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A Raney Nickel - Sodium Hypophosphite Combination System for Reductive Desulfurization without Racemization of Optically Active Secondary Alcohol[1]

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Abstract: Sulfides and sulfoxides bearing an optically active secondary alcohol were desulfurized with a Raney nickel (W-2)-sodium hypophosphite combination system to give optically active alcohols in high yields *without racemization*. However, the combination system was not effective with sulfides which comprise an alkylthio group and the corresponding sulfoxides. This system exhibited the reductive desulfurization of benzylthio or phenylthio ether in the presence of a benzyl ether.

INTRODUCTION

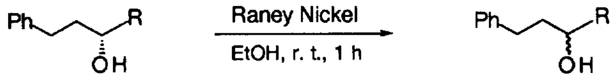
For the reduction of the carbon-sulfur bonds of sulfides, sulfoxides, and sulfones to the carbon-hydrogen bonds, Raney nickel is the most common reagent among others, namely, nickel(0) catalyst, nickel boride, dissolving metal, amalgam, and tin hydride.[2,3] Cyclic secondary alcohols are, however, known to suffer from epimerization with Raney nickel.[4] Epimerization of the secondary alcohols can be thought to involve reversible oxidation-reduction of the hydroxy group by Raney nickel, because Raney nickel was known to oxidize ethanol as the solvent to acetaldehyde, and to reduce the resultant acetaldehyde to ethanol, reversibly.[5] Although the reductive desulfurization with Raney nickel has been employed in the asymmetric synthesis using the sulfur atom,[6] partial racemization of optically active acyclic secondary alcohol was also suggested during reductive desulfinylation with Raney nickel (W-2)[7]. Therefore, prevention of the redox reaction by Raney nickel is imperative to retain the optical purity of the alcohol. This redox reaction can be prevented by means of protection of the chiral alcohol. For example, a benzoate[8a] of alcohol, and an acetonide[8b] of diol have been effectively used in reductive desulfinylation. Alternatively, Ohno *et al.* have presented a protocol of reductive desulfonylation with Raney nickel (W-4) saturated by hydrogen gas to prevent the redox reaction.[9]

In order to avoid racemization of an optically active alcohol with Raney nickel, a hydrogen source in the Raney nickel suspension should be added. Sodium hypophosphite in an acetate buffer as a hydrogen source would be promising, because this reagent system has been used for the conversion of nitriles to aldehydes[10] and the reductive Nef reaction of nitroolefins.[11] We report here a Raney nickel (W-2)-sodium hypophosphite combination system which is efficient for reductive desulfurization of sulfides and sulfoxides without racemization of secondary alcohol, as well as the reductive desulfurization of benzylthio or phenylthio ether in the presence of a benzyl ether.

RESULTS AND DISCUSSION

First of all, we tried to reconfirm the racemization of optically active acyclic secondary alcohols with Raney nickel. The results were compiled in Table 1. Thus, optically active (*S*)-4-phenyl-2-butanol (89 %ee, run 1) and (*R*)-1,3-diphenyl-1-propanol (76 %ee, run 3) were partially racemized to 72 %ee and 5 %ee, respectively, by treatment of Raney nickel (W-2)[12a] in ethanol for 1 h at room temperature. When (*S*)-4-phenyl-2-butanol (97 %ee) was treated with Raney nickel (W-4)[12b], which is more active than Raney nickel (W-2), the optical purity was decreased to 45 %ee (run 2). Furthermore, the reaction of (*R*)-1,3-diphenyl-1-propanol (96 %ee) with Raney nickel (W-4) (run 4) gave 1,3-diphenylpropane, which resulted from hydrogenolysis of the benzylic carbon-oxygen bond. These results for the racemization of chiral alcohols showed clearly that a benzylic alcohol was more sensitive to Raney nickel than an aliphatic alcohol.

Table 1. Racemization of Optically Active Secondary Alcohols with Raney Nickel (W-2 and W-4)



Run	Substrate			Raney Nickel	Product		
	R	o. p.[a]	Config.[b]		o. p.[a]	Config.[b]	yield[c]
1	Me	89 %ee	*S*	W-2	72 %ee	*S*	63 %
2	Me	97 %ee	*S*	W-4	45 %ee	*S*	42 %
3	Ph	76 %ee	*R*	W-2	5 %ee	*R*	34 %
4	Ph	96 %ee	*R*	W-4	—	—	26 %[d]

a) Determined by chiral HPLC analyses (DAICEL CHIRALCEL OD, Hex : *i*-PrOH = 95 : 5)
b) Configuration of major enantiomer c) Isolated yield d) 1,3-Diphenylpropane was obtained by hydrogenolysis.

Since racemization of an optically active alcohol with Raney nickel was confirmed, we investigated reductive desulfurization of several kinds of sulfur compounds (sulfides, sulfoxides, and sulfones) bearing an optically active alcohol with the Raney nickel (W-2)-sodium hypophosphite combination system as shown in Scheme 1.

Scheme 1

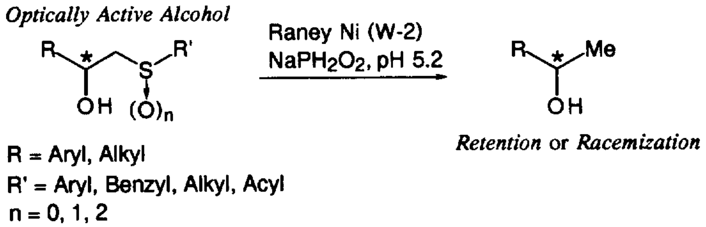
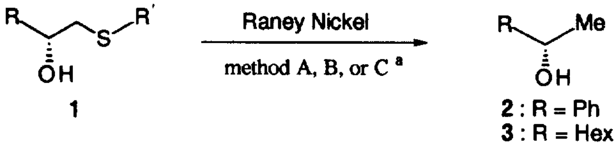


Table 2. Reductive Desulfurization of Sulfides Bearing an Optically Active Alcohol



