Rhodium-catalyzed Substitution Reaction of Aryl Fluorides with Disulfides:

***p*-Orientation in the Polyarylthiolation of Polyfluorobenzenes**

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Supporting Information

4-(*m*-Methoxyphenylthio)benzophenone 3. In a two-necked flask equipped with a reflux condenser were placed *p*-fluorobenzophenone **1** (400.4 mg, 2.0 mmol), di(*m*-methoxyphenyl) disulfide **2** (278.4 mg, 1 mmol), $RhH(PPh_3)_4$ (5.8 mg, 0.25 mol%), 1,2-bis(diphenylphosphino)benzene (4.5 mg, 0.5 mol%), and triphenylphosphine (262.3 mg, 50 mol%) in chlorobenzene (1 mL) under an argon atmosphere, and the solution was heated at reflux for 3 h. Then, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving **3** (573.7 mg, 87 %). Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.80 (3H, s), 6.92 (1H, dd, *J* = 8.0, 2.8 Hz), 7.05 (1H, d, *J* =2.0 Hz), 7.09 (1H, d, *J* = 7.2 Hz), 7.27 (2H, d, *J* = 8.4 Hz), 7.31 (1H, t, *J* = 8.0 Hz), 7.47 (2H, t, *J* = 8.0 Hz), 7.57 (1H, t, *J* = 7.6 Hz), 7.70 (2H, d, *J* = 8.8 Hz), 7.77 (2H, d, *J* = 8.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 55.4, 114.6, 118.6, 125.8, 127.5, 128.2, 129.8, 130.4, 130.7, 132.3, 133.3, 134.8, 137.6, 143.8, 160.3, 195.7. IR (neat) 1655, 1588, 1479, 1283, 1177, 1084, 1040, 922, 842, 787, 731, 699 cm^{-1}. MS (EI) *m*/*z* 320 (**M**$^+$, 100), 243 (**M**$^+$-Ph, 56). HRMS Calcd for $C_{20}H_{16}O_2S$: 320.0871. Found: 320.0856.

4-(*p*-Methoxyphenylthio)benzophenone. Colorless crystals. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.86 (3H, s), 6.97 (2H, d, *J* = 8.4 Hz), 7.12 (2H, d, *J* = 8.0 Hz), 7.46 (2H, t, *J* = 7.6 Hz), 7.50 (2H, d, *J* = 8.8 Hz), 7.56 (1H, t, *J* = 7.6 Hz), 7.67 (2H, d, *J* = 8.0 Hz), 7.75 (2H, d, *J* = 7.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 55.4, 115.3, 121.4, 125.6, 128.2, 129.8, 130.7, 132.2, 134.0, 136.8, 137.7, 146.2, 160.6, 195.8. IR (KBr) 3050, 3003, 2962, 2839, 1646, 1586, 1492, 1246, 829 cm^{-1}. MS (EI) *m*/*z* 320 (**M**$^+$, 100), 243 (**M**$^+$-Ph, 33). HRMS Calcd for $C_{20}H_{16}O_2S$: 320.0871. Found: 320.0852. Mp. 88 ºC (Hexane-Ethyl acetate). Lit. 89-90 °C.[1]

4-(*p*-Chlorophenylthio)benzophenone. $RhH(PPh_3)_4$ (1 mol%), 1,2-bis(diphenylphosphino)benzene (2 mol%), and triphenylphosphine (50 mol%) were used, and reacted in refluxing chlorobenzene for 3 h. Colorless crystals. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.25 (2H, dt, *J* = 9.0, 1.8 Hz), 7.36 (2H, dt, *J* = 9.0, 2.4 Hz),

7.43 (2H, dt, J = 9.0, 2.4 Hz), 7.47 (2H, tt, J = 7.8, 1.2Hz), 7.57 (1H, tt, J = 7.8, 1.2 Hz), 7.70 (2H, dt, J = 9.0, 1.8 Hz), 7.76 (2H, dt, J = 7.8, 1.8 Hz). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 127.7, 128.3, 129.83, 129.84, 130.8, 131.1, 132.4, 134.7, 134.9, 135.2, 137.5, 143.2, 195.6. IR (KBr) 1650, 1588, 1084, 814, 696 cm^{-1}. MS (EI) *m*/*z* 326 (**M**$^+$+2, 44), 324 (**M**$^+$, 100), 247 (**M**$^+$-Ph, 63). HRMS Calcd for $C_{19}H_{13}ClOS$: 324.0376. Found: 324.0362. Mp. 133-134 ºC (Hexane-Ethyl acetate). Lit. 128-130 °C.[2]

***p*-(*p*-Metoxyphenylthio)benzonitrile.** Reacted for 6 h. Colorless crystals. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.86 (3H, s), 6.98 (2H, d, J(H,H) = 8.8 Hz), 7.07 (2H, d, J = 8.8 Hz), 7.45 (2H, d, J(H,H) = 8.4 Hz), 7.47 (2H, d, J(H,H) = 8.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 55.4, 107.9, 115.5, 118.9, 120.3, 126.0, 132.2, 137.0, 147.3, 160.9. IR (KBr) 3083, 2224, 1591, 1493, 1403, 1295, 1251, 1024, 825, 544, 526 cm^{-1}. MS (EI) *m*/*z* 241 (**M**$^+$, 100), 226 (**M**$^+$-CH_3, 49). HRMS Calcd for $C_{14}H_{11}NOS$: 241.0561. Found: 241.0550. Mp. 98-99 ºC (Ethyl acetate). Lit. 90-91 °C.[5]

***p*-(*p*-Methoxyphenylthio)nitrobenzene.**[6] Reacted for 6 h. Yellow crystals. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.88 (3H, s), 7.00 (2H, d, J(H,H) = 8.8 Hz), 7.09 (2H, d, J(H,H) = 8.8 Hz), 7.50 (2H, d, J(H,H) = 8.8 Hz), 8.05 (2H, d, J(H,H) = 9.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 55.4, 115.6, 120.0, 123.9, 125.5, 137.2, 144.9, 150.1, 161.1. IR (KBr) 3095, 2836, 1593, 1575, 1503, 1336, 1252, 1172, 1082, 1032, 853, 823 cm^{-1}. MS (EI) *m*/*z* 261 (**M**$^+$, 100), 246 (**M**$^+$- CH_3, 20), 215(**M**$^+$-NO_2, 12), 139(**M**$^+$-$C_6H_4NO_2$, 14). HRMS Calcd for $C_{13}H_{11}NO_3S$: 261.0460. Found: 261.0452. Mp. 61-63 ºC (Hexane).

***p*-(*p*-Metoxyphenylthio)acetophenone.** $RhH(PPh_3)_4$ (1 mol%), 1,2-bis(diphenylphosphino)benzene (2 mol%), and triphenylphosphine (50 mol%) were used, and reacted in refluxing chlorobenzene for 6 h. Colorless crystals. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.52 (3H, s), 3.84 (3H, s), 6.95 (2H, d, J(H,H) = 8.8 Hz), 7.09 (2H, d, J(H,H) = 8.0 Hz), 7.47 (2H, d, J(H,H) = 8.8 Hz), 7.78 (2H, d, J(H,H) = 8.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 26.3, 55.3, 115.3, 121.3 125.7, 128.7, 133.8, 136.7, 146.8, 160.6, 197.0. IR (neat) 3003, 2940, 2837, 1683, 1590, 1495, 1249, 1090,1029, 828, 619, 590, 521 cm^{-1}. MS (EI) *m*/*z* 258 (**M**$^+$, 100), 243 (**M**$^+$-CH_3, 78), 215(**M**$^+$-$COCH_3$, 11), 139(**M**$^+$-$C_6H_4COCH_3$, 12), HRMS Calcd for $C_{15}H_{14}O_2S$: 258.0715. Found: 258.0694. Mp. 40-41 ºC (Hexane). Lit. 25-27 °C.[7]

