ISSN 1070-4280, Russian Journal of Organic Chemistry, 2014, Vol. 50, No. 4, pp. 469–477. © Pleiades Publishing, Ltd., 2014.
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α-Amino Acetals Containing a Phosphonate or Phosphine Oxide Group. Synthesis and Reactions with Resorcinols

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Received January 14, 2014

Abstract—New α-amino acetals containing a phosphonate or phosphine oxide group were synthesized by the Kabachnik–Fields reaction in the ternary system amino acetal–paraformaldehyde–dialkyl phosphonate (or dialkylphosphine oxide). Condensation of dialkyl (2,2-dimethoxyethylamino)methylphosphonates with resorcinol and its derivatives in ethanol in the presence of hydrochloric acid, apart from the corresponding 2,2-bis(polyhydroxyphenyl)ethylammonium salts, gave 2,5-bis(polyhydroxyphenyl)-1,4-bis[(dialkoxyphosphoryl)methyl]-piperazines. Dialkyl[(2,2-dimethoxyethylamino)methyl]phosphine oxides (Alk = C_8H_{17}, $C_{10}H_{21}$) did not react with resorcinol derivatives under similar conditions, and analogous ammonium salts were obtained by heating the reactants in boiling trifluoroacetic acid.

DOI: 10.1134/S1070428014040034

Amino acetals have long attracted researchers' attention due to their utility in various syntheses [1]. These compounds have been shown to be universal building blocks in the synthesis of many biologically important heterocycles and alkaloids [2] and diarylmethane derivatives exhibiting a broad spectrum of pharmacological activity [3].

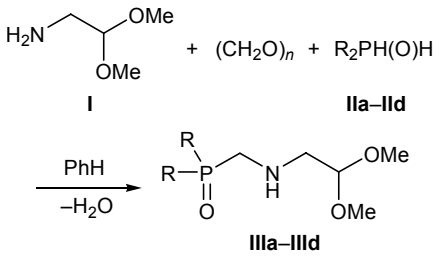
The condensation of functionally substituted acetals with resorcinol and its derivatives in acid medium provides a convenient method for the preparation of unique linear and cyclic polyphenols such as calix[4]-resorcinarenes having aminoalkyl [4] and phosphorus-containing substituents [5] on the lower rim, diarylmethane derivatives [6], including those based on a macrocyclic scaffold [7], and imidazolidin-2-ones with polyphenol fragments [8].

In continuation of our studies it seemed reasonable to synthesize acetals containing a phosphorylmethylamino group. Due to their complexing ability, amino phosphonates and amino phosphine oxides are used as extractants for rare earth metals [9] and amino acid carriers in membrane extraction processes [10] and are also promising for use in radioactive waste treatment processes [11].

The goal of the present work was to obtain new cyclic and acyclic polyphenol structures containing amino phosphonate (amino phosphine oxide) groups. For this purpose, we synthesized α-amino acetals functionalized with a phosphonate (phosphine oxide) group, and studied their condensation with resorcinol and its derivatives in acid medium.

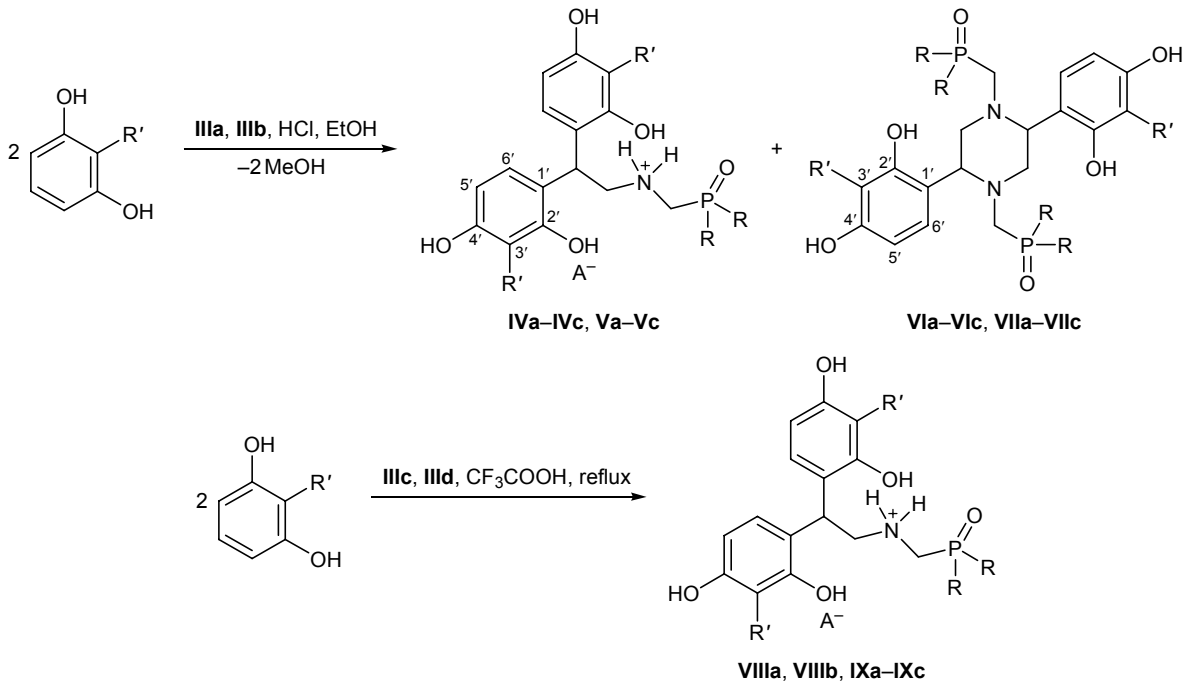
Phosphorylated acetals **IIIa**–**IIId** were prepared by reaction of aminoacetaldehyde dimethyl acetal (**I**) with

Scheme 1.



R = EtO (**a**), *i*-PrO (**b**), C_8H_{17} (**c**), $C_{10}H_{21}$ (**d**).

Scheme 2.



