N-Methylsulfonimidoyl-Substituted (2-Alkenyl)titanium Complexes: Application to the Synthesis of β- and δ-Sulfonimidoyl-Substituted Chiral Homoallylic Alcohols, X-ray Crystal Structure Analysis, and Fluxional Behavior

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Enantiopure acyclic (*E*)- and (*Z*)-configured allylic sulfoximines have been synthesized from *N*,*S*-dimethyl-*S*-phenylsulfoximine and aldehydes by the addition–elimination–isomerization route through the intermediate generation of the corresponding (*E*)-configured vinylic sulfoximines. Isomerization of the vinylic sulfoximines with DBU preferentially afforded the corresponding (*Z*)-configured allylic sulfoximines, which were subsequently isomerized by DBU to preferentially yield the (*E*)-isomers. Titanation of lithiated (*E*)-configured allylic sulfoximines with $ClTi(OiPr)_3$ furnished the corresponding bis(2-alkenyl)diisopropyloxytitanium(IV) complexes, which reacted with aldehydes in the presence of $ClTi(OiPr)_3$ with high regio- and diastereoselectivities at the γ-position to give the corresponding (*Z*)-*anti*-configured δ-*N*-methylsulfonimidoyl-substituted homoallylic alcohols in good yields. In the absence of $ClTi(OiPr)_3$ at low temperatures, only one allylic moiety of the bis(alkenyl)diisopropyloxytitanium complex is transferred to the aldehyde. In this way, a cyclic lithiated allylic sulfoximine has been converted with high regio- and diastereoselectivity to the corresponding homoallylic alcohols bearing a vinylic sulfonimidoyl group. Titanation of lithiated (*E*)- and (*Z*)-configured allylic sulfoximines with $ClTi(NEt_2)_3$ afforded the corresponding mono(2-alkenyl)tris(diethylamino)titanium(IV) complexes, which reacted with aldehydes with moderate to high regioselectivities and high diastereoselectivities preferentially at the α-position to give the corresponding *syn*-configured β-*N*-methylsulfonimidoyl-substituted homoallylic alcohols along with the (*Z*)-*anti*-configured δ-*N*-methylsulfonimidoyl-substituted homoallylic alcohols in good yields. In this way, the cyclic lithiated allylic sulfoximine was converted with high regio- and diastereoselectivity to the corresponding isomeric homoallylic alcohols bearing an allylic sulfonimidoyl group. In the case of mono(alkenyl)tris(diethylamino)titanium(IV) complexes, the regioselectivity of their reactions with aldehydes has been found to depend on the size of the substituent at the CC double bond and the aldehyde, as well as on the configuration of the double bond. Reaction of racemic lithiated *N*-methyl-*S*-(3,3-diphenyl-2-propenyl)-*S*-phenylsulfoximine with $ClTi(OiPr)_3$ afforded the corresponding bis(alkenyl)diisopropyloxytitanium(IV) complex. X-ray structure analysis revealed a distorted octahedral *cis*,*cis*,*cis*-configured bis(2-alkenyl)diisopropyloxytitanium(IV) complex, in which the allylic moieties are coordinated in a bidentate fashion through C-α and the N atom to the Ti atom, both having the relative configuration R_SS_C. In solution, the titanium complex shows fluxional behavior, which is characterized by topomerization of the isopropyloxy groups and allylic moieties. The exchange of the latter occurs with retention of the configuration at C-α.

Introduction

Sulfoximines have emerged as highly useful starting materials and auxiliaries in stereoselective synthesis.[1−3] Their versatility originates mainly from the endowment of the sulfonimidoyl group with an almost unique combination of the features, namely chirality, carbanion stabilization, nucleofugacity, basicity, nucleophilicity, and a low redox potential. Recent examples where several of these characteristics have been exploited are the asymmetric syntheses of prostacyclin analogs,[4,5] which utilize transition metal mediated cross-coupling reactions of vinylic and allylic sulfoximines with organometallics for the formation of key CC bonds.

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Having developed syntheses of enantiopure allylic *N*-methylsulfoximines of type **I**[6−9] (Scheme 1) during the course of the aforementioned work, we were interested to see whether both a regio- and stereoselective hydroxyalkylation of **I** leading to formation of the δ- and β-*N*-methylsulfonimidoyl-substituted homoallylic alcohols **II** and **III**, respectively, could be brought about. Although differently substituted homoallylic alcohols of types **II** or **III** can be obtained by several methods, no single method is available whereby both can be secured in enantio- and diastereopure form from a common substituted allylic carbanion through adjustment of the reaction conditions.[10−12] Selective conversions of the vinylic sulfoximines **II** and allylic sulfoximines **III** to the enantio- and diastereopure building blocks **IV**−**VIII** can be envisaged considering (i) the facile lithiation of vinylic sulfoximines[4,13−17] and allylic sulfoximines[2,5,11,12,18−24] at C-α, (ii) the ready nickel-catalyzed cross-coupling reaction of vinylic sulfoximines with

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organometallics,[4,15,25,26] (iii) the excellent Michael acceptor properties of vinylic sulfoximines and their (dialkylamino)sulfoxonium salts,[27−30] (iv) the facile reduction of sulfoximines,[31] (v) the ready S_N reaction of allylic sulfoximines with copper organyls,[5−7] (vi) the facile elimination of β-hydroxy (dialkylamino)sulfoxonium salts under formation of epoxides,[32,33] and (vii) the ready substitution of allylic sulfoximines.[34] Thus, if attainable, sulfoximines **II** and **III** would be expected to considerably expand the range of synthetic possibilities available through the use of either enantio- and diastereopure homoallylic alcohols of types **II** and **III** bearing an alkyloxy group,[35−42] a Cl atom,[43−45] a (dialkylamino)carbonyloxy group,[10e,46−51] or a silyl group[52−54] instead of the sulfonimidoyl group, or by utilizing aldol-type compounds[55,56] and vinylic epoxides as starting materials.[57] The feasibility of a synthesis of **II** from **I** was indicated by the work of Reggelin et al.,[11,12] who showed that lithium−titanium exchange using $ClTi(OiPr)_3$ of lithiated allyl and crotyl sulfoximines bearing a chiral *N*-(silyloxy)alkyl group instead of the *N*-methyl group allowed their γ-hydroxyalkylation under the highly regio- and diastereoselective formation of vinylic hydroxy sulfoximines of type **II** in medium to good yields.[58] Thus, we hoped that isopropyloxytitanium complexes of Li-**I** would behave similarly and react with aldehydes at the γ-position to give **II**. Although the allylic hydroxy sulfoximines **III** are accessible by the reaction of Li-**I** with aldehydes,[21−24] the diastereoselectivity of this transformation is too low to be synthetically useful. It is generally believed that the regioselective hydroxyalkylation of allylic titanium complexes is due to intramolecular C−C bond formation resulting in a cyclic six-membered transition state following coordination of the aldehyde to the Ti atom.[10e] We thus speculated that in view of the reduced electrophilicity of a tris(dialkylamino)titanyl group as compared to a tris(alkyloxy)titanyl group, dialkylaminotitanium complexes of Li-**I** might perhaps behave differently and react with aldehydes with high regio- and diastereoselectivity at the α-position to furnish the allylic hydroxy sulfoximines **III**. Admittedly, however, previous experience of such a change in the Ti ligands in the case of other hetero-substituted allylic titanium complexes[10e] was not too encouraging. Despite the accessibility of vinylic hydroxy sulfoximines of type **II** bearing a chiral *N*-(silyloxy)alkyl group, our efforts were directed towards the synthesis of the *N*-methylsulfoximines **II** and **III** from **I** for the reasons outlined below. A wide variety of not only cyclic but also acyclic (*Z*)- as well as (*E*)-configured allylic *N*-methylsulfoximines **I** is readily accessible by the routes we have described.[4−9] Of no less importance for our choice was, however, the fact that the chemistry required for the projected syntheses of **IV**−**VIII** from **II** and **III** has already been established for allylic and vinylic sulfoximines bearing an *N*-methyl group.

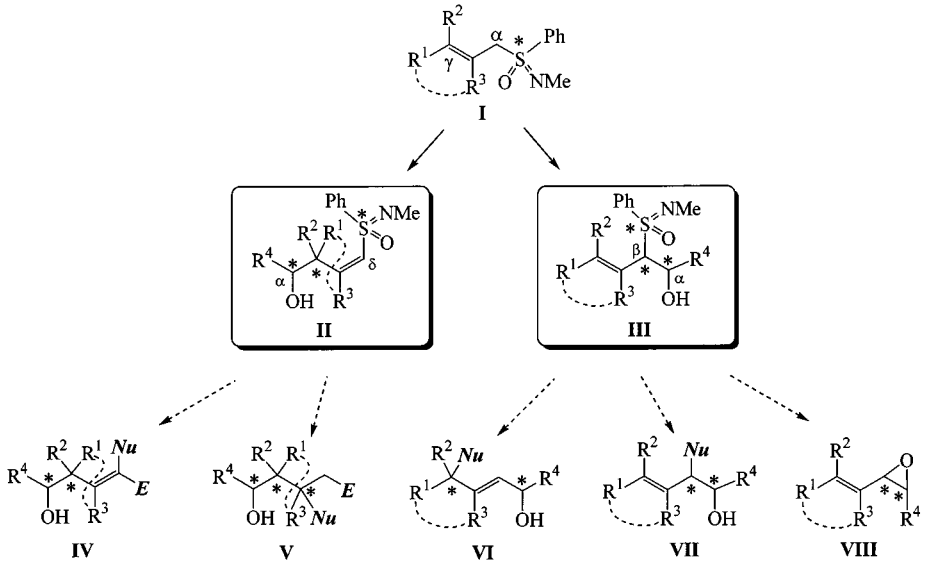
We report herein on studies of the reactions of isopropyloxy- and diethylaminotitanium(IV) complexes of Li-**I** with aldehydes, and on the investigation of the structure of a bis(2-alkenyl)diisopropyloxytitanium(IV) complex of Li-**I** in solution and in the crystal.[59]

Results and Discussion

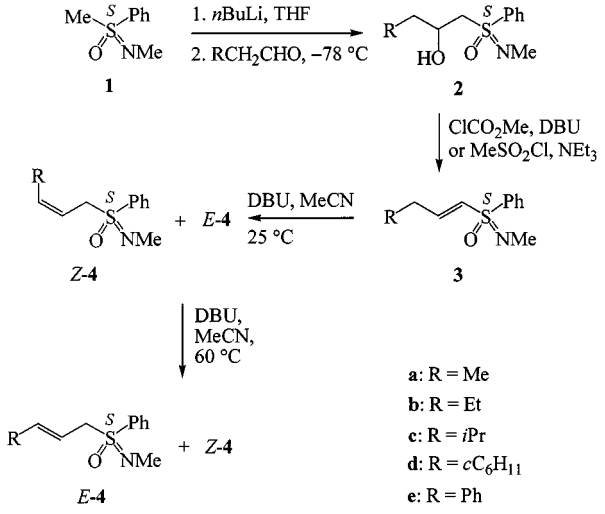
Synthesis of Allylic Sulfoximines

The allylic sulfoximines *E*-**4a**−**d**, *ent*-**4e**, *rac*-*E*-**4a**, *Z*-**4a**−**d**, and *rac*-*Z*-**4a** were synthesized from sulfoximines **1**, *ent*-**1**, and *rac*-**1**, respectively, and the corresponding aldehydes by the addition−elimination−isomerization route (AEI route) (Scheme 2).[4−7] The enantiopure sulfoximines **1** and *ent*-**1** were obtained from (+)- and (−)-*S*-methyl-*S*-phenylsulfoximine,[32,33]] which, in turn, are accessible in enantiopure form on a molar scale through an efficient racemate separation with (+)-10-camphorsulfonic acid[9] following the method of half-quantities. Treatment of **1** with *n*BuLi and propanal gave Li-**2a** as a mixture of epimers, which were not isolated but treated in situ with ClCOOMe and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)[60,61] to afford the (*E*)-configured vinylic sulfoximine **3a** in 78% yield. Reaction of **3a** with DBU at 60 °C in MeCN gave a mixture of the allylic sulfoximines *E*-**4a** and *Z*-**4a** in a ratio of 76:24 in 95% yield. Synthesis of the allylic sulfoximines *E*-**4b** and *Z*-**4b** was accomplished in a similar manner from **1** and *n*-butanal. Thus, reaction of **1** with *n*BuLi and *n*-butanal and subsequent acidic work-up led to the isolation of a mixture of the β-hydroxy sulfoximines **2b** and *epi*-**2b** in 99% yield. Conversion of **2b** and *epi*-**2b** to the corresponding mesylates and in situ treatment of the latter with DBU gave the (*E*)-configured vinylic sulfoximine **3b** in 98% yield. Isomerization of **3b** with DBU at 60 °C in MeCN afforded a mixture of the allylic sulfoximines *E*-**4b** and *Z*-**4b** in a ratio of 75:25 in 91% yield. Synthesis of the vinylic sulfoximine **3c** was carried out in a similar manner. Thus, reaction of **1** with *n*BuLi and 3-methylbutanal furnished a mixture of **2c** and *epi*-**2c** in 95% yield. Mesylation of **2c** and *epi*-**2c** and subsequent elimination as described above led to isolation of the (*E*)-configured vinylic sulfoximine **3c** in 89% yield. Finally, isomerization of **3c** with DBU furnished a mixture of the allylic sulfoximines *E*-**4c** and *Z*-**4c** in a ratio of 83:17 in 93% yield.

The synthesis of the vinylic sulfoximine **3d**, starting from **1** and cyclohexylethanal, was carried out without isolation of the corresponding β-hydroxy sulfoximines **2d** and *epi*-**2d**. Treatment of Li-**2d** and Li-*epi*-**2d** with $MeSO_2Cl$ and NEt_3 led to the isolation of the (*E*)-configured vinylic sulfoximine **3d** in 95% yield. Isomerization of **3d** with DBU at 60 °C in MeCN yielded a mixture of the allylic sulfoximines *E*-**4d** and *Z*-**4d** in a ratio of 90:10 in 96% yield. The (*Z*)- and (*E*)-isomers *Z*-**4a**−**d** and *E*-**4a**−**d** were quantitatively separated by either preparative HPLC or MPLC. It was found that the yields of *E*-**4a**−**d** could be increased by submitting *Z*-**4a**−**d** to DBU treatment at 60 °C in MeCN followed by a chromatographic separation of the isomers. Monitoring of the isomerization of **3a**−**d** with DBU at 25 °C in MeCN by GC analysis and NMR spectroscopy revealed the highly selective formation of the (*Z*)-configured allylic sulfoximines *Z*-**4a**−**d**, which subsequently underwent slow isomerization to *E*-**4a**−**d**. Only after prolonged treatment of the mixtures of (*Z*)- and (*E*)-configured allylic sulfoximines



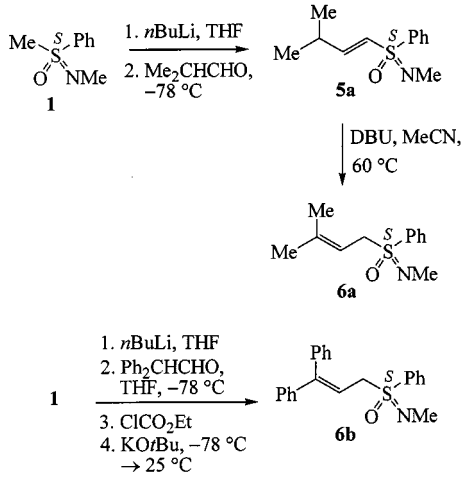
Scheme 1. δ- and β-*N*-Methylsulfonimidoyl-substituted homoallylic alcohols and their potential application to the synthesis of chiral building blocks



Scheme 2. Synthesis of monosubstituted allylic sulfoximines

with DBU at 60 °C in MeCN did the (*E*)-isomers become predominant. Thus, treatment of **3a** with DBU at 20 °C in MeCN until the starting material had been fully consumed yielded a mixture of *Z*-**4a** and *E*-**4a** in a ratio of 70:30. Subjecting this mixture to further treatment with DBU at 60 °C in MeCN afforded a mixture of the (*Z*)- and (*E*)-isomers in a reversed ratio of 24:76. Similar results were obtained in the isomerizations of the other alkyl-substituted vinylic sulfoximines **3b**−**d**. These results suggest that in the isomerization of **3a**−**d** with DBU, the (*Z*)-isomers *Z*-**4a**−**d** are the kinetic products, while the (*E*)-isomers *E*-**4a**−**d** are the thermodynamic products. Similar results have been reported previously for the isomerization of (*E*)-configured vinylic sulfones with DBU.[62] The reason for the preferential formation of (*Z*)-configured allylic sulfoximines and sulfones from the corresponding (*E*)-configured vinylic sulfoximines and sulfones, respectively, under the described conditions is not yet clear. Besides the mechanistic implications, the stepwise isomerization of **3a**−**d** by varying the temperature allows access not only to the (*E*)-configured allylic sulfoximines *E*-**4a**−**d**, but also to their (*Z*)-isomers *Z*-**4a**−**d** as the major component of the mixtures of both. The AEI route has hitherto been found to be best for the synthesis of (*Z*)-configured allylic sulfoximines.[8,11,12]

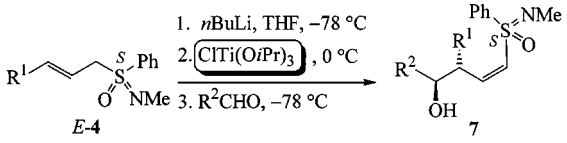
In the aforementioned syntheses of *Z*-**4a**−**d** and *E*-**4a**−**d**, the vinylic sulfoximines **3a**−**d**, and occasionally the hydroxy sulfoximines **2a**−**d** as well, were isolated and purified in order to characterize them. It should be noted, however, that for the attainment of the allylic sulfoximines these steps are not required. We have repeatedly prepared the allylic sulfoximines *Z*-**4a**−**d** and *E*-**4a**−**d** with the same efficiency by a shortened route omitting the isolation of the β-hydroxy sulfoximines **2a**−**d** and the purification of the vinylic sulfoximines **3a**−**d**. The synthesis of acyclic monosubstituted allylic sulfoximines by the AEI route generally requires a chromatographic separation of the (*E*)- and (*Z*)-isomers. If this proves difficult, the pure isomers can be obtained by an alternative stereoselective route starting from the α-chloro derivative of **1** and the corresponding (*E*)- or (*Z*)-configured vinylic lithium organyl.[8] The phenyl-substituted allylic sulfoximine *ent*-*E*-**4e** was obtained directly as the pure (*E*)-isomer in a one-pot process starting from *ent*-**1** and phenylethanal without isolation of any of the intermediates.[7] The disubstituted allylic sulfoximines **6a** and **6b** were prepared in a similar manner as the monosubstituted analogs starting from **1** and the corresponding aldehydes (Scheme 3). The successive treatment of **1** with *n*BuLi, 2-methylpropanal, $MeSO_2Cl$, and NEt_3, followed by the usual work-up, furnished the vinylic sulfoximine **5a** in 67% yield. Isomerization of **5a** with DBU at 60 °C in MeCN gave the allylic sulfoximine **6a** in 75% yield. The allylic sulfoximine **6b** was prepared in 60% yield in a one-pot process involving treatment of **1** with *n*BuLi and diphenylethanal and subsequent addition of ClCOOEt followed by KO*t*Bu.



Scheme 3. Synthesis of disubstituted allylic sulfoximines

Isopropyloxytitanium Complexes: Synthesis of (*Z*)-*anti*-Configured δ-*N*-Methylsulfonimidoyl-Substituted Chiral Homoallylic Alcohols

Titanation[63,64] of the lithiated (*E*)-configured allylic sulfoximines Li-*E*-**4a**−**d** and *ent*-Li-*E*-**4e**[7] with 1.2 equiv. of ClTi(O*i*Pr)$_3$ at −78 °C to 0 °C in THF presumably gave the corresponding bis(2-alkenyl)diisopropyloxytitanium complexes, admixed with equimolar amounts of Ti(O*i*Pr)$_4$ (vide infra). At −78 °C, these reacted with ethanal, propanal, 2-methylpropanal, and benzaldehyde, as anticipated, with high regioselectivities and generally also with high diastereoselectivities, to furnish the (*Z*)-*anti*-configured δ-*N*-methylsulfonimidoyl-substituted homoallylic alcohols **7a**−**c**, **7e**, **7g**, **7i**−**l**, and *ent*-**7n**, respectively (Scheme 4, Table 1, entries 1−3, 6−17). Formation of the corresponding isomeric allylic hydroxy sulfoximines *E*-**10** (vide infra, Scheme 5), derived from α-hydroxyalkylation, could either not be detected or amounted to less than 3%. Much to our surprise, however, the chemical yields (cy) of **7** under these conditions were generally only in the range 37−52%, and the yields of pure **7** were only in the range 31−45%. Approximately half of the starting allylic sulfoximine remained unchanged and could be recovered. Deuterative work-up of the reaction mixtures led to isolation of the (*E*)-configured allylic sulfoximines containing one D atom at the α-position. Increasing the temperature of the reaction mixture to ambient after the addition of the aldehyde did not lead to an increase in the yield of **7**. Instead, in a competing secondary reaction, the α-adducts *E*-**10** and *epi*-*E*-**10** were formed besides γ-adduct **7**. After having carried out most of the hydroxyalkylations, we eventually found that the use of 2.1 equiv. of ClTi(O*i*Pr)$_3$ in the titanation of Li-*E*-**4**, in combination with ambient temperatures for the hydroxyalkylation step, led to an increase in the chemical yields of **7** to 74−82% and in the yields of pure **7** to 45−72% (Table 1, entries 6, 9, 11, and 13). Under these conditions, formation of *E*-**10** and *epi*-*E*-**10** was not observed. It is interesting to note that Ti(O*i*Pr)$_4$, which was presumably present in all the aforementioned hydroxyalkylations, is not capable of effecting the γ-selective transfer of both allylic moieties of the bis(2-alkenyl)diisopropyloxytitanium complexes. Similar results were obtained when Cl$_2$Ti(O*i*Pr)$_2$ was used instead of the monochloro reagent. Thus, treatment of Li-*E*-**4d** with 0.50 equiv. of Cl$_2$Ti(O*i*Pr)$_2$ at −78 °C in THF followed by the addition of 2-methylpropanal gave **7l** in only 10% chemical yield (Table 1, entry 14). However, the use of 1.1 equiv. of Cl$_2$Ti(O*i*Pr)$_2$ under otherwise identical conditions led to an increase in the chemical yield of **7l** to 45% (Table 1, entry 15). Finally, when in the latter experiment the reaction mixture was allowed to warm to ambient temperature after the addition of the aldehyde, the chemical yield of **7l** increased to 78% (Table 1, entry 16) and it could be isolated in 70% yield. Again, the formation of *E*-**10l** and *epi*-*E*-**10l** was not observed under these conditions. Although not all of the described hydroxyalkylations were re-examined using 2.1 equiv. of ClTi(O*i*Pr)$_3$ and ambient reaction temperatures, we are convinced that with these modifications good yields of **7** can generally be achieved.



Scheme 4. Synthesis of acyclic δ-*N*-methylsulfonimidoyl-substituted homoallylic alcohols

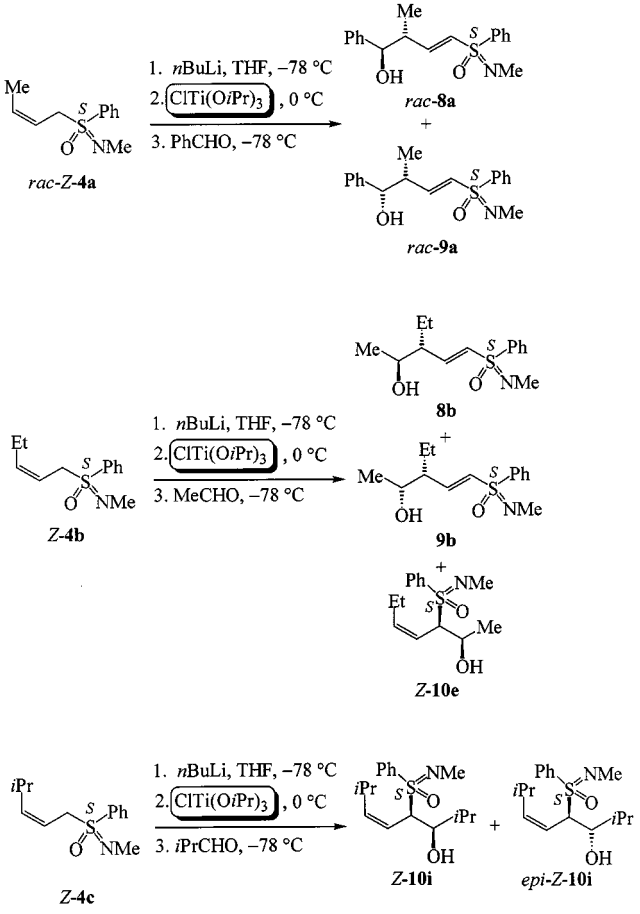
In view of the formation of bis(alkenyl)titanium complexes upon reaction of Li-*E*-**4** with ClTi(O*i*Pr)$_3$ (vide infra), it was of interest to see whether a difference in the selectivity of the hydroxyalkylation would be observed by using racemic instead of enantiopure Li-**4** as the starting material. Reaction of the isopropyloxytitanium complexes prepared from *rac*-Li-*E*-**4a** or *rac*-Li-*E*-**4e** and 1.2 equiv. of ClTi(O*i*Pr)$_3$ with 2-methylpropanal and benzaldehyde also proceeded with high regio- and diastereoselectivities and afforded the racemic (*Z*)-*anti*-configured vinylic hydroxy sulfoximines *rac*-**7c**, *rac*-**7d**, and *rac*-**7n**, respectively, in yields similar to those obtained with the enantiopure starting materials (Table 1, entries 4, 5, and 18).

The reactions of the isopropyloxytitanium complexes derived from Li-*Z*-**4a**−**d** having a (*Z*)-configured double bond with aldehydes were not only much slower than those of their (*E*)-isomers, but occurred at the γ- as well as the α-position, thereby affording the corresponding hydroxy sulfoximines with low stereoselectivities. The selectivity was found to depend on the size of the alkyl group of the allylic sulfoximine and on the size of the aldehyde (Scheme 5). Most interestingly, the sulfoximines derived from a γ-attack were found to have the (*E*)- rather than (*Z*)-configuration. In the series of isopropyloxytitanium complexes derived from *rac*-Li-*Z*-**4a**, Li-*Z*-**4b**, and Li-*Z*-**4c**, that bearing a methyl group at the γ-position reacted most rapidly with the aldehydes. Thus, reaction of the isopropyloxytitanium complex derived from *rac*-Li-*Z*-**4a** and 1.2 equiv. of

Table 1. Synthesis of the δ-*N*-methylsulfonimidoyl-substituted acyclic homoallylic alcohols **7**

Entry	Starting material	Aldehyde	Product	R^1	R^2	*ds* (%)[a][b]	Yield (%)[c]
1	*E*-**4a**	MeCHO	**7a**	Me	Me	≥98 (≥96)	31 (44)
2	*E*-**4a**	EtCHO	**7b**	Me	Et	≥98 (≥96)	32 (37)
3	*E*-**4a**	*i*PrCHO	**7c**	Me	*i*Pr	≥98 (≥96)	36 (46)
4	*rac*-*E*-**4a**	*i*PrCHO	*rac*-**7c**	Me	*i*Pr	≥98 (≥96)	32 (52)[d]
5	*rac*-*E*-**4a**	PhCHO	*rac*-**7d**	Me	Ph	97 (96)[e]	45 (53)[f]
6	*E*-**4b**	MeCHO	**7e**	Et	Me	≥98 (92)[e]	44 (74)[g,d]
[h]	–	–	**7f**	Et	*i*Pr	–	–
7	*E*-**4c**	MeCHO	**7g**	*i*Pr	Me	≥98 (≥96)	32 (48)
[h]	–	–	**7h**	*i*Pr	Et	–	–
8	*E*-**4c**	*i*PrCHO	**7i**	*i*Pr	*i*Pr	≥98 (≥96)	44 (48)
9	*E*-**4c**	*i*PrCHO	**7i**	*i*Pr	*i*Pr	≥98 (≥96)	72 (82)[g]
10	*E*-**4c**	PhCHO	**7j**	*i*Pr	Ph	≥98 (≥96)	43 (48)
11	*E*-**4d**	EtCHO	**7k**	cC_6H_{11}	Et	≥98 (96)[e]	69 (77)[g]
12	*E*-**4d**	*i*PrCHO	**7l**	cC_6H_{11}	*i*Pr	(≥96)	(52)
13	*E*-**4d**	*i*PrCHO	**7l**	cC_6H_{11}	*i*Pr	≥98 (≥96)	72 (82)[g]
14	*E*-**4d**	*i*PrCHO	**7l**	cC_6H_{11}	*i*Pr	–	(10)[i]
15	*E*-**4d**	*i*PrCHO	**7l**	cC_6H_{11}	*i*Pr	(≥96)	(45)[j]
16	*E*-**4d**	*i*PrCHO	**7l**	cC_6H_{11}	*i*Pr	≥98 (≥96)	70 (78)[k]
[h]	–	–	**7m**	cC_6H_{11}	Ph	–	–
17	*ent*-*E*-**4e**	*i*PrCHO	*ent*-**7n**	Ph	*i*Pr	≥98 (≥96)	29 (40)[d]
18	*rac*-*E*-**4e**	*i*PrCHO	*rac*-**7n**	Ph	*i*Pr	(≥96)	(42)

[a] From ^{1}H-NMR spectroscopic analysis. Where *ds* values are quoted as ≥98 % and ≥96 %, no other isomer could be detected in the isolated and in the crude product, respectively. – [b] Values in parentheses refer to crude products. – [c] Values in parentheses refer to chemical yields (cy). – [d] Isolated as triethylsilyl ether. – [e] A second (*Z*) diastereomer was observed in the ^{1}H NMR spectrum. – [f] Isolated as *tert*-butyldimethylsilyl ether. – [g] Titanation with 2.1 equiv. of $ClTi(OiPr)_3$ at −78 °C to 25 °C. – [h] Not investigated. – [i] Titanation with 0.50 equiv. of $Cl_2Ti(OiPr)_2$. – [j] Titanation with 1.1 equiv. of $Cl_2Ti(OiPr)_2$ at −78 °C. – [k] Titanation with 1.1 equiv. of $Cl_2Ti(OiPr)_2$ at −78 °C.

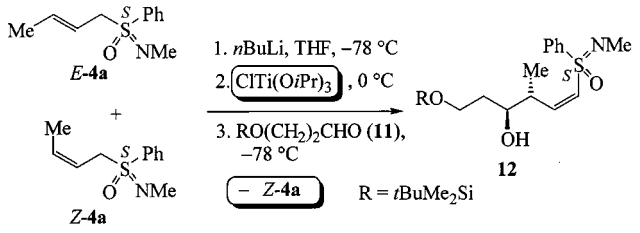


Scheme 5. Reaction of the isopropyloxytitanium complexes of Li-*Z*-**4** with aldehydes

$ClTi(OiPr)_3$ with benzaldehyde proceeded with high regioselectivity but with low *syn*/*anti* selectivity to give the (*E*)-*anti*-configured vinylic hydroxy sulfoximine *rac*-**8a** and the (*E*)-*syn*-configured vinylic hydroxy sulfoximine *rac*-**9a** in a 2:1 ratio in only 26% yield (isolated as the *tert*-butyldimethylsilyl ether). The corresponding reaction of the isopropyloxytitanium complex derived from Li-*Z*-**4b** and 2.1 equivalents of $ClTi(OiPr)_3$ with ethanal furnished a mixture of the (*E*)-*anti*-configured vinylic hydroxy sulfoximine **8b**, its (*E*)-*syn*-configured epimer **9b**, and the (*Z*)-*syn*-configured allylic hydroxy sulfoximine *Z*-**10a** (vide infra) in a ratio of 58:2:40 in 56% chemical yield. Crystallization of this mixture afforded pure **8b** in 26% yield. The reaction of the isopropyl-substituted isopropyloxytitanium complex of Li-*Z*-**4c**, prepared using 1.2 equiv. of $ClTi(OiPr)_3$, with 2-methylpropanal occurred exclusively at the α-position to furnish a mixture of the (*Z*)-*anti*- and the (*Z*)-*syn*-configured allylic hydroxy sulfoximines *epi*-*Z*-**10b** and *Z*-**10b** (vide infra) in a 2:1 ratio in 45% chemical yield.

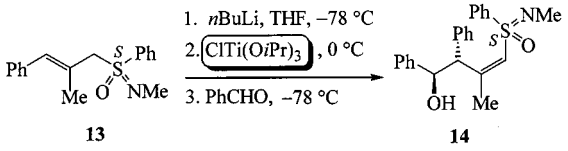
The reactivity differences between the isopropyloxytitanium complexes of Li-*E*-**4** and Li-*Z*-**4** were generally sufficient to allow for a selective synthesis of the corresponding vinylic hydroxy sulfoximine **7** starting from an (*E*)/(*Z*)-mixture of the allylic sulfoximine. Hence, separation of the (*Z*)- and (*E*)-isomers of **4** was generally not required in the syntheses of compounds **7**. An illustrative example is the synthesis of the silyloxy-substituted (*Z*)-*anti*-configured vinylic hydroxy sulfoximine **12**, which was obtained in diastereopure form in 32% yield starting from a 70:30 mixture of Li-*E*-**4a** and Li-*Z*-**4a** and the aldehyde **11**[65] (Scheme 6). Formation of the corresponding (*E*)-*anti*-configured dia-

stereomer of **12**, as would be derived from *Z*-**4a**, was not observed. The sulfoximines *E*-**4a** and *Z*-**4a** were recovered in 53% yield in a 1:1 ratio. Treatment of this mixture with DBU in MeCN gave the two isomers in a 70:30 ratio. Since in the synthesis of **12** only 1.2 equiv. of $ClTi(OiPr)_3$ were used, a considerable improvement in the yield of the vinylic hydroxy sulfoximine should be possible by using 2.1 equiv. of the titanium reagent and pure *E*-**4a** as the starting material (vide supra).



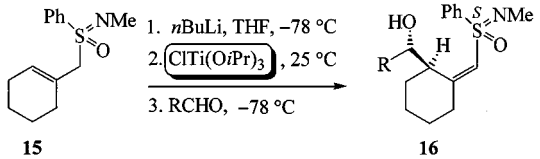
Scheme 6. Synthesis of the δ-*N*-methylsulfonimidoyl-substituted homoallylic alcohol **12** starting from a mixture of *E*-**4a** and *Z*-**4a**

β,γ-Disubstituted allylic sulfoximines are also amenable to selective γ-hydroxyalkylation. Thus, treatment of sulfoximine Li-**13**, obtained by lithiation of **13**,[7] with 1.2 equiv. of $ClTi(OiPr)_3$ at −78 °C in THF and subsequent addition of benzaldehyde led to the isolation of the (*Z*)-*anti*-configured vinylic hydroxy sulfoximine **14** incorporating a trisubstituted double bond in 41% yield with ≥98% *ds* (Scheme 7).



Scheme 7. Synthesis of the δ-*N*-methylsulfonimidoyl-substituted homoallylic alcohol **14**

Not only isopropyloxytitanium complexes of acyclic but also those of cyclic allylic sulfonimidoyl carbanions react with aldehydes with high regio- and diastereoselectivity at the γ-position to yield the corresponding vinylic sulfoximines (Scheme 8, Table 2). Thus, successive treatment of **15**, prepared from cyclohexanone and **1** in 93% overall yield by the shortened AEI route,[6] with *n*BuLi and 2.2 equiv. of $ClTi(OiPr)_3$, and subsequent reaction of the thus formed isopropyloxytitanium complex with ethanal, 2-methylpropanal, or benzaldehyde afforded the (*Z*)-*anti*-configured vinylic hydroxy sulfoximines **16b**−**d** with ≥96% *ds* in 62−77% chemical yield. The diastereopure sulfoximines **16c** and **16d** were isolated in 59% and 47% yield, respectively.



Scheme 8. Synthesis of cyclic δ-*N*-methylsulfonimidoyl-substituted homoallylic alcohols

Finally, it is important to note that incomplete lithium−titanium exchange of Li-*E*-**4**, Li-**13**, and Li-**15** with $ClTi(OiPr)_3$ leads to a competing and unselective formation of the corresponding allylic hydroxy sulfoximines derived from an α-attack of the aldehyde on the lithiated allylic sulfoximines.[66]

The acyclic and cyclic vinylic hydroxy sulfoximines (Table 1 and 2) were purified by either crystallization, chromatography, or chromatography following silylation. In some cases, formation of *N*-methyl-*S*-phenylsulfinamide as a minor side product was observed, which proved to be easy to separate by crystallization but difficult by chromatography. Thus, in the latter case, the crude mixture was treated with either $ClSiEt_3$ or $ClSitBuMe_2$, which gave a mixture of the corresponding *O*-silylated vinylic sulfoximine, *N*-silyl-*N*-methyl-*S*-phenylsulfinamide, and the allylic sulfoximine, which could readily be separated by chromatography.

The (*Z*)-*anti*-configuration of the vinylic hydroxy sulfoximines **7g** (Figure 1), **7j** (Figure 2), **16c** (Figure 3), and **16d** (Figure 4) was confirmed by X-ray structure analyses.[67] Internal correlation based on the known (*S*)-configuration of **1** led to the assignment of the absolute configurations of **7g**, **7j**, **16c**, and **16d** as shown in Schemes 8 and 12. Because of the similarity of the key NMR spectroscopic data (vide infra), we also assigned the configurations depicted in Schemes 8, 10, and 11 to sulfoximines **7a**−**e**, **7g**, **7i**−**l**, *ent*-**7n**, **12**, **14**, and **16b**. Interestingly, besides a pseudoaxial hydroxyalkyl group, in the crystal the hydroxy sulfoximines **16c** and **16d** feature an intramolecular hydrogen bond between the hydroxy group and the N atom belonging to an eight-membered ring (Figure 3 and 4). As a result, α-H and β-H[68a] of **16c** and **16d** are antiperiplanar. According to the magnitude of the coupling constant ^3J(α-H,β-H) in the NMR spectra, and in the light of the results of the NOE experiments, the basic structure of sulfoximines **16c** and **16d** seen in the crystal is retained in solution. In contrast to **16c** and **16d**, sulfoximines **7g** and **7j** do exhibit an intermolecular hydrogen bond between the hydroxy group and the N atom in the crystal. As a consequence, α-H and β-H of **7g** and **7j** are synclinal in the crystal. However, according to the magnitudes of the coupling constants ^3J(α-H,β-H) and ^3J(β-H,γ-H) in the NMR spectra of **7a**−**e**, **7g**, **7i**−**l**, *ent*-**7n**, **12**, and **14**, and in view of the results of NOE experiments on **7g** and **7j**, in solution these sulfoximines preferentially adopt a conformation similar to that of **16c** and **16d** in the crystal, with an intramolecular hydrogen bond between the hydroxy group and the O atom or N atom of the sulfoximine group. This conformation is characterized by antiperiplanar positions of α-H and β-H as well as of β-H and γ-H. In contrast, the ethers **7g**-$SiEt_3$ and **7j**-$SiEt_3$, which cannot form such a hydrogen bond, preferentially exist in solution in a conformation similar to that of the parent sulfoximine **7g** or **7j** in the crystal.

