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Metal(II) *d*-Tartrates Catalyzed Asymmetric Ring Opening of Oxiranes with Various Nucleophiles

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The asymmetric ring opening of *meso*-2,3-disubstituted oxiranes with thiols, aniline, and trimethylsilyl azide was studied by the use of metal(II) *d*-tartrates as heterogeneous chiral Lewis acid catalysts. The enantioselectivity varied widely with the combination of oxirane, nucleophile, and metal(II) *d*-tartrate, and Zn(II) *d*-tartrate gave the best enantioselectivity in the respective reactions of 1,2-epoxycyclohexane with 1-butanethiol, aniline, and trimethylsilyl azide to afford the corresponding adducts in 85, 58, and 42% ee, respectively. Furthermore, the kinetic resolution of racemic oxiranes with thiols catalyzed by Zn(II) *d*-tartrate was studied.

Catalytic asymmetric synthesis has attracted much attention because a large quantity of optically active compound can be effectively produced by using a small quantity of chiral source.

Although various types of catalytic asymmetric synthesis have been reported, only a little have been known about catalytic enantiotopos differentiating reaction, namely, the differentiation between two equivalent moieties in a symmetrical molecule by a chiral catalyst. To our knowledge, the asymmetric reduction of cyclic anhydride to lactone1) and the asymmetric oxidation of *cis*-1,2-bis(hydroxymethyl)-cycloalkane to lactone2) by a chiral ruthenium complex have been reported in this category, but their enantioselectivities were not satisfactory.

Only a few chiral Lewis acid catalysts have been known, for example, alkoxydichloroaluminium3) and dialkoxydichlorotitanium4) in the Diels–Alder reaction, and diphenoxyzinc5) in the cyclization of unsaturated aldehyde. Optically active alkoxyl or phenoxyl group is involved in these catalysts as a chiral source and they were used by in situ preparation because of their instabilities.

In the course of our studies on the preparation of optically active polyfunctionalized synthetic building blocks by asymmetric synthesis starting from symmetrical compounds,6) we recently communicated the asymmetric ring opening reaction of *meso*-2,3-disubstituted oxiranes with some nucleophiles catalyzed by Zn(II) *d*-tartrate or Cu(II) *d*-tartrate.7) This reaction is classified as a catalytic enantiotopos differentiating reaction. These metal(II) *d*-tartrates act as heterogeneous chiral Lewis acid catalysts which have the advantages of the stability to air, moisture, and heat, and the easy recovery from reaction mixture simply by filtration.

Results and Discussion

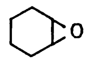
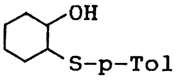
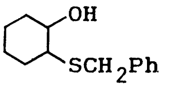
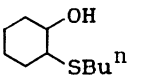
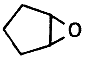
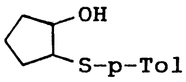
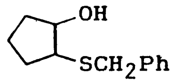
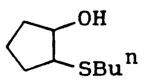
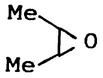
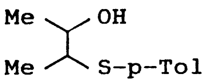
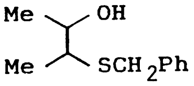
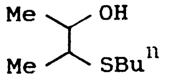
Various metal(II) *d*-tartrates such as BeT·H_2O,8) MgT·H_2O,9) CaT·H_2O,10) SrT·H_2O,10) BaT,10,11) MnT,12) FeT,12) CoT,12,13) NiT·H_2O,12,14) CuT,15) ZnT,12,16) CdT,12,17) HgT,12,18) SnT, and PbT12) (T=*d*-tartrate) were examined as chiral catalysts by the use of 10 mol% of metal(II) *d*-tartrate in dichloromethane at room temperature in the reactions of 1,2-epoxycyclohexane with thiols such as *p*-toluenethiol, phenylmethanethiol, and 1-butanethiol to give the corresponding optically active *trans*-2-substituted cyclohexanols. In these reactions, active metal ions were Zn^{2+} and Mn^{2+} which have almost same electronegativities,19) 8.0 and 7.5, respectivery. Other metal ions with lower or higher electronegativities exhibited no catalytic activities.

Next, instead of thiols, we tried various nucleophiles in the presence of 15 metal(II) *d*-tartrates described above, and found that aniline and trimethylsilyl azide gave optically active *trans*-2-anilinocyclohexanol and *trans*-1-azido-2-(trimethylsilyloxy)cyclohexane, respectively. In the reaction with aniline, MnT, FeT, ZnT, CoT, SnT, and CuT were active, and the electronegativities of these metal ions ranged from 7.5 to 9.5. When trimethysilyl azide was employed as a nucleophile, ZnT, CuT, MnT, SnT, CdT, FeT, and MgT·H_2O were active, and the electronegativities of these metal ions ranged widely from 6.0 to 9.5. Other nucleophiles such as benzylamine, ammonia, phenol, benzyl alcohol, methanol, benzoic acid, phenylacetic acid, and acetic acid resulted in no reactions by the use of metal(II) *d*-tartrates screened.

Reaction of *meso*-Oxiranes with Thiols. The results of the asymmetric ring opening of 1,2-epoxycyclohexane, 1,2-epoxycyclopentane, and *cis*-2,3-dimethyloxirane catalyzed by ZnT or MnT are summerized in Table 1. Comparing the chemical yields in the reactions for 5d, the reactivity of oxiranes decreased in the order of 1,2-epoxycyclohexane>*cis*-2,3-dimethyloxirane>1,2-epoxyclopentane with each thiol. No reaction took place in the cases of 1,2-epoxycyclooctane and *exo*-2,3-epoxynorbornane probably because of their steric hindrance around their oxirane rings. The same steric effects had been noticed in the reduction of oxiranes with lithium aluminium hydride20) or sodium borohydride.21)

The reactivity of thiols decreased in the order of *p*-toluenethiol > phenylmethanethiol > 1-butanethiol

Table 1. Reaction of *meso*-Oxiranes with Thiols[a]

Oxirane	Thiol	Catalyst	Product	Yield %	$[\alpha]_D^{23}$ /°[b]	ee %	Abs. Conf.[c]
	*p*-TolSH	ZnT	 **1**	96	−45.0	68	(1*R*, 2*R*)
		MnT		95	+21.8	33	(1*S*, 2*S*)
	PhCH$_2$SH	ZnT	 **2**	88	−34.4	77	(1*R*, 2*R*)
		MnT		56	−10.1	23	(1*R*, 2*R*)
	n-BuSH	ZnT	 **3**	82	−44.7	85	(1*R*, 2*R*)
		MnT		14	+10.5	20	(1*S*, 2*S*)
	*p*-TolSH	ZnT	 **4**	85	−8.0	45	(1*R*, 2*R*)
		MnT		72	0.0	0	
	PhCH$_2$SH	ZnT	 **5**	43	−7.8	50	(1*R*, 2*R*)
		MnT		Trace			
	n-BuSH	ZnT	 **6**	30	−15.1	72	(1*R*, 2*R*)
		MnT		Trace			
 cis	*p*-TolSH	ZnT	 **7**	98	−25.8	60	(2*R*, 3*R*)
		MnT		65	−17.3	40	(2*R*, 3*R*)
	PhCH$_2$SH	ZnT	 **8**	70	−18.5	75	(2*R*, 3*R*)
		MnT		Trace			
	n-BuSH	ZnT	 **9**	58	−29.0	71	(2*R*, 3*R*)
		MnT		Trace			

a) The mixture of oxirane (2 mmol), thiol (2 mmol), and catalyst (0.2 mmol) in CH$_2$Cl$_2$(5 cm^3) was stirred at room temperature for 5 d. b) (*c* 5.0, CH$_2$Cl$_2$). c) Absolute configuration.

with each oxirane. This order can be ascribed to the reverse order of the electron densities on their sulfur atoms.

