Synthesis of 3,3′-, 6,6′- and 3,3′,6,6′-substituted binaphthols and their application in the asymmetric hydrophosphonylation of aldehydes—an obvious effect of substituents of BINOL on the enantioselectivity

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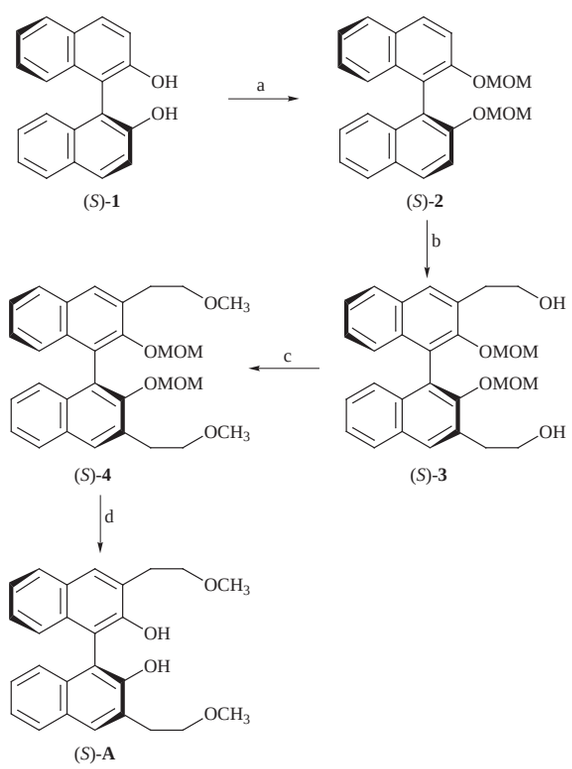
By using a direct *ortho*-lithiation strategy and/or Ni-catalysed coupling reaction, we have conveniently synthesized three new chiral polysubstituted BINOLs of vast synthetic potential from (*S*)-BINOL 1 in reasonable yields. Moreover, we have examined closely their influence on the enantioselectivity of the asymmetric Pudovik reaction catalyzed by chiral binaphthol-modified lanthanum alkoxides. The results show that the steric bulk of 3,3′-substituents of BINOL is responsible for a lowering of the enantioselectivity of the reaction, while coordination between the oxygens of the *ortho*-substituents and the lanthanum ion is beneficial in improving the asymmetric induction. 6,6′-Diphenyl-BINOL has the advantage over simple BINOL in giving the best asymmetric results. Further studies on this aspect are in progress.

Introduction

The C_2 symmetric 1,1′-bi-2-naphthol ligand has emerged as an important chiral auxiliary and ligand for an increasing range of asymmetric organometallic transformations.[1,2,3] Recently, chiral Lewis acid complexes of 3,3′-disubstituted-1,1′-bi-2-naphthols (BINOL derivatives) with main-group or transition metals have shown highly promising catalytic activity for asymmetric induction in Diels–Alder,[4] Claisen rearrangement[5] and ene[6] reactions, amongst others;[7] in particular, the use of sterically hindered BINOLs often leads to excellent enantioselectivity. However, the enantioselectivity of reactions with rare earth metal-substituted BINOLs, as compared to simple BINOL, has not been investigated to the same extent.[8] Rare earth metal-substituted BINOLs should show specific and interesting properties because of their higher coordination number, larger ionic radius, strong oxyphilicity and especially their strong electrostatic bond-forming interactions with ligands. Thus, it was thought that the introduction of oxygen-containing substituents at the *ortho*-position of BINOL would result in coordination between the oxygens of the 3,3′-substituents and the central lanthanide metal ion, which would further strengthen the contact between ligand and metal, and thus produce a favorable steric environment to give improved asymmetric induction. In addition, it was also considered that substituents at the 6,6′-positions of BINOL would affect the Lewis acidity of the central metal ion and make the asymmetric space around the chiral catalysts smaller simultaneously *via* their electronic and steric effects.[8,9] Our aim was to synthesize some new chiral 3,3′-, 6,6′- and 3,3′,6,6′-BINOL ligands substituted by diverse oxygen-containing substituents or phenyl groups and to explore their influence on the asymmetric hydrophosphonylation of aldehydes. Accordingly, we first took advantage of a convenient and direct *ortho*-lithiation strategy and/or Ni-catalysed coupling reaction to accomplish the regiospecific construction of polysubstituted BINOL derivatives.

Results and discussion

Oxidative coupling of β-naphthol was followed by resolution of racemic (±)-BINOL **1** with (−)-cinchonidine benzyl chloride to give both enantiomers of **1** simultaneously in optically pure form [(*S*)-BINOL (70% yield, >99% ee) and (*R*)-BINOL (60% yield, >99% ee)].[10] The hydroxy groups of (*S*)-BINOL **1** were protected with methoxymethoxy (MOM) groups to afford (*S*)-binaphthol ether **2** ($R = CH_2OCH_3$). The lithium organocyanocopper(I) salt of **2** was reacted with ethylene oxide to afford (*S*)-3,3′-bis(2-hydroxyethyl)-2,2′-bis(methoxymethoxy)-1,1′-bi-2-naphthol **3**, which was treated with sodium hydride and iodomethane to produce (*S*)-3,3′-bis(2-methoxyethyl)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene **4**. Removal of the MOM protecting groups gave the target molecule (*S*)-**A** (Scheme 1).



Scheme 1 *Reagents and conditions*: (a) (i) NaH, rt, (ii) $ClCH_2OCH_3$; (b) (i) 3 equiv. Bu″Li, (ii) CuCN, (iii) ethylene oxide; (c) NaH, MeI; (d) trace HCl, MeOH, 60 °C

Table 1 Opening of ethylene oxide by dilithium salt of **2**[a]

Entry	Ethylene oxide (mmol)	*T*/°C	*t*/h	Solvent	Yield (%)[b,c]
1	10	−78 ⟶ rt	12	diethyl ether	23
2	50	−78 ⟶ rt	12	diethyl ether	37
3	50	−78 ⟶ 0	12	THF	56
4	200	−78 ⟶ 0	12	THF	42

[a] 1 mmol of **2** was used in each reaction. [b] Yields are based on **2**. [c] Isolated yields.

However, the efficiency of the synthetic route was very low because the yield of the key step, the opening of ethylene oxide, was only 22%, which resulted in a total yield of only 14.5%. In order to enhance the synthetic efficiency, we have improved the reaction conditions of the key step. We found that (see Table 1) (a) the dilithium salt of **2** could also ring-open ethylene oxide, avoiding the tedious preparative procedure of the lithium organocyanocopper(I) salt of **2**; (b) the best ratio of ethylene oxide : **2** was 50 : 1 and any more or less than this would produce a lower yield; (c) tetrahydrofuran was superior to diethyl ether as reaction solvent; (d) a lower reaction temperature (−78 ⟶ 0 °C) was more suitable. Thus the optimal reaction conditions of the step were 1 equiv. of the dilithium salt of **2** reacting with 50 equiv. of ethylene oxide at low temperature in tetrahydrofuran, to afford the opened product **3** in 56% yield, which was higher than the previously mentioned yield. As a result of this modification, the total yield was improved from 14.5 to 36.6%. The enantiomeric purity (ee) of (*S*)-3,3′-bis(2-methoxyethyl)-1,1′-bi-2-naphthol, as determined by ^{1}H NMR spectroscopy of its corresponding MTPA ester, was found to be more than 99%.

