Lewis Base Activation of Lewis Acids: Asymmetric Allylations of Aromatic Aldehydes

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SUPPORTING INFORMATION

General Experimental

All reactions were performed in oven-dried (140 °C) or flame-dried glassware under an atmosphere of dry argon or N_2. The following reaction solvents were distilled from the indicated drying agents: dichloromethane (P_2O_5), chloroform (P_2O_5), tetrahydrofuran (sodium, benzophenone), solvents for crystallization benzene (Fisher ACS grade), hexanes (Fisher ACS grade) were used as received. Solvents for chromatography and filtration were technical grade and distilled from the indicated drying agents: hexane ($CaCl_2$); ethyl acetate (K_2CO_3); dichloromethane ($CaCl_2$); isopropanol (Fisher ACS grade) was used as received. Column chromatography was performed using EM Science 230-400-mesh silica gel. Benzaldehyde (**1a**), *trans* cinnamaldehyde (**1b**), α-methyl *trans* cinnamaldehyde (**1c**), 1-naphthaldehyde (**1f**), and furfural (**1h**) were freshly distilled before use. 2-Naphthaldehyde (**1g**) (Aldrich) was used as received. Allyltributylstannane (GFS) was stored over 3Å molecular sieves. Silicon tetrachloride (Aldrich) and trichlorosilane (Aldrich) were heated at reflux for 24 h and then distilled prior to use. Methyltrichlorosilane and phenyltrichlorosilane (Aldrich) were stored in Sure/Seal™ bottles and used as received.

^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on a Varian Unity 400 (400 MHz, ^{1}H; 100 MHz, ^{13}C, 162 MHz ^{31}P), Unity 500 (500 MHz, ^{1}H; 126 MHz, ^{13}C, 202 MHz ^{31}P). Spectra were referenced to residual chloroform (δ 7.26 ppm, ^{1}H; δ 77.23 ppm, ^{13}C), ^{31}P spectra were referenced externally to H_3PO_4 (0.00 ppm). Chemical shifts are reported in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet) h (hextet) m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz. Mass spectroscopy was performed by the University of Illinois Mass Spectrometer Center. FAB mass

spectra were performed on a Finnigan-MAT CH-5 spectrometer. Data are reported in the form of (*m/z*). Infrared spectra (IR) were recorded on a Mattson Galaxy 5020 spectrophotometer in NaCl cells. Peaks are reported in cm^{-1} with indicated relative intensities: s (strong, 67-100%); m (medium, 34-66%); w (weak, 0-33%). Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory. Melting points (mp) were determined on a Thomas-Hoover capillary melting point apparatus in sealed tubes and are uncorrected. Analytical thin-layer chromatography was performed on Merck silica gel plates with QF-254 indicator. Visualization was accomplished with $KMnO_4$. All reaction temperatures correspond to internal temperatures measured by Teflon-coated thermocouples unless otherwise noted.

Optical rotation data was obtained on a JASCO DIP-360 digital polarimeter and are reported as follows: concentration (*c* = g/100 mL), and solvent. Analytical supercritical fluid chromatography (SFC) was performed on a Berger Instruments packed-column SFC with built-in photometric detector (λ = 220, 258 nm) using Daicel Chiralpak OD, AD and AS columns. Analytical capillary gas chromatography (GC) was performed on a Hewlett Packard 5890 Series II fitted with a flame ionization detector (H_2 carrier gas, 16 mL/min). The following column was used: Astec (Chiraldex) GTA 30m x 0.25mm x 0.125μm. The injector temperature was 225 °C, the detector temperature was 300 °C Retention times (t_R) and peak ratios were determined with a Hewlett Packard 3396 Series II integrator.

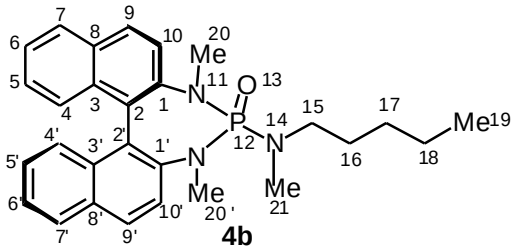
Literature Preparations

Phenylpropynal (**1e**),[1] (*R*)-(–)-2,4-dimethyl-3,4-dihydro-3-piperidinyldinaptho[2,1-d:1'2'-f]-1H-[1,3,2]diazaphosphepine 3-oxide ((*R*)-**4a**),[2] allenyltributylstannane (**7**),[3] and *N*,*N*-dimethylbinaphthyldiamine[4] were prepared by literature methods.

Experimental Procedures.

Synthesis of Phosphoramide Promoters.

Preparation of (*R*)-4,5-Dihydro-3,5-dimethyl-4-(*N*-methyl-*N*-pentylamino)-3H-dinaphtho]2,1-d:1',2'-f][1,3,2]-diazaphosphepine 4-Oxide ((*R*)-4b)



A flame-dried, 25-mL, 2-neck flask containing a solution of 250 mg (*R*)-*N*,*N*'-dimethylbinapthyldiamine (0.8 mmol, 1.1 equiv) in THF (5 mL) was cooled to -78 °C and then 1.14 mL of a solution of *n*-butyllithium (1.55 M in hexanes, 1.6 mmol, 2.2 equiv) was added dropwise under argon. The resultant, orange solution was allowed to warm to -20 °C over 20 min then was cooled back down to -78 °C, prior to the slow (dropwise) addition of 66 μL of PCl_3 (0.76 mmol, 2.0 equiv). The reaction mixture was allowed to slowly warm to room temperature and was stirred for 12 h. The reaction mixture was then cooled back down to -78 °C, whereupon 104 μL of methylpentylamine (0.76 mmol, 77.6 mg) and 111 μL of triethylamine (0.8 mmol, 80 mg, 2.2 equiv) were added and the reaction mixture was slowly warmed to room temperature and was stirred for 12 h. The reaction mixture was then cooled back down to -20 °C and a solution of 138 mg of *m*-CPBA (0.8 mmol, 1.1 equiv) in THF (1 mL) was added dropwise. The reaction mixture was then allowed to stir at room temperature for 12 h, after which a sat. aq. $NaHCO_3$ solution (5 mL) was added. The resulting biphasic mixture was washed with CH_2Cl_2 (3 x 25 mL), and the combined extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification of the residue by silica gel chromatography (CH_2Cl_2/*i*-PrOH, 19/1) afforded 261 mg (71%) of (*R*)-**4b** as a waxy solid, which was recrystallized from a mixture of Et_2O and hexanes.

Analytical Data for (*R*)-**4b**

mp: 190-192 °C (Et_2O/hexane)

^{1}H NMR: (400 MHz, $CDCl_3$)

7.97 (d, *J* = 9.0, 1 H, HC(4)), 7.94 (d, *J* = 9.0, 1 H, HC(4')), 7.89 (d, *J* = 8.1, 1 H, HC(7)), 7.87 (d, *J* = 8.1, 1 H, HC(7')), 7.72 (d, *J* = 8.8, 1 H, HC(10)), 7.62 (d, *J* = 8.8, 1 H, HC(10')), 7.40 (ddd, *J* = 8.1, 6.2, 1.5, 1 H, HC(6)), 7.36 (ddd, *J* = 8.1, 7.5, 0.7, 1 H, HC(5)), 7.24 (d, *J* = 7.3, 1 H, HC(9)), 7.21 (ddd, *J* = 7.5, 6.2, 1.0, 1 H, HC(6')), 7.13 (ddd, *J* = 7.9, 6.7, 1.3, 1 H, HC(5')), 7.05 (d, *J* = 8.6, 1 H, HC(9')), 3.15-3.0 (m, 1 H, HC(15)N), 3.06 (d, *J* = 9.0, 3 H, H_3C(20)N), 3.03 (d, *J* = 10.2, 3 H, H_3C(20')N), 2.95-2.80 (m, 1 H, HC(15)N), 2.30 (bd, *J* = 8.2, 3 H, H_2C(21)N), 1.61-1.53 (m, 2 H, H_2C(16)), 1.34 (h, *J* = 7.2, 2 H, H_2C(18)), 1.27-1.19 (m, 2 H, H_2C(17)), 0.91(t, 7.2, 3 H, H_3C(19))

^{13}C NMR: (100 MHz, $CDCl_3$)

143.6 (C(2)), 142.0 (C(2')), 133.0 (C(3)), 132.8 (C(3')), 131.4 (C(8)), 131.2 (C(8')), 129.9 (C(4)), 129.2 (C(4')), 128.5 (C(1)), 128.3 (C(10)), 128.2 (10')), 127.6 (C(9)), 127.5 (C(9')), 126.3 (C(1')), 126.2 (C(7)), 125.2 (C(7')), 125.0 (C(6)), 123.1 (C(6')), 123.0 (C(5)), 49.8 (d *J* = 3.2, C(15)), 35.9 (d, *J* = 5.5 C(21)), 35.2 (d *J* = 5.5, C(20')), 34.5 (d, *J* = 3.5, C(20)), 29.1 (C(16)), 26.6 (d, *J* = 1.8 C(17)), 22.8 (C(18)), 14.3 (C(19))

^{31}P NMR: (162 MHz, $CDCl_3$)

29.52

IR: (neat)

3054 (w), 2954 (m), 2929 (m), 2858 (w), 1617 (w), 1592 (m), 1506 (m), 1467 (m), 1332 (m), 1280 (m), 1224 (s), 1174 (w), 1147 (w), 1091 (m), 1025 (w), 964 (w), 937 (m), 819 (m), 750 (m), 728 (m)

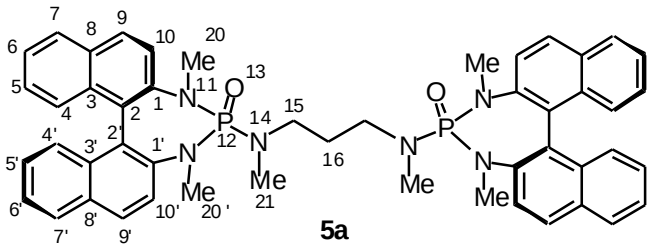
HRMS: (FAB M+1)

calcd. for $C_{28}H_{33}N_3OP$ (M^+-H): 458.2362; found: 458.2360

TLC: R_f 0.47 (EtOAc/EtOH, 85/15) [$KMnO_4$]

Opt. Rot.: $[\alpha]_D^{24}$ -409.7 (*c* = 1.00, EtOH)

(*R,R*)-*N,N*'-Bis[4,5-dihydro-3,5-dimethyl-4-(3H-dinaphtho[2,1-d:1',2'-f][1,3,2]-2-oxo-diazaphosphepino)]-*N,N*'-dimethyl-1,3-propanediamine (5a)



5a

A flame-dried, 25-mL, 2-neck flask containing a solution of 250 mg of (*R*)-*N,N*'-dimethylbinapthyldiamine (0.8 mmol 2.2 equiv) in THF (5 mL) was cooled to -78 °C and then 1.14 mL of a solution of *n*-butyllithium (1.55 M in hexanes, 1.6 mmol, 4.4 equiv) was added dropwise under argon. The resultant, orange solution was allowed to warm to -20 °C over 20 min then was cooled back down to -78 °C, prior to the slow (dropwise) addition of 66 μL of PCl_3 (0.76 mmol, 2.0 equiv). The reaction mixture was allowed to slowly warm to room temperature and was stirred for 12 h. The reaction mixture was then cooled back down to -78 °C, whereupon 38.8 mg of *N-N*'-dimethyl-1,3-propanediamine (47 μL, 0.38 mmol) and 111 μL of triethylamine (80 mg, 0.8 mmol, 2.2 equiv) were added and the reaction mixture was slowly warmed to room temperature and was stirred for 12 h. The reaction mixture was then cooled back down to -20 °C and a solution of 138 mg of *m*-CPBA (0.8 mmol, 2.2 equiv) in THF (1 mL) was added dropwise. The reaction mixture was then allowed to stir at room temperature for 12 h, after which a sat. aq. $NaHCO_3$ solution (5 mL) was added. The resulting biphasic mixture was washed with CH_2Cl_2(3 x 25 mL), and the combined extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification of the residue by silica gel chromatography (CH_2Cl_2/i-PrOH, 19/1 → 10/1) afforded 261 mg (71%) of (*R,R*)-**5a**. The resulting wax-like solid was dried by heating in a Kugelrohr oven for 3 h at 150 °C at 0.1 mm Hg.