The (*E*)-*anti*-configuration of the vinylic hydroxy sulfoximine **8b** was determined by the following chemical correlation. Successive treatment of the (*Z*)-configured vinylic hydroxy sulfoximine **7e** with *n*BuLi and acetic acid furnished

Table 2. Synthesis of the δ-*N*-methylsulfonimidoyl-substituted cyclic homoallylic alcohols **16**

Entry	Starting material	Aldehyde	Product	R	*ds* (%)[a]	Yield (%)
[b]	–	–	**16a**	Me	–	–
1	**15**	EtCHO	**16b**	Et	(≥96)[c]	(77)[d]
2	**15**	*i*PrCHO	**16c**	*i*Pr	≥98 (≥96)[c]	59 (77)[d]
3	**15**	PhCHO	**16d**	Ph	≥98 (≥96)[c]	47 (62)[d]

[a] From ^{1}H-NMR spectroscopic analysis. Where *ds* values are quoted as ≥98% and ≥96%, no other isomer could be detected in the isolated and in the crude product, respectively. – [b] Not investigated. – [c] Values in parentheses refer to crude products. – [d] Values in parenthesis refer to chemical yields.

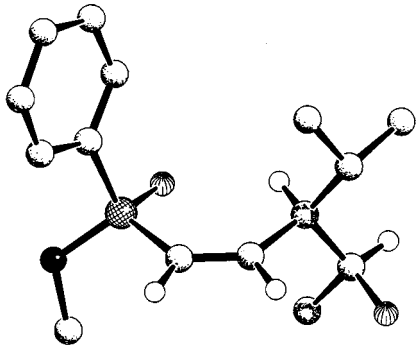


Figure 1. Crystal structure of sulfoximine **7g** (some H atoms have been omitted for the sake of clarity); selected bond lengths [A]: S–N 1.542(4), S–O 1.447(3), S–C 1.755(5), S–Ph 1.777(5)

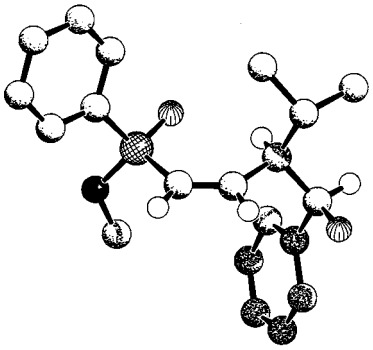


Figure 2. Crystal structure of sulfoximine **7j** (some H atoms have been omitted for the sake of clarity); selected bond lengths [A]: S–N 1.548(5), S–O 1.460(4), S–C 1.772(5), S–Ph 1.778(5)

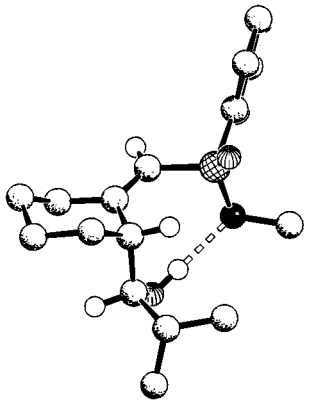


Figure 3. Crystal structure of sulfoximine **16c** (some H atoms have been omitted for the sake of clarity); selected bond lengths [A]: S–N 1.524(3), S–O 1.452(2), S–C 1.749(3), S–Ph 1.793(3)

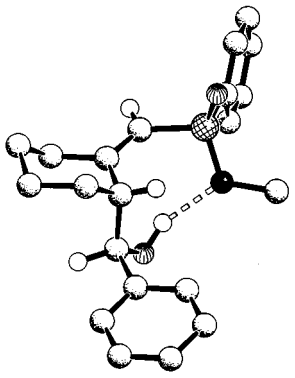


Figure 4. Crystal structure of sulfoximine **16d** (some H atoms have been omitted for the sake of clarity); selected bond lengths [A]: S–N 1.530(3), S–O 1.454(3), S–C 1.744(4), S–Ph 1.788(3)

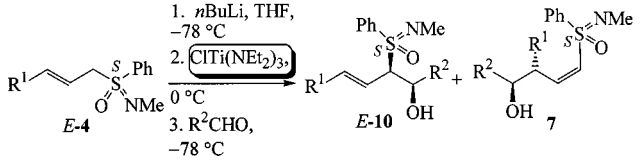
the (*E*)-isomer **8b** in quantitative yield.[34a,69] Because of the close similarity of the NMR spectroscopic data of **8b** and *rac*-**8a**, the (*E*)-*anti*-configuration was also assigned to the latter sulfoximine. The configurations of the vinylic sulfoximines *rac*-**9a** and **9b** were provisionally assigned as depicted on the basis of their ^{1}H NMR spectroscopic data.

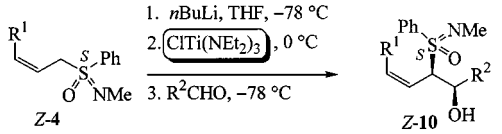
The configuration of *epi*-*Z*-**10b** was assigned by ^{1}H NMR spectroscopy through comparison with data for an analogous allylic hydroxy sulfoximine, the configuration of which has been confirmed by X-ray structure analysis (vide infra).

(Diethylamino)titanium Complexes: Synthesis of *syn*-Configured β-*N*-Methylsulfonimidoyl-Substituted Chiral Homoallylic Alcohols

Titanation of Li-*E*-**4a**–**d** with 1.1–1.2 equiv. of ClTi(NEt$_2$)$_3$ at –78 °C to 0 °C in THF or diethyl ether presumably afforded the corresponding mono(2-alkenyl)tris(diethylamino)titanium complexes (vide infra). At –78 °C, these reacted with ethanal, propanal, 2-methylpropanal, and benzaldehyde to give, as hoped for, the corresponding diastereopure (*E*)-*syn*-configured β-*N*-methylsulfonimidoyl-substituted homoallylic alcohols *E*-**10** in moderate to good yields (Scheme 9, Table 3, entries 1–8). However, a more detailed study of the reactions of the diethylaminotitanium complexes of Li-*E*-**4a**–**d** bearing different alkyl groups at the double bond with a number of aldehydes revealed in a few cases the formation of significant amounts of the vinylic hydroxy sulfoximines **7** besides the allylic sulfoximines *E*-**10** (Table 4, entries 1, 5, 7, and 8). The regioselectivity of the hydroxyalkylation was found to be strongly dependent on both the size of the aldehyde and the substituent on

the allylic sulfoximine. The α-selectivity increased markedly with increasing size of both reactants. From inspection of the data in Table 4, it would seem that the size of the aldehyde has a stronger effect on the α-selectivity than the size of the substituent on the allylic sulfoximine. It is interesting to note that the α-selectivity also increases at higher temperatures (Table 4, entries 2, 3, 7, 8, 9, and 10). In summary, a highly selective α-hydroxyalkylation can generally be achieved except in those cases where both reactants bear small groups. It is noteworthy that, in general, not only the allylic hydroxy sulfoximine *E*-**10** but also the corresponding vinylic hydroxy sulfoximine **7** was formed with high diastereoselectivity.





Scheme 9. Synthesis of acyclic β-*N*-methylsulfonimidoyl-substituted homoallylic alcohols

configured allylic sulfoximines. Only in the reaction of the diethylaminotitanium complex derived from crotyl sulfoximine Li-*Z*-**4a** with ethanal was the formation of a mixture of *Z*-**10a** and the (*E*)-isomer of **7a** observed (Table 4, entries 16 and 17). In all cases investigated, the (*Z*)-configured allylic hydroxy sulfoximines were formed with high diastereoselectivity. The results in Table 4 show that most reactions of the (*E*)- and (*Z*)-configured diethylaminotitanium complexes with ethanal, which ought to be the most reactive aldehyde of those investigated, were only sluggish, and that most of the starting allylic sulfoximine was recovered. Although not verified experimentally, the apparent low reactivity of ethanal may perhaps be due to a competing transfer of a diethylamino group[64] from the allylic aminotitanium complex to the aldehyde with formation of the aminal complex **IX** (Scheme 10). Alternatively, the allylic aminotitanium complex may react with the aldehyde under elimination of diethylamine to give the enolate complex **X**. Such side reactions would be expected to be more pronounced with ethanal than with the other aldehydes used on steric grounds.

Hydroxyalkylation of the diethylaminotitanium complex of the γ,γ-disubstituted sulfoximine Li-**6a** with 2-methylpropanal took place exclusively at the α-position to furnish the *syn*-configured allylic hydroxy sulfoximine **17a** with ≥98% *ds* in 75% yield (92% cy) (Scheme 11). Reaction of Li-**6b** with propanal under similar conditions afforded the *syn*-

Table 3. Synthesis of the β-*N*-methylsulfonimidoyl-substituted acyclic homoallylic alcohols **10**

Entry	Starting material	Aldehyde	Product	R^1	R^2	*ds* (%)[a]	Yield (%)
1	*E*-**4a**	MeCHO	*E*-**10c**	Me	*i*Pr	≥98	76
2	*E*-**4b**	MeCHO	*E*-**10e**	Et	Me	≥98	48
3	*E*-**4b**	*i*PrCHO	*E*-**10f**	Et	*i*Pr	≥98	47
4	*E*-**4c**	EtCHO	*E*-**10h**	*i*Pr	Et	≥98	87
5	*E*-**4c**	*i*PrCHO	*E*-**10i**	*i*Pr	*i*Pr	≥98	81
6	*E*-**4c**	PhCHO	*E*-**10j**	*i*Pr	Ph	≥98	70
7	*E*-**4d**	*i*PrCHO	*E*-**10l**	cC_6H_{11}	*i*Pr	≥98	86
8	*E*-**4d**	PhCHO	*E*-**10m**	cC_6H_{11}	Ph	≥98	68
9	*Z*-**4a**	MeCHO	*Z*-**10a**	Me	Me	≥98	20
10	*Z*-**4a**	EtCHO	*Z*-**10b**	Me	Et	≥98	90
11	*Z*-**4b**	MeCHO	*Z*-**10e**	Et	Me	≥98	64
12	*Z*-**4b**	*i*PrCHO	*Z*-**10f**	Et	*i*Pr	≥98	91
13	*Z*-**4c**	*i*PrCHO	*Z*-**10i**	*i*Pr	*i*Pr	≥98	73
14	*Z*-**4c**	PhCHO	*Z*-**10j**	*i*Pr	Ph	≥98	73

[a] From ^{1}H-NMR spectroscopic analysis, where a *ds* value is quoted as 98%, no other isomer could be detected in the isolated product.

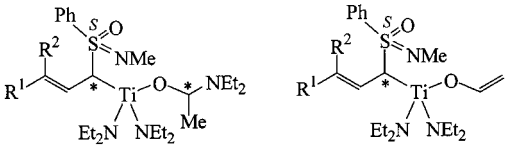
Titanation of Li-*Z*-**4a**−**c** with 1.1−1.2 equiv. of $ClTi(NEt_2)_3$ at −78 °C to 0 °C in THF and reaction of the thus formed diethylaminotitanium complexes (vide infra) with ethanal, propanal, 2-methylpropanal, and benzaldehyde led to the isolation of the corresponding diastereopure (*Z*)-*syn*-configured β-*N*-methylsulfonimidoyl-substituted homoallylic alcohols *Z*-**10** in moderate to good yields (Scheme 9, Table 3, entries 9−14). Again, the regioselectivity of the hydroxyalkylation was investigated by variation of the aldehyde and of the substituent on the allylic sulfoximine (Table 4, entries 16−24). Inspection of the data in Table 4 reveals that for the (*Z*)-configured allylic sulfoximines the regioselectivity, which increases with increasing temperature, is significantly higher than for the corresponding (*E*)-configured allylic hydroxy sulfoximine **17b** with 90% *ds* in 87% chemical yield. Recrystallization of the crude material furnished **17b** containing 2% of a diastereomer in 56% yield. The apparently lower diastereoselectivity of the formation of **17b** can most probably be attributed to a competing unselective α-hydroxyalkylation of a small amount of Li-**6b**,[70] present due to incomplete lithium−titanium exchange, as was subsequently revealed by NMR spectroscopic monitoring of the lithium−titanium exchange under similar conditions.

The selective α-hydroxyalkylation could also be extended to the cyclic allylic sulfoximine Li-**15**. Titanation of Li-**15** with $ClTi(NEt_2)_3$ and the subsequent reactions of the resulting diethylaminotitanium complex with ethanal, pro-

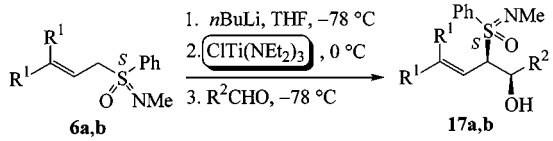
Table 4. Reactions of the diethylaminotitanium complexes of the acyclic allylic *N*-methylsulfonimidoyl carbanions Li-**4** with aldehydes

Entry	Starting material	Aldehyde	*T* [°C]	Conv. (%)	**10**/**7**	**10**, *ds* (%)[a]	**7**, *ds* (%)[a]	R^1	R^2
1	*E*-**4a**	MeCHO	−78	77	1:1.5	*E*-**10a**, ≥96	**7a**, 92[b]	Me	Me
2	*E*-**4a**	EtCHO	−78	62	4.1:1	*E*-**10b**, ≥96	**7b**, ≥96	Me	Et
3	*E*-**4a**	EtCHO	25	91	7.2:1	*E*-**10b**, ≥96	**7b**, ≥96	Me	Et
4	*E*-**4a**	*i*PrCHO	−78	97	23:1	*E*-**10c**, ≥96	**7c**, ≥96	Me	*i*Pr
[c]	–	–	–	–	–	*E*-**10d**	**7d**	Me	Ph
5	*E*-**4b**	MeCHO	−30	50	1.1:1	*E*-**10e**, ≥96	**7e**, ≥96	Et	Me
6	*E*-**4b**	*i*PrCHO	−78	97	31:1	*E*-**10f**, ≥96	**7f**, ≥96	Et	*i*Pr
7	*E*-**4c**	MeCHO	−78	53	1:1	*E*-**10g**, ≥96	**7g**, 85[b]	*i*Pr	Me
8	*E*-**4c**	MeCHO	25	28	1.8:1	*E*-**10g**, ≥96	**7g**, 90[b]	*i*Pr	Me
9	*E*-**4c**	EtCHO	−78	67	21:1	*E*-**10h**, ≥96	**7h**, –	*i*Pr	Et
10	*E*-**4c**	EtCHO	25	98	21:1	*E*-**10h**, ≥96	**7h**, –	*i*Pr	Et
11	*E*-**4c**	*i*PrCHO	−78	98	≥100:1	*E*-**10i**, ≥96	**7i**, –	*i*Pr	*i*Pr
12	*E*-**4c**	*i*PrCHO	25	99	≥100:1	*E*-**10i**, ≥96	**7i**, –	*i*Pr	*i*Pr
13	*E*-**4c**	PhCHO	−78	94	≥100:1	*E*-**10j**, ≥96	**7j**, –	*i*Pr	Ph
[c]	–	–	–	–	–	*E*-**10k**	**7k**	cC_6H_{11}	Et
14	*E*-**4d**	*i*PrCHO	−78	98	≥100:1	*E*-**10l**, ≥96	**7l**, –	cC_6H_{11}	*i*Pr
15	*E*-**4d**	PhCHO	−78	78	≥100:1	*E*-**10m**, ≥96	**7m**, –	cC_6H_{11}	Ph
[c]	–	–	–	–	–	*E*-**10n**	**7n**	Ph	*i*Pr
16	*Z*-**4a**	MeCHO	−78	36	2.6:1	*Z*-**10a**, ≥96	[d]	Me	Me
17	*Z*-**4a**	MeCHO	25	19	8.5:1	*Z*-**10a**, ≥96	[d]	Me	Me
18	*Z*-**4a**	EtCHO	−78	98	≥100:1	*Z*-**10b**, ≥96	–	Me	Et
19	*Z*-**4a**	EtCHO	25	99	≥100:1	*Z*-**10b**, ≥96	–	Me	Et
20	*Z*-**4b**	MeCHO	−78	63	≥100:1	*Z*-**10e**, ≥96	–	Et	Me
21	*Z*-**4b**	MeCHO	−30	76	≥100:1	*Z*-**10e**, ≥96	–	Et	Me
22	*Z*-**4b**	*i*PrCHO	−78	99	≥100:1	*Z*-**10f**, ≥96	–	Et	*i*Pr
23	*Z*-**4c**	*i*PrCHO	−78	92	≥100:1	*Z*-**10i**, ≥96	–	*i*Pr	*i*Pr
24	*Z*-**4c**	PhCHO	−78	90	≥100:1	*Z*-**10j**, ≥96	–	*i*Pr	Ph

[a] From ^{1}H-NMR spectroscopic analysis. Where a *ds* value is quoted as ≥98%, no other isomer could be detected in the isolated product. – [b] A second (*Z*) diastereomer was observed in the ^{1}H NMR spectrum. – [c] Not investigated. – [d] Several diastereomers.

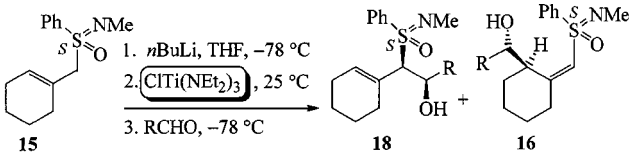


Scheme 10. Putative side products of the reaction of the diethylaminotitanium complexes of Li-**4** with ethanal



Scheme 11. Synthesis of acyclic β-*N*-methylsulfonimidoyl-substituted homoallylic alcohols

panal, 2-methylpropanal, and benzaldehyde gave with moderate to high α-regioselectivities and high diastereoselectivities the (*Z*)-*syn*-configured allylic hydroxy sulfoximines **18a–d** (Scheme 12, Table 5). We ascribe the slightly lower diastereoselectivities in the case of the formation of **18a** and **18d** to incomplete lithium–titanium exchange reactions. In-



Scheme 12. Synthesis of cyclic β-*N*-methylsulfonimidoyl-substituted homoallylic alcohols

spection of the data in Table 5 reveals a similar dependence of the regioselectivity on the size of the aldehyde as in the case of the hydroxyalkylation of the diethylaminotitanium complexes of acyclic lithiated allylic sulfoximines (vide supra). The α-selectivity increases with increasing size of the aldehyde. The diastereopure vinylic hydroxy sulfoximines **18c** and **18d** were isolated in 57% and 66% yield, respectively, by crystallization.

Table 5. Reaction of the diethylaminotitanium complex of the cyclic allylic *N*-methylsulfonimidoyl carbanion Li-**15** with aldehydes

Entry	Aldehyde	*T* [°C]	Conv. (%)	**18**/**16**	**18**, *ds* (%)[a]	**16**, *ds* (%)[a]
1	MeCHO	−78	94	2.6:1	**18a**, 95[b]	**16a**, ≥96
2	EtCHO	−78	98	13:1	**18b**, ≥96	**16b**, ≥96
3	*i*PrCHO	−78	91	22:1	**18c**, ≥96	**16c**, ≥96
4	PhCHO	−78	86	≥100:1	**18d**, 95[b]	**16d**, ≥96

[a] From ^{1}H NMR spectroscopic analysis. Where a *ds* value is quoted as ≥96%, no other isomer could be detected in the crude product. – [b] A second diastereomer was observed in the ^{1}H NMR spectrum.

Isolation of the aforementioned acyclic and cyclic substituted allylic hydroxy sulfoximines was accomplished either by crystallization or chromatography. For the latter, the silica gel had to be deactivated by the addition of triethylamine to the eluent owing to the instability of some of the allylic hydroxy sulfoximines on standard silica gel.

The *syn*-configuration of the allylic hydroxy sulfoximines *Z*-**10e** (Figure 5) and *E*-**10i** (Figure 6) was confirmed by X-ray structure analyses.[67] Internal correlation based on the known (*S*)-configuration of **1** led to the assignment of the

absolute configurations of *Z*-**10e** and *E*-**10i** as shown in Scheme 5−7. On the basis of these results and because of the similarity of key NMR spectroscopic data (vide infra), we assigned to sulfoximines *E*-**10a**−**c**, *E*-**10e**−**j**, *Z*-**10a**−**j**, **17a**, **17b**, and **18a**−**d** the configurations depicted in Schemes 5−7. In the crystal, *Z*-**10e** exhibits an intramolecular hydrogen bond between the hydroxy group and the N atom incorporated in a six-membered ring. As a consequence, α-H and β-H[68b] are antiperiplanar, the butenyl and methyl groups are both pseudoequatorial, and β-H and γ-H are antiperiplanar. Sulfoximine *E*-**10i** adopts a similar conformation as *Z*-**10e** in the crystal. Although the H atom of the hydroxy group of *E*-**10i** could not be located, the existence of an intramolecular hydrogen bond between the hydroxy group and the N atom seems to be highly likely in this case as well. The results of NOE experiments on *E*-**10i** and **17b**, together with the magnitudes of the coupling constants ^3J(α-H,β-H) and ^3J(β-H,γ-H) in the NMR spectra, indicate that in solution both hydroxy sulfoximines preferentially adopt a similar hydrogen-bond stabilized conformation as adopted by *Z*-**10e** and *E*-**10i** in the crystal. Since the coupling constants ^3J(α-H,β-H) and ^3J(β-H,γ-H) in the NMR spectra of *E*-**10a**−**c**, *E*-**10e**−**j**, *Z*-**10a**−**j**, **17a**, and **17b** are of the same magnitude in each case, it seems reasonable to assume that in solution these sulfoximines preferentially adopt a similar hydrogen-bond stabilized conformation.

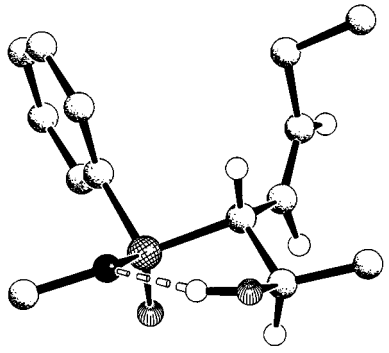


Figure 5 Crystal structure of sulfoximine *Z*-**10e** (some H atoms have been omitted for the sake of clarity); selected bond lengths [A]: S−N 1.532(3), S−O 1.444(3), S−C 1.816(2), S−Ph 1.790(4)

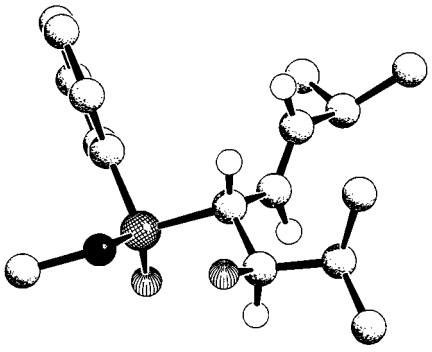


Figure 6. Crystal structure of sulfoximine *E*-**10i** (some H atoms have been omitted for the sake of clarity); selected bond lengths [A]: S−N 1.507(3), S−O 1.449(2), S−C 1.810(3), S−Ph 1.774(3)

Dynamics of Cyclohexenyl-Substituted Allylic Hydroxy Sulfoximines

Interestingly, in the ^{1}H NMR spectrum (500 MHz) of the cyclohexenyl-substituted hydroxy sulfoximine **18c** in [D_8]THF at room temperature, nearly all of the signals are broadened. In addition, the ^{13}C NMR spectrum (125 MHz) of **18c** in [D_8]THF at room temperature shows very broad signals due to C-α, C-β, and the *ortho* C atoms of the phenyl group. A similar line-broadening has also been observed in the NMR spectra of **18a**,**b**,**d**.[71] The ^{1}H and ^{13}C NMR spectra of **18c** at −60 °C reveal the existence of two isomeric species in a ratio of 2.4:1, the signals of which were assigned by two-dimensional methods. Activation barriers of $\Delta G^{\neq}_{278}$ = 53.2 ± 1.3 kJ/mol and 55.9 ± 1.3 kJ/mol were estimated for the equilibration of the isomers at the coalescence temperature.[72] In their ^{1}H NMR spectra, the isomers are characterized by a coupling constant ^3J(α-H,β-H) = 10.1 Hz and by similar chemical shifts for the hydroxy group signals. These observations were taken as an indication that both isomers form an intramolecular hydrogen bond between the hydroxy group and the N atom incorporated in a six-membered ring, at which the phenyl, cyclohexenyl, and isopropyloxy groups are pseudoequatorially arranged.[73] Characteristic chemical shift differences were observed for the signals of the =C*H* and CH_2 groups of the cyclohexene rings of the isomers. Whereas in the major isomer the =C*H* signal is subject to a significant high-field shift, it is the CH_2 signal of the minor isomer that shows a significant high-field shift as compared with the respective isomers (cf. Experimental Section). In the light of these results, we assign to the two isomers of **18c** observed in the NMR spectra the structures of the conformers **18c** (A) and **18c** (B) (Figure 7). Rotation of the cyclohexene ring about the Cβ−Cα′ bond of **18c** (A) and **18c** (B) is hindered mainly because of steric interactions with the neighboring phenyl and isopropyloxy groups. The estimated barriers of 53.2 kJ/mol and 55.9 kJ/mol for the rotation of the cyclohexene rings of **18c** (A) and **18c** (B), respectively, compare favorably in magnitude with those for other substituted cyclic alkenes having restricted sp^2-sp^3 bond rotation.[74] The differences in the chemical shifts of the =C*H* and CH_2 signals in the ^{1}H NMR spectra of **18c** (A) and **18c** (B) arise because of the phenyl ring current, which affects mainly the =C*H* group in the former and the CH_2 group in the latter. A final proof of the above structural assignment was provided by ROESY[75] experiments. The ROESY spectra of **18c** (A) and **18c** (B) in [D_8]THF at −90 °C showed no negative, off-diagonal cross-peaks. Thus, an exchange between **18c** (A) and **18c** (B) did not occur on the NMR time scale at this temperature. Appropriate positive cross-peaks indicated the close proximity of =C*H* and β-H as well as CH_2 and α-H in **18c** (A), and of =C*H* and α-H as well as CH_2 and β-H in **18c** (B). Thus, the notion of the observed isomerism of **18c** being due to a restricted inversion of the chiral cyclohexene ring and, hence, of isomers having the structures **18c** (C) and **18c** (D), can be dismissed. This is consistent with the expectation that the barriers associated

with inversion of the cyclohexene ring in **18c** (C) and **18c** (D) should be much lower[74] than that estimated for **18c** (A) and **18c** (B) at the coalescence temperature. Indeed, the NMR spectra of **18c** (A) and **18c** (B) at −60 °C reveal an averaging of the vicinal coupling constants for the H atoms of the cyclohexene ring. This shows that the inversion of the cyclohexene ring of **18c** (A) and **18c** (B) is still fast at low temperatures relative to the NMR time scale.

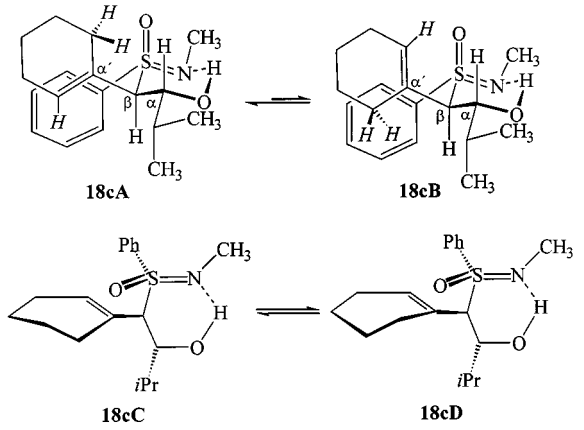
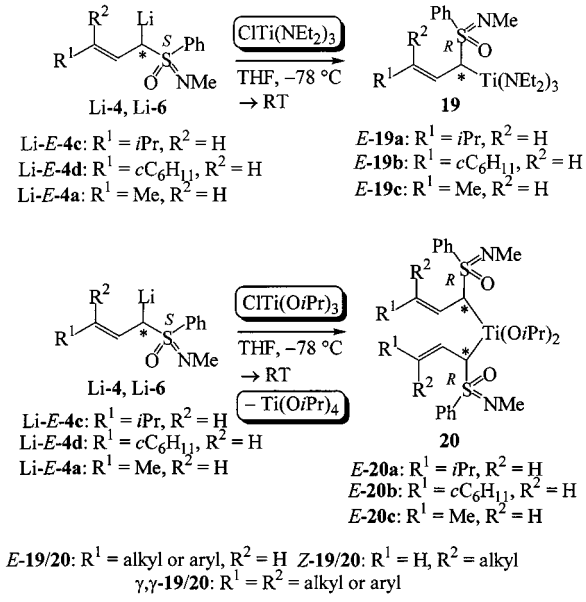


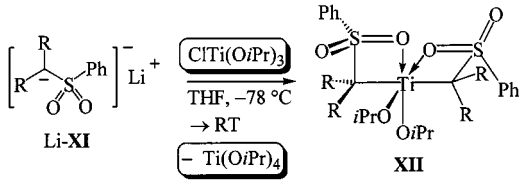
Figure 7. Conformers of the cyclohexenyl-substituted hydroxy sulfoximine **18c**

X-ray Crystal Structure, Fluxional Behavior, and Reactivity of a Bis(2-alkenyl)diisopropyloxytitanium(IV) Complex

A prerequisite for the rationalization of the regio- and diastereoselectivities of the reactions of the amino- and isopropyloxytitanium complexes of the sulfonimidoyl-substituted allylic carbanions with aldehydes is the delineation of their structures and dynamics. Despite the considerable importance of (2-alkenyl)titanium(IV) complexes in stereoselective synthesis, knowledge about their structures and dynamics is scarce.[2,10−12] Only very few (allyl)- and (crotyl)titanium(IV) complexes, where the allylic moieties have been devoid of functional groups, have been isolated and characterized by NMR spectroscopy[76] and X-ray structure analysis.[76e] The (allyl)titanium complexes show fluxional behavior due to a fast [1,3-C/C]-shift of the titanyl group. For the (crotyl)titanium complexes, where the titanyl group is bonded to the less substituted C atom, such a shift, although highly likely, has not yet been demonstrated experimentally. We have previously shown by NMR spectroscopy that reaction of Li-*E*-**4c** with 1.2 equiv. of $ClTi(NEt_2)_3$ at −78 °C in THF gives the mono(2-alkenyl)tris(amino)titanium(IV) complex *E*-**19a**, while its reaction with 1.2 equiv. of $ClTi(OiPr)_3$ under the same conditions affords the bis(2-alkenyl)dialkyloxytitanium complex *E*-**20a** along with an equimolar amount of $Ti(OiPr)_4$ (Scheme 13).[59b,77] A similar study of the titanation of Li-*E*-**4d** and Li-*E*-**4a** with $ClTi(OiPr)_3$ and $ClTi(NEt_2)_3$ revealed the formation of the complexes *E*-**19b**,**c** and *E*-**20b**,**c** [+ $Ti(OiPr)_4$], respectively.[78] The bis(alkenyl)titanium complexes could also be obtained by using 0.5 equiv. of $Cl_2Ti(OiPr)_2$.[78] In view of these results, we believe that titanation of lithiated allylic *N*-methylsulfoximines with $ClTi(OiPr)_3$ generally gives the corresponding bis(alkenyl)dialkyloxytitanium complexes, while titanation with $ClTi(NEt_2)_3$ yields the corresponding mono(alkenyl)tris(amino)titanium complexes. Although the formation of *E*-**20a**−**c** rather than the corresponding mono(alkenyl)titanium complexes was somewhat surprising, it is not totally unprecedented. We have previously observed that the reaction of lithiated dialkyl sulfones Li-**XI** with equimolar amounts of $ClTi(OiPr)_3$ proceeds in a similar fashion to give, besides equimolar amounts of $Ti(OiPr)_4$, the six-coordinate diorganotitanium complexes **XII**, which have been characterized by X-ray structure analysis and NMR spectroscopy (Scheme 14).[79,80] Titanation of Li-**4a**,**c**,**d** with $ClTi(OiPr)_3$ can be expected to initially afford the corresponding mono(alkenyl)tris(alkyloxy)titanium complexes. These complexes could then undergo disproportionation with formation of *E*-**20a**−**c** and $Ti(OiPr)_4$. A prerequisite for such a disproportionation would be a dimerization of the mono(alkenyl)tris(alkyloxy)titanium complex. In fact, aggregation of four-coordinate alkyloxytitanium complexes is quite common, although less pronounced for (dialkylamino)titanium complexes.[64] While the Ti atom in monomeric *E*-**20a**−**c** can be six-coordinate (vide infra), that in the corresponding monomeric mono(alkenyl)tris(alkyloxy)titanium complexes can only be five-coordinate. Thus, a driving force for such a disproportionation may be the formation of a coordinatively saturated titanium complex.

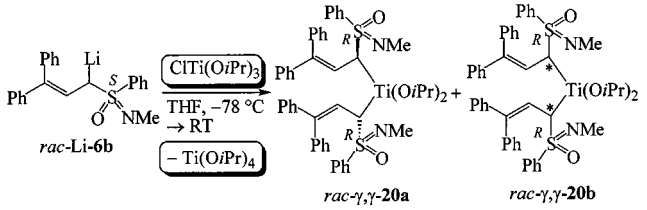


Scheme 13. Titanation of lithiated allylic *N*-methylsulfoximines with $ClTi(NEt_2)_3$ and $ClTi(OiPr)_3$



Scheme 14. Lithium−titanium exchange of α-sulfonyl carbanions Li-**XI** with $ClTi(OiPr)_3$

^{1}H NMR spectroscopic investigations of *E*-**19a** in [D$_8$]THF and [D$_8$]toluene at low temperatures showed it to be a mixture of three rapidly equilibrating species in a ratio of approximately 30:3:1.[77,81] Similar NMR analyses of *E*-**20a**−**c** in [D$_8$]THF and [D$_8$]toluene revealed in each case the existence of two equilibrating bis(alkenyl)titanium complexes, the rate of equilibration of which was found to decrease in the presence of ClTi(O*i*Pr)$_3$.[77,78] The preliminary NMR data collected for the equilibrium components of *E*-**19a** would seem to be compatible with mono(alkenyl)titanium complexes having an (*E*)-configured double bond and bearing the titanyl group at C-α or the N atom, but not at C-γ (vide infra). Equilibration of such complexes could occur by a [1,3-C/N]-shift of the titanyl group. However, the presence of minute amounts of isomers of *E*-**19a** bearing the titanyl group at C-γ, which may equilibrate through a fast [1,3-C/C]-shift, cannot be excluded. The preliminary NMR data collected for the equilibrium components of *E*-**20a**−**c** would seem to be compatible with bis(alkenyl)titanium complexes having an (*E*)-configured double bond and the titanyl group at C-α and differing perhaps in the configuration at C-α and/or the Ti atom. Recently, Reggelin et al. have reported that the reactions of lithiated allyl and crotyl *N*-(silyloxy)alkylsulfoximines with ClTi(O*i*Pr)$_3$ furnish mono(alkenyl)tris(isopropyloxy)titanium and not bis(alkenyl)diisopropyloxytitanium complexes.[2] However, the NMR data did not allow a conclusion as to the configuration and dynamics of these titanium complexes. While we are still engaged in structural studies of *E*-**19a**−**c** and *E*-**20a**−**c**, we have succeeded in isolating and structurally characterizing the γ,γ-diphenyl-substituted bis(2-alkenyl)diisopropyloxytitanium complex *rac*-γ,γ-**20a** (Scheme 15). Reaction of *rac*-Li-**6b** with 1.1 equiv. of ClTi(O*i*Pr)$_3$ in diethyl ether at −78 °C with subsequent warming of the reaction mixture to room temperature quantitatively afforded a mixture of the bis(alkenyl)titanium complex *rac*-γ,γ-**20a**, the putative complex *rac*-γ,γ-**20b**, and Ti(O*i*Pr)$_4$ in a molar ratio of 1:1:2 (Scheme 15). Crystallization of this mixture from diethyl ether furnished complex *rac*-γ,γ-**20a**·Et$_2$O as orange-red crystals in 25% yield based on *rac*-Li-**6b**. According to the relevant NMR data, the use of enantiopure Li-**6b** as the starting material in the reaction with ClTi(O*i*Pr)$_3$ likewise afforded a mixture of complex γ,γ-**20a**, complex γ,γ-**20b**, and Ti(O*i*Pr)$_4$ in a molar ratio of 1:1:2.



Scheme 15. Synthesis of the bis(alkenyl)diisopropyloxytitanium complex *rac*-γ,γ-**20a**

X-ray structure analysis of *rac*-γ,γ-**20a**·Et$_2$O[67] revealed an asymmetric bis(2-alkenyl)diisopropyloxytitanium(IV) complex, in which the Ti atom is coordinated by the two allylic moieties and the two isopropyloxy groups in a distorted octahedral fashion (Figure 8). Most interestingly, the allylic moieties in *rac*-γ,γ-**20a**·Et$_2$O are each bound to the Ti atom in a bidentate fashion through C-1 and the N atom, but not through C-3 or the O atom. The C-1, O, and N atoms of *rac*-γ,γ-**20a**·Et$_2$O are each arranged in a *cis*-fashion around the Ti atom, thus giving this complex a *cis*,-*cis*,*cis*-configuration. The C-1 atoms of the enantiomer of *rac*-γ,γ-**20a**·Et$_2$O depicted in Figure 8, which exhibits a distorted tetrahedral coordination geometry, both have the (*S*)-configuration, while both S atoms have the (*R*) configuration.[82] Interestingly, the *S*-phenyl group and the diphenylvinyl group are oriented *trans* in relation to the four-membered ring composed of the Ti, N, S, and C atoms. While one allylic moiety (A) features a short Ti−N bond of 2.09(1) Å and a rather long Ti−C1 bond of 2.45(1) Å, the other allylic moiety (B) is coordinated to the Ti atom through Ti−C1 and Ti−N bonds of almost equal length [2.21(1) and 2.29(2) Å]. It is of interest to note that the C1−Ti bond *trans* to the O atom is the longest. In the case of the octahedral diorganotitanium complexes **XII**, which feature a similar bidentate coordination of the Ti atom by the O atoms and the C-α atoms of the anions, but have the *cis*,*trans*,*cis*-configuration, the Ti−C-α bonds [2.174(4)−2.251(6) Å] and the Ti−O bonds [2.204(4)−2.278(2) Å] are of almost uniform length.[79,80] The Ti−N bond lengths in *rac*-γ,γ-**20a** compare favorably well with those found in, e.g., bis(benzamidinato)dialkyltitanium complexes.[83] The C1−C2 and C2−C3 bond lengths in *rac*-γ,γ-**20a**·Et$_2$O [1.47(2)/1.46(2) and 1.31(2)/1.35(2) Å] compare well with those observed in the (crotyl)titanium(IV) complex [{Ti(η^5-C$_5$Me$_5$)(μ-O)}$_3$(σ-CH$_2$CH=CHMe)$_3$] [1.47 and 1.34 Å (average)],[76e] and thus fall in the ranges for single and double bonds, respectively. However, the Ti−Cα bond in the latter complex [2.13 Å (average)] is significantly shorter. Finally, comparison of the bond lengths in *rac*-γ,γ-**20a**·Et$_2$O, *rac*-Li-**6b**, and *rac*-**6b** (Table 6) reveals that the sulfonimidoyl-substituted allylic unit of the titanated species resembles more closely that of the carbon acid than that of the lithium salt.

