Supporting Information For

Readily Accessible, Modular and Tuneable BINOL 3,3'-Perfluoroalkylsulfones: Highly Efficient Catalysts for Enantioselective In-Mediated Imine Allylation

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General: Thin layer chromatography (TLC) was performed on silica gel Whatman-60F glass plates, and components were visualized by illumination with UV light or by staining with potassium permanganate solution. Chromatography was performed using silica E. Merck silica gel 60 (230-400 mesh). NMR spectra were recorded in DMSO or CDCl₃ on a Varian Inova 500 MHz, 400 MHz, Varian Mercury 300 MHz, Jeol 400, and Jeol 300 MHz spectrometers. ¹³C NMR was recorded using broad-band proton decoupling. Chemical shifts are reported in δ relative to TMS and coupling constants in Hz. Optical rotations were recorded on a JASCO-CIP-370 instrument. Elemental analyses were performed on a Perkin Elmer Series II CHNS/O Analyzer 2400. High-resolution mass spectra (HRMS) [Positive Ion FAB (FAB⁺) or Electrospray (ES)] were obtained at the Mass Spectrometry Laboratory in the Department of Chemistry and Molecular Biology at North Dakota State University, or at the University of Bristol School of Chemistry. Melting points were determined without correction. Reactions were carried out under an inert atmosphere of nitrogen or argon. Solvents were dried using a nitrogen pressurized alumina column system from Solvtek or Anhydrous Engineering.

(R)-3,3'-bis(trifluoromethanesulfonyl)-2,2'-dihydroxy-1,1'-binaphthalene 4a. To a stirred solution of diisopropylamine (DIPA) (0.037 ml, 0.26 mmol) in dry THF (1 ml) at -78°C under nitrogen was added *n*BuLi (0.156 ml, 0.25 mmol, 1.6 M in hexanes). The solution was then warmed to room temperature and stirred for 1h. The solution was then cooled to -78°C and (*R*) 1,1'-binaphthalene-2,2'-bis(trifluoromethanesulfonate) (137 mg, 0.25 mmol in dry THF, 1 cm³) added and the mixture allowed to warm to room temperature. To a stirred solution of diisopropylamine (0.037 ml, 0.26 mmol) in dry THF (1 ml) at -78°C under nitrogen was added *n*BuLi (0.156ml, 0.25 mmol, 1.6 M in hexanes). The LDA solution was then warmed to room temperature and stirred for 1h. This solution was then added to the reaction mixture drop-wise at -78°C and the solution was allowed to warm to room temperature and stir for one hour. The reaction was quenched with 10 % HCl solution and extracted three times with dichloromethane. The dichloromethane extracts were combined and washed with 10 % HCl and brine, before drying over anhydrous magnesium sulphate. The product was purified by column chromatography 100 % dichloromethane and recrystallised from hot toluene to give a white crystalline solid (71 mg, 51% yield). Mp 194-196 °C; ¹H NMR (CDCl₃, 300 MHz) δ 8.69 (2H, s), 8.04 (2H, m), 7.52 (4H, m), 7.15 (2H, m); ¹³C NMR (CDCl₃, 75 MHz) δ 138.5, 136.7, 132.2, 131.9, 130.4, 127.5, 126.0, 125.8, 124.7, 120.6, 116.5 (CF₃ q, *J* = 309 Hz); ¹⁹F NMR (CDCl₃, 282 MHz) δ -78.6 (3F, s); [α]_D²⁰ = +80 (c = 0.4, ethyl acetate, 24 °C); IR ν 3427, 2923, 1620, 1584, 1504, 1456, 1350, 1299, 1199, 1110, 1080, 1040, 983, 874, 822, 779, 697; *m/z* (EI) 550 (M⁺, 100%), 532 (8%), 418 (12%), 399 (10%), 284 (24%), 267 (15%), 255 (20%), 239 (16%), 226 (22%), 207 (20%). HRMS(EI) C₂₂H₁₂F₆O₆S₂ calculated 549.9979, found 549.9986.

