***N*-Propargylcyclohexylamine**: IR (neat) 3360, 2100 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 3.4 (d, J = 3 Hz, 2 H), 2.3 (m, 1 H), 1.95 (t, J = 3 Hz, 1 H), 1.2-1.8 (m, 10 H). Anal. Calcd for $C_9H_{15}N$: C, 78.78; H, 11.02; N, 10.20. Found: C, 78.60; H, 11.01; N, 10.39.

***N*-Cyclohexylbenzamide**: mp 144-145 °C (lit.[18b] mp 147 °C); IR (neat) 3340, 1660 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 7.7 (m, 2 H), 7.25 (m, 3 H); 2.4 (m, 1 H), 1.1-1.8 (m, 10 H). Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.36; N, 6.88. Found: C, 76.4; H, 8.21; N, 6.74.

Acknowledgment. We thank Dr. A. V. Rama Rao for his encouragement and keen interest in this work.

Nonracemic Frontalin via Copper- and Palladium-Based Skeletal Construction and the Asymmetric Dihydroxylation[1]

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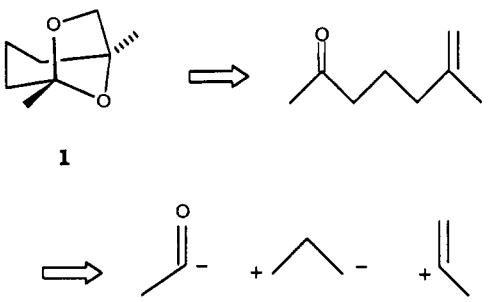
The new higher order organocuprate, $Li_2Cu(CN)(C(OMe):CH_2)_2$, prepared through a Sn → Li → Cu transmetalation sequence, was found to efficiently couple with allyl bromide producing 2-methoxy-1,4-pentadiene (**3**) which is efficiently converted to the ketal **4**. Hydroboration of **4** with 9-BBN-H and the selective oxidation of this adduct with trimethylamine *N*-oxide (TMANO) produces 9-oxa-10-borabicyclo[3.3.2]decane **5**, which undergoes Pd-catalyzed cross coupling with 2-bromopropene producing **6**, thereby accomplishing the construction of the frontalin carbon skeleton in 63% overall yield from allyl bromide. The Os-based dihydroxylation of **6** followed by ketalization either produces the racemic pheromone ((±)-**1**) or, with the Sharpless catalytic asymmetric dihydroxylation (dihydroquinine ligand) procedure, results in the selective formation of the *S* enantiomer in 35% ee. The de determined from the ^{13}C NMR spectra of the diastereomeric Mosher's monoesters (**9**) was found to provide useful corroborative information on the optical purity of the intermediate 1,2-diols **7**.

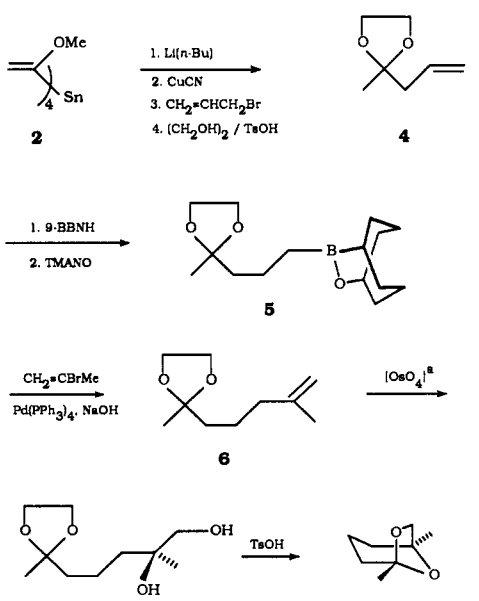
Our recent interest in new applications for the cross coupling of either higher order organocuprates[3] (Lipshutz reagents)[4] or organoboranes[5] (Suzuki coupling)[6] with electrophilic substrates led us to seek a simple synthetic target where the value of these reagents could be efficiently demonstrated. For this purpose, (*S*)-(−)-frontalin (**1**),[7] the aggregation pheromone of the southern pine beetle, *Dendroctonus frontalis*, was selected because both of these organometallic intermediates could be envisioned to play key roles in its novel 2 + 3 + 3 skeletal construction (Scheme I).

