Chiral 2,2′-Binaphthyldiimine–Nickel(II) Complexes as Lewis Acid Catalysts for Enantioselective Diels–Alder Reactions

Hiroyuki Suga,* Akikazu Kakehi, and Masashi Mitsuda

Department of Chemistry and Material Engineering, Faculty of Engineering, Shinshu University, Wakasato, Nagano 380-8553

Received September 1, 2003; E-mail: sugahio@gipwc.shinshu-u.ac.jp

The preparation and application of a novel class of chiral Lewis acid catalysts based on chiral 2,2′-binaphthyldiimine ligands are described. Among the binaphthyldiimine–metal complexes tested, *N*,*N*′-bis(2-quinolylmethylene)-1,1′-binaphthyl-2,2′-diamine–Ni(II) complex was found to be an efficient chiral Lewis acid catalyst for asymmetric Diels–Alder reactions (*endo*: up to 96% ee) between cyclopentadiene and 3-alkenoyl-2-oxazolidinones. This catalyst is easy to prepare and is efficient; that is, 1 mol% of the Ni(II) catalyst promoted a Diels–Alder reaction between cyclopentadiene and 3-acryloyl-2-oxazolidinone smoothly with high enantioselectivity (*endo*: 90% ee).

Diels–Alder reactions[1] have been one of the most powerful organic synthetic methods for the construction of 6-membered cyclic compounds. In particular, asymmetric catalytic variants[2] of Diels–Alder reactions have received special attention due to their potential ability to rapidly provide enantiomerically pure and complex compounds from simple substrates. Chiral Lewis acid catalysts have played an important role in these Lewis acid-promoted reactions. From a practical point of view, developing highly efficient chiral Lewis acids with low catalyst loading and minimal deactivation by moisture is one of the most important objectives in organic synthesis. Diels–Alder reactions of cyclopentadiene with 3-alkenoyl-2-oxazolidinones have also been used as model systems for developing such a new chiral Lewis acid catalyst and testing the degree of asymmetric induction.[2]

Recently, we reported that chiral *N*,*N*′-bis(2,6-dichlorobenzylidene)-1,1′-binaphthyl-2,2′-diamine (**BINIM-DC**, Chart 1) is an efficient ligand in Cu(I)-catalyzed asymmetric cyclopropanation reactions[3,4] of 1,1-diarylethylene with *l*-menthyl diazoacetate, and in asymmetric aziridination reactions[4] of 3-arylpropenoates with *N*-[(*p*-tolylsulfonyl)imino]phenyliodinane. Since 1,1′-binaphthyl-2,2′-diimines (**BINIM**s)[5] have both axial chirality and a diimine moiety, the complexes of **BINIM**s with metal salts would be expected to act as effective chiral Lewis acids for Lewis acid-promoted reactions. Furthermore, these ligands could coordinate to cations of different sizes by changes in the dihedral angle between the two naphthyl rings with flexibility; the resulting complexes have the potential to create a unique chiral environment for enantioselective reactions by placing appropriate substituents on the imino-carbons. Indeed, the nickel(II)-complex of **BINIM-DC** was the most effective chiral Lewis acid among several **BINIM**–metal complexes in an asymmetric 1,3-dipolar cycloaddition reaction of *N*-benzylideneaniline *N*-oxide with 3-crotonoyl-2-oxazolidinone.[6] In the reactions, $Ni(ClO_4)_2 \cdot 6H_2O$ in the presence of 4 Å molecular sieves (MS 4A) was a better Ni(II) source in terms of the catalytic activity than a combination of $NiBr_2$–2 equivalents of $AgClO_4$. The enantioselectivity and rate were also affected by the absence or presence of MS 4A in the reaction mixture. For a further evaluation of the versatility of the chiral metal–**BINIM** catalysts, the Diels–Alder reaction was chosen because of its synthetic importance. After screening studies of combinations between several **BINIM**s and metal salts, we found that a chiral complex of *N*,*N*′-bis(2-quinolylmethylene)-1,1′-binaphthyl-2,2′-diamine (**BINIM-2QN**) and $Ni(ClO_4)_2 \cdot 6H_2O$ is an efficient chiral Lewis acid catalyst for asymmetric Diels–Alder reactions between cyclopentadiene and 3-alkeno-

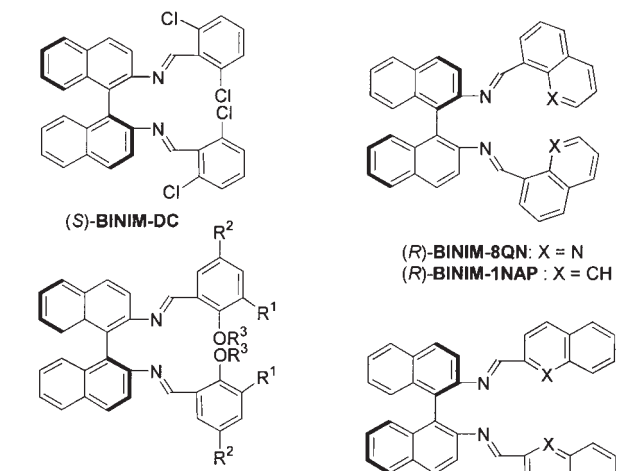

Chart 1. Structures of 1,1′-binaphthyl-2,2′-diimine (**BINIM**) ligands.

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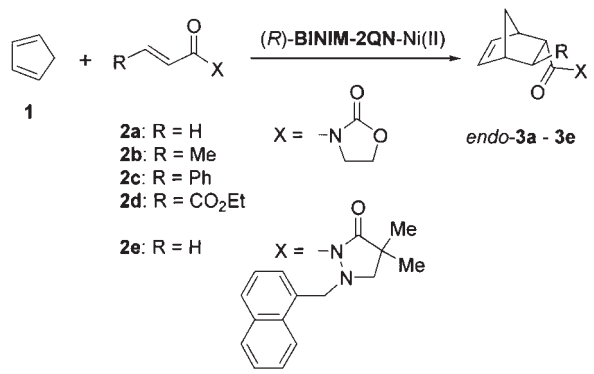
yl-2-oxazolidinones.[7,8] In the presence of 1 mol% of the Ni(II) catalyst, the reaction of cyclopentadiene with 3-acryloyl-2-oxazolidinone proceeded smoothly (85% yield) at −40 °C with high enantioselectivity (*endo*: 90% ee).[9] We also investigated the role of water in preparing complexes, and the scope and limitations of the reactions. The details of those investigations are reported herein.

Results and Discussion

Screening Study of Chiral BINIM–Metal Catalysts for the Reaction between Cyclopentadiene and 3-Acryloyl-2-oxazolidinone. Initially, a reaction of cyclopentadiene (**1**) with 3-acryloyl-2-oxazolidinone (**2a**) was conducted in CH_2Cl_2 at −40 °C in the presence of complexes (10 mol%), which were prepared from three (*S*)-**BINIM**s [(*S*)-**BINIM-DC**, (*S*)-**BINIM-OH**, and (*S*)-**BINIM-DCOH**; see Chart 1] and several metal salts or combinations of metal halides and 2 equivalents of silver salts (Scheme 1 and Table 1). In spite of good-to-moderate enantioselectivities of the minor *exo*-adducts in the **BINIM-DC**–Ni(II) catalyzed reactions, the enantioselectivities of preferentially obtained *endo*-adducts were low (entries 1–4).