The ^{1}H and ^{13}C NMR spectra (500 MHz and 125 MHz) of the *cis*,*cis*,*cis*-complex *rac*-γ,γ-**20a**·Et$_2$O in [D$_8$]THF at 25 °C feature only one set of signals for each of the diastereotopic allylic moieties and each of the diastereotopic isopropyloxy groups. However, several signals show signs of broadening at room temperature, and at −70 °C almost all the signals are split into two signals of equal intensity. Coalescence phenomena are observed for the signals of the allylic moieties as well as for those of the isopropyloxy groups, thus suggesting a fluxional behavior of the complex. According to the pattern of the signal sets of the two allylic moieties of *rac*-γ,γ-**20a**, both are coordinated to the Ti atom through C-1 and not through C-3. The ^{1}H NMR signals of *rac*-γ,γ-**20a** were assigned with the aid of a COSY spectrum recorded at −90 °C. A ROESY spectrum[75] of *rac*-γ,γ-**20a** in [D$_8$]THF at −90 °C showed no negative, off-diagonal cross-peaks (Figure 9). Thus, no exchange of the allylic moieties occurred on the NMR time scale at this temperature. The observation of positive cross-peaks between the

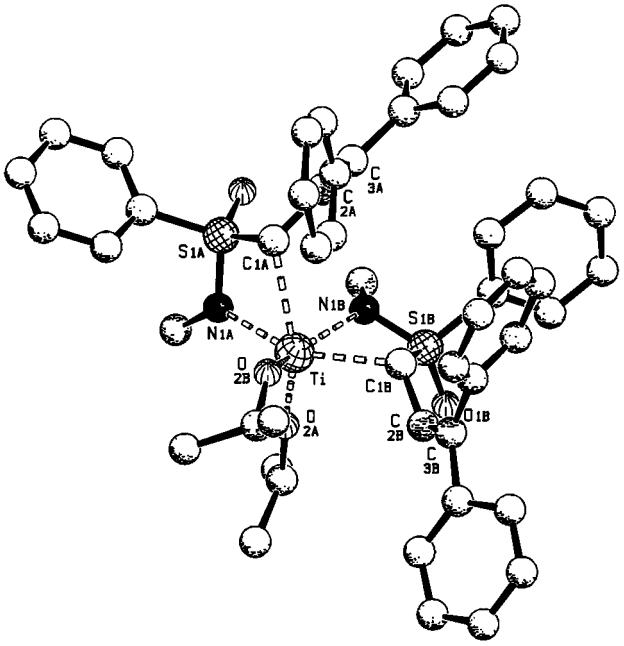
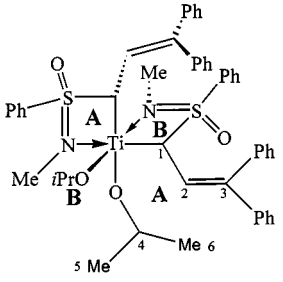


Figure 8. Crystal structure of the bis(alkenyl)diisopropyloxytitanium complex *rac*-γ,γ-**20a**·Et_2O (the ether molecule and the H atoms have been omitted for the sake of clarity); selected bond lengths [Å] and bond angles [°]: Ti−C1A 2.447(13), Ti−C1B 2.292(15), Ti−N1A 2.09(1), Ti−N1B 2.21(1), C1A−C2A 1.47(2), C1B−C2B 1.46(2), C2A−C3A 1.31(2), C2B−C3B 1.35(2), S1A−C1A 1.71(1), S1B−C1B 1.74(1); C1A−Ti−N1A 64.9(4), C1B−Ti−N1B 65.9(5), N1A−Ti−N1B 90.1(5), C1A−Ti−C1B 101.0(5), S1A−C1A−C2A 115.0(9), Ti−C1A−S1A 87.6(5), Ti−C1A−C2A 124.3(9), S1B−C1B−C2B 115(1), Ti−C1B−S1B 119(1), Ti−C1B−C2B 90.2(6)

Table 6. Selected bond lengths [Å] in *rac*-γ,γ-**20a**·Et_2O, *rac*-Li-**6b**, and *rac*-**6b**

Bond	*rac*-γ,γ-**20a**·Et_2O	*rac*-Li-**6b**	*rac*-**6b**
C1−C2	1.47(2)/1.46(2)	1.402(5)	1.494(5)
C2−C3	1.31(2)/1.35(2)	1.375(4)	1.336(4)
S−C1	1.71(2)/1.74(1)	1.659(3)	1.773(4)
S−Ph	1.78(2)/1.80(2)	1.798(3)	1.792(4)
S−N	1.53(1)/1.54(1)	1.526(3)	1.506(3)
S−O	1.447(9)/1.438(9)	1.456(2)	1.451(3)

signals of the two isopropyloxy groups and the two allylic moieties of *rac*-γ,γ-**20a** proves unequivocally that the new sets of signals observed at low temperatures belong to one species and not to two equilibrating diastereomers. The further ROESY data of *rac*-γ,γ-**20a** point to a close similarity between its structure in solution and that in the crystal. Based on the coalescence of the NMe signals in the ^1H NMR spectrum (500 MHz), a $\Delta G^{\neq}_{233}$ value of 47.3 ± 1.3 kJ/mol was estimated[72] for the exchange of the allylic moieties at the coalescence temperature. A similar barrier has been determined for the exchange of symmetrical diketonate ligands in octahedral titanium(IV) complexes of the type $Ti(chel)_2(OR)_2$.[84,85] The NMR data of *rac*-γ,γ-**20a** show unequivocally that the exchange of the allylic moieties proceeds under retention of the configuration at C-1. The exchange of all ligands could occur through an intramolecular mechanism encompassing two twists about two different imaginary C_3 axes via two six-coordinate trigonal prismatic transition states **TS1** and **TS2** and the *cis*,*trans*,*cis*-configured diastereomer (Figure 10). This twist mechanism does not require the rupture of any of the Ti−O, Ti−C, or Ti−N bonds.[86] Such a mechanism is plausible considering the exchange of unsymmetrical β-diketonate ligands in octahedral bis(chelate) complexes of the type $Ti(u\text{-}chel)_2X_2$ (X = Cl, Br, F, OR).[85,87] However, because of the limited data available at present, it cannot be ruled out that the ligand exchange of *rac*-γ,γ-**20a** occurs through an alternative mechanism involving rupture of the Ti−N and/or Ti−C bond(s) (vide infra) with generation of a five- or four-coordinate intermediate. Indeed, the rather long Ti−C1(**A**) bond in *rac*-γ,γ-**20a** could even be taken as an indication that the cleavage of the Ti−C-α bond leading to formation of a five-coordinate intermediate having an N−Ti-bonded allylic aminosulfoxonium ylide as ligand (vide infra) may be a facile process. The latter mechanistic scenario would imply that the C-1 atoms of *rac*-γ,γ-**20a** are configurationally labile, and that their configuration is determined by that of the S atom. The observed relative configuration,



rac-**21**

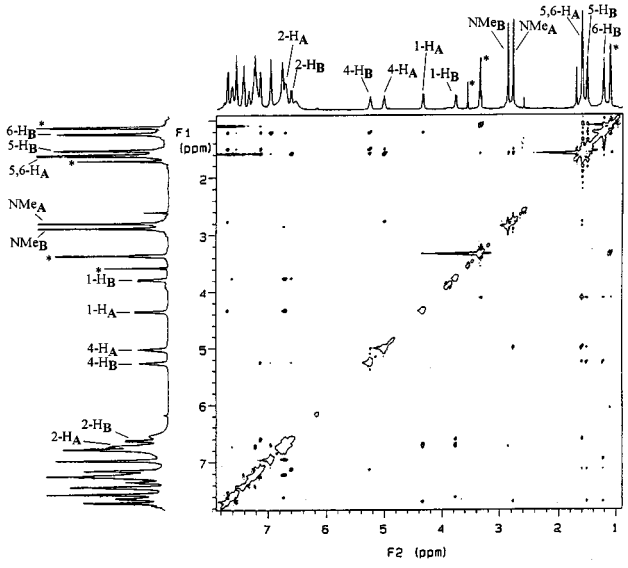


Figure 9. ROESY spectrum of the bis(alkenyl)diisopropyloxytitanium complex *rac*-γ,γ-**20a** in [D_8]THF at −90 °C; filled spots indicate positive and unfilled spots negative signals; signals marked with * are due to diethyl ether and/or [D_8]THF

R_S,S_C, would be in accordance with this line of thought since it has the vinylic group and the *S*-phenyl group in the thermodynamically more stable *trans* position.

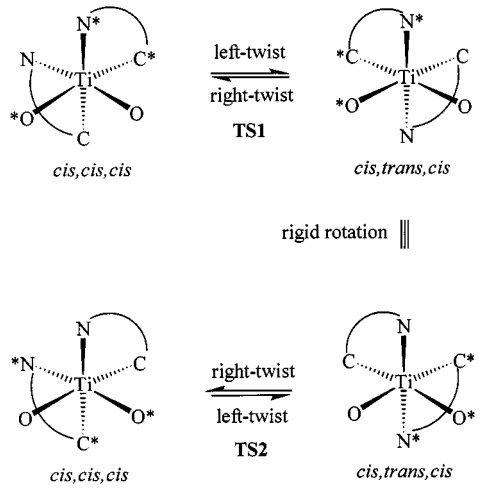
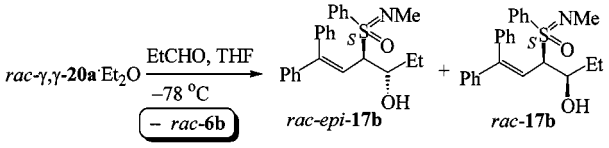


Figure 10. Putative twist mechanism of the ligand exchange of *rac*-γ,γ-**20a** (transition states **TS1** and **TS2** are not shown); the diastereotopic bidentate ligands are symbolized with C∩N and C*∩N*, and the diastereotopic isopropyloxy groups with O and O*; the complexes are viewed along the imaginary C_3 axis about which the twist is performed; the lower face of the octahedron (dotted bonds) is twisted with respect to the upper face (bold bonds), which is thought of as remaining constant

We have so far been unable to isolate the putative complex *rac*-γ,γ-**20b**. The incomplete NMR data set obtained for *rac*-γ,γ-**20b** in the mixture with *rac*-γ,γ-**20a** and Ti(O*i*Pr)$_4$ may also be compatible with a structure differing from *rac*-γ,γ-**20a** in the configuration at the Ti atom or/and at C-α. Although ^{1}H NMR spectroscopy (500 MHz) of a mixture of *rac*-γ,γ-**20a** and *rac*-γ,γ-**20b** [D$_8$]THF in the presence of Ti(O*i*Pr)$_4$ at 25 °C gave no indication (line broadening) of an equilibrium between the two complexes,[77] a re-examination of a sample of pure *rac*-γ,γ-**20a**·Et$_2$O in [D$_8$]THF, which had been kept at room temperature in a sealed NMR tube for 12 d, revealed the formation of up to 20% of *rac*-γ,γ-**20b** besides other unidentified products.[77] NMR saturation-transfer experiments[88] at 25 °C showed a slow exchange between the isopropyloxy groups of Ti(O*i*Pr)$_4$ and those of *rac*-γ,γ-**20a** and *rac*-γ,γ-**20b**,[78] which was, however, much faster in the case of *rac*-γ,γ-**20b**. Unfortunately, similar saturation-transfer experiments with the allylic moieties of the two complexes were unsuccessful because of signal overlap.

The six-coordinate bis(alkenyl)complex *rac*-γ,γ-**20a** can exist in eight diastereomeric forms, not counting those that are possible by changing the configurations at C-α and the S atom. However, within the limits of detection, the low-temperature NMR spectra of the *cic*,*cis*,*cis*-complex *rac*-γ,γ-**20a** gave no indication of an equilibrium with other diastereomers.

Finally, it was of interest to determine the reactivity of *rac*-γ,γ-**20a**·Et$_2$O towards aldehydes. Treatment of a solution of the pure complex *rac*-γ,γ-**20a** in THF at −78 °C with propanal gave a mixture of the *anti*- and *syn*-configured allylic sulfoximines *rac*-*epi*-**17b** and *rac*-**17b** in a ratio of 68:32 in 67% chemical yield (Scheme 16). The allylic sulfoximine *rac*-**6a** was recovered in 28% yield. An increase in the chemical yield of *rac*-*epi*-**17b** and *rac*-**17b** (69:31) to 79% was observed when, in the above experiment, the temperature of the reaction mixture was gradually allowed to increase from −78 °C to ambient. Likewise, the reaction of a 1:1 mixture of the complexes *rac*-γ,γ-**20a** and *rac*-γ,γ-**20b**, admixed with Ti(O*i*Pr)$_4$, with propanal at −78 °C in THF reached 72% completion and afforded a mixture of *rac*-*epi*-**17b** and *rac*-**17b** in a ratio of 69:31 in 51% chemical yield. No difference in reactivity was seen between the racemic and enantiopure complexes. This was demonstrated by the fact that starting from **6b** and *rac*-**6b**, the reactions furnished a mixture of *epi*-**17b** and **17b** in a ratio of 69:31 in 52% chemical yield, and a mixture of *rac*-*epi*-**17b** and *rac*-**17b** in a ratio of 69:31 in 52% chemical yield, respectively. Crystallization of the former mixture afforded diastereopure *epi*-**17b** in 38% yield. These results show that the bis(alkenyl)diisopropyloxytitanium complexes derived from Li-**6b**, γ,γ-**20a**, and γ,γ-**20b**, react with propanal in the same way as the bis(alkenyl)diisopropyloxytitanium complex derived from *Z*-Li-**4c** (*cf.* Scheme 5) and the mono(alkenyl)-tris(diethylamino)titanium complex derived from Li-**6b** (*cf.* Scheme 11), with high regioselectivity at the α-position. However, the facial selectivity of the aldehyde towards the aminotitanium complex is much higher than that towards the isopropyloxytitanium complexes.



Scheme 16. Reaction of the bis(alkenyl)diisopropyloxytitanium complex *rac*-γ,γ-**20a** with propanal

The configuration of *epi*-**17b** was confirmed by X-ray structure analysis (Figure 11).[67] In the crystal, *epi*-**17b** exhibits an intramolecular hydrogen bond between the hydroxy group and the N atom incorporated in a six-membered ring. The ethyl group is in a pseudoequatorial position, while the vinylic and *S*-phenyl groups are in pseudoaxial positions. According to NOE experiments and in view of the magnitude of the coupling constants ^3J(α-H,β-H) and ^3J(β-H,γ-H), in solution *epi*-**17b** also preferentially adopts such a hydrogen-bond stabilized conformation.

Attempted Rationalization of the Regio- and Stereoselectivities of the Titanium Complexes

Mono(alkenyl)tris(diethylamino)titanium Complexes

The selectivities of the reactions of the mono(alkenyl)tris-(diethylamino)titanium complexes of acyclic and cyclic allylic sulfoximines (cf. Schemes 13 and 15) with aldehydes can be summarized as follows:

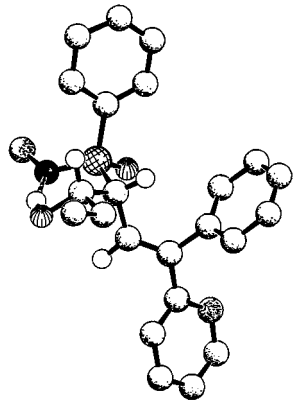


Figure 11. Crystal structure of sulfoximine *epi*-**17b** (some H atoms have been omitted for the sake of clarity); selected bond lengths [Å]: S−N 1.537(6), S−O 1.453(5), S−C 1.812(7), S−Ph 1.780(6)

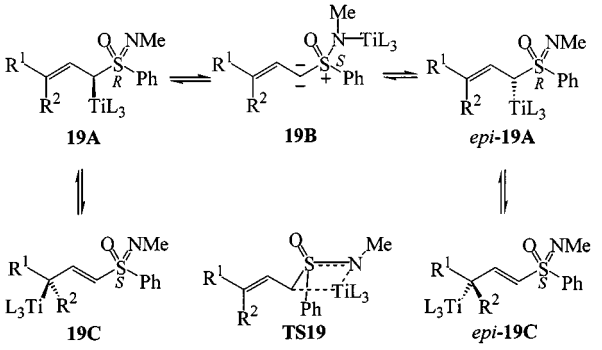
(a) The (*E*)-configured complexes *E*-**19** react with high diastereoselectivities at both the α- and γ-positions to give the (*E*)-*syn*-configured α-adduct *E*-**10** and the (*Z*)-*anti*-configured γ-adduct **7**, respectively. The regioselectivity is strongly dependent on the size of the aldehyde and of the substituent at the CC double bond. Except in cases where both are small, the reaction occurs with high selectivity at the α-position. The (*S*)-configuration of the sulfonimidoyl group in the starting allylic sulfoximine leads to a *Si*,*Si* process in the α-hydroxyalkylation and a *Re*,*Re* process in the γ-hydroxyalkylation.

(b) The (*Z*)-configured complexes *Z*-**19** and the γ,γ-disubstituted complexes γ,γ-**19** react with high regio- and diastereoselectivities at their α-positions, irrespective of the size of the reactants, to give the corresponding (*Z*)-*syn*-configured α-adduct *Z*-**10** and the *syn*-configured α-adduct **17**, respectively. The (*S*)-configuration of the sulfonimidoyl group in the starting allylic sulfoximine leads to a *Si*,*Si* process, and the configuration at the double bond in the starting material is retained.

(c) The reactions of complexes *E*-**19**, *Z*-**19**, and γ,γ-**19** are equally fast.

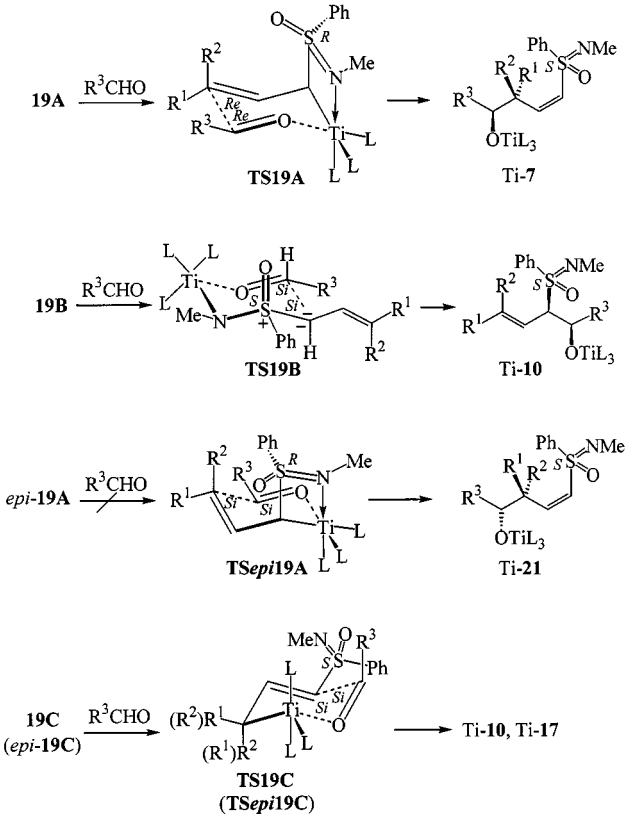
(d) The titanium complex derived from the cyclic allylic sulfoximine **15** reacts with high diasteroselectivities at both the α- and γ-positions to give the *syn*-configured α-adducts **18** and the (*Z*)-*anti*-configured γ-adducts **16**. The regioselectivity depends on the size of the aldehyde. Except with small aldehydes, reaction occurs with high selectivity at the α-position. The (*S*)-configuration of the sulfonimidoyl group in **15** leads to a *Si*,*Si* process.

For the rationalization of the regio- and stereoselectivities of the reactions of the mono(alkenyl)aminotitanium complexes *E*-**19**, *Z*-**19**, and γ,γ-**19** with aldehydes, we make the following assumptions, which are mainly based on the results of a variable-temperature NMR study of *E*-**19a** and the crystal structure of *rac*-γ,γ-**20a**·Et_2O. Complex **19** is an equilibrium mixture of the Cα-titanium complexes **19A** and *epi*-**19A** and the N-titanium complex **19B** (Scheme 17). Secondly, the reactions of **19A**, *epi*-**19A**, and **19B** with aldehydes are governed by the Curtin−Hammett principle,[89] i.e. the establishment of the equilibria between the complexes is fast relative to the time scale of their reactions with aldehydes. Thirdly, the reactions of the titanium complexes with aldehydes proceed through cyclic six-membered transition states. On the basis of these assumptions, the following proposals are made: Complex **19A** reacts preferentially via the chair-like transition state **TS19A**, in which the sulfoximine N atom is coordinated to the six-coordinate Ti atom, to give the *anti*-configured γ-adduct Ti-**7**, while **19B** reacts preferentially via the chair-like transition state **TS19B**, having a five-coordinate Ti atom, to furnish the *syn*-configured α-adduct Ti-**10** (Scheme 18). Transition states **TS19A** and **TS19B** are of similar energy in the case of small groups R^1 and R^3 and when the CC double bond has the (*E*) configuration. Hence, Ti-**7** and Ti-**10** will be formed with low regio- but high diastereoselectivities. In cases where the groups R^1 and R^3 are sterically more demanding, and the double bond has either the (*Z*)-configuration or bears two substituents at the γ-position, transition state **TS19A** is less favorable as a result of destabilizing steric interactions and transition state **TS19B** is preferred. Consequently, Ti-**10** and Ti-**17** are formed with high regio- and diastereoselectivities. Complex *epi*-**19A** is less reactive than complex **19A** because in the transition state **TS***epi***19A**, in which the sulfoximine N atom is also coordinated to the six-coordinate Ti atom, the phenyl group is in the sterically hindering *endo* position, whereas in transition state **TS19A** it is in the sterically nonhindering *exo* position. The fact that no Ti-**21** was formed is in accordance with these assumptions and proposals. The regio- and stereoselectivity of the reaction of the diethylaminotitanium complex derived from the cyclic carbanion Li-**15** with aldehydes could also be rationalized as outlined in Scheme 17.



Scheme 17. (L = NEt_2) Alleged dynamic behavior of the mono(alkenyl)tris(amino)titanium complexes **19**

The two key assumptions expressed in Schemes 17 and 18 are the existence of configurationally and constitutionally labile complexes **19A**, *epi*-**19A**, and **19B**, and the stereoselectivity of the hydroxyalkylation thus being dependent only on the configuration of the sulfonimidoyl group. The key complex **19B** may be regarded as an (*N*-titanyl-*N*-methylamino)sulfoxonium ylide. (*N*,*N*-Dialkylamino)sulfoxonium ylides bearing alkyl groups at C-α are synthetically well-established stable *S*-ylides, which are endowed with a high reactivity towards aldehydes.[2,90] An efficient stabil-



Scheme 18. (L = NEt_2) Attempted rationalization of the selectivities of the reaction of mono(alkenyl)tris(amino)titanium complexes **19** with aldehydes

ization of the negative charge on **19B** should not only be provided by the group $[PhS(O)(N(Me)TiL_3)]^+$, but also by allylic delocalization. The efficiency with which the dialkyl-substituted group $[PhS(O)(NR_2)]^+$ stabilizes a carbanion is illustrated by a pK_a value of 14.4 for the (dimethylamino)-methylphenylsulfoxonium cation, $[PhS(O)(NMe_2)Me]^+$.[90f] The isomeric ylides containing the group $[Ph(SOR)(NR)]^+$ are not known. Thus, we believe that the structure of **19B**, in which the titanyl group is bonded to the N and not to the O atom, should be more stable. This would be consistent with the bonding situation in the complex *rac*-γ,γ-**20a**·Et_2O. The [1,3-C/N]-shift of the titanyl group of **19A** could occur via the four-membered transition state **TS19**, a model for which may be seen in the complex *rac*-γ,γ-**20a**·Et_2O, where the allylic moieties are coordinated to the Ti atom through C-α and the N atom. A further key assumption inherent in Scheme 18 is the involvement of cyclic six-membered transitions states of the type depicted. While the evidence for the existence of such transition states is only circumstantial[2,10e] and cyclic four-membered transition states[10c,64,91] (S_E reaction) must, in principle, also be considered, they have regularly been invoked with much success for the rationalization of the regio- and stereoselectivities of reactions of allylic titanium reagents. Transition state **TS19B** features a Cα−S conformation of the ylide, in which the lone-pair orbital at C-α is periplanar to the S−Ph bond. Such a conformation has been found for the anion of the solvent-separated contact ion-pair of a lithiated allylic *N*-methyl-*S*-phenylsulfoximine in the crystal and for the free counterion of an allylic *N*-methyl-*S*-phenylsulfoximine by ab initio calculations.[18] According to the calculations, in this conformation the anion gains an additional stabilization through an n_C-σ^*_{SPh} interaction. In addition, experiment and calculation show that allylic sulfonimidoyl carbanions have a low Cα−S rotational barrier and thus a low configurational stability at C-α, even at low temperatures. Although, the Cα−S rotational barrier for **19B** is not known, it may well be that the allylic ylide also has a low configurational stability at C-α. Further possible equilibrium species of **19** not discussed thus far are the four-coordinate Cγ-titanium complexes **19C** and *epi*-**19C** (cf. Scheme 17), derived from **19A** and *epi*-**19A** by a [1,3-C/C]-shift. These complexes could, in principle, also react with aldehydes to give the α-adducts Ti-**10** and Ti-**17**. Although not observed by low-temperature NMR spectroscopic analysis of *E*-**19a**, the presence of **19C** and *epi*-**19C** as minor equilibrium components cannot be excluded. Such a fast [1,3-C/C]-shift has been proposed for sulfenyl-substituted (2-alkenyl)titanium complexes in order to rationalize the observed dependence of the regioselectivity of hydroxyalkylation on the structure of the allylic moiety.[92] However, as yet there is no direct experimental proof for such fluxional behavior of these S-substituted titanium complexes.[93] For the reactions of **19C** and *epi*-**19C** with aldehydes, a chair-like transition state of type **TS19C** or the corresponding boat-like transition state (not shown) would have to be considered (cf. Scheme 18). However, it is difficult to see why in the case of sterically demanding groups R^1 and R^3, a (*Z*)-configured double bond, and a γ,γ-disubstituted double bond, where exclusive α-attack leading to highly selective formation of the *syn*-adducts was observed, these transition states should be preferred to such an extent over **TS19A**. Similar arguments can be put forward in the case of the transition state **TS***epi***19C**. It seems interesting to note in this context that the α-attack of aldehydes on the above discussed sulfenyl-substituted (2-alkenyl)titanium complexes, where the existence of a γ-isomer of type **19C** as an equilibrium component has been held responsible for the formation of the corresponding α-hydroxyalkyl derivative,[10e] is highly *anti*- but not *syn*-selective as in the case of **19**.

Bis(alkenyl)diisopropyloxytitanium Complexes

The selectivities of the reactions of the bis(alkenyl)diisopropyloxytitanium complexes of acyclic and cyclic allylic sulfoximines (cf. Schemes 13 and 15) with aldehydes can be summarized as follows:

(a) The (*E*)-configured complexes *E*-**20** react with high regio- and diastereoselectivities at the γ-position, irrespective of the size of the aldehyde and the substituent at the CC double bond, with formation of the γ-adducts **7**. The (*S*)-configuration of the sulfonimidoyl group in the starting allylic sulfoximine leads to a *Re*,*Re* process. At low temperatures, only one allylic moiety of *E*-**20** is transferred with

high γ- and (*E*)-*anti*-selectivities. The second allylic moiety is transferred at ambient temperatures with high α-selectivity. However, the stereoselectivity is high only with regard to C-α, which bonds to the aldehyde in a *Re* process. In the presence of one equivalent of $ClTi(OiPr)_3$, however, both allylic moieties of *E*-**20** are transferred at low to ambient temperatures with high γ- and (*E*)-*anti*-selectivities to yield **7**.

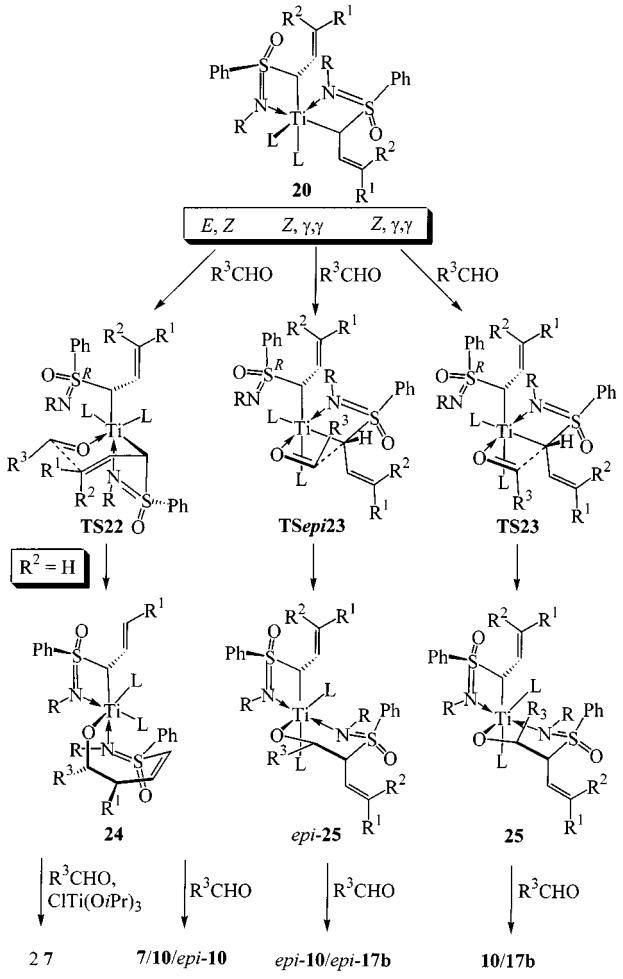
(b) The (*Z*)-configured complexes *Z*-**20** react with low diastereoselectivities at the α- and γ-positions to yield the corresponding (*E*)-*anti*- and (*E*)-*syn*-configured γ-adducts and the (*Z*)-*syn*- and (*Z*)-*anti*-configured α-adducts, respectively. The regioselectivity depends on the size of the substituent at the CC double bond. In the case of large substituents, only α-hydroxyalkylation occurs. However, in cases where the sulfonimidoyl group has the (*S*)-configuration, the diastereoselectivity is high only with regard to C-α, which bonds to the aldehyde in a *Re* process. Complexes *Z*-**20** react much more slowly than the isomeric complexes *E*-**20**.

(c) The γ,γ-disubstituted complexes γ,γ-**20** react with high selectivities at the α-position. However, in cases where the sulfonimidoyl group has the (*S*)-configuration, the diastereoselectivity is high only with regard to C-α, which bonds to the aldehyde in a *Re* process.

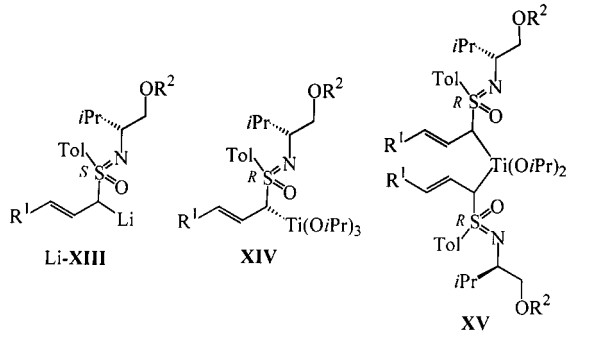
(d) The titanium complex derived from the cyclic allylic sulfoximine **15** reacts with high γ-selectivity and high diastereoselectivity to give the (*Z*)-*anti*-configured γ-adducts **16**. The (*S*)-configuration of the sulfonimidoyl group in **15** leads to a *Re*,*Re* process.

The reactions of the six-coordinate bis(alkenyl)isopropyloxytitanium complexes *E*-, *Z*-, and γ,γ-**20** and those derived from Li-**15** with aldehydes are more complicated and thus more difficult to rationalize than those of **19** because of the presence of two allylic moieties. These are expected to be transferred in a stepwise manner. Thus, six-coordinate mono(alkenyl)diisopropyloxytitanium complexes of types **24**, *epi*-**25**, and **25**, where the Ti atom bears a vinylic or allylic hydroxy sulfoximine as a ligand, have to be considered as reactive intermediates (Scheme 19). An indication of the formation of such intermediates may be seen in the noteworthy results obtained with *E*-**20** in the presence and absence of $ClTi(OiPr)_3$ at low and ambient temperatures (vide supra). It is remarkable that *E*-**20** and the mono(alkenyl)isopropyloxytitanium complexes **24** derived therefrom both react with aldehydes with similarly high γ- and *anti*-selectivities, at least in cases where only the γ-adduct is formed. Moreover, it is striking that in all reactions of complexes **20** with aldehydes, the (*S*)-configuration of the sulfonimidoyl group in the starting allylic sulfoximine leads to a *Re* process at C-α and to a *Si* process at C-γ. While some aspects of the transfer of the first allylic moiety in the reaction of **20** with aldehydes may be rationalized by making similar assumptions and proposals as in the case of **19** (cf. Schemes 17 and 18), other aspects can not. For example, the invariance of the regioselectivity of the γ-hydroxyalkylation of *E*-**20** using a variety of groups R^1 and R^3 and the low facial selectivity of the aldehyde in the reactions of *Z*-**20** and γ,γ-**20** fall into the latter category. Despite the structural information gained in the case of *rac*-γ,γ-**20a**, knowledge of the structure and dynamics of the bis(alkenyl)titanium complexes **20** is meagre. Hence, it cannot be excluded that, for example, complexes **20** are configurationally and constitutionally more stable than **19**, and that the selectivities of their hydroxyalkylation are determined by the regio- and diastereoselectivity of the titanation of the starting lithiated allylic sulfoximine, both of which might be high. Considering this scenario, the reactivity of the bis(alkenyl)-titanium complexes may be partly rationalized by making the following proposals: Complex *E*-**20** (R^1 = alkyl, R^2 = H), having a similar structure as *rac*-γ,γ-**20a** (R^1 = R^2 = Ph), reacts with the aldehyde via transition state **TS22** to yield the (2-alkenyl)titanium complex **24** incorporating **7** as a ligand. While intermediate **24** is attacked at C-γ by a second molecule of the aldehyde in the presence of $ClTi(OiPr)_3$ to yield two molecules of the γ-adduct **7**, in the absence of the titanium reagent attack occurs at the α-position to ultimately afford the α-adducts **10** and *epi*-**10** besides the γ-adduct **7**. Although the role of the chlorotitanium reagent has not yet been elucidated, one mode of action might involve its coordination to one of the sulfonimidoyl groups of **24**, thereby generating a free coordination side at the Ti atom. Complexes *Z*-**20** (R^1 = H, R^2 = Me, Et) bearing one small group at the γ-position may react via a transition state similar to **TS22**, but having the sulfonimidoyl group in an equatorial position, the group R^2 in an axial position, and the group R^3 in either an equatorial or axial position, to finally afford a mixture of **8** and **9** (cf. Scheme 5). Secondly, because of steric hindrance, complexes *Z*-**20** (R^1 = H, R^2 = *i*Pr) and γ,γ-**20** (R^1 = R^2 = alkyl, aryl) bearing either one large group or two groups at the γ-position would react with the aldehyde not at the γ-position but via transition state **TS***epi***23** at the α-position to give the (2-alkenyl)titanium complex *epi*-**25** incorporating *epi*-**10** or *epi*-**17b** as a ligand. Transition state **TS***epi***23** would arise in an S_E reaction of *Z*-**20** and γ,γ-**20** involving a frontside attack of the aldehyde at the Ti−Cα bond, which would thus proceed under retention of configuration at C-α. In the final step, intermediate *epi*-**25** would combine with a second molecule of the aldehyde in a similar S_E reaction to give two molecules of the α-adduct. Because of similar steric interactions between the group R^3 and the allylic moiety in **TS***epi***23** and between the group R^3 and the vinylic group in **TS23**, the transition states are similar in energy and the facial selectivity of the aldehyde is thus low, leading to mixtures of *epi*-**10** and **10** or *epi*-**17b** and **17b**.

It has already been stated in the introductory section that the titanation of lithiated cyclic and acyclic allylic sulfoximines bearing a chiral (silyloxy)alkyl group at the N atom (Scheme 20) with $ClTi(OiPr)_3$ furnishes (2-alkenyl)titanium complexes, which react with aldehydes with high *anti*-(*Z*)-stereoselectivity exclusively at the γ-position.[11,12,30] However, besides Li-**XIII**, no further lithiated acyclic allylic sulfoximines of this type have been investigated. Thus, little can be said at present concerning the dependence of the regioselectivity of the hydroxyalkylation on the substituents on the allylic moiety and the configuration at the double



Scheme 19. (L = O*i*Pr, R = Me) Attempted rationalization of the selectivities of the reaction of the bis(alkenyl)diisopropyloxytitanium complexes **20** with aldehydes



Scheme 20. (R^1 = H, Me; R^2 = Si*t*BuMe$_2$) Lithiated and titanated allylic sulfoximines having a (silyloxy)alkyl substituent at the N atom

bond. Recently, Reggelin et al. reported that the reaction of Li-**XIII** with ClTi(O*i*Pr)$_3$ furnishes the mono(2-alkenyl)titanium complexes **XIV** rather than the bis(2-alkenyl)titanium complexes **XV** and provided selected room temperature NMR spectroscopic data for **XIV** in the case of R^1 = H.[2,94] The apparently different reactivity of the *N*-methyl sulfoximines Li-**4** and the *N*-(silyloxy)alkyl sulfoximines Li-**XIII** towards ClTi(O*i*Pr)$_3$ was attributed to an inhibition of the formation of **XV** from **XIV**[95] due to an intramolecular saturation of the coordination sphere of the Ti atom by the O atom of the substituent at the N atom. Although the dynamic behavior of the titanium complexes derived from Li-**XIII** is not known at present, it has been suggested that it is the complex **XIV** having the $S_{C\alpha},R_S$ configuration that reacts with the aldehyde through a transition state of type **TS19A** to give the γ-hydroxyalkylation product.[2]

Conclusion

Cyclic and acyclic allylic *N*-methylsulfoximines are readily accessible in good yields from aldehydes or ketones and sulfoximines **1** or *ent*-**1** by the AEI route. Whereas this route is unproblematic in the case of symmetrical ketones, with aldehydes and acyclic unsymmetrical ketones mixtures of the (*E*)- and (*Z*)-configured allylic sulfoximines are obtained, which necessitates a chromatographic separation. Of synthetic advantage, however, is the fact that by judicious choice of the reaction conditions, the (*E*)- and (*Z*)-configured acyclic allylic sulfoximines can each be obtained as the major isomer.

Titanation of lithiated allylic *N*-methylsulfoximines with ClTi(O*i*Pr)$_3$ gives the corresponding bis(2-alkenyl)diisopropyloxytitanium(IV) complexes, while that with ClTi(NEt$_2$)$_3$ yields the corresponding mono(2-alkenyl)tris(diethylamino)-titanium(IV) complexes. Reaction of the bis(alkenyl)isopropyloxytitanium complexes of acyclic and cyclic allylic *N*-methyl sulfonimidoyl carbanions with aldehydes in the presence of one equivalent of ClTi(O*i*Pr)$_3$ furnishes δ-sulfonimidoyl-substituted *anti*-configured homoallylic alcohols in good yields with high selectivities, whereas the reaction of the corresponding mono(alkenyl)diethylaminotitanium complexes gives the isomeric β-sulfonimidoyl-substituted *syn*-configured homoallylic alcohols, also in good yields and with high selectivities. The only exception to this rule is the reaction of the mono(crotyl)aminotitanium complex with ethanal, which proceeds with low regioselectivity. It is noteworthy that the bis(alkenyl)isopropyloxytitanium complexes and the corresponding mono(alkenyl)diethylaminotitanium complexes give the same α- and γ-adducts and show similarly high stereoselectivities.

The determination of the structure of *rac*-γ,γ-**20a**, the first C-functionalized allylic titanium(IV) complex to be structurally characterized, revealed a bis(2-alkenyl)diisopropyloxytitanium complex with a distorted octahedral coordination geometry, where the allylic moieties are bound via their C and N atoms to the Ti atom and undergo rapid topomerization with retention of the configuration at C-α.

Although a considerable body of indirect and direct information has been gathered on the structure of the titanium complexes of allylic *N*-methylsulfonimidoyl carbanions, further structural studies are clearly required before a less speculative rationalization of the regio- and stereochemistry of their reactions with aldehydes can be proposed. The origin and the mechanism of the dynamic phenomena observed and, in particular, the question of a

[1,3-C/N]- and/or a [1,3-C/C]-shift of the titanyl group in these titanium complexes need further clarification.

