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A Catalytic Enantioselective Reaction Using a C_2-Symmetric Disulfonamide as a Chiral Ligand: Simmons-Smith Cyclopropanation of Allylic Alcohols by the Et_2Zn-CH_2I_2-Disulfonamide System

Hideyo Takahashi[†,1a], Masato Yoshioka[†,1b], Masakatsu Shibasaki[†], Masaji Ohno[†,1c], Nobuyuki Imai[‡,1d], and Susumu Kobayashi[‡*]

[†] Faculty of Pharmaceutical Sciences, University of Tokyo
Hongo, Bunkyo-ku, Tokyo 113, Japan

[‡] Sagami Chemical Research Center
Nishi-Ohnuma, Sagamihara 229, Japan

*Abstract: A catalytic and enantioselective Simmons-Smith cyclopropanation of an allylic alcohol was developed by the reaction of an allylic alcohol with Et_2Zn and CH_2I_2 in the presence of a catalytic amount of chiral disulfonamide **4**.*

The development of catalytic and enantioselective reactions has been one of the most important and challenging topics in organic synthesis. As one approach to solve this problem, we[2] and Corey *et al.*[3] have independently demonstrated the potential utility of Lewis acid catalysts modified by electron-withdrawing chiral disulfonamides. In this paper is described the full detail of the catalytic and enantioselective Simmons-Smith cyclopropanation of disubstituted allylic alcohols in the presence of a catalytic amount of disulfonamide-modified zinc complex.[4]

Among the various types of catalytic, enantioselective reaction investigated, cyclopropanation has attracted continuing and increasing attention since the pioneering work by Nozaki *et al.* in 1966,[5] and, indeed, reactions catalyzed by bis(oxazoline)copper complexes were independently reported by Masamune *et al.*[6a] and Evans *et al.*[6b] Further, bis(oxazolinyl)pyridine-ruthenium catalyst was recently reported by Nishiyama *et al.*[6c] However, the carbene sources employed in previous studies have been limited to diazoacetate derivatives, and there have been no examples using the Simmons-Smith type of reagent. Independent of our work, Ukaji *et al.*[7] and Denmark *et al.*[8] reported the enantioselective Simmons-Smith reaction in 1992. Further, highly enantioselective chiral boron complex was also developed by Charette *et al.*[9] These methodologies, however, require a stoichiometric amount of chiral auxiliaries, and to our knowledge there has been no catalytic and enantioselective Simmons-Smith reaction except our method utilizing disulfonamide-modified metal complexes. Improvement of our method[4] has very recently been reported by Denmark *et al.*[10], which also prompted us to describe our own results.

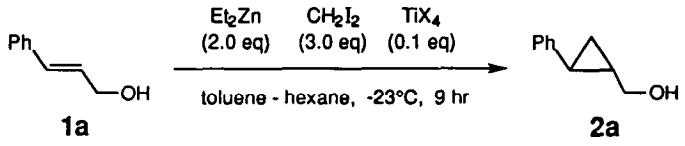
It is well recognized that the Simmons-Smith reaction of an allylic alcohol or its ether derivative proceeds much faster than that of a simple olefin,[11] and this enhancement of reactivity is explained by considering the proximity effect attributed to the strong affinity between the organozinc reagent and the oxygen atom.[12]

On the other hand, Friedrich *et al.* observed that the addition of catalytic amount of titanium tetrachloride facilitates the Simmons-Smith reaction of a simple olefin such as cyclohexene and α-pinene.[13] Although the function of titanium tetrachloride is not clear, we assumed that one possibility might be due to the activation of the carbenoid.

Based on these facts, we became interested in examining the Simmons-Smith reaction of an allyl alcohol derivative in the presence of a disulfonamide-modified Lewis acid catalyst. Carbene source employed in the present study is diethylzinc-methylene iodide developed by Furukawa *et al.*[14]

Since there has been only one example of the Lewis acid-mediated Simmons-Smith reaction,[13] we initially carried out the cyclopropanation of cinnamyl alcohol **1a** in the presence of $Ti(O\text{-}i\text{-}Pr)_4$ or $TiCl_4$.

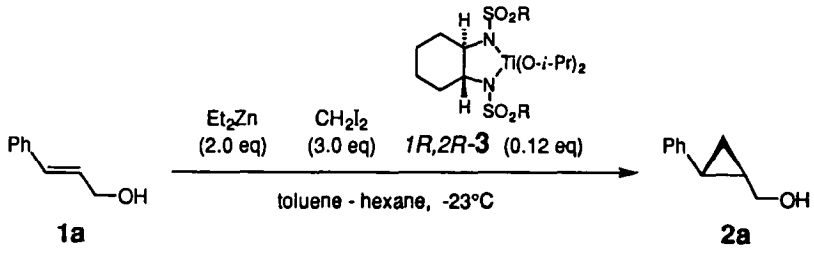
Scheme 1



TiX_4 (Yield): none (22%), $Ti(O\text{-}i\text{-}Pr)_4$ (35%), $TiCl_4$ (77%)

The results shown in Scheme 1 clearly demonstrate that the cyclopropanation of an allylic alcohol is indeed facilitated by Lewis acid. Encouraged with these results, we then examined the cyclopropanation of cinnamyl alcohol **1a** in the presence of disulfonamide-modified titanium catalyst which we have shown to be an excellent catalyst for the alkylation of an aldehyde with dialkylzinc.[2] The chiral tiatanium catalysts **3** were prepared *in situ* according to our original procedure.[2] Cyclopropanation proceeded smoothly to afford the cyclopropane **2a** in good yields. However, the enantioselectivities were found very poor as shown in Table 1.

Table 1

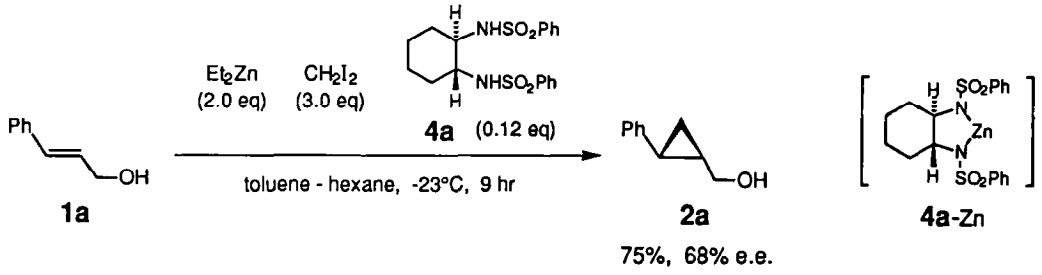


Entry	3	R	Time (h)	Yield (%)	e.e. (%)
1	3a	α-naphthyl	10	70	7
2	3b	CF_3	9	82	16
3	3c	n-C_4F_9	9	58	~0

After extensive experimentations, disulfonamide-modified zinc complex was found effective in Simmons-Smith reaction which was described below.

