New aspects in the chemistry of perphosphorylated calix[4]resorcinarenes

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Dedicated to Prof. Konovalov on the occasion of his 70th birthday
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Abstract
Interaction between calix[4]resorcinarenes 1 and 2-amino-1,3,2-diheterophosphorinanes 2 resulted in sterically pure polyphosphocyclic conjugates 3. The structure of which was supported by NMR spectroscopy and X-ray diffraction analysis. The possibility of further modification of perphosphorylated resorcinarenes 3 was studied. It was shown that compounds 3a,b containing *t*-Bu–N groups at the phosphorus atoms do not enter into reactions increasing the coordination number of phosphorus because of steric hindrance. Sterically less hindered phosphoresorcinarenes 3c-i readily add sulfur, oxygen, and form octanuclear and chelate complexes with transition metals (Mo and Pd, respectively).

Keywords: Calixarenes, phosphorylation, configuration, sulfurization, oxidation, complexation

Introduction

Polyhydroxycalixarenes and their modified derivatives are suitable matrices for the creation of receptor and coordination systems. [1] This has stimulated continuous studies using calixarenes as starting compounds.[2,3] The presented work, which is devoted to the design of new polyphosphocyclic calix[4]resorcinarene derivatives, is also related to this field of chemistry.

Calix[4]resorcinarenes are stable macrocyclic molecules containing eight hydroxyl groups on the upper rim forming intramolecular hydrogen bonds. Their functionalization destroys the system of hydrogen bonds, which can result in conformational changes of the molecule. [4-7] This allows a change the direction of phosphorylation and to synthesize cavitand systems with different orientation of phosphorus fragments with respect to each other and the macrocycle cavity.

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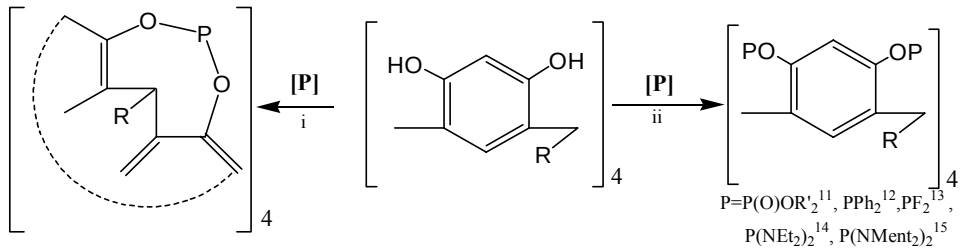
Two main directions of the phosphorylation of calix[4]resorcinarene at the hydroxy groups are considered at present: (i) cyclophosphorylation resulting in the formation of phosphocavitands with a rigid skeleton, which are dealt with in most papers, [8-10] and (ii) octaphosphorylation resulting in the formation of relatively labile systems, of which the chemistry is less explored. [11-15]



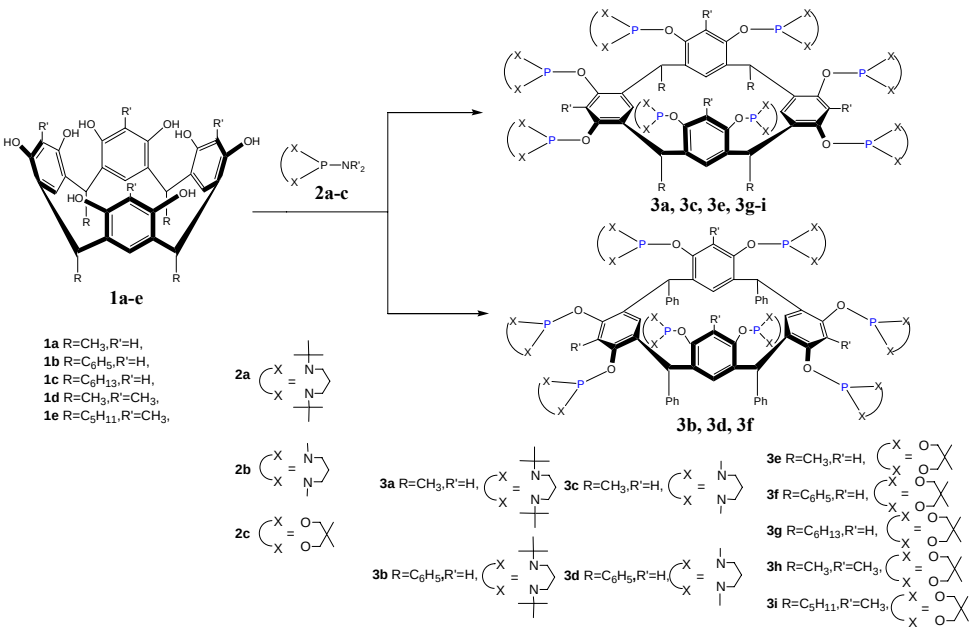
Scheme 1

The first perphosphorylated resorcinarenes were described by L.N. Markovskii *et al*. in the early 1990s.[11] Diorganyl chlorophosphates were used as phosphorylating agents. Later on, fragments containing trivalent phosphorus were introduced into the molecules of resorcinarenes[12-15] (Scheme 1). Note that phosphorous acid amides, including 2-amino-1,3,2-diheterophosphocyclanes have a high phosphorylating capacity for proton-containing nucleophiles due to the rupture of the P–N bond,[16] and found wide use for the design of complex polyphosphorylated compounds.

For the further elucidation of the chemistry of perphosphorylated calixarenes, we herein have studied the octaphosphorylation of calix[4]resorcinarenes **1** by 2-amino-1,3,2-dihetero-phospho-rinanes **2,** as well as the structure and subsequent modification of the resulting polycyclic conjugates **3**.

Results and Discussion

The perphosphorylation of calix[4]resorcinarenes 1a-e by 2-amino-1,3,2-diheterophosphorinanes 2a-c was performed in dioxane at a reagent ratio of 1 : 2 = 1 : 10. The reaction temperature depended on the nature of the phosphorylating agent. Octaphosphorylation of resorcinarenes 1a,b by diazaphosphorinanes 2a,b occurred at 20–25°C. The perphosphorylation of resorcinarenes 1a-e by dioxaphosphorinane 2c required heating of the reaction mixture to 90–95°C. Under the reaction conditions applied, octaphosphorylated resorcinarenes 3a-i crystallized directly from the reaction mixture. Note that compounds 3a-i form stable complexes with dialkylamines released in the course of reaction, which are decomposed only upon long-term exposure to 85–90°C in high vacuum.



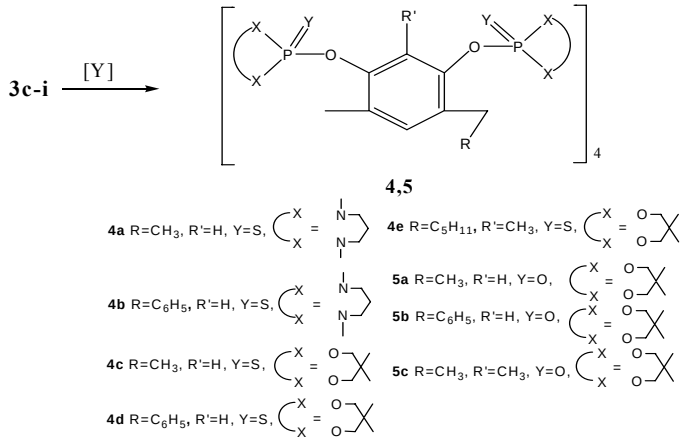
Scheme 2

Phosphocalixarenes **3a-i** (Scheme 2) have been isolated as individual stereoisomers with yields of 52–76%. The data of elemental analysis and the molecular weights of compounds **3** as determined by MALDI MS spectrometry, are in agreement with the calculated values.

The structure of phosphoresorcinarenes **3a,b,e,f** was established by correlated NMR spectroscopy and X-ray diffraction analysis.[17] It was found that compounds **3a,b,e,f**, like the initial resorcinarenes **1**, have the *all-cis* configuration of R groups at the methylidene bridges of the calixarenes system but different orientation of phenyl rings and phosphorinane fragments in respect to each another and to the macrocycle plane. Perphosphorylated resorcinarenes **3a,e** with R=Me adapt a *flattened cone* conformation with the phosphorinane fragments on the same side of the macrocycle plane. Conformations of perphosphorylated resorcinarenes **3b,f** with R=Ph change to intermediate ones between *flattened cone* and *1,3-alternate*. The phosphorus fragments in these compounds are located on the opposite sides of the macrocycle plane. The complete analogy of the spectral data of phosphoresorcinarenes **3a, 3b, 3e** and **3c, 3d, 3g-i** suggests the structural analogy of these compounds.

In terms of their chemical nature, the synthesized phosphor-resorcinarenes are diamidophosphites (**3a-d**) or neutral phosphites (**3e-d**) and should therefore give typical reactions for trivalent phosphorus derivatives. However, compounds **3a,b** containing *t*-Bu–N groups at the phosphorus atoms do not show reactions increasing the coordination number of phosphorus atoms such as sulfurization, oxidation, complexation. Attempts to force the process by increased reaction temperature resulted in the decomposition of the polycyclic system. Apparently, the introduction of eight bulky fragments overloads molecules **3a,b** sterically, which makes their further functionalization unfeasible. Sterically less hindered phosphoresorcinarenes **3c-i** readily add sulfur, and oxygen, and form complexes with transition metals (Scheme 3-5).