As anticipated, the substituted homoallylic alcohols **II** and **III** represent interesting starting materials for the synthesis of enantio- and diastereopure building blocks of types **IV**−**VII** (cf. Scheme 20). We and others have already succeeded in the realization of transformations **II** → **IV**,[15,96] **II** → **V**,[30][97] **III** → **VI**,[98] and **III** → **VII**.[34]

Experimental Section

General: All reactions were carried out in absolute solvents under an argon atmosphere in oven-dried glassware using syringe and Schlenk techniques. Solutions of titanium complexes for NMR spectroscopic investigations were placed in oven-dried, argon-filled NMR tubes, which were then sealed. THF and diethyl ether were distilled under argon from potassium/benzophenone and sodium/benzophenone, respectively, or from sodium/lead alloy. CH_2Cl_2 and MeCN were distilled from calcium hydride; toluene was distilled from sodium. The titanium reagents $ClTi(OiPr)_3$,[64,99] $Cl_2Ti(OiPr)_2$,[99,100] and $ClTi(NEt_2)_3$[101,102] were prepared with purities ≥96% (^{1}H NMR) according to literature procedures. Enantiopure (+)- and (−)-*N*,*S*-dimethyl-*S*-phenylsulfoximines were prepared according to the literature.[9,32,33] − TLC: Merck silica gel 60 F_{254} plates. − Column chromatography: Merck silica gel 60 (0.063−0.200 mm). − MPLC: Kronwald, Merck LiChroprep Si 60 (15−25 μm). − HPLC: Merck Nova Prep 5000, Merck Hibar LiChrosorb Si 60 (7 μm). − Melting points: Büchi apparatus, uncorrected values. − Optical rotations: Perkin−Elmer model 241; measurements were made at ca. 22 °C, specific rotations are in grad × mL/dm × g, *c* in g/100 mL. − ^{1}H and ^{13}C NMR: Varian VXR 300, Varian Gemini 300, Varian Inova 400, and Varian Unity 500; peaks in the ^{13}C NMR spectra are denoted as "u" for carbons with zero or two attached protons or "d" for carbons with one or three attached protons, as determined using the APT pulse sequence. − GC analyses: Chrompack CP-9000 (DB-5: 30 m × 0.32 mm; 50 kPa H_2). − IR spectra: Perkin−Elmer PE 1759 FT, only peaks of $\tilde{\nu} > 700$ cm^{-1} are listed. − GC-MS: Magnum Finnigan (HT-5: 25 m, 0.25 mm; 50 kPa He, CI, 40 eV, MeOH). − MS: Varian MAT 212S (EI, 70 eV); other than the parent peak, only peaks of $m/z > 70$ and with an intensity > 10% are listed. − Elemental analyses: Microanalytical laboratories of the Institut für Organische Chemie and of the Institut für Anorganische Chemie, RWTH Aachen. − The term "diastereopure" is used for cases where no other diastereomer could be detected in the ^{1}H NMR spectrum (≥98% *ds*); cy = chemical yield.

X-ray Analyses: The crystal data and the most salient experimental parameters relating to the X-ray measurements and the crystal structure analyses are reported in Table 7, Table 8, and Table 9. The crystal structures of **7g**, **7j**, *E*-**10i**, *Z*-**10e**, **16c**, **16d**, and *epi*-**17b** were solved using direct methods as implemented in the XTAL3.2 package of crystallographic routines.[103] The crystal structure of *rac*-γ,γ-**20a**·Et_2O was solved by direct methods using SHELX-86[104] and refined using XTAL3.2. The high *R* value and the relatively high residual electron density of *rac*-γ,γ-**20a** are due to the poor quality of the crystal, which stems in part from the co-crystallization of the complex with one molecule of diethyl ether in the asymmetric unit. Furthermore, interpretation of the structural parameters is hampered by the disorder of the two isopropyloxy groups, which has been resolved in two isotropically refined components with equal population distribution. Molecular structures were visualized with the program SCHAKAL 92.[105]

Table 7. Crystal data and parameters of data collection for sulfoximines **7g** and **7j**

	7g	**7j**
Formula	$C_{15}H_{23}NO_2S$	$C_{20}H_{25}NO_2S$
M_r	281.42	343.49
Color and habit	colorless, irregular	colorless, irregular
Crystal size, ca. mm	0.5 × 0.5 × 0.5	0.3 × 0.3 × 0.4
Crystal system	orthorhombic	orthorhombic
Space group (No.)	$P\,2_12_12_1$ (19)	$P\,2_12_12_1$ (19)
a [Å]	9.1474(5)	8.951(1)
b [Å]	12.8943(8)	9.846(2)
c [Å]	13.7833(8)	21.544(2)
α [°]	90.0	90.0
β [°]	90.0	90.0
γ [°]	90.0	90.0
V [Å^3]	1625.73	1898.71
Z	4	4
D_{calcd} [g cm^{-3}]	1.150	1.202
μ [cm^{-1}]	17.12	15.54
Diffractometer	CDA4 Enraf−Nonius	CDA4 Enraf−Nonius
T [°C]	25	25
Radiation	Cu-K_α	Cu-K_α
λ [Å]	1.54179	1.54179
Monochromator	graphite	graphite
Scan method	Ω/2θ	Ω/2θ
Θ_{max} [°]	75.2	75.2
No. of data colld.	3995	9319
No. of unique data	3310	3929
Obsn. criterion	$I > 2\sigma(I)$	$I > 2\sigma(I)$
No. of params. refd.	173	218
No. of data obsd.	2162	2893
R, R_w[a]	0.062, 0.062	0.071, 0.068
Δ(ρ) [e Å^{-3}]	−0.8/+0.4	−0.4/+0.5
GoF	2.168	3.213

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w\,|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o)$, where F_o and F_c are observed and calculated structure factors.

(+)-(*E*,*S*)-*N*-Methyl-*S*-(1-butenyl)-*S*-phenylsulfoximine (3a): To a solution of **1** (10.26 g, 60.6 mmol) in THF (150 mL) at −78 °C was added *n*BuLi (41.2 mL, 1.60 M solution in hexane, 66 mmol). After stirring the mixture for 30 min, propanal (4.8 mL, 66 mmol) was added. The mixture was stirred for 2 h and then ClCOOMe (5.1 mL, 66 mmol) was added. After allowing the mixture to warm to room temperature, it was stirred for 1 h. It was then cooled to −78 °C once more, whereupon DBU (10 mL, 66 mmol) was added, which led to the deposition of a colorless precipitate. After allowing the mixture to warm to room temperature over a period of 12 h, it was treated with saturated aqueous NH_4Cl solution and extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and the solvent was removed in vacuo. Purification of the residue by chromatography (EtOAc/hexane, 4:1) gave **3a** (9.75 g, 78%) as a colorless oil; $[\alpha]_D$ = +25.8 (*c* = 1.00, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06 (t, *J* = 7.4 Hz, 3 H, CH_3), 2.26 (qdd, *J* = 7.4, *J* = 6.0, *J* = 1.7 Hz, 2 H, CH_2), 2.73 (s, 3 H, N−CH_3), 6.33 (dt, *J* = 15.1, *J* = 1.7 Hz, 1 H, 1-H), 6.92 (dt, *J* = 15.1, *J* = 6.0 Hz, 1 H, 2-H) 7.48−7.62 (m, 3 H, Ph), 7.84−7.90 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.8 (d), 24.7 (u), 29.4 (d), 128.7 (d), 129.2 (d), 129.3 (d), 132.5 (d), 136.8 (u), 148.3 (d). − IR ($CHCl_3$): $\tilde{\nu}$ = 2968 (m), 2934 (m), 2913 (m), 1628 (m), 1445 (s), 1288 (m), 1246 (s), 1150 (s), 1109 (m), 1081 (m), 1069 (m), 868 (m), 835 (m). − MS: *m*/*z* (%) = 210 [M$^+$ + 1] (2), 209 [M$^+$] (11), 181 (6), 154 (7), 126 (14), 125 (19), 109 (12), 107 (17), 106 (25), 97 (14), 84 (100), 78 (46), 77 (50). − $C_{11}H_{15}NOS$ (209.3): calcd. C 63.12, H 7.22, N 6.69; found C 63.01, H 7.46, N 6.97.

Table 8. Crystal data and parameters of data collection for sulfoximines *Z*-**10e**, *E*-**10i**, and **16c**

	Z-**10e**	*E*-**10i**	**16c**
Formula	$C_{14}H_{21}NO_2S$	$C_{17}H_{27}NO_2S$	$C_{18}H_{27}NO_2S$
M_r	267.39	309.47	321.49
Color and habit	colorless, irregular	colorless, irregular	colorless, irregular
Crystal size, ca. mm	0.5 × 0.5 × 0.5	0.3 × 0.3 × 0.5	0.3 × 0.3 × 0.3
Crystal system	monoclinic	monoclinic	orthorhombic
Space group (No.)	$P2_1$ (4)	$P2_1$ (4)	$P2_12_12_1$ (19)
a [Å]	9.2125(4)	5.767(1)	9.2016(4)
b [Å]	8.0612(4)	16.577(2)	9.912(4)
c [Å]	9.876(2)	10.265(1)	19.062(1)
α [°]	90.0	90.0	90.0
β [°]	90.83(1)	106.043(8)	90.0
γ [°]	90.0	90.0	90.0
V [Å^3]	733.35	943.07	1738.56
Z	2	2	4
D_{calcd} [g cm^{-3}]	1.211	1.090	1.228
μ [cm^{-1}]	18.74	15.11	16.57
Diffractometer	CDA4 Enraf−Nonius	CDA4 Enraf−Nonius	CAD4 Enraf−Nonius
T [°C]	−123	25	−123
Radiation	Cu-K_α	Cu-K_α	Cu-K_α
λ [A]	1.54179	1.54179	1.54179
monochromator	graphite	graphite	graphite
scan method	ω/2θ	Ω/2θ	ω/2θ
Θ_{max} [°]	75.2	74.8	75.5
No. of data colld.	4841	8230	7992
No. of unique data	1621	3891	3605
Obsn. criterion	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
No. of params. refd.	162	189	199
No. of data obsd.	1597	3568	3491
R, R_w[a]	0.077, 0.069	0.055, 0.057	0.067, 0.063
Δ(ρ) [e Å^{-3}]	−1.24/+1.27	−0.3/+0.3	−1.68/+0.96
GoF	2.128	2.909	2.220

[a] $R = \Sigma| |F_o| - |F_c| |/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w |F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o)$, where F_o and F_c are observed and calculated structure factors.

Table 9. Crystal data and parameters of data collection for sulfoximines **16d**, *epi*-**17b**, and *rac*-γ,γ-**20a**·Et_2O

	16d	*epi*-**17b**	*rac*-γ,γ-**20a**·Et_2O
Formula	$C_{21}H_{25}NO_2S$	$C_{25}H_{27}NO_2S$	$C_{54}H_{64}N_2O_5S_2Ti$
M_r	355.55	405.56	933.15 (incl. Et_2O)
Color and habit	colorless, irregular	colorless, irregular	orange-red, irregular
Crystal size, ca. mm	0.6 × 0.4 × 0.4	0.3 × 0.3 × 0.3	0.3 × 0.3 × 0.3
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group (No.)	$P2_12_12_1$ (19)	$P2_12_12_1$ (19)	$P2_1/c$ (19)
a [Å]	5.8355(4)	8.872(1)	21.62(2)
b [Å]	11.352(1)	15.110(1)	11.003(7)
c [Å]	28.217(6)	16.264(5)	21.680(9)
α [°]	90.0	90.0	90.0
β [°]	90.0	90.0	99.70(2)
γ [°]	90.0	90.0	90.0
V [Å^3]	1869.23	2180.37	5083.61
Z	4	4	4
D_{calcd} [g cm^{-3}]	1.263	1.236	1.219
μ [cm^{-1}]	15.97	14.31	25.44
Diffractometer	CAD4 Enraf−Nonius	CDA4 Enraf−Nonius	CDA4 Enraf−Nonius
T [°C]	−123	−123	−20
radiation	Cu-K_α	Cu-K_α	Cu-K_α
λ [Å]	1.54179	1.54179	1.54179
Monochromator	graphite	graphite	graphite
Scan method	Ω/2θ	ω/2θ	Ω/2θ
Θ_{max} [°]	75.2	75.5	55.1
No. of data colld.	4683	5267	7113
No. of unique data	3869	2574	6777
Obsn. criterion	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
No. of params. refd.	226	262	538
No. of data obsd.	3485	1881	3148
R, R_w[a]	0.056, 0.065	0.104, 0.056	0.100, 0.098
Δ(ρ) [e Å^{-3}]	−0.5/+1.0	1.67	−1.5/+1.2
GoF	2.294	1.372	2.488

[a] $R = \Sigma| |F_o| - |F_c| |/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w |F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o)$, where F_o and F_c are observed and calculated structure factors.

Following the same procedure, but starting from *rac*-**1**, sulfoximine *rac*-**3a** was prepared.

General Procedure for the Rearrangement of Vinylic to Allylic Sulfoximines (*GP1*): A solution of the vinylic sulfoximine **3** (50 mmol) in MeCN (150 mL) was treated with DBU (9.7 mL, 65 mmol) at room temperature.

Synthesis of *Z*-4 (*GP1.1*): Stirring of the aforementioned reaction mixture at room temperature was continued until TLC of GC indicated complete consumption of the starting material (approximately 15 h). Work-up as described below gave a mixture of *Z*-**4** and *E*-**4**, with the former being predominant.

Synthesis of *E*-4 (*GP1.2*): The temperature of the mixture obtained according to *GP 1.1* was increased to 60 °C and stirring was continued until the ratio of the (*E*) and (*Z*) isomers remained constant (approximately 48 h). Diethyl ether (750 mL) was then added and the mixture was washed with water (2×), saturated aqueous NH_4Cl solution, and 10% aqueous Na_2CO_3. The organic phase was dried ($MgSO_4$) and concentrated in vacuo to give a mixture of *E*-**4** and *Z*-**4**, with the former being predominant. The isomers were separated by MPLC or HPLC.

(+)-(*E,S*)- and (+)-(*Z,S*)-*N*-Methyl-*S*-(2-butenyl)-*S*-phenylsulfoximine (*E*-4a and *Z*-4a): Treatment of **3a** (6.90 g, 33 mmol) with DBU according to *GP1.1* and *GP1.2* gave mixtures of *E*-**4a** and *Z*-**4a** in ratios of 30:70 and 76:24, respectively, as colorless oils (6.55 g, 95%). Sulfoximines *E*-**4a** and *Z*-**4a** were isolated as colorless oils by HPLC (EtOAc/cyclohexane, 7:1) of the latter mixture. Their analytical data were identical to those reported in the literature.[7]

Following the same procedure, but starting from *rac*-**3a**, sulfoximines *rac*-*E*-**4a** and *rac*-*Z*-**4a** were obtained.

Synthesis of *E*-4a and *Z*-4a by the Shortened Route: To a solution of **1** (24.0 g, 0.14 mol) in THF (250 mL) at −78 °C was added *n*BuLi (97 mL, 1.60 M solution in hexane, 0.16 mol). After stirring the mixture for 30 min, propanal (11.2 mL, 0.16 mol) was added. The mixture was stirred for 2 h and then ClCOOMe (12 mL, 0.16 mmol) was added. After warming the resulting mixture to room temperature, it was stirred for 1 h. It was then cooled to −78 °C once more, whereupon DBU (27 mL, 0.18 mol) was added, which led to the deposition of a colorless precipitate. After allowing the mixture to warm to room temperature over a period of 12 h, it was treated with half-saturated aqueous NH_4Cl solution and extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and the solvent was removed in vacuo. The residue was redissolved in acetonitrile (300 mL) and DBU (27 mL, 0.18 mol) was added. After heating the mixture to 50 °C for 4 d, it was allowed to cool to room temperature, treated with half-saturated aqueous NH_4Cl, and extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and the solvent was removed in vacuo. Purification of the residue by chromatography (EtOAc/hexane, 4:1) gave a mixture of *E*-**4a** and *Z*-**4a** (22.5 g, 76%) in a ratio of 70:30 as a colorless oil.

(2*R*)- and (2*S*)-1-[(*S*)-*N*-Methyl-*S*-phenylsulfonimidoyl]pentan-2-ol (2b and *epi*-2b): To a solution of **1** (8.63 g, 51 mmol) in THF (120 mL) at −35 °C was added *n*BuLi (35.4 mL, 1.60 M solution in hexane, 57 mmol). The mixture was allowed to warm to room temperature, then cooled to −78 °C, whereupon *n*-butanal (5.2 mL, 59 mmol) was added dropwise. After stirring the mixture for 2 h at −78 °C, it was allowed to warm to room temperature. Stirring was continued for 13 h at room temperature, and then the mixture was poured into saturated aqueous NH_4Cl solution. The aqueous phase was extracted with EtOAc and the combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification of the residue by chromatography (EtOAc/hexane, 4:1) afforded a mixture of **2b** and *epi*-**2b** (12.30 g, 99%, 70:30) as a colorless oil; $[\alpha]_D$ = +71.1 (*c* = 1.91, MeOH).

2b: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.30−1.63 (m, 4 H, CH_2), 2.62 (s, 3 H, N−CH_3), 2.95 (dd, *J* = 13.6, *J* = 1.0 Hz, 1 H, 1-H), 3.23 (dd, *J* = 10.1, *J* = 13.6 Hz, 1 H, 1-H), 4.49 (m, 1 H, 2-H), 5.8 (br. s, OH), 7.57−7.72 (m, 3 H, Ph), 7.86−7.94 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8 (d), 18.2 (u), 29.0 (d), 38.6 (u), 62.2 (u), 65.0 (d), 129.1 (d), 129.7 (d), 133.3 (d), 138.0 (u).

epi-**2b:** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.30−1.63 (m, 4 H, CH_2), 2.70 (s, 3 H, N−CH_3), 3.03 (dd, *J* = 14.1, *J* = 1.7 Hz, 1 H, 1-H), 3.18 (dd, *J* = 14.4, *J* = 9.7 Hz, 1 H, 1-H), 3.85 (m, 1 H, 2-H), 5.8 (br. s, 1 H, OH), 7.57−7.72 (m, 3 H, Ph), 7.86−7.94 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2 (d), 18.2 (u), 29.0 (d), 38.5 (u), 61.5 (u), 65.7 (d), 129.5 (d), 129.7 (d), 133.4 (d), 137.0 (u). − MS: *m*/*z* (%) = 241 [M^+] (1), 194 (35), 156 (37), 155 (21), 154 (41), 126 (28), 125 (100), 107 (76), 106 (55), 105 (24), 98 (63), 97 (22), 78 (59), 77 (52). − $C_{12}H_{19}NO_2S$ (241.3): calcd. C 59.72, H 7.93, N 5.80; found C 59.78, H 8.44, N 5.77.

(+)-(*E,S*)-*N*-Methyl-*S*-(1-pentenyl)-*S*-phenylsulfoximine (3b): To a solution of a 7:3 mixture of **2b** and *epi*-**2b** (12.30 g, 51 mmol) in CH_2Cl_2 (100 mL) at 0 °C were added dropwise NEt_3 (14.2 mL, 102 mmol) and $MeSO_2Cl$ (6.2 mL, 66 mmol). The mixture was stirred for 3 h at 0 °C, filtered, and DBU (9.9 mL, 66 mmol) was added to the filtrate. After stirring the resulting mixture for 15 h at room temperature, diethyl ether (1200 mL) was added, and the solution was washed with water (200 mL), saturated aqueous NH_4Cl solution (200 mL), and 10% aqueous Na_2CO_3 (200 mL). The organic phase was dried ($MgSO_4$) and concentrated in vacuo. Purification of the residue by chromatography (EtOAc/hexane, 4:1) gave **3b** (11.15 g, 98%), R_f = 0.42 (EtOAc/hexane, 4:1); $[\alpha]_D$ = +6.9 (*c* = 1.08, MeOH). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.4 Hz, 3 H, CH_3), 1.48 (sext, *J* = 7.4 Hz, 2 H, 4-H), 2.20 (td, *J* = 7.4, *J* = 1.3 Hz, 2 H, 3-H), 2.74 (s, 3 H, N−CH_3), 6.31 (dt, *J* = 15.1, *J* = 1.3 Hz, 1 H, 1-H), 6.85 (dt, *J* = 15.1, *J* = 6.7 Hz, 1 H, 2-H), 7.49−7.61 (m, 3 H, Ph), 7.88 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.6 (d), 21.0 (u), 29.4 (d), 33.4 (u), 128.7 (d), 129.3 (d), 130.3 (d), 132.5 (d), 139.6 (u), 146.7 (d). − IR (neat): $\tilde{\nu}$ = 3060 (w), 2958 (s), 2929 (m), 2871 (m), 2803 (w), 1630 (w), 1466 (m), 1446 (s), 1382 (w), 1338 (w), 1246 (s), 1150 (s), 1109 (m), 1082 (m), 1069 (m), 969 (m), 866 (m), 812 (w), 752 (m). − MS: *m*/*z* (%) = 223 [M^+] (20), 195 (19), 194 (55), 156 (17), 155 (19), 154 (49), 126 (27), 125 (59), 117 (14), 109 (18), 107 (57), 106 (59), 105 (19), 98 (100), 97 (17), 78 (59), 77 (50). − $C_{12}H_{17}NOS$ (223.3): calcd. C 64.54, H 7.67, N 6.27; found C 64.57, H 7.87, N 6.43.

(+)-(*E,S*)- and (−)-(*Z,S*)-*N*-Methyl-*S*-(2-pentenyl)-*S*-phenylsulfoximine (*E*-4b and *Z*-4b): Treatment of **3b** (11.15 g, 49.9 mmol) with DBU according to *GP1.1* and *GP1.2* gave mixtures of *E*-**4b** and *Z*-**4b** in ratios of 25:75 and 75:25, respectively, as colorless oils (10.14 g, 91%). Sulfoximines *E*-**4b** and *Z*-**4b** were isolated as colorless oils by HPLC (EtOAc/cyclohexane, 4:1) of the latter mixture.

E-**4b:** R_f = 0.39 (EtOAc/hexane, 4:1); $[\alpha]_D$ = +59.7 (*c* = 1.51, MeOH). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.4 Hz, 3 H, CH_3), 1.98 (m, 2 H, 4-H), 2.72 (s, 3 H, N−CH_3), 3.79 (d, *J* = 6.1 Hz, 2 H, 1-H), 5.38 (dm, *J* = 15.4 Hz, 1 H, 3-H), 5.47 (dd, *J* = 15.4, *J* = 5.5 Hz, 1 H, 2-H), 7.63−7.50 (m, 3 H, Ph), 7.80 (dt, *J* = 6.4, *J* = 2.0 Hz, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.0 (d), 26.0 (u), 29.7 (d), 60.2 (u), 115.8 (d), 129.1 (d), 129.8 (d),

132.8 (d), 136.9 (u), 142.6 (d). − IR (neat): $\tilde{\nu}$ = 3060 (w), 2959 (s), 2929 (s), 2871 (s), 2803 (m), 1662 (w), 1582 (w), 1465 (m), 1446 (s), 1403 (m), 1376 (w), 1340 (w), 1247 (s), 1147 (s), 1108 (m), 1082 (m), 970 (m), 922 (w), 873 (m), 858 (m), 769 (m), 738 (s). − MS: *m*/*z* (%) = 223 [M^+] (2), 194 (100), 155 (22), 154 (61), 125 (48), 107 (50), 106 (49), 105 (21), 98 (16), 78 (55), 77 (38). − $C_{12}H_{17}NOS$ (223.3): calcd. C 64.54, H 7.67, N 6.27; found C 64.18, H 7.79, N 6.65.

Z-**4b:** R_f = 0.41 (EtOAc/hexane, 4:1); $[\alpha]_D$ = +59.5 (*c* = 2.38, MeOH). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.70 (t, *J* = 7.4 Hz, 3 H, CH_3), 1.70 (m, 2 H, 4-H), 2.73 (s, 3 H, N−CH_3), 3.91 (m, 2 H, 1-H), 5.41 (m, 1 H, 2-H), 5.65 (m, 1 H, 3-H), 7.51−7.64 (m, 3 H, Ph), 7.84 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.4 (d), 20.6 (u), 29.7 (d), 55.0 (u), 115.3 (d), 129.1 (d), 129.8 (d), 132.8 (d), 137.0 (u), 140.5 (d). − IR (neat): $\tilde{\nu}$ = 3062 (w), 3020 (w), 2961 (s), 2930 (m), 2870 (m), 2803 (m), 1655 (w), 1582 (w), 1466 (m), 1446 (s), 1411 (w), 1393 (w), 1305 (w), 1246 (s), 1145 (s), 1107 (s), 1082 (m), 1019 (w), 999 (w), 906 (m), 855 (m), 793 (w), 758 (m), 718 (s). − MS: *m*/*z* (%) = 223 [M^+] (2), 194 (89), 156 (42), 155 (28), 154 (100), 125 (58), 107 (59), 106 (70), 105 (32), 98 (21), 97 (14), 78 (61), 77 (52). − $C_{12}H_{17}NOS$ (223.3): calcd. C 64.54, H 7.67, N 6.27; found C 64.19, H 7.89, N 6.56.

Synthesis of *E*-4b and *Z*-4b by the Shortened Route: Following the procedure described for the synthesis of *E*-**4a** and *Z*-**4a**, a mixture of *E*-**4b,** *Z*-**4b**, and *E*-**3b** in a ratio of 86:12:2 was obtained in 95% overall yield starting from **1** and *n*-butanal.

(2*R*)- and (2*S*)-1-[(*S*)-*N*-Methyl-*S*-phenylsulfonimidoyl]-4-methylpentan-2-ol (2c and *epi*-2c): To a solution of **1** (13.60 g, 80.3 mmol) in THF (100 mL) at −35 °C was added *n*BuLi (58.7 mL, 1.50 M solution in hexane, 88 mmol). The mixture was allowed to warm to room temperature, then cooled to −78 °C, whereupon 3-methylbutanal (9.5 mL, 88 mmol) was added dropwise. After stirring the resulting mixture for 2 h at −78 °C, it was allowed to warm to room temperature and stirring was continued for a further 13 h. It was then poured into saturated aqueous NH_4Cl solution and the aqueous phase was extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification of the residue by chromatography (EtOAc/hexane, 4:1) furnished a mixture of **2c** and *epi*-**2c** (19.40 g, 95%, 66:34) as a colorless oil.

2c: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (d, *J* = 6.7 Hz, 3 H, CH_3), 0.93 (d, *J* = 6.7 Hz, 3 H, CH_3), 1.08 (m, 1 H, 3-H), 1.13 (m, 1 H, 3-H), 1.82 (sept, *J* = 6.7 Hz, 1 H, 4-H), 2.62 (s, 3 H, N−CH_3), 2.92 (dd, *J* = 13.6, *J* = 1.0 Hz, 1 H, 1-H), 3.24 (dd, *J* = 13.6, *J* = 10.1 Hz, 1 H, 1-H), 4.57 (tdd, *J* = 9.6, *J* = 4.7, *J* = 1.0 Hz, 1 H, 2-H), 6.8 (br. s, OH), 7.56−7.70 (m, 3 H, Ph), 7.86−7.94 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.9 (d), 23.2 (d), 24.1 (d), 28.9 (d), 45.6 (u), 62.5 (u), 63.5 (d), 129.1 (d), 129.7 (d), 133.4 (d), 137.9 (u).

epi-**2c:** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.78 (d, *J* = 6.7 Hz, 3 H, CH_3), 0.83 (d, *J* = 6.4 Hz, 3 H, CH_3), 1.44−1.58 (m, 2 H, 3-H), 1.72 (sept d, *J* = 6.4, *J* = 1.7 Hz, 1 H, 4-H), 2.70 (s, 3 H, N−CH_3), 3.02 (dd, *J* = 14.1, *J* = 1.7 Hz, 1 H, 1-H), 3.17 (dd, *J* = 14.4, *J* = 9.7, 1 H, 1-H), 3.90 (dtd, *J* = 9.2, *J* = 4.7, *J* = 1.7 Hz, 1 H, 2-H), 6.8 (br. s, 1 H, OH), 7.56−7.70 (m, 3 H, Ph), 7.86−7.94 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.0 (d), 22.9 (d), 24.1 (d), 29.0 (d), 45.3 (d), 61.8 (d), 64.2 (u), 129.5 (d), 129.7 (d), 133.5 (d), 136.9 (u). − MS: *m*/*z* (%) = 255 [M^+] (2), 198 (20), 156 (100), 125 (67), 107 (32), 78 (21). − $C_{13}H_{21}NO_2S$ (255.3): calcd. C 61.14, H 8.29, N 5.48; found C 61.36, H 8.52, N 5.83.

(+)-(*E*,*S*)-*N*-Methyl-*S*-(4-methyl-1-pentenyl)-*S*-phenylsulfoximine (3c): To a solution of a mixture of **2c** and *epi*-**2c** (66:34) (19.40 g, 76.0 mmol) in CH_2Cl_2 (300 mL) at 0 °C were added dropwise NEt_3 (21 mL, 158 mmol) and $MeSO_2Cl$ (7.7 mL, 103 mmol). The mixture was stirred at this temperature for 3 h, and then DBU (28.4 mL, 130 mmol) was added. After stirring the resulting mixture for 15 h at room temperature, diethyl ether (600 mL) was added and the solution was washed with water, saturated aqueous NH_4Cl solution, and 10% aqueous Na_2CO_3. The organic phase was dried ($MgSO_4$) and concentrated in vacuo. Purification of the residue by chromatography (EtOAc/hexane, 4:1) gave **3c** (16.10 g, 89%) as a colorless oil, R_f = 0.41 (EtOAc/hexane, 4:1); $[\alpha]_D$ = +5.2 (*c* = 1.58, MeOH). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (d, *J* = 6.4 Hz, 3 H, CH_3), 0.90 (d, *J* = 6.7 Hz, 3 H, CH_3), 1.76 [sept, *J* = 6.7 Hz, 1 H, C*H*(CH_3)$_2$], 2.10 (td, *J* = 7.4, *J* = 1.3 Hz, 2 H, 3-H), 2.74 (s, 3 H, N−CH_3), 6.31 (dt, *J* = 15.1, *J* = 1.3 Hz, 1 H, 1-H), 6.83 (dt, *J* = 15.1, *J* = 7.4 Hz, 1 H, 2-H), 7.50−7.60 (m, 3 H, Ph), 7.88 (dt, *J* = 6.4, *J* = 2.0 Hz, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.2 (d), 22.3 (d), 27.7 (d), 29.4 (d), 40.6 (u), 128.6 (d), 129.3 (d), 131.0 (d), 132.5 (d), 139.5 (u), 146.0 (d). − IR (neat): $\tilde{\nu}$ = 3060 (w), 2958 (s), 2929 (m), 2871 (m), 2803 (w), 1630 (w), 1466 (m), 1446 (m), 1386 (w), 1368 (w), 1246 (s), 1150 (s), 1109 (m), 1082 (m), 1069 (m), 975 (m), 866 (m), 804 (w), 791 (w), 750 (m). − GC/MS: *m*/*z* (%) = 239 (14), 238 [M^+ + 1] (100), 236 (12), 209 (4), 192 (4), 149 (5), 126 (7), 125 (18), 117 (7), 115 (8), 112 (31), 109 (8), 107 (17), 106 (12), 97 (12), 81 (21), 79 (12), 78 (13), 77 (16). − $C_{13}H_{19}NOS$ (237.3): calcd. C 65.76, H 8.07, N 5.92; found C 65.50, H 8.28, N 6.07.

(+)-(*E*,*S*)- and (+)-(*Z*,*S*)-*N*-Methyl-*S*-(4-methyl-2-pentenyl)-*S*-phenylsulfoximine (*E*-4c and *Z*-4c): Treatment of **3c** (16.10 g, 67.8 mmol) with DBU according to *GP1.1* and *GP1.2* gave mixtures of *E*-**4c** and *Z*-**4c** in ratios of 17:83 and 83:17, respectively, as colorless oils (14.5 g, 90%). Sulfoximines *E*-**4c** and *Z*-**4c** were isolated as colorless oils by MPLC (EtOAc/cyclohexane, 6:1) of the latter mixture.

E-**4c:** R_f = 0.37 (EtOAc/hexane, 4:1); $[\alpha]_D$ = +62.2 (*c* = 6.53, MeOH). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84 (d, *J* = 6.6 Hz, 3 H, CH_3), 0.86 (d, *J* = 6.0 Hz, 3 H, CH_3), 2.22 (oct, *J* = 6.6 Hz, 1 H, 4-H), 2.73 (s, 3 H, N−CH_3), 3.78 (d, *J* = 6.3 Hz, 2 H, 1-H), 5.30 (dd, *J* = 15.4, *J* = 5.8 Hz, 1 H, 3-H), 5.37 (dt, *J* = 15.4, *J* = 6.9 Hz, 1 H, 2-H), 7.63−7.50 (m, 3 H, Ph), 7.80 (dt, *J* = 6.6, *J* = 1.9 Hz, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.8 (d), 29.8 (d), 31.2 (d), 60.1 (u), 129.0 (d), 129.9 (d), 132.8 (d), 134.0 (d), 136.6 (u), 147.9 (d). − IR (neat): $\tilde{\nu}$ = 3060 (w), 2959 (s), 2929 (s), 2871 (s), 2803 (m), 1662 (w), 1582 (w), 1465 (m), 1446 (s), 1403 (m), 1384 (w), 1364 (w), 1247 (s), 1147 (s), 1108 (m), 1082 (m), 973 (m), 955 (w), 893 (m), 858 (m), 769 (m), 738 (s). − GC/MS: *m*/*z* (%) = 238 [M^+ + 1] (8), 194 (84), 125 (100), 107 (28), 106 (17), 97 (23), 78 (30), 77 (28). − $C_{13}H_{19}NOS$ (237.3): calcd. C 65.76, H 8.07, N 5.92; found C 65.53, H 8.30, N 6.10.

Z-**4c:** R_f = 0.39 (EtOAc/hexane, 4:1); $[\alpha]_D$ = +63.0 (*c* = 3.54, MeOH). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.63 (d, *J* = 6.4 Hz, 3 H, CH_3), 0.72 (d, *J* = 6.7 Hz, 3 H, CH_3), 2.18 (dseptd, *J* = 9.7, *J* = 6.7, *J* = 0.7 Hz, 1 H, 4-H), 2.72 (s, 3 H, N−CH_3), 3.88 (ddd, *J* = 14.1, *J* = 7.7, *J* = 1.3 Hz, 1 H, 1-H), 3.94 (ddd, *J* = 14.1, *J* = 8.0, *J* = 1.3 Hz, 1 H, 1-H), 5.30 (dtd, *J* = 10.7, *J* = 7.7, *J* = 0.7 Hz, 1 H, 2-H), 5.47 (ddt, *J* = 11.1, *J* = 9.7, *J* = 1.0 Hz, 1 H, 3-H), 7.51−7.63 (m, 3 H, Ph), 7.84 (dt, *J* = 1.7, *J* = 6.4 Hz, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.4 (d), 22.4 (d), 26.9 (d), 29.7 (d), 55.1 (u), 113.5 (d), 129.1 (d), 129.9 (d), 132.8 (d), 137.0 (u), 145.8 (d). − IR (neat): $\tilde{\nu}$ = 3062 (w), 3020 (w), 2958 (s), 2924 (m), 2870 (m), 2803 (m), 1655 (w), 1582 (w), 1466 (m), 1446 (m), 1411 (w), 1379 (w), 1362 (w), 1305 (w), 1246 (s), 1149 (s), 1107 (s), 1082 (m), 1013 (w), 999 (w), 926 (w), 898 (w), 856 (w), 824 (w),

793 (w), 758 (m), 733 (s). − GC/MS: *m*/*z* (%) = 238 [M^+ + 1] (35), 194 (49), 156 (52), 154 (31), 125 (69), 112 (19), 107 (54), 106 (50), 105 (24), 97 (22), 78 (44), 77 (43). − $C_{13}H_{19}NOS$ (237.3): calcd. C 65.76, H 8.07, N 5.92; found C 65.90, H 8.25, N 6.25.

Synthesis of *E*-4c and *Z*-4c by the Shortened Route: Following the procedure described for the synthesis of *E*-**4a** and *Z*-**4a**, a mixture of *E*-**4c**, *Z*-**4c**, and *E*-**3c** in a ratio of 88:9:3 was obtained in 92% overall yield starting from **1** and 3-methylbutanal.

(+)-(*E*,*S*)-*N*-Methyl-*S*-(3-cyclohexyl-1-propenyl)-*S*-phenylsulfoximine (3d): To a solution of **1** (8.46 g, 50.0 mmol) in THF (100 mL) at −78 °C was added *n*BuLi (40.3 mL, 1.49 M solution in hexane, 60 mmol). The mixture was allowed to warm to room temperature, then cooled to −78 °C, whereupon cyclohexylethanal (9.11 mL, 65 mmol) was added dropwise. The resulting mixture was allowed to warm to room temperature and stirred for 3 h, then cooled to 0 °C, whereupon NEt_3 (20.8 mL, 150 mmol) and $MeSO_2Cl$ (5.0 mL, 65 mmol) were added dropwise. After stirring the resulting mixture for 20 h at room temperature, it was poured into saturated aqueous NH_4Cl solution (150 mL), and the aqueous phase was extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification of the residue by chromatography (EtOAc/hexane, 4:1) furnished **3d** (13.20 g, 95%) as a slowly crystallizing colorless oil; $[\alpha]_D$ = +26.9 (*c* = 2.32, acetone). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.81−0.97 (m, 2 H, C_6H_{11}), 1.01−1.30 (m, 3 H, C_6H_{11}), 1.35−1.50 (m, 1 H, 4-H), 1.55−1.70 (m, 5 H, C_6H_{11}), 2.10 (td, *J* = 7.4, *J* = 1.4 Hz, 2 H, 3-H), 2.74 (s, 3 H, N−CH_3), 6.31 (dt, *J* = 14.8, *J* = 1.4 Hz, 1 H, 1-H), 6.84 (dt, *J* = 14.8, *J* = 7.4 Hz, 1 H, 2-H), 7.48−7.61 (m, 3 H, Ph), 7.86 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.1 (u), 26.2 (u), 29.5 (d), 33.0 (u), 33.0 (u), 37.1 (d), 39.3 (u), 128.6 (d), 129.3 (d), 130.8 (d), 132.5 (d), 139.6 (u), 145.9 (d). − IR (neat): ṽ = 3013 (m), 2918 (s), 2849 (s), 2799 (m), 1633 (m), 1580 (w), 1475 (w), 1447 (s), 1242 (s), 1151 (s), 1106 (s), 1080 (s), 977 (m), 871 (s), 856 (s), 805 (s), 755 (s). − MS: *m*/*z* (%) = 277 [M^+] (9), 249 (15), 195 (21), 156 (22), 155 (20), 152 (69), 126 (36), 125 (68), 121 (22), 117 (21), 116 (12), 115 (15), 109 (16), 108 (10), 107 (100), 106 (36), 97 (20), 95 (42), 93 (20), 83 (19), 81 (15), 79 (27), 78 (30), 77 (33), 70 (56). − $C_{16}H_{23}NOS$ (277.4): calcd. C 69.27, H 8.36, N 5.05; found C 69.23, H 8.52, N 5.06.

(+)-(*E*,*S*)- and (+)-(*Z*,*S*)-*N*-Methyl-*S*-(3-cyclohexyl-2-propenyl)-*S*-phenylsulfoximine (*E*-4d and *Z*-4d): Treatment of **3d** (13.00 g, 46.8 mmol) with DBU according to *GP1.1* and *GP 1.2* gave mixtures of *E*-**4d** and *Z*-**4d** in ratios of 20:80 and 90:10, respectively, as colorless oils (11.7 g, 90%). Sulfoximines *E*-**4d** and *Z*-**4d** were isolated as a colorless oil and as colorless crystals, respectively, by MPLC (EtOAc/hexane, 4:1) of the latter mixture.

