Asymmetric Synthesis of Functionalized Secondary Alcohols by Catalytic Ring-Cleavage Reactions of Cyclic Acetals Derived from (*R*)-1,3-Butanediol

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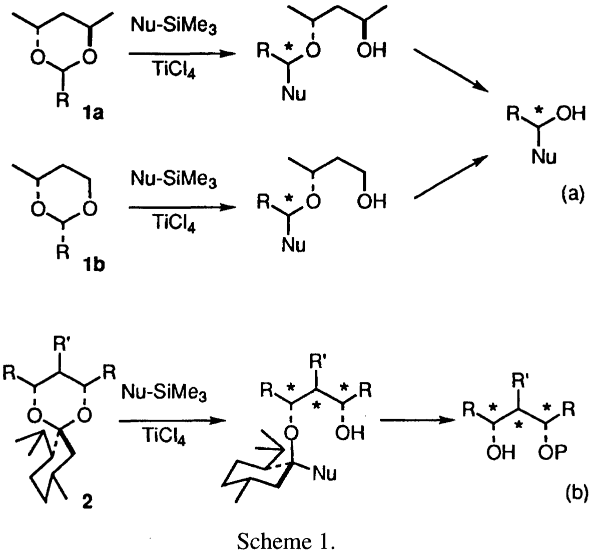
In the presence of a catalytic amount (0.1—0.2 molar amount) of a 2-phenyl-1,3,2-oxazaborolidin-5-one, prepared by the reaction of dichlorophenylborane and *N*-(trifluoromethylsulfonyl)-L- phenylalanine, and enol silyl ethers ($(R^2)_2C{=}C(R^3)OTMS$; $R^3 = t$-BuS, EtS, EtO, Ph) (1.1-1.5 molar amount), chiral cyclic acetals **6** derived from (*R*)-1,3-butanediol and aldehydes undergo an efficient ring-cleavage reaction with the inversion of the stereochemistry at the acetal carbon to give the *anti* isomer of the corresponding products with high stereoselectivity. The reaction is applicable to acetals derived from aromatic, aliphatic, and α,β-unsaturated aldehydes. Not only enol silyl ethers, but also methallyltrimethylsilane and allyltributyltin, can be employed as nucleophiles, leading to the selective formation of the *anti* isomer of the corresponding allylated ring-cleavage products. Removal of the chiral auxiliary from these ring-cleavage products by a two-step sequence ((i) PCC (ii) $Bn_2NH_2(CF_3CO_2)$) furnishes enantiomerically enriched β-hydroxy carbonyl compounds and homoallyl alcohols. A modest level of kinetic resolution is observed in the ring cleavage of a racemic acetal catalyzed by a phenylboron compound derived from *N*-mesyl-L-phenylalanine.

The Lewis acid-mediated cleavage of chiral cyclic acetals has been intensively investigated in recent years, and has proven to be a useful tool in asymmetric synthesis.[1] A $TiCl_4$-mediated reaction of chiral acetals **1a**, derived from enantiomerically pure 2,4-pentanediol, proceeds with a stereoselective introduction of a variety of carbon nucleophiles in an invertive manner, affording a powerful method for asymmetric carbon–carbon bond formation (Scheme 1-a).[2,3] Acetals **1b** in which inexpensive and readily available 1,3-butanediol[4] is used as a chiral auxiliary also serve as substrates, exhibiting high stereoselectivity.[5] The $TiCl_4$-mediated cleavage reaction is also utilized in an enantiodifferentiating transformation of prochiral diols (Scheme 1-b).[6] The cleavage of the equatorial C–O bond of *l*-menthone-derived spiroacetals **2** proceeds exclusively, leading to the formation of protected derivatives of the prochiral diols in an enantiodifferentiating manner.

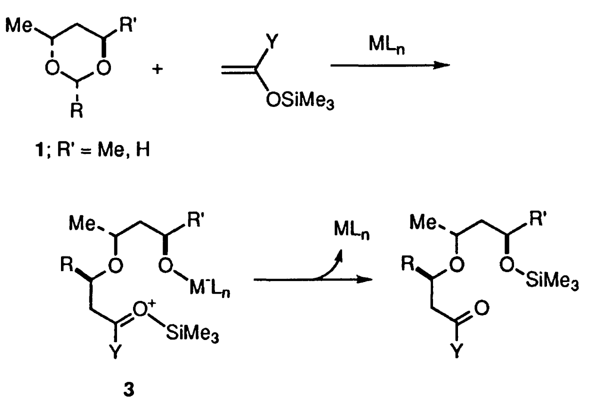


Scheme 1.

In both types of ring-cleavage reactions, either a stoichiometric or excess amount of Lewis acids is required to obtain high diastereoselectivity.[7,8] It has been reported that the use of a 5.5 molar amount (abbrev. to mol. amt. hereafter) of "Ti-blend", a 6 : 5 mixture of $TiCl_4$ and $Ti(OPr^i)_4$, gave a higher selectivity in the reaction shown in Scheme 1-a.[9] A search for efficient Lewis acid complexes which catalyze the cleavage of cyclic acetals is important not only for preparative uses of the reaction, but also for the future development of an enantioselective ring cleavage without the aid of chiral auxiliaries.

With enol silyl ethers as nucleophiles, the Lewis acid (ML_n) mediated reaction of acetal **1** gives zwitterion **3** as an intermediate (Scheme 2). The migration of the silyl group to the oxygen atom of the ring-cleavage product with a regeneration of ML_n should be crucial for achieving an efficient catalytic cycle. It has recently been reported that 1,3,2-oxazaborolidin- 5-ones derived from *N*-sulfonyl α-amino acids[10] act as effective catalysts for the mechanistically related asymmetric Mukaiyama aldol reaction.[11] The facile migration of the silyl group observed there prompted us to investigate the ring cleavage mediated by the oxazaborolidinones.[12]

We now report that oxazaborolidinones **5** catalyze the ring

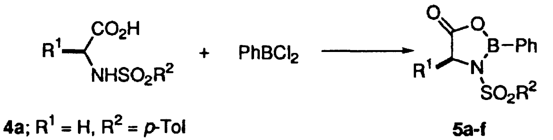


Scheme 2.

cleavage of chiral acetals derived from (R)-1,3-butanediol in a stereoselective manner. A wide applicability of the catalytic reaction to a variety of acetals and nucleophilic reagents is described.[13]

Results and Discussion

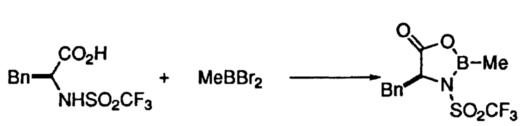
Organoboron compounds **5a**—**f** were prepared simply by treatment of the corresponding sulfonamides of L-amino acids (**4a**—**f**) with an equimolar amount of dichlorophenylborane in CH_2Cl_2 and a subsequent removal of produced HCl and the solvent in vacuo (Eq. 1). ^1H and ^{11}B NMR analyses of the residue showed a clean formation of **5a**—**f**. Alkylboron compounds derived from N-sulfonyl amino acids have been prepared by the dehydration of alkylboronic acids.[14] However, the reaction is sometimes sluggish and phenylboron compounds, in our hands, could not be prepared by this method. The reaction using dichlorophenylborane proceeded cleanly in a facile manner. Methylboron compound **5g** was also prepared by using dibromomethylborane (Eq. 2). Oxazaborolidinone **5h** was prepared by the reaction of BH_3–THF and **4d**.[10]



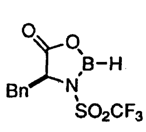
4a; R^1 = H, R^2 = p-Tol
4b; R^1 =Bn, R^2 = p-Tol
4c; R^1 = Bn, R^2 = Me
4d; R^1 =Bn, R^2 = CF_3
4e; R^1 = i-Pr, R^2 = p-Tol
4f; R^1 = i-Pr, R^2 = CF_3

5a-f

(1)



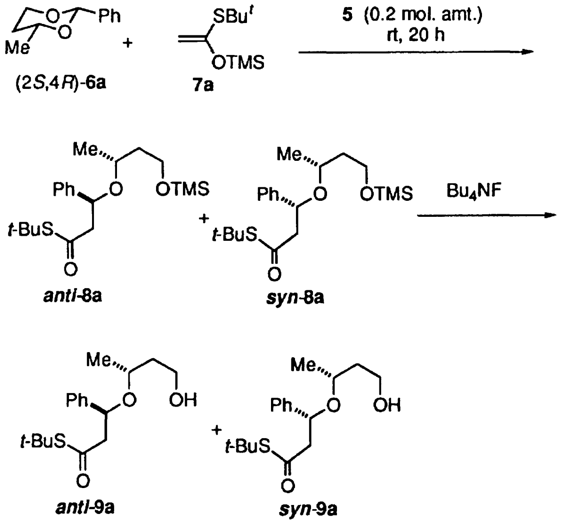
4d **5g**



5h

(2)

Ring-cleavage reaction of chiral acetal (2S,4R)-**6a** with enol silyl ether **7a** (3 mol. amt.) derived from thioic S-ester was examined in the presence of oxazaborolidinones **5** in CH_2Cl_2 at rt (Eq. 3 and Table 1). In most reactions, a GC analysis of the crude reaction mixture showed the formation of silyl ether derivative **8a** as the sole product, suggesting a smooth migration of the silyl group. Because the hydrolysis of the silyl group took place in part during isolation by silica gel chromatography, the crude mixture was treated with Bu_4NF, and the product was isolated as alcohol **9a**.[15]



(3)

The reaction using phenylboron compound **5a** derived from N-tosylglycine proceeded stereoselectively to give *anti*-**9a**, but in low yield (Entry 1). The reaction is also highly regioselective; no product derived from a C(2)–O(3) bond cleavage was detected. The yield of **9a** was improved considerably by using of valine- and phenylalanine-derived complexes **5b**,**e** (Entries 2 and 6). As shown in Entries 4—6, the structure of the sulfonamide moiety is also influential. The most satisfactory result was obtained when phenylboron compound **5d**, derived from N-(trifluoromethylsulfonyl)phenylalanine, was used: Even when a 10 mol. amt. of the catalyst was employed with a 1.5 mol. amt. of the nucleophile, the ring-cleavage product was obtained in high yield with a high stereoselectivity of 98 : 2 (Entry 4).

