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

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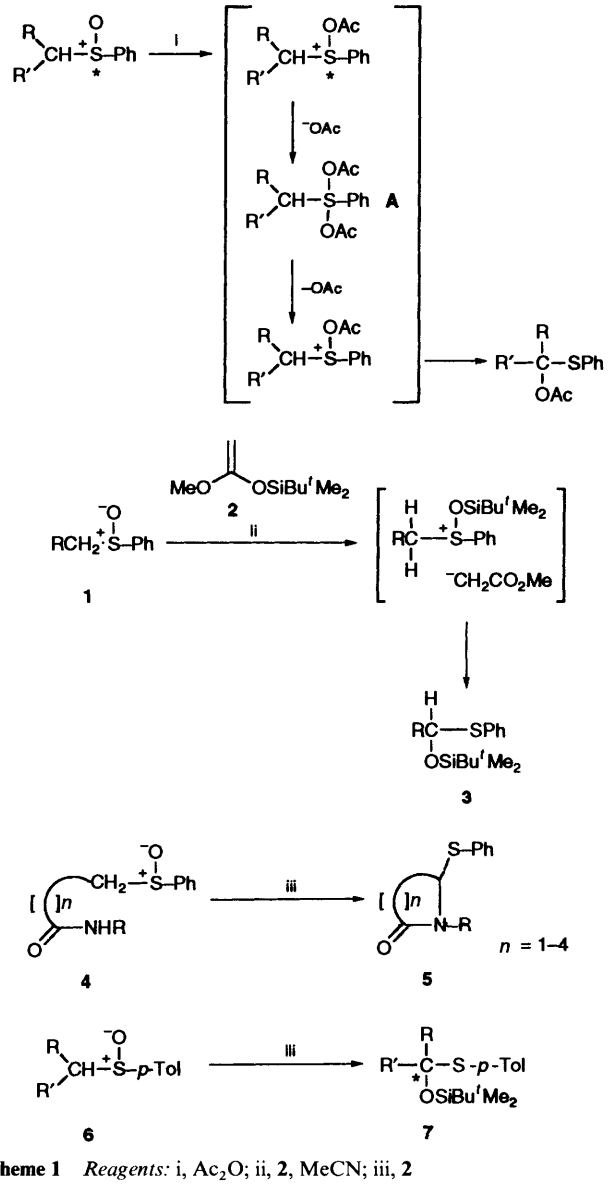
Various types of *syn*- and *anti*-β-substituted sulfoxides **6b–e, g** reacted with ketene *tert*-butyldimethylsilyl acetal **2** in the presence of a catalytic amount of zinc iodide in acetonitrile to give high yields of the corresponding α-siloxy sulfides **7b–e, g** stereoselectively. Similarly, 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 sulfides[1] 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 transformation[3] and is of considerable interest, because it would provide a means for the synthesis of chiral, non-racemic α-substituted sulfides.†[,4] 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 reported[6] 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 communicated[8] 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.‡[,9] 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.



Scheme 1 *Reagents:* i, Ac_2O; ii, **2**, MeCN; iii, **2**

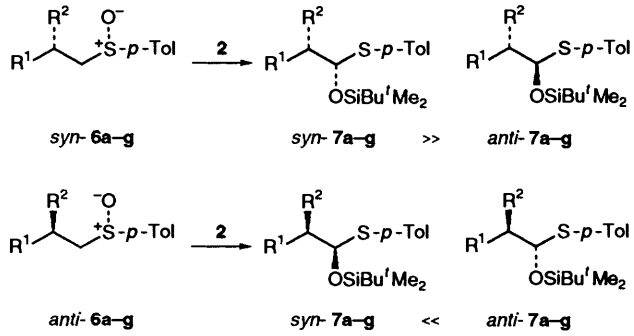
Results and Discussion

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 stereochemical ratio (*syn*:*anti*) of the diastereoisomeric α-siloxy sulfides was determined by Heathcock's method using ^{1}H 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 ^{1}H NMR resonance of the group *gauche* to it on the vicinal stereocentre.

