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Synthesis of New Heterofunctionalized Resorcinarene Derivatives

**V. I. Maslennikova, T. V. Guzeeva, O. S. Serkova,
L. K. Vasyanina, V. V. Glushko, and E. E. Nifant'ev**

Moscow State Pedagogical University, Nesvizhskii per. 3, Moscow, 119021 Russia
e-mail: him-vim@mail.ru

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Abstract—New derivatives of heterofunctionalized resorcinarenes differing by the nature, number, ratio, and orientation of functional groups were obtained by modification of free reactive centers in the phosphoresorcinarenes of different types.

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Currently great attention is paid to the design of the receptor systems that can act as chemosensors or extractants. The most common matrices for their creation are macrocyclic molecules containing free cavities and a large number of reaction centers located in a certain mode relative to each other [1–4]. These compounds include resorcinarenes and their modified analogs. Due to the conformational lability of these molecules and presence of hydroxy groups and the *ortho* position of benzene rings at the macrocycle whose reactivity can be controlled, the resorcinarenes form a convenient basis for the design of complex compounds with polyfunctionalized cavity systems [5–10].

Our goal was to synthesize derivatives of the new heterofunctional resorcinarenes and consider the ways to modify the free reaction sites of phosphoresorcinolarenes of various types.

To implement this task we used a common scheme: the resorcinarenes were phosphorylated with phosphorous amides, the phospho(IV)resorcinarenes formed were transformed in the phosphorus(IV) resorcinollarenes, and various functional groups were introduced into the latter molecules.

Depending on the required regioselectivity of the process, we selected as the basic compounds the resorcinollarenes **I** with certain substituents in methylidene bridges and *ortho* position of benzene rings of the macro-cyclic framework.

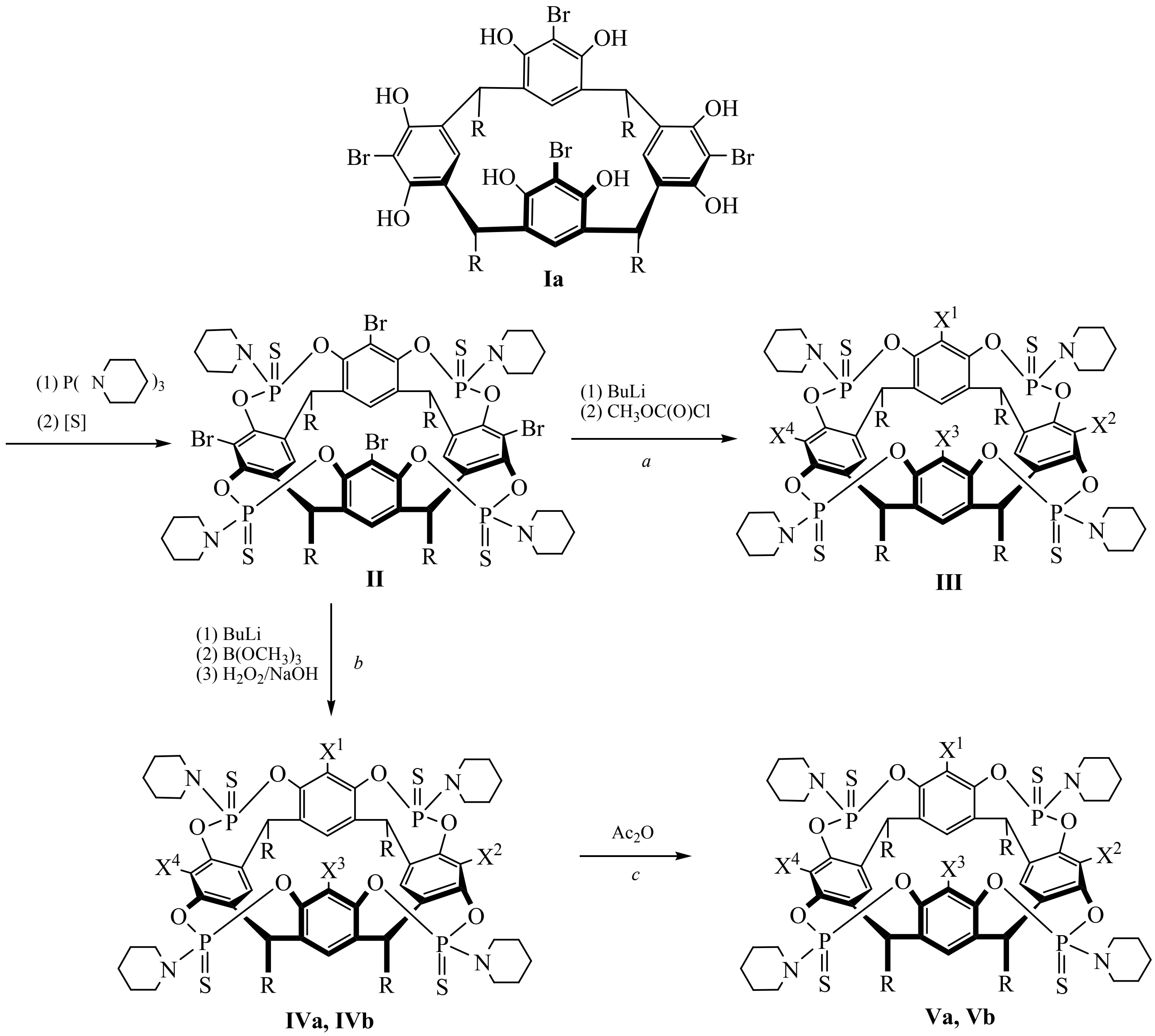
As a platform for the synthesis of new *ortho*-functionalized phosphocavitands served *ortho*-bromotetra(phenylethyl)resorcinarene **Ia**, due to its *boat* conformation, that is convenient for the phosphocyclization [9, 11], and to the presence of easily replaceable bromine atoms in the *ortho* positions of benzene rings of the macrocyclic skeleton [12–15] (Scheme 1).

The cyclophosphorylation of **Ia** with tripiperidylphosphite was performed by the standard method [16, 17] in dioxane at room temperature. To the formed phosphorus(III)cavitand was added sulfur without its isolation from the reaction mixture (Scheme 1). Two singlet signals with equal integral intensities appeared in the ^{31}P NMR spectrum of the isolated tionamidophosphatocavitand **II** and the doubling of signals of the the benzene rings *meta*-protons of the framework in the ^{1}H NMR spectrum indicated the implementation of the *kite* conformation [17, 18].

The phosphorus(IV)cavitand **II** was brpoght into the reaction of electrophilic substitution. Compound **II** was treated with BuLi, then to it was added either methylchloroformate, which led to *ortho*-methoxycarbonyl derivative **III** (Scheme 1, *a*), or sequentially trimethylborate and hydrogen peroxide with sodium hydroxide solution, which completed by the formation of the *ortho*-hydroxylated cavitands **IV** (Scheme 1, *b*). Further, in the interaction of **IV** with acetic anhydride *ortho*-acetylated cavitand **V** was obtained (Scheme 1, *c*).

Compounds **III–V** were characterized using the methods of MALDI mass-spectrometry, IR and NMR spectroscopy. The IR spectrum of cavitand **III** includes the bands characteristic of carbonyl (1770.5 cm^{-1}) and

Scheme 1.



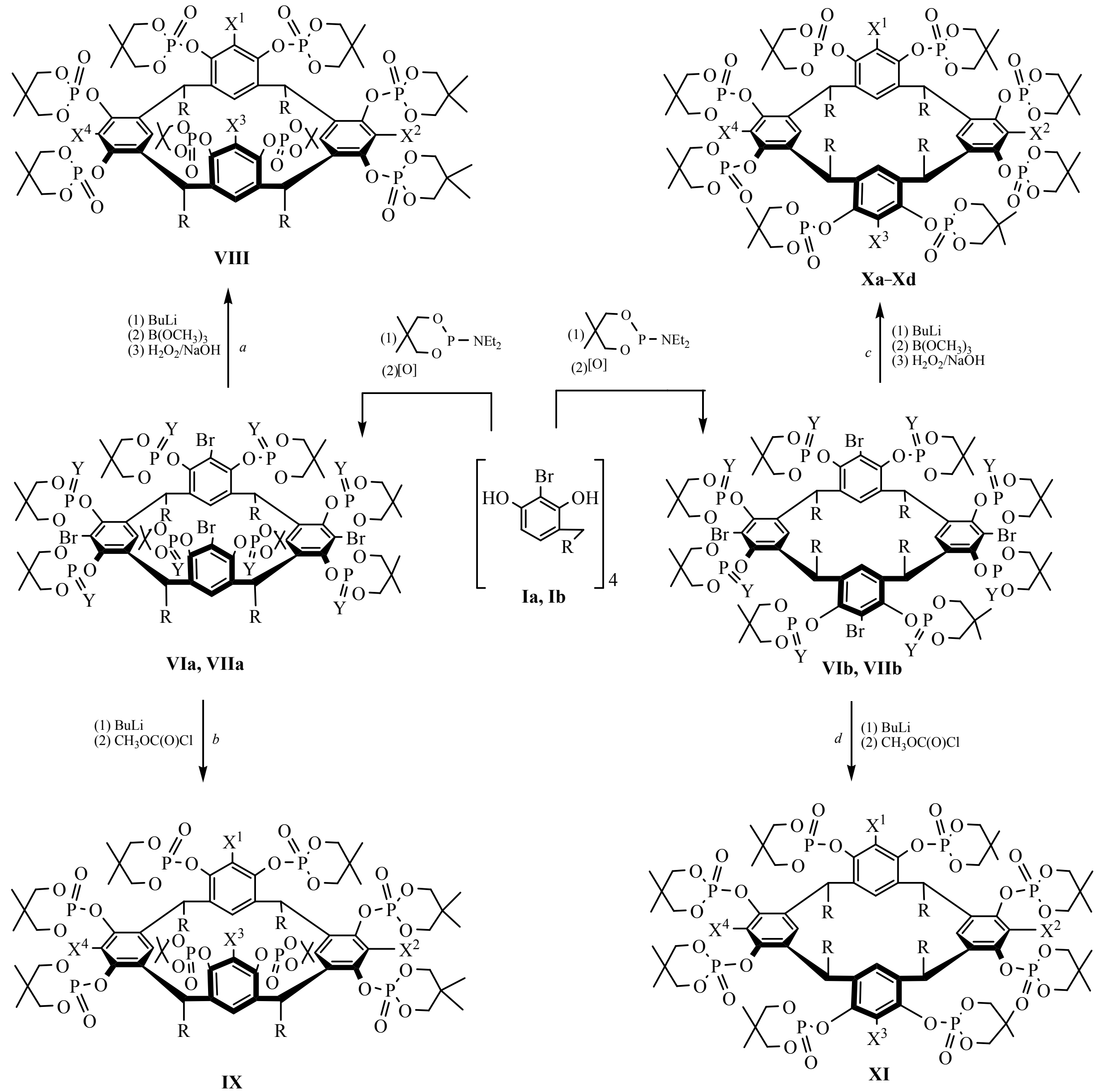
R = $CH_2CH_2C_6H_5$; **III**, X^{1-4} = $(O)COCH_3$; **IVa**, X^{1-4} = OH; **IVb**, X^{1-3} = OH, X^4 = Br; **V**a, X^{1-4} = $OC(O)CH_3$; **Vb**, X^{1-3} = $OC(O)CH_3$, X^4 = Br.