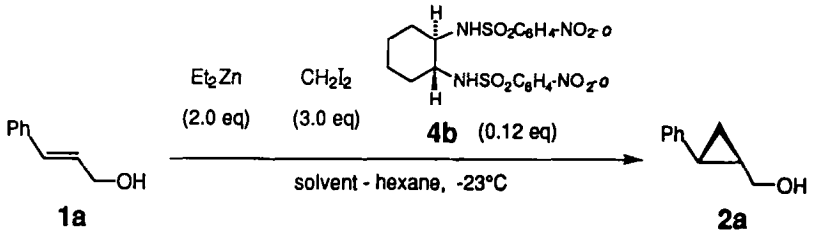
When cinnamyl alcohol **1a** was reacted with diethylzinc (2.0 eq), methylene iodide (3.0 eq), and disulfonamide **4a** (0.12 eq) in methylene chloride at -23°C for 9h, the corresponding cyclopropane **2a** (3-phenyl-2,3-methano-1-propanol) was isolated in 75% yield with 68% e.e. Enantiomeric excess was directly determined by HPLC analysis using a Daicel chiral column OD (eluent system; 5% *i*-PrOH in hexane). The absolute configuration of **2a** was determined to be as shown (2*R*,3*R*) by comparison of specific rotation value ($[\alpha]_D^{21}$ -56.2° (*c* 0.60, EtOH)) with that in literature[15] ($[\alpha]_D^{2}$ -46.6° (*c* 2.64, EtOH) for 2*R*,3*R*-**2a** with 75% e.e.). This is the first example of a catalytic and enantioselective Simmons-Smith reaction. We tentatively assumed that the chiral zinc complex **4a**-Zn is immediately formed *in situ* even at -23°C although we have not succeeded to isolate and characterize it. Concerning the active species of the zinc complex, Denmark *et al.* proposed in their recent paper[10b] that the NH group on the sulfonamide is still present after the addition of Et_2Zn under the reaction condition.

Scheme 2



It was also found that, under the same reaction conditions, the cyclopropanation of **1a** proceeded faster using the *o*-nitro derivative **4b** affording **2a** in 92% yield with 75% e.e. The effect of altering the solvent on the reaction is also shown in Table 2. In contrast to the Furukawa's original procedure,[14] cyclopropanation did not proceed in ether or THF. These results clearly suggest that the chiral zinc complex **4b**-Zn facilitates the reaction through its Lewis acid character, which, in turn, is attained through the substitution with electron-withdrawing sulfonamide ligands.

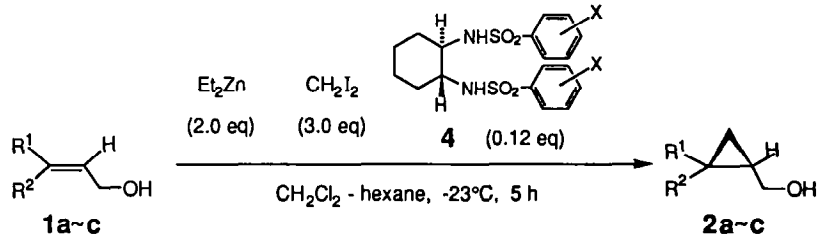
Table 2



Entry	Solvent	Time (h)	Yield (%)	e.e. (%)
1	toluene	9	81	69
2	CH_2Cl_2	5.5	92	75
3	THF	8.5	~0	-
4	Et_2O	8.5	~0	-

The reaction of cinnamyl alcohol **1a** with diethylzinc and methylene iodide was then examined in detail in the presence of differently substituted benzene sulfonamides, **4a~4f**. Some typical results are summarized in Table 3. (Entry 1~6) In all cases the absolute configuration of the resulting cyclopropane **2a** was 2*R*,3*R*. Although *p*-trifluoromethylbenzenesulfonamide **4e** facilitated the cyclopropanation, enantioselectivity was slightly low compared to *o*-nitro- and *p*-nitrobenzenesulfonamide, **4b** and **4d**. (Entry 2, 4 and 5) Substitution at *meta*-position resulted in the significant decrease in an enantioselectivity (Entry 3 and 6) probably due to the steric reason. Cyclopropanation of (*Z*)-3-phenyl-2-propen-1-ol (**1b**) was also examined and the results are summarized in Table 3. (Entry 7~9) Enantiomeric excess and the absolute configuration of the resulting *syn*-cyclopropane **2b** (2*R*,3*S*) were determined by HPLC analysis (Daicel chiral column OD, eluent system; 5% *i*-PrOH in hexane), and comparison of the specific rotation value ($[\alpha]_D^{23}$ -41.1° (*c* 1.42, $CHCl_3$)) with that in literature[16] ($[\alpha]_D^{20}$ +39° (*c* 2.42, $CHCl_3$) for 2*S*,3*R*-**2b** with 50% e.e.), respectively. Furthermore, (*E*)-5-phenyl-2-penten-1-ol (**1c**) was subjected to a cyclopropanation to obtain the corresponding cyclopropane (5-phenyl-2,3-methano-1-pentanol (**2c**); $[\alpha]_D^{20}$ -24.6° (*c* 1.13, $CHCl_3$)[17]) with 80% e.e. determined by HPLC analysis using Daicel Chiralpak AD. (Entry 10, 11) Absolute configuration of **2c** was unambiguously established to be 2*R*,3*R* by correlating to the known (2*R*,3*R*)-2,3-methano-1,4-butanediol 9[19] by the sequence shown in Scheme 3.

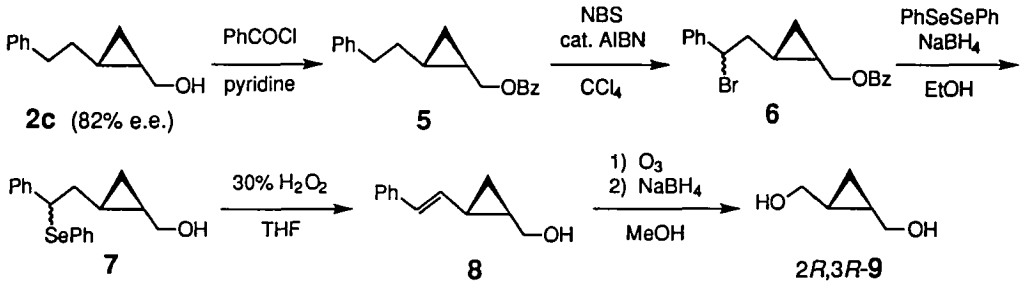
Table 3



Entry	Allyl Alcohol			Sulfonamide			Yield	e.e.
	1	R^1	R^2	**4**	X	**2**	(%)	(%)
1	**1a**	Ph	H	**4a**	H	**2a**	75	68
2	**1a**	Ph	H	**4b**	*o*-NO_2	**2a**	92	75
3	**1a**	Ph	H	**4c**	*m*-NO_2	**2a**	72	33
4	**1a**	Ph	H	**4d**	*p*-NO_2	**2a**	82	76
5	**1a**	Ph	H	**4e**	*p*-CF_3	**2a**	99	67
6	**1a**	Ph	H	**4f**	3,5-$(CF_3)_2$	**2a**	99	29
7	**1b**	H	Ph	**4b**	*o*-NO_2	**2b**	82	51
8	**1b**	H	Ph	**4c**	*m*-NO_2	**2b**	71	31
9	**1b**	H	Ph	**4d**	*p*-NO_2	**2b**	71	75
10	**1c**	$PhCH_2CH_2$	H	**4b**	*o*-NO_2	**2c**	82	80
11	**1c**	$PhCH_2CH_2$	H	**4d**	*p*-NO_2	**2c**	quant	82

Thus, the cyclopropylmethanol **2c** (82% e.e.) was initially converted to the benzoate **5** and the latter was transformed to the olefin **8** *via* the bromide **6** and the phenylselenide **7**. The olefin **8** was then subjected to an ozonolysis followed by the reductive work-up with $NaBH_4$ to obtain 2,3-methano-1,4-butanediol which has a negative rotation value (**9**; $[\alpha]_D^{20}$ -12.1° (*c* 0.6, EtOH)). Therefore, the absolute configuration of **2c** was determined to be 2*R*,3*R*.

