Supporting Information for

$NiCl_2(PCy_3)_2$: Simple and Efficient Catalyst for the Suzuki Cross-Coupling of Aryl Tosylates and Arylboronic Acids.

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General Methods

All reactions were carried out under an argon atmosphere in oven dried resealable Schlenk tube. 4-$MeCOC_6H_4OH$, 2-$MeO_2CC_6H_4OH$, 4-$NO_2C_6H_4OH$, 3-MeC_6H_4OH and dimethylformamide were purchased from Merck. 4-CNC_6H_4OH, 2, 3, 6-trimethylphenol and 4-*tert*-butylphenol were purchased from Aldrich. 2-MeC_6H_4OH, C_6H_5OH and 4-MeC_6H_4OH, 1-naphtol, 2-naphtol, 4-$MeOC_6H_4OH$ were purchased from Across. 4-BrC_6H_4OH and toluene-4-sulfonyl-chloride were purchased from Fluka. Arylboronic acids were prepared according to the previously published procedure[1]. Chemicals were used without further purification. Dioxane was dried over metallic sodium. 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.

General Procedure for the Synthesis of Aryl Tosylates[2]

To a solution of phenol (10 mmol) in pyridine (10 ml), TsCl (11 mmol) was added portionwise at room temperature and the whole misture was stirred at 45º C overnight. After cooling to room temperature, 25 mL of water was added to the mixture and stirred at room temperature for 3 h. This mixture was diluted with toluene (200 mL) and washed with water (150 mL), 10% aqueous HCl (150 mL x 3), water (150 mL x 2), saturated aqueous $NaHCO_3$ (150mL x

2) and brine (150 mL x 2), and then dried over $MgSO_4$. After filtration, solvent was evaporated to give a solid. Recrystallization from toluene-hexane gave tosylate.

4-Cyanophenyl tosylate. The general procedure gave 2.430 g (89%) of white solid: mp 84– 86 ºC (lit.[3]: 88-90ºC). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.71 (d, J=8.3 Hz, 2H), 7.62 (d, J=8.9 Hz, 2H), 7.35 (d, J=8.0 Hz, 2H), 7.14 (d, J=8.9 Hz, 2H), 2.97 (s, 3H), ^{13}C NMR ($CDCl_3$, 75.4 MHz): 152.4, 146.1, 133.8, 131.6, 130.0, 128.3, 123.4, 117.7, 111.0, 21.7. GC-MS (IE, 70 eV) m/z (%):91 (100), 155 (48), 65 (32), 63 (12), 90 (9), 69 (9), 92 (8), 273 (3, M^+). IR (neat, cm^{-1}) 2925, 2855, 2234, 1596, 1495, 1460, 1371, 1295, 1179, 1156, 1088, 859, 812, 772, 688, 654.

4-Acetylphenyl tosylate. The general procedure gave 2,320 g (80%) of white solid: mp 65-67^{o}C (lit.[2]: 62.5-63.5ºC). ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.81 (d, J=8.6 Hz, 2H), 7.62 (d, J=8.1 Hz, 2H), 7.24 (d, J=7.9 Hz, 2H), 7.00 (d, J=8.6 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): 196.6, 152.8, 145.7, 135.5, 131.9, 130.0, 129.8, 128.3, 122.4, 26.5, 21.6. GC-MS (IE, 70 eV) m/z (%):135 (100), 91 (53), 155 (20), 290 (15, M^+), 65 (15), 136 (11), 79 (8), 92 (6). IR (neat, cm^{-1}) 2925, 2855, 1681, 1595, 1498, 1458, 1379, 1297, 1270, 1270, 1177, 1156, 1092, 867, 816, 759, 687, 651.

Phenyl tosylate. The general procedure gave 2,257 g (91%) of white solid: mp: 89-91^{o}C. ^{1}HNMR ($CDCl_3$, 300 MHz) δ 7.71 (d, J=8.2 Hz, 2H), 7.33-7.27 (m, 5H), 7.00 (d, J=7.7 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): 149.9, 145.7, 132.6, 130.0, 129.9, 128.8, 127.9, 122.6, 22.0. GC–MS (IE, 70 eV) m/z (%) 91 (100), 155 (91), 65 (43), 248 (14, M^+), 63 (10), 51 (9), 92 (7), 89 (6). IR (neat, cm^{-1}) 2907, 2856, 1456, 1379, 1196, 1174, 860, 779, 730, 689, 658.

