Asymmetric Synthesis of Cycloalkenyl and Alkenyloxiranes From Allylic Sulfoximines and Aldehydes and Application to Solid-Phase Synthesis

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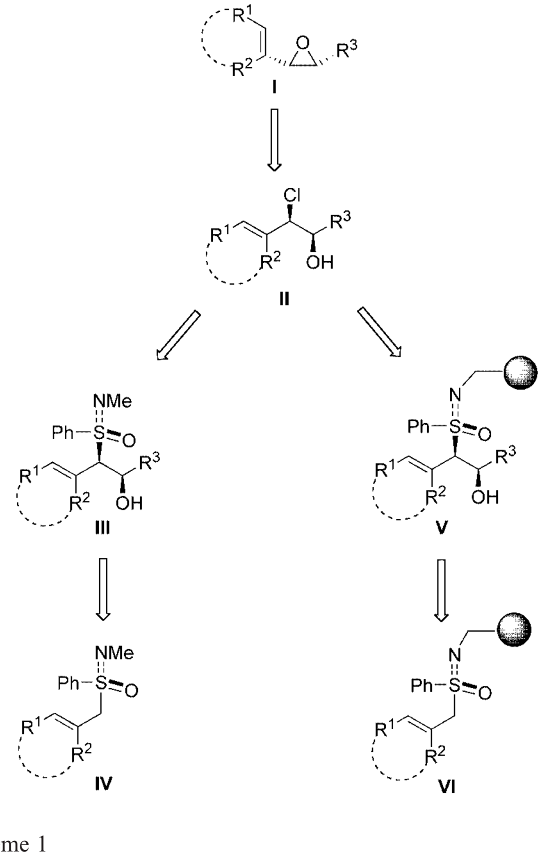
An asymmetric synthesis of cycloalkenyl and alkenyloxiranes from allylic sulfoximines and aldehydes is described. Lithiation and titanation of cyclic and acyclic allylic sulfoximines with chlorotris(diethylamino)titanium and subsequent treatment with aldehydes gave, as described previously, enantio- and diastereomerically pure, *syn*-configured, sulfoximine-substituted homoallylic alcohols. Treatment of the sulfoximine-substituted homoallylic alcohols with chloroethyl chloroformate resulted in a facile substitution of the sulfoximine group by a Cl atom, with formation of the corresponding alkenyl chlorohydrins. In the case of the cycloalkenyl derivatives the substitution proceeded with high diastereoselectivities with retention of configuration, while in the case of the alkenyl derivatives, medium diastereoselectivities with inversion of configuration were observed. While elimination reactions of the cycloalkenyl chlorohydrins gave the corresponding enantio- and diastereomerically pure *cis*-configured cycloalkenyloxiranes in good overall yields, the alkenyl chlorohydrins afforded mixtures of enantiomerically pure *trans* and *cis* isomers in which the *trans* isomers dominated. The solution-phase synthesis was extended to the solid phase by the synthesis of an enantiomerically pure, polymer-bound allylic sulfoximine and its conversion into an alkenyloxirane. The initial results proved that the concept of the utilization of the sulfoximine group as a traceless chiral linker is feasible and suggest that the solid-phase asymmetric synthesis of cycloalkenyloxiranes by this route should be possible.

Introduction

Chiral vinylic oxiranes are valuable intermediates in organic synthesis.[1,2] Their asymmetric synthesis has been accomplished by several methods, including the epoxidation of allylic alcohols in combination with an oxidation and olefination,[3] the epoxidation of dienes,[4] the chloroallylation of aldehydes in combination with an 1,2-elimination,[5,6] and reactions between S-ylides and aldehydes.[7] Although some of these methods are very efficient for the synthesis of alkenyloxiranes, they are all only poorly suited for the attainment of cycloalkenyloxiranes of type **I** (Scheme 1).[7c] We therefore developed an interest in the asymmetric synthesis of both cycloalkenyl and alkenyloxiranes from aldehydes and allylic sulfoximines. We had previously shown that treatment of derivatives of the cyclic and acyclic allylic sulfoximines **IV**, bearing a tris(diethylamino)titanium group at the α-position,[8−10] with aldehydes gives the sulfoximine-substituted homoallylic alcohols **III** with high regio- and diastereoselectivities.[9−11] It was speculated that the sulfoximine group of the homoallylic alcohols **III** might perhaps be stereoselectively replaceable by a Cl atom with formation of the corresponding chlorohydrins **II**, which upon base treatment should give the alkenyloxiranes



Scheme 1

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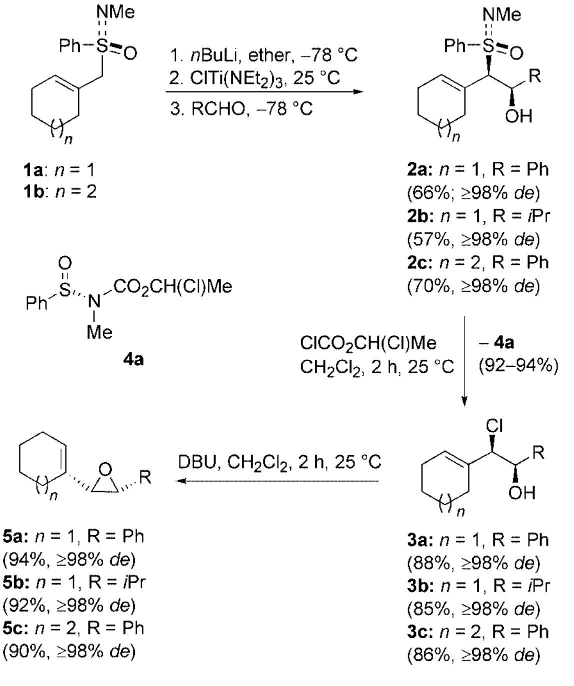
I.[5,6] The feasibility of a Cl substitution of the sulfoximine group had previously been shown in the case of *S*-alkylsulfoximines.[10b,12] A further stimulus for perusal of this route was its potential for application to solid-phase synthesis. We had previously described the synthesis of enantiomerically pure, *N*-polymer-bound *S*-methyl-*S*-phenylsulfoximine,[13] a potential starting material for the synthesis of the polymer-bound allylic sulfoximines **VI** from aldehydes and ketones by the addition−elimination−isomerization route.[9] Hydroxyalkylation of the polymer-bound allylic sulfoximines **VI** followed by a Cl substitution of the polymer-bound homoallylic alcohols **V** might deliver the corresponding chlorohydrins **II**. If successful, the sulfoximine group would function in this scheme as a chiral traceless linker, a concept of considerable interest.[14]

Here we describe a new method for the asymmetric synthesis of cycloalkenyl and alkenyloxiranes from aldehydes and allylic sulfoximines and its extension to solid-phase synthesis, a key step of which is facile Cl substitution of the allylic sulfoximine group.

Results and Discussion

Solution-phase Synthesis

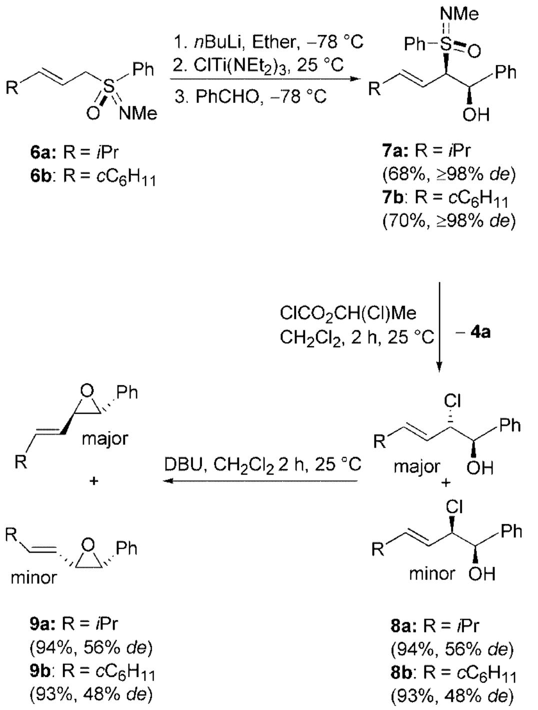
Successive lithiation and titanation of the six-membered cyclic allylic sulfoximine **1a**[15] with 1.1 equiv. of *n*BuLi and 1.2 equiv. of $ClTi(NEt_2)_3$ at −78 °C in diethyl ether afforded the corresponding allylic titanium complex, which upon treatment with benzaldehyde and isobutyraldehyde at −78 °C gave, as described previously, the diastereomerically pure *syn*-configured sulfoximine-substituted homoallylic alcohols **2a** and **2b**, respectively, in medium to good yields (Scheme 2).[9,10] Similarly, the new diastereomerically pure seven-membered homoallylic alcohol **2c** was obtained in good yield from the allylic sulfoximine **1b**[15] and benzaldehyde. NMR spectroscopic analysis of the crude reaction product showed the hydroxyalkylation to be, as in all previously described cases, highly diastereoselective (≥ 95% *de*) and regioselective (≥ 98:2). To our delight, treatment of the sulfoximines **2a−c** with 1.2 to 1.3 equiv. of $ClCO_2CH(Cl)Me$ at room temperature in CH_2Cl_2 for 1.5 h readily afforded the chlorohydrins **3a−c**, respectively, each in ≥ 98% *de* and in high yield. Substitution of the allylic sulfoximine group of **2a−c** occurred much more rapidly than in *S*-alkyl sulfoximines.[10,12] In addition to **3a−c** the sulfinamide **4a** was obtained in 92−94% yield (vide infra). The chlorohydrins and the sulfinamide were separated by flash chromatography. Cyclization of the chlorohydrins **3a−c** with DBU gave the enantio- and diastereomerically pure cycloalkenyloxiranes **5a−c**, respectively, in high yields. The oxiranes **5a−c** had *cis* configurations, as shown by the magnitudes of the vicinal coupling constants (^3J = 4.2−4.4 Hz) in their ^{1}H NMR spectra. Oxirane formation is expected to occur with inversion of configuration.[5,6] The chlorohydrins **3a−c** thus had *syn* configurations and, remarkably, the substitution of the sulfoximine groups of **2a−c** by Cl atoms had occurred with retention of configuration (vide infra). Attempts to convert the homoallylic alcohols **2a−c** into the oxiranes by methylation of the sulfoximine group with Me_3OBF_4 followed by cyclization with DBU failed.[16,17]



