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Chiral Binaphthyl Ligands with Buttressing Substituents

Yuan-Yong Yan and **Michael Widhalm***

Institut für Organische Chemie, Universität Wien, A-1090 Wien, Austria

Summary. Four macrocyclic and one non-cyclic chiral diphosphine ligand containing a 2,2′-substituted 1,1′-binaphthyl unit were synthesized in 6 steps from (*R*)-2,2′-dimethoxy-1,1′-binaphthyl in overall yields of 8–51%. Their asymmetric induction in allylic alkylation reactions was investigated showing enantioselectivities up to 98%.

Keywords. 2,2′,3,3′-Tetrasubstituted 1,1′-binaphthyls; Allylic alkylation; Asymmetric catalysis; Macrocyclic chiral diphosphine ligands.

Chirale Binaphthyl-Liganden mit Stützsubstituenten

Zusammenfassung. Vier makrozyklische und ein offenkettiger chiraler Diphosphinligand mit einem 2,2′-substituierten 1,1′-Binaphthylfragment wurden ausgehend von (*R*)-2,2′-Dimethoxy-1,1′-binaphthyl in sechs Schritten in 8–51% Gesamtausbeute synthetisiert. Die asymmetrische Induktion in allylischen Alkylierungsreaktionen wurde untersucht und zeigte Enantioselektivitäten bis zu 98% *ee*.

Introduction

In the field of asymmetric transformations, carbon-carbon bond forming reactions have gained considerable interest during last decades [1,2], since the construction of a complex carbon skeleton with introduction of one or more asymmetric centers takes place in an enantio- and diastereoselective manner thus saving time and costs by avoiding the formation of undesired stereoisomers and their tedious separation. In particular, transition metal catalyzed coupling reactions have found widespread application in natural compound synthesis, and promising results have stimulated mechanistic investigations. In a limited number of cases the accumulation of experimental data resulted in reasonable suggestions for catalytic cycles, often supported by kinetic and spectroscopic data. Among the best understood reactions are those mediated by chiral palladium(0) complexes, particularly *Heck* type [3] and allylic substitution reactions [4]. The extension of the scope of these synthetically valuable reactions to new substrates and improved selectivity and reactivity has been the subject of numerous investigations, and excellent results

* Corresponding author

have been reported. Beside the variation of typical parameters like temperature, solvent polarity, pressure and relative concentration of ligand, transition metal precursor, and additives, which all influence basically the kinetics of the system, the ''steric fit'' of the coordinated substrate and/or reagent at one hand and the chiral ligand at the other hand will determine relative thermodynamic stabilities of diastereomeric intermediates. Without detailed knowledge of the complex geometry, particularly in the configuration determining step, the optimization of the ligand-to-substrate complementarity remains so far an empirical and time consuming process.

Results and Discussion

In continuation of our work on asymmetric allylic substitutions we searched for more efficient ligand structures. The proposed mechanism which requires outer-sphere chiral control of the prochiral Pd-allyl precursor for allylic alkylation reactions prompted us to investigate primarily ligands with remote chiral interaction which are prone to envelope the substrate coordination sites [4].

The outstanding broadness of scope and efficiency of 2,2′-disubstituted 1,1′-binaphthyls as chiral auxiliaries has been amply demonstrated in a plenitude of stoichiometric and catalytic reactions. Extension of scope was achieved by modification of complexation sites in position 2 [5] and introduction of additional substituents in positions 3 [6], 6 [7], or 7 [8].

Within the group of optically active key intermediates, 2,2′-dihydroxy-1,1′-binaphthyl (*BINOL*) seems most versatile and is also accessible on a multigram scale in optically pure form. Modification of the original procedure [9] recently led to a semi-technical process which afforded racemic *BINOL* in high purity [10]; for its optical resolution various methods are available [11]. The most convenient procedure makes use of the different solubility of diastereomeric inclusion complexes formed with benzylcinchonidinium chloride and affords both enantiomers in 99% yield in enantiomeric purities of 99% and 96%, respectively [12].

We have recently reported the synthesis of a number of macrocyclic binaphthyl ligands schematically depicted in Fig. 1 [13–16] and their application in allylic

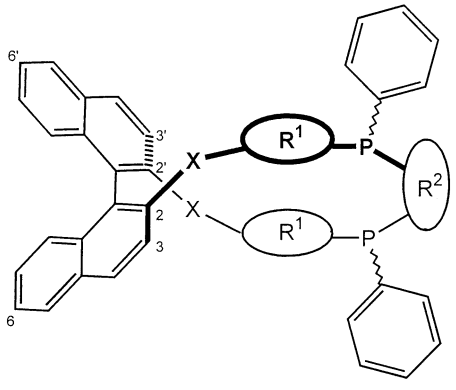
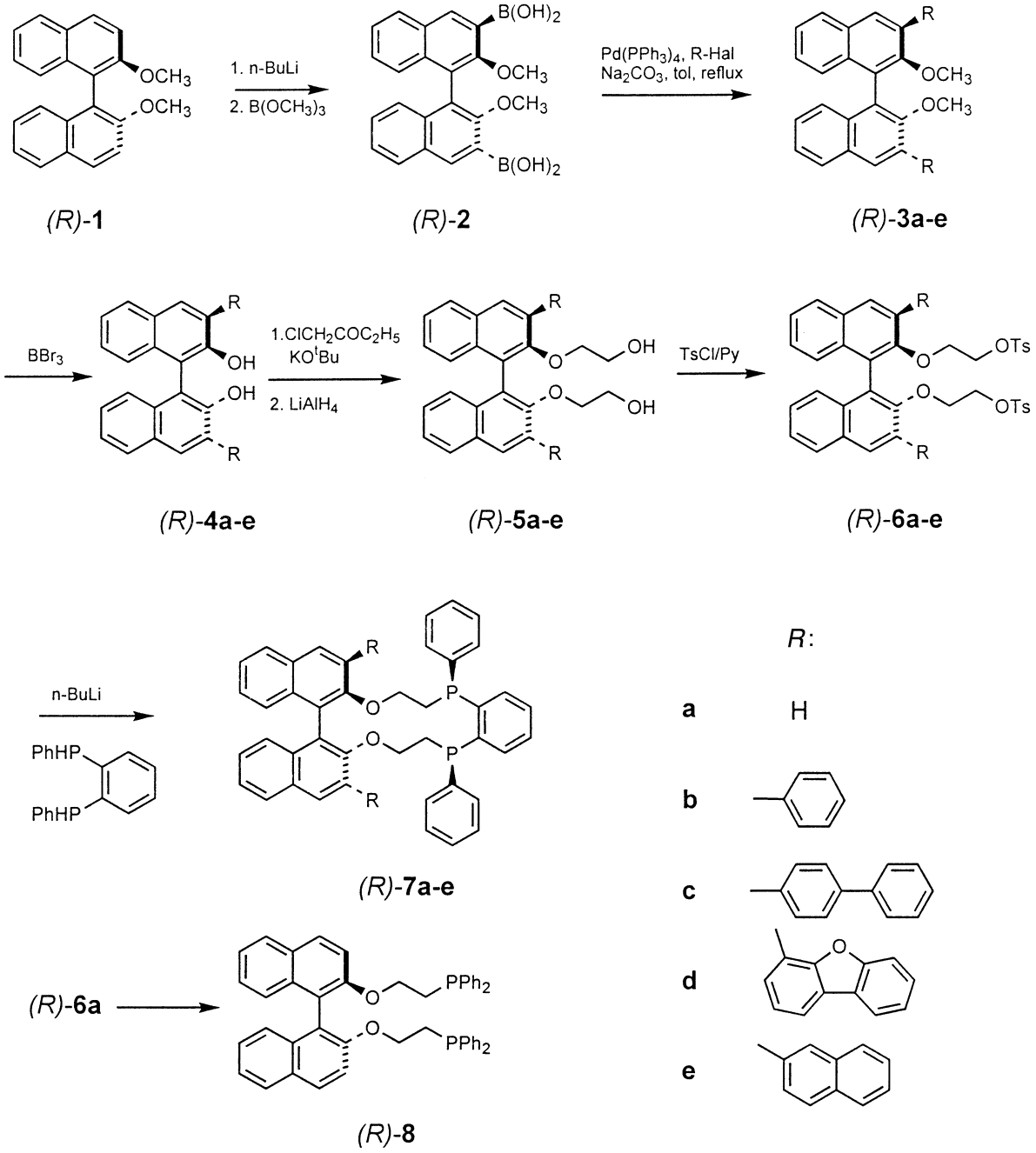