† 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]

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	$OSiBu^tMe_2$	0 °C, 1 h–r.t., 1 h	75	88:12
2	*anti*-**6a**[b]	Ph	$OSiBu^tMe_2$	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	$OSiBu^tPh_2$	r.t., 4 h	85	95:5
6	*anti*-**6c**	Ph	$OSiBu^tPh_2$	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	$NHCH_2Ph$	r.t., overnight	69	92:8
10	*anti*-**6e**	Ph	$NHCH_2Ph$	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	$OSiBu^tMe_2$	0 °C, 2 h	71	88:12
14	*anti*-**6g**	Me	$OSiBu^tMe_2$	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.

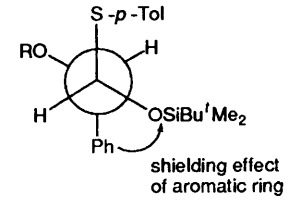


Fig. 1

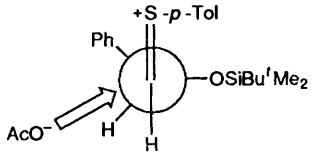
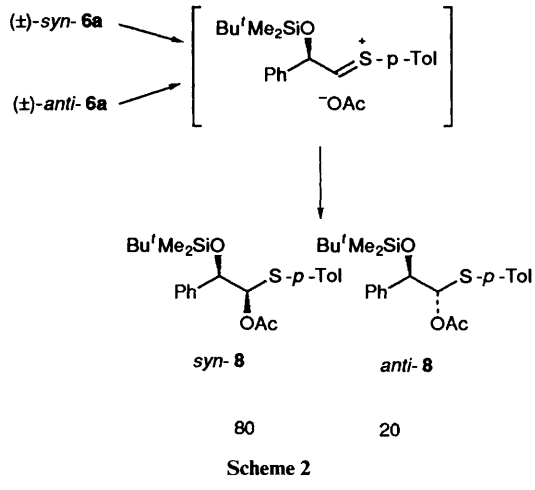


Fig. 2



Scheme 2

Therefore, the resonance of the *tert*-butyl group of *anti*-isomers occurs at a substantially higher field than does that of the *syn*-isomers[10] (Fig. 1).

The results are summarized in Table 1.

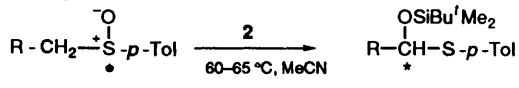
All reactions proceeded under mild conditions with a remarkably high degree of stereospecificity. We were surprised to find that extremely high retention occurred in all β-siloxy-, β-acylamino-, β-alkylamino-, β-alkyl- and β-aryl-substituted sulfoxides and, of course, in both racemic (entries 3–10, 13 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 stereogenic 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 $FeCl_3$ 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

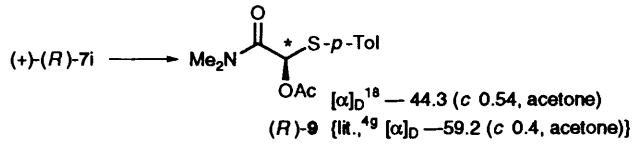
Table 2 Asymmetric silicon-induced Pummerer-type reactions



