# 2,2'-Disubstituted $F_{12}$Binaphthyl Derivatives: Stannanes, Boranes, and (*R*)-$F_{12}$BINOL

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## S.1 General Considerations:

### S1.1 Solvents and Reagents

Tetrahydrofuran (THF) was dried over sodium/benzophenone ketal and freshly distilled before use. $CH_2Cl_2$ was dried over $CaH_2$ and freshly distilled before use. Dimethylsulfoxide (DMSO) was fractionally distilled under vacuum and stored over activated 4 Å molecular sieves. Benzaldehyde and titanium isopropoxide were freshly

distilled before use. Octafluoronaphthalene (Oakwood Products, Inc.) and all other solvents and reagents (Aldrich) were purchased and used as received.

### S1.2 NMR Spectroscopy

Nuclear magnetic resonance spectroscopy (1-dimensional $^{1}H$, $^{11}B$, $^{13}C$, $^{19}F$, and $^{119}Sn$; 1-dimensional $^{1}H$-$^{19}F$ decoupling; and 2-dimensional $^{19}F$-$^{19}F$ and $^{1}H$-$^{1}H$ COSY) were performed on Bruker AMX-300 ($^{1}H$, 300.1 MHz; $^{11}B$, 96.3 MHz; $^{13}C$, 75.5 MHz; $^{19}F$, 282.4 MHz) or Bruker DRX-400 ($^{1}H$, 400.1 MHz; $^{11}B$, 128.4 MHz; $^{13}C$, 100.6 MHz; $^{119}Sn$, 149.0 MHz) spectrometers. All $^{1}H$ NMR spectra were referenced relative to $SiMe_4$ (δ 0.00 ppm) through the residual $^{1}H$ resonance(s) of the solvents employed (δ: $CDCl_3$, 7.27 ppm; $C_6D_6$, 7.16 ppm; $CD_2Cl_2$, 5.32 ppm; toluene-$d_8$, 2.09 ppm ($C(H/D)_3$); THF-$d_8$, 1.73 and 3.58 ppm). $^{11}B$ NMR spectra were referenced relative to $BF_3{\cdot}OEt_2$ (δ 0.0 ppm) in $C_6D_6$. $^{13}C$ NMR spectra were referenced relative to $SiMe_4$ (δ 0.0 ppm) through the resonance(s) of the solvents employed (δ: $CDCl_3$, 77.23 ppm; $CD_2Cl_2$, 54.0 ppm). $^{19}F$ NMR spectra were referenced relative to $CFCl_3$ (δ 0.0 ppm) relative to external $C_6F_6$ (δ -162.0 ppm) in $C_6D_6$ at room temperature.

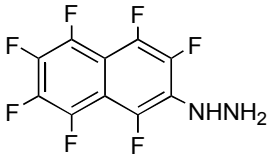
### S1.3 Other Instrumentation and Analysis

Analytical chiral HPLC separations were performed using a Daicel Chiralcel OD column with a Waters 1525 Binary HPLC Pump using isocratic hexane:*i*-PrOH mixtures at room temperature with UV detection at 254 nm on a Waters 2487 detector. Elemental analyses were performed on a Control Equipment Corporations 440 Elemental Analyzer by Mrs. Dorothy Fox, Mrs. Roxanna Smith, and Ms. Olivera Blagojevic. Single crystal

X-ray crystallographic analyses were performed by Dr. Masood Parvez (University of Calgary) on a Nonius KappaCCD diffractometer or by Dr. Robert McDonald (University of Alberta) on a Bruker P4/RA/SMART 1000 CCD diffractometer.

## S2 Experimental Details

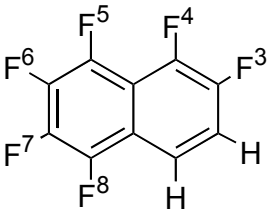
### S2.1 Synthesis of 1,3,4,5,6,7,8-Heptafluoro-2-naphthylhydrazine:




1, 3,4,5, 6,7,8-Heptafluoronaphthylhydrazine was prepared via the method described by Gething *et al.*[1] Hydrazine monohydrate, $NH_2NH_2{\cdot}H_2O$, (3.95 mL, 4.08 g, 81.6 mmol, 1.1 equiv.) was added via syringe to a stirred EtOH solution (100% absolute, 105 mL, 0.7 M) of octafluoronaphthalene (20.0 g, 73.5 mmol, 1 equiv.) at room temperature. The orange solution was heated at reflux (~80 °C) for 4 h, then poured into water (~200 mL) and extracted with $CH_2Cl_2$ (3 × ~150 mL). The combined $CH_2Cl_2$ extracts were dried over $MgSO_4$, filtered, and concentrated in vacuo to give an orange solid. In a modification of the literature procedure, the orange solid was suspended in petroleum spirits (~400 mL), stirred rapidly for 1 h, and filtered to give the fluoronaphthyl hydrazine as a pale orange solid (12.8 g, 61 %; Lit.[1] 57%). The product was found to be >95% pure by $^{19}F$ NMR with the only contaminant being unreacted octafluoronaphthalene (<5%). $^{1}H$ NMR ($CDCl_3$): δ 5.51 (br s, 1H, N*H*$NH_2$), 4.10 (br s, 2H, NHN$H_2$). $^{19}F$ NMR ($CDCl_3$): δ -142.6 (dm, $^{4}J_{peri}$ = 63.0 Hz), -146.7 (app. dtm, $^{4}J_{peri}$ = 56.5 and $J$ = 16.3 Hz), -147.4 (app. dtm, $^{4}J_{peri}$ = 63.8 and $J$ = 16.3 Hz), -148.5 (app. dtm, $^{4}J_{peri}$ = 56.8 and $J$ = 16.0 Hz), -149.3 (m), -155.7 (m), -158.1 (app. tm, $J$ = 18.8 Hz). The orange petroleum spirit filtrate was