Scheme 1. Asymmetric Diels–Alder reactions between cyclopentadiene (**1**) and 3-alkenoyl-2-oxazolidinones (**2a**–**2d**) and 2-acryloyl-3-pyrazolidinone **2e**.

Although opposite enantioselection by using **BINIM-DC**–Fe(II) catalysts compared with other metal catalysts appeared to be interesting, unsatisfactory results were obtained in terms of the enantioselectivity (entries 5 and 6). In contrast, among the combinations of **BINIM-OH** and several metal salts tested (entries 7–11), the complex prepared by mixing (*S*)-**BINIM-OH** and $Ni(ClO_4)_2 \cdot 6H_2O$ showed moderate enantioselectivities (74% and 73% ee, respectively) of both the *endo*- and *exo*-cycloadducts (entry 8). Although the enantioselectivity was modest, the use of (*S*)-**BINIM-DCOH** in combination with $Ni(ClO_4)_2 \cdot 6H_2O$ resulted in the opposite asymmetric induction (entry 12) compared with utilizing (*S*)-**BINIM-OH** as a ligand.

We then studied the effects of substitution patterns on the benzene rings of chiral **BINIM-OH** derivatives for the enantioselectivity of the cycloadducts (Table 2). When (*R*)-**BINIM-3ClOH** (entry 3) or (*R*)-**BINIM-5ClOH** (entry 4) was used instead of (*S*)-**BINIM-DCOH** for preparing the catalyst, the corresponding *endo*-cycloadduct having an *R* configuration at 2-C was preferentially obtained in both cases. This indicates that the substitution of chlorine atoms at both the 3- and 5-positions was required for the opposite enantioselection compared to the use of **BINIM-OH** as a ligand if the same configuration of the **BINIM**s was used. When **BINIM-DBOH** (entry 5), **BINIM-3OMeOH** (entry 6), and **BINIM-5MeOH** (entry 7) were utilized as ligands, the opposite asymmetric induction was also observed compared with **BINIM-OH**. Although the enantioselectivity was changed by the substituents or substitution patterns, no systematic trend was observed.

Subsequently, we focused our attention on the observation that substituting the hydroxy group of **BINIM-OH** with an OBn group (entry 9) resulted in a remarkable reduction of the enantioselectivity, which suggests that a coordinating group, such as the existing hydroxy group located in the vicinity of the diimino moiety, is needed to improve the enantioselectivity. This led to an investigation of ligands containing pyridine-type functionalities that can tightly coordinate to the Ni atom. Two quinolinecarbaldehyde-based **BINIM**s (**BINIM-8QN** and **BINIM-2QN**) were synthesized and tested for their catalytic

Table 1. **BINIM**–Metal Complexes Catalyzed Asymmetric Diels–Alder Reactions of Cyclopentadiene (**1**) with 3-Acryloyl-2-oxazolidinone (**2a**)[a)]

Entry	**BINIM**	Metal salt	MS 4A	Time	Yield	*endo*:*exo*[b)]	% ee[b)]	
				h	%		*endo* ( )[c)]	*exo*
1	(*S*)-**BINIM-DC**	$NiBr_2 + 2AgBF_4$	no	41	quant	80:20	53 (*S*)	81
2	(*S*)-**BINIM-DC**	$NiBr_2 + 2AgSbF_6$	no	16	85	89:11	32 (*S*)	46
3	(*S*)-**BINIM-DC**	$Ni(ClO_4)_2 \cdot 6H_2O$	yes	18	99	74:26	24 (*S*)	78
4	(*S*)-**BINIM-DC**	$Ni(ClO_4)_2 \cdot 6H_2O$	no	88	94	85:15	38 (*S*)	73
5	(*S*)-**BINIM-DC**	$FeCl_2 \cdot 4H_2O + 2AgSbF_6$	yes	14	95	91:9	52 (*R*)	50
6	(*S*)-**BINIM-DC**	$FeCl_2 \cdot 4H_2O + 2AgBF_4$	yes	84	93	92:8	11 (*R*)	38
7	(*S*)-**BINIM-OH**	$NiBr_2 + 2AgBF_4$	no	112	94	91:9	35 (*S*)	50
8	(*S*)-**BINIM-OH**	$Ni(ClO_4)_2 \cdot 6H_2O$	yes	38	quant	87:13	74 (*S*)	73
9	(*S*)-**BINIM-OH**	$Co(ClO_4)_2 \cdot 6H_2O$	yes	38	quant	93:7	27 (*S*)	39
10	(*S*)-**BINIM-OH**	$Zn(ClO_4)_2 \cdot 6H_2O$	yes	21	94	77:23	22 (*S*)	57
11	(*S*)-**BINIM-OH**	$Mg(ClO_4)_2$	yes	63	93	88:12	18 (*R*)	44
12	(*S*)-**BINIM-DCOH**	$Ni(ClO_4)_2 \cdot 6H_2O$	yes	18	69	88:12	49 (*R*)	24

a) Reactions were carried out at −40 °C in the presence of catalysts which were prepared by mixing the corresponding **BINIM** (10 mol%) and metal salts (10 mol%) in CH_2Cl_2 at room temperature for 6 h. b) Determined by HPLC analysis (Daicel Chiralpak AD). c) The absolute configuration of 2-C.

Table 2. Asymmetric Diels–Alder Reactions between Cyclopentadiene (**1**) and 3-Acryloyl-2-oxazolidinone (**2a**) Catalyzed by Ni(II)–**BINIM-OH** Derivatives[a]

Entry	Config[b]	R^1	R^2	R^3	**BINIM**	Time	Yield	*endo*:*exo*[c]	% ee[c]	
						h	%		*endo* ( )[d]	*exo*
1	*S*	H	H	H	**BINIM-OH**	38	quant	87:13	74 (*S*)	73
2	*S*	Cl	Cl	H	**BINIM-DCOH**	18	69	88:12	49 (*R*)	24
3	*R*	Cl	H	H	**BINIM-3ClOH**	116	95	97:3	16 (*R*)	35
4	*R*	H	Cl	H	**BINIM-5ClOH**	41	73	98:2	49 (*R*)	nd[e]
5	*R*	Br	Br	H	**BINIM-DBOH**	43	90	88:12	16 (*S*)	43
6	*R*	OMe	H	H	**BINIM-3-OMeOH**	42	quant	95:5	44 (*S*)	9
7	*S*	H	Me	H	**BINIM-5-MeOH**	40	87	90:10	27 (*R*)	38
8	*S*	*t*-Bu	*t*-Bu	H	**BINIM-DTBOH**	84	87	92:8	3 (*S*)	4
9	*S*	H	H	Bn	**BINIM-OBn**	64	quant	84:16	14 (*S*)	10

a) Reactions were carried out at −40 °C in the presence of catalysts which were prepared by mixing the corresponding **BINIM** (10 mol%) and $Ni(ClO_4)_2 \cdot 6H_2O$ (10 mol%) in the presence of MS 4A in CH_2Cl_2 at room temperature for 6 h. b) The absolute configuration of **BINIM**. c) Determined by HPLC analysis (Daicel Chiralpak AD). d) The absolute configuration of 2-C. e) Not determined.

