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N,N,N′,N′-Tetraalkyl-2,2′-dihydroxy-1,1′-binaphthyl-3,3′-dicarboxamides: Novel Chiral Auxiliaries for Asymmetric Simmons–Smith Cyclopropanation of Allylic Alcohols and for Asymmetric Diethylzinc Addition to Aldehydes

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The newly introduced title compounds were found to be efficient chiral auxiliaries for the asymmetric Simmons–Smith cyclopropanation of allylic alcohols and for asymmetric addition of diethylzinc to aldehydes. For example, Simmons-Smith cyclopropanation of cinnamyl alcohol in the presence of *N,N,N′,N′*-tetraethyl-2,2′-dihydroxy-1,1′-binaphthyl-3,3′-dicarboxamide (**1b**) proceeded with high enantioselectivity of 94% ee and addition of diethylzinc to benzaldehyde in the presence of *N,N,N′,N′*-tetraisopropyl-2,2′-dihydroxy-1,1′-binaphthyl-3,3′-dicarboxamide (**1e**) proceeded with enantioselectivity of 99% ee. Although the reaction mechanism of these reactions is still nuclear, a monomeric seven-membered 2,2′-dihydroxy-1,1′-binaphthyl-3,3′-dicarboxamide (**1**)–Zn complex is considered to be an active species which catalyzes the above reactions, on the basis of NMR experiments.

Carbon–carbon bond formation is a fundamental and indispensable method for constructing organic substances and the development of its enantioselective version is one of the most challenging task in organic synthesis. Toward this goal, many excellent reagents and catalysts have been introduced and high enantioselectivity has now been realized in several carbon–carbon bond forming reactions.[1] However, there still remains room for improvement in some reactions. The asymmetric Simmons–Smith reaction is one of such reactions. Simmons–Smith reaction of cyclic allylic alcohols,[2] chiral allylic ethers,[3] chiral enol ethers,[4] and unsaturated chiral acetals[5] has been known to proceed with high diastereoselectivity,[6] wherein oxygen functionalities of the substrates are ligated by iodomethylzinc species. As an extension of these reactions, asymmetric Simmons–Smith reaction of allylic alcohols has been studied and a moderate to excellent level of enantioselectivity has thus far been achieved by using various chiral auxiliaries including β-amino alcohol **A**,[7] bis(sulfonamido) derivatives **B**,[8] tartrate **C**,[9] tartaramide $\mathbf{D_1}$,[10] and tartrate-derived diol $\mathbf{E_1}$[11] (Chart 1). Though tartaramide $\mathbf{D_1}$ and diol $\mathbf{E_1}$ are used as catalysts in the form of the corresponding boron and titanium complexes ($\mathbf{D_2}$ and $\mathbf{E_2}$), other chiral auxiliaries (**A**—**C**) have been considered to form five-membered zinc chelates in situ. Although the mechanism of the reactions using these chiral auxiliaries has not been established unequivocally, the association of the respective metal complexes with allylic alcohols and iodomethylzinc species has been considered to be essential for effectively inducing asymmetry in the products.[7—11]

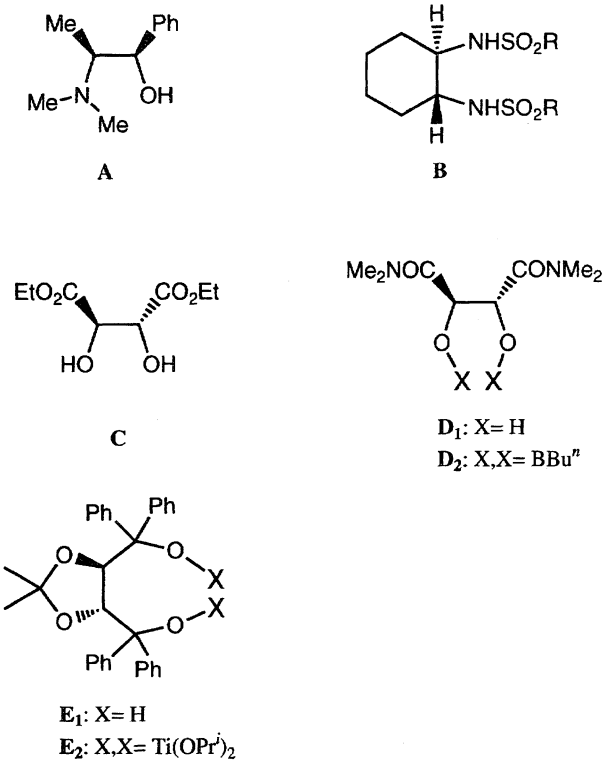


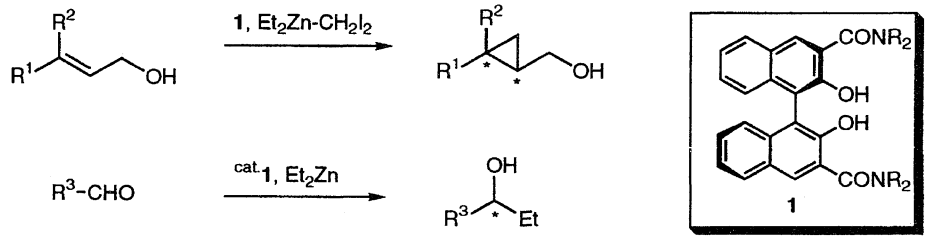
Chart 1.

Thus, the complexes having a Lewis acidic site for accepting allylic alcohols and a coordination site for iodomethylzinc

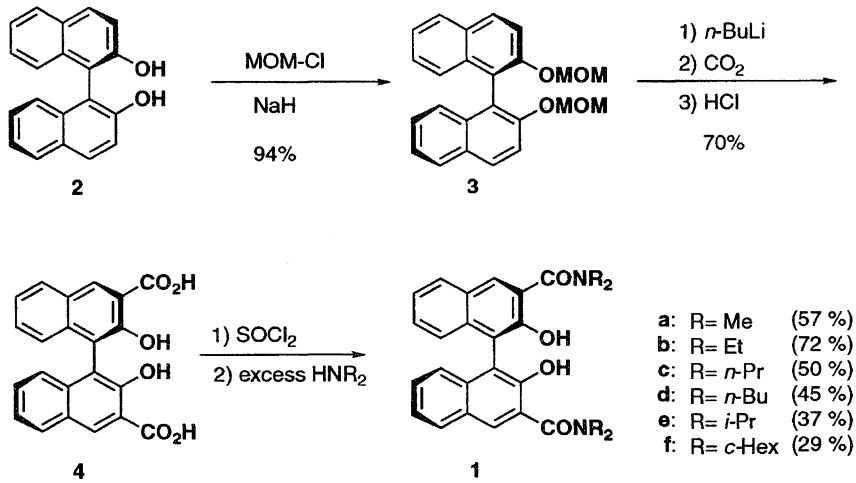
species are considered to provide a desirable reaction site for Simmons–Smith reaction. It is well-known that salicylic acid derivatives form chelate-complexes with various metal ions. It is also known that binaphthol-metal complex serves as an efficient chiral Lewis acid.[12] Considering these two results, we newly designed novel 2,2′-dihydroxy-1,1′-binaphthyl-derived compounds, *N*,*N*,*N*′,*N*′-tetraalkyl-2,2′-dihydroxy-1,1′-binaphthyl-3,3′-dicarboxamides (**1**: Hereafter, 2,2′-dihydroxy-1,1′-binaphthyl is referred to as BINOL.) as chiral auxiliaries for Simmons–Smith cyclopropanation (Scheme 1).[13] These compounds were also found to serves as effective chiral auxiliaries for enantioselective addition of dialkylzinc to aldehydes.[14] In this report, we discuss the title reactions using BINOL-3,3′-dicarboxamides and their reaction mechanisms.

