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New types of Lewis acids used in organic synthesis

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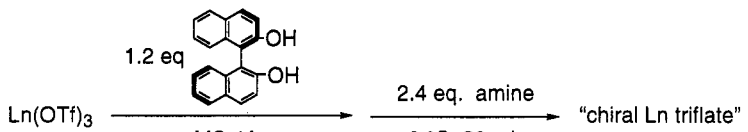
Abstract: New types of Lewis acids based on group 3 and 4 elements (Sc, Y, La, Zr, and Hf) have unique properties compared to typical Lewis acids. This article describes our recent results on Lewis acid-catalyzed enantioselctive reactions using these elements and their unique properties. Asymmetric versions of Diels-Alder reactions, [2+2] cycloaddition, aza Diels-Alder reactions, 1,3-dipolar cycloaddition, and Mannich-type reactions using chiral rare earth and zirconium catalysts are discussed.

INTRODUCTION

Lewis acid-catalyzed carbon-carbon bond forming reactions are of great current interest in organic synthesis because of the unique reactivities and selectivities that can be achieved as well as for the mild conditions. While various kinds of Lewis acid-promoted reactions including application in industry have been developed, these reactions must be carried out under strict anhydrous conditions. The presence of even a small amount of water stops the reaction, because most Lewis acids immediately react with water rather than the substrates and decompose or deactivate. Recently, rare earth triflates are found to be stable in water and to work efficiently as Lewis acid catalysts in several carbon-carbon bond forming reactions.[1] The reactions proceeded smoothly in the presence of a catalytic amount of the triflate under mild conditions in both aqueous and organic solvents. Moreover, the catalysts could be recovered after the reactions were completed and could be reused. In addition to rare earths, it has also been found that zirconium and hafnium Lewis acids have unique properties compared to typical Lewis acids, and several efficient catalytic reactions have been developed.[2] In this paper, chiral Lewis acid catalysis based on these new types of Lewis acids are focused. Several catalytic asymmetric reactions, especially important carbon-carbon bond-forming reactions, with unique reactivities and selectivities under mild conditions are discussed.

ASYMMETRIC DIELS-ALDER REACTIONS

It was found that a chiral Yb triflate was prepared *in situ* from $Yb(OTf)_3$, (*R*)-(+)-binaphthol ((*R*)-(+)-BINOL), and a tertiary amine at 0 °C for 0.5 h in dichloromethane. While $Yb(OTf)_3$ or (*R*)-(+)-BINOL dissolved only sluggishly in dichloromethane, the mixture of $Yb(OTf)_3$, (*R*)-(+)-BINOL, and an amine became an almost clear solution.



Ln = Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu

In the presence of the chiral Yb triflate, 3-(2-butenoyl)-1,3-oxazolidin-2-one (**1**) reacted with cyclopentadiene at room temperature to afford the Diels-Alder adduct in an 87% yield (*endo/exo* = 76/24) and the enantiomeric excess of the *endo* adduct was shown to be 33%. The amine employed at the stage of the preparation of the chiral catalyst strongly influenced the diastereo- and enantioselectivities. In general, bulky amines gave better results and 70%, 75%, and 71% ee's were observed when diisopropylethylamine, *cis*-2,6-dimethylpiperidine, and *cis*-1,2,6-trimethylpiperidine were used, respectively. In addition, a better result was obtained when the amine was combined with molecular sieves 4A (*cis*-1,2,6-trimethylpiperidine, 91% yield, *endo/exo* = 86/14, *endo* = 90% ee), and the enantiomeric excess was further improved to 95% when the reaction was carried out at 0 °C.[3]

It was also found that aging of the catalyst took place. High selectivities were obtained when the diene and the dienophile were added just after $Yb(OTf)_3$, (*R*)-(+)-BINOL, and a tertiary amine were stirred at 0 °C for 0.5 h in dichloromethane (the original catalyst system). On the other hand, the selectivities lowered in accordance with the stirring time of the catalyst solution and the temperature. These results seemed to be ascribed to the aging of the catalyst, but the best result (77% yield, *endo/exo* = 89/11, *endo* = 95% ee) was obtained when the mixture (the substrates and 20 mol% of the catalyst) was stirred at 0 °C for 20 h. It was suggested from this result that the substrates or the product stabilized the catalyst. The effect of the substrates or the product on the stabilization of the catalyst was then examined, and the dienophile (**1**) was found to be effective in preventing the catalyst from aging. When 20 mol% of the original catalyst system and **1** (additive) were stirred at 0 °C for 5.5 h in dichloromethane, the product was obtained in a 66% yield, *endo/exo* = 87/13, and the enantiomeric excess of the *endo* adduct was 88%.