The addition of sulfur to compounds **3c,d** containing Me–N groups at the phosphorus atoms proceeded at room temperature within 30 min. The sulfurization of compounds **3e,f**, whose molecules contain dioxaphosphorinane fragments, required heating of the reaction mixture to 80°C for 5 h. In all cases, the reactions were performed with a stoichiometric ratio of the reagents in a solvent mixture (chloroform: benzene = 1 : 1) (Scheme 3).



Scheme 3

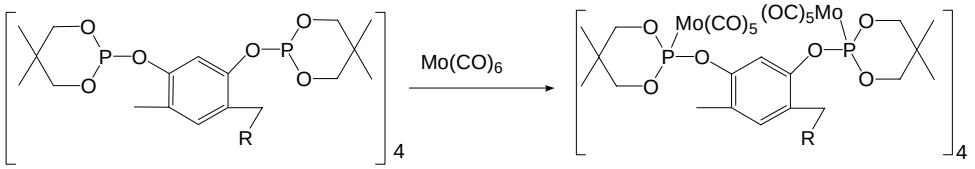
The oxidation of phosphoresorcinarenes **3e,f,h,i** with the urea–hydrogen peroxide adduct was performed with a stoichiometric ratio of the reagents in methylene chloride at 20–25°C (Scheme 3).

Octathiophosphates **4a-e** and octaphosphates **5a-c** were isolated with yields of 74–84 and 70–96%, respectively. The elemental analyses for compounds **4, 5** are in agreement with the calculated values.

The structures of compounds **4** and **5** were supported by NMR spectroscopy. The ^{31}P NMR spectra of thiophosphates **4a,b,d** and phosphates **5b,c** showed two singlets with similar chemical shifts and equal integral intensities; the ^{31}P NMR spectra of thiophosphates **4c,e** and phosphates **5b,c** gave broadened singlets. The averaging of signals in the spectra of resorcinarenes **4c,e** and **5b,c** is due to interconversion.[3,4] The ^{1}H and ^{13}C NMR spectral features of phospho(III)resorcinarenes **3** remain in the spectra of phospho(V)resorcinarenes **4, 5**, which suggests the structural analogy of the corresponding tri- and pentavalent phosphorus derivatives.

Phospho(III)resorcinarenes **3**, which have eight phosphorinane cycles attached to the periphery of their resorcinarene skeletons, are potential octadentate ligands. Because of their structural characteristics, they can interact with transition metals in different ways to form octanuclear complexes, where each metal atom is coordinated to only one phosphorus atom, and chelate complexes, where each metal atom is complexed by two phosphorus atoms. Using molybdenum hexacarbonyl and (1,5-cyclooctadienyl)palladium dichloride, we obtained complexes of both types.

The ligand exchange reaction between molybdenum hexacarbonyl and resorcinarenes **3f,g** was performed with a stoichiometric reagent ratio (**3** : $Mo(CO)_6$ = 1 : 8) in dioxane at 95–100°C for 12 h (Scheme 4).



3f,g **6,7**

3f, **6** R=C_6H_5
3g, **7** R=C_6H_{13}

Scheme 4

At the end of the reaction, a set of new signals at 144–149 ppm and no signals for the initial ligands were observed in the ^{31}P NMR spectra of the reaction mixtures. The elemental analysis of the complexation products indicated that compounds **6** and **7** each contain eight pentacarbonyl molybdenum fragments in their molecules.

The NMR study of octanuclear complexes **6,7** showed that they are mixtures of diastereomers, which exist in solution in a dynamic equilibrium. Individual stereoisomers were isolated by TLC in both cases. The ^{31}P NMR spectra of the isolated diastereomers **6a,7a** showed four singlets with equal integral intensities, and the ^{1}H NMR spectra gave a signal doubling for the protons of the phosphorinane cycles and the hydrocarbon bridges of the calixarene skeleton compared to the spectra of the initial ligands **3f,g** (Figs. 1c,d and 1a,b respectively). These NMR patterns of complexes **6a,7a** are due to a diastereomeric anisochronicity.

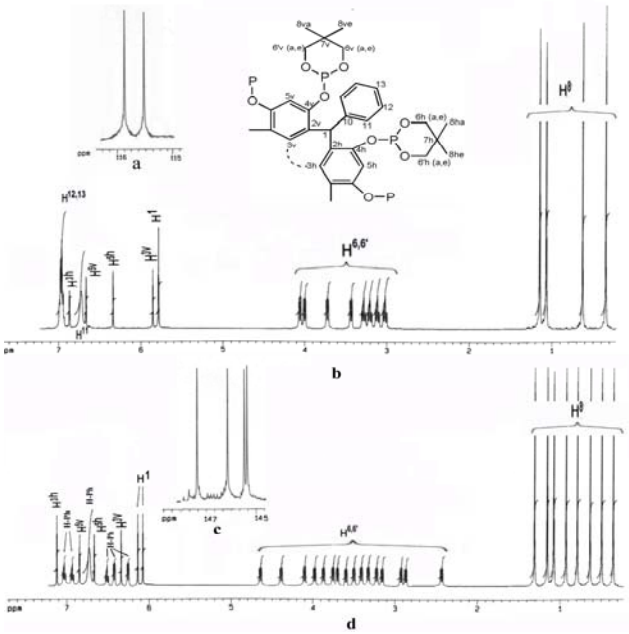
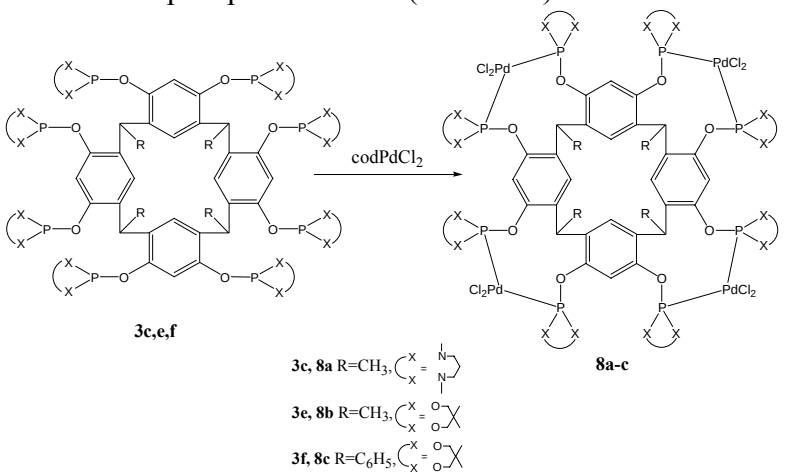


Figure 1. ^{31}P and ^{1}H NMR spectra of **3f (**a,b**)** and **6a (**c,d**)**.

The reaction of calix[4]resorsinarenes **3c,e,f** with (1,5-cyclooctadienyl)palladium dichloride was performed in chloroform with reagent ratios of 1 : 4 and 1 : 8. The reaction mixture was kept at 20–25°C for 30 min. In all cases, a singlet at 98 ppm and no signals for the initial ligands were observed in the ^{31}P NMR spectra of the reaction mixture at the end of the reaction. The elemental analysis of the complexation products showed that compounds **8a-c** have four metalphospho-containing fragments in their molecules. Hence, **8a-c** represent chelate complexes with each metal atom coordinated to two phosphorus atoms (Scheme 5).



Scheme 5

The ^{1}H NMR spectra of metal complexes **8a-c** (Fig. 2c,d) are simpler than those of the initial ligands (Fig. 2a,b). A narrow singlet in the ^{31}P NMR spectrum and a set of signals for the protons of the resorcinarene matrix in the ^{1}H NMR spectrum are typical for rigid phosphocyclic calixarene structures[18,19]. The averaging of signals for the protons of the macrocyclic skeleton in phosphocavitands is due to the symmetry of their molecules. NMR data suggest that complexes **8a-c** are metallaphosphocavitands, in which palladium atoms are coordinated to the phosphorus atoms of the diazaphosphorinane cycles located on adjacent benzene rings of the calixarene matrix.

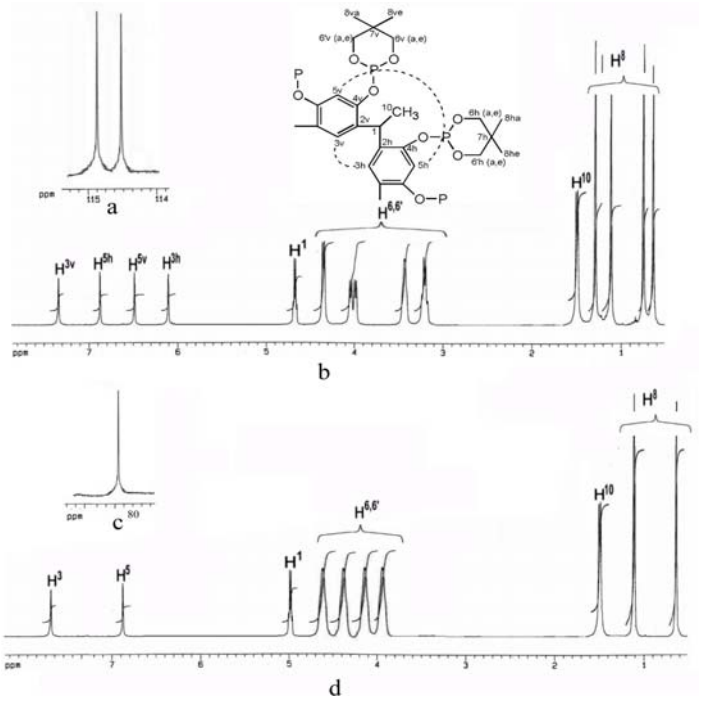


Figure 2. ^{31}P and ^{1}H NMR spectra of **3e** (a,b) and **8b** (c,d).