1

2 : R = Ph
3 : R = Hex

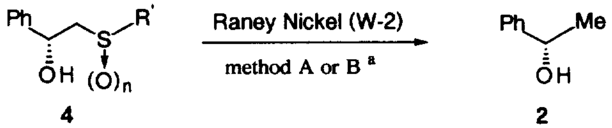
Entry	Substrate (mmol)	R	R'	o.p. (%)[b]	Method [a]	Product		
							Yield (%) [c]	o.p. (%)[b]
1	**1a** (0.30)	Ph	Bn	99 [d]	A	**2**	84	99 [e]
2	**1a** (0.12)	Ph	Bn	99 [d]	B	**2**	54	68 [e]
3	**1a** (0.36)	Ph	Bn	99 [d]	C	**2**	43 [h]	5 [e]
4	**1b** (0.24)	Ph	Ph	99 [d]	A	**2**	89	99 [e]
5	**1c** (0.22)	Ph	*p*-Tol	99 [d]	A	**2**	82	99 [e]
6	**1d** (0.18)	Hex	Bn	91 [f]	A	**3**	85	91 [g]
7	**1d** (0.28)	Hex	Bn	91 [f]	B	**3**	75	89 [g]
8	**1d** (0.35)	Hex	Bn	91 [f]	C	**3**	60 [h]	87 [g]
9	**1e** (0.27)	Hex	Ph	91 [f]	A	**3**	84	91 [g]
10	**1f** (0.29)	Hex	*p*-Tol	91 [f]	A	**3**	82	91 [g]
11	**1g** (0.25)	Ph	Ac	99 [e]	A	**2**	90 [h]	99 [e]
12	**1h** (0.26)	Ph	Et	99 [d]	A	**2**	28 [h]	54 [e]
13	**1h** (0.26)	Ph	Et	99 [d]	B	**2**	26 [h]	8 [e]

a) Method A: Raney Ni (W-2) - Sodium hypophosphite - Acetate buffer (pH 5.2) - EtOH, r. t., 0.5 h. method B: Raney Ni (W-2) - EtOH, r. t., 0.5 h. method C: Raney Ni (W-4) - EtOH, r. t., 0.5 h. b) Optical purity c) GC yield [Hewlett PACKARD HP-5890A, OV-1701 (25 m x 0.20 mm id), col. 120 °C, 1.0 ml He, split ratio 1 / 50] unless otherwise noted d) DAICEL CHIRALPAK AS (hexane / *i*-PrOH = 99 / 1) e) DAICEL CHIRALCEL OB (hexane / *i*-PrOH = 90 / 10) f) DAICEL CHIRALCEL OF (hexane / *i*-PrOH = 99 / 1) g) DAICEL CHIRALCEL OF (hexane) after benzoylation h) Isolated yield i) No reaction

The results on the reductive desulfurization of various sulfides with the Raney nickel (W-2)-sodium hypophosphite combination system (method A) are compiled in Table 2, compared with those of the usual Raney nickel (W-2 and W-4) (method B and C, respectively). Optically active arylthio and benzylthio alcohols **1a-f** (entries 1, 4-6, 9, and 10) were easily desulfurized with the Raney nickel (W-2)-sodium hypophosphite combination system to give secondary alcohols **2** or **3** in high yields *without any racemization*. For thiolester **1g**, this combination system was also effective (entry 11). The reactions with the Raney nickel combination system were superior to those with the usual Raney nickel (W-2 or W-4) in yields and optical purities (entries 1, 2, 3 and 6, 7, 8). Especially, in the case of benzylthio alcohols **1a**, the obtained alcohol **2** was almost racemized with the treatment of Raney nickel (W-4) (entry 3). Optically active ethylthio alcohol **1h** was, however, desulfurized with partial racemization to give **2** in low yield and a trace amount of acetophenone as a by-product (entry 12). Reductive desulfurization of **1h** with method B gave an almost racemized alcohol **2** (entry 13).

Results on the reductive desulfurization of sulfoxides or sulfones containing an optically active alcohol were summarized in Table 3. The same trend on substituents (R') in the desulfurization with the combination system was observed in the sulfoxides **4a**, **4b**, and **4c**. Thus, arylsulfinyl alcohols **4a** and **4b** were desulfurized effectively to afford alcohol **2** with the complete retention of its configuration (entries 1 and 2), but ethylsulfinyl alcohol **4c** gave alcohol **2** with partial racemization in moderate yield (entry 3). Reductive desulfurization of **4c** with Raney nickel itself gave **4** with complete racemization in low yield (entry 4). The aryl- and alkylsulfonyl alcohols **4d** and **4e** remained intact (entries 5 and 6). No reaction of **4d** was occurred by pH change of acetate buffer from pH 5.2 to pH 4.5 or pH 3.8. A combination of Raney nickel (W-4) - sodium hypophosphite in acetate buffer (pH 5.2) was also inefficient for the reductive desulfurization of **4d**.

Table 3. Reductive Desulfurization of Sulfoxides and Sulfones Bearing an Optically Active Alcohol

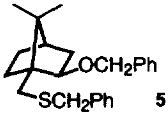
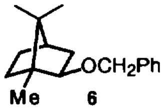
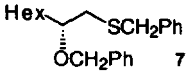
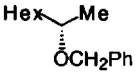
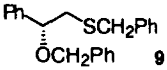
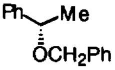
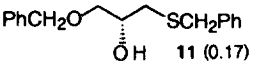
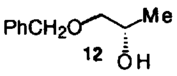
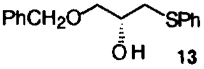


Entry	Substrate (mmol)	R'	n	o.p. (%)[b]	Method [a]	Product **2** Yield (%) [c]	Product **2** o.p. (%)[b]
1	**4a** (0.09)	Ph	1	99	A	92	99 [d]
2	**4b** (0.16)	*p*-Tol	1	99	A	93	99 [d]
3	**4c** (0.20)	Et	1	99	A	50	65 [d]
4	**4c** (0.23)	Et	1	99	B	14	0 [d]
5	**4d** (0.18)	Ph	2	99	A	n.r. [e]	—
6	**4e** (0.23)	Et	2	99	A	n.r. [e]	—

a) The same reaction conditions (Method A, B) as described in Table 2 b) Optical purity
c) Isolated yield d) DAICEL CHIRALCEL OB (hexane / *i*-PrOH = 90 / 10) e) No reaction

Raney nickel is commonly used for deprotection of the benzyl ether of alcohols, in which the usual hydrogenolysis on the palladium carbon is not suitable due to catalyst poisons of the sulfur-containing substrate itself.[13] Raney nickel (W-2) was also very useful for selective hydrogenolysis of benzyl ethers in the presence of other functional groups, such as 4-methoxybenzyl, methoxymethyl, and silyl ethers, isolated or conjugated olefins, and acetals.[14] Since this Raney nickel combination system is anticipated to be a milder reagent than Raney nickel itself, we attempted the desulfurization of benzylthio- and phenylthio ethers in the presence of benzyl ether using the Raney nickel combination system. The results are summarized in Table 4. All benzylthio ethers bearing benzyl ether were successfully desulfurized to give benzyl ethers. Even dibenzyl ether group in **9** remained intact (entry 3), which is susceptible to hydrogenolysis conditions. Racemization of chiral hydroxy group in **11** or **13** was not observed in those reductive desulfurization (entries 4, 5). The observed unique chemoselectivity shows also the mildness of this reagent system.

