Asymmetric Cyclopropanation and Aziridination Reactions of Olefins Catalyzed by Cu(I)-Binaphthyldiimine Complexes

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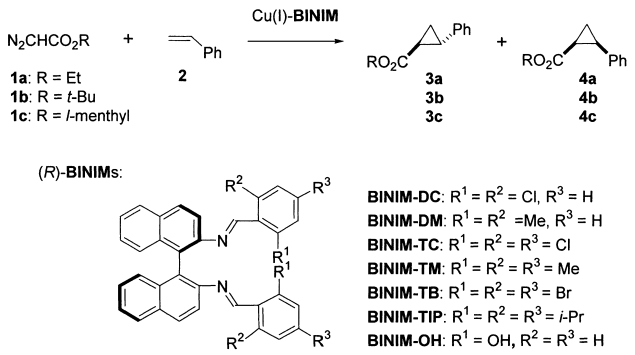
The chiral Cu(I)-*N*,*N*′-bis(2,6-dichlorobenzylidene)-1,1′-binaphthyl-2,2′-diamine complex was found to be an efficient catalyst for asymmetric cyclopropanation and aziridination reactions of olefins with *l*-menthyl diazoacetate and [*N*-(*p*-tolylsulfonyl)imino]phenyliodinane, respectively. Among mono- and disubstituted olefins, 1,1-diarylethylenes showed extremely high enantioselectivities (up to 98% ee) in the cyclopropanation reactions in the presence of a chiral Cu(I)-catalyst (2 mol%). In the case of aziridination reactions catalyzed by the same Cu(I)-catalyst (10 mol%), the reaction of *trans*-substituted 3-aryl-2-propenoates and 1-substituted *trans*-3-aryl-2-propen-1-ones showed satisfactory results in term of the enantioselectivities (up to 98% ee).

It is well-known that chiral binaphthyl derivatives, such as 1,1′-binaphthyl-2,2′-diol[1] and 1,1′-dinaphthyl-2,2′-bisphosphine[2] derivatives, are highly efficient ligands in asymmetric synthesis.[3] Concerning the mechanistic aspects, the C_2-symmetry of the axial chirality in the binaphthyl moiety plays an important role for asymmetric induction. On the other hand, chiral diimino compounds, such as bis(oxazoline)s[4] and salens,[5] are also known to be highly effective ligands in asymmetric synthesis.[3] Since chiral binaphthyldiimines have both axial chirality and a diimine structure, these derivatives are expected to serve as effective ligands in enatioselective reactions. Furthermore, those ligands could coordinate to metal of different sizes by changing in the dihedral angle between the two naphthyl rings with flexibility; the resulting complexes may create unique chiral environments for highly enantioselective reactions by placing appropriate substituents on the iminocarbons. Among this type of chiral binaphthyldiimine ligand, however, salen-type ligands containing 2-hydroxybenzylidene moieties were mainly paid attention, and have been applied to asymmetric synthesis.[6] Few examples were reported using simple chiral binaphthyldiimines having only a diimino-functionality for the coordination site.[8,11d] In this paper, we provide a full account of our investigations dealing with the combination of bidentate chiral binaphthyldiimines and Cu(I) salts as a catalytic system operated efficiently in the enantioselective cyclopropanation[7,8] and aziridination[9–12] reactions.

Results and Discussion

Cyclopropanation Reactions of Styrene. Initially, a cyclopropanation reaction of styrene (**2**) with ethyl diazoacetate (**1a**) was investigated in the presence of several Cu(I)-binaphthyldiimine-complexes (1 mol%) in dichloromethane at room temperature (Scheme 1). The complexes were prepared in situ



Scheme 1.

by mixing CuOTf·0.5C_6H_6 with several (*R*)-binaphthyldiimines ((*R*)-**BINIMs**), which were prepared by the reaction of (*R*)-1,1′-dinaphthyl-2,2′-diamine with 2,6-dichlorobenzaldehyde, 2,6-dinitrobenzaldehyde, 9-anthracenecarboxaldehyde, or 3,5-bis(benzyloxy)benzaldehyde, in dichloromethane at room temperature for 1 h under an argon atmosphere. Among the **BINIMs** used, *N*,*N*′-bis(2,6-dichlorobenzylidene)-1,1′-binaphthyl- 2,2′-diamine (**BINIM-DC**) exhibited moderate enantioselectivity (*trans*-adduct **3a**: 34% ee, *cis*-adduct **4a**: 47% ee, *trans*:*cis* = 79:21) in 75% total yield (Table 1, Entry 1).[13] Next, the steric effect of the alkoxy group on diazoacetate (Entries 2 and 3) and the solvent effect (Entries 4–8) were examined. Higher *trans*-selectivity was observed with larger alkoxy substituents, and an *l*-menthyloxy group on the diazoacetate showed the best results in terms of the enantioselectivity[26] of *trans*-product **3c**. From an investigation of the solvents, CH_2Cl_2 showed the highest enantioselectivity for both *trans*- and *cis*-cyclopropanes. The substituent effect of the benzene ring in the ligands for enantioselectivity was also

Table 1. Cu(I)-**BINIM**-Catalyzed Cyclopropanation Reactions of Styrene (**2**) with Diazoacetate **1**[a)]

Entry	R	Ligand	Solvent	Yield/%	*trans*:*cis*[b)]	% ee[b)]	*trans*	*cis*
1	Et	**BINIM-DC**	CH_2Cl_2	75	79:21		34[c)]	47[c)]
2	*t*-Bu	**BINIM-DC**	CH_2Cl_2	77	81:19		50[c)]	28[c)]
3	*l*-menthyl	**BINIM-DC**	CH_2Cl_2	81	83:17		57	43
4	*l*-menthyl	**BINIM-DC**	$CHCl_3$	84	77:23		42	35
5	*l*-menthyl	**BINIM-DC**	CH_3CHCl_2	81	73:27		27	7
6	*l*-menthyl	**BINIM-DC**	$CH_3CH_2CHCl_2$	83	76:24		34	13
7	*l*-menthyl	**BINIM-DC**	Benzene	88	71:29		10	8
8	*l*-menthyl	**BINIM-DC**	THF	83	81:19		0	20
9	*l*-menthyl	**BINIM-DM**	CH_2Cl_2	85	75:25		39	6
10	*l*-menthyl	**BINIM-TC**	CH_2Cl_2	95	81:19		50	41
11	*l*-menthyl	**BINIM-TM**	CH_2Cl_2	87	73:27		36	9
12	*l*-menthyl	**BINIM-TB**	CH_2Cl_2	84	69:31		15	6
13	*l*-menthyl	**BINIM-TIP**	CH_2Cl_2	89	71:29		37	25
14	*l*-menthyl	**BINIM-OH**	CH_2Cl_2	86	77:23		24	14

a) The reaction was carried out in the presence of 1 mol% of the catalysts, which were prepared from (*R*)-**BINIM**s and CuOTf·0.5C_6H_6, by adding **2** in a period of 6 h to **1** and then stirring was continued for 16 h at room temperature. b) Determined by GC (Quadrex Bonded-Fused Silica). c) Determined by GC after transformation into *l*-menthyl ester.

Table 2. Reactions of *l*-Menthyl Diazoacetate (**1c**) with Styrene (**2**)[a)]

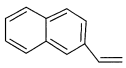
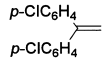
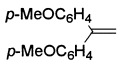
Entry	Copper Salt (Cat., mol%)	Conc.[b)]/molL^{-1}	Yield/%	*trans*:*cis*[c)]	% ee[c)]	*trans*	*cis*
1	CuOTf (1)	1.1	81	83:17		57	43
2	CuOTf (1)	0.55	92	85:15		62	84
3	CuOTf (2)	0.55	93	90:10		68	81
4	CuOTf (2)	0.55[d)]	92	85:15		55	63
5	CuOTf (2)	0.55[e)]	94	87:13		67	76
6	CuOTf (2)[f)]	0.55	96	82:18		57[g)]	85[g)]
7	CuOTf (2)	0.28	92	87:13		65	82
8	CuOTf (5)	0.55	92	86:14		65	83
9	$[Cu(MeCN)_4]PF_6$ (2)	0.55	92	86:14		62	89
10	$Cu(OTf)_2$ (2)	0.55	82	71:29		14	2

a) The reaction was carried out in the presence of the catalysts, which were prepared from (*R*)-**BINIM-DC** and copper salts, by adding the solution of **1c** in CH_2Cl_2 to **2** in a period of 6 h and then stirring was continued for 16 h at room temperature. See experimental section. b) The concentration of **1c** in CH_2Cl_2, which was added to **2** by a syringe pump. c) Determined by GC (Quadrex Bonded-Fused Silica). The absolute configuration was determined as *trans*: (1*S*,2*S*), *cis*: (1*S*,2*R*) in comparison with the optical rotation reported. d) The reaction was carried out at 0 °C. e) The solution of **1c** was added in a period of 24 h and then the mixture was stirred for 22 h. f) (*S*)-**BINIM-DC** was used. g) Absolute configuration; *trans*: (1*R*,2*R*), *cis*: (1*R*,2*S*).