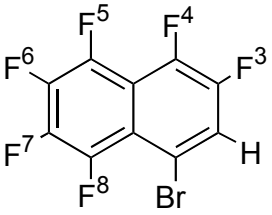
concentrated to give a dark orange solid which was purified by silica gel column chromatography (100% hexanes) to give octafluoronaphthalene (6.3 g, 32% recovery) as a colourless crystalline solid. Resonances for octafluoronaphthalene $C_{10}F_8$: $^{19}$F NMR ($CDCl_3$): δ -145.0 (m, 4F), -153.5 (m, 4F).

### S2.2 Synthesis of 1,2,3,4,5,6-Hexafluoronaphthalene (2-H):



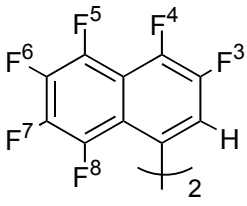

Hexafluoronaphthalene **2-H** was prepared from 1,3,4,5,6,7,8-heptafluoro-2-naphthyl hydrazine via a modification of the method described by Bolton and Sandall.[2] Solid 1,3,4,5,6,7,8-heptafluoro-2-naphthyl hydrazine (10.9 g, 38.4 mmol, 1 equiv.) was added to a MeOH solution of NaOMe (0.5 M, freshly prepared by dissolving Na {3.53 g, 153 mmol} in 300 mL MeOH, 4 equiv.) and the resulting dark solution was stirred at room temperature until the evolution of $N_2$ ceased (~0.5 h). The reaction mixture was poured into water (~250 mL) to give a yellow mixture that was extracted with $CH_2Cl_2$ (3 × ~200 mL). The combined $CH_2Cl_2$ extracts were dried over $MgSO_4$, filtered, and concentrated to give an orange oil that was purified by silica gel column chromatography (100% hexanes) to give **2-H** as a pale yellow oil (8.28 g, 91%). $^1$H and $^{19}$F NMR spectroscopic properties matched those reported in the literature.[2,3] $^1$H NMR ($CDCl_3$): δ 7.83 (dm, $J$ = 9.4 Hz, 1H), 7.47 (app. td, $J$ = 9.4 and 7.0 Hz, 1H). $^{19}$F NMR ($CDCl_3$): δ -137.1 (m, $F^3$), -144.6 (dm, $^4J_{peri(F4-F5)}$ = 51.0 Hz, $F^4$), -146.5 (app. dtd, $^4J_{peri(F5-F4)}$ = 51.0 Hz, and $J$ = 16.6 and 5.1 Hz, $F^5$), -147.8 (m, $F^8$), -155.3 (m, $F^6$), -157.5 (app. tdd, $J$ = 18.5 Hz for $^3J_{ortho(F7-F6)}$ and $^3J_{ortho(F7-F8)}$, and $J$ = 7.7 and 4.2 Hz, $F^7$).

### S2.3 Synthesis of 1-Bromo-3,4,5,6,7,8-hexafluoronaphthalene (2-Br):




Hexafluoronaphthalene **2-H** (8.28 g, 35.1 mmol, 1 equiv.) was added dropwise to a stirred mixture of $Br_2$ (9.0 mL, 28.0 g, 175 mmol, 5 equiv.) and Fe powder (3.92 g, 70.2 mmol, 2 equiv.). The mixture was stirred at room temperature for 15 min then diluted with $CH_2Cl_2$ (20 mL) and carefully added in portions to a stirred and cooled (ice bath) saturated aqueous solution of $Na_2S_2O_3$ (~250 mL). The yellow mixture was then extracted with $CH_2Cl_2$ (3 × ~250 mL) and the combined extracts were dried over $MgSO_4$, filtered, and concentrated to give an orange oil contaminated with solid yellow sulfur. Silica gel column chromatography gave **2-Br** as a pale yellow oil (10.5 g, 95%) that was approx. 85% pure by GC/MS. The pale yellow oil crystallized upon standing and was recrystallized from hexane at -30 °C to give **2-Br** as a colourless crystalline solid (7.74 g, 70%). $^{1}H$ and $^{19}F$ NMR spectroscopic characteristics matched those reported by Matthews,[3] although a more thorough analysis is given here. $^{1}H$ NMR ($CDCl_3$): δ 7.76 (dd, $^{3}J_{ortho(H\text{-}F3)}$ = 9.5 and $^{4}J_{meta(H\text{-}F4)}$ = 6.7 Hz). $^{19}F$ NMR ($CDCl_3$): δ -136.2 (m, $F^3$), -139.9 (app. tm, $J$ = 17.1 Hz for $^{3}J_{ortho(F8\text{-}F7)}$ and $^{5}J_{para(F8\text{-}F5)}$, $F^8$), -144.2 (ddm, $^{4}J_{peri(F4\text{-}F5)}$ = 68.3 and $^{3}J_{ortho(F4\text{-}F3)}$ = 17.6 Hz, $F^4$), -145.0 (app. dtm, $^{4}J_{peri(F5\text{-}F4)}$ = 68.8 and $J$ = 17.1 Hz for $^{3}J_{ortho(F5\text{-}F6)}$ and $^{5}J_{para(F5\text{-}F8)}$, $F^5$), -153.3 (app. tm, $J$ = 18.7 Hz for $^{3}J_{ortho(F6\text{-}F5)}$ and $^{3}J_{ortho(F6\text{-}F7)}$, $F^6$), -154.5 (app. tm, $J$ = 18.7 Hz for $^{3}J_{ortho(F7\text{-}F6)}$ and $^{3}J_{ortho(F7\text{-}F8)}$, $F^7$). Anal. calcd. for $C_{10}HBrF_6$: C, 38.13; H, 0.32. Found: C, 37.89; H, 0.30.