Synthesis of Optically Active *N*,*N*,*N*′,*N*′-Tetraalkyl-BINOL-3,3′-dicarboxamides (1). Synthesis of the chiral auxiliaries (**1a**—**f**) was started from commercially available (*R*)- BINOL (**2**), as shown in Scheme 2. The hydroxy groups of **2** were protected as methoxymethyl (MOM) ethers. The resulting **3** was subjected to ortholithiation,[15] followed by carboxylation to give the corresponding 3,3′-dicarboxylic acid, which was hydrolyzed by treatment with hydrogen chloride in isopropyl alcohol-tetrahydrofuran (THF) to give BINOL-3,3′-dicarboxlic acid **4**. Compound **4** was then exposed to thionyl chloride[16] and the resulting acid chloride was treated with excess (> 10 molar amount) dialkylamines to give the corresponding amides (**1a**—**f**). The optical purity of **1a**—**f** was confirmed to be > 99% ee by HPLC analysis using an optically active column.

Asymmetric Simmons–Smith Cyclopropanation of Allylic Alcohols by Using *N*,*N*,*N*′,*N*′-Tetraalkyl-BINOL-3,3′-dicarboxamide. With optically active dicarboxamides (**1**) in hand, we first examined cyclopropanation of cinnamyl alcohol (**5a**) by using diethylzinc and diiodomethane as a carbenoid precursor. Since it has been reported that enantioselectivity of asymmetric Simmons–Smith reaction is strongly dependent on experimental conditions used,[8e] we extensively studied the reaction conditions using **1a** as a chiral auxiliary and found that stoichiometry of diethylzinc affected the degree and the sense of enantioselectivity (Table 1). The use of 2 molar amounts of diethylzinc gave (1*S*,2*S*)-2-phenylcyclopropanemethanol as the major enantiomer, although the chemical yield and enantiomeric excess were poor (Entry 1). However, (1*R*,2*R*)-isomer was obtained preferentially when more than 3 molar amounts of diethylzinc were used. The enantioselectivity improved as the amount of diethylzinc increased, and reached 67% ee, when 6 molar amounts of diethylzinc were used (Entry 5). Under these optimized reaction conditions, we next examined the effect of amide alkyl group of **1** on enantioselectivity (Entries 8, 11, 13, and 15) and found that ethylamide **1b** showed the highest enantioselectivity of 94% ee (Entry 8). Recently, Denmark and co-workers reported that the enantioselectivity in Simmons–Smith reaction of cinnamyl alcohol with chiral bis(sulfonamido) derivatives as a chiral ligand was improved by the addition of zinc iodide.[8e] According to this report, we also examined the reaction in the presence of 1 molar amount



Scheme 1.



Scheme 2.

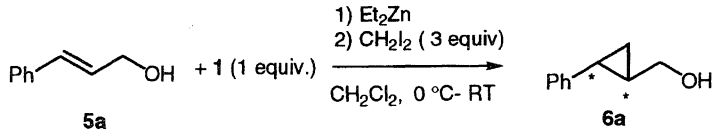


Table 1. Asymmetric Simmons–Smith Reaction of Cinnamyl Alcohol (**5a**) Using **1a—d** as Chiral Auxiliaries

Entry	Chiral auxiliary	Et_2Zn	Yield (%)	Ee(%)[a]	Confign[b]
1	**1a**	2 equiv.	7	14	1*S*, 2*S*
2	**1a**	3 equiv.	34	14	1*R*, 2*R*
3	**1a**	4 equiv.	85	26	1*R*, 2*R*
4	**1a**	5 equiv.	84	64	1*R*, 2*R*
5	**1a**	6 equiv.	90	67	1*R*, 2*R*
6[c]	**1a**	6 equiv.	80	42	1*R*, 2*R*
7	**1a**	6 equiv.+ZnI_2	87	75	1*R*, 2*R*
8	**1b**	6 equiv.	55	94	1*R*, 2*R*
9	**1b**	6 equiv.+ZnI_2	87	90	1*R*, 2*R*
10	**1b**	6 equiv.+THF	85	91	1*R*, 2*R*
11	**1c**	6 equiv.	51	85	1*R*, 2*R*
12	**1c**	6 equiv.+ZnI_2	88	79	1*R*, 2*R*
13	**1d**	6 equiv.	58	89	1*R*, 2*R*
14	**1d**	6 equiv.+ZnI_2	75	78	1*R*, 2*R*
15	**1e**	6 equiv.	60	51	1*R*, 2*R*
16	**1e**	6 equiv.+ZnI_2	87	29	1*R*, 2*R*

a) Enantiomeric excess was determined by HPLC analysis using a Daicel chiralcel OJ (eluent system; hexane : *i*-PrOH = 9 : 1). b) The absolute configuration was assigned by comparison of specific rotation (Ref. 8a). c) Chloroiodomethane was used instead of diiodomethane.

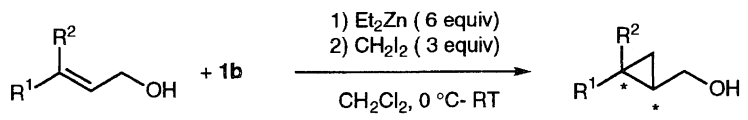
of zinc iodide but the addition of zinc iodide gave a negative effect on enantioselectivity, though the chemical yield were increased (Entries 9, 12, 14, and 16). The reaction using **1a** as the chiral auxiliary was an exception, here addition of zinc iodide also improved enantioselectivity to some extent (Entry 7). We also explored the possibility that addition of a polar solvent such as THF might improve enantioselectivity. However, the reaction in the presence of 1 molar amount of THF showed slightly diminished enantioselectivity of 91% ee, when 6 molar amounts of diethylzinc were used (Entry 10).

We next examined the cyclopropanation of other allylic alcohols by using **1b** as a chiral auxiliary (Table 2). The reaction of (*E*)-allylic alcohols proceeded smoothly with good enantioselectivity of > 85% ee (Entries 2—6). In contrast to this, the reaction of (*Z*)-allylic alcohols was relatively slow and showed substrate-dependent enantioselectivity. For example, the reaction of (Z)-cinnamyl alcohol (**5b**) showed high enantioselectivity of 92% ee (Entry 1), but that of (*Z*)-4-trityloxy-2-buten-1-ol gave a value of only 65% ee (Entry 7).

Although a stoichiometric amount of **1b** was used as a chiral auxiliary, it could be recovered intact from the reaction mixture by simple work-up procedure and used for another run without decay of enantioselectivity.

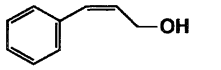
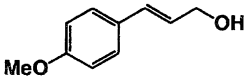
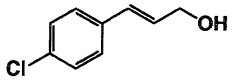
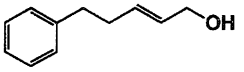
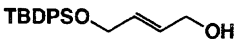
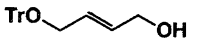
NMR and X-Ray Studies on the Structure of *N,N,N′,N′*-Tetraalkyl-BINOL-3,3′-dicarboxamide (1)–Diethylzinc Complex. As already mentioned, the mechanism of asymmetric Simmons–Smith reactions has not been established clearly. In order to get some clues to understand the mechanism, we performed the NMR experiment on the structure of **1a**–Et_2Zn complex in the solution. After compound **1a** was treated with 1 molar amount of diethylzinc in CD_2Cl_2 at room temperature, the reaction mixture was subjected to NMR analysis (Fig. 1,B). Disappearance of phenolic proton indicated the formation of zinc phenoxide. This was supported by another experiment: When the above reaction was carried out in CH_2Cl_2 in a 0.5 mmol scale, evolution of almost twice the molar amount of ethane (0.98 mmol) was observed.[17] The NMR spectrum also indicated that a newly formed species in the solution had a structure of C_2-symmetry, suggesting the formation of a seven-menbered chelate ring. However, the unusual high field shift of one of the *N*-methyl groups ($\delta = 1.76$) strongly suggested the association of the seven-membered chelate complex in solution. The NMR study of **1b**–Et_2Zn complex gave almost the same results as that of **1a**–Et_2Zn complex.

