Synthesis and Alkylation of Cyclic α-Sulfonimidoyl Carbanions: Non-transferable Chiral Carbanionic Ligands in Copper-Mediated Enantioselective Conjugate Addition

Stephan Boßhammer, Hans-Joachim Gais*

Institut für Organische Chemie der Rheinisch-Westfälischen Technischen Hochschule Aachen, Professor-Pirlet-Straße 1, D-52056 Aachen, Germany

Fax +49(241)8888127; E-mail: Gais@RWTH-Aachen.de

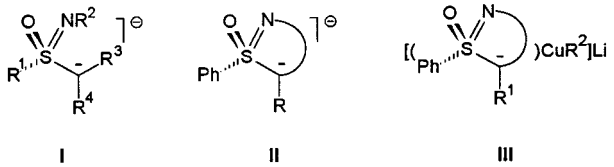
Received 31 January 1998

Abstract: The cyclic sulfoximines **4a** and **4b** have been prepared from (+)-(*S*)-*S*-methyl-*S*-phenylsulfoximine (**1**). Deprotonation of **4a** and **4b** and alkylation of lithiosulfoximines Li-**4a** and Li-**4b** gave α-alkyl substituted sulfoximines **5a** (89% de), **5b** (90% de), **6a** (≥98% de), **6b** (≥98% de), **7b** (≥98% de) and **8b** (≥98% de). The configuration of **6b** was determined by X-ray structure analysis. Consecutive treatment of **5b**, **6b** and **8b** with BuLi and CF_3CO_2H gave epimers *epi*-**5b** (64% de), *epi*-**6b** (89% de) and *epi*-**8b** (81% de). α,α-Dialkyl substituted sulfoximines **9** (≥98% de) and *epi*-**9** (≥98% de) were obtained by alkylation of Li-**5b** and Li-**6b**. Conjugate addition of cuprates **11–14**, containing the acyclic sulfonimidoyl carbanions **Ia–c**, to cyclohex-2-en-1-one gave ketones **15** and **16** in good yields but with low asymmetric induction (8–49% ee). However, conjugate addition of cuprates **19b**, **20b**, **21b** and **22b**, derived from the cyclic lithiosulfoximines Li-**7b** and Li-**8b**, to cyclopent-2-en-1-one, cyclohex-2-en-1-one and cyclohept-2-en-1-one gave ketones **15a–c**, **23b** and **24b** with good to high asymmetric inductions (77–99% ee) in good yields. The bicyclic ketone **27** (79% ee) was prepared from cyclohex-2-en-1-one via **24b** in three steps.

Key words: cyclic lithiosulfoximines, diastereoselective alkylation, Cu(I)-mediated enantioselective conjugate addition, chiral non-transferable C-ligands, acyclic lithiosulfoximines

Introduction

The chemistry of acyclic sulfonimidoyl carbanions, **I**, which have found many applications in asymmetric synthesis,[1] is well established.[2] Cyclic sulfonimidoyl carbanions, **II**, however, have escaped attention so far almost completely.[3] Because of the incorporation of the anionic C-atom and the S-atom in a ring, reactions with electrophiles should be highly stereoselective, and, thus, interesting applications of **II** in asymmetric synthesis can be envisioned. We were especially interested in the synthesis of chiral cuprates of type **III** from **II** and in the use of the former in enantioselective conjugate addition. The cuprates studied so far in enantioselective conjugate addition contained as chiral non-transferable ligands either alkoxides, amides, thiolates or phosphanes but not carbanions.[4] We have observed some time ago that **Ia** (R^1 = Ph, R^2 = Me, R^3 = R^4 = H) serves as a non-transferable ligand in conjugate addition of cuprates.[5] However, the asymmetric induction in conjugate addition of cuprates derived from **Ia** was only very low. In this paper we describe the synthesis and alkylation of carbanions **II** as well as their conversion to **III** and the use of the latter in enantioselective conjugate addition.

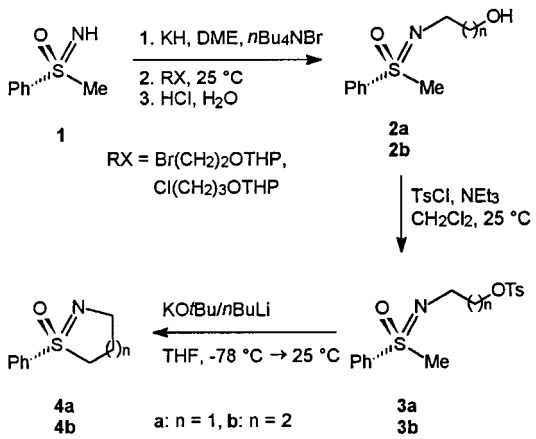


I **II** **III**

Results and Discussion

Synthesis and Alkylation of Cyclic Sulfonimidoyl Carbanions

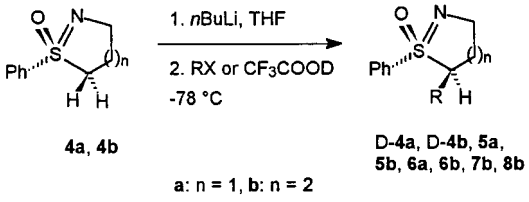
The unsubstituted 5- and 6-membered sulfoximines **4a** and **4b** were prepared in three steps from (+)-(*S*)-*S*-methyl-*S*-phenylsulfoximine (**1**), which is readily available by an efficient racemate separation[6] (Scheme 1). Alkylation of **1** at the N-atom[7] with THP-protected bromoethanol and chloropropanol[8] and cleavage of the acetals formed gave the *N*-hydroxyalkyl sulfoximines **2a** and **2b** in 77 and 72% yield. Tosylation of **2a** and **2b** afforded tosylates **3a** and **3b**, each in 92% yield. Treatment of **3a** and **3b** with *t*-BuOK/BuLi in THF led to their cyclization and afforded the cyclic sulfoximines **4a**[9] and **4b** in 66 and 57% yield.



Scheme 1

Metallation and deuteration experiments showed that sulfoximines **4a** and **4b** are readily deprotonated by BuLi in THF in the α-position (Scheme 2, Table 1, Entries 1 and 4). Deuteration of Li-**4a** and Li-**4b** occurred stereoselectively and gave D-**4a** and D-**4b**. The configurations of D-**4a** and D-**4b** were determined by NOE experiments on the basis of a complete assignment of the signals in the ^{1}H NMR spectra of **4a, 4b**, D-**4a** and D-**4b**. Consecutive treatment of **4a** and **4b** with BuLi and an alkylating reagent readily furnished the corresponding α-alkyl substituted sulfoximines with high diastereoselectivity (Table

1). With methyl iodide as the alkylating reagent the diastereomerically enriched sulfoximines **5a** and **5b** were obtained in high yields (Table 1, Entries 2 and 5). The use of the sterically more demanding benzyl bromide, isopropyl iodide and 2,4,6-trimethylbenzyl chloride as the alkylating reagents afforded the diastereomerically pure sulfoximines **6a**, **6b**, **7b** and **8b** in good to high yields (Table 1, Entries 3, 6, 7 and 8). In these cases formation of the epimeric sulfoximines could not be detected by NMR spectroscopy.



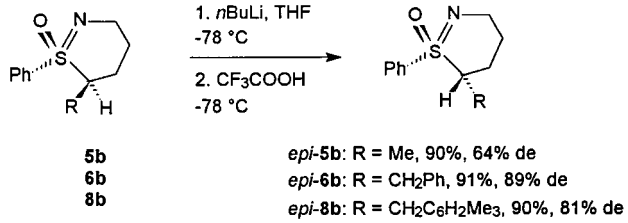
Scheme 2

Table 1. Deuteration and Alkylation of Cyclic Lithiosulfoximines

Entry	Substrate	Product	Yield[a] (%)	de (%)
1	**4a**	D-**4a**: R = D (> 95% D)	95	74
2	**4a**	**5a**: R = Me	94	89
3	**4a**	**6a**: R = CH_2Ph	85	≥98
4	**4b**	D-**4b**: R = D (≥ 95% D)	95	81
5	**4b**	**5b**: R = Me	88	90
6	**4b**	**6b**: R = CH_2Ph	71	≥98
7	**4b**	**7b**: R = $CHMe_2$	57	≥98
8	**4b**	**8b**: R = $CH_2C_6H_2Me_3$	69[b]	≥98

[a] Reaction time: 3 h.
[b] Reaction time: 15 h.

The similar stereochemical course of the deuteration and the alkylation of lithiosulfoximines Li-**4a** and Li-**4b** suggested, however, a facile synthesis of the epimeric alkyl sulfoximines as well. Thus, treatment of **5b**, **6b** and **8b** with BuLi and protonation of Li-**5b**, Li-**6b** and Li-**8b** with CF_3CO_2H gave the diastereomerically enriched epimeric sulfoximines *epi*-**5b**, *epi*-**6b** and *epi*-**8b** in high yields (Scheme 3). Sulfoximines *epi*-**6b** and *epi*-**8b** could be obtained diastereomerically pure by chromatography.

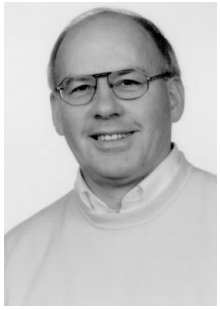


Scheme 3

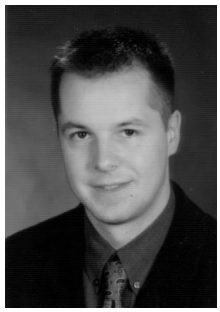
The configurations of **5a**, **6a**, **6b**, **7b** and **8b** as well as of epimers *epi*-**5b**, *epi*-**6b** and *epi*-**8b** were determined by NOE experiments on the basis of a complete assignment of the signals in their ^{1}H NMR spectra. The NMR spectroscopic assignment of configuration was substantiated in the case of **6b** by an X-ray structure analysis (Figure)[10] which showed **6b** to have the *S,S*-configuration. In the crystal and in solution **6b** adopts a conformation in which the phenyl and the benzyl group occupy the pseudo-equatorial position.