methoxy (1440 cm^{-1}) groups. In the ^{1}H NMR spectrum a signal of the protons of methoxyl groups in was observed alongside the signals of protons of the original thionoamidophosphate **II**. The mass spectrum contained a peak at *m/z* 1730 corresponding to the complex of **III** with two Li$^+$ cations.

Hydroxylation of cavitand **II** proceeded with formation of a mixture of products, **IVa** and **IVb**. The mass spectrum of the obtained compounds **IV** contains peaks at *m/z* 1547, 1570, 1621 belonging to the tetrahydroxy-cavitand **IVa**, complex **IVa** with Na$^+$ cations, and complexes of monobromo-trihydroxy-cavitand **IVb** with the cation Li$^+$, respectively. In the ^{1}H NMR spectrum of the cavitands **IVa**, **IVb** a broadening of the signals of all proton groups occurs due to the contribution of signals of similar protons of each compound.

Acylation of *ortho*-hydroxy-cavitands **IVa**, **IVb** with acetic anhydride leads to the corresponding tetra- and triacetylated derivatives **Va**, **IVb**. The IR spectrum

Scheme 2.



R = $CH_2CH_2C_6H_5$ (**Ia, VIa, VIIa, VIII, IX**), $C_{10}H_7$ (**Ib, VIb, VIIb, X, XI**); Y = НЭП (**VIa, VIb**), O (**VIIa, VIIb**); $X^{1–4}$ = OH (**VIII, Xa**), (O)$COCH_3$ (**IX, XI**); $X^{1–3}$ = OH, X^4 = Br (**Xb**); $X^{1,2}$ = OH, $X^{3,4}$ = Br (**Xc**); X^1 = OH, $X^{2–4}$ = Br (**Xd**).

of the cavitand **V** included an absorption band of carbonyl groups (1771 cm^{-1}). The ^1H NMR spectrum contained the signals of the methyl protons of acetyl groups. The MALDI spectrum contained the peaks corresponding to masses of tetra- and tri-acetylated (1715 and 1753, respectively) thionoamidophosphatocavitands **V**, the latter holds two lithium ions.

To determine the effect of conformation of the resorcinarene matrix on the selectivity of the *ortho*-modification, we used *ortho*-bromo-tetra(phenylethyl)- (**Ia**) and *ortho*-bromo-tetranaphthyl- (**Ib**) resorcinollarenes as the basic compounds for the synthesis of *ortho*-functionalized octaphosphorylated resorcinarenes **VIII–XI.** Compounds **Ia** and **Ib** are in the *boat* and *chair* conformations, respectively.

The octaphosphorylation of **Ia, Ib** and the subsequent oxidation of the obtained perphosphorylated products **VIa** and **VIb** was carried out using the previously developed technique [19, 20]. According to the data of ^{31}P and ^{1}H NMR spectroscopy, the steric organization of octaphosphates **VIIa**, **VIIb** was similar to that of their tricoordinated precursors **VIa**, **VIb** and corresponded to the conformation of the initial resorcinarenes **Ia**, **Ib** (Scheme 2).

For the *ortho*-functionalization of phosphoresorcinolarenes **VII** (Scheme 2) we used the same reaction as for the modification of phosphocavitand **II** (Scheme 1).

At the hydroxylation and methoxyformylation of phosphoresorcinarene **VIIa**, which existed in the *boat* conformation, all bromine atoms of the molecule were replaced, which led to the formation of tetrafunctionalized derivatives **VIII** and **IX**, respectively (Scheme 2, *a*, *b*).

In the ^{31}P NMR spectrum of *ortho*-hydroxyresorcinolarene **VIII** two singlet signals of equal integral intensity with chemical shifts –14.0 and –15.1 ppm were registered, in the ^{1}H NMR spectrum there are broad proton signals of dioxaphosphinane rings and the resorcinarene framework. Such a broadening of the signals was due to the formation of a complex of **VIII** with two sodium ions, as evidenced by a peak at *m/z* 2199 in the mass spectrum and the decreased intensity of the absorption bands in the infrared spectrum at 3390 cm^{-1} characteristic of the hydroxy groups.

The *ortho*-methoxyformylated resorcinarene **IX** was isolated as a complex with the Na^{+} cation (*m/z* 2346). Intense bands in the IR spectrum at 1768 and 1433 cm^{-1}, characteristic of the carbonyl and methoxy fragments, as well as a signal of methoxy protons at δ 3.84 ppm in the ^{1}H NMR spectrum confirm the presence of methoxycarbonyl groups in the molecules of compound **IX**.

At the hydroxylation of the phosphoresorcinarene **VIIb**, which is in the *chair* conformation, a mixture of compounds **X** formed differing by the degree of substitution of the bromine atoms for the OH groups (Scheme 2, *c*), as evidenced by the data of MALDI spectrometry of the product. The mass spectrum of **X** has peaks at *m/z* 2271 (**Xa** + Li^{+} + Na^{+}), 2344 (**Xb** + K^{+}), 2369 (**Xc**), 2435 (**Xd** + Li^{+}), and 2454 (**Xd** + Na^{+}), corresponding to the molecular masses of tetra-, tri-, di- and monohydroxy derivatives with a different number of alkali metal cations.

In the reaction with methylchloroformate only a part of octaphosphate molecules **VIIIb** is subjected to the modification (Scheme 2, *d*). In the MALDI spectrum of isolated product two intense peaks at *m/z* 2419 and 2500 were observed corresponding to molecular masses of the methyl *ortho*-methylformiate **XI** and *ortho*-bromoresorcinarene **VIIb** with the Li^{+} cation. In the IR spectrum of the resulting substance absorption of methylformate group {1768 cm^{-1} (C=O), 1453 cm^{-1} [C(O)OMe]} and C–Br (1004 cm^{-1}) were registered. In the ^{1}H NMR spectrum there were broad proton signals of the phosphoresorcinarene framework and methylformiate groups. These facts suggest that the methyl *ortho*-methylformylated resorcinarene **XI** forms an associate with the *ortho*-bromoresorcinarene **VIIb** with the participation of Li^{+} cations, which actually was separated from the reaction mixture.

Thus, the degree of *ortho*-modification of the phosphrus-containing resorcinarenes **II** and **VII** depends on the structure of the macrocyclic matrix and the ability of the produced derivatives to behave as an acceptor with respect to the alkali metal cations occurred in the reaction mixture.

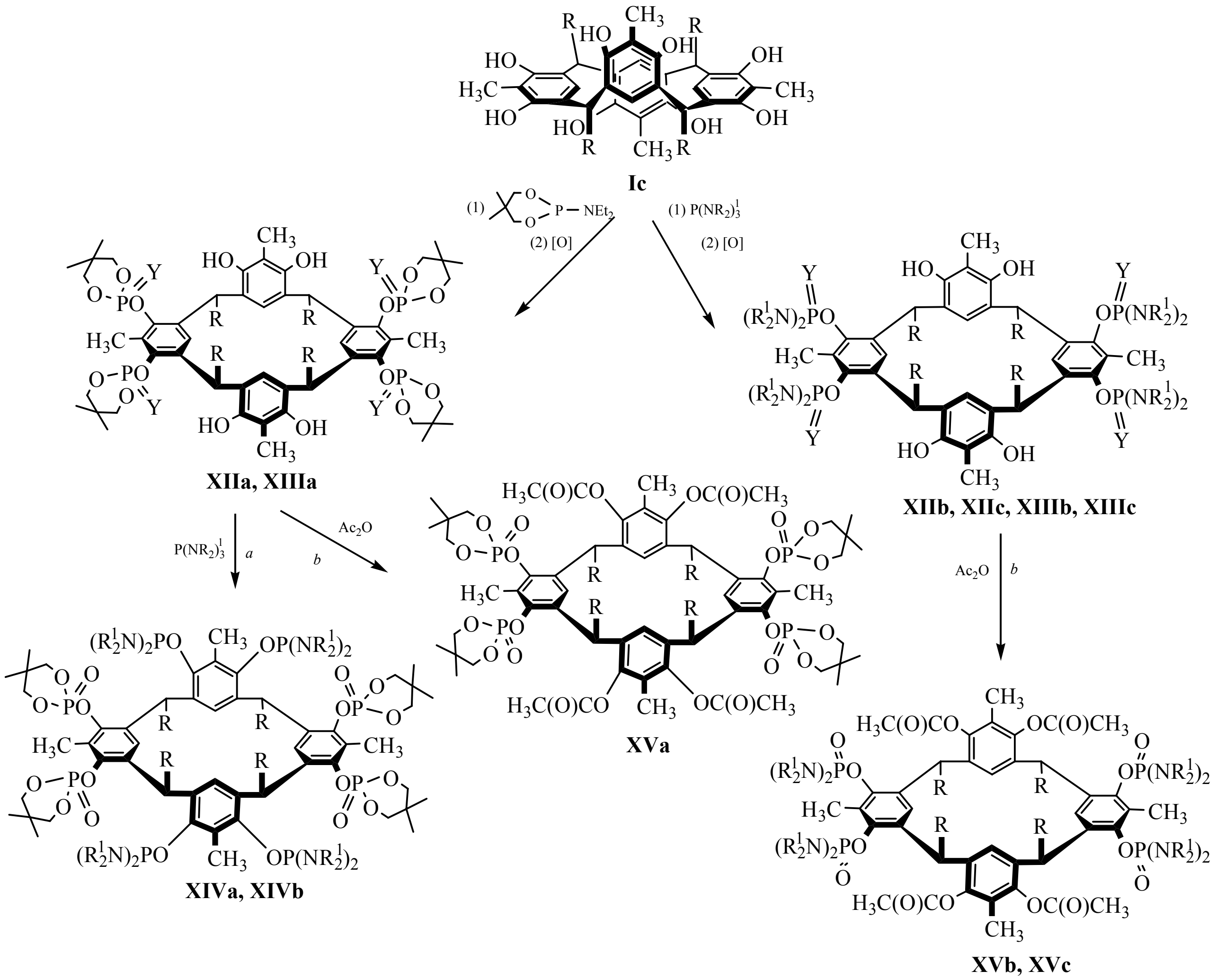
The synthesis of the tetraphosphorylated resorcinolarenes **XII** was performed using *ortho*-methyltetranaphthylresorcinarene **Ic**, which had the *chair* conformation (Scheme 3). This pre-arrangement of the macrocyclic matrix allows regioselective oligophosphorylation of the resorcinarenes with the reagents that differ by nature and number of the reactive substituents at the phosphorus atom [20]. In addition, in the *ortho*-methyl-*rctt*-tetranaphthylresorcinarene **Ic** the hydroxy groups of vertically oriented benzene rings are screened due to the sterically close methyl and two naphthyl groups. This situation contributes to the selective phosphorylation of planar benzene rings.