(*S*)-3,3′-Bis(2-methoxyethyl)-1,1′-bi-2-naphthol was further characterised by X-ray diffraction (see Fig. 1). Prismatic colorless crystals of (*S*)-**A** were obtained by recrystallisation from diethyl ether at room temperature. There are one and a half independent molecules in the asymmetric unit, but the distinction between these molecules does not persist in solution, where the ^{1}H NMR spectrum indicates a single molecular species. The dihedral angles between the naphthalene rings (C1–C10 and C14–C23, Fig. 1) is 72°, which is smaller than that of BINOL (82°). From the X-ray studies it was deduced that a hydrogen bond is present in ligand (*S*)-**A**. The O4–H2 and O6–H27 distances were determined from the X-ray diffraction data and were shown to be 2.13 and 1.72 Å, respectively. These distances between the methoxy oxygen and hydroxy hydrogen atom are indicative of the presence of an intramolecular hydrogen bond in (*S*)-3,3′-bis(2-methoxyethyl)-1,1′-bi-2-naphthol as shown in Fig. 1. The O4–H2–O3 and O6–H27–O5 bond angles are 149.9 and 164.7°, respectively. This implies indirectly that the oxygen atoms of both methoxyethyl groups seem to be able to form intramolecular coordination bonds with the central metal ion simultaneously when dilithium 3,3′-bis(2-methoxyethyl)-bi-2-naphthoxide binds lanthanide ion to form a chiral catalyst.

Next the required (*S*)-**B** ligand was also readily obtained from the known (*S*)-BINOL in four steps. Reaction of (*S*)-BINOL with Br_2 (2.5 equiv.) in CH_2Cl_2 at −78 °C for 2.5 h afforded (*S*)-6,6′-dibromo-1,1′-bi-2-naphthol **5** almost quantitatively, which without further purification was treated with chloromethyl methyl ether (3 equiv.) and sodium hydride (2.5 equiv.) in a solvent mixture of DMF and diethyl ether (1 : 5) at room temperature for 1 h, producing (*S*)-bis(methoxymethyl) ether **6** in 91% yield. Treatment of **6** with phenylmagnesium bromide in the presence of a catalytic amount of Ni[P(C_6H_5)$_3$]$_2$$Cl_2$ in Et_2O furnished the corresponding (*S*)-6,6′-diphenyl-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene **7** in 80% yield. Demethoxymethylation of **7** afforded the desired (*S*)-6,6′-diphenyl-1,1′-bi-2-naphthol **B**. The total yield was

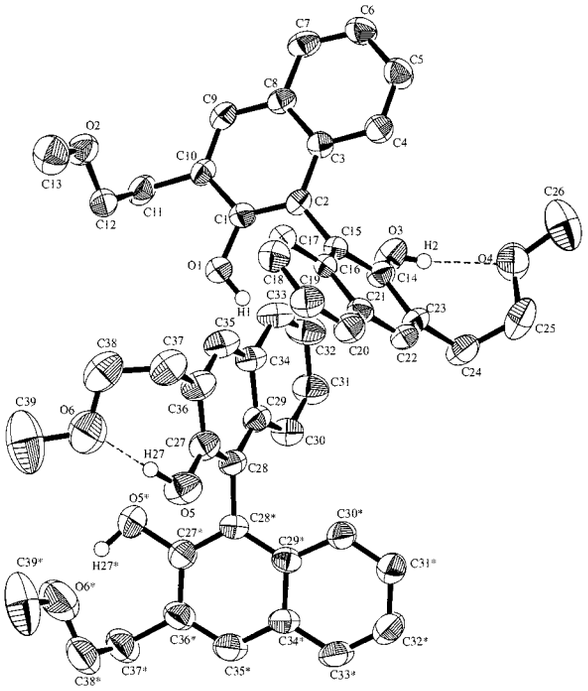
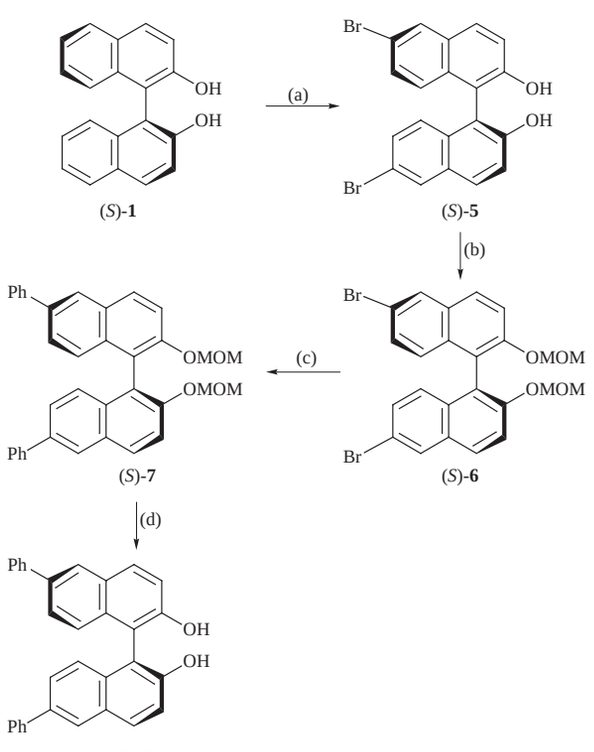


Fig. 1 Molecular structure of (*S*)-3,3′-bis(2-methoxyethyl)-1,1′-bi-2-naphthol **A** and the atom-numbering scheme. The asymmetric unit contains one and a half molecules and the latter is shown with its symmetry-related half. Starred atoms are related to their unstarred equivalents by the operation of a two-fold rotation axis.

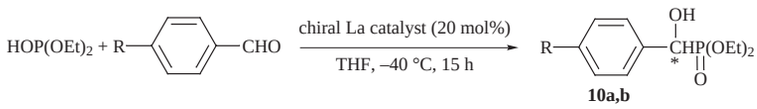


Scheme 2 *Reagents and conditions*: (a) Br_2, −78 °C, CH_2Cl_2; (b) NaH, $ClCH_2OCH_3$, rt; (c) PhMgBr, Ni[P(C_6H_5)$_3$]$_2$$Cl_2$, Et_2O, reflux; (d) trace HCl, MeOH

64.9% (Scheme 2). Its optical purity was also determined by ^{1}H NMR spectroscopy of its corresponding MTPA ester (>99% ee).

