**Enantioselective Synthesis of 1,5-*Anti* and 1,5-*Syn* Diols Using a Highly
Diastereoselective One-Pot Double Allylboration Reaction Sequence**

Eric M. Flamme and William R. Roush*

Department of Chemistry, University of Michigan, Ann Arbor, MI, 48109-1055

Email Address: roush@umich.edu

SUPPORTING INFORMATION

Experimental procedures and tabulated spectroscopic data for **1a-1e**, **2a-2f**, **3**, **10**,
and **9a - 9f**.

General Details: All reaction solvents were purified before use. Diethyl ether was dried by distillation from sodium benzophenone ketyl. Toluene was dried by distillation from sodium metal. Dichloromethane was purified ether by passage through a solvent column composed of activated alumina (A-1) or by distillation from CaH_2 .¹ All reactions were conducted under a nitrogen atmosphere using oven dried (140 °C) glassware. Nitrogen was dried by passage through a long drying column containing DrieriteTM. Removal of solvents was accomplished on a rotary evaporator at reduced pressure. Enantiomeric excess was determined by the method of Dale and Mosher.²

Physical Properties and Spectroscopic Measurements: ^1H NMR spectra were recorded on a Varian VXR-400 spectrometer at 400 MHz or on a Varian Inova-500 spectrometer at 500 MHz. ^{13}C NMR spectra were recorded on a Varian VXR-400 spectrometer at 100 MHz or a Varian Inova-500 spectrometer at 125 MHz. The proton signal of residual, non-deuterated solvent (δ 7.24 ppm for CHCl_3) was used as an internal reference for ^1H spectra. For ^{13}C spectra, the chemical shifts are reported relative to the δ 77.0 ppm resonance of CDCl_3 .

Infrared (IR) spectra were recorded as thin films using CH_2Cl_2 as the solvent on a Perkin-Elmer Spectrum 1000 FTIR. Optical rotations were measured on a Rudolph Autopol III polarimeter using a quartz cell with 1 mL capacity and a 10 cm path length. Melting points were determined on a Mel-Temp II hot stage melting point apparatus and are uncorrected. Mass spectra were recorded on a VG 70-250-s spectrometer manufactured by Micromass Corp. (Manchester UK) at the University of Michigan Mass Spectrometry Laboratory.

Analytical thin layer chromatography (TLC) was performed on Kieselgel 60 F_{254} glass plates precoated with a 0.25 mm thickness of silica gel. The TLC plates were visualized with UV light and/or by staining with *p*-anisaldehyde stain (a mixture of ethanol, sulfuric acid, and *p*-anisaldehyde). Column chromatography was generally performed according to the method of Still using Kieselgel 60 (230-400 mesh) silica gel.³

HPLC purifications were performed by using an HPLC system composed of two Rainin HPXL pumps connected to a Dynamax axial compression column packed with Rainin 60 Å irregular silica gel. Samples were loaded into the system with a 2 mL Rheodyne 7125 injector and were detected by using either a Rainin Dynamax UV-C detector or a Rainin Dynamax RI-1 detector. Integration of the various signals was performed using the Reprocessing program within the Dynamax HPLC Method Manager.

2-Allenyl-1,3,2-dioxaborinane (3). Freshly distilled trimethylborate (21.7 mL, 196 mmol) was added to a round bottom flask containing 150 mL of ether and cooled to $-78\text{ }^{\circ}\text{C}$. A $0\text{ }^{\circ}\text{C}$ solution of allenylmagnesium bromide⁴ (1 M in ether, 196 mmol) was added via syringe or canula at a rate as to keep the internal reaction temperature below $-65\text{ }^{\circ}\text{C}$. A white precipitate formed upon addition and the reaction was stirred 3 h at $-78\text{ }^{\circ}\text{C}$. The reaction was warmed to $0\text{ }^{\circ}\text{C}$ over 1 h and stirred at $0\text{ }^{\circ}\text{C}$ for an additional hour. Aqueous HCl (2M, 392 mmol) was added via an addition funnel to form the boronic acid. The reaction was stirred for 1 h and then the organic layer was separated from the aqueous layer with a separatory funnel. The aqueous layer was washed with ether (2 x 200 mL) and the organics were dried over Na_2SO_4 for 30 min. The organics were filtered under nitrogen and solvent removed in vacuo until ~250 mL of solvent remained (rotary evaporator was flushed and backfilled using an argon balloon). 1,3-Propane diol (10.4 g, 137 mmol) was added to the flask and reaction stirred for 24 h at room temperature at which time 10 g of MgSO_4 was added and the mixture stirred for an additional 18 h at room temperature. The reaction was filtered under nitrogen using a coarse fritted funnel and solvent removed in vacuo using argon to backfill the rotary evaporator. The remaining clear yellow oil was distilled under vacuum (bp 20 mm Hg, $81\text{--}82\text{ }^{\circ}\text{C}$) to yield 12.5 g (76%) of **3** as a clear, colorless oil. The oil was transferred to small vials and stored under nitrogen within a dessicator in a $-20\text{ }^{\circ}\text{C}$ freezer and could be used neat over several months without loss of efficiency. Spectral data obtained for **3** matched that reported in the literature.⁵

