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Enantioselective catalysis. Part 143: Astonishingly high enantioselectivity in the transfer hydrogenation of acetophenone with 2-propanol using Ru complexes of the Schiff base derived from (*S*)-2-amino-2′-hydroxy-1,1′-binaphthyl (NOBIN) and 2-pyridinecarbaldehyde†

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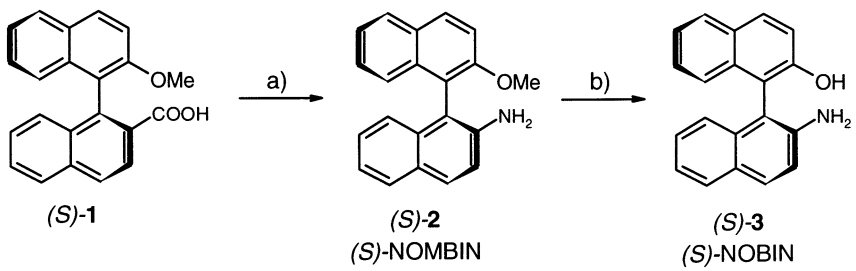
Abstract—A series of bidentate and tridentate (*S*)-NOBIN derivatives was synthesised and tested as chiral ligands in the Ru-catalysed enantioselective transfer hydrogenation of acetophenone with 2-propanol. Despite the similarities in chemical structure, only the imine derived from (*S*)-NOBIN and 2-pyridinecarbaldehyde and the corresponding amine (obtained by $NaBH_4$ reduction of the imine) afforded (*S*)-1-phenylethanol in nearly quantitative yields and outstanding enantioselectivities of up to 97% e.e.

1. Introduction

(*S*)-2-Amino-2′-hydroxy-1,1′-binaphthyl (NOBIN) can be synthesised by the unsymmetrical oxidative coupling of the carcinogenic 2-naphthylamine with 2-naphthol and subsequent resolution.[1,2] An alternative synthesis involves the diastereoselective nucleophilic aromatic substitution of (−)-menthyl 1-(−)-menthoxynaphthalene-2-carboxylate with 2-methoxy-1-naphthylmagnesium bromide to give (*S*)-2′-methoxy-1,1′-binaphthyl-2-carboxylic acid (*S*)-**1** after hydrolysis. Subsequent Curtius rearrangement of (*S*)-**1** leads to (*S*)-2-amino-2′-methoxy-1,1′-binaphthyl (*S*)-**2**, NOMBIN,[3] which can be submitted to BBr_3 cleavage of the methyl ether to afford (*S*)-**3**, (*S*)-NOBIN, in 92% yield, a new approach which we disclose herein (Scheme 1).



Scheme 1. Synthesis of (*S*)-**3**: (a) (i) $SOCl_2$, reflux 4 h, (ii) NaN_3, acetone, water, rt to 0°C, (iii) THF, water, reflux, 12 h, 70%; (b) BBr_3, methylene chloride, 92%.

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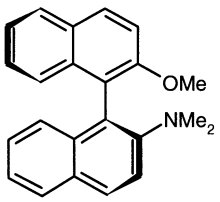
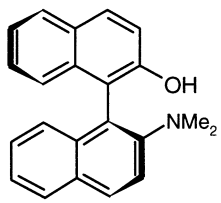
2. Results and discussion

By methylation of the hydroxyl group and/or the amine group of (*S*)-NOBIN the *O*- and *N*-methylated ligands (*S*)-**4** and (*S*)-**5**[4] were obtained (Scheme 2).

We prepared the imine derivatives (*S*)-**6**,[5] (*S*)-**8**,[6] (*S*)-**10** from (*S*)-NOBIN and (*S*)-**7**, (*S*)-**9** from (*S*)-NOMBIN by reaction with salicylaldehyde, 2-pyridinecarbaldehyde and 2-formylphenyl(diphenyl)phosphine. The ligand (*S*)-**11** was obtained from (*S*)-**8** by $NaBH_4$ reduction (Scheme 3). We used the starting materials (*S*)-**2**–(*S*)-**5**, the Schiff base ligands (*S*)-**6**–(*S*)-**10** and the amine (*S*)-**11** together with the procatalyst $Ru(PPh_3)_3Cl_2$ in the enantioselective transfer hydrogenation of acetophenone with 2-propanol. The in situ catalysts with binaphthyls (*S*)-**2**–(*S*)-**5** gave conversions below 10% and racemic 1-phenylethanol product (Table 1, entries 1–4).



