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Supporting Information

Syntheses, Crystal and Solution Structures, Ligand Exchange, and Ligand Coupling Reactions of Mixed Pentaarylantimony Compounds

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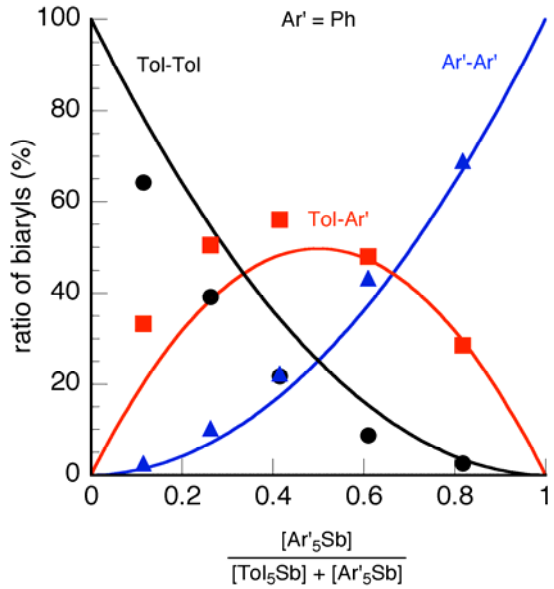

Figure S1. Distribution of biaryls generated from the LCR using a mixture of **1** and Ph_5Sb. Circles, squares, and triangles: experimental ratio of Tol-Tol, Tol-Ar', and Ar'-Ar', respectively. Solid lines: calculated statistical ratios.

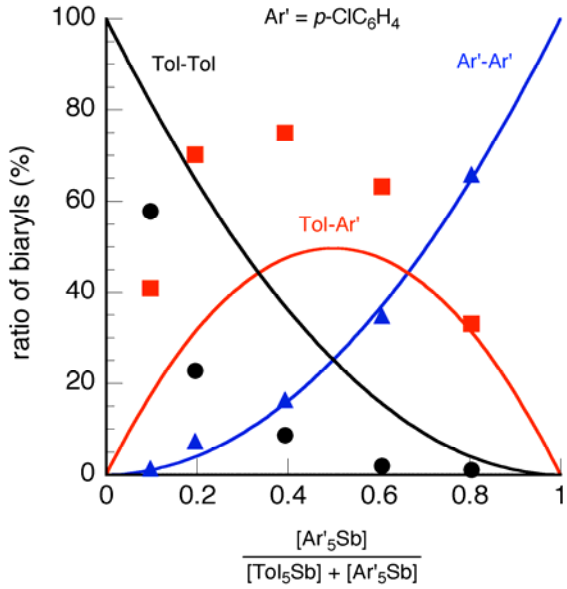

Figure S2. Distribution of biaryls generated from the LCR using a mixture of **1** and $(p\text{-}ClC_6H_4)_5Sb$. Circles, squares, and triangles: experimental ratio of Tol-Tol, Tol-Ar', and Ar'-Ar', respectively. Solid lines: calculated statistical ratios.

Experimental Section

General: Melting points were measured using a Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (100 MHz) spectra were recorded using a JEOL EX-400 spectrometer. ^{1}H NMR (90 MHz) and ^{19}F NMR (85 MHz) spectra were also routinely recorded using a Hitachi R-90H spectrometer. Chemical shifts are reported (δ scale) from internal tetramethylsilane for ^{1}H and ^{13}C or from fluorotrichloromethane for ^{19}F. Elemental analyses were performed using a Perkin-Elmer 2400CHN elemental analyzer. Flash column chromatography was carried out with Merck silica gel 9385. Preparative thin layer chromatography was carried out on plates of Merck silica gel 60 GF-254. HPLC was carried out using a JAI LC-908. All reactions involving organometallic compounds or diethylaminosulfur trifluoride were carried out under Ar. Tetrahydrofuran (THF) and diethyl ether were freshly distilled from sodium-benzophenone. Tris(*p*-methylphenyl)antimony, tris(*p*-methylphenyl)antimony dichloride, tris(*p*-methylphenyl)antimony dibromide, and pentakis(*p*-methylphenyl)antimony were prepared according to published procedures.[S1]

Tris(*p*-trifluoromethylphenyl)antimony (8: Ar_3Sb). To a solution of *p*-trifluoromethylphenyllithium prepared from *n*BuLi (*c* = 1.55 M in *n*-hexane, 200 mL,

