

Enantio- and Diastereoselectivity in 1,3-Dipolar Cycloaddition Reactions of Nitrones with 3-Crotonoyl-2-oxazolidinone Catalyzed by Ni(II)-Binaphthyl-diimine Complexes

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Chiral Ni(II)-1,1'-binaphthyl-2,2'-diimine complexes were found to be effective Lewis-acid catalysts for an asymmetric 1,3-dipolar cycloaddition reaction of *N*-benzylideneaniline *N*-oxide with 3-crotonoyl-2-oxazolidinone. In the presence of molecular sieves (4 Å), when the chiral *N,N'*-bis(2,6-dichlorobenzylidene)-1,1'-binaphthyl-2,2'-diamine (**BINIM-DC**) and Ni(ClO₄)₂·6H₂O were used to prepare the catalyst, up to 81% ee of the corresponding *endo*-cycloadduct was obtained with *endo*-selectivity (87:13, and up to 96:4). The use of *N,N'*-bis(3-chloro-substituted 2-hydroxybenzylidene) derivatives as ligands under similar conditions showed high *exo*-selectivity (up to 95:5) with moderate enantioselectivity. Although almost no diastereoselectivity was observed, *endo*- and *exo*-cycloadducts were obtained with promising levels of enantioselectivity (up to > 98%) in the presence of catalysts, which were prepared from chiral **BINIM-DC**, NiBr₂, and AgBF₄, AgSbF₆, or AgPF₆.

1,3-Dipolar cycloaddition reactions of nitrones with olefins are the most useful and convenient methods for preparing isoxazolidine derivatives, which are readily converted to synthetically useful 1,3-amino alcohols by reductive reagents.¹ Because of the importance of chiral amino alcohol units for the synthesis of biologically important alkaloids, amino acids, β -lactams, and amino sugars,² enantioselective cycloaddition reactions of nitrones³ using chiral Lewis acid catalysts have been studied intensively in recent years. On the other hand, we found that chiral *N,N'*-bis(2,6-dichlorobenzylidene)-1,1'-binaphthyl-2,2'-diamine (**BINIM-DC**) is an efficient ligand in a Cu(I)-catalyzed asymmetric cyclopropanation reaction⁴ of 1,1-diphenylethylene with *l*-menthyl diazoacetate and in asymmetric aziridination reactions⁵ of 3-arylpropenoates with *N*[(*p*-tolylsulfonyl)imino]phenyliodinane. Since 1,1'-binaphthyl-2,2'-diimines (**BINIMs**) have both axial chirality and a diimine moiety, the complexes of **BINIMs** with metal salts would be expected to act as chiral Lewis acids for Lewis acid-promoted reactions.¹¹ Furthermore, these ligands could coordinate to metals of different sizes by changes in the dihedral angle between the two naphthyl rings with flexibility; the resulting complexes may create a unique chiral environment for highly enantioselective reactions by placing appropriate substituents on the imino-carbons. To evaluate the versatility of the ligands, we investigated 1,3-dipolar cycloaddition reactions of *N*-benzylideneaniline *N*-oxide with 3-crotonoyl-2-oxazolidinone in the presence of these catalysts, which were prepared by mixing several **BINIMs** with various metal salts. In this paper, we report that chiral Ni(II)-**BINIM** complexes were found to be effective Lewis-acid catalysts in asymmetric 1,3-dipolar cycloaddition reactions of nitrones.³⁰

Results and Discussion

Reaction Using BINIM-DC as a Ligand. Initially, the reaction of *N*-benzylideneaniline *N*-oxide (**1**) with 3-crotonoyl-2-oxazolidinone (**2**) was examined in the presence of 10 mol% of the catalysts, which were prepared by mixing **BINIM-DC** (Chart 1) with different metal salts (such as Cu(OTf)₂, Sc(OTf)₃, Yb(OTf)₃, Ni(ClO₄)₂, Co(ClO₄)₂, CuCl + AgClO₄, FeCl₂ + 2AgClO₄, YbCl₃ + 3AgClO₄, and SmCl₃ + 3AgClO₄) in CH₂Cl₂ at room temperature for 6 h (Scheme 1). In this preliminary study, the catalyst prepared from

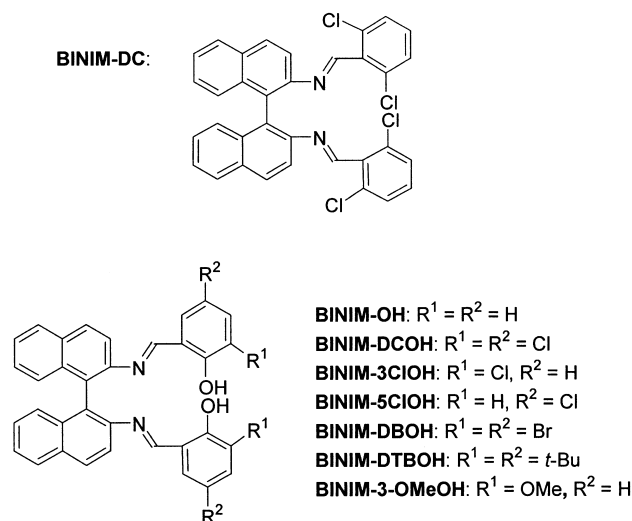
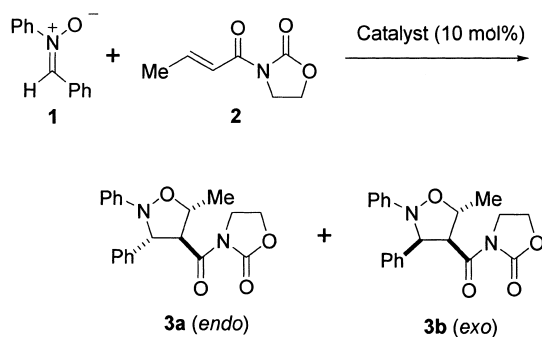


Chart 1.



Scheme 1.