(*S*)-**4**

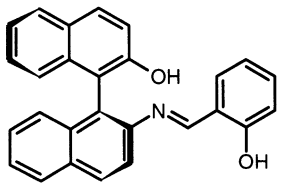


(*S*)-**5**

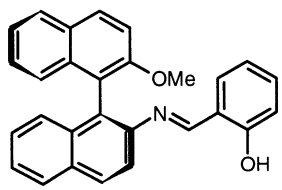
Scheme 2. The methylated compounds (*S*)-**4** and (*S*)-**5**.

As the metal precursor $Ru(PPh_3)_3Cl_2$ itself has low catalytic activity (entry 20), there is no ligand acceleration and no ligand influence with (*S*)-**2**–(*S*)-**5**. The same is true for the Schiff bases (*S*)-**6** and (*S*)-**9** (entries 5 and 8). Compound (*S*)-**7** gave a low conversion accompanied by chiral induction just outside the limits of error (entry 6) and the Schiff base (*S*)-**10**, derived from (*S*)-NOMBIN and 2-formylphenyl(diphenyl)phosphine, afforded (*R*)-1-phenylethanol with 15% e.e. (entry 9). Amazingly, the Schiff base (*S*)-**8**, derived from (*S*)-NOBIN and 2-pyridinecarbaldehyde, yielded (*S*)-1-phenylethanol in 97% e.e. (entry 7). Since the methoxy derivative (*S*)-**9** does not have any influence on the in situ catalyst, the OH group of (*S*)-**8** must be essential. (*S*)-**8** presumably binds to the metal atom as a phenolate. Inspection of Scheme 3 and Table 1 shows that (*S*)-**8** in combination with $Ru(PPh_3)_3Cl_2$ is a unique system affording outstanding enantioselectivities in the transfer hydrogenation of acetophenone. Interestingly, with the amine (*S*)-**11**, which is the reduction product of imine (*S*)-**8**, the same high enantioselectivity was obtained (entry 10).

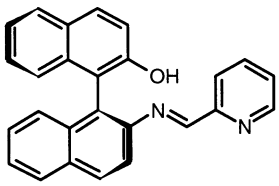
In order to increase the catalytic activity of (*S*)-**8** and (*S*)-**11** several parameters were varied. Changing the ratio of metal to ligand to substrate from 1/1.1/200 to 1/1.1/100 and 1/1.1/50 resulted in an increase in the yield, with the enantiomeric excess remaining excellent (entries 11–14 and 19). With the ratio 1/1.1/50 some precipitation of the catalyst occurred probably due to



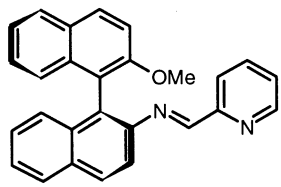
(*S*)-**6**



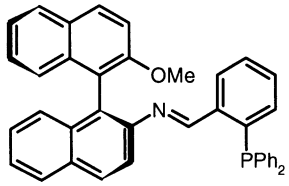
(*S*)-**7**



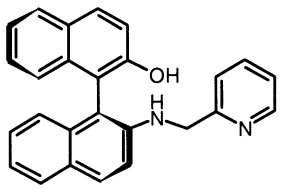
(*S*)-**8**



(*S*)-**9**



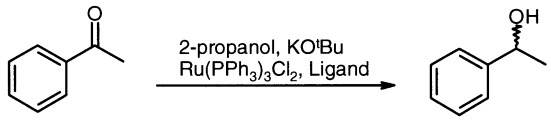
(*S*)-**10**



(*S*)-**11**

Scheme 3. Imines (*S*)-**6**–(*S*)-**10** and amine (*S*)-**11** derived from (*S*)-NOBIN and (*S*)-NOMBIN.

Table 1. Enantioselective transfer hydrogenation of acetophenone in presence of different (*S*)-NOBIN-derived Ligands[a]



