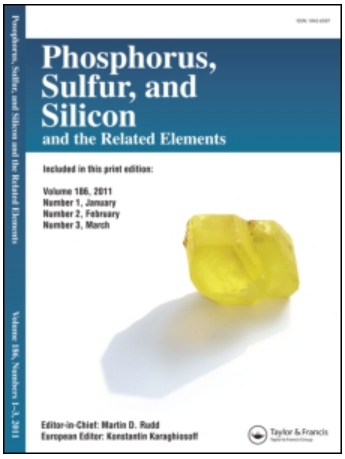

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Approaches to the Synthesis of Conjugates of Phosphocavitands and Natural Compounds

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Online publication date: 27 October 2010

To cite this Article Maslennikova, V. I. , Merkulov, R. V. , Vasyanina, L. K. , Bauer, I. , Weber, D. , Theumer, G. , Habicher, W. D. and Nifantyev, E. E.(2003) 'Approaches to the Synthesis of Conjugates of Phosphocavitands and Natural Compounds', Phosphorus, Sulfur, and Silicon and the Related Elements, 178: 7, 1489 — 1505

To link to this Article: DOI: 10.1080/10426500307874

URL: http://dx.doi.org/10.1080/10426500307874

Phosphorus, Sulfur, and Silicon, 178:1489–1505, 2003

ISSN: 1042-6507 print
DOI: 10.1080/10426500390212591

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APPROACHES TO THE SYNTHESIS OF CONJUGATES OF PHOSPHOCAVITANDS AND NATURAL COMPOUNDS

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(Received November 18, 2002; accepted January 16, 2003)

Possibilities for the design of phosphocavitand conjugates with natural alcohols and phenols were studied. First cavitand conjugates bearing biomolecular fragments at the periphery of the molecular cup were obtained by alcoholysis of tetrachlorophosphitocavitands and cyclophosphorylation of calix[4]resorcinarenes.

Keywords: Alcoholysis; calix[4]resorcinarenes; cyclophosphorylation; natural alcohols; phenols; phosphocavitands; phosphorous amides

The design of conjugates of synthetic polycyclic systems and natural compounds is a promising branch of modern organic chemistry. The insertion of fragments of these compounds into a polycyclic matrix can generate products for various applications, e.g., compounds with adjuvant properties and activity with respect to viruses and other microorganisms.[1–3] In recent times complex condensed systems, including calixarenes, have been used as cores of such conjugates.[4–8] We set ourselves an object to study the synthesis of hybrid systems from phosphocavitands whose molecules consist of a rigid cup-shaped skeleton framed by phosphorus functions. The latter can be considered as an affinity factor of the synthesized compounds to biological tissue.

This work was supported in part by the Russian Foundation for Basic Research (grant no. 00-03-32844a) and the German Ministry of Education and Research (BMBF, grant no. RUS 00/216).

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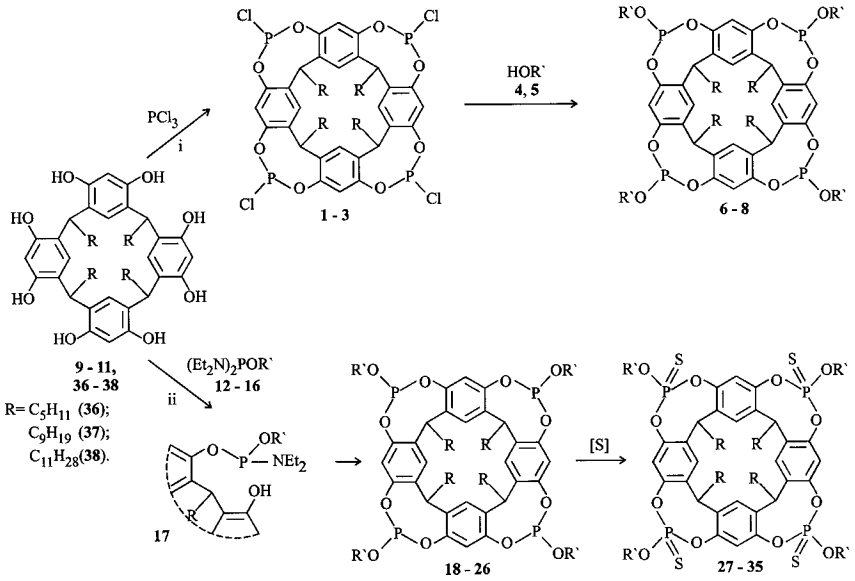
This article describes conjugates whose molecules combine fragments of phosphocavitands and natural alcohols (phenols) for the first time.* Two methods for their synthesis were considered: (1) alcoholysis (phenolysis) of phosphocavitands bearing active functions at the phosphorus atoms by natural hydroxides and (2) cyclophosphorylation of calix[4]resorcinarenes by phosphorus acid derivatives containing biomolecular fragments (Scheme 1).



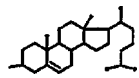
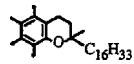
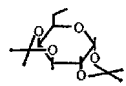
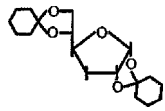
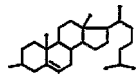
SCHEME 1

RESULTS AND DISCUSSION

The selection of the matrix type plays an important role in the efficient realization of the first synthetic method. The best studied derivatives of P(III)-phosphocavitands are amido- and chlorophosphitocavitands.[11–13] Amidophosphitocavitands are readily available and easy to handle, but they are passive in nucleophilic substitution reactions. Alcoholysis and hydrolysis of these compounds proceed under severe conditions; they are accompanied by the opening of the phosphocine rings.[13] Therefore, tetrachlorophosphitocavitands **1–3**, which are less stable but active in nucleophilic substitution reactions,[11,14] were

*Preliminary communications.[9,10]

TABLE I Initial Compounds and Obtained Cavitand Conjugates

Substrate		Reagent		Phosphito cavitand	Thiophosphato cavitand
No.	R	No.	R′	No.	No.
1	C_5H_{11}	**4**		**6**	
2	C_9H_{19}			**7**	
3	$C_{11}H_{23}$	**5**		**8**	
9	CH_3	**12**		**18**	**27**
10	C_3H_7			**19**	**28**
9	CH_3			**20**	**29**
10	C_3H_7	**13**		**21**	**30**
11	C_6H_{13}			**22**	**31**
9	CH_3	**14**		**23**	**32**
10	C_3H_7			**24**	**33**
9	CH_3	**15**		**25**	**34**
9	CH_3	**16**		**26** **26a**	**35** **35a**

used as initial substrates for the alcoholysis. Cholesterol (**4**) and α-tocopherol (**5**) were used as reagents (Scheme 1, Table I).

The reaction was carried out in toluene at 80°C in the presence of triethylamine. Phosphitocavitands **6–8** were isolated by column chromatography. Analysis of the NMR spectra showed that they were stereochemically pure isomers with an equatorial orientation of the exocyclic substituents at the phosphorus atoms. The stereospecifity of the syntheses depended on two factors: the use of symmetrical chlorophosphitocavitand stereoisomers with axial chlorine atoms[14] as substrates and the rigid structure of the cavitand.

