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Reactions of Glycosylamines with Diphenylphosphine Oxide and Ethyl and Phenyl Phenylphosphinates

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Abstract—A novel procedure has been proposed for the synthesis of chiral α-aminophosphoryl compounds from glycosylamines and PH compounds (diphenylphosphine oxide and ethyl and phenyl phenylphosphonates) under mild conditions. The reaction is accompanied by dehydration of the carbohydrate moiety in unprotected monosaccharides to form furan ring.

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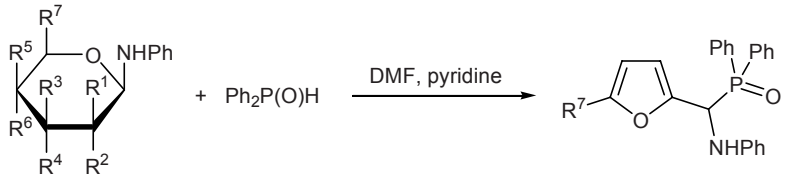
The Kabachnik–Fields reaction provides a convenient method for the synthesis of α-aminophosphoryl compounds that attract interest due to diversity of their useful properties, including broad spectrum of biological activity. Some α-aminophosphoryl derivatives were shown to act as antibacterial and antiviral agents, antibiotics, enzyme inhibitors, pesticides, and plant growth regulators [1].

Nowadays development of new procedures for the synthesis of α-aminophosphoryl compounds, specifically from naturally occurring materials such as sugars, steroids, amino acids, etc., remains an important problem. N-Glycosides occupy a specific place among carbohydrate derivatives capable of being involved in the Kabachnik–Fields reaction. They are structural fragments of biomolecules and some medicines [2]. With a view to combine *N*-glycoside and phosphoryl fragments in a single molecule we examined reactions of glycosylamines with PH-containing compounds.

In the first step of our study, diphenylphosphine oxide (**II**) [3] was brought into reactions with *N*-(β-D-pentopyranosyl)anilines **Ia**–**Id**. As a result, we obtained *N*-[(2-furyl)(diphenylphosphoryl)methyl]aniline (**III**) (Scheme 1). *N*-(β-D-Hexopyranosyl)anilines **IVa**–**IVc** reacted with compound **II** to give analogous substituted furan **V** having a hydroxymethyl group in the α-position of the furan ring. Presumably, the reaction involves ring–chain tautomeric transformation of pyranosylamines **I** and **IV** into imino forms **A** and **B** [4] which take up diphenylphosphine oxide to give adducts **C** and **D**, respectively. This step corresponds to a version of the Kabachnik–Fields reaction [5–7]. Dehydration of adducts **C** and **D** leads to stable furan structures **III** and **V** (Scheme 2). It should be emphasized that the dehydration of the carbohydrate moiety occurs under mild conditions (at a temperature of 25 to 55°C) in 3.5–4 h. The proposed mechanism is supported by experiments with *N*-(2,3 : 5,6-di-*O*-alkyli-

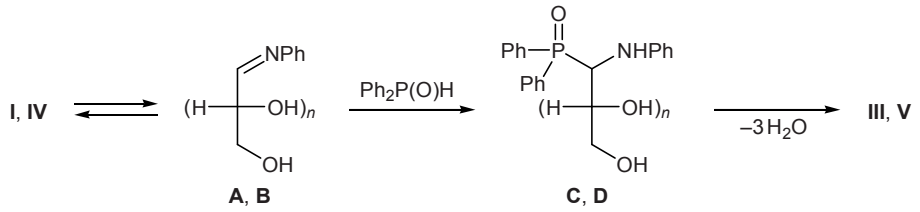
Scheme 1.



Ia–Id, **IVa–IVc** **II** **III**, **V**

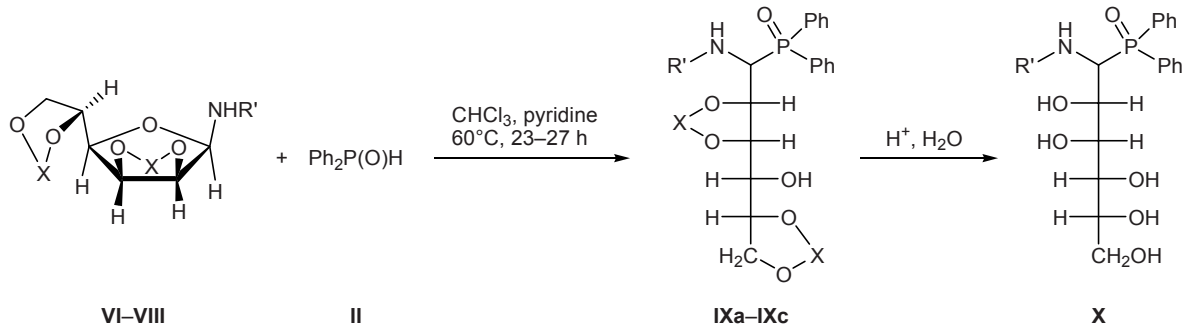
I, $R^1 = R^4 = R^5 =$H, $R^2 = R^3 = R^6 =$ OH (**a**); $R^1 = R^3 = R^5 =$ H, $R^2 = R^4 = R^6 =$ OH (**b**); $R^2 = R^3 = R^5 =$ H, $R^1 = R^4 = R^6 =$ OH (**c**); $R^2 = R^4 = R^5 =$ H, $R^1 = R^3 = R^6 =$ OH (**d**); **IV**, $R^1 = R^4 = R^5 =$ H, $R^2 = R^3 = R^6 =$ OH (**a**); $R^1 = R^4 = R^6 =$ H, $R^2 = R^3 = R^5 =$ OH (**b**); $R^2 = R^4 = R^5 =$ H, $R^1 = R^3 = R^6 =$ OH (**c**); **I**, **III**, $R^7 =$ H; **IV**, **V**, $R^7 = CH_2OH$.

