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Chiral rare earth organophosphates as homogeneous Lewis acid catalysts for the highly enantioselective hetero-Diels–Alder reactions

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Abstract—Various trivalent rare earth-chiral phosphate complexes [(*R*)-**1**-RE, (*R*)-**3**-RE, and (*R*)-**4**-Ce] were prepared and evaluated as a Lewis acid catalyst for the asymmetric hetero-Diels–Alder reaction of aldehydes with the Danishefsky's diene. Some of them effectively promoted the reaction at room temperature in the presence or absence of achiral additives under homogeneous conditions to afford the corresponding cycloadducts with high ee's (up to 99% ee). During these reactions, remarkably high asymmetric amplifications (positive nonlinear effects) were observed as the first example in the metal ion–chiral ligand 1:3 catalytic system. A scandium catalyst bearing the H_8-BNP ligand, (*R*)-**3**-Sc, could be recovered after the reaction and successfully reused for the next round of reactions. In addition, the hetero-Diels–Alder reaction of α-keto esters was effectively catalyzed by the ytterbium complex, (*R*)-**1**-Yb, without any additives thus producing the asymmetric quaternary carbon in excellent enantioselectivities (up to >99% ee).

1. Introduction

The trivalent state is the most stable oxidation state for the rare earths (RE), and according to Pearson's HSAB classification, RE^{3+} ions are considered to be hard acids, being located between Mg^{2+} and Ti^{4+}.[1] The effective Lewis acid catalysis with RE^{3+} ions may therefore be generally expected. Especially noteworthy is that the RE(III) salts of strong acids like the triflates,[2] perfluoroalkylsulfonates,[3–5] perchlorates,[3,6] bis(perfluoroalkylsulfonyl)amides,[7] and tris(perfluoroalkylsulfonyl)methides[7a–d,8] are sometimes able to work as effective Lewis acid catalysts in the presence of water, alcohols, or even amines, although most traditional Lewis acids lose their activities under such circumstances.[9] Reflecting such a stability, RE Lewis acids can often be recovered after the reactions and reused without any loss of activity. Another important aspect of rare earths is their high coordination numbers. Their large ionic radii often allow the accommodation of seven, eight, or nine ligands in the coordination sphere. These properties are highly advantageous for assembling various chiral and achiral ligands around the metal ions, thus creating an integrated chiral space in which the stereochemistry of the reaction may effectively be controlled. Actually, recent intensive studies on the chiral rare earth complexes are rapidly reporting various successful examples of the highly efficient asymmetric reactions catalyzed by them.[2,10–12] In most cases, however, the rare earth catalysts used were prepared in situ by mixing achiral rare earth metal salts such as $RE(OTf)_3$ and appropriate chiral ligands. In the present study, we tried to develop isolable and reusable chiral rare earth Lewis acid catalysts. For this purpose, chiral organophosphates were employed as a ligand for the rare earth complex catalysts since the reported pK_a value of 2.3 for 1,1′-binaphthyl-2,2′-diyl hydrogen phosphate (BNP–H)[13] seemed to be acidic enough to let the corresponding rare earths salts function as effective Lewis acid catalysts for certain reactions. In this paper are described the full details of the preparation of the RE[(*R*)-BNP]$_3$-type complexes and their application to hetero-Diels–Alder reactions.[3,14,15]

Keywords: chiral rare earth metal complex; chiral Lewis acid catalyst; homogeneous catalysis; enantioselective hetero-Diels–Alder reaction; asymmetric amplification.

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2. Results and discussion

2.1. Preparation of the rare earth metal catalysts

A variety of chiral rare earth complexes composed of different metal ions and chiral phosphate ligands were prepared. As shown in Figure 1, the three complexes [(*R*)-**1**-RE, (*R*)-**2**-RE, and (*R*)-**3**-RE] were prepared from trivalent rare earth metal chlorides or isopropoxides and the corresponding chiral phosphates according to methods A–D. For instance, a series of rare earth metal complexes of (*R*)-1,1′-binaphyly-2,2′-diyl phosphate, abbreviated RE[(*R*)-BNP]$_3$:(*R*)-**1**-RE, and the corresponding (*R*)-**2**-RE were synthesized as follows (method A). To a gently refluxing solution of (*R*)-BNP–H and an aqueous sodium hydroxide in methanol was added a solution of the appropriate rare earth(III) chloride in methanol or the methanol–water mixed-solvent, and the resulting mixture was stirred under the same conditions. The resulting precipitate was collected by filtration, washed with aqueous methanol, and dried in vacuo at 120°C to give the desired complex (*R*)-**1**-RE as a colorless or a pale colored powder. Alternatively, the crude precipitate was subjected to dialysis to remove the contaminated sodium chloride. Both procedures afforded the desired complex with a similar activity. In method B, chiral phosphate salts [e.g. (*R*)-BNP–Na] were first isolated and then reacted with $RECl_3$. In methods C and D, (*R*)-**1**-RE was prepared from RE(O-*i*-Pr)$_3$ and the free acid [(*R*)-BNP–H]. Interestingly, a trivalent cerium complex, (*R*)-**4**-Ce, was prepared from ammonium cerium(IV) nitrate (CAN) as shown in Scheme 1. The trivalent structure of (*R*)-**4**-Ce was confirmed by the magnetic susceptibility measurement. Elementary analysis of this complex suggested that it contained 0.5 equiv. of sodium nitrate.

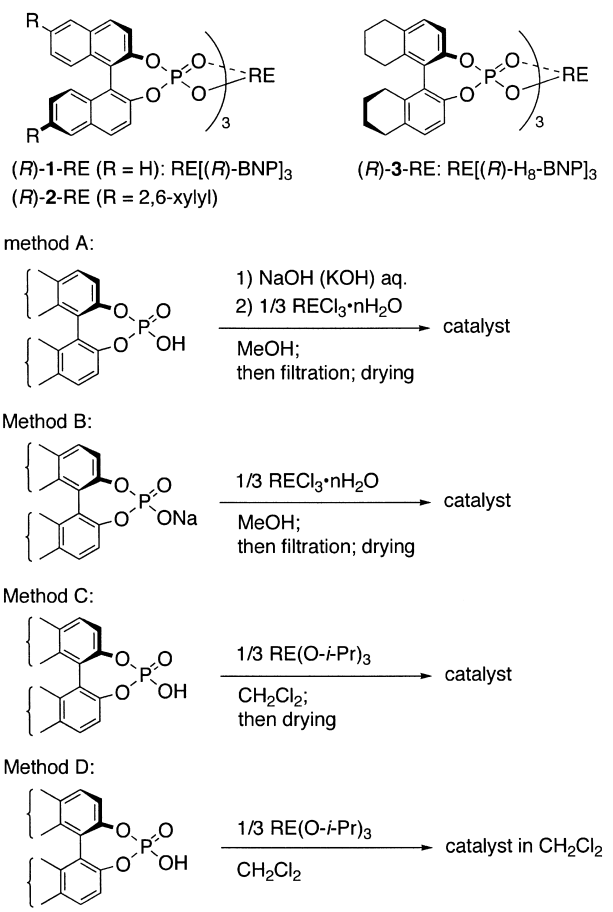
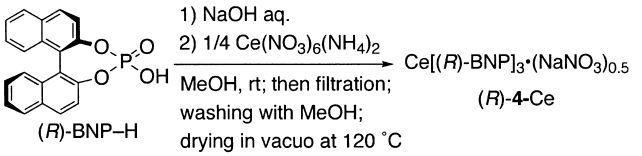


Figure 1. Novel rare earth metal complexes and their preparations [(*R*)-**1**-RE, (*R*)-**2**-RE, and (*R*)-**3**-RE].



Scheme 1. Preparation of (*R*)-**4**-Ce.

2.2. The RE[(*R*)-BNP]$_3$-catalyzed asymmetric hetero-Diels–Alder reaction

The complexes (*R*)-**1**-RE prepared by method A were used as a chiral Lewis acid catalyst for the hetero-Diels–Alder reaction of benzaldehyde **5a** with the Danishefsky's diene **6**.[16,17] The reactions were carried out using 10 mol% of the catalysts in dichloromethane at room temperature. As shown in Figure 2, the degrees of the asymmetric induction are highly dependent on the central metal ions of the catalysts, and (*R*)-**1**-Yb and (*R*)-**1**-Sc turned out to be relatively favorable catalysts affording the desired cycloadduct (*R*)-**7a** with 70 and 58% ee, respectively.[3]

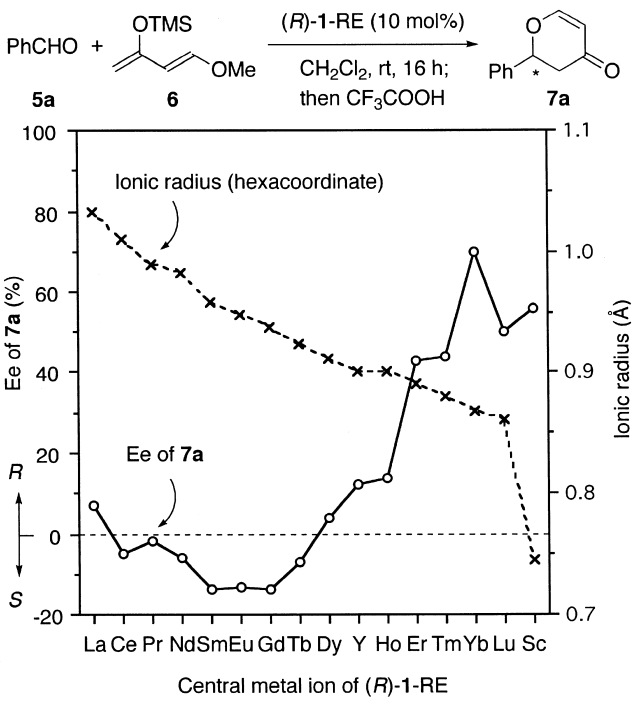
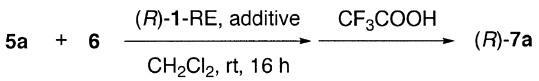


Figure 2. The (*R*)-**1**-RE-catalyzed asymmetric hetero-Diels–Alder reaction of **5a** with **6**.

In all cases, the reactions proceeded under heterogeneous conditions because of the low solubility of the catalysts in dichloromethane, which seemed to be one of the reasons for their unsatisfactory enantioselectivities. Therefore, using the ytterbium and the scandium catalysts, we examined the effect of various achiral additives on the solubility and efficiency of the catalysts. The hetero-Diels–Alder

reactions were carried out using 10 mol% of each catalyst and various achiral ligands at room temperature for 16 h. After many trials, some of the pyridine derivatives were found to be effectively promoted the desired reaction under homogeneous conditions. In Table 1 are shown some selected results.[14]

Table 1. Effect of the additives on the yield and enantioselectivity in the (*R*)-**1**-RE-catalyzed reaction



Entry	RE	Additive	Yield (%)[a]	Ee (%)[b]
1[c]	Yb	None	77	70
2	Yb	Pyridine	46	37
3	Yb	2-Picoline	63	77
4	Yb	2-Ethylpyridine	56	87
5	Yb	2,4-Lutidine	93	79
6	Yb	2,6-Lutidine	94	89
7[d]	Yb	2,6-Lutidine	76	90
8	Yb	3,5-Lutidine	49	78
9	Yb	2,4,6-Collidine	55	89
10[c]	Yb	2,6-Di-*tert*-butylpyridine	59	57
11[c]	Yb	2,6-Bis(phenylethynyl)pyridine	23	26
12	Yb	Quinaldine	96	88
13	Yb	7,8-Benzoquinoline	69	90
14[e]	Sc	None	93	56
15	Sc	Pyridine	78	56
16	Sc	2-Picoline	81	77
17	Sc	2,4-Lutidine	88	78
18	Sc	2,6-Lutidine	94	81
19[e]	Sc	2,6-Lutidine	86	80
20	Sc	3,5-Lutidine	54	56
21	Sc	2,4,6-Collidine	82	75
22[c]	Sc	2,6-Di-*tert*-butylpyridine	85	54
23[c]	Sc	2,6-Bis(phenylethynyl)pyridine	72	53

The reaction was carried out using (*R*)-**1**-RE (10 mol%) and the additive (10 mol%) under homogeneous conditions unless otherwise noted.
[a] Isolated yield.
[b] Determined by HPLC using a chiral column.
[c] The reaction proceeded under heterogeneous conditions.
[d] 40 mol% of 2,6-lutidine was used.
[e] 30 mol% of 2,6-lutidine was used.

In the (*R*)-**1**-Yb-catalyzed reactions, a notable increase in the enantioselectivity was observed when methyl- or ethyl-substituted pyridine derivatives were employed as the additive (entries 3–9). The effect of 2,6-lutidine was found to be particularly high thus giving **7a** with 89% ee in 94% yield (entry 6). An increase in the amount of the additive up to a 4-fold excess to the catalyst produced no decrease in the enantioselectivity (entry 7). The slightly reduced reaction rate may be explained by the competitive ligation of **5a** vs. 2,6-lutidine. The use of quinaldine also afforded a comparable result (entry 12). Interestingly, the use of pyridine rather decreased both the chemical and optical yields though the reaction proceeded under homogeneous conditions (entry 2). The use of bulkier ligands such as 2,6-di-*tert*-butylpyridine and 2,6-bis(phenylethynyl)pyridine was not effective (entries 10 and 11). Other additivies having high coordinating abilities such as 4-dimethylaminopyridine, 1,10-phenanthroline, 2,2′-bipyridyl, and HMPA seriously retarded the reaction. In the (*R*)-**1**-Sc-catalyzed reaction, a similarly tendency was observed, and (*R*)-**7a** was obtained in 94% yield and 81% ee when 2,6-lutidine was used as the additive (entry 18).