Fig. 1. $X = O$, NCH_3; $R^1 = -(CH_2)_n-$, $n = 2$–6, $-CH_2$-*m*-C_6H_4-, *o*-C_6H_4; $R^2 = o$-C_6H_4, $-(CH_2)_3-$

alkylation reactions [17]. From the structures investigated, **7a** (Scheme 1) proved to be most effective in allylic alkylation reactions giving asymmetric inductions of up to 86% ee. To further improve the enantioselectivity, we set out to extend the area of chiral interaction by introducing aromatic substituents of different size in positions 3 and 3′ of the binaphthyl skeleton [18]. Only aromatic fragments without

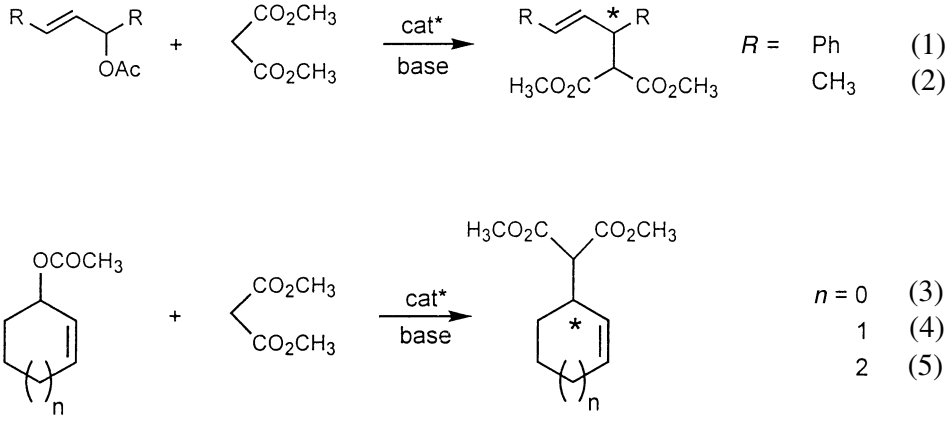


Scheme 1

functional groups but of different size and shape were chosen to vary gradually the interaction with the transition metal coordinated substrate. Another beneficial consequence expected from this substitution should be a buttressing effect which might increase the conformative stability of the macrocycle. If a *Suzuki* coupling is chosen to construct the biaryl moiety, a suitable precursor must bear either halogen or boronic acid functionalities. Fortunately, both compounds are easily obtained from **1** *via* an ortho lithiation protocol [19, 20]. We finally gave preference to the path *via* diboronic acid **2** since it was accessible without chromatographic purification [18a]. Moreover, the commercial availability of halo aromates rather than aromatic boronic acids made this route attractive. Employing *Suzuki* conditions yielded various 3,3′-substituted 2,2′-dimethoxy-1,1′-binaphthyl precursors **3b–e** [18a] which were treated with BBr_3 to give the corresponding diphenols **4b–e** in excellent yields. Alkylation with ethyl chloroacetate followed by $LiAlH_4$ reduction afforded diols **5a–e** which were converted into ditosylates **6a–e**. Cyclization with dilithio 1,2-*bis*(diphenylphosphinyl)benzene resulted in the nearly exclusive formation of the C_1-symmetrical stereoisomer which is in agreement with results obtained previously for the parent compound **7a** [14]. For comparative studies, also the non-cyclic analogue **8** was synthesized.

Ligands **7a–e** represent a set of chiral auxiliaries with increasingly extended chiral bias which should result in different chiral modeling of the reaction area. Nevertheless, the crucial question, *i.e.* if steric interaction will become sufficiently effective in proximity to the substrate coordination sites or not, cannot be answered without detailed knowledge of the preferred conformation of the macrocyclic palladium complex in course of the catalytic reaction. Since we have so far only information on the solid state geometry of the unsubstituted macrocycle **7a** and its palladium dichloride complex [17], the degree of asymmetric induction of **7b–e** cannot be predicted and must be determined empirically.

All new ligands were tested in Pd-catalyzed allylic substitution reactions (Scheme 2). Typical substrates are symmetrically disubstituted allyl acetate moieties which react *via* symmetrically substituted diastereomeric π-allyl palladium complexes with the nucleophile [4]. Results are summarized in Table 1.



Scheme 2

Table 1. Palladium catalyzed allylic alkylation reactions[a] with macrocyclic diphosphine ligands

Reaction	Solvent	(*R*)-**7a**[e]	(*R*)-**7b**[e]	(*R*)-**7c**[e]	(*R*)-**7d**[e]	(*R*)-**7e**[e]	(*R*)-**8**[e]
(1)	CH_2Cl_2	86 *S* (93)	96 *S* (93)	96 *S* (99)	97 *S* (94)	97 *S* (94)	66 *S* (91)
(1)	*THF*	87 *S* (94)	96 *S* (94)	96 *S* (87)	95 *S* (73)	97 *S* (93)	73 *S* (94)
(1)	CH_3CN	86 *S* (95)	97 *S* (97)	97 *S* (85)	97 *S* (92)	98 *S* (95)	70 *S* (96)
(1)[b]	CH_2Cl_2	81 *S* (89)	86 *S* (99)	90 *S* (74)	90 *S* (79)	91 *S* (82)	n.e.
(2)[c]	CH_2Cl_2	19 *S* (81)	4 *R* (98)	8 *S* (89)	4 *S* (78)	20 *S* (83)	28 *S* (87)
(2′)[c,d]	CH_2Cl_2	18 *S* (74)	21 *S* (55)	10 *S* (70)	11 *S* (86)	24 *S* (79)	25 *S* (89)
(3)	CH_2Cl_2	n.e.	13 *S* (90)	13 *S* (83)	10 *R* (70)	10 *S* (70)	10 *R* (87)
(4)	CH_2Cl_2	n.e.	17 *S* (83)	25 *S* (95)	5 *R* (88)	1 *R* (58)	9 *S* (66)
(5)	CH_2Cl_2	n.e.	n.e.	1 *R* (84)	2 *R* (88)	0	n.e.