Ni(ClO₄)₂·6H₂O in the presence of 4 Å molecular sieves (MS 4A, 0.25 g for 1 mmol scale) showed the best results at room temperature (Table 1, entry 1) in terms of diastereoselectivity (*endo*:*exo* = 96:4), enantioselectivity (*endo*: 66% ee), and chemical yield (86%). At 0 °C, the reaction did not go to completion, even after 187 h; stirring was then continued at room temperature for another 27 h to give *endo*-product preferentially with a slight increase in enantioselectivity (entry 2). In an investigation of solvent effects, CH₂Cl₂ and CHCl₃ promoted better diastereo- and enantioselectivity than benzene and toluene. The reaction in CHCl₃ showed a slightly higher enantioselectivity than in CH₂Cl₂, but a longer time was needed to complete the reaction. The effects of the amount of MS 4A used and the ratio of **BINIM-DC** to Ni(ClO₄)₂·6H₂O were also examined. When twice the amount of MS 4A was used, the enantioselectivity for the *endo*-adduct was decreased to 53% ee (entry 6), while the enantioselectivity increased to 76% ee in the absence of MS 4A (entry 7). The use of two molar amounts of **BINIM-DC** per Ni(ClO₄)₂·6H₂O for preparing the catalyst led to a slight increase in the enantioselectivity for the *endo*-adduct in both CH₂Cl₂ and CHCl₃ (entries 8 and 9), compared to equimolar amounts of ligand and metal. These results suggest that octahedral Ni(II) dication complexes participate in catalytic cycloaddition. They also suggest that the diastereo- and enantioselectivity of the reaction changes somewhat depending on whether water, another molecule of the ligand, nitrone **1**, or the solvent can coordinate to the remaining two co-

ordination sites of the metal, which are a result of the occupation of four coordination sites by the ligand and crotonoyloxazolidinone **2**.

To investigate the effect of the counter anion of the Ni(II)-complexes on the reaction, the catalysts were prepared by mixing NiBr₂ and two molar mounts of AgClO₄, AgSbF₆, AgBF₄, or AgPF₆ in CH₂Cl₂ at room temperature for 6 h; then, the reaction of **1** and **2** was carried out in the presence of 10 mol% of these catalysts (Table 2, entries 1–4). As shown in entry 1, the diastereo- and enantioselectivity observed with the catalyst prepared from NiBr₂ and AgClO₄ were almost equal to those obtained from the catalyst prepared with Ni(ClO₄)₂·6H₂O in the absence of MS 4A (Table 1, entry 7). In spite of drying the reaction media as much as possible, this result implies that the catalysts prepared by using silver salts may contain a small amount of water in situ, and the catalysts could be aqua-complexes. Although the reactions in the presence of these catalysts showed less-satisfactory results in terms of the diastereoselectivity, promising levels of enantioselectivity were observed. In particular, the Ni(II)-**BINIM-DC** complex containing BF₄[−] as a counter anion showed extremely high enantioselectivity (> 98% ee) of the *exo*-adduct (Table 2, entry 3). For the *endo*-adduct, we found that the complex containing SbF₆[−] showed the best result in terms of the enantioselectivity (entry 2). Surprisingly, the catalyst prepared by mixing NiBr₂ and AgSbF₆ in the presence of MS 4A did not promote the reaction, and only a trace amount of the cycloadduct was produced even after 264 h at room temperature. Similar Co-, Zn-, and Mn-complexes prepared by a similar procedure did not show higher enantioselectivities than those of the Ni(II)-complexes (entries 5–9). It is interesting that only the Mn(II)-complex gave an *exo*-adduct preferably (entry 9).

Effect of Additives on the Reaction Using BINIM-DC as a Ligand. The above results led us to examine the use of some additives, such as alcohols or phenols. The preparation of the catalyst in the presence of these additives was as follows. After mixing chiral **BINIM-DC** (10 mol%) and Ni(ClO₄)₂·6H₂O (10 mol%) in the presence of MS 4A in CH₂Cl₂ for 5 h, an additive was added (for most of the trials, an equimolar amount to nitrone **1**), and then stirring was continued for 1 h. The results of the selectivities found for the reac-

Table 1. Ni(II)-**BINIM-DC**-Catalyzed Cycloaddition of Nitrone **1** with Oxazolidinone **2**^{a)}

Entry	Ratio ^{b)}	Solvent	Temp/°C	Time/h	MS4A	Yield/%	<i>endo</i> : <i>exo</i>	% ee ^{c)} <i>endo</i>	<i>exo</i>
1	1:1	CH ₂ Cl ₂	rt	41	0.25 g	86	96:4	66	ND ^{d)}
2	1:1	CH ₂ Cl ₂	0, rt ^{e)}	187, 27 ^{e)}	0.25 g	89	92:8	71	ND ^{d)}
3	1:1	CHCl ₃	rt	91	0.25 g	73	89:11	70	20
4	1:1	Toluene	rt	120	0.25 g	80	47:53	27	3
5	1:1	Benzene	rt	235	0.25 g	79	56:44	32	1
6	1:1	CH ₂ Cl ₂	rt	114	0.5 g	83	95:5	53	24
7	1:1	CH ₂ Cl ₂	rt	187	none	66	81:19	76	72
8	2:1	CH ₂ Cl ₂	rt	98	0.25 g	87	94:6	73	ND ^{d)}
9	2:1 ^{f)}	CHCl ₃	rt	167	0.25 g	86	80:20	−78 ^{g)}	−44 ^{g)}

a) The reaction was carried out with 1 mmole scale in the presence of 10 mol% of the catalyst which was prepared by mixing (R)-**BINIM-DC** and Ni(ClO₄)₂·6H₂O in the solvent at room temperature for 6 h. b) The mole ratio of **BINIM-DC**:Ni(ClO₄)₂·6H₂O. c) Determined by HPLC analysis (*endo*: Daicel Chiralpak AS, *exo*: Daicel Chiralcel OD-H). d) Not determined. e) At 0 °C for 187 h and then at rt for 27 h. f) (S)-**BINIM-DC** was used. g) Opposite absolute configuration.