Not only the protonation but also the alkylation of Li-**5b** and Li-**6b** occurred with high diastereoselectivity. Thus,

Biographical Sketches



Hans-Joachim Gais was born in 1942 in Darmstadt, Germany. He studied chemistry at the TH Darmstadt where he received a diploma in chemistry and a Dr. Ing. in 1973, working under the supervision of Professor Hafner. After postdoctoral studies with Professor Woodward at Harvard University in 1974–1975, he returned to the TH Darmstadt. There he began his independent research and was appointed Privatdozent in 1981. In 1986 he joined the faculty at the University of Freiburg as Professor of Organic Chemistry. Since 1991 he has been a Professor of Organic Chemistry at the RWTH Aachen. He is a recipient of the Carl Duisberg Award of the Gesellschaft Deutscher Chemiker. His research interests comprise the synthesis of cyclopentanoid natural and non-natural compounds, the application of enzymes in asymmetric synthesis, the structure and reactivity of chiral sulfur-stabilized carbanions and the use of sulfoximines in asymmetric synthesis.



Stephan Boßhammer was born in 1968 in Würselen, Germany. He studied chemistry at the RWTH Aachen and received his diploma degree in 1995. He joined the research group of Professor Gais and received his Ph. D. degree in 1998. In his thesis he concentrated on new applications of sulfoximines in asymmetric synthesis.

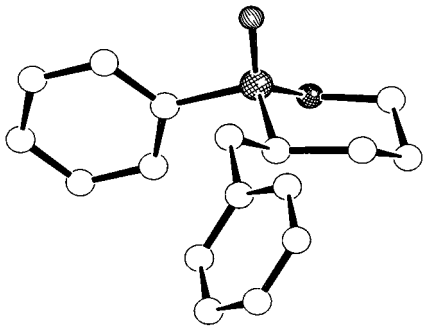
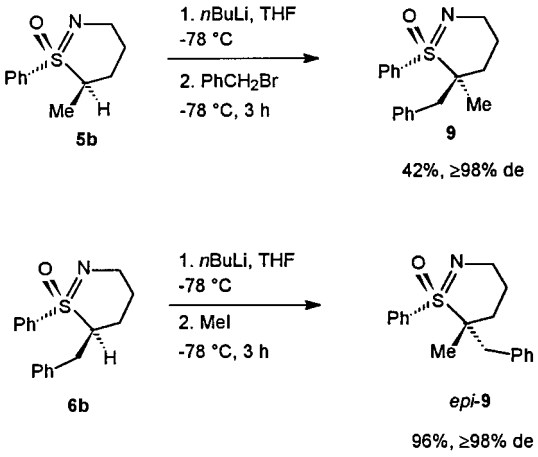


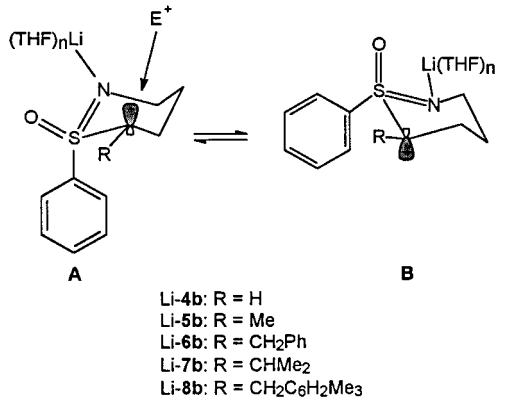
Figure. X-ray Crystal Structure of Sulfoximine **6b**. Selected bond lengths (Å): S-O 1.450(2), S-N 1.528(3), S-C_α 1.794(3).

consecutive treatment of **5b** with BuLi and benzyl bromide gave the α,α-dialkyl substituted sulfoximine **9** of ≥98% de in acceptable yield (Scheme 4). By the same sequence, but starting with sulfoximine **6b** and using methyl iodide as the alkylating reagent, sulfoximine *epi*-**9** of ≥98% de was obtained in high yield.



Scheme 4

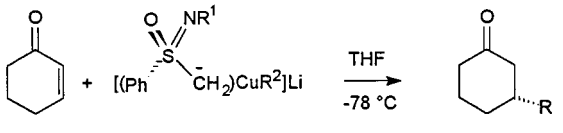
The above results show that attack of an electrophile at the anionic C-atom of lithiosulfoximines Li-**4a**, Li-**6a**, Li-**4b**, Li-**5b**, Li-**6b**, Li-**7b** and Li-**8b** occurs preferentially from the side of the sulfoximine O-atom, irrespective of the substituent at the C_α-atom. Similar observations were made in reactions of a racemic bicyclic lithiosulfoximine with electrophiles.[3] We propose structures **A** and **B** for the six-membered lithiosulfoximines Li-**4b**, Li-**5b**, Li-**6b**, Li-**7b** and Li-**8b**, on the basis of the structure of Li-**I**[11] (Scheme 5). The cyclic lithiosulfoximines are in THF solution most likely to be monomeric and/or dimeric contact ion pairs in which the Li-atom is coordinated to the N-atom in the monomer and to the N- and O-atoms in the dimer. The anion in **A** has a C_α-S-conformation in which the lone-pair orbital at the C_α-atom is periplanar to the S–Ph bond, because of a stabilizing n_C-σ^*-interaction.[11c] As a result the phenyl group occupies the pseudo-axial and the substituent R the pseudo-equatorial position, Because of a minimization of torsional interaction between the S–O bond and the substituent R, the C_α-atom is pyramidalized. In diastereomer **B** the lone-pair orbital is periplanar to the S-O bond, the C_α-atom is pyramidalized and the substituents at the S-atom and the C_α-atom occupy the pseudo-equatorial position. Whereas the $(THF)_nLi$ group and the phenyl ring are *trans* in **A** they are *cis* in **B**. The attainment of an equilibrium between **A** and **B** is expected to be fast even at low temperatures because of the low barriers towards C_α-S rotation and C_α-inversion. Attack of the electrophile at the C_α-atom in **A** syn to the O-atom is preferred because of the direction of the C_α-pyramidalization and a lack of a steric hindrance. Diastereomer **B** should be less reactive than **A**. Attack of E^+ at the C_α-atom *syn* as well as *anti* to the O-atom in **B** is disfavored because of the opposite direction of C_α-pyramidalization and the shielding by the phenyl group. A similar rationalization can be applied to the reactions of the five-membered lithiosulfoximines Li-**4a** and Li-**6a** which are expected to adopt similar structures.



Scheme 5

Conjugate Addition of Cuprates Containing Sulfonimidoyl Carbanions

The asymmetric induction in the reaction of cuprate **11**, containing the acyclic carbanion **Ia** (R^1 = Ph, R^2 = Me, R^3 = R^4 = H),[12a] with cyclohex-2-en-1-one (**10b**), was very low (Scheme 6). Ketone **15b** was isolated, however, in good yield. This showed that **Ia** can function like methylsulfinyl methanide and methylsulfonyl methanide[13] as a non-transferable ligand in conjugate addition of cuprates. Reaction of cuprates **12** and **13**, derived from the acylic carbanions **Ib** (R^1 = Ph, R^2 = CPh_3, R^3 = R^4 = H) (the precursor of **Ib** is designated as H-**Ib**, see experimental) and **Ic** (R^1 = Ph, R^2 = $SiPh_2$-*t*-Bu, R^3 = R^4 = H)[12b]



10b

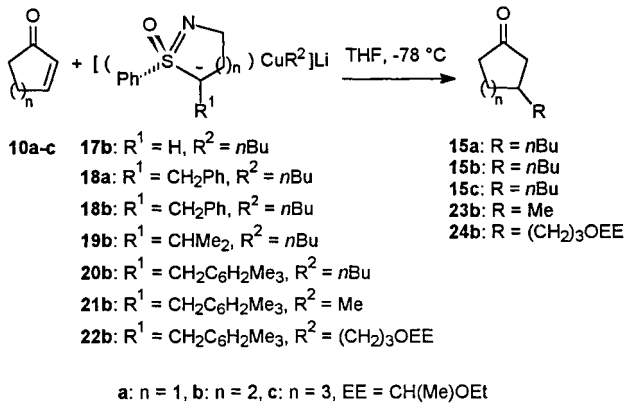
11: R^1 = Me, R^2 = *n*Bu
12: R^1 = CPh_3, R^2 = *n*Bu
13: R^1 = Si*t*BuPh$_2$, R^2 = *n*Bu
14: R^1 = Si*t*BuPh$_2$, R^2 = Ph

15b: R = *n*Bu, 84%, 8% ee
15b: R = *n*Bu, 49%, 30% ee
15b: R = *n*Bu, 70%, 24% ee
16b: R = Ph, 78%, 49% ee

Scheme 6

which carry bulky groups at the N-atom, with cyclohex-2-en-1-one gave ketone **15b**, having a higher ee-value. The highest enantioselectivity was observed in the case of reaction of cuprate **14** with **10b** which gave ketone **16b** of 49% ee in 78% yield.

Because of the low asymmetric induction recorded in conjugate addition with cuprates derived from flexible acyclic sulfonimidoyl carbanions **I**, we speculated that cuprates containing the more rigid cyclic sulfonimidoyl carbanions **II** would give perhaps better results. Thus, cuprates **17b**, **18a**, **18b**, **19b**, **20b**, **21b** and **22b** (Table 2) were prepared by the consecutive treatment of lithiosulfoximines Li-**4b**, Li-**6a**, Li-**6b**, Li-**7b** and Li-**8b** in THF with CuI (1 equiv) and BuLi, MeLi and $Li(CH_2)_3OCH(Me)OEt$[14] (0.9 equiv) (Scheme 7). Disappointingly, conjugate addition of unsubstituted and benzyl substituted cuprates **17b**, **18a** and **18b** to **10b** in THF proceeded with only very low asymmetric induction (Table 2, Entries 1–3). However, addition of the isopropyl and trimethylbenzyl substituted cuprates **19b**, **20b** and **21b** to cyclopent-2-en-1-one (**10a**), cyclohex-2-en-1-one (**10b**) and cyclohept-2-en-1-one (**10c**) afforded ketones **15a–c** and **23b**, having ee-values of 77–99%, in good yields (Table 2, Entries 4–9). Interestingly, conjugate addition of the isopropyl substituted cuprate **19b** and of the trimethylbenzyl substituted cuprate **20b** to cyclohex-2-en-1-one (**10b**) proceeded with opposite asymmetric induction (Table 2, Entries 4 and 5). Treatment of **10b** with the functionalized cuprate **22b** resulted in a transfer of the $(CH_2)_3OCH(Me)OEt$ group and gave ketone **24b** of 79% ee in 70% yield. In the above described conjugate additions sulfoximines **4b**, **6a**, **6b**, **7b** and **8b** were recovered almost quantitatively upon aqueous workup. Surprisingly, sulfoximines **6b**, **7b** and **8b** were mixed with *epi*-**6b**, *epi*-**7b** and *epi*-**8b**, respectively, in ratios of approximately 1:1. Because of the complete lack of information about the structures of cuprates **17b**, **18a**, **18b**, **19b**, **20b**, **21b** and **22b** as well as of cuprates **11–14**, rationalization of this observation is difficult at present.