Table 4. Reductive Desulfurization of Thioethers Bearing a Benzyl Ether with the Raney Nickel Combination System[a]

Entry	Substrate (mmol)	Product	Yield [b] (%)
1	 5 (0.11)	 6	87
2	 7 (0.14)	 8	81
3	 9 (0.19)	 10	83
4	 11 (0.17)	 12	87
5	 13 (0.17)	12	89

a) The same reaction conditions (Method A) as described in Table 2
b) Isolated yield

In addition, it must be noted that the order of addition of the reagents (Raney nickel, and sodium hypophosphite) to the solution of the starting material is critical in performing the desulfurization in this combination system [see General Procedure (Method A) in Experimental Section]. Combinations of the starting material, Raney nickel, and sodium hypophosphite in other orders of addition were unsuccessful.

CONCLUSION

We found that the Raney nickel (W-2)-sodium hypophosphite combination system was an excellent reagent for the reductive desulfurization of sulfides (Ar-S-, Bn-S-, and Ac-S-) or sulfoxides bearing an optically active alcohol *without any loss of the optical purity*, and for a chemoselective reduction of benzylthio or phenylthio ethers bearing benzyl ether. These features of the Raney nickel - sodium hypophosphite combination system would be useful in organic syntheses using organosulfur reagents. In practice, we effectively utilized this system in the desulfurization of sulfur-containing intermediates in a new asymmetric reduction of α,β-unsaturated ketones using chiral mercapto alcohols.[15]

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technical assistance. We are indebted to Daiso Co., Ltd. and Nippon Mining Co., Ltd. for the kind gift of (*S*)-(+)-benzyl glycidyl ethers and (*R*)-1,2-epoxyoctane, respectively.

EXPERIMENTAL SECTION

General: Melting points are taken with a micro hot-stage apparatus (Yanagimoto) and are uncorrected. Infrared (IR) spectra were recorded with a JASCO IR-810 diffraction grating infrared spectrophotometer and ^{1}H-NMR spectra were obtained with a JEOL JNM-GX-270, or a Varian XL-300 NMR spectrometer with tetramethylsilane as an internal standard. Mass spectra (MS) are determined on a JEOL JMS-SX 102A QQ or a JEOL JMS-GC-mate mass spectrometer. Combustion analysis was done with a PERKIN ELMER Series II CHNS/O Analyzer 2400. The gas chromatography (GC) yields were calculated using α-methylnaphthalene (5.0 mg) as an internal standard in OV-1701 fused silica column (25 m x 0.20 mm id) (conditions: column temp. 120 °C, 1.0 ml He, split ration 1 / 50) on a Hewlett PACKARD HP-5890A apparatus. The HPLC analyses were performed with a Shimadzu LC-9A and LC-10A Liquid Chromatograph series using Daicel chiral columns (CHIRALCEL OB, CHIRALCEL OD CHIRALPAK AS, or CHIRALCEL OF). Their data were recorded with a Shimadzu C-R6A Chromatopac. Acetate buffer was adjusted with a Horiba pH meter F-13. Wakogel C-200 (silica gel) (100-200 mesh, Wako) was used for open column chromatography. Flash column chromatography was performed with Silica Gel 60H (nakalai tesque). Kieselgel 60 F-254 plates (Merck) was used for thin layer chromatography (TLC). Preparative TLC (PTLC) was done with Kieselgel 60 F-254 plates (0.25mm, Merck) or Silica gel 60 F-254 plates (0.5mm, Merck).

Materials: Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl, and dichloromethane was distilled from CaH$_2$, after washing ten times with water to remove methanol contaminated, before use. *n*-BuLi (hexane solution) and *s*-BuLi (cyclohexane solution) were purchased from Wako Pure Chemical Industries, and Aldrich Chemical Company, Inc., respectively. (*S*)-(+)-Benzyl glycidyl ether, (*R*)-1,2-epoxyoctane, and (*R*)-styrene oxide were available from Daiso Co., Ltd., Nippon Mining Co., Ltd., and nakalai tesque, respectively.

The Preparation of Optically Active Acyclic Secondary Alcohols in Table 1

(*S*)-4-Phenylbutan-2-ol (97 %ee, run 2) and (*R*)-1,3-diphenylpropanol (96 %ee, run 4) were prepared by the reductive desulfurization of (2*S*,4*R*)-4-[(1*S*,4*R*)-2-oxobornane-10-sulfenyl]-4-phenyl-2-butanol and (1*R*)-3-[(1*S*,4*R*)-2-oxobornane-10-sulfenyl]-1,3-diphenyl-1-propanol, which were the products of a novel tandem Michael addition - Meerwein-Ponndorf-Verley reduction,[15] with this Raney nickel (W-2) - sodium hypophosphite combination system described in this paper. The low optically active (*S*)-4-phenylbutan-2-ol (89 %ee, run 1) and (*R*)-1,3-diphenylpropanol (76 %ee, run 3) were prepared by the reductive desulfurization of the same products described above, with Raney nickel (W-2) in ethanol. The enantiomeric excesses (%ee) were determined by chiral HPLC analyses [DAICEL CHIRALCEL OD (25 x 0.46); eluent: hexane / isopropanol = 95 / 5; flow rate: 1 mL/min.; Temp.: 25 °C; detector: 254 nm, (*S*)-4-phenylbutan-2-ol: 18.0 min; (*R*)-4-phenylbutan-2-ol: 12.4 min, and (*R*)-1,3-diphenylpropanol: 25.0 min; (*S*)-1,3-diphenylpropanol: 21.0 min, respectively].