Although we used enantiomerically pure oxazaborolidinones prepared from L-amino acids, chirality of the catalyst complex is not an important factor for the *anti* : *syn* selectivity. Indeed, the reaction of racemic acetal ***rac*-6a** in the presence of **5d** afforded **9a** similarly with high stereoselectivity (Entry 5). It should be noted that the phenyl group attached to the boron atom is essential to the catalytic activity. Thus, only a stoichiometric or less efficient reaction took place when methylboron compound **5g** or B-unsubstituted compound **5h** was used, respectively (Entries 7 and 8). Dichlorophenylborane, itself, also did not catalyze the ring-cleavage reaction (Entry 9). For a comparison, we also examined the use of TMSOTf[8] as a catalyst (Entry 10). The nonstereoselective reaction observed here excludes the possibility of a ring cleavage involving a silicon-catalyzed mechanism.[12]

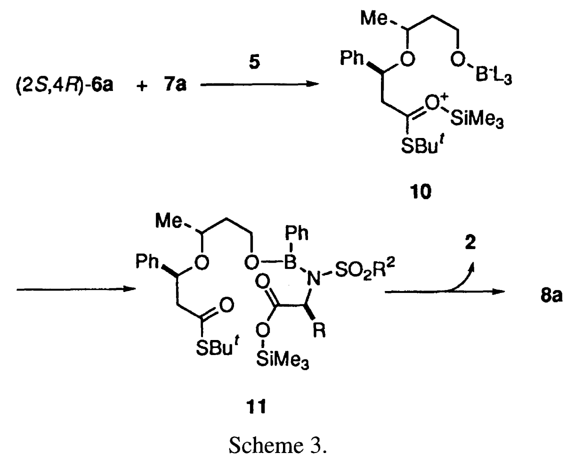
Table 1. Reaction of Acetal (2*S*,4*R*)-**6a** and Enol Silyl Ether **7a** in the Presence of Oxazaborolidinones **5**[a)]

Entry	Catalyst	Time (h)	Yield of **9a** (%)	*anti* : *syn*[b)]	Recovery of **6a** (%)
1[c)]	**5a**	21	31	94 : 6	55
2	**5b**	21	52	96 : 4	32
3	**5c**	20	94	94 : 6	—
4[d)]	**5d**	4	81	98 : 2	9
5[c,d)]		1	80	97 : 3	—
6	**5e**	20	81	96 : 4	13
7	**5g**	20	15	93 : 7	76
8	**5h**	21	Trace	—	97
9[c)]	$PhBCl_2$	23	14	63 : 37	63
10[c)]	TMSOTf	20	74	60 : 40	15

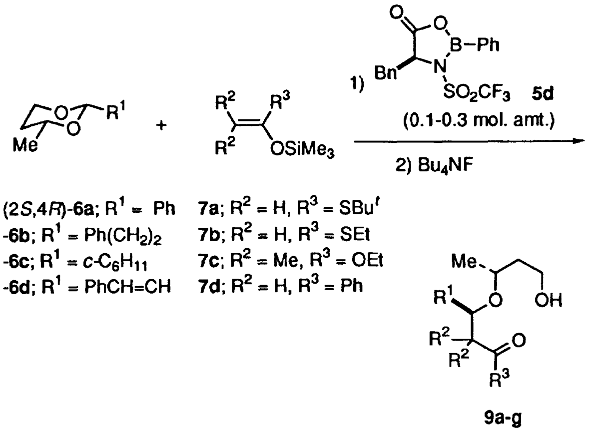
a) Unless otherwise noted, reactions were carried out by using 3 mol. amt. of **7a** and 0.2 mol. amt. of oxazaborolidinones **5** at rt. b) Ratios were determined by ^1H NMR (300 MHz) analyses. c) Racemic acetal ***rac*-6a** was used. d) 1.5 mol. amt. of **7a** and 0.1 mol. amt. of **5d** were used.

In the reaction using oxazaborolidinones **5b**—**e**, the ring-cleavage products existed as trimethylsilyl ether **8a** through the course of the reaction, judging from GC analyses of the reaction mixture. This observation implies that, in the present catalytic system, the intermediate **10** undergoes a facile silyl-group migration to give **8a**. On the other hand, when glycine-derived oxazaborolidinone **5a** was employed, the formation of **8a** as well as that of **9a** was observed during the early stage of the reaction. After 20 h of the reaction time, **8a** was the sole product and no **9a** was detected. The observed dependence of the rate of silyl- group migration on the structures of the catalysts can be rationalized if we assume that the migration proceeds via the trimethylsilyl ester derivative **11** (Scheme 3).[16)] Thus, the substituent R originated from the amino acid derived moiety may enhance the rate for the regeneration of the catalyst along with a simultaneous release of the silylated product **8** by a Thorpe–Ingold effect.[17)]

We then examined the ring-cleavage reaction of several acetals and enol silyl ethers using a 0.1—0.3 mol. amt. of the optimal catalyst **5d** (Eq. 4 and Table 2). Not only the enol silyl ethers of thioic *S*-esters, but also those of an ester and a ketone, can be employed as nucleophiles. Thus, the ring cleavage of (2*S*,4*R*)-**6a** with **7c**,**d** proceeded with high stereoselectivity to give the corresponding products **9c**,**d** (Table 2, Entries 3 and 4). Chiral acetals (2*S*,4*R*)-**6b**—**d**, derived from aliphatic and *α*,*β*- unsaturated aldehydes, also underwent a stereoselective ring-cleavage reaction (Entries 4—10). For these substrates, the stereoselectivities of the reaction at rt were lower than that of aromatic acetal (2*S*,4*R*)-**6a**. However, a satisfactory result was obtained when the reactions were carried out at −40 °C using a 0.2—0.3 mol. amt. of **5d**.



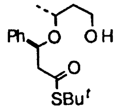
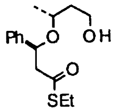
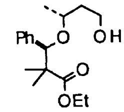
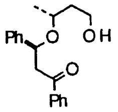
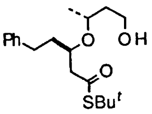
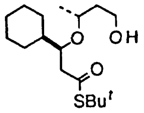
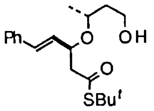
Scheme 3.



(4)

In order to extend the scope of the catalytic ring cleavage to the allylation of cyclic acetals, reactions using allylic silanes **12a**,**b** as nucleophiles were examined (Eq. 5). In the presence of **5d** (0.2 mol. amt.), the reaction of allylsilane **12a** and methallylsilane **12b** proceeded smoothly to give allylation products **13a** and **13b**, respectively, in high yields (Table 3, Entries 1 and 3). However, the level of the stereoselectivity was lower than those observed for the enol silyl ethers. A brief survey of other oxazaborolidinones as well as the reaction conditions showed that the most satisfactory results were obtained when catalyst **5d** was used in the reaction of **12b** at −50 °C (Entry 4). Tosyl and mesyl derivatives **5b**,**c** exhibited a higher stereoselectivity (Entries 8—11). However, these reactions did not reach completion. Triflates **5d**,**f** of higher Lewis acidity catalyzed the ring cleavage with **12b** at appreciable rate, even at −50 °C (Entries 4 and 12).

Table 2. Catalytic Ring-Cleavage of Acetals (2*S*,4*R*)-**6a**—**d** with Enol Silyl Ethers **7a**—**c**$^{a)}$

Entry	Acetal	Nucleophile	**5d** (mol. amt.)	Temp °C	Time h	Product	Yield %	*anti* : *syn*$^{b)}$
1	**6a**	**7a**	0.1	R.T.	4	 **9a**	81	98 : 2
2		**7b**	0.1	R.T.	4	 **9b**	78	98 : 2
3		**7c**	0.2	−20	1	 **9c**	88	>99 : 1
4$^{c)}$		**7d**	0.1	R.T.	3	 **9d**	86	93 : 7
5	**6b**	**7a**	0.3	−40	22	 **9e**	88	88 : 12
6			0.2	R.T.	18		74	75 : 25
7	**6c**	**7a**	0.3	−40	4	 **9f**	90	93 : 7$^{d)}$
8			0.2	R.T.	4		88	79 : 21$^{d)}$
9	**6d**	**7a**	0.2	−40	2	 **9g**	71	96 : 4$^{e)}$
10			0.1	R.T.	4		80	93 : 7$^{e)}$

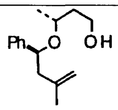
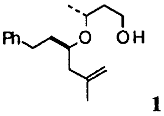
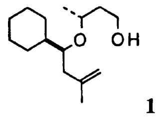
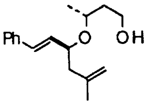
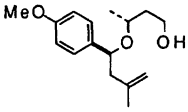
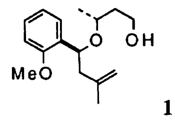
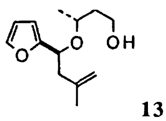
a) Unless otherwise noted, reactions were performed by using 1.5 mol. amt. of a nucleophile. b) Unless otherwise noted, ratios were determined by ^{1}H NMR (300 MHz) analyses. c) 1.1 mol. amt. of a nucleophile was used. d) The ratio was determined by a capillary GC analysis. e) The ratio was determined by the ^{1}H NMR (300 MHz) analysis of the aldehyde derivative **14g**.

Table 3. Reaction of Acetal **6a** and Allylic Silanes **12a**,**b** in the Presence of Oxazaborolidinones$^{a)}$

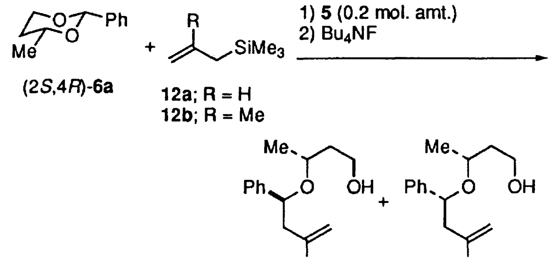
Entry	Catalyst	Allylic silane	Temp (°C)	Time (h)	Product	Yield (%)	*anti* : *syn*$^{b)}$
1	**5d**	**12a**	R.T.	2	**13b**	56	64 : 36
2			−20	3		77	71 : 29
3		**12b**	R.T.	3	**13b**	89	71 : 29
4			−50	3		91	83 : 17
5$^{c)}$			−50	3		86	92 : 8
6$^{d)}$			−50	4		92	95 : 5
7$^{e)}$			−50	6		90	90 : 10
8	**5b**		R.T.	21		20	91 : 9
9			−50	6		31	92 : 8
10	**5c**		R.T.	22		49	87 : 13
11			−50	6		18	90 : 10
12	**5f**		−50	3		90	85 : 15

a) Unless otherwise noted, reactions were carried out by using 0.2 mol. amt. of **5** in CH_2Cl_2. (2*S*,4*R*)-**6a** and ***rac*-6a** were used in Entries 1—4 and 5—12, respectively. b) Ratios were determined by ^{1}H NMR and capillary GC analyses for **13a** and **13b**, respectively. c) 1.0 mol. amt. of **5d** was used. d) **6a** was added in two portions (0.5 mol. amt. each) with time interval of 1 h. e) **6a** was added slowly by using syringe pump during 5 h and the mixture was stirred for 1 h.

Table 4. Catalytic Ring-Cleavage of Acetals **6** with Methallylsilane **12b**[a)]

Entry	Acetal	Time (h)	Product	Yield (%)	*anti* : *syn*[b)]
1	***rac*-6a**	3	 **13b**	91	83 : 17[c)]
2	(2*S*,4*R*)-**6b**	7	 **13c**	44	87 : 13
3	***rac*-6c**	8	 **13d**	62	87 : 13
4	(2*S*,4*R*)-**6d**	5	 **13e**	80	92 : 8
5[d)]	(2*S*,4*R*)-**6e**	6	 **13f**	95	92 : 8
6	***rac*-6f**	3	 **13g**	90	82 : 18
7[d)]	***rac*-6g**	6	 **13h**	81	94 : 6

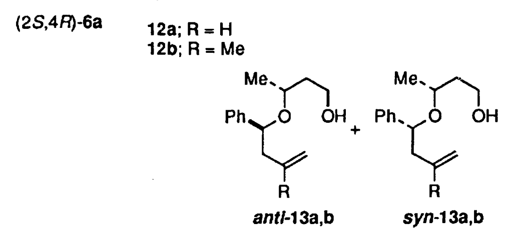
a) Unless otherwise noted, reactions were carried out by using 0.2 mol. amt. of **5d** in CH_2Cl_2 at −50 °C. b) Unless otherwise noted, ratios were determined by ^{1}H NMR analyses. c) The ratio was determined by a capillary GC analysis. d) Acetal **6e** or **6g** was added slowly by using syringe pump during 5 h and the mixture was stirred for 1 h.



