Diastereoselective Chloroallylboration of α-Chiral Aldehydes

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Double asymmetric reaction of chiral (*Z*)-(γ-chloroallyl)borane, **2**, with α-chiral aldehydes (**3**−**7**) provide a new practical method for the generation of 2,3-syn-3,4-anti and 2,3-syn-3,4-syn chiral vinylchlorohydrins (**8**−**17**) and vinyl epoxides (**18**−**27**). Both enantiomers of **2** exhibited excellent diatereoselectivity (≥90 de) for matched cases. The mismatched cases yielded moderate to good diastereoselectivity.

Introduction

Among stereoselective carbon−carbon bond-forming reactions, the coupling of allylic organometallic compounds with aldehydes is of considerable utility. This methodology provides an efficient strategy for simultaneous generation of two stereocenters (Scheme 1).[1]

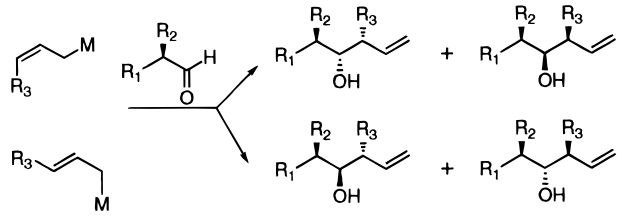
Whereas use of chiral aldehydes usually leads to low chiral induction at the new stereocenters, employment of chiral allylic reagents (Scheme 2) frequently leads to high chiral induction. The ease with which chiral ligands can be attached to boron makes allyl boron reagents particularly well suited for couplings in which chiral induction is desired and diastereoselectivity is desired between the new stereocenters and an α-chiral center in the aldehyde (Scheme 2).[1b,c,2]

The utility of the reactions of chiral allyl boron reagents with chiral aldehydes in the synthesis of natural products is well documented.[3] Recent examples include synthesis of D-1,6-diepicastanospermine by Burgess *et al.*[3d,3e] (Scheme 2, eq 1) and synthesis of the C(1)−C(15) segment of streptovaricin D by Roush *et al.*[3b,c] (Scheme 2, eq 2).

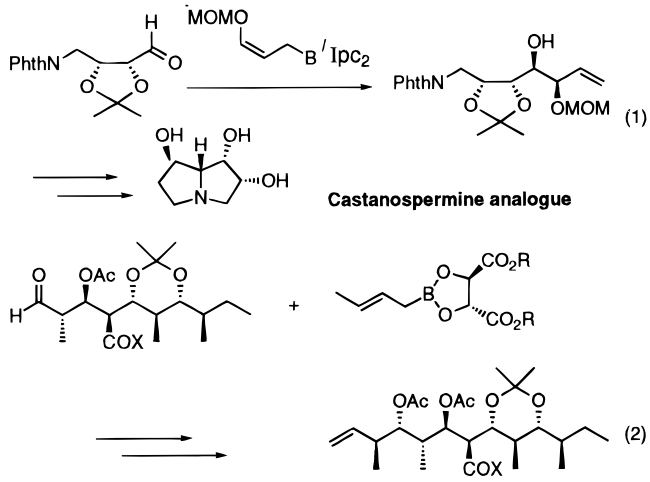
We have recently shown that (*Z*)-(γ-chloroallyl)diisopinocamphenylboranes **2a**,**b** (Scheme 3) are readily accessible.[4] The α-chloroallylboration of **2a** or **2b** with achiral aldehydes provides an excellent synthesis of chiral *syn*-vinylchlorohydrins and *cis*-vinyloxiranes arising from excellent diastereo- and enantioselectivities (≥90% de, 90−99% ee).[4] The methodology has been used in the synthesis of (±)-lamoxirene, the gamete-releasing and gamete-attracting pheromone of laminariales.[5]

We now report reactions of **2a**,**b** with α-chiral aldehydes. Our goal was to develop an efficient route to chiral *cis*-epoxides with an adjacent stereocenter (Scheme 4a).[6] Such epoxides are difficult to prepare by asymmetric epoxidation because an α-chiral center in the requisite starting (*Z*)-allylic alcohol slows the epoxidation and leads to low enantioselectivity[7] (Scheme 4b). We

Scheme 1



Scheme 2



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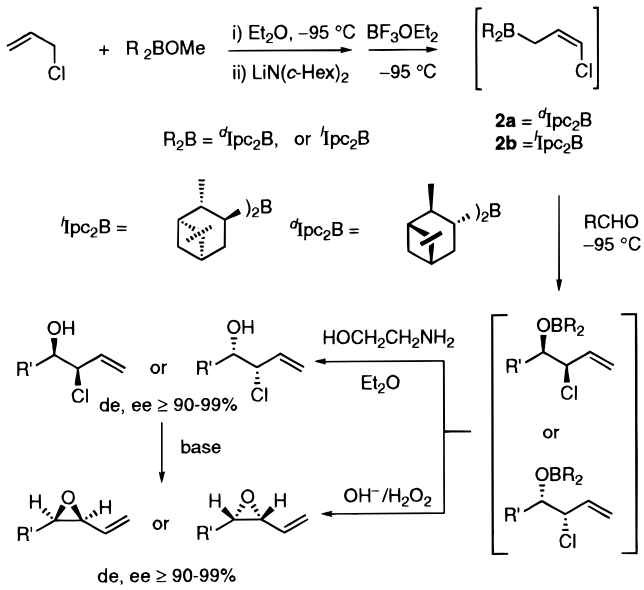
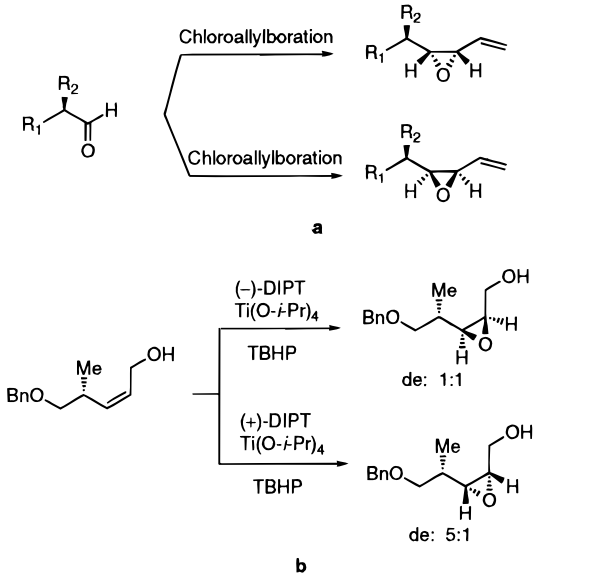
Scheme 3



Scheme 4



were pleased that in the reaction of **2a**,**b** with chiral aldehydes, both isomers of **2** exhibited excellent diastereoselectivities in matched cases.

Results and Discussion

(*Z*)-(γ-Chloroallyl)boranes **2a**,**b** are readily generated at −95 °C by BF_3·OEt_2-promoted decomposition of the ate complex obtained from the reaction of *B*-methoxydiisopinocamphenylborane (Ipc_2BOMe) and (α-chloroallyl)-lithium. The latter is prepared by metalation of allyl chloride with LiDCHA (lithium dicyclohexylamide) and used directly (Scheme 3).[4]

Preparation of Chiral Aldehydes. (*S*)-(+)-2-Methylbutanal, **3** (Chart 1), was prepared from commercially available (*S*)-(−)-2-methylbutanol in 80% yield and 94−97% ee by PCC oxidation.[8] Synthesis of *N*-Boc-L-valinal, **4**, proceeded from *N*-Boc-L-valine methyl ester in >97% ee by reduction to the α-amino alcohol with $LiAlH_4$ and oxidation with PCC.[9] (*R*)-2,3-O-Isopropylidene-D-glyceraldehyde, **5**, was synthesized from D-mannitol in two steps.[10] Aldehydes **6** and **7** (>98% ee) were prepared by PCC oxidation of silyl ether protected *β*-hydroxy-α-methylpropanols, which were obtained by reduction of (*R*)- and (*S*)-methyl-3-hydroxy-2-methylpropionates.[11] Protection with *tert*-butyldimethylsilyl or *tert*-butyldiphenylsilyl was necessary since the excess of BF_3·OEt_2 in chloroallylboration reaction mixtures removed *o*- or *p*-nitrobenzyl groups of these *β*-hydroxy-α-methyl aldehydes. All chiral aldehydes used in this study were used directly without purification since distillation or column chromatography have been reported to cause considerable racemization.[8a] The optical purity of each aldehyde was established by reduction to the alcohol with BMS and analysis of the latter by gas chromatography on a cyclodex-B column.