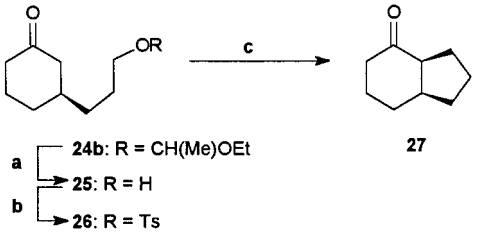
Scheme 7

Table 2. Conjugate Addition of Cuprates Containing Cyclic Sulfonimidoyl Carbanions

Entry	Cuprate	Substrate	Product	Yield (%)	ee (%)	Abs. Conf.
1	**17b**	**10b**	**15b**	45	12	*S*
2	**18a**	**10b**	**15b**	61	10	*R*
3	**18b**	**10b**	**15b**	95	20	*R*
4	**19b**	**10b**	**15b**	82	81	*R*
5	**20b**	**10b**	**15b**	90	99	*S*
6	**20b**	**10a**	**15a**	80	93	*S*
7	**20b**	**10c**	**15c**	90	77	*S*
8	**21b**	**10b**	**23b**	50	86	*S*
9	**22b**	**10b**	**24b**	70	79[a]	*R*

[a] For alcohol **25**.

Determination of the absolute configurations of **15a,**[15a] **15b**,[15b] **15c**,[15c] **16b**[15b] and **23b**[15d] was accomplished by comparison of their chiroptical data with those reported in the literature. The absolute configuration of **24b** was assigned by chemical correlation. Thus, acetal **24b** was converted via alcohol **25** to tosylate **26** in 42% overall yield from **10b** (Scheme 8). Treatment of tosylate **26** with $LiCuMe_2$ gave not **15b**, as expected, but led to cyclization of **26** and afforded ketone **27** in 90% yield. Comparison of the chiroptical data of **27** with those of its 7-methyl derivatives[16] led to assignment of the *R*-configuration to **24b**.



Reagents and conditions: a) HCl/HK_2O; ab) $TsCl/NEt_3/CH_2Cl_2$, 0 °C; c) $LiCuMe_2$/THF, –78 °C

Scheme 8

Conclusion

We have shown that enantiomerically pure cyclic α-sulfonimidoyl carbanions are easily accessible from the corresponding sulfoximines upon deprotonation with BuLi. Reaction of these carbanions with alkylating reagents proceeded highly stereoselective *syn* to the sulfoximine O-atom, giving the corresponding mono- and disubstituted cyclic sulfoximines. We have observed that acyclic and cyclic α-sulfonimidoyl carbanions are capable to act as non-transferable carbanionic ligands in conjugate addition of cuprates. High asymmetric induction was observed with cuprates derived from a six-membered cyclic α-sulfonimidoyl carbanion, bearing a trimethylbenzyl group at the anionic carbon atom.

All manipulations except workup and chromatography were performed in an atmosphere of dry argon, with Schlenk and syringe techniques in oven-dried glassware. Et_2O was distilled from sodium benzophenone ketyl, and THF was distilled from potassium benzophenone ketyl. Dimethoxyethane (DME) and NEt_3 were distilled

from CaH_2. MeOH was distilled from magnesium turnings. CuI was purified by the method described by Kauffman and Teter.[17] TLC was performed on E. Merck precoated plates (silica gel 60 F_{254}, 0.2 mm). Column chromatography was performed with E. Merck silica gel 60 (230–400 mesh). Melting points are uncorrected. ^{1}H NMR (300 MHz, $CDCl_3$) chemical shifts are reported in ppm relative to TMS as internal standard. Splitting patterns are designated as s, singlet; d, doublet; dd double doublet; t, triplet; m, multiplet; br, broad. ^{13}C NMR (75 MHz, $CDCl_3$) chemical shifts are reported in ppm relative to TMS as internal standard. Peaks in ^{13}C NMR spectra are denoted as "u" for carbons with zero or two attached protons or with "d" for carbons with one or three attached protons, as determined from the APT puls sequence. Determination of ee-values was performed by capillary GC analysis on an octakis-(2,3-di-*O*-pentyl-6-*O*-methyl)-γ-cyclodextrin column, a permethyl-β-cyclodextrin column and an octakis-(2,6-di-*O*-pentyl-3-*O*-butyryl)-γ-cyclodextrin column. Optical rotations were measured at room temperature. Elemental analyses were performed by the Institut für Organische Chemie Microanalytical Laboratory, Aachen.

(+)-(*S*)-*N*-(2-Hydroxyethyl)-*S*-methyl-*S*-phenylsulfoximine (2a); Typical Procedure:

A solution of **1** (15.0 g, 96.6 mmol) in DME (80 mL) was added to a suspension of KH (106 mmol, 14.2 g, 35% in mineral oil) in DME (80 mL). After stirring the suspension for 3 h at r.t., Bu_4NBr (1.56 g, 4.83 mmol) and 2-(2-bromoethoxy)tetrahydropyrane (30.3 g, 145 mmol) were added at 0 °C. The mixture was stirred for 20 h at r.t. and was subsequently poured into 2 M HCl (200 mL). The mixture was extracted with Et_2O (150 mL) and the aqueous phase was neutralized by the careful addition of solid Na_2CO_3. The aqueous phase was extracted with EtOAc (4 × 200 mL) and the combined organic phases were dried ($MgSO_4$) and concentrated in vacuum. Purification of the residue by chromatography (10% MeOH/EtOAc) gave **2a** (14.8 g, 77%) as a colorless oil; $[\alpha]_D$ +141.3 (*c* = 1.52, THF).

^{1}H NMR: δ = 2.98–3.14 (m, 2 H, NCH_2), 3.17 (s, 3 H, CH_3), 3.50 (br s, 1 H, O*H*), 3.65–3.70 (m, 2 H, OCH_2), 7.55–7.68 (m, 3 H, *m*/*p*-Ph*H*), 7.91–7.96 (m, 2 H, *o*-Ph*H*).

^{13}C NMR: δ = 44.97 (d, *C*H_3), 46.63 (u, N*C*H_2), 63.41 (u, O*C*H_2), 128.70 (d), 129.55 (d) (*o*/*m*-Ph*C*), 133.12 (d, *p*-Ph*C*), 138.78 (u, *ipso*-Ph*C*).

MS (EI, 70 eV): *m*/z (%) = 199 (M^+, 1), 170 (12), 169 (22), 168 (100), 142 (13), 141 (97), 140 (11), 126 (31), 125 (64), 124 (37), 97 (27), 91 (10), 78 (29), 77 (43), 65 (12), 63 (14), 51 (34).

Anal. $C_9H_{13}NO_2S$ (199.2): calcd C, 54.25; H, 6.58; N 7.03; found C, 54.20; H, 6.64; N, 7.04.

(+)-(S)-N-(3-Hydroxypropyl)-S-methyl-S-phenylsulfoximine (**2b**):

Following the above procedure, **2b** (14.8 g, 72%) was obtained from **1** (15.0 g, 96.6 mmol) and 2-(3-chloropropoxy)tetrahydropyrane (25.9 g, 145 mmol) as a colorless oil; $[\alpha]_D$ +147.7 (*c* = 1.36, THF).

^{1}H NMR: δ = 1.74–1.83 (m, 2 H, $CH_2CH_2CH_2$), 2.95 (ddd, *J* = 12.0, 6.4, 5.8 Hz, 1 H, NCH_2), 3.10 (s, 3 H, CH_3), 3.15 (ddd, *J* = 12.1, 6.7, 5.7 Hz, 1 H, NCH_2), 3.79–3.84 (m, 2 H, OCH_2), 7.55–7.67 (m, 3 H, *m*/*p*-Ph*H*), 7.90–7.94 (m, 2 H, *o*-Ph*H*).

^{13}C NMR: δ = 33.70 (u, $CH_2CH_2CH_2$), 42.02 (u, N*C*H_2), 45.07 (d, *C*H_3), 62.34 (u, O *C*H_2), 128.66 (d), 129.56 (d) (*o*/*m*-Ph*C*), 133.09 (d, *p*-Ph*C*), 138.99 (u, *ipso*-Ph*C*).

MS (EI, 70 eV): *m*/z (%) = 213 (M^+, 0.4), 180 (19), 168 (100), 141 (55), 140 (29), 126 (12), 125 (39), 124 (13), 117 (27), 92 (21), 91 (10), 78 (14), 77 (30), 51 (20).

Anal. $C_{10}H_{15}NO_2S$ (213.3): calcd C, 56.31; H, 7.09; N, 6.57; found C, 55.86; H, 7.18; N, 6.34.

(+)-(*S*)-*S*-Methyl-*S*-phenyl-*N*-(2-*p*-tosyloxyethyl)sulfoximine (3a); Typical Procedure:

To a solution of **2a** (13.3 g, 66.7 mmol) and *p*-TsCl (14.4 g, 75.3 mmol) in CH_2Cl_2 (55 mL) was added NEt_3 (15 mL) at 0 °C. After stirring the mixture for 20 h at r.t., satd aq NH_4Cl solution (100 mL) was added and the mixture was extracted with EtOAc (3 × 50 mL). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuum. Purification of the residue by chromatography (10% MeOH/EtOAc) gave **3a** (21.6 g, 92%) as a colorless oil; $[\alpha]_D$ +87.6 (*c* = 1.77, $CHCl_3$).

^{1}H NMR: δ = 2.43 (s, 3 H, ArCH_3), 3.01–3.21 (m, 2 H, NCH_2), 3.07 (s, 3 H, SCH_3), 4.04–4.15 (m, 2 H, OCH_2), 7.30–7.34 (m, 2 H, *m*-SO_2Ar*H*), 7.53–7.67 (m, 3 H, *m*/*p*-Ph*H*), 7.75–7.79 (m, 2 H, *o*-SO_2Ar*H*), 7.86–7.90 (m, 2 H, *o*-Ph*H*).

^{13}C NMR: δ = 21.60 (d, Ar*C*H_3), 42.49 (u, N*C*H_2), 44.82 (d, S*C*H_3), 71.00 (u, O*C*H_2), 127.91 (d), 128.64 (d), 129.54 (d), 129.76 (d) (*o*/*m*-Ph*C*), 133.02 (u, *p*-Ph*C*), 133.24 (d, *p*-Tol*C*), 138.54 (u), 144.66 (u) (*ipso*-Ph*C*).