Finally, according to a similar synthetic route to that of (*S*)-**A**, (*S*)-3,3′-bis(2-methoxyethyl)-6,6′-diphenyl-1,1′-bi-2-naphthol **C** was synthesized in a reasonable total yield (49.1%) from readily obtainable (*S*)-6,6′-diphenyl-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene **7** in three steps, which included

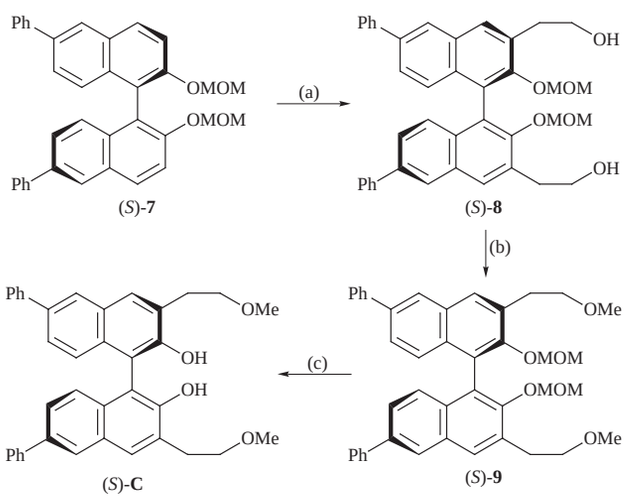
Table 2 Catalytic asymmetric reaction of aromatic aldehydes with diethyl phosphite



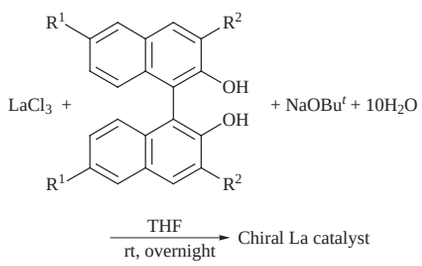
10a,b

Entry	Aldehyde	Ligand	Catalyst[a]	Product	Yield (%)[b]	ee (%)[c]
1	PhCHO	**1**	**I**	**10a**	92	20 (21)[d]
2	PhCHO	**A**	**II**	**10a**	83	21
3	PhCHO	**B**	**III**	**10a**	82	39
4	PhCHO	**C**	**IV**	**10a**	87	38
5	PhCHO	**D**	**V**	**10a**	93	0
6	*p*-tolualdehyde	**1**	**I**	**10b**	93	55 (58)[d]
7	*p*-tolualdehyde	**A**	**II**	**10b**	89	53
8	*p*-tolualdehyde	**B**	**III**	**10b**	93	69
9	*p*-tolualdehyde	**C**	**IV**	**10b**	89	62
10	*p*-tolualdehyde	**D**	**V**	**10b**	92	0

[a] Chiral lanthanide catalysts were prepared according to the published procedure.[12] [b] Yields based on aromatic aldehydes. [c] Enantioselectivity excess values were determined by ^{1}H NMR spectroscopy of their corresponding MTPA esters. [d] Figures in parentheses refer to ee values in the literature.[13a]



Scheme 3 *Reagents and conditions*: (a) i, 3 equiv. Bu^{n}Li, THF, rt, ii, ethylene oxide, −78 ⟶ 0 °C; (b) NaH, MeI; (c) trace HCl, MeOH, reflux



Catalyst	R^1	R^2
I	H	H
II	H	$CH_3OCH_2CH_2$
III	Ph	H
IV	Ph	$CH_3OCH_2CH_2$
V	H	Me_3Si

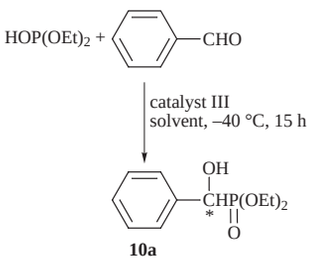
Scheme 4 Preparation of chiral La catalysts

initial lithiation of **7** and opening of ethylene oxide, subsequent methylation of the hydroxy groups and final demethoxymethylation (Scheme 3). The optical purity of product (*S*)-**C** (99% ee) indicated that no racemization took place during the total synthetic procedure.[11]

After obtaining these new chiral 3,3′-, 6,6′- and 3,3′,6,6′-polysubstituted BINOLs, we now report the application of their lanthanoid alkoxides in the enantioselective addition of dialkyl phosphite to aldehydes (Pudovik reaction) and the effect of substituents of BINOL on the enantioselectivity. The chiral lanthanide catalyst was prepared according to the published procedure (Scheme 4).[12] Benzaldehyde and *p*-tolualdehyde were selected as representative examples to study and the results are shown in Table 2.

As expected, the substituents on BINOL had a significant effect on the enantioselectivity of the asymmetric Pudovik reaction. This is exemplified by a comparison of ligand **B** and ligand **D** [(*S*)-3,3′-bis(trimethylsilyl)-1,1′-bi-2-naphthol[13b]]. Ligand **B** produced the α-hydroxyphosphonates in 39% ee and 69% ee for benzaldehyde and *p*-tolualdehyde respectively (entries 3 and 8 in Table 2), whereas ligand **D** produced racemic products for both aldehydes (entries 5 and 10 in Table 2). Although the relationship between the substituents on BINOL and enantioselectivity is not completely clear at present, certain features of the substituents seem to be responsible for the extent of enantioselection. In general, the steric bulk of the 3,3′-substituents on BINOL lowers the enantioselectivity of the reaction, which is in sharp contrast to that in the case of main-group and transition metals. We expected that the enantioselectivity would be related to the predominant electrostatic interaction between the lanthanide ion and ligand, but it is steric factors which become of overriding importance in determining the reactivity and structure of the lanthanide complexes. Because of the large radius of the lanthanide ion, the enhanced steric hindrance of the ligand would lengthen the M–O bonds of the lanthanide oxide, increasing the space around the chiral ligand and leading to the reduced asymmetric induction. However, the coordination between the oxygens of the *ortho*-substituents and the lanthanum ion improved the asymmetric induction; furthermore the coordination was supported by the following two facts[14a] in catalyst **II**: (i) the C–O–C absorption maximum of the methoxyethyl groups appeared at 1097 cm^{-1}, which is 9 cm^{-1} lower than the corresponding absorption maximum (1106 cm^{-1}) of ligand **A**; (ii) signals for the methoxy groups of the 3,3′-substituents of BINOL in the ^{1}H NMR spectrum of catalyst **II** appeared at δ 3.56 ppm, which is at 0.16 ppm lower field when compared with the corresponding absorption (δ 3.40) of those of ligand **A**. (*S*)-3,3′-Bis(2-methoxyethyl)-BINOL (ligand **A**) afforded products in almost the same optical purities as simple BINOL (entries 1, 2, 6, 7 in Table 2) during the reaction in spite of it showing a more promising optical induction than simple BINOL in the enantioselective trimethylsilylcyanation of aldehydes catalysed by chiral lanthanoid alkoxides.[14b] (*S*)-6,6′-Diphenyl-BINOL (ligand **B**) was found to give better results than simple BINOL. We have no good explanation why phenyl groups at the 6,6′-positions of BINOL were effective in obtaining α-hydroxyphosphonates in higher optical purities. One reason might be that phenyl groups at the 6,6′-positions of BINOL would affect the Lewis acidity of the chiral catalyst (catalyst **III**) *via* electronic effects.

Table 3 Effect of solvent on reactivity and enantioselectivity of catalyst III

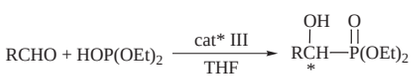


10a

Entry	Solvent	Yield (%)[a]	ee (%)[b]
1	CH_2Cl_2	33	17
2	toluene	13	0
3	diethyl ether	59	41
4	THF	82	39

[a] Yields based on aromatic aldehydes. [b] Ee values determined by ^{1}H NMR spectroscopy of the corresponding MTPA ester.