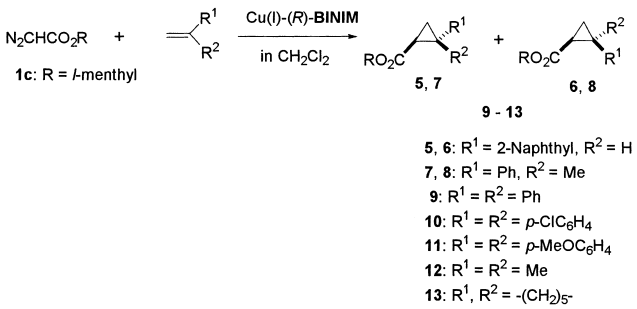
studied (Scheme 1, Entries 9–14). As a result, the **BINIM** containing 2,6-dicholorobenzylidene moieties gave the best result in terms of the enantioselctivity. Substitution of the *para*-position on the benzene ring did not largely affect the enantioselectivity in comparison to **BINIM-DC** and **BINIM-DM** with **BINIM-TC** and **BINIM-TM**, respectively (Entries 3 vs 10 and 9 vs 11). Replacing the Cl by a larger Br, or isopropyl groups on benzene rings, decreased the enantioselectivity as well as the diastereoselectivity. These results suggest that not only the size of the 2,6-substituents of the benzene ring, but also the electronic character, influence the enantioselectivity.

From examinations of the amount of the catalyst, the concentration of the diazoacetate in CH_2Cl_2, and the addition time, we found that the concentration greatly affected the enantioselctivity (Table 2). Thus, the enantioselectivity was improved especially for *cis*-adduct **4c** by diluting the solution of *l*-menthyl diazoacetate (**1c**) (Entries 2, 3, and 7) compared with the selectivity under the condition of Entry 1. In contrast, the slow addition of a solution of diazoacetate **1c** and lowering the reaction temperature did not improve the enantioselectivity (Entries 4 and 5). The amounts of the catalyst also did not significantly affect the enantioselectivity (Entries 2, 3, and 8). In the case of using the (*S*)-**BINIM-DC** instead of the (*R*)-**BINIM-DC**, the enantioselectivity of the *trans*-adduct **3c** was slightly decreased, probably due to stereochemical mismatching between the (*S*)-catalyst and *l*-menthyl diazoacetate (**1c**) (Entry 6). The use of easily handled $[Cu(MeCN)_4]PF_6$ as a copper salt in asymmetric cyclopropanation instead of CuOTf afforded a similar degree of enantioselectivity. However, the use of $Cu(OTf)_2$ as a copper salt showed an unsatisfactory result in terms of the enantioselectivities of both cyclopropanes. This result was quite a contrast from Cu-bis(oxazoline)-cata-

Table 3. Reactions of *l*-Menthyl Diazoacetate (**1c**) with Other Olefins[a)]

Entry	Olefin	Copper Salt	Temp/°C	Products	Yield/%	*E*:*Z*[b)]	% ee[b)]	*E*	*Z*
1		CuOTf	rt	**5**, **6**	89	90:10		76	62
2		CuOTf	rt	**7**, **8**	96	72:28[c)]		61[c)]	78[c)]
3		CuOTf	rt	**9**	69	—		74	
4		CuOTf	0	**9**	75	—		90	
5		CuOTf	−20	**9**	80	—		95	
6		CuOTf	−40	**9**	83	—		98	
7		$[Cu(MeCN)_4]PF_6$	rt	**9**	80	—		93	
8		$[Cu(MeCN)_4]PF_6$	−20	**9**	71	—		96	
9		$[Cu(MeCN)_4]PF_6$	rt	**10**	82	—		96[d)]	
10		$[Cu(MeCN)_4]PF_6$	rt	**11**	43	—		94[e)]	
11		CuOTf	rt	**12**	66	—		65	
12		CuOTf	−20	**12**	60	—		58	
13		$[Cu(MeCN)_4]PF_6$	rt	**13**	90	—		57	

a) To a solution of Cu(I)-(*R*)-**BINIM-DC** complex and olefin in CH_2Cl_2 was added *l*-menthyl diazoacetate (**1c**) in a period of 6 h at the temperature cited in Table 1, and then the mixture was stirred at the same temperature for 16 h. b) Determined by GC (Quadrex Bonded-Fused Silica). c) Determined by HPLC (Daicel Chiralpak AS). d) Determined by ^{1}H NMR (500 MHz). e) Determined by HPLC (Waters Radial-pak 8NVC18 4μ).



Scheme 2.

lyzed asymmetric cyclopropanations, in which the use of CuOTf and $Cu(OTf)_2$ showed similar enantioselectivities.[14]

We applied the Cu(I)-**BINIM-DC** complex to other olefins (Scheme 2) under similar conditions of Entry 3 in Table 2 (Table 3). The reactions of 2-vinylnaphthalene (Entry 1), α-methylstyrene (Entry 2), 2-methylpropene (Entries 11 and 12), and methylenecyclohexane (Entry 13) showed moderate enantioselectivities. On the other hand, it is noteworthy that the reactions of 1,1-diarylethylenes showed extremely high enantioselectivities (up to 98% ee). The enantioselectivity of the CuOTf-**BINIM-DC**-catalyzed cyclopropanation reaction of 1,1-diphenylethylene was quite dependent on the reaction temperature. Although only 74% ee was observed under the conditions at room temperature (Entry 3), the enantioselectivity increased by decreasing the temperature (Entry 4–6) and at −40 °C the corresponding cyclopropane was obtained in high chemical yield with 98% ee (Entry 6). When $[Cu(MeCN)_4]PF_6$ was used as a copper salt, a high level of enantioselectivity (93% ee) was afforded, even at room temperature (Entry 7). It is interesting to note that the cyclopropanation of 1,1-diphenylethylene with *l*-menthyl diazoacetate and *d*-menthyl diazoacetate proceeded only with 65% ee and 89% ee, respectively, both in 55% yield using Ru(II)-2,6-bis[(4*S*)-4-isopropyl-2-oxazolin-2-yl]pyridine complex, which catalyzed the cyclopropanation of styrene with extremely high enantioselectivity (up to 96% ee) in high yield.[15] The high enantioselectivity of the Cu(I)-**BINIM-DC**-catalyzed reaction was not affected by the electronic character of the substituent on the benzene ring of 1,1-diarylethylenes (Entries 9 and 10).

Model Study for Enantioselectivity in the Asymmetric Cyclopropanation. In order to elucidate the reason for the high enantioselectivity in Cu(I)-**BINIM-DC**-catalyzed cyclopropanation reactions of 1,1-diarylethylenes, the structure of the Cu(I)-**BINIM-DC**-carbenoide complex was studied by a PM3 calculation.[16] The optimized structure of the complex is shown in Figs. 1 and 2. From those views, the front side of the carbenoide carbon adjacent to copper in Fig. 2 is relatively more crowded by a 2,6-dichlorobenzylidene moiety than the back side of the carbon. Therefore, the back side approach of the olefin seems to be more accessible. If the phenyl group is

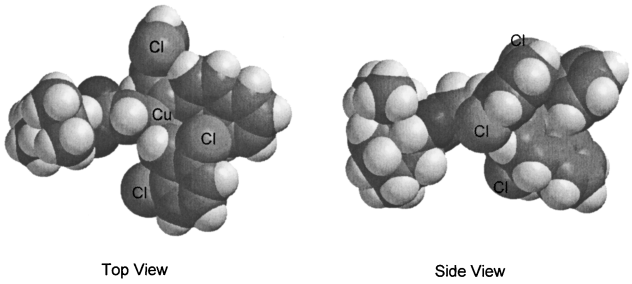


Fig. 1. Optimized structure of the Cu(I)-**BINIM-DC** complex calculated by PM3.

oriented *cis* from the *l*-menthyloxycalbonyl group through this approach, the steric hindrance between these groups may force the back side approach much more easily. Hence, the high enantioselctivities of the cyclopropanes derived from 1,1-diarylethylenes and the *cis*-adduct of styrene can be obtained.