IVa–IVc, **Va–Vc** **VIa–VIc**, **VIIa–VIIc**

VIIIa, **VIIIb**, **IXa–IXc**

IV, **VI**, R = EtO; **V**, **VII**, R = *i*-PrO; **VIII**, R = C_8H_{17}; **IX**, R = $C_{10}H_{21}$; R^1 = Me (**a**), H (**b**), OH (**c**); A = Cl, CF_3COO.

dialkyl phosphonates **IIa** and **IIb** or dialkylphosphine oxides **IIc** and **IId** and paraformaldehyde at a ratio of 1 : 1 : 1 in the presence of *p*-toluenesulfonic acid (Kabachnik–Fields reaction; Scheme 1). The structure of compounds **IIIa**–**IIId** was confirmed by ^{1}H and ^{31}P NMR and IR spectroscopy, MALDI mass spectrometry, and elemental analysis. The ^{31}P NMR spectra of **IIIa**–**IIId** contained a single phosphorus signal at δ_P 24 (**IIIa**, **IIIb**) or 47 ppm (**IIIc**, **IIId**). In the ^{1}H NMR spectra of **IIIa**–**IIId** the most informative were a doublet signal at δ 2.77–2.88 ppm from the PCH_2N methylene protons, a triplet at δ 4.42–4.47 ppm from the acetal CH proton, and a singlet at δ 3.3 ppm from the methoxy groups.

The condensation of acetals **IIIa** and **IIIb** with resorcinol and its derivatives was carried out at a reactant ratio of 1 : 2 in ethanol in the presence of concentrated aqueous HCl. The progress of the reactions was monitored by ^{31}P NMR, and the reaction mixtures were analyzed by MALDI mass spectrometry. We were the first to reveal that the reactions of resorcinol, 2-methylresorcinol, and pyrogallol with phosphorylated amino acetals **IIIa** and **IIIb** in acid medium led to the formation of diarylmethane derivatives **IVa**–**IVc** and **Va**–**Vc** containing polyphenol fragments (Scheme 2).

Compounds **IVa**–**IVc** and **Va**–**Vc** were isolated as light yellow hygroscopic crystalline substances which are soluble in alcohols, water, acetone, and DMSO. They characteristically showed in the ^{1}H NMR spectra doublets at δ 6.28–6.42 and 6.78–7.10 ppm from the aromatic protons (5′-H and 6′-H, respectively, a triplet at δ 4.51–5.1 ppm from the methine proton, and a doublet at δ 3.48–3.61 ppm from the PCH_2N protons ($^2J_{PH}$ = 13.4–14.0 Hz).

Detailed analysis of the reaction mixtures showed that the main process leading to the formation of diarylmethane derivatives **IV** and **V** is accompanied by a minor one. In the mass spectrum of the reaction mixture obtained in the reaction of amino phosphonate **IIIa** with 2-methylresorcinol, apart from ion peaks with *m*/*z* 440 $[M - HCl + H]^+$ and 462 $[M - HCl + Na]^+$ corresponding to compound **IVa**, we observed fairly strong peaks with *m*/*z* 631 and 653; analogous pattern was observed in the mass spectra of other reaction mixtures (Table 1). The ^{31}P NMR spectrum of the same reaction mixture contained a major signal at δ_P 15 ppm and a less intense signal at δ_P 19 ppm, their intensity ratio being 9 : 1.

By varying the reaction conditions (solvent, acid nature, reactant ratio) we found that products with *m*/*z* 631 (in the reaction with 2-methylresorcinol) and 634 (in the reaction with pyrogallol) separated from the reaction mixture when the reactions were carried out at a reactant ratio of 4 : 1 in ethanol in the presence

Table 1. MALDI mass spectra of reaction mixtures, *m*/*z*

Reactants	**IV**, **V**	**VI**, **VII**
2-Methylresorcinol + **IIIa**	440 $[M - HCl + H]^+$, 462 $[M - HCl + Na]^+$	631 $[M_1 + H]^+$, 653 $[M_1 + Na]^+$
Resorcinol + **IIIa**	412 $[M - HCl + H]^+$, 434 $[M - HCl + Na]^+$	603 $[M_1 + H]^+$, 625 $[M_1 + Na]^+$
Pyrogallol + **IIIa**	443 $[M - HCl + H]^+$, 465 $[M - HCl + Na]^+$	634 $[M_1 + H]^+$, 656 $[M_1 + Na]^+$
2-Methylresorcinol + **IIIb**	468 $[M - HCl + H]^+$, 490 $[M - HCl + Na]^+$	686 $[M_1 + H]^+$, 709 $[M_1 + Na]^+$
Resorcinol + **IIIb**	440 $[M - HCl + H]^+$, 462 $[M - HCl + Na]^+$	659 $[M_1 + H]^+$, 681 $[M_1 + Na]^+$
Pyrogallol + **IIIb**	472 $[M - HCl + H]^+$, 494 $[M - HCl + Na]^+$	691 $[M_1 + H]^+$, 713 $[M_1 + Na]^+$

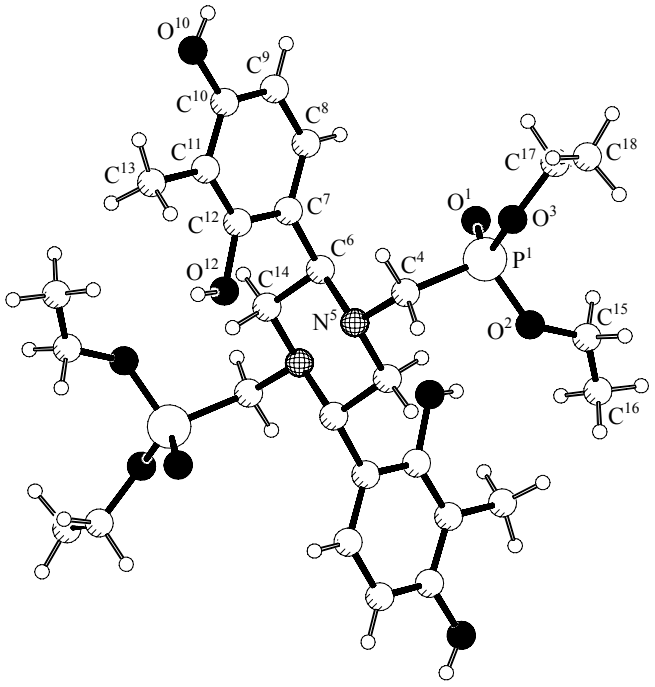
of HCl. In this case, the yield of these products was higher, and their isolation was easier. On the basis of the NMR data (including COSY, 2D ^1H–^{13}C HSQC, and 2D ^1H–^{13}C HMBC experiments), mass spectra, and elemental analyses, the minor products were assigned the structure of phosphorus-containing piperazines **VIa** and **VIc**.