Table 4 Catalytic asymmetric reaction of aldehydes with phosphite



10a–g

Entry	Substrate	*T*/°C	Product	Yield (%)[a]	ee (%)[b]
1	PhCHO	−40	**10a**	82	39
2	*p*-$CH_3C_6H_4CHO$	−40	**10b**	93	69
3	*p*-$CH_3OC_6H_4CHO$	−78	**10c**	89	74
4	*p*-ClC_6H_4CHO	−40	**10d**	95	52
5	PhCH=CHCHO	−20	**10e**	78	41
6	1-naphthylcarbaldehyde	−40	**10f**	80	35
7	$PhCH_2CH_2CHO$	−40	**10g**	75	0

[a] Catalyst III was used for all of these reactions (20 mol%), and yields based on aromatic aldehydes. [b] Ee values determined by ^{1}H NMR spectroscopy of the corresponding MTPA ester, monitoring of the ee of the products over time was made and no racemization was observed.

We next investigated the addition of benzaldehyde to diethyl phosphite in the presence of a catalytic amount (20 mol%) of catalyst **III** prepared *in situ* in several kinds of solvents (Table 3). Reaction in dichloromethane gave the α-hydroxyphosphonate **10a** enantioselectivity (17% ee) in 33% yield (entry 1 in Table 3). When the reaction was conducted in toluene, no facial selectivity was observed and a lower chemical yield was obtained (entry 2 in Table 3). However, when diethyl ether and tetrahydrofuran were used as donor solvents, the chemical and optical yields of **10a** increased to 59% (41% ee) and 82% (39% ee) respectively (entries 3 and 4 in Table 3).

The optimal conditions were finally applied to the reactions of various aldehydes. As shown in Table 4, the reaction of an aliphatic non-conjugated aldehyde afforded the corresponding α-hydroxyphosphonate without any optical induction in a good yield (entry 7), while aromatic and conjugated aldehydes gave satisfactory enantioselectivity (35–74% ee). The racemic product obtained in the reaction of an aliphatic aldehyde indicates that effective coordination of the substrate carbonyl group to lanthanum and also π–π interactions between the substrate π-system and the catalyst's binaphthyl ring play an important role in attaining the high asymmetric induction.

In conclusion, we have synthesized three new chiral 3,3′-, 6,6′- and 3,3′,6,6′-polysubstituted BINOLs of vast synthetic potential and examined the influence of ligands of binaphthol-modified lanthanum alkoxides on the enantioselectivity of the Pudovik reaction in detail. We found that the steric hindrance of the ligand was harmful to the asymmetric induction and that the intramolecular coordination of oxygen with the lanthanum ion improved the enantioselectivity, furthermore, 6,6′-diphenyl-BINOL was found to give the best results. Further application of the three new polysubstituted BINOLs to other asymmetric syntheses is now in progress.

Experimental

Melting points were determined on a Kofler hot stage and are not corrected. NMR spectra were recorded as $CDCl_3$ solutions on VXL-300 and Fx-90Q instruments. ^{1}H NMR (300 MHz and 90 MHz) chemical shifts are reported as δ values in parts per million (ppm) relative to tetramethylsilane ($\delta_H = 0.0$ 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 Finnigan 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 anhydrous solvents were purified and dried by standard techniques just before use. All reactions were monitored by thin layer chromatography (TLC) using silica gel GF254. Products were purified either by recrystallisation or flash column chromatography (FCG) on silica gel manufactured in Qing dao Marine Chemical Factory, eluting with solvent mixtures of light petroleum (bp 60–90 °C) and ethyl acetate. (±)-1,1′-Bi-2-naphthol was prepared by Wu's method.[15a] (*S*)-1,1′-Bi-2-naphthol was obtained *via* resolution of racemic (±)-BINOL according to our procedure which will be published soon.

Preparation of (*S*)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene 2

To a solvent mixture of dry Et_2O (50 ml) and DMF (20 ml) was added 1.2 g of NaH. (*S*)-1,1′-Bi-2-naphthol (5.72 g, 20 mmol) was dissolved in 50 ml of dry diethyl ether and added slowly to the stirred mixture. The reaction was stirred for an additional 15 min and then chloromethyl methyl ether (3.8 ml, 50 mmol) was added slowly. The reaction was followed with TLC and was complete within 0.5 h after the addition of chloromethyl methyl ether. The reaction mixture was added to 100 ml of water and the aqueous layer was separated and extracted three times with diethyl ether. The ethereal extraction was added to the organic layer and then washed three times with 10% aqueous NaOH and brine. This was dried with $MgSO_4$ and concentrated under vacuum. The crude product was purified by column chromatography and finally pure 2,2′-bis(methoxymethoxy)-1,1′-binaphthalene **2** was obtained (6.7 g, 90%), mp 92.5–94.5 °C (lit.,[15b] mp 93–94 °C); $[\alpha]_D^{20}$ −97.5 (*c* 1.3 in THF); ν_{max}(KBr)/cm^{-1} 3050, 1590, 1505, 1149, 1090, 811, 744; δ_H(90 MHz, $CDCl_3$) 7.97–7.86 (4H, m, Ar), 7.58 (2H, d, *J* 9.0, Ar), 7.14–7.37 (4H, m, Ar), 5.08 (2H, d, *J* 6.8, OCH_2OCH_3), 4.97 (2H, d, *J* 6.8, OCH_2OCH_3), 3.15 (6H, s, 2 × OCH_3).

Synthesis of (*S*)-3,3′-bis(2-hydroxyethyl)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene 3[15c]

To a stirred solution of 2,2′-bis(methoxymethoxy)-1,1′-binaphthalene **2** (3.7 g, 10 mmol) in anhydrous tetrahydrofuran (50 ml) was added dropwise at room temperature Bu^{n}Li (2.01 M, 15 ml, 30 mmol) in hexane. Upon completion of the addition, the reaction mixture was stirred for another 8 h and then cooled to −78 °C in an acetone–dry ice bath. To the reaction mixture was added dropwise *via* syringe a solution of ethylene oxide (0.5 mol) in THF (20 ml). The mixture was stirred for an additional 1 h at −78 °C and then allowed to warm to 0 °C gradually overnight. Water and diethyl ether were added to the mixture to quench the reaction. The organic layer was separated, the aqueous layer was extracted with diethyl ether and the combined organic phases were dried with anhydrous Na_2SO_4. Evaporation of the solvent *in vacuo* was followed by purification of

the residue by flash column chromatography to give the product in 56% yield (2.6 g), mp 74.5–76 °C; $[a]_D^{20}$ −97.8 (*c* 2.32 in $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3415, 3055, 1595, 1158, 1070, 753; δ_H(90 MHz, $CDCl_3$) 7.82 (4H, m, Ar), 7.23 (6H, m, Ar), 4.65 (2H, d, *J* 3.2, OCH_2OCH_3), 4.57 (2H, d, *J* 3.2, OCH_2OCH_3), 3.96 (4H, m, 2 × CH_2CH_2OH), 3.32 (4H, m, 2 × CH_2CH_2OH), 3.06 (6H, s, 2 × OCH_2OCH_3); *m*/*z* (EI) 462 (M^+, 8%), 430 (17), 398 (36), 338 (74).

