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Novel Asymmetric Desymmetrization of *meso*-1, 2-Diols *via* Diastereoselective β-Elimination of Chiral α-Arylsulfinyl Acetals

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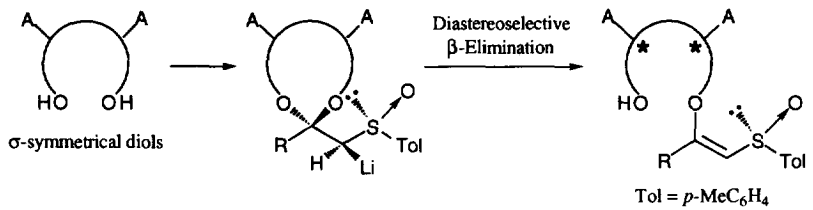
Abstract: Enantioselective desymmetrization of *meso*-1,2-diols was accomplished *via* diastereoselective C—O bond fission of acetals derived from various optically active β-ketosulfoxides with high diastereoselectivities. The substituent at the γ-position of the β-ketosulfoxide plays an important role in this cleavage.

Differentiation of enantiotopic groups in achiral bifunctional molecules with σ-symmetry has been widely used as a strategy for creating optically active molecules.[1] Furthermore, each diastereomer produced in this reaction can often be converted into either enantiomer by an appropriate manipulation, thereby enabling the enantioconvergent synthesis of a desired product, the so-called *meso* trick.[2] Asymmetrization of σ-symmetrical diols has recently received considerable attention as a fascinating methodology for synthesizing useful chiral building blocks for various natural products, and great effort has been devoted to the development of efficient methods.[3-7] While the induction of chirality for σ-symmetrical diols by enzymatic reactions is well known,[3] the use of chemical methods is less well established.[4-7] Since the application of the enzymatic method is limited due to the high specificity of substrates, the development of efficient chemical methods is very important.

In a previous work, we developed a chemical asymmetric desymmetrization of prochiral 1,3-diols *via* acetalization with an intramolecular chiral β-ketosulfoxide moiety followed by diastereoselective acetal fission to afford chiral mono-protected 1,3-diols.[4a, 4d-h] Based on this result, we planned to investigate the potency of β-ketosulfoxides as a tool for differentiating enantiotopic groups in σ-symmetrical diols, as shown in Scheme 1.

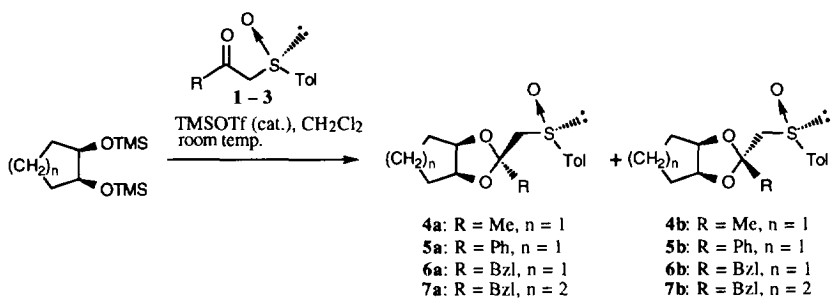
In this paper, we report a novel asymmetric desymmetrization of *meso*-1,2-diols with chiral β-ketosulfoxide as a chiral auxiliary.



Scheme 1

RESULTS AND DISCUSSION

Enantiomerically pure (*R*)-β-ketosulfoxides **1**–**3** [8] were acetalized with *cis*-1,2-bis(trimethylsiloxy)cyclopentane or *cis*-1,2-bis(trimethylsiloxy)cyclohexane in the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf) catalyst[9] to give a separable diastereomeric mixture of **4a**–**7a** and **4b**–**7b** (Scheme 2, Table 1). [10,11]



Scheme 2

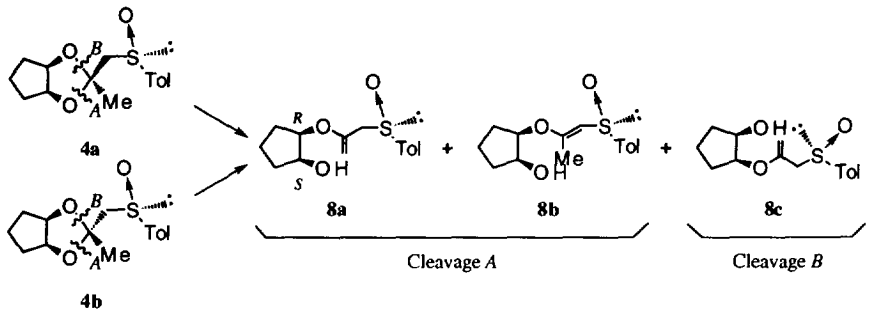
Table 1. Acetalization of β-Ketosulfoxides **1**–**3**.

Diol (n)	Sulfoxide	R	Product	Yield (%)[a]	
				a	**b**
1	**1**	Me	**4**	54	26
1	**2**	Ph	**5**	0	74
1	**3**	Bzl	**6**	24	48
2	**3**	Bzl	**7**	24	48

a) Isolated yield.

On treatment with one equivalent of lithium diisopropylamide (LDA), the acetal **4a** gave the alcohols **8a**–**c** in low yield along with a significant amount of **4a** and **4b**. This problem was overcome by increasing the

amount of base; i.e., the reaction was completed when six equivalents of base were used. Cleavage *A* gave a mixture of α,β- and β,γ-unsaturated sulfoxides. Bond cleavage *A* to **8a** and **8b** predominates over *B* to **8c**. The diastereomeric isomer **4b** showed better selectivity than **4a**. Selectivity in 1,2-dimethoxyethane (DME) was better than that in tetrahydrofuran (THF) (Scheme 3, Table 2).



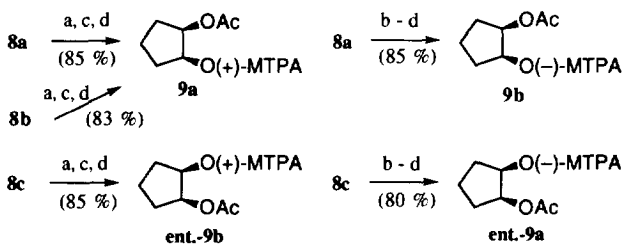
Scheme 3

Table 2. Diastereoselective Acetal Cleavage of **4a** and **4b**.

Substrate	Conditions (equiv.)	Yield (%)	Cleavage Ratio [a]	
			A	*B*
4a	LDA (6), THF, –78 ℃	95	74	26
	LDA (6), DME, –78 ℃	92	81	19
4b	LDA (6), THF, –78 ℃	81	82	18
	LDA (6), DME, –78 ℃	83	89	11

a) The ratio was determined by 200 MHz ^{1}H-NMR spectroscopy.

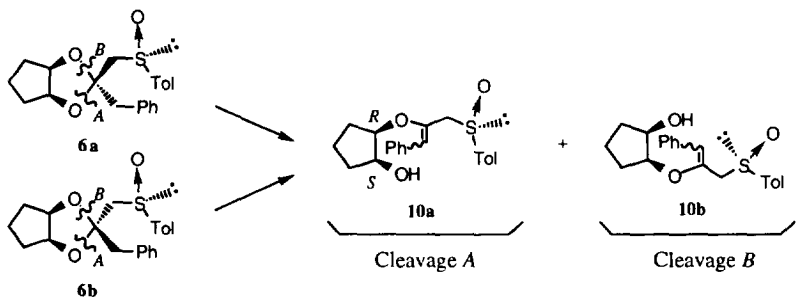
The olefin geometry of **8b** was determined by the observation of an NOE between the vinylic proton and the α-methine proton of vinylic ether on the cyclopentane ring.[12] The absolute configuration of these alcohols **8a–c** was determined by Mosher's method[13] after conversion into the α-methoxy-α-(trifluoromethyl)phenylacetic acid (MTPA) ester **9**[14] in 3 steps (MTPA esterification, hydrolysis of the vinylic ether, and acetylation), as shown in Scheme 4.



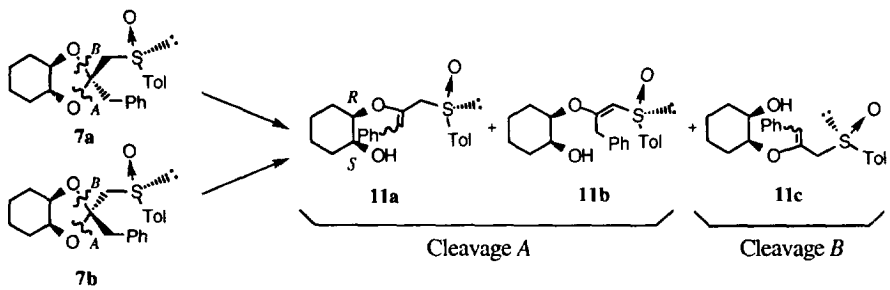
Reagents: a) (+)-MTPACl, Et_3N, DMAP, CH_2Cl_2, 0 °C. b) (–)-MTPACl, Et_3N, DMAP, CH_2Cl_2, 0 °C. c) 1N HCl, acetone, room temp. d) Ac_2O, pyridine, CH_2Cl_2, 0 °C.

Scheme 4

On the other hand, acetal **5b** (R=Ph) did not provide any cleaved products, but rather isomerized to **5a** in 98% yield on treatment with six equivalents of LDA in THF at –78 ℃. The resulting **5a** did not react under the same conditions. In contrast to the phenyl derivatives **5a** and **5b**, the benzyl derivatives **6a** and **6b** easily afforded the chiral alcohols **10a** and **10b**, each as a mixture of (*E*/*Z*)-isomers under the same conditions. Like **4a** and **4b**, the diastereomeric isomers **6a** and **6b** both preferentially gave the products arising from cleavage *A*. In addition, the selectivity was generally higher than that of **4a** and **4b**. In this case, three equivalents of base was enough to complete the reaction without decreasing the yield. Acetals **7a** and **7b** derived from *cis*-1,2-cyclohexanediol also selectively gave alcohols **11a** and **11b** with *S*-configuration. Acetals **6b** and **7b** with an *endo*-benzyl group showed better selectivity than the corresponding diastereomeric isomers **6a** and **7a**, respectively. The selectivity of **7a** was somewhat low compared with that of the corresponding cyclopentanediol derivative **6a**. For both **6** and **7**, fairly good selectivity was observed when *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) was added (Schemes 5 and 6, Table 3). The stereochemistry of the olefin in **10** and **11** was determined by an NOE experiments.[12] The absolute configurations of the products were confirmed by their transformation into the known compounds.[15,16]



Scheme 5



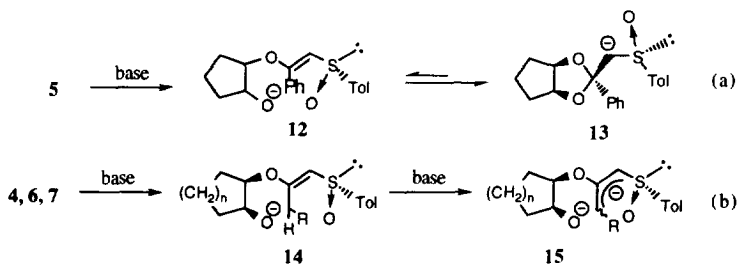
Scheme 6

Table 3. Diastereoselective Acetal Cleavage of **6** and **7**.