Entry	Ligand	Ratio[b]	Temp. (°C)	Time (h)	Yield (%)	E.e. (%)
1	(*S*)-**2**	1/1.1/1/200	28	15	6.4/6.4	rac.
2	(*S*)-**3**	1/1.1/2.1/200	28	15	3.6/5.2	rac.
3	(*S*)-**4**	1/1.1/1/200	28	15	5.8/8.9	rac.
4	(*S*)-**5**	1/1.1/2.1/200	28	15	4.0/16.5	rac.
5	(*S*)-**6**	1/1.1/3.1/200	28	15	1.2/0.8	rac.
6	(*S*)-**7**	1/1.1/2.1/200	28	15	8.6/4.3	2.6(*S*)/4.4(*S*)
7	(*S*)-**8**	1/1.1/2.1/200	28	15	22.8/22.6/25.1	97.1(*S*)/97.2(*S*)/96.6(*S*)
8	(*S*)-**9**	1/1.1/1/200	28	15	2.3/3.7	rac.
9	(*S*)-**10**	1/1.1/1/200	28	15	20.4/20.8	14.1(*R*)/15.9(*R*)
10	(*S*)-**11**	1/1.1/3.2/200	28	15	85.7	96.3(*S*)
11	(*S*)-**8**	1/1.1/2.1/100	28	15	94.3	95.7(*S*)
12	(*S*)-**11**	1/1.1/3.2/100	28	15	94.3	96.7(*S*)
13	(*S*)-**8**	1/1.1/2.1/50	28	15	88.3/86.0	96.3(*S*)/95.9(*S*)
14	(*S*)-**8**	1/1.1/2.5/50	28	15	96.4	95.2(*S*)
15	(*S*)-**8**	1/1.1/2.1/200	50	15	97.7/96.9/98.2/96.4	90.5(*S*)/88.1(*S*)/92.4(*S*)/93.8(*S*)
16	(*S*)-**8**	1/1.1/2.1/200	83	1	93.5	52.0(*S*)
17	(*S*)-**8**	1/1.1/1.6/200	28	15	31.4	97.8(*S*)
18	(*S*)-**8**	1/1.1/3.1/200	28	15	37.7	97.8(*S*)
19	(*S*)-**8**	1/1.1/2.1/100	50	15	98.6/97.0/98.1	81.1(*S*)/86.2(*S*)/91.9(*S*)
20	–	1/–/2.5/200[c]	28	15	3.5/5.7	–/–

[a] Representative procedure for entries 1–10: All experiments were performed under an inert nitrogen atmosphere using standard Schlenk techniques and absolute solvents. The ligand (9.4 μmol) was dissolved in 2-propanol (10.4 mL) under N_2 and a solution of KO^{t}Bu in 2-propanol (0.95 mL of 0.01 mol/L) was added for each hydroxy group of the ligand. $Ru(PPh_3)_3Cl_2$ (8.2 mg, 8.6 μmol) dissolved in 2-propanol (5 mL), was added. The solution was stirred at room temperature for 1.5 h to accomplish the formation of the catalyst. Then, the reaction vessel was thermostated to 28°C. Addition of acetophenone (0.2 mL) afforded a substrate concentration of 0.1 mol/L. The reaction was started by adding another 0.86 mL of the 0.01 mol/L KO^{t}Bu solution. After 15 h the reaction was stopped by addition of 0.1 mol/L solution of acetic acid in 2-propanol (0.30 mL). After removal of the solvent, acetophenone and 1-phenylethanol were isolated by bulb-to-bulb distillation. The yield and enantiomeric excess were determined by quantitative GC on a CP-Chirasil-Dex-CB-Column using biphenyl as an internal standard.

[b] Ratio of metal to ligand to base (KO^{t}Bu) to substrate.

[c] Base KOH.

its high concentration. Increasing the temperature raised the catalytic activity. At 50°C the enantiomeric excess decreased, but only slightly (entries 15 and 19), higher temperatures resulted in lower enantioselectivity (entry 16). Varying the amount of base affected the yield adversely but not the enantioselectivity of the reaction (entries 14, 17 and 18).

We monitored the performance of ligands (*S*)-**8** and (*S*)-**11** during the catalysis by analysing aliquots of the reaction mixture with time. In both cases the conversions reached 94% after 15 h reaction time (Fig. 1), resulting in a turnover number of 94 and a turnover frequency of 6 h^{-1}. Noyori et al. reported 95% conversion with a catalyst generated in situ from [(η^6-mesitylene)$RuCl_2$] and (*S*,*S*)-TsDPEN at a substrate to catalyst ratio of 200/1 under otherwise identical conditions.[7] This corresponds to a turnover number of 190 and a turnover frequency of 13 h^{-1}. The highest turnover frequencies of up to 3000 h^{-1} at room temperature with excellent enantioselectivities were achieved by Andersson et al. employing [(η^6-*p*-cymene)$RuCl_2$] and a bidentate chiral ligand.[8] We used $Ru(PPh_3)_3Cl_2$ and potentially tridentate ligands. Therefore, our catalysts are not analogous to those of Noyori and Andersson. Taking catalyst deterioration and a decreasing substrate concentration into account, turnover frequencies can be calculated at 50% conversion.[8] In this respect the ligands (*S*)-**8** and (*S*)-**11** display turnover frequencies of 25 and 10 h^{-1}.

At the beginning of the reaction the imine ligand (*S*)-**8** displayed a higher activity than the amine ligand (*S*)-**11**, for which an almost linear behaviour conversion/time up to 70% conversion was observed. With proceeding conversion the activity of the imine system decreased and after 12 h reaction time the performance of the amine system was very close to it. The decrease in reaction rate for the imine system may result from slow but steady catalyst decomposition (a yellow precipitate formed from the reddish–brown solution). On the other hand, when forming the catalyst from the amine (*S*)-**11**, base and $Ru(PPh_3)_3Cl_2$, the colour of the solution changed from brown to yellow and some yellow precipitate was formed initially, which disappeared during the reaction, presumably increasing the catalyst concentration.