Synthesis of (*S*)-3,3′-bis(2-methoxyethyl)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene 4

To a suspension of sodium hydride (0.24 g, 10 mmol) in anhydrous tetrahydrofuran (10 mmol) was added dropwise a solution of (*S*)-3,3′-bis(2-hydroxyethyl)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene **3** (2 g, 4.3 mmol) in anhydrous tetrahydrofuran (15 ml). After the addition was completed, iodomethane (1.42 g, 10 mmol) was added and stirring was continued overnight. Water was then added to quench the reaction, and after usual work-up, the analytically pure product was obtained in 91% yield (1.9 g, 3.9 mmol); $[a]_D^{20}$ −54.5 (*c* 1.14 in $CHCl_3$), mp 109–111.5 °C; ν_{max}(KBr)/cm^{-1} 3059, 1595, 1159, 1114, 1071, 753; δ_H(90 MHz, $CDCl_3$) 7.83 (4H, m, Ar), 7.39–7.12 (6H, m, Ar), 4.53 (2H, d, *J* 5.7, OCH_2OCH_3), 4.41 (2H, d, *J* 5.7, OCH_2OCH_3), 3.77 (4H, m, 2 × $CH_2CH_2OCH_3$), 3.41 (6H, s, 2 × OCH_2OCH_3), 3.23 (4H, m, 2 × $CH_2CH_2OCH_3$), 2.90 (6H, s, 2 × $CH_2CH_2OCH_3$); *m*/*z* (EI) 490 (M^+, 37%), 338 (57).

Synthesis of (*S*)-3,3′-bis(2-methoxyethyl)-1,1′-bi-2-naphthol (A)

To a solution of (*S*)-**4** (1.5 g, 3 mmol) in methanol (10 ml) was added 10% aqueous HCl (7.2 mmol) with stirring. After stirring for 1 h, the reaction mixture was evaporated *in vacuo*. The resulting residue was diluted with diethyl ether and washed with water and brine, and dried over $MgSO_4$. After evaporation of the solvent *in vacuo*, the resulting residue was purified by flash column chromatography to give **A** in 87% yield (1.03 mg, 2.6 mmol); $[a]_D^{20}$ −82 (*c* 1.25 in $CHCl_3$), mp 133.5–135.5 °C (Found: C, 77.59; H, 6.51. $C_{26}H_{26}O_4$ requires C, 77.32; H, 6.91%); ν_{max}(KBr)/cm^{-1} 3255, 3059, 1500, 1146, 1106, 1058, 747; δ_H(300 MHz, $CDCl_3$) 7.78 (4H, m, Ar), 7.30–7.08 (6H, m, Ar), 6.50 (2H, br, 2 × OH), 3.81 (4H, m, 2 × $CH_2CH_2OCH_3$), 3.40 (6H, s, 2 × $CH_2CH_2OCH_3$), 3.19 (4H, m, 2 × $CH_2CH_2OCH_3$); *m*/*z* (EI) 402 (M^+, 66%), 338 (40), 325 (31); (*S*)-MTPA-ester: δ_H(300 MHz, $CDCl_3$) 8.01–6.95 (20H, m, Ar), 3.75 (4H, m, 2 × $CH_2CH_2OCH_3$), 3.45 (6H, s, 2 × OCH_3), 3.38 (6H, s, 2 × $CH_2CH_2OCH_3$), 3.16 (4H, m, 2 × $CH_2CH_2OCH_3$).

X-Ray crystal structure of (*S*)-A

The single crystals of ligand (*S*)-**A** suitable for an X-ray diffraction study were obtained by recrystallization from diethyl ether at room temperature. The X-ray diffraction intensity data for (*S*)-**A** were collected with a Rigaku AFC 7R diffractometer at 20 °C using Mo-Kα radiation with an ω-2θ scan mode within the ranges (4.51° ≤ 2θ ≤ 50°).

The structure of ligand (*S*)-**A** was solved by direct methods (SHELXS-86) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 2334 observed reflections [$I > 2.00\sigma(I)$] and 407 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.039$ and $R_w = 0.046$. All the calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation.

Details of the crystallographic data and the procedure used for data collection and reduction for ligand (*S*)-**A** are given in Table 5. The procedure parameters and temperature factors of non-hydrogen atoms, H atomic coordination and B_{iso}/B_{eq}, anisotropic displacement parameters, bond lengths and angles, and least-square planes for ligand (*S*)-**A** have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 1*, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/218. The molecular structure of ligand (*S*)-**A** is given in Fig. 1.

Table 5 Crystal data and structure refinement for (*S*)-3,3′-bis(2-methoxyethyl)-1,1′-bi-2-naphthol

Empirical formula	$C_{26}H_{26}O_4$
Formula weight	402.49
T/°C	20.0
λ/Å	0.710 69
Crystal system	orthorhombic
Space group	$P2_12_12$ (#18)
Lattice parameters/Å	*a* = 11.394(4), *b* = 24.978(6), *c* = 11.244(4)
V/Å^3	3199(1)
Z	6
D_{calc}	1.253 g cm^{-3}
Absorption coeff/mm^{-1}	0.83 cm^{-1}
F_{000}	1284.00
Crystal size (mm)	0.20 × 0.20 × 0.20
θ range (°)	2θ 4.5 ~ 50°
Index ranges	0 ≤ *h* ≤ 13, 0 ≤ *k* ≤ 26, 0 ≤ *l* ≤ 17
Total reflections collected	3210
Independent reflection	3210
Observed data	2334
Refinement method	Full-matrix least- squares on *F*
Number of parameters	407
Goodness-of-fit on F^2 (*S*)	1.31
Residuals: *R*; R_w	0.039; 0.046
Final scheme	$W = 1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$
Residual diffraction max./min. (e Å^{-3})	0.15/−0.14

(*S*)-6,6′-Dibromo-1,1′-bi-2-naphthol 5

Compound **5** was prepared from (*S*)-BINOL by the published method.[16]

Synthesis of (*S*)-6,6′-dibromo-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene 6

Following the similar procedure used for **2**, a suspension of (*S*)-6,6′-dibromo-1,1′-bi-2-naphthol **5**, chloromethyl ether and sodium hydride was stirred at room temperature for 1 h. Recrystallization of the crude product from a solvent mixture of acetone–light petroleum afforded the analytically pure product (*S*)-**6** as a white powder in 91% yield; $[a]_D^{20}$ −27.8 (*c* 0.93 in $CHCl_3$), mp 108–109 °C; ν_{max}(KBr)/cm^{-1} 1565, 1152, 1068, 812, 516; δ_H(90 MHz, CCl_4/$SiMe_4$) 8.26–6.84 (10H, m, Ar), 5.03 (4H, m, 2 × OCH_2OCH_3), 3.16 (6H, s, 2 × OCH_2OCH_3); *m*/*z* (EI) 530 (M^+, 5%), 456 (9), 454 (5), 428 (9), 426 (6), 268 (7), 237 (5), 224 (4), 45 (100) (HRMS: Found: M^+ 529.9706. $C_{24}H_{20}O_4Br_2$ requires M^+, 529.9728).