2-allenyl-4,4,5,5-tetraphenyl-1,3,2-dioxaborolane (10). 1,1,2,2-Tetraphenylethylene⁶ glycol (18.4 g, 50 mmol) was placed in a 250 mL round bottom flask containing a magnetic stir bar. The flask was flushed with nitrogen and to the flask was added 50 mL of toluene and freshly distilled triisopropylborate (12.7 mL, 55 mmol) via syringe. The flask was fitted with a Dean-Stark condenser and the reaction was heated at $105\text{ }^{\circ}\text{C}$ for 24 h at which time the mixture was a clear homogenous solution. The mixture was distilled $150\text{ }^{\circ}\text{C}$ to remove isopropanol, toluene, and

residual triisopropylborate. The heating bath was turned off and when the bath temperature read 100 °C the mixture was stirred vigorously under high vacuum while allowing to cool. The resulting 2-isopropyl-4,4,5,5-tetraphenyl-1,3,2-dioxaborolane was stirred under vacuum overnight yielding a clear, colorless, glassy solid which was used without purification or characterization. The borolane was dissolved in 75 mL of diethyl ether and cooled to –78 °C. A 0 °C solution of allenylmagnesium bromide⁴ (1 M in ether, 50 mmol) was added dropwise at which time a white precipitate developed. The mixture was stirred 2 h at –78 °C and then warmed to room temperature and stirred for an additional 3 h. The reaction mixture was diluted with CH₂Cl₂ (200 mL), cooled to 0 °C, and quenched with aqueous 1 M HCl (0.8 equiv). The solution was adjusted to pH 4 with saturated aqueous ammonium chloride and additional 1 M HCl. The organic layer was separated and the aqueous layer extracted with CH₂Cl₂ (3 x 50 mL). The organic phase was washed with saturated sodium chloride, dried over Na₂SO₄, and concentrated. The crude oil was purified by column chromatography (3:1 hexanes : CH₂Cl₂) affording a white crystalline solid (12.4-16.5 g, 60-80%). The product **10** can be stored under nitrogen and handled in an air atmosphere, but for long term storage **10** was stored in a glove box: m.p. 160-64 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.18 - 7.13 (8 H, m), 7.08 – 7.03 (12 H, m), 5.27 (1 H, t, *J* = 7 Hz), 4.77 (2 H, d, *J* = 6.5 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 220.2, 142.3, 128.5, 127.2, 127.0, 96.1, 70.6; IR (thin film) 3059, 1956, 1932, 1368, 751, 698 cm⁻¹; HRMS (EI, 70 ev) calcd for C₂₉H₂₃O₂B [M + H]⁺: 414.1791, found 414.1978 *m/z*.

9a

(3*R*, 7*R*, 4*E*)-1,9-diphenylnon-4-ene-3,7-diol (9a): In a glove box ^dIpc₂BH⁷ (0.287 g, 1 mmol) was weighed into a round bottom flask containing a stir bar (Note: The crystalline borane should be crushed and pulverized with a glass rod prior to use in order to ensure efficient hydroboration). The flask was capped with a rubber septum and removed from the glove box and placed in an ice bath. Ether (3 mL) was added to the flask followed by the allenylboronic ester **3** (0.123 g, 1 mmol) added neat via a microliter syringe. The reaction was stirred 2 h in an ice bath during which time the solid ^dIpc₂BH dissolved to leave a colorless solution. The ice bath was removed and the reaction cooled to –78 °C. Distilled hydrocinnamaldehyde (0.188 g, 1.4 mmol) was added dropwise to the reaction mixture via microliter syringe and the reaction stirred at –78 °C

for 2 h. The cold bath was removed and the reaction was allowed to warm to room temperature and stir for an additional 24 h. The reaction was placed in an ice bath and 1 mL of aqueous 3M NaOH solution was added dropwise followed by slow addition of 0.4 mL of a 50% HOOH solution (Caution: Rapid addition of the peroxide can cause a vigorous exotherm). The reaction was stirred vigorously for 4 h at room temperature at which time it was diluted with 40 mL of CH₂Cl₂ and 20 mL of sat. NaHCO₃ and 5 mL of sat. NaCl solution. The organic layer was separated and the aqueous washed 2 x 10 mL of CH₂Cl₂. The reaction was dried over Na₂SO₄ and the solvent removed in vacuo. The residual oil was purified by column chromatography (gradient elution 10-45% EtOAc in hexanes) affording 0.119 g (38% based on mmol of **3**) of a colorless oil. An analytical sample was prepared by preparative HPLC (60 : 40 : EtOAc : hexanes): $[\alpha]_D^{24} + 13.6^\circ$ (*c* 1.0, CHCl₃); ee: 91%; ¹H NMR (500 MHz, CDCl₃) δ 7.29 – 7.15 (10 H, m), 5.71 (1 H, ddd, *J* = 7 Hz, 7 Hz, 15 Hz), 5.63 (1 H, dd, *J* = 7 Hz, 15 Hz), 4.12 (1 H, ddd (app q), *J* = 7 Hz), 3.7 (1 H, m), 2.83 – 2.62 (4 H, m), 2.32 – 2.26 (1 H, m), 2.20 – 2.13 (1 H, m), 1.90 – 1.71 (4 H, m), 1.58 (2 H, s, OH broad); ¹³C NMR (125 MHz, CDCl₃) δ 142.16, 142.07, 136.59, 128.61, 128.58, 127.61, 126.06, 126.03, 72.14, 70.54, 40.41, 38.94, 38.62, 32.24, 31.97; IR (thin film) 3351, 3026, 2928, 1602, 1495, 1454, 1051 cm⁻¹; HRMS (CI, NH₃) calcd for C₂₁H₃₀NO₂ [M + NH₄]⁺: 328.2277, found 328.2260 *m/z*; *Anal.* Calcd for C₂₁H₂₆O₂: C, 81.25; H, 8.44. Found: C, 80.95; H, 8.51.