Table 2. The Cycloaddition of Nitrone **1** with **2** in the Presence of the Catalyst Prepared with AgX^{a)}

Entry	Metal Salts	Time/h	Yield/%	endo:exo	% ee ^{b)} endo	exo
1	NiBr ₂ + 2AgClO ₄	119	79	78:22	76	75
2	NiBr ₂ + 2AgSbF ₆	114	75	57:43	85	85
3	NiBr ₂ + 2AgBF ₄	115	78	52:48	70	> 98
4	NiBr ₂ + 2AgPF ₆	113	76	62:38	84	80
5	CoCl ₂ + 2AgClO ₄	48	81	75:25	31	45
6	CoCl ₂ + 2AgSbF ₆	117	67	62:38	1	49
7	ZnCl ₂ + 2AgClO ₄	118	79	78:22	36	32
8	ZnCl ₂ + 2AgSbF ₆	93	63	87:13	66	15
9	MnCl ₂ ·4H ₂ O + 2AgClO ₄ + MS4A ^{c)}	117	66	14:86	ND ^{d)}	2

a) The reaction was carried out with 1 mmole scale in the presence of 10 mol% of the catalysts which were prepared by mixing (R)-**BINIM-DC** and metal salts listed in the table in CH₂Cl₂ at room temperature for 6 h. b) Determined by HPLC analysis (endo: Daicel Chiralpak AS, exo: Daicel Chiralcel OD-H). c) In the presence of 0.25 g of MS 4A powder. d) Not determined.

tion in the presence of various additives are given in Table 3. Among the additives examined, PhOH showed the best results in terms of the enantioselectivity. Although the diastereoselectivity decreased slightly (endo:exo = 82:18) compared to no additive, the enantioselectivity of the endo-adduct increased to 80% ee in the presence of an equimolar amount of PhOH (Table 3, entry 4). The use of a 50% equimolar amount of PhOH resulted in a decrease in the enantioselectivity (entry 5), whereas the reaction with a 1.5 molar amount of PhOH showed almost the same enantioselectivity as the equimolar trial (Table 3, entry 6). The addition of PhOH could replace water by PhOH in the octahedral Ni(II)-**BINIM-DC** aqua-complex (see Fig. 1). The resulting complex probably serves as better chiral catalyst than the aqua-complex in terms of the enantioselectivity.

Reaction Using BINIM-OH Derivatives as Ligands. If octahedral Ni(II) dication complexes participate as chiral

Lewis acids in catalytic cycloaddition, introducing coordination functionalities, such as hydroxy groups near the diimino moieties, may create a proper chiral environment for asymmetric induction. Accordingly, several *N,N'*-bis(2-hydroxybenzylidene)-1,1'-binaphthyl-2,2'-diamines were synthesized and tested as chiral ligands for the Ni(II)-catalyzed 1,3-dipolar cycloaddition of nitrone **1** (Table 4). Unfortunately, catalysts prepared by using Ni(ClO₄)₂·6H₂O did not show satisfactory results in terms of the enantioselectivity (entries 1–9). However, we found that substituents on the benzene rings of benzylidene moieties greatly affected the diastereoselectivity. In the presence of a catalyst prepared with **BINIM-OH**, the exo-adduct was produced somewhat preferentially (entry 1). In the case of **BINIM-DCOH**, the exo-adduct was obtained with extremely high diastereoselectivity (exo:endo = 92:8, entry 2). This exo-selectivity may be attributed to the production of octahedral Ni(II)-complexes, in which hydroxy groups coordi-

Table 3. The Effect of Additives in Ni(II)-**BINIM-DC**-Catalyzed Reaction^{a)}

Entry	Ligand	Additive (mol%)	Time/h	Yield/%	endo:exo	% ee endo ^{b)}	Config ^{c)}
1	(S)	<i>i</i> -PrOH (100)	45	91	95:5	69	(3 <i>S</i> , 4 <i>R</i> , 5 <i>S</i>)
2	(R)	(CF ₃) ₂ CHOH (100)	48	78	92:8	75	(3 <i>R</i> , 4 <i>S</i> , 5 <i>R</i>)
3	(S)	PhCH ₂ OH (100)	48	82	89:11	22	(3 <i>S</i> , 4 <i>R</i> , 5 <i>S</i>)
4	(S)	PhOH (100)	46	92	82:18	80	(3 <i>S</i> , 4 <i>R</i> , 5 <i>S</i>)
5	(S)	PhOH (50)	46	83	88:12	71	(3 <i>S</i> , 4 <i>R</i> , 5 <i>S</i>)
6	(S)	PhOH (150)	46	79	87:13	81	(3 <i>S</i> , 4 <i>R</i> , 5 <i>S</i>)
7	(S)	<i>o</i> -ClC ₆ H ₄ OH (100)	47	90	91:9	76	(3 <i>S</i> , 4 <i>R</i> , 5 <i>S</i>)
8	(R)	<i>p</i> -ClC ₆ H ₄ OH (100)	49	83	86:14	78	(3 <i>R</i> , 4 <i>S</i> , 5 <i>R</i>)
9	(R)	<i>o</i> -FC ₆ H ₄ OH (100)	48	79	81:19	73	(3 <i>R</i> , 4 <i>S</i> , 5 <i>R</i>)
10	(R)	<i>p</i> -FC ₆ H ₄ OH (100)	48	79	88:12	6	(3 <i>R</i> , 4 <i>S</i> , 5 <i>R</i>)
11	(R)	C ₆ F ₅ OH (100)	48	77	59:41	68	(3 <i>R</i> , 4 <i>S</i> , 5 <i>R</i>)
12	(R)	<i>m</i> -MeC ₆ H ₄ OH (100)	72	81	88:12	76	(3 <i>R</i> , 4 <i>S</i> , 5 <i>R</i>)
13	(R)	<i>p</i> -MeC ₆ H ₄ OH (100)	48	quant.	68:32	74	(3 <i>R</i> , 4 <i>S</i> , 5 <i>R</i>)
14	(R)	<i>p</i> -MeOC ₆ H ₄ OH (100)	48	quant.	70:30	76	(3 <i>R</i> , 4 <i>S</i> , 5 <i>R</i>)
15	(S)	2,6-Ph ₂ C ₆ H ₃ OH (100)	48	93	96:4	68	(3 <i>S</i> , 4 <i>R</i> , 5 <i>S</i>)
16	(S)	2,6- <i>t</i> -Bu ₂ -4-MeC ₆ H ₂ OH (100)	47	90	97:3	68	(3 <i>S</i> , 4 <i>R</i> , 5 <i>S</i>)
17	(R)	2-Naphthol (100)	48	85	81:19	74	(3 <i>R</i> , 4 <i>S</i> , 5 <i>R</i>)

a) The reaction was carried out with 1 mmole scale in the presence of 10 mol% of the catalysts which were prepared by mixing (R)- or (S)-**BINIM-DC**, Ni(ClO₄)₂·6H₂O, and MS 4A (0.25 g) in CH₂Cl₂ at room temperature for 5 h, and then in the presence of the additives for 1 h. b) Determined by HPLC analysis (Daicel Chiralpak AS). c) Absolute configuration of the adduct was determined by comparison of the optical rotation as well as retention time in a chiral HPLC.