4-(3-Methoxycarbonylpropylthio)benzophenone. $RhH(PPh_3)_4$ (2 mol%), 1,2-bis(diphenylphosphino)benzene (4 mol%), and tris(*p*-methoxyphenyl)phosphine (50 mol%) were used, and reacted in refluxing chlorobenzene for 6 h. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.04 (2H, quintet, J = 7.2 Hz), 2.51 (2H, t, J = 7.2 Hz), 3.07 (2H, t, J = 7.2 Hz), 3.69 (3H, s), 7.36 (2H, dt, J = 8.4, 2.0 Hz), 7.48 (2H, t, J = 8.0 Hz), 7.59 (1H, tt, J = 7.2, 1.6 Hz), 7.74 (2H, dd, J = 8.0, 1.6 Hz), 7.77 (2H, dt, J = 7.2, 2.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 24.0, 31.2, 32.5, 51.7, 126.4, 128.2, 129.8, 130.7, 132.2, 134.1, 137.7, 143.2, 173.2, 195.7. IR (neat) 2950, 1732, 1652, 1588, 1283, 1176, 840, 790 cm^{-1}. MS (EI) *m*/*z* 314 (**M**$^+$, 100), 105 (COPh, 39), 101 ($(CH_2)_3CO_2Me$, 68). HRMS Calcd for $C_{18}H_{18}O_3S$: 314.0977. Found: 314.0949.

4-[2-(*t*-Butoxycarbonylamino)ethylthio]benzophenone. $RhH(PPh_3)_4$ (2 mol%), 1,2-bis(diphenylphosphino)benzene (4 mol%), and tris(*p*-methoxyphenyl)phosphine (50 mol%) were used, and reacted in refluxing chlorobenzene for 6 h. Colorless crystals. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.45 (9H, s), 3.16 (2H, t, *J* = 6.4 Hz), 3.42 (2H, q, *J* = 6.4 Hz), 4.94 (1H, bs), 7.40 (2H, d, *J* = 8.8 Hz), 7.49 (2H, t, *J* = 7.6 Hz), 7.59 (1H, tt, *J* = 7.2, 1.2 Hz), 7.74-7.78 (4H. m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 28.4, 32.4, 39.6, 79.7, 126.8, 128.3, 129.8, 130.8, 132.3, 134.5, 137.6, 142.4, 155.7, 195.8. IR (KBr) 3361, 2980, 1682, 1639, 1522, 1272, 1169, 841 cm^{-1}. MS (EI) *m*/*z* 357 (**M**$^+$, 19), 301 (**M**$^+$-t-Bu, 77), 240 (**M**$^+$-*t*-BuOCONH$_2$, 100), 228 (**M**$^+$-*t*-BuOCONCH$_2$, 69), 105 (COPh, 54). HRMS Calcd for $C_{20}H_{23}NO_3S$: 357.1399. Found: 357.1363. Mp. 106-107 ºC (Hexane).

4-(*t*-Butylthio)benzophenone.[3] Reacted for 9 h. Colorless crystals. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.96 (3H, t, *J* = 7.2 Hz), 1.50 (2H, tq, *J* = 7.2, 7.2 Hz), 1.71 (2H, tt, *J* = 7.2, 7.2 Hz), 3.01 (2H, t, *J* = 7.2 Hz), 7.33 (2H, dt, *J* = 8.8, 1.6 Hz), 7.48 (2H, t, *J* = 8.0 Hz), 7.59 (1H, tt, *J* = 7.6, 1.6 Hz), 7.74 (2H, dt, *J* = 8.8, 2.0 Hz), 7.78 (2H, dd, *J* = 8.0, 1.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 13.6, 22.0, 30.8, 31.7, 126.1, 128.3, 129.8, 130.7, 132.2, 133.8, 137.8, 144.4, 195.9. IR (KBr) 2927, 1649, 1588, 1317, 1283, 1091, 834, 695 cm^{-1}. MS (EI) *m*/*z* 270 (**M**$^+$, 100), 214 (**M**$^+$-C_4H_9, 47), 137 (**M**$^+$-C_4H_9-Ph, 40), 105 (COPh, 42). HRMS Calcd for $C_{17}H_{18}OS$: 270.1078. Found: 270.1069. Mp. 44-45 ºC (Hexane).

Formation of difluorotriphenylphosphorane In a two-necked flask equipped with a reflux condenser were placed *p*-fluorobenzophenone **1** (400.4 mg, 2.0 mmol), di(*m*-methoxyphenyl) disulfide **2** (278.4 mg, 1.0 mmol), $RhH(PPh_3)_4$ (11.5 mg, 0.5 mol%), 1,2-bis(diphenylphosphino)benzene (8.9 mg, 1.0 mol%), and triphenylphosphine (262.3 mg, 50 mol%) in chlorobenzene (1.0 mL) under an argon atmosphere, and the solution was heated at reflux for 3 h. The ^{1}H-NMR yield of difluorotriphenylphosphorane (93%) was obtained using 1,1,2-trichloroethane as external reference. The solvent was removed under reduced pressure, the residue was recrystalyzed from ethanol under an argon atomosphere giving colorless crystals (212.1 mg, 71%). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 128.6 (d, *J* = 16.8 Hz), 131.6 (d, *J* = 4.0 Hz), 134.0 (dd, *J* = 9.2, 13.0 Hz), 134.1 (dd, *J* = 8.4, 13.0 Hz). ^{19}F-NMR (377 MHz, $CDCl_3$) δ -42.9 (d, *J* = 659 Hz). Lit[4] δ -39.6 (d, *J* = 666 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$) δ -54.9 (t, *J* = 659 Hz). Lit[4] δ -56.1 (d, *J* = 666 Hz). HRMS Calcd for $C_{18}H_{15}F_2P$: 300.0879. Found: 300.0865.

***o*-(*p*-Metoxyphenylthio)benzonitrile.** Reacted for 6 h. Colorless crystals. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.85 (3H, s), 6.93 (1H, d, *J*(H,H) = 8.0 Hz), 6.96 (2H, d, *J*(H,H) = 8.8 Hz), 7.18 (1H, dd, *J*(H,H) = 7.6, 8.4 Hz), 7.35 (1H, ddd, *J*(H,H) = 1.6, 8.0, 8.4 Hz), 7.49 (2H, d, *J*(H,H) = 8.8Hz), 7.60 (1H, d, *J* = 8.4Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 55.4, 110.8, 115.4, 116.9, 120.8, 125.4, 127.8, 132.8, 133.3, 136.7, 144.5, 160.8. IR (KBr) 3092, 2997, 2837, 2216, 1592, 1494, 1462, 1431, 1292, 1255, 1173, 1028, 824, 769, 535 cm^{-1}. MS (EI) *m*/*z* 241 (**M**$^+$, 100), 226 (**M**$^+$-CH_3, 42), 139(**M**$^+$-C_6H_4CN, 5). HRMS Calcd for $C_{14}H_{11}NOS$: 241.0561. Found: 241.0553. Mp. 105 ºC (Ethyl acetate). Lit. 98.5-100 °C.[8]

