Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Site-Selective Suzuki-Miyaura Cross-Coupling Reactions of 2,3,4,5-Tetrabromofuran

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Supporting Information

General procedure A for Suzuki-Miyaura Cross-Coupling Reactions: The reaction was carried out in a pressure tube. To a dioxane or toluene/dioxane (4:1) suspension (2.5 mL) of the brominated furan, $Pd(PPh_3)_4$ (2-3 mol%) and of the arylboronic acid **2** (1.0 to 1.1 equiv. per bromine atom of the substrate) was added an aqueous solution of K_2CO_3 (2 M, 0.5 mL). The mixture was heated at the indicated temperature (80 °C) under Argon atmosphere for the indicated period of time (3-5 h). The reaction mixture was diluted with water and extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography (silica gel, EtOAc / heptanes).

Synthesis of tetraarylfurans 3a-j

2,3,4,5-Tetraphenylfuran (3a). Following *general procedure A*, compound **3a** was prepared from **1** (96 mg, 0.25 mmol), $Pd(PPh_3)_4$ (9 mg, 3 mol%), 1,4-dioxane (2.5 mL), 2M K_2CO_3 (0.5 mL) and phenylboronic acid (132 mg, 1.10 mmol) as a white crystalline solid (86 mg, 92%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.05-7.10 (m, 4H, ArH), 7.13-7.22 (m, 8H, ArH), 7.41-7.46 (m, 4H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$) : δ = 125.1 (C), 125.9, 127.2, 127.3, 128.3, 128.4, 130.4 (CH), 130.9, 133.2, 147.7 (C). IR (KBr): ν = 3082, 3047, 2918, 2852 (w), 1482, 1443 (m), 1387, 1315, 1249, 1152 (w), 1071, 1024, 946, 917, 908, 793, 765, 756, 739, 704 (m), 689, 679 (s), 657, 648, 618 (m), 580, 536 (w) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%) = 72 ([M]$^+$, 100), 267 (23), 165 (05). HRMS (EI, 70 eV): calcd for $C_{28}H_{20}O$ [M]$^+$: 372.15087 found 472.150596.

2,3,4,5-Tetra-*p*-tolylfuran (3b). Following *general procedure A,* compound **3b** was prepared from **1** (96 mg, 0.25 mmol), $Pd(PPh_3)_4$ (09 mg, 2 mol%), toluene/dioxane (4:1, 2.5 mL), 2M K_2CO_3 (0.5 mL) and *p*-tolylboronic acid (136 mg, 1.0 mmol) as a white solid (108 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.23 (s, 12H, 4CH_3), 6.94-6.99 (m, 10H, ArH), 7.30-7.33 (m, 4H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.2, 21.3 (CH_3), 124.3 (C), 125.7 (CH), 128.4 (C), 128.9, 129.0, 130.2 (CH), 130.3, 136.4, 136.8, 147.5 (C). IR (KBr): ν = 2958, 2931, 2835 (w),

1782, 1604 (m), 1520, 1493, 1234 (m), 1161 (s), 1073, 944 (m), 820 (s), 640, 567 (m). cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 484 (M^+, 100), 351 (13). HRMS (EI, 70 eV): calcd. for $C_{36}H_{36}O$ (M^+): 484.27607; found: 484.27607.

2,3,4,5-Tetrakis(4-ethylphenyl)furan (3c). Following *general procedure A,* compound **3c** was prepared from **1** (96 mg, 0.25 mmol), $Pd(PPh_3)_4$ (09 mg, 3 mol%), 1,4-dioxane (2.5 mL), 2M K_2CO_3 (0.5 mL) and 4-ethylphenylboronic acid (165 mg, 1.10 mmol) as a white solid (111 mg, 92%). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.15 (t, 6H, *J* = 7.6 Hz, $2CH_3$), 1.16 (t, 6H, *J* = 7.6 Hz, $2CH_3$), 2.51-2.58 (m, 8H, $4CH_2$), 6.89-7.03 (m, 12H, ArCH), 7.35 (d, 4H, *J* = 8.2 Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 15.1, 15.3 ($2CH_3$), 28.5, 28.6 ($2CH_2$), 124.4 (C), 125.8, 127.7, 127.8 (CH), 128.7 (C), 130.3 (CH), 130.6, 142.7, 143.2, 147.5 (C). IR (KBr): $\tilde{\nu}$ = 3023 (w), 2964, 2929, 2869, 2859, 1518, 1454, 1372 (m), 1317, 1298, 1261, 1242, 1185 (w), 1184, 1114, 1104, 1062, 1045, 1018, 966, 944 (m), 832 (s), 795, 782, 747 (w), 686, 647, 637, 628 (m), 595, 587, 551 (w) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%) = 484 ($[M]^+$, 100), 469 (15), 351 (09). HRMS (EI, 70 eV): calcd for $C_{36}H_{36}O$ $[M]^+$: 484.27607 found 484.275860.

