Asymmetric Synthesis of Protected β-Substituted and β,β-Disubstituted β-Amino Acids Bearing Branched Hydroxyalkyl Side Chains and of Protected 1,3-Amino Alcohols with Three Contiguous Stereogenic Centers from Allylic Sulfoximines and Aldehydes

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We describe a new method for the asymmetric synthesis, from allylic sulfoximines and aldehydes, of *N*,*O*-protected, cyclic and acyclic, β-substituted and β,β-disubstituted δ-hydroxy-β-amino acids and of *N*,*O*-protected 1,3-amino alcohols, both possessing three contiguous stereogenic centers. Treatment of enantiomerically pure, acyclic allylic sulfoximines with aldehydes after successive lithiation and titanation afforded sulfonimidoyl-substituted homoallylic alcohols with high regio- and diastereoselectivities. Diastereomerically pure, cyclic, sulfonimidoyl-substituted homoallylic alcohols were synthesized in a similar manner from the corresponding enantiomerically pure, cyclic allylic sulfoximines and isobutyraldehyde. A highly diastereoselective amination of the sulfonimidoyl-substituted homoallylic alcohols with the generation of secondary and tertiary C atoms and formation of the sulfonimidoyl-substituted, protected 1,3-amino alcohols (oxazinones) was achieved by the carbamate method, through cyclization of the corresponding carbamates after their lithiation with *n*BuLi. The sulfonimidoyl-substituted, monocyclic and bicyclic oxazinones were converted into protected, acyclic and cyclic, β-substituted and β,β-disubstituted β-amino acids and protected 1,3-amino alcohols by two different routes: the carbanion route and the substitution route. The carbanion route involves: (1) a double lithiation of the protected β-amino sulfoximines, (2) treatment of the dilithiated sulfoximines with electrophiles, and (3) reductive removal of the sulfonimidoyl group. By the carbanion route, double lithiation of the sulfonimidoyl-substituted oxazinones with *n*BuLi gave the corresponding dilithium salts, which reacted readily with a number of electrophiles to give the corresponding α-substituted sulfoximines in good yields. Reduction of the sulfoximines with Raney nickel afforded the corresponding protected monocyclic and bicyclic 1,3-amino alcohols and the protected acyclic and cyclic β-amino acids in good yields. The substitution route involves: (1) a facile substitution of the sulfonimidoyl group by a Cl atom, and (2) a substitution of the Cl atom of the protected β-amino chlorides by a cyano group. Treatment of the sulfoximines with $ClCO_2Me$ readily afforded the corresponding β-amino chlorides in good yields, and so treatment of alkyl sulfoximines with chloroformates seems to be a general method for the replacement of an *N*-methylsulfonimidoyl group by a Cl atom. Introduction of a cyano group was achieved through treatment of chlorides with NaCN, which gave the corresponding β-amino nitriles in good yields. Finally, hydrolysis of the nitriles afforded the protected acyclic and cyclic, β-substituted and β,β-disubstituted β-amino acids. Treatment of the protected β-amino sulfoximines with $ClCO_2Me$ gave – besides the corresponding chlorides – methyl (*S*)-*N*-phenylsulfinylcarbamate with ≥ 99% *ee* in good yield. Treatment of the sulfinamide with MeMgCl afforded (*S*)-methyl phenyl sulfoxide with 97% *ee*, and this could be converted with complete retention of configuration into (*S*)-*N*,*S*-dimethyl-*S*-phenylsulfoximine, the starting material for the synthesis of the allylic sulfoximines used in this work.

Background and Synthetic Concept

β-Amino acids have attracted much attention[1] because of their incorporation in naturally occurring peptides and other biologically active compounds and their utilization as starting materials for the synthesis of β-lactams[2] and β-peptides,[3] oligomers of β-amino acids. This has resulted in ever-growing interest in the asymmetric synthesis of β-amino acids.[4] Cyclic and acyclic β,β-disubstituted β-amino acids are currently of much interest because of anticipated unusual structural and pharmacological properties of their derived β-peptides.[1i,3b,3c,3e] While numerous imaginative and efficient asymmetric syntheses of β-substituted β-amino acids have been described,[1,4] methods for the asymmetric synthesis of β,β-disubstituted β-amino acids are scarce.[5] The well established Arndt−Eistert homologation of α-amino acids, for example, fails in the case of α,α-disubstituted α-amino acids.[1i] Methods described for the asymmetric synthesis of β,β-disubstituted β-amino acids include the

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addition of nucleophiles to *N*-sulfinylimines,[5a−5c] the hydrogenation of *N*-sulfinylimine-derived aziridines,[5d] and the functionalization of aspartic acid derivatives.[5e] While the sulfinylimine method has been restricted to the synthesis of β-methyl-substituted derivatives and seems to be limited by *syn* and *anti* isomerization of ketosulfinimines, the selectivities of the aziridine method tend to be variable, while the aspartic acid method is confined to particular examples. As well as β,β-disubstituted derivatives, β-amino acids bearing hydroxy groups in their side chains are of particular interest. Hydroxy-β-amino acids occur as structural motifs in natural products and have been used as starting materials for the synthesis of biologically active compounds.[6a−6i,6k] The most interesting application of these functionalized β-amino acids, however, should be in the field of β-peptides,[6j] in particular in the synthesis of glycosylated β-peptides.[6l,6m] Glycosylated α-peptides,[7] oligomers of α-amino acids, are of high biological relevance, and so their glyco-β-peptide analogues may also exhibit interesting biological activities and structures.

We felt that β-substituted and β,β-disubstituted δ-hydroxy-β-amino acids of type **I**, with three contiguous stereogenic centers (Figure 1), ought to be particularly attractive as starting materials for the synthesis of glyco-β-peptides and peptide mimetics. Variation of R^1 to R^3 and the incorporation of R^1 and R^2 of **I** into a cyclic skeleton should provide a high degree of synthetic and structural flexibility. Asymmetric syntheses of acyclic derivatives of **I** bearing hydroxy groups at their γ-positions (R^1 = OH)[6a−6c] had been accomplished previously by use of the corresponding δ-hydroxy-α,β-unsaturated esters as starting materials and application of a stereoselective amination by the Hirma−Itô carbamate method. The asymmetric synthesis of β-amino acids of type **I** bearing functions other than a hydroxy group at the γ-position by this route, however, has with a few exemptions not been achieved.[6c,6i] This is perhaps due to the lack of direct methods for the asymmetric synthesis of the required γ-substituted δ-hydroxy-α,β-unsaturated esters from aldehydes,[8,9] which necessitates the use of indirect, albeit efficient, methods such as aldol or allylation reactions and Wittig homologation.[10]

Structurally closely related to **I** are the 1,3-amino alcohols **IV**, which have also aroused much attention because of their occurrence as structural motifs in natural products,[11] their use as starting materials for the synthesis of, for example, analgesics,[12] and their demonstrated or potential application as chiral auxiliaries and ligands in asymmetric synthesis.[13] As a consequence, much activity has been directed towards the asymmetric synthesis of 1,3-amino alcohols. While a number of methods have been developed,[14,15] those suitable for the asymmetric synthesis of type **IV** compounds with three contiguous stereogenic centers, situated either in a cyclic or in an acyclic carbon skeleton, are much less abundant.[16] Known methods include: (1) the addition of amino-substituted allenylindium,[16f] allylindium,[16g] and allyltitanium[16c] compounds (derived from α-amino acids, for example) to aldehydes, (2) the reduction of β-amino ketones,[16a,16b,16e] prepared through reduction of chiral dihydropyrimidines[16a,16b] or by asymmetric Mannich-type reactions,[17] and (3) asymmetric 1,3-dipolar cycloadditions with alkenes.[14b,14f,16d] While the selectivities of the allenylmetal and allylmetal routes tend to be variable, access to β-amino ketones with two stereogenic C atoms and a broad range of substituents is limited at present, and the 1,3-dipolar cycloaddition gives access only to 1,3-amino alcohols with particular substituents. Thus, in

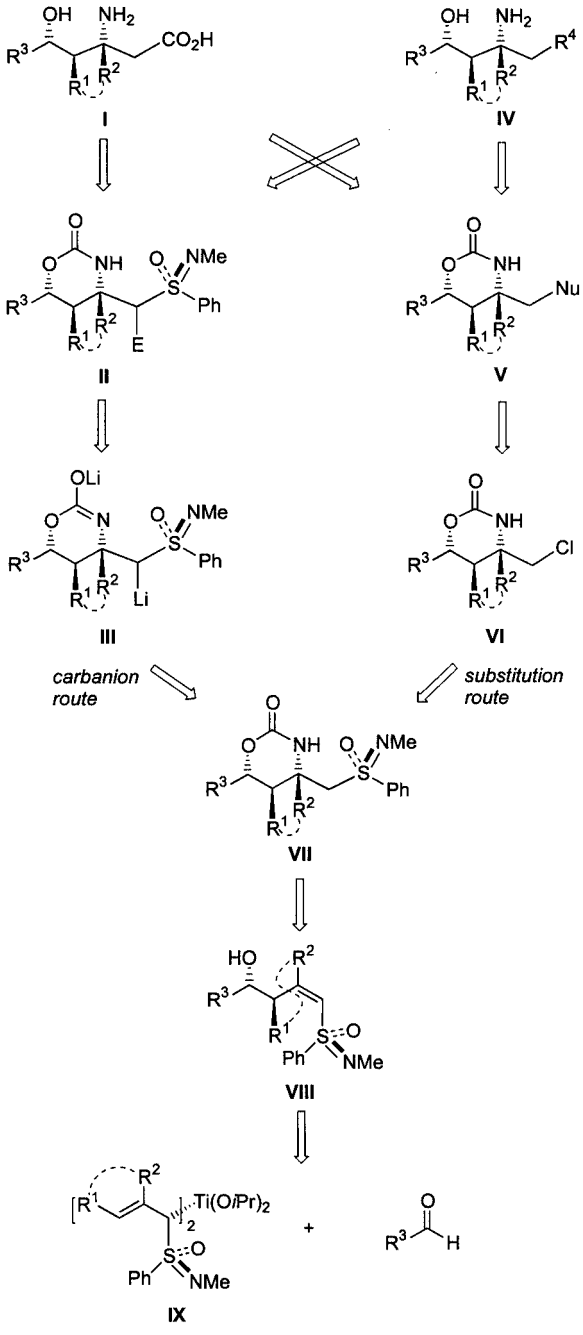


Figure 1. The carbanion and the substitution routes from δ-hydroxy-α,β-unsaturated sulfoximines to β-amino acids and 1,3-amino alcohols

view of the current strong interest both in β-amino acids and in 1,3-amino alcohols, we considered it desirable to have a method for the asymmetric synthesis of the β-amino acids **I** and the 1,3-amino alcohols **IV**, both with three contiguous stereogenic centers. In our view, sulfonimidoyl-substituted homoallylic alcohols of type **VIII** should be particularly attractive as starting materials for the asymmetric synthesis of **I** and **IV**.[18,19] Firstly, cyclic and acyclic derivatives of **VIII** with various substituents, including sterically demanding ones, are readily available enantiomerically and diastereomerically pure through treatment of the corresponding chiral, sulfonimidoyl-substituted bis(allyl)titanium complexes **IX** with aldehydes.[18] Secondly, the sulfonimidoyl group, because of its almost unique array of features − including nucleofugacity, basicity, nucleophilicity, carbanion-stabilizing and electron-withdrawing character, and favorable redox potential − offers a number of synthetic possibilities for the introduction of substituents and also for its replacement.[20] Some of these properties of the sulfonimidoyl group have already been advantageously exploited in the conversion of **VIII** (R^2 = H) into the corresponding enantiomerically and diastereomerically pure branched homopropargylic alcohols.[21] Synthesis of both the β-amino acids **I** and the 1,3-amino alcohols **IV** from **VIII** would require in a first step the installation of the amino group of the target molecules with the stereoselective generation of a secondary or tertiary C atom. This transformation could perhaps be accomplished through cyclization of the carbamates[6b] derived from the hydroxyalkenyl sulfoximines **VIII** with formation of *N*,*O*-protected δ-hydroxy-β-amino sulfoximines **VII**, since alkenyl sulfoximines are known to be good Michael acceptors for N-nucleophiles.[22] In a second step, the sulfonimidoyl group of **VII** would have to be replaceable by various groups, including a carboxy group. Because of the ability of the sulfonimidoyl group to act not only to stabilize a carbanion but also as a nucleofuge,[20] two different but complementary routes, the carbanion route and the substitution route, for the achievement of this goal could be envisaged. The carbanion route would include: (1) double deprotonation of the protected β-amino sulfoximines **VII** at the N atom and at the Cα atom with formation of the dilithiated sulfoximines **III**, (2) treatment of **III** with electrophiles including $ClCO_2R$ with formation of the substituted sulfoximines **II**, and (3) reduction of **II** with formation of **I** or **IV** after deprotection. While the feasibility of (1) lithiation of alkyl sulfoximines, (2) the facile reaction of lithiated alkyl sulfoximines with electrophiles, and (3) the reduction of alkyl sulfoximines have been amply demonstrated,[20] nothing is known, however, about the stability of the lithioalkyl sulfoximines **III** with potential nucleofuges at their β-positions. The substitution route would encompass: (1) substitution of the sulfonimidoyl group of **VII**, with formation of the protected β-amino chlorides **VI** by the chloroformate method developed recently in our laboratories,[23,24] and (2) the replacement of the Cl atom of **VI**, with the formation of derivatives **V**, upon treatment with various nucleophiles, including cyanide, to afford either **I** or **IV** after deprotection. Although the substitution of a sulfonimidoyl group by a Cl atom by treatment with $ClCO_2R$ works well for simple alkyl and allyl sulfoximines, nothing is known about the feasibility of the substitution of sulfoximines of type **VII** with secondary or tertiary carbon atoms at their β-positions. The nucleophilic substitution of chlorides **VI** by cyanide, for example, should pose no problem in the case of R^2 = H,[4a] but might face one in the case of $R^2 \neq$ H and the cyclic derivatives of **VI**.

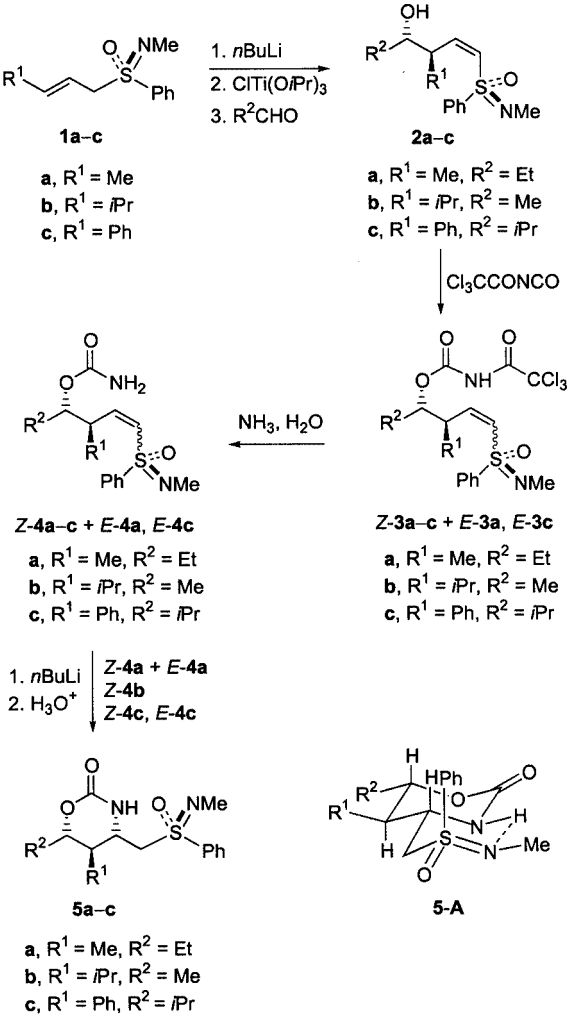
In this paper we describe a new method for the asymmetric synthesis of *N*,*O*-protected, cyclic and acyclic δ-hydroxy β-amino acids of type **I** and of *N*,*O*-protected, cyclic and acyclic 1,3-amino alcohols of type **IV** from the bis(allyl)titanium complexes **IX** and aldehydes.[25] This adds considerably to the synthetic usefulness of complexes **IX**, which have previously been shown to be excellent reagents not only for the asymmetric synthesis of branched homopropargylic alcohols from aldehydes,[21] but also for that of branched γ,δ-unsaturated α-amino acids from *N*-sulfonyl α-imino esters.[26]

Results and Discussion

I. Stereoselective Synthesis and Amination of δ-Hydroxy-α,β-Unsaturated Sulfoximines

Treatment of the enantiomerically and diastereomerically pure homoallylic alcohols **2a**−**c**, synthesized in good yields from the allylic sulfoximines **1a**−**c**[18c,27−29] and the corresponding aldehydes as described previously, with trichloroacetyl isocyanate and subsequent cleavage of the *N*-trichloroacetyl carbamates **3a**−**c** with aqueous ammonia gave a mixture of the (*Z*)-configured carbamate (*Z*)-**4a** and the (*E*)-configured carbamate (*E*)-**4a** in a ratio of 3:1, the pure (*Z*)-configured carbamate (*Z*)-**4b**, and a mixture of the (*Z*)-configured carbamate (*Z*)-**4c** and the (*E*)-configured carbamate (*E*)-**4c** in a ratio of 4.7:1, in 85%, 90% and 92% yields, respectively (Scheme 1). Carbamates **4a**−**c** were purified by chromatography, which also allowed separation of carbamates (*Z*)-**4c** and (*E*)-**4c**. The *N*-trichloroacetyl carbamates **3a**−**c** were not generally isolated, but ^{1}H NMR spectroscopy of the reaction product derived from alcohol **2b** and the isocyanate showed the formation of a mixture of (*Z*)-**3b** and (*E*)-**3b** in a ratio of approximately 11:1. This indicates that the isomerization of the C=C double bond has already taken place at the stage of the *N*-trichloroacetyl carbamates. Isomerization of the (*Z*) isomer to the more stable (*E*) isomer perhaps occurs through a reversible addition of the N atom of the fairly acidic trichloroacetyl carbamate group to the activated double bond after proton transfer to the basic sulfonimidoyl group. Treatment of the mixture of carbamates (*Z*)-**4a** and (*E*)-**4a**, and also of the pure carbamates (*Z*)-**4b** and (*Z*)-**4c**, each with 2−3 equiv. of *n*BuLi at −78 °C and warming of the reaction mixtures to room temperature resulted in highly diastereoselective cyclization reactions (≥ 95% *de*) and afforded the oxazinones **5a**−**c** after aqueous workup, each as a single diastereomer, in 93%, 94%, and 83% yields, respectively.[30] The configuration of the newly generated stereogenic center of

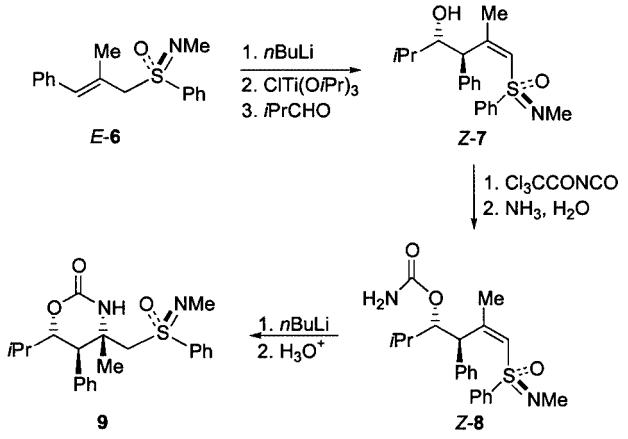
oxazinone **5b** was determined indirectly by X-ray crystal structure analysis of a derivative (vide infra). ^{1}H NMR spectroscopy of oxazinones **5a**−**c** showed that oxazinones **5a** and **5c** also have the same configuration as **5b**. Oxazinones **5a**−**c** are characterized by high magnitudes of the vicinal coupling constants for all protons in their oxazinone rings, which clearly demonstrates their *trans-trans* relationships. In solution, according to the NMR and IR data, oxazinones **5a**−**c** preferentially if not exclusively adopt a structure of type **5-A**, characterized by an intramolecular hydrogen bond between the N atoms of the oxazinone ring and the sulfonimidoyl group and a conformation of the oxazinone ring in which all substituents are in pseudoequatorial positions. A structure of this type was also found in the crystal in the case of the derivative of **5b** (vide infra).



Scheme 1. Amination of acyclic δ-hydroxy-α,β-unsaturated sulfoximines with formation of a secondary C atom

Formation of the diastereomerically pure oxazinone **5a** from the mixture of carbamates (*Z*)-**4a** and (*E*)-**4a** points to a stereoselective cyclization of both carbamates with the same sense and with similar degrees of asymmetric induction (stereoconvergence). In order to test this hypothesis, the cyclization of the (*E*)-configured carbamate (*E*)-**4c** was also studied. Treatment of (*E*)-**4c** with *n*BuLi under the same conditions as used in the case of (*Z*)-**4c** resulted in a highly stereoselective cyclization reaction (≥ 95% *de*) to give oxazinone **5c** as a single diastereomer in 82% yield. These results indicate that the formation of (*E*/*Z*) mixtures in the case of **4a** and **4c** is not detrimental to the success of the highly stereoselective amination of **2a** and **2c**.

Sulfoximines **5a**−**c** can serve as starting materials only for the synthesis of acyclic β-amino acids of type **I** (R^2 = H) and of acyclic 1,3-amino alcohols of type **IV** (R^2 = H) (cf. Figure 1). Synthesis of acyclic β,β-disubstituted β-amino acids of type **I** ($R^2 \neq$ H) and of acyclic 1,3-amino alcohols of type **IV** ($R^2 \neq$ H) requires the successful extension of the highly selective hydroxyalkylation of the monosubstituted bis(allyl)titanium complexes **IX** (R^2 = H) with aldehydes to that of the disubstituted titanium complexes **IX** ($R^2 \neq$ H). The hydroxyalkylation of the allylic sulfoximine (*E*)-**6**[27] was therefore studied (Scheme 2). Titanation of the allylic sulfoximine (*E*)-**6** with $ClTi(OiPr)_3$ after deprotonation with *n*BuLi furnished the corresponding bis(allyl)-titanium complex, which upon treatment with isobutyraldehyde gave the *anti*-configured homoallylic alcohol (*Z*)-**7** with high regioselectivity (≥ 95%) and diastereoselectivity (≥ 95% *de*), isolated as a single diastereomer in 59% yield. The allylic sulfoximine (*E*)-**6** was recovered in 25% yield. The depicted configuration of (*Z*)-**7** was determined by X-ray crystal structure analysis (Figure 2).



Scheme 2. Amination of acyclic (*E*)-configured δ-hydroxy-α,β-unsaturated sulfoximines with formation of a tertiary C atom

Successive treatment of alcohol (*Z*)-**7** with trichloroacetyl isocyanate and aqueous ammonia afforded carbamate (*Z*)-**8** in 89% yield. Besides (*Z*)-**8**, a small amount of the corresponding *N*-trichloroacetyl carbamate was also isolated. To our delight, cyclization of carbamate (*Z*)-**8** upon treatment with *n*BuLi also proceeded with high diastereoselectivity (≥ 95% *de*) to give the oxazinone **9** as a single diastereomer in 84% yield after aqueous workup. The configuration of **9** was verified by X-ray crystal structure analysis (Figure 3). Interestingly, sulfoximine **9** features an intramolecular hydrogen bond in the crystal, between the N atom of the oxazinone ring and the O atom of the sulfoximine group incorporated in a six-membered ring. In the absence of a steri-

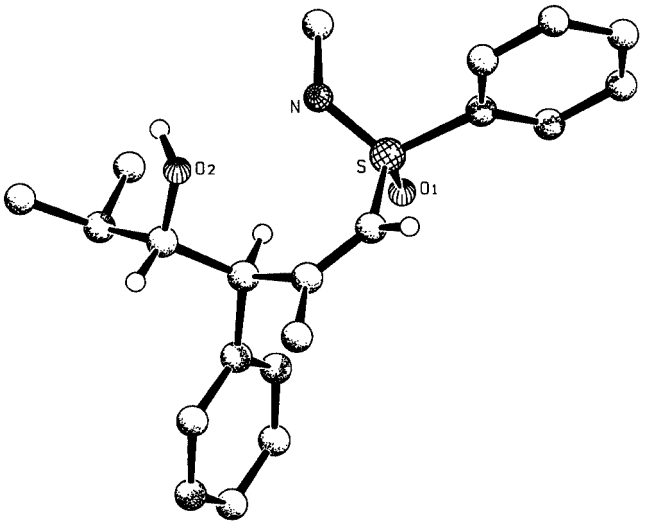


Figure 2. Structure of the δ-hydroxy-α,β-unsaturated sulfoximine (*Z*)-**7** in the crystal

cally demanding substituent at the N atom of the sulfonimidoyl group[19a] it is normally the N atom and not the O atom that engages in hydrogen bonding with hydroxy groups, as demonstrated by **2a**−**c**, **5a**−**c**, a derivative of **5b** (vide infra), and other sulfoximines.[18c] Formation of a hydrogen bond to the N atom of **9** is perhaps less favorable than to the O atom because of an otherwise resulting steric 1,3-interaction between the methyl group at the C atom and the *S*-phenyl group.

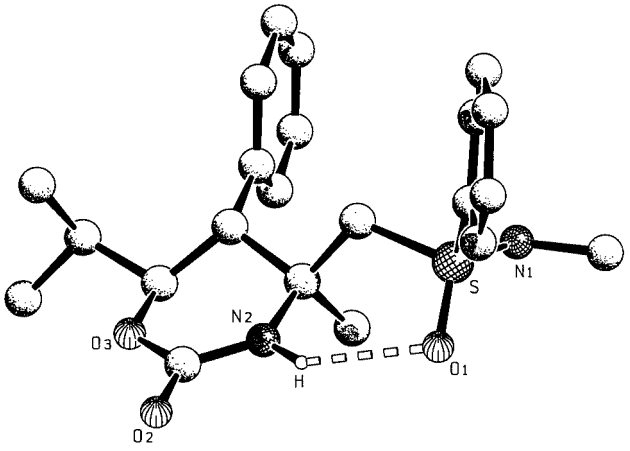
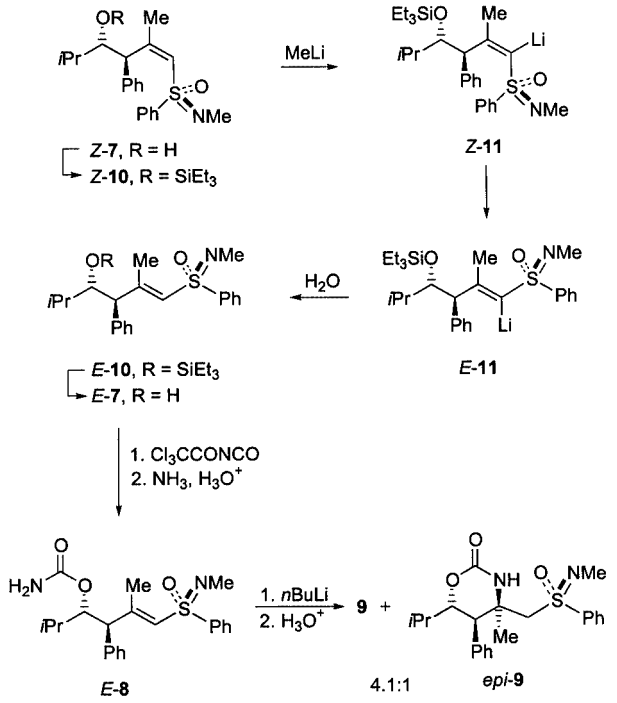


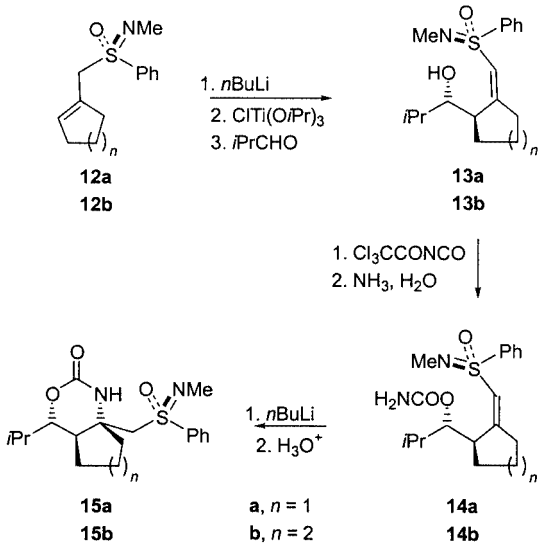
Figure 3. Structure of sulfonimidoyl-substituted 1,3-amino alcohol derivative **9** in the crystal; H···O1 223.3, N2···O1 297.9(3), N2−H 97.1 pm, N2−H···O1 132.7°

The cyclization of both carbamates (*Z*)-**4c** and (*E*)-**4c**, each possessing a disubstituted double bond, occurred with the same sense and with the same high degree of asymmetric induction. Although the synthesis of carbamate (*Z*)-**8**, with a trisubstituted double bond, was not accompanied by formation of the isomeric carbamate (*E*)-**8**, we were interested in whether (*E*)-**8** would also selectively give oxazinone **9** upon treatment with *n*BuLi. The synthesis of (*E*)-**8** was accomplished as shown in Scheme 3. Thus, treatment of the silyl ether (*Z*)-**10**, derived from alcohol (*Z*)-**7**, with MeLi in Et_2O at −35 °C initially afforded the alkenyllithium derivative (*Z*)-**11**, which rapidly isomerized to (*E*)-**11**. Protonation of (*E*)-**11** with water yielded the (*E*)-configured alkenyl sulfoximine (*E*)-**10** in 93% yield based on (*Z*)-**10**. Deprotection of the silyl ether (*E*)-**10** gave alcohol (*E*)-**7**, which was converted in two steps into carbamate (*E*)-**8** (78% yield based on (*E*)-**10**). Cyclization of carbamate (*E*)-**8** under the same conditions as employed for that of (*Z*)-**8** delivered a mixture of the oxazinones **9** and *epi*-**9** in a ratio of 4.4:1 in 76% yield. Thus, cyclization of (*E*)-**8** occurred with a lower diastereoselectivity than that of the isomer (*Z*)-**8**.



