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Synthetic Procedures and Structural Characterization Data of Novel Fluorine-Containing X-Branched Oligophenylenes

1,2,4,5-Tetra(4'-fluorobiphenyl-1'-yl)benzene (X-OPP(5)-F_1). A mixture of 1,2,4,5-tetra-(4'-iodophenyl)benzene **1** (443 mg, 0.5 mmol), 4-fluorophenylboronic acid (420 mg, 3 mmol), 1 : 2 palladium(II) acetate–triphenylphosphine (5 mol%), toluene (20 mL), methanol (10 mL) and 2 M K_2CO_3 (6 mL) under nitrogen atmosphere was heated at 75 °C for 4 h with magnetic stirring. After the reaction mixture was cooled to room temperature, it was poured into water and extracted with dichloromethane (3 × 50 mL). The combined organic layer was dried with anhydrous Na_2SO_4 and evaporated to dryness. The crude product was first purified by silica-gel column chromatography with 6 : 1 petroleum ether–dichloromethane as eluent and then by sublimation method affording a white solid with an isolated yield of 83 %. ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.62 (s, 2 H), 7.55 (d, J = 8.8 Hz, 4 H), 7.54 (d, J = 8.8 Hz, 4 H), 7.46 (d, J = 8.4 Hz, 8 H), 7.33 (d, J = 8.8 Hz, 8 H), 7.10 (t, J = 8.8 Hz, 8 H). ^{13}C NMR (100 MHz, $CDCl_3$, δ) 163.7, 161.2, 139.8, 139.2, 138.5, 136.6, 133.1, 130.3, 128.5, 128.4, 126.6, 115.7, 115.5. MS (FAB) *m/z* 759.6 (M^++1). Anal. calcd for $C_{54}H_{34}F_4$: C, 85.47; H, 4.52. Found: C, 85.67; H, 4.49%.

1,2,4,5-Tetra[4'-(3',5'-difluorophenyl)phenyl-1'-yl]benzene (X-OPP(5)-F_2). The Suzuki cross-coupling procedure described above was followed using **1** (886 mg, 1 mmol) and 3,5-difluorophenylboronic acid (883 mg, 6 mmol). The crude product was first purified by silica-gel column chromatography with 6 : 1 petroleum ether–dichloromethane as eluent and then

by sublimation affording a white solid with an isolated yield of 54%. ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.61 (s, 2 H), 7.46 (d, J = 8.0 Hz, 8 H), 7.34 (d, J = 8.0 Hz, 8 H), 7.07–7.12 (m, 8 H), 6.73–6.79 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$, δ) 164.6, 164.5, 162.1, 162.0, 143.9, 143.8, 143.7, 140.8, 139.2, 137.3, 133.1, 130.5, 126.7, 109.9, 109.8, 109.7, 109.6, 102.8, 102.6, 102.3. MS (FAB) *m/z* 830.6 (M^+). Anal. calcd for $C_{54}H_{30}F_8$: C, 78.07; H, 3.64. Found: C, 77.86; H, 3.72%.

1,2,4,5-Tetra[4'-(3',4',5'-trifluorophenyl)phenyl-1'-yl]benzene (X-OPP(5)-F_3). The Suzuki cross-coupling procedure described above was followed using **1** (0.89 g, 1 mmol) and 3,4,5-trifluorophenylboronic acid (1.06 g, 6 mmol). The crude product was first purified by silica-gel column chromatography with 6 : 1 petroleum ether–dichloromethane as eluent and then by sublimation affording a white solid with an isolated yield of 61%. ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.63 (s, 2 H), 7.42 (d, J = 8.4 Hz, 8 H), 7.36 (d, J = 8.4 Hz, 8 H), 7.11–7.18 (m, 4 H), 6.98–7.05 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$, δ) 140.5, 139.2, 133.1, 132.6, 130.1, 128.5, 128.4, 123.8, 123.7, 123.6, 123.5, 125.4, 112.3, 112.2, 112.0, 111.9. MS (FAB) *m/z* 902.8 (M^+). Anal. calcd for $C_{54}H_{26}F_{12}$: C, 71.84; H, 2.90. Found: C, 71.68; H, 2.95%.

1,2,4,5-Tetra(4'-trifluoromethylbiphenyl-1'-yl)benzene (X-OPP(5)-CF_3). The Suzuki cross-coupling procedure described above was followed using **1** (0.89 g, 1 mmol) and 4-trifluoromethylphenylboronic acid (1.14 g, 6 mmol). The crude product was first purified by silica-gel column chromatography with 6 : 1 petroleum ether–dichloromethane as eluent and then by sublimation affording a white solid with an isolated yield of 58%. ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.68 (d, J = 4.0 Hz, 16 H), 7.65 (s, 2 H), 7.53 (d, J = 8.4 Hz, 8 H), 7.38 (d, J = 8.4 Hz, 8 H). ^{13}C NMR (100 MHz, $CDCl_3$, δ) 144.5, 140.7, 139.5, 138.1, 133.1, 130.5,

127.2, 127.1, 127.0, 125.8, 109.5. MS (FAB) *m/z* 958.8 (M^+). Anal. calcd for $C_{58}H_{34}F_{12}$: C, 72.66; H, 3.57. Found: C, 72.60; H, 3.70%.

1,2,4,5-Tetra(4,4'-biphenyl-1-yl)benzene (X-OPP(5)-H). The Suzuki cross-coupling procedure described above was followed using **1** (886 mg, 1 mmol) and phenylboronic acid (732 mg, 6 mmol). The crude product was first purified by silica-gel column chromatography with 6 : 1 petroleum ether–dichloromethane as eluent and then by sublimation affording a white solid with an isolated yield of 66 %. ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.65 (s, 2 H), 7.58–7.61 (m, 8 H), 7.51 (d, J = 8.4 Hz, 8 H), 7.41 (dd, J = 7.6 Hz, 8 H), 7.35 (d, J = 8.4 Hz, 8 H), 7.31 (dd, J = 7.6 Hz, 4 H). MS (FAB) *m/z* 686.6 (M^+). Anal. calcd for $C_{54}H_{38}$: C, 94.42; H, 5.58. Found: C, 94.55; H, 5.70%.

1,2,4,5-Tetra(3',5'-difluorophenyl)benzene (X-OPP(3)-F_2). The Suzuki cross-coupling procedure described above was followed using 1,2,4,5-tetrabromobenzene (787 mg, 2 mmol) and 3,5-difluorophenylboronic acid (883 mg, 6 mmol). The crude product was first purified by silica-gel column chromatography with 10 : 1 petroleum ether–dichloromethane as eluent and then by sublimation affording a white solid with an isolated yield of 75 %. ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.42 (s, 2 H), 6.69–6.77 (m, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$, δ) 164.1, 163.9, 161.6, 161.5, 142.8, 142.7, 142.6, 138.5, 132.5, 112.7, 112.6, 112.5, 112.4, 103.4, 103.1, 102.9. MS (FAB) *m/z* 526.9 (M^+). Anal. calcd for $C_{30}H_{14}F_8$: C, 68.39; H, 2.68. Found: C, 68.45; H, 2.80%.