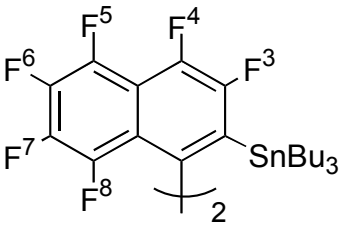
**S2.4 Synthesis of 3,3_,4,4_,5,5_,6,6_,7,7_,8,8_-Dodecafluoro-1,1_-binaphthyl (3):**




To a THF solution (0.4 M, 15 mL) of **2-Br** (2.00 g, 6.35 mmol, 1 equiv.) was added *i*-PrMgCl (2.0 M THF, 3.33 mL, 6.66 mmol, 1.05 equiv.) at room temperature. The resulting nearly colourless solution was cooled to -78 °C then transferred via canula onto a THF suspension (10 mL) of $CuBr{\cdot}SMe_2$ (1.31 g, 6.35 mmol, 1 equiv.) at -78 °C. To the colourless mixture at -78 °C was then added a THF solution (5 mL) of **2-Br** (2.00 g, 6.35 mmol, 1 equiv.) via syringe. The flask was sealed with a Teflon valve and the cold bath was removed and copious red precipitate began to appear as the mixture warmed to room temperature. The rust red mixture was heated to 90 °C for 48 hours then cooled to room temperature and filtered through a pad of Celite while washing with EtOAc. The yellow filtrate was diluted with aqueous HCl (1 M, ~150 mL) and extracted with EtOAc (3 × 150 mL). The combined yellow EtOAc extracts were dried over $MgSO_4$, filtered, and concentrated to give a yellow solid (3.2 g). Silica gel column chromatography (100% hexanes) gave the coupled product **3** as a nearly colourless crystalline solid (2.58 g, 86%). Single crystals suitable for X-ray crystallographic study were grown by cooling an $Et_2O$ solution to -30 °C. $^{1}$H NMR ($CDCl_3$): δ 7.29 (dd, $^{3}J_{ortho(H\text{-}F3)}$ = 9.9 and $^{4}J_{meta(H\text{-}F4)}$ = 7.1 Hz, 2H, aryl C-*H*). $^{19}$F NMR ($CDCl_3$): δ -137.6 (m, $F^3$), -140.7 (app. tm, $J$ = 16.6 Hz for $^{3}J_{ortho(F8\text{-}F7)}$ and $^{5}J_{para(F8\text{-}F5)}$, $F^8$), -143.4 (ddm, $^{4}J_{peri(F4\text{-}F5)}$ = 63.1 and $^{3}J_{ortho(F4\text{-}F3)}$ = 17.6 Hz, $F^4$), -145.2 (app. dtm, $^{4}J_{peri(F5\text{-}F4)}$ = 63.1 and $J$ = 16.6 Hz for $^{3}J_{ortho(F5\text{-}F6)}$ and $^{5}J_{para(F5\text{-}F8)}$, $F^5$), -154.0 (app. tm, $J$ = 18.1 Hz for $^{3}J_{ortho(F6\text{-}F5)}$ and $^{3}J_{ortho(F6\text{-}F7)}$, $F^6$), -155.5 (app. tm, $J$ = 18.6 Hz for $^{3}J_{ortho(F7\text{-}F6)}$ and $^{3}J_{ortho(F7\text{-}F8)}$, $F^7$). $^{13}$C NMR ($CDCl_3$): δ 146.5 (dd, $^{1}J_{C\text{-}F}$ = 252.3

and $J_{C\text{-}F}$ = 11.5 Hz, aryl *C*-F), 143.8 (dm, $^{1}J_{C\text{-}F}$ = 256.1 Hz, aryl *C*-F), 142.9 (dm, $^{1}J_{C\text{-}F}$ = 250.7 Hz, aryl *C*-F), 141.6 (dm, $^{1}J_{C\text{-}F}$ = 256.9 Hz, aryl *C*-F), 139.4 (app. dt, $^{1}J_{C\text{-}F}$ = 256.1 and $J_{C\text{-}F}$ = 15.0 Hz, aryl *C*-F), 138.9 (app. dt, $^{1}J_{C\text{-}F}$ = 256.1 and $J_{C\text{-}F}$ = 17.3 Hz, aryl *C*-F), 130.5 (m, quaternary aryl *C*), 121.0 (d, $^{2}J_{C\text{-}F}$ = 21.8 Hz, aryl *C*-H), 116.6 (m, quaternary aryl *C*), 112.2 (m, quaternary aryl *C*). Anal. calcd. for $C_{20}H_2F_{12}$: C, 51.09; H, 0.43. Found: C, 50.80; H, 0.26.