Aziridination Reactions of 3-Substituted Propenoate and 1,3-Disubstituted 2-Propen-1-one Derivatives. Asymmetric aziridination reactions of [*N*-(*p*-tolylsulfonyl)imino]-phenyliodinane (PhINTs, **14**) with methyl *trans*-cinnamate (5 equiv) were initially examined at room temperature in CH_2Cl_2 in the presence of 10 mol% chiral Cu(I)-**BINIM** complexes (Table 4, Entries 1–5). Various catalysts were prepared by mixing appropriate chiral **BINIMs** with $[Cu(MeCN)_4]PF_6$ (Scheme 3), followed by filtration under an argon atmosphere. The corresponding 2-methoxycarbonyl-3-phenylaziridine **15** was produced in good-to-high yields. Among the chiral ligands, the use of (*R*)-**BINIM-DC** showed the highest enantioselectivity (75–77% ee), which was similarly observed in the cyclopropanation reactions shown above. Although the aziridination reactions were probably completed in less than 3 h, the majority of the reactions were carried out for 19–20 h because the disappearance of highly polar PhINTs (**14**) could not be followed by TLC. In contrast to the Cu(II)-bis(oxazoline) complexes,[10b] it should be noted that the Cu(II) complex, which was prepared by $Cu(OTf)_2$ and (*R*)-**BINIM-DC** under similar conditions, did not catalyze the aziridination, and therefore aziridine was not obtained.

From an investigation of the reaction solvents, CH_2Cl_2 was found to be the most effective solvent in terms of the yield and enantioselectivity (Table 4, Entries 1 and 6–9). Using $CHCl_3$ or CCl_4, low or no yields of the aziridine were obtained, respectively, which were probably attributable to the low solubility of PhINTs in these solvents (Entries 6 and 7). Interestingly,

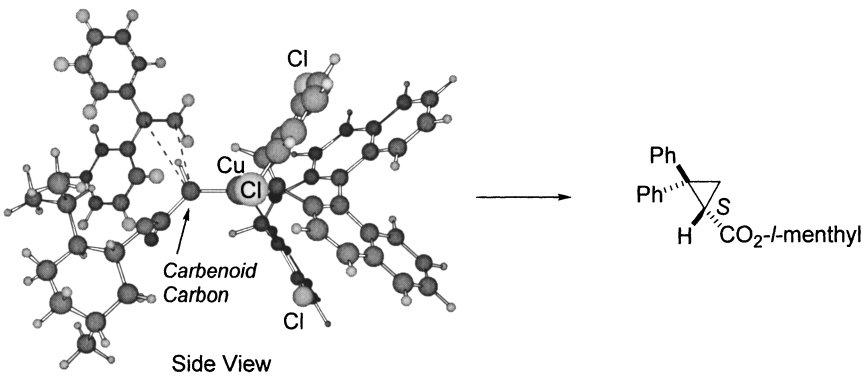
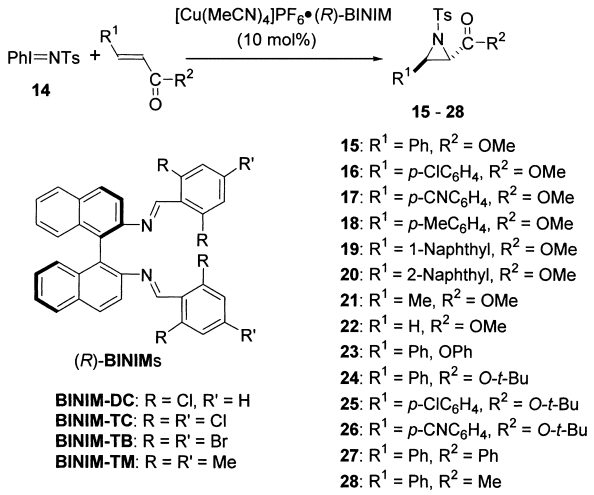


Fig. 2. Proposed approach of 1,1-diphenylethylene.

Table 4. Enantioselective Aziridination of Methyl Cinnamate[a)]

Entry	Ligand	Solvent	Temp, Time	Yield/%	% ee[b)]
1	(*R*)-**BINIM-DC**	CH_2Cl_2	rt, 3 h	71	77
2	(*R*)-**BINIM-DC**	CH_2Cl_2	rt, 19 h	77	75
3	(*R*)-**BINIM-TC**	CH_2Cl_2	rt, 20 h	95	66
4	(*R*)-**BINIM-TB**	CH_2Cl_2	rt, 19 h	75	55
5	(*R*)-**BINIM-TM**	CH_2Cl_2	rt, 19 h	86	32
6	(*R*)-**BINIM-DC**	$CHCl_3$	rt, 3 h	28	70
7	(*R*)-**BINIM-DC**	CCl_4	rt, 22 h	0	—
8	(*R*)-**BINIM-DC**	C_6H_6	rt, 3 h	64	41
9	(*R*)-**BINIM-DC**	MeCN	rt, 19 h	35	0
10	(*R*)-**BINIM-DC**	CH_2Cl_2	−20 °C, 1.5 h	88	80
11	(*R*)-**BINIM-DC**	CH_2Cl_2	−30 °C, 1.5 h	81	81
12	(*R*)-**BINIM-DC**	CH_2Cl_2	−45 °C, 2.5 h	83	83
13	(*R*)-**BINIM-DC**	CH_2Cl_2	−78 °C, 4 h	61	76

a) The reaction was carried out in the presence of 10 mol% of the catalyst, which was prepared by mixing $[Cu(MeCN)_4]PF_6$ (11 mol%) and the ligand (10 mol%) for 1 h at room temperature in the indicated solvent in this Table. b) Determined by HPLC using Chiralpak AS (hexane:2-propanol = 9:1).

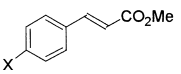
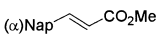
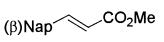
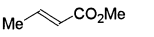
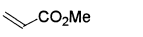
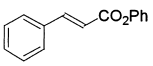
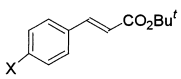
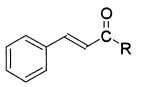


Scheme 3.

conducting the reactions at lower temperatures of −20, −30, and −45 °C (Entries 10–12, respectively) increased not only the enantioselectivities, which improved to over 80% ee, but also the overall yields. However, the reaction at −78 °C did not improve the results in either yield or enantioselectivity. It is noteworthy that, in terms of the reaction temperature, time, and yield, the rate acceleration effects of this catalyst seemed to be much higher than those of Cu(I)-bis(oxazoline) complexes[10b] and other reported catalysts without ligands, such as $CuClO_4$, $[Cu(acac)_2]$, and $Cu(OTf)_2$.[17]

In an investigation of the *trans*-3-arylpropenoates, *para*-substitution on the phenyl group, or a replacement of the phenyl group with 1-naphthyl or 2-naphthyl did not greatly affect the enantioselectivities (Table 5, Entries 1–5). Satisfactory enantioselectivities were observed regardless of the electron-withdrawing or electron-releasing character of the *para*-substituents. However, replacing the aromatic group at the 3-position by a hydrogen or a methyl group reduced the yields and

Table 5. Cu(I)-**BINIM-DC**-Catalyzed Enantioselective Aziridinations of Olefins[a)]

Entry	Olefin	Ligand	Temp, Time	Product	Yield/%	% ee[b)]	Config.[c)]
							
1	X = Cl	(*R*)-**BINIM-DC**	−20 °C, 22 h	**16**	82	81	(2*S*,3*R*)
2	X = CN	(*S*)-**BINIM-DC**	−20 °C, 26 h	**17**	69	90[e)]	(2*R*,3*S*)
3	X = Me	(*S*)-**BINIM-DC**	−20 °C, 75 h	**18**	41	83[e)]	(2*R*,3*S*)
4		(*R*)-**BINIM-DC**	−20 °C, 20 h	**19**	74	77[d)]	(2*S*,3*R*)
5		(*R*)-**BINIM-DC**	−20 °C, 25 h	**20**	74	68[d)]	(2*S*,3*R*)
6		(*S*)-**BINIM-DC**	rt, 24 h	**21**	13	36	ND[f]
7		(*S*)-**BINIM-DC**	rt, 18 h	**22**	30	43	ND[f]
8		(*R*)-**BINIM-DC**	−20 °C, 3 h	**23**	48	89	(2*S*,3*R*)
							
