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Highly efficient enantioselective epoxidation of α,β-enones catalyzed by cheap chiral lanthanum and gadolinium alkoxides

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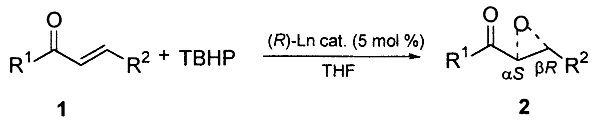
Abstract—(*S*)-6,6′-Dibromo-BINOL and (*S*)-6,6′-diphenyl-BINOL have been developed as efficient chiral ligands applicable to lanthanoid catalyzed asymmetric epoxidation of α,β-unsaturated ketones in the presence of cumene hydroperoxide. Excellent chemical yield and enantioselectivity have been achieved for several epoxides at room temperature by using 5 mol% of La(*O*-*i*-Pr)$_3$-(*S*)-6,6′-dibromo-BINOL and Gd(*O*-*i*-Pr)$_3$-(*S*)-6,6′-diphenyl-BINOL, respectively. Up to 95% ee was obtained for epoxychalcone with Gd(*O*-*i*-Pr)$_3$-(*S*)-6,6-diphenyl-BINOL catalyst at room temperature. A plausible catalyst structure as well as the catalytic cycle has also been suggested. © 2001 Elsevier Science Ltd. All rights reserved.

The asymmetric epoxidation of electron-deficient olefins, especially α,β-unsaturated ketones (**1**) gives excellent access to chiral α,β-epoxy ketones (**2**), which are very useful intermediates for the synthesis of a wide range of natural products and drug molecules.[1] Recently, great effort has been devoted to developing efficient methods for the enantioselective epoxidation of α,β-enones,[2] including chiral ligand–metal peroxide system,[3] asymmetric phase-transfer catalysis,[4] polyamino acid-catalyzed epoxidation,[5] and epoxidation with chiral dioxiranes.[6] Among these, the lanthanoid–BINOL system (Scheme 1) described by Shibasaki and coworkers has been attracted much attention,[7] as it provides an efficient and general method for obtaining good enantiomeric excesses of various epoxyketones even at room temperature with a small amount of chiral catalyst. In this case, chalcone was best epoxidized with 83% ee and in 93% yield by La-(*R*)-BINOL and cumene hydroperoxide (CMHP). Up to 91% ee for the epoxychalcone was further obtained with the improved chiral ligand of (*R*)-3-hydroxymethyl-BINOL.



Scheme 1. Epoxidation of α,β-unsaturated ketones.

More recently, Shibasaki et al., have improved the activity of the Yb-BINOL system by addition of water(4.5 equiv. relative to Yb(*O*-*i*-Pr)$_3$) to the catalyst generated from Yb(*O*-*i*-Pr)$_3$-(*R*)-BINOL, 86% ee was obtained for epoxychalcone **2a**.[8] Inanaga et al. have investigated the effect of a range of additives on Shibasaki's La-(*R*)-BINOL catalyst, and revealed that the addition of 15 mol% triphenylphosphine oxide producing an improvement in ee from 62 to 96% for **2a**.[9]

We have synthesized several kinds of chiral binaphthyl derivatives and applied them to a series of asymmetric reactions.[10–13] For an example, (*S*)-6,6′-diphenyl-BINOL exhibited obvious advantages over the simple (*S*)-BINOL on the asymmetric hydrophosphonylation of aldehydes catalyzed by a lanthanum complex.[10] Moreover, (*S*)-6,6′-dibromo-BINOL was screened as the best ligand in the Yb(*O*-*i*-Pr)$_3$ catalyzed glyoxylate-ene reaction.[12] We envisioned that these chiral catalysts would be useful for the asymmetric epoxidation of enones. Herein, we report our discovery that both Ln(*O*-*i*-Pr)$_3$-(*S*)-6,6′-dibromo-BINOL and Ln(*O*-*i*-Pr)$_3$-(*S*)-6,6′-diphenyl-BINOL show excellent chemical yield and enantioselectivity for the epoxidation of enones. After we finished this work, Shibasaki et al. reported 97% ee for **2a** using a two-component catalyst of La-(*R*)BINOL-triphenylarsine oxide.[14]

In order to screen some other good ligands applicable to epoxidation of enones, according to literature methods, we firstly synthesized some 3,3′- and 6,6′-disubstituted-BINOL derivatives started from (*S*)-BINOL **3**, such as (*S*)-3,3′-dimethyl-BINOL **4**,[15] (*S*)-3,3′-bis (trimethylsilyl)-BINOL

Keywords: asymmetric epoxidation; α,β-enones; chiral lanthanoid complexes.