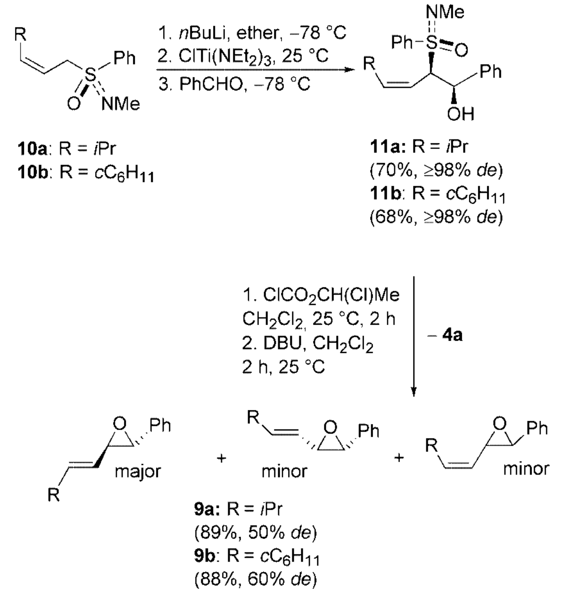
Scheme 2

Having recorded high selectivities in the synthesis of the cycloalkenyloxiranes **5a−c**, we next investigated the possibility of an analogous synthesis of alkenyloxiranes from acyclic allylic sulfoximines. Successive treatment of the *E*-configured allylic sulfoximines **6a** and **6b**[18] with *n*BuLi and $ClTi(NEt_2)_3$ gave the corresponding allylic titanium complexes,[8−10] which upon treatment with benzaldehyde afforded, as described previously, the enantio- and diastereomerically pure *syn*-configured sulfoximine-substituted homoallylic alcohols **7a** and **7b**, respectively, in good yields (Scheme 3).[9] Substitution of the sulfoximine groups of **7a** and **7b** upon treatment with $ClCO_2CH(Cl)Me$ proceeded readily and gave, beside **4a**, the chlorohydrins **8a** and **8b**, respectively, as mixtures of *anti* and *syn* diastereomers in ratios of 78:22 and 74:26, respectively, in high yields. Treatment of the mixtures of chlorohydrins with DBU furnished the oxiranes **9a** and **9b**, each as a mixture of *trans* and *cis* isomers in ratios of 78:22 and 74:26, respectively, and in high yields. The structures of the *trans*- and *cis*-configured oxiranes **9a** and **9b** were assigned on the basis of the magnitudes of the vicinal coupling constants in their ^{1}H NMR spectra, which amounted to ^3J = 1.9 Hz for the *trans* and ^3J = 4.3 Hz for the *cis* isomers.

In conclusion of the synthesis of the alkenyloxiranes from the acyclic allylic sulfoximines, the conversion of the *syn*-configured sulfoximine-substituted homoallylic alcohols **11a** and **11b**, with (*Z*)-configured double bonds, into the corresponding alkenyloxiranes was investigated (Scheme 4). This study was intended to probe the configurational stability of the double bond in the substitution of the sulfoximine group. The enantio- and diastereomerically pure



Scheme 3

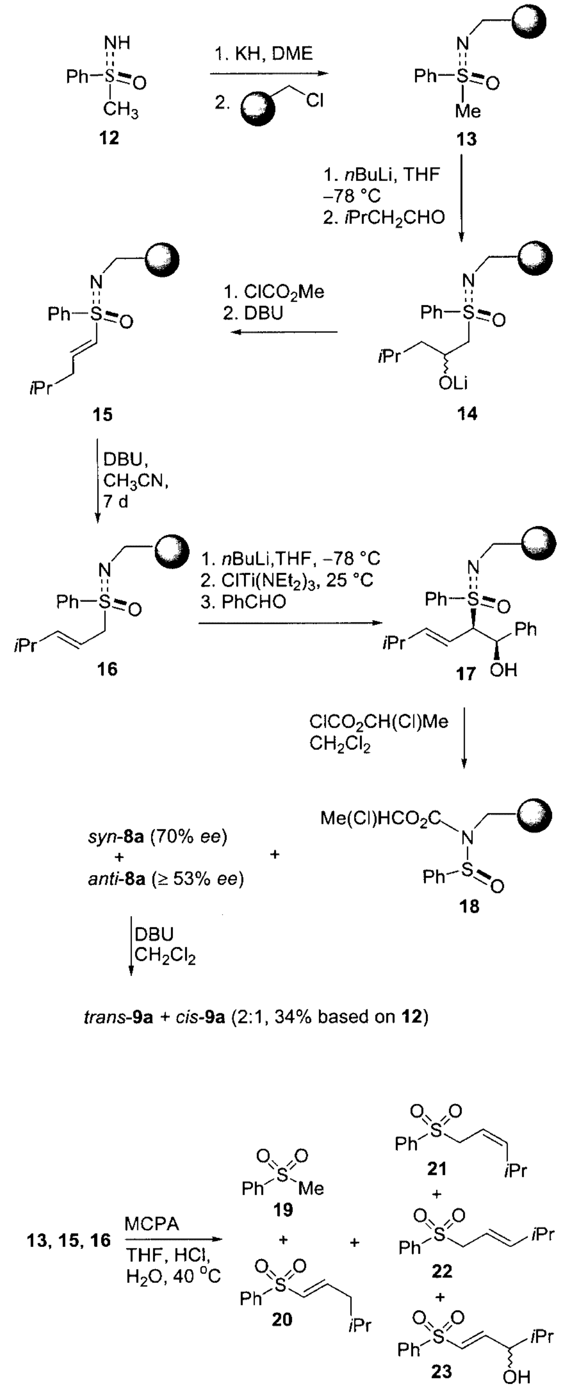


Scheme 4

homoallylic alcohols **11a** and **11b**[9,10] were synthesized in good yields, as described previously, from the (*Z*)-configured allylic sulfoximines **10a** and **10b**,[18] respectively, as outlined in Scheme 4. Successive treatment of sulfoximines **11a** and **11b** with $ClCO_2CH(Cl)Me$ and DBU afforded the alkenyloxiranes **9a** (89%) and **9b** (88%), but with (*E*)-configured double bonds, each as a mixture of *trans* and *cis* isomers in ratios of 75:25 and 80:20, respectively. ^1H NMR spectroscopy of the mixtures of *trans*-**9a**/*cis*-**9a** and *trans*-**9b**/*cis*-**9b** showed the presence of an additional 11% and 7% of the corresponding isomers with (*Z*)-configured double bonds. The substitution of the sulfoximine groups of **11a** and **11b** had thus to a large extent been accompanied by isomerization of the double bonds.