Analytical Data for (*R*,*R*)-**5a**

^{1}H NMR: (400 MHz, $CDCl_3$)

7.97 (d, *J* = 9.0, 2 H, 2 x HC(4)), 7.94 (d, *J* = 9.0, 2 H, 2 x HC(4')), 7.89 (d, *J* = 8.1, 2 H, 2 x HC(7)), 7.87 (d, *J* = 8.1, 2 H, 2 x HC(7')), 7.72 (d, *J* = 8.8, 2 H, 2 x HC(10)), 7.62 (d, *J* = 8.8, 2 H, 2 x HC(10')), 7.40 (ddd, *J* = 8.1, 6.2, 1.5, 2 H, 2 x HC(6)), 7.36 (ddd, *J* = 8.1, 7.5, 0.7, 2 H, 2 x HC(5)), 7.24 (d, *J* = 7.3, 2 H, 2 x HC(9)), 7.21 (ddd, *J* = 7.5, 6.2, 1.0, 2 H, 2 x HC(6')), 7.13 (ddd, *J* = 7.9, 6.7, 1.3, 2 H, 2 x HC(5')), 7.05 (d, *J* = 8.6, 2 H, 2 x HC(9')), 3.30-3.17 (m, 2 H, 2 x HC(15)), 3.06 (d, *J* = 9.0, 6 H, 2 x H_3CN(20)), 3.04 (d, *J* = 10.3, 6 H, 2 x H_3CN(20')) 3.10-3.00 (m, 2 H, 2 x HC(15)), 2.28 (brd, *J* = 8.0, 6 H, 2 x H_3CN(21)), 1.89 (p, *J* = 7.6, 2 H)

^{13}C NMR: (100 MHz, $CDCl_3$)

143.3 (C(2)), 141.8 (C(2')), 132.7 (C(3)), 131.4 (C(3')), 131.3 (C(8)), 129.8 (C(8')), 129.5 (C(4)), 128.7 (C(4')), 128.2 (C(1)), 128.1 (C(10)), 128.0 (10')), 127.6 (C(9)), 127.6 (C(9')), 127.4 (d, *J* = 1.9, C(1')), 126.3 (C(7)), 126.2 (C(7')), 125.3 (C(6)), 125.0 (C(6')), 123.5 (C(5)), 122.9 (C(5')), 47.7 (d, *J* = 2.4, C(15)), 36.0 (C(21)), 35.2 (d, *J* = 4.6, C(20')), 34.8 (d, *J* = 3.0, C(20)), 28.4 (C(16))

^{31}P NMR: (162 MHz, $CDCl_3$)

29.37

IR: (neat)

3052 (m), 2937 (m), 2908 (m), 2881 (m), 2817 (w), 1617 (m), 1592 (m), 1506 (m), 1469 (m), 1429 (w), 1359 (w), 1332 (s), 1280 (s), 1224 (s), 1176 (m), 1147 (m), 1091 (s), 1024 (m), 997 (m), 939 (s), 819 (s), 750 (s), 735 (s)

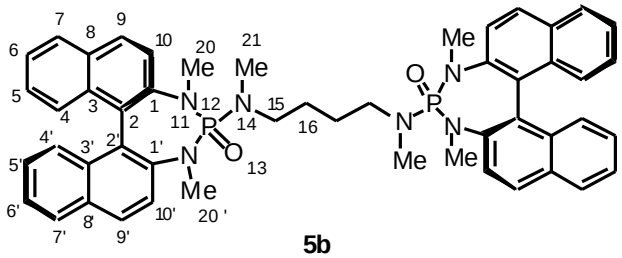
HRMS: (FAB M+1)

calcd. for $C_{49}H_{49}N_4O_2P_2$ (M^+-H): 815.3393; found: 815.3394

TLC: R_f 0.39 (EtOAc/EtOH, 7/3) [$KMnO_4$]

Opt. Rot.: $[\alpha]_D^{24}$ -374.6 (*c* = 0.94, EtOH)

(*R*,*R*)-*N*,*N*'-Bis[4,5-dihydro-3,5-dimethyl-4-(3H-dinaphtho[2,1-d:1',2'-f][1,3,2]-2-oxo-diazaphosphepino)]-*N*,*N*'-dimethyl-1,4-butanediamine (5b)



5b

A flame-dried, 25-mL, 2-neck flask containing a solution of 300 mg of (*R*)-*N*,*N*'-dimethylbinapthyldiamine (0.96 mmol 2.2 equiv) in THF (5 mL) was cooled to -78 °C and then 1.28 mL of a solution of *n*-butyllithium (1.55 M in hexanes, 1.92 mmol, 4.4 equiv) was added dropwise under argon. The resultant, orange solution was allowed to warm to -20 °C over 20 min then was cooled back down to -78 °C, prior to the slow (dropwise) addition of 79 μL of PCl_3 (0.91 mmol, 2.0 equiv). The reaction mixture was allowed to slowly warm to room temperature, and stirred for 12 h. The reaction mixture was then cooled back down to -78 °C, whereupon 50 mg of *N*-*N*'-dimethyl-1,4-butanediamine (0.43 mmol) and 97 mg of triethylamine (133 μL, 0.96 mmol, 2.2 equiv) were added, and the reaction mixture was slowly warmed to room temperature and stirred for 12 h. The reaction mixture was then cooled back down to -20 °C and a solution of 248 mg of *m*-CPBA (1.44 mmol, 3.3 equiv) in THF (1 mL) was added dropwise. The reaction mixture was then allowed to stir at room temperature for 12 h, after which a sat. aq. $NaHCO_3$ solution (5 mL) was added. The resulting biphasic mixture was washed with CH_2Cl_2 (3 x 25 mL), and the combined extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification of the residue by silica gel chromatography (CH_2Cl_2/i-PrOH, 19/1 → 9/1) afforded 194 mg (53%) of (*R*,*R*)-**5b**. The resulting wax like solid was dried by heating in a Kugelrohr oven for 3 h at 150 °C at 0.1 mm Hg.

Analytical Data for (*R*,*R*)-**5b**

^{1}H NMR: (400 MHz, $CDCl_3$)

7.97 (d, *J* = 9.0, 2 H, 2 x HC(4)), 7.94 (d, *J* = 9.0, 2 H, 2 x HC(4')), 7.89 (d, *J* = 8.1, 2 H, 2 x HC(7)), 7.87 (d, *J* = 8.1, 2 H, 2 x HC(7')), 7.72 (d, *J* = 8.8, 2 H, 2 x HC(10)), 7.62 (d, *J* = 8.8, 2 H, 2 x HC(10')), 7.40 (ddd, *J* = 8.1, 6.2, 1.5, 2 H, 2 x HC(6)), 7.36 (ddd, *J* = 8.1, 7.5, 0.7, 2 H, 2 x HC(5)), 7.24 (d, *J* = 7.3, 2 H, 2 x HC(9)), 7.21 (ddd, *J* = 7.5, 6.2, 1.0, 2 H, 2 x HC(6')), 7.13 (ddd, *J* = 7.9, 6.7, 1.3, 2 H, 2 x HC(5')), 7.05 (d, *J* = 8.6, 2 H, 2 x HC(9')), 3.25-3.17 (m, 2 H, 2 x HC(15)), 3.06 (d, *J* = 9.0, 6 H, 2 x H_3CN(20)), 3.04 (d, *J* = 10.3, 6 H, 2 x H_3CN(20')) 3.05-2.90 (m, 2 H, 2 x HC(15)), 2.28 (brd, 6 H, *J* = 8.0, 6 H, 2 x H_3CN(21)), 1.70-1.50 (bs, 4 H, 2 x H_2C(16))

^{13}C NMR: (100 MHz, $CDCl_3$)

143.4 (C(2)), 141.9 (C(2')), 132.9 (C(3)), 132.7 (C(3')), 131.4 (C(8)), 131.3 (C(8')), 129.9 (C(4)), 129.3 (C(4')), 128.6 (C(1)), 128.3 (C(10)), 128.2 (10')), 128.1 (C(9)), 127.6 (C(9')), 127.5 (C(1')), 126.4 (C(7)), 126.2 (C(7')), 125.3 (C(6)), 125.0 (C(6')), 123.2 (C(5)), 122.9 (C(5')), 49.8 (C(15)), 35.9 (d, *J* = 5.4 C(21)), 35.2 (d, *J* = 4.8, C(20')), 34.5 (d, *J* = 3.5, C(20)), 26.1 (C(16))

^{31}P NMR: (162 MHz, $CDCl_3$)

29.40

IR: (neat)

3052 (m), 2933 (m), 2877 (m), 2817 (w), 1617 (m), 1592 (m), 1506 (m), 1467 (m), 1429 (w), 1332 (s), 1280 (s), 1224 (s), 1174 (m), 1147 (m), 1091 (s), 1025 (m), 1000 (m), 937 (s), 819 (s), 750 (s), 732 (s)

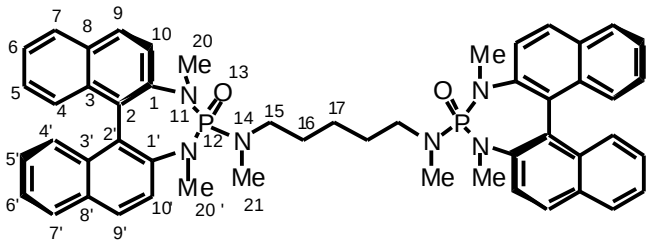
HRMS: (FAB M+1)

calcd. for $C_{50}H_{51}N_4O_2P_2$ (M^+-H): 829.3550; found: 829.3552

TLC: R_f 0.38 (EtOAc/EtOH, 7/3) [$KMnO_4$]

Opt. Rot.: $[\alpha]_D^{24}$ -396.1 ° (*c* = 1.14, EtOH)

(*R*,*R*)-*N*,*N*'-Bis[4,5-dihydro-3,5-dimethyl-4-(3H-dinaphtho[2,1-d:1',2'-f][1,3,2]-2-oxo-diazaphosphepino)]-*N*,*N*'-dimethyl-1,5-pentanediamine ((*R*,*R*)-5c)



