Phosphonation of 1,1′-binaphthalene-2,2′-diol (BINOL): synthesis of (*R*)- and (*S*)-2,2′-dihydroxy-1,1′-binaphthalene-6,6′-diyldiphosphonic acid

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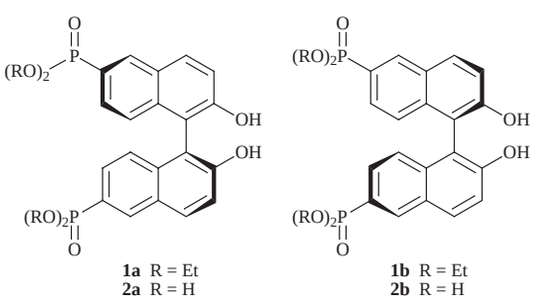
The synthesis of 6,6′-bis(diethoxyphosphoryl)-1,1′-binaphthalene-2,2′-diol 1 in racemic and chiral forms is described. This synthesis, which involves a palladium-assisted phosphonation step, allows study of the phosphonation of bromophenol as an electron-rich aryl bromide model. Furthermore, the synthesis of 2,2′-dihydroxy-1,1′-binaphthalene-6,6′-diyldiphosphonic acid 2, from its diester 1, leads to a key intermediate in the synthesis of hybrid organic-inorganic materials.

Introduction

Twenty years ago, Alberti *et al.*[1] described the synthesis of hybrid organic-inorganic materials which possess a layered structure such as in zirconium phosphate.[2] They were synthesised by the reaction between zirconyl chloride and phosphonic acids. Since this preliminary work, much attention has been devoted to new organic-inorganic layered phosphonates of tetravalent metals which may be porous.[3] Such materials can be used as stationary phases for chromatography[4] or as molecular sieves.[5] Another interesting field of development exists in using these materials as heterogeneous catalysts. There have been only a few reports where zirconium phosphate has been used as a catalyst.[6] The synthesis of hybrid materials which contain organometallic complexes is of great interest.[7] In order to obtain a more stable catalyst we looked to anchor the catalyst with covalent bonds to the zirconium backbone. We have recently described[8] a palladium triarylphosphine complex supported by covalent bonds to a zirconium phosphite sheet that is an efficient catalyst for Heck-type reactions. Furthermore, we observed that in the course of competitive reactions a shape selectivity occurs. Such a synthesis of a supported catalyst needs, as a first step, the preparation of functionalised phosphonic acids, which are then used for the synthesis of the supported catalyst according to Alberti's method.[1]

The first part of our research work concerning the synthesis of enantiopure binaphtholdiphosphonic acid **2** is described.



1a R = Et
2a R = H

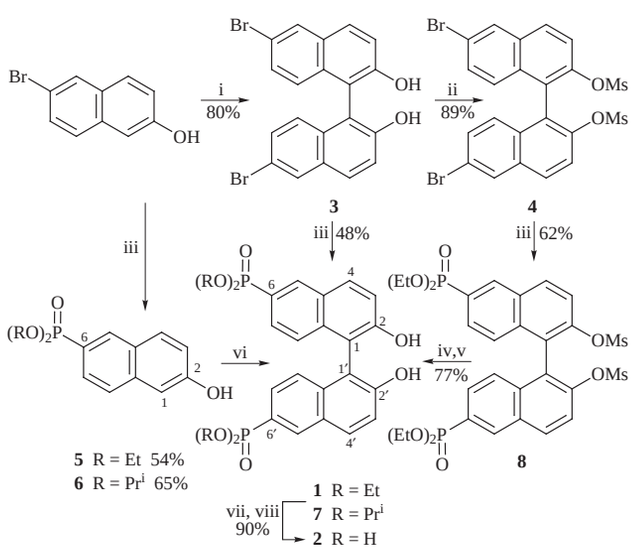
1b R = Et
2b R = H

The diphosphonic acid **2** will be used for the synthesis of organic-inorganic materials which will be tested both as a stationary chiral phase for HPLC and as supported ligands for metals such as Ti or Zr. These organometallic complexes are known as efficient catalysts in asymmetric synthesis under homogeneous conditions.[9]

Results and discussion

Several paths which could lead to diphosphonic acid **2** have been investigated. This substitution on the binaphthyl ring system was chosen for two reasons. First, the phosphonic acid functions, which will be the linker between the organic pendant and the inorganic backbone in the material, must be kept away from the phenol functions in order not to hinder these sites. Secondly, 6,6′-dibromo-1,1′-binaphthalene-2,2′-diol **3**, which is a key intermediate, is readily available.

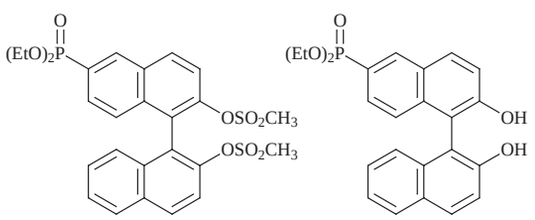
In the first instance work was carried out with racemic isomers and the best synthetic method was applied to the synthesis of enantiopure diacid **2**. 6,6′-Dibromo-1,1′-binaphthalene-2,2′-diol **3**, which is commercially available, can be also prepared in several ways. Bromination of 1,1′-binaphthalene-2,2′-diol[10] (binaphthol) depends on the purity of the binaphthol. Binaphthol, synthesised by oxidative coupling of 2-naphthol with a stoichiometric amount of iron(III) chloride,[11] needs several recrystallisations before the bromination step in order to remove all iron salts. Indeed, traces of iron(III) chloride, which catalyse the bromination reaction, induce many by-products and decrease the yield of the coupling reaction. An alternative method consists of an oxidative coupling of 6-bromo-2-naphthol (prepared in the laboratory[12] or available commercially) using a catalytic amount of chloro(hydroxy)-(tetramethylethylenediamine)copper(II) in the presence of air (Scheme 1). Such a coupling has previously been used for the



Scheme 1 *Reagents and conditions*: i, CuCl(OH)(TMEDA) air, CH_2Cl_2, 24 h; ii, MsCl, pyridine; iii, for ArBr (1 equiv.): 5% $PdCl_2(PPh_3)_2$, 5% $HSiEt_3$, 2.2 equiv. NEt_3, 1.1 equiv. $HP(O)(OR)_2$, toluene, reflux, 14–22 h; iv, EtMgBr; v, 1 M HCl; vi, CuCl(OH)(TMEDA), O_2, CH_2Cl_2, 4 days; vii, Me_3SiBr; viii, MeOH

synthesis of binaphthol,[13] but has never been employed for the synthesis of 6,6′-dibromo-1,1′-binaphthalene-2,2′-diol **3**. This reaction was carried out in good yield (86%) using 1% of catalyst, and can be carried out on a large scale.

Direct phosphonation of dibromobinaphthol **3** cannot be achieved by a photochemical process due to the presence of phenol functions.[14] Although many methods are available to synthesise arylphosphonates from aryl bromides,[15] palladium-assisted phosphonation, which is carried out under mild conditions, is an attractive method. Palladium(0) complexes are the catalytically active species and several palladium complexes can be used as precursor. Hirao *et al.*[16] used tetrakis(triphenylphosphine)palladium. In solution this complex is in equilibrium with the active form PdL_2. Another method uses a palladium(II) complex as the precursor. The main advantage is that such an air-stable complex is easier to handle. Dichlorobis(triphenylphosphine)palladium was used as precursor and was reduced *in situ* to palladium(0) complex under argon by triethylsilane. After purification, compound **1** was isolated in 48% yield. For this reaction the same amount of Pd^{II} complex and triethylsilane must be used and the reduction of the catalyst precursor must be complete before the addition of aryl bromide substrate. In the course of this reaction traces of phosphonate **10**, which result from a monophosphonation and a mono-



9 **10**

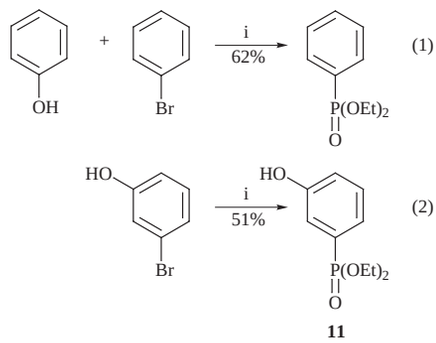
hydrodebromination of the dibromo substrate, were isolated. This observation is in agreement with recent work on the reduction of bromide compounds by triethylsilane in the presence of a catalytic amount of palladium dichloride.[17] Finally, the catalytic phosphonation step of dibromobinaphthol **3** was carried out in good yield compared with those obtained by Hirao[16] for the phosphonation of electron-rich aryl bromides such as 4-bromophenol or 4-bromoaniline, where yields never exceed 3%.

