Novel Chiral Bisoxazoline Ligands with a Biphenyl Backbone: Preparation, Complexation, and Application in Asymmetric Catalytic Reactions

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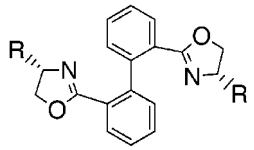
Novel C_2-symmetric chiral bisoxazoline ligands **1** were easily prepared from enantiomerically pure 2-amino alcohols and achiral 2,2′-biphenyldicarboxylic acid via the corresponding amide and mesylate as intermediates. Since these ligands bear only two *ortho*-substituents on the biphenyl backbone, the biphenyl axis is not fixed, and the two diastereomers of these ligands exist in equilibrium in solution. Interestingly, when the ligands **1** were coordinated with a metal ion, only one of the two possible diastereomer complexes, an (*S*,a*S*,*S*)-complex, can be formed depending on the combination of the ligand and the metal ion. Thus, copper(I) afforded only the (*S*,a*S*,*S*)-complexes with all ligands **1**, while zinc(II), palladium(II), and silver(I) afforded the (*S*,a*S*,*S*)-complexes as the sole product only with **1b**, which has a bulky *tert*-butyl group on the oxazoline ring, and a mixture of the two diastereomer complexes with **1a**,**c**,**d**. The copper(I)-catalyzed asymmetric cyclopropanation of styrene with diazoacetate proceeded successfully with these ligands and good to excellent enantioselectivities were afforded.

Introduction

Chiral oxazoline ligands derived from readily available amino acids have found widespread use in metal-catalyzed asymmetric reactions, and extensive efforts have been devoted to the preparation of their efficient structural derivatives.[1] Most of the earlier oxazoline ligands possess only the central chirality element in the oxazoline moiety. Within the coordination plane composed of two nitrogen atoms of the oxazoline rings and a metal ion, the plane of the oxazoline ring is involved, and the asymmetric induction is controlled only by the central chirality element in the oxazoline moiety. Our recent attention has been focused on the synthesis and application of novel oxazoline ligands with multiple elements of chirality. Besides the central chirality element in the oxazoline moiety, these ligands possess an additional chirality element in the backbone, such as 1,3-dioxolane,[2,3] ferrocene,[4,5] or biaryl.[6,7] Owing to the introduction of the chiral backbone, the plane of the oxazoline ring can be inclined to the coordination plane. Therefore, there is a possibility that the asymmetric induction by these ligands can be effectively controlled by a combination of the chirality elements in the oxazoline moiety and the backbone. Here we report novel C_2-symmetric chiral bisoxazoline ligands **1** bearing an axis-unfixed biphenyl backbone.[8]



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It has been pointed out that enantiomerically stable biaryls require at least three *ortho*-substituents to avoid the racemization due to the rotation around the internal bond of the biaryls.[9] Different from the bisoxazoline ligands with an axis-fixed biaryl backbone reported recently,[7a−d] in the case of ligands **1** which have only two

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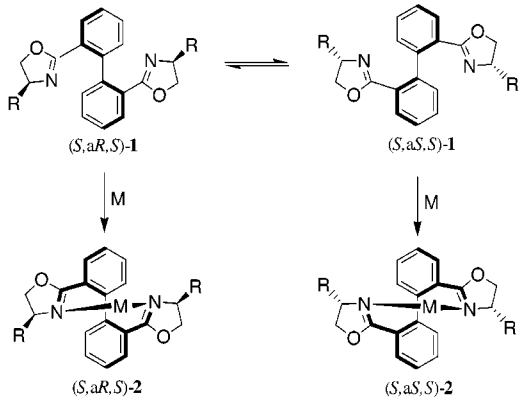
Scheme 1

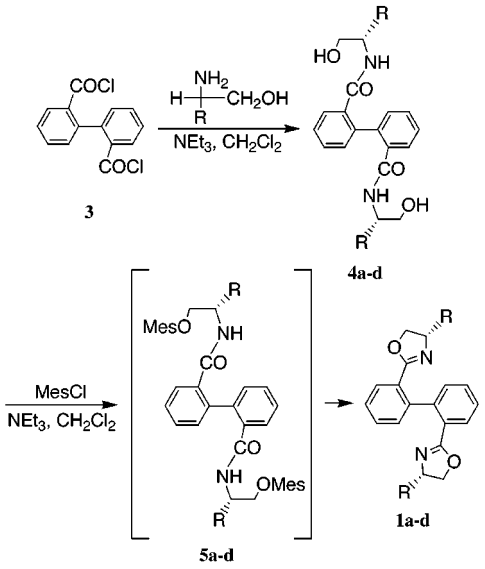


ortho-substituents on the biphenyl backbone, the two diastereomers, (*S*,a*S*,*S*)-**1** and (*S*,a*R*,*S*)-**1**, should be present in equilibrium in solution due to the rotation around the internal bond in the biphenyl backbone (Scheme 1). Upon coordinating with a metal ion, one of the two diastereomer complexes, (*S*,a*S*,*S*)-**2** and (*S*,a*R*,*S*)-**2**, may form in more preference to the other due to the difference in steric hindrance between them. If the ratio of the two diastereomer complexes is large enough, it may be possible to utilize the complex as a chiral catalyst in asymmetric reactions. On the basis of this idea, we prepared this kind of oxazoline ligands from achiral 2,2′-biphenyldicarboxylic acid and enantiomerically pure 2-amino alcohols, examined their complexation behavior with metal ions, and studied their application in asymmetric reactions. In fact, during our study, several bisoxazoline ligands with an axis-fixed biaryl backbone were reported.[7a−d] It was observed that the ligands with the same central chirality element but a different axial chirality element afforded a large difference in their catalytic activity and enantioselectivity. Namely, the diastereomer complex with less steric hindrance showed much higher catalytic activity and enantioselectivity than the other. These results showed the rationality of our design for ligands **1** with an axis-unfixed biaryl backbone because there is a possibility that the major complex derived from **1** shows much higher catalytic activity and enantioselectivity than the minor complex.

Results and Discussion

Ligand Preparation. Compounds **1** were readily prepared from 2,2′-biphenyldicarboxylic acid dichloride **3** and enantiomerically pure 2-amino alcohols via the corresponding *β*-hydroxylamides **4** and mesylates **5** successively as intermediates (Scheme 2).

Scheme 2



a: R=*i*-Pr, **b**: R=*t*-Bu, **c**: R= Ph, **d**: R=CH_2Ph

Table 1. Diastereomer Ratio of 1

	1a (*i*-Pr)	**1b** (*t*-Bu)	**1c** (Ph)	**1d** (CH_2Ph)
major-**1**:minor-**1**[a]	71:29	68:32	69:31	70:30

[a] Determined by ^{1}H NMR (400 MHz) in $CDCl_3$ at 26 °C.