Unlike ammonium salts **IVa**–**IVc** and **Va**–**Vc**, compounds **VIa** and **VIc** displayed in the ^1H NMR spectra strongly broadened signals from the methylene protons in the piperazine ring (δ 3.00–3.33 ppm), as well as from the CH protons (δ 4.50–4.89 ppm), and the PCH_2N proton signals appeared as doublets at δ 3.63–3.88 ppm.

The structure of piperazine derivatives **VIa** and **VIc** was unambiguously proved by X-ray analysis of the molecular complex formed by compound **VIa** with 2-methylresorcinol, hydrogen bromide, and water. This complex was formed after prolonged storage (7 days) of a solution of 2-methylresorcinol and amino acetal **IIIa** in aqueous HBr at room temperature. According to the X-ray diffraction data (see figure), molecule **VIa** consists of a piperazine ring, two phosphonate fragments linked to the piperazine nitrogen atoms through methylene spacers, and two 2,4-dihydroxy-3-methylphenyl substituents. Apart from molecules **VIa**, those of 2-methylresorcinol, water, and hydrogen bromide are present in crystal. The bond lengths and bond and torsion angles in molecule **VIa** do not differ from the corresponding standard values. The central piperazine fragment adopts a *boat* conformation. The phosphorus atoms have tetrahedral configuration with the torsion angles $O^1P^1O^2$ 116.7(4), $O^1P^1O^3$ 115.3(4), and $O^1P^1C^4$ 114.5(3)°.

Molecules of the complex in crystal are packed due mainly to classical hydrogen bonds (Table 2). In addition, a shortened intermolecular contact between the bromine and nitrogen atoms should be noted; the Br···N distance is 3.251(5) Å, which is shorter by 0.15 Å than the sum of the van der Waals radii of the bromine and nitrogen atoms. This contact is the only one connecting the bromine atom with one molecule **VIa**, whereas the other molecule of **VIa** and 2-methylresorcinol molecule are linked to the bromine atom through hydrogen bonds.

The crystal structure of the complex is represented by alternating layers made up of molecules **VIa** and 2-methylresorcinol, which are parallel to the *a*0*b* crystallographic plane, and H_3O^+ and Br^- ions reside between molecules **VIa**. No direct interaction was detected between molecules of **VIa** and 2-methylresorcinol, while the layers are linked to each other



Structure of the molecule of 1,4-bis[(diethoxyphosphoryl)-methyl]-2,5-bis(2,4-dihydroxy-3-methylphenyl)piperazine (**VIa**) in crystal according to the X-ray diffraction data.

Table 2. Hydrogen bonds formed by molecules **VIa** in crystal

Hydrogen bond	Symmetry operation	D–H, Å	D···A, Å	∠DHA, deg
$O^{10}\cdots H^{10}\cdots O^{4}$	$x, 1+y, z$	0.82	2.626(8)	167
$O^{12}\cdots H^{12}\cdots Br^{1}$	–	0.82	3.283(5)	144
$O^{17}\cdots H^{17}\cdots Br^{1}$	$1-x, 1-y, 1-z$	0.82	3.394(9)	160
$O^{21}\cdots H^{21}\cdots O^{4}$	$x, y, 1+z$	0.82	3.002(12)	136
$O^{4}\cdots H^{411}\cdots Br^{1}$	–	0.87	3.292(6)	144
$O^{4}\cdots H^{412}\cdots O^{1}$	$2-x, 1-y, 1-z$	0.87	2.715(9)	180
$C^{4}\cdots H^{41}\cdots O^{10}$	$1-x, 2-y, 1-z$	0.97	3.443(8)	150
$C^{13}\cdots H^{133}\cdots O^{10}$	–	0.96	2.769(10)	109
$C^{14}\cdots H^{142}\cdots O^{12}$	–	0.97	2.976(8)	119
$C^{15}\cdots H^{152}\cdots O^{21}$	$2-x, 1-y, 2-z$	0.97	3.390(18)	175
$C^{23}\cdots H^{231}\cdots O^{17}$	–	0.96	2.674(19)	110

through interactions of both organic components with H_3O^+ cations and Br^- anions.

Thus, we were the first to reveal that reactions of resorcinol, 2-methylresorcinol, and pyrogallol with phosphorylated amino acetals **IIIa** and **IIIb** in the presence of hydrochloric acid lead to the formation of [2,2-bis(polyhydroxyphenyl)ethyl](dialkoxyphosphorylmethyl)ammonium chlorides **IV** and **V** as the major products and phosphorylated polyhydroxyphenyl-substituted piperazines **VI** and **VII** as minor ones. Among the latter, we succeeded in isolating only those formed in the reactions of acetal **IIIa** with 2-methylresorcinol and pyrogallol; piperazine derivatives **VIb** and **VIIa**–**VIIc** were detected in the reaction mixtures by MALDI mass spectrometry.

Diarylmethane derivatives like **IV** and **V** attract interest as multidentate ligands [12] and building blocks for the synthesis of new macrocyclic compounds [5], and piperazine derivatives **VI** and **VII** are promising as biologically active compounds [13].

The structure of the condensation products formed in reactions with functionalized acetals is largely determined by the nature of the reactants and reaction conditions [4–6]. Amino acetals **IIIc** and **IIId** having dialkylphosphorylmethyl substituents (Alk = C_8H_{17}, $C_{10}H_{21}$) on the nitrogen atom failed to react with polyphenols under the above conditions (ethanol–HCl). The ^{31}P NMR spectra of the reaction mixtures contained signals in the region δ 53–55 ppm, indicating concurrent protonation of the P=O group in the presence of HCl. As a result, the catalyst (HCl) is deactivated, and generation of carbocations necessary for electrophilic substitution in the aromatic ring is hindered. Therefore, a larger amount of acid is required to effect the condensation.

However, it was impossible to increase the amount of acid catalyst (aqueous HCl) because of the low solubility of amino acetals **IIIc** and **IIId** in water. No condensation products were formed when the reaction was carried out in a nonpolar solvent (chloroform, benzene, toluene) in the presence of trifluoroacetic acid. We succeeded in obtaining the desired products only by heating acetals **IIIc** and **IIId** with resorcinol and its derivatives in boiling trifluoroacetic acid (Scheme 2). The results of a number of experiments showed that 4-fold excess of polyphenol with respect to amino acetal **III** ensured formation of condensation products **VIIIa**, **VIIIb**, and **IXa**–**IXc** in 45–55% yield; piperazine derivatives like **VI** (**VII**) were not detected in the reaction mixtures.