0.31 mol) and *p*-bromobenzotrifluoride (67.5 g, 0.3 mol) in ether (300 mL) was added an ether (100 mL) solution of antimony trichloride (25 g, 0.11 mol) at –78 °C. After the mixture was allowed to warm to room temperature, it was additionally stirred for 4 h and was heated under reflux for 1 h. The mixture was treated with ice water (400 mL). Extraction with ether, drying with $MgSO_4$, and removal of the solvent furnished an orange oil (37.2 g, 77%), which was crystallized from ether/methanol (1:1): mp 131-132 °C (lit.[S2] : 130-132 °C); ^{1}H NMR ($CDCl_3$) δ 7.54 (d, 6H, 2(6)-H, $^3J_{2(6)\text{-H},3(5)\text{-H}}$ = 8 Hz), 7.60 (d, 6H, 3(5)-H, $^3J_{3(5)\text{-H},2(6)\text{-H}}$ = 8 Hz); ^{13}C NMR ($CDCl_3$) δ 124.0 (q, C-7, $^1J_{\text{C-7,7-F}}$ = 272 Hz), 125.7 (dq, C-3(5), $^3J_{\text{C-3(5),7-F}}$ = 3.2 Hz), 131.4 (q, C-4, $^2J_{\text{C-2,7-F}}$ = 32 Hz), 136.4 (d, C-2(6)), 142.3 (s, C-1); ^{19}F NMR ($CDCl_3$) δ –63.46 (s, CF_3). Anal. Calcd for $C_{21}H_{12}F_9Sb$: C, 45.27; H, 2.17%. Found: C, 45.01; H, 2.03%.

Tris(*p*-trifluoromethylphenyl)antimony Dibromide (9: Ar_3SbBr_2). To a CCl_4 (100 mL) solution of tris(*p*-trifluoromethylphenyl)antimony (10.6 g, 0.019 mol) was added a CCl_4 (20 mL) solution of bromine (1.13 mL, 3.52 g, 0.022 mol) at room temperature. Evaporation of the volatiles and recrystallizion from 10 mL of diethyl ether and 75 mL of *n*-hexane yielded the product as a white solid (12.3 g, 90%): mp 150-151 °C; ^{1}H NMR ($CDCl_3$) δ 7.85 (d, 6H, 3(5)-H, $^3J_{3(5)\text{-H},2(6)\text{-H}}$ = 8 Hz), 8.33 (d, 6H, 2(6)-H, $^3J_{2(6)\text{-H},3(5)\text{-H}}$ = 8 Hz); ^{13}C NMR ($CDCl_3$) δ 123.2 (q, C-7, $^1J_{\text{C-7,7-F}}$ = 273 Hz), 126.5 (d, C-3(5)), 134.0 (q, C-4, $^2J_{\text{C-4,7-F}}$ = 32 Hz), 134.1 (d, C-2(6)), 144.2 (s, C-1); ^{19}F NMR ($CDCl_3$) δ –63.71

(s, CF_3). Anal. Calcd for $C_{21}H_{12}Br_2F_9Sb$: C, 35.18; H, 1.69%. Found: C, 35.05; H, 1.64%.

Pentakis(*p*-trifluoromethylphenyl)antimony (6: Ar_5Sb). To a solution of *p*-trifluoromethylphenyllithium prepared from *n*BuLi (*c* = 1.6 M in *n*-hexane, 31.5 mL, 50.4 mmol) and *p*-bromobenzotrifluoride (11.3 g, 50.4 mmol) in ether (100 mL) was added an ether (100 mL) solution of tris(*p*-trifluoromethylphenyl)antimony dibromide (**9**) (10.7 g, 14.9 mmol) at –78 °C. After the mixture was allowed to warm to room temperature, it was additionally stirred overnight. The mixture was treated with water (50 mL). Extraction with ether, drying with $MgSO_4$, and removal of solvent yielded a light yellow solid (9.05 g, 72%), which was recrystallized from benzene/*n*-hexane (1:1): mp 193-195 °C; ^{1}H NMR (C_6D_6) δ 7.13 (d, 10H, 3(5)-H, $^3J_{3(5)\text{-H},2(6)\text{-H}}$ = 8 Hz), 7.32 (d, 10H, 2(6)-H, $^3J_{2(6)\text{-H},3(5)\text{-H}}$ = 8 Hz); ^{13}C NMR (C_6D_6) δ 124.2 (q, C-7, $^1J_{\text{C-7,7-F}}$ = 272 Hz), 125.4 (dq, C-3(5), $^3J_{\text{C-3(5),7-F}}$ = 3.7 Hz), 131.8 (q, C-4, $^2J_{\text{C-4,F}}$ = 32.5 Hz), 135.4 (d, C-2(6)), 149.6 (s, C-1); ^{19}F NMR (C_6D_6) δ –62.73 (s, CF_3). Anal. Calcd for $C_{35}H_{20}F_{15}Sb$: C, 49.61; H, 2.38%. Found: C, 49.80; H, 2.23%.