Thus, 2,2′-biphenyldicarboxylic acid dichloride **3** was stirred with (*S*)-valinol and triethylamine in dichloromethane at 25 °C for 3 h to give amide **4a** in 77% yield. Then, **4a** was treated with methanesulfonyl chloride in the presence of triethylamine in dichloromethane at 25 °C for 4 h to give bisoxazoline compound **1a** in 83% yield, without isolation of the dimesylate intermediate **5a**.[4a] In the same way, the oxazolines **1b**−**d** were prepared in 61−63% overall yields from 2,2′-biphenyldicarboxylic acid dichloride and the corresponding enantiomerically pure 2-amino alcohols.

Behavior of Ligands 1 in Solution. As expected, two diastereomers were observed in solution for each ligand by ^{1}H NMR. These exist in an equilibrium due to the rotation around the internal bond of the biphenyl backbone. And one diastereomer dominated over the other, owing to the difference in the steric repulsion between the substituents on the oxazoline rings for the two diastereomers. It was found that the bulkiness of the substituent on the oxazoline ring had little effect on the ratio of the two diastereomers for the four kinds of ligands as shown in Table 1. In chloroform-*d* at 26 °C, the ratio of the two diastereomers was within 2.1−2.4:1. The temperature and solvent have a considerable effect on the ratio of the two diastereomers. As an example, the result with **1a** is shown in Table 2. It can be seen that lower temperature and a more polar solvent gave a higher ratio, and up to 8.5:1 ratio was obtained in methanol-d_4 at −90 °C.

By determining the NMR coalescence temperature, an activation barrier of 15.47 kcal/mol to axial torsion and an interconversion rate of 9.77 s^{-1} between the two diastereomers were calculated at 10 °C for ligand **1b**, which has a larger steric hindrance for the interconversion than **1a** due to a bulky *tert*-butyl group on the oxazoline ring and is suitable for the calculation due to the single proton peak of the *tert*-butyl group in ^{1}H

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(8) Part of this work has been communicated.[6a] During our study on this work, several bisoxazoline ligands with axis-fixed biaryl backbone have been reported.[7a−d]

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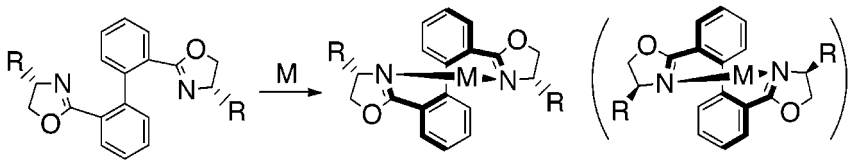
Scheme 3



R = *i*-Pr, *t*-Bu, Ph, CH_2Ph; M=CuOTf

Table 2. Diastereomer Ratio of 1a

entry	solvent	temp (°C)	major-**1**:minor-**1**[a]
1	C_6D_6	26	1.9:1
2	$CDCl_3$	26	2.4:1
3		−30	4.1:1
4		−60	5.5:1
5	CD_3OD	26	3.9:1
6		−30	4.3:1
7		−60	7.9:1
8		−90	8.5:1

[a] Determined by ^{1}H NMR (400 MHz).

NMR.[10] This result showed that for these kind of ligands, the activation barrier to axial torsion is very small and the interconversion rate between the two diastereomers is very fast.[11] Therefore, the isolation of the two diastereomers as an optically active form is substantially impossible.

Complexation Behavior of Ligands 1 with Metal Ions. The complexation behavior of ligands **1** with a copper(I) triflate benzene complex [Cu(I)OTf$(C_6H_6)_{0.5}$] in solution was examined. To a solution of **1a** in chloroform-*d* was added 1 equiv of the copper(I) triflate benzene complex, and then the suspension was stirred at room temperature under argon atmosphere until complete dissolution. Interestingly, the resultant solution afforded only one set of peaks in its ^{1}H NMR spectrum, and no new peak was observed by varying the temperature from −60 to 60 °C. The same behavior was also observed for the complexation in acetonitrile-d_3. Because it is not likely that the interconversion rate between the two diastereomer complexes is faster than that between the two diastereomers of the corresponding free ligand, which afforded two sets of peaks in its ^{1}H NMR spectrum, these results suggested the formation of only one of the two possible diastereomer complexes (Scheme 3). The structure of the formed complex was assigned to (*S*,a*S*,*S*)-**6a** by the analysis of the nuclear Overhauser effect (NOE). Thus, 11.2% and 6.2% NOE were observed between the methyl protons of the oxazolinyl isopropyl group and the 6-position proton of the phenyl group and between the 4-position proton of the oxazoline ring and the 3-position proton of the phenyl group, respectively. No obvious NOE was observed between the 4-position proton of the oxazoline ring and the 6-position proton of the phenyl group (Figure 1).

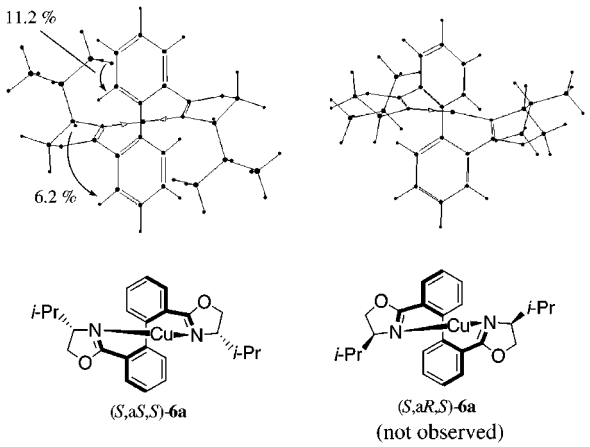


Figure 1. The observed NOE of (*S*,a*S*,*S*)-**6a**.

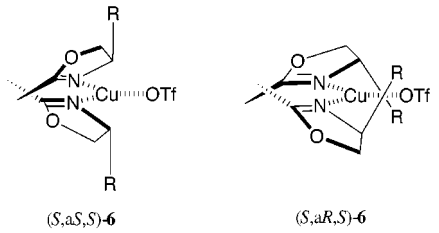


Figure 2. Model figures of (*S*,a*S*,*S*)-**6** and (*S*,a*R*,*S*)-**6**.

Similar to **1a**, ligands **1b**−**d** also afforded only one diastereomer complex, (*S*,a*S*,*S*)-**6b**−**d**, respectively, with the copper(I) triflate benzene complex. With copper(I) chloride and copper(I) iodide, ligands **1a**−**d** also afforded only one of the two possible diastereomer complexes, respectively.

