Axially Dissymmetric Chiral (*R*)-*N*, *N*′-Bis(2-hydroxy-3, 5-di-*tert*-butyl-arylmethyl)-1, 1′-binaphthalene-2, 2′-diamine as Chiral Ligands in the Reaction of Diethylzinc to Aldehydes†

SHI, Min*,[a](施敏) **DUAN, Wei-Liang**[b](段伟良) **RONG, Guo-Bin**[b](荣国斌)

[a] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*

[b] *East China University of Science and Technology, Shanghai 200237, China*

Chiral ligand (*R*)-*N*, *N*′-Bis(2-hydroxy-3,5-di-*tert*-butyl-arylmethyl)-1,1′-binaphthalene-2,2′-diamine derived from the reduction of Schiff base (*R*)-2,2′-bis (3,5-di-*tert*-butyl-2-hydroxybenzylideneamino)-1,1′-binaphthyl with $LiAlH_4$ is fairly effective in the asymmetric addition reaction of diethylzinc to aldehydes by which good yields (46%—94%) of the corresponding *sec*-alcohols can be obtained in moderate *ee* (51%—79%) with *R* configuration for a variety of aldehydes.

Keywords axially dissymmetric chiral ligand, (*R*)-*N*, *N*′-bis-(2-hydroxy-3, 5-di-*tert*-butyl-arylmethyl)-1, 1′-binaphthalene-2, 2′-diamine, diethylzinc, asymmetric addition reaction

Introduction

Axially dissymmetric 1, 1′-binaphthyl and 1, 1′-biphenyl ligands bearing two identical groups in the 2, 2′-position have proved to be remarkably useful in enantioselective catalysis, with optical yields close to 100% enantiomeric excess (*ee*) obtained in several preparatively important reactions.[1] Previously, we reported that axially dissymmetric chiral salen-type ligands **1**—**4** (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 salicylaldehyde, are excellent chiral ligands in the catalytic asymmetric aziridination of cinnamates catalyzed by Cu(MeCN)ClO_4.[2] In order to extend the scopes of these chiral ligands, we further examined the other types of catalytic asymmetric reactions using these chiral ligands or their derivatives. It was found that some derivatives of these chiral ligands having phenolic hydroxyl group are also very effective in the asymmetric addition reactions of di-

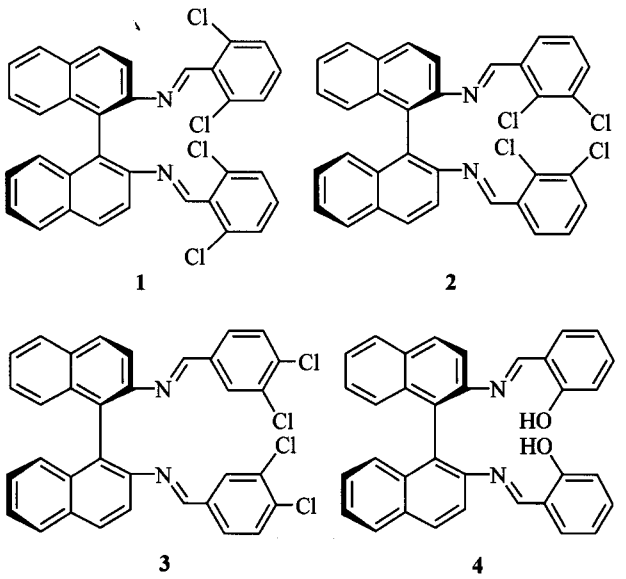


Fig. 1 Structures of Schiff bases **1**—**4**.

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

Received May 9, 2002; revised July 19, 2002; accepted August 16, 2002.

Project supported by the Major State Basic Research Development Program (No. G2000048007) and the National Natural Science Foundation of China (No. 20025206).

