

First Highly Asymmetric Pummerer-type Reaction in Chiral, Non-racemic Acyclic Sulfoxides Induced by *O*-Silylated Ketene Acetal

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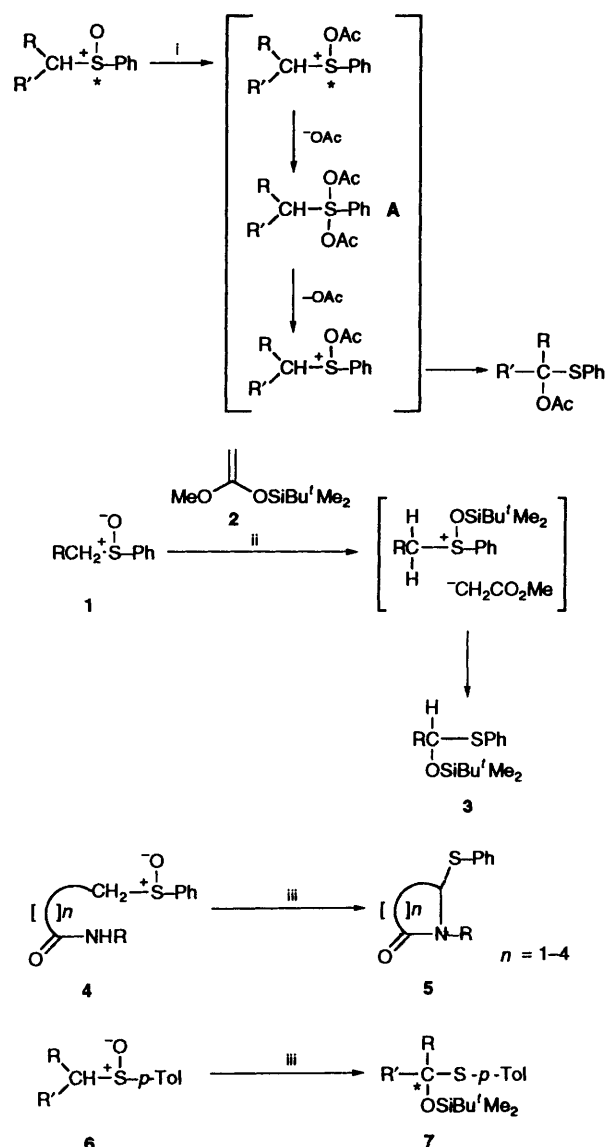
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Various types of *syn*- and *anti*- β -substituted sulfoxides **6b–e, g** reacted with ketene *tert*-butyldimethylsilyl acetal **2** in the presence of a catalytic amount of zinc iodide in acetonitrile to give high yields of the corresponding α -siloxy sulfides **7b–e, g** stereoselectively. Similarly, chiral, non-racemic sulfoxides **6a, f, h, i** reacted with acetal **2** in acetonitrile to give the chiral, non-racemic α -siloxy sulfides **7a, f, h, i** in high yields.

The Pummerer reaction of sulfoxides is a useful method for the synthesis of α -substituted sulfides¹ and has attracted considerable attention from both synthetic and mechanistic points of view.² The stereoselective Pummerer reaction of optically active sulfoxides is a self-immolative asymmetric transformation³ and is of considerable interest, because it would provide a means for the synthesis of chiral, non-racemic α -substituted sulfides.[†] In fact, the stereogenicity transfer from the sulfur of chiral, non-racemic sulfoxides to the carbon α to the sulfur in the sulfides has been reported^{4b–e,5} in recent investigations. The yields in enantiomeric excess (ee), however, were quite low in acyclic sulfoxides^{4b–e,g,h} probably due to the formation of the sulfurane intermediate **A** by reaction of the generated acetate anion. Several years ago, we reported⁶ a novel silicon-induced Pummerer-type reaction of sulfoxides **1** by using ketene *tert*-butyldimethylsilyl methyl acetal **2**, which gave α -siloxy sulfides **3** under mild conditions, and applied this method to novel and effective intramolecular Pummerer-type cyclizations of ω -amido sulfoxides **4** to afford sulfanyl-N- α -heterocycles **5** involving 4-to-7-membered α -sulfanyl lactams (Scheme 1).⁷ Very recently, we briefly communicated⁸ the first highly asymmetric transformation of chiral, non-racemic acyclic sulfoxides **6** leading to enantiomerically enriched α -siloxy sulfides **7** in high yields using our silicon-induced Pummerer-type reaction.[‡] In this paper, we report the generality of a highly stereoselective Pummerer-type reaction in various types of acyclic sulfoxides using *O*-silylated ketene acetal **2** in detail.

Results and Discussion

A typical experimental procedure is as follows for the reaction of sulfoxide *syn*-**6a** with siloxy compound **2**. A solution of reagents *syn*-**6a** and **2** and a catalytic amount of zinc iodide in dry acetonitrile was stirred at 0 °C for 1 h and then at room temperature for 1 h, followed by the usual work-up, to give (1*S*, 2*S*)-1,2-bis-(*tert*-butyldimethylsiloxy)-2-phenethyl 4-methylphenyl sulfide (*syn*-**7a** and *anti*-**7a**) in the ratio 88:12 in 75% yield (entry 1, Table 1). Similarly, various types of *syn* and *anti* β -substituted sulfoxides **6b–g** reacted with compound **2** in the presence of a catalytic amount of zinc iodide in acetonitrile under nearly the same conditions to give high yields of the corresponding α -siloxy sulfides **7b–g**. The relative stereochem-



Scheme 1 Reagents: i, Ac₂O; ii, **2**, MeCN; iii, **2**

[†] Although an unusually high asymmetric induction (70% ee) in the Pummerer reaction was achieved by the presence of dicyclohexylcarbodiimide as an effective scavenger of the generated acetic acid,^{4e} the chemical yield was quite low (10%).

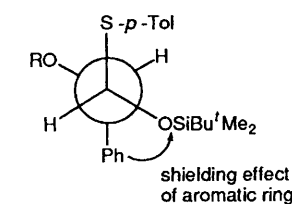
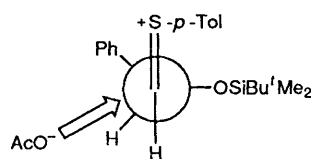
[‡] Other silicon-induced Pummerer-type reactions were reported using silylating reagents such as iodotrimethylsilane,^{9a} chlorotrimethylsilane,^{9a} and trialkyl triflate.^{9b}

ical ratio (*syn*:*anti*) of the diastereoisomeric α -siloxy sulfides was determined by Heathcock's method using ¹H NMR spectra. According to the definition, the molecules exist predominantly in conformations having the two hydrogens *anti* and the aryl group causes an upfield shift of the ¹H NMR resonance of the group *gauche* to it on the vicinal stereocentre.

Table 1 Asymmetric silicon-induced Pummerer-type reactions

Entry	Sulfoxide ^a	R ¹	R ²	Conditions ^d	Yield (%)	syn:anti
1	syn-6a ^b	Ph	OSiBu ^t Me ₂	0 °C, 1 h-r.t., 1 h	75	88:12
2	anti-6a ^b	Ph	OSiBu ^t Me ₂	0 °C, 4 h-r.t., 3 h	82	4:96
3	syn-6b	Ph	OSiMe ₃	0 °C, 4 h	62	87:13
4	anti-6b	Ph	OSiMe ₃	0 °C, 4 h	66	3:97
5	syn-6c	Ph	OSiBu ^t Ph ₂	r.t., 4 h	85	95:5
6	anti-6c	Ph	OSiBu ^t Ph ₂	0 °C, 4 h	74	1:99
7	syn-6d	Ph	NHAc	r.t., overnight	93	77:23
8	anti-6d	Ph	NHAc	r.t., overnight	76	5:95
9	syn-6e	Ph	NHCH ₂ Ph	r.t., overnight	69	92:8
10	anti-6e	Ph	NHCH ₂ Ph	r.t., overnight	60	15:85
11	syn-6f ^{b,c}	Ph	Me	r.t., overnight	45	90:10
12	anti-6f ^{b,c}	Ph	Me	r.t., overnight	56	24:76
13	syn-6g	Me	OSiBu ^t Me ₂	0 °C, 2 h	71	88:12
14	anti-6g	Me	OSiBu ^t Me ₂	r.t., 3 h	70	<1:99

^a Racemic sulfoxides were used except for entries 1, 2, 11 and 12. ^b Optically active sulfoxides were used. ^c The configuration of the phenylethyl carbon of compound **6f**, which was prepared from α -lithio (*S*)-methyl *p*-tolyl sulfoxide and phenylethyl bromide, was determined from the conversion into the known aldehyde ¹¹ using the reported method.¹² ^d r.t. = room temperature.

