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Supporting Information for

# Non-Basic, Room Temperature, Palladium-Catalyzed Coupling of Aryl and Alkenyl Iodides with Boronic Acids Mediated by Copper(I) Thiophene-2-carboxylate (CuTC)

by Cecile Savarin and Lanny S. Liebeskind*

Sanford S. Atwood Chemistry Center, Emory University
1515 Pierce Drive, Atlanta, GA, 30322

## GENERAL METHODS

$^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra were recorded on a Varian Mercury 300 MHz (300 MHz $^{1}H$, 75.0 MHz $^{13}C$) or Varian Inova 400 MHz (400 MHz $^{1}H$, 100.0 MHz $^{13}C$, 376.3 MHz $^{19}F$) spectrometer in deuteriochloroform ($CDCl_3$) or deuterioDMSO ($(CD_6)_2SO$) with either tetramethylsilane (TMS) (0.00 ppm $^{1}H$, 0.00 ppm) or chloroform (7.26 ppm $^{1}H$, 77.00 ppm) or DMSO (2.50 ppm, $^{1}H$) as internal reference unless otherwise stated. $^{19}F$ NMR spectra were referenced with trifluoromethyltoluene in benzene (-63.7 ppm) as external standard. Data are reported in the following order: chemical shifts are given (δ); multiplicities are indicated (br (broadened), s (singlet), d (doublet), t (triplet), q (quartet), pent (pentuplet), hex (hextet), hept (heptet), m (multiplet), exch (exchangeable), app (apparent)); coupling constants, *J*, are reported (Hz); integration is provided. Infrared spectra were recorded on a Nicolet 510 FT-IR spectrometer with a resolution of 4 $cm^{-1}$ or ASI ReactIR 1000FT-IR spectrometer with a silicone probe. Peaks are reported ($cm^{-1}$) with the following relative intensities: s (strong, 67-100%), m (medium, 40-67%), w (weak, 20-40%) and br (broad). GC-MS spectra were recorded on a Shimadzu Gas Chromatograph GC-17A, Mass Spectrometer QP-5000. GC/MS analysis was carried out on a bonded 5% diphenylsiloxane capillary column (30m, 0.25mm id, 0.25 μm df). Elementary analyses were performed by Atlantic Microlab, Inc., Norcross, Georgia. Melting points were recorded on a Thomas-Hoover melting point apparatus in open capillary tubes and are uncorrected. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel 60 plates, 0.25 mm thick with F-254 indicator. Visualization was accomplished by UV light and/or 5% phosphomolybdic acid solution in ethanol. Flash column chromatography was performed by the method of Still with 32-63 μm silica

gel (Woelm). Preparative plate chromatography was performed on Merck silica gel 60 plates, 0.5 mm thick with F-254 indicator. Solvents for extraction and chromatography were reagent grade and used as received. Dried solvents (THF, toluene, $CH_3CN$, benzene, DMA) used as reaction media were purchased from Aldrich and dried over 4Å molecular sieves and titrated for water level prior to use with a Fisher Coulomatic K-F titrator. All solvents, unless otherwise noted were sparged with nitrogen for several hours. All reactions were performed under dry nitrogen in oven- and/or flame-dried glassware, except for those reactions utilizing water as a solvent, which were run under air. "Brine" refers to a saturated aqueous solution of NaCl. Unless otherwise specified, solutions of HCl, $NH_4Cl$, $NaHCO_3$ refer to aqueous solutions.

## STARTING MATERIALS

Thiophene-2-carboxylic acid, phenylboronic acid, sodium tetraphenyloboronate, $Cu_2O$, 4-methyliodobenzene, 2-(methylthio)iodobenzene, 3-(trifluoromethyl)iodobenzene, 4-bromoacetophenone, 4-iodoacetophenone, chlorobenzene, 4-bromotoluene, 2-bromoiodobenzene, 2-naphthyl trifluoromethylsulfonate, 2-iodobenzylchloride, and 4,5-dimethoxy-3-iodobenzaldehyde were purchased from Aldrich Chemical Co. and used as received. Other boronic acid reagents were obtained from Frontier Scientific. Cu(I) thiophene-2-carboxylate (CuTC)[1], 2-iodonaphthalene[2], 5,5-dimethyl-3-iodocyclohex-2-en-1-one[3] were prepared according literature procedures.