Fortunately, **1b**–Et_2Zn complex crystallized out from a 1 : 1 solution of **1b** and Et_2Zn in dichloromethane and excess hexane as a single crystal; its structure was determined unambiguously by X-ray diffraction. As shown in Fig. 2, the chelate complex was associated as the trimer of C_2-symmetry. This X-ray structure showed that one of the two *N*-ethyl groups was located close over the naphthalene ring. This fact well-explained why one of the two *N*-alkyl groups greatly shifted to upper field and at the same time suggested that the complex existed as a trimer also in the solution. In this complex, all the zinc ions were ligated by six oxygen atoms (phenoxide oxygen and amide carbonyl oxygen atoms). Among them, the central zinc ion took a trigonal prismatic geometry and the other two terminal zinc ions took a slightly distorted octahedral geometry. Accordingly, the zinc ions are coordinatively saturated; this complex is therefore considerred to be inactive as a catalyst. This agrees



5b-h **6b-h**

Table 2. Asymmetric Simmons–Smith Reaction of Allylic Alcohols (**5b**—**h**) Using **1b** as the Chiral Auxiliary

Entry	Substrate		Time (h)	Product	Yield (%)[a]	Ee (%)	Confign
1		(**5b**)	24	**6b**	44	92[b]	1*R*,2*S*[c]
2		(**5c**)	18	**6c**	78	94[d]	ND[e]
3		(**5d**)	15	**6d**	59	90[f]	ND[e]
4		(**5e**)	18	**6e**	65	89[d]	1*R*,2*R*[g]
5		(**5f**)	15	**6f**	59	87[h]	ND[e]
6		(**5g**)	15	**6g**	64	88[i]	1*R*,2*R*[g]
7		(**5h**)	15	**6h**	34[j]	65[i]	1*R*,2*S*[k]
8[l]	〃	(〃)	15	〃	76	16[i]	1*R*,2*S*[g]

a) Isolated yield unless otherwise mentioned. b) Determined by HPLC analysis using Daicel Chiralcel OJ (hexane : *i*-PrOH = 45 : 1). c) Assigned by chiroptical comparison with the literature values (Ref. 9a). d) Determined by HPLC analysis using Daicel Chiralcel OD (hexane : *i*-PrOH = 15 : 1). e) Not determined. f) Determined by HPLC analysis using Daicel Chiralcel OD (hexane : *i*-PrOH = 100 : 1) after acetylation. g) Assigned by chiroptical comparison with the literature values (Ref. 8d). h) Determined by HPLC analysis using Daicel Chralcel OD (hexane : *i*-PrOH = 100 : 1) after benzoylation. i) Determined by HPLC analysis using Daicel Chiralcel OD (hexane : *i*-PrOH = 30 : 1). j) Estimated by ^{1}H NMR analysis of the work-up mixture since the chromatographic separation of **5h** and **6h** was difficult. k) Determined by the elution order of enantiomers in HPLC analysis using Daicel Chiralcel OD (hexane : *i*-PrOH = 30 : 1) l) The reaction was carried out in the presence of 1 equivalent of zinc iodide in order to complete the reaction.

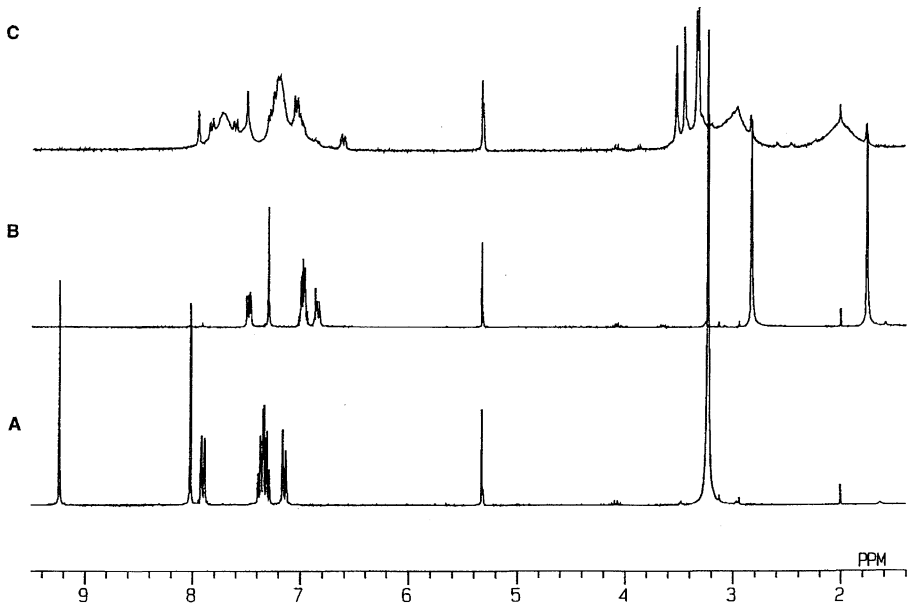


Fig. 1. 270 MHz ^{1}H NMR of **1a** in CD_2Cl_2 at room temperature (A), **1a**+Et_2Zn (1 equiv.) (B), and **1a**+Et_2Zn (5 equiv.) (C).

with the fact that Simmons-Smith reaction was very slow when two molar amounts of diethylzinc were used (One molar amount of diethylzinc should be used for generation of iodomethylzinc species: Table 1, Entry 1). The reaction proceeded smoothly and showed the highest enantioselectivity when six molar amounts of diethylzinc were used. To

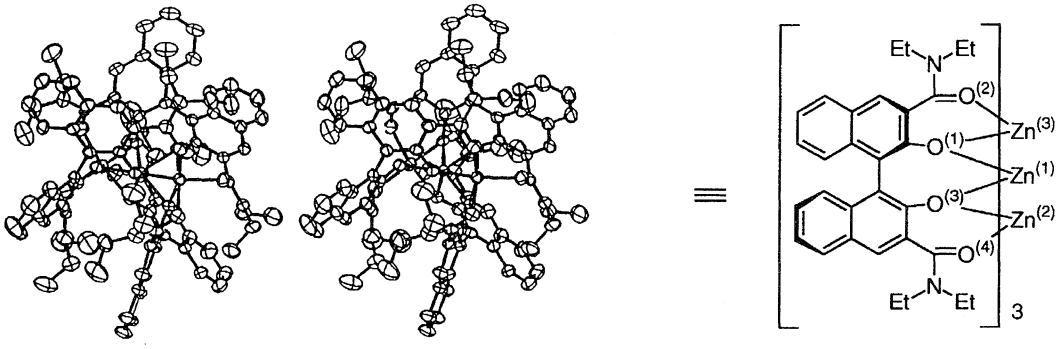
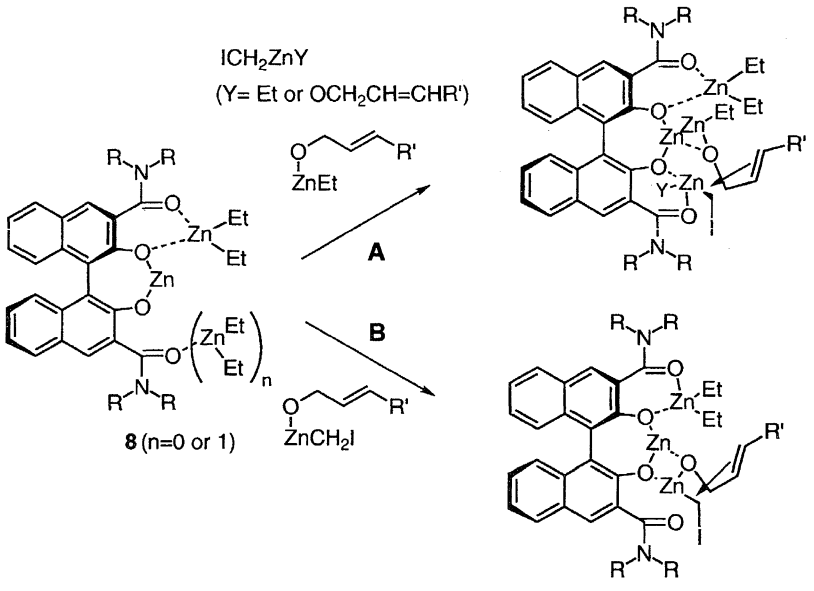


Fig. 2. Stereoview of crystal structure of **1b**–**Zn** complex; selected bond lengthes (Å) and bond angles (°) are as follows: O(1)–Zn-(1), 2.090(4); O(3)–Zn(1), 2.092 (4); O(1)–Zn(3), 2.112; O(2)–Zn(3), 2.055(4); O(3)–Zn(2), 2.090(4); O(4)–Zn(2), 2.062(4); O(1)–Zn(1)–O(3), 85.9(1); O(1)–Zn(3)–O(2), 87.2(1); O(3)–Zn(2)–O(4), 86.7(2); Zn(1)–O(1)–Zn(3), 85.0(1); Zn(1)–O(3)–Zn(2), 85.6 (1).