6h, i **7h, l**

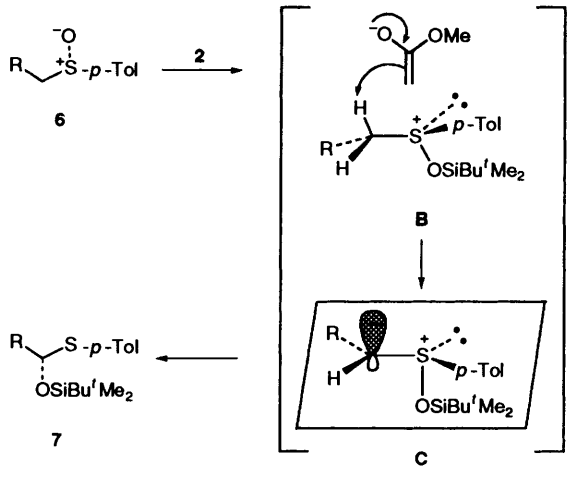
Sulfoxide[a]	R	Conditions	% ee[b] (% Yield[c])	$[\alpha]_D^{18}$ (*c*, acetone)	Configuration	Oae's approach[d] % ee (% Yield)
(*S*)-**6h**	CO_2Et	4 h	87 (75)	+35.8 (0.46)	*S*[f]	
(*R*)-**6h**	CO_2Et	4 h	86[e] (72)	−34.8 (0.67)	*R*[f]	70 (10)
(*S*)-**6i**	$CONMe_2$	12 h	88 (65)	−28.9 (1.40)	*S*	
(*R*)-**6i**	$CONMe_2$	12 h	88[e] (69)	+28.8 (1.23)	*R*	65 (35)

[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, $FeCl_3$ (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

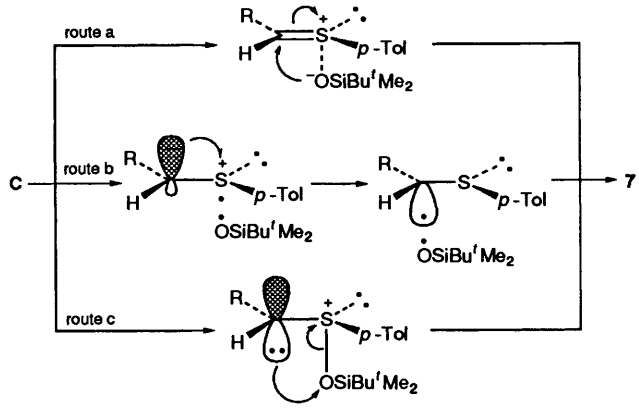


Scheme 4

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 $CHCl_3$ as solvent. ^1H NMR spectra were measured on JEOL JNM-FX90Q (90 MHz), JEOL JNM-EX270 (270 MHz) and JEOL JNM-GX500 (500 MHz)



Scheme 5

spectrometers with $CDCl_3$ 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 cm^3 capacity with a Perkin-Elmer 241 instrument; $[\alpha]_D$-values are given in units of 10^{-1} deg cm^2 g^{-1}. E. Merck silica gel 60 (70–230 mesh ASTM) for column chromatography and E. Merck precoated TLC plates with silica gel F_{254} for preparative TLC (PLC) were used. Organic layers were dried with anhydrous Na_2SO_4. 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 cm^3) gave *compound* syn-**6a** (510 mg, 93%) as an oil; $[\alpha]_D^{24}$ −64.8 (*c* 1.24, $CHCl_3$); δ_H −0.19 and 0.04 (each 3 H, each s, Me_2Si), 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. $C_{17}H_{21}O_2SSi$ 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 cm^3) gave *compound* anti-**6a** (112

* 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.

mg, 79%) as an oil; $[\alpha]_D^{24}$ −335 (*c* 0.74, $CHCl_3$); δ_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 (M^+ − Bu^t) [Found: (M^+ − Bu^t), 317.1060].

(S_S*)-[(2S*)-2-(tert-*Butyldiphenylsiloxy*)-2-*phenylethyl*] 4-*Methylphenyl Sulfoxide* syn-**6c**.—(S_S*,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; δ_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 (M^+ − Bu^t) [Found: (M^+ − Bu^t), 441.1340. $C_{27}H_{25}O_2SSi$ requires *m/z*, 441.1342].

(S_S*)-[(2R*)-2-(tert-*Butyldiphenylsiloxy*)-2-*phenylethyl*] 4-*Methylphenyl Sulfoxide* anti-**6c**.—(S_S*,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; δ_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. $C_{31}H_{34}O_2SSi$ requires M, 498.2046).