In Table 1, entries 7 and 10, the activity of the catalytic system with (*S*)-**11** seems to be a little higher than that

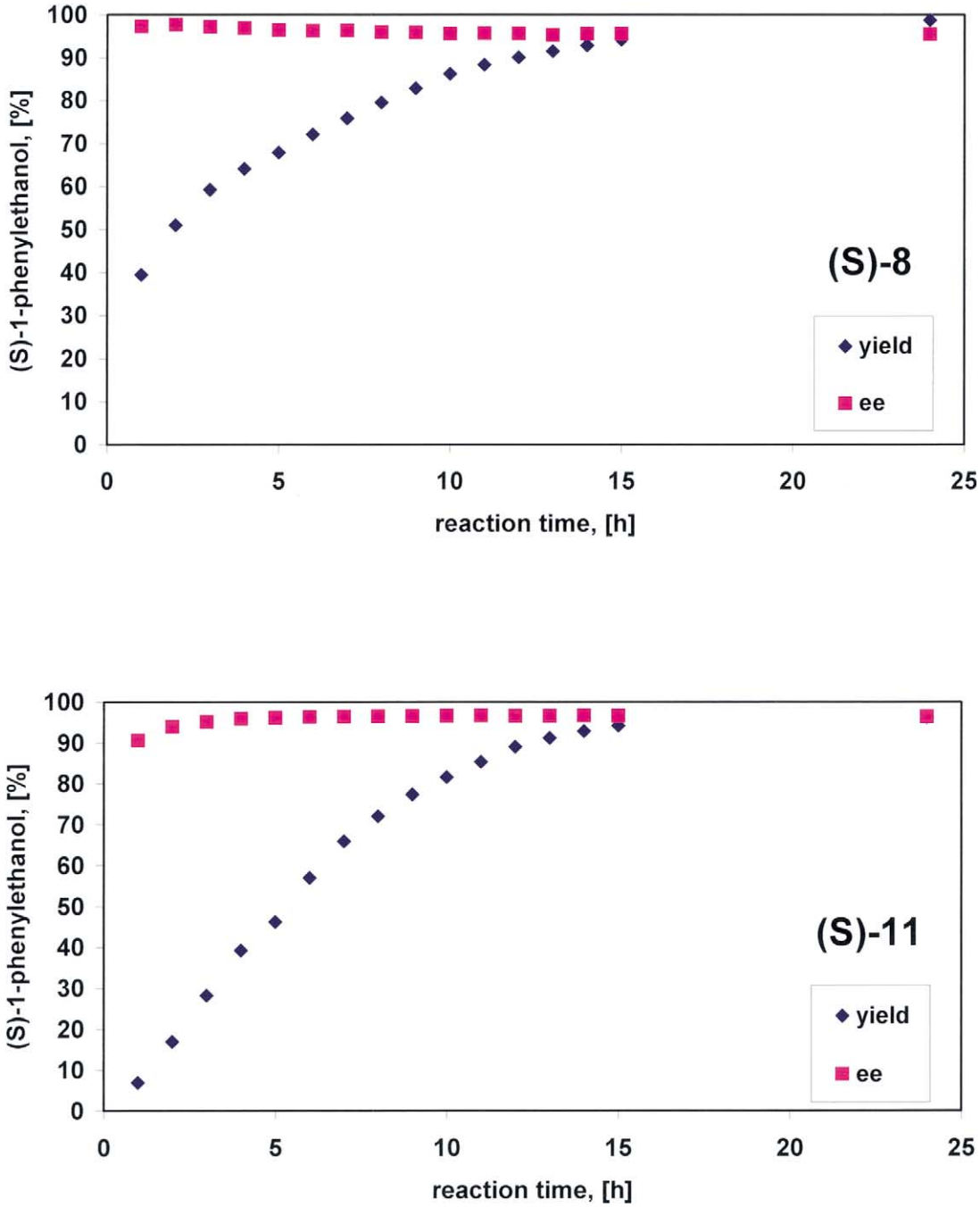


Figure 1. Transfer hydrogenation of acetophenone with $Ru(PPh_3)_3Cl_2$, KO^{t}Bu and the ligands (*S*)-**8**/(*S*)-**11** in 2-propanol (52 mL) at 28°C. Ratio Ru:ligand:base:substrate = 1:1.1:2.1(*S*)-**8**/3.2(*S*)-**11**:100. The catalyst was prepared by stirring the components at 28°C for 1.5 h. Addition of acetophenone (0.6 mL, 5.1 mmol) gave a substrate concentration of 0.1 mol/L. During the catalysis aliquots of 2.5 mL were diluted with 2.5 mL of petroleum ether 40–60, filtered over silica (washing with 1 mL of petroleum ether) and analysed by quantitative GC.