get more information on the structure of the complex in the presence of excess amount of diethylzinc, we added another diethylzinc to the 1 : 1 solution of **1a** and diethylzinc and we traced the change of the NMR signals. The signals at 1.8 and 2.8 ppm decreased gradually and two types of new signals [four singlet signals (δ = 3.33, 3.34, 3.46, and 3.53) and two broad signals (δ = 1.7—2.4 and 2.6—3.3)] appeared. When five molar amounts of diethylzinc were added, the signals at 1.8 and 2.8 ppm almost disappeared (Fig. 1, C). The four signals at 3.3—3.6 ppm suggested the formation of a new species which was neither trimeric nor C_2-symmetric. Although the structure of the new species is nuclear at present, we speculated that these four signals should be attributed to the *N*-methyl groups of monomeric species **8**. Coordination of an oxygen atom in the trimeric complex to an extra diethylzinc prompted dissociation of the trimer and provided a monomer **8** which had a Lewis acidic zinc ion[18] and a Lewis basic amide carbonyl which might be attached to diethylzinc (Scheme 3). We also speculated that two broad signals might be attributed to a mixture of dimeric or trimeric species which were randomly attached to diethylzinc. That monomeric, dimeric, and trimeric species existed in equilibrium in the presence of 6 molar amounts of diethylzinc was supported by observing slightly positive non-linear relationship between the ee of product and the ee of the chiral ligand **1b** in the cyclopropanation of cinnamyl alcohol (Fig. 3).[19] Ethylzinc allyloxide coordinates with the Lewis acidic zinc ion of **8** and the amide carbonyl traps ethyl(iodomethyl)zinc. Thus, methylene-transfer reaction is promoted in the asymmetric atmosphere to give an optically active product (route A).[20] Despite this description, we can not exclude the possibility that the reaction proceeds along the route B, wherein iodomethylzinc allyloxide complexes with the Lewis acidic zinc ion. It has been reported that iodomethylzinc allyloxide plays a very important role in Lewis acid-catalyzed asymmetric Simmons–Smith reaction.[11] According to this report, we treated iodomethylzinc cinnamyloxide in the presence of 1 molar amount of **1b** and 6 molar amount of diethylzinc. Enantioselectivity (92% ee) of the reaction was comparable with that observed under the standard reaction conditions (94% ee), but enhancement of the reaction rate was not observed. More experiments are needed to draw conclusions



Scheme 3.

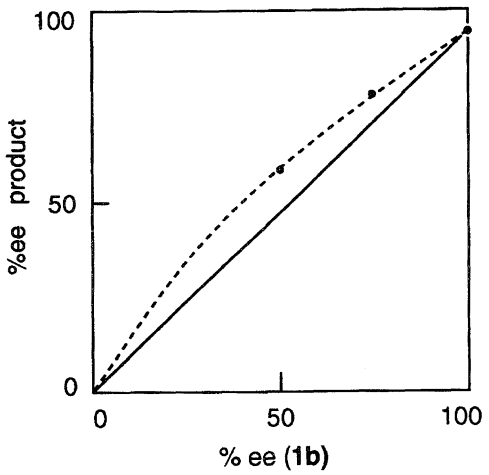
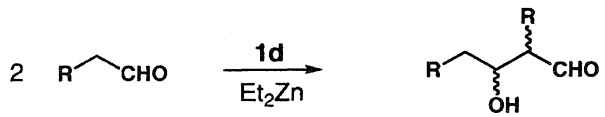


Fig. 3.

about the reaction mechanism.

Enantioselective Addition of Diethylzinc to Aldehydes Using *N,N,N′,N′*-Tetraalkyl-BINOL-3,3′-dicarboxamides as Chiral Auxiliaries. To date, various types of optically active β-amino alcohols and titanium alkoxides have been developed as chiral sources for enantioselective addition of dialkylzinc to aldehydes.[21] By the introduction of these chiral sources, an excellent level of enantioselectivity has been realized in most addition reactions, but the reaction of some substrates shows moderate enantioselectivity. With the mechanism of asymmetric induction of these reactions, β-amino alcohol-assisted enantioselective addition has been extensively studied. The transition state structure **9**, wherein the chirality of the amino alcohol moiety regulates the chirality of the vicinal oxygen atom caused by its coordination to dialkylzinc and in turn discriminates the enantioface of aldehydes, has been proposed to rationalize the stereochemistry of the addition reaction (Fig. 4).[21b,22] Furthermore, the addition reaction using a camphor-derived β-hydroxy amide has also been considered to proceed through a similar transition state **10**.[23] From our study about Simmons–Smith cyclopropanation, we could expect that the chelate **8** would catalyze the enantioselective addition which proceeded through a transition state **11**. Here, coordination of the amide car-



Scheme 4.

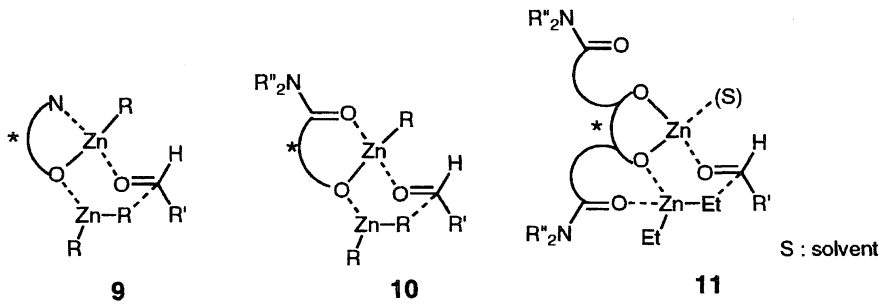


Fig. 4.

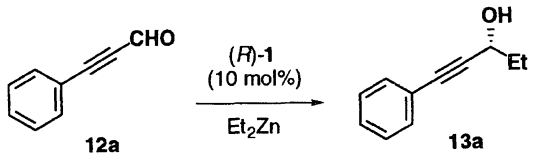


Table 3. Enantioselective Ethylation of 3-Phenyl-2-propynal (**12a**) Using *N,N,N′,N′*-Tetraalkyl-BINOL-3,3′-dicarboxamides (**1**) as Chiral Auxiliaries

Entry	Auxiliary	Solvent	Et_2Zn (eq)	Temp (°C)	Time (h)	Yield (%)	Ee (%)
1	**1a**	THF	1.3	0	15	82	79
2	**1b**	Toluene	1.3	0	6	69	56
3	**1b**	CH_2Cl_2	1.3	0	15	74	62
4	**1b**	Et_2O	1.3	0	6	88	66
5	**1b**	THF	1.3	0	6	92	78
6	**1c**	THF	1.3	0	15	70	82
7	**1d**	Toluene	1.3	0	15	79	59
8	**1d**	THF	1.3	0	15	68	84
9	**1e**	THF	1.3	0	6	77	88
10	**1e**	THF	1.3	−23	24	56	92
11	**1e**	THF	2.0	−23	24	90	92
12	**1f**	THF	1.3	0	6	56	80

Table 4. Enantioselective Ethylation of Aldehydes Using **1d** or **1e** as a Chiral Auxiliary

