# Synthesis and Characterization of 4- and 4,4′-Phosphorylated 2,2′-Bis(diphenylphosphanyl)-1,1′-binaphthyls

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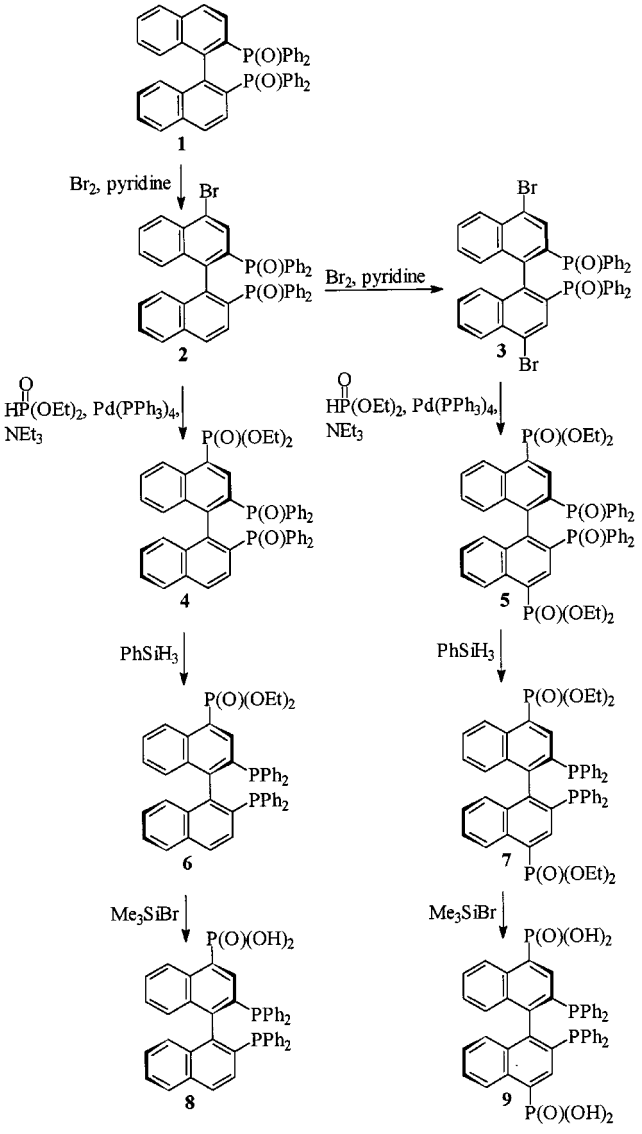
A convenient reaction sequence has been established to obtain selectively the mono- or bisphosphorylated BINAP derivatives **6**–**9**. The structure of the new compounds was confirmed by NMR spectroscopy. The sodium salts of the phosphonic acid derivatives **8** and **9** can be used in aqueous biphasic catalysis.

## Introduction

Catalytic hydroformylations of olefins in the homogeneous phase as well as in aqueous biphasic systems have become large-volume technical processes to produce aldehydes.[1−3] However, asymmetric hydroformylation, resulting in valuable chiral aldehydes as intermediates for fine chemicals, still requires further efforts for catalyst development. Numerous homogeneous catalysts have been investigated in this reaction but the majority of them showed only low or moderate selectivities. The best chiral homogeneous hydroformylation catalysts are formed with ligands containing phosphite groups, such as Takaya's BINAPHOS [(*R*)-2-(diphenylphosphanyl)-1,1′-binaphthalen-2′-yl-(*S*)-1,1′-binaphthalene-2,2′-diyl phosphite],[4−7] bulky diphosphite ligands[8,9] or a phosphane-phosphite developed by van Leeuwen.[10] Despite their exceptional catalytic properties these ligands suffer from instability against traces of water. Furthermore, their preparation and purification is complex and expensive. Thus, bisphosphanes which are stable against hydrolysis have attracted renewed attention. In contrast to previous results[11,12] recently published investigations[13] showed that rhodium bisphosphane catalysts can reach enantiomeric excesses (*ee*) of up to 76% in the asymmetric hydroformylation of styrene. Therefore, further attempts should be directed to the development of new, efficient chiral bisphosphanes.