9	X = H	(*R*)-**BINIM-DC**	−20 °C, 3 h	**24**	52	95	(2*S*,3*R*)
10	X = H	(*R*)-**BINIM-DC**	−40 °C, 24 h	**24**	57	98	(2*S*,3*R*)
11	X = Cl	(*S*)-**BINIM-DC**	−20 °C, 23 h	**25**	64	97	(2*R*,3*S*)
12	X = CN	(*S*)-**BINIM-DC**	−20 °C, 24 h	**26**	73	95	(2*R*,3*S*)[g)]
							
13	R = Ph	(*R*)-**BINIM-DC**	−20 °C, 3 h	**27**	87	84[e)]	(2*S*,3*R*)[g)]
14	R = Ph	(*S*)-**BINIM-DC**	−40 °C, 24 h	**27**	79	86[e)]	(2*R*,3*S*)[g)]
15	R = Me	(*S*)-**BINIM-DC**	−20 °C, 23 h	**28**	73	67[e)]	(2*R*,3*S*)[g)]

a) The reaction was carried out in the presence of 10 mol% of the catalyst, which was prepared by mixing $[Cu(MeCN)_4]PF_6$ (10 mol%) and **BINIM-DC** (11 mol%) for 1 h at room temperature in CH_2Cl_2. b) Determined by HPLC using Chiralpak AS (hexane:2-propanol = 9:1). c) Absolute configurations were established by the comparison of specific rotation with authentic sample. d) Determined by comparison of specific rotation with authentic sample (Ref. 2b). e) Determined by HPLC using Chiralpak AD (hexane:2-propanol = 9:1). f) Not determined. g) Absolute configurations were tentatively assigned related to the adducts of cinnamates.

enantioselctivities (Entries 6 and 7). Therefore, aryl-substituents of the propenoate at the 3-position seem to play an important role in appropriate enantiofacial selection.

We have observed that the size of the alkoxy moiety of the cinnamate affected the enantioselectivity of the aziridination reactions (Table 4, Entry 10; Table 5, Entries 8 and 9). In the case of the aziridination of *t*-butyl *trans*-cinnamate under similar conditions at −40 °C (Table 5, Entry 10), enantioselectivity was obtained with 98% ee in moderate yield. Reactions of *t*-butyl 3-*p*-chloro- and 3-*p*-cyanophenylpropenoates also showed extremely high enantioselectivity in good yields (Entries 11 and 12). Under similar conditions, the 1,3-disubstituted 2-propen-1-one derivatives, *trans*-chalcone and *trans*-benzylideneacetone (*trans*-4-phenyl-3-buten-2-one), also reacted in the presence of the chiral Cu(I)-**BINIM-DC** catalyst to give the corresponding aziridines in high yields with good enantioselectivity (Entries 13–15). Similar to the 3-arylpropenoates, the larger chalcone exhibited better enantioselectivity than that of benzylideneacetone. Unfortunately, the corresponding amido olefins, such as *N*-cinnamoylpyrrolidine and 3-cinnamoyl-2-oxazolidinone, did not react under those conditions.

Although reactions of styrene and *trans*-*β*-methylstyrene proceeded at −20 °C under similar conditions with high yields, the enantioselectivities of the corresponding aziridines were only 39% ee and 10% ee, respectively. It must be pointed out that, in the presence of the Cu(I)-(*R*)-**BINIM-DC** catalyst, the absolute configuration of the phenyl-bearing carbon (*S*) in the styrene adduct was opposite to those obtained from the 3-arylpropenoates. These results suggested that not only aromatic substituents, but also *trans*-substituted carbonyl moieties on the olefins, can play an important role in providing high enantioselectivity of the Cu(I)-**BINIM-DC**-catalyzed asymmetric aziridinations.

Model Study for Enantioselectivity in the Asymmetric Aziridinations. The structure of the nitrenoid intermediate, including the **BINIM-DC** ligand, was studied by semi-empirical molecular orbital calculations using the PM3 method.[16] Following calculations of the singlet species, the two optimised structures (Intermediates A and B) showed similar heat-of-formation values (Fig. 3). For these intermediates, the NSO_2-moiety has both N,O-bidentate coordinations to the Cu-diimine complex,[27] as described in the hybrid density functional theory calculations, as reported by Norrby.[18] The difference between the two intermediates is that either of the two sulfonyl oxygens can coordinate to the Cu-diimine complex. As shown in Fig. 3, the front side around the nitrenoid nitrogen in both intermediates A and B is shielded by the 2,6-dichlorophenyl group. In contrast, the back side of the nitrenoid nitrogen seems to be accessible, and it therefore seems that the approach of olefins from the backside is more facile. Since *trans*/*cis* isomerization was not observed in the aziridinations of *trans*-3-arylpropenoate and 1,3-disubstituted *trans*-2-propen-1-one derivatives, it is reasonable to consider a concerted mechanism. A possible approach of the cinnamate is shown in Fig. 4, in accordance with Norrby's Cu-aziridine complex model.[18] In this approach, the enantioselectivity is explained by the cleavage of the O–Cu of N,O-bidentate coordinations, followed by the coordination of carbonyl oxygen with Cu and the π-interaction of the 3-aryl group between the tosyl group.

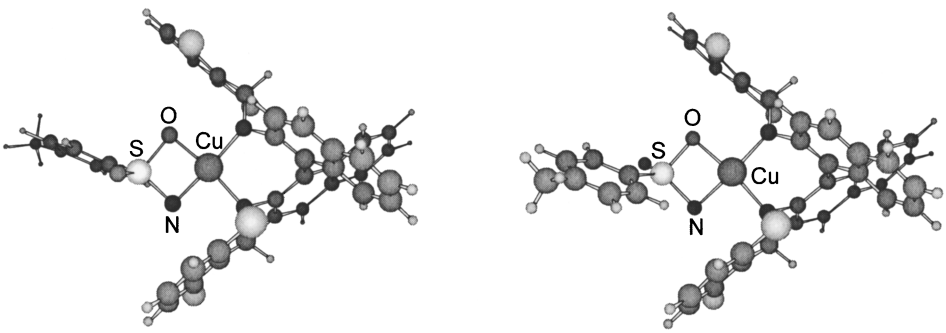


Fig. 3. Optimized structure of intermediates **A** and **B**.

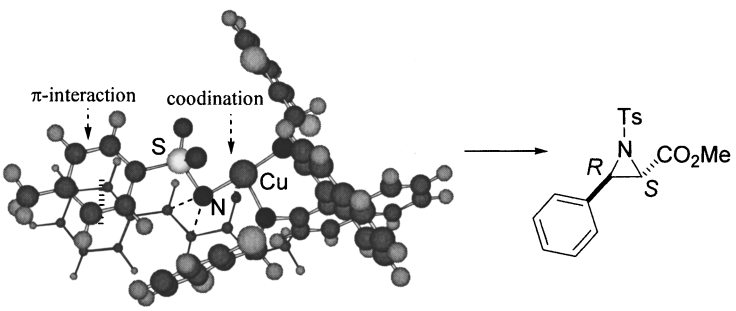


Fig. 4. Proposed approach of methyl cinnamate.

Conclusions

We have found that the chiral Cu(I)-**BINIM-DC** complex is an effective catalyst for asymmetric cyclopropanation and aziridination reactions. In the cyclopropanations, the reactions of *l*-menthy diazoacetate with 1,1-diarylethylenes showed extremely high enantioselctivity (up to 98% ee). High levels of enantioselectivity (up to 98% ee) were obtained in the aziridination reactions of 3-arylpropenoate and 1,3-disubstituted 2-propen-1-one derivatives using PhI=NTs as a nitrene precursor. Regarding model studies of the chiral carbene and nitrene complexes optimised by a PM3 calculation, the high levels of enantioselection could be explained by the proposed approaches (see Figs. 2 and 4). Experiments are currently underway to evaluate the versatility of the chiral **BINIM** ligands in other enantioselective reactions, such as Diels–Alder reactions[25] and 1,3-dipolar cycloaddition reactions.

