A Novel Synthesis Including Asymmetric Synthesis of α,β-Unsaturated γ-Hydroxy Carbonyl Compounds from Enones with Carbon Homologation[1)]

Tsuyoshi SATOH, Shigeyasu MOTOHASHI,† Norio TOKUTAKE,† and Koji YAMAKAWA*
Faculty of Pharmaceutical Sciences, Science University of Tokyo, Ichigaya-funagawara-machi, Shinjuku-ku, Tokyo 162
† College of Pharmacy, Nihon University, Narashinodai, Funabashi, Chiba 274
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Reaction of the carbanion derived from 1-chloroalkyl aryl sulfoxides with enones gave 1,2-adducts in good yields. Treatment of the adduct with potassium benzenethiolate afforded α-phenylthio β,γ-unsaturated carbonyl compound through an α,β-epoxy sulfoxide. Oxidation of the sulfide with 2.1 equivalents of *m*-chloroperbenzoic acid gave α,β-unsaturated γ-phenylsulfinyloxy carbonyl compound via sulfoxide–sulfenate rearrangement. The sulfinate was easily hydrolyzed with aqueous potassium hydroxide to afford α,β-unsaturated γ-hydroxy carbonyl compound in good yield. When optically active (−)-1-chloroalkyl *p*-tolyl sulfoxides were used in this procedure, a synthesis of optically active α,β-unsaturated γ-hydroxy carbonyl compounds with moderate to good optical purity was realized.

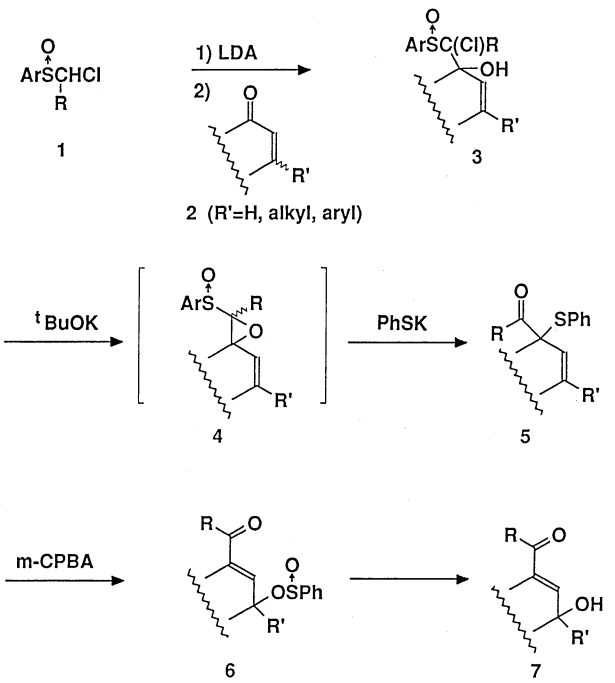
Carbonyl compounds are of most importance in synthetic organic chemistry. Especially, α,β-unsaturated carbonyl compounds are useful in various synthetic reactions such as the Diels–Alder reaction[2)] and Michael-type reactions.[3)] Innumerable studies on the preparation and chemistry of carbonyl compounds have already been reported;[4)] however, new procedure for their synthesis from readily available precursors is eagerly sought.

In the synthesis of carbonyl compounds, homologation of carbonyl compounds is most straightforward and reliable.[5)] In our recent studies on homologation of carbonyl compounds we reported the successful use of 1-chloroalkyl aryl sulfoxides **1** as acyl anion equivalents. Saturated ketones and aldehydes were used in the studies and various homologated carbonyl compounds, including α,β-unsaturated and optically active ones, were realized.[6)] In continuation of our studies on the use of 1-chloroalkyl aryl sulfoxides in homologation of carbonyl compounds, herein we report, in detail, a new homologation of α,β-unsaturated ketones **2** to α,β-unsaturated γ-hydroxy carbonyl compounds **7**, including optically active ones (Scheme 1).[7)]

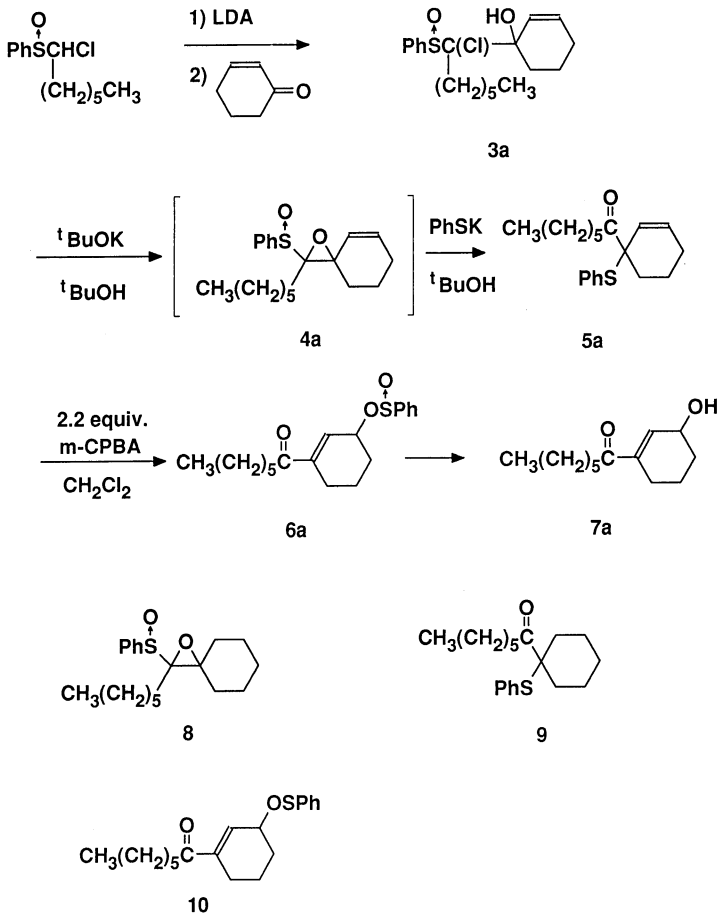
Results and Discussion

A Synthesis of α,β-Unsaturated γ-Hydroxy Carbonyl Compounds from α,β-Unsaturated Ketones Using 1-Chloroalkyl Phenyl Sulfoxides as Homologating Agents. A representative example of the synthesis of α,β-unsaturated γ-hydroxy carbonyl compounds **7** from α,β-unsaturated ketones **2** using 1-chloroheptyl phenyl sulfoxide and 2-cyclohexen-1-one is described (Scheme 2).

