Pergamon

Tetrahedron: *Asymmetry* 13 (2002) 2161–2166

TETRAHEDRON: *ASYMMETRY*

Axially dissymmetric binaphthyldiimine chiral Salen-type ligands for catalytic asymmetric addition of diethylzinc to aldehyde

Min Shi* and Chun-Jiang Wang

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China

Received 26 August 2002; accepted 11 September 2002

Abstract—The axially dissymmetric chiral Schiff base ligand **10**, prepared by the reaction of (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine with (*R*)-(+)-2,2′-dihydroxy-[1,1′]-binaphthalenyl-3-carbaldehyde, is a fairly effective chiral ligand for the catalytic asymmetric addition reaction of diethylzinc to aldehydes.

1. Introduction

Axially dissymmetric 1,1′-binaphthyl and 1,1′-biphenyl ligands bearing identical groups in the 2- and 2′-positions have proved remarkably useful in enantioselective catalysis, with enantiomeric purities close to 100% being obtained in several preparatively important reactions.[1] Previously, we have reported that axially dissymmetric chiral Salen-type ligands **A**–**D** (Fig. 1), derived from the reaction of (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine with 2,6-dichlorobenzaldehyde, 2,3-dichlorobenzaldehyde, 3,4-dichlorobenzaldehyde or

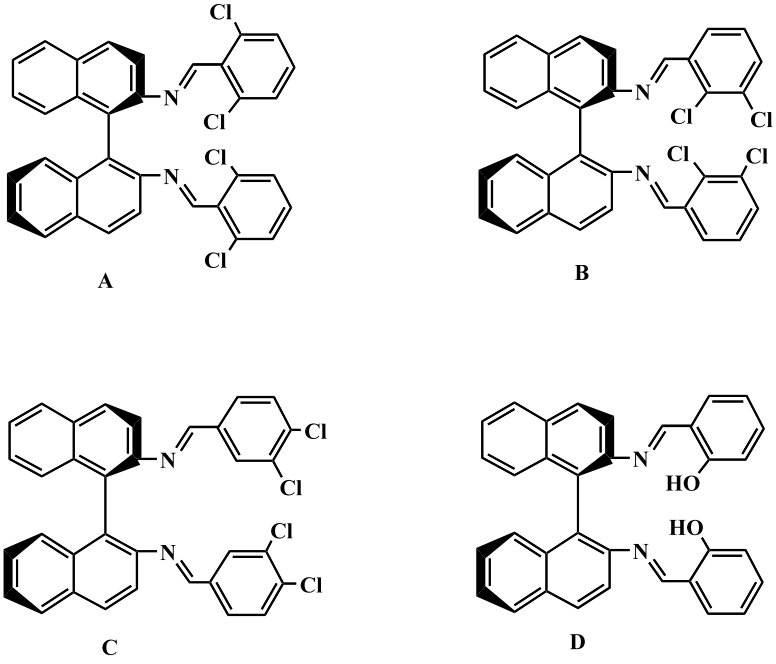


Figure 1. The structures of Schiff bases **A**–**D**.

* Corresponding author. Fax: 86-21-64166128; e-mail: mshi@pub.sioc.ac.cn

0957-4166/02/$ - see front matter
PII: S0957-4166(02)00571-2

salicylaldehyde, are excellent chiral ligands in the $Cu(MeCN)ClO_4$-catalyzed asymmetric aziridination of cinnamates.[2] In order to extend the scope of the applications of these ligands in asymmetric reactions, we further examined the other types of catalytic asymmetric reactions using these chiral ligands and their derivatives. We found that derivatives of these ligands having phenolic hydroxyl groups or hydroxyl groups are also very effective in the asymmetric addition reactions of diethylzinc to aldehydes, although some very common Salen type ligands, such as Schiff bases **D**–**F** having two phenolic hydroxy groups, showed no catalytic properties for this reaction (Fig. 2). In some cases, very high yields and good enantioselectivities were obtained.[3] Herein, we report on the application of axially dissymmetric chiral ligands **L1**–**L4** as promotors for the asymmetric addition reactions of diethylzinc to aldehydes.