(5)

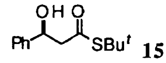
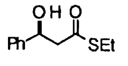
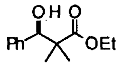
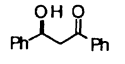
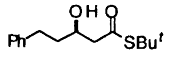
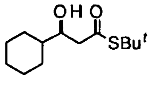
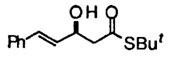
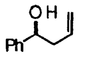
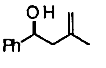
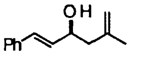
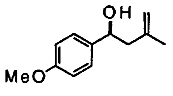
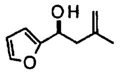
When a stoichiometric amount of **5d** was used in the reaction of **6a** and **12b** at −50 °C, the *anti* isomer of **13b** was obtained with higher stereoselectivity (*anti* : *syn*=92 : 8) (Entry 5). Interestingly, a similar level of high stereoselectivity (95 : 5) was also observed when **6a** was added in two portions (0.5 mol. amt. each) with a time interval of 4 h to a solution of 0.5 mol. amt. of **5d** (Entry 6). Of preparative interest, a 90 : 10 selectivity was obtained by the slow addition of acetal **6a** using a syringe-pump for 5 h (Entry 7). These results suggest the concomitant formation of a less stereoselective catalyst during the reactions.[18)] Although the catalytic activity of this species would be lower, it may catalyze the nonstereoselective reaction if a relatively large amount of **6a** is present in the reaction mixture. By a portionwise or slow addition of **6a**, the undesirable pathway would be considerably retarded.

By using catalyst **5d** at −50 °C, a variety of acetals **6** underwent ring-cleavage reactions to give the allylation product **13** with *anti* selectivity (Eq. 6, Table 4). The reaction of acetals **6a**,**d**—**g**, derived from aromatic and α,β-unsaturated aldehydes, proceeded efficiently. On the other hand, the yields of the ring-cleavage products for aliphatic acetals **6b**,**c** were moderate.



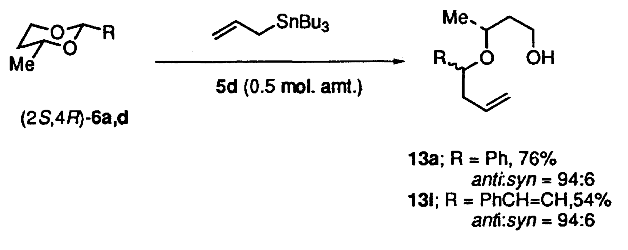
(6)

Table 5. Asymmetric Synthesis of Functionalized Alcohols **15** and **17**

Entry	Ring-cleavage product (*anti* : *syn*)	Aldehyde	Yield %	Product	Yield %	$[\alpha]_{\mathrm{D}}^{25}$[a)] (*c*, solvent)	Absolute configuration
1	**9a** (98 : 2)	**14a**	84	 **15a**	80	−43.4 (2.15, benzene)	*S*
2	**9b** (98 : 2)	**14b**	96	 **15b**	85	−60.7 (2.00, benzene)	*S*
3	**9c** (>99 : 1)	**14c**	81	 **15c**	96	−4.7 (0.96, MeOH)[b)]	*R*
4	**9d** (93 : 7)	**14d**	78	 **15d**	67	−27.9 (0.980, MeOH)	*S*
5	**9e** (88 : 12)	**14e**	82	 **15e**	69	−9.24 (2.51, benzene)	*R*
6	**9f** (93 : 7)	**14f**	79	 **15f**	84	−23.5 (1.50, CHCl$_3$)[b)]	*S*
7	**9g** (96 : 4)	**14g**	83	 **15g**	71	+18 (0.57, MeOH)[b)]	*S*
8	**13a** (94 : 6)	**16a**	90	 **17a**	63	−41 (0.26, benzene)	*S*
9	**13b** (83 : 17)	**16b**	84	 **17b**	80	−38.1 (1.97, benzene)	*S*
10	**13e** (>99 : 1)	**16c**	66	 **17c**	89	−1.48 (2.43, Et$_2$O)	*S*
11	**13f** (92 : 8)	**16d**	76	 **17d**	98	−41.0 (2.01, benzene)	*S*[c)]
12	**13h** (94 : 6)	**16e**	56	 **17e**	77	—	*S*[c)]

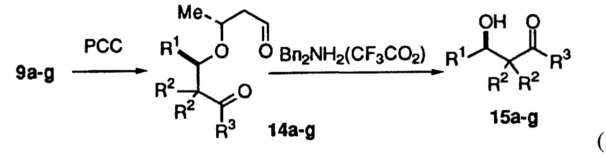
a) Specific rotation of **15** or **17** unless otherwise noted. b) Specific rotation was measured after converting into a carboxylic acid derivative. c) Tentative assignment.

In comparison with methallylsilane **12b**, allylsilane **12a** showed a lower stereoselectivity even when the reaction was performed at −20 °C (Table 3, Entry 2). However, it was found that the ring cleavage with allylation was achieved with high stereoselectivity by using more nucleophilic allyltributyltin; the *anti* isomers of **13a,i** were obtained with high stereoselectivity (94 : 6) in the reaction of **6a,d** by using a 0.5 mol. amt. of **5d** (Eq. 7).

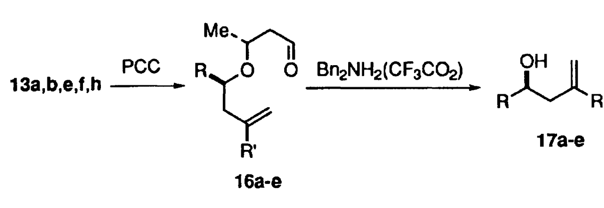


(7)

The chiral auxiliary of ring-cleavage products **9a**—**h** can be readily removed by a two-step sequence without any loss of stereochemical integrity (Eq. 8). Thus, pyridinium chlorochromate (PCC) oxidation of **9** and treatment of the resulting aldehydes **14** with dibenzylammonium trifluoroacetate in benzene[19] furnished the corresponding *β*-hydroxy carbonyl compounds **15** of high enantiomeric purities (Table 5, Entries 1—7). The ee value of **15a**, determined by converting into a (*S*)-*α*-methoxy-*α*-(trifluoromethyl)phenylacetic acid (MTPA) ester derivative, was 93%, being consistent with the *anti*/*syn* ratios of the ring-cleavage products **9a**. Similarly, homoallyl alcohols (*S*)-**17** were prepared starting from the allylation products **13** (Entries 8—14).



(8)

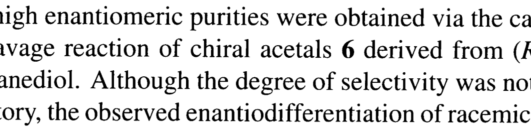


(9)

The absolute configurations of **15a,b,d,e**[20,21] and **17a,b,c**[22,23] were determined by a comparison with the literature values. For **15c,f,g**, the absolute configurations were determined after converting them into the known β-hydroxy carboxylic acids.[24—26]

The ring cleavage of chiral acetals (2*S*,4*R*)-**6a-d** took place exclusively at the less hindered C(2)–O(1) bonds with a stereoselective introduction of nucleophiles with an inversion of the C(2*S*) stereochemistry. These selectivities are well-consistent with the previously reported results on the $TiCl_4$-promoted ring-cleavage reaction. In spite of the use of chiral oxazaborolidinones **5** derived from enantiomerically pure L-amino acids, the chirality of the catalysts may not be an important factor for the *anti* : *syn* selectivity, because the selectivity is determined by the invertive vs retentive mode of the ring-cleavage reaction.

However, when racemic acetals are used as substrates and the reaction is quenched before a full conversion, the chirality of the catalysts should be of importance because one can expect differences in the reaction rates between enantiomeric acetals. Indeed, an appreciable degree of enantiodifferentiation was observed in the reaction of ***rac*-6a**. Thus, when the reaction of ***rac*-6a** and **7a** (3 mol. amt.) using oxazaborolidinone **5c** (0.2 mol. amt.) was quenched before a full conversion (r.t., 3 h), acetal (2*R*,4*S*)-**6a** of 51% ee was recovered in 27% yield together with **9a** (*anti* : *syn*=92 : 8, 69%) (Eq. 10).



(10)

In summary, we have shown that *B*-phenyl oxazaborolidinones **5**, derived from sulfonamides of α-amino acids serve as efficient catalysts for the cleavage of cyclic acetals with nucleophiles. Functionalized secondary alcohols **15** and **17** of high enantiomeric purities were obtained via the catalytic cleavage reaction of chiral acetals **6** derived from (*R*)-1,3-butanediol. Although the degree of selectivity was not satisfactory, the observed enantiodifferentiation of racemic acetal ***rac*-6a** suggests the possibility of catalytic asymmetric ring cleavage of achiral cyclic acetals using proper oxazaborolidinones.

Experimental

General. Unless otherwise noted, the ^1H, ^{11}B, and ^{13}C NMR spectra were recorded in $CDCl_3$ at 300, 96.5, and 75.6 MHz, respectively. ^{11}B NMR chemical shifts were recorded in units of parts per million relative to the external standard $BF_3{\cdot}Et_2O$. Microanalyses were performed at the Microanalysis Center of Kyoto University. Wakogel C-300 was used for flash chromatography. An enantiomeric excess of acetal **6a** was established by a capillary GC analysis using a chiral CP-Cyclodextrin-B-236-M-19 (25 m) column. Unless otherwise specified, all of the organic extracts were dried over Na_2SO_4. THF and CH_2Cl_2 were used after distillation from sodium benzophenone ketyl and from CaH_2, respectively. (*R*)-1,3-Butanediol was purchased from Wako Pure Chemical Industries Ltd.. Enol silyl ethers **7a— d**[27] and methallylsilane **12b**[28] were prepared according to the literature.

Acetals **6a—d,f,g** were prepared by condensation of the corresponding aldehydes and (*R*)-1,3,-butanediol.[1d] Acetal **6e** was prepared by treatment of cinnamaldehyde with the bis(TMS) ether derivative of (*R*)-1,3-butanediol in the presence of TMSOTf.[29] The spectral data of the acetals are as follows.

(2*S*,4*R*)-4-Methyl-2-phenyl-1,3-dioxane (6a): ^1H NMR δ= 1.33 (3H, d, *J*=6.2 Hz), 1.54 (1H, m), 1.82 (1H, m), 3.91—4.04 (2H, m), 4.27 (1H, ddd, *J*=1.3, 5.0, and 11.4 Hz), 5.52 (1H, s), 7.35 (3H, m), 7.54 (2H, m); ^{13}C NMR δ=21.71, 32.90, 66.94, 73.28, 101.22, 126.02, 128.10, 128.57, 138.77; IR (liquid film) 1100, 750, 695 cm^{-1}.

(2*S*, 4*R*)- 4- Methyl- 2- (2- phenylethyl)- 1, 3- dioxane (6b): ^1H NMR δ=1.25 (3H, d, *J*=6.0 Hz), 1.44 (1H, m), 1.68 (1H, m), 1.94 (2H, m), 2.75 (2H, m), 3.67—3.78 (2H, m), 4.11 (1H, ddd, *J*=1.4, 5.0, and 11.4 Hz), 4.51 (1H, t, *J*=5.3 Hz), 7.16—7.31 (5H, m); ^{13}C NMR δ=21.7, 30.2, 33.1, 36.4, 66.6, 72.7, 101.1, 125.7, 128.3, 128.4, 141.8; IR (film) 1130, 700 cm^{-1}.

(2*S*,4*R*)-2-Cyclohexyl-4-methyl-1,3-dioxane (6c): ^1H NMR δ=0.96—1.83 (15H, m including d (3H, *J*=6.3 Hz) at 1.20), 3.63—3.74 (2H, m), 4.08 (1H, ddd, *J*=1.2, 5.1, and 11.4 Hz), 4.21 (1H, d, *J*=5.7 Hz); ^{13}C NMR δ=20.8, 24.8 (2C), 25.5, 26.4, 26.7, 32.3, 41.5, 65.4, 71.7, 104.1; IR (liquid film) 1120 cm^{-1}.

