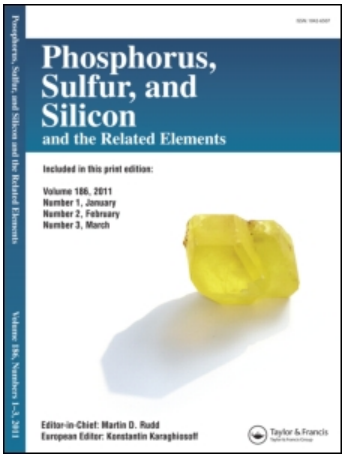

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SYNTHESIS OF NEW ALKYL DERIVATIVES OF 2,2'-DIHYDROXY-1,1'-BINAPHTHYL

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SYNTHESIS OF NEW ALKYL DERIVATIVES OF 2,2′-DIHYDROXY-1,1′-BINAPHTHYL

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2′-Hydroxy-1,1′-binaphthyl-2-yl phosphate **4** reacts with various alkylating agents under controlled conditions to give differently alkylated phosphoric esters **5–9**. The monoalkylation of binaphthol **1** with long-chain alkyl halides followed by reaction with phosphoryl chloride, propane-1,3-sultone or chlorosulfuric acid, respectively, yielded the amphiphilic binaphthyl derivatives **14–17**. The compounds prepared were fully characterized by spectroscopic methods.

Keywords: 2,2′-dihydroxy-1,1′-binaphthyl; 1,1′-binaphthyl-2-yl phosphates; amphiphiles; ^{1}H NMR; ^{13}C NMR; ^{31}P NMR

Dedicated to Prof. Dr. H. W. Krause on the Occasion of his 70th Birthday

INTRODUCTION

There is a considerable interest in the 2,2′-dihydroxy-1,1′-binaphthyl **1** and its derivatives. Although it has been known since 1926,[1,2] only quite recently the potential of this compound has been recognized for the application as chiral precursor or auxiliary in the asymmetric synthesis, as ligands in chiral complexes [3–16] and for analytical purposes.[17–23] In the last few years the application of amphiphiles as reaction medium for organic syntheses has been constantly raised.[24] Among them, binaphthyl derivatives were also used as amphiphiles.[25]

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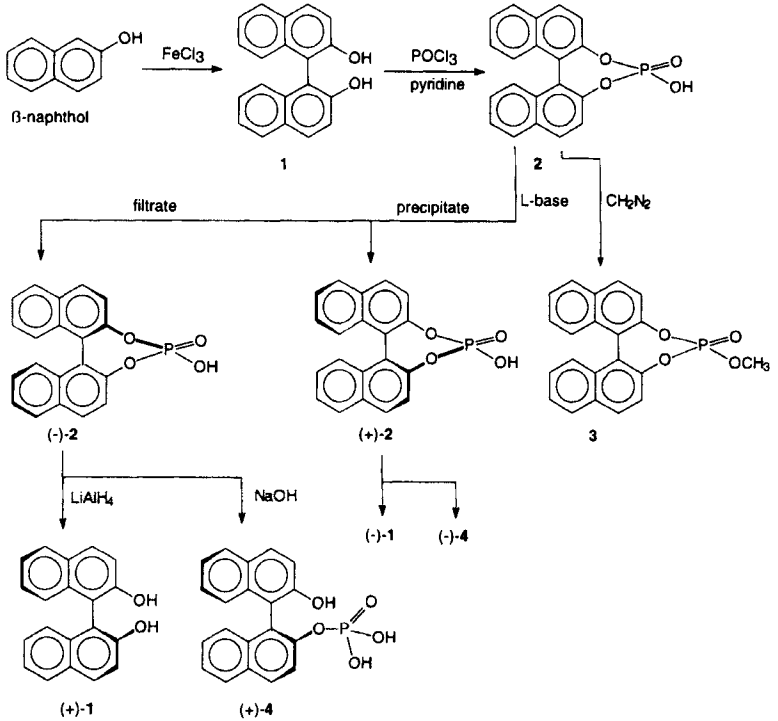
In the present paper, in continuation of our studies of chiral auxiliaries derived from **1**,[26] we want to report the synthesis and characterization of new optically active binaphthyl derivatives to use them both in the micellar catalysis and in the NMR spectroscopy.[21, 23]

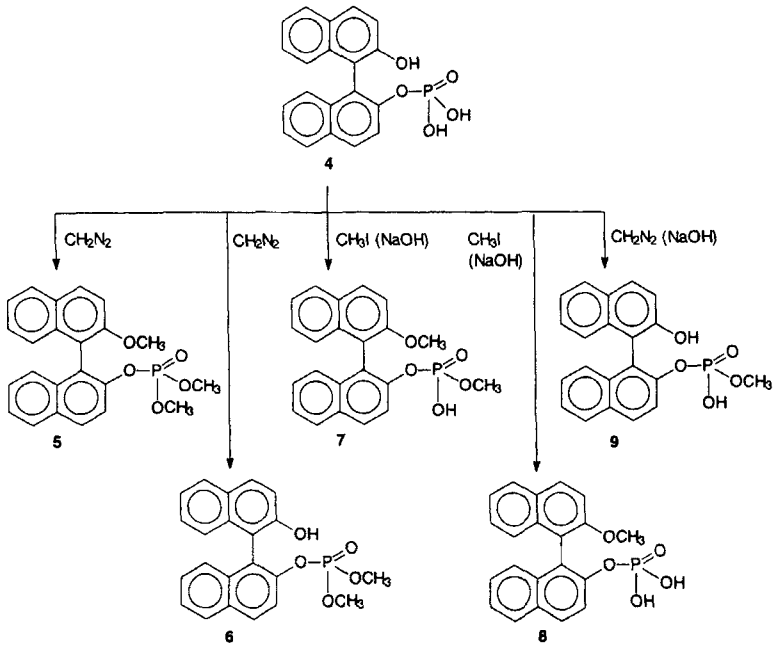
RESULTS AND DISCUSSION

1,1′-Binaphthyl-2,2′-diyl hydrogenphosphate **2** was prepared from 2,2′-dihydroxy-1,1′-binaphthyl **1** according to the procedure described by Jacques et al.[27,28] Racemic **2** was resolved with (1*S*,2*S*)-2-amino-1-(4-nitrophenyl)propane-1,3-diol, which is formed as byproduct (so-called "L-base") in the synthesis of chloramphenicol (Scheme 1).[29]



SCHEME 1

Further phosphoric acid derivatives of **1** were synthesized starting from **2**. Thus, the methylation of **2** with diazomethane led to compound **3**[27] (Scheme 1). By treatment of **2** with sodium hydroxide solution the ester **4** was obtained after precipitating the product with a diluted solution of hydrochloric acid. Compound **4** has been described by Jacques et al.[27] as intermediate to be formed in the synthesis of (-)-**5** (Scheme 2), but the authors did not isolate this product. The phosphoric ester **4** is interesting because of the three differently reactive OH groups. It was possible to carry out selectively reactions of the OH groups with various alkylating agents under controlled conditions. The isolation of **4** from the byproduct binaphthol **1** (ca. 10%) by column chromatography led to decomposition so that **4** was used without further purification.



SCHEME 2

In addition to **5** we prepared the compounds **6–9** by methylation with diazomethane and methyl iodide, respectively (Scheme 2).

Compounds **5** and **6** could be prepared with an etheric solution of diazomethane. Beside the racemates (±)-**5** and (±)-**6**, the optically active compounds (+)-**5** and (-)-**5** as well as (+)-**6** and (-)-**6** were prepared starting from (+)-**4** and (-)-**4**, respectively.

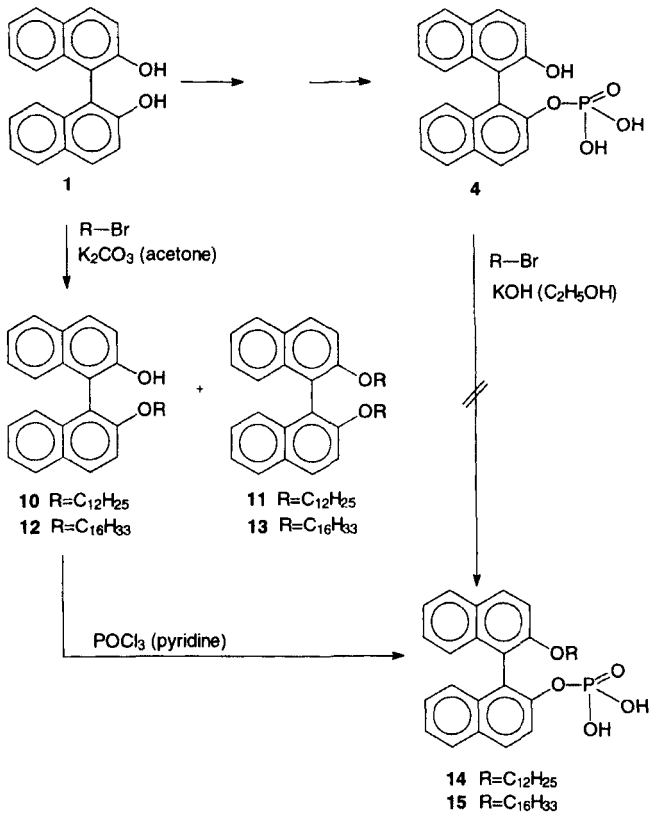
For preparation of **7–9** with diazomethane, the OH groups at the P atom in **4** have to be blocked selectively with an aqueous solution of sodium hydroxide. Thus, for 1 mmol of **4**, 8.56 mL of a 0.1N NaOH solution ($pH_1 = 4.93$) for the first and 17.36 mL ($pH_2 = 9.62$) for the second OH group are needed.