Reaction of (*Z*)-(γ-chloroallyl)diisopinocamphenylboranes, **2**, with chiral aldehydes gave the highest chiral induction when etheral solutions of aldehydes were added to (*Z*)-(γ-chloroallyl)diisopinocamphenylboranes **2** at −95 °C (Table 1). Reactions were completed in 3−5 h. Workup to generate α-chlorohydrins involved addition of ethanolamine to remove the boron auxiliary and is useful for **3**−**5**.[12] For aldehydes **6** and **7** direct oxidative workup by addition of aqueous NaOAc and H_2O_2 was used. The latter process destroys excess BF_3·OEt_2 resulting in a higher yield of products possessing silyl-protected alcohols. Diastereoselectivities were determined by gas chromatography.

Table 1. Double Asymmetric α-Chloroallylboration of α-Chiral Aldehydes

			α-chloroallylboration[a]				
entry	aldehyde	reagent	products	ratio[b]	yield[c]	epoxide[d]	yield[e]
1	**3**	**2b**	**8:9**	95:5	57	**18**	98
2	**3**	**2a**	**8:9**	15:85	59	**19**	98
3	**4**	**2b**	**10:11**	99:1	60	**20**	98
4	**4**	**2a**	**10:11**	15:85	61	**21**	98
5	**5**	**2a**	**12:13**	99.5:0.5	65	**22**	98
6	**5**	**2b**	**12:13**	39:61	65	**23**	98
7	**6**	**2a**	**14:15**	95:5	55	**24**	98
8	**6**	**2b**	**14:15**	14:86	58	**25**	99
9	**7**	**2b**	**16:17**	95:5	56	**26**	98
10	**7**	**2a**	**16:17**	15:85	55	**27**	98

[a] α-Chloroallylboration at −95 °C in Et_2O. Ethanolamine workup procedure was used for aldehydes **3**−**5** to yield chlorohydrins. Direct oxidation workup procedure was employed for aldehydes **6** and **7** to yield chlorohydrins. [b] Products ratio was determined by GC analysis of the crude chloroallylboration reaction mixture after filtration through a short silica gel plug. [c] Yields (%) of products isolated chromatographically. [d] Epoxides were prepared from the cyclization of corresponding chlorohydrins in MeOH/K_2CO_3. Alternatively, epoxides **18**−**23** can be prepared by oxidation workup in strong base medium. [e] Isolated yields (%) of cyclization of chlorohydrins.

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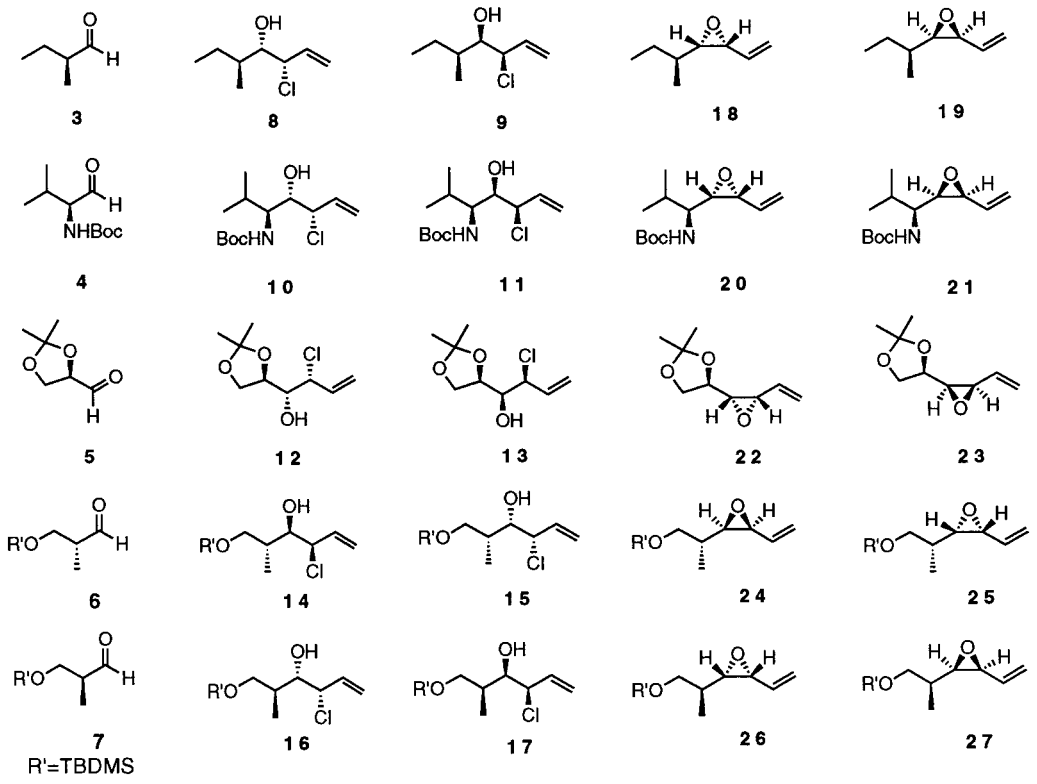
Chart 1



Reaction of (*S*)-2-methylbutanal, **3**, with **2a**,**b** proceeded with excellent diastereoselectivity (>95:5) to produce **8** in the matched case (**2b**). The mismatched case with **2a** provides 85:15 selectivity favoring **9** (Table 1, entries 1 and 2).

Reaction of **2b** with amino aldehyde **4** displays outstanding stereoselectivity, providing diastereoisomer **10** with ≥99:1 diastereoselectivity. The mismatched combination of **2a** and **4** leads to a 15:85 mixture of **10:11** (Table 1, entries 3 and 4).

The highest selectivity was found in the reaction of **2a** and **5** which gave **12:13** in a ratio of 99.5:0.5. The mismatched pair of reactants **2b** and **5** gave a 39:61 mixture of diastereoisomers (Table 1, entries 5 and 6).

Reaction of β-silyloxy-α-methyl aldehydes **6** and **7** gave excellent stereoselection (95:5) favoring **14** and **16**, respectively in matched cases (**6** with **2a** and **7** with **2b**; Table 1, entries 7 and 9). Reaction of mismatched **6** with **2b** and **7** with **2a** gave diastereoselectivities near 15:85 favoring **15** and **17**, respectively.

Vinyl epoxides **18**−**27** were easily obained by cyclization of the corresponding chlorohydrins **8**−**17** in methanolic K_2CO_3[4] or by oxidative workup of the allylboration product using strong base.[4]

Reactions of chiral γ-monosubstituted allylboranes with α-chiral aldehydes yield high diastereo- and enantioselectivities when Brown's chiral auxiliaries, ^{d}Ipc and ^{l}Ipc, are appended to boron.[13] Mechanism of double asymmetric induction in the reaction of chiral allyl boronates with α-chiral aldehydes is described elsewhere.[14] Diasteroselection in these reactions is attributed to the interaction of the γ-boron substituent with the more bulky alkyl aldehyde substituent. In the present cases one would expect preference for transition state A (Scheme 5) due to nonbonding interactions between the γ-Cl, boron and α-R aldehyde substituents that disfavors transition states B and C. In reactions of **2b** with **3** and **7** or **2a** with **6**, the combination of diastero- and enantioselectivities of Brown's chiral auxiliaries in **2a**,**b** with the intrinsic diastereofacial preference of the substrate leads to a high preference for diastereoisomers **8** (3,4-syn-4,5-anti), **16**, and **14** (2,3-anti-3,4-syn) (Table 1). The expected differences of these interactions among states A, B, and C in the mismatched pairs **2a** with **3** and **7** or **2b** with **6** yields lower diastereoselectivity for diastereoisomers **9** (3,4-*syn*-4,5-syn), **17**, and **15** (2,3-syn-3,4-syn). In these reactions the diastereo- and enantioselectivity of the boron auxiliaries compete with the diastereofacial preference of the chiral aldehydes.