As phosphorylating reagents we used hexaethyltriamidophosphite, tripiperidylphosphite, and 2-diethylamino-5,5-dimethyl-1,3,2-dioxaphosphinane. The reactions were carried out in dioxane at 80–85°C. The subsequent oxidation of phospho(III)resorcinarenes **XII** with the hydrogen peroxide adduct with urea afforded their P(IV)-analogs **XIII**.

Elemental analyses (Table 1) of compounds **XII** and **XIII** corresponded to immobilization of four phosphorus-containing fragments on the macrocyclic matrix. The same fact was indicated by the signals of four hydroxy groups in ^{1}H NMR spectra of **XII** and **XIII** (Table 2).

The presence in the ^{31}P NMR spectra of phosphoresorcinarenes **XII**, **XIII** of only one singlet signal (Table 2) and in the ^{13}C NMR spectra of one signal of

Scheme 3.



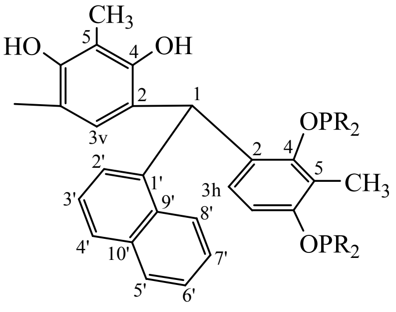
R = $C_{10}H_7$; $R^1 = CH_3$ (**XIVa**), C_2H_5 (**XIIb, XIIIb, XIVb, XVb**); $NR^1_2 = N(CH_2)_5$; Y = NET (**XIIa–XIIc**), O (**XIIIa–XIIIc**).

Table 1. Yields, melting points and elemental analyses data of phosphoresorcinarenes **VI, VII, XII–XV**

Comp. no.	Yield, %	mp, °C	Found, %				Formula	Calculated, %			
			C	H	N	P		C	H	N	P
XIIa	65	280–282[a]	70.06	5.90	–	7.87	$C_{92}H_{92}O_{16}P_4$	70.04	5.88	–	7.85
XIIb	65	305–307[a]	71.56	7.58	6.42	7.21	$C_{104}H_{132}N_8O_8P_4$	71.55	7.56	6.42	7.11
XIIc	51	268–270[a]	73.06	7.28	6.02	6.71	$C_{112}H_{132}N_8O_8P_4$	73.02	7.22	6.08	6.73
XIIIa	60	>360	67.33	5.68	–	5.57	$C_{92}H_{92}O_{20}P_4$	67.31	5.65	–	5.55
XIIIb	65	>360	69.06	7.38	6.12	6.41	$C_{104}H_{132}N_8O_{12}P_4$	69.02	7.30	6.19	6.85
XIIIc	65	298–300	70.55	6.94	8.82	6.51	$C_{112}H_{132}N_8O_{12}P_4$	70.57	6.98	8.88	6.50

[a] Melts with decomposition

Table 2. Parameters of ^{31}P and ^1H NMR spectra of phosphoresorcinarenes **XII** and **XIII** ($CDCl_3$, 25ºC)



Comp. no	δ_P, ppm	Resorcinarene matrix, δ, ppm	Phosphorus fragment (PR_2), δ, ppm	Naphthalene fragment (H-Naph), δ, ppm
XIIa[a]	120	H^1: 6.85 s (4H); H^3: 5.62 s ($2H^h$), 6.45 s ($2H^v$); CH_3: 2.47 s (6H), 2.80 s (6H); OH: 9.96 s (4H)	$OCH_2C(C\underline{H}_3)_2CH_2O$: 0.06 s (12H), 0.84 s (12H); $OC\underline{H}_2C(CH_3)_2C\underline{H}_2O$: 2.88 m ($4H^e$), 3.64 m ($4H^a$), 3.94 m ($4H^e$), 4.90 br.s ($4H^a$)	6.55 d (4H, $H^{2'}$, $^3J_{HH}$ 7.0 Hz), 6.88 d.d (4H, $H^{7'}$, $^3J_{HH}$ 7.9, $^3J_{HH}$ 7.3 Hz), 6.93 d.d (4H, $H^{3'}$, $^3J_{HH}$ 7.6, $^3J_{HH}$ 7.3 Hz), 7.04 d.d (4H, $H^{6'}$, $^3J_{HH}$ 7.6, $^3J_{HH}$ 7.3 Hz), 7.46 d (4H, $H^{4'}$, $^3J_{HH}$ 7.8 Hz), 7.54 d (4H, $H^{8'}$, $^3J_{HH}$ 8.3 Hz), 7.77 d (4H, $H^{5'}$, $^3J_{HH}$ 8.2 Hz)
XIIb	120	H^1: 6.22 s (2H), 6.19 s (2H); H^3: 4.79 s ($2H^h$), 6.42 s ($2H^v$); CH_3: 1.93 s (6H), 2.31 s (6H); OH : 6.69 s (2H), 6.67 s (2H)	$NCH_2C\underline{H}_3$: 0.57 t (24H, $^3J_{HH}$ 6.9 Hz), 0.81 t (24H, $^3J_{HH}$ 6.9 Hz); $NC\underline{H}_2CH_3$: 2.71 m (16H, $^3J_{PH}$ 10.3, $^3J_{HH}$ 6.9 Hz), 3.00 m (16H, $^3J_{PH}$ 14.0, $^3J_{HH}$ 7.3 Hz)	6.14 d (4H, $H^{2'}$, $^3J_{HH}$ 6.9 Hz), 6.77 d.d (4H, $H^{7'}$, $^3J_{HH}$ 7.3, $^3J_{HH}$ 7.3 Hz), 6.84 d.d (4H, $H^{3'}$, $^3J_{HH}$ 7.7, $^3J_{HH}$ 7.7 Hz), 6.99 d.d (4H, $H^{6'}$, $^3J_{HH}$ 7.3, $^3J_{HH}$ 7.3 Hz), 7.20 d (4H, $H^{4'}$, $^3J_{HH}$ 7.8 Hz), 7.25 d (4H, $H^{8'}$, $^3J_{HH}$ 5 Hz), 7.35 d (4H, $H^{5'}$, $^3J_{HH}$ 7.8 Hz)
XIIc	125	H^1: 6.37 s (4H); H^3: 4.80 s ($2H^h$), 7.25 s ($2H^v$); CH_3: 2.01 s (6H), 2.31 s (6H); OH : 6.16 s (2H), 6.18 s (2H)	$N(CH_2)_2C\underline{H}_2(CH_2)_2$: 0.86 m (8H, $^3J_{PH}$ 5.9, $^3J_{HH}$ 5.9 Hz), 1.03 m (8H, $^3J_{HH}$ 4.1 Hz); $CH_2C\underline{H}_2CH_2C\underline{H}_2CH_2$: 1.41 m (8H, $^3J_{PH}$ 5.0, $^3J_{HH}$ 4.6 Hz), 1.49 m (8H, $^3J_{HH}$ 4.6 Hz), 1.57 m (8H, $^3J_{PH}$ 5.0, $^3J_{HH}$ 4.6 Hz), 1.62 m (8H, $^3J_{HH}$ 4.6 Hz); $NC\underline{H}_2(CH_2)_3C\underline{H}_2$: 3.21 m (16H, $^3J_{PH}$ 5.0 Hz), 3.31 m (16H)	6.14 d (4H, $H^{2'}$, $^3J_{HH}$ 6.9 Hz), 6.80 d.d (4H, $H^{6'}$, $^3J_{HH}$ 7.8, $^3J_{HH}$ 7.3 Hz), 6.86 d.d (4H, $H^{3'}$, $^3J_{HH}$ 7.4, $^3J_{HH}$ 7.7 Hz), 7.02 d.d (4H, $H^{7'}$, $^3J_{HH}$ 7.3, $^3J_{HH}$ 7.8 Hz), 7.22 d (4H, $H^{4'}$, $^3J_{HH}$ 8.2 Hz), 7.29 d (4H, $H^{8'}$, $^3J_{HH}$ 8.7 Hz), 7.36 d (4H, $H^{5'}$, $^3J_{HH}$ 8.5 Hz)
XIIIa[a]	–10	H^1: 6.85 s (4H); H^3: 5.26 s ($2H^h$), 7.19 s ($2H^v$); CH_3: 1.94 s (6H), 2.80 s (6H); OH: 8.96 s (4H)	$OCH_2C(C\underline{H}_3)_2CH_2O$: 0.29 s (12H), 0.92 s (12H); $OC\underline{H}_2C(CH_3)_2C\underline{H}_2O$: 3.28 d.d ($4H^e$, $^2J_{HH}$ 10.5, $^3J_{PH}$ 11.4 Hz), 3.36 d.d ($4H^a$, $^2J_{HH}$ 10.1, $^3J_{PH}$ 2.3 Hz), 3.77 d.d ($4H^e$, $^2J_{HH}$ 10.6, $^3J_{PH}$ 12.3 Hz), 3.95 d.d ($4H^a$, $^2J_{HH}$ 10.5, $^3J_{PH}$ 2.2 Hz)	6.94 d (4H, $H^{2'}$, $^3J_{HH}$ 6.8 Hz), 6.96 d.d (4H, $H^{6'}$, $^3J_{HH}$ 6.9, $^3J_{HH}$ 8.8 Hz), 7.05 d.d (4H, $H^{3'}$, $^3J_{HH}$ 7.5, $^3J_{HH}$ 7.9 Hz), 7.14 d.d (4H, $H^{7'}$, $^3J_{HH}$ 7.5, $^3J_{HH}$ 7.9 Hz), 7.46 d (4H, $H^{4'}$, $^3J_{HH}$ 7.8 Hz), 7.54 d (4H, $H^{8'}$, $^3J_{HH}$ 8.3 Hz), 7.77 d (4H, $H^{5'}$, $^3J_{HH}$ 8.7 Hz)
XIIIb	12	H^1: 6.53 s (4H); H^3: 4.77 s ($2H^h$), 6.62 s ($2H^v$); CH_3: 2.00 s (6H), 2.30 s (6H); OH : 8.82 s (2H), 8.83 s (2H)	$NCH_2C\underline{H}_3$: 0.66 t (24H, $^3J_{HH}$ 6.9 Hz), 1.00 t (24H, $^3J_{HH}$ 6.9 Hz); $NC\underline{H}_2CH_3$: 2.11 m (8H, $^3J_{PH}$ 14.2, $^3J_{HH}$ 7.3 Hz), 2.58 m (8H, $^3J_{PH}$ 14.7, $^3J_{HH}$ 7.4 Hz), 3.02 m (16H, $^3J_{PH}$ 11.4, $^3J_{HH}$ 7.3 Hz)	6.26 d (4H, $H^{2'}$, $^3J_{HH}$ 6.8 Hz), 6.73 d.d (4H, $H^{6'}$, $^3J_{HH}$ 7.3, $^3J_{HH}$ 7.3 Hz), 6.91 d.d (4H, $H^{3'}$, $^3J_{HH}$ 7.8, $^3J_{HH}$ 7.8 Hz), 7.00 d.d (4H, $H^{7'}$, $^3J_{HH}$ 7.3, $^3J_{HH}$ 7.3 Hz), 7.18 d (4H, $H^{4'}$, $^3J_{HH}$ 8.3 Hz), 7.34 d (8H, $H^{5',8'}$, $^3J_{HH}$ 8.2 Hz)
XIIIc	10	H^1: 6.58 s (4H); H^3: 4.80 s ($2H^h$), 7.25 s ($2H^v$); CH_3: 2.01 s (6H), 2.31 s (6H); OH : 8.71 s (4H, OH)	$N(CH_2)_2C\underline{H}_2(CH_2)_2$: 0.63 m (8H), 1.03 m (8H); $NCH_2C\underline{H}_2CH_2C\underline{H}_2CH_2$: 1.49 m (16H), 1.50 m (16H); $NC\underline{H}_2(CH_2)_3C\underline{H}_2$: 2.89 m (16H, $^3J_{PH}$ 4.2 Hz), 3.15 m (16H, $^3J_{PH}$ 4.3 Hz)	6.21 d (4H, $H^{2'}$, $^3J_{HH}$ 6.9 Hz), 6.75 d.d (4H, $H^{6'}$, $^3J_{HH}$ 6.9, $^3J_{HH}$ 7.8 Hz), 6.89 d.d (4H, $H^{3'}$, $^3J_{HH}$ 7.6, $^3J_{HH}$ 7.4 Hz), 7.00 d.d (4H, $H^{7'}$, $^3J_{HH}$ 7.8, $^3J_{HH}$ 7.3 Hz), 7.16 d (4H, $H^{4'}$, $^3J_{HH}$ 7.8 Hz), 7.34 d (4H, $H^{8'}$, $^3J_{HH}$ 7.7 Hz), 7.36 d (4H, $H^{5'}$, $^3J_{HH}$ 8.8 Hz)