Experimental Section

General Procedures. ^{1}H NMR (TMS internal reference), ^{13}C NMR (TMS internal reference) and ^{31}P NMR spectra (85% H_3PO_4 external reference) of **3a,b,e,f, 6**; **3c,d** and **3g, 7** were recorded on a Bruker DRX-500; a AMX-400 and a AC-300 spectrometer, respectively, those of **3h,i**, **4a-d** and **5a-c** were performed on a Bruker WM-200 spectrometer. MALDI-TOF mass spectra were measured on a Kratos Kompact MALDI II (Shimadzu Europa GmbH) using N_2-laser source (λ = 337 nm), a positive polarity and 20 kV acceleration voltage. All syntheses were operated in dry solvents under argon. Calix[4]resorcinarenes **1** were synthesised according to previously described procedures.[20] 2-Amino-1,3,2-diheterophosphorinans **2** were synthesized using procedures described in literature.[21-23]

Phospho(III)resorcinarene (3a). A mixture of **1a** (0.1046 g, 0.192 mmol) and **2a** (0.3982 g, 1.54 mmol) in dioxane (1 ml) was stirred at 90–95^{o}C for 48h. The precipitate was filtered, washed with dioxane and maintained at 85–90^{o}C and 1 mm Hg for 10 h for the complete removal of dioxane and dialkylamine. Yield 63%. m.p. 250–252^{o}C. ^{1}H NMR (500 MHz, CDC1$_3$, 25^{o}C), δ, p.pm.: 1.00 (s, 12H, $H^{9'v}$), 1.11 (s, 12H, H^{9v}), 1.22 (s, 12H, H^{9h}), 1.31 (s, 12H, $H^{9'h}$), 1.42 (d, $^{3}J_{H,H}$=6.87 Hz, 12H, H^{10}), 1.68 (m, 4H, H^{7ve}), 1.85 (m, 8H, $H^{7he,va}$), 2.20 (m, 4H, H^{7ha}), 2.57 (m, 4H, $H^{6've}$), 2.73 (m, 4H, $H^{6'va}$), 2.77 (m, 4H, H^{6ve}), 2.94 (m, 8H, $H^{6,6'he}$), 3.39 (m, 8H, $H^{6,6'ha}$), 3.50 (m, 4H, H^{6va}), 4.52 (q, $^{3}J_{H,H}$=6.98 Hz, 4H, H^{1}), 6.64 (s, 2H, H^{3h}), 7.16 (s, 2H, H^{3v}), 7.21 (t, $^{4}J_{P,H}$=4.23 Hz, 2H, H^{5v}), 7.49 (t, $^{4}J_{P,H}$=4.10 Hz, 2H, H^{5h}). ^{13}C NMR (125.77 MHz,

CDC1з, 25˚C), δ, p.pm.: 23.94 (s, C^{10}), 26.60 (s, C^{7h}), 27.63 (s, C^{7v}), 29.44 (d, $^3J_{P,C}$=14.91 Hz, $C^{9\ or\ 9'}$), 29.65 (d, $^3J_{P,C}$=15.28 Hz, $C^{9\ or\ 9'}$), 29.90 (d, $^3J_{P,C}$=14.57 Hz, $C^{9\ or\ 9'}$), 29.92 (d, $^3J_{P,C}$=14.56 Hz, $C^{9\ or\ 9'}$), 31.37 (s, C^1), 38.28 (s, $C^{6'v}$), 38.63 (s, C^{6v}), 39.38 (s, $C^{6'h}$), 39.60 (s, C^{6h}), 54.66 (d, $^3J_{P,C}$=20.00 Hz, $C^{8\ or\ 8'}$), 54.83 (d, $^3J_{P,C}$=18.16 Hz, $C^{8\ or\ 8'}$), 55.01 (d, $^3J_{P,C}$=19.38 Hz, $C^{8\ or\ 8'}$), 55.03 (d, $^3J_{P,C}$=19.38 Hz, $C^{8\ or\ 8'}$), 106.59 (t, $^3J_{P,C}$=28.42 Hz, C^{5v}), 107.66 (t, $^3J_{P,C}$=25.77 Hz, C^{5h}), 124.81 (s, C^{2v}), 125.90 (s, C^{3h}), 129.16 (s, C^{2h}), 130.24 (s, C^{3v}), 151.46 (d, $^2J_{P,C}$=10.22 Hz, C^{4h}); 151.64 (d, $^2J_{P,C}$=10.43 Hz, C^{4v}). ^{31}P NMR (202.47 MHz, CDC1з, 25°C), δ, p.pm.: 113.23, 114.93. MS (MALDI): *m/z* (%)=2258 (100)[M^+]. Anal. Calcd. for $C_{120}H_{216}N_{16}O_8P_8$,%: C, 63.75; H, 9.56, N 9.92, P 10.98. Found,% : C 63.69, H 9.55, N 9.13, P 10.57.

Phospho(III)resorcinarene (3b). The compound was obtained analogously to **3a** by reaction of **1b** (0.1046 g, 0.17 mmol) with **2a** (0.3574 g, 1.74 mmol) for 3 h. Yield 76%. m.p. 267–269°C. ^{1}H NMR (500 MHz, CDC1з, 25˚C), δ, p.pm. 0.79 (s, 12H, H^{9h}), 1.07 (s, 12H, $H^{9'v}$), 1.20 (s, 24H, $H^{9v,9'h}$), 1.54 (m, 4H, H^{7he}), 1.67 (m, 8H, $H^{7ve,ha}$), 1.95 (m, 4H, H^{7va}), 2.12 (m, 4H, H^{6he}), 2.28 (m, 4H, H^{6ha}), 2.65 (m, 4H, $H^{6've}$), 2.72 (m, 4H, $H^{6'he}$), 2.84 (m, 4H, H^{6ve}), 2.93 (m, 4H, $H^{6'va}$), 3.26 (m, 4H, $H^{6'ha}$), 3.57 (m, 4H, H^{6va}), 5.75 (s, 4H, H^1), 5.93 (s, 2H, H^{3v}), 6.60 (b.s., 8H, H^{11}), 6.83 (s, 2H, H^{3h}), 6.84 (m, 12H, $H^{12,13}$), 7.24 (t, $^4J_{P,H}$=4.26 Hz, 2H, H^{5v}), 7.48 (t, $^4J_{P,H}$=5.51 Hz, 2H, H^{5h}). ^{13}C NMR (125.77 MHz, CDC1з, 25˚C), δ, p.pm.: 26.80(s, C^{7h}), 27.26(s, C^{7v}), 29.50 (d, $^3J_{P,C}$=14.69 Hz, $C^{9\ or\ 9'}$), 29.56 (d, $^3J_{P,C}$=15.54 Hz, $C^{9\ or\ 9'}$), 29.69 (d, $^3J_{P,C}$=15.73 Hz, $C^{9\ or\ 9'}$), 29.93 (d, $^3J_{P,C}$=15.14 Hz, $C^{9\ or\ 9'}$), 38.04 (s, C^{6h}), 38.69 (s, $C^{6'h,v}$), 38.98 (s, C^{6v}), 43.09 (s, C^1), 54.30 (d, $^3J_{P,C}$=24.22 Hz, C^{8h}), 54.77 (d, $^3J_{P,C}$=22.96 Hz, $C^{8'h}$), 55.02 (d, $^3J_{P,C}$=20,59 Hz, C^{8v}), 55.07 (d, $^3J_{P,C}$=21.76 Hz, $C^{8'v}$), 105.39 (t, $^3J_{P,C}$=27.86 Hz, C^{5h}), 106.06 (t, $^3J_{P,C}$=29.06 Hz, C^{5v}), 122.93 (s, C^{2h}), 123.76 (s, C^{13}), 125.01 (s, C^{2v}), 127.38 (s, C^{12}), 127.57 (s, C^{11}), 130.65 (s, C^{3h}), 136.97 (s, C^{3v}), 147.93 (s, C^{10}), 151.41 (d, $^2J_{P,C}$=10.89 Hz, C^{4v}), 152.48 (d, $^2J_{P,C}$=10.20 Hz, C^{4h}). ^{31}P NMR (202.47 MHz, CDC1з, 25°C), δ, p.pm.=111.99, 115.85. MS (MALDI): *m/z* (%)=2511 (100) [M^+]. Anal. Calcd. for $C_{140}H_{228}O_8N_{16}P_8$,%: C 66.94, H 9.15, N 8.92, P 9.84. Found, %: C 66.11, H 9.74, N 8.63, P 9.73.

