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Synthetic Approaches to Phosphasugars (2-oxo-1,2-oxaphosphacyclanes) Using the Anomeric Alkoxyl Radical β-Fragmentation Reaction as the Key Step

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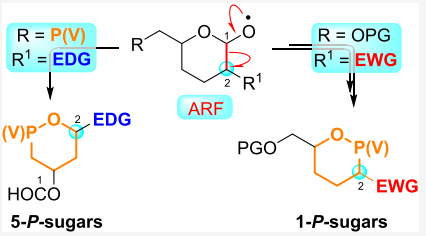
ABSTRACT: The anomeric alkoxyl radical β-fragmentation (ARF) of carbohydrates possessing an electron-withdrawing group (EWG) at C2, promoted by $PhI(OAc)_2/I_2$, gives rise to an acyclic iodide through which a pentavalent atom of phosphorus can be introduced via the Arbuzov reaction. After selective hydrolysis and subsequent cyclization, the phosphonate or phosphinate intermediates can be converted into 2-deoxy-1-phosphahexopyranose and 2-deoxy-1-phosphapentopyranose sugars. The ARF of carbohydrates with an electron-donor group (EDG) at C2 proceeds by a radical-polar crossover mechanism, and the cyclization occurs by nucleophilic attack of a conveniently positioned phosphonate or phosphinate group to the transient oxocarbenium ion. This alternative methodology leads to 5-phosphasugars with a 4-deoxy-5-phosphapentopyranose framework. The structure and conformation of the 2-oxo-1,2-oxaphosphinane and 2-oxo-1,2-oxaphospholane ring systems in different carbohydrate models have been studied by NMR and X-ray crystallography.



INTRODUCTION

1-Phosphapyranosyl and 1-phosphafuranosyl carbohydrates possessing a 2-oxo-1,2-oxaphosphacyclane skeleton have attracted considerable attention from synthetic chemists due to their unusual non-natural structures and great diversity of biological activities.[1] Cyclic phosphonate and phosphinate esters with a six-membered 2-oxo-1,2-oxaphosphinane ring system, also known as phostones and phostines, respectively, have been prepared almost exclusively by acid- or base-catalyzed Pudovik−Abramov addition of the phosphorus atom to the sugar carbonyl.[2] Originally reported by Thiem et al.[3] on a D-mannofuranose derivative, this methodology has been extended to other sugars giving always C1−P expanded 1,2-oxaphosphinane rings with respect to the original sugar.[4] Generally, the reaction occurs with little stereoselectivity on the adjacent phosphorus and carbon centers, and a mixture of the four possible isomers is formed. Nevertheless, asymmetric Abramov hydrophosphonylation enables optimization of the synthesis of phostones for the formation of the manno-isomers.[4f] The total synthesis of phostones using ring-closing metathesis has also been reported.[5]

What has been less well documented, however, is the preparation of 1-phosphafuranosyl carbohydrates. Cyclic phosphonates and phosphinates with a five-membered 2-oxo-1,2-oxaphospholane ring have been synthesized by the analogous unselective Abramov addition to the aldehyde in four-carbon-atom acyclic sugar derivatives.[6] The total synthesis of racemic cyclic phosphonate analogs of 2-deoxy-ribose and 2-deoxy-xylose has also been accomplished.[7] Some of these 2-oxo-1,2-oxaphosphacyclanes of a carbohydrates origin have been shown to exhibit biological activities as anticancer[8] and enzyme inhibitors.[9]

In previous papers, we have studied that the anomeric alkoxyl radical (i.e., **II**, Scheme 1) β-fragmentation (ARF) of sugars initiated under oxidative[10] or reductive[11] conditions. We have shown that with the system (diacetoxyiodo)benzene (DIB)/I_2, the reaction mechanism is strongly dependent on the polarity of the C2 substituent.[12] With an electron-withdrawing group (EWG), the C2 radical initially formed is trapped by the iodine atoms in the medium to give an open-chain iodide with one carbon less than the original carbohydrate (i.e., **III**). Notwithstanding, if the C2 substituent is an oxygen-containing electron-donor group (EDG), the intermediate radical is rapidly oxidized to an oxocarbenium ion by a radical-polar crossover mechanism,[13] which may subsequently react inter- or intramolecularly with nucleophiles (i.e., **VI**).[14]