The carbanion derived from 1-chloroheptyl phenyl sulfoxide[8)] with slight excess of lithium diisopropylamide (LDA) was reacted with 2-cyclohexen-1-one to afford a mixture of two diastereomers of the 1,2-adduct **3a** in 91% yield. As the stereochemistry of the carbon bearing the chlorine atom is completely controlled by the chirality of the sulfur center,[6,14b)] this reaction gave only two diastereomers though the adduct has three chiral centers. In order to get γ,δ-unsaturated α,β-epoxy sulfoxide **4a**, the mixture of **3a** was treated with potassium *t*-butoxide (*t*-BuOK) in *t*-butanol at room temperature. This reaction worked; however, the resulted α,β-epoxy sulfoxide **4a** was found to be quite unstable. For example, on exposure to silica gel or alumina, **4a** decomposed immediately to give a complex mixture. To overcome this problem, we planned a one-pot reaction for formation of the α,β-epoxy sulfoxide **4a** and simultaneous nucleophilic ring-opening of **4a** with thiolate.[9)] Thus, **3a** was treated with 2.4 equivalents of *t*-BuOK in *t*-BuOH in the



Scheme 1.



Scheme 2.

presence of 2.2 equivalents of benzenethiol at room temperature for 10 min to afford the desired α-phenylthio β,γ-unsaturated ketone **5a** in 61% yield. This reaction was thought to take place via the α,β-epoxy sulfoxide **4a**.

It is interesting to note that the ring-opening reaction of the corresponding saturated α,β-epoxy sulfoxide **8** with benzenethiolate required a large excess of thiolate in refluxing ethanol for 2.5 h to afford α-phenylthio ketone **9** (96% yield).[9] In contrast to the results in the previous paper,[9] the ring-opening reaction of **4a** with thiolate required much milder conditions, and the result indicated that the reactivity of γ,δ-unsaturated α,β-epoxy sulfoxides **4** toward nucleophiles might be much higher than that of γ,δ-saturated α,β-epoxy sulfoxides.

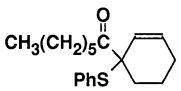
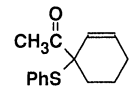
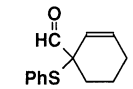
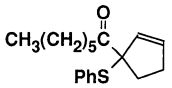
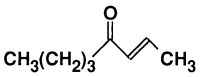
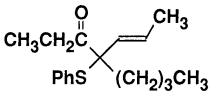
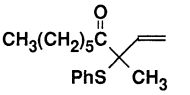
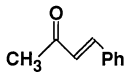
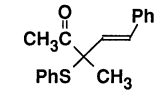
Table 1 shows the results for preparation of α-phenylthio β,γ-unsaturated carbonyl compounds **5** from 1-chloroalkyl phenyl sulfoxide **1** and enones **2** through the chloro alcohols **3**. In some cases, reaction of the carbanion of **1** with enones gave 1,4-adduct as a by-product (Entry d—f). Treatment of **3** with potassium benzenethiolate gave a moderate to good yield of α-phenylthio ketones **5**. When 1-chloroalkyl phenyl sulfoxide has a bulky alkyl group (**1**: R=isopropyl or cyclohexyl) the yield for the addition of **1** to enones was found to be low and treatment of the adduct with benzenethiolate gave only retro-alkylation products.

Next, oxidation of the sulfide **5a** was carried out with 1.1 equivalents of *m*-chloroperbenzoic acid (*m*-CPBA) at −60 to −30°C for 2 h. This reaction gave rearranged sulfenate **10** (26%) and sulfinate **6a** (20%), and no sulfoxide was observed. We were somewhat surprised by this result because sulfoxide-sulfenate equilibrium under ordinary conditions usually greatly favors the sulfoxide.[10] Formation of the thermodynamically stable enone seems to be the reason for this easy sulfoxide–sulfenate rearrangement. Further, the rate for the oxidation of the sulfenate **10** with *m*-CPBA was faster than that of the sulfide **5a**.

In order to convert all the starting material **5a** into the sulfinate **6a**, **5a** was treated with 2.1 equivalents of *m*-CPBA at 0°C for 15 min to give **6a** in 89% yield. As the sulfinate **6a** was found to be unstable, it was immediately hydrolyzed with 10% potassium hydroxide in methanol at room temperature to afford the desired α,β-unsaturated γ-hydroxy ketone **7a** in 93% yield. The results for preparation of α,β-unsaturated γ-hydroxy carbonyl compounds **7** from α-phenylthio ketones **5** are summarized in Table 2. The yields in each step are good except for two examples (Entry f, g).

The configuration of the double bond of the products (**7e**—**7g**) was determined from the chemical shift of the

Table 1. Preparation of α-Phenylthio β,γ-Unsaturated Carbonyl Compounds **5** from **1** (Ar=Ph) through Chloro Alcohols **3**

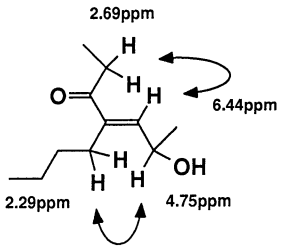
Entry	**1** R	Enone (2)	**3** Yield (%)[a]	**5** Yield (%)[a]
a	n-C_6H_{13}		**3a** (91)	 **5a** (61)
b	CH_3	〃	**3b** (95)	 **5b** (87)
c	H	〃	**3c** (86)	 **5c** (62)
d	n-C_6H_{13}		**3d** (42)[b]	 **5d** (59)
e	CH_3CH_2		**3e** (61)[c]	 **5e** (43)
f	n-C_6H_{13}		**3f** (61)[d]	 **5f** (52)
g	CH_3		**3g** (94)	 **5g** (93)

a) Isolated yield. b) With 1,4-adduct (28%). c) With 1,4-adduct (12%). d) With 1,4-adduct (32%).

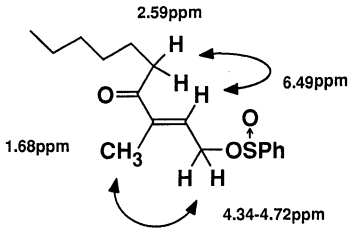
vinylic hydrogen[11] and NOESY spectrum.[12] For example, the NOESY experiment of **7e** shows two cross-peaks between protons at δ=2.29 and 4.75, and between protons at δ=2.69 and 6.44 (Fig. 1). In a similar way the configuration of **7f** was determined from the NOESY experiment of **6f**. These stereochemistries were consistent with the results reported by Evans.[10]

Asymmetric Synthesis of α,β-Unsaturated γ-Hydroxy Carbonyl Compounds. Optically active sulfoxides have recently received considerable attention for use in the synthesis of optically active compounds.[13] We recently reported some new asymmetric synthesis starting from optically active (−)-1-chloroalkyl p-tolyl sulfoxides.[14] We thought that when optically active **1** are used in the procedure described above, optically active α,β-unsaturated γ-hydroxy carbonyl compounds can be synthesized. Here we describe the successful use of optically active (−)-1-chloroalkyl p-tolyl sulfoxides **11** in the synthesis of optically active α,β-unsaturated γ-hydroxy carbonyl compounds (Scheme 3).