The Preparation of Optically Active Sulfides in Table 2

(*R*)-2-Acetylthio-1-phenylethanol (1g) To a dry THF solution (20 ml) of thioacetic acid (887 mg, 11.65 mmol) was added dropwise triethylamine (2.44 ml, 17.48 mmol) at 0 °C. After being stirred for 30 min, (*R*)-styrene oxide (0.66 ml, 11.65 mmol) was added dropwise, then the resultant mixture was stirred for 40 h. The reaction mixture was quenched with a saturated sodium bicarbonate solution, then the aqueous layer was extracted with chloroform (100 ml x 3). The organic layer was washed with brine, dried (MgSO$_4$), filtered and concentrated *in vacuo*. Silica gel chromatography (hexane : ethyl acetate = 15 : 1) of the residue gave (*R*)-**1g** (155 mg, 14 %). **1g**: colorless oil; $[\alpha]_D^{19}$ - 53.8 (0.94, CHCl$_3$); 99 %ee; chiral HPLC analysis [DAICEL

CHIRALCEL OB (25 x 0.46), eluent: hexane / isopropanol = 90 / 10, flow rate: 1 ml / min, temp.: 25 °C, detector: 254 nm, (*R*)-**1d**: 10.4 min, (*S*)-**1d**: 18.4 min]; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.42-7.30 (m, 5H), 4.84-4.78 (m, 1H), 3.33 (dd, A part of AB, *J* = 14.0 and 3.9 Hz, 1H), 3.12 (dd, B part of AB, *J* = 14.0 and 8.5 Hz, 1H), 2.61 (d, *J* = 3.6 Hz, 1H), 2.38 (s, 3H); IR ($CHCl_3$): 3600, 3540-3300, 3060, 2930, 1685, 1350, 1120, 1045, 625 cm^{-1}; FAB(+) MS *m/z*: 197 (M^++1, 7); HRMS calcd for $C_{10}H_{13}O_2S$ (M^++1) 197.0637, found: 197.0614.

A General Procedure for 1a-f, 1h in Table 2

To a dry THF solution (20 ml) of thiol (0.018 mol, 1.1 eq.) was added dropwise *n*-BuLi (1.6 M hexane solution, 0.018 mol, 1.1 eq.) at 0 °C. After being stirred for 30 min, a (*R*)-epoxide (0.017 mol) was added dropwise, then the resultant mixture was stirred for 1.5 h. The reaction mixture was quenched with a saturated ammonium chloride solution, then the aqueous layer was extracted with dichloromethane (100 ml x 3). The organic layer was washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. Silica gel chromatography (hexane : ethyl acetate = 15 : 1) of the residue gave a (*R*)-mercapto alcohol.

(*R*)-2-Benzylthio-1-phenylethanol (1a) Benzyl mercaptan (2.27 g, 0.018 mol) and (*R*)-styrene oxide (2 g, 0.017 mol) were used. **1a**: 78 % yield, colorless oil; $[\alpha]_D^{25}$ - 67.5 (1.25, $CHCl_3$); 99 %ee; chiral HPLC analysis [DAICEL CHIRALPAK AS (25 x 0.46), eluent: hexane / isopropanol = 99 / 1, flow rate: 1 ml / min, temp.: 25 °C, detector: 254 nm, (*S*)-**1a**: 22.0 min, (*R*)-**1a**: 24.4 min]; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.37-7.23 (m, 10H), 4.66 (br dt, *J* = 9 and 4.5 Hz, 1H), 3.71 (s, 2H), 2.84 (d, *J* = 2.7 Hz, 1H), 2.78 (dd, A part of AB, *J* = 14.0 and 3.0 Hz, 1H), 2.66 (dd, B part of AB, *J* = 14.0 and 9.1 Hz, 1H); IR ($CHCl_3$): 3600-3400, 2930, 2860, 1600, 1490, 1450, 1060, 1030, 550 cm^{-1}; FAB(+) MS *m/z*: 243 (M^+-1, 7); Anal. Calcd for $C_{15}H_{16}OS$: C, 73.74; H, 6.60. Found: C, 73.60; H, 6.73.

(*R*)-1-Phenyl-2-phenylthioethanol (1b) [16] Thiophenol (504 mg, 4.58 mmol) and (*R*)-styrene oxide (500 mg, 4.16 mmol) were used. **1b**: 86 % yield; colorless oil; $[\alpha]_D^{25}$ + 8.6 (1.07, $CHCl_3$); 99 %ee; chiral HPLC analysis [DAICEL CHIRALPAK AS (25 x 0.46), eluent: hexane / isopropanol = 99 / 1, flow rate: 1 ml / min, temp.: 25 °C, detector: 254 nm, (*S*)-**1b**: 25.3 min, (*R*)-**1b**: 28.2 min]; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.42-7.20 (m, 10H), 4.70 (ddd, *J* = 9.4, 3.5 and 2.5 Hz, 1H), 3.30 (dd, A part of AB, *J* = 13.8 and 3.6 Hz, 1H), 3.07 (dd, B part of AB, *J* = 13.8 and 9.4 Hz, 1H), 2.91 (d, *J* = 2.5 Hz, 1H); IR ($CHCl_3$): 3600, 3570-3200, 3060, 2995, 1600, 1580, 1470, 1435, 1050, 1020, 970, 905 cm^{-1}; FAB(+) MS *m/z*: 230 (M^+, 17); HRMS calcd for $C_{14}H_{14}OS$: 230.0766, found: 230.0780.

(*R*)-1-Phenyl-2-*p*-tolylthioethanol (1c) [17] *p*-Toluenethiol (568 mg, 4.57 mmol) and (*R*)-styrene oxide (502 mg, 4.16 mmol) were used. **1c**: 99 % yield; colorless oil; $[\alpha]_D^{25}$ + 17.3 (1.85, $CHCl_3$); 99 %ee; chiral HPLC analysis [DAICEL CHIRALPAK AS (25 x 0.46), eluent: hexane / isopropanol = 99 / 1, flow rate: 1 ml / min, temp.: 25 °C, detector: 254 nm, (*S*)-**1c**: 22.0 min, (*R*)-**1c**: 25.2 min]; MS (30 eV) *m/z*: 244 (M^+, 30), 138 (100), 107 (22), 91 (15), 79 (18); HRMS calcd for $C_{15}H_{16}OS$: 244.0921, found: 244.0919.

(*R*)-1-Benzylthio-2-octanol (1d) Benzyl mercaptan (2.13 g, 0.017 mol) and (*R*)-1,2-epoxyoctane (2.00 g, 0.016 mol) were used. **1e**: 86 % yield; colorless oil; $[\alpha]_D^{26}$ - 64.4 (0.93, $CHCl_3$); 91 %ee; chiral HPLC analysis [DAICEL CHIRALCEL OF (25 x 0.46), eluent: hexane / isopropanol = 99 / 1, flow rate: 1 ml / min, temp.: 25 °C, detector: 254 nm, (*R*)-**1d**: 18.0 min, (*S*)-**1d**: 20.1 min]; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.36-7.22 (m, 5H), 3.73 (s, 2H), 3.62-3.59 (m, 1H), 2.62 (dd, A part of AB, *J* = 13.8 and 3.3 Hz, 1H), 2.39 (d, *J* = 3.3 Hz, 1H), 2.38 (dd, B part of AB, *J* = 13.8 and 9.0 Hz, 1H), 1.50-1.17 (m, 10H), 0.88 (t, *J* = 6.6 Hz, 3H); IR ($CHCl_3$): 3610, 3550-3350, 3070, 3010, 2925, 1600, 1495, 1450, 1410, 1050, 1025, 985 cm^{-1}; FAB(+) MS *m/z*: 252 (M^+, 15.8); HRMS calcd for $C_{15}H_{24}OS$ (M^+) 252.1548, found: 252.1537.