Solid-Phase Synthesis

The synthesis of the polymer-bound allylic sulfoximine **16** was accomplished by the addition–elimination–isomerization route starting from the enantiomerically pure polymer-bound, (*S*)-configured *S*-methyl-*S*-phenyl sulfoximine **13**,[13] prepared as described previously from Merrifield resin and sulfoximine **12** with a loading of 84% according to CHN analysis (Scheme 5). Successive treatment of



Scheme 5

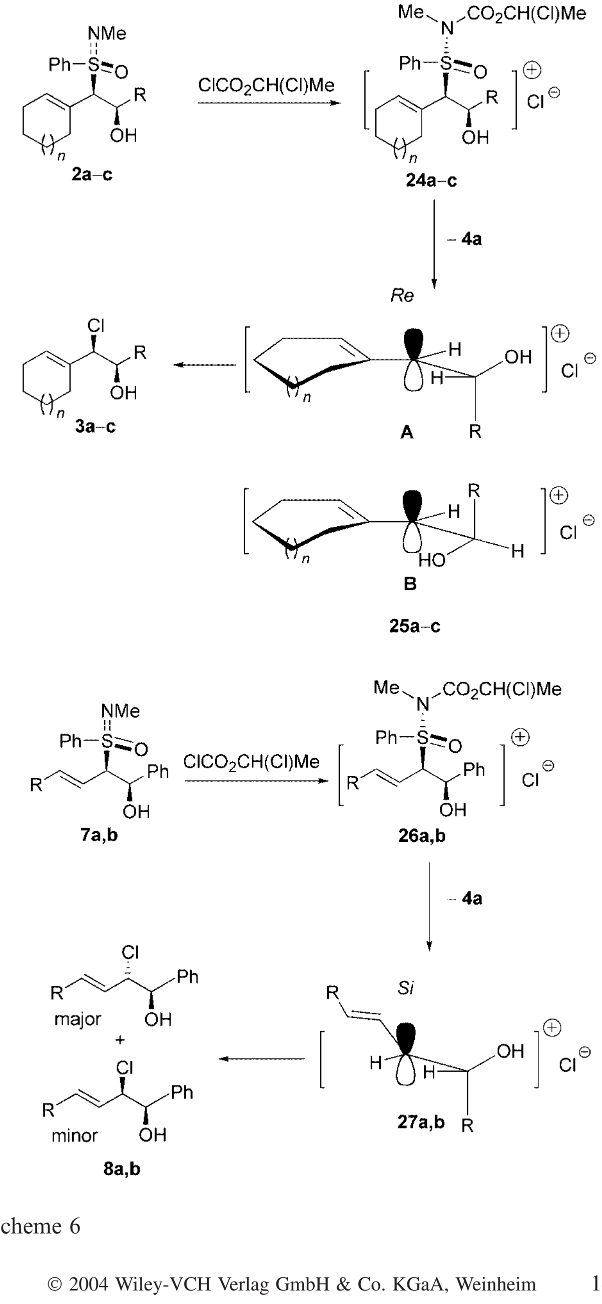
resin **13** with *n*BuLi in THF and isovaleraldehyde furnished the polymer-bound alkoxide **14**, which upon treatment with $ClCO_2Me$ and DBU afforded the polymer-bound vinylic sulfoximine **15**. The isomerization of **15** to the allylic sulfoximine **16** was carried out with DBU in MeCN at reflux.

The loading of the resin **16** and the success of each step of the synthesis was determined by an off-bead analysis involving the removal of the reaction products from the resin through an oxidative hydrolysis of the sulfoximine group at the S-N bond by a method we have described recently.[13] Treatment of the resin − potentially containing **13**, **14**, and **15** as well as **16** − with *m*-chloroperbenzoic acid (MCPA) and 0.1 m aqueous HCl in THF at 40 °C afforded a mixture of the sulfones **22**+**23**, **21**, **20**, and **19** in a ratio of 21:1.5:1:2 (^{1}H NMR). The γ-hydroxy sulfone **23** was presumably formed through epoxidation of the allylic sulfones **21** and **22**, followed by elimination of the corresponding epoxides. In summary, the off-bead analysis showed the successful anchoring of the allylic sulfoximine at the polymer in good yield.

The lithiation, titanation, and hydroxyalkalytion of the polymer-bound allylic sulfoximine **16** were carried out as follows. Resin **16** was treated with *n*BuLi in THF at −78 °C and, after the mixture had warmed to room temperature, the obtained resin **Li-16** was titanated by addition of $ClTi(NEt_2)_3$ at −78 °C. The titanated resin **Ti-16** was subsequently treated with benzaldehyde to afford the polymer-bound homoallylic alcohol **17** after workup. The cleavage of the linker group of **17** was achieved through treatment with $ClCO_2CH(Cl)Me$ in CH_2Cl_2 at room temperature, a mixture of the chlorohydrins *syn*-**8a** and *anti*-**8a** being obtained in a ratio of 2:1. HPLC analysis of the mixture of the *anti* and *syn* chlorohydrins, with the aid of a mixture of the enantiomerically pure compounds (HPLC) obtained by solution-phase synthesis as references, showed the *syn*-configured chlorohydrin *syn*-**8a** to be of 70% *ee* and the *anti*-configured chlorohydrin *anti*-**8a** to be of ≥ 53% *ee* (see Exp. Sect.). Treatment of **16** with benzaldehyde after lithiation and titanation had therefore given **17** with only 70% *de* at the C atom bearing the hydroxy group. We had previously observed that lithiated allylic sulfoximines react with aldehydes only with low diastereoselectivity at the α-position. We therefore assume that the lower diastereoselectivity of the formation of **17** is due to incomplete titanation of Li-**16** rather than to a lower diastereoselectivity of the hydroxyalkylation of the polymer-bound, titanated allylic sulfoximine. The chlorohydrins *anti*-**8a** and *syn*-**8a** were not purified, but were treated with DBU, which gave a mixture of the oxiranes *trans*-**9a** and *cis*-**9a** in a ratio of 2:1 in an overall yield of 34% based on sulfoximine **12**. Interestingly, the Cl substitution of **17** had occurred with a different selectivity than that of **7a**.

Mechanistic Consideration of the Cl substitution of Sulfoximines

The reactions between the cyclic allylic sulfoximines **2a**−**c** and $ClCO_2CH(Cl)Me$ proceeded with almost complete retention of configuration, while those between the acyclic allylic sulfoximines **7a** and **7b** and the chloroformate afforded the corresponding chlorohydrins predominantly with inversion of configuration. We had previously observed that *S*-alkyl-*N*-methyl sulfoximines are also amenable to this type of Cl substitution, the mechanism of which is not yet known. This substitution bears some resemblance to the dealkylation of tertiary amines upon treatment with chloroformates, which gives the corresponding alkyl chlorides and urethanes.[19] The first step seems to be acylation of the sulfoximine groups of **2a**−**c**, **7a**, and **7b** at the N atom[10b,12,20] with formation of the aminosulfoxonium salts **24a**−**c**, **26a**, and **26b**, respectively (Scheme 6). The allylic aminosulfoxonium groups of **24a**−**c**, **26a**, and **26b** would be expected to be excellent leaving groups.[21] Substitution of the allylic aminosulfoxonium salts by an S_N1 mechanism with formation of the allylic carbenium ions **25a**−**c**, **27a**, and **27b**, respectively and the sulfinamide **4a** thus seems to

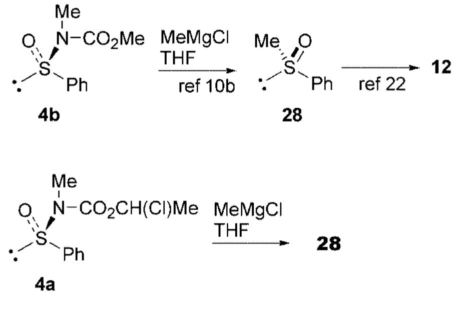


Scheme 6

be very likely. Such a mechanism could explain the (*Z*)/(*E*) isomerization that occurred in the case of the reactions of the (*Z*)-configured sulfoximine-substituted homoallylic alcohols. To explain the stereochemistry of the substitution it is postulated: (1) that the cyclic allylic carbenium ions **25a−c** preferentially adopt the C(OH)−C(sp^2)-conformation **A**, in which the hydroxy group is gauche to the H-atom at the C(sp^2)-atom, and (2) the chloride ion attacks with high selectivity from the *Re* face for steric reasons. The conformation **B** of **25a−c** should be less preferred because of a destabilizing interaction between the hydroxy group and the ring containing the double bond. In the case of the acyclic allylic cations **27a** and **27b**, an interpretation is more difficult. One would have to propose that the chloride attacks **27a** and **27b** in the conformation depicted preferentially from the *Si* face.

