Synthesis of Optically Active Lactones and 3-Cyclopentenone from Optically Active 3,3-Dialkyl-4-thianones

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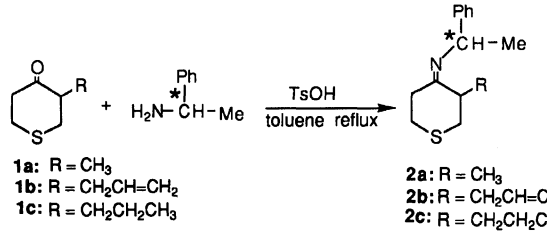
The Optically active 3,3-dialkyl-4-thianones **3** and **4** were prepared in moderate yields with about 90% enantiomeric purity using an asymmetric process involving a Michael-type alkylation of chiral 3-alkyl-4-thianimines with methyl vinyl ketone or methyl acrylate. The diketones **3** were then transformed into new heterocycles **5** by base-induced cyclization. 3-Methyl- and 3-allyl-3-(2-methoxycarbonylethyl)-4-thianone ((+)-**4a** and (+)-**4b**) were converted into the bicyclic lactones (−)-**6** and (−)-**7**, respectively. The stereochemistry of the sulfone (+)-**8** derived from the lactone (−)-**6a** was determined by a X-ray crystal structure analysis. Desulfurization of the lactone (−)-**6b** using nickel boride afforded the corresponding lactone (+)-**9**. A synthesis of optically active 2-alkyl-2-methyl-3-cyclopentenone (*S*)-(+)-**15** via the Ramberg–Bäcklund reaction from the keto ester (*R*)-(+)-**4a** was also accomplished.

The synthesis of enantiomerically pure compounds is an extremely important undertaking and a formidable challenge to any synthetic chemist. Considerable attention has been focused in recent years on cyclic sulfur compounds[1] for the synthesis of interesting natural compounds, since sulfur-containing heterocycles are useful synthons in an either ring-expansion[2] or ring-contraction[3] process. However, reports concerning the synthesis of cyclic sulfur compounds with chiral carbon atoms in the ring system have been limited;[4,5] e.g. to the stereoselective reduction of 2-alkyl- or 3-alkyl-4-thianones by enzymatic systems.[4] Our plan was to develop a synthetic procedure for optically active 4-thianone (tetrahydro-4*H*-thiopyran-4-one) derivatives which will be useful as optically active synthons for the synthesis of interesting natural compounds. Pfau et al.[6] have reported an asymmetric Michael-addition reaction of the chiral imine derivative of 2-methylcyclohexanone with electron-deficient olefins. We applied their procedure to 3-alkyl-4-thianimine derivatives, and found that this procedure is useful for the synthesis of optically active 4-thianone derivatives with high enantiomeric purity (about 90% ee). We now describe the studies concerning the synthesis of optically active 3,3-dialkyl-4-thianones and an attempt to synthesize optically active lactones[7] and 3-cyclopentenone.

Results and Discussion

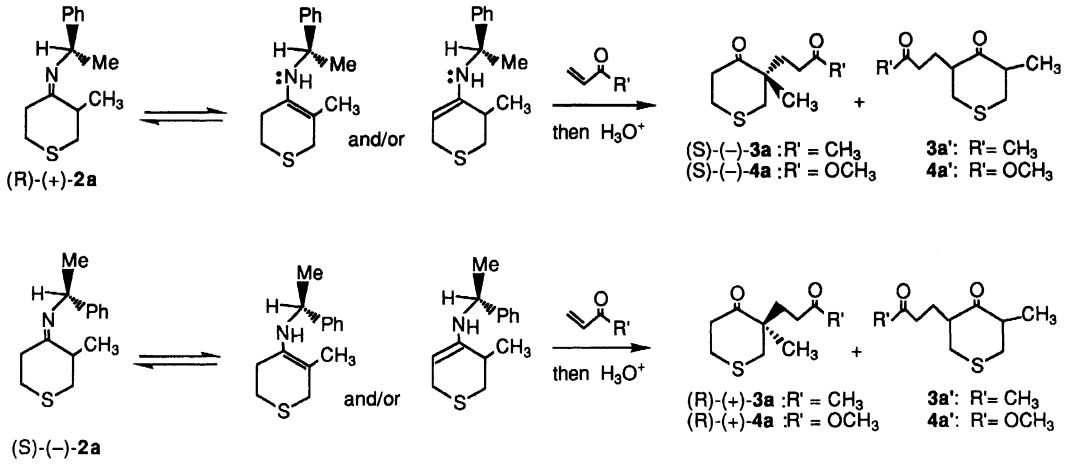
Michael-Type Reaction of Chiral Imines with Methyl Vinyl Ketones. The optically active 3-alkyl-4-thianimine derivatives **2** were prepared in 74—83% yields by the reaction of optically active (*R*)-(+)- or (*S*)-(−)-1-phenylethylamine and 3-alkyl-4-thianone (**1**) (R = Me, allyl, propyl) in the presence of a catalytic amount of *p*-toluenesulfonic acid under toluene reflux conditions (Eq. 1).



1a: R = CH_3
1b: R = $CH_2CH{=}CH_2$
1c: R = $CH_2CH_2CH_3$

2a: R = CH_3
2b: R = $CH_2CH{=}CH_2$
2c: R = $CH_2CH_2CH_3$ (1)

An asymmetric Michael-type addition reaction takes place via isomerization from the chiral imine to the enamine; the enamine reacts with electron-deficient olefins, such as methyl vinyl ketone and methyl acrylate (Scheme 1). The reaction of (*R*)-(+)-imine **2a** (R = Me) with 4 equiv of methyl vinyl ketone (THF, 25 °C, 3 d) afforded a Michael-type addition product. Hydrolysis of the adduct gave (*S*)-(−)-3-methyl-3-(3-oxobutyl)-4-thianone ((−)-**3a**) and the regioisomer, 3-methyl-5-(3-oxobutyl)-4-thianone (**3a′**), in 47% yield (ratio, (−)-**3a**/**3a′**=3.6/1) (Scheme 1). The enantiomeric purity of (−)-**3a** was determined to be 89% ee by an HPLC analysis of (+)-**5a** using a chiral column after the transformation of (−)-**3a** into bicyclic ketone (+)-**5a**. The absolute configuration of (−)-**3a** was established to be the (*S*)-form by a comparison of the CD spectra of (+)-**5a** with that of the related bicyclic ketone,[8] as described later. Similarly, (*R*)-(+)-diketone (+)-**3a** (88% ee) and the regioisomer **3a′** were obtained in 58% yield (ratio, (+)-**3a**/**3a′**=1.2/1) from the reaction of the chiral imine (*S*)-(−)-**2a** and methyl vinyl ketone in DMF. The reactions of the chiral imines of 3-allyl- or 3-propyl-4-thianone (**2b** or **2c**) with methyl vinyl ketone were also examined; the results are summarized in Table 1. The yields of the addition products (**3** and **3′**) were about 50% and the enantiomeric purity of **3** containing the quaternary carbon centers was about 90% ee in all cases. However, the amount of regioisomer **3′** derived form an addition reaction at the C-5 position of the enamine increased when the alkyl substituent of C-3 position was replaced



Scheme 1.

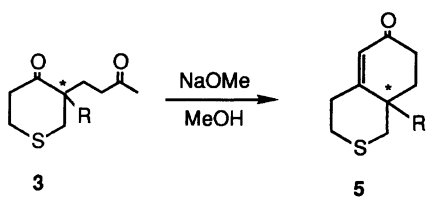
Table 1. Michael-Type Addition of **2** with Methyl Vinyl Ketone[a)]

Entry	R in imine **2**		Product			
			% Yield of **3**+**3**'[b)]	Ratio[c)] **3**/**3**'	%ee (R/S) of **3**[d)]	
1	(+)-**2a**	CH_3	47	3.6	(−)-**3a**	89 (S)
2	(−)-**2a**	CH_3	58[e)]	1.2	(+)-**3a**	88 (R)
3	(+)-**2b**	$CH_2CH{=}CH_2$	50	1.7	(−)-**3b**	96 (R)
4	(−)-**2b**	$CH_2CH{=}CH_2$	45	1.1	(+)-**3b**	89 (S)
5	(+)-**2c**	$CH_2CH_2CH_3$	44	0.32	(+)-**3c**	95 (S)
6	(−)-**2c**	$CH_2CH_2CH_3$	49	0.47	(−)-**3c**	90 (R)

a) Imine **2** was reacted with 4 equiv of methyl vinyl ketone (THF, 25 °C). b) Isolated yield as a mixture of **3** and **3**'. c) Determined by GC analysis of imine-adducts before hydrolysis. d) Enantiomeric excess was determined by HPLC analysis of the bicyclic ketone **5**, which was derived by base-induced cyclization of diketone **3**, using the chiral column (DAICEL CHIRALPAK AD). e) DMF was used as a solvent instead of THF.

from the methyl group to larger alkyl groups, such as allyl and propyl groups.

The base-induced cyclization of the diketone, (S)-(−)-**3a**, led to a bicyclic ketone, (S)-(+)-**5a**, in 52% yield (Eq. 2). The enantiomeric purity of (S)-(+)-**5a** was determined to be 89% ee by an HPLC analysis using a chiral column. The determination of the absolute configuration of (+)-**5a** was achieved as an (S)-form by a comparison of the CD spectra of (+)-**5a** with that of the bicyclic ketone, (S)-(+)-4,4a,5,6,7,8-hexahydro-4a-methyl-2(3H)-naphthalenone.[8)] Similarly, (R)-(−)-**5a** (88% ee) was prepared in 50% yield by a base-induced cyclization of the diketone (R)-(+)-**3a**. Base-induced cyclizations of other diketones, **3b** (R=allyl) and **3c** (R=propyl), were also examined; the results are summarized in Table 2.



(2)

Under the cyclization conditions, since no racemization of the quaternary carbon centers of **5** takes place, the enantiomeric purity (% ee) and absolute configuration of the diketones **3** could also be determined, as described above.