When MnT was used as a catalyst, these orders were clearly observed. While 1,2-epoxycyclohexane reacted with *p*-toluenethiol to give the corresponding product in an excellent yield, the combination of less reactive oxiranes such as 1,2-epoxycyclopentane and *cis*-2,3-dimethyloxirane and less reactive thiols such as phenylmethanethiol and 1-butanethiol resulted in almost no reactions.

Compared with ZnT, MnT showed less catalytic activity and enantioselectivity, but exhibited the following interesting feature, that is, MnT varied the stereoselectivity according to the combination of oxiranes and thiols to give (1*S*,2*S*)-**1**,**3**, (1*R*,2*R*)-**2**, and (2*R*,3*R*)-**7**, while ZnT gave (1*R*,2*R*) or (2*R*,3*R*)-product in all cases.

In the reaction of 1,2-epoxycyclohexane with *p*-toluenethiol, the salts such as Zn(II) (2*R*,3*R*)-2,3-dimethoxysuccinate (ZnDMS),[22] Zn(II) (2*R*,3*R*)-2-hydroxy-3-methoxysuccinate (ZnHMS),[23] Zn(II) (*S*)-2-hydroxysuccinate (ZnHS), and Zn(II) (*S*)-2-methoxysuccinate (ZnMS)[24] were catalytically active but scarcely selective.

Table 2. Reaction of 1,2-Epoxycyclohexane with Aniline[a]

Catalyst	10			
	Yield/%	$[\alpha]_D^{23}$/°[b]	ee/%	Abs. Conf.[c]
MnT	68	−24.6	24	(1*R*, 2*R*)
FeT	43	+ 1.38	1	(1*S*, 2*S*)
ZnT	28	−52.6	52	(1*R*, 2*R*)
CoT	18	−28.3	28	(1*R*, 2*R*)
SnT	16	− 2.48	3	(1*R*, 2*R*)
CuT	9	+24.5	24	(1*S*, 2*S*)

a) The mixture of 1,2-epoxycyclohexane (2 mmol), aniline (2 mmol), and catalyst (0.2 mmol) in CH$_2$Cl$_2$ (5 cm^3) was stirred at room temperature for 7 d. b) (*c* 2.0, CH$_2$Cl$_2$). c) Absolute configuration.

In order to confirm the absolute configurations of ring opening products, *trans*-2-(arylthio or alkylthio)-cyclohexanols **1**—**3**, -cyclopentanols **4**—**6**, and *threo*-3-(arylthio or alkylthio)-2-butanols **7**—**9** were converted into optically active 2-cyclohexen-1-ol,[25] 2-cyclopenten-1-ol,[26] and 3-buten-2-ol,[27] respectively, by oxidation with *m*-chloroperbenzoic acid and successive thermal decomposition of the resulting *S*-oxides without the formation of ketones. The enantiomeric exesses (ee) of **1**—**9** were determined by ^{19}F NMR measurements of their esters of (+)-α-methoxy-α-(trifluoromethyl)phenylacetic acid (MTPA).[28]

Reaction of *meso*-Oxiranes with Aniline. The results of the asymmetric ring opening of 1,2-epoxycyclohexane with aniline are summerized in Table 2. The salts such as ZnT, MnT, CoT, and SnT gave (1*R*,2*R*)-2-anilinocyclohexanol (**10**), while CuT and FeT gave (1*S*,2*S*)-**10**.

The enantiomeric excess of **10** was determined by ^{19}F NMR measurement of the MTPA ester of 2-(*N*-methylanilino)cyclohexanol (**11**) derived from **10** by *N*-methylation with Me_2SO_4. In order to confirm the absolute configuration, **11** was oxidized with *m*-chloroperbenzoic acid and the resulting *N*-oxide was transformed into optically acitve 2-cyclohexen-1-ol by thermal decomposition.

Compared with the reaction of 1,2-epoxycyclohexane with thiols, the chemical and optical yields were rather low in the reaction with aniline. One of the reasons could be considered that the amino alcohol **10** thus formed tightly coordinated to metal ion as a basic bidentate to decrease both catalytic activity and enantioselectivity of the salt. This possibility was clarified by the examination of the relationship between chemical yield and optical yield. As shown in Table 3, when 10 mol% of ZnT was used, the ee values were almost constant throughout the reaction in the case of *p*-toluenethiol. On the other hand, in the case of aniline, the ee values were gradually decreased and the reaction stopped completely after 28 d. When 50 mol% of ZnT was used, the reaction completed (95% yield) within 7 d, however, the enantioselectivity was not improved (37% ee).

Reaction of *meso*-Oxiranes with Trialkylsilyl Azide. The results of the reactions of 1,2-epoxycyclohexane, 1,2-epoxycyclopentane, and *cis*-2,3-dimethyloxirane with trimethylsilyl azide are summerized in Table 4. Throughout the experiments, (1*R*,2*R*)-products were produced in almost all cases except in the combination of 1,2-epoxycyclohexane and MnT resulting in the formation of (1*S*,2*S*)-product. The chemical yield was satisfactory, however, the optical yield was only 42% ee at best.

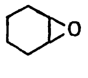
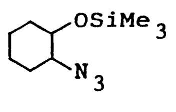
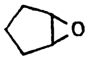
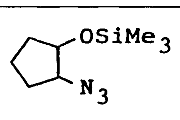
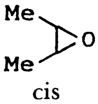
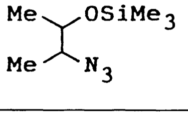
We screened several trialkylsilyl azides in place of trimethylsilyl azide to improve the enantioselectivity. When *t*-butyldimethylsilyl azide and triethylsilyl azide were employed, almost no products were obtained due to their severe steric hindrance, while ethyldimethylsilyl azide and isopropyldimethylsilyl azide gave the corresponding ring opening products **15**—**20** though in poor optical yields. These results are summerized in Table 5.