This unique behavior of the C2 radical during the ARF reaction motivated us to investigate the use of this dual

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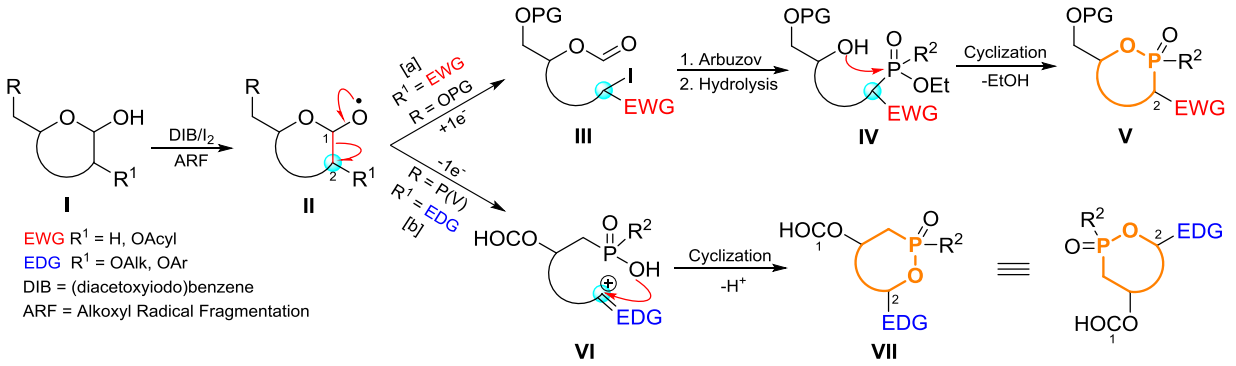
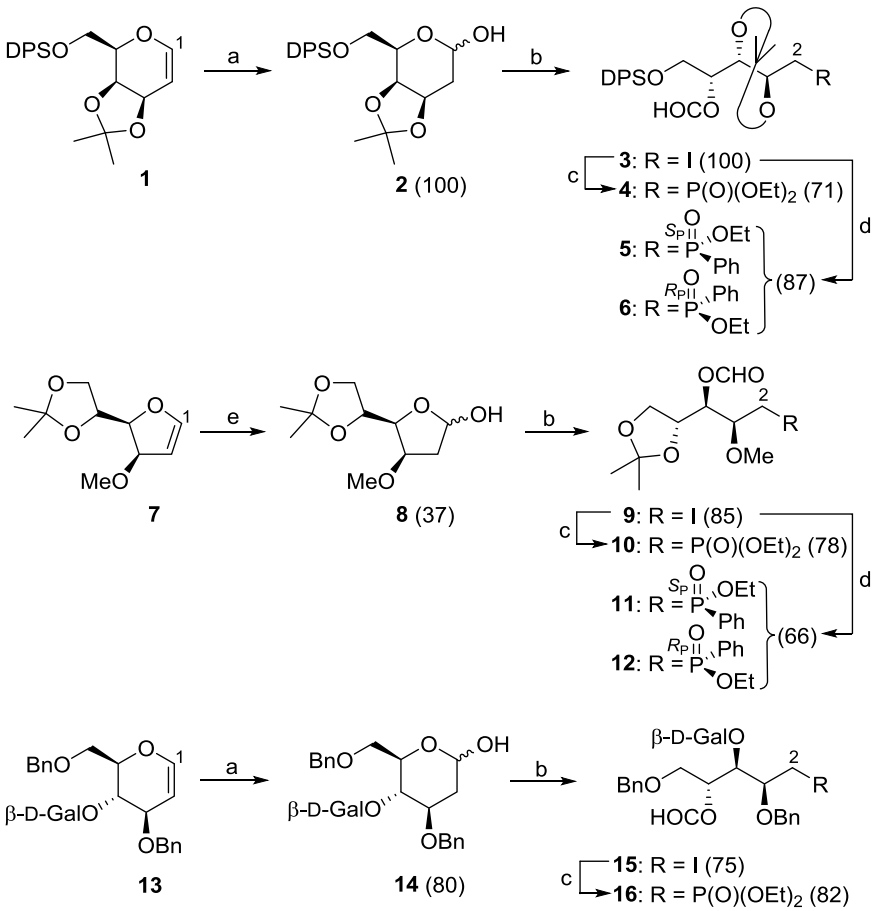
Scheme 1. Approaches for the Synthesis of Phosphasugars