Scheme 3. Amination of acyclic (*Z*)-configured δ-hydroxy-α,β-unsaturated sulfoximines with formation of a tertiary C atom

Having been shown that a stereoselective amination of acyclic homoallylic alcohols of type **VIII** with generation of secondary and tertiary carbon atoms can be accomplished efficiently by the carbamate method, its extension to cyclic homoallylic alcohols of type **VIII** was studied. Firstly, the feasibility of a regio- and stereoselective synthesis of the cyclic five-membered homoallylic alcohol **13a** was examined (Scheme 4). Treatment of a mixture of $Ti(OiPr)_4$ and the corresponding bis(allyl)titanium complex, prepared from the cyclopentenyl sulfoximine **12a**[29] by lithiation and subsequent titanation with one equivalent of $ClTi(OiPr)_3$, with isobutyraldehyde proceeded with high regioselectivity (≥ 95%) and diastereoselectivity (≥ 95% *de*) to give the homoallylic alcohol **13a**, which was purified through conversion into the corresponding triethylsilyl ether, as a single diastereomer in 68% yield. The diastereomerically pure cyclic six-membered homoallylic alcohol **13b** was obtained from the allylic sulfoximine **12b**[31] as described previously.[18c] Successive treatment of alcohols **13a** and **13b**



Scheme 4. Amination of cyclic sulfonimidoyl-substituted homoallylic alcohols with formation of a tertiary C atom

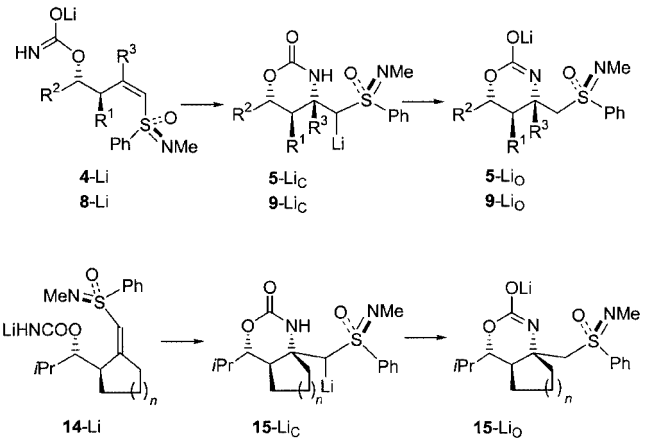


Figure 4. Cyclization of sulfonimidoyl-substituted lithiated homoallylic carbamates

with trichloroacetyl isocyanate and aqueous ammonia gave carbamates **14a** and **14b**, respectively, both in 90% yield; small amounts of the corresponding *N*-trichloroacetyl carbamates were also isolated. The cyclizations of carbamates **14a** and **14b** also occurred with high diastereoselectivities (≥ 95% *de*) upon treatment with 2 equiv. of *n*BuLi and gave the bicyclic oxazinones **15a** and **15b**, respectively, each as a single diastereomer, in 80% and 84% yields. The configuration of **15b** was determined indirectly by X-ray crystal structure analysis of derivatives (vide infra).

Stereochemical Consideration of the Intramolecular Amination

The formation of the oxazinones from the corresponding carbamates (cf. Schemes 1−4) most probably starts with deprotonation of the amino groups, with formation of the lithium salts **4**-Li, **8**-Li, and **14**-Li, respectively (Figure 4).[32] These lithium salts then undergo cyclization to give the *C*-lithiated sulfoximines **5**-Li$_C$, **9**-Li$_C$, and **15**-Li$_C$, respectively.[33,34] Since the acidity of the carbamates is much higher than that of alkyl sulfoximines,[35] the lithiated sulfoximines **5**-Li$_C$, **9**-Li$_C$, and **15**-Li$_C$ would be expected to undergo transmetalation, with formation of the *O*-lithiated oxazinones **5**-Li$_O$, **9**-Li$_O$, and **15**-Li$_O$, respectively. This transmetalation may be crucial to the success of the intramolecular amination, since the lithiated oxazinones should be much less prone to *retro*-Michael reaction than the lithiated sulfoximines because of the poorer leaving groups in their β-positions.

The generation of the new stereogenic centers in the monocyclic oxazinones and the bicyclic oxazinones occurs with the same sense and with the same high degree of asymmetric induction. The highly selective formation of the oxazinones **5a**−**c** from (*Z*)-**4a**-Li, (*E*)-**4a**-Li, (*Z*)-**4b**-Li, (*Z*)-**4c**-Li, and (*E*)-**4c**-Li, of oxazinone **9** from (*Z*)-**8**-Li, and of oxazinones **15a** and **15b** from **14a**-Li and **14b**-Li, respectively, implies that the C=C double bond of the lithiated carbam-

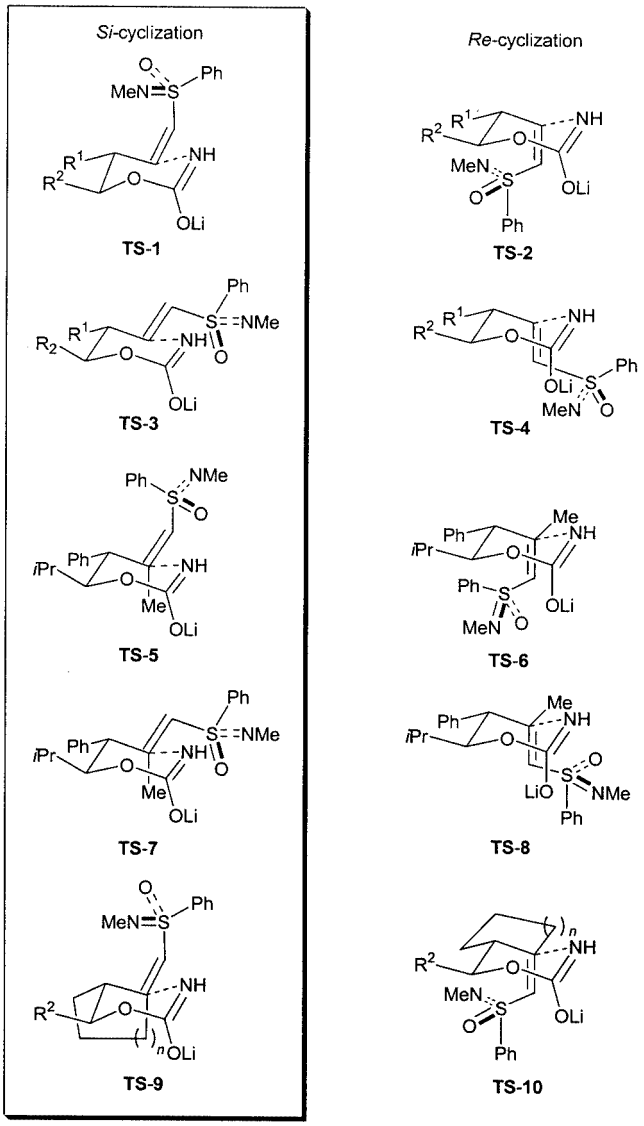


Figure 5. Transition state models for the intramolecular amination

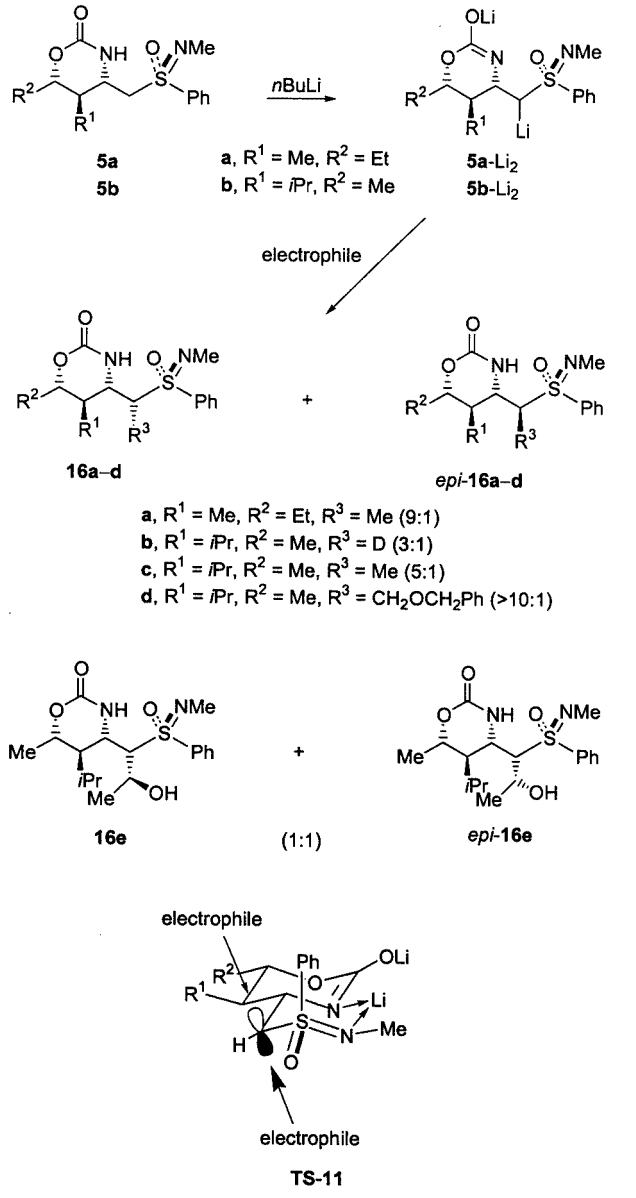
ates is attacked by the N atom from the *Si* face. This can be explained by invoking transition state models of type **TS-1** for the acyclic (*Z*) isomers and **TS-3** for the acyclic (*E*) isomers, in which the substituents R^1 and R^2 and the C=C double bond adopt pseudoequatorial positions (Figure 5). The alternative transition states **TS-2** and **TS-4**, which would feature attack of the N atom at the double bond from the *Re* face and afford the epimeric oxazinones, seem to be less favorable because of severe steric 1,3-interactions involving the sulfonimidoyl group and the double bond. Similar arguments can be applied to the transition states **TS-5** and **TS-6** for the cyclization of the (*Z*)-configured methyl-substituted lithiated carbamate and to **TS-7** and **TS-8** for the cyclization of the (*E*)-configured isomer. Why the selectivity is lower in the case of the cyclization of the latter salt is difficult to ascertain by these models. For the cyclization of the cyclic lithiated carbamates, transition state model **TS-9** has to be invoked, resulting in the bicyclic oxazinones with the *cis* ring fusion. The alternative transition state model **TS-10**, which would give isomeric bicyclic oxazinones with a *trans* ring fusion, is highly strained and destabilized by an unfavorable interaction between the sulfonimidoyl group and the lithiated carbamoyl group.

II. The Carbanion Route

Synthesis of Protected Dilithiated β-Amino Sulfoximines and Treatment with Electrophiles

We were delighted to see that the protected β-amino sulfoximines **5a** and **5b** readily afforded the dilithiated sulfoximines **5a**-Li_2 and **5b**-Li_2, respectively, upon treatment with 2.1 equiv. of *n*BuLi in THF at −10 °C (Scheme 5). The dilithiated sulfoximines **5a**-Li_2 and **5b**-Li_2 were stable in THF solution at −78 °C for at least 2 h. Treatment of **5a**-Li_2 with MeI gave a mixture of **16a** and *epi*-**16a** in a ratio of 9:1, chromatography delivering the diastereomerically pure derivative **16a** in 68% yield. No C,N-dimethylation of **5a**-Li_2 was observed under these conditions, within the limits of detection by ^{1}H NMR spectroscopy. Deuteration of **5b**-Li_2 with CD_3OD afforded a mixture of sulfoximines **16b** and *epi*-**16b** in a ratio of 3:1, with a D-content of ≥ 98%, in 99% yield. Methylation of **5b**-Li_2 yielded a mixture of **16c** and *epi*-**16c** in a ratio of 5:1 in 82% yield, chromatography furnishing diastereomerically pure **16c** in 75% yield. Similarly, treatment of **5b**-Li_2 with $PhCH_2OCH_2Cl$ proceeded readily and diastereoselectively to give the diastereomerically pure sulfoximine **16d** in 70% yield after chromatography of the crude reaction mixture. As a final example, treatment of **5b**-Li_2 with acetaldehyde was carried out, yielding a mixture consisting of alcohols **16e** and *epi*-**16e** in a ratio of 1.7:1 (67% yield) and of starting material **5b** (27% yield).

The configurations both of the newly generated stereogenic C atom of **16c**, at the position α to the sulfonimidoyl group, and, of no less importance, of the stereogenic C atom bearing the N atom were determined by X-ray crystal structure analysis (Figure 6). The structure of **16c** in the crystal is characterized by an intramolecular hydrogen bond between the N atoms of the oxazinone ring and of the sulfonimidoyl group incorporated in a six-membered ring. The methyl group and the phenyl group adopt pseudoaxial positions. From the magnitudes of the vicinal coupling constants of the protons of the oxazinone ring and the proton in the α-position in the ^{1}H NMR spectrum and NOE experiments, **16c** in solution preferentially adopts a structure similar to that in the crystal. On the basis of the unambiguous assignment of the configuration of **16c**, we tentatively assign the configurations depicted in Scheme 5 to the major diastereomers of sulfoximines **16a**−**d**. Treatment of **5b**-Li_2 with MeCHO gave a mixture of two diastereomers in a ratio of 1.7:1. Because of the almost unselective reaction between lithiated alkyl sulfoximines and aldehydes in general[20] and the observation of a 5:1 selectivity in the methylation of this dilithium salt with MeI, we tentatively assign



Scheme 5. Synthesis and reactivity of dilithium salts of protected β-amino sulfoximines having a secondary C atom

the structures **16e** and *epi*-**16e**, which differ in the configuration of the C atom bearing the hydroxy group.

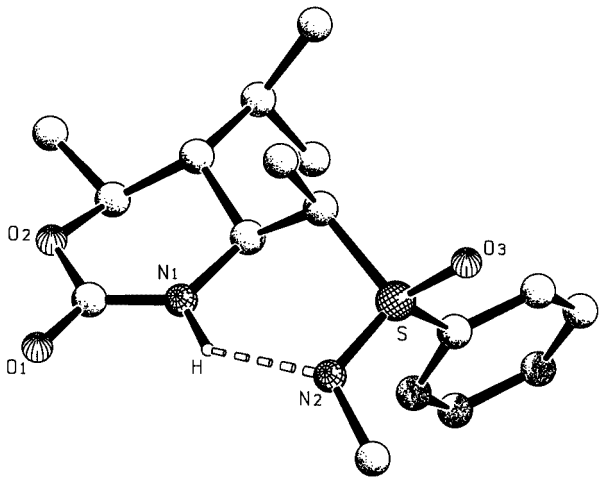
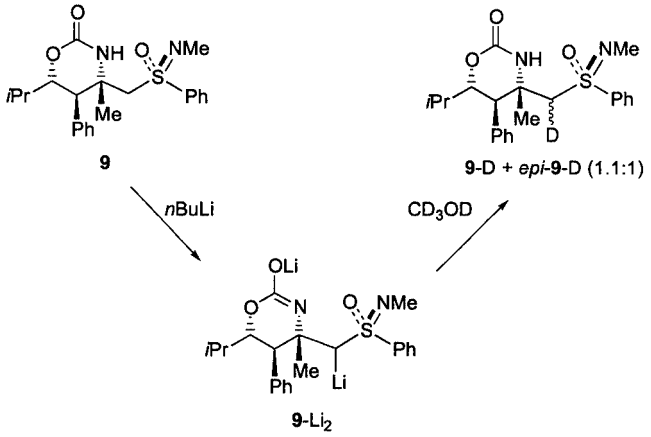


Figure 6. Structure of the sulfonimidoyl-substituted 1,3-amino alcohol derivative **16c** in the crystal; H···N2 198.8, N2···N1 280.5(5), N1−H 100.5 pm, N1−H···N2 136.7°

From previous structural investigations of lithiated alkyl and allyl sulfoximines,[33,34] a transition state model of type **TS-11** is proposed for the reaction of the dilithiated sulfoximines **5a**-Li_2 and **5b**-Li_2 giving rise to the major diastereomer. This transition state model is characterized by the lack of a C−Li bond and by the coordination of one of the two Li atoms by the two N atoms of the oxazinone ring and of the sulfonimidoyl group. Coordination of the N atom of the sulfonimidoyl group to the Li atom results in a C_α−S conformation of the carbanion, in which the lone pair orbital at the C_α atom and the S−Ph bond are approximately in one plane.[36] Theoretical calculations on α-sulfonimidoyl carbanions predict that this conformation should be energetically preferred because of a stabilizing $n_C-\sigma_{SPh}^*$ interaction.[33c] The preferential formation of the (*R*)-configured methyl derivative **16c** in the reaction between **5b**-Li_2 and MeI may be interpreted by assuming a preferential attack of MeI from the *Re* face of the carbanionic centers as depicted in **TS-11** because of steric shielding of the *Si* face by R^1 and the phenyl group. It is proposed that the reactions between **5a**-Li_2 and **5b**-Li_2 and the other electrophiles take a similar stereochemical course.

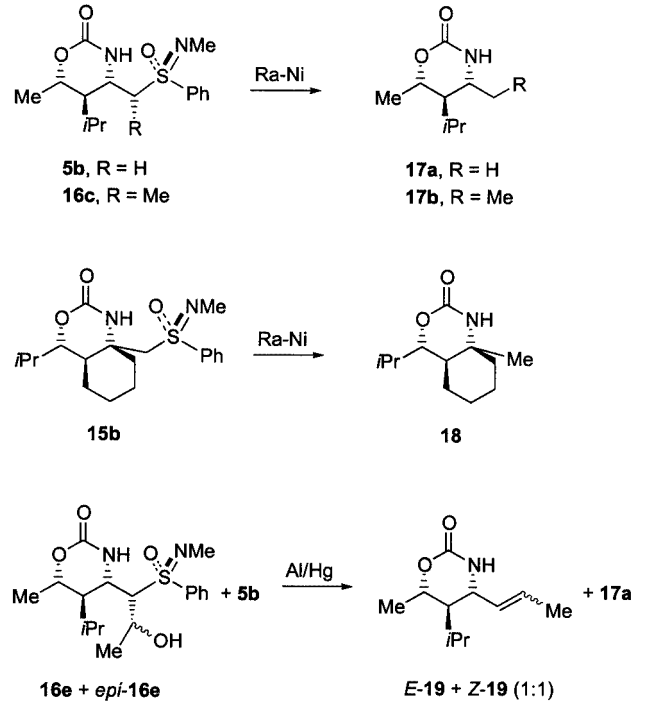
It is not only sulfoximines **5a** and **5b**, each with a secondary C atom in the β-position, that can be deprotonated twice; the procedure is also successful with sulfoximines incorporating tertiary C atoms. Treatment of sulfoximine **9** with 2 equiv. of *n*BuLi and trapping of the dilithium salts **9**-Li_2 with CD_3OD thus afforded a mixture of the deuterated sulfoximine **9**-D and *epi*-**9**-D in a ratio of approximately 1.1:1 in 99% yield (Scheme 6).



Scheme 6. Synthesis and reactivity of dilithium salts of protected β-amino sulfoximines having a tertiary C atom

Synthesis of Protected 1,3-Amino Alcohols

The above results show that substituents at the α-positions of protected β-amino sulfoximines **5a** and **5b** can readily be introduced through formation of the corresponding dilithiated sulfoximines and their treatment with electrophiles. Completion of the asymmetric synthesis of 1,3-amino alcohols by this route requires replacement of the sulfonimidoyl group, which should be possible either by reduction or by Cl-substitution (cf. Figure 1). Thus, treatment of the monocyclic sulfoximines **5b** and **16c** with Raney nickel[37] readily afforded the 1,3-amino alcohol derivatives **17a** and **17b**, respectively, each in 88% yield (Scheme 7). Similarly, reduction of the bicyclic sulfoximine **15b** furnished the cyclic 1,3-amino alcohol derivative **18** in 86% yield. The configuration of **18** and hence that of the oxazinone **15b** was determined by X-ray crystal structure analysis (Figure 7). The reductive substitution of the sulfonimidoyl groups of the β-hydroxy sulfoximines **16e** and *epi*-**16e**



Scheme 7. Synthesis of protected acyclic and cyclic 1,3-amino alcohols by reduction

was accomplished with the generation of a double bond. Thus, treatment of **16e** and *epi*-**16e** (admixed with **15b**) with Al/Hg[38] afforded a mixture of the unsaturated protected 1,3-amino alcohols (*E*)-**19** and (*Z*)-**19** in a ratio of 1:1 in 85% yield, together with **17a** in 46% yield.

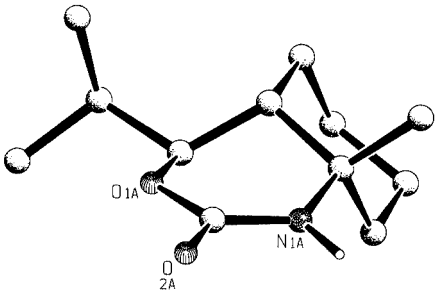
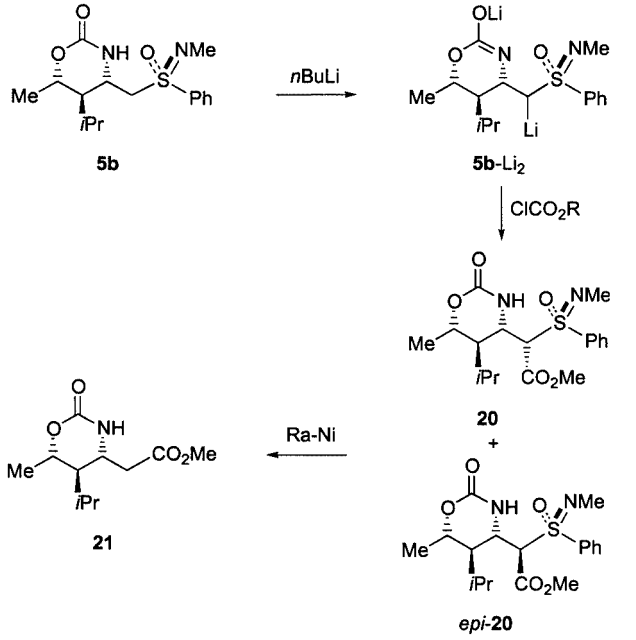


Figure 7. Structure of the protected 1,3-amino alcohol **18** in the crystal



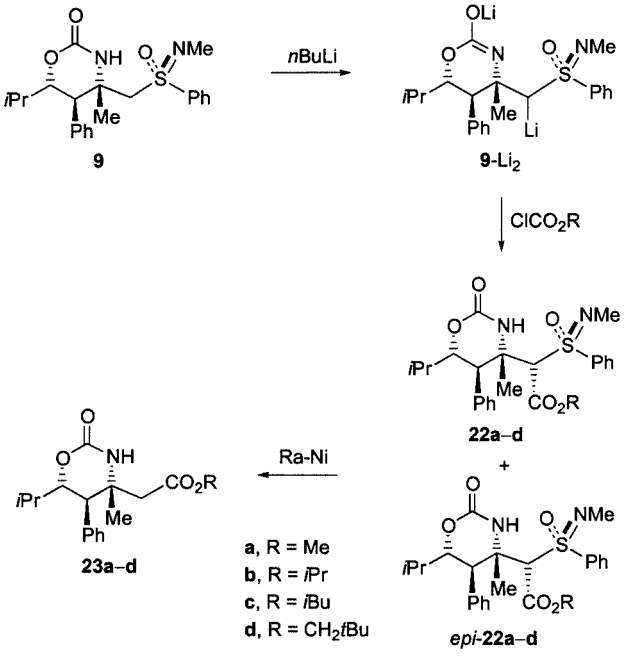
Scheme 8. Synthesis of protected acyclic β-substituted β-amino acids and protected 1,3-amino alcohols by the carbanion route

Synthesis of Protected β-Amino Acids

Conversion of the sulfonimidoyl-substituted monocyclic and bicyclic oxazinones to β-amino acid derivatives by the carbanion route first requires the introduction of a carboxy group into the molecules. Thus, treatment of the dilithiated sulfoximine **5b**-Li_2, derived from **5b**, with $ClCO_2Me$ furnished a mixture of the esters **20** and *epi*-**20** in a ratio of 5.2:1 in 64% yield (Scheme 8). The configurations of the esters **20** and *epi*-**20** were tentatively assigned as depicted. Finally, reduction of the sulfoximines **20** and *epi*-**20** with Raney nickel gave the protected β-amino acid **21** in 87% yield.

It was now of particular interest to see whether the carbanion route could also be successfully implemented for the synthesis of protected cyclic and acyclic β-amino acids with tertiary C_β atoms. Deprotonation of sulfoximine **9** with *n*BuLi in THF at −78 °C gave the dilithiated sulfoximine **9**-Li_2, which upon treatment with $ClCO_2R$ (R = Me, *i*Pr, *i*Bu, and CH_2tBu) furnished mixtures of esters **22a**−**d** and *epi*-**22a**−**d** and the starting sulfoximine **9**, the last of which was separated by chromatography (Scheme 9). Because of partial transmetalation between **9**-Li_2 and the esters formed, conversion of sulfoximine **9** was incomplete and 7−18% of the sulfoximine was recovered. Reduction of sulfoximines **22a**−**d** and *epi*-**22a**−**d** with Raney nickel afforded the protected β,β-disubstituted β-amino acids **23a**−**d** in 48% to 74% yields, based on **9**. The highest overall yield in the conversion of sulfoximine **9** into one of the β-amino ester derivatives was achieved in the case of ester **23c** (74%), for which isobutyl chloroformate was used for the introduction of the ester group into **9**-Li_2.

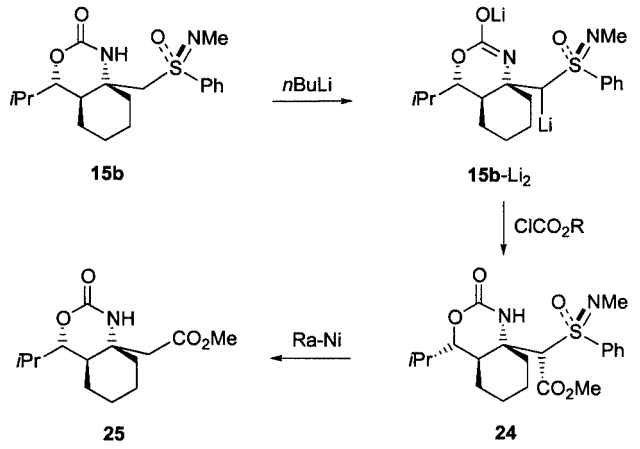
Finally, the conversion of the bicyclic sulfoximine **15b** into the amino acid derivative **25** by this route was investigated. Double deprotonation of sulfoximine **15b** with *n*BuLi



Scheme 9. Synthesis of protected acyclic β,β-disubstituted β-amino acids and protected 1,3-amino alcohols by the carbanion route

in THF at −78 °C cleanly gave the dilithiated sulfoximine **15b**-Li_2 (Scheme 10), which upon treatment with $ClCO_2Me$ delivered ester **24** as a single diastereomer in 70% yield. Reduction of sulfoximine **24** with Raney nickel furnished the protected cyclic β-amino acid **25** in 86% yield. The

structure of **25** was verified by X-ray crystal structure analysis (Figure 8).



