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Asymmetric Diels-Alder Reactions Catalyzed by Chiral Lanthanide(III) Trifluoromethanesulfonates. Unique Structure of the Triflate and Stereoselective Synthesis of Both Enantiomers Using a Single Chiral Source and a Choice of Achiral Ligands

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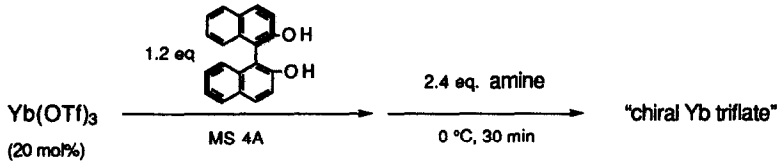
Abstract: *Chiral lanthanide trifluoromethanesulfonates (triflates) were developed and the unique structure of the triflates was revealed. In the presence of a catalytic amount of the triflate, acyl-1,3-oxazolidin-2-ones reacted with cyclopentadiene to afford the Diels-Alder adducts in high yields and with high enantiomeric excesses. According to the reactions, both enantiomers of the Diels-Alder adducts were stereoselectively prepared by using a single chiral source, R-(+)-binaphthol, and a choice of achiral ligands. When 3-acetyl-1,3-oxazolidin-2-one was combined with the original catalyst system consisting of lanthanide triflate, R-(+)-binaphthol, and cis-1,2,6-trimethylpiperidine, a new catalyst was generated (catalyst A). In the presence of this catalyst, 3-acyl-1,3-oxazolidin-2-ones reacted with cyclopentadiene to afford the endo adducts in high enantiomeric excesses. The absolute configuration of the products was 2S, 3R. On the other hand, when 3-phenylacetylacetone (PAA) was mixed with the original catalyst system (catalyst B), reverse enantiofacial selectivities were observed and endo adducts with the absolute configuration 2R, 3S were obtained in high enantiomeric excesses.*

Recently, some efficient asymmetric Diels-Alder reactions catalyzed by chiral Lewis acids have been reported.[1] The Lewis acids employed in these reactions are generally based on traditional acids such as titanium, boron, or aluminum reagents, and they are well modified to realize high enantioselectivities. Although lanthanide compounds were expected to be Lewis acid reagents, only a few asymmetric reactions catalyzed by chiral lanthanide Lewis acids were reported. Danishefsky's pioneer work demonstrated that $Eu(hfc)_3$ (an NMR shift reagent) catalyzed hetero-Diels-Alder reactions of aldehydes with siloxydienes, but enantiomeric excesses were moderate.[2]

In our previous paper, we reported that lanthanide(III) trifluoromethanesulfonates (lanthanide triflates, $Ln(OTf)_3$), especially ytterbium(III) triflate ($Yb(OTf)_3$), were good catalysts in the Diels-Alder reaction of some dienophiles with cyclopentadiene.[3] The reactions proceeded smoothly in the presence of a catalytic amount of $Yb(OTf)_3$ to give the corresponding adducts in high yields. Moreover, the catalyst was stable in water and was easily recovered

from the aqueous layer after the reaction was completed, and could be reused.[4] These unique properties were considered to be dependent on the specific coordination numbers and stereochemistry of the lanthanides(III),[5] and this prompted us to design a chiral lanthanide triflate which could work as an efficient catalyst in the asymmetric Diels-Alder reaction. In this paper, we report chiral lanthanide triflate-catalyzed Diels-Alder reactions of some dienophiles with cyclopentadiene, ***which afford both enantiomers of the corresponding cyclic compounds in high enantiomeric excesses by using a single chiral source and a choice of achiral ligands.***[6]

First, we chose $Yb(OTf)_3$ as a representative of the lanthanide triflates. The chiral ytterbium triflate was prepared *in situ* from $Yb(OTf)_3$, (R)-(+)-binaphthol, and a tertiary amine,[7] and a model reaction of 3-(2-butenoyl)-1,3-oxazolidin-2-one (**1**) with cyclopentadiene was examined.[8]



Thus, in the presence of a chiral ytterbium triflate prepared from $Yb(OTf)_3$, (R)-(+)-binaphthol, and triethylamine at 0 °C for 0.5 h in dichloromethane, **1** reacted with cyclopentadiene at 23 °C 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%. After screening several reaction conditions, we found that the amine employed at the stage of the preparation of the chiral ytterbium triflate strongly influenced the diastereo- and enantioselectivities (Table 1). In general, bulky amines gave better results and 70%, 75%, and 71% ees were observed when diisopropylethylamine, *cis*-2,6-dimethylpiperidine, and *cis*-1,2,6-trimethylpiperidine were used, respectively (entries 3,17, and 21). 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 (entry 25).

