A Novel Approach to the Asymmetric Synthesis of Epoxides, Allylic Alcohols, α-Amino Ketones, and α-Amino Aldehydes from Carbonyl Compounds through α,β-Epoxy Sulfoxides Using the Optically Active *p*-Tolylsulfinyl Group To Induce Chirality[1]

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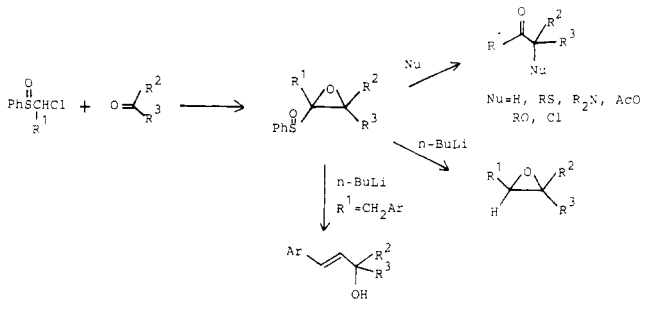
A practical and relatively inexpensive procedure for the preparation of (−)-chloromethyl *p*-tolyl sulfoxide of high optical purity was accomplished by the chlorination of optically pure (+)-methyl *p*-tolyl sulfoxide with *N*-chlorosuccinimide in the presence of K_2CO_3. The (−)-chloromethyl *p*-tolyl sulfoxide was alkylated to give a diastereomeric mixture of (−)-1-chloroalkyl *p*-tolyl sulfoxides. Addition of the anion derived from these sulfoxides to ketones or aldehydes afforded chlorohydrins in quite good yields with complete 1,2-asymmetric induction. Treatment of these chlorohydrins with a base gave optically active α,β-epoxy sulfoxides. On treatment with *n*-BuLi, the α,β-epoxy sulfoxides gave epoxides or allylic alcohols of high optical purity. This novel procedure was applied to a short synthesis of optically active (+)-disparlure, the sex attractant of the female gypsy moth. Aminolysis of the α,β-epoxy sulfoxides gave optically active α-amino ketones and α-amino aldehydes in quite good yields.

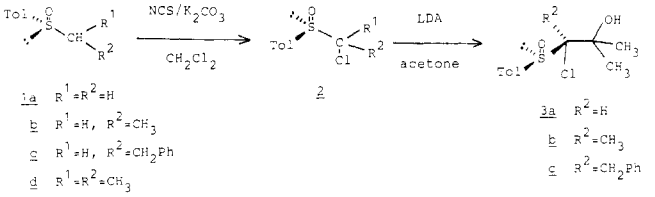
Since the pioneering work of Trost and others,[2] the synthetic utility of sulfinylated compounds in the elaboration of complex organic structures has become well established. Especially, optically active sulfoxides have recently received considerable attention for use in the synthesis of optically active compounds.[3] However, these fascinating chiral auxiliaries have not yet been put to full use in asymmetric synthesis.

The use of 1-chloroalkyl aryl sulfoxides in organic synthesis is relatively recent.[4] We reported a novel and versatile method for the synthesis of various kinds of carbonyl compounds,[5] epoxides,[6] and allylic alcohols[6] from α,β-epoxy sulfoxides which were derived from the reaction of carbonyl compounds and the anion of 1-chloroalkyl phenyl sulfoxides (Scheme I). We found that the methodology could be extended to asymmetric syntheses by using optically active sulfoxides.[7]

Scheme I



Scheme II



In this article we report the details of the preparation of 1-chloroalkyl *p*-tolyl sulfoxides of high optical purity and the successful use of these optically active sulfoxides in new asymmetric syntheses of epoxides, allylic alcohols, α-amino ketones, and α-amino aldehydes.

Results and Discussion

Preparation of 1-Chloroalkyl *p*-Tolyl Sulfoxides of High Optical Purity. In our chiral synthesis we required 1-chloroalkyl aryl sulfoxides of high optical purity. A survey of the literature revealed reports on only two methods of synthesis. One was the chlorination of optically active alkyl aryl sulfoxides with (dichloroiodo)benzene and silver(I) nitrate in acetonitrile,[8] and the other was chlo-

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Table I. Chlorination of Optically Active Alkyl p-Tolyl Sulfoxides 1 with NCS-K_2CO_3

	1			2			
	R^1	R^2	reactn time, h	chemical yield, %	$[\alpha]_D$,[a] deg	% ee[b]	highest $[\alpha]_D$, deg
1a	H	H	40	91	−207.9	87[c] 89[d]	−239.0
1b	H	CH_3	20	94	−154.1	93[d]	−[e]
1c	H	CH_2Ph	43	88	−85.1	87[d]	−[f]
1d	CH_3	CH_3	40	92	−115.2	94[c]	−122.6

[a] All specific rotations were measured in acetone at 25 °C. [b] Enantiomeric excess with respect to the sulfur chiral center. [c] Calculated on the basis of the highest value of specific rotation obtained in this study. [d] Calculated from NMR (the adduct with acetone in the presence of $Eu(hfc)_3$); see text. [e] A 3:1 diastereomeric mixture. [f] A 6.6:1 diastereomeric mixture.

rination with *N*-chlorosuccinimide (NCS) on silica gel.[9] These reactions both suffer from low optical yields, and the former is quite expensive. The latter could not be used to prepare a large quantity of the chloride.

The chlorination of alkyl aryl sulfoxides to obtain 1-chloroalkyl aryl sulfoxides has been accomplished by using various chlorinating agents.[10] First of all, we studied the chlorination of optically pure (+)-methyl *p*-tolyl sulfoxide (**1a**) and found that NCS in the presence of K_2CO_3 was the reagent of choice (Scheme II).

(+)-**1a** ($[\alpha]^{25}_D$ +149.5°) was synthesized from (−)-(*S*)-menthyl *p*-toluenesulfinate by a slight modification of Solladie's procedure.[3a] The chlorination of (+)-**1a** with NCS in CH_2Cl_2 gave racemic chloromethyl *p*-tolyl sulfoxide with significant amounts of dichloromethyl *p*-tolyl sulfoxide within 10 min at room temperature. On the other hand, this reaction was quite sluggish in the presence of K_2CO_3 powder at room temperature. After 40 h, with 2 equiv of NCS, the reaction was quenched by adding 4% NaI solution. The usual workup gave **2a** as colorless crystals in 91% yield. Unexpectedly, the product showed a quite high value of specific rotation ($[\alpha]^{25}_D$ −207.9°) compared with those reported for material prepared by other methods.[8,9] One recrystallization of this product from AcOEt–hexane gave a 72% yield (from **1a**) of **2a** having $[\alpha]^{25}_D$ −233.7°. Several further recrystallizations gave colorless plates with the highest value of specific rotation ($[\alpha]^{25}_D$ −239.0°). As discussed later, this was indeed optically pure (−)-**2a**.

This chlorination was applied to other optically active (+)-alkyl *p*-tolyl sulfoxides **1b–d**, and the results are summarized in Table I. As shown, the chemical yields were uniformly quite good. The enantiomeric purity of **2** is discussed below. As chlorides **2b** and **2c** were an inseparable diastereomeric mixture, it was clear that direct measurement of the enantiomeric purity of the sulfur center would be very difficult. We attempted to find a spectroscopic way of determining the enantiomeric purity of this center.