Table 3. Asymmetric Diels–Alder Reactions between Cyclopentadiene (**1**) and 3-Acryloyl-2-oxazolidinone (**2a**) Using Quinoline- and Naphthalenecarbaldehyde-Based **BIMIN**s as Ligands[a]

Entry	**BINIM**	Metal salt	mol%	MS 4A	Time	Yield	*endo*:*exo*[b]	% ee[b]	
					h	%		*endo* ( )[c]	*exo*
1	(*R*)-**BINIM-1NAP**	$Ni(ClO_4)_2 \cdot 6H_2O$	10	yes	14	96	93:7	63 (*R*)	31
2	(*R*)-**BINIM-8QN**	$Ni(ClO_4)_2 \cdot 6H_2O$	10	yes	39	98	93:7	60 (*R*)	37
3	(*R*)-**BINIM-2NAP**	$Ni(ClO_4)_2 \cdot 6H_2O$	10	yes	13	quant	88:12	50 (*R*)	48
4	(*R*)-**BINIM-2QN**	$Ni(ClO_4)_2 \cdot 6H_2O$	10	yes	17	94	>99:1	94 (*R*)	nd[d]
5	(*R*)-**BINIM-2QN**	$Ni(ClO_4)_2 \cdot 6H_2O$	10	no	182	93	94:6	59 (*R*)	55
6	(*R*)-**BINIM-2QN**	$Ni(ClO_4)_2 \cdot 6H_2O$	5	yes	13	89	92:8	93 (*R*)	77
7	(*R*)-**BINIM-2QN**	$Ni(ClO_4)_2 \cdot 6H_2O$	2	yes	33	87	93:7	92 (*R*)	79
8	(*R*)-**BINIM-2QN**	$Ni(ClO_4)_2 \cdot 6H_2O$	1	yes	38	85	93:7	90 (*R*)	72
9	(*R*)-**BINIM-2QN**	$Ni(ClO_4)_2 \cdot 6H_2O$	0.5	yes	160	93	93:7	45 (*R*)	41
10	(*R*)-**BINIM-2QN**	$Co(ClO_4)_2 \cdot 6H_2O$	10	yes	17	98	95:5	90 (*R*)	63
11	(*R*)-**BINIM-2QN**	$Zn(ClO_4)_2 \cdot 6H_2O$	10	yes	17	97	95:5	84 (*R*)	68
12	(*R*)-**BINIM-2QN**	$Cu(ClO_4)_2 \cdot 6H_2O$	10	yes	257	97	85:15	33 (*R*)	26
13	(*R*)-**BINIM-2QN**	$Mg(ClO_4)_2$	10	yes	39	85	>99:1	5 (*S*)	nd[d]

a) Reactions were carried out at −40 °C in the presence of catalysts which were prepared by mixing the corresponding **BINIM** and $Ni(ClO_4)_2 \cdot 6H_2O$ in the presence of MS 4A in CH_2Cl_2 at room temperature for 6 h. b) Determined by HPLC analysis (Daicel Chiralpak AD). c) The absolute configuration of 2-C. d) Not determined.

activities toward Ni(II)-catalyzed Diels–Alder reactions. The chiral catalyst prepared from (*R*)-**BINIM-2QN** and $Ni(ClO_4)_2 \cdot 6H_2O$ in the presence of MS 4A in CH_2Cl_2 afforded the *endo*-adduct in high yield (94%) with high diastereo- (*endo*:*exo* > 99:1) and enantioselectivity (94% ee) (Table 3, entry 4). In contrast, the use of (*R*)-**BINIM-8QN** as a ligand resulted in moderate enantioselectivity. To assess the influence of the ligand's nitrogen atom, naphthalene analogs **BINIM-1NAP** and **BINIM-2NAP** were also prepared and tested. Interestingly, the utilization of (*R*)-**BINIM-2NAP** instead of (*R*)-**BINIM-2QN** resulted in a loss of enantioselectivity, whereas the diastereo- and enantioselectivities of the reactions using (*R*)-**BINIM-8QN** and (*R*)-**BINIM-1NAP** were very similar (entries 1 and 2). It is also interesting that the (*R*)-**BINIM-2QN**–Ni(II) catalyst prepared in the absence of MS 4A showed a remarkable reduction in enantioselectivity, and a long reaction time was need for reaction completion (entry 5). This may be attribute to the interference of a sufficient coordination with four coordination sites of **BINIM-2QN** to the Ni(II) cation, or deactivation of the catalyst by the existence of excess water. The above results indicate that the coordination of Ni to the nitrogen functionalities, which are located three bonds-distance from imino-nitrogens, is important for high enantioselectivity. It is noteworthy that the catalyst loading could be reduced to a minimum of 1 mol% (entries 6–9). Thus, the Diels–Alder reaction of cyclopentadiene (**1**) with 3-acryloyl-2-oxazolidinone (**2a**) proceeded smoothly (85%) with 1 mol% of chiral **BINIM-2QN**–Ni(II) catalyst without any significant loss of diastereo- (*endo*:*exo* = 93:7) and enantioselectivities (90% ee (*endo*)) (entry 8). However, decreasing the catalyst loading to 0.5 mol% resulted in a remarkable reduction in the enantioselectivity and a long reaction time was need for reaction completion, probably due to competition of a non-catalyst process by deactivation of the catalyst proceeding under the conditions used. Catalysts obtained from (*R*)-**BINIM-2QN** in combination with $Co(ClO_4)_2 \cdot 6H_2O$ or $Zn(ClO_4)_2 \cdot 6H_2O$ also showed good *endo*- and enantioselectivities (entries 10 and 11).