Michael-Type Reaction of Chiral Imines with Methyl Acrylate. The reaction of the chiral imine (R)-(+)-**2a** with methyl acrylate was investigated in THF at room temperature for 3—5 d; the keto ester [(−)-3-methyl-3-(2-methoxycarbonylethyl)-4-thianone ((−)-**4a**)] and the regioisomer [3-methyl-5-(2-methoxycarbonylethyl)-4-thianone (**4a**')] were obtained in 15% yield (ratio, (−)-**4a**/**4a**'=11.7/1) (Scheme 1). The enantiomeric purity of (−)-**4a** was determined to be 92% ee by an HPLC analysis using a chiral column; the absolute configuration of (−)-**4a** was confirmed to be the (S)-form in analogy with the absolute configuration of (S)-(−)-**3a** prepared form a reaction of chiral imine (R)-(+)-**2a** and methyl vinyl ketone. The chemical yield of the addition product was improved in DMF as a solvent instead of THF.[9)] For example, the reaction of the chiral imine (R)-(+)-**2a** and methyl acrylate in DMF at room temperature for 3 d afforded the keto ester (S)-

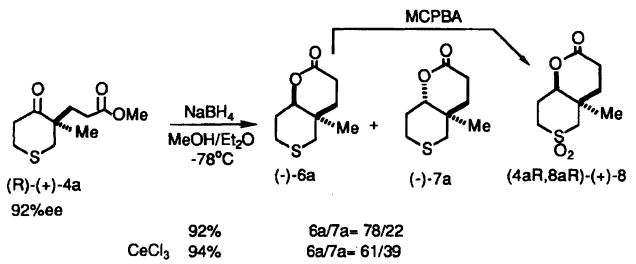
Table 2. Base-Induced Cyclization of Diketone **3**[a]

Entry	R in **3**		Product	
			% Yield of **5**[b]	%ee (R/S) of **5**[c]
1	(−)-**3a**	CH_3	(+)-**5a** 52	89 (S)
2	(+)-**3a**	CH_3	(−)-**5a** 50	88 (R)
3	(−)-**3b**	$CH_2CH{=}CH_2$	(+)-**5b** 52	96 (R)
4	(+)-**3b**	$CH_2CH{=}CH_2$	(−)-**5b** 45	89 (S)
5	(+)-**3c**	$CH_2CH_2CH_3$	(+)-**5c** 50	95 (S)
6	(−)-**3c**	$CH_2CH_2CH_3$	(−)-**5c** 51	90 (R)

a) Diketone **3** was stirred with 5% MeONa in methanol for 2 h at room temperature. b) Isolated yield. c) Enantiomeric excess was determined by HPLC analysis using the chiral column (DAICEL CHIRALPAK AD).

(−)-**4a** (92% ee) and the regioisomer **4a′** in 75% yield (ratio, (−)-**4a**/**4a′**=5.0/1). The Michael-type reactions of the imines of 3-allyl- or 3-propyl-4-thianone (**2b** and **2c**) with methyl acrylate were also examined in DMF; the results are summarized in Table 3.

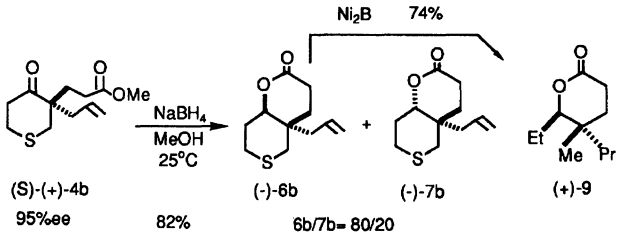
Synthesis of Optically Active Lactones. The compounds prepared as mentioned above will be useful as optically active synthons for the synthesis of interesting natural compounds; we attempted syntheses of optically active lactones. The reduction of the keto ester (R)-(+)-**4a** (92% ee) with 1 equiv of sodium borohydride at −78 °C in ether–MeOH (1/1) afforded the bicyclic lactones (−)-**6a** and (−)-**7a** as diastereomeric isomers (ratio, **6a**/**7a**=78/22) in 92% yield. Performing a reduction with sodium borohydride in the presence of 1 equiv of cerium trichloride[10] at −78 °C slightly increased the amount of the stereoisomer (−)-**7a** (94% yield; ratio, **6a**/**7a**=61/39). The major stereoisomer, (4aR, 8aR)-(−)-3,4,7,8-tetrahydro-4a-methyl-2H, 5H-thiopyrano[4,3-b]pyran-2-one ((−)-**6a**), was oxidized into the corresponding sulfone (+)-**8** with 3 equiv of m-chloroperbenzoic acid in dichloromethane; the recrystallized compound (+)-**8** was then subjected to a single-crystal X-ray structure analysis (Eq. 3).



(3)

Figure 1 shows an ORTEP drawing of compound (+)-**8**. The numbering given in Fig. 1 is arbitary and is not consistent with that of the IUPAC nomenclature. The bond length and bond angles are listed in Table 4. These results clearly show the structure of (+)-**8** with the absolute configuration (C-4a and C-8a having the (R)-configuration).

When the keto ester (S)-(+)-**4b** (95% ee) was reduced with 1 equiv of sodium borohydride, the corresponding lactones [(4aS,8aR)-(−)-3,4,7,8-tetrahydro-4a-allyl-2H, 5H-thiopyrano[4,3-b]pyran-2-one ((−)-**6b**) and the diastereoisomer (4aS, 8aS)-(−)-**7b**] were obtained in 82% yield (ratio, **6b**/**7b**=80/20). We then attempted to convert the C-S bonds of bicyclic lactone (−)-**6b** into C–H bonds with a variety of nickel reagents (e.g. Raney nickel, nickel boride). Nickel boride,[11] conveniently generated in situ from nickel chloride hexahydrate and sodium borohydride in MeOH–THF at 0 °C, has been used to desulfurize the major stereoisomer (−)-**6b**, and the corresponding lactone, (5S,6R)-(+)-5-methyl-5-propyl-6-ethyl-tetrahydro-2H-pyran-2-one ((+)-**9**), was obtained in 74% yield (Eq. 4).



(4)

Synthesis of Optically Active 3-Cyclopentenone. We previously reported a regioselective synthesis of 2-alkyl-3-cyclopenten-1-ones starting from 4-thianone by the selective alkylation and Ramberg–Bäcklund-type reactions.[3a] We therefore applied this method for the synthesis of optically active 2-alkyl-2-methyl-3-cyclopenten-1-one. The keto ester, (R)-(+)-3-methyl-3-(2-methoxycarbonylethyl)-4-thian-1-one ((R)-(+)-**4a**) (92% ee), was converted into the alcohol derivative **11** by protection of the carbonyl group (ethylene glycol, p-toluenesulfonic acid, benzene reflux), followed by a reduction of the methyl ester **10** with $LiAlH_4$. After the benzyl ether **12** was derived from alcohol **11** (benzyl bromide, NaH, THF), the oxidation of **12** with m-CPBA (3 equiv) gave a six-membered sulfone **13**. This six-membered sulfone **13** was transformed into the cyclopentene **14** in 71% yield by a Ramberg–Bäcklund-type reaction (t-BuOK, CCl_4, t-BuOH, 50 °C) under nitrogen. After an acid-catalyzed cleavage of the 1,

Table 3. Michael-Type Addition of **2** with Methyl Acrylate[a)]

Entry	R in **2**		Product			
			% Yield of **4**+**4′**[b)]	Ratio[c)] **4**/**4′**	%ee (R/S) of **4**[d)]	
1	(+)-**2a**	CH_3	75	5.0	(−)-**4a**	92 (S)
2	(−)-**2a**	CH_3	75	4.5	(+)-**4a**	92 (R)
3	(+)-**2b**	$CH_2CH{=}CH_2$	39	2.0	(−)-**4b**	96 (R)
4	(−)-**2b**	$CH_2CH{=}CH_2$	35	1.9	(+)-**4b**	95 (S)
5	(+)-**2c**	$CH_2CH_2CH_3$	35	1.2	(+)-**4c**	84 (S)

a) Imine **2** was reacted with 4 equiv of methyl acrylate in DMF at room temperature. b) Isolated yield as a mixture of **4** and **4′**. c) Determined by GC analysis before hydrolysis. d) Enantiomeric excess was determined by HPLC analysis using the chiral column (DAICEL CHIRALPAK AD) after purification of **4**.

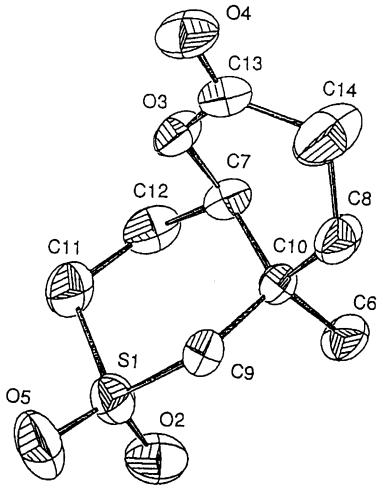


Fig. 1. ORTEP drawing of optically active lactone (+)-**8**, showing the numberimg scheme of the atoms.

Table 4. Bond Distances (Å) and Bond Angles (degrees) with esds in Parentheses

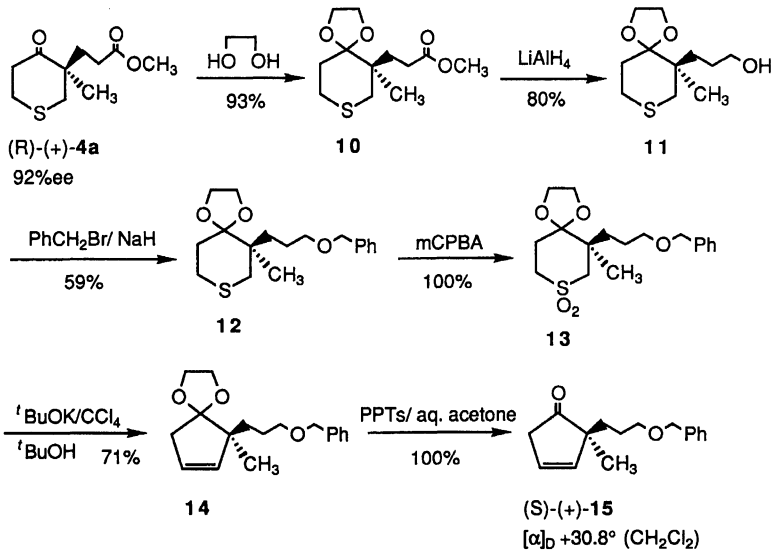
(a) Bond distances			
S1–O5	1.438(2)	C7–C12	1.510(3)
S1–O2	1.442(1)	C7–C10	1.538(2)
S1–C11	1.757(2)	C8–C14	1.434(3)
S1–C9	1.759(2)	C8–C10	1.559(3)
O3–C13	1.335(2)	C9–C10	1.530(2)
O3–C7	1.456(2)	C11–C12	1.520(3)
O4–C13	1.195(2)	C13–C14	1.516(4)
C6–C10	1.536(3)		
(b) Bond angles			
O5–S1–O2	117.3(1)	C9–C10–C6	111.7(1)
O5–S1–C11	110.3(1)	C9–C10–C7	111.1(1)
O5–S1–C9	108.2(1)	C9–C10–C8	107.3(1)
O2–S1–C11	108.5(1)	C6–C10–C7	109.0(1)
O2–S1–C9	110.1(1)	C6–C10–C8	109.1(2)
C11–S1–C9	101.2(1)	C7–C10–C8	108.5(1)
C13–O3–C7	119.4(1)	C12–C11–S1	111.0(2)
O3–C7–C12	104.8(1)	C7–C12–C11	113.6(2)
O3–C7–C10	110.6(1)	O4–C13–O3	119.3(2)
C12–C7–C10	115.9(1)	O4–C13–C14	126.0(2)
C14–C8–C10	115.8(2)	O3–C13–C14	114.4(2)
C10–C9–S1	116.1(1)	C8–C14–C13	114.4(2)