Durst[4a] and we[5] have already observed that the reaction of the anions derived from a diastereomeric mixture of 1-chloroalkyl phenyl sulfoxides with symmetric ketones (such as acetone and cyclohexanone) below −40 °C gives a single isomer of a chlorohydrin in high yield. This result means that the stereochemistry of this reaction was completely controlled by the chirality of the sulfur center. Thus, 1-chloroalkyl *p*-tolyl sulfoxides **2a–c** were treated

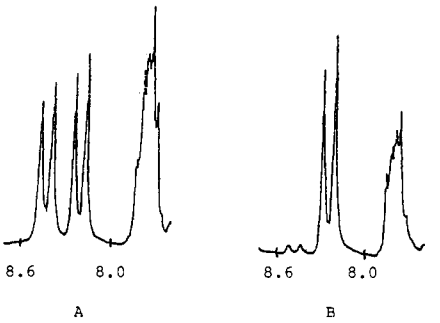
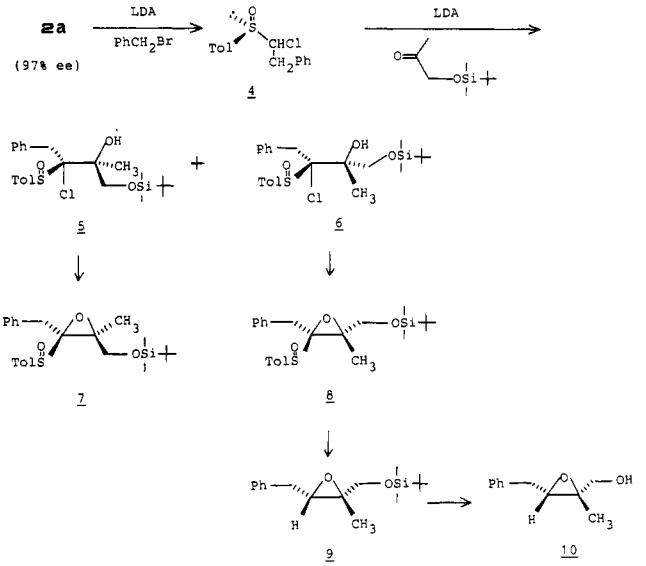


Figure 1. The ^1H NMR signals of the aromatic protons of the *p*-tolyl group of racemic (A) and optically active (B) **3c** in the presence of 20 mol % $Eu(hfc)_3$ in $CDCl_3$ (100 MHz).

Scheme III



with 1.1 equiv of lithium diisopropylamide (LDA) followed by acetone at −60 °C to afford only one diastereomer of the chlorohydrins **3a–c** in over 75% yield. These chlorohydrins were analyzed with ^1H NMR spectroscopy in the presence of 10–20 mol % of $Eu(hfc)_3$ as a chiral shift reagent, and it was observed that the protons on the carbon close to the sulfur atom exhibit a clear separation of signals. Figure 1 shows an example of **3c**. Integration of the signals of the aromatic protons of **3c** allowed the assignment of an 87% ee value for the enantiomeric purity of **2c** as shown in Table I. The same technique was applied to **3a** (H on the carbon bearing the chlorine atom was observed) and **3b** (methyl H on the carbon bearing the chlorine atom was observed), and it was calculated that the enantiomeric purities of **2a** and **2b** were 89% and 93% ee, respectively. The enantiomeric purity of **2d** was calculated on the basis of the value of specific rotation of optically pure (−)-**2d** which was synthesized from optically

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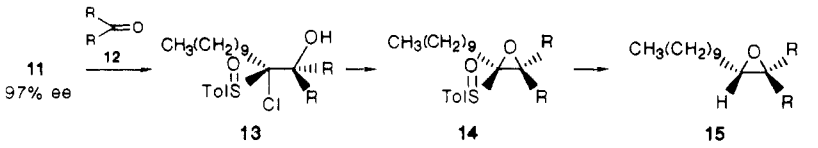
Table II. Synthesis of Chiral Epoxides from 11 and Symmetrical Ketones



	12 R	13 yield,[a] %	14 yield,[a] %	14 $[\alpha]_D$,[b] deg	15 yield,[a] %	15 $[\alpha]_D$,[b] deg
a	CH_3	100	98	+8.9	73	-13.7
b	Ph	-[c]	99	-91.7	89	-28.6
c	$-(CH_2)_5-$	93	95	+13.7	85	-14.0
d	$-(CH_2)_6-$	84	86	+18.5	61 (93)[d]	-13.7

[a] Isolated yield. [b] Measured in CCl_4 at 25 °C. [c] Not isolated. [d] Conversion yield.

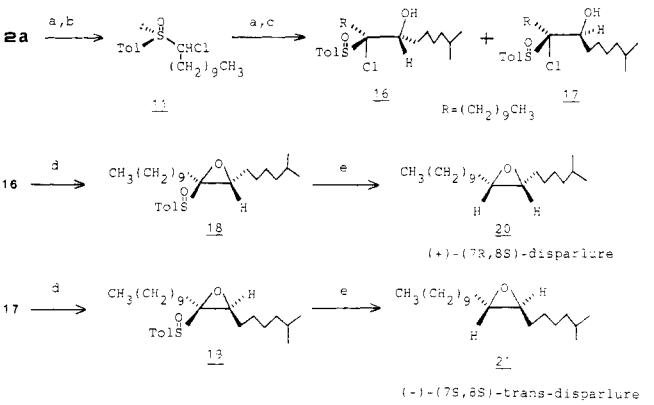
pure **2a** with excess LDA and iodomethane in 43% yield. After recrystallization from AcOEt–hexane, optically pure **2d** showed $[\alpha]^{25}_D$ -122.6° (lit.[8c] $[\alpha]^{25}_D$ -119°).

Asymmetric Synthesis of Epoxides. With this practical and less expensive procedure for obtaining optically active (-)-**2a**, the stage was set for the asymmetric synthesis of epoxides.

Alkylation of (-)-**2a** (97% ee) with benzyl bromide gave a diastereomeric mixture of **4** in 97% yield (Scheme III). This sulfoxide was treated with LDA followed by acetol *tert*-butyldimethylsilyl ether to afford the chlorohydrins **5** and **6**. Only two products were observed in this reaction. Since the chlorohydrins were rather unstable, the mixture was immediately treated with a base to afford the α,β-epoxy sulfoxides **7** and **8** in respective 22% and 35% yields from **4**. The stereochemistry of **7** and **8** was quite easily determined by ^1H NMR spectroscopy. The signal for the methyl group on the epoxide of **8** (δ 1.84) shows much lower absorption than that of **7** (δ 1.27).[6] Stereospecific desulfinylation[6] of **8** was conducted with 1.1 equiv of *n*-BuLi in THF at -100 °C to afford the desired epoxide **9** in 65% yield. The silyl group of **9** was removed in the usual way to give epoxide **10** in quantitative yield. The structure and absolute stereochemistry of **10** were determined to be as depicted in Scheme III by comparing the specific rotation with that reported by Sharpless et al.[11] From this result, the induced absolute stereochemistry of the carbon atoms bearing chlorine atoms of **5** and **6** was unambiguously determined to be *R*. The enantiomeric excess of **10** was calculated to be over 96% from a 500-MHz ^1H NMR spectrum of its (-)-MTPA (α-methoxy-α-(trifluoromethyl)phenylacetic acid) ester.[12]

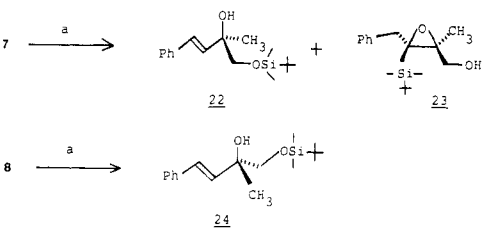
This method of obtaining chiral epoxides was most effective when symmetrical ketones were used. Representative results for this transformation using (-)-1-chloroundecyl *p*-tolyl sulfoxide (**11**; 97% ee), derived from (-)-**2a** (97% ee) and 1-iododecane, are summarized in Table II. The yields of each step were uniformly good, and (*S*)-(-)-epoxides **15** were obtained. The absolute configuration of **15** was determined to be *S* by comparison of the specific rotation of **15** with commerically available (*R*)-(+)-1,2-epoxydodecane ($[\alpha]^{25}_D$ +10.2°).[13] This would also be consistent with the result obtained in the synthesis of **10**. The optical yield of the epoxides **15** was calculated to be 97% based on ^1H NMR spectra in the presence of $Eu(hfc)_3$ as a chiral shift reagent.

