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Supporting Information

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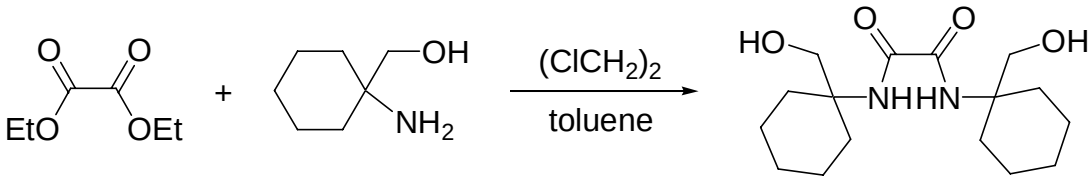
A new N-heterocyclic carbene ligand with flexible steric bulk allows room temperature Suzuki cross-coupling of sterically hindered arylchlorides

Gereon Altenhoff, Richard Goddard, Christian Lehmann, Frank Glorius

General remarks:

All chemicals, except 1-(4-chloro-3,5-dimethylphenyl)ethanone, which was synthesized from 2-chloro-1,3-dimethyl-benzene via Friedel-Crafts acylation,[1] were commercial and used as received. THF was distilled from sodium-potassium alloy under argon atmosphere. Water was degassed by three freeze-pump-thaw cycles.
All reactions were carried out in an argon filled glove box or under an argon atmosphere.

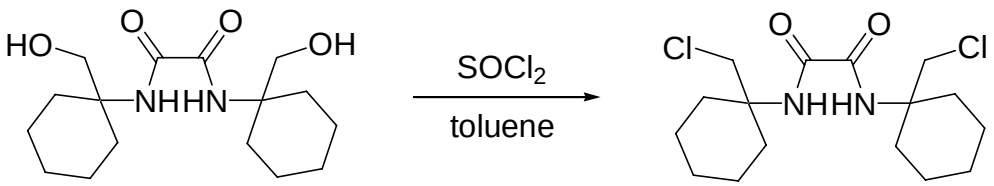
Synthesis of imidazolium triflate 2:



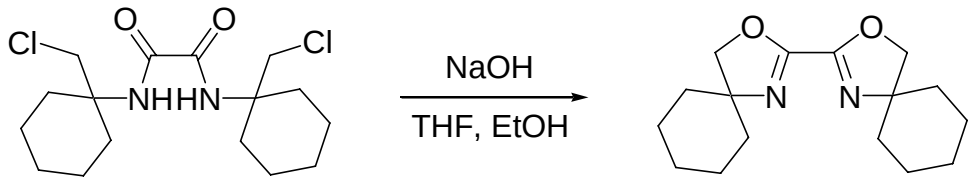
3

Synthesis of the amidoalcohol: Diethyl oxalate and aminoalcohol **3** were stirred in a toluene/1,2-dichloroethane mixture (50 mL, 75 mL) at 80 °C for 30 h (the reaction is complete in a much shorter time!). After the clear solution was cooled to r.t. the solvent was evaporated in vacuo and the residue was chromatographed on silica gel (4 x 15 cm, EtOAc/MeOH 20:1 to 7:1) giving 2.80 g (84%) of the amidoalcohol as a yellowish solid.

R_f = 0.64 (CH_2Cl_2/MeOH 10:1); IR (KBr) 3429, 3349, 3054, 2966, 2934, 2860, 1664, 1514, 1453, 1045, 847, 703, 629; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 2H, NH), 3.84 (s, 2H, OH), 3.72 (s, 4H, OCH_2), 1.93-1.88 (m, 4H, CH_2), 1.60-1.33 (m, 16H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8 (C=O), 68.3 (CH_2O), 58.5 (CN), 31.9 (CH_2), 25.4 (CH_2), 21.4 (CH_2); MS (EI), *m/z* (%) 312 (M^+, 3), 281 (76), 201 (11), 169 (100), 156 (11), 141 (5), 124 (8), 98 (94), 95 (43), 81 (23), 67 (12), 55 (11); HRMS (EI) calcd for $C_{16}H_{28}N_2O_4$: 312.2049, found 312.2051.