Phospho(III)resorcinarene (3c). The compound was obtained analogously to **3a** by reaction of **1a** (0.1046 g, 0.192 mmol) with **2b** (0.3982 g, 1.54 mmol) at 20–25°C for 48 h. Yield 73%. m.p. 222–223°C. ^{1}H NMR (400 MHz, $CDC1_3$, 25°C), δ, ppm: 1.50 (d, $^3J_{H,H}$ 7.20Hz, 12H, C^{10}), 1.51 (m, 4H, H^{7ve}), 1.68 (m, 4H, H^{7he}), 1.86 (m, 4H, H^{7va}), 2.08 (m, 4H, H^{7ha}), 2.37 (d, $^3J_{H,H}$ 16.00Hz, 12H, N-CH_3^v), 2.40 (m, 4H, $H^{6've}$), 2.49 (m, 4H, H^{6va}), 2.59 (d, $^3J_{H,H}$ 16.40Hz, 12H, N-CH_3^v), 2.65 (m, 8H, $H^{6,6'he}$), 2.72 (d, $^3J_{H,H}$ 16.81Hz, 12H, N-CH_3^h), 2.73 (d, $^3J_{H,H}$ 16.01 Hz, 12H, N-CH_3^h), 2.78 (m, 4H, H^{6ve}), 3.08 (m, 4H, H^{6va}), 3.31 (m, 8H, $H^{6,6'ha}$), 4.70 (q, $^3J_{H,H}$ 6.82Hz, 4H, H^1), 6.44(s, 2H, H^{3h}), 6.83 (t, $^4J_{P,H}$=2.8 Hz, 2H, H^{5v}), 6.95 (t, $^4J_{P,H}$=2.8 Hz, 2H, H^{5h}), 7.27 (s, 2H, H^{3v}). ^{13}C NMR (100.61 MHz, CDC1з, 25˚C), δ, p.pm.: 22.00 (s, C^{10}), 24.81 (s, C^{7h}), 25.43 (s, C^{7v}), 30.77 (s, C^1), 39.84 (d, $^2J_{P,C}$=31.69 Hz, N-CH_3^h), 39.89 (d, $^2J_{P,C}$=31.79 Hz, N-CH_3^v), 40.09 (d, $^2J_{P,C}$=31.39 Hz, N-CH_3^v), 43.86 (d, $^2J_{P,C}$=5.53 Hz, $C^{6'v}$), 44.47 (d, $^2J_{P,C}$=5.73 Hz, C^{6v}), 44.58 (d, $^2J_{P,C}$=5.73 Hz, $C^{6'h}$), 44.77 (d, $^2J_{P,C}$=5.73 Hz, C^{6h}), 107.56 (t, $^3J_{P,C}$=21.23 Hz, C^{5v}), 107.65 (t, $^3J_{P,C}$=18.01 Hz, C^{5h}), 124.72 (s, C^{3h}), 125.91 (s, C^{2v}), 129.11 (s, C^{3v}), 130.24 (s, C^{2h}); 151.18 (s, C^{4h}); 151.79 (s, C^{4v}). ^{31}P NMR (161.98 MHz, $CDCl_3$, 25°C), δ, p.pm.: 123.21, 123.55. MS

(MALDI): *m/z* (%)= 1589 (30) [M^+]. Anal. Calcd. for $C_{72}H_{120}N_{16}O_8P_8$, %: C 54.54; H 7.63; N 14.13; P 15.63. Found,%: C 54.50; H 7.66; N 14.15; P 15.60.

Phospho(III)resorcinarene (3d). The compound was obtained analogously to **3a** by reaction of **1b** (0.1378 g, 0.174 mmol) and **2b** (0.2825 g, 1.39 mmol). Yield 76%. m.p. 228–229°C. ^{1}H NMR (400 MHz, CDC1$_3$, 25°C), δ, ppm: 1.31 (m, 4H, H^{7he}), 1.51 (m, 4H, H^{7ve}), 1.78 (m, 4H, H^{7ha}), 1.90 (m, 4H, H^{7va}), 1.98 (d, $^3J_{P,H}$=16.81Hz, 12H, N-CH_3^h), 2.09 (m, 4H, H^{6he}), 2.28 (m, 4H, H^{6ha}), 2.40 (m, 4H, $H^{6've}$), 2.44 (d, $^3J_{P,H}$=16.01Hz, 12H, N-CH_3^v), 2.53 (m, 4H, $H^{6'he}$), 2.55 (d, $^3J_{P,H}$=16.80Hz, 12H, N-CH_3^v), 2.60 (m, 4H, H^{6ve}), 2.65 (d, $^3J_{P,H}$=16.41Hz, 12H, N-CH_3^h), 2.73 (m, 4H, $H^{6'ha}$), 2.93 (m, 4H, $H^{6'va}$), 3.11 (m, 4H, H^{6va}), 5.80 (s, 4H, H^1), 5.93 (s, 2H, H^{3v}), 6.60 (s, 2H, H^{3h}), 6.73 (b.s., 8H, H^{11}), 6.85 (t, $^4J_{P,H}$=2.4Hz, 2H, H^{5v}), 6.92 (m, 12H, $H^{12,13}$), 7.06 (t, $^4J_{P,H}$=2.8 Hz, 2H, H^{5h}). ^{13}C NMR (100.61 MHz, CDC1$_3$, 25°C), δ, p.pm.: 24.98 (s, C^{7h}), 25.25 (s, C^{7v}), 39.11 (d, $^2J_{P,C}$=30.59 Hz, N-CH_3^h), 39.76 (d, $^2J_{P,C}$=30.28 Hz, N-CH_3^h), 40.01 (d, $^2J_{P,C}$=30.28 Hz, N-CH_3^v), 40.31 (d, $^2J_{P,C}$=30.01 Hz, N-CH_3^v), 40.77 (s, C^1), 43.59 (d, $^2J_{P,C}$=5.53 Hz, C^{6h}), 43.86 (d, $^2J_{P,C}$=5.43 Hz, $C^{6'h}$), 44.23 (d, $^2J_{P,C}$=5.33 Hz, $C^{6'v}$), 44.77 (d, $^2J_{P,C}$=5.83 Hz, $C^6{}_v$), 105.02 (t, $^3J_{P,C}$=23.04 Hz, C^{5h}), 107.01 (t, $^3J_{P,C}$=19.62 Hz, C^{5v}), 124.55 (s, C^{13}), 124.60 (s, C^{2h}), 126.02 (s, C^{2v}), 127.57 (s, $C^{11,12}$), 129.64 (s, C^{3h}), 135.70 (s, C^{3v}), 145.99 (s, C^{10}), 151.28 (d, $^2J_{P,C}$=6.04 Hz, C^{4v}); 152.56 (d, $^2J_{P,C}$=6.04 Hz, C^{4h}). ^{31}P NMR (161.98 MHz, $CDCl_3$, 25°C), δ, p.pm.: 121.76, 123.51. MS (MALDI): *m/z* (%) = 1877 (20) [M^+]. Anal. Calcd. for $C_{92}H_{128}N_{16}O_8P_8$, %: C 60.25; H 7.04; N 12.22; P 13.51; Found,% : C 60.20; H 6.99; N 12.10; P 13.55.

Phospho(III)resorcinarene (3e). The compound was obtained analogously to **3a** by reaction of **1a** (0.231g, 0.42 mmol) and **2c** (0.87g, 4.25 mmol) at 90–95°C for 40.5 h. Yield 68%. m.p. 283–284°C. ^{1}H NMR (500.13 MHz, CDC1$_3$, 25°C), δ, ppm: 0.64 (s, 12H, H^{8va}), 0.75 (s, 12H, H^{8ha}), 1.12 (s, 12H, H^{8ve}), 1.29 (s, 12H, H^{8he}), 1.47 (d, $^3J_{H,H}$=7.19 Hz, 12H, H^{10}), 3.21 (dd, $^2J_{H,H}$=10.39 Hz, $^3J_{P,H}$=23.03 Hz, 8H, $H^{6,6've}$), 3.43 (dd, $^2J_{H,H}$=10.4 Hz, $^3J_{P,H}$=11.00 Hz, 8H, $H^{6,6'he}$), 4.01 (dd, $^2J_{H,H}$=10.11 Hz, $^3J_{P,H}$=27.17 Hz, 8H, $H^{6,6'va}$), 4.35 (d, $^2J_{H,H}$=9.92 Hz, 8H, $H^{6,6'ha}$), 4.67 (q, $^3J_{H,H}$=7.0 Hz, 4H, H^1), 6.10 (s, 2H, H^{3h}), 6.49 (s, 2H, H^{5v}), 6.88 (s, 2H, H^{5h}), 7.34 (s, 2H, H^{3v}). ^{13}C NMR (125.77 MHz, CDC1$_3$, 25°C), δ, p.pm.: 20.55 (s, C^{10}), 22.45 (s, C^{8e}), 22.63 (s, C^{8a}), 31.62 (s, C^1), 32.53 (s, C^{7v}), 32.70 (d, $^3J_{P,C}$=3.68 Hz, C^{7h}), 69.19 (s, $C^{6,6'v}$), 69.27 (s, $C^{6,6'h}$), 108.46 (t, $^3J_{P,C}$=10.33 Hz, C^{5h}), 110.50 (t, $^3J_{P,C}$=13.62 Hz, C^{5v}), 125.83 (s, C^{3h}), 126.15 (s, C^{3v}), 129.21 (s, C^{2v}); 133.09 (s, C^{2h}); 147.12 (d, $^2J_{P,C}$=7.16 Hz, C^{4h}); 149.12 (s, C^{4v}). ^{31}P NMR (202.47 MHz, CDC1$_3$, 25°C), δ, p.pm.: 114.54, 115.01. MS (MALDI): *m/z* (%)= 1602 (10) [M^+], 1666 (100) [M^+]+Na^++K^+. Anal. Calcd. for $C_{72}H_{104}O_{24}P_8$, %: C 54.00, H 6.55, P 15.47; Found,%: C 54.09, H 6.61, P 15.50.