[a] Experiments were run in 1 cm^3 of solvent with 1 mmol of substrate and 3 mmol of dimethylmalonate and *BSA* each, a trace of KOAc, and the catalyst prepared *in situ* from 0.5 mol% of $[Pd(C_3H_5)Cl]_2$ and 2 mol% of ligand; for experimental details see Ref. [17]; [b]NaH was used instead of *BSA*/KOAc; [c]tentative assignment of (*S*) configuration to the laevorotatory enantiomer [22]; [d]instead of pentenyl acetate, the corresponding carbonate was used as substrate; [e]figures refer to: *ee*/configuration of product/isolated yield (in parantheses): *ee* was determined by HPLC (Reaction (1), Chiralcel-ODH, 250×4.6 mm, 2-PrOH/*n*-hexane, 2:98), GC (Reaction (2), 50% of octa*bis*(6-O-methyl-2,3-di-O-pentyl)-γ-cyclodextrin, 0.25 mm×25 m, 0.5 bar H_2, 55°C), or on the basis of specific rotation ([21], Reactions (3)–(5): (*S*)-dimethyl 2-(cyclopent-2-en-1-yl)malonate, $[\alpha]_D^{20} = -98.7$ ($c = 2.27$, $CHCl_3$); (*S*)-dimethyl 2-(cyclohex-2-en-1-yl)malonate, $[\alpha]_D^{20} = -46.1$ ($c = 2.85$, $CHCl_3$); (*S*)-dimethyl 2-(cyclohept-2-en-1-yl)malonate, $[\alpha]_D^{20} = -7.8$ ($c = 3.04$, $CHCl_3$))

Reactions were run in CH_2Cl_2 with N,O-*bis*(trimethylsilyl)acetamide (*BSA*)/KOAc as base and 1 mol% of catalyst. Yields were found to be excellent, exceeding 90% in nearly all cases. In the presence of ligands with substituents in positions 3 and 3′, the asymmetric induction increased from 86% ee (**7a**) to 98% ee (**7e** in CH_3CN). Variation of the solvent did not affect the enantioselectivity, but the overall reaction rate reached a maximum of approximately 100 turn overs per h in CH_3CN. The use of sodium hydride instead of *BSA*/KOAc decreased the enantioselectivity to 81–91% ee (for **7a** and **7e**, respectively). This behavior was in sharp contrast to that of aliphatic substrates for which neither an improvement of the asymmetric induction nor a dependence from the bulkyness of substituents of the binaphthyl moiety could be observed. Disappointingly, for Reactions (2)–(5) the enantioselectivities did not exceed 25% ee (with **7c** and **7e**) and are in the same range as obtained with the non-cyclic ligand **8** (28% ee for Reaction (2)).

Conclusions

It was demonstrated that macrocyclic diphosphine ligands derived from chiral binaphthyl precursors are suitable auxiliaries in palladium catalyzed allylic alkylation reactions. Whereas chemical yields proved to be excellent, the enantioselectivity is highly dependent on substrate geometry and substitution pattern. High enantioselectivities of up to 98% were only observed with 1,3-diphenylpropenyl acetate, whereas for pent-3-en-2-yl acetate and cyclic substrates

(with *anti* configuration of the allyl fragment) the asymmetric induction was found to be low. For these cases, further structural modifications with emphasis to the area proximate to the phosphorus complexation sites will be attempted.

Experimental

General

Melting points: Kofler melting point apparatus, uncorrected. NMR: Bruker AM 400 spectrometer at 400.13 MHz (^{1}H), 100.61 MHz (^{13}C), and 161.98 MHz (^{31}P), $CDCl_3$, δ in ppm rel. to internal *TMS* (0.00 ppm), $CHCl_3$ (7.24 or 77.00 ppm, respectively) or H_3PO_4, 85% (0.00 ppm), respectively; coupling patterns are designated as s(ingulett), d(oublett), t(riplett), p(seudo), and br(oad). $^{13}C\{^1H\}$ NMR: spectra are recorded in the *J*-modulated mode (APT); undesignated signals refer to CH-resonances; *J* refers to PC-coupling. In spectral areas of extensive signal overlap, coupling patterns could not be identified; these signals of unclear relationship are underlined. MS: MAT 900 EI (70 eV) or FD. Optical rotations were measured on a Perkin-Elmer polarimeter 241 in a thermostatted 1 dm cell.

Petroleum ether (*PE*) CH_2Cl_2, and ethyl acetate (*EE*) were distilled; absolute CH_2Cl_2 and CH_3CN were distilled from CaH_2, *THF* from potassium benzophenone ketyl. Tosyl chloride was recrystallized from *PE*, *n*-BuLi was used as a 1.6 molar solution in hexane (Aldrich). Column chromatography was performed in silica gel Si 60, 25–40 µm (Merck), either used as purchased or deactivated with water [15]. All other chemicals were of analytical grade and used without further purification. Optically active compounds **1** [20b], **3a**, **4a**, **5a**, **6a** [13,14], and 1,2-*bis*(phenylphosphinyl)benzene [24] were prepared according to reported procedures.

(−)(R)-2,2′-Dimethoxy-1,1′-binaphthyl-3,3′-diboronic acid ((*R*)-**2**)

The preparation was conducted essentially the same way as previously reported for the racemic compound [18a]; the crude product was crystallized from a mixture of CH_2Cl_2/Et_2O/*PE* to give (*R*)-**2** as cream coloured crystals (49%). Drying under high vacuum afforded an analytically pure sample. M.p.: 237–240°C; $[\alpha]_D^{20} = -136$ ($c = 1.0$, CH_2Cl_2); Ref. [23]: $[\alpha]_D^{20} = -153.4$ ($c = 1.0$, $CHCl_3$).

(−)(R)-3,3′-Bis(2-naphthyl)-2,2′-dimethoxy-1,1′-binaphthyl ((*R*)-**3e**); *typical procedure*

A solution of 2-bromonaphthalene (1.67 g, 8.0 mmol) and $Pd(PPh_3)_4$ (100 mg, 0.087 mmol) in 100 cm^3 of toluene was prepared in a *Schlenk* tube and degassed. The solution was heated to reflux with stirring, and degassed solutions of (*R*)-**2** (1.10 g (2.7 mmol) in 9 cm^3 of ethanol) and Na_2CO_3 (2 *M*, 5 cm^3) were added dropwise and synchroneously *via* a teflon tube. The reaction mixture was protected from light and refluxed under argon for 24 h. The solvent was evaporated, and NaCl solution was added. The mixture was extracted three times with CH_2Cl_2, and the combined extracts were washed with saturated NaCl solution and dried ($MgSO_4$). After concentration the residue was chromatographed on silica gel (column: 4×27 cm). Elution with *PE*/CH_2Cl_2 (65/35) yielded 1.344 g of (*R*)-**3e**.

(+)(R)-3,3′-Diphenyl-2,2′-dimethoxy-1,1′-binaphthyl ((*R*)-**3b**; $C_{34}H_{26}O_2$)

Yield: 86%; white foam; m.p.: 97–98°C; $[\alpha]_D^{20} = +24.6$ ($c = 1.0$, CH_2Cl_2); ^{1}H NMR: $\delta = 3.17$ (s, 6H), 7.25 (m, 4H), 7.35–7.47 (m, 8H), 7.76 (m, 4H), 7.91 (br d, $J = 8.1$ Hz, 2H), 7.96 (s, 2H) ppm; ^{13}C NMR: $\delta = 60.52$ (CH_3), 124.98, 125.77, 125.89 (C), 126.25, 127.26, 128.04, 128.30, 129.31, 130.50, 130.79 (C), 133.62 (C), 135.02 (C), 138.91 (C), 154.07 (C) ppm; MS (150°C): $m/z = 466.3$ (M^+, 100%).