During our investigations on hydroformylation in aqueous biphasic systems and over heterogenized complexes we succeeded in the functionalization of a series of tertiary aryl- and arylalkylphosphanes with phosphonate groups.[14−16] Phosphorylated alkyldiarylphosphanes showed an outstanding performance in the hydroformylation of higher terminal olefins[14] in aqueous biphasic systems, which offer several technological advantages,[2,3] especially simplified catalyst recycling. To expand the application field of phosphorylated ligands to asymmetric hydroformylation in biphasic systems, we developed new methods to introduce phosphonate groups to a well-known atropisomeric ligand — BINAP [2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl] — as described below.




Scheme 1. Synthesis of phosphorylated 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyls

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BINAP is accessible in its chiral *R* and *S* forms.[17] It is one of the best examined and most successful chiral chelating ligands and has gained industrial importance for homogeneous catalysis.[18,19] However, sulfonation of BINAP or similar atropisomeric bisphosphanes to obtain water-soluble ligands does not lead to the pure products, but to mixtures of different isomers.[20,27] Other methods to make BINAP water-soluble have been reported,[21,22] but to the best of our knowledge enantiopure water-soluble BINAP derivatives have not been used for catalytic hydroformylation as yet.

## Results and Discussion

Starting from (*R*)-BINAP oxide[17] **(1)** we developed a four-stage method for the functionalization of BINAP with phosphonic acid groups (Scheme 1).

Bromination of **1** in the presence of pyridine resulted in the monobrominated product **2** after the first run. The twofold repetition of the brominating procedure with crude **1** and fresh bromine gave the bisbrominated compound **3**. Pyridine was added to eliminate hydrobromic acid from the reaction mixture thus avoiding conditions which could cause racemization.[23] The introduction of phosphonate groups succeeded with modified palladium-catalysed reactions of **2** and **3** with diethylphosphite.[24] The reduction of the phosphorylated phosphane oxides **4** and **5** to the corresponding phosphanes was carried out with phenylsilane as reducing agent.[25] For this step it was necessary to optimize the reaction time because too short a time for reduction caused low conversion, while long times led to an undesired reduction of the phosphonate group. The bisphosphanes **6** and **7** were purified by column chromatography (**6**) or recrystallized (**7**). Final hydrolysis of the dialkyl phosphonate groups resulted quantitatively in the phosphonic acid-substituted BINAP derivatives **8** and **9**. The $^{31}P$ NMR spectrum of **8** in *S*-(−)-1-phenylethylamine showed the signals of only one pure diastereomeric salt at $\delta = -15.0$ ($J = 4.7$ Hz) and $\delta = -16.4$ ($J = 6.1$ Hz) (phosphane groups) as well as at $\delta = 6.4$ (phosphonium salt). Thus, racemization during the described reaction sequence can be ruled out.

### Structure Determination of the New Ligands

The position of the phosphonic ester group in the binaphthyl skeleton was determined by NMR spectroscopy. A comparison of the $^1H$ NMR spectra of the unsubstituted BINAP oxide **1** and the bisphosphorylated phosphane oxide **5**, as well as the interpretation of the $^1H$-COSY spectrum of **5** (Figure 1), allowed the structure determination of this compound. The monobrominated product **2** is an intermediate product in the bromination of **1** to **3**. Therefore the position of the phosphonic ester group in 4 must be the same as in **5**.