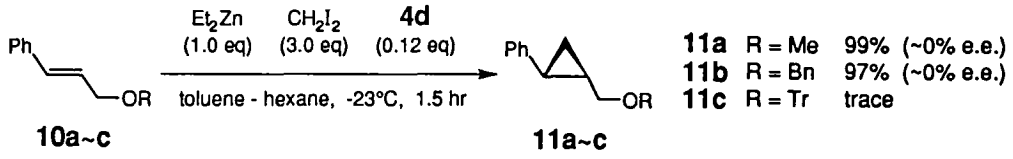
Scheme 3



These results clearly indicate that the stereochemical course of the present cyclopropanation is directed by the hydroxyl group, and upon use of a given enantiomer of **4**, cyclopropanation occurs from the same enantioface of the olefin regardless of its geometry.

Furthermore, free hydroxyl group was found to be essential to attain the relatively high enantioselectivity since methyl or benzyl ether of cinnamyl alcohol afforded almost racemic cyclopropanes even in the presence of **4d** under the same reaction condition. On the other hand, cyclopropanation did not proceed in the case of trityl derivative **10c**. (Scheme 4)

Scheme 4



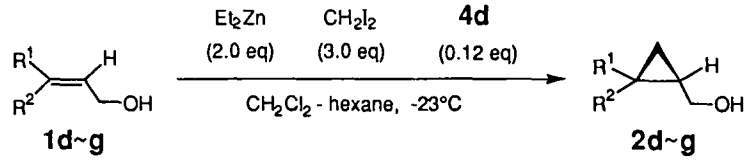
The remarkable contrast between the free cinnamyl alcohol and its ether derivative is quite interesting and was also reported by Charette *et al.* in the highly enantioselective Simmons-Smith reaction using a stoichiometric amount of chiral dioxaborolane.[9a] In addition we also observed that the cinnamyl ethers **10a** and **10b** underwent cyclopropanation readily even in the absence of disulfonamide giving the corresponding racemic cyclopropanes **11a** and **11b** in quantitative yields under the similar reaction conditions. From these results, we assume that the achiral zinc carbenoid directly coordinates to the ether oxygen of allylic ethers resulting the facile methylene transfer in a non-enantioselective manner even in the presence of chiral disulfonamide-Zn complex. In the case of free allylic alcohol, hydroxyl group is spontaneously converted into the zinc alkoxide, and we suppose that the zinc atom of the alkoxide, zinc carbenoid, and the chiral disulfonamide-Zn complex form a polynuclear complex through which the methylene transfer occurs in an

enantioselective manner. Although we can not draw the plausible transition state at present, free rotation of the allylic alcohol moiety might be restricted by the formation of the rigid polynuclear complex.

In order to evaluate the difference in the reactivity between free allylic alcohol and its ether as well as taking consideration of the synthetic utility of the resulting cyclopropanes, we were interested in examining the cyclopropanation of monoprotected 2-buten-1,4-diol derivatives which contain both a hydroxyl group and an alkoxyl group at the allylic positions. Results are summarized in Table 4.

In both *E*- and *Z*-butenediol derivatives, trityl ethers (**1e** and **1g**) gave relatively high enantioselectivities, while poor enantioselectivities were observed in the case of benzyl ethers, **1d** and **1f**. Apparently, competitive and non-enantioselective ether-directed cyclopropanation occurs in the case of benzyl ethers to result in lowering the enantioselectivities. Although we have not carried out the kinetic study, hydroxyl-directed and ether-directed cyclopropanation proceeds in comparable rate judging from the observed enantiomeric excesses. Another interesting observation is that the Z-monobenzyl ether **1f** gave low chemical yield as well as low enantioselectivity even for a prolonged reaction time. (Entry 3) We assume that the disulfonamide-Zn complex coordinates to both oxygen atoms of **2f** (ether oxygen and alkoxide oxygen) in a bidentate manner resulting the low catalytic efficiency. Furthermore, the low enantioselectivity might be due to the competitive achiral path which is not negligible in this case.

Table 4

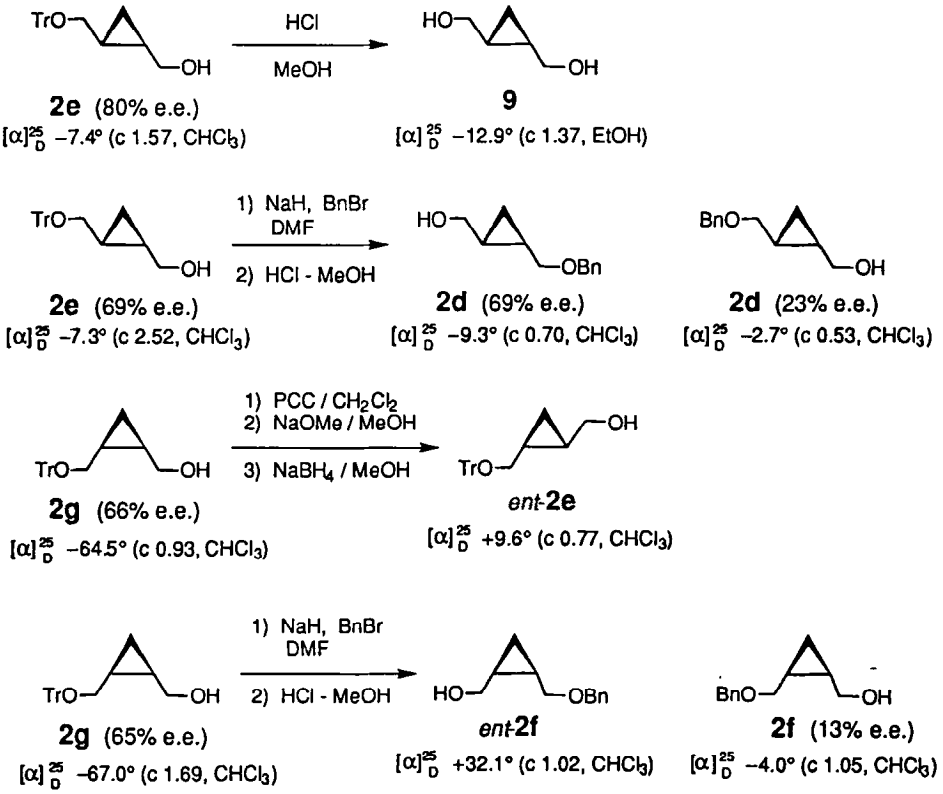


Entry	Allyl Alcohol 1	R^1	R^2	Time (h)	2	Yield (%)	e.e. (%)
1	**1d**	$BnOCH_2$	H	5	**2d**	70	36
2	**1e**	$TrOCH_2$	H	10	**2e**	86	80
3	**1f**	H	$BnOCH_2$	17	**2f**	36	13
4	**1g**	H	$TrOCH_2$	10	**2g**	77	65