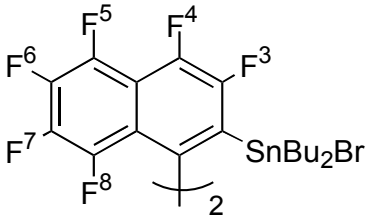
### S2.5 Synthesis of 2,2_-*Bis*(tri-*n*-butylstannyl)-3,3_,4,4_,5,5_,6,6_,7,7_,8,8_-dodecafluoro-1,1_-binaphthyl (4-Bu):




A THF solution (0.5 M, 60 mL) of LTMP was generated by the addition of *n*-BuLi (1.6 M hexane, 19.00 mL, 30.4 mmol, 6 equiv.) to a THF solution (40 mL) of 2,2,6,6-tetramethylpiperidine (5.16 mL, 4.29 g, 30.4 mmol, 6 equiv.) at room temperature and stirring for 30 min. The LTMP solution was cooled to -78 °C and to it was added $ClSnBu_3$ (8.24 mL, 9.89 g, 6 equiv.) via syringe at a rate slow enough to prevent warming of the LTMP/$ClSnBu_3$ solution above -70 °C. To this base/electrophile solution was added a THF solution (5 mL) of **3** (2.38g, 5.06 mmol, 1 equiv.) slowly via syringe to immediately give a dark blackish solution which was kept at -78 °C for 24 hours. The mixture was then warmed to room temperature, diluted with water (~60 mL), and extracted with $CH_2Cl_2$ (3 × 60 mL). The combined $CH_2Cl_2$ extracts were dried over $MgSO_4$, filtered, and concentrated to give a dark red/black oil. Silica gel column chromatography (100% hexanes) gave **4-Bu** as an analytically-pure colourless oil

(4.28 g, 81%). $^{1}$H NMR ($CDCl_3$): δ 1.36 – 1.12 (m, 4H, $SnCH_2CH_2CH_2CH_3$), 0.82 (t, $^{3}J_{H\text{-}H}$ = 7.2 Hz, $Sn(CH_2)_3CH_3$), 0.70 – 0.61 (m, 6H, $SnCH(H\_)(CH_2)_2CH_3$), 0.48 – 0.38 (m, 6H, $SnCH(H\_)(CH_2)_2CH_3$). $^{19}$F NMR ($CDCl_3$): δ -116.6 (m, $F^3$), -137.2 (m, $F^8$), -145.9 – -146.0 (m, $F^4$ and $F^5$), -155.3 (m, $F^6$), -156.8 (app. tm, $J$ = 18.8 Hz for $^{3}J_{ortho(F7\text{-}F6)}$ and $^{3}J_{ortho(F7\text{-}F8)}$, $F^7$). $^{13}$C NMR ($CDCl_3$; 3 overlapping aryl *C*-F resonances between 140 and 137 ppm are not tabulated and aryl *C*-$SnBu_3$ were not located): δ 150.9 (dm, $^{1}J_{C\text{-}F}$ = 236.9 Hz, aryl *C*-F), 141.5 (dm, $^{1}J_{C\text{-}F}$ = 244.9 Hz, aryl *C*-F), 118.1 (m, quat. aryl *C*), 112.8 (app. tm, $J$ = 9.8 Hz, quat. aryl *C*), 28.9 (s; Sn satellites: d, $^{3}J_{Sn\text{-}C}$ = 18.6 Hz, *n*-butyl $C_\gamma$), 27.4 (s; $^{119}$Sn satellites: d, $^{2}J_{119Sn\text{-}C}$ = 71.9 Hz; $^{117}$Sn satellites: d, $^{2}J_{117Sn\text{-}C}$ = 68.3 Hz, *n*-butyl $C_\beta$), 13.6 (s, *n*-butyl $C_\delta$), 11.2 (d, $^{4}J_{C\text{-}F}$ = 2.7 Hz; $^{119}$Sn satellites: dd, $^{1}J_{119Sn\text{-}C}$ = 353.1 and $^{4}J_{C\text{-}F}$ = 2.7 Hz; $^{117}$Sn satellites: dd, $^{1}J_{117Sn\text{-}C}$ = 338.9 and $^{4}J_{C\text{-}F}$ = 3.5 Hz, *n*-butyl $C_\alpha$). $^{119}$Sn NMR ($CDCl_3$): δ -35.0 (dm, $^{3}J_{Sn\text{-}F}$ = 41.0 Hz). Anal. calcd. for $C_{44}H_{54}F_{12}Sn_2$: C, 50.41; H, 5.19. Found: C, 50.19; H, 5.63.

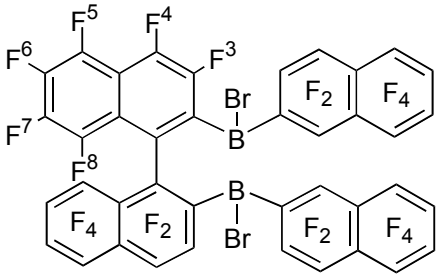
### S2.6 Synthesis of 2,2_-*Bis*(bromodi-*n*-butylstannyl)-3,3_,4,4_,5,5_,6,6_,7,7_,8,8_-dodecafluoro-1,1_-binaphthyl (4-Br):




$BBr_3$ (~1 mL, >10 equiv.) was vacuum transferred at -78 °C into a 25 mL glass bomb containing **4-Bu** (319 mg, 0.30 mmol, 1 equiv.). The bomb was sealed with a Teflon valve and the pink solution was stirred at room temperature for 2 h. The volatiles were then removed *in vacuo* to give a tan coloured powder (403 mg).