2. Results and discussion

It is well known that β-amino alcohols are excellent chiral ligands for the asymmetric addition reactions of diethylzinc to aldehydes. Thus, we first investigated the synthesis of chiral β-amino alcohols **4** and **5** using (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine **1** as a chiral scaffold. As Scheme 1 shows, the two chiral β-amino alcohols **4** and **5** were successfully prepared from (*R*)-(+)-*N*,*N*′-dimethyl-1,1′-binaphthyl-2,2′-diamine **3** (derived from (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine **1** by reaction with ethyl chloroformate and reduction of the resulting carbamate with $LiAlH_4$ in THF) by reaction with ethylene oxide in the presence of HOAc (Scheme 1). We found that the monosubstituted ligand **4** could be prepared in 86% yield by reaction of **3** with ethylene oxide at 0°C, whilst diol **5** was formed in slightly lower yield (80%) by completing the reaction at 10°C.

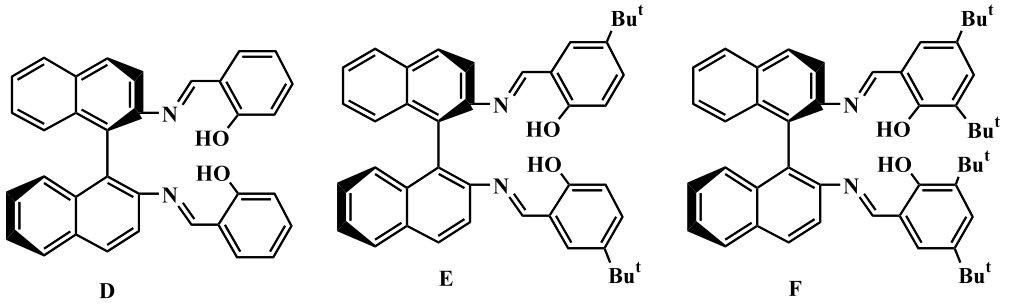
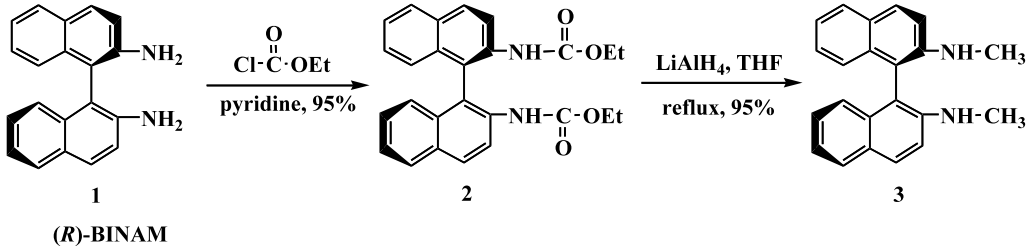
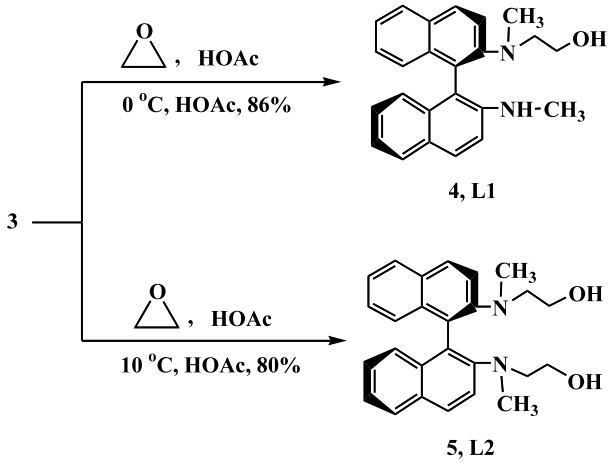


Figure 2. The Schiff bases having two phenolic hydroxy groups.