5c

A flame-dried, 250-mL, 2-neck flask containing a solution of 3.00 g of (*R*)-*N*,*N*'-dimethylbinapthyldiamine (9.6 mmol 2.2 equiv) in THF (5 mL) was cooled to -78 °C and then 12.8 mL of a solution of *n*-butyllithium (1.55 M in hexanes, 19.2 mmol, 4.4 equiv) was added dropwise under argon. The resultant, orange solution was allowed to warm to -20 °C over 20 min then was cooled back down to -78 °C, prior to the slow (dropwise) addition of 790 μL of PCl_3 (9.1 mmol, 2.0 equiv). The reaction mixture was allowed to slowly warm to room temperature and was stirred for 12 h. The reaction mixture was then cooled back down to -78 °C, whereupon 577 mg of *N*-*N*'-dimethyl-1,5-pentanediamine (4.3 mmol) and 926 mg of triethylamine (1.3 mL, 9.6 mmol, 2.2 equiv) were added, and the reaction mixture was slowly warmed to room temperature and was stirred for 12 h. The reaction mixture was then cooled back down to -20 °C and a solution of 2.48 g of *m*-CPBA (14.4 mmol, 3.3 equiv) in THF (10 mL) was added dropwise. The reaction mixture was then allowed to stir at room temperature for 12 h, after which a sat. aq. $NaHCO_3$ solution (50 mL) was added. The resulting biphasic mixture was washed with CH_2Cl_2 (3 x 75 mL), and the combined extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification of the residue by silica gel chromatography (CH_2Cl_2/i-PrOH, 19/1 → 9/1) afforded 2.64 g (72%) of (*R*,*R*)-**5c**. Analytically pure material was obtained by crystallization from benzene. The resulting crystals were dried by heating in a Kugelrohr oven for 3 h at 150 °C at 0.1 mm Hg.

Analytical Data for (*R*,*R*)-**5c**

mp: 216-218°C (benzene)

^{1}H NMR: (400 MHz, $CDCl_3$)

7.97 (d, *J* = 9.0, 2 H, 2 x HC(4)), 7.94 (d, *J* = 9.0, 2 H, 2 x HC(4')), 7.89 (d, *J* = 8.1, 2 H, 2 x HC(7)), 7.87 (d, *J* = 8.1, 2 H, 2 x HC(7')), 7.72 (d, *J* = 8.8, 2 H, 2 x HC(10)), 7.62 (d, *J* = 8.8, 2 H, 2 x HC(10')), 7.40 (ddd, *J* = 8.1, 6.2, 1.5, 2 H, 2 x HC(6)), 7.36 (ddd, *J* = 8.1, 7.5, 0.7, 2 H, 2 x HC(5)), 7.24 (d, *J* = 7.3, 2 H, 2 x HC(9)), 7.21 (ddd, *J* = 7.5, 6.2, 1.0, 2 H, 2 x HC(6')), 7.13 (ddd, *J* = 7.9, 6.7, 1.3, 2 H, 2 x HC(5')), 7.05 (d, *J* = 8.6, 2 H, 2 x HC(9')), 3.20 (m, 2 H, 2 x HC(15)), 3.06 (d, *J* = 9.0, 6 H, 2 x H_3CN(20)), 3.04 (d, *J* = 10.3, 6 H, 2 x H_3CN(20')) 3.05-2.90 (m, 2 H, 2 x HC(15)), 2.28 (bd, 6 H, *J* = 8.0, 6 H, 2 x H_3C(21), 1.65-1.59 (m, 4 H, 2 x H_2C(16)), 1.30-1.20 (m, 2 H, H_2C(17))

^{13}C NMR: (126 MHz, $CDCl_3$)

143.4 (C(2)), 141.7 (C(2')), 132.7 (C(3)), 132.5 (C(3')), 131.2 (C(8)), 131.0 (C(8')), 129.6 (C(4)), 129.0 (C(4')), 128.3 (C(1)), 128.0 (C(10)), 127.94 (10')), 127.9 (C(9)), 127.4 (C(9')), 127.3 (d, *J* = 1.9, C(1')), 126.1 (C(7)), 126.0 (C(7')), 125.1 (C(6)), 124.8 (C(6')), 123.0 (C(5)), 122.7 (C(5')), 49.6 (d, *J* = 2.4, C(15)), 35.7 (d, *J* = 5.4 C(21)), 35.0 (d, *J* = 4.8, C(20')), 34.2 (d, *J* = 3.5, C(20)), 28.5 (d, *J* = 1.8, C(16)), 23.9 (C(17)

^{31}P NMR: (202 MHz, $CDCl_3$)

27.86

IR: (neat)

3052 (m), 2933 (m), 2877 (m), 2817 (w), 1617 (m), 1592 (m), 1506 (m), 1467 (m), 1429 (w), 1332 (s), 1280 (s), 1224 (s), 1174 (m), 1147 (m), 1091 (s), 1025 (m), 1000 (m), 937 (s), 819 (s), 750 (s), 732 (s), 659 (s).

M.S.: (FAB M+1)

843 (M + 1, 100); 357 (37), 307 (20), 281 (45), 154 (58), 136 (38)

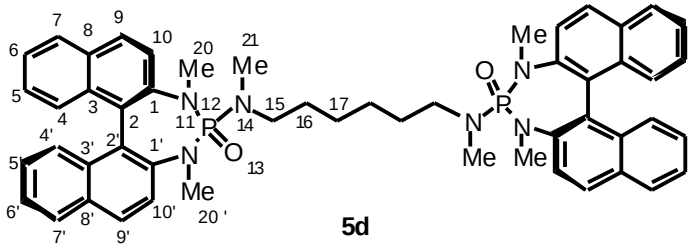
TLC: R_f 0.4 (EtOAc/EtOH, 4/1) [$KmnO_4$]

Opt. Rot.: $[\alpha]_D^{24}$ -390 ° (*c* = 1.07, MeOH)

Anal: $C_{51}H_{52}N_6P_2O_2$ (842.96)

Calcd.: C, 72.67;	H, 6.22;	N, 9.97;	P, 7.35
Found: C, 72.52;	H, 6.16;	N, 9.93;	P, 7.06

(*R*,*R*)-*N*,*N*'-Bis[4,5-dihydro-3,5-dimethyl-4-(3H-dinaphtho[2,1-d:1',2'-f][1,3,2]-2-oxo-diazaphosphepino)]-*N*,*N*'-dimethyl-1,6-hexanediamine ((*R*,*R*)-5d)



5d

A flame-dried, 25-mL, 2-neck flask containing a solution of 300 mg of (*R*)-*N*,*N*'-dimethylbinapthyldiamine (0.96 mmol 2.2 equiv) in THF (5 mL) was cooled to -78 °C and then 1.28 mL of a solution of *n*-butyllithium (1.55 M in hexanes, 1.92 mmol, 4.4 equiv) was added dropwise under argon. The resultant, orange solution was allowed to warm to -20 °C over 20 min then was cooled back down to -78 °C, prior to the slow (dropwise) addition of 79 μL of PCl_3 (0.91 mmol, 2.0 equiv). The reaction mixture was allowed to slowly warm to room temperature and was stirred for 12 h. The reaction mixture was then cooled back down to -78 °C, whereupon 63 mg of *N*-*N*'-dimethyl-1,6-butanediamine (0.43 mmol) and 133 μL of triethylamine (97 mg, 0.96 mmol, 2.2 equiv) were added, and the reaction mixture was slowly warmed to room temperature and was stirred for 12 h. The reaction mixture was then cooled back down to -20 °C and a solution of 248 mg of *m*-CPBA (1.44 mmol, 3.3 equiv) in THF (1 mL) was added dropwise. The reaction mixture was then allowed to stir at room temperature for 12 h, after which a sat. aq. $NaHCO_3$ solution (5 mL) was added. The resulting biphasic mixture was washed with CH_2Cl_2 (3 x 25 mL), and the combined extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification of the residue by silica gel chromatography (CH_2Cl_2/i-PrOH, 19/1 → 93/7) afforded 240 g (65%) of (*R*,*R*)-**5d**. The resulting wax-like solid was dried by heating in a Kugelrohr oven for 3 h at 150 °C at 0.1 mm Hg.

Analytical Data for (*R*,*R*)-**5d**

^{1}H NMR: (400 MHz, $CDCl_3$)

7.97 (d, *J* = 9.0, 2 H, 2 x HC(4)), 7.94 (d, *J* = 9.0, 2 H, 2 x HC(4')), 7.89 (d, *J* = 8.1, 2 H, 2 x HC(7)), 7.87 (d, *J* = 8.1, 2 H, 2 x HC(7')), 7.72 (d, *J* = 8.8, 2 H, 2 x HC(10)), 7.62 (d, *J* = 8.8, 2 H, 2 x HC(10')), 7.40 (ddd, *J* = 8.1, 6.2, 1.5, 2 H, 2 x HC(6)), 7.36 (ddd, *J* = 8.1, 7.5, 0.7, 2 H, 2 x HC(5)), 7.24 (d, *J* = 7.3, 2 H, 2 x HC(9)), 7.21 (ddd, *J* = 7.5, 6.2, 1.0, 2 H, 2 x HC(6')), 7.13 (ddd, *J* = 7.9, 6.7, 1.3, 2 H, 2 x HC(5')), 7.05 (d, *J* = 8.6, 2 H, 2 x HC(9')), 3.23-3.15 (m, 2 H, 2 x HC(15)), 3.06 (d, *J* = 9.0, 6 H, 2 x H_3CN(20)), 3.04 (d, *J* = 10.3, 6 H, 2 x H_3CN(20')) 3.05-2.90 (m, 2 H, 2 x HC(15)), 2.39-2.22 (bs, 6 H, 2 x H_3C(21)), 1.60 (bs, 4 H, 2 x H_2C(16)), 1.21(bs, 4 H, 2 x H_2C(17))

^{13}C NMR: (100 MHz, $CDCl_3$)

143.4 (C(2)), 141.9 (C(2')), 132.9 (C(3)), 132.7 (C(3')), 131.4 (C(8)), 131.2 (C(8')), 129.8 (C(4)), 129.2 (C(4')), 128.5 (C(1)), 128.2 (C(10)), 128.0 (10')), 127.6 (C(9)), 127.5 (C(9')), 126.4 (C(1')), 126.3 (C(7)), 126.1 (C(7')), 125.3 (C(6)), 125.0 (C(6')), 123.1 (C(5)), 122.9 (C(5')), 49.8 (C(15)), 35.8 (d, *J* = 5.5 C(21)), 35.2 (d *J* = 5.5, C(20')), 34.5 (d, *J* = 2.6, C(20)), 29.0 (C(16)), 26.8 (C(17)

^{31}P NMR: (162 MHz, $CDCl_3$)

29.48

IR: (neat)

3052 (m), 2933 (m), 2877 (m), 2817 (w), 1617 (m), 1592 (m), 1506 (m), 1467 (m), 1429 (w), 1332 (s), 1280 (s), 1224 (s), 1174 (m), 1147 (m), 1091 (s), 1025 (m), 1000 (m), 937 (s), 819 (s), 750 (s), 732 (s)