3-dioxolane ring of **14** (pyridinium *p*-toluenesulfonate, aqueous acetone reflux), the optically active 3-cyclopenten-1-one (S)-(+)-**15** was obtained in quantitative yield (Scheme 2).

In conclusion, the enantioselective synthesis of quaternary carbon centers through a Michael-type alkylation of the chiral 3-alkyl-4-thianimines with methyl vinyl ketone or methyl acrylate was accomplished. This synthetic procedure is useful for the synthesis of optically active 4-thianone derivatives with high enantiomeric purity (about 90% ee). The stereoselective synthesis of optically active lactones (**6a**, **6b** and (+)-**9**) from 3-alkyl-3-(2-methoxycarbonylethyl)-4-thianones (**4a** and **4b**) were investigated. A regioselective synthesis of the optically active 2-alkyl-2-methyl-3-cyclopenten-1-one (S)-(+)-**15** from the keto ester (R)-(+)-**4a** was also achieved.

Experimental

^{1}H NMR spectra were recorded on JEOL JNM-PMX 60SI (60 MHz) and JEOL FX90 (90 MHz) spectrometers; ^{13}C NMR specta were measured at 22.5 MHz. The mass and high-resolution mass spectra were determined with a JEOL JMX-DX 300 mass spectrometer with a JEOL JMA 5000 mass data system at an ionizing voltage of 70 eV. Optical rotations were measured with a JASCO DIP-140 digital polarimeter at 25 °C in a 1.0- or 0.5-dm cell. Circular dichroism (CD) spectra were recorded on a JASCO J-40A automatic recording spectropolarimeter in a 0.1-dm cell. The melting points were determined on a Yamato MP-21 apparatus in open capillary tubes, and are uncorrected. Infrared spectra were recorded on a Hitachi 260-10 spectrometer. GLPC were recorded on a Hitachi G-3000 with a 10% SE-30 1-m column or a 10% SE-30 25-m capillary column. The enantiomeric excess of optically active compounds was determined by HPLC (Hitachi 655) using a chiral column (Daicel Chemical, CHIRALPAK AD). Column Chromatography was performed with Wako gel C-200 (Wako Pure Chemical Ind.). Thin-layer chromatography was performed with a Merck Kieselgel 60F_{254}. Gel permeation chromatography was performed using a JAI LC-08 liquid chromatograph with JAIGEL-1H columns (20 mm×600 mm×2) using chloroform as the eluent. X-Ray data collection was carried out on a Mac Sci-



Scheme 2.

ence MXC 18 full-automatic four-circle diffractometer, and the computations were performed on a NS-SUN Work-Station System. All solvents were purified and dried by the usual procedure.

3-Methyl-4-thianone (**1a**, R=Me)[4a] and 3-allyl-4-thianone (**1b**. R=allyl)[3a] were prepared according to procedures described in the literature.

3-Propyl-4-thianone (1c, R=C_3H_7). Compound **1c** was prepared by the hydrogenation of 3-allyl-4-thianone (**1b**, R=allyl) (1.91 g, 12 mmol) in ethanol (80 cm^3) in the presence of platinum oxide (50 mg, 0.22 mmol): Yield, 1.90 g (100%); ^{1}H NMR ($CDCl_3$) δ=0.70—2.00 (7H, m), 2.37—3.20 (5H, m), 3.25—3.70 (2H, m); IR (neat) 1710 cm^{-1} (C=O); TLC (silica gel, hexane/ether=10/1) R_f=0.27. Calcd for $C_8H_{14}OS$: C, 60.72; H, 8.92%. Found: C, 60.60; H, 8.98%.

Synthesis of Chiral 3-Alkyl-4-thianimines. Chiral Imines, (*R*)-(+)-2a (R=Me). A toluene solution (50 cm^3) of 3-methyl-4-thianone (2.25 g, 17 mmol), (*R*)-(+)-1-phenylethylamine ($[\alpha]_D^{25}$ +39.0° (neat); 1.82 g, 15 mmol), and *p*-toluenesulfonic acid (20 mg) was refluxed for 5 h with an azeotropic removal of water by an apparatus fitted with a Dean–Stark condenser. After removing the solvent, chiral imine was purified by distillation: Yield, 2.52 g (72%); bp 131—133 °C (1.5 mmHg, 1 mmHg=133.322 Pa); ^{1}H NMR ($CDCl_3$) δ=1.00—1.53 (6H, m), 2.30—3.10 (7H, m), 4.65 (1H, q, J=6.0 Hz), 7.27 (5H, s); IR (neat) 1655 cm^{-1} (C=N); MS *m/z* 233 (M^+), 218, 200, 191; $[\alpha]_D^{25}$ +35.2° (*c* 1.05, EtOH). Calcd for $C_{14}H_{19}NS$: C, 72.05; H, 8.21; N, 6.00%. Found: C, 72.15; H, 8.20; N, 5.98%.

(*S*)-(−)-2a (R=Me). Following the general procedure described above for the preparation of (*R*)-(+)-**2a**, a toluene solution (30 cm^3) of 3-methyl-4-thianone (1.30 g, 10 mmol), (*S*)-(−)-1-phenylethylamine ($[\alpha]_D^{25}$ −39.0° (neat); 1.33 g, 11 mmol), and *p*-toluenesulfonic acid (20 mg) was refluxed: Yield, 1.94 g (83%); bp 141—145 °C (3 mmHg); ^{1}H NMR ($CDCl_3$) δ=1.00—1.53 (6H, m), 2.20—3.07 (7H, m), 4.63 (1H, q, J=6.0 Hz), 7.27 (5H, s); $[\alpha]_D^{25}$ −35.3° (*c* 1.05, EtOH). Calcd for $C_{14}H_{19}NS$: C, 72.05; H, 8.21; N, 6.00%. Found: C, 72.10; H, 8.18; N, 6.05%.

(±)-2a (R=Me). A toluene solution (50 cm^3) of 3-methyl-4-thianone (2.60 g, 20 mmol), (±)-1-phenylethylamine (2.18 g, 18 mmol), and *p*-toluenesulfonic acid (20 mg) was refluxed: Yield, 2.90 g (69%); bp 141—145 °C (3 mmHg); ^{1}H NMR ($CDCl_3$) δ=1.00—1.60 (6H, m), 2.20—3.10 (7H, m), 4.67 (1H, q, J=6.0 Hz), 7.30 (5H, s). Calcd for $C_{14}H_{19}NS$: C, 72.05; H, 8.21; N, 6.00%. Found: C, 72.10; H, 18.20; N, 6.08%.

(*R*)-(+)-2b (R=allyl). A toluene solution (50 cm^3) of 3-allyl-4-thianone (2.50 g, 16 mmol), (*R*)-(+)-1-phenylethylamine (1.82 g, 15 mmol), and *p*-toluenesulfonic acid (20 mg) was refluxed: Yield, 3.14 g (81%); bp 146—147 °C (3.0 mmHg); ^{1}H NMR ($CDCl_3$) δ=1.27—1.67 (3H, m), 2.17—3.33 (9H, m), 4.70 (1H, q, J=6.0 Hz), 4.80—5.90 (3H, m), 7.30 (5H, m); IR (neat) 1650 (C=N), 920 (C=CH_2) cm^{-1}; MS *m/z* 259 (M^+), 244, 222, 208, 168; $[\alpha]_D^{25}$ +34.4° (*c* 1.15, EtOH). Calcd for $C_{16}H_{21}NS$: C, 74.08; H, 8.16; N, 5.40%. Found: C, 74.10; H, 8.18; N, 5.38%.

(*S*)-(−)-2b (R=allyl). A toluene solution (50 cm^3) of 3-allyl-4-thianone (2.41 g, 15.4 mmol), (*S*)-(−)-1-phenylethylamine (2.06 g, 17 mmol), and *p*-toluenesulfonic acid (20 mg) was refluxed: Yield, 3.01 g (75%); bp 155—156 °C (3.5 mmHg); ^{1}H NMR ($CDCl_3$) δ=1.30—1.70 (3H, m), 2.20—3.13 (9H, m), 4.70 (1H, q, J=6.0 Hz), 4.80—6.00 (3H, m), 7.30 (5H, s); $[\alpha]_D^{25}$ −39.9° (*c* 1.08, EtOH). Calcd for $C_{16}H_{21}NS$: C, 74.08; H, 8.16; N, 5.40%. Found: C, 74.20; H, 8.16; N, 5.41%.

(*R*)-(+)-2c (R=propyl). A toluene solution (50 cm^3) of 3-propyl-4-thianone (2.18 g, 13.7 mmol), (*R*)-(+)-1-phenylethylamine (1.82 g, 15 mmol), and *p*-toluenesulfonic acid (20 mg) was refluxed: Yield, 2.29 g (64%); bp 147—150 °C (3.0 mmHg); ^{1}H NMR ($CDCl_3$) δ=0.67—2.00 (10H, m), 2.30—3.30 (7H, m), 4.70 (1H, q, J=6.0 Hz), 7.30 (5H, s); IR (neat) 1640 cm^{-1} (C=N); MS *m/z* 261 (M^+), 246, 219, 204, 186; $[\alpha]_D^{25}$ +35.6° (*c* 1.01, EtOH). Calcd for $C_{16}H_{23}NS$: C, 73.51; H, 8.87; N, 5.36%. Found: C, 73.60; H, 8.90; N, 5.30%.