Results of optimization studies of the double allylboration reaction are provided in the following table. These results show that it is necessary to use 1.4 equiv. of aldehyde to completely consume the in situ generated γ-borylallylborane **4** as well as the substituted methallylborane **5** (the product of the first allylboration reaction). The identity of the reducing agent that leads to the production of phenylpropanol (**C**) in these experiments is unclear at present. The double allylboration reactions summarized in Table 2 (see text of paper) have been optimized (by using 0.54 equiv of the first aldehyde) so as to minimize production of homocoupled diols, deriving from double allylboration of either the first aldehyde (if used in excess over the effective, useful concentration of **4**), or of double allylboration products of the second aldehyde (R²CHO), if an insufficient quantity of the first aldehyde (R¹CHO) is used such that all of reagent **4** is not consumed in the first allylboration step.

RCHO (equiv)	Ratio A : B (NMR)	Yield of A + B (combined)*	Yield of C
0.6	1 : 8.2	36%	n.d.
0.8	1 : 2.5	45%	14%
1.0	4.3 : 1	40%	17%
1.25	4.7 : 1	46%	28%
1.4	100 : 0	38%	38%
1.6	100 : 0	38%	48%
2.0	100 : 0	38%	48%

*Yield is based on allenylboronate **3**

ent-9a

(3S, 7S, 4E)-1,9-diphenylnon-4-ene-3,7-diol (ent-9a): $[\alpha]_{\text{D}}^{24} -12.8^\circ$ (*c* 1.0, CHCl₃); ee 92%; ¹H NMR (500 MHz, CDCl₃) δ 7.35–7.18 (10 H, m), 5.70 (1 H, ddd, *J* = 7 Hz, 7 Hz, 15 Hz), 5.63 (1 H, dd, *J* = 6 Hz, 15 Hz), 4.13 (1 H, m), 3.69 (1 H, m), 2.85 – 2.65 (4 H, m), 2.32 (1 H, m), 2.19 (1 H, m), 1.94 – 1.75 (6 H, m); ¹³C NMR (125 MHz, CDCl₃) δ 142.14, 142.01, 136.67, 128.64, 128.61, 127.68, 126.09, 126.07, 72.22, 70.47, 40.54, 38.97, 38.67, 32.25, 32.00; IR (thin film) 3350, 3026, 2928, 1603, 1495, 1454, 1051 cm⁻¹; HRMS (CI, NH₃) calcd for C₂₁H₃₀NO₂ [M + NH₄]⁺: 328.2277, found 328.2275 *m/z*.

9b

(1R, 5S, 2E)-1,5-dicyclohexylpent-2-ene-1,5-diol (9b): $[\alpha]_{\text{D}}^{24} - 8.8^\circ$ (c 1.06, CHCl_3); ee 84%; ^1H NMR (500 MHz, CDCl_3) δ 5.67 (1 H, ddd, $J = 6.5$ Hz, 7.5 Hz, 15.5 Hz), 5.59 (1 H, dd, $J = 7$ Hz, 15 Hz), 3.83 (1 H, dd (app t), $J = 6.5$ Hz), 3.39 (1 H, m), 2.33 (1 H, m), 2.14 (1 H, ddd, $J = 8.5$ Hz, 8.5 Hz, 16 Hz), 1.88 (1 H, s), 1.86 (1 H, s), 1.8 – 1.72 (4 H, m), 1.7 – 1.6 (m, 4H), 1.56 (2 H, s), 1.44 – 1.32 (2 H, m), 1.3 – 0.92 (10 H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 135.12, 128.85, 77.54, 75.31, 43.72, 43.02, 37.28, 29.25, 28.98, 28.58, 26.69, 26.65, 26.40, 26.28, 26.26, 26.22; IR (thin film) 3350, 2923, 2881, 1449 cm^{-1} ; HRMS (CI, NH_3) calcd for $\text{C}_{17}\text{H}_{34}\text{NO}_2$ $[\text{M} + \text{NH}_4]^+$: 284.2590, found 284.2588 m/z ; *Anal.* Calcd for $\text{C}_{17}\text{H}_{30}\text{O}_2$: C, 76.64; H, 11.35. Found: C, 76.91; H, 11.63.

9c

(3R, 7S, 4E)-2,8-dimethylnon-4-ene-3,7-diol (9c): $[\alpha]_{\text{D}}^{24} - 19.5^\circ$ (c 1.20, CHCl_3); ee 92%; ^1H NMR (500 MHz, CDCl_3) δ 5.64 (1 H, ddd, $J = 7$ Hz, 6.8 Hz, 15.8 Hz), 5.54 (1 H, dd, $J = 6.8$ Hz, 15.8 Hz), 3.78 (1 H, dd (app t), $J = 6.4$ Hz), 3.34 (1 H, m), 2.5 (1 H, m), 2.08 (1 H, m), 1.79 (1 H, s, OH-broad), 1.7 – 1.59 (3 H, m), 0.9 (3 H, d, $J = 4.8$ Hz), 0.88 (3H, d, $J = 4.8$ Hz), 0.88 (3 H, d, $J = 6.4$ Hz), 0.84 (3 H, d, $J = 6.8$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 134.69, 129.10, 78.14, 76.12, 37.42, 33.97, 33.29, 18.99, 18.42, 17.95; IR (thin film) 3352, 2959, 1469, 1013 cm^{-1} ; HRMS (CI, NH_3) calcd for $\text{C}_{11}\text{H}_{24}\text{NO}$ $[\text{M} + \text{NH}_4 - \text{H}_2\text{O}]^+$: 186.1852, found 186.1858 m/z .