We attempted to determine the structure of the complexes (*S*,a*S*,*S*)-**6** by the single-crystal X-ray analysis, but failed. However, a model study of the copper(I) complexes **6**, which have a trigonal planar coordination structure, suggests that the two planes of the oxazoline rings are inclined to the 2N-Cu(I)-OTf coordination plane by the introduction of the biphenyl backbone in the molecule (Figure 2). So the two substituents on the oxazoline rings of (*S*,a*R*,*S*)-**6** are almost in the coordination plane, while in (*S*,a*S*,*S*)-**6**, these two substituents are perpendicular to the plane in opposite directions and almost out of the plane. Therefore, the steric repulsion between the substituents on the oxazoline rings and the OTf group coordinated to copper(I) in (*S*,a*S*,*S*)-**6** is much smaller than that in (*S*,a*R*,*S*)-**6**.

Since a metal ion has its own peculiar atomic radius and coordination structure, we reasoned that the complexation behavior of ligands **1** with other metal ions

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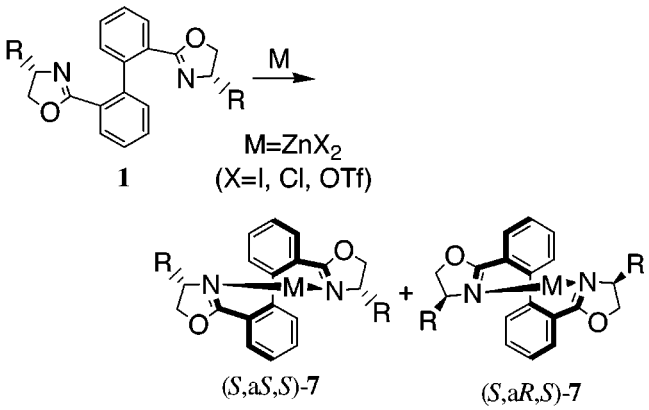
Table 3. Diastereomer Ratio of the Complexes of 1 with Zn(II) Salt



	(*S*,a*S*,*S*)-**7**:(*S*,a*S*,*S*)-**7**[a]		
	ZnI_2	$ZnCl_2$	$Zn(OTf)_2$
1a (*i*-Pr)	57:43	86:14	78:22
1b (*t*-Bu)	100:0	100:0	100:0
1c (Ph)	100:0	100:0	57:43
1d ($PhCH_2$)	87:13	99:1	89:11

[a] Determined by ^1H NMR in $CDCl_3$ at 26 °C.

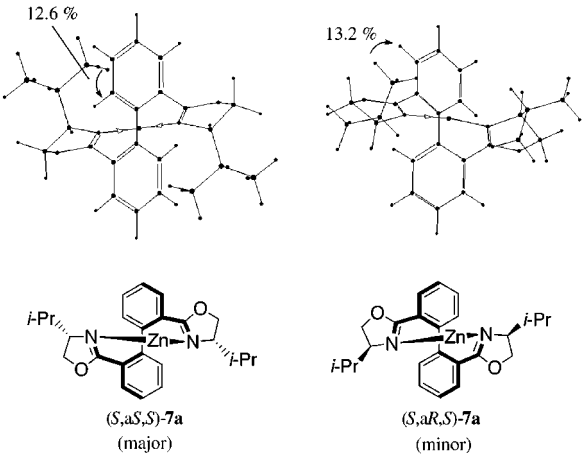


Figure 3. The observed NOE of (*S*,a*S*,*S*)-**7a** and (*S*,a*R*,*S*)-**7a**.

should be different from that with copper(I). Therefore, the complexation behavior of ligands **1** with several other metal ions was examined.

First, the complexation behavior of ligand **1a** with three kinds of zinc(II) salts, with which tetrahedrally coordinated complexes should be formed, was examined (Table 3). To a solution of ligand **1a** in chloroform-*d* was added 1 equiv of zinc(II) salt, and the suspension was stirred at room temperature under argon atmosphere until complete dissolution. The ^1H NMR spectrum of the solution showed the formation of both the two diastereomers, (*S*,a*S*,*S*)-**7a** and (*S*,a*R*,*S*)-**7a**. The counteranion affected the ratio of the two diastereomers. However, in all of these three cases, diastereomer (*S*,a*S*,*S*)-**7a** formed in preference to (*S*,a*R*,*S*)-**7a**. The structures of the two diastereomers were assigned by the determination of NOE (Figure 3). In the case of the complexation with $Zn(II)I_2$, the major diastereomer complex showed an NOE (12.6%) between the methyl protons of the oxazolinyl isopropyl group and the 6-position proton of the phenyl group. No obvious NOE was observed between the methyl protons of the oxazolinyl isopropyl group and the 3-position proton of the phenyl group. This NOE pattern is similar to that of (*S*,a*S*,*S*)-**6a**. So, the major diastereomer was assigned as (*S*,a*S*,*S*)-**7a**. Different from (*S*,a*S*,*S*)-**6a**, it is difficult here to determine the NOE between the 4-position proton of the oxazoline ring and the 3-position proton of the phenyl group due to the overlap of the signals in the ^1H NMR spectrum. The minor diastereomer complex showed an NOE (13.2%) between the methyl protons of the oxazolinyl isopropyl group and the 3-position proton of the phenyl group. No NOE was observed between the methyl protons of the oxazolinyl isopropyl group and the 6-position proton of the phenyl group, indicating the minor diastereomer to be (*S*,a*R*,*S*)-**7a**.

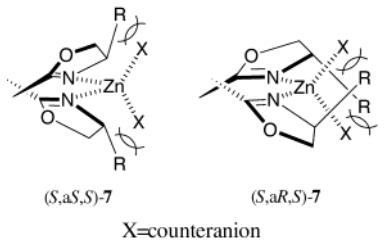


Figure 4. Model figures of (*S*,a*S*,*S*)-**7** and (*S*,a*R*,*S*)-**7**.

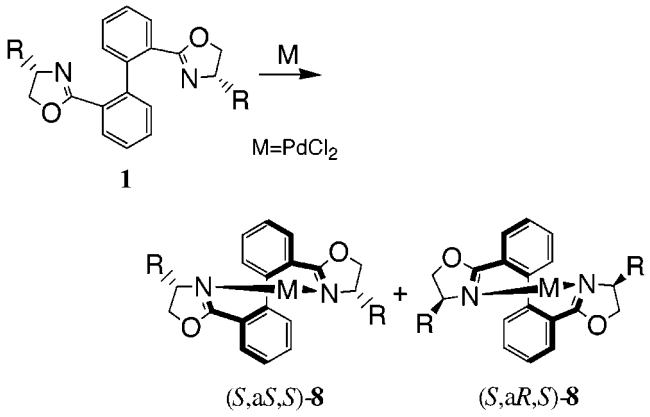
The complexation of ligand **1a** with zinc(II) iodide in chloroform-*d* at −60 °C afforded the same ratio of the two diastereomers as that at 26 °C. This result suggested the complexation might be a kinetically controlled process. Moreover, there was no change of the ratio after the above complex solution was heated at 60 °C for 7 days, showing no obvious interconversion between the two diastereomer complexes occurred under these conditions.

