Pergamon

Tetrahedron 58 (2002) 8321–8329

TETRAHEDRON

Chiral rare earth metal complex-catalyzed conjugate addition of *O*-alkylhydroxylamines. An efficient synthetic entry into optically active 2-acyl aziridines

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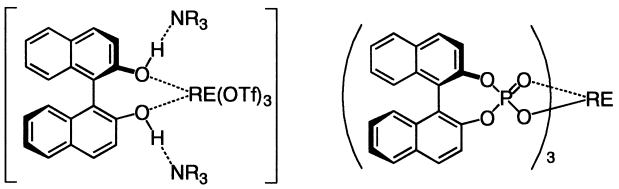
Received 28 May 2002; accepted 4 June 2002

Abstract—The conjugate addition of *O*-alkylhydroxylamines to α,β-unsaturated ketones is effectively catalyzed by chiral rare earth metal complexes to afford the corresponding β-amino ketones with high enantioselectivities (up to 99% ee) in almost quantitative yields, which are, upon treatment with a base catalyst, quantitatively converted into the 2-acyl aziridines without losing their enantiopurities. The protocol is highly practical thus providing an easy access to enantiopure 2-acyl aziridines and their derivatives in good quantities. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

One of the interesting properties of rare earth metal ions is their inherent strong Lewis acidities. A variety of rare earth metal salts of strong acids like the triflates,[1] perfluoroalkylsulfonates,[2–4] perchlorates,[2] bis(perfluoroalkylsulfonyl)amides,[5] and tris(perfluoroalkylsulfonyl)methides[6] have so far been prepared and successfully used in organic synthesis as an effective Lewis acid catalyst.[7] They are not only barely hydrolyzed under neutral or weakly acidic conditions, but also sometimes work as an efficient catalyst in the presence of water, alcohols, or even amines, although under similar circumstances, most traditional Lewis acids lose their activities.

Recently, we prepared the 1:3 complexes of a series of trivalent rare earth metal ions with chiral phosphate ligands, RE[(*R*)-BNP]$_3$ (RE=rare earth; BNP=1,1′-binapphthyl-2,2′-diyl phosphate; Fig. 1), as isolable chiral Lewis acids and demonstrated their usefulness for the enantioselective hetero-Diels–Alder reaction.[8] In the present study, we examined their catalytic abilities for the Michael reaction using amine nucleophiles and found that the chiral scandium complex, Sc[(*R*)-BNP]$_3$ (**B**-Sc, Fig. 1), can be an effective catalyst for the conjugate addition of *O*-alkylhydroxylamines to α,β-unsaturated ketones thus producing the corresponding β-amino ketones with high enantioselectivities (up to 99% ee).



A-RE (NR_3 = *i*-Pr_2NEt) **B**-RE, RE[(*R*)-BNP]$_3$,

Figure 1.

2. Results and discussion

Recently, we developed a practical and highly enantioselective epoxidation of conjugated enones using a La(O-*i*-Pr)$_3$–(*R*)-BINOL–Ph_3PO (1:1:3) precatalyst system (BINOL=1,1′-bi-2-naphthol).[9,10] From the analogy with the epoxidation, we first applied the same precatalyst system to the aziridination of chalcone **1a** using *O*-methylhydroxylamine **3** in place of an alkyl hydroperoxide (Scheme 1).

Although the chiral lanthanum complex in-situ prepared from La(O-*i*-Pr)$_3$, (*R*)-BINOL and Ph_3PO (1:1:3) or La(O-*i*-Pr)$_3$, (*R*)-BINOL and Et_3N (1:1:3) promoted the desired reaction with notable enantioselectivities (38% and 72% ee, respectively), the yields of the aziridine did not exceed the amount of the complex used.[11–14] Therefore, we turned our attention to a stepwise process, the Lewis acid-catalyzed

Keywords: *O*-alkylhydroxylamines; 2-acyl aziridine; chiral rare earth metal complex; asymmetric catalysis; asymmetric amplification.

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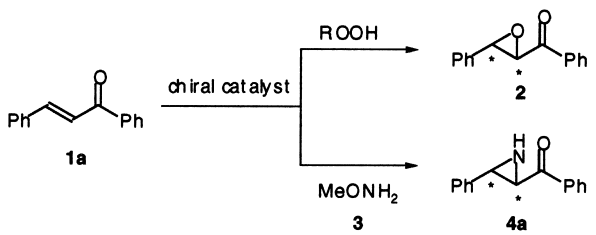
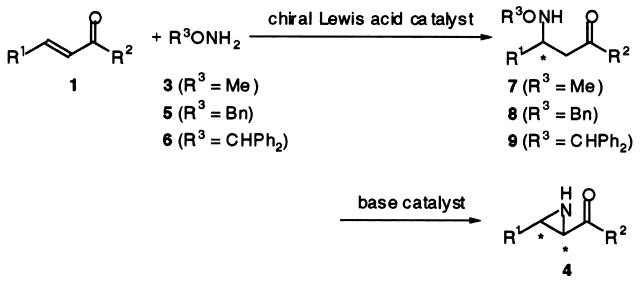
PII: S0040-4020(02)00983-3



Scheme 1.



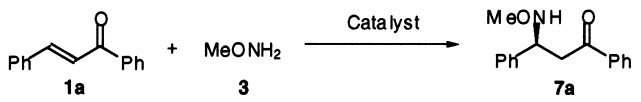
Scheme 2.

enantioselective Michael addition[15] followed by the base-catalyzed aziridine ring formation (Scheme 2).[16,17]

2.1. Chiral Lewis acid-catalyzed asymmetric Michael reaction

The rare earth metal triflate-based chiral complexes (**A**-RE, Fig. 1),[18] prepared in-situ from $RE(OTf)_3$, (*R*)-BINOL, and *N*,*N*-diisopropylethylamine (1:1:2) in an appropriate solvent, were initially examined as a chiral Lewis-acid catalyst for the Michael addition of **3** to **1a** under various conditions. Some selected results are summarized in Table 1. As can be seen in entries 1–3, the scandium and lanthanum

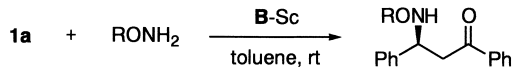
Table 1. Asymmetric Michael addition of **3** to **1a**



Entry	Catalyst	Solvent	Yield (%)[a]	Ee (%)[b]
1	**A**-Sc	THF	74	3
2	**A**-Sc	Toluene	64	14
3	**A**-La	THF	66	12
4	**A**-La	Toluene	30	14
5	**A**-Yb	THF	18	8
6	**A**-Yb	Toluene	14	2
7	**B**-Sc	Toluene	81	57
8[c]	**B**-Sc	Toluene	80	69
9	**B**-Sc	*m*-$(CF_3)_2$Ph	67	53
10	**B**-Sc	PhCl	42	39
11	**B**-Sc	PhOMe	44	60
12	**B**-Sc	CH_2Cl_2	50	33
13	**B**-Sc	AcOEt	36	30
14	**B**-Sc	CH_3CN	59	12
15	**B**-La	Toluene	33	6
16	**B**-Yb	Toluene	57	31

The reaction was carried out at room temperature for 14–18 h under argon in the presence of 10 mol% of the catalyst unless otherwise noted. 1.0–1.2 equiv. of **3** was used.
[a] Isolated yield.
[b] Determined by the HPLC analysis using chiral column.
[c] The reaction was carried out at −20°C for 72 h.

Table 2. Sc[(*R*)-BNP]$_3$-catalyzed asymmetric Michael addition of *O*-alkylhydroxylamine to **1a**



Entry	R	Nucleophile/adduct	Yield (%)[a]	Ee (%)[b]
1	Me	**3/7a**	81	57
2	Bn	**5/8a**	94	91
3	Ph_2CH	**6/9a**	94	99

The reaction was carried out for 18–24 h under argon in the presence of 10 mol% of **B**-Sc.
[a] Isolated yield.
[b] Ee of the crude product determined by the HPLC analysis using chiral column.