Experimental

General. Melting points were determined on a Yanagimoto melting-point apparatus and are uncorrected. IR spectra were taken with a JASCO FT/IR-5300S spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL JNM-MY60FT (60 MHz), a JEOL GSX-400 (400 MHz), a JEOL GX-500 (500 MHz), or a JEOL EX-270 instrument (270 MHz), and ^{13}C NMR on a JEOL GSX-400 or JEOL EX-270 spectrometer. Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. MS spectra were measured with a HITACHI M-80B mass spectrometer. Elemental analyses were performed on a Yanaco CHN recorder MT-3 or a Perkin-Elmer 2400 CHN recorder. High-performance liquid chromatography was measured on a SHIMADZU LC-VP system. Optical rotations were recorded with a JASCO P-1010 polarimeter. For preparative column chromatography, a Wakogel C-300 and a Silica gel 60 (Merck) were employed. Medium-pressure liquid chromatography was carried out using a column packed with Silica gel 60 (Merck, size 0.040–0.063 mm). All reactions were carried out under an argon atmosphere in dried glassware.

Materials. All alkyl diazoacetates were prepared by a method described in the literature by Pfaltz.[19] *N*-(*p*-Tolylsulfonyl)imino]phenyliodinane was prepared by the reported procedure.[20] CuOTf·0.5C_6H_6 and Cu(OTf)$_2$ were purchased from Tokyokasei Co. [Cu(MeCN)$_4$]PF_6 was prepared by a method described in the literature.[21] Benzene, toluene, and THF were freshly distilled from a sodium benzophenone ketyl still under argon. Dichloromethane, chloroform, CH_3CHCl_2, and $CH_3CH_2CHCl_2$ were purified by distillation, first from $CaCl_2$, and then CaH_2 under argon. Acetonitrile was purified by distillation, first from P_2O_5, and then CaH_2 under argon.

General Procedure is Given for the Asymmetric Cyclopropanation Reaction of *l*-Menthyl Diazoacetate with 1,1-Diphenlethylene. To a suspension of CuOTf·0.5C_6H_6 (14 mg, 0.055 mmol) in CH_2Cl_2 (5.0 mL) was added a solution of (*R*)-**BINIM-DC** (35 mg, 0.058 mmol) in dry CH_2Cl_2 (7.5 mL) at room temperature. Afer stirring for 1 h, 1,1-diphenyethylene (2.44 mL, 13.8 mmol) was added to the mixture. The mixture was cooled to −40 °C and a solution of *l*-menthyl diazoacetate (**1c**) (0.617 g, 2.75 mmol) in CH_2Cl_2 (5.0 mL) was added over a period of 6 h. The mixture was stirred for 16 h, and then concentrated in vacuo. The residue was chromatographed on silica gel (hexane–ethyl acetate, 99:1 v/v) to give 0.859 g (83% yield) of the corresponding cyclopropane.

Cyclopropanes **3a-c**,[15] **4a-c**,[15] **7**,[22, 23] **8**,[22, 23] and **9**[15, 22, 23] were identified by comparisons of their ^{1}H NMR signals with those given in the literature. The *trans*:*cis* ratio and/or enantioselectivity of cyclopropanes were determined by GC analysis using a Quadrex Bonded-Fused Silica Capillary Column (0.25 mm i.d. × 25 m × 0.25 μm) unless otherwise shown below. The *E*/*Z* ratio and enantioselectivities of cyclopropanes **7** and **8** were determined by an HPLC analysis (Daicel Chiralpak AS, hexane-*i*-PrOH 9:1 v/v, flow rate 1.0 mL/min).

l-Menthyl 2-naphthylcyclopropane-1-carboxylates (**5** and **6**) were obtained as 90:10 mixture of *trans*- and *cis*-isomers. Colorless solid; IR (KBr) 3420, 2952, 2927, 1717 (C=O), 1308, 1175 cm^{-1}; $[\alpha]_D^{24}$ = +7.6 ° (*c* 0.99, $CHCl_3$).

***l*-Menthyl *trans*-2-Naphthylcyclopropane-1-carboxylate (5):** ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.77–2.05 (21H, m, CH, CH_2, CH_3), 2.63–2.70 (1H, m, CH), 4.73 (1H, dt, *J* = 4.6, 10.9 Hz, CO_2CH), 7.18–7.81 (7H, m, Ar-H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 16.44, 17.07, 20.77, 22.01, 23.50, 24.34, 26.34, 31.38, 34.23, 40.96, 47.10, 74.50, 124.53, 124.69, 125.43, 126.22, 127.36, 127.59, 128.11, 132.23, 133.33, 137.66, 172.90.

***l*-Menthyl *cis*-2-Naphthylcyclopropane-1-carboxylate (6):** ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.22–1.60 (19H, m, CH, CH_2, CH_3), 1.86 (1H, m, CH), 2.15 (1H, m, CH), 2.72 (1H, m, CH), 4.37 (1H, dt, *J* = 4.3, 10.6 Hz, CO_2CH), 7.37–7.46 (3H, m, Ar-H), 7.70–7.78 (4H, m, Ar-H).

***l*-Menthyl 2,2-Diphenylcyclopropane-1-carboxylate (9):**[15, 22, 23] Colorless liquid; $[\alpha]_D^{24}$ = +9.4° (*c* 0.86, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.65–1.80 (19H, m, CH, CH_2, CH_3), 2.17 (1H, dd, *J* = 5.9, 5.0 Hz, CH), 2.55 (1H, dd, *J* = 7.9, 5.9 Hz, CH), 4.53 (1H, dt, *J* = 4.6, 10.9 Hz, CO_2CH), 7.14–7.59 (10H, m, Ar-H).

***l*-Menthyl 2,2-Bis(4-methoxyphenyl)cyclopropane-1-carboxylate (10):** Colorless liquid; $[\alpha]_D^{24}$ = +10.4° (*c* 0.80, $CHCl_3$); IR (Neat) 2954, 2869, 1727 (C=O), 1514, 1247, 1173, 1036 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.47–2.03 (19H, m, CH, CH_2, CH_3), 2.11 (1H, dd, *J* = 10.2, 4.6 Hz, CH), 2.46 (1H, t, *J* = 7.4 Hz, CH), 3.75 (6H, s, OCH_3), 4.49 (1H, dt, *J* = 4.2, 10.2 Hz, CO_2CH), 6.74–7.36 (8H, m, Ar-H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 16.22, 20.09, 20.84, 22.03, 23.28, 25.82, 29.37, 31.27, 34.21, 38.45, 41.09, 46.85, 55.04, 55.26, 74.25, 113.61, 113.73, 128.51, 130.77, 132.46, 137.72, 158.05, 158.35, 170.30. The enantioselectivity was determined by an HPLC analysis (Daicel Chiralpak AS, hexane-*i*-PrOH 9:1 v/v, flow rate 1.0 mL/min). HRMS (EI) Found: *m*/*z* 436.2602. Calcd for $C_{28}H_{36}O_4$: M, 436.2615.

***l*-Menthyl 2,2-Bis(4-chlorophenyl)cyclopropane-1-carboxylate (11):** Colorless liquid; $[\alpha]_D^{24}$ = +7.1° (*c* 0.97, $CHCl_3$); IR (Neat) 3445, 2956, 1718 (C=O), 1636, 1175, 1092 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.81–1.72 (19H, m, CH, CH_2, CH_3), 2.17 (1H, dd, *J* = 5.9, 5.3 Hz, CH), 2.52 (1H, dd, *J* = 8.3, 5.9 Hz, CH), 4.50 (1H, dt, *J* = 6.6, 10.9 Hz, CO_2CH), 7.14–7.37 (8H, m, Ar-H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 16.14, 20.01, 20.78, 21.99, 23.17, 25.82, 29.24, 31.22, 34.11, 38.35, 41.03, 46.76, 74.65, 128.61, 128.89, 131.11, 132.51, 133.08, 138.10, 142.95, 169.67. The enantioselctivity was determined by ^{1}H NMR (500 MHz). HRMS (EI) Found: *m*/*z* 444.1668. Calcd for $C_{26}H_{30}Cl_2O_2$: M, 444.1625.

***l*-Menthyl 2,2-Dimethylcyclopropane-1-carboxylate (12):** Colorless crystals; $[\alpha]_D^{24}$ = −2.4° (*c* 0.86, $CHCl_3$); IR (KBr) 3437, 2954, 1713 (C=O), 1635, 1459, 1401, 1269, 1173, 1015 cm^{-1}; ^{1}H NMR (270 Hz, $CDCl_3$) δ 0.74–2.04 (27H, m, CH, CH_2, CH_3), 4.66 (1H, dt, *J* = 4.3, 10.9 Hz, CO_2CH); ^{13}C NMR (67.8 MHz,

$CDCl_3$) δ 16.38, 18.74, 20.79, 21.60, 22.07, 22.61, 23.49, 26.23, 26.96, 27.13, 31.43, 34.34, 41.35, 47.09, 73.97, 172.42. A satisfactory analytical result was not obtained due to the instability of **12**.