In addition, during the NOE determination of **7a**, a saturation transfer signal was observed in the strength of less than 0.3% at the position of the methyl protons of the major complex upon irradiating the methyl protons of the minor complex. While, for the corresponding free ligand, a saturation transfer signal was observed in the strength of 100% at the 3-position proton of phenyl group of the major diastereomer upon irradiating the 3-position proton of phenyl group of the minor diastereomer. That is, the ratio of saturation transfer signal and the irradiated signal is consistent with the ratio of the two diastereomers for the free ligand. This result may also suggested that no obvious interconversion between the two diastereomer complexes occurred.

As listed in Table 3, ligand **1b** bearing a larger *tert*-butyl substituent on the oxazoline ring gave only one diastereomer, (*S*,a*S*,*S*)-**7b**, with each of the three kinds of zinc(II) salts, respectively. Higher diastereomer ratios were obtained for the complexation of all the ligands **1** with zinc(II) chloride which has a smaller counteranion than those with the other two kinds of zinc salts.

The different complexation behavior of ligands **1** with zinc(II) ion and with copper(I) ion can be explained by an examination of the CPK model of the zinc(II) complexes (Figure 4). In the tetrahedrally coordinated complex (*S*,a*S*,*S*)-**7**, the counteranions should be located nearer to the substituent on the oxazoline ring than those in the corresponding copper(I) complexes (*S*,a*S*,*S*)-**6** with a trigonal planar coordination. So, the steric repulsion between the substituent on the oxazoline ring and the counteranion in (*S*,a*S*,*S*)-**7** is larger compared to that in (*S*,a*S*,*S*)-**6**. While in (*S*,a*R*,*S*)-**7**, the steric repulsion

Table 4. Diastereomer Ratio of the Complexes of 1 with Pd(II) Chloride



	1a (*i*-Pr)	**1b** (*t*-Bu)	**1c** (Ph)	**1d** (CH_2Ph)
(*S*,a*S*,*S*)-**8**:(*S*,a*S*,*S*)-**8**[a]	81:19	100:0	90:12	98:3

[a] Determined by ^{1}H NMR in CD_3CN at 26 °C.

between the substituent and the counteranion is decreased compared to the case of (*S*,a*R*,*S*)-**6**, because the two counteranions are out of the N-Zn(II)-N coordination plane near where the two substituents were located. Therefore, the difference in steric hindrance between the two diastereomers, (*S*,a*S*,*S*)-**7** and (*S*,a*R*,*S*)-**7**, is diminished compared to the case of copper(I) complexes **6**, and in some cases it is not large enough to form exclusively one of the two diastereomers.

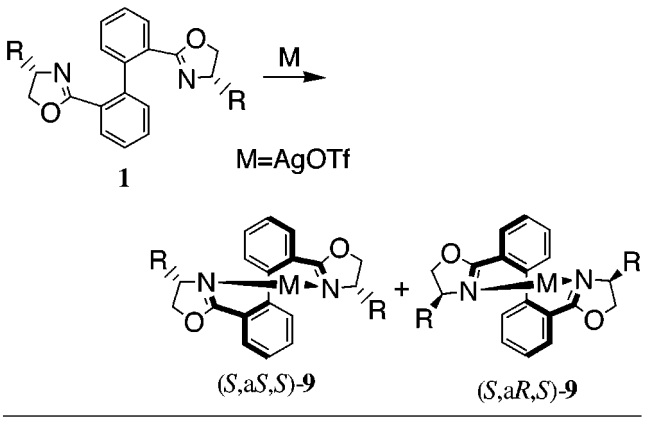
Next, the complexation behavior of ligands **1** with dichlorobis(acetonitrile)palladium(II), which should afford a square planar coordination complex, was examined by ^{1}H NMR in acetonitrile-d_3. As shown in Table 4, ligand **1b** gave only one of the two possible diastereomers, which could be tentatively assigned to (*S*,a*S*,*S*)-**8b**, while ligands **1a**,**c**,**d** gave a mixture of the two diastereomers. This may be caused by the larger torsion angle between the coordination and the oxazoline planes induced by a smaller bite angle of palladium(II) complex than the corresponding copper(I) complex. Therefore, the difference in steric repulsion between the substituent on oxazoline ring and the counteranion of the two diastereomers is diminished compared to that of the corresponding copper(I) complexes.

Finally, the complexation of **1** with silver(I) triflate, which has the same coordination style with copper(I), was examined (Table 5). As a result, only ligand **1b** afford only one diastereomer complex, (*S*,a*S*,*S*)-**9b**, as same as the complexation with copper(I). All the other ligands **1a**,**c**,**d**, gave a mixture of the two diastereomers; still the diastereomer (*S*,a*S*,*S*)-**9a**,**c**,**d** formed predominantly. This may be due to the difference in the coordination size of copper(I) and silver(I). Because the size of the silver(I) ion is larger than that of the copper(I) ion, the distance between the substituent on the oxazoline ring and the OTf group in silver(I) complex is longer than that in the corresponding copper(I) complex.

Catalytic Reactions. The catalytic activities of the copper(I) and copper(II) complexes of ligands **1** for cyclopropanation of styrene with diazoacetate and the zinc(II) complexes of ligands **1** for allylation of aldehyde with allyltri-*n*-butyltin were investigated.

Cu-catalyzed asymmetric cyclopropanation of olefin with diazoacetate is attracting considerable attention due

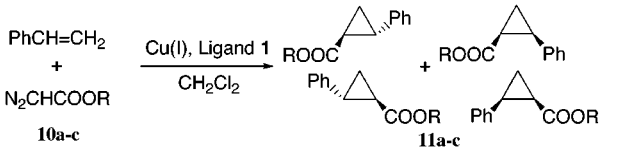
Table 5. Diastereomer Ratio of the Complexes of 1 with Ag(I) Triflate



	1a (*i*-Pr)	**1b** (*t*-Bu)	**1c** (Ph)	**1d** (CH_2Ph)
(*S*,a*S*,*S*)-**9**:(*S*,a*S*,*S*)-**9**[a]	88:12	100:0	93:7	87:13

[a] Determined by ^{1}H NMR in $CDCl_3$ at 26 °C.

