# SYNTHESIS OF $C_2$-SYMMETRICAL [1,1′-BINAPHTHALENE]-2,2′-DIAMINES WITH ADDITIONAL CHELATING GROUPS ATTACHED TO THE NITROGEN ATOMS AS POTENTIAL LIGANDS FOR ASYMMETRIC CATALYSIS

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Received March 1, 2000
Accepted April 4, 2000

*Dedicated to Professor Otakar Červinka on the occasion of his 75 birthday.*

Reductive amination of 2-hydroxybenzaldehyde, using a combination of $NaBH_4$ and (*R*)-[1,1′-binaphthalene]-2,2′-diamine, served as the key step in the synthesis of the potentially tetradentate ligands (*R*)-*N*,*N*′-bis(2-hydroxybenzyl)[1,1′-binaphthalene]-2,2′-diamine and (*R*)-*N*,*N*′-bis(2-hydroxybenzyl)-*N*,*N*′-dimethyl[1,1′-binaphthalene]-2,2′-diamine. In analogy, amination of 2-bromobenzaldehyde with (*R*)-[1,1′-binaphthalene]-2,2′-diamine produced (*R*)-*N*,*N*′-bis(2-bromobenzyl)[1,1′-binaphthalene]-2,2′-diamine, whose conversion into the novel diphosphine ligand (*R*)-*N*,*N*′-bis[2-(diphenylphosphino)benzyl]-*N*,*N*′-dimethyl-[1,1′-binaphthalene]-2,2′-diamine was readily attained in two steps. CD spectra of the new binaphthyl derivatives are presented.

**Key words**: Biaryls; Binaphthyls; Chiral ligands; Chiral phosphines; Amine reductive alkylation; Chiral cavity; Circular dichroism; Enantioselective catalysis; N-Ligands; P-Ligands.

Among the 1,1′-binaphthyl ligands with coordinating groups in positions 2 and 2′, such as BINOL[1] (**2**), BINAP[2] (**3**), NOBIN[3,4] (**4**), MOP[5] (**5**), MAP[3m,6] (**6**) and their counterparts[7], the simple diamine **1** appears to be a Cinderella with very few successful applications in asymmetric catalysis[7,8]. Nevertheless, owing to its straightforward, one-step synthesis from 2-naphthol and

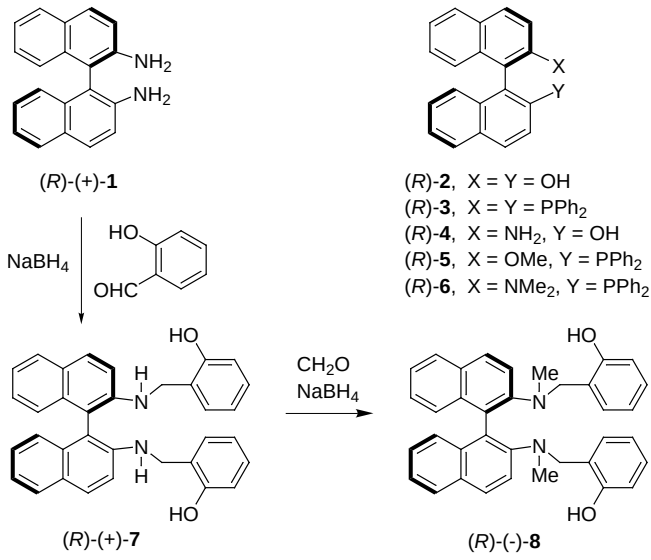
hydrazine and its ready resolution into enantiomers[9], **1** has the potential of becoming a very useful, $C_2$-symmetrical scaffold, provided that its derivatization offers a chiral cavity suitable for efficient asymmetric induction.

In our previous work, we have developed a straightforward protocol for introducing simple alkyl groups to the nitrogen atoms of NOBIN and diamine **1**, relying on the reductive amination of common aldehydes or ketones in the presence of $NaBH_4$ and $H_2SO_4$ at room temperature[3i,10]. While sterically non-hindered aldehydes, such as formaldehyde and acetaldehyde, were capable of planting two alkyl groups to each nitrogen atom of **1**, ketones, such as acetone or cyclohexanone, proved to be *N*-monoalkylating (with respect to each nitrogen of **1**). In the latter case, additional *N*-substituents (*e.g.*, $CH_3$) could be introduced *via* subsequent reductive amination with aldehydes[3i,10] (*e.g.*, $CH_2O$). Herein, we report on the extension of this methodology that allows to introduce more complex appendices, containing other functional groups, and the synthesis of novel ligands **7**, **8**, and **12**.