The $^1H$ NMR spectrum of 1 shows an ABCD pattern for the $H^A$, $H^B$, $H^C$ and $H^D$ protons in the annelated ring, as does the spectrum of **5**. Additionally, the ABCD coupling pattern was supported by simulation. As can be seen from Figure 1, four binaphthylic hydrogen nuclei ($H^A$, $H^B$, $H^C$ and $H^D$) of **5** exist, each one of them coupling with at least one neighbouring hydrogen nucleus. This implies that the

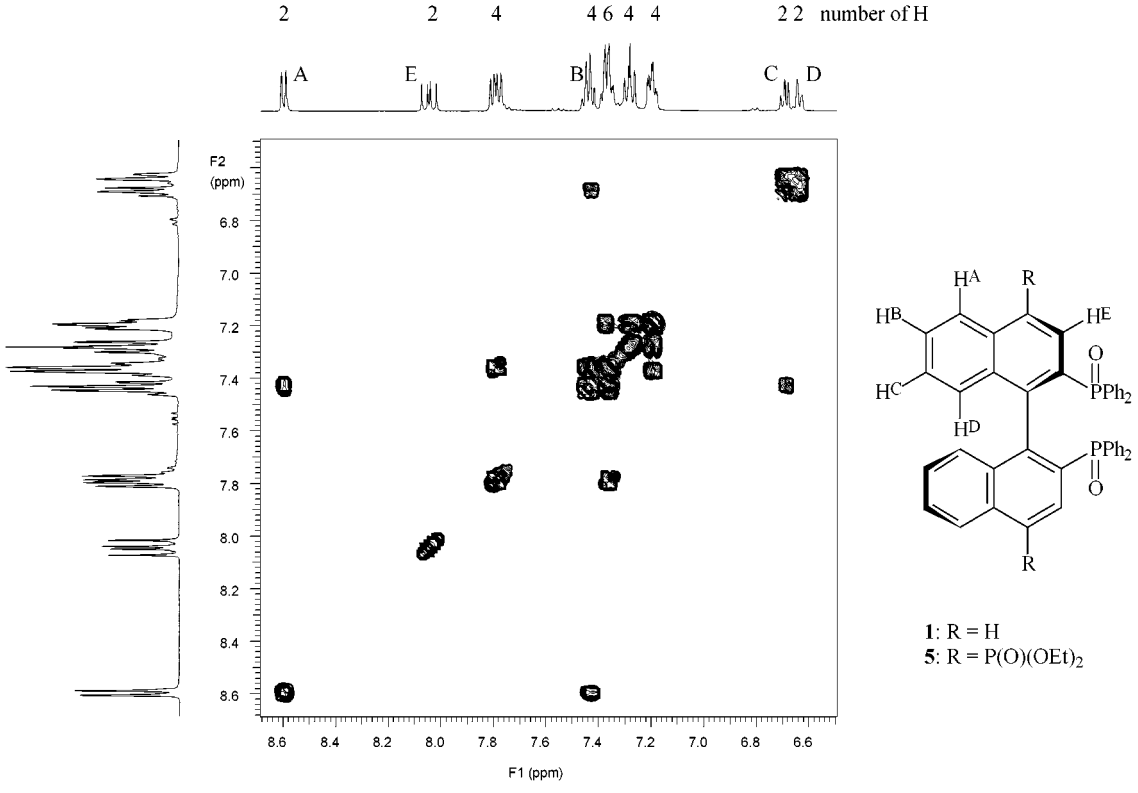


Figure 1. $^1H$ COSY spectrum of **5**

phosphorylation occurred either in the 3- or the 4-position. One proton ($H^E$) does not couple with any other hydrogen. $^1H$-$^{31}P$ coupling experiments showed that this "special" hydrogen nucleus couples with both phosphorus nuclei to a similar extent ($J$ = 16.6 and 11.7 Hz),[26] which means that $H^E$ must be located in the direct vicinity of both phosphorus substituents. This is only the case for a proton in the 3-position. Furthermore, $^3J_{PCCH}$ and $^4J_{PCCCH}$ for a proton in the 4-position should be very different in size, which is not the case.

From these findings we deduced the structure for the phosphorylated BINAP oxides described in Scheme 1. This is in agreement with the rules for electrophilic aromatic substitutions. Surprisingly, substitution did not take place either in the positions 6 or 7 of the binaphthyl nor in the phenyl rings.

## Conclusion

We have developed a convenient method to obtain selectively phosphorylated binaphthyl derivatives. Depending on the reaction conditions, one or two phosphonate groups can be introduced into binaphthyl structures. The solubility of the phosphonic acids **8** and **9** in water is moderate but the solubility of their sodium salts is excellent. So the new chiral BINAP ligands can be used both in biphasic catalysis and in heterogeneous catalysis with complexes anchored via the phosphonic acid groups. The catalytic properties of the new ligands will be published elsewhere next.