(2*S*,4*R*)-4-Methyl-2-(2-phenylethenyl)-1,3-dioxane (6d): Bp (Kugelrohr) 97—100 °C/0.4 mmHg (1 mmHg=133.322 Pa); ^1H NMR δ=1.03 (3H, d, *J*=6.0 Hz), 1.49 (1H, m), 1.74 (1H, m), 3.82—3.94 (2H, m), 4.19 (1H, ddd, *J*=1.4 5.0, and 11.4 Hz), 5.16 (1H, dd, *J*=1.2 and 4.8 Hz), 6.21 (1H, dd, *J*=4.8 and 16.2 Hz), 6.78 (1H, d, *J*=16.2 Hz), 7.21—7.42 (5H, m); ^{13}C NMR δ=21.7, 33.0, 66.7, 73.0, 100.5, 125.9, 126.8, 128.0, 128.4, 133.2, 136.2; IR (film) 1670, 960, 970 cm^{-1}.

(2*S*,4*R*)- 2- (4- Methoxyphenyl)- 4- methyl- 1,3- dioxane (6e): ^1H NMR δ=1.30 (3H, d, *J*=6.0 Hz), 1.52 (1H, m), 1.79 (1H, m), 3.79 (3H, s), 3.88—4.05 (2H, m), 4.23 (1H, ddd, *J*=1.1, 5.0, and 11.3 Hz), 5.46 (1H, s), 6.88 (2H, m), 7.42 (2H, m); ^{13}C NMR δ=21.8, 32.9, 55.2, 67.0, 101.2, 113.6, 127.3, 131.4, 159.8; IR (liquid film) 1110, 1030, 830 cm^{-1}.

(2*S*,4*R*)- 2- (2- Methoxyphenyl)- 4- methyl- 1,3- dioxane (6f): ^1H NMR δ=1.30 (3H, d, *J*=6.21 Hz), 1.52 (1H, m), 1.81 (1H, m), 3.83 (3H, s), 3.92—4.05 (3H, m), 4.22 (1H, br dd, *J*=5.0 and 11.4 Hz), 5.90 (1H, s), 6.86 (1H, d, *J*=8.3 Hz), 6.98 (1H, br t, *J*=ca. 8 Hz), 7.29 (1H, br t, *J*=ca. 8 Hz), 7.64 (1H, dd, *J*=1.7 and 7.2 Hz); ^{13}C NMR δ=21.9, 33.1, 55.6, 67.2, 73.5, 96.4, 110.7, 120.8, 127.1, 127.3, 129.9, 156.4;

(2*S*,4*R*)-2-(2-Furyl)-4-methyl-1,3-dioxane (6g): ^1H NMR δ=1.31 (3H, d, *J*=6.3 Hz), 1.52 (1H, m), 1.85 (1H, m), 3.87—4.04 (2H, m), 4.23 (1H, ddd, *J*=1.5, 5.0, and 11.6 Hz), 5.58 (1H, s), 6.35 (1H, dd, *J*=1.8 and 3.2 Hz), 6.44 (1H, br d, *J*=3.2 Hz), 7.39 (1H, dd, *J*=0.8 and 1.8 Hz); ^{13}C NMR δ=21.6, 32.8, 67.0, 73.5, 95.9, 107.3, 110.0, 142.3, 151.1; IR (liquid film) 1100, 1060, 1030, 740 cm^{-1}.

N-Tosyl- and *N*-mesyl amino acids **4a—c,e** were prepared by the reaction of the corresponding amino acids with *p*-toluenesulfonyl chloride and methanesulfonyl chloride, respectively, under Schotten–Baumann conditions.[10,30,31]

***N*-Tosylglycine (4a):**[30] Mp 149 °C (recrystallized from H_2O); ^1H NMR (acetone-d_6) δ=2.39 (3H, s), 6.62 (1H, s), 3.75 (2H, d, *J*=5.7 Hz), 7.36 (2H, d, *J*=8.1 Hz), 7.74 (2H, d, *J*=8.1 Hz).

***N*- Tosyl- L- phenylalanine (4b):**[30] Mp 161— 163 °C (recrystallized from MeOH and H_2O); ^1H NMR δ=2.39 (3H, s), 3.00 (1H, dd, *J*=6.3 and 13.9 Hz), 3.09 (1H, dd, *J*=5.5 and 13.9

Hz), 4.17—4.24 (1H, m), 5.03 (1H, d, J=8.5 Hz), 7.05—7.09 (2H, m), 7.20—7.26 (5H, m), 7.59 (2H, d, J=8.4 Hz).

***N*-Mesyl-L-phenylalanine (4c):**[31)] Mp 104—106 °C (recrystallized from benzene and ethyl acetate); ^{1}H NMR δ=2.65 (3H, s), 3.03 (1H, dd, J=7.8 and 13.8 Hz), 3.25 (1H, dd, J=4.8 and 13.8 Hz), 4.45 (1H, ddd, J=4.8, 7.8, and 9.3 Hz), 4.95 (1H, d, J=9.3 Hz), 7.23—7.37 (5H, m).

***N*-Tosyl-L-valine (4e):**[30)] Mp 149 °C (MeOH and H_2O) (recrystallized from MeOH and H_2O); ^{1}H NMR δ=0.87 (3H, d, J=6.9 Hz), 0.96 (3H, d, J=6.9 Hz), 2.05—2.15 (1H, m), 2.41 (3H, s), 3.79 (1H, dd, J=4.5 and 12.9 Hz), 5.07 (1H, m), 7.28 (2H, d, J=8.1 Hz), 7.72 (2H, d, J=8.1 Hz).

N-Trifluoromethylsulfonyl amino acids **4d,f** were prepared by the reaction of the methyl esters of the corresponding amino acids with trifluoromethanesulfonyl chloride in the presence of *i*-Pr_2NEt and subsequent saponification.[10b)]

***N*-(Trifluoromethylsulfonyl)-L-phenylalanine (4d):** Mp 121—122 °C (recrystallized from benzene); ^{1}H NMR δ=3.12 (1H, dd, J=5.7 and 13.8 Hz), 3.26 (1H, dd, J=5.4 and 13.8 Hz), 4.57—4.64 (1H, m), 5.33 (1H, m), 7.17—7.20 (2H, m), 7.33—7.36 (3H, m).

***N*-(Trifluoromethylsulfonyl)-L-valine (4f):** Mp 145—146 °C (recrystallized from ether); ^{1}H NMR (acetone-d_6) δ=0.98 (3H, d, J=6.9 Hz), 1.05 (3H, d, J=6.9 Hz), 2.22—2.33 (1H, m), 3.99 (1H, d, J=5.1 Hz).

General Method for the Preparation of Oxazaborolidinones 5a—f. To a solution of sulfonamide **4a—f** (0.10 mmol) in CH_2Cl_2 (1 mL) at rt under nitrogen was added dichlorophenylborane (13 µL, 0.10 mmol). After being stirred for 30 min the mixture was concentrated in vacuo to give phenylboron compounds **5a—f** as a white solid, which was then dissolved in CH_2Cl_2 (0.2 mL) and used for ring-cleavage reactions.

Oxazaborolidinone 5a: ^{1}H NMR δ=2.42 (3H, s), 4.24 (2H, s), 7.31 (2H, d, J=8.1 Hz), 7.45—7.52 (2H, m), 7.57—7.63 (1H, m), 7.70 (2H, d, J=8.1 Hz), 8.16 (2H, d, J=6.9 Hz); ^{11}B NMR δ=46.5.

Oxazaborolidinone 5b: ^{1}H NMR δ=2.39 (3H, s), 3.37 (1H, dd, J=2.7 and 14.1 Hz), 3.69 (1H, dd, J=5.4 and 14.1 Hz), 4.55 (1H, dd, J=2.7 and 5.4 Hz), 7.20—7.39 (8H, m), 7.46—7.55 (4H, m), 7.78—7.82 (2H, m); ^{11}B NMR δ=42.9.

Oxazaborolidinone 5c: ^{1}H NMR δ=3.01 (3H, s), 3.43 (1H, dd, J=3.0 and 14.1 Hz), 3.57 (1H, dd, J=5.4 and 14.1 Hz), 4.85 (1H, dd, J=3.0 and 5.4 Hz), 7.20—7.33 (5H, m), 7.37—7.43 (2H, m), 7.51—7.57 (1H, m), 7.90—7.93 (2H, m); ^{11}B NMR δ=47.1.

Oxazaborolidinone 5d: ^{1}H NMR δ=3.46 (1H, dd, J=2.4 and 14.4 Hz), 3.62 (1H, dd, J=5.7 and 14.4 Hz), 4.89 (1H, qdd, J=0.6, 2.4, and 5.7 Hz), 7.21—7.38 (6H, m), 7.48—7.56 (2H, m), 7.70—7.74 (2H, m); ^{11}B NMR δ=48.3.

Oxazaborolidinone 5e: ^{1}H NMR δ=0.89 (3H, d, J=6.9 Hz), 1.23 (3H, d, J=6.9 Hz), 2.38 (3H, s), 2.59—2.75 (1H, m), 4.26 (1H, d, J=3.6 Hz), 7.20—7.26 (2H, m), 7.42—7.62 (5H, m), 8.06—8.10 (2H, m); ^{11}B NMR δ=37.4.

Oxazaborolidinone 5f: ^{1}H NMR δ=0.97 (3H, d, J=6.9 Hz), 1.27 (3H, d, J=6.9 Hz), 2.55—2.67 (1H, m), 4.53 (1H, d, J=3.6 Hz), 7.45—7.66 (3H, m), 8.05—8.08 (2H, m); ^{11}B NMR δ=36.9.

Oxazaborolidinone 5g: The complex was prepared by the reaction of **4d** with $MeBBr_2$ according to a procedure similar to that described above. **5g**: ^{1}H NMR δ=0.60 (3H, s), 3.35 (1H, dd, J=2.4 and 14.1 Hz), 3.54 (3H, dd, J=5.7 and 14.1 Hz), 4.65 (1H, dd, J=2.4 and 5.7 Hz), 7.17—7.20 (2H, m), 7.30—7.35 (3H, m); ^{11}B NMR δ=40.4.

***S*-*t*-Butyl (3*S*)-3-[(1*R*)-3-Hydroxy-1-methylpropoxy]-3-phenylpropanethioate (9a) (Representative Procedure for Catalytic Ring Cleavage of Acetals 6 with Enol Silyl Ethers 7):** To a stirred solution of acetal **6a** (71.8 mg, 0.40 mmol) and **7a** (122 mg, 0.60 mmol) in CH_2Cl_2 (0.32 mL) at rt under argon was added a CH_2Cl_2 solution of **5d** (80 µL, 0.5 M, 1 M=1 mol dm^{-3}). After being stirred for 4 h, the reaction mixture was quenched by the addition of a CH_2Cl_2 solution of *i*-Pr_2NEt (1 M, 0.5 mL). A THF solution of Bu_4NF (1 mol dm^{-3} in THF, 0.5 mL) was added to the mixture and the whole was stirred at rt for 0.5 h. The mixture was diluted with Et_2O, poured into water, and extracted twice with Et_2O. Organic extracts were dried and concentrated in vacuo. Purification of the residue by flash chromatography (10% ethyl acetate/hexane) gave 101 mg (81% yield) of ring cleavage product **9a** (*anti* : *syn* 98 : 2): ^{1}H NMR δ=1.15 (3H, d, J=6.3 Hz), 1.44 (9H, s), 1.57—1.72 (2H, m), 2.46 (1H, br s), 2.62 (1H, dd, J=4.2 and 14.4 Hz), 2.90 (1H, dd, J=9.6 and 14.4 Hz), 3.49—3.61 (2H, m), 3.68—3.73 (1H, m), 4.88 (1H, dd, J=4.2 and 9.6 Hz), 7.27—7.38 (5H, m) [a minor diastereomer resonated at δ=0.92 (3H, d, J=6.0 Hz)]; ^{13}C NMR δ=18.4, 29.6, 39.1, 48.2, 52.8, 60.3, 71.4, 75.4, 126.8, 128.1, 128.6, 140.6, 197.3; IR (liquid film) 3400 (br), 1680, 760, 735, 695 cm^{-1}. Found: C, 65.64; H, 8.74; S, 10.54%. Calcd for $C_{17}H_{26}O_3S$: C, 65.77; H, 8.44; S, 10.33%.