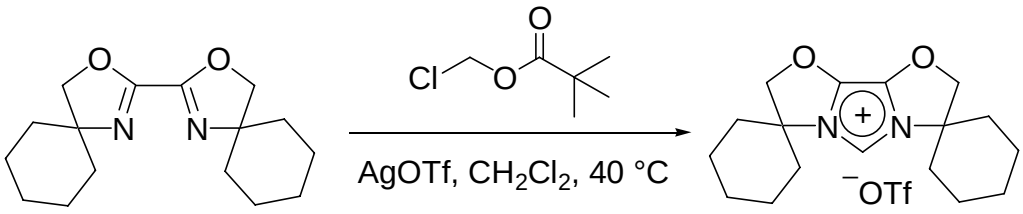
Synthesis of the amidochloride: To a suspension of amidoalcohol in toluene was added $SOCl_2$ at 60 °C. The solution was stirred at 60 °C for 1 h and then at 90 °C for 3 h. After the solution was cooled to r.t. it was added to a 20% (w/v) aq. solution of KOH (200 mL). Layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 200 mL). The combined organic phases were washed with brine (200 mL) and dried over Na_2SO_4. Filtration through a pad of Celite, folled by evaporation of the solvent gave 2.80 g (93%) of the amidochloride as a colorless solid.
R_f = 0.78 (CH_2Cl_2); IR (KBr) 3352, 2941, 2861, 1673, 1507, 1452, 737, 668, 606, 532; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 2H, NH), 3.87 (s, 4H, $ClCH_2$), 2.20-2.17 (m, 4H, CH_2), 1.64-1.41 (m, 14H, CH_2), 1.33-1.29 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2 (C=O), 56.6 (CN), 49.2 ($ClCH_2$), 32.3 (CH_2), 25.2 (CH_2), 21.4 (CH_2); MS (EI), *m*/*z* (%) 350 (6), 348 (M^+, 8), 313 (10), 299 (31), 219 (20), 174 (22), 169 (29), 131 (15), 95 (100), 89 (39), 81 (34), 67 (14); HRMS (EI) calcd for $C_{16}H_{26}N_2O_2$: 348.1371, found 348.1370.



4

*Synthesis of bioxazoline **4***: To a solution of amidochloride (2.7 g, 7.7 mmol) in THF (120 mL) was added a solution of NaOH (0.65 g, 16.2 mmol) in EtOH (40mL). After stirring at r.t. for 20 min the solution was heated to 80 °C for 1.5 h. The solution was cooled to r.t. and the solvent evaporated in vacuo. The residue was taken up in MTBE (400 mL), washed with a sat. aq. solution of Na_2CO_3 (100 mL) and the organic phase was dried over Na_2SO_4. Evaporation of the solvent gave 2.05 g (96%) of bioxazoline **4** as colorless crystals.
R_f = 0.59 (EtOAc); IR (KBr) 2930, 2853, 1623, 1453, 1106, 947, 793, 613; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.14 (s, 4H, OCH_2), 1.84-1.73 (m, 8H, CH_2), 1.62-1.51 (m, 6H,

CH_2), 1.40-1.24 (m, 6H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2 (C=O), 78.1 (CH_2O), 72.0 (CN), 37.2 (CH_2), 25.0 (CH_2), 22.7 (CH_2); MS (EI), *m*/*z* (%) 276 (M^+, 100), 248 (44), 234 (92), 220 (51), 205 (21), 193 (8), 180 (34), 166 (22), 153 (39), 138 (7), 124 (28), 110 (49), 95 (70), 81 (71), 67 (66), 55 (45); HRMS (EI) calcd for $C_{16}H_{24}N_2O_2$: 276.1838, found 276.1839.