The expected yield for 0.3 mmol of **4-Br** (MW = 1094, 0.3 mmol, 328 mg) and the by-product, *n*-$BuBBr_2$ (MW = 228, 0.6 mmol, 137 mg) was 465 mg total. The $^{19}F$ NMR spectrum of the tan powder shows one $C_2$-symmetric fluorine-containing product consistent with the structure of **4-Br**. The yield of **4-Br** was therefore assumed to be nearly quantitative. Small amounts (<50 mg) of colourless needle crystals of **4-Br** were obtained by cooling pentane solutions to -30 °C, although the similar solubilities of **4-Br** and the by-product *n*-$BuBBr_2$ led to contamination of samples of **4-Br** with *n*-$BuBBr_2$. $^1H$ NMR ($CDCl_3$): δ 1.48 – 1.2 (m, 5H), 1.01 (m, 1H), 0.85 (t, $^3J_{H\text{-}H}$ = 7.3 Hz, C*H*$_3$). $^{19}F$ NMR ($CDCl_3$): δ -118.9 (d, $^3J_{ortho(F3\text{-}F4)}$ = 21.7 Hz, $F^3$), -136.8 (app. t, *J* = 16.8 Hz for $^3J_{ortho(F8\text{-}F7)}$ and $^5J_{para(F8\text{-}F5)}$, $F^8$), -142.7 (ddm, $^4J_{peri(F4\text{-}F5)}$ = 62.6 and $^3J_{ortho(F4\text{-}F3)}$ = 22.8 Hz, $F^4$), -144.9 (app. dtm, $^4J_{peri(F5\text{-}F4)}$ = 62.6 and *J* = 17.1 Hz for $^3J_{ortho(F5\text{-}F6)}$ and $^5J_{para(F5\text{-}F8)}$, $F^5$), -152.7 (app. tm, *J* = 18.1 Hz for $^3J_{ortho(F6\text{-}F5)}$ and $^3J_{ortho(F6\text{-}F7)}$, $F^6$), -154.6 (app. tm, *J* = 18.1 Hz for $^3J_{ortho(F7\text{-}F6)}$ and $^3J_{ortho(F7\text{-}F8)}$, $F^7$). $^{13}C$ NMR ($CDCl_3$; only Sn*Bu* resonances are tabulated; $^{117}Sn$ and $^{119}Sn$ satellites were not observed due to the low concentration of the sample): δ 28.1, 26.6, 21.0 (d, $^4J_{C\text{-}F}$ = 4.2 Hz), 13.5. $^{119}Sn$ NMR ($CDCl_3$): δ 25.8 (dd, $^3J_{Sn\text{-}F}$ = 74.5 and $^4J_{Sn\text{-}F}$ = 14.5 Hz). Elemental analysis of the colourless powder suggests the formulation as the 2,2_-*bis*($SnBu_2Br$) derivative. Anal. calcd. for $C_{36}H_{36}Br_2F_{12}Sn_2$: C, 39.53; H, 3.32. Found: C, 39.86; H, 2.65. The other possibility, the 2,2_-*bis*($SnBuBr_2$) derivative, would have the theoretical composition for $C_{28}H_{18}Br_4F_{12}Sn_2$ of C, 29.51% and H, 1.59%.

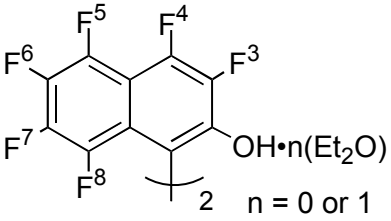
**S2-7 Synthesis of 2-Bromoboryl-3,3_,4,4_,5,5_,6,6_,7,7_,8,8_-dodecafluoro-1,1_-binaphthyl dimer (5):**




$BBr_3$ (8.4 g, 34 mmol, 8.7 equiv.) was vacuum transferred at -78 °C into a 25 mL glass bomb containing **2-Bu** (4.08 g, 3.9 mmol, 1 equiv.). The bomb was sealed with a Teflon valve and the pink solution darkened to intense dark blue as it was heated up to 90 °C. After stirring at 90 °C for 24 h, the black-green mixture was then cooled to room temperature and the volatiles removed in vacuo to give a mixture dark coloured oil and yellow crystalline solid. The yellow crystals were washed by vacuum transferring portions of pentane (~20 mL) into the flask, stirring for 5 – 10 min at room temperature and then decanting the dark blue pentane solution via canula into a second flask. This process was repeated twice more (or until the pentane wash is nearly colourless) and then the volatiles were removed in vacuo to give **5** as a canary yellow microcrystalline solid (1.62 g, 74%). The blue pentane solution was concentrated *in vacuo* and then treated with a second portion of $BBr_3$ (~5g) at 90 °C overnight followed by removal of volatiles and pentane washing as described above to give more yellow solid (0.26 g, 12%) for a total yield of **5** of 1.87 g (86%). The pentane washes were again concentrated to give a dark red oil (5.44g) consisting of $BuBBr_2$ and $Bu_2SnBr_2$ (theoretical yield: 1.76 and 3.06 g, respectively; total 4.82 g) and residual *bis*(bromodi-*n*-butylstannyl) derivative **4-Br** (theoretical for 14% unreacted material: 0.60 g). Single yellow block crystals of **5**·$(toluene)_2$ suitable for X-ray crystallographic analysis were obtained by cooling a saturated toluene solution to -