(S_S*,1S*)-N-*Benzyl*-2-[(4-*methylphenyl*)*sulfinyl*]-1-*phenylethanamine* syn-**6e**.—(S_S*,1*S**)-2-[(4-methylphenyl)sulfinyl]-1-phenylethanamine (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; δ_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_S*,1R*)-N-*Benzyl*-2-[(4-*methylphenyl*)*sulfinyl*]-1-*phenylethanamine* anti-**6e**.—(S_S*,1*R**)-2-[(4-methylphenyl)sulfinyl]-1-phenylethanamine (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; δ_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_S)-4-*Methylphenyl* (2S)-2-*Phenylpropyl Sulfoxide* syn-**6f** *and* (S_S)-4-*Methylphenyl* (2R)-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, $CHCl_3$); ν_{max}/cm^{-1} 3000, 1600, 1495, 1086 and 1053; δ_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. $C_{16}H_{18}OS$ 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, $CHCl_3$); ν_{max}/cm^{-1} 3000, 1600, 1495, 1086 and 1053; δ_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. $C_{16}H_{18}OS$ requires C, 74.35; H, 7.05; S, 12.40%).

(S_S*)-[(2S*)-2-(tert-*Butyldimethylsiloxy*)*propyl*] 4-*Methylphenyl Sulfoxide* syn-**6g**.—(S_S*,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; δ_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. $C_{16}H_{28}O_2SSi$ requires M, 312.1577).

(S_S*)-[(2R*)-2-(tert-*Butyldimethylsiloxy*)*propyl*] 4-*Methylphenyl Sulfoxide* anti-**6g**.—(S_S*,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; δ_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 O-*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%.

(1S,2S)-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, $CHCl_3$); ν_{max}/cm^{-1} 2920 and 1495; δ_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 × 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%. $C_{27}H_{44}O_2SSi_2$ requires M, 488.2597; C, 66.30; H, 9.10; S, 6.55%).

(1S,2R)-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, $CHCl_3$); ν_{max}/cm^{-1} 2940 and 1495;

δ_H −0.31, −0.20, −0.10 and −0.01 (each 3 H, each s, 2 × Me_2Si), 0.72 and 0.86 (each 9 H, each s, 2 × Bu^t), 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).

(1S*,2S*)-1-(tert-*Butyldimethylsiloxy*)-2-(tert-*butyldiphenylsiloxy*)-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), ZnI_2 (2.7 mg, 0.0087 mmol) and MeCN (3 cm^3) gave product **7c** (*syn*:*anti* 95:5; 44.0 mg, 85%). *Diastereoisomer* syn-**7c** was isolated in a pure state by column chromatography, oil; ν_{max}/cm ^{1} 2910 and 1495; δ_H −0.48 and 0.44 (each 3 H, each s, Me_2Si), 0.74 and 1.08 (each 9 H, each s, 2 × Bu^t), 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. $C_{37}H_{48}O_2SSi_2$ requires M, 612.2913).

(1S*,2R*)-1-(tert-*Butyldimethylsiloxy*)-2-(tert-*butyldiphenylsiloxy*)-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), ZnI_2 (2.5 mg, 0.0077 mmol) and MeCN (3 cm^3) gave compound **7c** (*syn*:*anti* 1:99; 34.0 mg, 74%). *Diastereoisomer* anti-**7c** was isolated in a pure state by column chromatography, oil; ν_{max}/cm^{-1} 2910 and 1495; δ_H −0.22 and −0.15 (each 3 H, each s, Me_2Si), 0.73 and 1.02 (each 9 H, each s, 2 × Bu^t), 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%. $C_{37}H_{48}O_2SSi_2$ requires M, 612.2911; C, 72.50, H, 7.90; S, 5.25%).