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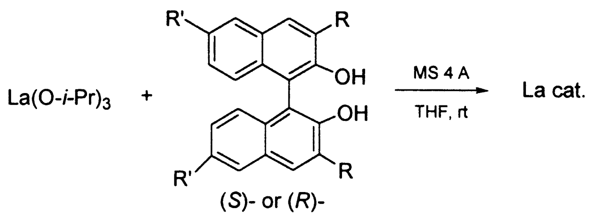
5,[15] (*S*)-3,3′-bis(methoxyethyl)-BINOL **6**,[11] (*S*)-3,3′-bis(*o*-methoxyphenyl)-BINOL **7**,[16] (*S*)-3,3′-dibromo-BINOL **8**,[17] (*S*)-6,6′-dibromo-BINOL **9**,[10] (*R*)-6,6′-dibromo-BINOL **9**[10] and (*S*)-6,6′-diphenyl-BINOL **10**[10] (Scheme 2). In addition, we have also prepared a series of TADDOLs, Salen as well as Py-box derivatives as the chiral ligands. Treatment of the corresponding ligand with 1.0 equiv. of La(*O*-*i*-Pr)$_3$ in THF in the presence of MS 4 A gave a suspension containing a catalytically active species for the asymmetric epoxidation of α,β-unsaturated enones. Epoxidation of chalcone was selected as a model reaction to study and the results were summarized in Table 1.

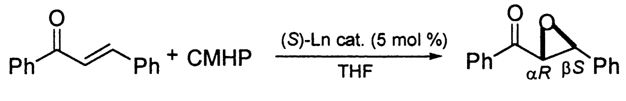
TADDOLs, Salen and Py-box ligands did not show any activity towards this epoxidation. The steric bulk of the 3,3′-substituents on BINOL lowers the enantioselectivity of the reaction. For an example, (*S*)-3,3′-bis(2-methoxyethyl)-BINOL **6** afforded the product with only 65% ee, which was lower than that obtained from (*S*)-**3** (Table 1, entries 5 and 1). Gratifyingly, ligands **9** and **10** exhibited better enantiomeric excesses than any other 3,3′-disubstituted ligands and (*S*)-BINOL (Table 1, entries 7 and 9 vs. 1). The same ee value was obtained with opposite optical rotation when (*S*)-**9** was replaced by (*R*)-**9** (Table 1, entry 8). The reason for the excellent enantioselectivity produced by (*S*)-**9** and (*S*)-**10** may be ascribed to the electronic effect of Br and Ph groups on the 6,6′-positions of BINOL, which produce a more favorable coordination environment between the ligand and lanthanoid, and lead to the improvement of the asymmetric induction. As a comparison, ligand (*S*)-**11** with methyl on the 6,6′-positions of BINOL was further synthesized and applied to this epoxidation. Just as expected, it gave lower ee values than either ligands **9** or **10** due to its lower inductive effect.



R=R'=H, (*S*)-**3**; R=Me, R'=H, (*S*)-**4**; R=SiMe$_3$, R'=H, (*S*)-**5**; R=CH$_2$CH$_2$OCH$_3$,R'=H, (*S*)-**6**; R=*o*-MeOC$_6$H$_4$, R'=H, (*S*)-**7**; R=Br, R'=H, (*S*)-**8**; R=H, R'=Br, (*S*)-**9**; R=H, R'=Br, (*R*)-**9**; R=H, R'=Ph, (*S*)-**10**; R=H, R'=Me, (*S*)-**11**

Scheme 2. Preparation of chiral BINOL derivatives.