Moreover, after screening several additives other than **1**, it was found that some additives were effective not only in stabilizing the catalyst but also *in controlling the enantiofacial selectivities in the Diels-Alder reaction* (Table 1). When 3-acetyl-1,3-oxazolidin-2-one (**2**) was combined with the original catalyst system (to form **catalyst A**), the *endo* adduct was obtained in 93% ee and the absolute configuration of the product was *2S, 3R*. On the other hand, when acetyl acetone derivatives were mixed with the catalyst, *reverse enantiofacial selectivities were observed.* The *endo*

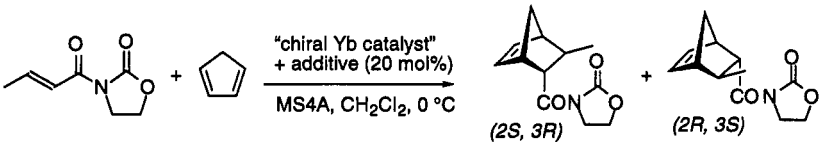
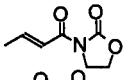


Table 1. Effect of Additives

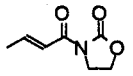
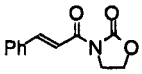
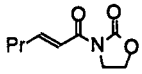
Additive		Yield (%)	*endo/exo*	*2S,3R/2R,3S*	(ee (%))[a]
	**1**	66	87/13	**94.0**/ 6.0	(88)
	**2**	77	89/11	**96.5**/ 3.5	(93)
		80	88/12	22.5/**77.5**	(55)
		36	81/19	19.0/**81.0**	(62)
		69	88/12	15.5/**84.5**	(69)
Ph		83	93/ 7	9.5/**90.5**	(81)[c]

a) Enantiomer ratios of *endo* adducts.
b) 1,2,2,6,6-Pentamethylpiperidine was used instead of *cis*-1,2,6-trimethylpiperidine. $Yb(OTf)_3$, MS4A, and the additive were stirred in dichloromethane at 40 °C for 3 h.

adduct with an absolute configuration of *2R, 3S* was obtained in 81% ee when 3-phenylacetylacetone (PAA) was used as an additive (**catalyst B**). In these cases, the chiral source was the same (*R*)-(+)-BINOL. Therefore, *the enantioselectivities were controlled by the achiral ligands, 3-acetyl-1,3-oxazolidin-2-one and PAA.*

The same selectivities were observed in the reactions of other 3-acyl-1,3-oxazolidin-2-ones (Table 2). Thus, by using the same chiral source ((*R*)-(+)-BINOL), both enantiomers of the Diels-Alder adducts between 3-acyl-1,3-oxazolidin-2-ones and cyclopentadiene were prepared. Traditional methods have required both enantiomers of chiral sources in order to prepare both enantiomers stereoselectively, but the counterparts of some chiral sources are of poor quality or are hard to obtain (for example, sugars, amino acids, alkaloids, etc.). *It is noted that the chiral catalysts with reverse enantiofacial selectivities could be prepared by using the same chiral source and a choice of achiral ligands.*[4]

Table 2. Synthesis of Both Enantiomers of the Diels-Alder Adducts between Cyclopentadiene and Dienophiles by Use of Catalysts A and B

Dienophile	Catalyst A				Catalyst B[a]			
	Yield/%	*endo*/*exo*	*2S,3R*/*2R,3S*	(ee (%))[b]	Yield/%	*endo*/*exo*	*2S,3R*/*2R,3S*	(ee (%))[b]
	77	89/11	**96.5**/ 3.5	(93)	83	93/ 7	9.5/**90.5**	(81)
	77	89/11	**97.5**/ 2.5	(95)[c]				
	40	81/19	**91.5**/ 8.5[d]	(83)	60	89/11	10.5/**89.5**[d]	(79)
					51	89/11	8.5/**91.5**[d]	(83)
					51	89/11	5.5/**94.5**[d]	(89)[e]
	34	80/20	**93.0**/ 7.0	(86)	81	91/ 9	10.0/**90.0**	(80)
	81	80/20	**91.5**/ 8.5	(83)[c]	85	91/ 9	9.0/**91.0**	(82)[e]
					60	91/ 9	7.5/**92.5**	(85)[f]