MS (EI, 70 eV): *m*/z (%) = 182 (M^+ – TsO, 3), 181 (19), 168 (100), 141 (22), 125 (12), 91 (18).

Anal. $C_{16}H_{19}NO_4S_2$ (353.4): calcd C, 54.37; H, 5.42; N, 3.96; found C, 54.21; H, 5.43 ; N, 3.98.

(+)-(S)-S-Methyl-S-phenyl-N-(3-p-tosyloxypropyl)sulfoximine (**3b**):

Following the above procedure, **3b** (18.9 g, 92%) was obtained from **2b** (13.0 g, 61.1 mmol) as a colorless oil; $[\alpha]_D$ +91.3 (*c* = 1.50, $CHCl_3$).

^{1}H NMR: δ = 1.82–1.92 (m, 2 H, $CH_2CH_2CH_2$), 2.44 (s, 3 H, ArCH_3), 2.85 (m, 1 H, NCH_2), 2.99 (m, 1 H, NCH_2), 3.04 (s, 3 H, SCH_3), 4.13 (m, 1 H, OCH_2), 4.27 (m, 1 H, OCH_2), 7.30–7.35 (m, 2 H, SO_2-m-Ar*H*), 7.54–7.66 (m, 3 H, *m*/*p*-Ph*H*), 7.75–7.80 (m, 2 H, SO_2-o-Ar*H*), 7.85–7.89 (m, 2 H, *o*-Ph*H*).

^{13}C NMR: δ = 21.63 (d, Ar*C*H_3), 31.61 (u, $CH_2CH_2CH_2$), 39.45 (u, N*C*H_2), 44.98 (d, S *C*H_3), 68.68 (u, O*C*H_2), 127.92 (d), 128.60 (d), 129.53 (d), 129.77 (d) (*o*/*m*-Ph*C*), 133.00 (d, *p*-Ph*C*), 133.21 (u, *p*-Tol*C*), 139.14 (u), 144.56 (u) (*ipso*-Ph*C*).

MS (EI, 70 eV): *m*/z (%) = 368 (M^+ + 1, 0.1), 212 (15), 168 (88), 142 (10), 141 (100), 140 (34), 125 (34), 124 (26), 94 (11), 91 (43), 78 (20), 77 (19), 65 (19), 56 (30), 51 (14).

Anal. $C_{17}H_{21}NO_4S_2$ (367.4): calcd C, 55.56; H, 5.76; N, 3.81; found C, 55.30; H, 5.78; N, 3.89.

(+)-(*S*)-1-Phenyl-4,5-dihydro-3*H*-isothiazol-1-oxide (4a); Typical Procedure:

To a solution of *t*-BuOK (7.20 g, 64.2 mmol) in THF (160 mL) at –78 °C was added BuLi (64.2 mmol, 41.1 mL of 1.6 M in hexane). After stirring the mixture for 30 min at –78 °C, a cold solution of sulfoximine **3a** (21.6 g, 61.1 mmol) in THF (160 mL) was added. Subsequently the mixture was warmed slowly to r.t. After stirring the mixture for 20 h, satd aq NH_4Cl solution (200 mL) was added and the mixture was extracted with EtOAc (4 × 150 mL). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuum. Purification of the residue by chromatography (10% MeOH/EtOAc) gave **4a** (7.3 g, 66%) as a colorless solid; mp 108–109 °C; $[\alpha]_D$ +25.1 (*c* = 0.90, EtOAc).

^{1}H NMR: δ = 2.19–2.35 (m, 1 H, NCH_2CH_2), 2.39–2.49 (m, 1 H, NCH_2CH_2), 3.17–3.29 (ddd, *J* = 12.9, 9.1, 8.2 Hz, 1 H, SCH_2), 3.35–3.46 (ddd, *J* = 12.9, 7.7, 5.8 Hz, 1 H, SCH_2), 3.82–3.92 (m, 1 H, NCH_2), 4.04–4.14 (m, 1 H, NCH_2), 7.51–7.58 (m, 2 H, *m*-Ph*H*), 7.60–7.67 (m, 1 H, *p*-Ph*H*), 7.93–7.99 (m, 2 H, *o*-Ph*H*).

^{13}C NMR: δ = 26.11 (u, NCH_2CH_2), 56.15 (u, N*C*H_2), 56.70 (u, S*C*H_2), 129.27 (d), 129.41 (d) (*o*/*m*-Ph*C*), 133.48 (d, *p*-Ph*C*), 139.78 (u, *ipso*-Ph*C*).

MS (EI, 70 eV): *m*/z (%) = 181 (M^+, 12), 180 (4), 153 (31), 125 (100), 97 (11), 77 (18), 51 (13).

Anal. $C_9H_{11}NOS$ (181.2): calcd C, 59.63; H, 6.12; N, 7.73; found C, 59.41; H, 6.14; N, 7.66.

(+)-(S)-1-Phenyl-3,4,5,6-tetrahydro[1,2]thiazin-1-oxide (**4b**):

Following the above procedure, **4b** (3.6 g, 57%) was obtained from **3b** (12.0 g, 32.6 mmol) as a colorless solid; mp 64 °C; $[\alpha]_D$ +69.4 (*c* = 1.11, $CHCl_3$).

^{1}H NMR: δ = 1.74–1.87 (m, 2 H, NCH$_2$CH_2), 2.18–2.26 (m, 1 H, SCH$_2$CH_2), 2.50–2.60 (m, 1 H, SCH$_2$CH_2), 2.90–2.97 (ddd, *J* = 13.5, 11.8, 4.9 Hz, 1 H, SCH_2), 3.15–3.20 (ddd, *J* = 11.8, 3.8, 3.8 Hz, 1 H, SCH_2), 3.50–3.56 (m, 1 H, NCH_2), 3.68–3.74 (m, 1 H, NCH_2), 7.53–7.58 (m, 2 H, *m*-Ph*H*), 7.60–7.65 (m, 1 H, *p*-Ph*H*), 8.05–8.09 (m, 2 H, *o*-Ph*H*).
^{13}C NMR: δ = 21.61 (u, SCH$_2$*C*H$_2$), 23.52 (u, NCH$_2$*C*H$_2$), 43.46 (u, N*C*H$_2$), 51.75 (u, S*C*H$_2$), 128.37 (d), 129.13 (d) (*o*/*m*-Ph*C*), 133.28 (d, *p*-Ph*C*), 139.64 (u, *ipso*-Ph*C*).
MS (EI, 70 eV): *m*/z (%) = 195 (M$^+$, 31), 126 (19), 125 (100), 118 (11), 117 (13), 110 (13), 105 (11), 97 (19), 91 (40), 78 (19), 77 (29), 70 (30), 69 (53), 68 (13), 55 (10), 51 (25).
Anal. $C_{10}H_{11}NOS$ (195.2): calcd C, 61.50; H, 6.71; N, 7.17; found C, 61.28; H, 6.97; N, 7.18.

α-Alkyl Sulfoximines 5–9; General Procedure:
To a solution of the sulfoximine **4** in THF (10 mL/mmol) was added BuLi (1.6 M in hexane, 1.1 equiv) at –50 °C. The resulting orange solution was warmed to r.t. for 10 min and cooled to –78 °C. Then the alkylating reagent (1.1 to 1.5 equiv) was added and the mixture was stirred for the appropriate time. Satd aq NH_4Cl solution was added and the mixture was extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuum. Purification of the residue by chromatography on silica gel gave the pure product.

(+)-(1S,5R)-5-Methyl-1-phenyl-4,5-dihydro-3H-isothiazol-1-oxide (**5a**):
From **4a** (501 mg, 2.76 mmol) and MeI; yield: 508 mg (94 %); colorless solid; mp 85-86 °C; $[\alpha]_D$ +68.8 (*c* = 0.99, $CHCl_3$); de = 89%.
^{1}H NMR: δ = 1.44 (d, *J* = 6.7 Hz, 3 H, CH_3), 2.00–2.15 (m, 1 H, NCH$_2$CH_2), 2.39–2.49 (m, 1 H, NCH$_2$CH_2), 3.19 (dq, *J* = 19.8, 6.7 Hz, 1 H, SC*H*), 3.63–3.72 (m, 1 H, NCH_2), 3.99–4.06 (m, 1 H, NCH_2), 7.51–7.58 (m, 2 H, *m*-Ph*H*), 7.60–7.66 (m, 1 H, *p*-Ph*H*), 7.92–7.99 (m, 2 H, *o*-Ph*H*).
^{13}C NMR: δ = 12.96 (d, *C*H$_3$), 32.67 (u, NCH$_2$ *C*H$_2$), 53.41 (u, N*C*H$_2$), 62.16 (d, S*C*H), 129.30 (d), 129.60 (d) (*o*/*m*-Ph*C*), 133.39 (d, *p*-Ph*C*), 139.02 (u, *ipso*-Ph*C*).
MS (EI, 70 eV): *m*/z (%) = 195 (M$^+$, 9), 153 (29), 126 (11), 125 (100), 97 (13), 77 (14), 51 (12).
Anal. $C_{10}H_{13}NOS$ (195.2): calcd C, 61.50; H, 6.71; N, 7.17; found C, 61.11; H, 6.39; N 7.02.

(+)-(1S,5R)-5-Benzyl-1-phenyl-4,5-dihydro-3H-isothiazol-1-oxide (**6a**):
From **4a** (480 mg, 2.65 mmol) and benzyl bromide; yield: 611 mg (85%); colorless solid; mp 108 °C; $[\alpha]_D$ +91.3 (*c* = 0.75, $CHCl_3$); de ≥98%.
^{1}H NMR: δ = 2.10–2.25 (m, 1 H, NCH$_2$CH_2), 2.32–2.34 (m, 1 H, NCH$_2$CH_2), 3.07 (dd, *J* = 14.4, *J* = 8.4 Hz, 1 H, PhCH_2), 3.21 (dd, *J* = 14.1, 6.7 Hz, 1 H, PhCH_2), 3.34–3.46 (m, 1 H, SC*H*), 3.61–3.70 (m, 1 H, NCH_2), 4.0l–4.08 (m, 1 H, NCH_2), 7.09–7.13 (m, 2 H, C-*o*-Ph*H*), 7.15–7.21 (m, 3 H, C-*m*/*p*-Ph*H*), 7.39–7.45 (m, 2 H, S-*m*-Ph*H*), 7.52–7.57 (m, 1 H, S-*p*-Ph*H*), 7.72–7.75 (m, 2 H, S-*o*-Ph*H*).
^{13}C NMR: δ = 30.95 (u), 34.69 (u) (NCH$_2$*C*H$_2$, PhCH_2), 53.22 (u, N*C*H$_2$), 68.29 (d, S*C*H), 126.78 (d, C-*p*-Ph*C*), 128.57 (d), 128.95 (d), 128.98 (d), 129.55 (d) (*o*/*m*-Ph*C*), 133.11 (d, S-*p*-Ph*C*), 137.43 (u), 138.81 (u) (*ipso*-Ph*C*).
MS (EI, 70 eV): *m*/z (%) = 271 (M$^+$, 4), 154 (18), 126 (11), 125 (100), 118 (20), 117 (38), 97 (10), 91 (21), 77 (14), 44 (40).
Anal. $C_{16}H_{17}NOS$ (271.3): calcd C, 70.81; H, 6.31; N, 5.16; found C, 70.60; H, 6.51; N, 4.85.