(S)-3-trifluoromethanesulfonyl-2,2'-dihydroxy-1,1'-binaphthalene 5a A solution of *n*BuLi (2.86 ml, 5.72 mmol, 1.6 M in hexanes) was added drop-wise to a solution of DIPA (0.80 ml, 5.72 mmol) in THF (5 ml) stirred at -78 °C. The reaction was stirred for one hour at -78 °C and then (*S*)-1,1'-binaphthalene-2,2'-bis(trifluoromethanesulfonate) (3.00 g, 5.44 mmol, in THF, 5 ml) was added drop-wise to the reaction. After stirring for one hour at -78 °C the reaction was allowed to warm to room temperature and stirred for a further 30 minutes. The reaction was quenched with 10 % HCl solution and extracted three times with dichloromethane. The dichloromethane extracts were combined and washed with 10 % HCl and brine, before drying over anhydrous magnesium sulphate. The product was purified by column chromatography 20 % dichloromethane 80 % hexane on silica. This gave a white friable solid (2.19 g, 73 % yield), which could be recrystallised from hot hexane to give (*S*)-3-trifluoromethanesulfonyl-2,2'-dihydroxy-1,1'-binaphthalene 2'-trifluoromethanesulfonate as a white crystalline material. Mp 112-114 °C; ¹H NMR (CDCl₃, 300 MHz) δ 8.71 (1H, s), 8.12 (1 H, d, *J* = 9.0 Hz), 8.10 (OH, s), 8.00-8.07 (2H, m), 7.40-7.63 (5H, m), 7.27(1H, d, *J* = 8.4 Hz), 7.10 (1H m); ¹³C NMR(CDCl₃, 72 MHz), δ 149.8, 145.4, 138.6, 137.2, 132.8, 132.6, 132.0, 131.6, 130.2, 128.6, 128.1, 127.3, 126.3, 126.0, 125.9, 125.3, 124.5,

120.1, 119.8 (CF₃, q, $J = 325$ Hz), 118.3 (CF₃, q, $J = 320$ Hz), 117.7, 115.7; ¹⁹F NMR (CDCl₃, 282 MHz), δ -74.7 (3F, s), -78.5 (3F, s); [α]_D²⁰ = -20 ($c = 0.4$, ethyl acetate, 24 °C); IR neat ν 3413, 3062, 1625, 1418, 1202, 1142, 1118, 945; MS (EI⁺), m/z 550 [M⁺], 551 [M⁺+1], 417, 418, 400, 389, 348; HRMS (EI⁺) for C₂₂H₁₂F₆O₆S₂ calculated 549.997951, found 549.997664. A 0.8 g sample of the (*S*)-3-trifluoromethanesulfonyl-2-dihydroxy-1,1'-binaphthalene 2'-trifluoromethanesulfonate (1.45 mmol) was dissolved in THF (15 ml) and stirred at 0 °C before drop-wise addition of 2M NaOH (10ml, 20 mmol). The reaction went yellow and was then allowed to warm to room temperature and stirred for 3 hours. The reaction was treated with 10 % HCl until the yellow colour had bleached, extracted three times with ethyl acetate and the combined extracts washed with 10 % HCl, brine then dried over magnesium sulphate. The crude product was purified by column chromatography 100 % dichloromethane on silica to give 0.53 g (88 %) of (*S*)-3-trifluoromethanesulfonyl-2,2'-dihydroxy-1,1'-binaphthalene **5a** as a white friable solid. Mp 156- 158 °C; ¹H NMR (CDCl₃, 300 MHz), δ 8.74 (1H, s), 8.05 (1H, m), 7.98 (1H, d, $J = 8.8$ Hz), 7.90 (1H, d, $J = 7.2$ Hz), 7.53 (2H, m), 7.26-7.41 (4H, m), 7.00 (1H, d, $J = 8.3$ Hz); ¹³C NMR (CDCl₃, 75 MHz) δ 151.8, 150.0, 138.6, 133.0, 131.4, 130.4, 129.3, 128.5, 127.7, 127.4, 126.2, 125.2, 124.0, 123.8, 119.5 (CF₃, q, $J = 326$ Hz), 118.5, 118.0, 117.9, 111.3; ¹⁹F NMR (CDCl₃, 282 MHz) δ -77.7 (3F, s); [α]_D²⁰ = - 90 ($c = 0.4$, ethyl acetate, 24 °C); IR ν 3432, 3061, 1695, 1619, 1580, 1356, 1194, 1112; MS (EI⁺), m/z 418 [M⁺], 419 [M⁺+1], 342, 286, 268; HRMS (EI⁺) for C₂₁H₁₃F₃O₄S calculated 418.0475, found 418.0475.