4 **2**

*Synthesis of imidazolium triflate **2***: To a suspension of AgOTf (2.16 g, 8.4 mmol) in CH_2Cl_2 (30 mL) was added chloromethyl pivalate (1.25 mL, 8.4 mmol) and the remaining suspension was stirred for 45 min. After filtration the filtrate was added to bioxazoline **4** (1.60 g, 5.8 mmol) and the solution was stirred in a sealed tube in the dark at 40 °C for 20 h. After the solution was cooled to r.t. the solvent was evaporated in vacuo and the resulting oil was chromatographed on silica gel (2.5 x 10 cm, CH_2Cl_2/MeOH 20:1 to 10:1). Subsequent crystallization from a solvent mixture comprising THF (10 mL), toluene (40 mL) and pentane (40 mL) gave 2.15 g (85 %) of imidazolium triflate **2** as colorless crystals.

R_f = 0.58 (CH_2Cl_2/MeOH 10:1); IR (KBr) 3113, 2945, 2862, 1727, 1516, 1459, 1266, 1224, 1151, 1031, 957, 913, 825, 754, 637; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.12 (s, 1H, NCHN), 4.80 (s, 4H, OCH_2), 2.32 (td, *J* = 3.8, 12.5 Hz, 4H, CH_2), 2.10-1.98 (m, 8H, CH_2), 1.74-1.58 (m, 4H, CH_2), 1.46-1.37 (m, 4H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.6 (NCO), 120.8 (q, *J* = 319 Hz, CF_3), 113.9 (NCHN), 85.6 (OCH_2), 67.5 (CCH_2), 34.7 (CH_2), 23.5 (CH_2), 23.1 (CH_2); ^{19}F NMR (300 MHz, $CDCl_3$) δ –78.5 (CF_3); MS (EI), *m*/*z* (%) 289 (100), 261 (5), 194 (5), 166 (5), 122 (12), 95 (20); HRMS (EI) calcd for $C_{17}H_{25}N_2O_2$ (cation): 289.1916, found 289.1918. Anal. Calcd. For $C_{18}H_{25}F_3N_2O_5S$: C, 49.31; H, 5.75; N, 6.39. Found C, 49.52; H, 5.75; N, 6.31.

General procedure for the Suzuki reaction:

Aryl boronic acid (1.1 mmol) and base (2.0 mmol) were dissolved in 2.5 mL solvent and stirred vigorously for 5 minutes. Arylhalide (1.0 mmol) was added, followed by addition of 0.5 mL of a previously prepared catalyst solution (vide infra). After 24 h at r.t. the solvent was removed in vacuo and the residue was chromatographed on silica gel.

Preparation of the catalyst solution: In a glove box, a mixture of imidazolium salt **2** (67 mg, 0.15 mmol), KH (10 mg, 0.25 mmol) and KO*t*Bu (3 mg, 0.03 mmol) was stirred in THF (0.5 mL) until hydrogen evolution ceased. The resulting suspension was filtered through a short pad of sand, and the vial was washed with THF to give 2 mL of filtrate. Finally, the filtrate was mixed with $Pd(OAc)_2$ (27 mg, 0.12 mmol) to give a clear brown solution.

Suzuki cross-coupling products:

4-Methyl-biphenyl (Table 1, entry 1).[2] The general procedure was followed, using 0.5 mL catalyst solution (0.06 M, 0.03 mmol), 1-chloro-4-methyl-benzene (0.118 mL, 1.0 mmol), phenylboronic acid (134 mg, 1.1 mmol) and CsF (304 mg, 2.0 mmol) in THF (2.5 mL). After 24 h at r.t., chromatography (hexane) yielded 138 mg (82 %) of the title compound as a white solid. Mp 37-39 °C; R_f = 0.34 (pentane); IR (film) 3080, 3054, 3029, 2938, 1944, 1908, 1878, 1749, 1657, 1601, 1568, 1519, 1488, 1445, 1403, 1379, 1340, 1313, 1266, 1155, 1129, 1113, 1076, 1039, 1008, 909, 823, 756, 736, 691, 546, 476; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (m, 2H), 7.67 (m, 2H), 7.58 (m, 2H), 7.49 (m, 1H), 7.41 (m, 2H), 2.55 (s, 3H); NMR (75 MHz, $CDCl_3$) δ 141.1, 138.3, 136.9, 129.4, 128.7, , 127.1, 126.9, 126.9, 21.0; MS (EI), *m*/*z* (%) 168 (100), 165 (19), 152 (16), 115 (5), 83 (6); HRMS (EI) calcd for $C_{13}H_{12}$: 168.0930, found 168.0938.