***o*-(*p*-Metoxyphenylthio)acetophenone.** $RhH(PPh_3)_4$ (2 mol%), 1,2-bis(diphenylphosphino)benzene (4 mol%), and triphenylphosphine (50 mol%) were used, and reacted in refluxing chlorobenzene for 6 h. Colorless crystals. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.64 (3H, s), 3.83 (3H, s), 6.80 (1H, d, *J*(H,H) = 8.0 Hz), 6.95 (2H, d, *J*(H,H) = 8.8 Hz), 7.11 (1H, dt, *J*(H,H) = 1.6, 7.2 Hz), 7.21 (1H, dt, *J*(H,H) = 1.6, 7.6 Hz), 7.45 (2H, d, *J*(H,H) = 8.8 Hz), 7.82 (1H, dd, *J*(H,H) = 1.6, 8.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 28.0, 55.3, 115.2, 123.2, 123.7, 127.1, 130.7, 132.0, 133.5, 137.2, 143.7, 160.5, 198.8. IR (KBr) 3001, 1661, 1591, 1493, 1250, 831, 762 cm^{-1}. MS (EI) *m*/*z* 258 (**M**$^+$, 100), 243 (**M**$^+$-CH_3, 78), HRMS Calcd for $C_{15}H_{14}O_2S$: 258.0715. Found: 258.0721. Mp. 98-99 ºC (Ethyl acetate). Lit. 100-101 °C.[9]

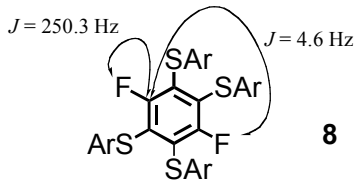
***o*-(*p*-Methoxyphenylthio)nitrobenzene.** $RhH(PPh_3)_4$ (0.25 mol%), 1,2-bis(diphenylphosphino)benzene (0.5 mol%), and triphenylphosphine (50 mol%) were used, and reacted in refluxing chlorobenzene for 6 h. Yellow crystals. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.88 (3H, s), 6.84 (1H, d *J*(H,H) = 8.0 Hz), 7.01 (2H, d, *J*(H,H) = 8.8 Hz), 7.19 (1H, dd, *J*(H,H) = 1.6, 8.0 Hz), 7.33 (1H, ddd, *J*(H,H) = 1.6, 7.2, 8.0 Hz), 7.50 (2H, d, *J*(H,H) = 8.8 Hz) 8.22 (1H, d, *J*(H,H) = 8.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 55.4, 115.7, 121.2, 124.6, 125.7, 127.9, 133.3, 137.7, 140.6, 144.6, 161.2. IR (KBr) 3110, 2954, 2835, 1590, 1564, 1489, 1459, 1449, 1442, 1333, 1305, 1292, 1250, 1183, 1172, 1102, 1027, 836, 734 cm^{-1}. MS (EI) *m*/*z* 261 (**M**$^+$, 100), 182 (**M**$^+$-CH_3-NO_2, 100), 154(**M**$^+$-$C_6H_4OCH_3$, 62), 139(**M**$^+$-$C_6H_4NO_2$, 10). HRMS Calcd for $C_{13}H_{11}NO_3S$: 261.0460. Found: 261.0453. Mp. 100-100.5 ºC (Hexane-Toluene). Lit. 95-96 °C.[10]

***m*-(*p*-Metoxyphenylthio)benzonitrile.**[6] $RhH(PPh_3)_4$ (5 mol%), 1,2-bis(diphenylphosphino)benzene (10 mol%), and triphenylphosphine (50 mol%) were used, and reacted in refluxing chlorobenzene for 6 h. Colorless crystals. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.86 (3H, s), 6.96 (2H, d, *J*(H,H) = 9.0 Hz), 7.26 (1H, d, *J*(H,H) = 1.0 Hz), 7.28-7.33 (2H, m), 7.36 (1H, ddd, *J*(H,H) = 1.5, 2.0, 7.0 Hz), 7.45 (2H, d, *J*(H,H) = 9.0 Hz). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 55.4, 113.1, 115.5, 118.4, 121.2, 128.6, 129.3, 129.6, 130.9, 136.6, 142.0, 160.8. IR (KBr) 3052, 2226, 1591, 1492, 1451, 1312, 1290, 1253, 1172, 1031, 824, 792, 684, 528 cm^{-1}. MS (EI) *m*/*z* 241 (**M**$^+$, 100), 226 (**M**$^+$-CH_3, 78), 139(**M**$^+$-C_6H_4CN, 11). HRMS Calcd for $C_{14}H_{11}NOS$: 241.0561. Found: 241.0550. Mp. 67-68 ºC (Ethyl acetate).

***m*-(*p*-Methoxyphenylthio)nitrobenzene.**[11] $RhH(PPh_3)_4$ (5 mol%), 1,2-bis(diphenylphosphino)benzene (10 mol%), and triphenylphosphine (50 mol%) were used, and reacted in refluxing chlorobenzene for 6 h. Yellow crystals. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.87 (3H, s), 6.98 (2H, d, *J* = 8.8 Hz), 7.37 (1H, d, *J* = 2.0 Hz), 7.38 (1H, d, *J* = 1.2 Hz), 7.49 (2H, d, *J* = 8.8 Hz), 7.89 (1H, s), 7.91 (1H, ddd, *J*(H,H) = ,2.0, 2.5, 7.0). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 55.3, 115.5, 119.9, 121.1, 129.4, 132.2, 136.6, 142.6, 148.5, 160.7. IR (KBr) 3068, 2940, 2837, 1591, 1525, 1348, 1249, 830, 797, 747, 730 cm^{-1}. MS (EI) *m*/*z* 261 (**M**$^+$, 100), 246 (**M**$^+$-CH_3, 20), 139(**M**$^+$-$C_6H_4NO_2$, 14). HRMS Calcd for $C_{13}H_{11}NO_3S$: 261.0460. Found: 261.0469. Mp. 57.5-58.5 ºC (Ethyl acetate).

5-Bromo-2-chloro-1-(*p*-tolylthio)benzene $RhH(PPh_3)_4$ (5 mol%), 1,2-bis(diphenylphosphino)benzene (10 mol%), and triphenylphosphine (50 mol%) were used, and reacted in refluxing chlorobenzene for 6 h. Colorless oil. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.40 (3H, s), 6.86 (1H, s), 7.16 (1H, d, *J*(H,H) = 8.4Hz), 7.18 (1H, d, *J*(H,H) = 9.0 Hz), 7.24 (2H, d, *J*(H,H) = 7.8 Hz), 7.39 (2H, d, *J*(H,H) = 7.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.3, 120.8, 126.8, 129.1, 130.1, 130.2, 130.6, 130.8, 134.8, 139.8, 140.6. IR (neat) 3022, 2920, 1597, 1563, 1491, 1402, 1246, 1080, 866, 810, 778, 503 cm^{-1}. MS (EI) *m*/*z* 316 (**M**$^+$+4,31), 315 (**M**$^+$+3, 18), 314 (**M**$^+$+2,95), 313 (**M**$^+$+1, 17), 312 (**M**$^+$, 74), 199 (**M**$^+$-$SC_6H_4CH_3$, 20), 198 (**M**$^+$-$HSC_6H_4CH_3$, 100), 91 (*p*-$C_6H_4CH_3$, 21). HRMS Calcd for $C_{13}H_{10}ClBrS$: 311.9375. Found: 311.9353.