9d

(2S, 6S, 3E)-1,7-dibenzyloxyhept-3-ene-2,6-diol (9d): $[\alpha]_{\text{D}}^{24} + 5.7^\circ$ (c 1.42, CHCl_3); ee 92%; ^1H NMR (500 MHz, CDCl_3) δ 7.4-7.3 (10 H, m), 5.80 (1 H, m), 5.54 (1 H, ddt, $J = 1.5$ Hz, 4.5 Hz, 15 Hz), 4.56 (4 H, m), 4.33 (1 H, m), 3.87 (1 H, ddddd (app nonet), $J = 3.5$), 3.52 (1 H, dd, $J = 1.5$ Hz, 3.5 Hz), 3.50 (1 H, dd, $J = 1.5$ Hz, 3.5 Hz), 3.38 (1 H, dd, $J = 1.5$ Hz, 7.5 Hz), 3.36 (1 H,

dd, $J = 1.5$ Hz, 7.5 Hz), 2.53 (1 H, d, OH, $J = 3.5$), 2.43 (1 H, d, OH, $J = 4$), 2.26 (2 H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 138.17, 138.07, 131.63, 129.04, 128.74, 128.72, 128.10, 128.05, 128.01, 74.38, 74.04, 73.60, 71.34, 70.02, 36.67; IR (thin film) 3351, 3025, 2929, 1602, 1495, 1453, 1030 cm^{-1} ; HRMS (CI, NH_3) calcd for $\text{C}_{21}\text{H}_{30}\text{NO}_4$ $[\text{M} + \text{NH}_4]^+$: 360.2175, found 360.2163 m/z ; *Anal.* Calcd for $\text{C}_{21}\text{H}_{26}\text{O}_4$: C, 73.66; H, 7.65. Found: C, 73.83; H, 7.58.

9e

(1S, 5S, 2E)-1,5-diphenylpent-2-ene-1,5-diol (9e): $[\alpha]_{\text{D}}^{24} - 17.1^\circ$ (c 1.0, CH_2Cl_2); ee 93%; ^1H NMR (500 MHz, CDCl_3) δ 7.32 – 7.22 (10 H, m), 5.76 – 5.65 (2 H, m), 5.07 (1 H, d, $J = 7$ Hz), 4.67 (1 H, t, $J = 8$ Hz), 2.98 (1 H, s, OH broad), 2.80 (1 H, s, OH broad), 2.44 (2 H, dd (app t), $J = 8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 143.97, 143.08, 136.08, 128.61, 128.57, 127.68, 127.60, 126.39, 125.99, 74.84, 73.64, 41.97; IR (thin film) 3351, 3029, 1603, 1493, 1452, 1261, 1028 cm^{-1} ; HRMS (CI, NH_3) calcd for $\text{C}_{17}\text{H}_{22}\text{NO}_2$ $[\text{M} + \text{NH}_4]^+$: 272.1651, found 272.1646 m/z ; *Anal.* Calcd for $\text{C}_{17}\text{H}_{18}\text{O}_2$: C, 80.28; H, 7.13. Found: C, 80.03; H, 6.93.

ent-9e

(1R, 5R, 2E)-1,5-diphenylpent-2-ene-1,5-diol (ent-9e): $[\alpha]_{\text{D}}^{24} + 18.0^\circ$ (c 1.0, CH_2Cl_2); ee 95%; ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.24 (10 H, m), 5.80 – 5.73 (2 H, m), 5.14 (1 H, m), 4.73 (1 H, m), 2.50 (2 H, dd (app t), $J = 7.5$ Hz), 2.43 (1 H, d, OH, $J = 4.5$ Hz), 2.35 (1 H, d, OH, $J = 4.5$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 143.99, 143.11, 136.19, 128.70, 128.65, 127.80, 127.66, 126.40, 126.02, 74.98, 73.78, 42.13; IR (thin film) 3359, 3029, 1455 cm^{-1} ; HRMS (CI, NH_3) calcd for $\text{C}_{17}\text{H}_{17}\text{O}_2$ $[\text{M} - \text{H}]^+$: 253.1229, found 253.1227 m/z .

9f

(3*R*, 7*S*, 4*E*)-2,2,8,8-tetramethylnon-2-ene-3,7-diol (9f): $[\alpha]_D^{24} - 31.0^\circ$ (c 1.02, CHCl_3); ee 92%; ^1H NMR (500 MHz, CDCl_3) δ 5.72 (1 H, ddd, $J = 6$ Hz, 8 Hz, 15.5 Hz), 5.65 (1 H, dd, $J = 7$ Hz, 15.5 Hz), 3.74 (1 H, dd, $J = 3.5$ Hz, 6.5 Hz), 3.25 (1 H, ddd, $J = 2.5$ Hz, 3.5 Hz, 10 Hz), 2.36 (1 H, m), 1.99 (1 H, m), 1.70 (1 H, d, OH, $J = 3.5$ Hz), 1.67 (1 H, d, OH, $J = 4$ Hz), 0.92 (9 H, s), 0.91 (9 H, s); ^{13}C NMR (125 MHz, CDCl_3) δ 132.98, 130.84, 80.75, 78.62, 35.02, 34.75, 34.69, 25.76; IR (thin film) 3351, 2955, 2866, 2903, 1476, 1360 cm^{-1} ; HRMS (CI, NH_3) calcd for $\text{C}_{13}\text{H}_{30}\text{NO}$ $[\text{M} + \text{NH}_4]^+$: 232.2277, found 232.2271 m/z .