When the reaction of **6a** and **7a** in the presence of **5d** (0.2 mol. amt.) was performed by a procedure like that described above, except that the initial reaction mixture was not treated with Bu_4NF, *S*-*t*-butyl (3*S*)-3-[(1*R*)-1-methyl-3-(trimethylsilyloxy)propoxy]-3-phenylpropanethioate (**8a**) was obtained in 86% yield (*anti* : *syn* 98 : 2). **8a**: ^{1}H NMR δ=0.02 (9H, s), 1.13 (3H, d, J=6.0 Hz), 1.44 (9H, s), 1.48—1.59 (1H, m), 1.65—1.77 (1H, m), 2.60 (1H, dd, J=4.5 and 14.4 Hz), 2.90 (1H, dd, J=9.3 and 14.4 Hz), 3.38—3.50 (2H, m), 3.53—3.61 (1H, m), 4.84 (1H, dd, J=4.5 and 9.0 Hz), 7.25—7.33 (5H, m) [a minor diastereomer resonated at 0.98 (3H, d, J=6.3 Hz)]; ^{13}C NMR δ=−0.6, 19.0, 29.7, 40.4, 47.9, 53.2, 59.4, 70.0, 75.6, 126.7, 127.7, 128.3, 141.6, 197.5; IR (liquid film) 1680, 1090, 840, 750, 695 cm^{-1}.

Ring-cleavage products **9b—g** were prepared by a procedure similar to that described above. For the reaction conditions, see Table 2. The spectral data are as follows:

***S*-Ethyl (3*S*)-3-[(1*R*)-3-Hydroxy-1-methylpropoxy]-3-phenylpropanethioate (9b):** ^{1}H NMR δ=1.16 (3H, d, J=6.0 Hz), 1.23 (3H, t, J=7.5 Hz), 1.61—1.67 (2H, m), 2.39 (1H, br t, J=ca. 5.5 Hz), 2.74 (1H, dd, J=4.5 and 14.7 Hz), 2.88 (2H, q, J=7.5 Hz), 3.02 (1H, dd, J=9.3 and 14.7 Hz), 3.49—3.64 (2H, m), 3.65—3.74 (1H, m), 4.93 (1H, dd, J=4.5 and 9.3 Hz), 7.28—7.39 (5H, m) [a minor diastereomer resonated at 0.93 (3H, d, J=6.2 Hz)]; ^{13}C NMR δ=14.7, 18.3, 23.5, 39.0, 52.3, 60.4, 71.4, 75.1, 126.8, 128.3, 128.7, 140.4, 196.7; IR (liquid film) 3400 (br), 1685, 760, 740, 700 cm^{-1}. Found: C, 63.52; H, 8.05; S, 11.63%. Calcd for $C_{15}H_{22}O_3S$: C, 63.80; H, 7.85; S, 11.35%.

Ethyl (3*R*)-3-[(1*R*)-3-Hydroxy-1-methylpropoxy]-2,2-dimethyl-3-phenylpropanoate (9c): ^{1}H NMR δ=1.02 (3H, s), 1.10 (3H, d, J=6.0 Hz), 1.11 (3H, s), 1.26 (3H, t, J=7.2 Hz), 1.58—1.76 (2H, m), 2.68 (1H, br s), 3.52 (1H, dqd, J=4.8, 6.0, and 12.0 Hz), 3.65—3.77 (2H, m), 4.09 (1H, qd, J=7.2 and 10.8 Hz), 4.17 (1H, qd, J=7.2 and 10.8 Hz) 4.72 (1H, s), 7.28—7.34 (5H, m) [a minor diastereomer resonated at 4.66 (s, 1H)]; ^{13}C NMR δ=14.1, 17.9, 19.2, 22.8, 39.2, 47.6, 60.4, 60.6, 71.4, 82.7, 127.8, 128.0, 128.7, 137.4, 176.4; IR (liquid film) 3425 (br), 1730, 770, 750, 705 cm^{-1}. Found: C, 69.15; H, 9.09%. Calcd for $C_{17}H_{26}O_4$: C, 69.36; H, 8.90%.

(3*S*)-3-[(1*R*)-3-Hydroxy-1-methylpropoxy]-1,3-diphenyl-1-propanone (9d): ^{1}H NMR δ=1.16 (3H, d, J=6.0 Hz), 1.61

(2H, q, J=5.5 Hz), 2.26 (1H, br t, J=5.1 Hz), 3.10 (1H, dd, J=4.5 and 16.2 Hz), 3.50—3.70 (4H including dd (J=8.1 and 16.2 Hz, 1H) at 3.59, m), 5.14 (1H, dd, J=4.5 and 8.1 Hz), 7.28—7.56 (8H, m), 7.91—7.96 (2H, m) [a minor diastereomer resonated at 0.94 (3H, d, J=6.1 Hz)]; ^{13}C NMR δ=18.5, 39.2, 47.1, 60.5, 71.3, 74.8, 126.9, 128.1, 128.2, 128.5, 128.7, 133.1, 137.3, 141.5, 197.5; IR (liquid film) 3420 (br), 1680, 745, 695 cm^{-1}; HRMS (CI) Calcd for $C_{19}H_{22}O_3$: (M$^+$+1), 299.1647. Found: *m*/*z* 299.1714.

***S*-*t*-Butyl (3*R*)-3-[(1*R*)-3-Hydroxy-1-methylpropoxy]-5-phenylpentanethio-ate (9e):** ^{1}H NMR (C_6D_6) δ=0.95 (3H, d, J=6.0 Hz), 1.35 (9H, s), 1.35—1.41 (1H, m), 1.45—1.56 (1H, m), 1.63—1.71 (2H, m), 1.85 (1H, br s), 2.31 (1H, dd, J=5.1 and 14.7 Hz), 2.41—2.47 (2H, m), 2.52 (1H, dd, J=7.5 and 14.7 Hz), 3.39—3.50 (2H, m), 3.55—3.63 (1H, m), 3.78 (1H, qd, J=5.3 and 7.6 Hz), 6.98—7.14 (5H, m) [a minor isomer resonated at 0.87 (3H, d J=6.2 Hz)]; ^{13}C NMR (C_6D_6) δ=20.5, 30.2, 31.9, 36.8, 40.2, 48.4, 50.7, 60.6, 73.1, 73.9, 126.7, 129.2, 129.2, 142.7, 198.1; IR (liquid film) 3440 (br), 1675, 740, 695 cm^{-1}. Found: C, 67.25; H, 8.88; S, 9.72%. Calcd for $C_{19}H_{30}O_3S$: C, 67.42; H, 8.93; S, 9.47%.

***S*-*t*-Butyl (3*S*)-3-Cyclohexyl-3-[(1*R*)-3-hydroxy-1-methylpropoxy]propanethioate (9f):** ^{1}H NMR δ=1.10 (3H, d, J=6.3 Hz), 0.86—1.77 (13H including s (9H) at 1.43, m), 2.46 (1H, dd, J=4.5 and 14.4 Hz), 2.54 (1H, dd, J=7.8 and 14.4 Hz), 2.59—2.63 (1H, m), 3.65—3.80 (4H, m) [a minor isomer resonated at 1.44 (9H, s)]; ^{13}C NMR δ=19.4, 26.3, 26.4, 26.6, 27.8, 28.8, 29.6, 39.0, 41.3, 47.0, 48.0, 60.5, 73.4, 77.8, 199.0; IR (liquid film) 3420 (br), 2920, 1685 cm^{-1}. Found: C, 64.48; H, 10.01; S, 10.13%. Calcd for $C_{17}H_{32}O_3S$: C, 64.51; H, 10.19; S, 10.13%.

***S*-*t*-Butyl (3*S*,4*E*-)-3-[(1*R*)-3-Hydroxy-1-methylpropoxy]-5-phenyl-4-pentenethioate (9g):** ^{1}H NMR δ=1.15 (3H, d, J=6.0 Hz), 1.44 (9H, s), 1.70—1.73 (2H, m), 2.61 (1H, dd, J=4.8 and 14.1 Hz), 2.71 (1H, br s), 2.78 (1H, dd, J=8.1 and 14.1 Hz), 3.65—3.85 (3H, m), 4.45 (1H, dt, J=4.8 and 8.3 Hz), 6.05 (1H, dd, J=8.4 and 15.9 Hz), 6.58 (1H, d, J=15.9 Hz), 7.22—7.39 (5H, m); ^{13}C NMR δ=18.8, 29.6, 39.0, 48.2, 50.7, 60.7, 71.9, 74.6, 126.5, 128.0, 128.4, 128.6, 133.1, 136.1, 197.1; IR (liquid film) 3440, 1680, 750, 695 cm^{-1}. Found: C, 67.82; H, 8.67; S, 9.36%. Calcd for $C_{19}H_{28}O_3S$: C, 67.82; H, 8.39; S, 9.53%.

Ring Cleavage Reaction with Allylic Silanes 12a,b. The reaction was carried out by a procedure similar to that described for enol silyl ethers **7**. Spectral data of the ring cleavage products **13a**—**i** are as follows.

(3*R*)-3-[(1*S*)-3-Phenyl-3-butenyloxy]-1-butanol (13a): ^{1}H NMR δ=1.16 (3H, d, J=6.3 Hz), 1.66 (2H, q, J=5.5 Hz), 2.35—2.45 (1H, m), 2.49—2.59 (1H, m), 2.70 (1H, br s), 3.51—3.62 (2H, m), 3.67—3.74 (1H, m), 4.43 (1H, dd, J=6.0 and 7.8 Hz), 4.99—5.08 (2H, m), 5.74 (1H, tdd, J=7.0, 10.2 and 17.0 Hz), 7.26—7.39 (5H, m); [a minor isomer resonated at 0.99 (3H, d, J=6.2 Hz)]; ^{13}C NMR δ=18.8, 39.5, 42.8, 60.5, 71.2, 78.8, 116.9, 127.0, 127.8, 128.5, 134.7, 142.0; IR (liquid film) 3400 (br), 920, 760, 705 cm^{-1}. Found: C, 76.12; H, 9.45%. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15%.