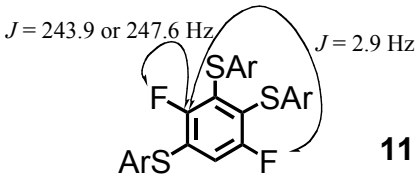
The reaction of hexafluorobenzene 6. In a two-necked flask equipped with a reflux condenser were placed **6** (93.1 mg, 0.5 mmol), di(*p*-tolyl) disulfide **5** (61.6 mg, 0.25 mmol), $RhH(PPh_3)_4$ (11.5 mg, 2.0 mol%), 1,2-bis(diphenylphosphino)benzene (8.9 mg, 4.0 mol%), and triphenylphosphine (65.7 mg, 50 mol%) in chlorobenzene (0.25 mL) under an argon atmosphere, and the solution was heated at reflux for 4 h. Then, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving 2,3,5,6-tetrafuluoro-1,4-bis(*p*-tolylthio)benzene **7** (93.9 mg, 95 %) and 3,6-difuluoro-1,2,4,5-tetrakis(*p*-tolylthio)benzene **8** (4.1. mg, 5 %). **7:** Colorless crystals. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.32 (6H, s), 7.11 (4H, d, *J*(H,H) = 8.4 Hz), 7.32 (4H, d, *J*(H,H) = 8.0 Hz). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 21.1, 115.7(m), 128.9, 130.1, 131.8, 138.5, 146.8(m). ^{19}F-NMR (565 MHz, $CDCl_3$) δ −136.02. IR (KBr) 2920, 1491, 1462, 1397, 1243, 957, 810, 640, 620, 512, 488 cm^{-1}. MS (EI) *m*/*z* 394 (**M**$^+$, 29), 271 (**M**$^+$-$SC_6H_4CH_3$, 14), 123 ($SC_6H_4CH_3$, 17), 91 ($C_6H_4CH_3$, 10). HRMS Calcd for $C_{20}H_{14}F_4S_2$: 394.0473. Found: 394.0487. Mp. 123-124 ºC (Ethyl Acetate). Lit. 116-117 °C.[12] **8:** Colorless Solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.29 (12H, s), 7.00 (8H, d, *J*(H,H) = 8.0 Hz), 7.07 (8H, d, *J*(H,H) = 8.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.1, 129.0 (dd, *J*(C,F) = 7.6, 13.8 Hz), 129.8, 129.9, 131.2, 137.0, 159.0 (dd, *J*(C,F) = 4.6, 250.3 Hz). ^{19}F-NMR (377 MHz, $CDCl_3$) δ -94.77. IR (KBr) 2910, 1491, 1387, 1081, 856, 803, 498, 484 cm^{-1}. MS (EI) *m*/*z* 604 (**M**$^+$+2H, 29), 603 (**M**$^+$+H, 44), 602 (**M**$^+$, 100), 356 (**M**$^+$-$2SC_6H_4CH_3$, 29), 123 ($SC_6H_4CH_3$, 1). HRMS Calcd for $C_{34}H_{28}F_2S_4$: 602.1024. Found: 602.1042. Mp. 193-194 ºC (Toluene). Lit. 188-189 °C.[13] **9:** Yellow Solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.27 (18H, s), 6.82 (12H, d, *J*(H,H) = 8.0 Hz), 6.93 (12H, d, *J*(H,H) = 8.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.0, 128.5 , 129.6, 134.3, 135.8, 147.8. IR (KBr) 3012, 2915, 1487, 1275, 1015, 807, 490 cm^{-1}. MS (EI) *m*/*z* 812 (**M**$^+$+2H, 45), 811 (**M**$^+$+H, 59), 810 (**M**$^+$, 100), 687 (**M**$^+$-$SC_6H_4CH_3$, 6), 91 ($C_6H_4CH_3$, 12). HRMS Calcd for $C_{48}H_{42}S_6$: 810.1611. Found: 810.1641. Mp. 206-208 ºC (Toluene). Lit. 196-197 °C.[13]



8

The reaction of pentafluorobenzene. $RhH(PPh_3)_4$ (5 mol%), 1,2-bis(diphenylphosphino)benzene (10 mol%), and triphenylphosphine (50 mol%) were used, and reacted in refluxing chlorobenzene for 6 h. **2,3,5,6-Tetrafluoro-1-(*p*-tolylthio)benzene 10.** Colorless oil. ^{1}H-NMR (594 MHz, $CDCl_3$) δ 2.32 (3H, s), 7.05

(1H, tt, J(H,F) = 7.2, 10.2 Hz), 7.10 (2H, dd, J(H,H) = 7.2, J(H,F) =0.6 Hz), 7.31 (2H, d, J(H,H) = 8.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.0, 106.6 (t, J(C,F) = 22.8 Hz), 115.6 (t, J(C,F) = 20.4 Hz), 129.2, 130.1, 131.4, 138.3, 146.0 (dddd, J(C,F) = 4.5, 10.6, 15.1, 259.9 Hz), 146.8 (dddd, J(C,F) = 2.0, 4.0, 12.9, 245.0 Hz). ^{19}F-NMR (559 MHz, $CDCl_3$) δ -133.88 (dddd, J(H,F) = 9.5 Hz, J(F,F) =1.1, 9.5, 11.2 Hz), -138.60 (ddd, J(H,F) = 7.3 Hz, J(F,F) = 7.3, 11.2 Hz). IR (neat) 3074, 2925, 1630, 1492, 1435, 1235, 1176, 919, 892, 849, 807, 714, 492 cm^{-1}. MS (EI) m/z 274 (**M**$^+$+2H, 7), 273 (**M**$^+$+H, 18), 272 (**M**$^+$, 100), 257 (**M**$^+$-CH_3, 21), 253 (**M**$^+$-F, 12), 238 (**M**$^+$-F-CH_3, 11), 91 ($C_6H_4CH_3$, 17). HRMS Calcd for $C_{13}H_8F_4S$: 272.0283. Found: 272.0280. **2,5-Difluoro-1,3,4-tris(*p*-tolylthio)benzene 11.** Colorless crystals. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.28 (3H, s), 2.30 (3H, s), 2.39 (3H, s), 6.47 (1H, dd, J(H,F) = 6.4, 8.8 Hz), 7.01 (2H, d, J(H,H) = 8.0 Hz), 7.04 (2H, d, J(H,H) = 8.0 Hz), 7.08 (2H, d, J(H,H) = 8.8 Hz), 7.15 (2H, d, J(H,H) = 8.4 Hz), 7.23 (2H, d, J(H,H) = 8.0 Hz), 7.40 (2H, d, J(H,H) = 8.0 Hz). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 21.0, 21.1, 21.3, 115.3 (dd, J(C,F) = 2.9,29.8 Hz), 123.7 (d, J(C,F) = 20.1 Hz), 125.7, 128.5 (d, J(C,F) = 18.2 Hz), 129.4, 129.7, 129.8, 130.1, 130.6 (dd, J(C,F) = 8.6, 22.0 Hz), 130.8, 131.5 (d, J(C,F) = 2.0 Hz), 132.1, 134.9, 136.6, 137.0, 140.1, 155.1 (dd, J(C,F) = 2.9, 243.9 Hz), 159.2 (dd, J(C,F) = 2.9, 247.6 Hz). ^{19}F-NMR (100 MHz, $CDCl_3$) δ -107.06 (dd, J(H,F) = 7.9 Hz, J(F,F) =15.1 Hz), -108.09 (dd, J(H,F) = 6.0 Hz, J(F,F) = 13.6 Hz). IR (KBr) 1491, 1422, 1232, 1192, 816, 803 cm^{-1}. MS (EI) m/z 482 (**M**$^+$+2, 23), 481 (**M**$^+$+1, 39), 480 (**M**$^+$, 100), 357 (**M**$^+$-$SC_6H_4CH_3$, 3), 123 ($SC_6H_4CH_3$, 8), 91 ($C_6H_4CH_3$, 3). HRMS Calcd for $C_{27}H_{22}F_2S_3$: 480.0852. Found: 480.0831. Mp. 133-134 ºC (Hexane).