Optically active 1-chloroalkyl p-tolyl sulfoxides (**11**: over 97% enantiomeric excess (ee) with respect to the sulfur chiral center) were synthesized from optically



7e



6f

Fig. 1. NOESY connective pattern of **7e** and **6f**.

Table 2. Preparation of α,β-Unsaturated γ-Hydroxy Carbonyl Compounds 7

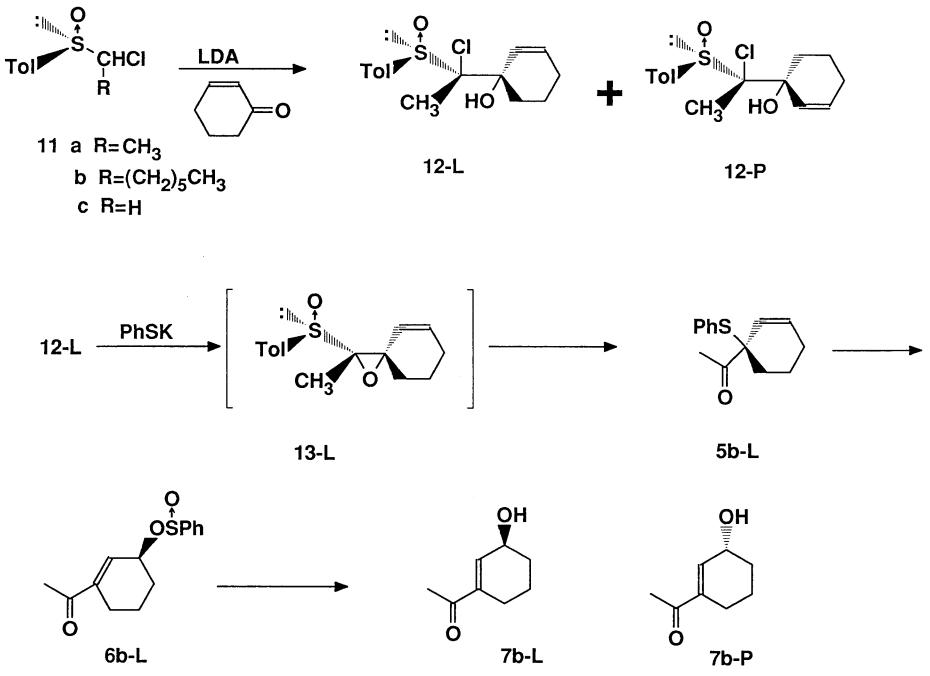
Entry	5	6 Yield (%)[a]	7 Yield (%)[a]
a	**5a**	**6a** (89)	**7a** (93)
b	**5b**	**6b** (84)	**7b**(94)
c	**5c**	**6c** (83)	**7c** (87)
d	**5d**	**6d** (88)	**7d** (98)
e	**5e**	**6e** (93)	**7e** (77)
f	**5f**	**6f** (55)	**7f** (60)
g	**5g**	**6g** (87)	**7g** (51)

a) Isolated yield.

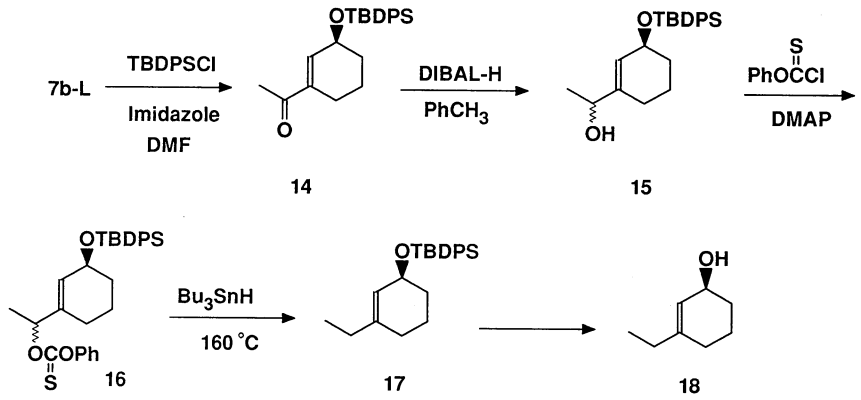
active methyl *p*-tolyl sulfoxide via (−)-chloromethyl *p*-tolyl sulfoxide.[14b] (−)-1-chloroethyl *p*-tolyl sulfoxide **11a** was reacted with 2-cyclohexen-1-one to afford the less polar adduct (**12-L**; 51%) and the more polar adduct (**12-P**; 40%). As already reported, the absolute stereochemistry of the carbon bearing the chlorine atom of **12-L** and **12-P** is *R*.[14b] The adduct **12-L** was treated with potassium benzenethiolate to afford optically active α-sulfenyl ketone **5b-L** ($[\alpha]_D$ +23°) via **13-L**. This compound was converted to optically active α,β-unsaturated γ-hydroxy ketone **7b-L** ($[\alpha]_D$ −51°) via the sulfinate **6b-L**. The ee of **7b-L** was calculated to be 77% by ^{1}H NMR (400 MHz) in the presence of 40 mol% of Eu(hfc)$_3$ as a chiral shift reagent. The same treatment of **12-P** gave the enantiomer **7b-P** ($[\alpha]_D$ +46.4°).

The absolute configuration of **7b-L** was determined as follows (Scheme 4). The hydroxyl group of **7b-L** was protected as *t*-butyldiphenylsilyl ether[15] to give **14** in quantitative yield. The ketone of **14** was reduced with diisobutylaluminum hydride (DIBAL-H) to give **15**, which was converted to phenoxythiocarbonyl derivative **16**. Reduction of **16** was carried out with tributyltin hydride under heating to afford **17** in moderate yield.[16] Deprotection of **17** under conventional conditions gave optically active allylic alcohol **18** ($[\alpha]_D$ −27.9°; 61% ee). Comparing the sign of the specific rotation of **18** with that of (*S*)-(−)-3-methyl-2-cycohexen-1-ol ($[\alpha]_D$ −96.3°),[17] the absolute configuration of **18** was unambiguously *S*. This result indicates that the absolute configuration of **7b-L** is also *S*.

Examples of the asymmetric synthesis of **7a**—**7c** from **11** and 2-cyclohexen-1-one are shown in Table 3. In the case of the synthesis of aldehyde **7c**, the alkylation of **11c**

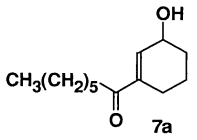
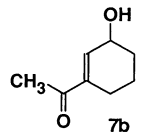
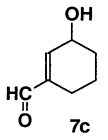


Scheme 3.