(*S*)-(−)-2c (R=propyl). A toluene solution (50 cm^3) of 3-propyl-4-thianone (1.88 g, 11.9 mmol), (*S*)-(−)-1-phenylethylamine (1.70 g, 14 mmol), and *p*-toluenesulfonic acid (20 mg) was refluxed: Yield, 3.01 g (74%); bp 160 °C (3.0

mmHg); ^{1}H NMR ($CDCl_3$) δ=0.63—2.00 (10H, m), 2.30—3.33 (7H, m), 4.70 (1H, q, J=6.0 Hz), 7.27 (5H, s); $[\alpha]_D^{25}$ −37.1° (c 1.42, EtOH). Calcd for $C_{16}H_{23}NS$: C, 73.51; H, 8.87; N, 5.36%. Found: C, 73.55; H, 8.90; N, 5.32%.

Asymmetric Michael-Type Addition of Chiral Imines 2a—c with Methyl Vinyl Ketone. (*S*)-(−)-3-Methyl-3-(3-oxobutyl)-4-thianone ((*S*)-(−)-3a). A THF solution (15 cm^3) of chiral imine (*R*)-(+)-**2a** (0.933 g, 4 mmol) and methyl vinyl ketone (1.40 g, 20 mmol) was stirred for 3 d at room temperature. The ratio of the regioisomer of the Michael-type addition products was determined by GC analyses of the imine adducts before hydrolysis (ratio, **3a**/**3a**′=3.6/1). After removing the solvent, the products were hydrolyzed in a mixed solution of acetic acid (3.8 cm^3), sodium acetate (1.65 g) in water (17.5 cm^3), and ether (25 cm^3) for 3 h at room temperature. The crude products were extracted with ether (20 cm^3×3), and the ether layer was washed with water (30 cm^3×3), dried over $MgSO_4$, and concentrated. Purification by column chromatography (silica gel, hexane/ether=4/1) afforded 0.379 g (47%) of diketones as a mixture of regioisomers. The regioisomers (**3a** and **3a**′) were further purified by gel permeation chromatography using a JAI LC-08 liquid chromatograph with two JAIGEL-1H columns (20 mm×600 mm) with chloroform used as the eluent. The enantiomeric purity (89%) of (−)-**3a** was determined by an HPLC measurement of the bicyclic ketone derivative (+)-**5a** using an optically active column (CHIRALPAC AD; hexane/EtOH=9/1). The absolute configuration of (−)-**3a** was determined to be (*S*)-form by a comparison of the CD spectra of (+)-**5a** with that of a known bicyclic ketone, (*S*)-(+)-4,4a,5,6,7,8-hexahydro-4a-methyl-2(3*H*)-naphthalenone.[8]

(*S*)-(−)-3a: Oil; ^{1}H NMR ($CDCl_3$) δ=1.17 (3H, s), 1.40—3.20 (10H, m), 2.10 (3H, s); IR (neat) 1700 cm^{-1} (C=O); MS m/z 200 (M^+), 182, 167, 142, 129; $[\alpha]_D^{25}$ −34.7° (c 1.19, EtOH); CD $[\theta]_{303}$ −423 (c 0.107, EtOH); UV (EtOH) λ_{max} (ε) 286 (71), 237 (458), 206 (531); TLC (silica gel, hexane/ethyl acetate=2/1) R_f=0.49. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59%. Found: C, 71.45; H, 9.60%.

(*R*)-(+)-3-Methyl-3-(3-oxobutyl)-4-thianone ((*R*)-(+)-3a). DMF solution (8 cm^3) of chiral imine (*S*)-(−)-**2a** (1.167 g, 5 mmol) and methyl vinyl ketone (1.40 g, 20 mmol) was stirred for 3 d at room temperature. After a similar work-up for the synthesis of (*S*)-(−)-**3a**, the regioisomers of diketone (**3a** and **3a**′; 0.76 g, 58% yield; ratio **3a**/**3a**′=1.2/1) were further purified by liquid chromatography ($CHCl_3$).

(*R*)-(+)-3a: Oil; ^{1}H NMR ($CDCl_3$) δ=1.17 (3H, s), 1.40—3.20 (10H, m), 2.10 (3H, s); IR (neat) 1700 cm^{-1} (C=O); MS m/z 200 (M^+), 182, 167, 142, 129; $[\alpha]_D^{25}$ +33.1° (c 0.97, EtOH); CD $[\theta]_{305}$ +429 (c 0.048, EtOH). Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59%. Found: C, 71.43; H, 9.62%.

(±)-3-Methyl-3-(3-oxobutyl)-4-thianone ((±)-3a). A THF solution (10 cm^3) of racemic imine (±)-**2a** (1.167 g, 5 mmol) and methyl vinyl ketone (0.70 g, 10 mmol) was stirred for 3 d at room temperature. The regioisomers of diketone (**3a** and **3a**′; 0.506 g, 50%; ratio, **3a**/**3a**′=1.9/1) were further purified by liquid chromatography ($CHCl_3$).

(±)-3a: Oil; ^{1}H NMR ($CDCl_3$) δ=1.17 (3H, s), 1.40—3.20 (10H, m), 2.13 (3H, s); IR (neat) 1700 cm^{-1} (C=O); MS m/z 200 (M^+), 182, 167, 142, 129. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59%. Found: C, 71.49; H, 9.60%.

(*R*)-(−)-3-Allyl-3-(3-oxobutyl)-4-thianone ((*R*)-(−)-3b). A THF solution (10 cm^3) of chiral imine (*R*)-(+)-**2b** (1.30 g, 5 mmol) and methyl vinyl ketone (1.40 g, 20 mmol) was stirred for 3 d at room temperature. The regioisomers of diketone (**3b** and **3b**′; 0.572 g, 50% yield; ratio, **3b**/**3b**′=1.7/1) were further purified by liquid chromatography ($CHCl_3$).

(*R*)-(−)-3b: Oil; ^{1}H NMR ($CDCl_3$) δ=1.53—3.20 (12H, m), 2.10 (3H, s), 4.83—6.00 (3H, m); IR (neat) 1700 (C=O), 1635 (C=C), 915 cm^{-1} (C=CH_2); MS m/z 226 (M^+), 185, 168, 155, 127; $[\alpha]_D^{25}$ −15.8° (c 1.34, EtOH); CD $[\theta]_{287}$ +605, $[\theta]_{253}$ 0, $[\theta]_{245}$ −151, $[\theta]_{239}$ 0, $[\theta]_{227}$ +664, $[\theta]_{217}$ 0 (c 0.060, EtOH); TLC (silica gel, hexane/ether=1/1) R_f=0.28. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34%. Found: C, 74.32; H, 9.40%.

(*S*)-(+)-3-Allyl-3-(3-oxobutyl)-4-thianone ((*S*)-(+)-3b). A THF solution (10 cm^3) of chiral imine (*S*)-(−)-**2b** (1.556 g, 6 mmol) and methyl vinyl ketone (2.10 g, 30 mmol) was stirred for 3 d at room temperature. The diketones (**3b** and **3b**′; 45% yield; ratio, **3b**/**3b**′=1.1/1) were immediately stirred with 5% sodium methoxide in methanol (10 cm^3) for 2 h at room temperature to afford the bicyclic ketones. The bicyclic ketones were purified by liquid chromatography ($CHCl_3$) to give (*S*)-(−)-**5b** (0.126 g) (See (*S*)-(−)-**5b**).

(*S*)-(+)-3-Propyl-3-(3-oxobutyl)-4-thianone ((*S*)-(+)-3c). A THF solution (10 cm^3) of chiral imine (*R*)-(+)-**2c** (1.05 g, 4 mmol) and methyl vinyl ketone (1.40 g, 20 mmol) was stirred for 4 d at room temperature. The regioisomers (**3c** and **3c**′; 0.43 g, 44% yield; ratio, **3c**/**3c**′=0.32/1) were purified by column chromatography on silica gel (hexane/ether=4/1).

(*S*)-(+)-3c: 84 mg; oil; ^{1}H NMR ($CDCl_3$) δ=0.73—1.20 (3H, m), 1.25—2.15 (6H, m), 2.20 (3H, s), 2.25—2.70 (2H, m), 2.80 (6H, s); ^{13}C NMR ($CDCl_3$) δ=14.48, 16.30, 27.88, 29.70, 29.89, 36.33, 37.89, 39.06, 40.82, 52.26 (s), 207.49, 211.20; IR (neat) 1700 cm^{-1} (C=O); MS m/z 228 (M^+), 210, 185, 167, 157; $[\alpha]_D^{25}$ +19.2° (c 1.07, EtOH); TLC (silica gel, hexane/ether=1/1) R_f=0.37. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27%. Found: C, 73.55; H, 10.30%.

(*R*)-(−)-3-Propyl-3-(3-oxobutyl)-4-thianone ((*R*)-(−)-3c). A THF solution (10 cm^3) of chiral imine (*S*)-(−)-**2c** (2.09 g, 8 mmol) and methyl vinyl ketone (1.12 g, 16 mmol) was stirred for 4 d at room temperature. The regioisomers (**3c** and **3c**′; 0.893 g, 49% yield; ratio, **3c**/**3c**′=0.47/1) were purified by column chromatography on silica gel (hexane/ether=4/1).

(*R*)-(−)-3c: 0.146 g; oil; ^{1}H NMR ($CDCl_3$) δ=0.73—1.20 (3H, m), 1.25—2.15 (6H, m), 2.20 (3H, s), 2.25—2.70 (2H, m), 2.80 (6H, s); IR (neat) 1700 cm^{-1} (C=O); MS m/z 228 (M^+), 210, 185, 167, 157; $[\alpha]_D^{25}$ −17.0° (c 1.05, EtOH); CD $[\theta]_{296}$ −850 (c 0.038, EtOH). Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27%. Found: C, 73.45; H, 10.28%.