2,3,4,5-Tetrakis(4-tert-butylphenyl)furan (3d). Following *general procedure A,* compound **3d** was prepared from **1** (96 mg, 0.25 mmol), $Pd(PPh_3)_4$ (9 mg, 3 mol%), 1,4-dioxane (2.5 mL), 2M K_2CO_3 (0.5 mL) and 4-*tert*-butylphenylboronic acid (195 mg, 1.10 mmol) as a white solid (137 mg, 92%). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.22 (s, 18H, $6CH_3$), 1.23 (t, 18H, $6CH_3$), 7.00 (d, 4H, *J* = 8.7 Hz, ArH), 7.16 (d, 4H, *J* = 8.9 Hz, ArH), 7.20 (d, 4H, *J* = 8.7 Hz, ArH), 7.4 0 (d, 4H, *J* = 8.7 Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$) : δ = 131.3, 31.4 ($6CH_3$), 34.5, 34.6, 124.7 (C), 125.0, 125.2, 125.3 (CH), 128.5 (C), 130.0 (CH), 130.4, 147.3, 149.7, 149.9 (C). IR (KBr): $\tilde{\nu}$ = 2960 (s), 2904, 2867 (m), 1789, 1766 (w) 1681, 1674, 1604, 1475, 1462, 1407, 1362, 1298 (m), 1267 (s), 1182, 1108, 1012 (m), 974, 942, 926, 887, 856 (w), 828 (s), 784, 770, 702, 687, 649, 626, 575, 545 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 484 ($[M]^+$, 100), 469 (15), 351 (09). HRMS (EI, 70 eV): calcd for $C_{44}H_{52}O$ $[M]^+$: 596.40182 found 596.40177.

2,3,4,5-Tetrakis(3-chlorophenyl)furan (3e). Following *general procedure A,* compound **3e** was prepared from **1** (96 mg, 0.25 mmol), $Pd(PPh_3)_4$ (9 mg, 3 mol%), 1,4-dioxane (2.5 mL), 2M K_2CO_3 (0.5 mL) and 3-chlorophenylboronic acid (171 mg, 1.10 mmol) as a white crystalline solid (101 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.93-7.00 (m, 2H, ArH), 7.06-7.23 (m, 12H, ArH), 7.47-7.48 (m, 2H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 124.0 (CH), 124.5 (C), 125.8, 128.0, 128.1, 128.4, 129.8, 130.0, 130.1 (CH), 131.6, 133.9, 134.5, 134.7, 147.2(C). IR (KBr): $\tilde{\nu}$ = 1598, 1569, 1470 (m), 1426, 1321, 1300, 1257, 1136 (w), 1111, 1100, 1090, 878, 789 (m), 780, 755, 681 (s), 665, 616, 550 (w) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 516 ([M, $^{37}Cl_4]^+$, 02), 514 ([M, ^{35}Cl, $^{37}Cl_3]^+$, 19), 512 ([M, $^{35}Cl_2$, $^{37}Cl_2]^+$, 52), 510 ([M, $^{35}Cl_3$, ^{37}Cl]$^+$, 100), 508 ([M, $^{35}Cl_4]^+$, 19), 369 (14), 263 (15). HRMS (EI, 70 eV): calcd for $C_{28}H_{16}Cl_4O$ [M, $^{35}Cl_4]^+$: 507.9955 found 507.99534.

2,3,4,5-Tetrakis(4-fluorophenyl)furan (3f). Following *general procedure A,* compound **3f** was prepared from **1** (96 mg, 0.25 mmol), $Pd(PPh_3)_4$ (09 mg, 3 mol%), 1,4-dioxane (2.5 mL), 2M K_2CO_3 (0.5 mL) and 4-fluorophenylboronic acid (154 mg, 1.10 mmol) as a white solid (94 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.86-6.85 (m, 8H, ArH), 6.98-7.04 (m, 4H, ArH), 7.31-7.41 (m, 4H, ArH). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -113.35, -111.25 . ^{13}C NMR (75.5 MHz, $CDCl_3$) : δ = 115.6 (d, $J_{F,C}$ = 21.9 Hz, CH), 115.7 (d, $J_{F,C}$ = 21.3 Hz, CH), 123.5 (C), 126.6 (d, $J_{F,C}$ = 3.3 Hz, C), 127.6 (d, $J_{F,C}$ = 8.2 Hz, CH), 128.6 (d, $J_{F,C}$ = 3.5 Hz, C), 131.9 (d, $J_{F,C}$ = 8.0 Hz, CH), 147.1, (C), 127.6 (d, $J_{F,C}$ = 248.5 Hz, 2CF). IR (KBr): $\tilde{\nu}$ = 3054, 2920, 2851 (w), 1738, 1732, 1589, 1475 (w), 1434 (m), 1393, 1378, 1307, 1260 (w), 1192, 1117 (s), 1089, 1068, 1025, 996 (m), 747, 743, 718, 691, 537 (s) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 444 ([M]$^+$, 100), 321 (30), 201 (5). HRMS (EI, 70 eV): calcd for $C_{28}H_{16}O_4$ [M]$^+$: 444.11318 found 444.11267.

