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A convenient protocol for the synthesis of axially chiral Brønsted acids

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Abstract

Partially hydrogenated binaphthol monophosphoric acids were prepared via an improved four-step sequence. It is demonstrated that typical protection and deprotection of the phenolic groups are dispensable. The vinyl-substituted derivative has been polymerized to give a novel polymerized organocatalyst.

Keywords: Brønsted acid; Organocatalysts; H8-BINOL diphosphates; Polymer

1. Introduction

Asymmetric reactions catalyzed by chiral Brønsted acids have attracted significant interest in recent years.[1] In general, the activation of the substrate is enabled via hydrogen bonding[2] or formation of ion pairs, depending on the acidic strength. Smooth transitions can be observed between both of these edge cases.

Among the different chiral Brønsted acids, especially axial chiral phosphoric acid diesters, e.g., BINOL derivatives, have been shown to be useful catalysts for a wide range of reactions like transfer hydrogenations,[3] hydrophosphonylation,[4] amidation of imines[5] and addition of *C*-nucleophiles to imines,[6] hetero-Diels–Alder reactions,[7] aza-ene-type reaction,[8] Strecker reaction,[9] allylboration of ketones,[10] Morita–Baylis–Hillman reactions,[11] Mannich[12] and Mannich-type reactions,[13] Pictet–Spengler reaction[14] and aza-Friedel–Crafts alkylation.[15] Thus, the development of new chiral Brønsted catalysts as well as their improved preparation is of major interest in organocatalysis.

Interestingly, in organotransition metal catalysis octahydrogenated BINOL-based (H8-BINOL) compounds were reported to induce higher enantioselectivity compared to the corresponding unsaturated BINOL derivatives.[16] Based on these observations we became interested to synthesize novel organocatalysts with partially hydrogenated aromatic backbone. In addition to the different steric features of these ligands we thought they might be easier to prepare.

The multi-step synthesis of the commonly known 3,3′-substituted binaphthyl-based chiral phosphates starts with protection of the hydroxy groups via methylation, bromination in 3,3′-position, Suzuki coupling with arylboronic acids, removal of the protective group, phosphorylation with phosphoryl chloride and hydrolysis of the P–Cl bond. Notably, the selective bromination in 3,3′-position is difficult, which leads to tedious purification.

Recently, Inanaga et al.[17] reported the synthesis of partially hydrogenated binaphthol monophosphoric acids and used them for complexation with rare earth metals. H8-BINOLS with phenyl, 3,5-bis(trifluoromethylphenyl) or mesityl substituents in 3,3′-position were prepared according to the above mentioned method using Pd/phosphine catalysts.[10,11a,b,18]

Other procedures for the synthesis of 3,3′-arylsubstituted BINOLS make use of a Ni-catalyzed arylation with arylmagnesium bromides[19,20] or the introduction of boronic acid

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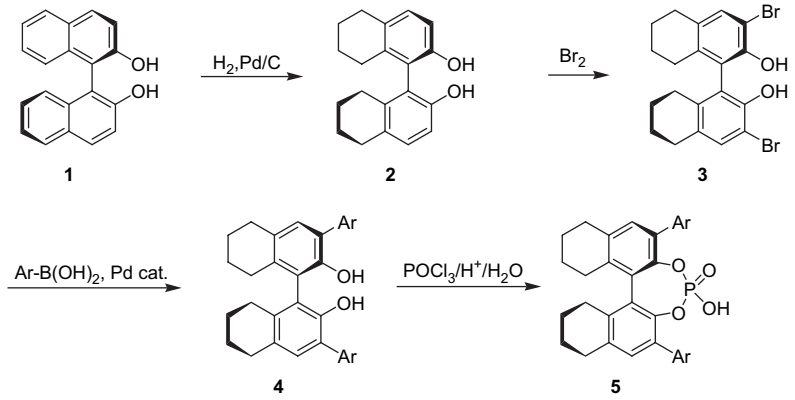


Scheme 1. Synthesis of the chiral Brønsted acids **5**.

groups in 3,3′-position followed by Suzuki cross-coupling with aryl bromides.[19,21,22] Both routes need protecting/deprotecting steps.

2. Results and discussion

Here, we report the synthesis of some new H8-binaphthyl-substituted phosphates as well as an improved procedure for the preparation of such chiral Brønsted acids in only four steps in gram-scale (Scheme 1). The (*R*)-binaphthol **1** was always used as educt.

Exploratory investigations showed that the protection of the phenolic groups in the Suzuki coupling is not necessary and so is the cleavage of the OMe group with BBr_3 omitted. The bromination of **2** which we have prepared by hydrogenation on 100 g scale to **3** can be carried out directly at low temperature (−30 °C), similar to the procedure reported by Cram et al.[23] Testing different palladium catalysts for the Suzuki coupling of **3** with phenylboronic acid, good results were achieved with $Pd(OAc)_2$/$BuPAd_2$ (*n*-butyl-di-1-adamantyl-phosphine; CataCXium A) catalyst (Table 1, entry 1).[24,25] This commercially available catalyst can be easily used with various arylboronic acids without special precautions. As shown in Table 1 the corresponding coupling products were obtained in general in 70 to >90% yield. Compared to other catalysts in similar coupling reactions the coupling products **4a**–**k** were observed in higher yield.[22]

Interestingly, the ^1H NMR spectrum of **4k** in $CHCl_3$ showed four signals for the OH group at 4.76, 4.77, 4.81 and 4.86, which disappeared by D_2O exchange. However, in DMSO-d_6 a downfield shift of a singlet signal to 7.45 ppm was recorded. We interpret this observation as a possible interaction through the space of sterically adjacent protons. The short distance between the OH proton and the hydrogen at H^{10} or $H^{10'}$ of 2.5 Å can be observed at the modelled structure of **4k** (Fig. 1). A NOESY spectrum of compound **4k** in $CHCl_3$ supports this modelling and showed a correlation between the OH hydrogen atoms and the aromatic hydrogen atoms H^{10} and $H^{10'}$ of the phenanthryl groups due to their close-by position.