The diastereomeric compounds **9a** and **9b** were formed by blocking of one OH group at the phosphorus with sodium hydroxide and following methylation with diazomethane. The ^{1}H NMR spectrum of **9** showed both diastereomers in the ratio of 0.70:0.30. In the ^{31}P NMR spectrum two different signals were found at $\delta = -3.7$ and -3.1 in the same ratio.

The reactions of **4** with diazomethane to give **7** and **8** were not so selective, and mixtures of the different methyl compounds were obtained. However, using an excess of methyl iodide, compound **7** could be prepared in the presence of sodium hydroxide with formation of only a small amount of **8** as byproduct. Only compound **8** was obtained with a threefold amount of methyl iodide.

In the same way, we tried to synthesize the amphiphilic compounds **14** and **15**. As the reactions of **4** with long-chain alkyl halides were not successful, we chose the other route, the monoalkylation of **1** followed by reaction with phosphoryl chloride (see Scheme 3). The reactions of **1** with dodecyl and hexadecyl bromide to **10** and **12** were carried out in the presence of potassium carbonate in acetone. The products were separated at first by a bulb tube distillation from the nonconverted alkyl halide and then by column chromatography from the starting material **1** and the dialkoxy products **11** and **13**, respectively.

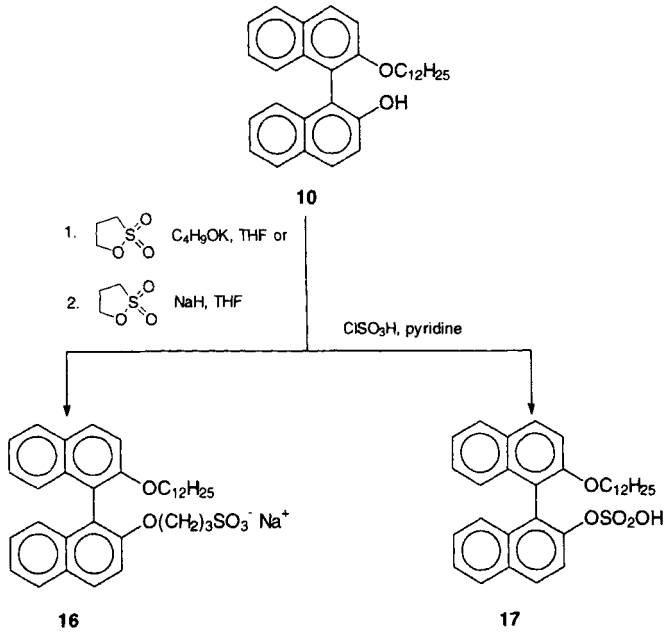
Starting from compounds **10** and **12**, respectively, the amphiphilic binaphthyl derivatives **14–17** were prepared (Schemes 3 and 4). The isolation and purification of **14** and **15** proved to be very complicated. Due to distributing into both the polar and nonpolar solvents because of its amphiphilic character, it was impossible to purify them by extraction as well as by column chromatography. After removal of the solvent the residue was carefully washed with water and dried to give the desired phosphoric ester. The isolation and purification of the reaction products seem to become more difficult with increasing chain length.



SCHEME 3

Furthermore, the sulfonate **16** was synthesized from the dodecyloxy compound **10** with propane-1,3-sultone in the presence of potassium *tert*-butanolate (Scheme 4). Better yields (85%) were observed by carrying out the reaction in the presence of sodium hydride. Finally, compound **17** was prepared by reaction of **10** with an excess of chlorosulfuric acid in pyridine at 0 °C.

As the product **17** decomposed both in solution and on the TLC plate, the purification had to be carried out quickly. After removal of the solvent and carefully drying it is stable for several months. The amphiphilic binaphthyl derivatives **14** and **16** were also synthesized as optically active compounds.



SCHEME 4

NMR Spectra and molecular structure of 6

The phosphoric acid esters **4–9** can be identified especially by ^{31}P NMR spectroscopy. ^{31}P chemical shifts as well as ^{1}H and ^{13}C data for the substituents are given in Table I.

The phosphorus NMR signal for **5** is observed at $\delta = -4.5$, for **6** at $\delta = -2.7$. For compound **4** a shift of $\delta = -4.9$ was found. In the coupled ^{31}P NMR spectrum the signal of **7** appears as a quartet at $\delta = -4.9$ due to ^{31}P-^{1}H coupling of the $POCH_3$ group while the signal of **8** is observed at $\delta = -5.3$ as a singlet.

Significant differences were also found in the ^{1}H NMR spectra. Thus, for the ester **5** two doublets at $\delta = 3.17$ and 3.32 are observed due to the non-equivalence of the two $POCH_3$ groups as well as a vicinal ^{31}P-^{1}H coupling ($^{3}J = 11.2$ Hz). The signal of the aryl methoxy group of **5** appears as a singlet at $\delta = 3.78$. For compound **6**, there are also two doublets at $\delta = 3.16$ and 3.55 with the coupling constants of 11.4 and 11.5 Hz, respec-

tively, but the signal of the phenolic OH group at $\delta = 6.16$ is found instead of a methoxy signal.

TABLE I ^{31}P, ^{1}H and ^{13}C NMR chemical shifts δ [ppm] and coupling constants $^{3}J(^{31}P, ^{1}H)$ and $^{2}J(^{31}P, ^{13}C)$ [Hz] (in parentheses) of compounds **2** and **4–9**

	Solvent	*^{31}P NMR*	*^{1}H NMR*			*^{13}C NMR*	
			OH	*C-OCH$_3$*	*P-OCH$_3$*	*C-OCH$_3$*	*P-OCH$_3$*
2	DMSO-d_6	+4.5	7.98	-	-	-	-
4	DMSO-d_6	-4.9	9.20	-	-	-	-
5	$CDCl_3$	-4.5	-	3.78 s	3.17 d	56.6	54.1 d
					(11.2)		(6.5)
					3.32 d		54.4 d
					(11.3)		(6.7)
6	$CDCl_3$	-2.7	6.16	-	3.16 d	-	54.3 d
					(11.4)		(6.4)
					3.55 d		54.8 d
					(11.5)		(6.6)
	DMSO-d_6	-3.9					
7	DMSO-d_6	-4.9	-	3.71 s	2.85 d	56.2	51.4 d
					(11.0)		(6.8)
8	DMSO-d_6	-5.3	8.31	3.72 s	-	56.4	-
9	$CDCl_3$	-3.1[a]	6.89	-	2.87 d[a]	-	53.9 d[a]
		-3.7[b]			(11.9)		(6.1)
					2.93 d[b]		54.1 d[b]
					(11.6)		(6.1)

[a, b] diastereomers, ratio 0.30[a]: 0.70[b].

The ^{1}H NMR spectrum of **7** displays a doublet at $\delta = 2.85$ ($^{3}J = 11.0$ Hz) for the $POCH_3$ group and a singlet at $\delta = 3.71$ for the methoxy group, while for compound **8** only a singlet at $\delta = 3.73$ for the aryl methoxy group is found.

TABLE II ^{1}H NMR chemical shifts δ [ppm] of selected compounds **1–17** (aromatic part) in $CDCl_3$ (**2** and **4** in DMSO-d_6)[a)]

	1	*2*	*4*	*6*	*10*	*14*	*17*
H-3	7.38d	7.58dd	7.83–7.89m[b)]	7.60dd	7.45d	7.70d	7.77d
H-3′			7.33d	7.38d	7.35d	7.23d	7.10d
H-4	7.97d	8.18dd	8.03d	8.02d	8.01d	7.65d	7.61d
H-4′				7.89d	7.89d	7.68d	7.56d
H-5	7.89dm	8.09dd	7.97d	7.93dt	7.89d	7.76dm	7.74dm
H-5′				7.83dm	7.85dm	7.62dm	7.53dm
H-6	7.37ddd	7.51dd	7.40ddd	7.47ddd	7.37ddd	7.34ddd	7.37ddd
H-6′			7.20–7.28m[c)]	7.28–7.33m[c)]	7.24–7.33m[c)]	7.03–7.14m[e)]	7.00–7.12m[e)]
H-7	7.30ddd	7.36ddd				7.18ddd	7.21ddd
H-7′			7.16m	7.20–7.28m[d)]	7.20–7.24m[d)]	6.95ddd	6.90m
H-8	7.15dm	7.24dd	6.95dm				
H-8′			6.87dm	7.04dm	7.06dm		

[a)]designation of atoms given in experimental part; [b)] H-3, H-4′, H-5′; [c)] H-6′, H-7; [d)] H-7′, H-8; [e)] H-6′, H-8, H-8′.