Scheme 2. Synthesis of Models for the Preparation of 1-Phosphasugars[a]



[a]Reagents and conditions: (a) $Ph_3P{\cdot}HBr$, tetrahydrofuran (THF), H_2O, 2−24 h; (b) $PhI(OAc)_2/I_2$, CH_2Cl_2, room temperature (rt), 1−2 h; (c) $(EtO)_3P$, Δ, 3−6 h; (d) $(EtO)_2PPh$, 160 °C, 6 h; (e) (i) $Hg(OAc)_2$, THF, H_2O, rt, 1 h, (ii) KI, H_2O, 0 °C, 0.5 h, (iii) $NaBH_4$, H_2O, 0 °C, 1.5 h. For brevity, β-D-Gal refers to the perbencylated moiety of galactose.

methodology for the preparation of two completely different 2-oxo-1,2-oxaphosphacyclane ring systems.

In the first method (path a), the synthesis starts with a 2-deoxy-sugar (**I**, R^1 = H) and the phosphorus is introduced in the final steps of the synthesis by the Michaelis−Arbuzov reaction of the iodide generated by the ARF reaction (**III**).[15] The obtained phosphinates or phosphonates after hydrolysis of the formyl group (**IV**, R^2 = Aryl, OAlkyl) can be conveniently cyclized to 2-oxo-1,2-oxaphosphinanes (**V**, R^2 = Aryl, OAlkyl). The final result of this method is the formation of 1-phosphasugars by net substitution of the anomeric carbon by an atom of pentavalent phosphorus, maintaining the ring size and the stereochemistry of the original 2-deoxy-sugar.[16]

The second approach (path b) requires the placement of an EDG at C2 (**I**, R^1 = OAlkyl), and phosphorus is now introduced at earlier steps of the synthesis, before the ARF reaction. As can be seen, the same four steps of the previous methodology are now introduced in a different order: Arbuzov−hydrolysis−ARF−cyclization. The strategically located monophosphonate ester (**VI**, R^2 = OAlkyl) or phosphinic acid (**VI**, R^2 = Aryl) is cyclized by a tandem ARF-nucleophilic addition on the intermediate oxocarbenium