The appearance of the hydroxyl groups as four singlets should be caused by the hindrance of the rotation of the phenanthryl moieties leading to rotamers. A coupling of an OH hydrogen atom with neighbouring hydrogen atoms can be ruled out because the HETCOR and COSY spectra of **4k** did not indicate such behaviour.

Esterification proceeded with phosphoryl chloride and subsequent hydrolysis led to the diphosphates **5** in good to excellent yield (Table 2). Notably, in case of **4c** more vigorous conditions were needed to hydrolyze the intermediately formed chlorophosphate to **5c**. Due to steric hindrance the yields of **4c** and **5c** are the lowest of all investigated compounds.

In addition to standard spectroscopic characterization of new products, LSIMS (Liquid Secondary Ion Mass Spectrometry) was used as a soft ionization method. All spectra were recorded with the so-called 'magic bullet' matrix (a mixture of

Table 1
Coupling products of **3** with arylboronic acids to **4** ((*R*)-enantiomers)

Entry	No.	Ar–$B(OH)_2$	Reaction time [h]	Yield [%]	Mp [°C]	$[\alpha]_D^T$ (T [°C], c, solvent)
1	**4a**	C_6H_5–	12	70	185	−29.5 (29.5, 0.5, $CHCl_3$)
2	**4b**	2-Naphthyl–	2.5	72	205–206	−150.5 (29.4, 0.5, $CHCl_3$)
3	**4c**	Mesityl	15	61	121–123	−36.2 (29.3, 0.4, $CHCl_3$)
4	**4d**	3,5-$((CF_3)_2$–$C_6H_3)$–	2	96	195–196	−29.2 (29.0, 0.5, $CHCl_3$)
5	**4e**	4-$(CH_2$=CH–$C_6H_4)$–	2	81	185–187	−168.2 (24.8, 0.4, $CHCl_3$)
6	**4f**	3,5-$(F_2$–$C_6H_3)$–	1	99	133–135	−34.6 (23.8, 0.49, $CHCl_3$)
7	**4g**	4-(F–C_6H_4)–	4	81	187–188	−28.3 (28.3, 0.39, $CHCl_3$)
8	**4h**	4-$(CH_3O$–$C_6H_4)$–	8	76	167–169	−32.8 (27.9, 0.4, $CHCl_3$)
9	**4i**	4-$(C_6H_5O$–$C_6H_4)$–	8	71	102–105	−35.3 (26.8, 0.4, $CHCl_3$)
10	**4j**	9-Anthracenyl–	3.5	58	179–181	−42.7 (29.2, 0.48, $CHCl_3$)
11	**4k**	9-Phenanthryl–	1	>99	193–195	−45.3 (23.0, 0.5, $CHCl_3$)

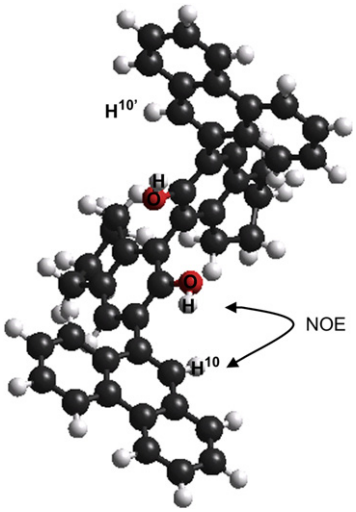
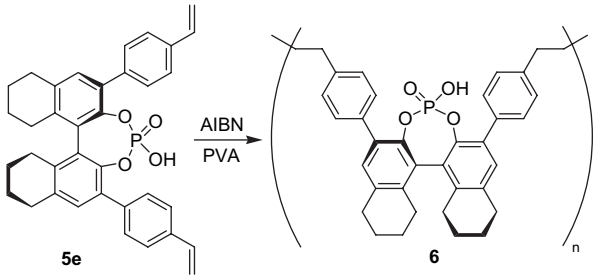


Figure 1. HyperChem structure of **4k**.

dithioerythritol and dithiothreitol). As expected, **4a–k** and the majority of the phosphoric acid esters **5** gave expected spectra mostly with $[M]^+$ as base peaks accompanied by $[M+1]^+$. Surprisingly, abundant cluster peaks were the base peaks in the spectra of **5c**, **5e** and **5i**, where potassium ions were added to the phosphoric ester molecules to generate $[M+K]^+$ peaks. Normally, $[M+Na]^+$ peaks which are accompanied by [M+1] peaks are expected in such spectra. Since comparable preparation and cleaning procedures were applied the different behaviour should be caused by the different aryl substituents. Whereas phenyl, naphthyl, anthracenyl and phenanthryl as well as fluorophenyl and methoxyphenyl substituents led to protonation in the LSIMS ionization process, mesityl, phenoxyphenyl, styryl and even trifluoromethylphenyl groups supported the formation of $[M+K]^+$ ions. These results can be interpreted as an indication for an increased ability of cation complexation of the corresponding ligands **5c**, **5e** and **5i**.

With regard to application a convenient separation of chiral Brønsted acids in catalytic reactions is desirable. Therefore, a strategy for the synthesis of a polymeric acid was also developed. Here, vinylphenylboronic acid was used as coupling agent to obtain **4e**. After phosphorylation, the vinyl group of



Scheme 2. Formation of the polymeric Brønsted acid **6**.