Scheme 2.



A, **C**, $n = 3$; **B**, **D**, $n = 4$.

Scheme 3.

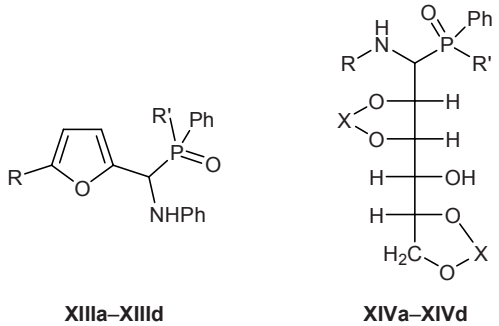


VI, **VII**, X = isopropylidene; **VIII**, X = cyclohexylidene; **VI**, **VIII**, R′ = Ph; **VII**, R′ = naphthyl.

dene-β-D-mannofuranosyl)anilines (Scheme 3). Hydrolysis of adducts **IXa**–**IXc** obtained from compounds **VI**–**VIII** and diphenylphosphine oxide (**II**) gave 1-deoxy-1-diphenylphosphoryl-1-phenylamino-D-mannite (**X**) which can be either isolated as individual substance or subjected to dehydration. The dehydration product of **X** was identical to substituted furan **V**.

The structure of the isolated compounds was confirmed by polarimetry, NMR spectroscopy, and X-ray analysis. The products obtained from D-xylose and D-ribose derivatives were identical to each other (mp 238–240°C, $[\alpha]_D^{20} = 0.0$, $c = 0.5$, DMSO) and were racemates (Fig. 1). The compounds obtained from D-arabinose and D-lyxose derivatives were individual dextrorotatory enantiomers (Fig. 2) having *S*-configuration of the chiral carbon atom (mp 248–250°C, $[\alpha]_D^{20} = +36.4°$, $c = 0.5$, DMSO). We believe that the above results are determined by the monosaccharide nature. Insofar as glycosylamines containing D-xylose or D-ribose differ from those derived from D-arabinose or D-lyxose by the position of hydroxy group on C^2, just its orientation is likely to be responsible for the observed stereochemical effect.

To develop studies in this line, we tried to extend the proposed approach to another class of PH compounds, phosphinic acid esters. Under analogous conditions, reactions of *N*-glycosides **Ia**–**Id**, **IVa**–**IVc**, and **VI**–**VIII** with readily accessible stable ethyl and phenyl phenylphosphinates **XI** and **XII** led to the formation of compounds **XIIIa**–**XIIId** and **XIVa**–**XIVd**. When the reaction was complete, the ^{31}P NMR spectra of the reaction mixtures contained three signals, two of which (δ_P 36–38 ppm) corresponded to the major products. The third minor signal (δ_P 11 ppm) indicated partial decomposition of phosphinic acid ester during the process with formation of free phenylphosphinic acid which failed to react with glycosylamines (presumably because of insufficient electron density on the phosphorus atom). The presence of two downfield signals in the ^{31}P NMR spectra is related to chirality of



XIII, R = H (**a**, **c**), $HOCH_2$ (**b**, **d**); R′ = OEt (**a**, **b**), OPh (**c**, **d**); **XIV**, X = isopropylidene (**a**, **b**, **d**), cyclohexylidene (**c**); R = Ph (**a**, **c**), 2-naphthyl (**b**, **d**); R′ = OEt (**a**, **b**), OPh (**c**, **d**).