[a] *d*-Py, 25ºC.

Table 3. Parameters of ^{13}C NMR spectra of phosphoresorcinarenes (**XII, XIII**), $CDCl_3$, 25ºC

Comp. no.	C^1	C^2	C^3	C^4	C^5	CH_3	C-Naph	PR_2
XIIb	42.4	128.3 128.7	128.9 131.3	150.8 d (COP, $^2J_{PC}$ 5.6 Hz); 152.1 (COH)	111.5 113.7	9.3 11.9	137.9 ($C^{1'}$), 126.2 ($C^{2'}$), 124.4 ($C^{3'}$), 126.1 ($C^{4'}$), 127.8 ($C^{5'}$), 124.7 ($C^{6'}$), 124.5 ($C^{7'}$), 124.1 ($C^{8'}$), 131.3 ($C^{9'}$), 132.8 ($C^{10'}$)	$NCH_2\underline{C}H_3$: 14.9; $N\underline{C}H_2CH_3$: 39.9 d ($^2J_{PC}$ 19.1 Hz), 40.1 d ($^2J_{PC}$ 15.3 Hz)
XIIc	41.6	127.9 128.0	128.8 128.9	151.1 d (COP, $^2J_{PC}$ 3.7 Hz); 151.8 (COH)	111.5 119.2	9.2 11.9	137.5 ($C^{1'}$), 128.5 ($C^{2'}$), 124.6 ($C^{3'}$, $C^{7'}$, $C^{8'}$), 126.4 ($C^{4'}$), 126.3 ($C^{5'}$), 124.9 ($C^{6'}$), 131.1 ($C^{9'}$), 132.9 ($C^{10'}$)	$N(CH_2)_2C\underline{H}_2(CH_2)_2$: 23.1, 23.9; $NCH_2C\underline{H}_2CH_2C\underline{H}_2CH_2$: 26.2, 26.9; $NC\underline{H}_2(CH_2)_3C\underline{H}_2$: 45.3, 45.7
XIIIb	41.6	126.6 128.9	131.9 132.5	146.9 d (COP, $^2J_{PC}$ 7.7 Hz); 152.8 (COH)	112.7 118.3	9.6 12.1	138.1 ($C^{1'}$), 126.5 ($C^{2'}$), 124.9 ($C^{3'}$), 125.9 ($C^{4'}$), 127.7 ($C^{5'}$), 125.0 ($C^{6'}$), 124.4 ($C^{7'}$), 124.6 ($C^{8'}$), 131.5 ($C^{9'}$), 132.6 ($C^{10'}$)	$NCH_2\underline{C}H_3$: 13.8, 14.9; $N\underline{C}H_2CH_3$: 39.0 d ($^2J_{PC}$ 3.9 Hz), 41.3 d ($^2J_{PC}$ 3.5 Hz)

the C^4 carbon atom connected with phos-phorous group, and one signal of the C^4 connected with the hydroxy group (Table 3) showed that phosphorus fragments are arranged symmetrically on diametrically opposite benzene rings. This is also supported by the data of X-ray diffraction investigation of tetraphosphinanylresorcinarene **XIIa**.[1] In the crystalline state the **XIIa** molecule is in *chair* conformation with *rctt* configuration of naphthyl substituents. The four phosphinane fragments are located on the horizontally oriented benzene rings of the resorcinarene.

Tetraphosphatoresorcinarenes **XIII** were subjected to further modification. Tetraphosphinanyl-resorcinarene **XIIIa** was phosphorylated with phos-phorous triamides (Scheme 3, *a*). The reaction mixture was maintained at 90–105°C for several days. The more rigid conditions of the second phosphorylation as compared with the primary one is due to the high steric loading of the **XIIIa** molecule and shielding of the hydroxy group of the vertical benzene with the naphthyl fragment. As a result, we obtained octaphosphorylated derivatives **XIV** containing in the molecule phosphorus atoms of different nature and coordination.

We failed to isolate compound **XIVb** owing to its high solubility in organic solvents. The phosphoresorcinarene **XIVa** was isolated in 67% yield as an individual stereoisomer with different phosphorus-containing fragments in the horizontal and vertical benzene rings of the macrocyclic matrix, which was confirmed by the data of NMR spectroscopy.

In the ^{31}P NMR spectrum of **XIVa** there are two singlet signals of equal integral intensity, with chemical shifts 130.5 and –14.0 ppm. In the ^{1}H NMR spectrum of **XIVa** (see the figure) the signals of hydroxy groups are absent, while appear two doublet signals of protons of methyl groups of amidophosphite fragments with chemical shifts 2.50 and 2.62 ppm and spin-spin coupling constants $^3J_{PH}$ 9.2 and 8.4 Hz, respectively. In the ^{13}C NMR spectrum there are two doublet signals of the carbon atoms C^4 associated with diamidophosphite (150.6 ppm, $^2J_{PC}$ 15.1 Hz) and phosphate groups (147.2 ppm, $^2J_{PC}$ 14.7 Hz)

The acetylation of tetraphosphatoresorcinarenes **XIIIa–XIIIc** with acetic anhydride (Scheme 3, *b*) proceeded under milder conditions (2 h, 75°C) than the phosphorylation of **XIIIa**. The ^{31}P NMR spectra of isolated products **XVa–XVc** contain one singlet signal in the region characteristic of the derivatives of tetracoordinated phosphorus. In the ^{1}H, ^{13}C NMR spectra there are the signals of the protons and carbon atoms of the resorcinarene framework, phosphate and acetyl groups. Ratio of integral intensities of proton signals of the resorcinarene framework and the methyl protons of acetyl groups in the ^{1}H NMR spectra is consistent with the presence of four acyl fragments in the **XVa–XVc** molecules.