E-**4d:** R_f = 0.48 (EtOAc/hexane, 4:1); $[\alpha]_D$ = +71.7 (*c* = 2.74, acetone). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.79−1.00 (m, 2 H), 1.00−1.15 (m, 4 H), 1.23−1.68 (m, 4 H), 1.82−1.97 (m, 1 H, 4-H), 2.73 (s, 3 H, N−CH_3), 3.78 (d, *J* = 6.4 Hz, 2 H, 1-H), 5.27 (dd, *J* = 15.4, *J* = 6.1 Hz, 1 H, 2-H), 5.37 (dtd, *J* = 15.4, *J* = 7.1, *J* = 0.6 Hz, 1 H, 3-H), 7.49−7.63 (m, 3 H, Ph), 7.79 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.7 (u), 26.0 (u), 29.8 (d), 32.3 (u), 32.3 (u), 40.7 (d), 60.3 (u), 114.4 (d), 129.0 (d), 129.9 (d), 132.7 (d), 136.6 (u), 146.7 (d). − IR (neat): ṽ = 3060 (w), 2924 (s), 2851 (s), 2802 (m), 1661 (w), 1582 (w), 1446 (s), 1403 (m), 1248 (s), 1147 (s), 1109 (s), 1082 (s), 970 (s), 896 (m), 856 (m), 766 (m), 736 (s). − MS: *m*/*z* (%) = 277 [M^+] (1), 194 (51), 156 (40), 155 (33), 154 (17), 152 (14), 126 (13), 125 (50), 123 (3), 107 (100), 106 (21), 105 (11), 81 (90), 79 (26), 78 (67), 77 (25). − $C_{16}H_{23}NOS$ (277.4): calcd. C 69.27, H 8.36, N 5.05; found C 69.42, H 8.33, N 4.94.

Z-**4d:** R_f = 0.49 (EtOAc/hexane, 4:1); m.p. 62 °C; $[\alpha]_D$ = +84.0 (*c* = 2.42, acetone). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.75−1.30 (m, 6 H, C_6H_{11}), 1.48−1.65 (m, 4 H, C_6H_{11}), 1.77 (dtt, *J* = 10.5, *J* = 10.5, *J* = 3.3 Hz, 1 H, 4-H), 2.73 (s, 3 H, N−CH_3), 3.89 (dd, *J* = 14.1, *J* = 7.7 Hz, 1 H, 1-H), 3.97 (dd, *J* = 14.1, *J* = 8.1 Hz, 1 H, 1-H), 5.30 (ddd, *J* = 10.5, *J* = 8.1, *J* = 7.7 Hz, 1 H, 2-H), 5.48 (dd, *J* = 10.5, *J* = 10.5 Hz, 1 H, 1-H), 7.51−7.63 (m, 3 H, Ph), 7.82−7.87 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.5 (u), 25.7 (u), 29.7 (d), 32.4 (u), 36.7 (d), 55.1 (u), 113.7 (u), 129.1 (d), 129.9 (d), 132.8 (d), 136.8 (u), 144.4 (d). − IR (KBr): ṽ = 2921 (s), 2850 (s), 2798 (m), 1699 (w), 1578 (w), 1445 (s), 1399 (m), 1247 (m), 1150 (s), 1106 (s), 1080 (s), 1004 (m), 908 (m), 882 (s), 850 (s), 800 (m), 759 (s), 729 (s). − GC/MS: *m*/*z* (%) = 277 [M^+] (1), 194 (58), 156 (54), 155 (18), 154 (27), 152 (11), 126 (15), 125 (90), 107 (62), 106 (31), 105 (13), 97 (22), 81 (100), 79 (32), 78 (48), 77 (52), 70 (11). − $C_{16}H_{23}NOS$ (277.4): calcd. C 69.27, H 8.36, N 5.05; found C 68.99, H 8.30, N 4.98.

Synthesis of *E*-4d and *Z*-4d by the Shortened Route: Following the procedure described for the synthesis of *E*-**4a** and *Z*-**4a**, a mixture of *E*-**4d**, *Z*-**4d**, and *E*-**3d** in a ratio of 88:9:3 was obtained in 90% overall yield starting from **1** and cyclohexanecarbaldehyde.

(−)-(*E*,*S*)-*N*-Methyl-*S*-(3-methyl-1-butenyl)-*S*-phenylsulfoximine (5a): To a solution of **1** (8.04 g, 47.5 mmol) in THF (100 mL) at −78 °C was added *n*BuLi (32.3 mL, 1.60 M solution in hexane, 51.7 mmol). The mixture was allowed to warm to room temperature, then cooled to −78 °C, whereupon 2-methylpropanal (3.2 mL, 56 mmol) was added dropwise. The mixture was allowed to warm to room temperature and stirred for 3 h, and then cooled to 0 °C, whereupon NEt_3 (19.5 mL, 141 mmol) and $MeSO_2Cl$ (4.7 mL, 61 mmol) were added dropwise. After stirring for 20 h at room temperature, the mixture was poured into saturated aqueous NH_4Cl solution (150 mL) and the aqueous phase was extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Chromatography of the residue (EtOAc/hexane, 4:1) gave **5a** (6.74 g, 64%) as a colorless oil; R_f = 0.42 (EtOAc/hexane, 4:1); $[\alpha]_D$ = −9.7 (*c* = 2.67, MeOH). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.04 (d, *J* = 2.0 Hz, 3 H, CH_3), 1.07 (d, *J* = 2.0 Hz, 3 H, CH_3), 2.49 (dt, *J* = 6.4, *J* = 1.7 Hz, 1 H, 3-H), 2.73 (s, 3 H, N−CH_3), 6.27 (dd, *J* = 15.1, *J* = 1.3 Hz, 1 H, 1-H), 6.86 (dd, *J* = 15.1, *J* = 6.4 Hz, 1 H, 2-H), 7.50−7.62 (m, 3 H, Ph), 7.84−7.90 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.9 (d), 21.0 (d), 29.5 (d), 30.6 (u), 128.0 (d), 128.7 (d), 129.3 (d), 132.5 (d), 139.5 (u), 152.7 (d). − IR (neat): ṽ = 3060 (w), 2964 (m), 2932 (m), 2827 (m), 2802 (m), 1670 (w), 1624 (m), 1582 (m), 1445 (s), 1304 (m), 1245 (s), 1149 (s), 1107 (m), 1082 (m), 1069 (m), 975 (m), 870 (m), 816 (m), 753 (m). − GC/MS: *m*/*z* (%) = 224 [M^+ + 1] (100), 222 (7), 156 (1), 125 (3), 107 (7), 98 (9). − $C_{12}H_{17}NOS$ (223.3): calcd. C 64.53, H 7.67, N 6.27; found C 64.36, H 6.83, N 6.27.

(+)-(*S*)-*N*-Methyl-*S*-(3-methyl-2-butenyl)-*S*-phenylsulfoximine (6a): Treatment of **5a** (6.36 g, 28.5 mmol) with DBU according to *GP1.2* and subsequent chromatography (EtOAc/hexane, 4:1) afforded **6a** (4.79 g, 75%) as a colorless oil; R_f = 0.29 (EtOAc/hexane, 4:1); $[\alpha]_D$ = +37.7 (*c* = 2.66, MeOH). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.23 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3), 2.73 (s, 3 H, N−CH_3), 3.81 (dd, *J* = 14.3, *J* = 8.0 Hz, 1 H, 1-H), 3.87 (dd, *J* = 14.3, *J* = 8.0 Hz, 1 H, 1-H), 5.20 (m, 1 H, 2-H), 7.49−7.64 (m, 3 H, Ph), 7.79−7.84 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.7 (d), 25.8 (d), 29.7 (d), 56.1 (u), 111.1 (d), 129.1 (d), 129.8 (d), 132.8 (d), 137.0 (u), 142.2 (u). − IR (neat): ṽ = 3060 (m), 2971 (m), 2915 (m), 2876 (m), 2803 (m), 1668 (w), 1582 (w), 1445 (s), 1378 (m), 1304 (w), 1246 (s), 1153 (s), 1103 (s),

1083 (s), 1060 (m), 910 (m), 860 (m), 755 (m), 740 (m). − MS: *m*/*z* (%) = 223 [M^+] (<1), 155 (73), 126 (11), 125 (39), 119 (12), 107 (100), 106 (26), 98 (27), 97 (20), 78 (81), 77 (40). − $C_{12}H_{17}NOS$ (223.3): calcd. C 64.53, H 7.67, N 6.27; found C 64.22, H 7.66, N 6.27.

(±)-(*RS*)- and (+)-(*S*)-*N*-Methyl-*S*-(3,3-diphenyl-2-propenyl)-*S*-phenylsulfoximine (6b and *rac*-6b): To a solution of *rac*-**1** (11.79 g, 69.7 mmol) in THF (50 mL) at −60 °C was added *n*BuLi (47.8 mL, 1.60 M solution in hexane, 76.5 mmol). The mixture was allowed to warm to room temperature, then cooled to −40 °C, whereupon a solution of diphenylethanal (13.84 g, 70.5 mmol) in THF (20 mL) was added dropwise. The resulting mixture was allowed to warm to room temperature, stirred for 1 h, then cooled to −78 °C and treated with ClCOOEt (6.7 mL, 70.0 mmol). The mixture was then allowed to warm to room temperature once more, cooled again to −78 °C, and treated with KO*t*Bu (7.82 g, 70.0 mmol). After stirring the resulting mixture for 13 h at room temperature, it was poured into saturated aqueous NH_4Cl solution and the aqueous phase was extracted with diethyl ether. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Chromatography (EtOAc/hexane/NEt_3, 75:24:1) of the residue and subsequent crystallization (diethyl ether) gave *rac*-**6b** (13.10 g, 54%) as a colorless solid. Following the same procedure, but starting from **1** (5.42 g, 32.0 mmol), chromatography (EtOAc/hexane/NEt_3, 75:24:1) furnished sulfoximine **6b** (6.60 g, 59%) as a slightly yellow oil; R_f = 0.54 (EtOAc/hexane, 4:1); $[\alpha]_D$ = +28.9 (*c* = 2.32, acetone). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.72 (s, 3 H, N−CH_3), 3.93 (dd, *J* = 14.1, *J* = 7.7 Hz, 1 H, 1-H), 3.99 (dd, *J* = 14.1, *J* = 8.1 Hz, 1 H, 1-H), 6.14 (t, *J* = 7.7 Hz, 1 H, 2-H), 6.61 (m, 2 H, Ph), 7.28−7.10 (m, 8 H, Ph), 7.45−7.55 (m, 2 H, Ph), 7.55−7.62 (m, 1 H, Ph), 7.60−7.71 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.7 (d), 57.1 (u), 115.1 (d), 127.6 (d), 128.1 (d), 128.2 (d), 127.4 (d), 128.3 (d), 129.2 (d), 129.3 (d), 129.8 (d), 132.8 (d), 137.0 (u) 138.0 (u), 141.0 (u), 149.0 (u). − IR (neat): $\tilde{\nu}$ = 3057 (s), 3027 (m), 2963 (m), 2913 (s), 2876 (s), 2804 (s), 2103 (w), 1964 (w), 1901 (w), 1816 (w), 1736 (m), 1664 (w), 1627 (w), 1599 (w), 1579 (w), 1494 (m), 1445 (s), 1399 (m), 1249 (s), 1143 (s), 1109 (s), 1082 (s), 914 (m), 861 (s), 765 (s), 743 (s), 702 (s). − MS: *m*/*z* (%) = 347 [M^+] (1), 222 (7), 194 (20), 193 (100), 191 (9), 178 (22), 165 (8), 115 (56), 91 (15), 77 (8). − $C_{22}H_{21}NOS$ (347.4): calcd. C 76.05, H 6.09, N 4.03; found C 75.73, H 6.11, N 4.01.

General Procedure for the γ-Hydroxyalkylation of Allylic Sulfoximines Using 1.2 Equiv. of ClTi(O*i*Pr)$_3$ (*GP2*): To a solution of the allylic sulfoximine **4** (1.0 mmol) in THF (10 mL) at −78 °C was added *n*BuLi (0.68 mL, 1.60 M solution in hexane, 1.1 mmol). After stirring the mixture for 10 min at −78 °C, ClTi(O*i*Pr)$_3$ (1.2 mmol), either neat or in THF (2 mL), was added. The resulting mixture was stirred for a further 10 min at −78 °C, allowed to warm to 0 °C, and stirred for 45 min at this temperature. The mixture was subsequently cooled to −78 °C once more, whereupon the aldehyde (2 mmol) was added dropwise and stirring was continued for 80 min at −78 °C. The mixture was then poured into saturated aqueous $(NH_4)_2CO_3$ solution and extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. The vinylic sulfoximine was isolated by chromatography, crystallization, or by chromatography following silylation.

General Procedure for the γ-Hydroxyalkylation of Allylic Sulfoximines Using 2.1 Equiv. of ClTi(O*i*Pr)$_3$ (*GP3*): To a solution of the allylic sulfoximine **4** (1.0 mmol) in THF (10 mL) at −78 °C was added *n*BuLi (0.68 mL, 1.60 M solution in hexane, 1.1 mmol). After stirring the mixture for 10 min at −78 °C, ClTi(O*i*Pr)$_3$ (2.1 mmol), either neat or in THF (2 mL), was added. The resulting mixture was stirred for 10 min at −78 °C, allowed to warm to 0 °C, and stirred for 45 min at this temperature. It was then cooled to −78 °C once more, whereupon the aldehyde (2 mmol) was added. The mixture thus obtained was stirred for 2 h at −78 °C and then slowly allowed to warm to room temperature over a period of 3 h. It was then poured into saturated aqueous $(NH_4)_2CO_3$ solution and extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. The vinylic sulfoximine was isolated by chromatography, crystallization, or by chromatography following silylation.

General Procedure for the Silylation of the Hydroxy Sulfoximine 7 (*GP4*): To a mixture of the hydroxy sulfoximine **7** (1 mmol), sulfoximine **4**, and *N*-methyl-*S*-phenylsulfinamide in DMF (2 mL) was added imidazole (273 mg, 4 mmol) and then $ClSiEt_3$ (4.0 mmol) was added dropwise. After stirring the mixture for 20 h at room temperature, half-saturated aqueous $NaHCO_3$ was added and the resulting mixture was extracted with diethyl ether. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Chromatography gave the silyl ether **7**-$SiEt_3$.

General Procedure for the Deprotection of the Silyl Ether 7-SiEt$_3$ (*GP5*): To a vigorously stirred solution of the silyl ether **7**-$SiEt_3$ (1 mmol) in THF (5 mL) and acetic acid (1 mL) at room temperature was added aqueous HCl (0.15 M, 5 mL). Stirring was continued at the same temperature until TLC showed complete consumption of the silyl ether. The mixture was then neutralized by the addition of saturated aqueous $NaHCO_3$ solution and extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Sulfoximine **7** was purified by chromatography.

(−)-(*Z*)-(2*S*,3*R*)-1-[(*S*)-*N*-Methyl-*S*-phenylsulfonimidoyl]-3-methylpent-4-en-2-ol (7a): Reaction of a mixture of *E*-**4a** and *Z*-**4a** (3.60 g, 17.2 mmol, 3:1) with ethanal according to *GP2* gave a mixture of **7a** (44% cy, ≥96% *ds*), an (*E*)-isomer and a (*Z*)-isomer of **7a** (7% cy) derived from *Z*-**4a** in a ratio of 3:2, recovered *E*-**4a** (21%), recovered *Z*-**4a** (25%), and *N*-methyl-*S*-phenylsulfinamide (2% cy). Crystallization (diethyl ether) afforded diastereopure **7a** (1.35 g, 31%) as colorless crystals, m.p. 74 °C; $[\alpha]_D$ = −142.7 (*c* = 0.92, MeOH). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 (d, *J* = 6.6 Hz, 3 H, CH_3), 1.27 (d, *J* = 6.0 Hz, 3 H, CH_3), 2.66 (s, 3 H, N−CH_3), 3.46 (m, 1 H) and 3.55 (m, 1 H) (2-H and 3-H), 3.80 (br. s, 1 H, OH), 6.14 (t, *J* = 10.7 Hz, 1 H, 4-H), 6.42 (d, *J* = 10.7 Hz, 1 H, 5-H), 7.57 (m, 3 H, Ph), 7.89 (m, 2 H, Ph). − ^{13}C NMR (75 MHz): δ = 17.0 (d), 22.7 (d), 29.7 (d), 40.8 (d), 71.8 (d), 129.4 (d), 129.9 (d), 133.4 (d), 132.4 (d), 140.3 (u), 148.8 (d). − IR (KBr): $\tilde{\nu}$ = 3265 (s), 2968 (s), 1235 (s), 1196 (s), 1147 (s), 1101 (s), 866 (s), 748 (s). − MS: *m*/*z* (%) = 253 [M^+] (12), 238 (10), 208 (6), 163 (18), 156 (43), 149 (34), 131 (21), 125 (100), 109 (33), 97 (46), 83 (42), 73 (37). − $C_{13}H_{19}NO_2S$ (253.4): calcd: C 61.63, H 7.56, N 5.53; found C 61.51, H 7.56, N 5.51.

(−)-(*Z*)-(3*S*,4*R*)-1-[(*S*)-*N*-Methyl-*S*-phenylsulfonimidoyl]-4-methylhex-5-en-3-ol (7b): Reaction of a mixture of *E*-**4a** and *Z*-**4a** (3.76 g, 18.0 mmol, 3:2) with propanal according to *GP2* furnished a mixture of **7b** (37% cy, ≥96% *ds*), recovered *E*-**4a** (18%), recovered *Z*-**4a** (37%), and two (*E*)-isomers of **7b** (4% cy) derived from *Z*-**4a** in a ratio of 6:1. Chromatography (EtOAc/hexane, 4:1) afforded, besides a 1:2 mixture of *E*-**4a** and *Z*-**4a** (1.72 g, 46%), the diastereopure sulfoximine **7b** (1.56 g, 32%) as colorless crystals; R_f = 0.17 (EtOAc/hexane, 4:1); m.p. 76 °C; $[\alpha]_D$ = −100.0 (*c* = 0.67, CH_2Cl_2). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.82 (d, *J* = 6.7 Hz, 3 H, CH_3), 1.01 (t, *J* = 7.4 Hz, 3 H, CH_3), 1.43 (dquin, *J* = 14.1, *J* = 7.2 Hz, 1 H, 2-H), 1.68 (dqd, *J* = 14.1, *J* = 7.4, *J* = 3.7 Hz, 1 H, 2-H), 2.65 (s, 3 H, N−CH_3), 3.34 (td, *J* = 7.3, *J* =

3.7 Hz, 1 H, 3-H), 3.57 (dquin, J = 11.0, J = 6.8 Hz, 1 H, 4-H), 3.57 (br. s, 1 H, OH), 6.17 (t, J = 11.0 Hz, 1 H, 5-H), 6.42 (d, J = 11.0 Hz, 1 H, 6-H), 7.52−7.64 (m, 3 H, Ph), 7.90 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.3 (d), 16.5 (d), 28.1 (u), 29.2 (d), 37.8 (d), 76.0 (d), 128.9 (d), 129.4 (d), 131.6 (d), 132.9 (d), 139.9 (u), 148.4 (d). − IR (KBr): ṽ = 3678 (w), 3219 (vs), 3088 (m), 3052 (m), 2999 (m), 2974 (s), 2962 (vs), 2925 (vs), 2891 (s), 2870 (s), 2799 (s), 2659 (m), 1624 (s), 1581 (w), 1475 (m), 1445 (vs), 1423 (s), 1412 (s), 1384 (m), 1376 (m), 1367 (s), 1353 (m), 1340 (w), 1315 (m), 1251 (vs), 1220 (vs), 1150 (vs), 1104 (vs), 1080 (vs), 1062 (s), 1039 (m), 1024 (m), 1000 (m), 983 (s), 965 (vs), 898 (m), 868 (vs), 835 (s), 744 (vs), 735 (vs). − MS: *m*/*z* (%) = 268 (3), 267 [M^+] (2), 238 (27), 209 (5), 182 (5), 163 (9), 161 (8), 156 (53), 131 (16), 129 (11), 126 (12), 125 (100), 109 (17), 107 (17), 97 (12), 83 (17), 78 (15), 77 (18). − $C_{14}H_{21}NO_2S$ (267.4): calcd. C 62.89, H 7.92, N 5.24; found C 62.85, H 8.05, N 5.23.

(±)-Triethyl-{(*Z*)-(1*RS*,2*SR*)-1-isopropyl-4-[(*RS*)-*N*-methyl-*S*-phenylsulfonimidoyl]-2-methylbut-3-enyloxy}silane (*rac*-7c-SiEt$_3$): Reaction of a mixture of *rac*-*E*-**4a** and *rac*-*Z*-**4a** (1.56 g, 7.46 mmol, 3:1) with 2-methylpropanal according to *GP2* gave a mixture of *rac*-**7c** (52% cy, ≥96% *ds*), recovered *rac*-*E*-**4a** (36%), recovered *rac*-*Z*-**4a** (23%), and *N*-methyl-*S*-phenylsulfinamide (6% cy). Silylation of this mixture according to *GP4* afforded, besides a mixture of *rac*-*E*-**4a**, *rac*-*Z*-**4a**, and *N*-methyl-*N*-triethylsilyl-*S*-phenylsulfinamide, the diastereopure silyl ether *rac*-**7c**-SiEt$_3$ (835 mg, 38%) as colorless crystals; m.p. 38−40 °C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.53−0.64 (m, 9 H), 0.90−1.01 (m, 15 H), 1.65 [oct, J = 6.5 Hz, 1 H, C*H*$(CH_3)_2$], 2.66 (s, 3 H, N−CH_3), 3.32 (dd, J = 6.4, J = 2.0 Hz, 1 H, 1-H), 3.62 (m, 1 H, 2-H), 6.30 (d, J = 11.1 Hz, 1 H, 4-H), 6.46 (dd, J = 11.1, J = 10.7 Hz, 1 H, 3-H), 7.50−7.61 (m, 3 H, Ph), 7.88−7.94 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 5.4 (u), 7.1 (d), 17.8 (d), 18.5 (d), 19.1 (d), 29.2 (d), 34.0 (d), 34.1 (d), 81.4 (d), 128.9 (u), 129.2 (u), 129.4 (d), 132.4 (d), 140.8 (u), 148.9 (d). − IR (KBr): ṽ = 3039 (s), 2956, 2936, 2910, 2875 (vs), 2800 (s), 1623 (m), 1386 (s), 1249 (s), 1218 (s), 1146 (s), 1124 (s), 1083 (s), 1045 (s), 1020 (vs), 970 (s), 864 (s), 832 (s), 810 (s), 765 (s), 737 (vs). − MS: *m*/*z* (%) = 395 [M^+] (6), 366 (14), 354 (12), 353 (29), 352 (100), 209 (14), 159 (13), 116 (11), 115 (89), 103 (18), 87 (70), 75 (20). − $C_{21}H_{37}NO_2SSi$ (395.6): calcd. C 63.74, H 9.43, N 3.54; found C 63.88, H 9.55, N 3.67.

(±)-(*Z*)-(3*RS*,4*SR*)-2,4-Dimethyl-6-[(*RS*)-*N*-methyl-*S*-phenylsulfonimidoyl]hex-5-en-3-ol (*rac*-7c): Deprotection of *rac*-**7c**-SiEt$_3$ (304 mg, 0.77 mmol) according to *GP5* afforded diastereopure *rac*-**7c** (184 mg, 85%) as a colorless solid; m.p. 119 °C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 (d, J = 6.4 Hz, 3 H, CH_3), 0.93 (d, J = 6.7 Hz, 3 H, CH_3), 1.05 (d, J = 6.7 Hz, 3 H, CH_3), 1.80 (septd, J = 6.6, J = 3.0 Hz, 1 H, 2-H), 2.64 (s, 3 H, N−CH_3), 3.17 (dd, J = 8.7, J = 3.0 Hz, 1 H, 3-H), 3.74 (m, 1 H, 4-H), 4.31 (br. s, 1 H, OH), 6.15 (dd, J = 11.1, J = 10.7 Hz, 1 H, 5-H), 6.38 (d, J = 10.7 Hz, 1 H, 6-H), 7.52−7.64 (m, 3 H, Ph), 7.85−7.90 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5 (d), 16.5 (d), 20.4 (d), 29.1 (d), 30.0 (d), 36.5 (d), 79.1 (d), 128.9 (d), 129.4 (d), 131.4 (d), 132.9 (d), 139.7 (u), 148.6 (d). − IR (KBr): ṽ = 3450 (m, br), 3230 (s), 2960 (m), 2925 (m), 2890 (m), 2850 (m), 1630 (m), 1480 (w), 1430 (m), 1240 (s), 1215 (vs), 1150 (s), 1110 (s), 1080 (s), 1000 (s), 860 (vs), 770 (s), 730 (s). − MS: *m*/*z* (%) = 281 [M^+] (7), 239 (10), 238 (74), 156 (65), 131 (14), 129 (11), 126 (12), 125 (100), 109 (11), 107 (18), 83 (18), 78 (17), 77 (17). − $C_{15}H_{23}NO_2S$ (281.4): calcd. C 64.02, H 8.24, N 4.98; found C 64.05, H 8.56, N 5.07.

(−)-Triethyl-{(*Z*)-(1*S*,2*R*)-1-isopropyl-4-[(*RS*)-*N*-methyl-*S*-phenylsulfonimidoyl]-2-methylbut-3-enyloxy}silane (7c-SiEt$_3$): Reaction of a mixture of *E*-**4a** and *Z*-**4a** (5.88 g, 28.1 mmol, 3:1) with 2-methylpropanal according to *GP2* gave a mixture of **7c** (44% cy, ≥96% *ds*), recovered *E*-**4a** (32%), recovered *Z*-**4a** (22%), and *N*-methyl-*S*-phenylsulfinamide (2% cy). Silylation of this mixture according to *GP4* afforded diastereopure **7c**-SiEt$_3$ (3.13 g, 38%); $[\alpha]_D$ = −103.7 (*c* = 1.12, MeOH). − $C_{21}H_{37}NO_2SSi$ (395.7): calcd. C 63.75, H 9.43, N 3.54; found C 63.35, H 9.60, N 3.37. The other analytical data were identical to those of *rac*-**7c**-SiEt$_3$.

Deprotection of **7c**-SiEt$_3$ (304 mg, 0.77 mmol) according to *GP6* furnished **7c** (184 mg, 85%) as a colorless solid; m.p. 119 °C; $[\alpha]_D$ = −141.5 (*c* = 1.03, MeOH). − $C_{15}H_{23}NO_2S$ (281.4): calcd. C 64.02, H 8.24, N 4.98; found C 63.80, H 8.32, N 4.90.

(−)-(*Z*)-(3*S*,4*R*)-2,4-Dimethyl-6-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]hex-5-en-3-ol (7c): Reaction of a mixture of *E*-**4a** and *Z*-**4a** (9.88 g, 47.2 mmol, 3:1) with 2-methylpropanal according to *GP2* gave a mixture of **7c** (46% cy, ≥96% *ds*), recovered *E*-**4a** (31%), recovered *Z*-**4a** (21%), and *N*-methyl-*S*-phenylsulfinamide (2% cy). Crystallization (cyclohexane) furnished diastereopure **7c** (4.78 g, 36%) as colorless crystals; m.p. 119 °C; $[\alpha]_D$ = −141.5 (*c* = 1.03, MeOH). − $C_{15}H_{23}NO_2S$ (281.4): calcd. C 64.02, H 8.24, N 4.98; found C 63.80, H 8.32, N 4.90. The other analytical data were identical to those of *rac*-**7c**.

Silylation of **7c** (1.97 g, 7.0 mmol) according to *GP5* gave **7c**-SiEt$_3$ (2.57 g, 93%).

(±)-*tert*-Butyl-{(*Z*)-(1*RS*,2*RS*)-4-[(*SR*)-*N*-methyl-*S*-phenylsulfonimidoyl]-2-methyl-1-phenylbut-3-enyloxy}dimethylsilane (*rac*-7d-Si*t*BuMe$_2$): Reaction of *rac*-*E*-**4a** (418 mg, 2.0 mmol) with benzaldehyde according to *GP2* and subsequent chromatography (EtOAc/hexane, 1:1) gave a mixture of *rac*-**7d** (53% cy, 96% *ds*) and recovered *rac*-*E*-**4a** (22%). This mixture was dissolved in DMF (10 mL), treated with imidazole (170 mg, 2.5 mmol), and then Cl-Si*t*BuMe$_2$ (300 mg, 2.0 mmol) was slowly added. After stirring for 16 h at room temperature, the mixture was poured into ice/water and extracted with cyclohexane. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Chromatography (EtOAc/hexane, 1:4) afforded *rac*-**7d**-Si*t*BuMe$_2$ (387 mg, 45%) containing 3% of a (*Z*)-diastereomer as a colorless oil.

rac-**7d:** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.73 (d, J = 6.7 Hz, 3 H, CH_3), 2.68 (s, 3 H, N−CH_3), 3.86−4.00 (m, 1 H, 2-H), 4.29 (d, J = 9.1 Hz, 1 H, 1-H), 6.20 (t, J = 11.1 Hz, 1 H, 3-H), 6.42 (d, J = 11.1 Hz, 1 H, 4-H), 7.20−7.40 (m, 5 H, Ph), 7.45−7.62 (m, 3 H, Ph), 7.86−7.92 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.7 (d), 29.3 (d), 40.7 (d), 78.2 (d), 126.8 (d), 127.5 (d), 128.3 (d), 128.8 (d), 129.4 (d), 132.0 (d), 132.9 (d), 139.3 (u), 143.5 (u), 148.0 (d).

rac-**7d**-Si*t*BuMe$_2$: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.19 (s, 3 H, Si−CH_3), 0.24 (s, 3 H, Si−CH_3), 1.08 (s, 9 H, *t*Bu), 0.95 (d, J = 6.7 Hz, 3 H, CH_3), 2.69 (s, 3 H, N−CH_3), 3.92−4.02 (m, 1 H, 2-H), 4.83 (d, J = 4.7 Hz, 1 H, 1-H), 6.27−6.36 (m, 2 H, 4-H, 3-H), 7.20−7.50 (m, 5 H, Ph), 7.61−7.75 (m, 3 H, Ph), 8.00−8.07 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = −5.1 (d), −4.6 (d), 15.6 (d), 25.8 (d), 29.2 (d), 40.0 (d), 77.7 (d), 126.6 (d), 127.2 (d), 127.9 (d), 128.5 (d), 129.0 (d), 130.1 (d), 133.3 (d), 140.7 (u), 142.6 (u), 147.8 (d). − MS: *m*/*z* (%) = 430 [M^+] (6), 429 (17), 372 (50), 274 (34), 222 (18), 221 (100), 217 (34), 142 (20), 128 (15), 75 (45), 73 (93).

(−)-(*Z*)-(2*S*,3*R*)-3-Ethyl-5-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]pent-4-en-2-ol (7e): Compound *E*-**4b** (300 mg, 1.34 mmol) was treated with ethanal according to *GP3*, with the modifications that the mixture was allowed to warm to room temperature, stirred at this temperature for 1 h, and cooled to −78 °C prior to addition of the aldehyde, and that the reaction mixture

was stirred for 10 h at room temperature. Work-up gave a mixture of **7e** (80% cy, 92% *ds*) and recovered *E*-**4b** (20%). Crystallization (diethyl ether) afforded diastereopure **7e** (156 mg, 44%) as colorless crystals; m.p. 68 °C; $[\alpha]_D$ = −132.1 (*c* = 0.93, CH_2Cl_2). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.57 (t, *J* = 7.7 Hz, 3 H, 7-H), 1.10 (dquad, *J* = 7.4, *J* = 13.2, *J* = 2.2 Hz, 1 H, 6-H), 1.30 (d, *J* = 6.0 Hz, 3 H, 5-H), 1.50 (dquad, *J* = 7.7, *J* = 13.3, *J* = 1.6 Hz, 1 H, 6-H), 2.64 (s, 3 H, N−CH_3), 3.21−3.32 (m, 1 H, 3-H), 3.61 (m, 1 H, 4-H), 3.84 (br. s, 1 H, OH), 6.10 (t, *J* = 11.0 Hz, 1 H, 2-H), 6.57 (d, *J* = 10.8 Hz, 1 H, 1-H), 7.52−7.63 (m, 3 H, Ph), 7.89 (m, 2 H, Ph). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.4 (d), 22.4 (d), 24.4 (u), 29.1 (u), 47.3 (d), 69.4 (d), 128.8 (d), 129.1 (d), 132.6 (d), 133.5 (u), 139.6 (d), 147.8 (d). − IR (KBr): $\tilde{\nu}$ = 3245 (s, br), 3067 (m), 3032 (m), 3009 (m), 2962 (s), 2920 (s), 2868 (s), 2798 (m), 2320 (w), 1896 (w), 1624 (s), 1586 (m), 1479 (m), 1458 (s), 1447 (s), 1418 (m), 1375 (m), 1313 (m), 1287 (m), 1243 (s), 1209 (s), 1150 (s), 1111 (s), 1084 (s), 1065 (s), 1041 (s), 1020 (s), 1000 (m), 956 (m), 898 (m), 861 (s), 847 (s), 789 (s), 755 (s), 731 (s), 684 (s), 621 (s). − MS: *m*/*z* (%) = 269 (15), 268 [M^+ + 1] (100), 266 (4), 239 (2), 224 (3), 155 (3). − $C_{14}H_{21}NO_2S$ (267.4): calcd. C 62.88, H 7.91, N 5.24; found C 62.85, H 8.34, N 5.25.

(−)-(*Z*)-(2*S*,3*R*)-3-Isopropyl-5-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]pent-4-en-2-ol (7g): Reaction of a mixture of *E*-**4c** and *Z*-**4c** (3.10 g, 13.1 mmol, 15:1) with ethanal according to *GP2* gave a mixture of **7g** (48% cy, ≥96% *ds*), recovered *E*-**4c** (42%), recovered *Z*-**4c** (6%), and *N*-methyl-*S*-phenylsulfinamide (3% cy). Crystallization (diethyl ether) afforded diastereopure **7g** (1.18 g, 32%) as colorless crystals. Chromatography (EtOAc/hexane, 4:1) of the mother liquor furnished, besides a mixture of *E*-**4c** and *Z*-**4c** (1.40 g, 45%, 7:1), an additional crop of **7g** (520 mg, 14%); R_f = 0.12 (EtOAc/hexane, 4:1); m.p. 109 °C; $[\alpha]_D$ = −218.0 (*c* = 0.66, MeOH). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.67 (d, *J* = 6.9 Hz, 3 H, CH_3), 0.70 (d, *J* = 6.9 Hz, 3 H, CH_3), 1.32 (d, *J* = 6.0 Hz, 3 H, CH_3), 1.80 (oct, *J* = 6.9 Hz, 1 H, 6-H), 2.64 (s, 3 H, N−CH_3), 3.25 (ddd, *J* = 11.8, *J* = 7.4, *J* = 5.5 Hz, 1 H, 3-H), 3.80 (sext, *J* = 6.4 Hz, 1 H, 2-H), 3.90 (br. s, 1 H, OH), 6.27 (dd, *J* = 11.8, *J* = 11.1 Hz, 1 H, 4-H), 6.61 (d, *J* = 11.1 Hz, 1 H, 5-H), 7.52−7.64 (m, 3 H, Ph), 7.90 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.9 (d), 21.3 (d), 22.9 (d), 28.3 (d), 29.2 (d), 50.9 (d), 67.8 (d), 129.1 (d), 129.3 (d), 132.8 (d), 134.3 (d), 139.8 (u), 145.2 (d). − IR (KBr): $\tilde{\nu}$ = 3281 (s, br), 3059 (w), 3028 (w), 2966 (s), 2930 (s), 2889 (s), 2871 (s), 2799 (m), 2101 (w), 1614 (m), 1470 (m), 1445 (s), 1386 (m), 1367 (m), 1310 (m), 1271 (m), 1243 (s), 1208 (vs), 1149 (vs), 1128 (s), 1105 (vs), 1078 (s), 1043 (s), 1026 (w), 999 (w), 982 (w), 952 (w), 916 (w), 865 (vs), 844 (m), 786 (s), 759 (s), 731 (s). − MS: *m*/*z* (%) = 281 [M^+] (5), 266 (2), 236 (5), 156 (28), 125 (57), 107 (20), 83 (18), 82 (10), 81 (23), 78 (39), 77 (29). − $C_{15}H_{23}NO_2S$ (281.4): calcd. C 64.02, H 8.24, N 4.98; found C 64.09, H 8.26, N 5.10.

(−)-(*Z*)-(3*S*,4*R*)-4-Isopropyl-2-methyl-6-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]hex-5-en-3-ol (7i): Reaction of a mixture of *E*-**4c** and *Z*-**4c** (3.38 g, 14.2 mmol, 9:1) with 2-methylpropanal according to *GP2*, with the modification that the reaction mixture was allowed to warmed to room temperature after the addition of the aldehyde, gave a mixture of **7i** (48% cy, ≥96% *ds*), recovered *E*-**4c** (20%), *Z*-**4c** recovered (4%), and **10i** (26% cy) as a mixture of diastereomers in a ratio of 31:32:30:7. Crystallization (diethyl ether/pentane, 2:1) furnished diastereopure **7i** (1.91 g, 44%) as colorless crystals. Reaction of *E*-**4c** (590 mg, 2.49 mmol) with 2-methylpropanal according to *GP3* gave a mixture of **7i** (82% cy, ≥96 *ds*), recovered *E*-**4c** (8%), and **10i** (9% cy) as a mixture of diastereomers. Crystallization (diethyl ether) afforded diastereopure **7i** as colorless crystals; m.p. 141 °C; $[\alpha]_D$ = −181.4 (*c* = 1.36, MeOH). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.62 (d, *J* = 6.9 Hz, 3 H, CH_3), 0.79 (d, *J* = 6.9 Hz, 3 H, CH_3), 0.94 (d, *J* = 6.8 Hz, 3 H, CH_3), 1.07 (d, *J* = 6.8 Hz, 3 H, CH_3), 1.81 (sept, *J* = 6.9 Hz, 1 H, 7-H), 1.82 (oct, *J* = 6.8 Hz, 1 H, 2-H), 2.62 (s, 3 H, N−CH_3), 3.38 (dd, *J* = 9.5, *J* = 2.7 Hz, 1 H, 3-H), 3.57 (ddd, *J* = 11.9, *J* = 9.5, *J* = 4.0 Hz, 1 H, 4-H), 4.3 (br. s, 1 H, OH), 6.31 (dd, *J* = 11.8, *J* = 11.0 Hz, 1 H, 5-H), 6.57 (d, *J* = 10.7 Hz, 1 H, 6-H), 7.51−7.63 (m, 3 H, Ph), 7.89 (dt, *J* = 7.0, *J* = 1.5 Hz, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.3 (d), 15.8 (d), 20.6 (d), 21.8 (d), 27.4 (d), 29.1 (d), 29.8 (d), 46.5 (d), 75.3 (d), 129.1 (d), 129.4 (d), 132.9 (d), 134.1 (d), 139.7 (u), 145.0 (d). − IR (KBr): $\tilde{\nu}$ = 3200 (s, br), 3067 (m), 3025 (m), 2960 (s), 2924 (m), 2898 (m), 2871 (m), 2802 (m), 1655 (w), 1618 (m), 1468 (m), 1446 (m), 1385 (w), 1369 (w), 1297 (m), 1251 (s), 1209 (s), 1157 (s), 1114 (s), 1067 (w), 1047 (m), 1026 (w), 862 (s), 836 (w), 782 (s), 760 (m), 735 (s). − MS: *m*/*z* (%) = 309 [M^+] (6), 266 (31), 236 (18), 156 (90), 125 (100), 111 (19), 107 (27), 81 (23), 78 (28), 77 (18). − $C_{17}H_{27}NO_2S$ (309.4): calcd. C 65.98, H 8.79, N 4.53; found C 66.02, H 8.95, N 4.70.