Scheme IV[a]



[a] (a) LDA, THF, -50 °C; (b) 1-iododecane; (c) 6-methyl-1-heptanal; (d) *t*-BuOK, *t*-BuOH, room temperature; (e) *n*-BuLi, THF, -100 °C.

Scheme V[a]



[a] (a) Three equivalents of *n*-BuLi in THF.

The interpretation of this 1,2-asymmetric induction was reported in the previous communication.[7b]

Brief Synthesis of Optically Active (+)-Disparlure. This method was then applied to a synthesis of (+)-disparlure,[14] the sex attractant of the female gypsy moth. Optically pure **11** was treated with LDA followed by 6-methyl-1-heptanal which was synthesized from 6-methyl-1-heptanol[15] to give two chlorodihydrins **16** and **17** in 39% and 51% yields, respectively (Scheme IV). No other products were observed (TLC). The chlorohydrins were easily separated by silica gel column chromatography

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and were treated with *t*-BuOK in *t*-BuOH to afford the desired α,β-epoxy sulfoxides **18** and **19** in 95% and 83% yields, respectively. The stereospecific desulfinylation of both α,β-epoxy sulfoxides **18** and **19** was conducted with *n*-BuLi in THF at −100 °C to give (+)-(7*R*,8*S*)-disparlure (**20**) ($[\alpha]^{25}_D$ +0.87° (lit.[14b] $[\alpha]^{25}_D$ +0.6 ± 0.4°; lit.[14d] $[\alpha]^{23}_D$ +0.8 ± 0.2°)) and (7*S*,8*S*)-*trans*-disparlure (**21**) ($[\alpha]^{25}_D$ −28.7° (lit.[14b] $[\alpha]^{25}_D$ −26.6 ± 0.8°)) in 55% and 62% yields, respectively. This three-step synthesis of (+)-**20** from the sulfoxide **11** was the shortest yet reported for the pheromone.

Synthesis of Optically Active Allylic Alcohols, α-Amino Ketones, and α-Amino Aldehydes. In previous papers,[6] we have reported that the α,β-epoxy sulfoxides having an arylmethyl group at the α-position gave allylic alcohols when treated with excess *n*-BuLi. Thus, α,β-epoxy sulfoxides **7** and **8** were treated with 3 equiv of *n*-BuLi in THF at −70 to −45 °C (Scheme V). The α,β-epoxy sulfoxide **7** gave the desired allylic alcohol **22** ($[\alpha]^{25}_D$ +3.0°) and epoxy silane **23** ($[\alpha]^{25}_D$ +63.5°) in 21% and 63% yields, respectively. The same treatment of **8** gave the allylic alcohol **24** ($[\alpha]^{25}_D$ −3.3°) in 90% yield. The enantiomeric excess of **22** and **24** was measured to be over 96% from the (+)-MTPA ester of the primary hydroxyl group of the desilylated glycols. These results show that this method allows both enantiomers of allylic alcohols to be synthesized from one chiral auxiliary. The epoxy silane **23** is a product worthy of note. It obviously came from **7** via 1,4 O → C silyl migration,[16] which implies that the stereospecific desulfinylation proceeded through the carbanion of epoxide.

On heating in piperidine followed by desilylation, **7** and **8** gave the α-amino ketones[5c] **29** and **30** in good yields. Both α-amino ketones showed a similar value of specific rotation except for the sign. From their (−)-MTPA esters the enantiomeric purity of **29** and **30** was shown to be 86% and 93%, respectively. Since **7** and **8** were of 97% optical purity, this indicates that the aminolysis took place with some racemization.

The examples of the synthesis of α-amino ketones and α-amino aldehydes are summarized in Table III. Treatment of the α,β-epoxy sulfoxides **25** and **26** of 97% optical purity with piperidine or aniline at room temperature gave α-amino aldehydes **31–34** in quantitative yields. The optical purity of these products was calculated to be 97% from ^{1}H NMR spectra with Eu(hfc)$_3$. The results from the α,β-epoxy sulfoxides **27** and **28** of 97% optical purity with piperidine is notable. The reaction was quite fast, giving α-amino ketone **35** in quantitative yield; however, complete racemization took place.

Although the procedure for preparing optically active α-amino carbonyl compounds was successful in some cases, several limitations were found in this study. First, primary amines, such as benzylamine and cyclohexylamine, gave complex mixtures with the α,β-epoxy sulfoxides. Second, cyclic secondary amines, such as piperidine and pyrrolidine, reacted well with the α,β-epoxy sulfoxides; however, acyclic ones reacted quite sluggishly and no satisfactory result was obtained. Third, the α-amino ketones which are trisubstituted at the asymmetric carbon racemized completely under the reaction conditions.

In conclusion, because of its overall simplicity and high overall yields, we believe that the presented method will prove valuable in the synthesis of chiral epoxides, allylic alcohols, α-amino ketones, and α-amino aldehydes having high enantiomeric purity.

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Experimental Section

All melting points are uncorrected. ^{1}H nuclear magnetic resonance (NMR) spectra were measured in a $CDCl_3$ solution at 100 or 500 MHz. Electron-impact mass spectra (MS) were obtained at 70 eV by direct insertion. Silica gel BW-127 ZH (Fuji-Devison) containing 2% fluorescence reagent 254 and a quartz column were used for column chromatography, and the products having UV absorption were detected by UV irradiation. In experiments requiring dry solvent, THF was distilled from benzophenone ketyl; toluene, CH_2Cl_2, and DMF were dried over CaH_2 and distilled. Some new compounds, especially oily products, did not give acceptable data for combustion analyses; however, the purity of all the title compounds was judged to be over 95% by ^{1}H NMR spectral determination and chromatographic analyses (GC and/or TLC).

General Procedure for the Synthesis of (+)-(*R*)-Alkyl *p*-Tolyl Sulfoxides 1. A synthesis of (+)-(*R*)-methyl *p*-tolyl sulfoxide (**1a**) is described. MeMgBr (3 M in ether; 18.4 mL) was added to a flame-dried flask (200 mL), and the ether was evaporated under vacuum. To the residue was added 25 mL of dry toluene, and the solution was cooled to −60 °C. To this solution was added a solution of *l*-menthyl (−)-(*S*)-*p*-toluenesulfinate[3a] (7.36 g; 25 mmol) in 50 mL of dry toluene dropwise with stirring. The temperature of the reaction mixture was allowed to warm to −20 °C, and then excess saturated aqueous NH_4Cl was added. The whole was extracted with ether. The usual workup followed by silica gel column chromatography (eluted with a mixture of hexane–AcOEt (1:1)) gave colorless crystals, which were recrystallized from AcOEt–hexane to afford 3.73 g (97%) of **1a** as colorless prisms: mp 72.5–73.5 °C (lit.[17] mp 73–74 °C); $[\alpha]^{25}_D$ +149.5° (*c* 0.9, acetone) (lit.[17] $[\alpha]^{21}_D$ +146°).