Preparation Procedure for Chiral BINIM-2QN–Ni(II) Catalyst. To obtain information on the structure of the **BINIM-2QN**–Ni(II) catalyst, preparing of the catalyst from

Table 4. Asymmetric Diels–Alder Reactions between Cyclopentadiene (**1**) and 3-Acryloyl-2-oxazolidinone (**2a**) in the Presence of Catalyst Prepared from (*R*)-**BINIM-2QN**, $NiBr_2$, and Silver Salts[a)]

Entry	Metal salt	Additive	Filtration[b)]	MS 4A	Time	Yield	*endo*:*exo*[c)]	% ee[c)]	
					h	%		*endo* ( )[d)]	*exo*
1	$NiBr_2 + 2AgClO_4$	none	yes	no	252	99	95:5	0	1
2	$NiBr_2 + 2AgClO_4$	$6H_2O$	yes	no	48	98	93:7	91 (*R*)	73
3	$NiBr_2 + 2AgClO_4$	$6H_2O$	no	no	58	99	93:7	85 (*R*)	64
4	$NiBr_2 + 2AgClO_4$	$6H_2O$	no	yes	62	quant	93:7	11 (*R*)	21
5	$NiBr_2 + 2AgClO_4$	$6H_2O$	yes	yes[e)]	52	87	93:7	86 (*R*)	71
6	$NiBr_2 + 2AgClO_4$	$4H_2O$	yes	yes[e)]	61	99	94:6	80 (*R*)	67
7	$NiBr_2 + 2AgClO_4$	$3H_2O$	yes	yes[e)]	39	99	93:7	87 (*R*)	75
8	$NiBr_2 + 2AgClO_4$	$2H_2O$	yes	yes[e)]	113	99	93:7	83 (*R*)	70
9	$NiBr_2 + 2AgClO_4$	$12H_2O$	yes	yes[e)]	216[f)]	98	95:5	3 (*R*)	6

a) Reactions were carried out at −40 °C in the presence of catalysts which were prepared by mixing (*R*)-**BINIM-2QN**, $NiBr_2$, and silver salts in CH_2Cl_2 at room temperature for 6 h. b) Filtered after preparation of the catalyst. c) Determined by HPLC analysis (Daicel Chiralpak AD). d) The absolute configuration of 2-C. e) MS 4A was added after filtration of the catalyst. f) The reaction was carried out at −40 °C for 216 h, and then at rt for 14 h.

$NiBr_2$ and $AgClO_4$ was examined. To a mixture of $NiBr_2$ (10 mol%) and $AgClO_4$ (20 mol%), a solution of (*R*)-**BINIM-2QN** (10 mol%) in CH_2Cl_2 was added, and the mixture was stirred for 6 h at room temperature. After filtration of an insoluble salt under an argon atmosphere, the resulting solution was used for the reaction of cyclopentadiene (**1**) with 3-acryloyl-2-oxazolidinone (**2a**) in a manner similar to the preparation of the catalyst from $Ni(ClO_4)_2 \cdot 6H_2O$. Surprisingly, a long time period was needed for completion of the reaction, and no asymmetric induction was observed (Table 4, entry 1). In contrast, when 6 equivalents of H_2O per $NiBr_2$ were added while preparing the Ni(II) catalyst, high enantioselectivity (91% ee) similar to the preparation procedure using $Ni(ClO_4)_2 \cdot 6H_2O$ was observed (entry 2). The use of a similarly prepared catalyst without filtration after stirring the same salts with (*R*)-**BINIM-2QN** in CH_2Cl_2 did not essentially decrease the enantioselectivity (entry 3). Not needing MS 4A in these cases is presumably due to the absorption of excess water by silver salt, which was produced during the complex formation, in this scale reaction. The addition of MS 4A to the filtrate, which was prepared by the same procedure as entry 2, also did not significantly reduced enantioselectivity (entry 5). From investigations into the use of water as an additive, three to six equivalents of water per $NiBr_2$ resulted in an acceptable reaction rate and good enantioselectivity (entries 5–8). The addition of twelve equivalents of water remarkably reduced the catalytic activity and enantioselectivity (entry 9). These results indicate that some amount of water is necessary for the formation of the active (*R*)-**BINIM-2QN**–Ni(II) complex, and that the chiral Ni(II) complex is likely to be an octahedral aqua cationic complex in which four nitrogen atoms on the **BINIM-2QN** and two molecules of water coordinate to Ni^{2+}.

Relation between the Enantiomeric Purity of BINIM-2QN and *endo*-Adduct. To gain additional information about the catalyst structure, the relation between the enantiomeric purity of the **BINIM-2QN**–Ni(II) catalyst and that of the *endo*-cycloadduct was investigated by a reaction of **1** with **2a** in the presence of 10 mol% catalyst at −40 °C. As shown in Fig. 1, a weak positive non-linear association was observed between the enantiomeric purity of the catalyst and the optical yield of the *endo*-cycloadduct, suggesting that dimeric or origomeric

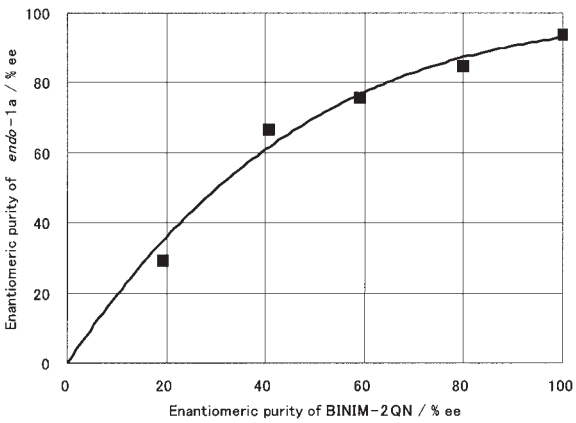


Fig. 1. Relation between the enantiomeric purity of **BINIM-2QN** and the optical purity of the *endo*-adduct in the reaction of **1** with **2a** catalyzed by the **BINIM-2QN**–Ni(II) complex.

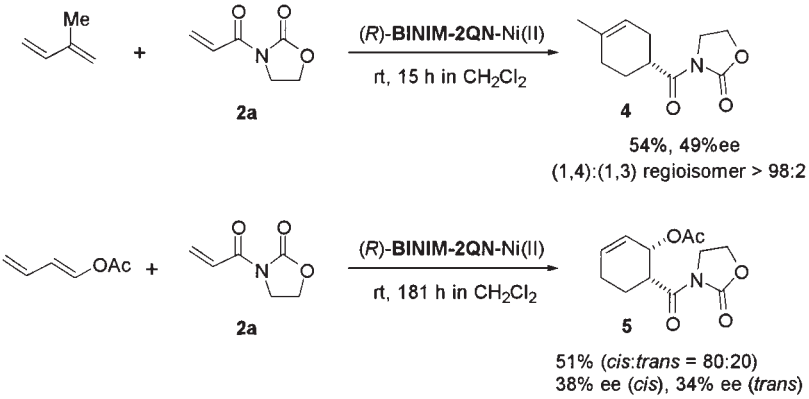
Ni complexes may exist as precursors of an active catalyst in those reactions. However, the level of asymmetric amplification was not high, in contrast to the Diels–Alder reaction catalyzed by 4,6-dibenzofurandiyl-2,2′-bis(4-phenyloxazoline)–Ni(II) (DBFOX/Ph–Ni(II)) complex.[7b] A small amount of water in our system presumably plays a role in changing the state of aggregation from dimeric or origomeric complexes to monomeric aqua complexes.