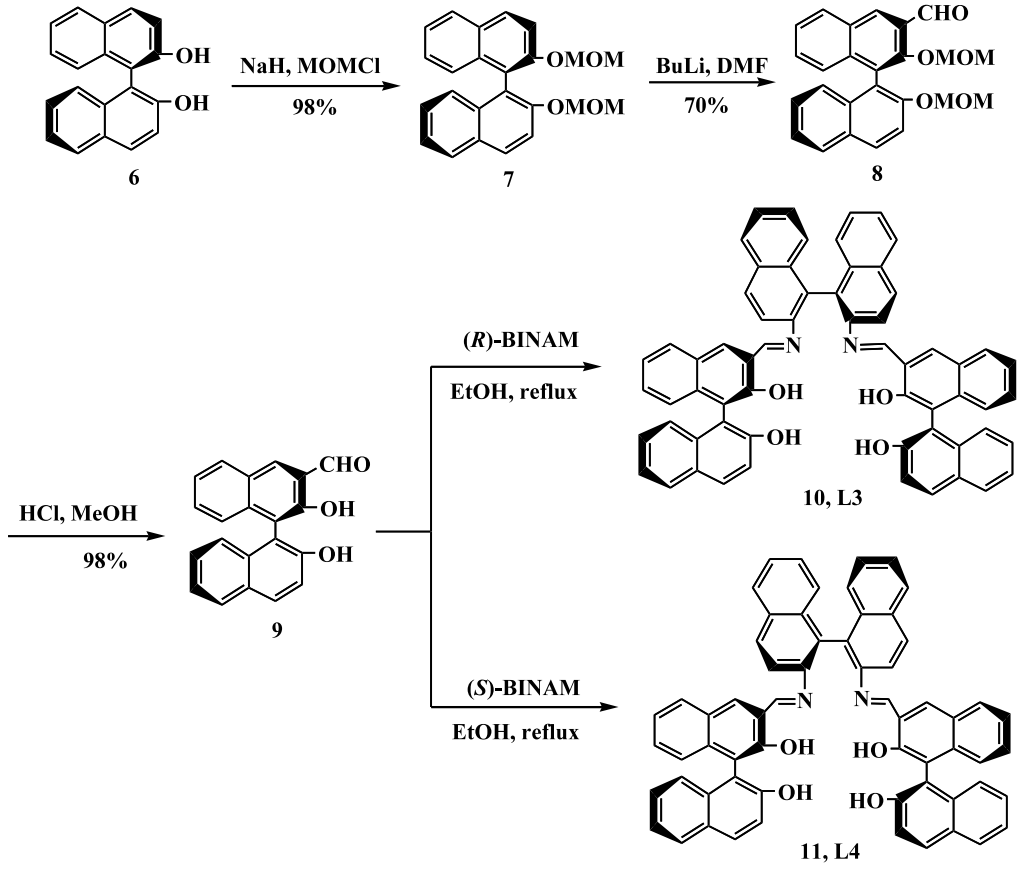




Scheme 1.

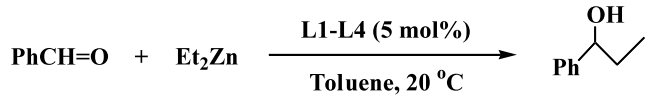
The axially dissymmetric chiral ligands Schiff bases **10** and **11** were prepared by the reaction of (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine **1** and (*S*)-(−)-1,1′-binaphthyl-2,2′-diamine **1** with (*R*)-(+)-2,2′-dihydroxy-[1,1′]-binaphthalenyl-3-carbaldehyde **9** (derived from (*R*)-(+)-binol **6** as shown in Scheme 2,[4] in anhydrous ethanol under reflux, Scheme 2).[5] After standard work-up and purification by silica gel column chromatography or recrystallization, **10** and **11** were obtained as yellow solids in about 95% yields, respectively.

We first examined the asymmetric addition reaction of diethylzinc to benzaldehydes in the presence of a catalytic amount (5 mol%) of chiral ligands **4** (**L1**), **5** (**L2**), **10** (**L3**) and **11** (**L4**). The results are summarized in Table 1. The ee of the products was determined by chiral HPLC analysis using a chiral stationary-phase column (CHIRALCEL OD and OJ) and the absolute configuration of the major enantiomer was assigned according to the sign of the specific rotations. As shown in Table 1, using **L1** as a ligand for the addition of diethylzinc to benzylaldehyde in toluene at room temperature, the *sec*-alcohol was obtained in 51% ee (58% yield) with *R* configuration. In contrast, using ligand **L2**, the *sec*-alcohol was obtained in 45% ee (40% yield) with *S* configuration under the same conditions (Table 1, entries 1 and 2). The axially dissymmetric chiral Schiff base ligand **L3** gave the best results under the



Scheme 2.