Entry	Aldehyde	Auxiliary	Temp (°C)	Product	Time (h)	Yield (%)	%Ee (confign)
1	C_6H_5CHO (**12b**)	**1d**	0	**13b**	24	88	99[a] (*R*)[b]
2	C_6H_5CHO (**12b**)	**1d**[c]	0	**13b**	72	63	98 (*R*)
3	C_6H_5CHO (**12b**)	**1e**	0	**13b**	24	82	97 (*R*)
4	*p*-ClC_6H_4CHO (**12c**)	**1d**	0	**13c**	24	88	97[d] (*R*)[b]
5	*p*-$CH_3OC_6H_4CHO$ (**12d**)	**1d**	0	**13d**	24	85	94[e] (*R*)[b]
6	*o*-FC_6H_4CHO (**12e**)	**1d**	0	**13e**	24	86	95[f] (*R*)[g]
7	*c*-$C_6H_{11}CHO$ (**12f**)	**1e**	0	**13f**	24	51	98[h] (R)[i]
8	4-*t*-Bu-$C_6H_{10}CHO$[j] (**12g**)	**1e**	0	**13g**	48	51	98[k] (ND)[l]
9	(*E*)-C_6H_5CH=$CHCHO$ (**12h**)	**1d**	-23	**13h**	24	53	91[m] (R)[b]

a) Determined by HPLC analysis using Daicel Chiralcel OJ (hexane : *i*-PrOH = 15 : 1) after benzoylation. b) Assigned by chiroptical comparison with the literature values (Ref. 27). c) Compound **1d** (2 mol %) was used. d) Determined by HPLC analysis using Daicel Chiralcel OB-H (hexane : *i*-PrOH = 30 : 1). e) Determined by HPLC analysis using Daicel Chiralcel OD (hexane : *i*-PrOH = 30 : 1). f) Determined by HPLC analysis using Daicel Chiralpak AD (hexane : *i*-PrOH = 50 : 1) after 3,5-dinitrobenzoylation. g) Assigned by chiroptical comparison with the literature values (Ref. 25a). h) Determined by HPLC analysis using Daicel Chiralpak AD (hexane : *i*-PrOH = 200 : 1) after benzoylation. i) Assigned by chiroptical comparison with the literature values (Ref. 28). j) *trans*-Isomer. k) Determined by HPLC analysis using Daicel Chiralpak AD (hexane : *i*-PrOH = 200 : 1) after 3,5-dinitrobenzoylation. l) Not determined. m) Determined by HPLC analysis using Daicel Chiralcel OD (hexane : *i*-PrOH = 9 : 1).

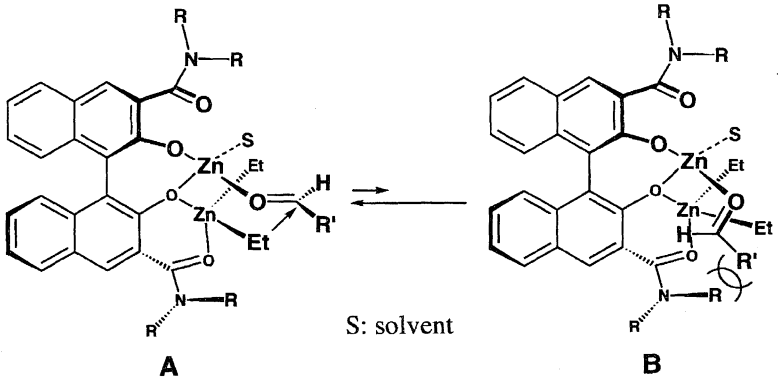


Fig. 5. Postulated reaction mechanism for diethylzinc addition to aldehyde using *N,N,N′,N′*-tetraalkyl-BINOL-3,3′-dicarboxamide.

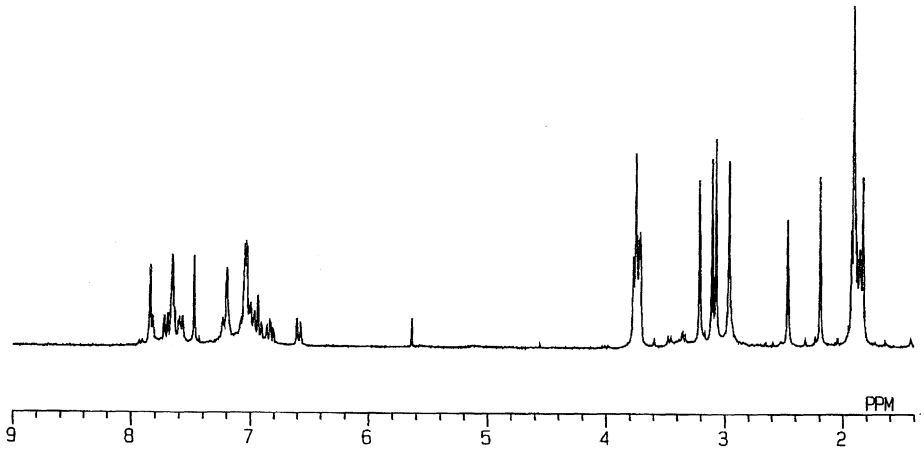


Fig. 6. 270 MHz ^{1}H NMR of **1a**+Et_2Zn (1 equiv.) in THF-d_8 at room temperature.

bonyl to diethylzinc was considered to fix its conformation to promote the transfer of one of ethyl groups to the carbonyl group, accelerating the desired reaction. Thus, we were intrigued by the catalytic addition reaction of diethylzinc to aldehyde with new ligands **1**.

We chose 3-phenyl-2-propynal (**12a**) as a test substrate, since the β-amino alcohol-promoted addition reaction to alkynals has been reported to show moderate enantioselectivity.[24,25] Table 3 summarizes the results obtained with 10 mol % of **1** as a chiral source under several reaction conditions. Interestingly, the reaction using (*R*)-**1b** in a polar solvent gave higher enantioselectivity as well as better chemical yield than that in a non-polar solvent such as toluene, which was generally used in this type of addition reaction (Entries 2—5). Tetrahydrofuran was found to be the solvent of choice. We next examined the effect

of the amide *N*-alkyl group on enantioselectivity and found that the isopropylamide (*R*)-**1e** showed the best enantioselectivity (Entry 9). Finally, the reaction with (*R*)-**1e** at −23 °C afforded (*R*)-1-phenyl-1-pentyn-3-ol (**13a**) of 92% ee in 90% yield (Entry 11). Enantiomeric excess was determined by HPLC analysis using Daicel chiralcel OJ (eluent system; hexane : *i*-PrOH = 9 : 1) and the absolute configuration was assigned by comparison of the specific rotation.[24a)]

Ethylation of other aldehydes was also examined under the above reaction conditions (Table 4). Although no explanation is available at present, the best chiral auxiliary [(*R*)-**1d** or (*R*)-**1e**)] to be used was dependent upon the substrates examined. All the substrates including aromatic, cycloalkyl, and alkenyl aldehydes gave (*R*)-secondary alcohols of high enantioselectivity, greater than 90% ee. It is noteworthy that high enantioselectivity was also achieved in the ethylation of *o*-fuluorobenzaldehyde. The same addition reaction in the presence of titanium(IV) $\alpha,\alpha,\alpha',\alpha'$-tetraaryl-2,2-dimethyl-1,3-dioxolan-4,5-dimethanolate which is one of the most efficient auxiliaries, has been reported to show only 62% ee, although quite high enantioselectivity was obtained for other substrates.[24a,25)] Reaction with a reduced amount (2 mol %) of **1d** also showed high enantioselectivity, equal to that with 10 mol % of **1d**, though the reaction rate became slow (Entry 2). However, linear alkanals such as heptanal, 3-phenylpropanal, and 3-methylbutanal underwent an undesired and poor stereoselective aldol reaction (Scheme 4) and no addition product was obtained, or at best a trace amount.

High enantioselectivity observed in the present reaction can be explained with the transition state model shown in Fig. 5. Chelation of the amide carbonyl and phenolic oxygen to diethylzinc fixes one of ethyl groups to direct toward the *re*-face of the aldehyde in conformer A, which is more favorable than the conformer B, which suffers from steric repulsion between the aldehyde and the amide *N*-alkyl group.

Furthermore, the favorable effect of polar solvent on chemical yield can be explained by the assumption that coordination of polar solvent to the central zinc ion prevents aggregation of the zinc complex which is catalytically active only in a monomeric form (Fig. 5). Indeed, ^{1}H NMR analysis of a 1 : 1 mixture of **1a** : Et_2Zn in THF-d_8 suggested the presence of three or four different isomers including monomeric and trimeric species (Fig. 6), while a 1 : 1 mixture of **1a** : Et_2Zn in dichloromethane existed only as a trimer (vide supra). However, we must wait for further study to explain the solvent effect on enantioselectivity.