(−)-(*Z*)-(1*R*,2*R*)-2-Isopropyl-4-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]-1-phenylbut-3-en-1-ol (7j): Reaction of a mixture of *E*-**4c** and *Z*-**4c** (4.13 g, 17.3 mmol, 9:1) with benzaldehyde according to *GP2* afforded a mixture of **7j** (48% cy, ≥96% *ds*), recovered *E*-**4c** (35%), and recovered *Z*-**4c** (15%). Crystallization (diethyl ether) gave diastereopure **7j** (2.56 g, 43%) as colorless crystals; m.p. 152 °C; $[\alpha]_D$ = −147.4 (*c* = 1.04, MeOH). − ^{1}H NMR (300 MHz): δ = 0.57 (d, *J* = 6.7 Hz, 3 H, CH_3), 0.87 (d, *J* = 6.3 Hz, 3 H, CH_3), 1.40 [septd, *J* = 7.0, *J* = 3.3 Hz, 1 H, C*H*(CH_3)$_2$], 2.69 (s, 1 H, N−CH_3), 3.88 (ddd, *J* = 10.4, *J* = 10.3, *J* = 3.3 Hz, 1 H, 2-H), 4.48 (d, *J* = 9.7 Hz, 1 H, 1-H), 5.93 (br. s, 1 H, OH), 6.42 (t, *J* = 11.4 Hz, 1 H, 3-H), 6.68 (d, *J* = 10.7 Hz, 1 H, 4-H), 7.26−7.45 (m, 5 H, Ph), 7.53−7.64 (m, 3 H, Ph), 7.91−7.96 (m, 2 H, Ph). − ^{13}C NMR (75 MHz): δ = 15.7 (d), 21.8 (d), 27.7 (d), 29.3 (d), 51.5 (d), 75.2 (d), 126.7 (d), 127.6 (d), 128.5 (d), 129.1 (d), 129.5 (d), 133.1 (d), 135.5 (d), 139.2 (u), 144.2 (u), 143.8 (d). − IR (KBr): $\tilde{\nu}$ = 3087 (s, br), 3021 (s), 2984 (s), 2962 (s), 2893 (s), 2871 (s), 2729 (m), 1617 (m), 1445 (s), 1246 (vs), 1214 (s), 1189 (s), 1152 (vs), 1114 (vs), 1055 (s), 863 (vs), 786 (vs), 764 (vs), 755 (vs), 703 (vs). − MS: *m*/*z* (%) = 343 [M^+] (10), 237 (36), 236 (22), 222 (30), 194 (14), 170 (25), 156 (69), 155 (21), 145 (59), 125 (100), 107 (47), 106 (46), 105 (50), 77 (67). − $C_{20}H_{25}NO_2S$ (343.5): calcd. C 69.94, H 7.34, N 4.08; found C 69.57, H 7.32, N 4.00.

(−)-(*Z*)-(3*S*,4*R*)-4-Cyclohexyl-1-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]hex-5-en-3-ol (7k): Reaction of *E*-**4d** (930 mg, 3.35 mmol) with propanal according to *GP3* gave a mixture of **7k** (77% cy, 96% *ds*), recovered *E*-**4d** (6%), *E*-**10k** (17% cy) as a mixture of diastereomers in a ratio of 19:37:22:11, and *N*-methyl-*S*-phenylsulfinamide (2% cy). Chromatography (EtOAc/hexane, 4:1) afforded diastereopure **7k** (710 mg, 69%) as a colorless solid, m.p. 86 °C; $[\alpha]_D$ = −105.9 (*c* = 1.06, acetone). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.65−0.87 (m, 2 H, C_6H_{11}), 0.90−1.22 (m, 3 H, C_6H_{11}), 1.03 (t, *J* = 7.4 Hz, 3 H, CH_3), 1.33−1.51 (m, 3 H, C_6H_{11}), 1.52−1.66 (m, 3 H, C_6H_{11}), 1.74 (dqd, *J* = 14.0, *J* = 7.4, *J* = 3.3 Hz, 2 H, CH_2), 2.63 (s, 3 H, N−CH_3), 3.34 (ddd, *J* = 12.1, *J* = 6.9, *J* = 5.2 Hz, 4-H), 3.63 (dt, *J* = 7.4, *J* = 3.3 Hz, 1 H, 3-H), 3.65 (br. s, 1 H, OH), 6.31 (dd, *J* = 12.1, *J* = 11.1 Hz, 1 H, 5-H), 6.55 (d, *J* = 11.0 Hz, 1 H, 6-H), 7.51 (m, 3 H, Ph), 7.86−7.92 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.4 (d), 26.4 (u), 26.4 (u), 26.6 (u), 27.8 (u), 28.5 (u), 29.2 (d), 31.7 (u), 38.4 (d), 48.0 (d), 71.8 (d), 129.2 (d), 129.3 (d), 132.8 (d), 133.5 (d), 139.9 (u), 146.2 (d). − IR (KBr): $\tilde{\nu}$ = 3205 (s, br), 3063 (m), 3021 (m), 2928 (s), 2854 (s), 2801 (m), 1991 (w), 1963 (w), 1896 (w), 1805 (w), 1765 (w), 1612 (m), 1586 (w), 1450 (s), 1385 (m), 1348 (m), 1317 (m), 1250 (s), 1222 (s), 1200 (s), 1153 (s), 1113 (s), 1054 (m), 1026 (s),

998 (m), 967 (m), 867 (s), 810 (s), 767 (s), 728 (s). − MS: *m/z* (%) = 336 [M$^+$] (2), 335 (7), 277 (13), 194 (17), 157 (7), 156 (100), 154 (10), 151 (16), 126 (13), 125 (99), 109 (13), 107 (73), 105 (12), 97 (25), 93 (16), 91 (16), 86 (34), 84 (57), 81 (79), 79 (32), 78 (45), 77 (44). − $C_{19}H_{29}NO_2S$ (336.5): calcd. C 67.81, H 8.99, N 4.17; found C 67.71, H 8.74, N 4.14.

(−)-(*Z*)-(3*S*,4*R*)-4-Cyclohexyl-2-methyl-6-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]hex-5-en-3-ol (7l):

With 1.2 Equiv. of ClTi(OiPr)$_3$: Reaction of *E*-**4d** (2.03 g, 7.31 mmol) with 2-methylpropanal according to *GP2* gave a mixture of **7l** (52% cy, ≥96% *ds*), recovered *E*-**4d** (47%), and *N*-methyl-*S*-phenylsulfinamide (1% cy).

With 2.1 Equiv. of ClTi(OiPr)$_3$: Reaction of *E*-**4d** (2.03 g, 7.31 mmol) with 2-methylpropanal according to *GP3* afforded a mixture of **7l** (82% cy, ≥96% *ds*), recovered *E*-**4d** (16%), and *N*-methyl-*S*-phenylsulfinamide (2% cy). Crystallization (diethyl ether) gave diastereopure **7l** (1.84 g, 72%) as colorless crystals; m.p. 149 °C; $[\alpha]_D$ = −77.3 (*c* = 1.20, acetone). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.74−1.25 (m, 6 H, C_6H_{11}), 0.94 (d, *J* = 6.7 Hz, 3 H, CH_3), 1.06 (d, *J* = 6.7 Hz, 3 H, CH_3), 1.35−1.90 (m, 6 H, 5-H, C_6H_{11}), 2.62 (s, 3 H, N−CH_3), 3.46 (dd, *J* = 9.4, *J* = 2.4 Hz, 1 H, 3-H), 3.58 (ddd, *J* = 11.4, *J* = 9.4, *J* = 4.0 Hz, 1 H, 4-H), 4.29 (br. s, 1 H, OH), 6.35 (t, *J* = 11.4 Hz, 1 H, 5-H), 6.52 (d, *J* = 11.1 Hz, 1 H, 6-H), 7.52−7.62 (m, 3 H, Ph), 7.87−7.93 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.4 (d), 20.6 (d), 26.5 (u), 26.7 (u), 29.2 (d), 29.9 (d), 32.1 (u), 38.0 (d), 46.4 (d), 74.8 (d), 129.1 (d), 129.3 (d), 132.8 (d), 133.6 (d), 139.8 (u), 145.9 (d). − IR (KBr): ṽ = 3216 (s, br), 3064 (m), 3021 (m), 2932 (s), 2905 (s), 2873 (s), 2852 (s), 2803 (m), 1804 (w), 1612 (m), 1448 (s), 1386 (m), 1366 (m), 1297 (m), 1249 (s), 1220 (s), 1199 (s), 1153 (s), 1112 (s), 1041 (s), 999 (w), 971 (w), 944 (w), 924 (w), 861 (s), 805 (s), 777 (s), 759 (m), 732 (s). − MS: *m/z* (%) = 349 [M$^+$] (4), 306 (22), 276 (12), 156 (100), 151 (27), 149 (13), 126 (11), 125 (96), 109 (13), 107 (29), 97 (14), 95 (11), 93 (14), 91 (14), 83 (15), 81 (24), 79 (22), 78 (18), 77 (21), 73 (11). − $C_{20}H_{31}NO_2S$ (349.5): calcd. C 68.73, H 8.94, N 4.01; found C 68.64, H 8.75, N 3.93.

With 0.50 Equiv. of Cl$_2$Ti(OiPr)$_2$ at −78 °C: To a solution of *E*-**4d** (370 mg, 1.34 mmol) in THF (20 mL) at −78 °C was added *n*BuLi (0.87 mL, 1.60 M solution in hexane, 1.39 mmol). After stirring the mixture for 20−30 min at −78 °C, $Cl_2Ti(OiPr)_2$ (160 mg, 0.67 mmol) was added, and the resulting mixture was stirred for 10 min at −78 °C, warmed to 25 °C, and stirred for 45 min at this temperature. It was subsequently cooled to −78 °C once more, whereupon 2-methylpropanal (0.243 mL, 2.68 mmol) was added dropwise. After stirring for 2 h at −78 °C, the mixture was poured into saturated aqueous $(NH_4)_2CO_3$ solution and extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo to give a mixture of **7l** (10% cy), recovered *E*-**4d** (80%), and *N*-methyl-*S*-phenylsulfinamide (10% cy).

With 1.1 Equiv. of Cl$_2$Ti(OiPr)$_2$ at −78 °C: To a solution of *E*-**4d** (370 mg, 1.34 mmol) in THF (20 mL) at −78 °C was added *n*BuLi (0.87 mL, 1.60 M solution in hexane, 1.4 mmol). After stirring the mixture for 20−30 min at −78 °C, $Cl_2Ti(OiPr)_2$ (348 mg, 1.47 mmol) was added, and the resulting mixture was stirred for 10 min at −78 °C, warmed to 25 °C, and stirred for 45 min at this temperature. It was subsequently cooled to −78 °C once more, whereupon 2-methylpropanal (0.243 mL, 2.68 mmol) was added dropwise. After stirring for 2 h at −78 °C, the mixture was poured into saturated aqueous $(NH_4)_2CO_3$ solution and extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo to give a mixture of **7l** (45% cy, ≥96% *ds*), recovered *E*-**4d** (54%), and *N*-methyl-*S*-phenylsulfinamide (1% cy).

With 1.1 Equiv. of Cl$_2$Ti(OiPr)$_2$ at −78 °C → 25 °C: To a solution of *E*-**4d** (2.00 g, 7.22 mmol) in THF (120 mL) at −78 °C was added *n*BuLi (4.73 mL, 1.6 M solution in hexane, 7.57 mmol). After stirring for 20−30 min at −78 °C, $Cl_2Ti(OiPr)_2$ (1.79 g, 7.57 mmol) was added, and the resulting mixture was stirred for 10 min at −78 °C, warmed to 25 °C, and stirred for 45 min at this temperature. It was then cooled to −78 °C once more, whereupon 2-methylpropanal (1.31 mL, 14.42 mmol) was added dropwise, stirring was continued for 2 h at −78 °C, and then the mixture was allowed to warm to room temperature over a period of 14 h. It was then poured into saturated aqueous $(NH_4)_2CO_3$ solution and extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo to give a mixture of **7l** (78% cy, ≥96% *ds*), recovered *E*-**4d** (16%), and *N*-methyl-*S*-phenylsulfinamide (6% cy). Crystallization (diethyl ether/hexane, 1:1) afforded diastereopure **7l** (1.74 g, 70%) as colorless crystals.

(−)-Triethyl-{(*Z*)-(1*S*,2*S*)-1-isopropyl-4-[(*R*)-*N*-methyl-*S*-phenylsulfonimidoyl]-2-phenylbut-3-enyloxy}silane (*ent*-7n-SiEt$_3$): Reaction of *ent*-*E*-**4e** (3.00 g, 11.06 mmol) with 2-methylpropanal according to *GP2* gave a mixture of *ent*-**7n** (40% cy, ≥96% *ds*), recovered *ent*-*E*-**4e** (34%), and *N*-methyl-*S*-phenylsulfinamide (24% cy). Treatment of this mixture with $ClSiEt_3$ according to *GP4* and subsequent chromatography (EtOAc/hexane, 2:1) furnished diastereopure *ent*-**7n**-$SiEt_3$ (1.75 g, 34%) as a colorless solid; m.p. 58−60 °C; R_f = 0.65 (EtOAc/hexane, 2:1); $[\alpha]_D$ = −9.4 (*c* = 0.57, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.18−0.36 (m, 6 H), 0.77 (t, *J* = 7.7 Hz, 9 H), 0.96 (d, *J* = 6.7 Hz, 3 H, CH_3), 1.01 (d, *J* = 7.0 Hz, 3 H, CH_3), 1.69 [d, *J* = 6.7 Hz, 1 H, C*H*$(CH_3)_2$], 2.63 (s, 3 H, N−CH_3), 3.64 (dd, *J* = 6.1, *J* = 2.7 Hz, 1 H, 1-H), 4.83 (dd, *J* = 10.7, *J* = 2.7 Hz, 1 H, 2-H), 6.50 (dd, *J* = 11.1, *J* = 0.7 Hz, 1 H, 4-H), 6.80−6.86 (m, 2 H, Ph), 6.92 (dd, *J* = 11.1, *J* = 10.7 Hz, 1 H, 3-H), 7.00−7.07 (m, 3 H, Ph), 7.12−7.20 (m, 2 H, Ph), 7.25−7.32 (m, 1 H, Ph), 7.51−7.56 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 5.1 (u), 7.0 (d), 18.7 (d), 19.0 (d), 29.1 (d), 33.8 (d), 44.2 (d), 82.6 (d), 126.2 (d), 128.00 (d), 128.1 (d), 128.6 (d), 128.7 (d), 131.1 (d), 132.0 (d), 139.3 (u), 141.4 (u), 145.8 (d). − IR (KBr): ṽ = 3450 (m, br), 3060 (m), 3026 (m), 2957 (s), 2911 (s), 2875 (vs), 2802 (m), 1627 (m), 1600 (m), 1583 (m), 1493 (s), 1448 (s), 1415 (s), 1379 (s), 1254 (vs), 1206 (s), 1175 (s), 1145 (vs), 1081 (vs), 1016 (s), 975 (s), 941 (s), 863 (vs), 853 (vs), 832 (vs), 812 (s), 781 (s), 740 (vs). − MS: *m/z* (%) = 458 [M$^+$ + 1] (10), 457 [M$^+$] (22), 428 (11), 416 (13), 415 (33), 414 (100), 271 (23), 187 (11), 159 (23), 125 (10), 117 (10), 116 (15), 115 (90), 103 (13), 87 (55). − $C_{26}H_{39}NO_2SSi$ (457.7): calcd. C 68.22, H 8.59, N 3.06; found C 67.94, H 8.65, N 3.23.

Reaction of *rac*-*E*-**4e** (1.00 g, 3.66 mmol) with 2-methylpropanal according to *GP2* gave a mixture of *rac*-**7n** (42% cy, ≥96% *ds*), recovered *rac*-*E*-**4e** (30%), and *N*-methyl-*S*-phenylsulfinamide (21% cy).

(−)-(*Z*)-(3*R*,4*S*)-1-[(*R*)-*N*-Methyl-*S*-phenylsulfonimidoyl]-2-methyl-4-phenylhex-5-en-3-ol (*ent*-7n): Deprotection of *ent*-**7n**-$SiEt_3$ (320 mg, 0.70 mmol) according to *GP5* afforded diastereopure *ent*-**7n** (209 mg, 87%) as a colorless oil; $[\alpha]_D$ = −105.1 (*c* = 0.68, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (d, *J* = 6.7 Hz, 3 H, CH_3), 0.97 (d, *J* = 7.0 Hz, 3 H, CH_3), 1.46 (septd, *J* = 6.8, *J* = 2.4 Hz, 1 H, 2-H), 2.67 (s, 3 H, N-CH_3), 3.73 (dd, *J* = 9.7, *J* = 2.4 Hz, 1 H, 3-H), 4.50 (br. s, 1 H, OH), 4.84 (ddd, *J* = 9.7, *J* = 8.4, *J* = 2.3 Hz, 1 H, 4-H), 6.47 (m, 2 H, 5-H, 6-H), 6.98−7.03 (m, 2 H, Ph), 7.15−7.28 (m, 3 H, Ph,), 7.49−7.63 (m, 3 H, Ph), 7.85−7.90 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$):

δ = 14.3 (d), 20.5 (d), 29.2 (d), 29.8 (d), 48.6 (d), 78.7 (d), 127.1 (d), 127.8 (d), 128.9 (d), 129.0 (d), 129.4 (d), 132.0 (d), 132.9 (d), 139.5 (u), 146.7 (d). − IR ($CHCl_3$): ṽ = 3480 (m), 3245 (m, br), 3062 (m), 3026 (m), 2962 (s), 2931, 2910 (m), 2873 (s), 1619 (m), 1600 (m), 1493 (m), 1446 (s), 1239 (m), 1146 (vs), 1104 (s), 1080 (s), 860 (s), 756 (vs), 702 (vs). − MS: *m*/*z* (%) = 343 [M^+] (13), 300 (45), 271 (15), 170 (11), 156 (65), 146 (16), 145 (18), 125 (69), 117 (100), 116 (34), 115 (80), 109 (12), 91 (26), 78 (13), 77 (21), 72 (24). − $C_{20}H_{25}NO_2S$ (343.5): calcd. C 69.95, H 7.34, N 4.08; found C 69.90, H 7.42, N 4.34.

(±)-*tert*-Butyl-{(*E*)-(1*RS*,2*RS*)-4-[(*SR*)-*N*-methyl-*S*-phenylsulfonimidoyl]-2-methyl-1-phenylbut-3-enyloxy}dimethylsilane (*rac*-8a-Si*t*BuMe$_2$) and (±)-*tert*-Butyl-{(*E*)-(1*RS*,2*SR*)-4-[(*RS*)-*N*-methyl-*S*-phenylsulfonimidoyl]-2-methyl-1-phenylbut-3-enyloxy}-dimethylsilane (*rac*-9a-Si*t*BuMe$_2$): Reaction of *rac*-*Z*-**4a** (418 mg, 1.99 mmol) with benzaldehyde according to *GP2* and subsequent chromatography (EtOAc/hexane, 2:1) gave a mixture of *rac*-**8a** and *rac*-**9a** (27% cy) in a ratio of 66:34, along with recovered *rac*-*Z*-**4a** (34%). The mixture was dissolved in DMF (5 mL), treated with imidazole (170 mg, 2.5 mmol), and then Cl-Si*t*BuMe$_2$ (300 mg, 2.0 mmol) was slowly added. After stirring for 16 h at room temperature, the mixture was poured into ice/water and extracted with cyclohexane. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Chromatography (EtOAc/hexane, 1:1) afforded a mixture of *rac*-**8a**-Si*t*BuMe$_2$ and *rac*-**9a**-Si*t*BuMe$_2$ (219 mg, 26%) in a ratio of 66:34.

rac-**8a:** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.09 (d, *J* = 6.7 Hz, 3 H, CH_3), 2.58−2.72 (m, 1 H, 2-H), 2.62 (s, 3 H, N−CH_3), 4.57 (d, *J* = 6.4 Hz, 1 H, 1-H), 6.14 (dd, *J* = 15.1, *J* = 1.3 Hz, 1 H, 4-H), 6.77 (dd, *J* = 15.1, *J* = 7.7 Hz, 1 H, 3-H), 7.13−7.21 (m, 5 H, Ph), 7.43−7.62 (m, 3 H, Ph), 7.68−7.72 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.6 (d), 29.3 (d), 43.7 (d), 76.4 (d), 126.4 (d), 127.6 (d), 128.2 (d), 128.6 (d), 129.2 (d), 130.4 (d), 132.4 (d), 139.4 (u), 142.7 (u), 148.8 (d).

rac-**9a:** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.99 (d, *J* = 6.7 Hz, 3 H, CH_3), 2.58−2.72 (m, 1 H, 2-H), 2.65 (s, 3 H, N−CH_3), 4.52 (d, *J* = 6.4 Hz, 1 H, 1-H), 6.22 (dd, *J* = 15.1, *J* = 1.0 Hz, 1 H, 4-H), 6.99 (dd, *J* = 15.2, *J* = 7.9 Hz, 1 H, 3-H), 7.13−7.21 (m, 5 H, Ph), 7.43−7.62 (m, 3 H, Ph), 7.76−7.81 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.0 (d), 29.3 (d), 43.8 (d), 77.2 (d), 126.4 (d), 127.5 (d), 128.1 (d), 128.5 (d), 129.2 (d), 130.4 (d), 132.4 (d), 139.2 (u), 142.4 (u), 148.6 (d).

rac-**8a**-Si*t*BuMe$_2$: ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.28 (s, 3 H, CH_3), −0.04 (s, 3 H, CH_3), 0.82 (s, 9 H, *t*Bu), 1.05 (d, *J* = 6.7 Hz, 3 H, CH_3), 2.55−2.64 (m, 1 H, 2-H), 2.69 (s, 3 H, N−CH_3), 4.44−4.49 (m, 1 H, 1-H), 6.13 (m, 1 H, 4-H), 6.66 (dd, *J* = 15.1, *J* = 8.4 Hz, 1 H, 3-H), 7.02−7.19 (m, 5 H, Ph), 7.46−7.62 (m, 3 H, Ph), 7.74−7.85 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = −5.2 (d), −4.7 (d), 16.4 (d), 29.4 (d), 29.8 (d), 45.2 (d), 78.5 (d), 126.4 (d), 127.3 (d), 127.9 (d), 127.8 (d), 128.8 (d), 129.2 (d), 138.2 (u), 142.8 (u), 148.7 (d).

rac-**9a**-Si*t*BuMe$_2$: ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.30 (s, 3 H, CH_3), −0.06 (s, 3 H, CH_3), 0.78 (s, 9 H, *t*Bu), 0.98 (d, *J* = 6.7 Hz, 3 H, CH_3), 2.55−2.64 (m, 1 H, 2-H), 2.71 (s, 3 H, N−CH_3), 4.44−4.49 (m, 1 H, 1-H), 6.13 (m, 1 H, 4-H), 6.89 (dd, *J* = 15.1, *J* = 8.1 Hz, 1 H, 3-H), 7.02−7.19 (m, 5 H, Ph), 7.46−7.62 (m, 3 H, Ph), 7.74−7.85 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = −5.2 (d), −4.7 (d), 15.0 (d), 29.8 (d), 29.4 (d), 45.1 (d), 77.8 (d), 126.5 (d), 127.3 (d), 127.8 (d), 128.7 (d), 128.8 (d), 129.2 (d), 139.5 (u), 142.1 (u), 148.5 (d).

(−)-(*E*)-(2*S*,3*R*)-3-Ethyl-5-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]pent-4-en-2-ol (8b): Sulfoximine *Z*-**4b** (300 mg, 1.34 mmol) was treated with ethanal according to *GP3*, with the modifications that after the titanation the mixture was allowed to warm to room temperature, stirred for 1 h, and then cooled to −78 °C, and that after the addition of the aldehyde the mixture was stirred at −78 °C for 1.5 h and thereafter at room temperature for 10 h. Work-up afforded a mixture of **8b** (32% cy), *epi*-**8b** (1%), recovered *Z*-**4b** (44%), and *Z*-**10e** (22% cy, ≥96% *ds*). Chromatography (EtOAc/cyclohexane, 4:1) followed by crystallization (diethyl ether) furnished diastereopure **8b** (105 mg, 26%) as colorless crystals; m.p. 75 °C; $[\alpha]_D$ = −121.5 (*c* = 1.29, CH_2Cl_2). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 7.4 Hz, 3 H, CH_3), 1.05 (d, *J* = 6.3 Hz, 3 H, CH_3), 1.38 (dq, *J* = 13.7, *J* = 7.4 Hz, 1 H, CH_2), 1.70 (dquad, *J* = 7.7, *J* = 13.7, *J* = 4.1 Hz, 1 H, CH_2), 2.15 (m, 1 H, 3-H), 2.43 (br. s, 1 H, OH), 2.74 (s, 3 H, N−CH_3), 3.75 (dqua, *J* = 6.1, *J* = 12.6 Hz, 1 H, 2-H), 6.35 (dd, *J* = 15.1, *J* = 0.8 Hz, 1 H, 5-H), 6.67 (dd, *J* = 15.1, *J* = 9.3 Hz, 1 H, 4-H), 7.50−7.60 (m, 3 H, Ph), 7.86 (m, 2 H, Ph). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.9 (d), 20.6 (d), 22.6 (u), 29.4 (u), 51.4 (d), 69.3 (d), 128.3 (d), 129.1 (d), 131.6 (d), 132.4 (d), 139.2 (u), 147.0 (d). − IR (KBr): ṽ = 3225 (s, br), 3051 (m), 2977 (s), 2951 (s), 2933 (s), 2893 (m), 2871 (s), 2798 (m), 2281 (w), 1627 (m), 1584 (w), 1448 (s), 1406 (w), 1383 (m), 1373 (m), 1338 (m), 1321 (m), 1308 (m), 1223 (s), 1149 (s), 1103 (s), 1082 (s), 1040 (m), 1020 (m), 994 (s), 943 (w), 898 (w), 872 (s), 859 (s), 797 (s), 750 (s), 701 (m), 689 (s), 607 (s), 541 (s). − MS: *m*/*z* (%) = 269 (16), 268 [M^+ + 1] (100), 266 (1), 239 (3), 224 (2), 192 (2), 155 (3). − $C_{14}H_{21}NO_2S$ (267.4): calcd. C 62.88, H 7.91, N 5.24; found C 63.07, H 7.77, N 5.21.

(*Z*)-(3*S*,4*R*)-2,7-Dimethyl-4-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]-oct-5-en-3-ol (*epi*-*Z*-10i): Sulfoximine *Z*-**4c** (136 mg, 0.57 mmol) was treated with 2-methylpropanal according to *GP2*. Work-up afforded a mixture of *epi*-*Z*-**10i** and *Z*-**10i** (45% cy) in a ratio of 2:1, recovered *Z*-**4c** (48%), and *N*-methyl-*S*-phenylsulfinamide (5% cy). Chromatography (EtOAc/hexane, 4:1) gave a mixture of *epi*-*Z*-**10i** and *Z*-**10i** (47.7 mg, 28%) in a ratio of 64:36.

epi-*Z*-**10i:** R_f = 0.63 (EtOAc/hexane, 4:1). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.59 (d, *J* = 6.7 Hz, 3 H, CH_3), 0.94 (d, *J* = 6.7 Hz, 3 H, CH_3), 0.96 (d, *J* = 6.7 Hz, 3 H, CH_3), 1.00 (d, *J* = 6.7 Hz, 3 H, CH_3), 1.60 [dsept, *J* = 9.1, *J* = 6.7 Hz, 1 H, C*H*(CH_3)$_2$], 2.49 [dsept, *J* = 10.4, *J* = 6.7 Hz, 1 H, C*H*(CH_3)$_2$], 2.71 (s, 3 H, N−CH_3), 3.54 (dd, *J* = 9.1, *J* = 1.0 Hz, 1 H, 3-H), 3.85 (d, *J* = 10.4 Hz, 1 H, 4-H), 5.63 (t, *J* = 10.8 Hz, 1 H, 6-H), 5.82 (dd, *J* = 10.8, *J* = 10.4 Hz, 1 H, 5-H), 7.50−7.69 (m, 3 H, Ph), 7.80−7.89 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.1 (d), 19.3 (d), 22.5 (d), 22.8 (d), 28.3 (d), 29.2 (d), 31.4 (d), 65.3 (d), 73.9 (d), 111.8 (d), 129.5 (d), 129.9 (d), 133.2 (d), 136.9 (u), 148.2 (d).

(−)-(*Z*)-(3*S*,4*R*)-1-(*tert*-Butyldimethylsilanyloxy)-4-methyl-6-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]hex-5-en-3-ol (12): Reaction of a mixture of *E*-**4a** and *Z*-**4a** (4.10 g, 19.6 mmol, 7:3) with aldehyde **11** according to *GP2* and subsequent chromatography (EtOAc/hexane, 4:1) gave, besides a mixture of recovered *E*-**4a** and *Z*-**4a** (53%) in a 1:1 ratio and recovered **11** (56%), the diastereopure sulfoximine **12** (2.50 g, 32%) as a colorless oil; R_f = 0.32 (EtOAc/hexane, 4:1); $[\alpha]_D$ = −134.9 (*c* = 1.18, MeOH). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.07 (s, 3 H, CH_3), 0.08 (s, 3 H, CH_3), 0.76 (d, *J* = 6.7 Hz, 3 H, CH_3), 0.90 (s, 9 H, *t*Bu), 1.58−1.75 (m, 1 H, 2-H), 1.75 (dtd, *J* = 14.4, *J* = 4.3, *J* = 2.3 Hz, 1 H, 2-H), 2.66 (s, 3 H, N−CH_3), 3.46 (dqd, *J* = 11.0, *J* = 6.7, *J* = 4.3 Hz, 1 H, 4-H), 3.72 (ddd, *J* = 9.7, *J* = 4.3, *J* = 4.3 Hz, 1 H, 3-H), 3.77−3.94 (m, 2 H, 1-H), 4.04 (br. s, 1 H, OH), 6.31 (dd, *J* = 11.0, *J* = 11.0 Hz, 1 H, 5-H), 6.45 (d, *J* = 11.0, 1 H, 6-H), 7.50−7.62

(m, 3 H, Ph), 7.87−7.93 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = −5.5 (d), 16.0 (d), 18.1 (u), 25.9 (d), 29.2 (d), 37.3 (u), 37.8 (d), 62.5 (u), 74.6 (d), 128.8 (d), 129.2 (d), 131.4 (d), 132.5 (d), 140.4 (u), 148.0 (d). − IR ($CHCl_3$): $\tilde{\nu}$ = 3500 (m, br), 2955 (s), 2929 (s), 2857 (s), 1622 (m), 1472 (m), 1463 (m), 1446 (s), 1250 (vs), 1148 (vs), 1099 (vs), 1082 (vs), 861 (m), 836 (s), 776 (s), 753 (s). − MS: *m*/*z* (%) = 397 [M^+] (21), 382 (5), 340 (66), 238 (31), 209 (20), 185 (32), 156 (55), 131 (92), 125 (81), 101 (91), 89 (20), 75 (100). − $C_{20}H_{35}NO_3SSi$ (397.6): calcd. C 60.41, H 8.87, N 3.52; found C 60.22, H 8.67, N 3.90.

(*Z*)-(1*R*,2*R*)-3-Methyl-4-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]-1,2-diphenylbut-3-en-1-ol (14): Reaction of **13** (571 mg, 2.0 mmol) with benzaldehyde according to *GP2* gave crude **14** (51% cy, 97% *ds*). Subsequent chromatography (EtOAc/hexane, 2:1) afforded **14** (317 mg, 41%) containing 3% of a diastereomer. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.85 (d, *J* = 1.3 Hz, 3 H, CH_3), 2.76 (s, 3 H, N−CH_3), 5.20 (d, *J* = 11.1 Hz, 1 H, 2-H), 5.70 (d, *J* = 11.1 Hz, 1 H, 1-H), 6.42 (br. s, 2 H, 4-H, OH), 7.04−7.18 (m, 6 H, Ph), 7.19−7.26 (m, 2 H, Ph), 7.41−7.46 (m, 2 H, Ph), 7.56−7.68 (m, 3 H, Ph), 7.89−8.02 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.8 (d), 29.6 (d), 54.4 (d), 74.3 (d), 127.0 (d), 127.1 (d), 127.4 (d), 128.3 (d), 128.3 (d), 129.2 (d), 129.3 (d), 129.6 (d), 129.8 (d), 133.1 (d), 137.3 (u), 139.3 (u), 143.7 (u), 155.8 (u). − MS: *m*/*z* (%) = 391 [M^+] (1), 236 (15), 167 (15), 160 (16), 131 (100), 129 (27), 124 (20), 115 (20), 106 (67), 105 (63), 91 (39), 78 (15), 77 (66).

General Procedure for γ-Hydroxyalkylation of the Allylic Sulfoximine 15 Using 2.1 Equiv. of ClTi(O*i*Pr)$_3$ (*GP6*): To a solution of **15** (1.0 mmol) in Et_2O (10 mL) at −78 °C was added *n*BuLi (0.68 mL, 1.6 M solution in hexane, 1.1 mmol). After stirring for 10 min at −78 °C, ClTi(O*i*Pr)$_3$ (2.1 mmol), either neat or in Et_2O (2 mL), was added. The resulting mixture was stirred for 10 min at −78 °C, allowed to warm to room temperature, and stirred for 2 h. It was then cooled to −78 °C once more, whereupon the aldehyde (2 mmol) was added dropwise and stirring was continued for 2 h at −78 °C. The mixture was then poured into aqueous $NaHCO_3$ solution and extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo.

(*Z*)-(*S*)-1-{(*R*)-2-[(*S*)-*N*-Methyl-*S*-phenysulfonimidoyl]1-methylenecyclohexyl}propan-1-ol (16b): Reaction of **15** (501 mg, 2.00 mmol) with propanal according to *GP6* furnished a mixture of recovered **15** (23%) and **16b** (77% cy, ≥96% *ds*). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (t, *J* = 7.4 Hz, 3 H, CH_3), 1.32−1.58 (m, 4 H, CH_2), 1.74−1.92 (m, 3 H, CH_2CH$_3$, CH_2), 2.15 (m, 2 H, CH_2CH$_3$, CH_2), 2.45 (td, *J* = 13.2, *J* = 5.2 Hz, 1 H, CH_2), 2.59 (s, 3 H, N−CH_3), 3.73 (br. dd, *J* = 10.4, *J* = 4.0 Hz, 1 H, CH), 3.79 (br. td, *J* = 8.5, *J* = 2.7 Hz, 1 H, C*H*OH), 6.30 (d, *J* = 1.7 Hz, 1 H, =CH), 7.49−7.64 (m, 3 H, *m*-, *p*-Ph), 7.78−7.92 (m, 2 H, *o*-Ph). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.6 (d), 20.1 (u), 22.4 (u), 25.4 (u), 29.6 (d), 32.7 (u), 42.4 (d), 71.0 (d), 126.3 (d), 128.6 (d), 129.6 (d), 132.5 (d), 139.6 (u), 160.8 (u).

(−)-(*Z*)-(*S*)-1-{(*R*)-2-[(*S*)-*N*-Methyl-*S*-phenylsulfonimidoyl]-methylenecyclohexyl}-2-methylpropan-1-ol (16c): Reaction of **15** (501 mg, 2.00 mmol) with 2-methylpropanal according to *GP6* furnished a mixture of recovered **15** (23%) and **16c** (77% cy, 96% *ds*). Crystallization of the residue (diethyl ether) gave the diastereopure sulfoximine **16c** (381 mg, 59%) as colorless crystals; m.p. 101 °C; $[\alpha]_D$ = −130.1 (*c* = 0.99, diethyl ether). − ^{1}H NMR (300 MHz, [D_8]THF): δ = 0.87 (d, *J* = 6.7 Hz, 3 H, CH_3), 1.08 (d, *J* = 7.1 Hz, 3 H, CH_3), 1.15−1.55 (m, 4 H, CH_2), 1.69 (m, 1 H, CH_2), 1.76−1.88 (m, 2 H, 2-H, CH_2), 2.08 (br. d, *J* = 14.1 Hz, 1 H, CH_2), 2.44 (dd, *J* = 4.9, *J* = 1.3 Hz, 1 H, CH_2), 2.45 (s, 3 H, N−CH_3), 3.66 (t, *J* = 10.1 Hz, 1 H, C*H*OH), 3.78 (dd, *J* = 11.1, *J* = 4.4 Hz, 1 H, CH), 4.36 (d, *J* = 9.4 Hz, 1 H, OH), 6.33 (br. s, 1 H, =CH), 7.56−7.61 (m, 3 H, *m*-, *p*-Ph), 7.81−7.88 (m, 2 H, *o*-Ph). − ^{13}C NMR (75 MHz, [D_8]THF): δ = 15.2 (d), 22.0 (u), 22.4 (d), 29.3 (u), 29.5 (u), 30.3 (d), 31.5 (d), 34.0 (d), 42.6 (d), 75.1 (d), 128.9 (d), 130.7 (d), 131.0 (d), 134.2 (d), 142.6 (u), 162.2 (u). − MS (CI): *m*/*z* (%) = 324 (7), 323 (20), 322 [M^+ + 1] (100), 293 (5), 250 (18), 167 (7), 156 (27), 75 (7). − $C_{18}H_{27}NO_2S$ (321.49): calcd. C 67.25, H 8.47, N 4.36; found C 67.10, H 8.42, N 4.24.

(−)-(*Z*)-(*R*)-1-{(*R*)-2-[(*S*)-*N*-Methyl-*S*-phenylsulfonimidoyl]-methylenecyclohexyl}-1-phenylmethanol (16d): Reaction of **15** (1.0 g, 4.01 mmol) with benzaldehyde according to *GP6* furnished a mixture of recovered **15** (38%) and **16d** (62% cy, ≥96% *ds*). Crystallization (diethyl ether) of the residue afforded diastereopure **16d** (667 mg, 47%, ≥98% *ds*) as colorless crystals; m.p. 149 °C; $[\alpha]_D$ = −10.24 (*c* = 1.25, CH_2Cl_2). − ^{1}H NMR (400 MHz, [D_8]THF): δ = 1.12−1.23 (m, 1 H, CH_2), 1.26−1.47 (m, 3 H, CH_2), 1.73 (br. s, 1 H, CH_2), 1.92 (m, 1 H, CH_2), 2.18 (m, 1 H, CH_2), 2.50−2.60 (tdd, *J* = 13.8, *J* = 4.8, *J* = 1.9 Hz, 1 H, CH_2), 2.63 (s, 3 H, N−CH_3), 4.00 (dd, *J* = 10.7, *J* = 4.4 Hz, 1 H, CH), 4.74 (t, *J* = 10.4 Hz, 1 H, C*H*OH), 5.77 (d, *J* = 9.1 Hz, 1 H, OH), 6.46 (d, *J* = 1.9 Hz, 1 H, =CH), 7.19−7.25 (m, 1 H, *p*-Ph), 7.29−7.35 (m, 2 H, *m*-Ph), 7.40−7.44 (m, 2 H, *o*-Ph), 7.55−7.63 (m, 3 H, *m*-, *p*-Ph), 7.90−7.93 (m, 2 H, *o*-Ph). − ^{13}C NMR (100 MHz, [D_8]THF): δ = 21.5 (u), 28.7 (u), 28.9 (u), 29.7 (d), 33.4 (u), 46.8 (d), 74.8 (d), 127.8 (d), 128.0 (d), 128.7 (d), 129.0 (d), 129.9 (d), 130.2 (d), 133.4 (d), 141.6 (u), 146.8 (u), 160.6 (u). − MS (EI): *m*/*z* (%) = 356 [M^+] (4), 250 (15), 171 (6), 158 (5), 157 (9), 156 (100), 125 (38), 124 (5), 107 (5), 96 (5), 95 (58), 76 (11).