(*R*)-6,6'-dibromo-3,3'-bis(trifluoromethanesulfonyl)-2,2'-dihydroxy-1,1'-binaphthalene and (*R*)-6,6'-dibromro 3-trifluoromethanesulfonyl-2,2'-dihydroxy-1,1'-binaphthalene 5a. Triflic anhydride (1.30 ml, 7.70 mmol) was added drop-wise to a solution of (*R*)-6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthalene (1.19 g, 3.50 mmol) in pyridine (8 ml) stirred at 0 °C. After 4 hours the reaction was quenched with water and extracted three times with dichloromethane. The dichloromethane extract was washed with 10 % HCl, brine and dried over magnesium sulphate. The product was purified by column chromatography, 100 % dichloromethane on silica to give (*R*)-6,6'-dibromo-1,1'-binaphthalene 2,2'-bis(trifluoromethanesulfonate) as a white friable solid (1.58 g, 75 %). Mp 94-96 °C ¹H NMR (CDCl₃, 300 MHz) δ 8.20 (2H, d, $J = 2.0$ Hz), 8.08 (2H, d, $J = 9.1$ Hz), 7.64 (2H, d, $J = 9.1$ Hz), 7.50 (2H, d, $J = 9.0$ Hz, $J = 2.0$ Hz), 7.09 (2H, d, $J = 8.9$ Hz); ¹³C NMR (CDCl₃, 75 MHz) δ 145.5, 133.5, 131.8, 131.6, 131.4, 130.6, 128.3, 123.5, 122.0, 120.8, 118.2 (CF₃, q, $J = 320$ Hz); ¹⁹F NMR (CDCl₃, 282 MHz) δ -74.3 (3F, s); [α]_D²⁰ = + 40 ($c = 0.73$, dichloromethane, 24 °C); IR ν 1584, 1495, 1416, 1351, 1317, 1247, 1207, 1172, 1156, 1132, 1059, 967, 933; MS (EI⁺), m/z 708 [M⁺], 707 [M⁺], 706 [M⁺], 496, 427, 426, 425; HRMS (EI⁺) for C₂₂H₁₀⁷⁹Br₂F₆O₆S₂ calculated 705.819775, found 705.818974. (*R*)-6,6'-dibromo-1,1'-binaphthalene 2,2'-bis(trifluoromethanesulfonate) (1.45 g 2.05 mmol) dissolved in THF (6 ml) was reacted sequentially with two equivalents of LDA, in an identical manner to that reported above for the preparation of **4a**. This gave a mixture of (*R*)-6,6'-dibromo-3,3'-bis(trifluoromethanesulfonyl)-2,2'-dihydroxy-1,1'-binaphthalene and (*R*)-6,6'-dibromo-3-trifluoromethanesulfonyl-2-hydroxy-1,1'-binaphthalene 2'-trifluoromethanesulfonate. The two products were separated by column chromatography using 20 % dichloromethane and 80 % hexane on silica. The mono-rearranged product eluted first and after evaporation was a yellow friable solid (0.40 g, 28 % yield). Mp 88-90 °C; ¹H NMR (CDCl₃, 300 MHz) δ 8.62 (1H, s), 8.22 (OH, s), 8.21 (1H, d, $J = 2.0$ Hz), 8.19 (1H, d, $J = 2.0$ Hz), 8.05 (1H, d, $J = 8.9$ Hz), 7.62 (1H, d, $J = 9.2$ Hz), 7.57 (1H, dd, $J = 9.2$ Hz, $J = 2.0$ Hz), 7.51 (1H, dd, $J = 8.9$ Hz, 2.0 Hz), 7.09 (1H, d, 9.2 Hz), 6.98 (1H, d, $J = 9.2$ Hz); ¹³C NMR (CDCl₃, 75 MHz) δ 150.4, 145.6, 136.3, 135.6, 133.8, 132.1, 131.9, 131.3, 131.0, 130.8, 128.2, 127.6, 126.9, 124.4, 122.0, 121.0, 120.3, 119.9 (CF₃, q, $J = 326$ Hz), 118.2 (CF₃, q, $J = 320$ Hz), 117.7; ¹⁹F NMR (CDCl₃, 282 MHz) δ -74.5 (3F, s), -78.3 (3F, s); [α]_D²⁰ = -70 ($c = 0.4$, ethyl acetate, 24 °C); IR ν 3416, 3072, 2929, 2349, 1617, 1584, 1488, 1420, 1363, 1205, 1172, 1136, 1117. MS (EI⁺), m/z 708 [M⁺], 707 [M⁺], 706 [M⁺], 576, 675, 574, 496, 361, 333, 226; HRMS (EI⁺) for C₂₂H₁₀⁷⁹Br₂F₆O₆S₂ calculated 705.818974, found 705.818831. The bis-rearranged product eluted from the column second and after evaporation of the solvent was an off white solid (0.27 g, 19 % yield). Mp 188-190 °C; ¹H NMR (CDCl₃, 300 MHz), δ 8.59 (2H, s), 8.21 (2H, d, $J = 2.0$ Hz), 7.59 (2H,