(1S*,2S*)-N-*Acetyl*-2-(tert-*butyldimethylsiloxy*)-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), ZnI_2 (5.5 mg, 0.0098 mmol) and MeCN (1 cm^3) 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 CH_2Cl_2–hexane); ν_{max}/cm^{-1} 3441, 3009, 1674 and 1550; δ_H −0.32 and −0.04 (total 6 H, each s, Me_2Si), 0.80 (9 H, s, Bu^t), 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. $C_{23}H_{33}NO_2SSi$ requires M, 358.1294).

(1R*,2S*)-N-*Acetyl*-2-(tert-*butyldimethylsiloxy*)-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), ZnI_2 (3.1 mg, 0.0096 mmol) and MeCN (1 cm^3) 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 CH_2Cl_2–hexane); ν_{max}/cm^{-1} 3447, 3011, 1674 and 1493; δ_H −0.076 and −0.05 (total 6 H, each s, Me_2Si), 0.88 (9 H, s, Bu^t), 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%). $C_{23}H_{33}NO_2SSi$ requires C, 66.45; H, 8.00; N, 3.35; S, 7.70%).

(1S*,2S*)-N-*Benzyl*-2-(tert-*butyldimethylsiloxy*)-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), ZnI_2 (3.9 mg, 0.0090 mmol) and MeCN (1 cm^3) 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; ν_{max}/cm^{-1} 3350, 2930, 1493 and 1454; δ_H(signals of *syn*-**7e**) −0.09 and 0.00 (total 92/100 × 6 H, each s, Me_2Si), 0.87 (92/100 × 9 H, s, Bu^t), 2.31 (92/100 × 3 H, s, Me), 3.49 and 3.75 (92/100 × 2 H, ABq, *J* 13.5, CH_2Ph), 3.89 and 5.08 (each 92/100 × 1 H, each d, *J* 5.9, 1- and 2-H) and 7.00–7.42 (92/100 × 14 H, m, ArH); *m/z* 406 (M^+) (Found: M^+, 406.1645. $C_{28}H_{37}NOSSi$ requires M, 406.1658).

(1R*,2S*)-N-*Benzyl*-2-(tert-*butyldimethylsiloxy*)-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), ZnI_2 (2.7 mg, 0.0085 mmol) and MeCN (1 cm^3) 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; ν_{max}/cm^{-1} 3325, 2930, 1493 and 1454; δ_H(signals of *anti*-**7e**) −0.41 and −0.07 (total 85/100 × 6 H, each s, Me_2Si), 0.7 (85/100 × 9 H, s, Bu^t), 2.35 (85/100 × 3 H, s, Me), 3.34 and 3.62 (85/100 × 2 H, ABq, *J* 13.2, CH_2Ph), 3.63 and 4.97 (each 85/100 × 1 H, each d, *J* 7.3, 1- and 2-H) and 7.06–7.42 (85/100 × 14 H, m, ArH) (Found: C, 72.35; H, 8.15; N, 3.05; S, 6.8. $C_{28}H_{37}NOSSi$ requires C, 72.50; H, 8.05; N, 3.00; S, 6.90%).

(1S,2S)-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), ZnI_2 (8.7 mg, 0.027 mmol) and MeCN (2 cm^3) 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 $[\alpha]_D^{24}$ −66.9 (*c* 0.639, $CHCl_3$); ν_{max}/cm^{-1} 2960, 1600 and 1493; δ_H −0.217 and −0.021 (each 10/100 × 3 H, each s, Me_2Si), −0.18 and 0.00 (each 90/100 × 3 H, each s, Me_2Si), 0.76 (10/100 × 9 H, s, Bu^t), 0.88 (90/100 × 9 H, s, Bu^t), 1.38 (10/100 × 3 H, d, *J* 6.9, 3-H_3), 1.44 (90/100 × 3 H, d, *J* 6.9, 3-H_3), 2.25 (90/100 × 3 H, s, Me), 2.35 (10/100 × 3 H, s, Me), 3.04 (10/100 × 1 H, quint, *J* 6.9, 2-H), 3.21 (90/100 × 1 H, dt, *J* 5.0 and 6.9, 2-H), 5.04 (10/100 × 1 H, d, *J* 6.9, 1-H), 5.13 (90/100 × 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. $C_{22}H_{32}OSSi$ requires M, 372.1943).