Historically, frontalin has been a popular synthetic target, whose asymmetric synthesis has been achieved through a variety of classic methods which employ chiral building blocks, auxiliaries, and reagents.[7] Considerable success with this last approach has been achieved with the Sharpless asymmetric epoxidation from either of two achiral allylic alcohol substrates.[7a] To adapt our synthetic approach to **1** to an asymmetric process would not have been feasible were it not for recent advances in the cata-

Scheme I



Scheme II[a]



[a] (±)-**7**: OsO_4, TMANO·$2H_2O$, *t*-BuOH; (*S*)-**7**: **8**, OsO_4, $K_3Fe(CN)_6$, K_2CO_3, *t*-BuOH.

(1) Dedicated to Professor Herbert C. Brown on the occasion of his 80th birthday in appreciation for his guidance and support over the years.

(2) Graduate student supported by the NIH-MBRS Program (RR08102).

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lytic asymmetric dihydroxylation (AD) of alkenes which contain no proximate directing functionality.[8,9] Vicinal diols can now be obtained in high optical purities from even 2-methyl-1-alkenes. While we felt that the steric similarity of Me vs primary alkyl substitution in **A** or its ketal **6** may present a particularly challenging substrate for the AD process, we were intrigued by both the novel aspects of the skeletal construction and by the possibility that significant asymmetric induction in **1** could be realized with such a simple modification of one step in the reaction sequence.

Results and Discussion

Our new synthesis of **1** in both racemic and nonracemic form is outlined in Scheme II.

The organocuprate reagent, $Li_2Cu(CN)(C(OMe)=CH_2)_2$,[10] was prepared from tetrakis(α-methoxyvinyl)tin (**2**)[11] via a new Sn → Li → Cu transmetalation sequence. The coupling of this Lipshutz reagent with allyl bromide proceeds smoothly to give the very volatile 2-methoxy-1,4-pentadiene (**3**),[12] which was isolated by distillation in 60% yield and efficiently converted to its dioxolane ketal **4** (90%). The **2** → **4** sequence can also be carried out without isolating **3** which gives **4** in 79% overall yield from allyl bromide, a significant improvement over the Al-based route to its dimethoxy ketal analogue.[13]

A few comments regarding the merits of the preparation of $Li_2Cu(CN)(C(OMe)=CH_2)_2$ by the above method are warranted. Employing α-methoxyvinyllithium which is generated from the deprotonation of methyl vinyl ether, α-methoxyvinyl Gilman reagents,[10a,b] while useful, is operationally more difficult to prepare because the deprotonation is neither clean nor stoichiometric.[11a,c] The Sn/Cu exchange route to the related higher order reagent, $Li_2Cu(CN)(Me)[C(OEt)=CH_2]$, in contrast to other vinyl derivatives, exhibits competitive methyl-group transfer.[10c] The present Sn → Li → Cu procedure is particularly simple and efficient because pure α-methoxyvinyllithium,[11] unlike other vinyl-[11b] or α-ethoxyvinyllithium[11e] reagents, quantitatively precipitates from pentane solution for its subsequent smooth conversion to the organocuprate reagent.

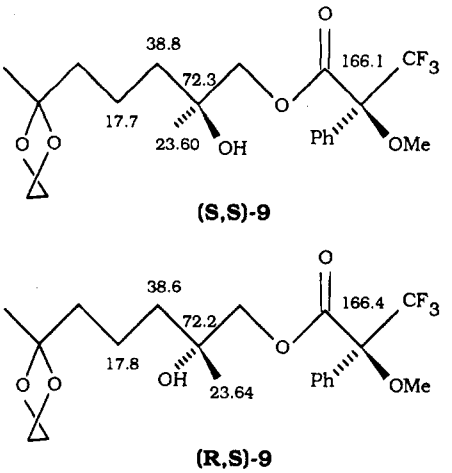
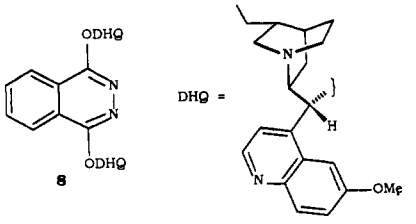


Figure 1.