2-Methyl-biphenyl (Table 1, entry 2).[3] The general procedure was followed, using 0.5 mL catalyst solution (0.06 M, 0.03 mmol), 1-chloro-2-methyl-benzene (0.119 mL, 1.0 mmol), phenylboronic acid (134 mg, 1.1 mmol) and CsF (304 mg, 2.0 mmol) in THF (2.5 mL). After 24 h at r.t., chromatography (pentane) yielded 140 mg (83 %) of the title compound as a colorless oil. R_f = 0.23 (pentane); IR (film) 3059, 3020, 2953, 2925, 2866, 1950, 1599, 1479, 1457, 1439, 1381, 1267, 1158, 1120, 1073, 1052, 1035, 1010, 943, 915, 774, 748, 726, 702, 619, 563, 548, 513, 455; ^{1}H

NMR (300 MHz, $CDCl_3$) δ 7.58-7.51 (m, 2H), 7.50-7.44 (m, 3H), 7.43-7.36 (m, 4H), 2.42 (s, 3H); NMR (75 MHz, $CDCl_3$) δ 141.9, 141.9, 135.3, 130.3, 129.8, 129.1, 128.7, 128.0, 127.2, 127.1, 126.7, 125.7, 20.4; MS (EI), *m*/*z* (%) 168 (100), 165 (29), 153 (27), 115 (6), 83 (9); HRMS (EI) calcd for $C_{13}H_{12}$: 168.0930, found 168.0937.

2,5,2'-Trimethyl-biphenyl (Table 1, entry 3).[4] The general procedure was followed, using 0.5 mL catalyst solution (0.06 M, 0.03 mmol), 1-chloro-2,5-dimethyl-benzene (0.134 mL, 1.0 mmol), 2-methyl-phenylboronic acid (150 mg, 1.1 mmol) and CsF (304 mg, 2.0 mmol) in THF (2.5 mL). After 24 h at r.t., chromatography (pentane) yielded 184 mg (84 %) of the title compound as a colorless oil. R_f = 0.25 (pentane); IR (film) 3058, 3016, 2947, 2921, 2864, 2733, 1913, 1612, 1602, 1573, 1499, 1482, 1453, 1379, 1278, 1178, 1157, 1139, 1114, 1033, 975, 942, 887, 811, 771, 740, 634, 596, 559, 462; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25-7.05 (m, 6H), 6.94 (s, 1H), 2.34 (s, 3H), 2.05 (s, 3H), 2.00(s, 3H); NMR (75 MHz, $CDCl_3$) δ 141.7, 141.4, 135.8, 134.9, 132.6. 129.9, 129.7, 129.6, 129.2, 127.8, 127.0, 125.5, 20.9, 19.8, 19.3; MS (EI), *m*/*z* (%) 196 (88), 181 (100), 178 (12), 165 (35), 83 (5), 76 (6); HRMS (EI) calcd for $C_{15}H_{16}$: 196.1252, found 196.1252.

2,6-Dimethyl-biphenyl (Table 1, entry 4).[4] The general procedure was followed, using 0.5 mL catalyst solution (0.06 M, 0.03 mmol), 1-chloro-2,6-dimethyl-benzene (0.133 mL, 1.0 mmol), phenylboronic acid (134 mg, 1.1 mmol) and CsF (304 mg, 2.0 mmol) in THF (2.5 mL). After 24 h at r.t., chromatography (pentane) yielded 144 mg (79 %) of the title compound as a colorless oil. R_f = 0.22 (pentane); IR (film) 3058, 3020, 2952, 2921, 2857, 2735, 1662, 1602, 1581, 1548, 1463, 1443, 1378, 1272, 1164, 1099, 1072, 1031, 1009, 990, 906, 767, 739, 703, 672, 564, 514; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43-7.34 (m, 2H), 7.33-7.25 (m, 1H), 7.17-7.04 (m, 5H), 2.02 (s, 6H); NMR (75 MHz, $CDCl_3$) δ 141.8, 141.0, 136.0, 129.0, 128.4, 127.2, 127.0, 126.6, 20.8; MS (EI), *m*/*z* (%) 182 (100), 167 (76), 152 (16), 115 (5), 89 (9), 76 (8); HRMS (EI) calcd for $C_{14}H_{14}$: 182.1095, found 182.1093.