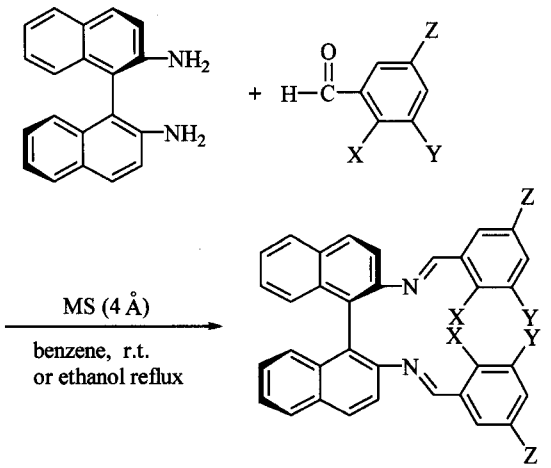
†Dedicated to Professor HUANG Yao-Zeng on the occasion of his 90th birthday.

ethylzinc to aldehydes. In some cases, very high yields and good enantioselectivities could be achieved in this very famous asymmetric addition reaction.[3] Herein, we report the details of axially dissymmetric chiral (*R*)-*N*, *N*′-bis(2-hydroxy-3,5-di-*tert*-butyl-arylmethyl)-1,1′-binaphthalene-2,2′-diamine promoted asymmetric addition reactions of diethylzinc to aldehydes.

Results and discussion

It is well-known that β-amino alcohols are the excellent chiral ligands for the asymmetric addition reactions of diethylzinc to aldehydes. Thus, we synthesized some Schiff bases having phenolic hydroxyl group, **4**, **5** and **6**, from chiral scaffold of (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine with the corresponding arylaldehydes and used them in the asymmetric addition reaction of diethylzinc to aldehydes. The axially dissymmetric chiral ligands, Schiff bases **4**—**6**, were prepared by the reaction of C_2-symmetric (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine with the corresponding arylaldehydes in anhydrous benzene or ethanol in the presence of molecular sieve (MS) (4 Å) according to the literature (Scheme 1).[4] After usual work-up and purification by silica gel column chromatography or recrystallization, ligands **4**—**6** were obtained as yellow solids in about 90% yields respectively.

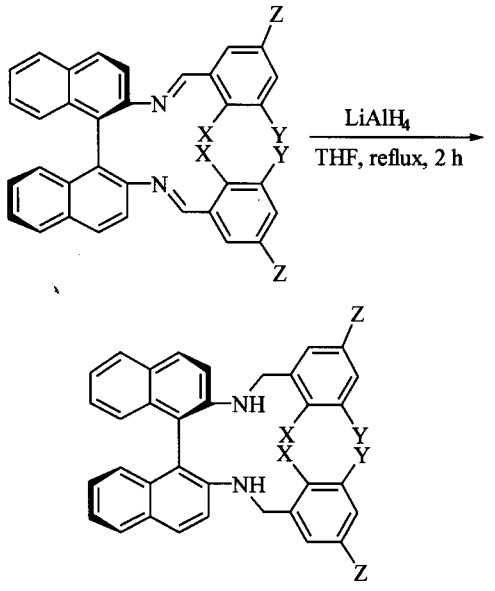
Scheme 1



4: X = OH, Y = Z = H; 92%
5: X = OH, Y = H, Z = Bu^t; 90%
6: X = OH, Y = Z = Bu^t; 89%

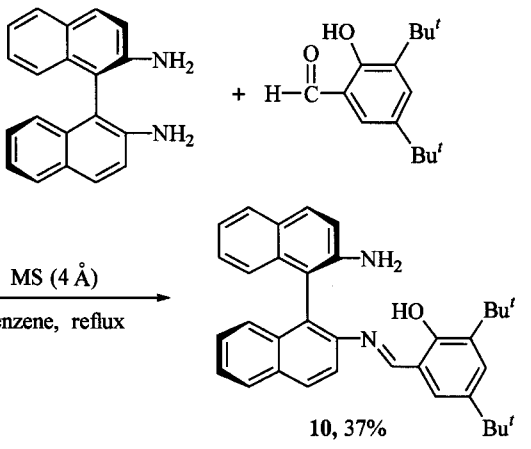
In addition, by reduction of Schiff bases **4**—**6** with $LiAlH_4$ in THF, chiral ligands **7**—**9** derived from the corresponding Schiff bases can be successfully synthesized in good yields (Scheme 2). It was also found that, in the reaction of (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine with 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde under the same conditions, an unsymmetric Schiff base **10** can be obtained in moderate yield (Scheme 3).