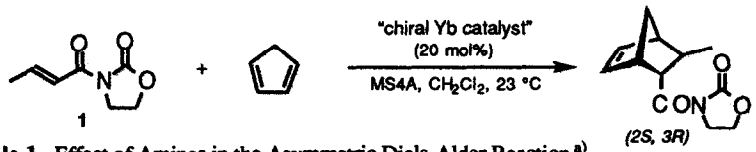
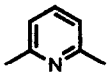
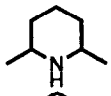
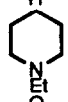
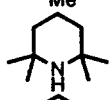
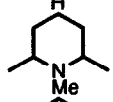
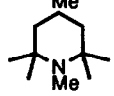
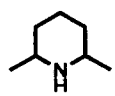
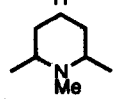
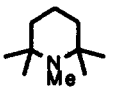


Table 1. Effect of Amines in the Asymmetric Diels-Alder Reaction [a]

Entry	Amine	MS [b]	Yield (%)	endo/exo	ee (%) [c]
1	Et_3N	—	87	76/24	33
2	Bu_3N	—	quant.	83/17	68
3	$^iPr_2NEt$	—	82	85/15	70
4	$^iPr_2NBu$	—	77	84/16	66
5	$^iPr_2NH$	—	67	82/18	57

6	$^{i}Pr(c\text{-}C_6H_{11})NH$	—	90	82/18	54
7	$(c\text{-}C_6H_{11})_2NH$	—	43	81/19	46
8	$Me_2N(CH_2)_2NMe_2$	—	91	78/22	40
9	$Me_2N(CH_2)_3NMe_2$	—	86	80/20	40
10	$Me_2N(CH_2)_4NMe_2$	—	84	78/22	42
11	$N(CH_2CH_2)_3N$	—	92	79/21	50
12	DBU	—	78	73/27	11
13		—	78	73/27	3
14		—	82	67/33	19
15	$PhNH_2$	—	86	73/27	2
16		—	72	76/24	27
17	 *(cis)*	—	95	84/16	75
18		—	85	81/19	50
19		—	71	76/24	16
20		—	93	80/20	51
21	 *(cis)*	—	96	85/15	71
22		—	96	85/15	69
23	$^{i}Pr_2NEt$	MS 3A	84	87/13	80
		MS 4A	88	87/13	83
		MS 5A	82	86/14	76
24	 *(cis)*	MS 4A	95	85/15	80
25	 *(cis)*	MS 4A	91	86/14	90
			77	89/11	95 [d]

26		MS 4A	92	86/14	76

a) The chiral catalysts were prepared at 0 °C and the reactions were carried out at 23 °C, unless otherwise noted. b) Molecular sieves. c) Enantiomer ratios of endo adducts. d) The reaction was carried out at 0 °C.

At this stage, although the reaction conditions were optimized, aging of the catalyst was found to take place. High selectivities (77% yield, endo/exo = 89/11, endo = 95% ee) were obtained when the diene and the dienophile were added just after $Yb(OTf)_3$, (R)-(+)-binaphthol, 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 (Table 2).

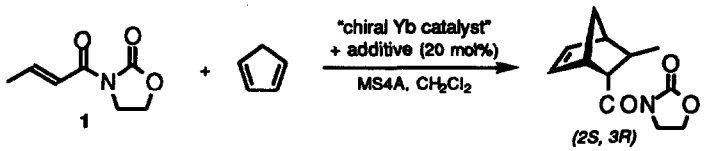
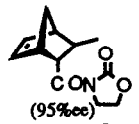
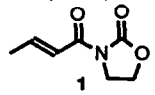


Table 2. Aging of the Catalyst

Conditions [b]	Additive	Yield (%)	endo/exo	ee (%) [a]
0 °C, 0.5 h	—	77	89/11	95
0 °C, 5.5 h	—	61	87/13	78
0 °C, 0.5 h; 23 °C, 5 h	—	77	86/14	65
0 °C, 0.5 h; 23 °C 5 h	 (95%ee)	84	84/16	66
0 °C, 0.5 h; 23 °C, 5 h	 1	76	89/11	81
0 °C, 5.5 h	1	66	87/13	88

a) Enantiomer ratios of endo adducts.
b) For preparation of the catalyst, see experimental.