Scheme 10. Synthesis of protected cyclic β,β-disubstituted β-amino acids and protected 1,3-amino alcohols by the carbanion route

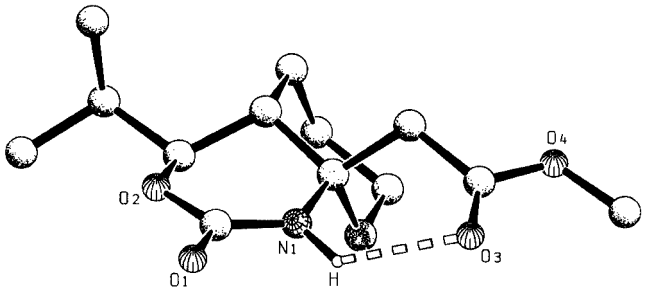
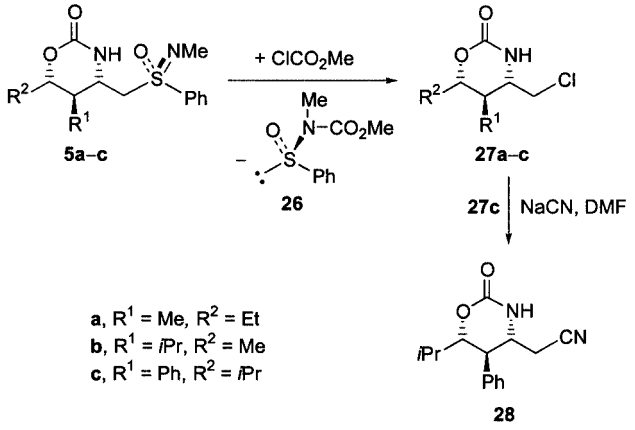


Figure 8. Structure of the protected cyclic β-amino ester **25** in the crystal; O3···H 214.9, N1···O3 285.5(8), N1−H 101.9 pm, N1−H···O3 124.7°

III. The Substitution Route

Synthesis of Protected β-Amino Chlorides and Protected β-Amino Acids

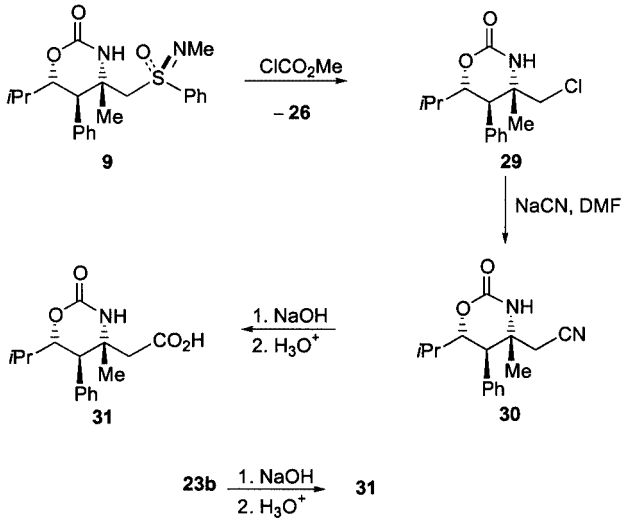
The carbanion route allows access to protected cyclic and acyclic β-amino acids of type **I** and to protected cyclic and acyclic 1,3-amino alcohols of type **IV**. This route ought to be particularly well suited for the synthesis of 1,3-amino alcohols **IV** with various substitution patterns, because of the potential for the introduction of a wide range of substituents R^4 through the reaction between the dilithiated sulfonimidoyl-substituted oxazinones and electrophiles. A principle shortcoming of the carbanion route may be seen, however, in the fact that the chirality of the sulfonimidoyl group is lost in the reduction step. The envisaged substitution route from sulfoximines **VII** to amino acids **I** and 1,3-amino alcohols **IV** via protected β-amino chlorides **VI** would not have this shortcoming, since we had found previously that the sulfonimidoyl groups of alkyl and allyl sulfoximines can readily be replaced by chlorine, proceeding with complete retention of configuration at the S atom, by treatment with $ClCO_2Me$.[23,24] The substitution route could perhaps therefore provide a valuable alternative to the carbanion route and at the same time open new synthetic possibilities, in particular for the synthesis of functionalized 1,3-amino alcohols. We were delighted to see that treatment of sulfoximines **5a−c** with $ClCO_2Me$ at room temperature in CH_2Cl_2 for 3 days gave clean substitution of the sulfonimidoyl group and afforded the β-chloroamines **27a−c** in 84%, 85% and 81% yields, respectively (Scheme 11). In addition, the sulfinamide **26** was isolated (vide infra). Treatment of chloride **27c** with NaCN in DMF readily gave the β-amino nitrile **28** in 87% yield.



Scheme 11. Synthesis of protected acyclic β-amino chlorides and nitriles by the substitution route

The sulfoximine **5c** having successfully been converted into the nitrile **28** by double substitution, it was of particular interest to see whether such transformations would also be feasible in the cases of sulfoximines **9**, **15a**, and **15b** and the corresponding chlorides with tertiary C atoms at their β-positions. To our delight, treatment of sulfoximine **9** with $ClCO_2Me$ in CH_2Cl_2 at room temperature for 2.5 days gave (besides sulfinamide **26**) the protected β-amino chloride **29** in 81% yield (Scheme 12). Treatment of chloride **29** with NaCN in DMF for 2 h furnished nitrile **30** in 87% yield, hydrolysis of nitrile **30** delivering the protected acyclic β-amino acid **31** in 72% yield. Interestingly, the oxazinone ring of **31** was not cleaved under these conditions. The structure of acid **31** was confirmed by X-ray crystal structure analysis (Figure 9).

Finally, the extension of the substitution route to the conversion of sulfoximines **15a** and **15b** into amino acid derivatives **34a** and **34b**, respectively, was attempted in order to study the scope and limitation of the substitution route. Substitution of the cyclic sulfoximines **15a** and **15b** proceeded uneventfully on treatment with $ClCO_2Me$ and gave, besides **26**, the protected β-amino chlorides **32a** in 83% yield and **32b** in 86% yield, respectively (Scheme 13). The structure of chloride **32b** was confirmed by X-ray crystal structure analysis (Figure 10). Treatment of chlorides **32a** and **32b** with NaCN in DMF readily furnished the nitrile **33a** in 92% yield and the nitrile **33b** in 95% yield, respectively. Finally, hydrolysis of nitriles **33a** and **33b** with aque-



Scheme 12. Synthesis of protected acyclic β,β-disubstituted β-amino acids by the substitution route

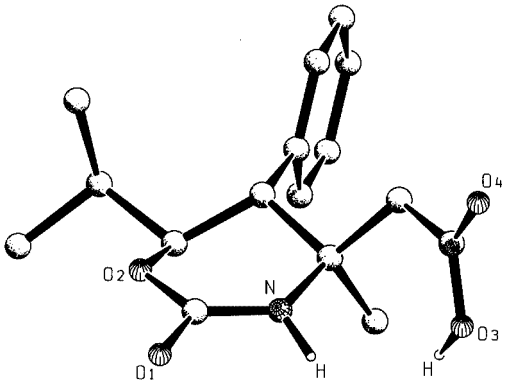
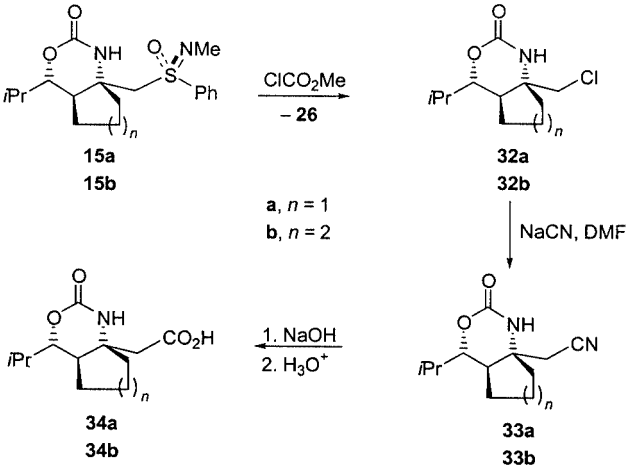


Figure 9. Structure of the protected acyclic β-amino acid **31** in the crystal



Scheme 13. Synthesis of protected cyclic β,β-disubstituted β-amino acids by the substitution route

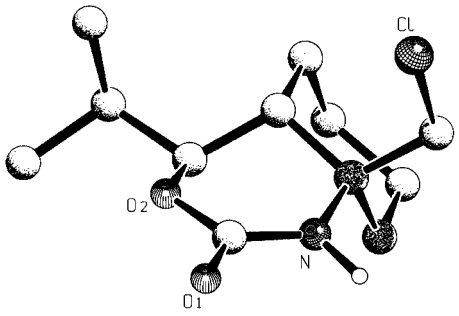
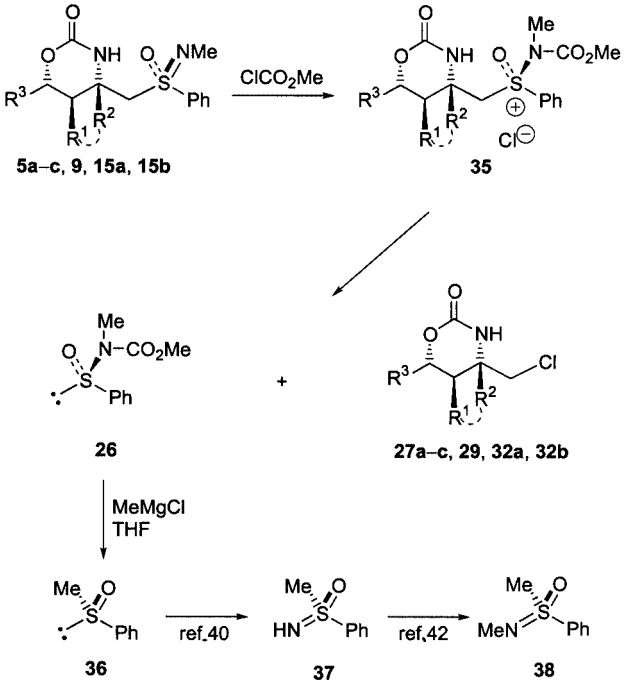


Figure 10. Structure of the chlorine-substituted cyclic 1,3-amino alcohol derivative **32b** in the crystal

ous NaOH at reflux afforded the protected cyclic β-amino acids **34a** in 70% yield and **34b** in 69% yield, respectively.

Recycling of the Chiral Auxiliary

Treatment of sulfoximines **5a**–**c**, **9**, **15a**, and **15b** with $ClCO_2Me$ in all cases delivered – in addition to the chlorides **27a**–**c**, **29**, **32a**, and **32b**, respectively – the sulfinamide **26** as a second reaction product, isolated in the case of – for example –the synthesis of **29** with ≥ 99% *ee* in 73% yield (Scheme 14). These results, together with those obtained previously,[23,24] indicate that treatment of *S*-alkyl-*N*-methyl-*S*-phenylsulfoximines with a chloroformate seems to be a general method for the replacement of the sulfonimidoyl group by a Cl atom. We assume that the substitution proceeds through the intermediate formation of the aminooxosulfonium chlorides **35**. It was now of interest to see whether the sulfoxide **36**[39] could be prepared from the sulfinamide **26** with complete inversion of configuration,

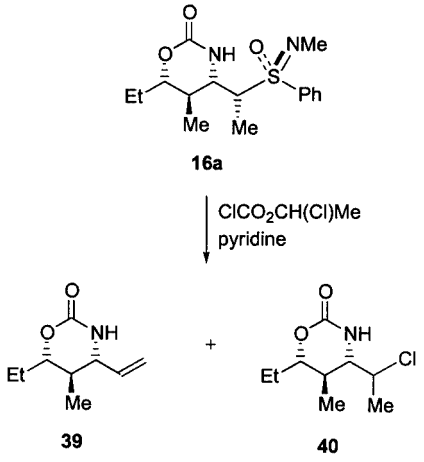


Scheme 14. Substitution of the sulfonimidoyl group and recycling of the chiral auxiliary

since a two-step conversion of **36** to sulfoximine **37** with complete retention of configuration had already been described.[40,41] Sulfoximine **37**, which is normally prepared through an efficient resolution,[29,42,43] can readily be methylated to give sulfoximine **38**,[44] the starting material for the synthesis of the allylic sulfoximines used in this work. Treatment of sulfinamide **26** with methylmagnesium chloride in THF at −78 °C resulted in the isolation of the sulfoxide **36** with 97% *ee* in 70% yield, so the synthesis of **36** from **26** represents a recycling of the chiral auxiliary.

Substitution of an α-Methylated Sulfoximine

Substitution of the sulfonimidoyl groups of **5a**−**c**, **9**, **15a**, and **15b**, without further substituents at their α-positions, by a Cl atom having been achieved, it was now of interest to study the reactivity of the α-methylated sulfoximine **16a** towards chloroformates (Scheme 15). Interestingly, treatment of sulfoximine **16a** with $ClCO_2CH(Cl)Me$ in the presence of pyridine in CH_2Cl_2 at room temperature for 1 h afforded a mixture of the unsaturated 1,3-amino alcohol derivative **39** and the chloride **40** in a ratio of 8:1 in 91% yield. This transformation could perhaps open a further route to synthetically highly valuable unsaturated 1,3-amino alcohols (cf. Scheme 7).



Scheme 15. Substitution of an α-methylated sulfoximine

Conclusion

We have presented a new method for the asymmetric synthesis of protected cyclic and acyclic β-substituted and β,β-disubstituted δ-hydroxy β-amino acids from aldehydes through the use of sulfonimidoyl-substituted bis(allyl)titanium complexes. The δ-hydroxy-β-amino acids are potentially useful not only for the synthesis of glycosylated β-peptides, but also for further derivatization of the amino acids. The method described also permits the asymmetric synthesis of protected cyclic and acyclic, unfunctionalized and sulfonimidoyl-, chlorine-, and cyano-functionalized 1,3-amino alcohols with three contiguous stereogenic C atoms and a secondary or tertiary C atom bearing the amino group. The key steps of this method are: (1) the highly regio- and stereoselective addition of the cyclic and acyclic sulfonimidoyl-substituted bis(allyl)titanium complexes to aldehydes, (2) the stereoselective intramolecular amination of sulfonimidoyl-substituted homoallylic alcohols by the carbamate method, (3) the substitution of protected β-amino sulfoximines with formation of protected β-amino chlorides, (4) the generation of lithiated alkyl sulfoximines with protected lithiated β-amino groups, (5) their treatment with electrophiles, and (6) the reduction of the substituted sulfoximines. The δ-hydroxy-β-amino acids and 1,3-amino alcohols described in this paper have protecting groups at the O and the N atom. We are currently studying the conversion of the β-amino nitriles into differently protected δ-hydroxy-β-amino acids.

Experimental Section

General: The enantiomerically and diastereomerically pure homoallylic alcohols **2a**−**c** and **13b** were synthesized from the allylic sulfoximines **1a**−**c** and **12b**, respectively, by literature procedures.[18c] The enantiomerically pure allylic sulfoximines **1a**−c,[27] (*E*)-**6**,[27] **12a**,[31] and **12b**[31] were prepared from sulfoximine **38** by the one-pot procedure described previously.[18c] All reactions were carried out in absolute solvents under an argon atmosphere by use of syringe and Schlenk techniques in oven-dried glassware. THF and Et_2O were distilled under argon from lead/sodium/benzophenone. CH_2Cl_2 and DMF were distilled from CaH_2. TLC: Merck silica gel 60 F_{254} plates. Column chromatography: Merck silica gel 60 (0.063−0.200 mm. Melting points: Büchi, melting points are uncorrected. Optical rotations: Perkin−Elmer Model 241, measurements were made at approximately 22 °C, specific rotations are in grad·mL/dm·g, and *c* is in g/100 mL. ^1H 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 from APT pulse sequences. The following abbreviations are used to designate the multiplicity of the peaks in ^1H NMR spectra: s = singlet, d = doublet, t = triplet, q = quadruplet, quin = quintet, sept = septet, m = multiplet, br. = broad, symm. = symmetrical and combinations thereof. IR spectra: Perkin−Elmer PE 1759 FT, only peaks of $\tilde{\nu} > 1000$ cm^{-1} are listed, vs = very strong, s = strong, m = medium, and w = weak. GC-MS (CI): Magnum Finnigan (HT-5: 25 m, 0.25 mm; 50 kPa He, 40 eV, MeOH). MS (EI): Varian MAT 212S, 70 eV. MS (CI): Finnigan SSQ 7000, 100 eV; only peaks of $m/z > 80$ and intensity > 10%, except for decisive ones, are listed.

X-ray Analyses: The crystal data and the most salient experimental parameters used in the X-ray measurements and in the crystal structure analyses are reported in Table 1. The crystal structures were solved by direct methods as implemented in the XTAL3.7 package of crystallographic routines.[45] The molecular structures were illustrated by use of the SCHAKAL 92 program.[46,47]

General Procedure for the Conversion of Alcohols into Carbamates (*GP1*): Trichloroacetyl isocyanate (1.05 mmol) was added at room temperature to a solution of the alcohol (1.00 mmol) in THF (20 mL). After the mixture had been stirred at room temperature for 2 h, concentrated aqueous ammonia (3 mL) was added. Stirring of the mixture was continued at room temperature for 1 h. Saturated aqueous NH_4Cl (20 mL) was then added, and the mixture was extracted with CH_2Cl_2. The combined organic phases were

Table 1. Crystal data and parameters of data collection for (*Z*)-**7**, **9**, **16c**, **18**, **25**, **31**, and **32b**

[a]	(*Z*)-**7**	**9**	**16c**	**18**	**25**	**31**	**32b**
Empirical formula	$C_{21}H_{27}NO_2S$	$C_{22}H_{28}N_2O_3S$	$C_{17}H_{26}N_2O_3S$	$2 \times (C_{12}H_{21}NO_2)$[a]	$C_{14}H_{23}NO_4$	$C_{16}H_{21}NO_4$	$C_{12}H_{20}ClNO_2$
M_r	357.52	400.54	338.47	2 × 211.31	269.34	291.35	245.75
Color and habit	colorless, irregular	colorless, irregular	colorless, irregular	Colorless, irregular	colorless, irregular	Colorless, block	Colorless, irregular
Crystal size, ca. mm	0.6 × 0.5 × 0.2	0.13 × 0.24 × 0.56	0.3 × 0.3 × 0.3	0.3 × 0.3 × 0.3	0.3 × 0.3 × 0.3	0.18 × 0.28 × 0.44	0.3 × 0.3 × 0.3
Crystal system	orthorhombic	monoclinic	orthorhombic	monoclinic	monoclinic	trigonal	orthorhombic
space group	$P2_12_12_1$	$P2_1$	$P2_12_12_1$	$P2_1$	$P2_1$	$P3_121$	$P\,2_12_12_1$
a, Å	7.394(2)	11.625(1)	8.338(1)	11.494(2)	5.8447(7)	9.9834(7)	9.138(4)
b, Å	10.175(3)	8.230(1)	9.397(1)	9.266(1)	12.713(2)	9.9834(7)	11.581(4)
c, Å	26.481(5)	12.144(2)	23.093(4)	11.685(3)	9.6417(9)	27.063(3)	12.053(5)
α, °	90.0	90.0	90.0	90.0	90.0	90.0	90.0
β, °	90.0	114.952(2)	90.0	101.69(2)	103.696(1)	90.0	90.0
γ, °	90.0	90.0	90.0	90.0	90.0	120.0	90.0
V, Å^3	1992.3(9)	1053.4(2)	1809.4(4)	1218.7(4)	696.9(2)	2336.0(4)	1275.5(9)
Z	4	2	4	2 × 2	2	6	4
$D_{calcd.}$, g cm^{-3}	1.192	1.263	1.242	1.152	1.283	1.243	1.280
μ, mm^{-1}	1.537	0.178	1.677	0.615	0.764	0.089	2.544
Data collection							
Diffractometer	CDA4 Enraf−Nonius	Bruker SMART APEX	CDA4 Enraf−Nonius	CDA4 Enraf−Nonius	CDA4 Enraf−Nonius	Bruker SMART APEX	CDA4 Enraf−Nonius
T, K	150	298	298	200	150	293	150
Radiation	Cu-K_α	Mo-K_α	Cu-K_α	Cu-K_α	Cu-K_α	Mo-K_α	Cu-K_α
λ, Å	1.54179	0.71073	1.54179	1.54179	1.54179	0.71073	1.54179
Scan method	ω/2θ	ω	ω/2θ	ω/2θ	ω/2θ	ω	ω/2θ
$\Theta_{max.}$, °	74.8	28.3	74.8	74.9	75.0	26.1	74.9
No. of data colld	4612	14686	4148	5373	3000	34565	3038
No. of unique data	3967	5232	3591	4848	2678	3100	2599
Obsevation criterion	$I > 2\sigma(I)$	$F > 4\sigma(F)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$F > 4\sigma(F)$	$I > 2\sigma(I)$
Refinement							
No. of parameters refined	226	253	209	270	172	190	145
No. of data observed in refinement	3548	3668	2149	4478	2662	1886	2239
R, R_w [b]	0.059, 0.069	0.042/0.042[c]	0.057, 0.061[c]	0.056/0.070	0.073/0.088	0.090/0.101[d]	0.056/0.076
Δ(ρ), e·Å^{-3}	−0.90/+0.70	−0.24/+0.32	−1.73/+0.88	−0.33/+0.37	−0.53/+0.52	−0.58/+0.74	−0.63/+0.65
GOF	1.969	0.944	1.351	2.700	4.675[e]	1.031	2.908

[a] Two symmetrically independent molecules. [b] $R = \Sigma| |F_o| - |F_c| |/\Sigma|F_o|$; $Rw = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w\,|F_o|^2]^{0.5}$; $w = 1/\sigma^2(F_o)$ where F_o and F_c are observed and calculated structure factors. [c] $w = 1/[\sigma^2(F_o) + 0.0004 \cdot F_o^2]$. [d] $w = 1/[11 \cdot \sigma^2(F_o)]$. [e] Poor crystal quality.

dried ($MgSO_4$) and concentrated in vacuo. Purification of the residue by chromatography or crystallization afforded the carbamate.

General Procedure for the Conversion of Carbamates into Oxazinones (*GP2*): *n*BuLi in hexane (1.05−1.30 mmol) was added at −78 °C to a solution of the carbamate (1.0 mmol) in THF (40 mL). The reaction mixture was then allowed to warm to room temperature over 18 h. Saturated aqueous NH_4Cl (40 mL) was added, and the aqueous phase was extracted with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification of the residue by chromatography or crystallization afforded the oxazinone.

General Procedure for the Introduction of Substituents at the α-Positions of Sulfoximines (*GP3*): *n*BuLi in hexane (3.00 mmol) was added at −50 °C to a solution of the sulfoximine (1.00 mmol) in THF (40 mL). The mixture was allowed to warm to −10 °C over 1 h, cooled to −50 °C, and then treated with the electrophile. The mixture was then allowed to warm to room temperature over 6 h, and saturated aqueous NH_4Cl (50 mL) was added. The aqueous phase was extracted with CH_2Cl_2, and the combined organic phases were dried ($MgSO_4$). Concentration in vacuo gave the sulfoximine, which was purified by chromatography or crystallization.

General Procedure for the Reduction of Sulfoximines with Raney Nickel (*GP4*): Raney nickel was prepared as follows: nickel aluminium alloy powder (50:50, 2.5 g) was suspended in desalted H_2O (100 mL) and treated with KOH until the evolution of hydrogen ceased. Subsequently, the suspension was heated at 80 °C for 30 min. After the mixture had cooled to room temperature, the aqueous layer was decanted, and the Raney nickel was washed with desalted H_2O (10 × 50 mL) and suspended in THF/H_2O (4:1, 50 mL).

The suspension was then added at room temperature to a solution of the sulfoximine (0.71 mmol) in THF/H_2O (4:1, 5 mL). Subsequently, the reaction mixture was stirred at room temperature until TLC or GC indicated complete conversion of the sulfoximine. The solution was then filtered, and the Raney nickel was washed with THF (5 × 25 mL). The combined organic phases were concentrated in vacuo, and the residue was dissolved in CH_2Cl_2. The aqueous phase was extracted with CH_2Cl_2 and the combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification of the residue by chromatography or crystallization afforded the reduction product.

General Procedure for the Conversion of Sulfoximines into Esters by the Carbanion Route (*GP5*): *n*BuLi in hexane (2.1 mmol) was added

at −78 °C to a solution of the sulfoximine (1.0 mmol) in THF (35 mL). After the mixture had been stirred at this temperature for 2 h, the chloroformate (2.1 mmol) was added and stirring was continued for 90 min. Subsequently, saturated aqueous NH_4Cl was added, and the aqueous phase was extracted with CH_2Cl_2. The combined organic phases were concentrated in vacuo, and the ester and the remaining starting sulfoximine were separated by chromatography (EtOAc). The obtained functionalized sulfoximine was reduced with Raney nickel as in *GP4*, and the ester was purified by chromatography (EtOAc/cyclohexane, 4:1).

General Procedure for the Conversion of Sulfoximines into Chlorides (*GP6*): $ClCO_2Me$ (15.0 mmol) was added at room temperature to a solution of the sulfoximine (1.00 mmol) in CH_2Cl_2 (12 mL). The mixture was stirred at room temperature until TLC or GC indicated almost complete conversion of the sulfoximine. Concentration in vacuo and purification of the residue by chromatography afforded the chloride.

General Procedure for the Conversion of Chlorides into Nitriles (*GP7*): NaCN (2.00 mmol) was added at room temperature to a solution of the chloride (1.00 mmol) in DMF (15 mL), and the resulting mixture was heated with stirring at 105 °C for 2 h. After the mixture had cooled to room temperature, the solvent was removed in vacuo. The remaining solid was purified by chromatography or recrystallization.

General Procedure for the Conversion of Nitriles into Acids (*GP8*): Aqueous NaOH (2 N, 2 mL) was added to a solution of the nitrile (0.32 mmol) in EtOH (8 mL), and the mixture was heated at reflux for 3 h. After the mixture had cooled to room temperature, EtOH was removed in vacuo and the solution was acidified with aqueous 3 N HCl until a colorless solid precipitated. The mixture was then extracted with $CHCl_3$, whereupon the solid dissolved, and the combined organic phases were concentrated in vacuo. Purification by chromatography or crystallization afforded the amino acid.

(3*S*,4*R*,5*Z*)- and (3*S*,4*R*,5*E*)-4-Methyl-6-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]-5-hexen-3-yl Carbamate [(*Z*)-4a and (*E*)-4a]: Treatment of alcohol **2a** (560 mg, 2.09 mmol) with trichloroacetyl isocyanate (0.26 mL, 2.19 mmol) according to *GP1* and purification by chromatography (EtOAc) gave a mixture of carbamates (*Z*)-**4a** and (*E*)-**4a** (550 mg, 85%) in a ratio of 3:1 as a colorless solid:

Compound (*Z*)-4a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.68 (d, *J* = 6.7 Hz, 3 H, CH*Me*), 0.93 (t, *J* = 7.4 Hz, 3 H, Et), 1.42−1.70 (m, 2 H, Et), 2.69 (s, 3 H, NMe), 3.67 (m, 1 H, C*H*Me), 4.63 (m, 1 H, CHO), 4.95 (br. s, 2 H, NH_2), 6.14 (t, *J* = 11.1 Hz, 1 H, SCH=C*H*), 6.39 (d, *J* = 11.1 Hz, 1 H, SC*H*=CH), 7.56 (m, 3 H, Ph), 7.91 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.62 (d), 15.96 (d), 26.12 (u), 29.27 (d), 35.27 (d), 78.37 (d), 128.88 (d), 129.34 (d), 131.71 (d), 132.69 (d), 146.82 (d), 140.50 (u), 157.23 (u) ppm.

Compound (*E*)-4a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84 (t, *J* = 7.4 Hz, 3 H, Et), 1.09 (d, *J* = 6.9 Hz, 3 H, CH*Me*), 1.42−1.70 (m, 2 H, Et), 2.74 (s, 3 H, NMe), 2.60 (m, 1 H, C*H*Me), 4.63 (m, 1 H, CHO), 4.82 (br. s, 2 H, NH_2), 6.39 (d, *J* = 15.0 Hz, 1 H, SC*H*=CH), 6.81 (dd, *J* = 15.0, *J* = 8.2 Hz, 1 H, SCH=C*H*), 7.56 (m, 3 H, Ph), 7.91 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.68 (d), 15.66 (d), 25.05 (u), 29.47 (d), 39.79 (d), 77.74 (d), 128.76 (d), 129.38 (d), 131.23 (d), 132.63 (d), 147.16 (d), 139.44 (u), 156.80 (u) ppm.