As demonstrated above, we found that the newly introduced BINOL-dicarboxamides were efficient chiral auxiliaries for both Simmons–Smith cyclopropanation of allylic alcohols and alkylation of aldehydes. These successful results were brought about by combination of the amide, a coordinating functional group, and binaphthol skeleton. The combination enables one to gather both the reagent and substrate onto the catalyst and the desired reaction proceeds in a strongly asymmetric atmosphere constituted by 3,3′-disubstituted binaphthyl skeleton.[29)]

Further studies on application of such auxiliaries to other asymmetric reactions are in progress in our laboratory.

Experimental

General. The melting points are uncorrected. NMR spectra were recorded at 270 MHz on a JOEL E-270 instrument. Signals were expressed as ppm down field from tetramethylsilane used as an internal standard (δ value in $CDCl_3$) unless otherwise described. IR spectra were obtained with a Shimadzu FTIR-8600 or JEOL JIR-6500W instrument. Optical rotation was measured with a JASCO DIP-360 automatic digital Polarimeter. EI mass spectra were recorded on a JEOL JMX DX-300 instrument. High-resolution mass (HRMS) spectra were recorded on a JOEL JMS-SX/SX 102A instrument. Column chromatography was conducted on Silica Gel BW-820-MH, 70-200 mesh ASTM, available from Fuji Silysia Chemical Ltd. Preparative thin-layer chromatography was performed on 0.5 mm×20 cm×20 cm E. Merck silica-gel plate (60 F-254). Solvents were dried and distilled shortly before use. Reactions were carried out under an atmosphere of nitrogen or argon, if necessary. For known compounds obtained, only the specific rotations are given.

(*R*)-2,2′-Bis(methoxymethoxy)-1,1′-binaphthyl (3):[30)] To a suspention of sodium hydride (60% dispersion in mineral oil, 922 mg, 23.1 mmol) in THF (40 ml) and *N*,*N*′-dimethylformamide (DMF, 20 ml) was added (*R*)-2,2′-dihydroxy-1,1′-binaphthyl (**2**, 3.0 g, 10.5 mmol) in THF (12 ml) at 0 °C. After the mixture was stirred for 1 h at the temperature, chloromethyl methyl ether (2.9 ml, 31.4 mmol) was added and the whole mixture was stirred overnight at room temperature. The reaction was quenched with water, extracted with ethyl acetate, washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residual solid was recrystallized from methanol to give **3** as white crystals (3.67 g, 94%). Mp 99—100 °C; $[\alpha]_D^{23} = +94.0°$ (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.14 (6H, s), 4.97 (2H, d, *J* = 6.9 Hz), 5.08 (2H, d, *J* = 6.9 Hz), 7.13—7.22 (4H, m), 7.31—7.37 (2H, m), 7.57 (2H, d, *J* = 9.1 Hz), 7.86 (2H, d, *J* = 8.3 Hz), 7.94 (2H, d, *J* = 9.1 Hz); IR (KBr) 1506, 1241, 1147, 1068, 1046, 1014, 921, 809, 754 cm^{-1}. Found: C, 77.10; H, 5.89%. Calcd for $C_{24}H_{22}O_4$: C, 76.99; H, 5.92%.

(*R*)-2,2′-Dihydroxy-1,1′-binaphthyl-3,3′-dicarboxylic acid (4): To a solution of **3** (3.00 g, 8.01 mmol) in anhydrous diethyl ether (32 ml) was added butyllithium [24.0 mmol, 14.6 ml of 1.6 M solution (M = mol dm^{-3}) in hexane] at room temperature under nitrogen atmosphere and the reaction mixture was stirred for 3 h. The mixture was cooled to 0 °C and dry CO_2 was bubbled through the mixture. Then the mixture was allowed to warm to room temperature and the reaction was quenched with H_2O. After the phases were separated, the aqueous layer was acidified to pH 2 with 5 % aqueous HCl and extracted with ethyl acetate two times. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, and then concentrated under reduced pressure. To the crude residue in THF (10 ml) was added saturated HCl in *i*-PrOH (20 ml) and this mixture was kept for 4 h at room temperature. After removal of solvent, the residue was partitioned into ethyl acetate and water. The organic layer was washed with water, and dried over anhydrous $MgSO_4$ and concentrated. The residue was triturated with chloroform and the resulting crystallines **4** were collected by filtration. This material was used for the next step without further purification. Mp > 290°C; $[\alpha]_D^{23} = +189°$ (*c* 1.06, pyridine). Lit, mp > 285°C, $[\alpha]_{589}^{25} = +185°$ (*c* 1.08, pyridine).[31)]

(*R*)-*N*,*N*,*N*′,*N*′-Tetramethyl-2,2′-dihydroxy-1,1′-binaphthyl-3,3′-dicarboxamide (1a): A solution of the above dicarboxylic acid **4** (1.83g, 4.89 mmol) in thionyl chloride (100 ml) was refluxed

for 4 h. After removal of thionyl chloride, the resulting acid chloride was dissolved in DMF (7.5 ml). The mixture was added to aqueous dimethylamine (50%, 10 ml) and stirred for 1 h at 0 °C. The reaction mixture was acidified to pH 2 with 5% HCl and extracted with chloroform two times. The combined organic layers were washed successively with 10% $NaHCO_3$ solution and brine, dried over $MgSO_4$, and concentrated. The residue was chromatographed on a silica gel ($CHCl_3$: MeOH = 50 : 1) to give the product as a solid, which was recrystallized from ethyl acetate to give **1a** as white crystals (1.20g, 57%). Mp 235 °C (decomp); $[\alpha]_D^{23} = +69.9°$ (*c* 1.0, $CHCl_3$); MS *m/z* 428 (M^+); ^1H NMR ($CDCl_3$) $\delta = 3.25$ (12H, s), 7.16 (2H, dd, $J = 1.7$, 7.6 Hz), 7.27—7.38 (4H, m), 7.86 (2H, dd, $J = 1.8$, 6.9 Hz), 7.99 (2H, s), 8.80 (2H, s); IR (KBr) 3402, 1633, 1500, 1394, 1273, 1134, 752 cm^{-1}. Found: C, 71.69; H, 5.72; N, 6.34%. Calcd for $C_{26}H_{24}N_2O_4 \cdot 0.5H_2O$: C, 71.37; H, 5.76; N 6.34%. HRMS Found: *m/z* 429.1828 ($M^+ + 1$). Calcd for $C_{26}H_{25}N_2O_4$: M + 1, 429.1814. The enantiomeric purity (> 99% ee) was measured by HPLC [Daicel CHIRALPAK AD, 5 mm × 25 cm; hexane : *i*-PrOH = 9 : 1; flow rate 0.5 ml min^{-1} retention time 60.6 min for (*R*)-**1a**, 77.9 min for (*S*)-**1a**].

(*R*)-*N*,*N*, *N*′,*N*′-Tetraethyl-2,2′-dihydroxy-1,1′-binaphthyl-3,3′-dicarboxamide (1b): The acid chloride prepared from **4** (4.1 mmol) as described above was suspended in dry benzene (80 ml). The this suspension was added diethylamine (4.2 ml, 41 mmol) at room temperature. The reaction mixture was stirred for 4 h and poured onto the cooled 5 % HCl solution. The product was extracted with ethyl acetate two times and the combined organic layers were washed with 10% $NaHCO_3$ solution and brine successively, dried over $MgSO_4$, and concentrated. The residue was chromatographed on a silica gel (ethyl acetate : hexane = 1 : 9) to give diethylamide **1b** (1.42 g, 72%). Mp 215 °C(decomp); $[\alpha]_D^{23} = +43.0°$ (*c* 1.0, $CHCl_3$); MS *m/z* 484 (M^+); ^1H NMR ($CDCl_3$) $\delta = 1.32$ (12H, t, $J = 7.1$ Hz), 3.52—3.69 (8H, m), 7.16 (2H, d, $J = 7.9$ Hz), 7.27—7.38 (4H, m), 7.87(2H, d, $J = 7.6$ Hz), 7.95 (2H, s), 8.26 (2H, s); IR (KBr) 2974, 2935, 1633, 1479, 1460, 1381, 1315, 1282, 1211, 1134, 750 cm^{-1}. Found: C, 74.00; H, 6.60; N, 5.45%. Calcd for $C_{30}H_{32}N_2O_4$: C, 74.36; H, 6.66; H 5.78%. HRMS Found: *m/z* 485.2437 ($M^+ + 1$). Calcd for $C_{30}H_{33}N_2O_4$: $M^+ + 1$, 485.2440. The enantiomeric purity (> 99% ee) was measured by HPLC [Daicel CHIRALPAK AD, 5 mm × 25 cm; hexane : *i*-PrOH = 9 : 1, flow rate 0.5 ml min^{-1}; retention time 23.2 min for (*R*)-**1b**, 39.7 min for (*S*)-**1b**].