Scheme 2



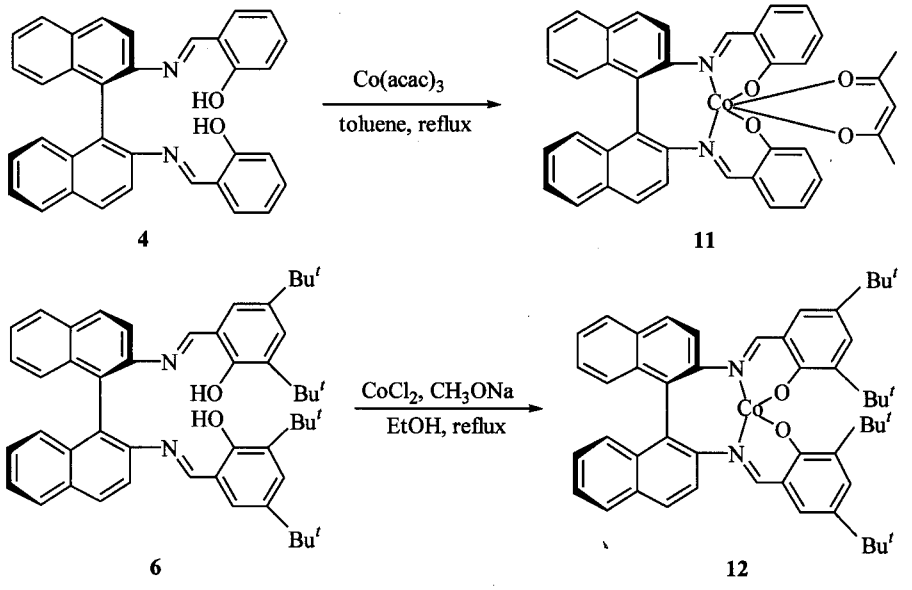
7: X = OH, Y = Z = H; 96%
8: X = OH, Y = H, Z = Bu^t; 94%
9: X = OH, Y = Z = Bu^t; 92%

Scheme 3



On the other hand, it is well known that some Salen-type catalysts of transition metal are also very effective for this asymmetric addition reaction.[5] Thus, we also prepared two chiral Salen-type Co catalysts from the reaction of Schiff bases **4** and **6** with $Co(acac)_3$ and $CoCl_2$, re-

Scheme 4



spectively (Scheme 4).[6] The structures of these chiral ligands were established by spectroscopic data.

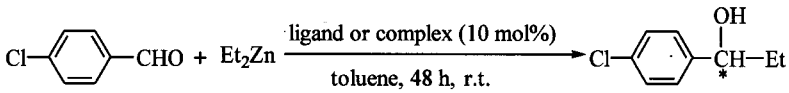
We examined the asymmetric addition reaction of diethylzinc to arylaldehydes in the presence of catalytic amount (10 mol%) of chiral ligands **6**, **9**—**12**. The results are summarized in Table 1. The enantiomeric excesses (*ee*) of the products were determined by HPLC analysis using chiral stationary-phase column (CHIRALCEL OD and OJ) and the absolute configuration of the major enantiomer was assigned according to the sign of their specific rotations. As shown in Table 1, using (*R*)-2,2′-bis-(3,5-di-*tert*-butyl-2-hydroxybenzylideneamino)-1,1′-binaphthyl (**6**) and unsymmetric Schiff base **10** as the chiral ligand in the asymmetric addition reaction of diethylzinc to *p*-chlorobenzylaldehyde, the corresponding *sec*-alcohol was obtained in very low yields with poor enantioselectivity (Table 1, Entries 1 and 3). The two chiral Salen-type Co complexes are also not effective in this reaction as the catalyst (Table 1, Entries 4 and 5). Only (*R*)-*N*,*N*′-bis (2-hydroxy-3,5-di-*tert*-butylarylmethyl)-1,1′-binaphthalene-2,2′-diamine (**9**) is fairly effective chiral ligand in this asymmetric reaction (Table 1, Entry 2).