of the (*S*)-**8** system. However, entries 11 and 12 show that their activities are almost identical and, according to Fig. 1, the (*S*)-**8** system is even more active than the (*S*)-**11** system. We attribute these inconsistencies to the fact that the components of the in situ catalysts had to be weighed in separately, effecting scattering of the results. Thus, it is an open question as to whether the imine is reduced to the amine (ruthenium complexes are known to catalyse the transfer hydrogenation of imines[9–11]) to give the active catalyst and metal–ligand bifunctional catalysis according to Noyori is operating.[12,13]

3. Experimental

^{1}H NMR spectra: Bruker ARX 400 (400 MHz) and AC 250 (250 MHz) with TMS as internal reference. ^{31}P NMR spectra: Bruker ARX 400 (162 MHz) with H_3PO_4 as external reference. (*S*)-**1**,[3] (*S*)-**2**[3] and (*S*)-**5**[4] were synthesised according to the literature.

3.1. (*S*)-2-Amino-2′-hydroxy-1,1′-binaphthyl (*S*)-3

A solution of (*S*)-**2** (8.0 g, 26.8 mmol) in CH_2Cl_2 (50 mL) at −15°C was treated with BBr_3 (3.0 mL, 7.9 g, 31.5 mmol). After stirring for 1 h the solution was allowed to warm to room temperature. To the white suspension cold water (20 mL) was added and with cooling 2N aqueous HCl (20 mL). The remaining suspension was extracted with diethyl ether (3×250 mL). The organic phases were collected and washed with 2N aqueous Na_2CO_3 and water and dried with Na_2SO_4. Removal of the solvent afforded the crude product. After recrystallisation from benzene (*S*)-**3** was obtained as white needles (7.0 g, 92%). Mp 168–170°C; $[\alpha]_D^{21}=-117$ (*c* 1.00, THF). Anal. calcd for $C_{20}H_{15}NO$ (285.3): C, 84.19; H, 5.30; N, 4.91. Found: C, 84.13; H, 5.20; N, 4.90%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, 1H, $^3J=8.8$ Hz, H_{ar}), 7.90–7.87 (m, 1H, H_{ar}), 7.84 (d, 1H, $^3J=8.8$ Hz, H_{ar}), 7.83–7.79 (m, 1H, H_{ar}), 7.39 (d, 1H, $^3J=8.7$ Hz, H_{ar}), 7.37–7.32 (m, 1H, H_{ar}), 7.30–7.21 (m, 3H, H_{ar}), 7.20–7.16 (m, 1H, H_{ar}), 7.12 (d, 1H, $^3J=8.8$ Hz, H_{ar}), 7.07–7.03 (m, 1H, H_{ar}), 4.89 (s, 1H, OH), 3.49 (s, 2H, NH_2); IR (KBr): 3403m, 3328m, 3199m br, 1620s, 1595s, 1512s, 1381s, 1218s, 1176s, 1145s, 822s, 751s, 661m cm^{-1}; MS (EI, 70 eV): *m*/*z* 285.2 (100, M^+).

3.2. (*S*)-2-(*N*,*N*-Dimethylamino)-2′-methoxy-1,1′-binaphthyl (*S*)-4

To a stirred solution of 20% aqueous H_2SO_4 (3.4 mL) and 35% formaldehyde (3.4 mL) in THF (10 mL) at 0°C was added a suspension of (*S*)-**2** (1 g, 3.3 mmol) and $NaBH_4$ (0.9 g, 23.8 mmol) in THF (50 mL) over 10 min. After a further 10 min the mixture was poured into 2% aqueous KOH (300 mL). The remaining suspension was extracted with ethyl acetate (3×100 mL). The organic phase was dried with $MgSO_4$ and evaporated. The residue was dissolved in benzene/ethanol (1:1, 100 mL). After half of the solvent was evaporated, a fine precipitate formed. Cooling to 5°C for 10 h gave (*S*)-**4** as a white solid (930 mg, 85%). Mp 191°C; $[\alpha]_D^{21}=-154$ (*c* 0.88, benzene). Anal. calcd for $C_{23}H_{21}NO$ (327.4): C, 84.37; H, 6.46; N, 4.27. Found: C, 84.09; H, 6.52; N, 4.16%; ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.98 (d, 1H, $^3J=9.1$ Hz, H_{ar}), 7.92 (d, 1H, $^3J=8.7$ Hz, H_{ar}), 7.88–7.82 (m, 2H, H_{ar}), 7.53 (d, 1H, $^3J=9.1$ Hz, H_{ar}), 7.47 (d, 1H, $^3J=9.1$ Hz, H_{ar}), 7.39–7.06 (m, 6H, H_{ar}), 3.81 (s, 3H, OCH_3), 2.55 (s, 6H, $N(CH_3)_2$); IR (KBr): 3060w, 2948w, 2860w, 2827w, 2784w, 1619m, 1592m, 1504s, 1462s, 1264s, 1254s, 1085s, 1054m, 981s, 809s, 753s cm^{-1}; MS (EI, 70 eV) *m*/*z* 327.2 (100, M^+).