Table 3. Relation between Yield and Enantiomeric Excess[a)]

Nucleophile	Reaction Time/d	Product	Yield %	ee %
p-TolSH	1	**1**	28	67
	2		51	66
	3		72	68
	4		88	68
	5		96	68
$PhNH_2$	3	**10**	19	58
	7		28	52
	14		42	45
	21		51	34
	28		53	32

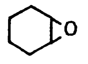
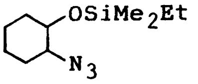
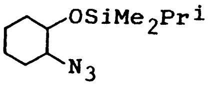
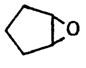
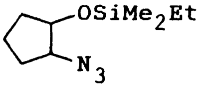
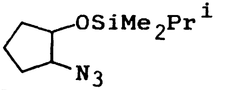
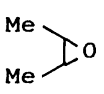
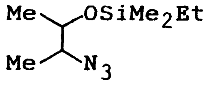
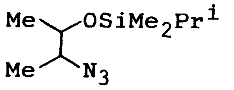
a) The mixture of 1,2-epoxycyclohexane (2 mmol), nucleophile (2 mmol), and ZnT (0.2 mmol) in CH_2Cl_2 (5 cm^3) was stirred at room temperature.

Table 4. Reaction of *meso*-Oxiranes with Trimethylsilyl Azide[a)]

Oxirane	Catalyst	Product	Yield %	$[\alpha]_D^{23}$ °b)	ee %	Abs. Conf.c)
	ZnT	 **12**	96	+10.9	42	(1*R*, 2*R*)
	CuT		96	+5.45	21	(1*R*, 2*R*)
	MnT		94	−2.95	11	(1*S*, 2*S*)
	SnT		95	0.0	0	
	CdT		92	+2.16	9	(1*R*, 2*R*)
	CoT		64	+1.00	4	(1*R*, 2*R*)
	FeT		41	+2.29	9	(1*R*, 2*R*)
	MgT·H_2O		95	+1.29	5	(1*R*, 2*R*)
	ZnT	 **13**	88	−8.86	27	(1*R*, 2*R*)
	CuT		85	−10.1	31	(1*R*, 2*R*)
	MnT		22	0.0	0	
 cis	ZnT	 **14**	85	−1.47	17	(2*R*, 3*R*)
	CuT		80	−3.35	40	(2*R*, 3*R*)
	MnT		52	−2.15	26	(2*R*, 3*R*)

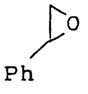
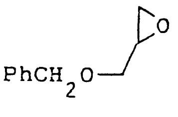
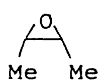
a) The mixture of oxirane (10 mmol), trimethylsilyl azide (12 mmol), and catalyst (1 mmol) in benzene (5 cm^3) was stirred at room temperature for 14 d. b) (*c* 2.0, CH_2Cl_2). c) Absolute configuration.

Table 5. Reaction of *meso*-Oxiranes with Trialkylsilyl Azides[a]

Oxirane	Azide	Catalyst	Product		Yield %	$[\alpha]^{23}_D$ °[b]	ee %	Abs. Conf.[c]
	EtMe$_2$SiN$_3$	ZnT		**15**	97	+2.40	15	(1*R*, 2*R*)
		CnT			58	+0.40	2	(1*R*, 2*R*)
	i-PrMe$_2$SiN$_3$	ZnT		**16**	85	+0.38	15	(1*R*, 2*R*)
		CuT			72	+0.30	12	(1*R*, 2*R*)
	EtMe$_2$SiN$_3$	ZnT		**17**	94	−9.08	24	(1*R*, 2*R*)
		CuT			85	−8.70	23	(1*R*, 2*R*)
	i-PrMe$_2$SiN$_3$	ZnT		**18**	73	−7.44	21	(1*R*, 2*R*)
		CuT			67	−7.87	22	(1*R*, 2*R*)
	EtMe$_2$SiM$_3$	ZnT		**19**	80	−3.56	20	(2*R*, 3*R*)
		CuT			50	−1.97	11	(2*R*, 3*R*)
cis	*i*-PrMe$_2$SiN$_3$	ZnT		**20**	82	−9.45	32	(2*R*, 3*R*)
		CuT			80	−3.59	12	(2*R*, 3*R*)

a) The mixture of oxirane (10 mmol), trialkylsilyl azide (12 mmol) and catalyst (1 mmol) in benzene (5 cm^3) was stirred at room temperature for 14 d. b) (*c* 2.0, CH$_2$Cl$_2$). c) Absolute configuration.

Table 6. Kinetic Resolution of Racemic Oxiranes[a]

Oxirane	Thiol	Reaction Time/d[c]	Recovered Oxirane		
			Yield/%[d]	ee/%	Abs. Conf.[f]
	*p*-TolSH	2	35	5	*R*
	PhCH$_2$SH	2	39	6	*R*
	n-BuSH	3	37	4	*R*
	t-BuSH	7	38	15	*R*
	*t*-BuSH	5	43	27	*R*
trans 	*p*-TolSH	14	47[e]	43[e]	(2*S*, 3R)[e]
	p-TolSH[b]	14	9[e]	72[e]	(2*S*, 3*R*)[e]

a) The mixture of oxirane (4 mmol), thiol (2 mmol), and ZnT (0.2 mmol) in CH$_2$Cl$_2$ (10 cm^3) was stirred at room temperature. b) 0.4 mmol. c) Complete consumption time of thiol checked by thin-layer chromatography. d) Based on oxirane. e) Ring opening product **21**. f) Absolute configuration.

These *O*-silylated *β*-azido alcohols **12**—**20** were desilylated by refluxing with methanol in the presence of a catalytic amount of concd HCl, and successive catalytic hydrogenolysis with 10% Pd-C resulted in the formation of corresponding *trans*-*β*-amino alcohols whose absolute configurations and maximum optical rotations have been known.

Kinetic Resolution of Racemic Oxiranes. As a model study, we examined the kinetic resolution of racemic oxiranes with thiols catalyzed by ZnT. At first, the reaction of 2-phenyloxirane with half molar equivalents of various thiols were carried out until thiols were completely consumed. When bulky 2-methyl-2-propanethiol was used as a nucleophile, (*R*)-2-phenyloxirane[29] was recovered in 15% ee. In the same reaction of 1-benzyloxy-2,3-epoxypropane, (*R*)-oxirane[30] was recovered in 27% ee. When *trans*-2,3-dimethyloxirane was treated with half molar equivalents of *p*-toluenethiol, (2*S*,3*R*)-3-(*p*-tolylthio)-2-butanol (**21**) was obtained in 43% ee, and in the case of 10 mol% of *p*-toluenethiol, the product **21** showed 72% ee. The recovery of unreacted *trans*-2,3-dimethyloxirane was failed because the separation from solvent (CH$_2$Cl$_2$) by distillation was difficult, however, (2*R*, 3*R*)-2,3-dimethyloxirane might be remained judging from the configuration of the ring opening product **21**.