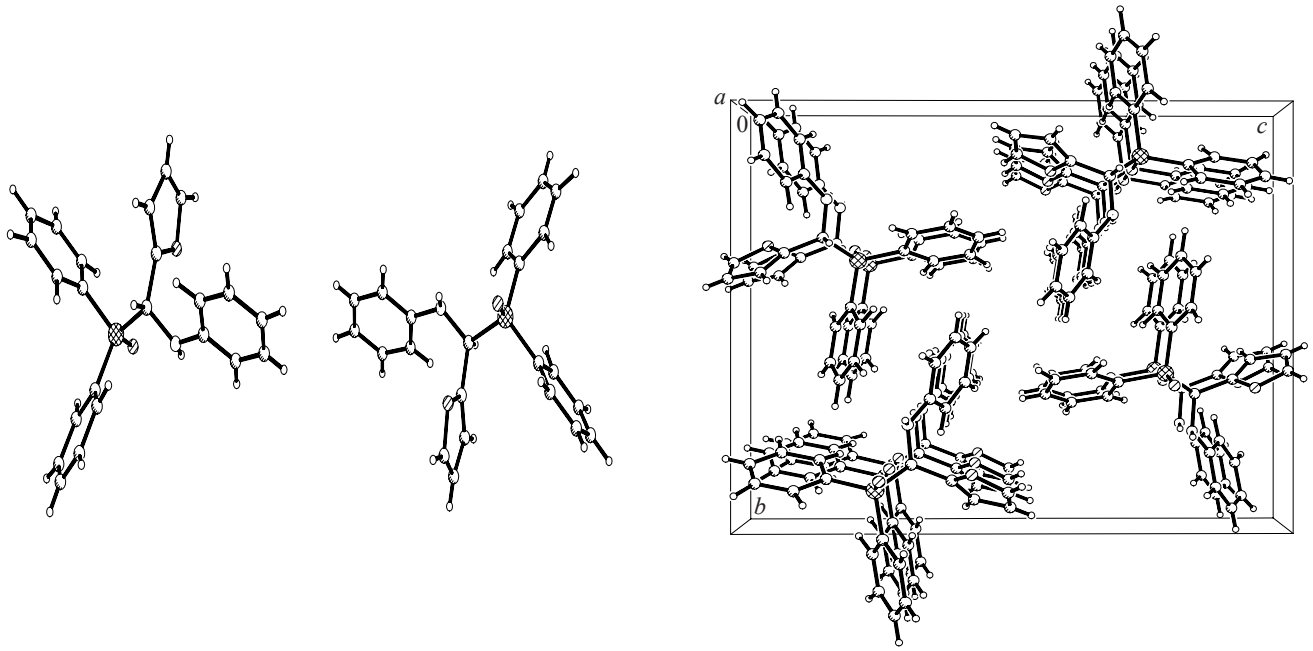


Fig. 1. Structure of the molecule and crystal packing of *N*-[(diphenylphosphoryl)(2-furyl)methyl]aniline (**III**) obtained from D-xylose or D-ribose. Different enantiomers are shown; a unit cell contains four molecules **III**.

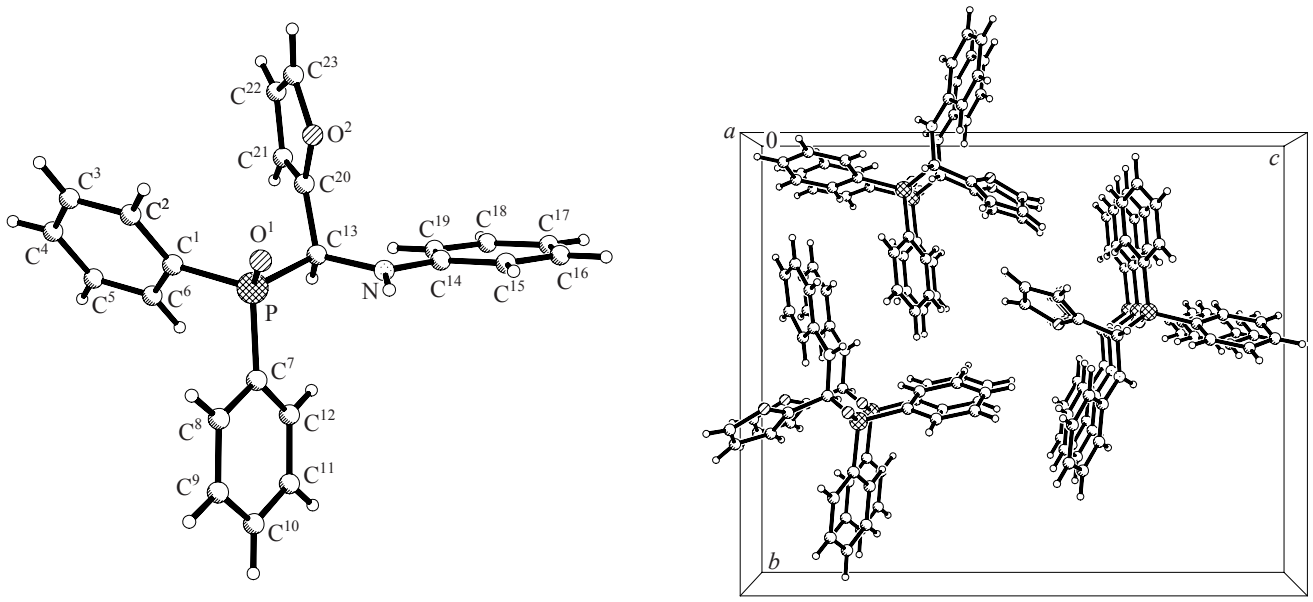


Fig. 2. Structure of the molecule and crystal packing of *N*-[(diphenylphosphoryl)(2-furyl)methyl]aniline (**III**) obtained from D-arabinose or D-lyxose. Only one stereoisomer is present; a unit cell contains three molecules **III**.

the phosphorus atom in the resulting phosphinates. The major products were characterized by similar chromatographic mobilities and were isolated as mixtures of stereoisomers by column chromatography on silica gel (benzene–dioxane, 1:3) in 30–35% yield. Their structure was confirmed by the ^{1}H, ^{13}C, and ^{31}P NMR spectra and elemental analyses. Compounds **XIIIa**–**XIIId** and **XIVa**–**XIVd** showed in the ^{31}P NMR spectra two signals in the region δ_P 36–38 ppm, and the difference in the phosphorus chemical shifts for stereoisomers was $\Delta\delta_P$ = 0.3–0.4 ppm. In the ^{1}H NMR spectra of **XIIIa**–**XIIId**, protons at the carbon atom attached to phosphorus give rise to two multiplets at δ 4.19–5.38 ppm due to the presence of geminal chiral centers (*S**,*R**), the coupling constant $^{2}J_{HP}$ being 17–18 Hz. Signals from the other protons are somewhat

broadened and are characterized by double relative intensity.

To conclude, we have developed a novel method for the synthesis of chiral α-aminophosphoryl compounds on the basis of glycosylamines and prepared a series of new phosphinates and tertiary phosphine oxides, including those containing a carbohydrate residue. The products attract interest as potential biologically active substances, as well as ligands for metal-complex catalysis. Our results extend the interdisciplinary research area implying the use of tervalent phosphorus reagents in the chemistry of carbohydrates and other natural compounds.