As 2,6-lutidine was found to be one of the most effective additives, the time course of the chemical yield and the enantioselectivity were investigated in the (*R*)-**1**-Yb-catalyzed reaction in the presence of this additive. Figure 3 shows that the reaction was almost completed in 16 h and essentially the same enantioselectivity was obtained regardless of the reaction time, suggesting that no structural change in the catalyst of the transition state occurs during the reaction. These results indicate that disaggregation of the complex catalyst by an appropriate ligand is important not only to solubilize the catalyst but also to make it thermodynamically stable so that it can work as the sole catalytically active species.

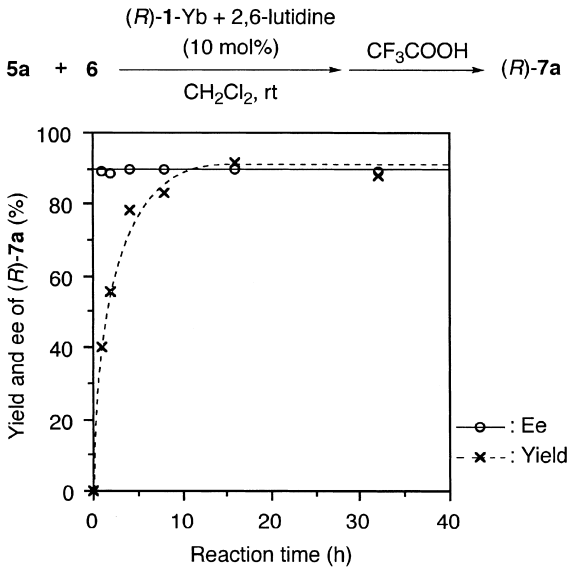


Figure 3. Time course of the chemical yield and enantioselectivity in the (*R*)-**1**-Yb-catalyzed reaction in the presence of 2,6-lutidine.

The effect of 2,6-lutidine was also examined for the reactions catalyzed by other (*R*)-**1**-RE complexes (RE=La, Nd, Gd, and Ho). The observed enantioselectivities are summarized in Figure 4 by comparison with the

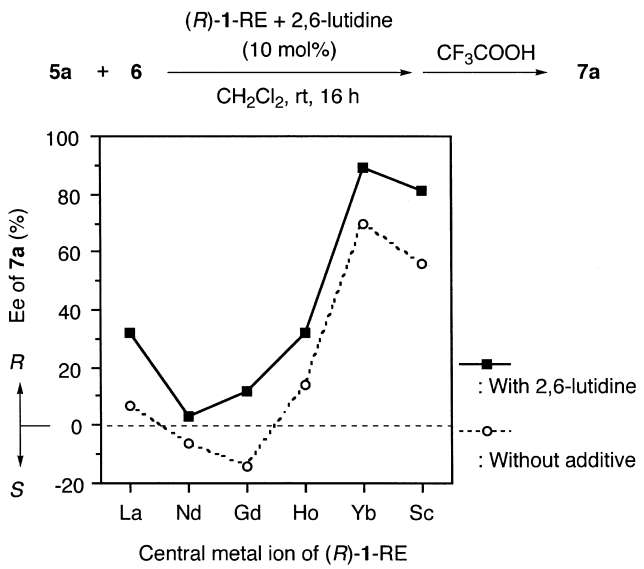
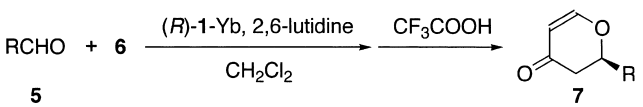


Figure 4. Influence of the central metal ions of (*R*)-**1**-RE and that of 2,6-lutidine on the enantioselectivity in the hetero-Diels–Alder reaction.

data obtained in the reactions without using 2,6-lutidine (cf. Fig. 2). Different from the scandium and the ytterbium catalysts, the lanthanum, neodymium and gadolinium complexes did not completely dissolve in dichloromethane in the presence of 1 equiv. of 2,6-lutidine, therefore, the reactions catalyzed by these complexes proceeded under heterogeneous conditions. In the case of the holmium complex-catalyzed reaction, an initially clear solution of the catalyst containing 2,6-lutidine became clouded when benzaldehyde was added. Whatever the appearance of the reaction mixture was, the addition of 2,6-lutidine uniformly increased the *R*-selectivity in all cases.

As the (*R*)-**1**-Yb/2,6-lutidine (1:1) system was found to be quite effective for the reaction of benzaldehyde (**5a**), the temperature effect on the enantioselectivity and also the effectiveness of the catalyst system to other aldehydes was examined (Table 2).

Table 2. The (*R*)-**1**–Yb-catalyzed hetero-Diels–Alder reaction of various aldehydes **5** with **6**



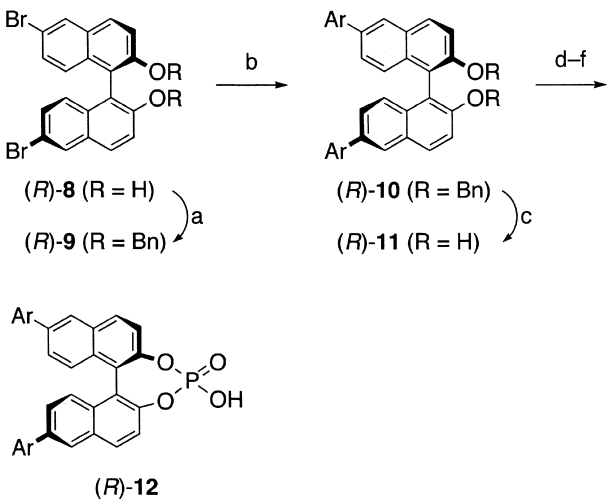
Entry	R	5/7	Yield (%)[a]	Ee (%)[b]
1	Ph	**5a/7a**	94 (77)	89 (70)
2[c]	Ph	**5a/7a**	79	91
3[d]	Ph	**5a/7a**	45	91
4[e]	Ph	**5a/7a**	92	91
5	4-MeO-C_6H_4	**5b/7b**	86 (56)	93 (65)[f]
6	4-Me-C_6H_4	**5c/7c**	79 (26)	89 (57)[f]
7	4-Biphenylyl	**5d/7d**	83 (44)	89 (64)[f]
8	4-Cl-C_6H_4	**5e/7e**	70 (57)	88 (61)[f]
9	4-NO_2-C_6H_4	**5f/7f**	84 (60)	65 (33)[f]
10	2-Naphthyl	**5g/7g**	79 (58)	84 (68)[f]
11	2-Furyl	**5h/7h**	83 (58)	76 (35)[f]
12	(*E*)-PhCH=CH	**5i/7i**	59 (19)	72 (35)
13	$Ph(CH_2)_2$	**5j/7j**	90 (68)	11 (11)

The reaction was carried out using (*R*)-**1**-Yb (10 mol%) and 2,6-lutidine (10 mol%) at room temperature for 16 h unless otherwise noted.
[a] Isolated yield. In parentheses is shown the yield obtained in the reaction without 2,6-lutidine.
[b] Determined by HPLC using a chiral column. In parentheses is shown the ee obtained in the reaction without 2,6-intidine.
[c] The reaction was carried out at 0°C for 16 h.
[d] The reaction was carried out at −25°C for 80 h.
[e] 2 Mol% each of (*R*)-**1**-Yb and 2,6-lutidine was used.
[f] The absolute configuration is tentatively assigned.

As can be seen in entries 1–3, the effect of the reaction temperature on the enantioselectivity is almost negligible. In most cases, both the chemical and optical yields were significantly improved by the addition of 2,6-lutidine, and up to 93% ee was realized in the reaction of 4-methoxybenzaldehyde (**5b**, entry 5). The amount of the catalyst could be reduced to 2 mol% without affecting the product yield and enantioselectivity (entry 4). The reaction of 4-nitrobenzaldehyde (**5f**) afforded a somewhat low ee (entry 9). A negative effect of the *p*-nitro substituent on the enantioselectivity suggests that the strong coordination of substrates to the chiral catalyst is crucial to gain a higher ee's, though a non-catalyzed process is also involved in this case. Unfortunately, the reaction of an aliphatic aldehyde did not afford a satisfactory optical yield even when 2,6-lutidine was added, although the chemical yield was significantly improved in the latter case (entry 13).

2.3. Modifications of the chiral phosphate ligand

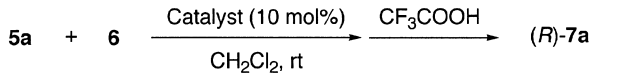
One of our concerns in this study is to develop new chiral rare earth complexes which may work as a reusable Lewis acid catalyst. Although (*R*)-**1**-Yb could be quantitatively recovered after the reaction and successfully reused for the second round of reactions without losing its activity, the enantioselectivity itself was not as satisfactorily high as previously mentioned. On the other hand, the addition of 2,6-lutidine to (*R*)-**1**-Yb significantly enhanced the enantioselectivity, but the recovery of the postulated (*R*)-**1**-Yb·2,6-lutidine adduct turned out to be difficult while maintaining its high catalytic activity. Therefore, two novel chiral rare earth phosphates, (*R*)-**2**-RE and and (*R*)-**3**-RE (Fig. 1), were prepared expecting that the 2,6-xylyl substituents on the binapthyl ring of the former or the octahydrobinaphthyl ring of the latter would play an important role not only in increasing the solubility of the catalysts in dichloromethane without 2,6-ltidine but also in providing a more effective chiral space for the reaction than the catalyst (*R*)-**1**-RE. Also, these catalysts were expected to be easily recovered after the reaction by changing the solvent and successfully reused if they do not require any additives to attain a high enantioselectivity. Based on these expectations, a new phosphate **12** was synthesized from 6,6′-dibromo-BINOL **8** in six steps using the standard conditions as shown in Scheme 2. Similarly, (*R*)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diyl hydrogen phosphate [(*R*)-H_8-BNP–H], the ligand of the (*R*)-**3**-RE complex, was also prepared from the corresponding octahydro-BINOL.[18]



Scheme 2. Preparation of (*R*)-**12** (Ar=2,6-xylyl). *Reagent*: (a) BnBr, NaH; (b) $ArB(OH)_2$, $Pd(PPh_3)_4$, $Ba(OH)_2$; (c) H_2, Pd–C, *i*-Pr_2NEt; (d) Cl_3PO_3 NEt_3; (e) Na_2CO_3 aq.; (f) HCl aq.

The hetero-Diels–Alder reaction of **5a** with **6** using the catalyst (*R*)-**2**-RE or (*R*)-**3**-RE proceeded under homogeneous conditions in dichloromethane without any additives, as expected. These results are shown in Table 3. Interestingly, the (*R*)-**2**-Yb-catalyzed reaction showed the opposite sense of enantioselection to afford (*S*)-**7a** with 57% ee, although the xylyl substituents at the 6,6′-positions of the ligand on the catalyst appears to be rather far from the

Table 3. The hetero-Diels–Alder reaction using the new catalysts bearing modified chiral ligands



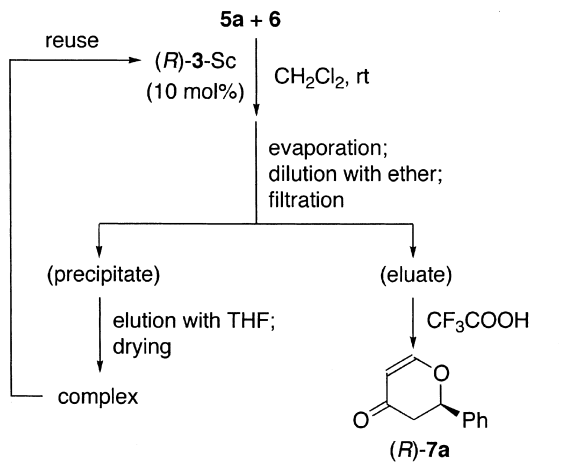
Entry	Catalyst	Method	Yield (%)[a]	Ee (%)[b]
1	(*R*)-**2**-Yb	A	76	*ent*-57[c]
2	(*R*)-**3**-Sc	B	99	93
3[d]	(*R*)-**3**-Sc	B	99	94
4	(*R*)-**3**-Sc	C	64	84
5	(*R*)-**3**-Yb	B	92	91
6	(*R*)-**3**-Yb	C	73	98
7	(*R*)-**3**-Er	C	76	98
8	(*R*)-**3**-Y	C	81	99
9	(*R*)-**3**-Y	D	80	98
10	(*R*)-**3**-Dy	C	58	91
11	(*R*)-**3**-Sm	C	79	93
12	(*R*)-**3**-La	C	68	92

[a] Isolated yield.
[b] Determined by HPLC using a chiral column.
[c] The absolute configuration is *S*.
[d] 4-Methoxybenzaldehyde (**5b**) was used instead of **5a**.

catalytic center (entry 1). Fortunately, the (*R*)-**3**-RE-catalyzed reactions afforded (*R*)-**7a** with good to excellent ee's (up to 99% ee) regardless of the type of central metal ions (entries 2–12). Although (*R*)-**3**-Sc prepared by method B gave a higher enantioselectivity than that prepared by method C (entries 2 vs. 4), the method-dependency was reserved in the corresponding ytterbium catalyst [(*R*)-**3**-Yb] (entries 5 vs. 6).