4-Methylphenyl tosylate. The general procedure gave 2,148 g (82%) of white solid: mp 58-60^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHZ) δ 7.68 (d, J=8.3 Hz, 2H), 7.30 (d, J=7.8 Hz, 2H), 7.06 (d, J=8.1 Hz, 2 H), 6.84 (d, J=8.5 Hz, 2H), 2.43 (s, 3H), 2.29 (s, 3H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): 147.9, 145.2, 136.9, 132.3, 130.0, 129.6, 122.0, 21.6, 20.8. GC–MS (IE, 70 eV) m/z (%) 91 (100), 155 (51), 65 (31), 77 (28), 107 (24), 262 (18, M^+), 79 (14), 52 (11). IR (neat, cm^{-1}) 2926, 2855, 1596, 1504, 1460, 1376, 1199, 1175, 1156, 1099, 864, 831, 788, 726, 696, 654.

3-Methylphenyl tosylate. The general procedure gave 1.965 g (75%) of white solid: mp 60-62°C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.69 (d, J=8.3 Hz, 2H), 7.30-6.99 (m, 4H), 6.71 (d, J=7.4 Hz, 2H), 2.41, (s, 3H), 2.26 (s, 3H). ^{13}C NMR ($CDCl_3$, 75.4 MHz) 149.5, 145.2, 139.8, 132.4, 129.6, 128.3, 127.7, 122.8, 119.0, 21.5, 21.1. GC–MS (IE, 70 eV) m/z (%) 91 (100), 155 (79), 65 (30), 262 (24, M^+), 77 (16), 92 (12), 51 (12), 63 (8). IR (neat, cm^{-1}) 2926, 2855, 1460, 1374, 1197, 1178, 1156, 1095, 889, 789, 710, 668.

2-Methylphenyl tosylate. The general procedure gave 1.965 g (75%) of white solid: mp 59-61°C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.73 (d, J=8.4 Hz, 2H), 7.31 (d, J=8.1 Hz, 2H), 7.04-6.98 (m, 4H), 2.44 (s, 3H), 2.07 (s, 3H). ^{13}C NMR ($CDCl_3$, 75.4 MHz) 148.2, 145.3, 133.0, 131.5, 129.7, 128.3, 126.9, 126.8, 122.2, 21.6, 16.2. GC-MS (IE, 70 eV) m/z (%) 91 (100), 155 (45), 65 (29), 77 (24), 51 (17), 262 (14, M^+), 107 (12), 52 (9). IR (neat, cm^{-1}) 2926, 2855, 1461, 1375, 1195, 1179, 1155, 1089, 874, 787, 751, 711, 661.

1-Naphthyl tosylate. The general procedure gave 2,532 g (85%) of white solid: mp 80-83°C (lit. [4]: 90-92°C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.94 (d, J=7.7 Hz, 1H), 7.84-7.75 (m, 4H), 7.52-7.36 (m, 3H), 7.30-7.21 (m, 3H), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 75.4 MHz) 146.0, 145.7, 135.0, 132.9, 130.1, 128.7, 128.0, 127.6, 127.4, 127.0, 126.9, 125.4, 122.0, 118.7, 21.9. GC-MS (IE, 70 eV) m/z (%) 115 (100), 143 (90), 91 (54), 65 (35), 298 (19, M^+), 89 (18), 155 (17), 63 (17), 144 (12), 116 (12). IR (neat, cm^{-1}) 2925, 2855,1596, 1367,1218, 1178, 1073,1034, 1012, 890, 808, 769, 712, 660.