With **4** in hand, its hydroboration with 9-BBN-H[14] was examined, first in C_6D_6, which by ^{13}C NMR clearly revealed the clean formation of the 1-(9-BBN) adduct **5'** (see Experimental Section). The selective oxidation of this adduct with TMANO[15] cleanly affords the more stable borinate ester intermediate **5** in 95% overall yield from **4**. Requiring no special catalyst,[6c] the Suzuki coupling of the primary alkylborane **5** with 2-bromopropene under basic conditions employing the standard $Pd(PPh_3)_4$ catalyst[5b,6d] cleanly produces **6** (84%) free of isomeric impurities.[16]

Having demonstrated that the carbon skeleton of frontalin could be efficiently (63%) assembled from very simple building blocks via this sequential organometallic approach, we turned our attention to the dihydroxylation of **6**. The desired racemic diol, (±)-**7**, was easily prepared employing Matteson's conditions.[17] To familiarize ourselves with the newest Sharpless dihydroquinine-based AD procedure,[9] we first carried out the process using 1-octene as a substrate which produced the desired (2*S*)-1,2-octanediol in both high yield (86%) and high ee (86%). Applying this approach to **6** gave the expected optically active diol (***S***)-**7** cleanly. To ascertain the ee of this latter product, the selective conversion of both this and (±)-**7** to the corresponding Mosher's monoesters **9**[18] was undertaken. By ^{13}C NMR analysis, several pairs of signals were resolved for each of the diastereomeric monoesters (cf. Figure 1). The signals in each of these pairs were of essentially equal area in the esters derived from the racemic diol, but were uniformly in an ca. 2:1 ratio for **9** derived from the nonracemic diol which allowed us to estimate the enantiomeric excess in (***S***)-**7** to be 30–36%.[18] It must be pointed out that the structures illustrated for **9** represent MMX conformational energy minima,[19] which, unlike the Mosher's esters derived from secondary alcohols, do not lend themselves to a simple relationship for predicting the absolute configuration of the alcohol from the NMR behavior.[20] The five sets of ^{13}C NMR signals which



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are either wholly or partially resolved at 75 MHz for **9** are identified in Figure 1.

After the known acid-catalyzed conversion of **7** to either (±)-**1** or to (−)-**1**, the specific rotation of the latter ($[\alpha]^{25}_D$ −19.0° (*c* 0.54, ether) corresponds to 35% ee,[7a] which is in complete accord with the diastereomeric excess determined for **9** by the ^{13}C NMR technique. The lower product ee for (*S*)-**7** compared to (2*S*)-1,2-octanediol is consistent with the fact that the chiral catalyst is forced to differentiate between two more similar reacting faces in **6** (i.e., primary alkyl, Me) when compared to those in 1-octene (i.e., primary alkyl, H). However, we can not rule out the possibility that the ketal functionality in **6** may play a deleterious role in the process since Sharpless observed higher asymmetric induction in related systems which lacked this functionality.[9,21]

In this work, the simple construction of the frontalin carbon framework with commercially available reagents was accomplished in 63% overall yield from allyl bromide via sequential cross-coupling reactions. Despite its being a "worst case scenario", having neither directing functionality nor sterically dissimilar 1,1-disubstitution, the AD of **6** produces (*S*)-**7** in 35% ee, a significant achievement when one considers the nature of the substrate.[22] While our approach to (−)-**1** will require further developments in the AD to improve the product's optical purity, in its present state, the method's value for the synthesis of this pheromone is less limited since its antipode, (+)-**1**, is biologically inactive.[7a]

Experimental Section

General Methods. All experiments were carried out in predried glassware (1 h, 150 °C) under a nitrogen atmosphere. Standard handling techniques for air-sensitive compounds were employed throughout this study.[11] ^1H and ^{13}C NMR data were recorded at 300 and 75 MHz, respectively. Standard COSY, HETCOR, APT, and/or DEPT experiments were carried out for the NMR assignments given in the procedures and elsewhere. The notation C-*n* is consistently used for the acyclic carbon chain based on the numbering system for **3** with a C-*n'* notation in **5**, **5'**, and **9** referring to the bicyclo or Mosher ester portion of the molecules, respectively. GC analyses were performed using 6-ft × $^1/_8$-in. 20% SE-30 on DCDMS-treated Chrom W packed columns and 30-m × 0.23-mm i.d. 20% SE-30 vitreous silica open tubular columns. Columns were silylated (MSTFA, Aldrich) prior to analytical runs. $CDCl_3$ was filtered through Al_2O_3 and stored in a sealed amber bottle. C_5H_5N, allyl bromide, 2-bromopropene, and CH_2Cl_2 were distilled from CaH_2 and stored in an ampule bottle under nitrogen. Hexanes and pentane were purified over concentrated sulfuric acid, decanted, extracted with a solution of 5% $NaHCO_3$, dried, and distilled from $LiAlH_4$. THF and ether were distilled from sodium/benzophenone prior to use. Other reagents were obtained from commercial sources or prepared as reported.