Phospho(III)resorcinarene (3f). The compound was obtained analogously to **3a** by reaction of **1b** (0.121g, 0.15 mmol) with **2c** (0.25g, 1.42 mmol) at 90-95 °C for 37.5 h. Yield 72%. m.p. 318-319°C. ^{1}H NMR (500.13 MHz, CDC1$_3$, 25°C), δ, p.pm.= 0.34 (s, 12H, H^{8ha}), 0.63 (s, 12H, H^{8va}), 1.07 (s, 12H, H^{8he}), 1.15 (s, 12H, H^{8ve}), 2.99 (dd, $^2J_{H,H}$=10.45 Hz, $^3J_{P,H}$=10.45 Hz, 4H, $H^{6'he}$), 3.12 (dd, $^2J_{H,H}$=10.62 Hz, $^3J_{P,H}$=10.68 Hz, 4H, H^{6he}), 3.21 (dd, $^2J_{H,H}$=10.62 Hz, $^3J_{P,H}$=10.59 Hz, 4H, $H^{6've}$), 3.28 (dd, $^2J_{H,H}$=10.62 Hz, $^3J_{P,H}$=10.39 Hz, 4H, H^{6ve}), 3.43 (dd, $^2J_{H,H}$=10.57 Hz,

$^{3}J_{P,H}$=2.37 Hz, 4H, $H^{6'ha}$), 3.72 (dd, $^{2}J_{H,H}$=10.45 Hz, $^{3}J_{P,H}$=2.23 Hz, 4H, H^{6ha}), 4.00 (dd, $^{2}J_{H,H}$=10.75 Hz, $^{3}J_{P,H}$=1.81 Hz, 4H, $H^{6'va}$), 4.06 (dd, $^{2}J_{H,H}$=10.62 Hz, $^{3}J_{P,H}$=1.70 Hz, 4H, H^{6va}), 5.79 (s, 4H, H^{1}), 5.85 (s, 2H, H^{3v}), 6.34 (s, 2H, H^{3h}), 6.66 (s, 2H, H^{5v}); 6.72 (b.s, 8H, H^{11}), 6,86 (s, 2H, H^{5h}), 6.93- 6.99 (m, 12H, $H^{12,13}$). ^{13}C NMR (125.77 MHz, CDC1з, 25˚C), δ, p.pm.: 22.15 (s, C^{8ha}), 22.27 (s, C^{8he}), 22.39 (s, C^{8ve}), 22.60 (s, C^{8va}), 32.29 (d, $^{3}J_{P,C}$=4.73 Hz, C^{7h}), 32.56 (d, $^{3}J_{P,C}$=4.21 Hz, C^{7v}), 43.96 (s, C^{1}) 68.61 (s, $C^{6'h}$), 69.27 (s, C^{6h}), 69.29 (s, $C^{6'v}$), 69.33 (s, C^{6v}), 106.32 (t, $^{3}J_{P,C}$=18.25 Hz, C^{5h}), 109.46 (t, $^{3}J_{P,C}$=15.69 Hz, C^{5v}), 125.53 (s, C^{13}), 127.14 (s, C^{2h}), 127.82 (s, C^{12}), 128.22 (s, C^{2v}), 128.46 (s,C^{11}), 129.71 (s, C^{3h}), 133.77 (s, C^{3v}), 143.48 (s, C^{10}), 149.20 (d, $^{2}J_{P,C}$=7.79 Hz, C^{4v}); 149.44 (d, $^{2}J_{P,C}$=6.75 Hz, C^{4h}). ^{31}P NMR (202.47 MHz, CDC1з, 25˚C), δ, p.pm.: 113.76, 115.88. MS (MALDI): *m/z* (%)=1852 (50) [M^{+}], 1916 (100) [M^{+}]+Na^{+}+K^{+}. Anal. Calcd. for $C_{92}H_{112}0_{24}P_{8}$, %: C 59.74; H 6.10; P 13.40; Found,%: C, 59.85; H, 6.18; P, 13.47.

Phospho(III)resorcinarene (3g). The compound was obtained analogously to **3a** by reaction of **1c** (0.099 g, 0.12 mmol) with **2c** (0.19 g, 9.7 mmol) at 90-95 ^{o}C for 20 h. The product was precipitated with acetonitrile (5 ml). Yield 52%. m.p. 151–152^{o}C. ^{1}H NMR (300.17 MHz, $CDC1_3$, 25^{o}C), δ, ppm: 0.66 (s, 12H, H^{8va}), 0.79 (s, 12H, H^{8ha}), 0.84 (t, $^{3}J_{H,H}$= 6.59 Hz, 12H, $(CH_2)_5CH_3$), 1.15 (s, 12H, H^{8ve}), 1.24 (s, 12H, H^{8he}), 1.33 (m, 32H, $CH_2(CH_2)_4CH_3$), 1.94 (m, $^{3}J_{H,H}$=7.24 Hz, 8H, $CH_2(CH_2)_4CH_3$), 3.24 (dd, $^{3}J_{H,H}$=10.33 Hz, $^{3}J_{P,H}$=10.26 Hz, 8H, $H^{6,6've}$), 3.46 (dd, $^{3}J_{H,H}$=8.50 Hz, $^{3}J_{H,H}$=7.71 Hz, 8H, $H^{6,6'he}$), 4.00 (d, $^{3}J_{H,H}$=9.91 Hz, 8H, $H^{6,6'va}$), 4.39 (d, $^{3}J_{H,H}$=9.95 Hz, 8H, $H^{6,6'ha}$), 4.60 (t, $^{3}J_{H,H}$=7.13 Hz, 4H, H^{1}), 6.20 (s, 2H, H^{3h}), 6.58 (s, 2H, H^{5v}), 6.94 (s, 2H, H^{5h}), 7.31 (s, 2H, H^{3v}). ^{13}C NMR (75.47 MHz, CDC1з, 25^{o}C), δ, p.pm.: 14.02 (s, $(CH_2)_5CH_3$), 22.54 (s, $(CH_2)_4CH_2CH_3$, H^{8e}), 22.76 (s, H^{8a}), 28.74 (s, $(CH_2)_3CH_2CH_2CH_3$), 29.87 (s, $(CH_2)_2CH_2(CH_2)_2CH_3$), 31.94 (s, $CH_2CH_2(CH_2)_3CH_3$), 32.62 (s, C^{7v}), 32.77 (s, C^{7h}), 35.94 (s, $CH_2(CH_2)_4CH_3$), 37.15 (s, C^{1}), 69.31 (s, $C^{6,6'}$), 108.12 (t, $^{3}J_{P,C}$=15.09 Hz, C^{5h}), 110.54 (t, $^{3}J_{P,C}$=15.09 Hz, C^{5v}), 126.52 (s, C^{3h}), 126.80 (s, C^{3v}), 127.10 (s, C^{2v}); 132.12 (s, C^{2h}); 148.11 (d, $^{2}J_{P,C}$=7.08 Hz, C^{4h}); 149.77 (s, C^{4v}). ^{31}P NMR (121.48 MHz, $CDCl_3$, 25^{o}C), δ, p.pm.: 114.27, 114.71. MS (MALDI): *m/z* (%)=1885 (18) [M^{+}], 1949 (100) [M^{+}]+Na^{+}+K^{+}. Anal. Calcd. for $C_{92}H_{144}O_{24}P_{8}$, %: C 58.72, H 7.71, P 13.17; Found,%: C 58.75, H 7.78, P 13.12.

Phospho(III)resorcinarene (3h). The compound was obtained analogously to **3a** by reaction of **1d** (0.198 g, 0.33 mmol) with **2c** (0.67 g, 3.3 mmol) at 90-95 ^{o}C for 24 h. Yield 65%. m.p. 310-312^{o}C. ^{1}H NMR (200.13 MHz, $CDC1_3$, 25^{o}C), δ, ppm: 0.71 (s, 12H, H^{8va}), 0.80 (s, 12H, H^{8ha}), 1.17 (s, 12H, H^{8ve}), 1.33 (s, 12H, H^{8he}), 1.51 (d, $^{3}J_{H,H}$=6.94 Hz, 12H, H^{10}), 2.06 (s, 6H, C^{5}-CH_3), 2.37 (s, 6H, C^{5}-CH_3), 3.30 (dd, $^{2}J_{H,H}$=10.60 Hz, $^{3}J_{P,H}$=21.20 Hz, 8H, $H^{6,6've}$), 3.49 (dd, $^{2}J_{H,H}$=10.96 Hz, $^{3}J_{P,H}$=22.29 Hz, 8H, $H^{6,6'he}$), 4.08 (d, $^{2}J_{H,H}$=10.60 Hz, 4H, $H^{6'va}$), 4.33 (d, $^{2}J_{H,H}$=10.24 Hz, 4H, H^{6va}), 4.44 (d, $^{2}J_{H,H}$=10.60 Hz, 4H, $H^{6'ha}$), 4.50 (q, $^{3}J_{H,H}$=6.58 Hz, 4H, H^{1}), 4.56 (d, $^{2}J_{H,H}$=9.87 Hz, 4H, H^{6va}), 5.95 (s, 2H, H^{3h}), 7.20 (s, 2H, H^{3v}). ^{31}P NMR (202.47 MHz, CDC1з, 25^{o}C), δ, p.pm.: 120.05, 119.34. Anal. Calcd. for $C_{76}H_{112}O_{24}P_{8}$, %: C 55.07, H 6.81, P 14,95; Found,%: C 55.09, H 6.83, P 15.00.