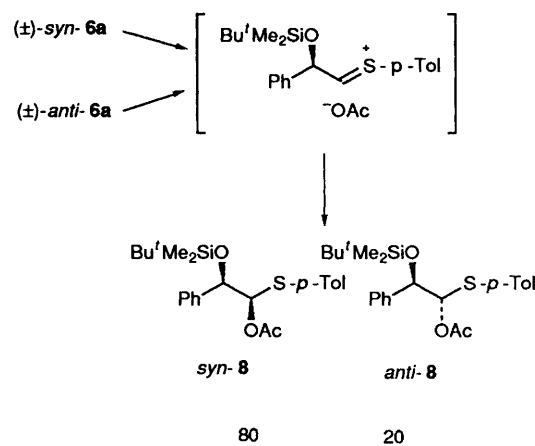
**Fig. 1****Fig. 2**

Therefore, the resonance of the *tert*-butyl group of *anti*-isomers occurs at a substantially higher field than does that of the *syn*-isomers¹⁰ (Fig. 1).

The results are summarized in Table 1.

All reactions proceeded under mild conditions with a remarkably high degree of stereospecificity. We were surprised to find that extremely high retention occurred in all β -siloxy-, β -acylamino-, β -alkylamino-, β -alkyl- and β -aryl- substituted sulfoxides and, of course, in both racemic (entries 3–10, 13 and 14) and non-racemic sulfoxides (entries 1, 2, 11 and 12). Contrary to these findings, a normal Pummerer reaction of both *syn*- and *anti*-**6a** with hot acetic anhydride gave the same 80:20 ratio of diastereoisomeric acetoxy sulfides **8** (Scheme 2). The predominant formation of the *syn*-isomer is predicted by the following Felkin–Anh model of the well documented^{10a} thionium ion intermediate (Fig. 2).

In order to ascertain the effect of the sulfoxide itself, we next examined the reaction of sulfoxides **6h**, **6i**, having one stereo-

**Scheme 2**

genic centre on the sulfur atom, with the silyl ether **2**. Known chiral, non-racemic sulfoxides **6h** and **6i**^{4g} were treated with compound **2** in the absence of a catalyst in acetonitrile to give the corresponding chiral, non-racemic α -siloxy sulfides **7h** and **7i**. In both cases, the optical purity and chemical yield of the Pummerer adducts were greater than those of Oae's approach^{4e,g} (Table 2).

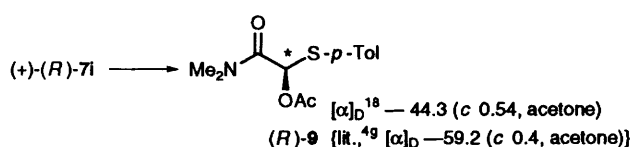
The stereochemistry of the newly generated stereogenic centre of compound **7i** was determined by conversion into a known derivative: treatment of compound **7i** with acetyl chloride in the presence of a catalytic amount of FeCl₃ in dry acetonitrile at room temperature for 1 h gave the (+)- α -acyloxy sulfide (*R*)-**9**, identical with the known sulfide^{4g,13} (Scheme 3).

Although details of the mechanism remain unknown, the asymmetric transformation of chiral, non-racemic sulfoxides is explained as follows: silylation of sulfoxides with compound **2** affords an intermediate **B**, which may yield an anion

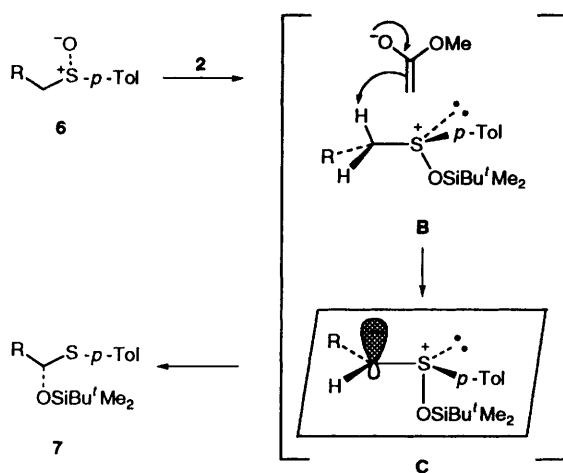
Table 2 Asymmetric silicon-induced Pummerer-type reactions

$\text{R}-\text{CH}_2-\overset{\text{O}}{\underset{\cdot}{\text{S}}}-\text{p-Tol} \xrightarrow[60-65^\circ\text{C, MeCN}]{2} \text{R}-\overset{\text{OSiBu}^t\text{Me}_2}{\underset{\cdot}{\text{CH}}}-\text{S}-\text{p-Tol}$						
6h, I			7h, I			
Sulfoxide ^a	R	Conditions	% ee ^b (% Yield ^c)	$[\alpha]_D^{18}$ (c, acetone)	Configuration	Oae's approach ^d % ee (% Yield)
(S)-6h	CO ₂ Et	4 h	87 (75)	+ 35.8 (0.46)	<i>S'</i>	70 (10)
(R)-6h	CO ₂ Et	4 h	86 ^e (72)	- 34.8 (0.67)	<i>R'</i>	
(S)-6i	CONMe ₂	12 h	88 (65)	- 28.9 (1.40)	<i>S</i>	65 (35)
(R)-6i	CONMe ₂	12 h	88 ^e (69)	+ 28.8 (1.23)	<i>R</i>	

^a (S)-6h: $[\alpha]_D^{20} - 189$ (c 1.80, acetone); (R)-6h: $[\alpha]_D^{20} + 195$ (c 0.97, acetone); (S)-6i: $[\alpha]_D^{19} - 187$ (c 1.24, acetone); (R)-6i: $[\alpha]_D^{18} + 192$ (c 0.83, acetone). ^b Determined by ¹H NMR spectroscopy with Eu(hfc)₃. ^c Isolated yield. ^d See reference 4 e.g. ^e ee-Value was calculated on the basis of the other ee-values determined with the shift reagent. ^f The stereochemistry of compound 7h was tentatively assigned based on the similarity of the shift patterns in the ¹H NMR spectra by addition of Eu(hfc)₃ to those of compound 7i.

**Scheme 3** Reagents and conditions: AcCl, FeCl₃ (cat.), MeCN, room temp., 1 h (64%)

intermediate **C** through abstraction of the *anti*-periplanar hydrogen with a generated ester enolate from the opposite face of the sulfoxide oxygen (Scheme 4).¹⁴ Then the siloxy group

**Scheme 4**

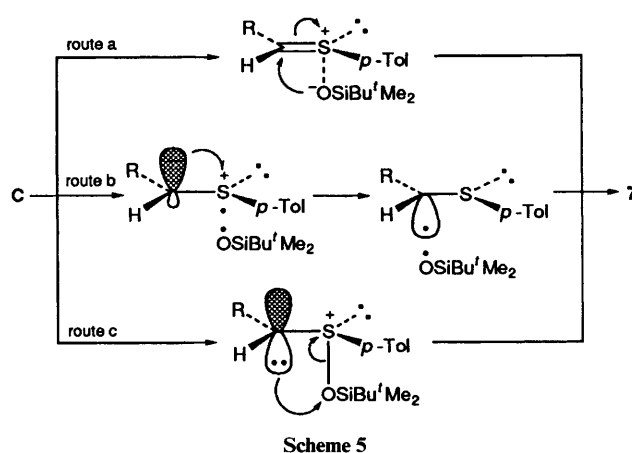
may be forced to migrate to the α -position *via* one of the following three mechanisms; (i) intimate ion-pair mechanism (route a), (ii) radical dissociation-recombination mechanism (route b),^{*,15} and direct carbanion attack (route c)[†] (Scheme 4, 5).