^1H and ^{13}C NMR data for the aromatic atoms of selected compounds are listed in Tables II–IV. The remaining data are given in the experimental section. Complete assignment of all signals was made by means of ^1H, ^1H-COSY and ^{13}C, ^1H-COR spectra. In the case of non-equivalence of the two naphthalene rings double sets of signals for the naphthalene atoms were found in the ^1H and ^{13}C NMR spectra. The assignment of the signals to both naphthalene rings as well as quarternary C atoms were possible by recording the COLOC and HMBC spectra, respectively. Thus, in the spectrum of **10** correlations were found for OH with C-1′, C-2′ and C-3′, H-3′ with C-1′ and C-10′, H-3 with C-1 and C-10, H-4′ with C-2′ and C-9′, H-4 with C-2 and C-9, C-1 with H-8, and C-1′ with H-8′, respectively. In addition, long-range correlations between H-4 and H-8 and H-4′ and H-8′, respectively, in the ^1H, ^1H-COSY spectra as well as H-4, H-5 and H-4′, H-5′ correlations in the ^1H, ^1H-NOESY spectra were found to be useful in assignment and interpretation of spectra. Moreover, for compounds with phosphorus containing substituents, the signals can be assigned to both naphthalene rings on the basis of ^{31}P, ^{13}C couplings. Twisting of the naphthalene rings about the C-1, C-1′ bond can be deduced from ^1H NMR spectra by the typical high-field shifts of H-8 and H-8′, which have also been found for other binaphthyl derivatives.[26]

TABLE III Coupling constants $J(^1H, ^1H)$ and $J(^{31}P, ^1H)$ [Hz] of selected compounds **1–17** (aromatic part)[a)]

	1	*2*	*4*	*6*	*10*	*14*	*17*
$^3J_{H\text{-}3,\,H\text{-}4}$	8.9	8.8	9.0	9.0	9.1	9.0	9.0
$^3J_{H\text{-}3',\,H\text{-}4'}$			9.0	8.9	8.9	9.1	9.1
$^3J_{H\text{-}5,\,H\text{-}6}$	8.0	8.3	8.0	8.1	8.0	8.0	8.0
$^3J_{H\text{-}5',\,H\text{-}6'}$				8.2	8.0	8.2	8.2
$^3J_{H\text{-}6,\,H\text{-}7}$	6.8	6.6	6.8	6.6	6.5	6.8	6.8
$^3J_{H\text{-}6',\,H\text{-}7'}$						6.8	
$^3J_{H\text{-}7,\,H\text{-}8}$	8.2	8.5	8.5			8.5	8.4
$^3J_{H\text{-}7',\,H\text{-}8'}$			8.3	8.3		8.0	8.0
$^4J_{H\text{-}5,\,H\text{-}7}$	1.6	1.5				1.3	
$^4J_{H\text{-}5',\,H\text{-}7'}$						1.3	
$^4J_{H\text{-}6,\,H\text{-}8}$	1.4	1.2	1.2	1.5	1.4	1.2	1.2
$^4J_{P,\,H\text{-}3}$		1.0		1.0			

[a)] designation of atoms given in experimental part.

TABLE IV ^{13}C NMR chemical shifts δ [ppm] and coupling constants $J(^{31}P, ^{13}C)$ [Hz] (in parentheses) of selected compounds **1–17** (aromatic part) in $CDCl_3$ (**2** and **4** in DMSO-d_6)[a)]

	1	*2*	*4*	*6*	*10*	*14*	*17*
C-1	110.8	121.2d (2.1)	122.5d (8.5)	122.6d (6.3)	116.4	122.9d (8.2)	124.0
C-1′			115.1	115.6	115.3	119.7	119.9
C-2	152.7	147.8d (9.3)	148.0d (5.8)	147.1d (7.0)	155.6	147.9d (6.0)	148.0
C-2′			153.1	152.2	151.3	154.5	152.2
C-3	117.7	121.4d (2.7)	120.0d (2.8)	119.9d (1.8)	115.7	120.3	120.7
C-3′			119.0	119.4	117.4	116.0	116.7
C-4	131.4	131.2d (1.0)	128.8	130.9d (1.8)	130.8	129.3	129.3
C-4′			129.2	130.2	129.6	129.0	129.8
C-5	128.4	128.8	127.9[b)]	128.2	128.1	127.9	128.0
C-5′			128.0[b)]	127.9	128.0	127.5	127.8
C-6	124.0	125.6	124.7	126.0	124.2	124.4	124.9
C-6′			122.5	123.6	123.1	123.4	123.9
C-7	127.5	127.0	126.4	127.5	127.2	125.8	126.0
C-7′			126.1	126.7	126.2	126.2	126.2
C-8	124.2	126.3	125.5	125.8	125.0	126.0	126.2
C-8′			124.5	124.6	125.0	126.0	125.9
C-9	133.4	131.2d (1.5)[b)]	133.6	133.7d (1.0)	134.1	133.9	123.7[b)]
C-9′			134.1	133.7	133.9	133.9	123.8[b)]
C-10	129.4	131.8d (1.3)[b)]	130.3	131.7d (1.0)	129.6	130.6	131.2
C-10′			128.2	129.1	129.1	128.9	129.1

[a)] designation of atoms given in experimental part; [b)] exchangable.

Additionally, the structure of **6** could be proved by an X-ray structure analysis (Figure 1).

SUMMARY

The 2′-hydroxy-1,1′-binaphthyl-2-yl phosphate **4** was prepared by ring-opening of 1,1′-binaphthyl-2,2′-diyl hydrogenphosphate **2** with

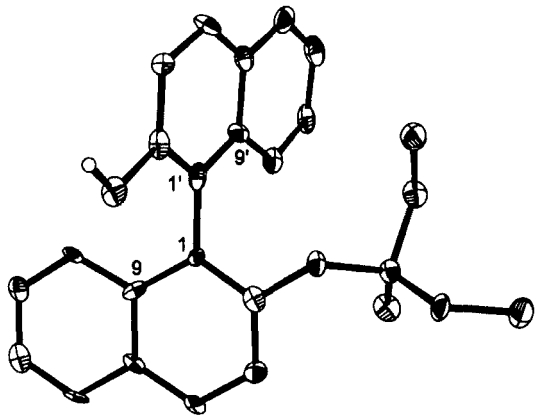


FIGURE 1 ORTEP-Plot (30% probability) of the molecular structure of **6** (torsion angle C(9)-C(1)-C(1′)-C(9′) = 64.9°)

sodium hydroxide solution. **4** reacted under controlled conditions to give the differently methylated derivatives **5–9**. The reactions of **4** with dodecyl or hexadecyl bromide to give the amphiphilic compounds **14** and **15** were not succesful, but **14** and **15** could be prepared by another route, i.e. by alkylation of **1** to the monoalkylated products **10** and **12**, respectively, followed by reaction with $POCl_3$. In the same way, the amphiphilic binaphthol derivatives **16** and **17** were available by reaction with propane-1,3-sultone and chlorosulfuric acid, respectively.

EXPERIMENTAL

2,2′-Dihydroxy-1,1′-binaphthyl **1** was purchased from Aldrich and Janssen. Reagents and solvents were dried and purified by distillation before used. Melting points were determined with a Boetius micro heating stage (Carl Zeiss Jena). Elemental analyses were performed using a CHNS-932 LECO analyzer. IR spectra (in KBr pellets) were recorded with a Nicolet Magna 550 FTIR spectrometer. Mass spectra were taken with an AMD 402/3 spectrometer (Intectra). The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX-300 spectrometer (^{1}H: 300.13 MHz, ^{13}C:

75.48 MHz, ^{31}P: 121.5 MHz). The calibration of ^{1}H and ^{13}C spectra was carried out by means of solvent peaks ($CDCl_3$: δ $^{1}H = 7.25$; δ $^{13}C = 77.0$; DMSO-d_6: δ $^{1}H = 2.50$; δ $^{13}C = 39.7$). The ^{31}P chemical shifts are referenced to 85% H_3PO_4. HPLC was done on a Knauer apparatus with UV detection and a column packed with *N*-(3,5-dinitrobenzoyl)phenylglycine (4.6×250 mm; 5 µm) (J. T. Baker Inc). Preparative TLC was performed on Merck silica gel 60 F_{254} precoated glass plates. TLC were performed on Merck silica gel 60 F_{254} aluminum foils as well as Silufol® foils (Sklo Union, Sklárny Kavalier, koncernový podnik, závod 01, Votice, Czech Republic). The detection was carried out by UV ($\lambda = 254$ nm) and/or a 10% alcoholic solution of wolframato phosphoric acid. The optical rotation was determined with the polarimeter "gyromat-HP" (Firma Dr. Kernchen) at 589 nm (sodium-D line). The determination of pH was carried out on the Microprocessor pH Meter, pH 539 from Wissenschaftlich-technische Werkstätten GmbH Weilheim.

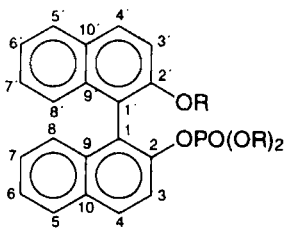
X-Ray crystal structure of 6

Single crystals were obtained by slow evaporation of an ethanol solution. Enraf-Nonius CAD4 MACH3 diffractometer, graphite monochromated Mo-K_α radiation, $\lambda = 0.71069$ Å, structure solution direct methods (SHELXS-86),[30] least square refinement against F^2(SHELXL-93),[31] structure representation: XP (Siemens), compound **6**: $0.5 \times 0.1 \times 0.05$ mm, colorless crystals, space group P $2_12_12_1$, orthorhombic, a = 7.205(2), b = 8.766(2), c = 29.317(4) Å, V = 1851.6 (7) Å^3, Z = 4, $\rho_{cal.} = 1.415$ g cm^{-3}, 1365 collected, 943 observed ($I = 2\sigma(I)$), R = 0.0622, wR^2 (all data) = 0.1708, 267 parameters. Crystallographic data (without Fo/Fc list) have been deposited at the Cambridge Crystallographic Data Centre. Copies can be obtained from the following address: The Director, CCDC, 12 Union Road. GB-Cambridge CB2 1EZ (fax: 1223/336033; e-mail: teched@chemcrys.cam.ac.uk).