(+)-(*R*)-Ethyl *p*-Tolyl Sulfoxide (1b). Ethylmagnesium bromide was used: colorless oil; 99% yield; $[\alpha]^{25}_D$ +202.6° (*c* 1.0, acetone).

(+)-(*R*)-2-Phenylethyl *p*-Tolyl Sulfoxide (1c). (2-Phenylethyl)magnesium chloride was used: colorless oil; 99% yield; $[\alpha]^{25}_D$ +119.9° (*c* 1.1, acetone).

(+)-(*R*)-Isopropyl *p*-Tolyl Sulfoxide (1d). Isopropylmagnesium bromide was used: colorless oil; 98% yield; $[\alpha]^{25}_D$ +194.0° (*c* 0.9, acetone).

General Procedure for the Synthesis of (−)-(*R*)-1-Chloroalkyl *p*-Tolyl Sulfoxides 2. A synthesis of (−)-(*R*)-chloromethyl *p*-tolyl sulfoxide (**2a**) is described. To a solution of **1a** (1.54 g; 10 mmol) in 10 mL of dry CH_2Cl_2 was added K_2CO_3 (800 mg) followed by NCS (2.64 g; 20 mmol). The suspension was stirred at room temperature for 40 h. The reaction mixture was diluted with ether (50 mL), and the solution was washed with 4% NaI (50 mL) followed by 10% $Na_2S_2O_3$ (50 mL). The organic layer was dried over Na_2SO_4, and the solvent was evaporated to leave a residue, which was purified by silica gel column chromatography to give 1.71 g (91%) of **2a** as colorless crystals: $[\alpha]^{25}_D$ −207.9° (*c* 1.0, acetone). One recrystallization from AcOEt–hexane afforded 1.36 g (72%) of colorless plates: $[\alpha]^{25}_D$ −233.7° (*c* 0.7, acetone); 97% ee. Additional recrystallization gave optically pure **2a**: mp 88–88.5 °C; $[\alpha]^{25}_D$ −239.0° (*c* 1.0, acetone); IR (KBr) 1080, 1050, 1040; ^{1}H NMR δ 2.43 (3 H, s), 4.35 (3 H, s), 7.25–7.65 (4 H, m); MS, *m/z* (relative intensity) 188 (M^+, 16), 139 (100).

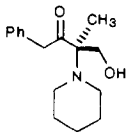
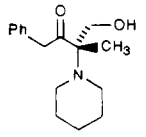
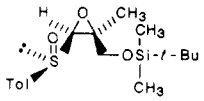
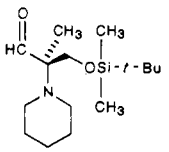
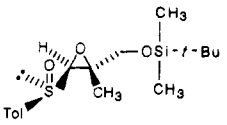
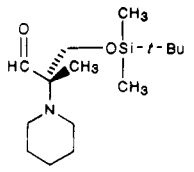
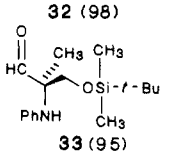
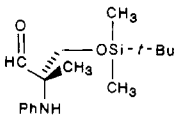
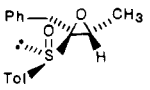
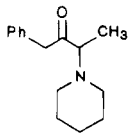
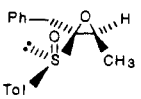
(−)-(*R*)-1-Chloroethyl *p*-Tolyl Sulfoxide (2b): diastereomeric mixture (3:1); colorless oil; IR (neat) 1095, 1085, 1060, 1040; ^{1}H NMR δ 1.60, 1.76 (each d, 3 H, *J* = 7 Hz), 2.43 (3 H, s), 4.49, 4.67 (each q, 1 H, *J* = 7 Hz), 7.16–7.62 (4 H, m); MS, *m/z* (relative intensity) 202 (M^+, 2), 140 (100), 92 (84).

(−)-(*R*)-1-Chloro-2-phenylethyl *p*-Tolyl Sulfoxide (2c): diastereomeric mixture (6.6:1); colorless oil; IR (neat) 1090, 1060; ^{1}H NMR δ 2.42 (3 H, s), 2.70 (dd, 0.87 H, *J* = 10, 15 Hz), 3.14 (dd, 0.13 H, *J* = 10, 15 Hz), 3.30–3.72 (1 H, m), 4.52 (dd, 0.13 H, *J* = 3, 10 Hz), 4.65 (dd, 0.87 H, *J* = 4, 10 Hz), 7.0–7.7 (9 H, m); MS, *m/z* (relative intensity) 278 (M^+, 10), 140 (100), 103 (87).

(−)-(*R*)-1-Chloro-1-methylethyl *p*-Tolyl Sulfoxide (2d): colorless crystals; IR (KBr) 1090, 1065; ^{1}H NMR δ 1.55 (3 H, s), 1.84 (3 H, s), 2.42 (3 H, s), 7.16–7.68 (4 H, m); MS, *m/z* (relative intensity) 140 (100), 92 (65). Optically pure (−)-**2d** was synthesized from optically pure (−)-**2a** (132 mg) with 4 equiv of MeI and 2.4

(17) Solladie, G.; Hutt, J.; Girardin, A. *Synthesis* **1987**, 173.

Table III. Synthesis of α-Amino Ketones and α-Amino Aldehydes from α,β-Epoxy Sulfoxides

α,β-epoxy sulfide	amine[a]	condtns[b]	α-amino ketone and α-amino aldehyde (yield,[c] %)	$[\alpha]_D$,[d] deg	% ee
7	A	100 °C, 4 h	 **29** (72)	−6.0[e]	86
8	A	100 °C, 4 h	 **30** (80)	+6.0[e]	93
 **25**	A	rt,[f] 1 day	 **31** (96)	+5.09	97
 **26**	A	rt, 1 day	 **32** (98)	−5.06	97
25	B	rt, 2 days	 **33** (95)	+36.1	97
26	B	rt, 2 days	 **34** (98)	−35.8	97
 **27**	A	rt, 40 min	 **35** (95)	0	0
 **28**	A	rt, 100 min	**35** (99)	0	0

[a] A: piperidine. B: aniline. [b] All reactions were conducted in the amine without solvent. [c] Isolated yield. [d] Unless otherwise noted, the specific rotations were measured in acetone. [e] Measured in EtOH. [f] Room temperature.

equiv of lithium diisopropylamide (LDA) in THF at −60 to −20 °C for 2 h. Recrystallization of the product from AcOEt–hexane gave 65 mg (43%) of colorless plates: mp 53–55 °C; $[\alpha]^{25}_D$ −122.6° (c 0.5, acetone). Anal. Calcd for $C_{10}H_{13}ClOS$: C, 55.42; H, 6.05. Found: C, 55.30; H, 6.05.