HRMS: (FAB M+1)

calcd. for $C_{52}H_{55}N_4O_2P_2$ (M^+-H): 857.3863; found: 857.3864

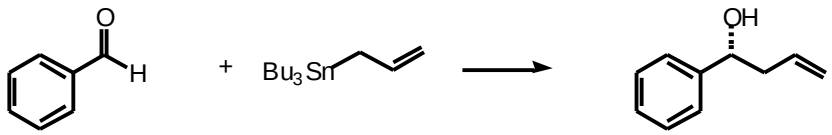
TLC: R_f 0.32 (EtOAc/EtOH, 3/1) [$KMnO_4$]

Opt. Rot.: $[\alpha]_D^{24}$ -394.4 (*c* = 0.58 EtOH)

General Procedure I: Optimization Studies

In a flame-dried, 10-mL, 2-neck flask, the phosphoramide was dissolved in the indicated solvent (1.5 mL) under N_2. To this solution was added allyltributylstannane and the resulting mixture was cooled to -78°C (bath temperature). Then the silicon source was added followed by benzaldehyde. The resulting mixture was allowed to stir at -78 °C (bath temperature) for 6 h whereupon the cold reaction mixture was poured into a rapidly stirring solution of 1/1 sat. aq. KF/1.0 M KH_2PO_4 (10 mL). This biphasic mixture was stirred vigorously for 2 h after which the mixture was filtered and aqueous layer was washed with CH_2Cl_2 (3 x 25 mL). The combined organic extracts were dried over Na_2SO_4, filtered and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography (CH_2Cl_2/pentane 3/1 → CH_2Cl_2). The product-containing fractions were combined and the solvent was removed *in vacuo*. The residue was then dissolved in 75 mL of CH_2Cl_2 and the resulting solution was filtered through a column containing solid anhydrous KF (10 mm) over silica gel (10 mm). The solvent was removed *in vacuo* to yield the (α*R*)-α-(2-propenyl)benzenemethanol ((*R*)-**3a**).

Allylation of Benzaldehyde Catalyzed by (*R*)-4a (Table 1 Entry 1)



1a **2** **3a**

Following General Procedure I, from 44 mg of **4a** (0.1 mmol, 0.1 equiv), 310 μL of allyltributylstannane (1.0 mmol, 331 mg, 1.0 equiv), 101 μL of benzaldehyde (1.0 mmol, 106.2 mg), and 229 μL of $SiCl_4$ (2.0 mmol, 340 mg, 2.0 equiv) was obtained 125 mg (85%) of (α*R*)-α-(2-propenyl)benzenemethanol ((*R*)-**3a**) as a clear, colorless oil.

^{1}H NMR: (400 MHz, $CDCl_3$)

7.37 (m, 2 H), 7.36 (m, 2 H), 7.29 (m, 1 H), 5.52 (ddt, *J* = 17.3, 10.1, 7.4, 1 H), 5.20-5.14 (m, 2 H), 4.74 (m, 1 H), 2.56-2.47 (m, 2 H), 2.06 (d, *J* = 3.2, 1 H)

SFC: t_R (*R*)-**3a**, 3.17 min (89.6%); t_R (*S*)-**3a**, 3.69 min (10.4%) (Chiralpak OD, 40 °C, 150 bar, 4% CH_3OH in CO_2, 3 mL/min, 258 nm)

Allylation of Benzaldehyde Catalyzed by (*R*)-4b (Table 1 Entry 2)

Following General Procedure I, from 23 mg (0.05 mmol, 0.05 equiv) of (*R*)-**4b**, 310 μL of allyltributylstannane (1.0 mmol, 331 mg, 1.0 equiv), 101 μL of benzaldehyde (1.0 mmol, 106.2 mg), and 229 μL of $SiCl_4$ (2.0 mmol, 340 mg, 2.0 equiv) was obtained 120 mg (83%) of (α*R*)-α-(2-propenyl)benzenemethanol ((*R*)-**3a**) as a clear, colorless oil.

^{1}H NMR: (400 MHz, $CDCl_3$)
7.37 (m, 2 H), 7.36 (m, 2 H), 7.29 (m, 1 H), 5.52 (ddt, *J* = 17.3, 10.1, 7.4, 1 H), 5.20-5.14 (m, 2 H), 4.74 (m, 1 H), 2.56-2.47 (m, 2 H), 2.06 (d, *J* = 3.2, 1 H)

SFC: t_R (*R*)-**3a**, 3.00 min (76.9%); t_R (*S*)-**3a**, 3.69 min (23.1%) (Chiralpak OD, 40 °C, 150 bar, 4% CH_3OH in CO_2, 3 mL/min, 258 nm)

Allylation of Benzaldehyde Catalyzed by (*R*,*R*)-5a (Table 1 Entry 3)

Following General Procedure I, from 40 mg (0.05 mmol, 0.05 equiv) of (*R*,*R*)-**5a**, 310 μL of allyltributylstannane (1.0 mmol, 331 mg, 1.0 equiv), 101 μL of benzaldehyde (1.0 mmol, 106.2 mg), and 229 μL of $SiCl_4$ (2.0 mmol, 340 mg, 2.0 equiv) was obtained 120 mg (81%) of (α*R*)-α-(2-propenyl)benzenemethanol ((*R*)-**3a**) as a clear, colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$)
7.37 (m, 2 H), 7.36 (m, 2 H), 7.29 (m, 1 H), 5.52 (ddt, *J* = 17.3, 10.1, 7.4, 1 H), 5.20-5.14 (m, 2 H), 4.74 (m, 1 H), 2.56-2.47 (m, 2 H), 2.06 (d, *J* = 3.2, 1 H)

SFC: t_R (*R*)-**3a**, 3.03 (92.1%); t_R (*S*)-**3a**, 3.56 min (7.9%) (Chiralpak OD, 40 °C, 150 bar, 4% CH_3OH in CO_2, 3 mL/min, 258 nm)

Allylation of Benzaldehyde Catalyzed by (*R*,*R*)-5b (Table 1 Entry 4)

Following General Procedure I, from 41 mg (0.05 mmol, 0.05 equiv) of (*R*,*R*)-**5b**, 310 μL of allyltributylstannane (1.0 mmol, 331 mg, 1.0 equiv), 101 μL of benzaldehyde (1.0 mmol,

106.2 mg), and 229 μL of $SiCl_4$ (2.0 mmol, 340 mg, 2.0 equiv) was obtained 127 mg (86%) of (α*R*)-α-(2-propenyl)benzenemethanol ((*R*)-**3a**) as a clear, colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$)
7.37 (m, 2 H), 7.36 (m, 2 H), 7.29 (m, 1 H), 5.52 (ddt, *J* = 17.3, 10.1, 7.4, 1 H), 5.20-5.14 (m, 2 H), 4.74 (m, 1 H), 2.56-2.47 (m, 2 H), 2.06 (d, *J* = 3.2, 1 H)
SFC: t_R (*R*)-**3a**, 2.80 (90.5%); t_R (*S*)-**3a**, 3.62 min (9.4%) (Chiralpak OD, 40 °C, 150 bar, 4% CH_3OH in CO_2, 3 mL/min, 258 nm)

Allylation of Benzaldehyde Catalyzed by (*R*,*R*)-5c (Table 1 Entry 5)

Following General Procedure I, from 42 mg (0.05 mmol, 0.05 equiv) of (*R*,*R*)-**5c**, 310 μL of allyltributylstannane (1.0 mmol, 331 mg, 1.0 equiv), 101 μL of benzaldehyde (1.0 mmol, 106.2 mg), and 229 μL of $SiCl_4$ (2.0 mmol, 340 mg, 2.0 equiv) was obtained 132 mg (89%) of (α*R*)-α-(2-propenyl)benzenemethanol ((*R*)-**3a**) as a clear, colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$)
77.37 (m, 2 H), 7.36 (m, 2 H), 7.29 (m, 1 H), 5.52 (ddt, *J* = 17.3, 10.1, 7.4, 1 H), 5.20-5.14 (m, 2 H), 4.74 (m, 1 H), 2.56-2.47 (m, 2 H), 2.06 (d, *J* = 3.2, 1 H)
SFC: t_R (*R*)-**3a**, 2.93 (96.4%); t_R (*S*)-**3a**, 3.46 min (3.6%) (Chiralpak OD, 40 °C, 150 bar, 4% CH_3OH in CO_2, 3 mL/min, 258 nm)

Allylation of Benzaldehyde Catalyzed by (*R*,*R*)-5d (Table 1 Entry 6)

Following General Procedure I, from 43 mg (0.05 mmol, 0.05 equiv) of (*R*,*R*)-**5d**, 310 μL of allyltributylstannane (1.0 mmol, 331 mg, 1.0 equiv), 101 μL of benzaldehyde (1.0 mmol, 106.2 mg), and 229 μL of $SiCl_4$ (2.0 mmol, 340 mg, 2.0 equiv) was obtained 124 mg (84%) of (α*R*)-α-(2-propenyl)benzenemethanol ((*R*)-**3a**) as a clear, colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$)
7.37 (m, 2 H), 7.36 (m, 2 H), 7.29 (m, 1 H), 5.52 (ddt, *J* = 17.3, 10.1, 7.4, 1 H), 5.20-5.14 (m, 2 H), 4.74 (m, 1 H), 2.56-2.47 (m, 2 H), 2.06 (d, *J* = 3.2, 1 H)

SFC: t_R (*R*)-**3a**, 2.90 (84.2%); t_R (*S*)-**3a**, 3.42 min (15.7%) (Chiralpak OD, 40 °C, 150 bar, 4% CH_3OH in CO_2, 3 mL/min, 258 nm)

Allylation of Benzaldehyde Catalyzed by (*R*,*R*)-5c; with $HSiCl_3$ (Table 2 Entry 2)

Following General Procedure I, from 42 mg (0.05 mmol, 0.05 equiv) of (*R*,*R*)-**5c**, 310 μL of allyltributylstannane (1.0 mmol, 331 mg, 1.0 equiv), 101 μL of benzaldehyde (1.0 mmol, 106.2 mg), and 201 μL of $HSiCl_3$ (2.0 mmol, 271 mg, 2.0 equiv) was obtained 137 mg (93%) of (α*R*)-α-(2-propenyl)benzenemethanol ((*R*)-**3a**) as a clear, colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$)
7.37 (m, 2 H), 7.36 (m, 2 H), 7.29 (m, 1 H), 5.52 (ddt, *J* = 17.3, 10.1, 7.4, 1 H), 5.20-5.14 (m, 2 H), 4.74 (m, 1 H), 2.56-2.47 (m, 2 H), 2.06 (d, *J* = 3.2, 1 H)

SFC: t_R (*R*)-**3a**, 2.96 (94.0%); t_R (*S*)-**3a**, 3.50 min (6.0%) (Chiralpak OD, 40 °C, 150 bar, 4% CH_3OH in CO_2, 3 mL/min, 258 nm)

Allylation of Benzaldehyde Catalyzed by (*R*,*R*)-5c; in $CHCl_3$ (Table 2 Entry 5)