(−)(R)-3,3′-Bis(p-diphenyl)-2,2′-dimethoxy-1,1′-binaphthyl ((*R*)-**3c**; $C_{46}H_{34}O_2$)

Yield: 74%; white foam; m.p.: 175–178°C; $[\alpha]_D^{20} = -112.7$ ($c = 1.0$, CH_2Cl_2); ^{1}H NMR: $\delta = 3.35$ (s, 6H), 7.27 (m, 4H), 7.33–7.38 (m, 2H), 7.39–7.48 (m, 6H), 7.67 (s, 2H), 7.69–7.72 (m, 6H), 7.86 (m, 4H), 7.93 (d, $J = 8.5$ Hz, 2H), 8.03 (s, 2H) ppm; ^{13}C NMR: $\delta = 60.65$ (CH_3), 125.04, 125.79, 125.95 (C), 126.33, 126.99, 127.05, 127.33, 128.08, 128.81, 129.69, 130.46, 130.84 (C), 133.67 (C), 134.55 (C), 137.90 (C), 140.02 (C), 140.77 (C), 154.15 (C) ppm; MS (235°C): $m/z = 618.7$ (M^+, 100%).

(+)(R)-3,3′-Bis(dibenzofuran-1-yl)-2,2′-dimethoxy-1,1′-binaphthyl ((*R*)-**3d**; $C_{46}H_{30}O_4$)

Yield: 74%; white foam; m.p.: 159–161°C; $[\alpha]_D^{20} = +47.6$ ($c = 1.0$, CH_2Cl_2); spectroscopic data are in agreement with (±)-**3d** [18a].

(−)(R)-3,3′-Bis(2-naphthyl)-2,2′-dimethoxy-1,1′-binaphthyl ((*R*)-**3e**; $C_{42}H_{30}O_2$)

Yield: 89%; white foam; m.p.: 128–131°C; $[\alpha]_D^{20} = -76.7$ ($c = 1.0$, CH_2Cl_2); ^{1}H NMR: $\delta = 3.21$ (s, 6H), 7.30 (br d, $J = 3.4$ Hz, 4H), 7.41–7.45 (m, 2H), 7.51 (m, 4H), 7.88–7.96 (m, 10H), 8.10 (s, 2H), 8.25 (br d, $J = 0.6$ Hz, 2H) ppm; ^{13}C NMR: $\delta = 60.67$ (CH_3), 125.07, 125.81, 126.00, 126.08, 126.37, 127.66, 127.69, 127.75, 127.93, 128.12, 128.21, 130.85, 130.90 (C), 132.63 (C), 133.59 (C), 133.73 (C), 134.91 (C), 136.58 (C), 154.23 (C) ppm; MS (260°C): $m/z = 566.6$ (M^+, 98.1%), 567.5 ($M^+ + 1$, 100%), 283.2 (61.8%).

(−)(R)-3,3′-Bis(2-naphthyl)-2,2′-dihydroxy-1,1′-binaphthyl ((*R*)-**4e**); *typical procedure*

To a solution of (*R*)-**3e** (1.32 g, 2.30 mmol) in 30 cm^3 of anhydrous CH_2Cl_2, BBr_3 (0.80 cm^3, 3.6 equiv.) was added at −78°C. The mixture was stirred for 30 min at −78°C and subsequently 5 h at room temperature. Water (20 cm^3) was added with external cooling. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (3×20 cm^3). The combined extracts were washed with saturated NaCl solution and dried ($MgSO_4$). After concentration *in vacuo* the crude product was purified by chromatography (silica gel, column 4×27 cm). Elution with CH_2Cl_2/hexane (50/50) gave 1.004 g of (*R*)-**4e**.

(+)(R)-3,3′-Diphenyl-2,2′-dihydroxy-1,1′-binaphthyl ((*R*)-**4b**; $C_{32}H_{22}O_2$)

Yield: 90%; white needles; m.p.: 203–205°C; $[\alpha]_D^{20} = +86.4$ ($c = 0.88$, CH_2Cl_2); Ref. [20b]: m.p.: 197–198°C. $[\alpha]_D^{20} = +106.5$ ($c = 1$, *THF*); Ref. [23]: m.p.: 202–204°C, $[\alpha]_D^{20} = +69.1$ ($c = 1$, $CHCl_3$); ^{1}H NMR: $\delta = 5.37$ (s, 2H), 7.22 (s, 2H), 7.31 (ddd, $J = 1.5$, 6.9, 8.4 Hz, 2H), 7.36–7.42 (m, 4H), 7.49 (m, 4H), 7.73 (m, 4H), 7.91 (br d, $J = 7.9$ Hz, 2H), 8.02 (s, 2H) ppm; ^{13}C NMR: $\delta = 112.43$ (C), 124.27, 124.31, 127.32, 127.74, 128.43, 128.46, 129.43 (C), 129.59, 130.68 (C), 131.36, 132.96 (C), 137.47 (C), 150.13 (C) ppm; MS (190°C): $m/z = 438.2$ (M^+, 100%).

(−)(R)-3,3′-Bis(p-diphenyl)-2,2′-dihydroxy-1,1′-binaphthyl ((*R*)-**4c**; $C_{44}H_{30}O_2$)

Yield: 97%; white needles; m.p.: 144–146°C; $[\alpha]_D^{20} = -45.0$ ($c = 1.0$, CH_2Cl_2); ^{1}H NMR: $\delta = 5.42$ (s, 2H), 7.26 (br d, $J = 8.4$ Hz, 2H), 7.32–7.43 (m, 6H), 7.47 (m, 4H), 7.67 (m, 4H), 7.73 (m, 4H), 7.84 (m, 4H), 7.95 (br d, $J = 7.9$ Hz, 2H), 8.09 (s, 2H) ppm; ^{13}C NMR: $\delta = 112.33$ (C), 124.26, 124.41, 127.13, 127.18, 127.40, 127.43, 128.49, 128.81, 129.52 (C), 130.01, 130.25 (C), 131.38, 132.95 (C), 136.43 (C), 140.60 (C), 140.74 (C), 150.24 (C) ppm; MS (250°C): $m/z = 590$ (M^+, 100%).

(+)(R)-3,3′-Bis(dibenzofuran-1-yl)-2,2′-dihydroxy-1,1′-binaphthyl ((*R*)-**4d**; $C_{44}H_{26}O_4$)

Yield: 69%; white needles; m.p.: 172–175°C; $[\alpha]_D^{20} = +103.1$ ($c = 1.0$, CH_2Cl_2); ^{1}H NMR: $\delta = 5.54$ (s, 2H), 7.35 (ddd, $J = 0.9$, 7.5, 8.0 Hz, 2H), 7.39–7.49 (m, 10H), 7.52 (br d, $J = 8.2$ Hz, 2H), 7.75 (m, 2H), 7.96–8.02 (m, 6H), 8.28 (s, 2H) ppm; ^{13}C NMR: $\delta = 111.86$, 112.79 (C), 120.32, 120.70, 122.07 (C), 122.78, 122.85, 124.29 (C), 124.33, 124.55, 124.67 (C), 127.22, 127.55, 128.63, 128.84, 129.06 (C), 129.31 (C), 132.56, 133.37 (C), 150.58 (C), 153.95 (C), 156.13 (C) ppm; MS (150°C): $m/z = 618.9$ (M^+, 100%).

(−)(R)-3,3′-Bis(2-naphthyl)-2,2′-dihydroxy-1,1′-binaphthyl ((*R*)-**4e**; $C_{40}H_{26}O_2$)

Yield: 81%; white needles; m.p.: 245–248°C; $[\alpha]_D^{20} = -28.7$ ($c = 1.0$, CH_2Cl_2); Ref. [23]: m.p.: 248–249°C, $[\alpha]_D^{20} = -40.2$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR: $\delta = 5.47$ (s, 2H), 7.30 (br d, $J = 8.4$ Hz, 2H), 7.35 (ddd, $J = 1.0$, 6.9, 7.9 Hz, 2H), 7.41 (ddd, $J = 1.0$, 6.4, 7.9 Hz, 2H), 7.51 (m, 4H), 7.86–7.96 (m, 10H), 8.13 (s, 2H), 8.20 (br d, $J = 1.5$ Hz, 2H) ppm; ^{13}C NMR: $\delta = 112.53$ (C), 124.34, 124.40, 126.23, 126.28, 127.43, 127.68, 127.93, 128.21, 128.51, 129.54 (C), 130.66 (C), 131.69, 132.78 (C), 133.06 (C), 133.47 (C), 135.02 (C), 150.33 (C) ppm; MS (240°C): $m/z = 538.3$ (M^+, 97.2%), 488.2 (100%).