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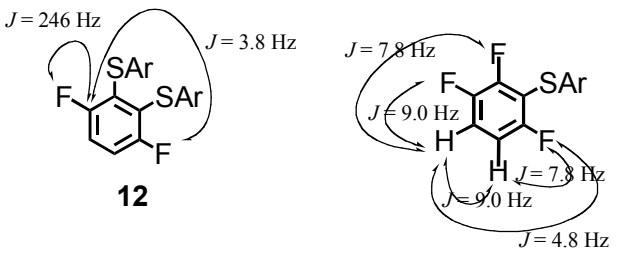
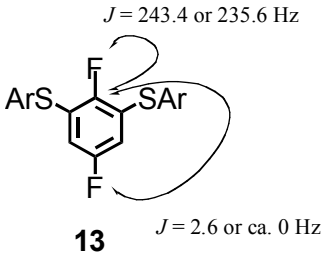
The reaction of 1,2,3,4-tetrafluorobenzene. $RhH(PPh_3)_4$ (5 mol%), 1,2-bis(diphenylphosphino)benzene (10 mol%), and triphenylphosphine (50 mol%) were used, and reacted in refluxing chlorobenzene for 6 h. **2,3,6-Trifluoro-1-(*p*-tolylthio)benzene.** Yellow oil. ^{1}H-NMR (594 MHz, $CDCl_3$) δ 2.30 (3H, s), 6.88 (1H, dddd, J(H,H) = 9.0 Hz, J(H,F) = 2.4, 3.6, 7.8 Hz), 7.09 (2H, d, J(H,H) = 8.4 Hz, J(H,F) = 0.6 Hz), 7.14 (1H, ddd, J(H,H) = 9.0 Hz, J(H,F) = 4.8, 7.8, 9.0 Hz), 7.26 (2H, d, J(H,H) = 8.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.0, 110.9 (ddd, J(C,F) = 4.6, 6.8, 25.8 Hz), 113.5 (dd, J(C,F) = 17.7, 24.1 Hz), 117.6 (ddd, J(C,F) = 1.6, 9.8, 19.7 Hz), 129.9, 130.2, 130.5, 137.6, 147.3 (ddd, J(C,F) = 3.8, 13.6, 245.9 Hz). 150.9 (ddd, J(C,F) = 3.8, 13.4, 248.9 Hz), 158.4 (ddd, J(C,F) = 2.0, 2.0, 244.7 Hz). ^{19}F-NMR (559 MHz, $CDCl_3$) δ -110.63 (ddd, J(H,F) = 5.0, 7.8 Hz, J(F,F) = 20.1 Hz), -127.41 (ddd, J(H,F) = 1.7, 8.4 Hz, J(F,F) =17.9 Hz), -141.05 (dddd, J(H,F) = 4.5, 9.5 Hz, J(F,F) = 11.2, 22.9 Hz). IR (neat) 2924, 1486, 1433, 1243, 1193, 1016, 1005, 889, 807, 739, 491 cm^{-1}. MS (EI) m/z 255 (**M**$^+$+H, 20), 254 (**M**$^+$, 100), 239 (**M**$^+$-CH_3, 13), 233 (**M**$^+$-F, 8), 123 ($SC_6H_4CH_3$, 4), 91 ($C_6H_4CH_3$, 28). HRMS Calcd for $C_{13}H_9F_3S$: 254.0377. Found: 254.0378. **3,6-Difluoro-1,2-bis(*p*-tolylthio)benzene 12.** Yellow oil. ^{1}H-NMR (594 MHz, $CDCl_3$) δ 2.29 (6H, s), 7.03 (4H, d, J(H,H) = 7.8 Hz), 7.05 (2H, dd, J(H,F) = 6.0, 6.6 Hz), 7.12 (4H, d, J(H,H) = 8.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.0, 117.0 (dd, J(C,F) = 6.0, 20.4 Hz), 128.3 (dd, J(C,F) = 6.9, 12.2 Hz), 129.7, 129.7, 131.7, 136.8, 159.2 (dd, J(C,F) = 3.8, 246.3 Hz). ^{19}F-NMR (377 MHz, $CDCl_3$) δ -108.38 (dd, J(H,F) = 6.0, 6.4 Hz). IR (neat) 3074, 3021, 2921, 2865, 1491, 1450, 1232, 1086, 1016, 939, 805, 717, 487 cm^{-1}. MS (EI) m/z 359 (**M**$^+$+H, 24), 358 (**M**$^+$, 90), 235 (**M**$^+$-$SC_6H_4CH_3$, 30), 123 ($SC_6H_4CH_3$,

11), 91 ($C_6H_4CH_3$, 10). HRMS Calcd for $C_{20}H_{16}F_2S_2$: 358.0661. Found: 358.0638.

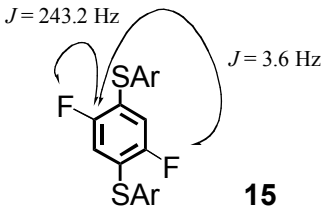


The reaction of 1,2,3,5-tetrafluorobenzene. $RhH(PPh_3)_4$ (5 mol%), 1,2-bis(diphenylphosphino)benzene (10 mol%), and triphenylphosphine (50 mol%) were used, and reacted in refluxing chlorobenzene for 6 h. **2,5-Difluoro-1,3-bis(*p*-tolylthio)benzene 13.** Colorless crystals. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.38 (6H, s), 6.36 (2H, dd, *J*(H,F) = 5.2, 8.0 Hz), 7.21 (4H, d, *J*(H,H) = 8.0 Hz), 7.38 (4H, d, *J*(H,H) = 8.0 Hz), ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.3, 113.3 (d, *J*(C,F) = 26.5 Hz), 127.0, 127.9 (dd, *J*(C,F) = 9.1, 20.1 Hz), 130.6, 134.3, 139.4, 151.8 (d, *J*(C,F) = 235.6 Hz). 158.5 (dd, *J*(C,F) = 2.6, 243.4 Hz). ^{19}F-NMR (377 MHz, $CDCl_3$) δ -118.71 (dt, *J*(H,F) = 6.0, *J*(F,F) = 15.4 Hz), -119.98 (dt, *J*(H,F) = 7.9, *J*(F,F) = 15.0 Hz). IR (KBr) 1491, 1443, 1424, 1398, 1174, 938, 845, 810, 527, 503 cm^{-1}. MS (EI) *m*/*z* 359 (**M**$^+$+H, 28), 358 (**M**$^+$, 100), 235 (**M**$^+$-$SC_6H_4CH_3$, 8), 91 ($C_6H_4CH_3$, 8). HRMS Calcd for $C_{20}H_{16}F_2S_2$: 358.0661. Found: 358.0655. Mp. 198-199 ºC (Ethyl acetate). **2,3,5-Trifluoro-1-(*p*-tolylthio)benzene 14.** Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.40 (3H, s), 6.35 (1H, ddd, *J*(H,H) = 5.2 Hz, *J*(H,F) =2.8, 10.8 Hz), 6.70 (1H, dddd, *J*(H,H) = 5.6 Hz, *J*(H,F) =2.8, 7.8, 7.5 Hz), 7.23 (2H, d, *J*(H,H) = 8.0 Hz), 7.39 (2H, d, *J*(H,H) = 8.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.2, 102.6 (dd, *J*(C,F) = 21.2, 27.3 Hz), 110.6 (d, *J*(C,F) = 25.8 Hz), 126.2, 130.0 (dd, *J*(C,F) = 9.1, 15.6 Hz), 130.7, 134.5, 139.8, 144.1 (ddd, *J*(C,F) = 2.5, 14.4, 240.8 Hz). 150.2 (ddd, *J*(C,F) = 13.7, 14.4, 250.8 Hz), 157.6 (ddd, *J*(C,F) = 3.0, 12.6, 244.0 Hz). ^{19}F-NMR (559 MHz, $CDCl_3$) δ -115.72 (dddd, *J*(H,F) = 7.8 Hz, *J*(F,F) =2.8, 7.8, 13.4 Hz), -134.32 (dddd, *J*(H,F) = 2.2, 3.4 Hz, *J*(F,F) = 9.5, 21.5 Hz), -142.42 (dddd, *J*(H,F) = 6.0 Hz, *J*(F,F) = 11.2, 12.9, 21.2 Hz) IR (neat) 2924, 1482, 1436, 1319, 1213, 1173, 1118, 998, 876, 849, 812, 777, 507 cm^{-1}. MS (EI) *m*/*z* 256 (**M**$^+$+2H, 7), 255 (**M**$^+$+H, 19), 254 (**M**$^+$, 100), 239 (**M**$^+$-CH_3, 16), 235 (**M**$^+$-F, 10), 220 (**M**$^+$-F-CH_3, 9), 123 ($SC_6H_4CH_3$, 3), 91 ($C_6H_4CH_3$, 22). HRMS Calcd for $C_{13}H_9F_3S$: 254.0377. Found: 254.0388.



