Asymmetric Diels–Alder Reactions Catalyzed by Chiral Ni(II)-Binaphthyldiimine Complexes

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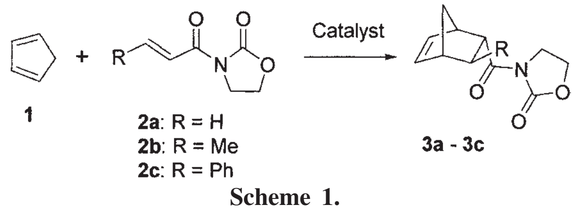
Ni(II)-*N*,*N*′-Bis(2-quinolylmethylene)-1,1′-binaphthyl-2,2′-diamine complex was found to be an efficient chiral Lewis acid catalyst for asymmetric Diels–Alder reactions (*endo*: up to 94% ee) between cyclopentadiene (**1**) and 3-alkenoyl-2-oxazolidinones (**2**). In the presence of Ni(II) catalyst (1 mol%), the reaction between cyclopentadiene and 3-acryloyl-2-oxazolidinone proceeded smoothly (85% yield) at −40 °C with high enantioselectivity (*endo*: 90% ee).

Since its discovery, Diels–Alder reactions[1] have been one of the most powerful organic synthetic methods. In particular, asymmetric catalytic variants of the reaction[2] have received exceptional attention, due to their capacity to rapidly provide enantiomerically pure and complex cyclic compounds from simple substrates. We have recently reported on the high catalytic activities of Cu(I)-binaphthyldiimine (BINIM) complexes for asymmetric cyclopropanation[3] and aziridination[4,5] reactions, and of Ni(II)-BINIM complexes for 1,3-dipolar cycloaddition reaction of *N*-benzylideneaniline *N*-oxide.[6] For these reactions, among the several BINIMs used in the study, *N*,*N*′-bis(2,6-benzylidene)-1,1′-binaphthyl-2,2′-diamine (BINIM-DC) was found to be the most effective ligand. For the evaluation of the versatility of the chiral metal-BINIM catalysts, reactions of the Diels–Alder type were chosen owing to their synthetic importance. Herein, we report on the versatile application of chiral Ni(II)-*N*,*N*′-bis(2-quinolylmethylene)-1,1′-binaphthyl-2,2′-diamine (BINIM-2QN) complex as an efficient chiral Lewis acid catalyst for asymmetric Diels–Alder reactions between cyclopentadiene and 3-alkenoyl-2-oxazolidinones.[7]



Scheme 1.

Initially, reactions were carried out between cyclopentadiene (**1**) and 3-acryloyl-2-oxazolidinone (**2a**) in CH_2Cl_2 at −40 °C in the presence of the Ni(II) complexes (10 mol%), which were prepared by mixing (*S*)-BINIM-DC with $Ni(ClO_4)_2 \cdot 6H_2O$, $NiBr_2 + 2AgBF_4$, or $NiBr_2 + 2AgSbF_6$ (Scheme 1; Table 1, Entries 1–4). In spite of good to moderate enantioselectivities of the minor *exo*-cycloadduct, the *endo*-cycloadduct was preferentially obtained with low enantioselectivity using these Ni(II)-BINIM-DC catalysts. In contrast, by using a combination of (*S*)-BINIM-OH and $Ni(ClO_4)_2 \cdot 6H_2O$ in the preparation of the catalyst, both *endo*- and *exo*-cycloadducts were obtained with moderate enantioselectivities (74% ee and 73% ee, respectively) (Entry 5). Although *endo*-selectivity was higher in some cases, the use of various BINIM-OH derivatives, such as BINIM-DCOH, BINIM-3ClOH, BINIM-5ClOH, and BINIM-TBOH (see Figure 1), did not improve the enantioselectivities. Use of other perchlorates in the preparation of the catalysts with different metal ions also did not show better results in terms of enantioselectivity.

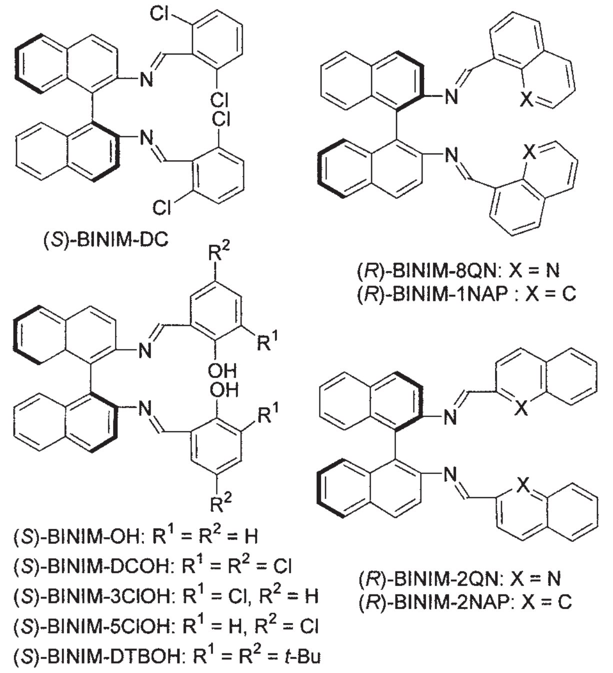


Figure 1. The Structures of BINIMs.