General Procedure for α-Hydroxyalkylation of Allylic Sulfoximines (*GP7*): To a solution of the allylic sulfoximine **4** or **6** (1.0 mmol) in THF (5 mL) at −78 °C was added *n*BuLi (0.68 mL, 1.60 M solution in hexane, 1.1 mmol). After stirring for 10 min at −78 °C, ClTi(-NEt_2)$_3$ (1.2 mmol), either neat of in THF (2 mL), was added dropwise and stirring was continued for a further 10 min at −78 °C. The mixture was then allowed to warm to 0 °C, stirred for 30 min at this temperature, and cooled to −78 °C once more, whereupon the aldehyde (1.5−2 mmol) was added dropwise. After stirring for 2 h at −78 °C, the mixture was poured into saturated aqueous $(NH_4)_2CO_3$ solution and extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. The allylic sulfoximine **10** was isolated by crystallization or chromatography.

(*E*)-(2*R*,3*R*)-3-[(*S*)-*N*-Methyl-*S*-phenylsulfonimidoyl]hex-4-en-2-ol (*E*-10a): Reaction of *E*-**4a** (210 mg, 1.00 mmol) with ethanal according to *GP7* gave a mixture of recovered *E*-**4a** (23%), *E*-**10a** (31% cy, ≥96% *ds*), and **7a** (46% cy, 92% *ds*) besides a (*Z*)-diastereomer.

E-**10a:** ^{1}H NMR (400 MHz, C_6D_6): δ = 1.14 (dd, *J* = 6.3, *J* = 1.6 Hz, 3 H, 6-H), 1.20 (d, *J* = 6.3 Hz, 3 H, 1-H), 2.61 (s, 3 H, N−CH_3), 3.47 (dd, *J* = 9.3, *J* = 9.3 Hz, 1 H, 3-H), 4.58 (dq, *J* = 15.1, *J* = 6.6 Hz, 1 H, 2-H), 4.87 (dq, *J* = 9.1, *J* = 6.3 Hz, 1 H, 5-H), 5.15 (ddq, *J* = 10.4, *J* = 10.4, *J* = 1.7 Hz, 1 H, 4-H), 7.2 (br. s, 1 H, OH), 6.92−6.96 (m, 3 H, *m*-Ph, *p*-Ph), 7.56−7.62 (m, 2 H, *o*-Ph).

(*E*)-(3*R*,4*R*)-4-[(*S*)-*N*-Methyl-*S*-phenylsulfonimidoyl]hept-5-en-3-ol (*E*-10b): Reaction of *E*-**4a** (230 mg, 1.10 mmol) with propanal according to *GP7* gave a mixture of *E*-**10b** (50% cy, ≥96% *ds*), recovered *E*-**4a** (38% cy), and **7b** (12% cy, ≥96% *ds*).

E-**10b:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.3 Hz, 3 H, 1-H), 1.27−1.40 (m, 1 H, 2-H), 1.50 (dd, *J* = 6.3, *J* = 1.7 Hz, 3

H, 7-H), 1.55−1.65 (m, 1 H, 2-H), 2.65 (s, 3 H, N−CH_3), 3.53 (dd, J = 9.9, J = 9.9 Hz, 1 H, 4-H), 4.38 (ddd, J = 9.3, J = 9.3, J = 3.0 Hz, 1 H, 3-H), 4.97 (dq, J = 15.4, J = 6.3 Hz, 1 H, 6-H), 5.20 (ddq, J = 10.4, J = 10.4, J = 1.7 Hz, 1 H, 5-H), 7.0 (br. s, 1 H, OH), 7.50−7.56 (m, 2 H, *m*-Ph), 7.57−7.62 (m, 1 H, *p*-Ph), 7.72−7.76 (m, 2 H, *o*-Ph). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.6 (d), 18.0 (d), 27.6 (u), 29.7 (d), 69.1 (d), 73.4 (d), 119.7 (d), 128.8 (d), 130.0 (d), 132.8 (d), 135.6 (d).

Reaction of *E*-**4a** (145 mg, 0.69 mmol) with propanal according to *GP7*, with the modifications that the aldehyde was added at room temperature and that the mixture was stirred for 2 h at room temperature, gave a mixture of *E*-**10b** (79% cy, ≥96% *ds*), recovered *E*-**4a** (9%), and **7b** (11% cy, ≥96% *ds*).

(+)-(*E*)-(3*R*,4*R*)-2-Methyl-4-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]hept-5-en-3-ol (*E*-10c): Reaction of *E*-**4a** (247 mg, 1.18 mmol) with 2-methylpropanal according to *GP7* gave a mixture of *E*-**10c** (93% cy, ≥96% *ds*), recovered *E*-**4a** (3%), and **7c** (4% cy, ≥96% *ds*). Subsequent chromatography (EtOAc/hexane/NEt_3, 75:24:1) furnished diastereopure *E*-**10c** (252 mg, 76%) as a colorless oil; $[\alpha]_D$ = +170.9 (c = 1.10, CH_2Cl_2). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.77 [d, J = 6.4 Hz, 3 H, $CH(CH_3)_2$], 1.07 [d, J = 6.9 Hz, 3 H, $CH(CH_3)_2$], 1.48 (dd, J = 6.6, J = 1.6 Hz, 3 H, 7-H), 1.71 (septd, J = 6.9, J = 2.2 Hz, 1 H, 2-H), 2.64 (s, 3 H, N−CH_3), 3.55 (dd, J = 9.9, J = 9.8 Hz, 1 H, 4-H), 4.33 (dd, J = 9.6, J = 1.9 Hz, 1 H, 3-H), 4.97 (dq, J = 15.4, J = 6.7 Hz, 1 H, 6-H), 5.20 (ddq, J = 10.4, J = 10.4, J = 1.7 Hz, 1 H, 5-H), 6.84 (br. s, 1 H, OH), 7.50−7.56 (m, 2 H, *m*-Ph), 7.57−7.62 (m, 1 H, *p*-Ph), 7.72−7.76 (m, 2 H, *o*-Ph). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5 (d), 18.4 (d), 20.4 (u), 29.9 (d), 31.0 (d), 72.0 (d), 73.0 (d), 119.7 (d), 129.1 (d), 130.4 (d), 133.2 (d), 135.9 (d), 136.1 (u). − IR ($CHCl_3$): $\tilde{\nu}$ = 3259 (w, br), 3063 (w), 3010 (w), 2965 (s), 2934 (m), 2916 (m), 2874 (m), 2806 (w), 1472 (m), 1446 (s), 1366 (w), 1281 (w), 1237 (vs), 1177 (w), 1151 (vs), 1111 (m), 1082 (s), 1023 (w), 1005 (m), 970 (m), 861 (m), 758 (vs), 728 (m), 713 (m). − MS (EI): m/z (%) = 238 [M^+ − $CH(CH_3)_2$] (16), 208 (22), 161 (14), 156 (73), 155 (24), 138 (27), 126 (13), 125 (62), 107 (100), 97 (11), 78 (55), 71 (28). − MS (CI): m/z (%) = 282 [M^+ + 1] (32), 156 (100), 127 (17).− $C_{15}H_{23}NO_2S$ (281.4): calcd. C 64.02, H 8.24, N 4.98; found C 63.93, H 8.39, N 5.02.

(+)-(*E*)-(2*R*,3*R*)-3-[(*S*)-*N*-Methyl-*S*-phenylsulfonimidoyl]-hept-4-en-2-ol (*E*-10e): Reaction of *E*-**4b** (610 mg, 2.73 mmol) with ethanal according to *GP7*, with the modification that the aldehyde was added at −30 °C, gave a mixture of *E*-**10e** (50% cy, ≥96 *ds*), recovered *E*-**4b** (8%), and **7e** (42% cy, ≥96% *ds*). Crystallization (diethyl ether) gave diastereopure *E*-**10e** (352 mg, 48%) as colorless crystals; m.p. 142 °C; $[\alpha]_D$ = +229.5 (c = 1.31, MeOH). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.74 (t, J = 7.4 Hz, 3 H, 7-H), 1.85 (m, 2 H, 6-H), 1.28 (d, J = 6.1 Hz, 3 H, 1-H), 2.65 (s, 3 H, N−CH_3), 3.49 (t, J = 9.6 Hz, 1 H, 3-H), 4.56 (dq, J = 9.4, J = 6.2 Hz, 1 H, 2-H), 5.04 (dd, J = 15.4, J = 6.3 Hz, 1 H, 4-H), 5.16 (dt, J = 15.4, J = 9.4 Hz, 1 H, 5-H), 6.89 (br. s, 1 H, OH), 7.53 (m, 2 H, Ph), 7.59 (m, 1 H, Ph), 7.76 (m, 2 H, Ph). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.4 (d), 21.4 (d), 24.3 (u), 29.7 (d), 65.3 (d), 69.2 (d), 118.0 (d), 129.0 (d), 130.1 (d), 133.1 (d), 135.8 (u), 148.0 (d). − IR (KBr): $\tilde{\nu}$ = 3240 (s, br), 3061 (m), 3028 (m), 2965 (s), 2930 (s), 2870 (s), 2801 (m), 2002 (w), 1910 (w), 1818 (w), 1779 (w), 1698 (w), 1656 (w), 1583 (m), 1467 (s), 1443 (s), 1371 (m), 1342 (m), 1317 (m), 1235 (s), 1210 (s), 1148 (s), 1120 (s), 1082 (s), 1069 (s), 1027 (m), 999 (m), 936 (m), 856 (s), 812 (w), 798 (w), 760 (m), 728 (s). − MS: m/z (%) = 268 [M^+ + 1] (1), 238 (21), 223 (43), 208 (17), 156 (38), 155 (29), 154 (21), 138 (13), 125 (60), 107 (100), 106 (20), 95 (24), 78 (48), 77 (19). − $C_{14}H_{21}NO_2S$ (267.3): calcd. C 62.89, H 7.92, N 5.24; found C 63.13, H 7.62, N 5.26.

(+)-(*E*)-(3*R*,4*R*)-4-[(*S*)-*N*-Methyl-*S*-phenylsulfonimidoyl]-2-methyloct-5-en-3-ol (*E*-10f): Reaction of *E*-**4b** (320 mg, 1.43 mmol) with 2-methylpropanal according to *GP7* gave a mixture of *E*-**10f** (94% cy, ≥96 *ds*) and **7f** (3% cy, ≥96 *ds*). Subsequent chromatography (EtOAc/hexane/NEt_3, 75:24:1) afforded diastereopure *E*-**10f** (200 mg, 47%) as a colorless oil; $[\alpha]_D$ = +231.5 (c = 1.22, CH_2Cl_2). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.73 (t, J = 7.5 Hz, 3 H, 8-H), 0.79 [d, J = 6.6 Hz, 3 H, $CH(CH_3)_2$], 1.08 [d, J = 6.8 Hz, 3 H, $CH(CH_3)_2$], 1.71 (dsept, J = 6.8, J = 2.0 Hz, 1 H, 7-H), 1.85 (m, 2 H, 7′-H, 2-H), 2.64 (s, 3 H, N−CH_3), 3.59 (dd, J = 9.9, J = 10.2 Hz, 1 H, 4-H), 4.33 (dd, J = 9.6, J = 2.2 Hz, 1 H, 3-H), 5.02 (dt, J = 15.4, J = 6.3 Hz, 1 H, 6-H), 5.18 (ddd, J = 15.4, J = 10.4, J = 1.4 Hz, 1 H, 5-H), 6.81 (br. s, 1 H, OH), 7.52−7.64 (m, 3 H, Ph), 7.76 (m, 2 H, Ph). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.9 (d), 13.0 (d), 20.0 (d), 25.5 (u), 29.7 (d), 30.6 (d), 71.6 (d), 72.6 (d), 117.3 (d), 128.8 (d), 130.0 (d), 132.9 (d), 135.6 (u), 142.3 (d). − IR ($CHCl_3$): $\tilde{\nu}$ = 3261 (s, br), 3064 (m), 3008 (m), 2964 (s), 2932 (s), 2874 (s), 2806 (m), 1969 (w), 1817 (w), 1663 (w), 1583 (m), 1446 (s), 1371 (m), 1383 (m), 1366 (m), 1355 (m), 1305 (w), 1282 (m), 1237 (s), 1202 (s), 1177 (s), 1150 (s), 1112 (s), 1082 (s), 1070 (s), 1025 (m), 1000 (s), 972 (m), 942 (m), 901 (w), 861 (s), 757 (s), 717 (m). − MS: m/z (%) = 296 [M^+ + 1] (1), 266 (6), 252 (10), 223 (15), 208 (5), 156 (61), 155 (20), 125 (52), 123 (14), 107 (100), 106 (13), 97 (13), 78 (41), 77 (14), 71 (34). − $C_{16}H_{25}NO_2S$ (295.4): calcd. C 64.99, H 8.53, N 4.74; found C 64.55, H 8.25, N 4.34.

(+)-(*Z*)-(2*R*,3*R*)-6-Methyl-3-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]hept-4-en-2-ol (*E*-10g): Reaction of *E*-**4c** (240 mg, 1.01 mmol) with ethanal according to *GP7* gave a mixture of recovered *E*-**4c** (46%), *E*-**10g** (27% cy, ≥96% *ds*), and **7g** (27% cy, 85% *ds*) besides a *Z*-diastereomer.

E-**10g:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.71 [d, J = 6.6 Hz, 3 H, $CH(CH_3)_2$], 0.76 [d, J = 6.9 Hz, 3 H, $CH(CH_3)_2$], 1.15 (d, J = 6.3 Hz, 3 H, 1-H), 2.10 (octd, J = 6.8, J = 1.2 Hz, 1 H, 6-H), 2.64 (s, 3 H, N−CH_3), 3.49 (dd, J = 9.9, J = 9.3 Hz, 1 H, 3-H), 4.56 (dq, J = 9.3, J = 6.3 Hz, 1 H, 2-H), 4.98 (dd, J = 15.4, J = 6.9 Hz, 1 H, 5-H), 5.11 (ddd, J = 15.4, J = 10.2, J = 1.2 Hz, 1 H, 4-H), 6.80 (br. s, 1 H, OH), 7.50−7.63 (m, 3 H, *m*-Ph, *p*-Ph), 7.74−7.82 (m, 2 H, *o*-Ph).

Reaction of *E*-**4c** (178 mg, 0.75 mmol) with ethanal according to *GP7*, with the modifications that the aldehyde was added at room temperature and that the mixture was stirred for 2 h at room temperature, gave a mixture of recovered *E*-**4c** (72%), *E*-**10g** (18% cy, ≥96% *ds*), and **7g** (10% cy, 90% *ds*) besides a (*Z*)-diastereomer.

(+)-(*E*)-(3*R*,4*R*)-7-Methyl-4-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]-oct-5-en-3-ol (*E*-10h): Reaction of *E*-**4c** (240 mg, 1.01 mmol) with propanal according to *GP7*, with the modifications that the aldehyde was added at room temperature and that the mixture was stirred for 2 h at room temperature, furnished crude *E*-**10h** with ≥96% *ds*, containing less than 1% of **7h**. Crystallization (diethyl ether) afforded diastereopure *E*-**10h** (259 mg, 87%) as colorless crystals; m.p. 82 °C; $[\alpha]_D$ = +134.8 (c = 0.95, CH_2Cl_2). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.70 [d, J = 6.6 Hz, 3 H, $CH(CH_3)_2$], 0.75 [d, J = 6.9 Hz, 3 H, $CH(CH_3)_2$], 0.95 (t, J = 7.4 Hz, 3 H, 1-H), 1.34 (dquin, J = 14.0, J = 7.4 Hz, 1 H, 2-H), 1.58 (dqd, J = 14.0, J = 7.4, J = 3.3 Hz, 1 H, 2-H), 2.10 (octd, J = 6.7, J = 1.1 Hz, 1 H, 7-H), 2.64 (s, 3 H, N−CH_3), 3.53 (dd, J = 9.9, J = 9.6 Hz, 1 H, 4-H), 4.39 (ddd, J = 9.3, J = 7.7, J = 3.3 Hz, 1 H, 3-H), 4.94 (dd, J = 15.4, J = 6.9 Hz, 1 H, 6-H), 5.13 (ddd, J = 15.4, J = 10.2, J = 1.2 Hz, 1 H, 5-H), 6.90 (br. s, 1 H,

OH), 7.50−7.55 (m, 2 H, *m*-Ph), 7.56 (m, 1 H, *p*-Ph), 7.73−7.77 (m, 2 H, *o*-Ph). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.4 (d), 21.4 (d), 21.9 (d), 27.5 (u), 29.7 (d), 31.1 (d), 69.1 (d), 73.3 (d), 115.7 (d), 128.8 (d), 130.0 (d), 132.8 (d), 135.7 (u), 147.7 (d). − IR (KBr): ṽ = 3254 (s, br), 3097 (s), 3065 (m), 3053 (m), 2961 (s), 2929 (s), 2872 (s), 2801 (m), 1659 (w), 1583 (w), 1467 (s), 1446 (s), 1416 (w), 1385 (w), 1366 (w), 1338 (m), 1309 (w), 1309 (w), 1228 (vs), 1151 (vs), 1116 (s), 1083 (s), 1007 (m), 981 (s), 945 (w), 890 (w), 861 (s), 803 (w), 770 (m), 742 (s). − MS: *m*/*z* (%) = 252 (19), 237 (53), 236 (20), 222 (33), 156 (68), 155 (42), 138 (14), 126 (11), 125 (94), 123 (63), 107 (100), 97 (29), 81 (14), 78 (30), 77 (22). − $C_{16}H_{25}NO_2S$ (295.4): calcd. C 65.05, H 8.53, N 4.74; found C 64.90, H 8.61, N 4.69.

Reaction of *E*-**4c** (247 mg, 1.04 mmol) with propanal according to *GP7* gave a mixture of *E*-**10h** (64% cy, ≥96% *ds*), recovered *E*-**4c** (33%), and **7h** (3% cy).

(+)-(*E*)-(3*R*,4*R*)-2,7-Dimethyl-4-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]oct-5-en-3-ol (*E*-10i): Reaction of *E*-**4c** (239 mg, 1.01 mmol) with 2-methylpropanal according to *GP7* gave crude *E*-**10i** with ≥96% *ds*, containing less than 1% of **7i**. Chromatography (EtOAc/hexane, 4:1) afforded diastereopure *E*-**10i** (252 mg, 81%) as colorless needles; m.p. 82 °C; R_f = 0.57 (EtOAc/hexane, 4:1); $[\alpha]_D$ = +127.7 (*c* = 1.64, MeOH). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.70 (d, *J* = 6.7 Hz, 3 H, CH_3), 0.74 (d, *J* = 7.0 Hz, 3 H, CH_3), 0.78 (d, *J* = 6.7 Hz, 3 H, CH_3), 1.08 (d, *J* = 7.0 Hz, 3 H, CH_3), 1.69 (septd, *J* = 6.9, *J* = 2.1 Hz, 1 H, 2-H), 2.10 (octd, *J* = 6.7, *J* = 1.2 Hz, 1 H, 7-H), 2.63 (s, 3 H, N−CH_3), 3.57 (dd, *J* = 10.1, *J* = 9.8 Hz, 1 H, 4-H), 4.34 (dd, *J* = 9.5, *J* = 2.1 Hz, 1 H, 3-H), 4.95 (dd, *J* = 15.2, *J* = 7.0 Hz, 1 H, 6-H), 5.14 (ddd, *J* = 15.3, *J* = 10.4, *J* = 1.2 Hz, 1 H, 5-H), 6.79 (br. s, 1 H, OH), 7.53 (m, 2 H, Ph), 7.59 (m, 1 H, Ph), 7.76 (m, 2 H, Ph). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.0 (d), 20.1 (d), 21.4 (d), 21.9 (d), 29.8 (d), 30.7 (d), 31.2 (d), 71.8 (d), 72.7 (d), 115.6 (d), 129.1 (d), 130.3 (d), 133.0 (d), 136.0 (u), 147.9 (d). − IR (KBr): ṽ = 3271 (s, br), 3064 (w), 2964 (s), 2931 (s), 2888 (s), 2871 (s), 2797 (m), 1655 (w), 1561 (w), 1491 (w), 1474 (m), 1466 (m), 1459 (m), 1449 (s), 1413 (w), 1384 (m), 1363 (m), 1307 (w), 1283 (m), 1235 (s), 1207 (s), 1179 (m), 1148 (s), 1112 (s), 1080 (s), 1030 (m), 1006 (s), 980 (s), 869 (s), 858 (m), 769 (m), 743 (s). − MS: *m*/*z* (%) = 309 [M^+] (1), 156 (57), 137 (27), 125 (53), 111 (16), 107 (94), 95 (22), 81 (24), 78 (57), 77 (19), 71 (55). − $C_{17}H_{27}NO_2S$ (309.4): calcd. C 65.98, H 8.79, N 4.53; found C 65.77, H 8.73, N 4.51.

Reaction of *E*-**4c** (223 mg, 0.94 mmol) with 2-methylpropanal according to *GP7*, with the modifications that the aldehyde was added at room temperature and that the reaction mixture was stirred for 2 h at room temperature, gave crude *E*-**10i** (98% cy, ≥96% *ds*).

(+)-(*E*)-(1*R*,2*R*)-5-Methyl-2-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]-1-phenylhex-3-en-1-ol (*E*-10j): Reaction of *E*-**4c** (471 mg, 1.98 mmol) with benzaldehyde according to *GP7* gave crude *E*-**10j** with ≥96% *ds* (86% cy), containing less than 1% of **7j**. Chromatography (EtOAc/hexane, 4:1) afforded diastereopure *E*-**10j** (476 mg, 70%) as colorless needles; m.p. 60 °C; R_f = 0.62 (EtOAc/hexane, 4:1); $[\alpha]_D$ = +44.3 (*c* = 1.53, MeOH). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.40 (d, *J* = 6.7 Hz, 3 H, CH_3), 0.45 (d, *J* = 6.7 Hz, 3 H, CH_3), 1.77 (octd, *J* = 6.8, *J* = 1.0 Hz, 1 H, 5-H), 2.72 (s, 3 H, N−CH_3), 3.72 (dd, *J* = 10.4, *J* = 9.4 Hz, 1 H, 2-H), 4.53 (dd, *J* = 15.4, *J* = 7.0 Hz, 4-H), 4.97 (ddd, *J* = 15.4, *J* = 10.4, *J* = 1.0 Hz, 1 H, 3-H), 5.39 (d, *J* = 9.4 Hz, 1 H, 1-H), 7.15−7.32 (m, 5 H, Ph), 7.38 (br. s, 1 H, OH), 7.48−7.62 (m, 3 H, Ph), 7.76−7.81 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2 (d), 21.4 (d), 29.8 (d), 30.9 (d), 72.9 (d), 74.2 (d), 115.9 (d), 127.3 (d), 128.0 (d), 128.1 (d), 129.1 (d), 130.2 (d), 133.1 (d), 136.0 (u), 140.5 (u), 147.9 (d). − IR (KBr): ṽ = 3202 (s, br), 3051 (m), 3032 (m), 2956 (s), 2934 (s), 2894 (m), 2867 (s), 2798 (m), 1906 (w), 1886 (w), 1823 (w), 1811 (w), 1688 (w), 1662 (w), 1582 (w), 1465 (s), 1445 (s), 1383 (w), 1327 (m), 1306 (w), 1238 (s), 1207 (m), 1147 (s), 1100 (s), 1082 (s), 1067 (m), 1036 (m), 1024 (m), 1008 (m), 1000 (m), 971 (s), 943 (w), 920 (w), 869 (m), 855 (s), 778 (s), 742 (s), 704 (s). − MS: *m*/*z* (%) = 343 [M^+] (< 1), 237 (37), 222 (19), 171 (32), 157 (10), 156 (59), 155 (46), 154 (11), 145 (18), 138 (10), 129 (13), 125 (47), 117 (12), 107 (79), 106 (39), 105 (100), 97 (10), 91 (24), 79 (14), 78 (57), 77 (64). − $C_{20}H_{25}NO_2S$ (343.4): calcd. C 69.94, H 7.34, N 4.08; found C 69.61, H 7.00, N 3.92.

(+)-(*E*)-(3*R*,4*R*)-6-Cyclohexyl-2-methyl-4-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]hex-5-en-3-ol (*E*-10l): Reaction of *E*-**4d** (1.04 g, 3.73 mmol) with 2-methylpropanal according to *GP7* gave crude *E*-**10l** with ≥96% *ds* (91% cy), containing less than 1% of **7l**. Crystallization (EtOAc/hexane, 4:1, or diethyl ether/hexane, 4:1) afforded diastereopure *E*-**10l** (1.12 g, 86%) as colorless needles; m.p. 113 °C; $[\alpha]_D$ = +102.8 (*c* = 1.16, acetone). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.64−0.90 (m, 2 H, C_6H_{11}), 0.77 (d, *J* = 6.7 Hz, 3 H, CH_3), 0.90−1.30 (m, 3 H, C_6H_{11}), 1.07 (d, *J* = 6.7 Hz, 3 H, CH_3), 1.31−1.50 (m, 2 H, C_6H_{11}), 1.52−1.64 (m, 2 H, C_6H_{11}), 1.64−1.85 (m, 2 H, C_6H_{11}), 2.63 (s, 3 H, N−CH_3), 3.55 (dd, *J* = 10.1, *J* = 9.7 Hz, 1 H, 4-H), 4.33 (dd, *J* = 9.7, *J* = 2.0 Hz, 1 H, 3-H), 4.91 (dd, *J* = 15.4, *J* = 6.9 Hz, 1 H, 6-H), 5.15 (dd, *J* = 15.4, *J* = 10.4 Hz, 1 H, 5-H), 6.80 (br. s, 1 H, OH), 7.49−7.63 (m, 3 H, Ph), 7.73−7.78 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.0 (d), 20.1 (d), 25.6 (u), 25.7 (u), 26.0 (u), 29.8 (d), 30.7 (d), 31.9 (u), 32.3 (u), 40.7 (d), 71.8 (d), 72.9 (d), 116.0 (d), 129.1 (d), 130.3 (d), 133.0 (d), 135.9 (u), 146.7 (d). − IR (KBr): ṽ = 3235 (s, br), 3087 (m), 3067 (m), 2960 (s), 2926 (s), 2852 (s), 2800 (m), 2090 (w), 2005 (w), 1824 (w), 1780 (w), 1661 (w), 1583 (w), 1472 (s), 1449 (s), 1383 (m), 1368 (m), 1285 (m), 1237 (s), 1208 (s), 1179 (s), 1145 (s), 1106 (s), 1080 (s), 1070 (s), 1027 (m), 1005 (s), 976 (s), 864 (s), 768 (m), 743 (s). − MS: *m*/*z* (%) = 349 [M^+] (< 1), 277 (4), 194 (11), 177 (15), 156 (49), 155 (14), 151 (18), 125 (58), 122 (13), 111 (33), 109 (24), 108 (17), 107 (100), 106 (15), 97 (30), 95 (24), 93 (12), 91 (11), 83 (14), 81 (38), 79 (24), 78 (42), 77 (39), 71 (50). − $C_{20}H_{31}NO_2S$ (349.5): calcd. C 68.73, H 8.94, N 4.01; found C 68.77, H 8.95, N 3.86.

(+)-(*E*)-(1*R*,2*R*)-4-Cyclohexyl-2-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]-1-phenylbut-3-en-1-ol (*E*-10m): Reaction of *E*-**4d** (277 mg, 1.00 mmol) with benzaldehyde according to *GP7* furnished crude *E*-**10m** with ≥96% *ds*. Crystallization (diethyl ether) gave diastereopure *E*-**10m** (259 mg, 68%) as colorless needles; m.p. 134 °C; $[\alpha]_D$ = +29.8 (*c* = 1.14, acetone). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.39−0.52 (m, 2 H, C_6H_{11}), 0.83−1.13 (m, 5 H, C_6H_{11}), 1.37−1.52 (m, 4 H, C_6H_{11}), 2.71 (s, 3 H, N−CH_3), 3.70 (dd, *J* = 10.1, *J* = 9.7 Hz, 1 H, 2-H), 4.52 (dd, *J* = 15.4, *J* = 7.1 Hz, 1 H, 4-H), 4.90 (ddd, *J* = 15.4, *J* = 10.4, *J* = 1.0 Hz, 1 H, 3-H), 5.37 (d, *J* = 9.4 Hz, 1 H, 1-H), 7.15−7.31 (m, 5 H, Ph), 7.40 (br. s, 1 H, OH), 7.48−7.61 (m, 3 H, Ph), 7.76−7.81 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.5 (u), 25.9 (u), 29.9 (d), 31.7 (u), 31.9 (u), 40.4 (d), 73.0 (d), 74.4 (d), 116.4 (d), 127.5 (d), 128.1 (d), 128.2 (d), 129.1 (d), 130.3 (d), 133.2 (d), 136.1 (u), 140.6 (u), 146.8 (d). − IR (KBr): ṽ = 3191 (s, br), 3084 (m), 3033 (m), 3005 (m), 2967 (m), 2917 (s), 2856 (s), 2805 (m), 1987 (w), 1964 (w), 1896 (w), 1812 (w), 1773 (w), 1662 (m), 1583 (w), 1496 (m), 1448 (s), 1341 (m), 1324 (m), 1240 (s), 1203 (s), 1156 (s), 1120 (s), 1084 (s), 1069 (m), 1044 (s), 1025 (m), 994 (m), 966 (s), 922 (m), 871 (s), 775 (s), 736 (s), 705 (s). − MS: *m*/*z* (%) = 383 [M^+] (< 1), 300 (3), 277 (19), 228 (10), 211 (27), 199 (16), 156 (64), 155 (51), 145 (30), 133 (19), 129 (15), 128 (10), 125 (53), 117 (46), 115 (14), 109 (17), 108 (14), 107 (93), 106 (33), 105 (100), 97 (17), 91 (38), 81 (31), 79 (23), 78

(40), 77 (73). − $C_{23}H_{29}NO_2S$ (383.5): calcd. C 72.03, H 7.62, N 3.65; found C 71.83, H 7.79, N 3.61.

(+)-(*Z*)-(2*R*,3*R*)-3-[(*S*)-*N*-Methyl-*S*-phenylsulfonimidoyl]-hex-4-en-2-ol (*Z*-10a): Reaction of *Z*-**4a** (209 mg, 1.00 mmol) with ethanal according to *GP7* gave a mixture of recovered *Z*-**4a** (64%), *Z*-**10a** (26% cy, ≥96% *ds*), and several γ-diastereomers (10% cy). Chromatography (EtOAc/hexane/NEt_3, 75:24:1) furnished diastereopure *Z*-**10a** (51 mg, 20%) as colorless needles; m.p. 102 °C; R_f = 0.63 (EtOAc/hexane/NEt_3, 75:24:1); $[\alpha]_D$ = +238.9 (*c* = 1.08, CH_2Cl_2). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91 (dd, *J* = 7.0, *J* = 1.8 Hz, 3 H, 6-H), 1.13 (d, *J* = 6.1 Hz, 3 H, 1-H), 2.64 (s, 3 H, N−CH_3), 3.90 (dd, *J* = 9.2, *J* = 8.9 Hz, 1 H, 3-H), 4.55 (dq, *J* = 8.9, *J* = 6.4 Hz, 1 H, 2-H), 5.20 (ddq, *J* = 11.3, *J* = 11.0, *J* = 1.8 Hz, 1 H, 4-H), 5.64 (dq, *J* = 11.0, *J* = 7.0 Hz, 1 H, 5-H), 7.0 (br. s, 1 H, OH), 7.52 (m, 2 H, *m*-Ph), 7.59 (m, 1 H, *p*-Ph), 7.77 (m, 2 H, *o*-Ph). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.4 (d), 21.0 (d), 29.5 (d), 65.7 (d), 68.5 (d), 119.5 (d), 129.1 (d), 130.2 (d), 133.1 (d), 133.2 (d), 136.1 (u). − IR (KBr): $\tilde{\nu}$ = 3168 (m, br), 3058 (m), 3025 (w), 2988 (m), 2970 (m), 2929 (m), 2870 (m), 2805 (m), 1584 (w), 1473 (s), 1450 (s), 1405 (w), 1374 (m), 1345 (w), 1307 (m), 1265 (m), 1235 (vs), 1209 (s), 1149 (vs), 1123 (s), 1083 (s), 1021 (w), 932 (w), 858 (s), 798 (w), 761 (m), 715 (vs). − MS: *m*/*z* (%) = 254 [M^+ + 1] (0.6), 209 (27), 208 (13), 198 (11), 161 (12), 156 (34), 155 (33), 154 (23), 138 (16), 131 (14), 129 (12), 128 (11), 126 (15), 125 (64), 109 (10), 107 (100), 106 (26), 105 (10), 100 (24), 97 (13), 82 (12), 78 (53), 77 (23). − $C_{13}H_{19}NO_2S$ (253.4): calcd. C 61.63, H 7.56, N 5.53; found C 61.59, H 7.60, N 5.35.

Reaction of *Z*-**4a** (197 mg, 0.94 mmol) with ethanal according to *GP7*, with the modifcations that the aldehyde was added at room temperature and that the mixture was stirred for 2 h at room temperature, gave a mixture of recovered *Z*-**4a** (81%), *Z*-**10a** (17% cy, ≥96% *ds*), and several γ-diastereomers (2% cy).

(+)-(*Z*)-(3*R*,4*R*)-4-[(*S*)-*N*-Methyl-*S*-phenylsulfonimidoyl]-hept-5-en-3-ol (*Z*-10b): Reaction of *Z*-**4a** (260 mg, 1.24 mmol) with propanal according to *GP7*, with the modifications that the aldehyde was added at room temperature and that the mixture was stirred for 2 h at room temperature, gave crude *Z*-**10b** with ≥96% *ds*, containing no γ-isomers. Crystallization (diethyl ether) afforded diastereopure *Z*-**10b** (297 mg, 90%) as colorless crystals; m.p. 97−98 °C; $[\alpha]_D$ = +261.4 (*c* = 1.04, CH_2Cl_2). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (dd, *J* = 7.1, *J* = 1.9 Hz, 3 H, 7-H), 0.93 (t, *J* = 7.4 Hz, 3 H, 1-H), 1.34 (dquin, *J* = 14.0, *J* = 7.4 Hz, 1 H, 2-H), 1.61 (dqd, *J* = 14.0, *J* = 7.4, *J* = 3.0 Hz, 1 H, 2-H), 2.66 (s, 3 H, N−CH_3), 3.96 (dd, *J* = 9.6, *J* = 9.4 Hz, 1 H, 4-H), 4.41 (ddd, *J* = 9.3, *J* = 9.3, *J* = 3.0 Hz, 1 H, 3-H), 5.21 (ddq, *J* = 11.1, *J* = 11.1, *J* = 1.9 Hz, 1 H, 5-H), 5.64 (dqd, *J* = 11.0, *J* = 7.1, *J* = 0.8 Hz, 1 H, 6-H), 7.06 (br. s, 1 H, OH), 7.50−7.56 (m, 2 H, *m*-Ph), 7.58−7.63 (m, 1 H, *p*-Ph), 7.78−7.82 (m, 2 H, *o*-Ph). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.6 (d), 12.4 (d), 27.3 (u), 29.5 (d), 67.1 (d), 69.5 (d), 119.1 (d), 128.9 (d), 130.1 (d), 132.9 (d), 135.9 (u). − IR (KBr): $\tilde{\nu}$ = 3194 (s, br), 3087 (m), 3060 (m), 3030 (m), 2983 (m), 2960 (m), 2919 (m), 2862 (s), 2800 (m), 1472 (s), 1450 (s), 1399 (w), 1372 (w), 1343 (s), 1313 (m), 1258 (s), 1234 (vs), 1199 (m), 1148 (vs), 1123 (s), 1105 (s), 1085 (s), 1069 (s), 1030 (m), 981 (s), 894 (w), 857 (s), 807 (w), 763 (m), 715 (vs).− MS (EI): *m*/*z* (%) = 209 (42), 208 (14), 161 (14), 158 (61), 155 (41), 154 (21), 138 (15), 131 (12), 126 (16), 125 (79), 107 (100), 106 (24), 97 (18), 96 (11), 78 (43), 77 (22). − MS (CI): *m*/*z* (%) = 268 [M^+ + 1] (100), 210 (10), 157 (18), 156 (92), 113 (15). − $C_{14}H_{21}NO_2S$ (267.4): calcd. C 62.89, H 7.92, N 5.24; found C 62.74, H 7.89, N 5.24.

Reaction of *Z*-**4a** (190 mg, 0.91 mmol) with propanal according to *GP7* led to the same results.

(+)-(*Z*)-(2*R*,3*R*)-3-[(*S*)-*N*-Methyl-*S*-phenylsulfonimidoyl]-hept-4-en-2-ol (*Z*-10e): Reaction of *Z*-**4b** (560 mg, 2.51 mmol) with ethanal according to *GP7*, with the modification that the aldehyde was added at −30 °C, gave crude *Z*-**10e** with ≥96% *ds* (76% cy), containing no γ-isomers. Crystallization (diethyl ether) furnished diastereopure *Z*-**10e** (432 mg, 64%) as colorless crystals; m.p. 153 °C; $[\alpha]_D$ = +232.4 (*c* = 1.06, MeOH). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.47 (t, *J* = 7.4 Hz, 3 H, 7-H), 1.14 (d, *J* = 6.3 Hz, 3 H, 1-H), 1.18 (dqd, *J* = 14.6, *J* = 7.2, *J* = 1.6 Hz, 1 H, 6-H), 1.54 (dqd, *J* = 14.6, *J* = 7.4, *J* = 1.6 Hz, 1 H, 6-H), 2.65 (s, 3 H, N−CH_3), 3.91 (tt, *J* = 11.1, *J* = 9.1 Hz, 1 H, 3-H), 4.55 (dt, *J* = 6.3, *J* = 9.1 Hz, 1 H, 2-H), 5.17 (dd, *J* = 11.0, *J* = 1.6 Hz, 1 H, 4-H), 5.53 (dt, *J* = 11.0, *J* = 7.4 Hz, 1 H, 5-H), 7.02 (br. s, 1 H, OH), 7.50−7.63 (m, 3 H, Ph), 7.80 (m, 2 H, Ph). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.1 (d), 20.5 (u), 21.2 (d), 29.6 (d), 65.6 (d), 68.9 (d), 117.7 (d), 129.2 (d), 130.2 (d), 133.1 (d), 136.1 (u), 140.5 (d). − IR (KBr): $\tilde{\nu}$ = 3160 (s, br), 3054 (m), 3010 (m), 2963 (s), 2938 (s), 2916 (s), 2868 (s), 2798 (m), 1977 (w), 1955 (w), 1908 (w), 1826 (w), 1782 (w), 1658 (w), 1580 (w), 1458 (s), 1444 (s), 1362 (w), 1335 (m), 1264 (m), 1233 (s), 1203 (m), 1147 (s), 1108 (s), 1082 (s), 1058 (s), 1030 (m), 998 (m), 920 (m), 871 (s), 847 (m), 824 (w), 807 (m), 764 (s), 737 (s), 707 (s). − MS: *m*/*z* (%) = 267 [M^+] (1), 237 (29), 222 (16), 159 (21), 156 (41), 155 (27), 154 (14), 145 (17), 138 (5), 126 (8), 125 (45), 117 (24), 115 (9), 107 (76), 106 (38), 105 (100), 97 (14), 91 (18), 78 (40), 77 (54). − $C_{14}H_{21}NO_2S$ (267.3): calcd. C 62.89, H 7.92, N 5.24; found C 62.94, H 8.00, N 5.23.

Reaction of *Z*-**4b** according to *GP7* gave the same result, except that the chemical yield of *Z*-**10e** was only 63%.