Reactions of **2a**,**b** with **4** and **5** involve additional dipolar interactions. Examination of molecular models of expected transition states D and E suggests that there are orientations of the C−Cl dipole and the lone pair on nitrogen of **4** that would lead to a favorable dipolar interactions stabilizing transition state D. In the matched case of **2b** and **4** a 99:1 preference for the diastereoisomer (**10**) derived from D is obtained. A similar situation can be envisioned for the reaction of **2a** and **5** in which an acetonide oxygen may stabilize transition state F with respect to G. This reaction leads to the highest diastereoselectivity observed (99.5:0.5) in favor of the diaste-

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Scheme 5. Transition State for Chloroallylboration of α-Chiral Aldehydes

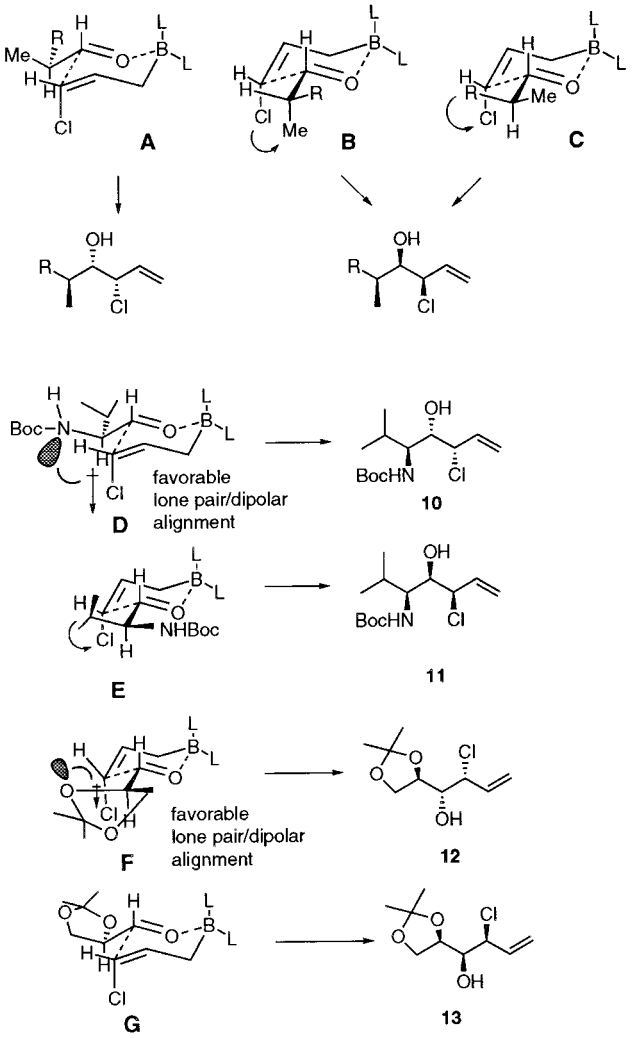
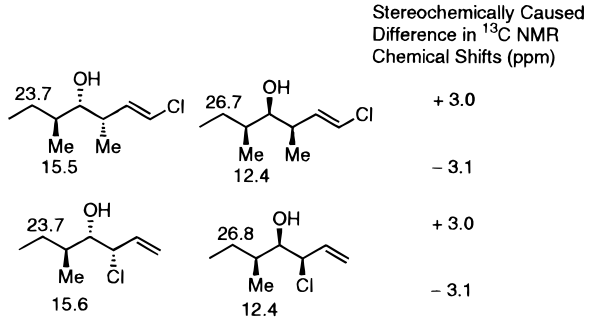


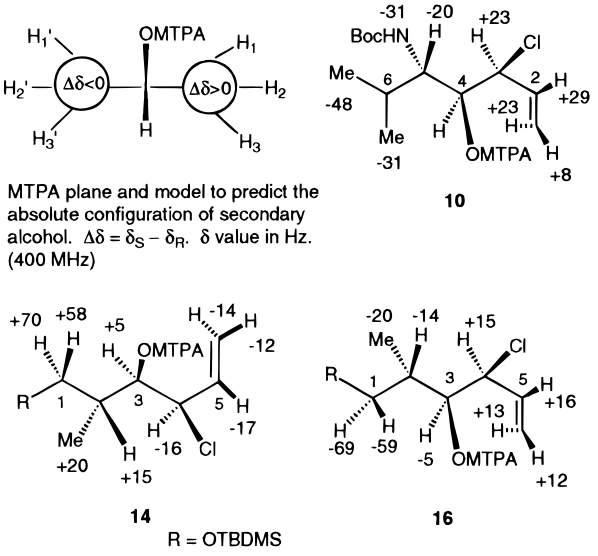
Chart 2



reoisomer (**12**) derived from F (Scheme 6). In the mismatched cases these additional interactions lead to lower selectivity than reactions in which they are absent.

Assignments of stereochemistry based on ^{1}H couplings[15] were possible for **16** and **17**. The [^3J(syn), ^3J(anti)] of these diastereoisomers fall within expected ranges for 2,3-anti, 3,4-syn stereochemistry in **16** and 2,3-syn, 3,4-syn stereochemistry in **17** (Chart 2). According to the method of Hoffmann, differences of ^{13}C chemical shifts between **12** and **13** unambiguously allowed assignment of relative stereochemistry in these diastereoisomers.[16] In the remaining sets of diastereoisomers it was not possible to make reliable stereochemical assignment using ^{1}H or ^{13}C NMR spectra.

Chart 3



Assignment of stereochemistry to the remaining sets of diastereoisomers was accomplished using the Mosher ester method for the determination of absolute configuration.[17] This method is based on diamagnetic shifts in the substrate caused by the aromatic substituent of the MTPA moiety [α-methoxy-α-(trifluoromethyl)phenylacetic acid]. In the ^{1}H NMR spectra of (*R*)-MTPA ester of alcohol the signals due to H_1, H_2, and H_3 are upfield compared with those of an (*S*)-MTPA ester (Chart 3). Similarly, signals due to $H_{1'}$, $H_{2'}$, and $H_{3'}$ of an (*R*)-MTPA ester occur downfield relative to those of the (*S*)-MTPA ester. The chemical shifts obtained in the ^{1}H NMR spectra of the MTPA esters of **8** and **10** suggest these diastereoisomers have a 4*S* configuration. On the basis of the chirality of the starting aldehyde, the configuration of **8** at C-5 is *S*. This allows assignment of a 4,5-anti stereochemistry to **8**. N-Boc-L-valinal, **4**, has a 2*S* configuration which allows assignment of a 4,5-anti stereochemistry to **10**. If a similar analysis is employed, a 2,3-anti stereochemistry of **14** can be assigned. In the ^{1}H NMR spectra of **8**, **10**, and **14** coupling of H_3 and H_4 are in the range of 3−4 Hz which is expected for 3,4-syn diastereoisomers.

Conclusions

Reaction of both enantiomers of **2** with five α-chiral aldehydes yielded chlorohydrins with excellent de in matched cases and moderate to good de for mismatched cases. Cyclization of the corresponding chlorohydrins furnished chiral vinyl epoxides in excellent yields. There-

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fore, chloroallylboration of α-chiral aldehydes with **2** provides a practical synthesis of chiral vinyl epoxides.

Experimental Section

General Chemical Procedures. ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively. GC analyses were conducted using a 30-m × 0.25-mm i.d. fused silica column coated with DB-1 with FID detection. THF and diethyl ether were distilled from sodium−benzophenone ketyl. Dicyclohexylamine [(c-Hex)$_2$NH] was freshly distilled from CaH_2 prior to use. Allyl chloride was freshly distilled over P_2O_5 prior to use. The ^{d}Ipc$_2$BOMe and ^{l}Ipc$_2$BOMe were purchased from Aldrich and used without purification. Moisture and air-sensitive reactions were conducted under argon in vacuum-dried glassware. A nitrogen glovebag was used to weigh moisture-sensitive compounds. Syringes and cannulas were used to transfer air-sensitive reagents.[18] Unless otherwise stated, standard workup refers the combination of organic extracts, washing with ice-cold brine, drying over anhydrous $MgSO_4$, and concentration in vacuo.