The combination of *trans*-2,3-dimethyloxirane and less reactive thiols such as phenylmethanethiol, 1-butanethiol, and 2-methyl-2-propanethiol resulted in no reactions. These results are summerized in Table 6.

In all these reactions catalyzed by ZnT, thiols attacked the back side of the asymmetric carbon having *S*-configuration faster than that of *R*-configuration. These results were in good accordance with the intramolecular enantioselectivity in the reaction of *meso*-oxiranes with thiols catalyzed by ZnT, that is, thiols attacked the side of *S*-configuration and (1*R*,2*R*)-*β*-substituted alcohols were obtained.

Structure of Metal (II) *d*-Tartrate. The salts such as $CaT\cdot 4H_2O$,[31,32] $SrT\cdot 3H_2O$,[31] $CuT\cdot 3H_2O$,[33] and $Ni_2T_2\cdot 5H_2O$[34] are known to have common polymeric structures stabilized by three dimensional networks of hydrogen bonds, but their detailed coordination structures are different in every salts. Furthermore, the structure of anhydrous ZnT has been reported to be X-ray crystallographycally amorphous.[35] Considering these structural variations, it is difficult to simply presume the structures of the other metal(II) *d*-tartrates employed in the present experiments.

The catalytically active metal ions existed in a certain range of electronegativity in accordance with thiols, aniline, and trialkylsilyl azide, and highly basic nucleophiles such as benzylamine and ammonia resulted in no reactions. The enantioselectivity was varied according to the combination of oxirane, nucleophile, and metal(II) *d*-tartrate. Based on these results, it may be possible to consider that both oxirane and nucleophile coordinate simultaneously to metal (II) *d*-tartrate which acts as a heterogeneous Lewis acid catalyst to activate the oxirane, and the entropically advantageous state enables the enantioselective ring opening reaction to proceed smoothly. The detailed mechanism of the enantiotopos differentiation is remained unknown at present.

Experimental

All the boiling points and the melting points were uncorrected. The IR spectra were recorded with a JASCO IRA-2 spectrometer. The ^{1}H NMR spectra were measured with a JEOL JNM-3H-60 spectrometer or a JEOL JNM-PMX-60SI spectrometer with tetramethylsilane as an internal standard, and ^{19}F NMR spectra were taken with a Varian EM-390 spectrometer. The optical rotations were measured with a Union Giken PM-101 polarimeter or a JASCO DIP-181 polarimeter. Kugelrohr distillation was carried out with a Sibata GTO-250RS distilling apparatus. Column chromatography was performed on silica gel (Wakogel C-200). Dichloromethane and benzene were stored over Molecular Sieves 4A.

Preparation of Metal(II) Dicarboxylates. Typical Procedures for the Preparation of ZnT. Method A. To an aqueous solution (100 cm^3) of $ZnCl_2$ (13.6 g, 0.10 mol) was added an aqueous solution (100 cm^3) of potassium sodium *d*-tartrate tetrahydrate (28.2 g, 0.10 mol). The mixture was stirred at room temperature for 1 h and was left overnight. The precipitated white powder was collected by filtration, washed with water (100 cm^3) and methanol (50 cm^3), and dried at 150 °C/1 Torr (1 Torr≈133.322 Pa) for 5 h to afford ZnT (21 g, 98%). Found: C, 22.49; H, 1.93; Zn, 30.27%. Calcd for $C_4H_4O_6Zn$: C, 22.51; H, 1.89; Zn, 30.63%.

Method B. An aqueous solution (100 cm^3) of Zn $(OAc)_2\cdot 2H_2O$ (27.9 g, 0.10 mol) was added to an aqueous solution (100 cm^3) of *d*-tartaric acid (15.0 g, 0.10 mol). The mixture was stirred for 1 h, and was left over night followed by the same work-up as Method A to give ZnT (21 g, 98%). Found: C, 22.53; H, 1.92; Zn, 30.32%. Calcd for $C_4H_4O_6Zn$: C, 22.51; H, 1.89; Zn, 30.63%.

The other salts such as $BeT\cdot H_2O$, $CaT\cdot H_2O$, $SrT\cdot H_2O$, BaT, MnT, FeT, and CuT were prepared from the corresponding metal(II) chlorides and potassium sodium *d*-tartrate by method A, and $MgT\cdot H_2O$, CoT, $NiT\cdot H_2O$, CdT, HgT, and PbT were prepared from the corresponding metal(II) diacetates and *d*-tartaric acid by method B.

The salts such as ZnDMS, ZnHMS, ZnHS, and ZnMS were prepared from $Zn(OAc)_2\cdot 2H_2O$ and the corresponding dicarboxylic acids by method B with a slight modification. These salts were very soluble in water. The aqueous reaction mixture was evaporated in vacuo, and the residual salt was washed with methanol and dried.

The yields and analytical data for metal(II) dicarboxylates: $BeT\cdot H_2O$ (54%), Found: C, 27.05; H, 3.62%. Calcd for $C_4H_6O_7Be$: C, 27.44; H, 3.45%. $MgT\cdot H_2O$ (37%), Found: C. 24.98; H. 3.42%. Calcd for $C_4H_6O_7Mg$: C, 25.23; H, 3.18%. $CaT\cdot H_2O$ (94%), Found: C, 23.14; H, 3.11%. Calcd for $C_4H_6O_7Ca$: C, 23.30, H, 2.93%. $SrT\cdot H_2O$ (82%), Found: C,19.01; H, 2.22%. Calcd for $C_4H_6O_7Sr$: C, 18.94; H, 2.38%. BaT (98%), Found: C, 16.18; H, 1.58%. Calcd for $C_4H_4O_6Ba$: C, 16.83; H, 1.41%. MnT (94%), Found: C, 23.28; H, 2.09%. Calcd for $C_4H_4O_6Mn$: C, 23.43; H, 1.97%. FeT (86%), Found: C, 23.52; H, 2.06%. Calcd for $C_4H_4O_6Fe$: C, 23.56; H, 1.98%. CoT (71%), Found: C, 23.54; H, 2.06%. Calcd for $C_4H_4O_6Co$: C, 23.21; H, 1.95%. $NiT\cdot H_2O$ (77%), Found: C, 21.11; H, 2.82%. Calcd for $C_4H_6O_7Ni$: C, 21.37; H, 2.69%. CuT (99%), Found: C,22.69; H, 2.01%. Calcd for $C_4H_4O_6Cu$: C, 22.70; H, 1.91%. CdT (88%), Found: C,18.43; H, 1.50%. Calcd for $C_4H_4O_6Cd$: C, 18.44; H, 1.55%. HgT (92%), Found: C, 13.77; H,1.11%. Calcd for $C_4H_4O_6Hg$: C, 13.78; H, 1.16%. PbT (96%), Found: C, 13.29; H, 1.04%. Calcd for $C_4H_4O_6Pb$: C, 13.52; H, 1.13%. SnT (90%), Found: C, 17.94; H, 1.60%. Calcd for $C_4H_4O_6Sn$: C, 18.01; H, 1.51%. ZnDMS (96%), Found: C, 29.75; H, 3.46%. Calcd for $C_6H_8O_6Zn$: C, 29.84; H, 3.34%. ZnHMS (92%), Found: C, 26.43; H, 2.81%. Calcd for $C_5H_6O_6Zn$: C, 26.40; H, 2.66%. ZnHS (85%), Found: C, 24.14; H, 2.19%. Calcd for $C_4H_4O_5Zn$: C, 24.33; H, 2.04%. ZnMS (95%), Found: C, 28.35; H, 2.93%. Calcd for $C_5H_6O_5Zn$: C, 28.40; H, 2.86%.