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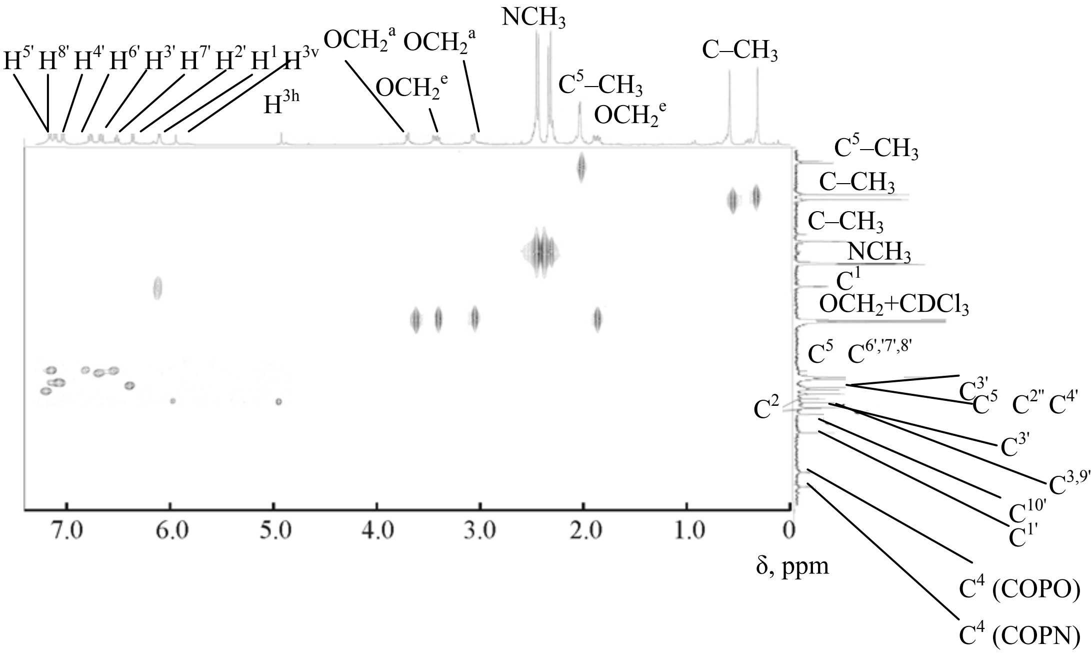
[1] Crystallographicdata of compound **XIIa** are deposited in the Cambridge crystallographic database (cc/dc 780946).



^{13}C–^{1}H NMR spectrum of phosphoresorcynolarene **XIVa** ($CDCl_3$, 25ºC).

The IR spectra of resorcinarenes **XVa–XVc** contain a strong absorption band of carbonyl group at 1759 cm^{-1}. Molecular mass of compounds **XVa** and **XVb** obtained by MALDI spectrometry and elemental analysis data correspond to the calculated values.

Thus, by the selective modification of resorcinolarene **Ic** heterofunctionalized derivatives were obtained with a predefined orientation of functional groups attached to the macrocyclic matrix.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra (internal reference TMS) and ^{31}P NMR spectra (external reference 85% H_3PO_4) were registered on a Jeol ECX-400 spectrometer (at the operating frequencies ^{1}H 400 MHz, ^{13}C 100.5 MHz, and ^{31}P 161.8 MHz). The MALDI-TOF mass spectra were obtained on a Bruker Ultraflex TOF/TOF mass spetrometer (Bruker Daltonics GmbH), the matrix is 1,8,9-trihydroxyanthracene. The IR spectra were recorded on a Nicolette 380 Thermo spectrometer in the reflection mode in the range of 4000–500cm^{-1} on a ZnSe slide.

All syntheses were performed under argon, with dry oxygen-free solvents.

Resorcinarenes **Ia–Ic**, 2-diethylamino-5,5-dimethyl-1,3,2-dioxaphosphinane, and octaphosphorylated resorcinarene **VIb** were obtained according to the procedures described in [20–22].

Phosphocavitand II. A mixture of 0.170 mmol of resorcinarene **Ia** and 0.760 mmol of tripiperidylphosphite in 20 ml of dioxane was kept for 14 days at 20°C. To the formed amidophosphitocavitand [^{31}P NMR (dioxane) δ, ppm: 136.9 s (2P), 137.7 s (2P)] was added 1.52 mmol of sulfur in 10 ml of benzene and the reaction mixture was heated for 4 h at 80°C. The solvents were then distilled off, and the residue was dissolved in 1 ml of methylene chloride. To the solution was added 10 ml of hexane, the precipitate formed was filtered off, washed with hexane, and dried for 3 h at 80–90°C (1 mm Hg). Yield 73%, mp 150–151°C. ^{1}H NMR spectrum ($CDCl_3$, 25ºC), δ, ppm: 1.56 br.s [12H, $NCH_2(C\underline{H_2})_3CH_2$]; 1.67 br.s [12H, $NCH_2(C\underline{H_2})_3CH_2$]; 2.48 m (8H, $CH_2C\underline{H_2}Ph$); 2.61 m (8H, $CH_2C\underline{H_2}Ph$); 3.46 m [16H, $NC\underline{H_2}(CH_2)_3CH_2$, $^{3}J_{PH}$ 9.7 Hz]; 5.33 m (2H, CH, $^{3}J_{HH}$ 7.0 Hz); 5.60 m (2H, CH, $^{3}J_{HH}$ 7.5 Hz), 6.61 to (2H, H^3), 6.90 s (2H, H^3), 7.13–7.25 m (20H, Ph). ^{31}P NMR spectrum ($CDCl_3$, 25ºC), δ, ppm: 63.2, 63.9 .Found, %: C 53.40, H 4.72; N 3.15; P 6.90. $C_{80}H_{84}Br_4N_4O_8P_4S_4$. Calculated, %: C 53.34, H 4.70; N 3.11; P 6.88.

***ortho*-Methyloxycarbonylated phosphocavitand III**. To a solution of 0.047 mmol of the cavitand **II** in 25 ml of THF at –78°C was added 2.2 ml of butyllithium (1.5 M solution in hexane). The reaction mixture was stirred for 2 h, 0.18 ml of methylchloroformate was added and the stirring was continued for another 30 min. The reaction mixture was heated to room temperature, 10 ml of water was added and the mixture was left overnight. Organic solvents were distilled off, and the product was extracted from water with methylene chloride (3×5 ml). CH_2Cl_2 was evaporated, the residue was dissolved in 1 ml of methylene chloride, and 5 ml of hexane was added. The resulting precipitate was filtered off and dried for 4 h at 80°C (1 mm Hg). Yield 79%, mp 155–157ºC (decomp.). IR spectrum, cm^{-1}: 1770.5 (C=O), 1440 [C(O)OMe]. ^{31}P NMR spectrum ($CDCl_3$, 25ºC), δ, ppm: 63–64. ^1H NMR spectrum ($CDCl_3$, 25ºC), δ, ppm: 1.62 br.s [12H, $NC\underline{H}_2(CH_2)_3C\underline{H}_2$–]; 1.67 br.s [12H, $NCH_2(C\underline{H}_2)_3CH_2$–]; 2.50 m (8H, $C\underline{H}_2CH_2Ph$); 2.63 m (8H, $C\underline{H}_2CH_2Ph$); 3.32 m [8H, $–NC\underline{H}_2(CH_2)_3·C\underline{H}_2$–]; 3.34 m [8H, $–NC\underline{H}_2(CH_2)_3C\underline{H}_2$–]; 3.73 m (12H, OCH_3), 5.12 m (4H, CH), 6.60 s (2H, H^3), 6.75 s (2H, H^3), 6.99–7.21 m (20H, Ph). Mass spectrum, *m/z*: 1730 (calculated 1731.82): $C_{88}H_{96}N_4O_{16}P_4S_4·2Li^+$.

***ortho*-Hydroxyated phosphocavitands IV**. To a solution of 0.120 mmol of cavitand **II** in 22 ml of THF at –78°C was poured 2.4 ml of BuLi solution (1.5 M in hexane). The reaction mixture was stirred for 15 min, 0.044 ml of trimethyl borate was adding to it and the mixture was stirred for 2 h, gradually warming to room temperature. Then to the reaction mixture at –78°C was added 5.18 ml of 1.5 M NaOH in 15% H_2O_2, the mixture was stirred for 1 h and left overnight at room temperature. To remove excess H_2O_2 to the reaction mixture was added 0.350 mmol of sodium hydrosulfite, and then organic solvents were distilled off, the product was extracted with methylene chloride (3×5 ml), which was further distilled off. The residue was dissolved in 1 ml of methylene chloride, to the solution was added 5 ml of hexane, the resulting precipitate was filtered off and dried for 4 h at 80°C (1 mm Hg). The total yield 85%, mp 110–112°C. ^1H NMR spectrum ($CDCl_3$, 25ºC), δ, ppm: 1.57 br.s [$NCH_2(C\underline{H}_2)_3CH_2$]; 1.67 br.s [$NCH_2(C\underline{H}_2)_3CH_2$]; 2.55 m ($CH_2C\underline{H}_2Ph$); 2.68 m ($C\underline{H}_2CH_2Ph$); 3.30 m [$NC\underline{H}_2(CH_2)_3C\underline{H}_2$]; 5.12 m (CH), 6.63 m ($H^3$), 6.70–7.29 m (Ph + OH). ^{31}P NMR spectrum ($CDCl_3$, 25ºC), δ, ppm: 63–64. Mass spectrum, *m/z*: 1547, $C_{80}H_{88}N_4O_{12}P_4S_4$ (calculated 1548.42); 1570, $C_{80}H_{88}N_4O_{12}P_4S_4·Na^+$ (calculated 1571.41); 1621, $C_{80}H_{87}BrN_4O_{11}P_4S_4·Li^+$ (calculated 1619.57).