In order to optimize the reaction conditions, we employed (*R*)-2,2′-bis (3,5-di-*tert*-butyl-2-hydroxybenzylideneamino)-1,1′-binaphthyl (**6**) and ligands **7**—**9** as the chiral ligand in this asymmetric reaction under various conditions. The results are summarized in Table 2. It was found that the reaction temperature and solvent play very important roles in this asymmetric reaction (Table 2). Using (*R*)-*N*,*N*′-bis(2-hydroxy-3,5-di-*tert*-butylarylmethyl)-1,1′-binaphthalene-2,2′-diamine (**9**) (10 mol%) as the chiral ligand in toluene at low temperature (−4 ℃) the *sec*-alcohol can be obtained in 79% ee and 81% yield with *R* configuration (Table 2, Entry 5). The similar result was obtained in the presence of ligand **9** (20 mol%) under the same conditions (Table 2, Entry 6). At lower reaction temperature (−30 ℃), no improvement on enantioselectivity could be realized and the yield of *sec*-alcohol decreased to 28% (Table 2, Entry 7). The chiral ligands **6**—**8** gave the *sec*-alcohol with very poor enantioselectivities (Table 2, Entries 1, 9 and 10). As the matter of fact, chiral ligand **9** is the best catalyst in this reaction (Table 2, Entry 5).

Based on these results, chiral ligand **9** was utilized as the catalyst to investigate the asymmetric addition reaction of diethylzinc to various aldehydes under the optimized reaction conditions. The results are summarized in Table 3. As can be seen from Table 3, good to excellent yields (46%—94%) of the corresponding *sec*-alcohols can be formed in moderate *ee* (51%—79%) with *R* configuration (Table 3).

In conclusion, it was found that the chiral ligand (*R*)-*N*,*N*′-bis(2-hydroxy-3,5-di-*tert*-butyl-arylmethyl)-1,1′-binaphthalene-2,2′-diamine (**9**) derived from the reduction of Schiff base (*R*)-2,2′-bis(3,5-di-*tert*-butyl-

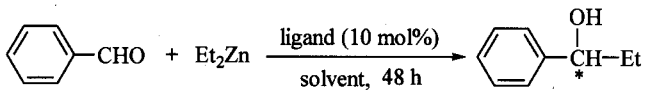
Table 1 Asymmetric addition reaction of diethylzinc to aldehydes in the presence of chiral catalysts **6**, **9**—**12** (10 mol%)



Entry	Chiral catalyst	Yield (%)[a]	*ee* (%)[b]	Absolute configuration
1	Ligand **6**	28	10	*S*
2	Ligand **9**	71	60	*R*
3	Ligand **10**	38	9	*S*
4	Complex **11**	18	24	*R*
5	Complex **12**	40	44	*R*

[a] Isolated yields. [b] Determined by chiral HPLC.

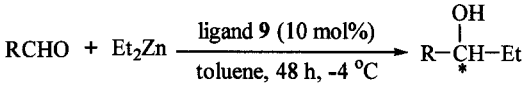
Table 2 Asymmetric addition reaction of diethylzinc to aldehydes in the presence of chiral ligands **6**—**9** (10 mol%)

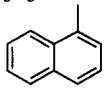


Entry	Ligand	Solvent	Temp. (℃)	Yield (%)[a]	*ee* (%)[b]	Absolute configuration
1	**6**	Toluene	r.t.	80[c]	8	*R*
2	**9**	Toluene	r.t.	74	66	*R*
3	**9**	CH_2Cl_2	r.t.	59	56	*R*
4	**9**	THF	r.t.	6	23	*R*
5	**9**	Toluene	−4	81	79	*R*
6	**9**	Toluene	−4	84[d]	75	*R*
7	**9**	Toluene	−30	47[e]	69	*R*
8	**9**	Toluene	−30	28[f]	69	*R*
9	**7**	Toluene	−4	21	36	*R*
10	**8**	Toluene	−4	9	—	*R*

[a] Isolated yields. [b] Determined by chiral HPLC. [c] The reaction was carried out in the presence of 1.5 equiv. $Ti(OPri)_4$. [d] The reaction was carried out in the presence of ligand **9** (20 mol%). [e] The reaction was carried out at −30 ℃ in the presence of ligand **9** (5 mol%). [f] The reaction was carried out at −30 ℃ in the presence of ligand **9** (2.5 mol%).

Table 3 Asymmetric addition reaction of diethylzinc to aldehydes in the presence of chiral ligand **9** (10 mol%)



Entry	R	Yield (%)[a]	*ee* (%)[b]	Absolute configuration
1	C_6H_5	81	79	*R*
2	*p*-ClC_6H_4	93	71	*R*
3	*p*-BrC_6H_4	91	70	*R*
4	*p*-$MeOC_6H_4$	81	63	*R*
5	*m*-MeC_6H_4	77	77	*R*
6	$C_6H_5CH=CH$	50	51	*R*
7		46	74	*R*
8	*p*-EtC_6H_4	94	70	*R*
9	*m*-FC_6H_4	84	60	*R*

[a] Isolated yields. [b] Determined by chiral HPLC.