2,3,4,5-Tetrakis(4-(trifluoromethyl)phenyl)furan (3g). Following *general procedure A,* compound **3g** was prepared from **1** (96 mg, 0.25 mmol), $Pd(PPh_3)_4$ (09 mg, 2 mol%), toluene/dioxane (4:1, 2.5 mL), 2M K_2CO_3 (0.5 mL) and 4-(trifluoromethyl)phenylboronic acid (190 mg, 0.25 mmol) as a white solid (143 mg, 89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.19 (d, 4H, *J* = 7.9 Hz, ArH), 7.48-7.51 (m, 12H, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -62.6, -62.8.

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 123.8 (q, $J_{F,C}$ = 272.2 Hz, CF_3), 125.1 (C), 125.7 (q, $J_{F,C}$ = 3.9 Hz, CH), 125.9 (q, $J_{F,C}$ = 3.4 Hz, CH), 126.2 (CH), 129.6 (q, $J_{F,C}$ = 32.8 Hz, C-CF_3), 129.7 (q, $J_{F,C}$ = 32.0 Hz, C-CF_3), 130.5 (CH), 132.9, 135.6, 148.0. IR (KBr): $\tilde{\nu}$ = 3052, 2923(w), 1695, 1612, 1446 (m), 1333 (s), 1168 (m), 1132 (m), 1080, 810, 740 (m), 682 (s), 642, 589 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 644 (M^+, 100), 625 (11), 471 (31), 173 (27), 145 (22). HRMS (EI, 70 eV): *m/z* = calcd. for $C_{32}H_{16}OF_{12}$ [M^+]: 644.10041, found: 644.100370.

2,3,4,5-Tetrakis(3-(trifluoromethyl)phenyl)furan (3h). Following *general procedure A,* compound **3i** was prepared from **1** (96 mg, 0.25 mmol), $Pd(PPh_3)_4$ (09 mg, 3 mol%), 1,4-dioxane (2.5 mL), 2M K_2CO_3 (0.5 mL) and 3-(trifluoromethyl)phenylboronic acid (208 mg, 1.10 mmol) as a white crystalline solid (132 mg, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.23-7.27 (m, 2H, ArH), 7.32-7.39 (m, 6H, ArH), 7.45-7.58 (m, 6H, ArH), 7.67 (brs, 2H, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -63.11, -63.20. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 122.7 (q, $J_{F,C}$ = 4.1 Hz, CH), 123.8 (q, $J_{F,C}$ = 272.2 Hz, CF_3), 123.9 (q, $J_{F,C}$ = 273.3 Hz, CF_3), 124.5 (C), 124.7 (q, $J_{F,C}$ = 3.9 Hz, CH), 124.8 (q, $J_{F,C}$ = 3.9 Hz, CH), 122.7 (q, $J_{F,C}$ = 3.6 Hz, CH), 128.9, 129.2, 129.4 (CH), 130.4 (C), 131.3 (q, $J_{F,C}$ = 36.7 Hz, C-CF_3), 131.4 (q, $J_{F,C}$ = 36.7 Hz, C-CF_3), 132.5 (C), 133.4 (CH), 147.7 (C). IR (KBr): $\tilde{\nu}$ = 1617, 1611, 1492, 1476, 1462, 1439, 1354 (w), 1324 (s), 1294, 1284, 1205 (m), 1160, 1113, 1097, 1068 (s), 1000, 967, 897, 850 (m), 800 (s), 739 (w), 707, 700, (s), 652 (w) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 644 ([M]$^+$, 100), 555 (11), 411 (12), 325 (10). HRMS (EI, 70 eV): *m/z* = 644.10095; calcd. for $C_{32}H_{16}F_{12}O$ (M^+), found: 644.099515.

2,3,4,5-Tetrakis(4-methoxyphenyl)furan (3i). Following *general procedure A,* compound **3i** was prepared from **1** (96 mg, 0.25 mmol), $Pd(PPh_3)_4$ (09 mg, 3 mol%), 1,4-dioxane (2.5 mL), 2M K_2CO_3 (0.5 mL) and 4-methoxyphenylboronic acid (167 mg, 1.10 mmol) as a white crystalline solid (120 mg, 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.70 (s, 12H, 4OCH_3), 6.67-6.98 (m, 8H, ArH), 6.96 (d, 4H, *J* = 8.3 Hz, ArH), 7.34 (d, 4H, *J* = 8.9 Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.1, 55.2 (OCH_3), 113.8, 113.9 (CH), 123.3, 124.1, 125.8 (C), 127.2, 131.6 (CH), 147.2, 158.5, 158.7 (C). IR (KBr): $\tilde{\nu}$ = 3433 (w), 3020, 3001, 2953, 2922, 2839, 1603 (m), 1501, 1492, 1283, 1172, 1029, 831 (s), 788 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%) = 492 ([M]$^+$,

100), 377 (15), 357 (09), 246 (05), 246 (22). HRMS (EI, 70 eV): calcd for $C_{32}H_{28}O_5$ $[M]^+$: 492.19313 found 492.193346.