(1S,2R)-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), ZnI_2 (9.2 mg, 0.029 mmol) and MeCN (2 cm^3) 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; $[\alpha]_D^{24}$ +95.0 (*c* 0.82, $CHCl_3$); ν_{max}/cm^{-1} 2960, 1601 and 1493; δ_H −0.217 and −0.021 (each 76/100 × 3 H, each s, Me_2Si), −0.18 and 0.00 (each 24/100 × 3 H, each s, Me_2Si), 0.76 (76/100 × 9 H, s, Bu^t), 0.88 (24/100 × 9 H, s, Bu^t), 1.38 (76/100 × 3 H, d, *J* 6.9, 3-H_3), 1.44 (24/100 × 3 H, d, *J* 6.9, 3-H_3), 2.25 (24/100 × 3 H, s, Me), 2.35 (76/100 × 3 H, s, Me), 3.04 (76/100 × 1 H, quint, *J* 6.9, 2-H), 3.21 (24/100 × 1 H, dt, *J* 5.0 and 6.9, 2-H), 5.04 (76/100 × 1 H, d, *J* 6.9, 1-H), 5.13 (24/100 × 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).

(1S*,2S*)-1,2-*Bis*-(tert-*butyldimethylsiloxy*)-1-[(4-*methylphenyl*)*sulfanyl*]*propane* syn-**7g**.—Compound *syn*-**6g** (50.0 mg, 0.160 mmol), the acetal **2** (150 mg, 0.799 mmol), ZnI_2 (5.1 mg, 0.016 mmol) and MeCN (2 cm^3) gave compound **7g** (*syn*:*anti* 88:12; 48.5 mg, 71%). *Diastereoisomer* syn-**7g** was isolated in a pure state by column chromatography, oil; ν_{max}/cm^{-1} 2957, 1493, 1471 and 1257; δ_H −0.11, −0.07, 0.06 and 0.07 (each 3 H, each s, 2 × Me_2Si), 0.86 and 0.90 (each 9 H, each s, 2 × Bu^t), 1.26 (3 H, d, *J* 6.2, 3-H_3), 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. $C_{22}H_{42}O_2SSi_2$ requires M, 426.2442).

(1S*,2R*)-1,2-*Bis*-(tert-*butyldimethylsiloxy*)-1-[(4-*methylphenyl*)*sulfanyl*]*propane* anti-**7g**.—Compound *anti*-**6g** (45.0 mg, 0.144 mmol), the acetal **2** (135 mg, 0.720 mmol), ZnI_2 (4.6 mg, 0.014 mmol) and MeCN (2 cm^3) gave compound **7g** (*syn*:*anti* 0:100; 43.2 mg, 70%). *Diastereoisomer* anti-**7g** was an oil; ν_{max}/cm^{-1} 2930, 1493, 1471 and 1257; δ_H −0.03 and −0.06 (each 3 H, each s, Me_2Si), 0.00 (6 H, s, 2 × $SiMe_2$), 0.87 and 0.88 (each 9 H, each s, 2 × Bu^t), 1.25 (3 H, d, *J* 6.3, 3-H_3), 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-*Butyldimethylsiloxy*)-2-*phenyl*-2-(*trimethylsiloxy*)*ethyl* 4-*Methylphenyl Sulfide* syn-**7b**.—To a stirred solution of (S_S*,1*S**)-2-[(4-methylphenyl)sulfinyl]-1-phenylethanol (51.3 mg, 0.197 mmol) and ZnI_2 (6.2 mg, 0.020 mmol) in dry MeCN (4 cm^3) 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; ν_{max}/cm^{-1} 2920 and 1495; δ_H(signals of *syn*-**7b**) −0.04 and −0.01 (each 87/100 × 3 H, each s, Me_2Si), 0.01 (87/100 × 9 H, s, Me_3Si), 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. $C_{24}H_{38}O_2SSi_2$ requires M, 446.2129).