### *General Procedure for the Cross-coupling Reaction of Aryliodide Derivatives:*

The boronic acid (1.0-1.2 equiv), Pd catalyst (2-5%), copper salt (CuTC, 1.0-1.2 equiv) and aryl iodide (1.0 equiv) were introduced in a 25 mL Schlenk tube. After a vacuum/argon cycle, dry and degassed solvent was added. When one of the starting materials was an oil, it was added last by syringe. The reaction mixture was stirred for 2-12 h at room temperature and monitored by GC/MS and TLC. After completion of the reaction, $CH_2Cl_2$ was added and the organic layer was washed with 2N HCl or $NH_4Cl$, and then $NaHCO_3$ or $NH_4OH$. The aqueous layer was then extracted once with

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[1] Zhang, S.; Zhang, D.; Liebeskind, L. S. *J. Org. Chem.* **1997**, *62*, 2312-2313.

[2] Suzuki, H.; Kondo, A.; Ogawa, T. *Chem. Lett.* **1985**, 411-412.

[3] Piers, E.; Grierson, J. R.; Lau, C. K.; Nagakura, I. *Can. J. Chem.* **1982**, *60*, 210-223.

$CH_2Cl_2$. The combined organic layers were dried ($MgSO_4$ or $Na_2SO_4$), filtered, and concentrated to a viscous oil or solid. Preparative thin layer chromatography (silica, 0.5 mm thick plate) provided the corresponding product, which in some cases was recrystallized.

**1-Methyl-4-phenylbenzene,[4] 1.** Following the general procedure, dry and degassed THF (8.0 mL) was added to 4-methyliodobenzene (494 mg, 2.3 mmol, 1.0 equiv), phenylboronic acid (304 mg, 2.5 mmol, 1.1 equiv), $Pd(PPh_3)_4$ (81 mg, 0.7 mmol, 3%), and CuTC (476 mg, 2.5 mmol, 1.1 equiv). The reaction was stirred for 3 h at room temperature. After purification by radial chromatography (hexanes), **1** (348 mg, 2.1 mmol, 90%) was obtained as a white solid. TLC (hexanes, $R_f = 0.47$); mp = 47-48 °C (lit. 47-48 °C [4]); IR (neat, $cm^{-1}$): 3057 (m), 3030 (m), 2922 (s), 2856 (m), 1490 (s), 1444 (m), 1405 (m), 1378 (w), 1266 (w), 1127 (w), 1038 (w), 1007 (w), 822 (s), 802 (m), 753 (s), 691 (s). $^1H$ NMR ($CDCl_3$, 400 MHz): δ 7.58 (app d, $J$ = 7.2 Hz, 2 H), 7.50 (app d, $J$ = 7.6 Hz, 2 H), 7.43 (app t, $J$ = 7.6 Hz, 2 H), 7.33 (tt, $J$ = 7.2, 1.2 Hz, 1 H), 7.26 (d, $J$ = 8.4 Hz, 2 H), 2.40 (s, 3 H).