2.4. Repeated use of the Lewis acid catalyst

Since the complexes (*R*)-**3**-RE were found to work as a highly efficient homogeneous Lewis acid catalyst in the absence of additives, we briefly examined the reusability of (*R*)-**3**-Sc for the reaction of **5a** with **6** (Fig. 5). After the first round of reaction, the solvent was evaporated. To the residue was added ether, and the resulting precipitate was filtered through a Celite column and then eluted with THF.



Run	Yield (%)	Ee (%)
1	99	93
2	99	89
3	95	87

Figure 5. The recovery and reuse of the catalyst (*R*)-**3**-Sc.

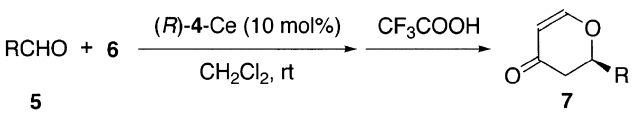
After evaporation of the solvent, the residual complex was dried under vacuum at room temperature for 3 h (52% recovery). The recovered catalyst was used for the next round of reactions, in which 10 equiv of **5a** and 15 equiv of **6** for the catalyst was utilized. Although the conditions for the recovery of the catalyst was not optimized, the high catalytic activity of (*R*)-**3**-Sc was retained even in the third round of reactions thus affording (*R*)-**7a** with an 87% ee in 95% yield.

2.5. The Ce(III)–BNP complex prepared from CAN

Although cerium is one of the most economical rare earth elements, little has been developed regarding the chiral cerium complexes that can work as effective Lewis acid catalysts.[19] The cerium complex (*R*)-**1**-Ce, prepared from $CeCl_3$ by method **A**, also turned out not to be effective for the reaction of **5a** with **6** (see Fig. 2), and the enantioselectivity could not be improved by the addition of 2,6-lutidine. The low catalytic activity of the Ce(III) complex prompted us to examine the corresponding Ce(IV) complex, because it can be a stronger Lewis acid by having a capacity of four chiral ligands and provide a higher selectivity. Therefore, we tried to prepare a chiral Ce(IV) complex from ammonium cerium(IV) nitrate (CAN) and (*R*)-BNP–Na (see Scheme 1).[20] Unfortunately, the desired Ce(IV) complex could not be produced but the corresponding Ce(III) complex [(*R*)-**4**-Ce] was generated; the Ce/P ratio was analyzed to be ca. 1:3.2 using as inductively coupled plasma (ICP) mass spectrometer, and the electron spectroscopy for chemical analysis (ESCA) study and magnetic susceptibility measurement also indicated the trivalent cerium structure.

Using various aldehydes, the (*R*)-**4**-Ce-catalyzed asymmetric hetero-Diels–Alder reaction was carried out at room temperature in the absence of an additive (Table 4). All the reactions proceeded under homogeneous conditions and, in the case of the aromatic aldehydes, generally high enantioselectivities were obtained (entries 1 and 3–12). The addition of 2,6-lutidine rather lowered the enantioselectivity (entry 2). The high performance of the cerium catalyst clearly indicated that the structure of (*R*)-**4**-Ce is different from the of (*R*)-**1**-Ce. It should be noted that (*R*)-**4**-Ce is so stable that its original activity could be maintained even after two years from its preparation (entry 10). Thus, (*R*)-**4**-Ce was proved to be the first successful example of the isolable and storable chiral cerium catalyst that can afford a high level of enantioselectivity. The relatively low ee's observed in the reactions of aliphatic aldehydes suggest the importance of some $\pi-\pi$ interactions between the aromatic ring of the aldehydes and that of the catalyst in the transition state. Although we do not have a clear explanation for the higher activity of (*R*)-**4**-Ce than (*R*)-**1**-Ce, the existence of a small amount of nitrate ion derived from CAN seems to play an important role in increasing the solubility of the catalyst and the selectivity during the reaction. Actually, when (*R*)-**1**-Ce was used for the reaction of **5a** with **6** in the presence of nitrate ions, the reaction mixture became clear and the enantioselectivity increased to 73% ee (with NH_4NO_3) and 68% ee (with $NaNO_3$). The use of the cerium complex prepared from CAN and (*R*)-BNP–Na (1:3) (cf. Scheme 1) did not show a meaningful result, e.g. **7n** with 51% ee was obtained in 57% yield.

Table 4. The (*R*)-**4**-Ce-catalyzed hetero-Diels–Alder reaction of various aldehydes with **6**



Entry	R	5/7	Yield (%)[a]	Ee (%)[b]
1	Ph	**5a/7a**	91	80
2[c]	Ph	**5a/7a**	91	74
3	4-MeO-C_6H_4	**5b/7b**	39	87[d]
4	4-Me-C_6H_4	**5c/7c**	96	88[d]
5	4-Et-C_6H_4	**5k/7k**	95	93[d]
6	4-*i*-Bu-C_6H_4	**5l/7l**	61	93[d]
7	4-*i*-Bu-C_6H_4	**5m/7m**	75	94[d]
8	4-Biphenylyl	**5d/7d**	46	93[d]
9	4-F-C_6H_4	**5n/7n**	91	85[d]
10[e]	4-Cl-C_6H_4	**5e/7e**	93	88[d]
11	4-Br-C_6H_4	**5o/7o**	80	92[d]
12	2-Naphthyl	**5g/7g**	42	89[d]
13[f]	(*E*)-PhCH=CH	**5i/7i**	50	44
14	*n*-Pr	**5p/7p**	36	61[d]
15[f]	*c*-Hex	**5q/7q**	58	45[d]

The reaction was carried out for 15 h unless otherwise noted.
[a] Isolated yield.
[b] Determined by HPLC using a chiral column.
[c] 10 mol% of 2,6-lutidine was used as an additive.
[d] The absolute configuration is tentatively assigned.
[e] The catalyst (*R*)-**4**-Ce stored in air for two years was used.
[f] The reaction time was 105 h.

2.6. Asymmetric amplifications (positive nonlinear effect)

Since the first example reported by Kagan and co-workers,[21] the positive nonlinear effect has frequently been observed in various asymmetric reactions using chiral metal catalysts.[10a,11,22,23] However, most of them are limited to the central metal ion-chiral ligand 1:1 system, and a high degree of asymmetric amplification concerning the 1:3 system has never been reported although mathematical treatment allows one to expect a considerable nonlinear effect in this system. We investigated the linear-nonlinear effect for the hetero-Diels–Alder reactions catalyzed by (*R*)-rich **1**-Yb and **4**-Ce. In all cases, the amount of the catalyst was adjusted for the excess enantiomer to be 10 mol% for the substrate, e.g., 20 mol% of the catalyst was used for the reaction when it was 50% ee.

First, the **1**-Yb-catalyzed reaction was checked.[15] As shown in Figure 6, the optically impure catalysts **13** and **14** were prepared by methods I and II, respectively. When solutions of enantiopure (*R*)-**1**-Yb and (*S*)-**1**-Yb containing 2,6-lutidine were mixed in different ratios (method I), the system became heterogeneous due to the resulting precipitates. The direct use of the suspension as a catalyst **13** for the reaction of **5a** with **6** showed a notable asymmetric amplification (Fig. 6). Very interestingly, the catalysts **14** prepared from the chiral ligands with various ee's according to method II further promoted the amplification under heterogeneous conditions, e.g., using only 20% ee of the BNP–Na (*R*/*S* 3:2), the adduct (*R*)-**7a** with 90% ee was obtained. These results strongly suggest that the active catalyst generated from an enantiomerically impure ligand has the same structure as that of the catalyst prepared from the enantiopure ligand.

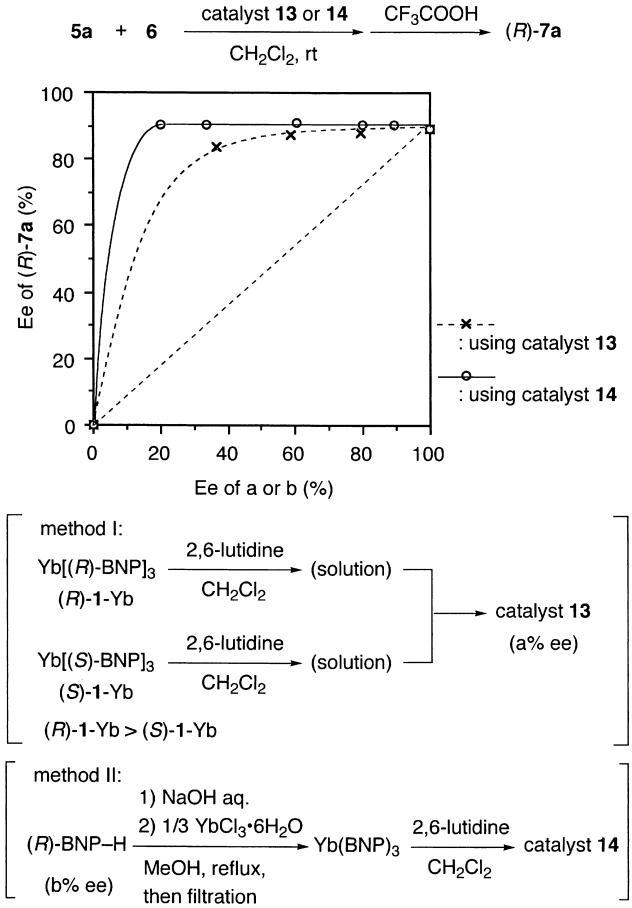


Figure 6. The asymmetric amplification observed in the hetero-Diels–Alder reaction catalyzed by **13** and **14**.

To gain an insight into the mechanism of the present highly positive nonlinear effect, we carried out the reactions shown in Figure 7. The ytterbium complex **15**-Yb prepared from 50% ee of the BNP–Na (*R*/*S* 3:1) was isolated, and then treated with 2,6-lutidine in dichloromethane. Separation of the CH_2Cl_2-soluble part (**16**) from the insoluble part (**17**) by centrifugation (**16**/**17** 41:59) followed by $LiAlH_4$ reduction of each part afforded the corresponding BINOLs with 98 and 7% ee, respectively. In addition, while **16**-catalyzed the hetero-Diels–Alder reaction to give the product (*R*)-**7a** with

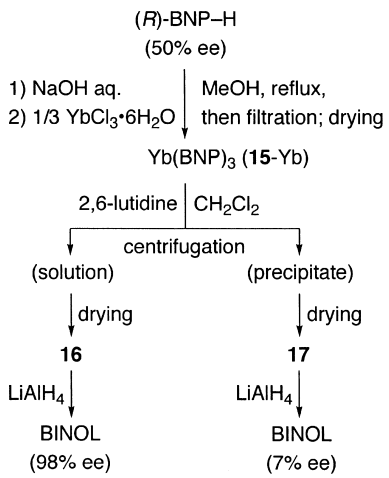
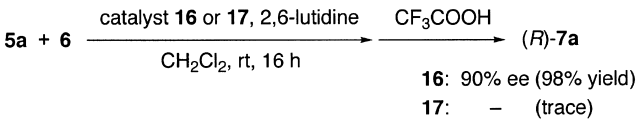


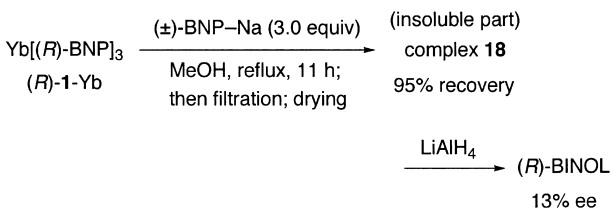
Figure 7. Correlation between solubility and optical purity of the catalysts.

90% ee in 98% yield, **17** hardly promoted the reaction under the same reaction conditions (Scheme 3). These results clearly indicate that the active catalyst **16** is composed entirely of the enantiopure ligands, whereas the inactive **17** is made up of almost a 1:1 mixture of enantiomers.

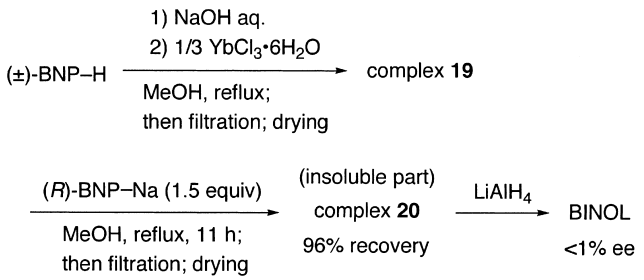


Scheme 3. Correlation between catalytic activity and solubility of the catalysts.