dd, $J = 8.9$ Hz, $J = 2.0$ Hz), 7.00 (2H, d, $J = 9.2$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz), δ 150.3, 137.0, 135.7, 135.6, 132.2, 129.2, 128.4, 128.3, 126.4, 120.01, 120.0 (CF_3 , q, $J = 309$ Hz), 118.5, 117.2; ^{19}F NMR (CDCl_3 , 282 MHz), δ -78.1 (3F, s); $[\alpha]_{\text{D}}^{20} = -50$ ($c = 0.4$, ethyl acetate, 24 °C); IR ν 3409, 3066, 1612, 1577, 1488, 1448, 1350, 1205, 1190, 1111, 1090, 1068; MS (CI^+), m/z 710 [$\text{M}+\text{H}^+$], 709 [$\text{M}+\text{H}^+$], 708 [M^+], 707 [M^+], 706 [M^+], 630, 629, 576, 575, 574, 496, 361, 333, 226; HRMS (CI^+) [$\text{M}+\text{H}^+$] for $\text{C}_{22}\text{H}_{11}\text{Br}_2\text{F}_6\text{O}_6\text{S}_2$ calculated 706.8268, found 706.8258. The (*R*)-6,6'-dibromo-3-trifluoromethanesulfonyl-2-hydroxy-1,1'-binaphthalene 2'-trifluoromethanesulfonate was hydrolysed (as for **5a**) to give (*R*)-6,6'-dibromo-3-trifluoromethanesulfonyl-2,2'-dihydroxy-1,1'-binaphthalene as a light brown solid (0.26 g, 90 %). Mp 120-124 °C. ^1H NMR (CDCl_3 , 300 MHz), δ 8.62 (1H, s), 8.21 (1H, d, $J = 2.0$ Hz), 8.03 (1H, d, $J = 1.9$ Hz), 7.86 (1H, d, $J = 9.0$ Hz), 7.56 (1H, dd, $J = 9.2$ Hz, $J = 2.0$ Hz), 7.36 (1H, dd, $J = 9.0$ Hz, $J = 1.9$ Hz), 7.33 (1H, d, $J = 9.0$ Hz), 7.09 (1H, d, $J = 9.1$ Hz), 6.83 (1H, d, $J = 8.8$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz) δ 152.1, 150.4, 137.2, 137.2, 135.9, 135.6, 132.1, 131.7, 130.8, 130.6, 130.5, 128.6, 126.9, 125.6, 120.3, 120.1 (CF_3 , q, $J = 325$ Hz), 119.1, 118.3, 118.0, 117.9, 111.7; ^{19}F NMR (CDCl_3 , 282 MHz) δ -77.3 (3F, s); $[\alpha]_{\text{D}}^{20} = -40$ ($c = 0.4$, ethyl acetate, 24 °C); IR ν 3418, 3073, 2962, 2927, 1705, 1615, 1578, 1488, 1420, 1362, 1205, 1172, 1137, 1118, 933; MS (EI^+), m/z 574 [M^+], 575 [M^+], 576 [M^+], 364, 335, 283; HRMS (EI^+) for $\text{C}_{21}\text{H}_{11}\text{Br}_2\text{F}_3\text{O}_4\text{S}$ calculated 573.8697, found 573.8678.

(*R*)-3,3'-bis(nonafluorobutanesulfonyl)-2,2'-dihydroxy-1,1'-binaphthalene 4b. This was prepared in an identical manner to **4a** from (*R*) 1,1'-binaphthalene-2,2'-bis(nonafluorobutanesulfonate) (5.00 g 5.88 mmol) to give **4b**, after recrystallisation from hot hexane, as a white solid (0.24 g, 5 %). Mp 156-158 °C. ^1H NMR (CDCl_3 , 300 MHz), δ 8.67 (2H, s), 8.06 (2H, m), 7.54 (4H, m), 7.17 (2H, m); ^{13}C NMR (CDCl_3 , 75 MHz) δ 149.9, 138.7, 137.1, 132.4, 130.6, 127.5, 126.1, 124.7, 118.5, 116.5 (F-bearing carbons not detected). ^{19}F NMR (CDCl_3 , 282 MHz) δ -80.5 (6F, t, 9.8 Hz), 111.5 (4F, t, $J = 14.1$ Hz), 120.7 (2F, m), 125.7 (2F, m), $[\alpha]_{\text{D}}^{20} = +82$ ($c = 0.5$, diethyl ether, 17.4 °C).