Scheme 4.

Table 3. The Absolute Configuration and Enantiomeric Excess of Optically Active α,β-Unsaturated γ-Hydroxy Carbonyl Compounds (**7a**—**7c**)

		$[\alpha]_D^{25}$ deg[a]	ee[b]	Absolute configuration
 **7a**	L	−32.9	82	(*S*)
	P	+30.7	75	(*R*)
 **7b**	L	−51.0	77	(*S*)
	P	+46.4	76	(*R*)
 **7c**		+63.0	67	(*R*)

a) All specific rotations were measured in acetone. b) Calculated from ^{1}H NMR in the presence of Eu(hfc)$_3$.

with 2-cyclohexen-1-one gave a mixture of two inseparable diastereomers (ratio about 9 : 1); however, the main product could be separated by recrystallization. The ee of the starting materials **11** was about 97%, but the ee of the products **7a**—**7c** was about 70—80%. Unfortunately, the ee of the intermediates (**5a**—**5c** and **6a**—**6c**) could not be successfully determined. At present we suppose that this racemization occurred at the last stage, basic hydrolysis of the sulfinates (**6a**—**6c**).

Experimental

All melting points are uncorrected. IR spectra were measured directly on a NaCl plate or in KBr disks. NMR spectra were measured in $CDCl_3$ solution on JEOL-EX90 (90 MHz), FX-100 (100 MHz), or GSX-400 (400 MHz) spectrometer using Me_4Si as an internal standard. EI and CI (isobutane) mass spectra (MS) were recorded on Hitachi M-2000 spectrometer. Specific rotation was measured on a JASCO DIP-360 polarimeter at 25 °C. Silica-gel containing 2% fluorescence reagent 254 and a quartz column were used for column chromatography, and the products having UV absorption were detected by UV irradiation. In experiments requiring a dry solvent, THF was distilled from diphenylketyl; diisopropylamine, CH_2Cl_2, toluene, and DMF were dried over CaH_2 and distilled.

General Procedure for the Synthesis of Chloro Alcohol (3a—3g). To a solution of LDA (5.5 mmol) in 10 ml of dry THF at −60 °C under N_2 atmosphere was added dropwise, with stirring, a solution of 1-chloroheptyl phenyl sulfoxide (1.3 g; 5 mmol) in 2.5 ml of dry THF. The mixture was stirred for 10 min, and then a solution of 2-cyclohexen-1-one (576 mg; 6 mmol) in 1 ml of THF was added. After 5 min the reaction was quenched with sat. aq NH_4Cl. The whole was extracted with benzene and the organic layer was washed with sat. aq NH_4Cl. The solution was dried over Na_2SO_4, and the solvent was evaporated to leave a residue, which was purified by silica-gel column chromatography to give 1.62 g (91%) of 1-[1-chloro-1-(phenylsulfinyl)heptyl]-2-cyclohexen-1-ol (**3a**) as a colorless oil (a mixture of two diastereomers). IR (neat) 3400 (OH) and 1050 (SO) cm^{-1}; ^{1}H NMR δ=0.62—2.52 (19H, m), 4.20 (1H, bs), 5.68 (2H, m), and 7.28—7.96 (5H, m); MS *m/z* (%) 229 ([M−PhSO]$^+$, 3), 200(21), 157(11), 129(86), and 97(100).

All other chloro alcohols (**3b**—**3g**) were synthesized in a similar way as described above.

3b: Colorless crystals; mp 110—112 °C (AcOEt–hexane); IR (KBr) 3300 (OH) and 1040 (SO) cm^{-1}; ^{1}H NMR δ=1.46 (1.5H, s), 1.48 (1.5H, s), 1.64—2.56 (6H, m), 3.29 (0.5H, s), 4.30 (0.5H, s), 5.84—6.28 (2H, m), and 7.40—7.84 (5H, m). Found: C, 59.13; H, 6.00; S, 11.11%. Calcd for $C_{14}H_{17}ClO_2S$: C, 59.04; H, 6.02; S, 11.26%.

3c: Colorless crystals; mp 122—124 °C (AcOEt–hexane); IR (KBr) 3350 (OH) and 1045 (SO) cm^{-1}; ^{1}H NMR δ=1.56—2.24 (6H, m), 3.20 (1H, bs), 4.46 (1H, s), 5.84—6.22 (2H, m), and 7.44—7.76 (5H, m). Found: C, 57.78; H, 5.48; S, 11.93%. Calcd for $C_{13}H_{15}ClO_2S$: C, 57.67; H, 5.58; S, 11.84%.

3d: Colorless oil; IR (neat) 3350 (OH) and 1050 (SO) cm^{-1}; ^{1}H NMR δ=0.87 (3H, t, *J*=6 Hz), 1.0—2.8 (14H, m), 3.96—4.28 (1H, m), 5.76—6.10 (2H, m), and 7.36—7.94 (5H, m); MS *m/z* (%) 234(5), 214 ([M−PhSOH]$^+$, 13), 179(46), 145(18), and 126(100).

3e: Colorless oil; IR (neat) 3400 (OH) and 1045 (SO) cm^{-1}; ^1H NMR δ=0.76—2.50 (17H, m), 4.90 (1H, bs), 5.24—6.34 (2H, m), and 7.40—7.88 (5H, m); MS *m/z* (%) 253(12), 203 ([M−PhSOH]$^+$, 13), 186(8), and 145(100).

3f: Colorless oil; IR (neat) 3350 (OH) and 1040 (SO) cm^{-1}; ^1H NMR δ=0.86 (3H, t, *J*=6 Hz), 0.98—2.12 (13H, m), 4.80 (1H, bs), 5.10—6.48 (3H, m), and 7.40—7.88 (5H, m); MS *m/z* (%) 241(5), 203(4), 167(22), and 126(100).

3g: Colorless crystals (major isomer); mp 87—88 °C (AcOEt–hexane); IR (KBr) 3380 (OH) and 1020 (SO) cm^{-1}; ^1H NMR δ=1.56 (3H, s), 1.60 (3H, s), 5.04—5.20 (1H, bs), 6.67, 7.12 (each 1H, d, *J*=16 Hz), and 7.2—7.8 (10H, m). Found: C, 64.33; H, 5.64; Cl, 10.48; S, 9.55%. Calcd for $C_{18}H_{19}ClO_2S$: C, 64.56; H, 5.72; Cl, 10.59; S, 9.57%.