Substrate	Conditions (equiv.)	Yield (%)	Cleavage Ratio [a]	
			A	*B*
	LDA (3), THF, –78 ℃	92	86	14
	LDA (3), HMPA [b] (3), THF, –78 ℃	91	66	34
6a	LDA (3), TMEDA (3), THF, –78 ℃	92	84	16
	LDA (3), DME, –78 ℃	92	90	10
	LiTMP [c] (3), THF, –78 ℃	90	74	26
	LDA (3), THF, –78 ℃	91	90	10
	LDA (3), HMPA (3), THF, –78 ℃	90	86	14
6b	LDA (3), TMEDA (3), THF, –78 ℃	92	94	6 [d]
	LDA (3), DME, –78 ℃	92	48	52
	LiTMP (3), THF, –78 ℃	93	87	13
7a	LDA (5), THF, –78 ℃	95	46	54
	LDA (5), TMEDA (5), THF, –78 ℃	88	63	37
7b	LDA (5), THF, –78 ℃	95	94	6 [e]
	LDA (5), TMEDA (5), THF, –78 ℃	90	92	8

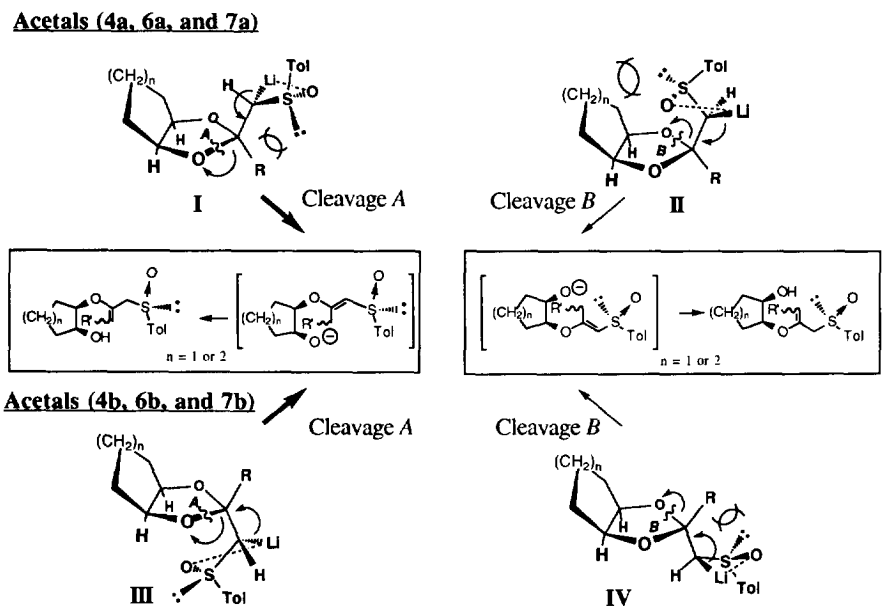
a) The ratio was determined by 200 or 270 MHz ^{1}H-NMR spectroscopy.
b) HMPA = hexamethylphosphoric triamide. c) LiTMP = lithium 2,2,6,6-tetramethylpiperidide.
d) (*Z*)-**10a** : (*E*)-**10a** : (*Z*)-**10b** : (*E*)-**10b** = 88 : 6 : 2 : 4.
e) (*Z*)-**11a** : (*E*)-**11a** : (*E*)-**11b** : (*Z*)-**11c** : (*E*)-**11c** = 76 : 4 : 14 : 3 : 3.

The different reactivities of the α-sulfinyl acetals can be explained as follows (Scheme 7). As shown in Scheme 7(a), for **5**, the initially formed alkoxide anion **12** would rapidly recyclize to a stable anion **13**. On the other hand, for **4**, **6** and **7**, further deprotonation occurred in the anion **14** (R=H or Ph, n=1 or 2) bearing a hydrogen at the γ-position of the sulfinyl group to give a dianion **15**, in which recyclization would be prevented by electronic repulsion between the anions, as shown in Scheme 7(b). Since the proton at the γ-position of the sulfinyl group in **6a** and **6b** is more acidic than that in **4a** and **4b**, less base is needed to generate dianion **15** from **6a** and **6b**, compared to that from **4a** and **4b**.



Scheme 7

The diastereoselectivity in this acetal fission can be explained as follows (Scheme 8). The *p*-tolyl group would be *anti* to a bulky bicyclic ring to minimize steric repulsion. For isomers with an *exo*-*p*-tolylsulfinylmethyl group **4b**, **6b**, and **7b**, the conformer **III** would predominate over the conformer **IV** since the partially positive sulfur atom benefits from so-called attractive *gauche* interaction[17] with the partially negative acetal oxygens in **III**. In contrast, conformer **IV** is destabilized by an unfavorable *gauche* interaction between the sulfinyl group and the bulky substituent R. Consequently, cleavage *A* would be more favorable than cleavage *B* because of diastereoselective deprotonation of the *pro-S* proton (a proton *gauche* to the sulfinyl oxygen),[18] followed by *anti* elimination. For **4a**, **6a**, and **7a**, the conformer **I** would be more favorable than **II** since the steric repulsion between the cyclopentane ring and the sulfinylmethyl group in **II** is greater than the *gauche* interaction between the sulfinyl group and R in **I**. As a result, cleavage *A* predominates over cleavage *B*. In the case of **6a** (R=Bzl, n=1), the steric repulsion between the cyclopentane ring and the sulfinylmethyl group in **II** is greater than that with the corresponding cyclohexane ring in **7a** (R=Bzl, n=2). Therefore, the diastereoselectivity of **6a** is somewhat higher than that of **7a**.



Scheme 8

In summary, we have developed a novel method for desymmetrizing σ-symmetrical diols *via* acetal formation with β-ketosulfoxides followed by base-promoted diastereoselective acetal cleavage. In these transformations, β-ketosulfoxides serve as a chiral auxiliary which gives rise to excellent diastereoselectivity. An important facet of this study is that both the diastereomeric isomers give the same product preferentially, although acetalization gives a diasetereomeic mixture. This transformation may be useful in the synthesis of natural products. Applications are under investigation and will be reported in due course.

EXPERIMENTAL

General. Melting points are uncorrected. Optical rotations were measured using a JASCO DIP-360 digital polarimeter. IR spectra were measured with a Hitachi 260-10 IR spectrometer or a Horiba FT-210 IR spectrometer. ^{1}H-NMR spectra were measured with a Varian VXR-200 spectrometer (200 MHz), a JEOL JNM-EX270 spectrometer (270 MHz), or a JEOL JNM-GX500 spectrometer (500 MHz). ^{13}C-NMR spectra were measured with a Varian VXR-200 spectrometer (50.3 MHz) or a JEOL JNM-EX270 spectrometer (67.8 MHz). Mass spectra were taken with a Shimadzu QP-1000 mass spectrometer and a JEOL JMS-D300 mass spectrometer. HPLC analyses were performed using a Waters 6000A pump, A Waters μ-PORASIL (3.9 mm× 30 cm)column, a Waters RCM 25×10 column and a Soma S-310 UV detector (at 254 nm). Unless otherwise stated, all reactions were performed with anhydrous solvents and the extract was dried over anhydrous $MgSO_4$ before evaporation. Merck Kieselgel 60 was used as an adsorbent for column chromatography. Merck Kieselgel 60 PF_{254} was used for preparative TLC.

(*Rs*)-3-Phenyl-1-(*p*-tolylsulfinyl)propan-2-one (3). A solution of methyl *p*-tolyl sulfoxide (1.28 g, 8.30 mmol) in THF (20 ml) was added to a stirred solution [prepared from n-BuLi (1.6 M in hexane; 11.4 ml, 18.3 mmol) and diisopropylamine (2.44 ml, 17.4 mmol) in THF (30 ml)] at −78 ℃ and the whole was stirred at −78 ℃ for 30 min. Methyl phenylacetate (1.31 ml, 9.13 mmol) was added to the mixture and the whole was stirred at −78 ℃ for 30 min. The reaction was quenched with saturated NH_4Cl. The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layers were washed with water and brine, and then dried. The solvent was evaporated and the residue was chromatographed on silica gel with AcOEt–hexane (1 : 2) to give **3** (1.99 g, 88 %) as colorless crystals, mp 107–108 ℃ (AcOEt–hexane). $[\alpha]_D^{27}$ +161.45 (c = 1.14, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 2.42 (s, 3H, Ar–C$\underline{H}_3$), 3.72 (d, 1H, J = 15.8 Hz, C$\underline{H}_2$SO or C$\underline{H}_2$Ph), 3.78 (d, 1H, J = 15.8 Hz, C$\underline{H}_2$SO or C$\underline{H}_2$Ph), 3.80 (d, 1H, J = 13.7 Hz, C$\underline{H}_2$SO or C$\underline{H}_2$Ph), 3.85 (d, 1H, J = 13.7 Hz, C$\underline{H}_2$SO or C$\underline{H}_2$Ph), 7.12 (d, 2H, J = 7.3 Hz, Ar–$\underline{H}$), 7.25–7.34 (m, 5H, Ar–$\underline{H}$) , 7.51 (d, 2H, J = 8.5 Hz, Ar–$\underline{H}$). ^{13}C-NMR ($CDCl_3$) δ: 21.4, 51.8, 66.8, 124.0, 127.3, 128.8, 129.5 130.1, 132.4, 139.4, 142.2, 199.1. IR (KBr): 3020, 1720, 1610, 1510, 1045 cm^{-1}. MS *m/z* (%): 272 (M^+, 100), 133 (100). *Anal.* Calcd for $C_{16}H_{16}O_2S$: C, 70.56 ; H, 5.92 ; S, 11.77. Found : C, 70.24 ; H, 6.01 ; S, 11.70.

(*Rs*)-3-*exo*-Methyl-3-*endo*-(*p*-tolylsulfinyl)methyl-2,4-dioxa-*cis*-bicyclo[3.3.0]octane and (*Rs*)-3-*endo*-Methyl-3-*exo*-(*p*-tolylsulfinyl)methyl-2,4-dioxa-*cis*-bicyclo[3.3.0]octane (4a and 4b). TMSOTf (0.187 ml, 0.969 mmol) was added to a stirred solution of β-ketosulfoxide **1** (1.90 g, 9.69 mmol) and *cis*-1,2-bis(trimethylsiloxy)cyclopentane (2.87 g, 11.6 mmol) in CH_2Cl_2 (95 ml), and the whole was stirred at 25 ℃ for 12 h. After the addition of saturated $NaHCO_3$, the whole was extracted with AcOEt. The extract was washed with water and brine, and then dried. The solvent was evaporated and the residue was chromatographed on silica gel with AcOEt–hexane (1 : 1) to afford **4a** (1.46 g, 54 %) as a colorless oil and **4b** (710 mg, 26 %) as colorless crystals. **4a:** $[\alpha]_D^{26}$ +101.9 (c = 1.00, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.43 (s, 3H, CC$\underline{H}_3$), 1.43–1.63 (m, 3H), 1.90–2.07 (m, 3H), 2.41 (s, 3H, Ar–C$\underline{H}_3$), 3.13 (d, 1H, J = 14.1 Hz, C$\underline{H}_2$SO), 3.23 (d, 1H, J = 14.1 Hz, C$\underline{H}_2$SO), 4.71 (t, 1H, J = 5.1 Hz, CH_2C$\underline{H}$O), 4.75 (t, 1H, J = 5.1 Hz, CH_2C$\underline{H}$O), 7.31 (d, 2H, J = 8.4 Hz, Ar–$\underline{H}$), 7.58 (d, 2H, J = 8.4 Hz, Ar–$\underline{H}$). ^{13}C-NMR ($CDCl_3$) δ: 21.3, 22.7, 23.3, 33.1, 33.1, 68.8, 81.4, 81.6, 107.3, 124.0, 129.8, 141.0, 142.3. IR ($CHCl_3$): 3000, 2940, 1040 cm^{-1}. MS *m/z* (%): 280 (M^+, 0.4), 127 (100). *Anal.* Calcd for $C_{15}H_{20}O_3S$: C, 64.26 ; H, 7.19 ; S, 11.44. Found : C, 64.23 ; H, 7.25 ; S, 11.28. **4b:** mp 107–108 ℃ (AcOEt–hexane). $[\alpha]_D^{27}$ +132.3 (c = 1.05,

$CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.37–1.46 (m, 2H), 1.55–1.62 (m, 1H), 1.64 (s, 3H, $CC\underline{H}_3$), 1.68–1.79 (m, 1H), 1.90 (d, 1H, J = 6.0 Hz), 1.93 (d, 1H, J = 6.0 Hz), 2.42 (s, 3H, Ar–$C\underline{H}_3$), 2.95 (d, 1H, J = 13.7 Hz, $C\underline{H}_2SO$), 3.07 (d, 1H, J = 13.7 Hz, $C\underline{H}_2SO$), 4.58 (t, 1H, J = 6.0 Hz, $CH_2C\underline{H}O$), 4.68 (d, 1H, J = 6.0 Hz, $CH_2C\underline{H}O$), 7.32 (d, 2H, J = 8.6 Hz, Ar–$\underline{H}$), 7.55 (d, 2H, J = 8.6 Hz, Ar–$\underline{H}$). ^{13}C-NMR ($CDCl_3$) δ: 21.4, 22.2, 25.2, 33.3, 33.4, 66.5, 81.7, 81.8, 107.4, 124.0, 130.0, 141.5, 141.7. IR ($CHCl_3$): 3000, 2975, 1600, 1040 cm^{-1}. MS *m/z* (%): 280 (M^+, 0.2), 127 (100). *Anal.* Calcd for $C_{15}H_{20}O_3S$: C, 64.26 ; H, 7.19 ; S, 11.44. Found : C, 63.94 ; H, 7.17 ; S, 11.24.