Tetrakis(*p*-trifluoromethylphenyl)antimony Fluoride (10: Ar_4SbF). To an ether (20 mL) of pentakis(*p*-trifluoromethylphenyl)antimony (1.0 g, 1.18 mmol) was added diethylaminosulfur trifluoride (210 mg, 0.16 mL, 1.3 mmol) at 0 °C. After the mixture was allowed to warm to room temperature, it was additionally stirred for 2 h. Removal

of the solvent yielded a colorless powder which was treated with *n*-hexane (20 mL) for 2 h. The insoluble white solid residue was collected as the product (560 mg, 66%): mp 177-178 °C; ^{1}H NMR ($CDCl_3$) δ 7.73 (d, 8H, 3(5)-H, $^{3}J_{3(5)\text{-H},2(6)\text{-H}}$ = 8 Hz), 7.81 (d, 8H, 2(6)-H, $^{3}J_{2(6)\text{-H},3(5)\text{-H}}$ = 8 Hz); ^{13}C NMR ($CDCl_3$) δ 123.6 (q, C-7, $^{1}J_{\text{C-7,7-F}}$ = 273 Hz), 126.0 (dq, C-3(5), $^{3}J_{\text{C-3(5),7-F}}$ = 3.6 Hz), 133.3 (q, C-4, $^{2}J_{\text{C-4,7-F}}$ = 33.1 Hz), 136.2 (d, C-2(6)), 140.3 (s, C-1); ^{19}F NMR ($CDCl_3$) δ –63.69 (s, 12F, CF_3), –84.16 (s, 1F, SbF). Anal. Calcd for $C_{28}H_{16}F_{13}Sb$: C, 46.63; H, 2.24%. Found: C, 46.61; H, 2.06%.

***p*-(Methylphenyl)tetrakis(*p*-trifluoromethylphenyl)antimony (5: Ar_4TolSb).** To an ether (10 mL) solution of tetrakis(*p*-trifluoromethylphenyl)antimony fluoride (430 mg, 0.6 mmol) was added an ether (10 mL) solution of *p*-tolylmagnesium bromide (0.7 mmol) dropwise within 3 min at 0 °C. After stirring the mixture for an additional 15 min at 0 °C, water (0.2 mL) was added followed by filtration through silica gel, which was subsequently purged with ether (200 mL). Removal of the solvent and recrystallization of the white residue from 2.5 mL of benzene and 5 mL of *n*-hexane yielded the product as a colorless powder (260 mg). From the mother liquor, another crop of 60 mg was isolated using preparative HPLC; total yield 320 mg (67%); mp 176-178 °C; ^{1}H NMR (C_6D_6) δ 2.11 (s, 3H, 7-H), 7.00 (d, 2H, 3(5)-H, $^{3}J_{3(5)\text{-H},2(6)\text{-H}}$ = 7.8 Hz), 7.17 (d, 8H, 2'(6')-H, $^{3}J_{2'(6')\text{-H},3'(5')\text{-H}}$ = 7.8 Hz), 7.27 (d, 8H, 3'(5')-H, $^{3}J_{3'(5')\text{-H},2'(6')\text{-H}}$ = 7.8 Hz), 7.35 (d, 2H, 2(6)-H, $^{3}J_{2(6)\text{-H},3(5)\text{-H}}$ = 7.8 Hz). ^{13}C NMR (C_6D_6) δ 21.20 (q, C-7),

124.7 (q, C-7', $^{1}J_{\text{C-7',7'-F}}$ = 273 Hz), 125.1 (dq, C-3'(5'), $^{3}J_{\text{C-3'(5'),7'-F}}$ = 3.7 Hz), 130.1 (d, C-3(5)), 131.2 (q, C-4', $^{2}J_{\text{C-4',7'-F}}$ = 32.5 Hz), 134.0 (s, C-1), 135.3 (d, C-2(6)), 135.4 (d, C-2'(6')), 141.1 (s, C-4), 152.2 (s, C-1'); ^{19}F NMR (C_6D_6) δ –62.59 (s, CF_3). Anal. Calcd for $C_{35}H_{23}F_{12}Sb$: C, 52.99; H, 2.92%. Found: C, 52.83; H, 2.59%.

Tris(*p*-trifluoromethylphenyl)antimony Difluoride (12: Ar_3SbF_2).

(a) To a cooled (–78 ˚C) suspension of 7.15 g (33 mmol) of antimony pentafluoride in 100 mL of ether was added dropwise a solution of *p*-trifluoromethylphenyllithium prepared from *n*BuLi (*c* = 1.66 M in *n*-hexane, 132.5 mL, 0.22 mol) and *p*-bromobenzotrifluoride (49.5 g, 0.22 mol) in ether (200 mL) at –78 °C. After the mixture was allowed to warm to room temperature, it was additionally stirred for 2 h and was heated under reflux for 2 h. The reaction mixture was filtered through silica gel (3 x 4 cm), which was then washed with 200 mL of ether. Evaporation of solvents and subsequent recrystallization from *n*-hexane yielded a white pasty mass, which was dissolved in 25 mL of ether and 75 mL of ethanol. Slow evaporation of ether at room temperature by means of a rotary evaporator yielded a white solid (12.5 g, 64%): mp 101-102 °C (lit[S3] : 109-110 °C); ^{1}H NMR ($CDCl_3$) δ 7.82 (d, 6H, 3(5)-H, $^{3}J_{\text{3(5)-H,2(6)-H}}$ = 8 Hz), 8.34 (d, 6H, 2(6)-H, $^{3}J_{\text{2(6)-H,3(5)-H}}$ = 8 Hz); ^{13}C NMR ($CDCl_3$) δ 123.4 (q, C-7, $^{1}J_{\text{C-7,7-F}}$ = 273 Hz), 126.4 (dq, C-3(5), $^{3}J_{\text{C-3(5),7-F}}$ = 3.3 Hz), 134.7 (q, C-4, $^{2}J_{\text{C-4,7-F}}$ = 33.1 Hz), 135.9 (dt, C-2(6), $^{3}J_{\text{C-2(6),Sb-F}}$ = 4.6 Hz), 137.3 (t, C-1, $^{2}J_{\text{C-1,Sb-F}}$ = 15.6 Hz); ^{19}F NMR