30 °C. $^{19}$F NMR (282.4 MHz, $CDCl_3$): δ -131.0 (dm, $^3J_{ortho(F3-F4)}$ = 16.0 Hz, $F^3$), -138.3 (app. tm, $J$ = 16.6 Hz for $^3J_{ortho(F8-F7)}$ and $^5J_{para(F8-F5)}$, $F^8$), -140.0 (ddm, $^4J_{peri(F4-F5)}$ = 61.6 and $^3J_{ortho(F4-F3)}$ = 18.1 Hz, $F^4$), -143.3 (app. dtm, $^4J_{peri(F5-F4)}$ = 62.1 and $J$ = 16.6 Hz for $^3J_{ortho(F5-F6)}$ and $^5J_{para(F5-F8)}$, $F^5$), -148.2 (app. tm, $J$ = 18.6 Hz for $^3J_{ortho(F6-F5)}$ and $^3J_{ortho(F6-F7)}$, $F^6$), -151.7 (m, $F^7$). $^{19}$F NMR (282.4 MHz, $C_6D_6$): δ -131.4 ($F^3$), -139.1 ($F^8$), -139.8 ($F^4$), -143.2 ($F^5$), -147.7 ($F^6$), -152.2 ($F^7$). $^{11}$B NMR 49.2 ppm. The low solubility of **5** and low intensities for *C*-F resonances prevented the acquisition of good quality $^{13}$C NMR spectral data. Anal. calcd. for $C_{40}B_2Br_2F_{24}$: C, 42.98. Found: C, 43.00.

**S2-8 Synthesis of 2,2_-Dihydroxy-3,3_,4,4_,5,5_,6,6_,7,7_,8,8_-dodecafluoro-1,1_-binaphthyl, $F_{12}$BINOL (1):**



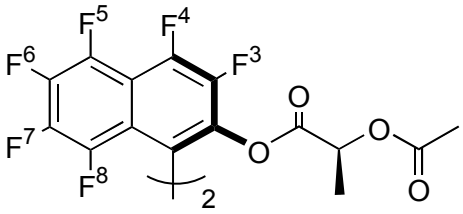

To a THF solution (5 mL) of **5** (1.57 g, 1.40 mmol) was added $H_2O_2$ (30% aqueous solution, 1.6 mL, 10 equiv., ~2.5 equiv. per B-C bond in **5**) dropwise by syringe at room temperature. The pale yellow solution immediately changed to yellow/orange with some precipitate formation and exothermicity during the addition of the first ~0.7 mL of 30% $H_2O_2$ solution. Upon further addition the reaction mixture turned clear yellow/orange without any further heat evolved. After stirring for 30 min at room temperature, the solution was poured into brine (~100 mL) and extracted with $Et_2O$ (3 × 150 mL). The combined $Et_2O$ extracts were dried over $MgSO_4$, filtered, and concentrated to give an orange solid (2.18 g). Silica gel column chromatography (0 – 40% EtOAc in hexanes) gave a red oil (1.66 g) that was pure by TLC ($R_f$ = 0.56, 40%

EtOAc:hexanes). The red oil was dissolved in $Et_2O$ (~100 mL) and washed with aqueous NaOH solution (1 M, 3 × 50 mL). The nearly colourless basic aqueous extracts were combined and acidified by the addition of aqueous HCl solution (6 M) and the resulting milky acidic layer was extracted with $Et_2O$ (3 × 150 mL). The combined $Et_2O$ extracts were then dried over $MgSO_4$, filtered, and concentrated to give a pale green oil (1.50 g) that began to crystallize on standing. Recrystallization from $Et_2O$ gave colourless block crystals of **1**·$(Et_2O)_2$ (1.40 g, 90 %). Single crystals of **1**·$(Et_2O)_2$ suitable for X-ray diffraction were grown by cooling an $Et_2O$ solution to -30 °C. **1**·$(Et_2O)_2$: $^1$H NMR ($CDCl_3$): δ 6.45 (br d, $^4J_{H\text{-}F3}$ = 2.0 Hz, 2H, O*H*), 3.50 (q, $^3J_{H\text{-}H}$ = 6.9 Hz, 8H, OC$H_2$CH$_3$), 1.19 (t, $^3J_{H\text{-}H}$ = 6.9 Hz, 12H, OCH$_2$C$H_3$). $^{19}$F NMR ($CDCl_3$; fluorine resonances were not symmetrical for unknown reasons): δ -140.9 (m, F$^4$), -146.0 (m, F$^8$), -146.1 (dm, $^4J_{peri(F5\text{-}F4)}$ = 61.5 Hz, F$^5$), -155.6 (m, F$^7$), -156.6 (m, F$^3$), -159.0 (m, F$^6$). $^{13}$C NMR ($CDCl_3$; 4 overlapping aryl *C*-F resonances between 142 and 136 ppm are not tabulated): δ 144.9 (dm, $^1J_{C\text{-}F}$ = 259.0 Hz, aryl *C*-F), 144.0 (d, $^2J_{C\text{-}F}$ = 13.3 Hz, aryl *C*-OH), 141.8 (dm, $^1J_{C\text{-}F}$ = 259.9 Hz, aryl *C*-F), 116.7 (m, quat. aryl *C*), 109.0 (m, quat. aryl *C*), 106.9 (app. tm, *J* = 9.8 Hz), 66.2 (s, O*C*H$_2$CH$_3$), 15.1 (s, OCH$_2$*C*H$_3$). Removal of the coordinated $Et_2O$ molecules was accomplished by grinding the crystalline **1**·$(Et_2O)_2$ into a powder and heating under dynamic vacuum at 50 °C overnight. **1**: $^1$H NMR ($CDCl_3$): δ 5.51 (br d, $^4J_{H\text{-}F3}$ = 3.8 Hz, 2H, O*H*). $^{19}$F NMR ($CDCl_3$): δ -140.4 (dm, $^4J_{peri(F4\text{-}F5)}$ = 59.0 Hz, F$^4$), -145.6 to -146.0 (overlapping signals for F$^5$ and F$^8$), -155.1 (m, F$^7$), -157.2 (m, F$^3$), -158.4 (m, F$^6$). Anal. calcd. for $C_{20}H_2F_{12}O_2$: C, 47.83; H, 0.40. Found: C, 47.58; H, 0.14.