**1,2-Methylenedioxy-4-(4-methylphenyl)benzene,[5] 2.** Following the general procedure, dry and degassed THF (2.0 mL) was added to 4-methyliodobenzene (103 mg, 0.47 mmol, 1.0 equiv), 3,4-(methylenedioxy)phenylboronic acid (87 mg, 0.52 mmol, 1.1 equiv), $Pd(PPh_3)_4$ (15 mg, 0.01 mmol, 3%), and CuTC (98 mg, 0.52 mmol, 1.1 equiv). The reaction was stirred for 12 h at room temperature. After purification by preparative plate chromatography (hexanes-$CH_2Cl_2$, 2:1), **2** (73 mg, 0.34 mmol, 73%) was obtained as a white solid. TLC (hexanes-$CH_2Cl_2$, 1:1, $R_f = 0.67$); mp = 60-61 °C; IR (neat, $cm^{-1}$): 3030 (m), 2922 (m), 2891 (m), 1478 (s), 1436 (s), 1409 (s), 1339 (s), 1274 (s), 1224 (s), 1131 (s), 1108 (s), 1034 (s), 930 (s), 888 (s), 865 (s), 811 (s), 726 (s). $^1H$ NMR ($CDCl_3$, 300 MHz): δ 7.44 (td, $J$ = 8.4, 1.8 Hz, 2 H), 7.24 (app d, $J$ = 8.1 Hz, 2 H), 7.09-7.05 (m, 2 H), 6.89 (dd, $J$ = 7.8, 0.6 Hz, 1 H), 6.00 (s, 2 H), 2.41 (s, 3 H). $^{13}C$ NMR ($CDCl_3$, 75 MHz): δ 148.0, 146.8, 138.0, 136.6, 135.5, 129.4, 126.7, 120.3, 108.5, 107.5, 101.0, 21.0. LRMS (FAB) : 212 ($M^+$). HRMS (FAB) Calcd for $C_{14}H_{12}O_2$ : 212.0837. Found: 212.0830 ([$M^+$], error -3.5 ppm).

**2-Phenylnaphthalene,[6] 3.** Following the general procedure, dry and degassed THF (2.0 mL) was added to 2-iodonaphthalene (51 mg, 0.19 mmol, 1.0 equiv), phenylboronic acid (27 mg, 0.22

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[4] Streitwieser, A.; Guibe, F. *J. Am. Chem. Soc.* **1978**, *100*, 4532-4534.

[5] Kuo, G-H.; Eissenstat, M. A. *Tetrahedron Lett.* **1997**, *38*, 19, 3343-3344.

mmol, 1.1 equiv), $Pd(PPh_3)_4$ (11 mg, 0.01 mmol, 5%), and CuTC (40 mg, 0.21 mmol, 1.1 equiv). The reaction was stirred for 2 h at room temperature. After preparative plate chromatography (hexanes), product **3** (36 mg, 0.18 mmol, 93%) was obtained as a white solid. TLC (hexanes, $R_f = 0.32$); mp = 100-101 °C (lit. 99-103 °C [6]); IR (neat, $cm^{-1}$): 3061 (m), 3038 (m), 1594 (m), 1575 (m), 1498 (m), 1455 (m), 892 (m), 861 (m), 822 (s), 772 (s), 755 (s), 737 (m), 687 (s). $^1H$ NMR ($CDCl_3$, 400 MHz): 8.08 (br s, 1 H), 7.96-7.88 (m, 3 H), 7.79-7.75 (m, 3 H), 7.56-7.49 (m, 4 H), 7.41 (tt, $J = 7.2$, 1.2 Hz, 1 H).