***ortho*-Acetylated phosphocavitands V**. A solution of 0.040 mmol of cavitand **IV** in 1 ml of acetic anhydride acidified with 1 drop of concentrated H_2SO_4 was stirred at 80°C for 3 h. After cooling to room temperature, to the reaction mixture was added 10 ml of water, and the product was extracted with methylene chloride (5x5 ml). CH_2Cl_2 was evaporated, the residue was dissolved in 0.5 ml of methylene chloride and to the solution was added 3 ml of hexane. The precipitate formed was filtered off and dried at 80°C (1 mm Hg). The total yield 42%, mp 188–189ºC (decomp.). IR spectrum, cm^{-1}: 1771 (C=O). ^1H NMR spectrum ($CDCl_3$, 25ºC), δ, ppm: 1.62 br.s [$NCH_2·(C\underline{H}_2)_3CH_2$], 2.02 s ($OCH_3$), 2.51 m ($CH_2C\underline{H}_2$ Ph); 2.64 m ($C\underline{H}_2CH_2$ Ph); 3.34 m [$NC\underline{H}_2(CH_2)_3C\underline{H}_2$], 4.55 m (CH), 6.75 m ($H^3$), 6.99–7.25 m (Ph). ^{31}P NMR spectrum ($CDCl_3$, 25ºC), δ, ppm: 63–64. Mass spectrum, *m/z*: 1715, $C_{88}H_{96}N_4O_{16}P_4S_4$ (calculated 1716.46); 1753, $C_{86}H_{93}BrN_4O_{14}P_4S_4·2Li^+$ (calculated 1752.74).

Phosphoresorcinarene VIa. To a suspension of 0.180 mmol of resorcinarene **Ia** in 1 ml of dioxane was added 1.180 mmol of 2-diethylamino-5,5-dimethyl-1,3,2-dioxaphosphinane. The reaction mix-ture was maintained for 65 h at 90–95°C. The pre-cipitate was filtered off and washed with dioxane. The product was dried for 3 h at 75°C (1 mm Hg). Yield 44%, mp 158–160°C. ^1H NMR spectrum ($CDCl_3$, 25ºC), δ, ppm: 0.72 s (12H, CCH_3), 0.79 s (12H, CCH_3), 1.20 s (12H, CCH_3), 1.32 s (12H, CCH_3), 2.24 m (8H, $CH_2C\underline{H}_2Ph$), 3.11 m (8H, $C\underline{H}_2CH_2Ph$), 3.31 m (8H, OCH_2^e, $^2J_{HH}$ 9.5 Hz, $^3J_{PH}$ 10.9 Hz), 3.52 m (8H, O–CH_2^e, $^2J_{HH}$ 9.9 Hz), 4.10 m (8H, OCH_2^a, $^2J_{HH}$ 9.9 Hz, $^3J_{PH}$ 4.7 Hz), 4.32 br.s (4H, H^1), 4.63 m (8H, O–CH_2^a, $^2J_{HH}$ 10.2 Hz), 6.33 s (2H, H^{3h}), 7.03 m (20H, Ph), 7.53 s (2H, H^{3v}). ^{31}P NMR spectrum ($CDCl_3$, 25ºC), δ, ppm: 115.5 s (4P), 121.1 C (4P). Found, %: C 52.58; H 5.51; P 10.85. $C_{100}H_{124}Br_4O_{24}P_8$. Calculated, %: C 52.74; H 5.49; P 10.88.

Phosphoresorcinarene VIIa. To a solution of 0.022 mmol of phosphoresorcinarene **VIa** in 2.5 ml of CH_2Cl_2 was added 0.350 mmol of the adduct $H_2O_2·(NH_2)_2CO$. The reaction mixture was stirred for 3 h at 20°C. The $H_2O·(NH_2)_2CO$ precipitate was filtered off and the filtrate was washed with water to remove urea. CH_2Cl_2 was evaporated, the residue was dried for 4 h at 80°C (1 mm Hg.). Yield 70%, mp 105–107°C. ^1H NMR spectrum ($CDCl_3$, 25ºC), δ, ppm: 0.78 s (12H, C–CH_3), 0.90 s (12H, C–CH_3), 1.14 s (12H, C–CH_3), 1.24 s (12H, C–CH_3), 2.17 t (8H, $CH_2C\underline{H}_2Ph$, $^3J_{HH}$ 10.1 Hz), 2.27 m (8H, $C\underline{H}_2CH_2Ph$), 3.97 m (16H, O–CH_2^e, 4H, H^1, $^2J_{HH}$ 10.2 Hz), 4.57 d.d (8H, O–CH_2^a, $^2J_{HH}$ 10.7 Hz, $^3J_{PH}$ 1.9 Hz), 4.72 d.d (8H, O–CH_2^a, $^2J_{HH}$

9.5 Hz, $^3J_{PH}$ 2.2 Hz), 6.31 s (2H, H^{3h}), 7.01–7.07 m (20H, Ph), 7.61 s (2H, H^{3v}). ^{31}P NMR spectrum ($CDCl_3$, 25ºC), δ, ppm: –13.7 s (4P), –14.5 s (4P). Found, %: C 50.00; H 5.23; P 10.32. $C_{100}H_{124}Br_4O_{32}P_8$. Calculated, %: C 49.93; H 5.20; P 10.30.

Phosphoresorcinarene VIIb was prepared analogously to **VIIa** by the reaction of 0.017 mmol of phosphoresorcinol **VIb** with 0.340 mmol of adduct $H_2O_2 \cdot (NH_2)_2CO$. Yield 70%, mp > 360°C. ^{1}H NMR spectrum ($CDCl_3$, 25ºC), δ, ppm: 0.66 s (12H, CCH_3), 0.73 s (12H, CCH_3), 0.84 s (12H, CCH_3), 1.25 s (12H, CCH_3), 2.35 d.d (4H, OCH_2^e, $^2J_{HH}$ 10.4 Hz, $^3J_{PH}$ 11.3 Hz), 3.47 d (4H, OCH_2^a, $^2J_{HH}$ 11.5 Hz), 3.74 m (8H, OCH_2^e, $^2J_{HH}$ 11.0 Hz, $^3J_{PH}$ 12.3 Hz), 3.90 d (4H, OCH_2, $^2J_{HH}$ 11.4 Hz), 4.05 m (4H, OCH_2^e, $^2J_{HH}$ 11.0 Hz, $^3J_{PH}$ 14.7 Hz), 4.31 d (4H, OCH_2^a, $^2J_{HH}$ 10.5 Hz), 4.63 d (4H, OCH_2^a, $^2J_{HH}$ 11.0 Hz), 5.32 s (2H, H^{3h}), 5.99 s (2H, H^{3v}), 6.40 d (4H, H$^{2'}$, $^3J_{HH}$ 7.3 Hz), 6.63 s (4H, H^1), 6.97 d.d (4H, H$^{3',7'}$, $^3J_{HH}$ 7.6 Hz, $^3J_{HH}$ 7.8 Hz), 7.7 d.d (4H, H$^{6'}$, $^3J_{HH}$ 7.3 Hz, $^3J_{HH}$ 6.9 Hz), 7.44 d (4H, H$^{4',8'}$, $^3J_{HH}$ 7.4 Hz), 7.57 d (4H, H$^{5'}$, $^3J_{HH}$ 8.2 Hz). ^{31}P NMR spectrum ($CDCl_3$, 25ºC), δ, ppm: –14.3 s (4P), –15.7 s (4P). Found, %: C 50.10, H 4.73, P 9.80. $C_{108}H_{116}Br_4O_{32}P_8$. Calculated, %: C 50.02, H 4.69, P 9.94.

***ortho*-Hydroxyated phosphoresorcinarene VIII** was prepared analogously to **IV** by a sequential treatment of 0.340 mmol of resorcinarene **VIIa** in 35 ml of THF with 2.640 mmol of butyllithium (within 30 min), 3.100 mmol of trimethyl borate, 0.9 ml of 1.5 M NaOH in 15% H_2O_2, and 1.000 mmol of sodium hydrosulfite. Yield 48%, mp 258–259ºC. IR spectrum, cm^{-1}: 3340 (OH). ^{1}H NMR spectrum ($CDCl_3$, 25ºC), δ, ppm: 0.91 br.s (24H, CCH_3), 1.27 br.s (24H, CCH_3), 1.87 m (8H, CH_2CH_2Ph), 2.05 m (8H, CH_2CH_2Ph), 3.76 –4.23 m (32H, OCH_2, 4H, H^1), 6.0 (2H, H^{3h}), 7.01–7.45 m (2H, H^{3v}, 20H, Ph), 7.54 br.s (2H, OH), 7.72 br.s (2H, OH). ^{31}P NMR spectrum ($CDCl_3$, 25ºC), δ, ppm: –14.0 br.s (4P), –15.1 br.s (4P). Mass spectrum, *m/z* 2199.53 (calculated 2199.83), $C_{100}H_{128}O_{36}P_8 \cdot 2Na^+$.

***ortho*-Methoxycarbonylated phosphoresorcinarene IX** was prepared analogously to **III** by sequential treatment of 0.035 mmol of phosphoresorcinarene **VIIa** in 30 ml of THF with 0.840 mmol of butyllithium and 0.15 ml of methylchloroformate. The product was extracted with chloroform (3×5 ml), the solvent was partially evaporated, to the residue was added 20 ml of hexane. The precipitate formed was filtered off and dried for 4 h at 80°C (1 mm Hg). Yield 48%, mp 198–200ºC. IR spectrum, cm^{-1}: 1768 (C=O), 1433 cm^{-1} [C(O)OMe]. ^{1}H NMR spectrum ($CDCl_3$, 25ºC), δ, ppm: 0.89 s (12H, CCH_3), 0.91 s (12H, CCH_3), 1.27 s (12H, CCH_3), 1.31 s (12H, CCH_3), 2.35 br.s (8H, CH_2CH_2Ph), 2.65 br.s (8H, CH_2CH_2Ph), 3.33 m (8H, O–CH_2^e), 3.84 s [9H, $C(O)OCH_3$], 3.98–4.75 m (24H, O–$CH_2^{e,a}$, 4H, H^1), 6.17 s (2H, H^{3h}), 7.01–7.07 m (20H, Ph), 7.46 s (2H, H^{3v}). ^{31}P NMR spectrum ($CDCl_3$, 25ºC), δ, ppm: –14.3 br.s (4P), –15.8 br.s (4P). Mass spectrum, *m/z*: 2346 (calculated 2321.99), $C_{108}H_{136}O_{40}P_8$.