**S2.9 Synthesis of 2,2_-*Bis*((*S*)-2-acetoxypropionato)-3,3_,4,4_,5,5_,6,6_,7,7_,8,8_-dodecafluoro-1,1_-binaphthyl (6):**

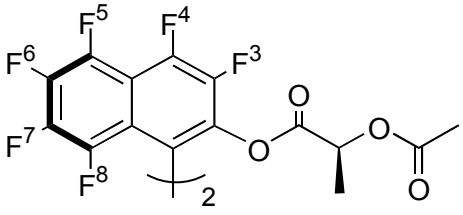
Modifications of the methods described by Hopkins and Keay,[4] and Kazlouskas[5] were employed for the synthesis of **6**. To a solution of **1** (828 mg, 1.64 mmol) in $Et_2O$ (0.05 M, 30 mL) was added $NEt_3$ (506 μL, 3.61 mmol, 2.2 equiv.) at room temperature. (*S*)-(-)-Acetoxypropionyl chloride (457 μL, 3.61 mmol, 2.2 equiv.) was then added dropwise via syringe and the mixture was stirred for 8 hours. The mixture was then diluted with hexanes, filtered, and the resulting filter cake washed with several portions of $Et_2O$. The volatiles were removed in vacuo and the residue was purified by silica gel column chromatography (gradient elution, 0 – 10% EtOAc:hexanes) to give **6** as an off-white semi-solid (1.14 g, 95%) that was found to be a 1:1 mixture of diastereomers, ($R_{ax}$,*S*,*S*)-**6** and ($S_{ax}$,*S*,*S*)-**6**. Fractional recrystallization from hexanes (~0.26 M, ~6 mL) at -10 °C gave 536 mg (47 %) of nearly colourless solid that was found to be 56 % de by $^1$H NMR spectroscopy. Recrystallizations of this fraction from hexanes gave colourless block crystals (407 mg, 36 %; 71 % of theoretical for one diastereomer) that were found to be 97 % de by $^1$H NMR. An X-ray diffraction study of single block crystals from this fraction did not assignment of the absolute configuration based on X-Ray data alone, due to the low scattering power of the light atoms in the structure. However, the known stereochemistry at C2 and C7 based on the starting material allowed assignment of this isomer as ($R_{ax}$,*S*,*S*)-**6** (*R* in the $F_{12}$-BINOL fragment). The combined mother liquors from the recrystallizations were concentrated to give a yellow oil product of 70 % de for the ($S_{ax}$,*S*,*S*)-**6** diastereomer.

**S2.10 Spectral data for (*R*)-(-)-2,2_-*Bis*((*S*)-2-acetoxypropionato)-3,3_,4,4_,5,5_,6,6_,7,7_,8,8_-dodecafluoro-1,1_-binaphthyl ((*R*$_{ax}$,*S*,*S*)-6):**




$^{1}$H NMR ($CDCl_3$): δ 4.76 (q, *J* = 7.2 Hz, 2H, propionoate C*H*$CH_3$), 2.00 (s, 6H, acetate C*H*$_3$), 1.35 (d, *J* = 7.2 Hz, 6H, propionoate CHC*H*$_3$). $^{19}$F NMR ($CDCl_3$): δ -139.1 (dd, $^{4}J_{peri(F4-F5)}$ = 63.1 Hz and $^{3}J_{ortho(F4-F3)}$ = 17.6 Hz, F$^4$), -141.1 (m, F$^8$), -144.9 (dm, $^{4}J_{peri(F5-F4)}$ = 63.1 Hz, F$^5$), -148.1 (m, F$^3$), -153.6 (m, F$^7$), -154.0 (app. t, *J* = 19.1 Hz for $^{3}J_{ortho(F6-F5)}$ and $^{3}J_{ortho(F6-F7)}$, F$^6$). $^{13}$C NMR ($CDCl_3$; only acetoxypropionate *C* resonances are tabulated): δ 170.1 (ester *C*=O), 167.6 (ester *C*=O), 68.3 (propionoate *C*H$CH_3$), 20.2 (acetoxy *C*H$_3$), 16.7 (propionoate CH*C*H$_3$). $[á]_D^{22}$ -121 (c = 12, $CH_2Cl_2$) for a sample of 97% de by $^{1}$H NMR).