General Procedure for Chloroallylboration of Aldehydes Using Ipc$_2$BOMe. (3*S*,4*S*,5*S*)-5-[*N*-(*tert*-Butyloxycarbonyl)amino]-3-chloro-6-methyl-1-hepten-4-ol (10). To a stirred and cooled (−78 °C) mixture of ^{l}Ipc$_2$BOMe (11.5 mmol) and allyl chloride (15 mmol) in anhydrous ether (50 mL) was added a solution of LiN(c-Hex)$_2$ (15 mmol) in THF (25 mL). After being stirred for 0.5 h, the mixture is cooled to −95 °C and BF_3·OEt_2 (30 mmol) was added followed by chiral aldehyde **4** (10 mmol). The reaction was maintained at −95 °C for 4 h. (For direct oxidative workup using NaOAc/H_2O_2, see synthesis of **14**).

Ethanolamine Workup. All solvents were removed in vacuo at room temperature, and the residue was triturated with *n*-pentane (40 mL) and precipitates were allowed to settle (12 h). The supernatant was transferred to a predried flask by cannula. The residue was further treated with pentane (2 × 30 mL), and the pentane extracts were combined. Removal of pentane *in vacuo* furnished a semisolid. (For synthesis of *cis*-vinyl epoxide by oxidation using NaOH/H_2O_2, see preparation of **20**). This residue was dissolved in ether and treated with ethanolamine following the reported procedure.[4] Standard workup followed by flash chromatography yielded a liquid (1.62 g, 60% yield; purity 95%, 93% of **10**, 2% of **11**). The reaction stereoselectivity was determined to be 99:1 (**10**:**11**) by GC analysis of the reaction mixture which was filtered through a silica gel plug prior to gas chromatographic analysis (analysis conditions: 30 m DB-1, 90 to 275 °C at 1 °C/min, t_R 47.99 min).

(3*S*,4*S*,5*S*)-5-[*N*-(*tert*-Butyloxycarbonyl)amino]-3-chloro-6-methyl-1-hepten-4-ol (10). R_f = 0.46 (hexane−Et$_2$O, 1:1); $[\alpha]^{23}_D$ +13.5 (*c* = 2.29, EtOH). ^{13}C NMR ($CDCl_3$): δ 155.87, 133.06, 120.33, 75.94, 65.21, 56.54, 28.32, 28.05, 19.92, 15.83. ^{1}H NMR ($CDCl_3$): δ 6.05 (ddd, *J* = 17.2, 10.9, 8.5 Hz, 1H), 5.38 (d, *J* = 17.2 Hz, 1H), 5.24 (d, *J* = 10.9 Hz, 1H), 4.58 (dd, $J_{2,3}$ = 8.5, $J_{3,4}$ = 2.9 Hz, 1H), 4.43 (d, *J* = 10.3 Hz, 1H), 3.73 (m, 1H), 3.60 (dt, *J* = 9.0, 3.7 Hz, 1H), 2.58 (br s, 1H), 2.18 (m, 1H), 1.43 (s, 9H), 0.91 (d, *J* = 6.9, 3H), 0.84 (d, *J* = 6.9 Hz, 3H). IR (neat): 3356, 1656, 1549, 1078 cm^{-1}. CIMS [*m*/*z* (isobutane, rel intensity)]: 278 (M^+ + 1, 6.7), 224 (32), 222 (100), 186 (36), 172 (21). Anal. Calcd for $C_{13}H_{24}ClNO_3$: C, 56.21; H, 8.71; N, 5.04. Found: C, 56.24; H, 8.79; N, 4.94.

(3*R*,4*R*,5*S*)-5-[*N*-(*tert*-Butyloxycarbonyl)amino]-3-chloro-6-methyl-1-hepten-4-ol (11). This diastereoisomer was prepared from reaction of **2a** (generated from 5.8 mmol of ^{d}Ipc$_2$BOMe, 7.5 mmol of allyl chloride, and 7.5 mmol of LiDCHA) and **4** (5 mmol). Flash column chromatography yielded 54 mg of **10** and 768 mg of **11**. Reaction stereoselectivity was determined by gas chromatographic analysis (30 m DB-1, 90 to 275 °C at 1 °C/min) of a portion of the reaction mixture that had been filtered through a plug of silica gel. Data for **11**: R_f = 0.31 (hexane−Et$_2$O, 1:1); $[\alpha]^{23}_D$ −2.8 (*c* = 4.33, EtOH); ^{13}C NMR ($CDCl_3$) δ 155.96, 135.51, 118.47, 75.10, 66.23, 56.59, 28.37, 27.78, 20.31, 16.47. ^{1}H NMR ($CDCl_3$) δ 6.02 (m, 1H), 5.38 (d, *J* = 16.9 Hz, 1H), 5.24 (d, *J* = 10.2 Hz, 1H), 4.58 (m, 1H), 3.70 (m, 1H), 3.60 (m, 1H), 2.36 (s, 1H), 2.14 (s, 1H), 1.64 (s, 1H), 1.44 (s, 9H), 0.89 (m, 6H). CIMS *m*/*z* (isobutane, rel intensity) 278 (M^+ + 1, 9.7), 222 (100), 186 (46), 172 (30). Anal. Calcd for $C_{13}H_{24}ClNO_3$: C, 56.21; H, 8.71; N, 5.04. Found: C, 56.22; H, 8.76; N, 4.97.

(3*S*,4*S*,5*S*)-3-Chloro-4-hydroxy-5-methyl-1-heptene (8). Diastereoisomer **8** was prepared from reaction of **2b** and **3** (as described for **11**) in 60% yield (91% purity, 90% of **8**, 1% of **9**). Reaction stereoselectivity was determined to be 99:1 (**8**:**9**) by gas chromatographic analysis (30 m DB-1, 60 °C for 4 min, then programmed to 275 °C at 4 °C/min) of a portion of the reaction mixture that had been filtered through a plug of silica gel. Data for **8**: R_f = 0.45 (hexane−Et$_2$O, 1:1); $[\alpha]^{23}_D$ −63.2 (*c* = 3.72, EtOH); ^{13}C NMR ($CDCl_3$) δ 135.45, 118.69, 76.87, 68.33, 37.03, 26.82, 12.48, 11.48; ^{1}H NMR ($CDCl_3$) δ 5.90 (ddd, *J* = 16.9, 10.8, 8.4 Hz, 1H), 5.37 (ddd, *J* = 16.9, 1, 1 Hz, 1H), 5.24 (ddd, *J* = 10.8, 1, 1 Hz, 1H), 4.48 (dd, *J* = 9.0, 7.4 Hz, 1H), 3.54 (dt, *J* = 7.4, 4.4 Hz, 1H), 2.12 (d, *J* = 4.4 Hz, 1H), 1.50 (m, 1H), 0.85−0.98 (m, 8H); CIMS *m*/*z* (isobutane, rel intensity) 163 (M^+ + 1, 5), 145 [(M^+ + 1) − 18, 100], 127 (80). Anal. Calcd for $C_8H_{15}ClO$: C, 59.07; H, 9.30. Found: C, 59.13; H, 9.35.

(3*R*,4*R*,5*S*)-3-Chloro-4-hydroxymethyl-1-heptene (9). Diastereoisomer **9** was prepared by reaction of **2a** and **3** (as described for **11**) in 60% yield (92% purity, 3% of **8**, 89% of **9**). Reaction stereoselectivity was determined to be 15:85 (**8**:**9**) by gas chromatographic analysis (30 m DB-1, 60 °C for 4 min, then programmed to 275 °C at 4 °C/min) of a portion of the reaction mixture that had been filtered through a plug of silica gel. GC: t_R of **8** = 20.07 min, t_R of **9** = 19.47 min. Data for **9**: R_f = 0.43 (hexane−Et$_2$O, 1:1); $[\alpha]^{23}_D$ +29.6 (*c* = 2.04, EtOH); ^{13}C NMR ($CDCl_3$) δ 136.91, 118.23, 78.15, 67.15, 37.82, 23.69, 15.55, 11.17; ^{1}H NMR ($CDCl_3$) δ 6.01 (ddd, *J* = 16.9, 10.8, 8.4 Hz, 1H), 5.36 (ddd, *J* = 16.9, 1, 1 Hz, 1H), 5.24 (ddd, *J* = 10.8, 1, 1 Hz, 1H), 4.56 (dd, *J* = 8.4, 4.4 Hz, 1H), 3.40 (dt, *J* = 8.4, 6.6 Hz, 1H), 1.95 (d, *J* = 6.6 Hz, 1H), 1.62 (m, 1H), 0.99−1.04 (m, 2H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H); CIMS *m*/*z* (isobutane, rel intensity) 163 (M^+ + 1, 5), 145 [(M^+ + 1) − 18, 100], 127 (62). Anal. Calcd for $C_8H_{15}ClO$: C, 59.07; H, 9.30. Found: C, 59.11; H, 9.40.