(+)-(1S,6R)-6-Methyl-1-phenyl-3,4,5,6-tetrahydro[1,2]thiazin-1-oxide (**5b**):
From **4b** (394 mg, 2.02 mmol) and MeI; yield: 372 mg (88%); colorless oil; $[\alpha]_D$ +102.1 (*c* = 0.82, $CHCl_3$); de = 90%.
^{1}H NMR: δ = 1.11 (d, *J* = 6.6 Hz, 3 H, CH_3), 1.77–1.83 (m, 1 H, NCH$_2$CH_2), 1.89–1.99 (m, 1 H, NCH$_2$CH_2), 2.04–2.10 (m, 1 H, SCHCH_2), 2.14–2.24 (m, 1 H, SCHCH_2), 2.94 (dqd, *J* = 12.7, 6.6, 4.3 Hz, 1 H, SC*H*), 3.44–3.49 (m, 1 H, NCH_2), 3.57–3.64 (m, 1 H, NCH_2), 7.51–7.56 (m, 2 H, *m*-Ph*H*), 7.60–7.64 (m, 1 H, *p*-Ph*H*), 8.0l–8.05 (m, 2 H, *o*-Ph*H*).
^{13}C NMR: δ = 16.51 (d, *C*H$_3$), 26.10 (u), 29.97 (u) (NCH$_2$*C*H$_2$, SCH*C*H$_2$), 43.46 (u, N*C*H$_2$), 56.61 (d, S*C*H), 128.96 (d), 129.13 (d) (*o*/*m*-Ph*C*), 133.22 (d, *p*-Ph*C*), 137.16 (u, *ipso*-Ph*C*).
MS (EI, 70 eV): *m*/z (%) = 209 (M$^+$, 26), 126 (15), 125 (100), 105 (12), 97 (11), 91 (10), 84 (72), 78 (16), 77 (16), 69 (16), 56 (11), 55 (14), 51 (12).
Anal. $C_{11}H_{15}NOS$ (209.3): calcd C, 63.12; H, 7.22; N 6.69; found C, 63.09; H, 7.39; N 6.41.

(+)-(1S,6S)-6-Benzyl-1-phenyl-3,4, 5,6-tetrahydro[1,2]thiazin-1-oxide (**6b**):
From **4b** (409 mg, 2.09 mmol) and benzyl bromide; yield: 441 mg (7l%); colorless solid; mp 110 °C; $[\alpha]_D$ +60.7 (*c* = 1.11, $CHCl_3$); de ≥98%.
^{1}H NMR: δ = 1.73–1.88 (m, 2 H, NCH$_2$CH_2), 2.00–2.07 (m, 1 H, SCHCH_2), 2.10–2.20 (m, 1 H, SCHCH_2), 2.69 (dd, *J* = 14.1, 10.1 Hz, 1 H, PhCH_2), 2.91 (dd, *J* = 14.1, 4.4 Hz, 1 H, PhCH_2), 3.09 (dddd, *J* = 12.6, 10.1, 4.4, 4.4 Hz, 1 H, SC*H*), 3.42–3.47 (m, 1 H, NCH_2), 3.59–3.66 (m, 1 H, NCH_2), 6.89–6.92 (m, 2 H, C-*o*-Ph*H*), 7.12–7.19 (m, 3 H, C-*m*/*p*-Ph*H*), 7.50–7.54 (m, 2 H, S-*m*-Ph*H*), 7.59–7.63 (m, l H, S-*p*-Ph*H*), 8.00–8.03 (m, 2 H, S-*o*-Ph*H*).
^{13}C NMR: δ = 25.81 (u), 27.09 (u) (NCH$_2$*C*H$_2$, SCH*C*H$_2$), 37.08 (u, PhCH_2), 43.52 (u, N*C*H$_2$), 61.73 (d, S*C*H), 126.67 (d, C-*p*-Ph*C*), 128.48 (d), 128.97 (d), 129.09 (d), 129.10 (d, *o*/*m*-Ph*C*), 133.21 (d, S-*p*-Ph*C*), 136.39 (u), 137.17 (u) (*ipso*-Ph*C*).
MS (EI, 70 eV): *m*/z (%) = 285 (M$^+$, 15), 194 (17), 160 (20), 131 (14), 125 (100), 91 (60), 77 (11), 70 (15), 65 (10).
Anal. $C_{17}H_{19}NOS$ (285.4): calcd C, 71.54; H, 6.71 ; N, 4.91; found C, 71.38; H, 6.50; N, 4.88.

(+)-(1S,6S)-6-Isopropyl-1-phenyl-3,4,5,6-tetrahydro[1,2]thiazin-1-oxide (**7b**):
From **4b** (353 mg, 1.81 mmol) and isopropyl iodide; yield: 243 mg (57%); colorless solid; mp 70 °C; $[\alpha]_D$ +54.8 (*c* =0.98, $CHCl_3$); de ≥98%.
^{1}H NMR: δ = 0.70 (d, *J* = 6.7 Hz, 3 H, CH_3), 1.00 (d, *J* = 6.7 Hz, 3 H, CH_3), 1.86–2.00 (m, 3 H, NCH$_2$CH_2, C*H*Me$_2$), 2.14–2.29 (m, 2 H, SCHCH_2), 2.86 (ddd, *J* = 11.8, 4.7, 4.0 Hz, 1 H, SC*H*), 3.41–3.46 (m, 1 H, NCH_2), 3.58–3.64 (m, 1 H, NCH_2), 7.52–7.56 (m, 2 H, *m*-Ph*H*), 7.59–7.63 (m, 1 H, *p*-Ph*H*), 8.01–8.04 (m, 2 H, *o*-Ph*H*).
^{13}C NMR: δ = 17.32 (d), 21.48 (d, *C*H$_3$), 23.40 (u), 26.59 (u, NCH$_2$*C*H$_2$, SCH*C*H$_2$), 28.37 (d, *C*HMe$_2$), 43.66 (u, N*C*H$_2$), 66.52 (d, S *C*H), 128.93 (d), 128.99 (d, *o*/*m*-Ph*C*), 133.07 (d, *p*-Ph*C*), 138.50 (u, *ipso*-PhC).
MS (EI, 70 eV): *m*/z (%) = 237 (M$^+$, 5), 194 (7), 125 (100), 112 (11), 70 (20), 55 (14).
Anal. $C_{13}H_{19}NOS$ (237.3): calcd C, 65.78; H, 8.07; N, 5.90; found C, 65.42, H, 8.10; N, 5.81.

(+)-(1S,6S)-1-Phenyl-6-(2,4,6-trimethylbenzyl)-3,4,5,6-tetrahydro-[1,2]thiazin-1-oxide (**8b**):
From **4b** (864 mg, 4.42 mmol) and 2,4,6-trimethylbenzyl chloride; yield: 1.00 g (69%); colorless solid; mp 172–173 °C; $[\alpha]_D$ +106.5 (*c* = 1.17, $CHCl_3$); de ≥98%.
^{1}H NMR: δ = 1.70–1.83 (m, 2 H, NCH$_2$CH_2), 1.91 [br s, 6 H, *o*-C$_6$H$_2$(CH_3)$_3$CH$_2$], 1.90–2.00 (m, 1 H, SCHCH_2), 2.19 [s, 3 H, *p*-C$_6$H$_2$(CH_3)$_3$CH$_2$], 2.20–2.35 (m, 1 H, SCHCH_2), 2.70 (dd, *J* = 13.4, 2.7 Hz, 1 H, C$_6$H$_2$Me$_3$CH_2), 2.89 (dd, *J* = 13.4, 11.1 Hz, 1 H, C$_6$H$_2$Me$_3$CH_2), 2.99 (dddd, *J* = 12.4, 11.1, 3.7, 2.7 Hz, 1 H, SC*H*), 3.40–3.49 (m, 1 H, NCH_2), 3.57–3.72 (m, 1 H, NCH_2), 6.73 (s, 2 H, C$_6$$H_2Me_3CH_2$), 7.53–7.60 (m, 2 H, *m*-Ph*H*), 7.62–7.68 (m, 1 H, *p*-Ph*H*), 8.09–8.13 (m, 2 H, *o*-Ph*H*).

^{13}C NMR: δ = 19.78 [d, *o*-$C_6H_2(CH_3)_3CH_2$], 20.72 [d, *p*-$C_6H_2(CH_3)_3CH_2$], 26.21 (u), 26.68 (u) (NCH_2CH_2, $SCHCH_2$), 29.64 (u, $C_6H_2Me_3CH_2$), 43.55 (u, NCH_2), 60.61 (d, SCH), 129.01 (d), 129.25 (d), 129.37 (d) (S-*o*/*m*-Ph*C*, *m*-*C*6$H_2Me_3CH_2$), 130.07 (u, *p*-$C_6H_2Me_3CH_2$), 133.37 (d, S-*p*-Ph*C*), 135.99 (u, *ipso*-$C_6H_2Me_3CH_2$), 136.86 (u, *o*-$C_6H_2Me_3CH_2$), 138.71 (u, S-*ipso*-Ph*C*).
MS (EI, 70 eV): *m*/z (%) = 327 (M^+, 7), 202 (22), 194 (21), 159 (12), 134 (11), 133 (98), 131 (12), 129 (11), 125 (100), 119 (11), 118 (16), 117 (20), 115 (10), 105 (13), 91 (14), 77 (19), 70 (48).
Anal. $C_{20}H_{25}NOS$ (327.4): calcd C, 73.35; H, 7.69; N, 4.28; found C, 73.12; H, 7.83; N, 4.25.