(3*R*)-3-[(1*S*)-3-Methyl-1-phenyl-3′-butenyloxy]-1-butanol (13b): ^{1}H NMR δ=1.16 (3H, d, J=6.1 Hz), 1.62—1.69 (2H, m), 1.72 (13H, br s), 2.32 (1H, dd, J=5.3 and 13.5 Hz), 2.52 (1H, dd, J=8.5 and 13.5 Hz), 2.8 (1H, br), 3.51—3.66 (2H, m), 3.72 (1H, m), 4.55 (1H, dd, J=5.3 and 8.5 Hz), 4.70 (1H, m), 4.76 (1H, m) 7.26—7.39 (5H, m) [a minor diastereomer resonated at δ=0.96 (3H, d, J=6.2 Hz)]; ^{13}C NMR δ=18.2, 22.5, 38.13, 38.8, 46.8, 60.4, 71.0, 77.0, 112.9, 126.8, 127.7, 128.4, 141.8, 142.0; IR (liquid film) 3400 (br), 1650, 1080, 1050, 890, 755, 700 cm^{-1}; MS *m*/*z* (rel intensity) 179 (M$^+$ − CH$_2$=C(Me)CH$_2$; 19), 145 (3), 107 (100), HRMS Calcd for $C_{11}H_{15}O_2$: (M$^+$ − CH$_2$=C(Me)CH$_2$), 179.1072. Found: *m*/*z* 179.1067. Found: C, 77.04; H, 9.60%. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46%.

(3*R*)-3-[(1*S*)-3-Methyl-1-(2-phenylethyl)-3-butenyloxy]-1-butanol (13c): ^{1}H NMR δ=1.14 (3H, d, J=6.2 Hz), 1.70—1.90 (5H, m, including br s (3H) at δ=1.74), 2.18—2.30 (2H, m), 2.60—2.90 (3H, m), 3.58 (1H, quint, J=ca. 6 Hz), 4.74 (1H, m), 4.84 (1H, m) [a minor diastereomer resonated at δ=1.17 (3H, d, J=6.2 Hz)]; ^{13}C NMR δ=19.8, 22.82, 31.3, 35.5, 39.0, 43.6, 60.7, 73.6, 74.6, 112.9, 125.7, 128.27, 128.33, 142.1, 142.6; IR (liquid film) 3400 (br), 1650, 1050, 890, 745, 700 cm^{-1}; MS (CI) *m*/*z* (rel intensity) 263 (MH$^+$; <1), 207 (55), 117 (98), 91 (100). HRMS Calcd for $C_{13}H_{19}O_2$: (M$^+$ − CH$_2$=C(Me)CH$_2$), 207.1385. Found: *m*/*z* 207.1376. Found: C, 77.60; H, 10.11%. Calcd for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99%.

(3*R*)-3-[(1*S*)-1-Cyclohexyl-3-methyl-3-butenyloxy]-1-butanol (13d): ^{1}H NMR δ=0.95—1.45 (8H, m including d (J=6.1 Hz, 3H) at δ=1.197), 1.45—1.85 (11H, m), 2.09 (1H, dd, J=7.5 and 4.0 Hz), 2.14 (1H, dd, J=5.3 and 14.0 Hz), 2.97 (1H, br s), 3.33 (1H, m), 3.65—3.85 (3H, m), 4.70 (1H, m), 4.76 (1H, m) [a minor diastereomer resonated at δ=1.122 (3H, d, J=6.2 Hz)]; ^{13}C NMR (C_6D_6) δ=20.1, 23.1, 27.0, 27.1, 28.5, 28.8, 39.8, 40.4, 41.3, 60.3, 72.7, 79.7, 112.9, 143.5; IR (liquid film) 3300 (br), 1685, 1090, 925 cm^{-1}; MS *m*/*z* (rel intensity) 185 (M$^+$ − CH$_2$=C(Me)-CH$_2$; 17), 113 (49), 107 (39), 95 (100). HRMS Calcd for $C_{11}H_{21}O_2$: (M$^+$ − CH$_2$=C(Me)CH$_2$), 185.1541. Found: *m*/*z* 185.1538. Found: C, 74.65; H, 11.87%. Calcd for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74%.

(3*R*)-3-[(1*S*)-3-Methyl-1-[(*E*)-2-phenylethenyl]-3-butenyloxy]-1-butanol (13e): ^{1}H NMR δ=1.17 (3H, d, J=6.1 Hz), 1.65—1.80 (5H, m, including br s (3H) at δ=1.77), 2.27 (1H, dd, J=5.8 and 13.7 Hz), 2.39 (1H, dd, J=7.7 and 13.5 Hz), 2.98 (1H, br s), 3.65—3.85 (2H, m), 3.87 (1H, sextet, J=6.1 Hz), 4.14 (1H, ddd, J=5.8, 7.7, and 8.4 Hz), 4.76 (1H, m), 4.80 (1H, m), 6.05 (1H, dd, J=8.4 and 15.9 Hz), 6.53 (1H, d, J=15.9 Hz), 7.20—7.45 (5H, m); ^{13}C NMR δ=18.7, 22.9, 38.8, 44.8, 61.1, 71.6, 76.1, 113.1, 126.5, 127.8, 128.6, 130.1, 132.5, 136.4, 141.8; IR (liquid film) 3420 (br), 1650, 1050, 965, 890, 750, 695 cm^{-1}; MS *m*/*z* (rel intensity) 205 (M$^+$ − CH$_2$=C(Me)CH$_2$; 23), 170 (8), 155 (11), 133 (100); HRMS Calcd for $C_{13}H_{17}O_2$: (M$^+$ − CH$_2$=C(Me)CH$_2$), 205.1229. Found: *m*/*z* 205.1234. Found: C, 78.42; H, 9.30%. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29%.

(3*R*)-3-[(1*R*)-3-Methyl-1-[(*E*)-2-phenylethenyl]-3-butenyloxy]-1-butanol (a Minor Isomer): ^{1}H NMR δ=1.18 (3H, d, J=6.2 Hz), 1.65—1.85 (5H, m, including br s (3H) at δ=1.79), 2.24 (1H, dd, J=7.4 and 13.8 Hz), 2.83 (1H, dd, J=7.7 and 13.8 Hz), 2.50, (1H, br s), 3.65—3.90 (3H, m), 4.13 (1H, q, J=ca. 6 Hz), 4.80 (1H, m), 4.84 (1H, m), 6.13 (1H, dd, J=7.4 and 16.0 Hz), 6.52 (1H, d, J=16.0 Hz), 7.15—7.40 (5H, m); ^{13}C NMR δ=21.1, 22.8, 38.9, 44.9, 60.4, 73.9, 78.0, 113.6, 126.4, 127.6, 128.6, 130.8, 131.5, 136.7, 141.8.

(3*R*)-3-[(1*S*)-3-Methyl-1-(4-methoxyphenyl)-3-butenyloxy]-1-butanol (13f): ^{1}H NMR δ=1.14 (3H, d, J=6.1 Hz), 1.60—1.70 (2H, m), 1.70 (3H, br s), 2.31 (1H, dd, J=5.6 and 13.9 Hz), 2.51 (1H, dd, J=8.3 and 13.9 Hz), 2.85 (1H, br t, J=ca. 5.5 Hz), 3.45—3.65 (2H, m), 3.72 (1H, m), 3.80 (3H, s), 4.51 (1H, dd, J=5.6 and 8.3 Hz), 4.69 (1H, m), 4.75 (1H, m), 6.89 (2H, m), 7.24 (2H, m) [a minor diastereomer resonated at δ=0.94 (3H, d, J=6.3 Hz) and 1.73 (3H, br s)]; ^{13}C NMR δ=18.3, 22.6, 38.8, 46.8, 55.2, 60.8, 71.0, 76.5, 112.9, 113.8, 128.1, 133.8, 142.2, 159.2; IR (liquid film) 3420 (br), 3075, 1610, 1245, 890, 835 cm^{-1}; MS *m*/*z* (rel intensity) 209 (M$^+$ − CH$_2$=C(Me)CH$_2$; 21), 175 (3), 137 (100); HRMS Calcd for $C_{12}H_{17}O_3$: (M$^+$ − CH$_2$= C(Me)CH$_2$), 209.1178. Found: *m*/*z*

209.1174. Found: C, 72.89; H, 9.25%. Calcd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15%.

(3*R*)-3-[(1*S*)-3-Methyl-1-(2-methoxyphenyl)-3-butenyloxy]-1-butanol (13g): ^{1}H NMR δ=1.16 (3H, d, J=6.1 Hz), 1.60—1.75 (5H, m including br s (3H) at J=1.76), 2.37 (1H, dd, J=5.3 and 13.8 Hz), 2.43 (1H, dd, J=8.2 and 13.8 Hz), 3.07 (1H, br s), 3.50—3.80 (2H, m), 3.83 (3H, s), 4.68 (1H, m), 4.74 (1H, m), 5.08 (1H, dd, J=5.3 and 8.2 Hz), 6.87 (1H, dd, J=1.0 and 8.2 Hz), 6.98 (1H, dt, J=1.0 and 7.5 Hz), 7.25 (1H, dt, J=1.7 and 7.8 Hz), 7.37 (1H, dd, J=1.7 and 7.5 Hz) [a minor diastereomer resonated at δ=0.98 (3H, d, J=6.3 Hz) and 4.99 (1H, dd, J=4.9 and 8.1 Hz)]; ^{13}C NMR δ=18.5, 22.5, 38.9, 45.5, 55.2, 60.7, 70.5, 71.5, 110.4, 112.4, 120.7, 127.3, 128.4, 130.1, 142.7, 157.1; IR (liquid film) 3420 (br), 1600, 1240, 890, 755 cm^{-1}; MS *m/z* (rel intensity) 209 ($M^+-CH_2{=}C(Me)CH_2$; 23), 175 (4), 137 (100); HRMS Calcd for $C_{12}H_{17}O_3$: ($M^+-CH_2{=}C(Me)CH_2$), 209.1178. Found: *m/z* 209.1184. Found: C, 72.99; H, 9.43%. Calcd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15%.

(3*R*)-3-[(1*S*)-1-(2-Furyl)-3-methyl-3-butenyloxy]-1-butanol (13h): ^{1}H NMR δ=1.16 (3H, d, J=6.1 Hz), 1.55—1.75 (5H, m including br s (3H) at J=1.69), 2.49 (1H, dd, J=6.6 and 13.9 Hz), 2.59 (1H, dd, J=7.7 and 13.9 Hz), 2.60 (1H, br), 3.45—3.85 (3H, m), 4.56 (1H, dd, J=6.6 and 7.7 Hz), 4.70 (1H, m), 4.76 (1H, m), 6.26 (1H, dd, J=0.6 and 3.3 Hz), 6.33 (1H, dd, J=1.8 and 3.3 Hz), 7.40 (1H, dd, J=0.6 and 1.8 Hz) [a minor diastereomer resonated at δ=0.97 (3H, d, J=6.2 Hz)]; ^{13}C NMR δ=18.9, 22.5, 38.9, 43.0, 60.8, 70.4, 71.9, 108.0, 110.0, 113.0, 141.5, 142.2, 154.2; IR (liquid film) 3410 (br), 1650, 1050, 890, 740 cm^{-1}; MS *m/z* (rel intensity) 169 ($M^+-CH_2{=}C(Me)CH_2$; 20), 135 (4), 97 (100); HRMS Calcd for $C_9H_{13}O_3$: ($M^+-CH_2{=}C(Me)CH_2$), 169.0865. Found: *m/z* 169.0877. Found: C, 69.41; H, 9.08%. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99%.

(3*R*)-3-[(1*S*)-1-[(*E*)-2-Phenylethenyl]-3-butenyloxy]-1-butanol (13i) (Ring Cleavage Reaction with Allyltributyltin). The reaction was carried out by a procedure similar to that described for the enol silyl ethers **7**.