The efficient implementation of the second synthetic method also depended on the correct choice of the reagent. Two pathways were used for the cyclophosphorylation of calix[4]resorcinarenes by phosphorus acid derivatives. The dichloroanhydride method[14–16] involves the addition of tertiary amines to the reaction mixture. This results in the contamination of the reaction products with the corresponding hydrochlorides,

and the purification of the cavitands from these compounds turns out to be difficult. The amide method is free from this disadvantage. This is easy to realize: Most reactions proceed at room temperature; the resulting secondary amines are easily removed from the reaction mixture, and the target products are obtained in high yields.[17,18] Thus, this method offers great opportunities for the formation of complex cavitand conjugates of calix[4]resorcinarenes.

We used calix[4]resorcinarenes **9–11** as substrates and bis-(*N*, *N*-diethylamido)phosphites **12–16** obtained from 1,2,3,4-diisopropylidene-D-galactopyranose (**12**), 1,2-isopropylideneglycerol (**13**), L-menthol (**14**), 1,2,5,6-dicyclohexylidene-D-glucofuranose (**15**), and cholesterol (**16**) as reagents (Scheme 1, Table I).

It was found previously that cyclophosphorylation of calix[4]-resorcinarenes proceeds most completely at a stoichiometric reagent ratio (octol : amide = 1 : 4) in dioxane.[17,18] Dioxane favors the selective reaction course and makes the isolation of the target product from the reaction mixture easier. Therefore, we chose these conditions for the synthesis of cavitand conjugates. Interaction of calix[4]resorcinarenes with bis-*N*,*N*-diethylamido–1,2,5,6-diisopropylideneglucofuranosylphosphite and bis-*N*,*N*-diethylamidomenthylphosphite in other conditions leads to a formation of calixarenes with various degrees of phosphorylation, containing both cyclic and noncyclic phosphorus fragments.[6–8] The reaction temperature varied in the range between 20°C and 100°C depending on the phosphorylating agent used.

Reaction of octols **9, 10** with bis-*N*,*N*-diethylamido-1,2,3,4-diisopropylidenegalactopyranosylphosphite **12** proceeded at room temperature within 10–14 days. Bis-*N*,*N*-diethylamidoisopropylideneglycerylphosphite **13** phosphorylated calixarenes **9–11** under similar conditions in 3–4 days. At the same time, the reaction of octols **9, 10** with diamidomenthyl- and 1,2,5,6-dicyclohexylideneglucofuranosylphosphites **14, 15** was carried out at 90–95°C. At room temperature the reaction with diamidophosphite **15** took 50 days, and it could not be accomplished with diamidophosphite **14** under mild conditions.

When bis-*N*,*N*-diethylamidocholesterylphosphite **16** was used, heating the reaction mixture to 90°C favored the stereoselective process, although cyclophosphorylation also proceeded at room temperature. In other cases, heating only accelerated the cyclization, without affecting its stereoregularity.

Thus, cyclophosphorylation of calix[4]resorcinarenes by diamidophosphites **12, 13** obtained from primary alcohols proceeds more easily than the reaction with phosphorous acid diamidoesters **14–16** bearing a secondary alcohol fragment. This can be explained by steric

hindrances at the stage of the cyclisation of primarily formed phosphorylated calixarenes **17**.

Phosphocavitands **18–20, 24**, and **26** were isolated from the reaction mixture by precipitation with hexane. Their composition was confirmed by elemental analysis, and their structure was supported by ^{31}P and ^{1}H NMR spectroscopy. In all cases the reaction yielded phosphocavitands with different arrangements of alkoxyl groups at the phosphorus atoms with respect to the macrocycle cup. This was evidenced by NMR spectroscopic data. The ^{31}P NMR spectra showed broadened and split signals; the ^{1}H NMR spectra displayed non-equivalent signals for the protons from the calixarene skeleton of the molecule. So, four signals for the *ortho*- (6.41, 6.45, 6.53, and 6.57 ppm) and two signals for the *meta*- (7.08 and 7.14 ppm) protons from benzene rings were observed in the ^{1}H NMR spectrum of menthylphosphitocavitand **24**, along with those for the methine bridges of the calixarene matrix (4.58 and 4.83 ppm), clear doublets for methyl groups (0.81 and 0.95 ppm), a multiplet for the proton from the methine group linked to the oxygen atom of the menthyl moiety (4.43 ppm), and multiplets for the methylene and methine protons from the menthyl and propyl moieties at 1.08–2.29 ppm (Fig. 1a). These spectra can be explained by the presence of diastereoisomers or conformers. However, signal averaging in the ^{31}P NMR spectra recorded at elevated temperatures indicated the presence of conformers.

Only in the case of cholesterylphosphitocavitand **26**, we succeeded in isolating the symmetrical stereoisomer **26a** with the similar arrangement of steroid fragments on the macrocycle cup. A narrow singlet was observed in the ^{31}P NMR spectrum of **26a** in the temperature range between $-60^{\circ}C$ and $60^{\circ}C$, which indicated the magnetic equivalence of the phosphorus nuclei; in the ^{1}H NMR spectrum, one set of signals was observed for all proton groups: singlets for the protons of the benzene rings with δ 6.64 (H_o) and 7.30 ppm (H_m), a quadruplet for the methine protons (δ 4.82 ppm), and a doublet for the methyl protons (δ 1.74 ppm) of the interring bridges of the calixarene structure, two doublets (δ 0.87 and 0.92 ppm), and two singlets (δ 0.68 and 1.05 ppm) for the methyl groups of cholesterol, a signal for the proton at the multiple bond (δ 5.41 ppm), a multiplet for the proton of the cholesterol methine group linked to the phosphite fragment (δ 4.52 ppm), a doublet for the protons of the cholesterol methylene group linked to the alcohol and unsaturated carbon atoms (δ 2.52 ppm), and signals for the methine and methylene protons of the cholesterol rings at 1.14–2.04 ppm.