Table 6. Cu(I)-Catalyzed Asymmetric Cyclopropanation[a]



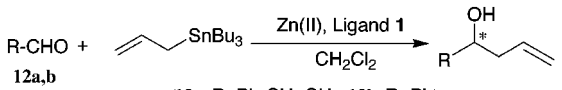
(**a**: R=Et, **b**: R=*l*-menthyl, **c**: R=*d*-menthyl)

ligand	diazoacetate	yield[b] (%)	ratio[c] of *trans*/*cis*	% ee[d] (config)[e] *trans*	*cis*
1a	**10a**	72	74/26	49 (1*R*, 2*R*)	59 (1*R*, 2*S*)
1a[f]	**10a**	75	74/26	45 (1*R*, 2*R*)	55 (1*R*, 2*S*)
1a	**10b**	60	79/21	70 (1*R*, 2*R*)	87 (1*R*, 2*S*)
1a	**10c**	59	78/22	69 (1*R*, 2*R*)	57 (1*R*, 2*S*)
1b	**10a**	69	68/32	74 (1*R*, 2*R*)	84 (1*R*, 2*S*)
1b[f]	**10a**	68	76/24	71 (1*R*, 2*R*)	84 (1*R*, 2*S*)
1b	**10b**	60	81/19	84 (1*R*, 2*R*)	92 (1*R*, 2*S*)
1b	**10c**	58	87/13	89 (1*R*, 2*R*)	82 (1*R*, 2*S*)
1c	**10a**	50	72/28	53 (1*R*, 2*R*)	58 (1*R*, 2*S*)
1c	**10b**	55	77/23	55 (1*R*, 2*R*)	84 (1*R*, 2*S*)
1d	**10a**	57	62/38	21 (1*R*, 2*R*)	27 (1*R*, 2*S*)

[a] Styrene (1.0 mmol), diazoacetate (1.3 mmol), [Cu(I)OTf(C_6H_6)$_{0.5}$] (10.3 μmol), ligand (11.0 μmol), in dichloromethane (2 mL), at room temperature under argon for 24 h. [b] Isolated yield of a mixture of *trans*- and *cis*-**11a**−**c**. [c] Determined by GC. [d] Determined by GC with Chiraldex G-TA for **11a**, and with DB-1 for **11b**,**c**. [e] By comparison of their specific rotation with the reported one for *trans*- and *cis*-**11a**,[13] and for **11b**,**c** after transformed to **11a**. [f] Styrene (5.0 mmol), diazoacetate (5.0 mmol), [Cu(II)$(OTf)_2$] (50 μmol), ligand (55 μmol), in 1,2-dichloroethane (10 mL), at room temperature under argon for 15 h.

to the demand for optically pure cyclopropanes, and some oxazoline ligands have been found to be effective for cyclopropanation of styrene with diazoacetate.[1a,b,e,f,12] Because ligands **1** afforded optically pure complexes with copper(I) salt, this reaction using a ligand **1**−copper(I) triflate complex was first investigated (Table 6). It was found that all the ligands afforded good to excellent enantioselectivities for substrates **10a**−**c**. The *trans*-cyclopropanes were formed as the major product, and higher enantiomeric excess was obtained for the *cis*-products than the *trans*-products for all the three substrates. The highest enantiomeric excesses for both *cis*- and *trans*-products were afforded for substrates **10b** which has a bulky *l*-menthyl group. The ligand structure has a considerable effect on the enantioselectivity for both *cis*- and *trans*-products and ligand **1b**, which has a *tert*-

Table 7. Asymmetric Allylation of Aldehydes Catalyzed by Zinc(II)−Bis(oxazolinyl)biphenyl[a]



(12a: R=Ph-CH=CH-, 12b: R=Ph)

ligand	aldehyde	zinc(II) salt	yield (%)[b]	% ee[c]
1a	**12a**	$Zn(II)Cl_2$	35	trace
1a	**12a**	$Zn(II)(OTf)_2$	40	13
1b	**12a**	$Zn(II)(OTf)_2$	30	trace
1c	**12a**	$Zn(II)(OTf)_2$	43	trace
1d[d]	**12a**	$Zn(II)Cl_2$	69	19
1d	**12a**	$Zn(II)(OTf)_2$	54	22
1a	**12a**	$Zn(II)(OTf)_2$	47	13
1d	**12a**	$Zn(II)(OTf)_2$	62	16

[a] Aldehyde (1.0 mmol), allyltri-*n*-butyltin (1.5 mmol), zinc(II) salt (0.1 mmol), ligand (0.1 mmol), in dichloromethane (5 mL), at room temperature under argon for 72 h. [b] Isolated yield. [c] Determined by HPLC (Chiralcel OB). [d] $AgNO_3$ added.

butyl group on oxazoline ring, afforded the highest enantiomeric excesses for all the three substrates. Particularly, when **1b** was used, up to 92% ee was afforded for the minor *cis*-product **11b**, while 84% ee was afforded for the major *trans*-product **11b**. This result is comparable to that obtained with the related bisoxazoline ligands which have an axis-fixed biaryl backbone.[7b]

Although the complexation behavior of ligands **1** with copper(II) cannot be examined by ^{1}H NMR due to the paramagnetic property of the copper(II) complex, the copper(II)-catalyzed cyclopropanation with **1** was also carried out and a comparable result with that obtained by a copper(I) complex was afforded (Table 6). The catalytically active species was suggested to be the corresponding copper(I) complex produced in situ by the reduction with the diazoacetate.[14]

For the related axis-fixed bisoxazoline ligands, the (*S*,a*R*,*S*)-diastereomers afforded a very low catalytic activity and enantioselectivity and are not useful for the asymmetric catalytic reactions.[7a−d] So, when these ligands were synthesized from racemic biaryl dicarboxylic acid and enantiomerically pure 2-amino alcohol, a diastereomer separation is necessary and a half of the ligand obtained has to be discarded. On the other hand, in the case of our axis-unfixed ligands **1**, the diastereomer separation is not necessary. All of the two diastereomers of ligands **1** in equilibrium transformed to the (*S*,a*S*,*S*)-complexes on complexation with copper(I), which show a good catalytic activity and enantioselectivity.

For the zinc(II)-catalyzed asymmetric allylation of aldehyde with allyltri-*n*-butyltin, which was reported by Cozzi's group recently,[15] ligands **1** exhibited an activity to give products in moderate to high yields (Table 7). However, satisfactory enantioselectivity was not obtained. The highest enantiomeric excess obtained is only 22% with ligand **1d** and zinc(II) triflate when *trans*-cinnamaldehyde **12a** was used as a substrate. No obvious enantioselectivity was observed for this reaction with ligand **1b**, although it afforded only one of the two possible diastereomer complexes with zinc(II) as stated above.

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(13) Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 726−728.
(14) Gupta, A. D.; Bhuniya, D.; Singh, V. K. *Tetrahedron* **1994**, *50*, 13725−13730.
(15) Cozzi, P. G.; Orioli, P.; Tagliavini, E.; Umani-Ronchi, A. *Tetrahedron Lett.* **1997**, *38*, 145−148.