Enantiomeric excesses of **2d~2g** were determined by HPLC analysis (see Experimental Section). Absolute configurations were unambiguously established as shown by comparing the sign of rotation value[20] with those of authentic sample prepared by the transformations shown in Scheme 5. First, trans trityloxy derivative **2e** with 80% e.e. ($[\alpha]_D^{25}$ -7.4° (*c* 1.57, $CHCl_3$)) was detritylated with HCl-MeOH to afford (2*R*,3*R*)-2,3-methano-1,4-butanediol **9**[19] ($[\alpha]_D^{25}$ -12.9° (*c* 1.37, EtOH)). Absolute configuration of **2e** was thus established as shown. Then, the stereochemically established **2e** with 69% e.e. ($[\alpha]_D^{25}$ -7.3° (*c* 2.52, $CHCl_3$)) was benzylated and detritylated to afford (2*R*,3*R*)-4-benzyloxy-2,3-methano-1-butanol (**2d**) which has the negative rotation value ($[\alpha]_D^{25}$ -9.3° (*c* 0.70, $CHCl_3$)). Since trans benzyloxy derivative (23% e.e.) obtained by the cyclopropanation of **1d** showed the same negative rotation value ($[\alpha]_D^{25}$ -2.7° (*c* 0.53, $CHCl_3$)), absolute configuration of **2d** was established as 2*R*,3*R*. Absolute configuration of cis trityloxy derivative **2g** was

established by correlating to the trans trityloxy derivative *ent*-**2e**. Thus, **2g** with 66% e.e. ($[\alpha]_D^{25}$ -64.5° (*c* 0.93, $CHCl_3$)) was oxidized with PCC to the aldehyde and the latter was epimerized to the thermodynamically more stable trans aldehyde with NaOMe[21] in methanol. Resulting aldehyde was then reduced with $NaBH_4$ to obtain trans trityloxy derivative which showed the positive rotation value (*ent*-**2e**, $[\alpha]_D^{25}$ +9.6° (*c* 0.77, $CHCl_3$)). Finally, absolute configuration of the cis benzyloxy derivative **2f** ($[\alpha]_D^{25}$ -4.0° (*c* 1.05, $CHCl_3$) as 13% e.e.) was determined to be 2*R*,3*S* by comparing with the authentic sample ((2*S*,3*R*)-4-benzyloxy-2,3-methano-1-butanol (*ent*-**2f**) with 65% e.e.; $[\alpha]_D^{25}$ +32.1° (*c* 1.02, $CHCl_3$)) prepared from the stereochemically established **2g** with 65% e.e. ($[\alpha]_D^{25}$ -67.0° (*c* 1.69, $CHCl_3$)) by benzylation followed by detritylation. Absolute configurations of the cyclopropanation products were thus unambiguously established.

Scheme 5



In conclusion, we have found that the sulfonamide-modified zinc complex catalyzed the Simmons-Smith cyclopropanation of an allylic alcohol. It should be noted that this is the first example of a catalytic and enantioselective Simmons-Smith reaction. As mentioned briefly in the introductory part, improvement of our methodology has been investigated by Denmark *et al.* by changing the reaction protocol and the modification of the sulfonyl group.[10] From a mechanistic point of view, we do not have any experimental evidence as to how the chiral disulfonamide-modified zinc complex participates in the transition state because of the multiplicity of zinc species such as zinc alkoxide, carbenoid zinc, and zinc iodide in addition to the chiral zinc complex. We

recently found that the disulfonamide-modified aluminum complex has also a catalytic activity in a similar Simmons-Smith reaction.[18,22] It is quite interesting that both aluminum and zinc complex showed similar enantioselectivities as well as the same enantioface selection, although the number of coordination sites is different. These results will be helpful for the understanding the reaction mechanism. The most important point is that only sulfonamide-modified metal complex has a catalytic activity in the Simmons-Smith cyclopropanation. Although excellent enantioselectivity was observed with the chiral boron complex developed by Charette *et al.*[9] their method requires a stoichiometric amount of chiral auxiliary. We speculate that the an increase in the Lewis acidity of the metal salts by the substitution with an electron-withdrawing group might be responsible for attaining a catalytic activity. From a synthetic point of view, it is important to note again that upon use of a given enantiomer of **4** the cyclopropanation occurs from the same enantioface of the olefin regardless of its geometry. Further, the present methodology is successfully applied to the cyclopropanation of stannyl and silyl-substituted allyl alcohol providing the first entry to the catalytic and enantioselective route to stannyl and silyl substituted cyclopropanes[23] of potential synthetic intermediates.

Experimental Section

All melting points were determined with a Yanagimoto MP-21 melting point apparatus and were uncorrected. Optical rotations were measured with a Horiba WEPA-200 auto digital polarimeter. Infrared (IR) spectra were recorded on a JASCO A-202 spectrometer. ^{1}H-NMR spectra were measured with a Brucker AM 200 (200MHz), and a Brucker AM 400 (400MHz) spectrometer. The chemical shifts are expressed in ppm downfield from tetramethylsilane, using tetramethylsilane (δ=0) and/or residual chloroform (δ=7.25) as an internal standard. Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad signal. Mass spectra were taken with a Hitachi RMU-6MG mass spectrometer. Unless otherwise noted, all experiments were carried out under an atmosphere of dry argon using anhydrous solvents. For thin layer chromatographic (TLC) analyses, Merck precoated TLC plates (silica gel 60 F254, 0.25mm, Art 5715) were used. The following abbreviations were used for solvents: tetrahydrofuran (THF), diethyl ether (Et_2O), ethyl acetate (AcOEt), methanol (MeOH), and dichloromethane (CH_2Cl_2).