Experimental

All m.p.s were determined on a Yanaco micro melting apparatus and are uncorrected. IR absorption spectra were recorded on JASCO HPIR-102 and Shimadzu FTIR-8100 spectrophotometers with CHCl₃ as solvent. ¹H NMR spectra were measured on JEOL JNM-FX90Q (90 MHz), JEOL JNM-EX270 (270 MHz) and JEOL JNM-GX500 (500 MHz)

* A similar mechanism involving homolysis of the α -anion intermediate, followed by recombination of the radical and radical anion fragments, is proposed in the Wittig rearrangement.

† This mechanism was suggested by a reviewer.

**Scheme 5**

spectrometers with CDCl₃ as solvent with tetramethylsilane as internal standard unless otherwise noted. *J*-Values are given in Hz. Mass spectra (MS) and high-resolution MS were obtained by ESCO EMD-05A and JEOL JMS-D300 mass spectrometers. Optical rotations were measured in 1 dm cells of 1 cm³ capacity with a Perkin-Elmer 241 instrument; $[\alpha]_D$ -values are given in units of 10⁻¹ deg cm² g⁻¹. E. Merck silica gel 60 (70–230 mesh ASTM) for column chromatography and E. Merck precoated TLC plates with silica gel F₂₅₄ for preparative TLC (PLC) were used. Organic layers were dried with anhydrous Na₂SO₄. The known sulfoxides 6d,¹⁶ 6h,^{4g} and 6i^{4g} were prepared by the reported method, and other starting sulfoxides were prepared by the same procedure as those reported methods.^{16,17}

(S_S)-[(2S)-2-(*tert*-Butyldimethylsiloxy)-2-phenylethyl] 4-Methylphenyl Sulfoxide syn-6a. —(S_S,1*S*)-2-[(4-methylphenyl)sulfinyl]-1-phenylethanol (379 mg, 1.46 mmol), *tert*-butyldimethylsilyl chloride (440 mg, 2.92 mmol), 4-(dimethylamino)pyridine (DMAP) (712 mg, 5.84 mmol) and dimethylformamide (DMF) (7 cm³) gave compound syn-6a (510 mg, 93%) as an oil; $[\alpha]_D^{24} - 64.8$ (c 1.24, CHCl₃); $\delta_H - 0.19$ and 0.04 (each 3 H, each s, Me₂Si), 0.86 (9 H, s, Bu^t), 2.41 (3 H, s, Me), 2.94 (1 H, dd, *J* 7.26 and 12.9, 1-H^a), 3.38 (1 H, dd, *J* 6.60 and 12.9, 1-H^b), 4.98 (1 H, dd, *J* 6.60 and 7.26, 2-H) and 7.26–7.51 (9 H, m, ArH); *m/z* 317 (M⁺ – Bu^t) [Found: (M⁺ – Bu^t), 317.1056. C₁₇H₂₁O₂Si requires *m/z*, 317.1031].

(S_S)-[(2R)-2-(*tert*-Butyldimethylsiloxy)-2-phenylethyl] 4-Methylphenyl Sulfoxide anti-6a. —(S_S,1*R*)-2-[(4-methylphenyl)sulfinyl]-1-phenylethanol (98.4 mg, 0.378 mmol), *tert*-butyldimethylsilyl chloride (114.3 mg, 0.757 mmol), DMAP (185 mg, 1.51 mmol) and DMF (2.5 cm³) gave compound anti-6a (112

mg, 79%) as an oil; $[\alpha]_D^{24} - 335$ (c 0.74, CHCl_3); $\delta_{\text{H}} - 0.08$ and 0.19 (each 3 H, each s, Me_2Si), 0.95 (9 H, s, Bu^t), 2.41 (3 H, s, Me), 2.87 (1 H, dd, J 2.74 and 12.8, 1- H^a), 2.94 (1 H, dd, J 10.1 and 12.8, 1- H^b), 5.27 (1 H, dd, J 2.74 and 10.1, 2-H) and 7.20 – 7.53 (9 H, m, ArH); m/z 317 ($\text{M}^+ - \text{Bu}^t$) [Found: ($\text{M}^+ - \text{Bu}^t$), 317.1060].

(S_5^*)-[(2 S^*)-2-(*tert*-Butyldiphenylsiloxy)-2-phenylethyl] 4-Methylphenyl Sulfoxide syn-**6c**.—(S_5^* , 1 S^*)-2-[(4-methylphenyl)sulfinyl]-1-phenylethanol (100 mg, 0.384 mmol), *tert*-butyldiphenylsilyl chloride (0.15 cm^3 , 0.576 mmol), imidazole (41.8 mg, 0.615 mmol) and DMF (2 cm^3) gave compound syn-**6c** (183 mg, 96%) as an oil; $\delta_{\text{H}} 1.03$ (9 H, s, Bu^t), 2.37 (3 H, s, Me), 2.91 (1 H, dd, J 7.92 and 12.9, 1- H^a), 3.34 (1 H, dd, J 5.61 and 12.9, 1- H^b), 5.04 (1 H, dd, J 5.61 and 7.92, 2-H) and 7.19 – 7.81 (19 H, m, ArH); m/z 441 ($\text{M}^+ - \text{Bu}^t$) [Found: ($\text{M}^+ - \text{Bu}^t$), 441.1340]. $\text{C}_{27}\text{H}_{25}\text{O}_2\text{SSi}$ requires m/z , 441.1342].

(S_5^*)-[(2 R^*)-2-(*tert*-Butyldiphenylsiloxy)-2-phenylethyl] 4-Methylphenyl Sulfoxide anti-**6c**.—(S_5^* , 1 R^*)-2-[(4-methylphenyl)sulfinyl]-1-phenylethanol (100 mg, 0.384 mmol), *tert*-butyldiphenylsilyl chloride (0.15 cm^3 , 0.576 mmol), imidazole (41.8 mg, 0.615 mmol) and DMF (2 cm^3) gave compound anti-**6c** (169 mg, 88%) as an oil; $\delta_{\text{H}} 1.10$ (9 H, s, Bu^t), 2.37 (3 H, s, Me), 2.94 (1 H, dd, J 2.97 and 13.2, 1- H^a), 3.14 (1 H, dd, J 9.57 and 13.2, 1- H^b), 5.21 (1 H, dd, J 2.97 and 9.57, 2-H) and 7.05 – 7.70 (19 H, m, ArH); m/z 498 (M^+) (Found: M^+ , 498.2038). $\text{C}_{31}\text{H}_{34}\text{O}_2\text{SSi}$ requires M , 498.2046.

(S_5^* , 1 S^*)-*N*-Benzyl-2-[(4-methylphenyl)sulfinyl]-1-phenylethylamine syn-**6e**.—(S_5^* , 1 S^*)-2-[(4-methylphenyl)sulfinyl]-1-phenylethylamine (200 mg, 0.771 mmol), benzaldehyde (0.078 cm^3 , 0.771 mmol), CH_2Cl_2 (4 cm^3), sodium boranuide (116.7 mg, 3.08 mmol) and MeOH (4 cm^3) gave compound syn-**6e** (242 mg, 90%) as an oil; $\delta_{\text{H}} 2.39$ (3 H, s, Me), 2.82 (1 H, dd, J 4.95 and 13.2, 2- H^a), 3.24 (1 H, dd, J 8.57 and 13.2, 2- H^b), 3.51 and 3.67 (each 1 H, each d, J 13.2, PhCH_2), 4.19 (1 H, dd, J 4.95 and 8.57, 1-H) and 7.21 – 7.47 (14 H, m, ArH).