(2*R*,3*R*,4*R*)-1,2-*O*,*O*′-Isopropylidene-4-chloro-5-hexene-1,2,3-triol (12). Diastereoisomer **12** was prepared from reaction of **2a** and **5** (as described for **11**) in 65% yield (97% purity, 97% of **12**). Reaction stereoselectivity was determined to be 99.5:0.5 (**12**:**13**) by gas chromatographic analysis (30 m DB-1, 60 °C for 5 min, then programmed to 275 °C at 5 °C/min) of a portion of the reaction mixture that had been filtered through a plug of silica gel. Data for **12**: R_f = 0.30 (hexane−Et$_2$O, 1:1); $[\alpha]^{23}_D$ +34.5 (*c* = 3.62, EtOH); ^{13}C NMR ($CDCl_3$) δ 135.15, 118.88, 109.54, 75.82, 74.72, 66.65, 64.65, 26.88, 25.21; ^{1}H NMR ($CDCl_3$) δ 6.04 (ddd, *J* = 16.9, 10.2, 7.8 Hz, 1H), 5.42 (ddd, *J* = 16.9, 1, 1 Hz, 1H), 5.28 (ddd, *J* = 10.2, 1, 1 Hz, 1H), 4.77 (dd, $J_{4,5}$ = 7.8, $J_{3,4}$ =2.2 Hz, 1H), 4.03−4.10 (m, 3H), 3.62 (ddd, $J_{3,4}$ = 2.2, $J_{3,O}$ = 8.8 Hz, $J_{2,3}$ = 7.0 Hz, 1H), 2.09 (d, $J_{3,O}$ = 8.8 Hz, 1H), 1.41 (s, 3H), 1.35 (s, 3H); CIMS *m*/*z* (isobutane, rel intensity) 207 (M^+ + 1, 100), 149 (42.5), 101 (84.5). Anal. Calcd for $C_9H_{15}ClO_3$: C, 52.31; H, 7.32. Found: C, 52.21; H, 7.40.

(2*R*,3*S*,4*S*)-1,2-*O*,*O*′-Isopropylidene-4-chloro-5-hexene-1,2,3-triol (13). Distereoisomer **13** was prepared by reaction of **2b** with **5** (as described for **11**) in 65% yield (97% purity). Reaction stereoselectivity was determined to be 39:61 (**12**:**13**) by gas chromatographic analysis (30 m DB-1, 60 °C for 5 min, then programmed to 275 °C at 5 °C/min) of a portion of the reaction mixture that had been filtered through a plug of silica gel. GC: t_R for **12** = 8.21 min; t_R for **13** = 8.44 min. Data for **13**: R_f = 0.38 (hexane−Et$_2$O, 1:1); $[\alpha]^{23}_D$ −28.5 (*c* = 2.96, EtOH); ^{13}C NMR ($CDCl_3$) δ 134.4, 119.4, 109.8, 75.0, 73.7, 66.4, 64.5, 26.3, 25.4; ^{1}H NMR ($CDCl_3$) δ 5.95 (ddd, *J* = 16.9, 10.2, 8.8 Hz, 1H), 5.40 (ddd, *J* = 16.9, 1, 1 Hz, 1H), 5.28 (ddd, *J* = 10.2, 1, 1 Hz, 1H), 4.40 (dd, $J_{4,5}$ = 8.8 Hz, $J_{3,4}$ = 5.8 Hz, 1H),

(18) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. *Organic Synthesis via Boranes*; Wiley-Interscience: New York, 1975.

4.30 (td, $J_{2,3}$ = 3.7 Hz, $J_{1,2}$ = 6.8 Hz, 1H), 4.06 (dd, $J_{1,2}$ = 6.8, $J_{1a,b}$ = 8.2 Hz, 1H), 3.85 (dd, $J_{1,2}$ = 6.9, $J_{1a,b}$ = 8.2 Hz, 1H), 3.64 (ddd, $J_{3,4}$ = 5.4, $J_{3,O}$ = 6.8, $J_{2,3}$ = 3.7 Hz, 1H), 2.59 (d, $J_{3,O}$ = 6.9 Hz, 1H), 1.43 (s, 3H), 1.35 (s, 3H); CIMS *m/z* (isobutane, rel intensity) 207 ($M^+ + 1$, 81.2), 149 (14.5), 101 (100). Anal. Calcd for $C_9H_{15}ClO_3$: C, 52.31; H, 7.32. Found: C, 52.37; H, 7.43.

Direct Oxidation Workup. The allyboration reaction (see representative procedure for preparation of **10**) was quenched by addition of MeOH (4 mL). Then, 3 M NaOAc (10 mL) and 30% H_2O_2 (6 mL) were sequentially added. Stirring was continued for 10 h, and H_2O (100 mL) was added. The reaction mixture was extracted with Et_2O (3 × 25 mL), and the combined extract was sequentially washed with saturated NH_4Cl solution (20 mL) and water (20 mL). Drying (anhydrous Na_2SO_4), removal of solvent, and flash chromatography over silica gel yielded chlorohydrins.

(2*R*,3*R*,4*R*)-4-Chloro-1-[(*tert*-butyldimethylsilyl)oxy]-2-methyl-5-hexen-3-ol (14). This was prepared by the reaction of **6** and **2a** in 55% yield (89% of **14**, 3% of **15**). The reaction stereoselectivity was determined to be 95:5 (**14**:**15**) by GC analysis of the reaction mixture that had been filtered through a plug of silica gel. GC: t_R 15.78 min (30 m DB-1, 60 °C, 4 min, then programmed to 275 °C at 7 °C/min). Data for **14**: $[\alpha]^{23}_D$ +3.9 (*c* = 3.76, EtOH); ^{13}C NMR ($CDCl_3$) δ 136.26, 117.68, 75.30, 67.09, 66.00, 37.93, 25.89, 18.21, 13.56, 9.82, 5.60; ^{1}H NMR ($CDCl_3$) δ 6.11 (ddd, *J* = 16.9, 10.4, 8 Hz, 1H), 5.36 (ddd, *J* = 16.9, 1, 1 Hz, 1H), 5.23 (ddd, *J* = 10.4, 1, 1 Hz, 1H), 4.50 (dd, *J* = 8.0, 3.2 Hz, 1H), 3.86 (m, 1H), 3.75 (dd, *J* = 10, 4.3 Hz, 1H), 3.64 (m, 2H), 2.01 (m, 1H), 0.91 (m, 12H), 0.1 (s, 6H); CIMS *m/z* (isobutane, rel intensity) 281 ($M^+ + 3$, 10), 280 ($M^+ + 2$, 5.4), 279 ($M^+ + 1$, 100), 243 (8.1), 185 (7.5). Anal. Calcd for $C_{13}H_{27}ClO_2Si$: C, 55.99; H, 9.76. Found: C, 56.12; H, 9.87.

(2*R*,3*S*,4*S*)-4-Chloro-1-[(*tert*-butyldimethylsilyl)oxy]-2-methyl-5-hexen-3-ol (15). Compound **15** was prepared by the reaction of **6** and **2b** in 55% yield (6% of **14**, 85% of **15**). The reaction stereoselectivity was determined to be 14:86 (**14**:**15**) by GC analysis of the reaction mixture that had been filtered through a plug of silica gel. GC: t_R 16.25 min (30 m DB-1, 60 °C for 4 min, then programmed to 275 °C at 7 °C/min). Data for **15**: $[\alpha]^{23}_D$ +29.5 (*c* = 4.53, EtOH); ^{13}C NMR ($CDCl_3$) δ 135.46, 118.60, 75.30, 67.71, 66.70, 37.60, 25.89, 18.24, 9.82, 5.53, 5.49; ^{1}H NMR ($CDCl_3$) δ 5.88 (ddd, *J* = 16.9, 10.2, 9 Hz, 1H), 5.36 (ddd, *J* = 16.9, 1, 1 Hz, 1H), 5.23 (ddd, *J* = 10.2, 1, 1 Hz, 1H), 4.46 (dd, *J* = 5, 9 Hz, 1H), 3.84 (m, 1H), 3.65 (m, 2H), 2.82 (s, 1H), 1.84 (m, 1H), 0.95 (d, *J* = 8 Hz, 3H), 0.91 (s, 9H), 0.1 (s, 6H); CIMS *m/z* (isobutane, rel intensity) 281 ($M^+ + 3$, 12), 280 ($M^+ + 2$, 5.4), 279 ($M^+ + 1$, 100), 243 (9.7). Anal. Calcd for $C_{13}H_{27}ClO_2Si$: C, 55.99; H, 9.76. Found: C, 56.10; H, 9.67.