**4-(2-Naphthyl)benzoic acid methyl ester,[7] 4.** Following the general procedure, dry and degassed THF (2.0 mL) was added to 2-iodonaphthalene (62 mg, 0.25 mmol, 1.0 equiv), 4-(methoxycarbonyl)phenylboronic acid (46 mg, 0.26 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (8 mg, 0.01 mmol, 3%), and CuTC (53 mg, 0.28 mmol, 1.1 equiv). The reaction was stirred for 12 h at room temperature. After preparative plate chromatography (hexanes-$CH_2Cl_2$, 1:1), product **4** (47 mg, 0.18 mmol, 72%) was obtained as a white solid. TLC (hexanes-$CH_2Cl_2$, 1:1, $R_f = 0.17$); mp = 149-150 °C; IR (neat, $cm^{-1}$): 3061 (w), 2949 (w), 1722 (s), 1606 (m), 1440 (m), 1297 (m), 1278 (s), 1028 (m), 1112 (s), 1015 (w), 857 (w), 822 (s), 776 (s), 699 (s). $^1H$ NMR ($CDCl_3$, 400 MHz): δ 8.15 (td, $J = 8.4$, 2.0 Hz, 2 H), 8.10 (br s, 1 H), 7.97-7.96 (m, 3 H), 7.81-7.75 (m, 3 H), 7.55-7.49 (m, 2 H), 3.96 (s, 3 H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ 167.0, 145.5, 137.3, 133.5, 132.9, 130.2, 128.9, 128.6, 128.3, 127.7, 127.3, 126.5, 126.4, 126.3, 125.2, 52.2. LRMS (FAB) : 269 ($M^+$+Li). HRMS (FAB) Calcd for $C_{18}H_{14}O_2Li$ : 269.1154. Found: 269.1161 ([$M^+$+Li]).

**3-[2-(Methylthio)phenyl]nitrobenzene, 5.** Following the general procedure, 2-(methylthio)iodobenzene (98 mg, 0.39 mmol, 1.0 equiv) was added to a mixture of 3-nitrophenylboronic acid (77 mg, 0.46 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (20 mg, 0.02 mmol, 4%), and CuTC (87 mg, 0.46 mmol, 1.2 equiv) in dry and degassed THF (2.0 mL). The reaction was stirred for 12 h at room temperature. After purification by preparative plate chromatography (hexanes-$CH_2Cl_2$, 1:1), product **5** (92 mg, 0.37 mmol, 96%) was obtained as a pale yellow oil. TLC (hexanes-$CH_2Cl_2$, 1:1, $R_f = 0.23$); IR (neat, $cm^{-1}$): 3069 (w), 2980 (w), 2922 (w), 2864 (w), 2849 (w), 1586 (w), 1529 (s), 1486 (m), 1459 (m), 1436 (m), 1347 (s), 1104 (w), 1077 (w), 1042 (w), 903 (w), 876 (w), 807 (w), 776

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[6] Seong, M. R.; Song, H. N.; Kim, J. N. *Tetrahedron Lett.* **1998**, *39*, 7101-7104.

[7] Blettner, C. G.; Konig, W. A.; Stenzel, W.; Scotten, T. *Synlett.* **1998**, 295-297.

(s), 757 (s), 737 (s), 687 (s). $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.31 (t, $J$ = 2.0 Hz, 1 H ), 7.24 (app d, $J$ = 8.0, 0.8 Hz, 1 H), 7.77 (td, $J$ = 7.6, 1.2 Hz, 1 H), 7.60 (t, $J$ = 7.6 Hz, 1 H), 7.43-7.38 (m, 1 H), 7.33 (d, $J$ = 7.6 Hz, 1 H), 7.27-7.21 (m, 2 H), 2.40 (s, 3 H). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 148.0, 142.0, 138.3, 137.0, 135.6, 129.9, 129.0, 128.9, 125.7, 125.1, 124.4, 122.4, 15.9. Anal. calcd for $C_{13}H_{11}NO_2S$: C, 63.65; H, 4.52; S, 13.07; N, 5.71. Found: C, 63.76; H, 4.61; S, 13.18; N, 5.65.