5e was polymerized according to a radical pathway described for styrene monomers (Scheme 2).[26]

The obtained solid product is insoluble in organic solvents. It exhibited a very small BET surface of 3.63 m^2/g. The particle size and surface texture is shown in the TEM image in Figure 2. The particle size shows a broad distribution between 4.5 and 100 μm. The image originates from the border area of a polymeric agglomerate which consists of adhered smaller units.

The size of primary particles could not be determined. The measurement of the particle size showed a definite dependence of the size distribution from the time of dispersion under ultrasound conditions. This fact argues for agglomeration as well

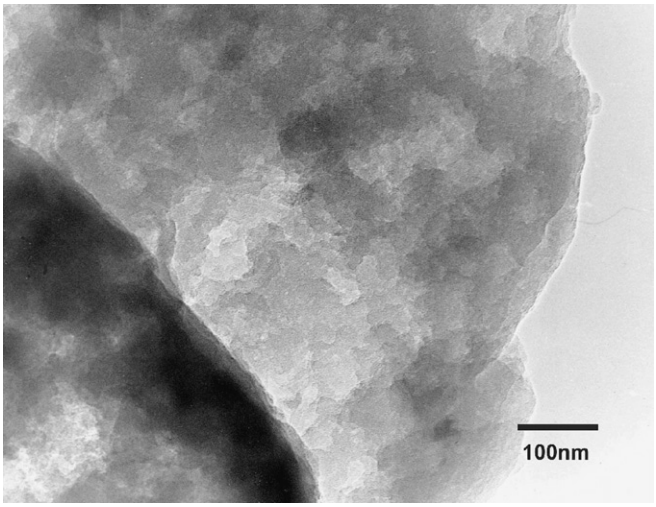


Figure 2. TEM image of the polymer **6**.

Table 2
Phosphoric acid diesters **5** ((*R*)-enantiomers)

Entry	No.	Ar	Reaction time [h]	Yield [%][a]	Mp [°C]	$[\alpha]_D^T$ (T [°C], c, solvent)
1	**5a**	C_6H_5–	1.5	99	290[b]	−283.8 (28.4, 0.4, $CHCl_3$)
2	**5b**	2-Naphthyl–	1.5	93	350[b]	−297.3 (27.5, 0.4, $CHCl_3$)
3	**5c**	Mesityl	2.5	63	174–176[b]	−181.3 (28.1, 0.35, $CHCl_3$)
4	**5d**	3,5-$((CF_3)_2$–$C_6H_3)$–	1.5	99.9	167–169	−192.7 (25.5, 0.38, $CHCl_3$)
5	**5e**	4-$(CH_2$=CH–$C_6H_4)$–	2	87	456[b]	−250.4 (29.7, 0.5, $CHCl_3$)
6	**5f**	3,5-$(F_2$–$C_6H_3)$–	2	90	293–295[b]	−267.6 (26.8, 0.4, $CHCl_3$)
7	**5g**	4-(F–$C_6H_4)$–	2.5	73	277–279[b]	−224.8 (26.8, 0.4, $CHCl_3$)
8	**5h**	4-$(CH_3O$–$C_6H_4)$–	2.5	71	241–243[b]	−217.9 (27.7, 0.39, $CHCl_3$)
9	**5i**	4-$(C_6H_5O$–$C_6H_4)$–	2.5	77	261–264[b]	−233.8 (28.3, 0.38, $CHCl_3$)
10	**5j**	9-Anthracenyl–	2	94	244–246[b]	−173.4 (27.9, 0.4, $CHCl_3$)
11	**5k**	9-Phenanthryl–	2	98	252–255[b]	−160.1 (22.4, 0.5, $CHCl_3$)

[a] Isolated yield.
[b] Decomposition.

as for the above described morphology of the powder. Typical vinyl bands (C=C, wagging und rocking CH), e.g., at 1626 cm^{-1}, disappeared or became less intensive in the FTIR and Raman spectra. The band at 1107 cm^{-1} related to PO vibrations was slightly switched to 1096 cm^{-1}. These results provide a strong indication for the formation of a polymer.

3. Conclusions

New H8-BINOL phosphoric acid diesters were prepared according to a convenient four-step reaction sequence. The typical protection of the OH groups of the BINOL before further functionalization is not necessary. $Pd(OAc)_2$/$BuPAd_2$ serves as an efficient catalyst for Suzuki coupling reactions of the bishydroxynaphthol derivative. This simplifies the preparation of this class of interesting organocatalysts. In addition, a heterogeneous phosphoric acid diester was prepared via a styryl-substituted monomer. Catalytic investigations of the novel Brønsted acids are in progress.

4. Experimental

4.1. General

The octahydro binaphthol **2** was prepared according to a literature procedure.[27] Elemental analyses were determined by the ICP-OES method using an Optima 3000 XL (Perkin Elmer) and an EA 1110 (CE Instruments). ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectra were recorded on a Varian UNITYPLUS 300 and 500 (300 and 500 MHz). Chemical shifts are given in parts per million with respect to TMS (^{1}H, ^{13}C), H_3PO_4 (^{31}P) or $CFCl_3$ (^{19}F), coupling constants are reported in hertz. Optical rotations were measured on a Perkin Elmer 241 polarimeter. Mass spectra were obtained on an Autospec (Micromass). Raman spectra were received on a fibre-optic RXN spectrometer (Kaiser Optical Systems, laser 785 nm, laser power 30 mW). The FTIR spectra were recorded on a Nicolet Avatar 370 (Thermo Electron, diamond ATR, resolution 4, 32 scans). FTIR and Raman values are given in cm^{-1}. TEM images were obtained with a CM-20 Phillips at 200 kW acceleration voltages. The particle size of polymer was measured in water with He–Ne-Laser on a Fritsch Particle Sizer Analysette 22.