2-Methoxy-1,4-pentadiene (3). To a solution of **2** (4.33 g; 12.5 mmol) in pentane (40 mL) at 0 °C was added Li(*n*-Bu) (17 mL of 2.55 M; 43 mmol) dropwise. After 15 min, the mixture was allowed to warm to rt and was stirred an additional 45 min. Centrifugation followed by decantation of the supernatant gave the solid reagent, α-methoxyvinyllithium (*Caution! Highly pyrophoric! Reacts explosively with atmospheric oxygen!*)[11] which was washed, as above, with pentane (3 × 20 mL). After being dried with a stream of N_2, the stirring solid was cooled to −78 °C and dry THF (20 mL) was added slowly via syringe. After dissolution, the solution was added to a stirring slurry of CuCN (1.8 g, 20 mmol) and dry THF (20 mL) at −78 °C. The combined mixture was allowed to warm to −45 °C for 1 h, and the resulting solution was recooled to −78 °C. Allyl bromide (2.4 g; 20 mmol) was added dropwise and this mixture was stirred for 2 h and subsequently allowed to warm to rt. A saturated solution of NH_4Cl in aqueous NH_4OH (10%) (20 mL) was added, the phases were separated, and the organic layer was repeatedly washed with the NH_4Cl mixture (4 × 10 mL) and water (20 × 20 mL) and distilled to give 1.8 g (60%) of **3** (bp 95 °C (760 Torr) (lit.[12] bp 32–33 °C (75 Torr): ^1H NMR ($CDCl_3$) δ 5.93 (m, 1 H), 5.17 (m, 2 H), 3.96 (s, 2 H), 3.63 (s, 3 H), 2.91 (d, *J* = 6.7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 162.5 (C-2), 134.7 (C-4), 116.4 (C-5), 81.0 (C-1), 54.7 (OMe), 39.3 (C-3); IR (TF) 3090, 3010, 2950, 1650, 1600 cm^{-1}; MS (70 eV) *m/e* (rel intensity) 98 (7, M^+), 83 (100).

2-Methyl-2-(2-propenyl)-1,3-dioxolane (4). To ethylene glycol (0.73 g, 4.0 mmol) and TsOH (ca. 0.1 g) was added **3** (0.29 g, 3.0 mmol), and after 4 h, $NaHCO_3$(sat.) solution (5 mL) and pentane (10 mL) were added. After separation, the organic layer was washed with water (3 × 10 mL), dried (K_2CO_3), and concentrated to give 0.35 g (90%) of **4**: ^1H NMR ($CDCl_3$) δ 5.85 (m, 1 H), 5.13 (m, 2 H), 3.97 (s, 4 H), 2.42 (d, *J* = 7.2 Hz, 2 H), 1.34 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 133.3 (C-4), 118.0 (C-5), 109.3 (C-2), 64.6 (OCH_2CH_2O), 23.7 (C-1); IR (TF) 3090, 2960, 1640, 1120 cm^{-1}; MS (70 eV) *m/e* (rel intensity) 113 (5, M − Me^+), 87 (100). Anal. Calcd for $C_7H_{12}O_2$: C, 61.27; H, 9.09. Found: C, 61.26; H, 9.08.

One-Pot Preparation of 4. As for **3** above, from **2** (2.51 g; 7.24 mmol) in pentane (10 mL), Li(*n*-Bu) 12.5 mL of 2.35 M; 29 mmol), CuCN (1.31 g, 14.6 mmol), and allyl bromide (1.85 g; 14.6 mmol) was obtained a dry solution of **3** in pentane which was added to ethylene glycol (1.86 g, 30 mmol), THF (10 mL), and TsOH (0.19 g, 1.0 mmol). After 4 h, $NaHCO_3$(sat.) solution (5 mL) and pentane (25 mL) were added. Workup as above gave 1.48 g (79%) of **4** (bp 139–140 °C (760 Torr), >99% GC purity). The spectroscopic data were identical to those of the above product.