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

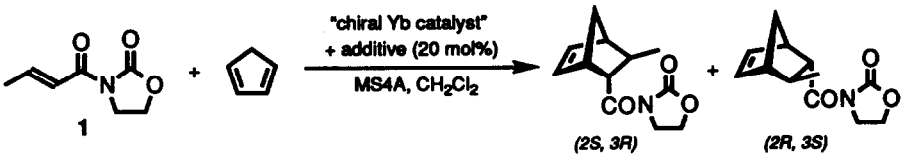
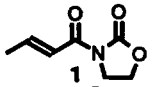
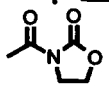
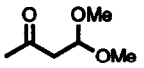
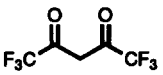
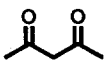
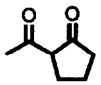
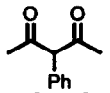
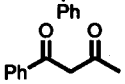
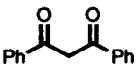
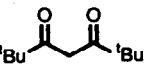
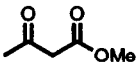
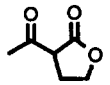
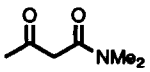
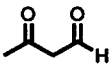
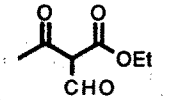
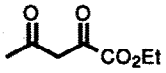


Table 3. Effect of Additives[a)]

Entry	Additive	Yield (%)	endo/exo	2S,3R/2R,3S (ee (%))[b)]
1		66	87/13	94.0/ 6.0 (88)
2		77	89/11	**96.5**/ 3.5 (93)
3		81	86/14	90.5/ 9.5 (81)
4		54	77/23	53.5/46.5 (7)[d)]
5		58 80	78/22 79/21	75.5/24.5 (51) 55.0/45.0 (10)[d)]
6		80 81	88/12 85/15	22.5/77.5 (55) 22.5/77.5 (55)[d)]
7		36	81/19	19.0/81.0 (62)
8		69 83	88/12 93/ 7	15.5/84.5 (69) 9.5/**90.5** (81)[c)]
9		77	78/22	33.0/67.0 (34)[d)]
10		77 78	72/28 75/25	42.5/57.5 (15) 39.0/61.0 (22)[d)]
11		48 35	60/40 58/42	47.0/53.0 (6) 40.5/59.5 (19)[d)]
12		51	70/30	45.5/54.5 (9)[d)]
13		60	83/17	30.5/69.5 (39)[d)]
14		55	73/27	41.5/58.5 (17)
15		81	78/22	43.0/57.0 (14)

16		74 79	75/25 77/23	39.0/61.0 42.5/57.5	(22) (15)[d]
17		82	87/13	44.5/55.5	(11)[d]

a) For preparation of the catalysts, see experimental. b) Enantiomer ratios of endo adducts. c) 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. d) $Yb(OTf)_3$, MS4A, and the additive were stirred in dichloromethane at 23 °C for 1 h.

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%.

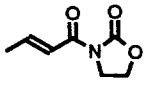
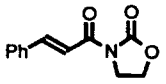
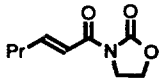
Moreover, after screening several additives other than **1**, it was found that some additives were effective not only in stabilizing the catalyst but also ***in controlling the enantiofacial selectivities in the Diels-Alder reaction.*** Selected examples are shown in Table 3. When 3-acetyl-1,3-oxazolidin-2-one was combined with the original catalyst system (to form catalyst A), the endo adduct was obtained in 93% ee (entry 2) 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 adduct with an absolute configuration of *2R, 3S* was obtained in 81% ee (entry 8) when 3-phenylacetylacetone (PAA) was used as an additive (catalyst B). In these cases, the chiral source was the same (R)-(+)-binaphthol. Therefore, ***the enantioselectivities were controlled by the achiral ligands, 3-acetyl-1,3-oxazolidin-2-one and PAA.***

As shown in Table 4, the same selectivities were observed in the reactions of other 3-acyl-1,3-oxazolidin-2-ones.