Following General Procedure I, from 42 mg (0.05 mmol, 0.05 equiv) of (*R*,*R*)-**5c**, 310 μL of allyltributylstannane (1.0 mmol, 331 mg, 1.0 equiv), 101 μL of benzaldehyde (1.0 mmol, 106.2 mg), and 229 μL of $SiCl_4$ (2.0 mmol, 340 mg, 2.0 equiv) in $CHCl_3$ (1.5 mL) was obtained 135 mg (91%) of (α*R*)-α-(2-propenyl)benzenemethanol ((*R*)-**3a**) as a clear, colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$)
7.37 (m, 2 H), 7.36 (m, 2 H), 7.29 (m, 1 H), 5.52 (ddt, *J* = 17.3, 10.1, 7.4, 1 H), 5.20-5.14 (m, 2 H), 4.74 (m, 1 H), 2.56-2.47 (m, 2 H), 2.06 (d, *J* = 3.2, 1 H)

SFC: t_R (*R*)-**3a**, 2.96 (92.0%); t_R (*S*)-**3a**, 3.50 min (8.0%) (Chiralpak OD, 40 °C, 150 bar, 4% CH_3OH in CO_2, 3 mL/min, 258 nm)

Allylation of Benzaldehyde Catalyzed by (*R*,*R*)-5c; 0.5 equiv $SiCl_4$ (Table 2 Entry 6)

Following General Procedure I, from 42 mg (0.05 mmol, 0.05 equiv) of (*R*,*R*)-**5c** 310 μL of allyltributylstannane (1.0 mmol, 331 mg, 1.0 equiv), 101 μL of benzaldehyde (1.0 mmol,

106.2 mg), and 57 μL of $SiCl_4$ (0.5 mmol, 85 mg, 0.5 equiv) was obtained 66 mg (45%) of (α*R*)-α-(2-propenyl)benzenemethanol ((*R*)-**3a**) as a clear, colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$)
7.37 (m, 2 H), 7.36 (m, 2 H), 7.29 (m, 1 H), 5.52 (ddt, *J* = 17.3, 10.1, 7.4, 1 H), 5.20-5.14 (m, 2 H), 4.74 (m, 1 H), 2.56-2.47 (m, 2 H), 2.06 (d, *J* = 3.2, 1 H)

SFC: t_R (*R*)-**3a**, 2.90 (97.4%); t_R (*S*)-**3a**, 3.50 min (2.6%) (Chiralpak OD, 40 °C, 150 bar, 4% CH_3OH in CO_2, 3 mL/min, 258 nm)

Allylation of Benzaldehyde Catalyzed by (*R*,*R*)-5c; 1.1 equiv $SiCl_4$ (Table 2 Entry 7)

Following General Procedure I, from 84 mg (0.1 mmol, 0.05 equiv) of (*R*,*R*)-**5c**, 680 μL of allyltributylstannane (2.2 mmol, 728 mg, 1.1 equiv), 202 μL of benzaldehyde (2.0 mmol, 212 mg), and 252 μL of $SiCl_4$ (2.2 mmol, 374 mg, 1.1 equiv) was obtained 269 mg (91%) of (α*R*)-α-(2-propenyl)benzenemethanol ((*R*)-**3a**) as a clear, colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$)
7.37 (m, 2 H), 7.36 (m, 2 H), 7.29 (m, 1 H), 5.52 (ddt, *J* = 17.3, 10.1, 7.4, 1 H), 5.20-5.14 (m, 2 H), 4.74 (m, 1 H), 2.56-2.47 (m, 2 H), 2.06 (d, *J* = 3.2, 1 H)

SFC: t_R (*R*)-**3a**, 2.89 (97.1%); t_R (*S*)-**3a**, 3.42 min (2.9%) (Chiralpak OD, 40 °C, 150 bar, 4% CH_3OH in CO_2, 3 mL min^{-1} 258 nm)

Allylation of Benzaldehyde Catalyzed by (*R*,*R*)-5c; 2.0 equiv $SiCl_4$ (Table 2 Entry 8)

Following General Procedure I, from 42 mg (0.05 mmol, 0.05 equiv) of (*R*,*R*)-**5c**, 310 μL of allyltributylstannane (1.0 mmol, 331 mg, 1.0 equiv), 101 μL of benzaldehyde (1.0 mmol, 106.2 mg), and 229 μL of $SiCl_4$ (2.0 mmol, 340 mg, 2.0 equiv) was obtained 131 mg (89%) of (α*R*)-α-(2-propenyl)benzenemethanol ((*R*)-**3a**) as a clear, colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$)
7.37 (m, 2 H), 7.36 (m, 2 H), 7.29 (m, 1 H), 5.52 (ddt, *J* = 17.3, 10.1, 7.4, 1 H), 5.20-5.14 (m, 2 H), 4.74 (m, 1 H), 2.56-2.47 (m, 2 H), 2.06 (d, *J* = 3.2, 1 H)

SFC: t_R (*R*)-**3a**, 2.90 (96.4%); t_R (*S*)-**3a**, 3.50 min (3.6%) (Chiralpak OD, 40 °C, 150 bar, 4% CH_3OH in CO_2, 3 mL/min, 258 nm)

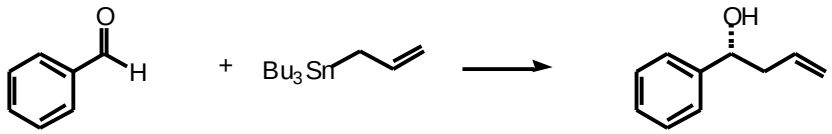
Allylation of Benzaldehyde Catalyzed by (*R*,*R*)-5c; 3.0 equiv $SiCl_4$ (Table 2 Entry 9)

Following General Procedure I, from 42 mg (0.05 mmol, 0.05 equiv) of (*R*,*R*)-**5c**, 310 μL of allyltributylstannane (1.0 mmol, 331 mg, 1.0 equiv), 101 μL of benzaldehyde (1.0 mmol, 106.2 mg), and 343 μL of $SiCl_4$ (3.0 mmol, 510 mg, 3.0 equiv was obtained 124 mg (84%) of (α*R*)-α-(2-propenyl)benzenemethanol ((*R*)-**3a**) as a clear, colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$)
7.37 (m, 2 H), 7.36 (m, 2 H), 7.29 (m, 1 H), 5.52 (ddt, *J* = 17.3, 10.1, 7.4, 1 H), 5.20-5.14 (m, 2 H), 4.74 (m, 1 H), 2.56-2.47 (m, 2 H), 2.06 (d, *J* = 3.2, 1 H)

SFC: t_R (*R*)-**3a**, 2.90 (92.1%); t_R (*S*)-**3a**, 3.52 min (7.9%) (Chiralpak OD, 40 °C, 150 bar, 4% CH_3OH in CO_2, 3 mL/min, 258 nm)

Representative Procedure I: Preparation of (α*R*)-α-2-Propenylbenzenemethanol ((*R*)-3a) (Table 3 entry 1)



1a **2** **3a**

In a flame-dried, 10-mL, 2-neck flask was placed 84 mg (0.1 mmol, 0.05 equiv) of (*R*,*R*)-**5c** in dry CH_2Cl_2 (3 mL) under dry N_2. To this solution was added 0.680 mL of allyltributylstannane (2.2 mmol, 728 mg, 1.1 equiv) and the resulting mixture was cooled to -78 °C (bath temperature). Then 252 μL of $SiCl_4$ (2.2 mmol, 374 mg, 1.1 equiv) was added followed by 202 μL of benzaldehyde (2.0 mmol, 212 mg). The resulting mixture was allowed to stir at -78 °C for 6 h whereupon the cold solution was added to a rapidly stirring solution of 1/1 sat. aq. KF/1.0 M KH_2PO_4 (20 mL). This biphasic mixture was stirred vigorously for 2 h after which

the separated, aqueous layer was washed with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were dried over Na_2SO_4, filtered and the solvent was removed *in vacuo*. The residue was purified by column chromatography ((SiO$_2$) CH_2Cl_2/pentane, 3/1 → CH_2Cl_2). The product-containing fractions were combined and the solvent was removed *in vacuo*. The oil was then dissolved in CH_2Cl_2 (75 mL) and the resulting solution was filtered through a column of solid anhydrous KF (10 mm) over silica gel (10 mm). The solvent was removed *in vacuo* to yield 269 mg (91%) of (α*R*)-α-(2-propenyl)benzenemethanol ((*R*)-**3a**) as a clear, colorless oil. The spectroscopic data matched those from the literature.[5]

Analytical Data for (*R*)-**3a**

^{1}H NMR: (500 MHz, $CDCl_3$)

7.37 (m, 2 H), 7.36 (m, 2 H), 7.29 (m, 1 H), 5.52 (ddt, *J* = 17.3, 10.1, 7.4, 1 H), 5.20-5.14 (m, 2 H), 4.74 (m, 1 H), 2.56-2.47 (m, 2 H), 2.06 (d, *J* = 3.2, 1 H)

^{13}C NMR: (100 MHz, $CDCl_3$)

144.03, 134.64, 128.61, 127.75, 125.99, 118.69, 73.46, 44.06

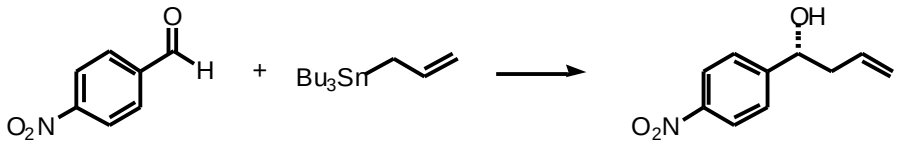
IR: (neat)

3305 (m), 3077 (m), 3030 (m), 2979 (w), 1811 (w), 1641 (m), 1493 (m), 1453 (m), 1311 (w), 1198 (w), 1000 (s), 758 (s)

SFC: t_R (*R*)-**3a**, 2.89 (97.1%); t_R (*S*)-**3a**, 3.42 min (2.9%) (Chiralpak OD, 40 °C, 150 bar, 4% CH_3OH in CO_2, 3 mL/min, 258 nm)

Opt. Rot.: $[\alpha]_D^{24}$ +51.2 (*c* = 1.10, benzene) [Lit.[5] (*R*)-**3a**: $[\alpha]_D^{24}$ +49.5 (*c* = 1.01, benzene]

Preparation of (α*R*)-4-Nitro-α-(2-propenyl)benzenemethanol ((*R*)-3b) (Table 3 entry 2)



1b **2** **3b**

Following Representative Procedure I, from 84 mg (0.1 mmol, 0.05 equiv) of (*R*,*R*)-**5c**, 212 mg of 4-nitrobenzaldehyde (**1b**) (2.0 mmol) (**1b** was dissolved in CH_2Cl_2 before the addition of allyltributylstannane and $SiCl_4$), 0.680 mL of allyltributylstannane (2.2 mmol, 728 mg, 1.1 equiv) and 252 μL of $SiCl_4$ (2.2 mmol, 374 mg, 1.1 equiv) was obtained 269 mg (91%) (α*R*)-4-nitro-α-(2-propenyl)benzenemethanol (*R*)-**3b** after column chromatography ((SiO_2) CH_2Cl_2/pentane, 3/1 → CH_2Cl_2) as a wax-like solid. The spectroscopic data matched those from the literature.[6]