## Experimental Section

**General:** All operations were carried out excluding air and moisture under an atmosphere of argon. Solvents were dried with sodium wire (toluene), molecular sieves 4 Å (dichloromethane) or distilled in an argon stream with $LiAlH_4$ (ethers). Solvents were deoxygenated before use by repeated evacuation and argon purging. NMR spectra were recorded on a Varian UNITYPLUS 300 or 500 (300 and 500 MHz). Chemical shifts are given in ppm with respect to TMS ($^1H$, $^{13}C$) or $H_3PO_4$ ($^{31}P$), coupling constants are reported in Hz. Optical rotations were measured on a Perkin−Elmer 241 polarimeter. Mass spectra were obtained on an Autospec (Micromass). Elemental analyses were determined with an Optima 3000 XL (Perkin−Elmer) and an EA 1110 (CE Instruments). It was difficult to obtain reliable elemental analyses for the air-sensitive compounds **6**−**9**. As an alternative LSI-MS spectra were recorded. (*R*)-BINAP oxide **(1)** was prepared according to a literature method.[17]

**(*R*)-4-Bromo-2,2′-bis(diphenylphosphoryl)-1,1′-binaphthyl (2), (*R*)-4,4′-dibromo-2,2′-bis(diphenylphosphoryl)-1,1′-binaphthyl (3):** Compound **1** (15.06 g, 23 mmol) was dissolved in $CH_2Cl_2$ (340 mL). While the solution was stirred, $Br_2$ (11.03 g, 69 mmol) and pyridine (1.82 g, 23 mmol) were added. The stirring was continued at room temperature for 20 hours. Thereafter the organic phase was extracted with 1 M aqueous sodium hydrogen sulfite (320 mL), brine and saturated sodium hydrogen carbonate solution. Drying over $Na_2SO_4$ was followed by filtration. After evaporation of the solvent, the crude oily product which mainly consisted of the 4-bromo-substituted product **2** was used for its phosphorylation to **4**.

Yield: 16.83 g (consisting of 62 mol-% of **2**, 18 mol-% of **3** and 20 mol-% of **1**, determined by $^{31}P$ NMR spectroscopy). − $^{31}P$ NMR ($CH_2Cl_2$): δ = 26.8, 28.0.

To obtain the bisbrominated product **3**, the above described bromination procedure was repeated twice and the crude products of the preceding brominations, containing **2**, were used as starting materials. The dichloromethane solution of **3** was reduced in volume, and the crude oily product was dried in vacuo and used for the following phosphorylation to obtain **5**.

Yield: 18.43 g (consisting of 86 mol-% of **3** and 14 mol-% of **2**, determined by $^{31}P$ NMR spectrosocpy). − $^{31}P$ NMR ($CH_2Cl_2$): δ = 26.5.