**2-Formyl-5-[3-(trifluoromethyl)phenyl]furan,[8] 6**. Following the general procedure, 3-(trifluoromethyl)iodobenzene (43 mg, 0.16 mmol, 1.0 equiv) was added to a mixture of 2-formyl-5-furanylboronic acid (24 mg, 0.17 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (10 mg, 0.01 mmol, 5%), and CuTC (33 mg, 0.17 mmol, 1.1 equiv) in dry and degassed THF (1.5 mL). The reaction was stirred for 12 h at room temperature. After preparative plate chromatography (hexanes-$CH_2Cl_2$, 1:1), product **6** (31 mg, 0.13 mmol, 81%) was obtained as a pale yellow oil. TLC ($CH_2Cl_2$, $R_f$ = 0.62); IR (neat, $cm^{-1}$): 1679 (s), 1521 (w), 1455 (w), 1432 (w), 1393 (w), 1332 (s), 1282 (w), 1170 (m), 1127 (s), 1100 (w), 1069 (w), 1031 (w), 969 (w), 938 (w), 799 (m), 764 (m), 695 (m). $^1$H NMR ($CDCl_3$, 400 MHz): δ 9.69 (s, 1 H), 8.05 (br s, 1 H), 7.99 (d, $J$ = 7.6 Hz, 1 H), 7.64 (d, $J$ = 7.6 Hz, 1 H), 7.57 (d, $J$ = 7.6 Hz, 1 H), 7.34 (d, $J$ = 4.0 Hz, 1 H), 6.93 (d, $J$ = 4.4 Hz, 1 H). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 177.4, 157.5, 152.4, 129.7, 129.6, 128.2, 126.0 (q, $J$ = 14.4 Hz), 123.2, 122.0 (q, $J$ = 14.4 Hz), 108.7 (the carbons from $CF_3$ and in alpha to $CF_3$ were not observed under the conditions of the experiment). $^{19}$F NMR ($CDCl_3$, 376 MHz): -64.2. LRMS (FAB): 247 ($M^+$+Li). HRMS (FAB) Calcd for $C_{12}H_7O_2F_3Li$ : 247.0558. Found: 247.0769 ([$M^+$+Li]).

**1-Acetyl-4-(styryl)benzene,[9] 7.** Following the general procedure, dry and degassed THF (2 mL) was added to 4-iodoacetophenone (99 mg, 0.40 mmol, 1.0 equiv), *trans*-β-styrylboronic acid (66 mg, 0.44 mmol, 1.1 equiv), $Pd(PPh_3)_4$ (25 mg, 0.02 mmol, 5%), and CuTC (82 mg, 0.43 mmol, 1.1 equiv). The reaction was stirred for 4 h at room temperature. After purification by preparative plate chromatography (hexanes-$CH_2Cl_2$, 1:1), product **7** (79 mg, 0.36 mmol, 89%) was obtained as a white

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[8]Peng, S. F.; Pelosi, S. S.; Wessels, F. L.; Yu, C.-N.; Burns, R. H.; White, R. E.; Anthony, D. R. *Arzneim. Forsch.* **1983**, *33*, 1411-1416.

[9] (a) Bezou, P.; Hilberer, A.; Hadziioannou, G. *Synthesis* **1996**, *4*, 449-451. (b) Kon, G. A. R. *J. Chem. Soc., Chem. Comm.* **1948**, 224-227.

solid. TLC (hexanes-$CH_2Cl_2$, 1:1, $R_f$ = 0.17); mp = 139-140 °C [lit. 141-142 °C (benzene, petroleum ether)[9b]]; IR (neat, $cm^{-1}$): 3022 (w), 1679 (s), 1602 (m), 1451 (s), 1413 (m), 1359 (m), 1270 (m), 1181 (w), 965 (s), 868 (m), 822 (s), 753 (s), 722 (w), 691 (s). $^1H$ NMR ($CDCl_3$, 400 MHz): δ 7.95 (app d, *J* = 8.4 Hz, 2 H ), 7.78 (d, *J* = 8.0 Hz , 2 H), 7.54 (d, *J* = 7.2 Hz , 2 H), 7.39 (app t, *J* = 7.2 Hz , 2 H), 7.31 (app t, *J* = 7.2 Hz , 1 H), 7.18 (AB, *J* = 16.0 Hz , 2 H), 2.60 (s, 3 H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ 197.4, 141.9, 136.6, 135.8, 131.4, 128.8, 128.7, 128.2, 127.3, 126.7, 126.4, 26.5.