We failed to isolate pure cavitands **21–23** because of their high solubility in organic solvents. They were characterised by conversion to the corresponding thiophosphatocavitands. For this purpose, as well as for

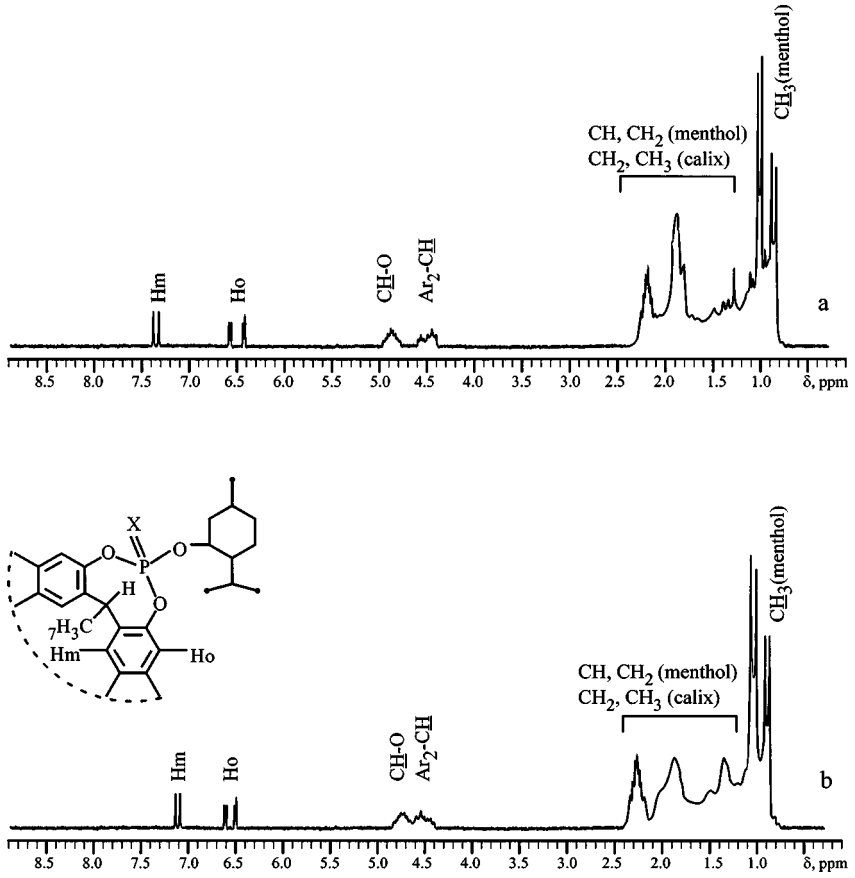


FIGURE 1 ^{1}H NMR spectra of (a) phosphitocavitand **24** (X = electron lone pair) and (b) thiophosphatocavitand **33** (X = S).

obtaining more stable macrocyclic systems, we performed the sulphurisation of the synthesised P(III) derivatives **18–26** (Scheme 1, Table I).

Addition of sulphur to phosphites **18–26** was performed in benzene for 3–5 h. The temperature varied depending on the phosphocavitand used. For example, sulphurisation of galactosyl- (**18**, **19**), glucosyl- (**25**), and cholesterylphosphocavitands (**26**) proceeded at 50°C; addition of sulphur to glyceryl- (**20–22**) and menthylphosphocavitands (**23**, **24**) required more severe conditions.

Analysis of the NMR spectra of thiophosphates **27–35** showed that their structure is determined by the configuration of the initial substrates. For illustration, ^{1}H NMR spectra of menthylthiophosphatocavitand **33** obtained from menthylphosphite **24** with different

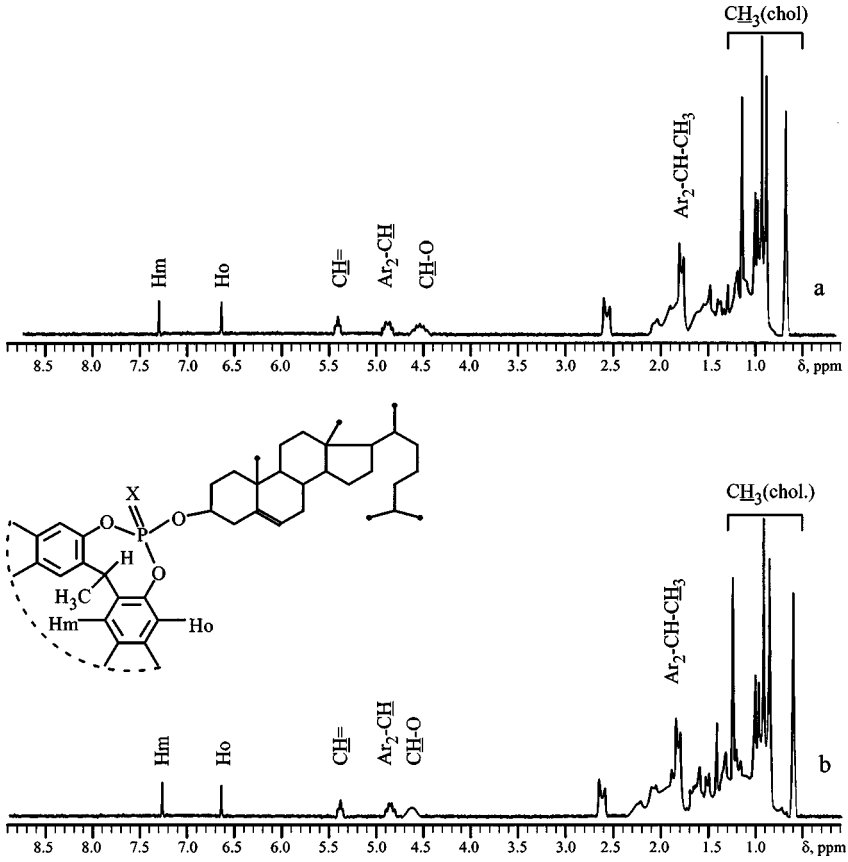


FIGURE 2 ^{1}H NMR spectra of (a) phosphitocavitand **26a** (X = electron lone pair) and (b) thiophosphatocavitand **35a** (X = S).

arrangement of menthyl groups with respect to the macrocyclic skeleton and cholesterylthiophosphatocavitand **35a** obtained by sulphurisation of the symmetrical cholesterylphosphite stereoisomer **26a** are presented in Figures 1b and 2b respectively. It is to be seen that the spectra of thiophosphates **33** and **35a** are analogous to those of the corresponding phosphites **24** and **26a**. A similar situation is observed for other pairs of phosphite and thiophosphate derivatives of cavitand conjugates. Hence, thiophosphates **27–35**, as well as phosphites **18–26**, are conformers with different arrangements of bioalcohol fragments with respect to the central axis of the macrocycle. Only the molecules of cholesterylphosphocavitands **26a** and **35a** have a C_{4v} symmetry.

Thus, we have obtained the first cavitands in which the macrocyclic cup is enclosed by a "belt" of chiral biomolecular fragments.

EXPERIMENTAL

All syntheses were carried out in dry deoxygenated solvents under argon atmosphere. ^{1}H NMR spectra of **6–8** were recorded on a Bruker AC-300 spectrometer; those of **18–35** were performed on a Bruker WM-200 spectrometer. ^{13}C NMR spectra (at 75.48 MHz) and ^{31}P NMR spectra of **1–3** and **6–8** (at 121.50 MHz) were recorded on a Bruker AC-300 spectrometer. ^{31}P NMR spectra of **18–35** (at 32.4 MHz) were run on a Bruker WP-80 spectrometer. MALDI-TOF MS measurements were carried out on a Kratos Kompact MALDI II instrument of Shimadzu Europa GmbH.