***ortho*-Hydroxyated phosphoresorcinarene X** was prepared analogously to **IV** by sequential treatment of 1.700 mmol of resorcinarenee **VIIb** in 60 ml of THF with 13.200 mmol of butyllithium (within 2 h), 15 mmol of trimethyl borate, 4.5 ml of 1.5 M NaOH in 15% H_2O_2 and 35 mmol of $Na_2S_2O_5$. The total yield 50%, mp > 360ºC. IR spectrum, cm^{-1}: 3375 (OH). ^{1}H NMR spectrum ($CDCl_3$, 25ºC), δ, ppm: 0.66 s (CCH_3), 0.73 s (CCH_3), 0.84 s (CCH_3), 1.25 s (CCH_3), 2.53 m (O CH_2^e), 3.44 d (OCH_2^a, $^2J_{HH}$ 10.6 Hz), 3.73 m (OCH_2^e), 3.90 d ($OCH_2^{a,e}$, $^2J_{HH}$ 11.0 Hz), 2.4 m (O–CH_2^e), 4.14 d.d (OCH_2^a, $^2J_{HH}$ 10.7 Hz, $^3J_{PH}$ 3.1 Hz), 4.61 d (OCH_2^a, $^2J_{HH}$ 10.4 Hz), 5.30 s (H^{3h}), 5.96 s (H^{3v}), 6.37 d (H$^{2'}$, $^3J_{HH}$ 7.3 Hz), 6.60 s (H^1), 6.94 d.d (H$^{3',6'}$, $^3J_{HH}$ 7.6 Hz, $^3J_{HH}$ 7.3 Hz), 7.7 d.d (H$^{7'}$, $^3J_{HH}$ 7.3 Hz, $^3J_{HH}$ 7.6 Hz), 7.40 d (H$^{5',8'}$, OH, $^3J_{HH}$ 8.0 Hz), 7.57 d (H$^{4'}$, $^3J_{HH}$ 7.6 Hz). ^{31}P NMR spectrum ($CDCl_3$, 25ºC), δ, ppm: –14.2 br.s (4P), –15.3 br.s (4P). Mass spectrum, *m/z* 2271 (calculated 2271.81), $C_{108}H_{120}O_{36}P_8 \cdot Li^+ \cdot Na^+$; 2344 (calculated 2309.87), $C_{108}H_{119}BrO_{34}P_8$, 2369 (calculated 2367.67), $C_{108}H_{118}Br_2O_{34}P_8$, 2435 (calculated 2437.51), $C_{108}H_{117}Br_3O_{33}P_8 \cdot Li^+$; 2454 (calculated 2453.57), $C_{108}H_{117}Br_3O_{33}P_8 \cdot Na^+$.

***ortho*-Methoxyformylated phosphoresorcinarene XI** was prepared analogously to **III** by sequential treatment of 0.035 mmol of phosphoresorcinarene **VIIb** in 30 ml of THF with 0.840 mmol of butyllithium and 0.15 ml of methyl chloroformate. The product was extracted with chloroform (3×5 ml), the solvent was partially evaporated, and to the residue was added 20 ml of hexane. The precipitate formed was filtered off and dried for 4 h at 80°C (1 mm Hg). Yield 55%, mp 301–307ºC (decomp.). IR spectrum, cm^{-1}: 1768 (C=O), 1453 [C(O)OMe], 1004 (C–Br). ^{1}H NMR spectrum ($CDCl_3$, 25ºC), δ, ppm: 0.67 s (12H, CCH_3), 0.74 s (12H, CCH_3), 0.85 s (12H, CCH_3), 1.26 s (12H, CCH_3), 2.30 m (4H, OCH_2^e), 2.43 m (4H, OCH_2^e), 3.44 m (4H, OCH_2^e), 3.79 s [6H, $C(O)OCH_3$], 3.81–3.91 m (8H, $OCH_2^{a,e}$), 4.12 br.d (4H, OCH_2^a,

$^2J_{HH}$ 10.0 Hz), 4.31 br.d (4H, OCH$_2^a$, $^2J_{HH}$ 10.9 Hz), 4.62 br.d (4H, OCH$_2^a$, $^2J_{HH}$ 10.5 Hz), 5.30 s (2H, H^{3h}), 5.97 s (2H, H^{3v}), 6.39 d (4H, H$^{2'}$, $^3J_{HH}$ 7.3 Hz) , 6.62 s (4H, 1 H), 6.97 d.d (4H, H$^{3',7'}$, $^3J_{HH}$ 7.6 Hz, $^3J_{HH}$ 6.9 Hz), 8.7 d.d (4H, H$^{6'}$, $^3J_{HH}$ 7.3 Hz, $^3J_{HH}$ 6.9 Hz), 7.45 d (8H, H$^{4',8'}$, $^3J_{HH}$ 8.0 Hz), 7.57 d (4H, H$^{5'}$, $^3J_{HH}$ 7.6 Hz). ^{31}P NMR spectrum (CDCl$_3$, 25ºC), δ, ppm: –14.0 br.s (4P), –15.2 br.s (4P). Mass spectrum, *m/z*: 2419 (calculated 2416.96), $C_{116}H_{128}O_{40}P_8 \cdot Li^+$; 2500 (calculated 2500.40), $C_{108}H_{116}Br_4O_{32}P_8 \cdot Li^+$).

Tetraphosphorylated resorcinarene XIIa. To a suspension of 0.945 mmol of resorcinarene **Ic** in 1 ml of dioxane was added 9.450 mmol of 2-diethylamino-5,5-dimethyl-1,3,2-dioxaphosphinane, and the reaction mixture was kept for 3 h at 80–85°C. The precipitate formed was filtered off, washed with dioxane, and dried for 6 h at 75°C (1 mm Hg).

Tetraphosphorylated resorcinarene XIIb was prepared analogously to **XIIa** by the reaction of 0.120 mmol of resorcinol **Ic** with 1.200 mmol of phosphoric hexaethyltriamide in 0.6 ml of dioxane for 2 h.

Tetraphosphorylated resorcinarene XIIc was prepared analogously to **XIIa** by the reaction of 0.110 mmol of resorcinarene **Ic** with 2.650 mmol of phosphoric tripiperidylamide in 0.6 ml of dioxane for 2 h.

Tetraphosphorylated resorcinarene XIIIa was prepared analogously to **VIIa** in the reaction of 0.002 mmol of phosphoresorcinol **XIIa** with 0.016 mmol of $H_2O_2 \cdot (NH_2)_2CO$ adduct in 5 ml of methylene chloride. Mass spectrum, *m/z*: 1663 (M + Na$^+$), 1726 ($M + C_4H_8O_2$).

Tetraphosphorylated resorcinarene XIIIb was prepared analogously to **VIIa** in the reaction of 0.040 mmol of phosphoresorcinol **XIIb** with 0.650 mol adduct of $H_2O_2 \cdot (NH_2)_2CO$ adduct in 2 ml of dry methylene chloride. Mass spectrum *m/z*: 1808 (M^+).

Tetraphosphorylated resorcinarene XIIIc was prepared analogously to **VIIa** by the reaction of 0.002 mmol of phosphoresorcinol **XIIc** with 0.016 mmol of $H_2O_2 \cdot (NH_2)_2CO$ adduct in 5 ml of methylene chloride. Mass spectrum *m/z*: 1906 (M^+).

Heterophosphorylated resorcinarene XIVa. To a solution of 0.06 mmol of phosphoresorcinarene **XIIIa** in 0.7 ml dioxane was added 0.590 mmol of hexamethyltriamidophosphite. The reaction mixture was heated for 60 h at 85–95ºC, and then 40 h at 110–115ºC. The precipitate was filtered off, washed with dioxane,and dried for 4 h at 80°C (1 mm Hg). Yield 67%, mp > 360ºC. ^{1}H NMR spectrum (CDCl$_3$, 25ºC), δ, ppm: 0.54 s (12H, C–CH$_3$), 0.75 s (12H, C–CH$_3$), 2.15 d.d (4H, O–CH$_2^e$, ^2J 10.2 Hz, NH , $^3J_{PH}$ 19.2 Hz), with 2.21 (6H, CH$_3$), with 2.22 (6H, CH$_3$), 2.50 d (24H, NCH$_3$, $^3J_{PH}$ 9.2 Hz), 2.62 d (24H, NCH$_3$, $^3J_{PH}$ 8.4 Hz), 3.24 d.d (4H, OCH$_2^a$, $^2J_{HH}$ 4.11 Hz, $^3J_{PH}$ 2.3 Hz), 3.60 d.d (4H, OCH$_2^e$, $^2J_{HH}$ 11.9 Hz, $^3J_{PH}$ 19.2 Hz), 3.89 d.d (4H, OCH$_2^a$, $^2J_{HH}$ 8.3 Hz, $^3J_{PH}$ 2.7 Hz), 5.14 s (2H, H^{3h}), 6.16 s (2H, H^{3v}), 6.33 s (4H, H^1), 6.59 d (4H, H$^{2'}$, $^3J_{HH}$ 6.8 Hz), 6.74 d.d (4H, H$^{7'}$, $^3J_{HH}$ 8.2 Hz, $^3J_{HH}$ 7.3 Hz), 6.89 d.d (4H, H$^{3'}$, $^3J_{HH}$ 8.2 Hz, $^3J_{HH}$ 6.8 Hz), 7.00 d.d (4H, H$^{6'}$, $^3J_{HH}$ 8.2 Hz, $^3J_{HH}$ 7.3 Hz) , 7.26 d (4H, H$^{4'}$, $^3J_{HH}$ 8.2 Hz), 7.35 d (4H, H$^{8'}$, $^3J_{HH}$ 8.2 Hz), 7.38 d (4H, H$^{5'}$, $^3J_{HH}$ 8.2 Hz). ^{13}C NMR (CDCl$_3$, 25ºC), δ, ppm: 11.9 s (CH$_3$), 12.5 s (CH$_3$), 20.1 s (CCH$_3$), 31.4 s (CCH$_3$), 31.5 s (CCH$_3$), 36.8 d (NCH$_3$, $^2J_{PC}$ 3.7 Hz), 36.9 d (NCH$_3$, $^2J_{PC}$ 3.7 Hz), 42.5 s (C 1), 77.3–77.6 m (OCH$_2$), 122.6 s (C^5), 123.7 s (C^5), 124.2 s (C$^{6',7',8'}$), 124.9 s (C$^{3'}$), 126.7 s (C$^{4'}$), 127.2 s (C$^{2'}$), 128.2 s (C$^{5'}$), 129.4 s (C^2), 130.4 s (C^2), 131.5 s (C$^{3,9'}$), 131.7 s (C^3), 133.0 s (C$^{10'}$), 137.5 s (C$^{1'}$), 147.2 d (C^4, $^2J_{PC}$ 14.7 Hz, COPO), 150.6 d (C^4, $^2J_{PC}$ 15.1 Hz, COPN). ^{31}P NMR spectrum (CDCl$_3$, 25ºC), δ, ppm: 130.5 s (4P), –14.0 C (4P). Found, %: C 61.34; H 6.43; N 5.38; P 11.75. $C_{108}H_{136}N_8O_{20}P_8$. Calculated, %: C 61.36; H 6.48; N 5.38; P 11.72.