Synthesis of Optically Active Bicyclic Ketones. (*S*)-(+)-1,3,4,4a,5,7,8,8a-octahydro-8a-methyl-6*H*-2-benzothiopyran-6-one ((*S*)-(+)-5a). The diketone (*S*)-(−)-**3a** (60 mg, 0.3 mmol) was stirred with 5% sodium methoxide in methanol (10 cm^3) for 2 h at room temperature. After removing the solvent in vacuo, water (50 cm^3) was added to the residue, and the cyclization product was extracted with ether (50 cm^3×3). The ether solution was washed with water (60 cm^3×3), dried over $MgSO_4$, filtered and concentrated. Purification by column chromatog-

raphy (silica gel, CH_2Cl_2) afforded 28 mg (52%) of (*S*)-(+)-**5a** as a solid: Mp 75—78 °C (hexane/CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ=1.43 (3H, s), 1.70—2.97 (10H, m), 5.67 (1H, s); ^{13}C NMR ($CDCl_3$) δ=22.31, 29.85, 34.34, 34.47, 36.87, 37.07, 42.73, 126.10, 166.22, 198.34; IR (KBr) 1662 (C=O), 1605 cm^{-1} (C=C); MS *m/z* 182 (M^+), 167, 154, 149, 136; Calcd for $C_{10}H_{14}OS$: M, 182.0765; Found: *m/z* 182.0770; $[\alpha]_D^{25}$ +201° (*c* 1.02, EtOH); CD $[\theta]_{360}$ +98, $[\theta]_{353}$ 0, $[\theta]_{320}$ −1020, $[\theta]_{300}$ 0, $[\theta]_{269}$ +3610 (*c* 0.056, EtOH); TLC (silica gel, hexane/ether=1/1) R_f=0.33. The enantiomeric purity (89% ee) was determined by an HPLC measurement using chiral column (CHIRALPAK AD; hexane/EtOH=9/1; flow rate 1.4 cm^3 min^{-1}; detection, UV 254 nm; retention time, t_r=17.77 (*R*-form) and 21.40 min (*S*-form)). The absolute configuration of (+)-**5a** was determined to be (*S*)-form by a comparison of the CD spectra of (+)-**5a** with that of the known bicyclic ketone, (*S*)-(+)-4,4a,5,6,7,8-hexahydro-4a-methyl-2(3*H*)-naphthalenone (purchased from Wako Pure Chemical Ind.).[8)]

(*S*)-(+)-4,4a,5,6,7,8-Hexahydro-4a-methyl-2(3*H*)-naphthalenone: Oil; $[\alpha]_D^{25}$ +215° (*c* 1.20, MeOH); 98% ee; CD $[\theta]_{355}$ +218, $[\theta]_{332}$ 0, $[\theta]_{306}$ −527, $[\theta]_{271}$ 0 (*c* 0.073, MeOH).

(*R*)-(−)-5a. The diketone (*R*)-(+)-**3a** (60 mg, 0.3 mmol) was stirred with 5% MeONa in methanol (10 cm^3) for 2 h at room temperature. After the usual workup for the synthesis of (*S*)-(+)-**5a**, purification by column chromatography (silica gel, CH_2Cl_2) yielded 30 mg (50%) of (*R*)-(−)-**5a**: Oil; ^{1}H NMR ($CDCl_3$) δ=1.43 (3H, s), 1.70—2.97 (10H, m), 5.67 (1H, s); IR (neat) 1660, 1605 cm^{-1}; MS *m/z* 182 (M^+), 167, 154, 149, 136; Calcd for $C_{10}H_{14}OS$: M, 182.0765; Found: *m/z* 182.0731; $[\alpha]_D^{25}$ −199° (*c* 0.064, EtOH); CD $[\theta]_{360}$ −85, $[\theta]_{353}$ 0, $[\theta]_{318}$ +950, $[\theta]_{300}$ 0, $[\theta]_{270}$ −3400 (*c* 0.062, EtOH); enantiomeric purity, 88% ee (CHIRALPAK AD; hexane/EtOH=9/1; flow rate 1.4 cm^3 min^{-1}; detection, UV 254 nm; retention time, t_r=17.79 (*R*-form) and 21.50 min (*S*-form)). The absolute configulation of (−)-**5a** was determined to be (*R*)-form by a comparison of the CD spectra of (−)-**5a** with that of the known bicyclic ketone (*R*)-(−)-4,4a,5,6,7,8-hexahydro-4a-methyl-2(3*H*)-naphtalenone (Wako Pure Chemical Ind.): Oil; $[\alpha]_D^{25}$ −215° (*c* 0.962, MeOH); 98% ee; CD $[\theta]_{355}$ −196, $[\theta]_{332}$ 0, $[\theta]_{306}$ +520, $[\theta]_{270}$ 0 (*c* 0.059, MeOH).

(±)-5a. Base-induced cyclization of the diketone (±)-**3a** (100 mg, 0.5 mmol) with 5% MeONa in methanol (10 cm^3) afforded (±)-**5a** (44 mg, 48%): Oil; purified by column chromatography (silica gel; CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ= 1.43 (3H, s), 1.70—2.97 (10H, m), 5.70 (1H, s); IR (neat) 1660, 1605 cm^{-1}; MS *m/z* 182 (M^+), 167, 154, 149, 136; Calcd for $C_{10}H_{14}OS$: M, 182.0765; Found: *m/z* 182.0729.

(*R*)-(+)-1,3,4,4a,5,7,8,8a-Octahydro-8a-allyl-6*H*-2-benzothiopyran-6-one ((*R*)-(+)-5b). Base-induced cyclization of the diketone (*R*)-(−)-**3b** (90.5 mg, 0.4 mmol) with 5% MeONa in methanol (10 cm^3) afforded (−)-**5b** (43 mg, 52% yield) as a solid: Mp 55—57 °C (hexane/CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ=1.23—3.33 (12H, m), 4.80—6.27 (3H, m), 5.80 (1H, s); ^{13}C NMR ($CDCl_3$) δ=29.85, 32.91, 34.21, 37.52, 39.28, 39.80, 119.40, 126.94, 132.73, 165.76, 198.41; IR (KBr) 1670 (C=O), 1640 (C=C), 1610 cm^{-1} (C=C); MS *m/z* 208 (M^+), 180, 167, 139, 125; Calcd for $C_{12}H_{16}OS$: M, 208.0922; Found: *m/z* 208.0910; $[\alpha]_D^{25}$ +179° (*c* 0.93, EtOH); CD $[\theta]_{352}$ +794, $[\theta]_{330}$ 0, $[\theta]_{315}$ −716, $[\theta]_{304}$ 0, $[\theta]_{264}$ +9610 (*c* 0.045, EtOH); TLC (silica gel, hexane/ether=1/1) R_f=0.31; enantioimeric purity, 96.0% ee (CHIRALPACK AD; hexane/EtOH=9/1; flow rate 1.4 cm^3 min^{-1}; detection, UV 254 nm; retention time, t_r=12.35 (*S*-form) and 20.90 min (*R*-form)). The absolute configuration of (+)-**5b** was determined to be (*R*)-form by CD spectrum of (+)-**5b**.

(*S*)-(−)-1,3,4,4a,5,7,8,8a-Octahydro-8a-allyl-6*H*-2-benzothiopyran-6-one ((*S*)-(−)-5b). The cyclization of the diketone (*S*)-(+)-**3b** to the bicyclic ketone **5b** took place upon stirring the diketone with 5% sodium methoxide in methanol at 25 °C for 2 h (see, synthesis of diketone (*S*)-(+)-**3b**): Yield, 45%; mp 54—56 °C (hexane/CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ=1.37—3.10 (12 H, m), 4.90—6.10 (3 H, m), 5.70 (1 H, s); ^{13}C NMR ($CDCl_3$) δ=29.85, 32.84, 34.21, 37.46, 39.21, 39.80, 119.33, 126.88, 132.79, 165.63, 198.21; IR (KBr) 1665 (C=O), 1640 (C=O), 1605 cm^{-1} (C=C); MS *m/z* 208 (M^+), 180, 167, 147, 125; Calcd for $C_{12}H_{16}OS$: M, 208.0922; Found: *m/z* 208.0939; $[\alpha]_D^{25}$ −168° (*c* 1.23, EtOH); CD $[\theta]_{348}$ −331, $[\theta]_{332}$ 0, $[\theta]_{317}$ +408, $[\theta]_{304}$ 0, $[\theta]_{265}$ −3440 (*c* 0.059, EtOH); enantiomeric purity, 88.8% ee (CHIRALPAK AD; hexane/EtOH=9/1; flow rate 1.4 cm^3 min^{-1}; detection, UV 254 nm; t_r=15.63 (*S*-form) and 20.89 min (*R*-form)). The absolute configuration of (−)-**5b** was determined to be (*S*)-form by CD spectrum of (−)-**5b**.

(*S*)-(+)-1,3,4,4a,5,7,8,8a-Octahydro-8a-propyl-6*H*-2-benzothiopyran-6-one ((*S*)-(+)-5c). The base-induced cyclization of the diketone (*S*)-(+)-**3c** (58 mg, 0.25 mmol) with 5% MeONa in methanol afforded (+)-**5c** (26 mg, 50%) as an oil: ^{1}H NMR ($CDCl_3$) δ=0.80—2.83 (17 H, m), 5.73 (1 H, s); IR (neat) 1670 (C=O), 1610 cm^{-1} (C=C); MS *m/z* 210 (M^+), 193, 181, 167, 149; Calcd for $C_{12}H_{18}OS$: M, 210.1078; Found: *m/z* 210.1042; $[\alpha]_D^{25}$ +227° (*c* 0.81, EtOH); CD $[\theta]_{361}$ +1400, $[\theta]_{329}$ 0, $[\theta]_{313}$ −803, $[\theta]_{301}$ 0, $[\theta]_{253}$ +17200 (*c* 0.0096, EtOH); TLC (silica gel, hexane: ether=1/1) R_f=0.31; enantiomeric purity, 95.3% ee (CHIRALPAK AD; hexane/EtOH=9/1; flow rate 1.4 cm^3 min^{-1}; detection, UV 254 nm; retention time, t_r=13.12 (*R*-form) and 15.33 min (*S*-form)). The absolute configuration of (+)-**5c** was determined to be the (*S*)-form based on the CD spectrum of (+)-**5c**.