**(*R*)-(+)-4-Diethoxyphosphoryl-2,2′-bis(diphenylphosphoryl)-1,1′-binaphthyl (4):** Crude **2** (7.34 g containing 6.2 mmol of **2**), diethyl phosphite (4.88 g, 40 mmol), tetrakis(triphenylphosphane)palladium (1.15 g, 1 mmol) and triethylamine (4.04 g, 40 mmol) were dissolved in absolute toluene (20 mL) and stirred for 22 hours at 90 °C. After cooling, the solution was diluted with $CH_2Cl_2$ (80 mL), extracted three times with $H_2O$ (30 mL) and dried with $Na_2SO_4$. The solvent was evaporated and the crude product chromatographed on a silica gel column (eluent: ethyl acetate/hexane/ethanol, 7:3:1) giving a colourless oil. Yield: 2.65 g (54%). − MS: (*m*/*z*) = 791 [$M^+$ + 1]. − $[\alpha]_D^{20}$ = +98.6 (DMSO, *c* = 1.0). − $^1H$ NMR ($CDCl_3$): δ = 1.24, 1.26 (2t, 6 H, $CH_3$), 4.07 (m, 4 H, $CH_2$), 6.64 (d, *J* = 8.5, 1 H), 6.74 (m, 3 H), 7.21 (m, 4 H), 7.30−7.45 (m, 15 H), 7.65−7.78 (m, 4 H) 7.82 (d, *J* = 7.9, 1 H), 7.88 (dd, *J* = 8.5, 2.4, 1 H), 8.04 (dd, *J* = 16.5, 11.6, 1 H), 8.59 (d, *J* = 8.8, 1 H, $CH_{naphthyl}$ + $CH_{phenyl}$). − $^{13}C$ NMR ($CDCl_3$): δ = 16.2, 16.3 ($CH_3$), 62.4 (d, *J* = 5.5), 62.6 (d, *J* = 5.9, $CH_2$), 126.0, 126.1, 126.5, 126.8, 127.3, 127.7, 127.8, 127.9, 127.94, 128.0, 128.1, 128.2, 128.26, 128.3, 128.4, 128.6, 131.0, 131.1, 131.4, 131.5, 131.9, 132.0, 132.1, 132.2, 132.4, 132.5, 132.53, 132.6, 141.9, 148.2 ($C_{naphthyl}$ + $C_{phenyl}$). − $^{31}P$ NMR ($CH_2Cl_2$): δ = 16.7 (d, *J* = 3.6, phosphonate), 27.3 (d, *J* = 3.6), 27.5 (phosphane oxide). − $C_{48}H_{41}O_5P_3$ (790.8): calcd. C 72.91, H 5.23, P 11.75; found C 72.66, H 5.48, P 11.46.

**(*R*)-(+)-4,4′-Bis(diethoxyphosphoryl)-2,2′-bis(diphenylphosphoryl)-1,1′-binaphthyl (5):** Crude **3** (2.00 g containing 2.1 mmol of **3**), diethyl phosphite (1.22 g, 10 mmol), tetrakis(triphenylphosphane)-palladium (0.58 g, 0.5 mmol) and triethylamine (1.11 g, 11 mmol) were dissolved in absolute toluene (5 mL) and stirred for 40 hours at 90 °C. Then the solution was treated in the same manner as described above for the solution of **4**. After chromatography **5** was isolated as a glassy mass. − Yield: 1.03 g (53%). − MS: (*m*/*z*) = 927 [$M^+$ + 1]. − $[\alpha]_D^{20}$ = +157.9 ($CHCl_3$, *c* = 1.0). − $^1H$ NMR ([$D_6$]DMSO): δ = 1.25, 1.35 (2m, 12 H, $CH_3$), 4.03−4.29 (3m, 8 H, $CH_2$), 6.63 (d, *J* = 8.2, 2 H, $H^D$), 6.69 (dt, *J* = 6.8, 1.0, 2 H, $H^C$), 7.18−7.39 (m, 14 H, $H_{phenyl}$), 7.44 (m, 4 H, $H^B$+$H_{phenyl}$), 7.79 (dd, *J* = 12.5, 4 H, $H_{phenyl}$, 7.3), 8.04 (dd, *J* = 16.5, 11.6, 2 H, $H^F$), 8.59 (d, *J* = 8.5, 2 H, $H^A$). − $^{13}C$ NMR ([D6]DMSO): δ = 15.9, 16.0 (2d, *J* = 3.1, $CH_3$), 62.1, 62.3 (2d, *J* = 5.8, $CH_2$), 124.4 (dd, *J* = 172.8, 11.3), 126.2, 126.3, 126.7, 126.9, 128.3, 128.4, 128.5, 128.5 (dd, *J* = 87.0, 14.3), 128.9, 130.5, 131.2, 131.3, 131.7, 131.8, 132.0, 132.2, 132.5 (m), 133.2 (m), 134.8, 146.6. − $^{31}P$ NMR ($CH_2Cl_2$): δ = 16.4 (d, *J* = 4.6, phosphonate), 27.1 (d, *J* = 4.6, phosphane oxide). − $C_{52}H_{50}O_8P_4$ (926.9): calcd. C 67.38, H 5.44, P 13.37; found C 67.70, H 5.56, P 13.59.