Chiral BINIM-2QN–Ni(II)-Catalyzed Diels–Alder Reaction of Other Dienes and Dienophiles. The (*R*)-**BINIM-2QN**–Ni(II) catalyst prepared from (*R*)-**BINIM-2QN** and $Ni(ClO_4)_2 \cdot 6H_2O$ was applied to Diels–Alder reactions of cyclopentadiene (**1**) with 3-alkenoyl-2-oxazolidinones **2b–2d** (Scheme 1, Table 5). Although diastereoselectivities of reactions with **2b–2d** were somewhat decreased, the (*R*)-**BINIM-2QN**–Ni(II) catalyst could interact satisfactorily with these 3-alkenoyl-2-oxazolidinones to provide high enantioselectivity (90–96% ee) of *endo*-adducts (entries 2–4). The reaction with 2-acryloyl-3-pyrazolidinone **2e** was also examined to improve the enantioselectivity using a chiral relay in the catalytic asymmetric Diels–Alder reaction, as reported by Sibi.[10] The same level of enantioselectivity (94% ee) as that obtained by a reac-

Table 5. Asymmetric Diels–Alder Reactions between Cyclopentadiene (**1**) and 3-Alkenoyl-2-oxazolodinones (**2b**–**2d**) and 2-Acryloyl-3-pyrazolidinone **2e**[a)]

Entry	Dienophile	R	mol%	Temp	Time	Yield	*endo*:*exo*[b)]	% ee[b)]	
				°C	h	%		*endo*	*exo*
1	**2a**	H	10	−40	17	94	>99:1	94	nd[c)]
2	**2b**	Me	10	rt	13	85	80:20	92	68
3	**2c**	Ph	20	rt	48	96	73:27	90	51
4	**2d**	CO_2Et	10	−40	17	quant	78:22	96	77
5	**2e**	H	10	−40	41	73	92:8	94	nd[c)]

a) Reactions were carried out in the presence of catalysts which were prepared by mixing (*R*)-**BINIM-2QN** and $Ni(ClO_4)_2 \cdot 6H_2O$ in the presence of MS 4A in CH_2Cl_2 at room temperature for 6 h. b) Determined by HPLC analysis (Daicel Chiralpak AD). c) Not determined.



Scheme 2. Diels–Alder reactions of isoprene and 1-acetoxybutadiene with 3-acryloyl-2-oxazolidinone (**2a**), which were catalyzed by the (*R*)-**BINIM-2QN**–Ni(II) complex.

tion with **2a** was observed (entry 5).

For applications to other dienes, (*R*)-**BINIM-2QN**–Ni(II)-catalyzed Diels–Alder reactions of isoprene or 1-acetoxybutadiene[13] with 3-acryloyl-2-oxazolidinone (**2a**) were investigated (Scheme 2). The yield and enantioselectivity were less satisfactory in reactions involving these dienes. The catalytic activity of (*R*)-**BINIM-2QN**–Ni(II) toward the less-reactive dienes was a problem, which requires improvement.

Model Study for Enantioselectivity. As described above, we found that several equivalents of water per Ni were needed to prepare the active chiral **BINIM-2QN**–Ni(II) complex from chiral **BINIM-2QN**, $NiBr_2$, and $AgClO_4$. This observation suggests that the active complex is a six-coordinated aqua cationic Ni^{2+} complex having two ClO_4^- anions as counter ions. A square bipyramidal structure containing an octahedral nickel ion was also proposed for the reacting-catalyst substrate complexes in the Diels–Alder reactions between cyclopentadiene and 3-alkenoyl-2-oxazolidinone catalyzed by the DBFOX/Ph–Ni(II) complex.[7b] Since chiral **BINIM-2QN** bears four nitrogen coordination sites, two molecules of water presumably coordinate to Ni^{2+} in the complex. For the activation of dienophiles in the chiral **BINIM-2QN**–Ni(II)-catalyzed Diels–Alder reaction, two molecules of water must be replaced by the dienophiles, which have two carbonyl oxygens to coordinate. Thus, the complex of **2a** coordinated to the (*R*)-**BINIM-2QN**–Ni(II) catalyst was constructed by a molecular modeling program, and the structure of the complex was optimized using semi-empirical molecular orbital calculations (PM3).[14] The optimized structure is shown in Figs. 2 and 3 as a cylindrical-bonds model and space-filling model, respectively. The back side view in

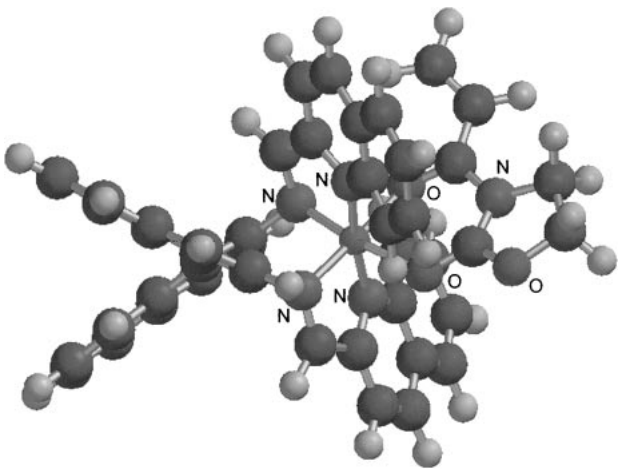


Fig. 2. Optimized structure of **2a** coordinated to the Ni(II) complex (cylindrical-bonds model).

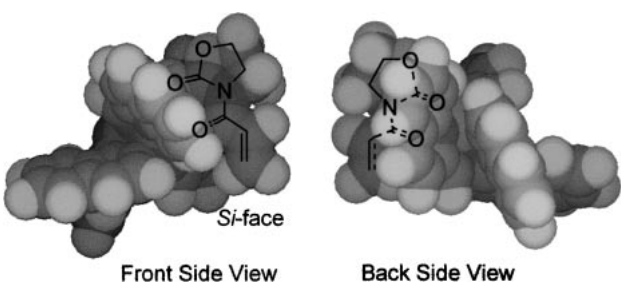
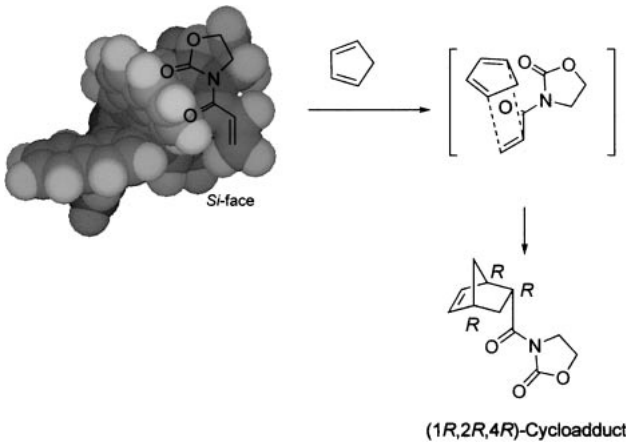


Fig. 3. Optimized structure of **2a** coordinated to the Ni(II) complex (space-filling model).



Scheme 3. Proposed mechanism in the (*R*)-**BINIM-2QN**–Ni(II)-catalyzed Diels–Alder reaction.

Fig. 3 suggests that the area around the olefin is shielded by a quinoline ring; therefore, the approach of cyclopentadiene from the front side (*Si*-face) is more facile.[15] This *Si*-face approach can reasonably explain the selective formation of the (1*R*,2*R*,4*R*)-*endo*-cycloadduct, which has the same configuration, determined by the optical rotation (Scheme 3).