10-(4-(2-Methyl-1,3-dioxolan-2-yl)propyl)-9-oxa-10-borabicyclo[3.3.2]decane (5). To a mixture of 9-BBN-H (2.7 g, 22 mmol)[14] in pentane (10 mL) was added a solution of **4** (2.56 g, 20 mmol) in pentane (10 mL). After 4 h, the solution was cooled to 0 °C and a solution of TMANO (1.5 g, 20 mmol)[15] in CH_2Cl_2 (10 mL) was added dropwise. After 1.5 h, the mixture was concentrated in vacuo to afford **5** (95%, ca. 90% chemical purity by GC and NMR (see supplementary material)). The attempted further purification of this material by distillation (bp 145 °C (0.3 Torr)) gave 4.9 g (91%) of **5** which contained variable amounts of decomposition products: ^1H NMR ($CDCl_3$) δ 4.63 (bs, 1 H), 4.00 (bs, 4 H), 1.9–1.8 (m, 4 H), 1.8–1.4 (m, 13 H), 1.36 (s, 3 H), 0.89 (t, *J* = 7.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 110.3 (C-2), 73.2 (C-1'), 64.4 (OCH_2CH_2O), 42.1 (C-3), 31.7 (C-2',C-8'), 25.9 (C-4', C-6'), 25.0 (C-5'), 23.6 (C-1), 23.0 (C-5), 22.3 (C-3',C-7'), 18.7 (C-4); ^{11}B NMR (C_6D_6) 53.9; IR (TF 2950, 1140, 936 cm^{-1}; MS (70 eV) *m/e* (rel intensity) 251 (2, M − Me^+), 140 (6), 87 (100). To characterize the hydroboration product, an equimolar mixture of **4** and 9-BBN-H in C_6D_6 was allowed to stir for 2 h at 25 °C resulting, by NMR analysis, in the formation of the single adduct.

9-(4-(2-Methyl-1,3-dioxolan-2-yl)propyl)-9-borabicyclo-[3.3.1]nonane (5'): ^{13}C NMR (C_6D_6) δ 110.9 (C-2), 64.4 (OCH_2CH_2O), 41.9 (C-3), 33.4 (C-2',4',6',8'), 30.7 (C-1',5'), 27.2 (C-5), 23.9 (C-1), 23.7 (C-3',7'), 19.6 (C-4); ^{11}B NMR (C_6D_6) δ 83.

2-Methyl-2-(4-methyl-4-pentenyl)-1,3-dioxolane (6). A mixture of **5** (2.44 g, 9.1 mmol), NaOH (1.27 g, 31.7 mmol), THF (20 mL), and water (20 mL) was added to $Pd(PPh_3)_4$ (0.33 g, 0.29 mmol) and 2-bromopropene (1.16 g, 9.6 mmol) in THF (20 mL). After the stirred mixture was heated for 2 h at 55–60 °C, pentane (50 mL) was added to the cooled mixture. The organic layer was washed with water (5 × 20 mL), filtered through neutral alumina (25 g) with pentane (100 mL), concentrated, and distilled to give 1.3 g (84%) of **6**[16] (bp 49 °C (0.4 Torr), >99% GC purity): ^1H NMR ($CDCl_3$) δ 4.66 (bs, 1 H), 1.63 (bs, 1 H), 3.89 (s, 4 H), 1.97 (t, *J* = 6.7 Hz, 2 H), 1.67 (s, 3 H), 1.7–1.4 (m, 4 H), 1.27 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 145.5 (C-6), 110.0 (C-2), 109.9 (C-7), 64.5

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(22) Compare, for example: (a) Zhang, W.; Loebach, G. L.; Wilson, S. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1990**, *112*, 2801 and references cited therein. (b) Burgess, K.; Ohlmeyer, M. J. *J. Org. Chem.* **1988**, *53*, 5178. (c) Masamune, S.; Kim, B. M.; Petersen, J. S.; Sato, T.; Veenstra, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 4549. (d) Srebnik, M.; Ramachandran; P. V. *Aldrichimica Acta* **1987**, *20*, 9.

(OCH_2CH_2O), 38.6 (C-3), 37.7 (C-5), 23.7 (C-1), 22.2 (Me), 21.9 (C-4); IR (TF) 3079, 2970, 1650, 1268, 840 cm^{-1}; MS (70 eV) *m/e* (rel intensity) 170 (0.1, M^+), 155 (13), 115 (5), 111 (3), 99 (97), 87 (100), 59 (72), 55 (72).