(2*S*,3*R*,4*Z*)-3-(1-Methylethyl)-5-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]-4-penten-2-yl Carbamate [(*Z*)-4b]: Treatment of alcohol **2b** (2.02 g, 7.18 mmol) with trichloroacetyl isocyanate (0.89 mL, 7.54 mmol) according to *GP1* and purification by crystallization (Et_2O/CH_2Cl_2, 25:1) gave carbamate (*Z*)-**4b** (2.09 g, 90%) as a colorless solid: M.p. 209 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.47 (d, *J* = 6.9 Hz, 3 H, *i*Pr), 0.80 (d, *J* = 6.7 Hz, 3 H, *i*Pr), 1.33 (d, *J* = 6.4 Hz, 3 H, Me), 1.60 (m, 1 H, *i*Pr), 2.68 (s, 3 H, NMe), 3.31 (ddd, *J* = 11.5, *J* = 6.7, *J* = 4.4 Hz, 1 H, C*H*i*Pr*), 4.78 (br. s, 2 H, NH_2), 5.04 (qd, *J* = 6.4, *J* = 4.4 Hz, 1 H, CHO) 6.13 (t, *J* = 11.5 Hz, 1 H, SCH=C*H*), 6.52 (d, *J* = 11.5 Hz, 1 H, SC*H*=CH), 7.50−7.60 (m, 3 H, Ph), 7.90 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.10 (d), 19.47 (d), 20.63 (d), 28.61 (d), 29.24 (d), 47.41 (d), 70.90 (d), 129.13 (d), 129.31 (d), 132.71 (d), 133.38 (d), 145.03 (d), 140.12 (u), 156.55 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3856 (w), 3437 (s), 3328 (s), 3290 (s), 3201 (m), 3052 (m), 2999 (m), 2966 (s), 2926 (m), 2903 (m), 2862 (s), 2792 (m), 1735 (vs), 1701 (vs), 1627 (m), 1611 (m), 1582 (w), 1474 (m), 1446 (s), 1391 (s), 1360 (s), 1333 (s), 1317 (s), 1253 (vs), 1214 (s), 1144 (vs), 1103 (s), 1081 (s), 1070 (s), 1048 (vs), 1010 (m) cm^{-1}. MS (EI): *m*/*z* (relative intensity, %) = 325 [M^+ + 1] (2), 324 [M^+] (8), 265 (10), 264 (54), 236 (17), 156 (58), 126 (16), 125 (100), 111 (14), 109 (28), 108 (23), 107 (25), 97 (22), 96 (14), 93 (35), 91 (41), 83 (19), 81 (38). $C_{16}H_{24}N_2O_3S$ (324.44): calcd. C 59.23, H 7.46, N 8.63; found C 58.77, H 7.22, N 8.75.

(2*S*,3*R*,4*Z*)- and (2*S*,3*R*,4*E*)-3-(1-Methylethyl)-5-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]-5-penten-2-yl *N*-Trichloroacetylcarbamate [(*Z*)-3b and (*E*)-3b]: Trichloroacetyl isocyanate (49 μL, 0.41 mmol) was added at 0 °C to a solution of alcohol (*Z*)-**2b** (78 mg, 0.28 mmol) in CH_2Cl_2 (8 mL). After the mixture had been stirred at 0 °C for 3.5 h, it was concentrated in vacuo to give a mixture of (*Z*)-**3b** and (*E*)-**3b** in a ratio of 11:1, together with trichloroacetyl isocyanate (^{1}H NMR). Purification by chromatography (EtOAc/hexane, 4:1) afforded a mixture of carbamates (*Z*)-**3b** and (*E*)-**3b** (75 mg, 58%) in a ratio of 6:1 as a colorless solid.

Compound (*Z*)-3b: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.63 (d, *J* = 6.7 Hz, 3 H, *i*Pr), 0.78 (d, *J* = 6.7 Hz, 3 H, *i*Pr), 1.45 (d, *J* = 6.3 Hz, 3 H, Me), 1.74 (m, 1 H, *i*Pr), 2.67 (s, 3 H, NMe), 3.52 (dt, *J* = 11.1, *J* = 6.3 Hz, 1 H, C*H*i*Pr*), 5.08 (quin, *J* = 6.3 Hz, 1 H, CHO), 6.17 (t, *J* = 11.1 Hz, 1 H, SCH=C*H*), 6.50 (d, *J* = 11.1 Hz, 1 H, SC*H*=CH), 7.54−7.66 (m, 3 H, Ph), 7.86 (m, 2 H, Ph), 9.65 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.71 (d), 18.90 (d), 21.01 (d), 28.01 (d), 29.46 (d), 47.50 (d), 73.92 (d), 77.38 (u), 129.27 (d), 129.70 (d), 133.24 (d), 133.97 (d), 143.56 (d), 139.07 (u), 150.30 (u), 158.56 (u) ppm, signal of CCl_3 was not observed.

Compound (*E*)-3b: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (d, *J* = 6.7 Hz, 3 H, *i*Pr), 0.98 (d, *J* = 6.7 Hz, 3 H, *i*Pr), 1.19 (d, *J* = 6.3 Hz, 3 H, Me), 1.85 (m, 1 H, *i*Pr), 2.06 (m, 1 H, C*H*i*Pr*), 2.77 (s, 3 H, NMe), 5.22 (quin, *J* = 6.3, *J* = 4.4 Hz, 1 H, CHO), 6.42 (d, *J* = 15.0 Hz, 1 H, SC*H*=CH), 6.78 (dd, *J* = 15.0, *J* = 10.4 Hz, 1 H, SCH=C*H*), 7.50−7.64 (m, 3 H, Ph), 7.88 (m, 2 H, Ph), 8.50 (br. s, 1 H, NH) ppm.

(+)-(3*S*,4*R*,5*Z*)-2-Methyl-6-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]-4-phenyl-5-hexen-3-yl Carbamate [(*Z*)-4c)] and (+)-(3*S*,4*R*,5*E*)-2-Methyl-6-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]-4-phenyl-5-hexen-3-yl Carbamate [(*E*)-4c]: Treatment of alcohol **2c** (1.47 g, 4.28 mmol) with trichloroacetyl isocyanate (0.53 mL, 4.49 mmol) according to *GP1* and purification by chromatography (EtOAc/*i*PrOH, 4:1) gave carbamates (*Z*)-**4c** (1.26 g, 76%) and (*E*)-**4c** (270 mg, 16%) as colorless solids.

Compound (*Z*)-4c: M.p. 46−49 °C. $[\alpha]_D$ = +68.6 (*c* = 0.60, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (d, *J* = 6.9 Hz, 3 H, *i*Pr), 0.91 (d, *J* = 6.9 Hz, 3 H, *i*Pr), 1.57 (septd, 1 H, *J* = 6.9, *J* = 3.5 Hz, *i*Pr), 2.68 (s, 3 H, NMe), 4.86 (m, 1 H, C*H*Ph), 4.97

(br. s, 2 H, NH_2), 4.98 (dd, J = 9.4, J = 3.5 Hz, 1 H, CHO), 6.39 (d, J = 11.0 Hz, 1 H, SC*H*=CH), 6.47 (dd, J = 11.0, J = 11 Hz,1 H, SCH=*CH*), 6.93−6.96 (m, 2 H, Ph), 7.15−7.21 (m, 3 H, Ph), 7.43−7.57 (m, 3 H, Ph), 7.82−7.86 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.52 (d), 19.75 (d), 28.90 (d), 29.18 (d), 45.03 (d), 79.82 (d), 126.96 (d), 127.66 (d), 128.58 (d), 128.60 (d), 128.97 (d), 131.17 (d), 132.32 (d), 138.16 (u), 139.90 (u), 144.98 (d), 157.16 (u) ppm. IR (KBr): ṽ = 3428 (m), 3356 (m), 3171 (w), 3061 (w), 3030 (w), 2965 (m), 2935 (m), 2875 (m), 2803 (w), 1724 (s), 1600 (m), 1495 (m), 1448 (m), 1390 (s), 1331 (m), 1305 (m), 1246 (s), 1214 (m), 1184 (w), 1147 (s), 1110 (m), 1080 (m), 1041 (s) cm^{-1}. MS (EI): *m*/*z* (relative intensity, %) = 387 [M^+ + 1] (4), 386 (16), 343 (35), 326 (32), 300 (10), 271 (18), 171 (42), 170 (97), 156 (43), 155 (60), 146 (11), 145 (21), 144 (21), 143 (17), 129 (15), 128 (11), 127 (13), 125 (68), 118 (12), 117 (77), 116 (28), 115 (100), 109 (19), 97 (13), 91 (32). $C_{21}H_{26}N_2O_3S$ (386.51): calcd.C 65.26, H 6.78, N 7.25; found C 64.97, H 6.79, N 7.24.

Compound (*E*)-4c: M.p. 56−58 °C. $[\alpha]_D$ +62.1 (c = 0.38, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.81 (d, J = 6.7 Hz, 3 H, *i*Pr), 0.82 (d, J = 6.7 Hz, 3 H, *i*Pr), 1.57 (septd, 1 H, J = 6.7, J = 3.7 Hz, *i*Pr), 2.70 (s, 3 H, NMe), 3.65 (7, J = 9.1, 1 H, C*H*Ph), 4.64 (s, 2 H, NH_2), 5.00 (dd, J = 9.1, J = 3.7 Hz, 1 H, CHO), 6.35 (dd, J = 15.1, J = 0.8 Hz, 1 H, SC*H*=CH), 7.04 (dd, J = 15.1, J = 9.1 Hz, 1 H, SCH=C*H*), 7.19−7.34 (m, 5 H, Ph), 7.48−7.56 (m, 3 H, Ph), 7.85−7.89 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.39 (d), 19.62 (d), 28.99 (d), 29.30 (d), 50.88 (d), 78.97 (d), 127.36 (d), 127.93 (d), 128.64 (d), 128.91 (d), 129.04 (d), 131.39 (d), 132.33 (d), 137.94 (u), 138.97 (u), 145.75 (d), 156.34 (u) ppm. IR (KBr): ṽ = 3840 (m), 3426 (s), 3060 (w), 3030 (w), 2965 (m), 2935 (m), 2875 (m), 2804 (w), 2373 (w), 1725 (s), 1602 (m), 1563 (w), 1545 (w), 1496 (w), 1448 (m), 1385 (s), 1331 (m), 1243 (s), 1184 (w), 1150 (m), 1109 (w), 1081 (w), 1040 (s) cm^{-1}. MS (EI): *m*/*z* (relative intensity, %) = 387 [M^+ + 1] (3), 386 (17), 271 (18), 270 (33), 261 (10), 248 (14), 225 (24), 200 (42), 193 (12), 191 (10), 171 (24), 170 (32), 158 (24), 156 (23), 146 (14), 145 (44), 144 (60), 125 (62), 117 (28), 116 (39), 115 (100), 107 (19), 106 (10), 91 (38). $C_{21}H_{26}N_2O_3S$ (386.51): calcd. C 65.26, H 6.78, N 7.25; found C 65.00, H 6.87, N 7.02.

(+)-(4*S*,5*R*,6*S*)-Tetrahydro-6-ethyl-5-methyl-4-{[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]methyl}-2*H*-1,3-oxazin-2-one (5a): Treatment of a mixture of carbamates (*Z*)-**4a** and (*E*)-**4a** (928 mg, 2.99 mmol, in a ratio of 3:1) with *n*BuLi (2.43 mL of 1.60 M in hexane, 3.89 mmol) according to *GP2* and purification by crystallization (Et_2O) gave oxazinone **5a** (863 mg, 93%) as a colorless solid. M.p. 240 °C, $[\alpha]_D$ = +179.1 (c = 0.45, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.75 (d, J = 6.7 Hz, 3 H, CH*Me*), 0.99 (t, J = 7.4 Hz, 3 H, Et), 1.53 (m, 2 H, CH*Me*, Et), 1.80 (dqd, J = 14.4, J = 7.4, J = 3.0 Hz, 1 H, Et), 2.71 (s, 3 H, NMe), 3.09 (dd, J = 14.0, J = 10.3 Hz, 1 H, CH_2S), 3.26 (dd, J = 14.0, J = 1.0 Hz, 1 H, CH_2S), 3.31 (td, J = 10.3, J = 1.0 Hz, 1 H, C*H*NH), 3.85 (ddd, J = 10.0, J = 7.4, J = 3.0 Hz, 1 H, CHO), 7.48 (s, 1 H, NH), 7.60−7.72 (m, 3 H, Ph), 7.86 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.24 (d), 12.61 (d), 24.93 (u), 29.32 (d), 34.63 (d), 52.74 (d), 59.66 (u), 81.11 (d), 129.44 (d), 129.98 (d), 133.80 (d), 136.89 (u), 153.20 (u) ppm. IR (KBr): ṽ = 3271 (s), 3061 (w), 2973 (m), 2929 (m), 2877 (m), 2802 (w), 1710 (vs), 1581 (w), 1529 (w), 1469 (s), 1445 (s), 1418 (m), 1403 (m), 1386 (m), 1362 (m), 1341 (m), 1310 (m), 1271 (m), 1242 (vs), 1143 (vs), 1106 (s), 1078 (s), 1018 (s) cm^{-1}. MS (EI): *m*/*z* (relative intensity, %) = 311 [M^+ + 1] (2), 282 (12), 281 (21), 157 (13), 156 (75), 154 (14), 140 (42), 126 (18), 125 (100), 112 (26), 107 (39), 106 (27), 105 (38), 98 (10), 97 (24), 96 (32), 95 (24), 94 (15), 91 (31), 88 (40), 83 (11), 82 (18), 81 (10). $C_{15}H_{22}N_2O_3S$ (310.41): calcd. C 58.04, H 7.14, N 9.02; found C 57.86, H 7.05, N 8.97.

(+)-(4*S*,5*R*,6*S*)-Tetrahydro-6-methyl-5-(1-methylethyl)-4-{[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]methyl}-2*H*-1,3-oxazin-2-one (5b): Treatment of carbamate **4b** (1.63 g, 5.02 mmol) with *n*BuLi (4.10 mL of 1.60 M in hexane, 6.56 mmol) according to *GP2* and purification by crystallization (Et_2O) gave oxazinone **5b** (1.54 g, 94%) as a colorless solid. M.p. 113 °C, $[\alpha]_D$ = +130.5 (c = 0.55, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.66 (d, J = 7.1 Hz, 3 H, *i*Pr), 0.79 (d, J = 7.1 Hz, 3 H, *i*Pr), 1.32 (m, 1 H, C*H*iPr), 1.35 (d, J = 6.2 Hz, 3 H, Me), 1.63 (m, 1 H, *i*Pr), 2.73 (s, 3 H, NMe), 3.14−3.26 (m, 2 H, CH_2S), (td, J = 8.5, J = 2.7 Hz, 1 H, C*H*NH), 4.15 (dq, J = 9.4, J = 6.2 Hz, 1 H, CHO), 7.22 (s, 1 H, NH), 7.60−7.73 (m, 3 H, Ph), 7.87 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.80 (d), 18.98 (d), 20.02 (d), 27.29 (d), 29.20 (d), 47.42 (d), 48.16 (d), 62.21 (u), 74.30 (d), 129.35 (d), 129.90 (d), 133.69 (d), 137.13 (u), 154.03 (u) ppm. IR (KBr): ṽ = 3451 (m), 3241 (s), 3156 (s), 3046 (m), 3007 (m), 2971 (vs), 2930 (s), 2899 (s), 2874 (s), 2809 (m), 1733 (vs), 1579 (m), 1551 (w), 1465 (m), 1445 (s), 1425 (m), 1414 (m), 1394 (s), 1385 (s), 1369 (m), 1354 (m), 1345 (m), 1321 (m), 1294 (s), 1232 (s), 1187 (m), 1173 (m), 1157 (s), 1147 (s), 1127 (m), 1110 (s), 1079 (s), 1066 (s), 1045 (m), 1007 (m) cm^{-1}. MS (EI): *m*/*z* (relative intensity, %) = 325 [M^+ + 1] (3), 296 (10), 295 (15), 171 (10), 170 (62), 156 (20), 154 (12), 140 (48), 128 (16), 127 (27), 126 (39), 125 (100), 112 (29), 110 (20), 109 (37), 107 (41), 106 (30), 105 (14), 97 (27), 94 (16), 91 (34), 88 (25), 84 (23), 83 (50), 82 (22), 81 (10). $C_{16}H_{24}N_2O_3S$ (324.44): calcd. C 59.23, H 7.46, N 8.63; found C 58.89, H 7.46, N 8.63.

(+)-(4*S*,5*R*,6*S*)-Tetrahydro-6-(1-methylethyl)-4-{[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]methyl}-5-phenyl-2*H*-1,3-oxazin-2-one (5c). From Carbamate (*Z*)-4c: Treatment of carbamate (*Z*)-**4c** (1.63 g, 4.21 mmol) with *n*BuLi (2.76 mL of 1.60 M in hexane, 4.42 mmol) according to *GP2* and purification by crystallization (EtOAc/*i*PrOH, 1:1) and chromatography (EtOAc) of the remaining mother liquor gave oxazinone **5c** (1.34 g, 83%) as a colorless solid, together with sulfoximine **1c** (20 mg, 2%).

From Carbamate (*E*)-4c: Treatment of carbamate (*E*)-**4c** (221 mg, 0.57 mmol) with *n*BuLi (0.37 mL of 1.60 M in hexane, 0.60 mmol) according to *GP2* and purification by crystallization (EtOAc/*i*PrOH, 1:1) and chromatography (EtOAc) of the mother liquor gave oxazinone **5c** (183 mg, 82%) as a colorless solid, together with sulfoximine **1c** (5 mg, 3%).

5c: M.p. 180 °C (dec.). $[\alpha]_D$ = +98.6 (c = 0.70, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83 (d, J = 6.9 Hz, 3 H, *i*Pr), 0.96 (d, J = 6.9 Hz, 3 H, *i*Pr), 1.40 (septd, J = 6.9, J = 1.7 Hz, 1 H, *i*Pr), 2.62 (t, J = 10.6 Hz, 1 H, C*H*Ph), 2.71 (s, 3 H, NMe), 2.76 (dd, J = 14.1, J = 1.2 Hz, 1 H, CH_2S), 3.06 (dd, J = 14.1, J = 10.7 Hz, 1 H, CH_2S), 3.65 (ddd, J = 10.7, J = 10.6, J = 1.2 Hz, 1 H, C*H*NH), 4.20 (dd, J = 10.6, J = 1.7 Hz, 1 H, CHO), 6.75−6.78 (m, 2 H, Ph), 7.12−7.24 (m, 3 H, Ph), 7.49−7.56, 7.60−7.67 (m, 6 H, Ph, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.12 (d), 20.01 (d), 29.04 (d), 29.58 (d), 46.43 (d), 52.93 (d), 58.83 (u), 84.01 (d), 127.97 (d), 128.49 (d), 129.41 (d), 129.60 (d), 129.85 (d), 133.65 (d), 134.97 (u), 136.51 (u), 153.12 (u) ppm. IR (KBr): ṽ = 3822 (s), 3278 (m), 3089 (w), 3066 (w), 3028 (w), 3003 (w), 2969 (m), 2916 (m), 2880 (m), 2809 (w), 2734 (w), 2659 (w), 2579 (w), 2373 (w), 2343 (w), 2183 (w), 2106 (w), 2001 (w), 1956 (w), 1931 (w), 1906 (w), 1708 (s), 1604 (m), 1583 (m), 1525 (w), 1497 (w), 1449 (s), 1420 (w), 1373 (m), 1326 (m), 1298 (w), 1246 (s), 1143 (s), 1105 (m), 1080 (m), 1037 (m), 1001 (w) cm^{-1}. MS (CI): *m*/*z* (relative intensity, %) = 387 [M^+ + 1] (29), 235 (13), 234 (69), 233 (15), 132 (74), 156

(100). $C_{21}H_{26}N_2O_3S$ (386.51): calcd. C 65.26, H 6.78, N 7.25; found C 65.09, H 6.84, N 7.17.

(+)-(3*S*,4*R*,5*Z*)-2,5-Dimethyl-6-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]-4-phenyl-5-hexen-3-ol [(*Z*)-7]: *n*BuLi (10.7 mL of 1.60 M in hexane, 17.0 mmol) was added at −78 °C to a solution of the allylic sulfoximine (*E*)-**6** (4.42 g, 15.5 mmol) in THF (85 mL). After the mixture had been stirred at this temperature for 10 min, $ClTi(OiPr)_3$ (4.44 mL, 18.6 mmol) was added. The mixture was then stirred at −78 °C for 10 min, allowed to warm to 0 °C, and stirred at this temperature for 45 min. Subsequently, the mixture was cooled to −78 °C and isobutyraldehyde (2.8 mL, 31.0 mmol) was added dropwise. After the mixture had been stirred at −78 °C for 80 min, it was poured into saturated aqueous $(NH_4)_2CO_3$ and extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification by chromatography (EtOAc/cyclohexane, 4:1) gave alcohol (*Z*)-**7** (3.27 g, 59%) as a colorless solid, together with sulfoximine (*E*)-**6** (1.01 g, 25%). M.p. 105 °C. $[\alpha]_D$ = +194.7 (*c* = 1.02, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.90 (d, *J* = 6.9 Hz, 3 H, *i*Pr), 1.05 (d, *J* = 6.9 Hz, 3 H, *i*Pr), 1.68 (septd, *J* = 7.3, *J* = 1.1 Hz, 1 H, *i*Pr), 1.74 (d, *J* = 1.4 Hz, 3 H, Me), 2.64 (s, 3 H, NMe), 4.10 (dd, *J* = 11.1, *J* = 1.3 Hz, 1 H, CHO), 5.04 (br. s, 1 H, OH), 5.21 (d, *J* = 11.1 Hz, 1 H, C*H*Ph), 6.32 (p, *J* = 1.1 Hz, 1 H, C=CH), 7.00−7.03 (m, 2 H, Ph), 7.17−7.28 (m, 3 H, Ph), 7.57−7.68 (m, 3 H, Ph), 7.94−7.98 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.80 (d), 19.64 (d), 20.94 (d), 29.36 (d), 29.74 (d), 50.68 (d), 74.74 (d), 126.87 (d), 128.34 (d), 128.82 (d), 128.90 (d), 128.94 (d), 129.29 (d), 132.66 (d), 138.00 (u), 139.59 (u), 156.94 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3222 (m), 3067 (m), 3032 (w), 2960 (s), 2935 (m), 2903 (s), 2869 (s), 2769 (m), 2319 (w), 1619 (m), 1601 (m), 1582 (w), 1494 (m), 1467 (m), 1444 (s), 1385 (m), 1298 (w), 1217 (s), 1159 (m), 1139 (s), 1100 (s), 1079 (s), 1034 (m), 1009 (m) cm^{-1}. MS (EI): *m*/*z* (relative intensity, %) = 358 [M^+ + 1] (5), 314 (42), 206 (14), 205 (18), 202 (12), 185 (12), 184 (54), 160 (15), 159 (65), 158 (13), 156 (73), 132 (12), 131 (100), 130 (30), 129 (57), 128 (23), 127 (11), 125 (79), 116 (12), 115 (33), 91 (40). $C_{21}H_{27}NO_2S$ (357.51): calcd. C 70.55, H 7.61, N 3.92; found C 70.88, H 7.63, N 3.89.

(+)-(3*S*,4*R*,5*Z*)-2,5-Dimethyl-6-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]-4-phenyl-5-hexen-3-yl Carbamate [(*Z*)-8]: Treatment of alcohol (*Z*)-**7** (4.21 g, 11.78 mmol) with trichloroacetyl isocyanate (1.47 mL, 12.37 mmol) according to *GP1* and purification by chromatography (EtOAc/*i*PrOH, 8:1) gave carbamate (*Z*)-**8** (4.31 g, 89%) as a colorless solid, together with the corresponding *N*-trichloroacetyl carbamate (450 mg, 7%). M.p. 62−64 °C. $[\alpha]_D$ = +169.1 (*c* = 0.72, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.90 (d, *J* = 6.9 Hz, 3 H, *i*Pr), 0.96 (d, *J* = 6.9 Hz, 3 H, *i*Pr), 1.75 (septd, *J* = 6.9, *J* = 1.8 Hz, 1 H, *i*Pr), 1.81 (d, *J* = 1.1 Hz, 3 H, Me), 2.68 (s, 3 H, NMe), 5.15 (br. s, 2 H, NH_2), 5.31 (d, *J* = 11.1 Hz, 1 H, C*H*Ph), 5.38 (dd, *J* = 11.1, *J* = 1.8 Hz, 1 H, CHO), 6.25 (d, *J* = 1.4 Hz, 1 H, C=CH), 6.84−6.87 (m, 2 H, Ph), 7.16−7.18 (m, 3 H, Ph), 7.57−7.66 (m, 3 H, Ph), 7.97−7.99 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.76 (d), 20.01 (d), 20.88 (d), 29.07 (d), 29.18 (d), 46.66 (d), 75.86 (d), 126.99 (d), 128.17 (d), 128.34 (d), 128.83 (d), 128.91 (d), 129.27 (d), 132.36 (d), 137.36 (u), 140.42 (u), 154.59 (u), 157.32 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3421 (s), 3357 (s), 3179 (m), 3061 (m), 3030 (m), 2965 (s), 2932 (m), 2875 (m), 2803 (w), 1724 (s), 1615 (s), 1601 (s), 1496 (m), 1467 (m), 1446 (s), 1393 (s), 1383 (s), 1334 (m), 1308 (m), 1236 (s), 1147 (s), 1105 (s), 1081 (s), 1047 (s), 1001 (w) cm^{-1}. MS (EI): *m*/*z* (relative intensity, %) = 401 [M^+ + 1] (3), 185 (24), 184 (100), 169 (30), 159 (17), 156 (25), 141 (11), 131 (12), 129 (25), 128 (16), 125 (23), 115 (11), 191 (14). $C_{22}H_{28}N_2O_3S$ (400.54): calcd. C 65.67, H 7.05, N 6.99; found C 65.63, H 7.12, N 6.91.

***N*-Trichloroacetyl Carbamate:** ^1H NMR (400 MHz, $CDCl_3$): δ = 0.94 (d, *J* = 6.9 Hz, 3 H, *i*Pr), 0.99 (d, *J* = 7.1 Hz, 3 H, *i*Pr), 1.72 (d, *J* = 1.4 Hz, 3 H, Me), 1.87 (septd, *J* = 6.9, *J* = 1.9 Hz, 1 H, *i*Pr), 2.73 (s, 3 H, NMe), 5.39 (dd, *J* = 11.0, *J* = 1.9 Hz, 1 H, CHO), 5.62 (d, *J* = 11.0 Hz, 1 H, CHPh), 6.19 (d, *J* = 1.4 Hz, 1 H, C=CH), 7.05−7.09 (m, 2 H, Ph), 7.20−7.29 (m, 3 H, Ph), 7.56−7.66 (m, 3 H, Ph), 7.94−7.98 (m, 2 H, Ph), 9.24 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.71 (d), 20.20 (d), 20.65 (d), 29.01 (d), 29.22 (d), 46.23 (d), 77.78 (d), 127.22 (d), 128.50 (d), 128.55 (d), 128.87 (d), 128.92, (d), 129.35 (d), 132.51 (d), 136.90 (u), 139.69 (u), 152.57 (u), 154.17 (u), 154.62 (u) ppm, signal of CCl_3 was not observed.

(+)-(4*S*,5*R*,6*S*)-Tetrahydro-4-methyl-6-(1-methylethyl)-4-{[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]methyl}-5-phenyl-2*H*-1,3-oxazin-2-one (9): Treatment of carbamate (*Z*)-**8** (2.19 g, 5.47 mmol) with *n*BuLi (3.76 mL of 1.60 M in hexane, 6.02 mmol) according to *GP2* and purification by crystallization (Et_2O) and chromatography (EtOAc/*i*PrOH, 8:1) of the mother liquor gave oxazinone **9** as a colorless solid (1.83 g, 84%), together with the allylic sulfoximine (*E*)-**6** (160 mg, 10%). M.p. 178 °C. $[\alpha]_D$ = +59.8 (*c* = 1.01, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.75 (d, *J* = 7.0 Hz, 3 H, *i*Pr), 1.05 (d, *J* = 7.0 Hz, 3 H, *i*Pr), 1.52−1.59 (m, 1 H, *i*Pr), 1.53 (s, 3 H, Me), 2.64 (s, 3 H, NMe), 3.03 (d, *J* = 11.4 Hz, 1 H, C*H*Ph), 3.19 (d, *J* = 14.3 Hz, 1 H, CH_2S), 3.25 (d, *J* = 14.3 Hz, 1 H, CH_2S), 4.66 (dd, *J* = 11.4, *J* = 1.8 Hz, 1 H, CHO), 7.10−7.12 (m, 2 H, Ph), 7.30−7.36 (m, 3 H, Ph), 7.71 (br. s, 1 H, NH), 7.54−7.65 (m, 3 H, Ph), 7.78−7.82 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.43 (d), 19.78 (d), 23.90 (d), 28.79 (d), 28.59 (d), 50.85 (d), 56.53 (u), 64.83 (u), 79.42 (d), 128.15 (d), 128.54 (d), 128.77 (d), 129.54 (d), 133.12 (d), 133.76 (u), 139.45 (u), 154.59 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3676 (m), 3653 (w), 3404 (s), 3067 (w), 3027 (w), 2971 (s), 2930 (m), 2878 (m), 2806 (m), 2285 (w), 1978 (w), 1706 (s), 1607 (m), 1583 (m), 1498 (m), 1459 (s), 1426 (s), 1390 (s), 1361 (m), 1333 (s), 1304 (m), 1240 (s), 1226 (s), 1184 (s), 1136 (s), 1097 (s), 1046 (s) cm^{-1}. MS (CI): *m*/*z* (relative intensity, %) = 401 [M^+ + 1] (13), 249 (18), 248 (85), 246 (30), 156 (100). $C_{22}H_{28}N_2O_3S$ (400.54): calcd. C 65.97, H 7.05, N 6.99; found C 65.90, H 6.72, N 6.92.