Recycling of the Chiral Auxiliary

We had previously shown that treatment of (*S*)-configured *S*-alkyl-*N*-methyl sulfoximines with $ClCO_2Me$ resulted in the formation of the sulfinamide **4b** with ≥ 98% *ee* (Scheme 7).[10b,12] Sulfinamide **4b** was converted on treatment with MeMgCl into the sulfoxide **28** of ≥ 98% *ee*, the conversion of which into the (*S*)-configured sulfoximine **12** of ≥ 98% *ee* had already been described in the literature.[22] Sulfoximine **12** is in turn the starting material for the synthesis of allylic sulfoximines **1a**, **1b**, **6a**, **6b**, **10a**, and **10b**. In order to examine whether **4a** could also be used as starting material for the synthesis of **12**, the sulfinamide was treated with MeMgCl, which gave sulfoxide **28** with 96% *ee* and in 85% yield. A similar experiment with the polymer-bound sulfinamide **18** has not yet been carried out. However, recycling of the chiral auxiliary from **18** by the route depicted in Scheme 7 should be possible.



Scheme 7

Conclusion

A highly selective asymmetric synthesis of *cis*-configured cycloalkenyloxiranes, not hitherto efficiently accessible by existing methods, has been developed. The three-step sequence consists of an allylation of an aldehyde with a cyclic allylic sulfoximine bearing a tris(diethylamino)titanium group, a Cl substitution of the sulfoximine group of the resulting homoallylic alcohol, and a cyclization of the resulting chlorohydrin. The synthesis of the cyclic allylic sulfoximines is accomplished from commercially available enantiomerically pure *S*-methyl-*S*-phenyl sulfoximine and the cycloalkanone by a six-step sequence of transformations requiring the isolation and purification of only one intermediate, *N*,*S*-dimethyl-*S*-phenyl sulfoximine. A solid-phase asymmetric synthesis of cycloalkenyloxiranes by this route through the use of the sulfoximine group as a traceless chiral linker seems feasible. The asymmetric synthesis of alkenyloxiranes by this route is also possible, but yields mixtures of *cis* and *trans* isomers, in which the latter dominate. The facile Cl substitution of the sulfoximine group with retention of configuration at the S atom and the recycling of the sulfinamide provide the basis for a full utilization of the sulfoximine group as a chiral auxiliary.

Experimental Section

General Comments and Materials: All reactions were carried out under argon in oven-dried glassware by use of Schlenk and syringe techniques. $ClTi(NEt_2)_3$[23] of ≥ 96% purity (^1H NMR) was prepared according to the literature. The allylic sulfoximine **1b**[15] of ≥ 98% *ee* was synthesized from (*S*)-*S*-methyl-*S*-phenyl sulfoximine and cycloheptanone according to the literature. Sulfoximine **12**[24] of ≥ 99% *ee* was prepared as described previously. The sulfoximine-substituted homoallylic alcohols **2a**, **2b**, **7a**, and **7b** were synthesized according to the literature.[9] The polymer-bound sulfoximine **13**[13] was prepared from sulfoximine **12** of ≥ 98% *ee* and Merrifield resin (PL-CMS resin, 1% cross-linked, 1.02 mmol/g, 35−75 µ m, 200−400 mesh) as described previously. Et_2O and THF were distilled from sodium-lead/benzophenone. CH_2Cl_2 was distilled from CaH_2. Reagents were obtained from commercial sources and used without further purification unless otherwise stated. *n*BuLi was standardized by titration with diphenylacetic acid. Analytical thin-layer chromatography (TLC) was performed with Merck pre-coated TLC plates (silica gel 60 F_{254}, layer thickness 0.2 mm). Gravity column chromatography (denoted as chromatography) was performed with E. Merck silica gel 60 (0.063−0.200 mm). Melting points were determined with a Büchi 535 apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded with a Varian VXR 300, an Inova 400, or a Varian Unity 500 instrument. Chemical shifts are reported relative to TMS (δ = 0.00 ppm) as internal standard. Splitting patterns in the ^1H NMR spectra are designated as s, singlet; d, doublet; dd, double doublet; t, triplet; q, quadruplet; sept, septet; m, multiplet. Peaks in the ^{13}C NMR spectra are denoted as "*u*" for carbon atoms with zero or two attached protons or as "*d*" for carbon atoms with one or three attached protons, as determined from the APT pulse sequence. Low-resolution mass spectra were recorded with a Varian MAT 212 mass spectrometer and secondary ion mass spectra were recorded with a Finnigan MAT mass spectrometer. Optical rotations were measured with a Perkin−Elmer Model 241 polarimeter at approximately 25 °C. Elemental analyses were performed by the microanalytical laboratory of the Institut für Organische Chemie.

(1*R*,2*R*)-2-(Cyclohept-1-enyl)-2-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]-1-phenylethanol (2c): *n*BuLi (3.12 mL, 5.0 mmol, 1.6 m solution in hexane) was added at −78 °C to a solution of the cyclic allylic sulfoximine **1b** (1.20 g, 4.56 mmol) in Et_2O (50 mL). After the mixture had been stirred for 10 min at −78 °C, neat $ClTi(NEt_2)_3$ (1.76 mL, 5.7 mmol) was added. The resulting mixture was stirred for 10 min at −78 °C, warmed to room temperature, and stirred for 2 h. After the mixture had again been cooled to −78 °C, benzaldehyde (869 mg, 8.2 mmol) was added dropwise. After the mixture had been stirred for 2 h at −78 °C, it was poured into aqueous $(NH_4)_2CO_3$ solution and extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Recrystallization from diethyl ether afforded **2c (**1.17 g, 70%, ≥ 98% *de*) as colorless crystals. M.p. 115−116 °C. $[\alpha\ ]_D$ = −21.4 (*c* = 1.00, CH_2Cl_2). ^1H NMR ($CDCl_3$,400 MHz): δ = 0.90−1.06 (m, 4 H), 1.30−1.74 (m, 6 H), 2.70 (s, 3 H), 3.75 (m, 1 H), 5.46 (br. d, *J* = 9.7 Hz, 1 H), 7.48−7.72 (m, 5 H), 7.78−7.84 (m, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.1 (u), 24.3 (u), 28.2 (u), 28.5 (u), 28.6 (d), 28.7 (u), 71.9 (d), 72.4 (d), 125.9 (d), 126.0 (d), 126.4 (d), 126.6 (d), 126.7 (d), 127.5 (d), 127.8 (d), 131.9 (d), 135.3 (u), 139.2 (u) ppm. MS (CI, isobutane): *m*/*z* (%) = 370 (10) $[M^+ +1]$, 264 (44), 231 (10), 215 (43), 156 (100), 140 (13), 107 (19). IR (capillary): ṽ = 3631 (s), 3460 (s, br), 3183 (w), 3056 (m), 3025 (s), 2962 (m), 2802 (w), 2802 (w), 2696 (S), 2475 (s), 2373 (s), 2344 (s), 2282 (s), 2160 (s), 2064 (s), 1985 (s), 1964 (s), 1918 (s), 1890 (s), 1809 (s), 1737 (s), 1702 (s), 1687 (s), 1605 (s), 1582 (s), 1545 (s), 1496 (s), 1170 (m), 896 (s), 856 (w), 822 (s) cm^{-1}. $C_{22}H_{27}NO_2S$ (369.52): calcd. C 71.51, H 7.36, N 3.79; found C 71.64, H 7.77, N 3.65.

General Procedure for the Substitution of Sulfoximine-Substituted Homoallylic Alcohols (*GP1*): $ClCO_2CH(Cl)Me$ (1.3 mmol) was added at room temperature to a solution of the sulfoximine-substituted homoallylic alcohol (1 mmol) in CH_2Cl_2 (10 mL). The progress of the reaction was monitored by TLC (EtOAc/*n*-hexane, 1:9). After the mixture had been stirred at room temperature for 1.5 h, it was concentrated in vacuo. Purification by flash chromatography (EtOAc/*n*-hexane, 1:9) gave the alkenyl/cycloalkenyl chlorohydrin and sulfinamide **4** as colorless oils.

General Procedure for the Elimination of Alkenyl/Cycloalkenyl Chlorohydrins (*GP2*): DBU (1 mmol) was added at room temperature to a solution of chlorohydrin (1 mmol) in CH_2Cl_2 (10 mL). The progress of the reaction was monitored by TLC (EtOAc/*n*-hexane, 1:9). After the mixture had been stirred at room temperature for 1.5 h, CH_2Cl_2 was carefully evaporated under reduced pressure (highly volatile compound!). Conventional workup followed by purification by flash chromatography (EtOAc/*n*-hexane, 1:9) gave the alkenyloxirane as a colorless oil.