2,6-dimethyl-4'-(trifluoromethyl)-1,1'-biphenyl (Table 1, entry 5). The general procedure was followed, using 0.5 mL catalyst solution (0.06 M, 0.03 mmol), 2-chloro-1,3-dimethylbenzene (0.134 mL, 1.0 mmol), 4-trifluoromethyl-phenylboronic acid (209 mg, 1.1 mmol) and CsF (304 mg, 2.0 mmol) in THF (2.5 mL). After 24 h at r.t., chromatography (hexane) yielded 213 mg (85 %) of the title compound as a white solid. Mp 52-54 °C; R_f = 0.28 (pentane); IR (KBr) 3022, 2981, 2946, 2921, 2857, 1932,1616, 1581, 1522, 1465, 1443, 1404, 1382, 1322, 1146, 1102, 1065,

1026,1006, 846, 829, 771, 749, 686, 615; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, 2H, *J* = 7.9 Hz), 7.33 (d, 2H, *J* = 7.9 Hz), 7.29-7.18 (m, 3H), 2.09 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.0, 140.4, 135.7, 129.5, 129.1 (q, ^{2}J(CF) = 32.4 Hz), 127.6, 127.5, 125.5 (q,^{3}J(CF) = 3.8Hz), 124.3 (q, ^{1}J(CF) = 272.1 Hz), 20.7; MS (EI), *m*/*z* (%) 250 (100), 235 (41), 215 (6), 181 (34), 165 (26), 89 (4); HRMS (EI) calcd for $C_{15}H_{13}F_3$: 250.0967, found 250.0969.

2,6-Dimethyl-4'-methoxy-biphenyl (Table 1, entry 6). The general procedure was followed, using 0.5 mL catalyst solution (0.06 M, 0.03 mmol), 2-chloro-1,3-dimethylbenzene (0.134 mL, 1.0 mmol), 4-methoxy-phenylboronic acid (167 mg, 1.1 mmol) and CsF (304 mg, 2.0 mmol) in THF (2.5 mL). After 24 h at r.t., chromatography (3% Et_2O in hexane) yielded 184 mg (87 %) of the title compound as a white solid. Mp 46-47 °C; R_f = 0.10 (pentane); IR (film) 3062, 2999, 2953, 2855, 2834, 1610, 1575, 1516, 1465, 1441, 1377, 1288, 1240, 1175, 1105, 1041, 1001, 832, 806, 770, 638, 622, 569, 538, 521; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15-7.02 (m, 5H), 6.96-6.92 (m, 2H), 3.81(s, 3H), 2.03 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.2, 141.5, 136.4, 133.2, 129.9, 127.1, 126.8, 113.8, 55.1, 20.8; MS (EI), *m*/*z* (%) 212 (100), 197 (23), 181 (15), 169 (10), 165 (14), 153 (11), 141 (4),128 (4), 115 (4), 105 (4), 55 (8); HRMS (EI) calcd for $C_{15}H_{16}O$: 212.1201, found 212.1200.