(*R*)-3,3'-bis(heptafluorohexanesulfonyl)-2,2'-dihydroxy-1,1'-binaphthalene 4c. This was prepared in an identical manner to **4a** from (*R*) 1,1'-binaphthalene-2,2'-bis(heptafluorohexanesulfonate) (3.40 g 3.24 mmol) to give **4c**, after recrystallisation from hot hexane, as a white solid (0.23 g, 7 %) Mp 178-184 °C. ^1H NMR (CDCl_3 , 300 MHz), δ 8.67 (2H, s), 8.11 (2OH, s), 8.06 (2H, m), 7.54 (4H, m), 7.17 (2H, m); ^{13}C NMR (CDCl_3 , 50 °C, 75 MHz) δ 149.9, 138.7, 137.0, 132.1, 130.5, 127.6, 126.0, 124.7, 118.6, 116.9 (F-bearing carbons not detected); ^{19}F NMR (CDCl_3 , 282 MHz) δ -80.7 (6F, t, 9.7 Hz), 111.4 (4F, t, $J = 14.1$ Hz), 119.6 (4F, m), 121.3 (4F, m), 121.6 (4F, m), 121.8 (4F, m), 122.6 (4F, m), 126.0 (4F, m); $[\alpha]_{\text{D}}^{20} = -54$ ($c = 0.5$, diethyl ether, 17.6 °C).

(*R*)-3,3'-bis(methanesulfonyl)-2,2'-dihydroxy-1,1'-binaphthalene 4d. Methyl magnesium bromide (3M) (2.63 ml, 7.89 mmol) was added drop-wise to a solution of (*R*)-3,3'-bis(trifluoromethanesulfonyl)-2,2'-dihydroxy-1,1'-binaphthalene **4a** (0.54 g 0.98 mmol) in THF (10 ml) at 0 °C. The reaction was left to stir and warm to ambient temperature overnight. The reaction was quenched with acetic acid, the solvent evaporated and the residue purified by column chromatography 50 % ethyl acetate 50 % hexane on silica, to yield **4d** 0.29 g (66 %) as a white powder. Mp >310 °C. ^1H NMR (CDCl_3 , 300 MHz) δ 9.75 (2 OH, s), 8.64 (2H, s), 8.19 (2H, m), 7.41 (4H, m), 6.88 (2H, m), 3.34 (6H, s), ^{13}C (CDCl_3 , 75 MHz) δ 150.4, 136.2, 131.1, 129.9, 129.8, 129.4, 126.8, 124.1, 123.6, 115.28, 42.7; $[\alpha]_{\text{D}}^{20} = +60$ ($c = 0.1$, ethyl acetate, 24 °C); IR ν 3354, 2924, 2159, 2022, 1977, 1732, 1619, 1587, 1277, 1129; MS (EI^+), m/z 442 [M^++1], 443 [M^+], 424, 364, 345, 333; HRMS (EI^+) M^+ for $\text{C}_{22}\text{H}_{18}\text{O}_6\text{S}_2$ calculated 442.0544, found 442.0543.

(*R*)-3,3'-bis(cyclohexylsulfonyl)-2,2'-dihydroxy-1,1'-binaphthalene 4e was prepared from (*R*)-3,3'-bis(trifluoromethanesulfonyl)-2,2'-dihydroxy-1,1'-binaphthalene **4a** (1.00 g, 1.82 mmol) by an analogous procedure to **4d** but using cyclohexyl magnesium bromide (1.3 M) (11.9 ml, 14.54 mmol) and was isolated as a white powder (0.80 g, 73 %). Mp 164-168 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 8.74 (2OH, s), 8.44 (2H, s), 7.97 (2H, m), 7.42 (4H, m), 7.12 (2H, m), 3.11 (2H, tt, $J = 12.2$ Hz, 3.5 Hz), 2.18 (4H, d, $J = 13.2$ Hz),