(S_5^* , 1 R^*)-*N*-Benzyl-2-[(4-methylphenyl)sulfinyl]-1-phenylethylamine anti-**6e**.—(S_5^* , 1 R^*)-2-[(4-methylphenyl)sulfinyl]-1-phenylethylamine (200 mg, 0.771 mmol), benzaldehyde (0.078 cm^3 , 0.771 mmol), CH_2Cl_2 (4 cm^3), sodium boranuide (116.7 mg, 3.08 mmol) and MeOH (4 cm^3) gave compound anti-**6e** (228 mg, 84%) as an oil; $\delta_{\text{H}} 2.39$ (3 H, s, Me), 2.91 (1 H, dd, J 2.97 and 13.5, 2- H^a), 3.06 (1 H, dd, J 10.6 and 13.5, 2- H^b), 3.59 and 3.69 (each 1 H, each d, J 13.2, PhCH_2), 4.22 (1 H, dd, J 2.97 and 10.6, 1-H) and 7.24 – 7.47 (14 H, m, ArH).

(S_5)-4-Methylphenyl (2 S)-2-Phenylpropyl Sulfoxide syn-**6f** and (S_5)-4-Methylphenyl (2 R)-2-Phenylpropyl Sulfoxide anti-**6f**.—To a solution of (*S*)-methyl *p*-tolyl sulfoxide (2.08 g, 13.5 mmol) in tetrahydrofuran (THF) (10 cm^3) was added a solution of lithium diisopropylamide (LDA) [prepared from diisopropylamine (2.4 cm^3 , 17.1 mmol) and a 1.6 mol dm^{-3} solution of butyllithium in hexane (10.6 cm^3 , 17.0 mmol)] in THF (40 cm^3). The mixture was cooled to -78°C dropwise under nitrogen, stirred for 30 min at -78°C , and α -phenylethyl bromide (3.6 g, 19.5 mmol) was then added to the mixture. After 30 min, the reaction mixture was then quenched with saturated aq. NH_4Cl , then was extracted with CH_2Cl_2 . The extract was washed with brine, dried, and concentrated under reduced pressure. The residue was purified by column chromatography with 50–100% AcOEt in hexane to give title compound **6f** (3.69 g, 100%) as crystals, which were repurified by HPLC and recrystallized to give pure samples of each diastereoisomer: syn-**6f** (92% de): crystals; m.p. 89 – 91°C (from CH_2Cl_2 –hexane); $[\alpha]_D^{23} - 129$ (c 1.08, CHCl_3); $\nu_{\text{max}}/\text{cm}^{-1}$ 3000, 1600, 1495, 1086

and 1053; $\delta_{\text{H}} 1.40$ (3 H, d, J 7.3, 2-Me), 2.40 (3 H, s, Me), 2.88 (1 H, dd, J 9.6 and 12.9, 1- H^a), 3.07 (1 H, dd, J 5.3 and 12.9, 1- H^b), 3.39 (1 H, m, 2-H) and 7.24 – 7.56 (9 H, m, ArH); m/z 258 (M^+) (Found: M^+ , 258.1063). $\text{C}_{16}\text{H}_{18}\text{OS}$ requires M , 258.1076; anti-**6f** (93% de): crystals; m.p. 95 – 98°C (from CH_2Cl_2 –hexane); $[\alpha]_D^{23} - 176$ (c 1.06, CHCl_3); $\nu_{\text{max}}/\text{cm}^{-1}$ 3000, 1600, 1495, 1086 and 1053; $\delta_{\text{H}} 1.52$ (3 H, d, J 6.9, 2-Me), 2.40 (3 H, s, Me), 2.79 (1 H, dd, J 10.5 and 12.9, 1- H^a), 3.12 (1 H, dd, J 4.6 and 12.9, 1- H^b), 3.32 (1 H, m, 2-H) and 7.18 – 7.53 (9 H, m, ArH); m/z 258 (M^+) (Found: M^+ , 258.1096; C, 74.2; H, 7.05; S, 12.45. $\text{C}_{16}\text{H}_{18}\text{OS}$ requires C, 74.35; H, 7.05; S, 12.40%).

(S_5^*)-[(2 S^*)-2-(*tert*-Butyldimethylsiloxy)propyl] 4-Methylphenyl Sulfoxide syn-**6g**.—(S_5^* , 2 S^*)-1-[(4-methylphenyl)sulfinyl]propan-2-ol (1.15 g, 5.82 mmol), *tert*-butyldimethylsilyl chloride (2.06 g, 13.6 mmol), DMAP (3.33 g, 27.3 mmol) and DMF (18 cm^3) gave compound syn-**6g** (1.42 g, 78%) as an oil; $\delta_{\text{H}} - 0.02$ and 0.00 (each 3 H, each s, Me_2Si), 0.81 (9 H, s, Bu^t), 1.32 (3 H, d, J 6.27, 3- H_3), 2.35 (3 H, s, Me), 2.68 (1 H, dd, J 7.59 and 12.9, 1- H^a), 2.99 (1 H, dd, J 4.95 and 12.9, 1- H^b), 4.09 (1 H, m, 2-H) and 7.26 and 7.59 (each 2 H, each d, J 7.59, ArH); m/z 312 (M^+) (Found: M^+ , 312.1567). $\text{C}_{16}\text{H}_{28}\text{O}_2\text{SSi}$ requires M , 312.1577.

(S_5^*)-[(2 R^*)-2-(*tert*-Butyldimethylsiloxy)propyl] 4-Methylphenyl Sulfoxide anti-**6g**.—(S_5^* , 2 R^*)-1-[(4-methylphenyl)sulfinyl]propan-2-ol (380 mg, 1.92 mmol), *tert*-butyldimethylsilyl chloride (580 mg, 3.83 mmol), DMAP (937 mg, 7.68 mmol) and DMF (10 cm^3) gave compound anti-**6g** (587 mg, 98%) as an oil; $\delta_{\text{H}} 0.13$ and 0.20 (each 3 H, each s, Me_2Si), 0.94 (9 H, s, Bu^t), 1.23 (3 H, d, J 6.27, 3- H_3), 2.40 (3 H, s, Me), 2.70 (1 H, dd, J 9.24 and 12.9, 1- H^a), 2.78 (1 H, dd, J 3.30 and 12.9, 1- H^b), 4.41 (1 H, m, 2-H) and 7.30 and 7.50 (each 2 H, each d, J 8.25, ArH); m/z 312 (M^+) (Found: M^+ , 312.1581).

General Procedure for the Pummerer-type Reaction of α -Silylated Ketene Acetal 2 with Sulfoxides 6a, 6c–g.—To a stirred solution of a sulfoxide **6** (0.100 mmol) and ZnI_2 (0.01–0.02 mmol) in dry MeCN (3 cm^3) was added dropwise ketene *tert*-butyldimethylsilyl methyl acetal **2** (0.500–1.00 mmol) at the temperature indicated in Table 1 for 2–12 h under nitrogen. The mixture was then poured into saturated aq. sodium hydrogen carbonate and repeatedly extracted with methylene dichloride. The organic layer was washed with brine, dried, and evaporated. The residue was purified by PLC to give the corresponding α -siloxy sulfide **7** in yields between 45 and 93%.