(*Rs*)-3-*endo*-Phenyl-3-*exo*-(*p*-tolylsulfinyl)methyl-2,4-dioxa-*cis*-bicyclo[3.3.0]octane (5b). TMSOTf (12 μl, 0.062 mmol) was added to a solution of β-ketosulfoxide **2** (159 mg, 0.615 mmol) and *cis*-1,2-bis(trimethylsiloxy)cyclopentane (182 mg, 0.739 mmol) in CH_2Cl_2 (10 ml) with stirring at 25 ℃ and the mixture was stirred at 25 ℃ for 36 h. After the addition of saturated $NaHCO_3$, the whole was extracted with AcOEt. The extract was washed with water and brine, and then dried. The solvent was evaporated and the residue was chromatographed on silica gel with AcOEt–hexane (1 : 1) to give **5b** (156 mg, 74 %) as colorless crystals, mp 82–83 ℃ (AcOEt–hexane). $[\alpha]_D^{30}$ +91.9 (c = 1.13, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.23–1.35 (m, 1H), 1.38–1.54 (m, 3H), 1.84–1.96 (m, 2H), 2.38 (s, 3H, Ar–$C\underline{H}_3$), 3.23 (d, 1H, J = 14.1 Hz, $C\underline{H}_2SO$), 3.39 (d, 1H, J = 14.1 Hz, $C\underline{H}_2SO$), 4.94 (t, 1H, J = 5.6 Hz, $CH_2C\underline{H}O$), 5.04 (d, 1H, J = 5.6 Hz, $CH_2C\underline{H}O$), 7.26 (d, 2H, J = 7.7 Hz, Ar–$\underline{H}$), 7.31–7.37 (m, 3H, Ar–$\underline{H}$), 7.45 (d, 2H, J = 8.1 Hz, Ar–$\underline{H}$), 7.54–7.58 (m, 2H, Ar–$\underline{H}$). ^{13}C-NMR ($CDCl_3$) δ: 21.2, 22.4, 33.2, 33.3, 70.5, 83.0, 83.3, 108.9, 123.8, 125.3, 128.1, 128.3, 129.8, 141.0, 141.4, 141.9. IR ($CHCl_3$): 2976, 1600, 1495, 1040 cm^{-1}. MS *m/z* (%): 342 (M^+, 0.2), 127 (100). *Anal.* Calcd for $C_{20}H_{22}O_3S$: C, 70.15 ; H, 6.47 ; S, 9.36. Found : C, 69.95 ; H, 6.48 ; S, 9.11.

(*Rs*)-3-*exo*-Phenyl-3-*endo*-(*p*-tolylsulfinyl)methyl-2,4-dioxa-*cis*-bicyclo[3.3.0]octane (5a). A solution of **5b** (17.2 mg, 0.0503 mmol) in THF (1 ml) was added to a stirred LDA solution [prepared from *n*-BuLi (1.6 M in hexane; 0.189 ml, 0.302 mmol) and diisopropylamine (42 μl, 0.30 mmol) in THF (5 ml)] at –78 ℃ and the whole was stirred at –78 ℃ for 30 min. The reaction was quenched with saturated NH_4Cl. The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layers were washed with brine, and then dried. The solvent was evaporated and the residue was chromatographed on silica gel with AcOEt–hexane (1 : 2) to give **5a** (16.9 mg, 98 %) as colorless crystals, mp 70–72 ℃ (AcOEt–hexane). $[\alpha]_D^{30}$ +106.1 (c = 1.34, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.42–1.54 (m, 2H), 1.64–1.70 (m, 1H), 2.09–2.14 (m, 1H), 2.16–2.27 (m, 2H), 2.39 (s, 3H, Ar–$C\underline{H}_3$), 3.28 (d, 1H, J = 14.3 Hz, $C\underline{H}_2SO$), 3.35 (d, 1H, J = 14.3 Hz, $C\underline{H}_2SO$), 4.45–4.49 (m, 2H, $C\underline{H}OC$), 7.27–7.36 (m, 5H, Ar–$\underline{H}$), 7.49 (d, 2H, J = 7.3 Hz, Ar–$\underline{H}$), 7.57 (d, 2H, J = 8.1 Hz, Ar–$\underline{H}$). ^{13}C-NMR ($CDCl_3$) δ: 21.2, 23.1, 32.9, 33.0, 69.7, 81.8, 81.8, 107.6, 123.8, 125.7, 128.4, 128.5, 129.7, 140.5, 140.8, 142.5. IR ($CHCl_3$): 3020, 2980, 1603, 1501, 1042 cm^{-1}. MS *m/z* (%): 342 (M^+, 0.3), 189 (100). *Anal.* Calcd for $C_{20}H_{22}O_3S$: C, 70.15 ; H, 6.47 ; S, 9.36. Found : C, 70.06 ; H, 6.46 ; S, 9.30.

(*Rs*)-3-*exo*-Benzyl-3-*endo*-(*p*-tolylsulfinyl)methyl-2,4-dioxa-*cis*-bicyclo[3.3.0]octane and (*Rs*)-3-*endo*-3-Benzyl-3-*exo*-(*p*-tolylsulfinyl)methyl-2,4-dioxa-*cis*-bicyclo[3.3.0]octane (6a and 6b). TMSOTf (46 μl, 0.24 mmol) was added to a solution of β-ketosulfoxide **3** (650 mg, 2.39 mmol) and *cis*-1,2-bis(trimethylsiloxy)cyclopentane (708 mg, 2.87 mmol) in CH_2Cl_2 (70 ml) with stirring at 25 ℃ and the mixture was stirred at 25 ℃ for 60 h. After the addition of saturated $NaHCO_3$, the whole was extracted with AcOEt. The extract was washed with water and brine, and then dried. The solvent was evaporated and the residue was chromatographed on silica gel with AcOEt–hexane (1 : 1) to afford **6a** (373 mg, 24 %) as a colorless

oil and **6b** (746 mg, 48 %) as colorless crystals. **6a:** $[\alpha]_D^{25}$ +90.2 (c = 1.12, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.42–1.53 (m, 2H), 1.54–1.64 (m, 1H), 1.90–2.02 (m, 2H), 2.04–2.10 (m, 1H), 2.39 (s, 3H, Ar-C$\underline{H}_3$), 3.01 (d, 1H, *J* = 13.7 Hz, C$\underline{H}_2$SO), 3.02 (s, 2H, Ar–C$\underline{H}_2$), 3.17 (d, 1H, *J* = 13.7 Hz, C$\underline{H}_2$SO), 4.63 (t, 1H, *J* = 5.2 Hz, C$\underline{H}$OC), 4.65 (t, 1H, *J* = 5.2Hz, C$\underline{H}$OC), 7.20–7.30 (m, 7H, Ar–$\underline{H}$), 7.50 (d, 2H, *J* = 8.6 Hz, Ar–$\underline{H}$). ^{13}C-NMR ($CDCl_3$) δ: 21.4, 21.9, 33.2, 33.2, 44.0, 65.0, 81.8, 81.9, 108.3, 124.0, 126.6, 127.7, 129.9, 131.3, 135.1, 141.4, 141.6. IR ($CHCl_3$): 2955, 2925, 1605, 1498, 1033 cm^{-1}. MS *m/z* (%): 356 (M^+, 0.6), 264 (100). *Anal.* Calcd for $C_{21}H_{24}O_3S$: C, 70.76 ; H, 6.79 ; S, 8.99. Found : C, 70.46 ; H, 6.83 ; S, 8.75. **6b:** mp 118–119 ℃ (AcOEt–hexane). $[\alpha]_D^{22}$ +109.3 (c = 1.00, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 0.91–1.05 (m, 1H), 1.25–1.38 (m, 3H), 1.72–1.81 (m, 2H), 2.40 (s, 3H, Ar–C$\underline{H}_3$), 2.89 (d, 1H, *J* = 14.1 Hz, C$\underline{H}_2$SO), 3.08 (d, 1H, *J* = 14.1 Hz, C$\underline{H}_2$SO), 3.19 (d, 1H, *J* = 14.1 Hz, Ar–C$\underline{H}_2$), 3.24 (d, 1H, *J* = 14.1 Hz, Ar-C$\underline{H}_2$), 4.59 (t, 1H, *J* = 5.3 Hz, C$\underline{H}$OC), 4.69 (t, 1H, *J* = 5.3 Hz, C$\underline{H}$OC), 7.20–7.35 (m, 7H, Ar–$\underline{H}$), 7.49 (d, 2H, *J* = 8.1 Hz, Ar–$\underline{H}$). ^{13}C-NMR ($CDCl_3$) δ: 21.3, 22.9, 33.3, 33.3, 43.2, 66.9, 82.4, 82.5, 109.5, 123.9, 126.8, 128.2, 129.8, 130.4, 135.7, 140.9, 142.3. IR ($CHCl_3$): 2920, 1600, 1025 cm^{-1}. MS *m/z* (%): 356 (M^+, 0.3), 264 (100). *Anal.* Calcd for $C_{21}H_{24}O_3S$: C, 70.76 ; H, 6.79 ; S, 8.99. Found : C, 70.70 ; H, 6.77 ; S, 8.94.

(*Rs*)-8-*exo*-Benzyl-8-*endo*-(*p*-tolylsulfinyl)methyl-7,9-dioxa-*cis*-bicyclo[4.3.0]nonane and (*Rs*)-8-*endo*-Benzyl-8-*exo*-(*p*-tolylsulfinyl)methyl-7,9-dioxa-*cis*-bicyclo[4.3.0]nonane (7a and 7b). TMSOTf (14 μl, 0.073 mmol) was added to a solution of β-ketosulfoxide **3** (200 mg, 0.734 mmol) and *cis*-1,2-bis(trimethylsiloxy)cyclohexane (500 mg, 1.92 mmol) in CH_2Cl_2 (30 ml) with stirring at 25 ℃ and the mixture was stirred at 25 ℃ for 140 h. After the addition of saturated $NaHCO_3$, the whole was extracted with AcOEt. The extract was washed with water and brine, and then dried. The solvent was evaporated and the residue was chromatographed on silica gel with AcOEt–hexane (2 : 5) to afford **7a** (65.0 mg, 24 %) as a colorless oil and **7b** (130 mg, 48 %) as colorless crystals. **7a**: $[\alpha]_D^{29}$ +71.1 (c = 0.50, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.21–1.33 (m, 2H), 1.48–1.60 (m, 2H), 1.70–1.84 (m, 4H), 2.40 (s, 3H, Ar-C$\underline{H}_3$), 2.99 (d, 1H, *J* = 13.7 Hz, C$\underline{H}_2$SO), 3.14 (s, 2H, Ar-C$\underline{H}_2$), 3.26 (d, 1H, *J* = 13.7 Hz, C$\underline{H}_2$SO), 4.06–4.12 (m, 2H, C$\underline{H}$OC), 7.20–7.33 (m, 5H, Ar–$\underline{H}$), 7.32 (d, 2H, *J* = 7.7 Hz, Ar–$\underline{H}$), 7.51 (d, 2H, J = 7.7 Hz, Ar–$\underline{H}$). ^{13}C-NMR ($CDCl_3$) δ: 20.3, 20.3, 21.4, 27.9, 28.0, 44.5, 67.9, 74.6, 74.7, 107.5, 124.1, 126.7, 128.2, 129.8, 130.9, 135.9, 141.2, 142.1. IR (KBr): 2925, 2860, 1730, 1495, 1454, 1261, 1228, ,1128, 1090, 1003 cm^{-1}. MS *m/z* (%): 370 (M^+, 11.4), 279 (100). High MS Calcd for $C_{22}H_{26}O_3S$–O: 354.1651. Found: 354.1650. **7b:** mp 125–126 ℃ (AcOEt). $[\alpha]_D^{25}$ +104.3 (c = 0.51, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.20–1.28 (m, 2H), 1.40–1.47 (m, 2H), 1.54–1.61 (m, 2H), 1.64–1.72 (m, 2H), 2.39 (s, 3H, Ar-C$\underline{H}_3$), 2.91 (d, 1H, *J* = 13.7 Hz, C$\underline{H}_2$SO), 3.11 (s, 2H, Ar-C$\underline{H}_2$), 3.28 (d, 1H, *J* = 13.7 Hz, C$\underline{H}_2$SO), 4.15 (dd, 1H, *J* = 6.0 , 5.2 Hz, C$\underline{H}$OC), 4.19 (dd, 1H, *J* = 6.0 , 5.2 Hz, C$\underline{H}$OC), 7.22–7.31 (m, 5H, Ar–$\underline{H}$), 7.38 (d, 2H, *J* = 6.8 Hz, Ar–$\underline{H}$), 7.45 (d, 2H, *J* = 7.7 Hz, Ar–$\underline{H}$). ^{13}C-NMR ($CDCl_3$) δ: 20.4, 20.5, ,21.4, 27.7, 27.9, 46.0, 65.7, 74.3, 74.3, 107.0, 124.0, 126.8, 128.0, 129.8, 131.4, 135.5, 141.2, 141.9. IR (KBr): 2927, 2854, 1733, 1495, 1456, 1259, 1093, 1039 cm^{-1}. MS *m/z* (%): 370 (M^+, 16.2), 217 (100). *Anal.* Calcd for $C_{22}H_{26}O_3S$: C, 71.32 ; H, 7.07 ; S, 8.66. Found : C, 71.10 ; H, 7.04 ; S, 8.61.