The effect of other lanthanide triflates was also examined. As shown in Table 5, lanthanide elements strongly influenced the yields and selectivities. A slight difference between the two catalyst systems (catalysts A and B) on the effect of the lanthanide elements was also observed. In catalyst A, lutetium triflate ($Lu(OTf)_3$) was also effective in generating the endo Diels-Alder adduct in 93% ee. The yields and selectivities diminished rapidly in accordance with the enlargement of the ionic radii. In catalyst B, on the other hand, the best results were obtained when thulium triflate ($Tm(OTf)_3$) or erbium triflate ($Er(OTf)_3$) was employed. Deviations to either larger or smaller ionic radii resulted in decreased selectivities, however the Diels-Alder adduct was obtained in an 85% yield with good selectivities (endo/exo = 92/8, endo isomer = 61% ee) even when holmium triflate ($Ho(OTf)_3$) was used.

As for the chiral lanthanide catalyst, we have postulated the following structure (Scheme 1). ^{13}C NMR spectroscopy of the chiral ytterbium catalyst (both catalyst A and B) indicated the existence of a weak interaction between the nitrogen of *cis*-1,2,6-trimethylpiperidine and the phenolic hydrogen of (R)-(+)-binaphthol. IR data also supported this interaction (Table 6).[9] The coordination form of the $Yb(OTf)_3$-(R)-(+)-binaphthol complex may be similar to that of lanthanide(III)-water or -alcohol complexes[10] and this is quite different from the forms of

Table 4. Synthesis of Both Enantiomers of the Diels-Alder Adducts between Cyclopentadiene and Dienophiles by Use of Catalyst A and B

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

a) See experimental. b) 1,2,2,6,6-Pentamethylpiperidine was used instead of 1,2,6-trimethylpiperidine. c) Enantiomer ratios of endo adducts. d) $Yb(OTf)_3$, MS4A, and the additive were stirred in dichloromethane at 40 °C for 3 h. e) Without additive. f) 2R,3R/2S,3S. g) The reaction was carried out at 40 °C for 22 h. h) $Tm(OTf)_3$ was used instead of $Yb(OTf)_3$. $Tm(OTf)_3$, MS4A, and the additive were stirred in dichloromethane at 40 °C for 3 h. i) $Er(OTf)_3$ was used instead of $Yb(OTf)_3$. $Er(OTf)_3$, MS4A, and the additive were stirred in dichloromethane at 40 °C for 3 h.

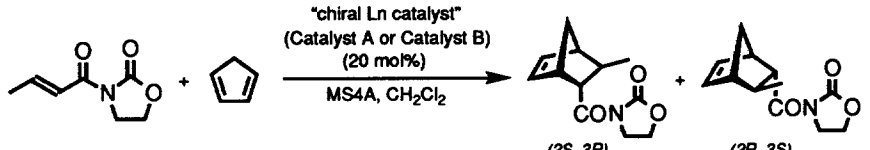
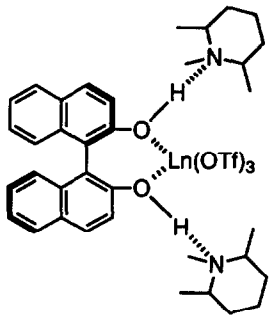


Table 5. Effect of $Ln(OTf)_3$

Ln	Catalyst A[a] Yield (%)	endo/exo	2S,3R/2R,3S (ee(%))[c]		Catalyst B[a] Yield (%)	endo/exo	2S,3R/2R,3S (ee (%))[b]	
Lu	60	89/11	96.5/3.5	(93)	30	89/11	24.5/75.5	(51)
Yb	77	89/11	96.5/3.5	(93)	88	92/8	15.0/85.0	(70)
Tm	46	86/14	87.5/12.5	(75)	72	91/9	13.0/87.0	(74)
Er	24	83/17	84.5/15.5	(69)	59	90/10	13.0/87.0	(74)
Ho	12	73/27	62.5/37.5	(25)	70	84/16	21.0/79.0	(58)
Y	6	70/30	60.0/40.0	(20)	85	91/9	19.5/80.5	(61)
Gd	0	—	—	—	61	85/15	28.5/71.5	(43)

a) See experimental. b) Enantiomer ratios of endo adducts.