Compounds **VIIIa**, **VIIIb**, and **IXa**–**IXc** were isolated as white powders with low melting points, which were soluble in chloroform, alcohols, acetone, and benzene. Their structure was confirmed by the IR, ^{31}P, ^{1}H, and ^{13}C NMR, and MALDI mass spectra and elemental analyses.

To conclude, we have revealed a new path in the reaction of phosphorylated α-amino acetals with resorcinol and its derivatives in ethanol in the presence of hydrochloric acid, which leads to the formation of phosphorus-containing piperazine derivatives in addition to products of the diarylmethane series. Analogous amino acetals containing a phosphine oxide fragment exhibit a lower reactivity toward resorcinol derivatives. Dialkyl(2,2-dimethoxyethylaminomethyl)-phosphine oxides (Alk = C_8H_{17}, $C_{10}H_{21}$) do not form

condensation products in ethanol under catalysis with concentrated aqueous HCl, and heating of the reactants in boiling trifluoroacetic acid is necessary to obtain the corresponding diarylmethane derivatives.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-600 spectrometer at 600.1 and 150.9 MHz, respectively; the chemical shifts were measured relative to the residual proton and carbon signals of the deuterated solvents. The ^{31}P NMR spectra were recorded on a Bruker Avance II-400 instrument at 161.9 MHz using 85% phosphoric acid as external reference. The IR spectra (4000–400 cm^{-1}) were obtained on a Bruker Vector-22 spectrometer. The MALDI-TOF mass spectra were recorded on a Bruker Ultraflex III instrument using plastic and metal targets and 2,5-dihydroxybenzoic acid as matrix.

The X-ray diffraction data for a single crystal of the complex of **VIa** with 2-methylresorcinol, HBr, and H_2O were acquired on a Bruker SMART Apex II diffractometer (λMoK_α radiation, λ 0.71073 Å; graphite monochromator). The structure was solved by the direct method using SHELXS software package [14]. The positions of non-hydrogen atoms were refined first in isotropic and then in anisotropic approximation using SHELXL-97 [15]. Hydrogen atoms attached to carbons were placed in calculated positions. All calculations were carried out using WinGX [16] and APEX2 [17]. The molecular structure was plotted with the aid of PLATON [18]. The complex crystallized in triclinic crystal system; $C_{42}H_{64}Br_2N_2O_{16}P_2$. Unit cell parameters (20°C): a = 9.1050(9), b = 11.2785(11), c = 13.8547(13) Å; α = 81.6740(10), β = 73.2540(10), γ = 70.6250(10)°; V = 1283.3(2) Å^3; Z = 1, d_{calc} = 1.391 g×cm^{-3}; space group P-1; μ_{Mo} = 1.707 cm^{-1}. Intensities of 4958 reflections were measured; 3258 reflections were characterized by $I \geq 2\sigma(I)$. Final divergence factors R = 0.0549, R_w = 0.1538. The X-ray diffraction data for compound **VIa** were deposited to the Cambridge Crystallographic Data Centre (entry no. CCDC 982639).

Phosphorylated α-amino acetals **IIIa** and **IIIb** were synthesized according to the procedures described in [19, 20].

[(2,2-Dimethoxyethyl)aminomethyl]dioctylphosphine oxide (IIIc). A mixture of 1.5 g (5.47 mmol) of dioctylphosphine oxide (**IIc**), 0.57 g (5.42 mmol) of aminoacetaldehyde dimethyl acetal, 0.16 g (5.33 mmol) of paraformaldehyde, and 0.01 g of *p*-toluenesulfonic acid in 20 mL of benzene was heated for 6 h under reflux in a flask equipped with a Dean–Stark trap. When the reaction was complete, 0.12 g of potassium carbonate was added, the mixture was heated under reflux for an additional 10 min and cooled, and the precipitate was filtered off. The organic layer was washed with three portions of water and dried over $MgSO_4$, and the solvent was distilled off. Yield 2.05 g (93%). IR spectrum, ν, cm^{-1}: 3294 br (NH), 1263 s (P=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.85 t (6H, CH_3, J = 6.9 Hz), 1.25 br.s (16H, CH_2), 1.36 m (4H, CH_2), 1.53 m (4H, CH_2), 1.70 m (4H, CH_2P), 2.77 d (2H, NCH_2, J = 5.4 Hz), 2.92 d (2H, PCH_2N, J = 7.9 Hz), 3.34 s (6H, OCH_3), 4.32 t (1H, CH, J = 5.4 Hz). ^{31}P NMR spectrum ($CDCl_3$): δ_P 47.64 ppm. Mass spectrum, m/z: 392 $[M + H]^+$, 414 $[M + Na]^+$, 430 $[M + K]^+$. Found, %: C 64.19; H 11.84; N 3.54; P 7.98; $C_{21}H_{46}NO_3P$. Calculated, %: C 64.35; H 11.86; N 3.52; P 7.99.

Didecyl[(2,2-dimethoxyethyl)aminomethyl]-phosphine oxide (IIId) was synthesized in a similar way from 1.63 g (5.39 mmol) of didecylphosphine oxide (**IId**), 0.56 g (5.33 mmol) of aminoacetaldehyde dimethyl acetal, and 0.16 g (5.33 mmol) of paraformaldehyde. Yield 2.3 g (95%), mp 40–42°C. IR spectrum, ν, cm^{-1}: 3283 br (NH), 1258 s (P=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.88 t (6H, CH_3, J = 7.1 Hz), 1.24 br.s (24H, CH_2), 1.39–1.42 m (4H, CH_2), 1.57 m (4H, CH_2), 1.73 m (4H, CH_2P), 2.82 d (2H, NCH_2, J = 5.4 Hz), 2.96 d (2H, PCH_2N, J = 7.9 Hz), 3.38 s (6H, OCH_3), 4.47 t (1H, CH, J = 5.4 Hz). ^{31}P NMR spectrum ($CDCl_3$): δ_P 47.6 ppm. Mass spectrum, m/z: 448 $[M + H]^+$, 470 $[M + Na]^+$, 487 $[M + K]^+$. Found, %: C 67.07; H 12.05; N 3.14; P 6.95. $C_{25}H_{54}NO_3P$. Calculated, %: C 67.11; H 12.08; N 3.13; P 6.94.