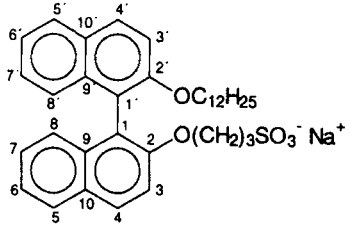
Preparation of compounds

1,1'-Binaphthyl-2,2'-diyl hydrogenphosphate 2

To a suspension of 42.9 g (0.15 mol) of **1** in 240mL abs. pyridine, 19.2mL (0.21 mol) of phosphoryl chloride were added dropwise with stirring at



4-9, 14, 15



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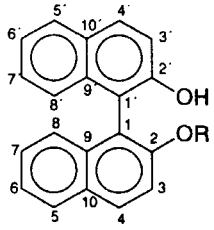
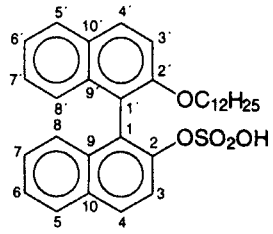


10, 12



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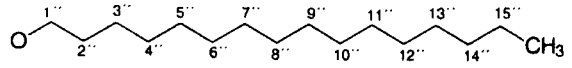

SCHEME 5 Designation of atoms in the binaphthyl system and in the chain

0 °C during 30 min. The temperature must be kept below 20 °C. After stirring the reaction mixture for 1 h at 0 °C, 5 mL of water were added and 370 mL of a 2N NaOH solution were added slowly. The clear mixture was left to stand for 1 h and 650 mL of a 6N HCl solution were then added dropwise. After stirring for 3 h the resulting precipitate was filtered off, washed with water several times and dried at 60 °C. The crude product was recrystallized from ethanol.

(±)-**2**: Colorless crystals, *mp* = 232–235 °C; yield: 95%.

NMR: ^{1}H, ^{13}C and ^{31}P: Tables I–IV.

MS (70 eV): m/z = 348 (M^+, 63), 286 (95), 268 (72), 257 (25), 239 (61), 226 (20).

IR (KBr): ν = 3416 (OH); 3063 (arom.); 2900–2500 (br, OH); 1621, 1593, 1506, 1489 (arom.); 1347; 1226 (P=O); 1072; 971; 815, 749 (arom.) cm^{-1}.

HPLC: eluent: *n*-hexane/isopropanol/ethanol (80:20:30).

$C_{20}H_{13}O_4P$ (348.06)	Calcd. C 68.95 H 3.76 P 8.90
	Found C 68.73 H 3.96 P 8.55

Determination of the equivalence point and pH value: 1 mmol of 2 were dissolved in a methanol/water solution (2:1). By titration with 0.1N NaOH (f_{NaOH}= 1.002) the following equivalence point and pH were obtained: $V_{equ.}$ = 9.9 mL; *pH* = 7.0 (three measurements).

Resolution of 2 with (1S,2S)-2-amino-1-(4-nitrophenyl)propane-1,3-diol (L-base)[29]

52.2 g (0.15 mol) of **2** and 15.9 g (0.075 mol) of L-base were dissolved in 150 mL of hot methanol, filtered, and then 1.8 L of acetone were added. The crystallization of the diastereomeric salt began after 20 min. After cooling overnight the salt was filtered off and washed with acetone.

Colorless needles, *mp* = 220–230 °C; $[\alpha]_D^{25}$ = 592.7 (*c* = 1, methanol); yield: 13%.

(+)-1,1′-Binaphthyl-2,2′-diyl hydrogenphosphate (+)-2

The diastereomeric salt was suspended with stirring in 500 mL of water and 20 mL of concentrated HCl solution were added dropwise. The mixture was then heated to 95 °C. After cooling the resulting precipitate was filtered off, washed with water several times and recrystallized from ethanol.

Colorless crystals, $[\alpha]_D^{22}$ = 606.0 (*c* = 1, methanol); yield: 96%.

HPLC: eluent: *n*-hexane/isopropanol/ethanol (80:20:30); 99.9% *ee*.

(-)-1,1′-Binaphthyl-2,2′-diyl hydrogenphosphate (-)-2

The filtrate was evaporated and the residue suspended with stirring in 500 mL of water. Then, 20 mL of concentrated HCl solution were added dropwise and the temperature was increased to 95 °C. After cooling the resulting precipitate was filtered off, washed with water several times and recrystallized from ethanol. Colorless crystals, $[\alpha]_D^{22}$ = −593 (*c* = 1, methanol); yield: 98%.

HPLC: eluent: *n*-hexane/isopropanol/ethanol (80:20:30); 99.9% *ee*.

(+)- and (-)-2,2′-Dihydroxy-1,1′-binaphthyl (+)-1 and (-)-1

To 5.0 g (0.132 mol) of lithium aluminum hydride, 100 mL of abs. ether were slowly added at 0 °C. Then, 10.44 g (0.03 mol) of (+)-**2** and (-)-**2**, respectively, were added in portions with stirring. The reaction mixture was stirred for 1.5 h at room temperature and then refluxed for 1 h. Afterwards the mixture was cooled to 0 °C and 20 mL of distilled water were added carefully. At the end of addition aluminum hydroxide precipitated, which was dissolved by adding 100 mL of a 10% sulfuric acid solution. The phases formed were separated, the etheric phase was washed repeatedly with water and dried with sodium sulfate. After removing the ether the resulting precipitate was recrystallized from toluene.

(+)-**1**: Colorless crystals, *mp* = 211–213 °C; $[\alpha]_D^{20} = 35.0$ (*c* = 1, THF); yield: 77%.

NMR: ^1H ($CDCl_3$): δ [ppm] 5.02 (s, 1H, OH); Tables II and III; ^{13}C: Table IV.

MS (70 eV): *m/z* = 286 (M^+ 100), 268 (5), 258 (4), 257 (5), 239 (5), 229 (5), 226 (5), 215 (2), 134 (5), 119 (6), 115 (6).

IR (KBr): *v* = 3487, 3404 (OH); 3060, 1618, 1560, 1509, 1471 (arom.); 1382; 1322; 1273; 1253; 1217; 1176: 1126; 827; 816, 751 (arom.) cm^{-1}.

$C_{20}H_{14}O_2$ (286.10):	Calcd. C 83.89 H 4.93
	Found C 83.84 H 5.01

HPLC: eluent: *n*-hexane/isopropanol (95:5); 100% *ee*.

(-)-**1**: Colorless crystals, *mp* = 211–212 °C; $[\alpha]_D^{24} = -24.8$ (*c* = 1, methanol); yield: 93%.

HPLC: eluent: *n*-hexane/isopropanol (95:5); 100% *ee*.

1,1′-Binaphthyl-2,2′-diyl methyl phosphate 3

3.48 g (0.01 mol) of **2** were dissolved in a methanol/water solution (10:1) at room temperature. Then, an etheric diazomethane solution was added dropwise until a weak yellow coloring was observed. The precipitate formed was filtered off, the filtrate evaporated and the residue dried in air.

(+)-**3**: Colorless solid, *mp* = 182 °C; $[\alpha]_D^{23} = 516.9$ (*c* = 0.21, methanol).

NMR: ^1H ($CDCl_3$): δ [ppm] 3.98 (d, 3H, $J_{P,H} \approx 11.5$ Hz, CH_3); 7.25–7.40 (m, 4H, H-7, H-7′, H-8, H-8′); 7.44–7.51 (m, 2H, H-6, H-6′); 7.48 (dd, 1H, $J_{H\text{-}3,H\text{-}4} \approx 8.8$ Hz, $J_{P,H} \approx 1.0$ Hz), 7.60 (dd, 1H, $J_{H\text{-}3,H\text{-}4} \approx 8.8$ Hz, $J_{P,H} \approx 1.0$ Hz) (H-3, H-3′); 7.94 (d, 2H, $J_{H\text{-}5,H\text{-}6} \approx 8.2$ Hz, H-5, H-5′); 8.02 (d, 1H, $J_{H\text{-}3,H\text{-}4} \approx 8.8$ Hz), 8.04 (d, 1H, $J_{H\text{-}3,H\text{-}4} \approx 8.8$ Hz) (H-4,

H-4′); ^{13}C ($CDCl_3$): δ [ppm] 55.8 (d, $J_{P,C} \approx 6.0$ Hz, CH_3); 120.1 (d, $J_{P,C} \approx 3.2$ Hz), 120.6 (d, $J_{P,C} \approx 2.7$ Hz) (C-3, C-3′); 121.2 (d, $J_{P,C} \approx 2.2$ Hz), 121.4 (d, $J_{P,C} \approx 2.2$ Hz) (C-1, C-1′): 125.8 (C-6, C-6′); 126.78, 126.83 (C-7, C-7′); 127.0, 127.2 (C-8, C-8′); 128.4, 128.5 (C-5, C-5′); 131.2 (d, $J_{P,C} \approx 1.5$ Hz), 131.5 (d, $J_{P,C} \approx 1.0$ Hz) (C-4, C-4′); 131.7 (d, $J_{P,C} \approx 1.5$ Hz), 131.9 (d, $J_{P,C} \approx 1.5$ Hz), 132.28 (d, $J_{P,C} \approx 1.5$ Hz), 132.31 (d, $J_{P,C} \approx 1.3$ Hz) (C-9, C-9′, C-10, C-10′); 146.3 (d, $J_{P,C} \approx 8.2$ Hz), 147.4 (d, $J_{P,C} \approx 9.2$ Hz) (C-2, C-2′); ^{31}P ($CDCl_3$): δ [ppm] 4.5.

MS (70 eV): $m/z = 362$ (M^+, 100), 347 (23), 268 (51), 239 (36), 226 (16).