Table 4. The Cycloaddition of Nitron 1 with 2 Using *N,N'*-Bis(2-hydroxybenzylidene)-1,1'-binaphthyl-2,2'-diamine Derivatives as Ligands^{a)}

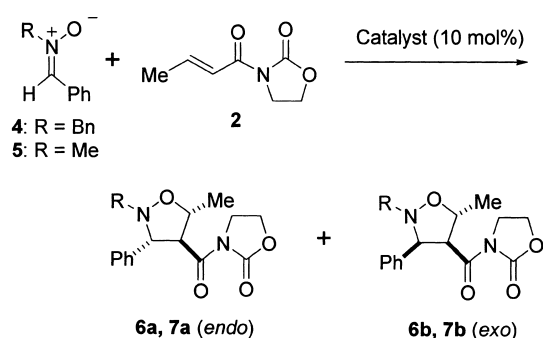
Entry	Ligand	R ¹	R ²	MLn	Time/h	Yield/%	endo:exo	% ee	endo ^{b)} (Config.) ^{c)}	exo ^{b)} (Config.) ^{c)}
1	(<i>S</i>)- BINIM-OH	H	H	Ni(ClO ₄) ₂ ·6H ₂ O ^{d)}	120	73	26:74	25	(3 <i>S</i> , 4 <i>R</i> , 5 <i>S</i>)	54 (3 <i>R</i> , 4 <i>R</i> , 5 <i>S</i>)
2	(<i>S</i>)- BINIM-DCOH	Cl	Cl	Ni(ClO ₄) ₂ ·6H ₂ O ^{d)}	95	86	8:92	33	(3 <i>R</i> , 4 <i>S</i> , 5 <i>R</i>)	63 (3 <i>S</i> , 4 <i>S</i> , 5 <i>R</i>)
3	(<i>S</i>)- BINIM-DCOH	Cl	Cl	Co(ClO ₄) ₂ ·6H ₂ O ^{d)}	240	42	18:82	2	(3 <i>S</i> , 4 <i>R</i> , 5 <i>S</i>)	5 (3 <i>S</i> , 4 <i>S</i> , 5 <i>R</i>)
4	(<i>S</i>)- BINIM-DCOH	Cl	Cl	Cu(ClO ₄) ₂ ·6H ₂ O ^{d)}	239	57	21:79	2	(3 <i>S</i> , 4 <i>R</i> , 5 <i>S</i>)	1 (3 <i>R</i> , 4 <i>R</i> , 5 <i>S</i>)
5	(<i>R</i>)- BINIM-3ClOH	Cl	H	Ni(ClO ₄) ₂ ·6H ₂ O ^{d)}	51	94	5:95	50	(3 <i>S</i> , 4 <i>R</i> , 5 <i>S</i>)	52 (3 <i>R</i> , 4 <i>R</i> , 5 <i>S</i>)
6	(<i>R</i>)- BINIM-5ClOH	H	Cl	Ni(ClO ₄) ₂ ·6H ₂ O ^{d)}	168	70	34:66	12	(3 <i>R</i> , 4 <i>S</i> , 5 <i>R</i>)	60 (3 <i>S</i> , 4 <i>S</i> , 5 <i>R</i>)
7	(<i>S</i>)- BINIM-DBOH	Br	Br	Ni(ClO ₄) ₂ ·6H ₂ O ^{d)}	216	58	24:76	7	(3 <i>S</i> , 4 <i>R</i> , 5 <i>S</i>)	58 (3 <i>S</i> , 4 <i>S</i> , 5 <i>R</i>)
8	(<i>S</i>)- BINIM-DTBOH	Bu ^t	Bu ^t	Ni(ClO ₄) ₂ ·6H ₂ O ^{d)}	168	60	41:59	26	(3 <i>S</i> , 4 <i>R</i> , 5 <i>S</i>)	2 (3 <i>R</i> , 4 <i>R</i> , 5 <i>S</i>)
9	(<i>R</i>)- BINIM-3OMeOH	OMe	H	Ni(ClO ₄) ₂ ·6H ₂ O ^{d)}	191	81	63:37	54	(3 <i>R</i> , 4 <i>S</i> , 5 <i>R</i>)	16 (3 <i>S</i> , 4 <i>S</i> , 5 <i>R</i>)
10	(<i>R</i>)- BINIM-OH	H	H	NiBr ₂ + 2AgSbF ₆	120	68	55:45	83	(3 <i>R</i> , 4 <i>S</i> , 5 <i>R</i>)	66 (3 <i>S</i> , 4 <i>S</i> , 5 <i>R</i>)
11	(<i>R</i>)- BINIM-OH	H	H	NiBr ₂ + 2AgBF ₄	139	78	58:42	74	(3 <i>R</i> , 4 <i>S</i> , 5 <i>R</i>)	75 (3 <i>S</i> , 4 <i>S</i> , 5 <i>R</i>)
12	(<i>R</i>)- BINIM-OH	H	H	NiBr ₂ + 2AgPF ₆	142	82	56:44	84	(3 <i>R</i> , 4 <i>S</i> , 5 <i>R</i>)	68 (3 <i>S</i> , 4 <i>S</i> , 5 <i>R</i>)
13	(<i>S</i>)- BINIM-DCOH	Cl	Cl	NiBr ₂ + 2AgSbF ₆	112	63	42:58	82	(3 <i>S</i> , 4 <i>R</i> , 5 <i>S</i>)	24 (3 <i>R</i> , 4 <i>R</i> , 5 <i>S</i>)
14	(<i>S</i>)- BINIM-DCOH	Cl	Cl	NiBr ₂ + 2AgBF ₄	141	73	60:40	77	(3 <i>S</i> , 4 <i>R</i> , 5 <i>S</i>)	69 (3 <i>R</i> , 4 <i>R</i> , 5 <i>S</i>)

a) The reaction was carried out with 1 mmole scale in the presence of 10 mol% of the catalysts which were prepared by mixing **BINIMs** and metal salts listed in the table in CH₂Cl₂ at room temperature for 6 h. b) Determined by HPLC analysis (*endo*: Daicel Chiralpak AS, *exo*: Daicel Chiralcel OD-H). c) Absolute configuration of the adduct was determined by comparison of the optical rotation as well as retention time in a chiral HPLC. d) In the presence of MS 4A (0.25 g).

nate to the Ni atom, as shown in model studies. Furthermore, although the enantioselectivity was moderate, the opposite sense of asymmetric induction was found using **BINIM-DCOH** as the ligand, compared with the use of **BINIM-DC** and **BINIM-OH**. The combination of **BINIM-DCOH** with other metal perchlorates (Co(ClO₄)₂·6H₂O and Cu(ClO₄)₂·6H₂O) also showed *exo*-selectivity. In an investigation of the substitution positions of chlorine atoms on the benzene ring, the 3-position for a chlorine atom was shown to be important for high *exo*-selectivity (**BINIM-3ClOH**; *exo:endo* = 95:5) and a reversal of the sense of enantioselection (entries 5 and 6).