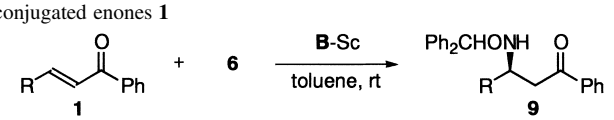
complexes promoted the reaction at room temperature, but the observed enantioselectivities were very low.

We then applied the RE[(*R*)-BNP]$_3$ complex (**B**-RE, Fig. 1) to the above reaction as a catalyst. As shown in Table 1, among the complexes tested, Sc[(*R*)-BNP]$_3$ (**B**-Sc) was found to be the most effective. Thus, the reaction catalyzed by **B**-Sc in toluene afforded the corresponding β-methoxyamino ketone **7a** in good yield with modest enantioselectivity (57% ee) (entry 7). A higher enantioselectivity (69% ee) was obtained by lowering the reaction temperature to −20°C (entry 8), but the use of 2,6-lutidine[8a] or molecular sieves 4A as an additive did not improve either the chemical or optical yields.

We further found that the use of *O*-benzylhydroxylamine **5** or *O*-diphenylmethylhydroxylamine **6**[19] as an amine nucleophile was particularly effective (Table 2). Thus, an almost perfect enantioselectivity (99% ee) was attained at room temperature when **6** was employed (entry 3). The π−π interaction between the phenyl groups of the amine nucleophiles and that of the catalyst may be anticipated because the decrease in the reaction rate due to the bulkiness of the nucleophiles was not significant.

The optimized protocol, i.e. the use of the **B**-Sc catalyst and *O*-diphenylmethylhydroxylamine in toluene, was found to be quite effective for other substrates as shown in Table 3.

Table 3. Sc[(*R*)-BNP]$_3$-catalyzed asymmetric Michael addition of **6** to conjugated enones **1**



Entry	R	**1/9**	Reaction time (h)	Ee (%)[a]
1	Ph	**1a/9a**	48	99
2	4-MePh	**1b/9b**	96	98
3	4-MeOPh	**1c/9c**	133	94
4	4-ClPh	**1d/9d**	48	99
5	3-ClPh	**1e/9e**	72	98
6	4-FPh	**1f/9f**	24	98
7	4-CNPh	**1g/9g**	24	94
8	4-NO_2Ph	**1h/9h**	16	99
9	*i*-Pr	**1i/9i**	72	98

10 mol% of **B**-Sc was used. Isolated yield was >98%.
[a] Ee of the crude product determined by the HPLC analysis using chiral column.

The phenyl group of **1** was adopted in the hope that the phenyl ketone would provide (1) high crystallinity, (2) no oxime formation,[16] and (3) an easy access to the ester group if required. Actually, the desired β-amino ketones (**9**) were quantitatively obtained in excellent ee values, and simple recrystallization of the crude products easily afforded the enantiopure compounds.

2.2. Asymmetric amplification (positive nonlinear effect)

Since Kagan's first report regarding the positive nonlinear effect, such an asymmetric amplification has frequently been observed in various catalytic asymmetric reactions, especially using chiral metal complexes.[20–22] However, most of them are limited within the range of Kagan's ML_2 model (L=chiral ligand),[22a] and a high degree of asymmetric amplification concerning the ML_3 system has not been reported until we found such a phenomenon in the Yb(BNP)$_3$-catalyzed hetero-Diels–Alder reaction.[8b] As expected, the reaction of **1h** with **6** using the enantiomerically impure scandium catalyst showed a remarkably high asymmetric amplification as shown in Fig. 2. For example, **9h** with 97% ee was obtained using the catalyst with 50% ee. The observed positive nonlinear effect suggests that the active catalyst may not be monomeric but rather dimeric or oligomeric, and it may also be explained by the formation of thermodynamically stable heterochiral complexes having almost no catalytic activity as previously discussed in detail.[8b]

2.3. Base-catalyzed aziridine ring formation

In a preliminary experiment, the β-methoxyamino ketone **7a** was first treated with 10 mol% of sodium methoxide in THF at room temperature for 24 h. Unfortunately, the aziridine ring formation did not cleanly proceed thus affording the corresponding **4a** in 62% isolated yield.[17] We anticipated that the high coordination number and strong Lewis acidity of the lanthanoid ions would be effective for the activation of the N–OMe bond through double coordination of the oxygen and nitrogen atoms as shown in Fig. 3. As expected, when 10 mol% of La(O-*i*-Pr)$_3$ or Yb(O-*i*-Pr)$_3$ was employed as a catalyst, the desired ring formation was completed within 4 h at room temperature to give the 2-acyl aziridine **4a** in 99% isolated yield. Any loss in the optical purity of **7a** or the retro-Michael reaction leading back to the chalcone **1a** was not detected.

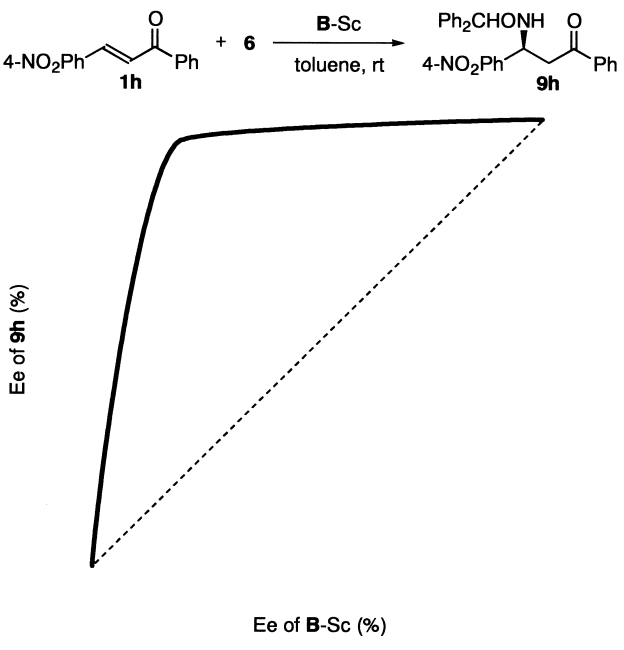


Figure 2. Asymmetric amplification observed in the Sc[(*R*)-BNP]$_3$-catalyzed Michael addition of **6** to **1h**.

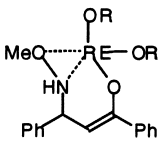


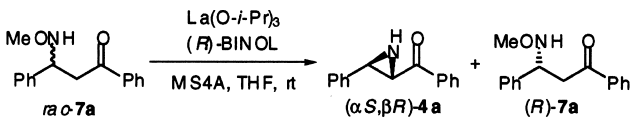
Figure 3.

At this stage, we postulated that if the two OR groups on the metal ion in Fig. 3 are chiral, there must be a difference in the cyclization speed of the two enantiomers, (*R*)-**7a** and (*S*)-**7a**. We then investigated the kinetic resolution of **7a** using a chiral lanthanum alkoxide catalyst prepared in situ from 10 mol% each of La(O-*i*-Pr)$_3$ and (*R*)-BINOL in the presence of molecular sieves 4A. These results are shown in Table 4; 16% yield (maximum 50% in theory) of (*R*)-**7a** with 93% ee was recovered starting from *rac*-**7a** after the 48 h reaction.

Based on these results, (*S*)-enriched **7a** (69% ee, cf. entry 8 in Table 1) was treated with the La(O-*i*-Pr)$_3$–(*S*)-BINOL catalyst and after a 28% conversion, the ee of the recovered (*S*)-**7a** reached 86% (Scheme 3).