Acetone Adduct of 2a, 2b, and 2c. The general procedure is described for the adduct of **2a** with acetone. To a solution of LDA (0.89 mmol) in 3 mL of dry THF at −60 °C was added dropwise with stirring a solution of **2a** ($[\alpha]^{25}_D$ −207.9°; 152 mg; 0.81 mmol) in 0.5 mL of THF. The stirring was continued for 10 min, and then acetone (0.89 mmol) was added; after 5 min, the reaction was quenched by saturated aqueous NH_4Cl solution. The usual workup gave 146 mg (73%) of **3a** as colorless crystals: mp 150–153 °C; IR (KBr) 3410, 1095, 1045; ^{1}H NMR δ 1.56 (6 H, s), 2.40 (3 H, s), 4.24 (1 H, s), 7.15–7.55 (4 H, m). Anal. Calcd for $C_{11}H_{15}ClO_2S$: 53.54; H, 6.13; Cl, 14.37; S, 12.99. Found: C, 53.35; H, 6.08; Cl, 14.18; S, 13.15.

With 20 mol % (+)-Eu(hfc)$_3$, the proton at the carbon bearing the chlorine atom of racemic **3a** showed δ 5.85 and δ 5.92, respectively.

3b: 81% yield; colorless crystals; mp 102–104.5 °C; IR (KBr) 3410, 1090, 1065, 1015, ^{1}H NMR δ 1.46 (6 H, s), 1.47 (3 H, s), 2.44 (3 H, s), 7.22–7.66 (4 H, m). Anal. Calcd for $C_{12}H_{17}ClO_2S$: C, 55.27; H, 6.57; Cl, 13.59; S, 12.29. Found: C, 55.36; H, 6.62; Cl, 13.66; S, 12.25.

With 10 mol % (+)-Eu(hfc)$_3$, the methyl H at the carbon bearing the chlorine atom of racemic **3b** showed δ 2.17 and δ 2.28, respectively.

3c: 85% yield: colorless oil; IR (neat) 3425, 1090, 1050; ^{1}H NMR δ 1.21 (3 H, s), 1.58 (3 H, s), 2.40 (3 H, s), 3.30, 3.40 (each 1 H, d, J = 15 Hz), 7.10–7.60 (9 H, m).

With 20 mol % (+)-Eu(hfc)$_3$, the aromatic H (*p*-tolyl group) of racemic **3c** showed δ 8.22 (d, J = 8 Hz) and δ 8.44 (d, J = 8 Hz), respectively. See Figure 1.

(−)-(*R*)-1-Chloro-2-phenylethyl *p*-Tolyl Sulfoxide (4). A solution of (−)-**2a** (97% ee; 500 mg; 2.65 mmol) in 2.5 mL of dry THF was added dropwise with stirring to a solution of LDA (3 mmol) in 5 mL of THF at −78 °C. After 30 min, benzyl bromide (3.45 mmol) was added to the reaction mixture, and the stirring was continued for 17 min. The reaction was quenched with saturated aqueous NH_4Cl. The usual workup followed by silica gel column chromatography gave **4** (718 mg; 97%) as a colorless oil; $[\alpha]^{25}_D$ −85.0° (*c* 1.0, acetone). This product was a 1.2:1 mixture of diastereomers, and the spectral data were similar to those of **2c**.

(−)-(2*S*,3*R*)-2,3-Epoxy-1-(*tert*-butyldimethylsiloxy)-2-methyl-4-phenyl-3-(*p*-tolylsulfinyl)butane (7) and Its (−)-(2*R*,3*R*) Isomer 8. A solution of **4** (545 mg; 1.95 mmol) in 2 mL of dry THF was added to a solution of LDA (2.15 mmol) in 5 mL of THF at −78 °C with stirring. The reaction mixture was stirred for 50 min at −78 °C, and then a solution of acetol *tert*-butyldimethylsilyl ether (739 mg; 3.9 mmol; this compound was prepared from acetol and *tert*-butyldimethylsilyl chloride with imidazole in DMF) in 2 mL of THF was added. Shortly after the addition, the reaction was quenched with saturated aqueous NH_4Cl. The usual workup followed by silica gel column chromatography gave 547 mg (60%) of a mixture of **5** and **6**. This mixture was dissolved in 20 mL of MeOH, 30% KOH (7 mL) was added, and the whole was stirred at room temperature for 25 min. The reaction was quenched by adding powdered NH_4Cl, and the MeOH was evaporated. The residue was extracted with ether–benzene. The usual workup followed by silica gel column chromatography gave **7** (186 mg; 22%) and **8** (291 mg; 35%). (−)-**7**: mp 52–53 °C (pentane); $[a]^{25}_D$ −33.7° (*c* 2.8, acetone); IR (KBr) 1265, 1255, 1090, 1055; ^1H NMR δ 0.13, 0.16, (each 3 H, s), 0.96 (9 H, s), 1.27 (3 H, s), 2.39 (3 H, s), 3.08, 3.36 (each 1 H, d, *J* = 17 Hz), 4.08, 4.20 (each 1 H, d, *J* = 11 Hz), 6.8–7.6 (9 H, m); MS, *m/z* (relative intensity) 373 (0.1), 315 (0.8), 91 (100). Anal. Calcd for $C_{24}H_{34}O_3SSi$: C, 66.93; H, 7.96; S, 7.44. Found: C, 67.04; H, 8.06; S, 7.70. (−)-**8**: colorless oil; $[\alpha]^{25}_D$ −1.8° (*c* 4.4, acetone); IR (neat) 1260, 1255, 1100, 1080, 1055; ^1H NMR δ −0.10, −0.07 (each 3 H, s), 0.84 (9 H, s), 1.84 (3 H, s), 2.40 (3 H, s), 3.15, 3.30 (each 1 H, d, *J* = 17 Hz), 3.35 (2 H, s), 6.7–7.6 (9 H, m); MS, *m/z* (relative intensity) 373 (0.1), 91 (100).

(+)-(2*S*,3*S*)-2,3-Epoxy-3-methyl-1-phenyl-4-(*tert*-butyldimethylsiloxy)butane (9). A solution of **8** (291 mg; 0.68 mmol) in 1.4 mL of dry THF was added to a solution of *n*-BuLi (1.5 M; 0.68 mL) in 1.4 mL of dry THF at −100 °C with stirring. After 5 s, the reaction was quenched by saturated aqueous NH_4Cl, and the whole was extracted with ether. The usual workup followed by silica gel column chromatography gave 128 mg (65%) of **9** and recovered **8** (68 mg; 23%). **9**: colorless oil; $[\alpha]^{25}_D$ +8.7° (*c* 1.6, $CHCl_3$); IR (neat) 1265, 1260, 1100, 840; ^1H NMR δ 0.08, 0.11 (each 3 H, s), 0.93 (9 H, s), 1.37 (3 H, s), 2.8–3.1 (3 H, m), 3.75 (2 H, s), 7.25 (5 H, br s); MS *m/z* (relative intensity) 274 (0.3), 235 (22), 91 (100).

(−)-(2*R*,3*S*)-2,3-Epoxy-2-methyl-4-phenylbutan-1-ol (10). To a solution of **9** (117 mg; 0.4 mmol) in 1.3 mL of dry THF was added a solution of TBAF (1 mL; 1 mmol); and the reaction mixture was stirred at room temperature for 1.3 h. The reaction was quenched by adding saturated aqueous NH_4Cl, and the whole was extracted with ether. The usual workup followed by silica gel column chromatography gave 71 mg (100%) of **10** as a colorless oil; $[\alpha]^{25}_D$ −37.0° (*c* 1.4, EtOH) (lit.[11] $[\alpha]^{20}_D$ −33.05°; 91% ee); IR (neat) 3420, 1035; ^1H NMR δ 1.40 (3 H, s), 2.8–3.2 (3 H, m), 3.78 (2 H, s), 7.24 (5 H, m). The methyl H at the epoxy group of the (−)-MTPA ester of **10** showed δ 1.34, and the proton of its enantiomer showed δ 1.25. MS: *m/z* (relative intensity) 160 (0.01), 147 (100), 91 (71).