Conclusion

Novel C_2-symmetric chiral bisoxazoline ligands **1** were prepared with ease from enantiomerically pure 2-amino alcohols and achiral 2,2′-biphenyldicarboxylic acid via the corresponding amide and mesylate as intermediates. Because these ligands bear only two *ortho*-substituents at the biphenyl backbone, the biphenyl axis is not fixed, and the two diastereomers of these ligands exist in equilibrium in solution. These ligands showed interesting complexation behavior with metal ions. Thus, Cu(I)X (X = OTf, Cl, I) gave only one of the two possible diastereomer complexes with all the ligands, while $Zn(II)X_2$ (X = OTf, Cl, I), $Pd(II)Cl_2$, and Ag(I)OTf afforded only one of the two possible diastereomer complexes with only ligand **1b** which has a bulky *tert*-butyl group on the oxazoline ring. With these ligands, the copper(I)-catalyzed asymmetric cyclopropanation of styrene with diazoacetate successfully proceeded to afford the products with good to excellent enantioselectivities. This result is comparable to that obtained with the related axis-fixed bisoxazoline ligands. In zinc(II)-catalyzed asymmetric allylation of aldehyde with allyltri-*n*-butyltin using these ligands, satisfactory enantioselectivity was not obtained.

Experimental Section

General. Complete descriptions of the general methods and apparatus have been published before.[4c]

2,2′-Bis[*N*-(1′*S*)-(1′-isopropyl-2′-hydroxyethyl)carboxamido]-1,1′-biphenyl (4a). A solution of (*S*)-valinol (4.0 g, 38.8 mmol) in dry dichloromethane (20 mL) was added dropwise over 0.5 h to a solution of 2,2′-biphenyldicarboxylic acid dichloride **3** (5.0 g, 17.9 mmol) in the presence of triethylamine (8.0 mL, 57.4 mmol) in dry dichloromethane (30 mL) with stirring at −5 °C. After being stirred for 3 h at room temperature, the resulting mixture was washed with water and then brine, dried over magnesium sulfate, and then concentrated in vacuo. The residue was purified by silica gel column chromatography with acetone/dichloromethane (1:1) as an eluent to give **4a** (5.7 g, 13.8 mmol, 77% yield) as a colorless solid. The ^{1}H NMR of **4a** showed two sets of signals. major/minor (55:45). ^{1}H NMR (600 MHz, $CDCl_3$) major: δ 0.80 (d, 6H, *J* 6.3 Hz), 0.84 (d, 6H, *J* 6.3 Hz), 1.77 (m, 2H), 3.32 (m, 2H), 3.45 (m, 2H), 3.61 (m, 2H), 7.10 (m, 2H), 7.17 (d, 2H, *J* 9.0 Hz), 7.37 (m, 4H), 7.54 (m, 2H); minor: δ 0.67 (d, 6H, *J* 7.2 Hz), 0.71 (d, 6H, *J* 7.2 Hz), 1.63 (m, 2H), 3.32 (m, 2H), 3.45 (m, 2H), 3.61 (m, 2H), 7.14 (m, 2H), 7.37 (m, 6H), 7.60 (m, 2H). IR (KBr, cm^{-1}), 1549, 1628, 1639, 3265. MS (CI) *m*/*z* 413 ($[M + 1]^+$).

2,2′-Bis[*N*-(1′*S*)-(1′-*tert*-butyl-2′-hydroxyethyl)carboxamido]-1,1′-biphenyl (4b). Following a procedure identical to that described for the preparation of **4a**, the reaction of (*S*)-*tert*-leucinol (1.0 g, 8.5 mmol) with **3** (1.0 g, 3.6 mmol) in the presence of triethylamine (1.5 mL, 10.8 mmol) in dry dichloromethane (30 mL) afforded **4b** (1.1 g, 2.5 mmol, 69% yield) as a yellow solid. The ^{1}H NMR of **4b** also showed two sets of signals. major/minor (52:48). ^{1}H NMR (600 MHz, $CDCl_3$) major: δ 0.88 (s, 18H), 3.26 (q, 2H, *J* 8.2, 11.2 Hz), 3.64 (dd, 2H, *J* 3.2, 11.2 Hz), 3.78 (m, 2H), 7.14 (d, 2H, *J* 9.2 Hz), 7.23−7.47 (m, 6H), 7.57 (m, 2H); minor: δ 0.84 (s, 18H), 3.35 (q, 2H, *J* 7.4, 11.2 Hz), 3.71 (dd, 2H, *J* 3.2, 11.2 Hz), 3.78 (m, 2H), 6.66 (d, 2H, *J* 9.2 Hz), 7.23−7.47 (m, 6H), 7.57 (m, 2H). IR-(KBr, cm^{-1}) 1531, 1633, 3236. MS (CI) *m*/*z* 441 ($[M + 1]^+$).

2,2′-Bis[*N*-(1′*S*)-(1′-phenyl-2′-hydroxyethyl)carboxamido]-1,1′-biphenyl (4c). Following a procedure identical to that described for the preparation of **4a**, the reaction of (*S*)-phenylglycinol (5.4 g, 39.4 mmol) with **3** (5.0 g, 17.9 mmol) in the presence of triethylamine (8.0 mL, 57.4 mmol) in dry dichloromethane (70 mL) afforded **4c** (6.2 g, 12.9 mmol, 72% yield) as a yellow solid. The ^{1}H NMR of **4c** also showed two sets of signals. Major/minor (52:48). ^{1}H NMR (400 MHz,

$CDCl_3$) major: δ 3.63 (m, 2H), 3.75 (m, 2H), 4.91 (m, 2H), 6.90−7.62 (m, 20H); minor: δ 3.57 (m, 4H), 5.00 (m, 2H), 6.90−7.62 (m, 20H). IR (KBr, cm^{-1}) 1539, 1633. MS (CI) *m*/*z* 481 ([M + 1]$^+$).

2,2′-Bis[*N*-(1′*S*)-(1′-benzyl-2′-hydroxyethyl)carboxamido]-1,1′-biphenyl (4d). Following a procedure identical to that described for the preparation of **4a**, the reaction of (*S*)-phenylalaninol (6.3 g, 41.7 mmol) with **3** (5.0 g, 17.9 mmol) in the presence of triethylamine (8.0 mL, 57.4 mmol) in dry dichloromethane (70 mL) afforded **4d** (6.6 g, 13.0 mmol, 73% yield) as a yellow solid. The ^{1}H NMR of **4d** also showed two sets of signals. Major/minor (52:48). ^{1}H NMR (400 MHz, $CDCl_3$) major: δ 2.39 (m, 2H), 2.64 (m, 2H), 3.19−4.00 (m, 6H), 6.75−7.31 (m, 20H), 7.36 (m, 2H); minor: δ 2.39 (m, 2H), 2.64 (m, 2H), 3.19−4.00 (m, 6H), 6.75−7.31 (m, 20H), 7.42 (m, 2H). IR (KBr, cm^{-1}) 1539, 1651, 3244. MS (CI) *m*/*z* 509 ([M + 1]$^+$).