The experiment shown in Scheme 4 indicates how easily the ligands of the complex (*R*)-**1**-Yb can be exchanged by the sodium salt (BNP–Na) of the opposite enantiomer, giving the heterochiral complex, i.e., when enantiopure (*R*)-**1**-Yb was refluxed with racemic BNP-Na under similar conditions for the preparation of (*R*)-**1**-Yb (see Fig. 1), the resulting precipitate (complex **18**, 95% recovery) contained the chiral ligand with only 13% ee, which was clarified by converting **18** to the corresponding BINOL. On the other hand, complex **19** prepared from racemic BNP–H hardly promoted such a ligand exchange reaction with enantiopure (*R*)-BNP–Na under similar conditions (Scheme 5). These results demonstrate the remarkable thermodynamic stability of the heterochiral complex.



Scheme 4. The ligand exchange reaction of (*R*)-**1**-Yb with (±)-BNP–Na.



Scheme 5. The ligand exchange reaction of the complex **19** with (*R*)-BNP–Na.

Taking all these facts into consideration, we propose the origin of the present asymmetric amplification as shown in Figure 8. For the formation of YbL_3, there are four possibilities in choosing three chiral ligands: $(L_R)_3$, $(L_R)_2L_S$, L_R $(L_S)_2$, and $(L_S)_3$, where L_R=(*R*)-BNP, and L_S=(*S*)-BNP. From these four complexes, heterochiral pairs such as $Yb(L_R)_3$ and $Yb(L_S)_3$ and/or $Yb(L_R)_2L_S$ and $YbL_R(L_S)_2$ seem to irreversibly assemble, forming the thermodynamically very stable complexes which have almost no catalytic activity for the hetero-Diels–Alder reaction. As a result, the enantiopure ytterbium complex

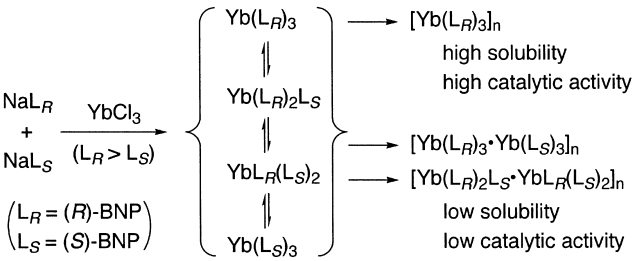
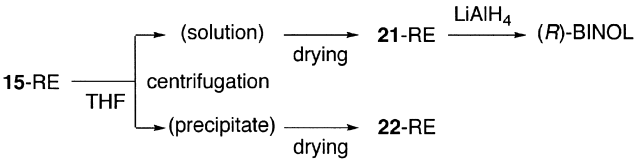


Figure 8. A possible chirality discrimination process for the formation of $[Yb(L_R)_3]_n$.

based on an excess amount of the enantiomer, $Yb(L_R)_3$, would remain in solution as the catalyst.

This autogenetic chiral discrimination process, which can afford a solution of the enantiopure complex $[Yb(L_R)_3]$, was found to also occur in THF instead of the 2,6-lutidine-containing dichloromethane, as shown by entry 6 of Table 5. It is interesting to note that this phenomenon is quite general within the lanthanide metal ions with similar ionic radii to that of the ytterbium ion like neodymium, gadolinium, and holmium ions (entries 3–5). On the other hand, the lanthanum and the cerium complexes, the metal ions of which have larger ionic radii, were sparingly soluble in THF indicating that they might exist as oligomeric mixtures with high molecular weights (entries 1 and 2). In the case of the scandium complex, which contains the smallest rare earth metal ion, almost half of the complex was soluble in THF, but the $LiAlH_4$ reduction of it revealed that the autogenetic process to form the enantiopure complex did not effectively operate in this system (entry 7).

Table 5. Correlation between the THF-soluble complex **21** and optical purity of the ligand



Entry	RE	**21**:**22**	Ee of (*R*)-BINOL (%)[a]
1	La	3:97	–
2	Ce	3:97	–
3	Nd	36:64	99
4	Gd	37:63	98
5	Ho	41:59	97
6	Yb	46:54	98 (5)[b]
7	Sc	54:46	64

The complexes **15**–RE was prepared from 50% ee of (*R*)-BNP–H.
[a] Ee of the BINOL derived from **21**–RE unless otherwise noted. Determined by HPLC using a chiral column.
[b] Ee of the BINOL derived from **22**–Yb.

Since the cerium complex [(*R*)-**4**-Ce] prepared from CAN is soluble in dichloromethane, the linear-nonlinear effect was also investigated for the **4**-Ce-catalyzed reaction of 4-ethylbenzaldehyde (**5k**) with the Danishefsky's diene (**6**).[20] The procedure and the results are shown in Figure 9. Different from the previous case using the **1**-Ce catalyst (entry 2 in Table 5), significant positive nonlinear effects were observed. For example, when the optically impure complex **23** prepared by mixing the optically pure (*R*)-and

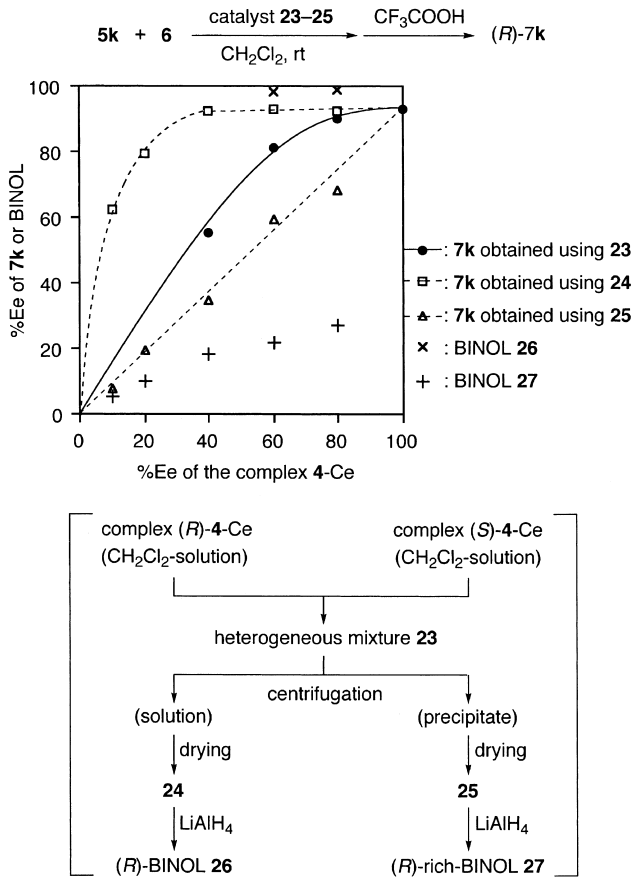


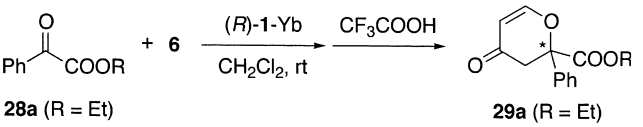
Figure 9. The relation between optical purities of the Ce-catalyst and ee's of (*R*)-**7k** obtained by using it.

(*S*)-**4**-Ce complexes in 9:1 (80% ee) and 4:1 (60% ee) ratios were used (see method I in Fig. 6), the product **7k** was produced in 90 and 81% ee, respectively. These reactions proceeded under heterogeneous conditions because the mixing of (*R*)- and (*S*)-**4**-Ce produced precipitates. Therefore, the precipitate was separated by centrifugation, and the soluble complex **24** and the insoluble one **25** were independently used as a catalyst for the hetero-Diels–Alder reaction. As anticipated form the results of the **13**-Yb-catalyzed reactions (see Fig. 6), the soluble complex **24** showed a high asymmetric amplification, and also the $LiAlH_4$ reduction of **24** afforded the almost enantiopure (*R*)-BINOL (**26**). Unexpectedly, however, the insoluble complex **25** also exhibited considerable catalytic activity and the enantioselectivity linearly increased. More interestingly, the (*R*)-rich-BINOLs (**27**) derived from **25** showed uniformly lower ee's than the corresponding products [(*R*)-**7k**] obtained using **25** as a catalyst. These behaviors are much different from those observed in the **1**-Yb-catalyzed reactions (cf. Fig. 7 and Scheme 3). There must be a rapid ligand exchange process effectively promoted by the nitrate ion.

2.7. Asymmetric hetero-Diels–Alder reaction of α-keto esters

Finally, we briefly checked the effectiveness of (*R*)-**1**-Yb for the hetero-Diels–Alder reaction of α-keto esters **28** with the Danishefsky's diene **6** (Table 6).[24] Although such a reaction can produce a quaternary stereogeneic center, there has been

Table 6. The (*R*)-**1**-Yb-catalyzed hetero-Diels–Alder reaction of α-keto esters **28** with **6**



28a (R = Et)
28b (R = Me)

29a (R = Et)
29b (R = Me)

Entry	α-Keto ester	Catalyst (mol%)	Time (h)	Yield (%)[a]	Ee (%)[b]
1	**28a**	10	11	90	>99
2[c]	**28a**	10	26	80	91
3	**28a**	5	12	88	>99
4	**28a**	2	60	89	96
5	**28b**	10	11	99	98
6	**28b**	5	21	99	97

[a] Isolated yield.
[b] Determined by HPLC using a chiral column.
[c] The reaction was carried out in the presence of 2,6-lutidine (10 mol%).

no example of its highly enantioselective version until the recent report by Jϕrgensen and co-workers.[24d] The (*R*)-**1**-Yb-catalyzed reactions of phenylglyoxylates (**28a** and **28b**) proceeded at room temperature under homogeneous conditions in the absence of 2,6-lutidine, and almost enantiopure products (**29a** and **29b**) were obtained. Different from the reactions of aldehydes (see Table 2), the addition of 2,6-lutidine rather decreased the enantioselectivity as well as the reaction rate (entry 2). These results suggest that the substrate may coordinate to the catalyst as a bidentate ligand and the resulting rigid transition structure may be responsible for such high enantioselectivities. The quantity of the catalyst could be reduced to 2 mol% and still maintain its high enantioselectivity (entries 3, 4, and 6).

3. Conclusion

We succeeded in developing four kinds of chiral rare earth metal complexes that can work as isolable and storable Lewis acid catalysts. These catalysts effectively promoted, in some cases with the aid of 2,6-lutidine, the hetero-Diels–Alder reactions of aromatic aldehydes and α-keto esters with the Danishefsky's diene at room temperature to give the corresponding cycloadducts with excellent enantioselectivities (up to >99% ee). In the two cases examined, remarkably high asymmetric amplifications were observed as the first notable example of the metal-chiral ligand 1:3 system. These results strongly suggest that aggregation and disaggregation processes play an extremely important role in creating a certain chiral space that would be favorable for a high enantioselectivity. We also demonstrated the high potential of the (*R*)-**3**-Sc complex as a reusable Lewis acid catalyst. These findings would lead to a new phase of asymmetric catalysis using chiral metal (especially rare earth) complexes.

4. Experimental

4.1. General methods

Melting points were measured with a Yanako MP-500D micro melting point apparatus and are uncorrected. IR

spectra were taken with JASCO FT/IR-420, JEOL JIR-WINSPEC 50 or Shimadzu FTIR-8600. ^1H and ^{13}C NMR spectra were measured on JEOL JMN-EX 400 at 400 and 100 MHz, respectively. Chemical shifts are given by δ relative to that of internal tetramethylsilane in $CDCl_3$ or the solvent signal of $CDCl_3$ or CD_3OD. High performance liquid chromatography (HPLC) was done with a Shimadzu LC-9A or a LC-10ATVP using ϕ 0.46 cm×25 cm chiral column (Daicel CHIRALCEL OD, CHIRALPAK AD or CHIRALPAK AS). The spectra were analyzed on a Shimadzu C-R6A. Optical rotations were measured on a Horiba SEPA-300 polarimeter. FAB mass spectra were obtained with JEOL JMS-HX110A. Thin layer chromatography (TLC) was performed on a silica gel plates (Merck Kieselgel 60 F-254, 20 cm×20 cm×0.25 mm). Column chromatography was carried out with silica gel as an absorbent (Merck Kieselgel 60, 70–230 mesh or Kanto Chemical, silica gel 60N 70–230 mesh). Dichloromethane was dried over calcium hydride.

4.2. Preparation of catalysts

4.2.1. Typical procedure for the preparation of chiral rare earth metal phosphate (method A): Ytterbium(III) (*R*)-1,1′-binaphthyl-2,2′-diyl phosphate, Yb[(*R*)-BNP]$_3$ [(*R*)-1-Yb]. To a refluxing solution of (*R*)-BNP–H (506 mg, 1.45 mmol) and 3N aqueous sodium hydroxide (0.470 ml, 1.41 mmol) in methanol (12 ml) was slowly added a solution of ytterbium chloride hexahydrate (179 mg, 0.461 mmol) in methanol, and the resulting mixture was stirred for 12 h under the same conditions. After cooling, the precipitate was filtered, washed with methanol, and dried at 120°C for 15 h in vacuo to give the complex (*R*)-**1**-Yb (535 mg, 96%) as colorless solids. Gradually decomposes around 145°C. $[\alpha]_D^{21}$=395.0 (*c* 1.00, THF). IR (KBr): 3616, 3065, 1621, 1592, 1509, 1466, 1329, 1238, 1215, 1112, 1071, 967, 945, 870, 817, 750, 568 cm^{-1}. Anal. calcd for $C_{60}H_{36}O_{12}P_3Yb{\cdot}H_2O$: C, 58.45; H, 3.11. Found: C, 58.17; H, 3.11.