Scheme 1. The chiral lanthanide catalyst

Table 6. Comparison of ^{13}C NMR Chemical Shifts (CD_2Cl_2) of the Carbons of the *N*-Methyl Groups of *cis*-1,2,6-Trimethylpiperidine (TMP) and IR Wave Numbers (CH_2Cl_2) in the Region 930-1000 cm^{-1}

Compound	δ (ppm)	Wave Number (cm^{-1})
TMP	38.2	947
TMP + (R)-(+)-binaphthol (1 : 1)	35.1	989, 947
TMP + TfOH (1 : 1)	34.1	958
TMP + $Yb(OTf)_3$ + (R)-(+)-binaphthol + 3-acetyl-1,3-oxazolidin-2-one (Catalyst A)	37.5	997, 955
TMP + $Yb(OTf)_3$ + (R)-(+)-binaphthol + PAA (Catalyst B)	38.5	982, 935

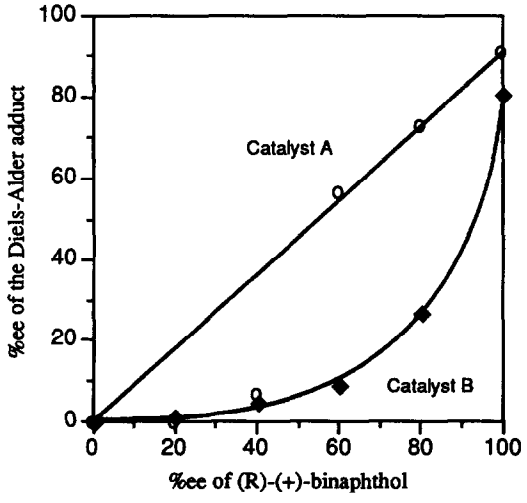
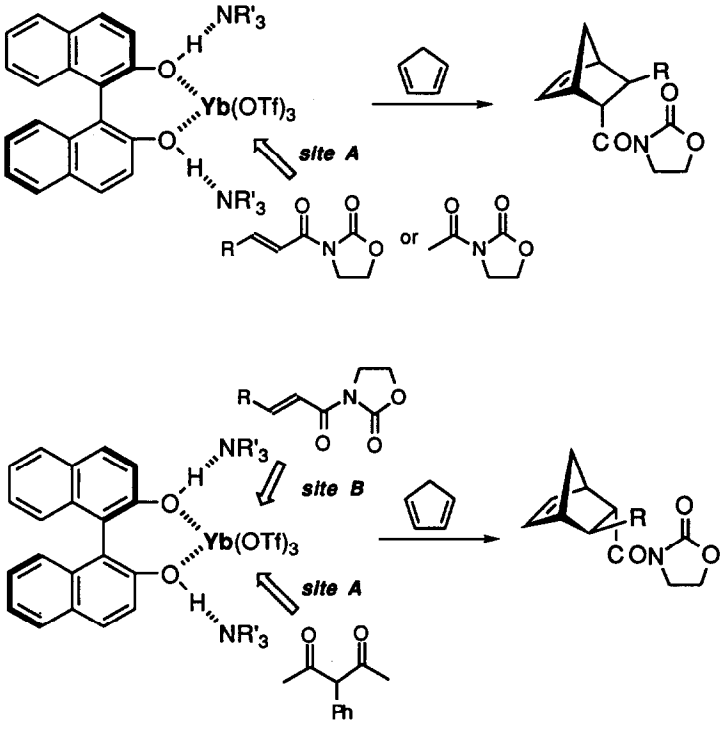