13i: ^{1}H NMR δ=1.17 (3H, d, J=6.0 Hz), 1.65—1.80 (2H, m), 2.25—1.45 (2H, m), 2.92 (1H, br s), 3.65—3.92 (3H, m including sextet (1H, J=ca. 6 Hz) at δ=3.85), 4.04 (1H, td, J=6.3 and 8.4 Hz), 5.05—5.17 (2H, m), 5.83 (1H, tdd, J=7.0, 10.2, and 17.1 Hz), 6.08 (1H, dd, J=8.4 and 15.9 Hz), 6.54 (1H, d, J=15.9 Hz), 7.20—7.45 (5H, m) [a minor diastereomer resonated at δ=1.18 (3H, d, J=6.2 Hz)]; ^{13}C NMR δ=19.0, 38.9, 40.8, 61.1, 71.9, 77.3, 117.3, 126.5, 127.9, 128.6, 129.8, 132.7, 134.2, 136.3; IR (liquid film) 3420 (br), 1055, 970, 915, 750, 690 cm^{-1}; MS *m/z* (rel intensity) 205 ($M^+-CH_2{=}CHCH_2$; 22), 133 (100); HRMS Calcd for $C_{13}H_{17}O_2$: ($M^+-CH_2{=}CHCH_2$), 205.1229. Found: *m/z* 205.1232. Found: C, 77.75 H, 9.20%. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00%.

***S-t*-Butyl (3*S*)-3-[(1*S*)-1-Methyl-2-formylethoxy]-3-phenylpropanethioate (14a) (Representative Procedure for PCC Oxidation).** To a solution of **9a** (93 mg, 0.30 mmol) in CH_2Cl_2 (1 mL) was added PCC (215 mg, 1.0 mmol). After being stirred for 5 h, the mixture was diluted with Et_2O and filtered through Cellite. The filtrate was concentrated in vacuo. Purification of the residue by flash chromatography (3% ethyl acetate/hexane) gave 77 mg (84% yield) of **14a**: ^{1}H NMR δ=1.22 (3H, d, J=6.3 Hz), 1.44 (9H, s), 2.35 (1H, ddd, J=1.8, 5.1, and 15.9 Hz), 2.48 (1H, ddd, J=3.0, 6.9, and 15.9 Hz), 2.59 (1H, dd, J=4.2 and 14.7 Hz), 2.90 (1H, dd, J=9.6 and 14.7 Hz), 3.79—3.89 (1H, m), 4.88 (1H, dd, J=4.2 and 9.6 Hz), 7.25—7.36 (5H, m), 9.55 (1H, dd, J=1.8 and 3.0 Hz) [a minor diastereomer resonated at δ=9.79 (1H, dd, J=1.8 and 5.7 Hz)]; ^{13}C NMR δ=19.0, 29.6, 48.1, 50.7, 52.8, 68.1, 75.7, 126.6, 128.1, 128.6, 140.7, 197.3, 201.7; IR (liquid film) 2720, 1720, 1680, 760, 740, 700 cm^{-1}.

Aldehydes **14b**—**g** and **16a**—**e** were prepared by a procedure similar to that described above. The spectral data are as follows:

***S*-Ethyl (3*S*)-3-[(1*S*)-1-Methyl-2-formylethoxy]-3-phenylpropanethioate (14b):** ^{1}H NMR δ=1.22 (3H, t, J=6.0 Hz), 1.23 (3H, t, J=7.5 Hz), 2.34 (1H, ddd, J=1.8, 5.1, and 15.9 Hz), 2.49 (1H, ddd, J=3.0, 7.2, and 15.9 Hz), 2.71 (1H, dd, J=4.2 and 15.0 Hz), 2.87 (2H, q, J=7.5 Hz), 3.02 (1H, dd, J=9.3 and 15.0 Hz), 3.89—3.79 (1H, m), 4.93 (1H, dd, J=4.2 and 9.3 Hz), 7.27—7.38 (5H, m), 9.55 (1H, dd, J=1.8 and 3.0 Hz) [a minor diastereomer resonated at δ=9.76 (1H, dd, J=1.2 and 3.3 Hz)]; ^{13}C NMR δ=14.7, 18.9, 23.4, 50.7, 52.4, 68.1, 75.5, 126.7, 128.3, 128.6, 140.6, 196.7, 201.6; IR (liquid film) 2720, 1720, 1680, 765, 740, 700 cm^{-1}.

Ethyl (3*R*)-2,2-Dimethyl-3-[(1*R*)-1-methyl-2-formylethoxy]-3-phenylpropanoate (14c): ^{1}H NMR δ=0.96 (3H, s), 1.11 (3H, s), 1.16 (3H, d, J=6.3 Hz), 1.25 (3H, t, J=7.2 Hz), 2.37 (1H, ddd, J=2.1, 5.1, and 15.9 Hz), 2.49 (1H, ddd, J=3.0, 6.9, and 15.9 Hz), 3.86—3.76 (1H, m), 4.08 (1H, qd, J=7.2 and 10.8 Hz), 4.16 (1H, qd, J=7.2 and 10.8 Hz), 4.76 (1H, s), 7.23—7.35 (5H, m), 9.66 (1H, dd, J=2.1 and 3.0 Hz); ^{13}C NMR δ=14.2, 18.7 (2C), 22.5, 47.8, 50.9, 60.5, 68.1, 82.8, 127.8, 128.0, 128.7, 137.5, 176.4, 201.5; IR (liquid film) 2725, 1720, 770, 745, 710 cm^{-1}.

(3*S*)-3-[(1*R*)-1-Methyl-2-formylethoxy]-1,3-diphenyl-1-propanone (14d): ^{1}H NMR δ=1.21 (3H, d, J=6.3 Hz), 2.31 (1H, ddd, J=1.8, 4.8, and 15.9 Hz), 2.43 (1H, ddd, J=3.0, 7.5, and 15.9 Hz), 3.00 (1H, dd, J=4.2 and 16.2 Hz), 3.60 (1H, dd, J=8.7 and 16.2 Hz), 3.88 (1H, dqd, J=4.8, 6.3, and 7.5 Hz), 5.14 (1H, dd, J=4.2 and 8.7 Hz), 7.30—7.57 (8H, m), 7.91—7.95 (2H, m), 9.51 (1H, dd, J=1.8 and 3.0 Hz) [a minor diastereomer resonated at 9.72 (1H, dd, J=1.8 and 2.7 Hz)]; ^{13}C NMR δ=18.9, 47.1, 50.8, 67.8, 75.0, 126.9, 128.1, 128.2, 128.5, 128.6, 133.1, 137.2, 141.5, 197.7, 201.8; IR (liquid film) 2725, 1720, 1690, 750, 700, 695 cm^{-1}.

***S-t*-Butyl (3*R*)-3-[(1*R*)-1-Methyl-2-formylethoxy]-5-phenylpentanethioate (14e):** ^{1}H NMR δ=1.19 (3H, d, J=6.3 Hz), 1.46 (9H, s), 1.78—1.86 (2H, m), 2.45 (1H, ddd, J=1.8, 5.4, and 16.5 Hz), 2.54—2.66 (4H, m), 2.70 (2H, dd, J=7.2 and 14.4 Hz), 3.87—3.95 (1H, m), 3.97—4.07 (1H, m), 7.15—7.30 (5H, m), 9.79 (1H, dd, J=1.8 and 2.1 Hz) [a minor diastereomer resonated at 9.76 (1H, t, J=2.1 Hz)]; ^{13}C NMR δ=20.5, 29.7, 31.2, 36.1, 48.2, 49.9, 50.6, 69.2, 73.7, 125.9, 128.2, 128.4, 141.6, 198.1, 201.2; IR (liquid film) 2710, 1720, 1680, 735, 700 cm^{-1}.

***S-t*-Butyl (3*S*)-3-Cyclohexyl-3-[(1*R*)-1-methyl-2-formylethoxy]propanethioate (14f):** ^{1}H NMR δ=1.16 (3H, d, J=6.0 Hz), 1.44 (9H, s), 0.89—1.75 (11H, m), 2.43 (1H, ddd, J=2.1, 5.4, and 16.2 Hz), 2.50—2.63 (3H, m), 3.66—3.71 (1H, m), 3.93—4.02 (1H, m), 9.78 (1H, dd, J=2.1 and 2.7 Hz) [a minor diastereomer resonated at δ=9.75 (1H, dd, J=1.8 and 2.7 Hz)]; ^{13}C NMR δ=20.4, 26.2, 26.3, 26.5, 27.9, 28.8, 29.7, 41.6, 47.0, 48.0, 50.7, 69.4, 78.2, 199.1, 201.7; IR (liquid film) 2770, 1720, 1680 cm^{-1}.

***S-t*-Butyl (3*S*,4*E*)-3-[(1*R*)-1-Methyl-2-formylethoxy]-5-phenyl-4-pentenethioate (14g):** ^{1}H NMR δ=1.21 (3H, d, J=6.0 Hz), 1.44 (9H, s), 2.43 (1H, ddd, J=1.8, 5.1, and 16.2 Hz), 2.58 (1H, ddd, J=2.7, 7.5, and 16.2 Hz), 2.59 (1H, dd, J=5.1 and 14.4 Hz), 2.78 (1H, dd, J=8.7 and 14.4 Hz), 4.03—4.13 (1H, m), 4.44—5.51 (1H, m), 6.01 (1H, dd, J=8.1 and 15.9 Hz), 6.57 (1H, d, J=15.9 Hz), 7.22—7.39 (5H, m), 9.73 (1H, dd, J=1.8 and 2.7 Hz) [a minor diastereomer resonated at 9.78 (1H, dd, J=2.1 and 2.4 Hz)]; ^{13}C NMR δ=19.3, 29.7, 48.2, 50.7, 50.8, 67.9, 74.9, 126.6, 128.0, 128.6 (2C), 132.9, 136.1, 197.1, 201.4; IR (liquid film) 2725, 1720, 1680, 750, 695 cm^{-1}.

(3*R*)-3-[(1*S*)-1-Phenyl-3-butenyloxy]butanal (16a): ^{1}H NMR δ=1.23 (3H, d, J=6.0 Hz), 2.31—2.40 (1H, m), 2.47—2.58 (1H, m), 3.80—3.90 (1H, m), 4.38 (1H, dd, J=5.7 and 7.8 Hz), 4.97—5.06 (2H, m), 5.67—5.81 (1H, m), 7.25—7.37 (5H, m), 9.57 (1H, dd, J=1.8 and 3.0 Hz); ^{13}C NMR δ=19.2, 42.7, 50.9, 67.7, 79.2, 116.8, 126.9, 127.8, 128.4, 134.8, 141.9, 201.7; IR (film) 2720, 1720, 760, 700 cm^{-1}.

(3*R*)-3-[(1*S*)-3-Methyl-1-phenyl-3-butenyloxy]butanal (16b): ^{1}H NMR δ=1.22 (3H, d, J=6.3 Hz), 1.71 (3H, br s), 2.22—2.40 (2H, m), 2.24—2.55 (2H, m), 3.83 (1H, m), 4.51 (1H, dd, J=5.7 and 8.1 Hz), 4.67 (1H, m), 4.74 (1H, m), 7.24—7.37 (5H, m), 9.57 (1H, dd, J=ca. 2 and 3 Hz) [a minor diastereomer resonated at δ=1.06 (3H, d, J=6.3 Hz) and 9.82 (1H, t, J=2 Hz)]; IR (film) 2720, 1725, 890, 755, 700 cm^{-1}.

(3*R*)-3-[(1*S*)-3-Methyl-1-[(*E*)-2-phenylethenyl]-3-butenyloxy]butanal (16c): ^{1}H NMR δ=1.22 (3H, d, J=6.3 Hz), 1.75 (3H, br s), 2.24 (1H, dd, J=6.0 and 13.8 Hz), 2.37 (1H, dd, J=7.2 and 13.8 Hz), 2.45 (1H, ddd, J=1.8, 4.8, and 16.2 Hz), 2.58 (1H, ddd, J=ca. 3, 7.5, and 16.2 Hz), 4.06—4.17 (2H, m), 4.75 (1H, m), 4.79 (1H, m), 6.02 (1H, dd, J=8.3 and 15.9 Hz), 6.51 (1H, d, J=15.9 Hz), 7.22—7.41 (5H, m), 9.74 (dd, J=ca. 2 and 3 Hz); IR (film) 2725, 1725, 890, 750, 695 cm^{-1}.