## RESULTS AND DISCUSSION

With the *N*-alkylating methodology at hand[3i,10], we have now focused on the *N*-derivatization of diamine (*R*)-**1** with *ortho*-substituted benzyl moieties, aiming at the synthesis of $C_2$-symmetrical diphenol **8** and diphosphine **12**. Sakiyama reacted **1** with substituted 2-hydroxybenzaldehyde to afford the corresponding bisimine as a stable compound[11] and preparation of a related imine ligand starting from NOBIN (**4**) has been reported by Carreira[4a]. These findings demonstrate that the presence of hydroxy and other groups is not detrimental to the imine formation. We could envisage that the imine, once generated, should be prone to an *in situ* reduction along the lines of our strategy.

Diamine (*R*)-**1** (≥99% ee)[9] was treated with 2-hydroxybenzaldehyde in the presence of $NaBH_4$ under our standard conditions ($H_2SO_4$, $H_2O$, THF, room temperature, 15 min)[3i,10] to give the disubstituted diamine (*R*)-**7** (93%). Reductive bismethylation of the latter product ($CH_2O$, $NaBH_4$, $H_2SO_4$, $H_2O$, THF, room temperature, 15 min) also proceeded readily to furnish the desired ligand (*R*)-**8** (95%)[12]. These results clearly demonstrate that the reductive amination of bulky aldehydes with this type of amines stops at the monoalkylation product (*i.e.*, secondary amine). This behavior is in sharp contrast to the reactivity of sterically non-hindered aldehydes that produce dialkylated derivatives (*i.e.*, tertiary amines).

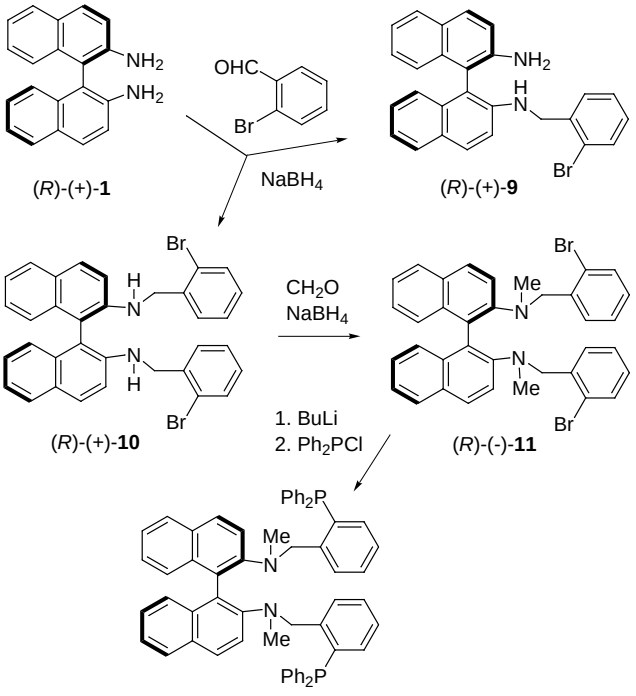



SCHEME 1

Reductive amination ($NaBH_4$, $H_2SO_4$, $H_2O$, THF, room temperature, 15 min), using (*R*)-**1** (≥99% ee)[9] and 2-bromobenzaldehyde, afforded mainly the bis-derivative (*R*)-**10** (73%) along with a small amount of the monosubstituted diamine (*R*)-**9** (23%). The latter mixture was readily separated by flash chromatography. The main product (*R*)-**10** was then bis-*N*-methylated ($CH_2O$, $NaBH_4$, $H_2SO_4$, $H_2O$, THF, room temperature, 15 min) to give the tertiary diamine (*R*)-**11** (97%). Lithiation of the latter derivative (BuLi, THF, –78 °C, 1 h), followed by quenching the dilithio intermediate with $Ph_2PCl$ (–78 °C → room temperature, overnight), produced the desired diphosphine (*R*)-**12** in 84% yield.