4.2.2. Scandium(III) (*R*)-1,1′-binaphthyl-2,2′-diyl phosphate, Sc[(*R*)-BNP]$_3$ [(*R*)-1-Sc]. Colorless solid. $[\alpha]_D^{25}$=−492.2 (*c* 1.06, THF). IR (KBr): 3060, 1621, 1592, 1509, 1466, 1328, 1237, 1210, 1155, 1109, 1071, 993, 968, 949, 888, 871, 816, 750, 722, 659, 568, 542, 486 cm^{-1}. Anal. calcd for $C_{60}H_{36}O_{12}P_3Sc{\cdot}3H_2O$: C, 63.17; H, 3.71. Found: C, 63.27; H, 3.55.

4.2.3. Lanthanum(III) (*R*)-1,1′-binaphthyl-2,2′-diyl phosphate, La[(*R*)-BNP]$_3$ [(*R*)-1-La]. Colorless solid. $[\alpha]_D^{25}$=356.0 (*c* 1.00, THF). IR (KBr): 3060, 1620, 1592, 1508, 1466, 1329, 1238, 1215, 1103, 1071, 992, 965, 945, 867, 841, 817, 750, 720, 659, 595, 582, 568, 538, 495, cm^{-1}. Anal. calcd for $C_{60}H_{36}O_{12}P_3La{\cdot}H_2O$: C, 60.12; H, 3.20. Found: C, 59.72; H, 3.30.

4.2.4. Cerium(III) (*R*)-1,1′-binaphthyl-2,2′-diyl phosphate, Ce[(*R*)-BNP]$_3$ [(*R*)-1-Ce]. Colorless solid. $[\alpha]_D^{25}$=−325.0 (*c* 1.00, THF). IR (KBr): 3065, 1621, 1592, 1508, 1466, 1329, 1238, 1215, 1103, 1071, 991, 966, 948, 868, 817, 750, 568 cm^{-1}. Anal. calcd for $C_{60}H_{36}O_{12}P_3Ce{\cdot}3H_2O$: C, 58.30; H, 3.43. Found: C, 58.24; H, 3.28.

4.2.5. Neodymium(III) (*R*)-1,1′-binaphthyl-2,2′-diyl phosphate, Nd[(*R*)-BNP]$_3$ [(*R*)-1-Nd]. Colorless solid. $[\alpha]_D^{25}$=−389.9 (*c* 1.08, THF). IR (KBr): 3062, 1592, 1058, 1466, 1329, 1238, 1213, 1104, 1071, 992, 966, 946, 868, 817, 750, 568 cm^{-1}. Anal. calcd for $C_{60}H_{36}O_{12}P_3Nd{\cdot}2H_2O$: C, 58.97; H, 3.30. Found: C, 58.84; H, 3.27.

4.2.6. Gadolinium(III) (*R*)-1,1′-binaphthyl-2,2′-diyl phosphate, Gd[(*R*)-BNP]$_3$ [(*R*)-1-Gd]. Colorless solid. $[\alpha]_D^{25}$=−398.0 (*c* 1.00, THF). IR (KBr): 3068, 1620, 1592, 1508, 1467, 1329, 1238, 1209, 1108, 1071, 992, 966, 946, 868, 817, 750, 568 cm^{-1}. Anal. calcd for $C_{60}H_{36}O_{12}P_3Gd{\cdot}3H_2O$: C, 57.51; H, 3.38. Found: C, 57.88; H, 3.27.

4.2.7. Holmium(III) (*R*)-1,1′-binaphthyl-2,2′-diyl phosphate, Ho[(*R*)-BNP]$_3$ [(*R*)-1-Ho]. Pale orange solid. $[\alpha]_D^{25}$=−359.4 (*c* 1.03, THF). IR (KBr): 3065, 1621, 1592, 1508, 1466, 1329, 1238, 1212, 1109, 1071, 992, 966, 948, 869, 817, 750, 720, 659, 568 cm^{-1}. Anal. calcd for $C_{60}H_{36}O_{12}P_3Ho{\cdot}2H_2O$: C, 57.99; H, 3.24. Found: C, 58.29; H, 3.14.

4.2.8. Ytterbium(III) (*R*)-6,6′-bis(2,6-xylyl)-1,1′-binaphthyl-2,2′-diyl phosphate, [(*R*)-2-Yb]. Gradually decomposes around 275°C. $[\alpha]_D^{25}$=−17.7 (1.00, $CHCl_3$). IR (KBr): 3853, 3649, 3307, 1240, 1103 cm^{-1}. Anal. calcd for $C_{108}H_{84}O_{12}P_3Yb{\cdot}5H_2O$: C, 67.22; H, 4.91. Found: C, 67.08; H, 4.71.

4.2.9. Typical procedure for the preparation of chiral rare earth metal phosphate (method B): Scandium(III) (*R*)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diyl phosphate, Sc[(*R*)-H$_8$-BNP]$_3$ [(*R*)-3-Sc]. To a solution of (*R*)-H$_8$-BNP–Na (351 mg, 0.928 mmol) in methanol (3 ml) and water (1 ml) was slowly added a solution of scandium chloride hexadydrate (77.8 mg, 0.300 mmol) in water (1 ml) and then methanol (3 ml) at 70°C, and the resulting suspension was stirred for 12 h under the same conditions. After cooling, the precipitate was filtered, washed with a mixture of methanol and water (4:1), and dried in vacuo at 120°C to give (*R*)-**3**-Sc (278 mg, 83.3%) as colorless solids. Gradually decomposes around 248°C. $[\alpha]_D^{25}$=−246.8 (*c* 1.02, ethanol). IR (KBr): 2931, 2858, 1471, 1448, 1437, 1423, 1252, 1225, 1111, 1057, 962, 889, 877, 833, 812 cm^{-1}. Anal. calcd for $C_{60}H_{60}O_{12}P_3Sc{\cdot}4H_2O$: C, 60.91; H, 5.79. Found: C, 61.05; H, 5.45.

4.2.10. Typical procedure for the preparation of chiral rare earth metal phosphate (method C and D). Yttrium(III) (*R*)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diyl phosphate, Y[(*R*)-H$_8$-BNP]$_3$ [(*R*)-3-Sc]. To a suspension of (*R*)-H$_8$-BNP–H (830 mg, 2.33 mmol) in dichloromethane (10 ml) was added a solution of yttrium isopropoxide (207 mg, 0.775 mmol) in dichloromethane (12 ml) at room temperature under argon, and the resulting solution was refluxed for 1 min. After cooling, the mixture was directly for 1 min. After Diels–Alder reaction as a 0.05M solution of the catalyst (method D). Alternatively, the solvent was removed under reduced pressure, and the colorless solid was dried in vacuo at 120°C for 6 h to give (*R*)-**3**-Y (953 mg, 100%) (method C). $[\alpha]_D^{25}$=−98.2 (*c* 1.07, THF). Anal. calcd for $C_{60}H_{60}O_{12}P_3Y{\cdot}$

$C_3H_7OH{\cdot}H_2O$: C, 61.37; H, 5.72; P, 7.54; Y, 7.2. Found: C, 61.4; H, 5.7; P, 7.3; Y, 7.6.

4.2.11. Dysprosium(III) (*R*)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diyl phosphate, Dy[(*R*)-H_8-BNP]$_3$ [(*R*)-3-Dy]. $[\alpha]_D^{25}=-122.2$ (*c* 0.157, THF). Anal. calcd for $C_{60}H_{60}O_{12}P_3Dy{\cdot}C_3H_7OH{\cdot}2H_2O$: C, 57.12; H, 5.48; P, 7.01; Dy, 12.27. Found: C, 57.5; H, 5.6; P, 7.0; Y, 12.

4.2.12. Samarium(III) (*R*)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diyl phosphate, Sm[(*R*)-H_8-BNP]$_3$ [(*R*)-3-Sm]. $[\alpha]_D^{25}=-88.2$ (*c* 0.103, THF). Anal. calcd for $C_{60}H_{60}O_{12}P_3Sm{\cdot}C_3H_7OH{\cdot}2H_2O$: C, 57.65; H, 5.53; P, 7.08; Sm, 11.46. Found: C, 57.9; H, 5.8; P, 6.9; Sm, 11.

4.2.13. Preparation of the Ce(III)-BNP complex from CAN [(*R*)-4-Ce]. To a solution of (*R*)-BNP–H (2.19 g, 6.3 mmol) and 3N aqueous sodium hydroxide (2.0 ml, 6.0 mmol) in methanol (45 ml) was slowly added a solution of CAN (822 mg, 1.5 mmol) in methanol at room temperature, and the resulting mixture was stirred for 12 h. The precipitate was filtered, washed with methanol, and dried in vacuo at 120°C for 15 h to give the complex **4** (1.34 g, 59%) as pale gray solids. $[\alpha]_D^{16}=-490.8$ (*c* 1.00, $CHCl_3$). Anal. calcd for $C_{60}H_{36}CeO_{12}P_3{\cdot}3H_2O{\cdot}0.5NaNO_3$: C, 56.37; H, 3.31; N, 0.55. Found: C, 56.24; H, 3.50; N, 0.39. ICP spectrometry analysis: Ce, 10; P, 7.0 (calculated data for the composition ratio: Ce/P 1:3.2). Effective magnetic moment (rt): μ_{eff}, 2.35 μ_B.

4.3. Asymmetric hetero-Diels–Alder reaction of aldehydes

4.3.1. Typical procedure for the chiral rare earth metal phosphate-catalyzed asymmetric hetero-Diels–Alder reaction of aldehydes. Synthesis of (*R*)-2,3-dihydro-2-phenyl-4*H*-pyran-4-one [(*R*)-7a] using (*R*)-1-Yb and 2,6-lutidine. Yb[(*R*)-BNP]$_3$ [(*R*)-**1**-Yb] (12.2 mg, 0.01 mmol) was dried in vacuo at ca. 100°C, and dichloromethane (1 ml) and 0.515 M solution of 2,6-lutidine in dichloromethane (20.0 ml, 0.01 mmol), which was prepared by mixing 2,6-lutidine (27.6 mg, 0.258 mmol) and dichloromethane (0.470 ml), was added to the catalyst under argon. To the resulting solution were added **5a** (10.4 mg, 0.098 mmol) and **6** (26.6 mg, 0.154 mmol), and the mixture was stirred at room temperature for 16 h. The reaction mixture was successively treated with two drops of trifluoroacetic acid and three drops of pyridine, and the resulting mixture was directly subjected to column chromatography to give the desired product (*R*)-**7a** (16.1 mg, 94%) as a colorless oil. R_f 0.35 (ethyl acetate–hexane 3:7). $[\alpha]_D^{27}=-97.9$ (*c* 1.55, $CHCl_3$, 96.3% ee by HPLC analysis), $[\alpha]_D^{20}=-92.4$ (*c* 1.49, THF, 90.8% ee by HPLC analysis), $[\alpha]_D^{20}=-97.7$ (*c* 1.39, CH_3OH, 90.8% ee by HPLC analysis). HPLC (CHIRALCEL OD, 2-propanol–hexane 1:9, 1.0 ml/min): t_R 16.6 min for the (*R*)-**7a** [14.4 min for (*S*)-**7a**]. IR (neat): 3063, 2901, 1676, 1593, 1404, 1269, 1227, 1038, 991, 935, 795, 758, 698 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 7.49 (d, *J*=5.86 Hz, 1H), 7.45–7.37 (m, 5H), 5.53 (dd, *J*=1.46, 5.86 Hz, 1H), 5.44 (dd, *J*=3.42, 14.16 Hz, 1H), 2.92 (dd, *J*=14.16, 16.84 Hz, 1H), 2.67 (ddd, *J*=1.46, 3.42, 16.84 Hz 1H). ^{13}C NMR ($CDCl_3$, δ): 192.09, 163.15, 137.81, 128.87, 126.07, 107.35, 81.06, 43.36. Anal. calcd for $C_{11}H_{10}O_2$: C, 75.83; H, 5.80. Found: C, 75.89; H, 5.75. CAS registry no. 88198-68-9 (*R*), 124578-13-8 (*S*), 40989-96-6 (*rac*).

4.3.2. 2,3-Dihydro-2-(4-methoxyphenyl)-4*H*-pyran-4-one (7b). $[\alpha]_D^{20}=-129.0$ (*c* 1.07, $CHCl_3$, 89.1% ee by HPLC analysis). HPLC (CHIRALPAK AD, 2-propanol–hexane 1:9, 0.5 ml/min): t_R 25.2 min for the major enantiomer (28.4 min for the minor one), (CHIRALCEL OD, 2-propanol–hexane 1:9, 0.5 ml/min): t_R 45.0 min for the major enantiomer (40.5 min for the minor one). ^1H NMR ($CDCl_3$, δ): 7.46 (d, *J*=6.10 Hz, 1H), 7.33 (dt, *J*=8.79, 2.44 Hz, 2H), 6.94 (dt, 2H, *J*=8.79, 2.44 Hz), 5.51 (dd, *J*=0.98, 6.10 Hz, 1H), 5.38 (dd, *J*=3.42, 14.16 Hz, 1H), 3.83 (s, 3H) 2.93 (dd, *J*=14.16, 16.85 Hz, 1H), 2.63 (ddd, *J*=0.98, 3.42, 16.85 Hz, 1H). Anal calcd for $C_{12}H_{12}O_3$: C, 70.58; H, 5.92. Found: C, 70.63; H, 6.09. CAS registry no. 256222-20-5 (*R*), 333719-17-8 (*S*), 60380-11-2 (*rac* or undetermined).