Table 1. Catalytic asymmetric addition reaction of diethylzinc to benzaldehyde in the presence of chiral ligands **L1**–**L4**



Entry	Chiral ligand	Time (h)	Yield[a]	ee[b] (%)	Config.[c]
1	**L1**	48	58	51	*R*
2	**L2**	48	40	45	*S*
3	**L3**	48	85	75	*R*
4	**L4**	48	40	7	*R*

[a] Isolated yield.
[b] Determined by chiral HPLC.
[c] Determined by the sign of the specific rotation.

same conditions in 75% ee (85% yield) with *R* configuration (Table 1, entry 3). Obviously, **L4** is not suitable for this asymmetric addition reaction (Table 1, entry 4). The results suggest that **L3** is an effective chiral ligand in this asymmetric reaction.

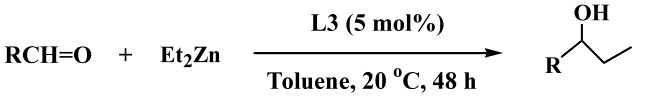
Under the optimized reaction conditions, we employed **L3** as the chiral ligand in this asymmetric reaction for various aldehydes. The results are summarized in Table 2.

As can be seen from Table 2, the corresponding *sec*-alcohols can be formed in excellent yields (82–98%) and good *ee* (60–83%) with *R* configuration for aromatic aldehydes (Table 2, entries 1–4, 6–8). On the other hand, in the reactions of aliphatic aldehydes, although high yields of the *sec*-alcohols were achieved, poor enantioselectivities (23–30% ee) were realized (Table 2, entries 5 and 9). It is known that in the catalytic asymmetric addition reaction of diethylzinc, the enantioselectivity is usually much lower with aliphatic aldehydes than the equivalent reaction with aromatic aldehydes.

To the best of our knowledge, it is only known that some Salen-type catalysts of transition metals can catalyze the asymmetric addition reaction[6] and the chiral Schiff bases themselves have not been investigated in detail for this purpose. Also, during our own investigations, we found that the readily available Schiff bases **D**–**F** have no catalytic activity in this reaction. Therefore, we have disclosed for the first time that axially dissymmetric chiral Schiff base ligands having specific structure can be effective chiral ligands in this reaction.

In conclusion, we have found that axially dissymmetric chiral ligands Schiff base **10** derived from the reaction of (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine with (*R*)-(+)-2,2′-dihydroxy-[1,1′]-binaphthalenyl-3-carbaldehyde **9** is also fairly effective in the asymmetric addition reaction of diethylzinc with aldehydes. At the present time we cannot clearly explain why **10** (**L3**) is so effective for this reaction, while its diastereomer **11** (**L4**) is a less effective ligand under the same conditions. For chiral ligands **L1** and **L2**, we believe that the flexible structures and the distance of the active site from the stereogenic center cause the low enantioselectivities. Efforts are now underway to elucidate the scope and limitations of (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine-derived Schiff base ligands in asymmetric catalysis.

Table 2. Catalytic asymmetric addition reaction of diethylzinc to aldehydes in the presence of chiral ligand **L3**



Entry	R	Yield[a] (%)	ee[b] (%)	Config.[c]
1	C_6H_5	85	75	*R*
2	*p*-MeC_6H_4	82	60	*R*
3	*p*-EtC_6H_4	95	72	*R*
4	1-Naphthyl	88	60	*R*
5	$PhCH{=}CH_2$	95	30	*R*
6	*p*-F-C_6H_4	91	71	*R*
7	*p*-ClC_6H_4	97	83	*R*
8	*p*-BrC_6H_4	98	79	*R*
9	*iso*-Butyl	86	23	*R*

[a] Isolated yields.
[b] Determined by chiral HPLC.
[c] Determined by the sign of the specific rotation.