(1*R*,2*R*)-2-Chloro-2-(cyclohex-1-enyl)-1-phenylethanol (3a): Treatment of **2a** (550 mg, 1.55 mmol) with $ClCO_2CH(Cl)Me$ (0.2 mL, 1.86 mmol) as described in *GP2* afforded chlorohydrin **3a** (322 mg, 88%, ≥ 98% *de*) and sulfinamide **4** (380 mg, 94%). $[\alpha]_D$ = −10.8 (*c* = 0.45, CH_2Cl_2). ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.34−1.54 (m, 4 H), 1.75−2.00 (m, 2 H), 2.05−2.15 (m, 2 H), 2.66 (br. s, 1 H), 4.51 (d, *J* = 8.5 Hz, 1 H), 4.79 (d, *J* = 8.5 Hz, 1 H), 5.52 (m, 1 H), 7.27−7.35 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.8 (u), 22.2 (u), 24.5 (u), 25.0 (u), 75.3 (d), 76.2 (d), 126.6 (d), 128.0 (d), 128.1 (d), 129.0 (d), 133.7 (u), 139.3 (u) ppm. MS (CI, isobutane): *m*/*z* (%) = 236 $[M^+]$ (11), 218 (66), 201(9), 183 (43), 159 (17), 141(100), 128(18), 115(31), 91 (35). IR (capillary): ṽ = 3450 (m, br), 3062 (m), 3031 (m), 2709 (s), 2667 (s), 1951 (s), 1884 (s),1767 (s), 1632 (s), 1600 (s), 1496 (m), 1372 (s), 1349 (m), 1324 (m), 1249 (m), 1190 (m), 1142 (m), 1085 (m), 1028 (m), 969 (w), 912 (s), 891 (s), 845 (s) cm^{-1}. $C_{14}H_{17}ClO$ (236.74): calcd. C 71.03, H 7.24; found C 71.16, H 6.86.

(1*R*,2*R*)-1-Chloro-1-(cyclohex-1-enyl)-3-methylbutan-2-ol (3b): Treatment of **2b** (520 mg, 1.62 mmol) with $ClCO_2CH(Cl)Me$ (0.21 mL, 1.94 mmol) as described in *GP3* afforded chlorohydrin **3b** (294 mg, 85%, ≥ 98% *de*) and sulfinamide **4a** (393 mg, 93%). $[\alpha\ ]_D$ = −14.2 (*c* = 0.30, CH_2Cl_2). ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.85 (d, *J* = 6.8 Hz, 3 H), 0.95 (d, *J* = 6.8 Hz, 3 H), 1.40−1.70 (m, 4 H), 1.75−1.90 (m, 4 H), 1.95−2.05 (m, 1 H), 2.10−2.20 (br. s, 1 H), 3.55 (dd, *J* = 8.2, *J* = 3.3 Hz, 1 H), 4.35 (d, *J* = 8.2 Hz, 1 H), 5.75 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz)**:** δ = 15.2 (d), 20.9 (d), 24.4 (u), 22.7 (u), 24.1 (u) 25.5 (u) 30.3 (d),74.3 (d), 76.9 (d), 128.5 (d), 135.3 (u) ppm. MS (CI, isobutane): *m*/*z* (%) = 201 $[M^+ -1]$ (2), 180 (4), 185 (9), 167 (35), 150 (33), 149 (100), 135 (14), 123 (22), 107 (14), 95 (19), 79 (11), 69 (19). IR (capillary): ṽ = 3470 (m, br), 3043 (m), 2660 (s), 1730 (s), 1659 (s), 1465 (m), 1368 (m), 1302 (s), 1270 (s), 1235 (m), 1173 (m), 1138 (m), 1061 (m), 971 (s), 920 (m), 891 (s), 848 (s), 817 (s), 778 (s), 715 (w) cm^{-1}. HRMS (EI, 70 eV) calcd. for $C_{11}H_{19}ClO$ 202.112505; found 202.112443.

(1*R*,2*R*)-2-Chloro-2-(cyclohept-1-enyl)-1-phenylethanol (3c): Treatment of **2c** (525 mg, 1.42 mmol) with $ClCO_2CH(Cl)Me$ (0.18 mL, 1.70 mmol) as described in *GP3* afforded the chlorohydrin **3c** (306 mg, 86%, ≥ 98% *de*) and the sulfinamide **4a** (341 mg, 92%). $[\alpha]_D$ = −18.8 (*c* = 1.00, CH_2Cl_2). ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.30−1.45 (m, 3 H), 1.50−1.60 (m, 2 H), 1.8−2.0 (m, 3 H), 2.1−2.2 (m, 1 H), 2.30 (m, 1 H), 2.81 (br. s, 1 H), 4.58 (d, *J* = 8.9 Hz, 1 H), 4.79 (d, *J* = 8.9 Hz, 1 H), 5.65 (m, 1 H), 7.22−7.40 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 26.2 (u), 26.8 (u), 28.2 (u), 29.1 (u), 32.2 (u), 76.4 (d), 77.2 (d), 127.0 (d), 128.30 (d), 128.4 (d), 134.4 (d), 139.5 (u), 139.26 (u) ppm. MS (CI, isobutane): *m*/*z* (%) = 250 (1.5) $[M^+]$, 232 (11), 155 (8), 144 (9), 141 (30), 129 (11), 108 (33), 107 (100), 105 (29), 91 (17), 79 (33), 77 (22). IR (capillary): ṽ = 3444 (s, br), 3020 (m), 2927 (w), 2853 (m), 1954 (s), 1882 (s),1703 (w), 1601 (s), 1493 (s), 1383 (s), 1318 (s), 1275 (s), 1147 (s), 1053 (m), 965 (s), 915 (s), 852 (s) cm^{-1}. HRMS (EI, 70 eV) calcd. for $C_{15}H_{19}ClO$: 250.112421; found 250.112443.

(2*S*,3*R*)-2-(Cyclohex-1-enyl)-3-phenyloxirane (5a): Treatment of **3a** (430 mg, 1.82 mmol) with DBU (0.29 mL, 2.00 mmol) as described in *GP2* afforded the oxirane **5a** (342 mg, 94%, ≥ 98% *de*). $[\alpha]_D$ = −14.0 (*c* = 0.30, CH_2Cl_2). ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.20−1.34 (m, 4 H), 1.40−1.50 (m, 2 H), 1.65−2.00 (m, 2 H), 3.62 (m, 1 H), 4.12 (d, *J* = 4.4 Hz, 1 H), 5.71 (m, 1 H), 7.20−7.25 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.1 (u), 22.3 (u), 22.5 (u), 25.4 (u), 58.3 (d), 61.1 (d), 126.7 (d), 127.3(d), 127.5(d), 125.4 (d), 130.2 (u), 135.4 (u) ppm. MS (CI, isobutane): *m*/*z* (%) = 201 (9) $[M^+ +1]$, 200 (63) $[M^+]$, 199 (100), 171 (72), 157(36), 143 (19), 129 (91), 105 (78), 91 (71). IR (capillary): ṽ = 3087 (m), 3061 (m), 3031 (m), 2859 (w), 2835 (w), 2673 (s), 1951 (s), 1885 (s), 1723 (m), 1671 (m), 1605 (m), 1585 (s), 1451 (w), 1410 (m), 1337 (m), 1315 (m), 1270 (m), 1251 (m), 1195 (m), 1137 (m), 1001 (m), 967 (m), 921 (w), 830 (m), 801 (m) cm^{-1}. HRMS (EI, 70 eV) calcd. for $C_{14}H_{16}O$ 200.120047; found 200.120115.

(2*S*,3*R*)-2-(Cyclohex-1-enyl)-3-isopropyloxirane (5b): Treatment of **3b** (420 mg, 2.08 mmol) with DBU (0.34 mL, 2.29 mmol) as described in *GP2* afforded the oxirane **5b** (318 mg, 92%, ≥ 98% *de*). $[\alpha]_D$ = −43.4 (*c* = 0.35, CH_2Cl_2). ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.85 (d, *J* = 6.6 Hz, 3 H), 1.05 (d, *J* = 6.6 Hz, 3 H), 1.38−1.47 (m, 1 H), 1.50−1.70 (m, 4 H), 1.90−2.08 (m, 4 H), 2.68 (dd, *J* = 4.1, *J* = 9.0 Hz, 1 H), 3.29 (m, 1 H), 5.61 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 18.8 (d), 20.1 (d) 22.5 (u), 22.6 (u), 24.5 (u), 25.7 (d), 26.4 (u), 58.8 (d), 64.6 (d), 122.7 (d), 131.0 (u) ppm. MS (CI, isobutane): *m*/*z* (%) = 166 (45) $[M^+]$, 150 (11), 149 (100), 113 (11), 71 (18), 70 (14), 57 (26), 55 (11). IR (capillary)**:** ṽ **=** 2932 (w), 2669 (s), 1729 (s), 1673 (s), 1462 (m), 1387 (s), 1364 (s), 1340 (s), 1252 (s), 1162 (s), 1136 (s), 1075 (s), 958 (m), 922 (m), 828 (s), 801 (s) cm^{-1}. HRMS (EI, 70 eV) calcd. for $C_{11}H_{18}O$ 166.135698; found 166.135765.