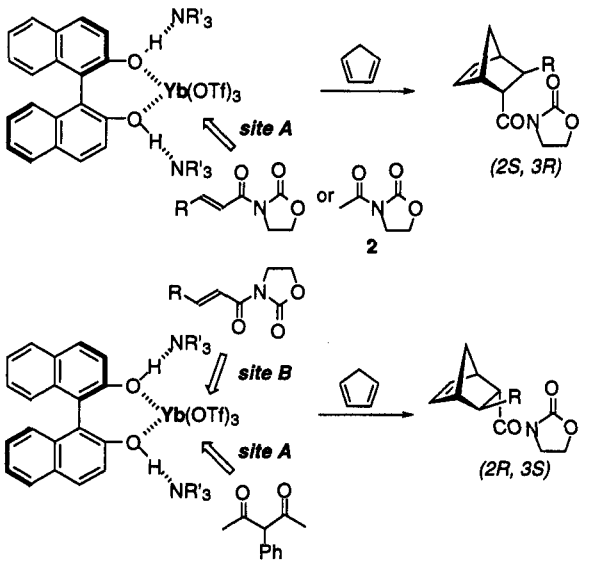
Catalyst A: $Yb(OTf)_3$ + (R)-(+)-binaphthol + *cis*-1,2,6-trimethylpiperidine + MS4A + 3-acetyl-1,3-oxazolidin-2-one (**2**)
Catalyst B: $Yb(OTf)_3$ + (R)-(+)-binaphthol + *cis*-1,2,6-trimethylpiperidine + MS4A + 3-phenylacetylacetone (PAA)

a) 1,2,2,6,6-Pentamethylpiperidine was used instead of 1,2,6-trimethylpiperidine. b) Enantiomer ratios of *endo* adducts. c) Without additive. d) *2R,3R*/*2S,3S*. e) $Tm(OTf)_3$ was used instead of $Yb(OTf)_3$. f) $Er(OTf)_3$ was used instead of $Yb(OTf)_3$.

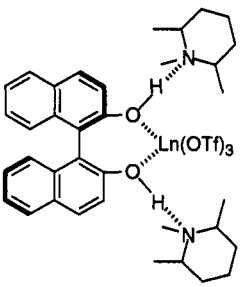
These exciting selectivities are believed to be strongly dependent on the specific coordination number of Yb(III)[5] (Scheme 1). Two binding sites for the ligands are now postulated in the Yb catalysts. Denophile **1** or additive **2** coordinates in **site A** under equilibrium conditions to stabilize the original catalyst system. When **1** coordinates Yb(III), cyclopentadiene attacks from the *si* face of **1** (**site A** favors *si* face attack). On the other hand, in **catalyst B** (the original catalyst system and PAA), **site A** is occupied by PAA. 3-Acyl-1,3-oxazolidin-2-ones are weakly coordinating ligands, whereas PAA is stronger coordinating. From the experiments, **site A** seems to be more easily available for coordination than **site B**. Since another coordination site still remains in the Yb(III) catalyst owing to the specific coordination numbers, **1** coordinates at **site B** and cyclopentadiene attacks from the *re* face (**site B** favors *re* face attack).

Although $Sc(OTf)_3$ has slightly different properties compared to lanthanide triflates, the chiral Sc catalyst could be prepared from $Sc(OTf)_3$, (*R*)-(+)-BINOL, and a tertiary amine in dichloromethane.[6] The catalyst was also found to be effective in the Diels-Alder reactions of acyl-1,3-oxazolidin-2-ones with dienes.