**(*R*)-(+)-4-Diethoxyphosphoryl-2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl (6):** Compound **4** (1.88 g, 2.38 mmol) and phenylsilane

(10 mL) were refluxed for 60 h. The silane was removed in vacuo and the foamy residue was chromatographed on silica gel (eluent: ethyl acetate/hexane, 1:2) giving a glassy oil. − Yield: 1.15 g (64%). − MS: (*m*/*z*) = 759 [$M^+$ + 1]. − $[\alpha]_D^{20}$ = +84.9 (DMSO, *c* = 1.0). − $^1$H NMR ($CDCl_3$): δ = 1.17, 1.18 (2t, 6 H, $CH_3$), 3.90−4.10 (m, 4 H, $CH_2$), 6.66 (d, *J* = 8.3, 1 H), 6.74−6.86 (m, 3 H), 6.92−7.12 (m, 20 H), 7.26 (t, *J* = 8.3, 1 H), 7.35 (m, 2 H), 7.74 (d, *J* = 7.8, 1 H), 7.82 (d, *J* = 8.8, 1 H), 7.90 (d, *J* = 16.6, 1 H), 8.54 (d, *J* = 8.8, 1 H, $CH_{naphthyl}$ + $CH_{phenyl}$). − $^{13}$C NMR ($CDCl_3$): δ = 15.2, 15.3 ($CH_3$), 61.3, 61.5 (2d, *J* = 6.1, $CH_2$), 123.9 (d, *J* = 184.3), 125.0, 125.2, 125.6, 126.1, 126.6, 126.7, 126.9, 127.0, 127.1, 127.2, 127.3, 127.4, 127.5, 127.6, 129.4, 131.5, 131.6, 131.7, 131.8, 131.9, 132.0, 132.2, 132.6 (m), 132.9, 133.0, 133.2, 133.3, 133.5, 133.6, 133.8 (m), 134.4 (d, *J* = 8.2), 135.6 (m), 136.2 (d, *J* = 6.1), 136.4 (d, *J* = 10.1), 136.8 (m), 138.2, 143.3 (m), 149.4 (m, $C_{naphthyl}$ + $C_{phenyl}$). − $^{31}$P NMR (acetone/hexane, 1:1): δ = 17.4 (phosphonate), −14.6 (dd, *J* = 29.0, 15.3, phosphane).

**(*R*)-(+)-4,4′-Bis(diethoxyphosphoryl)-2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl (7):** Compound **5** (0.93 g, 1 mmol) and phenylsilane (6 mL) were refluxed for 65 h. The mixture was cooled down and kept in the refrigerator overnight. Colourless crystals precipitated. These were filtered off, washed with *n*-hexane and dried in vacuo. − Yield: 0.50 g (56%). − m.p.: 221−224 °C. − MS: (*m*/*z*) = 895 [$M^+$ + 1]. − $[\alpha]_D^{20}$ = +102.6 ($CH_2Cl_2$, *c* = 1.0). − $^1$H NMR ($CDCl_3$): δ = 0.89, 0.93 (2t, 12 H, $CH_3$), 3.63−4.26 (3m, 8 H, $CH_2$) 6.68 (d, *J* = 8.5, 2 H), 6.82 (dt, *J* = 8.1, 1.3, 2 H), 7.37 (dt, *J* = 8.1, 1.3, 2 H), 7.90 (dd, *J* = 16.6, 2.1, 2 H), 8.55 (d, *J* = 8.5, 2 H, $CH_{naphthyl}$), 6.91−6.94 (m, 2 H), 7.01−7.07 (m, 4 H), 7.11−7.15 (m, 4 H, $CH_{phenyl}$). − $^{13}$C NMR ($CDCl_3$): δ = 16.2, 16.3 ($CH_3$), 62.4, 62.6 (2d, *J* = 6.0), 124.4 (d, *J* = 184.1), 126.4, 126.7 (d, *J* = 4.5), 127.9, 128.0, 128.1, 128.3 (t, *J* = 3.9), 128.4 (t, *J* = 2.5), 128.8, 128.9, 130.9, 132.5, 132.7 (m), 134.4 (m), 135.9 (m), 137.2 (m), 149.5 (m, $C_{naphthyl}$ + $C_{phenyl}$). − $^{31}$P NMR ($CH_2Cl_2$): δ = 17.3 (phosphonate), −15.0 (phosphane).