3. Experimental

Mps were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. Optical rotations were determined in a solution of $CHCl_3$ or acetone at 20°C by using a Perkin–Elmer-241 MC digital polarimeter; $[\alpha]_D$ values are given in unit of 10^{-1} deg cm^2 g^{-1}. ^1H NMR spectra were determined for solutions in $CDCl_3$ with tetramethylsilane (TMS) as internal standard on a Bruker AMX-300 spectrometer; *J*-values are in Hz. IR spectra were determined by a Perkin–Elmer 983 spectrometer. Mass spectra were recorded with an HP-5989 instrument. High mass spectra were recorded on a Finnigan MA+ instrument. All solid compounds reported in this paper gave satisfactory CHN microanalyses with an Italian Carlo-Erba 1106 analyzer. (*R*)-(+)-1,1′-Binaphthyl-2,2′-diamine was prepared according to the literature.[7]

3.1. Preparation of (*R*)-2,2′-bis(ethoxycarbonylamino)-1,1′-binaphthyl, 2

This is a known compound and was prepared according to the literature method.[7] To a stirred, ice-cooling solution of (*R*)-binaphthyldiamine (568 mg, 2.0 mmol) in benzene (12 mL) and pyridine (1.5 mL) was added dropwise a solution of ethyl chloroformate (0.47 mL, 5.0 mmol) in benzene (3.0 mL). After the addition was completed, the mixture was stirred for 3 h at room temperature. The reaction was quenched by adding 10% NaOH (20 mL). The resulting organic layer and benzene extracts from the aqueous layer were combined, washed with water and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel. Elution with hexane/ethyl acetate (8:1) gave compound **2** as a colorless oil (813 mg, 95%). ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.70 (t, $J=7.1$ Hz, 3H), 4.30 (q, $J=7.1$ Hz, 2H), 6.27 (s, 2H, 2 NH), 6.96 (d, $J=8.2$ Hz, 2H, ArH), 7.14 (m, 2H, ArH), 7.22 (m, 2H, ArH), 7.93 (d, $J=7.9$ Hz, 2H, ArH), 8.06 (d, $J=9.1$ Hz, 2H, ArH), 8.56 (d, $J=9.1$ Hz, 2H, ArH).

3.2. Preparation of (*R*)-2,2′-bis(methylamino)-1,1′-binaphthyl, 3

This is a known compound and was prepared according to the literature method.[7] To a stirred solution of LAH (130 mg, 3.4 mmol), in anhydrous THF (15 mL) was

added dropwise a solution of (*R*)-2,2′-bis(ethoxycarbonylamino)-1,1′-binaphthyl **2** (256 mg, 0.6 mmol) in anhydrous THF (5 mL). The mixture was heated under reflux for 1 h, the reaction was quenched by water and 10% NaOH. After separation, the aqueous layer was extracted with ethyl acetate (2×20 mL). The organic layers were combined and dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography on silica gel. Elution with hexane/ethyl acetate (10:1) gave compound **3** (178 mg, 95%) as a colorless oil. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.84 (s, 6H, 2Me), 6.96 (d, J=8.2 Hz, 2H, ArH), 7.10 (m, 4H, ArH), 7.36 (d, J=9.7 Hz, 2H, ArH), 7.83 (d, J=7.6 Hz, 2H, ArH), 7.97 (d, J=8.2 Hz, 2H, ArH).