3.3. General procedure for the Schiff bases (*S*)-6, (*S*)-7, (*S*)-8, (*S*)-9 and (*S*)-10

(*S*)-**2** or (*S*)-**3** (5 mmol) and $MgSO_4$ (400 mg) were suspended in benzene (30 mL). After adding the desired aldehyde (5.5 mmol) the suspension was stirred for 20 h. The yellow–orange mixture was filtered and the solvent and excess aldehyde were evaporated by gentle warming in vacuo. The crude product was purified as indicated for the individual compounds.

3.3.1. (*S*)-2-(2-Hydroxybenzylideneamino)-2′-hydroxy-1,1′-binaphthyl (*S*)-6[5]

Recrystallisation from benzene yielded (*S*)-**6** as orange crystals (875 mg, 45%). Mp 221–223°C; $[\alpha]_D^{21}=-179$ (*c* 0.96, benzene). Anal. calcd for $C_{27}H_{19}NO_2$ (389.5): C, 83.27; H, 4.92; N, 3.60. Found: C, 82.89; H, 4.90; N, 3.38%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.01 (s, 1H, OH), 8.70 (s, 1H, N=CH), 8.12 (d, 1H, $^3J=8.8$ Hz, H_{ar}), 8.01–7.93 (m, 2H, H_{ar}), 7.90–7.86 (m, 1H, H_{ar}), 7.67 (d, 1H, $^3J=9.0$ Hz, H_{ar}), 7.55–7.45 (m, 1H, H_{ar}), 7.40–7.18 (m, 7H, H_{ar}), 7.05–7.01 (m, 1H, H_{ar}), 6.84–6.74 (m, 2H, H_{ar}), 4.94 (s, 1H, OH); IR (KBr): 3333m br, 3057w, 1611s, 1505s, 1433m, 1346s, 1278s, 1203s, 1149s, 978m, 815s, 752s cm^{-1}; MS (EI, 70 eV): *m*/*z* 389.1 (38, M^+), 372.2 (60, M^+–OH), 268.2 (100, M^+–C_6H_7NO).

3.3.2. (*S*)-2-(2-Hydroxybenzylideneamino)-2′-methoxy-1,1′-binaphthyl (*S*)-7

Recrystallisation from ethanol yielded (*S*)-**7** as a yellow powder (1.9 g, 80%). Mp 178–180°C; $[\alpha]_D^{21}=+40$ (*c* 1.03, benzene). Anal. calcd for $C_{28}H_{21}NO_2$ (403.5): C, 83.35; H, 5.25; N, 3.47. Found: C, 83.03; H, 5.30; N, 3.50%; ^{1}H NMR (250 MHz, C_6D_6): δ 12.74 (s, 1H, OH), 8.24 (s, 1H, N=CH), 7.86–7.65 (m, 4H, H_{ar}), 7.53 (d, 1H, $^3J=8.3$ Hz, H_{ar}), 7.32 (d, 1H, $^3J=8.7$ Hz, H_{ar}), 7.25–6.97 (m, 6H, H_{ar}), 6.90–6.73 (m, 3H, H_{ar}), 6.56–6.46 (m, 1H, H_{ar}), 3.29 (s, 3H, OCH_3); IR (KBr): 3055w, 2839w, 1613s, 1569s, 1504s, 1462s, 1268s, 1253s, 1188m, 1149s, 1085s, 1054s, 1022m, 967m, 903m, 808s, 751s, 681m, 531m cm^{-1}; MS (EI, 70 eV) *m*/*z* 403.1 (100, M^+).