(*Rs*)-2-[(1*R*,2*S*)-2-Hydroxycyclopentyloxy]-3-(*p*-tolylsulfinyl)propene (8a), (*E*,*Rs*)-2-[(1*R*,2*S*)-2-Hydroxycyclopentyloxy]-1-(*p*-tolylsulfinyl)propene (8b), and (*Rs*)-2-[(1*S*,2*R*)-2-Hydroxycyclopentyloxy]-3-(*p*-tolylsulfinyl)propene (8c). Representative Procedure in Table 2: A solution of **4a** (52.1 mg, 0.186 mmol) in DME (1 ml) was added to a stirred LDA solution [prepared from *n*-BuLi (1.6 M in hexane; 0.697 ml, 1.12 mmol) and diisopropylamine (0.156 ml, 1.12 mmol) in DME (4 ml)] at –78 ℃ and the mixture was stirred at –78 ℃ for 30 min. The reaction was quenched with saturated NH_4Cl.

The organic layer was separated and the aqueous layer was extracted with AcOEt. The extract was washed with brine, and then dried. The solvent was evaporated and the residue was purified by preparative TLC with AcOEt–hexane (1 : 1) to afford **8a** (31.4 mg, 60 %), **8b** (7.6 mg, 15 %) and **8c** (8.9 mg, 17 %) each as a colorless oil. **8a:** $[\alpha]_D^{30}$ +169.5 (c = 1.09, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.47–1.62 (m, 1H), 1.70–1.93 (m, 5H), 2.42 (s, 3H, Ar–C$\underline{H}_3$), 3.35 (d, 1H, *J* = 13.3 Hz, C$\underline{H}_2$SO), 3.36–3.42 (bs, 1H, OH), 3.73 (d, 1H, *J* = 13.3 Hz, C$\underline{H}_2$SO), 3.81 (d, 1H, *J* = 2.6 Hz, C=C$\underline{H}_2$), 4.16 (d, 1H, *J* = 2.6 Hz, C=C$\underline{H}_2$), 4.18–4.26 (m, 1H, C$\underline{H}$OH), 4.18–4.26 (m, 1H, C$\underline{H}$OC), 7.32 (d, 2H, *J* = 8.6 Hz, Ar–$\underline{H}$), 7.49 (d, 2H, *J* = 8.6 Hz, Ar–$\underline{H}$). ^{13}C-NMR ($CDCl_3$) δ: 19.3, 21.3, 27.5, 30.6, 61.5, 71.1, 79.6, 89.6, 124.2, 129.7, 139.3, 141.5, 150.5. IR ($CHCl_3$): 3200–3400, 3000, 1630, 1290, 1035 cm^{-1}. MS *m/z* (%): 280 (M^+, 0.2), 140 (100). *Anal.* Calcd for $C_{15}H_{20}O_3S \cdot 1/3H_2O$: C, 62.91 ; H, 7,27 ; S, 11.19. Found : C, 62.94 ; H, 7.20 ; S, 11.26. **8b:** $[\alpha]_D^{29}$ +58.2 (c = 0.85, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.48 (m, 6H), 2.33 (s, 3H, CC$\underline{H}_3$), 2.41 (s, 3H, Ar–C$\underline{H}_3$), 4.02–4.13 (m, 1H, C$\underline{H}$OH), 4.24–4.28 (m, 1H, C$\underline{H}$OC), 5.44 (s, 1H, C=C$\underline{H}$), 7.30 (d, 2H, *J* = 8.6 Hz, Ar–$\underline{H}$), 7.48 (d, 2H, *J* = 8.6 Hz, Ar–$\underline{H}$). ^{13}C-NMR ($CDCl_3$) δ: 18.3, 19.6, 21.3, 27.7, 30.8, 72.7, 80.0, 109.2, 124.0, 129.8, 140.6, 142.6, 165.1. IR ($CHCl_3$): 3150–3550, 2990, 1600, 1385, 1305, 1085, 1026 cm^{-1}. MS *m/z* (%): 280 (M^+, 0.5), 127 (100). High MS Calcd for $C_{15}H_{20}O_3S$: 280.1133. Found: 280.1133. **8c:** $[\alpha]_D^{30}$ +201.9 (c = 1.20, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.47–1.57 (m, 1H), 1.67–1.92 (m, 5H), 2.42 (s, 3H, Ar–C$\underline{H}_3$), 2.80 (bs, 1H, OH), 3.48 (d, 1H, *J* = 12.8 Hz, C$\underline{H}_2$SO), 3.56 (d, 1H, *J* = 12.8 Hz, C$\underline{H}_2$SO), 4.12–4.17 (m, 1H, C$\underline{H}$OH), 4.20 (d, 1H, *J* = 3.1 Hz, C=C$\underline{H}_2$), 4.22–4.27 (m, 1H, C$\underline{H}$OC), 4.24 (d, 1H, *J* = 3.1 Hz, C=C$\underline{H}_2$), 7.32 (d, 2H, *J* = 8.2 Hz, Ar–$\underline{H}$), 7.55 (d, 2H, *J* = 8.2 Hz, Ar–$\underline{H}$). ^{13}C-NMR ($CDCl_3$) δ: 19.5, 21.4, 27.6, 30.9, 63.0, 72.0, 79.6, 89.5, 124.2, 129.8, 140.5, 141.7, 151.5. IR ($CHCl_3$): 3200–3600, 2950, 1630, 1290, 1039 cm^{-1}. MS *m/z* (%): 280 (M^+, 0.5), 140 (100). *Anal.* Calcd for $C_{15}H_{20}O_3S \cdot 1/4H_2O$: C, 62.91 ; H, 7,27 ; S, 11.19. Found : C, 62.94 ; H, 7.20 ; S, 11.26.

(1*S*,2*R*)-2-Acetoxycyclopentyl (*R*)-α-Methoxy-α-(trifluoromethyl)phenylacetate (9a). From 8a: Triethylamine (64 μl, 0.46 mmol) and dimethylaminopyridine (DMAP) (18.7 mg, 0.153 mmol) were added to a solution of **8a** (85.6 mg, 0.306 mmol) in CH_2Cl_2 (4 ml) at 0 ℃ and the whole was stirred at 0 ℃ for 10 min. (+)-MTPACl (86 μl, 0.46 mmol) was added to the stirred mixture at 0 ℃ and the mixture was stirred at 0 ℃ for 30 min. After the addition of saturated $NaHCO_3$, the whole was extracted with $CHCl_3$. The extract was washed with water and brine, and then dried. The solvent was evaporated and the residue was chromatographed on silica gel with AcOEt–hexane (1 : 2) to give (+)-MTPA ester (147 mg, 97 %) as a colorless oil. $[\alpha]_D^{24}$ +78.4 (c = 1.53, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.50–1.68 (m, 2H), 1.76–2.03 (m, 4H), 2.41 (s, 3H, Ar–C$\underline{H}_3$), 3.23 (d, 1H, *J* = 12.8 Hz, C$\underline{H}_2$SO), 3.34 (d, 1H, *J* = 12.8 Hz, C$\underline{H}_2$SO), 3.55 (s, 3H, OC$\underline{H}_3$), 4.00 (d, 1H, *J* = 2.6 Hz, C=C$\underline{H}_2$), 4.05 (d, 1H, *J* = 2.6 Hz, C=C$\underline{H}_2$), 4.38 (dd, 1H, *J* = 11.1, 6.0 Hz, C$\underline{H}$OC), 5.32 (dd, 1H, *J* = 11.1, 6.0 Hz, C$\underline{H}$OC), 7.25–7.30 (m, 2H, Ar–$\underline{H}$), 7.37–7.44 (m, 5H, Ar–$\underline{H}$), 7.52–7.56 (m, 2H, Ar–$\underline{H}$). ^{13}C-NMR ($CDCl_3$) δ: 19.1, 21.4, 27.5, 28.1, 55.3, 63.1, 76.4, 76.8, 89.1, 121.1, 124.3, 125.4, 127.5, 128.3, 129.5, 129.6, 132.0, 140.2, 141.5, 151.0, 165.9. IR ($CHCl_3$): 3000, 2950, 1760, 1645, 1305, 1185, 1033 cm^{-1}. MS *m/z* (%): 496 (M^+, 35.9), 189 (100). *Anal.* Calcd for $C_{25}H_{27}F_3O_5S$: C, 60.47 ; H, 5.48 Found : C, 60.20 ; H, 5.63. 1N HCl (0.03 ml) was added to a solution of the (+)-MTPA ester of **8a** (78.2 mg, 0.158 mmol) in acetone (5 ml) at 25 ℃ and the mixture was stirred at 25 ℃ for 30 min. After the addition of saturated $NaHCO_3$, acetone was evaporated and the residue was extracted with AcOEt. The extract was washed with brine and dried. The solvent was evaporated and the resulting alcohol was used in the next step without further purification. Acetic anhydride (45 μl, 0.47 mmol) was added to a solution of the crude alcohol in pyridine (2ml) at 25 ℃ and the mixture was stirred at 25 ℃ for 10 h. After the addition of 1N HCl, the whole was extracted with CH_2Cl_2. The extract was washed with brine and dried. The solvent was evaporated and the

residue was purified by preparative TLC with AcOEt–hexane (1 : 5) to give **9a** [14] (50.1 mg, 88 %) as a colorless oil. $[\alpha]_D^{24}$ +42.8 (c = 1.27, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.61–1.70 (m, 1H), 1.71–1.80 (m, 1H), 1.84–1.94 (m, 2H), 1.90 (s, 3H, $OCOC\underline{H}_3$), 1.99–2.10 (m, 2H), 3.55 (s, 3H, $OC\underline{H}_3$), 5.13 (td, 1H, *J* = 7.7, 4.3 Hz, C<u>H</u>OAc), 5.44 (dd, 1H, *J* = 9.4, 4.3 Hz, C<u>H</u>O(+)-MTPA), 7.38–7.42 (m, 3H, Ar–<u>H</u>), 7.53–7.56 (m, 2H, Ar–<u>H</u>). ^{13}C-NMR ($CDCl_3$) δ: 19.0, 20.7, 27.7, 28.5, 55.3, 74.1, 76.3, 121.2, 125.4, 127.4, 128.4, 129.6, 132.2, 165.7, 170.4. IR ($CHCl_3$): 2990, 1745, 1605, 1172, 1045 cm^{-1}. MS *m/z* (%): 360 (M^+, 0.6), 189 (100). High MS Calcd for $C_{17}H_{19}F_3O_5$: 360.1182. Found: 360.1179.

From 8b: By a similar procedure to that described for (+)-MTPA esterification of **8a**, **8b** (16.6 mg, 0.0593 mmol) was converted into the (+)-MTPA ester (27.0 mg, 92 %) as colorless crystals, mp 95–96℃ (AcOEt–hexane). $[\alpha]_D^{25}$ +6.7 (c = 1.00, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.56–1.71 (m, 2H), 1.81–2.06 (m, 4H), 2.05 (s, 3H, $CC\underline{H}_3$), 2.40 (s, 3H, Ar–$C\underline{H}_3$), 3.56 (s, 3H, $OC\underline{H}_3$), 4.53 (dd, 1H, *J* = 10.3, 6.0 Hz, C<u>H</u>OC), 5.36 (s, 1H, C=C<u>H</u>), 5.34–5.39 (m, 1H, C<u>H</u>OC), 7.30 (d, 2H, *J* = 8.6 Hz, Ar–<u>H</u>), 7.41–7.44 (m, 3H, Ar–<u>H</u>), 7.47 (d, 2H, *J* = 8.6 Hz, Ar–<u>H</u>), 7.53–7.56 (m, 2H, Ar–<u>H</u>). ^{13}C-NMR ($CDCl_3$) δ: 17.8, 19.1, 21.2, 27.6, 28.0, 55.3, 76.0, 77.2, 108.8, 121.0, 123.9, 125.3, 127.3, 128.3, 129.6, 129.7, 132.0, 140.4, 142.7, 164.7, 165.6. IR ($CHCl_3$): 3000, 1750, 1600, 1100–1300 cm^{-1}. MS *m/z* (%): 496 (M^+, 5.7), 480 (100). *Anal.* Calcd for $C_{25}H_{27}F_3O_5S$: C, 60.47 ; H, 5.48. Found : C, 60.37 ; H, 5.48. By a similar procedure to that described for the preparation of **9a**, the (+)-MTPA ester of **8b** (109 mg, 0.220 mmol) was converted into **9a** [14] (71.3 mg, 90 %) as a colorless oil.