General Procedure for the Synthesis of α-Phenylthio β,γ-Unsaturated Carbonyl Compounds (5a—5g). A synthesis of 1-(1-phenylthio-2-cyclohexenyl)-1-heptanone (**5a**) is described as a typical experiment. To a solution of 2.4 equivalents of PhSK in 4 ml of *t*-BuOH at room temperature under N_2 atmosphere was added dropwise, with stirring, a solution of **3a** (237 mg; 0.67 mmol) in 2 ml of *t*-BuOH. The reaction mixture was stirred for 10 min, and then the reaction was quenched by adding pulverized NH_4Cl. The solvent was evaporated and the residue was extracted with benzene. The organic layer was successively washed with 10% aq NaOH and sat. aq NH_4Cl, and dried over Na_2SO_4. The solvent was evaporated to leave a residue, which was purified by silica-gel column chromatography to give 123 mg (61%) of **5a** as a colorless oil. IR (neat) 1700 (CO) cm^{-1}; ^1H NMR δ=0.90 (3H, t, *J*=6 Hz), 1.08—2.28 (14H, m), 2.60—2.86 (2H, m), 5.64—6.08 (2H, m), and 7.12—7.50 (5H, m); MS *m/z* (%) 302 (M$^+$, 2) and 189 ([M−$C_6H_{13}CO$]$^+$, 100). Found: *m/z* 302.1684. Calcd for $C_{19}H_{26}OS$: M, 302.1702.

1-(1-Phenylthio-2-cyclohexenyl)ethanone (5b). Colorless oil; IR (neat) 1710 (CO) cm^{-1}; ^1H NMR δ=1.5—1.6 (1H, m), 1.8—2.2 (5H, m), 2.37 (3H, s), 5.76 (1H, d, *J*=10 Hz), 5.97 (1H, dt, *J*=10, 4 Hz), and 7.3—7.4 (5H, m); MS *m/z* (%) 232 (M$^+$, 3) and 189 ([M−CH_3CO]$^+$, 100). Found: *m/z* 232.0921. Calcd for $C_{14}H_{16}OS$: M, 232.0921.

1-Pheylthio-2-cyclohexenecarbaldehyde (5c). Colorless oil; IR (neat) 1715 (CO) cm^{-1}; ^1H NMR δ=1.6—2.2 (6H, m), 5.57 (1H, d, *J*=10 Hz), 6.07 (1H, dt, *J*=10, 4 Hz), 7.3—7.4 (5H, m), and 9.36 (1H, s); MS *m/z* (%) 218 (M$^+$, 6) and 189 ([M−CHO]$^+$, 100). Found: *m/z* 218.0768. Calcd for $C_{13}H_{14}OS$: M, 218.0765.

1-(1-Phenylthio-2-cyclopentenyl)-1-heptanone (5d). Colorless oil; IR (neat) 1700 (CO) cm^{-1}; ^1H NMR δ=0.89 (3H, t, *J*=6 Hz), 1.08—1.80 (8H, m), 2.04—2.60 (4H, m), 2.73 (2H, t, *J*=7 Hz), 5.72—5.84 (1H, m), 5.90—6.04 (1H, m), and 7.20—7.48 (5H, m); MS *m/z* (%) 175 ([M−$C_6H_{13}CO$]$^+$, 100), 142(4), and 109(6).

(*E*)-4-Butyl-4-phenylthio-5-hepten-3-one (5e). Colorless oil; IR (neat) 1710 (CO) cm^{-1}; ^1H NMR δ=0.88 (3H, t, *J*=6 Hz), 1.08 (3H, t, *J*=7 Hz), 1.18—1.48 (4H, m), 1.56—1.84 (5H, m), 2.48—3.08 (2H, m), 5.50—5.92 (2H, m), and 7.32 (5H, s); MS *m/z* (%) 276 (M$^+$, 2), 219 ([M−C_2H_5CO]$^+$, 100), and 167(9). Found: *m/z* 276.1522. Calcd for $C_{17}H_{24}OS$: M, 276.1545.

3-Methyl-3-phenylthio-1-decen-4-one (5f). Colorless oil; IR (neat) 1710 (CO) cm^{-1}; ^1H NMR δ=0.90 (3H, t, *J*=6 Hz), 1.08—1.96 (8H, m), 1.46 (3H, s), 2.52—2.88 (2H, m), 5.16—5.40 (2H, m), 6.16 (1H, dd, *J*=15, 8 Hz), and 7.16—7.52 (5H, m); MS *m/z* (%) 276 (M$^+$, 9), 193(7), 167(4), 165(5), 164(12), and 163 ([M−$C_6H_{13}CO$]$^+$, 100). Found: *m/z* 276.1529. Calcd for $C_{17}H_{24}OS$: M, 276.1546.

(*E*)-3-Methyl-5-phenyl-3-phenylthio-4-penten-2-one (5g). Colorless crystals; mp 61—62 °C (hexane); IR (KBr) 1710 (CO) cm^{-1}; ^1H NMR δ=1.60 (3H, s), 2.45 (3H, s), 6.48, 6.60 (each 1H, d, *J*=16 Hz), and 7.20—7.52 (10H, m); MS *m/z* (%) 282 (M$^+$, 9), 239 ([M−CH_3CO]$^+$, 95), 173(90), and 129(100). Found: C, 76.53; H, 6.38; S, 11.05%. Calcd for $C_{18}H_{18}OS$: C, 76.56; H, 6.42; S, 11.35%.

General Procedure for the Synthesis of Sulfinate (6a—6g). A synthesis of 1-(3-phenylsulfinyloxy-1-cyclohexenyl)-1-heptanone (**6a**) is described as a typical procedure. To a solution of **5a** (693 mg; 2.3 mmol) in 23 ml of CH_2Cl_2 at 0 °C was added 2.1 equivalents of *m*-CPBA. The reaction mixture was stirred for 10 min. The reaction mixture was diluted with CH_2Cl_2 and the solution was successively washed with 10% aq NaOH and sat. aq NH_4Cl. The solution was dried over Na_2SO_4, and the solvent was evaporated to leave a residue, which was purified by silica-gel column chromatography to give 683 mg (89%) of **6a** as a colorless oil. IR (neat) 1685 (CO) and 1140 (SO) cm^{-1}; ^1H NMR δ=0.89 (3H, t, *J*=6 Hz), 1.08—2.84 (16H, m), 4.86—5.20 (1H, m), 6.30—6.42 (0.5H, m), 6.68—6.82 (0.5H, m), and 7.30—7.88 (5H, m); MS *m/z* (%) 222(4), 193 ([M−$PhSO_2$]$^+$, 100), and 165(25).

When 1.1 equivalents of *m*-CPBA was used in this reaction, 1-(3-phenylsulfenyloxy-1-cyclohexenyl)-1-heptanone (**10**) was obtained. Colorless oil; IR (neat) 1685 (CO) cm^{-1}; ^1H NMR δ=0.88 (3H, t, *J*=6 Hz), 1.08—2.76 (16H, m), 4.24—4.56 (1H, m), 6.50—6.92 (1H, m), and 7.20—7.80 (5H, m); MS *m/z* (%) 250(13), 218(70), 125(82), and 109(100).