(*R*)-(−)-5c. Base-induced cyclization of the diketone (*R*)-(−)-**3c** (58 mg, 0.25 mmol) with 5% MeONa in methanol afforded (−)-**5c** (27 mg, 51%) as an oil: ^{1}H NMR ($CDCl_3$) δ=0.50—3.33 (17H, m), 5.77 (1H, s); ^{13}C NMR ($CDCl_3$) δ=14.63, 16.97, 29.91, 32.58, 34.14, 34.34, 35.57, 39.28, 39.86, 126.42, 166.93, 198.54; IR (neat) 1670, 1610 cm^{-1}; MS *m/z* 210 (M^+), 193, 181, 167, 149; Calcd for $C_{12}H_{18}OS$: M, 210.1078; Found: *m/z* 210.1071; $[\alpha]_D^{25}$ −214° (*c* 1.43, EtOH); CD $[\theta]_{345}$ −448, $[\theta]_{330}$ 0, $[\theta]_{315}$ +492, $[\theta]_{302}$ 0, $[\theta]_{268}$ −4660 (*c* 0.068, EtOH); enantiomeric purity, 90.0% ee (CHIRALPAK AD; hexane/EtOH=9/1; flow rate 1.4 cm^3 min^{-1}; detection, UV 254 nm; retention time, t_r=13.04 (*R*-form) and 15.32 min (*S*-form)). The absolute configuration of (−)-**5c** was determined to be (*R*)-form by CD spectrum of (−)-**5c**.

Asymmetric Michael-Type Addition of Chiral Imines 2a—c with Methyl Acrylates. (*R*)-(+)-3-Methyl-3-(2-methoxycarbonylethyl)-4-thianone ((*R*)-(+)-4a). Chiral imine (*S*)-(−)-**2a** (2.06 g, 8.8 mmol) and methyl acrylate (3.01 g, 35 mmol) were dissolved in 10 cm^3 of DMF; the mixture was then stirred for 3 d at room temperature. The ratio of the regioisomer of the addi-

tion products was determined by GC analysis of the imine adducts before hydrolysis. After removing the solvent in vacuo, imine derivatives were hydrolyzed by mixing with acetic acid (3.8 cm^3), sodium acetate (1.7 g) in water (18 cm^3), and ether for 3 h at room temperature. The product was extracted with ether (20 $cm^3 \times 3$), dried over $MgSO_4$, filtered, and concentrated. Purification by column chromatography (silica gel; hexane/ether=4/1) yielded 1.44 g (75%) of Michael-type addition products as a mixture of regioisomers (**4a**/**4a'**=**4.5**/1). The regioisomers were further purified by gel permeation chromatography using a JAI LC-08 liquid chromatograph with two JAIGEL-1H columns (20 mm×600 mm) with chloroform as eluent.

(*R*)-(+)-4a: Oil; ^{1}H NMR ($CDCl_3$) δ=1.20 (3H, s), 1.67–3.07 (10H, m), 3.63 (3H, s); IR (neat) 1730 (C=O), 1700 cm^{-1} (C=O); MS *m/z* 216 (M^+), 198, 184, 169, 157; Calcd for $C_{10}H_{16}O_3S$: M, 216.0820; Found:*m/z* 216.0866; $[\alpha]_D^{25}$ +67.1° (*c* 1.11, EtOH); CD $[\theta]_{299}$ +1130 (*c* 0.052, EtOH); The enantiomeric purity (91.9% ee) of (+)-**4a** was determined by an HPLC measurement using an optically active column (DAICEL CHIRALPAK AD; hexane/EtOH= 9/1; flow rate 1.4 cm^3 min^{-1}; detection, UV 254 nm; retention time, t_r=29.04 (*S*-form) and 39.13 min (*R*-form)).

(*S*)-(−)-3-Methyl-3-(2-methoxycarbonylethyl)-4-thianone ((*S*)-(−)-4a). A DMF solution (10 cm^3) of chiral imine (*R*)-(+)-**2a** (0.933 g, 4 mmol) and methyl acrylate (1.72 g, 20 mmol) was stirred for 3 d at room temperature. After the usual workup for the synthesis of (*R*)-(+)-**4a**, purification by column chromatography (silica gel; hexane/ether=4/1) yielded 0.65 g (75%) of Michael-type addition products as a mixture of regioisomers (**4a**/**4a'**= 5.0/1). The regioisomers were further separated by liquid chromatography ($CHCl_3$ as eluent).

(*S*)-(−)-4a: Oil; ^{1}H NMR ($CDCl_3$) δ=1.20 (3H, s), 1.63—3.07 (10H, m), 3.67 (3H, s); ^{13}C NMR ($CDCl_3$) δ=21.72, 29.00, 30.50, 32.19, 40.64, 41.95, 49.62 (s), 51.63, 173.50, 211.35; IR (neat) 1730, 1700 cm^{-1}; MS *m/z* 216 (M^+), 198, 184, 169, 157; Calcd for $C_{10}H_{16}O_3S$: M, 216.0820; Found: *m/z* 216.0824; $[\alpha]_D^{25}$ −66.7° (*c* 0.98, EtOH); CD $[\theta]_{299}$ −908 (*c* 0.045, EtOH); TLC (silica gel, hexane/ether=1/1) R_f=0.38; enantiomeric purity 92% ee (CHIRALPAK AD; hexane/EtOH=9/1; flow rate 1.4 cm^3 min^{-1}; detection, UV 254 nm; retention time, t_r=28.56 (*S*-form) and 42.95 min (*R*-form)).

(*S*)-(+)-3-Allyl-3-(2-methoxycarbonylethyl)-4-thianone ((*S*)-(+)-4b). A DMF (10 cm^3) solution of chiral imine (*S*)-(−)-**2b** (1.04 g, 4 mmol) and methyl acrylate (1.72 g, 20 mmol) was stirred for 5 d. After a similar hydrolysis as that described above for the synthesis of (*R*)-(+)-**4a**, purification by column chromatography (silica gel; hexane/ether=4/1) yielded 0.336 g (35%) of Michael-type addition products as a mixture of regioisomers (ratio **4b**/**4b'**=1.9/1). The regioisomers were further purified by liquid chromatography ($CHCl_3$ as eluent).

(*S*)-(+)-4b: Oil; ^{1}H NMR ($CDCl_3$) δ=1.70—3.07 (12H, m), 3.60 (3H, s), 4.83—6.07 (3H, m); ^{13}C NMR ($CDCl_3$) δ=28.46, 29.24, 29.89, 38.15, 38.93, 40.88, 51.42, 52.07 (s), 119.05, 132.25, 173.22, 210.22; MS *m/z* 242 (M^+), 224, 211, 201, 169, 155; Calcd for $C_{12}H_{18}O_3S$: M, 242.0976; Found: *m/z* 242.0989; $[\alpha]_D^{25}$ +17.0° (*c* 1.83, EtOH), $[\alpha]_{546}^{25}$ +20.8° (*c* 1.03, EtOH), $[\alpha]_{435}^{25}$ +48.9° (*c* 1.03, EtOH); CD $[\theta]_{296}$ −330 (*c* 0.038, EtOH); enantiomeric purity 94.6% ee (CHIRALPAK AD; hexane/EtOH=9/1; flow rate 1.4 cm^3 min^{-1}; detection, UV 254 nm; retention time, t_r=25.22 (*R*-form) and 27.38 min (*S*-form); TLC (silica gel, hexane/ether=1/1) R_f=0.48.

(*R*)-(−)-3-Allyl-3-(2-methoxycarbonylethyl)-4-thianone ((*R*)-(−)-4b). A THF (15 cm^3) solution of chiral imine (*R*)-(+)-**2b** (1.30 g, 5 mmol) and methyl acrylate (1.72 g, 20 mmol) was stirred for 3 d at room temperature. After hydrolysis, purification by column chromatography (silica gel; hexane/ether=4/1) yielded 0.472 g (39%) of Michael-type additiin products as a mixture of regioisomers (ratio, **4b**/**4b'**=2/1). The regioisomers were further purified by liquid chromatography ($CHCl_3$ as eluent).

(*R*)-(−)-4b: Oil; ^{1}H NMR ($CDCl_3$) δ=1.73—2.90 (12H, m), 3.67 (3H, s), 4.83—5.97 (3H, m); IR (neat) 1730, 1700 cm^{-1}; MS *m/z* 242 (M^+), 211, 201, 169, 155; Calcd for $C_{12}H_{18}O_3S$: M, 242.0976; Found: *m/z* 242.0955; $[\alpha]_D^{25}$ −16.9° (*c* 1.38, EtOH); $[\theta]_{296}$ +412 (*c* 0.057, EtOH); enantiomeric purity 96.0% ee (CHIRALPAK AD; hexane/EtOH=9/1; flow rate 1.4 cm^3 min^{-1}; detection, UV 254 nm; retention time, t_r=25.30 (*R*-form) and 28.39 min (*S*-form); TLC (silica gel; hexane/ether=1/1) R_f=0.42.

(*S*)-(+)-3-(2-Methoxycarbonylethyl)-3-propyl-4-thianone ((*S*)-(+)-4c). A DMF (10 cm^3) solution of chiral imine (*R*)-(+)-**2c** (1.05 g, 4 mmol) and methyl acrylate (1.72 g, 20 mmol) was stirred for 4 d at room temperature. After hydrolysis, purification by column chromatography (silica gel; hexane/ether=4/1) yielded 342 mg (35%) of Michael addition products as a mixture of regioisomers (ratio, **4c**/**4c'**=1.2/1). The regioisomers were further purified by liquid chromatography ($CHCl_3$ as eluent).

(*S*)-(+)-4c: Oil; ^{1}H NMR ($CDCl_3$) δ=0.70—1.10 (3H, m), 1.20—2.40 (8H, m), 3.06 (6H, s), 3.62 (3H, s); ^{13}C NMR ($CDCl_3$) δ=14.63, 16.58, 28.87, 29.46, 30.24, 36.42, 39.34, 41.03, 51.63, 52.61 (s), 173.70, 211.09; IR (neat) 1740, 1700 cm^{-1}; MS *m/z* 244 (M^+), 226, 213, 201, 169; Calcd for $C_{12}H_{20}O_3S$: M, 244.1133; Found: *m/z* 244.1127; $[\alpha]_D^{25}$ +12.9° (*c* 1.01, EtOH), $[\alpha]_{546}^{25}$ +19.7° (*c* 0.98, EtOH), $[\alpha]_{435}^{25}$ +42.6° (*c* 0.98, EtOH); CD $[\theta]_{298}$ +534 (*c* 0.041, EtOH); enantiomeric purity 84.3% ee (CHIRALPAK AD; hexane/EtOH=9/1; flow rate 1.4 cm^3 min^{-1}; detection, UV 254 nm; retention time, t_r=23.74 (*S*-form) and 27.88 min (*R*-form)); TLC (silica gel; hexane/ether=1/1) R_f=0.43.