**4-(2-Bromophenyl)anisole,[10] 8.** Following the general procedure, dry and degassed THF (3 mL) was added to 2-bromoiodobenzene (104 mg, 0.37 mmol, 1.0 equiv), 4-methoxyphenylboronic acid (63 mg, 0.42 mmol, 1.1 equiv), $Pd(PPh_3)_4$ (20 mg, 0.02 mmol, 5%), and CuTC (77 mg, 0.41 mmol, 1.1 equiv). The reaction was stirred for 12 h at room temperature. After purification by preparative plate chromatography (hexanes-$CH_2Cl_2$, 1:1), product **8** (79 mg, 0.30 mmol, 81%) was obtained as a colorless oil. TLC (hexanes-$CH_2Cl_2$, 1:1, $R_f$ = 0.71); IR (neat, $cm^{-1}$): 3057 (m), 3003 (m), 2957 (m), 2934 (m), 2907 (m), 2837 (m), 1610 (s), 1579 (m), 1517 (s), 1467 (s), 1440 (s), 1409 (m), 1297 (s), 1247 (s), 1117 (s), 1108 (s), 1065 (s), 1027 (s), 1000 (s), 830 (s), 807 (s), 757 (s), 733 (s). $^1H$ NMR ($CDCl_3$, 400 MHz): δ 7.68 (d, *J* = 8.4 Hz, 1 H ), 7.39-7.33 (m, 4 H), 7.21-7.17 (m, 1 H), 6.99 (app d, *J* = 9.2 Hz , 2 H), 3.87 (s, 3 H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ 159.0, 142.1, 133.5, 133.0, 131.3, 130.5, 128.4, 127.3, 122.8, 113.3, 55.2.

**5,5-Dimethyl-3-phenylcyclohex-2-en-1-one,[11] 9.** Following the general procedure, dry and degassed THF (3 mL) was added to 5,5-dimethyl-3-iodocyclohex-2-en-1-one (130 mg, 0.52 mmol, 1.0 equiv), phenylboronic acid (71 mg, 0.51 mmol, 1.1 equiv), $Pd(PPh_3)_4$ (25 mg, 0.02 mmol, 4%), and CuTC (108 mg, 0.57 mmol, 1.1 equiv). The reaction was stirred for 4 h at room temperature. After purification by preparative plate chromatography ($CH_2Cl_2$), product **9** (88 mg, 0.44 mmol, 85%) was obtained as a white solid. TLC ($CH_2Cl_2$, $R_f$ = 0.23); mp = 49-50 °C [lit. 51-52 °C (benzene, petroleum ether)[11]]; IR (neat, $cm^{-1}$): 3497 (br w), 3061 (w), 2957 (s), 2872 (s), 2826 (w), 1660 (s), 1610 (s), 1575 (s), 1494 (m), 1467 (m), 1447 (s), 1413 (m), 1366 (s), 1305 (s), 1278 (s), 1251 (s), 1143 (s), 1119 (m),

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[10] Blake, A. J.; Cooke, P. A.; Doyle, K. J.; Gair, S.; Simpkins, N. S. *Tetrahedron Lett.* **1998**, *39*, 9093-9096.

[11] House, H. O.; Huber, L. E.; Umen, M. J. *J. Am. Chem. Soc.* **1972**, *94*, 8471-8475.

922 (m), 903 (s), 872 (m), 853 (m), 757 (s), 691 (s). $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.54-7.51 (m, 2 H), 7.41-7.39 (m, 3 H), 6.41 (t, $J$ = 1.6 Hz, 1 H), 2.64 (s, 2 H), 2.33 (s, 2 H), 1.12 (s, 6 H). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 200.0, 157.5, 138.9, 129.9, 128.7, 126.0, 124.3, 50.8, 42.2, 33.7, 28.3.