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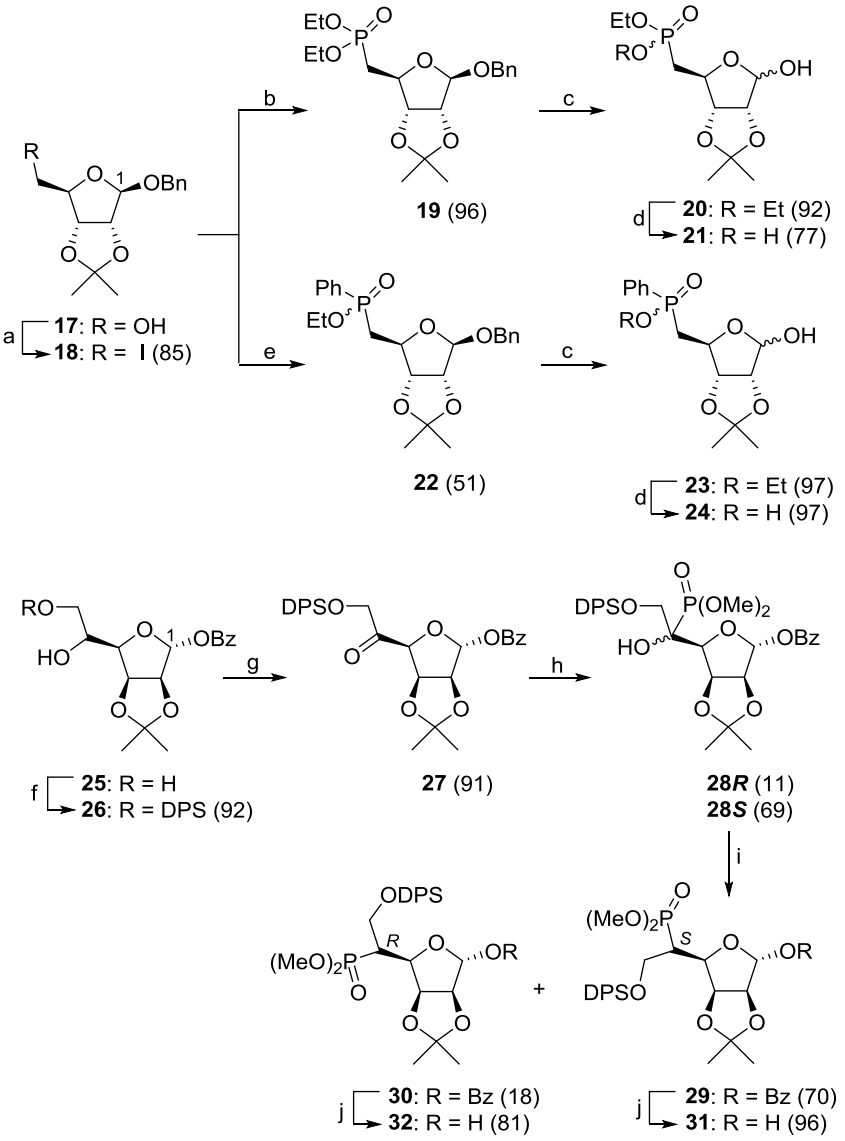
Scheme 3. Synthesis of Models for the Preparation of 5-Phosphasugars[a]



[a]Reagents and conditions: (a) I_2, PPh_3, imidazole, PhH, Δ, 0.5 h; (b) $(EtO)_3P$, Δ, 28 h; (c) H_2, Pd/C 10%, EtOAc, 2.5−20 h; (d) NaOH, EtOH, rt, 42−48 h; (e) $(EtO)_2PPh$, 160 °C, 28 h; (f) TBDPSiCl, imidazole, 4-dimethylaminopyridine (DMAP), dimethylformamide (DMF), rt, 2 h; (g) pyridinium chlorochromate (PCC), MS 3 Å, CH_2Cl_2, rt, 9 h; (h) $(MeO)_2P(O)H$, DBU, 0 °C, 0.5 h; (i) (i) $MeO(CO)_2Cl$, DMAP, MeCN, 0 °C, 1 h, (ii) Bu_3SnH, AIBN, $PhCH_3$, Δ, 2 h; (j) NaOMe, MeOH, rt, 2 h.

ion. In the new 2-oxo-1,2-oxaphosphinane (**VII**, R^2 = Aryl, OAlkyl) formed, the ether bridge is now linked to C2 and the ring has been expanded in relation to the original sugar. This structure can actually be considered to be a 4-deoxy-5-phosphapyranose sugar.

RESULTS AND DISCUSSION

Preparation of Carbohydrate Models. Intermediates primary alkyl iodides **3**, **9**, and **15** were prepared from the corresponding 2-deoxy-sugars **2**, **8**, and **14** via anomeric alkoxyl radical fragmentation with DIB and iodine in good to excellent yield (Scheme 2). The 2-deoxy-sugars **2** and **14** were in turn synthesized using a modification of the procedure developed by Mioskowsky and Falck[17] by catalytic hydration of glycals **1** and **13** employing triphenylphosphine hydrobromide and water as nucleophile. This reaction failed in the case of 2-deoxy-pent-1-enitol **7**, and an oxymercuration-demercuration protocol[18] with the glycal **7** was utilized instead (Scheme 2). The required phosphonates **4**, **10**, and **16** and phosphinates **5**, **6**, **11**, and **12** were prepared by the Michaelis−Arbuzov reaction: by heating the corresponding primary iodides with triethyl phosphate and diethyl phenylphosphonite, respectively.