In order to enhance the catalytic phosphonation of dibromobinaphthol **3**, the catalytic phosphonation of 4-bromophenol as an electron-rich aryl model was studied. Bis(triphenylphosphine)palladium complex, prepared by the reduction of dichlorobis(triphenylphosphine)palladium with triethylsilane, was used as catalyst. Furthermore, an excess of triethylamine (2.2 equiv.) was used because phenol groups can react with it. Under these conditions, diethyl phenylphosphonate was obtained in a better yield than under Hirao's conditions, but the yield was still poor (18 instead of 3%).

In order to investigate the effect of the phenol group on the catalytic process, phosphonation of bromobenzene in the presence of phenol was carried out [reaction (1), Scheme 2]. The yield was 62%, instead of 95% without phenol. Catalytic phosphonation of 3-bromophenol was also carried out without protection of the phenol function in 51% yield [reaction (2)].

These two experiments indicate that this reaction is controlled mainly by electronic effects, but is also affected by the presence of a phenol function.

In view of these results it seems that the catalytic process could be slowed due to an electron-donating group which is able to stabilise the palladium complex resulting from the insertion of palladium into the C–Br bond. In order to reduce such hypothetical stabilisation, dichlorobis(tri-*o*-tolylphosphine)-palladium complex was used as catalyst precursor, which is a sterically more hindered catalyst, but an enhanced yield was not observed.



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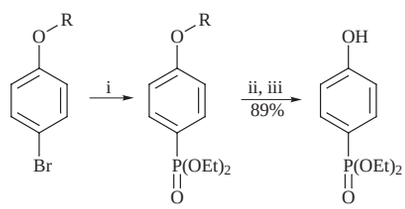
Scheme 2 *Reagents and conditions*: i, 5% $PdCl_2(PPh_3)_2$, 5% $HSiEt_3$, 2.2 equiv. NEt_3, $HP(O)(OEt)_2$, toluene, reflux, 22 h

The phenol function was therefore protected with an electron-withdrawing group in order to enhance the catalytic phosphonation step. The phenol function of 4-bromophenol was protected, according to literature methods, by acetate,[18] methanesulfonate[19] and toluene-*p*-sulfonate (tosylate).[20] Then the phosphonation step was carried out in good yield (Scheme 3). The best yield was obtained with mesylate (methanesulfon-



	R	Yield (%)
12	Ac	58
13	Ts	88
14	Ms	90

Scheme 3 *Reagents and conditions*: i, 5% $PdCl_2(PPh_3)_2$, 5% $HSiEt_3$, 2.2 equiv. NEt_3, $HP(O)(OEt)_2$, toluene, reflux, 22 h; ii, (R = Ms) EtMgBr; iii, 1 M HCl

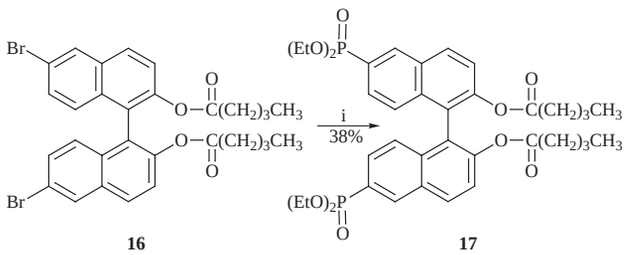
ate) as protecting group, which was removed by reaction with ethylmagnesium bromide in 89% yield. The removal of mesylate by a Grignard reagent, which have previously been used to deprotect an alcohol function,[21] is also efficient for phenols.

This simple work-up, which yields diethyl 4-hydroxyphenylphosphonate **15** in 18% yield from 4-bromophenol, allows use of a palladium-assisted phosphonation in the course of phosphonation of an electron-rich aryl bromide. This strategy was applied to the phosphonation of dibromobinaphthol **3** (Scheme 1). The dimesylate **4** was synthesised in 89% yield. The phosphonation step was achieved in 62% yield, but if this protection increased the yield of the phosphonation step, this increase was not sufficient to compensate for the loss of yield due to the extra step. If an excess of triethylsilane (30 instead of 5%) is employed to reduce formation of Pd^{II} complex in the course of the phosphonation, compound **9**, which results from a monophosphonation and a monohydrodebromination of the dibromo substrate **4**, is isolated in 24% yield. Compound **9**, which possesses a binaphthyl ring system with a dissymmetrical substitution, may be also useful for the synthesis of mixed organic-inorganic materials.

Another method to synthesise tetraalkyl 2,2′-dihydroxy-1,1′-binaphthalene-6,6′-diphosphonate **1** is an oxidative coupling of dialkyl 6-hydroxynaphthylphosphonate by a copper salt (Scheme 1). Phosphonates **5** and **6** were isolated by a palladium-assisted phosphonation of 6-bromo-2-naphthol in 54 and 65% yield, respectively. Oxidative coupling of the naphthylphosphonates was carried out with 5% chloro(hydroxy)(tetramethylethylenediamine)copper under oxygen. Despite the use of dioxygen instead of air, the yields were never higher than 25 (R = Et) and 60% (R = Pr^i). The mechanism of this oxidative

coupling involves the formation, as an intermediate, of a carbanion, in position 1, which is oxidised to a radical. The presence of electron-withdrawing groups on the naphthyl ring decreases its electron density and therefore makes the oxidation more difficult. Furthermore, phosphonate functions are able to complex transition metals[22] and the copper complex may therefore be rendered less reactive.

In order to describe the synthesis of all the intermediates which may be useful in obtaining enantiopure 2,2′-dihydroxy-1,1′-binaphthalene-6,6′-diphosphonates **1a** and **1b**, compound **17** (Scheme 4) was synthesised by a palladium-assisted phos-



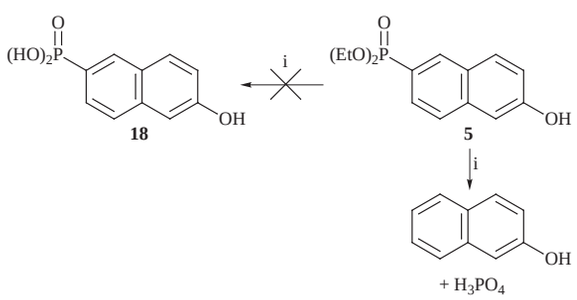
16 **17**

Scheme 4 *Reagents and conditions*: i, 5% $PdCl_2(PPh_3)_2$, 5% $HSiEt_3$, 2.5 equiv. NEt_3, 2.1 equiv. $HP(O)(OEt)_2$, toluene, reflux, 6 h

phonation of dipentanoate **16**. Compound **17** is an intermediate on which a kinetic enzymic resolution can be tested. This type of method was previously applied by Kazlauskas to resolve binaphthol.[23]

Synthesis of phosphonic acids

Two methods are commonly used in order to transform phosphonate into phosphonic acid. Hydrolysis with HCl,[24] HBr[25] or reaction between phosphonate and bromotrimethylsilane followed by alcoholysis. The former method was used to synthesise the 6-hydroxy-2-naphthylphosphonic acid **18**. Both acids lead to the unexpected formation of 2-naphthol and phosphoric acid (Scheme 5).



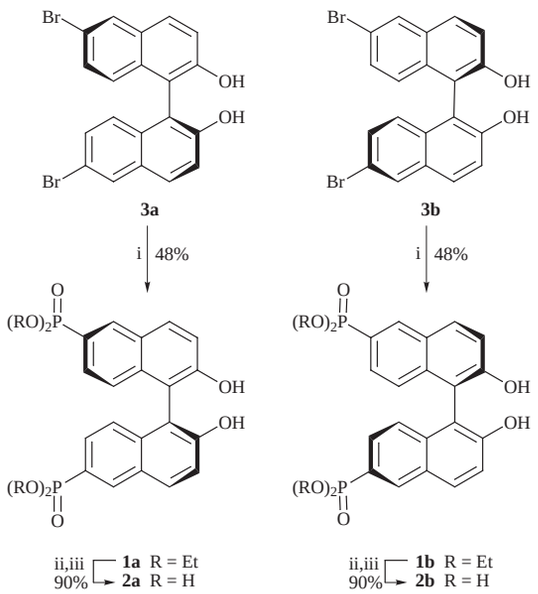
18 **5**

Scheme 5 *Reagents and conditions*: i, 11 M HCl or 48% HBr, reflux, 24 h

This unexpected reaction, which has no precedent, cannot be completely explained although the presence of the phenol function on the naphthyl group seems crucial. The second method was therefore used to synthesise phosphonic acid **2** (Scheme 1).

Synthesis of enantiopure 2,2′-dihydroxy-1,1′-binaphthalene-6,6′-diyldiphosphonic acid 2

Optically pure 6,6′-dibromo-1,1′-binaphthol **3** is easily available by chemical resolution with *N*-benzylcinchonidinium salt from the racemic mixture.[26] (*S*)- and (*R*)-6,6′-Dibromo-1,1′-binaphthol were isolated in 97.8 and 99.5% ee, respectively.[27] Afterwards these chiral substrates were used in the course of the palladium-assisted phosphonation. (*S*)- and (*R*)-Diethyl 2,2′-dihydroxy-1,1′-binaphthalene-6,6′-diphosphonate [(*S*)-**1a** and (*R*)-**1b**] were isolated with the same ee as the chiral substrate. These ees were determined by HPLC using the same column used by Combret and co-workers[28] (Scheme 6). No epimerisation was observed in the course of the phosphonation step which was carried out in refluxing toluene.