1-(2,6-Dimethyl-1,1'-biphenyl-4-yl)ethanone (Table 1, entry 8) The general procedure was followed, using 5 μL catalyst solution (0.06 M, 0.0003 mmol), 1-(4-chloro-3,5-dimethylphenyl)ethanone (182 mg, 1.0 mmol), phenylboronic acid (135 mg, 1.1 mmol) and CsF (304 mg, 2.0 mmol) in THF. After 24 h at 60 °C, chromatography (1% Et_2O in hexane) yielded 210 mg (94 %) of the title compound as a pale yellow solid. Mp 70-72 °C; R_f = 0.26 (10% Et_2O in hexane); IR (film) 3347, 3057, 3022, 3000, 2968, 2920, 2859, 1682, 1598, 1565, 1496, 1474, 1443, 1411, 1380, 1355, 1306, 1273, 1202, 1073, 1008, 979, 942, 896, 873, 769, 704, 641, 614, 581, 486, 473; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (m, 2H), 7.45-7.40 (m, 2H), 7.37-7.32 (m, 1H), 7.11-7.08 (m, 2H), 2.60 (s, 3H), 2.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 146.8, 136.6, 140.1, 135.9, 128.6, 128.3, 127.2, 127.1, 26.6, 20.8; MS (EI), *m*/*z* (%) 224 (44), 209 (100), 181 (9), 165 (28), 104 (4), 89 (5), 76 (4), 43 (10); HRMS (EI) calcd for $C_{16}H_{16}O_1$: 224.1201, found 224.1199.

2,6,4'-Trimethyl-biphenyl (Table 2, entry 1). The general procedure was followed, using 0.5 mL catalyst solution (0.06 M, 0.03 mmol), 1-chloro-4-methyl-benzene (0.118 mL, 1.0 mmol), 2,6-dimethyl-phenylboronic acid (164 mg, 1.1 mmol)

and KO*t*Bu (224 mg, 2.0 mmol) in THF/H_2O (10/1) (2.5 mL). After 24 h at r.t., chromatography (pentane) yielded 137 mg (70 %) of the title compound as a white solid. Mp 31-33 °C; R_f = 0.25 (pentane); IR (film) 3045, 3019, 2950, 2921, 2862, 2733,1658, 1615, 1581, 1519, 1465, 1443, 1398, 1377, 1210, 1181, 1164, 1108, 987, 966, 818, 769, 748, 726, 641, 564, 515, 446; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27-7.02 (m, 7H), 2.42 (s, 3H), 2.07 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.8, 138.0, 136.2, 136.0, 129.1, 128.8, 127.2, 126.9, 21.2, 20.8; MS (EI), *m*/*z* (%) 196 (100), 181 (81), 179 (11), 165 (31), 152 (5), 89 (9), 83 (5), 76 (5); HRMS (EI) calcd for $C_{15}H_{16}$: 196.1252, found 196.1251.

2,6,2'-Trimethyl-biphenyl (Table 2, entry 2).[5] The general procedure was followed, using 0.5 mL catalyst solution (0.06 M, 0.03 mmol) to a mixture of 1-chloro-2-methyl-benzene (0.119 mL, 127 mg, 1.0 mmol), 2,6-dimethyl-phenylboronic acid (164 mg, 1.1 mmol) and KO*t*Bu (224 mg, 2.0 mmol) in THF/H_2O (10/1) (2.5 mL). After 24 h at r.t., chromatography (pentane) yielded 135 mg (69 %) of the title compound as a colorless oil. R_f = 0.35 (pentane); IR (film) 3060, 3017, 2920, 2947, 2857, 2734, 1919, 1602, 1582, 1463, 1377, 1274, 1163, 1120, 1096, 1033, 1006, 985, 761, 747, 731, 665, 572, 561, 463;^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.09 (m, 6H), 7.03-7.00 (1H), 1.97 (s, 3H), 1.94 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.2, 140.7, 136.0, 135.8, 130.1, 129.0, 127.4, 127.1, 127.1, 126.2, 20.6, 19.7; MS (EI), *m*/*z* (%) 196 (75), 181 (100), 165 (31), 83 (5); HRMS (EI) calcd for $C_{15}H_{16}$: 196.1252, found 196.1252.