(2*S*,3*R*)-2-(Cyclohept-1-enyl)-3-phenyloxirane (5c): Treatment of **3c** (450 mg, 1.80 mmol) with DBU (0.29 mL, 1.98 mmol) as described in *GP2* afforded the oxirane **5c** (347 mg, 90%, ≥ 98% *de*). $[\alpha]_D = -7.1$ (c = 1.80, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.20−1.34 (m, 4 H), 1.40−1.55 (m, 4 H), 1.60−2.00 (m, 2 H), 3.67 (m, 1 H), 4.13 (d, J = 4.2 Hz, 1 H), 5.88−5.93 (m, 1 H), 7.22−7.28 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 25.7 (u), 26.7 (u), 28.0 (u), 29.7 (u), 32.1 (u), 58.6 (d), 62.2 (d), 126.9 (d), 127.4 (d), 127.5 (d), 129.8 (d), 135.2 (u), 135.6 (u) ppm. MS (CI, isobutane): m/z (%) = 215 (100) [M$^+$ +1], 214 [M$^+$] (27) 197 (34), 105 (27). IR (capillary): ṽ = 3030 (m), 2696 (s), 1946 (s), 1880 (m), 1730 (s), 1671 (s), 1605 (s), 1540 (s), 1495 (s), 1450 (w), 1407 (s), 1377 (s), 1274 (s), 1221 (s), 1193 (s), 1075 (s), 1027 (s), 966 (s), 899 (m), 860 (m) cm^{-1}. $C_{15}H_{18}O$ (214.30): calcd. C 84.07, H 8.47; found C 84.28, H 8.27.

(1*R*,2*S*)- and (1*R*,2*R*)-2-Chloro-5-methyl-1-phenylhex-3-en-1-ol (*anti*-8a and *syn*-8a): Treatment of **7a** (650 mg, 1.89 mmol) with $ClCO_2CH(Cl)Me$ (0.26 mL, 2.46 mmol) as described in *GP1* afforded a mixture of chlorohydrins *anti*-**8a** and *syn*-**8a** (377 mg, 89%) in a ratio of 78:22 together with sulfinamide **4a** (465 mg, 94%).

Compound *syn*-8a: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.80 (d, J = 6.7 Hz, 3 H), 0.86 (d, J = 6.7 Hz, 3 H), 2.22−2.30 (m, 1 H), 2.32−2.40 (br. s, 1 H), 4.52 (dd, J = 7.3, J = 8.2 Hz, 1 H), 4.69 (d, J = 7.3 Hz, 1 H), 5.36−5.46 (m, 2 H), 7.28−7.36 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.6 (d), 21.7 (d), 30.6 (d), 70.0 (d), 77.6 (d), 123.6 (d), 139.2 (u), 142.9 (d) ppm.

Compounds *syn*-8a + *anti*-8a: MS (CI, isobutene): m/z (%) = 207 (23), 190 (14), 189 (100), 173 (10), 107 (13). IR (capillary): ṽ = 3425 (m, br), 3085 (s), 3062 (m), 3031 (m), 2929 (w), 2870 (w), 2386 (s), 2286 (s), 1951 (s), 1882 (s), 1807 (s), 1663 (m), 1601 (s), 1546 (s), 1494 (m), 1454 (w), 1385 (m), 1366 (m), 1328 (m), 1232 (s), 1189 (m), 1054 (w), 1028 (w), 917 (s), 854 (m) cm^{-1}.

Compound *anti*-8a: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.90 (d, J = 6.7 Hz, 3 H), 0.93 (d, J = 6.7 Hz, 3 H), 2.22−2.30 (m, 1 H), 2.32−2.40 (br. s, 1 H), 4.50 (m, 1 H), 4.90 (d, J = 4.7 Hz, 1 H), 5.46−5.54 (m, 2 H), 7.25−7.35 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.8 (d), 31.1 (d), 68.1 (d), 77.1 (d), 122.4 (d), 139.3 (u), 143.6 (d) ppm.

(1*R*,2*S*)- and (1*R*,2*R*)-2-Chloro-4-cyclohexyl-1-phenylbut-3-en-1-ol (*anti*-8b and *syn*-8b): Treatment of **7b** (400 mg, 1.04 mmol) with $ClCO_2CH(Cl)Me$ (0.26 mL, 2.46 mmol) as described in *GP1* afforded a mixture of chlorohydrins *anti*-**8b** and *syn*-**8b** (249 mg, 90%) in a ratio of 74:26 together with sulfinamide **4a** (255 mg, 93%).

Compound *syn*-8b: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.85−1.35 (m, 5 H), 1.48−1.72 (m, 5 H), 1.80−1.86 (m, 1 H), 2.55−2.59 (br. s, 1 H), 4.50−4.55 (m, 1 H), 4.68 (d, J = 7.6 Hz, 1 H), 5.38−5.54 (m, 2 H), 7.28−7.36 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 25.6 (u), 25.7 (u), 25.9 (u), 32.1 (u), 32.2 (u), 40.1 (d), 68.1 (d), 70.3 (d), 123.9 (d), 139.1 (u), 141.9 (d) ppm.

Compounds *syn*-8b + *anti*-8b: MS (CI, isobutane): m/z (%) = 264 (38) [M$^+$], 263 (14), 262 (100), 183 (8), 126 (14). IR (capillary): ṽ = 3188 (m, br), 3028 (m), 2924 (w), 2853 (w), 2800 (m), 1656 (m), 1448 (w), 1384 (m), 1330 (m), 1235 (w), 1203 (m), 1177 (m), 1146 (w), 1107 (m), 1081 (w), 1049 (w), 997 (m), 913 (m), 865 (w), 851 (w) cm^{-1}. $C_{16}H_{21}ClO$ (264.79): calcd. C 72.58, H 7.99; found C 72.59, H 8.20.

Compound *anti*-8b: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.85−1.35 (m, 5 H), 1.48−1.72 (m, 5 H), 1.90−1.98 (m, 1 H), 2.84 (br. s, 1 H), 4.50−4.55 (m, 1 H), 4.90 (d, J = 4.6 Hz, 1 H), 5.38−5.54 (m, 2 H), 7.28−7.36 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 25.7 (u), 25.7 (u), 25.9 (u), 32.1 (u), 32.2 (u), 39.9 (d), 68.1 (d), 70.3 (d), 122.7 (d), 139.1 (u), 142.6 (d) ppm.

(3*R*,2*R*)- and (3*R*,2*S*)-2-(3-Methylbut-1-enyl)-3-phenyloxirane (*trans*-9a and *cis*-9a): Treatment of a mixture of *anti*-**8a** and *syn*-**8a** (640 mg, 2.85 mmol) with DBU (0.43 mL, 2.85 mmol) as described in *GP2* afforded a mixture of the oxiranes *trans*-**9a** and *cis*-**9a** (504 mg, 94%) in a ratio of 78:22.

Compound *cis*-9a: ^{1}H NMR ($CDCl_3$,400 MHz): δ = 0.88 (d, J = 7.4 Hz, 3 H), 0.91 (d, J = 6.9 Hz, 3 H), 2.21 (octd, J = 6.6, J = 1.1 Hz, 1 H), 3.64 (dd, J = 4.1, J = 8.5 Hz, 1 H), 4.20 (d, J = 4.4 Hz, 1 H), 4.97 (ddd, J = 8.5, J = 15.4, J = 1.1 Hz, 1 H), 5.94 (dd, J = 6.9, J = 15.4 Hz, 1 H), 7.25−7.37 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.9 (d), 30.9 (d), 58.9 (d), 59.8 (d), 120.2 (d), 126.3 (d), 127.1 (d), 127.9 (d), 135.29 (u), 146.5 (d) ppm.

Compounds *cis*-9a + *trans*-9a: MS (CI, isobutane): m/z (%) = 188 (6) [M$^+$], 171 (16), 106 (10), 105 (100), 77 (34), 51 (12). IR (capillary): ṽ = 3063 (s), 3031 (m), 2963 (w), 2872 (m), 1963 (s), 1884 (s), 1692 (m), 1623 (s), 1598 (s), 1580 (s), 1495 (m), 1465 (m), 1386 (m), 1315 (s), 1179 (s), 1136 (s), 1106 (w), 1068 (w), 1009 (m), 969 (m), 894 (m), 842 (s), 760 (w) cm^{-1}. $C_{13}H_{16}O$ (188.27): calcd. C 82.93, H 8.57; found C 82.94, H 8.69.