IR (KBr): $\nu = 3067$ (arom.); 2957, 2855 (CH_3); 1619, 1591, 1507 (arom.); 1466; 1330; 1310; 1230 (P=O); 1204; 1048; 1029; 988; 969; 950; 893; 818, 750 (arom.); 563 cm^{-1}.

2′-Hydroxy-1,1′-binaphthyl-2-yl phosphate **4**

10.44 g (0.03 mol) of **2** were suspended in 90mL of 1N sodium hydroxide solution and refluxed for 3 h. After cooling to room temperature 100 mL of distilled water were added and the precipitate formed was filtered off. After adding 28 mL of a 6N HCl solution (pH = 2) the precipitate was extracted with ether, and the etheric layer washed twice with water, dried with sodium sulfate and then evaporated.

(±)-**4**: Colorless solid, *mp* = 201–203 °C: yield: 70%.

NMR: ^1H, ^{13}C and ^{31}P: Tables I–IV.

MS (FD pos., DMSO): $m/z = 366$ (M^+, 100), 348 (31).

IR (KBr): $\nu = 3422$ (OH); 3058 (arom.); 2800–2450 (br, OH); 1621, 1593, 1507 (arom.); 1460; 1433; 1346; 1330; 1271; 1212 (P=O); 1145; 1074; 1031; 999 (P-OH); 975; 934; 815, 752 (arom.); 589; 494 (P=O) cm^{-1}.

$C_{20}H_{15}O_5P$ (366.07):	Calcd. C 65.56 H 4.13 P 8.46
	Found C 66.61 H 4.97 P 7.91

Determination of the equivalence points and pH values: 1 mmol of **4** was dissolved in a methanol/water solution (10:1). By titration with 0.1N NaOH (f_{NaOH}= 1.002) the following values were obtained: $V_{equ.1}$= 8.56 mL: $pH_1 = 4.93$; $V_{equ.2} = 17.36$ mL; $pH_2 = 9.62$ (three measurements).

(+)-**4**: Colorless solid, *mp* = 201–203 °C; $[\alpha]_D^{22} = 30.1$ ($c = 1$, methanol); yield: 45%.

(-)-**4**: Colorless solid, *mp* = 201–203 °C; $[\alpha]_D^{24} = -33.1$ (*c* = 1, methanol); yield: 43%.

2′-Methoxy-1,1′-binaphthyl-2-yl dimethyl phosphate 5

0.366 g (1 mmol) of (-)-**4** were dissolved in 10 mL of a methanol/water solution (10:1) at room temperature. An excess of an etheric diazomethane solution was then added dropwise. The reaction was controlled by TLC ($R_f = 0.55$, eluent $CHCl_3$/MeOH 20:1). After staying overnight the ether was removed and the resulting precipitate recrystallized from ethanol.

(-)-**5**: Colorless crystals, *mp* = 140–144 °C; $[\alpha]_D^{19} = -13.23$ (*c* = 1, methanol); yield: 69%.

NMR: ^{1}H ($CDCl_3$): δ [ppm] 3.17 (d, 3H, $J_{P,H} \approx 11.2$ Hz, $POCH_3$); 3.32 (d, 3H, $J_{P,H} \approx 11.3$ Hz, $POCH_3$); 3.78 (s, 3H, OCH_3); 7.15 (dm, 1H, $J_{H\text{-}7',H\text{-}8'} \approx 8.4$ Hz, H-8′); 7.20–7.30 (m, 3H, H-7, H-7′, H-8); 7.32 (ddd, 1H, $J_{H\text{-}5',H\text{-}6'} \approx 8.0$ Hz, $J_{H\text{-}6',H\text{-}7'} \approx 6.8$ Hz, $J_{H\text{-}6',H\text{-}8'} \approx 2.0$ Hz, H-6′); 7.42 (ddd, 1H, $J_{H\text{-}5,H\text{-}6} \approx 8.2$ Hz, $J_{H\text{-}6,H\text{-}7} \approx 6.2$ Hz, $J_{H\text{-}6,H\text{-}8} \approx 2.0$ Hz, H-6); 7.44 (d, 1H, $J_{H\text{-}3',H\text{-}4'} \approx 9.0$ Hz, H-3′); 7.73 (dd, 1H, $J_{H\text{-}3,H\text{-}4} \approx 9.0$ Hz, $J_{P,H\text{-}3} \approx 1.0$ Hz, H-3); 7.84 (dm, 1H, $J_{H\text{-}5',H\text{-}6'} \approx 8.0$ Hz, H-5′); 7.91 (dt, 1H, $J_{H\text{-}5,H\text{-}6} \approx 8.2$ Hz, $J \approx 1.0$ Hz, H-5); 7.97 (d, 1H, $J_{H\text{-}3,H\text{-}4} \approx 9.0$ Hz, H-4); 7.98 (d, 1H, $J_{H\text{-}3',H\text{-}4'} \approx 9.0$ Hz, H-4′); ^{13}C ($CDCl_3$): δ [ppm] 54.1 (d, $J_{P,C} \approx 6.5$ Hz, $POCH_3$); 54.4 (d, $J_{P,C} \approx 6.7$ Hz, $POCH_3$); 56.6 (OCH_3); 113.6 (C-3′); 117.8 (C-1′); 119.6 (d, $J_{P,C} \approx 1.6$ Hz, C-3); 123.5 (d, $J_{P,C} \approx 7.6$ Hz, C-1); 123.7 (C-6′); 125.2 (C-6); 125.3 (C-8′); 126.0 (C-8); 126.6 (C-7, C-7′); 127.7 (C-5′); 128.0 (C-5); 128.9 (C-10′); 129.6 (d, $J_{P,C} \approx 1.0$ Hz, C-4); 129.9 (C-4′); 131.2 (d, $J_{P,C} \approx 1.0$ Hz, C-10); 133.8 (C-9, C-9′); 146.3 (d, $J_{P,C} \approx 7.0$ Hz, C-2); 155.1 (C-2′); ^{31}P ($CDCl_3$): δ [ppm] –4.5, (DMSO-d_6): δ [ppm] –3.9.

MS (70eV): *m/z* = 408 (M^+, 70), 281 (100), 268 (98), 252 (51), 239 (82), 226 (26).

IR (KBr): *v* = 3057 (arom.); 2998, 2954, 2843 (CH_3); 1620, 1593, 1508, 1477 (arom.); 1463 (CH_3); 1291; 1273; 1264; 1251; 1231; 1088; 1055; 1032; 1007; 869; 852; 813 (arom.); 765; 748 (arom.); 484; 458 cm^{-1}.

$C_{23}H_{21}O_5P$ (408.11)	Calcd. C 67.63 H 5.19 P 7.59
	Found C 67.83 H 5.11 P 7.68

(+)-**5**: Colorless crystals, *mp* = 146–147 °C; $[\alpha]_D^{19} = 11.6$ (*c* = 1, methanol); yield: 57%.

2′-Hydroxy-1,1′-binaphthyl-2-yl dimethyl phosphate 6

0.366 g (1 mmol) of (-)-**4** were dissolved in 10 mL of a methanol/water solution (10:1) at room temperature. An etheric diazomethane solution was added with stirring and the reaction controlled by TLC ($R_f = 0.46$, eluent $CHCl_3$/MeOH 20:1). After cooling the reaction mixture the precipitated crystals were recrystallized from ethanol.

(-)-**6**: Colorless crystals, *mp* = 158–160 °C; $[\alpha]_D^{27} = -6.3$ ($c = 1$, methanol); yield: 39%.

NMR: ^1H, ^{13}C and ^{31}P: Tables I–IV.

MS (CI, isobutane): $m/z = 395$ (M+1).

IR (KBr): $\nu = 3150$ (br, OH); 1624, 1594, 1506 (arom.); 1464; 1437; 1430; 1347; 1330; 1258; 1219 (P=O); 1210; 1185; 1145; 1062 (P-O-CH_3); 1030; 993; 978; 940; 876; 860; 815; 776; 765; 751; 473 cm^{-1}.

$C_{22}H_{19}O_5P$ (394.10):	Calcd. C 66.99 H 4.86 P 7.86
	Found C 67.06 H 4.78 P 7.92

(+)-**6**: Colorless crystals, *mp* = 164–166 °C; $[\alpha]_D = 5.0$ ($c = 1$, methanol); yield: 39%.

2′-Methoxy-1,1′-binaphthyl-2-yl methyl phosphate 7

0.2 g (5 mmol) of sodium hydroxide were dissolved in 20 mL of water at room temperature and 0.366 g (1 mmol) of **4** and 0.62 mL (10 mmol) of methyl iodide were added. The reaction mixture was refluxed for 2 h and the precipitate formed was filtered off. The filtrate was treated with a 6N HCl solution ($pH = 2$). The formed precipitate was filtered off, washed with water several times and then extracted with chloroform. The extract was washed with water, dried with sodium sulfate, and the solvent was then distilled off.

(±)-**7**: Light-brown solid, *mp* = 95–97 °C, $R_f = 0.70$ (eluent $CHCl_3$/MeOH 1:2).; yield: 44%.