4.2. 3,3′-Dibromo-5,6,7,8,5′,6′,7′,8′-octahydro-(1,1′-binaphthalene)-2,2′-diol **3**

Compound **2** of 8.83 g (30 mmol) was dissolved in 300 ml CH_2Cl_2 and cooled down to −30 °C. Under stirring, 11 g bromine (69 mmol) was added in one portion. The stirring was continued at −30 °C for 30 min (TLC control, eluent hexane/CH_2Cl_2 1:1). Then 400 ml of a saturated solution of $NaHSO_3$ was added and the reaction mixture was slowly warmed up to room temperature. The organic phase was subsequently washed with saturated $NaHCO_3$ solution and with cold H_2O, dried over Na_2SO_4 and finally the solvent was evaporated. The crude product was recrystallized from heptane or purified by column chromatography (eluent hexane/ethyl acetate). Yield 95–100%. Mp: 142 °C. The melting point, NMR and MS data were in accordance with literature[23] results.

4.3. 3,3′-Diaryl-5,6,7,8,5′,6′,7′,8′-octahydro-(1,1′-binaphthalene)-2,2′-diols **4**

General procedure: 10 mg $Pd(OAc)_2$ (2 mol %) and 20 mg (adamantyl)$_2$-butyl-phosphine (2.5 mol %) were added in an inert atmosphere to a solution of 1 g of **3** (2.2 mol) and 2.5–3 equiv of the corresponding boronic acid, dissolved in 1,2-dimethoxyethane and 10 ml 1 M K_2CO_3 solution. The mixture was heated up to 95 °C for 1–15 h (TLC control, eluent hexane/CH_2Cl_2 1:1). After cooling down the organic phase was separated, diluted with CH_2Cl_2, washed with saturated NH_4Cl solution as well as with H_2O and dried with Na_2SO_4. Then the solvent was evaporated and the solid residue was purified by column chromatography (eluent hexane/CH_2Cl_2).

4.3.1. Compound **4a**[11b]

White solid; ^{1}H NMR ($CDCl_3$) δ 1.75 (m, 8H), 2.26 (m, 2H), 2.41 (m, 2H), 2.80 (t, 4H, J=6.2), 4.89 (s, 2H, OH), 7.15 (s, 2H, ArH, BINOL), 7.32 (m, 2H, ArH), 7.42 (m, 4H, ArH), 7.59 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$) δ 23.1, 27.2, 29.3, 120.1, 126.0, 127.1, 128.4, 129.2, 130.2, 131.7, 136.6, 137.9, 148.1; MS (FAB pos.) m/z 446.1 $[M]^+$, 447.1 $[M+H]^+$. Anal. Calcd for $C_{32}H_{30}O_2$: C, 86.06; H, 6.77. Found: C, 86.12; H, 6.23.

4.3.2. Compound **4b**

White solid; ^{1}H NMR ($CDCl_3$) δ 1.77 (m, 8H), 2.31 (m, 2H), 2.47 (m, 2H), 2.84 (m, 4H), 5.01 (s, 2H, OH), 7.27 (s, 2H, ArH, BINOL), 7.48 (m, 4H, ArH), 7.75 (dd, 2H, J=8.45, 1.45, ArH), 7.87 (m, 6H, ArH), 8.06 (s, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 23.1, 27.2, 29.3, 120.2, 125.9, 126.0, 126.1, 127.6, 127.8, 127.9, 128.1, 130.4, 132.0, 132.5, 133.5, 135.5, 136.8, 148.3; MS (FAB) m/z 547.5 $[M+H]^+$. Anal. Calcd for $C_{40}H_{34}O_2$: C, 87.88; H, 6.27. Found: C, 87.60; H, 6.21.

4.3.3. Compound **4c**[20]

White solid; ^{1}H NMR ($CDCl_3$) δ 1.76 (m, 8H), 2.00 (3s, 18H, 6CH_3), 2.32 (m, 4H), 2.76 (t, 4H, J=6.2), 4.53 (s, 2H, OH), 6.80 (s, 2H, ArH, BINOL), 6.93 (2s, 4H, ArH); ^{13}C NMR ($CDCl_3$) δ 19.7, 20.4, 21.0, 23.1, 27.0, 29.1, 120.3, 124.5, 128.1, 128.2, 129.6, 131.0, 133.6, 135.8, 136.9, 147.8; MS (FAB) m/z 530.1 $[M]^+$. Anal. Calcd for $C_{38}H_{42}O_2$: C, 85.99; H, 7.98. Found: C, 86.32; H, 8.38.

4.3.4. Compound **4d**[11b]

White solid; ^{1}H NMR ($CDCl_3$) δ 1.76 (m, 8H), 2.32 (m, 4H), 2.83 (m, 4H), 4.93 (s, 2H, OH), 7.22 (s, 2H, ArH, BINOL), 7.82 (s, 2H, ArH), 8.09 (s, 4H, ArH); ^{13}C NMR ($CDCl_3$) δ 22.8, 27.3, 29.2, 119.3, 120.6, 123.3, 123.5 (q, J_{CF}=272.6), 129.4, 130.7, 131.2, 131.4 (q, J_{CF}=33.1), 131.5, 138.5, 139.9, 148.3; ^{19}F NMR ($CDCl_3$) δ −63.3; MS (FAB pos.) m/z 718.2 $[M]^+$, 719.2 $[M+H]^+$. Anal. Calcd for $C_{36}H_{26}F_{12}O_2$: C, 60.17; H, 3.65. Found: C, 60.40; H, 3.64.