Phospho(III)resorcinarene (3i). The compound was obtained analogously to **3a** by reaction of **1e** (0.198 g, 0.33 mmol) with **2c** (0.67 g, 3.3 mmol) at 90-95 ^{o}C for 24 h. Yield 75%. m.p. 288-

289°C. ^{1}H NMR (200.13 MHz, CDC1$_3$, 25°C), δ, ppm: 0.70 (s, 12H, H^{8va}), 0.80 (s, 12H, H^{8ha}), 0.82 (t, $^3J_{H,H}$= 6.59 Hz, 12H, $(CH_2)_4CH_3$), 1.16 (s, 12H, H^{8ve}), 1.24 (m, 24H, $CH_2(CH_2)_3CH_3$), 1.33 (s, 12H, H^{8he}), 1.94 (m, $^3J_{H,H}$=7.24 Hz, 8H, $CH_2(CH_2)_3CH_3$), 2.05 (s, 6H, C^5-CH_3), 2.38 (s, 6H, C^5-CH_3), 3.29 (dd, $^2J_{H,H}$=10.45 Hz, $^3J_{P,H}$=20.90 Hz, 8H, $H^{6,6've}$), 3.47 (dd, $^2J_{H,H}$=10.45 Hz, $^3J_{P,H}$=21.35 Hz, 8H, $H^{6,6'he}$), 4.08 (d, $^2J_{H,H}$=9.35 Hz, 4H, H^{6va}), 4.31 (t, $^3J_{H,H}$=7.15 Hz, 4H, H^1), 4.33 (d, $^2J_{H,H}$=9.35 Hz, 4H, $H^{6'va}$), 4.43 (d, $^2J_{H,H}$=9.90 Hz, 4H, $H^{6'ha}$), 4.61 (d, $^2J_{H,H}$=10.45 Hz, 4H, H^{6ha}), 5.92 (s, 2H, H^{3h}), 7.08 (s, 2H, H^{3v}). ^{31}P NMR (202.47 MHz, CDC1з, 25°C), δ, p.pm.: 119.05, 119.34. Anal. Calcd. for $C_{92}H_{144}O_{24}P_8$, %: C 58.72, H 7.71, P 13.17; Found,%: C 58.71, H 7.73, P 13.15.

Thiophosphatoresorcinarene (4a). A solution of sulphur (0.0078 g, 0.24 mmol) and phosphocalixarene **3c** (0.0482 g, 0.03 mmol) in 1 ml of a chloroform–benzene mixture (1 : 1) was stirred at 20-25°C for 0.5 h. Hexane (4 ml) was added to the reaction mixture; the precipitate was filtered off and dried in vacuum (1 mm Hg) at 85–90°C. Yield 74%. m.p. 308–309°C. ^{1}H NMR (200 MHz, $CDCl_3$, 25^{0}C), δ, p.pm.: 1.52 (m, 4H, H^{7ve}), 1.59 (d, $^3J_{H,H}$ = 6,59 Hz, 12H, H^{10}), 1,94 (m, 4H, H^{7he}), 2,23 (m, 4H, H^{7va}), 2.58-3.23 (28H, signals of $H^{6,6've}$, $H^{6,6'va}$, $H^{6,6'he}$, H^{7ha} aren't resolved due to signals superposition N-$CH_3^{v,h}$), 2,77 (d, $^3J_{P,H}$ = 13,19 Hz, 12H, NCH_3^v), 2,83 (d, $^3J_{P,H}$ = 13,20 Hz, 12H, NCH_3^h), 2,99 (d, $^3J_{P,H}$ = 13,75 Hz, 12H, NCH_3^v), 3,02 (d, $^3J_{P,H}$ = 13,75 Hz, 12H, NCH_3^h), 3,49 (m, 8H, $H^{6.6`ha}$), 4,78 (q, $^3J_{H,H}$ = 7,7 Hz, 4H, H^1), 6,32 (s, 4H, H^{3h}), 7,40 (s, 4H, H^{5v}), 7,53 (s, 4H, H^{5h}), 7,90 (s, 4H, H^{3v}). ^{31}P NMR (32,4 MHz, $CDCl_3$, 25°C), δ, p.pm.: 71,88. Anal. Calcd. for $C_{72}H_{120}N_{16}O_8P_8S_8$, %: C 46.96, H 6.52, N 12.17, O 6.96, P 13.48, S 13.91; Found, %: C 46.94, H 6.55, N 12.16, P 13.48, S 13.92.

Thiophosphatoresorcinarene (4b). The compound was obtained analogously to **4a** by reaction of **3d** (0,0502 g, 0.027 mmol) with sulphur (0,007 g, 0.22 mmol). Yield 74%. m.p. >350°C. ^{1}H NMR (200 MHz, $CDCl_3$, 25°C), δ, p.pm.: 1,61 (m, 4H, H^{7he}), 1,84 (m, 4H, H^{7ve}), 2,03 (m, 4H, H^{7ha}), 2,46-2,92 (32H, signals of $H^{6'va}$, $H^{6,6've}$, $H^{6,6'ha}$; $H^{6,6'he}$, H^{7va} aren't resolved due to signals superposition N-$CH_3^{v,h}$), 2,60 (d, $^3J_{P,H}$ = 13.2 Hz, 12H, NCH_3^h), 2,72 (d, $^3J_{P,H}$ = 14.29 Hz, 12H, NCH_3^v), 2,81 (d, $^3J_{P,H}$ = 14.85 Hz, 12H, NCH_3^v), 2,87 (d, $^3J_{P,H}$ = 14.85 Hz, 12H, NCH_3^h), 3,04 (m, 4H, $H^{6`va}$), 3,21 (m, 4H, H^{6va}), 5,85 (s, 2H, H^{3v}), 5,98 (s, 4H, H^1), 6,41 (bs., 8H, H^{11}), 6,96 (bs., 12H, $H^{12,13}$), 7,35 (s, 2H, H^{3h}), 7,69 (s, 2H, H^{5v}), 7,97 (s, 2H, H^{5h}). ^{31}P NMR (32,4 MHz, $CDCl_3$, 25°C), δ, p.pm.: 71,99; 70,51. Anal. Calcd. for $C_{92}H_{128}N_{16}O_8P_8S_8$, %: C 52.87, H 6.13, N 10.73, P 11.88, S 12.26. Found, %: C 52.85, H 6.14, N 10.72, P 11.88, S 12.31

Thiophosphatoresorcinarene (4c). The compound was obtained analogously to **4a** by reaction of **3e** (0.1473 g, 0.092 mmol) with sulphur (0.0237 g, 0.74 mmol) at 75–80°C for 4 h. Yield 80%. m.p. 327–328°C. ^{1}H NMR (200 MHz, $CDCl_3$, 30^{0}C), δ, p.pm.: 0.81 (s, 12H, H^{8va}); 0.93 (s, 12H, H^{8ha}); 1.17 (s, 12H, H^{8ve}); 1.35 (s, 12H, H^{8he}); 1.57 (d, $^3J_{H,H}$ =7.02 Hz, 12H, H^{10}); 3.96-4.40 (m, 32H, $H^{6,6'}$); 4.78 (q, $^3J_{H,H}$ =7.33 Hz, 4H, H^1); 6.36 (s, 2H, H^{3h}); 6.94 (s, 2H, H^{5v}); 7.42 (s, 2H, H^{5h}); 7.46 (s, 2H, H^{3v}). ^{13}C NMR (50.32 MHz, $CDCl_3$, 30^{0}C), δ, p.pm.: 20.54 (s, C^{10}), 21.21 (s, C^{8e}); 21.95 (s, C^{8a}); 31.23 (s, C^1); 32.07 (s, C^7); 76.35 (s, $C^{6,6'v}$); 76.99 (s, $C^{6,6'h}$); 110.93 (b.s., C^{5h}); 113.11 (b.s, C^{5v}); 126.22 (s, C^{3h}); 126.99 (s, C^{3v}); 130.89 (s, C^{2v}); 133.52 (s, C^{2h}); 146.06 (s, C^{4h}); 147.09 (s, C^{4v}). ^{31}P NMR (80.97 MHz, $CDCl_3$, 30°C), δ, p.pm.: 54.77. Anal. Calcd. for

$C_{72}H_{104}O_{24}P_8S_8$, %: C 46.55; H 5.64; P 13.34, S 13.81. Found, %: C 46.58; H 5.69; P 13.41; S 13.86.

Thiophosphatoresorcinarene (4d). The compound was obtained analogously to **4a** by reaction of **3f** (0,1461 g, 0.079 mmol) with sulphur (0,0202 g, 0.63 mmol). Yield 84%. m.p. 344-345°C. ^{1}H NMR (200 MHz, $CDCl_3$, 30°C), δ, p.pm.: 0.88 (s, 12H, H^{8ha}); 1.18 (s, 12H, H^{8va}); 1.26 (s, 12H, H^{8he}); 1.26 (s, 12H, H^{8ve}); 3.61-4.47 (m, 32H, $H^{6,6'}$); 6.02 (s, 4H, H^1); 6.17 (s, 2H, H^{3v}); 6.55 (s, 2H, H^{3h}); 7.00 (s, 2H, H^{5v});.7.08 (b.s, 8H, H^{11}); 7.48 (m, 12H, $H^{12,13}$); 7.56 (s, 2H, H^{5h}). ^{13}C NMR (50.32 MHz, $CDCl_3$, 30°C), δ, p.pm.: 20.05 (s, C^{8h}); 21.94 (s, C^{8v}); 31.73 (d, $^3J_{P,C}$ =6.20 Hz, C^{7h}); 32.11 (d, $^3J_{P,C}$ =6.40 Hz, C^{7v}); 43.43 (s, C^1); 76.38 (s, $C^{6,6'h}$); 77.01 (s, $C^{6,6'v}$); 109.82 (b.s, C^{5h}); 114.31 (b.s, C^{5v}); 126.23(s, C^{13}); 127.97 (s, C^{2h}); 128.14 (s, C^{12}); 128.33 (s, C^{2v}); 129.75 (s, C^{11}); 130.61 (s, C^{3h}); 133.91 (s, C^{3v}); 142.15(s, C^{10}), 147.19 (d, $^2J_{P,C}$ =7.81 Hz, C^{4v}); 147.31 (d, $^2J_{P,C}$ =7.79 Hz, C^{4h}). ^{31}P NMR (80.97 MHz, $CDCl_3$, 30°C), δ, p.pm.: 51.94, 53.56. Anal. Calcd. for $C_{92}H_{112}O_{24}P_8S_8$, %: C 52.46; H 5.36; P 11.76, S 12.18. Found, %: C 52.49; H 5.39; P 11.81; S 12.20.

