yield based on aryl bromide) of the title compound as a white solid, mp 97-99^{o}C.. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12-8.11 (m, 1H), 7.99-7.91 (m, 3H), 7.83-7.78 (m, 3H), 7.59-7.52 (m, 4H), 7.47-7.44 (m, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$) 141.4, 138.9, 134.0, 132.9, 129.2, 128.7, 127.9, 127.7, 127.6, 126.6, 126.2, 126.1, 125.9. IR (neat) ν (cm^{-1}) 3056, 1495, 1453, 860, 771, 757, 688. GC-MS (IE, 70 eV) m/z (%): 204 (100, M^+), 202 (35), 203 (29), 101 (24), 205 (17), 102 (11), 89 (10), 88 (9).

p-Terphenyl. . The coupling of 4-bromobiphenyl with phenylboronic acid was effected using the general procedure to afford 229 mg (99% yield based on aryl bromide) of the title compound as a white solid, mp 201-204 ^{o}C. ^{1}H NMR (300 MHz, C_6D_6) δ 7.50 (m, broad, 6H), 7.24-7.15 (m, broad, 8H). IR (neat) ν (cm^{-1}) 1455, 1377, 838, 745, 688. GC-MS (IE, 70 eV) m/z (%): 230 (100, M^+), 231 (21), 115 (16), 228 (14), 229 (12), 101 (9), 226 (8), 152 (8).

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