2,3,4,5-Tetrakis(3,5-dimethylphenyl)furan (3j). Following *general procedure A,* compound **3j** was prepared from **1** (96 mg, 0.25 mmol), $Pd(PPh_3)_4$ (09 mg, 3 mol%), 1,4-dioxane (2.5 mL), 2M K_2CO_3 (0.5 mL) and 3,5-dimethylphenylboronic acid (165 mg, 1.10 mmol) as a white crystalline solid (91 mg, 76%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.11 (s, 12H, $4CH_3$), 2.15 (s, 12H, $4CH_3$), 6.71 (s, 2H, ArH), 6.72 (s, 2H, ArH), 6.76 (s, 4H, ArH), 7.08 (s, 4H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.1, 21.4, 123.6 (CH), 125.2 (C), 128.3, 128.5, 128.8 (CH), 131.1, 133.2, 137.3, 137.6, 147.5 (C). IR (KBr): $\tilde{\nu}$ = 3003, 2915, 2860 (w), 1618, 1599, 1462, 1444, 1377, 1299, 1213, 1198, 1176, 1148, 1036, 913, 894 (m), 848 (s), 801, 729, 702, 692, 675 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 484 ($[M]^+$, 100), 351 (33), 321 (5), 242 (6). HRMS (EI, 70 eV): calcd for $C_{36}H_{36}O$ $[M]^+$: 484.27607 found 484.27587.

Synthesis of 2,5-diaryl-3,4-dibromofurans 4

3,4-Dibromo-2,5-bis(3-chlorophenyl)furan (4a). Following *general procedure A,* compound **4a** was prepared from **1** (96 mg, 0.25 mmol), $Pd(PPh_3)_4$ (06 mg, 2 mol%), toluene/dioxane (4:1, 2.5 mL), 2M K_2CO_3 (0.5 mL) and 3-chlorophenylboronic acid (78 mg, 0.50 mmol) as a white solid (87 mg, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26-7.33 (m, 4H, ArH), 7.83 (dt, *J* = 1.6, 7.4 Hz, 2H, ArH), 7.89-7.91 (m, 2H, ArH). ^{13}C NMR (75.7 MHz, $CDCl_3$): δ = 103.7 (C), 123.7, 125.5, 128.2, 130.0 (CH), 130.4, 134.8, 147.1 (C). IR (KBr): $\tilde{\nu}$ = 1596, 1567, 1471, 1461 (m), 1426, 1401, 1321, 1302, 1258, 1241, 1136 (w), 1112, 1102, 1092, 1074, 991, 958, 878, 789 (m), 779, 754, 681 (s), 664, 615, 549, 529 (w) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 446 ([M, ^{79}Br,^{81}Br, ^{35}Cl ^{35}Cl] $^+$ or [M, ^{79}Br,^{79}Br, ^{35}Cl ^{37}Cl]$^+$, 100), 444 ([M, ^{79}Br,^{79}Br, ^{35}Cl, ^{35}Cl]$^+$, 36), 450 ([^{81}Br,^{81}Br, ^{37}Cl, ^{37}Cl]$^+$, 31), 339 (10), 223 (14). HRMS (EI, 70 eV): *m/z* = 443.83135, calcd. for $C_{16}H_8OBr_2Cl_2$ (M^+, [^{79}Br,^{79}Br, ^{35}Cl, ^{35}Cl]) found: 443.832061.

3,4-Dibromo-2,5-bis(3-(trifluoromethyl)phenyl)furan (4c). Following *general procedure A,* compound **4c** was prepared from **1** (96 mg, 0.25 mmol), $Pd(PPh_3)_4$ (6 mg, 2 mol%), toluene/dioxane (4:1, 2.5 mL), 2M K_2CO_3 (0.5 mL) and 3-(trifluoromethyl)phenylboronic acid (95 mg, 0.50 mmol) as a white solid (109 mg, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.50-7.59 (m, 4H, ArH), 8.12-8.15 (m, 2H, ArH), 8.21 (brs, 2H, ArH). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 62.87. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ= 104.0 (C), 122.4 (q, $J_{F,C}$ = 4.0 Hz, CH), 124.23 (q, $J_{F,C}$ = 272.6 Hz, CF_3), 125.4 (q, $J_{F,C}$ = 3.7 Hz, CH), 128.7, 129.3 (CH), 129.4 (C), 131.3 (q, $J_{F,C}$ = 32.7 Hz, C-CF_3), 147.4 (C). IR (KBr): ν = 3028 , 2922, 2867, 1746, 1692, 1610, 1511, 1445, 1428 (w), 1327, 1307, 1147 (m), 1122, 1071 (s), 1052, 961, 946, 902, 845 (w), 801 (m), 750, 740, 715 (w), 693 (s), 664, 655, 573 (w) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 514 ([M, ^{79}Br,^{79}Br]$^+$, 52), 514 ([M, ^{81}Br,^{81}Br]$^+$, 100), 516 ([M, ^{81}Br,^{81}Br]$^+$, 49), 495 (07), 407 (12), 326 (07), 257 (15), 173 (37). HRMS (EI, 70 eV): *m/z* = 511.88406, calcd. for $C_{18}H_8Br_2OF_6$ (M^+, [^{79}Br,^{79}Br]) found: 511.884645; 513.88201, calcd. for (M^+, [^{81}Br,^{79}Br]) found 513.882475; 515.87997, calcd. for (M^+, [^{81}Br,^{81}Br]) found 515.880736