Conclusion

A chiral **BINIM-2QN**–Ni(II) complex, which was prepared from chiral **BINIM-2QN** and $Ni(ClO_4)_2 \cdot 6H_2O$ in the presence of MS 4A in CH_2Cl_2, was an efficient chiral Lewis acid catalyst for the asymmetric Diels–Alder reaction of cyclopentadiene with several 3-alkenoyl-2-oxazolidinones, which yielded greater than 90% ee *endo*-cycloadduct. In the reaction of cyclopentadiene with 3-acryloyl-2-oxazolidinone, catalyst loading could be reduced to 1 mol% without any essential loss of enantioselectivity. The structure of the active complex was proposed based on investigations of a preparation method using $NiBr_2$, $AgClO_4$, and water. The high enantioselectivity observed in the reaction was also reasonably explained by optimizing the structure of acryloyl-2-oxazolidinone coordinated to the Ni(II) complex using semi-empirical molecular orbital calculations (PM3). Experiments are currently underway to evaluate the versatility of the chiral **BINIM-2QN**–Ni(II) catalyst in other Lewis acid-promoted asymmetric reactions.

Experimental

General. All reactions were carried out under an argon atmosphere in dried glassware. Air- and moisture-sensitive compounds were introduced by using a cannula through a rubber septum. ^{1}H NMR spectra were recorded in $CDCl_3$ on a 60 MHz or 400 MHz instrument. The chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. Enantiomeric ratios were determined using a chiral column via HPLC analysis. Analytical thin-layer chromatography was performed using silica gel $60F_{254}$ aluminium sheets. For preparative column chromatography, Wakogel C-300 and Silica gel 60 (size 0.040–0.063 mm) were employed. Medium-pressure liquid chromatography was carried out using a column packed with Silica gel 60 (size 0.040–0.063 mm).

Materials. Chiral 1,1′-binaphthyl-2,2′-diamine and 2-quinolinecarbaldehyde were purchased from Aldrich Co. 3-Alkenoyl-2-oxazolidinones were prepared according to reported procedures.[7a,11a,b] Dichloromethane, ethyl acetate, and hexane were purified by distillation, first from $CaCl_2$ and then CaH_2 under argon. Benzene and THF were freshly distilled from a sodium diphenylketyl still under argon. Powdered 4 Å molecular sieves were commercially available and dried in vacuo at 250 °C for 12 h before use.

A General Procedure for Diels–Alder Reactions Catalyzed by BINIM-2QN–Ni(II) Complex Prepared from $Ni(ClO_4)_2 \cdot 6H_2O$ was Exemplified by the Reaction of 1 with 2a. To a mixture of $Ni(ClO_4)_2 \cdot 6H_2O$ (18 mg, 0.05 mmol) and MS 4A (0.125 g) was added a solution of (*R*)-**BINIM-2QN** (28 mg, 0.05 mmol) in CH_2Cl_2 (2 mL); the mixture was then stirred at room temperature for 6 h. To the above mixture was added a solution of 3-acryloyl-2-oxazolidinone (**2a**) (72 mg, 0.50 mmol) in CH_2Cl_2 (1 mL). After cooling to −40 °C, the mixture was allowed to react with cyclopentadiene (**1**) (0.331 g, 5.0 mmol) for 17 h. The reaction mixture was quenched with a saturated NH_4Cl solution (3 mL) and then filtered through Cerite. The filtrate was extracted with CH_2Cl_2 (5 mL × 3). The combined extracts were dried over $MgSO_4$ and evaporated in vacuo. The residue was chromatographed on silica gel with hexane–diethyl ether (7:3 v/v) to give cycloadduct **3a** (0.099 g, 94%). The *endo*:*exo* ratio and enantiomeric purity were evaluated by an HPLC analysis (Daicel Chiralpak AD, hexane–2-PrOH, 39:1 v/v, detector: UV 254 nm, flow rate = 0.5 mL/min, 35 °C, exo_{major}: t_R = 62.6 min, $endo_{major}$: t_R = 65.7 min, exo_{minor}: t_R = 83.2 min, $endo_{minor}$: t_R = 94.1 min).

(1*R*,2*R*,4*R*)-3-(Bicyclo[2.2.1]hept-5-en-2-ylcarbonyl)-2-oxazolidinone (3a):[7b,11a] Colorless solid; mp 80–81 °C; $[\alpha]_D^{25}$ +145.40° (*c* 1.04, $CHCl_3$); 94% ee estimated on the basis of HPLC using a chiral column (Daicel Chiralpak AD); IR (KBr) 2978, 2876, 1768 (C=O), 1682 (C=O), 1651, 1485, 1385, 1340, 1280, 1249, 1215, 1114, 1064, 1039, 1005, 978, 958, 931, 904, 860, 837, 814, 761, 723, 702, 675, 679 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.36–1.48 (3H, m), 1.89–1.96 (1H, m), 2.91 (1H, m), 3.28 (1H, m), 3.87–4.03 (3H, m), 4.32–4.42 (2H, m), 5.84 (1H, dd, J = 5.6, 2.9 Hz), 6.21 (1H, dd, J = 5.6, 2.9 Hz).

(1*R*,2*R*,3*S*,4*S*)-3-(3-Methylbicyclo[2.2.1]hept-5-en-2-ylcarbonyl)-2-oxazolidinone (3b):[7b,11a,11c] A mixture of 80:20 *endo*- and *exo*-isomers; Colorless solid; mp 93–94 °C; $[\alpha]_D^{25}$ +159.50° (*c* 1.02, $CHCl_3$); 92% ee estimated on the basis of HPLC using a chiral column (Daicel Chiralpak AD with hexane–2-PrOH, 39:1 v/v, detector: UV 254 nm, flow rate = 0.5 mL/min, 35 °C, exo_{minor}: t_R = 44.1 min, $endo_{minor}$: t_R = 46.6 min, exo_{major}: t_R = 49.9 min, $endo_{major}$: t_R = 54.0 min); IR (KBr) 2968, 2928, 2870, 1768 (C=O), 1693 (C=O), 1381, 1329, 1292, 1221, 1120, 1095, 1078, 1035, 1008, 761, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 0.80 (3H × 20/100, d, J = 6.6 Hz, *exo*), 1.06 (3H × 80/100, d, J = 7.0 Hz, *endo*), 1.28–1.73 (2H, m), 1.92–2.13 (1H, m), 2.47 (1H, bs), 3.23 (1H, bs), 3.40–3.54 (1H, m), 3.73–4.01 (2H, m), 4.23–4.51 (2H, m), 5.72 (1H, dd, J = 5.6, 2.9 Hz), 6.21 (1H, dd, J = 5.6, 2.9 Hz).