(1 S ,2 S)-1,2-Bis-(*tert*-butyldimethylsiloxy)-2-phenylethyl 4-Methylphenyl Sulfide syn-**7a**.—syn-**6a** $\{[\alpha]_D^{24} - 64.8$ (c 1.24, CHCl_3), 48.0 mg, 0.128 mmol}, the acetal **2** (120 mg, 0.642 mmol), ZnI_2 (4.1 mg, 0.0128 mmol) and MeCN (2 cm^3) gave compound **7a** (syn:anti 88:12; 45.3 mg, 75%). Compound syn-**7a** was isolated in a pure state by column chromatography, oil; $[\alpha]_D^{24} - 17.5$ (c 1.16, CHCl_3); $\nu_{\text{max}}/\text{cm}^{-1}$ 2920 and 1495; $\delta_{\text{H}} - 0.08$ (9 H, s, Me_3Si), 0.07 (3 H, s, MeSi), 0.89 and 0.91 (each 9 H, each s, $2 \times \text{Bu}^t$), 2.32 (3 H, s, Me), 4.87 and 5.11 (each 1 H, each d, J 4.3, 1- and 2-H) and 7.05 – 7.64 (9 H, m, ArH); m/z 488 (M^+) (Found: M^+ , 488.2594; C, 66.35; H, 8.95; S, 6.35%. $\text{C}_{27}\text{H}_{44}\text{O}_2\text{SSi}_2$ requires M , 488.2597; C, 66.30; H, 9.10; S, 6.55%).

(1 S ,2 R)-1,2-Bis-(*tert*-butyldimethylsiloxy)-2-phenylethyl 4-Methylphenyl Sulfide anti-**7a**.—anti-**6a** $\{[\alpha]_D^{24} - 335$ (c 0.74, CHCl_3), 39.3 mg, 0.105 mmol}, the acetal **2** (98.8 mg, 0.525 mmol), ZnI_2 (3.3 mg, 0.0105 mmol) and MeCN (2 cm^3) gave compound **7a** (syn:anti 4:96; 40.7 mg, 82%). Diastereoisomer anti-**7a** was isolated in a pure state by column chromatography, oil; $[\alpha]_D^{24} - 7.4$ (c 1.75, CHCl_3); $\nu_{\text{max}}/\text{cm}^{-1}$ 2940 and 1495;

δ_{H} –0.31, –0.20, –0.10 and –0.01 (each 3 H, each s, 2 \times Me₂Si), 0.72 and 0.86 (each 9 H, each s, 2 \times Bu'), 2.32 (3 H, s, Me), 4.74 and 5.02 (each 1 H, each d, *J* 5.9, 1- and 2-H) and 7.06–7.41 (9 H, m, ArH); *m/z* 488 (*M*⁺) (Found: *M*⁺, 488.2603).

(1*S**,2*S**)-1-(tert-Butyldimethylsiloxy)-2-(tert-butylphenylsiloxy)-2-phenylethyl 4-Methylphenyl Sulfide syn-7c.—Compound syn-6c (43.3 mg, 0.087 mmol), the acetal 2 (81.8 mg, 0.435 mmol), ZnI₂ (2.7 mg, 0.0087 mmol) and MeCN (3 cm³) gave product 7c (*syn:anti* 95:5; 44.0 mg, 85%). Diastereoisomer syn-7c was isolated in a pure state by column chromatography, oil; $\nu_{\text{max}}/\text{cm}^{-1}$ 2910 and 1495; δ_{H} –0.48 and 0.44 (each 3 H, each s, Me₂Si), 0.74 and 1.08 (each 9 H, each s, 2 \times Bu'), 2.28 (3 H, s, Me), 4.91 and 4.96 (each 1 H, each d, *J* 4.3, 1- and 2-H) and 7.15–7.82 (19 H, m, ArH); *m/z* 612 (*M*⁺) (Found: *M*⁺, 612.2915). C₃₇H₄₈O₂SSi₂ requires *M*, 612.2913).

(1*S**,2*R**)-1-(tert-Butyldimethylsiloxy)-2-(tert-butylphenylsiloxy)-2-phenylethyl 4-Methylphenyl Sulfide anti-7c.—Compound anti-6c (38.5 mg, 0.077 mmol), the acetal 2 (72.7 mg, 0.387 mmol), ZnI₂ (2.5 mg, 0.0077 mmol) and MeCN (3 cm³) gave compound 7c (*syn:anti* 1:99; 34.0 mg, 74%). Diastereoisomer anti-7c was isolated in a pure state by column chromatography, oil; $\nu_{\text{max}}/\text{cm}^{-1}$ 2910 and 1495; δ_{H} –0.22 and –0.15 (each 3 H, each s, Me₂Si), 0.73 and 1.02 (each 9 H, each s, 2 \times Bu'), 2.30 (3 H, s, Me), 4.86 and 5.13 (each 1 H, each d, *J* 4.0, 1- and 2-H) and 6.94–7.71 (19 H, m, ArH); *m/z* 612 (*M*⁺) (Found: *M*⁺, 612.2911; C, 72.55; H, 7.90; S, 5.35%. C₃₇H₄₈O₂SSi₂ requires *M*, 612.2911; C, 72.50; H, 7.90; S, 5.25%).

(1*S**,2*S**)-N-Acetyl-2-(tert-butylphenylsiloxy)-2-[(4-methylphenyl)sulfanyl]-1-phenylethylamine syn-7d.—Compound syn-6d (29.6 mg, 0.098 mmol), the acetal 2 (185 mg, 0.983 mmol), ZnI₂ (5.5 mg, 0.0098 mmol) and MeCN (1 cm³) gave compound 7d (*syn:anti* 77:23; 38.1 mg, 93%). Compound syn-7d was isolated in a pure state by column chromatography, crystals; m.p. 91–93 °C (from CH₂Cl₂–hexane); $\nu_{\text{max}}/\text{cm}^{-1}$ 3441, 3009, 1674 and 1550; δ_{H} –0.32 and –0.04 (total 6 H, each s, Me₂Si), 0.80 (9 H, s, Bu'), 2.08 (3 H, s, OAc), 2.36 (3 H, s, Me), 5.13 (1 H, d, *J* 2.0, 2-H), 5.20 (1 H, dd, *J* 2.0 and 8.2, 1-H), 6.36 (1 H, d, *J* 8.2, NH) and 7.10–7.64 (9 H, m, ArH); *m/z* 358 (*M*⁺) (Found: *M*⁺, 358.1294). C₂₃H₃₃NO₂SSi requires *M*, 358.1294).

(1*R**,2*S**)-N-Acetyl-2-(tert-butylphenylsiloxy)-2-[(4-methylphenyl)sulfanyl]-1-phenylethylamine anti-7d.—Compound anti-6d (28.9 mg, 0.096 mmol), the acetal 2 (90.2 mg, 0.48 mmol), ZnI₂ (3.1 mg, 0.0096 mmol) and MeCN (1 cm³) gave compound 7d (*syn:anti* 5:95; 37.6 mg, 76%). Diastereoisomer anti-7d was isolated in a pure state by column chromatography, crystals; m.p. 133–135 °C (from CH₂Cl₂–hexane); $\nu_{\text{max}}/\text{cm}^{-1}$ 3447, 3011, 1674 and 1493; δ_{H} –0.076 and –0.05 (total 6 H, each s, Me₂Si), 0.88 (9 H, s, Bu'), 2.00 (3 H, s, OAc), 2.33 (3 H, s, Me), 5.13 (1 H, dd, *J* 7.6 and 4.6, 1-H), 5.39 (1 H, d, *J* 4.6, 2-H), 6.18 (1 H, d, *J* 7.6, NH) and 7.11–7.43 (9 H, m, ArH); *m/z* 358 (*M*⁺) (Found: *M*⁺, 358.1296; C, 66.2; H, 8.0; N, 3.35; S, 7.75%). C₂₃H₃₃NO₂SSi requires C, 66.45; H, 8.00; N, 3.35; S, 7.70%).