2,3,6-Trimethylphenyl tosylate. The general procedure gave 2,223 g (77%) of white solid: mp 57-60°C ^{1}H NMR ($CDCl_3$, 300 MHZ) δ 7.83 (d, J=8.3 Hz, 2H), 7.35 (d, J=8.3 Hz, 2H), 6.93 (d, J=7.6 Hz, 2H), 2.46 (s, 3H), 2.20 (s, 3H), 2.10, (s, 3H), 2.01 (s, 3H). ^{13}C NMR ($CDCl_3$, 75.4 MHz) 147.3, 145.0, 136.2, 134.3, 130.7, 129.8, 129.3, 128.2, 128.1, 128.0, 29.7, 21.6, 19.9, 17.1, 14.0. GC–MS (IE, 70 eV) m/z (%) 135 (100), 91 (71), 65 (24), 155 (19), 290 (13, M^+), 79 (12), 136 (11), 77 (9), 92 (8). IR (neat, cm^{-1}) 2933, 2856, 1594, 1461, 1363, 1195, 1174, 1157, 1094, 1055, 893, 817, 776, 728, 670.

2-Naphthyl tosylate: The general procedure gave 2,384 g (80%) of white solid: mp 124-126 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.85-7.82 (t, 1H), 7.79-7.74 (m, 4H), 7.52 (t, 3H), 7.31 (d, J=8.5 Hz, 2H), 7.13 (d, J=8.8 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR ($CDCl_3$, 75.4 MHz) 147.5, 145.7, 133.7, 132.6, 132.1, 130.1, 130.0, 128.8, 128.1, 128.0, 127.1, 126.7, 121.4, 120.3, 22.0. GC-MS (IE, 70 eV) m/z (%):115 (100), 91 (66), 65 (35), 143 (33), 155 (27), 298 (18, M^+), 63 (17), 89 (15), 116 (11). IR (neat, cm^{-1}) 2926, 2855,1596, 1460,1378, 1191, 1145, 1092, 959, 909, 889, 865, 750, 639.

4-Methoxyphenyl tosylate. The general procedure gave 2,303 g (83%) of white solid: mp: 69-71^{o}C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.59 (d, J=8.4 Hz, 2H), 7.21 (d, J=8.1 Hz, 2H), 6.81-6.65 (m, 4H), 3.66, (s, 3H), 2.35 (s, 3H). ^{13}C NMR ($CDCl_3$, 75.4 MHz) 158.1, 145.2, 142.9, 132.1, 129.6, 128.4, 123.2, 114.3, 55.4, 21.6. GC–MS (IE, 70 eV) m/z (%) 123 (100), 65 (19), 95 (16), 91 (15), 278 (10, M^+), 52 (10), 124 (8), 51 (7). IR (neat, cm^{-1}) 2928, 2855, 1592, 1500, 1460, 1378, 1295, 1249, 1169, 1148, 1092, 10243, 817, 730, 706, 680.

4-*tert*-Butylphenyl tosylate. The general procedure gave 2.523 g (83%) of white solid: mp 109-111^{o}C (lit. [5]: 109-110^{o}C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.75 (d, J=8.2 Hz, 2H), 7.35-7.29 (m, 4H), 6.92 (d, J=8.8 Hz, 2H), 2.47 (s, 3H), 1.30 (s, 9H). ^{13}C NMR ($CDCl_3$, 75.4 MHz) 150.4, 147.6, 145.5, 132.9, 130.0, 128.7, 126.8, 121.9, 34.8, 31.6, 22.0. GC–MS (IE, 70 eV) m/z (%) 91 (100), 289 (80), 155 (47), 65 (26). 304 (22, M^+), 109 (19), 290 (14), 121 (13). IR (neat, cm^{-1}) 2962, 2868, 1596, 1504, 1203, 1182, 1094, 1018, 870, 848, 818, 761, 735, 684, 650.

4-Nitrophenyl tosylate. The general procedure gave 2.578 g (88%) of white solid: mp 79-82^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.20 (d, J=9.3 Hz, 2H), 7.74 (d, J=8.2 Hz, 2H), 7.37 (d, J=8.0 Hz, 2H), 7.18 (d, J=8.2 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR ($CDCl_3$, 75.4 MHz) 154.2, 146.6, 146.4, 131.8, 130.4, 128.7, 125.7, 123.5, 22.0. GC–MS (IE, 70 eV) m/z (%) 91 (100), 155 (50), 65 (31), 63 (16), 64(9), 92 (8), 51 (7), 89 (6), 293 (2, M^+). IR (neat, cm^{-1}) 2857, 1617, 1591, 1483, 1462, 1352, 1290, 1200, 1109, 1035, 1009, 812, 762, 690, 665, 631.