(−)-1-Chloroundecyl *p*-Tolyl Sulfoxide (11). A solution of (−)-**2a** (97% ee; 750 mg; 4 mmol) in 1 mL of dry THF was added dropwise with stirring to a solution of LDA (4.3 mmol) in 7.5 mL of dry THF at −60 °C. After 25 min, 1-iododecane (4.4 mmol) was added to the mixture, and it was gradually allowed to warm to −20 °C for 1 h. The reaction was quenched with saturated aqueous NH_4Cl, and the whole was extracted with ether–benzene. The usual workup followed by silica gel column chromatography gave **11** (1.01 g; 77%) as a colorless oil (3:2 diastereomeric mixture): $[\alpha]^{25}_D$ −87.7° (*c* 0.4, CCl_4); IR (neat) 1090, 1065; ^1H NMR δ 0.87 (3 H, t, *J* = 6 Hz), 1.0–1.8 (18 H, m), 2.41 (3 H, s), 4.37 (0.6 H, dd, *J* = 3, 9 Hz), 4.50 (0.4 H, dd, *J* = 3, 8 Hz), 7.2–7.7 (4 H, m); MS, *m/z* (relative intensity) 328 (M^+, 0.6), 140 (100). Found: *m/z* 328.1622. Calcd for $C_{18}H_{29}ClOS$: M, 328.1625.

General Procedure for the Synthesis of α,β-Epoxy Sulfoxides 14. A synthesis of **14a** is described. A solution of **11** (197 mg; 0.6 mmol) in 1 mL of dry THF was added dropwise with stirring to a solution of LDA (0.66 mmol) in 3 mL of dry THF at −45 °C. The mixture was stirred for 10 min, and then acetone (0.72 mmol) was added. After 5 min, the reaction was quenched by saturated aqueous NH_4Cl. The usual workup gave 230 mg (100%) of the chlorohydrin **13a** as a colorless oil: IR (neat) 3410, 1090, 1050, 1025. **13a** (230 mg) was dissolved in 10 mL of *t*-BuOH, and *t*-BuOK (0.65 mmol) was added. The reaction mixture was stirred at room temperature for 15 min and then quenched with powdered NH_4Cl. The solvent was evaporated under vacuum, and the residue was extracted with ether–benzene. The usual workup followed by silica gel column chromatography gave **14a** (202 mg; 98%) as a colorless oil: $[\alpha]^{25}_D$ +8.9° (*c* 0.5, CCl_4); IR (neat) 1090, 1060, 1025; ^1H NMR δ 0.88 (3 H, t, *J* = 6 Hz), 1.39, 1.79 (each 3 H, s), 2.41 (3 H, s), 7.1–7.6 (4 H, m); MS, *m/z* (relative intensity) 350 (M^+, 0.2), 211 (66), 140 (100). Found: *m/z* 350.2277. Calcd for $C_{21}H_{34}O_2S$: M, 350.2277.

α,β-Epoxy Sulfoxide 14b. Reaction of **11** with benzophenone afforded **14b** in quantitative yield: $[\alpha]^{25}_D$ −91.7° (*c* 0.2, CCl_4); IR (neat) 1505, 1460, 1095, 1060, 705; ^1H NMR δ 0.2–2.2 (21 H, m), 2.02 (3 H, s), 7.1–7.7 (14 H, m); MS, *m/z* (relative intensity) 335 (10), 167 (18), 140 (100). Anal. Calcd for $C_{31}H_{38}O_2S$: C, 78.44; 8.07; S, 6.75. Found: C, 77.99; H, 8.33; S, 7.04.

α,β-Epoxy Sulfoxide 14c. Chlorohydrin **13c**: colorless oil; IR (neat) 3410, 1090, 1045, 1025. **14c**: colorless oil; $[\alpha]^{25}_D$ +13.7° (*c* 0.5, CCl_4); IR (neat) 1095, 1060, 1025; ^1H NMR δ 0.87 (3 H, t, *J* = 6 Hz), 0.8–1.4 (18 H, m), 1.4–1.9 (10 H, m), 2.41 (3 H, s), 7.16–7.64 (4 H, m); MS, *m/z* (relative intensity) 250 (13), 124 (100).

α,β-Epoxy Sulfoxide 14d. Chlorohydrin **13d**: colorless oil; IR (neat) 3430, 1090, 1050, 1025. **14d**: colorless oil; $[\alpha]^{25}_D$ +18.5° (*c* 0.5, CCl_4); IR (neat) 1095, 1060, 1025; ^1H NMR δ 0.87 (3 H, t, *J* = 6 Hz), 0.8–2.4 (28 H, m), 2.40 (3 H, s), 7.1–7.6 (4 H, m); MS, *m/z* (relative intensity) 264 (13), 123 (100).

Epoxides 15. Epoxides **15** were synthesized from **14** with *n*-BuLi at −100 °C in THF as described above. The enantiomeric purity of **15** was measured to be 97% from ^1H NMR with 20 mol % (+)-Eu(hfc)$_3$; for example, the proton at the epoxy group of racemic **15c** showed δ 5.93 and δ 6.13 (each t, *J* = 6 Hz), respectively.

(−)-(*S*)-2,3-Epoxy-2-methyltridecane (15a): colorless oil; $[\alpha]^{25}_D$ −13.7° (*c* 1.4, CCl_4); IR (neat) 1480, 1390, 1260, 1130; ^1H NMR δ 0.87 (3 H, t, *J* = 6 Hz), 1.0–1.6 (21 H, m); 1.26, 1.30 (each 3 H, s), 2.70 (1 H, t, *J* = 5 Hz); MS, *m/z* (relative intensity) 212 (trace), 197 (trace), 59 (100).

(−)-(*S*)-1,2-Epoxy-1,1-diphenyldodecane (15b): colorless oil; $[\alpha]^{25}_D$ −28.6° (*c* 2.3, CCl_4); IR (neat) 1505, 1480, 1460, 700; ^1H NMR δ 0.87 (3 H, t, *J* = 6 Hz), 1.0–1.6 (21 H, m), 3.35 (1 H, t, *J* = 6 Hz), 7.1–7.3 (10 H, m); MS, *m/z* (relative intensity) 336 (M^+, 33), 128 (6), 166 (100). Found: *m/z* 335.2469. Calcd for $C_{24}H_{32}O$: M, 336.2451.

(−)-(*S*)-3′-Decylspiro[cyclohexane-1,2′-oxirane] (15c): colorless oil; $[\alpha]^{25}_D$ −14.0° (*c* 1.6, CCl_4); IR (neat) 1480, 1470, 1460; ^1H NMR δ 0.88 (3 H, t, *J* = 6 Hz), 1.0–1.9 (28 H, m), 2.69 (1 H, t, *J* = 6 Hz); MS, *m/z* (relative intensity) 252 (M^+, 3), 154 (3), 125 (12), 99 (100). Found: *m/z* 252.2456. Calcd for $C_{17}H_{32}O$: M, 252.2452.