Although the high temperature required was feared to be a problem with these sensitive substrates, the reaction proceeded efficiently.[19] The pairs of phosphorus-centered diastereomers of phenylphosphinates **5**, **6** and **11**, **12** could be separated by high-performance liquid chromatography (HPLC), although the absolute stereochemistry was more conveniently determined at later stages after the cyclization step (vide infra).

The preparation of models **21**, **24**, **31**, and **32** for the synthesis of 1,2-oxaphosphinanes using the second methodology (route b, Scheme 1) is described in Scheme 3. To access the 5-phosphonate **19** and 5-phosphinate **22**, benzyl 2,3-*O*-

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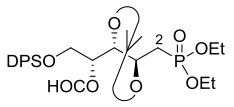
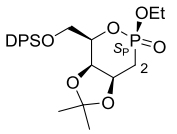
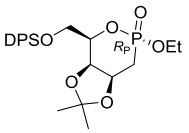
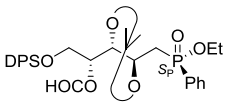
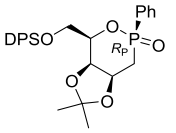
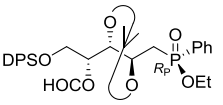
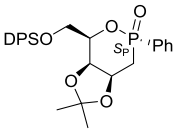
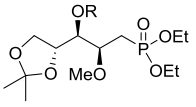
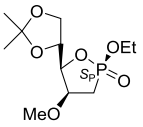
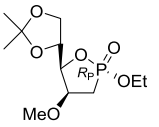
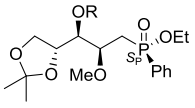
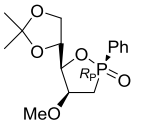
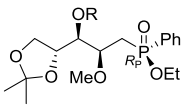
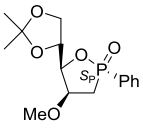
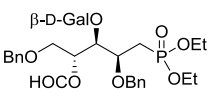
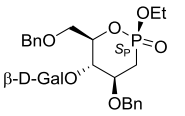
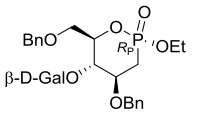
Table 1. Synthesis of 1-Phosphasugars

entry	substrate	time (h)	products (yield)	
1	 **4**[a]	102	 **36** (23)	 **37** (67)
2	 **5**[a]	24	 **38** (69)	
3	 **6**[a]	24	 **39** (75)	
4	 a → **10**: R = CHO; **33**: R = H[b]	86.5	 **40** (9)	 **41** (52)
5	 a → **11**: R = CHO; **34**: R = H[b]	94	 **42** (92)	
6	 a → **12**: R = CHO; **35**: R = H[b]	94	 **43** (69)	
7	 **16**[a,c]	27	 **44** (20)	 **45** (42)

[a]Reagents and conditions per mmol of substrate: NaOEt/EtOH (0.01 M, 0.09 mmol), rt. [b]Pyridinium *p*-toluenesulfonate (PPTS) (2.0 mmol), MS 4 Å, $CHCl_3$, reflux. [c]For brevity, β-D-Gal refers to the perbencylated moiety of galactose.

isopropylidene-β-D-ribofuranoside (**17**) was converted into the 5-iodo derivative **18** in 85% yield by treatment with triphenylphosphine in the presence of iodine and imidazole. Iodide **18** was subsequently submitted to Michaelis–Arbuzov conditions, as described above, to afford 5-phosphonate **19** and 5-phosphinate **22** derivatives, that were then debenzylated by catalytic hydrogenolysis in the presence of Pd/C 10% under 1 atm of H_2 to deprotect the anomeric alcohols to give **20** and **23**, respectively. Selective hydrolysis of the phosphonate diester **20** and the phosphinate ester **23** was performed using sodium hydroxide in ethanol to furnish the required monoester **21** and phosphinic acid derivative **24**, respectively.