Compounds IVa–IVc, VIa, and VIIc (*general procedure*). *a*. A mixture of 5.65 mmol of the corresponding polyphenol and 0.70 g (2.75 mmol) of amino phosphonate **IIIa** in 5 mL of ethanol was cooled to 5°C, 1.5 mL of aqueous HCl was added dropwise under vigorous stirring, and the mixture was stirred for 1 h at room temperature and heated for 4–6 h at 55–60°C. When the reaction was complete, a part of the solvent was evaporated under reduced pressure (water-jet pump), and the precipitate (compound **VIa** or **VIc**) was filtered off, washed with acetone, and dried under reduced pressure (water-jet pump). The filtrate was evaporated, the oily residue was dissolved in water, the solution was extracted twice with diethyl ether, the aqueous layer was evaporated under reduced pressure

(water-jet pump), and the precipitate (compound **IVa**–**IVc**) was dried in a vacuum desiccator over P_2O_5 until constant weight.

b. Amino acetal **IIIa**, 3 g (11 mmol), was added dropwise to a mixture of 36.40 mmol of the corresponding polyphenol, 30 mL of ethanol, and 8 mL of aqueous HCl, and the mixture was heated for 4 h at 60–75°C and left to stand for 24 h. The precipitate (compound **VIa** or **VIc**) was filtered off and dried under reduced pressure (water-jet pump) until constant weight. The filtrate was evaporated under reduced pressure, the oily residue was dissolved in water, the solution was extracted with diethyl ether and methylene chloride, the aqueous layer was separated by decanting and evaporated under reduced pressure, and the residue (compound **IVa** or **IVc**) was dried under reduced pressure.

***N*-[2,2-Bis(2,4-dihydroxy-3-methylphenyl)ethyl]-*N*-[(diethoxyphosphoryl)methyl]ammonium chloride (IVa).** Yield 0.95 g (74%, *a*), 2.53 g (45%, *b*); mp 180–182°C. IR spectrum, ν, cm^{-1}: 3406, 3259 br (OH); 1609 s (C=C_{arom}); 1232 s (P=O), 1019, 1073 s (POC). ^{1}H NMR spectrum (D_2O), δ, ppm: 1.21 t (6H, CH_3, J = 6.9 Hz), 2.00 s (6H, 3′-CH_3), 3.48 d (2H, PCH_2, J = 14.0 Hz), 3.67 d (2H, NCH_2, J = 7.9 Hz), 4.06–4.13 m (4H, OCH_2), 4.89 t (1H, CH, J = 7.6 Hz), 6.42 d (2H, 5′-H, ^3J = 8.6 Hz), 6.78 d (2H, 6′-H, J = 8.6 Hz). ^{31}P NMR spectrum (D_2O): δ_P 16.83 ppm. Mass spectrum, *m*/*z*: 440 [M – HCl + H]$^+$, 462 [M – HCl + Na]$^+$, 478 [M – HCl + K]$^+$. Found, %: C 52.85; H 6.69; Cl 7.45; N 2.49; P 6.43. $C_{21}H_{30}NO_7P\cdot HCl$. Calculated, %: C 53.00; H 6.57; Cl 7.45; N 2.94; P 6.51.

***N*-[2,2-Bis(2,4-dihydroxyphenyl)ethyl]-*N*-[(diethoxyphosphoryl)methyl]ammonium chloride (IVb).** Yield 0.72 g (59%), mp 140–141°C. IR spectrum, ν, cm^{-1}: 3422, 3243 br (OH); 1620 s (C=C_{arom}); 1227 s (P=O); 1019, 1039 s (POC). ^{1}H NMR spectrum (CD_3OD), δ, ppm: 1.36 t (6H, CH_3, J = 6.9 Hz), 3.54 d (2H, PCH_2, J = 14.0 Hz), 3.79 d (2H, NCH_2, J = 7.6 Hz), 4.18–4.23 m (4H, OCH_2), 6.28 d (2H, 5′-H, $^3J_{HH}$ = 8.2 Hz), 6.40 s (2H, 3′-H), 6.93 d (2H, 6′-H, J = 8.2 Hz), 8.90 br.s (4H, OH). ^{31}P NMR spectrum (CD_3OD): δ_P 16.62 ppm. Mass spectrum, *m*/*z*: 412 [M – HCl + H]$^+$, 434 [M – HCl + Na]$^+$, 451 [M – HCl + K]$^+$. Found, %: C 50.35; H 6.09; Cl 7.86; N 3.19; P 6.94. $C_{19}H_{26}NO_7P\cdot HCl$. Calculated, %: C 50.96; H 6.08; Cl 7.92; N 3.13; P 6.92.

***N*-[2,2-Bis(2,3,4-trihydroxyphenyl)ethyl]-*N*-[(diethoxyphosphoryl)methyl]ammonium chloride (IVc).** Yield 1.27 g (69%, *a*), 5.12 g (40%, *b*); mp 148–150°C. IR spectrum, ν, cm^{-1}: 3420 br (OH), 1626 w (C=C_{arom}), 1215 s (P=O), 1045 s (POC). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 1.25 t (6H, CH_3, J = 7.1 Hz), 3.51 d (2H, PCH_2, J = 14.0 Hz), 3.68 d (2H, NCH_2, J = 7.8 Hz), 4.11 m (4H, OCH_2), 4.82 t (1H, CH, J = 7.8 Hz), 6.42 d (2H, 5′-H, ^3J = 8.6 Hz), 7.10 br.s (2H, 6′-H, ^3J = 8.6 Hz). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 14.8 (CH_3), 24.9 (CH), 45.4 (PCH_2N), 60.3 (CH_2), 62.0 (OCH_2), 110.4 (C$^{5'}$), 123.7 (C$^{6'}$), 126.8 (C$^{1'}$), 136.5 (C$^{3'}$), 146.2 (C$^{2'}$), 147.6 (C$^{4'}$). ^{31}P NMR spectrum (acetone-d_6): δ_P 16.9 ppm. Mass spectrum, *m*/*z*: 444 [M – HCl + H]$^+$, 466 [M – HCl + Na]$^+$, 482 [M – HCl + K]$^+$. Found, %: C 47.15; H 5.73; Cl 7.42; N 2.79; P 6.43. $C_{19}H_{26}NO_9P\cdot HCl$. Calculated, %: C 47.55; H 5.67; Cl 7.39; N 2.92; P 6.45.