($CDCl_3$) δ –63.87 (s, 9F, CF_3), –152.6 (s, 2F, SbF_2). Anal. Calcd for $C_{21}H_{12}F_{11}Sb$: C, 42.38; H, 2.03%. Found: C, 42.20; H, 1.83%.

(b) To an ether (100 mL) solution of Ar_3Sb (8.6 g, 15.4 mmol) was added diethylaminosulfur trifluoride (1.0 mL, 7.6 mmol) at 0 °C. After the mixture was stirred for 30 min it was treated with water, the organic layer was washed with water several times. Drying with $MgSO_4$ and removal of the solvent yielded a colorless solid (6.7 g, 73%), which was recrystallized from ethanol/water.

Bis(*p*-methylphenyl)tris(*p*-trifluoromethylphenyl)antimony (4: Ar_3Tol_2Sb). To an ether (50 mL) solution of tris(*p*-trifluoromethylphenyl)antimony difluoride (2.98 g, 5.0 mmol) was added an ether (111.1 mL) solution of *p*-tolylmagnesium bromide (10 mmol) at 0 °C. After the mixture was stirred for 20 min at 0 °C, it was treated with water (60 mL). Extraction with ether, drying with $MgSO_4$, and removal of the solvent yielded the product as a gummy, white residue which was crystallized from 20 mL of benzene and 75 mL of acetonitrile; 2.16 g (58%): mp 168-169 °C; ^{1}H NMR (C_6D_6) δ 2.09 (s, 6H, 7-H), 6.98 (d, 4H, 3(5)-H, $^3J_{3(5)\text{-H},2(6)\text{-H}}$ = 8 Hz), 7.26 (s, 12H, 2'(6')-H, 3'(5')-H), 7.41 (d, 4H, 2(6)-H, $^3J_{2(6)\text{-H},3(5)\text{-H}}$ = 8 Hz); ^{13}C NMR (C_6D_6) δ 21.18 (q, C-7), 124.9 (q, C-7', $^1J_{\text{C-7',7'-F}}$ = 272 Hz), 124.8 (d, C-3'(5')), 129.9 (d, C-3(5)), 130.6 (q, C-4', $^2J_{\text{C-4',7'-F}}$ = 31.9 Hz), 136.1 (s, C-1), 135.2 (d, C-2(6)), 135.5 (d, C-2'(6')), 140.4 (s, C-4), 155.3 (s, C-1'); ^{19}F NMR (C_6D_6) δ –62.49 (s, CF_3). Anal. Calcd for $C_{35}H_{26}F_9Sb$: C,

56.85; H, 3.54%. Found: C, 56.68; H, 3.41%.

***p*-Methylphenylantimony Dichloride (TolSbCl$_2$).** A mixture of Tol$_3$Sb (5.9 g, 15 mmol) and SbCl$_3$ (6.9 g, 30 mmol) was heated at 40 °C for 30 min. The reaction mixture was extracted with dry dichloromethane. Evaporation of the solvent yielded a colorless solid, which was recrystallized from dichloromethane to give colorless crystals (6.3 g, 49%): mp 94-96 °C; ^{1}H-NMR (CDCl$_3$) δ 2.41 (s, 3H), 7.40 (d, 2H, J = 7.8 Hz), 7.75 (d, 2H, J = 7.8 Hz).

***p*-Methylphenylbis(*p*-trifluoromethylphenyl)antimony (14: Ar$_2$TolSb).** To a solution of *p*-trifluoromethylphenyllithium prepared from *n*BuLi (c = 1.6 M in *n*-hexane, 22.5 mL, 36.0 mmol) and *p*-bromobenzotrifluoride (5.0 mL, 35.71 mmol) in ether (25 mL) was added an ether (25 mL) solution of MgBr$_2$ prepared from Mg (0.9 g, 37.04 mmol) and 1,2-dibromoethane (3.1 mL, 35.97 mmol) at –78 °C. The mixture was stirred for 30 min at –78 °C. The prepared ArMgBr was transferred to an ether (50 mL) suspension of TolSbCl$_2$ (5.0 g, 17.63 mmol) at 0 °C. After the mixture was allowed to warm to room temperature, it was heated under reflux for 3 h. It was then treated with water (50 mL). Extraction was done with ether followed by usual workup. Short column chromatography (ether on silica gel) furnished the product (5.2 g, 59%) as a yellow oil along with a small amount (ca. 5 %) of Ar$_3$Sb. The product was crystallized from methanol: mp 69-71 °C; ^{1}H NMR (CDCl$_3$) δ 2.37 (s, 3H, 7-H), 7.20