*4.3.5. Compound **4e***

White solid; ^{1}H NMR ($CDCl_3$) δ 1.74 (m, 8H), 2.24 (m, 2H), 2.40 (m, 2H), 2.80 (t, 4H, J=6.1), 4.91 (s, 2H, OH), 5.25 (dd, 2H, J=11.5, ~1, −CH=CH_2), 5.77 (dd, 2H, J=17.6, 0.7, −CH=CH_2), 6.74 (dd, 2H, J=17.5, 11, −CH=CH$_2$), 7.16 (s, 2H, ArH, BINOL), 7.47 and 7.57 (dd, 4H, J=8.3, 1.7, ArH); ^{13}C NMR ($CDCl_3$) δ 23.0, 27.2, 29.3, 113.8, 120.1, 125.7, 126.2, 129.3, 130.3, 131.6, 136.3, 136.5, 136.7, 137.4, 148.2; MS (EI) *m/z* 498.4 $[M]^+$. Anal. Calcd for $C_{36}H_{34}O_2$: C, 86.71; H, 6.87. Found: C, 86.23; H, 6.41.

*4.3.6. Compound **4f***

White solid; ^{1}H NMR ($CDCl_3$) δ 1.75 (m, 8H), 2.23 (m, 2H), 2.34 (m, 2H), 2.80 (m, 4H), 4.88 (s, 2H, OH), 6.75 (m, 2H, ArH), 7.16 (m, 6H, ArH and ArH−BINOL); ^{13}C NMR ($CDCl_3$) δ 22.9, 27.2, 29.2, 102.3 (t, J_{CF}=25.4), 112.1 (q, J_{CF}=17.4, 8.0), 119.6, 124.0, 130.9, 131.8, 137.8, 141.0 (t, J_{CF}=9.9), 148.1, 162.8 (dd, J_{CF}=247.2, 13.1); ^{19}F NMR ($CDCl_3$) δ −111.1 (m); MS (FAB pos.) *m/z* 518.1 $[M]^+$, 519.1 $[M+H]^+$. Anal. Calcd for $C_{32}H_{26}F_4O_2$: C, 74.12; H, 5.05. Found: C, 73.62; H, 4.93.

*4.3.7. Compound **4g***

White solid; ^{1}H NMR ($CDCl_3$) δ 1.75 (m, 8H), 2.31 (m, 4H), 2.80 (t, 4H, J=5.9), 4.85 (s, 2H, OH), 7.10 (m, 6H, ArH), 7.57 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$) δ 22.9, 23.0, 27.1, 29.2, 115.0 (d, J=21.4), 119.8, 125.1, 130.4, 130.8, 130.9, 131.8, 133.8, 133.84, 136.6, 148.1, 160.4 (d, J=246.3); ^{19}F NMR ($CDCl_3$) δ −116.1 (m); MS (FAB) *m/z* 482.1 $[M]^+$, 483.2 $[M+H]^+$. Anal. Calcd for $C_{32}H_{28}F_2O_2$: C, 79.65; H, 5.85. Found: C, 79.91; H, 6.09.

*4.3.8. Compound **4h***

White solid; ^{1}H NMR ($CDCl_3$) δ 1.74 (m, 8H), 2.31 (m, 4H), 2.79 (t, 4H, J=6.2), 3.84 (s, 3H, OCH_3), 4.88 (s, 2H, OH), 7.03 (m, 6H, ArH), 7.52−7.53 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$) δ 23.1, 27.1, 29.3, 55.3 (OCH_3), 113.8, 114.2, 120.1, 125.6, 127.7, 130.1, 130.3, 131.4, 136.0, 148.1, 158.8; MS (FAB) *m/z* 506.2 $[M]^+$, 507.2 $[M+H]^+$. Anal. Calcd for $C_{34}H_{34}O_4$: C, 80.60; H, 6.76. Found: C, 80.97; H, 7.12.

*4.3.9. Compound **4i***

White solid; ^{1}H NMR ($CDCl_3$) δ 1.74 (m, 8H), 2.31 (m, 4H), 2.80 (t, 4H, J=5.6), 4.89 (s, 2H, OH), 7.29 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 23.0, 27.1, 29.2, 30.3, 118.1, 118.3, 118.6, 118.9, 119.0, 119.1, 120.0, 123.2, 123.3, 123.33, 125.4, 128.2, 129.4, 129.7, 129.8, 130.3, 130.5, 131.7, 132.8, 135.6, 136.4, 148.1, 156.4, 156.6, 157.1, 157.15, 157.2; MS (FAB) *m/z* 630.2 $[M]^+$, 631.2 $[M+H]^+$. Anal. Calcd for $C_{44}H_{38}O_4$: C, 83.78; H, 6.07. Found: C, 84.13; H, 6.41.

*4.3.10. Compound **4j***

White solid; ^{1}H NMR ($CDCl_3$) δ 1.70 (m, 8H), 2.21 (m, 4H), 2.80 (m, 4H), 5.11 (s, 2H, OH), 7.28 (m, 2H, ArH, BINOL), 7.54 (m, 8H, ArH), 8.45 (m, 4H, ArH), 8.50 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 22.7, 22.74, 26.9, 29.0, 122.1, 122.3, 125.6, 127.0, 127.1, 127.6, 128.6, 130.5, 131.5, 132.1, 132.5, 136.7, 147.1; MS (FAB pos.) *m/z* 647.4 $[M+H]^+$. Anal. Calcd for $C_{48}H_{38}O_2$: C, 89.13; H, 5.92. Found: C, 89.43; H, 5.97.