Catalysts prepared from NiBr, silver salts, and **BINIM-OH** or **BINIM-DCOH** were also examined (Table 4, entries 10–14). Although almost no diastereoselectivity was observed, in contrast to the **BINIM**-Ni(ClO₄)₂·6H₂O catalysts, the enantioselectivity of the *endo*-adduct was relatively high (up to 84% ee). The enantio- and diastereoselectivities found were very similar to the selectivities obtained using **BINIM-DC** as the chiral ligand. These results imply that the 2-hydroxy groups on the benzene rings probably did not coordinate to the Ni cation, and that aqua-complexes may participate as catalysts under those conditions. The higher enantioselectivities of the *endo*-adduct obtained by the SbF₆[−] complexes than BF₄[−] complexes were also similar to those of complexes using **BINIM-DC** as a chiral ligand.

The Ni(II)-BINIM Catalyzed Reactions of Other Nitrones. Cycloaddition reactions of nitrones 4 and 5 with 3-crotonoyl-2-oxazolidinone (2) were also carried out under the typical conditions using chiral **BINIM-DC** and **BINIM-DCOH** as ligands (Scheme 2, Table 5). Although satisfactory results were not obtained in terms of the enantioselectivities, the diastereoselectivities were successfully controlled by selecting these Ligands. Thus, the use of **BINIM-DC** in combination with Ni(ClO₄)₂·6H₂O as a catalyst showed high *endo*-selectivity (entries 3 and 5), while the use of **BINIM-DCOH** as a ligand afforded *exo*-products in high diastereoselectivity



Scheme 2.

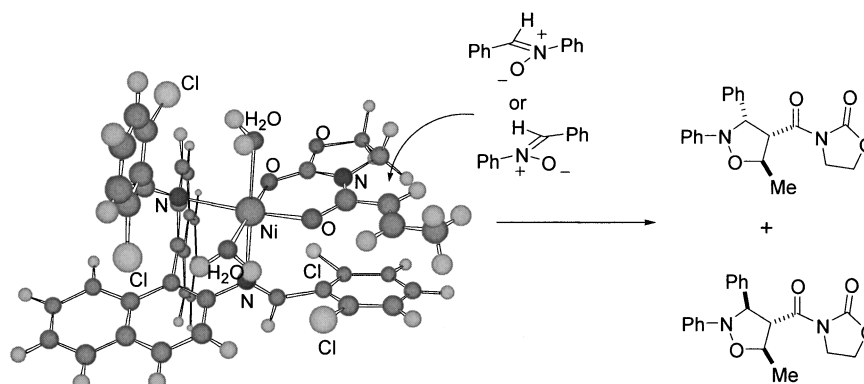
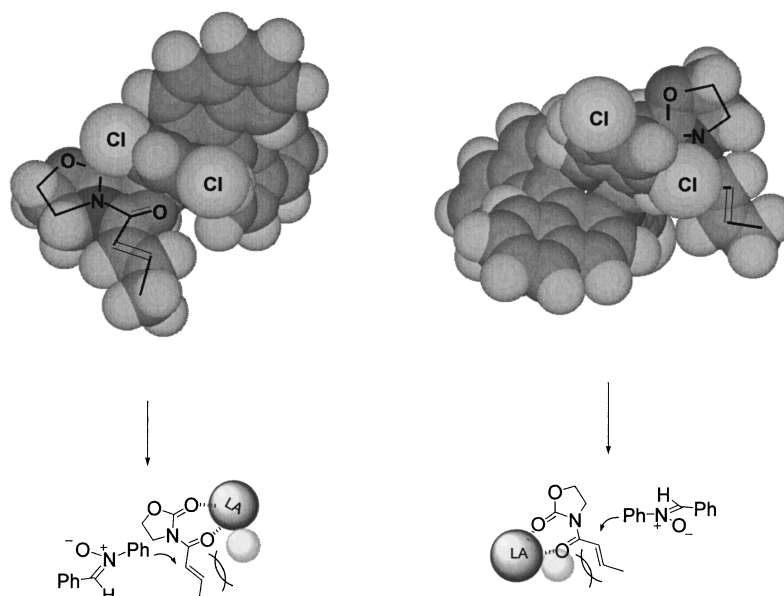
(entries 4 and 6). It is interesting that the Ni(II)-**BINIM-DCOH** catalyzed reactions of nitron showed *exo*-selectivity regardless of the kind of nitrones, because the high enantioselectivities reported in the cycloaddition reactions of nitrones with 3-crotonoyl-2-oxazolidinone (2) usually showed high *endo*-selectivity.³ A further study to develop the Metal-**BINIM** catalysts, which afford high *exo*-selectivity with high enantioselectivity, is in progress.

Model Studies for Enantio- and Diastereoselection. Because it was difficult to obtain good single crystals of the Ni(II)-**BINIM** complexes to carry out an X-ray crystal analysis, the structures of Ni(II)-**BINIM** complexes coordinated to 3-crotonoyl-2-oxazolidinone (2) were studied by semiempirical molecular-orbital calculations (PM3).⁶ The optimized structure of the (*R*)-**BINIM-DC** aqua-complex arrived at is shown in Fig. 1. From this model, the lower side of the 3-crotonoyl-2-oxazolidinone olefin moiety is shielded by the 2,6-dichlorobenzene group of the ligand. In contrast, the upper side of the olefin is accessible, and therefore the approach of the nitron from the upper side is much more facile. This geometry of the aqua-complex could explain the good enantioselectivity found in the reaction, where an *endo* approach of the

Table 5. The Cycloaddition of Nitrones **4** and **5** with **2** Catalyzed by Ni(II)-**BINIM** Complexes.^{a)}