Thiophosphatoresorcinarene (4e). The compound was obtained analogously to **4a** by reaction of **3f** (0,0785 g, 0.044 mmol) with sulphur (0,0112 g, 0.35 mmol). Yield 80%. m.p. 232-233°C. ^{1}H NMR (200.13 MHz, CDC1$_3$, 25°C), δ, ppm: 0.79 (s, 12H, H^{8va}), 0.85 (t, $^3J_{H,H}$= 6.00 Hz, 12H, $(CH_2)_4CH_3$), 1.05 (s, 12H, H^{8ha}), 1.15 (s, 12H, H^{8ve}), 1.26 (s, 12H, H^{8he}), 1.29 (m, 24H, $CH_2(CH_2)_3CH_3$), 1.94 (m, $^3J_{H,H}$=7.24 Hz, 8H, $CH_2(CH_2)_3CH_3$), 2.03 (s, 6H, C^5-CH_3), 2.44 (s, 6H, C^5-CH_3), 3.83 (dd, $^2J_{H,H}$=11.55 Hz, $^3J_{P,H}$=19.25 Hz, 8H, $H^{6,6've}$), 3.96 (dd, $^2J_{H,H}$=9.90 Hz, $^3J_{P,H}$=19.25 Hz, 8H, $H^{6,6'he}$), 4.12 (d, $^2J_{H,H}$=9.35 Hz, 4H, H^{6va}), 4.21 (dd, $^2J_{H,H}$=10.99 Hz, $^3J_{P,H}$=11.55 Hz, 4H, $H^{6'va}$), 4.40 (dd, $^2J_{H,H}$=10.45 Hz, $^3J_{P,H}$=19.79 Hz, 4H, $H^{6'ha}$), 4.51 (t, $^3J_{H,H}$=11.00 Hz, 4H, H^1), 4.74 (dd, $^2J_{H,H}$=10.23 Hz, $^3J_{P,H}$=19.74 Hz, 4H, H^{6ha}), 5.95 (s, 2H, H^{3h}), 7.35 (s, 2H, H^{3v}). ^{31}P NMR (202.47 MHz, CDC1з, 25°C), δ, p.pm.: 53.69. Anal. Calcd. for $C_{92}H_{144}O_{24}P_8S_8$,%: C 51.64, H 6.79, P 11.59, S 12.00; Found,%: C 51.66, H 6.58, P 11.95, S 12.08.

Phosphatoresorcinarene (5a). A solution of phosphocalixarene **3e** (0.1478 g, 0.0923 mmol) in CH_2Cl_2 (1 ml) was added to an adduct of hydrogen peroxide and urea (0.0694 g, 0.738 mmol). The reaction mixture was stirred at 20–25°C for 4 h. The precipitate was filtered off; the filtrate was washed with water, and the organic layer was separated. The solvent was completely removed, and the product was dried in vacuum (1 mm Hg) at 85–90°C. Yield 70%. m.p. 209–210°C. ^{1}H NMR (200 MHz, $CDCl_3$, 30°C), δ, p.pm.: 0.81 (s, 12H, H^{8va}); 0.90 (s, 12H, H^{8ha}); 1.15 (s, 12H, H^{8ve}); 1.33 (s, 12H, H^{8he}); 1.53 (d, $^2J_{H,H}$=7.25 Hz, 12H, H^{10}); 3.84 (m, 8H, $H^{6,6've}$); 4.04 (d, $^2J_{H,H}$ =12.81 Hz, 8H, $H^{6,6'he}$); 4.34 (d, $^2J_{H,H}$ =11.10 Hz, 8H, $H^{6,6'va}$); 4.48 (d, $^2J_{H,H}$ =9.39 Hz, 8H, $H^{6,6'ha}$); 4.75 (q, $^3J_{H,H}$=7.25 Hz, 4H, H^1); 5.95 (s, 2H, H^{3h}); 6.95 (s, 2H, H^{5v}); 7.39 (s, 2H, H^{5h}); 7.44 (s, 2H, H^{3v}). ^{31}P NMR (80.97 MHz, $CDCl_3$, 30^{0}C), δ, p.pm.: -14.18, -14.40. Anal. Calcd. for $C_{72}H_{104}O_{32}P_8$, %: C 50.01; H 6.06; P 14.33; Found, %: C 50.06, H 6.12, P 14.37.

Phosphatoresorcinarene (5b). The compound was obtained analogously to **5a** by reaction of **3f** (0.065 g, 0.0351 mmol) with an adduct of hydrogen peroxide and urea (0.028 g, 0.294 mmol). Yield 87%. m.p. 243–244°C. ^{1}H NMR (200 MHz, $CDCl_3$, 30^{0}C), δ, p.pm.: 0.54 (s, 12H, H^{8ha});

0.87 (s, 12H, H^{8va}); 1.15 (s, 12H, H^{8he}); 1.22 (s, 12H, H^{8ve}); 3.57-3.97 (m, 32H, $H^{6,6'}$); 5.83 (s, 2H, H^{3v}); 5.96 (s, 4H, H^{1}); 6.15 (s, 2H, H^{3h}); 6.70 (b.s., 8H, H^{11}); 7.04 (m, 12H, $H^{12,13}$); 7.29 (s, 2H, H^{5v});.7.64 (s, 2H, H^{5h}). ^{13}C NMR (50.32 MHz, $CDCl_3$, 30°C), δ, p.pm.: 19.63 (s, C^{8h}); 21.47 (s, C^{8v}); 31,59 (d, $^3J_{P,C}$ =5.88 Hz, C^{7h}); 31.9 (d, $^3J_{P,C}$ =5.80 Hz C^{7v}); 43.80 (s, C^{1}); 76,36 (s, $C^{6,6'h}$); 77,00 (s, $C^{6,6'v}$); 108.48 (b.s, C^{5h}); 111,48 (b.s, C^{5v}); 126.39 (s, C^{13}), 127.66 (s, C^{2h}); 127.84 (s, C^{12}), 128.18 (s, C^{2v}), 129.43 (s, C^{11}), 130.06 (s, C^{3h}); 133.77 (s, C^{3v}); 140.78, (s, C^{10}), 146.95 (d, $^2J_{P,C}$ =6.92 Hz, C^{4v}); 147.13 (d, $^2J_{P,C}$ =6.94 Hz, C^{4h}). ^{31}P NMR (80.97 MHz, $CDCl_3$, 30^{0}C), δ, p.pm.: -14.50, -15.56. Anal. Calcd. for $C_{92}H_{112}O_{32}P_8$, %: C 55.87; H 5.71; P 12.53. Found, %: C 55.85; H 5.73; P 12.50.

Phosphatoresorcinarene (5c). The compound was obtained analogously to **5a** by reaction of **3h** (0.133 g, 0.0803 mmol) with an adduct of hydrogen peroxide and urea (0.06 g, 0.643 mmol). Yield 96%. m.p. 224-225°C. ^{1}H NMR (200 MHz, $CDCl_3$, 30°C), δ, p.pm.: 0.82 (s, 12H, H^{8va}); 0.95 (s, 12H, H^{8ha}); 1.15 (s, 12H, H^{8ve}); 1.31 (s, 12H, H^{8he}); 1.58 (d, $^2J_{H,H}$=7.31 Hz, 12H, H^{10}); 2.12 (s, 6H, C^5-CH_3); 2.46 (s, 6H, C^5-CH_3); 3.82 (dd, $^2J_{H,H}$ =9.90 Hz, $^3J_{P,H}$ =17.05 Hz, 8H, $H^{6,6've}$); 3.92 (d, $^2J_{H,H}$ =11.00 Hz, 4H, $H^{6'he}$); 4.08 (dd, $^2J_{H,H}$ =10.44 Hz, $^3J_{P,H}$ =20.34 Hz, 8H, $H^{6he,6'va}$); 4.20 (dd, $^2J_{H,H}$ =9.39 Hz, $^3J_{P,H}$ =9.90 Hz, 4H, H^{6va}); 4.41 (dd, $^2J_{H,H}$ =10.99 Hz, $^3J_{P,H}$ =11.55 Hz, 4H, $H^{6'ha}$); 4.60 (dd, $^2J_{H,H}$ =9.90 Hz, $^3J_{P,H}$ =12.1 Hz, 4H, H^{6ha}); 4.64 (q, $^3J_{H,H}$=7.25 Hz, 4H, H^{1}); 5.96 (s, 2H, H^{3h}); 7.25 (s, 2H, H^{3v}). ^{31}P NMR (80.97 MHz, $CDCl_3$, 30°C), δ, p.pm.: -13.43, -14.36. Anal. Calcd. for $C_{76}H_{112}O_{32}P_8$, %: C 51.12; H 6.32; P 13.88. Found, %: C 51.15; H 6.35; P 13.90.