3,4-Dibromo-2,5-bis(4-fluorophenyl)furan (4e). Following *general procedure A,* compound **5e** was prepared from **1** (96 mg, 0.25 mmol), $Pd(PPh_3)_4$ (06 mg, 2 mol%), toluene/dioxane (4:1, 2.5 mL), 2M K_2CO_3 (0.5 mL) and 4-fluorophenylboronic acid (70 mg, 0.50 mmol) as a white solid (90 mg, 87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.05-7.17 (m, 4H, ArH), 7.91-7.96 (m, 4H, ArH). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -111.4. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 102.1 (C), 115.6, 116.0 (CH), 125.2 (d, $J_{C,F}$ = 3.6 Hz, C), 127.6, 127.8 (CH), 147.4, 162.3 (d, $J_{C,F}$ = 251.9 Hz, CF). IR (KBr): ν = 1786, 1760, 1605, 1497, 1523, 1492 (m), 1410, 1298, 1275 (w), 1233, 1159 (s), 1072, 996, 943, 829 (m), 729, 641, 632, 597, 587 (w) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 416 ([M, ^{81}Br,^{81}Br]$^+$, 50), 414 ([M, ^{79}Br,^{81}Br]$^+$, 100), 412 ([M, ^{79}Br,^{79}Br]$^+$, 50), 305 (18), 225 (18), 207 (10). HR-MS (EI, 70 eV): *m/z* = 411.89100, calcd. for $C_{16}H_8OBr_2F_2$ (M^+, [^{79}Br,^{79}Br]) found: 411.890019; 413.88840, calcd. for (M^+, [^{79}Br,^{81}Br]) found 413.888075; 415.88635, calcd. for (M^+, [^{81}Br,^{81}Br]) found 415.886165.

Synthesis of 2-aryl-3,4,5-tribromofurans 5a-e

2,3,4-Tribromo-5-(3-chlorophenyl)furan (**5a**). Following *general procedure A,* compound **5a** was prepared from **1** (96 mg, 0.25 mmol), $Pd(PPh_3)_4$ (6 mg, 2 mol%), toluene/dioxane (4:1, 5 mL), 2M K_2CO_3 (0.5 mL) and 3-chlorophenylboronic acid (39 mg, 0.25 mmol) as a highly viscous colourless oil (90 mg, 87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25-7.33 (m, 2H, ArH), 7.73-7.76 (m, 2H, ArH), 7.82 (brs, 1H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 100.9, 107.3, 122.1, 122.2 (C), 122.4, 124.3, 127.9, 128.9 (CH), 133.8, 149.2 (C). IR (KBr): $\tilde{\nu}$ = 3093, 3066, 2961, 2921 (w), 1789, 1769, 1596 (s), 1514, 1471 (m), 1418, 1401, 1315, 1260, 1204 (w), 1164, 1111, 1089, 1065, 1003, 958, 884 (m), 681 (s) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 416 (M^+, [$^{81}Br_2{}^{79}Br$], 100), 379 (9), 351 (16), 307 (94), 256 (19), 228 (17). HRMS (EI, 70 eV): calcd. for $C_{10}H_4OClBr_3$ (M^+, [$^{79}Br_3$]): 411.74953, found: 411.749450; calcd. For (M^+, [$^{81}Br^{79}Br_2$]): 413.74749, found 413.747368; calcd. for (M^+, [$^{81}Br_2{}^{79}Br$]): 415.74544, found 415.745451; (M^+, [$^{81}Br_3$]): 417.74339, found 417.743243.

2,3,4-Tribromo-5-(4-(trifluoromethyl)phenyl)furan (5c). Following *general procedure A,* compound **5c** was prepared from **1** (96 mg, 0.25 mmol), $Pd(PPh_3)_4$ (06 mg, 2 mol%), toluene/dioxane (4:1, 2.5 mL), 2M K_2CO_3 (0.5 mL) and 3-(trifluoromethyl)phenylboronic acid (51 mg, 0.27 mmol) as a highly viscous colourless oil (95 mg, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46-7.57 (m, 2H, ArH), 8.03-8.10 (m, 2H, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -62.9. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 102.2, 108.4 (C), 122.1 (q, $J_{F,C}$ = 3.9 Hz, CH), 123.4 (C), 123.8 (q, $J_{F,C}$ = 272.3 Hz, CF_3), 125.4 (q, $J_{F,C}$ = 3.6 Hz, CH), 128.3 (CH), 129.1 (C), 129.2 (CH), 132.8 (q, $J_{F,C}$ = 32.9 Hz, C-CF_3), 150.1 (C). IR (KBr): $\tilde{\nu}$ = 3083, 3060, 2951, 2931 (w), 1776, 1757, 1583 (s), 1504, 1461 (m), 1418, 1403, 1317, 1261, 1203 (w), 1167, 1088, 1064, 998, 884 (m), 676 (s) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 451 ([M^+, $^{81}Br_3$], 12), 449 ([M^+, $^{79}Br^{81}Br_2]^+$, 12), 447 ([M^+, $^{81}Br^{79}Br_2]^+$, 100), 445 ([M^+, $^{79}Br_3]^+$, 33), 343 (49), 342 (11), 341 (97), 339 (49), 290 (11), 288 (12), 262 (22), 260 (22), 181 (31), 161 (11). HRMS (EI, 70 eV): *m/z* = calcd. for $C_{11}H_4OBr_3F_3$ (M^+, [^{79}Br,^{79}Br,^{79}Br]): 445.77589, found: 445.775839; calcd. for (M^+, [^{81}Br,^{79}Br,^{79}Br]): 447.77384, found 447.773857; calcd. for (M^+, [^{81}Br,^{81}Br,^{79}Br]): 449.77180, found 449.771888; calcd. for (M^+, [^{81}Br,^{81}Br,^{81}Br]): 451.76975, found 451.76975.