The observed higher reactivity of 2-salicylaldehyde in reductive amination (as compared to 2-bromobenzaldehyde) is likely to be associated with the equilibrium that is favorably shifted toward the imine formation in the first step, presumably originating from the stabilization by the hydrogen bonding between the OH and the imine nitrogen (which is absent in the case of the bromoanalogue). Note that the Schiff base, arising from **4** and 2-salicylaldehyde, is sufficiently stable under the conditions of chromatography on silica gel[4a].

The basic shape of the CD spectra of the diamines **7**–**12** (Figs 1, 2) is determined by the binaphthyl moiety. Since all these compounds are of the same absolute configuration, it is not surprising that the dominant feature found in the CD curves is identical in all cases. It is an intense CD couplet




SCHEME 2

centered at ≈240 nm (non-*N*-methylated diamines **7**, **9**, and **10**) or 220–230 nm (*N*-methylated compounds **8**, **11**, and **12**), which exhibits its negative lobe at higher wavelength. It corresponds to the intense absorption band with

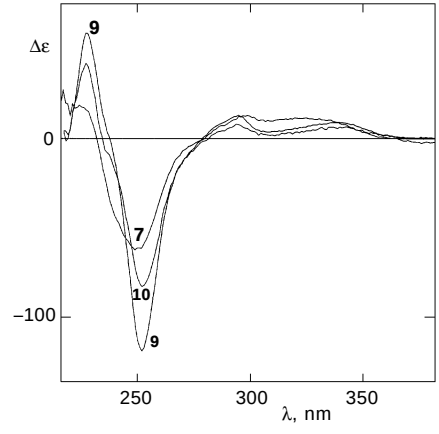



FIG. 1
CD spectra of diamines *R*-(+)-**7**, *R*-(+)-**9**, and *R*-(+)-**10** measured in chloroform. The intensity differences are largely caused by sample deterioration in chloroform solution

the maximum slightly blue shifted (≈5 nm) with respect to the zero crossing of the CD couplet. At higher wavelengths, there are two additional, much weaker CD couplets of the same sign pattern, one centered around 290, the other around 340 nm. This general shape of CD spectra is largely unaffected by substitution of the phenyl ring by alternative bromine or hydroxy substituents (compounds **7**, **9**, and **10**). Even the derivatization of only one of the amino groups with the 2-bromobenzyl substituent (**9**) does not bring very significant changes. Only when the phenyl rings are substituted with diphenylphosphino group (compound **12**), we observed large changes and additional bands, but these are easy to explain qualitatively on the basis of the much more complex π-electron system in this compound. It is generally easier to detect the effect of methylation on the nitrogen atom. Thus, the methylated compounds (**8**, **11**, and **12**) exhibit the blue shift (*vide supra*) of the intense CD couplet (and of the associated absorption band) and, in addition, there are intensity changes in the region of about 290 nm, where the bands of the methylated compounds are more intense. In fact, the spectra of non-methylated diamines **7**, **9**, and **10** closely follow the CD and absorption spectra of (*R*)-*N*,*N*′-dimethyl-[1,1′-binaphthalene]-2,2′-diamine[13]. It appears that further N-substitution by phenyl rings does not bring significant electronic or conformational changes to the molecule. Similar conclusions can be deduced for the methylated diamines **8**, **11**, and **12** using (*R*)-*N*,*N*,*N*′,*N*′-tetramethyl[1,1′-binaphthalene]-2,2′-diamine[13] as a model.