EXPERIMENTAL*

The ^{31}P NMR spectra of compounds **III**, **V**, and **IXa**–**IXc** were recorded on a Bruker WP-80 spectrometer at 32.4 MHz, and the ^{31}P NMR spectra of **XIIIa**–**XIIId** and **XIVa**–**XIVd** were measured on a Bruker Avance-400 instrument at 161.98 MHz; the chemical shifts were determined relative to 85% H_3PO_4 as external reference. The ^{1}H NMR spectra were recorded on a Bruker H-250 spectrometer (250 MHz) relative to tetramethylsilane as internal reference. The ^{13}C NMR spectra were obtained on a Bruker AC-200 spectrometer at 50 MHz using tetramethylsilane as internal reference. Thin-layer chromatography was performed on Silufol UV-254 plates; spots were detected by calcination. Silica gel L 40–100 μm was used for column chromatography (10 mm i.d.; benzene–dioxane, 1:3). The optical rotations were measured on a Jasco DIP-360 polarimeter. The elemental compositions were determined on a Perkin–Elmer 2400 analyzer. X-Ray analysis was performed on an Enraf–Nonius CAD 4 diffractometer (see table).

Phosphine oxides III and V (*general procedure***).** A mixture of 5 mmol of compound **Ia**–**Id** or **IVa**–**IVc** and 5 mmol of diphenylphosphine oxide (**II**) in 5 ml of DMF and 1 ml of pyridine was stirred under argon for 3.5–4 h at 25°C (**III**) or 55°C (**V**). The solvent was removed under reduced pressure, and the residue was purified by chromatography on silica gel.

***N*-[(Diphenylphosphoryl)(2-furyl)methyl]aniline (III).** Yield 40–45%, R_f 0.64. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.00 m (2H, NCHP, NH); furan fragment: 6.21 m (1H, 4-H, $^3J_{4,3}$ = 3.0 Hz), 6.30 m (1H, 3-H, $^3J_{3,4}$ = 3.0, $^4J_{HP}$ = 2.7 Hz), 7.37 m (1H, 5-H, $^4J_{5,3}$ = 1.2 Hz); aniline fragment: 6.56 t (1H, 4-H, $^3J_{4,3}$ = 7.3 Hz), 6.92 d (2H, 2-H, 6-H, $^3J_{2,3}$ = 7.3 Hz), 7.01 d.d (2H, 3-H, 5-H, $^3J_{5,4}$ = 7.0 Hz); diphenylphosphoryl fragment: 7.4–7.5 m (6H, 3-H, 4-H, 5-H), 7.80–7.98 m (4H, 2-H, 6-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 50.3 d (NCHP, $^1J_{CP}$ = 81.6 Hz); furan fragment: 109.5 d (C^3, $^3J_{CP}$ = 5.0 Hz), 110.4 (C^4), 142.4 (C^5), 149.9 (C^2); aniline fragment: 113.9 (C^2, C^6), 117.5 (C^4), 128.6 (C^3, C^5), 147.1 d (C^1, $^3J_{CP}$ = 10.9 Hz); diphenylphosphoryl fragment: 128.1–128.4 m (C^3, C^5), 130.3–133.2 m (C^1, C^4, C^2, C^6). ^{31}P NMR spectrum (DMSO-d_6): δ_P 29.1 ppm. Found, %: C 74.08, 74.06; H 5.45, 5.44; N 3.62, 3.65; P 8.52, 8.51. $C_{23}H_{20}NO_2P$. Calculated, %: C 73.99; H 5.36; N 3.75; P 8.32.

{5-[(Diphenylphosphoryl)(phenylamino)methyl]-furan-2-yl}methanol (V). Yield 38–45%, R_f 0.70, mp 179–181°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.97–6.04 m (3H, NCHP, NH, 4′-H); furan fragment: 4.11 m (2H, CH_2), 5.07 t (1H, OH, $^3J_{HH}$ =

Parameters of X-ray diffraction experiments and principal crystallographic data for compound **III**

Parameter	From **Ia** or **Ib**	From **Ic** or **Id**
Formula	$C_{23}H_{20}NO_2P$	$C_{23}H_{20}NO_2P$
M	373.37	373.37
Temperature, K	293	293
a, Å	5.777(1)	5.774(1)
b, Å	16.421(3)	16.471(3)
c, Å	20.215(4)	20.176(4)
β, deg	90.91(3)	90
V, Å^3	1917.4(6)	1918.8(6)
d_{calc}, g/cm^3	1.293	1.480
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$
N	4	4
F(000)	784	904
Scan mode	ω/2Θ	ω/2Θ
Total number of reflections	3783	2001
Number of independent reflections (R_{int})	3417 (0.0276)	2001 (0.0)
Number of refined parameters	325	245
Absorption coefficient, cm^{-1}	1.61	1.82
R_1 [$I > 2\sigma(I)$]	0.0421	0.0260
wR_2	0.1271	0.0609

* Some experiments were performed with participation of S.V. Metlitskikh.

6.0 Hz), 6.28 m (1H, 3′-H); aniline fragment: 6.57 t (1H, 4-H, $^3J_{4,3}$ = 6.4 Hz), 6.93 d (2H, 2-H, 6-H, $^3J_{2,3}$ = 7.6 Hz), 7.02 d.d (2H, 3-H, 5-H, $^3J_{5,4}$ = 7.2 Hz); diphenylphosphoryl fragment: 7.43–7.50 m (6H, 3-H, 4-H, 5-H), 7.77–8.01 m (4H, 2-H, 6-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 50.2 d (NCHP, $^1J_{CP}$ = 82.2 Hz); furan fragment: 55.3 (CH_2), 107.3 ($C^{3'}$), 109.9 d ($C^{4'}$, $^4J_{CP}$ = 5.0 Hz), 148.7 ($C^{5'}$), 154.6 ($C^{2'}$); aniline fragment: 113.7 (C^2, C^6), 117.2 (C^4), 128.6 (C^3, C^5), 146.8 d (C^1, $^3J_{CP}$ = 11.3 Hz); diphenylphosphoryl fragment: 127.8–128.5 m (C^3, C^5), 130.6–132.4 m (C^1, C^4, C^2, C^6). ^{31}P NMR spectrum (DMSO-d_6): δ_P 29.2 ppm. Found, %: C 71.78, 71.75; H 5.49, 5.51; N 3.68, 3.69; P 7.73, 7.48. $C_{24}H_{22}NO_3P$. Calculated, %: C 71.47; H 5.46; N 3.47; P 7.69.