(d, 2H, 3(5)-H, $^{3}J_{3(5)\text{-H},2(6)\text{-H}}$ = 7.8 Hz), 7.29 (d, 2H, 2(6)-H, $^{3}J_{2(6)\text{-H},3(5)\text{-H}}$ = 7.8 Hz), 7.54 (d, 4H, 2'(6')-H, $^{3}J_{2'(6')\text{-H},3'(5')\text{-H}}$ = 8.3 Hz), 7.57 (d, 4H, 3'(5')-H, $^{3}J_{3'(5')\text{-H},2'(6')\text{-H}}$ = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 21.37 (q, C-7), 124.1 (q, C-7', $^{1}J_{\text{C-7',7'-F}}$ = 273 Hz), 125.4 (q, C-3'(5'), $^{3}J_{\text{C-3'(5'),7'-F}}$ = 3.7 Hz), 130.2 (d, C-3(5)), 130.9 (q, C-4', $^{2}J_{\text{C-4',7'-F}}$ = 31.9 Hz), 133.3 (s, C-1), 136.2 (d, C-2(6)), 136.4 (d, C-2'(6')), 139.4 (s, C-4), 143.2 (s, C-1'); ^{19}F NMR ($CDCl_3$) δ –63.37 (s, CF_3). Anal. Calcd for $C_{21}H_{15}F_6Sb$: C, 50.13; H, 3.01%. Found: C, 50.22; H, 2.75%.

***p*-Methylphenylbis(*p*-trifluoromethylphenyl)antimony Difluoride (15: $Ar_2TolSbF_2$).** To an ether (10 mL) solution of *p*-methylphenylbis(*p*-trifluoromethylphenyl)antimony (0.99 g, 1.97 mmol) was added an ether (10 mL) solution of diethylaminosulfur trifluoride (0.27 mL, 355 mg, 2.2 mmol) at 0 °C. After the mixture was stirred for 2 h at 0 °C it was treated with water (50 mL). Extraction with ether, drying with $MgSO_4$, and removal of the solvent yielded the product as a yellow oil which was crystallized from 20 mL of methanol and a small amount of water. The crystallization is rather difficult and time consuming, but gives a pure product: yield 710 mg (65%); mp 67-68 °C; ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3H, 7-H), 7.39 (d, 2H, 3(5)-H, $^{3}J_{3(5)\text{-H},2(6)\text{-H}}$ = 8.8 Hz), 7.79 (d, 4H, 3'(5')-H, $^{3}J_{3'(5')\text{-H},2'(6')\text{-H}}$ = 8.8 Hz), 8.02 (d, 2H, 2(6)-H, $^{3}J_{2(6)\text{-H},3(5)\text{-H}}$ = 8.8 Hz), 8.31 (d, 4H, 2'(6')-H, $^{3}J_{2'(6')\text{-H},3'(5')\text{-H}}$ = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 21.50 (q, C-7), 123.5 (q, C-7', $^{1}J_{\text{C-7',7'-F}}$ =

273 Hz), 126.1 (d, C-3'(5')), 130.7 (d, C-3(5)), 134.2 (q, C-4', $^2J_{C\text{-}4',7'\text{-}F}$ = 32.5 Hz), 128.9 (t, C-1, $^2J_{C\text{-}1,Sb\text{-}F}$ = 14.7 Hz), 135.1 (d, C-2(6)), 135.8 (dt, C-2'(6'), $^3J_{C\text{-}2',Sb\text{-}F}$ = 5.5 Hz), 138.6 (t, C-1', $^2J_{C\text{-}1',Sb\text{-}F}$ = 16.6 Hz), 143.5 (s, C-4); ^{19}F NMR ($CDCl_3$) δ –63.77 (s, 6 F, CF_3), –152.7 (s, 2 F, SbF_2). Anal. Calcd for $C_{21}H_{15}F_8Sb$: C, 46.61; H, 2.79%. Found: C, 46.46; H, 2.55%.