1-*l*-Menthyloxycarbonylspiro[2.5]octane (13): Colorless crystals; $[\alpha]_D^{24} = -2.0°$ (*c* 0.97, $CHCl_3$); IR (KBr) 3437, 2942, 2850, 1709 (C=O), 1445, 1403, 1172 cm^{-1}; ^1H NMR (270 Hz, $CDCl_3$) δ 0.75–1.71 (29H, m, CH, CH_2, CH_3), 1.89–2.05 (2H, m, CH), 4.66 (1H × 78.5/100, dt, J = 4.3, 10.9 Hz, CO_2CH), 4.68 (1H × 21.5/100, dt, J = 4.3, 10.9 Hz, CO_2CH); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 16.37, 20.36, 20.80, 22.08, 23.48, 25.70, 25.77, 26.18, 26.22, 26.32, 26.41, 28.80, 31.42, 34.36, 37.44, 41.13, 47.08, 73.76, 172.31. A satisfactory analytical result was not obtained due to the instability of **13**.

Typical Experimental Procedure for the Aziridination was Exemplified by the Reaction of *t*-Butyl *trans*-Cinnamate. To a suspension of $[Cu(MeCN)_4]PF_6$ (18 mg, 0.050 mmol) in CH_2Cl_2 (1.0 mL) was added (*R*)-**BINIM-DC** (33 mg, 0.055 mmol) in CH_2Cl_2 (4.0 mL) at room temperature. After stirring for 1.5 h, the mixture was filtered and washed with CH_2Cl_2 (6.0 mL) under an argon atmosphere. To this mixture was added *t*-butyl *trans*-cinnamate (510 mg, 2.5 mmol) and PhI=NTs (187 mg, 0.5 mmol) successively. The mixture was stirred at −40 °C for 24 h, and then filtered through a short plug of silica gel (2 × 5 cm). The silica gel was washed with 50% hexane–ethyl acetate (100 mL), and the filtrate was concentrated by rotary evaporation. The residue was chromatographed over silica gel (hexane-AcOEt 6:1 v/v) to give (2*S*,3*R*)-2-(*t*-butoxycarbonyl)-3-phenyl-1-(*p*-tolylsulfonyl)-aziridine (**24**) (145 mg, 57%). The enantiomeric excess was determined as 98% ee by an HPLC analysis (Daicel Chiralpak AS).

Aziridine **15**,[10b] **19**,[10b] **20**,[10b] **22**,[17] **23**,[10b] **24**,[11b] and **25**[11b] were identified by comparisons of their ^1H NMR signals with those given in the literature.

(2*S*,3*R*)-2-(Methoxycarbonyl)-3-phenyl-1-(*p*-tolylsulfonyl)-aziridine (15):[10b] Pale yellow viscous oil; $[\alpha]_D^{28} = -18.32°$ (*c* 0.18, CH_2Cl_2); 83% ee; IR (neat) 3056, 2955, 1747 (C=O), 1336 (SO_2), 1161 (SO_2) cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 2.48 (3H, s, Me), 3.61 (1H, d, J = 4.1 Hz, CH), 3.95 (3H, s, OMe), 4.54 (1H, d, J = 4.1 Hz, CH), 7.43 (7H, s, Ar-H), 7.94 (2H, d, J = 7.3 Hz, Ar-H); HPLC (CHIRALPAK AS, 1:9 2-PrOH–hexane, flow rate = 0.5 mL/min, Temp 35 °C, major = 48.6 min, minor = 71.6 min).

(2*S*,3*R*)-3-(4-Chlorophenyl)-2-(methoxycarbonyl)-1-(*p*-tolylsulfonyl)aziridine (16): Colorless solid; mp 110.0–110.7 °C; $[\alpha]_D^{23} = -26.57°$ (*c* 1.35, $CHCl_3$); 81% ee; IR (KBr) 2957, 1745 (C=O), 1597, 1494, 1444, 1369 (SO_2), 1267, 1226, 1182, 1161 (SO_2), 1087, 1012, 947, 837, 810, 792, 723, 672, 652 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 2.43 (3H, s, Me), 3.50 (1H, d, J = 3.9 Hz , CH), 3.86 (3H, s, OMe), 4.39 (1H, d, J = 3.9 Hz , CH), 7.25–7.87 (8H, m, Ar-H). Anal. Calcd for $C_{17}H_{16}ClNO_4S$: C, 55.81; H, 4.41; N, 3.83%. Found: C, 55.78; H, 4.49; N, 3.77%. HPLC (CHIRALPAK AS, 1:19 2-PrOH–hexane, flow rate = 0.5 mL/min, Temp 35 °C, major = 56.7 min, minor = 85.5 min).

(2*R*,3*S*)-3-(4-Cyanophenyl)-2-(methoxycarbonyl)-1-(*p*-tolylsulfonyl)aziridine (17): Colorless solid; mp 109.2–109.8 °C; $[\alpha]_D^{25} = +25.53°$ (*c* 0.79, $CHCl_3$); 90% ee; IR (KBr) 3040, 2957, 2361, 2231 (CN), 1919, 1757 (C=O), 1597, 1506, 1444, 1425, 1402, 1329 (SO_2), 1309, 1249, 1209, 1163 (SO_2), 1109, 1086 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 2.44 (3H, s, Me), 3.47 (1H, d, J = 4.0 Hz, CH), 3.88 (3H, s, OMe), 4.48 (1H, d, J = 4.0 Hz, CH), 7.27–7.89 (8H, m, Ar-H). Anal. Calcd for $C_{18}H_{16}N_2O_4S$: C, 60.66; H, 4.53; N, 7.86%. Found: C, 60.60; H, 4.68; N, 7.78%. HPLC (CHIRALPAK AS, 1:9 2-PrOH–hexane, flow rate = 0.5 mL/min, Temp 35 °C, major = 139.1 min, minor = 154.0 min).

(2*R*,3*S*)-2-(Methoxycarbonyl)-3-(4-methylphenyl)-1-(*p*-tolylsulfonyl)aziridine (18): Yellow oil; $[\alpha]_D^{24} = +14.72°$ (*c* 0.84, $CHCl_3$); 83% ee; IR (neat) 3030, 2955, 2361, 2339, 1747 (C=O), 1597, 1518, 1494, 1442, 1402, 1336 (SO_2), 1215, 1161 (SO_2), 1089, 1018, 935, 812, 783, 761, 721 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 2.33 (3H, s, Me), 2.42 (3H, s, Me), 3.38 (1H, d, J = 3.9 Hz, CH), 3.80 (3H, s, OMe), 4.34 (1H, d, J = 3.9 Hz, CH), 7.21–7.88 (8H, m, Ar-H). Anal. Calcd for $C_{18}H_{19}NO_4S$: C, 62.59; H, 5.54; N, 4.06%. Found: C, 62.75; H, 5.67; N, 3.79%. HPLC (CHIRALPAK AS, 1:9 2-PrOH–hexane, flow rate = 0.5 mL/min, Temp 35 °C, major = 75.8 min, minor = 35.6 min).

(2*S*,3*R*)-2-(Methoxycarbonyl)-3-(1-naphthyl)-1-(*p*-tolylsulfonyl)aziridine (19):[10b] Colorless solid; mp 49.0–50.0 °C; $[\alpha]_D^{24} = +26.20°$ (*c* 1.03, CH_2Cl_2); 77% ee; IR (KBr) 3051, 2953, 2361, 1745 (C=O), 1597, 1510, 1439, 1392, 1336 (SO_2), 1290, 1213, 1161 (SO_2), 1087, 1037, 1018, 916, 802 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 2.41 (3H, s, Me), 3.60 (1H, d, J = 4.4 Hz, CH), 3.93 (3H, s, OMe), 4.95 (1H, d, J = 4.4 Hz, CH), 7.16–8.19 (11H, m, Ar-H).

(2*S*,3*R*)-2-(Methoxycarbonyl)-3-(2-naphthyl)-1-(*p*-tolylsulfonyl)aziridine (20):[10b] Colorless solid; mp 105.5–106.8 °C; $[\alpha]_D^{24} = -8.76°$ (*c* 1.07, $CHCl_3$); 68%; IR (KBr) 3040, 2953, 2359, 1745 (C=O), 1597, 1506, 1494, 1440, 1406, 1323 (SO_2), 1240, 1205, 1161 (SO_2), 1087, 1018 , 993 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 2.40 (3H, s, Me), 3.65 (1H, d, J = 4.0 Hz, CH), 3.89 (3H, s, OMe), 4.59 (1H, d, J = 4.0 Hz, CH), 7.20–7.85 (11H, m, Ar-H).