Phosphine oxides IXa–IXc (*general procedure*). A solution of 5 mmol of compound **VI**–**VIII** and 5 mmol of phosphine oxide **II** in a mixture of 5 ml of chloroform and 3 ml of pyridine was stirred for 23–27 h at 60°C under argon. The solvent was removed under reduced pressure, and the residue was purified by chromatography on silica gel.

1-Deoxy-1-diphenylphosphoryl-2,3 : 5,6-di-*O*-isopropylidene-1-phenylamino-D-mannite (IXa). Yield 50%, oily substance, R_f 0.66. ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: carbohydrate fragment: 25.3–27.3 m (CH_3), 54.7 d (C^1, $^1J_{CP}$ = 77.8 Hz), 66.4 (C^6), 69.6 (C^4), 74.9 d (C^3, $^3J_{CP}$ = 5.4 Hz), 76.0 (C^5), 80.2 d (C^2, $^2J_{CP}$ = 8.6 Hz), 108.2 (O^2CO^3), 108.8 (O^5CO^6); aniline fragment: 112.8 (C^2, C^6), 116.5 (C^4), 128.6 (C^3, C^5), 147.3 d (C^1, $^3J_{CP}$ = 3.5 Hz); diphenylphosphoryl fragment: 127.6–128.2 m (C^3, C^5), 130.6–133.7 m (C^1, C^4, C^2, C^6). ^{31}P NMR spectrum (DMSO-d_6): δ_P 31.0 ppm. Found, %: C 67.28, 67.29; H 6.57, 6.60; N 2.54, 2.55; P 5.89, 5.92. $C_{30}H_{36}NO_6P$. Calculated, %: C 67.16; H 6.53; N 2.62; P 5.78.

2,3:5,6-Di-*O*-cyclohexylidene-1-deoxy-1-diphenylphosphoryl-1-phenylamino-D-mannite (IXb). Yield 60%, oily substance, R_f 0.85. ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: carbohydrate fragment: 21.2–24.4 and 34.2–36.1 m (CH_2), 54.2 d (C^1, $^1J_{CP}$ = 77.6 Hz), 65.7 (C^6), 69.0 (C^4), 73.4 d (C^3, $^3J_{CP}$ = 3.4 Hz), 78.9 (C^5), 79.8 d (C^2, $^2J_{CP}$ = 9.6 Hz), 108.3 (O^2CO^3), 108.6 (O^5CO^6); aniline fragment: 112.2 (C^2, C^6), 116.0 (C^4), 128.2 (C^3, C^5), 146.7 d (C^1, $^3J_{CP}$ = 3.1 Hz); diphenylphosphoryl fragment: 127.5–128.7 m (C^3, C^5), 130.4–133.5 m (C^1, C^4, C^2, C^6). ^{31}P NMR spectrum (DMSO-d_6): δ_P 30.9 ppm. Found, %: C 70.15, 70.19; H 7.25, 7.22; N 2.13, 2.12; P 5.36, 5.29. $C_{36}H_{43}NO_6P$. Calculated, %: C 70.02; H 7.13; N 2.27; P 5.02.

1-Deoxy-1-diphenylphosphoryl-2,3 : 5,6-di-*O*-isopropylidene-1-(2-naphthylamino)-D-mannite (IXc). Yield 53%, oily substance, R_f 0.73. ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: carbohydrate fragment: 25.8–27.6 m (CH_3), 55.4 d (C^1, $^1J_{CP}$ = 77.5 Hz), 66.2 (C^6), 69.4 (C^4), 75.1 d (C^3, $^3J_{CP}$ = 5.3 Hz), 76.1 (C^5), 80.0 d (C^2, $^2J_{CP}$ = 8.4 Hz), 108.4 (O^2CO^3), 108.9 (O^5CO^6); naphthalene fragment: 105.6 (C^1), 118.8 (C^3), 122.1 (C^6), 125.8 (C^8), 126.2 (C^7), 127.3 (C^5), 127.5 (C^{10}), 128.8 (C^4), 134.6 (C^9), 145.0 d (C^2, $^3J_{CP}$ = 9.8 Hz); diphenylphosphoryl fragment: 128.3–128.6 m (C^3, C^5), 130.4–133.1 m (C^1, C^4, C^2, C^6). ^{31}P NMR spectrum (DMSO-d_6): δ_P 33.7 ppm. Found, %: C 69.70, 69.67; H 6.57, 6.54; N 2.14, 2.19; P 5.45, 5.51. $C_{34}H_{38}NO_6P$. Calculated, %: C 69.51; H 6.47; N 2.39; P 5.28.

Phosphinates XIIIa–XIIId (*general procedure*). A solution of 1.2 mmol of compound **Ia**–**Id** or **IVa**–**IVc** and 1.2 mmol of ethyl or phenyl phenylphosphinate **XI** or **XII** in 2.5 ml of DMF was stirred for 3.5–4 h at 65°C under argon. The solvent was removed under reduced pressure, the residue was dissolved in 15 ml of ethanol, 5 g of activated charcoal was added, the mixture was heated under reflux until clarification and filtered, the filtrate was concentrated, and the residue was purified by chromatography on silica gel.