The reaction of 1,2,4,5-tetrafluorobenzene. $RhH(PPh_3)_4$ (10 mol%), 1,2-bis(diphenylphosphino)benzene (20 mol%), and triphenylphosphine (50 mol%) were used, and reacted in refluxing chlorobenzene for 6 h. **2,5-Difluoro-1,4-bis(*p*-tolylthio)benzene 15.** Colorless crystals. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.37 (6H, s), 6.67 (2H, dd, *J*(H,F) = 7.6, 8.0 Hz), 7.19 (4H, d, *J*(H,H) = 8.0 Hz), 7.33 (4H, d, *J*(H,H) = 8.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.2, 116.8 (dd, *J*(C,F) = 9.8, 28.8 Hz), 124.7 (dd, *J*(C,F) = 12.1, 15.1 Hz), 127.8, 130.5, 133.4,

139.0, 155.8 (dd, J(C,F) = 3.6, 243.2 Hz). ^{19}F-NMR (377 MHz, $CDCl_3$) δ -118.94 (dd, J(H,F) = 7.5, 9.0 Hz). IR (KBr) 2918, 1486, 1458, 1375, 1281, 1165, 1085, 1018, 870, 840, 811, 789, 509 cm^{-1}. MS (EI) m/z 360 (**M**$^+$+2H, 15), 359 (**M**$^+$+H, 28), 358 (**M**$^+$, 100), 235 (**M**$^+$-$SC_6H_4CH_3$, 46), 91 ($C_6H_4CH_3$, 6). HRMS Calcd for $C_{20}H_{16}F_2S_2$: 358.0661. Found: 358.0644. Mp. 167-168 ºC (Ethyl acetate). **1,2,4,5-Tetrakis(*p*-tolylthio)benzene** Colorless crystals. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.28 (12H, s), 6.73 (2H, s,), 7.03 (8H, d, J(H,H) = 8.0 Hz), 7.13 (8H, d, J(H,H) = 8.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.2, 129.6, 130.0, 131.5, 132.5, 136.2, 137.7. IR (KBr) 1911, 1490, 1254, 1056, 806 cm^{-1}. MS (EI) m/z 568 (**M**$^+$+2, 28), 567 (**M**$^+$+1, 44), 566 (**M**$^+$, 100), 320 (**M**$^+$-$2SC_6H_4CH_3$, 25). HRMS Calcd for $C_{34}H_{30}S_4$: 566.1230. Found: 560.1247. Mp. >235 ºC (Chloroform).



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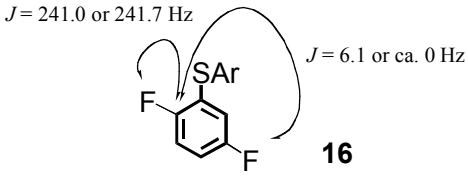
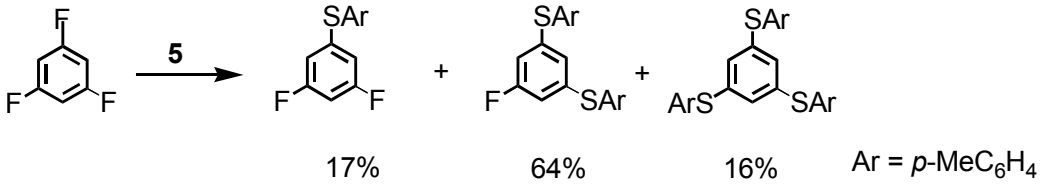
The reaction of 1,2,4-trifluorobenzene. $RhH(PPh_3)_4$ (5 mol%), 1,2-bis(diphenylphosphino)benzene (10 mol%), and triphenylphosphine (50 mol%) were used, and reacted in refluxing chlorobenzene for 24 h. **1,4-Difluoro-2-(*p*-tolylthio)benzene 16.** Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.38 (3H, s), 6.62 (1H, ddd, J(H,H) = 3.2 Hz, J(H,F) =6.0, 8.8 Hz), 6.81 (1H, ddd, J(H,H) = 7.2 Hz, J(H,F) =3.6, 11.6 Hz), 6.99 (1H, ddd, J(H,H) = 8.8 Hz, J(H,F) = 4.4, 8.8 Hz), 7.21 (2H, d, J(H,H) = 8.0 Hz), 7.38 (2H, d, J(H,H) = 8.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.2, 113.7 (dd, J(C,F) = 8.4, 24.4 Hz), 116.1 (dd, J(C,F) = 8.4, 24.2 Hz), 116.3 (d, J(C,F) = 26.5 Hz), 127.4, 127.5 (dd, J(C,F) = 8.4, 20.3 Hz). 130.5, 133.9, 139.2, 155.6 (dd, J(C,F) = 6.1, 241.7 Hz), 157.8 (d, J(C,F) = 241.0Hz). ^{19}F-NMR (377 MHz, $CDCl_3$) δ -120.61 (m), -120.93 (dddd, J(H,H) = 4.5, 7.5, 7.9 Hz, J(H,F) = 16.9 Hz). IR (neat) 3073, 3023, 2922, 2866, 1612, 1590, 1481, 1401, 1243, 1211, 1186, 1112, 1052, 1018, 907, 860, 810, 759, 528, 505 cm^{-1}. MS (EI) m/z 238 (**M**$^+$+2H, 7), 237 (**M**$^+$+H, 20), 236 (**M**$^+$, 100), 221 (**M**$^+$-CH_3, 14), 123 ($SC_6H_4CH_3$), 3), 91 ($C_6H_4CH_3$, 21). HRMS Calcd for $C_{13}H_{10}F_2S$: 236.0471. Found: 236.0457. **1,2,4-Tris(*p*-tolylthio)benzene** Colorless crystals. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.34 (6H, s), 2.36 (3H, s), 6.79 (1H, d, J(H,H) = 2.0 Hz), 6.86 (1H, dd, J(H,H) = 2.0, 7.5 Hz), 6.96 (1H, d, J(H,H) = 7.5 Hz), 7.06 (2H, d, J(H,H) = 7.5 Hz), 7.09 (2H, d, J(H,H) = 8.0 Hz), 7.13 (2H, d, J(H,H) = 8.0 Hz), 7.20 (2H, d, J(H,H) = 8.0 Hz), 7.23 (2H, d, J(H,H) = 8.0 Hz), 7.25 (2H, d, J(H,H) = 8.0 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 21.1, 21.2, 21.2, 126.8, 129.2, 129.3, 129.8, 130.0, 130.1, 130.2, 130.8, 131.6, 131.8, 133.0, 133.2, 133.6, 137.3, 137.6, 138.0, 138.2, 139.9. IR (KBr) 2914, 1491, 1441, 1029, 1016, 809, 803 cm^{-1}. MS (EI) m/z 446 (**M**$^+$+2, 21), 445 (**M**$^+$+1, 35), 444 (**M**$^+$, 100), 123 ($SC_6H_4CH_3$, 3), 91 ($C_6H_4CH_3$, 3). HRMS Calcd for $C_{27}H_{24}S_3$: 444.1040. Found: 444.1056. Mp. 116-117 ºC (Chloroform).