Analytical Data for(*R*)-**3b**

^{1}H NMR: (400 MHz, $CDCl_3$)

8.21 (d, *J* = 8.5, 2 H), 7.53 (d, *J* = 8.5, 2 H), 5.84-5.73 (m, 1 H), 5.22-5.17 (m, 2 H), 4.87 (p, *J* = 3.9, 1 H), 2.60-2.43 (m, 1 H), 2.49-2.42 (m, 1 H), 2.22 (d, *J* = 2.9, 1 H)

^{13}C NMR: (100 MHz, $CDCl_3$)

151.24, 133.37, 126.75, 123.56, 119.98, 72.31, 44.16

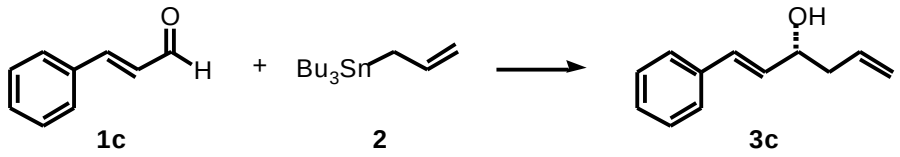
IR: (neat)

3401 (m), 3079 (w), 1604 (w), 1517 (s), 1346 (s), 1108 (w), 1054 (w), 1000 (w), 919 (m), 854 (m), 700 (m)

SFC: t_R (*R*)-**3b**, 6.26 (91.7%); t_R (*S*)-**3b**, 6.82 min (8.3%) (Chiralpak AS, 200 bar, 40 °C, 5% CH_3OH in CO_2, 2 mL/min, 220 nm)

Opt. Rot.: $[\alpha]_D^{24}$ +21.5 (*c* = 1.84, benzene) [Lit.[6] (*R*)-**3b**: $[\alpha]_D^{24}$ +14.9 (*c* = 1.6, benzene)]

Preparation of (1*E*,3*R*)-1-Phenyl-1,5-hexadiene-3-ol ((*R*)-3c) (Table 3 entry 3)



1c **2** **3c**

Following Representative Procedure I, from 84 mg (0.1 mmol, 0.05 equiv) of (*R*,*R*)-**5c**, 0.682 mL of allyltributylstannane (2.2mmol, 728 mg, 1.1 equiv), 202 μL of (*E*)-cinnamaldehyde (2.0 mmol, 212 mg), and 252 μL of $SiCl_4$ (2.2 mmol, 374 mg, 1.1 equiv) after 8 h was obtained 325 mg (89%) of (1*E*,3*R*)-1-phenyl-1,5-hexadiene-3-ol (*R*)-**3c** after column chromatography ((SiO_2), CH_2Cl_2) as a clear, colorless oil. The spectroscopic data matched those from the literature.[5]

Analytical Data for (*R*)-**3c**

^{1}H NMR: (400 MHz, $CDCl_3$)

7.40 (d, *J* = 7.1, 2 H), 7.33 (t, *J* = 7.1, 2 H), 7.26 (t, *J* = 7.1, 1 H), 6.62 (d, *J* = 15.9, 1 H), 6.26 (dd, *J* = 15.9, 6.3, 1 H), 5.87 (ddt, *J* = 17.3, 10.1, 7.4, 1 H), 5.23-5.17 (m, 2 H), 4.37 (dd *J* = 12.5, 6.1, 1 H), 2.50-2.36 (m, 1 H), 1.82 (s, 1 H)

^{13}C NMR: (100 MHz, $CDCl_3$)

136.81, 134.21, 131.69, 130.55, 128.77, 127.86, 126.67, 118.79, 71.88, 42.21

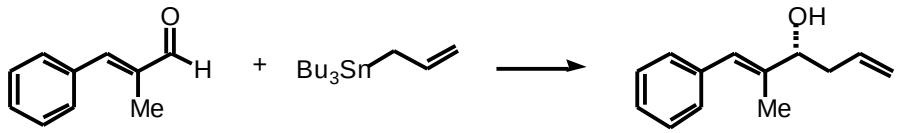
IR: (neat)

3368 (s), 3078 (m), 3026 (m), 2979 (m), 2930 (m), 2905 (m), 1948 (w), 1876 (w), 1805 (w), 1749 (w), 1641 (m), 1599 (w), 1578 (w), 1448 (m), 1309 (m), 1128 (m), 1030 (s), 967 (s), 917 (s), 749 (s)

SFC: t_R (*R*)-**3c**, 1.92 (82.5%); t_R (*S*)-**3c**, 2.43 min (17.5%) (Chiralpak OD, 40 °C, 150 bar, 10% CH_3OH in CO_2, 4 mL/min, 220 nm)

Opt. Rot.: $[\alpha]_D^{24}$ +2.92 (*c* = 1.01, benzene) (Lit.[5] (*R*)-**3c**: $[\alpha]_D^{24}$ +3.3 (*c* = 0.87, benzene)

Preparation of (1*E*)-2-Methyl-1-phenyl-1,5-hexadiene-3-ol (3d) (Table 3 entry 4)



1d **2** **3d**

Following Representative Procedure I, from 84 mg (0.1 mmol, 0.05 equiv) of (*R*,*R*)-**5c**, 0.682 mL of allyltributylstannane (2.2mmol, 728 mg, 1.1 equiv), 279 μL of (*E*)-2-methyl-cinnamaldehyde (2.0 mmol, 292 mg) and 252 μL of $SiCl_4$ (2.2 mmol, 374 mg, 1.1 equiv) after 8 h was obtained 284 mg (75%) of (1*E*)-2-methyl-1-phenyl-1,5-hexadiene-3-ol **(3d)** after column chromatography ((SiO_2) CH_2Cl_2) as a clear, colorless oil. The spectroscopic data matched those from the literature.[7]

Analytical Data for **3d**

^{1}H NMR: (400 MHz, $CDCl_3$)

7.35 (d, *J* = 7.1, 2 H), 7.27 (t, *J* = 7.1, 2 H), 7.21 (t, *J* = 7.1, 1 H), 6.54 (s, 1 H), 5.84 (ddt, *J* = 17.1, 10.3, 7.4, 1 H), 5.22-5.14 (m, 2 H), 4.23 (q *J* = 3.9, 1 H), 2.50-2.36 (m, 2 H), 1.89 (d *J* = 1.2, 3H) 1.82 (s, 1 H)

^{13}C NMR: (100 MHz, $CDCl_3$)

139.67, 137.71, 134.71, 129.19, 128.30, 126.65, 125.92, 118.35, 76.71, 40.31, 13.91

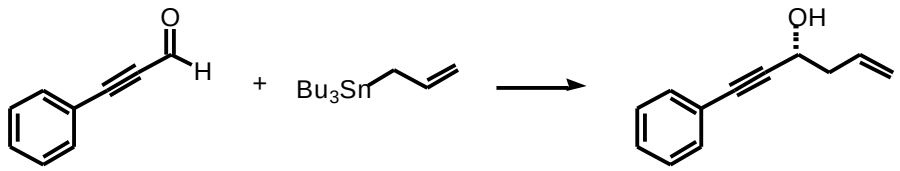
IR: (neat)

3369 (s), 3077 (m), 3024 (m), 2979 (m), 2935 (m), 2915 (m), 1641 (m), 1600 (m), 1492 (m), 1443 (s), 1328 (m), 1113 (w), 1045 (s), 998 (s), 916 (s), 874 (m), 748 (s)

SFC: t_R major-**3d**, 5.50 (55.6%); t_R minor-**3d**, 5.96 min (44.35%) (Chiralpak AD, 200 bar, 40 °C, 2% CH_3OH in CO_2, 3 mL/min, 220 nm)

Opt. Rot.: $[\alpha]_D^{24}$ -2.12 (*c* = 1.01, benzene)

Preparation of (3*R*)-1-Phenyl-5-hexen-1-yn-3-ol ((*R*)-3e) (Table 3 entry 5)



1e **2** **3e**

Following Representative Procedure I, from 84 mg (0.1 mmol, 0.05 equiv) of (*R*,*R*)-**5c**, 0.682 mL of allyltributylstannane (2.2 mmol, 728 mg, 1.1 equiv), 249 μL of phenylpropynal (2.0 mmol, 260 mg) and 252 μL of $SiCl_4$ (2.2 mmol, 374 mg, 1.1 equiv) was obtained 315 mg (92%) of (3*R*)-1-phenyl-5-hexen-1-yn-3-ol (*R*)-**3e** after column chromatography ((SiO_2) CH_2Cl_2/pentane, 3/1 → CH_2Cl_2) as a clear, colorless oil. The spectroscopic data matched those from the literature.[8]

Analytical Data for (*R*)-**3e**

^{1}H NMR: (500 MHz, $CDCl_3$)

7.45-7.41 (m, 2 H), 7.33-7.28 (m, 3H), 5.96 (ddt, *J* = 17.1, 10.3, 7.2, 1 H), 5.28-5.21 (m, 2 H), 4.66 (dd, *J* = 12.2, 6.1, 1 H), 2.60-2.56 (m, 2 H), 2.04-2.02 (m, 1 H)

^{13}C NMR: (100 MHz, $CDCl_3$)

133.18, 131.90, 128.66, 128.49, 122.68, 119.40, 89.51, 85.41, 62.23, 42.41

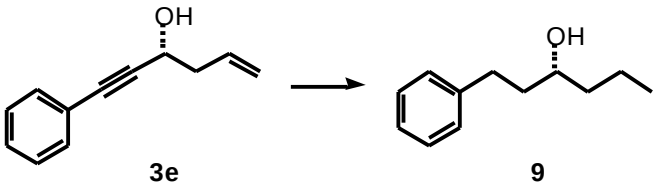
IR: (neat)

3351 (s), 3079 (m), 2981 (w), 2940 (w), 2913 (m), 1967 (w), 1882 (w), 1843 (w), 1669 (w), 1641 (m), 1598 (m), 1490 (s), 1442 (s), 1338 (m), 1030 (s), 993 (s), 920 (s), 756 (s), 691 (s)

SFC: t_R (*R*)-**3e**, 2.36 (61.1%); t_R (*S*)-**3e**, 2.98 min (38.9%) (Chiralpak OD, 200 bar, 40 °C, 2% CH_3OH in CO_2, 3 mL/min, 220 nm)

Opt. Rot.: $[\alpha]_D^{24}$ -5.36 (*c* = 2.1, EtOH)

Preparation (α*R*)-α-(Propyl)benzenepropanol (*R*-(9))



3e **9**

In a 10-mL flask containing a solution of 50 mg (0.29 mmol) of (3*R*)-1-phenyl-5-hexen-1-yn-3-ol ((*R*)-**3e**) in MeOH (4 mL) was added 5 mg of 5% Pd/C. The flask was then placed under 1 atm of H_2. The resulting mixture was allowed to stir for 3 h after which the mixture was filtered through a pad of Celite which was washed with CH_2Cl_2 (3 x 10 mL). The combined organic filtrates were then concentrated *in vacuo* and the resulting oil was purified by chromatography ((SiO$_2$) hexane/EtOAc, 9/1) to yield 41 mg (80%) of (α*R*)-α-(propyl)benzenepropanol (*R*-(**9**)) as a clear, colorless oil. The spectroscopic data matched those from the literature.[9]