Synthesis of (*S*)-6,6′-diphenyl-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene 7

To a suspension of (*S*)-6,6′-dibromo-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene **6** (3.2 g, 6 mmol) $Ni[P(C_6H_5)_3]_2Cl_2$ (0.21 g, 0.32 mmol) in 40 ml of diethyl ether stirred under N_2 was added a solution of 15 mmol of phenylmagnesium bromide in 20 ml of diethyl ether. The mixture was refluxed for 20 h, cooled, and quenched with 20 ml of water. After usual work-up, analytically pure **7** was obtained in 80% yield (2.5 g, 2.8 mmol); $[a]_D^{20}$ −89.6 (*c* 0.67 in $CHCl_3$), mp 76–78 °C (Found: C, 81.83; H, 5.34. $C_{36}H_{30}O_4$ requires C, 82.13; H, 5.70%); ν_{max}(KBr)/cm^{-1} 1593, 1153, 1078, 761; δ_H(300 MHz, $CDCl_3$) 8.10 (2H, s, Ar), 8.02 (2H, d, *J* 8.9, Ar), 7.70–7.25 (16H,

m, Ar), 5.07 (4H, q, 2 × OCH_2OCH$_3$), 3.17 (6H, s, 2 × OCH$_2$OCH_3); *m/z* (EI) 527 (M + H$^+$, 17%), 526 (M$^+$, 43), 450 (79), 422 (73), 421 (60), 420 (40), 167 (81), 165 (38), 134 (100), 45 (46).

Synthesis of (*S*)-6,6′-diphenyl-1,1′-bi-2-naphthol B

(*S*)-6,6′-Diphenyl-1,1′-bi-2-naphthol was prepared in a similar manner to that for **A**. Yield, 89.2%; $[\alpha]_D^{20}$ −19.5 (*c* 1.3 in CHCl$_3$), mp 98–100 °C (Found: C, 87.63; H, 5.18. $C_{36}H_{30}O_4$ requires C, 87.67; H, 5.02%); ν_{max}(KBr)/cm^{-1} 3446, 1596, 1492, 760; δ_H(300 MHz, CDCl$_3$) 8.10 (2H, s, Ar), 8.04 (2H, d, *J* 9.0, Ar), 7.68–7.25 (16H, m, Ar), 5.09 (2H, s, 2 × OH); *m/z* (EI) 439 (M + H$^+$, 36%), 438 (M$^+$, 100), 420 (8), 409 (6), 219 (8), 191 (13), 77 (10); (*S*)-MTPA-ester: δ_H(300 MHz, CDCl$_3$) 7.10–8.25 (30H, m, Ar), 3.25 (6H, s, 2 × OCH$_3$).

Synthesis of (*S*)-6,6′-diphenyl-3,3′-bis(2-hydroxyethyl)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene 8

Following the similar procedure used for the preparation of **3**, (*S*)-**8** was afforded in 62% yield; $[\alpha]_D^{20}$ −153.8 (*c* 0.92 in CHCl$_3$), mp 74–76 °C (Found: C, 78.37; H, 6.29. $C_{40}H_{38}O_6$ requires C, 78.18; H, 6.14%); ν_{max}(KBr)/cm^{-1} 3430, 1596, 1113, 1075, 763; δ_H(300 MHz, CDCl$_3$) 7.26–8.07 (18H, m, Ar), 4.55 (4H, m, 2 × OCH_2OCH$_3$), 4.07 (4H, t, *J* 6.3, 2 × CH$_2$CH_2OH), 3.25 (4H, m, 2 × CH_2CH$_2$OH), 3.05 (6H, s, 2 × OCH$_3$); *m/z* (EI) 614 (M$^+$, 2%), 550 (11), 538 (12), 490 (20), 414 (14), 246 (13), 121 (21), 119 (67), 117 (70), 84 (12), 82 (15), 47 (12), 45 (100), 43 (18).

Synthesis of (*S*)-6,6′-diphenyl-3,3′-bis(2-methoxyethyl)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene 9

(*S*)-6,6′-Diphenyl-3,3′-bis(2-methoxyethyl)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene was prepared by the similar procedure used for the preparation of **4**; yield 87%, mp 40–42 °C; $[\alpha]_D^{20}$ −169.7 (*c* 1.57 in CHCl$_3$); ν_{max}(KBr)/cm^{-1} 1596, 1161, 1116, 1076, 763; δ_H(300 MHz, CDCl$_3$) 8.1–7.0 (18H, m, Ar), 4.45 (4H, m, 2 × OCH_2OCH$_3$), 3.75 (4H, t, *J* 5.4, 2 × CH$_2$CH_2OCH$_3$), 3.4 (6H, s, 2 × OCH$_2$OCH_3), 3.17 (4H, m, 2 × CH_2CH$_2$OCH$_3$), 3.0 (6H, s, 2 × CH$_2$CH$_2$OCH_3); *m/z* (EI) 642 (M$^+$, 1%), 567 (10), 566 (22), 491 (15), 490 (10), 473 (7), 4.61 (6), 447 (6), 45 (100).

Synthesis of (*S*)-6,6′-diphenyl-3,3′-bis(2-methoxyethyl)-1,1′-bi-2-naphthol C

Following the similar deprotection procedure used for the preparation of **A**, (*S*)-**C** was obtained in 91% yield; $[\alpha]_D^{20}$ −49.4 (*c* 1.36 in CHCl$_3$), mp 60–62 °C (Found: C, 82.19; H, 6.26. $C_{38}H_{34}O_4$ requires C, 82.31; H, 6.14%); ν_{max}(KBr)/cm^{-1} 3516, 3057, 1596, 1106, 762; δ_H(300 MHz, CDCl$_3$) 7.17–8.04 (18H, m, Ar), 3.84 (4H, t, *J* 6.0, 2 × CH_2OCH$_3$), 3.41 (6H, s, 2 × CH$_2$-OCH_3), 3.22 (4H, t, *J* 5.8, 2 × (CH_2CH$_2$OCH$_3$); *m/z* (EI) 478 (25%), 121 (36), 119 (98), 117 (100), 82 (30), 69 (37), 57 (47), 55 (46), 43 (62); (*S*)-MTPA-ester: δ_H(300 MHz, CDCl$_3$) 7.10–7.75 (30H, m, Ar), 3.85 (4H, t, *J* 6.1, 2 × CH$_2$CH_2OCH$_3$), 3.40 (6H, s, 2 × OCH$_3$), 3.25 (6H, s, 2 × CH$_2$CH$_2$OCH_3), 3.09 (4H, t, *J* 5.8, 2 × CH_2CH$_2$OCH$_3$).

Representative procedure for Pudovik reaction with chiral binaphthol-modified lanthanoid alkoxides

A suspension of chiral binaphthol-modified lanthanoid alkoxide in THF was prepared from LaCl$_3$ (49.1 mg, 0.2 mmol), dilithium (*S*)-substituted bi-2-naphthoxide (0.2 mmol), NaOBu′ (19.2, 0.2 mmol) and water (36 μl, 2 mmol) according to the method of Shibasaki.[8] To the stirred suspension was added successively a THF solution of the aldehyde (1 mmol) and a THF solution of diethyl phosphite (166 mg, 1.2 mmol) at low temperature (−20 to −78 °C). After being stirred for 15 h at the same temperature, the reaction mixture was quenched with 1 M aqueous hydrochloride acid and extracted with Et$_2$O. The combined extracts were washed with brine, dried (Na$_2$SO$_4$) and concentrated to give a residue. Purification of this flash chromatography (ethyl acetate–light petroleum 2:1) afforded **10a**–**g**. Ee values of **10a**–**g** were determined by ^{1}H NMR spectroscopy of their MTPA esters.