As for the chiral lanthanide and scandium catalysts, the following structures have been postulated (Scheme 2).[7] The unique structure shown in Scheme 2 was indicated by ^{13}C NMR and IR spectra. The most characteristic point of the catalysts was the existence of hydrogen bonds between the phenolic hydrogens of (*R*)-(+)-BINOL and the nitrogens of the tertiary amines. The ^{13}C NMR



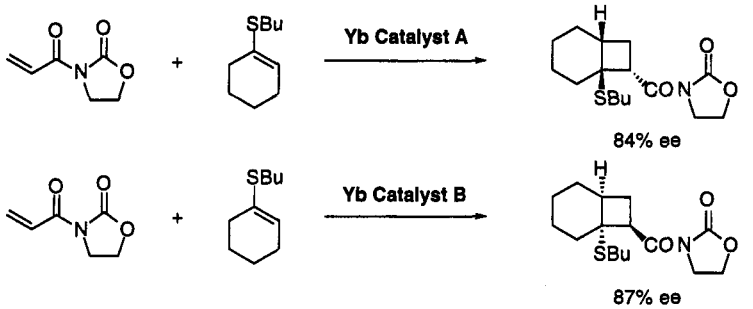
Scheme 1. Synthesis of Both Enantiomers Using the Same Chiral Source



Scheme 2. Chiral Lanthanide Catalysts

spectra indicated these interactions, and the existence of the hydrogen bonds was confirmed by the IR spectra.[8] The coordination form of these catalysts may be similar to that of the lanthanide(III)-water or -alcohol complex.[9] It is noted that the structure is quite different from those of conventional chiral Lewis acids based on other typical Lewis acids such as aluminum, boron, or titanium. In the present chiral catalysts, the axial chirality of (*R*)-(+)-BINOL is transferred via the hydrogen bonds to the amine parts, which shield one side of the dienophile effectively. This is consistent with the experimental results showing that amines employed in the preparation of the chiral catalysts strongly influenced the selectivities and that bulky amines gave better selectivities. Moreover, since the amine part can be freely chosen, the design of the catalyst is easier than other catalysts on the basis of (*R*)-(+)-BINOL. Although some "modified" binaphthols were reported to be effective as chiral sources, their preparations often require long steps.

ASYMMETRIC [2+2] CYCLOADDITION



Scheme 3. Asymmetric [2+2] Cycloaddition. Synthesis of Both Enantiomers Using the Same Chiral Source and a Choice of Achiral Ligands

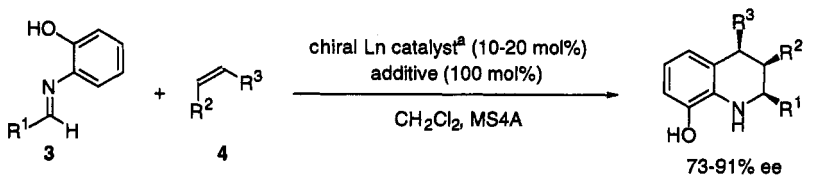
Enantioselctive [2+2] cycloaddition of a vinyl sulfide with an oxazolidone derivative proceeds smoothly in the presence of a catalytic amount of the chiral lanthanide catalyst.[10] Both enantiomers can be prepared by using a single chiral source and a choice of achiral ligands (Scheme 3).

ASYMMETRIC AZA DIELS-ALDER REACTIONS

Chiral Lewis acid-catalyzed asymmetric reactions of nitrogen-containing substrates are rare, probably because most chiral Lewis acids would be trapped by the basic nitrogen atoms to block the catalytic cycle. For example, although aza Diels-Alder reactions are one of the most basic and versatile reactions for the synthesis of nitrogen-containing heterocyclic compounds, and asymmetric versions using chiral auxiliaries or a stoichiometric amount of a chiral Lewis acid have been reported,[11] examples using a catalytic amount of a chiral source were unprecedented.

We have found that the reaction of *N*-benzylidene-2-hydroxyaniline (**3a**, R^1 = Ph) with cyclopentadiene proceeded under the influence of 20 mol% of a chiral ytterbium Lewis acid prepared from $Yb(OTf)_3$, (*R*)-(+)-BINOL, and diazabicyclo-[5,4,0]-undec-7-ene (DBU), to afford the corresponding 8-hydroxyquinoline derivative in a high yield. The enantiomeric excess of the *cis*-adduct was 40%. It was indicated that the phenolic hydrogen of **3a** would interact with DBU, which should interact with the hydrogen of (*R*)-(+)-BINOL, to decrease the selectivity. Additives which interact with the phenolic hydrogen of **3a** were examined. When 20 mol% *N*-methylimidazole (MID) was used, 91% ee of the *cis* adduct was obtained, however, the chemical yield was low. Other additives were screened and it was found that the desired tetrahydroquinoline derivative was obtained in a 92% yield with high selectivities (*cis*/*trans* = >99/1, 71% ee), when 2,6-di-*t*-butyl-4-methylpyridine (DTBMP) was used.[12]