(1*S*,2*R*)-2-Acetoxycyclopentyl (*S*)-α-Methoxy-α-(trifluoromethyl)phenylacetate (9b). By a similar procedure to that described for (+)-MTPA esterification of **8a**, **8a** (51.0 mg, 0.182 mmol) was converted into the (–)-MTPA ester (84.9 mg, 94 %) as a colorless oil. $[\alpha]_D^{28}$ +42.6 (c = 1.50, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.52–1.71 (m, 2H), 1.74–1.86 (m, 2H), 1.88–2.02 (m, 2H), 2.40 (s, 3H, Ar–$C\underline{H}_3$), 3.30 (d, 1H, *J* = 12.8 Hz, $C\underline{H}_2SO$), 3.51 (d, 1H, *J* = 12.8 Hz, $C\underline{H}_2SO$), 3.58 (s, 3H, $OC\underline{H}_3$), 4.09 (d, 1H, *J* = 2.6 Hz, C=C<u>H</u>$_2$), 4.12 (d, 1H, *J* = 2.6 Hz, C=C<u>H</u>$_2$), 4.36–4.40 (m, 1H, C<u>H</u>OC), 5.34 (dd, 1H, *J* = 9.4, 4.3 Hz, C<u>H</u>OC), 7.26–7.30 (m, 2H, Ar–<u>H</u>), 7.38–7.44 (m, 5H, Ar–<u>H</u>), 7.56–7.60 (m, 2H, Ar–<u>H</u>). ^{13}C-NMR ($CDCl_3$) δ: 19.0, 21.4, 27.3, 28.1, 55.4, 63.5, 76.5, 77.4, 89.4, 121.2, 124.3, 125.4, 127.5, 128.3, 129.6, 129.6, 132.2, 140.2, 141.6, 151.2, 165.8. IR ($CHCl_3$): 3000, 1750, 1639, 1295, 1179, 1042 cm^{-1}. MS *m/z* (%): 496 (M^+, 4.7), 189 (100). *Anal.* Calcd for $C_{25}H_{27}F_3O_5S$: C, 60.47 ; H, 5.48. Found : C, 60.48 ; H, 5.55. By a similar procedure to that described for the preparation of **9a**, the (–)-MTPA ester of **8a** (81.1 mg, 0.164 mmol) was converted into **9b** (53.0 mg, 90 %) as a colorless oil. $[\alpha]_D^{22}$ –9.0 (c = 1.82, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.60–1.68 (m, 1H), 1.74–1.91 (m, 3H), 1.96 (s, 3H, $OCOC\underline{H}_3$), 1.97–2.09 (m, 2H), 3.58 (s, 3H, $OC\underline{H}_3$), 5.17 (td, 1H, *J* = 7.7, 4.3 Hz, C<u>H</u>OAc), 5.44 (dd, 1H, *J* = 8.6, 4.3 Hz, C<u>H</u>O(+)-MTPA), 7.38–7.42 (m, 3H, Ar–<u>H</u>), 7.56–7.59 (m, 2H, Ar–<u>H</u>). ^{13}C-NMR ($CDCl_3$) δ: 19.0, 20.7, 27.6, 28.4, 55.3, 74.2, 76.5, 121.2, 125.4, 127.4, 128.3, 129.6, 132.2, 165.8, 170.3. IR ($CHCl_3$): 2990, 2955, 1745, 1169, 1045 cm^{-1}. MS *m/z* (%): 360 (M^+, 0.6), 189 (100). High MS Calcd for $C_{17}H_{19}F_3O_5$: 360.1185. Found: 360.1185.

(1*R*,2*S*)-2-Acetoxycyclopentyl (*S*)-α-Methoxy-α-(trifluoromethyl)phenylacetate (ent.-9a). By a similar procedure to that described for (+)-MTPA esterification of **8a**, **8c** (62.7 mg, 0.126 mmol) was converted into the (–)-MTPA ester (101 mg, 91 %) as a colorless oil. $[\alpha]_D^{26}$ +92.2 (c = 1.25, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.58–1.67 (m, 1H), 1.78–2.08 (m, 5H), 2.41 (s, 3H, Ar–$C\underline{H}_3$), 3.04 (d, 1H, *J* = 12.8 Hz, $C\underline{H}_2SO$), 3.34 (d, 1H, *J* = 12.8 Hz, $C\underline{H}_2SO$), 3.55 (s, 3H, $OC\underline{H}_3$), 4.14 (d, 1H, *J* = 2.6 Hz, C=C<u>H</u>$_2$), 4.16 (d, 1H, *J* = 2.6 Hz, C=C<u>H</u>$_2$), 4.47 (dd, 1H, *J* = 10.3, 6.0 Hz, C<u>H</u>OC), 5.33 (dd, 1H, *J* = 10.3, 6.0 Hz, C<u>H</u>OC), 7.26–7.28 (m, 2H, Ar–<u>H</u>), 7.34–7.39 (m, 3H, Ar–<u>H</u>), 7.41–7.43 (m, 2H, Ar–<u>H</u>), 7.54–7.56 (m, 2H, Ar–<u>H</u>).

^{13}C-NMR ($CDCl_3$) δ: 19.0, 21.3, ,27.7, 28.3, 55.3, 64.3, 76.4, 76.7, 89.5, 121.1, 124.1, 125.3, 127.5, 128.3 129.5, 129.7, 132.1, 140.7, 141.5, 151.0, 165.9. IR ($CHCl_3$): 3002, 1750, 1639, 1299, 1178, 1050 cm^{-1}. MS *m/z* (%): 496 (M^+, 7.5), 189 (100). *Anal.* Calcd for $C_{25}H_{27}F_3O_5S \cdot 1/4H_2O$: C, 59.93 ; H, 5.53. Found : C, 60.00 ; H, 5.57. By a similar procedure to that described for the preparation of **9a**, the (–)-MTPA ester of **8c** (155 mg, 0.312 mmol) was converted into **ent.-9a** (99 mg, 88 %) as a colorless oil. $[\alpha]_D^{24}$ –46.0 (c = 1.11 $CHCl_3$). The spectroscopic data (^{1}H-NMR, ^{13}C-NMR, IR, and MS) was consistent with data for **9a**.

(1*R*,2*S*)-2-Acetoxycyclopentyl (*R*)-α-Methoxy-α-(trifluoromethyl)phenylacetate (ent.-9b). By a similar procedure to that described for (+)-MTPA esterification of **8a**, **8c** (35.4 mg, 0.126 mmol) was converted into the (+)-MTPA ester (59.0 mg, 94 %) as a colorless oil. $[\alpha]_D^{25}$ +117.6 (c = 1.65, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.56–1.66 (m, 1H), 1.77–1.88 (m, 3H), 1.92–2.05 (m, 2H), 2.41 (s, 3H, Ar–C$\underline{H}_3$), 3.24 (d, 1H, *J* = 12.8 Hz, C$\underline{H}_2$SO), 3.46 (d, 1H, *J* = 12.8 Hz, C$\underline{H}_2$SO), 3.58 (s, 3H, OC$\underline{H}_3$), 4.20 (s, 1H, *J* = 3.5 Hz, C=C$\underline{H}_2$), 4.21 (s, 1H, *J* = 3.5 Hz, C=C$\underline{H}_2$), 4.44–4.48 (m, 1H, CH_2C$\underline{H}$O), 5.34–5.38 (m, 1H, CH2C$\underline{H}$O), 7.29 (d, 2H, *J* = 8.6 Hz, Ar–$\underline{H}$), 7.36–7.40 (m, 3H, Ar–$\underline{H}$), 7.47 (d, 2H, *J* = 8.6 Hz, Ar–$\underline{H}$), 7.55–7.58 (m, 2H, Ar–$\underline{H}$). ^{13}C-NMR ($CDCl_3$) δ: 19.0, 21.4, 27.5, 28.3, 55.4, 64.3, 76.5, 77.3, 89.8, 121.2, 124.1, 125.4, 127.5, 128.3, 129.6, 129.8, 132.1, 140.6, 141.6, 151.1, 165.9. IR ($CHCl_3$): 2980, 1740, 1625, 1285, 1162, 1038 cm^{-1}. MS *m/z* (%): 496(M^+, 7.5), 189 (100). *Anal.* Calcd for $C_{25}H_{27}F_3O_5S \cdot 1/4H_2O$: C, 59.93 ; H, 5.53. Found : C, 59.90 ; H, 5.53. By a similar procedure to that described for the preparation of the **9a**, the (+)-MTPA ester of **8c** (139 mg, 0.281 mmol) was converted into **ent.-9b** [14] (91 mg, 90 %) as a colorless oil. $[\alpha]_D^{23}$ +8.9 (c = 1.07, $CHCl_3$). The spectroscopic data (^{1}H-NMR, ^{13}C-NMR, IR, and MS) was consistent with data for **9b**.

(1*R*,2*S*)- and (1*S*,2*R*)-2-[(*R*)-α-Methoxy-α-(trifluoromethyl)phenylacetoxy]cyclopentyl (*Rs*)-(*p*-Tolylsulfinyl)acetate (16a and 16b). Representative Procedure in Table 3: TMEDA (0.382 ml, 2.53 mmol) was added to a stirred LDA solution [prerared from *n*-BuLi (1.6 M in hexane; 1.58 ml, 2.53 mmol) and diisopropylamine (0.354 ml, 2.53 mmol) in THF (30 ml)] at –78 ℃ and the mixture was stirred at –78 ℃ for 5 min. A solution of **6b** (300 mg, 0.843 mmol) in THF (10 ml) was added dropwise to the stirred mixture at –78 ℃ and the whole was stirred at –78 ℃ for 30 min. The reaction was quenched with saturated NH_4Cl. The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layers were washed with water and brine, and then dried. The solvent was evaporated and the residue was chromatographed on silica gel with AcOEt–hexane (2 : 1) to give a mixture of **10a** and **10b** (277 mg, 92 %). The diastereomeric mixture was used in the next step without further purification. Triethylamine (0.163 ml, 1.17mmol) and DMAP (47.5 mg, 0.389 mmol) were added to a solution of the mixture of **10a** and **10b** (277 mg, 0.778 mmol) in CH_2Cl_2 (10 ml) at 0 ℃ and the whole was stirred at 0 ℃ for 10 min. (+)-MTPACl (0.218 ml, 1.17 mmol) was added to the stirred mixture at 0 ℃ and the mixture was stirred at 0 ℃ for 30 min. After the addition of saturated $NaHCO_3$, the whole was extracted with $CHCl_3$. The extract was washed with water and brine, and then dried. The solvent was evaporated and the residue was chromatographed on silica gel with AcOEt–hexane (1 : 2) to give (+)-MTPA ester (436 mg, 98 %). The crude product was used in the next step without further purification. A stream of ozone was bubbled through the solution of (+)-MTPA ester (436 mg, 0.762 mmol) in MeOH (8 ml) at –78 ℃ until a pale blue color developed. Nitrogen was allowed to bubble through the solution to remove excess ozone. Dimethyl sulfide (0.60 ml, 7.6 mmol) was added to the solution. The whole was allowed to warm to 25 ℃ and stirred for 1 h. The solvent was evaporated and the residue was chromatographed on silica gel with AcOEt–hexane (1 : 1) to give a mixture of **16a** and **16b** (372 mg, 98 %). The mixture was separated by HPLC [AcOEt : hexane = 2 : 5, flow rate = 4 ml/min, tR = 39.7 min (**16a**), tR =

45.8 min (**16b**)] to afford **16a** (350 mg, 92 %) and **16b** (22.0 mg, 6 %) each as a colorless oil. **16a**: $[\alpha]_D^{28}$ –20.9 (c = 1.05, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.58–1.70 (m, 2H), 1.79–2.10 (m, 4H), 2.42 (s, 3H, Ar–C$\underline{H}_3$), 3.40 (d, 1H, *J* = 13.7 Hz, C$\underline{H}_2$SO), 3.53 (brs, 3H, OC$\underline{H}_3$), 3.63 (d, 1H, *J* = 13.7 Hz, C$\underline{H}_2$SO), 5.11 (td, 1H, *J* = 6.8, 4.3 Hz, C$\underline{H}$OC), 5.36 (dd, 1H, *J* = 10.3, 4.3 Hz, C$\underline{H}$OC), 7.32 (d, 2H, *J* = 8.1 Hz, Ar–$\underline{H}$), 7.38–7.42 (m, 3H, Ar–$\underline{H}$), 7.50–7.55 (m, 4H, Ar–$\underline{H}$). ^{13}C-NMR ($CDCl_3$) δ: 19.0, 21.4, 27.7, 28.3, 55.3, 61.2, 75.4, 76.1, 121.1, 124.2, 125.3, 127.4, 128.4, 129.7, 130.0, 132.1, 139.8, 142.4, 163.9, 165.8. IR ($CHCl_3$): 3005, 2950, 1737, 1585, 1031 cm^{-1}. MS *m/z* (%): 498 (M^+, 5.5), 139 (100). *Anal.* Calcd for $C_{24}H_{25}F_3O_6S$: C, 57.82 ; H, 5.05. Found : C, 57.76 ; H, 5.19. **16b**: $[\alpha]_D^{30}$ +124.4 (c = 1.19, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.58–1.76 (m, 2H), 1.80–1.92 (m, 2H), 1.95–2.10 (m, 2H), 2.43 (s, 3H, Ar–C$\underline{H}_3$), 3.39 (d, 1H, *J* = 13.9 Hz, C$\underline{H}_2$SO), 3.51 (brs, 3H, OC$\underline{H}_3$), 3.60 (d, 1H, *J* = 13.9 Hz, C$\underline{H}_2$SO), 5.15 (td, 1H, *J* = 6.8, 4.3 Hz, C$\underline{H}$OC), 5.36 (dd, 1H, *J* = 9.6, 4.3 Hz, C$\underline{H}$OC), 7.33 (d, 2H, *J* = 8.2 Hz, Ar–$\underline{H}$), 7.35–7.40 (m, 3H, Ar–$\underline{H}$), 7.47–7.51 (m, 2H, Ar–$\underline{H}$), 7.53 (d, 2H, *J* = 8.2 Hz, Ar–$\underline{H}$). ^{13}C-NMR ($CDCl_3$) δ: 18.9, 21.3, 27.6, 28.3, 55.2, 61.2, 75.3, 76.0, 121.0, 124.1, 125.2, 127.3, 128.3, 129.5, 130.0, 132.0, 140.0, 142.3, 164.2, 165.6. IR ($CHCl_3$): 3040, 2980, 1745, 1600, 1040 cm^{-1}. MS *m/z* (%): 498 (M^+, 7.6), 139 (100). *Anal.* Calcd for $C_{24}H_{25}F_3O_6S$: C, 57.82 ; H, 5.05. Found : C, 57.78 ; H, 5.11.