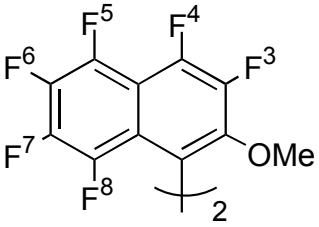
**S2.11 Spectral data for (*S*)-(+)-2,2_-*Bis*((*S*)-2-acetoxypropionato)-3,3_,4,4_,5,5_,6,6_,7,7_,8,8_-dodecafluoro-1,1_-binaphthyl ((*S*$_{ax}$,*S*,*S*)-6):**




$^{1}$H NMR ($CDCl_3$): δ 4.79 (q, *J* = 7.2 Hz, 2H, propionoate C*H*$CH_3$), 1.86 (s, 6H, acetate C*H*$_3$), 1.38 (d, *J* = 7.2 Hz, 6H, propionoate CHC*H*$_3$). $^{19}$F NMR ($CDCl_3$): δ -138.8 (dd, $^{4}J_{peri(F4-F5)}$ = 63.1 Hz and $^{3}J_{ortho(F4-F3)}$ = 17.6 Hz, F$^4$), -141.1 (m, F$^8$), -145.4 (dm, $^{4}J_{peri(F5-F4)}$ = 63.1 Hz, F$^5$), -148.0 (m, F$^3$), -154.2 (m, F$^7$), -154.7 (app. t, *J* = 18.6 Hz for $^{3}J_{ortho(F6-F5)}$ and $^{3}J_{ortho(F6-F7)}$, F$^6$). $^{13}$C NMR ($CDCl_3$; only acetoxypropionate *C* resonances are tabulated): δ 169.8 (ester *C*=O), 167.4 (ester *C*=O), 67.9 (propionoate *C*H$CH_3$), 20.1 (acetoxy *C*H$_3$), 16.6 (propionoate CH*C*H$_3$).

**S2.13 Saponification of ($R_{ax}$,*S*,*S*)-6: Synthesis of (*R*)-$F_{12}$BINOL ((*R*)-1):**

The saponification procedure described by Hopkins and Keay[4] was adapted for the saponification of ($R_{ax}$,*S*,*S*)-**6**. To a THF solution (0.2 M, 1.6 mL) of ($R_{ax}$,*S*,*S*)-**6** (230 mg, 0.31 mmol, 1 equiv.) was added an aqueous solution of LiOH (1.45 mL of a 1.07 M solution, 1.55 mmol, 5 equiv.) at room temperature. The yellow reaction mixture was stirred overnight at room temperature then diluted with 1N aqueous HCl (~15 mL), and extracted into $Et_2O$ (3 × 15 mL). The combined ethereal extracts were then dried over $MgSO_4$, filtered, and concentrated in vacuo to give a yellow oil (225 mg) that was subjected to silica gel column chromatography (gradient elution, 0 – 40% EtOAc:hexanes) to give a pale yellow oil that solidified on standing. Heating the sample at 60 °C under dynamic vacuum to remove residual solvent gave (*R*)-**1** as a pale yellow solid (155 mg, 99%). $^1$H and $^{19}$F NMR spectroscopic properties matched those described above for racemic, solvent-free **1**. [á]$_D^{22}$ -46 (c = 3.9, $CH_2Cl_2$). A sample of (*R*)-**7** prepared from a representative aliquot of (*R*)-**1** was found to be 98.6 % ee by chiral stationary phase HPLC (*vide infra*).




**S2.14 Synthesis of 2,2_-Dimethoxy-3,3_,4,4_,5,5_,6,6_,7,7_,8,8_-dodecafluoro-1,1_-binaphthyl (7):**

To a DMF solution/suspension (5 mL) of **1** (77 mg, 0.15 mmol, 1 equiv.) and $K_2CO_3$ (207 mg, 1.50 mmol, 10 equiv.) was added MeI (93 µL, 1.5 mmol,

10 equiv.) via syringe at room temperature. The yellow mixture was stirred at room temperature for 18 hours then diluted with aqueous HCl (0.05 M, 15 mL) and extracted with $Et_2O$ (3 × 15 mL). The combined $Et_2O$ extracts were dried over $MgSO_4$, filtered, and concentrated to give a yellow semi-solid that was recrystallized from $Et_2O$ to give **7** as yellow crystals (68 mg, 86%). Samples of (*R*)-**7** prepared from (*R*)-**1** were not recrystallized so that the optical purities determined by HPLC would be representative of the samples of (*R*)-**1** used. Instead, crude samples of (*R*)-**7** were analyzed directly by HPLC. $^1$H NMR ($CDCl_3$): δ 3.81 (d, $^5J_{H\text{-}F3}$ = 2.3 Hz, 6H, O*Me*). $^{19}$F NMR ($CDCl_3$): δ -140.4 (ddm, $^4J_{peri(F4\text{-}F5)}$ = 62.6 and $^3J_{ortho(F4\text{-}F3)}$ = 16.6 Hz, $F^4$), -143.7 (app. tm, $J$ = 16.0 Hz for $^5J_{para(F8\text{-}F5)}$ and $^3J_{ortho(F8\text{-}F7)}$, $F^8$), -145.8 (dm, $^4J_{peri(F5\text{-}F4)}$ = 62.6 Hz, $F^5$), -150.5 (m, $F^3$), -155.5 (app. tm, $J$ = 18.6 Hz for $^3J_{ortho(F7\text{-}F6)}$ and $^3J_{ortho(F7\text{-}F8)}$, $F^7$), -157.2 (app. tm, $^3J_{ortho(F6\text{-}F5)}$ and $^3J_{ortho(F6\text{-}F7)}$, $F^6$). Anal. calcd. for $C_{22}H_6F_{12}O_2$: C, 49.83; H, 1.14. Found: C, 49.82; H, 1.06. Chiral HPLC: $t_R$ (*S*)-**7**, 8.3 min; $t_R$ (*R*)-**7**, 9.4 min (Daicel Chiralcel OD, 100% hexane, 1 mL/min).

## S3 References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