(1*R*,2*R*)-1,2-*N*,*N*'-Bis(substitutedbenzenesulfonylamino)cyclohexane (4a~4f):

Sulfonamides, **4a~4f**, were prepared from (1*R*,2*R*)-1,2-diaminocyclohexane[24] and the corresponding sulfonylchlorides in the presence of diisopropylethylamine[2c]. Physical and spectral data of **4a~4f** are as follows: **4a** m.p. 106.0 °C: $[\alpha]_D^{20}$ -4.0° (*c* 0.49, acetone): IR (KBr) 3438, 3283, 2940, 2868, 1638, 1449, 1420, 1321, 1163, 1094, 1057, 1017, 918, 868, 752, 723, 687 cm^{-1}: ^{1}H-NMR ($CDCl_3$) δ 1.11 (4H, m), 1.56 (4H, m), 2.76 (2H, m), 4.72 (2H, d, *J*=5.8Hz), 7.57 (6H, m), 7.89 (4H, m): HRMS calcd for $C_{18}H_{23}N_2O_4S_2$ ([M+H]$^+$) 395.1099, found 395.1101. **4b**: m.p. 187.0 °C: $[\alpha]_D^{20}$ -59.2° (*c* 1.52, acetone): IR (KBr) 3418, 3054, 2939, 1504, 1451, 1328, 1158 cm^{-1}: ^{1}H-NMR (DMSO-*d*$_6$) δ 1.04 (2H, m), 1.27 (2H, m), 1.52 (4H, m), 3.14 (2H, m), 7.82 (2H, br), 7.83 (4H, m), 7.92 (2H, m), 8.04 (2H, m): HRMS calcd for $C_{18}H_{21}N_4O_8S_2$ ([M+H]$^+$) 485.0801, found 485.0803. **4c**: m.p. 168.0 °C: $[\alpha]_D^{20}$ -36.6° (*c* 1.13, acetone): IR (KBr) 3260, 2938, 1528, 1439, 1356, 1165, 1123, 1073, 912, 878, 735, 667 cm^{-1}: ^{1}H-NMR (DMSO-*d*$_6$) δ 1.05 (2H, m), 1.17 (2H, m), 1.45 (4H, m), 2.94 (2H, m), 7.86 (4H, m), 8.14 (2H, ddd, *J*=1.0, 1.6, 8.0Hz), 8.43 (2H, ddd, *J*=1.0, 2.3, 8.0Hz), 8.50 (2H, dd, *J*=2.0, 2.0Hz): HRMS calcd for

$C_{18}H_{21}N_4O_8S_2$ ([M+H]$^+$) 485.0801, found 485.0807. **4d**: m.p. 225.0 °C: $[\alpha]_D^{20}$ -19.9° (*c* 0.52, acetone): IR (KBr) 3247, 3112, 2940, 2863, 1935, 1802, 1609, 1530, 1437, 1402, 1350, 1310, 1165, 1080, 1013, 968, 909, 857, 739, 685, 650 cm^{-1}: ^{1}H-NMR (DMSO-*d*6) δ 1.05 (2H, m), 1.17 (2H, m), 1.46 (4H, m), 2.96 (2H, m), 7.91 (2H, d, *J*=7.8Hz), 8.00 (4H, d, *J*=8.9Hz), 8.35 (4H, d, *J*=8.9Hz): HRMS calcd for $C_{18}H_{20}N_4O_8S_2$ (M$^+$) 484.0722, found 484.0698. **4e**: m.p. 222.0 °C: $[\alpha]_D^{20}$ -10.7° (*c* 0.54, acetone): IR (KBr) 3382, 3310, 3279, 3108, 2949, 2926, 2863, 1941, 1659, 1611, 1545, 1453, 1404, 1335, 1240, 1136, 1092, 1065, 1017, 976, 951, 903, 855, 837, 787, 754, 716, 619 cm^{-1}: ^{1}H-NMR ($CDCl_3$) δ 1.15 (4H, m), 1.56 (4H, m), 2.85 (2H, br), 4.00 (2H, d, *J*=6.3Hz), 7.81 (4H, d, *J*=8.3Hz), 8.02 (4H, d, *J*=8.3Hz): HRMS calcd for $C_{20}H_{20}F_5N_2O_4S_2$ ([M-F]$^+$) 511.0785, found 511.0762. **4f**: m.p. 215.0 °C: $[\alpha]_D^{20}$ -4.3° (*c* 1.12, acetone): IR (KBr) 3297, 3090, 2946, 2868, 1626, 1456, 1362, 1335, 1283, 1138, 1003, 982, 953, 905, 845, 700, 683, 633 cm^{-1}: ^{1}H-NMR (DMSO-*d*6) δ 1.13 (4H, m), 1.45 (4H, m), 3.02 (2H, br), 8.02 (2H, s), 8.31 (4H, s), 8.40 (2H, s): HRMS calcd for $C_{22}H_{18}F_{11}N_2O_4S_2$ ([M-F]$^+$) 647.0532, found 647.0525: Anal. calcd for $C_{22}H_{18}F_{12}N_2O_4S_2$, C 39.65, H 2.72, N 4.20, found C 39.41, H 2.63, N 4.13.

Typical Procedure for the Cyclopropanation of an Allylic Alcohol (Table 3, Entry 11):

To a solution of **4d** (354 mg, 0.73 mmol, 12 mol%) and (*E*)-5-phenyl-2-penten-1-ol **1c** (988 mg, 6.1 mmol) in 200 mL of anhydrous CH_2Cl_2 was added successively a hexane solution of Et_2Zn (0.98 M, 12.4 mL, 12.2 mmol) and CH_2I_2 (4.89 g, 18.3 mmol) in 20 mL of CH_2Cl_2 at -23°C. The reaction mixture was stirred at that temperature for 5 hr, then 40 mL of 2*N* NaOH solution was added, and the product was extracted with Et_2O. The organic phase was washed with Sat. NaCl solution, dried over anhydrous Na_2SO_4, and condensed under reduced pressure. The residue was chromatographed on silica gel (AcOEt/n-hexane=1/4) to afford (2*R*,3*R*)-5-phenyl-2,3-methano-1-pentanol as a colorless oil (**2c**, 1.06 g, quant, $[\alpha]_D^{20}$ -20.3° (*c* 1.14, $CHCl_3$)). The sulfonamide **4d** was recovered quantitatively from the combined aqueous solution after being acidified with HCl solution. The enantiomeric excess of **2c** was determined by HPLC analysis (CHIRALPAK AD (Daicel Chemical Ind. Ltd.); eluent, 2% 2-propanol in hexane; flow rate, 0.5 mL/min; detection, 254-nm light) t_R of 2*R*,3*R*-isomer, 30 min; t_R of 2*S*,3*S*-isomer, 33 min.; IR (neat) 3345, 3062, 3025, 2997, 2921, 2855, 1723, 1603, 1584, 1495, 1453, 1289, 1202, 1140, 1062, 1018 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.36 (2H, m), 0.63 (1H, m), 0.84 (1H, m), 1.17 (1H, t, *J*=5.5Hz), 1.58 (2H, m), 2.72 (2H, m), 3.40 (2H, m), 7.26 (5H, m); EIMS *m/z* (M$^+$) 176, 158, 143, 129, 117, 105, 91, 41; HRMS calcd for $C_{12}H_{16}O$ (M$^+$) 176.1201, found 176.1175.