Synthesis of Optically Active Lactones, (−)-6a and (−)-7a. To an ether–MeOH solution (1/1; 10 cm^3) of (*R*)-(+)-**4a**, $[\alpha]_D^{25}$ +67.1° (*c* 1.11, EtOH), 92% ee, (145 mg, 0.67 mmol) was added sodium borohydride (25 mg, 0.67 mmol) at −78 °C. The reaction mixture was stirred for 15 min at −78 °C, and then warmed slowly to room temperature. To the solution was added 7.2 g of 1% HCl solution; the mixture was stirred for 30 min at room temperature. After removing the organic solvent under vacuum, the products were extracted with dichloromethane (20 $cm^3 \times 2$). The organic layers were combined, washed with water (30 $cm^3 \times 3$), brine (30 cm^3), dried over $MgSO_4$, filtered, and concentrated in vacuo to afford an oil. Purification by short-column chromatography (ca. 10 cm hight of silica gel, CH_2Cl_2 as eluent) yielded 115 mg (92%) of (−)-**6a** and (−)-**7a** as a mixture of diastereomeric isomers (ratio of isomers was determined by GC analysis; **6a**/**7a**=78/22). Both diastereomeric isomers, (−)-**6a** and (−)-**7a**, were further purified by column

chromatography (silica gel, hexane/ether=1/1).

(−)-6a: Yield 68 mg; oil; ^{1}H NMR ($CDCl_3$) δ=1.27 (3H, s), 1.67—3.17 (10H, m), 4.13 (1H, t, J=4.0 Hz); ^{13}C NMR ($CDCl_3$) δ=23.09, 23.93, 26.73, 29.07, 31.48 (s), 31.87, 34.34, 81.81, 171.03; IR (neat) 1725 cm^{-1}; MS m/z 186 (M^+), 168, 158, 140, 126, 113; Calcd for $C_9H_{14}O_2S$: M, 186.0714; Found: m/z 186.0680; $[\alpha]_D^{25}$ −12.9° (c 0.99, EtOH); CD $[\theta]_{235}$ −498 (c 0.053, EtOH); TLC (silica gel; hexane/ether=1/1) R_f=0.30.

(−)-7a: Yield 9 mg; oil; ^{1}H NMR ($CDCl_3$) δ=1.23 (3H, s), 1.50—2.90 (10H, m), 3.80—4.07 (1H, m); ^{13}C NMR ($CDCl_3$) δ=15.15, 27.51, 28.03, 28.81, 33.95 (s), 34.79, 40.58, 83.69, 170.25; IR (neat) 1730 cm^{-1}; MS m/z 186 (M^+), 171, 158, 138, 130, 113; Calcd for $C_9H_{14}O_2S$: M, 186.0714; Found: m/z 186.0698; $[\alpha]_D^{25}$ −128° (c 0.87, EtOH); CD $[\theta]_{251}$ +53, $[\theta]_{245}$ 0, $[\theta]_{228}$ −607 (c 0.047, EtOH); TLC (silica gel, hexane/ether=1/1) R_f=0.26.

A reduction of keto ester (*R*)-(+)-**4a** with sodium borohydride in the presence of cerium trichloride was performed. According to the procedure described above for the preparation of lactones (−)-**6a** and (−)-**7a**, to a mixture of (*R*)-(+)-**4a** (108 mg, 0.50 mmol) and cerium trichloride hexahydrate (186 mg, 0.50 mmol) in 10 cm^3 of ether–MeOH (1/1) was added sodium borohydride (19 mg, 0.50 mmol) at −78 °C. Purification of the product by short-column chromatography (ca. 10 cm hight of silica gel; CH_2Cl_2 as eluent) yielded 87 mg (94%) of (−)-**6a** and (−)-**7a** as a mixture of diastereomeric isomers (ratio of isomers was determined by GC; **6a**/**7a**=61/39). Lactones (−)-**6a** and (−)-**7a** were further purified by column chromatography (silica gel, hexane/ether=1/1). (−)-**6a**: yield 50 mg; (−)-**7a**: yield 18 mg.

Synthesis of Lactones (−)-6b and (−)-7b. A MeOH (15 cm^3) solution of 121 mg (0.50 mmol) of (+)-**4b** ($[\alpha]_D^{25}$ +17.0° (c 1.83, EtOH), 95% ee), was treated with 19 mg (0.50 mmol) of sodium borohydride at room temperature. After the mixture was stirred for 2.5 h at room temperature, 3.6 cm^3 of 1% HCl was added; the mixture was then stirred for 0.5 h. After removing the organic solvent under vacuum, to the residue was added water (10 cm^3); the products were then extracted with CH_2Cl_2 (20 cm^3×3). The organic layer was washed with water (50 cm^3×2), dried over $MgSO_4$, filtered, and concentrated in vacuo to give 88 mg (82%) of lactones, (−)-**6b** and (−)-**7b**, as a mixture of diastereomeric isomers (ratio of isomers was determined by GC: **6b**/**7b**=78/22). Lactones (−)-**6b** and (−)-**7b** were further separated by column chromatography (silica gel, hexane/ether=4/1).

(−)-6b: Yield 54 mg; oil; ^{1}H NMR ($CDCl_3$) δ=1.20—3.20 (12H, m), 4.17 (1H, t, J=4.0 Hz), 4.93—6.13 (3H, m); ^{13}C NMR ($CDCl_3$) δ=22.89, 26.73, 28.61 (2×C), 32.65, 34.34 (s), 39.47, 80.18, 119.85, 131.69, 171.16; IR (neat) 1740, 1640 cm^{-1}; MS m/z 212 (M^+), 197, 184, 170, 156; Calcd for $C_{11}H_{16}O_2S$: M, 212.0871; Found: m/z 212.0838; $[\alpha]_D^{25}$ −19.4° (c 1.34, CH_2Cl_2); CD $[\theta]_{237}$ −738 (c 0.063, CH_2Cl_2); TLC (silica gel; hexane/ether=1/1) R_f=0.26.

(−)-7b: Yield 14 mg; oil; ^{1}H NMR ($CDCl_3$) δ=0.77—3.00 (12H, m), 4.03 (1H, t, J=6.0 Hz), 4.93—5.77 (3H, m); IR (neat) 1730, 1640 cm^{-1}; MS m/z 212 (M^+), 197, 184, 170, 155; Calcd for $C_{11}H_{16}O_2S$: M, 212.0871; Found: m/z 212.0842; $[\alpha]_D^{25}$ −59.2° (c 0.32, CH_2Cl_2); CD $[\theta]_{232}$ −591 (c 0.015, CH_2Cl_2); TLC (silica gel; hexane/ether=1/1) R_f=0.19.

Sulfone (+)-8. To a CH_2Cl_2 (10 cm^3) solution of lactone (−)-**6a** (102 mg, 0.55 mmol; $[\alpha]_D^{25}$ −12.9° (c 0.99, EtOH)), was added *m*-chloroperbenzoic acid (285 mg, 1.65 mmol) over 5 min at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and then for 3 h at room temperature. Water (5 cm^3) and CH_2Cl_2 (20 cm^3) were added to the reaction mixture; the organic layer was then washed with 10% potassium carbonate solution (20 cm^3×4), dried over $MgSO_4$, filtered, and concentrated in vacuo to give 22 mg (18%) of sulfone (+)-**8** as a white solid: Mp 192—194 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ=1.40 (3H, s), 1.50—3.67 (10H, m), 4.23 (1H, t, J=3.0 Hz); IR (KBr) 1720, 1320, 1120 cm^{-1}; MS m/z 219 (M^+ + 1), 203, 201, 154, 139; Calcd for $C_9H_{14}O_4S$: M, 218.0613; Found: m/z 218.0582; $[\alpha]_D^{25}$ +13.9° (c 0.81, CH_2Cl_2).

Lactone (+)-9. To a MeOH—THF (3/1; 8 cm^3) solution of lactone (−)-**6b** (24 mg, 0.11 mmol), $[\alpha]_D^{25}$ −19.4° (c 1.34, CH_2Cl_2), 95% ee, was added nickel chloride hexahydrate (188 mg, 0.79 mmol) at 0 °C. This mixture was stirred for 10 min and then treated with sodium borohydride (90 mg, 2.37 mmol) in portions at 0 °C. The mixture was stirred at 0 °C for 1 h, and then at room temperature for 2 h. After removing the precipitate by filtration using short-column chormatography (10 cm hight of silica gel, CH_2Cl_2 as eluent), the product was isolated from the filtrate and purified by column chromatography (silica gel; hexane/ether=4/1); yield 15 mg (74%); oil; ^{1}H NMR ($CDCl_3$, 90 MHz) δ=0.91 (3H, s), 0.91—0.93 (3H, m), 1.07 (3H, t, J=6.6 Hz), 1.27—1.79 (8H, m), 2.53 (2H, t, J=7.4 Hz), 3.91 1H, dd, J=8.8 and 2.9 Hz); IR (neat) 1730 cm^{-1}; MS m/z 184 (M^+), 155, 149, 141, 126, 108; Calcd for $C_{11}H_{20}O_2$: M, 184.1464; Found: m/z 184.1460; $[\alpha]_D^{25}$ +85.3°(c 0.27, EtOH).

X-Ray Single Crystal Structure Analysis of Sulfone (+)-8. Crystal Data for Compound (+)-8. $C_9H_{14}O_4S$, M=218.10. Monoclinic, a=7.772(2), b=10.592(2), c=6.268(2) Å, β=102.74(2)°, V=503.4(2) Å^3, space group $P2_1$, Z=2, D_x=1.44 g cm^{-3}. Colorless rods. Crystal dimensions: 1.10×0.50×0.35 mm^3, μ(Mo $K\alpha$)=2.56 cm^{-1}. F(000)=232. T=295 K.