2,2′-Bis[(4′*S*)-isopropyloxazolin-2′-yl]-1,1′-biphenyl (1a). A solution of methanesulfonyl chloride (2.5 mL, 32.3 mmol) in dry dichloromethane (5 mL) was added dropwise for 1 h to a solution of crude **4a** (5.7 g, 13.8 mmol) in the presence of triethylamine (8.0 mL, 57.4 mmol) in dry dichloromethane (50 mL) with stirring at −5 °C. After being stirred for 4 h at room temperature, the resulting mixture was washed with water and then brine, dried over magnesium sulfate, and then concentrated in vacuo. The residue was purified by silica gel column chromatography with ethyl acetate as an eluent to give **1a** (4.3 g, 11.4 mmol, 83% yield) as a colorless viscous liquid. The ^{1}H NMR of **1a** showed two sets of signals. major/minor (71:29). ^{1}H NMR (600 MHz, $CDCl_3$) major: δ 0.81(m, 12H), 1.69 (m, 2H), 3.74 (t, 2H, *J* 7.8 Hz), 3.85 (m, 2H), 4.13 (t, 2H, *J* 9.3 Hz), 7.32 (d, 2H, *J* 7.2 Hz), 7.37 (m, 2H), 7.47 (t, 2H, *J* 7.2 Hz), 7.80 (d, 2H, *J* 7.8 Hz); minor: δ 0.81 (m, 6H), 0.87 (d, 6H, *J* 6.6 Hz), 1.64 (m, 2H), 3.85 (m, 4H), 4.01 (t, 2H, *J* 7.2 Hz), 7.23 (d, 2H, *J* 7.2 Hz), 7.37 (m, 2H), 7.40 (t, 2H, *J* 7.2 Hz), 7.86 (d, 2H, *J* 7.2 Hz). IR (neat, cm^{-1}) 1657. $[\alpha]^{26}_D$ = −141.5 (*c* 0.50, $CHCl_3$). HRMS (EI) calcd for $C_{24}H_{28}N_2O_2$: 376.2152, found 376.2156. Anal. Calcd for $C_{24}H_{28}N_2O_2$ $0.5H_2O$: C, 74.78; H, 7.58; N, 7.27. Found: C, 74.98; H, 7.53; N, 7.17.

2,2′-Bis[(4′*S*)-*tert*-butyloxazolin-2′-yl]-1,1′-biphenyl (1b). Following a procedure identical to that described for the preparation of **1a**, the reaction of crude **4b** (1.1 g, 2.5 mmol) with methanesulfonyl chloride (0.5 mL, 6.5 mmol) in the presence of triethylamine (1.5 mL, 10.8 mmol) in dry dichloromethane (25 mL) afforded **1b** (0.9 g, 2.2 mmol, 89% yield) as a colorless viscous liquid. The ^{1}H NMR of **1b** showed two sets of signals: major/minor (68:32). ^{1}H NMR (600 MHz, $CDCl_3$) major: δ 0.79 (s, 18H), 3.78 (t, 2H, *J* 8.6 Hz), 3.83 (m, 2H), 4.07 (t, 2H, *J* 8.6 Hz), 7.27 (m, 2H), 7.37 (m, 2H), 7.44 (m, 2H), 7.84 (d, 2H, *J* 7.8 Hz); minor: δ 0.79 (s, 18H), 3.83 (m, 2H), 3.94 (m, 4H), 7.21 (d, 2H, *J* 7.2 Hz), 7.37 (m, 4H), 7.88 (d, 2H, *J* 7.8 Hz). IR (neat, cm^{-1}) 1655. $[\alpha]^{26}_D$ = −101.4 (*c* 0.50, $CHCl_3$). HRMS (EI) calcd for $C_{26}H_{32}N_2O_2$: 404.2466, found 404.2474. Anal. Calcd for $C_{26}H_{32}N_2O_2$ $0.5H_2O$: C, 75.51; H, 8.04; N, 6.77. Found: C, 75.35; H, 7.89; N, 6.44.

2,2′-Bis[(4′*S*)-phenyloxazolin-2′-yl]-1,1′-biphenyl (1c). Following a procedure identical to that described for the preparation of **1a**, the reaction of crude **4c** (6.2 g, 12.9 mmol) with methanesulfonyl chloride (2.5 mL, 32.3 mmol) in the presence of triethylamine (8.0 mL, 57.4 mmol) in dry dichloromethane (55 mL) afforded **1c** (5.0 g, 11.3 mmol, 87% yield) as a colorless viscous liquid. The ^{1}H NMR of **1a** showed two sets of signals. major/minor (69:31). ^{1}H NMR (400 MHz, $CDCl_3$) major: δ 3.89 (t, 2H, *J* 8.4 Hz), 4.51 (q, 2H, *J* 8.4, 10.1 Hz), 5.22 (m, 2H), 7.14−7.98 (m, 18H); minor: δ 4.00 (t, 2H, *J* 8.4 Hz), 4.41 (q, 2H, *J* 8.4, 10.2 Hz), 5.22 (m, 2H), 7.14−7.98 (m, 18H). IR (neat, cm^{-1}) 1645. $[\alpha]^{26}_D$ = −194.6 (*c*, 0.50, $CHCl_3$). HRMS (EI) calcd for $C_{30}H_{24}N_2O_2$: 444.1839, found 444.1845. Anal. Calcd for $C_{30}H_{24}N_2O_2$ $0.6H_2O$: C, 79.13; H, 5.58; N, 6.15. Found: C, 79.40; H, 5.64; N, 6.00.

2,2′-Bis[(4′*S*)-benzyloxazolin-2′-yl]-1,1′-biphenyl (1d). Following a procedure identical to that described for the preparation of **1a**, the reaction of crude **4d** (6.6 g, 13.0 mmol) with methanesulfonyl chloride (2.5 mL, 32.3 mmol) in the presence of triethylamine (8.0 mL, 57.4 mmol) in dry dichloromethane (70 mL) afforded **1d** (5.2 g, 11.0 mmol, 85% yield) as a colorless viscous liquid. The ^{1}H NMR of **1a** showed two sets of signals: major/minor (70:30). ^{1}H NMR (400 MHz, $CDCl_3$) major: δ 2.62 (q, 2H, *J* 8.4, 13.8 Hz), 2.96 (dd, 2H, *J* 5.4, 13.8 Hz), 3.81 (t, 2H, *J* 7.8 Hz), 4.11 (t, 2H, *J* 9.0 Hz), 4.37 (m, 2H), 7.13−7.47 (m, 16H), 7.80 (d, 2H, *J* 7.8 Hz). minor: δ 2.56 (q, 2H, *J* 9.0, 13.8 Hz), 3.07 (dd, 2H, *J* 5.4, 13.8 Hz), 3.87 (t, 2H, *J* 7.8 Hz), 3.98 (t, 2H, *J* 9.0 Hz), 4.37 (m, 2H), 7.13−7.47 (m, 16H), 7.87 (d, 2H, *J* 7.8 Hz). IR (neat, cm^{-1}) 1649. $[\alpha]^{26}_D$ = −208.2 (*c* 0.50, $CHCl_3$). HRMS (EI) calcd for $C_{32}H_{28}N_2O_2$: 472.2152, found 472.2144. Anal. Calcd for $C_{32}H_{28}N_2O_2 \cdot 0.1H_2O$: C, 78.06; H, 6.18; N, 5.69. Found: C, 77.81; H, 5.95; N, 5.54.