(*R*)-1-Phenylthio-2-octanol (1e) [17] Thiophenol (473 mg, 4.29 mmol) and (*R*)-1,2-epoxyoctane (500 mg, 3.90 mmol) were used. **1e**: 78 % yield; colorless oil; $[\alpha]_D^{25}$ - 30.4 (1.04, $CHCl_3$); 91 %ee; chiral HPLC analysis [DAICEL

CHIRALCEL OF (25 x 0.46), eluent: hexane / isopropanol = 99 / 1, flow rate: 0.5 ml / min, temp.: 25 °C, detector: 254 nm, (*R*)-**1e**: 32.5 min, (*S*)-**1e**: 36.3 min]; FAB(+) MS *m/z*: 238 (M^+, 100); HRMS calcd for $C_{14}H_{22}OS$ (M^+) 238.1391, found: 238.1397.

(*R*)-1-*p*-Tolylthio-2-octanol (1f) *p*-Toluenethiol (532 mg, 4.28 mmol) and (*R*)-1,2-epoxyoctane (500 mg, 3.89 mmol) were used. **1f**: 99 % yield; colorless oil; $[\alpha]_D^{24}$ - 31.0 (1.50, $CHCl_3$); 91 %ee; chiral HPLC analysis [DAICEL CHIRALCEL OF (25 x 0.46), eluent: hexane / isopropanol = 99 / 1, flow rate: 0.5 ml / min, Temp.: 25 °C, detector: 254 nm, (*R*)-**1f**: 33.4 min, (*S*)-**1f**: 36.1 min]; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.30 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 8.1 Hz, 2H), 3.68-3.57 (m, 1H), 3.10 (dd, A part of AB, J = 13.7 and 3.3 Hz, 1H), 2.78 (dd, B part of AB, J = 13.7 and 8.9 Hz, 1H), 2.46 (d, J = 3.3 Hz, 1H), 2.32 (s, 3H), 1.60-1.22 (m, 10H), 0.87 (t, J = 5.5 Hz, 3H); IR ($CHCl_3$): 3600, 3550-3400, 3000, 2922, 2855, 1600, 1490, 1010 cm^{-1}; MS (70 eV) *m/z*: 252 (M^+, 37), 138 (100), 123 (18), 91 (20), 41 (12); HRMS calcd for $C_{15}H_{24}OS$ (M^+) 252.1547, found: 252.1536.

(*R*)-2-Ethylthio-1-phenylethanol (1h)[18] Ethanethiol (700 mg, 5.83 mmol) and (*R*)-styrene oxide (398 mg, 6.41 mmol) were used. **1h**: 91 % yield; colorless oil; $[\alpha]_D^{20}$ - 75.8 (2.19, $CHCl_3$); 99 %ee; chiral HPLC analysis [DAICEL CHIRALPAK AS (25 x 0.46), eluent: hexane / isopropanol = 99 / 1, flow rate: 0.5 ml / min, temp.: 25 °C, detector: 254 nm, (*S*)-**1h**: 29.4 min, (*R*)-**1h**: 31.3 min]; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.40-7.26 (m, 5H), 4.74 (ddd, J = 9.3, 3.4, and 2.3 Hz, 1H) 3.01 (d, J = 2.3 Hz, 1H), 2.95 (dd, A part of AB, J = 13.8 and 3.4 Hz, 1H), 2.72 (dd, B part of AB, J = 13.8 and 9.3 Hz, 1H), 2.58 (q, J = 7.4 Hz, 2H), 1.28 (t, J = 7.4 Hz, 3H); IR ($CHCl_3$): 3610, 3550-3300, 3050, 2975, 2925, 1450, 1060, 980 cm^{-1}; FAB(+) MS *m/z*: 182 (M^+, 4); HRMS calcd for $C_{10}H_{14}OS$ (M^+) 182.0765, found: 182.0764.

A General Procedure for Sulfoxide (4a-c) in Table 3

To a methanol solution (30 ml) of a sulfide (ca. 0.2 mmol) was added sodium metaperiodate (3 eq.), then the resultant mixture was stirred at room temperature. The reaction mixture was quenched with 1*N* HCl and evaporated. To a resultant residue was added water (20 ml), then the aqueous layer was extracted with ethyl acetate (100 ml x 3). The organic layer was washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. Silica gel chromatography (hexane : ethyl acetate = 2 : 1) of the residue gave the corresponding sulfoxide.

(*R*)-1-Phenyl-2-phenylsulfinylethanol (4a)[19] (*R*)-1-Phenyl-2-phenylthioethanol (**1b**) (33.1 mg, 0.144 mmol, 99 %ee) and sodium metaperiodate (92 mg, 0.432 mmol) were used. The reaction time was 21 h. **4a**: two diastereomeric mixtures; 95 % yield; colorless needles; IR ($CHCl_3$): 3600, 3500-3300, 2995, 1440, 1080, 1040 cm^{-1}; FAB(+) MS *m/z*: 247 (M^++1, 46); HRMS calcd for $C_{14}H_{15}O_2S$ (M^++1) 247.0793, found: 247.0779.

(*R*)-1-Phenyl-2-*p*-tolylsulfinylethanol (4b)[8a, 20] (*R*)-1-Phenyl-2-*p*-tolylthioethanol (**1c**) (413 mg, 1.693 mmol, 99 %ee) and sodium metaperiodate (1.09 g, 5.08 mmol) were used. The reaction time was 18 h. **4b**: two diastereomeric mixtures, 89 % yield; colorless needles; ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 7.59-7.50 (m, 2H), 7.31-7.20 (m, 7H), 5.41 (br d, J = 9.9 Hz, 0.3H), 5.24 (br d, J = 10.2 Hz, 0.7H), 4.29 (d, J = 1.3 Hz, 0.3H), 4.09 (d, J = 2.6 Hz, 0.7H), 3.36-3.15 (m, 1H), 2.93-2.75 (m, 1H), 2.44 (s, 2.1H), 2.41 (s, 0.9H); IR ($CHCl_3$): 3600, 3550-3200, 2995, 1590, 1485, 1445, 1080, 1045, 1010 cm^{-1}; FAB(+) MS *m/z*: 261 (M^++1, 72); HRMS calcd for $C_{15}H_{17}O_2S$ (M^++1) 261.0950, found: 261.0935.