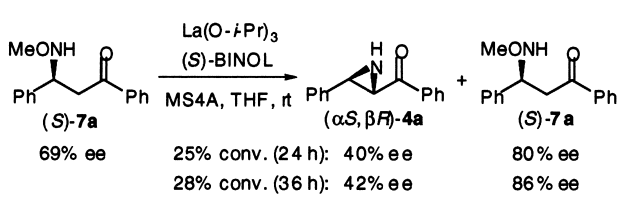
Despite these findings, the dehydroalkoxylation of the *O*-diphenylmethoxyamino ketone **9a** could not cleanly be converted into the aziridine ketone **4a** by the catalysis with La(O-*i*-Pr)$_3$. The bulkiness of the diphenylmethyl group might be responsible for this inefficiency; the N–O bond activation anticipated in Fig. 3 may no longer be possible

Table 4. La(O-*i*-Pr)$_3$-(*R*)-BINOL complex-catalyzed kinetic resolution of racemic **7a**



Entry	Time (h)	Conversion (%)	Ee of **4a** (%)[a]	Ee of **7a** (%)[a]
1	3	25	48	18
2	20	78	22	74
3	48	84	10	93

Ten mol% each of La(O-*i*-Pr)$_3$ and (*R*)-BINOL was used.
[a] Determined by the HPLC analysis using chiral column.



Scheme 3. La(O-*i*-Pr)$_3$–(*S*)-BINOL complex-catalyzed kinetic resolution of (*S*)-enriched **7a**.

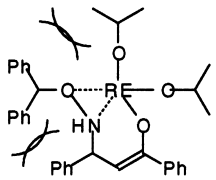
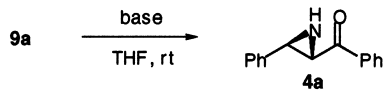


Figure 4.

Table 5. Aziridine ring formation using base catalyst



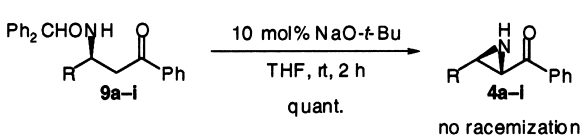
Entry	Base/(mol%)	Reaction time (h)	Yield (%)[a]
1	La(O-*i*-Pr)$_3$/10	24	43
2	Sm(O-*i*-Pr)$_3$/10	48	14
3	Yb(O-*i*-Pr)$_3$/10	48	14
4	NaOMe/100	48	62
5	NaO-*i*-Pr/10	17	46[b]
6	NaO-*t*-Bu/5	20	>99
7	NaO-*t*-Bu/10	2	>99
8	NaO-*t*-Bu/50	Instant.[c]	>99
9	DBU[d]/10	24	NR[e]

[a] Isolated yield.
[b] Benzophenone was also yielded.
[c] The reaction completed instantaneously.
[d] 1,8-Diazabicyclo[5,4,0]undec-7-ene.
[e] No reaction.

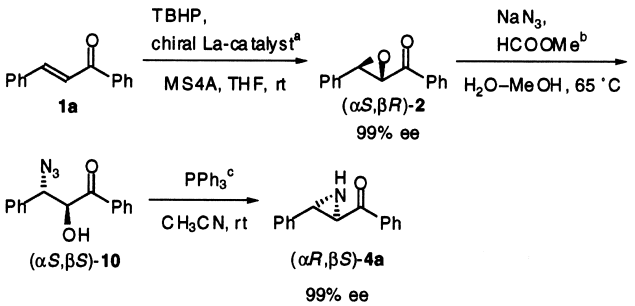
due to the steric repulsion shown in Fig. 4. After some unsuccessful trials, we finally found that the catalytic conversion of **9a** to **4a** was best performed using NaO-*t*-Bu.[17] Thus, the reaction was completed within 2 h at room temperature and **4a** was obtained in quantitative yield without racemization (Table 5). Other bases like NaOMe or NaO-*i*-Pr were found to be much less effective. For example, in the case of NaO-*i*-Pr, **4a** was isolated in 46% yield and a significant amount of benzophenone was detected, which might be derived from sodium diphenylmethoxide via the Meerwein–Pondrof–Verley–Oppennauer process. Organic bases such as DBU did not promote the desired reaction at all.

Other substrates **9b–i** were also quantitatively converted into the corresponding 2-acyl aziridines **4b–i** without losing their enantiopurities (Scheme 4).

The absolute configuration of (α*R*,β*S*)-**4a** was determined by comparing its optical rotation and also its retention time on the HPLC using a chiral column with those of the authentic sample [(α*R*,β*S*)-**4a**, 99% ee] prepared from the corresponding epoxy ketone [(α*S*,β*R*)-**2**, 99% ee], which was obtained by the enantioselective epoxidation of **1a**



Scheme 4.



Scheme 5. The synthesis of (α*R*,β*S*)-**4a**. (a) La(O-*i*-Pr)$_3$-(*R*)-BINOL (1:1, 5 mol%), Ph_3PO (15 mol%), 0.5 h, 99%. (b) 5 h, 39%. (c) 4 h, 66%.

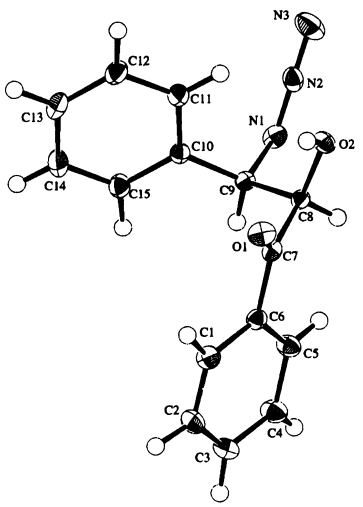


Figure 5. The ORTEP drawing of **10**.

using an efficient catalyst system recently developed in this laboratory,[9] according to the literature methods (Scheme 5).[23] The structure of the (α*S*,β*S*)-α-hydroxy-β-azido ketone **10** was unambiguously determined by an X-ray crystallographic analysis (Fig. 5).

3. Conclusion

The chiral scandium complex, Sc[(*R*)-BNP]$_3$, was found to be an excellent Lewis acid catalyst for the conjugate addition of *O*-diphenylmehylhydroxylamine to α,β-unsaturated ketones thus affording the corresponding β-amino ketones with high ee values (up to 99% ee) in almost quantitative yields. A remarkably high asymmetric amplification (positive nonlinear effect) was observed in this reaction. It was also found that the chiral lanthanum complex prepared in-situ from La(O-*i*-Pr)$_3$ and (*S*)-BINOL, La[(*S*)-binaphthoxide·(O-*i*-Pr)], brought about kinetic resolution of a racemic β-methoxyamino ketone in the dehydromethoxylation step. The aziridine ring-forming reaction of the β-diphenylmethoxyamino ketones could be best performed using a catalytic amount of NaO-*t*-Bu. The catalytic two-step process is so convenient and efficient that the protocol provides an easy access to enantiopure 2-acyl aziridines and their derivatives in good quantities.

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. ^{1}H and ^{13}C NMR spectra were measured on JEOL JNM-EX 400 at 400 MHz and at 100 MHz, respectively. Chemical shifts are given by δ relative to that of internal tetramethylsilane in $CDCl_3$. FAB mass spectra were obtained with JEOL JMS-HX110A. Enantiomeric excesses were determined by high performance liquid chromatography (HPLC) with Shimadzu LC-9A or LC-10ATVP using ∅0.46 cm×25 cm chiral column (Daicel CHIRALCEL OD, CHIRALCEL OB-H or CHIRALPAK AD). The spectra were detected with a Simadzu SPD-6A or SPD-10AV UV-VIS detector and analyzed on Shimadzu C-R6A. Optical rotations were measured on a Horiba SEPA-300 polarimeter. Elemental analyses were accomplished at Center of Elementary Analysis, Faculty of Science, Kyushu University. TLC was performed on a silica gel plate (Merck, Kieselgel 60 F254, 20 cm×20 cm×0.25 mm). Column chromatography was carried out with silica gel as an absorbent (Merck, Kieselgel 60, 70–230 mesh). THF was dried over sodium metal-9-fluorenone.[24] Other solvents were dried over calcium hydride.