16

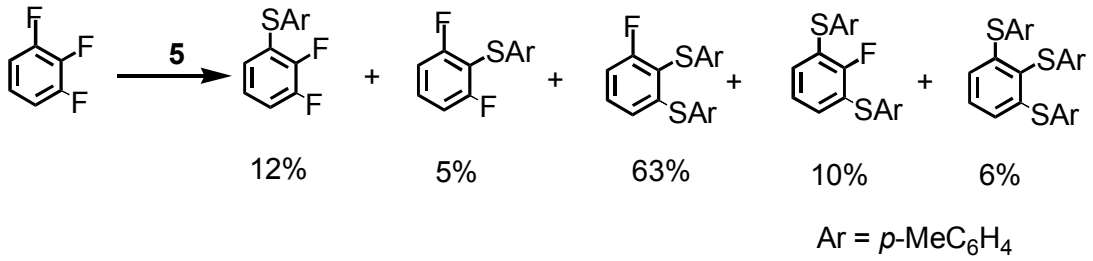
The reaction of 1,3,5-trifluorobenzene. $RhH(PPh_3)_4$ (5 mol%), 1,2-bis(diphenylphosphino)benzene (10

mol%), and triphenylphosphine (50 mol%) were used, and reacted in refluxing chlorobenzene for 24 h. **3,5-Difluoro-1-(*p*-tolylthio)benzene.** Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.39 (3H, s), 6.55 (1H, tt, *J*(H,H) = 2.4 Hz, *J*(H,F) = 8.8 Hz), 6.61 (2H, dd, *J*(H,H) = 2.0 Hz, *J*(H,F) = 8.0 Hz), 7.23 (2H, d, *J*(H,H) = 8.0 Hz), 7.40 (2H, d, *J*(H,H) = 8.0 Hz). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 21.3, 101.0 (t, *J*(C,F) = 26.2 Hz), 110.1 (dd, *J*(C,F) = 6.7, 21.2 Hz), 127.7, 130.6, 134.5, 139.6, 143.0 (t, *J*(C,F) = 9.7Hz), 163.1 (dd, *J*(C,F) = 13.5, 250.5Hz). ^{19}F-NMR (377 MHz, $CDCl_3$) δ -112.51 (t, *J*(H,F) = 7.5 Hz). IR (neat) 2925, 2854, 1607, 1586, 1458, 1285, 1119, 985, 874, 843, 810, 667, 538, 499 cm^{-1}. MS (EI) *m/z* 238 (**M**$^{+}$+2H, 8), 237 (**M**$^{+}$+H, 21), 236 (**M**$^{+}$, 100), 221 (**M**$^{+}$-CH_3, 23), 123 ($SC_6H_4CH_3$, 3), 91 ($C_6H_4CH_3$, 18). HRMS Calcd for $C_{13}H_{10}F_2S$: 236.0471. Found: 236.0471. **5-Fluoro-1,3-bis(*p*-tolylthio)benzene.** Colorless crystals. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.37 (3H, s), 6.56 (2H, dd, *J*(H,H) = 1.6 Hz, *J*(H,F) = 9.6 Hz), 6.74 (1H, t, *J*(H,H) = 1.6 Hz), 7.16 (4H, d, *J*(H,H) = 8.0 Hz), 7.32 (4H, d, *J*(H,H) = 8.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 22.3, 111.9 (d, *J*(C,F) = 23.5 Hz), 122.2, 128.4, 130.4, 134.0, 139.0, 141.5 (d, *J*(C,F) = 8.4 Hz), 163.0 (d, *J*(C,F) = 249.0 Hz). ^{19}F-NMR (377 MHz, $CDCl_3$) δ -114.91 (t, *J*(H,F) = 9.0 Hz). IR (KBr) 3085, 1581, 1491, 1437, 1399, 1227, 1212, 1179, 1019, 924, 837, 809, 705, 668, 505, 485 cm^{-1}. MS (EI) *m/z* 342 (**M**$^{+}$+2H, 16), 341 (**M**$^{+}$+H, 31), 340 (**M**$^{+}$, 100), 217 (**M**$^{+}$-$SC_6H_4CH_3$, 10), 123 ($SC_6H_4CH_3$, 5), 91 (*p*-$C_6H_4CH_3$, 6). HRMS Calcd for $C_{20}H_{17}FS_2$: 340.0756. Found: 340.0753. Mp. 140-141 ºC (Hexane). **1,3,5-Tris(*p*-tolylthio)benzene.** Colorless crystals. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.35 (9H, s), 6.74 (3H, s), 7.09 (6H, d, *J*(H,H) = 8.0 Hz), 7.23 (6H, d, *J*(H,H) = 8.0 Hz). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 21.2, 125,2, 129.2, 130.1, 133.4, 138.3, 139.8. IR (neat) 2359, 2343, 1550, 1491, 803, 684, 668, 485 cm^{-1}. MS (EI) *m/z* 446 (**M**$^{+}$+2, 22), 445 (**M**$^{+}$+1, 38), 444 (**M**$^{+}$, 100), 321 (**M**$^{+}$-$SC_6H_4CH_3$, 2), 198 (**M**$^{+}$-2$SC_6H_4CH_3$, 23), 123 ($SC_6H_4CH_3$, 2), 91 ($C_6H_4CH_3$, 2). HRMS Calcd for $C_{27}H_{24}S_3$: 444.1040. Found: 444.1045. Mp. 87-88 ºC (Hexane).



The reaction of 1,2,3-trifluorobezene. $RhH(PPh_3)_4$ (5 mol%), 1,2-bis(diphenylphosphino)benzene (10 mol%), and triphenylphosphine (50 mol%) were used, and reacted in refluxing chlorobenzene for 6 h. **2,3-Difluoro-1-(*p*-tolylthio)benzene** Yellow oil. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.36 (3H, s), 6.82 (1H, dddd, *J*(H,H) = 1.8, 7.8 Hz, *J*(H,F) = 1.2, 6.0 Hz), 6.93 (1H, dddd, *J*(H,H) = 8.4, 8.4 Hz, *J*(H,F) = 1.8, 5.4 Hz), 7.00 (1H, dddd, *J*(H,H) = 1.8, 8.4 Hz, *J*(H,F) = 7.2, 8.4 Hz), 7.17 (2H, d, *J*(H,H) = 7.8 Hz), 7.34 (2H, d, *J*(H,H) = 7.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.2, 115.4 (d, *J*(C,F) = 17.4 Hz), 124.1 (dd, *J*(C,F) = 4.4, 7.2 Hz), 126.0 (d, *J*(C,F) = 3.0 Hz), 127.4 (d, *J*(C,F) = 14.5 Hz), 128.6, 130.3, 133.1, 138.6, 148.4 (dd, *J*(C,F) = 13.0, 247.2 Hz), 150.7 (dd, *J*(C,F) = 13.0, 250.1 Hz). ^{19}F-NMR (377 MHz, $CDCl_3$) δ -138.40 (d, *J*(F,F) = 17.4 Hz), -140.85 (d, *J*(F,F) = 17.4 Hz). IR (neat) 2924, 1609, 1492, 1478, 1456, 1271, 899, 813, 770 cm^{-1}. MS (EI) *m/z* 237 (**M**$^{+}$+1, 20), 236 (**M**$^{+}$, 100), 221 (**M**$^{+}$-CH_3, 21), 91 (*p*-$C_6H_4CH_3$, 27). HRMS Calcd for $C_{13}H_{10}F_2S$. 236.0471. Found: 236.0448. **1,3-Difluoro-2-(*p*-tolylthio)benzene** Colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.29 (3H, s), 6.95 (2H, dd, *J*(H,H) = 8.5 Hz, *J*(H,F) = 7.0 Hz), 7.06 (2H, d, *J*(H,H) = 8.5 Hz), 7.21 (2H, d, *J* = 8.0 Hz), 7.32 (1H, tt, *J*(H,H) = 8.0 Hz, *J*(H,F) = 6.5 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.0, 111.8 (d, *J*(C,F) = 4.8 Hz), 111.9 (d, *J*(C,F) = 5.8 Hz), 129.7, 129.8, 130.8 (t, *J*(C,F) = 10.6 Hz), 131.3, 136.9, 163.3 (dd, *J*(C,F) = 4.8, 249.5 Hz).