Tris(*p*-methylphenyl)bis(*p*-trifluoromethylphenyl)antimony (3: Ar_2Tol_3Sb). To an ether (10 mL) solution of *p*-methylphenylbis(*p*-trifluoromethylphenyl)antimony difluoride (298 mg, 0.50 mmol) was added an ether (20 mL) solution of *p*-methylphenylmagnesium bromide (1.54 mmol) at 0 °C. After the mixture was stirred for 20 min at 0 °C it was treated with water. Extraction was done with ether followed by usual workup. Short column chromatography (ether on silica gel) furnished the product as a colorless powder, which was recrystallized from 0.5 ml of benzene and 5 ml of *n*-hexane. An additional crop was obtained by evaporation of the mother liquor and separation of the residue by means of preparative HPLC: total yield 290 mg (55%): mp 155-165 °C; ^{1}H NMR (C_6D_6) δ 2.08 (s, 9H, 7-H), 6.98 (d, 6H, 3(5)-H, $^3J_{3(5)\text{-}H,2(6)\text{-}H}$ = 7.8 Hz), 7.27 (d, 4H, 3'(5')-H, $^3J_{3'(5')\text{-}H,2'(6')\text{-}H}$ = 7.8 Hz), 7.35 (d, 4H, 2'(6')-H, $^3J_{2'(6')\text{-}H,3'(5')\text{-}H}$ = 7.8 Hz), 7.50 (d, 6H, 2(6)-H, $^3J_{2(6)\text{-}H,3(5)\text{-}H}$ = 7.8 Hz); ^{13}C NMR (C_6D_6) δ 21.18 (q, C-7), 125.1 (q, C-7', $^1J_{C\text{-}7',7'\text{-}F}$ = 272 Hz), 124.4 (dq, C-3'(5'), $^3J_{C\text{-}3'(5'),7'\text{-}F}$ = 3.6 Hz), 129.7 (d, C-3(5)), 129.7 (q, C-4', $^2J_{C\text{-}4',7'\text{-}F}$ = 31.9 Hz), 138.0 (s, C-1), 135.2 (d, C-2(6)), 135.6 (d,

C-2'(6')), 139.7 (s, C-4), 159.5 (s, C-1'); ^{19}F NMR (C_6D_6) δ –62.33 (s, CF_3). Anal. Calcd for $C_{35}H_{29}F_6Sb$: C, 61.33; H, 4.27%. Found: C, 61.41; H, 4.32%.

Bis(*p*-methylphenyl)antimony Chloride (Tol_2SbCl). A stirred mixture of Tol_3Sb (2.25 g, 5.69 mmol) and $SbCl_3$ (1.0 g, 4.38 mmol) was heated at 50 °C overnight. The product became a mixture of Tol_2SbCl (major) and $TolSbCl_2$ and Tol_3SbCl_2. The mixture was used without further purification in the following reaction. It was not possible to obtain a pure product by recrystalization. ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 6H), 7.23 (d, 4H, J = 7.8 Hz), 7.51 (d, 4H, J = 7.8 Hz).

Bis(*p*-methylphenyl)*p*-trifluoromethylphenylantimony (17: $ArTol_2Sb$).

To a solution of *p*-trifluoromethylphenyllithium prepared from *n*BuLi (*c* = 1.6 M in *n*-hexane, 30.6 mL, 48.99 mmol) and *p*-bromobenzotrifluoride (6.86 mL, 48.99 mmol) in ether (25 mL) was added an ether (25 mL) solution of $MgBr_2$ prepared from Mg (1.2 g, 49.38 mmol) and 1,2-dibromoethane (4.25 mL, 49.32 mmol) at –78 °C. The mixture was stirred for 30 min at –78 °C. The prepared ArMgBr was transferred at –78 °C to an ether (50 mL) suspension of Tol_2SbCl prepared from Tol_3Sb (10.4 g, 26.4 mmol) and $SbCl_3$ (4.64 g, 20.3 mmol). After the mixture was allowed to warm to room temperature it was heated under reflux for 4 h. It was then treated with water (50 mL). Extraction was done with ether followed by usual workup. Short column chromatography (ether on silica gel) furnished a yellow oil which was distilled by

Kugelrohr (200 °C / 10^{-2} torr). Preparative HPLC yielded the product as colorless crystals (1.67 g, 8%) which was recrystallized from methanol. Mp 77-78 °C; ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 6H, 7-H), 7.21 (d, 4H, 3(5)-H, $^{3}J_{3(5)\text{-H},2(6)\text{-H}}$ = 8.8 Hz), 7.37 (d, 4H, 2(6)-H, $^{3}J_{2(6)\text{-H},3(5)\text{-H}}$ = 8.8 Hz), 7.54 (d, 4H, 2'(6')-H, $^{3}J_{2'(6')\text{-H},3'(5')\text{-H}}$ = 8.3 Hz), 7.57 (d, 4H, 3'(5')-H, $^{3}J_{3'(5')\text{-H},2'(6')\text{-H}}$ = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 21.35 (q, C-7), 124.3 (q, C-7', $^{1}J_{\text{C-7',7'-F}}$ = 272 Hz), 125.1 (dq, C-3'(5'), $^{3}J_{\text{C-3'(5'),7'-F}}$ = 3.6 Hz), 129.9 (d, C-3(5)), 130.5 (q, C-4', $^{2}J_{\text{C-4',7'-F}}$ = 32.2 Hz), 134.0 (s, C-1), 136.3 (d, C-2(6)), 136.2 (d, C-2'(6')), 138.8 (s, C-4), 144.1 (s, C-1'); ^{19}F NMR ($CDCl_3$) δ –63.27 (s, CF_3). Anal. Calcd for $C_{21}H_{18}F_3Sb$: C, 56.16; H, 4.04%. Found: C, 55.88; H, 3.98%.