4.2. Preparation of catalyst

4.2.1. Typical procedure of the preparation of chiral rare earth phosphate: scandium(*R*)-1,1′-binaphthyl-2,2′-diyl phosphate, Sc[(*R*)-BNP]$_3$ (B-Sc). To a refluxing solution of (*R*)-1,1′-binaphthyl-2,2′-diyl hydrogen phosphate (358 mg, 1.03 mmol) and 3N aqueous sodium hydroxide (0.333 ml, 0.999 mmol) in methanol (7 ml) was slowly added a solution of scandium chloride hexahydrate (84.4 mg, 0.326 mmol) in methanol–water, and the resulting mixture was stirred for 12 h under same conditions. After cooling the suspension to room temperature, the precipitate was filtered and wash with methanol. The colorless solid was dried at 120°C for 15 h in vacuo to give Sc[(*R*)-BNP]$_3$·3H$_2$O (325 mg, 87%). IR (KBr): 3060, 1621, 1592, 1509, 1466, 1328, 1237, 1210, 1155, 1109, 1071, 993, 968, 949, 888, 871, 816, 750, 722, 659, 568 cm^{-1}. $[\alpha]_D^{25}=-492.2$ (*c* 1.06, THF). Anal. calcd for $C_{60}H_{36}O_{12}P_3Sc\cdot 3H_2O$: C, 63.17; 3.71. Found: C, 63.27; H, 3.55. This catalyst was dried again for 5 min by heat-gun under vacuum just before use.

4.2.2. Lanthanum (*R*)-1,1′-binaphthyl-2,2′-diyl phosphate, La[(*R*)-BNP]$_3$ (B-La). Colorless solid. IR (KBr): 3060, 1620, 1592, 1508, 1466, 1392, 1238, 1215, 1103, 1071, 992, 965, 945, 867, 841, 817, 750, 720, 659, 595, 582, 568, 538, 495 cm^{-1}. $[\alpha]_D^{25}=-356.0$ (*c* 1.00, THF). Anal. calcd for $C_{60}H_{36}O_{12}P_3La\cdot H_2O$: C, 60.12; 3.20. Found: C, 59.72; H, 3.30.

4.2.3. Ytterbium (*R*)-1,1′-binaphthyl-2,2′-diyl phosphate, Yb[(*R*)-BNP]$_3$ (B-Yb). Colorless solid. IR (KBr): 3616, 3065, 1621, 1592, 1509, 1466, 1329, 1238, 1215, 1112, 1071, 967, 945, 870, 817, 750, 568 cm^{-1}. $[\alpha]_D^{25}=-395.0$ (*c* 1.00, THF). Anal. calcd for $C_{60}H_{36}O_{12}P_3Yb\cdot H_2O$: C, 58.45; 3.11. Found: C, 58.17; H, 3.11.

4.3. Chiral lanthanide complex-catalyzed Michael addition of *O*-alkylhdroxylamines

4.3.1. Asymmetric reacton of chalcone (1a) with *O*-methylhydroxylamine (3) catalyzed by Sc(OTf)$_3$-BINOL-*i*-Pr$_2$NEt complex (A-Sc). To a mixture of Sc(OTf)$_3$ (4.9 mg, 0.01 mmol) and (*R*)-1,1′-bi-2-naphthol (2.9 mg, 0.01 ml) in dry THF (0.5 ml) was added *N*,*N*-diisopropylethylamine (2.6 mg, 0.02 mmol) under Ar, and the solution was stirred at room temperature for 1 h. After addition of chalcone (31.5 mg, 0.11 mmol) and 0.2 M *O*-methylhydroxylamine in THF (0.55 ml, 0.11 mmol), the resulting solution was stirred for 18 h at room temperature, and passed through a short column of silica gel. The eluent was evaporated and the residue was purified by preparative TLC (AcOEt–hexana 1:4) to give 3-methoxyamino-1,3-diphenylpropan-1-one **7a** (18.9 mg, 74%) as a colorless crystal.

4.3.2. Typical procedure of the RE[(*R*)-BNP]$_3$-catalyzed Michael addition: synthesis of (3*S*)-1,3-diphenyl-3-diphenylmethoxyaminopropan-1-one (9a). To a suspension of Sc[(*R*)-BNP]$_3$·3H$_2$O (10.9 mg, 0.01 mmol) in dry toluene (1 ml) were successively added **1a** (20.8 mg, 0.1 mmol) and **6** (31.9 mg, 0.16 mmol) under Ar, and the mixture was stirred for 24 h at room temperature. The reaction mixture was passed through a short column of silica gel. The eluent was evaporated and the residue was purified by column chromatography on silica gel (hexane–AcOEt 4:1) to give **9a** (40.4 mg, 99%) as colorless needles. Mp 79.5–79.7°C. R_f 0.42 (AcOEt–hexane 1:4). $[\alpha]_D^{26}=-23.3$ (*c* 1.00, $CHCl_3$, 99.8% ee by the HPLC analysis). HPLC (CHIRALPAK AD, 2-propanol–hexane 1:19, 0.5 ml/min): t_R 23.9 min for the major enantiomer (30.5 min for the minor one). IR (KBr): 3062, 3030, 2899, 1671, 1596, 1493, 1450, 1349, 1280, 1207, 1182, 1079, 1006, 985, 921, 847, 747, 705, 657, 599, 411 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 3.30 (1H, dd, *J*=4.9, 17.3 Hz), 3.50 (1H, dd, *J*=8.1, 17.3 Hz), 4.78 (1H, dd, *J*=4.9, 8.1 Hz), 5.53 (1H, s), 6.18 (1H, s), 6.95–6.98 (2H, m), 7.15–7.53 (16H, m), 7.85–7.87 (2H, m). ^{13}C NMR ($CDCl_3$, δ): 42.68, 61.22, 86.93, 127.21, 127.43, 127.48, 127.70, 127.91, 128.06, 128.12, 128.34, 128.45, 128.53, 141.25, 141.30, 198.32. Anal. calcd for $C_{28}H_{25}NO_2$: C, 82.53; H, 6.18; N, 3.44. Found: C, 82.56; H, 6.16; N, 3.43.

4.3.3. (3*S*)-1,3-Diphenyl-3-methoxyaminopropan-1-one (7a). R_f 0.30 (AcOEt–hexane 1:4). $[\alpha]_D^{22}=-9.5$ (*c* 1.00, $CHCl_3$, 50% ee by the HPLC analysis). HPLC (CHIRALPAK OD, 2-propanol–hexane 1:50, 0.5 ml/min): t_R 17.5 min for the major enantiomer (23.8 min for the minor one). ^{1}H NMR ($CDCl_3$, δ): 3.28 (1H, dd, *J*=4.9, 17.1 Hz), 3.40 (3H, s), 3.49 (1H, dd, *J*=8.3, 17.2 Hz), 4.69 (1H, dd, *J*=5.0, 8.2 Hz), 6.20 (1H, s), 7.26–7.53 (8H, m), 7.90 (2H, t). ^{13}C NMR ($CDCl_3$, δ): 42.44, 60.80, 61.97, 127.38, 127.46, 127.84, 128.26, 128.37, 133.00, 136.56, 140.90, 198.07. CAS registry no. 52322-76-6 (*rac*).