4-Bromophenyl tosylate. The general procedure gave 2.453 g (75%) of white solid: mp 69-71^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.69 (d, J=8.3 Hz, 2H), 7.42-7.30 (m, 4H), 6.86 (d,

J=9.0 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR ($CDCl_3$, 75.4 MHz) 148.5, 145.7, 132.6, 131.8, 129.8, 128.5, 124.0, 120.5, 21.7. GC–MS (IE, 70 eV) m/z (%):91 (100), 155 (53), 65 (29), 63 (19), 64 (10), 92 (9), 89 (6), 51 (6), 328 (5, M^+). IR (neat, cm^{-1}) 2926, 2856, 1595, 1477, 1198, 1166, 1094, 1067, 1010, 863, 841, 814, 747, 708, 666.

Methyl-2-tosylbenzoate. The general procedure gave 2.669 g (87%) of white solid: mp 89-90^{o}C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.87 (d, J=7.6 Hz, 2H), 7.71 (d, J=8.4 Hz, 2H), 7.40-7.30 (m, 4H), 7.08 (d, J=8.1 Hz, 2H), 3.80 (s, 3H), 2.44 (s, 3H). ^{13}C NMR ($CDCl_3$, 75.4 MHz) 165.0, 147.7, 145.4, 133.2, 132.4, 131.9, 129.6, 128.4, 127.0, 125.4, 123.8, 52.2, 21.6. GC–MS (IE, 70 eV) m/z (%) 91 (100), 120 (68), 65 (33), 155 (32), 92 (23), 63 (19), 63 (18), 64 (13), 306 (4, M^+). IR (neat, cm^{-1}) 2926, 2856, 2361, 1734, 1596, 1487, 1429, 1373, 1302, 1282, 1198, 1132, 963, 865, 816, 778, 729, 665.

Typical experiment for the Suzuki coupling of aryl tosylates

An oven-dried resealable Schlenk flask was evacuated and back-filled with argon and charged with K_3PO_4 (212 mg, 1.0 mmol), aryl tosylate (0.5 mmol), phenylboronic acid (91.5mg, 0.75mmol), PCy_3 (16.8 mg, 0.06 mmol) and $NiCl_2(PCy_3)_2$ (10.3 mg, 0.015 mmol, 3 mol %). The flask was evacuated, back-filled with argon and then were added 5 mL of dioxane. The reaction mixture was stirred at 130°C until the starting aryl tosylate had been completely consumed as judged by GC or after 60 hours even if starting aryl tosylate remained. 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). The organic layer was dried over $MgSO_4$, filtered, concentrated in vacuo and then the crude material was purified by flash chromatography on silica gel. The procedures described in this section are representative, and thus the yields may differ from those given in Table 1.

4-Methylbiphenyl. The coupling of 4-methylphenyl tosylate with phenylboronic acid was effected using the general procedure to afford 67 mg (80% yield based on aryl tosylate) of the title compound as a white solid, mp 40-41 ^{o}C (lit. 42-45 ^{o}C[6]). ^{1}H 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 141.7, 141.5, 138.6, 130.0,

129.1, 129.0, 128.9, 128.8, 128.3, 128.2, 127.5, 124.6, 21.8. IR (neat) ν (cm^{-1}) 2927, 2853, 1600, 1482, 1376, 1191, 1179, 1093, 930, 792, 753, 698. GC-MS (IE, 70 eV) m/z (%): 168 (100, M^+), 167 (58), 82(38), 165 (25), 152 (24), 153 (18), 169 (14), 166 (9).

3-Methylbiphenyl. The coupling of 3-methylphenyl tosylate with phenylboronic acid was effected using the general procedure to afford 73 mg (87% yield based on aryl tosylate) of the title compound as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74-7.16 (m, 9H), 2.43 (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).