Ethyl [(2-furyl)(phenylamino)methyl]phenylphosphinate (XIIIa). Yield 0.13 g (31%), oily substance, R_f 0.85. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.21 [5.32]** m (2H, NCHP, $^2J_{HP}$ = 17.17 Hz), 5.95 br.s (2H, NH); furan fragment: 6.28 m (2H, 4-H, $^3J_{4,3}$ = 3.05 Hz), 6.39 m (2H, 3-H, $^3J_{3,4}$ = 3.05, $^4J_{HH}$ = 2.7 Hz), 7.44 m (2H, C^5); aniline fragment: 6.74 t (2H, 4-H, $^3J_{4,5}$ = 7.3 Hz), 6.96 d (4H, 2-H, 6-H, $^3J_{2,3}$ = 7.31 Hz), 7.02 d.d (4H, 3-H, 5-H, $^3J_{3,4}$ = 7.0 Hz); phosphoryl fragment: 1.21 m (6H, C**H**$_3$CH$_2$), 4.14 m (8H, C**H**$_2$OP, $^3J_{HP}$ = 8.04 Hz), 7.48–7.62 m (6H, 3-H, 4-H, 5-H), 7.69–7.8 m (4H, 2-H, 6-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 49.9 d (NCHP, $^1J_{CP}$ = 80.8 Hz); furan fragment: 107.8 d (C^3, $^3J_{CP}$ = 5.2 Hz), 109.7 (C^4), 142.5 (C^5), 154.8 (C^2); aniline fragment: 113.4 (C^2, C^6), 117.2 (C^4), 129.4 (C^3, C^5), 146.9 d (C^1, $^3J_{CP}$ = 10.5 Hz); phosphoryl fragment: 16.29 (**C**H$_3$CH$_2$), 66.38 (CH_2O), 128.5 m (C^3, C^5), 130.5–132.3 m (C^1, C^4, C^2, C^6). ^{31}P NMR spectrum (DMSO-d_6), δ_P, ppm: 35.76, 36.04. Found, %: C 66.89, 66.9; H 5.9, 5.92;

** Hereinafter, the chemical shifts for the second enantiomer are given in brackets.

N 4.02, 4.04; P 9.25, 9.28. $C_{19}H_{20}NPO_3$. Calculated, %: C 66.86; H 5.86; N 4.11; P 9.09.

Ethyl [(5-hydroxymethylfuran-2-yl)(phenylamino)methyl]phenylphosphinate (XIIIb). Yield 0.13 g (29%), oily substance, R_f 0.75. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.19 [5.26] m (2H, NCHP, $^2J_{HP}$ = 17.91 Hz), 5.92 br.s (2H, NH); furan fragment: 4.19 m (4H, 5-CH_2), 6.09 t (2H, OH, $^3J_{HH}$ = 2.92 Hz), 6.24 m (2H, 4-H, $^3J_{4,3}$ = 2.75 Hz), 6.41 m (2H, 3-H, $^3J_{3,4}$ = 2.75 Hz); aniline fragment: 6.54 t (2H, 4-H, $^3J_{4,3}$ = 6.4 Hz), 6.73 d (4H, 2-H, 6-H, $^3J_{2,3}$ = 7.6 Hz), 7.03 d.d (4H, 3-H, 5-H, $^3J_{3,4}$ = 7.2 Hz); phosphoryl fragment: 1.23 m (6H, C**H**$_3$CH$_2$), 4.04 m (4H, CH_2OP, $^3J_{HP}$ = 8.04 Hz), 7.4–7.6 m (6H, 3-H, 4-H, 5-H), 7.7–7.85 m (4H, 2-H, 6-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 55.6 d (NCHP, $^1J_{CP}$ = 79.8 Hz); furan fragment: 61.12 (CH_2OH), 107.9 d (C^3, $^3J_{CP}$ = 5.0 Hz), 109.8 (C^4), 146.2 (C^5), 155.1 (C^2); aniline fragment: 113.6 (C^2, C^6), 117.3 (C^4), 128.6 (C^3, C^5), 148.8 d (C^1, $^3J_{CP}$ = 10.9 Hz); phosphoryl fragment: 16.28 (**C**H$_3$CH$_2$), 66.36 (CH_2OP), 128.3 m (C^3, C^5), 130.4–133.0 m (C^1, C^4, C^2, C^6). ^{31}P NMR spectrum (DMSO-d_6), δ_P, ppm: 35.89, 36.17. Found, %: C 64.74, 64.76; H 5.98, 5.96; N 3.73, 3.70; P 8.46, 8.48. $C_{20}H_{22}NO_4P$. Calculated, %: C 64.69; H 5.93; N 3.77; P 8.36.

Phenyl [(2-furyl)(phenylamino)methyl]phenylphosphinate (XIIIc). Yield 0.126 g (27%), oily substance, R_f 0.86. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.47 [5.55] m (2H, NCHP, $^2J_{HP}$ = 17.37 Hz), 5.65 br.s (2H, NH); furan fragment: 6.28 m (2H, 4-H, $^3J_{4,3}$ = 3.04 Hz), 6.39 m (2H, 3-H, $^3J_{3,4}$ = 3.04, $^4J_{HH}$ = 2.75 Hz), 7.2 m (2H, 5-H); aniline fragment: 6.6 t (2H, 4-H, $^3J_{4,3}$ = 7.32 Hz), 6.85 d (4H, 2-H, 6-H, $^3J_{2,3}$ = 7.3 Hz), 7.08 d.d (4H, 3-H, 5-H, $^3J_{3,4}$ = 7.1 Hz); phosphoryl fragment: 7.5–7.67 m (12H, 3-H, 4-H, 5-H), 7.87–8.00 m (8H, 2-H, 6-H). ^{31}P NMR spectrum (DMSO-d_6), δ_P, ppm: 36.30, 36.65. Found, %: C 70.98, 71.00; H 5.15, 5.17; N 3.56, 3.57; P 7.86, 7.89. $C_{23}H_{20}NO_3P$. Calculated, %: C 70.95; H 5.14; N 3.60; P 7.97.