Chlorophosphitocavitands 1–3

A solution of 0.01 mmol of the corresponding calix[4]resorcinarene **36–38** and 0.07 mol of TEA in 250 ml of toluene was added dropwise to a solution of 0.06 mol of phosphorus trichloride in 100 ml of toluene at room temperature. The mixture was stirred at 80°C for 4 h, the triethylammonium hydrochloride was filtered off and all liquids were removed under vacuum. The residue was dissolved in the given amount of toluene and used for further reactions as described below. ^{31}P NMR of cavitands **1–3** ($CDCl_3$) δ, ppm: 125–126.[14]

Phosphitocavitands 6, 7

A solution of the corresponding chlorophosphitocavitand **1** or **2**, respectively, (0.01 mmol) in 150 ml of toluene was rapidly added to a solution of cholesterol **4** (0.04 mmol) and triethylamine (0.05 mmol) in 150 ml of toluene. The mixture was stirred at 80°C for 4 h. Triethylammonium hydrochloride was filtered off; the solvent was removed under vacuum, and the residue was rubbed with acetonitrile. The resulting yellow substance was purified by column chromatography (Silicagel 60, chloroform) to obtain colourless crystals.

Phosphitocavitand 6

Yield 53%. m.p. 130–135°C. ^{31}P NMR ($CDCl_3$) δ, ppm: 133.33. ^{1}H NMR ($CDCl_3$) δ, ppm: 0.50–2.50 (176 H, signals for CH_3-, CH_2- and

CH-groups from cholesterol and calix[4]resorcinarene side-chain), 4.53 (t, $^{2}J_{HH} = 7.2$ Hz, 4H, Ar—C<u>H</u>R—Ar), 5.32 (br, 4H, —C<u>H</u>= from cholesterol), 6.58 (s, 4H, Ar—<u>H</u>), 7.08 (s, 1H, Ar—<u>H</u>). ^{13}C NMR ($CDCl_3$) δ, ppm: 11.86 (<u>C</u>H$_3$, cholesterol), 14.15 (<u>C</u>H$_3$, calixarene), 18.71 (<u>C</u>H$_3$, cholesterol), 19.33 (<u>C</u>H$_3$, cholesterol), 21.05 (<u>C</u>H$_2$, cholesterol), 22.56 (<u>C</u>H$_3$, cholesterol), 22.67 (<u>C</u>H$_2$, calixarene), 22.81 (<u>C</u>H$_3$, cholesterol), 23.82 (<u>C</u>H$_2$, cholesterol), 24.29 (<u>C</u>H$_2$, cholesterol), 27.55 (<u>C</u>H$_2$, calixarene), 28.01 (<u>C</u>H, cholesterol), 28.23 (<u>C</u>H$_2$, cholesterol), 30.70 (<u>C</u>H$_2$, calixarene), 31.19 (<u>C</u>H$_2$, calixarene), 30.68 (<u>C</u>H$_2$, cholesterol), 31.23 (<u>C</u>H$_2$, cholesterol), 31.87 (<u>C</u>H, cholesterol), 31.91 (<u>C</u>H$_2$, cholesterol), 35.72 (Ar—<u>C</u>H—Ar), 35.78 (<u>C</u>H, cholesterol), 36.19 (<u>C</u>H$_2$, cholesterol), 36.55 (*tert*-<u>C</u>, cholesterol), 37.20 (<u>C</u>H$_2$, cholesterol), 39.51 (<u>C</u>H$_2$, cholesterol), 39.77 (<u>C</u>H$_2$, cholesterol), 41.10 (<u>C</u>H$_2$, cholesterol), 42.33 (*tert*-C, cholesterol), 50.10 (<u>C</u>H, cholesterol), 56.15 (<u>C</u>H, cholesterol), 56.76 (<u>C</u>H, cholesterol), 75.60 (<u>C</u>H, cholesterol) 117.11 (Ar—<u>C</u>), 121.78 (Ar—<u>C</u>), 122.47 (—<u>C</u>H=, cholesterol), 136.32 (Ar—<u>C</u>), 140.29 (*ipso*-<u>C</u>=, cholesterol), 147.11 (Ar—<u>C</u>). $C_{172}H_{268}O_{12}P_4$ (2427.3): $m/z = 2593$ [M+$CHCl_3$+K^+].

Phosphitocavitand 7

Yield 45%. m.p. 78–83°C. ^{31}P NMR ($CDCl_3$) δ, ppm: 133.15. ^{1}H NMR ($CDCl_3$) δ, ppm: 0.50–2.50 (208H, signals for C<u>H</u>$_3$-, C<u>H</u>$_2$- and C<u>H</u>-groups from cholesterol and calix[4]resorcinarene side-chain), 4.53 (t, $^{2}J_{HH} = 7.2$ Hz, 4H, Ar—C<u>H</u>R—Ar), 5.32 (br., 4H, —C<u>H</u>= from cholesterol), 6.58 (s, 4H, Ar—<u>H</u>), 7.08 (s, 1H, Ar—<u>H</u>). ^{13}C NMR ($CDCl_3$) δ, ppm: 11.85 (<u>C</u>H$_3$, cholesterol), 14.13 (<u>C</u>H$_3$, calixarene), 18.71 (<u>C</u>H$_3$, cholesterol), 19.32 (<u>C</u>H$_3$, cholesterol), 21.05 (<u>C</u>H$_2$, cholesterol), 22.55 (<u>C</u>H$_3$, cholesterol), 22.73 (<u>C</u>H$_2$, calixarene), 22.80 (<u>C</u>H$_3$, cholesterol), 23.81 (<u>C</u>H$_2$, cholesterol), 24.28 (<u>C</u>H$_2$, cholesterol), 27.84 (<u>C</u>H$_2$, calixarene), 28.01 (<u>C</u>H, cholesterol), 28.22 (<u>C</u>H$_2$, cholesterol), 29.40 (<u>C</u>H$_2$, calixarene), 29.70–29.75 (<u>C</u>H$_2$, calixarene), 30.68 (<u>C</u>H$_2$, cholesterol), 31.23 (<u>C</u>H$_2$, cholesterol), 31.86 (<u>C</u>H, cholesterol), 31.91 (<u>C</u>H$_2$, cholesterol), 35.72 (Ar—<u>C</u>H—Ar), 35.77 (<u>C</u>H, cholesterol), 36.19 (<u>C</u>H$_2$, cholesterol), 36.55 (*tert*-<u>C</u>, cholesterol), 37.22 (<u>C</u>H$_2$, cholesterol), 39.51 (<u>C</u>H$_2$, cholesterol), 39.77 (<u>C</u>H$_2$, cholesterol), 41.13 (<u>C</u>H$_2$, cholesterol), 42.33 (*tert*-C, cholesterol), 50.11 (<u>C</u>H, cholesterol), 56.15 (<u>C</u>H, cholesterol), 56.77 (<u>C</u>H, cholesterol), 75.60 (<u>C</u>H, cholesterol) 117.48 (Ar—<u>C</u>), 121.90 (Ar—<u>C</u>), 122.45 (—<u>C</u>H=, cholesterol), 136.28 (Ar—<u>C</u>), 140.30 (*ipso*-<u>C</u>=, cholesterol), 147.05 (Ar—<u>C</u>). $C_{172}H_{268}O_{12}P_4$ (2651.7): $m/z = 2815$ [M+$CHCl_3$+K^+].