Finally, the introduction of the 5-dimethoxyphosphoryl group in a mannofuranose skeleton was accomplished through a methodology developed by Hanaya et al.,[20] which essentially consists of an Abramov addition to a 5-ulose carbohydrate (Scheme 3). The sequence was initiated by the selective protection of 1-*O*-benzoyl-*O*-isopropylidene-α-D-mannofuranose (**25**) with ^{t}BuPh$_2$SiCl to give **26**. The 5-ulose **27** was efficiently obtained by the oxidation of the secondary alcohol with PCC, and the addition of dimethyl phosphite to the carbonyl group in the presence of DBU afforded a mixture of α-hydroxyphosphonate esters **28*R*** and **28*S***. Both isomers can be separated by chromatography, but since the next step is the deoxygenation of the tertiary 5-hydroxyl group, the determination of 5-stereochemistry at **28** was deemed to be unnecessary. Nevertheless, the stereochemistry has been

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tentatively assigned in analogy with that observed in a similar case.[20]

The deoxygenation was carried out by the Dolan and MacMillan protocol;[21] the 5-*O*-methyl oxalyl derivative prepared by methyl oxalyl chloride in the presence of DMAP was then reduced with the *n*-Bu_3SnH/AIBN system to give a mixture of **29** and **30** (88%, 80:20). The C-5 stereochemistry was also more easily accomplished in the next step after the cyclization. Debenzoylation with NaOMe in MeOH afforded models **31** and **32** with the free anomeric alcohol prepared for the ARF reaction.

Synthesis of 1-Phosphasugars. Open-chain diethoxyphosphoryl intermediate **4** cyclized by a base-catalyzed intramolecular transesterification process furnished S_P and R_P diastereomeric mixtures of 1-phospha-1-oxo-D-*lyxo*-hexopyranose derivatives **36** and **37** (Table 1, entry 1). The sensitive δ-formate ester was hydrolyzed rapidly under the reaction conditions. The R_P-isomer **37** in which the ethyl group is disposed at the less sterically congested α-side of the ring is the major component. Nuclear over-Hauser effect spectroscopy (NOESY) experiments were used for the assignment of the H2α and H2β protons and the relative configuration of the phosphorus chiral center [see Figures S1 and S2 in the Supporting Information (SI)]. The conformational situation of the 1,2-oxophosphacyclane ring was evaluated on the basis of $^3J_{HH}$, $^3J_{PH}$, and $^3J_{PC}$ vicinal NMR coupling constants suggesting a preferential $B_{2,5}$ conformation in both compounds.[22] The values of the ^3J constants calculated on minimized structures of **36** and **37**, using the corresponding Karplus equations,[23] agree well with the experimental data (see Tables S1 and S2 in the SI).

The cyclization proceeded analogously with pure phenylphosphinates **5** and **6** to give 2-phenyl-1,2-oxaphosphinanes **38** and **39**, respectively, in good overall yield (Table 1, entries 2 and 3). The ring conformations are similar to those previously commented for compounds **36** and **37** and very close to a theoretical $B_{2,5}$ boat (Cremer-Pople parameters: φ = 290°, θ = 94°, Q = 0.7 Å) confirmed by the large $^3J_{PCCH_3}$ (24 Hz) coupling constant observed, consistent with an almost antiperiplanar arrangement of the atoms (torsion angle ≈ 170°) (Figures and Tables S3 and S4 in the SI). The *P*-stereochemistry has also been established with the aid of NOESY experiments. The NOESY spectrum of **38** unequivocally related the phenylphosphinate protons to β-face hydrogens (H2β and the endo methyl group of the isopropylidene), while in the spectrum of **39**, the phenyl protons are related to α-face hydrogens (H2α and H5). In this context, the substantial deshielding of the endo methyl group of the isopropylidene (ca. 0.26 ppm) is also significant, with the consequent shielding of the 2Hα (−0.25 ppm) and 5H (−0.58 ppm) protons observed on going from the ^{1}H NMR spectrum of **38**−**39** caused by the anisotropic shielding effect of the P−Ph group. Under these conditions, the cyclization proceeded stereospecifically; only one isomer was formed in each case, as detected by ^{31}P NMR spectroscopy of the crude reaction mixture. As described in the literature, the phosphorus nucleophilic substitution mechanism is produced through an intermediary with trigonal bipyramidal geometry, the final result being a *P*-stereochemical inversion.[24] Consequently, the configuration of open-chain precursors **5** and **6** can now be determined as S_p and R_p, respectively.