Data Collection and Processing. A Mac Science MXC18 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation (0.7107 Å) was used. The unit-cell parameters were determined from 25 reflections with $30° \leqq 2\theta \leqq 35°$. The intensity data with $2\theta < 55°$ ($-10 \leqq h \leqq 10$, $0 \leqq k \leqq 14$, $0 \leqq 1 \leqq 8$) were collected with the 2θ–ω-scan technique (scan speed 8° min^{-1}) at 1732 reflections. The deviation of three standard reflections measured every 100 reflections was less than 2.6% decay over the time of the entire data correction. Although the intensities were corrected for Lorentz and polarization factors, they were not corrected for absorption.

Structure Analysis and Refinement. The structure was solved by the Monte-Carlo direct methods[12] by the use of MULTAN-78 program.[13] A full-matrix least-squares refinement for non-H atoms was carried out for $\Sigma w (|F_o|^2 - |F_c|^2)^2$, where the weight $w = 1.0/[(\sigma|F_o|)^2 + 0.0001(|F_o|)^2]$ was used for 1434 independent reflections with $F_o > 3.0\sigma$ (F_o). The final discrepancy factors were R=0.040 and R_w=0.043, and $(\Delta/\sigma)_{max}$ in the final refinement cycle was 0.36. The scattering factors were taken from International Tables of X-Ray Crystallography, Vol. 4.[14] All the

calculation were carried out on a Mac Science MXC18 SYSTEM; ORTEP[15] was employed for drawing the molecular structure.[16]

Synthesis of Optically Active 3-Cyclopenten-1-one, (*S*)-(+)-2-[3-(Benzyloxy)propyl]-2-methyl-3-cyclopenten-1-one (15). 6-Methyl-6-(2-methoxycarbonylethyl)-1,4-dioxa-8-thiaspiro[4.5]decane (10). A benzene (30 cm^3) solution of 178 mg (0.82 mmol) of keto ester (*R*)-(+)-**4a** ($[\alpha]_D^{25}$ +67.1° (*c* 1.11, EtOH), 92% ee), 124 mg (2 mmol) of ethylene glycol, and a catalytic amount of *p*-toluenesulfonic acid (5 mg) was put in a 50 cm^3 round-bottom flask fitted with a Dean–Stark trap. The ketone was acetalized by heating to reflux for 14 h and then removing water by azeotropic distillation. After the reaction mixture was cooled to room temperature, benzene was removed under vacuum. The residual oil was purified by silica-gel column chromatography (CH_2Cl_2 as eluent) to give **10**: Oil; yield 200 mg (93%); ^{1}H NMR ($CDCl_3$) δ=1.03 (3H, s), 1.63—3.07 (10H, m), 3.60 (3H, s), 3.87 (4H, s); IR (neat) 1740 cm^{-1} (ester C=O); MS *m/z* 260 (M^+), 299, 199, 186, 173; TLC (silica gel, hexane/ether=1/1) R_f=0.49.

(*R*)-(+)-6-Methyl-6-(3-hydroxypropyl)-1,4-dioxa-8-thiaspiro[4.5]decane (11). After the ester **10** (196 mg, 0.75 mmol) was dissolved in 10 cm^3 of THF, the solution was cooled in an ice-water bath under a N_2 atmosphere. To the solution was added $LiAlH_4$ (29 mg, 0.75 mmol) and the mixture was stirred for 15 min at 0 °C and for 1 h at room temperature. After the addition of 6 equiv HCl solution to make pH 2—3, the product was extracted with ether (20 cm^3×3). The ether solution was washed with water (30 cm^3×3) and dried over $MgSO_4$. After removing the solvent, the product was purified by silica-gel column chromatography (CH_2Cl_2 as eluent): Oil; yield, 140 mg (80%); $[\alpha]_D^{25}$ +19.0° (*c* 1.05, EtOH); ^{1}H NMR ($CDCl_3$) δ=1.00 (3H, s), 1.23—2.87 (11H, m), 3.58 (2H, t, *J*=6.0 Hz), 4.87 (4 H, s); IR (neat) 3350 cm^{-1} (OH); MS *m/z* 232 (M^+), 171, 132, 113, 99, 86.

6-Methyl-6-[3-(benzyloxy)propyl]-1,4-dioxa-8-thiaspiro[4.5]-decane ((*R*)-(+)-12). The alcohol **11** (130 mg, 0.56 mmol) was treated with NaH (48 mg, 2 mmol) in 10 cm^3 of THF at room temperature for 15 min under a N_2 atmosphere. After the addition of benzyl bromide (162 mg, 0.95 mmol) to the above-mentioned solution, the THF solution was refluxed for 19 h. After the solution was cooled to room temperature, a small amount of water was added. After removing the THF under vacuum, the crude product was extracted with ether (20 cm^3×3) and the ether solution was washed with water (30 cm^3×3) and dried over $MgSO_4$. Filtration and solvent evaporation gave an oil, which was purified by column chromatography (hexane/ether=1/1); oil; yield, 106 mg (59%); $[\alpha]_D^{25}$ +24.0° (*c* 1.62, EtOH); ^{1}H NMR ($CDCl_3$) δ=1.00 (3H, s) 1.20—2.07 (6H, m), 2.47—2.83 (4H, m), 3.17—3.73 (2H, m), 3.87 (4H, s), 4.47 (2H, s), 7.23 (5H, s); IR (neat) 3040 cm^{-1} (aromatic CH); MS *m/z* 322 (M^+), 261, 231, 173, 132, 113, 99, 91; TLC (silica gel, hexane/ether=1/1) R_f=0.48. The unreacted alcohol **11** (31 mg, 24%) was also recovered.

6-Methyl-6-[3-(benzyloxy)propyl]-1,4-dioxa-8-thiaspiro[4.5]-decane 8,8-dioxide ((*R*)-(+)-13). The benzyl ether **12** (74 mg, 0.23 mmol) was dissolved in 5 cm^3 of CH_2Cl_2 and cooled to 0 °C. *m*-Chloroperbenzoic acid (119 mg, 0.69 mmol) was added over 5 min to the above-mentioned solution with stirring at 0 °C. The solution was stirred at 0 °C for 1 h and then at room temperature for 3 h. Water (5 mL) and CH_2Cl_2 (25 cm^3) were added to the above mixture, and the CH_2Cl_2 solution was washed with 10% potassium carbonate solution (10 cm^3×3). The organic layer was dried over $MgSO_4$ and evaporated under vacuum to afford **13** as an oil; 82 mg (100%); $[\alpha]_D^{25}$ +3.48° (*c* 1.64, EtOH); ^{1}H NMR ($CDCl_3$) δ=1.07 (3H, s), 1.37—1.77 (4H, m), 2.00—2.37 (2H, m), 2.83—3.57 (6H, m), 3.87 (4H, s), 4.37 (2H, s), 7.17 (5H, s); IR (neat) 3080, 3040 (aromatic CH), 1320, 1300, 1120, 1110 cm^{-1} (SO_2); MS *m/z* 354 (M^+), 309, 279, 262, 247, 203, 171; Calcd for $C_{18}H_{26}O_5S$: M, 354.1501; Found: *m/z* 354.1483.

6-[3-(Benzyloxy)propyl]-6-methyl-1,4-dioxaspiro-[4.4]non-7-ene ((*S*)-(+)-14). Six-membered sulfone **13** (75 mg, 0.21 mmol) was dissolved in carbon tetrachloride (10 cm^3) and dry *t*-butyl alcohol (5 cm^3), and to the above-mentioned solution was added potassium *t*-butoxide (236 mg, 2.1 mmol) below 50 °C under a N_2 atmosphere. The mixture was stirred for 40 h at 50—55 °C. After the reaction solution was cooled to room temperature, the solution was poured into water (30 cm^3); the product was then extracted with ether (40 cm^3×3). The ether extract was washed with water (30 cm^3×3) and brine (30 cm^3), and dried over $MgSO_4$. Filtration and solvent evaporation gave 43 mg (71%) of an oil, which was mostly pure **14**: ^{1}H NMR ($CDCl_3$) δ=1.07 (3H, s), 1.20—1.97 (4H, m), 2.50 (2H, s), 3.20—3.33 (2H, m), 3.90 (4H, s), 4.43 (2H, s), 5.63 (2H, s), 7.27 (5H, s); ^{13}C NMR ($CDCl_3$) δ=19.70, 25.43, 29.72, 32.52, 42.60, 51.31 (s), 64.45, 64.84, 71.47, 72.90, 125.71, 127.46, 127.66, 128.31, 138.84, 139.17; IR (neat) 3050, 3020 (aromatic CH), 1610 cm^{-1} (C=C); MS *m/z* 288 (M^+), 273, 245, 197, 182, 153, 139; Calcd for $C_{18}H_{24}O_3$: M, 288.1725; Found: *m/z* 288.1746; $[\alpha]_D^{25}$ +29.7° (*c* 1.01, EtOH); TLC (silica gel, hexane/ether=1/1) R_f=0.56.

2-[3-(Benzyloxy)propyl]-2-methyl-3-cyclopenten-1-one ((*S*)-(+)-15). An aqueous acetone solution (10 cm^3, water/acetone=1/4) of ketal **14** (40 mg, 0.14 mmol) and pyridinium *p*-toluenesulfonate (3 mg) was refluxed for 5 h. After removing the acetone under vacuum, water (15 cm^3) was added to the residue and cyclopentenone was extracted with ether (20 cm^3×3). The ether extract was washed with water (20 cm^3×3) and brine (20 cm^3), and dried over $MgSO_4$. Filtration and solvent evaporation gave 34 mg (100%) of an oil, which was mostly pure 3-cyclopenten-1-one **15**: ^{1}H NMR ($CDCl_3$) δ=1.10 (3H, s), 1.17—1.83 (4H, m), 2.83 (2H, s), 3.23—3.57 (2H, m), 4.43 (2H, s), 5.80—6.17 (2H, m), 7.27 (5H, s): IR (neat) 3050 (aromatic CH), 1740 cm^{-1} (C=O); MS *m/z* 244 (M^+), 226, 216, 198, 188, 172, 157; Calcd for $C_{16}H_{20}O_2$: M, 244.1463; Found: *m/z* 244.1415; $[\alpha]_D^{25}$ +30.8° (*c* 1.75, CH_2Cl_2); TLC (silica gel, hexane/ether=1/1) R_f=0.56.

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