2-Methylbiphenyl. The coupling of 2-methylphenyl tosylate with phenylboronic acid was effected using the general procedure to afford 50 mg (60% yield based on aryl tosylate) of the title compound as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-7.20 (m, 9H), 2.24 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) . δ 141.9, 135.3, 131.5, 130.3, 129.8, 129.2, 128.4, 128.0, 127.2, 126.7, 125.7, 20.4. IR (film) ν (cm^{-1}) 3060, 2927, 2853, 1599, 1480, 1378, 1193, 1180, 1158, 1091, 1010, 873, 748, 701.GC-MS (IE, 70 eV) m/z (%): 168 (100, M^+), 167 (91), 82(55), 153 (41), 165 (40), 152 (32), 51 (15), 63 (14).

4-*tert*-Buthylbiphenyl. The coupling of 4-*tert*-buthylphenyl tosylate with phenylboronic acid was effected using the general procedure to afford 88 mg (84% yield based on aryl tosylate) of the title compound as a white solid, mp 49-50 ^{o}C (lit. 47-49 ^{o}C[6]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67-7.38 (m, 9H), 1.42 (s, 9H). ^{13}C NMR (75.4 MHz, $CDCl_3$) . δ 150.5, 141.3, 138.6, 129.0, 127.3, 127.2, 127.0, 126.0, 34.8, 31.7. IR (neat) ν (cm^{-1}) 2962, 1486, 1179, 836, 766. GC-MS (IE, 70 eV) m/z (%): 195 (100), 83 (43), 210(33, M^+), 167 (29), 196 (17), 152 (12), 165 (12), 155 (12).

2-Carbomethoxybiphenyl. The coupling of methyl-4-tosylbenzoate with phenylboronic acid was effected using the general procedure to afford 50 mg (47% yield based on aryl tosylate) of the title compound as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62-7.33 (m, 8H), 3.67 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) . δ 169.5, 142.7, 141.6, 131.5, 131.0, 130.0, 129.0, 128.6,

127.5, 127.4, 66.1, 52.2. IR (film) ν (cm^{-1}) 2949, 1731, 1478, 1451, 1439, 1431, 1283, 1249, 1126, 1090, 1050, 746, 700. GC-MS (IE, 70 eV) m/z (%): 181 (100), 152 (67), 212 (44, M^+), 76 (41), 153 (38), 151 (23), 51 (20), 75 (15).

4-Acetylbiphenyl. The coupling of 4-acetylphenyl tosilate with phenylboronic acid was effected using the general procedure to afford 93 mg (95% yield based on aryl tosylate) of the title compound as a white solid, mp 115-118 ^oC (lit. 120-121 ^oC[6]). ^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).

4-Methoxybiphenyl. . The coupling of 4-methoxyphenyl tosylate with phenylboronic acid was effected using the general procedure to afford 82 mg (89% yield based on aryl tosylate) of the title compound as a white solid, mp 81-83.5 ^oC (lit. 77-78.5 ^oC[6]). ^1H 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).

4-Cyanobiphenyl. The coupling of 4-cyanophenyl tosylate with phenylboronic acid was effected using the general procedure to afford 85 mg (95% yield based on aryl tosylate) of the title compound as a white solid, mp 89-92 ^oC (lit. 86-87 ^oC[6]). ^1H 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).

1-Phenylnaphthalene. The coupling of 1-naphtyl tosylate with phenylboronic acid was effected using the general procedure to afford 97 mg (95% yield based on aryl tosylate) 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-naphtyl tosylate with phenylboronic acid was effected using the general procedure at room temperature to afford 100 mg (98% yield based on aryl tosylate) of the title compound as a white solid, mp 97-99°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).