(3*R*)-3-[(1*S*)-3-Methyl-1-(4-methoxyphenyl)-3-butenyloxy]butanal (16d): ^{1}H NMR δ=1.20 (3H, d, J=6.0 Hz), 1.69 (1H, br s), 2.23—2.37 (2H, m), 2.42—2.54 (2H, m), 3.81 (3H, s), 3.82 (1H, m), 4.46 (1H, dd, J=5.9 and 8.0 Hz), 4.65 (1H, m), 4.73 (1H, m), 6.76 (2H, m), 7.19 (2H, m), 9.55 (1H, dd, J=ca. 2 and 3 Hz) [a minor isomer resonated at δ=1.05 (3H, d, J=6.0 Hz) and 9.81 (1H, t, J=ca. 2.5 Hz)].

(3*R*)-3-[(1*S*)-3-Methyl-1-(2-furyl)-3-butenyloxy]butanal (16e): ^{1}H NMR δ=1.22 (3H, d, J=6.3 Hz), 1.69 (3H, br s), 2.34 (1H, ddd, J=2.0, 6.0, and 13.8 Hz), 2.42—2.62 (3H, m), 3.92 (1H, m), 4.55 (1H, t, J=7.2 Hz), 4.70 (1H, m), 4.75 (1H, m), 6.25 (1H, dd, J=0.5 and 3.3 Hz), 6.32 (1H, dd, J=ca. 2.0 and 3.3 Hz), 7.38 (1H, dd, J=0.5 and 2.0 Hz), 9.55 (1H, dd, J=2.0 and 3.2 Hz) [a minor isomer resonated at δ=1.05 (3H, t, J=6.3 Hz) and 9.82 (3H, t, J=2.2 Hz)].

***S*-*t*-Butyl (*S*)-3-Hydroxy-3-phenylpropanethioate (15a) (Representative Procedure for the Liberation of Enantiomerically Enriched Secondary Alcohols).** To a solution of aldehyde **14a** (71 mg, 0.23 mmol) in benzene (3 mL) at rt was added dibenzylammonium trifluoroacetate (78 mg, 0.25 mmol). After being stirred for 3 h, the mixture was poured into water and extracted twice with ethyl acetate. Organic extracts were dried and concentrated in vacuo. Purification of the residue by flash chromatography (5% ethyl acetate/hexane) gave 44 mg (80% yield) of **15a**: $[\alpha]_{\mathrm{D}}^{25}$ −43.4 (c 2.15, benzene) (lit,[20] $[\alpha]_{\mathrm{D}}^{25}$ −41.4). (*S*)-MTPA ester of **15a**: ^{1}H NMR δ=1.39 (9H, s), 2.86 (1H, dd, J=4.2 and 16.2 Hz), 3.21 (1H, dd, J=9.6 and 16.2 Hz), 3.41—3.43 (3H, m), 6.45 (1H, dd, J=4.2 and 9.6 Hz), 7.27—7.42 (10H, m) [a minor diastereomer resonated at δ=1.44 (9H, s)].

The following compounds were obtained by a procedure similar to that described above starting from **14b**—**g** and **16a**—**e**:

***S*-Ethyl (*S*)-3-Hydroxy-3-phenylpropanethioate (15b):** $[\alpha]_{\mathrm{D}}^{25}$ −60.7 (c 2.00, benzene) (lit,[20] $[\alpha]_{\mathrm{D}}^{25}$ −56.3).

Ethyl (*R*)-2,2-Dimethyl-3-hydroxy-3-phenylpropanoate (15c): ^{1}H NMR δ=1.10 (3H, s), 1.13 (3H, s), 1.26 (3H, t, J=7.2 Hz), 3.19 (1H, br s), 4.17 (2H, q, J=7.2 Hz), 4.88 (1H, s), 7.29—7.32 (5H, m); ^{13}C NMR δ=14.1, 19.1, 23.0, 47.5, 60.9, 78.7, 127.7 (3C), 140.0, 177.7; IR (liquid film) 3450 (br), 2980, 1720, 770, 745, 705 cm^{-1}. Treatment of **15c** with aq NaOH in THF afforded (*R*)-2,2-dimethyl-3-hydroxy-3-phenylpropanoic acid: $[\alpha]_{\mathrm{D}}^{25}$ −4.7 (c 0.96, MeOH) (lit,[24] $[\alpha]_{\mathrm{D}}^{25}$ +4.5 for the *S* enantiomer).

(*S*)-3-Hydroxy-1,3-diphenyl-1-propanone (15d): $[\alpha]_{\mathrm{D}}^{25}$ −27.9 (c 0.980, MeOH) (lit,[21] $[\alpha]_{\mathrm{D}}^{25}$ −31.97 for the *R* enantiomer).

***S*-*t*-Butyl (*R*)-3-Hydroxy-5-phenylpentanethioate (15e):** $[\alpha]_{\mathrm{D}}^{25}$ −9.24 (c 2.51, benzene) (lit,[20] $[\alpha]_{\mathrm{D}}^{25}$ −7.5).

***S*-*t*-Butyl (*S*)-3-Cyclohexyl-3-hydroxypropanethioate (15f):** ^{1}H NMR δ=0.96—1.40 (6H, m), 1.46 (9H, s), 1.63—1.84 (5H, m), 2.55 (1H, dd, J=9.0 and 15.6 Hz), 2.65 (1H, dd, J=3.0 and 15.6 Hz), 2.72 (1H, d, J=3.9 Hz), 3.75—3.82 (1H, m); ^{13}C NMR δ=26.0, 26.1, 26.4, 28.1, 28.8, 29.7, 43.1, 48.2, 48.4, 72.8, 201.1; IR (liquid film) 3450 (br), 2920, 1680 cm^{-1}. Treatment of **15f** with aq NaOH in THF afforded (*S*)-3-cyclohexyl-3-hydroxypropanoic acid: $[\alpha]_{\mathrm{D}}^{25}$ −23.5 (c 1.50, CHCl$_3$) (lit,[25] $[\alpha]_{\mathrm{D}}^{25}$ −31.8 for the *R* enantiomer).

***S*-*t*-Butyl (*S*)-3-Hydroxy-5-phenyl-4-pentenoate (15g):** ^{1}H NMR δ=1.47 (9H, s), 2.71—2.82 (2H, m), 2.97 (1H, br s), 4.71—4.77 (1H, m), 6.18 (1H, dd, J=6.3 and 15.6 Hz), 6.64 (1H, dd, J=0.9 and 15.6 Hz), 7.21—7.38 (5H, m); ^{13}C NMR δ=29.7, 48.7, 50.9, 69.5, 126.5, 127.7, 128.5, 129.9, 130.7, 136.5, 199.6; IR (liquid film) 3450, 2960, 1680, 755, 700 cm^{-1}. Treatment of **15c** with aq NaOH in THF afforded (*S*)-3-hydroxy-5-phenyl-4-pentenoic acid: $[\alpha]_{\mathrm{D}}^{25}$ +18 (c 0.57, MeOH) (lit,[26] $[\alpha]_{\mathrm{D}}^{25}$ −16.2).

(*S*)-1-Phenyl-3-buten-1-ol (17a): $[\alpha]_{\mathrm{D}}^{25}$ −41 (c 0.26, benzene) (lit,[22] $[\alpha]_{\mathrm{D}}^{25}$ −44.92).

(*S*)-3-Methyl-1-phenyl-3-buten-1-ol (17b): $[\alpha]_{\mathrm{D}}^{21}$ −38.1 (c 1.97, benzene) (lit,[23] $[\alpha]_{\mathrm{D}}^{25}$ −46.6).

(*S*)-5-Methyl-1-phenyl-1,5-hexadien-3-ol (17c):[32] $[\alpha]_{\mathrm{D}}^{22}$ −1.48 (c 2.43, Et$_2$O) (lit,[23] $[\alpha]_{\mathrm{D}}^{25}$ −1.69). The ee of **17c** was determined to be 92% by ^{1}H NMR analysis of the (*S*)-MTPA ester. (*S*)-MTPA ester of **17c**: ^{1}H NMR δ=1.73 (3H, br s), 2.39 (1H, dd, J=5.6 and 14.1 Hz), 2.54 (1H, ddd, J=0.6, 8.1, and 14.1 Hz), 3.54 (3H, q, J=1.2 Hz), 4.71 (1H, m), 4.77 (1H, m), 5.85 (1H, m), 6.20 (1H, dd, J=7.8 and 15.9 Hz), 6.73 (1H, d, J=15.9 Hz), 7.25—7.43 (8H, m), 7.54 (2H, m) [a minor diastereomer resonated at δ=1.80 (3H, br s), 3.57 (3H, q, J=1.2 Hz), 4.83 (1H, m), 4.88 (1H, m), 6.06 (1H, dd, J=7.8 and 16.0 Hz), 6.62 (1H, d, J=16.0 Hz)].

(*S*)-1-(4-Methoxyphenyl)-3-methyl-3-buten-1-ol (17d):[32] $[\alpha]_{\mathrm{D}}^{25}$ +41.0 (c 2.01, benzene). The ee of **17d** was determined to be 81% by ^{1}H NMR analysis of the (*S*)-MTPA ester. (*S*)-MTPA ester of **17d**: ^{1}H NMR δ=1.78 (3H, br s), 2.45 (1H, dd, J=5.4 and 14.3 Hz), 2.70 (1H, dd, J=8.9 and 14.3 Hz), 3.41 (3H, br s), 3.81 (3H, s), 4.64 (1H, m), 4.71 (1H, m), 6.12 (1H, dd, J=5.5 and 8.6 Hz), 6.88 (2H, m), 7.2—7.45 (7H, m) [a minor diastereomer resonated at δ=1.76 (3H, br s), 3.51 (3H, br s), 4.79 (1H, m), 4.85 (1H, m)].

(*S*)-1-(2-Furyl)-3-methyl-3-buten-1-ol (17e):[32] The ee of **17e** was determined to be 77% by ^{1}H NMR analysis of the (*S*)-MTPA ester. (*S*)-MTPA ester of **17e**: ^{1}H NMR δ=1.69 (3H, br s), 2.64 (1H, dd, J=5.8 and 14.3 Hz), 2.75 (1H, dd, J=8.6 and 14.3 Hz), 3.44 (3H, q, J=1.2 Hz), 4.67 (1H, m), 4.74 (1H, m), 6.25 (1H, dd, J=5.9 and 8.6 Hz), 6.35 (1H, dd, J=2.0 and 3.1 Hz), 6.43 (1H, br d, J=3.1 Hz), 7.28—7.45 (6H, m) [a minor diastereomer resonated at δ=1.76 (3H, br s), 3.51 (3H, q, J=1.2 Hz), 4.81 (1H, m), 4.86 (1H, m)].

Reaction of Racemic Acetal *rac*-6a and Enol Silyl Ether 7a Catalyzed by Phenyl Boron Complex 5c. The reaction of ***rac*-6a** and **7a** was carried out at r.t. for 3 h using a 0.2 mol. amt. of **5c** according to a procedure similar to that described in the representative procedure for a catalytic ring-cleavage reaction. The purification of crude products by flash chromatography (5—10% ethyl acetate/hexane) gave **9a** (*anti*:*syn*=92:8, 69% yield) and (2*R*,4*S*)-**6a** (27% yield), whose ee was determined to be 51% by a capillary GC analysis.

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