In a similar manner, the cyclopropanation of allylic alcohols, **1a**, **1b**, and **1d~1g**, were performed to obtain the corresponding cyclopropanes, **2a**, **2b** and **2d~2g**. Physical and spectral data of **2a**, **2b** and **2d~2g** are as follows: (2*R*,3*R*)-3-phenyl-2,3-methano-1-propanol (**2a**): $[\alpha]_D^{20}$ -56.2° (*c* 0.60, $CHCl_3$) for 75% e.e.; HPLC analysis (CHIRALCEL OD (Daicel Chemical Ind. Ltd.); eluent, 5% 2-propanol in hexane; flow rate, 1.0 mL/min) t_R of 2*R*,3*R*-isomer, 21 min; t_R of 2*S*,3*S*-isomer, 14 min; IR (neat) 3335, 3064, 3026, 2923, 2871, 1605, 1497, 1462, 1444, 1413, 1091, 1032, 1020 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.96 (2H, m), 1.43 (1H, br), 1.44 (1H, m), 1.84 (1H, ddd, *J*=8.5, 5.9, 5.0Hz), 3.64 (2H, br), 7.08 (2H, m), 7.16 (1H, m), 7.26 (2H, m); EIMS *m/z* (M$^+$) 148, 130, 117, 115, 104, 91, 77, 51; HRMS calcd for $C_{10}H_{12}O$ (M$^+$) 148.0888, found 148.0874. (2*R*,3*S*)-3-phenyl-2,3-methano-1-propanol (**2b**): $[\alpha]_D^{20}$ -41.1° (*c* 1.42, $CHCl_3$) for 75% e.e.; HPLC analysis (CHIRALCEL OD (Daicel Chemical Ind. Ltd.); eluent, 5% 2-propanol in hexane; flow rate, 0.5 mL/min) t_R of 2*R*,3*S*-isomer, 12 min; t_R of 2*S*,3*R*-isomer, 17 min.; IR (neat) 3345, 3061, 3025, 2936, 2876, 1603, 1497, 1449, 1325, 1088, 1026, 770 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ

0.89 (1H, ddd, *J*=5.4, 5.4, 5.4Hz), 1.05 (1H, ddd, *J*=8.5, 8.5, 5.4Hz), 1.11 (1H, br), 1.51 (1H, m), 2.31 (1H, ddd, *J*=8.5, 8.5, 5.4Hz), 3.27 (1H, dd, *J*=11.6, 8.7Hz), 3.47 (1H, br), 7.27 (5H, m); EIMS *m/z* (M^+) 148, 130, 117, 115, 104, 91, 77; HRMS calcd for $C_{10}H_{12}O$ (M^+) 148.0888, found 148.0875. (2*R*,3*R*)-4-benzyloxy-2,3-methano-1-butanol (**2d**): $[\alpha]_D^{20}$ -2.7° (*c* 0.53, $CHCl_3$) for 23% e.e.; HPLC analysis (CHIRALCEL OJ (Daicel Chemical Ind. Ltd.); eluent, 2% 2-propanol in hexane; flow rate, 0.5 mL/min) t_R of 2*R*,3*R*-isomer, 87 min; t_R of 2*S*,3*S*-isomer, 105 min.; IR (neat) 3391, 3065, 3003, 2863, 1719, 1532, 1497, 1455, 1364, 1204, 1167, 1073 1028 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.51 (2H, m), 1.14 (2H, m), 1.60 (1H, br), 3.28 (1H, m), 3.35-3.60 (3H, m), 4.53 (2H, s), 7.34 (5H, m); EIMS *m/z* 193 ($[M+1]^+$), 161, 129, 107, 121, 107, 91; 41; HRMS calcd for $C_{12}H_{16}O_2$ (M^+) 192.1150, found 192.1166. (2*R*,3*R*)-4-trityloxy-2,3-methano-1-butanol (**2e**): $[\alpha]_D^{20}$ -7.3° (*c* 2.52, $CHCl_3$) for 69% e.e.; HPLC analysis (CHIRALCEL OD (Daicel Chemical Ind. Ltd.); eluent, 2% 2-propanol in hexane; flow rate, 1.0 mL/min) t_R of 2*R*,3*R*-isomer, 23 min; t_R of 2*S*,3*S*-isomer, 17 min.; IR (neat) 3335, 3057, 3029, 2921, 2857, 1595, 1491, 1447, 1379, 1215, 1154, 1121 1073, 1038 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.47 (2H, m), 0.99 (2H, m), 1.36 (1H, br), 2.89 (1H, dd, *J*=6.6, 9.7Hz), 3.06 (1H, dd, *J*=9.7, 5.7Hz), 3.45 (1H, br), 3.53 (1H, br), 7.26 (9H, m), 7.44 (6H, m); EIMS *m/z* 344 (M^+), 313, 267, 259, 243, 183, 165; 105; HRMS calcd for $C_{24}H_{24}O_2$ (M^+) 344.1776, found 344.1780. (2*R*,3*S*)-4-benzyloxy-2,3-methano-1-butanol (**2f**): $[\alpha]_D^{20}$ -4.0° (*c* 1.05, $CHCl_3$) for 13% e.e.; HPLC analysis (CHIRALCEL OD (Daicel Chemical Ind. Ltd.); eluent, 5% 2-propanol in hexane; flow rate, 0.5 mL/min) t_R of 2*R*,3*S*-isomer, 59 min; t_R of 2*S*,3*R*-isomer, 54 min.; IR (neat) 3441, 3067, 3029, 2867, 1960, 1815, 1605, 1453, 1422, 1375, 1329, 1250 1210, 1161, 1071 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.22 (1H, ddd, *J*=5.3, 5.3, 5.3Hz), 0.81 (1H, ddd, *J*=8.2, 8.2, 5.3Hz), 1.36 (2H, m), 1.60 (1H, br), 3.14 (2H, m), 3.94 (2H, m), 4.51 (1H, d, *J*=11.7Hz), 4.59 (1H, d, *J*=11.7Hz), 7.35 (5H, m); EIMS *m/z* 192 (M^+), 175, 161, 130, 121, 107, 91; HRMS m/z calcd for $C_{12}H_{16}O_2$ (M^+) 192.1150, found 192.1138. (2*R*,3*S*)-4-trityloxy-2,3-methano1-butan-ol (**2g**): $[\alpha]_D^{20}$ -64.5° (*c* 0.93, $CHCl_3$) for 66% e.e.; HPLC analysis (CHIRALCEL OD (Daicel Chemical Ind. Ltd.); eluent, 2% 2-propanol in hexane; flow rate, 0.5 mL/min) t_R of 2*R*,3*S*-isomer, 22 min; t_R of 2*S*,3*R*-isomer, 19 min.; IR (neat) 3513, 3085, 3059, 3019, 2953, 2878, 1964, 1815, 1595, 1489, 1451, 1412, 1348, 1318, 1258, 1219, 1183, 1086, 1042 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ -0.08 (1H, ddd, *J*=5.2, 5.2, 5.2Hz), 0.71 (1H, ddd, *J*=8.3, 8.3, 5.2Hz), 1.38 (2H, m), 2.37 (1H, dd, *J*=10.6, 10.6Hz), 2.86 (1H, ddd, *J*=12.0, 10.6, 1.4Hz), 3.18 (1H, dd, *J*=10.6, 1.4Hz), 3.81 (2H, m), 7.24 (3H, m), 7.31 (6H, m), 7.46 (6H, m); EIMS *m/z* 344 (M^+), 267, 267, 259, 243, 183, 165; 105; HRMS calcd for $C_{24}H_{24}O_2$ (M^+) 344.1776, found 344.1801.