All other sufinates (**6b—6g**) were synthesized from **5b—5g**, respectively, in a similar manner as described above.

6b: Colorless oil; IR (neat) 1675 (CO) and 1135 (SO) cm^{-1}; ^1H NMR δ=1.40—2.40 (6H, m), 2.22, 2.36 (each 1.5H, s), 4.88—5.20 (1H, m), 6.32—6.44 (0.5H, m), 6.68—6.82 (0.5H, m), and 7.40—7.88 (5H, m); MS *m/z* (%) 264 (M$^+$, 1), 123 ([M−$PhSO_2$]$^+$, 82), 107(5), 77(22), and 43(100). Found: *m/z* 264.0825. Calcd for $C_{14}H_{16}O_3S$: M, 264.0819.

6c: Colorless oil; IR (neat) 1695 (CO) and 1135 (SO) cm^{-1}; ^1H NMR δ=1.40—2.30 (6H, m), 4.90—5.20 (1H, m), 6.28—6.40 (0.5H, m), 6.70—6.80 (0.5H, m), 7.44—7.90 (5H, m), and 9.42, 9.56 (each 0.5H, s); MS *m/z* (%) 250 (M$^+$, 4), 143(28), 109 ([M−$PhSO_2$]$^+$, 100), and 81(95). Found: *m/z* 250.0642. Calcd for $C_{13}H_{14}O_3S$: M, 250.0662.

6d: Colorless oil; IR (neat) 1675 (CO) and 1135 (SO) cm^{-1}; ^1H NMR δ=0.88 (3H, *J*=6 Hz), 1.08—2.94 (14H, m), 5.32—5.64 (1H, m), 6.20—6.32 (0.5H, m), 6.60—6.68 (0.5H, m), and 7.40—7.88 (5H, m); MS *m/z* (%) 320 (M$^+$, 2), 208(3), and 179 ([M−$PhSO_2$]$^+$, 100). Found: *m/z* 320.1434. Calcd for $C_{18}H_{24}O_3S$: M, 320.1444.

6e: Colorless oil; IR (neat) 1680 (CO) and 1135 (SO) cm^{-1}; ^1H NMR δ=0.80—1.56 (13H, m), 1.80—2.88 (4H, m), 5.08—5.66 (1H, m), 6.30, 6.48 (each 0.5H, d, *J*=8 Hz), and 7.40—7.80 (5H, m); MS *m/z* (%) 308 (M$^+$, trace) and 167 ([M−$PhSO_2$]$^+$, 100). Found: *m/z* 308.1422. Calcd for $C_{17}H_{24}O_3S$: M, 308.1444.

6f: Colorless oil; IR (neat) 1675 (CO) and 1135 (SO) cm^{-1}; ^1H NMR δ=0.90 (3H, t, *J*=6 Hz), 1.08—2.04 (11H, m), 2.62 (2H, t, *J*=9 Hz), 4.24—4.88 (2H, m), 6.40—6.60 (1H, m), and 7.44—7.88 (5H, m); MS *m/z* (%) 250(13), 218(13), 167 ([M−$PhSO_2$]$^+$, 35), 125(37), and 95(100).

6g: Colorless oil; IR (neat) 1720, 1685 (CO), and 1145 (SO) cm^{-1}; ^1H NMR δ=1.65, 1.88 (each 1.5H, d, *J*=2 Hz), 2.16, 2.35 (each 1.5H, s), 5.93—7.00 (2H, m), and 7.10—7.80 (10H, m).

General Procedure for the Hydrolysis of the Sulfinates (6a—6h). A synthesis of 1-(3-hydroxy-1-cyclohexenyl)-1-heptanone

(**7a**) is described as a typical experiment. To a solution of **6a** (218 mg; 0.65 mmol) in 6 ml of MeOH at room temperature was added, with stirring, a solution of 10% aq KOH (2 equivalents). The reaction mixture was stirred for 15 min, then the solvent was evaporated under reduced pressure to give a residue, which was dissolved in benzene. The solution was washed successively with 10% aq KOH and sat. aq NH_4Cl, then dried over Na_2SO_4. The solvent was evaporated and the residue was purified by silica-gel column chromatography to give 128 mg (93%) of **7a** as a colorless oil. IR (neat) 3430 (OH) and 1670 (CO) cm^{-1}; ^1H NMR δ=0.88 (3H, t, J=7 Hz), 1.26—1.34 (6H, m), 1.52—1.64 (4H, m), 1.76—2.02 (3H, m), 2.18—2.24 (2H, m), 2.65 (2H, t, J=7 Hz), 4.40—4.45 (1H, m), 6.75 (1H, bs); MS m/z (%) 210 (M^+, 21), 153(12), 140(29), 125(40), 97 ($[M-C_6H_{13}CO]^+$, 100). Found: m/z 210.1614. Calcd for $C_{13}H_{22}O_2$: M, 210.1617.

1-(3-Hydroxy-1-cyclohexenyl)ethanone (7b). Colorless oil; IR (neat) 3400 (OH) and 1670 (CO) cm^{-1}; ^1H NMR δ=1.40—2.36 (6H, m), 2.36 (3H, s), 2.84 (1H, bs), 4.44 (1H, bs), and 6.76—6.88 (1H, m); MS m/z (%) 140 (M^+, 60), 97 ($[M-CH_3CO]^+$, 100), 69(27), and 43(77). Found: m/z 140.0832. Calcd for $C_8H_{12}O_2$: M, 140.0835.

3-Hydroxy-1-cyclohexene-1-carbaldehyde (7c). Colorless oil; IR (neat) 3400 (OH) and 1690 (CO) cm^{-1}; ^1H NMR δ=1.30—2.32 (6H, m), 2.72 (1H, bs), 4.40—4.64 (1H, m), 6.68—6.80 (1H, m), and 9.52 (1H, s); MS m/z (%) 126 (M^+, 65), 97 ($[M-CHO]^+$, 100), and 79(27). Found: m/z 126.0678. Calcd for $C_7H_{10}O_2$: M, 126.0680.

1-(3-Hydroxy-1-cyclopentenyl)-1-heptanone (7d). Colorless oil; IR (neat) 3450 (OH) and 1675 (CO) cm^{-1}; ^1H NMR δ=0.90 (3H, t, J=6 Hz), 1.00—2.80 (15H, m), 4.92—5.16 (1H, m), and 6.60—6.68 (1H, m); MS m/z (%) 196 (M^+, 11), 153(7), 125(50), 111(93), and 83 ($[M-C_6H_{13}CO]^+$, 100). Found: m/z 196.1463. Calcd for $C_{12}H_{20}O_2$: M, 194.1462.