1b

(1*S*, 5*R*, 3*E*)-1,7-diphenylhept-3-ene-1,5-diol (1b): In a glove box $^d\text{Ipc}_2\text{BH}^7$ (0.287 g, 1 mmol) was weighed into a round bottom flask containing a stir bar (Note: The crystalline borane should be crushed and pulverized with a glass rod prior to use in order to ensure efficient hydroboration). The flask was capped with a rubber septum and removed from the glove box and placed in an ice bath. Ether (3 mL) was added to the flask followed by the allenyl boronic ester **3** (0.123 g, 1 mmol) added neat via a microliter syringe. The reaction was stirred 2 h in an ice bath during which time the solid $^d\text{IpcBH}$ reacted to leave a colorless solution. The ice bath was removed and the reaction cooled to -78°C . Distilled hydrocinnamaldehyde (0.072 g, 0.54 mmol) was added dropwise via a microliter syringe. The flask was stirred at -78° for 2 h and then distilled benzaldehyde (0.106 g, 1 mmol) was added dropwise via microliter syringe and the reaction was stirred an additional 2 h. The flask was removed from the cold bath and allowed to warm to room temperature and stir for 24 h. The reaction was cooled in an ice bath and 1 mL of 3M NaOH solution was added dropwise followed by 0.4 mL of a 50% HOOH solution. The reaction was stirred for 4 h at room temperature at which time it was diluted with 40 mL of CH_2Cl_2 and 20 mL of sat. NaHCO_3 and 5 mL of sat. NaCl solution. The organic layer was separated and the aqueous washed with CH_2Cl_2 (2 x 10 mL). The reaction was dried over Na_2SO_4 and the solvent removed in vacuo. The residual oil was purified by column chromatography (gradient elution 10-45% EtOAc

in hexanes) affording 0.126 g (83%, based on benzaldehyde) of a colorless oil. An analytical sample was prepared by preparative HPLC (60 : 40 : EtOAc : hexanes): $[\alpha]_{\text{D}}^{24} - 28.4^\circ$ (c 1.08, CHCl_3); ee 89%; ^1H NMR (500 MHz, CDCl_3) δ 7.38 – 7.17 (10 H, m), 5.72 – 5.66 (1 H, m), 5.62 (1 H, dd, $J = 6.5$ Hz, 15.5 Hz), 4.76 (1 H, ddd, $J = 3$ Hz, 6.5 Hz, 6.5 Hz), 4.12 (1 H, m), 2.74 – 2.62 (2 H, m), 2.54 – 2.52 (2 H, m), 2.01 (1 H, d, OH, $J = 3.5$ Hz), 1.92 – 1.76 (2 H, m), 1.54 (1 H, d, OH, $J = 4$ Hz), ^{13}C NMR (100 MHz, CDCl_3) δ 144.03, 142.10, 136.60, 128.63, 128.54, 127.76, 127.48, 126.01, 125.97, 73.75, 72.11, 42.05, 38.72, 31.85; IR (thin film) 3360, 3027, 2925, 1949, 1878, 1807, 1669, 1603, 1495, 1454 cm^{-1} ; HRMS (CI, NH_3) calcd for $\text{C}_{19}\text{H}_{26}\text{NO}_2$ $[\text{M} + \text{NH}_4]^+$: 300.1964 found 300.1951 m/z ; Anal. Calcd for $\text{C}_{19}\text{H}_{22}\text{O}_2$: C, 80.82; H, 7.85. Found: C, 80.61; H, 7.98.

1a

(3R, 7R, 5E)-1-phenyl-8-methylnon-5-ene-3,7-diol (1a): $[\alpha]_{\text{D}}^{24} - 8.3^\circ$ (c 1.00, CHCl_3); ee 92%.; ^1H NMR (500 MHz, CDCl_3) δ 7.32 – 7.27 (2 H, m), 7.24 – 7.18 (3 H, m), 5.71 – 5.65 (1 H, m), 5.59 (1 H, dd, $J = 6.5$ Hz, 15 Hz), 3.84 (1 H, m), 3.69 (1 H, m), 2.85 – 2.78 (1 H, m), 2.73 – 2.66 (1 H, m), 2.35 – 2.30 (1 H, m), 2.23 – 2.16 (1 H, m), 1.91 (1 H, d, OH, $J = 4$ Hz), 1.85 (1 H, d, OH, $J = 3.5$ Hz), 1.83 – 1.77 (2 H, m), 1.76 – 1.68 (1 H, m), 0.94 (3 H, d, $J = 6.5$ Hz), 0.90 (3 H, d, $J = 7$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 142.22, 135.18, 128.64, 128.28, 126.07, 78.07, 70.53, 40.70, 38.64, 34.03, 32.26, 18.45, 18.24; IR (thin film) 3367, 2956, 1603, 1495, 1454, 1013 cm^{-1} ; HRMS (CI, NH_3) calcd for $\text{C}_{16}\text{H}_{28}\text{NO}_2$ $[\text{M} + \text{NH}_4]^+$: 266.2120 found 266.2116 m/z .