In a similar manner, compounds **1c**—**1f** were prepared from diacid **4** and corresponding dialkylamines.

(*R*)-*N*,*N*,*N*′,*N*′-Tetrapropyl-2,2′-dihydroxy-1,1′-binaphthyl-3,3′-dicarboxamide (1c): Pale yellow amorphous; yield 50 %; $[\alpha]_D^{22} = +47.4°$ (*c* 1.0, $CHCl_3$). MS *m/z* 540 (M^+); ^1H NMR ($CDCl_3$) $\delta = 0.94$ (12H, t, $J = 7.1$ Hz), 1.76 (8H, m), 3.43—3.55 (8H, m), 7.16 (2H, d, $J = 7.9$ Hz), 7.27—7.39 (4H), 7.87 (2H, d, $J = 7.6$ Hz), 7.89 (2H, s), 7.93 (2H, s); IR (KBr) 2962, 2933, 2873, 1633, 1466, 1427, 1379, 1207, 1134, 748 cm^{-1}. Found: C, 73.23; H, 7.25; N, 5.09%. Calcd for $C_{34}H_{40}N_2O_4 \cdot H_2O$:C, 73.09; H, 7.58; N 5.01%.

(*R*)-*N*,*N*,*N*′,*N*′-Tetrabutyl-2,2′-dihydroxy-1,1′-binaphthyl-3,3′-dicarboxamide (1d): Pale yellow amorphous; yield 45%; $[\alpha]_D^{22} = +45.6°$ (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) $\delta = 0.92$ (12H, t, $J = 7.3$ Hz), 1.34 (8H, m), 1.76 (8H, m), 3.46—3.63 (8H, m), 7.14 (2H, d, $J = 8.1$ Hz), 7.28—7.38 (4H, m), 7.84 (2H, d, $J = 7.6$ Hz), 7.86 (2H, s), 7.92 (2H, s); IR (KBr) 2958, 2931, 2871, 1633, 1465, 1427, 1377, 1317, 1207, 1134, 748 cm^{-1}. Found: C, 75.80; H, 8.13; N, 4.74%. Calcd for $C_{38}H_{49}N_2O_4 \cdot 0.25\ H_2O$: C, 75.78; H, 8.28; N 4.65%. HRMS Found: *m/z* 597.3698 ($M^+ + 1$). Calcd for $C_{38}H_{49}N_2O_4$: $M^+ + 1$, 597.3692.

(*R*)-*N*,*N*,*N*′,*N*′-Tetra-isopropyl-2,2′-dihydroxy-1,1′-binaphthyl-3,3′-dicarboxamide (1e): White crystals; yield 37%; mp 178—180 °C; $[\alpha]_D^{22} = +59.6°$ (*c* 1.0, $CHCl_3$); MS *m/z* 540 (M^+). ^1H NMR ($CDCl_3$) $\delta = 1.43$ (24H, d, $J = 5.6$ Hz), 3.96 (4H, m), 7.16 (2H, d, $J = 8.3$ Hz), 7.28—7.39 (6H, m), 7.85 (2H, d, $J = 7.6$ Hz), 7.86 (2H, s); IR (KBr) 2970, 2933, 1633, 1460, 1371, 1344, 1209, 1151, 750 cm^{-1}. Found: C, 74.52; H, 7.43; N, 5.14%. Calcd for $C_{34}H_{40}N_2O_4 \cdot 0.5\ H_2O$: C, 74.29; H, 7.52; N 5.10%.

(*R*)-*N*,*N*,*N*′,*N*′-Tetra-cyclohexyl-2,2′-dihydroxy-1,1′-binaphthyl-3,3′-dicarboxamide (1f): White powder; yield 29%; mp 195 °C (decomp); $[\alpha]_D^{22} = +51.5°$ (*c* 1.0, $CHCl_3$); MS *m/z* 700 (M^+). ^1H NMR ($CDCl_3$) $\delta = 1.20$—1.58 (24H, m), 1.80 (16H, m), 3.48 (4H, m), 7.15 (2H, d, $J = 7.9$ Hz). 7.28—7.37 (6H), 7.84 (2H, d, $J = 7.3$ Hz), 7.85 (2H, s); IR (KBr) 2929, 2854, 1633, 1454, 1365, 1317, 1209, 1184, 1142, 748 cm^{-1}. Found: C, 77.80; H, 7.93; N, 3.74%. Calcd for $C_{46}H_{56}N_2O_4 \cdot 0.5\ H_2O$: C, 77.82; H, 8.09; N 3.95%.

General Procedure for Asymmetric Simmons–Smith Cyclopropanation of Allylic Alcohols Using *N*,*N*,*N*′,*N*′-Tetraethyl-BINOL-3,3′-dicarboxamide (1b) as a Chiral Auxiliary. To a solution of (*R*)-**1b** (48 mg, 0.1 mmol) and (*E*)-3-(4-methoxyphenyl)-2-propen-1-ol (**5c**, 16 mg, 0.1 mmol) in anhydrous dichloromethane (1 ml) were added diethylzinc (1.0 M solution in hexane, 0.6 ml) and diiodomethane (0.024 ml, 0.3 mmol) at 0 °C under a nitrogen atmosphere, and the mixture was stirred for 15 h at the same temperature. The mixture was allowed to warm to room temperature, and the reaction was quenched with a 2 M NaOH solution. After extraction three times with diethyl ether, the combined organic layers were successively washed with 2 M aqueous NaOH and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by TLC on silica gel (developed with diisopropyl ether) to give *trans*-2-(4-methoxyphenyl)cyclopropanemethanol (**6c**, 13.9 mg, 78%) as a colorless oil. The enantiomeric excess was determined to be 94% ee by HPLC as described in the footnote of Table 2. $[\alpha]_D^{23} = -63.5°$ (*c* 1.05, EtOH); ^1H NMR ($CDCl_3$) $\delta = 0.89$ (2H, m), 1.40 (1H, m), 1.58 (1H, brs), 1.79 (1H, m), 3.61 (2H, m), 3.78 (3H, s), 6.81 (2H, d, $J = 8.9$ Hz), 7.01 (2H, d, $J = 8.9$ Hz); IR (KBr) 3318, 1518, 1461, 1255, 1178, 1032, 818 cm^{-1}. Found: C, 74.17; H, 7.78%. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92%.

Compound **1b** was recovered in 87% yield without loss of the optical purity by acidification of the aqueous layer and the extraction with chloroform.

In a similar manner, compounds, **6a**, **6b** and **6d**—**6f** were prepared. Analytical data were as follows:

(1*R*, 2*R*)-2-Phenylcyclopropanemethanol (6a): $[\alpha]_D^{23} = -68.3°$ (*c* 0.56, EtOH, 94% ee). Lit, $[\alpha]_D^{21} = -56.2°$ (*c* 0.6, EtOH, 75% ee).[8a)]

(1*R*, 2*S*)-2-Phenylcyclopropanemethanol (6b): $[\alpha]_D^{23} = -49.7°$ (*c* 1.02, EtOH, 92% ee). Lit, $[\alpha]_D^{23} = -52°$ (*c* 1.3, EtOH, 70% ee).[9a)]

***trans*-2-(4-Chlorophenyl)cyclopropanemethanol (6d):** An oil; $[\alpha]_D^{23} = -67.5°$ (*c* 0.89, EtOH, 90% ee); ^1H NMR ($CDCl_3$) $\delta = 0.95$ (2H, m), 1.44 (1H, m), 1.60 (1H, br, s), 1.81 (1H, m), 3.62 (2H, d, $J = 6.6$ Hz), 7.00 (2H, d, $J = 7.3$ Hz), 7.22 (2H, d, $J = 7.3$ Hz); IR (Nujol) 3317, 1497, 1092, 1014, 825, 525 cm^{-1}. HRMS Found: *m/z* 182.0502. Calcd for $C_{10}H_{11}ClO$: M, 182.0498.