(+)-(*S*)-*S*-[(1*Z*,3*R*,4*S*)-2,5-dimethyl-3-phenyl-4-(triethylsilyloxy)hex-1-enyl]-*N*-methyl-*S*-phenylsulfoximine [(*Z*)-10]: Imidazole (1.34 g, 19.65 mmol) and $ClSiEt_3$ (1.0 mL, 5.9 mmol) were successively added at room temperature to a solution of alcohol (*Z*)-**7** (1.76 g, 4.92 mmol) in DMF (35 mL). After the mixture had been stirred at room temperature for 12 h, half-saturated aqueous $NaHCO_3$ was added and the resulting mixture was extracted with diethyl ether. The combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. Chromatography (EtOAc/cyclohexane, 1:1) gave silyl ether (*Z*)-**10** (2.30 g, 99%) as a colorless oil. $[\alpha]_D$ = +123.6 (*c* = 2.04, EtOAc). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.55 (q, *J* = 8.0 Hz, 6 H, Et), 0.80 (d, *J* = 6.9 Hz, 3 H, *i*Pr), 0.93 (t, *J* = 8.0 Hz, 9 H, Et), 1.02 (d, *J* = 6.9 Hz, 3 H, *i*Pr), 1.66 (septd, *J* = 6.9, *J* = 3.1 Hz, 1 H, *i*Pr), 1.96 (d, *J* = 1.4 Hz, 3 H, Me), 2.74 (s, 3 H, NMe), 4.21 (dd, *J* = 8.7, *J* = 3.2 Hz, 1 H, CHO), 5.33 (qd, *J* = 8.7 Hz, 1 H, C*H*Ph), 6.11 (q, *J* = 1.1 Hz, 1 H, C=CH), 6.98−7.02 (m, 2 H, Ph), 7.10−7.16 (m, 3 H, Ph), 7.35−7.44 (m, 3 H, Ph), 7.46−7.51 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 5.93 (u), 7.59 (d), 17.15 (d), 20.46 (d), 22.41 (d), 29.72 (d), 32.47 (d), 47.63 (d), 78.78 (d), 126.67 (d), 128.48 (d), 128.60 (d), 128.81 (d), 128.98 (d), 129.10 (d), 132.22 (d), 139.81 (u), 141.13 (u), 156.26 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3060 (m), 3027 (w), 2958 (s), 2912 (s), 2876 (s), 2802 (m), 1614 (m), 1600 (m), 1583 (w), 1582 (w), 1494 (w), 1446 (m), 1415 (w), 1385 (w), 1373 (w), 1243 (s), 1182 (w), 1147 (s), 1107 (s), 1079 (s), 1010 (s) cm^{-1}. MS (EI): *m*/*z*

(relative intensity, %) = 471 [M^+] (1), 442 (24), 429 (17), 428 (56), 316 (17), 301 (14), 287 (21), 274 (10), 273 (43), 206 (11), 205 (14), 187 (16), 185 (22), 184 (55), 159 (17), 156 (27), 129 (19), 125 (11), 116 (12), 115 (100), 103 (19). CI 472 [M^+ + 1] (100). $C_{27}H_{41}NO_2SSi$ (471.77): calcd. C 68.74. H 8.76, N 2.97; found C 68.36, H 8.93, N 3.15.

(+)-(*S*)-*S*-[(1*E*,3*R*,4*S*)-2,5-Dimethyl-3-phenyl-4-(triethylsilyloxy)-1-hexenyl]-*N*-methyl-*S*-phenylsulfoximine [(*E*)-10]: MeLi (0.40 mL of 1.60 M in Et_2O, 0.64 mmol) was added at −78 °C to a solution of silyl ether (*Z*)-**10** (200 mg, 0.42 mmol) in Et_2O (20 mL). The mixture was warmed to −35 °C and stirred at this temperature for 2 h. It was then cooled to −78 °C, and saturated aqueous NH_4Cl was added. The aqueous phase was extracted with diethyl ether and the combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. Chromatography (EtOAc/cyclohexane, 1:1) afforded silyl ether (*E*)-**10** (186 mg, 93%) as a colorless oil. $[\alpha]_D$ = +27.4 (*c* = 0.90, Et_2O). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.30−0.46 (m, 6 H, Et), 0.73 (d, *J* = 6.7 Hz, 3 H, *i*Pr), 0.82 (t, *J* = 8.0 Hz, 9 H, Et), 0.89 (d, *J* = 6.7 Hz, 3 H, *i*Pr), 1.68−1.73 (m, 1 H, *i*Pr), 1.99 (d, *J* = 1.1 Hz, 3 H, Me), 2.64 (s, 3 H, NMe), 3.42 (d, *J* = 7.4 Hz, 1 H, C*H*Ph), 4.02 (dd, *J* = 7.4, *J* = 4.0 Hz, 1 H, CHO), 6.70 (br. s, 1 H, C=CH), 7.07−7.11 (m, 2 H, Ph), 7.16−7.26 (m, 3 H, Ph), 7.46−7.56 (m, 3 H, Ph), 7.86−7.89 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 5.55 (u), 7.35 (d), 17.03 (d), 17.74 (d), 20.48 (d), 29.54 (d), 31.92 (d), 59.70 (d), 79.47 (d), 127.251 (d), 128.343 (d), 128.75 (d), 128.84 (d), 128.94 (d), 129.16 (d), 132.35 (d), 139.94 (u), 140.90 (u), 156.19 (u) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3061 (m), 3026 (m), 2957 (s), 2912 (s), 2876 (s), 2801 (m), 2732 (w), 1626 (m), 1600 (w), 1584 (w), 1494 (w), 1448 (m), 1416 (m), 1382 (m), 1243 (s), 1145 (s), 1106 (s), 1080 (s), 1009 (s) cm^{-1}. MS (EI): *m*/*z* (relative intensity, %) = 272 [M^+ + 1] (3), 442 (21), 428 (10), 287 (12), 286 (11), 285 (50), 273 (24), 270 (10), 245 (11), 244 (26), 237 (17), 214 (17), 206 (38), 205 (43), 187 (55), 185 (14), 184 (15), 160 (17), 159 (56), 158 (14), 157 (11), 156 (24), 143 (10), 131 (17), 130 (29), 129 (40), 128 (15), 125 (19), 116 (15), 115 (100), 103 (23), 91 (16), 87 (69). $C_{27}H_{41}NO_2SSi$ (471.77): calcd. C 68.74, H 8.76, N 2.97; found C 68.40, H 8.71, N 3.19.

(+)-(3*S*,4*R*,5*E*)-2,5-Dimethyl-6-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]-4-phenyl-5-hexen-3-ol [(*E*)-7]: Aqueous HCl (0.15 M, 13 mL) was added at room temperature to a vigorously stirred solution of the silyl ether (*E*)-**10** (1.06 g, 2.25 mmol) in THF (15 mL) and acetic acid (3 mL). Stirring of the mixture was continued at this temperature for 2 h. The mixture was then neutralized by the addition of saturated aqueous $NaHCO_3$ and extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Chromatography (EtOAc/cyclohexane, 4:1) afforded alcohol (*E*)-**7** (660 mg, 82%) as a colorless solid. M.p. 135 °C. $[\alpha]_D$ = +4.0 (*c* = 0.60, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.81 (d, *J* = 7.0 Hz, 3 H, *i*Pr), 0.92 (d, *J* = 7.0 Hz, 3 H, *i*Pr), 1.51 (septd, *J* = 7.0, *J* = 2.8 Hz, 1 H, *i*Pr), 1.89 (d, *J* = 1.1 Hz, 3 H, Me), 2.60 (br. s, 1 H, OH), 2.65 (s, 3 H, NMe), 3.41 (d, *J* = 9.9 Hz, 1 H, C*H*Ph), 3.96 (dd, *J* = 9.9, *J* = 2.8 Hz, 1 H, CHO), 6.74 (br. s, 1 H, C=CH), 7.09−7.13 (m, 2 H, Ph), 7.18−7.28 (m, 3 H, Ph), 7.46−7.55 (m, 3 H, Ph), 7.89−7.92 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.16 (d), 16.78 (d), 20.52 (d), 29.22 (d), 29.27 (d), 59.42 (d), 75.16 (d), 127.12 (d), 127.40 (d), 128.18 (d), 128.37 (d), 128.54 (d), 128.83 (d), 132.00 (d), 138.21 (u), 140.26 (u), 156.17 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3676 (w), 3652 (w), 3400 (m), 3256 (m), 3062 (w), 3039 (w), 2967 (s), 2930 (m), 2905 (m), 2873 (m), 2802 (m), 2370 (w), 2343 (w), 1736 (w), 1703 (w), 1617 (m), 1493 (m), 1465 (m), 1446 (s), 1381 (m), 1335 (w), 1302 (m), 1229 (s), 1135 (s), 1108 (s), 1083 (s), 1004 (s) cm^{-1}. MS (CI): *m*/*z* (relative intensity, %) = 358 [M^+ + 1] (41), 287 (14), 286 (69), 187 (11), 160 (18), 156 (100), 140 (12), 133 (29), 132 (38), 131 (50), 129 (13). $C_{21}H_{27}NO_2S$ (357.51): calcd. C 70.55, H 7.61, N 3.92; found C 70.55, H 7.75, N 3.78.

(+)-(3*S*,4*R*,5*E*)-2,5-Dimethyl-6-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]-4-phenyl-5-hexen-3-yl Carbamate [(*E*)-8]: Treatment of alcohol (*E*)-**7** (418 mg, 1.17 mmol) in THF (15 mL) with trichloroacetyl isocyanate (0.15 mL, 1.23 mmol) according to *GP1* and purification by chromatography (EtOAc/*i*PrOH, 8:1) gave carbamate (*E*)-**8** (443 mg, 95%) as a colorless solid. M.p. 64−70 °C. $[\alpha]_D$ = +23.6 (*c* = 0.95, Et_2O). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.77 (d, *J* = 6.9 Hz, 3 H, *i*Pr), 0.87 (d, *J* = 6.9 Hz, 3 H, *i*Pr), 1.70 (septd, *J* = 6.9, *J* = 2.7 Hz, 1 H, *i*Pr), 1.88 (d, *J* = 0.8 Hz, 3 H, Me), 2.67 (s, 3 H, NMe), 3.59 (d, *J* = 10.5 Hz, 1 H, C*H*Ph), 4.69 (s, 2 H, NH_2), 5.28 (dd, *J* = 10.5, *J* = 2.7 Hz 1 H, CHO), 6.61 (br. d, *J* = 0.8 Hz, 1 H, C=CH), 7.16−7.19 (m, 2 H, Ph), 7.21−7.31 (m, 3 H, Ph), 7.47−7.56 (m, 3 H, Ph), 7.89−7.92 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.88 (d), 14.98 (d), 19.94 (d), 29.14 (d), 29.18 (d), 57.86 (d), 76.14 (d), 127.43 (d), 127.92 (d), 128.40 (d), 128.43 (d), 128.61 (d), 128.81 (d), 132.05 (d), 137.05 (u), 140.34 (u), 154.73 (u), 156.31 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3428 (m), 3175 (w), 3061 (w), 3029 (w), 2965 (m), 2934 (m), 2874 (m), 2802 (w), 1724 (s), 1620 (m), 1496 (m), 1448 (m), 1389 (s), 1333 (s), 1236 (s), 1144 (s), 1107 (s), 1081 (m), 1043 (s) cm^{-1}. MS (EI): *m*/*z* (relative intensity, %) = 401 [M^+ + 1] (3), 400 (30), 340 (40), 298 (14), 285 (12), 265 (32), 260 (19), 259 (14), 237 (18), 236 (14), 217 (11), 214 (17), 206 (40), 205 (52), 204 (11), 194 (11), 185 (11), 184 (23), 183 (10), 172 (12), 169 (28), 159 (11), 158 (30), 157 (11), 156 (33), 145 (31), 143 (18), 142 (100), 141 (21), 131 (24), 130 (47), 129 (100), 128 (64), 127 (18), 126 (11), 125 (64), 117 (16), 116 (11), 115 (43), 109 (12), 107 (10), 105 (25), 103 (10), 97 (10), 91 (72). $C_{22}H_{28}N_2O_3S$ (400.54): calcd. C 65.97, H 7.05, N 6.99; found C 65.82, H 7.21, N 6.94.

(+)-(4*S*,5*R*,6*S*)- and (−)-(4*R*,5*R*,6*S*)-Tetrahydro-4-methyl-6-(1-methylethyl)-4-{[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]-methyl}-5-phenyl-2*H*-1,3-oxazin-2-one (9 and *epi*-9): Treatment of carbamate (*E*)-**8** (453 mg, 1.13 mmol) with *n*BuLi (0.78 mL of 1.60 M in hexane, 1.24 mmol) according to *GP2* and purification by chromatography (EtOAc/*i*PrOH, 8:1) gave oxazinones **9** (279 mg, 62%) and *epi*-**9** (65 mg, 14%) as colorless solids, together with (*E*)-**6** (32 mg, 10%) and (*Z*)-**6** (26 mg, 8%).

***epi*-9:** M.p. 183−187 °C. $[\alpha]_D$ = −63.4 (*c* = 0.55, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.75 (d, *J* = 7.0 Hz, 3 H, *i*Pr), 1.03 (d, *J* = 7.0 Hz, 3 H, *i*Pr), 1.62 (septd, *J* = 7.0, *J* = 1.8 Hz, 1 H, *i*Pr), 1.67 (s, 3 H, Me), 2.59 (s, 3 H, NMe), 2.97 (m, 2 H, CH_2S), 3.56 (d, *J* = 13.7 Hz, 1 H, C*H*Ph), 4.46 (dd, *J* = 11.4, *J* = 1.9 Hz, 1 H, CHO), 7.02−7.03 (m, 2 H, Ph), 7.30−7.34 (m, 3 H, Ph), 7.54−7.65 (m, 4 H, Ph, NH), 7.78−7.81 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.24 (d), 19.74 (d), 27.04 (d), 28.59 (d), 29.39 (d), 53.72 (d), 56.01 (u), 63.31 (u), 79.34 (d), 128.14 (d), 128.69 (d), 128.74 (d), 129.54 (d), 132.99 (d), 133.44 (u), 138.97 (u), 152.85 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3676 (w), 3405 (m), 3060 (m), 3030 (w), 2967 (m), 2931 (m), 2875 (m), 2803 (w), 1710 (s), 1583 (w), 1498 (w), 1445 (m), 1384 (m), 1335 (w), 1302 (w), 1235 (s), 1182 (w), 1148 (m), 1105 (w), 1075 (m), 1044 (w) cm^{-1}. MS (CI): *m*/*z* (relative intensity, %) = 401 [M^+ + 1] (34), 248 (21), 247 (18), 246 (100), 156 (73). $C_{22}H_{28}N_2O_3S$ (400.54): calcd. C 65.97, H 7.05, N 6.99; found C 65.57, H 6.28, N 6.77.

(−)-(α*S*,1*R*,2*Z*)-α-(1-Methylethyl)-2-{[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]methylene}cyclopentylmethanol (13a): *n*BuLi (16.1 mL of 1.6 M in hexane, 25.7 mmol) was added at −78 °C to a solution of the allylic sulfoximine **12a** (5.77 g, 24.5 mmol) in THF (130 mL). After the mixture had been stirred at this temperature for 1 h, $ClTi(OiPr)_3$ (12.3 mL, 51.5 mmol) was added. The mixture was

then stirred at −78 °C for 1 h, allowed to warm to 0 °C, and stirred at this temperature for 2 h. Subsequently the mixture was cooled to −78 °C, and isobutyraldehyde (4.7 mL, 51.5 mmol) was added dropwise. The mixture was then allowed to warm to room temperature over a period of 5 h and was then poured into saturated aqueous $(NH_4)_2CO_3$ and extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification by chromatography (cyclohexane/EtOAc, 4:1) gave a mixture of alcohol **13a**, sulfoximine **12a**, and *N*-methyl-*S*-phenylsulfinamide in a ratio of 45:12:1. This mixture was dissolved in DMF (200 mL), and imidazole (7.06 g, 103.7 mmol) and $ClSiEt_3$ (6.4 mL, 38.4 mmol) were added successively. After the mixture had been stirred at room temperature for 12 h, half-saturated aqueous $NaHCO_3$ was added and the mixture was extracted with diethyl ether. The combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. Chromatography (EtOAc/hexane, 3:1) gave silyl ether **13a**-$SiEt_3$ (7.34 g, 71%) as a colorless oil, together with sulfoximine **12a** (750 mg, 13%). The silyl ether **13a**-$SiEt_3$ (7.34 g, 17.45 mmol) was dissolved in THF (200 mL), and acetic acid (40 mL) and aqueous HCl (0.15 M, 210 mL) were added to the vigorously stirred solution at room temperature. Stirring of the mixture was continued at this temperature for 2 h. 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. Chromatography (EtOAc) afforded alcohol **13a** (5.11 g, 68%, based on **12a**) as a colorless solid.

Compound 13a−SiEt$_3$: $[\alpha]_D = -249.5$ ($c = 0.20$, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.65−0.73 (m, 6 H, Et), 0.92 (d, J = 6.9 Hz, 3 H, *i*Pr), 0.96−1.02 (m, 12 H, Et, *i*Pr), 1.41−1.53 (m, 1 H, CH_2), 1.63−1.81 (m, 3 H, *i*Pr, CH_2), 2.06−2.16 (m, 1 H, CH_2), 2.30−2.38 (m, 1 H, CH_2), 2.51−2.63 (m, 1 H, CH_2), 2.71 (s, 3 H, NMe), 3.54−3.62 (m, 1 H, CHC=C), 4.33−4.37 (m, 1 H, CHO), 6.17−6.19 (m, 1 H), 7.49−7.58 (m, 3 H, Ph), 7.88−7.92 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 5.51 (u), 7.48 (d), 18.61 (d), 22.71 (d), 23.03 (u), 27.74 (u), 29.78 (d), 31.36 (d), 38.07 (u), 47.50 (d), 77.56 (d), 122.35 (d), 128.74 (d), 129.29 (d), 132.37 (d), 140.77 (u), 164.04 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3062 (m), 2957 (s), 2876 (s), 2801 (m), 1624 (m), 1461 (s), 1447 (s), 1416 (m), 1389 (w), 1374 (w), 1241 (s), 1152 (s), 1118 (s), 1080 (s), 1008 (s) cm^{-1}. MS (EI): *m*/*z* (relative intensity, %) = 422 [M$^+$ + 1] (2), 394 (10), 393 (31), 392 (95), 391 (93), 379 (14), 378 (56), 345 (11), 344 (47), 270 (32), 266 (13), 251 (24), 238 (16), 237 (15), 235 (74), 235 (11), 223 (19), 191 (14), 189 (14), 188 (11), 187 (67), 159 (48), 157 (15), 156 (28), 155 (27), 149 (12.84), 135 (13), 125 (15), 125 (14), 116 (14), 115 (100), 110 (11), 109 (19), 107 (17), 105 (11), 103 (33), 97 (13), 93 (10), 91 (13), 87 (86), 85 (10), 81 (14). $C_{23}H_{39}NO_2SSi$ (421.72): calcd. C 65.51, H 9.32, N 3.32; found C 65.38, H 9.23, N 3.65.

Compound 13a: M.p. 53 °C. $[\alpha]_D = -94.1$ ($c = 1.70$, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.99 (d, J = 6.9 Hz, 3 H, *i*Pr), 1.07 (d, J = 6.9 Hz, 3 H, *i*Pr), 1.61−1.89 (m, 5 H, *i*Pr, CH_2), 2.30−2.40 (m, 1 H, CH_2), 2.63 (s, 3 H, NMe), 2.64−2.74 (m, 1 H, CH_2), 3.22 (dd, J = 10.6, J = 2.0 Hz, 1 H, CHC=C), 3.87−3.93 (m, 1 H, CHO), 6.00 (br. s, 1 H, OH), 6.20−6.22 (m, 1 H, C=CH), 7.52−7.62 (m, 3 H, Ph), 7.88−7.92 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.67 (d), 21.54 (d), 21.65 (u), 29.31 (d), 30.16 (u), 31.30 (d), 34.52 (u), 46.38 (d), 77.26 (d), 123.52 (d), 128.89 (d), 129.48 (d), 132.89 (d), 139.97 (u), 164.21 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3144 (s), 3024 (w), 2957 (s), 2870 (m), 2800 (w), 1627 (s), 1582 (w), 1447 (s), 1383 (w), 1365 (w), 1289 (w), 1218 (s), 1142 (s), 1101 (s), 1077 (s), 1020 (s) cm^{-1}. MS (CI): *m*/*z* (relative intensity, %) = 308 [M$^+$ + 1] (100), 236 (43), 156 (48). $C_{17}H_{25}NO_2S$ (307.44): calcd. C 66.41, H 8.20, N 4.55; found C 66.51, H 8.36, N 4.55.

(−)-(α*S*,1*R*,2*Z*)-α-(1-Methylethyl)-2-{[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]-methylene]cyclopentylmethyl Carbamate (14a): Treatment of alcohol **13a** (2.38 g, 7.44 mmol) with trichloroacetyl isocyanate (0.96 mL, 8.13 mmol) according to *GP1* and purification by chromatography (EtOAc/*i*PrOH, 8:1) gave carbamate **14a** (2.44 g, 90%) as a colorless solid, together with the corresponding *N*-trichloroacetyl carbamate (370 mg, 10%). M.p. 45−47 °C. $[\alpha]_D = -237.7$ ($c = 1.85$, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (d, J = 6.9 Hz, 3 H, *i*Pr), 1.05 (d, J = 6.9 Hz, 3 H, *i*Pr), 1.50−1.61 (m, 1 H, CH_2), 1.63−1.70 (m, 2 H, CH_2), 1.78−1.90 (m, 1 H, CH_2), 2.00 (septd, J = 6.9, J = 3.6 Hz, 1 H, *i*Pr), 2.21−2.31 (m, 1 H, CH_2), 2.61 (s, 3 H, NMe), 2.60−2.70 (m, 1 H, CH_2), 3.90−3.97 (m, 1 H, CHC=C), 4.42 (dd, J = 10.0, J = 3.6 Hz, 1 H, CHO), 5.85 (br. s, 2 H, NH_2), 6.35 (m, 1 H, C=CH), 7.52−7.58 (m, 3 H, Ph), 7.86−7.89 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.38 (d), 20.37 (d), 20.98 (u), 29.28 (d), 29.66 (u), 30.46 (d), 34.51 (u), 42.28 (d), 76.80 (d), 122.80 (d), 128.76 (d), 128.17 (d), 132.10 (d), 139.56 (u), 158.38 (u), 161.59 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3410 (m), 3159 (m), 3062 (m), 2964 (s), 2875 (m), 2803 (m), 1723 (s), 1609 (m), 1467 (w), 1446 (m), 1380 (s), 1333 (s), 1306 (m), 1235 (s), 1152 (s), 1104 (m), 1079 (s), 1047 (s) cm^{-1}. MS (EI): *m*/*z* (relative intensity, %) = 351 [M$^+$ + 1] (2), 307 (29), 306 (81), 291 (20), 290 (100), 264 (14), 236 (13), 235 (87), 189 (12), 187 (15), 157 (12), 156 (39), 155 (37), 135 (25), 134 (26), 129 (12), 125 (60), 110 (10), 109 (26), 107 (17), 105 (11), 97 (12), 93 (11), 91 (17), 81 (16). $C_{18}H_{26}N_2O_3S$ (350.48): calcd. C 61.69, H 7.48, N 7.99; found C 61.56, H 7.48, N 7.91.

***N*-Trichloroacetyl Carbamate:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.07 (d, J = 6.9 Hz, 3 H, *i*Pr), 1.09 (d, J = 6.9 Hz, 3 H, *i*Pr), 1.55−1.88 (m, 4 H, CH_2), 2.08 (septd, 1 H, J = 6.9, J = 3.4 Hz, *i*Pr), 2.22−2.34 (m, 1 H, CH_2), 2.48−2.58 (m, 1 H, CH_2), 2.69 (s, 3 H, NMe), 4.38−4.42 (m, 1 H, C*H*C=C), 4.39 (dd, J = 10.0, J = 3.4 Hz, 1 H, CHO), 6.26 (br. d, J = 1.4 Hz, 1 H, C=CH), 7.49−7.62 (m, 3 H, Ph), 7.86−7.90 (m, 2 H, Ph), 10.43 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.49 (d), 20.41 (d), 21.39 (u), 29.10 (d), 29.93 (u), 30.82 (d), 34.53 (u), 42.03 (d), 75.86 (d), 123.29 (d), 128.89 (d), 129.27 (d), 132.33 (u), 138.71 (u), 154.66 (u), 155.18 (u), 159.78 (u) ppm, signal of CCl_3 was not observed.

(−)-(α*S*,1*R*,2*Z*)-α-(1-Methylethyl)-2-{[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]methylene}cyclohexylmethyl Carbamate (14b): Treatment of alcohol **13b** (1.26 g, 3.92 mmol) with trichloroacetyl isocyanate (0.49 mL, 4.12 mmol) according to *GP1* and purification by chromatography (EtOAc/*i*PrOH, 4:1) gave carbamate **14b** (1.29 g, 90%) as a colorless solid, together with the corresponding *N*-trichloroacetyl carbamate (190 mg, 10%). M.p. 53−55 °C, $[\alpha]_D = -210.0$ ($c = 0.20$, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 (d, J = 6.8 Hz, 3 H, *i*Pr), 0.91 (d, J = 6.8 Hz, 3 H, *i*Pr), 0.90−0.95 (m, 1 H), 1.10−1.40 (m, 3 H), 1.80−2.00 (m, 4 H), 2.50−2.60 (m, 4 H), 3.60 (dd, J = 10.5, J = 2.4 Hz, 1 H, CHC=C), 4.95 (dd, J = 10.5, J = 2.2 Hz, 1 H, CHO), 5.00 (br. s, 2 H, NH_2), 6.30 (d, J = 1.4 Hz, 1 H, C=CH), 7.45−7.55 (m, 3 H, Ph), 7.80−7.85 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.70 (d), 20.15 (d), 20.33 (d), 20.46 (u), 27.76 (u), 28.60 (d), 29.33 (d), 33.61 (u), 38.35 (d), 75.47 (d), 126.73 (d), 129.10 (d), 129.26 (d) 132.37 (d), 141.32 (u), 157.83 (u), 159.84 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3431 (s), 3356 (s), 3177 (m), 1723 (vs), 1654 (s), 1446 (s), 1240 (vs), 1148 (s) 1070 (s) cm^{-1}. MS (EI): *m*/*z* (relative intensity, %) = 365 [M$^+$ + 1] (3), 364 [M$^+$] (3), 304 (10), 116 (16), 156 (100), 149 (55), 148 (28), 133 (40), 125 (63), 123 (59), 105 (27), 91 (18). $C_{19}H_{28}N_2O_3S$ (364.50): calcd. C 62.61, H 7.69, N 7.69; found C 62.27, H 7.88, N 7.52.

***N*-Trichloroacetyl Carbamate:** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.97 (d, *J* = 6.9 Hz, 3 H, *i*Pr), 1.01 (d, *J* = 6.7 Hz, 3 H, *i*Pr), 1.21−1.54 (m, 4 H, CH_2), 1.60−1.71 (m, 2 H, CH_2), 2.02−2.07 (m, 4 H, *i*Pr, CH_2), 2.41−2.47 (m, 1 H, CH_2), 2.67 (s, 3 H, NMe), 3.95−4.05 (m, 1 H, C*H*C=CH), 5.10 (dd, *J* = 11.0, *J* = 2.1 Hz, 1 H, CHO), 6.26 (d, *J* = 1.7 Hz, 1 H, C=CH), 7.52−7.62 (m, 3 H, Ph), 7.88−7.94 (m, 2 H, Ph), 8.70 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.51 (d), 20.11 (d), 20.30 (u), 27.33 (u), 27.89 (u), 28.49 (d), 29.05 (d), 33.20 (u), 37.38 (d), 77.47 (d), 126.23 (d), 128.70 (d), 129.10 (d), 132.35 (d), 139.83 (u), 153.74 (u), 154.42 (u), 157.65 (u) ppm, signal of CCl_3 was not observed.