(−)(R)-3,3′-Bis(2-naphthyl)-2,2′-bis(2-hydroxyethoxy)-1,1′-binaphthyl ((*R*)-**5e**); *typical procedure*

To a stirred solution of (*R*)-**4e** (980 mg, 1.82 mmol) in 40 cm^3 of dry *THF*, *t*-BuOK (510 mg, 2.5 equiv.) was added and the mixture was heated to reflux under argon for 1 h. A solution of ethyl chloroacetate (0.45 cm^3, 2.5 equiv.) in 5 cm^3 of dry *THF* was slowly added, and reflux was continued for 20 h. The solvent was evaporated, and the residue was distributed between 100 cm^3 of CH_2Cl_2 and 50 cm^3 of water. The organic layer was separated, and the water layer was repeatedly extracted with CH_2Cl_2 (3×30 cm^3). The combined organic extracts were washed with water and saturated NaCl solution and dried ($MgSO_4$). After evaporation of the solvent the residue was carefully dried under high vacuum for 5 h and redissolved in 30 cm^3 of dry *THF*. The solution of the crude diester was added dropwise to an ice-cooled suspension of $LiAlH_4$ (280 mg, 4.0 equiv.) in 30 cm^3 of *THF* with stirring. Stirring was continued for 20 h at room temperature. The reaction was quenched by careful addition of 50 cm^3 of water, followed by 80 cm^3 of 6 *N* HCl (ice bath). The mixture was stirred for 4 h. The organic layer was separated, and the aqueous phase was extracted with three 30 cm^3 portions of CH_2Cl_2. The combined organic extracts were washed successively with saturated $NaHCO_3$ solution, water, and saturated NaCl solution and dried ($MgSO_4$). Removal of the solvent afforded the crude diol which was purified by column chromatography (column: 2×25 cm). Elution with *EE*/*PE* (30/70) afforded 813 mg of (*R*)-**5e**.

(−)(R)-3,3′-Diphenyl-2,2′-bis(2-hydroxyethoxy)-1,1′-binaphthyl ((*R*)-**5b**; $C_{36}H_{30}O_4$)

Yield: 89%; white foam; m.p.: 82–84°C; $[\alpha]_D^{20} = -96.1$ ($c = 1.0$, CH_2Cl_2); ^{1}H NMR: $\delta = 1.17$ (p t, $J = 6.5$ Hz, 2H), 3.14 (m, 4H), 3.31 (m, 2H), 3.49 (m, 2H), 7.23 (br d, $J = 8.5$ Hz, 2H), 7.28 (ddd, $J = 1.5$, 7.0, 8.5 Hz, 2H), 7.37–7.49 (m, 8H), 7.72 (m, 4H), 7.91 (br d, $J = 8.2$ Hz, 2H), 7.97 (s, 2H) ppm; ^{13}C NMR: $\delta = 61.69$ (CH_2), 74.41 (CH_2), 125.32, 125.71, 126.66, 127.64, 128.22, 128.48, 129.36, 130.71 (C), 130.80, 133.36 (C), 135.23 (C), 138.65 (C), 152.49 (C) ppm; MS (180°C): $m/z = 526.2$ (M^+, 100%).

(−)(R)-3,3′-Bis(p-diphenyl)-2,2′-bis(2-hydroxyethoxy)-1,1′-binaphthyl ((*R*)-**5c**; $C_{48}H_{38}O_4$)

Yield: 66%; white foam; m.p.: 225–227°C; $[\alpha]_D^{20} = -196$ ($c = 1.0$, CH_2Cl_2); ^{1}H NMR: $\delta = 1.23$ (p t, $J = 6.5$ Hz, 2H), 3.19 (m, 4H), 3.38 (m, 2H), 3.58 (m, 2H), 7.26 (br d, $J = 8.5$ Hz, 2H), 7.29–7.38 (m, 4H), 7.42–7.48 (m, 6H), 7.67 (m, 4H), 7.72 (m, 4H), 7.82 (m, 4H), 7.94 (br d, $J = 8.0$ Hz, 2H), 8.03

(s, 2H) ppm; ^{13}C NMR: $\delta = 61.74$ (CH_2), 74.44 (CH_2), 125.39, 125.75, 126.73, 127.07, 127.14, 127.45, 128.27, 128.83, 129.76, 130.78 (C), 130.84, 133.38 (C), 134.74 (C), 137.62 (C), 140.41 (C), 140.55 (C), 152.54 (C) ppm; MS (200°C): $m/z = 678$ (M^+, 100%).

(+)(R)-3,3′-Bis(dibenzofuran-1-yl)-2,2′-bis(2-hydroxyethoxy)-1,1′-binaphthyl ((*R*)-**5d**; $C_{48}H_{34}O_6$)

Yield: 58%; white foam; m.p.: 150–152°C; $[\alpha]_D^{20} = +42.4$ ($c = 1.0$, CH_2Cl_2); ^{1}H NMR: $\delta = 1.47$ (p t, $J = 6.5$ Hz, 2H), 3.00–3.11 (m, 4H), 3.31–3.36 (m, 2H), 3.47–3.52 (m, 2H), 7.33–7.42 (m, 8H), 7.47 (m, 6H), 7.74 (m, 2H), 7.96–8.02 (m, 6H), 8.22 (s, 2H) ppm; ^{13}C NMR: $\delta = 61.71$ (CH_2), 74.53 (CH_2), 111.94, 120.28, 120.74, 122.83, 122.85, 123.14 (C), 124.17 (C), 124.59 (C), 125.09 (C), 125.27, 125.91, 126.89, 127.35, 128.43, 128.56, 130.01 (C), 130.59 (C), 131.82, 133.86 (C), 153.18 (C), 153.89 (C), 156.18 (C) ppm; MS (280°C): $m/z = 706.6$ (M^+, 100%), 662.9 (54%), 618.8 (96%).

(−)(R)-3,3′-Bis(2-naphthyl)-2,2′-bis(2-hydroxyethoxy)-1,1′-binaphthyl ((*R*)-**5e**; $C_{44}H_{34}O_4$)

Yield: 71%; white foam; m.p.: 124–126°C, $[\alpha]_D^{20} = -162$ ($c = 1.0$, CH_2Cl_2); ^{1}H NMR: $\delta = 1.22$ (p t, $J = 6.5$ Hz, 2H), 3.08–3.20 (m, 4H), 3.33–3.38 (m, 2H), 3.55 (m, 2H), 7.28–7.35 (m, 4H), 7.45 (ddd, $J = 1.5$, 6.4, 8.0 Hz, 2H), 7.49–7.55 (m, 4H), 7.88–7.97 (m, 10H), 8.09 (s, 2H), 8.19 (br d, $J = 1.6$ Hz, 2H) ppm; ^{13}C NMR: $\delta =$ 61.70 (CH_2), 74.41 (CH_2), 125.38 (C), 125.42, 125.77, 126.36, 126.77, 127.60, 127.77, 127.90, 128.02, 128.15, 128.29, 130.83 (C), 131.22, 132.66 (C), 133.45 (C), 133.54 (C), 135.06 (C), 136.34 (C), 152.62 (C) ppm; MS (260°C): $m/z = 627.1$ (M^+, 100%).