4.3.4. 3-Benzyloxyamino-1,3-diphenylpropan-1-one (8a). Colorless solid. Mp 80.9–81.1°C. R_f 0.52 (AcOEt–hexane 1:4). HPLC (CHIRALPAK AD, ethanol–hexane 1:19, 0.5 ml/min): t_R 39.3 min for the major enantiomer (35.4 min for the minor one). IR (KBr): 3282, 3026, 2908,

1671, 1596, 1496, 1449, 1409, 1369, 1276, 1230, 1131, 1067, 1003, 984, 759, 742, 701, 605, 583 cm^{-1}. ^1H NMR (CDCl3, δ): 3.29 (1H, dd, J=4.9, 17.1 Hz), 3.49 (1H, dd, J=7.8, 17.1 Hz), 4.52 and 4.56 (2H, each d, J=11.7 Hz), 4.71 (1H, d, J=4.9, 7.8 Hz), 6.18 (1H, s), 7.18–7.45 (12H, m), 7.54 (1H, t, J=7.3 Hz), 7.89 (2H, d, J=7.3 Hz). ^{13}C NMR ($CDCl_3$, δ): 42.65, 61.14, 127.71, 127.76, 128.06, 128.26, 128.46, 128.55, 133.19, 136.74, 137.60, 141.02, 198.30. Anal. calcd for $C_{22}H_{21}NO_2$: C, 79.67; H, 6.40; N, 4.20. Found: C, 79.73; H, 6.39; N, 4.23.

4.3.5. 3-Diphenylmethoxyamino-3-(4-methylphenyl)-1-phenyl-propan-1-one (9b). Colorless solid. Mp 93.7–93.9°C. R_f 0.44 (AcOEt–hexana 1:4). $[\alpha]_D^{26}=-21.4$ (c 1.00, $CHCl_3$, 99.7% ee by the HPLC analysis). HPLC (CHIRALPAK AD, 2-propanol–hexane 1:19, 0.5 ml/min): t_R 24.0 min for the major enantiomer (35.3 min for the minor one). IR (KBr): 3255, 3062, 3029, 2888, 1960, 1678, 1597, 1582, 1511, 1496, 1449, 1402, 1360, 1343, 1277, 1204, 1008, 984, 814, 752, 700, 419 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 2.34 (3H, s), 3.28 (1H, dd, J=5.1, 17.3 Hz), 3.51 (1H, dd, J=7.9, 17.3 Hz), 4.74 (1H, dd, J=5.1, 7.9 Hz), 5.55 (1H, s), 6.10 (1H, s), 7.01–7.03 (2H, m), 7.14–7.40 (14H, m), 7.51 (1H, t, J=7.1 Hz), 7.85 (2H, d, J=7.1 Hz). ^{13}C NMR ($CDCl_3$, δ): 21.13, 42.76, 60.98, 86.89, 127.23, 127.41 127.46, 127.79, 128.06, 128.13, 128.31, 128.50, 129.11, 133.12, 136.76, 137.33, 138.09, 141.21, 141.36, 198.40. Anal. calcd for $C_{29}H_{27}NO_2$: C, 82.63; H, 6.46; N, 3.32. Found: C, 82.61; H, 6.47; N, 3.32.

4.3.6. 3-Diphenylmethoxyamino-3-(4-methoxyphenyl)-1-phenylpropan-1-one (9c). Colorless solid. Mp 105.7–105.8°C. R_f 0.32 (AcOEt–hexane 1:4). $[\alpha]_D^{20}=-24.7$ (c 1.00, $CHCl_3$, >99.8% ee by the HPLC analysis). HPLC (CHIRALPAK AD, 2-propanol–hexane 1:19, 0.5 ml/min): t_R 38.4 min for the major enantiomer (52.1 min for the minor one). IR (KBr): 3060, 3030, 2887, 1678, 1512, 1452, 1244, 1207, 1176, 1028, 835, 752, 702 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 3.28 (1H, dd, J=5.4, 17.1 Hz), 3.51 (1H, dd, J=7.8, 17.1 Hz), 3.81 (3H, s), 4.73 (1H, dd, J=5.4, 7.8 Hz), 5.53 (1H, s), 6.08 (1H, s), 6.87 (2H, d, J=8.5 Hz), 7.03–7.04 (1H, m), 7.18–7.42 (12H, m), 7.52 (1H, t, J=7.3 Hz), 7.86 (2H, d, J=7.3 Hz). ^{13}C NMR ($CDCl_3$, δ): 42.77, 55.29, 60.64, 86.93, 113.80, 127.22, 127.43, 127.45, 128.07, 128.16, 128.32, 128.52, 129.02, 133.14, 136.78, 141.22, 141.37, 159.13, 198.45. Anal. calcd for $C_{29}H_{27}NO_3$: C, 79.61; H, 6.22; N, 3.20. Found: C, 79.50; H, 6.22; N, 3.25.

4.3.7. 3-(4-Chlorophenyl)-3-diphenylmethoxyamino-1-phenylpropan-1-one (9d). Colorless needles. Mp 135.5–135.7°C. R_f 0.44 (AcOEt–hexane 1:4). $[\alpha]_D^{26}=-22.1$ (c 1.00, $CHCl_3$, 99.7% ee by the HPLC analysis). HPLC (CHIRALPAK AD, 2-propanol–hexane 1:19, 0.5 ml/min): t_R 27.5 min for the major enantiomer (40.1 min for the minor one). IR (KBr): 3264, 3063, 3025, 2905, 2873, 2360, 1680, 1490, 1450, 1356, 1270, 1202, 1090, 1003, 816, 750, 701, 688, 542, 418 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 3.18 (1H, dd, J=5.1, 17.6 Hz), 3.38 (1H, dd, J=7.9, 17.6 Hz), 4.67 (1H, dd, J=5.1, 7.9 Hz), 5.44 (1H, s), 6.09 (1H, s), 6.91–6.94 (2H, m), 7.11–7.26 (10H, m), 7.30–7.35 (4H, m), 7.46 (1H, t, J=7.3 Hz), 7.77–7.79 (2H, m). ^{13}C NMR ($CDCl_3$, δ): 42.40, 60.47, 87.03, 127.16, 127.39, 127.51, 128.02, 128.18, 128.38, 128.56, 128.59, 129.26, 133.34, 136.53, 139.87, 140.97, 141.19, 197.96. Anal. calcd for $C_{28}H_{24}ClNO_2$: C, 76.09; H, 5.47; N, 3.17. Found: C, 76.10; H, 5.48; N, 3.15.

4.3.8. 3-(3-Chlorophenyl)-3-diphenylmethoxyamino-1-phenylpropan-1-one (9e). Colorless needles. Mp 93.6–93.8°C. R_f 0.46 (AcOEt–hexana 1:4). $[\alpha]_D^{19}=-24.9$ (c 1.00, $CHCl_3$, 99.8% ee by the HPLC analisis). HPLC (CHIRALPAK AD, 2-propanol–hexane 1:19, 0.5 ml/min): t_R 20.8 min for the major enantiomer (25.4 min for the minor one). IR (KBr): 3263, 3063, 3029, 2902, 1675, 1597, 1449, 1424, 1359, 1299, 1273, 1204, 1070, 1003, 791, 748, 701, 686, 606 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 3.26 (1H, dd, J=4.6, 17.6 Hz), 3.46 (1H, dd, J=8.3, 17.6 Hz), 4.74 (1H, dd, J=4.6, 8.3 Hz), 5.52 (1H, s), 6.21 (1H, s), 6.98–7.01 (2H, m), 7.19–7.35 (11H, m), 7.41 (2H, t, J=7.8 Hz), 7.47 (1H, s), 7.54 (1H, t, J=7.3 Hz), 7.85–7.87 (2H, m). ^{13}C NMR ($CDCl_3$, δ): 42.28, 60.63, 87.07, 126.19, 127.21, 127.41, 127.53, 127.82, 128.04, 128.19, 128.40, 128.60, 129.70, 133.38, 134.27, 136.49, 140.91, 141.12, 143.53, 197.88. Anal. calcd for $C_{28}H_{24}ClNO_2$: C, 76.09; H, 5.47; N, 3.17. Found: C, 76.07; H, 5.50; N, 3.15.