Bis(*p*-methylphenyl)*p*-trifluoromethylphenylantimony Difluoride (18: $ArTol_2SbF_2$). To an ether (10 mL) solution of bis(*p*-methylphenyl)(*p*-trifluoromethylphenyl)antimony (1.00 g, 2.23 mmol) was added an ether (10 mL) solution of diethylaminosulfur trifluoride (0.31 mL, 400 mg, 2.5 mmol) at 0 °C. After the mixture was stirred for 2 h at 0 °C it was treated with water (50 mL). Extraction with ether, drying with $MgSO_4$, and removal of the solvent yielded the product as a yellow oil. It was used without further purification in the following reaction. An analytical sample was prepared by means of preparative HPLC; ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 6H, 7-H), 7.36 (d, 4H, 3(5)-H, $^{3}J_{3(5)\text{-H},2(6)\text{-H}}$ = 8 Hz), 7.76 (d, 2H, 3'(5')-H, $^{3}J_{3'(5')\text{-H},2'(6')\text{-H}}$ = 8.3 Hz), 8.02 (d, 4H, 2(6)-H, $^{3}J_{2(6)\text{-H},3(5)\text{-H}}$ = 8 Hz),

8.30 (d, 2H, 2'(6')-H, $^{3}J_{2'(6')\text{-H},3'(5')\text{-H}}$ = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 21.50 (q, C-7), 123.6 (q, C-7', $^{1}J_{\text{C-7',7'-F}}$ = 272 Hz), 125.9 (d, C-3'(5')), 130.5 (d, C-3(5)), 133.8 (q, C-4', $^{2}J_{\text{C-4',7'-F}}$ = 33.1 Hz), 129.7 (t, C-1, $^{2}J_{\text{C-1,Sb-F}}$ = 15.7 Hz), 135.1 (dt, C-2(6), $^{3}J_{\text{C-2,Sb-F}}$ = 4.6 Hz), 135.8 (dt, C-2'(6'), $^{3}J_{\text{C-2',Sb-F}}$ = 5.6 Hz), 139.4 (t, C-1', $^{2}J_{\text{C-1',Sb-F}}$ = 17.1 Hz), 143.0 (s, C-4); ^{19}F NMR ($CDCl_3$) δ –63.72 (s, 3F, CF_3), –152.5 (s, 2F, SbF_2). Anal. Calcd for $C_{21}H_{18}F_5Sb$: C, 51.78; H, 3.72%. Found: C, 51.49; H, 3.41%.

Tetrakis(*p*-methylphenyl)*p*-trifluoromethylphenylantimony (2: ArTol$_4$Sb). To an ether (20 mL) solution of bis(*p*-methylphenyl)(*p*-trifluoromethylphenyl)antimony difluoride (1.22 g, 2.5 mmol) was added an ether (20 mL) solution of *p*-methylphenylmagnesium bromide (5.5 mmol) at 0 °C. After the mixture was stirred for 20 min at 0 °C it was treated with water. Extraction was done with ether followed by usual workup. Short column chromatography (ether on silica gel) furnished the product as a colorless powder, which was recrystallized from 1 mL of benzene and 10 ml of *n*-hexane. An additional crop was obtained by evaporation of the mother liquor and separation of the residue by means of preparative HPLC: total yield 690 mg (49%): mp 163-164 °C; ^{1}H NMR (C_6D_6) δ 2.08 (s, 12H, 7-H), 6.98 (d, 8H, 3(5)-H, $^{3}J_{\text{3(5)-H,2(6)-H}}$ = 7.8 Hz), 7.27 (d, 2H, 3'(5')-H, $^{3}J_{\text{3'(5')-H,2'(6')-H}}$ = 7.8 Hz), 7.42 (d, 2H, 2'(6')-H, $^{3}J_{\text{2'(6')-H,3'(5')-H}}$ = 7.8 Hz), 7.57 (d, 8H, 2(6)-H, $^{3}J_{\text{2(6)-H,3(5)-H}}$ = 7.8 Hz); ^{13}C NMR (C_6D_6) δ 21.20 (q, C-7), 125.3 (q, C-7', $^{1}J_{\text{C-7',7'-F}}$ = 272 Hz), 124.1 (dq, C-3'(5'), $^{3}J_{\text{C-3'(5'),7'-F}}$ = 3.6

Hz), 129.4 (d, C-3(5)), 129.3 (q, C-4', $^2J_{C\text{-}4',7'\text{-}F}$ = 31.9 Hz), 141.4 (s, C-1), 135.5 (d, C-2(6)), 135.8 (d, C-2'(6')), 138.9 (s, C-4), 162.0 (s, C-1'); ^{19}F NMR (C_6D_6) δ –62.21 (s, CF_3). Anal. Calcd for $C_{35}H_{32}F_3Sb$: C, 66.57; H, 5.11%. Found: C, 66.28; H, 5.00%.