Compound *trans*-9a: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.01 (d, J = 6.6 Hz, 3 H), 1.03 (d, J = 6.6 Hz, 3 H), 2.32−2.41 (octd, J = 6.9, J = 1.4 Hz, 1 H), 3.33 (dd, J = 1.9, J = 8.0 Hz, 1 H), 3.76 (d, J = 2.2 Hz, 1 H), 5.26−5.30 (ddd, J = 8.0, J = 15.7, J = 1.4 Hz, 1 H), 5.94−5.98 (dd, J = 6.6, J = 15.4 Hz, 1 H), 7.25−7.37 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.1 (d), 30.9 (d), 60.2 (d), 63.3 (d), 124.0 (d), 125.5 (d), 127.1 (d), 127.9 (d), 137.40 (u), 144.2 (d) ppm.

(3*R*,2*R*)- and (3*R*,2*S*)-2-(2-Cyclohexylvinyl)-3-phenyloxirane (*trans*-9b and *cis*-9b): Treatment of a mixture of *anti*-**8b** and *syn*-**8b** (450 mg, 1.7 mmol) with DBU (0.28 mL, 1.87 mmol) as described in *GP2* afforded a mixture of oxiranes *trans*-**9b** and *cis*-**8b** (361 mg, 93%) in a ratio of 74:26.

Compound *cis*-9b: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.90−1.30 (m, 5 H), 1.60−1.80 (m, 5 H), 3.64 (dd, J = 4.4, J = 8.8 Hz, 1 H), 4.20 (d, J = 4.4 Hz, 1 H), 1.95−2.05 (m, 1 H), 4.97 (ddd, J = 8.5, J = 15.4, J = 1.1 Hz, 1 H), 5.89 (dd, J = 6.6, J = 15.3 Hz, 1 H), 7.25−7.37 (m, 5 H,) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 26.2 (u), 26.5 (u), 29.7 (u), 32.7 (u), 32.8 (u), 41.1 (d), 60.6 (d), 63.7 (d), 120.9 (d), 145.5 (d), 125.8 (d), 128.7 (d), 128.3 (d), 135.7 (u) ppm.

Compounds *cis*-9b + *trans*-9b: MS (CI, isobutane): m/z (%) = 228 (5) [M$^+$], 145 (100), 144 (12), 146 (26), 127 (8), 117 (36), 105 (10), 91 (29), 77 (13), 55 (18). IR (capillary): ṽ = 3087 (s), 3063 (s), 2666 (s), 1948 (s), 1881 (s), 1807 (s), 1762 (s), 1691 (s), 1663 (s), 1604 (m), 1542 (s), 1497 (m), 1449 (w), 1421 (s), 1374 (m), 1349 (s), 1255 (s), 1197 (s), 1152 (s), 1072 (s), 1027 (s), 966 (w), 916 (s), 878 (w), 849 (m) cm^{-1}. HRMS (EI, 70 eV) calcd. for $C_{16}H_{20}O$ 228.151504; found 228.151415.

Compound *trans*-9b: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.90−1.30 (m, 5 H), 1.55−1.80 (m, 5 H), 3.32 (dd, J = 1.9, J = 8.0 Hz, 1 H), 3.76 (d, J = 1.9 Hz, 1 H), 1.95−2.05 (m, 1 H), 5.28 (ddd, J = 8.0, J = 15.6, J = 1.4 Hz, 1 H), 5.90 (dd, J = 6.6, J = 15.3 Hz, 1 H), 7.25−7.37 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 26.3

(u), 26.4 (u), 30.1 (u), 32.8 (u), 32.9 (u), 40.8 (d), 59.4 (d), 60.3 (d), 120.9 (d), 143.3 (d), 126.7 (d), 127.8 (d), 127.7 (d), 137.6 (u) ppm.

Synthesis of the Alkenyloxiranes *trans*-9a and *cis*-9a from 11a: Treatment of **11a** (400 mg, 1.04 mmol) with $ClCO_2CH(Cl)Me$ (1.32 mL, 1.25 mL) as described in *GP1* afforded a mixture of chlorohydrins *anti*-**8a** and *syn*-**8a** together with sulfinamide **4a** (253 mg, 93%). Treatment of the mixture of chlorohydrins with DBU (0.15 mL, 1 mmol) as described in *GP2* afforded a mixture of *trans*-**9a** and *cis*-**9a** (203 mg, 89%) in a ratio of 75:25, also containing 11% of the corresponding *Z* isomers.

Synthesis of the Alkenyloxiranes *trans*-9b and *cis*-9b from 11b: Treatment of **11b** (344 mg, 1.00 mmol) with $ClCO_2CH(Cl)Me$ (0.13 mL, 1.2 mmol) as described in *GP1* afforded a mixture of chlorohydrins *syn*-**8b** and *anti*-**8b** together with sulfinamide **4a** (243 mg, 93%). Treatment of the mixture of chlorohydrins with DBU (0.15 mL, 1 mmol) as described in *GP2* afforded a mixture of the oxiranes *trans*-**9b** and *cis*-**9b** (166 mg, 88%) in a ratio of 80:20, also containing 7% of the corresponding (*Z*) isomers.

Sulfinamide (4a): $[\alpha]^{20}_{D} = -69.4$ ($c = 1.00$, CH_2Cl_2). ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 1.90$ (d, $J = 6.0$ Hz, 3 H), 2.70 (d, $J = 5.5$ Hz, 3 H), 6.55−6.60 (m, 1 H), 7.25−7.37 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 25.2$ (d), 25.3 (d), 83.5 (d) 124.9 (d), 129.2 (d), 131.95 (d), 141.71 (u) ppm. MS (CI, isobutane): *m*/*z* (%) = 261 [M^+] (2), 201 (3), 199 (40), 142 (22), 126 (10), 125 (100), 105 (12), 97 (21), 94 (25), 78 (12), 74 (10), 59 (11), 51 (16), 45 (18). IR (capillary): $\tilde{\nu} = 3063$ (m), 2940 (m), 1906 (w), 1949 (s), 1728 (s), 1726 (s), 1663 (s), 1495 (m), 1449 (m), 1371 (s), 1348 (s), 1260 (s), 1196 (s), 1071 (s), 1027 (s), 967 (w), 916 (s), 879 (m), 843 (s) cm^{-1}. HRMS (EI, 70 eV) calcd. for $C_{10}H_{12}SClNO_3$ 261.022674; found 261.022644.

Synthesis of Polymer-Bound Vinylic Sulfoximine 15: A suspension of resin **13** (10.94 g of 0.78 mmol/g, 8.57 mmol) in dry THF (140 mL) was stirred at room temperature for 30 min and then cooled to −78 °C. *n*BuLi (7.0 mL of 1.6 m in hexane, 11.2 mmol) was added. After the mixture had been stirred at −78 °C for 30 min, the cooling bath was removed for 15 min, the mixture was then again cooled to −78 °C, and isovaleraldehyde (1.2 mL, 11.1 mmol) was added dropwise. The mixture was stirred for 30 min at −78 °C and then for 1.5 h at room temperature, and $ClCO_2Me$ (0.87 mL, 11.2 mmol) was subsequently added at −78 °C. After the mixture had been stirred for 15 min at −78 °C, it was warmed to room temperature and stirring at this temperature was continued for 1 h. The mixture was then once more cooled to −78 °C, and DBU (1.70 mL, 11.3 mmol) was added. The mixture was warmed to room temperature over 15 h, and aqueous NH_4Cl (30 mL) was added. The resin was filtered and washed successively with water (3 × 30 mL), EtOH (3 × 30 mL), and CH_2Cl_2 (3 × 30 mL). Drying in vacuo gave resin **15** (11.10 g). IR (KBr): $\tilde{\nu} = 3081$ (s), 3057 (s), 3024 (s), 2960 (s), 1944 (m), 1872 (m), 1804 (m), 1745 (s), 1678 (m), 1628 (m), 1601 (s), 1583 (m), 1510 (m), 1493 (s), 1442 (s), 1420 (s), 1368 (s), 1251 (s), 1126 (s), 1080 (s), 1021 (s), 972 (s), 937 (s), 906 (s), 840 (m), 815 (m) cm^{-1}.