Vinyl ethers also worked well to afford the corresponding tetrahydroquinoline derivatives in good to high yields with good to excellent diastereo- and enantioselectivities. Use of 10 mol% of the chiral catalyst also gave the adduct in high yields and selectivities. As for additives, 2,6-di-*t*-butylpyridine (DTBP) gave the best result in the reaction of imine **3a** with ethyl vinyl ether (**4a**, R^2 = OEt, R^3 = H), while higher selectivities were obtained when DTBMP or 2,6-diphenylpyridine (DPP) was used in the reaction of imine **3b** (R^1 = 1-naphthyl) with **4a**. This could be explained by the slight difference in the asymmetric environment created by $Yb(OTf)_3$, (*R*)-(+)-BINOL, DBU, and the additive. While use of butyl vinyl ether decreased the selectivities, dihydrofurane reacted smoothly to achieve high levels of selectivity. It was found that imine **3c** (R^1 = c-C_6H_{11}) prepared from cyclohexanecarboxaldehyde and 2-hydroxyaniline was unstable and difficult to purify. The asymmetric aza Diels-Alder reaction was successfully carried out using the three component coupling procedure (successively adding the aldehyde, the amine, and cyclopentadiene) in the presence of $Sc(OTf)_3$ (instead of $Yb(OTf)_3$), (*R*)-(+)-BINOL, DBU, and DTBMP.

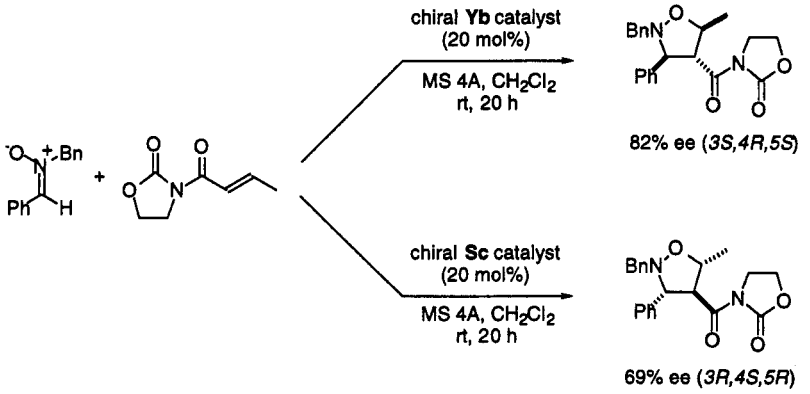


[a]Prepared from $Yb(OTf)_3$ or $Sc(OTf)_3$, (*R*)-(+)-BINOL, and DBU. Additive = DTBP (2,6-di-*t*-butylpyridine), DTBMP (2,6-di-*t*-butyl-4-methylpyridine), or DPP (2,6-diphenylpyridine). Ln = Yb, Sc

ASYMMETRIC 1,3-DIPOLAR CYCLOADDITION

A catalytic asymmetric 1,3-dipolar cycloaddition of a nitrone with a dipolarophile was carried out using a chiral lanthanide catalyst.[13] The chiral catalyst, which was effective in asymmetric Diels-Alder reactions, was readily prepared from $Yb(OTf)_3$, (*R*)-(+)-BINOL, and *cis*-1,2,6-trimethylpiperidine, and the reaction of benzylbenzylideneamine *N*-oxide with 3-(2-butenoyl)-1,3-oxazolidin-2-one was performed in the presence of the chiral catalyst (20 mol%). The reaction proceeded smoothly in dichloromethane at rt, and the desired isoxazolidine was obtained in a 75%

yield with perfect diastereoselectivity (*endo*/*exo* = >99/1), and the enantiomeric excess of the *endo* adduct was 82% determined by HPLC analysis. On the other hand, it was found that reverse enantioselectivity was observed when a chiral scandium catalyst was used in stead of the chiral ytterbium catalyst (Scheme 4).[14]