1,4-Bis[(diethoxyphosphoryl)methyl]-2,5-bis(2,4-dihydroxy-3-methylphenyl)piperazine (VIa). Yield 0.10 g (12%, *a*), 0.62 g (16.7%, *b*); mp 205–208°C. IR spectrum, ν, cm^{-1}: 3426, 3201 br (OH); 1604 m (C=C_{arom}); 1253 m (P=O); 1080, 1013 s (POC). ^{1}H NMR spectrum (D_2O), δ, ppm: 1.25 t (12H, CH_3, J = 6.9 Hz), 2.13 s (6H, 3′-CH_3), 3.11–3.33 m (4H, NCH_2), 3.88 d (4H, PCH_2, J = 16.4 Hz), 4.06–4.13 m (8H, OCH_2), 4.89 br.s (2H, CH), 6.42 d (2H, 5′-H, ^3J = 8.4 Hz), 7.10 br.s (2H, 6′-H). ^{31}P NMR spectrum (D_2O): δ_P 19.83 ppm. Mass spectrum, *m*/*z*: 631 [M + H]$^+$, 653 [M + Na]$^+$, 669 [M + K]$^+$. Found, %: C 52.85; H 7.05; N 4.46; P 9.84. $C_{28}H_{44}N_2O_{10}P_2$. Calculated, %: C 53.33; H 7.03; N 4.44; P 9.82.

1,4-Bis[(diethoxyphosphoryl)methyl]-2,5-bis(2,3,4-trihydroxyphenyl)piperazine (VIIc). Yield 0.15 g (12%, *a*), 0.70 g (19%, *b*); mp 199–201°C. IR spectrum, ν, cm^{-1}: 3418, 3243 br (OH); 1628 m (C=C_{arom}); 1213 m (P=O); 1048, 1019 s (POC). ^{1}H NMR spectrum (D_2O) δ, ppm: 1.16 t (12H, CH_3, J = 6.9 Hz), 3.00–3.26 m (4H, NCH_2), 3.63 d (4H, PCH_2, J = 11.4 Hz), 3.88–3.92 m (8H, OCH_2), 4.55 br.s (2H, CH), 6.39 d (2H, 5′-H, ^3J = 8.4 Hz), 6.81 d (2H, 6′-H, ^3J = 8.4 Hz). ^{13}C NMR spectrum (D_2O), δ_C, ppm: 16.0 (CH_3), 47.4 (NCH_2), 57.1 (PCH_2NH), 59.3 (CH), 62.0 (OCH_2), 107.6 (C$^{5'}$), 117.5 (C$^{6'}$), 120.8 (C$^{1'}$), 132.9 (C$^{3'}$), 145.1 (C$^{2'}$), 146.6 (C$^{4'}$). ^{31}P NMR spectrum (D_2O): δ_P 20.01 ppm. Mass spectrum, *m*/*z*: 635 [M + H]$^+$, 657 [M + Na]$^+$, 673 [M + K]$^+$. Found, %: C 48.75; H 6.41; N 4.38; P 9.82. $C_{26}H_{40}N_2O_{12}P_2$. Calculated, %: C 49.21; H 6.31; N 4.42; P 9.78.

Compounds Va–Vc (*general procedure*). A mixture of 7.06 mmol of the corresponding polyphenol

and 0.50 g (1.76 mmol) of amino phosphonate **IIIb** in 5 mL of ethanol was cooled to 10°C, 1 mL of aqueous HCl was added dropwise under continuous stirring, and the mixture was stirred for 2 h at room temperature and heated for 4 h at 60°C. The solvent was distilled off on a rotary evaporator, the residue was ground with diethyl ether, and the precipitate was filtered off and dried in a vacuum desiccator over P_2O_5 until constant weight.

***N*-[2,2-Bis(2,4-dihydroxy-3-methylphenyl)ethyl]-*N*-[(diisopropoxyphosphoryl)methyl]ammonium chloride (Va).** Yield 0.55 g (66%), mp 76–78°C. IR spectrum, ν, cm^{-1}: 3415 s (OH), 1609 m (C=C_{arom}), 1199 m (P=O), 1073 s (POC). ^{1}H NMR spectrum (D_2O), δ, ppm: 1.25 d and 1.28 d (6H each, CH_3, J = 6.2 Hz), 2.05 s (6H, 3′-CH_3), 3.50 d (2H, NCH_2P, J = 13.9 Hz), 3.76 d (2H, NCH_2, J = 7.9 Hz), 4.73 m (2H, OCH), 4.94 t (1H, CH, J = 7.9 Hz), 6.50 d (2H, 5′-H, J = 8.5 Hz), 6.88 d (2H, 6′-H, J = 8.5 Hz). ^{31}P NMR spectrum (D_2O): δ_P 14.91 ppm. Mass spectrum, *m*/*z*: 468 [M – HCl + H]$^+$, 490 [M – HCl + Na]$^+$. Found, %: C 54.52; H 6.99; Cl 7.02; N 2.82; P 6.24. $C_{23}H_{34}NO_7P\cdot HCl$. Calculated, %: C 54.81; H 6.95; Cl 7.05; N 2.78; P 6.16.

***N*-[2,2-Bis(2,4-dihydroxyphenyl)ethyl]-*N*-[(diisopropoxyphosphoryl)methyl]ammonium chloride (Vb).** Yield 0.45 g (58%), mp 70–73°C. IR spectrum, ν, cm^{-1}: 3271 br (OH), 1614 m (C=C_{arom}), 1220 m (P=O), 1074 s (POC). ^{1}H NMR spectrum (D_2O) δ, ppm: 1.30 d and 1.31 d (6H each, CH_3, J = 6.0 Hz), 3.61 d (2H, NCH_2P, J = 13.4 Hz), 3.89 d (2H, NCH_2, J = 7.4 Hz), 4.78 m (2H, OCH), 4.96 t (1H, CH, J = 7.4 Hz), 6.29 d.d (2H, 5′-H, ^3J = 8.3, ^4J = 2.4 Hz), 6.56 d (2H, 3′-H, ^4J = 2.4 Hz), 6.94 d (2H, 6′-H, J = 8.3 Hz). ^{31}P NMR spectrum (D_2O): δ_P 16.0 ppm. Mass spectrum, *m*/*z*: 440 [M – HCl + H]$^+$, 462 [M – HCl + Na]$^+$. Found, %: C 52.72; H 6.52; Cl 7.44; N 2.90; P 6.48. $C_{21}H_{30}NO_7P\cdot HCl$. Calculated, %: C 52.9; H 6.52; Cl 7.47; N 2.94; P 6.52.