*4.3.11. Compound **4k***

White solid; ^{1}H NMR (DMSO-d_6) δ 1.74 (m, 8H), 2.50 (m, 4H), 2.76 (m, 4H), 6.94 (m, 2H, ArH, BINOL), 7.33 (d, 1H, J=2.5, ArH), 7.45 (m, 12H, ArH, OH), 7.96 (m, 3H, ArH), 8.87 (m, 4H, ArH); ^{13}C NMR (DMSO-d_6) δ 22.8, 22.9, 23.0, 27.0, 28.8, 122.7, 123.0, 123.3 (d), 123.6, 123.8, 124.8, 125.0, 125.2, 126.4 (d), 126.5, 126.8 (d), 127.0, 127.5 (d), 127.6, 127.6, 127.7, 127.8, 128.0, 128.5, 129.5 (d), 129.9 (dd), 130.7, 130.9, 131.3 (d), 131.5 (d), 135.8, 136.0, 136.2, 136.3, 149.8, 150.0; MS (FAB pos.) *m/z* 647.4 $[M+H]^+$. Anal. Calcd for $C_{48}H_{38}O_2$: C, 89.13; H, 5.92. Found: C, 88.52; H, 5.74.

*4.4. 3,3′-Diaryl-5,6,7,8,5′,6′,7′,8′-octahydro-1,1′-binaphthyl-2,2′-diyl-hydrogenphosphates **5***

General procedure: to a solution of 1 mmol **4** in 2 ml dry pyridine a solution of 1.5−2 mmol freshly distilled phosphorus oxychloride in 1 ml dry pyridine was added at room temperature over a period of 10 min. The mixture was stirred at 80 °C until no educt could be observed in an accompanying thin layer chromatogram (eluents CH_2Cl_2/hexane 5:2; CH_2Cl_2/EtOH 10:1, 7:1). The solution was allowed to cool down to 40 °C, then 1 ml H_2O and after 10 min 5 ml 6 N HCl were added dropwise. The resulting mixture was heated to 100 °C for 5 min (**5c** 30 min), cooled down and filtrated. The isolated solid was reprecipitated from ethanol/6 N HCl, washed with H_2O and reprecipitated again from CH_2Cl_2/hexane. If necessary, the product was finally purified by column chromatography.

*4.4.1. Compound **5a**[28]*

White solid; ^{1}H NMR (DMSO-d_6) δ 1.58 (m, 2H), 1.77 (m, 6H), 2.21 (m, 2H), 2.64 (m, 2H), 2.85 (m, 4H), 7.21 (s, 2H, ArH, BINOL), 7.37 (m, 6H, ArH), 7.62 (d, 4H, J=7.6, ArH); ^{13}C NMR (DMSO-d_6) δ 22.1, 27.3, 28.5, 127.1 (d, J_{CP}=3.3), 128.1, 129.3, 130.8, 130.9 (d, J_{CP}=3.7), 134.4 (d, J_{CP}=1.2), 136.6, 137.1, 143.2 (d, J_{CP}=9.2); ^{31}P NMR (DMSO-d_6) δ −0.5 (s); MS (FAB neg.) *m/z* 507.2 $[M-H]^-$. Anal. Calcd for $C_{32}H_{29}O_2P$: C, 75.58; H, 5.75; P, 6.09. Found: C, 75.73; H, 5.63; P, 5.82.

*4.4.2. Compound **5b**[29]*

White solid; ^{1}H NMR (DMSO-d_6) δ 1.62 (m, 2H), 1.81 (s, 6H), 2.29 (m, 2H), 2.69 (m, 2H), 2.89 (m, 4H), 7.36 (s, 2H, ArH, BINOL), 7.52 (m, 4H, ArH), 7.81 (m, 2H, ArH), 7.94 (m, 6H, ArH), 8.14 (s, 2H, ArH); ^{13}C NMR (DMSO-d_6) δ 22.1, 27.4, 28.5, 126.1 (d, J_{CP}=4.9), 127.3, 127.4, 127.7, 128.0, 130.9 (d, J_{CP}=3.1), 131.0, 132.0, 132.9, 134.6, 134.7, 136.9, 143.4 (d, J_{CP}=9.2); ^{31}P NMR (DMSO-d_6) δ −1.0 (s); MS (FAB neg.) *m/z* 607.6 $[M-H]^-$, (FAB pos.) *m/z* 609 $[M+H]^+$, 631.4 $[M+Na]^+$, 647.4 $[M+K]^+$. Anal. Calcd for $C_{40}H_{33}O_4P$: C, 78.93; H, 5.46; P, 5.09. Found: C, 78.63; H, 5.64; P, 5.18.

4.4.3. Compound ***5c***

White solid; ^{1}H NMR ($CDCl_3$) δ 1.65 (m, 2H), 1.82 (m, 6H), 2.01 (3s, 18H, $6CH_3$), 2.29 (m, 2H), 2.82 (m, 2H), 2.84 (m, 4H), 6.93 (m, 6H, ArH); ^{13}C NMR ($CDCl_3$) δ 21.0, 21.02, 21.1, 21.3, 22.5, 22.6, 27.7, 27.8, 29.2, 29.3, 126.5, 126.53, 126.6, 126.7, 127.5, 128.2, 128.4, 128.7, 129.4 (d, J_{CP}=4.8), 130.7, 130.8, 132.2, 132.3, 132.4, 132.43, 132.5 (d, J_{CP}=1.8), 132.7, 132.72, 135.6, 135.7, 135.89, 135.9, 136.2, 136.25, 136.3, 136.34, 136.96, 136.98, 137.0 (d, J_{CP}=2.8), 137.04, 137.1, 142.9 (d, J_{CP}=10.7), 143.5 (d, J_{CP}=12.2); ^{31}P NMR ($CDCl_3$) δ 6.6 (s); MS (FAB) *m/z* 593.3 $[M+H]^+$, 631.3 $[M+K]^+$. Anal. Calcd for $C_{38}H_{41}O_4P$: C, 77.00; H, 6.97; P, 5.23. Found: C, 77.27; H, 7.19; P, 5.58.