Phosphitocavitand 8

A solution of chlorophosphitocavitand **3** (0.01 mmol) in 150 ml of toluene was rapidly added to a solution of α-tocopherol **5** (0.04 mmol) and triethylamine (0.05 mmol) in 100 ml of toluene. The reaction mixture was stirred at 80°C for 5 h. Triethylammonium hydrochloride was filtered off; the solvent was removed under vacuum, and the residue was purified by column chromatography (Silicagel 60, chloroform) to give a viscous oil. Yield 30%. ^{31}P NMR ($CDCl_3$) δ, ppm: 136.45. ^{1}H NMR ($CDCl_3$) δ, ppm: 0.75–2.30 (280H, C$\underline{H}_3$ and C$\underline{H}_2$ from tocopherol and calixarene), 2.53 (t, br, 8H, C$\underline{H}_2$ from tocopherol), 4.63 (t, $^3J_{HH} = 7.0$ Hz, 4H, Ar—C$\underline{H}$R—Ar), 6.50 (s, 4H, Ar—$\underline{H}$), 7.14 (s, 4H, Ar—$\underline{H}$). ^{13}C—NMR ($CDCl_3$) δ, ppm: 11.23, 11.75, 11.98, 12.17, 13.44, 14.07, 14.31, 19.60-19.74, 20.78, 20.84, 21.07, 22.61, 22.69, 23.80, 24.45, 24.80, 27.95 (C$\underline{H}_2$), 27.97, 29.39, 29.71, 31.24, 31.57, 31.62, 31.95, 32.73, 32.80, 35.74 (Ar—C$\underline{H}$R—Ar), 37.32–37.63 (C$\underline{H}_2$), 39.40, 39.90, 39.97, 40.41, 75.05 (*tert*.-$\underline{C}$), 117.37, 117.55, 122.14, 123.02, 125.44, 127.43, 136.68, 144.58, 146.68, 148.48 (Ar—$\underline{C}$). $C_{188}H_{300}O_{16}P_4$ (2940.2): $m/z = 2940$ [M+H$^+$].

Phosphitocavitand 18

A solution of octol **9** (0.14 mmol) and diamidophosphite **12** (0.56 mmol) in dioxane (2 ml) was exposed at 25°C for 10 days. Two-thirds of the solvent was evaporated under vacuum; hexane was added to the residue, and the precipitate formed was filtered off and dried under vacuum (1 mm Hg) at 50°C. Yield 87%. m.p. 225–227°C (decomp). ^{31}P NMR (C_6D_6) δ, ppm.: 129.2. ^{1}H NMR (C_7D_8) δ, ppm.: 1.31 (s, 12H, $(CH_3)_2$C-galactose); 1.42 (s, 12H, $(CH_3)_2$C-galactose); 1.64 (s, 12H, $(CH_3)_2$C-galactose); 1.67 (s, 12H, $(CH_3)_2$C-galactose); 1.79 (d, $^3J_{HH}$ 7.4 Hz, 6H, CH_3, calixarene); 1.83 (d, $^3J_{HH}$ 7.8 Hz, 6H, CH_3, calixarene); 4.34–5.17 (24H, CH, CH_2, galactose); 4.89 (m, 4H, CH, calixarene); 5.62 (d, $^3J_{HH}$ 5.1 Hz, 1H, C^{1}H, galactose); 5.67 (d, $^3J_{HH}$ 4.7 Hz, 3H, C^{1}H, galactose); 6.73 (s, 2H, H-arom., calixarene); 6.89 (s, 2H, H-arom., calixarene); 7.55 (s, 2H, H-arom., calixarene); 7.63(s, 2H, H-arom., calixarene). Anal. Calcd for $C_{80}H_{100}O_{32}P_4$ (1697.53): C, 56.60; H, 5.94; P, 7.30. Found: C, 56.67; H, 5.48; P, 7.63.

Phosphitocavitand 19

Phosphitocavitand **19** was obtained analogously to **18** in the reaction of octol **10** (0.21 mmol) with diamidophosphite **12** (0.84 mmol) for 14 days. Yield 86%. m.p. 195–197°C (decomp). ^{31}P NMR ($CDCl_3$) δ, ppm: 126.9–129.5. ^{1}H NMR ($CDCl_3$) δ, ppm: 1.02 (t, 12H,

$(CH_2)_2$-C<u>H</u>$_3$, calixarene); 1.26 (m, 8H, CH_2—C<u>H</u>$_2$—CH_3, calixarene); 1.34 (s, 12H, $(CH_3)_2$C-galactose); 1.36 (s, 12H, $(CH_3)_2$C-galactose); 1.47 (s, 12H, $(CH_3)_2$C-galactose); 1.53 (s, 12H, $(CH_3)_2$C-galactose); 2.21 (m, 8H, C<u>H</u>$_2$—CH_2—CH_3, calixarene); 4.16–4.62 (28H, CH, CH_2, galactose and CH, calixarene); 5.55 (d, $^3J_{HH}$ 4.4 Hz, 4H, C^1H, galactose); 6.44(s, 2H, H-arom., calixarene); 6.65 (s, 2H, H-arom., calixarene); 7.19 (s, 2H, H-arom., calixarene); 7.21(s, 2H, H-arom., calixarene). Anal. Calcd for $C_{88}H_{116}O_{32}P_4$ (1809.74): C, 58.40; H, 6.46; P, 6.85. Found: C, 57.98; H, 6.21; P, 6.97.

Phosphitocavitand 20

Phosphitocavitand **20** was obtained analogously to **18** in the reaction of octol **9** (0.24 mmol) with diamidophosphite **13** (0.96 mmol) for 3 days. Yield 89%. m.p. 198–200°C. ^{31}P NMR ($CDCl_3$) δ, ppm: 127.9. ^{1}H NMR ($CDCl_3$) δ, ppm: 1.36 (s, 6H, $(CH_3)_2$C-glycerol); 1.40(s, 6H, $(CH_3)_2$C-glycerol); 1.43 (s, 6H, $(CH_3)_2$C-glycerol); 1.47 (s, 6H, $(CH_3)_2$C-glycerol); 1,75(d, $^3J_{HH}$ 7.3 Hz, 12H, CH_3, calixarene); 3.80–4.42 (20H, CH, CH_2, glycerol); 4.56 (q, 1H, CH, calixarene); 4.75 (q, 3H, CH, calixarene); 6.41 (s, 3H, H-arom., calixarene); 6.64 (s, 1H, H-arom., calixarene); 7.16 (s, 1H, H-arom., calixarene); 7.32 (s, 3H, H-arom., calixarene). Anal. Calcd for $C_{56}H_{68}O_{20}P_4$ (1185.02): C, 56.76; H, 5.78; P, 10.46. Found: C, 56.33; H, 5.93; P, 10.62.