(1*S**,2*S**)-N-Benzyl-2-(tert-butylphenylsiloxy)-2-[(4-methylphenyl)sulfanyl]-1-phenylethylamine syn-7e.—Compound syn-6e (31.3 mg, 0.090 mmol), the acetal 2 (84.3 mg, 0.449 mmol), ZnI₂ (3.9 mg, 0.0090 mmol) and MeCN (1 cm³) gave compound 7e (*syn:anti* 92:8; 28.7 mg, 69%). The diastereoisomers could not be separated in a pure state by column chromatography. The product was an oil; $\nu_{\text{max}}/\text{cm}^{-1}$ 3350, 2930, 1493 and 1454; δ_{H} (signals of syn-7e) –0.09 and 0.00 (total 92/100 \times 6 H, each s, Me₂Si), 0.87 (92/100 \times 9 H, s, Bu'), 2.31 (92/100 \times 3 H, s, Me), 3.49 and 3.75 (92/100 \times 2 H, ABq, *J*

13.5, CH₂Ph), 3.89 and 5.08 (each 92/100 \times 1 H, each d, *J* 5.9, 1- and 2-H) and 7.00–7.42 (92/100 \times 14 H, m, ArH); *m/z* 406 (*M*⁺) (Found: *M*⁺, 406.1645). C₂₈H₃₇NOSSi requires *M*, 406.1658).

(1*R**,2*S**)-N-Benzyl-2-(tert-butylphenylsiloxy)-2-[(4-methylphenyl)sulfanyl]-1-phenylethylamine anti-7e.—Compound anti-6e (29.8 mg, 0.085 mmol), the acetal 2 (80.2 mg, 0.427 mmol), ZnI₂ (2.7 mg, 0.0085 mmol) and MeCN (1 cm³) gave compound 7e (*syn:anti* 15:85; 23.6 mg, 60%). The diastereoisomers could not be separated in a pure state by column chromatography. The product was an oil; $\nu_{\text{max}}/\text{cm}^{-1}$ 3325, 2930, 1493 and 1454; δ_{H} (signals of anti-7e) –0.41 and –0.07 (total 85/100 \times 6 H, each s, Me₂Si), 0.7 (85/100 \times 9 H, s, Bu'), 2.35 (85/100 \times 3 H, s, Me), 3.34 and 3.62 (85/100 \times 2 H, ABq, *J* 13.2, CH₂Ph), 3.63 and 4.97 (each 85/100 \times 1 H, each d, *J* 7.3, 1- and 2-H) and 7.06–7.42 (85/100 \times 14 H, m, ArH) (Found: C, 72.35; H, 8.15; N, 3.05; S, 6.8. C₂₈H₃₇NOSSi requires C, 72.50; H, 8.05; N, 3.00; S, 6.90%).

(1*S*,2*S*)-1-(tert-Butyldimethylsiloxy)-1-[(4-methylphenyl)sulfanyl]-2-phenylpropane syn-7f.—Compound syn-6f (35.0 mg, 0.136 mmol), the acetal 2 (128 mg, 0.678 mmol), ZnI₂ (8.7 mg, 0.027 mmol) and MeCN (2 cm³) gave substrate syn-6f (18.6 mg, 53% recovery) and compound 7f (*syn:anti* 90:10; 22.6 mg, 45%). The diastereoisomers could not be separated in a pure state by column chromatography. The product had $[\alpha]_{\text{D}}^{24}$ –66.9 (*c* 0.639, CHCl₃); $\nu_{\text{max}}/\text{cm}^{-1}$ 2960, 1600 and 1493; δ_{H} –0.217 and –0.021 (each 10/100 \times 3 H, each s, Me₂Si), –0.18 and 0.00 (each 90/100 \times 3 H, each s, Me₂Si), 0.76 (10/100 \times 9 H, s, Bu'), 0.88 (90/100 \times 9 H, s, Bu'), 1.38 (10/100 \times 3 H, d, *J* 6.9, 3-H₃), 1.44 (90/100 \times 3 H, d, *J* 6.9, 3-H₃), 2.25 (90/100 \times 3 H, s, Me), 2.35 (10/100 \times 3 H, s, Me), 3.04 (10/100 \times 1 H, quint, *J* 6.9, 2-H), 3.21 (90/100 \times 1 H, dt, *J* 5.0 and 6.9, 2-H), 5.04 (10/100 \times 1 H, d, *J* 6.9, 1-H), 5.13 (90/100 \times 1 H, d, *J* 5.0, 1-H) and 7.09–7.61 (9 H, m, ArH); *m/z* 372 (*M*⁺) (Found: *M*⁺, 372.1955). C₂₂H₃₂OSSi requires *M*, 372.1943).

(1*S*,2*R*)-1-(tert-Butyldimethylsiloxy)-1-[(4-methylphenyl)sulfanyl]-2-phenylpropane anti-7f.—Compound anti-6f (37.2 mg, 0.144 mmol), the acetal 2 (136 mg, 0.723 mmol), ZnI₂ (9.2 mg, 0.029 mmol) and MeCN (2 cm³) gave substrate anti-6f (14.1 mg, 38% recovery) and compound 7f (*syn:anti* 24:76; 30.2 mg, 56%) as an oil. The isomers could not be separated in a pure state by column chromatography; $[\alpha]_{\text{D}}^{24}$ +95.0 (*c* 0.82, CHCl₃); $\nu_{\text{max}}/\text{cm}^{-1}$ 2960, 1601 and 1493; δ_{H} –0.217 and –0.021 (each 76/100 \times 3 H, each s, Me₂Si), –0.18 and 0.00 (each 24/100 \times 3 H, each s, Me₂Si), 0.76 (76/100 \times 9 H, s, Bu'), 0.88 (24/100 \times 9 H, s, Bu'), 1.38 (76/100 \times 3 H, d, *J* 6.9, 3-H₃), 1.44 (24/100 \times 3 H, d, *J* 6.9, 3-H₃), 2.25 (24/100 \times 3 H, s, Me), 2.35 (76/100 \times 3 H, s, Me), 3.04 (76/100 \times 1 H, quint, *J* 6.9, 2-H), 3.21 (24/100 \times 1 H, dt, *J* 5.0 and 6.9, 2-H), 5.04 (76/100 \times 1 H, d, *J* 6.9, 1-H), 5.13 (24/100 \times 1 H, d, *J* 5.0, 1-H) and 7.09–7.61 (9 H, m, ArH); *m/z* 372 (*M*⁺) (Found: *M*⁺, 372.1940).

(1*S**,2*S**)-1,2-Bis-(tert-butylphenylsiloxy)-1-[(4-methylphenyl)sulfanyl]propane syn-7g.—Compound syn-6g (50.0 mg, 0.160 mmol), the acetal 2 (150 mg, 0.799 mmol), ZnI₂ (5.1 mg, 0.016 mmol) and MeCN (2 cm³) gave compound 7g (*syn:anti* 88:12; 48.5 mg, 71%). Diastereoisomer syn-7g was isolated in a pure state by column chromatography, oil; $\nu_{\text{max}}/\text{cm}^{-1}$ 2957, 1493, 1471 and 1257; δ_{H} –0.11, –0.07, 0.06 and 0.07 (each 3 H, each s, 2 \times Me₂Si), 0.86 and 0.90 (each 9 H, each s, 2 \times Bu'), 1.26 (3 H, d, *J* 6.2, 3-H₃), 2.32 (3 H, s, Me), 3.94 (1 H, dq, *J* 4.2 and 6.2, 2-H), 5.14 (1 H, d, *J* 4.2, 1-H) and 7.08 and 7.40 (each 2 H, each d, *J* 8, ArH); *m/z* 426 (*M*⁺) (Found: *M*⁺, 426.2437). C₂₂H₄₂O₂SSi₂ requires *M*, 426.2442).