Scheme 6 *Reagents and conditions*: i, 5% $PdCl_2(PPh_3)_2$, 5% $HSiEt_3$, 4.4 equiv. NEt_3, 2.1 equiv. $HP(O)(OEt)_2$, toluene, reflux, 6 h; ii, Me_3SiBr; iii, MeOH

The transformation of diphosphonates (*S*)-**1a** and (*R*)-**1b** into phosphonic acids was carried out under mild conditions with bromotrimethylsilane followed by methanolysis. Chiral 2,2′-dihydroxy-1,1′-binaphthalene-6,6′-diphosphonic acids (*S*)-**2a** and (*R*)-**2b** were isolated in 90% yield.

Conclusions

Catalytic phosphonation of an electron-rich aryl bromide by a palladium complex, which allows the synthesis of 4-hydroxyphenylphosphonate in good yield, has been studied. Several routes to prepare racemic 2,2′-dihydroxy-1,1′-binaphthalene-6,6′-diphosphonic acid were attempted. Eventually the best path was found to be the direct palladium-assisted phosphonation of 6,6′-dibromo-1,1′-binaphthalene-2,2′-diol **3**. The resulting diphosphonate **1** was transformed into a diphosphonic acid **2** under mild conditions by bromotrimethylsilane. This synthesis was carried out with a chiral substrate, and chiral diphosphonic acids **2a** and **2b** were isolated and are now available for the synthesis of chiral organic-inorganic materials.

Experimental

General

^1H and ^{13}C NMR spectra were recorded on a Bruker AC 250 spectrometer. ^{31}P NMR spectra were recorded on a Bruker WP 80 SY instrument. [^2H]Chloroform and [$^2H_2$]water were used as NMR solvents and chemical shifts are reported as δ-values in parts per million relative to tetramethylsilane. *J*-Values are in Hz. IR spectra were determined with a Perkin-Elmer 16 PC FT-IR spectrometer. Optical rotations were measured on a Perkin-Elmer polarimeter 241; $[\alpha]_D$ values are given in units of 10^{-1} deg cm^2 g^{-1}. The products were purified by preparative column chromatography on silica gel (E. Merck). Chiral HPLC was performed using a cholic acid-bonded phase,[27] UV detector 254 nm, flow: 0.8 ml min^{-1}. In experiments requiring dry solvents, THF was distilled from sodium–benzophenone. Toluene was dried over sodium metal. 6-Bromo-2-naphthol,[12] dichlorobis(triphenylphosphine)palladium(II)[29] and chloro(hydroxy)(*N*,*N*,*N*′,*N*′-tetramethylethylene-1,2-diamine)copper[13] [CuCl(OH)(TMEDA)] were prepared by the reported methods. Light petroleum refers to the fraction with distillation range 35–60 °C.

Synthesis of aryl bromide

6,6′-Dibromo-1,1′-binaphthalene-2,2′-diol 3. CuCl(OH)-(TMEDA) (15 mg, 0.067 mmol) and 6-bromo-2-naphthol (1.5 g, 6.72 mmol) in dichloromethane (50 ml) were stirred for 24 h in an open conical flask. The organic layer was washed successively with 2 M HCl (2 × 20 ml) and brine (2 × 20 ml) before being dried over $MgSO_4$ and concentrated. The resulting oil was purified by chromatography with 60:40 light petroleum–diethyl ether as eluent or by crystallisation (toluene–cyclohexane), to afford compound **3** as a solid (1.19 g, 80%). Resolution of compound **3** was accomplished according to the literature,[25] mp 196 °C; $\delta_H(CDCl_3)$ 5.13 (s, O*H*, 2 H), 6.95 (d, $^3J_{HH}$ 8.9, H^8 and $H^{8'}$, 2 H), 7.37 (dd, $^3J_{HH}$ 8.9, $^4J_{HH}$ 1.9, H^7 and $H^{7'}$, 2 H), 7.38 (d, $^3J_{HH}$ 9.0, H^3 and $H^{3'}$, 2 H), 7.88 (d, $^3J_{HH}$ 9.0, H^4 and $H^{4'}$, 2 H) and 8.04 (d, $^4J_{HH}$ 1.9, H^5 and $H^{5'}$, 2 H); $\delta_C(CDCl_3)$ 110.77 (s, C^1 and $C^{1'}$), 118.12 (s, C^6 and $C^{6'}$), 119.09 (s, C^3 and $C^{3'}$), 125.99, 130.55, 130.67 and 130.79 (4 s, C^4, C^5, C^7, C^8 and $C^{4'}$, $C^{5'}$, $C^{7'}$, $C^{8'}$), 128.45 and 131.99 (2 s, C^9, C^{10} and $C^{9'}$, $C^{10'}$) and 153.08 (s, C^2 and $C^{2'}$); *m/z* 443–445 and 447 (M + 1, 0.3–0.5 and 0.3%), 442–444 and 446 ($M^{\cdot+}$, 0.8–1.7 and 0.8), 284 (1.0), 108 (12.8), 84 (32.3), 69 (46.5), 57 (63.9), 56 (61.6), 43 (100) and 41 (78.9).

6,6′-Dibromo-1,1′-binaphthalene-2,2′-diyl bis(methanesulfonate) 4. Mesyl chloride (0.6 ml, 7.7 mmol) was added dropwise to a cooled solution (5 °C) of DMAP (0.085 g, 0.7 mmol), 2,4,6-trimethylpyridine (collidine) (1.05 g, 8.8 mmol) and compound **3** (1.5 g, 3.4 mmol) in dichloromethane (30 ml). The solution was stirred for 5 h at rt. After the addition of dichloromethane (50 ml), triethylamine hydrobromide was removed by filtration. The filtrate was washed successively with 1 M sodium hydroxide (2 × 20 ml) and brine (2 × 20 ml). The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by recrystallisation (toluene–cyclohexane) and afforded compound **4** as a solid (1.78 g, 89%), R_f (Et_2O) 0.70; mp 234 °C (Found: S, 10.58. $C_{22}H_{16}Br_2O_6S_2$ requires S, 10.68%); $\delta_H(CDCl_3)$ 2.57 (s, SO_2CH_3, 6 H), 7.07 (d, $^3J_{HH}$ 9.2, H^8 and $H^{8'}$, 2 H), 7.46 (dd, $^3J_{HH}$ 9.2, $^4J_{HH}$ 1.8, H^7 and $H^{7'}$, 2 H), 7.76 (d, $^3J_{HH}$ 9.2, H^3 and $H^{3'}$, 2 H), 7.99 (d, $^3J_{HH}$ 9.2, H^4 and $H^{4'}$, 2 H) and 8.14 (d, $^4J_{HH}$ 1.8, H^5 and $H^{5'}$, 2 H); $\delta_C(CDCl_3)$ 38.91 (SO_2CH_3), 121.15 (s, C^6 and $C^{6'}$), 122.31 (s, C^3 and $C^{3'}$), 123.20 (s, C^1 and $C^{1'}$), 128.11 (s, C^8 and $C^{8'}$), 130.15 (s, C^4 and $C^{4'}$), 130.43 (s, C^5 and $C^{5'}$), 131.29 (s, C^7 and $C^{7'}$), 131.72 and 132.86 (s, C^9–C^{10} and $C^{9'}$–$C^{10'}$) and 145.61 (s, C^2 and $C^{2'}$); *m/z* 602–600 and 598 ($M^{\cdot+}$, 1.8–2.7 and 1.8%), 426 (4.7), 266 (49.7), 249 (51.5), 186 (27.3), 111 (43.0) and 43 (100.0); ν_{max}(KBr)/cm^{-1} 1166 (S=O), 1356 and 1368 (S=O), 3016 and 3026 (C–H).