4.3.9. 3-Diphenylmethoxyamino-3-(4-fluorophenyl)-1-phenylpropan-1-one (9f). Colorless solid. Mp 115.4–115.6°C. R_f 0.44 (AcOEt–hexana 1:4). $[\alpha]_D^{25}=-24.0$ (c 1.00, $CHCl_3$, 99.4% ee by the HPLC analisis). HPLC (CHIRALPAK AD, 2-propanol–hexane 1:19, 0.5 ml/min): t_R 25.7 min for the major enantiomer (34.6 min for the minor one). IR (KBr): 3267, 3062, 3030, 2905, 2889, 1677, 1601, 1506, 1450, 1353, 1271, 1204, 1152, 1082, 1003, 980, 842, 752, 701, 687, 546 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 3.26 (1H, dd, J=5.1, 17.3 Hz), 3.47 (1H, dd, J=7.8, 17.3 Hz), 4.76 (1H, dd, J=5.1, 7.8 Hz), 5.51 (1H, s), 6.15 (1H, s), 7.00–7.05 (2H, m), 7.19–7.34 (8H, m), 7.39–7.43 (4H, m), 7.54 (1H, dt, J=0.7, 7.6 Hz), 7.86 (2H, d, J=7.6 Hz). ^{13}C NMR ($CDCl_3$, δ): 42.59, 60.45, 87.03, 115.13, 115.34, 127.17, 127.40, 127.50, 128.04, 128.18, 128.38, 128.58, 129.44, 129.52, 133.30, 136.60, 137.01, 137.04, 141.02, 141.23, 161.04, 163.48, 198.11. Anal. calcd for $C_{28}H_{24}FNO_2$: C, 79.04; H, 5.67; N, 3.29. Found: C, 79.05; H, 5.73; N, 3.29.

4.3.10. 3-Diphenylmethoxyamino-1-phenyl-3-(4-cyanophenyl)propan-1-one (9g). Colorless solid. Mp 139.0–139.2°C. R_f 0.36 (AcOEt–hexana 1:4). $[\alpha]_D^{19}=-34.5$ (c 1.00, $CHCl_3$, >99.8% ee by the HPLC analysis). HPLC (CHIRALPAK AD, 2-propanol–hexane 1:19, 1.0 ml/min): t_R 47.1 min for the major enantiomer (57.8 min for the minor one). IR (KBr): 3259, 3064, 3030, 2890, 2232, 1678, 1450, 1359, 1276, 1207, 1002, 984, 839, 764, 750, 703, 685, 562, 403 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 3.26 (1H, dd, J=5.0, 17.8 Hz), 3.43 (1H, dd, J=8.1, 17.8 Hz), 4.82 (1H, br s), 5.51 (1H, s), 6.25 (1H, s), 6.96–6.98 (2H, m), 7.19–7.20 (3H, m), 7.24–7.34 (5H, m), 7.41 (2H, t, J=7.6 Hz), 7.53–7.63 (5H, m), 7.84–7.86 (2H, m). ^{13}C NMR ($CDCl_3$, δ): 41.98, 60.62, 87.07, 111.34, 118.78, 127.06, 127.26, 127.44, 127.58, 127.97, 128.18, 128.42, 128.59, 128.63, 132.20, 133.54 136.23, 140.71, 140.94, 147.03, 197.40. Anal. calcd for $C_{29}H_{24}N_2O_2$: C, 80.53; H, 5.59; N, 6.48. Found: C, 80.49; H, 5.63; N, 6.46.

4.3.11. 3-Diphenylmethoxyamino-3-(4-nitrophenyl)-1-phenylpropan-1-one (9h). Yellow needles. Mp 138.1–138.3°C. R_f 0.29 (AcOEt–hexane 1:4).

$[\alpha]_D^{25}=-32.5$ (*c* 1.00, $CHCl_3$, >99.8% ee by the HPLC analysis). HPLC (CHIRALPAK AD, 2-propanol–hexane 1:9, 0.5 ml/min): t_R 46.1 min for the major enantiomer (60.9 min for the minor one). IR (KBr): 3260, 3062, 3030, 2902, 2880, 1682, 1598, 1515, 1450, 1274, 1205, 1002, 980, 754, 701, 688, 626, 540 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 3.28 (1H, dd, *J*=5.0, 17.6 Hz), 3.46 (1H, dd, *J*=8.1, 17.6 Hz), 4.87 (1H, dd, *J*=5.0, 8.1 Hz), 5.53 (1H, s), 6.27 (1H, s), 6.98–6.99 (2H, m), 7.18–7.34 (8H, m), 7.43 (2H, t, *J*=7.8 Hz), 7.56 (1H, dt, *J*=1.2, 8.1 Hz), 7.62 (2H, d, *J*=8.1 Hz), 7.86 (2H, d, *J*=8.5 Hz), 8.19 (2H, d, *J*=7.8 Hz). ^{13}C NMR ($CDCl_3$, δ): 42.05, 60.43, 87.14, 123.64, 127.11, 127.29, 127.64, 127.67, 128.02, 128.23, 128.48, 128.70, 133.63, 136.25, 140.74, 140.96, 147.39, 149.14, 197.33. Anal. calcd for $C_{28}H_{24}N_2O_4$: C, 74.32; H, 5.35; N, 6.19. Found: C, 74.44; H, 5.41; N, 6.18.

4.3.12. 3-Diphenylmethoxyamino-4-methyl-1-phenylpentan-1-one (9i). An oil. R_f 0.46 (AcOEt–hexane 1:4). $[\alpha]_D^{23}=-38.4$ (*c* 1.58, $CHCl_3$, 97.8% ee by the HPLC analysis). HPLC (CHIRALPAK AD, ethanol–hexane 1:300, 0.5 ml/min): t_R 25.1 min for the major enantiomer (20.7 min for the minor one). IR (KBr): 2959, 2360, 1734, 1717, 1684, 1653, 1558, 1541, 1521, 1507, 1456, 745, 696, 668, 484, 468, 458 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 0.94 (3H, d, *J*=6.8 Hz), 0.98 (3H, d, *J*=6.8 Hz), 2.03–2.11 (1H, m), 2.99 (1H, dd, *J*=4.2, 16.6 Hz), 3.20 (1H, dd, *J*=8.3, 16.6 Hz), 3.36–3.41 (1H, m), 5.63 (1H, s), 5.88 (1H, s), 7.21–7.29 (10H, m), 7.42 (2H, t, *J*=7.8 Hz), 7.54 (1H, t, *J*=7.3 Hz), 7.91 (2H, d, *J*=7.3 Hz). ^{13}C NMR ($CDCl_3$, δ): 18.56, 19.39, 29.20, 37.40, 62.31, 86.52, 127.02, 127.16, 127.30, 127.36, 128.08, 128.23, 128.45, 132.91, 137.20, 141.61, 141.71, 199.92. HRMS-FAB (*m*/*z*): [M+H] calcd for $C_{25}H_{28}NO_2$, 374.2120; found, 374.2125.