Analytical Data for (*R*)-**9**

^{1}H NMR: (400 MHz, $CDCl_3$)

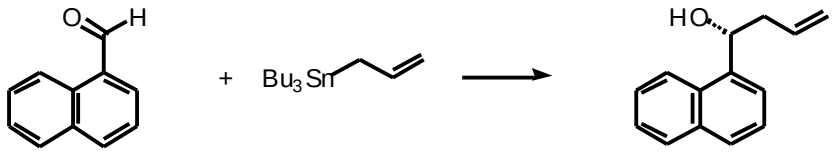
7.32-7.27 (m, 2 H), 7.23-7.19 (m, 3H), 3.67-3.66 (m, 1 H), 2.86-2.73 (m, 1 H), 2.72-2.19 (m, 1 H), 1.86-1.70 (m, 2 H), 1.51-1.33 (m, 5 H), 0.95 (t, *J* = 7.1, 3H)

^{13}C NMR: (100 MHz, $CDCl_3$)

142.43, 128.62, 128.61, 126.0, 71.34, 39.98, 39.33, 32.23, 19.02, 14.33

Opt. Rot.: $[\alpha]_D^{24}$ -4.05 (*c* = 1.85, EtOH) (Lit.[9] (*S*)-**9**: $[\alpha]_D^{24}$ +12.8 (*c* = 1.00, EtOH))

Preparation of (2*R*)-α-(2-Propenyl)-1-naphthalenemethanol ((*R*)-3f) (Table 3 entry 6)



1f **2** **3f**

Following Representative Procedure I, from 84 mg (0.1 mmol, 0.05 equiv) of (*R*,*R*)-**5c**, 0.682 mL of allyltributylstannane (2.2 mmol, 728 mg, 1.1 equiv), 271 μL of 1-naphthaldehyde (2.0 mmol, 312 mg, 1.0 equiv), and 252 μL of $SiCl_4$ (2.2 mmol, 374 mg, 1.1 equiv) was obtained 375 mg (93%) of (2*R*)-α-(2-propenyl)-1-naphthalenemethanol (*R*)-**3f** after column chromatography ((SiO_2) CH_2Cl_2/pentane, 3/1 → CH_2Cl_2) as a clear, colorless oil. The spectroscopic data matched those from the literature.[5]

Analytical Data for (*R*)-**3f**

^{1}H NMR: (500 MHz, $CDCl_3$)

8.08 (d, *J* = 8.4, 1 H), 7.89 (d, *J* = 8.0, 1 H), 7.80 (d, *J* = 8.1, 1 H), 7.68 (d, *J* = 6.2 1 H), 7.55-7.47 (m, 3 H), 5.95 (ddt, *J* = 17.1, 10.3, 7.3, 1 H), 5.54 (dd, *J* = 8.6, 4.1, 1 H), 5.23 (dq, *J* = 17.2, 1.5 1 H), 5.19 (dp, *J* = 10.3, 1.1, 1 H), 2.81-2.75 (m, 1 H), 2.65-2.60 (m, 1 H), 2.18 (s, 1 H).

^{13}C NMR: (100 MHz, $CDCl_3$)

139.60, 134.99, 133.99, 130.45, 129.18, 128.20, 126.26, 125.73, 125.66, 123.18, 123.05, 118.64, 70.16, 43.08

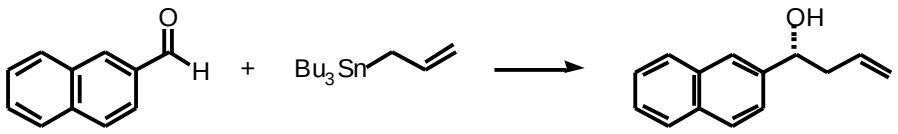
IR: (neat)

3388 (s), 3066 (m), 3008 (w), 2976 (w), 1638 (m), 1509 (w), 1509 (w), 1054 (m), 915 (m)

SFC: t_R (*S*)-**3f**, 3.27 min (3.4%); t_R (*R*)-**3f**, 4.90 min (96.6%) (Chiralpak OD, 40 °C, 150 bar, 10% CH_3OH in CO_2, 4 mL/min, 220 nm)

Opt. Rot.: $[\alpha]_D^{24}$ +94.69 (*c* = 1.06, benzene) (Lit.[5] (*R*)-**3f**: $[\alpha]_D^{24}$ +72.6 (*c* = 2.36, benzene)

Preparation of (2*R*)-α-(2-Propenyl)-2-naphthalenemethanol ((*R*)-3g) (Table 3 entry 7)



1g **2** **3g**

Following Representative Procedure I, from 84 mg (0.1 mmol, 0.05 equiv) of (*R*,*R*)-**5c**, and 312 mg (2.0 mmol,1.0 equiv) of 2-naphthaldehyde (**1g**) (**1g** was dissolved in CH_2Cl_2 before the addition of stannane and $SiCl_4$), 0.680 mL of allyltributylstannane (2.2 mmol, 728 mg, 1.1 equiv) and 252 μL of $SiCl_4$ (2.2 mmol, 374 mg, 1.1 equiv) was obtained 365 mg (92%) of (2*R*)-α-(2-propenyl)-2-naphthalenemethanol (*R*)-**3g** after column chromatography ((SiO_2) CH_2Cl_2/pentane, 3/1 → CH_2Cl_2) as a wax-like solid. The spectroscopic data matched those from the literature.[5]

Analytical Data for (*R*)-**3g**

^{1}H NMR: (500 MHz, $CDCl_3$)

7.85-7.82 (m, 4 H), 7.52-7.45 (m, 3 H), 5.85 (ddt, *J* = 17.1, 10.3, 7.2, 1 H), 5.22-5.14 (m, 2 H), 4.91 (dd, *J* = 7.6, 5.4, 1 H), 2.65- 2.54 (m, 2 H), 2.21 (s, 1 H)

^{13}C NMR: (100 MHz, $CDCl_3$)

141.40, 134.53, 133.42, 133.12, 128.39, 128.14, 127.86, 126.32, 126.00, 124.68, 124.18, 118.78, 73.54, 43.95

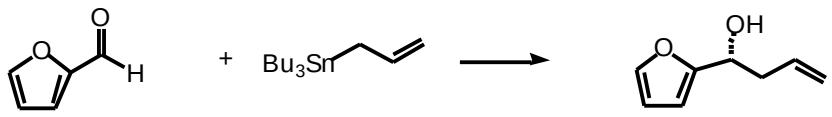
IR: (neat)

3526 (w), 3402 (s), 3056 (m), 2978 (w), 2931 (w), 2905 (w), 1640 (m), 1602 (m), 1508 (m), 1125 (m), 1048 (m), 916 (m), 819 (s), 747 (s)

SFC: t_R (*S*)-**3g**, 4.15 min (3.6%); t_R (*R*)-**3g**, 4.7 min (96.4%) (Chiralpak OD, 40 °C, 150 bar, 10% CH_3OH in CO_2, 4 mL/min, 220 nm)

Opt. Rot.: $[\alpha]_D^{24}$ +37.48 (*c* = 0.995, benzene) (Lit.[5] (*R*)-**3g**: $[\alpha]_D^{24}$ +22.4 (*c* = 1.85, benzene))

Preparation of (α*R*)-α-(2-Propenyl)-2-furanmethanol ((*R*)-3h) (Table 3 entry 8)



1h **2** **3h**

Following Representative Procedure I, from 84 mg (0.1 mmol, 0.05 equiv) of (*R*,*R*)-**5c**, 0.682 mL of allyltributylstannane (2.2mmol, 728 mg, 1.1 equiv), 165 μL of 1-furfural (2.0 mmol, 192 mg, 1.0 equiv) and 252 μL of $SiCl_4$ (2.2 mmol, 374 mg, 1.1 equiv) was obtained 180 mg (65%) of (α*R*)-α-(2-propenyl)-2-furanmethanol (*R*)-**3h** after column chromatography ((SiO_2) CH_2Cl_2/pentane, 3/1 → CH_2Cl_2) as a clear, colorless oil. The spectroscopic data matched those from the literature.[10]

Analytical Data for (*R*)-**3h**

^{1}H NMR: (500 MHz, $CDCl_3$)

7.38 (dd, *J* = 1.0, 0.9, 1 H), 6.33 (dd, *J* = 3.2, 2.0 1 H), 6.26 (d *J* = 3.2, 1 H), 5.81 (ddt, *J* = 17.1, 10.3, 7.2, 1 H), 5.21-5.14 (m, 2 H), 4.75 (dt, *J* = 7.1, 5.5, 1 H), 2.65-2.60 (m, 2 H), 2.02 (m, 1 H)

^{13}C NMR: (100 MHz, $CDCl_3$)

156.16, 142.21, 133.86, 118.87, 110.34, 106.31, 67.31, 40.29

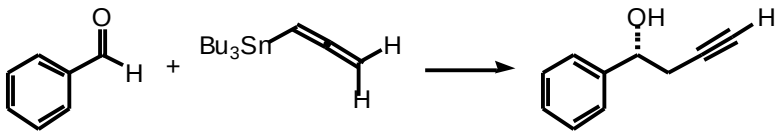
IR: (neat)

3548 (w), 3401 (s), 3078 (m), 2980 (m), 2912 (m), 1642 (m), 1504 (m), 1434 (m), 1228 (w), 1149 (s), 1055 (m), 1011 (s), 920 (s), 811 (w), 738 (s)

GC: t_R (*S*)-**3h**, 8.82 min (19.2%); t_R (*R*)-**3h**, 9.26 min (80.8%) (Chiraldex GTA) 80 °C isothermal, 16 mL/min)

Opt. Rot.: $[\alpha]_D^{24}$ +27.31 (*c* = 1.22, $CHCl_3$) (Lit.[10] (*R*)-**3h**: $[\alpha]_D^{24}$ +24.9 (*c* = 1.0, $CHCl_3$))

Preparation of (α*R*)-α-(2-Propynyl)benzenemethanol ((*R*)-8a)



1a **7** **8a**

Following Representative Procedure I, from 84 mg (0.1 mmol, 0.05 equiv) of (*R*,*R*)-**5c**, 723 mg of allenyltributylstannane (2.2 mmol, 1.1 equiv) 202 μL of benzaldehyde (2.0 mmol, 212 mg), and 252 μL of $SiCl_4$ (2.2 mmol, 374 mg, 1.1 equiv) in 1.5 mL of CH_2Cl_2, after 8 h was obtained 236 mg (80%) of (α*R*)-α-(2-propynyl)benzenemethanol ((*R*)-**8a**) after column chromatography ((SiO_2) hexane/EtOAc, 10/1 → 6/1) as a clear, colorless oil. The spectroscopic data matched those from the literature.[11]

Analytical Data for (*R*)-**8a**

^{1}H NMR: (500 MHz, $CDCl_3$)

7.40 (d, *J* = 6.8, 2 H), 7.37 (t, *J* = 7.2, 2 H), 7.31 (m, 1 H), 4.89 (dt, *J* = 3.5, 6.4, 1 H), 2.66-2.64 (m, 2 H), 2.36 (d, *J* = 3.5, 1 H), 2.08 (t, *J* = 2.5, 1 H)