6,6′-Dibromo-1,1′-binaphthalene-2,2′-diyl dipentanoate 16. To a solution of 6,6′-dibromo-1,1′-binaphthalene-2,2′-diol **3** (2.2 g, 4.95 mmol), triethylamine (1.25 g, 12.4 mmol), DMAP (0.14 g, 1.2 mmol) and diethyl ether (24 ml) at 0 °C under nitrogen, was added dropwise pentanoyl chloride (1.49 g, 12.4 mmol) over a period of 10 min. The solution was stirred at rt overnight. The organic layer was washed successively with aq. sodium carbonate and brine, dried over $MgSO_4$, and concentrated. The residue was recrystallised from diethyl ether to give compound **16** as a solid (2.5 g, 82%), R_f (CH_3CO_2Et–cyclohexane 20:80) 0.60; mp 125 °C; $\delta_H(CDCl_3)$ 0.66 (t, $^3J_{HH}$ 7.1, CH_3, 6 H), 0.81–0.96 (m, CH_2CH_3, 4 H), 1.00–1.16 (m, $CH_2CH_2CH_3$, 4 H), 2.07 (t, $OCOCH_2$, $^3J_{HH}$ 7.1, 4 H), 7.02 (d, $^3J_{HH}$ 9, H^8 and $H^{8'}$, 2 H), 7.34 (dd, $^3J_{HH}$ 9, $^4J_{HH}$ 2, H^7 and $H^{7'}$, 2 H), 7.39 (d, $^3J_{HH}$ 8.9, H^3 and $H^{3'}$, 2 H), 7.87 (d, $^3J_{HH}$ 8.9, H^4 and $H^{4'}$, 2 H) and 8.06 (d, $^4J_{HH}$ 2, H^5 and $H^{5'}$, 2 H); $\delta_C(CDCl_3)$ 13.53 (s, CH_3), 21.75 (s, CH_2CH_3), 26.53 (s, $CH_2CH_2CH_3$), 33.68 (s, $OCOCH_2$), 120.01 (s, C^1 and $C^{1'}$), 123.19 (s, C^3 and $C^{3'}$), 123.40 (s, C^6 and $C^{6'}$), 127.79, 128.71, 129.99 and 130.25 (4 s, C^4, C^5, C^7, C^8 and $C^{4'}$, $C^{5'}$, $C^{7'}$, $C^{8'}$), 131.75 and 132.62 (2 s, C^9, C^{10} and $C^{9'}$, $C^{10'}$), 147.12 (s, C^2 and $C^{2'}$) and 171.73 (s, *C*O); *m/z* 614, 612 and 610 ($M^{\cdot+}$, 0.61–0.90 and 0.61%), 530, 528 and 526 (14.41–27.58 and 14.76), 447, 446, 445, 444 and 443 (40.75, 44.19, 81.74, 61.15 and 64.23), 366, 364 and 362 (12.14, 25.78 and 18.36), 281 (18.78), 252 and 251 (19.16 and 20.96), 222 (29.55), 85 (38.48) and 57 (100); ν_{max}(KBr)/cm^{-1} 1170 (C–O), 1760 (C=O) and 2930–2954 (C–H).

Synthesis of aryl phosphonate

General procedure for the catalytic phosphonation. To dichlorobis(triphenylphosphine)palladium(II) (5%) under argon was added triethylsilane (5%) in toluene (1 ml) and the resulting mixture was stirred at 90 °C for 10 min to yield a black solution. Then diethyl hydrogen phosphite (1.1 equiv. by bromide function), aryl bromide (1.8 mmol), triethylamine (1.2 equiv. by bromide function and 1 equiv. by phenol function) and toluene (1 ml) were added. The mixture was heated at 90 °C for 22 h. After cooling of the mixture, 2 M hydrochloric acid was added (60 ml) and the solution was extracted with dichloromethane (3 × 20 ml). The organic layer was dried over $MgSO_4$ and the solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel (CH_2Cl_2–EtOH: 98:2) to give the phosphonate.

Diethyl 3-hydroxyphenylphosphonate 11. (0.21 g, 51%); R_f (CH_2Cl_2–EtOH 95:5) 0.35; $\delta_H(CDCl_3)$ 1.32 (t, $^3J_{HH}$ 7.1, OCH_2CH_3, 6 H), 4.10 (m, OCH_2CH_3, 4 H), 7.07 (~dd, $^3J_{HH}$ 7.9, $^5J_{HP}$ 2.5, H^4, 1 H), 7.15 (dd, $^3J_{HH} \approx 7.9$, $^3J_{HP}$ 12.5, H^6, 1 H), 7.32 (dt, $^3J_{HH} = {}^3J_{HH}$ 7.9, $^4J_{HP}$ 5.6, H^5, 1 H), 7.82 (~d, $^3J_{HP}$ 15.6, H^2, 1 H) and 9.68 (s, O*H*); $\delta_C(CDCl_3)$ 16.33 (d, $^3J_{CP}$ 6.3, OCH_2CH_3), 62.66 (d, $^2J_{CP}$ 5.4, OCH_2CH_3), 116.52 and 121.86 (2 d, $^2J_{CP}$ 12.6 and 8.1, C^2 and C^6), 120.50 (d, $^4J_{CP}$ 2.7, C^4), 127.80 (d, $^1J_{CP}$ 188.5, C^1), 130.17 (d, $^3J_{CP}$ 17.9, C^5) and 157.91 (d, $^3J_{CP}$ 19.7, C^3); $\delta_P(CDCl_3)$ 19.4; *m/z* 231 ($M^{\cdot+}$ + 1, 6.7%), 230 (M^+, 40.8), 202 (70.1), 174 (100.0), 158 (67.2) and 157 (36.3).

4-(Diethoxyphosphoryl)phenyl acetate 12. (0.28 g, 58%); R_f (CH_2Cl_2–MeOH 98:2) 0.10; $\delta_H(CDCl_3)$ 1.35 (t, $^3J_{HH}$ 7.1, OCH_2CH_3, 6 H), 2.31 (s, CH_3, 3 H), 4.1 (m, OCH_2CH_3, 4 H), 7.21 (dd, $^3J_{HH}$ 8.5, $^4J_{HP}$ 3.3, H^2 and H^6, 2 H) and 7.84 (dd, $^3J_{HH}$ 8.5, $^3J_{HP}$ 12.8, H^3 and H^5, 2 H); $\delta_C(CDCl_3)$ 16.13 (d, $^3J_{CP}$ 6.3, OCH_2CH_3), 20.79 (s, CH_3), 62.08 (d, $^2J_{CP}$ 5.4, OCH_2CH_3), 121.74 (d, $^3J_{CP}$ 16.2, C^2 and C^6), 125.73 (d, $^1J_{CP}$ 191.2, C^4), 133.14 (d, $^2J_{CP}$ 11.7, C^3 and C^5), 153.81 (d, $^4J_{CP}$ 3.6, C^1) and 168.40 (s, C=O); $\delta_P(CDCl_3)$ 17.7; *m/z* 273 ($M^{\cdot+}$ + 1, 2.1%), 272 ($M^{\cdot+}$, 10.7), 230 (30.2), 202 (58.5), 174 (82.1), 157 (23.2), 94 (31.1) and 43 (100.0); ν_{max}(KBr)/cm^{-1} 1020 and 1052 (P–O), 1250 (P=O) and 1770 (C=O).

4-(Diethoxyphosphoryl)phenyltoluene-*p*-sulfonate 13. (0.60 g, 88%); R_f (CH_2Cl_2–MeOH 98:2) 0.20 (Found: S, 8.14. $C_{17}H_{21}O_6PS$ requires S, 8.32%); $\delta_H(CDCl_3)$ 1.31 (t, $^3J_{HH}$ 7.0, OCH_2CH_3, 6 H), 2.46 (s, CH_3, 3 H), 4.1 (m, OCH_2CH_3, 4 H), 7.09 (dd, $^3J_{HH}$ 8.5, $^4J_{HP}$ 3.4, H^2 and H^6, 2 H), 7.33–7.71 (2 d, $^3J_{HH}$ 8.2, ArH, 4 H) and 7.75 (dd, $^3J_{HH}$ 8.5, $^3J_{HP}$ 12.8, H^3 and H^5, 2 H); $\delta_C(CDCl_3)$ 16.40 (d, $^3J_{CP}$ 6.4, OCH_2CH_3), 21.83 (s, CH_3), 62.43 (d, $^2J_{CP}$ 5.5, OCH_2CH_3), 122.58 (d, $^3J_{CP}$ 15.7, C^2 and C^6), 127.50 (d, $^1J_{CP}$ 190.6, C^4), 128.55, 130.02 and 132.20 (3 s, C^{Ar}), 133.59 (d, $^2J_{CP}$ 11.3, C^3 and C^5), 145.88 (s, $C^{1'}$) and 152.63 (d, $^4J_{CP}$ 3.8, C^1); $\delta_P(CDCl_3)$ 17.0; *m/z* 385 ($M^{\cdot+}$ + 1, 7.8%), 384 ($M^{\cdot+}$, 12.9), 229 (0.6), 201 (1.1), 174 (1.2), 155 (16.9), 91 (100.0), 65 (74.4) and 64 (14.1); ν_{max}(KBr)/cm^{-1} 1018.0 and 1050.0 (P–O), 1158–1180 and 1376 (S=O) and 1252.0 (P=O).