(*E*)-4-Butyl-6-hydroxy-4-hepten-3-one (7e). Colorless oil; IR (neat) 3450 (OH) and 1680 (CO) cm^{-1}; ^1H NMR δ=0.90 (3H, t, J=6 Hz), 1.10 (3H, t, J=7 Hz), 1.20—1.56 (7H, m), 2.10—2.46 (3H, m), 2.72 (2H, q, J=7 Hz), 4.60—4.92 (1H, m), and 6.50 (1H, d, J=8 Hz); MS m/z (%) 184 (M^+, 3), 166 ($[M-H_2O]^+$, 21), 141(32), 99(37), 43(100). Found: m/z 184.1438. Calcd for $C_{11}H_{20}O_2$: M, 184.1461.

(*E*)-1-Hydroxy-3-methyl-2-decen-4-one (7f). Colorless oil; IR (neat) 3450 (OH) and 1680 (CO) cm^{-1}; ^1H NMR δ=0.90 (3H, t, J=6 Hz), 1.04—1.84 (11H, m), 2.28—2.80 (3H, m), 4.46 (2H, bd, J=6 Hz), and 6.60—6.82 (1H, m); MS m/z (%) 153 ($[M-CH_2OH]^+$, 100), 99(43), and 71 ($[M-C_6H_{13}CO]^+$, 58).

(*E*)-5-Hydroxy-3-methyl-5-phenyl-3-penten-2-one (7g). Colorless oil; IR (neat) 3430 (OH) and 1680 (CO) cm^{-1}; ^1H NMR δ=1.87 (3H, d, J=2 Hz), 2.32 (3H, s), 2.72 (1H, bs), 5.62 (1H, d, J=7 Hz), 6.76 (1H, dq, J=7, 2 Hz), and 7.20—7.50 (5H, m); MS m/z (%) 190 (M^+, 14), 161(85), 147 ($[M-CH_3CO]^+$, 100), 129(30), and 105(95). Found: m/z 190.0980. Calcd for $C_{12}H_{14}O_2$: M, 190.0992.

(1*S*)-1-[(1*R*)-1-Chloro-1-[(*R*)-*p*-tolylsulfinyl]ethyl]-2-cyclohexen-1-ol (12-L, abbrev. to (1*S*,1′*R*,*R*s)-isomer hereafter) and (1*R*,1′*R*,*R*s)-Isomer (**12-P**). These compounds were synthesized from (−)-1-chloroethyl *p*-tolyl sulfoxide and 2-cyclohexen-1-on as described for the synthesis of **3a**.

12-L: Colorless oil; $[\alpha]_D$ −30.8° (*c* 1.0, acetone); IR (neat) 3396 (OH) and 1057 (SO) cm^{-1}; ^1H NMR δ=1.44 (3H, s), 1.82—2.17 (6H, m), 2.44 (3H, s), 4.27 (1H, bs), 5.92 (1H, bd, J=10 Hz), 6.05 (1H, dt, J=10, 4 Hz), and 7.27—7.61 (4H, m); MS (CI) m/z (%) 299 ($[M+H]^+$, 3), 205(87), 203(100), and 175(33).

12-P: Colorless oil; $[\alpha]_D$ −27.1° (*c* 1.0, acetone); IR (neat) 3386 (OH) and 1045 (SO) cm^{-1}; ^1H NMR δ=1.43 (3H, s), 1.67—2.20 (6H, m), 2.44 (3H, s), 3.93 (1H, bs), 6.10 (1H, bd, J=10 Hz), 6.18 (1H, dt, J=10, 4 Hz), and 7.31—7.65 (4H, m); MS (CI) m/z (%) 299 ($[M+H]^+$, 11), 283(11), 241(13), 203(18), and 197(100).

Optically Active 5b and 6b. These compounds were obtained from **12-L** and **12-P** in the same way as described for racemic compounds. Specific rotations are reported.

5b-L: $[\alpha]_D$ +23.0° (*c* 1.0, acetone),
5b-P: $[\alpha]_D$ −21.7° (*c* 1.0, acetone).
6b-L: $[\alpha]_D$ −96.5° (*c* 1.0, acetone),
6b-P: $[\alpha]_D$ +93.4° (*c* 1.0, acetone).

Synthesis of Optically Active 7a. Optically active **7a** (Table 3) was synthesized starting from (−)-1-chloroheptyl *p*-tolyl sulfoxide **11b** and 2-cyclohexen-1-one. Addition of the carbanion of **11b** to 2-cyclohexenone gave less polar adduct (**L**); (1*S*,1′*R*,*R*s)-1-[1-chloro-1-(*p*-tolylsulfinyl)heptyl]-2-cyclohexen-1-ol and more polar adduct (**P**), (1*R*,1′*R*,*R*s)-isomer.

Less polar adduct: Colorless oil; $[\alpha]_D$ −11.7° (*c* 1.0, acetone); IR (neat) 3390 (OH) and 1037 (CO) cm^{-1}; ^1H NMR δ=0.83 (3H, t, J=7 Hz), 1.00—2.48 (17H, m), 2.44 (3H, s), 5.88—6.04 (2H, m), and 7.32—7.67 (4H, m); MS (CI) m/z (%) 369 ($[M+H]^+$, 7), 351(10), 264(12), 263(70), and 211(100).

More polar adduct: Colorless oil; $[\alpha]_D$ −24.2° (*c* 1.0, acetone); IR (neat) 3394 (OH) and 1048 (SO) cm^{-1}; ^1H NMR δ=0.86 (3H, t, J=7 Hz), 1.08—2.48 (17H, m), 2.43 (3H, s), 5.86—6.08 (2H, m), and 7.29—7.66 (4H, m); MS (CI) m/z (%) 369 ($[M+H]^+$, 5), 264(14), 263(78), and 211(100). Optically active **5a** and **6a** were derived from these adducts in a similar way as described above. Specific rotations are reported.

5a-L: $[\alpha]_D$ +27.5° (*c* 1.0, acetone).
5a-P: $[\alpha]_D$ −20.5° (*c* 1.0, acetone).
6a-L: $[\alpha]_D$ −77.0° (*c* 1.0, acetone).
6a-P: $[\alpha]_D$ +73.7° (*c* 1.0, acetone).