(1S*,2R*)-1,2-Bis-(tert-butyltrimethylsiloxy)-1-[(4-methylphenyl)sulfanyl]propane anti-**7g**.—Compound anti-**6g** (45.0 mg, 0.144 mmol), the acetal **2** (135 mg, 0.720 mmol), ZnI₂ (4.6 mg, 0.014 mmol) and MeCN (2 cm³) gave compound **7g** (*syn:anti* 0:100; 43.2 mg, 70%). Diastereoisomer anti-**7g** was an oil; $\nu_{\max}/\text{cm}^{-1}$ 2930, 1493, 1471 and 1257; δ_{H} −0.03 and −0.06 (each 3 H, each s, Me₂Si), 0.00 (6 H, s, 2 × SiMe₂), 0.87 and 0.88 (each 9 H, each s, 2 × Bu^t), 1.25 (3 H, d, *J* 6.3, 3-H₃), 2.32 (3 H, s, Me), 3.96 (1 H, dq, *J* 3.3 and 6.3, 2-H), 4.93 (1 H, d, *J* 3.3, 1-H) and 7.09 and 7.35 (each 2 H, each d, *J* 8.0, ArH); *m/z* 426 (M⁺) (Found: M⁺, 426.2444).

(1S*,2S*)-1-(tert-Butyltrimethylsiloxy)-2-phenyl-2-(trimethylsiloxy)ethyl 4-Methylphenyl Sulfide *syn-7b*.—To a stirred solution of (S_S*,1S*)-2-[(4-methylphenyl)sulfanyl]-1-phenylethanol (51.3 mg, 0.197 mmol) and ZnI₂ (6.2 mg, 0.020 mmol) in dry MeCN (4 cm³) was added dropwise 1,2-dimethoxy-1-(trimethylsiloxy)ethylene (104 mg, 0.592 mmol) at room temperature for 1 h under nitrogen to give a crude solution of *syn-β*-trimethylsiloxy sulfoxide *syn-6b*, then the acetal **2** (185 mg, 0.985 mmol) was added at 0 °C for 4 h under nitrogen, and the mixture was poured into saturated aq. sodium hydrogen carbonate and repeatedly extracted with methylene dichloride. The organic layer was washed with brine, dried, and evaporated. The residue was purified by PLC to give the α-siloxy sulfide **7b** (*syn:anti* 87:13; 54.7 mg, 62%) as a pale yellow oil. The diastereoisomers could not be separated in a pure state by column chromatography; $\nu_{\max}/\text{cm}^{-1}$ 2920 and 1495; δ_{H} (signals of *syn-7b*) −0.04 and −0.01 (each 87/100 × 3 H, each s, Me₂Si), 0.01 (87/100 × 9 H, s, Me₃Si), 0.89 (87/100 × 9 H, s, Bu^t), 2.32 (87/100 × 3 H, s, Me), 4.77 and 5.01 (each 87/100 × 1 H, each d, *J* 5.6, 1- and 2-H) and 7.07–7.41 (87/100 × 9 H, m, ArH); *m/z* 446 (M⁺) (Found: M⁺, 446.2129. C₂₄H₃₈O₂SSi₂ requires M, 446.2129).

(1S*,2R*)-1-(tert-Butyltrimethylsiloxy)-2-phenyl-2-(trimethylsiloxy)ethyl 4-Methylphenyl Sulfide anti-**7b**.—To a stirred solution of (S_S*,1R*)-2-[(4-methylphenyl)sulfanyl]-1-phenylethanol (38.8 mg, 0.149 mmol) and ZnI₂ (4.8 mg, 0.015 mmol) in dry MeCN (3 cm³) was added dropwise 1,2-dimethoxy-1-(trimethylsiloxy)ethylene (78.8 mg, 0.448 mmol) at room temperature for 1 h under nitrogen to give a crude solution of anti-β-trimethylsiloxy sulfoxide anti-**6b**, then the acetal **2** (140 mg, 0.745 mmol) was added at 0 °C for 4 h under nitrogen. The mixture was then poured into saturated aq. sodium hydrogen carbonate and repeatedly extracted with methylene dichloride. The organic layer was washed with brine, dried, and evaporated. The residue was purified by PLC to give the α-siloxy sulfide **7b** (*syn:anti* 3:97; 44.0 mg, 66%) as a pale yellow oil. The diastereoisomers could not be separated in a pure state by column chromatography; $\nu_{\max}/\text{cm}^{-1}$ 2940 and 1495; δ_{H} (signals of anti-**7b**) −0.33 and −0.08 (each 3 H, each s, Me₂Si), −0.06 (97/100 × 9 H, s, Me₃Si), 0.72 (97/100 × 9 H, s, Bu^t), 2.34 (97/100 × 3 H, s, Me), 4.62 and 4.99 (each 97/100 × 1 H, each d, *J* 6.8, 1- and 2-H) and 7.08–7.42 (97/100 × 9 H, m, ArH); *m/z* 446 (M⁺) (Found: M⁺, 446.2139).

General Procedure for the Pummerer Reaction of Ac₂O with Sulfoxides 6a.—A stirred solution of sulfoxide **6a** (0.100 mmol) in Ac₂O (3 cm³) was refluxed for 2 days under nitrogen, and then the mixture was concentrated under reduced pressure. The crude oil was purified by PLC to give the α-acetoxy sulfide **8**.

(1R*,2R*)-2-(tert-Butyltrimethylsiloxy)-1-[(4-methylphenyl)sulfanyl]-2-phenylethyl Acetate *syn-8*.—Sulfoxide *syn-6a* (70.0 mg, 0.187 mmol) and Ac₂O (3 cm³) gave acetate **8** (*syn:anti* 4:1, 44.1 mg, 57%).

(1S*,2R*)-2-(tert-Butyltrimethylsiloxy)-1-[(4-methylphenyl)sulfanyl]-2-phenylethyl Acetate anti-**8**.—Compound anti-**6a** (49.6 mg, 0.133 mmol) and Ac₂O (2 cm³) gave compound **8** (*syn:anti* 4:1; 18.2 mg, 33%) as an oil; $\nu_{\max}/\text{cm}^{-1}$ 2930, 1743 and 1493; δ_{H} −0.17 and 0.04 (each 3/4 × 6 H, each s, Me₂Si), −0.10 and 0.10 (each 1/4 × 6 H, each s, Me₂Si), 0.84 (3/4 × 9 H, s, Bu^t), 0.93 (1/4 × 9 H, s, Bu^t), 1.97 (1/4 × 3 H, s, OAc), 1.98 (3/4 × 3 H, s, OAc), 2.28 (1/4 × 3 H, s, Me), 2.30 (3/4 × 3 H, s, Me), 4.82 (3/4 × 1 H, d, *J* 6.6, 2-H), 4.96 (1/4 × 1 H, d, *J* 4.3, 2-H), 6.13 (1/4 × 1 H, d, *J* 4.3, 1-H), 6.17 (3/4 × 1 H, d, *J* 4.3, 1-H) and 6.995–7.449 (9 H, m, ArH); *m/z* 416 (M⁺) (Found: M⁺, 416.1842. C₂₃H₃₂O₃SSi requires M, 416.1841).

General Procedure for the Pummerer-type Reaction of O-Silylated Ketene Acetal 2 with Sulfoxides 6h, 6i.—To a stirred solution of a sulfoxide **6** (0.100 mmol) in dry MeCN (1 cm³) was added dropwise ketene tert-butyltrimethylsilyl methyl acetal **2** (0.500–1.00 mmol) at 60–65 °C as indicated in Table 2 for 4–12 h under nitrogen, and then the solvent was evaporated off. The residue was purified by PLC to give the corresponding α-siloxy sulfide **7** in yields between 65 and 75%.

Ethyl (1S)-(tert-Butyltrimethylsiloxy)-[(4-methylphenyl)sulfanyl]acetate (S)-7h.—Compound (S)-**6h** {[α]_D²⁰ −189 (c 1.80, acetone), 193 mg, 0.854 mmol}, the acetal **2** (1.605 g, 8.54 mmol) and MeCN (3 cm³) gave compound (S)-**7h** (217 mg, 75%; 87% ee) as an oil; [α]_D¹⁸ +35.8 (c 0.46, acetone); $\nu_{\max}/\text{cm}^{-1}$ 2858 and 1747; δ_{H} 0.031 and 0.062 (3 H × 2, each s, Me₂Si), 0.88 (s, 9 H, Bu^t), 1.21 (3 H, t, *J* 7.3, OCH₂Me), 2.33 (s, 3 H, Me), 4.10 and 4.11 (each 1 H, each q, *J* 7.3, OCH₂H_bMe), 5.40 (s, 1 H, 1-H) and 7.08 and 7.43 (each 2 H, each d, *J* 8.3, ArH); *m/z* 340 (M⁺) (Found: M⁺, 340.1527; C, 59.75; H, 8.15; S, 9.45%. C₁₇H₂₈O₃SSi requires M, 340.1527; C, 59.95; H, 8.30; S, 9.40%).