(−)-(*S*)-3′-Decylspiro[cycloheptane-1,2′-oxirane] (15d): colorless oil; $[\alpha]^{25}_D$ −13.7° (*c* 1.1, CCl_4); IR (neat) 1475, 1460, 1455; ^1H NMR δ 0.87 (3 H, t, *J* = 6 Hz), 1.0–1.9 (30 H, m), 2.67 (1 H, t, *J* = 5 Hz); MS, *m/z* (relative intensity) 266 (M^+, 9), 248 (6), 169 (15), 125 (94), 133 (100). Found: *m/z* 266.2595. Calcd for $C_{18}H_{34}O$: M, 266.2607.

α,β-Epoxy Sulfoxides 18 and 19. A solution of **11** (390 mg; 1.18 mmol) in 1 mL of dry THF was added dropwise with stirring to a solution of LDA (1.31 mmol) in 3 mL of dry THF at −55 °C. After 10 min, 6-methyl-1-heptanal (1.4 mmol) was added, and the stirring was continued for another 10 min. The reaction was quenced with saturated aqueous NH_4Cl, and the whole was extracted with ether–benzene. The usual workup followed by separation on a silica gel column gave **16** (210 mg; 39%) and **17** (273 mg; 51%) as a colorless oil. **16**: IR (neat) 3375, 1090, 1045,

1020. **17**: IR (neat) 3400, 1085, 1060, 1040, 1020. To a solution of **16** (200 mg) in 10 mL of *t*-BuOH was added *t*-BuOK (54 mg), and the mixture was stirred at room temperature for 10 min. The reaction was quenched with NH_4Cl, and *t*-BuOH was evaporated to give a residue, which was extracted with ether–benzene. The usual workup followed by purification by silica gel column chromatography gave **18** (175 mg; 95%) as a colorless oil; $[\alpha]^{25}_D$ −1.6° (*c* 0.5, CCl_4); IR (neat) 1095, 1065, 1025; ^1H NMR δ 0.85 (6 H, d, *J* = 7 Hz), 0.89 (3 H, t, *J* = 6 Hz), 1.0–1.8 (27 H, m), 2.41 (3 H, s), 3.63 (1 H, t, *J* = 6 Hz), 7.2–7.6 (4 H, m); MS, *m/z* (relative intensity) 420 (M^+, 3), 281 (16), 195 (11), 169 (77), 43 (100). Found: *m/z* 420.3074. Calcd for $C_{26}H_{44}O_2S$: M, 420.3060.

A similar treatment of **17** with *t*-BuOK gave **19** as a colorless oil in 83% yield: $[\alpha]^{25}_D$ −8.8° (*c* 0.4, CCl_4); IR (neat) 1090, 1060, 1020; ^1H NMR δ 0.86 (3 H, t, *J* = 6 Hz), 0.90 (6 H, d, *J* = 7 Hz), 0.9–2.2 (27 H, m), 2.41 (3 H, s), 3.22 (1 H, t, *J* = 6 Hz), 7.2–7.8 (4 H, m); MS, *m/z* (relative intensity) 420 (M^+, 4), 281 (22), 217 (4), 169 (98), 43 (100). Found: *m/z* 420.3054. Calcd for $C_{26}H_{44}O_2S$: M, 420.3060.

(+)-(7*R*,8*S*)-Disparlure (20). A solution of **18** (84 mg; 0.2 mmol) in 0.4 mL of dry THF was added with stirring to a solution of *n*-BuLi (0.22 mmol) in 0.4 mL of dry THF at −100 °C. After 3 min, the reaction was quenched with saturated aqueous NH_4Cl, and the whole was extracted with ether–benzene. The usual workup followed by silica gel column chromatography gave **20** (31 mg; 55%) as a colorless oil: $[\alpha]^{25}_D$ +0.87° (*c* 1.2, CCl_4); IR (neat) 1475, 1395, 1375, ^1H NMR δ 0.88 (6 H, d, *J* = 7 Hz), 0.89 (3 H, t, *J* = 6 Hz), 1.0–1.7 (27 H, m), 2.90 (2 H, m); MS, *m/z* (relative intensity) 282 (M^+, 1.6), 183 (20), 152 (8), 141 (11), 69 (100). Found: *m/z* 282.2906. Calcd for $C_{19}H_{38}O$: M, 282.2920.

A similar treatment of **19** with *n*-BuLi gave (−)-**21** as a colorless oil in 62% yield, and **19** was recovered in 34% yield. **21**: $[\alpha]^{25}_D$ −28.7° (*c* 0.3, CCl_4); IR (neat) 1480, 1395, 1375; ^1H NMR δ 0.96 (6 H, d, *J* = 7 Hz), 0.98 (3 H, t, *J* = Hz), 1.0–1.7 (27 H, m), 2.65 (2 H, m); MS, *m/z* (relative intensity) 282 (M^+, 1.6), 183 (19), 152 (7), 141 (11), 69 (100). Found: *m/z* 282.2893. Calcd for $C_{19}H_{38}O$: M, 282.2920.

Allylic Alcohol 22 and Epoxy Silane 23. A solution of **7** (71 mg; 0.16 mmol) in 0.25 mL of dry THF was added dropwise with stirring to a solution of *n*-BuLi (0.49 mmol) in 0.25 mL of dry THF at −70 °C. The reaction mixture was allowed to warm to −45 °C, and then the reaction was quenched with saturated aqueous NH_4Cl. The whole was extracted with AcOEt. The usual workup followed by silica gel column chromatography afforded **22** (10 mg; 21%) and **23** (30 mg; 63%) as colorless oils. **22**: $[\alpha]^{25}_D$ +3.0° (*c* 0.5, EtOH); IR (neat) 3540, 1270, 1100; ^1H NMR δ 0.06, 0.07 (each 3 H, s), 0.90 (9 H, s), 1.33 (3 H, s), 3.50, 3.55 (each 1 H, d, *J* = 10 Hz), 6.20, 6.64 (each 1 H, d, *J* = 16 Hz), 7.1–7.4 (5 H, m). The enantiomeric purity of desilylated **22** was measured to be 97% from the 500-MHz ^1H NMR of its (+)-MTPA ester. The methylene H of the MTPA ester showed δ 4.25 (d, *J* = 11 Hz) and δ 4.40 (d, *J* = 11 Hz). MS: *m/z* (relative intensity) 292 (M^+, 0.3), 274 (0.7), 235 (15), 147 (100). Found: *m/z* 292.1838. Calcd for $C_{17}H_{28}O_2Si$: M, 292.1857. **23**: $[\alpha]^{25}_D$ +63.5° (*c* 0.3, EtOH); IR (neat) 3425, 1465, 1265, 1255, 1030; ^1H NMR δ −0.14, 0.14 (each 3 H, s), 0.93 (9 H, s), 1.46 (3 H, s), 2.81, 3.31 (each 1 H, d, *J* = 17 Hz), 3.72 (1 H, s), 7.0–7.4 (5 H, m); MS, *m/z* (relative intensity) 261 (1), 157 (6), 143 (31), 75 (100).

Allylic Alcohol (24). The similar treatment of **8** with *n*-BuLi gave **24** as a colorless oil in 90% yield: $[\alpha]^{25}_D$ −3.3° (*c* 0.2, EtOH). The enantiomeric purity of desilylated **24** was measured to be 96% from the 500-MHz ^1H NMR of its (+)-MTPA ester. The methylene H of the MTPA ester showed δ 4.22 (d, *J* = 11 Hz) and δ 4.46 (d, *J* = 11 Hz).