2-hydroxybenzylideneamino)-1, 1′-binaphthyl (**6**) with $LiAlH_4$ is also fairly effective in the asymmetric addition reaction of diethylzinc to aldehydes. Now we can not clearly explain why **9** is more effective than **6** in this famous asymmetric reaction. It was believed that because of the more sterically flexible structure of the chiral ligand **9** (by comparison with ligand **6**), the reactive intermediate formed by the reaction of chiral ligand **9** with diethylzinc may possess such structure in which the zinc atom can coordinate with both of the nitrogen atoms. However, for chiral ligand **6**, it may be quite difficult to form such sterically rigid active species. Thus, much higher enatioselectivities can be achieved by the catalysis of chiral ligand **9** in this reaction. Efforts are underway to elucidate the scope and limitations of this kind of Schiff base ligand derived from (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine in asymmetric catalysis. Work along these lines is currently in progress.

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 ℃ by using a Perkin-Elmer-241 MC digital polarimeter; $[\alpha]_D$-values are given in unit of 10^{-1} deg·cm^2·g^{-1}. ^{1}H NMR spectra were determined for solutions in $CDCl_3$ with tetramethylsilane (TMS) as internal standard on a Bruker AMX-300 spectrometer. IR spectra were determined by a Perkin-Elmer 983 spectrometer. Mass spectra were recorded on 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 a Italian Carlo-Erba 1106 analyzer. Compounds **4**—**6** were prepared according to the literatures.[5]

Preparation of N, N′-bis(2-hydroxyarylmethyl)-1,1′-binaphthalene-2,2′-diamine (**7**)

To a solution of (*R*)-2,2′-bis(2-hydroxybenzylideneamino)-1,1′-binaphthyl **4** (98 mg, 0.2 mmol) in THF (20 mL) was added $LiAlH_4$ (80 mg, 2.0 mmol) and the reaction mixture was stirred for 2 h under reflux. After cooling to room temperature, 20% NaOH aqueous solution (5 mL) was added into the reaction mixture. The solution was filtered off and washed with brine (20 mL). The organic phase was extracted with ether (10 mL × 2) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography to give **7** (95 mg, 96%) as a colorless oil (eluent: ethyl acetate/petroleum ether = 1/14, *V*/*V*). $[\alpha]_D$ +15.3 (*c* 0.41, acetone); m.p. 180—183 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 4.02 (br, 2H, NH), 4.40 (d, *J* = 12.2 Hz, 2H, CH_2), 4.48 (d, *J* = 12.2 Hz, 2H, CH_2), 6.77 (d, *J* = 8.1 Hz, 2H, Ar), 6.83 (td, *J* = 8.1, 1.2 Hz, 2H, Ar), 7.01 (d, *J* = 8.1 Hz, 2H, Ar), 7.09—7.33 (m, 8H, Ar), 7.40 (d, *J* = 9.3 Hz, 2H, Ar), 7.83 (dd, *J* = 8.4, 1.2 Hz, 2H, Ar), 7.90 (d, *J* = 9.3 Hz, 2H, Ar); IR (film) ν: 3412, 3350, 3051, 1616, 1594, 1510, 1490, 1456, 1335, 1242, 812, 750 cm^{-1}; MS (EI) *m*/*z* (%): 497 (M^+ + 1, 0.59), 496 (M^+, 0.36), 390 (M^+ − 106, 17.40), 284 (M^+ − 212, 100), 147 (M^+ − 349, 24.88). Anal. calcd for $C_{34}H_{28}N_2O_2$: C 82.23, H 5.68, N 5.64; found C 81.70, H 5.96, N 5.26.