Fig. 1. Correlation between the ee of the Diels-Alder adduct and the ee of (R)-(+)-binaphthol

usual Lewis acids.[11] In the chiral catalysts, the axial chirality of (R)-(+)-binaphthol is transferred via the hydrogen bonds to the amine parts, which shield one side of the dienophile. This is consistent with the experimental results that amines employed in the preparation of the chiral catalysts strongly influenced the selectivities and that bulky amines gave better selectivities. Although the full structure of the catalysts including the additives (3-acetyl-1,3-oxazolidin-2-one and PAA) is not yet clear, a difference between states of aggregation of the catalysts was indicated by experiments using (R)-(+)-binaphthol in lower enantiomeric excesses in the Diels-Alder reaction of **1** with cyclopentadiene (20 mol% catalysts). As shown in Fig. 1, a negative nonlinear effect[12] was observed in catalyst B. While the extent of asymmetric induction in catalyst A did not deviate from the enantiomeric excesses of (R)-(+)-binaphthol at the range of 60-100% ee, lower enantiomeric excesses of the product was observed when (R)-(+)-binaphthol in less than 60% ee was used.[13]



Scheme 2. Synthesis of Both Enantiomers Using the Same Chiral Source

These exciting selectivities are believed to be strongly dependent on the specific coordination number of ytterbium(III)[4] (Scheme 2). Two binding sites for the ligands are now postulated in the Yb catalysts. **1** or 3-acetyl-1,3-oxazolidin-2-one 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.[14] 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). It should be noted that the axial chirality of (R)-(+)-binaphthol is transfered to the amine, which would work as a "wall" in the transition state to shield one side of the dienophile. This is consistent with the strong effect of the amines on the selectivities.

In summary, chiral lanthanide triflates have been developed and both enantiomers of the Diels-Alder adducts between 3-acyl-1,3-oxazolidin-2-ones and cyclopentadiene were prepared by the triflates using the same chiral source, R-(+)-binaphthol. Traditional methods have required both enantiomers of chiral sources in order to prepare both enantiomers stereoselectively,[15] 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.***

Further investigations to clarify the precise transition states and the reaction mechanism as well as to develop other asymmetric reactions using the chiral lanthanide catalysts are now actively in progress.

Experimental

General. IR spectra were recorded on a Horiba FT-300 infrared spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Hitachi R-1100 or JEOL JNR-EX270L spectrometer, and tetramethylsilane (TMS) served as internal standard. HPLC was carried out using a Hitachi LC-Organizer, L-4000 UV Detector, L-6200 Intelligent Pump, and D-2500 Chromato-Integrator. Optical rotations were recorded on a Jasco DIP-360 digital polarimeter. Column chromatography was performed on Silica gel 60 (Merck) or Wakogel B5F. All reactions were carried out under argon atmosphere in dried glassware.

Dichloromethane was distilled from P_2O_5, then CaH_2, and dried over MS4A. *cis*-1,2,6-Trimethylpiperidine[16] and 1,2,2,6,6-pentamethylpiperidine[17] were prepared according to the literature.

All lanthanide triflates ($Ln(OTf)_3$) were prepared by the modification method based on the literature.[18]

Preparation of Lanthanide Triflates ($Ln(OTf)_3$)

Lanthanide oxide (30 mmol) was mixed with TfOH-H_2O (v/v = 1/1, 21.2 ml), and the suspension was heated at 100 °C for 2 h. Unreacted oxide was removed by filtration and the

filtrate was concentrated under reduced pressure. The hydrate thus prepared was dried *in vacuo* (200 °C/0.5 mmHg for 40 h) to give anhydrous lanthanide triflate.

$Yb(OTf)_3$: IR (KBr) 3650, 3350, 2300, 1650, 1300, 1040 cm^{-1}; ^{13}C NMR (D_2O) δ 122.4 (q, J = 317 Hz) (sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) served as an internal standard.

Preparation of Catalyst A: To a mixture of $Yb(OTf)_3$ (0.10 mmol), (R)-(+)-binaphthol (0.12 mmol), and MS4A (125 mg) was added *cis*-1,2,6-trimethylpiperidine (0.24 mmol) in dichloromethane (0.75 ml) at 0 °C. The mixture was stirred for 30 min at this temperature, then 3-acetyl-1,3-oxazolidin-2-one (0.10 mmol) in dichloromethane (0.25 ml) was added.