Determination of the Absolute Configuration of 5-Phenyl-2,3-methano-1-pentanol (2c):

5-Phenyl-2,3-methanopentyl benzoate (**5**): A mixture of 5-phenyl-2,3-methano-1-pentanol (**2c**, $[\alpha]_D^{20}$ -20.3° (*c* 1.14, $CHCl_3$), 82% e.e., 1.07 g, 6.09 mmol), benzoyl chloride (1.03 g, 7.31 mmol), and pyridine (723 mg, 9.14 mmol) in 20 mL of anhydrous CH_2Cl_2 was stirred at room temperature for 30 min. After addition of 1*N* HCl (10 mL), the product was extracted with ether. Organic phase was combined, washed with brine, and dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel (AcOEt/n-hexane=1/50) to afford 5-phenyl-2,3-methanopentyl benzoate (1.64 g, 96% yield) as a colorless oil. $[\alpha]_D^{20}$ -3.7° (*c* 0.70, $CHCl_3$); IR (neat) 3850, 3741, 3418, 3063, 3026, 2300, 2923, 2854, 2359, 2339, 1716, 1652, 1602, 1585, 1558, 1539, 1495, 1418, 1376, 1314, 1273, 1176, 1110, 1070, 1026 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.44 (1H, m), 0.55 (1H, m), 0.80 (1H, m), 1.04 (1H, m), 1.52 (1H, m), 1.65 (1H, m), 2.72 (2H, m), 4.14 (2H, m), 7.17 (3H, m), 7.27 (2H, m), 7.45 (2H, m), 7.56 (1H, m), 8.07 (2H, m);

EIMS *m/z* (M^+) 280, 159. 5-Bromo-5-phenyl-2,3-methanopentyl benzoate (**6**): A mixture of 5-phenyl-2,3-methanopentyl benzoate (**5**, 1.54 g, 5.48 mmol), *N*-bromosuccinimide (1.07 g, 6.03 mmol), and AIBN (9.0 mg, 0.06 mmol) in CCl_4 (90 mL) was heated under refluxing for 2 hr. The reaction mixture was cooled to room temperature, and the insoluble material was filtered off. The filtrate was diluted with Et_2O, washed with brine, and dried over Na_2SO_4. After removal of the solvent, the residue was chromatographed on silica gel (AcOEt/n-hexane=1/50) to afford 5-bromo-5-phenyl-2,3-methanopentyl benzoate (**6**, 1.63g, 83% yield) as a diastereomeric mixture. 5-Phenylseleno-5-phenyl-2,3-methano-1-pentanol (**7**): To a solution of diphenyldiselenide (1.05 g, 3.37 mmol) in EtOH (60 mL) was added $NaBH_4$ (265 mg, 7.02 mmol). After an exothermic reaction was ceased, 5-bromo-5-phenyl-2,3-methanopentyl benzoate (**6**, 1.01 g, 2.81 mmol) in EtOH (16 mL) was added dropwise, and the reaction mixture was heated under refluxing overnight. The reaction mixture was cooled to room temperature, and was added water. The product was extracted with $CHCl_3$, and the organic phase was washed with brine, and dried over Na_2SO_4. After removal of the solvent, the residue was chromatographed on silica gel (AcOEt/n-hexane=1/5) to afford 5-phenylseleno-5-phenyl-2,3-methano-1-pentanol (**7**, 513 mg, 55% yield) as a diastereomeric mixture. 5-Phenyl-2,3-methano-4-penten-1-ol (**8**): To a THF solution (20 mL) of 5-phenylseleno-5-phenyl-2,3-methano-1-pentanol (**7**, 495 mg, 1.49 mmol) was added 30% aqueous H_2O_2 (4 mL) at 0°C, and the mixture was stirred for 2 hr. The product was extracted with AcOEt, and the organic phase was washed with brine, and dried over Na_2SO_4. After removal of the solvent, the residue was chromatographed on silica gel (AcOEt/n-hexane=1/2) to afford 5-phenyl-2,3-methano-4-penten-1-ol as a colorless oil (**8**, 87.8 mg, 34%). $[\alpha]_D^{20}$ -86.6° (*c* 0.78, $CHCl_3$); IR (neat) 3346, 3022, 2348, 1648, 1596, 1494, 1446, 1050, 958, 745 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.95 (2H, m), 1.41 (1H, m), 0.79 (2H, m), 1.29 (1H, m), 1.36 (2H, m), 3.57 (2H, m), 5.79 (1H, dd, *J*=15.8, 8.4Hz), 6.47 (1H, d, *J*=15.8Hz), 7.30 (5H, m); EIMS *m/z* 174 (M^+), 156, 143. (2*R*,3*R*)-2,3-Methano-1,4-butanediol (**9**): Ozone gas was passed into a solution of 5-phenyl-2,3-methano-4-penten-1-ol (**8**, 130 mg, 0.75 mmol) in MeOH (50 mL) at -78°C until the reaction mixture became blue. Sodium borohydride (241 mg, 6.35 mmol) was added, and the mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure, and the residue was acidified with 1*N* HCl. The product was extracted with AcOEt, and the organic phase was washed with brine, and dried over Na_2SO_4. After removal of the solvent, the residue was chromatographed on silica gel (AcOEt) to afford (2*R*,3*R*)-2,3-methano-1,4-butanediol as a colorless oil (**9**, 52 mg, 68%). $[\alpha]_D^{20}$ -12.1° (*c* 0.63, EtOH). Spectral data (IR and ^{1}H-NMR) were in good accordance with those in literature.[19]

Determination of the Absolute Configuration of *trans*-4-Trityloxy-2,3-methano-1-butanol (2e):

To a solution of *trans*-4-trityloxy-2,3-methano-1-butanol (**2e**, $[\alpha]_D^{20}$ -7.4° (*c* 1.57, $CHCl_3$) for 80% e.e., 94.0 mg, 0.27 mmol) in MeOH (5 mL) was added 1*N* HCl (0.3 mL), and the mixture was stirred at room temperature for 5 hr. The solution was neutralized with $NaHCO_3$ and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel (MeOH/CH_2Cl_2=1/10) to afford (2*R*,3*R*)-2,3-methano-1,4-butanediol (**9**, 25.4 mg, 91%). $[\alpha]_D^{20}$ -12.9° (*c* 0.63, EtOH).

Preparation of Authentic (2*R*,3*R*)-4-Benzyloxy-2,3-methano-1-butanol (2d):