1.90 (4H, d, $J = 13.2$ Hz), 1.69 (2H, d, $J = 12.2$ Hz), 1.53 (4H, m), 1.25 (4H, m), 0.86 (2H, m); ^{13}C NMR (CDCl_3 , 75 MHz) δ 149.8, 137.1, 133.3, 130.2, 129.9, 127.4, 125.1, 124.8, 127.8, 118.0, 65.18, 25.3, 25.2, 25.1, 25.0; $[\alpha]_{\text{D}}^{20} = +60$ ($c = 0.4$, ethyl acetate, 24 °C); IR ν 3416, 3026, 2970, 2935, 2856, 1738, 1216, 1205, 1116; MS (EI^+), m/z 578 [M^+], 579 [$\text{M}^+ + 1$], 514, 478, 442, 432, 424; HRMS (EI^+) M^+ for $\text{C}_{32}\text{H}_{34}\text{O}_6\text{S}_2$ calculated 578.1797 found 578.1793.

Asymmetric Allylation of 1 to 2 This was conducted by way of previously reported procedures, but using BINOLs **4a-e** and **5ab**. Characterisation data for all substrates (**1a-l**) and products (**2a-l**) as well as analytical methods for ee determination have been reported before.^{S1}

Representative Procedure for Asymmetric Allylation of Hydrazone Using Allyl Iodide: To an oven dried Schlenk flask was added activated 4Å molecular sieves (100 mg per 1.5 mL THF) under argon atmosphere. Indium powder (2.0 equiv.) was added followed by THF (0.17M with respect to hydrazone) and allyl iodide (3.0 equiv.). The mixture was stirred until all indium powder was dissolved. Heating the reaction mixture at 50 °C under argon atmosphere aids in the organoindium generation, which is signified by the dissolution of the indium powder. The ligand (0.1 equiv.) was added and reaction mixture stirred for 10 minutes. The flask was cooled down to 0 °C followed by addition of the substrate under argon atmosphere. The reaction was stirred for 24 h (the ice bath was allowed to slowly melt to rt), then poured onto a silica gel column and eluted (graduated 15% to 30% ethyl acetate/hexane) to afford the pure homoallylic hydrazine. Enantiomeric excess was determined by HPLC analysis.^{S1}

Representative Procedure for Asymmetric Allylation of Hydrazone Using Allyl Bromide: To an oven dried Schlenk flask was added activated 4Å molecular sieves (100 mg per 1.5 mL THF) under argon atmosphere. Indium powder (2.0 equiv.) was added followed by 0.5 mL THF and allyl bromide (3.0 equiv.). The mixture was heated at 50 °C until all indium powder dissolved. The reaction mixture was allowed to cool to rt and 1.0 mL of THF is added followed by the ligand (0.1 equiv.) under argon atmosphere. The reaction mixture was stirred for 10 minutes. The flask was cooled down to 0 °C followed by addition of the substrate under argon atmosphere. The reaction was stirred for 24 h (the ice bath was allowed to slowly melt to rt), then poured onto a silica gel column and eluted (graduated 15% to 30% ethyl acetate/hexane) to afford the pure homoallylic hydrazine. Enantiomeric excess was determined by HPLC analysis.^{S1}

¹H NMR Experiments to Probe the Interactions between **1a**, **3a** and Allyl Indium Species

Figure S1 ¹H NMR spectrum of **1a** and **3a** (THF-d₈, 400 MHz)

Upper Spectrum – **1a** + **3a**
 Lower Spectrum – **1a**
*No change in chemical shifts of **1a** observed*

Figure S2 ^1H NMR spectrum of Allyl Indium Reagents (THF- d_8 , 500 MHz)

Upper Spectrum – allyl iodide + InI (1:1). Allylic peaks at 2.18 ppm for $[(\text{allyl})_2\text{In}_2\text{I}_4]$

Lower Spectrum – allyl iodide + In(0) (3:2). Allylic peaks at 2.18 and 1.87 ppm

Figure S3 ^1H NMR spectrum of **3a** + allyl indium species (THF- d_8 , 500 MHz)

Allyl iodide + In(0) (allylic peaks at 1.87 ppm decrease, no change at 2.18 ppm)

New BINOLate aromatic resonances upfield from parent BINOL

Possible chiral Lewis acid generated *in situ* from allyl indium species at 1.87 ppm + **3a** by deprotonation to form propene

Reference:

[S1] Cook, G. R.; Kargbo, R.; Maity, B. *Org. Lett.* **2005**, 7, 2767.