4'-Methoxybiphenyltosylate. The compound was prepared according to the previously published procedure[7]. An oven-dried resealable Schlenk flask was evacuated and backfilled with argon and charged with K_3PO_4 (4.24 g, 20.0 mmol), 4-bromophenyltosylate (3.27 g, 10 mmol), 4-methoxyphenylboronic (2.28 g, 15 mmol) and $Pd(OAc)_2$ (11.2 mg, 0.05 mmol, 0.5 mol %). The flask was evacuated and backfilled with argon and then were added 5 mL of dimethylformamide. The reaction mixture was stirred at 130°C for 20 hours. The solution was then allowed to cool to room temperature, taken up in dichloromethane (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 3.36 g of a white solid, mp 130-132°C (95% yield based on 4-bromophenyltosylate). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78-7.77 (m, 2H), 7.76-7.45 (m, 4H), 7.36-7.29 (m, 2H), 7.05-6.97 (m, 4H), 3.87 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) 159.7, 148.6, 145.6, 140.0, 132.7, 132.5, 130.0, 128.8, 128.4, 128.0, 122.9, 114.5, 55.6, 22.0. IR (neat) ν (cm^{-1}) 2854, 1496, 1463, 1377, 1291, 1208, 1192, 1175, 1156, 1094, 1039, 865, 822, 753, 730, 678. GC-MS (IE, 70 eV) m/z (%): 199 (100), 91 (22), 128 (19), 171 (18), 200 (15), 65 (15), 354 (10, M^+), 156 (10).

1-(4'-Methoxyphenyl)-4-(3'-trifluoromethylphenyl)benzene. An oven-dried resealable Schlenk flask was evacuated and back-filled with argon and charged with K_3PO_4 (212 mg, 1.0 mmol), 4'-methoxybiphenyltosylate (177 mg, 0.5 mmol), 3-trifluorophenylboronic acid (143 mg, 0.75mmol), PCy_3 (16.8 mg, 0.06 mmol) and $NiCl_2(PCy_3)_2$ (10.3 mg, 0.015 mmol, 3 mol %). The

flask was evacuated, back-filled with argon and then were added 5 mL of dioxane. The reaction mixture was stirred at 130°for 60 hours. The solution was then allowed to cool to room temperature, taken up in dichloromethane (20 mL) and washed with aqueous NaOH (1 M, 5 mL) and brine (2x5 mL). The organic layer was dried over $MgSO_4$, filtered, concentrated in vacuo and then the crude material was purified by flash chromatography on silica gel to afford 133 mg of a white solid, mp 124-129°C (81% yield based on 4'-methoxybiphenyltosylate). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84-7.50 (m, 10H), 6.99-6.96 (m, 2H), 3.83 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) 159.7, 141.8, 140.8, 138.2, 133.1, 131.2, 130.5, 129.5, 128.6, 127.8, 127.5, 124.1 (q, J=15.90 Hz), 114.6, 55.6. IR (neat) ν (cm^{-1}) 2925, 2854, 1606, 1484, 1338, 1292, 1259, 1171, 1127, 1075, 1037, 832, 803, 696, 683. GC-MS (IE, 70 eV) m/z (%): 328 (100, M^+), 313 (41), 285 (36), 164 (27), 215 (25), 329 (22), 94 (18), 115 (16). Anal. Calcd. for $C_{20}H_{15}F_3O$: C, 73.16; H, 4.60. Found: C, 73.00; H, 4.50.

Competitive Suzuki coupling between *t*-butylphenyl tosylate and 4-tolylchloride

An oven-dried resealable Schlenk flask was evacuated and back-filled with argon and charged with K_3PO_4 (61 mg, 0.29 mmol), *t*-butylphenyltosylate (436 mg, 1.43 mmol), 4-tolylchloride (181 mg, 1.43 mmol), phenylboronic acid (26.5 mg, 0.22 mmol) PCy_3 (4.9 mg, 0.0174 mmol) and $NiCl_2(PCy_3)_2$ (3,0 mg, 0.00435 mmol, 2 mol % based on the phenylboronic acid). The flask was evacuated, back-filled with argon and then were added 5 mL of dioxane. The reaction mixture was stirred at 130°C for 1 hour and then analysed by CG. After 1 hour 0.011 mmol of 4-methylbiphenyl had been generated while the production of 4-*t*-butylbiphenyl was 0.023 mmol.