(1*R*,2*R*,3*S*,4*S*)-3-(3-Phenylbicyclo[2.2.1]hept-5-en-2-ylcarbonyl)-2-oxazolidinone (3c):[7b,11a,11c,12] A mixture of 73:27 *endo*- and *exo*-isomers; Colorless solid; mp 115–116 °C; $[\alpha]_D^{25}$ +130.83° (*c* 1.00, $CHCl_3$); 90% ee estimated on the basis of HPLC using a chiral column (Daicel Chiralpak AD with hexane–2-PrOH, 39:1 v/v, detector: UV 254 nm, flow rate = 0.5 mL/min, 35 °C, exo_{major}: t_R = 47.0 min, $endo_{major}$: t_R = 54.8 min, exo_{minor}: t_R = 71.7 min, $endo_{minor}$: t_R = 113.2 min), IR (KBr) 3410, 2982, 1774 (C=O), 1693 (C=O), 1386, 1332, 1277, 1222, 1026, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 1.25–1.93 (2H, m), 3.13

(2H, bs), 3.68–3.78 (1H, m), 3.99–4.15 (3H, m), 4.30–4.41 (2H, m), 5.72 (1H, dd, $J = 5.6$, 3.0 Hz), 6.21 (1H, dd, $J = 5.6$, 3.0 Hz), 7.20 (5H, s).

(1*R*,2*R*,3*S*,4*S*)-3-(3-Ethoxycarbonylbicyclo[2.2.1]hept-5-en-2-ylcarbonyl)-2-oxazolidinone (3d):[11a,12] A mixture of 78:22 *endo*- and *exo*-isomers; Colorless oil; $[\alpha]_D^{25}$ +159.45° (*c* 0.98, $CHCl_3$); 96% ee estimated on the basis of HPLC using a chiral column (Daicel Chiralpak AD with hexane–2-PrOH, 39:1 v/v, detector: UV 220 nm, flow rate = 0.5 mL/min, 35 °C, exo_{minor}: t_R = 95.5 min, $endo_{major}$: t_R = 106.6 min, exo_{major}: t_R = 114.3 min, $endo_{minor}$: t_R = 123.2 min), IR (neat) 2984, 1778 (C=O), 1726 (C=O), 1695 (C=O), 1386, 1365, 1325, 1280, 1221, 1114, 1037, 435, 408 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 1.23 (3H × 22/100, t, $J = 7.1$ Hz, *exo*), 1.26 (3H × 78/100, t, $J = 7.1$ Hz, *endo*), 1.42–1.69 (2H, m), 2.90 (1H, dd, $J = 1.7$, 4.6 Hz), 3.24 (1H, bs), 3.46 (1H, bs), 3.67–5.32 (7H, m), 5.72 (1H, dd, $J = 5.6$, 2.9 Hz), 6.21 (1H, dd, $J = 5.6$, 2.9 Hz).

(1*R*,2*R*,4*R*)-2-(Bicyclo[2.2.1]hept-5-en-2-ylcarbonyl)-4,4-dimethyl-1-(1-naphthylmethyl)-3-pyrazolidinone (3e): Colorless solid; mp 143–144 °C; $[\alpha]_D^{26}$ +80.52° (*c* 1.00, $CHCl_3$); 94% ee estimated on the basis of HPLC using a chiral column (Daicel Chiralpak AD with hexane–2-PrOH, 39:1 v/v, detector: UV 254 nm, flow rate = 0.5 mL/min, 17 °C, $endo_{minor}$: t_R = 35.3 min, $endo_{major}$: t_R = 39.4 min), IR (KBr) 2978, 2945, 1768 (C=O), 1684 (C=O), 1350, 1336, 1300, 1211, 1182, 798, 779, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.02–1.60 (4H, m), 1.29 (6H, s), 2.69–2.81 (3H, m), 2.96 (1H, bs), 3.44 (1H, bs), 4.40 (1H, d, $J = 13.4$ Hz), 4.52 (1H, d, $J = 13.4$ Hz), 5.67 (1H, dd, $J = 5.6$, 2.7 Hz), 6.07 (1H, dd, $J = 5.6$, 2.7 Hz), 7.25–8.22 (7H, m); HRMS *m*/*z* 374.2009. Calcd for $C_{24}H_{26}N_2O_2$: M, 374.1996. Anal. Calcd for $C_{24}H_{26}N_2O_2$: C, 76.98; H, 7.00; N, 7.48%. Found: C, 76.93; H, 7.15; N, 7.38%.

3-[(1*R*)-4-Methyl-3-cyclohexenylcarbonyl]-2-oxazolidinone (4):[11a,11b,12] Colorless solid; mp 66–67 °C; $[\alpha]_D^{26}$ +19.34° (*c* 0.38, $CHCl_3$); 49% ee determined by HPLC after conversion to the corresponding (*R*)-α-methylbenzyl amide[11b] (Daicel Chiralpak AS with hexane–2-PrOH, 19:1 v/v, detector: UV 254 nm, flow rate = 0.5 mL/min, 35 °C, minor: t_R = 27.1 min, major: t_R = 30.0 min); IR (KBr) 2922, 1782 (C=O), 1693 (C=O), 1392, 1367, 1336, 1259, 1228, 1211, 1043, 758, 707 cm^{-1}; ^1H MNR ($CDCl_3$, 400 MHz) δ 1.64–2.26 (6H, m), 1.68 (3H, s), 3.66 (1H, m), 4.03 (2H, t, $J = 8.3$ Hz), 4.00 (2H, t, $J = 8.3$ Hz), 5.40 (1H, bs).

3-[(1*R*,2*S*)-2-Acetoxy-3-cyclohexenylcarbonyl]-2-oxazolidinone (5):[11b] A mixture of 80:20 *cis*- and *trans*-isomers; Colorless solid; mp 74–75 °C; $[\alpha]_D^{26}$ +66.75° (*c* 0.20, $CHCl_3$); 38% ee (*cis*) and 34% ee (*trans*) estimated on the basis of HPLC using a chiral column (Daicel Chiralcel OD-H with hexane–2-PrOH, 4:1 v/v, detector: UV 220 nm, flow rate = 1.0 mL/min, 35 °C, cis_{major}: t_R = 8.9 min, cis_{minor}: t_R = 12.2 min, $trans_{major}$: t_R = 15.4 min, $trans_{minor}$: t_R = 17.8 min), IR (KBr) 2939, 1778 (C=O), 1739 (C=O), 1693 (C=O), 1487, 1437, 1392, 1369, 1313, 1224, 1120, 1095, 1032, 999, 985, 964, 916, 887, 761, 711, 684 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 1.62–2.24 (4H, m), 1.95 (3H, s), 3.73–4.59 (5H, m), 5.68–6.02 (3H, m).