4.3.3. 2,3-Dihydro-2-(4-tolyl)-4*H*-pyran-4-one (7c). $[\alpha]_D^{21}=-114.7$ (*c* 2.41, $CHCl_3$, 91.9% ee by HPLC analysis). HPLC (CHIRALCEL OD, 2-propanol–hexane 1:9, 0.5 ml/min): t_R 25.3 min for the major enantiomer (22.5 min for the minor one). ^1H NMR ($CDCl_3$, δ): 7.47 (d, *J*=5.86 Hz, 1H), 7.30 (d, *J*=8.06 Hz, 2H), 7.23 (d, *J*=8.06 Hz, 2H), 5.52 (dd, *J*=0.98, 5.86 Hz, 1H), 5.40 (dd, *J*=3.42, 14.65 Hz, 1H), 2.92 (dd. *J*=14.65, 17.09 Hz, 1H), 2.64 (ddd, *J*=0.98, 3.42, 17.09 Hz, 1H), 2.38 (s, 3H). Anal. calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.27; H, 6.59. CAS registry no. 478488-10-7 (*R*), 188116-41-8 (*rac* or undetermined).

4.3.4. 2-(1,1′-Biphenyl-4-yl)-2,3-dihydro-4*H*-pyran-4-one (7d). $[\alpha]_D^{22}=-106.5$ (*c* 0.808, $CHCl_3$, 89.9% ee by HPLC analysis). HPLC (CHIRALPAK AD, 2-propanol–hexane 1:9, 0.5 ml/min): t_R 24.3 min for the major enantiomer (32.8 min for the minor one). ^1H NMR ($CDCl_3$, δ): 7.66–7.59 (m, 4H), 7.51–7.44 (m, 5H), 7.37 (tt, *J*=1.95, 7.32 Hz, 1H), 5.55 (dd, *J*=0.97, 5.85 Hz), 5.49 (dd, *J*=3.42, 14.16 Hz, 1H), 2.96 (dd, *J*=14.16, 17.09 Hz, 1H), 2.71 (ddd, *J*=0.97, 3.42, 17.09 Hz, 1H). CAS registry no. 244614-14-0 (*S*), 188116-42-9 (undetermined).

4.3.5. 2-(4-Chlorophenyl)-2,3-dihydro-4*H*-pyran-4-one (7e). $[\alpha]_D^{20}=-105.8$ (*c* 0.675, $CHCl_3$, 92.0% ee by HPLC analysis). HPLC (CHIRALCEL OD, 2-propanol–hexane 1:9, 0.5 ml/min): t_R 35.6 min for the major enantiomer (29.7 min for the minor one). ^1H NMR ($CDCl_3$, δ): 7.47 (d, *J*=5.85 Hz, 1H), 7.41–7.33 (mm, 4H), 5.54 (dd, *J*=0.98, 5.85 Hz, 1H), 5.41 (dd, *J*=3.41, 14.16 Hz, 1H), 2.86 (dd, *J*=14.16, 16.60 Hz, 1H), 2.65 (ddd, *J*=0.98, 3.41, 16.60 Hz, 1H). CAS registry no. 335609-84-2 (*R*), 244614-13-9 (*S*), 188116-43-0 (undetermined).

4.3.6. 2,3-Dihydro-2-(4-nitrophenyl)-4*H*-pyran-4-one (7f). $[\alpha]_D^{24}=-34.5$ (*c* 1.29, $CHCl_3$, 59.1% ee by HPLC analysis). HPLC (CHIRALPAK AD, 2-propanol–hexane 1:4, 1.0 ml/min): t_R 17.2 min for the major enantiomer (21.7 min for the minor one). ^1H NMR ($CDCl_3$, δ): 8.30 (d, *J*=8.79 Hz, 2H), 7.60 (d, *J*=8.79 Hz, 2H,), 7.51 (d, *J*=6.34 Hz, 1H), 5.59 (dd, *J*=0.97, 6.35 Hz, 1H), 5.55 (dd, *J*=3.90, 14.16 Hz, 1H), 2.85 (dd, *J*=14.16, 16.85 Hz, 1H), 2.73 (ddd, *J*=0.98, 3.90, 16.85 Hz, 1H). Anal. calcd for

$C_{11}H_9NO_4$: C, 60.28; H, 4.14; N, 6.39. Found: C, 60.43; H, 4.39; N, 6.10. CAS registry no. 350688-07-2 (*R*), 162299-82-3 (*S*), 188116-44-1 (*rac* or undetermined).

4.3.7. 2,3-Dihydro-2-(2-naphthyl)-4*H*-pyran-4-one (7g). $[\alpha]_D^{22}=-74.2$ (*c* 0.708, $CHCl_3$, 92.3% ee by HPLC analysis). HPLC (CHIRALCEL OD, 2-propanol–hexane 1:4, 1.0 ml/min): t_R 23.2 min for the major enantiomer (15.5 min for the minor one). ^1H NMR ($CDCl_3$, δ): 7.93–7.86 (m, 4H), 7.54–7.50 (m, 4H), 5.61 (dd, *J*=3.42, 14.16 Hz, 1H) 5.57 (dd, *J*=0.98, 5.86 Hz, 1H), 3.02 (dd, *J*=14.16, 16.60 Hz, 1H), 2.76 (ddd, *J*=0.98, 3.42, 16.60 Hz, 1H). Anal. calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 80.31; H, 5.43. CAS registry no. 188116-45-2 (undetermined).

4.3.8. 2,3-Dihydro-2-(2-furyl)-4*H*-pyran-4-one (7h). $[\alpha]_D^{21}=-286.9$ (*c* 2.57, $CHCl_3$, 84.4% ee by HPLC analysis). HPLC (CHIRALPAK AD, 2-propanol–hexane 1:9, 0.5 ml/min): t_R 17.6 min for the major enantiomer (25.8 min for the minor one). ^1H NMR ($CDCl_3$, δ): 7.48 (dd, *J*=0.98, 1.95 Hz, 1H), 7.37 (d, *J*=6.34 Hz, 1H), 6.45 (dd, *J*=0.98, 3.42 Hz, 1H), 6.41 (dd, *J*=1.95, 3.42 Hz, 1H), 5.51 (dd, *J*=0.98, 6.35 Hz, 1H), 5.48 (dd, *J*=3.90, 12.69 Hz, 1H), 3.09 (dd, *J*=12.69, 17.09 Hz, 1H), 2.74 (ddd, *J*=0.98, 3.91, 17.09 Hz, 1H). Anal. calcd for $C_9H_8O_3$: C, 65.85; H, 4.91. Found: C, 65.79; H, 4.80 CAS registry no. 145624-55-1 (*R*), 85613-03-2 (*rac* or undetermined).

4.3.9. (*R*)-2,3-Dihydro-2-[(*E*)-styryl]-4*H*-pyran-4-one [(*R*)-7i]. HPLC (CHIRALPAK AD, 2-propanol–hexane 1:9, 0.5 ml/min): t_R 35.1 min for (*R*)-**7n** [43.0 min for (*S*)-**7n**]. ^1H NMR ($CDCl_3$, δ): 7.42 (d, *J*=6.35 Hz, 1H), 7.37–7.28 (m, 5H), 6.73 (d, *J*=16.11 Hz), 6.31 (dd, *J*=6.84, 16.11 Hz, 1H), 5.48 (d, *J*=6.35 Hz, 1H), 5.11–5.05 (m, 1H), 2.74 (dd, *J*=12.69, 17.09 Hz, 1H), 2.63 (dd, *J*=3.91, 17.09 Hz, 1H). CAS registry no. 139627-54-6 (*R*), 122046-62-2 (*R*), 190835-53-1 (*S*), 85613-04-3 (*rac* or undetermined), 82093-23-0 (*rac*).

4.3.10. (*S*)-2,3-Dihydro-2-(2-phenylethyl)-4*H*-pyran-4-one [(*S*)-7j]. $[\alpha]_D^{21}=-20.9$ (*c* 0.717, $CHCl_3$, 9.3% ee by HPLC analysis).HPLC (CHIRALPAK AD, 2-propanol–hexane 1:50, 1.0 ml/min): t_R 16.4 min for (*S*)-**7j** [21.4 min for (*R*)-**7j**]. ^1H NMR ($CDCl_3$, δ): 7.38 (d, *J*=5.86 Hz, 1H), 7.35–7.18 (m, 5H), 5.41 (dd, *J*=0.98, 5.86 Hz, 1H), 4.43–4.36 (m, 1H), 2.87–2.71 (m, 2H) 2.55 (dd, *J*=13.19, 16.60 Hz, 1H), 2.43 (ddd, *J*=0.98, 3.91, 16.60 Hz, 1H), 2.20–2.11 (m, 1H), 2.00–1.91 (m, 1H). Anal calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.09; H, 7.07. CAS registry no. 145624-57-3 (*S*), 366463-10-7 (*R*), 188116-46-3 (undetermined).

4.3.11. 2,3-Dihydro-2-(4-ethylphenyl)-4*H*-pyran-4-one (7k). A colorless oil. R_f 0.43 (ethyl acetate–hexane 3:7). $[\alpha]_D^{24}=-58.8$ (*c* 0.55, $CHCl_3$, 77.7% ee by HPLC analysis). HPLC (CHIRALPAK OD, 2-propanol–hexane 1:9, 0.5 ml/min): t_R 24.4 min for the major enantiomer (20.4 min for minor one). IR (KBr): 2966, 2360, 1678, 1595, 1402, 1271, 1228, 1211, 1038, 988, 934, 837, 793, 482cm^{-1}. ^1H NMR ($CDCl_3$, δ): 7.47 (d, *J*=6.34 Hz, 1H), 7.32 (d, *J*=8.30 Hz, 2H), 7.25 (d, *J*=6.35 Hz, 2H), 5.52 (d, *J*=5.58 Hz, 1H), 5.41 (dd, *J*=3.42, 14.64 Hz, 1H), 2.93 (dd, *J*=14.65, 17.09 Hz, 1H), 2.71–2.63 (m, 3H), 1.25 (t, *J*=7.32 Hz, 3H). ^{13}C NMR ($CDCl_3$, δ): 192.01, 163.02, 144.97, 134.85, 128.11, 126.05, 107.09, 80.92, 43.16, 28.51, 15.43. HRMS-FAB (*m*/*z*): $[M+H]^+$ calcd for $C_{13}H_{15}O_2$, 203.1072. Found: 203.1071. Anal. calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.03; H, 6.97.

4.3.12. 2,3-Dihydro-2-(4-isobutylphenyl)-4*H*-pyran-4-one (7l). A pale yellow oil. R_f 0.57 (ethyl acetate–hexane 1:1). $[\alpha]_D^{21}=-70.1$ (*c* 0.63 $CHCl_3$, 87.9% ee by HPLC analysis). HPLC (CHIRALPAK OD, 2-propanol–hexane 1:19, 0.25 ml/min): t_R 50.7 min for the major enantiomer (45.8 min for the minor one). IR (KBr): 2955, 2869, 1680, 1596, 1517, 1466, 1402, 1271, 1228, 1211, 1038, 989, 934, 847, 790, 550, 483cm^{-1}. ^1H NMR ($CDCl_3$, δ): d 7.47 (d, *J*=6.11 Hz, 1H), 7.30 (d, *J*=8.24 Hz, 2H), 7.20 (d, *J*=8.23 Hz, 2H), 5.52 (d, *J*=6.11 Hz, 1H), 5.40 (dd, *J*=3.35, 14.35 Hz, 1H), 2.92 (dd, *J*=14.65, 16.78 Hz, 1H), 2.65 (dd, *J*=2.74, 16.78 Hz, 1H), 2.50 (d, *J*=7.02 Hz, 2H) 1.91–1.83 (m, 1H), 0.91 (d, *J*=6.41 Hz, 6H). ^{13}C NMR ($CDCl_3$, δ): 192.19, 163.13, 142.61, 134.93, 129.45, 125.93, 107.23, 81.09, 45.11, 43.27, 30.22, 22.38. HRMS-FAB (*m*/*z*): $[M+H]^+$ calcd for $C_{15}H_{19}O_2$, 231.1385. Found: 231.1388. Anal. calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.07; H, 7.89.