Phosphitocavitand 24

Phosphitocavitand **24** was obtained analogously to **18** in the reaction of octol **10** (0.3 mmol) with diamidophosphite **14** (0.12 mmol) at 90–95°C for 14 h. Yield 45%. m.p. 176–179°C. ^{31}P NMR ($CDCl_3$) δ, ppm: 135.0–135.3. ^{1}H NMR ($CDCl_3$) δ, ppm: 0.81 (d, $^3J_{HH}$ 6.8 Hz, 12H, CH_3, menthol); 0.95 (d, $^3J_{HH}$ 6.0 Hz, 24H, CH_3, menthol); 1.08–2.29 (64H, CH, CH_2, menthol; CH_2, CH_3, calixarene); 4.43 (m, 4H, CHO, menthol); 4.58 (t, 1H, CH, calixarene); 4.83 (t, 3H, CH, calixarene); 6.41 (s, 1H, H-arom., calixarene); 6.45 (s, 1H, H-arom., calixarene); 6.53 (s, 1H, H-arom., calixarene); 6.57 (s, 1H, H-arom., calixarene); 7.32 (s, 2H, H-arom., calixarene); 7.38 (s, 2H, H-arom., calixarene). Anal. Calcd for $C_{80}H_{116}O_{12}P_4$ (1393.66):C, 68.94; H, 8.39; P, 8.89. Found: C, 68.53; H, 8.33; P, 8.62.

Phosphitocavitand 26

Phosphitocavitand **26** was obtained analogously to **18** in the reaction of octol **9** (0.28 mmol) with diamidophosphite **16** (1.12 mmol) for 12 days.

Yield 80%. m.p. 200–203°C. ^{31}P NMR ($CDCl_3$) δ, ppm: 133.2. ^{1}H NMR ($CDCl_3$), δ, ppm: 0.68 (s, 12H, CH_3, cholesterol); 0.87 (d, $^3J_{HH}$ 6.4 Hz, 24H, CH_3, cholesterol); 0.92 (d, $^3J_{HH}$ 6.4 Hz, 12H, CH_3, cholesterol); 1.05 (s, 12H, CH_3, cholesterol); 1.77 (d, $^3J_{HH}$ 8.0 Hz, 12H, CH_3, calixarene); 1.04–2.06 (104H, CH, CH_2, cholesterol); 2.52 (d, $^3J_{HH}$ 6.4 Hz, 8H, OCH–C$\underline{H}_2$–C=, cholesterol); 4.55 (m, 4H, HCO, cholesterol); 4.71 (m, 4H, CH, calixarene); 5.41 (t, 4H, =CH, cholesterol); 6.48 (s, 1H, H-arom., calixarene); 6.65 (s, 3H, H-arom., calixarene); 7.31 (s, 2H, H-arom., calixarene); 7.38 (s, 2H, H-arom., calixarene). Anal. Calcd for $C_{140}H_{204}O_{12}P_4$ (2203.01): C, 76.33; H, 9.33; P, 5.62. Found: C, 76.41; H, 9.24; P, 5.52.

Phosphitocavitand 26a

Phosphitocavitand **26a** was obtained analogously to **18** in the reaction of octol **9** (0.18 mmol) with diamidophosphite **16** (0.72 mmol) at 90°C for 8 h. Yield 40%. m.p. 193–195°C. ^{31}P NMR ($CDCl_3$) δ, ppm: 133.0. ^{1}H NMR ($CDCl_3$), δ, ppm: 0.68 (s, 12H, CH_3, cholesterol); 0.87 (d, $^3J_{HH}$ 6.4 Hz, 24H, CH_3, cholesterol); 0.92 (d, $^3J_{HH}$ 6.4 Hz, 12H, CH_3, cholesterol); 1.05 (s, 12H, CH_3, cholesterol); 1.74 (d, $^3J_{HH}$ 8.1 Hz, 12H, CH_3, calixarene); 1.13–2.04 (104H, CH, CH_2, cholesterol); 2.52 (d, $^3J_{HH}$ 6.4 Hz, 8H, OCH–C$\underline{H}_2$–C=, cholesterol); 4.52 (m, 4H, HCOP, cholesterol); 4.82 (q, 4H, CH, calixarene); 5.41 (t, 4H, =CH, cholesterol); 6.64 (s, 4H, H-arom., calixarene); 7.30 (s, 4H, H-arom., calixarene). Anal. Calcd for $C_{140}H_{204}O_{12}P_4$ (2203.01): C, 76.33; H, 9.33; P, 5.62 Found: C, 76.25; H, 9.42; P, 5.71.

Thiophosphatocavitand 27

Sulphur (0.56 mmol) was added to a solution of cavitand **18** (0.24 mmol) in benzene (2 ml). The reaction mixture was stirred at 50–60°C for 3 h. Two-thirds of the solvent was evaporated under vacuum. Hexane was added to the residue, and the precipitate formed was filtered off and dried under vacuum (1 mm Hg) at 50°C. Yield 51%. m.p. 205–207°C. ^{31}P NMR ($CDCl_3$) δ, ppm: 56.5 (br., s). ^{1}H NMR ($CDCl_3$) δ, ppm: 1.34 (s, 12H, $(CH_3)_2$C-galactose); 1.36 (s, 12H, $(CH_3)_2$C-galactose); 1.47 (s, 12H, $(CH_3)_2$C-galactose); 1.55 (s, 12H, $(CH_3)_2$C-galactose); 1.72 (d, $^3J_{HH}$ 7.6 Hz, 6H, CH_3, calixarene); 1.80 (d, $^3J_{HH}$ 7.3 Hz, 6H, CH_3, calixarene); 4.23–4.65 (24H, CH, CH_2, galactose); 4.84 (m, 4H, CH, calixarene); 5.55 (d, $^3J_{HH}$ 4.9 Hz, 4H, C^{1}H, galactose); 6.43 (s, 2H, H-arom., calixarene); 6.49 (s, 1H, H-arom., calixarene); 6.64 (s, 1H, H-arom., calixarene); 7.15 (s, 1H, H-arom., calixarene); 7.18 (s, 2H, H-arom., calixarene); 7.22 (s,

1H, H-arom., calixarene). Anal. Calcd for $C_{80}H_{100}O_{32}P_4S_4$ (1825.79): C, 52.63; H, 5.52; P, 6.79. Found: C, 52.42; H, 5.78; P, 7.01.