(*R*)-2-Ethylsulfinyl-1-phenylethanol (4c) (*R*)-2-Ethylthio-1-phenylethanol (**1h**) (408 mg, 2.24 mmol, 99 %ee) and sodium metaperiodate (1.44 g, 6.73 mmol) were used. The reaction time was 15 h. **4c**: single diastereomer after recrystallization from ether; 48 % yield; colorless needles; mp 124-127 °C (ether); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.45-7.27 (m, 5H), 5.44 - 5.34 (m, 1H), 3.81 (d, J = 3.7 Hz, 1H), 3.09-3.00 (m, 1H), 2.92-2.75 (m, 3H), 1.37 (t, J = 7.5 Hz, 3H); IR ($CHCl_3$): 3600, 3500-3100, 2995, 1450, 1055, 1045, 1010 cm^{-1}; FAB(+) MS *m/z*: 199 (M^++1, 82); HRMS calcd for $C_{10}H_{15}O_2S$ (M^++1) 199.0792, found: 199.0779. Anal. Calcd for $C_{10}H_{14}O_2S$: C, 60.57; H, 7.12. Found: C, 60.40; H, 7.13.

A General Procedure for Sulfones (4d,e) in Table 3

To a methanol - water (5 : 1) solution (70 ml) of a sulfide (ca. 0.2 mmol) was added oxone (5 eq.), then the resultant mixture was stirred at room temperature. After concentration of the reaction mixture, water (20 ml) was added to the residue, then the aqueous layer was extracted with ethyl acetate (100 ml x 3). The organic layer was washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. Recrystallization from hexane gave the corresponding sulfone.

(*R*)-1-Phenyl-2-phenylsulfonylethanol (4d) [21] (*R*)-1-Phenyl-2-phenylthioethanol (**1b**) (493 mg, 2.14 mmol, 99 %ee), oxone (6.59 g, 10,71 mmol) were used. The reaction time was 20 h. Twice recrystallization gave **4d** (452 mg, 81 %). **4d**: colorless needles; mp. 111-113 °C (hexane); $[\alpha]_D^{17}$ - 30.3 (1.00, $CHCl_3$); ^1H-NMR (300 MHz, $CDCl_3$) δ: 7.99-7.95 (m, 2H), 7.75-7.67 (m, 1H), 7.65-7.55 (m, 2H), 7.35-7.23 (m, 5H), 5.29 (dt, *J* = 10.0 and 2.0 Hz, 1H), 3.67 (d, *J* = 2.0 Hz, 1H), 3.51 (dd, A part of AB, *J* = 14.4 and 10.0 Hz, 1H), 3.35 (dd, B part of AB, *J* = 14.4 and 2.0 Hz, 1H); IR ($CHCl_3$): 3600-3450, 1450, 1305, 1150, 1135, 1085, 990 cm^{-1}; FAB(+) MS *m/z*: 263 (M^++1, 19); HRMS calcd for $C_{14}H_{15}O_3S$ (M^++1) 263.0742, found: 263.0755.; Anal. Calcd for $C_{14}H_{14}O_3S$: C, 64.10; H, 5.38. Found: C, 63.95; H, 5.41.

(*R*)-2-Ethylsulfonyl-1-phenylethanol (4e) (*R*)-2-Ethylthio-1-phenylethanol (**1h**) (407 mg, 2.24 mmol, 99 %ee) and oxone (6.87 g, 11.17 mmol) were used. The reaction time was 17 h. Twice recrystallization gave **4e** (417 mg, 88 %). **4e**: colorless needles; mp. 96-97 °C (hexane); $[\alpha]_D^{19}$ - 56.2 (1.04, $CHCl_3$); ^1H-NMR (300 MHz, $CDCl_3$) δ: 7.41-7.33 (m, 5H), 5.38 (dt, *J* = 10.4 and 2.4 Hz, 1H), 3.42 (dd, A part of AB, *J* = 14.6 and 10.4 Hz, 1H), 3.16 (dd, B part of AB, *J* = 14.6 and 2.4 Hz, 1H), 3.25-3.10 (m, 2H), 3.04 (d, *J* = 2.4 Hz, 0.5H), 3.03 (d, *J* = 0.9 Hz, 0.5H), 1.44 (t, *J* = 7.5 Hz, 3H); IR ($CHCl_3$): 3600, 3550-3450, 3050, 2970, 1450, 1300, 1120, 1040 cm^{-1}; FAB(+) MS *m/z*: 215 (M^++1, 4); HRMS calcd for $C_{10}H_{15}O_3S$ (M^++1) 215.0742, found: 215.0756.

Reductive Desulfurization (Table 2, 3 and 4)

Method A: To a solution of a starting material (indicated amount in Table 2) in an acetate buffer (pH 5.2) and ethanol (1 : 2, 9 ml) was added freshly prepared Raney nickel (W-2) (suspension in ethanol, 5 ml), followed by the addition of water (2 ml) solution of sodium hypophosphite monohydrate (10 eq.) immediately, and the resultant solution was stirred for 0.5 h at room temperature. The reaction mixture was filtered with celite (washing with dichloromethane for a GC analysis, or washing with hot methanol in the other cases). To this solution was added water (20 ml), then the aqueous layer was extracted with dichloromethane (30 ml x 3), washed with brine, dried ($MgSO_4$). The GC yield of (*S*)-phenethyl alcohol (**2**) or (*S*)-2-octanol (**3**) was calculated using α-methylnaphthalene (5.0 mg) as an internal standard (entries 1, 4-7, 10, and 11). After concentration *in vacuo*, the preparative TLC of the residue gave a product, whose ee was determined by a chiral HPLC analysis.

Method B: To a solution of a starting material (indicated amount in Table 2) in ethanol (10 ml) was added Raney nickel (W-2) (suspension in ethanol, 5 ml), and the resultant mixture was stirred for 0.5 h at room temperature. The reaction mixture was filtered with celite (washing with dichloromethane for a GC analysis, or washing with hot methanol in the other cases). The GC yield of **2** or **5** was calculated using α-methylnaphthalene (5.0 mg) as an internal standard (entries 2 and 7). After the usual work-up, the preparative TLC of the residue gave a product, whose ee was determined by a chiral HPLC analysis.