Entry	Nitrone	Ligand	mol%	Time/h	Yield/% ^{b)}	<i>endo:exo</i> ^{b)}	% ee ^{c)}
1	1	(<i>S</i>)- BINIM-DC	10 ^{d)}	46	92 ^{e)}	82:18 ^{e)}	80 (<i>endo</i>)
2	1	(<i>S</i>)- BINIM-DCOH	10	95	86 ^{e)}	8:92 ^{e)}	63 (<i>exo</i>)
3	4	(<i>S</i>)- BINIM-DC	10 ^{d)}	66	51	95:5	32 (<i>endo</i>)
4	4	(<i>S</i>)- BINIM-DCOH	20 ^{f)}	287	55	12:88	52 (<i>exo</i>)
5	5	(<i>R</i>)- BINIM-DC	10 ^{d)}	215	77	91:9	59 (<i>endo</i>)
6	5	(<i>S</i>)- BINIM-DCOH	10	425	66	15:85	31 (<i>exo</i>)

a) The reaction was carried out with 1 mmole scale in the presence of 10 mol% of the catalysts which were prepared by mixing **BINIMs** and Ni(ClO₄)₂·6H₂O in CH₂Cl₂ at room temperature for 6 h. b) Determined by ¹H NMR analysis. c) Determined by HPLC analysis. d) In the presence of PhOH (100 mol%). e) The value of isolated products. f) The reaction was carried out with 0.5 mmol scale.

Fig. 1. Proposed approach using **BINIM-DC** as a chiral ligand.Fig. 2. *Endo* approaches to the complex of the Ni(II)-**BINIM-DCOH** catalyst.

nitrone from the upper side gave (3*R*,4*S*,5*R*)-isoxazolidine, and an *exo* approach of the nitrone from the same side afforded (3*S*,4*S*,5*R*)-isoxazolidine preferably.

The high *exo*-selectivities using the **BINIM-DCOH** and **BINIM-3ClOH** ligands could be explained by a model of coordinated hydroxy groups, which was also optimized by a

PM3 calculation (Fig. 2). The space-filling models in Fig. 2 show two views from opposite sides relative to the 3-crotonoyl-2-oxazolidinone part of the Ni(II)-(*R*)-**BINIM-DCOH** complex. In both views, the 3-chlorine atoms on the benzene rings prevent an *endo*-approach of nitrone **1** because of a steric hindrance between the *N*-phenyl group on the nitrone and the

chorine atom that must be passed through this approach. Therefore, the sterically less hindered *exo*-approach predominates to give *exo*-cycloadducts with high diastereoselectivity.

Conclusions

We found that chiral Ni(II)-**BINIM** complexes were effective Lewis acid catalysts for an asymmetric 1,3-dipolar cycloaddition reaction of *N*-benzylideneaniline *N*-oxide (**1**) with 3-crotonoyl-2-oxazolidinone (**2**). The catalyst prepared from **BINIM-DC**, Ni(ClO₄)₂·6H₂O and PhOH in the presence of MS 4A showed the highest enantioselectivity (up to 81% ee) of the corresponding *endo*-cycloadduct with *endo*-selectivity (87:13) for the reaction. The use of chiral *N,N'*-bis(3-dichloro-substituted 2-hydroxybenzylidene) derivatives (**BINIM-DCOH** and **BINIM-3ClOH**) with Ni(ClO₄)₂·6H₂O and MS 4A as catalysts under similar conditions showed high *exo*-selectivity (up to 95:5) with moderate enantioselectivity. In the case of catalysts prepared with chiral **BINIM-DC**, NiBr₂, and AgBF₄, AgSbF₆, or AgPF₆, cycloadducts were obtained with promising levels of enantioselectivity (up to > 98%) with low diastereoselectivity. Experiments are currently underway to evaluate the versatility of the chiral Ni(II)-**BINIM** catalysts in other Lewis acid-promoted asymmetric reactions.¹¹

Experimental

General. The melting points were determined on a Yanagimoto melting-point apparatus, and are uncorrected. IR spectra were taken with a JASCO FT/IR-5300S spectrophotometer. ¹H NMR spectra were recorded on a JEOL JNM-MY60FT (60 MHz) or a JEOL EX-270 instrument (270 MHz). The chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. Elemental analyses were performed on a Yanaco CHN recorder MT-3, or a Perkin-Elmer 2400 CHN recorder. High-performance liquid chromatography was performed on a SHIMADZU LC-VP system. Optical rotations were recorded with a JASCO P-1010 polarimeter. For preparative column chromatography, Wakogel C-300 and 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. Nitrones **1**,^{7a} **4**,^{7b} **5**^{7c} and 3-crotonoyl-2-oxazolidinone (**2**)⁸ were prepared by the reported procedures. Chiral 1,1'-binaphthyl-2,2'-diamine was purchased from Aldrich Co. Benzene and toluene were freshly distilled from a sodium benzophenone ketyl still under argon. Dichloromethane and chloroform were purified by distillation, first from CaCl₂ and then CaH₂ under argon.

General Procedure for the Reactions of Nitrones with 3-Crotonoyl-2-oxazolidinone (2**) Catalyzed by the Ni(II)-**BINIM-DC** Complex Prepared from Ni(ClO₄)₂·6H₂O.** A solution of (*S*)-**BINIM-DC** (60 mg, 0.10 mmol) in CH₂Cl₂ (5.0 mL) was added to a mixture of oven-dried powdered MS 4A (0.253 g) and Ni(ClO₄)₂·6H₂O (37 mg, 0.10 mmol) at room temperature. After stirring for 5 h at room temperature, PhOH (94 mg, 0.088 mL, 1.0 mmol) was added to the mixture, and then the suspension was stirred for an additional 1 h. A solution of oxazolidinone **2** (0.155 g, 1.0 mmol) in CH₂Cl₂ (1.5 mL) and nitrone **1** (0.197 g, 1.0 mmol) were added successively to the catalyst suspension.

After stirring at room temperature for 46 h, the reaction mixture was quenched with a saturated NH₄Cl solution (10 mL) and then filtered through Cerite. The filtrate was extracted with CH₂Cl₂ (10 mL × 3). The combined extracts were dried over MgSO₄ and evaporated in vacuo. The residue was chromatographed on silica gel with hexane–diethyl ether (65:35 v/v) to give *exo*-adduct **3b** (0.059 g) and *endo*-adduct **3a** (0.264 g). Total yield: 92%. The enantiomeric excesses of both adducts were determined by HPLC analysis (*endo*: Daicel Chiralpak AS; *exo*: Daicel Chiralcel OD-H).