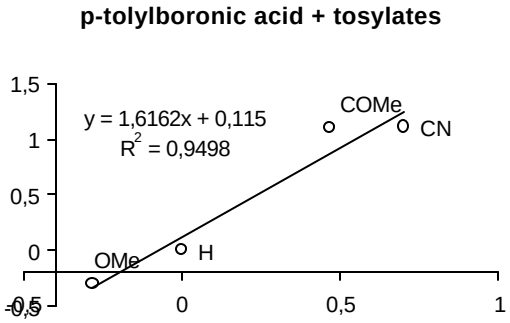
Typical experiment using Hammett parameters: effect of substituents arylboronic acid

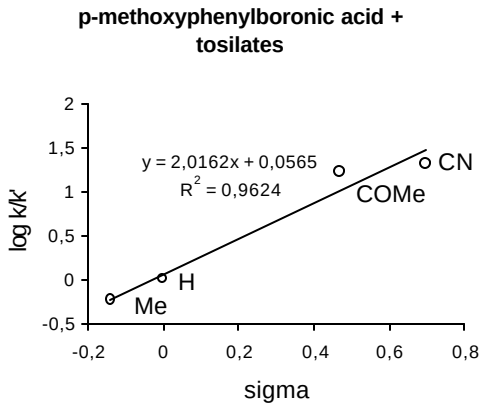
An oven-dried resealable Schlenk flask was evacuated and back-filled with argon and charged with K_3PO_4 (42.4 mg, 0.2 mmol), aryl tosylate (1.0 mmol), aryl boronic acids (1 ml of a solution 25M, 0.025 mmol of each one) PCy_3 (4.9 mg, 0.008 mmol) and $NiCl_2(PCy_3)_2$ (6,9 mg, 0.001 mmol, 0.1 mol % based on the total amount of arylboronic acid). The flask was evacuated, back-

filled with argon and then were added 5 mL of dioxane. The reaction mixture was stirred at 130°C and the reaction profile was monitored by CG.

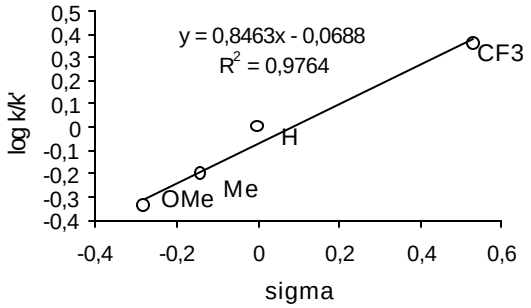
Typical experiment using Hammett parameters: effect of substituents aryl tosylates

An oven-dried resealable Schlenk flask was evacuated and back-filled with argon and charged with K_3PO_4 (42.4 mg, 0.2 mmol), arylboronic acid (1.0 mmol), aryl tosylates (1 ml of a solution 25M, 0.025 mmol of each one) PCy_3 (4.9 mg, 0.008 mmol) and $NiCl_2(PCy_3)_2$ (6,9 mg, 0.001 mmol, 0.1 mol % based on the total amount of aryl tosylate). The flask was evacuated, back-filled with argon and then were added 5 mL of dioxane. The reaction mixture was stirred at 130°C and the reaction profile was monitored by CG.

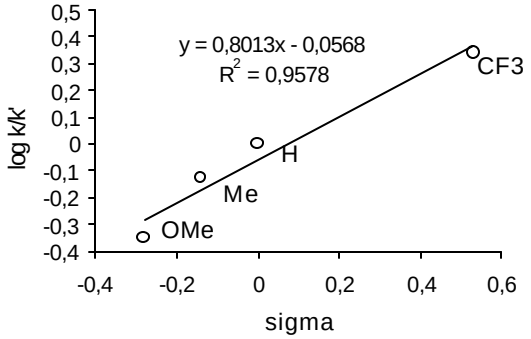




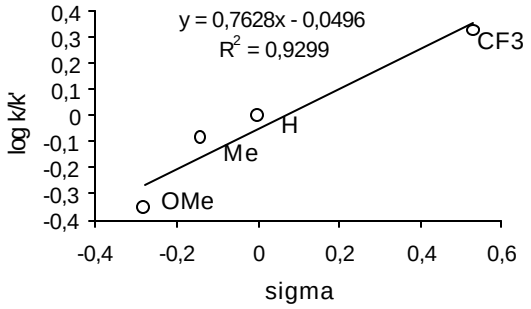
4-methylphenyl tosylate + arylboronic acids



phenyl tosylate + arylboronic acids



4-cyanophenyl tosylate + arylboronic acids



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