Preparation of Catalyst B: 3-Phenylacetylacetone (PAA, 0.12 mmol) in dichloromethane (0.5 ml) was added to $Yb(OTf)_3$ (0.10 mmol) and MS4A (125 mg), and the mixture was stirred at 40 °C for 1 h. After cooling to 23 °C, (R)-(+)-binaphthol (0.12 mmol) was added. The mixture was cooled to 0 °C and *cis*-1,2,6-trimethylpiperidine (or 1,2,2,6,6-pentamethylpiperidine, see Tables) (0.24 mmol) in dichloromethane (0.5 ml) was added and the mixture was stirred for an additional 30 min at the same temperature.

A typical experimental procedure for the reaction of 1 with cyclopentadiene: To catalyst A or B, **1** (0.50 mmol) in dichloromethane (0.25 ml) and cyclopentadiene (1.5 mmol, freshly distilled before use) in dichloromethane (0.25 ml) were successively added at 0 °C, and the mixture was stirred for 20 h at this temperature (catalyst A) or at 23 °C (catalyst B). Water was then added to quench the reaction and the insoluble materials were filtered off. After a usual work up, the crude product was purified by silica gel column chromatography on silica gel to afford the desired Diels-Alder adduct. The structure assignment of the product was performed by comparison of the ^1H NMR spectrum with that of the literature.[1b] The diastereomer ratio was determined by ^1H NMR analysis and the enantiomeric excess of the endo adduct was determined by HPLC analysis. The absolute configuration was assigned by comparison of the optical rotation with that reported in the literature.[1b]

Similarly, the structure assignments, determinations of diastereomer ratios, enantiomeric excesses, and absolute configuration of other Diels-Alder adducts were made by comparison with the literature.[1b]

3-(((1'S,2'S,3'R,4'R)-3'-Methylbicyclo[2.2.1]hept-5'-en-2'yl)carbonyl)-1,3-oxazolidin-2-one. 95% ee. $[\alpha]_D^{28}$ -201 ° (c 1.6, CCl_4). Mp. 110.5-111.5 °C. IR (KBr) 1780, 1690 cm^{-1}; ^{1}HNMR ($CDCl_3$) δ 1.13 (d, 3H, J = 6.9 Hz), 1.45 (dd, 1H, J = 1.3, 8.6 Hz), 1.71 (d, 1H, J = 8.6 Hz), 2.04-2.11 (m, 1H), 2.53 (brs, 1H), 3.27 (brs, 1H), 3.51-3.54 (m, 1H), 3.89-4.10 (m, 2H), 4.41 (t, 2H, J = 8.1 Hz), 5.78 (dd, 1H, J = 2.6, 5.3 Hz), 6.36 (dd, 1H, J = 2.6, 4.6 Hz); ^{13}C NMR ($CDCl_3$) δ 20.2, 36.2, 42.8, 46.9, 47.2, 49.3, 51.1, 61.7, 130.7, 139.5, 153.3, 174.1. HPLC (Daicel Chiralpak AD, hexane/*i*-PrOH = 19/1, flow rate = 1.0 mL/ min): t_R = 11.5 min (major), t_R = 13.0 min (minor).

3-(((1'R,2'R,3'S,4'S)-3'-Methylbicyclo[2.2.1]hept-5'-en-2'yl)carbonyl)-1,3-oxazolidin-2-one. 81% ee. $[\alpha]_D^{28}$ +154 ° (c 1.2, CCl_4).

3-(((1'S,2'R,3'R,4'R)-3'-Phenylbicyclo[2.2.1]hept-5'-en-2'yl)carbonyl)-1,3-oxazolidin-2-one. 83% ee. $[\alpha]_D^{27}$ -146 ° (c 5.1, CCl_4). IR (KBr) 1780, 1690 cm^{-1}; ^{1}HNMR ($CDCl_3$) δ 1.58 (dd, 1H, J = 1.6, 8.6 Hz), 1.95 (d, 1H, J = 8.6 Hz), 3.00 (d, 1H, J = 1.3 Hz), 3.33-3.37 (m, 1H), 3.47 (brs, 1H), 3.90-4.05 (m, 2H), 4.19 (dd, 1H, J = 3.3, 5.0 Hz), 4.32-4.40 (m, 2H), 5.92 (dd, 1H, J = 2.6, 5.6 Hz), 6.53 (dd,

1H, *J* = 3.3, 5.6 Hz); ^{13}C NMR ($CDCl_3$) δ 42.9, 46.7, 47.4, 48.0, 49.6, 50.2, 61.8, 126.0, 127.5, 128.4, 132.1, 140.1, 143.6, 153.3, 173.8. HPLC (Daicel Chiralpak AD, hexane/*i*-PrOH = 19/1, flow rate = 1.0 mL/ min): t_R = 15.6 min (minor), t_R = 31.3 min (major).