1c

(1S, 5R, 2E)-1,7-diphenylhept-2-ene-1,5-diol (1c): $[\alpha]_{\text{D}}^{24} + 16.52^\circ$ (c 0.96, CHCl_3); ee 91%.; ^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.10 (10 H, m), 5.78 – 5.68 (2 H, m), 5.12 (1 H, m), 3.68 – 3.58 (1 H, m), 3.2 (1 H, d, $J = 3.2$ Hz); 2.78 – 2.69 (1 H, m), 2.66 – 2.56 (1 H, m), 2.48 (1 H, d, $J = 4.4$ Hz), 2.28 – 2.21 (1 H, m), 2.18 – 2.08 (1 H, m), 1.78 – 1.69 (2 H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 142.98, 141.89, 135.73, 128.42, 128.34, 128.31, 127.52, 127.47, 126.14, 125.74,

74.64, 70.20, 39.94, 38.26, 31.95; IR (thin film) 3351, 3026, 2929, 1493, 1453 cm^{-1} ; HRMS (CI, NH_3) calcd for $\text{C}_{19}\text{H}_{26}\text{NO}_2$ $[\text{M} + \text{NH}_4]^+$: 300.1964 found 300.1974 m/z .

1d

(1S, 5R, 3E)-1-Phenyl-5-cyclohexylpent-3-ene-1,5-diol (1d): $[\alpha]_{\text{D}}^{24} - 36.9^\circ$ (c 1.08, CHCl_3); ee 96%; ^1H NMR (500 MHz, CDCl_3) δ 7.7.4 – 7.24 (5 H, m), 5.65 – 5.54 (2 H, m), 4.75 (1 H, dd (app t), $J = 6.5$ Hz), 3.79 (1 H, dd (app t), $J = 6.5$ Hz), 2.56 – 2.47 (2 H, m), 2.20 (1 H, s, broad OH), 1.85 – 1.56 (6 H, m), 1.38 (1 H, m), 1.28 – 1.10 (3 H, m), 1.98 – 1.88 (2 H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 144.07, 135.68, 128.66, 127.99, 127.79, 126.09, 77.54, 73.83, 43.77, 42.41, 29.00, 28.84, 26.73, 26.34, 26.27; IR (thin film) 3368, 2924, 2851, 1450 cm^{-1} ; HRMS (CI, NH_3) calcd for $\text{C}_{17}\text{H}_{28}\text{NO}_2$ $[\text{M} + \text{NH}_4]^+$: 278.2120, found 278.2107 m/z .

1e

(1S, 5S, 2E)-1-phenyl-6,6-dimethylhept-2-ene-1,5-diol (1e): $[\alpha]_{\text{D}}^{24} - 3.6^\circ$ (c 2.33, CHCl_3); ee 95%; ^1H NMR (500 MHz, CDCl_3) δ 7.36 – 7.30 (4 H, m), 7.28 – 7.22 (1 H, m), 5.89 – 5.78 (2 H, m), 5.21 (1 H, m), 3.27 (1 H, m), 2.38 – 2.34 (2 H, m), 2.04 – 1.98 (1 H, m), 1.69 (1 H, d, OH, $J = 4$ Hz), 0.91 (9 H, s); ^{13}C NMR (125 MHz, CDCl_3) δ 143.34, 135.60, 129.94, 128.77, 127.81, 126.36, 78.86, 75.13, 34.93, 25.92; IR (thin film) 3368, 2956, 2907, 2869, 1453, 1363, 1070, 1007 cm^{-1} ; HRMS (CI, NH_3) calcd for $\text{C}_{15}\text{H}_{24}\text{NO}$ $[\text{M} + \text{NH}_4 - \text{H}_2\text{O}]^+$: 234.1849, found 234.1858 m/z .

2a

(3R, 7R, 4Z)-1,9-Diphenylnon-4-ene-3,7-diol (2a): In a glove box $^d\text{Ipc}_2\text{BH}^7$ (0.287 g, 1 mmol) was weighed into a round bottom flask containing a stir bar and capped with a rubber septum (Note: If the borane is crystalline, then it should be crushed and pulverized with a glass rod prior to use in order to ensure efficient hydroboration). In the glove box allenyl boronate **10** (0.414 g, 1 mmol) was weighed into a round bottom flask containing a stir bar and capped with a septum. The flask containing the borane was placed in an ice bath and CH_2Cl_2 (2 mL) was added to the flask. Dichloromethane (2 mL) was added to the allenylboronate and the mixture was stirred until the boronate had dissolved. The resulting solution was added via canula to the borane and stirred vigorously for 2 h. The borane does not easily go into solution and during the 2 h period CH_2Cl_2 (4-6 mL) was added in order to rinse solid borane from the sides of the flask. If the reaction is not homogeneous after 90 min the reaction can be warmed to room temperature until the reaction is homogeneous and then recooled to 4 °C in an ice bath. The ice bath was removed and the reaction cooled to -78 °C with a dry ice/acetone bath. Distilled hydrocinnamaldehyde (0.110 g, 0.82 mmol) was added dropwise to the reaction mixture via a microliter syringe and the mixture stirred at -78 °C for 2 h. Then distilled hydrocinnamaldehyde (0.228 g, 1.7 mmol) was added dropwise via microliter syringe and the reaction mixture was stirred an additional 2 h. The cold bath was removed and the reaction was allowed to warm to room temperature and stir for an additional 24 h. The reaction was cooled in an ice bath and diluted with CH_2Cl_2 (10 mL) and 3M NaOH solution was added dropwise followed by 0.4 mL of a 50% HOOH solution at which time a white precipitate formed. The mixture was stirred for 3 h at room temperature at which time it was diluted with 50 mL of CH_2Cl_2 and 20 mL of sat. NaHCO_3 and 10 mL of sat. NaCl solution. The biphasic mixture was stirred for 30 min or until the precipitate had dissolved. The organic layer was separated and the aqueous washed 2 x 10 mL of CH_2Cl_2 . The reaction was dried over Na_2SO_4 and the solvent removed in vacuo. The residual oil was purified by column chromatography (gradient elution 10-45% EtOAc in hexanes) affording 0.224 g (72%) of a colorless oil. An analytical sample was prepared by preparative HPLC (60 : 40 : EtOAc : hexanes). $[\alpha]_{\text{D}}^{24} + 38.5^\circ$ (c 1.04, CHCl_3); ee 91%; ^1H NMR (500 MHz, CDCl_3) δ 7.38 – 7.28 (4 H, m), 7.22 – 7.19 (6 H, m), 5.71 – 5.66 (1 H, m), 5.64 – 5.58 (1 H, m), 4.42 (1 H, ddd (app q), J = 7 Hz), 3.77 – 3.71 (1 H, dddd (app quintet), J = 6.5), 2.83 – 2.66 (4 H, m), 2.45 – 2.38 (1 H, dddd, J = 14, 8.5, 4.5, 1), 2.37 (1 H, s, OH broad), 2.28 – 2.21 (1 H, m), 2.06 (1 H, s, OH broad), 1.99 – 1.92 (1 H, dddd, J = 13.5 Hz, 9.5 Hz, 7 Hz, 6.5 Hz), 1.86 – 1.77 (3 H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 142.06, 141.98, 136.08, 128.67, 128.63, 128.61, 128.60, 127.77, 126.14, 126.04, 70.38, 66.77, 38.93, 38.18, 35.13, 32.44, 31.91; IR (thin film) 3351, 3025, 2930, 1602, 1495, 1454, 1030 cm^{-1} ; HRMS (FAB, Na) calcd for $\text{C}_{21}\text{H}_{26}\text{O}_2\text{Na}$ [$\text{M} +$