(1*R*,2*S*)- and (1*S*,2*R*)-2-[(*R*)-α-Methoxy-α-(trifluoromethyl)phenylacetoxy]cyclopentyl (*R*s)-(*p*-Tolylsulfinyl)acetate (16a and 16b). A solution of **6b** (23.2 mg, 0.0651 mmol) in THF (1 ml) was added dropwise to a stirred LDA solution [prerared from *n*-BuLi (1.6 M in hexane; 122 μl, 0.195 mmol) and diisopropylamine (27.3 μl, 0.195 mmol) in THF (3 ml)] at –78 ℃ and the mixture was stirred at –78 ℃ for 30 min. The reaction was quenched with saturated NH_4Cl. The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layers were washed with water and brine, and then dried. The solvent was evaporated and the residue was purified by preparative TLC with AcOEt–hexane (1 : 1) to give a mixture of (*Z*)-**10a** and (*Z*)-**10b** [18.6 mg, 80%, (*Z*)-**10a** : (*Z*)-**10b** = 87 : 13] and (*E*)-**10a** and (*E*)-**10b** [2.5 mg, 11%, (*E*)-**10a** : (*E*)-**10b** = 83 : 17]. By a similar procedure to that described for the preparation of a mixture of **16a** and **16b** from a mixture of (*E*/*Z*)-**10a** and (*E*/*Z*)-**10b**, a mixture of (*Z*)-**10a** and (*Z*)-**10b** [7.4 mg, 0.021 mmol, (*E*)-**10a** : (*E*)-**10b** = 87 : 13] was converted into a mixture of **16a** and **16b**, which was purified by preparative TLC with AcOEt–hexane (1 : 1) [9.3 mg, 90 % in 2 steps, **16a** : **16b** = 81 : 19]. By a similar procedure to that described for the preparation of a mixture of **16a** and **16b** from a mixture of (*E*/*Z*)-**10a** and (*E*/*Z*)-**10b**, a mixture of (*E*)-**10a** and (*E*)-**10b** [2.4 mg, 0.0070 mmol, (*E*)-**10a** : (*E*)-**10b** = 83 : 17] was converted into a mixture of **16a** and **16b** [3.3 mg, 94 % in 2 steps, **16a** : **16b** = 86 : 14].

(1*S*,2*R*)-2-Acetoxycyclopentyl (*R*)-α-Methoxy-α-(trifluoromethyl)phenylacetate (9a).
From 16a: An excess of Raney Ni (W2) was added to a solution of **16a** (14.2 mg, 0.0285 mmol) in EtOH (1 ml) at 25 ℃ and stirred at 25 ℃ for 5 min, then filtered. The solvent was evaporated and the residue was chromatographed on silica gel with AcOEt–hexane (1 : 2) to give **9a**[14] (10.2 mg, quant.) as a colorless oil.

(1*S*,2*R*)-2-Acetoxycyclopentyl (*S*)-α-Methoxy-α-(trifluoromethyl)phenylacetate (ent.-9b).
From 16b: By a similar procedure to that described for the preparation of **9a** from **16a**, **16b** (18.2 mg, 0.0365 mmol) was converted into **ent.-9b**[14] (13.1 mg, quant.) as a colorless oil.

(*E*,*R*s)- and (*Z*,*R*s)-2-[(1*R*,2*S*)-2-Hydroxycyclohexyloxy]-1-phenyl-3-(*p*-tolylsulfinyl)]-propene [(*E*)- and (*Z*)-11a], (*E*,*R*s)-2-[(1*R*,2*S*)-2-Hydroxycyclohexyloxy]-3-phenyl-1-(*p*-tolylsulfinyl)]propene [(*E*)-11b], and (*E*,*R*s)- and (*Z*,*R*s)-2-[(1*S*,2*R*)-2-Hydroxycyclohexyl-

oxy]-1-phenyl-3-(*p*-tolylsulfinyl)]propene [(*E*)- and (*Z*)-11c]. Representative Procedure in Table 3: A solution of acetal **7b** (100 mg, 0.270 mmol) in THF (2ml) was added to a stirred LDA solution [prepared from *n*-BuLi (1.6 M in hexane; 0.844 ml, 1.35 mmol) and diisopropylamine (0.188 ml, 1.35 mmol) in THF (8 ml)] at –78 °C and the mixture was stirred at –78 °C for 30 min. The reaction was quenched with saturated NH_4Cl. The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layers were washed with brine and dried. The solvent was evaporated and the residue was chromatographed on silica gel with AcOEt–hexane (1 : 2) to give a mixture of (*Z*)-**11a** and (*Z*)-**11c** [75.1 mg, 75 %, (*Z*)-**11a** : (*Z*)-**11c** = 96 : 4], (*E*)-**11a** (3.8 mg, 4 %), (*E*)-**11b** (13.3 mg, 13 %), and (*E*)-**11c** (2.9 mg, 3%) each as colorless crystals. A mixture of (*Z*)-**11a** and (*Z*)-**11c**: ^{1}H-NMR ($CDCl_3$) δ: 1.19–1.33 (m, 2H, C$\underline{H}_2$), 1.41–1.67 (m, 4H, C$\underline{H}_2$), 1.70–1.83 (m, 2H, C$\underline{H}_2$), 2.39 (s, 3×4/100H, Ar–C$\underline{H}_3$), 2.41 (s, 3×96/100H, Ar–C$\underline{H}_3$), 3.53 (d, 1×96/100H, *J* = 13.7 Hz, C$\underline{H}_2$SO), 3.73 (d, 1×4/100H, *J* = 13.7 Hz, C$\underline{H}_2$SO), 3.66–3.75 (m, 1H, C$\underline{H}$OH), 3.79 (d, 1×4/100H, *J* = 13.7 Hz, C$\underline{H}_2$SO), 3.97 (d, 1×96/100H, *J* = 13.7 Hz, C$\underline{H}_2$SO), 4.11–4.19 (m, 1H, C$\underline{H}$OC), 5.40 (s, 1×4/100H, C=C$\underline{H}$), 5.60 (s, 1×96/100H, C=C$\underline{H}$), 7.19 (d, 1×96/100H, *J* = 7.7 Hz, Ar–$\underline{H}$), 7.20 (d, 1×4/100H, *J* = 7.7 Hz, Ar–$\underline{H}$), 7.27–7.34 (m, 4H, Ar–$\underline{H}$), 7.43(d, 2×4/100H, *J* = 7.7 Hz, Ar–$\underline{H}$), 7.49 (d, 2×96/100H, *J* = 7.7 Hz, Ar–$\underline{H}$), 7.55 (d, 2×4/100H, *J* = 8.5 Hz, Ar–$\underline{H}$), 7.57 (d, 2×96/100H, *J* = 8.5 Hz, Ar–$\underline{H}$). IR (KBr): 3388, 2937, 2862, 1727, 1641, 1597, 1493, 1446, 1363, 1170, 1083, 1039 cm^{-1}. MS *m/z* (%): 370 (M^+, 18.7), 91 (100). (*E*)-**11a:** mp 103–105 °C (AcOEt–hexane). $[\alpha]_D^{26}$ –45.8 (c = 0.58, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.30–1.44 (m, 2H), 1.56–1.78 (m, 4H), 1.82–1.89 (m, 1H), 2.01–2.09 (m, 1H), 2.38 (s, 3H, Ar-C$\underline{H}_3$), 3.73 (d, 1H, *J* = 13.3 Hz, C$\underline{H}_2$SO), 3.93 (d, 1H, *J* = 13.3 Hz, C$\underline{H}_2$SO), 3.94–3.99 (m, 1H, C$\underline{H}$OH), 4.32–4.37 (m, 1H, C$\underline{H}$OC), 5.92 (s, 1H, C=C$\underline{H}$Ph), 6.92 (d, 2H, *J* = 6.9 Hz, Ar–$\underline{H}$), 7.11–7.20 (m, 5H, Ar–$\underline{H}$), 7.38 (d, 2H, *J* = 8.5 Hz, Ar–$\underline{H}$). ^{13}C-NMR ($CDCl_3$) δ: 21.4, 21.6, 22.1, 26.7, 30.5, 57.6, 67.6, 76.9, 107.3, 124.2, 126.1, 128.1, 128.8, 129.8, 135.5, 139.4, 141.6, 146.6. IR (KBr): 3375, 2927, 2854, 1734, 1641, 1495, 1446, 1400, 1240, 1180 1140, 1084, 1041 cm^{-1}. MS *m/z* (%): 370 (M^+, 1.7), 133 (100). *Anal.* Calcd for $C_{22}H_{26}O_3S$: C, 71.32 ; H, 7.07 ; S, 8.66. Found : C, 71.12 ; H, 7.06 ; S, 8.63. (*E*)-**11b:** mp 109–110 °C (AcOEt–hexane). $[\alpha]_D^{27}$ –67.5 (c = 0.58, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.15–1.80 (m, 8H), 2.39 (s, 3H, Ar-C$\underline{H}_3$), 3.73–3.78 (m, 1H, C$\underline{H}$OH), 3.95 (d, 1H, *J* = 14.1 Hz, C$\underline{H}_2$SO), 4.08 (d, 1H, *J* = 14.1 Hz, C$\underline{H}_2$SO), 4.13–4.18 (m, 1H, C$\underline{H}$OC), 5.52 (s, 1H, C=C$\underline{H}$), 7.28–7.39 (m, 7H, Ar–$\underline{H}$), 7.43 (d, 2H, *J* = 8.6 Hz, Ar–$\underline{H}$). ^{13}C-NMR ($CDCl_3$) δ: 20.8, 21.3, 21.8, 25.7, 30.2, 38.3, 68.1, 77.7, 109.3, 124.1, 127.2, 128.8, 128.9, 129.9, 136.9, 140.6, 142.5, 166.0. IR (KBr): 3394, 3346, 2937, 2860, 1734, 1593, 1495, 1450, 1313, 1219, 1163, 1082, 1032 cm^{-1}. MS *m/z* (%): 370 (M^+, 25.7), 224 (100). *Anal.* Calcd for $C_{22}H_{26}O_3S$: C, 71.32 ; H, 7.07 ; S, 8.66. Found : C, 71.08 ; H, 7.03 ; S, 8.57. (*E*)-**11c:** mp 107–108 °C (AcOEt–hexane). $[\alpha]_D^{25}$ +270.2 (c = 0.69, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.34–1.42 (m, 2H), 1.58–1.75 (m, 4H), 1.80–1.89 (m, 1H), 2.03–2.12 (m, 1H), 2.40 (s, 3H, Ar-C$\underline{H}_3$), 3.64 (d, 1H, *J* = 12.8 Hz, C$\underline{H}_2$SO), 3.74 (d, 1H, *J* = 12.8 Hz, C$\underline{H}_2$SO), 3.85–3.94 (m, 1H, C$\underline{H}$OH), 4.39–4.12 (m, 1H, C$\underline{H}$OC), 6.03 (s, 1H, C=C$\underline{H}$Ph), 7.20 (d, 2H, *J* = 8.6 Hz, Ar–$\underline{H}$), 7.22–7.29 (m, 5H, Ar–$\underline{H}$), 7.50 (d, 2H, *J* = 8.6 Hz, Ar–$\underline{H}$). ^{13}C-NMR ($CDCl_3$) δ: 21.4, 21.6, 22.0, 26.9, 30.5, 59.8, 68.3, 77.5, 107.1, 123.9, 126.4, 128.3, 128.8, 129.9, 135.8, 140.7, 141.7, 148.4. IR (KBr): 3425, 2929, 2854, 1735, 1639, 1495, 1446, 1400, 1243, 1182, 1128, 1083, 1041 cm^{-1}. MS *m/z* (%): 370 (M^+, 25.1), 91 (100). *Anal.* Calcd for $C_{22}H_{26}O_3S$: C, 71.32 ; H, 7.07 ; S, 8.66. Found : C, 71.11 ; H, 7.04 ; S, 8.59.