In conclusion, we have synthesized novel, enantiomerically pure $C_2$-symmetrical ligands (*R*)-**7**, (*R*)-**8**, and (*R*)-**12**, derived from 2,2′-diamino- 1,1′-binaphthyl (*R*)-**1**. These ligands possess other potentially coordinating

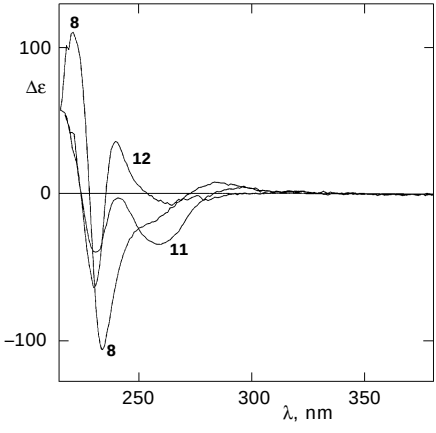



FIG. 2
CD spectra of diamines *R*-(–)-**8**, *R*-(–)-**11**, and *R*-(–)-**12** measured in chloroform

groups, namely OH, as in the former, and $PPh_2$, as in the latter instance, capable of creating chiral, tetradental cavities. The key step in the synthesis was the reductive amination of *ortho*-substituted benzaldehydes with (*R*)-**1**. No loss of enantiopurity was observed along the synthetic sequences. The utility of the ligands thus obtained in transition metal catalysis is now being investigated and the results will be reported in due course.

## EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. The optical rotations ($[\alpha]_D$ values given in $10^{-1}$ deg $cm^2$ $g^{-1}$) were measured in THF at 25 °C with an error of $<\pm 0.1$. The $^1H$ NMR spectra were recorded on 250 or 400 MHz instruments (FT mode) for $CDCl_3$ solutions at 25 °C with TMS as the internal reference. The $^{13}C$ NMR spectra were recorded on 63 or 101 MHz instruments (FT mode) for $CDCl_3$ solutions at 25 °C. The $^{31}P$ NMR spectra were recorded on a 162 MHz instrument (FT mode) for $CDCl_3$ solutions at 25 °C with $H_3PO_4$ as the external reference. Chemical shifts are given in ppm (δ-scale), coupling constants (*J*) in Hz. The IR spectra (wavenumbers in $cm^{-1}$) were measured in dichloromethane or chloroform. The high-resolution mass spectra were measured on a JEOL JMS D-100 double focusing spectrometer (70 eV, 50 μA) using direct inlet and the lowest temperature enabling evaporation; the accuracy was ≤5 ppm. The FAB spectra were measured on a VG 71070E spectrometer (resolution 1 100, FAB Argon 6 kVe, matrix: 3-nitrobenzyl alcohol–glycerin 1 : 3 mixture (low volatility), mass range 80–1 300, 15 s/decade). Yields are given in milligrams of isolated product, showing one spot on a chromatographic plate and no impurities detectable in the NMR spectrum. The CD spectra were measured using Jobin Yvon Mark VI Dichrographe for $CHCl_3$ and/or acetonitrile solutions (the compounds **9**–**11** were not soluble in acetonitrile), at $\approx 5 \cdot 10^{-4}$ mol $l^{-1}$ concentrations. Quartz cells with the optical path length of 0.1–0.01 cm were used. Since we observed notable degradation of the CD signal with time for all the $CHCl_3$ solutions (the change could be discerned after only several minutes, two subsequent runs were usually significantly different), the spectra were generally recorded in a fast mode. The rather high light absorption by the samples allowed the spectra to be measured in the region 400–190 nm (acetonitrile) and 400–220 nm ($CHCl_3$). Spectracalc and Gramms (Galaxy Industries) software packages were used for the final evaluation and plotting of the spectra.

### Reactions of (*R*)-(+)-**1** with Substituted Benzaldehydes. General Procedure

A solution of the enantiomerically pure (*R*)-(+)-**1** (ref.[9]) (284 mg, 1 mmol) in THF (10 ml) and solid $NaBH_4$ (530 mg, 14 mmol) were added to a mixture of 2-substituted benzaldehyde (7 mmol) and 20% aqueous $H_2SO_4$ (2 ml) in THF (10 ml) over a period of 15 min, while cooling in a water bath. The mixture was stirred for an additional 15 min and then poured into a 2% aqueous KOH (100 ml). The resulting suspension was extracted with AcOEt (3 × 20 ml) and the extract was dried with $MgSO_4$ and evaporated. The crude product was purified by flash chromatography on silica gel (20 g) with toluene.