4-(Diethoxyphosphoryl)phenyl methanesulfonate 14. (0.50 g, 90%); R_f (CH_2Cl_2–MeOH 98:2) 0.20 (Found: S, 10.21. $C_{11}H_{17}O_6PS$ requires S, 10.38%); $\delta_H(CDCl_3)$ 1.34 (d, $^3J_{HH}$ 7.1, CH_3CH_2O, 6 H), 3.20 (s, CH_3SO_2, 3 H), 4.13 (m, CH_3CH_2O, 4 H), 7.40 (dd, $^3J_{HH}$ 8.5, $^4J_{HP}$ 3.4, H^2 and H^6) and 7.90 (dd, $^3J_{HH}$ 8.5, $^3J_{HP}$ 12.8, H^3 and H^5); $\delta_C(CDCl_3)$ 16.40 (d, $^3J_{CP}$ 6.3, CH_3CH_2O), 37.92 (CH_3SO_2), 62.50 (d, $^2J_{CP}$ 5.5, CH_3CH_2O), 122.21 (d, $^3J_{CP}$ 16.2, C^2 and C^6), 128.00 (d, $^1J_{CP}$ 190.2, C^4), 134.00 (d, $^2J_{CP}$ 10.8, C^3 and C^5) and 152.11 (d, $^4J_{CP}$ 3.6, C^1); $\delta_P(CDCl_3)$ 16.8.

Diethyl 4-hydroxyphenylphosphonate 15. (*a*) *By catalytic process from* 4-*bromophenol.*—After the standard work-up compound **15** was isolated as an oil (0.07 g, 18%).

(*b*) *From* 4-(*diethoxyphosphoryl*)*phenyl methanesulfonate*

14.—Ethylmagnesium bromide (3.67 mmol) [from ethyl bromide (0.4 g, 3.67 mmol) and magnesium (0.18 g) in THF (5 ml)] was added, with constant stirring under nitrogen, to a solution of 4-(diethoxyphosphoryl)phenyl methanesulfonate **14** (0.3 g, 0.97 mmol) in THF (3 ml). The solution was refluxed for 6 h, cooled, and hydrolysed with 2 M hydrochloric acid (20 ml). The solution was extracted with dichloromethane (3 × 20 ml). The combined organic layers were washed with water (2 × 15 ml), dried over $MgSO_4$, and concentrated. The residue was purified by Kugelrohr distillation (180 °C; 2×10^{-2} mbar) to afford compound **15** as an oil (0.2 g, 89%), R_f (CH_2Cl_2–EtOH 98:2) 0.20; $\delta_H(CDCl_3)$ 1.31 (t, $^3J_{HH}$ 7.1, OCH_2CH_3, 6 H), 4.08 (dq, $^3J_{HH}$ 7.1, $^3J_{HP}$ 14.5, OCH_2CH_3, 4 H), 7.00 (dd, $^3J_{HH}$ 8.5, $^4J_{HP}$ 3.7, H^3 and H^5, 2 H), 7.63 (dd, $^3J_{HH}$ 8.5, $^3J_{HP}$ 12.1, H^2 and H^6, 2 H) and 9.85 (s, O*H*, 1 H); $\delta_C(CDCl_3)$ 16.34 (d, $^3J_{CP}$ 6.8, OCH_2CH_3), 62.44 (d, $^2J_{CP}$ 5.4, OCH_2CH_3), 116.13 (d, $^3J_{CP}$ 16.5, C^3 and C^5), 116.35 (d, $^1J_{CP}$ 116.3, C^1), 133.86 (d, $^2J_{CP}$ 11.7, C^2 and C^6) and 161.91 (d, $^4J_{CP}$ 3.5, C^4); $\delta_P(CDCl_3)$ 20.9; *m/z* 231 ($M^{\bullet+}$ + 1, 4.9%), 230 ($M^{\bullet+}$, 22.5), 202 (37.0), 174 (100.0), 158 (30.8) and 157 (28.2); ν_{max}(KBr)/cm^{-1} 838 (γ C–H), 1024 and 1050 (P–O), 1212 (P=O) and 3124 (OH).

Diethyl 6-hydroxy-2-naphthylphosphonate 5. To dichlorobis(triphenylphosphine)palladium(II) (63 mg, 0.09 mmol) under argon was added triethylsilane (0.09 mmol) in toluene (1 ml) and the resulting mixture was stirred at 90 °C for 10 min to yield a black solution. Diethyl hydrogen phosphite (0.27 g, 2.0 mmol), 6-bromo-2-naphthol (0.4 g, 1.8 mmol), triethylamine (0.37 g, 3.7 mmol) and toluene (3 ml) were added. The mixture was heated at 90 °C for 22 h. After cooling of the mixture, 2 M hydrochloric acid was added (60 ml) and the solution was extracted with dichloromethane (3 × 20 ml). The organic layer was dried over $MgSO_4$ and the solvent was removed *in vacuo*. The residue (450 mg) was purified by column chromatography on silica gel (95:5 dichloromethane–ethanol as eluent) to give compound **5** (0.27 g, 54%), R_f (CH_2Cl_2–EtOH 95:5) 0.15; $\delta_H(CDCl_3)$ 1.34 (t, $^3J_{HH}$ 7.1, OCH_2CH_3, 6 H), 4.1 (m, OCH_2CH_3, 4 H), 7.25–7.30 (m, H^5 and H^7, 2 H), 7.63–7.66 (m, H^3 and H^4, 2 H), 7.76 (d, $^3J_{HH}$ 9.5, H^8, 1 H), 8.30 (~d, $^3J_{HP}$ 15.6, H^1, 1 H) and 9.22 (s, O*H*, 1 H); $\delta_C(CDCl_3)$ 16.43 (d, $^3J_{CP}$ 6.3, OCH_2CH_3), 62.63 (d, $^2J_{CP}$ 5.4, OCH_2CH_3), 109.94 and 119.94 (2 s, C^5 and C^7), 120.68 (d, $^1J_{CP}$ 192.0, C^2), 126.02 (d, $^3J_{CP}$ 14.4, C^4), 126.59 and 134.11 (2 d, $^2J_{CP}$ 9.9 and 10.8, C^1 and C^3), 127.32 (d, $^3J_{CP}$ 17.1, C^9), 130.75 (s, C^8), 137.18 (d, $^4J_{CP}$ 2.7, C^{10}) and 157.62 (s, C^6); $\delta_P(CDCl_3)$ 20.6; *m/z* 281 ($M^{\bullet+}$ + 1, 17.4%), 280 ($M^{\bullet+}$, 30.4), 252 (33.7), 224 (100), 208 (224 − O, 33.7), 206 (78.3), 144 (82.6), 131 (66.3), 115 (94.6) and 77 (51.1); ν_{max}(KBr)/cm^{-1} 1024 and 1052 (P–O) and 1248 (P=O).

Diisopropyl 6-hydroxy-2-naphthylphosphonate 6. To dichlorobis(triphenylphosphine)palladium(II) (158 mg, 0.22 mmol) under argon was added triethylsilane (0.22 mmol) in toluene (1 ml) and the resulting mixture was stirred at 90 °C for 10 min to yield a black solution. Diisopropyl hydrogen phosphite (0.82 g, 4.9 mmol), 6-bromo-2-naphthol (1.0 g, 4.5 mmol), triethylamine (0.95 g, 9.4 mmol) and toluene (3 ml) were added. The mixture was heated at 90 °C for 22 h. After cooling of the mixture, 2 M hydrochloric acid was added (60 ml) and the solution was extracted with dichloromethane (3 × 20 ml). The organic layer was dried over $MgSO_4$ and the solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel (97:3 dichloromethane–ethanol as eluent) to give compound **6** (0.90 g, 65%), R_f (CH_2Cl_2–EtOH 95:5) 0.20; mp 195 °C; $\delta_H(CDCl_3)$ 1.24 and 1.40 [2 d, $^3J_{HH}$ 6.1, $OCH(CH_3)_2$, 12 H], 4.73 [dseptet, $^3J_{HP}$ 7.9, $^3J_{HH}$ 6.1, $OCH(CH_3)_2$, 2 H], 7.24–7.28 (m, H^5 and H^7, 2 H), 7.64–7.68 (m, H^3 and H^4, 2 H), 7.75 (d, $^3J_{HH}$ 9.5, H^8, 1 H), 8.22 (~d, $^3J_{HP}$ 15.6, H^1, 1 H) and 8.71 (s, O*H*, 1 H); $\delta_C(CDCl_3)$ 23.95 and 24.17 [2 d, $^3J_{CP}$ 3.6 and 5.4, $OCH(CH_3)_2$], 71.35 [d, $^2J_{CP}$ 5.4, $OCH(CH_3)_2$], 109.60 and 119.79 (2 s, C^5 and C^7), 122.42 (d, $^1J_{CP}$ 193.0, C^2), 126.79 and 133.93 (2 d, $^2J_{CP}$ 9.9 and 10.8, C^1 and C^3), 126.82 (d, $^3J_{CP}$ 14.4, C^4), 127.32 (d, $^3J_{CP}$ 17.1, C^9), 130.74 (s, C^8), 137.03 (d, $^4J_{CP}$ 2.7, C^{10}) and 157.47 (s, C^6); $\delta_P(CDCl_3)$ 18.1; *m/z* 309 ($M^{\bullet+}$ + 1, 2.2%), 308 ($M^{\bullet+}$, 14.9), 266 (11.0), 224 (74.6), 206 (34.5), 115 (31.2), 69 (69.2) and 43 (100); ν_{max}(KBr)/cm^{-1} 982 and 1024 (P–O) and 1234 (P=O).