^{13}C NMR: (100 MHz, $CDCl_3$)

142.60, 128.71, 128.24, 125.94, 80.85, 72.54, 71.21, 29.69

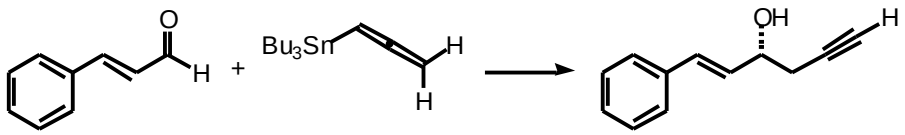
IR: (neat)

3523 (w), 3392 (m), 3293 (s), 3064 (w), 3031 (w), 2912 (w), 2119 (w), 1955 (w), 1882 (w), 1810 (w), 1604 (w), 1494 (m), 1454 (m), 1421 (m), 1317 (w), 1201 (w), 1081 (w), 1049 (s), 863 (w), 755 (s), 700 (s)

GC: t_R (*S*)-**8a**, 8.63 (99.0%); t_R (*S*)-**8a**, 9.73 min (1.0%) ((Chiraldex GTA) 100 °C isothermal, 16 mL/min)

Opt. Rot.: $[\alpha]_D^{24}$ +12.9 (*c* = 1.55, MeOH) (Lit.[11] (*R*)-**8a**: $[\alpha]_D^{24}$ +7.36 (*c* = 3.8, MeOH))

Preparation of (1*E*,3*R*) 1-Phenyl-1-hexen-5-yn-3-ol ((*R*)-8b)



1c **7** **8b**

Following Representative Procedure I, from 84 mg (0.1 mmol, 0.05 equiv) of (*R*,*R*)-**5c**, 723 mg of allenyltributylstannane (2.2 mmol, 1.1 equiv), 202 μL of (*E*)-cinnamaldehyde (2.0 mmol, 212 mg), and 252 μL of $SiCl_4$ (2.2 mmol, 374 mg, 1.1 equiv) in 1.5 mL of CH_2Cl_2, after 8 h was obtained 325 mg (89%) of (1*E*,3*R*)-1-phenyl-1-hexen-5-yn-3-ol ((*R*)-**8b**) after column chromatography ((SiO_2) hexane/EtOAc, 10/1 → 6/1) as a clear, colorless oil. The spectroscopic data matched those from the literature.[12]

Analytical Data for (*R*)-**8b**

^{1}H NMR: (500 MHz, $CDCl_3$)

7.41 (d, *J* = 7.1, 2 H), 7.34 (t, *J* = 7.1, 2 H), 7.27 (t, *J* = 7.1, 1 H), 6.67 (d, *J* = 15.9, 1 H), 6.29 (dd, *J* = 15.9, 6.2, 1 H), 4.51-4.46 (m, 1 H), 2.60 (ddd, *J* = 15.9, 5.5, 2.5, 1 H), 2.53 (ddd, *J* = 16.7, 6.6, 2.5, 1 H), 2.10 (m, 1 H)

^{13}C NMR: (100 MHz, $CDCl_3$)

136.49, 131.56, 130.11, 128.80, 128.11, 126.79, 80.38, 71.35, 70.93, 27.94

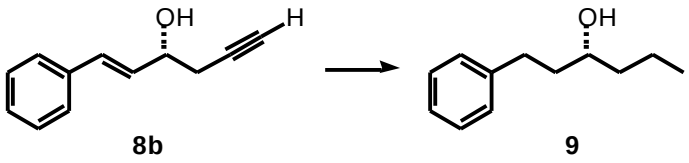
IR: (neat)

3539 (w), 3383 (m), 3295 (s), 3103 (w), 3081 (w), 3059 (w), 3027 (m), 2911 (m), 1807 (w), 1655 (w), 1598 (m), 1578 (m), 1494 (m), 1449 (m), 1421 (m), 1391 (m), 1330 (m), 1102 (m), 1071 (m), 1038 (s), 967 (s), 858 (w)

SFC: t_R (*R*)-**3c**, 2.21 (93.1%); t_R (*S*)-**3c**, 2.54 min (6.9%) (Chiralpak OD, 40 °C, 150 bar, 15% CH3OH in CO2, 3 mL/min, 220 nm)

Opt. Rot.: $[\alpha]_D^{24}$ -59.27 (*c* = 1.35, benzene)

Preparation (α*R*)-α-(Propyl)benzenepropanol (*R*-(9))



8b **9**

In a 10-mL flask containing a solution of 50 mg (0.29 mmol) of 1-phenyl-hexen-5-yn-3-ol (**8b**) in MeOH (4 mL) was placed 5 mg of 5% Pd/C. The flask was then placed under 1 atm of H_2. The resulting mixture was allowed to stir for 3 h after which the mixture was filtered through a pad of Celite which was washed with CH_2Cl_2 (3 x 10 mL). The combined organic filtrates were then concentrated *in vacuo* and the resulting oil was purified by chromatography ((SiO_2) hexane/EtOAc, 9/1) to yield 35 mg (68%) of (α*R*)-α-(propyl)benzenepropanol (*R*-(**9**)) as a clear, colorless oil. The spectroscopic data matched those from the literature.[9]

Analytical Data for (*R*)-**9**

^{1}H NMR: (400 MHz, $CDCl_3$)

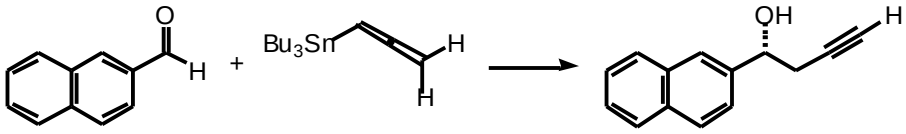
7.32-7.27 (m, 2 H), 7.23-7.19 (m, 3 H), 3.67-3.66 (m, 1 H), 2.86-2.73 (m, 1 H), 2.72-2.19 (m, 1 H), 1.86-1.70 (m, 2 H), 1.51-1.33 (m, 5 H), 0.95 (t, *J* = 7.1, 3 H)

^{13}C NMR: (100 MHz, $CDCl_3$)

142.43, 128.62, 128.61, 126.0, 71.34, 39.98, 39.33, 32.23, 19.02, 14.33

Opt. Rot.: $[\alpha]_D^{24}$ -14.47 (*c* = 1.3, EtOH) (Lit.[9] (*S*)-**9**: $[\alpha]_D^{24}$ +12.8 (*c* = 1.00, EtOH))

Preparation of (α*R*)-α-(2-Propynyl)-2-naphthalenemethanol ((*R*)-8c)



1g **7** **8c**

Following Representative Procedure I, from 84 mg (0.1 mmol, 0.05 equiv) of (*R,R*)-**5c**, and 312 mg (2.0 mmol) of 2-naphthaldehyde (**1g**) (**1g** was dissolved in CH_2Cl_2 before the addition of allenyltributylstannane and $SiCl_4$), 723 mg of allenyltributylstannane (2.2 mmol, 1.1 equiv) and 252 μL of $SiCl_4$ (2.2 mmol, 374 mg, 1.1 equiv) in 1.5 mL of CH_2Cl_2, after 8 h, was obtained 376 mg (95%) of (α*R*)-α-(2-propynyl)-2-naphthalenemethanol ((*R*)-**8c**) after column chromatography ((SiO_2) hexanes/EtOAc, 10/1 → 6/1) as a wax-like solid. The spectroscopic data matched those from the literature.[13]

Analytical Data for (*R*)-**8c**

^{1}H NMR: (400 MHz, $CDCl_3$)

7.86-7.84 (m, 4 H), 7.51-7.50 (m, 3 H), 5.05 (dt, *J* = 6.1, 3.4, 1 H), 2.74 (m, 2 H), 2.46 (d, *J* = 3.7, 1 H), 2.10 (t, *J* = 2.7, 1 H)

^{13}C NMR: (100 MHz, $CDCl_3$)

139.97, 133.34, 133.30, 128.54, 127.00, 126.44, 126.24, 124.86, 123.87, 123.87, 80.80, 72.63, 71.32, 29.61

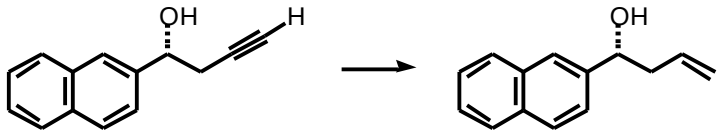
IR: (neat)

3546 (w), 3401 (s), 3294 (s), 3055 (m), 2912 (m), 1601 (w), 1508 (w), 1420 (w), 1320 (w), 1271 (w), 1122 (w), 1054 (m), 953 (w), 853 (w), 895 (w), 858 (m), 820 (m), 750 (m)

SFC: t_R (*S*)-**3g**, 5.58 min (96.6%); t_R (*R*)-**3g**, 6.00 min (3.4%) (Chiralpak AD, 40 °C, 150 bar, 8% CH_3OH in CO_2, 3 mL/min, 220 nm)

Opt. Rot.: $[\alpha]_D^{24}$ -2.67 (*c* = 1.16, EtOH)

Preparation of (2*R*)-α-(2-Propenyl)-2-naphthalenemethanol ((*R*)-3g)



8c **3f**

In a 10-mL flask containing a solution of 50 mg (0.25 mmol) of (α*R*)-α-(2-propynyl)-2-naphthalenemethanol (**8c**) in 3 mL of MeOH was placed 5 mg of 5% Pd/Ba_2SO_4, and 100 μL of pyridine. The flask was then placed under 1 atm of H_2. The resulting mixture was allowed to stir for 20 min at room temperature after which the mixture was filtered through a pad of Celite which was washed with CH_2Cl_2 (3 x 10 mL). The combined organic filtrates were then concentrated *in vacuo* and the resulting oil was purified via column chromatography ((SiO_2) hexane/EtOAc, 9/1) to yield 35 mg (68%) of (2*R*)-α-(2-propenyl)-2-naphthalenemethanol (containing 10% of (α*R*)-α−(propyl)-2-naphthylenepropanol). The *R* absolute configuration was assigned by order of elution of the peaks by CSP SFC compared to an authentic sample.

Analytical Data for (*R*)-**3f**

^{1}H NMR: (400 MHz, $CDCl_3$)

7.85-7.82 (m, 4 H), 7.52-7.45 (m, 3 H), 5.85 (ddt, *J* = 17.1, 10.3, 7.2, 1 H), 5.22-5.14 (m, 2 H), 4.91 (dd, *J* = 7.6, 5.4, 1 H), 2.65- 2.54 (m, 2 H), 2.21 (s, 1 H)

^{13}C NMR: (100 MHz, $CDCl_3$)

141.40, 134.53, 133.42, 133.12, 128.39, 128.14, 127.86, 126.32, 126.00, 124.68, 124.18, 118.78, 73.54, 43.95

SFC: t_R (*S*)-**3g**, 4.15 min (3.4%); t_R (*R*)-**3g**, 4.7 min (96.6%) (Chiralpak OD, 40 °C, 150 bar, 10% CH_3OH in CO_2, 4 mL/min, 220 nm)

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