Methylation of *N,N′*-Disubstituted-2,2′-diamino-1,1′-binaphthyls with Formaldehyde. General Procedure

A solution of (*R*)-*N,N′*-disubstituted-2,2′-diamino-1,1′-binaphthyl (1 mmol) in THF (20 ml) and solid $NaBH_4$ (530 mg, 14 mmol) were added to a solution of 40% aqueous formaldehyde (2 ml, 24 mmol) and 20% aqueous $H_2SO_4$ (2 ml) in THF (20 ml) over a period of 15 min, while cooling in a water bath. The mixture was stirred for an additional 15 min and then poured into a 2% aqueous KOH (100 ml). The resulting suspension was extracted with AcOEt (3 × 20 ml) and the extract was dried with $MgSO_4$ and evaporated. The crude product was purified by flash chromatography on silica gel (20 g) with toluene.

*(R)-(+)-N,N′-Bis(2-hydroxybenzyl)[1,1′-binaphthalene]-2,2′-diamine* [(*R*)-(+)-**7**]. Reaction of (*R*)-(+)-**1** with salicylaldehyde (855 mg, 7 mmol) was carried out as given in the general procedure to give (*R*)-(+)-**7** (461 mg, 93%), m.p. 66–68 °C (toluene); $[\alpha]_D$ +57.9 (*c* 0.5, THF). $^1$H NMR (250 MHz): 4.38 (s, 4 H); 6.72 (d, *J* = 7.8, 2 H); 6.75–6.81 (m, 2 H); 6.98–7.08 (m, 6 H); 7.18–7.28 (m, 4 H); 7.35 (d, *J* = 8.8, 2 H); 7.76–7.80 (m, 2 H); 7.84 (d, *J* = 9.1, 2 H). $^{13}$C NMR: 67.91 (t), 115.09 (s), 115.62 (d), 116.46 (d), 120.08 (d), 123.30 (d), 123.67 (s), 123.91 (d), 127.13 (d), 128.22 (d), 128.48 (d), 128.67 (d), 128.92 (s), 130.15 (d), 133.33 (s), 143.88 (s), 155.93 (s). IR ($CH_2Cl_2$): 3 582, 3 348, 1 620, 1 592. MS, *m/z* (%): 390 (6), 284 (100), 267 (38), 107 (23), 94 (19). FAB, *m/z* (%): 496 ($M^{+\bullet}$, 13), 389 (100). HR MS (EI): calculated for $C_{34}H_{28}N_2O_2$ 496.2151; found 496.2151.

*(R)-(–)-N,N′-Bis(2-hydroxybenzyl)-N,N′-dimethyl[1,1′-binaphthalene]-2,2′-diamine* [(*R*)-(–)-**8**]. Reaction of (*R*)-(+)-**7** (496 mg, 1 mmol) with formaldehyde was carried out as given in the general procedure to afford (*R*)-(–)-**8** (498 mg, 95%), m.p. 103–105 °C (toluene); $[\alpha]_D$ –34.2 (*c* 0.5, THF). $^1$H NMR (250 MHz): 2.47 (s, 6 H); 4.07 (s, 4 H); 6.51 (d, *J* = 8.2, 2 H); 6.60–6.66 (m, 2 H); 6.89 (d, *J* = 7.2, 2 H); 6.93–7.02 (m, 2 H); 7.06 (d, *J* = 8.5, 2 H); 7.16–7.22 (m, 2 H); 7.36–7.43 (m, 2 H); 7.86 (d, *J* = 8.8, 2 H); 7.95 (d, *J* = 7.9, 2 H); 8.18 (d, *J* = 8.8, 2 H); 8.61 (s, 2 H). $^{13}$C NMR: 41.94 (q), 61.99 (t), 115.74 (d), 118.79 (d), 120.76 (s), 120.91 (d), 125.82 (d), 126.59 (d), 126.62 (d), 128.37 (d), 128.56 (d), 128.94 (d), 130.55 (d), 130.92 (s), 132.30 (s), 133.56 (s), 148.37 (s), 156.93 (s). IR ($CH_2Cl_2$): 3 592, 1 622, 1 592. MS, *m/z* (%): 312 (100), 294 (7), 281 (40), 267 (28), 170 (91). FAB, *m/z* (%): 525 ($[M + H]^+$, 23), 417 (10). HR MS (EI): calculated for $C_{34}H_{28}N_2O_2$ 524.2464; found 524.2464.