6,6′-Bis(diethoxyphosphoryl)-1,1′-binaphthalene-2,2′-diyl bis(methanesulfonate) 8. To dichlorobis(triphenylphosphine)-palladium(II) (17 mg, 0.02 mmol) under argon was added triethylsilane (0.02 mmol) in toluene (1 ml) and the resulting mixture was stirred at 90 °C for 10 min to yield a black solution. Diethyl hydrogen phosphite (0.17 g, 1.2 mmol), compound **4** (0.30 g, 0.5 mmol), triethylamine (0.14 g, 1.4 mmol) and toluene (2 ml) were added. The mixture was heated at 90 °C for 14 h. After cooling of the mixture, 2 M hydrochloric acid was added (50 ml) and the solution was extracted with dichloromethane (3 × 20 ml). The organic layer was dried over $MgSO_4$ and the solvent was removed *in vacuo*. The residue (510 mg) was purified by column chromatography on silica gel (95:5 dichloromethane–ethanol as eluent) to give compound **8** (0.22 g, 62%) and traces of the phosphonate **9**, R_f (CH_2Cl_2–EtOH 95:5) 0.50; $\delta_H(CDCl_3)$ 1.35 (t, $^3J_{HH}$ 7.0, OCH_2CH_3, 12 H), 2.62 (s, SO_2CH_3, 6 H), 4.18 (m, OCH_2CH_3, 8 H), 7.26 (dd, $^3J_{HH}$ 8.5, $^4J_{HP}$ 3.7, H^8 and $H^{8'}$, 2 H), 7.65 (ddd, $^3J_{HH}$ 8.5, $^3J_{HP}$ 10.7, $^4J_{HH}$ 1.2, H^7 and $H^{7'}$, 2 H), 7.85 (d, $^3J_{HH}$ 9.2, H^3 and $H^{3'}$, 2 H), 8.19 (d, $^3J_{HH}$ 9.2, H^4 and $H^{4'}$, 2 H) and 8.55 (dd, $^3J_{HP}$ 15.3, $^4J_{HH}$ 1.2, H^5 and $H^{5'}$, 2 H); $\delta_C(CDCl_3)$ 16.44 (d, $^3J_{CP}$ 6.3, OCH_2CH_3), 38.93 (s, SO_2CH_3), 62.52 (d, $^2J_{CP}$ 5.4, OCH_2CH_3), 121.97 (s, C^3 and $C^{3'}$), 124.10 (d, $^1J_{CP}$ 163.4, C^6 and $C^{6'}$), 126.71 (d, $^3J_{CP}$ 14.4, C^8 and $C^{8'}$), 128.43 (s, C^1 and $C^{1'}$), 128.38 and 134.12 (2 d, $^2J_{CP}$ 9.9, C^5–C^7 and $C^{5'}$–$C^{7'}$), 130.72 (d, $^3J_{CP}$ 17.0, C^{10} and $C^{10'}$), 132.18 (s, C^4 and $C^{4'}$), 134.90 (d, $^4J_{CP}$ 2.7, C^9 and $C^{9'}$), 147.12 (s, C^2 and $C^{2'}$); $\delta_P(CDCl_3)$ 17.6; *m/z* 716 ($M^{\bullet+}$ + 2, 0.6%), 715 ($M^{\bullet+}$ + H, 1.5), 266 (6.2), 249 (5.0), 109 (61.9), 97 (45.0), 79 (90.5) and 44 (100).

6-Diethoxyphosphoryl-1,1′-binaphthalene-2,2′-diyl bis(methanesulfonate) 9. The same procedure was followed except that 30% of triethylsilane instead of 5% was used. After purification by chromatography (95:5 dichloromethane–ethanol as eluent), phosphonate **9** was isolated in 24% yield, R_f (CH_2Cl_2–EtOH 95:5) 0.75 (Found: S, 11.22. $C_{26}H_{27}O_9PS_2$ requires S, 11.07%); $\delta_H(CDCl_3)$ 1.34 (t, $^3J_{HH}$ 7.0, OCH_2CH_3, 6 H), 2.49 and 2.57 (2 s, SO_2CH_3, 6 H), 4.16 (m, OCH_2CH_3, 4 H), 7.20 (~dd, $^3J_{HH}$ 8.2, $^4J_{HH} \approx 0.9$, $H^{8'}$, 1 H), 7.33 (dd, $^3J_{HH}$ 8.5, $^4J_{HP}$ 3.7, H^8, 1 H), 7.39 and 7.63 (2 ddd, $^3J_{HH}$ 8.2, $^3J_{HH}$ 7.2, $^4J_{HH} \approx 0.9$, $H^{6'}$ and $H^{7'}$, 2 H), 7.63 (ddd, $^3J_{HH}$ 8.5, $^3J_{HP}$ 10.9, $^4J_{HH}$ 1.2, H^7, 1 H), 7.73 and 7.83 (2 d, $^3J_{HH}$ 9.2, H^3 and $H^{3'}$, 2 H), 7.99 (dd, $^3J_{HH}$ 8.2, $^4J_{HH} \approx 0.9$, $H^{5'}$, 1 H), 8.09 and 8.17 (2 d, $^3J_{HH}$ 9.2, H^4 and $H^{4'}$, 2 H) and 8.55 (dd, $^3J_{HP}$ 15.6, $^4J_{HH} \approx 1.2$, H^5, 1 H); $\delta_C(CDCl_3)$ 16.48 (d, $^3J_{CP}$ 7.2, OCH_2CH_3), 38.80 and 38.87 (2 s, SO_2CH_3), 62.52 (d, $^2J_{CP}$ 5.4, OCH_2CH_3), 121.04 and 122.22 (2 s, C^3 and $C^{3'}$), 123.52 and 128.33 (2 s, C^1 and $C^{1'}$), 123.93 (d, $^1J_{CP}$ 172.3, C^6), 126.27, 126.82, 127.92, 128.49 and 131.23 (5 s, $C^{4'}$, $C^{5'}$, $C^{6'}$, $C^{7'}$ and $C^{8'}$), 127.01 (d, $^3J_{CP}$ 13.5, C^8), 128.25 and 134.10 (d, $^2J_{CP}$ 9.9, C^7 and C^5), 130.76 (d, $^3J_{CP}$ 17.0, C^{10}), 131.87 (s, C^4), 133.13 and 131.81 (2 s, $C^{9'}$ and $C^{10'}$), 135.10 (d, $^4J_{CP}$ 2.7, C^9) and 145.56 and 147.20 (2 s, C^2 and $C^{2'}$); $\delta_P(CDCl_3)$ 17.6; *m/z* 579 ($M^{\bullet+}$ + 1, 0.6%), 578 ($M^{\bullet+}$, 1.5), 404 (0.9), 357 (1.9), 279 (13.2), 278 (54.0), 277 (100.0), 201 (29.2), 199 (34.6), 152 (27.5) and 77 (91.7); ν_{max}(KBr)/cm^{-1} 1048 (P–O), 1166 (S=O), 1242 (P=O), 1360 and 1372 (S=O), 2936 and 2986 (C–H).

Diethyl 2,2′-dihydroxy-1,1′-binaphthalene-6,6′-diphosphonate 1. (*a*) *By catalytic process from* 6,6′-*dibromo*-1,1′-*binaphthalene*-2,2′-*diol* **3**.—To dichlorobis(triphenylphosphine)palladium(II) (79 mg, 0.11 mmol) under argon was added triethylsilane (0.11 mmol) in toluene (1 ml) and the resulting mixture was stirred at 90 °C for 10 min to yield a black solution. Diethyl hydrogen phosphite (0.68 g, 4.9 mmol), compound **3** (1.00 g, 2.2 mmol), triethylamine (0.91 g, 9.0 mmol) and toluene (4 ml) were added. The mixture was heated at 90 °C for 14 h. After cooling of the mixture, 2 M hydrochloric acid was added (50 ml) and the solu-

tion was extracted with dichloromethane (3 × 20 ml). The organic layer was dried over $MgSO_4$ and the solvent was removed *in vacuo*. The residue (1.04 g) was purified by column chromatography on silica gel (95:5 dichloromethane–ethanol as eluent) to give compound **1** (0.60 g, 48%) and traces of phosphonate **10**. Diphosphonates **1a** and **1b** were isolated by phosphonation of both enantiomers **3a** and **3b**.

(*b*) *From* 6,6′-*bis*(*diethoxyphosphoryl*)-1,1′-*binaphthalene*-2,2′-*diyl bis*(*methanesulfonate*) **8**.—Ethylmagnesium bromide (1.4 mmol) [from ethyl bromide (0.15 g, 1.4 mmol) and magnesium (41 mg) in THF (3 ml)] was added, with constant stirring under nitrogen, to a solution of 6,6′-bis(diethoxyphosphoryl)-1,1′-binaphthalene-2,2′-diyl bis(methanesulfonate) **8** (100 mg, 0.14 mmol) in THF (2 ml). The resulting solution was stirred at reflux for 15 h, cooled and hydrolysed with 2 M hydrochloric acid (10 ml). The solution was extracted with dichloromethane (3 × 15 ml). The combined organic layers were washed with water (2 × 15 ml), dried over $MgSO_4$ and concentrated. Chromatography of the residue with 98:2 dichloromethane–ethanol as eluent afforded compound **1** (0.06 g, 77%).