Table 1. Ligand effects on the epoxidation of chalcone in the presence of chiral La catalyst



Entry	Ligand	Yield (%)[a]	ee (%)[b]
1	(*S*)-**3**	90	82
2	(*S*)-**4**	65	8
3	(*S*)-**5**	75	22
4	(*S*)-**6**	82	65
5	(*S*)-**7**	86	26
6	(*S*)-**8**	33	14
7	(*S*)-**9**	93	92[c]
8	(*R*)-**9**	92	92[d]
9	(*S*)-**10**	91	86
11	(*S*)-**11**	81	75

La (*O*-*i*-Pr)$_3$ 5 mol%, ligand/La=1:1, CMHP (30 equiv. to La), rt, THF, *t*=8 h.

[a] Yield of isolated epoxide, no *cis*-epoxide was observed.

[b] Determined by HPLC analysis on chiral OD column, configuration of the major enantiomer is α*R*, β*S*, which was determined by comparison with literature data.[18]

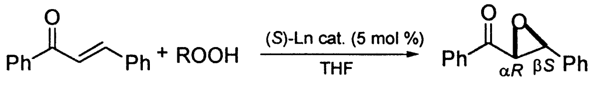
[c] $[\alpha]_{589}^{20}=-230.2$ (*c* 0.73, CHCl$_3$).

[d] $[\alpha]_{589}^{20}=+229.6$ (*c* 0.71, CHCl$_3$).

Then, we chose (*S*)-**9** and (*S*)-**10** as the candidates for further optimizing this epoxidation, and the results are summarized in Table 2. In the case of ligand (*S*)-**9**, both La and Gd showed very good enantioselectivity, 92% ee was obtained in both systems. For La, the ee value could be increased to 94% at lower temperature of 0°C. When (*S*)-**10** was selected as the ligand, both Gd and Yb were found to be excellent rare earth metals affording the highest ee of 95% for epoxychalcone **2a**. Gd(*O*-*i*-Pr)$_3$-(*S*)-**10** catalyst was not affected by lowering the reaction temperature. According to the method reported by Shibasaki,[8] we added 4.5 equiv. water to the Yb-(*S*)-**10** catalyst, but to our disappointment, there was no further improvement in the enantiomeric excess of epoxychalcone.

In this lanthanoid catalyzed epoxidation of chalcone, CMHP showed an obvious advantage over the *tert*-butyl hydroperoxide (TBHP) in all cases. For an example, only 86% ee for epoxychalcone **2a** was found when CMHP was replaced by TBHP in the Gd-**10** catalytic system (Table 2, entry 15). The activity and enantioselectivity of the catalyst

Table 2. Effect of lanthanoid alkoxides on the epoxidation of chalcone



Entry	Chiral ligand	Ln (*O*-*i*-Pr)$_3$	Yield (%)[a]	ee (%)
1	(*S*)-**9**	Sc	15	62
2	(*S*)-**10**	Sc	11	54
3	(*S*)-**9**	Ho	82	90
4	(*S*)-**10**	Ho	79	81
5	(*S*)-**9**	Dy	74	82
6	(*S*)-**10**	Dy	61	92
7	(*S*)-**9**	Sm	89	90
8	(*S*)-**10**	Sm	93	90
9	(*S*)-**9**	La	93	92
10	(*S*)-**9**	La	86	94[b]
11	(*S*)-**10**	La	91	86
12	(*S*)-**9**	Gd	89	92
13	(*S*)-**10**	Gd	95	95
14	(*S*)-**10**	Gd	95	95[c]
15	(*S*)-**10**	Gd	91	86[d]
16	(*S*)-**9**	Yb	81	62
17	(*S*)-**10**	Yb	91	95

Ln(*O*-*i*-Pr)$_3$ 5 mol%, Ln(*O*-*i*-Pr)$_3$/ligand=1:1, CMHP as the oxidant, THF, rt 8 h.

[a] Yield of isolated epoxide, no *cis*-epoxide was observed.

[b] 0°C, 24 h.

[c] Ligand (*S*)-**10** was reused.

[d] TBHP used instead of CMHP.

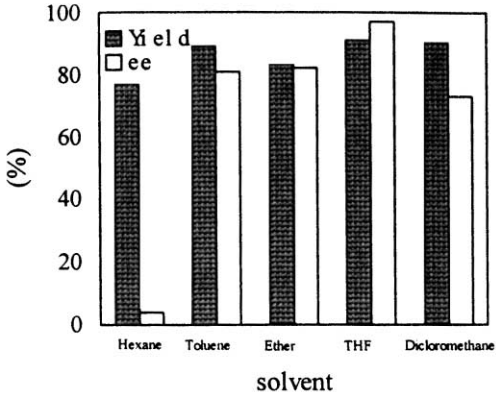


Figure 1. Effect of solvents on the yield and ee value with La(O-i-Pr)$_3$-(S)-**9**.