Thiophosphatocavitand 28

Thiophosphatocavitand **28** was obtained analogously to **27** in the reaction of cavitand **19** (0.14 mmol) with sulphur (0.56 mmol) for 3 h. Yield 36%. m.p. 173–175°C. ^{31}P NMR ($CDCl_3$) δ, ppm: 57.3, 58.0, 58.4. ^{1}H NMR ($CDCl_3$) δ, ppm: 0.96 (t, 12H, $(CH_2)_2$—C<u>H</u>$_3$, calixarene); 1.12 (s, 12H, $(CH_3)_2$C-galactose); 1.18 (m, 8H, CH_2—C<u>H</u>$_2$—CH_3, calixarene); 1.22 (s, 12H, $(CH_3)_2$C-galactose); 1.52 (s, 12H, $(CH_3)_2$C-galactose); 1.59 (s, 12H, $(CH_3)_2$C-galactose); 2.20 (m, 8H, C<u>H</u>$_2$-CH_2-CH_3, calixarene); 4.21–4.88 (28H, CH, CH_2, galactose and CH, calixarene); 5.57 (b s, 4H, C^{1}H, galactose); 6.82 (b s, 4H, H-arom., calixarene); 7.48 (b s, 4H, H-arom., calixarene). Anal. Calcd for $C_{88}H_{116}O_{32}P_4S_4$ (1938.00): C, 54.54; H, 6.03; P, 6.39. Found: C 54.32; H 6.24; P, 6.71.

Thiophosphatocavitand 29

Thiophosphatocavitand **29** was obtained analogously to **27** in the reaction of cavitand **20** (0.08 mmol) with sulphur (0.32 mmol) at 80°C for 3 h. Yield 83%. m.p. 205–207°C (decomp.). ^{31}P NMR (C_6H_6) δ, ppm: 56.7. ^{1}H NMR ($CDCl_3$) δ, ppm: 1.41(s, 12H, $(CH_3)_2$C-glycerol); 1.49(s, 12H, $(CH_3)_2$C-glycerol); 1.72 (b s, 6H, CH_3, calixarene); 1.82 (b s, 6H, CH_3, calixarene); 3.98 (m, 4H, CH_2O, glycerol); 4.17 (m, 4H, CH_2O, glycerol); 4.36 (m, 8H, CH_2O, glycerol); 4.46 (m, 4H, CHO, glycerol); 4.64 (q, 1H, CH, calixarene); 4,81 (q, 3H, CH, calixarene); 6.36 (s, 1H, H-arom., calixarene); 6.44 (s, 2H, H-arom., calixarene); 6.66 (s, 1H, H-arom., calixarene); 7.20 (s, 1H, H-arom., calixarene); 7.26 (s, 2H, H-arom., calixarene); 7.33 (s, 1H, H-arom., calixarene). Anal. Calcd for $C_{56}H_{68}O_{20}P_4S_4$ (1313.29): C, 51.21; H, 5.22; P, 9.43. Found: C, 51.38; H, 5.13; P, 9.42.

Thiophosphatocavitand 30

A solution of octol **10** (0.24 mmol) and diamidophosphite **13** (0.96 mmol) in dioxane (2 ml) was stirred at 25°C for 4 days. Sulphur (0.96 mmol) was added to the phosphitocavitand **21** formed (δ_P 127 ppm), and the reaction mixture was stirred at 80°C for 3 h. Two-thirds of the solvent was removed under vacuum. Hexane was added to the residue, and the precipitate formed was filtered off and dried under vacuum (1 mm Hg) at 50°C. Yield 55%. m.p. 195–197°C (decomp.). ^{31}P NMR ($CDCl_3$) δ, ppm: 53.5–57.0. ^{1}H NMR ($CDCl_3$) δ, ppm: 0.95 (t, 6H, CH_3, calixarene);

1.05 (t, 6H, CH_3, calixarene); 1.26 (m, 8H, CH_2—$C\underline{H}_2$—CH_3, calixarene); 1.38 (s, 12H, $(CH_3)_2$C-glycerol); 1.47 (s, 12H, $(CH_3)_2$C-glycerol); 2.21 (b s, 8H, $C\underline{H}_2$—CH_2—CH_3, calixarene); 3.97–4.56 (24H, CH, CH_2, glycerol and CH, calixarene); 6.35 (s, 1H, H-arom., calixarene); 6.45 (s, 1H, H-arom., calixarene); 6.64 (s, 2H, H-arom., calixarene); 7.05 (s, 2H, H-arom., calixarene); 7.18 (s, 2H, H-arom., calixarene). Anal. Calcd for $C_{64}H_{84}O_{20}P_4S_4$ (1425.50): C, 53.92; H, 5,94; P, 8.69. Found: C, 54.13; H, 6.02; P, 8.93.

Thiophosphatocavitand 31

Thiophosphatocavitand **31** was obtained analogously to **30** in the reaction of octol **11** (0.23 mmol) with diamidophosphite **13** (0.92 mmol) for 4 days followed by the addition of sulphur (0.92 mmol) to the resulting phosphitocavitand **22** (δ_P 127.5 ppm). Yield 77%. m.p. 96–98°C. ^{31}P NMR ($CDCl_3$) δ, ppm: 56.6–56.9. ^{1}H NMR ($CDCl_3$) δ, ppm: 0.88 (m, 12H, $(CH_2)_5C\underline{H}_3$, calixarene); 1.31 (m, 32H, CH_2—$(C\underline{H}_2)_4$—CH_3, calixarene); 1.39 (s, 12H, $(CH_3)_2$C-glycerol); 1.47 (s, 12H, $(CH_3)_2$C-glycerol); 2.23 (m, 8H, $C\underline{H}_2$-$(CH_2)_4$-CH_3, calixarene); 3.96–4.31 (20H, CH_2, CH, glycerol); 4.45 (m, 4H, CH, calixarene); 6.49 (s, 2H, H-arom., calixarene); 6.63 (s, 2H, H-arom., calixarene); 7.04 (s, 2H, H-arom., calixarene); 7.18 (s, 2H, H-arom., calixarene). Anal. Calcd for $C_{76}H_{108}O_{20}P_4S_4$ (1593.82): C, 57.27; H, 6.83; P, 7.77. Found: C, 56.87; H, 6.70; P, 7.44.