(*c*) *By coupling of diethyl* 6-*hydroxy*-2-*naphthylphosphonate* **5**.—To a solution of CuCl(OH)(TMEDA) (3 mg, 0.013 mmol) in dichloromethane, under O_2, was added diethyl 6-hydroxy-2-naphthylphosphonate **5** (184 mg, 0.66 mmol). The resulting solution was stirred for 24 h. After a second addition of CuCl(OH)(TMEDA) (3 mg, 0.013 mmol), stirring was continued for 72 h. The solvent was removed and the residue was purified by column chromatography on silica gel (98:2 dichloromethane–ethanol as eluent) to give phosphonate **1** (0.09 g, 25%), R_f (CH_2Cl_2–EtOH 95:5) 0.10; mp 150 °C; $\delta_H(CDCl_3)$ 1.29 (dt, $^3J_{HH}$ 7.0, $^4J_{HP}$ 3.0, OCH_2CH_3, 12 H), 4.1 (m, OCH_2CH_3, 8 H), 7.14 (dd, $^3J_{HH}$ 8.5, $^4J_{HP}$ 4.0, H^8 and $H^{8'}$, 2 H), 7.45 (ddd, $^3J_{HH}$ 8.5, $^3J_{HP} \approx 12$, $^4J_{HH}$ 1.5, H^7 and $H^{7'}$, 2 H), 7.48 (d, $^3J_{HH}$ 8.8, H^3 and $H^{3'}$, 2 H), 7.77 (s, O*H*, 2 H), 7.87 (d, $^3J_{HH}$ 8.8, H^4 and $H^{4'}$, 2 H) and 8.36 (~d, $^3J_{HP}$ 15.2, H^5 and $H^{5'}$, 2 H); $\delta_C(CDCl_3)$ 16.35 (d, $^3J_{CP}$ 6.3, OCH_2CH_3), 62.41 (d, $^2J_{CP}$ 5.4, OCH_2CH_3), 113.27 (s, C^1 and $C^{1'}$), 119.48 (s, C^3 and $C^{3'}$), 121.69 (d, $^1J_{CP}$ 190.3, C^6 and $C^{6'}$), 125.15 (d, $^3J_{CP}$ 14.4, C^8 and $C^{8'}$), 127.32 (d, $^2J_{CP}$ 10.0, C^7 and $C^{7'}$), 127.96 (d, $^3J_{CP}$ 17.1, C^{10} and $C^{10'}$), 131.58 (s, C^4 and $C^{4'}$), 134.46 (d, $^2J_{CP}$ 10.8, C^5 and $C^{5'}$), 136.19 (d, $^4J_{CP}$ 2.7, C^9 and $C^{9'}$) and 155.42 (s, C^2 and $C^{2'}$); $\delta_P(CDCl_3)$ 19.5; *m/z* 559 ($M^{\bullet+}$ + 1, 2.4%), 558 ($M^{\bullet+}$, 6.7), 280 (1.0), 252 (1.6), 224 (2.5), 165 (31.1), 144 (12.2), 143 (10.5), 142 (28.8) and 43 (100); ν_{max}(KBr)/cm^{-1} 1020 and 1046 (P–O), 1218 (P=O) and 3134 (O–H); **1a** $[\alpha]_D^{20}$ −89.70 (*c* 1.17, CH_2Cl_2, ee 97.8%); **1b** $[\alpha]_D^{20}$ −89.74 (*c* 1.17, CH_2Cl_2, ee 99.5%); HPLC retention time (hexane–propan-2-ol 75:25) 22.4 min (**1a**) and 25.7 min (**1b**).

Diethyl 2,2′-dihydroxy-1,1′-binaphthalene-6-phosphonate 10. R_f (CH_2Cl_2–EtOH 95:5) 0.25; $\delta_H(CDCl_3)$ 1.27 (dt, $^3J_{HH}$ 7.1, $^4J_{HP}$ 3.0, OCH_2CH_3, 6 H), 4.1 (m, OCH_2CH_3, 4 H), 6.22 (s, O*H*, 2 H), 7.08 (~d, $^3J_{HH} \approx 7.7$, $H^{8'}$, 1 H), 7.19 (dd, $^3J_{HH}$ 8.3, $^4J_{HP}$ 3.4, H^8, 1 H), 7.26 and 7.44 (2 dt, $^3J_{HH} \approx {}^3J_{HH} \approx 7.7$, $^4J_{HH}$ 1.2, $H^{6'}$ and $H^{7'}$, 2 H), 7.41 and 7.44 (2 d $^3J_{HH}$ 8.8, H^3 and $H^{3'}$, 2 H), 7.47 (ddd, $^3J_{HH}$ 8.3, $^3J_{HP} \approx 12.5$, $^4J_{HH}$ 1.2, H^7, 1 H), 7.86 (~d, $^3J_{HH} \approx 7.7$, $H^{5'}$, 1 H), 7.92 and 7.93 (2 d, $^3J_{HH}$ 8.8, H^4 and $H^{4'}$, 2 H) and 8.39 (~d, $^3J_{HP}$ 15.3, H^5, 1 H); $\delta_C(CDCl_3)$ 15.44 (d, $^3J_{CP}$ 6.3, OCH_2CH_3), 61.46 (d, $^2J_{CP}$ 5.4, OCH_2CH_3), 110.23 and 111.76 (2 s, C^1 and $C^{1'}$), 117.22 and 118.17 (2 s, C^3 and $C^{3'}$), 121.35 (d, $^1J_{CP}$ 190.3, C^6), 122.96, 123.33, 126.43 and 127.52 (4 s, $C^{5'}$, $C^{6'}$, $C^{7'}$ and $C^{8'}$), 124.19 (d, $^3J_{CP}$ 14.4, C^8), 126.75 and 133.57 (2 d, $^2J_{CP}$ 10.8, C^5 and C^7), 127.29 (d, $^3J_{CP}$ 17.0, C^{10}), 127.82 (s, $C^{10'}$), 128.41 and 130.37 (2 s, C^4 and $C^{4'}$), 132.71 (s, $C^{9'}$), 135.01 (d, $^4J_{CP}$ 2.7, C^9) and 152.17 and 154.01 (2 s, C^2 and $C^{2'}$); $\delta_P(CDCl_3)$ 19.7; *m/z* 424 ($M^{\bullet+}$ + 2, 14.7%), 423 ($M^{\bullet+}$ + 1, 45.3), 422 ($M^{\bullet+}$, 27.9), 366 (11.3), 349 (23.4), 239 (66.0), 226 (67.9), 183 (100) and 115 (41.1); ν_{max}(KBr)/cm^{-1} 1024 and 1048 (P–O), 1222 (P=O) and 3174 (O–H).

Diisopropyl 2,2′-dihydroxy-1,1′-binaphthalene-6,6′-diphosphonate 7. To a solution of CuCl(OH)(TMEDA) (6 mg, 0.026 mmol) in dichloromethane (20 ml) under O_2 was added compound **6** (0.4 g, 1.3 mmol). The resulting solution was stirred for 40 h. After a second addition of CuCl(OH)(TMEDA) (15 mg, 0.065 mmol), stirring was continued for 46 h. The solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel (98:2 dichloromethane–ethanol as eluent) to afford compound **7** (0.24 g, 60%), R_f (CH_2Cl_2–EtOH 90:10) 0.30; mp 170 °C; $\delta_H(CDCl_3)$ 1.20 and 1.36 [2 d, $^3J_{HH}$ 6.2, $OCH(CH_3)_2$, 24 H], 4.69 and 4.70 [2 m, $OCH(CH_3)_2$, 4 H], 6.2 (s, O*H*, 2 H), 7.14 (ddt, $^3J_{HH}$ 8.7, $^4J_{HP}$ 4.0, $^5J_{HH} = {}^5J_{HH} = 0.8$, H^8 and $H^{8'}$, 2 H), 7.47 (d, $^3J_{HH}$ 9.0, H^3 and $H^{3'}$, 2 H), 7.52 (ddd, $^3J_{HP}$ 11.2, $^3J_{HH}$ 8.7, $^4J_{HH}$ 1.6, H^7 and $H^{7'}$, 2 H), 7.99 (dd, $^3J_{HH}$ 9.0, $^5J_{HH}$ 0.8, H^4 and $H^{4'}$, 2 H) and 8.42 (dd, $^3J_{HP}$ 15.3, $^4J_{HH}$ 1.6, H^5 and $H^{5'}$, 2 H); $\delta_C(CDCl_3)$ 23.98 and 24.17 [2 d, $^3J_{CP}$ 4.5, $OCH(CH_3)_2$], 71.10 [d, $^2J_{CP}$ 5.4, $OCH(CH_3)_2$], 112.36 (s, C^1 and $C^{1'}$), 119.18 (s, C^3 and $C^{3'}$), 123.97 (d, $^1J_{CP}$ 192.1, C^6 and $C^{6'}$), 124.84 (d, $^3J_{CP}$ 13.5, C^8 and $C^{8'}$), 127.86 (d, $^2J_{CP}$ 9.9, C^7 and $C^{7'}$), 128.14 (d, $^3J_{CP}$ 16.2, C^{10} and $C^{10'}$), 132.03 (s, C^4 and $C^{4'}$), 134.30 (d, $^2J_{CP}$ 9.8, C^5 and $C^{5'}$), 135.76 (d, $^4J_{CP}$ 2.7, C^9 and $C^{9'}$) and 152.12 (s, C^2 and $C^{2'}$); $\delta_P(CDCl_3)$ 16.0; *m/z* 615 ($M^{\bullet+}$ + 1, 0.1%), 530 (0.3), 488 (1.3), 446 (10.5), 97 (23.9), 85 (19.5), 69 (32.6), 57 (45.9), 43 (46.9), 42 (89.7) and 41 (100.0); ν_{max}(KBr)/cm^{-1} 984 and 1014 (P–O), 1218 (P=O) and 3146 (O–H).