*(+)-(1S,6S)-6-Methyl-1-phenyl-3,4,5,6-tetrahydro[1,2]thiazin-1-oxide (epi-***5b**):
From **5b** (30 mg, 0.14 mmol) and CF_3CO_2H (82 mg, 0.72 mmol), a mixture of *epi*-**5b** and **5b** in a ratio of 82:18 (27 mg, 90%) was obtained as a colorless oil; $[\alpha]_D$ +30.8 (*c* = 1.30, $CHCl_3$).
^{1}H NMR: δ = 1.07 (d, *J* = 7.1 Hz, 3 H, CH_3), 1.43–1.54 (m, 1 H, NCH_2CH_2), 1.73–2.03 (m, 2 H, NCH_2CH_2, $SCHCH_2$), 2.72–2.85 (m, 1 H, $SCHCH_2$), 3.21 (qdd, *J* = 7.1, 3.7, 3.5 Hz, 1 H, SC*H*), 3.47–3.53 (m, 1 H, NCH_2), 3.65–3.76 (m, 1 H, NCH_2), 7.50–7.57 (m, 2 H, *m*-Ph*H*), 7.58–7.65 (m, 1 H, *p*-Ph*H*), 8.00–8.05 (m, 2 H, *o*-Ph*H*).
^{13}C NMR: δ = 16.28 (d, *C*H_3), 17.41 (u, NCH_2CH_2), 27.86 (u, $SCHCH_2$), 43.28 (u, NCH_2), 52.88 (d, SCH), 128.80 (d), 129.25 (d, *o*/*m*-Ph*C*), 133.12 (d, *p*-h*C*), 136.63 (u, *ipso*-Ph*C*).

*(–)-(1S,6R)-6-Benzyl-1-phenyl-3,4,5,6-tetrahydro(1,2)thiazin-1-oxide (epi-***6b**):
From **6b** (225 mg, 0.79 mmol) and CF_3CO_2H (0.45 g, 3.94 mmol), *epi*-**6b** (205 mg, 91%) was obtained with de = 89%. Chromatography (EtOAc) gave pure *epi*-**6b** (180 mg, 80%) as a colorless solid; mp 63–64 °C; $[\alpha]_D$ –35.4 (*c* = 1.18, $CHCl_3$).
^{1}H NMR: δ = 1.44–1.48 (m, 1 H, NCH_2CH_2), 1.86–2.03 (m, 2 H, NCH_2CH_2, $SCHCH_2$), 2.50 (dd, *J* = 13.7, 4.3 Hz, 1 H, $PhCH_2$), 2.53–2.61 (m, 1 H, $SCHCH_2$), 2.83 (dd, *J* = 13.7, 11.3 Hz, 1 H, $PhCH_2$), 3.32 (dddd, *J* = 11.3, 4.3, 4.3, 4.0 Hz, 1 H, SC*H*), 3.54–3.58 (m, 1 H, NCH_2), 3.71–3.77 (m, 1 H, NCH_2), 6.94–6.96 (m, 2 H, C-*o*-Ph*H*), 7.15–7.24 (m, 3 H, C-*m*/*p*-Ph*H*), 7.54–7.57 (m, 2 H, S-*m*-Ph*H*), 7.61–7.64 (m, 1 H, S-*p*-Ph*H*), 8.07–8.10 (m, 2 H, S-*o*-Ph*H*).
^{13}C NMR: δ = 17.59 (u, NCH_2CH_2), 23.61 (u, SCH CH_2), 34.99 (u, $PhCH_2$), 43.31 (u, NCH_2), 58.41 (d, SCH), 126.73 (d, C-*p*-Ph*C*), 128.68 (d), 128.97 (d), 129.39 (d) (*o*/*m*-Ph*C*), 133.30 (d, S-*p*-Ph*C*), 136.49 (u), 136.77 (u) (*ipso*-Ph*C*).
MS (EI, 70 eV): *m*/z (%) = 285 (M^+, 10), 194 (15), 160 (57), 131 (16), 126 (10), 125 (100), 117 (11), 104 (10), 97 (13), 91 (57), 78 (10), 77 (17), 65 (10), 51 (10).
Anal. $C_{17}H_{19}NOS$ (285.4): calcd C, 71.54; H, 6.71; N, 4.91; found C, 71.21; H, 6.78; N, 4.87.

*(–)-(1S, 6R)- 1-Phenyl-6-(2,4,6-trimethylbenzyl)-3,4,5,6-tetrahydro-[1,2]thiazin-1-oxide (epi-***8b**):
From **8b** (642 mg, 1.96 mmol) and CF_3CO_2H (671 mg, 5.88 mmol), *epi*-**8b** (578 mg, 90%) was obtained with de = 81%. Chromatography (EtOAc) gave pure *epi*-**8b** (480 mg, 75%) as a colorless solid; mp 125–126 °C; $[\alpha]_D$ –64.0 (*c* = 1.09, $CHCl_3$).
^{1}H NMR: δ = 1.54–1.63 (m, 1 H, NCH_2CH_2), 1.79–l.90 (m, 1 H, NCH_2CH_2), 2.10 [br s, 6 H, *o*-$C_6H_2(CH_3)_3CH_2$], 2.06–2.17 (m, 1 H, $SCHCH_2$), 2.22 [s, 3 H, *p*-$C_6H_2(CH_3)_3CH_2$], 2.40 (dd, *J* = 14.4, 2.4 Hz, 1 H, $C_6H_2Me_3CH_2$), 2.42–2.53 (m, 1 H, $SCHCH_2$), 2.85 (dd, *J* = 13.8, 12.1 Hz, 1 H, $C_6H_2Me_3CH_2$), 3.19 (dddd, *J* = 12.1, 4.7, 4.4, 2.4 Hz, 1 H, SC*H*), 3.55–3.64 (m, 1 H, NCH_2), 3.72–3.83 (m, 1 H, NCH_2), 6.79 (s, 2 H, $C_6H_2Me_3CH_2$), 7.57–7.72 (m, 3 H, *m*/*p*-Ph*H*), 8.16–8.20 (m, 2 H, *o*-Ph*H*).
^{13}C NMR: δ = 19.08 (u), 23.64 (u), 28.43 (u) (NCH_2CH_2, $SCHCH_2$, $C_6H_2Me_3CH_2$), 20.38 [d, *o*-$C_6H_2(CH_3)_3CH_2$], 20.81 [d, *p*-$C_6H_2(CH_3)_3CH_2$], 43.43 (u, NCH_2), 57.78 (d, SCH), 128.96 (d), 129.51 (d), 129.84 (d) (S-*o*/*m*-Ph*C*, *m*-$C_6H_2Me_3CH_2$), 130.93 (u. *p*-*C*6$H_2Me_3CH_2$), 133.53 (d, S-*p*-Ph*C*), 136.21 (u, *o*-$C_6H_2Me_3CH_2$), 136.66 (u, S-*ipso*-Ph*C*).
MS (EI, 70 eV): *m*/z (%) = 327 (M^+, 2), 202 (21), 194 (14), 159 (10), 134 (11), 133 (100), 131 (12), 129 (10), 125 (90), 118 (15), 117 (18), 105 (14), 97 (10), 91 (14), 77 (23), 70 (47).
Anal. $C_{20}H_{25}NOS$ (327.4): calcd C, 73.35; H, 7.69; N, 4.28; found C, 72.97; H, 7.84; N, 3.96.

(+)-(1S,6S)-6-Benzyl-6-methyl-1-phenyl-3,4,5,6-tetrahydro[1,2]thiazin-1-oxide (**9**):
From **5b** (198 mg, 0.95 mmol) and benzyl bromide; yield: 119 mg (42%); colorless oil; $[\alpha]_D$ +45.05 (*c* = 1.90, $CHCl_3$); de ≥98%.
^{1}H NMR: δ = 1.14 (s, 3 H, CH_3), 1.50–1.56 (m, 1 H, NCH_2CH_2), 1.70–l.80 (m, 1 H, NCH_2CH_2), 1.81–1.99 (m, 1 H, $SCCH_2$), 2.44–2.56 (m, 1 H, $SCCH_2$), 2.72 (d, *J* = 13.1 Hz, 1 H, $PhCH_2$), 3.38 (d, *J* = 13.1 Hz, 1 H, $PhCH_2$), 3.40–3.48 (m, 1 H, NCH_2), 3.62–3.74 (m, 1 H, NCH_2), 7.01–7.04 (m, 2 H, C-*o*-Ph*H*), 7.21–7.24 (m, 3 H, C-*m*/*p*-Ph*H*), 7.52–7.59 (m, 2 H, S-*m*-Ph*H*), 7.62–7.69 (m, 1 H, S-*p*-Ph*H*), 8.05–8.08 (m, 2 H, S-*o*-Ph*H*).
^{13}C NMR: δ = 20.62 (d, *C*H_3), 20.34 (u), 32.37 (u) (NCH_2CH_2, $SCCH_2$), 43.11 (u), 43.53 (u) (NCH_2, $PhCH_2$), 58.96 (u, SC), 126.76 (d, C-*p*-Ph*C*), 128.05 (d), 128.61 (d), 130.53 (d), 130.80 (d) (*o*/*m*-Ph*C*), 133.22 (d, S-*p*-Ph*C*), 134.30 (u), 134.91 (u) (*ipso*-Ph*C*).
MS (EI, 70 eV): *m*/z (%) = 299 (M^+, 2), 208 (60), 174 (10), 126 (10), 125 (100), 91 (36), 77 (12).
HRMS ($C_{18}H_{21}NOS$): *m*/*z* calcd 299.134387; found 299.134580.