General Procedure for the Reaction of *meso*-Oxiranes with Thiols. To a dichloromethane (5 cm^3) solution of oxirane (2 mmol) and thiol (2 mmol) was suspended metal(II) *d*-tartrate (0.2 mmol). The heterogeneous mixture was stirred at room temperature for 5 d. After filtration of metal(II) *d*-tartrate, the filtrate was concentrated and purified by column chromatography on silica gel (hexane : ethyl acetate=10 : 1) to give *trans*-*β*-(alkylthio or arylthio) alcohol. The isolated yields, optical rotations, and enantiomeric excesses of the adducts **1**—**9** in the various combination of oxiranes thiols, and metal(II) *d*-tartrates are listed in Table 1. Spectral and analytical data for **1**—**9** are as follows.

(1*R*,2*R*)-2-(*p*-Tolylthio)cyclohexanol (1): IR (neat) 3450, 800 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.02—1.48 (4H, m), 1.52—1.83

(2H, m), 1.83—2.12 (2H, m), 2.32 (3H, s), 2.43—2.78 (1H, m), 2.90 (1H, s), 2.98—3.39 (1H, m), 7.04 (2H, d, *J*=8 Hz), 7.32 (2H, d, *J*=8 Hz). Found: C, 70.03; H, 8.27; S, 14.37%. Calcd for $C_{13}H_{18}OS$: C, 70.22; H, 8.16; S, 14.42%.

(1*R*,2*R*)-2-(Benzylthio)cyclohexanol (2): IR (neat) 3450, 690 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.02—1.48 (4H, m), 1.50—1.82 (2H, m), 1.72—2.12 (2H, m), 2.15—2.42 (1H, m), 2.83 (1H, s), 3.08—3.36 (1H, m), 3.62 (2H, s), 7.18 (5H, s). Found: C, 69.93; H, 8.10; S, 14.38%. Calcd for $C_{13}H_{18}OS$: C, 70.22; H, 8.16; S, 14.42%.

(1*R*,2*R*)-2-(Butylthio)cyclohexanol (3): IR (neat) 3450, 730 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.93 (3H, t, *J*=8 Hz), 1.00—2.25 (12H, m), 2.52 (2H, t, *J*=7 Hz), 2.25—2.50 (1H, m), 2.80 (1H, s), 3.08—3.45 (1H, m). Found: C, 63.50; H, 10.59; S, 16.95%. Calcd for $C_{10}H_{20}OS$; C, 63.77; H, 10.70; S, 17.03%.

(1*R*,2*R*)-2-(*p*-Tolylthio)cyclopentanol (4): IR (neat) 3410, 780 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.10—2.38 (6H, m), 2.27 (3H, s), 3.16—3.37 (1H, m), 3.45 (1H. s), 3.80—4.18 (1H, m), 7.00 (2H, d, *J*=8 Hz), 7.25 (2H, d, *J*=8 Hz). Found: C, 68.93; H, 8.03; S. 15.05%. Calcd for $C_{12}H_{16}OS$: C, 69.19; H, 7.74; S, 15.39%.

(1*R*,2*R*)-2-(Benzylthio)cyclopentanol (5): IR (neat) 3410, 690 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.10—2.30 (6H, m), 2.60—2.84 (1H, m), 3.19 (1H, s), 3.66 (2H, s), 3.78—4.04 (1H, m), 7.26 (5H, s). Found: C, 69.25; H, 8.03; S, 15.10%. Calcd for $C_{12}H_{16}OS$: C, 69.19; H, 7.74; S. 15.39%.

(1*R*,2*R*)-2-(Butylthio)cyclopentanol (6): IR (neat) 3410 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.96 (3H, t, *J*=6 Hz), 1.05—2.38 (10H, m), 2.17 (1H, s), 2.53 (2H, t, *J*=7 Hz), 2.65—2.96 (1H, m), 3.87—4.18 (1H. m). Found: C, 62.28; H, 10.26; S, 18.21%. Calcd for $C_9H_{18}OS$: C. 62.02, H, 10.41; S, 18.39%.

(2*R*,3*R*)-3-(*p*-Tolylthio)-2-butanol (7): IR (neat) 3430, 810 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.87 (3H, d, *J*=7 Hz), 1.24 (3H, d, *J*=7 Hz),2.35 (3H, s), 2.43 (1H, s). 2.67—3.08 (1H, m), 3.32—3.75 (1H, m), 7.07 (2H, d, *J*=8 Hz), 7.32 (2H, d, *J*=8 Hz). Found: C, 67.14; H, 7.99; S, 16.43%. Calcd for $C_{11}H_{16}OS$: C, 67.30; H, 8.22; S, 16.33%.

(2*R*,3*R*)-3-(Benzylthio)-2-butanol (8): IR (neat) 3430, 690 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.15 (3H, d, 7 Hz), 1.21 (3H, d, *J*=7 Hz), 2.29 (1H, s), 2.37—2.65 (1H, m), 3.40—3.66 (1H, m), 3.74 (2H, s), 7.34 (5H, s). Found: C. 67.56; H, 8.38; S, 16.21%. Calcd for $C_{11}H_{16}OS$: C, 67.30; H, 8.22; S, 16.33%.

(2*R*,3*R*)-3-(Butylthio)-2-butanol (9): IR (neat) 3430 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.94 (3H, t, *J*=7 Hz), 1.09 (3H, d, *J*=6 Hz), 1.33 (3H, d, *J*=7 Hz), 1.34—1.82 (4H, m), 2.03 (1H, s), 2.38—2.69 (1H, m), 2.35 (2H, t, *J*=7 Hz), 3.32—3.58 (1H, m). Found C, 59.43; H, 10.97; S, 19.58%. Calcd for $C_8H_{18}OS$: C, 59.21; H, 11.18; S, 19.75%.