Stereochemically established (2*R*,3*R*)-4-trityloxy-2,3-methano-1-butanol (**2e**, $[\alpha]_D^{20}$ -7.3° (*c* 2.52, $CHCl_3$) for 69% e.e., 103.2 mg, 0.30 mmol) in DMF (10 mL) was added NaH (*ca* 60% in mineral oil, 14.4

mg, 0.36 mmol) at 0°C, and the reaction mixture was stirred for 30 min. Benzyl bromide (0.04 mL, 0.36 mmol) was then added slowly at 0°C, and the reaction mixture was stirred at room temperature for 12 hr. Water was added, and the product was extracted with Et_2O. The organic phase was washed with brine, dried over Na_2SO_4, and condensed under reduced pressure. The residue was chromatographed on silica gel (AcOEt/n-hexane=3/100) to afford (2*R*,3*R*)-1-benzyloxy-4-trityloxy-2,3-methanobutane (84.4 mg, 65%). $[\alpha]_D^{20}$ -13.2° (*c* 0.52, $CHCl_3$). IR (neat) 3412, 2949, 1835, 1067 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.46 (2H, m), 0.99 (2H, m), 2.95 (1H, dd, *J*=6.3, 11.7Hz), 2.99 (1H, dd, *J*=9.5, 6.3Hz), 3.38 (2H, d, *J*=6.6Hz), 4.54 (1H, d, *J*=12.0Hz), 4.61 (1H, d, *J*=12.0Hz), 7.27 (15H, m), 7.45 (5H, m); EIMS *m/z* 434 (M^+), 357, 343, 243, 191, 165, 91; HRMS calcd for $C_{24}H_{23}O_2$ ([M-$C_6H_5CH_2$]$^+$) 343.1698, found 343.1709. (2*R*,3*R*)-1-Benzyloxy-4-trityloxy-2,3-methanobutane (72.9 mg, 0.17 mmol) in MeOH (5 mL) was added 1*N* HCl (0.2 mL), and the mixture was stirred at room temperature for 12 hr. The solution was neutralized with $NaHCO_3$ and the product was extracted with Et_2O. The organic phase was washed with brine, dried over Na_2SO_4, and condensed under reduced pressure. The residue was chromatographed on silica gel (AcOEt/n-hexane=1/5) to afford (2*R*,3*R*)-4-benzyloxy-2,3-methano-1-butanol (**2d**, 31.7 mg, 98%). $[\alpha]_D^{20}$ -9.3° (*c* 0.70, $CHCl_3$).

Determination of *cis*-4-Trityloxy-2,3-methano-1-butanol (2g):

To a stirred solution of PCC (318.0 mg, 1.48 mmol) and MS3A (80 mg) and NaOAc (242.1 mg, 2.95 mmol) in anhydrous CH_2Cl_2 was added *cis*-4-trityloxy-2,3-methano-1-butanol (**2g**, $[\alpha]_D^{20}$ -64.5° (*c* 0.93, $CHCl_3$) for 66% e.e., 81.3 mg, 0.24 mmol) at room temperature, and the mixture was stirred for 1h. Et_2O (15mL) and $MgSO_4$ were added, and the mixture was stirred for an additional 5 min. Insoluble materials were filtered off, and the filtrate was condensed under reduced pressure. The residue was chromatographed on silica gel (AcOEt/n-hexane=1/10) to afford *cis*-4-trityloxy-2,3-methanobutyraldehyde (58.2 mg, 72%). $[\alpha]_D^{20}$ -6.0° (*c* 0.50, $CHCl_3$); IR (neat) 3447, 3021, 2922, 2853, 1698, 1489, 1447, 1262 1219, 1177, 1154 1071, 1032, 961, 928, 901, 804, 768, 750, 708, 633 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.18 (2H, m), 1.78 (1H, m), 1.94 (1H, m), 2.99 (1H, dd, *J*=10.4, 8.6Hz), 3.57 (1H, dd, *J*=10.4, 5.9Hz), 7.27 (10H, m), 7.42 (5H, m); EIMS *m/z* 259 ([M-C_5H_7O]$^+$), 243, 165, 83; HRMS calcd for C_5H_7O 83.0497, found 83.0494. A mixture of *cis*-4-trityloxy-2,3-methanobutyraldehyde (58.2 mg, 0.17 mmol) and NaOMe (13.8 mg, 0.26 mmol) in MeOH (20 mL) was heated under refluxing for 48 hr. After being cooled to room temperature, the reaction mixture was added sat. NH_4Cl, and the product was extracted with Et_2O. The organic phase was washed with brine, dried over Na_2SO_4, and condensed under reduced pressure. The residue was chromatographed on silica gel (AcOEt/n-hexane=1/10) to afford a mixture (trans/cis=6/1) of 4-trityloxy-2,3-methanobutyraldehyde (38.7 mg, 67%). Without separation, the mixture was dissolved in MeOH (5 mL), and was added $NaBH_4$ (4.7 mg, 0.12 mmol). The mixture was stirred for 30 min, and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel (AcOEt/n-hexane=1/10) to afford (2*S*,3*S*)-4-trityloxy-2,3-methano-1-butanol (*ent*-**2e**, 24.4 mg, 63%). $[\alpha]_D^{20}$ +9.6° (*c* 0.77, $CHCl_3$)^{20}: Spectral data (IR and ^{1}H-NMR) of *ent*-**2e** were identical with those of **2e**.

Preparation of Authentic (2*S*,3*R*)-4-Benzyloxy-2,3-methano-1-butanol (*ent*-2f):

To a solution of stereochemically established (2*R*,3*S*)-4-trityloxy-2,3-methano-1-butanol (**2g**, $[\alpha]_D^{20}$ -67.0° (*c* 1.69, $CHCl_3$) for 65% e.e., 106.8 mg, 0.31 mmol) in anhydrous DMF (10 mL) was added NaH (*ca* 60% in mineral oil, 14.9 mg, 0.37 mmol) at 0°C, and the reaction mixture was stirred for 30 min. Benzyl

bromide (0.04 mL, 0.36 mmol) was then added slowly at 0°C, and the reaction mixture was stirred at room temperature for 12 hr. Water was added, and the product was extracted with Et_2O. The organic phase was washed with brine, dried over Na_2SO_4, and condensed under reduced pressure. The residue was chromatographed on silica gel (AcOEt/n-hexane=1/20) to afford (2*R*,3*S*)-1-benzyloxy-4-trityloxy-2,3-methanobutane (99.8 mg, 74 %). $[\alpha]_D^{20}$ -1.3° (*c* 0.81, $CHCl_3$) as 66 % e.e.; IR (neat) 3387, 1896, 1385, 1071, 698 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.11 (1H, ddd, *J*=4.9, 4.9, 4.9Hz), 0.80 (1H, ddd, *J*=4.9, 8.3, 8.3Hz), 1.27 (2H, m), 2.94 (1H, dd, *J*=7.4, 10.2Hz), 3.22 (1H, dd, *J*=6.5, 10.0Hz), 3.26 (1H, dd, *J*=7.0, 10.0Hz), 3.39 (1H, dd, *J*=6.6, 10.2Hz), 4.39 (2H, s), 7.27 (15H, m), 7.44 (5H, m); HRMS calcd for $C_{31}H_{30}O_2$ (M^+) 434.2246, found 434.2226. (2*R*,3*S*)-1-benzyloxy-4-trityloxy-2,3-methanobutane (78.2 mg, 0.18 mmol) in MeOH (5 mL) was added 1*N* HCl (0.2 mL), and the mixture was stirred at room temperature for 12 hr. The solution was neutralized with $NaHCO_3$ and the product was extracted with Et_2O. The organic phase was washed with brine, dried over Na_2SO_4, and condensed under reduced pressure. The residue was chromatographed on silica gel (AcOEt/n-hexane=1/5) to afford (2*S*,3*R*)-4-benzyloxy-2,3-methano-1-butanol (*ent*-**2f**, 36.1 mg, quant). $[\alpha]_D^{20}$ +32.1° (c 1.02, $CHCl_3$) as 66 % e.e. Spectral data (IR and ^{1}H-NMR) of *ent*-**2f** were identical with those of **2f**.

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References and Notes

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