Ethyl (1R)-(tert-Butyltrimethylsiloxy)-[(4-methylphenyl)sulfanyl]acetate (R)-7h.—Compound (R)-**6h** {[α]_D²⁰ +195 (c 0.97, acetone), 58.0 mg, 0.257 mmol}, the acetal **2** (482 mg, 2.57 mmol) and MeCN (1 cm³) gave compound (R)-**7h** (63.1 mg, 72%; 86% ee) as an oil; [α]_D¹⁸ −34.8 (c 0.67, acetone); $\nu_{\max}/\text{cm}^{-1}$ 2858 and 1747; δ_{H} 0.03 and 0.06 (3 H × 2, each s, Me₂Si), 0.88 (9 H, s, Bu^t), 1.21 (3 H, t, *J* 7.3, OCH₂Me), 2.33 (3 H, s, Me), 4.10 and 4.11 (each 1 H, each q, *J* 7.3, OCH₂H_bMe), 5.40 (1 H, s, 1-H) and 7.08 and 7.43 (each 2 H, each d, *J* 8.3, ArH); *m/z* 340 (M⁺) (Found: M⁺, 340.1546; C, 59.65; H, 8.20; S, 9.20%).

(1S)-1-(tert-Butyltrimethylsiloxy)-N,N-dimethylamino-1-[(4-methylphenyl)sulfanyl]acetamide (S)-7i. —Compound (S)-**6i** {[α]_D²⁰ −187 (c 1.24, acetone), 38.3 mg, 0.170 mmol}, the acetal **2** (320 mg, 1.70 mmol) and MeCN (1 cm³) gave compound (S)-**7i** (37.3 mg, 65%; 88% ee) as an oil; [α]_D¹⁸ −28.9 (c 1.4, acetone); $\nu_{\max}/\text{cm}^{-1}$ 2932 and 1641; δ_{H} −0.06 (6 H, s, Me₂Si), 0.84 (9 H, s, Bu^t), 2.34 (3 H, s, Me), 2.94 and 3.19 (2 × 3 H, each s, Me₂N), 5.57 (1 H, s, 1-H) and 7.13 and 7.43 (each 2 H, each d, *J* 8.2, ArH); *m/z* 282 (M⁺ − Bu^t) [Found: (M⁺ − Bu^t), 282.0971; C, 60.05; H, 8.4; N, 4.15; S, 9.55%. C₁₃H₂₀NO₂SSi requires *m/z*, 282.0981; C₁₇H₂₉NO₂SSi requires C, 60.10; H, 8.60; N, 4.15; S, 9.45%].

(1R)-1-(tert-Butyltrimethylsiloxy)-N,N-dimethyl-1-[(4-methylphenyl)sulfanyl]acetamide (R)-7i. —Compound (R)-**6i** {[α]_D²⁰ +192 (c 0.83, acetone), 233 mg, 1.03 mmol}, the acetal **2** (1.88 g, 10.3 mmol) and MeCN (3 cm³) gave compound (R)-**7i** (244 mg, 69%; 88% ee) as an oil; [α]_D¹⁸ +28.8 (c 1.23, acetone); $\nu_{\max}/\text{cm}^{-1}$ 2932 and 1642; δ_{H} −0.06 (6 H, s, Me₂Si), 0.84 (9 H, s, Bu^t), 2.34 (3 H, s, Me), 2.94 and 3.19 (2 × 3 H, each s, Me₂N), 5.57 (1 H, s, 1-H) and 7.13 and 7.43 (each 2 H, each d, *J* 8.2, ArH); *m/z* 282 (M⁺ − Bu^t) [Found: (M⁺ − Bu^t), 282.0979; C, 59.8; H, 8.5; N, 4.2; S, 9.35%].

(R)-(Dimethylcarbamoyl)-[4-methylphenyl)sulfanyl]methyl Acetate **9**.—To a stirred solution of sulfide (R)-**7i** (30.0 mg, 0.085 mmol) and FeCl₃ (1.4 mg, 0.0085 mmol) in dry MeCN (1 cm³) was added dropwise acetyl chloride (35.0 mg, 0.443 mmol) at room temperature for 1 h under nitrogen. The mixture was then poured into saturated aq. sodium hydrogen carbonate and repeatedly extracted with methylene dichloride. The organic layer was washed with brine, dried, and evaporated. The residue was purified by PLC to give the α -acetoxy sulfide **9** (15.2 mg, 64%) as crystals; m.p. 60–62 °C; $[\alpha]_D^{18}$ –44.3 (c 0.54, acetone) {lit.,^{4g} m.p. 59–60 °C; $[\alpha]_D^{18}$ –59.2 (c 0.4, acetone)}.

Determination of Absolute Stereochemistry of (S_S)-4-Methylphenyl 2-Phenylpropyl Sulfoxide: Conversion into 2-Phenylpropanal.—(S)-2-Phenylpropanal. To a stirred solution of (S_S)-4-methylphenyl (2S)-2-phenylpropyl sulfoxide syn-**6f** (188 mg, 0.729 mmol) and 2,6-lutidine (2,6-dimethylpyridine) (156 mg, 1.458 mmol) in dry MeCN (4 cm³) was added dropwise trifluoroacetic anhydride (TFAA) (0.202 cm³, 1.458 mmol) at 0 °C under nitrogen. After 30 min, aq. CuCl₂ (137 mg, 1.02 mmol in 10 cm³) was added, and the mixture was then stirred for 3 h at room temperature before being repeatedly extracted with ethyl acetate. The organic layer was washed with brine, dried and evaporated. The residue was purified by PLC to give (S)-2-phenylpropanal (30.0 mg, 31%) as an oil; $[\alpha]_D^{25}$ +6.14 (c 0.26, benzene) {lit.,¹¹ $[\alpha]_D^{25}$ +209.1 (c 1.49, benzene)}; $\nu_{\max}/\text{cm}^{-1}$ 2370, 1730 and 1490; δ_{H} 1.47 (3 H, d, *J* 7.2, 3-H₃), 3.64 (1 H, q, *J* 7.2, 2-H), 7.19–7.42 (5 H, m, ArH) and 9.69 (1 H, s, CHO); *m/z* 134 (M⁺) (Found: M⁺, 134.0741. C₉H₁₀O requires M, 134.0731).

(R)-2-Phenylpropanal. To a stirred solution of (S_S)-4-methylphenyl (2R)-2-phenylpropyl sulfoxide anti-**6f** (148 mg, 0.574 mmol) and 2,6-lutidine (83 mg, 1.148 mmol) in dry MeCN (4 cm³) was added dropwise TFAA (0.202 cm³, 1.458 mmol) at 0 °C under nitrogen. After 30 min, aq. HgCl₂ (234 mg, 0.861 mmol in water 10 cm³) was added, and the mixture was then stirred for 3 h at room temperature before being repeatedly extracted with ethyl acetate. The organic layer was washed with brine, dried and evaporated. The residue was purified by PLC to give (R)-2-phenylpropanal (25.0 mg, 33%) as an oil; $[\alpha]_D^{25}$ –11.0 (c 0.83, benzene); $\nu_{\max}/\text{cm}^{-1}$ 2370, 1730 and 1490; δ_{H} 1.47 (3 H, d, *J* 7.2, 3-H₃), 3.64 (1 H, q, *J* 7.2, 2-H), 7.19–7.42 (5 H, m, ArH) and 9.69 (1 H, s, CHO).

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