Complex 6a. A mixture of calixarenes **3f** (0.221 g, 0.0317 mmol) and molybdenum hexacarbonyl (0.252 g, 0.253 mmol) in 1 ml of dioxane was maintained at 95–100°C for 12 h. The complex was isolated by preparative TLC with a benzene–hexane–chloroform (3 : 3 : 0.5) mixture as eluent. The product was dried in vacuum (1 mm Hg) at 20°C. Yield 75%. M.dec. 183–185°C. R_f 0.82. ^{1}H NMR (300.17 MHz, $CDC1_3$, 25°C), δ, p.pm.: 0.33 (s, 3H, H^8), 0.75 (s, 3H, H^8), 0.82 (s, 3H, H^8), 0.90 (s, 3H, H^8), 1.11 (s, 3H, H^8), 1.26 (s, 3H, H^8), 1.28 (s, 3H, H^8), 1.28 (s, 3H, H^8), 1.37 (s, 3H, H^8), 2.37 (d, $^2J_{HH}$=10.09Hz, 2H, H^6), 2.94 (d, $^2J_{HH}$=11.35Hz, 2H, H^6), 2.98 (d, $^2J_{HH}$=10.72Hz, 2H, H^6), 3.44 (d, $^2J_{HH}$=9.77Hz, 2H, H^6), 3.50 (d, $^2J_{HH}$=8.82Hz, 2H, H^6), 3.65(d, $^2J_{HH}$=10.14Hz, 2H, H^6), 3.75 (d, $^2J_{HH}$=12.78Hz, 2H, H^6), 3.78 (d, $^2J_{HH}$=11.49Hz, 2H, H^6), 3.98 (d, $^2J_{HH}$=10.24Hz, 2H, H^6), 4.01 (d, $^2J_{HH}$=9.77Hz, 2H, H^6), 4.10 (d, $^2J_{HH}$=10.72Hz, 2H, H^6), 4.12 (d, $^2J_{HH}$=8.83Hz, 2H, H^6), 4.18 (d, $^2J_{HH}$=9.46Hz, 2H, H^6), 4.44 (d, $^2J_{HH}$=9.77Hz, 2H, H^6), 4.75 (d, $^2J_{HH}$=9.77Hz, 2H, H^6), 5.92 (s, 2H, H^1), 6.13 (s, 2H, H^1), 6.37(d, $^3J_{HH}$=7.25Hz, 2H, CH-arom.), 6.40 (s, 2H, H^{3h}), 6.54(d, $^3J_{HH}$=8.19Hz, 2H, CH-arom.), 6.72 (t, $^3J_{HH}$=7.25Hz, 2H, CH-arom.) 6.99 (s, 2H, H^{3v}), 7.04 (s, 2H, H^{5v}), 6.99- 7.10 (m, 10H, CH-arom.), 7.12 (t, $^3J_{HH}$=7.25Hz, 2H, CH-arom.), 7.23 (t, $^3J_{HH}$=7.25Hz, 2H, CH-arom.), 7.33 (s, 2H, H^{5h}). ^{31}P NMR (202.47 MHz, $CDC1_3$, 25°C), δ, p.pm.: 149.65, 147.04, 144.90, 144.73. Anal. Calcd. for $C_{132}H_{112}Mo_8O_{64}P_8$, %: C 42.42; H 3.02; P 6.63. Found, %: C 42.47; H 3.03; P 6.69.

Complex 7a. The compound was obtained analogously to **6a** by reaction of **4b** (0.133 g, 0.0803 mmol) with molybdenum hexacarbonyl (0.12 g, 0.25 mmol) in 1 ml of dioxane was maintained at 95–100°C for 12 h. Yield 51%. M.dec. 148-151°C. Rf=0.89. ^{1}H NMR (300.17

MHz, CDC1$_3$, 25^{o}C), δ, p.pm.: 0.71 (t, 12H, $CH_2(CH_2)_4CH_3$), 0.78 (s, 12H, H^8), 0.82 (s, 12H, H^8), 1.17 (s, 12H, H^8), 1.18 (s, 12H, H^8), 1.45 (m, 32H, $CH_2(CH_2)_4CH_3$), 1.84 (m, $^3J_{HH}$=7.85Hz, 8H, $CH_2(CH_2)_4CH_3$), 3.50 (d, $^2J_{HH}$=10.63Hz, 4H, H^6), 3.62 (d, $^2J_{HH}$=10.63Hz, 4H, H^6), 3.72 (d, $^2J_{HH}$=10.53Hz, 4H, H^6), 3.98 (d, $^2J_{HH}$=11.15Hz, 4H, H^6), 4.21 (d, $^2J_{HH}$=10.68Hz, 4H, H^6), 4.34 (t, $^3J_{HH}$=7.95Hz, 4H, H^1), 4.61 (d, $^2J_{HH}$=9.76Hz, 4H, H^6), 4.67 (d, $^2J_{HH}$=9.06Hz, 4H, H^6), 4.86 (d, $^2J_{HH}$=10.63Hz, 4H, H^6), 6.96 (s, 2H, H^{3h}), 6.98 (s, 2H, H^{5v}), 7.34 (s, 2H, H^{5h}), 7.49 (s, 2H, H^{3v}). ^{31}P NMR (202.47 MHz, CDC1з, 25˚C), δ, p.pm.: 149.80, 148.70, 145.50, 144.90. Anal. Calcd. for $C_{132}H_{144}Mo_8O_{64}P_8$, %: C 51.16; H 4.64; P 8.01. Found, %: C 51.10; H 4.54 P 8.05.

Complex 8a. A solution of calixarene **3c** (0,05 g, 0.032 mmol) in 1 ml of chloroform was added to (1,5-cyclooctadienyl)palladium dichloride (0,0485 g, 0.126 mmol). The reaction mixture was stirred at room temperature for 0.5 h. The precipitate formed was filtered off, washed with hexane, dried at room temperature and 1 mm Hg. Yield 70%; m.p. 240–242^{o}C. ^{1}H NMR (200 MHz, $CDCl_3$, 30^{o}C), δ, p.pm.: 1.80 (d, $^3J_{H,H}$=7.33 Hz, 12H, H^{10}), 1.97 (m, 8H, H^7), 2.94-3.25 (40H, signals of $H^{6,6'}$, H^7 aren't resolved due to signals superposition of N-CH_3), 2,97 (d, $^3J_{P,H}$ = 7.02 Hz, 24H, NCH_3), 3,22 (d, $^3J_{P,H}$ = 7.02 Hz, 24H, NCH_3), 4.72 (q, $^3J_{H,H}$=7.63 Hz, 4H, H^1); 6.85 (s, 4H, H^3); 8.04 (s, 4H, H^5). ^{31}P NMR (80.97 MHz, $CDCl_3$, 30^{o}C), δ, p.pm.: 91.28. Anal. Calcd. for $C_{72}H_{104}O_{24}P_8Pd_4Cl_8$, %: C 37.43; H 4.54; P 10.72. Found, %: C 37.22; H 4.57; P 10.70.

Complex 8b. The compound was obtained analogously to **7a** by reaction of **3e** (0.0744g, 0.046mmol) with (1,5-cyclooctadienyl)palladium dichloride (0.053g, 0.186mmol). Yield 87%. m.p. 240-242^{o}C. ^{1}H NMR (200 MHz, $CDCl_3$, 30^{o}C), δ, p.pm.: 0.72 (s, 24H, H^8); 1.14 (s, 24H, H^8); 1.77 (d, $^3J_{H,H}$=6.44 Hz, 12H, H^{10}); 4.09 (d, 8H, $^3J_{H,H}$ =5.02 Hz, $H^{6,6've}$); 4.24 (d, $^3J_{H,H}$ =5.48 Hz, 8H, $H^{6,6'he}$); 4.33 (d, $^3J_{H,H}$ =5.49 Hz, 8H, $H^{6,6'va}$); 4.45 (d, $^3J_{H,H}$ =5.94 Hz, 8H, $H^{6,6'ha}$); 4.98 (q, $^3J_{H,H}$=6.85 Hz, 4H, H^1); 6.92 (s, 4H, H^3); 7.67 (s, 4H, H^5). ^{31}P NMR (80.97 MHz, $CDCl_3$, 30^{o}C), δ, p.pm.: 83.63. Anal. Calcd. for $C_{92}H_{112}O_{24}P_8Pd_4Cl_8$, %: C 43.18; H 4.41; P 9.68. Found, %: C 43.20; H 4.57; P 9.80.

Complex 8c. The compound was obtained analogously to **7a** by reaction of **3f** (0,083 g, 0.045 mmol) with (1,5-cyclooctadienyl)palladium dichloride (0,0512 g, 0.179 mmol). Yield 80%. m.p. 200-222^{o}C. ^{1}H NMR (200 MHz, $CDCl_3$, 30^{o}C), δ, p.pm.: 0.88 (s, 24H, H^8); 1.20 (s, 24H, H^8); 3.97 (m, 8H, $H^{6,6've}$); 4.12 (m, 8H, $H^{6,6'he}$); 4.30 (m, 8H, $H^{6,6'va}$); 4.43 (m, 8H, $H^{6,6'ha}$); 5.49(s, 4H, H^1); 6.94 (s, 4H, H^3); 7.01 (b.s., 8H, H^{11}), 7.12 (s, 4H, H^5), 7.25(b.s., 12H, $H^{12,13}$). ^{31}P NMR (80.97 MHz, $CDCl_3$, 30^{o}C), δ, p.pm.: 81.33. Anal. Calcd. for $C_{72}H_{120}N_{16}O_8P_8Pd_4Cl_8$, %: C 37.68; H 5.27; N 9.77; P 10.80. Found, %: C 37.50; H 5.57; N 9.80; P 10.70.

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