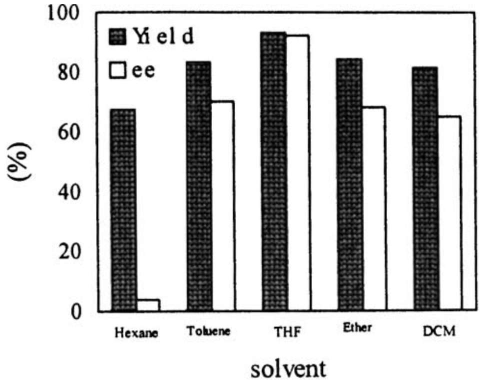


Figure 2. Effect of solvents on the yield and ee value with Gd(O-i-Pr)$_3$-(S)-**10**.

could be adjusted for the reaction by tuning the donor or acceptor ability of the solvents used. Hexane gave very low ee values and tetrahydrofuran proved to be the most favorable solvent for the enantioselectivity of the reaction due to its coordination effect with the lanthanide ion. Figs. 1 and 2 summarized the results with La(O-i-Pr)$_3$-(S)-**9**, and Gd(O-i-Pr)$_3$-(S)-**10**, respectively.

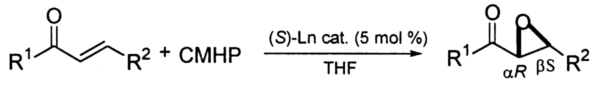
The scope and the potential of the epoxidation catalyzed by the La(O-i-Pr)$_3$-**9** and Gd(O-i-Pr)$_3$-**10** were demonstrated for the reaction of several kinds of α,β-unsaturated enones under the optimized reaction conditions. The results are summarized in Table 3. All the aromatic substituted enones showed good activity and enantiomeric excesses in both La-**9** and Gd-**10** systems at room temperature. Substitutions on the β-phenyl by p-Cl, p-MeO, p-Me or p-MeO had almost no effect on the ee values of the corresponding epoxides. However, **1g** afforded the corresponding epoxide with somewhat lower enantioselectivities compared to the results obtained from chalcone.

Just as the discovery of Shibasaki,[7] we also found that an almost 1:1 ratio of ligand and lanthanide alkoxide gave the maximum chemical yield and enantiomeric excesses in both the La-**9** and Gd-**11** system (Figs. 3 and 4).

We have made several efforts to collect information on the structure of the Gd-**10** catalyst. Measurement of the MS of powder-dried Gd-**10** revealed that this complex has an oligomeric structure. There existed a series of peaks higher than M$^+$(monomeric molecular weight) peak in the FAB spectrum. In the IR spectrum, both the characteristic absorption peaks of phenyl group and isopropyl oxide were clearly found. The elemental analysis of the powder-dried Gd-**10** was in agreement with the calculated results. ^{1}H and ^{13}C NMR spectra were obscure. However, the precise structure of the real catalyst for the present epoxidation is not clear at present.

We propose the following catalytic cycles for the epoxidation of chalcone (Scheme 3). The powder oligomeric gadolinium catalyst is solvated by THF when the epoxidation reaction occurs in tetrahydrofuran, which is very liable to coordinate with the lanthanide ion and thereby control the orientation of the hydroperoxides to form an appropriate

Table 3. Results of asymmetric catalytic epoxidation of different substituted α,β-enones