(+)-(4*S*,4a*R*,7a*S*)-Hexahydro-4-(1-methylethyl)-7a-{[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]methyl}cyclopenta[*d*][1,3]oxazin-2(1*H*)-one (15a): Treatment of carbamate **14a** (2.35 g, 6.71 mmol) with *n*BuLi (4.39 mL of 1.6 M in hexane, 7.02 mmol) according to *GP2* and purification by crystallization (Et_2O) and chromatography (EtOAc/*i*PrOH, 8:1) of the mother liquor gave oxazinone **15a** as a light yellow solid (1.88 g, 80%), together with sulfoximine **12a** (93 mg, 6%). M.p. 147 °C. $[\alpha]_D$ = +84.5 (*c* = 0.40, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (d, *J* = 7.0 Hz, 3 H, *i*Pr), 1.05 (d, *J* = 7.0 Hz, 3 H, *i*Pr), 1.46−1.54 (m, 1 H, CH_2), 1.61−1.71 (m, 1 H, CH_2), 1.76−2.00 (m, 5 H, CH_2, *i*Pr), 2.62−2.69 (m, 1 H, C*H*CNH), 2.67 (s, 3 H, NMe), 3.26 (dd, *J* = 14.3, *J* = 0.8 Hz, 1 H, CH_2S), 3.55 (d, *J* = 14.3 Hz, 1 H, CH_2S), 3.72 (dd, *J* = 9.9, *J* = 3.0 Hz, 1 H, CHO), 6.82 (s, 1 H, NH), 7.56−7.66 (m, 3 H, Ph), 7.84−7.88 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.10 (d), 19.82 (d), 22.93 (u), 27.16 (u), 28.90 (d), 29.67 (d), 38.52 (u), 44.78 (d), 63.28 (u), 65.64 (u), 82.80 (d), 128.47 (d), 129.57 (d), 133.00 (d), 139.59 (u), 154.83 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3404 (w), 3309 (m), 2968 (s), 2918 (m), 2888 (m), 2805 (m), 1707 (s), 1579 (w), 1447 (m), 1432 (m), 1415 (m), 1396 (m), 1372 (m), 1330 (m), 1295 (m), 1237 (s), 1196 (w), 1141 (s), 1103 (m), 1074 (m), 1015 (s) cm^{-1}. MS (CI): *m*/*z* (relative intensity, %) = 351 [M^+ + 1] (16), 199 (17), 198 (100), 196 (26), 156 (67). $C_{18}H_{26}N_2O_3S$ (350.48): calcd. C 61.69, H 7.48, N 7.99; found C 61.64, H 7.45, N 7.75.

(+)-(4*S*,4a*R*,8a*S*)-Octahydro-4-(1-methylethyl)-8a-{[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]methyl}-2*H*-3,1-benzoxazin-2-one (15b): Treatment of carbamate **14b** (1.15 g, 3.15 mmol) with *n*BuLi (2.1 mL of 1.60 M in hexane, 3.32 mmol) according to *GP2* and purification by crystallization (EtOAc) gave oxazinone **15b** (965 mg, 84%) as a light yellow solid. M.p. 206−207 °C, $[\alpha]_D$ = +89.3 (*c* = 0.70, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.80 (d, *J* = 6.7 Hz, 3 H, *i*Pr), 1.10 (d, *J* = 6.7 Hz, 3 H, *i*Pr), 1.15−1.80 (m, 8 H, CH_2), 1.95 (septd, *J* = 7.0, *J* = 2.0 Hz, 1 H, *i*Pr), 2.55−2.60 (m, 1 H, C*H*CNH), 2.70 (s, 3 H, NMe), 3.10 (dd, *J* = 14.4, *J* = 1.6 Hz, 1 H, CH_2S), 3.90 (dd, *J* = 14.4, *J* = 2.2 Hz, 1 H, CH_2S), 4.30 (dd, *J* = 10.4, *J* = 2.0 Hz, 1 H, CHO), 7.50 (s, 1 H, NH), 7.55−7.65 (m, 3 H, Ph), 7.80−7.85 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.44 (d), 19.84 (d), 20.05 (u), 22.31 (u), 28.01 (d), 29.67 (d), 33.55 (u), 39.00 (d), 55.88 (u), 62.66 (u), 78.39 (d) 128.81 (d), 128.95 (d), 129.76 (d), 133.31 (d), 140.06 (u), 153.18 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3390(s), 2967 (s), 2934 (s), 2884 (m), 1699 (vs), 1580 (w), 1441 (s), 1373 (m), 1277 (s), 1169 (s) cm^{-1}. MS (EI): *m*/*z* (relative intensity, %) = 365 [M^+ + 1] (1), 364 [M^+] (1), 336 (28), 321 (14), 210 (45), 170 (34), 167 (16), 166 (37), 156 (17), 150 (57), 140 (100), 138 (28), 125 (50), 95 (39). $C_{19}H_{28}N_2O_3S$ (364.50): calcd. C 62.61, H 7.69, N 7.69; found C 62.30, H 7.91, N 7.55.

(+)-(4*S*,5*R*,6*S*)-Tetrahydro-6-ethyl-5-methyl-4-{(1*R*)-1-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]ethyl}-2*H*-1,3-oxazin-2-one (16a): Successive treatment of sulfoximine **5a** (216 mg, 0.70 mmol) with *n*BuLi (1.09 mL of 1.60 M in hexane, 1.74 mmol) and MeI (0.50 mL, 8.03 mmol) according to *GP3* gave a mixture of sulfoximines **16a**, *epi*-**16a**, and **5a** in a ratio of 18:2:1. Purification by chromatography (EtOAc/cyclohexane, 4:1) and crystallization (Et_2O) afforded sulfoximine **16a** (154 mg, 68%) as a colorless solid. M.p. 147 °C. $[\alpha]_D$ = +134.0 (*c* = 0.70, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.68 (d, *J* = 6.5 Hz, 3 H, CH*Me*), 1.00 (t, *J* = 7.3 Hz, 3 H, Et), 1.38 (d, *J* = 7.0 Hz, 3 H, CH(*Me*)S], 1.51 (dquin, *J* = 14.8, *J* = 7.3 Hz, 1 H, Et), 1.57 (tq, *J* = 10.0, *J* = 6.5 Hz, 1 H, C*H*Me), 1.78 (dqd, *J* = 14.8, *J* = 7.3, *J* = 3.0 Hz, 1 H, Et), 2.71 (s, 3 H, NMe), 3.07 (brq, *J* = 7.0 Hz, 1 H, CHS), 3.50 (dd, *J* = 10.0, *J* = 1.0 Hz, 1 H, C*H*NH), 3.81 (ddd, *J* = 10.0, *J* = 7.3, *J* = 3.0 Hz, 1 H, CHO), 7.12 (s, 1 H, NH), 7.62 (m, 2 H, Ph), 7.68 (m, 1 H, Ph), 7.82 (m, 2 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 5.82 (d), 8.32 (d), 12.44 (d), 24.89 (u), 29.06 (d), 32.58 (d), 55.09 (d), 59.94 (d), 80.91 (d), 129.71 (d), 133.52 (d), 136.07 (u), 154.17 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3397 (m), 3226 (vs), 3089 (m), 3066 (m), 2974 (vs), 2944 (s), 2921 (s), 2880 (s), 2805 (m), 1708 (vs), 1582 (w), 1529 (w), 1463 (s), 1448 (s), 1417 (s), 1405 (s), 1387 (m), 1377 (m), 1358 (s), 1332 (m), 1304 (s), 1268 (s), 1237 (vs), 1227 (vs), 1174 (m), 1148 (s), 1133 (vs), 1107 (s), 1078 (s), 1060 (m), 1028 (s) cm^{-1}. MS (EI): *m*/*z* (relative intensity, %) = 325 [M^+ + 1] (5), 183 (20), 170 (22), 169 (76), 156 (39), 154 (20), 126 (44), 125 (100), 110 (90), 107 (17), 106 (18), 105 (31), 97 (18), 96 (44). $C_{16}H_{24}N_2O_3S$ (324.44): calcd. C 59.23, H 7.46, N 8.63; found C 58.99, H 7.40, N 8.59.

(4*S*,5*R*,6*S*)-Tetrahydro-6-methyl-5-(1-methylethyl)-4-{[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl)deuteriomethyl}-2*H*-1,3-oxazin-2-one (16b and *epi*-16b): Successive treatment of sulfoximine **5b** (46 mg, 0.14 mmol) with *n*BuLi (0.27 mL of 1.60 M in hexane, 0.43 mmol) and CD_3OD (0.5 mL) according to *GP3* gave a mixture of sulfoximines **16b** and *epi*-**16b** in a ratio of 3:1 (46 mg, 99%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.66 (d, *J* = 7.1 Hz, 3 H, *i*Pr), 0.79 (d, *J* = 7.1 Hz, 3 H, *i*Pr), 1.32 (td, *J* = 9.2, *J* = 2.5 Hz, 1 H, C*Hi*Pr), 1.35 (d, *J* = 6.2 Hz, 3 H, Me), 1.63 (septd, *J* = 7.1, *J* = 2.5 Hz, 1 H, *i*Pr), 2.73 (s, 3 H, NMe), 3.18 (br. d, *J* = 10.2 Hz, 0.25 H, CH_2S), 3.24 (br. s, 0.75 H, CH_2S), 3.58 (br. d, *J* = 9.0 Hz, 1 H, C*H*NH), 4.15 (dq, *J* = 9.2, *J* = 6.2 Hz, 1 H, CHO), 7.22 (s, 1 H, NH), 7.60−7.73 (m, 3 H, Ph), 7.87 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.80 (d), 18.98 (d), 20.02 (d), 27.29 (d), 29.20 (d), 47.42 (d), 48.16 (d), 62.21 (u), 74.30 (d), 129.35 (d), 129.90 (d), 133.69 (d), 137.13 (u), 154.03 (u) ppm.

(+)-(4*S*,5*R*,6*S*)-Tetrahydro-6-methyl-5-(1-methylethyl)-4-{(1*R*)-1-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]ethyl}-2*H*-1,3-oxazin-2-one (16c): Successive treatment of sulfoximine **5b** (162 mg, 0.50 mmol) with *n*BuLi (0.80 mL of 1.60 M in hexane, 1.28 mmol) and MeI (0.40 mL, 6.43 mmol) according to *GP3* gave a mixture of sulfoximines **16c**, *epi*-**16c**, and **5b** in a ratio of 10:2:1. Purification by chromatography (EtOAc/cyclohexane, 4:1) afforded sulfoximine **16c** (127 mg, 75%) and a mixture of *epi*-**16c** and **5b** (16 mg) in a ratio of 5:1 as colorless solids.

Compound 16c: M.p. 134 °C, $[\alpha]_D$ = +140.4 (*c* = 0.29, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.55 (d, *J* = 7.1 Hz, 3 H, *i*Pr), 0.73 (d, *J* = 7.1 Hz, 3 H, *i*Pr), 1.34 (d, *J* = 6.4 Hz, 3 H, CH*Me*), 1.33−1.58 (m, C*Hi*Pr), 1.40 (d, *J* = 7.0 Hz, 3 H, *i*Pr), 1.40 [d, *J* = 7.0 Hz, 3 H, CH(*Me*)S], 1.58 (m, 1 H, *i*Pr), 2.73 (s, 3 H, NMe), 3.03 (m, 1 H, CHS), 3.76 (br. d, *J* = 9.0 Hz, 1 H, C*H*NH), 4.08 (dq, *J* = 10.4, *J* = 6.1 Hz, 1 H, CHO), 6.98 (s, 1 H, NH), 7.62 (m, 2 H, Ph), 7.68 (m, 1 H, Ph), 7.84 (m, 2 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 5.82 (d), 18.46 (d), 18.66 (d), 19.76 (d), 27.03 (d), 28.95 (d), 45.84 (d), 50.34 (d), 62.76 (d), 74.19 (d), 129.74 (d), 129.84 (d), 133.52 (d), 136.52 (u), 155.65 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3854 (m), 3399 (w), 3231 (s), 3089 (m), 3061 (m), 2995 (s),

2975 (vs), 2938 (s), 2901 (s), 2878 (s), 2813 (m), 1718 (vs), 1713 (vs), 1581 (w), 1531 (w), 1466 (s), 1445 (s), 1423 (m), 1403 (m), 1392 (s), 1375 (s), 1364 (m), 1350 (m), 1330 (w), 1307 (s), 1284 (m), 1268 (m), 1244 (vs), 1233 (vs), 1188 (m), 1150 (s), 1129 (s), 1112 (s), 1078 (s), 1051 (s), 1018 (s) cm^{-1}. MS (EI): *m*/*z* (relative intensity, %) = 339 [M^+ + 1] (1), 184 (18), 183 (70), 156 (34), 154 (24), 141 (100), 138 (11), 126 (66), 125 (65), 124 (30), 112 (11), 110 (17), 109 (10), 107 (23), 106 (18), 105 (30), 98 (10), 97 (23), 96 (22), 83 (13), 82 (17), 81 (15). $C_{17}H_{26}N_2O_3S$ (338.5): calcd. C 60.33, H 7.74, N 8.28; found C 60.08, H 7.71, N 8.18.

Compound *epi*-16c: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84 (d, *J* = 6.7 Hz, 3 H, *i*Pr), 0.88 (d, *J* = 6.5 Hz, 3 H, *i*Pr), 1.21 [d, *J* = 7.2 Hz, 3 H, CH(*Me*)S], 1.41 (d, *J* = 6.7 Hz, 3 H, CH*Me*), 1.52 (m, 1 H, C*Hi*Pr), 1.68 (m, 1 H, *i*Pr), 2.73 (s, 3 H, NMe), 3.33 (dq, *J* = 8.7, *J* = 7.2 Hz, 1 H, CHS), 3.63 (m, 1 H, C*H*NH), 4.40 (qd, *J* = 6.7, *J* = 3.7 Hz, 1 H, CHO), 7.45 (s, 1 H, NH), 7.58−7.72 (m, 3 H, Ph), 7.81 (m, 2 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.85 (d), 19.40 (d), 20.44 (d), 20.69 (d), 29.45 (d), 30.86 (d), 43.48 (d), 52.49 (d), 66.02 (d), 73.58 (d), 129.60 (d), 130.66 (d), 133.59 (d), 137.36 (u), 153.27 (u) ppm.

(+)-(4*S*,5*R*,6*S*)-Tetrahydro-6-methyl-5-(1-methylethyl)-4-[(1*S*)-1-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl)-2-(phenylmethoxy)-ethyl]-2*H*-1,3-oxazin-2-one (16d): Successive treatment of sulfoximine **5b** (207 mg, 0.64 mmol) with *n*BuLi (1.21 mL of 1.60 M in hexane, 1.93 mmol) and $PhCH_2OCH_2Cl$ (0.67 mL, 4.79 mmol) according to *GP3* and purification by chromatography (EtOAc/cyclohexane, 4:1) afforded sulfoximine **16d** (198 mg, 70%) as a slightly yellow oil. $[\alpha]_D$ = +81.2 (*c* = 1.05, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.50 (d, *J* = 7.1 Hz, 3 H, *i*Pr), 0.70 (d, *J* = 7.1 Hz, 3 H, *i*Pr), 1.27 (d, *J* = 6.1 Hz, 3 H, Me), 1.50 (septd, *J* = 7.1, *J* = 2.0 Hz, 1 H, *i*Pr), 1.83 (td, *J* = 9.9, *J* = 2.0 Hz, 1 H, C*Hi*Pr), 2.70 (s, 3 H, NMe), 3.29 (dd, *J* = 6.4, *J* = 3.7 Hz, 1 H, CHS), 3.73 (d, *J* = 9.5 Hz, 1 H, C*H*NH), 3.96 (dd, *J* = 10.4, *J* = 6.4 Hz, 1 H, CH_2O), 4.03 (dq, *J* = 10.2, *J* = 6.1 Hz, 1 H, CHO), 4.23 (dd, *J* = 10.4, *J* = 3.7 Hz, 1 H, CH_2O), 4.40 (symm m, 2 H, PhCH_2O), 7.00 (s, 1 H, NH), 7.23−7.36 (m, 5 H, Ph), 7.57−7.70 (m, 3 H, Ph), 7.84 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.03 (d), 18.99 (d), 19.93 (d), 26.81 (d), 29.14 (d), 44.73 (d), 50.61 (d), 63.10 (u), 73.71 (u), 66.65 (d), 74.52 (d), 127.94 (d), 128.05 (d), 128.44 (d), 129.83 (d), 130.00 (d), 133.73 (d), 136.42 (u), 137.27 (u), 155.41 (u) ppm. IR (neat): $\tilde{\nu}$ = 3381 (w), 3290 (m), 3062 (m), 3031 (w), 2964 (s), 2937 (s), 2878 (s), 2809 (w), 2337 (w), 1724 (vs), 1582 (w), 1496 (w), 1447 (s), 1422 (s), 1373 (s), 1303 (s), 1246 (s), 1146 (s), 1109 (s), 1077 (s), 1047 (s), 1025 (m) cm^{-1}. MS (EI): *m*/*z* (relative intensity, %) = 445 [M^+] (1), 290 (4), 289 (4), 288 (4), 198 (16), 183 (10), 182 (11), 156 (13), 155 (14), 141 (14), 125 (21), 124 (22), 107 (27), 91 (100). $C_{24}H_{32}N_2O_4S$ (444.59): calcd. C 64.84, H 7.25, N 6.30; found C 64.95, H 7.34, N 6.54.

(4*S*,5*R*,6*S*)-Tetrahydro-4-{(1*S*,2*S*)-2-hydroxy-1-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]propyl}-6-methyl-5-(1-methylethyl)-2*H*-1,3-oxazin-2-one (16e) and (4*S*,5*R*,6*S*)-Tetrahydro-4-{(1*S*,2*R*)-2-hydroxy-1-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]propyl}-6-methyl-5-(1-methylethyl)-2*H*-1,3-oxazin-2-one (*epi*-16e): Successive treatment of sulfoximine **5b** (78 mg, 0.24 mmol) with *n*BuLi (0.45 mL of 1.60 M in hexane, 0.72 mmol) and ethanal (0.3 mL, 5.3 mmol) according to *GP3* and purification by chromatography (EtOAc/cyclohexane, 4:1) gave a mixture of sulfoximines **16e**, *epi*-**16e**, and **5b** (78 mg) in a ratio of 1.7:1:1 as a colorless solid.

Compound 16e: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.47 (d, *J* = 7.1 Hz, 3 H, *i*Pr), 0.78 (d, *J* = 7.1 Hz, 3 H, *i*Pr), 1.35 (d, *J* = 6.0 Hz, 3 H, CH*Me*), 1.30−1.38 (m, 1 H, *i*Pr), 1.48 [d, *J* = 6.5 Hz, 3 H, CH(OH)*Me*], 1.71 (td, *J* = 10.1, *J* = 1.7 Hz, 1 H, C*Hi*Pr), 2.79 (s, 3 H, NMe), 3.04 (br. d, *J* = 5.6 Hz, 1 H, CHS), 3.69 (br. d, *J* = 10.1 Hz, 1 H, C*H*NH), 4.04 (m, 1 H, CHO), 4.64 (quin, *J* = 6.3 Hz, 1 H, C*H*OH), 6.55 (s, 1 H, NH), 7.60−7.76 (m, 3 H, Ph), 7.85−7.92 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.03 (d), 19.92 (d), 20.22 (d), 23.14 (d), 26.68 (d), 29.06 (d), 45.47 (d), 51.33 (d), 65.84 (d), 70.50 (d), 74.58 (d), 129.92 (d), 130.10 (d), 134.15 (d), 137.12 (u), 154.53 (u).

Compound *epi*-16e: ^{1}H NMR (300 MHz, $CDCl_3$) signals for *epi*-**16** are partially superposed by those for **16**; only those signals that could be unequivocally assigned are listed: δ = 0.37 (d, *J* = 7.1 Hz, 3 H, *i*Pr), 0.67 (d, *J* = 7.1 Hz, 3 H, *i*Pr), 1.33 (d, *J* = 6.0 Hz, 3 H, CH*Me*), 1.76 [d, *J* = 6.5 Hz, 3 H, CH(OH)*Me*], 1.83 (td, *J* = 9.5, *J* = 2.0 Hz, 1 H, C*Hi*Pr), 2.77 (s, 3 H, NMe), 3.14 (bdd, *J* = 3.7, *J* = 1.0 Hz, 1 H, CHS), 3.62 (br. d, *J* = 9.5 Hz, 1 H, C*H*NH), 4.04 (m, 1 H, CHO), 4.53 (m, 1 H, C*H*OH), 7.17 (s, 1 H, NH), 7.60−7.76 (m, 3 H, Ph), 7.85−7.92 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) only those signals are listed, which could be unequivocally assigned: δ = 17.85 (d), 23.20 (d), 27.00 (d), 45.38 (d), 50.75 (d), 65.29 (d), 71.07 (d), 74.42 (d), 136.19 (u), 155.33 (u) ppm.

(+)-(4*S*,5*R*,6*S*)-Tetrahydro-4-methyl-6-(1-methylethyl)-4-{[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]deuteriomethyl}-5-phenyl-2*H*-1,3-oxazin-2-one (9-D and *epi*-9-D): Successive treatment of sulfoximine **9** (85 mg, 0.21 mmol) with *n*BuLi (0.29 mL of 1.60 M in hexane, 0.46 mmol) and CD_3OD (0.75 mL) according to *GP3* gave a mixture of sulfoximines **9**-D and *epi*-**9**-D in a ratio of 1.1:1 (84 mg, 99%) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.75 (d, *J* = 6.9 Hz, 3 H, *i*Pr), 1.05 (d, *J* = 6.9 Hz, 3 H, *i*Pr), 1.52−1.59 (m, 1 H, *i*Pr), 1.53 (s, 3 H, Me), 2.64 (s, 3 H, NMe), 3.03 (d, *J* = 11.3 Hz, 1 H, C*H*Ph), 3.18 (s, 0.5 H, CHD), 3.23 (s, 0.5 H, CHD), 4.65 (dd, *J* = 11.3, *J* = 1.9 Hz, 1 H, CHO), 7.10−7.13 (m, 2 H, Ph), 7.30−7.37 (m, 3 H, Ph), 7.54−7.65 (m, 3 H, Ph), 7.70 (br. s, 1 H, NH), 7.78−7.82 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.44 (d), 19.79 (d), 23.90 (d), 28.81 (d), 28.58 (d), 50.87 (d), 56.47 (u), 64.50 (d), 79.44 (d), 128.15 (d), 128.56 (d), 128.78 (d), 129.54 (d), 133.12 (d), 133.79 (u), 139.46 (u), 152.54 (u) ppm.

(−)-(4*R*,5*R*,6*S*)-Tetrahydro-4,6-dimethyl-5-(1-methylethyl)-2*H*-1,3-oxazin-2-one (17a): Treatment of sulfoximine **5b** (230 mg, 0.71 mmol) with Raney nickel, prepared from 2.5 g Ni/Al, for 5.5 h according to *GP4* and purification by chromatography (EtOAc/cyclohexane, 4:1) afforded oxazinone **17a** (107 mg, 88%) as a colorless solid. M.p. 54 °C. $[\alpha]_D$ = −44.7 (*c* = 0.55, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.97 (d, *J* = 7.1 Hz, 3 H, *i*Pr), 1.01 (d, *J* = 7.1 Hz, 3 H, *i*Pr), 1.26 [d, *J* = 6.1 Hz, 3 H, CH(N)*Me*], 1.31 (td, *J* = 9.3, *J* = 2.2 Hz, 1 H, C*Hi*Pr), 1.40 [d, *J* = 6.1 Hz, 3 H, CH(O)*Me*], 1.92 (septd, *J* = 7.1, *J* = 2.2 Hz, 1 H, *i*Pr), 3.37 (dq, *J* = 8.8, *J* = 6.1 Hz, 1 H, C*H*N), 4.23 (dq, *J* = 9.5, *J* = 6.1 Hz, 1 H, CHO), 6.48 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.11 (d), 19.78 (d), 20.46 (d), 23.18 (d), 27.13 (d), 48.43 (d), 49.96 (d), 75.76 (d), 155.68 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3383 (m), 3245 (m), 3136 (m), 2963 (s), 2904 (m), 1708 (vs), 1489 (m), 1458 (s), 1416 (s), 1390 (s), 1372 (s), 1343 (m), 1305 (s), 1245 (m), 1197 (s), 1151 (m), 1110 (m), 1054 (s) cm^{-1}. MS (EI): *m*/*z* (relative intensity, %) = 172 [M^+ + 1] (1), 171 [M^+] (2), 112 (13), 84 (51). $C_9H_{17}NO_2$ (171.24): calcd. C 63.13. H 10.01. N 8.18; found C 62.87, H 10.09, N 8.10.

(−)-(4*R*,5*R*,6*S*)-Tetrahydro-4-ethyl-6-methyl-5-(1-methylethyl)-2*H*-1,3-oxazin-2-one (17b): Treatment of sulfoximine **16c** (94 mg, 0.28 mmol) with Raney nickel, prepared from 1.6 g Ni/Al, for 18 h according to *GP4* and purification by chromatography (EtOAc/cyclohexane, 4:1) afforded oxazinone **17b** (45 mg, 88%) as

a colorless oil. $[\alpha]_D = -28.0$ ($c = 0.69$, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.97 (d, $J = 7.0$ Hz, 3 H, *i*Pr), 0.97 (t, $J = 7.4$ Hz, 3 H, Et), 1.00 (d, $J = 7.0$ Hz, 3 H, *i*Pr), 1.41 (d, $J = 6.3$ Hz, 3 H, Me), 1.44 (ddd, $J = 8.8$, $J = 7.7$, $J = 2.7$ Hz, 1 H, C*H*i*Pr*), 1.53 (sept, $J = 7.2$ Hz, 1 H, Et), 1.68 (dqd, $J = 14.4$, $J = 7.4$, $J = 3.9$ Hz, 1 H, Et), 1.87 (septd, $J = 7.0$, $J = 2.7$ Hz, 1 H, *i*Pr), 3.19 (ddd, $J = 7.7$, $J = 7.2$, $J = 3.9$ Hz, 1 H, C*H*NH), 4.23 (dq, $J = 8.8$, $J = 6.3$ Hz 1 H, CHO), 5.76 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.05 (d), 18.92 (d), 19.82 (d), 20.57 (d), 27.84 (d), 29.31 (u), 46.84 (d), 53.48 (d), 75.35 (d), 156.42 (u) ppm. IR (neat): $\tilde{\nu}$ = 3256 (m), 3136 (w), 2965 (s), 2938 (m), 2879 (m), 2240 (w), 1713 (s), 1462 (m), 1417 (m), 1392 (m), 1381 (m), 1353 (w), 1301 (m), 1268 (w), 1185 (w), 1143 (w), 1098 (w), 1068 (m), 1031 (w), 1010 (w) cm^{-1}. GC-MS: *m*/*z* (relative intensity, %) = 187 [$M^+ + 2$] (4), 186 [$M^+ + 1$] (26), 156 (10), 112 (40), 102 (9), 89 (12). $C_{10}H_{19}NO_2$ (185.26): calcd. C 64.83, H 10.34, N 7.56; found C 64.74, H 10.47, N 7.85.

(−)-(4*S*,4a*R*,8a*S*)-Octahydro-4-(1-methylethyl)-8a-methyl-2*H*-3,1-benzoxazin-2-one (18): Treatment of **15b** (320 mg, 0.88 mmol) with Raney nickel, prepared from 2.6 g Ni/Al, for 6 h according to *GP4* and purification by chromatography (EtOAc/cyclohexane, 1:1) afforded **18** (160 mg, 86%) as a colorless solid. M.p. 190 °C, $[\alpha]_D = -37.3$ ($c = 0.23$, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.80 (d, $J = 6.7$ Hz, 3 H, *i*Pr), 1.10 (d, $J = 6.7$ Hz, 3 H, *i*Pr), 1.07−1.80 (m, 12 H, CH_2), 1.95 (septd, $J = 6.8$, $J = 2.3$ Hz, 1 H, *i*Pr), 4.30 (dd, $J = 10.08$, $J = 2.02$ Hz, 1 H, C*H*NH), 6.30 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.68 (d), 20.02 (d), 20.55 (u), 22.75 (u), 22.92 (u), 26.85 (d), 28.14 (d), 36.92 (u), 39.02 (d), 52.83 (u), 79.99 (d), 155.02 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3242 (w), 2945 (s), 2870 (m), 1700 (s), 1446 (s), 1371 (m) 1141 (m), 1070 (m) cm^{-1}. MS (EI): *m*/*z* (relative intensity, %) = 211 [M^+] (12), 169 (10), 168 (100). $C_{12}H_{21}NO_2$ (211.30): calcd. C 68.21, H 10.02, N 6.63; found C 68.08, H 10.14, N 6.59.