(±)-2-(4,5-Dihydroxy-4-methylpentyl)-2-methyl-1,3-dioxolane (7). To **6** (1.7 g, 10 mmol), $TMANO{\cdot}2H_2O$ (2.22 g, 20 mmol), water (8 mL), and *t*-BuOH (20 mL) was added OsO_4 in PhMe (0.75 mL of 0.40 M, 0.33 mmol), and after 7 h at rt, 20% aqueous $NaHSO_3$ (50 mL) was added and the mixture was stirred for 1 h. Concentration to remove the *t*-BuOH, followed by saturation of the aqueous residue with NaCl and extraction with ether (5 × 10 mL), concentration, and distillation, gave 1.43 g (70%) of (±)-**7** (bp 80 °C, (0.2 Torr), 99% GC purity):[7e] ^1H NMR ($CDCl_3$) δ 4.00 (s, 4 H), 3.42 (d, *J* = 10.7 Hz, 1 H), 3.39 (d, *J* = 10.7 Hz, 1 H), 2.99 (bs, 1 H), 2.96 (bs, 1 H), 1.64 (m, 2 H), 1.43 (m, 4 H), 1.32 (s, 3 H), 1.15 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 109.9 (C-2), 69.4 (C-7), 64.4 (OCH_2CH_2O), 39.4 (C-3), 38.4 (C-5), 23.6 (Me), 22.9 (C-1), 18.1 (C-4), IR (TF) 3410, 2950, 1100 cm^{-1}; MS (70 eV) *m/e* (rel intensity) 189 (1, M − Me^+), 87 (100), 71 (30), 59 (16).

(*4S*)-(4,5-Dihydroxy-4-methylpentyl)-2-methyl-1,3-dioxolane ((*S*)-7). To a well-stirred solution of **8** (0.078 g, 0.1 mmol), $K_3Fe(CN)_6$ (9.9 g, 30 mmol), K_2CO_3 (4.2 g, 30 mmol), and OsO_4 in PhMe (0.05 mL of 0.40 M, 0.02 mmol) in water/*t*-BuOH (100 mL 1:1) at 0 °C was added **6** (1.5 g, 8.8 mmol) all at once. After 19 h, $Na_2S_2O_5$ (15 g) was slowly added and the mixture was stirred for 1 h. After rt was reached, EtOAc (100 mL) was added, the separated aqueous layer was extracted with EtOAc (3 × 50 mL), and the combined organic material was dried (Na_2SO_4), concentrated, and distilled to afford 1.3 g (72%) of (*S*)-**7**. The bp and spectroscopic data were identical to those of the above racemic material.

2-(4-Hydroxy-4-methyl-5-((2*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyloxy)pentyl)-2-methyl-1,3-dioxolane (9). To a mixture of either (±)-**7** or (*S*)-**7** (0.1 g, 0.5 mmol) in CH_2Cl_2 (5 mL) and pyridine (0.5 mL) at 0 °C was added (2*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyl chloride (0.14 g, 0.54 mmol). The stirred mixture was allowed to reach rt and, after 1 h, was quenched with saturated K_2CO_3 solution (10 mL) and ether (15 mL) was added. The organic layer was washed with saturated NH_4Cl solution (3 × 10 mL), dried (Na_2SO_4), and concentrated to provide essentially pure **9** for spectroscopic analysis. (*S,S*)-**9**: ^{13}C NMR ($CDCl_3$) δ 166.1 (C=O), 131.9, 129.4, 128.4, 127.1 (Ph), 123.1 (q, J_{CF} = 288.3 Hz, CF_3), 109.6 (C-2), 84.5 (q, J_{CF} = 27.7 Hz, C-2′), 72.3 (C-6), 70.6 (C-7), 64.3 (OCH_2CH_2O), 55.2 (OMe), 39.2 (C-3), 38.8 (C-5), 23.60 (Me(C-6), 23.5 (C-1), 17.7 (C-4). (*R,S*)-**9**: ^{13}C NMR ($CDCl_3$) δ 166.4 (C=O), 131.9, 129.4, 128.4, 127.1 (Ph), 123.1 (q, J_{CF} = 288.3 Hz, CF_3), 109.6 (C-2), 84.5 (q, J_{CF} = 27.7 Hz, C-2′), 72.2 (C-6), 70.6 (C-7), 64.3 (OCH_2CH_2O), 55.2 (OMe), 39.2 (C-3), 38.6 (C-5), 23.64 (Me(C-6), 23.5 (C-1), 17.8 (C-4); IR (TF) 3440, 2910, 1710, 1050 cm^{-1}; MS (70 eV) *m/e* (rel intensity) 405 (1, M − Me^+), 259 (3), 189 (37), 105 (17), 87 (100). Employing a standard pulse sequence, the integration of the five sets of ^{13}C NMR signals noted in Figure 1 revealed that these peaks were in a 1:1 ratio for **9** derived from (±)-**7**. However, from (*S*)-**7**, these peaks from (*S,S*)-**9** were consistently in an ca. 2:1 area ratio (65–68:35–32) compared to those from (*R,S*)-**9** which corresponds to 30–36% ee, in good agreement with the 35% ee determined from the specific rotation measured for (−)-**1** (vide infra).