NMR: ^1H (DMSO-d_6): δ [ppm] 2.85 (d, 3H, $J_{P,H} \approx 11.0$ Hz, $POCH_3$); 3.71 (s, 3H, OCH_3); 6.88 (d, 1H, $J_{H\text{-}7,\,H\text{-}8} \approx 8.4$ Hz, H-8); 6.99 (d, 1H, $J_{H\text{-}7',\,H\text{-}8'} \approx 8.4$ Hz, H-8′); 7.13–7.22 (m, 2H, H-7, H-7′); 7.25–7.33 (m, 2H, H-6, H-6′); 7.58 (d, 1H, $J_{H\text{-}3',\,H\text{-}4'} \approx 9.0$ Hz, H-3′); 7.87–7.94 (m, 3H, H-4, H-5, H-5′); 8.04 (d, 1H, $J_{H\text{-}3',\,H\text{-}4'} \approx 9.0$ Hz, H-4′); 8.12 (d, 1H, $J_{H\text{-}3,\,H\text{-}4} \approx 9.0$ Hz, H-3); ^{13}C (DMSO-d_6): δ [ppm] 51.4 (d, $J_{P,C} \approx 6.8$ Hz, $POCH_3$); 56.2 (OCH_3); 114.4 (C-3′); 119.3 (C-1′); 120.0 (d, $J_{P,C} \approx 8.4$ Hz, C-1); 121.3 (d, $J_{P,C} \approx 2.2$ Hz, C-3); 123.3, 123.4 (C-6, C-6′); 124.8 (C-8);

125.2 (C-8′); 125.8 (C-7); 126.1 (C-7′); 127.9 (C-5, C-5′); 127.9 (C-4); 128.8 (C-10′); 129.1 (C-10); 129.2 (C-4′); 133.6, 133.7 (C-9, C-9′); 150.3 (d, $J_{P,C} \approx 5.5$ Hz, C-2); 154.8 (C-2′); ^{31}P (DMSO-d_6): δ[ppm] –4.9.

MS (70 eV): $m/z = 394$ (M^+, 100).

IR (KBr): $\nu = 3440$ (OH); 3050, 3000 (arom.); 2940, 2840 (CH_3); 1622, 1592, 1507, 1475 (arom.); 1462 (CH_3); 1430; 1358; 1332; 1263; 1251 (br, P=O); 1236; 1147; 1088 (P-O-CH_3); 1056; 994 (P-OH); 833; 812, 749 (arom.); 507 cm^{-1}.

$C_{20}H_{19}O_5P$ (394.10):	Calcd. C 66.99 H 4.86 P 7.86
	Found C 65.33 H 4.87 P 7.86

2′-Methoxy-1,1′-binaphthyl-2-yl dihydrogenphosphate 8

0.2 g (5 mmol) of sodium hydroxide were dissolved in 20 mL of water at room temperature, and then 0.366 g (1 mmol) of **4** and 0.1 mL (1.5 mmol) of methyl iodide were added. The reaction mixture was refluxed for 2h and let stand overnight. After adding 30 mL of water the mixture was acidified with 6N HCl solution (*pH* = 2). The precipitate formed was extracted with chloroform, washed with water several times, dried with sodium sulfate, and the solvent was then distilled off.

(±)-**8**: Brown solid, *mp* = 120–140 °C, $R_f = 0.43$ (eluent $CHCl_3$/MeOH 1:2).; yield: 5%.

NMR: ^{1}H (DMSO-d_6): δ [ppm] 3.72 (s, 3H, OCH_3); 6.86–8.12 (m, 12H, H_{aryl}); 8.31 (s, OH); ^{13}C (DMSO-d_6): δ [ppm] 56.4 (OCH_3); 114.4–155.0 (C_{aryl}); ^{31}P (DMSO-d_6): δ [ppm] –5.3.

MS (70 eV): $m/z = 380$ (M^+, 10); 300 (94); 286 (100).

IR (KBr): $\nu = 3420$ (OH); 3058 (arom.); 1622, 1592, 1507 (arom.); 1462 (CH_3); 1432; 1329; 1263; 1216; 1146; 1073; 1032; 1002; 813, 748 (arom.); 491 cm^{-1}.

2′-Hydroxy-1,1′-binaphthyl-2-yl methyl hydrogenphosphate 9

0.366 g (1 mmol) of **4** were dissolved in 10 mL of methanol at room temperature and 8.56 mL of 0.1N sodium hydroxide solution (34 mg, 0.86 mmol) were added. Then 2.5 mL of an etheric diazomethane solution were added to the mixture with stirring. The reaction was controlled by TLC ($R_f = 0.13$ and 0.21, eluent $CHCl_3$/MeOH 20:1). The solvent was then distilled off, the residue treated with 25 mL of water and acidified with 6N HCl solution (*pH* = 2). The resulting precipitate was extracted

with chloroform, the chloroformic layer washed with water, dried with sodium sulfate and then evaporated in vacuo.

(±)-**9**: Amorphous substance, *mp* = 93 °C; yield: 53%.

NMR: ^{1}H ($CDCl_3$): δ [ppm] 2.87 (d, 3H, $J_{P,H} \approx 11.9$ Hz), 2.93 (d, 3H, $J_{P,H} \approx 11.6$ Hz), (ratio 0.30:0.70, $POCH_3$); 6.89 (br s, OH); 6.99–8.02 (m, H_{aryl}); ^{13}C ($CDCl_3$): δ [ppm] 53.9 (d, $J_{P,C} \approx 6.1$ Hz), 54.1 (d, $J_{P,C} \approx 6.1$ Hz), (ratio 0.30:0.70, $POCH_3$); 111.0–155.1 (C_{aryl}); ^{31}P ($CDCl_3$): δ [ppm] −3.1, −3.7 (ratio 0.30:0.70).

MS (70 eV): *m/z* = 380 (M^+, 48), 348 (25), 300 (25), 286 (54), 268 (100), 239 (50), 134 (24), 119 (30).

IR (KBr): *v* = 3427 (OH); 3058 (arom.); 2955, 2853 (CH_3); 1622, 1593, 1507 (arom.); 1461 (CH_3); 1432; 1251; 1218; 1146; 1056; 1030; 1000; 871; 815, 749 (arom.) cm^{-1}.

$C_{21}H_{17}O_5P$ (380.09):	Calcd. C 66.30 H 4.51 P 8.15
	Found C 66.05 H 4.87 P 7.64

2-Dodecyloxy-2′-hydroxy-1,1′-binaphthyl 10 and 2-Hexadecyloxy-2′-hydroxy-1,1′-binaphthyl 12

7.15 g (25 mmol) of **1** were dissolved with stirring in 100 mL of acetone and 4.84 g (35 mmol) of anhydrous potassium carbonate were added. After stirring for 1 h at room temperature 7.2 mL (30 mmol) of dodecyl bromide or 9.2 mL (30 mmol) of hexadecyl bromide, respectively, were added and the mixture was refluxed for 8 h. The reaction was controlled by TLC (Silufol® foils, eluent *n*-hexane/ethyl acetate (9:1), detection by 10% ethanolic wolframato phosphoric acid solution, R_f = 0.18 (**10**) and 0.19 (**12**)). Then, the potassium carbonate was filtered off. The filtrate was evaporated and the residue subjected to a bulb tube distillation in order to remove unreacted alkyl bromide. The crude product was dissolved in a small amount of ethyl acetate and purified by means of column chromatography.

(±)-**10**: Colorless, waxy solid, *mp* = 53–55 °C; yield: 53%.

NMR: ^{1}H ($CDCl_3$): δ [ppm] 0.91 (t, 3H, CH_3); 0.89–1.38 (m, 18H, H-3″-H-11″); 1.44 (m, 2H, H-2″); 3.98 (m, 2H, H-1″); 4.95 (s, OH); Tables II and III; ^{13}C ($CDCl_3$): δ [ppm] 14.1 (CH_3); 22.7 (C-11″); 25.5 (C-3″); 29.1, 29.37, 29.39, 29.5, 29.63, 29.65 (C-4″-C-9″); 29.2 (C-2″); 31.9 (C-10″); 69.8 (C-10″); Table IV.

MS (CI, isobutane): m/z = 455 ($[M+1]^+$, 100), 287 (8).

IR (KBr): ν = 3535 (OH); 3057 (arom.); 2917, 2850 (CH_2, CH_3); 1620, 1591, 1508 (arom.); 1469 (CH_2, CH_3); 1431, 1379 (CH_3); 1330; 1264 (C-O); 1245 (C-O-C); 1206; 1172; 1127; 1077 (C-O-C); 1046; 1016; 808, 745 (arom.) cm^{-1}.

$C_{32}H_{38}O_2$ (454.29):	Calcd. C 84.53 H 8.43
	Found C 84.27 H 8.32

(+)-**10**: Colorless, waxy solid, mp = 51–53 °C; $[\alpha]_D^{24}$ = 16.0 (c = 1, THF) yield: 46%.

(-)-**10**: Colorless, waxy solid, mp = 52 °C; $[\alpha]_D^{24}$ = –16.0 (c = 1, THF) yield: 36%.

(±)-**12**: Yellowish, waxy solid, mp = 63–66 °C; yield: 47%.