4.4.4. Compound ***5d***

White solid; ^{1}H NMR ($CDCl_3$) δ 1.66 (m, 2H), 1.87 (m, 6H), 2.39 (m, 2H), 2.70 (m, 2H), 2.89 (m, 4H), 6.46 (s, 2H, OH), 7.11 (s, 2H, ArH, BINOL), 7.61 (s, 2H, ArH), 7.87 (s, 4H, ArH); ^{13}C NMR ($CDCl_3$) δ 22.3, 22.4, 27.9, 29.1, 121.0 (d, J=3.5), 123.3 (q, J_{CF}=272.6), 126.9 (d, J=1.5), 129.2 (d, J_{CP}=3.4), 129.6 (d, J=1.9), 131.2, 131.3 (q, J_{CF}=33.3), 136.2 (d, J_{CP}=1.8), 138.8, 139.2, 142.4 (d, J_{CP}=9.2); ^{31}P NMR ($CDCl_3$) δ 0.6 (s); ^{19}F NMR ($CDCl_3$) δ −63.6; MS (FAB neg.) *m/z* 779.3 $[M-H]^-$, (FAB pos.) *m/z* 761.3 $[M-F]^+$, 781.3 $[M+H]^+$, 803.3 $[M+Na]^+$, 819.3 $[M+K]^+$. Anal. Calcd for $C_{36}H_{25}F_{12}O_4P$: C, 55.4; H, 3.23; P, 3.97. Found: C, 55.00; H, 3.10; P, 4.20.

4.4.5. Compound ***5e***

White solid; ^{1}H NMR (DMSO-d_6) δ 1.57 (m, 2H), 1.76 (m, 6H), 2.18 (m, 2H), 2.64 (m, 2H), 2.85 (m, 4H), 5.02 (br s, 2H, OH), 5.28 (d, 2H, J=11.2, −CH=CH_2), 5.87 (d, 2H, J=17.6, −CH=CH_2), 6.76 (dd, 2H, J=17.8, 11, −CH=CH$_2$), 7.23 (s, 2H, ArH, BINOL), 7.51 and 7.62 (d, 4H, J=8.3, ArH); ^{13}C NMR (DMSO-d_6) δ 22.1, 27.3, 28.5, 114.3, 125.9, 127.2 (d, J_{CP}=1.7), 129.5, 130.5 (d, J_{CP}=3.4), 130.6, 134.4, 135.9, 136.3, 136.7 (d, J_{CP}=3.7), 143.3 (d, J_{CP}=9.5); ^{31}P NMR (DMSO-d_6) δ −0.5 (s); MS (FAB neg.) *m/z* 558.6 $[M-2H]^-$, 559.6 $[M-H]^-$, 560.6 $[M]^-$, (FAB pos.) *m/z* 599.2 $[M+K]^+$; FTIR (KBr) ν 1627, 1605, 1288, 1235, 1106, 988, 902, 843; Raman (KBr) ν 1627, 1607, 1412. Anal. Calcd for $C_{36}H_{33}O_4P$: C, 77.13; H, 5.93; P, 5.52. Found: C, 77.49; H, 5.88; P, 5.26.

4.4.6. Compound ***5f***

White solid; ^{1}H NMR ($CDCl_3$) δ 1.68 (m, 2H), 1.87 (m, 6H), 2.41 (m, 2H), 2.71 (m, 2H), 2.90 (m, 4H), 6.34 (tt, 2H, ArH), 6.95 (m, 4H, ArH), 7.14 (s, 2H, ArH−BINOL), 8.41 (s, 2H, OH); ^{13}C NMR ($CDCl_3$) δ 22.4, 22.5, 27.8, 29.2, 102.5 (t, J_{CF}=25.4), 112.4 (q, J_{CF}=17.3, 8.2), 127.1 (d, J_{CP}=1.5), 130.0 (d, J_{CP}=2.1), 130.8, 135.8 (d, J_{CP}=1.9), 138.5, 139.8 (t, J_{CF}=10.2), 142.5 (d, J_{CP}=9.2), 162.6 (dd, J_{CF}=247.6, 13.2); ^{31}P NMR ($CDCl_3$) δ 3.2 (s); ^{19}F NMR ($CDCl_3$) δ −111.1 (m); MS (FAB pos.) *m/z* 581.3 $[M+H]^+$. Anal. Calcd for $C_{32}H_{25}F_4O_4P$: C, 66.21; H, 4.34; P, 5.34. Found: C, 65.47; H, 4.02; P, 5.48.

4.4.7. Compound ***5g***[28]

White solid; ^{1}H NMR ($CDCl_3$) δ 1.63 (m, 2H), 1.80 (m, 6H), 2.34 (m, 2H), 2.67 (m, 2H), 2.83 (m, 4H), 7.11 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 22.5, 22.6, 27.8, 29.2, 114.7 (d, J_{CF}=21.3), 126.9, 130.6, 131.0, 131.1, 132.9, 135.4, 137.6, 142.9 (d, J_{CP}=9.1), 160.5 (d, J_{CF}=245.7); ^{31}P NMR ($CDCl_3$) δ 2.0 (s); ^{19}F NMR ($CDCl_3$) δ −116.4 (s); MS (FAB) *m/z* 545.1 $[M+H]^+$. Anal. Calcd for $C_{32}H_{27}F_2O_4P$: C, 70.58; H, 5.00; P, 5.69. Found: C, 70.82; H, 5.39; P, 5.99.