1 **2**

Entry	Enones	Epoxide	Ln catalyst (5 mol%)	Yield (%)	ee (%)
1	**1a**, R^1=R^2=Ph	**2a**	La-**9**	93	92
	1a, R^1=R^2=Ph	**2a**	La-**9**	86	94[a]
3	**1b**, R^1=Ph, R^2=4-MeC$_6$H$_4$	**2b**	La-**9**	88	86
4	**1c**, R^1=Ph, R^2=4-MeOC$_6$H$_4$	**2c**	La-**9**	86	82
5	**1d**, R^1=Ph, R^2=4-ClC$_6$H$_4$	**2d**	La-**9**	91	87
6	**1e**, R^1=Ph, R^2=2-MeOC$_6$H$_4$	**2e**	La-**9**	88	81
7	**1f**, R^1=Ph, R^2=1-C$_{10}$H$_7$	**2f**	La-**9**	89	84
8	**1a**, R^1=R^2=Ph	**2a**	Gd-**10**	95	95
9	**1b**, R^1=Ph, R^2=4-MeC$_6$H$_4$	**2b**	Gd-**10**	83	93
10	**1a**, R^1=Ph, R^2=4-MeOC$_6$H$_4$	**2c**	Gd-**10**	85	91
11	**1c**, R^1=Ph, R^2=4-ClC$_6$H$_4$	**2d**	Gd-**10**	85	94
12	**1d**, R^1=Ph, R^2=2-MeOC$_6$H$_4$	**2e**	Gd-**10**	81	92
13	**1g**, R^1=2-MOMOC$_6$H$_4$, R^2=Ph	**2g**	Gd-**10**	85	73
14	**1h**, R^1=i-Pr, R^2=Ph	**2h**	Gd-**10**	82	82

Room temperature, CMHP, THF, 8 h.

[a] 0°C; t=24 h.

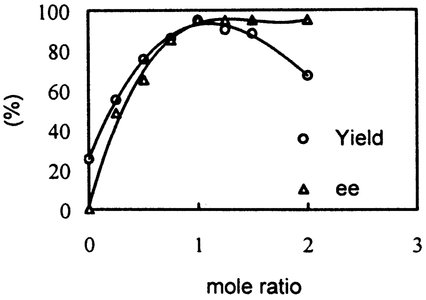


Figure 3. Influences of the mole ratio of (*S*)-**9** and La(*O*-*i*-Pr)$_3$ on yield and ee.

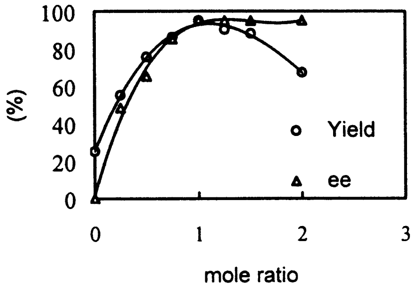


Figure 4. Influences of the mole ratio of (*S*)-**10** and Gd(*O*-*i*-Pr)$_3$ on yield and ee.

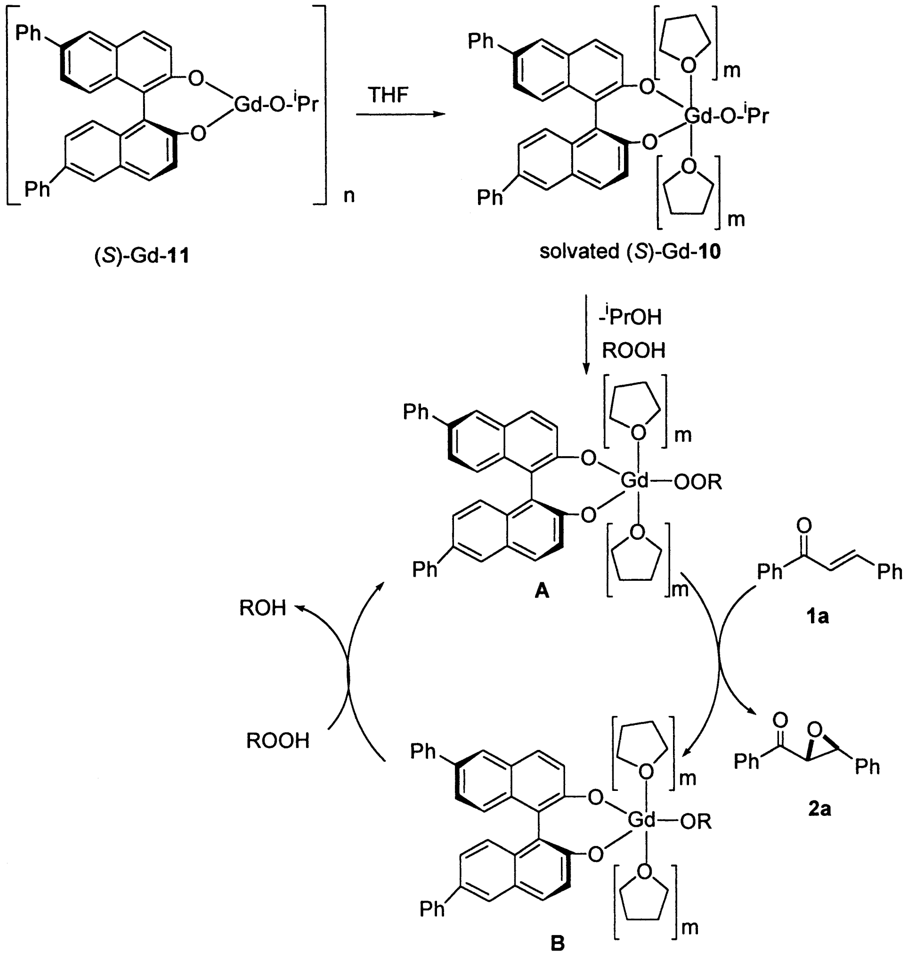
asymmetric environment for epoxidation, just as water molecules do in Inagana's catalyst system. As a result, the oligomeric structure is broken to produce a non-polymeric catalyst having uni-structure, which then reacts with hydroperoxide to form chiral gadolinium peroxide **A** as the active intermediate. It oxides the chalcone **1a** to **2a** and generates the gadolinium oxide **B**. The latter continues to react with ROOH to regenerate chiral gallium peroxide **A**, which enters into the next cycle once more.