*(R)-(+)-N-(2-Bromobenzyl)[1,1′-binaphthalene]-2,2′-diamine* [(*R*)-(+)-**9**]. The more polar by-product from the reductive amination of 2-bromobenzaldehyde with (*R*)-**1** (after the isolation of **10**; see below) was identified as the monosubstituted diamine (*R*)-(+)-**9** (102 mg, 23%), m.p. 213–215 °C (toluene); $[\alpha]_D$ +133 (*c* 0.1, THF). $^1$H NMR (400 MHz): 3.85 (bs, 3 H); 4.43 (s, 2 H); 7.02–7.26 (m, 12 H); 7.46 (dd, *J* = 7.8, *J* = 1.4, 1 H); 7.74–7.77 (m, 1 H); 7.78–7.84 (m, 2 H). $^{13}$C NMR (101 MHz): 47.85 (t), 112.10 (s), 113.73 (s), 114.10 (d), 118.30 (d), 122.14 (d), 122.48 (d), 123.04 (s), 123.77 (d), 124.00 (d), 126.75 (d), 126.82 (d), 127.31 (d), 127.81 (s), 128.10 (d), 128.15 (d), 128.40 (d), 128.55 (d), 129.60 (d), 129.65 (d), 129.66 (s), 132.61 (d), 133.58 (s), 133.97 (s), 138.38 (s), 143.03 (s), 143.41 (s). IR ($CHCl_3$): 3 492, 3 439, 3 392, 1 620, 1 598. MS, *m/z* (%): 452 ($M^{+\bullet}$, 100), 373 (8), 371 (9), 310 (12), 283 (22), 280 (25), 268 (57), 230 (17), 184 (3), 169 (5), 143 (30), 91 (28). HR MS (EI): calculated for $C_{27}H_{21}BrN_2$ 452.0888; found 452.0887.

*(R)-(+)-N,N′-Bis(2-bromobenzyl)[1,1′-binaphthalene]-2,2′-diamine* [(*R*)-(+)-**10**]. Reaction of (*R*)-(+)-**1** with 2-bromobenzaldehyde (1.3 g, 7 mmol) was carried out as given in the general procedure. The crude product mixture was separated by flash chromatography on silica gel

(20 g) with toluene to furnish (*R*)-(+)-**10** (450 mg, 73%) as the less polar component, m.p. 237–239 °C (toluene); $[\alpha]_D$ +72 (*c* 0.1, THF). $^1$H NMR (400 MHz): 4.36–4.47 (m, 6 H); 7.02–7.12 (m, 6 H); 7.17–7.27 (m, 8 H); 7.49 (dd, *J* = 7.7, *J* = 1.5, 2 H); 7.75–7.79 (m, 2 H); 7.83 (dd, *J* = 8.8, *J* = 0.5, 2 H). $^{13}$C NMR (101 MHz): 47.82 (t), 112.20 (s), 114.05 (d), 122.22 (d), 123.00 (s), 123.84 (d), 126.83 (d), 127.33 (d), 127.90 (s), 128.16 (d), 128.44 (d), 128.48 (d), 129.81 (d), 132.64 (d), 133.87 (s), 138.34 (s), 143.71 (s). IR ($CHCl_3$): 3 427, 1 619, 1 599. MS, *m/z* (%): 622 ($M^{+\bullet}$, 53), 620 ($M^{+\bullet}$, 26), 541 (1), 540 (1), 451 (100), 371 (14), 354 (12), 280 (20), 267 (30), 252 (6), 184 (2), 169 (12). HR MS (EI): calculated for $C_{34}H_{26}Br_2N_2$ 620.0642; found 620.0642).