2-(Methoxycarbonyl)-3-methyl-1-(*p*-tolylsulfonyl)aziridine (21): Yellow oil; $[\alpha]_D^{23} = -3.86°$ (*c* 0.088, $CHCl_3$); 36% ee; IR (neat) 2955, 2361, 1747, 1683 (C=O), 1597, 1494, 1442, 1329 (SO_2), 1244, 1161 (SO_2), 1089, 1060, 970, 877, 817, 684 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 1.73 (1H, d, J = 5.6 Hz, Me), 2.43 (3H, s, Me), 2.95–3.30 (1H, m, CH), 3.35 (1H, d, J = 4.1 Hz, CH), 7.32 (2H, d, J = 8.3 Hz, Ar-H), 7.86 (2H, d, J = 8.3 Hz, Ar-H). HPLC (CHIRALPAK AS, 1:29 2-PrOH–hexane, flow rate = 0.5 mL/min, Temp 35 °C, major = 13.0 min, minor = 14.1 min). A satisfactory analytical result was not obtained due to the instability of **21**.

2-(Methoxycarbonyl)-1-(*p*-tolylsulfonyl)aziridine (22):[17] Yellow oil; $[\alpha]_D^{24} = -19.11°$ (*c* 0.736, $CHCl_3$); 43% ee; IR (neat) 2957, 1748 (C=O), 1597, 1442, 1394, 1332 (SO_2), 1292, 1232, 1163 (SO_2), 1093, 1035, 908, 815, 781, 707, 692, 642 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 2.43 (3H, s, Me), 2.56 (1H, d, J = 3.9 Hz, one of CH_2), 2.76 (1H, d, J = 7.1 Hz, one of CH_2), 3.35 (1H, dd, J = 7.1, 3.9 Hz, CH), 3.74 (3H, s, OMe), 7.32 (2H, d, J = 8.3 Hz, Ar-H), 7.84 (2H, d, J = 8.3 Hz, Ar-H). HPLC (CHIRALPAK AD, 1:9 2-PrOH–hexane, flow rate = 0.5 mL/min, Temp 35 °C, major = 44.0 min, minor = 42.1 min).

(2*S*,3*R*)-2-(Phenoxycarbonyl)-3-phenyl-1-(*p*-tolylsulfonyl)-aziridine (23):[10b] Pale yellow viscous oil; $[\alpha]_D^{24} = -51.75°$ (*c* 1.21, $CHCl_3$); 89% ee; IR (neat) 3065, 3034, 2924, 2361, 1919, 1749 (C=O), 1653, 1595, 1493, 1456, 1417, 1338 (SO_2), 1292, 1197 (SO_2), 1087, 1026, 945, 869, 815, 748, 696, 599 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 2.42 (3H, s, Me), 3.69 (1H, d, J = 4.0 Hz, CH), 4.61 (1H, d, J = 4.0 Hz, CH), 7.33 (12H, s, Ar-H), 7.86 (2H, d, J = 8.6 Hz, Ar-H). HPLC (CHIRALPAK AS, 1:19 2-PrOH–hexane, flow rate = 0.5 mL/min, Temp 35 °C, major = 48.3 min, minor = 45.0 min).

(2*S*,3*R*)-2-(*t*-Butoxycarbonyl)-3-phenyl-1-(*p*-tolylsulfonyl)-aziridine (24):[11b] Pale yellow viscous oil; $[\alpha]_D^{24} = -36.18°$ (*c* 1.13, $CHCl_3$); 98% ee; IR (neat) 2980, 2361, 1738 (C=O), 1597, 1456, 1417, 1369 (SO_2), 1338, 1240, 1161 (SO_2), 1087, 929, 814, 763, 694, 594, 567, 441 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 1.54 (9H, s, *t*-Bu), 2.42 (3H, s, Me), 3.41 (1H, d, J = 4.0 Hz, CH), 4.38 (1H, d, J = 4.0 Hz, CH), 7.34–7.28 (7H, m, Ar-H), 7.82 (2H, d, J = 8.1 Hz, Ar-H). HPLC (CHIRALPAK AS, 1:19 2-PrOH-hexane, flow rate = 0.5 mL/min, Temp 35 °C, major = 19.7 min, minor = 21.5 min).

(2*R*,3*S*)-2-(*t*-Butoxycarbonyl)-3-(4-chlorophenyl)-1-(*p*-tolylsulfonyl)aziridine (25):[11b] Colorless solid; mp 82.0–83.0 °C; $[\alpha]_D^{24} = +27.19°$ (*c* 0.56, $CHCl_3$); 97% ee; IR (KBr) 2974, 2930, 1739 (C=O), 1597, 1496, 1435, 1400, 1371, 1332 (SO_2), 1300, 1259, 1155 (SO_2), 1089, 1014, 925, 875, 815, 723, 685 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 1.54 (9H, s, *t*-Bu), 2.42 (3H, s, Me), 3.38 (1H, d, J = 3.9 Hz, CH), 4.34 (1H, d, J = 3.9 Hz, CH), 7.21–7.88 (8H, m, Ar-H). Anal. Calcd for $C_{20}H_{22}ClNO_4S$: C, 58.89; H, 5.44; N, 3.43%. Found: C, 58.90; H, 5.44; N, 3.41%. HPLC (CHIRALPAK AD, 1:29 2-PrOH–hexane, flow rate = 0.5 mL/min, Temp 35 °C, major = 93.9 min, minor = 99.1 min).

(2*R*,3*S*)-2-(*t*-Butoxycarbonyl)-3-(4-cyanophenyl)-1-(*p*-tolylsulfonyl)aziridine (26): Colorless solid; mp 44.5–45.0 °C; $[\alpha]_D^{24} = +30.73°$ (*c* 1.07, $CHCl_3$); 95% ee; IR (KBr) 3420, 2982, 2932, 2229, 1738 (C=O), 1597, 1433, 1396, 1369, 1338, 1307 (SO_2), 1230, 1163 (SO_2), 1116, 1087, 1018, 939, 815, 707, 690 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 1.55 (9H, s, *t*-Bu), 2.43 (3H, s, Me), 3.35 (1H, d, J = 4.2 Hz, CH), 4.41 (1H, d, J = 4.2 Hz, CH), 7.23–7.89 (8H, m, Ar-H). Anal. Calcd for $C_{21}H_{22}N_2O_4S$: C, 63.30; H, 5.57; N, 7.03%. Found: C, 63.50; H, 5.59; N, 6.81%. HPLC (CHIRALPAK AS, 1:19 2-PrOH–hexane, flow rate = 0.5 mL/min, Temp 35 °C, major = 68.1 min, minor = 94.0 min).

(2*R*,3*S*)-2-Benzoyl-3-phenyl-1-(*p*-tolylsulfonyl)aziridine (27): Yellow solid; mp 109.0–110.5 °C; $[\alpha]_D^{25} = -4.65°$ (*c* 1.00, $CHCl_3$); 86% ee; IR (KBr) 3032, 2922, 2478, 2328, 1967, 1913, 1826, 1799, 1693 (C=O), 1597, 1450, 1323 (SO_2), 1292, 1236, 1184, 1161 (SO_2), 1099, 1082, 997, 947, 920, 846, 812, 744, 711 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 2.40 (3H, s, Me), 4.28 (1H, d, J = 4.4 Hz, CH), 4.52 (1H, d, J = 4.4 Hz, CH), 7.15–7.80 (14H, m, Ar-H). Anal. Calcd for $C_{22}H_{19}NO_3S$: C, 70.00; H, 5.07; N, 3.71%. Found: C, 70.07; H, 5.05; N, 3.55%. HPLC (CHIRALPAK AD, 1:9 2-PrOH–hexane, flow rate = 0.5 mL/min, Temp 35 °C, major = 95.6 min, minor = 73.7 min).