Scheme 4. Asymmetric 1,3-Dipolar Cycloaddition. Synthesis of Both Enantiomers Using the Same Chiral Source and a Choice of Rare Earth Elements

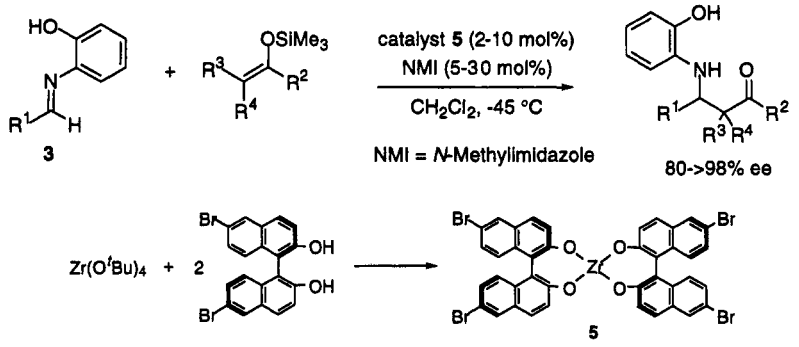
CATALYTIC ENANTIOSELECTIVE MANNICH-TYPE REACTIONS USING A NOVEL ZIRCONIUM CATALYST

Asymmetric Mannich-type reactions provide useful routes for the synthesis of optically active β-amino ketones or esters, which are versatile chiral building blocks in the preparation of many nitrogen-containing biologically important compounds. While several diastereoselective Mannich-type reactions have already been reported, very little is known about the enantioselective versions. Asymmetric Mannich-type reactions using small amounts of chiral sources have not been reported to the best of our knowledge.

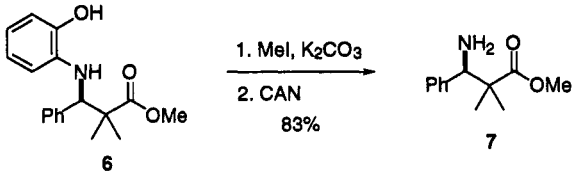
While rather rapid progress has been made on the enantioselective reactions of carbonyl compounds using chiral Lewis acids (aldol reactions, allylation reactions, Diels-Alder reactions, etc.),[15] very few examples have been reported for their aza analogues.[16] We thought that this was due to two main difficulties. First, many Lewis acids are deactivated or sometimes decomposed by the nitrogen atoms of starting materials or products as already mentioned in the previous section, and even when the desired reactions proceed, more than stoichiometric amounts of the Lewis acids are needed because the acids are trapped by the nitrogen atoms. Secondly, aldimine-chiral Lewis acid complexes are rather flexible and often have several stable conformers (including E/Z isomers of aldimines), while aldehyde-chiral Lewis acid complexes are believed to be rigid. Therefore, in the additions to aldimines activated by chiral Lewis acids, plural transition states would exist to decrease selectivities. In order to solve these problems, we first screened various metal salts in the achiral reactions of aldimines with silylated nucleophiles. After careful investigation of the catalytic ability of the salts, we found unique characteristics in zirconium (IV) (Zr (IV)) and decided to design a chiral Lewis acid based on Zr (IV) as a center metal. On the other hand, as for the problem of the conformation of the aldimine-Lewis acid complex, we planned to utilize the bidentate chelation (see the section of *AYMMETRIC AZA DILES-ALDER REACTIONS*). A necessary condition is easy removal of the chelation part of the substrates after the reactions.

A chiral zirconium catalyst was prepared *in situ* according to Scheme 5. In the presence of 10 mol% of catalyst **5**, the aldimine prepared from 1-naphthaldehyde and 2-aminophenol **3b** (R^1 = 1-naphthyl) was treated with the ketene silyl acetal derived from methyl isobutylate (**7**) in dichloromethane at 45 °C, to afford the desired adduct in a 95% ee. It should be noted that the same