Preparation of N, N′-bis(2-hydroxy-4-tert-butyl-arylmethyl)-1,1′-binaphthalene-2,2′-diamine (**8**)

This compound was prepared in the same manner as that described above. Yield 114 mg, 94%; $[\alpha]_D$ −52.0 (*c* 0.22, acetone); m.p. 74—76 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.26 (s, 18H, Me_3C), 4.00 (s, br, 2H, NH), 4.40 (d, *J* = 12.2 Hz, 2H, CH_2), 4.48 (d, *J* = 12.2 Hz, 2H, CH_2), 6.70 (d, *J* = 8.4 Hz, 2H, Ar), 7.01 (d, *J* = 8.4 Hz, 2H, Ar), 7.08—7.32 (m, 8H, Ar), 7.41 (d, *J* = 9.3 Hz, 2H, Ar), 7.70 (br., 2H, OH), 7.82 (d, *J* = 8.4 Hz, 2H, Ar), 7.95 (d, *J* = 12.9 Hz, 2H, Ar); IR (film) ν: 3418, 3353, 2961, 1618, 1596, 1504, 1424, 1267, 811, 745 cm^{-1}; MS (EI) *m*/*z* (%): 609 (M^+ + 1, 1.62), 608 (M^+, 1.26), 446 (M^+ − 162, 17.10), 284 (M^+ − 324, 100), 147 (M^+ − 461, 24.88). Anal. calcd for $C_{42}H_{44}N_2O_2$: C 82.86, H 7.28, N 4.60; found C 82.74, H 7.53, N 4.43.

Preparation of N, N′-bis(2-hydroxy-3,5-di-tert-butylarylmethyl)-1,1′-binaphthalene-2,2′-diamine (**9**)

This compound was prepared in the same manner as that described above. Yield 133 mg, 92%; $[\alpha]_D$ −31.0 (*c* 0.30, acetone); m.p. 104—106 ℃; ^{1}H

NMR ($CDCl_3$, 300 MHz) δ: 1.25 (s, 18H, Me_3C), 1.29 (s, 18H, Me_3C), 3.78—3.84 (m, 2H, NH), 4.42—4.48 (m, 4H, CH_2), 6.92 (d, J = 2.7 Hz, 2H, Ar), 7.03 (d, J = 7.8 Hz, 2H, Ar), 7.21—7.32 (m, 6H, Ar), 7.51 (d, J = 8.7 Hz, 2H, Ar), 7.83 (dd, J = 8.7, 1.2 Hz, 2H, Ar), 7.95 (d, J = 9.0 Hz, 2H, Ar), 8.34 (s, 2H, OH); IR (film) ν: 3361, 2953, 1618, 1591, 1478, 1421, 1289, 1229, 805, 749 cm^{-1}; MS (EI) m/z (%): 502 (M^+, 3.47), 284 (M^+ - 218, 100), 267 (M^+ - 235, 38.18), 219 (M^+ - 283, 13.57). Anal. calcd for $C_{50}H_{60}N_2O_2$: C 83.29, H 8.39, N 3.89; found C 83.02, H 8.22, N 3.78.

Preparation of (*R*)-2-*amino*-2′-(3,5-*di*-*tert*-*butyl*-2-*hydroxybenzylideneamino*)-1,1′-*binaphthyl* (**10**)

The starting materials (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine (142 mg, 0.5 mmol) and 3,5-di-*tert*-butyl-2-hydroxylbenzaldehyde (117 mg, 0.5 mmol) were refluxed for 6 h in anhydrous benzene in the presence of catalytic amount of camphorsulfonic acid (CSA). The solvent was removed under reduced pressure and the residue was purified by flash chromatography to give **10** (92 mg, 37%) as a solid compound (eluent: ethyl acetate/petroleum ether = 1/19, *V*/*V*). $[\alpha]_D$ - 4.8 (*c* 0.50, $CHCl_3$); ^1H NMR (CDCl3, 300 MHz) δ: 1.25 (s, 9H, CMe_3), 1.26 (s, 9H, CMe_3), 3.62 (s, 2H, NH_2), 6.90—8.10 (m, 14H, Ar), 8.67 (s, 1H, CH=N), 11.62 (s, 1H, OH); IR (film) ν: 1621 (C=N) cm^{-1}. The spectroscopic data are in consistent with those reported in literature.[7]

Preparation of [[2,2′-[[1,1′-*binaphthalene*]-2,2′-*diylbis*[*nitrilomethylidyne*]]*bisphenolato*](2-)](2,4-*pentanedionato*)-*cobalt*(III) (**11**)[6]