(2*S*,3*S*,4*S*)-4-Chloro-1-[(*tert*-butyldimethylsilyl)oxy]-2-methyl-5-hexen-3-ol (16). Compound **16** was prepared by the reaction of **7** and **2b** in 56% yield (89% of **16**, 3% of **17**). The reaction stereoselectivity was determined to be 95:5 (**16**:**17**) by GC analysis of the reaction mixture that had been filtered through a plug of silica gel. GC: t_R 15.78 min (30 m DB-1, 60 °C for 4 min, then programmed to 275 °C at 7 °C/min). Data for **16**: $[\alpha]^{23}_D$ −3.5 (*c* = 4.53, EtOH). Anal. Calcd for $C_{13}H_{27}ClO_2Si$: C, 55.99; H, 9.76. Found: C, 56.10; H, 9.85.

(2*S*,3*R*,4*R*)-4-Chloro-1-[(*tert*-butyldimethylsilyl)oxy]-2-methyl-5-hexen-3-ol (17). Compound **17** was prepared by the reaction of **7** and **2a** in 55% yield (8% of **16**, 84% of **17**). The reaction stereoselectivity was determined to be 15:85 (**16**:**17**) by GC analysis of the reaction mixture that had been filtered through a plug of silica gel. GC: t_R 16.25 min (30 m DB-1, 60 °C for 4 min, then programmed to 275 °C at 7 °C/min). Data for **17**: $[\alpha]^{23}_D$ −30.1 (*c* = 4.53, EtOH). Anal. Calcd for $C_{13}H_{27}ClO_2Si$: C, 55.99; H, 9.76. Found: C, 56.15; H, 9.89.

Synthesis of Vinyl Epoxides. (i) General Procedure for Oxidation Workup. The residue obtained (see experimental procedure for preparation of **10**) was dissolved in THF (20 mL) with stirring and cooled to 0 °C. Then, 3 M NaOH (12 mL) and 30% H_2O_2 (12 mL) were sequentially added. The reaction mixture was allowed to warm to room temperature (14 h). Standard workup followed by flash chromatography yielded a colorless liquid, **20** (1.4 g, 60% yield).

(ii) General Procedure for Cyclization of α-Chlorohydrins (8−17). To a solution of α-chlorohydrin **10** (1.37 g, 5 mmol) in MeOH (20 mL) was added K_2CO_3 (1.2 g, 10.0 mmol). The mixture was stirred for 4 h, after which time most of MeOH was removed in vacuo. The resulting slurry was then diluted with water (20 mL), and the mixture was extracted with Et_2O (3 × 40 mL). Standard workup followed by flash chromatography gave vinyl epoxide **20** (1.2 g, 98% yield).

(3*R*,4*S*,5*S*)-5-[*N*-(*tert*-Butyloxycarbonyl)amino]-3,4-epoxy-6-methyl-1-heptene (20): R_f = 0.46 (hexane−Et_2O, 1:1); $[\alpha]^{23}_D$ −17.6 (*c* = 1.54, Et_2O); ^{13}C NMR ($CDCl_3$) δ 132.48, 120.52, 59.40, 56.93, 53.98, 31.55, 28.32, 18.91, 17.39; ^{1}H NMR ($CDCl_3$) δ 5.85 (m, 1H), 5.48 (d, *J* = 17 Hz, 1H), 5.38 (d, *J* = 10 Hz, 1H), 4.48 (m, 1H), 3.45 (dd, *J* = 7, 4 Hz, 1H), 3.31 (m, 1H), 2.99 (dd, *J* = 9, 4 Hz, 1H), 1.95 (m, 1H), 1.41 (s, 9H), 1.00 (d, *J* = 3 Hz, 3H), 0.97 (d, *J* = 3 Hz, 3H); EIMS *m/z* (rel intensity) 198 ($M^+ - i$-Pr, 9), 185 ($M^+ - i$-butene, 20), 142 (39), 114 (68), 57 (100). Anal. Calcd for $C_{13}H_{23}NO_3$: C, 64.70; H, 9.61; N, 5.80. Found: C, 64.86; H, 9.71; N, 5.70.

(3*S*,4*R*,5*S*)-5-[*N*-(*tert*-Butyloxycarbonyl)amino]-3,4-epoxy-6-methyl-1-heptene (21): R_f = 0.34 (hexane−Et_2O, 1:1); $[\alpha]^{23}_D$ −12.5 (*c* = 2.63, Et_2O); ^{13}C NMR ($CDCl_3$) δ 132.49, 120.54, 59.42, 56.95, 53.98, 31.56, 28.34, 18.92, 17.41; ^{1}H NMR ($CDCl_3$) δ 5.85 (m, 1H), 5.46 (d, *J* = 17 Hz, 1H), 5.36 (d, *J* = 11 Hz, 1H), 4.51 (m, 1H), 3.41 (dd, *J* = 7.2, 4 Hz, 1H), 3.31 (m, 1H), 3.0 (dd, *J* = 8.8, 4 Hz, 1H), 1.94 (sextet, *J* = 6.6 Hz, 1H), 1.41 (s, 9H), 1.00 (d, *J* = 3 Hz, 3H), 0.97 (d, *J* = 3 Hz, 3H); EIMS *m/z* (rel intensity) 198 ($M^+ - i$-Pr, 6), 185 ($M^+ - i$-butene, 12), 142 (28), 114 (31), 57 (100). Anal. Calcd for $C_{13}H_{23}NO_3$: C, 64.70; H, 9.61; N, 5.80. Found: C, 64.66; H, 9.47; N, 5.85.

(3*R*,4*S*,5*S*)-3,4-Epoxy-5-methyl-1-heptene (18): $[\alpha]^{23}_D$ −17.1 (*c* = 2.18, Et_2O); ^{13}C NMR ($CDCl_3$) δ 132.90, 119.90, 68.10, 63.95, 33.24, 26.56, 15.36, 11.32; ^{1}H NMR ($CDCl_3$) δ 5.71 (ddd, *J* = 10.4, 8.0, 7.4 Hz, 1H), 5.45 (ddd, *J* = 8.0, 1, 1 Hz, 1H), 5.33 (ddd, *J* = 10.4, 1, 1 Hz, 1H), 3.44 (dd, *J* = 4.4, 7.3 Hz, 1H), 3.38 (dd, *J* = 4.4, 7.5 Hz, 1H), 1.63 (m, 1H), 1.37 (m, 2H), 1.21 (t, *J* = 7.3 Hz, 3H), 1.08 (d, *J* = 5.9 Hz, 3H); CIMS *m/z* (isobutane, rel intensity) 127 ($M^+ + 1$, 57.9), 109 [($M^+ + 1$) − 18, 100]; HRMS calcd for $C_8H_{14}O$ 126.1045, found 126.1043.

(3*S*,4*R*,5*S*)-3,4-Epoxy-5-methyl-1-heptene (19): $[\alpha]^{23}_D$ +32.6 (*c* = 3.60, Et_2O); ^{13}C NMR ($CDCl_3$) δ 133.19, 120.09, 63.54, 56.54, 33.73, 27.05, 17.50, 11.15; ^{1}H NMR ($CDCl_3$) δ 5.71 (ddd, *J* = 10.4, 8.0, 7.4 Hz, 1H), 5.48 (ddd, *J* = 8.0, 1, 1 Hz, 1H), 5.33 (ddd, *J* = 10.4, 1, 1 Hz, 1H), 3.44 (dd, *J* = 4.4, 7.3 Hz, 1H), 3.38 (dd, *J* = 4.4, 7.5 Hz, 1H), 1.63 (m, 1H), 1.37 (m, 2H), 1.21 (t, *J* = 7.3 Hz, 3H), 1.08 (d, *J* = 5.9 Hz, 3H); CIMS *m/z* (isobutane, rel intensity) 127 ($M^+ + 1$, 55.6), 109 [($M^+ + 1$) − 18, 100]; HRMS calcd for $C_8H_{14}O$ 126.1045, found 126.1046.