(2*R*,3*S*)-2-Acetyl-3-phenyl-1-(*p*-tolylsulfonyl)aziridine (28): Yellow oil; $[\alpha]_D^{24} = -5.24°$ (*c* 0.85, $CHCl_3$); 67%; IR (neat) 3065, 3034, 2924, 1716 (C=O), 1597, 1496, 1454, 1410, 1336 (SO_2), 1240, 1205, 1159 (SO_2), 1087, 929, 815, 744, 690 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 2.33 (3H, s, COMe), 2.42 (3H, s, Me), 3.73 (1H, d, J = 4.1 Hz, CH), 4.27 (1H, d, J = 4.1 Hz, CH), 7.20–7.80 (9H, m, Ar-H). Anal. Calcd for $C_{17}H_{17}NO_3S$: C, 64.74; H, 5.43; N, 4.44%. Found: C, 64.85; H, 5.49; N, 4.26%. HPLC (CHIRALPAK AS, 1:9 2-PrOH–hexane, flow rate = 0.5 mL/min, Temp 35 °C, major = 62.9 min, minor = 70.3 min).

(*R*)-*N*,*N*′-Bis(2,6-dichlorobenzylidene)-1,1′-binaphthyl-2,2′-diamine ((*R*)-BINIM-DC). A suspension of MS 4A (3.2 mm pellets, 12.0 g), (*R*)-1,1′-binaphthyl-2,2′-diamine (0.602 g, 2.12 mmol), and 2,6-dichlorobenzaldehyde (0.742 g, 4.24 mmol) in benzene (18 mL) was stirred at room temperature for 16 h. After MS 4A was removed by filtration, the filtrate was concentrated in vacuo. The resulting solids were recrystallized from benzene-hexane to give (*R*)-**BINIM-DC** (1.00 g, 79%): Yellow plate (benzene-hexane); mp 216–218 °C; $[\alpha]_D^{24} = -10.1°$ (*c* 0.96, CH_2Cl_2); IR (KBr) 3051, 1636, 1615 (C=N), 1577, 1429, 814, 777, 748 cm^{-1}; ^1H NMR (270 MHz, C_6D_6) δ 6.17 (2H, t, J = 7.9 Hz, 4-H of 2,6-$Cl_2C_6H_3$), 6.60 (4H, d, J = 7.9 Hz, 3-, 5-H of 2,6-$Cl_2C_6H_3$), 7.05–7.09 (2H, m, Ar-H), 7.19–7.22 (2H, m, Ar-H), 7.42 (2H, d, J = 8.6 Hz, Ar-H), 7.56 (2H, J = 8.3 Hz, Ar-H), 7.73 (2H, d, J = 7.9 Hz, Ar-H), 7.81 (2H, d, J = 8.6 Hz, Ar-H), 8.69 (2H, s, CH=N). Anal. Calcd for $C_{34}H_{20}Cl_4N_2$: C, 68.2; H, 3.37; N, 4.68%. Found: C, 68.4; H, 3.52; N, 4.60%.

(*R*)-**BINIM-TC**, (*R*)-**BINIM-TM**, (*R*)-**BINIM-DM**, (*R*)-**BINIM-TB**, and (*R*)-**BINIM-TIP** were prepared by the same procedure as (*R*)-**BIMIN-DC**.

(*R*)-*N*,*N*′-Bis(2,4,6-trichlorobenzylidene)-1,1′-binaphthyl-2,2′-diamine ((*R*)-BINIM-TC): Yellow plates (diethyl ether–hexane); mp 162.3–163.7 °C; $[\alpha]_D^{24} = -5.9°$ (*c* 0.82, CH_2Cl_2); IR (KBr) 3443, 1642, 1617 (C=N), 1573, 1540, 1504, 1361 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.16–8.00 (16H, m, Ar-H), 8.57 (2H, s, CH=N). Anal. Calcd for $C_{34}H_{18}Cl_6N_2$: C, 61.20; H, 2.72; N, 4.20%. Found: C, 61.63; H, 2.91; N, 4.23%.

(*R*)-*N*,*N*′-Bis(2,4,6-trimethylbenzylidene)-1,1′-binaphthyl-2,2′-diamine ((*R*)-BINIM-TM): Yellow prisms (benzene-hexane); mp 191.5–193.0 °C; $[\alpha]_D^{24} = -9.3°$ (*c* 0.99, CH_2Cl_2); IR (KBr) 3051, 2965, 2917, 1629 (C=N), 1608, 1563, 808, 748 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.90 (12H, s, Me), 2.17 (6H, s, Me), 6.67 (4H, s, Ar-H), 7.95–7.24 (12H, m, Ar-H), 8.68 (2H, s, CH=N). Anal. Calcd for $C_{40}H_{36}N_2$: C, 88.20; H, 6.66; N, 5.14%. Found: C, 88.20; H, 6.74; N, 5.06%.

(*R*)-*N*,*N*′-Bis(2,6-dimethylbenzylidene)-1,1′-binaphthyl-2,2′-diamine ((*R*)-BINIM-DM): Yellow prisms (diethyl ether-hexane) mp 45.5–48.8 °C; $[\alpha]_D^{24} = -4.3°$ (*c* 0.82, CH_2Cl_2); IR (KBr) 2954, 2912, 2359, 1685, 1614 (C=N), 1590, 1506, 1465, 1424 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.92 (12H, s, Me), 6.84–7.98 (18H, m, Ar-H), 8.72 (2H, s, CH=N). Anal. Calcd for $C_{38}H_{32}N_2$: C, 88.3; H, 6.24; N, 5.42%. Found: C, 87.0; H, 6.51; N, 5.55%.

(*R*)-*N*,*N*′-Bis(2,4,6-tribromobenzylidene)-1,1′-binaphthyl-2,2′-diamine ((*R*)-BINIM-TB): Yellow plates (benzene-hexane); mp 102.0–104.0 °C; $[\alpha]_D^{24} = +7.6°$ (*c* 0.99, CH_2Cl_2); IR (KBr) 1616 (C=N), 1531, 1528, 1429, 1330, 856, 814, 735 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.26–8.00 (16H, m, Ar-H), 8.46 (2H, s, CH=N). Anal. Calcd for $C_{34}H_{18}Br_6N_2$: C, 43.73; H, 1.94; N, 3.00%. Found: C, 43.65; H, 2.20; N, 2.83%.

(*R*)-*N*,*N*′-Bis(2,4,6-triisopropylbenzylidene)-1,1′-binaphthyl-2,2′-diamine ((*R*)-BINIM-TIP): Yellow prisms (benzene-hexane); mp 74.8–76.4 °C; $[\alpha]_D^{24} = -15.1°$ (*c* 0.93, CH_2Cl_2); IR (KBr) 2960, 2927, 2868, 1615 (C=N), 1591, 1459, 743 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.76 (12H, d, J = 6.9 Hz, Me of *i*-Pr), 0.92 (12H, d, J = 6.9 Hz, Me of *i*-Pr), 1.16 (12H, d, J = 6.9 Hz, Me of *i*-Pr), 2.78–2.69 (6H, m, CH of *i*-Pr), 7.21–8.01 (16H, m, Ar-H), 8.82 (2H, s, CH=N). Anal. Calcd for $C_{52}H_{60}N_2$: C, 87.59; H, 8.48; N, 3.93%. Found: C, 87.44; H, 8.51; N, 3.94%.

(*R*)-*N*,*N*′-Bis(2-hydroxybenzylidene)-1,1′-binaphthyl-2,2′-diamine ((*R*)-BINIM-OH). (*R*)-**BINIM-OH** was prepared according to a procedure reported by Stack.[24] A solution of 1,1′-binaphthyl-2,2′-diamine (0.100 g, 0.35 mmol) and salicylaldehyde (0.080 mL, 0.70 mmol) in ethanol (3.0 mL) was heated under reflux for 6 h. The resulting crystals were filtered and then recrystallized from benzene-hexane to give (*R*)-**BINIM-OH** (0.152 g, 88%): Yellow plates (from benzene-hexane); mp 255–256.5 °C; $[\alpha]_D^{25} = +382.9°$ (*c* 0.16, CH_2Cl_2); ^1H NMR (60 MHz, $CDCl_3$) δ 6.63–8.19 (20H, m, Ar-H), 8.66 (2H, s, CH=N), 12.08 (2H, s, OH); IR (KBr) 3440 (OH), 3053, 1609 (C=N), 1568, 1493, 1462,

1283, 1196, 818 cm^{-1}. Anal. Calcd for $C_{34}H_{24}N_2O_2$: C, 82.91; H, 4.91; N, 5.69%. Found: C, 83.18; H, 4.82; N, 5.41%.

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27 In contrast, Scott reported that the density functional theory calculations of similar biaryldiimine-Cu(I) catalytic intermediates did not locate N,O-bidentate coordinated structure.[11b]