(1S*,2R*)-1-(tert-*Butyldimethylsiloxy*)-2-*phenyl*-2-(*trimethylsiloxy*)*ethyl* 4-*Methylphenyl Sulfide* anti-**7b**.—To a stirred solution of (S_S*,1*R**)-2-[(4-methylphenyl)sulfinyl]-1-phenylethanol (38.8 mg, 0.149 mmol) and ZnI_2 (4.8 mg, 0.015 mmol) in dry MeCN (3 cm^3) 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; ν_{max}/cm^{-1} 2940 and 1495; δ_H(signals of *anti*-**7b**) −0.33 and −0.08 (each 3 H, each s, Me_2Si), −0.06 (97/100 × 9 H, s, Me_3Si), 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 Ac_2O *with Sulfoxides* **6a**.—A stirred solution of sulfoxide **6a** (0.100 mmol) in Ac_2O (3 cm^3) 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-*Butyldimethylsiloxy*)-1-[(4-*methylphenyl*)-*sulfanyl*]-2-*phenylethyl Acetate* syn-**8**.—Sulfoxide *syn*-**6a** (70.0 mg, 0.187 mmol) and Ac_2O (3 cm^3) gave acetate **8** (*syn*:*anti* 4:1, 44.1 mg, 57%).

(1S*,2R*)-2-(tert-*Butyldimethylsiloxy*)-1-[(4-*methylphenyl*)-*sulfanyl*]-2-*phenylethyl Acetate* anti-**8**.—Compound *anti*-**6a** (49.6 mg, 0.133 mmol) and Ac_2O (2 cm^3) gave *compound* **8** (*syn*:*anti* 4:1; 18.2 mg, 33%) as an oil; ν_{max}/cm^{-1} 2930, 1743 and 1493; δ_H −0.17 and 0.04 (each 3/4 × 6 H, each s, Me_2Si), −0.10 and 0.10 (each 1/4 × 6 H, each s, Me_2Si), 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. $C_{23}H_{32}O_3SSi$ 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 cm^3) was added dropwise ketene *tert*-butyldimethylsilyl 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-*Butyldimethylsiloxy*)-[(4-*methylphenyl*)*sulfanyl*]*acetate* (S)-**7h**.—Compound (*S*)-**6h** {$[\alpha]_D^{20}$ −189 (*c* 1.80, acetone), 193 mg, 0.854 mmol}, the acetal **2** (1.605 g, 8.54 mmol) and MeCN (3 cm^3) gave *compound* (S)-**7h** (217 mg, 75%; 87% ee) as an oil; $[\alpha]_D^{18}$ +35.8 (*c* 0.46, acetone); ν_{max}/cm^{-1} 2858 and 1747; δ_H 0.031 and 0.062 (3 H × 2, each s, Me_2Si), 0.88 (s, 9 H, Bu^t), 1.21 (3 H, t, *J* 7.3, OCH_2Me), 2.33 (s, 3 H, Me), 4.10 and 4.11 (each 1 H, each q, *J* 7.3, OCH_aH_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%. $C_{17}H_{28}O_3SSi$ requires M, 340.1527; C, 59.95; H, 8.30; S, 9.40%).