(2*R*,3*R*,4*S*)-1,2-*O*,*O*′-Isopropylidene-3,4-epoxy-5-hexene-1,2-diol (22): R_f = 0.42 (hexane−Et_2O, 1:1); $[\alpha]^{23}_D$ −18.3 (*c* = 3.54, Et_2O); ^{13}C NMR ($CDCl_3$) δ 131.27, 120.91, 109.89, 72.15, 67.98, 58.51, 56.90, 26.73, 25.27; ^{1}H NMR ($CDCl_3$) δ 5.79 (ddd, *J* = 16.9, 10.6, 6.6 Hz, 1H), 5.49 (ddd, *J* = 16.9, 1, 1 Hz, 1H), 5.42 (ddd, *J* = 10.6, 1, 1 Hz, 1H), 4.17 (dd, *J* = 8.6, 6.3 Hz, 1H), 4.03 (d, *J* = 8.6, 5.2 Hz, 1H), 3.88 (ddd, *J* = 8.5, 6.3, 5.2 Hz, 1H), 3.53 (dd, *J* = 6.6, 4.1 Hz, 1H), 3.11 (dd, *J* = 8.5, 4.1 Hz, 1H); IR (neat) 1454, 1255, 1063 cm^{-1}; EIMS *m/z* (rel intensity) 155 (M^+ − Me, 60), 99 (51), 71 (45), 43 (100). Anal. Calcd for $C_9H_{14}O_3$: C, 63.49; H, 8.30. Found: C, 63.40; H, 8.36.

(2*R*,3*S*,4*R*)-1,2-*O*,*O*′-Isopropylidene-3,4-epoxy-5-hexene-1,2-diol (23): R_f = 0.35 (hexane−Et_2O, 1:1); $[\alpha]^{23}_D$ −7.16 (*c* = 1.84, Et_2O); ^{13}C NMR ($CDCl_3$) δ 134.47, 119.40, 109.84, 75.05, 73.73, 68.45, 64.55, 26.35, 25.43; ^{1}H NMR ($CDCl_3$) δ 5.68 (ddd, *J* = 17.2, 10.5, 7.2 Hz, 1H), 5.51 (ddd, *J* = 17.2, 1, 1 Hz, 1H), 5.35 (ddd, *J* = 10.5, 1, 1 Hz, 1H), 4.03 (dd, *J* = 8.2, 6.7 Hz, 1H), 3.95 (d, *J* = 14.3, 6.7 Hz, 1H), 3.70 (dd, *J* = 8.2, 6.7 Hz, 1H), 3.46 (dd, *J* = 7.2, 4.4 Hz, 1H), 3.14 (dd, *J* = 7.6, 4.4 Hz, 1H); IR (neat) 2986, 1461, 1372, 1089 cm^{-1}; EIMS *m/z* (rel intensity) 155 (M^+ − Me, 56), 99 (61), 71 (40), 43 (100). Anal. Calcd for $C_9H_{14}O_3$: C, 63.49; H, 8.30. Found: C, 63.42; H, 8.39.

(2*R*,3*R*,4*S*)-3,4-Epoxy-1-[(*tert*-butyldimethylsilyl)oxy]-2-methyl-5-hexene (24). Compound **24** was obtained by cyclization of **14** (98% yield). Data for **24**: $R_f = 0.63$ (hexane−Et_2O, 1:1); $[\alpha]^{23}_D$ +33.5 (c = 1.99, Et_2O); ^{13}C NMR ($CDCl_3$) δ 132.65, 120.21, 65.74, 60.28, 56.55, 35.08, 25.93, 13.01, 5.44; ^1H NMR ($CDCl_3$) δ 5.71 (ddd, J = 17.2, 10.5, 7.2 Hz, 1H), 5.48 (ddd, J = 17.2, 1, 1 Hz, 1H), 5.34 (ddd, J = 10.5, 1, 1 Hz, 1H), 3.73 (dd, J = 9.7, 3.8 Hz, 1H), 3.66 (dd, J = 9.7, 6.0 Hz, 1H), 3.42 (dd, J = 7.2, 4.4 Hz, 1H), 2.94 (dd, J = 9.4, 4.4 Hz, 1H), 1.52 (m, 1H), 0.94 (d, J = 6.9 Hz, 3H), 0.90 (s, 9H), 0 (s, 6H); CIMS m/z (isobutane, rel intensity) 243 ($M^+ + 1$, 32.7), 201 (16.8), 185 (22.8), 111 (100). Anal. Calcd for $C_{13}H_{26}O_2Si$: C, 64.41; H, 10.81. Found: C, 64.48; H, 10.71.

(2*R*,3*S*,4*R*)-3,4-Epoxy-1-[(*tert*-butyldimethylsilyl)oxy]-2-methyl-5-hexene (25). Compound **25** was prepared by cyclization of **15** (98% yield). Data for **25**: $R_f = 0.60$ (hexane−Et_2O, 1:1); $[\alpha]^{23}_D$ +10.5 (c = 2.66, Et_2O); ^{13}C NMR ($CDCl_3$) δ 133.17, 119.88, 65.55, 62.19, 58.00, 34.74, 25.91, 14.45, 5.47; ^1H NMR ($CDCl_3$) δ 5.74 (ddd, J = 17.2, 9.6, 7.2 Hz, 1H), 5.36 (ddd, J = 17.2, 1, 1 Hz, 1H), 5.23 (ddd, J = 9.6, 1, 1 Hz, 1H), 3.53 (dd, J = 10.0, 5.5 Hz, 1H), 3.50 (dd, J = 10.0, 6.5 Hz, 1H), 3.43 (dd, J = 7.2, 4.3 Hz, 1H), 2.88 (dd, J = 9.3, 4.3 Hz, 1H), 1.63 (m, 1H), 1.09 (d, J = 6.8 Hz, 3H), 0.89 (s, 9H), 0 (s, 6H); CIMS m/z (isobutane, rel intensity) 243 ($M^+ + 1$, 29.7), 185 (22.8), 111 (100). Anal. Calcd for $C_{13}H_{26}O_2Si$: C, 64.41; H, 10.81. Found: C, 64.53; H, 10.87.

(2*S*,3*S*,4*R*)-3,4-Epoxy-1-[(*tert*-butyldimethylsilyl)oxy]-2-methyl-5-hexene (26). Compound **26** was prepared by the cyclization of **16** (98% yield). Data for **26**: $R_f = 0.63$ (hexane−Et_2O, 1:1); $[\alpha]^{23}_D$ −34.0 (c = 2.19, Et_2O). Anal. Calcd for $C_{13}H_{26}O_2Si$: C, 64.41; H, 10.81. Found: C, 64.55; H, 10.94.

(2*S*,3*R*,4*S*)-3,4-Epoxy-1-[(*tert*-butyldimethylsilyl)oxy]-2-methyl-5-hexene (27). Compound **27** was prepared by cyclization of **17** (98% yield). Data for **27**: $R_f = 0.60$ (hexane−Et_2O, 1:1); $[\alpha]^{23}_D$ −11.5 (c = 1.96, Et_2O). Anal. Calcd for $C_{13}H_{26}O_2Si$: C, 64.41; H, 10.81. Found: C, 64.55; H, 10.72.

General Procedure for Preparation of MTPA Esters. MTPA-Cl was prepared following the reported procedure.[19] To the residue of MTPA-Cl was added compound **10** (2.7 mg, 0.01 mmol), Et_3N (4 μL), DMAP (1 mg), and CH_2Cl_2 (5 mL) sequentially. The reaction mixture was stirred for 3 h at room temperature during which time it was monitored by TLC. Then, saturated $NaHCO_3$ solution (3 mL) and Et_2O (10 mL) were sequentially added. The organic layer was separated, and the aqueous layer was extracted with Et_2O (3 × 5 mL). The combined organic extract was washed with brine and dried (anhydrous $MgSO_4$). Removal of solvents followed by flash chromatography furnished MTPA-ester.