α,β-Epoxy Sulfoxides 25–28. The α,β-epoxy sulfoxides **25–28** were synthesized from **1a** (97% ee) or **4** (97% ee) with acetol *tert*-butyldimethylsilyl ether or acetaldehyde through chlorohydrins as described above. **25**: colorless oil: 34% overall yield; $[\alpha]^{25}_D$ +1.98° (*c* 1.2, acetone); IR (neat) 1115, 1055; ^1H NMR δ 0.15 (6 H, s), 0.95 (9 H, s), 1.45 (3 H, s), 2.42 (3 H, s), 3.70 (1 H, s), 4.01, 4.10 (each 1 H, d, *J* = 11 Hz), 7.24–7.62 (4 H, m); MS, *m/z* (relative intensity) 283 (5), 201 (8), 139 (33), 73 (100). **26**: colorless oil; 23% overall yield; $[\alpha]^{25}_D$ −35.6° (*c* 1.1, acetone); IR (neat) 1120, 1055; ^1H NMR δ 0.00, 0.03 (each 3 H, s), 0.89 (9 H, s), 1.69 (3 H, s), 2.42 (3 H, s), 3.62, 3.74 (each 1 H, d, *J* = 12 Hz), 3.83 (1 H, s), 7.22–7.64 (4 H, m); MS, *m/z* (relative intensity) 254 (2), 201 (10), 139 (34), 73 (100). **27**: colorless prisms: mp 81–82 °C (AcOEt-hexane); 33% overall yield; $[\alpha]^{25}_D$ −13.2° (*c* 1.0, acetone); IR (KBr) 1050; ^1H NMR δ 1.31 (3 H, d, *J* = 6 Hz), 2.39 (3 H, s), 3.00, 3.04 (each 1 H, d, *J* = 16 Hz), 3.74 (1 H, q, *J* = 6 Hz), 6.8–7.6 (9 H, m). Anal. Calcd for $C_{17}H_{18}O_2S$: C, 70.98; H, 6.36; S, 11.06. Found: C, 71.30; H, 6.34; S, 11.19 **28**: colorless oil: 50% overall yield; $[\alpha]^{25}_D$ +13.4° (*c* 1.0, acetone); IR (neat) 1090, 1060; ^1H NMR δ 1.64 (3 H, d, *J* = 6 Hz), 2.45 (3 H, s), 2.58 (1 H, d, *J* = 15 Hz), 2.75 (1 H, q, *J* = 6 Hz), 3.50 (1 H, d, *J* = 15 Hz), 6.8–7.8 (9 H, m); MS, *m/z* (relative intensity) 286 (M^+, 14), 178 (5), 140 (62), 91 (100). Found: *m/z* 286.1033. Calcd for $C_{17}H_{18}O_2S$: M, 286.1027.

α-Amino Ketones 29 and 30. A solution of **7** (99 mg; 0.23 mmol) in 2 mL of piperidine was heated at 100 °C under N_2 for 4 h. The piperidine was evaporated under vacuum to give a residue, which was purified by silica gel column chromatography to give colorless crystals (72 mg; mp 62–65 °C). This product was treated with 3 equiv of TBAF in 1 mL of THF at room temperature for 2 h. The usual workup followed by silica gel column chromatography afforded **29** in 72% overall yield as a colorless oil: $[\alpha]^{25}_D$ −6.0° (*c* 0.5, EtOH); IR (neat) 3450, 1710, 1030; ^1H NMR δ 1.19 (3 H, s), 1.3–1.8 (6 H, m), 2.3–2.7 (4 H, m), 3.55, 3.85 (each 1 H, d, *J* = 12 Hz), 3.96 (2 H, s), 7.0–7.4 (5 H, m). The enantiomeric purity of **29** was measured to be 86% from the 500-MHz ^1H NMR of its (−)-MTPA ester. The methylene H at the carbon bearing acyloxy group showed δ 3.77 (d, *J* = 16 Hz) and δ 4.00 (d, *J* = 16 Hz). MS: *m/z* (relative intensity) 230 ($[M - CH_2OH]^+$, 3), 142 (100), 112 (85).

30: colorless oil; 80% overall yield; $[\alpha]^{25}_D$ +6.0° (*c* 1.2, EtOH). The enantiomeric purity of **30** was measurd to be 93% from the 500-MHz ^1H NMR of its (−)-MTPA ester. The methylene H at the carbon bearing acyloxy group showed δ 3.87 (d, *J* = 17 Hz) and δ 3.97 (d, *J* = 17 Hz).

α-Amino Aldehydes 31 and 32. A solution of α,β-epoxy sulfoxide **25** (68 mg; 0.2 mmol) in 1 mL of piperidine was stirred at room temperature for 1 day. The piperidine was evaporated, and the residue was purified by silica gel column chromatography to give 55 mg (96%) of **31** as a colorless oil: $[\alpha]^{25}_D$ +5.09° (*c* 1.9, acetone); IR (neat) 1750, 1740, (CO); ^1H NMR δ 0.03 (6 H, s), 0.86 (9 H, s), 1.07 (3 H, s), 1.50 (6 H, m), 2.46 (4 H, m), 3.70, 3.86 (each 1 H, d, *J* = 10 Hz), 9.36 (1 H, s); MS, *m/z* (relative intensity) 285 (M^+, 1), 257 (21), 256 (100). Found: *m/z* 285.2122. Calcd for $C_{15}H_{31}NO_2Si$: M, 285.2122.

32: colorless oil: 98% yield; $[\alpha]^{25}_D$ −5.06° (*c* 1.7, acetone). The enantiomeric purity of **31** and **32** was measured to be 97% from 500-MHz ^1H NMR with 75 mol % (+)-Eu(hfc)$_3$. The *tert*-butyl group of **31** and **32** showed δ 1.18 and δ 1.12, respectively.

α-Anilino Aldehydes 33 and 34. A solution of **25** (46 mg) in 1 mL of aniline was stirred at room temperature for 2 days. The aniline was evaporated under vacuum, and the residue was purified by silica gel column chromatography eluted with benzene to give 38 mg (95%) of **33** as a colorless oil: $[\alpha]^{25}_D$ +36.1° (*c* 1.8, acetone); IR (neat) 3425 (NH), 1735 (CO); ^1H NMR δ 0.00, 0.03 (each 3 H, s), 0.88 (9 H, s), 1.37 (3 H, s), 3.62, 3.79 (each 1 H, d, *J* = 10 Hz), 6.5–7.2 (5 H, m), 9.72 (1 H, s); MS, *m/z* (relative intensity) 293 (M^+, 6) 264 (100). Found: *m/z* 293.1818. Calcd for $C_{16}H_{27}NO_2Si$: M, 293.1809.

34: colorless oil: 98% yield; $[\alpha]^{25}_D$ −35.8° (*c* 1.9, acetone). The enantiomeric purity of **33** and **34** was measured to be 97% from ^1H NMR with 50 mol % (+)-Eu(hfc)$_3$. The methyl H at the chiral center of **33** and **34** showed δ 2.63 and δ 2.40, respectively.

α-Amino Ketone 35. The reactions of the α,β-epoxy sulfoxides **27** and **28** with piperidine gave racemic **35**[5c] in 95% and 99% yields, respectively. The products showed no optical activity. With 25 mol % of (+)-Eu(hfc)$_3$, the methyl H of racemic **35** showed δ 2.25 (d, *J* = 7 Hz) and δ 2.40 (d, *J* = 7 Hz), respectively.

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