Ditosylate of (R)-3,3′-bis(2-naphthyl)-2,2′-bis(2-hydroxyethoxy)-1,1′-binaphthyl ((*R*)-**6e**); *typical procedure*

To a solution of diol (*R*)-**5e** (800 mg, 1.27 mmol) in 10 cm^3 of dry pyridine, *p*-tosyl chloride (1.45 g, 6 equiv.) was added. The mixture was kept in a tightly stoppered flask in a refrigerator at 2°C. After 24 h it was poured into 50 cm^3 of ice-cold water and extracted sufficiently with CH_2Cl_2 (3×40 cm^3). The combined extracts were successively washed with 50 cm^3 of 6 *N* HCl, water, and saturated NaCl solution and dried over $MgSO_4$. Removal of the solvent at room temperature *in vacuo* gave a crude product which was chromatographed on a silica gel (column: 2×26 cm). Elution with *EE*/*PE* (30/70) to afforded 1.07 g of (*R*)-**6e**.

(−)(R)-Ditosylate of (−)(R)-3,3′-diphenyl-2,2′-bis(2-hydroxyethoxy)-1,1′-binaphthyl ((*R*)-**6b**; $C_{50}H_{42}O_8S_2$)

Yield: 84%; white foam; m.p.: 66–68°C; $[\alpha]_D^{20} = -91$ ($c = 1.0$, CH_2Cl_2); ^{1}H NMR: $\delta = 2.34$ (s, 6H), 3.28 (m, 2H), 3.41 (m, 2H), 3.48–3.59 (m, 4H), 7.06 (d, $J = 8.0$, 4H), 7.12 (d, $J = 8.6$, 2H), 7.24 (m, 2H), 7.31–7.44 (m, 12H), 7.60 (m, 4H), 7.89 (s, 2H), 7.90 (d, $J = 7.8$ Hz, 2H) ppm; ^{13}C NMR: $\delta =$ 21.55 (CH_3), 68.37 (CH_2), 69.43 (CH_2), 125.23, 125.70, 126.45, 127.51, 127.68, 128.22, 128.34, 129.39, 129.52, 130.68, 130.93 (C), 132.68 (C), 133.31 (C), 134.97 (C), 138.19 (C), 144.33 (C), 152.28 (C) ppm; MS (245°C): $m/z = 834.9$ (M^+, 100%).

(−)(R)-Ditosylate of (−)(R)-3,3′-bis(p-diphenyl)-2,2′-bis(2-hydroxyethoxy)-1,1′-binaphthyl ((*R*)-**6c**; $C_{62}H_{50}O_8S_2$)

Yield: 87%; white foam; m.p.: 95–96°C; $[\alpha]_D^{20} = -141$ ($c = 1.0$, *THF*); ^{1}H NMR: $\delta = 2.28$ (s, 6H), 3.37 (m, 2H), 3.49 (m, 2H), 3.57 (m, 2H), 3.66 (m, 2H), 6.99 (br d, $J = 8.0$ Hz, 4H), 7.15 (br d, $J = 8.0$ Hz, 2H), 7.27 (m, 2H), 7.32–7.50 (m, 12H), 7.62–7.73 (m, 12H), 7.92 (br d, $J = 8.0$ Hz, 2H), 7.96 (s, 2H) ppm; ^{13}C NMR: $\delta =$ 21.51 (CH_3), 68.35 (CH_2), 69.49 (CH_2), 125.30, 125.74, 125.80

(C), 126.52, 127.02, 127.09, 127.41, 127.66, 128.26, 128.85, 129.52, 129.82, 130.68, 130.99 (C), 132.64 (C), 133.36 (C), 134.53 (C), 137.15 (C), 140.24 (C), 140.70 (C), 144.34 (C), 152.32 (C) ppm; MS (260°C): $m/z = 986.3$ (M^+, 100%).

(−)(R)-Ditosylate of (+)(R)-3,3′-bis(dibenzofuran-1-yl)-2,2′-bis(2-hydroxyethoxy)-1,1′-binaphthyl ((*R*)-**6d**; $C_{62}H_{46}O_{10}S_2$)

Yield: 89%; white foam; m.p.: 98–101°C; $[\alpha]_D^{20} = -29.2$ ($c = 1.0$, *THF*); ^{1}H NMR: $\delta = 2.22$ (s, 6H), 3.30–3.37 (m, 6H), 3.56–3.64 (m, 2H), 6.89 (br d, $J = 8.4$ Hz, 4H), 7.18 (m, 4H), 7.27–7.48 (m, 14H), 7.63 (m, 2H), 7.94–8.02 (m, 6H), 8.18 (s, 2H) ppm; ^{13}C NMR: $\delta =$ 21.42 (CH_3), 68.31 (CH_2), 69.75 (CH_2), 111.87, 120.18, 120.71, 122.50 (C), 122.81, 122.88, 124.32 (C), 124.48 (C), 125.33, 125.47 (C), 125.81, 126.83, 127.21, 127.52, 128.39, 129.05, 129.37, 129.75 (C), 130.69 (C), 131.83, 132.49 (C), 133.74 (C), 144.15 (C), 152.80 (C), 153.75 (C), 156.09 (C) ppm; MS (250°C): $m/z = 1014.2$ (M^+, 100%).

(−)(R)-Ditosylate of (−)(R)-3,3′-bis(2-naphthyl)-2,2′-bis(2-hydroxyethoxy)-1,1′-binaphthyl ((*R*)-**6e**; $C_{58}H_{46}O_8S_2$)

Yield: 90%; white foam; m.p.: 86–88°C; $[\alpha]_D^{20} = -124$ ($c = 1.0$, *THF*); ^{1}H NMR: $\delta = 2.25$ (s, 6H), 3.30–3.35 (m, 2H), 3.40–3.45 (m, 2H), 3.50–3.55 (m, 2H), 3.58–3.64 (m, 2H), 6.93 (br d, $J = 8.0$ Hz, 4H), 7.18 (br d, $J = 8.0$ Hz, 2H), 7.23 (m, 4H), 7.28 (ddd, $J = 1.5$, 7.0, 8.5 Hz, 2H), 7.45 (ddd, $J = 1.0$, 6.5, 8.0 Hz, 2H), 7.53 (m, 4H), 7.77 (m, 2H), 7.85 (br d, $J = 8.5$ Hz, 2H), 7.89 (m, 4H), 7.95 (br d, $J = 8.5$ Hz, 2H), 8.02 (s, 2H), 8.14 (br d, $J = 1.5$ Hz, 2H) ppm; ^{13}C NMR: $\delta =$ 21.47 (CH_3), 68.35 (CH_2), 69.49 (CH_2), 125.32, 125.77, 125.78 (C), 126.15, 126.18, 126.57, 127.57, 127.69, 127.76, 128.11, 128.30, 129.45, 131.03 (C), 131.08, 132.58 (C), 132.69 (C), 133.44 (C), 133.49 (C), 134.86 (C), 135.93 (C), 144.24 (C), 152.44 (C) ppm; MS (240°C): $m/z = 934.6$ (M^+, 100%).