Reaction of 1,2-Epoxycyclohexane with Aniline Catalyzed by ZnT. To a dichloromethane (5 cm^3) solution of 1,2-epoxycyclohexane (196 mg, 2 mmol) and aniline (186 mg, 2 mmol) was suspended ZnT (43 mg, 0.2 mmol). The heterogeneous mixture was stirred at room temperature for 7 d. After filtration of ZnT, the filtrate was concentrated and purified by column chromatography on silica gel ($CHCl_3$) to afford 108 mg (28% yield) of (1*R*,2*R*)-2-anilinocyclohexanol (**10**): $[\alpha]^{23}_{\mathrm{D}}$ −52.6° (*c* 2.0, CH_2Cl_2); mp 78—81 °C; IR (KBr) 3370, 3450, 1590, 1280 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.00—1.52 (4H, m), 1.55—1.88 (2H, m), 1.88—2.24 (2H, m), 2.86—3.45 (2H, m), 3.34 (2H, s), 6.48—6.51 (3H, m), 6.96—7.23 (2H, m). Found: C, 75.12; H, 8.86; N, 7.48%. Calcd for $C_{12}H_{17}NO$: C, 75.36, H, 8.96, N, 7.32%. The isolated yields, optical rotations, and enantiomeric excesses of **10** in the use of various metal(II) *d*-tartrates are listed in Table 2.

Preparation of Trialkylsilyl Azide. Trimethylsilyl azide was commercially available (Tokyo Kasei) and was used without further purification. The following trialkylsilyl azides were prepared from the corresponding trialkylsilyl chlorides and sodium azide according to the literature for the preparation of trimethylsilyl azide.[36]

Ethyldimethylsilyl Azide: Yield 56%; bp 72 °C/150 Torr; IR (neat) 2160 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.14 (6H, s), 0.72 (2H, q, *J*=8 Hz), 1.04 (3H, t, *J*=8 Hz). Found: C, 37.29; H, 8.51, N, 32.40%. Calcd for $C_4H_{11}N_3Si$: C, 37.18; H, 8.58; N, 32.51%.

Isopropyldimethylsilyl Azide: Yield 72%; bp 75 °C/90 Torr; IR (neat) 2140 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.23 (6H, s), 1.04 (6H, d, *J*=5 Hz), 1.03 (1H, q, *J*=5 Hz). Found: C, 41.73; H, 9.04; N, 29.45%. Calcd for $C_5H_{13}N_3Si$: C, 41.91; H, 9.15; N, 29.33%.

***t*-Butyldimethylsilyl Azide:** Yield 84%; bp 78 °C/67 Torr; IR (neat) 2140 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.22 (6H, s), 0.97 (9H, s). Found: C, 45.90; H, 9.75; N, 26.47%. Calcd for $C_6H_{15}N_3Si$: C, 45.81; H, 9.61; N, 26.72%.

Triethylsilyl Azide: Yield 80%; bp 82 °C/35 Torr; IR (neat) 2130 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.79 (6H, q, *J*=9 Hz), 1.05 (9H, t, *J*=9 Hz). Found: C, 45.82; H, 9.75; N, 26.51%. Calcd for $C_6H_{15}N_3Si$: C, 45.81; H, 9.61; N, 26.72%.

General Procedure for the Reaction of *meso*-Oxiranes with Trialkylsilyl Azides. To a benzene (5 cm^3) solution of oxirane (10 mmol) and trialkylsilyl azide (12 mmol) was suspended metal(II) *d*-tartrate (1 mmol). The heterogeneous mixture was stirred at room temperature for 14 d. After filtration of metal(II) *d*-tartrate, the filtrate was concentrated and purified by Kugelrohr distillation to afford *trans-O*-trialkylsilyl β-azido alcohol. The isolated yields, optical rotations, and enantiomeric excesses of the adducts in the various combination of oxiranes, trialkylsilyl azides, and metal(II) *d*-tartrates are listed in Tables 4 and 5. Spectral and analytical data of the adducts **12**—**20** are as follows.

(1*R*,2*R*)-1-Azido-2-(trimethylsilyloxy)cyclohexane (12): Bp 110 °C/5 Torr; IR (neat) 2110 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.16 (9H, s), 1.02—1.05 (4H, m), 1.55—2.20 (4H, m), 3.00—3.60 (2H, m). Found: C, 50.58: H, 8.93; N, 19.83%. Calcd for $C_9H_{19}N_3OSi$: C, 50.65; H, 8.98; N, 19.70%.

(1*R*,2*R*)-1-Azido-2-(trimethylsilyloxy)cyclopentane (13): Bp 105 °C/5 Torr; IR (neat) 2100 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.12 (9H, s), 1.23—2.25 (6H, m), 3.40—3.76 (1H, m), 3.78—4.10 (1H, m). Found: C, 48.01, H, 8.47; N, 21.32%. Calcd for $C_8H_{17}N_3OSi$: C, 48.20: H, 8.60, N. 21.08%.

(2*R*,3*R*)-2-Azido-3-(trimethylsilyloxy)butane (14): Bp 100 °C/5 Torr; IR (neat) 2100 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.13 (9H, s), 1.15 (3H, d, *J*=10 Hz), 1.16 (3H, d, *J*=10 Hz), 2.98—3.40 (1H, m), 3.50—3.89 (1H, m). Found: C, 44.72; H, 8.98; N, 22.51%. Calcd for $C_7H_{17}N_3OSi$: C, 44.88; H, 9.15; N, 22.43%.

(1*R*,2*R*)-1-Azido-2-(ethyldimethylsilyloxy)cyclohexane (15): Bp 120 °C/6 Torr; IR (neat) 2100 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.10 (6H, s), 0.58 (2H, q, *J*=8 Hz), 0.96 (3H, t, *J*=8 Hz), 1.02—2.35 (8H, m), 2.70—3.63 (2H, m). Found: C,52.69; H, 9.13; N, 18.40%. Calcd for $C_{10}H_{21}N_3OSi$: C, 52.82; H, 9.31; N, 18.48%.

(1*R*,2*R*)-1-Azido-2-(ethyldimethylsilyloxy)cyclopentane (17): Bp 105 °C/5 Torr; IR (neat) 2100 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.10 (6H, s), 0.58 (2H, q, *J*=8 Hz), 0.96 (3H, t, *J*=8 Hz); 1.16—2.24 (6H, m), 3.48—3.82 (1H, m), 3.84—4.19 (1H, m). Found: C, 50.51; H, 8.79%; N, 19.79%. Calcd for $C_9H_{19}N_3OSi$: C, 50.65; H, 8.98; N, 19.70%.