Method C: To a solution of a starting material (indicated amount in Table 2) in ethanol (10 ml) was added Raney nickel (W-4) (suspension in ethanol, 5 ml), and the resultant mixture was stirred for 0.5 h at room temperature. The reaction mixture was filtered with celite. After the usual work-up, the preparative TLC of the residue gave a product, whose ee was determined by a chiral HPLC analysis.

(*S*)-Phenethyl alcohol (2) [22] (Table 2, entries 1-5, 11-13 and Table 3, entries 1-4) The enantiomeric excess was determined by a chiral HPLC analysis [DAICEL CHIRALCEL OB (25 x 0.46), eluent: hexane / isopropanol = 90 / 10, flow rate: 1 ml / min, temp.: 25 °C, detector: 254 nm, (*S*)-**2**: 6.0 min, (*R*)-**2**: 8.5 min].

(*S*)-2-Benzoyloxyoctane (Table 2, entries 6-10) After the determination of GC yield of (*S*)-2-octanol (**3**), the mixture was evaporated. To a pyridine (10 ml) solution of the residue was added benzoyl chloride (3 eq. to the theoretical amount of (*S*)-2-octanol) and the resultant solution was stirred for 12 h at room temperature. The reaction mixture was quenched with 10 % HCl solution, then extracted with dichloromethane (30 ml x 3), washed brine, dried ($MgSO_4$), concentrated *in vacuo*. Preparative TLC of the residue gave (*S*)-2-benzoyloxyoctane, whose ee (indicated in Table 2) was determined by a chiral HPLC analysis [DAICEL CHIRALCEL OF (25 x 0.46), eluent: hexane, flow rate: 1 ml / min, temp.: 25 °C, detector: 254 nm, (*R*)-2-benzoyloxyoctane: 14.5 min, (*S*)-2-benzoyloxyoctane: 15.8 min].

The Preparation of Substrates in Table 4

(-)-10-Benzylthioisoborneol *O*-Benzyl Ether (5) (-)-10-Mercaptoisoborneol (500 mg, 2.70 mmol) was added dropwise to a slurry of 50 % sodium hydride (324 mg, 8.10 mmol), which was washed 3 times with dry ether, in dry DMF (10 ml) at 0 °C. After being stirred for 30 min, benzyl bromide (412 μl, 8.10 mmol) was added dropwise and then the mixture was stirred for 1.5 h. The reaction mixture was quenched with 1*N* HCl solution, then the aqueous layer was extracted with diethyl ether (100 ml x 3). The organic layer was washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. Silica gel chromatography (hexane : ethyl acetate = 40 : 1) of the residue gave **5** (393 mg, 46 % yield). **5**: colorless oil; $[\alpha]_D^{27}$ - 46.8 (1.84, $CHCl_3$); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.33-7.15 (m, 10H), 4.54 (d, A part of AB, J = 11.8 Hz, 1H), 4.41 (d, B part of AB, J = 11.8 Hz, 1H), 3.72 (d, A part of AB, J = 13.2 Hz, 1H), 3.69 (d, B part of AB, J = 13.2 Hz, 1H), 3.61 (dd, J = 7.6 and 3.4 Hz, 1H), 2.90 (d, A part of AB, J = 11.7 Hz, 1H), 2.39 (d, B part of AB, J = 11.7 Hz, 1H), 1.89-1.78 (m, 1H), 1.75-1.48 (m, 4H), 1.33-1.25 (m, 1H), 1.07-0.98 (m, 1H), 1.03 (s, 3H), 0.81 (s, 3H); IR ($CHCl_3$): 3070, 2955, 2880, 1600, 1490, 1455, 1090 cm^{-1}; FAB(+) MS *m/z*: 366 (M$^+$, 5); HRMS calcd for $C_{24}H_{30}OS$ (M$^+$) 366.2017; found, 366.2007.

(*R*)-2-Benzyloxy-1-benzylthiooctane (7) (*R*)-1-Benzylthio-2-octanol (**1e**) (293 mg, 1.16 mmol, 91 %ee) was added dropwise to a slurry of 50 % sodium hydride (93 mg, 2.32 mmol), which was washed 3 times with dry ether, in dry DMF (10 ml) at 0 °C. After being stirred for 30 min, benzyl bromide (397 mg, 2.32 mmol) was added dropwise and then stirred for 16 h. The reaction mixture was quenched with 1*N* HCl solution, then the aqueous layer was extracted with diethyl ether (100 ml x 3). The organic layer was washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. Silica gel chromatography (hexane : ethyl acetate = 50 : 1) gave **7** (272 mg, 69 %). **7**: colorless oil; $[\alpha]_D^{16}$ + 23.2 (0.88, $CHCl_3$); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.42-7.22 (m, 10H), 4.53 (d, A part of AB, J = 11.7 Hz, 1H), 4.51 (s, 2H), 4.44 (d, B part of AB, J = 11.7 Hz, 1H), 3.47-3.41 (m, 1H), 2.64 (dd, A part of AB, J = 13.3 and 5.6 Hz, 1H), 2.55 (dd, B part of AB, J = 13.3 Hz and 6.2 Hz, 1H), 1.65-1.48 (m, 2H), 1.35-1.19 (m, 8H), 0.88 (t, J = 6.7 Hz, 3H); IR ($CHCl_3$): 3075, 3005, 2930, 2860, 1605, 1490, 1455, 1090, 1070, 605, 550 cm^{-1}; FAB(+) MS *m/z*: 343 (M$^+$+1, 4.3); HRMS calcd for $C_{22}H_{31}OS$ (M$^+$+1) 343.2096, found 343.2082.

(*R*)-1-Benzyloxy-2-benzylthio-1-phenylethane (9) (*R*)-2-Benzylthio-1-phenylethanol (**1a**) (296 mg, 1.22 mmol, 99 %ee) was added dropwise to a slurry of 50 % sodium hydride (88 mg, 2.43 mmol), which was washed 3 times with dry ether, in dry DMF (10 ml) at 0 °C. After being stirred for 30 min, benzyl bromide (415 mg, 2.43 mmol) was added dropwise and then the mixture was stirred for 2.5 h. The reaction mixture was quenched with 1*N* HCl solution, then aqueous layer was extracted with diethyl ether (100 ml x 3). The organic layer was washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. Silica gel chromatography (hexane : ethyl acetate = 50 : 1) of the residue gave **9** (296 mg, 73 %). **9**: colorless oil; $[\alpha]_D^{15}$ - 62.3 (0.89, $CHCl_3$); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.39-7.22 (m, 15H), 4.47 (d, A part of AB, J = 11.8 Hz, 1H), 4.40 (dd, J = 8.1 and 5.4 Hz, 1H), 4.27 (d, B part of AB, J = 11.8 Hz, 1H), 3.65 (d, A part of AB, J = 13.4 Hz, 1H), 3.59 (d, B part of AB, J = 13.4 Hz, 1H), 2.88 (dd, A part of AB, J = 13.7 and 8.1 Hz, 1H), 2.62 (dd, B part of AB, J = 13.7 and 5.4 Hz, 1H); IR ($CHCl_3$): 3070, 3010, 2930, 2875, 1495, 1455, 1090, 1075, 1030 cm^{-1}; MS (16 eV) *m/z*: 334 (M$^+$, 1.2), 228 (7), 197 (100), 137 (7), 91 (89); HRMS calcd for $C_{22}H_{22}OS$ (M$^+$) 334.1391, found 334.1409.