X-ray Structure Determination of 2, 3, 4, 5 and 6. Crystal data and numeric details of the structure determinations are given in Table S1. Crystals suitable for X-ray structure determination were mounted on a Mac Science MXC3 diffractometer and irradiated with graphite-monochromated Mo *K*α radiation (λ = 0.71073 Å) for data collection. Lattice parameters were determined by least-squares fitting of 29, 42, 32, 28 and 31 reflections with 31° < 2θ < 35°, 31° < 2θ < 39°, 31° < 2θ < 42°, 31° < 2θ < 35° and 31° < 2θ < 35° for **3**, **4**, **5**, **6** and **2**, respectively. Data were collected with the 2θ/ω-scan mode. All data were corrected for absorption[S4] and extinction.[S5] The structures were solved by a direct method using the SHELX-97 program. [S6] Refinement on F^2 was carried out by full-matrix least squares using the SHELX-97 program.[S6] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms with isotropic thermal parameters. The F atoms in some of the CF_3 groups show considerable disorder along the 3-fold axis and these "split" stoms were refined isotropically.

Table S1. Crystallographic data for **2**, **3**, **4**, **5** and **6**.

	2	**3**	**4** • 0.5 Et_2O
Formula	$C_{35}H_{32}F_3Sb$	$C_{35}H_{29}F_6Sb$	$C_{37}H_{31}F_9O_{0.5}Sb$
Molecular weight	631.36	685.33	776.37
Crystal system	*monoclinic*	*monoclinic*	*triclinic*
Space group	$P2_1/n$	$P2_1/n$	P-1
Color	colorless	colorless	colorless
Habit	plate	plate	plate
Cryst dimens, mm	0.90, 0.60, 0.30	0.55, 0.50, 0.20	0.60, 0.40, 0.20
a, Å	17.257(3)	17.508(8)	10.2002(11)
b, Å	12.172(3)	12.380(4)	11.4868(17)
c, Å	14.723(3)	14.823(5)	15.929(2)
α, deg	90	90	106.512(10)
β, deg	103.151(15)	102.93(3)	91.241(10)
γ, deg	90	90	96.206(10)
V, Å^3	3011.6(11)	3131(2)	1776.3(4)
Z	4	4	2
D_{calc}, g cm^{-3}	1.392	1.454	1.452
Abs coeff, mm^{-1}	0.956	0.939	0.849
F(000)	1280	1376	778
Radiation: λ, Å	Mo $K\alpha$, 0.71073	Mo $K\alpha$, 0.71073	Mo $K\alpha$, 0.71073
Temp, K	296	296	296
Index range	$-22 \le h \le 21$	$-20 \le h \le 20$	$-12 \le h \le 0$
	$-1 \le k \le 15$	$-7 \le k \le 14$	$-13 \le k \le 13$
	$-7 \le l \le 19$	$0 \le l \le 17$	$-18 \le l \le 18$
Reflections collected	7256	5814	6745
Independent reflections	6917	5494	6258
R_{int}	0.0379	0.0184	0.0152
No of params refined	366	380	422
R_1 ($I>2\sigma(I)$)	0.0504	0.0652	0.0609
wR_2 (all data)	0.1600	0.1929	0.1787
Goodness of fit	1.071	1.039	1.068
Max shift in final cycle	0.001	0.001	0.001
Final diff map, max, e/Å	0.855	0.743	1.361

Table S1 (continued).

	5 • 2.5 benzene	**6**
Formula	$C_{50}H_{38}F_{12}Sb$	$C_{35}H_{20}F_{15}Sb$
Molecular weight	988.55	847.26
Crystal system	*triclinic*	*triclinic*
Space group	*P*-1	*P*-1
Color	colorless	colorless
Habit	plate	plate
Cryst dimens, mm	0.80, 0.70, 0.60	0.80, 0.50, 0.25
a, Å	12.272(4)	13.374(6)
b, Å	13.022(3)	13.608(6)
c, Å	16.697(5)	19.415(7)
α, deg	69.63(2)	92.54(3)
β, deg	80.30(2)	103.45(3)
γ, deg	68.45(2)	90.11(3)
V, Å^3	2324.0(11)	3433(2)
Z	2	4
D_{calc}, g cm^{-3}	1.413	1.639
Abs coeff, mm^{-1}	0.674	0.910
F(000)	994	1664
Radiation: λ, Å	Mo *K*α, 0.71073	Mo *K*α, 0.71073
Temp, K	296	296
Index range	$-14 \le h \le 14$	$-15 \le h \le 15$
	$-14 \le k \le 15$	$0 \le k \le 16$
	$-7 \le l \le 19$	$-23 \le l \le 23$
Reflections collected	8637	12773
Independent reflections	8200	12088
R_{int}	0.0133	0.0139
No of params refined	572	911
R_1 ($I>2\sigma(I)$)	0.0673	0.0633
wR_2 (all data)	0.2028	0.1818
Goodness of fit	1.065	1.042
Max shift in final cycle	0.001	0.001
Final diff map, max, e/Å	1.532	1.003

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