(*R*)-MTPA Ester of (3*S*,4*S*,5*S*)-5-[*N*-(*tert*-Butyloxycarbonyl)amino]-3-chloro-6-methyl-1-hepten-4-ol (10): ^1H NMR ($CDCl_3$) δ 7.61 (m, 2H), 7.41 (m, 3H), 5.84 (ddd, J = 16.9, 10, 9 Hz, 1H), 5.41 (dd, J = 8.2, 4 Hz, 1H), 5.33 (d, J = 16.9 Hz, 1H), 5.25 (d, J = 10 Hz, 1H), 4.56 (dd, J = 9, 4 Hz, 1H), 4.38 (d, J = 10.7 Hz, 1H), 3.88 (ddd, J = 10.7, 8.2, 4 Hz, 1H), 3.48 (s, 3H), 1.78 (m, 1H), 1.44 (s, 9H), 0.88 (d, J = 6.8 Hz, 3H), 0.74 (d, J = 6.8 Hz, 3H); HRMS calcd for $C_{23}H_{31}ClF_3NO_5$ 493.1843, found 493.1847.

(*S*)-MTPA Ester of (3*S*,4*S*,5*S*)-5-[*N*-(*tert*-Butyloxycarbonyl)amino]-3-chloro-6-methyl-1-hepten-4-ol (10): ^1H NMR ($CDCl_3$) δ 7.60 (m, 2H), 7.41 (m, 3H), 5.91 (ddd, J = 17, 10, 9 Hz, 1H), 5.39 (dd, J = 8.4, 4 Hz, 1H), 5.36 (d, J = 17 Hz, 1H), 5.30 (d, J = 10 Hz, 1H), 4.61 (dd, J = 9, 4 Hz, 1H), 4.31 (d, J = 10.7 Hz, 1H), 3.82 (ddd, J = 10.7, 8.4, 3.2 Hz, 1H), 3.61 (s, 3H), 1.57 (m, 1H), 1.43 (s, 9H), 0.76 (d, J = 6.8 Hz, 3H). 0.66 (d, J = 6.8 Hz, 3H).

(*R*)-MTPA Ester of (3*R*,4*R*,5*S*)-5-[*N*-(*tert*-Butyloxycarbonyl)amino]-3-chloro-6-methyl-1-hepten-4-ol (11): ^1H NMR ($CDCl_3$) δ 7.60 (m, 2H), 7.41 (m, 3H), 5.86 (ddd, J = 16.8, 10, 9.6 Hz, 1H), 5.41 (m, 1H), 5.36 (d, J = 16.8 Hz, 1H), 5.24 (d, J = 10 Hz, 1H), 4.58 (m, 1H), 4.44 (d, J = 10.3 Hz, 1H), 3.94 (m, 1H), 3.41 (s, 3H), 1.82 (m, 1H), 1.47 (s, 9H), 0.79 (d, J = 6.8 Hz, 3H), 0.73 (d, J = 6.8 Hz, 3H); HRMS calcd for $C_{23}H_{31}ClF_3NO_5$ 493.1843, found 493.1844.

(*S*)-MTPA Ester of (3*R*,4*R*,5*S*)-5-[*N*-(*tert*-Butyloxycarbonyl)amino]-3-chloro-6-methyl-1-hepten-4-ol (11): ^1H NMR ($CDCl_3$) δ 7.61 (m, 2H), 7.41 (m, 3H), 5.93 (m, 1H), 5.41 (t, J = 6.0 Hz, 2H), 5.39 (d, J = 16.8 Hz, 1H), 5.28 (d, J = 10.2 Hz, 1H), 4.56 (m, 1H), 4.19 (d, J = 10.3 Hz, 1H), 3.82 (dt, J = 6.0, 3.0 Hz, 1H), 3.69 (s, 3H), 1.60 (m, 1H), 1.46 (s, 9H), 0.74 (d, J = 6.8 Hz, 3H), 0.44 (d, J = 6.8 Hz, 3H).

(*S*)-MTPA Ester of (2*R*,3*R*,4*R*)-4-Chloro-1-[(*tert*-Butyldimethylsilyl)oxy]-2-methyl-5-hexen-3-ol (14): ^{13}C NMR ($CDCl_3$) δ 134.54, 129.62, 128.33, 128.08, 119.18, 78.93, 63.62, 62.12, 55.38, 37.72, 31.56, 25.86, 22.62, 18.27, 14.02, −5.54, −5.61, −5.67; ^1H NMR ($CDCl_3$) δ 7.60 (m, 2H), 7.41 (m, 3H), 5.78 (ddd, J = 16.8, 10.2, 7.4 Hz, 1H), 5.36 (d, J = 16.8 Hz, 1H), 5.30 (t, J = 5.8 Hz, 1H), 5.23 (d, J = 10.2 Hz, 1H), 4.74 (dd, J = 7.3, 5.5 Hz, 1H), 3.56 (dd, J = 10, 5.5 Hz, 3H), 3.50 (s, 3H), 3.42 (dd, J = 10, 5.5 Hz, 1H), 2.18 (m, 1H), 1.28 (m, 6H), 0.89 (m, 12H); HRMS calcd for $C_{23}H_{34}ClF_3O_4Si$ 494.1867, found 494.1871.

(*R*)-MTPA Ester of (2*R*,3*R*,4*R*)-4-Chloro-1-[(*tert*-butyldimethylsilyl)oxy]-2-methyl-5-hexen-3-ol (14): ^{13}C NMR ($CDCl_3$) δ 134.58, 129.62, 128.32, 127.66, 119.39, 79.09, 63.39, 62.45, 55.39, 37.56, 34.73, 31.61, 25.88, 25.33, 22.67, 14.10, −5.54, −5.65; ^1H NMR ($CDCl_3$) δ 7.60 (m, 2H), 7.41 (m, 3H), 5.82 (ddd, J = 16.8, 10.2, 7.3 Hz, 1H), 5.39 (d, J = 16.8 Hz, 1H), 5.29 (t, J = 5.8 Hz, 1H), 5.26 (d, J = 10.2 Hz, 1H), 4.78 (t, J = 7.2 Hz, 1H), 3.62 (s, 3H), 3.40 (dd, J = 10, 5.7 Hz, 1H), 3.28 (dd, J = 10, 5.7 Hz, 1H), 2.18 (m, 1H), 1.30 (m, 6H), 0.91 (m, 12H).

(*S*)-MTPA Ester of (2*S*,3*S*,4*S*)-4-Chloro-1-[(*tert*-butyldimethylsilyl)oxy]-2-methyl-5-hexen-3-ol (16): ^{13}C NMR ($CDCl_3$) δ 134.55, 129.60, 128.29, 127.63, 119.36, 79.07, 63.36, 62.42, 55.37, 37.53, 34.70, 31.59, 25.85, 25.30, 22.65, 14.08, −5.51, −5.63; ^1H NMR ($CDCl_3$) δ 7.60 (m, 2H), 7.41 (m, 3H), 5.87 (ddd, J = 16.8, 10.2, 7.3 Hz, 1H), 5.42 (d, J = 16.8 Hz, 1H), 5.34 (t, J = 5.8 Hz, 1H), 5.26 (d, J = 10.2 Hz, 1H), 4.78 (t, J = 7.2 Hz, 1H), 3.62 (s, 3H), 3.40 (dd, J = 10, 5.7 Hz, 1H), 3.28 (dd, J = 10, 5.7 Hz, 1H), 2.18 (m, 1H), 1.30 (m, 6H), 0.91 (m, 12H); HRMS calcd for $C_{23}H_{34}ClF_3O_4Si$ 494.1867, found 494.1864.

(*R*)-MTPA Ester of (2*S*,3*S*,4*S*)-4-Chloro-1-[(*tert*-butyldimethylsilyl)oxy]-2-methyl-5-hexen-3-ol (16): ^{13}C NMR ($CDCl_3$) δ 134.53, 129.61, 128.32, 128.07, 119.17, 78.92, 63.61, 62.11, 55.37, 37.71, 31.55, 25.85, 22.61, 18.24, 14.00, −5.51, −5.58, −5.65; ^1H NMR ($CDCl_3$) δ 7.60 (m, 2H), 7.41 (m, 3H), 5.83 (ddd, J = 16.8, 10.2, 7.4 Hz, 1H), 5.42 (d, J = 16.8 Hz, 1H), 5.35 (t, J = 5.8 Hz, 1H), 5.23 (d, J = 10.2 Hz, 1H), 4.74 (dd, J = 7.3, 5.5 Hz, 1H), 3.56 (dd, J = 10, 5.5 Hz, 3H), 3.50 (s, 3H), 3.42 (dd, J = 10, 5.5 Hz, 1H), 2.18 (m, 1H), 1.28 (m, 6H), 0.89 (m, 12H).

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