(*R*)-1-Benzyloxy-3-benzylthiopropan-2-ol (11) [23] According to the general procedure for 1a-f, 1h in Table 2, benzyl mercaptan (416 mg, 3.35 mmol) and (*S*)-(+)-benzyl glycidyl ether (500 mg, 3.05 mmol) (Daiso Co. Ltd., 98 %ee) were used to give **11** in quantitative yield. **11**: colorless oil; $[\alpha]_D^{17}$ - 14.8 (1.00, $CHCl_3$) (99 %ee) ; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.36-7.25 (m, 10H), 4.55 (s, 2H), 3.92-3.85 (m, 1H), 3.74 (s, 2H), 3.56 (dd, A part of AB, *J* = 9.6 and 4.1 Hz, 1H), 3.48 (dd, B part of AB, *J* = 9.6 and 6.2 Hz, 1H), 2.62 (dd, A part of AB, *J* = 13.8 and 5.4 Hz, 1H), 2.55 (dd, B part of AB, *J* = 13.8 and 7.3 Hz, 1H), 2.58 (d, *J* = 1.2 Hz, 1H); IR ($CHCl_3$): 3600-3450, 3060, 2920, 2860, 1600, 1480, 1450, 1100 cm^{-1}; FAB(+) MS *m/z*: 288 (M^+, 7.6); HRMS calcd for $C_{17}H_{20}O_2S$ (M^+) 288.1184, found: 288.1185.

(*R*)-1-Benzyloxy-3-phenylthiopropan-2-ol (13) [24] According to the general procedure for 1a-f, 1h in Table 2, thiophenol (369 mg, 3.35 mmol) and (*S*)-(+)-benzyl glycidyl ether (500 mg, 3.05 mmol) (Daiso Co. Ltd., 98 %ee) were used to give **13** in 92 % yield. **13**: colorless oil; $[\alpha]_D^{19}$ + 16.0 (0.97, $CHCl_3$) [(*S*)-**13** Lit.[24] $[\alpha]_D$ - 14.4 (4.176, $CHCl_3$)].

Reductive Desulfurization (Table 4)

The same procedure (Method A) described in Table 2 was preformed for reductive desulfurization.

(-)-Isoborneol *O*-Benzyl Ether (6) [25] **6**: colorless oil; $[\alpha]_D^{20}$ - 76.4 (0.83, $CHCl_3$); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.33-7.23 (m, 5H), 4.62 (d, A part of AB, *J* = 12.5 Hz, 1H), 4.31 (d, B part of AB, *J* = 12.5 Hz, 1H), 3.32 (dd, *J* = 7.6 and 3.6 Hz, 1H), 1.85-1.79 (m, 1H), 1.73-1.42 (m, 6H), 1.05 (s, 3H), 0.95 (s, 3H), 0.82 (s, 3H); IR ($CHCl_3$) 3070, 2955, 2875, 1455, 1110, 1090, 1075, 905 cm^{-1}; MS (70 eV) *m/z*: 244 (M^+, 9.7), 153 (19), 109 (100), 91 (75), 69 (22), 55 (15), 41 (19); HRMS calcd for $C_{17}H_{24}O$ (M^+) 244.1827, found 244.1824.

(*S*)-2-Benzyloxyoctane (8) **8**: colorless oil; $[\alpha]_D^{15}$ + 16.5 (0.47, $CHCl_3$); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.35-7.25 (m, 5H), 4.61 (d, A part of AB, *J* = 11.8 Hz, 1H), 4.41 (d, B part of AB, *J* = 11.8 Hz, 1H), 3.57-3.43 (m, 1H), 1.67-1.22 (m, 10H), 1.19 (d, *J* = 6.1 Hz, 3H), 0.88 (t, *J* = 6.7 Hz, 3H); IR ($CHCl_3$): 2995, 2925, 2855, 1600, 1490, 1460, 1450, 1375, 1335, 1135, 1080, 1060, 1050, 905 cm^{-1}; FAB(+) MS *m/z*: 221 (M^++1, 5.5); HRMS calcd for $C_{15}H_{25}O$ (M^++1) 221.1905, found 221.1915.

(*S*)-1-Benzyloxy-1-phenylethane (10) [26] **10**: colorless oil; $[\alpha]_D^{13}$ - 87.1 (1.19, $CHCl_3$).

(*S*)-1-Benzyloxy-propan-2-ol (12) [27] **12**: colorless oil; $[\alpha]_D^{23}$ + 15.8 (1.57, $CHCl_3$) (98 %ee) (obtained in entry 4 in Table 4), $[\alpha]_D^{23}$ + 15.4 (2.02, $CHCl_3$) (98 %ee) (obtained in entry 5 in Table 4), [Lit.[27] $[\alpha]_D^{24}$ + 13.2 (1.0, $CHCl_3$)]; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.39-7.27 (m, 5H), 4.56 (s, 2H), 4.03-3.96 (m, 1H), 3.47 (dd, A part of AB, *J* = 9.4 and 3.1 Hz, 1H), 3.28 (dd, B part of AB, *J* = 9.4 and 8.2 Hz, 1H), 2.5 (s, 1H), 1.15 (d, *J* = 6.4 Hz, 3H); IR ($CHCl_3$): 3700, 3600, 2900, 1600, 1450, 1090 cm^{-1}; MS (70 eV) *m/z*: 166 (M^+, 12), 107 (13), 91 (100), 65 (17), 45 (26); HRMS calcd for $C_{10}H_{14}O_2$ (M^+) 166.0994, found 166.098. The ee's were determined by chiral HPLC analyses [DAICEL CHIRALCEL OD (25 x 0.46), eluent: hexane / *i*-PrOH = 95 / 5, flow rate: 1 ml / min, temp.: 25 °C, detector: 254 nm, (*R*)-**12**: 12.5 min, (*S*)-**12**: 13.6 min].

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