NMR: ^1H ($CDCl_3$): δ [ppm] 0.87–1.37 (m, 26H, H-3″-H-15″); 0.90 (t, 3H, CH_3); 1.44 (m, 2H, H-2″); 3.98 (m, 2H, H-1″); 4.95 (s, OH); 7.06 (dm, 1H, $J_{H\text{-}7',\ H\text{-}8'} \approx$ 8.2 Hz, H-8′); 7.18–7.24 (m, 2H, H-7′, H-8); 7.24–7.33 (m, 2H, H-6′, H-7); 7.35 (d, 1H, $J_{H\text{-}3',\ H\text{-}4'} \approx$ 8.9 Hz, H-3′); 7.37 (ddd, 1H, $J_{H\text{-}5,\ H\text{-}6} \approx$ 8.0 Hz, $J_{H\text{-}6,\ H\text{-}7} \approx$ 6.5 Hz, $J_{H\text{-}6,\ H\text{-}8} \approx$ 1.4 Hz, H-6); 7.45 (d, 1H, $J_{H\text{-}3,\ H\text{-}4} \approx$ 9.1 Hz, H-3); 7.85 (dm, 1H, $J_{H\text{-}5',\ H\text{-}6'} \approx$ 8.0 Hz, H-5′); 7.89 (d, 1H, $J_{H\text{-}5,\ H\text{-}6} \approx$ 8.0 Hz, H-5); 7.89 (d, 1H, $J_{H\text{-}3',\ H\text{-}4'} \approx$ 8.9 Hz, H-4′); 8.01 (d, 1H, $J_{H\text{-}3,\ H\text{-}4} \approx$ 9.1 Hz, H-4); ^{13}C ($CDCl_3$): δ [ppm] 14.1 (CH_3); 22.7 (C-15″); 25.5 (C-3″); 29.1, 29.37, 29.39, 29.5, 29.66, 29.67(2×), 29.7(3×) (C-4″-C-13″); 29.2 (C-2″); 31.9 (C-14″); 69.8 (C-1″); 115.3 (C-1′); 115.7 (C-3); 116.4 (C-1); 117.4 (C-3′); 123.1 (C-6′); 124.2 (C-6); 124.96 (C-8′); 125.0 (C-8); 126.2 (C-7′); 127.2 (C-7); 128.0 (C-5′); 128.1 (C-5); 129.1 (C-10′); 129.6 (C-10); 129.6 (C-4′); 130.8 (C-4); 133.9 (C-9′); 134.1 (C-9); 151.3 (C-2′); 155.6 (C-2).

MS (CI, isobutane): m/z = 511 ($[M+1]^+$ 100), 287 (10).

IR (KBr): ν = 3534 (OH); 3056 (arom.); 2917, 2849 (CH_2, CH_3); 1620, 1592, 1508 (arom.); 1469 (CH_2, CH_3); 1330; 1273; 1265 (C-O); 1245 (C-O-C); 1144; 1128; 1077; 809, 745 (arom.) cm^{-1}.

$C_{36}H_{46}O_2$ (510.35):	Calcd. C 84.65 H 9.08
	Found C 84.42 H 8.63

(+)-**12**: Yellowish, waxy solid, mp = 63–64 °C; $[\alpha]_D^{24}$ = 34.9 (c = 1, THF); yield: 41%.

2,2′-Didodecyloxy-1,1′-binaphthyl 11 and 2,2′-Dihexadecyloxy-1,1′-binaphthyl 13

11 and **13** were formed as byproducts in the synthesis of **10** and **12**, respectively. They were separated from the monoalkyl compounds by means of column chromatography (eluent *n*-hexane/ethyl acetate (9:1), TLC: Silufol® foils, detection by 10% ethanolic wolframato phosphoric acid solution, R_f = 0.38 (**11**) and 0.45 (**13**)). The excessive alkyl bromide was removed by a bulb tube distillation.

(+)-**11**: Brown oil, $[\alpha]_D^{28}$ = 36.0 (*c* = 0.6; THF).

NMR: ^{1}H ($CDCl_3$): δ [ppm] 0.85–1.30 (m, 36H; H-3″-H-11″); 0.89 (t, 6H, J ≈ 7.2 Hz, CH_3); 1.35 (m, 4H, H-2″); 3.91 (m, 4H, H-1″); 7.10–7.22 (m, 4H, H-7, H-7′, H-8, H-8′); 7.29 (ddd, 2H, $J_{H\text{-}5,\,H\text{-}6} \approx 8.3$ Hz, $J_{H\text{-}6,\,H\text{-}7} \approx$ 6.8 Hz, $J_{H\text{-}6,\,H\text{-}8} \approx 1.8$ Hz, H-6, H-6′); 7.39 (d, 2H, $J_{H\text{-}3,\,H\text{-}4} \approx 9.0$ Hz, H-3, H-3′); 7.83 (dt, 2H, $J_{H\text{-}5,\,H\text{-}6} \approx 8.3$ Hz, $J \approx 1.2$ Hz, H-5, H-5′); 7.91 (d, 2H, $J_{H\text{-}3,\,H\text{-}4} \approx 9.0$ Hz, H-4, H-4′); ^{13}C ($CDCl_3$); δ [ppm] 14.1 (CH_3); 22.7 (C-11″); 25.6 (C-3″); 29.2 (C-2″); 29.38, 29.43, 29.46, 29.5, 29.65, 29.68 (C-4″-C-9″); 31.9 (C-10″); 69.8 (C-1″); 115.9 (C-3, C-3′); 120.8 (C-1, C-1′); 123.4 (C-6, C-6′); 125.5 (C-8, C-8′); 126.0 (C-7, C-7′); 127.7 (C-5, C-5′); 129.0 (C-4, C-4′); 129.3 (C-10, C-10′); 134.3 (C-9, C-9′); 154.6 (C-2, C-2′).

MS (70 eV): *m/z* = 622 (M^+, 100), 454 (12), 286 (42), 268 (6), 257 (5).

IR (neat): ν= 3056 (arom.); 2924, 2853 (CH_2, CH_3); 1622, 1592, 1509 (arom.); 1466 (CH_3); 1430; 1354; 1334; 1263; 1242; 1146; 1087; 1018; 805, 746 (arom.); 408 cm^{-1}.

$C_{44}H_{62}O_2$ (622.47): Calcd. C 84.82 H 10.04
Found C 85.46 H 10.10

(+)-**13**: Light-brown, waxy solid, *mp* = 45–48 °C; $[\alpha]_D^{24}$= 22.8 (*c* = 1, THF).

NMR: ^{1}H ($CDCl_3$): δ [ppm] 0.85–1.30 (m, 52H, H-3″-H-15″); 0.88 (t, 6H *J* ≈ 7.0 Hz, CH_3); 1.37 (m, 4H, H-2″); 3.91 (m, 4H, H-1″); 7.10–7.22 (m, 4H, H-7, H-7′, H-8, H-8′); 7.29 (ddd, 2H, $J_{H\text{-}5,\,H\text{-}6} \approx 8.0$ Hz, $J_{H\text{-}6,\,H\text{-}7} \approx$ 6.2 Hz, $J_{H\text{-}6,\,H\text{-}8} \approx 1.6$ Hz, H-6, H-6′); 7.39 (d, 2H, $J_{H\text{-}3,\,H\text{-}4} \approx 8.9$ Hz, H-3, H-3′) ; 7.83 (dt, 2H, $J_{H\text{-}5,\,H\text{-}6} \approx 8.0$ Hz, $J \approx 1.2$ Hz, H-5, H-5′); 7.91 (d, 2H, $J_{H\text{-}3,\,H\text{-}4} \approx 8.9$ Hz, H-4, H-4′); ^{13}C ($CDCl_3$): δ [ppm] 14.1 (CH_3); 22.7 (C-15″): 25.6 (C-3″); 29.2 (C-2″); 29.38, 29.47(2×), 29.51, 29.69(3×), 29.74(3×) (C-4″-C-13″); 31.9 (C-14″); 69.9 (C-1″); 116.0 (C-3, C-3′); 120.9 (C-1, C-1′); 123.4 (C-6, C-6′); 125.5 (C-8, C-8′); 126.0 (C-7, C-7′);

127.8 (C-5, C-5′); 129.0 (C-4, C-4′); 129.3 (C-10, C-10′); 134.3 (C-9, C-9′); 154.6 (C-2, C-2′).

MS (CI, isobutane): m/z = 735 ($[M+H]^+$, 100), 511 (17).

IR (KBr): ν = 3062 (arom.); 2919, 2850 (CH_2, CH_3); 1622, 1591, 1509 (arom.); 1468 (CH_2, CH_3); 1428; 1354; 1324; 1280; 1265; 1244 (C-O-C); 1225; 1213; 1146; 1132; 1089; 1070; 1056; 1019; 804 (arom.); 776; 742 (arom.); 721 cm^{-1}.

$C_{52}H_{78}O_2$ (734.60): Calcd. C 84.94 H 10.70
Found C 84.25 H 10.38

2′-Dodecyloxy-1,1′-binaphthyl-2-yl dihydrogenphosphate 14 and 2′-Hexadecyloxy-1,1′-binaphthyl-2-yl dihydrogenphosphate 15

To a solution of 2 mmol of **10** (0.91 g) or **12** (1.02g) respectively, in 20 mL of abs. pyridine, 1.8 mL (19 mmol) of phosphoryl chloride were added dropwise under argon with stirring at 0 °C. After stirring for 30 min, 10 mL of distilled water were added dropwise, the mixture was stirred for further 3 h and left to stay overnight. Afterwards water and pyridine were distilled off and the residue was dried in vacuo to remove the remaining pyridine. The crude product was washed with water several times, then with a little amount of methanol and dried in vacuo.

(±)-**14**: Light-brown, viscous substance, yield: 50%.

NMR: ^1H ($CDCl_3$): δ [ppm] 0.70–1.35 (m, 20H, H-2″-H-11″); 0.88 (t, 3H, CH_3); 3.81 (m, 2H, H-1″); 10.26 (s, 2H, OH); Tables II and III; ^{13}C ($CDCl_3$) δ [ppm] 14.1 (CH_3); 22.7 (C-11″); 25.5 (C-3″); 29.1, 29.38, 29.44, 29.5, 29.66, 29.68 (C-4″-C-9″); 29.2 (C-2″); 31.9 (C-10″); 69.8 (C-1″); Table IV. ^{31}P ($CDCl_3$): δ [ppm] –4.4.

MS (FD pos.): m/z = 534 (M^+, 100), 454 (10).