(2*R*,3*R*)-2-Azido-3-(ethyldimethylsilyloxy)butane (19): Bp 100 °C/5 Torr; IR (neat) 2100 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.09 (6H, s), 0.58 (2H, q, *J*=8 Hz), 0.97 (3H, t, *J*=8 Hz), 1.13 (3H, d, *J*=6 Hz), 1.15 (3H, d, *J*=6 Hz), 3.02—3.42 (1H, m), 3.44—3.86 (1H, m). Found: C, 47.76; H, 9.38; N, 20.98%. Calcd for $C_8H_{19}N_3OSi$: C, 47.72; H, 9.51; N, 20.87%.

(1*R*,2*R*)-1-Azido-2-(isopropyldimethylsilyloxy)cyclohexane (16): Bp 135 °C/5 Torr; IR (neat) 2100 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.09 (6H, s), 0.92 (1H, q, *J*=5 Hz), 0.97 (6H, d, *J*=5 Hz), 1.00—2.32 (8H, m), 2.83—3.85 (2H, m). Found: C, 54.71; H, 9.48; N, 17.46%. Calcd for $C_{11}H_{23}N_3OSi$: C, 54.72; H, 9.60; N, 17.41%.

(1*R*,2*R*)-1-Azido-2-(isopropyldimethylsilyloxy)cyclopentane (18): Bp 120 °C/5 Torr; IR (neat) 2100 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.07 (6H, s), 0.92 (1H, q. *J*=5 Hz), 0.97 (6H, d, *J*=5 Hz), 1.35—2.32 (6H, m), 3.40—3.83 (1H, m), 3.84—4.17 (1H, m). Found: C, 52.91; H, 9.57; N, 18.47%. Calcd for $C_{10}H_{21}N_3OSi$: C, 52.82; H, 9.31; N, 18.48%.

(2*R*,3*R*)-2-Azido-3-(isopropyldimethylsilyloxy)butane (20): Bp 110 °C/5 Torr; IR (neat) 2100 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.08 (6H, s), 0.92 (1H, q, *J*=5 Hz), 0.97 (6H, d, *J*=5 Hz), 1.17 (3H, d, *J*=9 Hz), 1.26 (3H, d, *J*=9 Hz); 3.02—3.83 (2H, m). Found: C, 50.46; H, 9.63; N, 19.47%. Calcd for $C_9H_{21}N_3OSi$: C, 50.19: H, 9.83; N, 19.51%.

Kinetic Resolution of *trans*-2,3-Dimethyloxirane. To a dichloromethane (100 cm^3) solution of *trans*-2,3-dimethyloxirane (2.88 g, 40 mmol) and *p*-toluenethiol (2.48 g, 20 mmol) was suspended ZnT (0.43 g, 2 mmol). This heterogeneous mixture was stirred at room temperature for 14 d. After filtration of ZnT, the filtrate was concentrated and purified by column chromatography on silica gel (hexane : ethyl acetate=10 : 1) to afford (2*S*,3*R*)-3-(*p*-tolylthio)-2-butanol (**21**) (3.70 g, 47%). $[\alpha]_D^{23}$ +2.16° (*c* 5.00, CH_2Cl_2). IR (neat) 3440, 800 cm^{-1}. ^{1}H NMR (CCl_4) δ=1.16 (3H, d, *J*=8 Hz), 1.27 (3H, d, *J*=8 Hz), 2.08 (1H, s), 2.37 (3H, s), 2.96—3.27 (1H, m), 3.50—3.86 (1H, m), 7.07 (2H, d, *J*=8 Hz), 7.30 (2H, d, *J*=8 Hz). Found: C, 67.07; H, 8.26; S, 16.39%. Calcd for $C_{11}H_{16}OS$: C, 67.30; H, 8.22; S, 16.33%.

Typical Procedures for the Conversion of (1*R*,2*R*)-1 into (*R*)-2-Cyclohexen-1-ol. Oxidation of 1. To a $CHCl_3$ (50 cm^3) solution of **1** (4.04 g, 20 mmol, $[\alpha]_D^{23}$ −45.0°, (*c* 5.00, CH_2Cl_2)) was added *m*-chloroperbenzoic acid (5.2 g, 30 mmol) little by little on ice cooling with stirring. Afer stirring for 30 min at room temperature, the reaction mixture was washed with 20 cm^3 of 5% aqueous $KHCO_3$ three times, dried over Na_2SO_4, concentrated, and purified by column chromatography on silica gel ($CHCl_3$: MeOH=50 : 1) to afford the corresponding S-oxide (4.4 g, 92%). Mp 135—139 °C. IR (KBr) 3380, 1020 cm^{-1}.

Thermal Decomposition of *S*-Oxide of 1. The mixture of *S*-oxide of **1** (3.2 g, 13 mmol) and $CaCO_3$ (1.3 g, 13 mmol) was heated at 150 °C/10 Torr for 3 h. During the thermal decomposition, the distillate was collected in a reciever with Dry Ice-acetone cooling, and was purified by Kugelrohr distillation (100 °C/15 Torr) to give (*R*)-2-cyclohexen-1-ol (0.90 g, 69%, $[\alpha]_D^{23}$ +92.4° (*c* 0.60, $CHCl_3$)).

By the same way, (1*R*,2*R*)-**2** ($[\alpha]_D^{23}$ −34.4°) and (1*R*,2*R*)-**3** ($[\alpha]_D^{23}$ −44.7°) were transformed into (*R*)-2-cyclohexen-1-ol ($[\alpha]_D^{23}$ +102.7 and +110.8°) in 41 and 58% yields, respectively.

The 2-substituted cyclopentanols such as (1*R*,2*R*)-**4** ($[\alpha]_D^{23}$ −7.97°), (1*R*,2*R*)-**5** ($[\alpha]_D^{23}$ −7.80°), and (1*R*,2*R*)-**6** ($[\alpha]_D^{23}$ −15.1°) were converted into (*R*)-2-cyclopenten-1-ol ($[\alpha]_D^{23}$ +46.8, +52.3, and +81.9° (*c* 1.0, $CHCl_3$)) in 80, 62, and 48% yields, respectively.

The 3-substituted 2-butanols such as (2*R*,3*R*)-**7** ($[\alpha]_D^{23}$ −25.8°), (2*R*,3*R*)-**8** ($[\alpha]_D^{23}$ −18.5°), and (2*R*,3*R*)-**9** ($[\alpha]_D^{23}$ −29.0°) were converted into (*R*)-3-buten-2-ol ($[\alpha]_D^{23}$ −16.9, −23.1, and −21.8° (neat)) in 57, 41, and 53% yields, respectively. Furthermore, (2*S*,3*R*)-**21** ($[\alpha]_D^{23}$ +2.16°) was also converted into (*S*)-3-buten-2-ol ($[\alpha]_D^{23}$ −14.1° (neat)) in 51% yield.