Na]⁺: 333.1831, found 333.1817 *m/z*; *Anal.* Calcd for C₂₁H₂₆O₂: C, 81.25; H, 8.44. Found: C, 81.30; H, 8.75.

2b

(1*S*, 5*R*, 3*Z*)-1-phenyl-6-methylhept-3-ene-1,5-diol (2b): $[\alpha]_{\text{D}}^{24} + 89.3^\circ$ (*c* 1.27, CHCl₃); ee 92%; ¹H NMR (500 MHz, CDCl₃) δ 7.3 – 7.24 (5 H, m), 5.57 – 5.51 (1 H, m), 5.49 – 5.42 (1 H, m), 4.79 (1 H, dd (app t), *J* = 5.5 Hz), 3.97 (1 H, dd (app t), *J* = 7.5 Hz), 2.72 – 2.65 (1 H, m), 2.55 – 2.48 (2 H, m), 1.79 (1 H, s, broad OH), 1.70 – 1.60 (1 H, m), 0.92 (3 H, d, *J* = 6.5 Hz), 0.82 (3 H, d, *J* = 7 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 143.88, 134.55, 128.57, 127.84, 127.67, 126.09, 73.43, 72.47, 37.25, 33.91, 18.45, 18.33; IR (thin film) 3351, 2958, 1452, 1014 cm⁻¹; HRMS (CI, NH₃) calcd for C₁₄H₂₄NO₂ [M + NH₄]⁺: 238.1807, found 238.1817 *m/z*.

2c

(1*S*, 5*R*, 2*Z*)-1,7-diphenylhept-2-ene-1,5-diol (2c): $[\alpha]_{\text{D}}^{24} + 94.6^\circ$ (*c* 1.20, CHCl₃); ee 95%; ¹H NMR (500 MHz, CDCl₃) δ 7.40 – 7.37 (2 H, m), 7.36 – 7.31 (2 H, m), 7.30 – 7.25 (3 H, m), 7.20 – 7.16 (3 H, m), 5.86 – 5.81 (1 H, m), 5.66 – 5.59 (1 H, m), 5.49 (1 H, d, *J* = 8.5 Hz), 3.75 (1 H, m), 2.59 – 2.48 (2 H, m), 2.40 – 2.34 (1 H, m), 1.93 (1 H, s, broad OH), 1.83 – 1.79 (2 H, m); ¹³C NMR (100 MHz, CDCl₃) δ 143.62, 141.95, 135.76, 128.80, 128.67, 128.62, 127.77, 127.59, 126.19, 126.14, 70.48, 69.70, 38.40, 35.42, 32.39; IR (thin film) 3350, 3026, 2931, 1602, 1494, 1453, 1030 cm⁻¹; HRMS (EI, 70 eV) calcd for C₁₉H₂₁O₂ [M - H]⁺: 281.1542, found 281.1540 *m/z*; *Anal.* Calcd for C₁₉H₂₂O₂: C, 80.82; H, 7.85. Found: C, 80.75; H, 7.96.

2d

(3R, 7R, 4Z)-1-phenyl-8-methylnon-4-ene-3,7-diol (2d): $[\alpha]_{\text{D}}^{24} + 40.7^\circ$ (*c* 0.85, CHCl₃); ee 94%; ¹H NMR (500 MHz, CDCl₃) δ 7.30 – 7.20 (2 H, m), 7.20 – 7.10 (3 H, m), 5.66–5.53 (2 H, m), 4.38 (1 H, ddd (app q), *J* = 4 Hz), 3.40 – 3.32 (1 H, m), 2.76 – 2.60 (2 H, m), 2.34 – 2.26 (1 H, m), 2.24 – 2.12 (2 H, m), 1.96 – 1.84 (1 H, m), 1.82 – 1.70 (2 H, m), 1.60 (1 H, octet, *J* = 8 Hz), 0.90 (3 H, d, *J* = 8 Hz), 0.88 (3 H, d, *J* = 8 Hz), ¹³C NMR (100 MHz, CDCl₃) δ 142.13, 135.77, 128.64, 128.58, 128.41, 126.02, 76.31, 66.95, 38.98, 33.07, 32.33, 31.90, 19.10, 18.21; IR (thin film) 3351, 3026, 2958, 1603, 1496, 1454, 1043, cm⁻¹; HRMS (CI, NH₃) calcd for C₁₆H₂₈NO₂ [M + NH₄]⁺: 266.2120, found 266.2119 *m/z*.