*(R)-(–)-N,N′-Bis(2-bromobenzyl)-N,N′-dimethyl[1,1′-binaphthalene]-2,2′-diamine* [(*R*)-(–)-**11**]. Reaction of (*R*)-(+)-**10** (620 mg, 1 mmol) with formaldehyde was carried out as given in the general procedure to give (*R*)-(–)-**11** (630 mg, 97%), m.p. 203–205 °C (toluene); $[\alpha]_D$ –61 (*c* 0.1, THF). $^1$H NMR (400 MHz): 2.48 (s, 6 H); 3.92–4.04 (m, 4 H); 6.65 (dd, *J* = 7.8, *J* = 2, 2 H); 6.90–6.99 (m, 4 H); 7.12–7.19 (m, 4 H); 7.25–7.32 (m, 4 H); 7.43 (d, *J* = 8.8, 2 H); 7.74–7.81 (m, 4 H). $^{13}$C NMR: 40.44 (q), 60.36 (t), 120.92 (d), 122.96 (s), 123.81 (d), 125.98 (d), 126.22 (d), 126.90 (d), 126.97 (s), 127.62 (d), 127.73 (d), 128.66 (d), 128.75 (d), 130.13 (s), 131.95 (d), 134.62 (s), 137.86 (s), 149.48 (s). IR ($CHCl_3$): 1 619, 1 596. MS, *m/z* (%): 650 ($M^{+\bullet}$, 2), 648 ($M^{+\bullet}$, 1), 479 (100), 309 (17), 294 (32), 280 (29), 267 (13), 169 (8). HR MS (EI): calculated for $C_{36}H_{30}Br_2N_2$ 648.0775; found 648.0771.

(*R*)-(–)-*N,N′*-Bis[2-(diphenylphosphino)benzyl]-*N,N′*-dimethyl[1,1′-binaphthalene]-2,2′-diamine [(*R*)-(–)-**12**]

(*R*)-(–)-**11** (650 mg, 1 mmol) was dissolved in dry THF, cooled to –78 °C, and 1.4 ml of butyllithium (1.6 M solution in hexanes, 2.2 mmol) was added. The reaction mixture was stirred at –78 °C for 1 h and chlorodiphenylphosphine (484 mg, 2.2 mmol) was then added. The reaction mixture was stirred at –78 °C for an additional 1 h and then allowed to reach room temperature overnight. The mixture was quenched with saturated brine, the resulting suspension was extracted with AcOEt (3 × 20 ml), and the extract was dried with $MgSO_4$ and evaporated. The crude product was purified by flash chromatography on silica gel (20 g) with toluene to produce (*R*)-(–)-**12** (671 mg, 78%) as an amorphous solid; $[\alpha]_D$ –56.3 (*c* 0.5, THF). $^1$H NMR (400 MHz): 2.27 (s, 6 H); 4.01 (dd, *J* = 16.4, *J* = 1.7, 2 H); 4.21 (dd, *J* = 15.3, *J* = 3.7, 2 H); 6.58–6.64 (m, 4 H); 6.86–6.98 (m, 4 H); 7.05–7.17 (m, 12 H); 7.21–7.29 (m, 14 H); 7.42 (d, *J* = 8.8, 2 H); 7.74 (d, *J* = 8.1, 2 H); 7.81 (d, *J* = 9.0, 2 H). $^{13}$C NMR: 40.04 (q), 58.12 (t), 58.38 (t), 121.40 (d), 123.65 (d), 126.00 (d), 126.14 (d), 127.58 (s), 127.63 (d), 127.65 (d), 128.40 (d), 128.46 (d), 128.49 (d), 128.52 (d), 128.58 (d), 128.65 (d), 130.18 (s), 132.46 (d), 133.64 ($J_{C,P}$ = 20, d), 134.03 ($J_{C,P}$ = 20, d), 134.49 (s), 134.65 ($J_{C,P}$ = 14, s), 136.47 ($J_{C,P}$ = 10, s), 136.54 ($J_{C,P}$ = 11, s), 143.25 ($J_{C,P}$ = 21, s), 149.76 (s). $^{31}$P NMR: –15.93. IR ($CHCl_3$): 1 619, 1 594. MS, *m/z* (%): 675 (2), 662 (3), 585 (100), 275 (58), 197 (32). FAB, *m/z* (%): 861 ($[M + H]^+$, 10), 586 (72), 275 (100).

*We thank the Grant Agency of the Czech Republic for grant No 203/98/1185, Grant Agency of Charles University for grant No 18/98.*

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