(+)-(*Z*)-(3*R*,4*R*)-4-[(*S*)-*N*-Methyl-*S*-phenylsulfonimidoyl]-2-methyloct-5-en-3-ol (*Z*-10f): Reaction of *Z*-**4b** (460 mg, 2.06 mmol) with 2-methylpropanal according to *GP7* gave crude *Z*-**10f** with ≥96 *ds* (98% cy). Crystallization (diethyl ether) afforded diastereopure *Z*-**10f** (551 mg, 91%) as colorless crystals; m.p. 69 °C; $[\alpha]_D$ = +244.5 (*c* = 1.07, CH_2Cl_2). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.44 [t, *J* = 7.5 Hz, 3 H, $CH(CH_3)_2$], 0.76 (d, *J* = 6.6 Hz, 3 H, 1-H), 0.96−1.09 (dqua, *J* = 7.4, *J* = 1.6 Hz, 1 H, 7-H), 1.50−1.63 (dsept, *J* = 7.4, *J* = 1.6 Hz, 1 H, 2-H), 1.68−1.77 [dqua, *J* = 6.9, *J* = 2.0 Hz, 1 H, $CH(CH_3)_2$], 2.64 (s, 3 H, N−CH_3), 4.01 (ddd, *J* = 9.3, *J* = 11.2, *J* = 0.5 Hz, 1 H, 3-H), 4.36 (ddd, *J* = 9.3, *J* = 11.2, *J* = 1.9 Hz, 1 H, 4-H), 5.16 (ddt, *J* = 11.2, *J* = 9.3, *J* = 1.9 Hz, 1 H, 5-H), 5.47 (dt, *J* = 11.0, *J* = 7.4 Hz, 1 H, 6-H), 6.93 (br. s, 1 H, OH), 7.51−7.62 (m, 3 H, Ph), 7.81 (m, 2 H, Ph). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.9 (d), 13.6 (d), 20.1 (d), 20.7 (u), 29.5 (d), 30.8 (d), 66.9 (d), 72.2 (d), 117.0 (d), 128.9 (d), 130.2 (d), 132.9 (d), 135.8 (u), 140.1 (d). − IR (KBr): $\tilde{\nu}$ = 3215 (s, br), 3068 (m), 3051 (m), 3018 (m), 2958 (s), 2932 (s), 2915 (s), 2873 (s), 2811 (m), 1998 (w), 1912 (w), 1788 (w), 1655 (w), 1581 (m), 1463 (s), 1447 (s), 1417 (m), 1405 (m), 1378 (m), 1367 (m), 1357 (m), 1311 (m), 1288 (m), 1241 (s), 1197 (s), 1178 (s), 1146 (s), 1116 (s), 1082 (s), 1024 (s), 998 (s), 932 (m), 856 (s), 832 (m), 758 (m), 722 (s), 689 (s), 631 (s), 617(s). − MS: *m*/*z* (%) = 296 [M^+ + 1] (100), 224 (15), 156 (62), 123 (5). − $C_{16}H_{25}NO_2S$ (295.4): calcd. C 64.99, H 8.53, N 4.74; found C 64.92, H 8.88, N 4.98.

(+)-(*Z*)-(3*R*,4*R*)-2,7-Dimethyl-4-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]oct-5-en-3-ol (*Z*-10i): Reaction of *Z*-**4c** (235 mg, 0.99 mmol) with 2-methylpropanal according to *GP7* gave crude *Z*-**10i** with ≥96 *ds* (92% cy). Chromatography (EtOAc/hexane, 4:1) furnished diastereopure *Z*-**10i** (224 mg, 73%) as colorless crystals; m.p. 102 °C; R_f = 0.64 (EtOAc/hexane, 4:1); $[\alpha]_D$ = +205.4 (*c* = 1.22, MeOH). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.07 (d, *J* = 6.6 Hz, 3 H, CH_3), 0.77 (d, *J* = 6.6 Hz, 3 H, CH_3), 0.82 (d, *J* = 6.6 Hz, 3 H, CH_3), 1.08 (d, *J* = 6.6 Hz, 3 H, CH_3), 1.75 (septd,

J = 6.6, J = 1.7 Hz, 1 H, 2-H), 1.94 (dsept, J = 10.7, J = 6.4 Hz, 1 H, 7-H), 2.59 (s, 3 H, N−CH_3), 4.09 (dd, J = 11.3, J = 9.3 Hz, 1 H, 4-H), 4.35 (dd, J = 9.3, J = 1.9 Hz, 3 H, 3-H), 5.09 (dd, J = 11.3, J = 10.7 Hz, 1 H, 6-H), 5.32 (t, J = 11.3, J = 11.3 Hz, 1 H, 6-H), 7.03 (br. s, 1 H, OH), 7.50−7.63 (m, 3 H, Ph), 7.82 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9 (d), 20.4 (d), 21.4 (d), 22.5 (d), 27.5 (d), 29.5 (d), 30.5 (d), 76.1 (d), 72.8 (d), 115.3 (d), 129.3 (d), 130.4 (d), 133.2 (d), 136.3 (u), 145.4 (d). − IR (KBr): ṽ = 3215 (s, br), 2963 (s), 2931 (s), 2872 (s), 2804 (s), 1947 (w), 1906 (w), 1818 (w), 1655 (w), 1582 (w), 1469 (m), 1449 (s), 1382 (m), 1362 (m), 1315 (w), 1284 (m), 1231 (s), 1201 (s), 1175 (m), 1147 (m), 1111 (m), 1082 (s), 1033 (m), 1024 (m), 1005 (m), 871 (s), 835 (w), 824 (w), 807 (m), 764 (s), 737 (s). − MS: *m*/*z* (%) = 310 [M^+ + 1] (3), 266 (59), 238 (13), 237 (78), 236 (25), 222 (54), 158 (14), 157 (31), 156 (98), 155 (81), 154 (68), 140 (14), 139 (17), 138 (62), 137 (94), 127 (15), 126 (39), 125 (100), 112 (16), 111 (37), 110 (15), 109 (30), 108 (36), 107 (98), 106 (66), 105 (20), 97 (77), 95 (65), 94 (16), 83 (19), 82 (31), 81 (52), 79 (33), 78 (93), 77 (91), 73 (15), 71 (88). − $C_{17}H_{27}NO_2S$ (309.4): calcd. C 65.98, H 8.79, N 4.53; found C 66.23, H 8.76, N 4.30.

(+)-(*Z*)-(1*R*,2*R*)-5-Methyl-2-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]-1-phenylhex-3-en-1-ol (*Z*-10j): Reaction of *Z*-**4c** (247 mg, 1.04 mmol) with benzaldehyde according to *GP7* afforded crude *Z*-**10j** with ≥96% *ds* (90% cy). Chromatography (EtOAc/hexane, 4:1) gave diastereopure *Z*-**10j** (210 mg, 73%) as colorless crystals; m.p. 131 °C; R_f = 0.62 (EtOAc/hexane, 4:1); $[\alpha]_D$ = +70.4 (*c* = 1.07, MeOH). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.10 (d, J = 6.4 Hz, 3 H, CH_3), 0.10 (d, J = 6.4 Hz, 3 H, CH_3), 1.56 (dsept, J = 10.1, J = 6.4 Hz, 1 H, 5-H), 2.70 (s, 3 H, N−CH_3), 4.18 (dd, J = 10.8, J = 9.2 Hz, 1 H, 2-H), 4.94 (dd, J = 11.1, J = 10.1 Hz, 1 H, 4-H), 5.05 (dd, J = 11.4, J = 11.1 Hz, 1 H, 3-H), 5.37 (d, J = 9.1 Hz, 1 H, 1-H), 7.14−7.30 (m, 3 H, Ph), 7.31−7.36 (m, 2 H, Ph), 7.50−7.61 (m, 3 H, Ph), 7.64 (br. s, 1 H, OH), 7.81−7.87 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2 (d), 21.7 (d), 27.0 (d), 29.7 (d), 68.7 (d), 73.2 (d), 115.2 (d), 127.4 (d), 128.0 (d), 128.1 (d), 129.2 (d), 130.3 (d), 133.3 (d), 136.3 (u), 140.7 (u), 145.5 (d). − IR (KBr): ṽ = 3162 (s, br), 3057 (m), 3037 (m), 3017 (m), 2957 (s), 2934 (s), 2916 (s), 2867 (s), 2798 (m), 1977 (w), 1910 (w), 1826 (w), 1657 (w), 1581 (w), 1456 (s), 1444 (s), 1335 (m), 1234 (s), 1204 (m), 1148 (s), 1106 (s), 1083 (s), 1058 (m), 1034 (m), 1025 (m), 920 (m), 870 (s), 847 (m), 825 (m), 808 (m), 765 (s), 733 (s), 708 (m). − MS: *m*/*z* (%) = 343 [M^+] (< 1), 237 (34), 222 (22), 171 (21), 159 (10), 157 (15), 156 (78), 155 (46), 154 (24), 138 (12), 129 (23), 128 (12), 126 (15), 125 (70), 117 (20), 115 (16), 109 (11), 107 (100), 106 (57), 105 (99), 97 (26), 91 (38), 79 (26), 78 (75), 77 (95). − $C_{20}H_{25}NO_2S$ (343.4): calcd. C 69.94, H 7.34, N 4.08; found C 69.57, H 7.36, N 3.82.

(+)-(3*R*,4*R*)-2,6-Dimethyl-4-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]hept-5-en-3-ol (17a): Reaction of **6a** (1.01 g, 4.52 mmol) with 2-methylpropanal according to *GP7* gave crude **17a** with ≥96% *ds* (92% cy). Crystallization (diethyl ether) afforded diastereopure **17a** (997 mg, 75%) as colorless crystals; m.p. 87 °C; $[\alpha]_D$ = +124.4 (*c* = 1.11, acetone). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.73 (d, J = 6.7 Hz, 3 H, CH_3), 0.80 (d, J = 1.4 Hz, 3 H, CH_3), 1.06 (d, J = 7.0 Hz, 3 H, CH_3), 1.58 (d, J = 1.3 Hz, 3 H, CH_3), 1.70 (septd, J = 6.7, J = 1.7 Hz, 1 H, 2-H), 2.67 (s, 3 H, N−CH_3), 3.84 (dd, J = 11.4, J = 9.4 Hz, 1 H, 4-H), 4.33 (dd, J = 9.1, J = 2.0 Hz, 1 H, 3-H), 4.94 (dt, J = 11.4, J = 1.3 Hz, 1 H, 5-H), 6.90 (br. s, 1 H, OH), 7.48−7.63 (m, 3 H, Ph), 7.74−7.79 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8 (d), 17.3 (d), 20.1 (d), 25.7 (d), 29.6 (d), 30.9 (d), 68.3 (d), 72.4 (d), 113.4 (d), 129.0 (d), 130.4 (d), 133.0 (d), 136.4 (u), 141.9 (u). − IR (KBr): ṽ = 3235 (s, br), 3062 (m), 2968 (s), 2931 (s), 2872 (s), 2806 (m), 2090 (w), 1966 (w), 1907 (w), 1816 (w), 1777 (w), 1711 (w), 1669 (m), 1609 (w), 1583 (w), 1445 (s), 1383 (s), 1366 (s), 1305 (m), 1282 (m), 1238 (s), 1150 (s), 999 (s), 976 (s), 922 (m), 861 (m), 753 (s). − MS: *m*/*z* (%) = 295 [M^+] (< 1), 171 (1), 155 (4), 125 (17), 107 (38), 97 (21), 78 (14), 77 (18), 74 (67), 73 (18), 71 (11). − $C_{17}H_{27}NO_2S$ (295.4): calcd. C 65.05, H 8.53, N 4.74; found C 64.81, H 8.54, N 4.68.

(−)-(3*R*,4*R*)-4-[(*S*)-*N*-Methyl-*S*-phenylsulfonimidoyl]-6,6-diphenylhex-5-en-3-ol (17b): Reaction of **6b** (839 mg, 2.30 mmol) with propanal according to *GP7* afforded a mixture of **17b** and *epi*-**17b** (87% cy) in a ratio of 9:1, recovered **6b**, and *N*-methyl-*S*-phenylsulfinamide. Crystallization (diethyl ether) gave **17b** (526 mg, 56%) as colorless crystals; m.p. 116 °C; $[\alpha]_D$ = −109.7 (*c* = 1.12, acetone). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06 (t, J = 7.4 Hz, 3 H, 1-H), 1.52 (ddq, J = 13.4, J = 10.2, J = 7.4 Hz, 1 H, 2-H), 1.72 (ddq, J = 13.4, J = 7.4, J = 2.3 Hz, 1 H, 2-H), 2.57 (s, 3 H, N−CH_3), 3.91 (dd, J = 11.4, J = 9.1 Hz, 1 H, 4-H), 4.46 (ddd, J = 10.1, J = 9.1, J = 2.4 Hz, 1 H, 3-H), 5.92 (d, J = 11.4 Hz, 1 H, 5-H), 6.23 (br. d, J = 7.1 Hz, 2 H, Ph), 7.02−7.30 (m, 7 H, Ph), 7.38−7.46 (m, 3 H, Ph), 7.57−7.64 (m, 3 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.6 (d), 28.7 (u), 29.5 (d), 69.8 (d), 70.8 (d), 117.1 (d), 127.4 (d), 127.4 (d), 128.1 (d), 128.2 (d), 128.3 (d), 129.0 (d), 129.3 (d), 130.3 (d), 133.0 (d), 136.3 (u), 137.5 (u), 141.0 (u), 149.2 (u). − IR (KBr): ṽ = 3201 (s, br), 3053 (w), 2963 (m), 2923 (m), 2872 (m), 2810 (w), 2084 (w), 1966 (w), 1818 (w), 1627 (w), 1599 (w), 1578 (w), 1471 (m), 1445 (m), 1344 (m), 1262 (s), 1234 (s), 1178 (m), 1142 (s), 1107 (s), 1024 (s), 982 (m), 876 (m), 858 (m), 802 (s), 771 (m), 744 (m), 703 (m). − MS: *m*/*z* (%) = 405 [M^+] (< 1), 347 (2), 251 (22), 250 (22), 233 (20), 221 (16), 205 (20), 194 (12), 193 (100), 191 (32), 189 (14), 178 (26), 165 (18), 125 (21), 115 (56), 107 (39), 97 (12), 91 (21), 78 (12), 77 (19). − $C_{25}H_{27}NO_2S$ (405.5): calcd. C 74.04, H 6.71, N 3.45; found C 73.91, H 6.70, N 3.35.

General Procedure for α-Hydroxyalkylation of the Allylic Sulfoximine 15 (*GP8*): To a solution of **15** (1.0 mmol) in Et_2O (10 mL) at −78 °C was added *n*BuLi (0.68 mL, 1.6 M solution in hexane, 1.1 mmol). After stirring for 10 min at −78 °C, $ClTi(NEt_2)_3$ (1.25 mmol), either neat or in Et_2O (2 mL), was added. The resulting mixture was stirred for 10 min at −78 °C, allowed to warm to room temperature, and stirred for 2 h. It was then cooled to −78 °C once more, whereupon the aldehyde (2 mmol) was added dropwise and stirring was continued for 2 h at −78 °C. The mixture was then poured into aqueous $NaHCO_3$ solution and extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo.

(1*R*,2*R*)-1-(Cyclohex-1-enyl)-1-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]propan-2-ol (18a): Reaction of **15** (298 mg, 1.20 mmol) with acetaldehyde according to *GP8* furnished a mixture of recovered **15** (5%), **18a** (69% cy, 95% *ds*) along with a diastereomer, and **16a** (26% cy, ≥96% *ds*).

18a: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12 (d, J = 3.6 Hz, 3 H, CH_3), 1.27−1.48 (m, 3 H, CH_2), 1.59−1.70 (m, 1 H, CH_2), 1.72−1.89 (m, 2 H, CH_2), 2.00−2.07 (m, 1 H, CH_2), 2.54 (s, 3 H, N−CH_3), 3.38 (br. d, J = 9.4 Hz, 1 H, CHS), 4.61 (dq, J = 9.4, J = 6.4 Hz, 1 H, C*H*OH), 6.23 (s, 1 H, OH), 7.42−7.57 (m, 3 H, *m*-, *p*-Ph), 7.68−7.76 (m, 2 H, *o*-Ph). − ^{13}C NMR (100 MHz, [D_8]THF): δ = 22.0 (d), 22.9 (u), 23.8 (u), 26.6 (u), 29.8 (d), 66.3 (d), 78.9 (d), 127.4 (u), 130.3 (u), 130.5 (d), 131.3 (u), 133.9 (d), 138.2 (u).

16a: ^{1}H NMR (400 MHz, $CDCl_3$, only those signals which could be unequivocally identified are given): δ = 1.26 (d, J = 4.0 Hz, 3 H, CH_3), 2.52 (s, 3 H, NCH_3), 3.59 (m, 1 H, C*H*OH), 3.87 (m, 1

H, CH), 6.23 (d, J = 1.7 Hz, 1 H, α-H). − ^{13}C NMR (100 MHz, [D$_8$]THF): δ = 46.8 (d), 161.3 (u).

(1*R*,2*R*)-1-(Cyclohex-1-enyl)-1-[(*S*)-methyl-*S*-phenylsulfonimidoyl]butan-2-ol (18b): Reaction of **15** (500 mg, 2.01 mmol) with propanal according to *GP8* furnished a mixture of recovered **15** (2%), **18b** (91% cy, ≥96% *ds*), and **16b** (7% cy, ≥96% *ds*).

23: ^{1}H NMR (400 MHz, [D$_8$]THF): δ = 0.94 (t, J = 7.2 Hz, 3 H, CH$_3$), 1.07−1.58 (m, 6 H, CH$_2$, CH$_2$CH$_3$), 1.69−1.76 (m, 1 H, CH$_2$), 1.81−1.91 (m, 2 H, CH$_2$, CH$_2$CH$_3$), 2.22−2.31 (br. s, 1 H, CH$_2$), 2.54 (s, 3 H, N−CH$_3$), 3.58 (br. s, 1 H, CHS), 4.34 (td, J = 9.0, J = 2.8 Hz, 1 H, C*H*OH), 5.20−5.42 (br. s, 1 H, =CH), 6.46 (br. s, 1 H, OH), 7.53−7.65 (m, 3 H, *m*-, *p*-Ph), 7.77−7.81 (m, 2 H, *o*-Ph). − ^{13}C NMR (100 MHz, CDCl$_3$): δ = 9.4 (d), 21.7 (u), 22.6 (u), 25.7 (u), 27.6 (u), 29.6 (d), 68.5 (d, br), 77.2 (d), 128.2 (u), 128.9 (d), 129.7 (d), 129.9 (d), 132.8 (d), 136.3 (u).

(+)-(1*R*,2*R*)-1-(Cyclohex-1-enyl)-1-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]-3-methylbutan-2-ol (18c): Reaction of **15** (199 mg, 0.80 mmol) with 2-methylpropanal according to *GP8* furnished a mixture of recovered **15** (9%), **18c** (87% cy, ≥96% *ds*), and **16c** (4% cy, ≥96% *ds*). Crystallization (diethyl ether) gave diastereopure **18c** (148 mg, 57%) as yellow crystals; m.p. 87 °C; [α]$_D$ = +31.4 (c = 0.96, diethyl ether). − ^{1}H NMR (300 MHz, [D$_8$]THF, 25 °C): δ = 0.79 (d, J = 6.7 Hz, 3 H, CH$_3$), 1.02 (d, J = 7.1 Hz, 3 H, CH$_3$), 1.31−1.91 (m, 9 H, CH$_2$), 2.54 (s, 3 H, N−CH$_3$), 3.63 (br. d, J = 10.1 Hz, 1 H, CHS), 4.34 (br. d, J = 9.4 Hz, 1 H, C*H*OH), 5.10 (br. s, 1 H, =CH), 6.37 (br. s, 1 H, OH), 7.53−7.66 (m, 3 H, Ph), 7.77−7.83 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, [D$_8$]THF, 25 °C): δ = 13.5 (d), 20.0 (d), 21.6 (u), 22.6 (u), 25.4 (u), 28.7 (d), 30.6 (d), 70.5 (d, br), 74.9 (d, br), 128.6 (u), 128.9 (d), 130.1 (d), 132.7 (d, br), 137.0 (u). − MS (CI): *m*/*z* (%) = 324 (8), 323 (22), 322 [M$^+$ + 1] (100), 311 (9), 304 (6), 280 (7), 167 (5), 157 (5), 156 (57), 151 (12), 150 (7), 149 (37), 124 (24). − C$_{18}$H$_{27}$NO$_2$S (321.4): calcd. C 67.25, H 8.47, N 4.36; found C 66.96, H 8.26, N 4.29. − **18cA:** ^{1}H NMR (500 MHz, [D$_8$]THF, −60 °C): δ = 0.76 (d, J = 6.4 Hz, 3 H, CH$_3$*a*), 1.01 (d, J = 7.0 Hz, 3 H, CH$_3$*e*), 1.21−1.38 (m, 2 H, CH$_2$), 1.39−1.51 (m, 3 H, CH$_2$), 1.58 (m, 1 H, CH$_2$), 1.75−1.83 (m, 2 H, CH$_2$), 2.50 (s, 3 H, NCH$_3$), 2.55−2.61 (m, 1 H, CH$_2$), 3.72 (d, J = 10.1 Hz, 1 H, α-H), 4.37 (dd, J = 10.1, J = 0.9 Hz, 1 H, C*H*OH), 4.95 (br. s, 1 H, =CH), 6.52 (d, J = 0.9 Hz, 1 H, OH), 7.59−7.72 (m, 3 H, *m*-, *p*-Ph), 7.79−7.85 (m, 2 H, *o*-Ph). − ^{13}C NMR (125 MHz, [D$_8$]THF, −60 °C): δ = 14.0 (d), 20.7 (d), 22.4 (u), 23.2 (u), 25.0 (u), 26.2 (u), 29.7 (d), 31.5 (d), 70.4 (d), 76.5 (d), 129.2 (u), 129.7 (d), 130.7 (d), 133.2 (d), 133.8 (d), 136.4 (u). − **18cB:** ^{1}H NMR (500 MHz, [D$_8$]THF, −60 °C): δ = 0.61 (br. d, J = 17.4 Hz, 1 H, CH$_2$), 0.78 (d, J = 7.0 Hz, 3 H, CH$_3$*a*), 0.89 (m, 1 H, CH$_2$), 0.96 (d, J = 6.7 Hz, 3 H, CH$_3$*e*), 1.21−1.38 (m, 1 H, CH$_2$), 1.39−1.51 (m, 1 H, CH$_2$), 1.68 (m, 1 H, CH$_2$), 1.88 (m, 1 H, CH$_2$), 2.01 (br. s, 2 H, CH$_2$), 2.51 (s, 3 H, NCH$_3$), 3.62 (d, J = 10.0 Hz, 1 H, α-H), 4.22 (dd, J = 10.0, J = 1.2 Hz, 1 H, C*H*OH), 5.96 (br. s, 1 H, =CH), 6.43 (br. s, 1 H, OH). − ^{13}C NMR (125 MHz, [D$_8$]THF, −60 °C): δ = 14.9 (d), 20.9 (d), 22.1 (d), 23.2 (u), 25.2 (u), 25.9 (u), 29.5 (d), 30.8 (d), 31.9 (u), 72.4 (d), 74.1 (d), 128.3 (u), 129.8 (d), 131.4 (d), 132.0 (d), 134.0 (d), 137.0 (u).

(1*R*,2*R*)-2-(Cyclohex-1-enyl)-2-[(*S*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]-1-phenylethanol (18d): Reaction of **15** (1.2 g, 4.80 mmol) with benzaldehyde (867 mg, 8.16 mmol) according to *GP8* furnished a mixture of recovered **15** (5%) and **18d** (95% cy, ≥97% *ds*). Formation of **16d** was not observed. Crystallization (diethyl ether) gave diastereopure **18d** (1.1 g, 66%) as colorless crystals; m.p. 115 °C; [α]$_D$ = −22.8 (c = 0.25, CH$_2$Cl$_2$). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.21−2.19 (m, 8 H, CH$_2$), 2.71 (s, 3 H, N−CH$_3$), 3.77 (br. d, J = 8.7 Hz, 1 H, CHS), 5.46 (br. d, J = 9.7 Hz, 1 H, C*H*OH), 7.48−7.72 (m, 5 H, Ph), 7.78−7.84 (m, 3 H, *m*-, *p*-Ph), 7.86−7.95 (m, 2 H, *o*-Ph). − ^{13}C NMR (100 MHz, CDCl$_3$): δ = 21.3 (u), 22.3 (u), 25.4 (u), 29.6 (d), 71.6 (d, br), 73.6 (d, br), 127.9 (u), 129.0 (u), 133.1 (u), 136.7 (u), 140.6 (u). − MS (CI): *m*/*z* (%) = 355 [M$^+$] (0.06), 249 (14), 248 (14), 230 (21), 200 (11), 183 (20), 171 (11), 169 (14), 156 (47), 155 (19), 141 (21), 129 (17), 125 (33), 107 (56), 106 (18), 105 (100), 91 (40), 81 (15), 79 (23), 78 (41), 77 (54), 51 (14). − C$_{21}$H$_{25}$NO$_2$S (355.5): calcd. C 70.96, H 7.03, N 3.94, found C 70.87, H 6.86, N 3.78.

(±)-(*OC*-6−32-*AC*,*SR*$_C$,*RS*$_S$)-Bis[3,3-diphenyl-1-(*N*-methyl-*S*-phenylsulfonimidoyl)-2-propenyl]bis(isopropyloxy)titanium Diethyl Ether (*rac*-γ,γ-20a·Et$_2$O): To a solution of *rac*-**8b** (1.05 g, 3.03 mmol) in diethyl ether (30 mL) at −78 °C was added *n*BuLi (2.09 mL, 1.60 M solution in hexane, 3.34 mmol). After stirring for 10 min, the mixture was treated with ClTi(O*i*Pr)$_3$ (0.83 mL, 3.47 mmol), stirred for a further 10 min at −78 °C, and thereafter for 4 h at room temperature. The LiCl deposited was filtered off under argon and the filtrate was concentrated in vacuo to give a mixture of *rac*-γ,γ-**20a**, *rac*-γ,γ-**20b**, and Ti(O*i*Pr)$_4$ in a molar ratio of 2:1:1. This mixture was redissolved in diethyl ether/hexane (10 mL, 1:1) and the resulting solution was kept at −80 °C for 24 h. The mother liquor was then decanted off and the orange solid that had separated was redissolved in diethyl ether (5 mL). This solution was kept at 5 °C for 24 h. Decantation of the mother liquor and washing of the solid with diethyl ether afforded *rac*-γ,γ-**20a**·Et$_2$O (345 mg, 25%) as orange-red, hexagonal-prismatic crystals. − ^{1}H NMR (500 MHz, [D$_8$]THF, 25 °C): δ = 1.13 (t, J = 7.0 Hz, 6 H, Et$_2$O), 1.28 (br. s, 6 H, 5-H), 1.42 (d, J = 6.1 Hz, 6 H, 6-H), 2.81 (s, 6 H, N−CH$_3$), 3.41 (q, J = 7.0 Hz, 4 H, Et$_2$O), 3.87 (d, J = 11.9 Hz, 2 H, 1-H), 4.96 (sept, J = 6.1 Hz, 2 H, 4-H), 6.63 (m, 4 H, *o*-Ph$_Z$), 6.67 (d, J = 11.9 Hz, 2-H), 6.96 (m, 6 H, *o*-, *p*-Ph$_Z$), 7.14 (m, 6 H, *o*-, *p*-Ph$_E$), 7.21 (m, 4 H, *m*-Ph$_E$), 7.4 (br. m, 4 H, *m*-Ph$_S$), 7.52 (m, 2 H, *p*-Ph$_S$), 7.73 (d, J = 7.6 Hz, 4 H, *o*-Ph$_S$). − ^{1}H NMR (500 MHz, [D$_8$]THF, −70 °C): δ = 1.13 (t, J = 7.0 Hz, 6 H, Et$_2$O), 1.20 (d, J = 4.9 Hz, 3 H, 6-H$_B$), 1.49 (d, J = 5.4 Hz, 3 H, 5-H$_B$), 1.59 (d, J = 4.0 Hz, 4 H, 5-H$_A$, 6-H$_A$), 2.78 (s, 6 H, N−CH$_{3A}$), 2.89 (s, 6 H, N−CH$_{3B}$), 3.35 (q, J = 7.0 Hz, 4 H, Et$_2$O), 3.75 (d, J = 11.9 Hz, 1 H, 1-H$_B$), 4.30 (d, J = 11.9 Hz, 1 H, 1-H$_A$), 5.04 (sept, J = 5.8 Hz, 1 H, 4-H$_A$), 5.17 (sept, J = 5.7 Hz, 1 H, 4-H$_B$), 6.54 (m, 2 H, *o*-Ph$_{ZB}$), 6.61 (d, J = 11.9 Hz, 1 H, 2-H$_B$), 6.66 (d, J = 6.2 Hz, 2 H, *o*-Ph$_{ZA}$), 6.74 (d, J = 11.9 Hz, 1 H, 2-H$_A$), 6.79 (m, 3 H, *p*-, *m*-Ph$_{ZB}$), 6.86 (m, 2 H, *m*-Ph$_{SB}$), 6.97 (m, 3 H, *p*-, *m*-Ph$_{ZA}$), 7.13 (d, J = 7.3 Hz, 2 H, *o*-Ph$_{EB}$), 7.19 (d, J = 7.3 Hz, 2 H, *o*-Ph$_{EA}$), 7.25 (m, 3 H, *m*-, *p*-Ph$_{EB}$), 7.31 (t, J = 7.3 Hz, 1 H, *p*-Ph$_{EA}$), 7.39 (t, J = 7.3 Hz, 2 H, *m*-Ph$_{EA}$), 7.45 (t, J = 7.3 Hz, 1 H, *p*-Ph$_{SB}$), 7.52−7.58 (m, 3 H, *m*-, *p*-Ph$_{SA}$), 7.65 (d, J = 7.6 Hz, 2 H, *o*-Ph$_{SB}$), 7.70 (d, J = 6.7 Hz, 2 H, *o*-Ph$_{SA}$). − ^{13}C NMR (125 MHz, [D$_8$]THF, 25 °C): δ = 16.0 (d, Et$_2$O), 27.2 (d, $J_{C,H}$ = 124 Hz, C-5, C-6), 27.3 (d, $J_{C,H}$ = 125 Hz, C-5, C-6), 32.4 (br. d, $J_{C,H}$ = 137 Hz, N−CH$_3$), 63.0 (br. s, $J_{C,H}$ = 144 Hz, C-1), 66.6 (u, Et$_2$O), 79.9 (d, $J_{C,H}$ = 143 Hz, C-4), 126.9 (d, $J_{C,H}$ = 160 Hz, *p*-Ph$_E$), 127.1 (d, $J_{C,H}$ = 156 Hz, C-2), 127.3 (d, $J_{C,H}$ = 156 Hz, *p*-Ph$_Z$), 128.5 (d, $J_{C,H}$ = 160 Hz, *o*-P$_E$), 128.8 (d, $J_{C,H}$ = 166 Hz, *o*-Ph$_S$), 129.0 (d, $J_{C,H}$ = 159 Hz, *m*-Ph$_E$), 129.3 (d, *m*-Ph$_Z$), 130.5 (d, $J_{C,H}$ = 155 Hz, *m*-Ph$_S$), 131.5 (d, *o*-Ph$_Z$), 133.3 (d, $J_{C,H}$ = 158 Hz, *p*-Ph$_S$), 136.5 (br. s, C-3), 141.4 (u, *i*-Ph$_Z$), 141.7 (u, *i*-Ph$_S$), 144.9 (u, *i*-Ph$_E$). − ^{13}C NMR (125 MHz, [D$_8$]THF, −70 °C): δ = 16.2 (d, Et$_2$O), 26.1 (d, C-6$_B$), 26.8 (d), 27.0 (d, C-5, C-6$_A$), 27.2 (d, C-5$_B$), 31.7 (d, $J_{C,H}$ = 138 Hz, N−CH$_{3B}$), 33.8 (d, $J_{C,H}$ = 138 Hz, N−CH$_{3A}$), 55.7 (d, $J_{C,H}$ = 147 Hz, C-1$_A$), 66.9 (u, Et$_2$O), 68.4 (d, $J_{C,H}$ = 142 Hz, C-1$_B$), 79.4 (d, $J_{C,H}$ = 133 Hz, C-4$_B$), 81.2 (d, $J_{C,H}$ = 136 Hz, C-4$_A$), 126.2 (d, *m*-Ph$_{ZA}$), 126.8 (d), 126.9 (d, C-2$_B$, *p*-Ph$_{EA}$), 127.6 (d, C-2$_A$), 127.9 (d, *o*-Ph$_{EA}$), 128.1 (d), 128.2 (d,

o-Ph_{SA}, *o*-Ph_{EB}), 128.9 (d, *p*-Ph_{ZA}), 129.1 (d, *o*-Ph_{SB}), 129.3 (d, *m*-Ph_{EB}), 129.4 (d, *m*-Ph_{EA}), 129.6 (d, *m*, *p*-Ph_{ZB}), 130.5 (d, *p*-Ph_{EB}), 130.7 (d, *o*-Ph_{ZA}), 130.9 (d, *m*-Ph_{SA}), 131.1 (d, *o*-Ph_{ZB}), 131.4 (d, *m*-Ph_{SA}), 131.8 (u, C-3), 133.5 (d, *p*-Ph_{SB}), 133.9 (d, *p*-Ph_{SA}), 138.9 (u, C-3), 139.9 (u), 140.5 (u), 140.8 (u), 141.3 (u, *i*-Ph_Z, *i*-Ph_S), 145.0 (u), 145.5 (u, *i*-Ph_E). − MS (direct inlet): *m*/*z* (%) = 859 [M^+ − Et_2O] (< 1), 572 (2), 384 (12), 363 (10), 346 (5), 285 (8), 269 (53), 224 (13), 223 (10), 222 (20), 221 (28), 220 (100), 218 (38), 204 (14), 194 (12), 193 (56), 191 (23), 164 (16), 139 (47), 125 (19), 115 (23), 110 (11), 109 (55), 107 (25), 97 (13), 91 (10), 78 (11), 77 (26). − $C_{54}H_{64}N_2O_5S_2Ti$ (933.1): calcd. C 69.51, H 6.97, N 3.00; found (V_2O_5) C 69.71, H 6.93, N 3.14.

rac-**22:** ^{1}H NMR (300 MHz, [D_8]THF, 25 °C): δ = 1.19 (d, *J* = 6.6 Hz, 12 H, 5-H, 6-H), 2.81 (s, 6 H, NCH_3), 3.87 (d, *J* = 12.6 Hz, 2 H, 1-H), 4.66 (sept, *J* = 6.1 Hz, 2 H, 7-H), 6.52 (br. s, 1 H, 2-H), 6.95−7.30 (m, 20 H, *o*-, *m*-, *p*-Ph), 7.50−7.65 (m, 6 H, *m*-, *p*-Ph), 7.87 (br. d, *J* = 7.4 Hz, 2 H, *o*-Ph).

(+)- and (±)-(3*S*,4*R*)-4-[(*S*)-*N*-Methyl-*S*-phenylsulfonimidoyl]-6,6-diphenylhex-5-en-3-ol (*epi*-17b and *rac-epi*-17b): Starting from rac-γ,γ-20a·Et_2O: To a solution of crystalline *rac*-γ,γ-**20a**·Et_2O (325 mg, 0.35 mmol) in THF (8 mL) at −78 °C was added propanal (0.10 mL, 0.70 mmol). After stirring for 1 h at −78 °C, the mixture was poured into saturated aqueous $(NH_4)_2CO_3$ solution and extracted with diethyl ether. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo to give a mixture of *rac-epi*-**17b** and *rac*-**17b** (67% cy) in a ratio of 68:32, *rac*-**6b** (28% cy), and *N*-methyl-*S*-phenylsulfinamide (5% cy). Treatment of *rac*-γ,γ-**20a**·Et_2O (224 mg, 0.26 mmol) with propanal according to the above procedure but allowing the reaction mixture to warm to room temperature over a period of 13 h after addition of the aldehyde gave a mixture of *rac-epi*-**17b** and *rac*-**17b** (79% cy) in a ratio of 69:31, *rac*-**6b** (19% cy), and *N*-methyl-*S*-phenylsulfinamide (2% cy).

Starting from 6b: Reaction of **6b** (839 mg, 2.30 mmol) with propanal according to *GP2* gave a mixture of *epi*-**17b** and **17b** (52% cy) in a ratio of 69:31, recovered **6b** (33%), and *N*-methyl-*S*-phenylsulfinamide (15% cy). Crystallization (diethyl ether) afforded diastereopure *epi*-**17b** (154 mg, 38%) as colorless needles; m.p. 111 °C; $[\alpha]_D$ = +2.0 (*c* = 1.20, CH_2Cl_2); $[\alpha]_D$ = +4.6 (*c* = 1.30, MeOH). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.73 (t, *J* = 7.4 Hz, 3 H, CH_3), 1.27 (m, 1 H, 2-H), 1.67 (ddq, *J* = 13.8, *J* = 8.7, *J* = 7.4 Hz, 1 H, 2-H), 2.72 (s, 3 H, N−CH_3), 3.67 (dd, *J* = 11.1, *J* = 1.7 Hz, 1 H, 4-H), 3.83 (dddd, *J* = 8.7, *J* = 4.7, *J* = 2.0, *J* = 1.5 Hz, 1 H, 3-H), 6.16 (d, *J* = 2.0 Hz, 1 H, OH), 6.46 (d, *J* = 11.1 Hz, 1 H, 5-H), 7.10 (m, 2 H, Ph), 7.25−7.36 (m, 8 H, Ph), 7.50 (m, 2 H, Ph), 7.58 (m, 1 H, Ph), 7.72 (m, 2 H, Ph). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.2 (d), 27.5 (u), 29.2 (d), 68.9 (d), 71.7 (d), 114.7 (d), 127.6 (d), 128.2 (d), 128.2 (d), 129.4 (d), 129.6 (d), 129.7 (d), 133.1 (d), 137.7 (u), 138.7 (u), 141.1 (u), 151.3 (u). − IR (KBr): $\tilde{\nu}$ = 3224 (s), 3081 (w), 3059 (w), 2964 (m), 2924 (m), 2873 (m), 2854 (m), 2815 (m), 1624 (w), 1598 (w), 1579 (w), 1493 (m), 1466 (m), 1445 (s), 1385 (w), 1339 (m), 1287 (m), 1245 (s), 1226 (s), 1150 (s), 1111 (s), 1081 (s), 1045 (m), 1029 (m), 996 (m), 946 (m), 886 (m), 866 (m), 789 (m), 770 (s), 742 (s), 713 (s). − MS: *m*/*z* (%) = 405 [M^+] (< 1), 250 (19), 221 (17), 194 (12), 193 (100), 191 (23), 189 (11), 178 (26), 165 (17), 155 (6), 149 (8), 143 (8), 128 (6), 125 (26), 115 (84), 107 (57), 105 (9), 97 (21), 91 (38), 89 (7), 78 (19), 77 (33). − $C_{25}H_{27}NO_2S$ (405.5): calcd. C 74.04, H 6.71, N 3.45; found C 73.81, H 6.91, N 3.35.

Starting from *rac*-6b: Reaction of *rac*-**6b** with propanal according to *GP2* gave a mixture of *rac-epi*-**17b** and *rac*-**17b** (51% cy) in a ratio of 69:31.

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[68] [68a] For a better comparison, the C atom of **7**, **8**, **9**, **12**, **14**, and **16** bearing the hydroxy group is designated as α and that bearing the sulfonimidoyl group as δ. − [68b] For a better comparison, the C atom of **10**, **17**, and **18** bearing the hydroxy group is designated as α and that bearing the sulfonimidoyl group as β.
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[94] It seems interesting that in approximately half of the reported hydroxyalkylations of titanium complexes derived from Li-**XIII**, the yields of the γ-hydroxyalkylation products have been only in the range 44−57% (see refs.[11,12]). We have found that such yields are typical for the reactions of the bis(2-alkenyl)titanium complexes *E*-**20** with aldehydes at low temperatures in the absence of $ClTi(OiPr)_3$.
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Note Added in Proof (October 10, 2000): X-ray crystal structure analyses of **18c** and **18d** not only confirmed the configurations shown in Scheme 12 but revealed also hydrogen bond stabilized conformations of type (B) depicted in Figure 7.

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