high level of ee was obtained when 2 mol% of the catalyst was employed. When the aldimine prepared from aniline or 2-methoxyaniline was used under the same reaction conditions, the corresponding β-amino esters were obtained in good yields but with less than 5% ee's. We then tested other aldimines (**3**) and silyl enolates and the results are summarized in Table 4. Not only aldimines derived from aromatic aldehydes but also aldimines from heterocyclic and aliphatic aldehydes[17] worked well in this reaction, and good to high yields and enantiomeric excesses were obtained. Similar high levels of ees were also obtained when the silyl enol ether derived from *S*-ethyl thioacetate was used. The *N*-substituent of the product was easily removed according to Scheme 6. Thus, methylation of the phenolic OH of **6** using methyl iodide and potassium bicarbonate, and deprotection using cerium ammonium nitrate (CAN)[18] gave β-amino ester **7**. The absolute configuration assignment was made by comparison of the optical rotation of **7** with that in the literature.[19]



Scheme 5. Catalytic Asymmetric Mannich-Type Reactions

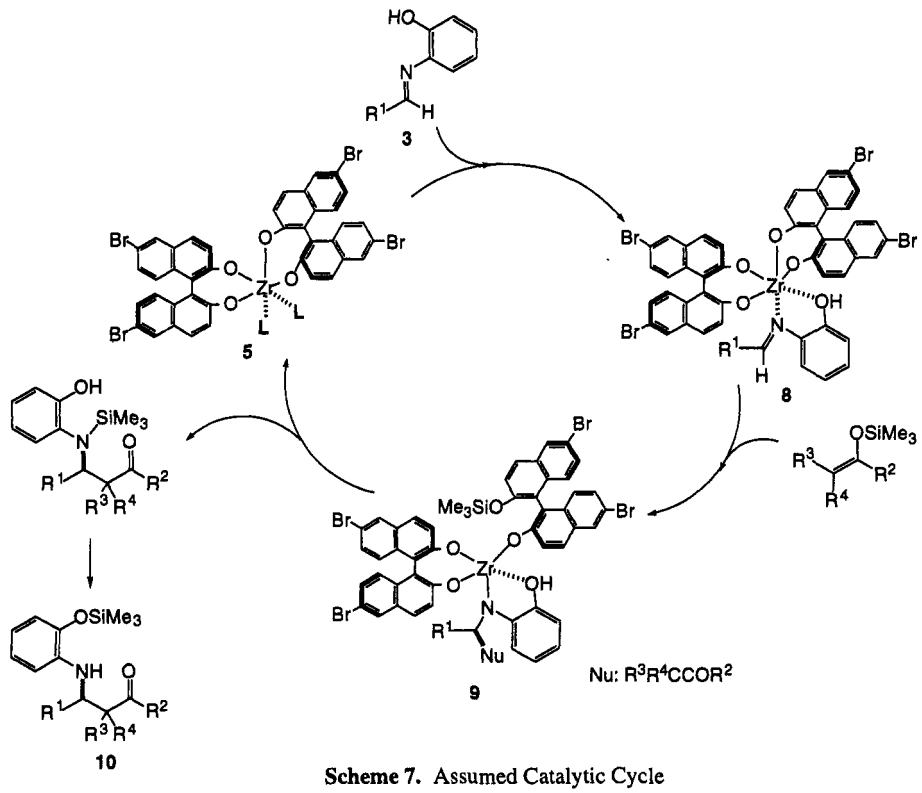


Scheme 6. Conversion to β-Amino Ester

The assumed catalytic cycle of this enantioselective reaction is shown in Scheme 7. Catalyst **5** is postulated to coordinate aldimine **3** to form zirconium complex **8**. A silyl enolate attacks the aldimine from the *si* face to produce **9**, whose trimethylsilylated oxygen atom attacks the zirconium center to afford the product along with the regeneration of catalyst **5**. The product was obtained as a trimethylsilylated form (**10**) without the acidic work up.

Thus, the first catalytic enantioselective Mannich-type reactions of aldimines with silyl enolates have been achieved by using a novel chiral zirconium catalyst.[20] High levels of enantioselectivities in the synthesis of chiral β-amino ester derivatives have been obtained according to these reactions. The novel zirconium catalyst has been shown to be effective for the catalytic activation of aldimines.

Acknowledgement. I thank and express my deep gratitude to my co-workers whose names appear in references. Financial support by CREST, Japan Science and Technology Corporation (JST), a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture, Japan, and a SUT Special Grant for Research Promotion, is also acknowledged.



Scheme 7. Assumed Catalytic Cycle

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