***N*-[2,2-Bis(2,3,4-trihydroxyphenyl)ethyl]-*N*-[(diisopropoxyphosphoryl)methyl]ammonium chloride (Vc).** Yield 0.56 g (62%), mp 73–75°C. IR spectrum, ν, cm^{-1}: 3300 br (OH), 1605 m (C=C_{arom}), 1208 m (P=O), 1061 s (POC). ^{1}H NMR spectrum (D_2O), δ, ppm: 1.26 d and 1.27 d (6H each, CH_3, J = 6.2 Hz), 3.51 d (2H, NCH_2P, J = 13.8 Hz), 3.76 d (2H, NCH_2, J = 7.9 Hz), 4.74 m (2H, OCH), 4.86 t (1H, CH, J = 7.9 Hz), 6.47 d (2H, 5′-H, ^3J = 8.5 Hz), 6.62 d (2H, 6′-H, J = 8.5 Hz). ^{31}P NMR spectrum (D_2O): δ_P 14.93 ppm. Mass spectrum, *m*/*z*: 472 [M – HCl + H]$^+$, 494 [M – HCl + Na]$^+$. Found, %: C 49.55; H 6.16; Cl 7.06; N 2.73; P 6.03. $C_{21}H_{30}NO_9P\cdot HCl$. Calculated, %: C 49.65; H 6.11; Cl 6.99; N 2.76; P 6.10.

Compounds VIIIa, VIIIb, and IXa–IXc (*general procedure*). A mixture of 4 mmol of the corresponding polyphenol and 1 mmol of amino phosphine oxide **IIIc** or **IIId** in 4 mL of trifluoroacetic acid was heated for 8 h under reflux. When the reaction was complete, trifluoroacetic acid was distilled off on a rotary evaporator, the residue was ground with diethyl ether, and the precipitate was filtered off and dried in a vacuum desiccator over P_2O_5 until constant weight.

***N*-[2,2-Bis(2,4-dihydroxy-3-methylphenyl)ethyl]-*N*-[(dioctylphosphoryl)methyl]ammonium trifluoroacetate (VIIIa).** Yield 0.36 g (53%), mp 93–95°C. IR spectrum, ν, cm^{-1}: 3423 br (OH), 1672 s (C=O), 1610 s (C=C_{arom}), 1203 m (P=O). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 0.91 t (6H, CH_3, J = 6.32 Hz), 1.30 br.s (16H, CH_2), 1.41 m (4H, CH_2), 1.57 m (4H, C**H**$_2$CH$_2$P), 1.98 m (4H, CH_2P), 2.13 s (6H, 3′-CH_3), 3.55 d (2H, PCH_2N, J = 6.2 Hz), 3.86 d (2H, CH_2N, J = 7.6 Hz), 5.14 t (1H, CH, J = 7.6 Hz), 6.41 d (2H, 5′-H, ^3J = 8.4 Hz), 6.85 d (2H, 6′-H, ^3J = 8.4 Hz). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 7.9 (3′-CH_3), 20.5–31.1 [$(CH_2)_7$P], 26.6 d (CH_2P, J = 66.3 Hz), 34.6 (CH), 41.9 d (PCH_2NH, J = 59.7 Hz), 52.3 (NCH_2), 106.9 (C$^{5'}$), 111.9 (C$^{3'}$), 115.5 q (CF_3, J = 294.0 Hz), 118.3 (C$^{1'}$), 124.5 (C$^{6'}$), 152.7 (C$^{2'}$), 154.6 (C$^{4'}$), 160.5 q (C=O, J = 40.0 Hz). ^{31}P NMR spectrum (acetone-d_6): δ_P 46 ppm. Mass spectrum, *m*/*z*: 575 [M – CF_3COOH + H]$^+$, 598 [M – CF_3COOH + Na]$^+$, 614 [M – CF_3COOH + K]$^+$. Found, %: C 59.14; H 7.99; N 2.83; P 4.91. $C_{33}H_{54}NO_5P\cdot CF_3COOH$. Calculated, %: C 59.27; H 7.97; N 2.87; P 5.02.

***N*-[2,2-Bis(2,4-dihydroxyphenyl)ethyl]-*N*-[(di-octylphosphoryl)methyl]ammonium trifluoroacetate (VIIIb).** Yield 0.30 g (41%), mp 110–112°C. IR spectrum, ν, cm^{-1}: 3436 br (OH), 1672 v.s (C=O), 1615 s (C=C_{arom}), 1205 m (P=O). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 0.89 br.s (6H, CH_3), 1.30 br.s (20H, CH_2), 1.43–1.47 m (4H, CH_2), 1.58–1.62 m (4H, CH_2P), 3.53 br.s (2H, PCH_2N), 3.80 d (2H, CH_2N, J = 6.7 Hz), 5.07 br.s (1H, CH), 6.30 d (2H, 5′-H, ^3J = 8.4 Hz), 6.57 s (2H, 3′-H), 6.96 d (2H, 6′-H, J = 8.4 Hz). ^{31}P NMR spectrum (acetone-d_6): δ_P 48.11 ppm. Mass spectrum, *m*/*z*: 548 [M – CF_3COOH + H]$^+$, 570 [M – CF_3COOH + Na]$^+$, 586 [M – CF_3COOH + K]$^+$. Found, %: C 59.84; H 7.69; N 2.06; P 4.65. $C_{31}H_{50}NO_5P\cdot CF_3COOH$. Calculated, %: C 59.90; H 7.77; N 2.12; P 4.68.