(4*R*,5*R*,6*S*)-Tetrahydro-6-methyl-5-(1-methylethyl)-4-[(1*E*)-propenyl]-2*H*-1,3-oxazin-2-one [(*E*)-19] and (4*R*,5*R*,6*S*)-Tetrahydro-6-methyl-5-(1-methylethyl)-4-[(1*Z*)-propenyl]-2*H*-1,3-oxazin-2-one [(*Z*)-19]: Amalgamated aluminium was prepared as follows: aluminium powder (1.5 g) was treated with a solution of $HgCl_2$ in water (2%, 50 mL) for 2 min. The aqueous phase was decanted and the residue was washed with water (2 × 25 mL). A suspension of the obtained amalgamated aluminium in THF/H_2O/HOAc (2:1:1, 40 mL) was added at room temperature to a rapidly stirred solution of a mixture of **16e**, *epi*-**16e**, and **5b** (190 mg, in a ratio of 1.8:1:1) in THF (20 mL). After the mixture had been stirred for 2 h, it was filtered through a pad of Celite. The residue was washed with CH_2Cl_2 (4 × 25 mL). The combined organic phases were washed with water (2 × 25 mL) and aqueous NaOH (10%, 2 × 25 mL), dried ($MgSO_4$), and concentrated in vacuo. Purification by chromatography (EtOAc/cyclohexane, 4:1) gave a mixture of alkenes (*E*)-**19** and (*Z*)-**19** (66 mg, 85%) in a ratio of 1:1, together with oxazinone **17a** (11 mg, 46%) as colorless solids.

Compounds (*E*)-19/(*Z*)-19: ^1H NMR (300 MHz, $CDCl_3$): δ = 0.94 (d, $J = 7.1$ Hz, 3 H, Me), 0.95 (d, $J = 7.1$ Hz, 3 H, Me), 0.99 (br. d, $J = 7.1$ Hz, 6 H, 2 × Me), 1.40 [d, $J = 6.1$ Hz, 3 H, CH(O)*Me*], 1.41 [d, $J = 6.2$ Hz, 3 H, CH(O)*Me*], 1.44 (m, 2 H, 2 × C*H*i*Pr*), 1.71 (m, 6 H, 2 × CH=CH*Me*), 1.93 (m, 2 H, 2 × *i*Pr), 3.71 (t, $J = 9.1$ Hz, 1 H, C*H*NH), 4.14 (t, $J = 9.6$ Hz, 1 H, C*H*NH), 4.23 (dq, $J = 9.7$, $J = 6.2$ Hz, 1 H, CHO), 4.27 (dq, $J = 9.9$, $J = 6.1$ Hz 1 H, CHO), 5.27 (m, 1 H, C*H*=CHMe), 5.33 (dq, $J = 8.6$, $J = 1.7$ Hz, 1 H, C*H*=CHMe), 5.62−5.76 (m, 4 H, 2 × CH=C*H*Me, 2 × NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.16 (d), 17.63 (d), 18.72 (d), 18.84 (d), 19.95 (d), 20.09 (d), 20.24 (d), 26.53 (d), 26.66 (d), 47.88 (d), 48.03 (d), 49.57 (d), 56.03 (d), 75.63 (d), 75.75 (d), 128.73 (d), 130.17 (d), 131.08 (d), 131.98 (d), 154.58 (u) ppm. IR (neat): $\tilde{\nu}$ = 3251 (m), 3127 (m), 2962 (s), 2937 (s), 2878 (m), 1713 (vs), 1456 (m), 1407 (s), 1378 (s), 1351 (m), 1330 (m), 1307 (m), 1294 (m), 1264 (m), 1223 (w), 1187 (w), 1165 (m), 1135 (m), 1048 (m), 1019 (w) cm^{-1}. GC-MS: *m*/*z* (relative intensity, %) = 199 [$M^+ + 2$] (10), 198 [$M^+ + 1$] (100), 114 (24), 110 (13). $C_{11}H_{19}NO_2$ (197.27): calcd. C 66.97, H 9.71, N 7.10; found C 66.41, H 9.22, N 6.98. $C_{11}H_{19}NO_2$: calcd. 197.14158; found (HRMS, EI) 197.14154.

Methyl (α*S*,4*S*,5*R*,6*S*)- and (α*R*,4*S*,5*R*,6*S*)-[Tetrahydro-6-methyl-5-(1-methylethyl)-2-oxo-2*H*-1,3-oxazin-4-yl][(*S*)-*N*-methyl-*S*-phenyl sulfonimidoyl]acetate (20 and *epi*-20): Successive treatment of sulfoximine **5b** (220 mg, 0.68 mmol) with *n*BuLi (1.06 mL of 1.60 M in hexane, 1.70 mmol) and $ClCO_2Me$ (0.13 mL, 1.69 mmol) according to *GP3* and purification by chromatography (EtOAc/cyclohexane, 1:1) gave a mixture of esters **20** and *epi*-**20** (165 mg, 64%) in a ratio of 5.2:1 as a colorless solid.

Compound 20: ^1H NMR (400 MHz, $CDCl_3$): δ = 0.91 (d, $J = 7.1$ Hz, 3 H, *i*Pr), 0.96 (d, $J = 7.1$ Hz, 3 H, *i*Pr), 1.45 (d, $J = 6.3$ Hz, 3 H, Me), 1.64−1.78 (m, 2 H, C*H*i*Pr*, *i*Pr), 2.61 (s, 3 H, NMe), 3.78 (s, 3 H, CO_2Me), 4.04−4.16 (m, 3 H, CHN, CHS, CHO), 6.60 (br. s, 1 H, NH), 7.60−7.70 (m, 3 H, Ph), 7.85−7.90 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.71 (d), 19.29 (d), 20.12 (d), 27.89 (d), 29.86 (d), 46.25 (d), 50.82 (d), 53.64 (d), 73.02 (d), 74.02 (d), 129.86 (d), 130.05 (d), 134.10 (d), 137.23 (u), 155.25 (u), 163.89 (u) ppm.

Compound *epi*-20: ^1H NMR (400 MHz, $CDCl_3$): δ = 0.78 (d, $J = 7.1$ Hz, 3 H, *i*Pr), 0.90 (d, $J = 7.0$ Hz, 3 H, *i*Pr), 1.38 (d, $J = 6.4$ Hz, 3 H, Me), 2.75 (s, 3 H, NMe), 3.65 (s, 3 H, CO_2Me), 4.38 (m, 1 H), 4.42 (d, $J = 10.0$ Hz, 1 H), 6.25 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.00 (d), 20.43 (d), 21.99 (d), 31.09 (d), 51.64 (d), 53.33 (d), 75.61 (d) ppm. IR (KBr): $\tilde{\nu}$ = 3303 (s), 2960 (m), 1754 (vs), 1725 (s), 1447 (m), 1338 (w), 1260 (s), 1163 (m), 1018 (m) cm^{-1}. MS (EI): *m*/*z,* relative intensity, %) = 354 (2), 228 (89), 227 (40), 198 (27), 196 (38), 185 (21), 170 (18), 154 (59), 146 (21), 125 (100), 107 (57). $C_{18}H_{26}N_2O_5S$ (382.48): calcd. C 56.52, H 6.85, N 7.32; found C 56.35, H 7.01, N 7.24.

Methyl (+)-(4*R*,5*R*,6*S*)-[Tetrahydro-6-methyl-5-(1-methylethyl)-2-oxo-2*H*-1,3-oxazin-4-yl]acetate (21): Treatment of sulfoximines **20** and *epi*-**20** (230 mg, 0.60 mmol) with Raney nickel, prepared from 1.8 g Ni/Al, for 8 h according to *GP4* and purification by chromatography (EtOAc/cyclohexane, 1:1) afforded **21** (120 mg, 87%) as a viscous liquid. $[\alpha]_D = +51.42$ ($c = 0.70$, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.85 (d, $J = 7.1$ Hz, 3 H, *i*Pr), 0.95 (d, $J = 7.1$ Hz, 3 H, *i*Pr), 1.40 (d, $J = 6.5$ Hz, 3 H, Me), 1.40 (symm. m, 1 H, C*H*i*Pr*), 1.80−1.85 (m, 1 H, *i*Pr), 2.50 (dd, $J = 17.1$, $J = 10.1$ Hz, 1 H, CH_2), 2.65 (dd, $J = 17.1$, $J = 2.7$ Hz, 1 H, CH_2), 3.60 (m, 1 H, C*H*NH), 3.70 (s, 3 H, CO_2Me), 4.20 (dq, $J = 9.3$, $J = 6.5$ Hz, 1 H, CHO), 5.80 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.53 (d), 19.61 (d), 20.55 (d), 28.34 (d), 42.12 (u), 48.36 (d), 49.12 (d), 52.42 (d), 75.17 (d), 155.17 (u), 171.94 (u) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3261 (m), 3141 (w), 2961(s), 1714 (vs), 1439 (s), 1373 (m), 1047 (m) cm^{-1}. MS (EI): *m*/*z* (relative intensity, %) = 229 [M^+] (8), 198 (8), 186 (18), 170 (11), 156 (28), 142 (100), 112 (32), 84 (17). $C_{11}H_{19}NO_4$ (229.27): calcd. C 57.62, H 8.35, N 6.11; found C 57.08, H 8.30, N 6.34.

Methyl (−)-(4*R*,5*R*,6*S*)-[Tetrahydro-4-methyl-6-[(1-methylethyl)-2-oxo-5-phenyl-2*H*-1,3-oxazin-4-yl]acetate (23a): Successive treatment of sulfoximine **9** (223 mg, 0.56 mmol) with *n*BuLi (0.77 mL of 1.60 M in hexane, 1.23 mmol) and $ClCO_2Me$ (0.09 mL, 1.23 mmol) and reduction of the functionalized sulfoximine **22a** with Raney nickel,

prepared from 3.5 g Ni/Al, according to *GP5* and purification by chromatography afforded ester **23a** (82 mg, 48%) as a colorless solid, together with sulfoximine **9** (16 mg, 7%). M.p. 104 °C. $[\alpha]_D$ = −53.0 (*c* = 0.77, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.78 (d, *J* = 7.0 Hz, 3 H, *i*Pr), 1.06 (d, *J* = 7.0 Hz, 3 H, *i*Pr), 1.29 (s, 3 H, Me), 1.62 (septd, *J* = 6.9, *J* = 1.9 Hz, 1 H, *i*Pr), 2.37 (d, *J* = 15.7 Hz, 1 H, CH_2), 2.48 (d, *J* = 15.7 Hz, 1 H, CH_2), 2.98 (d, *J* = 11.4 Hz, 1 H, C*H*Ph), 3.67 (s, 1 H, OMe), 4.66 (dd, *J* = 11.4, *J* = 1.9 Hz, 1 H, CHO), 6.48 (br. s, 1 H, NH), 7.06−7.12 (m, 2 H, Ph), 7.23−7.33 (m, 3 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.79 (d), 20.23 (d), 23.56 (d), 29.08 (d), 44.87 (u), 51.04 (d), 52.32 (d), 55.05 (u), 80.17 (d), 128.32 (d), 128.96 (d), 134.70 (u), 153.48 (u), 171.22 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3375 (m), 3253 (w), 3088 (w), 3033 (w), 2966 (m), 2920 (m), 2877 (w), 1715 (s), 1499 (w), 1439 (s), 1422 (m), 1389 (m), 1370 (m), 1355 (m), 1332 (w), 1300 (m), 1266 (w), 1243 (m), 1227 (m), 1204 (w), 1178 (m), 1159 (w), 1114 (m), 1096 (m), 1055 (s), 1004 (w) cm^{-1}. MS (CI): *m*/*z* (relative intensity, %) = 306 [M^+ + 1] (100), 248 (14). $C_{17}H_{23}NO_4$ (305.37): calcd. C 66.86, H 7.59, N 4.59; found C 66.88, H 7.48, N 4.59.

Isopropyl (−)-(4*R*,5*R*,6*S*)-[Tetrahydro-4-methyl-6-(1-methylethyl)-2-oxo-5-phenyl-2*H*-1,3-oxazin-4-yl]acetate (23b): Successive treatment of sulfoximine **9** (114 mg, 0.28 mmol) with *n*BuLi (0.39 mL of 1.60 M in hexane, 0.63 mmol) and $ClCO_2$*i*Pr (0.63 mL of 1.0 M in toluene, 0.63 mmol), reduction of the functionalized sulfoximine **22b** with Raney nickel, prepared from 1.7 g Al-Ni, according to *GP5*, and purification by chromatography afforded ester **23b** (56 mg, 59%) as a colorless solid, together with sulfoximine **9** (21 mg, 18%). M.p. 151 °C. $[\alpha]_D$ = −42.7 (*c* = 0.95, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.73 (d, *J* = 6.6 Hz, 3 H, *i*Pr), 1.01 (d, *J* = 6.9 Hz, 3 H, *i*Pr), 1.15 (d, *J* = 6.0 Hz, 3 H, *i*Pr), 1.17 (d, *J* = 5.8 Hz, 3 H, *i*Pr), 1.31 (s, 3 H, Me), 1.56 (septd, *J* = 7.0, *J* = 1.8 Hz, 1 H, *i*Pr), 2.28 (d, *J* = 15.4 Hz, 1 H, CH_2), 2.40 (d, *J* = 15.4 Hz, 1 H, CH_2), 2.96 (d, *J* = 11.5 Hz, 1 H, C*H*Ph), 4.61 (dd, *J* = 11.4, *J* = 1.8 Hz, 1 H, CHO), 4.98 (sept, *J* = 6.3 Hz, 1 H, O*i*Pr), 6.58 (s, 1 H, NH), 7.10−7.16 (m, 2 H, Ph), 7.26−7.34 (m, 3 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.41 (d), 19.88 (d), 21.70 (d), 21.78 (d), 23.34 (d), 28.71 (d), 44.90 (u), 50.54 (d), 54.85 (u), 68.78 (d), 79.88 (d), 128.05 (d), 128.74 (d), 134.66 (u), 153.36 (u), 170.21 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3415 (s), 3029 (m), 2975 (m), 2934 (m), 2879 (m), 1721 (s), 1497 (m), 1442 (m), 1388 (m), 1369 (m), 1334 (m), 1226 (m), 1179 (m), 1149 (m), 1105 (m), 1059 (m) cm^{-1}. MS (CI): *m*/*z* (relative intensity, %) = 334 [M^+ + 1] (100). $C_{19}H_{27}NO_4$ (333.42): calcd. C 68.44. H 8.16. N 4.20; found C 68.35, H 8.04, N 4.04.

Isobutyl (−)-(4*R*,5*R*,6*S*)-[Tetrahydro-4-methyl-6-(1-methylethyl)-2-oxo-5-phenyl-2*H*-1,3-oxazin-4-yl]acetate (23c): Successive treatment of sulfoximine **9** (1.18 g, 2.94 mmol) with *n*BuLi (3.86 mL of 1.60 M in hexane, 6.18 mmol) and $ClCO_2$*i*Bu (0.81 mL, 2.95 mmol), reduction of the functionalized sulfoximine **22c** with Raney nickel, prepared from 1.8 g Ni/Al, according to *GP5*, and purification by chromatography furnished ester **23**c (754 mg, 74%) as a colorless solid, together with sulfoximine **9** (141 mg, 12%). M.p. 119 °C. $[\alpha]_D$ = +34.0 (*c* = 1.21, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.79 (d, *J* = 6.9 Hz, 3 H, *i*Pr), 0.91 (dd, *J* = 6.6, *J* = 3.1 Hz, 6 H, *i*Pr), 1.07 (d, *J* = 6.9 Hz, 3 H, *i*Pr), 1.32 (s, 3 H, Me), 1.63 (septd, *J* = 6.9, *J* = 1.9 Hz, 1 H, *i*Pr), 1.83−1.96 (m, 1 H, *i*Pr), 2.36 (d, *J* = 15.7 Hz, 1 H, CH_2), 2.50 (d, *J* = 15.7 Hz, 1 H, CH_2), 3.01 (d, *J* = 11.4 Hz, 1 H, C*H*Ph), 3.86 (dd, *J* = 12.2, *J* = 6.7 Hz, 1 H, OCH_2), 3.88 (dd, *J* = 12.2, *J* = 6.7 Hz, 1 H, OCH_2), 4.67 (dd, *J* = 11.4, *J* = 1.7 Hz, 1 H, CHO), 6.60 (br. s, 1 H, NH), 7.16−7.18 (m, 2 H, Ph), 7.32−7.40 (m, 3 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.42 (d), 19.04 (d), 19.85 (d), 23.23 (d), 27.55 (d), 28.70 (d), 44.59 (u), 50.70 (d), 54.68 (u), 71.09 (u), 79.80 (d), 127.90 (d), 128.57 (d), 134.43 (u), 153.06 (u), 170.52 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3413 (s), 3085 (w), 3063 (w), 3030 (w), 2968 (s), 2896 (m), 1712 (s), 1604 (w), 1497 (w), 1471 (m), 1438 (s), 1394 (m), 1372 (m), 1346 (m), 1222 (s), 1179 (m), 1146 (s), 1120 (m), 1103 (m), 1056 (m) cm^{-1}. MS (EI): *m*/*z* (relative intensity, %) = 348 [M^+ + 1] (100). $C_{20}H_{29}NO_4$ (347.45): calcd. C 69.14, H 8.41, N 4.03; found C 68.96, H 8.21, N 4.00.

Neopentyl (−)-(4*R*,5*R*,6*S*)-[Tetrahydro-4-methyl-6-(1-methylethyl)-2-oxo-5-phenyl-1,3-oxazine-4-yl]acetate (23d): Successive treatment of sulfoximine **9** (226 mg, 0.56 mmol) with *n*BuLi (0.77 mL of 1.60 M in hexane, 1.23 mmol) and $ClCO_2CH_2t$Bu (0.18 mL, 1.23 mmol), reduction of the functionalized sulfoximine **22d** with Raney nickel, prepared from 3.3 g of Ni/Al, according to *GP5*, and purification by chromatography afforded ester **23d** (104 mg, 51%) as a colorless solid, together with sulfoximine **9** (38 mg, 17%). M.p. 133 °C. $[\alpha]_D$ = −3.7 (*c* = 0.83, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.79 (d, *J* = 6.9 Hz, 3 H, *i*Pr), 0.91 (s, 9 H, *t*Bu), 1.07 (d, *J* = 7.1 Hz, 3 H, *i*Pr), 1.33 (s, 3 H, Me), 1.63 (septd, *J* = 6.9, *J* = 1.8 Hz, 1 H, *i*Pr), 2.37 (d, *J* = 15.7 Hz, 1 H, CH_2), 2.52 (d, *J* = 15.7 Hz, 1 H, CH_2), 3.03 (d, *J* = 11.5 Hz, 1 H, C*H*Ph), 3.79 (symm m, 2 H, OCH_2), 4.68 (dd, *J* = 11.4, *J* = 1.8 Hz, 1 H, CHO), 6.60 (br. s, 1 H, NH), 7.16−7.21 (m, 2 H, Ph), 7.32−7.41 (m, 3 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.40 (d), 19.85 (d), 23.28 (d), 26.37 (d), 28.66 (d), 31.16 (u), 44.51 (u), 50.62 (d), 54.65 (u), 74.25 (u), 79.75 (d), 127.88 (d), 128.56 (d), 134.41 (u), 153.07 (u), 170.59 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3368 (m), 3035 (w), 2959 (m), 2920 (m), 2876 (m), 1711 (s), 1499 (m), 1467 (m), 1439 (m), 1411 (m), 1383 (m), 1368 (m), 1352 (m), 1339 (w), 1299 (w), 1268 (w), 1241 (m), 1228 (m), 1178 (m), 1110 (m), 1095 (m), 1057 (m) cm^{-1}. MS (CI): *m*/*z* (relative intensity, %) = 362 [M^+ + 1] (100). $C_{21}H_{31}NO_4$ (361.48): calcd. C 69.78, H 8.64, N 3.87; found C 69.26, H 8.71, N 3.74.

Methyl (+)-(α*R*,4*S*,4a*R*,8a*S*)-{Octahydro-4-(1-methylethyl)-2-oxo-8a*H*-3,1-benzoxazin-8a-yl}-α-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]-acetate (24): Successive treatment of sulfoximine **15b** (538 mg, 1.48 mmol) with *n*BuLi (2.31 mL of 1.60 M in hexane, 3.70 mmol) and $ClCO_2Me$ (0.28 mL, 3.70 mmol) according to *GP3* and purification by chromatography (EtOAc/cyclohexane, 2:1) gave ester **24** (437 mg, 70%) as a colorless solid. M.p. 64−65 °C, $[\alpha]_D$ = +49.3 (*c* = 0.15, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (d, *J* = 6.8 Hz, 3 H, *i*Pr), 1.05 (d, *J* = 6.8 Hz, 3 H, *i*Pr), 1.10−1.80 (m, 8 H, CH_2), 1.90 (septd, *J* = 6.8, *J* = 2.2 Hz, 1 H, *i*Pr), 2.75 (s, 3 H, NMe), 2.95 (m, 1 H), 3.70 (s, 3 H, CO_2Me), 4.20 (dd, *J* = 10.9, *J* = 2.2 Hz, 1 H, CHO), 4.70 (s, 1 H, CHS), 6.09 (s, 1 H, NH), 7.50−7.70 (m, 3 H, Ph), 7.75−7.80 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.62 (d), 19.84 (u), 20.08 (u), 22.47 (u), 28.20 (d), 29.86 (d), 32.60 (d), 37.31 (u), 53.36 (d), 56.98 (u), 70.28 (d), 70.66 (d), 129.57 (d), 129.76 (d), 133.72 (d), 138.04 (u), 152.94 (u), 166.96 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3394 (s), 2943 (s), 2876 (m), 1711 (s), 1446 (s), 1379 (m), 1263 (s), 1073 (m) cm^{-1}. MS (EI): *m*/*z* (relative intensity, %) = 394 (1), 278 (3), 228 (6), 227 (8), 198 (9), 195 (21), 156 (10), 154 (100), 150 (11), 136 (21), 125 (46), 108 (32). $C_{21}H_{30}N_2O_5S$ (422.54): calcd. C 59.69, H 7.16, N 6.63; found C 59.18, H 7.09, N 6.33.

Methyl (+)-(4*S*,4a*R*,8a*R*)-{Octahydro-4-(1-methylethyl)-2-oxo-8a*H*-[3,1]benzoxazin-8a-yl}acetate (25): Treatment of sulfoximine **24** (160 mg, 0.38 mmol) with Raney nickel, prepared from 1.6 g Ni/Al, according to *GP4* and purification by chromatography (EtOAc/cyclohexane, 1:1) afforded **20** (80 mg, 78%) as a colorless solid. M.p. 132 °C, $[\alpha]_D$ = +23.33 (*c* = 0.24, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (d, *J* = 6.7 Hz, 3 H, *i*Pr), 1.05 (d, *J* = 6.7 Hz, 3 H, *i*Pr), 1.10−1.30 (m, 4 H), 1.50−1.85 (m, 9 H),

1.95 (septd, J = 7.0, J = 2.1 Hz, 1 H, *i*Pr), 2.40 (dd, J = 15.5, J = 1.5 Hz, 1 H, CH_2CO), 3.02 (d, J = 15.5 Hz, 1 H, CH_2CO), 3.70 (s, 3 H, CO_2Me), 4.30 (dd, J = 10.6, J = 2.1 Hz, 1 H, CHO), 6.35 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.54 (d), 19.93 (d), 20.43 (u), 22.43 (u), 22.66 (u), 28.12 (d), 33.98 (u), 38.55 (d), 41.66 (u), 52.12 (d), 53.90 (u), 79.06 (d), 153.76 (u), 171.28 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3372 (s), 3000 (w), 2961 (s), 2930 (s), 1697 (vs), 1525 (w), 1464 (s), 1379 (m), 1207 (s) cm^{-1}. MS (EI): *m*/*z* (relative intensity, %) = 269 [M$^+$] (2), 238 (2), 227 (13), 226 (100), 213 (35), 196 (25), 194 (19), 170 (63), 152 (15). $C_{14}H_{23}NO_4$ (269.34): calcd. C 62.43, H 8.61, N 5.20; found C 62.25, H 8.56, N 4.90.

(−)-(4*S*,5*R*,6*S*)-4-(Chloromethyl)-tertahydro-6-ethyl-5-methyl-2*H*-1,3-oxazin-2-one (27a): Treatment of sulfoximine **5a** (77 mg, 0.25 mmol) with $ClCO_2Me$ (0.28 mL, 3.7 mmol) at room temperature for 3 days (95% conversion) according to *GP6* and purification by chromatography (EtOAc) afforded chloride **27a** (40 mg, 84%) as a colorless solid. M.p. 138 °C. $[\alpha]_D$ = −1.0 (c = 0.67, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01 (d, J = 6.7 Hz, 3 H, CH*Me*), 1.04 (t, J = 7.4 Hz, 3 H, Et), 1.59 (dquin, J = 14.4, J = 7.4 Hz, 1 H, Et), 1.75 (tq, J = 10.0, J = 6.7 Hz, 1 H, C*H*Me), 1.86 (dqd, J = 14.4, J = 7.4, J = 3.0 Hz, 1 H, Et), 3.33 (ddd, J = 9.7, J = 7.1, J = 2.7 Hz, 1 H, C*H*NH), 3.48 (dd, J = 11.4, J = 7.1 Hz, 1 H, CH_2Cl), 3.78 (dd, J = 11.4, J = 2.7 Hz, 1 H, CH_2Cl), 3.93 (ddd, J = 10.1, J = 7.4, J = 3.0 Hz, 1 H, CHO), 6.29 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.27 (d), 13.02 (d), 24.74 (u), 33.16 (d), 46.76 (u), 57.58 (d), 81.51 (d), 154.59 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3310 (s), 3172 (m), 2980 (s), 2930 (s), 2883 (s), 1712 (vs, br), 1664 (s), 1531 (m), 1478 (s), 1435 (s), 1411 (s), 1386 (s), 1358 (s), 1327 (s), 1304 (s), 1269 (s), 1244 (s), 1216 (s), 1140 (s), 1117 (s), 1075 (s), 1045 (m), 1023 (s) cm^{-1}. MS (EI): *m*/*z* (relative intensity, %) = 192 [M$^+$ + 1] (3), 162 (2), 143 (5), 142 (61), 117 (3), 99 (7), 98 (100), 81 (36). $C_8H_{14}ClNO_2$ (191.66): calcd. C 50.13, H 7.36, N 7.31; found C 50.15, H 7.28, N 7.06.

(+)-(4*S*,5*R*,6*S*)-4-(Chloromethyl)-tertahydro-6-methyl-5-(1-methylethyl)-2*H*-1,3-oxazin-2-one (27b): Treatment of sulfoximine **5b** (280 mg, 0.86 mmol) with $ClCO_2Me$ (0.33 mL, 4.32 mmol) for 3 days (95% conversion) according to *GP6* and purification by chromatography (EtOAc/pentane, 1:1) afforded chloride **27b** (151 mg, 85%) as a low-melting, colorless solid. $[\alpha]^d$ = +4.0 (c = 0.30, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (d, J = 1.4 Hz, 3 H, *i*Pr), 0.95 (d, J = 1.6 Hz, 3 H, *i*Pr), 1.35 (d, J = 6.3 Hz, 3 H, CH*Me*), 1.55 (ddd, J = 9.0, J = 6.7, J = 3.0 Hz, 1 H, C*H*Me), 1.85 (septd, J = 7.1, J = 3.0 Hz, 1 H, *i*Pr), 3.45 (dd, J = 14.1, J = 7.6 Hz, 1 H, CH_2Cl), 3.60 (dd, J = 14.8, J = 7.1 Hz, 1 H, CH_2Cl), 4.15 (dq, J = 9.0, J = 2.7 Hz, 1 H, CHO), 6.30 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.15 (d), 19.89 (d), 20.46 (d), 28.23 (d), 46.13 (d), 49.39 (u), 53.55 (d), 75.20 (d), 155.94 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3253 (m), 2879 (s), 1709 (vs), 1412 (s), 1301 (s), 1116 (m), 1039 (m) cm^{-1}. MS (EI): *m*/*z* (relative intensity, %) = 205 [M$^+$] (1), 157 (6), 155 (90), 112 (100), 95 (10). $C_9H_{16}ClNO_2$ (205.68): calcd. C 52.56, H 7.84, N 6.81; found C 52.56, H 7.86, N 6.85.