^{19}F-NMR (377 MHz, $CDCl_3$) δ -107.20 (dd, *J*(H,F) = 7.5 Hz, *JJ*(F,F) = 6.0 Hz). IR (neat) 2922, 1604, 1492, 1462, 1235, 992, 782 cm^{-1}. MS (EI) *m/z* 237 (**M**$^+$+1, 20), 236 (**M**$^+$, 100), 221 (**M**$^+$-CH_3, 5), 91 (*p*-$C_6H_4CH_3$, 22). HRMS Calcd for $C_{13}H_{10}F_2S$. 236.0471. Found: 236.0459. **2-Fluoro-1,3-bis(*p*-tolylthio)benzene** Colorless crystals. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.36 (6H, s), 6.88 (3H, m), 7.16 (4H, d, *J*(H,H) = 7.2 Hz), 7.33 (4H, d, *J*(H,H) = 7.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.2, 124.5 (d, *J*(C,F) = 4.4 Hz), 125.4 (d, *J*(C,F) = 18.9 Hz), 129.0, 129.6, 130.2, 132.9, 138.3, 157.4 (d, *J* = 244.3 Hz). ^{19}F-NMR (377 MHz, $CDCl_3$) δ -109.79 (t, *J*(H,F) = 6.4 Hz). IR (KBr) 1489, 1430, 1178, 809, 763 cm^{-1}. MS (EI) *m/z* 342 (**M**$^+$+2, 15), 341 (**M**$^+$+1, 29), 340 (**M**$^+$, 100), 217 (**M**$^+$- S(*p*-$C_6H_4CH_3$), 9), 123 (S(*p*-$C_6H_4CH_3$), 6), 91 (*p*-$C_6H_4CH_3$, 9). HRMS Calcd for $C_{20}H_{17}FS_2$: 340.0756. Found: 340.0733. Mp 158-159 ℃ (Hexane). **3-Fluoro-1,2-bis(*p*-tolylthio)benzene.** Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.29 (3H, s), 2.38 (3H, s), 6.52 (1H, d, *J*(H,H) = 8.0 Hz), 6.84 (1H, dd, *J*(H,H) = 8.0, *J*(H,F) =8.0 Hz), 7.06 (2H, d, *J*(H,H) = 8.0 Hz), 7.10 (1H, ddd, *J*(H,H) = 8.0, 8.0 Hz *J*(H,F) = 5.2 Hz), 7.18 (2H, d, *J*(H,H) = 8.0 Hz), 7.21 (2H, d, *J*(H,H) = 8.0 Hz), 7.39 (2H, d, *J*(H,H) = 8.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.0, 21.3, 112.1 (d, *J*(C,F) = 24.4 Hz), 117.3 (d, *J*(C,F) = 1.0 Hz), 117.5 (d, *J*(C,F) = 2.9 Hz), 122.1 (d, *J*(C,F) = 3.1 Hz), 128.4, 129.7, 130.6, 130.6, 130.7, 131.9, 135.3, 136.2, 139.4, 149.0, 163.4 (d, *J*(C,F) = 247.0 Hz). ^{19}F-NMR (377 MHz, $CDCl_3$) δ -107.22 (dd, *J*(H,F) = 6.0 Hz). IR (neat) 3020, 2921, 1581, 1562, 1491, 1443, 1246, 1017, 886, 810, 778 cm^{-1}. MS (EI) *m/z* 342 (**M**$^+$+2, 14), 341 (**M**$^+$+1, 28), 340 (**M**$^+$, 100), 217 (**M**$^+$-S(*p*-$C_6H_4CH_3$), 17), 123 (S(*p*-$C_6H_4CH_3$), 3), 91 (*p*-$C_6H_4CH_3$, 9). HRMS Calcd for $C_{20}H_{17}FS_2$: 340.0756. Found: 340.0757. **1,2,3-Tris(*p*-tolylthio)benzene** Colorless crystals. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.32 (3H, s), 2.37 (6H, s), 6.45 (2H, d, *J*(H,H) = 8.0 Hz), 6.92 (1H, t, *J*(H,H) = 8.0 Hz), 7.10 (2H, d, *J*(H,H) = 8.0 Hz), 7.15 (2H, d, *J*(H,H) = 8.0 Hz), 7.19 (4H, d, *J*(H,H) = 8.0 Hz), 7.38 (4H, d, *J*(H,H) = 8.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$). 21.0, 21.3, 122.8, 126.9, 128.9, 129.8, 129.9, 130.4, 132.1, 134.2, 135.4, 135.5, 139.2, 149.0. IR (KBr) 2918, 1550, 1489, 1425, 812, 805, 770 cm^{-1}. MS (EI) *m/z* 446 (**M**$^+$+2, 22), 445 (**M**$^+$+1, 37), 444 (**M**$^+$, 100), 198 (**M**$^+$-2S(*p*-$C_6H_4CH_3$), 14), 123 (S(*p*-$C_6H_4CH_3$), 2), 91 (*p*-$C_6H_4CH_3$, 3). HRMS Calcd for $C_{27}H_{24}S_3$: 444.1040. Found: 444.1030. Mp 79.5-80.5 ℃ (Ethyl acetate).



Reference

1) Allen, N. S.; Corrales, T.; Edge, M.; Catalina, F.; Blanco-Pina, M.; Green, A. *Polymer*, **1998**, *39*, 903.

2) Denney, D. B.; Denny, D. Z.; Perez, A. J. *Tetrahedron* **1993**, *49*, 4463.

3) Zheng, N.; McWilliams, J. C.; Fleitz, F. J.; Armstrong III, J. D.; Volante, R. P. *J. Org. Chem*. **1998**, *63*, 9606.

4) Marshall, W. J.; Grushin, V. V. *Organometallics* **2003**, *22*, 555.

5) Schopfer, U.; Schlapbach, A. *Tetrahedron* **2001**, *57*, 3069.

6) Sawyer, J. S.; Schmittling, E. A.; Palkowitz, J. A.; Smith, III, W. J. *J. Org. Chem*.. **1998**, *63*, 6338.

7) Gorczynski, M. J.; Leal, R. M.; Mooberry, S. L.; Bushweller, J. H.; Brown, M. L. *Bioorg. Med. Chem*. **2004**, *12*, 1029.

8) Urban J.; Sedivy, Z.; Holubek, J.; Svatek, E.; Ryska, M.; Koruna, I.; Dlabac, A.; Valchar, M.; Metysova, J.; Polivka, Z.; Sindelar, K.; Pomykacek, J.; Hrubantova, M.; Protiva, M. *Collect. Czech. Chem. Commun*. **1990**, *55*, 1077.

9) Sindelar, K.; Kakac, B.; Svatek, E.; Metysova, J.; Protiva, M. *Collect. Czech. Chem. Commun*. **1973**, *38*, 1579.

10) Constantino, L.; Ferrari, A. M.; Gamberini, M. C.; Rastelli, G. *Bioorg. Med. Chem*. **2002**, *10*, 3923.

11) Davis, F A.; Horner, C, J.; Fretz, E. R.; Stackhouse, J. F. *J. Org. Chem*. **1973**, *38*, 695.

12) Hynes, R. C.; Peach, M. E. *J. Fluorine Chem*. **1986**, *31*, 129.

13) Malichenko, B. F.; Robota, L. P. *J. Org. Chem. USSR*. **1975**, *11*, 772.