(1*R*, 2*S*)-2-Methoxyethoxymethoxycyclohexyl (*R*)-α-Methoxy-α-(trifluoromethyl)phenylacetate (17a). From (*E*)-11a: MEMCl (43 μl, 0.38 mmol) was added to a mixture of alcohol (*E*)-**11a** (70.0 mg, 0.189 mmol) and diisopropylethylamine (99 μl, 0.57 mmol) in CH_2Cl_2 (1 ml) at 25 °C and the mixture was stirred at 25 °C for 36 h. After the addition of saturated $NaHCO_3$, the whole was extracted with Et_2O.

The extract was washed with saturated NH_4Cl and brine, and then dried. The solvent was evaporated and the residue was chromatographed on silica gel with AcOEt–hexane (2 : 1) to give MEM ether (75.0 mg, 87 %) as a colorless oil. $[\alpha]_D^{26}$ +25.5 (c = 0.99, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.35–1.46 (m, 2H), 1.60–1.76 (m, 4H), 1.91–2.07 (m, 2H), 2.38 (s, 3H, Ar–C$\underline{H}_3$), 3.37 (s, 3H, OC$\underline{H}_3$), 3.57 (t, 2H, J = 4.7 Hz, C$\underline{H}_2$OCH$_3$), 3.64 (d, 1H, J = 12.8 Hz, C$\underline{H}_2$SO), 3.74–3.79 (m, 1H, OC$\underline{H}_2$CH$_2$OCH$_3$), 3.80–3.85 (m, 1H, OC$\underline{H}_2$CH$_2$OCH$_3$), 3.91–3.94 (m, 1H, C$\underline{H}$OC), 3.95 (d, 1H, J = 12.8 Hz, C$\underline{H}_2$SO), 4.36–4.40 (m, 1H, C$\underline{H}$OC), 4.88 (s, 2H, OC$\underline{H}_2$O), 5.90 (s, 1H, C=C$\underline{H}$), 7.05 (d, 2H, J = 7.3 Hz, Ar–$\underline{H}$), 7.14 (t, 1H, J = 7.3 Hz, Ar–$\underline{H}$), 7.21 (t, 4H, J = 8.1 Hz, Ar–$\underline{H}$), 7.46 (d, 2H, J = 8.1 Hz, Ar–$\underline{H}$). ^{13}C-NMR ($CDCl_3$) δ: 21.4, 21.8, 22.0, 26.5, 28.4, 59.0, 60.5, 66.9. 71.8, 74.8, 75.7, 94.6, 107.0, 124.2, 126.1, 128.1, 128.9, 129.7, 135.6, 140.9, 141.5, 147.6. IR (KBr): 2939, 1639, 1492, 1446, 1398, 1240, 1184, 1130, 1047 cm^{-1}. MS *m/z* (%): 458 (M^+, 11.3), 89 (100). *Anal.* Calcd for $C_{26}H_{34}O_5S$: C, 67.43 ; H, 7.51 ; S, 6.92. Found : C, 67.46 ; H, 7.59 ; S, 6.52. 1N HCl (0.03 ml) was added to a solution of MEM ether (14.5 mg, 0.0316 mmol) in acetone (1 ml) at 25 ℃ and the mixture was stirred at 25 ℃ for 15 min. After the addition of saturated $NaHCO_3$, acetone was evaporated and the residue was extracted with AcOEt. The extract was washed with brine and dried. The solvent was evaporated and the residue was diluted with CH_2Cl_2 (2 ml). DMAP (19.3 mg, 0.158 mmol) was added to the solution with stirring at 0 ℃ and the whole was stirred at 0 ℃ for 10 min. (+)-MTPACl (18 μl, 0.095 mmol) was added to the stirred mixture at 0 ℃ and the whole was stirred at 25 ℃ for 30 min. After the addition of saturated $NaHCO_3$, the whole was extracted with Et_2O. The extract was washed with saturated NH_4Cl and brine, and then dried. The solvent was evaporated and the residue was chromatographed on silica gel with AcOEt–hexane (2 : 1) to give **17a** (10.6 mg, 80 % in 2 steps) as a colorless oil.

From (*E*)-11b: By a similar procedure to that described for the preparation of the MEM ether from (*E*)-**11a**, (*E*)-**11b** (35.2 mg, 0.0951 mmol) was converted into MEM ether (38.5 mg, 88 %) as a colorless oil. $[\alpha]_D^{24}$ –41.1 (c = 1.32, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.10–1.39 (m, 4H), 1.48–1.86 (m, 4H), 2.39 (s, 3H, Ar-C$\underline{H}_3$) 3.37 (s, 3H, OC$\underline{H}_3$), 3.48–3.55 (m, 2H, C$\underline{H}_2$OCH$_3$), 3.62–3.66 (m, 2H, OC$\underline{H}_2$CH$_2$OCH$_3$), 3.72–3.77 (m, 1H, C$\underline{H}$OC), 3.85 (d, 1H, J = 13.7 Hz, Ar-C$\underline{H}_2$), 4.19 (d, 1H, J = 13.7 Hz, Ar-C$\underline{H}_2$), 4.23–4.28 (m, 1H, C$\underline{H}$OC), 4.65 (d, 1H, J = 6.7 Hz, OC$\underline{H}_2$O), 4.70 (d, 1H, J = 6.7 Hz, OC$\underline{H}_2$O), 5.44 (s, 1H, C$\underline{H}$=C), 7.23–7.40 (m, 9H, Ar–$\underline{H}$). ^{13}C-NMR ($CDCl_3$) δ: 21.3, 21.3, 21.8, 26.0, 28.0, 38.3, 59.0, 66.9, 71.7, 74.4, 76.2, 94.3, 108.3, 124.2, 126.8, 128.5, 128.9, 129.8, 137.2, 140.4, 142.7, 166.7. IR (KBr): 2937, 1595, 1495, 1454, 1313, 1220, 1161, 1107, 1082, 1041 cm^{-1}. MS *m/z* (%): 458 (M^+, 3.8), 89 (100). *Anal.* Calcd for $C_{26}H_{34}O_5S$: C, 67.43 ; H, 7.51 ; S, 6.92. Found : C, 67.59 ; H, 7.61 ; S, 6.67. By a similar procedure to that described for the preparation of **17a** from MEM ether of (*E*)-**11a**, MEM ether of (*E*)-**11b** (22.0 mg, 0.048 mmol) was converted into **17a** (16.5 mg, 82 % in 2 steps) as a colorless oil. $[\alpha]_D^{20}$ –1.0 (c = 0.73, $CHCl_3$). ^{1}H-NMR spectroscopic property of **17a** was consistent with the authentic data written in reference 5b.

(1*S*,2*R*)-2-Methoxyethoxymethoxycyclohexyl (*R*)-α-Methoxy-α-(trifluoromethyl)phenylacetate (17b). By a similar procedure to that described for the preparation of the MEM ether from (*E*)-**11a**, (*E*)-**11c** (20.0 mg, 0.0540 mmol) was converted into MEM ether (22.0 mg, 89 %) as a colorless oil. $[\alpha]_D^{24}$ +39.6 (c = 0.70, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.35–1.46 (m, 2H), 1.51–1.80 (m, 4H), 1.91–2.01 (m, 1H), 2.10–2.20 (m, 1H), 2.39 (s, 3H, Ar-C$\underline{H}_3$), 3.38 (s, 3H, OC$\underline{H}_3$), 3.50 (d, 1H, J = 12.8 Hz, C$\underline{H}_2$SO), 3.55–3.58 (m, 2H, C$\underline{H}_2$OCH$_3$), 3.74–3.83 (m, 2H, OC$\underline{H}_2$CH$_2$OCH$_3$), 3.88–3.94 (m, 1H, C$\underline{H}$OC), 4.03(d, 1H, J = 12.8 Hz, C$\underline{H}_2$SO), 4.45–4.49 (m, 1H, C$\underline{H}$OC), 4.86 (d, 2H, J = 1.3 Hz, OC$\underline{H}_2$O), 5.99 (s, 1H, C=C$\underline{H}$), 7.14–7.18 (m, 2H, Ar–$\underline{H}$), 7.22–7.28 (m, 5H, Ar–$\underline{H}$), 7.54 (d, 2H, J = 8.2 Hz, Ar–$\underline{H}$). ^{13}C-NMR ($CDCl_3$) δ: 21.2, 21.4, 22.5, 26.5, 27.8, 59.0, 60.5, 66.9, 71.7, 75.1, 75.2, 94.2, 107.5, 124.2, 126.1, 128.1, 129.0, 129.7, 135.7, 141.0, 141.4, 147.3. IR (KBr): 2937, 1732, 1641, 1492, 1446, 1398, 1240, 1182, 1086, 1045 cm^{-1}.

MS *m/z* (%): 458 (M^+, 3.6), 89 (100). *Anal.* Calcd for $C_{26}H_{34}O_5S$: C, 67.43 ; H, 7.51 ; S, 6.92. Found : C, 67.56 ; H, 7.58 ; S, 6.65. By a similar procedure to that described for the preparation of **17a** from MEM ether of (*E*)-**11a**, MEM ether of (*E*)-**11c** (14.5 mg, 0.0316 mmol) was converted into known **17b** (11.4 mg, 86 %) as a colorless oil. $[\alpha]_D^{24}$ +29.4 (c = 0.25, $CHCl_3$). ^{1}H-NMR spectroscopic poperty of **17b** was consistent with the authentic data written in reference 5b.

(1*R*,2*S*)-2-Acetoxycyclohexyl (*Rs*)-(*p*-Tolylsulfinyl)acetate (18a). DMAP (50.2 mg, 0.411 mmol) were added to a solution of (*E*)-**11a** (38.0 mg, 0.103 mmol) in CH_2Cl_2 (3 ml) at 0 ℃ and the mixture was stirred at 0 ℃ for 10 min. Acetyl chloride (15 μl, 0.21 mmol) was added to the stirred mixture at 0 ℃ and the mixture was stirred at 0 ℃ for 30 min. After the addition of saturated $NaHCO_3$, the whole was extracted with Et_2O. The extract was washed with saturated NH_4Cl and brine, and then dried. The solvent was evaporated and the residue was chromatographed on silica gel with AcOEt–hexane (1 : 1) to give the acetate (40.0 mg, 94 %) as a colorless oil. $[\alpha]_D^{33}$ +29.7 (c = 1.43, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.40–1.52 (m, 2H), 1.65–1.80 (m, 4H), 1.92–2.12 (m, 2H), 2.12 (s, 3H, $OC\underline{H}_3$), 2.39 (s, 3H, Ar–$C\underline{H}_3$), 3.62 (d, 1H, *J* = 12.9 Hz, $C\underline{H}_2SO$), 3.93 (d, 1H, *J* = 12.9 Hz, $C\underline{H}_2SO$), 4.46–4.51 (m, 1H, C<u>H</u>OC), 4.99–5.04 (m, 1H, C<u>H</u>OC), 5.91 (s, 1H, C=C<u>H</u>), 7.07 (d, 2H, *J* = 7.7 Hz, Ar–<u>H</u>), 7.13–7.25 (m, 5H, Ar–<u>H</u>), 7.47 (d, 2H, *J* = 8.6 Hz, Ar–<u>H</u>). ^{13}C-NMR ($CDCl_3$) δ: 21.0, 21.3, 21.4, 22.4, 27.1, 27.5, 60.6, 71.9, 73.7, 107.4, 124.2, 126.2, 128.1, 128.9, 129.7, 135.4, 141.0, 141.5, 147.8, 170.8. IR (KBr): 2941, 1732, 1641, 1493, 1446, 1373, 1238, 1184, 1132, 1086, 1051 cm^{-1}. MS *m/z* (%): 396 (M^+–O, 0.7), 133 (100). High MS Calcd for $C_{24}H_{28}O_4S$: 412.1706. Found: 412.1704. A stream of ozone was bubbled through the solution of the acetate (66.0 mg, 0.160 mmol) in MeOH (5 ml) at –78 ℃ until a pale blue color developed. Nitrogen was allowed to bubble through the solution to remove excess ozone. Dimethyl sulfide (118 μl, 1.60 mmol) was added to the mixture. The solution was allowed to warm to 25 ℃ and stirred for 1h. The solvent was evaporated and the residue was chromatographed on silica gel with AcOEt–hexane (1 : 1) to give **18a** (50.0 mg, 92 %) as a colorless oil. $[\alpha]_D^{32}$ +94.9 (c = 0.90, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.38–1.46 (m, 2H), 1.57–1.70 (m, 4H), 1.78–1.86 (m, 2H), 2.02 (s, 3H, $OC\underline{H}_3$), 2.42 (s, 3H, Ar–$C\underline{H}_3$), 3.66 (d, 1H, *J* = 13.7 Hz, $C\underline{H}_2SO$), 3.82 (d, 1H, *J* = 13.7 Hz, $C\underline{H}_2SO$), 4.95–4.99 (m, 1H, C<u>H</u>OC), 5.06–5.10 (m, 1H, C<u>H</u>OC), 7.34 (d, 2H, *J* = 8.5 Hz, Ar–<u>H</u>), 7.59 (d, 2H, *J* = 8.5 Hz, Ar–<u>H</u>). ^{13}C-NMR ($CDCl_3$) δ: 21.1, 21.4, 21.4, 21.6, 27.4, 27.5, 61.9, 70.7, 72.9, 124.2, 130.1, 140.1, 142.3, 164.3, 170.4. IR (KBr): 2943, 2866, 1732, 1495, 1450, 1369, 1267, 1236, 1120, 1086 1051 cm^{-1}. MS *m/z* (%): 338 (M^+, 35.7), 139 (100). High MS Calcd for $C_{17}H_{22}O_5S$: 338.1186. Found: 338.1179.