4.4. Base-catalyzed aziridine ring formation

4.4.1. Synthesis of (2*S*,3*R*)-2-Benzoyl-3-phenylaziridine (4a). To a solution of **9a** (20.35 mg, 0.05 mmol) in dry THF (0.5 ml) was added NaO-*t*-Bu (0.1 M in THF, 50 μl, 0.005 mmol) under Ar and the mixture was stirred for 1.5 h at room temperature. The reaction mixture was passed through a short column of silica gel, the eluent was evaporated, and the residue was purified by chromatography on silica gel (AcOEt–hexane 1:8) to give (2*S*,3*R*)-**4a** (11.2 mg, 100%) as a colorless solid. Mp 124.6–124.8°C. R_f 0.34 (AcOEt–hexane 1:4). $[\alpha]_D^{19}=+268.7$ (*c* 1.00, $CHCl_3$, 99.8% ee by the HPLC analysis). HPLC (CHIRALCEL OD, 2-propanol–hexane 1:19, 0.5 ml/min): t_R 21.4 min for the major enantiomer (27.8 min for the minor one). IR (KBr): 3222, 1660, 1449, 1413, 1264, 1032, 1011, 844, 756, 698, 594, 529 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 2.67 (1H, br t), 3.18 (1H, br d, *J*=7.1 Hz), 3.51 (1H, br d, *J*=5.6 Hz), 7.29–7.39 (5H, m), 7.47–7.51 (2H, m), 7.60–7.63 (1H, m), 7.99–8.01 (2H, m). ^{13}C NMR ($CDCl_3$, δ): 43.51, 44.07, 126.18, 127.86, 128.30, 128.53, 128.79, 133.79, 135.89, 138.30, 195.68. Anal. calcd for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.49; H, 5.90; N, 6.22. CAS registry no. 74280-88-9 (2*S*,3*R*), 7570-84-5 (2*R*,3*S*), 65309-87-7 (2*R*,3*S*).

4.4.2. *trans*-2-Benzoyl-3-(4-methylphenyl)aziridine (4b). Yellow solid. Mp 88.8–90.0°C. R_f 0.37 (AcOEt–hexane 1:4). $[\alpha]_D^{19}=+311.7$ (*c* 1.00, $CHCl_3$, 99.7% ee by the HPLC analysis). HPLC (CHIRALCEL OD, 2-propanol–hexane 1:19, 0.5 ml/min): t_R 16.6 min for the major enantiomer (23.5 min for the minor one). IR (KBr): 3216, 1657, 1450, 1398, 1266, 1234, 1042, 1010, 855, 807, 783, 692, 529 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 2.36 (3H, s), 2.65 (1H, br s), 3.15 (1H, br s), 3.48 (1H, br s), 7.17 (2H, d, *J*=8.1 Hz), 7.26 (2H, d, *J*=8.1 Hz), 7.45–7.50 (2H, m), 7.58–7.63 (1H, m), 7.98–8.00 (2H, m). ^{13}C NMR ($CDCl_3$, δ): 21.16, 43.50, 44.18, 126.07, 128.78, 129.23, 133.75, 135.35, 135.94, 137.66, 195.77. Anal. calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 80.94; H, 6.38; N, 5.94. CAS registry no. 101854-88-0 (2*R*,3*S*).

4.4.3. *trans*-2-Benzoyl-3-(4-methoxylphenyl)aziridine (4c). An orange oil. R_f 0.22 (AcOEt–hexane 1:4). $[\alpha]_D^{20}=+334.2$ (*c* 1.00, $CHCl_3$, >99.8% ee by the HPLC analysis). HPLC (CHIRALCEL OD, 2-propanol–hexane 1:19, 0.5 ml/min): t_R 28.1 min for the major enantiomer (43.5 min for the minor one). IR (KBr): 3264, 2836, 1666, 1612, 1516, 1450, 1403, 1303, 1252, 1177, 1033, 814, 693 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 2.65 (1H, br s), 3.14 (1H, br d, *J*=2.2 Hz), 3.48 (1H, br d, *J*=2.4 Hz), 3.81 (3H, s), 6.88–6.90 (2H, m), 7.28–7.30 (2H, m), 7.46–7.50 (2H, m), 7.58–7.62 (1H, m), 7.98–8.00 (2H, m). ^{13}C NMR ($CDCl_3$, δ): 43.34, 44.11, 55.29, 113.97, 127.29, 128.27, 128.77, 130.34, 133.74, 135.93, 159.39, 195.72. HRMS-FAB (*m*/*z*): [M+H] calcd for $C_{16}H_{16}NO_2$, 254.1181; found, 254.1211.

4.4.4. *trans*-2-Benzoyl-3-(4-chlorophenyl)aziridine (4d). Yellow needles. Mp 97.2–97.4°C. R_f 0.37 (AcOEt–hexane 1:4). $[\alpha]_D^{19}=+291.9$ (*c* 1.00, $CHCl_3$, 99.7% ee by the HPLC analysis). HPLC (CHIRALCEL OD, 2-propanol–hexane 1:4, 0.5 ml/min): t_R 12.7 min for the major enantiomer (20.4 min for the minor one). IR (KBr): 3278, 1659, 1450, 1394, 1259, 1234, 1008, 812, 705 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 2.68 (1H, br t), 3.15 (1H, br d, *J*=6.8 Hz), 3.45 (1H, br d, *J*=5.6 Hz), 7.29–7.35 (4H, m), 7.50 (2H, t, *J*=7.3 Hz), 7.63 (1H, t, *J*=7.3 Hz), 7.97–8.00 (2H, m). ^{13}C NMR ($CDCl_3$, δ): 42.76, 44.06, 126.51, 127.53, 128.29, 128.46, 128.72, 128.86, 133.66, 133.94, 135.77, 136.87, 195.37. Anal. calcd for $C_{15}H_{12}ClNO$: C, 69.91; H, 4.69; N, 5.43. Found: C, 70.08; H, 4.67; N, 5.51. CAS registry no. 10854-87-9 (2*R*,3*S*).

4.4.5. *trans*-2-Benzoyl-3-(3-chlorophenyl)aziridine (4e). An oil. R_f 0.52 (AcOEt–hexane 1:4). $[\alpha]_D^{19}=+277.8$ (*c* 1.04, $CHCl_3$, 99.8% ee by the HPLC analysis). HPLC (CHIRALCEL OD, 2-propanol–hexane 1:19, 0.5 ml/min): t_R 19.2 min for the major enantiomer (43.6 min for the minor one). IR (KBr): 3266, 1667, 1599, 1578, 1449, 1408, 1259, 1228, 1010, 773, 712, 688 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 2.68 (1H, br t, *J*=8.5 Hz), 3.14 (1H, dd, *J*=2.2, 9.3 Hz), 3.48 (1H, dd, *J*=2.2, 8.1 Hz), 7.24–7.28 (3H, m), 7.36 (1H, s), 7.47–7.51 (2H, m), 7.59–7.64 (1H, m), 7.97–8.00 (2H, m). ^{13}C NMR ($CDCl_3$, δ): 42.63, 43.90, 124.55, 126.15, 127.99, 128.29, 128.82, 129.75, 133.93, 134.57, 135.68, 140.45, 195.26. Anal. calcd for $C_{15}H_{12}ClNO$: C, 69.91; H, 4.69; N, 5.43. Found: C, 69.87; H, 4.73; N, 5.40.

4.4.6. *trans*-2-Benzoyl-3-(4-fluorophenyl)aziridine (4f). Yellow solid. Mp 71.8–72.0°C. R_f 0.34 (AcOEt–hexana 1:4). $[\alpha]_D^{19}=+234.6$ (*c* 1.00, $CHCl_3$, 99.4% ee by the HPLC

analysis). HPLC (CHIRALCEL OD, 2-propanol–hexane 1:4, 0.5 ml/min): t_R 12.9 min for the major enantiomer (23.9 min for the minor one). IR (KBr): 3260, 1659, 1598, 1510, 1449, 1397, 1264, 1215, 1032, 1013, 817, 690 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 2.67 (1H, br s), 3.16 (1H, br s), 3.46 (1H, br s), 7.01–7.08 (2H, m), 7.32–7.36 (2H, m), 7.5 (2H, t, J=8.1 Hz), 7.63 (1H, dt, J=1.2, 7.8 Hz), 7.99 (2H, dd, J=1.0, 8.1 Hz). ^{13}C NMR ($CDCl_3$, δ): 42.82, 44.04, 115.38, 115.60, 127.76, 127.84, 128.30, 128.86, 133.90, 134.07, 134.10, 135.87, 161.28, 163.73, 195.52. Anal. calcd for $C_{15}H_{12}FNO$: C, 74.67; H, 5.01; N, 5.81. Found: C, 74.31; H, 5.06; N, 5.84. CAS registry no. 101854-86-8 (2*R*,3*S*).