1-(2',6'-Dimethyl-biphenyl-4-yl)-ethanone (Table 2, entry 3).[4] The general procedure was followed, using 0.5 mL catalyst solution (0.06 M, 0.03 mmol) to a mixture of 4-chloro-acetophenone (0.130 mL, 1.0 mmol), 2,6-dimethyl-phenylboronic acid (164 mg, 1.1 mmol) and KO*t*Bu (224 mg, 2.0 mmol) in THF/H_2O (10/1) (2.5 mL). After 24 h at r.t., chromatography (3 % Et_2O in hexane) yielded 213 mg (95 %) of the title compound as a white solid. Mp 67-69 °C; R_f = 0.23 (10 % Et_2O in hexane); IR (KBr) 3339, 3063, 2998, 2966, 2947, 2919, 2855, 1948, 1679, 1641, 1603, 1558, 1507, 1464, 1440, 1423, 1398, 1377, 1354, 1303, 1266, 1254, 1178, 1162, 1109, 1073, 1004, 956, 840, 775, 751, 730, 618, 605, 566, 555, 512, 483; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (m, 2H), 7.25 (m, 2H), 7.18 (m, 1H), 7.10 (m, 2H), 2.65 (s, 3H), 2.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 146.4, 140.6, 135.6, 135.5,129.3, 128.5, 127.4, 127.4, 26.5, 20.6; MS (EI), *m*/*z* (%) 224 (47), 209 (100), 181 (5), 165 (26), 97 (8), 89 (5), 43 (17); HRMS (EI) calcd for $C_{16}H_{16}O$: 224.1201, found 224.1199.

4'-Methoxy-2,6-dimethyl-biphenyl (Table 2, entry 4). The general procedure was followed, using 0.5 mL catalyst solution (0.06 M, 0.03 mmol), 4-chloranisol (0.123 mL, 1.0 mmol), 2,6-dimethyl-phenylboronic acid (164 mg, 1.1 mmol) and KO*t*Bu (224 mg, 2.0 mmol) in THF/H_2O (10/1) (2.5 mL). After 24 h at r.t., chromatography (3% Et_2O in hexane) yielded 153 mg (72 %) of the title compound as a white solid. R_f value, melting point and NMR data were identical to those of entry 6 in Table 1.

2,6-Dimethyl-3',5'-dimethoxy-1,1'-biphenyl (Table 2, entry 5). The general procedure was followed, using 0.5 mL catalyst solution (0.06 M, 0.03 mmol), 1-chloro-3,5-dimethoxybenzene (173 mg, 1.0 mmol), 2,6-dimethyl-phenylboronic acid (164 mg, 1.1 mmol) and KO*t*Bu (224 mg, 2.0 mmol) in THF/H_2O (10/1) (2.5 mL). After 24 h at r.t., chromatography (1% Et_2O in hexane) yielded 184 mg (76 %) of the title compound as a colorless oil. R_f = 0.49 (10% Et_2O in hexane); IR (film) 3063, 2999, 2954, 2835, 1605, 1591, 1456, 1421, 1377, 1344, 1327, 1296, 1250, 1205, 1154, 1104, 1065, 1033, 992, 929, 836, 772, 751, 730, 704, 625, 584, 539, 470; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17-7.07 (m, 3H), 6.45 (t, *J* = 2.3 Hz, 1H), 6.30 (d, *J* = 2.3, 2H), 3.78 (s, 6H), 2.08 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.8, 143.1, 141.8, 135.8, 127.2, 126.9, 106.9, 98.6, 55.2, 20.5; MS (EI), *m*/*z* (%) 242 (100), 227 (13), 211 (69), 199 (7), 196 (12), 181 (5), 167 (9), 165, (8), 152 (9), 141 (6), 128 (7), 120 (9), 155 (6); HRMS (EI) calcd for $C_{16}H_{18}O_2$: 242.1307, found 242.1306.

2,6,2'-Trimethyl-biphenyl (Table 2, entry 6). The general procedure was followed, using 0.5 mL catalyst solution Pd/NHC = 1/2 (0.06 M, 0.03 mmol), 1-chloro-2,6-dimethyl-benzene (0.133 mL, 1.0 mmol), 2-methyl-phenylboronic acid (150 mg, 1.1 mmol) and KO*t*Bu (224 mg, 2.0 mmol) in THF/H_2O (10/1) (2.5 mL). After 24 h at 60 °C, chromatography (pentane) yielded 129 mg (66 %) of the title compound as a colorless oil. R_f value, melting point and NMR data were identical to those of entry 2 in Table 2.

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