Thiophosphatocavitand 32

Thiophosphatocavitand **32** was obtained analogously to **30** in the reaction of octol **9** (0.15 mmol) with diamidophosphite **14** (0.6 mmol) at 90°C for 8 h followed by the addition of sulphur (0.6 mmol) to the resulting phosphitocavitand **23** (δ_P 131.6–132 ppm) and keeping the mixture at 80°C for 5 h. Yield 57%. m.p. 268–270°C (decomp.). ^{31}P NMR ($CDCl_3$) δ, ppm: 55.2, 56.7. ^{1}H NMR ($CDCl_3$) δ, ppm: 0.87 (d, $^3J_{HH}$ 6.8 Hz, 12H, CH_3, menthol); 0.95 (d, $^3J_{HH}$ 6.4 Hz, 24H, CH_3, menthol); 1.05–2.36 (36H, CH, CH_2, menthol.); 1.77 (d, $^3J_{HH}$ 8.4 Hz, 6H, CH_3, calixarene); 1.81 (d, $^3J_{HH}$ 7.4 Hz, 6H, CH_3, calixarene); 4.62 (m, 4H, HCO, menthol); 4.84 (q, 4H, CH, calixarene); 6.50 (s, 1H, H-arom., calixarene); 6.54 (s, 1H, H-arom., calixarene); 6.62 (s, 2H, H-arom., calixarene); 7.22 (s, 2H, H-arom., calixarene); 7.34 (s, 2H, H-arom., calixarene). Anal. Calcd for $C_{72}H_{100}O_{12}P_4S_4$ (1409.72): C, 61.34; H, 7.15; P, 8.79. Found: C, 61.13; H, 7.39; P, 8.42.

Thiophosphatocavitand 33

Thiophosphatocavitand **33** was obtained analogously to **27** in the reaction of cavitand **24** (0.07 mmol) with sulphur (0.28 mmol) at 80°C for 5 h. Yield 55%. m.p. 203–205°C. ^{31}P NMR (C_6H_6) δ, ppm: 54.4–56.7. ^{1}H NMR ($CDCl_3$) δ, ppm: 0.88 (d, $^{3}J_{HH}$ 6.8 Hz, 12H, CH_3, menthol); 0.95 (d, $^{3}J_{HH}$ 6.0 Hz, 24H, CH_3, menthol); 1.08–2.23 (64H, CH, CH_2, menthol and CH_2, CH_3, calixarene); 4.45 (m, 4H, CHO, menthol); 4.58 (m, 4H, CH, calixarene); 6.49 (s, 1H, H-arom., calixarene); 6.53 (s, 1H, H-arom., calixarene); 6.58 (s, 1H, H-arom., calixarene); 6.62 (s, 1H, H-arom., calixarene); 7.08 (s, 2H, H-arom., calixarene); 7.14 (s, 2H, H-arom., calixarene). Anal. Calcd for $C_{80}H_{116}O_{12}P_4S_4$ (1521.63): C, 63.13; H, 7.68; P, 8.14. Found: C, 63.32; H, 7.24; P, 8.01.

Thiophosphatocavitand 34

Thiophosphatocavitand **34** was obtained analogously to **30** in the reaction of octol **9** (0.16 mmol) with diamidophosphite **15** (0.64 mmol) at 80–90°C for 7 h followed by the addition of sulphur (0.64 mmol) to the resulting phosphitocavitand **25** (δ_P 129.7–132.5 ppm) and keeping the mixture at 80°C for 3 h. Yield 60%. m.p. 223–225°C (decomp.). ^{31}P NMR ($CDCl_3$) δ, ppm: 54.9–55.6. ^{1}H NMR ($CDCl_3$) δ, ppm: 1.40–1.82 (92H, cyclo-C_6H_{10}-glucose and CH_3, calixarene); 4.05–5.27 (28H, $C^{2-6}H$, glucose and CH, calixarene); 6.00 (b s, 4H, $C^{1}H$, glucose); 6.47 (s, 1H, H-arom., calixarene); 6.51 (s, 1H, H-arom., calixarene); 6.70 (s, 2H, H-arom., calixarene); 7.20 (s, 2H, H-arom., calixarene); 7.34 (s, 2H, H-arom., calixarene). Anal. Calcd for $C_{80}H_{100}O_{32}P_4S_4$ (1825.79): C, 52.63; H, 5.52; P, 6.79. Found: C, 52.20; H, 5.33; P, 6.41.

Thiophosphatocavitand 35

Thiophosphatocavitand **35** was obtained analogously to **27** in the reaction of cavitand **26** (0.02 mmol) with sulphur (0.08 mmol) in benzene (1 ml) for 3 h. Yield 90%. m.p. 236–238°C. ^{31}P NMR ($CDCl_3$) δ, ppm: 53.9, 54.7. ^{1}H NMR ($CDCl_3$), δ, ppm: 0.69 (s, 12H, CH_3, cholesterol); 0.87 (d, $^{3}J_{HH}$ 6.4 Hz, 24H, CH_3, cholesterol); 0.92 (d, $^{3}J_{HH}$ 6.8 Hz, 12H, CH_3, cholesterol); 1.05 (s, 12H, CH_3, cholesterol); 1.03–2.17 (104H, CH, CH_2, cholesterol); 1.80 (br., s, 12H, CH_3, calixarene); 2.58 (d, $^{3}J_{HH}$ 6.7 Hz, 8H, OCH–C$\underline{H}_2$–C=, cholesterol); 4.63 (m, 4H, HCO, cholesterol); 4.82 (q, 4H, CH, calixarene); 5.43 (t, 4H, =CH–, cholesterol); 6.63 (s, 1H, H-arom., calixarene); 6.66 (s, 3H, H-arom., calixarene); 7.21 (s, 2H, H-arom., calixarene); 7.34 (s, 2H, H-arom., calixarene). Anal. Calcd for

$C_{140}H_{204}O_{12}P_4S_4$ (2331.27): C, 72.13; H, 8.82; P, 5.31. Found: C, 72.29; H, 8.61; P, 5.40.

Thiophosphatocavitand 35a

Thiophosphatocavitand **35a** was obtained analogously to **27** in the reaction of phosphitocavitand **26a** (0.02 mmol) with sulphur (0.08 mmol) for 3 h. Yield 83%. m.p. 234–236°C. ^{31}P NMR ($CDCl_3$) δ, ppm: 57.3. ^{1}H NMR ($CDCl_3$), δ, ppm: 0.67 (s, 12H, CH_3, cholesterol); 0.86 (d, $^3J_{HH}$ 6.8 Hz, 24H, CH_3, cholesterol); 0.92 (d, $^3J_{HH}$ 6.8 Hz, 12H, CH_3, cholesterol); 1.03 (s, 12H, CH_3, cholesterol); 1.11–2.15 (104H, CH, CH_2, cholesterol); 1.77 (d, $^3J_{HH}$ 7.7 Hz, 12H, CH_3, calixarene); 2.57 (d, $^3J_{HH}$ 7.7 Hz, 8H, OCH–C$\underline{H}_2$–C=, cholesterol); 4.63 (m, 4H, HCO, cholesterol); 4.83 (q, 4H, CH, calixarene); 5.39 (t, 4H, =CH–, cholesterol); 6.62 (s, 4H, H-arom., calixarene); 7.26 (s, 4H, H-arom., calixarene). Anal. Calcd for $C_{140}H_{204}O_{12}P_4S_4$ (2331.27): C, 72,13; H, 8,82; P, 5,31. Found: C, 72,25; H, 8,64; P, 5,32.

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