(*R*)-Diethyl phenyl(hydroxy)methylphosphonate 10a. Mp 58–60 °C; ν_{max}(KBr)/cm^{-1} 3263, 3025, 1600, 1230, 1030, 763; δ_H(300 MHz, CDCl$_3$) 7.2–7.5 (5H, m, Ph), 4.1–3.7 (5H, m), 1.2–1.05 (6H, m, 2 × OCH$_2$CH_3); *m/z* (EI) 245 (M + H$^+$, 100%), 227 (91), 138 (73), 111 (78), 107 (36), 82 (47), 79 (45), 77 (55) (HRMS: Found M$^+$, 244.0844. $C_{11}H_{17}O_4P$ requires *M*$^+$, 244.0864); (*R*)-MTPA-ester: δ_H(300 MHz, CDCl$_3$) 3.41, 3.54 (OCH$_3$); ligand **1** gave **10a** in 20% ee {92% yield, $[\alpha]_D^{20}$ +5.9 (*c* 1.61 in CHCl$_3$)}; ligand **A**, 21% ee {83% yield, $[\alpha]_D^{20}$ +6.2 (*c* 0.92 in CHCl$_3$)}; ligand **B**, 39% ee {82% yield, $[\alpha]_D^{20}$ +11.8 (*c* 1.68 in CHCl$_3$)}; ligand **C**, 38% ee {87% yield, $[\alpha]_D^{20}$ +11.6 (*c* 1.07 in CHCl$_3$)}, ligand **D**, 0% ee {93% yield, $[\alpha]_D^{20}$ 0 (*c* 1.51 in CHCl$_3$)}.

(*R*)-Diethyl hydroxy(4-methylphenyl)methylphosphonate 10b. Mp 93–95 °C; ν_{max}(KBr)/cm^{-1} 3262, 3015, 1508, 1234, 1025, 759; δ_H(300 MHz, CDCl$_3$) 7.1–7.5 (4H, m, C$_6$H$_4$), 4.05 (5H, m), 2.3 (3H, s, CH$_3$), 1.1–1.3 (6H, m, 2 × OCH$_2$CH_3); *m/z* (EI) 258 (M$^+$, 23%), 138 (81), 121 (61), 119 (38), 111 (100), 93 (43), 91 (67), 83 (34), 82 (43) (HRMS: Found M$^+$, 258.1043. $C_{12}H_{19}O_4P$ requires *M*$^+$, 258.1021); (*R*)-MTPA-ester: δ_H(300 MHz, CDCl$_3$) 3.49, 3.60 (OCH$_3$). Ligand **1** gave **10b** in 55% ee {93% yield, $[\alpha]_D^{20}$ +19.7 (*c* 2.25 in CHCl$_3$)}; ligand **A**, 53% ee {89% yield, $[\alpha]_D^{20}$ +19.4 (*c* 1.19 in CHCl$_3$)}; ligand **B**, 69% ee {93% yield, $[\alpha]_D^{20}$ +24.1 (*c* 1.63 in CHCl$_3$)}; ligand **C**, 62% ee {89% yield, $[\alpha]_D^{20}$ +22.1 (*c* 1.62 in CHCl$_3$)}; ligand **D**, 0% ee {92% yield, $[\alpha]_D^{20}$ 0 (*c* 1.01 in CHCl$_3$)}.

(*R*)-Diethyl hydroxy(4-methoxyphenyl)methylphosphonate (*R*)-(+)-10c. Mp 119–121 °C; $[\alpha]_D^{20}$ +29.8 (*c* 1.49 in CHCl$_3$) for a sample of 74% ee; ν_{max}(KBr)/cm^{-1} 3246, 3010, 1509, 1228, 1174, 1032, 761; δ_H(300 MHz, CDCl$_3$) 7.1–7.5 (4H, m, C$_6$H$_4$), 4.2–3.8 (5H, m), 3.52 (3H, s, OCH$_3$), 1.25–1.05 (6 H, m, 2 × OCH$_2$CH_3); *m/z* (EI) 274 (M$^+$, 20%), 138 (33), 137 (100), 136 (36), 135 (60), 111 (45), 109 (27), 83 (23), 77 (22) (HRMS: Found M$^+$, 274.0998. $C_{13}H_{21}O_4P$ requires *M*$^+$, 274.0970); (*R*)-MTPA-ester: δ_H(300 MHz, CDCl$_3$) 3.40, 3.56 (OCH$_3$).

(*R*)-Diethyl hydroxy(4-chlorophenyl)methylphosphonate (*R*)-(+)-10d. Mp 65–67 °C; $[\alpha]_D^{20}$ +24.3 (*c* 1.71 in CHCl$_3$) for a sample of 52% ee; ν_{max}(KBr)/cm^{-1} 3251, 3035, 1490, 1236, 1029, 842, 772; δ_H(300 MHz, CDCl$_3$) 7.3–7.7 (4H, m, C$_6$H$_4$), 4.1–3.7 (5H, m), 1.3–1.1 (6H, m, 2 × OCH$_2$CH_3); *m/z* (EI) 278 (M$^+$, 100%), 261 (89) (HRMS: Found M$^+$, 278.0499. $C_{11}H_{16}O_4PCl$ requires *M*$^+$, 278.0475); (*R*)-MTPA-ester: δ_H(300 MHz, CDCl$_3$) 3.45, 3.60 (OCH$_3$).

(+)-10e. Mp 73–75 °C; $[\alpha]_D^{20}$ +4.7 (*c* 0.59 in CHCl$_3$) for a sample of 41% ee; ν_{max}(KBr)/cm^{-1} 3258, 3035, 1630, 1494, 1229, 1023, 762; δ_H(300 MHz, CDCl$_3$) 7.6–7.2 (5H, m, Ph), 6.45 (1H, d, *J* 15.8, HC=CH), 6.05 (1H, dd, *J* 16, 4.1, CH=CH), 4.3–3.9 (5H, m), 1.32–1.04 (6H, m, 2 × OCH$_2$CH_3); *m/z* (EI) 270 (M$^+$, 9%), 241 (100), 147 (44), 138 (45), 133 (66), 131 (55), 115 (52), 111 (79), 103 (46); (HRMS: Found M$^+$, 270.0998. $C_{13}H_{19}O_4P$ requires *M*$^+$, 270.0975); (*R*)-MTPA-ester: δ_H(300 MHz, CDCl$_3$) 3.40, 3.57 (OCH$_3$).

(+)-10f. Mp 109–110 °C; $[\alpha]_D^{20}$ +19.4 (*c* 1.19 in CHCl$_3$) for a sample of 35% ee; ν_{max}(KBr)/cm^{-1} 3314, 3016, 1683, 1231, 1025, 756; δ_H(300 MHz, CDCl$_3$) 7.4–8.2 (7H, m, Ar), 4.1–3.1 (5H, m), 1.2–0.92 (6H, m, 2 × OCH$_2$CH_3); *m/z* (EI) 294 (M$^+$, 77%), 157 (59), 156 (82), 155 (60), 129 (71), 128 (100), 127 (82), 111 (65) (HRMS: Found M$^+$ 294.1012. $C_{15}H_{19}O_4P$ requires *M*$^+$, 294.1021). (*R*)-MTPA-ester: δ_H(300 MHz, CDCl$_3$) 3.42, 3.58 (OCH$_3$).