Conversion of (1*R*,2*R*)-10 into (*R*)-2-Cyclohexen-1-ol. *N*-Methylation of 10. To a methanol (50 cm^3) solution of (1*R*,2*R*)-**10** (4.2 g, 22 mmol, $[\alpha]_D^{23}$ −52.6° (*c* 5.0, CH_2Cl_2)) was added 50 cm^3 of 25% aqueous K_2CO_3, and Me_2SO_4 (12.6 g, 100 mmol) during 2 h with vigorous stirring. After adding 10 cm^3 of 5% aqueous NaOH, the reaction mixture was extracted with 50 cm^3 of ethyl acetate, dried over Na_2SO_4, cocentrated, and purified by column chromatography on silica gel (hexane : ethyl acetate=6 : 1) to yield (1*R*,2*R*)-**11** (4.2 g, 94%,). $[\alpha]_D^{23}$ +46.4° (*c* 5.0, CH_2Cl_2). IR (neat) 3450 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.10—1.85 (8H, m), 2.18 (1H, s), 2.76 (3H, s), 3.20—3.85 (2H, m), 6.60—7.38 (5H, m). Found: C, 76.18; H, 9.28; N, 6.86%. Calcd for $C_{13}H_{19}NO$: C, 76.06; H, 9.33; N, 6.82%.

Oxidation of (1*R*,2*R*)-11. To a dichloromethane (50 cm^3) solution of **11** (4.2 g, 20 mmol) was added *m*-chloroperbenzoic acid (4.0 g, 23 mmol) little by little. After being stirred for 1 h at room temperature, the mixture was washed with 50 cm^3 of 10% aqueous K_2CO_3 three times, dried over Na_2SO_4, concentrated, and purified by column chromatography on silica gel ($CHCl_3$: MeOH=20 : 1) to afford the corresponding *N*-oxide (3.7 g, 82%). Mp 123—125 °C. IR (KBr) 3420, 1450, 1110 cm^{-1}.

Thermal Decomposition of *N*-Oxide. The *N*-oxide of **11** (1.0 g, 4.5 mmol) was heated at 140 °C/20 Torr for 3 h. The distillate was collected in a reciever with Dry Ice-acetone cooling, and was purified by Kugelrohr distillation to yield (*R*)-2-cyclohexen-1-ol (0.30 g, 67%, $[\alpha]_D^{23}$ +69.3° (*c* 0.60, $CHCl_3$).

Desilylation of *O*-Trialkylsilyl *β*-Azido Alcohols 12—20. Typical Procedure for the Desilylation of (1*R*,2*R*)-12 into (1*R*,2*R*)-2-Azidocyclohexanol. A methanol solution (8 cm^3) of (1*R*,2*R*)-**12** (2.13 g, 10 mmol, $[\alpha]_D^{23}$ +10.9° (*c* 2.0, CH_2Cl_2)) and 0.05 cm^3 of concd HCl was refluxed for 2 h. After being concentrated in vacuo, the residue was purified by Kugelrohr distilation (105 °C/4.5 Torr) to give (1*R*,2*R*)-2-azidocyclohexanol (1.4 g, 92%). $[\alpha]_D^{23}$ −30.8° (*c* 2.0, CH_2Cl_2). IR (neat) 3320, 2100 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.00—2.28 (8H, m), 2.26 (1H, s), 3.00—3.70 (2H, m). Found: C, 50.89; H, 7.64; N, 29.71%. Calcd for $C_6H_{11}N_3O$: C, 51.05; H, 7.85; N, 29.77%.

By the same way, (1*R*,2*R*)-**15** and **16** ($[\alpha]_D^{23}$ +2.40 and +0.38°) were transformed into (1*R*,2*R*)-2-azidocyclohexanol ($[\alpha]_D^{23}$ −10.5 and −11.1°) in 85 and 87%, respectively.

Desilylation of (1*R*,2*R*)-**13**, **17**, and **18** ($[\alpha]_D^{23}$ −10.1, −9.08, and −7.44° (*c* 2.0, CH_2Cl_2)) were similarly carried out to afford (1*R*,2*R*)-2-azidocyclopentanol ($[\alpha]_D^{23}$ −21.0, −16.5, and −14.3° (*c* 2.0, CH_2Cl_2)) in 91, 88, and 86%. Bp 105 °C/5 Torr (Kugelrohr distillation). IR (neat) 3290, 2120 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.30—2.56 (6H, m), 3.36 (1H, s), 3.40—3.78 (1H, m), 3.80—4.42 (1H, m). Found: C.47.30; H, 7.09; N, 33.12%. Calcd for $C_5H_9N_3O$: C, 47.22; H, 7.13, N, 33.05%.

Desilylation of (2*R*,3*R*)-**14**,**19**, and **20** ($[\alpha]_D^{23}$ −3.35, −3.56, and −9.45° (*c* 2.0, CH_2Cl_2)) yielded (2*R*,3*R*)-3-azido-2-butanol ($[\alpha]_D^{23}$ −37.8, −18.3, and −29.2° (*c* 2.0, CH_2Cl_2)) in

86, 86, 81%, respectively. Bp 100 °C/5 Torr (Kugelrohr distillation). IR (neat) 3370, 2100 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.12 (2H, d, J=12 Hz), 1.25 (2H, d, J=12 Hz), 2.30 (1H, s), 3.03—3.79 (2H, m). Found: C, 41.79; H, 7.67; N, 36.42%. Calcd for $C_4H_9N_3O$: C, 41.72; H, 7.88; N, 36.42%.

Hydrogenolysis of Azido Alcohols. Typical Procedure for the Hydrogenolysis of (1*R*,2*R*)-2-Azidocyclohexanol. The catalytic hydrogenolysis of (1*R*,2*R*)-2-azidocyclohexanol (1.3 g, 9.2 mmol, $[\alpha]_D^{23}$ −30.8° (*c* 2.0, CH_2Cl_2)) was carried out in methanol (12 cm^3) with 10% Pd–C (0.1 g) under atmospheric pressure at room temperature for 1 h. The catalyst was filtered off, and the filtrate was concentrated and purified by Kugelrohr distillation (165 °C/5 Torr) to afford (1*R*,2*R*)-2-aminocyclohexanol (1.2 g, 86%). $[\alpha]_D^{23}$ −15.9° (*c* 1.3, H_2O), (lit,[37] $[\alpha]_D^{22}$ −37.6°).

In a similar manner, the catalytic hydrogenolysis of (1*R*,2*R*)-2-azidocyclopentanol and (2*R*,3*R*)-3-azido-2-butanol ($[\alpha]_D^{23}$ −21.0 and −37.8° (*c* 2.0, CH_2Cl_2)) gave (1*R*,2*R*)-2-amonocyclopentanol (95% yield, $[\alpha]_D^{23}$ −10.2° (*c* 1.7, EtOH lit,[38] $[\alpha]_D^{20}$ −33.3°) and (2*R*,3*R*)-3-amino-2-butanol (95% yield, $[\alpha]_D^{23}$ −6.84° (neat); lit,[39] $[\alpha]_D^{25}$ −17.05°), respectively.

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