3.3.3. (*S*)-2-(2-Pyridinylmethyleneamino)-2′-hydroxy-1,1′-binaphthyl (*S*)-8[6]

Recrystallisation from toluene gave (*S*)-**8** as a fine yellow powder (1.2 g, 65%). Mp 179–181°C; $[\alpha]_D^{21}=+275.5$ (*c* 1.12, benzene). Anal. calcd for $C_{26}H_{18}N_2O$ (374.4): C, 83.40; H, 4.85; N, 7.48. Found: C, 82.95; H, 4.92; N, 7.40%; ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.53 (s, 1H, N=CH), 8.45 (ddd, 1H, $^3J=4.8$ Hz, $^4J=1.7$ Hz, $^5J=1.0$ Hz, py-H^6), 8.05–7.77 (m, 4H, H_{ar}), 7.65–6.98 (m, 11H, H_{ar}), 6.21 (s, 1H, OH); IR (KBr): 3333m br, 3057w, 1611s, 1571m, 1505s, 1433m, 1346s, 1278s, 1203m, 1149m, 978m, 815s, 752s, 633m cm^{-1}; MS (EI, 70 eV): *m*/*z* 374.1 (40, M^+), 357.2 (88, M^+–OH), 268.2 (100, M^+–$C_6H_6N_2$).

3.3.4. (*S*)-2-(2-Pyridinylmethyleneamino)-2′-methoxy-1,1′-binaphthyl (*S*)-9

Bulb-to-bulb distillation at 165°C (0.005 torr) yielded (*S*)-**9** as a yellow glass (1.2 g, 62%). Mp 78–82°C; $[\alpha]_D^{21}=-224$ (*c* 1.10, benzene). Anal. calcd for $C_{27}H_{20}N_2O$ (388.5): C, 83.48; H, 5.19; N, 7.21. Found: C, 83.25; H, 5.36; N, 7.01%; ^{1}H NMR (250 MHz, C_6D_6): δ 8.86 (d, 1H, $^4J=0.5$ Hz, N=CH), 8.32 (ddd, 1H, $^3J=4.8$ Hz, $^4J=1.8$ Hz, $^5J=1.0$ Hz, py-H^6), 7.79–7.42 (m, 7H, H_{ar}), 7.33–6.96 (m, 6H, H_{ar}), 6.71–6.61 (m, 1H, py-H^4), 6.41 (ddd, 1H, $^3J=7.5$ Hz, $^4J=4.8$ Hz, $^5J=1.3$ Hz, py-H^5), 3.22 (s, 3H, OCH_3); IR (KBr): 3055m, 3006w, 2937w, 2838w, 1620s, 1590s, 1506s, 1467s, 1433m, 1334m, 1264s, 1254s, 1211m, 1148m, 1085s, 1054s, 813s, 748s, 682m, 617m cm^{-1}; MS (EI, 70 eV): *m*/*z* 388.1 (100, M^+), 357.2 (52, M^+–OCH_3).

3.3.5. (*S*)-2-(2-Diphenylphosphanylbenzylideneamino)-2′-methoxy-1,1′-binaphthyl (*S*)-10. Recrystallisation from methanol (400 mL) yielded (*S*)-**10** as a fine yellow powder (1.8 g, 64%). Mp 146–148°C; $[\alpha]_D^{21}=-177$ (*c* 1.01, benzene). Anal. calcd for $C_{40}H_{30}NOP$ (571.7): C, 84.04; H, 5.29; N, 2.45. Found: C, 83.36; H, 5.30; N, 2.21%; $^1H\{^{31}P\}$ NMR (400 MHz, C_6D_6): δ 9.46 (s, 1H, N=CH), 7.82–7.61 (m, 6H, H_{ar}), 7.52–7.40 (m, 2H, H_{ar}), 7.32–6.88 (m, 16H, H_{ar}), 6.79–6.69 (m, 2H, H_{ar}), 3.21 (s, 3H, OCH_3); ^{31}P NMR (162 MHz, C_6D_6): δ −14.39; IR (KBr): 3054w, 2838w, 1618s, 1591s, 1507s, 1461s, 1432s, 1641m, 1265s, 1148m, 1085s, 1054s, 1023m, 967m, 808s, 746s, 695s, 516m, 498s, 471s, 436m cm^{-1}; MS (EI, 70 eV): *m*/*z* 571.1 (8, M^+), 556.1 (8, M^+-CH_3); 540.0 (100, M^+-OCH_3), 494.1 (22, $M^+-C_6H_5$).