Phenyl [(5-hydroxymethylfuran-2-yl)(phenylamino)methyl]phenylphosphinate (XIIId). Yield 0.131 g (26%), oily substance, R_f 0.68. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.41 [5.48] m (2H, NCHP, $^2J_{HP}$ = 17.48 Hz), 5.78 br.s (2H, NH); furan fragment: 4.10 m (4H, C**H**$_2$OH), 6.10 t (2H, OH, $^3J_{HH}$ = 3.94 Hz), 6.22 m (2H, 4-H, $^3J_{4,3}$ = 2.74 Hz), 6.32 m (2H, 3-H, $^3J_{3,4}$ = 2.74 Hz); aniline fragment: 6.45 t (2H, 4-H, $^3J_{4,3}$ = 6.4 Hz), 6.82 d (4H, 2-H, 6-H, $^3J_{2,3}$ = 7.6 Hz), 7.07 d.d (4H, 3-H, 5-H, $^3J_{3,4}$ = 7.2 Hz); phosphoryl fragment: 7.51–7.67 m (12H, 3-H, 4-H, 5-H), 7.89–8.03 m (8H, 2-H, 6-H). ^{31}P NMR spectrum (DMSO-d_6), δ_P, ppm: 36.19, 36.43. Found, %: C 68.80, 68.77; H 5.28, 5.27; N 3.30, 3.29; P 7.32, 7.36. $C_{24}H_{22}NO_4P$. Calculated, %: C 68.74; H 5.25; N 3.34; P 7.40.

Phosphinates XIVa–XIVd (*general procedure*). A solution of 1.2 mmol of glycosylamine **VI–VIII** and 1.2 mmol of ethyl or phenyl phenylphosphinate **XI** or **XII** in a mixture of 2 ml of chloroform and 0.5 ml of pyridine was stirred for 5–6 h at 60°C under argon. The solvent was removed, and the residue was purified by chromatography on silica gel.

1-Deoxy-1-[ethoxy(phenyl)phosphoryl]-2,3:5,6-di-*O*-isopropylidene-1-phenylamino-D-mannite (XIVa). Yield 0.18 g (30%), oily substance, R_f 0.8. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: carbohydrate fragment: 1.55 m (12H, CH_3), 3.84 m (1H, 4-H, $^3J_{4,5}$ = 6.26, $^3J_{H,OH}$ = 4.6 Hz), 3.98–4.02 m (2H, 6-H, 6′-H, $^3J_{6,5}$ = 6.21, $^3J_{6',5}$ = 6.58 Hz), 4.3 m (1H, 5-H, $^3J_{5,6}$ = 6.21, $^3J_{5,6'}$ = 6.58, $^3J_{5,4}$ = 6.26 Hz), 4.4 m (1H, 3-H, $^3J_{3,2}$ = 3.29 Hz), 4.65 m (1H, 2-H, $^3J_{2,1}$ = 5.8, $^3J_{2,3}$ = 3.29 Hz), 5.13 m (1H, 1-H, $^3J_{1,2}$ = 5.8, $^2J_{HP}$ = 12.50 Hz); aniline fragment: 5.60 br.s (1H, NH), 6.4–6.6 t (1H, 4-H, $^3J_{4,3}$ = 6.4 Hz), 6.76 d (2H, 2-H, 6-H, $^3J_{2,3}$ = 7.6 Hz), 7.04 d.d (2H, 3-H, 5-H, $^3J_{3,4}$ = 7.2 Hz); phosphoryl fragment: 1.24 m (3H, C**H**$_3$CH$_2$), 3.9 m (4H, CH_2OP, $^3J_{HP}$ = 9.04 Hz), 7.46 m (3H, 3-H, 4-H, 5-H), 7.75 m (2H, 2-H, 6-H). ^{31}P NMR spectrum (DMSO-d_6), δ_P, ppm: 37.93, 38.43. Found, %: C 61.80, 61.82; H 7.17, 7.18; N 2.74, 2.75; P 6.30, 6.26. $C_{26}H_{36}NO_7P$. Calculated, %: C 61.78; H 7.13; N 2.77; P 6.14.

1-Deoxy-1-[ethoxy(phenyl)phosphoryl]-2,3:5,6-di-*O*-isopropylidene-1-(2-naphthylamino)-D-mannite (XIVb). Yield 0.21 g (32%), oily substance, R_f 0.88. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: carbohydrate fragment: 1.5 m (12H, CH_3), 3.89 m (1H, 4-H, $^3J_{4,5}$ = 6.01, $^3J_{H,OH}$ = 4.6 Hz), 3.98–4.01 m (2H, 6-H, 6′-H, $^3J_{6,5}$ = 6.12, $^3J_{6',5}$ = 6.15 Hz), 4.35 m (1H, 5-H, $^3J_{5,4}$ = 6.01, $^3J_{5,6}$ = 6.12, $^3J_{5,6'}$ = 6.15 Hz), 4.43 m (1H, 3-H, $^3J_{3,2}$ = 3.29 Hz), 4.62 m (1H, 2-H, $^3J_{2,1}$ = 5.88, $^3J_{2,3}$ = 3.29 Hz), 5.13 m (1H, 1-H, $^3J_{1,2}$ = 5.88, $^2J_{HP}$ = 12.50 Hz); naphthalene fragment: 6.43 br.s (1H, NH), 6.8 m (2H, 1-H, 3-H), 7.00 m (1H, 6-H), 7.1 m (1H, 7-H), 7.3 m (3H, 4-H, 5-H, 8-H); phosphoryl fragment: 1.29 m (3H, C**H**$_3$CH$_2$), 4.06 m (4H, CH_2OP, $^3J_{HP}$ = 9.34 Hz), 7.5–7.7 m (3H, 3-H, 4-H, 5-H), 7.77–7.95 m (2H, 2-H, 6-H). ^{31}P NMR spectrum (DMSO-d_6), δ_P,