(+)-(4*S*,5*R*,6*S*)-4-(Chloromethyl)tetrahydro-6-(1-methylethyl)-5-phenyl-2*H*-1,3-oxazin-2-one (27c) and Methyl (*S*)-*N*-Phenylsulfinylcarbamate (26): Treatment of sulfoximine **5c** (1.30 g, 3.36 mmol) with $ClCO_2Me$ (2.60 mL, 33.50 mmol) according to *GP6* and purification by HPLC (EtOAc) gave chloride **27c** (730 mg, 81%) as a colorless solid, carbamic acid ester **26** (540 mg, 75%) as a colorless oil, and oxazinone **5c** (190 mg, 15%). **27c**: M.p. 154 °C. $[\alpha]_D$ = +1.4 (c = 1.05, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (d, J = 6.9 Hz, 3 H, *i*Pr), 1.02 (d, J = 6.9 Hz, 3 H, *i*Pr), 1.53 (septd, J = 7.1, J = 1.9 Hz, 1 H, *i*Pr), 2.95 (t, J = 10.7 Hz, 1 H, C*H*Ph), 3.28 (dd, J = 11.6, J = 6.0 Hz, 1 H, CH_2), 3.52 (dd, J = 11.6, J = 2.7 Hz, 1 H, CH_2), 3.86 (ddd, J = 10.6, J = 6.0, J = 2.7 Hz, 1 H, C*H*N), 4.67 (dd, J = 10.7, J = 1.9 Hz, 1 H, CHO), 6.75 (br. s, 1 H, NH), 7.17−7.21 (m, 2 H, Ph), 7.31−7.42 (m, 3 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.66 (d), 19.66 (d), 28.43 (d), 44.05 (d), 46.04 (u), 57.60 (d), 83.50 (d), 127.98 (d), 128.07 (d), 129.23 (d), 135.46 (u), 154.62 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3362 (w), 3231 (s), 3138 (m), 3029 (m), 2972 (s), 2935 (m), 2877 (m), 1697 (s), 1605 (m), 1496 (m), 1473 (s), 1435 (s), 1387 (m), 1369 (m), 1338 (m), 1313 (m), 1289 (s), 1251 (w), 1210 (m), 1130 (s), 1087 (w), 1062 (m), 1036 (s) cm^{-1}. MS (CI): *m*/*z* (relative intensity, %) = 268 [M$^+$ + 1] (100), 234 (16), 232 (12). $C_{14}H_{18}ClNO_2$ (267.75): calcd. C 62.80, H 6.78, N 5.23; found C 62.73, H 6.85, N 5.13.

(+)-(4*R*,5*R*,6*S*)-4-(Cyanomethyl)-tertahydro-6-(1-methylethyl)-5-phenyl-2*H*-1,3-oxazin-2-one (28): Treatment of chloride **27c** (440 mg, 1.64 mmol) with NaCN (160 mg, 3.27 mmol) according to *GP7* gave nitrile **28** (370 mg, 87%) as a colorless solid. Nitrile **28** was isolated by filtration of the reaction mixture after addition of water. M.p. 244−246 °C (decomposition). $[\alpha]_D$ = +30.6 (c = 0.31, DMSO). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 0.74 (d, J = 6.9 Hz, 3 H, *i*Pr), 0.86 (d, J = 6.9 Hz, 3 H, *i*Pr), 1.30 (septd, J = 6.9, J = 1.8 Hz, 1 H, *i*Pr), 2.11 (dd, J = 17.2, J = 3.1 Hz, 1 H, CH_2), 2.65 (dd, J = 17.2, J = 4.3 Hz, 1 H, CH_2), 2.70 (t, J = 10.4 Hz, 1 H, C*H*Ph), 3.86 (ddd, J = 10.6, J = 4.3, J = 3.1 Hz, 1 H, C*H*N), 4.52 (dd, J = 10.5, J = 1.8 Hz, 1 H, CHO), 7.27−7.39 (m, 5 H, Ph), 7.71 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 14.38 (d), 20.29 (d), 22.41 (u), 28.85 (d), 46.18 (d), 52.54 (d), 80.60 (d), 117.72 (u), 128.64 (d), 129.03 (d), 129.85 (d), 136.49 (u), 153.48 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3220 (m), 3123 (m), 2969 (m), 2929 (m), 2879 (m), 2245 (w), 1693 (s), 1500 (w), 1473 (w), 1428 (m), 1386 (w), 1369 (w), 1351 (w), 1327 (w), 1290 (m), 1260 (w), 1220 (m), 1187 (w), 1151 (m), 1132 (w), 1107 (w), 1089 (w), 1065 (w), 1034 (s) cm^{-1}. MS (CI): *m*/*z* (relative intensity, %) = 259 [M$^+$ + 1] (100). $C_{15}H_{18}N_2O_2$ (258.32): calcd. C 69.74, H 7.02, N 10.84; found C 69.53, H 7.02, N 10.83.

(−)-(4*S*,5*R*,6*S*)-4-(Chloromethyl)-tertahydro-4-methyl-6-(1-methylethyl)-5-phenyl-2*H*-1,3-oxazin-2-one (29) and Methyl (*S*)-*N*-Phenylsulfinylcarbamate (26): Treatment of sulfoximine **9** (204 mg, 0.51 mmol) with $ClCO_2Me$ (0.39 mL, 5.10 mmol) according to *GP5* and purification by chromatography (EtOAc) gave chloride **29** (116 mg, 81%) as a colorless solid, carbamic acid ester **26** (79 mg, 73%) of ≥99% *ee* (GC, permethyl-β-cyclodextrin, chemically bound, t_R (*R*) = 24.61 min, t_R (*S*) = 24.71 min) as a colorless oil, and oxazinone **9** (28 mg, 14%).

Compound 29: M.p. 161 °C. $[\alpha]_D$ = −57.2 (c = 1.25, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.81 (d, J = 6.6 Hz, 3 H, *i*Pr), 1.09 (d, J = 6.9 Hz, 3 H, *i*Pr), 1.26 (s, 3 H, Me), 1.72 (septd, J = 6.9, J = 1.8 Hz, 1 H, *i*Pr), 3.33 (d, J = 11.4 Hz, 1 H, C*H*Ph), 3.41 (symm. m, 2 H, CH_2), 4.67 (dd, J = 11.4, J = 1.8 Hz, 1 H, CHO), 6.95 (br. s, 1 H, NH), 7.17−7.22 (m, 2 H, Ph), 7.30−7.39 (m, 3 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.44 (d), 19.88 (d), 23.18 (d), 28.60 (d), 46.05 (d), 51.79 (u), 56.73 (u), 79.96 (d), 127.90 (d), 128.59 (d), 134.14 (u), 154.73 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3239 (m), 3111 (w), 2971 (m), 2932 (m), 2876 (w), 1702 (s), 1604 (w), 1583 (w), 1497 (w), 1469 (m), 1456 (m), 1430 (s), 1413 (s), 1386 (m), 1368 (m), 1352 (m), 1335 (m), 1312 (m), 1300 (s), 1267 (w), 1251 (m), 1193 (m), 1146 (m), 1115 (m), 1092 (m), 1071 (w), 1048 (s) cm^{-1}. MS (CI): *m*/*z* (relative intensity, %) = 282 [M$^+$ + 1] (100). $C_{15}H_{20}ClNO_2$ (281.78): calcd. C 63.94, H 7.15, N 4.97; found C 63.68, H 7.00, N 4.82.

Compound 26: $[\alpha]_D = -78.1$ ($c = 0.78$, Et_2O). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.69 (s, 3 H, Me), 3.30 (s, 3 H, OMe), 7.52−7.57 (m, 3 H, Ph), 7.61−7.67 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.67 (d), 54.01 (d), 125.15 (d), 129.33 (d), 131.85 (d), 142.31 (u), 155.55 (u) ppm. IR (neat): $\tilde{\nu}$ = 3058 (w), 3001 (w), 2955 (m), 2844 (w), 1725 (s), 1582 (w), 1444 (s), 1414 (m), 1313 (s), 1201 (m), 1145 (s), 1108 (s), 1078 (m), 1066 (m), 1023 (w) cm^{-1}. MS (CI): *m*/*z* (relative intensity, %) = 214 [M^+ + 1] (7), 125 (100), 97 (24). $C_9H_{11}NOS$ (213.25): calcd. C 50.69, H 5.20, N 6.57; found C 50.69, H 5.41, N 6.89.

(−)-(4*R*,5*R*,6*S*)-4-(Cyanomethyl)-tertahydro-4-methyl-6-(1-methylethyl)-5-phenyl-2*H*-1,3-oxazin-2-one (30): Treatment of chloride **29** (1.14 g, 4.05 mmol) with NaCN (40 mg, 0.82 mmol) according to *GP6* and purification by chromatography (EtOAc) gave nitrile **30** (960 mg, 87%) as a colorless solid. M.p. 164 °C. $[\alpha]_D = -28.7$ ($c = 0.55$, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.84 (d, *J* = 6.9 Hz, 3 H, *i*Pr), 1.09 (d, *J* = 7.1 Hz, 3 H, *i*Pr), 1.34 (s, 3 H, Me), 1.70 (septd, *J* = 6.9, *J* = 1.7 Hz, 1 H, *i*Pr), 2.38 (d, *J* = 17.0 Hz, 1 H, CH_2), 2.61 (d, *J* = 17.0 Hz, 1 H, CH_2), 3.30 (d, *J* = 11.4 Hz, 1 H, C*H*Ph), 4.69 (dd, *J* = 11.4, *J* = 1.9 Hz, 1 H, CHO), 7.24−7.27 (m, 2 H, Ph), 7.34−7.42 (m, 3 H, Ph), 7.73 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.51 (d), 19.88 (d), 24.81 (d), 28.77 (d), 30.30 (u), 48.40 (d), 55.08 (u), 80.52 (d), 116.08 (u), 128.51 (d), 129.07 (d), 133.73 (u), 154.92 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3455 (w), 3219 (w), 3108 (w), 2961 (m), 2931 (w), 2876 (w), 2257 (w), 1700 (s), 1451 (w), 1418 (s), 1389 (w), 1371 (m), 1350 (m), 1338 (m), 1315 (m), 1268 (w), 1189 (w), 1167 (w), 1101 (w), 1056 (m) cm^{-1}. MS (CI): *m*/*z* (relative intensity, %) = 273 [M^+ + 1] (100). $C_{16}H_{20}N_2O_2$ (272.34): calcd. C 70.56, H 7.40, N 10.29; found C 70.30, H 7.49, N 10.04.

(−)-(4*R*,5*R*,6*S*)-{Tetrahydro-4-methyl-6-(1-methylethyl)-2-oxo-5-phenyl-2*H*-[1,3]-oxazin-4-yl}acetic Acid (31). From Nitrile 30: Treatment of **30** (170 mg, 0.62 mmol) with NaOH (2 N, 5 mL) according to *GP8* and purification by recrystallization ($CHCl_3$/hexane, 5:1) afforded amino acid **31** (130 mg, 72%) as fine, colorless needles.

From Ester 23b: Aqueous NaOH (2 N, 2 mL) was added to a solution of the amino ester **23b** (101 mg, 0.29 mmol) in EtOH (6 mL) and the mixture was heated at 55 °C for 3 h. After the mixture had cooled to room temperature, EtOH was removed in vacuo and the solution was acidified with aqueous 3 N HCl until a colorless solid precipitated. The mixture was then extracted with $CHCl_3$, whereupon the solid dissolved, and the combined organic phases were concentrated in vacuo. Purification by recrystallization ($CHCl_3$/hexane, 5:1) afforded the amino acid **31** (70 mg, 82%) as fine, colorless needles.

Compound 31: M.p. 185 °C (dec.). $[\alpha]_D = -26.7$ ($c = 0.45$, MeOH). ^1H NMR (400 MHz, CD_3OD): δ = 0.82 (d, *J* = 6.9 Hz, 3 H, *i*Pr), 1.10 (d, *J* = 7.1 Hz, 3 H, *i*Pr), 1.30 (s, 3 H, Me), 1.70 (septd, *J* = 6.9, *J* = 1.7 Hz, 1 H, *i*Pr), 2.37 (d, *J* = 15.7 Hz, 1 H, CH_2), 2.53 (d, *J* = 15.7 Hz, 1 H, CH_2), 3.44 (d, *J* = 11.5 Hz, 1 H, C*H*Ph), 4.88 (dd, *J* = 11.5, *J* = 1.9 Hz, 1 H, HCO), 7.33−7.45 (m, 5 H, Ph) ppm. ^{13}C NMR (100 MHz, CD_3OD): δ = 12.76 (d), 19.04 (d), 23.46 (d), 28.79 (d), 43.21 (u), 48.52 (d), 54.89 (u), 80.35 (d), 127.82 (d), 128.43 (d), 135.01 (u), 155.38 (u), 172.75 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3372 (m), 3266 (m), 3068 (m), 2974 (m), 2935 (m), 2881 (m), 2734 (w), 2557 (w), 1730 (s), 1717 (s), 1667 (s), 1500 (w), 1469 (m), 1432 (s), 1389 (m), 1377 (m), 1346 (m), 1317 (m), 1288 (w), 1237 (m), 1206 (m), 1192 (m), 1154 (w), 1113 (w), 1101 (w), 1062 (m) cm^{-1}. MS (CI): *m*/*z* (relative intensity, %) = 292 [M^+ + 1] (100), 267 (34), 248 (18), 183 (16), 165 (33), 141 (31), 123 (10), 99 (11).

(−)-(4*S*,4a*R*,7a*S*)-7a-(Chloromethyl)-hexahydro-4-(1-methylethyl)-cyclopenta[*d*][1,3]oxazin-2(1*H*)-one (32a) and Methyl (*S*)-*N*-Phenylsulfinylcarbamate (26): Treatment of sulfoximine **15a** (1.02 g, 2.91 mmol) with $ClCO_2Me$ (3.5 mL, 45.45 mmol) according to *GP5* and purification by double chromatography (EtOAc/cyclohexane, 4:1; aluminium oxide, EtOAc/MeOH, 10:1) gave chloride **32a** (560 mg, 83%) as a white solid and carbamic acid ester **26** (420 mg, 68%) as a colorless oil. **32a:** M.p. 96 °C. $[\alpha]_D = -9.8$ ($c = 1.20$, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.01 (d, *J* = 6.9 Hz, 3 H, *i*Pr), 1.10 (d, *J* = 6.9 Hz, 3 H, *i*Pr), 1.49−1.68 (m, 2 H, CH_2), 1.74−2.06 (m, 5 H, CH_2, *i*Pr), 2.28 (ddd, *J* = 10.2, *J* = 8.5, *J* = 4.1 Hz, 1 H, C*H*CN), 3.54 (symm. m, 2 H, CH_2Cl), 3.74 (dd, *J* = 10.2, *J* = 3.0 Hz, 1 H, CHO), 6.84 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.16 (d), 19.91 (d), 23.29 (u), 28.77 (u), 29.31 (d), 38.11 (u), 41.28 (d), 52.72 (u), 64.79 (u), 83.77 (d), 157.25 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3249 (w), 3128 (w), 2964 (s), 2878 (m), 1713 (s), 1469 (w), 1407 (m), 1371 (w), 1333 (m), 1303 (w), 1144 (w), 1085 (w), 1038 (w), 1021 (w) cm^{-1}. MS (CI): *m*/*z* (relative intensity, %) = 332 [M^+ + 1] (100). $C_{11}H_{18}ClNO_2$ (231.72): calcd. C 57.02, H 7.83, N 6.04; found C 57.08, H 7.48, N 5.83.

(+)-(4*S*,4a*R*,8a*S*)-8a-(Chloromethyl)-octahydro-4-(1-methylethyl)-2*H*-3,1-benzoxazin-2-one (32b): Treatment of sulfoximine **15b** (392 mg, 1.08 mmol) with $ClCO_2Me$ (1.25 mL, 16.2 mmol) for 3 days according to *GP5* and purification by chromatography (EtOAc/pentane, 1:1) afforded chloride **32b** (227 mg, 86%) as a colorless solid and carbamic acid ester **26** (152 mg, 66%). M.p. 145−146 °C, $[\alpha]_D$ = +4.8 ($c = 0.25$, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.85 (d, *J* = 6.8 Hz, 3 H, *i*Pr), 1.00 (d, *J* = 6.8 Hz, 3 H, *i*Pr), 1.10−1.80 (m, 8 H), 1.92 (septd, *J* = 6.8, *J* = 2.2 Hz, 1 H, *i*Pr), 2.00−2.05 (m, 1 H), 3.45 (dd, *J* = 11.3, *J* = 1 Hz, 1 H, CH_2Cl), 3.85 (d, *J* = 11.3 Hz, 1 H, CH_2Cl), 4.25 (dd, *J* = 10.4, *J* = 2.2 Hz, 1 H, CHO), 5.65 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.05 (d), 20.21 (d), 20.76 (u), 22.57 (u), 22.99 (u), 28.44 (d), 33.10 (u), 36.20 (d), 51.05 (u), 55.59 (u), 80.01 (d), 154.59 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3351 (m), 2935 (s), 1725 (s), 1678 (s), 1433 (m), 1332 (m), 1031 (s) cm^{-1}. MS (EI): *m*/*z* (relative intensity, %) = 205 (1), 204 (9), 202 (33), 196 (100), 152 (88), 145 (14), 95 (25), 80 (14). $C_{12}H_{20}ClNO_2$ (245.75): calcd. C 58.65, H 8.20, N 5.70; found C 58.46, H 8.00, N 5.67.

(−)-(4*R*,4a*R*,7a*S*)-7a-(Cyanomethyl)-hexahydro-4-(1-methylethyl)-2*H*-3,1-cyclopenta[*d*][1,3]oxazin-2(1*H*)-one (33a): Treatment of chloride **32a** (348 mg, 1.50 mmol) with NaCN (147 mg, 3.00 mmol) according to *GP6* and purification by chromatography (EtOAc) gave nitrile **33a** (308 mg, 92%) as a colorless solid. M.p. 132 °C. $[\alpha]_D = -34.8$ ($c = 1.63$, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.96 (d, *J* = 6.9 Hz, 3 H, *i*Pr), 1.05 (d, *J* = 6.9 Hz, 3 H, *i*Pr), 1.47−1.69 (m, 2 H), 1.73−2.03 (m, 5 H), 2.28 (td, *J* = 0.9, *J* = 9.8, *J* = 4.1 Hz, 1 H, CHCN), 2.59 (d, *J* = 16.7 Hz, 1 H, CH_2CN), 2.66 (d, *J* = 16.8 Hz, 1 H, CH_2CN), 3.69 (dd, *J* = 10.0, *J* = 3.4 Hz, 1 H, CHO), 7.53 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.76 (d), 20.15 (d), 23.60 (u), 29.12 (u), 29.79 (d), 31.27 (u), 40.43 (u), 43.04 (d), 62.41 (u), 84.51 (d), 117.12 (u), 157.48 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3326 (s), 2971 (m), 2937 (m), 2880 (m), 2256 (m), 1716 (s), 1456 (w), 1412 (m), 1386 (m), 1334 (m), 1301 (m), 1272 (w), 1254 (w), 1192 (w), 1158 (w), 1126 (w), 1055 (w), 1036 (m), 1018 (m) cm^{-1}. MS (EI): *m*/*z* (relative intensity, %) = 223 [M^+ + 1] (1), 182 (84), 180 (12), 179 (21), 139 (10), 138 (100), 137 (23), 136 (51), 135 (12), 122 (12), 121 (69), 110 (21), 109 (10), 108 (60), 107 (21), 96 (16), 95 (22), 94 (13), 93 (54), 82 (54), 81 (50), 80 (19). $C_{12}H_{18}N_2O_2$ (222.28): calcd. C 64.84, H 8.16, N 12.60; found C 64.83, H 8.33, N 12.64.

(+)-(4*R*,4a*R*,8a*S*)-8a-(Cyanomethyl)-octahydro-4-(1-methylethyl)-2*H*-3,1-benzoxazin-2-one (33b): Treatment of chloride **32b** (186 mg, 0.76 mmol) with NaCN (74 mg, 1.51 mmol) according to *GP6* and purification by chromatography (EtOAc) afforded nitrile **33b** (170 mg, 95%) as a colorless solid. M.p. 48−50 °C. $[\alpha]_D$ = +2.86 (*c* = 0.21, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.97 (d, *J* = 6.7 Hz, 3 H, *i*Pr), 1.13 (d, *J* = 6.7 Hz, 3 H, *i*Pr), 1.19−1.35 (m, 2 H), 1.51−1.61 (m, 2 H), 1.69−1.76 (m, 1 H), 1.80−1.90 (m, 3 H), 2.00 (septd, *J* = 6.9, *J* = 3.0 Hz, 1 H, *i*Pr), 2.08 (dt, *J* = 9.8, *J* = 2.2, *J* = 2.2 Hz, 1 H, CHCN), 2.74 (d, *J* = 17.1 Hz, 1 H, CH_2CN), 2.86 (d, *J* = 17.1 Hz, 1 H, CH_2CN), 4.28 (dd, *J* = 9.8, *J* = 3.0 Hz, 1 H, CHO), 7.42 (s, 1 H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.13 (d), 19.76 (d), 20.40 (u), 22.29 (u), 22.98 (u), 28.10 (u), 28.52 (d), 35.54 (u), 36.23 (d), 53.83 (u), 80.59 (d), 116.26 (u), 155.42 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3677 (w), 3652 (w), 3340 (m), 3123 (w), 2939 (s), 2875 (m), 2247 (w), 1707 (s), 1468 (m), 1421 (m), 1383 (m), 1334 (m), 1276 (w), 1244 (w), 1192 (w), 1166 (w), 1142 (w), 1102 (w), 1077 (w), 1034 (m) cm^{-1}. MS (CI): *m*/*z* (relative intensity, %) = 237 [M^+ + 1] (100). $C_{13}H_{20}N_2O_2$ − CH_2CN: calcd. 196.1338; found (HRMS, EI) 196.1337.

(−)-(4*R*,4a*R*,7a*S*)-[Hexahydro-4-(1-methylethyl)-2-oxocyclopenta[*d*][1,3]oxazin-7a(4*H*)-yl]acetic Acid (34a): Treatment of nitrile **33a** (107 mg, 0.48 mmol) with aqueous NaOH (2 N, 1 mL) according to *GP8* and purification by chromatography (EtOAc/AcOH, 95:5) afforded amino acid **33a** (81 mg, 70%) as a colorless oil. $[\alpha]_D$ = −4.4 (*c* = 1.45, MeOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (d, *J* = 6.6 Hz, 3 H, *i*Pr), 1.09 (d, *J* = 6.9 Hz, 3 H, *i*Pr), 1.45−1.69 (m, 2 H, CH_2), 1.73−2.02 (m, 5 H, CH_2, *i*Pr, CHCN), 2.25−2.35 (m, 1 H, CH_2), 2.59 (d, *J* = 17 Hz, 1 H, CH_2CO), 2.65 (d, *J* = 17 Hz, 1 H, CH_2CO), 3.69 (dd, *J* = 10.2, *J* = 2.8 Hz, 1 H, CHO), 7.72 (s, 1 H, NH), 10.6 (br. s, 1 H, CO_2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.91 (d), 19.90 (d), 22.58 (u), 26.95 (u), 28.71 (d), 38.55 (u), 43.95 (d), 44.94 (u), 61.83 (u), 83.39 (d), 157.97 (u), 173.85 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3376 (m), 2970 (s), 2879 (m), 2727 (w), 2627 (w), 1718 (s), 1640 (s), 1545 (w), 1440 (s), 1417 (m), 1394 (w), 1372 (w), 1333 (w), 1287 (w), 1239 (m), 1217 (s), 1182 (m), 1138 (w), 1106 (w), 1070 (m), 1050 (w) cm^{-1}. MS (EI): *m*/*z* (relative intensity, %) = 242 [M^+ + 1] (1), 199 (28), 198 (13), 182 (11), 156 (100), 155 (11), 138 (22), 137 (22), 101 (23), 93 (10), 82 (10), 81 (17).

(−)-(4*R*,4a*R*,8a*S*)-Octahydro-4-(1-methylethyl)-2-oxo-8a*H*-3,1-benzoxazin-8a-yl)acetic Acid (34b): Treatment of nitrile **33b** (78 mg, 0.33 mmol) with aqueous NaOH (2 N, 2 mL) according to *GP8* and purification by chromatography (EtOAc/AcOH, 95:5) afforded the amino acid **34b** (58 mg, 69%) as a colorless solid. M.p. 215 °C (dec.). $[\alpha]_D$ = −2.6 (*c* = 1.25, MeOH). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (d, *J* = 6.6 Hz, 3 H, *i*Pr), 1.13 (d, *J* = 6.9 Hz, 3 H, *i*Pr), 1.18−1.42 (m, 2 H, CH_2, CHCN), 1.49−1.84 (m, 6 H, CH_2), 1.98 (septd, *J* = 6.9, *J* = 1.9 Hz, 1 H, *i*Pr), 2.30−2.43 (m, 2 H, CH_2CO, C*H*CNH), 3.10 (d, *J* = 16.8 Hz, 1 H, CH_2CO), 4.39 (dd, *J* = 10.5, *J* = 1.9 Hz, 1 H, CHO), 7.67 (s, 1 H, NH), 8.3 (br. s, 1 H, CO_2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.41 (d), 19.79 (d), 20.39 (u), 22.20 (u), 22.50 (u), 27.64 (d), 33.03 (u), 39.17 (d), 40.86 (u), 53.77 (u), 79.27 (d), 156.07 (u), 173.93 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3360 (m), 2985 (m), 2944 (m), 2882 (w), 2515 (w), 1716 (s), 1646 (s), 1442 (s), 1386 (w), 1340 (w), 1307 (w), 1263 (m), 1209 (m), 1169 (w), 1140 (w), 1123 (w), 1101 (w), 1044 (m) cm^{-1}. MS (CI): *m*/*z* (relative intensity, %) = 256 [M^+ + 1] (100).

(−)-(*S*)-(Methylsulfinyl)benzene (36): MeMgCl (0.9 mL, 22 wt% in THF, 2.66 mmol) was added at −78 °C to a solution of sulfinamide **26** (284 mg, 1.33 mmol) in THF (6 mL). After the mixture had been stirred at this temperature for 45 min, saturated aqueous NH_4Cl was added and the aqueous phase was extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Chromatography (EtOAc/*i*PrOH, 8:1) afforded sulfoxide **36** (131 mg, 70%) of 97% *ee* [GC, octakis(2,6-di-*O*-pentyl-3-*O*-butyryl)-γ-cyclodextrin, t_R (**36**) = 25.10, t_R (*ent*-**36**) = 21.40 min] as a colorless oil. $[\alpha]_D$ = −140.2 (*c* = 2.05, acetone). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.73 (s, 3 H, CH_3), 7.47−7.56 (m, 3 H, Ph), 7.63−7.67 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.89 (d), 123.28 (d), 129.15 (d), 130.82 (d), 145.47 (u) ppm.

(4*R*,5*R*,6*S*)-Tetrahydro-4-ethenyl-6-ethyl-5-methyl-2*H*-1,3-oxazin-2-one (39): $ClCO_2CH(Cl)Me$ (0.13 mL, 1.20 mmol) and four drops of pyridine were added at room temperature to a solution of **16a** (40 mg, 0.12 mmol) in CH_2Cl_2 (2 mL). The yellow mixture was stirred at room temperature for 1 h and then concentrated in vacuo. Purification by chromatography (EtOAc) gave a mixture of **39** and **40** in a ratio of 8:1 (119 mg) as a colorless solid.

Compound 39: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (d, *J* = 6.7 Hz, 3 H, CH*Me*), 1.03 (t, *J* = 7.4 Hz, 3 H, Et), 1.61 (tq, *J* = 10.0, *J* = 6.7 Hz, 1 H, *CH*Me), 1.58 (dquin, *J* = 14.8, *J* = 7.4 Hz, 1 H, Et), 1.85 (dqd, *J* = 14.8, *J* = 7.4, *J* = 3.0 Hz, 1 H, Et), 3.46 (dd, *J* = 10.0, *J* = 8.3 Hz, 1 H, CHN), 3.93 (ddd, *J* = 10.0, *J* = 7.4, *J* = 3.0 Hz, 1 H, CHO), 5.28 (br. d, *J* = 9.9 Hz, 1 H, *CH*=CH_2), 5.29 (br. d, *J* = 17.1 Hz, 1 H, CH=CH_2), 5.38 (s, 1 H, NH), 5.65 (ddd, *J* = 17.1, *J* = 9.9, *J* = 8.3 Hz, 1 H, *CH*=CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.25 (d), 12.54 (d), 24.94 (u), 35.16 (d), 61.02 (d), 82.19 (d), 119.75 (u), 136.84 (d), 154.18 (u) ppm. GC-MS: *m*/*z* (relative intensity, %) = 170 [M^+ + 1] (99), 109 (13), 100 (21), 96 (22), 86 (10), 84 (18), 82 (14).

Compound 40: ^{1}H NMR (400 MHz, $CDCl_3$) (signals for **40** are partially superposed by those for **39**, so only those signals that could be unequivocally assigned are listed): δ = 1.00 (d, *J* = 6.7 Hz, 3 H, Me), 1.04 (t, *J* = 7.4 Hz, 3 H, Et), 3.13 (dd, *J* = 9.3, *J* = 1.7 Hz, 1 H, C*H*NH), 3.90 (m, 1 H, C*H*O), 4.20 (qd, *J* = 7.0, *J* = 1.7 Hz, 1 H, C*H*Cl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) (only those signals are listed, which could be unequivocally assigned): δ = 8.37, 13.40, 21.89, 24.88, 33.09, 56.85, 61.99, 81.42 ppm.

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