*(+)-(1S,6R)-6-Benzyl-6-methyl-1-phenyl-3,4,5,6-tetrahydro[1,2]thiazin-1-oxide (epi-***9**):
From **6b** (216 mg, 0.76 mmol) and MeI; yield: 218 mg (96%); colorless oil; $[\alpha]_D$ +31.98 (*c* = 1.06, $CHCl_3$); de ≥98%.
^{1}H NMR: δ = 1.24 (s, 3 H, CH_3), 1.54–1.63 (m, 1 H, NCH_2CH_2), 1.72–l.81 (m, 1 H, NCH_2CH_2), 1.98 (d, *J* = 13.1 Hz, 1 H, $PhCH_2$), 2.16–2.41 (m, 2 H, $SCCH_2$), 3.50–3.58 (m, 1 H, NCH_2), 3.58 (d, *J* = 13.1 Hz, 1 H, $PhCH_2$), 3.65–3.77 (m, 1 H, NCH_2), 7.00–7.05 (m, 2 H, C-*o*-Ph*H*), 7.19–7.28 (m, 3 H, C-*m*/*p*-Ph*H*), 7.53–7.60 (m, 2 H, S-*m*-Ph*H*), 7.61–7.68 (m, 1 H, S-*p*-Ph*H*), 8.06–8.09 (m, 2 H, S-*o*-Ph*H*).
^{13}C NMR: δ = 22.70 (d, *C*H_3), 21.11 (u), 30.82 (u) (NCH_2CH_2, $SCCH_2$), 39.38 (u), 43.29 (u) (NCH_2, $PhCH_2$), 59.87 (u, SC), 127.00 (d, C-*p*-Ph*C*), 128.33 (d), 128.82 (d), 130.43 (d), 130.47 (d) (*o*/*m*-Ph*C*), 133.36 (d, S-*p*-Ph*C*), 134.37 (u), 135.57 (u) (*ipso*-Ph*C*).
MS (EI, 70 eV): *m*/z (%) = 299 (M^+, 3), 208 (49), 174 (13), 126 (11), 125 (100), 91 (28), 57 (14), 55 (11).
HRMS ($C_{18}H_{21}NOS$): *m*/*z* calcd 299.134387; found 299.134292.

(+)-(*S*)-*S*-Methyl-*S*-phenyl-*N*-triphenylmethylsulfoximine (H-Ib):
To a solution of **1** (0.50 g, 3.22 mmol) in pyridine (15 mL) was added slowly chlorotriphenylmethane (1.80 g, 6.44 mmol). After stirring the mixture for 7 h at r.t., brine (30 mL) was added and the mixture was extracted with EtOAc (3 × 50 mL). After washing the combined organic phases with 0.1 M HCl (3 × 50 mL), satd aq $NaHCO_3$ solution (2 × 50 mL) and water, they were dried ($MgSO_4$) and concentrated in vacuum. Purification of the residue by chromatography (50% hexane/EtOAc) gave H-**Ib** (0.85 g, 66%) as a colorless solid; mp 212–213 °C, $[\alpha]_D$ +110.0 (*c* = 1.01, THF).
^{1}H NMR: δ = 2.75 (s, 3 H, CH_3), 7.06–7.20 (m, 9 H, Ph*H*), 7.24–7.41 (m, 3 H, *m*/*p*-Ph*H*), 7.50–7.55 (m, 6 H, C-*o*-Ph*H*), 7.64–7.68 (m, 2 H, S-*o*-Ph*H*).
^{13}C NMR: δ = 42.88 (u, *C*Ph_3), 47.81 (d, *C*H_3), 126.26 (d, C-*p*-Ph*C*), 127.31 (d), 128.53 (d) (S-*o*/*m*-Ph*C*), 127.35 (d), 129.16 (d) (C-*o*/*m*-Ph*C*), 131.39 (d, S-*p*-Ph*C*), 143.33 (u, S-*ipso*-Ph*C*), 147.48 (u, C-*ipso*-Ph*C*).
MS (El, 70 eV): *m*/z (%) = 320 (M^+ - Ph, 35), 258 (21), 257 (100), 256 (12), 243 (15), 180 (52), 165 (20), 77 (33).
Anal. $C_{26}H_{23}NOS$ (397.5): calcd C, 78.55 ; H, 5.83; N, 3.52; found C, 78.20; H, 6.05; N, 3.72.

Conjugate Addition with Cuprates Containing Sulfonimidoyl Carbanions (Scheme 6); General Procedure:
To a solution of the sulfoximine (1.0 mmol) in THF (5 mL) at –50 °C was added BuLi (1.0 mmol, 0.62 mL of 1.6 M in hexane). The resulting mixture was warmed to r.t. and stirred for 10 min. Subsequently CuI (190 mg, 1.0 mmol) was added at 0 °C and the mixture was stirred for 10 min at this temperature. After cooling the mixture to –78 °C, the lithiumorganyl (1.0 mmol) was added and the mixture was stirred for l0 min at 0 °C. The resulting mixture was cooled to –78 °C and the enone (1.0 mmol) was added dropwise. After stirring the mixture for 1.5 to 2 h at this temperature, a 10:1 mixture of satd aq NH_4Cl and concd aq NH_3 was added. The resulting mixture was extracted with Et_2O (3 × 20 mL). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuum. Purification of the residue by chromatography (50% hexane/EtOAc) afforded the addition product. In addition, the sulfoximine was recovered quantitatively by chromatography. α-Alkylated sulfoximines were isolated as a mixture of epimers.

(+)-(R)-3-Phenylcyclohexanone (**16b**):
From **10b** (101 mg, 1.05 mmol), H-**Ib** (413 mg, 1.05 mmol), BuLi (1.05 mmol, 0.66 mL of 1.6 M in hexane) and PhLi (1.05 mmol, 0.58 mL of 1.8 M in cyclohexane/ether, 7:3), **16b** (143 mg, 78%) was obtained as a colorless oil; $[\alpha]_D$ +9.0 (*c* = 0.90, $CHCl_3$); ee = 49% [GC, octakis-(2,3-*O*-dipentyl-6-*O*-methyl)-γ-cyclodextrin column: R_f (**16b**) = 24.6 min, R_f (*ent*-**16b**) = 24.8 min].

(–)-(S)-3-Butylcyclopentanone (**15a**):
From **10a** (35 mg, 0.43 mmol), **8b** (156 mg, 0.48 mmol), BuLi (0.48 mmol, 0.30 mL of 1.6 M in hexane) and BuLi (0.43 mmol, 0.27 mL of 1.6 M in hexane), **15a** (48 mg, 80%) was obtained as a colorless oil; ee = 93% [GC, octakis-(2,3-di-*O*-pentyl-6-*O*-methyl)-γ-cyclodextrin column: R_f (**15a**) = 20.2 min, R_f (*ent*-**15a**) = 21.0 min].
ent-**15a**: $[\alpha]_D$ +66.5 (*c* = 1.65, toluene); ee = 49%.

(–)-(S)-3-Butylcyclohexanone (**15b**):
From **10b** (40 mg, 0.41 mmol), **8b** (151 mg, 0.46 mmol), BuLi (0.46 mmol, 0.29 mL of 1.6 M in hexane) and BuLi (0.41 mmol, 0.26 mL of 1.6 M in hexane), **15b** (58 mg, 90%) was obtained as a colorless oil; $[\alpha]_D$ –7.84 (*c* = 1.70, toluene); ee = 99% [GC, octakis-(2,3-di-*O*-pentyl-6-*O*-methyl)-γ-cyclodextrin column: R_f (**15b**) = 44.7 min, R_f (*ent*-**15b**) = 44.0 min].

(–)-(S)-3-Butylcycloheptanone (**15c**):
From **10c** (51 mg, 0.47 mmol), **8b** (173 mg, 0.53 mmol), BuLi (0.52 mmol, 0.32 mL of 1.6 M in hexane) and BuLi (0.47 mmol, 0.29 mL of 1.6 M in hexane), **15c** (70 mg, 90%) was obtained as a colorless oil; ee = 77% [GC, octakis-(2,3-di-*O*-pentyl-6-*O*-methyl)-γ-cyclodextrin column: R_f (**15c**) = 23.0 min, R_f (*ent*-**15c**) = 23.6 min].
ent-**15c**: $[\alpha]_D$ = +14.7 (*c* = 1.11, $CHCl_3$); ee = 43%.

(–)-(S)-3-Methylcyclohexanone (**23b**):
From **10b** (46 mg, 0.48 mmol), **8b** (174 mg, 0.53 mmol), BuLi (0.53 mmol, 0.33 mL of 1.6 M in hexane) and MeLi (0.48 mmol, 0.30 mL of 1.6 M in Et_2O was evaporated and the residue dissolved in 3 mL THF), **23b** (27 mg, 50%) was obtained as a colorless oil; $[\alpha]_D$ –14.3 (*c* = 0.48, MeOH), ee = 86% [GC, permethyl-β-cyclodextrin column: R_f (**18**) = 19.0 min, R_f (*ent*-**18**) = 18.9 min].

(+)-(R)-3-(3-Hydroxypropyl)cyclohexanone (**25**):
From **10b** (81 mg, 0.85 mmol) and 3-(1-ethoxyethoxy)-propyllithium[14] (0.85 mmol, 1.30 mL of 0.65 M in THF), **25** (92 mg, 70%) was obtained after treatment of **24b** with 2 M HCl and neutralization with satd aq Na_2CO_3 solution as a colorless oil; $[\alpha]_D$ +1.26 (*c* = 1.03, MeOH); ee = 79% [GC, octakis-(2,6-di-*O*-pentyl-3-*O*-butyryl)-γ-cyclodextrin column: R_f (**25**) = 30.6 min, R_f (*ent*-**25**) = 30.7 min].
^{1}H NMR: δ = 1.28–2.10 (m, 11 H), 2.20–2.49 (m, 3 H), 3.65 (t, *J* = 6.4 Hz, 2 H, OCH_2).
^{13}C NMR: δ = 25.23 (u), 29.85 (u), 31.29 (u), 32.71 (u) ($COCH_2CH_2$, $COCH_2CH_2CH_2$, OCH_2CH_2, $OCH_2CH_2CH_2$), 38.94 (d, C*H*CH_2), 41.48 (u), 48.14 (u) (COCH_2, COCH_2), 62.88 (u, OCH_2).
MS (EI, 70 eV): *m*/z (%) = 157 (M^+ + 1, 9), 156 (M^+, 6), 112 (12), 98 (10), 97 (100), 96 (10), 69 (19), 68 (14), 67 (41), 57 (13), 56 (13), 55 (55), 53 (10).
HRMS ($C_9H_{16}O_2$): *m*/*z* calcd 156.11503 ; found 156.11573.