General Procedure for the Reaction Catalyzed by the **BINIM-Ni(II) Complexes Prepared from NiBr₂ and Silver Salts.** A mixture of NiBr₂ (22 mg, 0.10 mmol), silver salt (0.20 mmol), and chiral **BINIM** (0.10 mmol) in CH₂Cl₂ (5.0 mL) was stirred at room temperature for 6 h. The resulting suspension was used without filtration for the cycloaddition reactions following the same procedures as shown above. After completion of the reactions, similar quenching and purification procedures were applied.

Other **BINIM** complexes were prepared according to a similar procedure by using metal halides, such as CoCl₂, ZnCl₂, and MnCl₂.

Cycloadducts **3a**, **3b**, **6a**, **6b**, **7a**, and **7b** were identified by comparing their ¹H NMR signals with those in the literature.^{3b,m,o}

(–)-(3*S*,4*R*,5*S*)-5-Methyl-4-(2-oxo-1,3-oxazoline-3-carbonyl)-2,3-diphenylisoxazolidine (**3a**): Colorless viscous oil; [α]_D²³ –15.7° (c 1.00, CHCl₃); 80% ee estimated on the basis of HPLC (Daicel Chiralpak AS, hexane–2-PrOH, 21:1 v/v, detector: UV 254 nm, flow rate = 0.5 mL/min, 35 °C, *t*_{minor} = 55.0 min, *t*_{major} = 73.9 min); ¹H NMR (60 MHz, CDCl₃) δ 1.55 (3H, d, *J* = 6.3 Hz, Me), 4.00–5.25 (7H, m, CH, CH₂), 6.91–7.43 (10H, m, Ph–H).

(–)-(3*S*,4*S*,5*R*)-5-Methyl-4-(2-oxo-1,3-oxazoline-3-carbonyl)-2,3-diphenylisoxazolidine (**3b**): Colorless viscous oil; [α]_D²² –17.4° (c 1.01, CHCl₃); > 98% ee estimated on the basis of HPLC (Daicel Chiralcel OD-H, hexane–2-PrOH, 21:1 v/v, detector: UV 254 nm, flow rate = 0.5 mL/min, 35 °C, *t*_{minor} = 45.6 min, *t*_{major} = 50.2 min); ¹H NMR (60 MHz, CDCl₃) δ 1.45 (3H, d, *J* = 6.3 Hz, Me), 3.04 (1H, m, CH), 3.75–5.05 (6H, m, CH, CH₂), 7.01–7.37 (10H, m, Ph–H).

endo-2-Benzyl-5-methyl-4-(2-oxo-1,3-oxazoline-3-carbonyl)-3-phenylisoxazolidine (**6a**): Colorless viscous oil; [α]_D²⁰ +4.9° (c 1.00, CHCl₃); 32% ee estimated on the basis of HPLC (Daicel Chiralcel OD-H, hexane–2-PrOH, 80:20 v/v, detector: UV 220 nm, flow rate = 0.3 mL/min, 35 °C, *t*_{major} = 35.8 min, *t*_{minor} = 53.6 min); ¹H NMR (60 MHz, CDCl₃) δ 1.58 (3H, d, *J* = 6.1 Hz, Me), 3.82–4.61 (9H, m, CH, CH₂), 7.16–7.49 (10H, m, Ph–H).

exo-2-Benzyl-5-methyl-4-(2-oxo-1,3-oxazoline-3-carbonyl)-3-phenylisoxazolidine (**6b**): Colorless viscous oil; [α]_D²⁰ –29.5° (c 1.00, CHCl₃); 52% ee estimated on the basis of HPLC (Daicel Chiralcel OD-H, hexane–2-PrOH, 19:1 v/v, detector: UV 220 nm, flow rate = 0.3 mL/min, 35 °C, *t*_{minor} = 54.8 min, *t*_{major} = 60.1 min). ¹H NMR (60 MHz, CDCl₃) δ 1.33 (3H, d, *J* = 6.1 Hz, Me), 2.99–5.05 (9H, m, CH, CH₂), 7.19–7.46 (10H, m, Ph–H).

endo-2,5-Dimethyl-4-(2-oxo-1,3-oxazoline-3-carbonyl)-3-phenylisoxazolidine (**7a**): Colorless viscous oil; [α]_D²⁰ –14.5° (c 1.00, CHCl₃); 59% ee estimated on the basis of HPLC (Daicel Chiralcel OJ-R, methanol–water, 60:40 v/v, detector: UV 220 nm, flow rate = 0.5 mL/min, *t*_{minor} = 78.9 min, *t*_{major} = 100.0 min). ¹H NMR (60 MHz, CDCl₃) δ 1.59 (3H, d, *J* = 5.8 Hz, Me), 2.66 (3H, s, N–Me), 3.88–4.75 (7H, m, CH, CH₂), 7.27–7.35 (5H, m, Ph–

H).

exo-2,5-Dimethyl-4-(2-oxo-1,3-oxazoline-3-carbonyl)-3-phenylisoxazolidine (7b): Colorless viscous oil; $[\alpha]_D^{20} -33.4^\circ$ (*c* 1.00, CHCl₃); 31% ee estimated on the basis of HPLC (Daicel Chiralcel OJ-R, methanol–water, 60:40 v/v, detector: UV 220 nm, flow rate = 0.5 mL/min, $t_{\text{major}} = 27.0$ min, $t_{\text{minor}} = 32.9$ min). ¹H NMR (60 MHz, CDCl₃) δ 1.37 (3H, d, *J* = 5.8 Hz, Me), 2.61 (3H, s, N-Me), 2.93–5.15 (7H, m, CH, CH₂), 7.32–7.82 (5H, m, Ph-H).

(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 the 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 (from benzene–hexane); mp 216–218 °C; $[\alpha]_D^{24} -10.1^\circ$ (*c* 0.96, CH₂Cl₂); ¹H NMR (270 MHz, C₆D₆) δ 6.17 (2H, t, *J* = 7.9 Hz, H-4 of 2,6-Cl₂C₆H₃), 6.60 (4H, d, *J* = 7.9 Hz, H-3 and H-5 of 2,6-Cl₂C₆H₃), 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, d, *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); IR (KBr) 3051, 1636, 1615 (C=N), 1577, 1429, 814, 777, 748 cm⁻¹. Anal. Calcd for C₃₄H₂₀Cl₄N₂: C, 68.2; H, 3.37; N, 4.68%. Found: C, 68.4; H, 3.52; N, 4.60%.