4.3.13. 2,3-Dihydro-2-(4-*tert*-butylphenyl)-4*H*-pyran-4-one (7m). Colorless solid. Mp 86.0–87.0°C. R_f 0.57 (ethy1 acetate–hexane 1:1). $[\alpha]_D^{21}=-80.6$ (*c* 0.73, $CHCl_3$, 87.7% ee by HPLC analysis). HPLC (CHIRALPAK OD, 2-propanol–hexane 1:9, 0.5 ml/min): t_R 24.1 min for the major enantiomer (15.8 min for the minor one). IR (KBr): 3060, 2960, 2902, 2868, 1673, 1594, 1515, 1462, 1410, 1362, 1273, 1230, 1041, 996, 637, 835, 572, 492 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 7.47 (d, *J*=6.10 Hz, 1H), 7.45 (d, *J*=8.24 Hz, 2H), 7.33 (d, *J*=8.24 Hz, 2H), 5.52 (d, *J*=5.80 Hz, 1H), 5.41 (dd, *J*=3.66, 14.65 Hz, 1H), 2.93 (dd, *J*=14.64, 17.09 Hz, 1H), 2.66 (dd, *J*=3.36, 16.79 Hz, 1H), 1.33 (s, 9H). ^{13}C NMR ($CDCl_3$, δ): 192.20, 163.16, 152.05, 134.63, 125.92, 125.71, 107.24, 81.00, 43.19, 34.72, 31.31. HRMS-FAB (*m*/*z*): $[M+H]^+$ calcd for $C_{15}H_{19}O_2$, 231.1385. Found: 231.1386. Anal. calcd for $C_{15}H_{18}O_2$; C, 78.23; H, 7.88. Found: C, 78.11; H, 7.85.

4.3.14. 2,3-Dihydro-2-(4-fluorophenyl)-4*H*-pyran-4-one (7n). $[\alpha]_D^{21}=-41.7$ (*c* 0.52, $CHCl_3$, 75.8% ee by HPLC analysis). HPLC (CHIRALPAK OD, 2-propanol–hexane 1:9, 0.5 ml/min): t_R 29.1 min for the major enantiomer (25.8 min for the minor one). ^1H NMR ($CDCl_3$, δ): 7.48 (d, *J*=5.86 Hz, 1H), 7.39 (d, *J*=8.79 Hz, 2H), 7.12 (d, *J*=8.79 Hz, 2H), 5.55 (d, *J*=5.86 Hz, 1H), 5.42 (dd, *J*=3.42, 14.65 Hz, 1H), 2.90 (dd, *J*=14.65, 17.09 Hz, 1H), 2.66 (dd, *J*=3.42, 17.09 Hz, 1H). HRMS-FAB (*m*/*z*): $[M+H]^+$ calcd for $C_{11}H_{10}FO_2$, 193.0665. Found: 193.0650. CAS registry no. 226714-93-8 (*rac*).

4.3.15. 2-(4-Bromophenyl)-2,3-dihydro-4*H*-pyran-4-one (7o). $[\alpha]_D^{21}=-42.0$ (*c* 0.53, $CHCl_3$, 78.8% ee by HPLC analysis). HPLC (CHIRALPAK OD, 2-propanol–hexane 1:9; 0.5 ml/min: t_R 43.9 min for the major enantiomer (35.1 min for the minor one). ^1H NMR ($CDCl_3$, δ): 7.56 (d, *J*=7.32 Hz, 2H), 7.47 (d, *J*=4.89 Hz, 1H), 7.28 (d, *J*=7.81, 2H), 5.53 (d, *J*=4.39 Hz, 1H), 5.40 (d, *J*=13.18 Hz, 1H),

2.85 (dd, J=14.65, 16.11 Hz, 1H), 2.65 (d, J=16.60 Hz, 1H). HRMS-FAB (m/z): $[M+H]^+$ calcd for $C_{11}H_{10}BrO_2$, 252.9864. Found: C, 252.9863. Anal. calcd for $C_{11}H_9BrO_2$: C, 52.20; H, 3.58. Found: C, 52.25; H, 3.62. CAS registry no. 387388-81-0 (undetermined).

4.3.16. 2,3-Dihydro-2-propyl-4*H*-pyran-4-one (7p). HPLC (CHIRALPAK AD, 2-propanol–hexane 1:50, 0.5 ml/min): t_R 24.2 min for the major enantiomer (33.9 min for the minor one). ^{1}H NMR ($CDCl_3$, δ): 7.35 (d, J=6.34 Hz, 1H), 5.40 (d, J=6.34 Hz, 1H), 4.42–4.41 (m, 1H), 2.52 (dd, J=13.67, 16.60 Hz, 1H), 1.83–1.45 (m, 4H), 0.97 (t, J=7.32 Hz, 3H). CAS registry no. 129548-17-0 (*S*), 89171-64-2 (undetermined).

4.3.17. 2-Cyclohexyl-2-3,dihydro-4*H*-pyran-4-one (7q). HPLC (CHIRALPAK AD, 2-propanol–hexane 1:50, 0.25 ml/min): t_R 25.4 min for the major enantiomer (21.6 min for the minor one). ^{1}H NMR ($CDCl_3$, δ): 7.37 (d, J=5.86 Hz, 1H), 5.39 (d, J=5.86 Hz, 1H), 4.17 (d, J=14.16 Hz, 1H), 2.56 (dd, J=14.65, 16.60 Hz, 1H), 2.40 (dd, J=2.93, 16.60 Hz, 1H), 1.90–1.69 (m, 5H), 1.26–1.06 (m, 6H). Anal. calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.91. Found: C, 73.20; H, 8.89. CAS registry no. 145624-56-2 (*R*), 60380-10-1 (*rac*).

4.4. Synthesis of the chiral ligand

4.4.1. (*R*)-2,2′-Bis(benzyloxy)-6,6′-di(2,6-xylyl)-1,1′-binaphthyl (10). A mixture of 2,2′-bis(benzyloxy)-6,6′-dibromo-1,1′-binaphthyl (**9**)[25] (4.80 g, 7.69 mmol), 2,6-xylylboronic acid (3.00 g, 20.0 mmol), tetrakis(triphenylphosphine)palladium (889 mg, 0.760 mmol) and a solution of barium hydroxide octahydrate (7.28 g, 23.1 mmol) in 1,2-dimethoxyethane (DME) (46.2 ml) and water (7.7 ml) was stirred at 80°C for 2.5 h under argon. After cooling, the resulting mixture was extracted with toluene. The organic layer was washed with brine, dried over anhydrous magnesium sulfate, and concentrated. The residue was subjected to column chromatography to give the desired product **10** (5.3 g, 99%) as a colorless crystalline. Mp 93–94°C. R_f 0.44 (ethyl acetate–hexane 1:9). $[\alpha]_D^{20}$=+89.0 (c 1.0, $CHCl_3$). IR (KBr): 3712, 3061, 3030, 2947, 2918, 1589, 1483, 1452 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 7.92 (d, J=8.79 Hz, 2H), 7.66 (s, 2H), 7.45 (dd, J=8.79, 8.30 Hz, 4H), 7.20–7.07 (m, 14H), 6.96 (d, J=6.83 Hz, 4H), 5.08 (s, 4H), 2.08 (d, J=4.39 Hz, 2H). ^{13}C NMR ($CDCl_3$, δ): 153.85, 141.78, 137.41, 136.35, 132.94, 129.54, 129.27, 128.99, 128.19, 128.06, 127.55, 127.29, 127.24, 126.98, 126.78, 125.77, 120.69, 115.94, 71,02, 21.04, 21.00. HRMS-FAB (m/z): $[M]^+$ calcd for $C_{50}H_{42}O_2$, 674.3185. Found: 674.3142. Anal. calcd for $C_{50}H_{42}O_2 \cdot H_2O$: C, 86.67; H, 6.40. Found: C, 86.60; H, 6.15.

4.4.2. (*R*)-6,6′-Di(2,6-xylyl)-1,1′-bi-2-naphthol (11). To a mixture of **10** (1.49 g, 2.21 mmol) and 10% palladium carbon (149 mg) were added ethyl acetate (22 ml) and *N*,*N*-diisopropylethylamine (286 mg, 2.21 mmol) under argon, and then the atmosphere was changed to hydrogen. After stirring at room temperature for 12 h, the reaction mixture was passed through Celite. The filtrate was concentrated, and subjected to column chromatography to give the desired product **11** (1.07 g, 95%) as a colorless crystalline. Mp 133–135°C. R_f 0.31 (ethyl acetate–hexane 1:4). $[\alpha]_D^{27}$=−62.9 (c 1.0, $CHCl_3$). IR (KBr): 3521, 1720, 1621, 1598, 1483, 767 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 7.97 (d, J=8.79 Hz, 2H), 7.68 (s, 2H), 7.42 (d, J=8.79 Hz, 2H). 7.33 (d, J=8.79 Hz, 2H), 7.21–7.14 (m, 8H), 2.07 (s, 12H). ^{13}C NMR ($CDCl_3$, δ): 152.69, 141.34, 136.82, 136.31, 132.10, 131.35, 129.56, 129.30, 128.23, 127.35, 127.16, 124.29, 117.87, 110.92, 21.06. HRMS-FAB (m/z): $[M]^+$ calcd for $C_{36}H_{30}O_2$, 494.2246. Found: 494.2240. Anal. calcd for $C_{36}H_{30}O_2 \cdot H_2O$: C, 84.35; H, 6.29. Found: C, 84.05; H, 6.19.

4.4.3. (*R*)-6,6′-Di(2,6-xylyl)-1,1′-binaphthyl-2,2′-diyl chlorophosphate. To a cold solution of **11** (614 mg, 1.24 mmol) and phosphoryl chloride (355 mg, 2.32 mmol) in dichloromethane (2.8 ml) was added dropwise triethylamine (326 mg, 3.22 mmol), and the mixture was stirred at 0°C for 40 min under argon. After additional stirring for 4.5 h at room temperature, water was added, and the crude product was extracted with dichloromethane. The organic layer was washed with water, dried over anhydrous magnesium sulfate, and concentrated to give the analytically almost pure (*R*)-6,6′-di(2,6-xylyl)-1,1′-binaphthyl-2,2′-diyl chlorophosphate (719 mg) as colorless solids, which was used for the next hydrolysis without further purification. R_f 0.55 (ethyl acetate–hexane 4:1). IR (KBr): 3733, 3338, 3020, 2975, 1475, 1461, 1317, 960, 687 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 8.08 (q, J=4.40 Hz, 2H), 7.79 (d, J=5.86 Hz, 2H), 7.67 (d, J=8.79 Hz, 1H), 7.58 (d, J=8.79 Hz, 2H), 7.55 (d, J=8.79 Hz, 1H), 7.22–7.12 (m, 8H), 2.13 (s, 6H), 2.01 (s, 3H), 1.98 (s, 3H). ^{13}C NMR ($CDCl_3$, δ): 146.17, 140.62, 139.23, 136.09, 135.96, 135.85, 132.38, 132.19, 131.85, 131.61, 130.93, 128.96, 128.33, 127.44, 127.37, 127.27, 127.15, 126.32, 121.57, 120.42, 119.98, 20.95, 20.89, 20.82. HRMS-FAB (m/z): $[M]^+$ calcd for $C_{36}H_{28}ClO_3P$, 574.1465. Found: 574.1460.

4.4.4. (*R*)-6,6′-di(2,6-xylyl)-1,1′-binaphthyl-2,2′-diyl hydrogen phosphate (11). To a suspension of (*R*)-6,6′-di(2,6-xylyl)1,1′-binaphthyl-2,2′-diyl chlorophosphate (1.57 g, 2.73 mmol) in 2% aqueous sodium carbonate was stirred at 90°C for 1 h, and the reaction mixture was placed in refrigerator for 12 h. The precipitate was filtered, washed with 2% aqueous sodium carbonate and added to water (22 ml). To the mixture was added 35% aqueous hydrochloric acid (1.7 ml), and the resulting suspension was stirred at 95°C for 1 h. After cooling, the mixture was extracted with dichloromethane, and the organic layer was washed with water, dried over anhydrous magnesium sulfate, and concentrated. The residue was purified by recrystallization from ethanol and dried in vacuo at 120°C for 16 h to give the desired phosphoric acid **11** (495 mg, 33%) as colorless solids. Mp 246–248°C. $[\alpha]_D^{26}$=−267.0 (c 1.0, $CHCl_3$). IR (KBr): 3853, 3648, 3307, 1226, 1207, 1027, 950, 892, 767 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 8.03 (d, J=8.79 Hz, 2H), 7.76 (s, 2H), 7.64 (d, J=8.79 Hz, 2H), 7.58 (d, J=8.79 Hz, 2H), 7.22–7.12 (m, 8H) 2.14 (s, 6H), 1.99 (s, 6H). ^{13}C NMR ($CDCl_3$, δ): 147.28, 147.19, 140.94, 138.32, 136.07, 135.96, 131.85, 131.10, 131.02, 128.32, 128.10, 127.38, 127.31, 127.24, 121.61, 120.91, 20.91, 20.80. HRMS-FAB (m/z): [M]+ calcd for $C_{36}H_{29}O_4P$, 557.1882. Found: 557.1879.