2,2′-Bis[(4′*S*)-isopropyloxazolin-2′-yl]-1,1′-biphenyl Copper(I) Triflate Complex (6a, M = Cu(OTf)). To a solution of ligand **1a** (3.8 mg, 10.1 μmol) in dichloromethane-d_2 was added 1 equiv of $[Cu(I)OTf(C_6H_6)_{0.5}]$ (2.6 mg, 10.3 μmol), and the suspension was stirred at room temperature under argon atmosphere until complete dissolution. The ^{1}H NMR of this solution showed only one set of signals. (*S*,a*S*,*S*)-**6a** (M = Cu(OTf)): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 0.42 (d, 6H, *J* 6.8 Hz), 0.47 (d, 6H, *J* 6.8 Hz), 1.47 (m, 2H), 4.03 (m, 2H), 4.31 (m, 2H), 4.54 (t, 2H, *J* 9.4 Hz), 7.06 (m, 2H), 7.41 (m, 4H), 7.60 (m, 2H). MS (FAB) *m*/*z* 439 ([M − OTf]$^+$).

2,2′-Bis[(4′*S*)-*tert*-butyloxazolin-2′-yl]-1,1′-biphenyl Copper(I) Triflate Complex (6b, M = Cu(OTf)). The ^{1}H NMR of **6b** showed only one set of signals. (*S*,a*S*,*S*)-**6b** (M = Cu(OTf)): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 0.53 (s, 18H), 4.04 (m, 2H), 4.43 (m, 2H), 4.53 (t, 2H, *J* 9.6 Hz), 7.05 (m, 2H), 7.41 (m, 4H), 7.67 (m, 2H). MS (FAB) *m*/*z* 467 ([M − OTf]$^+$).

2,2′-Bis[(4′*S*)-phenyloxazolin-2′-yl]-1,1′-biphenyl Copper(I) Triflate Complex (6c, M = Cu(OTf)). The ^{1}H NMR of **6c** showed only one set of signals. (*S*,a*S*,*S*)-**6c** (M = Cu(OTf)): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.36 (q, 2H, *J* 7.4, 9.0 Hz), 4.82 (q, 2H, *J* 9.0, 10.2 Hz), 5.27 (q, 2H, *J* 7.4, 10.2 Hz), 6.58 (m, 4H), 7.01 (m, 4H), 7.08 (m, 2H), 7.16 (m, 2H), 7.43−7.51 (m, 4H), 7.57 (dd, 2H, *J* 1.6, 7.6 Hz). MS (FAB) *m*/*z* 507 ([M − OTf]$^+$).

2,2′-Bis[(4′*S*)-benzyloxazolin-2′-yl]-1,1′-biphenyl Copper(I) Triflate Complex (6d, M = Cu(OTf)). The ^{1}H NMR of **6d** showed only one set of signals. (*S*,a*S*,*S*)-**6d** (M = Cu(OTf)): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.93 (dd, 2H, *J* 5.4, 13.4 Hz), 2.50 (dd, 2H, *J* 5.4, 13.4 Hz), 4.30 (m, 2H), 4.44 (m, 4H), 6.83 (m, 4H), 7.08−7.14 (m, 8H), 7.42−7.51 (m, 4H), 7.59 (m, 2H). MS (FAB) *m*/*z* 535 ([M − OTf]$^+$).

Typical Procedure for Copper(I)-Catalyzed Asymmetric Cyclopropanation of Styrene. To a copper(I) triflate benzene complex $[Cu(I)OTf(C_6H_6)_{0.5}]$ (2.6 mg, 10.3 μmol) was added a solution of ligand **1** (11.0 μmol) in dichloromethane (1.0 mL), and then the suspension was stirred at room temperature for 2 h under argon atmosphere. The resulting solution was filtered through a membrane filter. After addition of styrene (104.2 mg, 1.0 mmol), a solution of ethyl or *l*-menthyl diazoacetate (1.3 mmol) in dichloromethane (1.0 mL) was slowly added over a period of 4 h, and then the reaction solution was stirred at room temperature for additional 24 h. The reaction mixture was filtered through an alumina short column, and the filtrate was concentrated in vacuo to give an oil which was chromatographed on a silica gel column with hexane/ethyl acetate (9:1) to separate *trans*- and *cis*-cycropropane carboxylates **11a**−**c**. The ratio of the *trans*- and *cis*-products was determined by GC with DB-1 of the oil before chromatography. The enantiomeric excess of **11a**−**c** was determined by GC with Chiraldex G-TA and DB-1. Absolute configuration of *trans*- and *cis*-**11a** was determined by comparison of their specific rotation with the reported one.[13] The absolute configuration of *trans*- and *cis*-**11b**,**c** was determined after the transesterification of *trans*- and *cis*-**11b**,**c** to *trans*- and *cis*-**11a**, respectively, in the presence of a sulfuric acid catalyst.

Typical Procedure for the Zinc(II)-Catalyzed Asymmetric Allylation of Aldehyde. To a stirred solution of ligand **1** (0.1 mmol) in dichloromethane (5 mL) was added zinc(II) salt (0.1 mmol), and the resulting mixture was stirred for

2 h at room temperature under argon atmosphere. Then aldehyde (1.0 mmol) and allyltri-*n*-butyltin (496.7 mg, 1.5 mmol) were added to this mixture, and the mixture was further stirred at room temperature for 72 h. The reaction was quenched by adding a saturated aqueous solution of $NaHCO_3$, and the organic phase was separated. The aqueous phase was extracted with dichloromethane (50 mL × 3), and the organic phases were combined, dried, and concentrated under reduced pressure to give an oil which was purified by flash silica gel column chromatography with cyclohexane/ether (2:1). Enantiomeric excess was determined by HPLC analysis [CHIRALCELL OB].

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Supporting Information Available: Experimental procedures and spectral data (^{1}H NMR and MS) of the complexes **6a**−**d** (M = CuCl, CuI), **7a**−**d** (M = ZnI_2, $ZnCl_2$, $Zn(OTf)_2$), **8a**−**d**, and **9a**−**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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