3.4. (*S*)-2-(2-Pyridinylmethylamino)-2′-hydroxy-1,1′-binaphthyl (*S*)-11

(*S*)-**8** (0.6 g, 1.6 mmol) was dissolved in methanol (50 mL) and $NaBH_4$ (73 mg, 1.9 mmol) was added with stirring at room temperature. The yellow colour disappeared and after 2 h diethyl ether (100 mL) and water (100 mL) were added. The aqueous layer was extracted further with diethyl ether (2×50 mL). The combined organic layers were dried with Na_2SO_4 and evaporated. Purification by silica gel column chromatography with petroleum ether (40/60) and ethyl acetate (1:1) gave (*S*)-**11** as a white solid (364 mg, 60%). Mp 138–140°C; $[\alpha]_D^{21}=-155$ (*c* 0.99, benzene). Anal. calcd for $C_{26}H_{20}N_2O$ (376.5): C, 82.95; H, 5.35; N, 7.44. Found: C, 82.31; H, 5.35; N, 7.39%; ^1H NMR (400 MHz, $CDCl_3/D_2O$): δ 8.40 (ddd, 1H, $^3J=4.9$ Hz, $^4J=1.7$ Hz, $^5J=0.9$ Hz, py-H^6), 7.95 (d, 1H, $^3J=8.9$ Hz, H_{ar}), 7.91–7.87 (m, 1H, H_{ar}), 7.79–7.71 (m, 2H, H_{ar}), 7.58 (ddd, 1H, $^3J=7.5$ Hz, $^3J=7.7$ Hz, $^4J=1.5$ Hz, py-H^5), 7.42 (d, 1H, $^3J=9.1$ Hz, H_{ar}), 7.38–7.32 (m, 1H, H_{ar}), 7.46–6.94 (m, 8H, H_{ar}), 4.76 (s, 1H, NH), 4.67 (d, 1H, $^3J=16.9$ Hz, NCH^A), 4.49 (d, 1H, $^3J=17.0$ Hz, NCH^B); IR (KBr): 3494w, 3418m, 3056m, 1618s, 1597s, 1510s, 1430s, 1377m, 1341s, 1310s, 1274m, 1217s, 1179m, 1148s, 974m, 813s, 753s, 621m, 428m cm^{-1}; MS (EI, 70 eV): *m*/*z* 376.4 (100, M^+), 358.4 (40, M^+-H_2O); 280.3 (34, $M^+-C_5H_4N$), 268.3 (45, $M^+-C_6H_8N_2$).

References

1. (a) Smrčina, M.; Lorenc, M.; Hanuš, V.; Kočovský, P. *Synlett* **1991**, 231–232; (b) Smrčina, M.; Lorenc, M.; Hanuš, V.; Sedmera, P.; Kočovský, P. *J. Org. Chem.* **1992**, *57*, 1917–1920; (c) Vyskočil, Š.; Smrčina, M.; Lorenc, M.; Hanuš, V.; Polášek, M.; Kočovský, P. *Chem. Commun.* **1998**, 585–586.
2. (a) Ding, K.; Xu, Q.; Wang, Y.; Jinxia, L.; Yu, Z.; Du, B.; Wu, Y.; Koshima, H.; Matsuura, T. *Chem. Commun.* **1997**, 693–694; (b) Ding, K.; Wang, Y.; Yun, H.; Liu, J.; Wu, J.; Terada, M.; Okubo, Y.; Mikami, K. *Chem. Eur. J.* **1999**, *5*, 1734–1737; (c) Mahmoud, H.; Han, Y.; Segal, B. M.; Cai, L. *Tetrahedron: Asymmetry* **1998**, *9*, 2035–2042.
3. (a) Hattori, T.; Hotta, H.; Suzuki, T.; Miyano, S. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 613–622; (b) Hattori, T.; Shijo, M.; Sakamoto, J.; Kumagai, S.; Nakajima, A.; Miyano, S. *J. Chem. Res. (M)* **1995**, 124–134.
4. Smrčina, M.; Vyskočil, Š.; Polívková, J.; Sejbal, J.; Hanuš, V.; Polášek, M.; Verrier, H.; Kočovský, P. *Tetrahedron: Asymmetry* **1997**, *8*, 537–546.
5. Mahmoud, H.; Han, Y.; Segal, B. M.; Cai, L. *Tetrahedron: Asymmetry* **1998**, *9*, 2035–2042.
6. Zhang, X. Patent 1/4/2001, WO 0,100,581.
7. Hashiguchi, S.; Fuji, A.; Takehara, J.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1995**, *117*, 7562–7563.
8. Nordin, S. J. M.; Roth, P.; Tarnai, T.; Alonso, D. A.; Brandt, P.; Andersson, P. G. *Chem. Eur. J.* **2001**, *7*, 1431–1436.
9. Vedejs, E.; Trapencieris, P.; Suna, E. *J. Org. Chem.* **1999**, *64*, 6724–6729.
10. Meuzelaar, G. J.; van Vliet, M. C. A.; Maat, L.; Sheldon, R. A. *Eur. J. Org. Chem.* **1999**, 2315–2321.
11. Samano, V.; Ray, J. A.; Thompson, J. B.; Mook, R. A.; Jung, D. K.; Koble, C. S.; Martin, M. T.; Bigham, E. C.; Regitz, C. S.; Feldman, P. L.; Boros, E. E. *Org. Lett.* **1999**, *1*, 1993–1996.
12. Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97–102.
13. Yamakawa, M.; Ito, H.; Noyori, R. *J. Am. Chem. Soc.* **2000**, *122*, 1466–1478.