**(*R*)-(+)-2,2′-Bis(diphenylphosphanyl)-4-phosphono-1,1′-binaphthyl (8):** Compound **6** (1.00 g, 1.31 mmol) was stirred with bromotrimethylsilane (5 mL) at room temperature for 24 hours. Then volatile components were evaporated in vacuo and the residue was dissolved in a mixture of THF (5 mL) and water (2 mL), stirred for 1 h and concentrated in vacuo. A dry foam of **8** resulted. − Yield: 0.92 g (quantitative). − MS: (*m*/*z*) = 703 [$M^+$ + 1]. − $[\alpha]_D^{20}$ = +92.4 (DMSO, *c* = 1.0). − $^1$H NMR ($CD_3OD$): δ = 6.53 (d, *J* = 8.5, 1 H), 6.69 (d, *J* = 8.2, 1 H), 6.75 (dt, *J* = 7.9, 1.3, 1 H), 6.80 (t, *J* = 7.2, 1 H), 7.24 (dt, *J* = 8.2, 1.3, 1 H), 7.29 (dd, *J* = 8.8, 2.8, 1 H), 7.31 (dt, *J* = 8.0, 1.5, 1 H), 7.76 (d, *J* = 8.1, 1 H), 7.81 (d, *J* = 8.5, 1 H), 8.13 (dd, *J* = 16.2, 1.6, 1 H), 8.61 (d, *J* = 8.5, 1 H), 6.90−7.11 (m, 20 H). − $^{13}$C NMR ($CD_3OD$): δ = 128.0, 128.7 (d, *J* = 156.2), 128.9, 129.4, 130.0 (m), 130.2 (m), 130.3−130.5 (m), 130.9, 131.0, 132.7, 135.0 (m), 135.2 (m), 136.3, 136.5, 136.6, 136.7. − $^{31}$P NMR (DMSO): δ = 11.8 (phosphonic acid), −16.3 (dd, *J* = 64.1, 9.2, phosphane); [(*S*)-(−)-phenyl ethylamine]: δ =6.4 (phosphonic acid salt), −15.0 (d, *J* = 4.6), −16.4 (d, *J* = 6.1, phosphane).

**(*R*)-(+)-2,2′-Bis(diphenylphosphanyl)-4,4′-bisphosphono-1,1′-binaphthyl (9):** Compound **7** (2.00 g, 2.23 mmol) was subjected to the same procedure as described above for **6**. − Yield: 1.74 g (quantitative). − MS: (*m*/*z*) = 782 [$M^+$]. − $[\alpha]_D^{20}$ = +92.4 (DMSO, *c* = 1.0). − $^1$H NMR ($CD_3OD$): δ = 6.64 (d, *J* = 8.5, 2 H), 6.80 (dt, *J* = 8.1, 1.3, 2 H), 7.34 (dt, *J* = 8.1, 1.3, 2 H), 8.15 (d, *J* = 16.2, 2 H), 8.62 (d, *J* = 8.5, 2 H, $CH_{naphthyl}$), 6.96−6.99 (m, 8 H), 7.02−7.08 (m, 10 H), 7.11 (t, *J* = 7.2, 7.3, 2 H, $CH_{phenyl}$). − $^{13}$C NMR ($CD_3OD$): δ = 129.1 (d, *J* = 163.5), 129.6 (d, *J* = 4.6), 130.1, 130.3, 130.6 (m), 131.2, 135.1 (m), 135.8 (m), 136.5 (m), 138.9 (m), 139.6 (m), 151.5 (m). − $^{31}$P NMR: δ = 14.4 (phosphonic acid), −15.7 (phosphane).

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