2,3,4-Tribromo-5-(4-methoxyphenyl)furan (5d). Following *general procedure A,* compound **5d** was prepared from **1** (96 mg, 0.25 mmol), $Pd(PPh_3)_4$ (06 mg, 2 mol%), toluene/dioxane (4:1, 2.5 mL), 2M K_2CO_3 (0.5 mL) and 4-methoxyphenylboronic acid (41 mg, 0.27 mmol) as a highly viscous colourless oil (90 mg, 91%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.77 (s, 3H, OCH_3), 6.87 (d, J = 8.7 Hz, 2H, ArH), 7.75 (d, J = 8.9 Hz, 2H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 55.3 (OCH_3), 99.1, 107.7 (C), 114.0 (CH), 121.2, 121.3 (C), 127.1 (CH), 151.8, 160.0 (C). IR (KBr): ν = 3070, 1886 (w), 1781, 1601 (m), 1520, 1481, 1222, 1145 (s), 1064, 932 (m), 815 (s), 634, 577 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 414 (M^+, [$^{81}Br_3$], 4), 412 (M^+, [$^{81}Br_2{}^{79}Br$], 12) 410 (M^+, [$^{81}Br_2{}^{79}Br_2$], 43), 408 (M^+, [$^{79}Br_3$], 100), 376 (10), 300 (13). HRMS (EI, 70 eV): calcd. for $C_{11}H_7Br_3O_2$ (M^+, [$^{81}Br_3$]): 414.89397, found: 414.893850; calcd. for (M^+, [$^{79}Br^{81}Br_2$]): 412.99102, found 412.991369; calcd. for (M^+, [$^{79}Br_2{}^{81}Br$]): 410.88710, found 410.887321; calcd. for (M^+, [$^{81}Br_3$]): 408.76424, found 408.764562.

2,3,4-Tribromo-5-(4-fluorophenyl)furan (5e). Following *general procedure A,* compound **5e** was prepared from **1** (96 mg, 0.25 mmol), $Pd(PPh_3)_4$ (06 mg, 2 mol%), toluene/dioxane (4:1, 2.5 mL), 2M K_2CO_3 (0.5 mL) and 4-fluorophenylboronic acid (38 mg, 0.27 mmol) as a highly viscous colourless oil (87 mg, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.01-7.09 (m, 2H, ArH), 7.77-7.85 (m, 2H, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -110.9. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 100.5, 108.0 (C), 115.8 (d, $J_{F,C}$ = 22.3 Hz, CH), 122.3 (C), 124.8 (d, $J_{F,C}$ = 1.0 Hz, C), 127.5 (d, $J_{F,C}$ = 8.1 Hz, CH), 150.9 (C), 162.6 (d, $J_{F,C}$ = 249.2 Hz, CF). IR (KBr): $\tilde{\nu}$ = 3072, 1887 (w), 1782, 1604 (m), 1523, 1491, 1233, 1159 (s), 1071, 943 (m), 828 (s), 641, 597 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 402 (M^+, [$^{81}Br_3$], 5), 400 (M^+, [$^{81}Br_2{}^{79}Br$], 10), 398 (M^+, [$^{81}Br_2{}^{79}Br_2$], 34), 396 (M^+, [$^{79}Br_3$], 100), 376 (10). HRMS (EI, 70 eV): *m/z* = calcd. for $C_{10}H_4Br_3FO$ (M^+, [$^{81}Br_3$]): 402.79186, found: 402.791732; calcd. for (M^+, [$^{79}Br^{81}Br_2$]): 400.87112, found 400.871257; calcd. for (M^+, [$^{79}Br_2{}^{81}Br$]): 398.77613, found 398. 776221; calcd. for (M^+, [$^{81}Br_3$]): 396.67324, found 396.6731562.

Synthesis of unsymmetrical tetraarylfurans 6

General procedure B for the one-pot synthesis of products **6.** The reaction was carried out in a pressure tube. To a suspension of **1** (0.75 mmol), $Pd(PPh_3)_4$ (27 mg, 3 mol%) and **2a,b,d,j** (1.5 mmol) in toluene/dioxane (4:1, 10 mL) was added a 2M solution of K_2CO_3 (1 mL). The mixture was heated at 80 °C under Argon atmosphere for 3 h. The reaction mixture was cooled to 20 °C and was distributed carefully into three equal portions in separate pressure tubes. One arylboronic acid (**2a**, **2b**, **2d** or **2j**) (0.55 mmol) was added to each reaction vessel. The reaction mixture was heated under Argon atmosphere for 3 h at 80 °C. After cooling to 20 °C, each mixture was diluted with water and extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were dried (Na_2SO_4) and concentrated in vacuo. The residues of each reaction were purified by column chromatography (EtOAc/heptanes) to give **6b-d,e**, respectively.