Synthesis of Polymer-Bound Allylic Sulfoximine 16: Resin **15** (11.1 g) was suspended in dry CH_3CN (70 mL), and DBU (2.5 mL, 16.7 mmol) was added. After the mixture had been stirred at 60 °C for 7 days, aqueous NH_4Cl (30 mL) was added and the resin was filtered and washed successively with water (3 × 30 mL), EtOH (3 × 30 mL), and CH_2Cl_2 (3 × 30 mL). Drying in vacuo afforded resin **16** (10.2 g). IR (KBr): $\tilde{\nu} = 3081$ (s), 3058 (m), 3024 (m), 2919 (s), 2848 (m), 1943 (m), 1870 (w), 1803 (w), 1748 (w), 1709 (w), 1662 (w), 1600 (m), 1492 (s), 1448 (s), 1364 (m), 1261 (m), 1217 (m), 1131 (m), 1068 (m), 1026 (m), 969 (m), 904 (m), 842 (m), 757 (s), 696 (s) cm^{-1}.

Off-Bead Analysis of Polymer-Bound Allylic Sulfoximine 16: *m*-$ClC_6H_4CO_3H$ (1 g, 30% water, 4 mmol) and aqueous HCl (0.3 mL of 0.1 m, 0.03 mmol) were added to a suspension of resin **16** (1 g) in THF (15 mL). The mixture was then heated at 40 °C for 15 h and then cooled to room temperature. After addition of aqueous NaOH (50 mL of 1 m) to the mixture, the resin was filtered and washed successively with water (5 × 20 mL) and Et_2O (5 × 20 mL). The aqueous layer was extracted with Et_2O (3 × 20 mL), and the combined organic phases were dried ($MgSO_4$). Concentration in vacuo gave a mixture of sulfones **22**+**23**, **21**, **20**, and **19** (165 mg) in a ratio of 21:1.5:1:2 (^1H NMR). Chromatography of the mixture (EtOAc/*n*-hexane, 4:1) afforded the pure sulfones.

4-Methyl-1-(phenylsulfonyl)pent-1-en-3-ol (23): ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.91$ (d, $J = 6.9$ Hz, 3 H), 0.95 (d, $J = 6.9$ Hz, 3 H), 1.82 (br. S, 1 H), 1.87 (dsept, $J = 6.9$, $J = 4.9$ Hz, 1 H), 4.21 (m, 1 H), 6.62 (dd, $J = 14.8$, $J = 1.9$ Hz, 1 H), 7.01 (dd, $J = 14.8$, $J = 3.9$ Hz, 1 H), 7.52−7.67 (m, 3 H), 7.87−7.97 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 17.1$ (d) 18.2 (d), 33.6 (d), 74.8 (d), 127.4 (d) 129.1 (d), 130.40 (d) 133.2 (d), 140.19 (u), 146.7 (d) ppm.

(*E*)-(4-Methylpent-2-enylsulfonyl)benzene (22): ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.87$ (d, $J = 6.6$ Hz, 6 H), 2.23 (d, $J = 6.6$ Hz, 1 H), 3.74 (d, $J = 6.3$ Hz, 2 H), 5.32−5.45 (m, 2 H), 7.50−7.67 (m, 3 H), 7.83−7.94 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 22.1$ (d), 31.4 (d), 60.3 (u), 113.5 (d), 128.7 (d) 129.1 (d), 133.9 (d), 138.2 (u), 148.5 (d) ppm.

(*Z*)-(4-Methylpent-2-enylsulfonyl)benzene (21): ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.71$ (d, $J = 6.6$ Hz, 6 H), 2.19−2.29 (m, 1 H), 3.87 (d, $J = 8.0$ Hz, 2 H), 5.25−5.35 (m, 1 H), 5.52 (tt, $J = 10.7$, $J = 1.1$ Hz, 1 H), 7.50−7.59 (m, 2 H), 7.61−7.67 (m, 1 H), 7.87−7.92 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 22.2$ (d), 26.8 (d), 55.2 (u), 112.5 (d), 128.3 (d) 128.8 (d), 133.4 (d), 138.3 (u) 146.1 (d) ppm.

(*E*)-(4-Methylpent-1-enylsulfonyl)benzene (20): ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.91$ (d, $J = 6.9$ Hz, 6 H), 1.72−1.84 (m, 1 H), 2.11 (m, 2 H), 6.32 (dm, $J = 15.1$ Hz, 1 H), 6.98 (dt, $J = 15.1$, $J = 7.4$ Hz, 1 H), 7.50−7.62 (m, 3 H), 7.86−7.90 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 22.2$ (d), 27.6 (d), 40.47 (u), 127.3 (d) 129.0 (d), 131.0 (d) 133.2 (d), 140.5 (u), 145.9 (d) ppm.

(Methylsulfonyl)benzene (19): ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.06$ (s, 3 H), 7.54−7.71 (m, 3 H), 7.90−7.98 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 44.6$ (d), 127.4 (d) 129.5 (d), 133.8 (d), 140.6 (u) ppm.

Synthesis of Polymer-Bound Sulfoximine-Substituted Homoallylic Alcohol 17: A suspension of resin 16 (6 g) in dry THF (80 mL) was stirred for 30 min at room temperature and then cooled to −78 °C. *n*BuLi (4.1 mL of 1.6 m in hexane, 6.6 mmol) was added dropwise. The mixture was warmed to room temperature, then cooled to −78 °C, and $ClTi(NEt_2)_3$ (2.1 mL, 6.6 mmol) was added dropwise. The mixture was stirred for 15 min at −78 °C and then warmed to room temperature. After the mixture had been stirred for 2 h at this temperature, benzaldehyde (1.2 mL, 12.0 mmol) was added dropwise and stirring was continued for 3 h. Aqueous $(NH_4)_2CO_3$ (100 mL) was then added and the mixture was stirred for 30 min. The resin was filtered and washed successively with aqueous $(NH_4)_2CO_3$ (3 × 20 mL), water (3 × 20 mL), EtOH (3 × 20 mL), and CH_2Cl_2 (3

× 20 mL). Drying in vacuo gave resin **17** (6.79 g). IR (KBr): $\tilde{\nu}$ = 3651 (w), 3424 (m), 3081 (w), 3058 (w), 3023 (m), 2917 (s), 2848 (m), 1942 (w), 1870 (w), 1802 (w), 1655 (w), 1600 (s), 1543 (w), 1491 (s), 1448 (s), 1382 (w), 1364 (w), 1253 (w), 1202 (m), 1124 (m), 1078 (m), 1025 (m), 967 (w), 906 (m) cm^{-1}.

Substitution of the Polymer-Bound Sulfoximine-Substituted Homoallylic Alcohol 17: Resin **17** (5 g) was suspended in dry CH_2Cl_2 (50 mL), and $ClCO_2CH(Cl)Me$ (0.53 mL, 4.85 mmol) was added dropwise. After the mixture had been stirred for 2.5 h at room temperature, the resin was filtered and washed with CH_2Cl_2 (5 × 20 mL). Concentration of the combined organic phases in vacuo gave a crude mixture of *syn*-**8a** with 70% *ee* and *anti*-**8a** of ≥ 53% *ee* in a ratio of 2:1 (^{1}H NMR). Chiracel-OD-H; *n*-hexane/*i*PrOH, 99:1 isocratic, flow 0.7 mL/min, 20 °C, t_R [(1*S*,2*S*)-**8a**] = 25.37 min, t_R [(1*S*,2*R*)-**8a**] = 28.79 min, t_R [(1*R*,2*R*)-**8a**] = 32.79 min, t_R [(1*R*,2*S*)-**8a**] = 49.41 min. Because of an overlap of the peaks of (1*S*,2*R*)-**8a** and that of an impurity, no more accurate determination of the *ee*-value of *anti*-**8a** was possible.

The mixture of the crude chlorohydrins *syn*-**8a** and *anti*-**8a** was dissolved in dry CH_2Cl_2 (10 mL) and then treated with DBU (0.6 mL, 4.0 mmol), and the mixture was stirred for 2 h at room temperature. Concentration in vacuo and purification by column chromatography (silica gel, EtOAc/*n*-hexane, 1:9) gave a mixture of the oxiranes *cis*-**9a** and *trans*-**9a** (232 mg, 34% overall yield based on **12**) in a ratio of 2:1.

(*S*)-Methyl Phenyl Sulfoxide (28): MeMgCl (1.76 mL, 22wt% in THF, 5.22 mmol) was added at −78 °C to a solution of **4a** (681 mg 2.61 mmol) in THF (15 mL). After the mixture had been stirred for 1 h, saturated aqueous NH_4Cl was added and the aqueous phase was extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification by chromatography (EtOAc/*n*-hexane, 4:1) afforded the sulfoxide **28** (310 mg, 85%) of 96% *ee* [GC, octakis(2,3-*O*-dipentyl-*O*-methyl)-γ-cyclodextrin column] as a colorless oil. $[\alpha]^{25}_D = -159.6$ (*c* = 3.05, CH_2Cl_2).

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