**4,5-Dimethoxy-[3-(3-methoxyphenyl)]benzaldehyde, 10.** Following the general procedure, dry and degassed THF (2 mL) was added to 4,5-dimethoxy-3-iodobenzaldehyde (101 mg, 0.34 mmol, 1.0 equiv), 3-methoxyphenylboronic acid (63 mg, 0.42 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (17 mg, 0.02 mmol, 4%), and CuTC (78 mg, 0.41 mmol, 1.2 equiv). The reaction was stirred for 4 h at room temperature. After preparative plate chromatography ($CH_2Cl_2$), product **10** (68 mg, 0.25 mmol, 73%) was obtained as an colorless oil. TLC ($CH_2Cl_2$, $R_f$ = 0.50); IR (neat, cm$^{-1}$): 3073 (w), 3000 (m), 2941 (m), 2837 (m), 2729 (w), 1695 (s), 1579 (s), 1463 (s), 1382 (s), 1343 (s), 1293 (s), 1254 (s), 1146 (s), 1042 (m), 1000 (s), 907 (s), 857 (s), 776 (s). $^1$H NMR ($CDCl_3$, 400 MHz): δ 9.92 (s, 1 H), 7.47 (d, $J$ = 2.0 Hz, 1 H), 7.45 (d, $J$ = 2.0 Hz, 1 H), 7.35 (t, $J$ = 7.6 Hz, 1 H), 7.13-7.09 (m, 2H), 6.93 (ddd, $J$ = 8.4, 2.8, 1.2 Hz, 1H), 3.97 (s, 3 H), 3.84 (s, 3 H), 3.70 (s, 3 H). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 191.2, 159.4, 153.7, 151.9, 138.3, 135.8, 132.3, 129.3, 127.3, 121.5, 114.6, 133.3, 109.4, 60.8, 56.0, 55.2. LRMS (FAB) : 279 ($M^+$+Li). HRMS (FAB) Calcd for $C_{16}H_{16}O_4Li$ : 279.1209. Found: 279.1201 ([$M^+$+Li]).

**2-Phenylbenzylchloride (11).**[12] Following the typical procedure, dry and degassed THF (2.5 mL) was added to 2-iodobenzylchloride (207 mg, 0.82 mmol, 1.0 equiv), phenylboronic acid (130 mg, 1.06 mmol, 1.3 equiv), $Pd(PPh_3)_4$ (40 mg, 0.03 mmol, 4%), and CuTC (172 mg, 0.90 mmol, 1.1 equiv). The reaction was stirred for 12 h at room temperature. After preparative plate chromatography (hexanes), product **11** (119 mg, 0.59 mmol, 72%) was obtained as a colorless oil. TLC (hexanes, $R_f$ = 0.40); IR (neat, cm$^{-1}$): 3057 (m), 3030 (m), 2964 (m), 1600 (m), 1480 (s), 1440 (m), 1270 (s), 1100 (m), 1020 (m). $^1$H NMR ($CDCl_3$, 400 MHz): 7.59-7.56 (m, 1 H), 7.49-7.37 (m, 7 H), 7.32-7.30 (m, 1 H), 4.56 (s, 2 H). $^{13}$C NMR ($CDCl_3$, 100 MHz): 142.0, 140.1, 134.9, 130.5, 130.3, 129.1, 128.5, 128.3, 127.9, 127.4, 44.4.

[12] Streitwieser, A.; Hammond, H. A.; Jagow, R. H.; Williams, R. M.; Jesaitis, R. G.; Chang, C. J.; Wolf, R. *J. Am. Chem. Soc.* **1970**, *92*, 5141-5150.