(±)- and (−)-Frontalin (1). To a solution of TsOH (0.95 g, 5.0 mmol) in CH_2Cl_2 (25 mL) was added **7** (0.86 g, 4.2 mmol) dropwise. After 2 h, saturated $NaHCO_3$ solution (20 mL) was added, and the organic phase was washed with water (3 × 10 mL) and brine (2 × 10 mL), dried (Na_2SO_4), concentrated, and distilled to give 0.57 g (95%) of (±)-**1** (bp 85 °C (35 Torr) (lit.[7a] bp 92 °C (110 Torr))). On a 3.38-mmol scale, (*S*)-**7** gave 0.38 g (80%) of (−)-**1** in 35% ee ($[\alpha]^{25}_D$ −19.0° (*c* 0.54, ether (lit.[7h] $[\alpha]^{23}_D$ −54.4° (*c* 1.33, ether)): ^1H NMR ($CDCl_3$) δ 3.92 (d, *J* = 6.7 Hz, 1 H), 3.48 (d, *J* = 6.7 Hz, 1 H), 1.93 (m, 1 H), 1.72 (m, 2 H), 1.64 (m, 3 H), 1.47 (s, 3 H), 1.33 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 108.0 (C-5), 79.9 (C-1), 74.1 (C-7), 34.5 (C-4), 33.9 (C-2), 24.6 (Me(C-5)), 23.0 (Me(C-1)), 18.0 (C-3); IR (TF) 2942, 2885, 1119, 1097 cm^{-1}; MS (70 eV) *m/e* (rel intensity) 142 (17, M^+), 112 (29), 100 (92), 72 (100), 58 (23).

(2*S*)-(+)-1,2-Octanediol. To a well-stirred solution of **8** (0.039 g, 0.05 mmol), $K_3Fe(CN)_6$ (4.95 g, 15 mmol), K_2CO_3 (2.1 g, 15 mmol), and OsO_4 in PhMe (0.025 mL of 0.40 M, 0.01 mmol) in water/*t*-BuOH (50 mL 1:1) at 0 °C was added 1-octene (0.56 g, 5.0 mmol) all at once. After 19 h, $Na_2S_2O_5$ (7.5 g) was slowly added, and the mixture was stirred for 1 h. After rt was reached, EtOAc (50 mL) was added, the separated aqueous layer was extracted with EtOAc (3 × 25 mL), and the combined organic material was dried (Na_2SO_4), concentrated, and distilled to afford 0.61 g (86%) of the diol (bp 120 °C (0.5 Torr), >99% chemical purity, 86% ee): ^1H NMR δ 0.99 (t, *J* = 5.5 Hz, 3 H), 1.1-1.3 (m, 10 H), 3.01 (m, 1 H), 3.50 (t, *J* = 7.8 Hz, 2 H), 5.11 (bs, 1 H), 5.50 (bs, 1 H); ^{13}C NMR 14.0, 22.7, 25.8, 29.6, 32.0, 32.3, 66.9, 72.4 ppm;[23a] $[\alpha]^{25}_D$ + 9.1° (*c* 0.60, ether (lit.[23b] $[\alpha]^{25}_D$ +11.1° (EtOH))).

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Supplementary Material Available: An expanded view of representative resolved ^{13}C NMR signals which were used to determine the de for **9** as well as the ^{13}C NMR spectrum of **5** (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from ACS; see any current masthead page for ordering information.

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