Subsequently, we focused our attention to the observation that substituting the hydroxyl group of BINIM-OH with an OBn group (Entry 6) resulted remarkably in reduction of the enantioselectivity. The results imply that a coordinating group, such as the existing hydroxyl group located in the vicinity of the diimino moiety, is needed for the improvement of enantioselectivity. This observation led us to investigate ligands containing pyridine-type functionalities, which can tightly coordinate to the Ni atom. Two quinolinecarboxaldehyde-based BINIMs (Figure 1, BINIM-8QN and BINIM-2QN), were synthesized and tested for their catalytic activities toward Ni(II)-catalyzed Diels–Alder reactions. To assess the influence of the ligand's nitrogen atom, naphthalene analogs, BINIM-1NAP and BINIM-2NAP, were also prepared and tested. As shown as Entry 10, chiral Ni(II) catalysts that were prepared from (*R*)-BINIM-2QN and

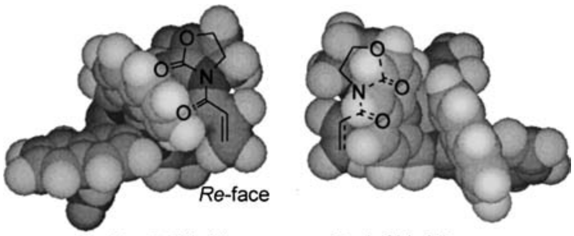
Table 1. Diels–Alder Reactions of Cyclopentadiene with 3-Alkenoyl-2-oxazolidinones[a]

Entry	R	Ligand	Metal Salt	mol%	MS 4A	Temp./°C	Time/h	Yield/%	*endo* : *exo*[b]	% ee[b] *endo*( )[c]	*exo*
1	H	(*S*)-BINIM-DC	$Ni(ClO_4)_2 \cdot 6H_2O$	10	yes	−40	18	99	74 : 26	24 (*S*)	78
2	H	(*S*)-BINIM-DC	$Ni(ClO_4)_2 \cdot 6H_2O$	10	no	−40	88	94	85 : 15	38 (*S*)	73
3	H	(*S*)-BINIM-DC	$NiBr_2 + 2AgBF_4$	10	no	−40	41	quant.	80 : 20	53 (*S*)	81
4	H	(*S*)-BINIM-DC	$NiBr_2 + 2AgSbF_6$	10	no	−40	16	85	89 : 11	32 (*S*)	46
5	H	(*S*)-BINIM-OH	$Ni(ClO_4)_2 \cdot 6H_2O$	10	yes	−40	37	quant.	87 : 13	74 (*S*)	73
6	H	(*S*)-BINIM-OBn	$Ni(ClO_4)_2 \cdot 6H_2O$	10	yes	−40	64	quant.	84 : 16	14 (*S*)	10
7	H	(*R*)-BINIM-1NAP	$Ni(ClO_4)_2 \cdot 6H_2O$	10	yes	−40	14	96	93 : 7	63 (*R*)	31
8	H	(*R*)-BINIM-8QN	$Ni(ClO_4)_2 \cdot 6H_2O$	10	yes	−40	39	98	93 : 7	60 (*R*)	37
9	H	(*R*)-BINIM-2NAP	$Ni(ClO_4)_2 \cdot 6H_2O$	10	yes	−40	13	quant.	88 : 12	50 (*R*)	48
10	H	(*R*)-BINIM-2QN	$Ni(ClO_4)_2 \cdot 6H_2O$	10	yes	−40	17	94	>99 : 1	94 (*R*)	nd[d]
11	H	(*R*)-BINIM-2QN	$Co(ClO_4)_2 \cdot 6H_2O$	10	yes	−40	17	98	95 : 5	90 (*R*)	nd[d]
12	H	(*R*)-BINIM-2QN	$Zn(ClO_4)_2 \cdot 6H_2O$	10	yes	−40	17	97	95 : 5	84 (*R*)	nd[d]
13	H	(*R*)-BINIM-2QN	$Ni(ClO_4)_2 \cdot 6H_2O$	5	yes	−40	13	89	92 : 8	93 (*R*)	nd[d]
14	H	(*R*)-BINIM-2QN	$Ni(ClO_4)_2 \cdot 6H_2O$	2	yes	−40	33	87	93 : 7	92 (*R*)	nd[d]
15	H	(*R*)-BINIM-2QN	$Ni(ClO_4)_2 \cdot 6H_2O$	1	yes	−40	38	85	93 : 7	90 (*R*)	nd[d]
16	Me	(*R*)-BINIM-2QN	$Ni(ClO_4)_2 \cdot 6H_2O$	10	yes	rt	13	85	80 : 20	92 (*R*)	68
17	Ph	(*R*)-BINIM-2QN	$Ni(ClO_4)_2 \cdot 6H_2O$	20	yes	rt	48	96	73 : 27	90 (*R*)	51