6,6′-Bis(diethoxyphosphoryl)-1,1′-binaphthalene-2,2′-diyl dipentanoate 17. To dichlorobis(triphenylphosphine)palladium(II) (23 mg, 0.03 mmol) under argon was added triethylsilane (0.03 mmol) in toluene (1 ml) and the resulting mixture was stirred at 90 °C for 10 min to yield a black solution. Diethyl hydrogen phosphite (0.19 g, 1.37 mmol), 6,6-dibromo-1,1′-binaphthalene-2,2′-diyl dipentanoate **16** (0.40 g, 0.65 mmol), triethylamine (0.16 g, 1.6 mmol) and toluene (2 ml) were added. The mixture was heated at 90 °C for 22 h. After cooling of the mixture, 2 M hydrochloric acid was added (50 ml) and the solution was extracted with dichloromethane (3 × 20 ml). The organic layer was dried over $MgSO_4$ and the solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel (95:5 dichloromethane–ethanol as eluent) to give compound **17** (0.18 g, 38%); R_f (CH_2Cl_2–MeOH 98:2) 0.15; $\delta_H(CDCl_3)$ 0.63 (t, $^3J_{HH}$ 7.1, CH_3, 6 H), 0.90 (sextet, $^3J_{HH} = {}^3J_{HH} = 7.1$, CH_2, 4 H), 1.12 (m, CH_2, 4 H), 1.32 (t, $^3J_{HH}$ 7.0, CH_3, 12 H), 2.11 (t, $^3J_{HH}$ 7.5, $COCH_2$, 4 H), 4.1 (m, OCH_2, 8 H), 7.26 (dd, $^3J_{HH}$ 8.5, $^4J_{HP}$ 3.7, H^8 and $H^{8'}$, 2 H), 7.50 (d, $^3J_{HH}$ 8.8, H^3 and $H^{3'}$, 2 H), 7.57 (~ddd, $^3J_{HH}$ 8.5, $^3J_{HP} \approx 10$, $^4J_{HH}$ 1.2, H^7 and $H^{7'}$, 2 H), 8.11 (d, $^3J_{HH}$ 8.8, H^4 and $H^{4'}$, 2 H) and 8.53 (~d, $^3J_{HP}$ 15.4, H^5 and $H^{5'}$, 2 H); $\delta_C(CDCl_3)$ 13.6 (s, CH_3), 16.44 (d, $^3J_{CP}$ 6.3, OCH_2CH_3), 21.75 (s, $CH_2CH_2CH_3$), 26.55 (s, $CH_2CH_2CH_2$), 33.72 (s, $COCH_2$), 62.35 (d, $^2J_{CP}$ 5.4, OCH_2CH_3), 123.26–123.31 (2 s, C^1–C^3 and $C^{1'}$–$C^{3'}$), 125.68 (d, $^1J_{CP}$ 190.3, C^6 and $C^{6'}$), 126.51 (d, $^3J_{CP}$ 14.4, C^8 and $C^{8'}$), 127.58 (d, $^2J_{CP}$ 9.9, C^7 and $C^{7'}$), 130.57 (d, $^3J_{CP}$ 16.2, C^{10} and $C^{10'}$), 130.84 (s, C^4 and $C^{4'}$), 134.12 (d, $^2J_{CP}$ 10.8, C^5 and $C^{5'}$), 135.11 (d, $^4J_{CP}$ 2.7, C^9 and $C^{9'}$), 148.83 (s, C^2 and $C^{2'}$) and 171.72 (s, C=O); $\delta_P(CDCl_3)$ 18.4.

Hydrolysis of phosphonates

General procedure. Trimethylsilyl bromide (3 equiv. by phosphonate function) was added to a dichloromethane (2 ml) solution of dialkyl phosphonate (1.4 mmol) under nitrogen. The resulting solution was stirred at rt for 24 h. Excess of reagents and solvent were evaporated off and methanol was added (15 ml) to the residue. The solution was stirred for 30 min, and the solvent was removed *in vacuo* to give the phosphonic acid in good purity.

6-Hydroxy-2-naphthylphosphonic acid 18. (82%); mp >250 °C; $\delta_H(D_2O)$ 7.34 (dd, $^3J_{HH}$ 8.8, $^4J_{HH}$ 2.4, H^7, 1 H), 7.38 (d, $^4J_{HH}$ 2.4, H^5, 1 H), 7.80–7.95 (m, H^3 and H^4, 2 H), 8.04 (d, $^3J_{HH}$ 8.8, H^8, 1 H) and 8.33 (~d, $^3J_{HP}$ 15.0, H^1, 1 H); $\delta_C(D_2O)$ 107.35 and 116.78 (2 s, C^5 and C^7), 124.72 (d, $^3J_{CP}$ 13.5, C^4),

125.35 and 129.2 (2 d, $^2J_{CP}$ 9.9 and ~11, C^1 and C^3), 125.75 (d, $^3J_{CP}$ 15.2, C^9), 127.7 (d, $^1J_{CP} \approx 181$, C^2), 129.11 (s, C^8), 133.64 (s, C^{10}) and 152.96 (s, C^6); $\delta_P(D_2O$ and $Na_2CO_3)$ 13.8; *m/z* 225 ($M^{\bullet+}$ + 1, 9.9%), 224 ($M^{\bullet+}$, 44.2), 207 (10.2), 144 (12.6), 115 (18.6), 69 (55.0) and 43 (100); ν_{max}(KBr)/cm^{-1} 1012 (P–O).

2,2′-Dihydroxy-1,1′-binaphthalene-6,6′-diyldiphosphonic acid 2. Chiral acids **2a** and **2b** were obtained by hydrolysis of diphosphonates **1a** and **1b** (90%); mp >250 °C; $\delta_H(D_2O)$ 1–2.5 (br s, O*H*, ~2 H), 5.0 (s, PO*H*, ~4 H), 6.34 (dd, $^3J_{HH}$ 8.6, $^4J_{HP}$ 3.4, H^8 and $H^{8'}$, 2 H), 6.75 (~t, $^3J_{HH} \approx {}^3J_{HP} \approx 9$, H^7 and $H^{7'}$, 2 H), 7.16 (d, $^3J_{HH}$ 8.8, H^3 and $H^{3'}$, 2 H), 7.80 (d, $^3J_{HH}$ 8.8, H^4 and $H^{4'}$, 2 H) and 8.17 (~d, $^3J_{HP}$ 15.6, H^5 and $H^{5'}$, 2 H); $\delta_C(D_2O)$ 112.46 (s, C^1 and $C^{1'}$), 117.21 (s, C^3 and $C^{3'}$), 122.59 (d, $^3J_{CP}$ 13.5, C^8 and $C^{8'}$), 122.68 (d, $^1J_{CP}$ 187.6, C^6 and $C^{6'}$), 124.71 (d, $^2J_{CP}$ 11.7, C^7 and $C^{7'}$), 126.06 (d, $^3J_{CP}$ 17.0, C^{10} and $C^{10'}$), 129.73 (s, C^4 and $C^{4'}$), 130.77 (d, $^2J_{CP}$ 10.8, C^5 and $C^{5'}$), 133.48 (s, C^9 and $C^{9'}$) and 155.42 (s, C^2 and $C^{2'}$); $\delta_P(D_2O)$ 17.8; *m/z* 447 ($M^{\bullet+}$ + 1, 1.1%), 446 ($M^{\bullet+}$, 1.2), 193 (16.8), 83 (36.9), 69 (58.1), 57 (68.5), 55 (69.9) and 43 (100.0); **2a** $[a]_D^{20}$ +27.82 (*c* 1.15, CH_3OH); **2b** $[a]_D^{20}$ −27.83 (*c* 1.15, CH_3OH).

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