ppm: 37.87, 38.48. Found, %: C 64.90, 64.89; H 6.86, 6.88; N 2.50, 2.48; P 5.72, 5.69. $C_{30}H_{38}NO_7P$. Calculated, %: C 64.86; H 6.85; N 2.52; P 5.58.

2,3:5,6-Di-*O*-cyclohexylidene-1-deoxy-1-[phenoxy(phenyl)phosphoryl]-1-phenylamino-D-mannite (XIVc). Yield 0.23 g (30%), oily substance, R_f 0.85. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: carbohydrate fragment: 1.15–1.53 m (20H, CH_2), 3.83 m (1H, 4-H, $^3J_{4,5}$ = 5.5 Hz), 3.98 m (2H, 6-H, 6′-H, $^3J_{6,5}$ = 8.4, $^3J_{6',5}$ = 8.6 Hz), 4.24 m (1H, 5-H, $^3J_{5,4}$ = 5.5, $^3J_{5,6}$ = 8.4, $^3J_{5,6'}$ = 8.6 Hz), 4.45 m (1H, 3-H, $^3J_{3,2}$ = 3.29 Hz), 4.73 m (1H, 2-H, $^3J_{2,1}$ = 5.85, $^3J_{2,3}$ = 3.29 Hz), 5.15 m (1H, 1-H, $^3J_{1,2}$ = 5.85, $^2J_{HP}$ = 12.50 Hz); aniline fragment: 5.5 br.s (1H, NH), 6.5 t (1H, 4-H, $^3J_{4,3}$ = 6.4 Hz), 6.86 d (2H, 2-H, 6-H, $^3J_{2,3}$ = 7.6 Hz), 7.11 d.d (2H, 3-H, 5-H, $^3J_{3,4}$ = 7.2 Hz); phosphoryl fragment: 7.5–7.6 m (6H, 3-H, 4-H, 5-H), 7.77 m (4H, 2-H, 6-H). ^{31}P NMR spectrum (DMSO-d_6), δ_P, ppm: 38.85, 39.04. Found, %: C 68.30, 68.28; H 6.97, 6.98; N 2.12, 2.15; P 5.02, 5.04. $C_{35}H_{44}NO_7P$. Calculated, %: C 68.25; H 6.95; N 2.21; P 4.90.

1-Deoxy-2,3:5,6-di-*O*-isopropylidene-1-[phenoxy(phenyl)phosphoryl]-1-(2-naphthylamino)-D-mannite (XIVd). Yield 0.24 g (33%), oily substance, R_f 0.84. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: carbohydrate fragment: 1.25–1.35 m (12H, CH_3), 3.84 m (1H, 4-H, $^3J_{4,5}$ = 6.16, $^3J_{H,OH}$ = 4.76 Hz), 3.98–4.02 m (2H, 6-H, 6′-H, $^3J_{6,5}$ = 6.21, $^3J_{6',5}$ = 6.58 Hz), 4.25 m (1H, 5-H, $^3J_{5,4}$ = 6.16, $^3J_{5,6'}$ = 6.21, $^3J_{5,6'}$ = 6.58 Hz), 4.46 m (1H, 3-H, $^3J_{3,2}$ = 3.29 Hz), 4.72 m (1H, 2-H, $^3J_{2,1}$ = 5.85, $^3J_{2,3}$ = 3.29 Hz), 5.13 m (1H, 1-H, $^3J_{1,2}$ = 5.85, $^2J_{HP}$ = 12.50 Hz); naphthalene fragment: 6.48 br.s (1H, NH), 6.74 m (2H, 1-H, 3-H), 7.15 m (1H, 6-H), 7.2 m (1H, 7-H), 7.3 m (3H, 4-H, 5-H, 8-H); phosphoryl fragment: 7.53–7.65 m (6H, 3-H, 4-H, 5-H), 7.95 m (4H, 2-H, 6-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: carbohydrate fragment: 25.3–26.6 m (CH_3), 55.4 d (C^1, $^1J_{CP}$ = 77.5 Hz), 65.9 (C^6), 73.2 (C^4), 79.5 d (C^3, $^3J_{CP}$ = 5.3 Hz), 85.5 (C^5), 100.5 d (C^2, $^2J_{CP}$ = 8.4 Hz), 108.4 (O^2CO^3), 108.9 (O^5CO^6); naphthalene fragment: 155.3 (C^1), 118.8 (C^3), 122.1 (C^6), 125.8 (C^8), 126.2 (C^7), 127.3 (C^5), 127.5 (C^{10}), 129.4 (C^4), 134.6 (C^9), 147.6 (C^2); phosphoryl fragment: 128.3–128.6 m (C^3, C^5), 130.4–133.1 m (C^1, C^4, C^2, C^6). ^{31}P NMR spectrum (DMSO-d_6), δ_P, ppm: 37.09, 37.75. Found, %: C 67.72, 67.71; H 6.33, 6.34; N 2.30, 2.29; P 5.23, 5.26. $C_{34}H_{38}NO_7P$. Calculated, %: C 67.67; H 6.30; N 2.32; P 5.14.

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