Macrocyclic diphosphine (*R*)-**7e**; *typical procedure*

A 250 cm^3 *Schlenk* tube fitted with a magnetic stirring bar and reflux condenser was charged with 120 cm^3 of anhydrous, degassed *THF*. Solutions of ditosylate (*R*)-**6e** (1.00 g, 1.06 mmol) in 10 cm^3 of *THF* and of 1.5 equiv. of the dilithium salt of 1,2-*bis*(phenylphosphinyl)benzene (prepared from 1,2-*bis*(phenylphosphinyl)benzene (474 mg, 1.61 mmol) and 2.0 ml of *n*-BuLi solution) in 8 cm^3 of the same solvent were added synchronously to boiling *THF* during 1 h. Stirring was continued overnight at room temp. The solvent was distilled off, and the residue was partitioned between 100 cm^3 of CH_2Cl_2 and 60 cm^3 of saturated NaCl solution. The organic phase was separated and dried ($MgSO_4$). Removal of the solvent yielded the crude mixture which was purified by chromatography on silica gel deactivated with 13% (w/w) of water (column: 2×27 cm). Elution with CH_2Cl_2/*PE* (20/80) afforded 715 mg of (*R*)-**7e**.

Macrocyclic diphosphine (+) (*R*)-**7a** [13,14]

(+) (*R*)-**7a** could be obtained in better yield than reported previously if the chromatographic purification was performed on deactivated silica gel (13% water content [15]). Elution with CH_2Cl_2/*PE* (25/75) afforded 94% of (*R*)-**7a** as a white powder, m.p.: 229–230°C, $[\alpha]_D^{20} = +655$ ($c = 1.0$, CH_2Cl_2)[1].

[1] The previously reported optical rotation for compound **7a** [14] is too low. A considerable amount of CH_2Cl_2 is trapped even after prolonged drying under vacuum at room temperature; only heating under vacuum at 80°C for 24 h yielded an analytically pure sample

Macrocyclic diphosphine (+)(*R*)-**7b** ($C_{54}H_{42}O_2P_2$)

Yield: 88%; white powder; m.p.: 143–146°C; $[\alpha]_D^{20} = +419$ ($c = 1.0$, CH_2Cl_2); ^{1}H NMR: $\delta = 1.93$–2.01 (m, 1H), 2.07–2.30 (m, 3H), 3.52–3.66 (m, 2H), 3.73–3.81 (m, 1H), 3.85–3.93 (m, 1H), 6.68–6.73 (m, 1H), 6.80 (m, 1H), 6.97 (m, 2H), 7.03–7.23 (m, 15H), 7.29–7.41 (m, 9H), 7.82 (s, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.88 (d, $J = 7.3$ Hz, 2H), 7.91 (d, $J = 7.8$ Hz, 1H), 8.00 (s, 1H) ppm; ^{13}C NMR: $\delta = 26.90$ (CH_2, d×d, $J = 3.0$, 16.0 Hz), 29.12 (CH_2, d×d, $J = 2.5$, 13.0 Hz), 70.17–70.60 (CH_2, m), 124.89, 124.91, 125.54, 125.60, 126.01 (C), 126.23, 126.39, 126.40 (C), 126.41, 126.98, 127.20, 127.71, 127.87, 128.06, 128.15, 128.19, 128.25, 128.30, 128.36, 128.47, 128.57, 128.70, 129.40, 129.66, 129.67, 130.45, 130.50 (C), 130.88 (C), 130.92, 131.76 (d, $J = 3.5$ Hz), 131.90 (d, $J = 3.0$ Hz), 132.01 (d, $J = 3.4$ Hz), 132.15 (d, $J = 3.0$ Hz), 132.66 (d, $J = 5.5$ Hz), 132.90 (d, $J = 6.5$ Hz), 133.65 (C), 133.81 (C), 135.30 (C), 135.40 (C), 138.74 (C, d×d, $J = 5.5$, 7.5 Hz), 138.95 (C, d×d, $J = 5.5$, 7.5 Hz), 139.13 (C), 139.38 (C), 144.37 (C, d×d, $J = 8.4$, 26.3 Hz), 145.49 (C, d×d, $J = 8.4$, 26.3 Hz), 152.02 (C), 152.79 (C) ppm; ^{31}P NMR: $\delta = -27.13$ (d, $J = 149.2$ Hz), −28.93 (d, $J = 149.2$ Hz) ppm; MS (230°C): $m/z = 784.9$ (M^+, 100%).

Macrocyclic diphosphine (+)(*R*)-**7c** ($C_{66}H_{50}O_2P_2$)

Yield: 78%; white powder; m.p.: 160–166°C; $[\alpha]_D^{20} = +197$ ($c = 1.0$, CH_2Cl_2); ^{1}H NMR: $\delta = 2.08$–2.18 (m, 3H), 2.28–2.40 (m, 1H), 3.60–3.90 (m, 3H), 4.00–4.11 (m, 1H), 6.68–6.74 (m, 1H), 6.84–6.90 (m, 1H), 6.99–7.17 (m, 11H), 7.21–7.56 (m, 16H), 7.58–7.74 (m, 7H), 7.82–7.89 (m, 2H), 7.91 (s, 1H), 7.95 (d, $J = 8.3$ Hz, 1H), 8.02 (d, $J = 8.5$ Hz, 1H), 8.08 (s, 1H) ppm; ^{13}C NMR: $\delta = 26.85$ (CH_2, m), 29.85 (CH_2, d×d, $J = 4.6$, 16.1 Hz), 70.05 (CH_2, d, $J = 21.4$ Hz), 70.42 (CH_2, d, $J = 21.4$ Hz), 124.95, 125.00, 125.55, 125.67, 126.13 (C), 126.36, 126.41, 126.75 (C), 127.03, 127.07, 127.14, 127.20, 127.44, 127.53, 127.89, 127.94, 128.11, 128.20, 128.25, 128.33, 128.38, 128.56, 128.72, 128.81, 128.89, 129.89, 130.01, 130.11, 130.13, 130.30, 130.55 (C), 130.74, 130.97 (C), 131.60 (d, $J = 16.8$ Hz), 132.10 (d, $J = 18.3$ Hz), 132.65 (d, $J = 7.7$ Hz), 133.05 (d, $J = 5.3$ Hz), 133.71 (C), 133.83 (C), 134.89 (C), 135.07 (C), 137.90 (C), 138.20 (C, d×d, $J = 5.4$, 14.7 Hz), 138.46 (C), 139.40 (C, d×d, $J = 7.4$, 15.7 Hz), 139.83 (C), 139.91 (C), 140.70 (C), 145.05 (C, d×d, $J = 12.9$, 20.3 Hz), 145.50 (C, d×d, $J = 12.7$, 17.8 Hz), 150.25 (C), 151.85 (C), 152.88 (C) ppm; ^{31}P NMR: $\delta = -26.45$ (d, $J = 151.6$ Hz), −29.93 (d, $J = 151.6$ Hz) ppm; MS (260°C): $m/z = 936$ (M^+, 100%).