3.3. Preparation of (*R*)-2-[methyl-(2′-methylamino-[1,1′]-binaphthalenyl-2-yl)-amino]ethanol, 4

To a stirred, ice-cooling solution of (*R*)-2,2′-bis(methylamino)-1,1′-binaphthyl **3** (508 mg, 1.63 mmol) in CH_2Cl_2 (40 mL) and acetic acid (10 mL) was added ethylene oxide (10 mL, 0.5 mol). The mixture was stirred for 24 h at 0°C, then the reaction was quenched by slowly adding 20% NaOH until pH >7. After separation, the aqueous layer was extracted with ethyl acetate (2×20 mL). The organic layers were combined and dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography on silica gel. Elution with hexane/ethyl acetate (3:1) gave compound **4** (467 mg, 86%) as colorless solid. Mp 141–142°C; $[\alpha]_D$=−152 (*c* 0.4, $CHCl_3$); IR ($CHCl_3$) ν 3383, 3050, 2980, 1681, 1615, 1594, 1506, 1490, 1440, 1421, 1337, 817, 756 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.32 (s, 3H, Me), 2.82 (s, 3H, Me), 3.10–3.46 (m, 4H, CH_2CH_2), 6.95–7.54 (m, 8H, ArH), 7.81–7.99 (m, 4H, ArH); MS (EI) *m*/*e* 356 (M^+, 7.10), 325 (M^+−31, 100), 308 (M^+−48, 84.66), 280 (M^+−76, 47.80). Anal. calcd for $C_{24}H_{24}N_2O$ requires: C, 80.89; H, 6.74; N, 7.86. Found: C, 80.93; H, 6.77; N, 7.80%.

3.4. (*R*)-2-({2′-[(2-Hydroxyethyl)-methylamino]-[1,1′]-binaphthalenyl-2-yl}-methylamino)ethanol, 5

The preparation of compound **5** was completed in the same manner as that of compound **4** except that the mixture was stirred for 24 h at 10°C. Compound **5** was obtained (520 mg, 80%) as a colorless solid. Mp 152–153°C; $[\alpha]_D$=−19.1 (*c* 4.4, $CHCl_3$); IR ($CHCl_3$) ν 3381, 3050, 2982, 1685, 1618, 1597, 1506, 1490, 1445, 1420, 1337, 815, 755 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.52 (s, 6H, Me), 2.83–3.28 (m, 8H, $2CH_2CH_2$), 7.05 (d, J=7.6 Hz, 2H, ArH), 7.17 (m, 2H, ArH), 7.20 (m, 2H, ArH), 7.57 (d, J=9 Hz, 2H, ArH), 7.86 (d, J=8.1 Hz, 2H, ArH), 7.96 (d, J=8.7 Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 41.95, 58.56, 59.39, 120.76, 124.62, 126.30, 126.32, 126.71, 128.05, 128.29, 129.39, 130.68, 134.74; MS (EI) *m*/*e* 400 (M^+, 1.28), 369 (M^+−31, 38.24), 352 (M^+−48, 23.26), 294 (M^+−106, 100); HRMS calcd for $C_{26}H_{28}N_2O_2$ (M^+) requires 400.2151, found 400.2153.

3.5. Preparation of (*R*)-2,2′-bis(methoxymethoxy)-1,1′-binaphthyl, 7

This is a known compound and was prepared according to the literature.[4] Under a nitrogen atmosphere, (*R*)-1,1′-binaphthol (5.72 g, 20 mmol) was added to a suspension of NaH (2.4 g, 100 mmol) in anhydrous THF (40 mL) at 0°C with stirring. The resulting solution was stirred at 0°C for 10 min, and then methoxymethyl chloride (3.65 mL, 48 mmol) was slowly added. The mixture was allowed to warm to room temperature and stirred for 4 h. Then the reaction was quenched by water. After separation, the aqueous layer was extracted with ethyl acetate (2×20 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. After removal of the solvent, compound **7** was obtained (7.33 g, 98%), which was pure enough for the next step. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 3.14 (s, 6H, 2 Me), 4.97 (d, J=6.6 Hz, 2H, CH_2), 5.08 (d, J=6.6 Hz, 2H, CH_2), 7.13–7.37 (m, 6H, ArH), 7.58 (d, J=9.0 Hz, 2H, ArH), 7.86 (d, J=8.1 Hz, 2H, ArH), 7.94 (d, J=9.0 Hz, 2H, ArH).