[a] See a typical procedure [Ref. 8]. [b] Determined by HPLC analysis. [c] The absolute configuration of 2-C. [d] Not determined.

$Ni(ClO_4)_2 \cdot 6H_2O$ afforded the *endo*-cycloadduct in high yield (94%) with high enantioselectivity (*endo*: 94% ee).[8] It is interesting to note that BINIM-2NAP resulted in a loss of enantioselectivity, whereas the diastereo- and enantioselectivities of the reaction using BINIM-1NAP and BINIM-8QN were almost similar (Entries 7 and 8). Catalysts obtained from the combination of BINIM-2QN with $Co(ClO_4)_2 \cdot 6H_2O$ and $Zn(ClO_4)_2 \cdot 6H_2O$ also showed good *endo*- and enantioselectivities (Entries 11 and 12). It is noteworthy that the Diels–Alder reaction proceeded smoothly with 1 mol% of the Ni(II) catalyst without significant loss of selectivity (Entry 15). Reaction between cyclopentadiene and 3-crotonoyl-2-oxazolidinone (**2b**) or 3-cinnamoyl-2-oxazolidinone (**2c**) under the Ni(II)-catalyzed conditions also showed satisfactory results in terms of enantioselectivity (Entries 16 and 17).

Semiempirical molecular orbital calculations (PM3)[9] were carried out using the structure of **2a** coordinated to Ni(II)-(*R*)-BINIM-2QN to yield an optimized structure, as shown in Figure 2. From the backside view, it can be suggested that the area around the olefin is shielded by a quinoline ring, and therefore the approach of cyclopentadiene from the frontside (*Re*-face) is more facile. This *Re*-face approach can reasonably explain the selective formation of the (1*R*, 2*R*, 4*R*)-cycloadduct in the reaction using (*R*)-BINIM-2QN as the ligand.



Front Side View Back Side View

Figure 2. The Optimized Structure of the Ni(II) Complex.

In conclusion, we have found that the chiral Ni(II)-BINIM-2QN complex is a highly efficient chiral Lewis acid catalyst for asymmetric Diels–Alder reactions of cyclopentadiene with 3-alkenoyl-2-oxazolidinones. Experiments are currently under way to evaluate the further versatility of the chiral Ni(II)-BINIM catalysts in other Lewis acid-promoted asymmetric reactions.

References and Notes

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7 Ni(II)-Catalyzed asymmetric Diels–Alder reactions using Chiral 4,6-dibenzofurandiyl-2,2′-bis(4-phenyloxazoline) were reported by Kanemasa: S. Kanemasa, Y. Oderaotoshi, S. Sakaguchi, H. Yamamoto, J. Tanaka, E. Wada, and D. P. Curran, *J. Am. Chem. Soc.*, **120**, 3074 (1998), and references therein.

8 A typical procedure using (*R*)-BINIM-2QN as a chiral ligand: A mixture of $Ni(ClO_4)_2 \cdot 6H_2O$ (19 mg, 0.05 mmol), 4 Å molecular sieves (0.125 g), and (*R*)-BINIM-2QN (28 mg, 0.05 mmol) in dry CH_2Cl_2 (2.0 mL) was stirred at room temperature for 6 h under argon atmosphere. To the above mixture was added a solution of **2a** (72 mg, 0.50 mmol) in dry CH_2Cl_2 (1.0 mL). After cooling the mixture to −40 °C, the reaction mixture was allowed to react with cyclopentadiene (0.331 g, 5.0 mmol) for 17 h. Usual workup and chromatographic procedures afforded the cycloadducts (99 mg, 94%). The *endo* : *exo* ratio and enantiomeric purity were evaluated using HPLC (Daicel Chiralpak AD).

9 Geometry optimizations were performed using PC Spartan Pro (Version 1.0.5) program.