Ethyl (1R)-(tert-*Butyldimethylsiloxy*)-[(4-*methylphenyl*)*sulfanyl*]*acetate* (R)-**7h**.—Compound (*R*)-**6h** {$[\alpha]_D^{20}$ +195 (*c* 0.97, acetone), 58.0 mg, 0.257 mmol}, the acetal **2** (482 mg, 2.57 mmol) and MeCN (1 cm^3) gave *compound* (R)-**7h** (63.1 mg, 72%; 86% ee) as an oil; $[\alpha]_D^{18}$ −34.8 (*c* 0.67, acetone); ν_{max}/cm^{-1} 2858 and 1747; δ_H 0.03 and 0.06 (3 H × 2, each s, Me_2Si), 0.88 (9 H, s, Bu^t), 1.21 (3 H, t, *J* 7.3, OCH_2Me), 2.33 (3 H, s, Me), 4.10 and 4.11 (each 1 H, each q, *J* 7.3, OCH_aH_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-*Butyldimethylsiloxy*)-N,N-*dimethylamino*-1-[(4-*methylphenyl*)*sulfanyl*]*acetamide* (S)-**7i**.—Compound (*S*)-**6i** {$[\alpha]_D^{20}$ −187 (*c* 1.24, acetone), 38.3 mg, 0.170 mmol}, the acetal **2** (320 mg, 1.70 mmol) and MeCN (1 cm^3) gave *compound* (S)-**7i** (37.3 mg, 65%; 88% ee) as an oil; $[\alpha]_D^{18}$ −28.9 (*c* 1.4, acetone); ν_{max}/cm^{-1} 2932 and 1641; δ_H −0.06 (6 H, s, Me_2Si), 0.84 (9 H, s, Bu^t), 2.34 (3 H, s, Me), 2.94 and 3.19 (2 × 3 H, each s, Me_2N), 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%. $C_{13}H_{20}NO_2SSi$ requires *m*/*z*, 282.0981; $C_{17}H_{29}NO_2SSi$ requires C, 60.10; H, 8.60; N, 4.15; S, 9.45%].

(1R)-1-(tert-*Butyldimethylsiloxy*)-N,N-*dimethyl*-1-[(4-*methylphenyl*)*sulfanyl*]*acetamide* (R)-**7i**.—Compound (*R*)-**6i** {$[\alpha]_D^{20}$ +192 (*c* 0.83, acetone), 233 mg, 1.03 mmol}, the acetal **2** (1.88 g, 10.3 mmol) and MeCN (3 cm^3) gave compound (R)-**7i** (244 mg, 69%; 88% ee) as an oil; $[\alpha]_D^{18}$ +28.8 (*c* 1.23, acetone); ν_{max}/cm^{-1} 2932 and 1642; δ_H −0.06 (6 H, s, Me_2Si), 0.84 (9 H, s, Bu^t), 2.34 (3 H, s, Me), 2.94 and 3.19 (2 × 3 H, each s, Me_2N), 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 $FeCl_3$ (1.4 mg, 0.0085 mmol) in dry MeCN (1 cm^3) 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 (2*S*)-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 cm^3) was added dropwise trifluoroacetic anhydride (TFAA) (0.202 cm^3, 1.458 mmol) at 0 °C under nitrogen. After 30 min, aq. $CuCl_2$ (137 mg, 1.02 mmol in 10 cm^3) 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)}; ν_{max}/cm^{-1} 2370, 1730 and 1490; δ_H 1.47 (3 H, d, *J* 7.2, 3-H_3), 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. $C_9H_{10}O$ requires M, 134.0731).

(R)-2-*Phenylpropanal*. To a stirred solution of (S_S)-4-methylphenyl (2*R*)-2-phenylpropyl sulfoxide *anti*-**6f** (148 mg, 0.574 mmol) and 2,6-lutidine (83 mg, 1.148 mmol) in dry MeCN (4 cm^3) was added dropwise TFAA (0.202 cm^3, 1.458 mmol) at 0 °C under nitrogen. After 30 min, aq. $HgCl_2$ (234 mg, 0.861 mmol in water 10 cm^3) 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); ν_{max}/cm^{-1} 2370, 1730 and 1490; δ_H 1.47 (3 H, d, *J* 7.2, 3-H_3), 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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