3.6. Preparation of (*R*)-3-formyl-2,2′-bis(methoxymethoxy)-1,1′-binaphthyl, 8

This is a known compound and was prepared according to the literature.[4] Under a nitrogen atmosphere, *n*-BuLi (2 M in hexene, 2.83 mL, 5.65 mmol) was added to a solution of (*R*)-2,2′-bis(methoxymethoxy)-1,1′-binaphthyl **7** (1.87 g, 5 mmol) in anhydrous THF (30 mL) at room temperature. The mixture was stirred for 2 h, which produced a grey suspension. After the mixture was cooled to 0°C, DMF (0.46 mL, 6 mmol) was added. The reaction was allowed to warm to room temperature and stirred for 4 h. The reaction was then quenched by saturated NH_4Cl (20 mL). After separation, the aqueous layer was extracted with ethyl acetate (2×20 mL). The organic layers were combined and dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography on silica gel. Elution with hexane/ethyl acetate (10:1) gave compound **8** (1.4 g, 70%). ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 3.07 (s, 3H, Me), 3.20 (s, 3H, Me), 4.64 (d, J=6.1 Hz, 1H, CH), 4.75 (d, J=6.1 Hz, 1H, CH), 5.04 (d, J=7.3 Hz, 1H, CH), 5.16 (d, J=7.3 Hz, 1H, CH), 7.16–7.62 (m, 7H, ArH), 7.82–8.16 (m, 3H, ArH), 8.58 (s, 1H, ArH), 10.59 (s, 1H, CH=O).

3.7. Preparation of (*R*)-2,2′-dihydroxy-[1,1′]-binaphthyl-3-carbaldehyde, 9

This is a known compound and was prepared according to the literature method.[4] To a stirred solution of (*R*)-3-formyl-2,2′-bis(methoxymethoxy)-1,1′-binaphthyl **8** (1.44 g, 3.6 mmol) in methanol (20 mL) was added 10 drops of concentrated HCl at 60°C. Then the mixture was stirred for 0.5 h at the same temperature. After removal of the solvent, the residue was purified by column chromatography on silica gel. Elution with hexene/ethyl acetate (6:1) gave the compound **9** (1.18 g, 98%) as a yellow solid. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 4.94 (s, 1H, OH), 7.02–7.46 (m, 7H, ArH),

7.81–8.10 (m, 3H, ArH), 8.21 (s, 1H, ArH), 10.21 (s, 1H, OH), 10.65 (s, 1H, CH=O).

3.8. Preparation of Salen-type ligands, 10 and 11

3.8.1. Preparation of Salen-type ligand, 10. A mixture of (*R*)-binaphthyldiamine (57 mg, 0.2 mmol) and (*R*)-2,2′-dihydroxy -[1,1′]-binaphthyl-3-carbaldehyde **9** (126 mg, 0.4 mmol) in absolute ethanol (10 mL) was refluxed for about 10 h to yield a yellow precipitate. The crude product was filtered at room temperature and washed with ice-cold ethanol to afford pure Salen-type ligand **10** (166 mg, 95%). Mp 197–198°C; $[\alpha]_D = -377$ (*c* 0.105, acetone); IR ($CHCl_3$) *v* 3521, 3056, 1622, 1603, 1588, 1466, 1433, 1352, 814, 752 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 4.92 (s, 2H, 2OH), 6.92–8.02 (m, 32H, ArH), 8.67 (s, 2H, ArH), 12.22 (s, 2H, 2OH); MS (ESI) *m*/*e* 899.5 (M^++Na^+). Anal. calcd for $C_{62}H_{40}N_2O_4 \cdot CH_2Cl_2$ requires: C, 78.66; H, 4.57; N, 3.19. Found: C, 78.79, H, 4.63; N, 2.87%.

3.8.2. The preparation of Salen-type ligand, 11. This compound was prepared in the same manner as that of compound **10** except that (*S*)-binaphthyldiamine was used. Mp 186–187°C; $[\alpha]_D = +646$ (*c* 0.12, acetone); IR ($CHCl_3$) *v* 3515, 3381, 3056, 1698, 1622, 1603, 1588, 1466, 1434, 1353, 814, 748 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 5.15 (s, 2H, 2OH), 6.94–8.04 (m, 32H, ArH), 8.60 (s, 2H, ArH), 12.30 (s, 2H, 2OH); MS (ESI) *m*/*e* 899.5 (M^++Na^+). Anal. calcd for $C_{62}H_{40}N_2O_4 \cdot CH_2Cl_2$ requires: C, 78.66; H, 4.57; N, 3.19. Found: C, 78.74; H, 4.79; N, 2.92%.