***N*-[2,2-Bis(2,4-dihydroxy-3-methylphenyl)ethyl]-*N*-[(didecylphosphoryl)methyl]ammonium trifluoroacetate (IXa).** Yield 0.39 g (52%), mp 160–162°C. IR spectrum, ν, cm^{-1}: 3308 br (OH), 1676 s (C=O), 1608 s (C=C_{arom}), 1200 m (P=O). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 0.89 t (6H, CH_3, J = 6.9 Hz), 1.30 br.s (24H, CH_2), 1.41 br.s (4H, CH_2), 1.58 m (4H, C**H**$_2$$CH_2$P), 1.98 m (4H, CH_2P), 2.10 s (6H, 3′-CH_3), 3.55 d (2H, PC**H**$_2$N, J = 6.2 Hz), 3.87 d (2H, CH_2N, J = 7.4 Hz), 5.14 t (1H, CH, J = 7.4 Hz), 6.43 d (2H, 5′-H, ^3J = 8.4 Hz), 6.85 d (2H, 6′-H, ^3J = 8.4 Hz). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 7.9 (3′-CH_3), 13.0 (CH_3), 20.5–30.3 [$(CH_2)_7$P], 26.5 d (CH_2P, J = 66.0 Hz), 34.8 (CH), 41.9 d (PC**H**$_2$N, J = 60.8 Hz), 52.3 (CH_2N), 106.9 (C$^{5'}$), 111.9 (C$^{3'}$), 115.5 q (CF_3, J = 294.0 Hz), 118.5 (C$^{1'}$), 124.6 (C$^{6'}$), 152.7 (C$^{2'}$), 154.5(C$^{4'}$), 160.1 q (C=O, J = 40.0 Hz). ^{31}P NMR spectrum (acetone-d_6): δ_P 47.07 ppm. Mass spectrum, *m*/*z*: 632 [M – CF_3COOH + H]$^+$, 654 [M – CF_3COOH + Na]$^+$, 670 [M – H + K]$^+$. Found, %: C 62.65; H 8.48; N 7.87; P 4.43. $C_{37}H_{62}NO_5P\cdot CF_3COOH$. Calculated, %: C 62.81; H 8.45; N 7.57; P 4.16.

***N*-[2,2-Bis(2,4-dihydroxyphenyl)ethyl]-*N*-[(dioctylphosphoryl)methyl]ammonium trifluoroacetate (IXb).** Yield 0.30 g (41%), mp 130°C. IR spectrum, ν, cm^{-1}: 3314 br (OH), 1668 s (C=O), 1604 s (C=C_{arom}), 1205 m (P=O). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 0.92 t (6H, CH_3, J = 7.0 Hz), 1.32 br.s (24H, CH_2), 1.42 m (4H, CH_2), 1.67 m (4H, C**H**$_2$$CH_2$P), 1.85 m (4H, CH_2P), 3.88 d (2H, PC**H**$_2$N, J = 5.1 Hz), 4.12 d (2H, CH_2N, J = 7.9 Hz), 5.11 t (1H, CH, J = 7.9 Hz), 6.27 d.d (2H, 5′-H, ^3J = 8.4, ^4J = 2.2 Hz), 6.38 d (2H, 3′-H, ^4J = 2.2 Hz), 6.99 d (2H, 6′-H, ^3J = 8.4 Hz), 8.05 s (4H, OH). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 13.0 (CH_3), 20.5–31.2 [$(CH_2)_7$P], 26.2 (CH_2P, J = 63.8 Hz), 34.5 (CH), 40.0 (PC**H**$_2$NH, J = 59.7 Hz), 51.1 (NCH_2), 103.1 (C$^{3'}$), 106.1 (C$^{5'}$), 115.5 q (CF_3, J = 295.0 Hz), 117.8 (C$^{1'}$), 129.0 (C$^{6'}$), 155.8 (C$^{2'}$), 158.3 (C$^{4'}$) 160.1 q (C=O, J = 38.0 Hz). ^{31}P NMR spectrum (acetone-d_6): δ_P 49.6 ppm. Mass spectrum, *m*/*z*: 604 [M – CF_3COOH + H]$^+$, 626 [M – CF_3COOH + Na]$^+$, 642 [M – CF_3COOH + K]$^+$. Found, %: C 61.85; H 8.24; N 1.87; P 4.43. $C_{35}H_{58}F_3NO_5P\cdot CF_3COOH$. Calculated, %: C 61.91; H 8.28; N 1.95; P 4.31.

***N*-[2,2-Bis(2,3,4-trihydroxyphenyl)ethyl]-*N*-[(dioctylphosphoryl)methyl]ammonium trifluoroacetate (IXc).** Yield 0.34 g (45%), mp 62–64°C. IR spectrum, ν, cm^{-1}: 3322 br (OH), 1668 s (C=O), 1597 s (C=C_{arom}), 1201 m (P=O). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 0.88 t (6H, CH_3, J = 6.8 Hz), 1.28 br.s (24H, CH_2), 1.39 m (4H, CH_2), 1.59 m (4H, C**H**$_2$$CH_2$P), 1.95 m (4H, CH_2P), 3.78 d (2H, PC**H**$_2$N, J = 6.1 Hz), 3.93 d (2H, CH_2N, J = 7.6 Hz), 5.06 t (1H, CH, J = 7.6 Hz), 6.37 d (2H, 5′-H, ^3J = 8.4 Hz), 6.51 d (2H, 6′-H, ^3J = 8.4 Hz), 7.97 s (2H, OH). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 13.0 (CH_3), 21.9–31.2 [$(CH_2)_7$P], 26.6 (CH_2P, J = 66.3 Hz), 35.1 (CH), 42.1 (PC**H**$_2$N, J = 59.0 Hz), 53.3 (NCH_2), 106.9 (C$^{5'}$), 115.2 q (CF_3, J = 291.0 Hz), 118.6 (C$^{1'}$), 125.5 (C$^{6'}$), 132.2 (C$^{3'}$), 144.5 (C$^{2'}$), 145.4 (C$^{4'}$), 159.7 q (C=O, J = 36.6 Hz). ^{31}P NMR spectrum (acetone-d_6): δ_P 51.7 ppm. Mass spectrum, *m*/*z*: 636 [M – CF_3COOH + H]$^+$, 658 [M – CF_3COOH + Na]$^+$. Found, %: C 59.05; H 7.94; N 1.86; P 4.12. $C_{35}H_{58}NO_7P\cdot CF_3COOH$. Calculated, %: C 59.28; H 7.88; N 1.87; P 4.14.

This study was performed under financial support by the Russian Foundation for Basic Research (project nos. 12-03-31 138_mol_a, 14-03-31 740mol_a, 13-03-97073-a, 14-03-00191-a).

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