3,4-Diphenyl-2,5-bis(3-(trifluoromethyl)phenyl)furan (6b). Following *general procedure B,* compound **6b** was prepared from phenylboronic acid (67 mg, 0.55 mmol) as a highly viscous colorless oil (109 mg, 86%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.06-7.09 (m, 4H, ArH), 7.18-7.22 (m, 6H, ArH), 7.29-7.46 (m, 4H, ArH), 7.57 (d, 2H, J = 7.7 Hz, ArH), 7.69 (brs, 2H, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -63.0. ^{13}C NMR (65.5 MHz, $CDCl_3$): δ = 122.4 (q, $J_{F,C}$ = 3.9 Hz, CH), 123.9(q, $J_{F,C}$ = 272.7 Hz, CF_3), 124.0 (q, $J_{F,C}$ = 3.9 Hz, CH), 125.2 (C), 126.0, 127.7, 128.7, 128.9, 130.1 (CH), 130.9 (d, $J_{F,C}$ = 32.3 Hz, C-CF_3), 131.3, 132.1, 146.9 (C). IR (KBr): $\tilde{\nu}$ = 3062, 2926 (w), 1693, 1610, 1448 (m), 1330 (s), 1166 (m), 1122 (m), 1070, 801, 750 (m), 692 (s), 652, 579 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 508 (M^+8), 368 (10), 367 (39), 257 (13), 236 (12), 173 (87), 165 (10), 145 (27), 137 (14), 135 (13), 125 (14), 123 (15), 121 (10), 112 (12), 111 (25), 110 (13), 109 (16), 105 (100), 99 (11), 98 (17), 97 (42), 96 (23), 95 (27), 93 (10), 91 (10), 85 (28), 84 (20), 83 (46), 82 (25), 81 (44), 78 (13), 77 (30), 73 (13), 71 (44), 70 (24), 69 (96), 68 (17), 67 (22), 63 (11), 57 (71), 56 (21), 55 (51), 43 (50), 41 (38). HRMS (EI, 70 eV): *m/z* = calcd. for $C_{30}H_{18}OF_6$ [M^+]: 508.12564, found: 508.125078.

3,4-Bis(4-tolyl)-2,5-bis(3-(trifluoromethyl)phenyl)furan (6c). Following *general procedure B,* compound **6c** was prepared from **4c** (102 mg, 0.20 mmol), $Pd(PPh_3)_4$ (06 mg, 2 mol%),

toluene/dioxane (4:1, 2.5 mL), 2M K_2CO_3 (0.5 mL) and *p*-tolylboronic acid (74 mg, 0.44 mmol) as a highly viscous colorless oil (100 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.25 (s, 6H, CH_3), 6.94-7.02 (m, 8H, ArH), 7.25-7.30 (m, 2H, ArH), 7.38 (d, J = 7.95, 2H, ArH), 7.55 (d, J = 7.95, 2H, ArH), 7.71 (brs, 2H, ArH). ^{19}F NMR (300 MHz, $CDCl_3$): δ = -63.01. ^{13}C NMR (62.9 MHz, $CDCl_3$): □ = 21.3 (CH_3), 122.4 (q, $J_{F,C}$ = 4.1 Hz, CH), 123.8 (q, $J_{F,C}$ = 3.8 Hz, CH), 123.9 (q, $J_{F,C}$ = 272.6 Hz, CF_3), 126.6 (C), 128.8 (CH), 129.1 (C), 129.4, 129.9 (CH), 130.9 (q, $J_{F,C}$ = 32.4 Hz, C-CF_3), 131.4, 137.4, 146.8 (C). IR (KBr): $\tilde{\nu}$ = 3028, 2922, 2867 (w), 1746, 1691, 1609, 1511, 1327, 1222, 1164 (w), 1123 (s), 1071, 961, 801 (m), 693 (s), 655, 572 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 536 [M^+], 100), 363 (18). HRMS (EI, 70 eV): *m/z* = calcd. for $C_{32}H_{22}OF_6$ [M^+]: 536.15694, found: 536.157343.