(–)-(*R*)-Toluene-4-sulfonic Acid 3-(3-Oxocyclohexyl)propyl Ester (26):
To a solution of **25** (90 mg, 0.58 mmol) and *p*-TsCl (121 mg, 0.63 mmol) in CH_2Cl_2 (3 mL) at 0 °C was added NEt_3 (0.2 mL). After stirring the mixture 20 h at this temperature, satd aq NH_4Cl solution was added. The resulting mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuum. Purification of the residue by chromatography (50% hexane/EtOAc) afforded **26** (107 mg, 60%) as a colorless oil; $[\alpha]_D$ –4.35 (*c* = 2.0, CH_2Cl_2).
^{1}H NMR: δ = 1.22–1.46 (m, 3 H), 1.51–1.75 (m, 4 H), 1.77–2.08 (m, 3 H), 2.17–2.38 (m, 3 H), 2.46 (s, 3 H, CH_3), 4.01 (t, *J* = 6.2 Hz, 2 H, OCH_2), 7.36 (m, 2 H, SO_2-*m*-Ph*H*), 7.78 (m, 2 H, SO_2-o-Ph*H*).
^{13}C NMR: δ = 21.69 (d, *C*H_3), 25.12 (u), 26.15 (u), 31.06 (u), 32.23 (u) ($COCH_2CH_2$, $COCH_2CH_2CH_2$, OCH_2CH_2, $OCH_2CH_2CH_2$), 38.44 (d, C*H*CH_2), 41.40 (u), 47.87 (u, COCH_2, COCH_2), 70.48 (u, OCH_2), 127.92 (d), 129.96 (d) (*o*/*m*-Ph*C*), 133.08 (u, *p*-Ph*C*), 144.94 (u, *ipso*-Ph*C*), 211.31 (u, *C*O).
MS (EI, 70 eV): *m*/z (%) = 311 (M^+ + 1, 9), 310 (M^+, 29), 155 (44), 139 (16), 138 (11), 137 (11), 110 (84), 97 (100), 96 (23), 95 (24), 91 (45), 82 (21), 81 (11), 69 (13), 68 (10), 67 (35), 65 (15), 55 (39).
Anal. $C_{16}H_{22}O_4S$ (310.4): calcd C, 61.91; H, 7.14; found C, 61.68; H, 7.36.

(+)-(1*S*,6*S*)-Bicyclo[4.3.0]nonan-2-one (27):
To a solution of CuI (74 mg, 0.39 mmol) in THF (3 mL) at –40 °C was added MeLi (0.39 mmol, 0.24 mL of 1.6 M in Et_2O) and the mixture was stirred for 45 min at this temperature. After cooling the mixture to –78 °C, it was treated with a solution of **26** (0.13 mmol, 40 mg) in THF (3 mL). The mixture was stirred for 15 h and warmed slowly to r.t. Subsequently a mixture of satd aq NH_4Cl and concd aq NH_3 (10:1) was added and the solution was extracted with Et_2O (3 × 30 mL). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuum. Purification of the residue by chromatography (50% hexane/EtOAc) afforded **27** (16 mg, 90%) as a colorless oil; $[\alpha]_D$ +16.9 (*c* = 0.80, THF); ee = 78% [GC, octakis-(2,3-di-*O*-pentyl-6-*O*-methyl)-γ-cyclodextrin column: R_f (**27**) = 31.4 min, R_f (*ent*-**27**) = 30.3 min].
^{1}H NMR: δ = 1.25–2.11 (m, 10 H), 2.24–2.51 (m, 3 H), 2.56–2.66 (m, 1 H).
^{13}C NMR: δ = 23.14 (u), 23.88 (u), 26.77 (u), 27.31 (u), 31.09 (u), 39.69 (u, *C*H_2), 43.01 (d), 53.21 (d, *C*H), 216.52 (u, *C*O).
GC/MS: *m*/z (%) = 138 (M^+, 26), 110 (25), 97 (100), 95 (36), 94 (32), 82 (12), 81 (13), 79 (35), 68 (11), 67 (73), 55 (12), 54 (12), 53 (11).
Anal. $C_9H_{14}O$ (138.2): calcd C, 78.21; H, 10.21; found C, 77.93; H, 10.31.

Financial support of this work by the Deutsche Forschungsgemeinschaft (SFB 380) and the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Dr. G. Raabe for the X-ray structure analysis and Dr. J. Runsink for NOE experiments.

(1) For recent examples, see: (a) Hainz, R.; Gais, H.-J.; Raabe, G. *Tetrahedron: Asymmetry* **1996**, *7*, 2505.
(b) Pyne, S. G.; Dong, Z. *J. Org. Chem.* **1996**, *61*, 5517.
(c) Reggelin, M.; Weinberger, H.; Gerlach, M.; Welcker, R. *J. Am. Chem. Soc.* **1996**, *118*, 4765.

(d) Pyne, S. G.; Dong, Z.; Skelton, B. W.; White, A. H. *J. Org. Chem.* **1997**, *62*, 2337.

(2) (a) Johnson, C. R. In *Comprehensive Organic Chemistry*; Barton, D.; Ollis, W. D., Eds.; Pergamon Press: Oxford, 1979; Vol. 1, p 223.
(b) Barbachyn, M. R.; Johnson, C. R. In *Asymmetric Synthesis*; Morrison, J. D.; Scott, J. W., Eds.; Academic Press: New York, 1984; Vol. 4, 227.
(c) Johnson, C. R. *Aldrichimica Acta* **1985**, *18*, 3.
(d) Pyne, S. G. *Sulfur Reports* **1992**, *12*, 57.

(3) (a) Harmata, M.; Jones, D. E. *Tetrahedron Lett.* **1995**, *36*, 4769.
(b) Harmata, M.; Herron, B. F. *Tetrahedron* **1991**, *47*, 8855.

(4) (a) Rossiter, B. E.; Swingle, N. M. *Chem. Rev.* **1992**, *92*, 771.
(b) Lipshutz, B. H.; Sengupta, S. *Org. React.* **1992**, *41*, 135.
(c) Lipshutz, B. H. In *Organometallics in Synthesis*; Schlosser, M., Ed.; Wiley: New York, 1994; p 283.
(d) Alexakis, A. In *Organocopper Reagents*; Taylor, R. J. K., Ed.; Oxford University Press: Oxford; 1994, pp 159.
(e) Yamamoto, Y. In *Stereoselective Synthesis* (Houben-Weyl); Helmchen, G.; Hoffmann, R. W.; Mulzer, J.; Schaumann, E., Eds.; Thieme: Stuttgart, 1996; E21 Vol. 4, p 2041.
(f) Krause, N.; Gerold, A. *Angew. Chem*, **1997**, *109*, 194; *Angew. Chem., lnt. Ed. Engl.* **1997**, *36*, 186.

(5) Bund, J. *Ph. D. Thesis*, Universität Freiburg, 1991.

(6) Brandt, J.; Gais, H.-J. *Tetrahedron: Asymmetry* **1997**, *8*, 909.

(7) Johnson, C. R.; Lavergne, O. M. *J. Org. Chem.* **1993**, *58*, 1922.

(8) 2-(2-Bromoethoxy)tetrahydropyrane and 2-(3-chloropropoxy)tetrahydropyrane were prepared from 2-bromoethanol and 3-chloropropan-1-ol, respectively, according to Genardy, K. F.; Floyd, M. B.; Poletto, J. F.; Weiss, M. J. *J. Org. Chem.* **1979**, *44*, 1438.

(9) For the synthesis of *rac*-**4a** by a different route, see: Johnson, C. R.; Katekar, G. F.; Huxol, R. F.; Janiga, E. R. *J. Am. Chem. Soc.* **1971**, *93*, 3771.

(10) X-ray crystallographic analysis of **6b**:
$C_{17}H_{19}NOS$ (M_r = 267.27), monoclinic, space group P 2_1 (No. 4), a = 5.8377(5) Å, b = 9.173(2) Å, c = 14.6265(5) Å, α = 90.0°, β = 97.665(5)°, γ = 90.0°, V = 776.22 Å^3, Z = 2, D_{calc} = 1.221 g·cm^{-3}, CuKα radiation, crystal dimensions = 0.3 × 0.3 × 0.3 mm, 3641 reflections were measured up to θ_{max} = 75.2° at 298 K on an CAD4 Enraf-Nonius diffractometer with graphite employing monochromated CuKα radiation (λ = 1.54179 Å). 3122 symmetry independent reflections, μ(CuKα) = 17.5 cm^{-1}, no absorption correction, 2842 reflections with I > 2σ (I) were treated as observed. The structure was solved by means of direct methods as implemented in the *XTAL3.2* package of crystallographic routines, employing *GENSIN* to generate structure invariant relationships and *GENTAN* for the general tangent phasing procedure. The final full-matrix least-squares refinement (on *F*) of 180 parameters terminated at *R* = 0.044 (R_w = 0.047) and an error of fit of 2.174. The chirality of **6b** as shown in the Figure was determined by calculation of Flack's absolute structure parameter [X_{abs} = 0.003(33)]. Crystallographic data (excluding structure factors) for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax:(internat.) +44 (0)1223 336033, e-mail: deposit@chemcrys.cam.ac.uk].

(11) (a) Gais, H.-J.; Erdelmeier, I.; Lindner, H. J.; Vollhardt, J. *Angew. Chem.* **1986**, *98*, 914; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 938.
(b) Gais, H.-J.; Dingerdissen, U.; Krüger, C.; Angermund, K. *J. Am. Chem. Soc.* **1987**, *109*, 3775.
(c) Gais, H.-J.; Lenz, D.; Raabe, G. *Tetrahedron Lett.* **1995**, *36*, 7437.
(d) Müller, J. F. K.; Batra, R.; Spingler, B.; Zehnder, M. *Helv. Chim. Acta* **1996**, *79*, 820.
(e) Müller, J. F. K.; Neuburger, M.; Zehnder, M. *Helv. Chim. Acta* **1997**, *80*, 2182.

(12) (a) Johnson, C. R.; Zeller, J. R. *Tetrahedron* **1984**, *40*, 1225.
(b) S. G. Pyne, B. Dikic, *Tetrahedron Lett.* **1990**, *36*, 5231.

(13) Johnson, C. R.; Dhanoa, D. S. *J. Org. Chem.* **1987**, *52*, 1885.

(14) Eaton, P. E.; Cooper, G. F.; Johnson, R. C.; Mueller, H. *J. Org. Chem.* **1972**, *37*, 1947.

(15) (a) Corey, E. J.; Naef, R.; Hannon, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 7114.
(b) Posner, G. H.; Frye, L. L. *Isr. J. Chem.* **1984**, *24*, 88.
(c) Rossiter, B. E.; Eguchi, M.; Miao, G.; Swingle, N. M.; Hernandez, A. E.; Vickers, D.; Fluckiger, E.; Patterson, R. G.; Reddy, K. V. *Tetrahedron* **1993**, *49*, 965.
(d) Langer, W.; Seebach, D. *Helv. Chim. Acta* **1979**, *62*, 1710.

(16) (a) Cicero, B. L.; Weisbuch, F.; Dana, G. *J. Org. Chem.* **1981**, *46*, 914.
(b) Dana, G.; Weisbuch, F.; Drancourt, J.-M. *Tetrahedron* **1985**, *41*, 1233.

(17) Kauffman, G. B.; Teter, L. A. *Inorg. Synth.* **1963**, *7*, 10.