3.9. Typical asymmetric addition procedure: typical procedure for the asymmetric addition of Et_2Zn to benzaldehyde

To a solution of ligand **10** (22 mg, 0.025 mmol) in toluene (1.5 mL) was added dropwise a solution of Et_2Zn (1.1 mL, 1 M in hexene) at room temperature. After the mixture stirred for 1 h, benzaldehyde (53 mg, 0.5 mmol) was added at room temperature, and the reaction was stirred for 48 h at room temperature. Optically active 1-phenylpropan-1-ol (58 mg, 85%) was obtained after acid workup and purification by silica gel TLC which was subjected to the chiral HPLC for the analysis of enantioselectivity.

Acknowledgements

We thank the State Key Project of Basic Research (Project 973) (No. G2000048007) and the National Natural Science Foundation of China for financial support (20025206).

References

1. (a) Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345; (b) Noyori, R.; Suga, S.; Kawai, K.; Okada, S.; Kitamura, M. *Pure Appl. Chem.* **1988**, *60*, 1597; (c) Tomioka, K. *Synthesis* **1990**, 541; (d) Brunner, H. *Synthesis* **1988**, 645; (e) Narasaka, K. *Synthesis* **1991**, 1; (f) Noyori, R. *Chem. Soc. Rev.* **1989**, *18*, 187; (g) Kaufmann, D.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 545.
2. Shi, M.; Wang, C.-J. *Tetrahedron: Asymmetry* **2001**, *12*, 3105.
3. (a) Noyori, R.; Kitamura, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 49 and references cited therein; (b) Pu, L.; Yu, H.-B. *Chem. Rev.* **2001**, *101*, 757; (c) Kitamura, M.; Okada, S.; Suga, S.; Noyori, R. *J. Am. Chem. Soc.* **1989**, *111*, 4028; (d) Oguni, N.; Matsuda, Y.; Kaneko, T. *J. Am. Chem. Soc.* **1988**, *110*, 7877; (e) Kang, J.; Lee, J. W.; Kim, J. I. *J. Chem. Soc., Chem. Commun.* **1994**, 2009; (f) Kitamura, M.; Suga, S.; Niwa, M.; Noyori, R. *J. Am. Chem. Soc.* **1995**, *117*, 4832; (g) Shi, M.; Satoh, Y.; Makihara, T.; Masaki, Y. *Tetrahedron: Asymmetry* **1995**, *6*, 2109; (h) Shi, M.; Satoh, Y.; Masaki, Y. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2547; (i) Shi, M.; Jiang, J.-K. *Tetrahedron: Asymmetry* **1999**, *10*, 1673; (j) Shi, M.; Jiang, J.-K.; Feng, Y.-S. *Tetrahedron: Asymmetry* **2000**, *11*, 4923.
4. (a) Matsunaga, S.; Das, J.; Roels, J.; Vogl, E. M.; Yamamoto, N.; Lida, T.; Yamaguchi, K.; Shibasaki, M. *J. Am. Chem. Soc.* **2000**, *122*, 2252; (b) Zhang, H.; Huang, W.; Pu, L. *J. Org. Chem.* **2001**, *66*, 481.
5. (a) Bernardo, K.; Robert, A.; Dahan, F.; Meunier, B. *New J. Chem.* **1995**, *19*, 129; (b) Evans, D. A.; Janey, J. M.; Magomedov, N.; Tedrow, J. S. *Angew. Chem., Int. Ed.* **2001**, *40*, 1884.
6. (a) Review for using chiral metal (Salen) complexes in asymmetric catalysis: Canali, L.; Sherrington, D. C. *Chem. Soc. Rev.* **1999**, *28*, 85; (b) Cozzi, P. G.; Papa, A.; Umani-Ronchi, A. *Tetrahedron Lett.* **1996**, *37*, 4613; (c) Rippert, A. J.; Keller, F. *Helv. Chim. Acta* **1999**, *82*, 125; (d) Kozlowski, M. C.; Dimauro, E. F. *Org. Lett.* **2001**, *3*, 3053.
7. Miyano, S.; Nawa, M.; Mori, A.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2171.