3-(((1'R,2'S,3'S,4'S)-3'-Phenylbicyclo[2.2.1]hept-5'-en-2'yl)carbonyl)-1,3-oxazolidin-2-one. 89% ee. $[\alpha]_D^{27}$ +157 ° (c 3.5, CCl_4).

3-(((1'S,2'S,3'R,4'R)-3'-Propylbicyclo[2.2.1]hept-5'-en-2'yl)carbonyl)-1,3-oxazolidin-2-one. 86% ee. $[\alpha]_D^{28}$ -144 ° (c 1.1, CCl_4). IR (KBr) 1780, 1700 cm^{-1}; ^{1}HNMR ($CDCl_3$) δ 0.89 (d, 3H, *J* = 7.3 Hz), 1.24-1.48 (m, 5H), 1.67 (d, 1H, *J* = 8.6 Hz), 1.96-2.03 (brs, 1H), 2.63 (brs, 1H), 3.27 (brs, 1H), 3.58 (dd, 1H, *J* = 3.6, 4.5 Hz), 3.89-4.07 (m, 2H), 4.41 (t, 2H, *J* = 8.3 Hz), 5.78 (dd, 1H, *J* = 2.6, 5.6 Hz), 6.36 (dd, 1H, *J* = 3.0, 5.6 Hz); ^{13}C NMR ($CDCl_3$) δ 14.2, 21.9, 37.7, 42.3, 42.9, 47.0, 47.50, 47.53, 49.8, 61.8, 131.0, 139.6, 153.4, 174.4. HPLC (Daicel Chiralpak AD, hexane/*i*-PrOH = 200/1, flow rate = 1.0 mL/ min): t_R = 34.3 min (minor), t_R = 38.7 min (major).

3-(((1'R,2'R,3'S,4'S)-3'-Propylbicyclo[2.2.1]hept-5'-en-2'yl)carbonyl)-1,3-oxazolidin-2-one. 85% ee. $[\alpha]_D^{28}$ +140 ° (c 1.0, CCl_4).

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(7) While $Yb(OTf)_3$ or (R)-(+)-binaphthol dissolved only sluggishly in dichloromethane, the mixture of $Yb(OTf)_3$, (R)-(+)-binaphthol, and an amine became an almost clear solution.

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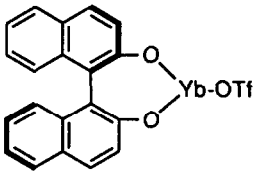
(11) Following experiments also supported the structure shown in Scheme 1. (a) The Diels-Alder reactions proceeded sluggishly in the presence of only $Yb(OTf)_3$ and *cis*-1,2,6-trimethylpiperidine (without (R)-(+)-binaphthol). In this case, the amine coordinated to $Yb(OTf)_3$ to decrease its Lewis acidity. From this experiment, it was indicated that the amine did not coordinate to $Yb(OTf)_3$ in the chiral Yb triflate. (b) When a chiral catalyst was prepared from $Yb(OTf)_3$ and lithium or sodium salt of (R)-(+)-binaphthol, only less than 10% ee was obtained in the reaction of **1** with cyclopentadiene. In this case, [(R)-1,1'-bi-2-naphthalenediolato(2-)-O,O']scandium triflate (**2**) would be produced, and **2** is not the catalyst prepared from $Yb(OTf)_3$, (R)-(+)-binaphthol, and a tertiary amine. This is consistent with the result that no triflic acid-tertiary amine salt was observed by ^1H and ^{13}C NMR when $Yb(OTf)_3$, (R)-(+)-binaphthol, and a tertiary amine were combined.



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(13) This may be ascribed to turnover of the catalyst.

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