BINIM-DC, **BINIM-OH**, **BINIM-DCOH**, **BINIM-3ClOH**, **BINIM-5ClOH**, **BINIM-DBOH**, **BINIM-3OMeOH**, **BINIM-5MeOH**, **BINIM-DTBOH**, and **BINIM-OBn** were prepared according to the procedures reported previously.[6]

A General Procedure for Preparation of the Other BINIMs was Exemplified by the Reaction of (*R*)-1,1′-Binaphthyl-2,2′-diamine with 2-Quinolinecarbaldehyde. A suspension of MS 4A (3.2 mm pellets, 6.0 g), (*R*)-1,1′-binaphthyl-2,2′-diamine (0.300 g, 1.1 mmol), and 2-quinolinecarbaldehyde (0.742 g, 4.24 mmol) was heated under reflux in benzene (9.0 mL) for 4 h. After the MS 4A was removed by filtration, the filtrate was concentrated in vacuo. The resulting solids were recrystallized from diethyl ether to give (*R*)-**BINIM-2QN** (0.278 g, 49%): Yellow plates; mp 125.5–129 °C (diethyl ether); $[\alpha]_D^{25}$ +34.50° (*c* 1.00, CH_2Cl_2); IR (KBr) 1614 (C=N), 1591, 1558, 1502, 1425, 1203, 1111, 968, 895 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 7.26–8.13 (24H, m, Ar-H), 8.65 (2H, s, CH=N); HRMS (EI) *m*/*z* 562.2134. Calcd for $C_{40}H_{26}N_4$: M, 562.2156. Anal. Calcd for $C_{40}H_{26}N_4$: C, 85.38; H, 4.66; N, 9.96%. Found: C, 85.22; H, 4.90; N, 9.76%.

(*S*)-*N*,*N*′-Bis[2-(benzyloxy)benzylidene]-1,1′-binaphthyl-2,2′-diamine ((*S*)-BINIM-OBn): Pale-yellow powder; mp 173–174 °C (benzene–hexane); $[\alpha]_D^{26}$ −1.52° (*c* 1.01, CH_2Cl_2); IR (KBr) 1610 (C=N), 1487, 1452, 1373, 1294, 1246, 1224, 1159, 1105, 1016, 972, 812, 750, 696 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 4.92 (4H, s, CH_2), 6.70–8.00 (30H, m, Ar-H), 8.81 (2H, s, CH=N); HRMS (EI) *m*/*z* 672.2813. Calcd for $C_{48}H_{36}N_2O_2$: M, 672.2775. Anal. Calcd for $C_{48}H_{36}N_2O_2$: C, 85.69; H, 5.39; N, 4.16%. Found: C, 85.71; H, 5.38; N, 4.15%.

(*R*)-*N*,*N*′-Bis(8-quinolylmethylene)-1,1′-binaphthyl-2,2′-diamine ((*R*)-BINIM-8QN): Yellow plates; mp 220–225.5 °C (dichloromethane–hexane); $[\alpha]_D^{24}$ +442.45° (*c* 1.00, CH_2Cl_2); IR (KBr) 3051, 2953, 2924, 1616 (C=N), 1591, 1570, 1317, 1201, 891 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 7.00–8.45 (24H, m, Ar-H), 8.58 (2H, s, CH=N); HRMS (EI) *m*/*z* 562.2138. Calcd for $C_{40}H_{26}N_4$: M, 562.2156. Anal. Calcd for $C_{40}H_{26}N_4$: C, 85.38; H, 4.66; N, 9.96%. Found: C, 85.59; H, 4.83; N, 9.68%.

(*R*)-*N*,*N*′-Bis(2-naphthylmethylene)-1,1′-binaphthyl-2,2′-diamine ((*R*)-BINIM-2NAP): Pale-yellow plates; mp 113–115.5 °C (benzene–hexane); $[\alpha]_D^{25}$ +255.09° (*c* 1.01, CH_2Cl_2); IR (KBr) 3053, 2955, 2954, 1614 (C=N), 1502, 1120, 970, 825, 752 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 7.12–8.05 (26H, m, Ar-H), 8.28 (2H, s, CH=N); HRMS (EI) *m*/*z* 560.2250. Calcd for $C_{42}H_{28}N_2$: M, 560.2251. Anal. Calcd for $C_{40}H_{28}N_2$: C, 89.97; H, 5.03; N, 5.00%. Found: C, 89.65; H, 5.75; N, 4.61%.

(*R*)-*N*,*N*′-Bis(1-naphthylmethylene)-1,1′-binaphthyl-2,2′-diamine ((*R*)-BINIM-1NAP): Pale-yellow plates; mp 56.0–63.0 °C (benzene–hexane); $[\alpha]_D^{25}$ +105.82° (*c* 1.00, CH_2Cl_2); IR (KBr) 1631, 1608 (C=N), 1587, 1504, 1205, 817, 802, 773, 746 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 6.98–8.23 (26H, m, Ar-H), 8.83 (2H, s, CH=N); HRMS (EI) *m*/*z* 560.2251. Calcd for $C_{42}H_{28}N_2$: M, 560.2251. Anal. Calcd for $C_{40}H_{28}N_2$: C, 89.97; H, 5.03; N, 5.00%. Found: C, 89.49; H, 5.42; N, 4.71%.

2-Acryloyl-4,4-dimethyl-1-(1-naphthylmethyl)-3-pyrazolidinone (2e):[10] To a solution of acrylic acid (1.44 g, 1.36 mL, 20.0 mmol) in ethyl acetate (100 mL) at 0 °C was first added triethylamine (2.02 g, 2.80 mL, 20.0 mmol), followed by acryloyl chloride (1.81 g, 1.62 mL, 20 mmol) over a period of 2 min. The reaction mixture was stirred at 0 °C for 40 min, and then at room temperature for 30 min. After the mixture was filtered through filter paper, the filter cake was washed with ethyl acetate. The filtrate was concentrated in vacuo. The residue was taken up in hexane (40 mL) and swirled, then filtered and concentrated in vacuo again. The anhydride was dissolved in THF (14 mL) and immediately used in the following step. To a suspension of 4,4-dimethyl-1-(1-naphthylmethyl)-3-pyrazolidinone[10a] (2.54 g, 10.0 mmol) and LiCl (0.85 g, 20 mmol) in THF (15 mL) was added triethylamine (2.02 g, 2.80 mL, 20.0 mmol), followed by the anhydride solution prepared above by the use of a cannula. The resulting slurry was stirred at room temperature for 4 h. After removal of the solvent, 40 mL of a 1 mol/L HCl solution was added and extracted with CH_2Cl_2

(10 mL × 3). The combined organic layers were washed with 1:1 sat. aq $NaHCO_3/H_2O$ (40 mL) and brine (40 mL), and then dried over $MgSO_4$. After filtration and concentration in vacuo, the resulting oil was chromatographed on silica gel with hexane–ethyl acetate (2:1 v/v) to yield 1.74 g (54%) of desired product as colorless solids: mp 128–129 °C; IR (KBr) 2978, 2945, 1768 (C=O), 1684 (C=O), 1350, 1336, 1300, 1211, 1182, 798, 779, 692 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 1.41 (6H, s), 2.74 (2H, s), 4.45 (2H, s), 5.01 (1H, dd, $J = 10.0$, 2.4 Hz), 5.80 (1H, dd, $J = 17.1$, 2.4 Hz), 6.35 (1H, dd, $J = 17.1$, 10.0 Hz), 7.27–8.28 (7H, m); HRMS (EI) m/z 308.1511. Calcd for $C_{19}H_{20}N_2O_2$: M, 308.1524. Anal. Calcd for $C_{19}H_{20}N_2O_2$: C, 74.00; H, 6.54; N, 9.08%. Found: C, 73.95; H, 6.57; N, 9.09%.

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