2e

(3S, 7R, 5Z)-1-phenyl-8-methylnon-5-ene-3,7-diol (2e): $[\alpha]_{\text{D}}^{24} + 5.29^\circ$ (*c* 0.68, CHCl₃); ee 95%; ¹H NMR (500 MHz, CDCl₃) δ 7.35 – 7.28 (2 H, m), 7.22 – 7.19 (3 H, m), 5.68 – 5.60 (2 H, m), 4.12 (1 H, dd (app t), *J* = 7.5), 3.76 (1 H, m), 2.84 – 2.78 (1 H, m), 2.72 – 2.66 (1 H, m), 2.49 – 2.44 (1 H, m), 2.32 – 2.60 (1 H, m), 2.05 (2 H, s, broad OH), 1.85 – 1.79 (2 H, m), 1.73 (1 H, octet, *J* = 7 Hz), 0.98 (3 H, d, *J* = 7 Hz), 0.90 (3 H, d, *J* = 7 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 142.03, 134.65, 128.67, 128.63, 128.28, 126.13, 72.49, 70.55, 38.37, 35.45, 34.19, 32.43, 18.43, 18.40; IR (thin film) 3350, 2955, 2926, 1603, 1496, 1454, 1014 cm⁻¹; HRMS (CI, NH₃) calcd for C₁₆H₂₈NO₂ [M + NH₄]⁺: 266.2120, found 266.2119 *m/z*.

2f

(3*R*, 7*R*, 4*Z*)-1-phenyl-7-cyclohexylhept-4-ene-3,7-diol (2f): $[\alpha]_{\text{D}}^{24} + 47.1^\circ$ (*c* 1.01, CHCl₃); ee 94%; ¹H NMR (500 MHz, CDCl₃) δ 7.32 – 7.27 (2 H, m), 7.24 – 7.17 (3 H, m), 5.67 (1 H, dd, *J* = 11 Hz, 7.5 Hz), 5.62 (1 H, ddd, *J* = 11 Hz, 8 Hz, 7.5 Hz), 4.42 (1 H, ddd (app q), *J* = 7.5), 3.41 (1 H, ddd, *J* = 7 Hz, 7 Hz, 4 Hz), 2.72 (3 H, m), 2.37 (1 H, m), 2.26 (1 H, m), 2.13 (1 H, s, OH broad), 1.99 – 1.65 (7 H, m), 1.36 (1 H, m), 1.30 – 1.1 (3 H, m), 1.06 – 0.92 (2 H, m); ¹³C NMR (100 MHz, CDCl₃) δ 141.92, 135.61, 128.40, 128.31, 128.12, 125.74, 75.23, 66.62, 42.49, 38.70, 31.87, 31.67, 29.14, 28.55, 26.36, 26.11, 25.94; IR (thin film) 3343, 2924, 2852, 1496, 1450, 1031 cm⁻¹; HRMS (FAB, Na) calcd for C₁₉H₂₈O₂Na [M + Na]⁺: 311.1987, found 311.1977 *m/z*.

Stereochemical Assignments.

The 1,5-anti stereochemistry of the diols produced in Table 1 was assigned by hydrogenation, which provided the C2 symmetric, optically active diols summarized below.

Evidence that the diols in Tables 2 and 3 have different 1,5-diol stereochemistry was provided by the hydrogenation experiments summarized below. In particular, hydrogenation of **1b** and **2c** gave diastereomeric 1,5-anti and 1,5-syn diols **12** and **13**, respectively. The isolation of the hydrogenolysis product **14** also established that **1b** and **2c** are heterochirally related.

Finally, and most importantly, the absolute stereochemistry of diols **9a**, **9b**, **9c**, **9d**, **9e**, and **9f** (Table 1), **1b**, **1d**, and **1e** (Table 2), and **2a**, **2b**, **2d** and **2f** (Table 3) were assigned by application of the modified Mosher ester method.⁸ Details of the differential shifts of the pairs of diastereomeric MTPA esters are provided in the following structures. Owing the homochirality of the two hydroxyl centers in the anti 1,5-diols, it is predicted that negative $\Delta\delta$ values will be realized for the hydrogen atoms on carbons 2, 3, and 4, where as positive $\Delta\delta$ values should be observed for protons associated with the R^1 and R^2 substituents of the original aldehydes used in the double allylboration reaction. This is exactly what is observed (Table 4)..

In contrast, the heterochiral relationship of the two hydroxyl centers in the 1,5-syn diols of Table 3 indicates that the differential shielding/deshielding promoted by the MTPA esters will be dissonantly paired, such that the differential shielding of C(2) and C(4) in the diastereomeric pairs of MTPA esters should be opposite, as should be the differential shifts of protons in the R^1 and R^2 substituents of the original aldehydes. This is exactly what is observed in the absolute stereochemical assignments of the diastereomeric Mosher ester derivatives prepared from **2b**, **2d** and **2f** (Table 5).

Table 4. Absolute Stereochemical Assignments for 1,5-Anti Diols

Table 5. Absolute Stereochemical Assignments for 1,5-Syn Diols

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