(±)-10g. Oil; $[\alpha]_D^{20}$ 0 (*c* 1.49 in CHCl$_3$) for a sample of 0% ee; ν_{max}(KBr)/cm^{-1} 3230, 3030, 1596, 1204, 1035, 776; δ_H(300 MHz, CDCl$_3$) 7.1–7.5 (5H, m, Ph), 4.1–3.7 (5H, m), 2.4 (2H, t, *J* 7.3, CH$_2$), 2.0 (2H, m, CH$_2$), 0.95–1.2 (6H, m, 2 × OCH$_2$CH_3); *m/z* (EI) 273 (M + H$^+$, 77%), 168 (100), 140 (29), 112 (27), 111 (24), 91 (54), 92 (23), 65 (20) (HRMS: Found M$^+$, 272.1178. $C_{13}H_{21}O_4P$ requires *M*$^+$, 272.1178); (*R*)-MTPA-ester: δ_H(300 MHz, CDCl$_3$) 3.41, 3.60 (OCH$_3$).

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References

1 (*a*) M. Suzuki, Y. Morite, H. Koyano, M. Koga and R. Noyori, *Tetrahedron*, 1990, **46**, 4809; (*b*) R. Noyori, I. Tomino, M. Yamada and M. Nishizawa, *J. Am. Chem. Soc.*, 1984, **106**, 6717; (*c*) R. Noyori, *Chem. Soc. Rev.*, 1989, **18**, 187.

2 (*a*) P. Magalioli, O. De Lucchi, G. Delogu and G. Valle, *Tetrahedron: Asymmetry*, 1992, **3**, 365; (*b*) K. Fuji, M. Node and F. Tanaka, *Tetrahedron Lett.*, 1990, **31**, 6553.

3 (*a*) Ch. Chapuis and J. Jurezak, *Helv. Chim. Acta*, 1987, **70**, 436; (*b*) J. Bao, W. Wulff and A. L. Rheingold, *J. Am. Chem. Soc.*, 1993, **115**, 3814; (*c*) K. Maruoka, T. Itoh, T. Shirasaka and H. Yamamoto, *J. Am. Chem. Soc.*, 1988, **110**, 310; (*d*) K. Tani, T. Yamagata, S. Akutagawa, H. Kumobayashi, T. Taketomi, H. Takaya, A. Miyashita, R. Noyori and S. Otsuka, *J. Am. Chem. Soc.*, 1984, **106**, 5208; (*e*) M. Terada, Y. Motoyama and K. Mikami, *Tetrahedron Lett.*, 1994, **35**, 5693; (*f*) K. Mikami and S. Matsukawa, *Tetrahedron Lett.*, 1994, **35**, 3133; (*g*) S. Sakane, K. Maruoka and H. Yamamoto, *Tetrahedron Lett.*, 1985, **20**, 5535.

4 (*a*) T. R. Kelly, A. Whiting and N. S. Chandrakumar, *J. Am. Chem. Soc.*, 1986, **108**, 3510; (*b*) K. Maruoka and H. Yamamoto, *ibid.*, 1989, **111**, 789; (*c*) K. Ishihara and H. Yamamoto, *J. Am. Chem. Soc.*, 1994, **116**, 1561; (*d*) K. Maruoka, N. Murase and H. Yamamoto, *J. Org. Chem.*, 1993, **58**, 2938; (*e*) K. Ishihara, H. Kurihara and H. Yamamoto, *J. Am. Chem. Soc.*, 1996, **118**, 3049.

5 K. Maruoka, H. Banno and H. Yamamoto, *J. Am. Chem. Soc.*, 1990, **112**, 7791.

6 (*a*) K. Maruoka, Y. Hoshino, T. Shirasaka and H. Yamamoto, *Tetrahedron Lett.*, 1988, **29**, 3967; (*b*) M. Terada, K. Mikami and T. Nakai, *Tetrahedron Lett.*, 1991, **32**, 935; (*c*) K. Mikami, M. Terada and T. Nakai, *J. Am. Chem. Soc.*, 1990, **112**, 3949; (*d*) K. Mikami, M. Terada and T. Nakai, *J. Am. Chem. Soc.*, 1989, **111**, 1940; (*e*) K. Mikami, M. Terada, S. Narisawa and T. Nakai, *Synlett*, 1992, 155; (*f*) M. Terada and K. Mikami, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 833; (*g*) K. Mikami, Y. Motoyama and M. Terada, *J. Am. Chem. Soc.*, 1994, **116**, 2812; (*h*) M. Terada, S. Matsukawa and K. Mikami, *J. Chem. Soc.*, *Chem. Commun.*, 1993, 327.

7 K. Narasaka, *Synthesis*, 1991, 1.

8 H. Sasai, T. Tokunaga, S. Watanabe, T. Suzuki, N. Itoh and M. Shibasaki, *J. Org. Chem.*, 1995, **60**, 7388.

9 M. Terada, Y. Motoyama and K. Mikami, *Tetrahedron Lett.*, 1992, **33**, 2253.

10 (*a*) D. Cai, D. L. Hughes, T. R. Verhoeven and P. J. Reider, *Tetrahedron Lett.*, 1995, **36**, 7991; (*b*) Q. Hu, D. Vitharana and L. Pu, *Tetrahedron: Asymmetry*, 1995, **6**, 2123; (*c*) our procedure for resolution of racemic (±)-BINOL will be published.

11 The optical purity of (*S*)-3,3′-bis(2-methoxyethyl)-6,6′-diphenyl-1,1′-bi-2-naphthol [(*S*)-**C**] was also determined by ^{1}H NMR spectroscopy of its corresponding MTPA ester.

12 The preparation procedure for chiral binaphthol-modified lanthanoid alkoxide from $LaCl_3$: to a solution of (*S*)-modified binaphthol (0.2 mmol dried at 50 °C for 2 h under reduced pressure) in THF (1 ml) was added Bu″Li (0.4 mmol) under Ar at 0 °C. A suspension of $LaCl_3$ (49.1 mg, 0.2 mmol) in THF (2 ml) was stirred overnight at room temperature. To this suspension was then added the above-prepared solution of dilithium modified naphthoxide dropwise and NaOBu′ (19.2 mg, 0.2 mmol) and water (36 μl, 2 mmol). After being stirred overnight at room temperature and then for 30 h at 50 °C, chiral binaphthol-modified lanthanoid alkoxide was carried out.

13 (*a*) T. Yokomatsu, T. Yamagishi and S. Shibuya, *Tetrahedron: Asymmetry*, 1993, 1783; (*b*) P. J. Cox, W. Wang and V. Snieckus, *Tetrahedron Lett.*, 1992, **33**, 2253.

14 (*a*) B. Wang, D. Deng and C. Qian, *New J. Chem.*, 1995, **19**, 515; (*b*) This part of the work will be published soon.

15 (*a*) K. Ding, Y. Wang, L. Zhang, Y. Wu and T. Matsuura, *Tetrahedron*, 1996, **52**, 1005; (*b*) S. S. Peacock, D. M. Walba, F. C. A. Gaeta, R. C. Helgeson and D. J. Cram, *J. Am. Chem. Soc.*, 1980, **102**, 2043; (*c*) J. Li, W. Li, Y. Li, Yu. Li and S. Yang, *Org. Prep. Proced. Int.*, 1995, **27**, 685.

16 G. Dotsevi, Y. Sogah and D. J. Cram, *J. Am. Chem. Soc.*, 1979, **101**, 3035.

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