In conclusion, we have developed two kinds of cheap and efficient La, Gd catalyst systems for the epoxidation of α,β-unsaturated ketones with either aromatic or alkyl substituents. Up to 95% ee for epoxychalcone could be obtained in the presence of 5 mol% of Gd(*O*-*i*-Pr)$_3$-(*S*)-6,6′-diphenyl-BINOL at room temperature, which will exhibit great potential applications in organic synthesis. The chiral ligand could be quantitatively recovered and reused without any lose of the chemical yield and ee values. A plausible catalyst structure as well as the catalytic cycle has also been suggested.

1. Experimental

1.1. General methods

Melting points were determined on a Kofler hot stage and



Scheme 3. A proposed catalytic cycle for Gd-(*S*)-**10** catalyzed asymmetric epoxidation of chalcone.

are not corrected. NMR spectra were recorded as $CDCl_3$ solutions on VXL-300 and Fx-90Q instruments ^1H NMR (300 and 90 MHz) chemical shifts are reported as δ values in parts per million (ppm) relative to tetramethylsilane (δ_H=0.0 ppm) as internal standard. Infrared spectra were recorded on a Perkin–Elmer 983 FT-IR spectrometer as liquid films on potassium bromide plates unless otherwise noted. Mass spectral measurements were performed on a Finnigan 4021 or Finningan MAT 8430 gas chromatograph/mass spectrometer at 70 eV and mass data were tabulated as *m/z* values. Elemental analyses were carried out on an MOD-1106 elemental analyzer. All reactions were monitored by thin layer chromatography (TLC) using silica gel GF254. Products were purified either by recrystallization or flash column chromatography (FCC) on silica gel manufactured in Qingdao Marine Chemical Factory, eluting with solvent mixtures of light petroleum (bp 60–90°C) and ethyl acetate.

Enantiomeric excess determination was performed by using chiral phase HPLC analysis (OD column, 46 mm×250 mm, from Daicel Chemical Industries, hexane/2-propanol, 9:1, 0.7 mL min^{-1}) based on comparison of retention times with the racemic ones. Optical rotations were measured on materials isolated by column chromatography using a Perkin–Elmer polarimeter 341.

1.2. Materials

All anhydrous solvents were purified and dried by standard techniques just before use. (*S*)-BINOL was commercial material. Substrates of **1a–h** were synthesized as described in Refs. 4b and 7. Liangds of (*S*)-6,6′-dibromo-BINOL and (*S*)-6,6′-diphenyl-BINOL were synthesized according the procedures described in Ref. 10.