4.4.7. *trans*-2-Benzoyl-3-(4-cyanophenyl)aziridine (4g). Yellow solid. Mp 113.5–113.7°C. R_f 0.18 (AcOEt–hexane 1:4). $[\alpha]_D^{19}$=+326.3 (*c* 1.00, $CHCl_3$, >99.8% ee by the HPLC analysis). HPLC (CHIRALCEL OD, 2-propanol–hexane 1:4, 0.5 ml/min): t_R 26.7 min for the major enantiomer (36.5 min for the minor one). IR (KBr): 3273, 3072, 2224, 1658, 1450, 1261, 1232, 1009, 815, 683 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 2.74 (1H, br t, J=8.3 Hz), 3.21 (1H, dd, J=2.2, 9.1 Hz), 3.49 (1H, dd, J=2.2, 8.3 Hz), 7.48–7.53 (4H, m), 7.63–7.67 (3H, m), 7.97–7.99 (2H, m). ^{13}C NMR ($CDCl_3$, δ): 42.50, 44.10, 111.61, 118.67, 126.99, 128.33, 128.94, 132.38, 134.16, 135.60, 143.80, 194.91. Anal. calcd for $C_{16}H_{12}N_2O$: C, 77.40; H, 4.87; N, 11.28. Found: C, 77.36; H, 4.94; N, 11.22.

4.4.8. *trans*-2-Benzoyl-3-(4-nitrophenyl)aziridine (4h). An orange solid. Mp 136.8–137.0°C. R_f 0.25 (AcOEt–hexane 1:4). $[\alpha]_D^{19}$=+282.5 (*c* 1.00, $CHCl_3$, >99.8% ee by the HPLC analysis). HPLC (CHIRALCEL OD, 2-propanol–hexane 1:4, 0.5 ml/min): t_R 27.9 min for the major enantiomer (39.4 min for the minor one). IR (KBr): 3266, 1667, 1601, 1516, 1449, 1345, 1261, 1232, 1019, 829, 746, 709 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 2.78 (1H, br t, J=8.5 Hz), 3.26 (1H, dd, J=2.2, 9.1 Hz), 3.51 (1H, dd, J=2.2, 8.1 Hz), 7.49–7.56 (4H, m), 7.63–7.67 (1H, m), 7.98–8.00 (2H, m), 8.23 (2H, d, J=8.5 Hz). ^{13}C NMR ($CDCl_3$, δ): 42.28, 44.16, 123.85, 127.09, 128.35, 128.97, 134.21, 135.58, 145.80, 147.60, 194.83. Anal. calcd for $C_{15}H_{12}N_2O_3$: C, 67.16; H, 4.51; N, 10.44. Found: C, 67.20; H, 4.56; N, 10.42. CAS registry No. 76336-95-3 (2*R*,3*S*), 51659-22-4 (*rac*).

4.4.9. *trans*-2-Benzoyl-3-(2-propyl)aziridine (4i). An oil. R_f 0.22 (AcOEt–hexane 1:4). $[\alpha]_D^{22}$=−27.8 (*c* 1.56, $CHCl_3$, 97.7% ee by the HPLC analysis). HPLC (CHIRALCEL OD, 2-propanol–hexane 1:19, 0.5 ml/min): t_R 12.1 min for the major enantiomer (20.3 min for the minor one). IR (neat): 2961, 1669, 1598, 1450, 1421, 1356, 1259, 1019, 940, 859, 700, 516 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 1.05 (3H, d, J=6.8 Hz), 1.09 (3H, d, J=6.8 Hz), 1.47–1.56 (1H, m), 1.98 (1H, dd, J=2.2, 7.8 Hz), 2.14 (1H, br s), 3.32 (1H, d, J=2.2 Hz), 7.50–7.54 (2H, m), 7.60–7.64 (1H, m), 8.03–8.05 (2H, m). ^{13}C NMR (CDCl3, δ): 19.62, 20.18, 32.05, 38.96, 49.72, 128.05, 128.72, 133.54, 136.04, 197.18. HRMS-FAB (*m*/*z*): [M+H] calcd for $C_{12}H_{16}NO$, 190.1232; found, 190.1233. CAS registry no. 167707-87-1 (2*R*,3*S*).

4.5. Determination of absolute configuration of 4a

4.5.1. (2*S*,3*S*)-3-Azido-1,3-diphenyl-2-hydroxypropan-1-one (10). To a solution of (2*S*,3*R*)-2,3-epoxy-1,3-diphenylpropan-1-one **3**[9b,c] (280 mg, 1.2 mmol) in water–methanol (1:6, 7 ml) was added methyl formate (1 ml) and sodium azide (350 mg, 5.4 mmol), and the resulting solution was stirred for 5 h at 60°C and passed through a short column of anhydrous $MgSO_4$ on silica gel. The eluent was evaporated, and the residue was subjected to column chromatography on silica gel (AcOEt–hexane 1:30) to give the desired (2*S*,3*S*)-**10** (131 mg, 39%) as a colorless crystal. Mp 86.1–86.9°C. R_f 0.31 (AcOEt–hexane 1:4). $[\alpha]_D^{25}$=+76.0 (*c* 1.00, CHCl3). IR (KBr): 3422, 3057, 3036, 2946, 2569, 2469, 2105, 1969, 1677, 1493, 1450, 1398, 1343, 1273, 1182, 1111, 1074, 1031, 990, 848, 694, 611 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 3.79 (1H, d, J=7.3 Hz), 4.81 (1H, d, J=3.9 Hz), 5.29 (1H, dd, J=3.9, 7.3 Hz), 6,99–7.01 (2H, m), 7.11–7.18 (3H, m), 7.29–7.38 (2H, m), 7.47 (1H, t, J=7.3 Hz), 7.63–7.65 (2H, m). ^{13}C NMR (CDCl3, δ): 67.82, 75.57, 127.68, 128.39, 128.52, 128.65, 128.72, 128.77, 130.05, 133.95, 134.11, 134.28, 198.40. Anal. calcd for $C_{15}H_{13}N_3O_2$: C, 67.41; H, 4.90; N, 15.72. Found: C, 67.40; H, 4.86; N, 15.79. HRMS-FAB (*m*/*z*): [M] calcd for $C_{15}H_{13}N_3O_2$, 268.1086; found, 268.1078.

4.5.2. (2*R*,3*S*)-2-Benzoyl-3-phenylaziridine (4a). A mixture of (2*S*,3*S*)-**10** (18.6 mg, 0.07 mmol) and triphenylphosphine (18.2 mg, 0.07 mmol) in acetonitrile (1 ml) was stirred at room temperature for 4 h. After evaporation, the residue was subjected to column chromatography on silica gel (AcOEt–hexane 1:30) to give the desired (2*R*,3*S*)-**4a** (10.3 mg, 66%). $[\alpha]_D^{23}$=−307.8 (*c* 1.00, $CHCl_3$).

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Culture, Sports, Science and Technology, Japan, the Japan Society for the Promotion of Science, and also by the Kyushu University P&P Programs 'Green Chemistry' (to J. I.).

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