4.4.5. (*R*)-5,5′,6,6′,7,7′,8,8′-Octahydro-1,1′-binaphthyl-2,2′-diyl chlorophosphate. To a solution of (*R*)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-bi-2-naphthol (1.14 g,

3.87 mmol)[18] and phosphoryl chloride (1.17 g, 7.62 mmol) in dichloromethane (8 ml) was added dropwise triethylamine (1.16 g, 11.5 mmol) at room temperature under argon, and the resulting mixture was vigorously stirred for 12 h under the same conditions. After quenching with water, the product was extracted with dichloromethane. The organic layer was washed with water, dried over anhydrous magnesium sulfate, concentrated, and dried in vacuo to give the analytically almost pure (*R*)-chlorophosphate (1.45 g, 99.9%) as colorless voluminous solids, which was used for the following hydrolysis without further purification. ^{1}H NMR ($CDCl_3$, δ): 7.19–7.17 (m, 3H), 7.06 (dd, J=1.95, 8.30 Hz, 1H), 2.90–2.78 (m, 4H), 2.72–2.63 (m, 2H), 2.28 (dt, J=5.37, 16.11 Hz, 2H), 1.86–1.77 (m, 6H), 1.63–1.51 (m, 2H); (CD_3OD, δ): 7.32 (dd, J=3.91, 8.30 Hz, 2H), 7.18 (ddd, J=1.95, 5.86, 8.30 Hz, 2H), 2.97–2.87 (m, 4H), 2.82–2.74 (m, 2H), 2.34–2.25 (m, 2H), 1.93–1.82 (m, 6H), 1.66–1.57 (m, 2H). CAS registry no. 39648-65-2.

4.4.6. Sodium (*R*)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-, 2,2′ diyl phosphate [(*R*)-H$_8$-BNP–Na]. To a mixture of (*R*)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diyl cholorophosphate (1.45 g, 3.87 mmol) and 2% aqueous sodium carbonate (85 ml) was added THF (ca. 10 ml), and if necessary, water and additional THF, enough to make a clear solution of the reaction mixture at 65°C. The resulting solution was stirred for 3 h under same conditions and further 10 h at room temperature. Most of the THF was evaporated under reduced pressure, and the resulting suspension was warmed at 70°C to make a clear solution of the mixture, and cooled at 0°C for 12 h. The precipitate was filtered, washed with 2% aqueous sodium carbonate, and dried in vacuo at 70°C to give (*R*)-H$_8$-BNP-Na (1.42 g, 97%) as colorless solids. IR (KBr): 2932, 2857, 2839, 1653, 1633, 1472, 1436, 1254, 1228, 1104, 1058, 955, 854, 710, 592, 485 cm^{-1}.

4.4.7. (*R*)-5,5′,6,6′,7,7′,8,8′-Octahydro-1,1′-binaphthyl-2,2′-diyl hydrogen phosphate [(*R*)-H$_8$-BNP–H]. To a solution of the sodium phosphate (1.01 g, 2.67 mmol) in water (45 ml) was slowly added 35% hydrochloric acid (6 ml), and the resulting suspension was vigorously stirred at 70°C for 2 h. After cooling, the precipitate was filtered, washed with water, and dried in vacuo at 120°C for 10 h to give (*R*)-H$_8$-BNP-H (892 mg, 94%) as colorless solids. Gradually decomposes around 289°C. $[\alpha]_D^{20}=-249.9$ (c 1.00, ethanol). IR (KBr): 2935, 2858, 1471, 1439, 1423, 1311, 1063, 1252, 1227, 1157, 1056, 1049, 962, 904, 895, 833, 816, 710 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 7.12 (d, J=8.30 Hz, 2H), 7.08 (d, J=8.30 Hz, 2H), 3.20 (brs), 2.87–2.77 (m, 4H), 2.67 (ddd, J=4.88, 8.30, 16.60 Hz, 2H), 2.28 (dt, J=4.88, 16.60 Hz, 2H), 1.82–1.76 (m, 6H), 1.58–1.52 (m, 2H); (CD_3OD, δ): 7.22 (d, J=8.30 Hz, 2H), 7.08 (d, J=8.30 Hz, 2H), 2.91–2.86 (m, 4H), 2.80–2.72 (m, 2H), 2.30–2.23 (m, 2H), 1.89–1.80 (m, 6H), 1.61–1.55 (m, 2H). ^{13}C NMR (CD_3OD, δ): 147.98, 147.88, 139.45, 136.86, 131.11, 127.47, 119.34, 30.02, 28.87, 23.60, 23.47. HRMS-FAB (m/z): $[M+H]^+$ calcd for $C_{20}H_{22}O_4P$, 357.1256. Found: 357.1255. CAS registry no. 39648-63-0.

4.5. Repeated use of the catalyst

To a solution of the catalyst (*R*)-**3**-Sc (22.2 mg, 0.02 mmol) in dichloromethane (2 ml) were added **5a** (20.9 mg, 0.197 mmol) and **6** (53.1 mg, 0.308 mmol) under argon, and the reaction mixture was stirred at room temperature for 16 h. After concentration, the residue was diluted with ether (4 ml) and passed through Celite using additional ether. The filtrate was successively treated with three drops of trifluoroacetic acid and four drops of pyridine, and the resulting mixture was directly subjected to column chromatography to give 93% ee of the cycloadduct (*R*)-**7a** (34.0 mg, 99%) as a colorless oil. On the other hand, the precipitate on the Celite was eluted with THF. After concentration of the solvent, the complex (11.5 mg, 52% recovery) was dried in vacuo at room temperature for 3 h, and that was used for the next round of reactions.

4.6. Asymmetric amplifications and the related experiments

4.6.1. Typical procedure for the hetero-Diels–Alder reaction using the catalyst 13 (a=37, Fig. 6). To a solution of the catalyst (*S*)-**1**-Yb (7.5 mg, 0.0062 mmol) and 2,6-lutidine (0.715 mg, 0.0067 mmol) in dichloromethane (0.35 ml) was added a solution of the catalyst (*R*)-**1**-Yb (16.3 mg, 0.0134 mmol) and 2,6-lutidine (1.42 mg, 0.0133 mmol) in dichloromethane (0.40 ml) under argon. To the resulting suspension (the catalyst **13**) were added **5a** (8.4 mg, 0.079) and **6** (21.2 mg, 0.123 mmol), and the mixture was stirred at room temperature for 16 h. The reaction mixture was successively treated with two drops of trifluoroacetic acid and three drops of pyridine, and the resulting mixture was directly subjected to column chromatography to give the desired product (*R*)-**7a** (9.7 mg, 71%), the enantiomeric purity of which was determined to be 84% ee by HPLC using Daicel CHIRALCEL OD.

4.6.2. Typical procedure for the preparation of Yb(BNP)$_3$ from optically impure ligands (method II, b=34, Fig. 6). To a refluxing solution of 34% ee of (*R*)-BNP-H (224 mg, 0.624 mmol) and 3N aqueous sodium hydroxide (0.208 ml, 0.624 mmol) in methanol (4 ml) was slowly added a solution of ytterbium chloride hexahydrate (78.7 mg, 0.203 mmol) in methanol, and the resulting mixture was stirred for 9 h under the same conditions. After cooling, the resulting precipitate was centrifuged and wash with methanol. The colorless solid was dried at 120°C for 12 h in vacuo to give the desired complex (235 mg, 95%).

4.6.3. Typical procedure for the hetero-Diels–Alder reaction using the catalyst 14 (b=34 Fig. 6). To a suspension of Yb(BNP)$_3$ (36.6 mg, 0.0301 mmol), prepared above in 4.6.2, and 2,6-lutidine (3.31 mg, 0.0309 mmol) in dichloromethane (1 ml) were added **5a** (10.4 mg, 0.0984 mmol) and **6** (26.6 mg, 0.154 mmol) under argon, and the mixture was stirred at room temperature for 16 h. The reaction mixture was successively treated with two drops of trifluoroacetic acid and three drops of pyridine, and the resulting mixture was directly subjected to column chromatography to give the desired product (R)-**7a** (12.4 mg, 73%), the enantiomeric purity of which was determined to be 90.2% ee by HPLC using Daicel CHIRALCEL OD.

4.6.4. Complex 15-Yb prepared from 50% ee of (*R*)-rich BNP-H. Colorless solid. Anal. calcd for $C_{60}H_{36}O_{12}P_3$-Yb·H_2O: C, 58.45; H, 3.11. Found: C, 58.09; H, 3.14.

4.6.5. Typical procedure for the determination of the enantiopurity of the chiral ligand of the complex RE(BNP)$_3$: Complex 16. To a solution of the complex **16** [18.9 mg, 0.0156 mmol as Yb(BNP)$_3$] in THF was added a 1.0 M solution of LiA1H_4 in ether (0.160 ml, 0.160 mmol) at 0°C under argon. The regulating mixture was stirred for 46 h at room temperature, and then quenched with dilute hydrochloric acid. The crude product was extracted with dichloromethane, and the organic layer was dried over anhydrous magnesium sulfate. After concentration, the residue was subjected to column chromatography to give (*R*)-1,1′-bi-2-naphthol (13.2 mg, 99%), the enantiomeric purity of which was determined to be 98.0% ee by HPLC using Daicel CHIRALPAK AD (ethanol–hexane 1:9, 0.5 ml/min): t_R 44.5 min for the *R* isomer (49.4 min for the *S* isomer).

4.6.6. Complex 18. This complex was prepared according to Scheme 4 and isolated in a similar way to the preparation of (*R*)-**1**-Yb. Colorless solid. Anal. calcd for $C_{60}H_{36}O_{12}P_3$-Yb·$2H_2O$: C, 57.61; H, 3.22. Found: C, 57.30; H, 3.10.

4.6.7. Complex 20. This complex was prepared via the complex **19** according to Scheme 5 and isolated in a similar way to the preparation of (*R*)-**1**-Yb. Colorless solid. Anal. calcd for $C_{60}H_{36}O_{12}P_3Yb·H_2O$: C, 58.45; H, 3.11. Found: C, 58.67; H, 3.04.

4.6.8. Complexes 21-Yb and 22-Yb. These complexes were derived from **15**-Yb (Section 4.6.4) as described in Table 5. For **21**-Yb. Anal. calcd for $C_{60}H_{36}O_{12}P_3Yb·H_2$-$O·C_4H_8O$ [=Yb(BNP)$_3$·H_2O·THF]: C, 58.90; H, 3.55. Found: C, 58.62; H, 3.63. For **22**-Yb. Anal. calcd for $C_{60}H_{36}O_{12}P_3Yb·H_2O$: C, 58.45; H, 3.11. Found: C, 58.67; H, 3.02.

4.7. Asymmetric Hetero-Diels–Alder reaction of α-keto esters

4.7.1. Typical procedure for the asymmetric hetero-Diels–Alder reaction of α-keto esters. Synthesis of ethyl 3,4-dihydro-4-oxo-2-phenyl-2*H*-pyran-2-carboxylate (29a). To a suspension of the catalyst (*R*)-**1**-Yb (12.2 mg, 0.0100 mmol) in dichloromethane (1 ml) was added **28a** (18.0 mg, 0.101 mmol) and **6** (26.6 mg, 0.154 mmol), and the reaction mixture was stirred at room temperature for 11 h. The mixture was successively treated with two drops of trifluoroacetic acid and three drops of pyridine, and the resulting solution was directly subjected to column chromatography to give the desired product **29a** (22.2 mg, 90%). $[\alpha]_D^{22}=-46.8$ (*c* 1.00, $CHCl_3$, 99.6% ee for HPLC analysis). HPLC (CHIRALPAK AD, 2-propanol–hexane 1:50, 0.5 ml/min): t_R 40.8 min for the major enantiomer (44.9 min for the minor one). ^{1}H NMR ($CDCl_3$, δ): 7.57–7.50 (m, 3H), 7.44–7.36 (m, 3H), 5.52 (dd, *J*=0.97, 5.86 Hz, 1H), 4.20 (dq, *J*=0.97, 7.32 Hz, 2H), 3.45 (dd. *J*=0.97, 16.60 Hz, 1H) 3.07 (d, *J*=16.60 Hz, 1H), 1.20 (t, *J*=7.32 Hz, 3H). CAS registry no. 200421-47-2 (*R*), 238737-21-8 (undetermined).

4.7.2. Methyl 3,4-dihydro-4-oxo-2-phenyl-2*H*-pyran-2-carboxylate (29b). Colorless needle. Mp 77.5–78.5°C. R_f 0.37 (ethyl acetate–hexane 3:7). $[\alpha]_D^{23}=-34.3$ (*c* 1.00, $CHCl_3$, 97.1% ee for HPLC analysis). HPLC (CHIRALPAK AD, 2-propanol–hexane 1:50, 0.5 ml/min): t_R 48.3 min for the major enantiomer (53.3 min for the minor one). IR (KBr): 3082, 1749, 1736, 1677, 1599, 1451, 1401, 1273, 1229, 1212, 1125, 1024, 993, 892, 858, 812, 777, 725, 695 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 7.54–7.50 (m, 3H), 7.45–7.37 (m, 3H), 5.52 (dd, *J*=0.98, 6.35 Hz, 1H), 3.74 (s, 3H), 3.45 (dd, *J*=0.98, 16.60 Hz, 1H) 3.08 (d, *J*=16.60 Hz, 1H). ^{13}C NMR ($CDCl_3$ δ): 189.42, 169.89, 161.23, 136.45, 129.07, 128.77, 124.85, 108.25, 85.61, 53.48, 44.27.

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