1.3. General procedure for the catalytic asymmetric epoxidation with Gd(*O*-*i*-Pr)$_3$-(*S*)-6,6′-diphenyl-BINOL complex

To a suspension of MS 4 A (1.0 g) in THF (10 mL) was added (*S*)-6,6′-diphenyl-BINOL (56 mg, 0.125 mmol) and then Gd(*O*-*i*-Pr)$_3$ (42 mg, 0.0125 mmol) at room temperature. After stirring at room temperature overnight, chalcone **2a** (520 mg, 125 mmol) was added and the resulting mixture was stirred for an additional 30 min at the same temperature. To this solution was added a toluene solution of the cumene hydroperoxide (1.05 mL, 3.75 mmol) in toluene. After stirring for a certain time at room temperature, the reaction mixture was treated with saturated NH_4Cl aq. (1.5 mL) and extracted with EtOAc (10 mL×3). The combined organic extracts were washed with brine, dried with Na_2SO_4, and concentrated, and purified by flash chromatography (EtOAc/hexane=1:30).

1.3.1. Compounds 2a–h. (−)-(2*R*,3*S*)-Epoxy-1,3-diphenylpropan-1-one (**2a**) in 95% ee as a colorless solid, mp 64–65°C; $[\alpha]_{589}^{20}=-253.7^\circ$ (*c* 0.81, $CHCl_3$).

(−)-(2*R*,3*S*)-Epoxy-3-(4-methylphenyl)-1-phenylpropan-1-one (**2b**): colorless solid, mp 70–71°C; $[\alpha]_{589}^{20}=-219.9^\circ$ (*c* 0.70, $CHCl_3$) (93% ee).

(−)-(2*R*,3*S*)-Epoxy-3-(4-methoxyphenyl)-1-phenylpropan-1-one (**2c**): colorless solid, mp 60–62°C; $[\alpha]_{589}^{20}=-256.5^\circ$(*c* 0.66, $CHCl_3$) (91% ee).

(−)-(2*R*,3*S*)-Epoxy-3-(4-chlorophenyl)-1-phenylpropan-1-one (**2d**): colorless solid, mp 68–69°C; $[\alpha]_{589}^{20}=-216.9^\circ$ (*c* 0.99, $CHCl_3$) (94% ee).

(−)-(2*R*,3*S*)-Epoxy-3-(2-methoxyphenyl)-1-phenylpropan-1-one (**2e**): colorless solid, mp 90–91°C; $[\alpha]_{589}^{20}=-32.9^\circ$ (*c* 1.11, $CHCl_3$) (92% ee).

(−)-(2*R*,3*S*)-Epoxy-3-(1-naphthyl)-1-phenylpropan-1-one (**2f**): colorless solid, mp 106–107°C; $[\alpha]_{589}^{20}=+81.3^\circ$ (*c* 0.50, $CHCl_3$) (84% ee).

(−)-(2*R*,3*S*)-Epoxy-3-phenyl-1-(2-methoxymethyloxyphenyl)propan-1-one(**2g**): colorless solid, mp 77–78°C; $[\alpha]_{589}^{20}=-116.8^\circ$(*c* 0.415, $CHCl_3$) (73% ee).

(−)-(4*R*,5*S*)-Epoxy-2-methyl-5-phenylpenta-3-one (**2h**): colorless oil; $[\alpha]_{589}^{20}=-103.1^\circ$ (*c* 0.55 $CHCl_3$) (82% ee).

1.3.2. Synthesis of Gd(*O*-*i*-Pr)$_3$-(*S*)-6,6′-diphenyl-BINOL complex. (*S*)-6,6′-diphenyl-BINOL (56 mg, 0.125 mmol) in THF (5 mL) was added to Gd(*O*-*i*-Pr)$_3$ (42 mg, 0.0125 mmol) in THF (5 mL) at room temperature. After stirring at room temperature overnight, the resulting solution was dried under reduced pressure for 12 h at room temperature. FAB (*m/z*): 972, 927, 855, 837, 816, 782, 744, 701, 667, 629, 607, 568, 514, 476, 454, 438, 420, 389, 362, 340, 313, 295, 267, 248, 219. IR (film): 3024, 2971, 2870, 1615, 1586, 1574, 1172, 1242, 1293 cm^{-1}. Anal. Calcd for C, 64.42%; H, 4.14%. Found for C, 64.11%; H, 4.34%.

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