(1*S*,2*R*)-2-Acetoxycyclohexyl (*Rs*)-(*p*-Tolylsulfinyl)acetate (18b). By a similar procedure to that described for the preparation of the acetate from (*E*)-**11a**, (*E*)-**11c** (60.2 mg, 0.163 mmol) was converted into the acetate (61.0 mg, 91 %) as a colorless oil. $[\alpha]_D^{30}$ +52.9 (c = 0.65, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.40–1.52 (m, 2H), 1.65–1.80 (m, 4H), 1.92–2.15 (m, 2H), 2.11 (s, 3H, $OC\underline{H}_3$), 2.39 (s, 3H, Ar–$C\underline{H}_3$), 3.55 (d, 1H, *J* = 12.8 Hz, $C\underline{H}_2SO$), 3.98 (d, 1H, *J* = 12.8 Hz, $C\underline{H}_2SO$), 4.42–4.47 (m, 1H, C<u>H</u>OC), 5.04–5.10 (m, 1H C<u>H</u>OC), 5.93 (s, 1H, C=C<u>H</u>), 7.07 (d, 2H, *J* = 6.9 Hz, Ar–<u>H</u>), 7.13–7.25 (m, 5H, Ar–<u>H</u>), 7.50 (d, 2H, *J* = 7.7 Hz, Ar–<u>H</u>). ^{13}C-NMR ($CDCl_3$) δ: 21.0, 21.3, 21.3, 22.3, 27.0, 27.2, 60.6, 72.0, 73.8, 107.6, 124.2, 126.2, 128.1, 128.9, 129.7, 135.3, 140.9, 141.5, 147.2, 170.6. IR (KBr): 2945, 2862, 1736, 1641, 1599, 1493, 1446, 1371, 1234, 1182, 1132, 1047 cm^{-1}. MS *m/z* (%): 412 (M^+, 0.7), 133 (100). High MS Calcd for $C_{24}H_{28}O_4S$: 412.1706. Found: 412.1695. By a similar procedure to that described for the preparation of **18a** from the acetate of (*E*)-**11a**, the acetate of (*E*)-**11c** (33.9 mg, 0.0822 mmol) was converted into **18b** (25.0 mg, 90 %) as a colorless oil. $[\alpha]_D^{31}$ +91.7 (c = 1.27, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.38–1.44 (m, 2H),

1.56–1.69 (m, 4H), 1.73–1.84 (m, 2H), 2.05 (s, 3H, $OC\underline{H}_3$), 2.42 (s, 3H, Ar–$C\underline{H}_3$), 3.66 (d, 1H, J = 13.7 Hz, $C\underline{H}_2SO$), 3.87 (d, 1H, J = 13.7 Hz, $C\underline{H}_2SO$), 4.95–4.99 (m, 1H, $C\underline{H}OC$), 5.05–5.09 (m, 1H, $C\underline{H}OC$), 7.34 (d, 2H, J = 8.5 Hz, Ar–$\underline{H}$), 7.60 (d, 2H, J = 8.5 Hz, Ar–$\underline{H}$). ^{13}C-NMR ($CDCl_3$) δ: 21.1, 21.1, 21.4, 21.8, 27.3, 27.7, 61.9, 70.8, 72.8, 124.2, 130.0, 140.1, 142.3, 164.1, 170.4. IR (KBr): 2941, 2866, 1736, 1495, 1450, 1371, 1269, 1236, 1120, 1084, 1053, 1018 cm^{-1}. MS *m/z* (%): 338 (M^+, 35.7), 139 (100). High MS Calcd for $C_{17}H_{22}O_5S$: 338.1188. Found: 338.1188.

(1*R*,2*S*)- and (1*S*,2*R*)-2-Acetoxycyclohexyl (*Rs*)-(*p*-Tolylsulfinyl)acetate (18a and 18b). From a mixture of (*Z*)-11a and (*Z*)-11c: By a similar procedure to that described for the preparation of the acetate from (*E*)-**11a**, a mixture of (*Z*)-**11a** and (*Z*)-**11c** [99.8 mg, 0.270 mmol, (*Z*)-**11a** : (*Z*)-**11c** = 96 : 4] was converted into a mixture of the acetate (110 mg, 99 %, 96 : 4). Then, by a similar procedure to that described for the preparation of **18a** from the acetate of (*E*)-**11a**, a mixture of the acetate (100 mg, 0.243 mmol) was converted into a mixture of **18a** and **18b** (75.0 mg, 91 %, **18a** : **18b** = 96 : 4).

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REFERENCES AND NOTES

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8. β-Ketosulfoxides **1** and **2** were prepared as previously described by the reaction of the corresponding esters with enantiomerically pure (*R*)-methyl *p*-tolyl sulfoxide (Solladié, G. *Synthesis* 1981, 185–196.) in the presence of LDA. The optical purity was determined by comparison with the reported specific rotation (Banfi, L.; Colombo, L.; Gennari, C.; Annunziata, R.; Cozzi, F. *Synthesis* 1982, 829–831. Kunieda, N.; Nokami, J.; Kinoshita, M *Chem. Lett.* 1974, 369–372.).
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10. The stereochemistry of the acetals in **4–7a** and **4–7b** was determined based on nuclear Overhauser effect (NOE) experiments, in which marked NOE enhancements were observed between the angular methine protons on the bicyclic ring and the substituent R or the sulfinylmethyl group (Fig. 1).

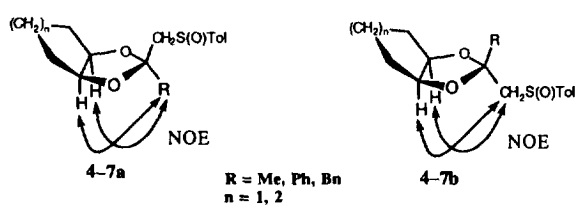

Fig. 1. NOE Observaon of α-Sulfinyl Actals.

11. Diasteteoselectivity of acetalization can be explained as follows. Acetalization of β-ketosulfoxides would proceed *via* the most stable oxonium intermediates (a or b), in which the smaller substituent (Rs) eclipses with the hydrogen (H*) to minimize the steric interaction, therby affording mainly the acetals with the *endo*-larger group (RL). The higher selectivity for the acetal **5b** is due to the great difference in size between the phenyl group (RL) and the sulfinylmethyl group (Rs) (Fig.2).

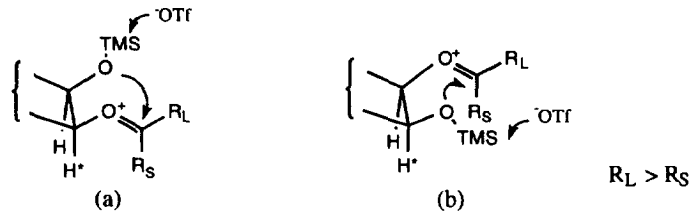

Fig. 2. Plausible Reaction Mechanism for Acetalization.

12. The stereochemistry of the olefin in **8b**, **10a–b**, and **11a–c** was determined by NOE experiment (Fig. 3).

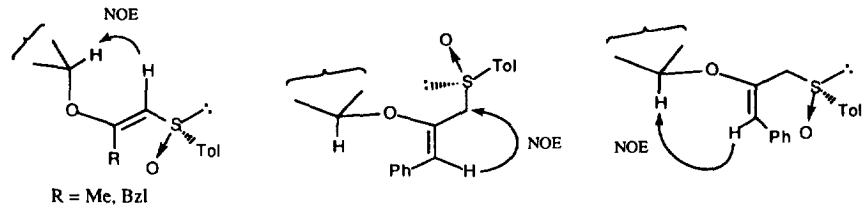

Fig. 3. Geometry of the Olefin Moieties.

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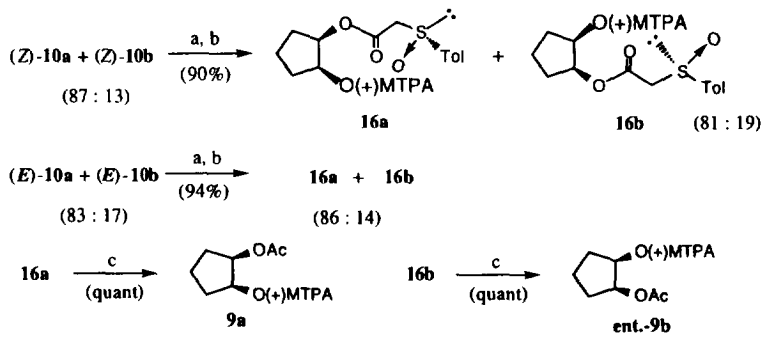
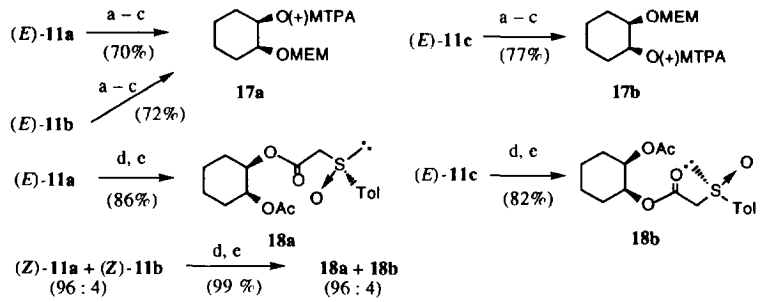
14. Xie Z.-F.; Suemune H.; Nakamura I.; Sakai K. *Chem. Pharm. Bull.* **1987**, *35*, 4454–4459.
15. The stereochemistry of alcohols **10a** and **10b** was determined as follows. The diastereomeric isomers were separated into a mixture of (*Z*)-**10a** and (*Z*)-**10b** and a mixture of (*E*)-**10a** and (*E*)-**10b**. Since further separation was difficult at this stage, they were first converted into **16a** and **16b** by esterification and, ozonolysis and then separated. Products **16a** and **16b** were assumed to be derived from **10a** and **10b**, respectively, since the ratio of **10a** to **10b** was almost equal to that of **16a** to **16b** in each case. Desulfurization of **16a** and **16b** with Raney Ni (W2) afforded the known **9a** and **ent.-9b**, respectively (Scheme 9).



Reagents: a) (+)-MTPACl, DMAP, CH_2Cl_2, 0 °C; b) O_3, MeOH, –78 °C then Me_2S; c) Raney Ni (W2), EtOH, room temp.

Scheme 9

16. The absolute configurations of (*E*)-**11a**, (*E*)-**11b**, and (*E*)-**11c** were confirmed by their transformation into known compounds **17a** or **17b**[9b]. After protection of the alcohols as 2-methoxyethoxymethyl (MEM) ether, (*E*)-**11a** and (*E*)-**11b** were hydrolyzed with dilute hydrochloric acid followed by esterification with (+)-MTPACl to afford known **17a**. (*E*)-**11c** was also converted into known **17b**. Since separation of (*Z*)-**11a** and (*Z*)-**11c** was difficult, the mixture was converted into **18a** and **18b** *via* acetylation and ozonolysis without separation. Compounds (*Z*)-**11a** and (*Z*)-**11c** were considered to be derived from **18a** and **18b**, respectively, because the ratio of (*Z*)-**11a** to (*Z*)-**11c** (96:4) was the same as that of **18a** to **18b** (96:4). The absolute configurations of **18a** and **18b** were determined by ^{1}H-NMR spectroscopic analysis in comparison with those derived from (*E*)-**11a** and (*E*)-**11c** with known absolute configurations (Scheme 10).



Reagents: a) MEMCl, Pr^i_2NEt, CH_2Cl_2, room temp. b) 1N HCl, acetone, room temp.
c) (+)-MTPACl, DMAP, CH_2Cl_2, 0 °C. d) AcCl, DMAP, CH_2Cl_2, 0 °C. e) O_3, MeOH, –78 °C then Me_2S.

Scheme 10

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