IR (KBr): ν = 3412 (OH); 3137, 3065 (arom.); 2924, 2853 (CH_2, CH_3); 2647–2143 (br, OH); 1622, 1591, 1507, 1488 (arom.); 1460 (CH_2, CH_3); 1429; 1357; 1332; 1236 (br, P=O); 1084; 992 (P-OH); 813, 752 (arom.); 685; 608; 501 cm^{-1}.

$C_{32}H_{39}O_5P$ (534.25): Calcd. C 71.88 H 7.36 P 5.80
Found C 71.11 H 7.21 P 5.81

(-)-**14**: Brown, viscous substance; $[\alpha]_D^{24} = -6.7$ ($c = 1$, methanol); yield: 42%,

(±)-**15**: Brown, viscous substance; yield: 40%.

NMR: ^1H ($CDCl_3$): δ [ppm] 0.70–1.35 (m, 28H, H-2″-H-15″); 0.87 (t, 3H, CH_3); 3.69–3.92 (m, 2H, H-1″): 6.90–7.10 (m, 4H, H-6′, H-7′, H-8, H-8′); 7.11–7.21 (m, 2H, H-3′, H-7); 7.33 (m, 1H, H-6); 7.50–7.80 (m, 5H, H-3, H-4, H-4′, H-5, H-5′); 8.20 (br s, OH); ^{13}C ($CDCl_3$): δ [ppm] 14.1 (CH_3); 22.7 (C-15″): 25.5 (C-3″); 29.2 (C-2″); 29.1, 29.4(2×), 29.46, 29.5, 29.69(2×), 29.7, 29.74(2×) (C-4″-C-13″); 31.9 (C-14″); 70.0 (C-1″); 116.1 (C-3′); 119.8 (C-1′); 120.3 (C-3); 122.7 (d, $J_{P,C} \approx 8.0$ Hz, C-1); 123.4 (C-6′); 124.4 (C-6); 125.9 (C-7, C-8, C-8′); 126.2 (C-7′); 127.5 (C-5′); 127.8 (C-5); 129.0 (C-4′, C-10′); 129.2 (C-4); 130.6 (C-10); 133.9 (C-9, C-9′); 147.9 (d, $J_{P,C} \approx 6.0$ Hz, C-2); 154.6 (C-2′); ^{31}P ($CDCl_3$): δ [ppm] –4.3.

MS (70eV): m/z = 590 (M^+, 20), 510 (100), 366 (25), 348 (16), 286 (85), 268 (32), 239 (18).

IR (KBr): ν = 3434 (OH); 3063 (arom.); 2922, 2851 (CH_2, CH_3); 1622, 1592, 1507 (arom.); 1467 (CH_3); 1430; 1358; 1333; 1262; 1231 (br, P=O); 1147; 1084; 996 (br, P-OH); 863; 810 (arom.); 775; 747 (arom.); 681; 495 cm^{-1}.

$C_{36}H_{47}O_5P \cdot 1H_2O$ (608.76):	Calcd. C 71.03 H 8.11 P 5.09
	Found C 70.80 H 7.53 P 5.28

Sodium 3-(2′-dodecyloxy-1,1′-binaphthyl-2-yloxy)propane-1-sulfonate 16

To a solution of 227.3 mg (0.5 mmol) of **10** in 4 mL of THF, 21.6 mg (0.9 mmol) of sodium hydride were added and the reaction mixture was stirred for 30 min at room temperature. Afterwards 7.94 mL (0.6 mmol) of propane-1,3-sultone, dissolved in 4 mL of THF, were added and the mixture was stirred for further 30 min at room temperature, and then refluxed for 5 h. The precipitate formed was filtered off and the filtrate evaporated. The resulting residue was purified by means of column chromatography (R_f = 0.06, eluent: methylene chloride/methanol 9:1).

(±)-**16**: Colorless solid, *mp* = 125–130 °C; yield: 85%.

NMR: ^1H (DMSO-d_6): δ [ppm] 0.86 (t, 3H, $J \approx 6.8$ Hz, CH_3); 0.89–1.27 (m, 18H, H-3″-H-11″); 1.31 (m, 2H, H-2″); 1.72 (m, 2H, $\underline{CH_2}$-CH_2-SO_3^-); 2.23 (m, 2H, CH_2-SO_3^-); 3.95 (m, 2H, H-1″); 4.06 (m, 2H, $\underline{CH_2}$-$(CH_2)_2$-SO_3^-); 6.88–6.96 (m, 2H, H-8, H-8′); 7.14–7.24 (m, 2H, H-7,

H-7′); 7.24–7.34 (m, 2H, H-6, H-6′); 7.53 (d, 1H, $J_{H\text{-}3,\,H\text{-}4} \approx 5.5$ Hz), 7.56 (d, 1H, $J_{H\text{-}3,\,H\text{-}4} \approx 5.5$ Hz) (H-3, H-3′); 7.89 (ddd, 1H, $J_{H\text{-}5,\,H\text{-}6} \approx 5.0$ Hz, $J_{H\text{-}5,\,H\text{-}7} \approx 1.5$ Hz, $J_{H\text{-}5,\,H\text{-}8} \approx 0.8$ Hz), 7.92 (ddd, 1H, $J_{H\text{-}5,\,H\text{-}6} \approx 5.0$ Hz, $J_{H\text{-}5,\,H\text{-}7} \approx 1.5$ Hz, $J_{H\text{-}5,\,H\text{-}8} \approx 0.8$ Hz) (H-5, H-5′); 7.99 (dd, 1H, $J_{H\text{-}3,\,H\text{-}4} \approx 5.5$ Hz, $^5J_{H\text{-}4,\,H\text{-}8} \approx 0.8$ Hz), 8.02 (dd, 1H, $J_{H\text{-}3,\,H\text{-}4} \approx 5.5$ Hz, $^5J_{H\text{-}4,\,H\text{-}8} \approx 0.8$ Hz) (H-4, H-4′); ^{13}C (DMSO-d_6): δ [ppm] 14.1 (CH_3); 22.2 (C-11″); 25.2 (C-3″); 25.5 ($\underline{CH_2}$-CH_2-SO_3^-); 28.6, 28.8, 28.9, 29.0(2×), 29.1 (C-4″-C-9″); 29.1 (C-2″); 31.4 (C-10″); 47.9 (CH_2-SO_3^-); 68.2 ($\underline{CH_2}$-$(CH_2)_2$-SO_3^-); 68.8 (C-1″); 115.5, 115.8 (C-3, C-3′); 119.4, 119.5 (C-1, C-1′); 123.2, 123.4 (C-6, C-6′); 124.7 (C-8, C-8′); 126.1, 126.2 (C-7, C-7′); 128.0, 128.1 (C-5, C-5′); 129.2, 129.3 (C-4, C-4′); 133.6, 133.7 (C-9, C-9′); 154.1, 154.2 (C-2; C-2′).

MS (FAB neg.): *m/z* = 576 (M-Na, 5), 454 (18), 267 (50), 183 (59), 121 (45), 80 (82), 46 (100).

IR (KBr): *v* = 3059 (arom.); 2953, 2919, 2869, 2850 (CH_2, CH_3); 1622, 1591, 1506 (arom.); 1467 (CH_2, CH_3); 1458; 1427; 1354; 1321; 1217–1168 (several bands: SO_3, C-O-C); 1048; 803, 750 (arom.) cm^{-1}.

$C_{35}H_{43}O_5SNa{\cdot}2H_2O$ (634.29):	Calcd. C 66.22 H 7.47 S 5.04
	Found C 66.16 H 7.55 S 4.82

(+)-**16**: Colorless solid, *mp* = 70–72 °C; $[\alpha]_D^{24} = 34.8$ (*c* = 1, THF); yield: 79%.

(-)-**16**: Colorless solid, *mp* = 70–73 °C; $[\alpha]_D^{24} = -35.1$ (*c* = 1, THF); yield: 91 %.

2′-Dodecyloxy-1,1′-binaphthyl-2-yl hydrogensulfate 17

To a solution of 0.908 g (2 mmol) of **10** in 10 mL of abs. pyridine, 2.7 mL (40 mmol) of chlorosulfuric acid were added slowly under argon at 0 °C. After termination of reaction the excessive pyridine was distilled off and the residue dissolved in water. The precipitate formed was separated and purified by means of preparative TLC (silica gel (Merck), R_f = 0.17, eluent: chloroform/methanol 5:1) and then dried in vacuo.

(±)-**17**: Brown, viscous substance, yield: 25%.

NMR: ^{1}H ($CDCl_3$): δ [ppm] 0.88 (t, 3H, $J \approx 7.0$ Hz, CH_3); 0.50–1.35 (m, 20H, H-2″-H-11″); 3.66 (m, 2H, H-1″); Tables II and III; ^{13}C ($CDCl_3$): δ [ppm] 14.1 (CH_3); 22.7 (C-11″); 25.4 (C-3″); 29. 1 (C-2″); 29.1, 29.4, 29.5, 29.6, 29.68, 29.71 (C-4″-C-9″); 32.0 (C-10″); 66.8 (C-1″); Table IV.

MS (FAB neg., nitrobenzyl alcohol): *m/z* = 533 ([M-H]$^-$, 100).

IR (KBr): ν = 3460 (OH); 3058 (arom.); 2924, 2853 (CH_2, CH_3); 1623, 1592, 1507 (arom.); 1459 (CH_2, CH_3); 1261; 1246; 1054; 973 cm^{-1}.

$C_{32}H_{38}O_5S \cdot 2H_2O$ (570.74):	Calcd. C 67.34 H 7.24 S 5.62
	Found C 66.70 H 7.69 S 5.41

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