4.4.8. Compound ***5h***

White solid; ^{1}H NMR ($CDCl_3$) δ 1.61 (m, 2H), 1.79 (m, 6H), 2.33 (m, 2H), 2.82 (m, 2H), 2.84 (m, 4H), 3.63 (s, 6H, 2×OCH_3), 6.80 (s, 4H, ArH), 7.12 (s, 2H, ArH), 7.44 (d, 4H, ArH); ^{13}C NMR ($CDCl_3$) δ 22.5, 22.6, 29.2, 29.7, 55.1 (OCH_3), 113.6, 126.9, 129.1, 130.4, 131.1, 135.3, 136.9, 142.7 (d, J_{CP}=9.2), 158.9; ^{31}P NMR ($CDCl_3$) δ 2.5 (s); MS (FAB) *m/z* 569.2 $[M+H]^+$. Anal. Calcd for $C_{34}H_{33}O_6P$: C, 71.82; H, 5.85; P, 5.45. Found: C, 72.17; H, 6.11; P, 5.79.

4.4.9. Compound ***5i***[30]

White solid; ^{1}H NMR ($CDCl_3$) δ 1.62 (m, 2H), 1.80 (s, 6H), 2.26 (m, 2H), 2.65 (m, 2H), 2.91 (m, 4H), 7.25 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 22.5, 22.6, 27.8, 29.2, 118.6, 118.8, 119.0, 119.1, 122.8, 123.3, 127.0 (d, J_{CP}=2.2), 128.2, 129.6, 129.8, 130.8, 131.0, 131.1 (d, J_{CP}=3.6), 131.8, 135.5 (d, J_{CP}=2.1), 135.6, 137.3 (d, J_{CP}=1.5), 142.7 (d, J_{CP}=9.1), 156.4, 156.6, 157.3; ^{31}P NMR ($CDCl_3$) δ 2.8 (s); MS (FAB) *m/z* 693.4 $[M+H]^+$, 715.4 $[M+Na]^+$; 731.4 $[M+K]^+$. Anal. Calcd for $C_{44}H_{37}O_6P$: C, 76.29; H, 5.38; P, 4.47. Found: C, 76.57; H, 5.73; P, 4.89.

4.4.10. Compound ***5j***

White solid; ^{1}H NMR ($CDCl_3$) δ 1.81 (m, 8H), 2.34 (m, 2H), 2.68 (m, 2H), 2.84 (m, 4H), 7.12 (s, 2H, ArH, BINOL), 7.46 (m, 10H, ArH), 7.84 (m, 8H, ArH); ^{13}C NMR ($CDCl_3$) δ 125.8, 126.9, 127.1, 127.8, 128.0, 129.3, 131.1 (d, J_{PC}=3.3), 131.6, 133.4, 135.3, 136.7, 137.4, 142.7 (d, J_{PC}=9.1); ^{31}P NMR ($CDCl_3$) δ 2.3 (s); MS (FAB pos.) *m/z* 708.2 $[M+H]^+$. Anal. Calcd for $C_{48}H_{37}O_4P$: C, 81.34; H, 5.26; P, 4.37. Found: C, 81.87; H, 5.41; P, 4.19.

4.4.11. Compound ***5k***[30]

White solid; ^{1}H NMR (DMSO-d_6) δ 1.84 (m, 8H), 2.50 (m, 2H), 2.90 (m, 6H), 7.23 (s, 2H, ArH, BINOL), 7.63 (m, 10H, ArH), 7.90 (m, 4H, ArH), 8.86 (m, 4H, ArH); ^{13}C NMR (DMSO-d_6) δ 22.2, 22.3, 27.6, 28.6, 122.8, 123.1, 125.9, 126.2, 126.4, 126.5, 126.8, 126.9, 127.3, 127.5, 128.6, 128.7, 129.4, 129.5, 129.7 (d, J_{CP}=2.1), 130.2, 130.6, 130.8, 131.0, 131.8, 132.2, 132.8, 133.8 (d, J_{CP}=5.8), 134.7, 136.8, 137.2, 144.0, 144.2 (d, J_{CP}=9.1); ^{31}P NMR (DMSO-d_6) δ 0.5 (s); MS (FAB neg.) *m/z* 707.2 $[M-H]^-$, (FAB pos.) *m/z* 709.2 $[M+H]^+$. Anal. Calcd for $C_{48}H_{37}O_4P$: C, 81.34; H, 5.26; P, 4.37. Found: C, 81.91; H, 5.47; P, 3.94.

4.5. Polymerization of **5e**

To a stirred solution of 206 mg of **5e** (0.36 mmol) and 7.5 mg azobisisobutyronitrile in 4 ml of a benzene/THF mixture (1.5:1), was added a warm (45 °C) aqueous solution of polyvinyl alcohol (12 mg in 1.2 ml, Mw 85,000–124,000, 87–89% hydrolyzed). After vigorously stirring at room temperature for 15 min to homogenize the particle size, the temperature was slowly raised up to 75–80 °C and the stirring was continued at this temperature until the educt spot disappeared during TLC control (ca. 10 h). The heterogeneous mixture was filtered and washed with hot water, ethanol/water, ethanol, THF, ethanol and hexane. White polymer beads of **6** were obtained in quantitative yield after drying under high vacuum. FTIR (KBr) ν 1626, 1603, 1235, 1096, 1005, 827; Raman (KBr) ν 1607, 1433; elemental analysis found: C, 63.91; H, 5.76; P, 3.13.

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