(1*R*, 2*R*)- 2- (2- Phenylethyl)cyclopropanemethanol (6e): $[\alpha]_D^{23} = -33°$ (*c* 0.25, $CHCl_3$, 89% ee). Lit, $[\alpha]_D^{20} = -20.3°$ (*c* 1.14, $CHCl_3$, 82% ee).[8d)]

***trans*-2-[*t*-Butyldiphenylsilyloxy)methyl]cyclopropanemethanol (6f):** An oil; $[\alpha]_D^{22} = -12°$ (*c* 0.32, $CHCl_3$, 87% ee); ^1H NMR ($CDCl_3$) $\delta = 0.37$—0.48 (2H, m), 0.96 (2H, m), 1.05 (9H, s), 1.28

(1H, brs), 3.40—3.48 (H, m), 3.69 (1H, dd, J = 3.3, 5.3 Hz), 7.35—7.46 (5H, m), 7.65—7.68 (5H, m); IR (Nujol) 2931, 2858, 1471, 1427, 1113, 1074, 1030, 823, 741, 702, 613, 505 cm^{-1}. Found: C, 73.82; H, 8.29%. Calcd for $C_{21}H_{28}O_2Si$: C, 74.07; H, 8.29%.

(1*R*, 2*R*)- 2- (Trityloxymethyl)cyclopropanemethanol (6g): $[\alpha]_D^{22} = -10.1°$ (*c* 1.39 $CHCl_3$, 88% ee). Lit, $[\alpha]_D^{20} = -7.3°$ (*c* 2.52, $CHCl_3$, 69% ee).[8d]

(1*R*, 2*S*)- 2- (Trityloxymethyl)cyclopropanemethanol (6h): $[\alpha]_D^{22} = -15.9°$ (*c* 1.43, $CHCl_3$, 16% ee). Lit, $[\alpha]_D^{20} = -64.5°$ (*c* 0.93, $CHCl_3$, 66% ee).[8d]

Genaral Procedure for Addition of Diethylzinc to Aldehydes Using *N,N,N′,N′*-Tetraisopropyl-BINOL-3,3′-dicarboxamide (1e) as a Chiral Auxiliary. A hexane solution of diethylzinc (1.0 M, 0.67 ml) was added to a solution of (*R*)-**1e** (18 mg, 0.033 mmol) in anhydrous THF (1.5 ml) at −23 °C and stirred for 15 min. To this solution was added a solution of 3-phenyl-2-propynal (**12a**, 44 mg, 0.33 mmol) in THF (0.5 ml) and the mixture was stirred for 24 h at the same temperature. After quenching the reaction with 5% HCl solution, the product was extracted with diethyl ether three times. The combined organic layers were washed successively with 2 M NaOH solution and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified on a silica gel (ethyl acetate : hexane = 1 : 4) to afford (*R*)-1-phenyl-1-pentyn-3-ol (**13a**, 48.0 mg, 90%) as a colorless oil. $[\alpha]_D^{23} = +19.8°$ (*c* 1.96, Et_2O, 92% ee). Lit, $[\alpha]_D^{25} = -13.7°$ (*c* 2.00, Et_2O, 70% ee) for (*S*)-form.[24a] The enantiomeric excess was determined by HPLC analysis as described in the text.

In a similar manner, compounds **13b—h** were produced. Analytical data were as follows:

(*R*)-1-Phenyl-1-propanol (13b): $[\alpha]_D^{23} = +48.4°$ (*c* 3.35, $CHCl_3$, 99% ee). Lit, $[\alpha]_D^{22} = -47.6$ (*c* 3.35, $CHCl_3$, 98% ee) for (*S*)-form.[27]

(*R*)-1-(4-Chlorophenyl)-1-propanol (13c): $[\alpha]_D^{23} = +24.9°$ (*c* 3.83, benzene, 97% ee). Lit, $[\alpha]_D^{22} = -23.5°$ (*c* 0.82, benzene, 93% ee) for (*S*)-form.[27]

(*R*)-1-(4-Methoxyphenyl)-1-propanol (13d): $[\alpha]_D^{23} = +34.0°$ (*c* 2.95, benzene, 94% ee). Lit, $[\alpha]_D^{22} = -32.1°$ (*c* 1.25, benzene, 93% ee) for (*S*)-form.[27]

(*R*)-1-(2-Fluorophenyl)-1-propanol (13e): $[\alpha]_D^{23} = +33.1°$ (*c* 4.04, $CHCl_3$, 95% ee). Lit, $[\alpha]_D^{rt} = -20.06°$ (*c* 1.77, $CHCl_3$, 62% ee) for (*S*)-form.[25a]

(*R*)-1-Cyclohexyl-1-propanol (13f): $[\alpha]_D^{23} = +8.2°$ (*c* 7.28, Et_2O, 98% ee). Lit, $[\alpha]_D^{23} = -8.02°$ (*c* 8.02, Et_2O, 98% ee) for (*S*)-form.[28]

1-(*trans*-4-*t*-Butylcyclohexyl)-1-propanol (13g): An oil; $[\alpha]_D^{23} = +4.5°$ (*c* 3.97, Et_2O, 98% ee); ^{1}H NMR ($CDCl_3$) δ = 0.85 (9H, s), 0.93—1.13 (7H, m), 1.20—1.62 (5H, m), 1.69—1.89 (4H, m), 3.28 (1H, m); IR (KBr) 2912, 1450, 1393, 1366, 1238, 1148, 1115, 1082, 979, 955 cm^{-1}. Found: C, 78.51; H, 13.19%. Calcd for $C_{13}H_{26}O$: C, 78.72; H, 13.21%.

(1*E*, 3*R*)-1-Phenyl-1-penten-3-ol (13h): $[\alpha]_D^{23} = +4.7°$ (*c* 1.77, $CHCl_3$, 91% ee). Lit, $[\alpha]_D^{22} = -5.7°$ (*c* 1.00, $CHCl_3$, 96% ee) for (*S*)-form.[27]

^{1}H NMR Experiment on the Structure of (*R*)-*N,N,N′,N′*-Tetramethyl-2,2′-dihydroxy-1,1′-binaphtyl-3,3′-dicarboxamide (1a)–Et_2Zn Complex: Compound **1a** (21.4 mg, 0.05 mmol) was dissolve in CH_2Cl_2 (1 ml), dried over activated molecular sieves 4 Å, and carefully concentrated under reduced pressure so as not to absorb moisture. Compound **1a** thus obtained was dissolved in CD_2Cl_2 (0.5 ml) and treated with Et_2Zn (10% solution (v/v) in CD_2Cl_2, 0.051 ml, 0.05 mmol) at 0 °C. The sample was warmed to room temperature and transferred via a Teflon® tube to an oven-dried NMR tube. The tube was capped with septum seal under argon atmosphere. Chemical shifts are expressed with residual dichloromethane as an internal standard (δ = 5.33 for ^{1} NMR, δ = 53.8 for ^{13}C NMR). Data for Fig. 1(B): ^{1}H NMR (CD_2Cl_2) δ = 1.76 (6H, s), 2.84 (6H, s), 6.84—6.87 (1H, m), 6.97—7.01 (2H, m), 7.30 (1H, s), 7.47—7.51 (1H, m); ^{13}C NMR (67.8 MHz, CD_2Cl_2) δ = 36.8, 40.7, 120.7, 121.5, 124.2, 124.9, 125.9, 127.2, 128.7 (2 peaks), 136.4, 159.2, 176.9. To this NMR tube, an additional solution of Et_2Zn (0.204 ml, 0.2 mmol) was added and the mixture was subjected to NMR analysis. The signals of *N*-methyl groups (^{1}H NMR, CD_2Cl_2) δ = 1.7—2.4 (ca. 3H, brs), 2.6—3.3 (ca. 3H, brs), 3.33 (ca. 1.5H, s), 3.34 (ca. 1.5H, s), 3.46 (ca. 1.5H, s), 3.53 (ca. 1.5H, s).

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