Variation using $K_2CO_3$:

Following the typical procedure, dry and degassed THF (2.5 mL) was added to 2-iodobenzylchloride (252 mg, 1.00 mmol, 1.0 equiv), phenylboronic acid (154 mg, 1.26 mmol, 1.3 equiv), $Pd(PPh_3)_4$ (46 mg, 0.04 mmol, 4%), and $K_2CO_3$ (452 mg, 3.30 mmol, 3.3 equiv). After stirring for 12 h at room temperature, only the starting material 2-iodochlorobenzene was observed according to GC/MS. After heating at 60 °C for 12 hours, a myriad of products, including starting material, was detected by GC/MS.

## *CONTROL EXPERIMENTS*

*Cross-coupling of 4-methyliodobenzene and $PhB(OH)_2$ with CuTC.* Following the general procedure, dry and degassed THF (1.5 mL) was added to 4-methyliodobenzene (33 mg, 0.15 mmol, 1.0 equiv), phenylboronic acid (21 mg, 0.17 mmol, 1.1 equiv), $Pd(PPh_3)_4$ (4 mg, 0.01 mmol, 3%), and CuTC (33 mg, 0.17 mmol, 1.1 equiv). The reaction was stirred for 17 h at room temperature. 1-Methyl-4-phenylbenzene was detected quantitatively by GC/MS; no 4-methyliodobenzene was observed by GC/MS [octadecane (41 mg, 0.16 mmol) was used as internal standard].

*Cross-coupling of 4-methyliodobenzene and $PhB(OH)_2$ with CuTC in the absence of palladium catalyst.* Following the general procedure, dry and degassed THF (1.5 mL) was added to 4-methyliodobenzene (32 mg, 0.15 mmol, 1.0 equiv), phenylboronic acid (22 mg, 0.18 mmol, 1.2 equiv), and CuTC (31 mg, 0.16 mmol, 1.1 equiv). The reaction was stirred for 17 h at room temperature, then 10 h at 50 °C. No product was detected by GC/MS, whereas the starting material 4-methyliodobenzene was detected quantitatively [octadecane (40 mg, 0.16 mmol) was used as internal standard]

*Cross-coupling of 4-methyliodobenzene and $PhB(OH)_2$ with NaTC in the absence of Cu(I).* Following the general procedure, dry and degassed THF (1.5 mL) was added to 4-methyliodobenzene (31 mg, 0.14 mmol, 1.0 equiv), phenylboronic acid (22 mg, 0.18 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (4 mg, 0.01 mmol, 3%), and NaTC (23 mg, 0.16 mmol, 1.1 equiv). The reaction was stirred for 17 h at room temperature, then 10 h at 50 °C. No product was detected by GC/MS, whereas the starting material

4-methyliodobenzene was detected quantitatively [octadecane (40 mg, 0.16 mmol) was used as internal standard].

*Cross-coupling of 4-methyliodobenzene and $PhB(OH)_2$ with KOAc in the absence of Cu(I).* Following the general procedure, dry and degassed THF (1.5 mL) was added to 4-methyliodobenzene (33 mg, 0.15 mmol, 1.0 equiv), phenylboronic acid (23 mg, 0.18 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (5 mg, 0.01 mmol, 3%), and KOAc (21 mg, 0.21 mmol, 1.4 equiv). The reaction was stirred for 17 h at room temperature, then 10 h at 50 °C. No product was detected by GC/MS, whereas the starting material 4-methyliodobenzene was detected [octadecane (41 mg, 0.16 mmol) was used as internal standard].

*Cross-coupling of 4-methyliodobenzene and $PhB(OH)_2$ in the absence of Cu(I).* Following the general procedure, dry and degassed THF (1.5 mL) was added to 4-methyliodobenzene (30 mg, 0.14 mmol, 1.0 equiv), phenylboronic acid (23 mg, 0.18 mmol, 1.2 equiv), and $Pd(PPh_3)_4$ (4 mg, 0.01 mmol, 3%). The reaction was stirred for 17 h at room temperature, then 10 h at 50 °C. No product was detected by GC/MS, whereas the starting material 4-methyliodobenzene was detected [octadecane (41 mg, 0.16 mmol) was used as internal standard]