Heterophosphorylated resorcinarene XIVb was prepared analogously to **XIVa** in the reaction of 0.060 mmol of phosphoresorcinarene **XIIIa** with 0.620 mmol of hexaethyltriamidophosphite in 1 ml of dioxane for 12 h at 110–115ºC. ^{31}P NMR spectrum (dioxane), δ, ppm: 131.5 s (4P), –15.9 C (4P).

Tetraphosphatotetraacethylresorcinarene XVa. A solution of 0.070 mmol of phosphoresorcinarene **XIIIa** in 1 ml of acetic anhydride acidified with 2 drops of concentrated H$_2$SO$_4$ was stirred for 2 h at 75°C. To the reaction mixture was added 10 ml of water, the precipitate was filtered off, washed with water and hexane to the disappearance of the acetic acid smell, and dried 8 h at 80°C (1 mm Hg). Yield 56%, mp 229–232ºC. ^{1}H NMR spectrum (CDCl$_3$, 25ºC), δ, ppm: 0.15 s (12H, CCH$_3$), 0.86 s (12H, CCH$_3$), 2.01 s (6H, CH$_3$), 2.22 s (6H, CH$_3$), 2.27 s [12H, (O)CCH$_3$], 2.32 s [12H, (O)CCH$_3$], 3.58 m (16N, OCH$_2$), 5.33 s (2H, H^{3h}), 5.95 m (4H, H$^{2'}$), 6.07 s (H, H^1), 6.20 s (2H, H^{3v}), 6.59 m (4H, H$^{7'}$), 6.95 d.d (4H, H$^{3'}$, $^3J_{HH}$ 7.6 Hz, $^3J_{HH}$ 7.3 Hz), 7.03 d.d (4H, H$^{6'}$, $^3J_{HH}$ 7.5 Hz, $^3J_{HH}$ 7.3 Hz), 7.30 d (4H, H$^{4'}$, $^3J_{HH}$ 7.8 Hz), 7.37 d (4H , H$^{8'}$, $^3J_{HH}$ 8.3 Hz), 7.43 d (4H, $H^{5'}$, $^{3}J_{HH}$ 8.2 Hz). ^{31}P NMR spectrum ($CDCl_3$, 25ºC), δ, ppm: –13.2. Mass spectrum, *m/z*: 1808.5 (M^+). Found, %: C 66.36; H 5.50; P 6.82. $C_{100}H_{100}O_{24}P_4$. Calculated, %: C 66.37; H 5,57; P 6.85.

Tetra(amidophosphato)tetraacethylresorcinolarene XVb was prepared analogously to **XVa** in the reaction of 0.050 mmol of phosphoresorcinarene **XIIIb** with 1 ml of acetic anhydride for 3 h. Yield 76%, mp 337–339ºC. ^{1}H NMR spectrum ($CDCl_3$, 25ºC), δ, ppm: 0.53 m (24H, $NCH_2C\underline{H}_3$, $^{3}J_{HH}$ 6.9 Hz), 0.65 m (24H, $NCH_2\ C\underline{H}_3$, $^{3}J_{HH}$ 6.9 Hz), 2.01 s (6H , CH_3), 2.22 s [12H, $(O)CCH_3$], 2.30 s (6H, CH_3), 2.28 m (16H, $NC\underline{H}_2CH_3$), 2.44 m (16H, $NC\underline{H}_2CH_3$, $^{3}J_{PH}$ 11.5 Hz, $^{3}J_{HH}$ 6.9 Hz), 5.32 s (2H, H^{3h}), 6.20 s (2H, H^{3v}), 6.56 s (4H, H^{1}), 6.59 d (4H, $H^{2'}$, $^{3}J_{HH}$ 6.9 Hz), 6.79 d.d (4H, $H^{7'}$, $^{3}J_{HH}$ 7.4 Hz, $^{3}J_{HH}$ 6.0 Hz), 6.87 d.d (4H, $H^{3'}$, $^{3}J_{HH}$ 7.8 Hz, $^{3}J_{HH}$ 7.3 Hz), 7.01 d.d (4H, $H^{6'}$, $^{3}J_{HH}$ 7.3 Hz, $^{3}J_{HH}$ 7.4 Hz), 7.22 d (4H, $H^{4'}$, $^{3}J_{HH}$ 8.7 Hz), 7.26 d (4H, $H^{8'}$, $^{3}J_{HH}$ 10.1 Hz), 7.33 d (4H, $H^{5'}$, $^{3}J_{HH}$ 8.2 Hz). ^{13}C NMR ($CDCl_3$, 25ºC), δ, ppm: 10.8 s (CH_3), 13.4 s ($NCH_2\underline{C}H_3$), 14.2 s ($NCH_2\underline{C}H_3$), 14.4 (CH_3), 20.5 s ($OC\underline{C}H_3$), 39.0 g ($N\underline{C}H_2CH_3$, $^{2}J_{PC}$ 3.9 Hz), 40.1 d ($N\underline{C}H_2CH_3$, $^{2}J_{PC}$ 4.0 Hz), 41.4 s (C^{1}), 123.5 s (C^{5}), 123.9 s (C^{5}), 124.2 s ($C^{3'}$), 124.5 s ($C^{8'}$), 124.8 s ($C^{6'}$), 125.4 s ($C^{7'}$), 126.5 s ($C^{4'}$), 126.6 s ($C^{2'}$), 127.7 s ($C^{5'}$), 130.3 s (C^{2}), 131.4 s ($C^{2,9'}$), 131.9 s (C^{3}), 133.1 s (C^{10}), 133.4 s (C^{3}), 136.9 s (C^{1}), 146.9 s (C^{4}), 148.0 d (C^{4}, $^{2}J_{PC}$ 14.8 Hz), 168.0 s ($OC(O)CH_3$). ^{31}P NMR spectrum ($CDCl_3$, 25ºC), δ, ppm: 12.64 s (2P), 12.65 s (2P). Mass spectrum *m/z*: 1978 (M^+). Found, %: C 68.03; H 7.12; N 5.67; P 6.28. $C_{112}H_{140}N_8O_{16}P_4$. Calculated, %: C 68.00; H 7.13; N 5.66; P 6.26.

Tetra(amidophosphato)tetraacethylresorcinarene XVc was prepared analogously to **XVa** in the reaction of 0.015 mmol of phosphoresorcinarene **XIIIc** with 0.5 ml of acetic anhydride at 75°C for 4 h. Yield 65%, mp 300–302ºC. ^{1}H NMR spectrum ($CDCl_3$, 25ºC), δ, ppm: 1.10–1.26 m [24H, $NCH_2(C\underline{H}_2)_3CH_2$], 2.00 s [12H, $(O)CCH_3$] 2.23–2.34 m [28H, CH_3, $NC\underline{H}_2(CH_2)_3\cdot C\underline{H}_2$], 5.32 m (2H, H^{3h}); 6.10 m (4H, H^{1}), 6.57–6.80 m (2H, H^{3v}, 4H, $H^{2'}$), 6.88–7.09 m (12H, $H^{3',6',7'}$), 7.25–7.35 m (12H, $H^{4',5',8'}$). ^{13}C NMR ($CDCl_3$, 25ºC), δ, ppm: 9.2 s (CH_3), 11.9 s (CH_3), 23.1 s [$N(CH_2)_2\underline{C}H_2\cdot(CH_2)_2$], 23.9 s [$N(CH_2)_2\underline{C}H_2(CH_2)_2$], 26.2 s ($NCH_2\underline{C}H_2CH_2\underline{C}H_2CH_2$), 26.9 s ($NCH_2\underline{C}H_2CH_2\underline{C}H_2CH_2$), 41.6 s ($C^{1}$), 45.3 s [$N\underline{C}H_2(CH_2)_3\underline{C}H_2$], 45.7 s [$N\underline{C}H_2\cdot(CH_2)_3\underline{C}H_2$], 124.2–125.8 m ($C^{5,3',7',8',6'}$), 126.3 s ($C^{5'}$), 124.8 s ($C^{4'}$), 125.4 s ($C^{2}$), 126.4 s ($C^{2}$), 126.6 s ($C^{2'}$), 127.8 s ($C^{3}$), 130.3 s ($C^{3}$), 131.4 s ($C^{9'}$), 133.3 s ($C^{10'}$), 136.9 s ($C^{1'}$), 146.8 s ($C^{4}$), 146.9 d ($C^{4}$, $^{2}J_{PC}$ 5.8 Hz), 167.9 s [$O\underline{C}(O)CH_3$]. ^{31}P NMR spectrum ($CDCl_3$, 25ºC), δ, ppm: 9.80. Found, %: C 69.45; H 6.81; N 5.43; P 5.94. $C_{120}H_{140}N_8O_{16}P_4$. Calculated, %: C 69.48; H 6.80; N 5.40; P 5.90.

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