3,4-Bis(4-*tert*-butylphenyl)-2,5-bis(3-(trifluoromethyl)phenyl)furan (6d). Following *general procedure B,* compound **6d** was prepared using *4-tert*-butylphenylboronic acid (98 mg, 0.55 mmol) as a highly viscous colorless oil (144 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.23 (s, 18H, 6CH_3), 8.03 (d, 4H, J = 8.4 Hz, ArH), 7.23 (d, 4H, J = 8.4 Hz, ArH), 7.32-7.39 (m, 4H, ArH), 7.54 (brs, 2H, ArH), 7.62-7.66 (m, 2H, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -63.1. ^{13}C NMR (62.8 MHz, $CDCl_3$): δ = 31.2 (6CH_3), 34.6 (C), 122.5 (q, $J_{F,C}$ = 3.9 Hz, CH), 123.7 (q, $J_{F,C}$ = 3.9 Hz, CH), 124.2 (q, $J_{F,C}$ = 278 Hz, CF_3), 125.5 (CH), 126.6 (C), 128.7, 128.8, 129.7 (CH), 129.9 (C), 130.7 (d, $J_{F,C}$ = 32.7 Hz, C-CF_3), 131.4, 146.9, 150.7. IR (KBr): $\tilde{\nu}$ = 3023, 3060, 2953, 2911 (w), 1782, 1760, 1556 (s), 1510, 1462 (m), 1405, 1314, 1260, 1203 (w), 1162, 1114, 1080, 1060, 999, 948, 871 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 620 (M^+, 71), 605 (26), 565 (11), 564 (33), 492 (11), 491 (37), 479 (14), 173 (100), 161 (84), 145 (20), 57 (24), 43 (12). HRMS (EI, 70 eV): *m/z* = calcd. for $C_{38}H_{34}OF_6$ [M^+]: 620.25084, found: 620.250900.

3,4-Bis(3,5-dimethylphenyl)-2,5-bis(3-(trifluoromethyl)phenyl)furan (6e). Following *general procedure B,* compound **6e** was prepared using 3,5-dimethylphenylboronic acid (82 mg, 0.55 mmol) as a highly viscous colorless oil (124 mg, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.13 (s, 12H, 4CH_3), 6.71 (s, 4H, ArH), 6.82 (s, 2H, ArH), 7.27-7.39 (m, 4H, A rH), 7.56-7.61 (m, 2H, ArH), 7.72 (brs, 2H, ArH). ^{19}F NMR (300 MHz, $CDCl_3$): δ = -63.05. ^{13}C NMR (62.9 MHz,

$CDCl_3$): δ = 21.3 (CH_3), 122.4 (q, $J_{F,C}$ = 4.1 Hz, CH), 123.7 (q, $J_{F,C}$ = 4.1 Hz, CH), 124.0 (q, $J_{F,C}$ = 270.3 Hz, CF_3), 126.9 (C), 127.8, 128.6, 128.8, 129.3 (CH), 130.7 (q, $J_{F,C}$ = 31.2 Hz, C-CF_3), 131.5, 131.9, 137.9, 146.6 (C). IR (KBr): $\tilde{\nu}$ = 3076, 3066, 2919, 2862 (w), 1789, 1769, 1596 (s), 1514, 1471 (m), 1418, 1401, 1315, 1260, 1204 (w), 1164, 1111, 1089, 1065, 1601, 1485, 1446, 1353, 1322, 1164 (m), 1113, 1072 (s), 899, 864, 797 (m), 688 (s), 694 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 564 (M^+, 100), 391 (19). HRMS (EI, 70 eV): *m/z* = calcd. for $C_{34}H_{26}OF_6$ [M^+]: 564.18824, found: 564.188743.

2,3,4-Tris(4-*tert*-butylphenyl)-5-(3-(trifluoromethyl)phenyl)furan (7). Following *general procedure B,* compound **7** was prepared from **5c** (112 mg, 0.25 mmol), $Pd(PPh_3)_4$ (06 mg, 2 mol%), dioxane .5 mL), 2M K_2CO_3 (0.5 mL) and 4-*tert*-butylphenylboronic acid (146 mg, 0.82 mmol) as a highly viscous colourless oil (141 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.23 (s, 9H, $3CH_3$), 1.24 (s, 9H, $3CH_3$), 1.24 (s, 9H, $3CH_3$), 6.98-7.05 (m, 4H, ArH), 7.17-7.25 (m, 8H, ArH), 7.39-7.43 (m, 2H, ArH), 7.56-7.61 (m, 2H, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ= -63.1. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ= 31.2, 31.3, 31.3 (CH_3), 34.5, 34.6 (C), 122.3 (q, $J_{F,C}$ = 4.2 Hz, CH), 123.2 (q, $J_{F,C}$ = 3.9 Hz, CH), 124.2 (q, $J_{F,C}$ = 277.8 Hz, CF_3), 124.6 (C), 125.1, 125.3, 125.4, 125.5 (CH), 126.6, 128.0 (C),128.4 (CH), 128.9, 129.6 (C), 129.8, 129.9 (CH), 130.3 (q, $J_{F,C}$ = 31.3 Hz, C-CF_3), 131.8, 145.8, 148.4, 149.9, 150.4, 150.5 (C). IR (KBr): $\tilde{\nu}$ = 3064, 2922 (w), 1692, 1603, 1437 (m), 1320 (s), 1155 (m), 1103 (m), 1055, 740 (m), 682 (s), 642, 569 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 608 (M^+, 50), 593 (14), 251 (18), 173 (11), 163 (16), 162 (15), 161 (100), 57 (14). HRMS (EI, 70 eV): *m/z* = calcd. for $C_{41}H_{43}OF_3$ [M^+]: 608.32605, found: 608.326028.