Macrocyclic diphosphine (+)(*R*)-**7d** ($C_{66}H_{46}O_4P_2$)

Yield: 83%; white powder; m.p.: 189–191°C; $[\alpha]_D^{20} = +283$ ($c = 1.10$, CH_2Cl_2); ^{1}H NMR: $\delta = 1.94$–2.02 (m, 1H), 2.06–2.16 (m, 3H), 3.54–3.65 (m, 2H), 3.77–3.85 (m, 1H), 3.91–3.99 (m, 1H), 6.24–6.29 (m, 1H), 6.51 (t, $J = 7.4$ Hz, 1H), 6.59–6.63 (m, 1H), 6.74 (t, $J = 7.2$ Hz, 1H), 6.82–6.90 (m, 4H), 7.04–7.15 (m, 5H), 7.27–7.48 (m, 15H), 7.55 (d, J = 8.5 Hz, 1H), 7.83 (m, 1H), 7.88 (d, $J = 8.0$ Hz, 1H), 7.92–8.03 (m, 5H), 8.08 (s, 1H), 8.30 (s, 1H) ppm; ^{13}C NMR: $\delta = 26.68$ (CH_2, d×d, $J = 3.7$, 16.8 Hz), 29.28 (CH_2, d×d, $J = 3.8$, 16.0 Hz), 70.57–71.12 ($2CH_2$, m), 112.00, 112.17, 119.57, 119.86, 120.53, 120.60, 122.53, 122.76, 122.79, 123.04, 123.62 (C), 123.87 (C), 124.39 (C), 124.44 (C), 124.94, 125.42 (C), 125.54 (C), 125.90, 126.02, 126.59, 126.64, 126.89, 127.10, 127.52, 127.61, 127.96, 128.02, 128.06, 128.11, 128.23, 128.26, 128.42, 128.90, 129.21, 129.23, 129.81 (C), 130.24 (C), 130.27 (C), 130.65 (C), 131.57, 131.76 (d, $J = 5.4$ Hz), 131.93 (d, $J = 6.1$ Hz), 132.17, 132.24, 134.20 (C), 134.37 (C), 138.60 (C, d×d, $J = 7.8$, 14.3 Hz), 138.83 (C, d×d, $J = 7.8$, 15.2 Hz), 144.14 (C, d×d, $J = 14.3$, 33.6 Hz), 144.75 (C, d×d, $J = 13.1$, 32.2 Hz), 152.72 (C), 153.55 (C), 153.72 (C), 153.92 (C), 156.16 (C), 156.30 (C) ppm; ^{31}P NMR: $\delta = -26.17$ (d, $J = 149.6$ Hz), −29.30 (d, $J = 149.6$ Hz) ppm; MS (260°C): $m/z = 964.3$ (M^+, 100%).

Macrocyclic diphosphine (+)(*R*)-**7e** ($C_{62}H_{46}O_2P_2$)

Yield: 76%; white powder; m.p.: 149–152°C; $[\alpha]_D^{20} = +190$ ($c = 1.0$, CH_2Cl_2); ^{1}H NMR: $\delta = 2.00$–2.16 (m, 3H), 2.30–2.38 (m, 1H), 3.58–3.72 (m, 2H), 3.74–3.82 (m, 1H), 4.02–4.10 (m, 1H), 6.48 (m, 1H), 6.82 (m, 7H), 6.99 (t, $J = 7.5$ Hz, 3H), 7.04–7.11 (m, 2H), 7.18 (d, $J = 8.5$ Hz, 2H), 7.25–7.31 (m, 2H), 7.34–7.45 (m, 5H), 7.56 (m, 3H), 7.69 (m, 1H), 7.77 (d×d, $J = 2.0$, 8.5 Hz, 2H), 7.86–7.94 (m, 4H), 7.97 (t, $J = 4.0$ Hz, 2H), 8.06 (br s, 1H), 8.09 (d×d, $J = 1.5$, 8.5 Hz, 1H), 8.14 (s, 1H), 8.38 (s, 1H) ppm; ^{13}C NMR: $\delta = 26.71$–27.02 (CH_2, m), 29.80 (CH_2, d×d, $J = 4.1$, 17.2 Hz), 70.16 (CH_2, d, $J = 21.0$ Hz), 70.67 (CH_2, d, $J = 21.0$ Hz), 124.96, 125.02, 125.59, 125.73, 125.78, 125.87, 126.07 (C), 126.08, 126.22, 126.43, 126.46, 126.52 (C), 127.31, 127.54, 127.73, 127.79, 127.87, 127.91, 127.97, 128.03, 128.08, 128.13, 128.14, 128.17, 128.28, 128.30, 128.33, 128.41, 128.52, 128.64, 130.58 (C), 130.71, 131.00 (C), 131.21, 131.32 (d, $J = 0.9$ Hz), 131.58 (d, $J = 0.9$ Hz), 131.90 (d, $J = 1.3$ Hz), 132.20 (d, $J = 1.4$ Hz), 132.39 (d, $J = 0.9$ Hz), 132.51 (d, $J = 0.9$ Hz), 132.57 (C), 132.87 (d, $J = 1.3$ Hz), 132.98 (d, $J = 1.0$ Hz), 133.43 (C), 133.67 (C), 133.83 (C), 133.93 (C), 135.29 (C), 135.44 (C), 136.61 (C), 137.29 (C), 137.97 (C, d×d, $J = 9.9$, 15.2 Hz), 139.12 (C, d×d, $J = 7.6$, 15.8 Hz), 145.05 (C, d×d, $J = 12.4$, 30.4 Hz), 145.48 (C, d×d, $J = 13.8$, 20.2 Hz), 150.33 (C), 152.08 (C). 153.00 (C) ppm; ^{31}P NMR: $\delta = -26.00$ (d, $J = 152.1$ Hz), -29.85 (d, $J = 152.1$ Hz) ppm; MS (280°C): $m/z = 884$ (M^+, 100%).

2,2′-Bis(2-diphenylphosphinoethoxy)-1,1′-binaphthyl (*R*)-**8**; ($C_{48}H_{40}O_2P_2$)

A 50 cm^3 *Schlenk* tube was charged with 40 mg of lithium strips, 20 ml of anhydrous, degassed *THF*, and chlorodiphenylphosphine (270 mm^3, 1.5 mmol). The mixture was stirred at room temperature for 1 h to give a deep red solution. The excess of lithium strips was removed with a spatula, and the resultant solution of diphenyllithium phosphide was added at 0°C to a solution of ditosylate (*R*)-**6a** (340 mg, 0.5 mmol) in 5 cm^3 of anhydrous *THF* over a period of 30 min. Stirring was continued for 5 h at room temperature. The solvent was distilled off, and the residue was partitioned between 100 cm^3 of CH_2Cl_2 and 60 cm^3 of saturated NaCl solution. The organic phase was separated and dried ($MgSO_4$). After removal of the solvent the crude mixture was subjected to column chromatography on silica gel (2×26 cm) with CH_2Cl_2/*PE* (35/65) to give 258 mg (24%) of (*R*)-**8** as a white powder.

M.p.: 47–50°C; $[\alpha]_D^{20} = +0.6$ ($c = 1.0$, CH_2Cl_2); ^{1}H NMR: $\delta = 2.11$ (p t, $J = 7.9$ Hz, 4H), 3.96–4.10 (m, 4H), 7.09 (br d, $J = 8.4$ Hz, 2H), 7.15–7.27 (m, 24H), 7.30 (ddd, $J = 1.0$, 6.4, 7.9 Hz, 2H), 7.83 (br d, $J = 8.4$ Hz, 2H), 7.87 (br d, $J = 8.8$ Hz, 2H) ppm; ^{13}C NMR: $\delta = 28.37$ (CH_2, d, $J = 13.7$ Hz), 67.48 (CH_2, d, $J = 28.9$ Hz), 116.34, 121.08 (C), 123.70, 125.49, 126.21, 127.86, 128.38 (d, $J = 6.9$ Hz), 128.39 (d, $J = 6.7$ Hz), 128.54, 128.59, 129.27, 129.49 (C), 132.51 (d, $J = 18.9$ Hz), 132.55 (d, $J = 19.3$ Hz), 134.08 (C), 137.82 (C, d, $J = 3.0$ Hz), 137.95 (C, d, $J = 3.7$ Hz), 153.98 (C) ppm; ^{31}P NMR: $\delta = -22.49$ (s) ppm; MS (160°C): $m/z = 710$ (M^+, 100%).

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