BINIM-OH, BINIM-DCOH, BINIM-3ClOH, BINIM-5ClOH, BINIM-3OMeOH, and BINIM-DBOH were prepared according to a procedure reported by Stack.⁹ A solution of 1,1'-binaphthyl-2,2'-diamine (0.100 g, 0.70 mmol) and the corresponding salicylaldehyde derivative (0.35 mmol) in ethanol (3.0 mL) was heated under reflux for 6 h. The resulting crystals were filtered and then recrystallized from benzene–hexane. Yields: **BINIM-OH**, 88%; **BINIM-DCOH**, 80%; **BINIM-3ClOH**, 69%; **BINIM-5ClOH**, 63%; **BINIM-3OMeOH**, 65%; **BINIM-DBOH**, 88%.

(S)-N,N'-Bis(2-hydroxybenzylidene)-1,1'-binaphthyl-2,2'-diamine ((S)-BINIM-OH): Yellow plates (from benzene–hexane); mp 255–256.5 °C; $[\alpha]_D^{25} +382.9^\circ$ (*c* 0.16, CH₂Cl₂); ¹H NMR (60 MHz, CDCl₃) 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 C₃₄H₂₄N₂O₂: C, 82.91; H, 4.91; N, 5.69%. Found: C, 83.18; H, 4.82; N, 5.41%.

(S)-N,N'-Bis(3,5-dichloro-2-hydroxybenzylidene)-1,1'-binaphthyl-2,2'-diamine ((S)-BINIM-DCOH): Orange plates (from benzene–hexane); mp 189–191 °C; $[\alpha]_D^{25} +471.8^\circ$ (*c* 0.50, CH₂Cl₂); ¹H NMR (60 MHz, CDCl₃) δ 7.10–8.19 (16H, m, Ar-H), 8.55 (2H, s, CH=N), 12.74 (2H, s, OH); IR (KBr) 3409 (OH), 1605 (C=N), 1557, 1449, 1202, 1179, 868, 737 cm⁻¹. Anal. Calcd for C₃₄H₂₀Cl₄N₂O₂: C, 64.78; H, 3.20; N, 4.44%. Found: C, 64.94; H, 3.37; N, 4.21%.

(R)-N,N'-Bis(3-chloro-2-hydroxybenzylidene)-1,1'-binaphthyl-2,2'-diamine ((R)-BINIM-3ClOH): Orange plates (from benzene–hexane); mp 230–230.5 °C; $[\alpha]_D^{25} = -458.2^\circ$ (*c* 0.32, CH₂Cl₂); ¹H NMR (60 MHz, CDCl₃) δ 6.57–8.17 (18H, m, Ar-H), 8.60 (2H, s, CH=N), 12.77 (2H, s, OH); IR (KBr) 3436 (OH), 1644, 1615 (C=N), 1481, 1447, 1383, 1362, 1298, 1221, 833 cm⁻¹. Anal. Calcd for C₃₄H₂₂Cl₂N₂O₂: C, 72.73; H, 3.95; N, 4.99%. Found: C, 72.59; H, 4.21; N, 4.71%.

(R)-N,N'-Bis(5-chloro-2-hydroxybenzylidene)-1,1'-binaph-

thyl-2,2'-diamine ((R)-BINIM-5ClOH): Orange plates (from benzene–hexane); mp 165–166.5 °C; $[\alpha]_D^{25} -360.5^\circ$ (*c* 0.034, CH₂Cl₂); ¹H NMR (60 MHz, CDCl₃) δ 6.55–8.21 (18H, m, Ar-H), 8.59 (2H, s, CH=N), 12.04 (2H, s, OH); IR (KBr) 3445 (OH), 1609 (C=N), 1559, 1478, 1277, 1179, 816, 747, 677 cm⁻¹. Anal. Calcd for C₃₄H₂₂Cl₂N₂O₂: C, 72.73; H, 3.95; N, 4.99%. Found: C, 72.97; H, 4.00; N, 4.71%.

(S)-N,N'-Bis(3,5-dibromo-2-hydroxybenzylidene)-1,1'-binaphthyl-2,2'-diamine ((S)-BINIM-DBOH): Orange plates (from benzene–hexane); mp 183–185 °C; $[\alpha]_D^{25} +398.7^\circ$ (*c* 1.03, CH₂Cl₂); ¹H NMR (60 MHz, CDCl₃) δ 7.25–8.19 (16H, m, Ar-H), 8.50 (2H, s, CH=N), 12.91 (2H, s, OH); IR (KBr) 3439 (OH), 1603 (C=N), 1588, 1549, 1443, 1202, 1163, 812 cm⁻¹. Anal. Calcd for C₃₄H₂₀Br₂N₂O₂: C, 50.53; H, 2.49; N, 3.47%. Found: C, 50.80; H, 2.55; N, 3.24%.

(R)-N,N'-Bis(2-hydroxy-3-methoxybenzylidene)-1,1'-binaphthyl-2,2'-diamine ((R)-BINIM-3OMeOH): Orange plates (from benzene–hexane); mp 274–275 °C; $[\alpha]_D^{25} -364.5^\circ$ (*c* 0.030, CH₂Cl₂); ¹H NMR (60 MHz, CDCl₃) δ 3.76 (6H, s, OMe), 6.78–8.13 (18H, m, Ar-H), 8.59 (2H, s, CH=N), 12.31 (2H, s, OH); IR (KBr) 3439 (OH), 1607 (C=N), 1589, 1574, 1460, 1400, 1252, 1204, 970 cm⁻¹. Anal. Calcd for C₃₆H₂₈N₂O₄: C, 78.24; H, 5.11; N, 5.07%. Found: C, 78.54; H, 5.00; N, 4.88%.

BINIM-DTBOH was prepared according to the procedure reported by Evans.¹⁰

(S)-N,N'-Bis(3,5-di-*t*-butyl-2-hydroxybenzylidene)-1,1'-binaphthyl-2,2'-diamine ((S)-BINIM-DTBOH): Orange plates (from benzene–hexane); mp 112–114 °C; $[\alpha]_D^{25} +433.9^\circ$ (*c* 1.01, CH₂Cl₂); ¹H NMR (60 MHz, CDCl₃) δ 1.22 (18H, s, *t*-Bu), 7.02–8.13 (16H, m, Ar-H), 8.66 (2H, s, CH=N), 12.72 (2H, s, OH); IR (KBr) 3451 (OH), 2957, 2907, 2870, 1613 (C=N), 1582, 1466, 1359, 1248, 818 cm⁻¹. Anal. Calcd for C₅₀H₅₆N₂O₂: C, 83.76; H, 7.87; N, 3.91%. Found: C, 83.83; H, 8.11; N, 3.62%.

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