$Co(acac)_3$(71 mg, 0.2 mmol) was added to a solution of **4** (98 mg, 0.2 mmol) in toluene (20 mL). The reaction solution was refluxed for 3 d under argon atmosphere. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (silica gel) to give **11** (98 mg, 73%) as a green solid (eluent: ethyl acetate/petroleum ether = 1/2, *V*/*V*). $[\alpha]_D$ - 317 (*c* 0.0175, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ: 1.17 (s, 3H, Me), 2.05 (s, 3H, Me), 5.33 (s, 1H, CH), 6.32 (t, J = 7.5 Hz, 1H, Ar), 6.40—6.45 (m, 1H, Ar), 6.79 (dd, J = 7.8, 1.8 Hz, 1H, Ar), 7.02—7.34 (m, 13H, Ar), 7.43 (t, J = 7.5 Hz, 1H, Ar), 7.48—7.54 (m, 1H, Ar), 7.77 (d, J = 8.7 Hz, 1H, Ar), 7.80 (s, 1H, HC=N), 7.83 (s, 1H, HC=N), 7.93(d, J = 8.4 Hz, 1H, Ar); IR (film) ν: 1608 (C=N), 1587 (C=O) cm^{-1}; MS (EI) m/z (%): 549 (M^+ - acac, 95.16), 430 (M^+ - 119, 4.20), 342 (M^+ - 207, 8.69), 100 (M^+ - 449, 1.51). Anal. calcd for $C_{39}H_{29}CoN_2O_4 \cdot 0.5H_2O$: C 71.23, H 4.60, N 4.26; found C 71.33, H 5.06, N 4.02.

Preparation of [[2,2′-[[1,1′-*binaphthalene*]-2,2′-*diylbis*(*nitrilomethylidyne*)] *bis*[3,5-*di*-*tert*-*butylphenolato*]](2-)]-*cobalt*(II) (**12**)

A solution of compound **6** (143 mg, 0.2 mmol) and $CoCl_2$(26 mg, 0.2 mmol) in absolute ethanol (20 mL) was refluxed for 24 h under argon atmosphere in the presence of CH_3ONa (43 mg, 0.4 mmol). After cooling to room temperature, the solution was filtered off. The solvent was removed under reduced pressure and the residue was recrystallized from CH_2Cl_2:CH_3OH (3:1, *V*/*V*) to give **12** (73 mg, 47%) as a red compound. $[\alpha]_D$ - 240 (*c* 0.025, $CHCl_3$); IR (film) ν: 1588 (C=N) cm^{-1}; MS (EI) m/z (%): 774 (M^+, 98.80), 759 (M^+ - 15, 100), 372 (M^+ - 402, 29.32), 219 (M^+ - 555, 15.85). Anal. calcd for $C_{50}H_{54}CoN_2O_2$: C 77.60, H 7.03, N 3.62; found C 77.20, H 6.96, N 3.60.

Typical asymmetric addition procedure

To a suspension of *N*,*N*′-bis(2-hydroxy-3,5-di-*tert*-butyl-arylmethyl)-1,1′-binaphthalene-2,2′-diamine (**9**) (36 mg, 0.05 mmol) in toluene (2.0 mL), diethylzinc (1.0 mmol, 1.0 mL of 1 mol/L hexane solution) was added at - 4 ℃. After stirring for 0.5 h, benzaldehyde (53 mg, 0.5 mmol) was added and the reaction mixture was stirred for 48 h at - 4 ℃. The reaction was quenched by 2 mol/L HCl aqueous solution (2.0 mL) and the organic product was extracted with ether. The solvent was dried over Na_2SO_4 and was evaporated under reduced pressure. The residue was purified by a flash column chromatography (silica gel) to give the optically active 1-phenylpropanol (55 mg, 81%, *ee* 79%).

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) 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.

5 (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.

6 (a) Cheng, M.-C.; Chan, M. C.-W.; Peng, S.-M.; Cheung, K.-K.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1997**, 3479.
(b) Bernardo, K.; Leppard, S.; Robert, A.; Commenges, G.; Dahan, F.; Meunier, B. *Inorg. Chem.* **1996**, *35*, 387.

7 Zhou, X.-G.; Huang, J.-S.; Ko, P.-H.; Cheung, K.-K.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1999**, 3303.

(E0205094 PAN, B. F.; DONG, H. Z.)