Synthesis of Optically Active 7c. Optically active **7c** (Table 3) was synthesized starting from (−)-chloromethyl *p*-tolyl sulfoxide **11c** and 2-cyclohexen-1-one. Addition of the carbanion of **11c** to 2-cyclohexen-1-one gave an inseparable mixture of two diastereomers (ratio about 9 : 1). The main product was obtained from the mixture by recrystallization (twice with AcOEt); (1*R*,1′*R*,*R*s)-1-[1-chloro-1-(*p*-tolylsulfinyl)methyl]-2-cyclohexen-1-ol. Colorless crystals; mp 155—157°C; $[\alpha]_D$ −226.0° (*c* 1.0, acetone); IR (KBr) 3360 (OH) and 1034 (SO) cm^{-1}; ^1H NMR δ=1.65—2.18 (6H, m), 2.43 (3H, s), 3.09 (1H, bs), 4.38 (1H, s), 5.97 (1H, d, J=10 Hz), 6.09 (1H, dt, J=10, 4 Hz), and 7.33—7.51 (4H, m); MS m/z (%) 284 (M^+, 1), 171(8), 145(13), and 140 ($[CH_3C_6H_4SO]^+$, 100). Found: m/z 284.0638. Calcd for $C_{14}H_{17}ClO_2S$: M, 284.0639. Optically active **5c**: $[\alpha]_D$ +19.1° (*c* 1.0, acetone). Optically active **6c**: $[\alpha]_D$ +79.3° (*c* 1.0, acetone).

(*S*)-1-[3-*t*-Butyldiphenylsiloxy-1-cyclohexenyl]ethanone (14). To a solution of **7b-L** (312 mg; 2.23 mmol) in dry DMF (2.3 ml) was added, with stirring, imidazole (1.15 g; 16.9 mmol) and *t*-butyldiphenylsilyl chloride (1.94 g; 7.1 mmol) at room temperature. The reaction mixture was stirred overnight. After the usual workup, the crude product was purified by silica-gel column chromatography to give 827 mg (98%) of **14** as a colorless oil. $[\alpha]_D$ −67.0° (*c* 1.0, acetone); IR (neat) 1672 (CO) cm^{-1}; ^1H NMR δ=1.08 (9H, s), 1.38—1.82 (4H, m), 2.04—2.22 (2H, m), 2.12 (3H, s), 4.40 (1H, m), 6.48 (1H, m), and 7.38—7.72 (10H, m); MS m/z (%) 378 (M^+, trace), 321(14), and 199(100). Found: m/z 378.2013. Calcd for $C_{24}H_{30}O_2Si$: M, 378.2013.

1-[3-*t*-Butyldiphenylsiloxy-1-cyclohexenyl]ethanol (15). To a solution of **14** (803 mg; 2.12 mmol) in dry toluene (1 ml) at

−60 °C was added, with stirring, a solution of DIBAL-H in toluene (4.25 mmol). The reaction mixture was stirred for 10 min, and then the reaction was quenched with MeOH. Evaporation of the solvent gave a residue, which was extracted with benzene. The solution was washed with 10% HCl and then brine. The solution was dried over Na_2SO_4 and the solvent was evaporated. The residue was purified by silica-gel column chromatography to give **15** (801 mg; 99%) as a colorless oil. $[\alpha]_D$ −54.0° (*c* 1.0, acetone); IR (neat) 3356 (OH) cm^{-1}; ^1H NMR δ=1.07 (9H, s), 1.25, 1.27 (3H, each doublet, *J*=8 Hz), 1.57—2.27 (6H, m), 3.10 (1H, m), 4.12, 4.29 (each 1H, q, *J*=8 Hz), 5.70—6.01 (2H, m), and 7.35—7.73 (10H, m); MS (CI) *m/z* (%) 381 ($[M+H]^+$, trace), 363 ($[M-OH]^+$, 100), 323(26), and 303(33).

1-[3-(*t*-Butyldiphenylsiloxy)-1-cyclohexenyl]ethyl Phenyl Thiocarbonate (16). To a solution of **15** (768 mg; 2.02 mmol) in dry CH_2Cl_2 (20 ml) was added, with stirring, 4-dimethylaminopyridine (542 mg; 4.44 mmol) and a solution of *o*-phenyl chlorothioformate (418 mg; 2.42 mmol) in 1 ml of dry CH_2Cl_2 at 0 °C. The reaction mixture was stirred at 0 °C for 15 min, and then at room temperature overnight. The reaction mixture was diluted with CH_2Cl_2 and washed successively with sat. aq $NaHCO_3$, 10% HCl, and brine. The solution was dried over Na_2SO_4 and the solvent was evaporated to give a residue, which was purified by silica-gel column chromatography to give **16** (945 mg; 91%) as a colorless oil. $[\alpha]_D$ −34.5° (*c* 1.0, acetone); IR (neat) 1729 (C=S) cm^{-1}; ^1H NMR δ=1.06, 1.09 (9H, each singlet), 1.52—1.91 (6H, m), 1.63, 1.68 (each 1.5H, d, *J*=8 Hz), 3.84—4.28 (2H, m), 5.39, 5.57 (each 0.5H, q, *J*=8 Hz), and 7.05—7.73 (15H, m); MS (CI) *m/z* (%) 517 ($[M+H]^+$, 3), 363(17), 273(7), 261(34), and 231(100).

(*S*)-3-(*t*-Butyldiphenylsiloxy)-1-ethylcyclohexene (17). A mixture of **16** (500 mg; 0.97 mmol) and tributyltin hydride (1.2 ml) was heated at 160 °C under N_2 atmosphere for 7 h. Excess tributyltin hydride was evaporated under reduced pressure and the residue was purified by silica-gel column chromatography to give **17** (148 mg; 42%) as a colorless oil. $[\alpha]_D$ −49.4° (*c* 1.7, acetone); IR (neat) 1666 (C=C) cm^{-1}; ^1H NMR δ=0.93 (3H, t, *J*=8 Hz), 1.05—1.09 (9H, m), 1.27—2.50 (8H, m), 4.24 (1H, bs), 5.31 (1H, bs), 7.34—7.43 (6H, m), and 7.65—7.73 (4H, m); MS *m/z* (%) 308(12), 307 ($[M-C_4H_9]^+$, 44), 305(5), 201(15), 200(46), and 199(100).

(*S*)-3-Ethyl-2-cyclohexen-1-ol (18). To a solution of **17** (103 mg; 0.283 mmol) in THF (1 ml) was added a solution of *n*-Bu_4NF (1M solution; 1 ml). The mixture was stirred at room temperature overnight, and then diluted with ether. The solution was washed with water, and the usual workup was followed by silica-gel column chromatography to afford **18** (21 mg; 58%) as a colorless oil. $[\alpha]_D$ −27.9° (*c* 0.4, $CHCl_3$); IR (neat) 3344 (OH) cm^{-1}; ^1H NMR δ=1.01 (3H, t, *J*=8 Hz), 1.32—2.20 (7H, m), 1.99 (2H, q, *J*=8 Hz), 4.21 (1H, bs), and 5.49 (1H, m); MS *m/z* (%) 126 (M^+, 11), 108 ($[M-H_2O]^+$, 14), and 98(21). Found: *m/z* 126.1052. Calcd for $C_8H_{14}O$: M, 126.1044.

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