This methodology can readily be extended to the synthesis of five-membered 1,2-oxaphospholanes ring compounds. Starting from a hexose sugar in furanose form [e.g., 2-deoxy-5,6-*O*-isopropylidene-3-*O*-methyl-D-*arabino*-hexofuranose (**8**), Scheme 2], the alkoxyl radical fragmentation led, across γ-hydroxy-phosphonates (e.g., **33**) or -phosphinates (e.g., **34** and **35**), finally to the required 1,2-oxaphospholanes (e.g., **40**−**43**).

In this particular model, the cyclization step was performed using PPTS in anhydrous $CHCl_3$ after hydrolysis of the formyl ester. This two-step method provides better yields than the direct cyclization used previously for the six-membered rings. It has been reported in the literature that the intramolecular transesterification is highly favored in the case of five-membered 1,2-oxaphospholanes.[25] This may be the reason why small amounts of the corresponding cyclized compounds can be detected during the hydrolysis of the formyl group in the preparation of γ-hydroxy-precursors **33**−**35** (Table 1, entries 4−6), or even in the Arbuzov reactions of iodide **9**. Indeed, a mixture of cyclized **42** and **43** can be obtained directly when heating **9** with $PhP(OEt)_2$ at 120 °C for a long period of time (68 h), although in moderate yield (37%, 6:4, three steps). The *P*-stereochemistries were assigned by analysis of their NOESY spectra (Figures S5−S8 in the SI) and in the case of 2-phenyl-1,2-oxaphospholanes **42** and **43** confirmed by the chemical shift displacement of H2α (−0.32 ppm), H2β (0.14 ppm), and 3β-methoxyl group (0.1 ppm) observed on going from the ^{1}H NMR spectrum of **42**−**43** motivated by the aromatic ring current effect. According to the $^3J_{HH}$, $^3J_{PH}$, and $^3J_{PC}$ coupling constants, the 1,2-oxaphospholane rings in compounds **40**−**43** adopt preferentially very similar $^3T_2$ conformation patterns. The experimental ^3J values are consistent with those calculated on a minimized $^3T_2$ structure. This is also in accordance with a pseudorotational analysis of the $^3J_{HH}$ ring constants. The most populated conformers appear at phase angles of P = 0−42° ($^3T_2$−^3E−$^3T_4$) of the northern region of the pseudorotational itinerary (see Tables S5−S8 in the SI for details).[26]

For the sake of completeness, this methodology was also extended to a disaccharide model derived from perbenzylated D-lactose [β-D-Gal*p*-(1 → 4)-D-Glc*p*]. The diethyl phosphonate **16** was effectively cyclized under similar reaction conditions to give a 1,2-oxaphosphinane derivative as a mixture of *P*-diastereomers **44** and **45** (62%, 1:2) (Table 1, entry 7). The reaction can be expected to come under some steric control and to lead to the major diastereomer **45** having the ethyl group positioned on the less hindered α-side of the ring. NOE interactions observed between this ethyl group and the H2α and H3α protons are also in agreement with the R_P stereochemistry assigned to this isomer (Figures S9 and S10 in the SI). In this case, the 1,2-oxaphosphinane ring adopts preferentially a $^4C_1$ chair conformation in both isomers.[27] This is evident from the $^3J_{HH}$ vicinal coupling values between the axial ring protons (H2β, H3, H4, and H5) and further supported by the relatively small $^3J_{PCCH_3}\beta$ (ca. 2 Hz) observed, which is consistent with a P−C_2−C_3−H dihedral angle of approximately 60° (Table S9 and S10 in the SI).[5b] This is the first synthesis of a β-D-Gal*p*-(1 → 4)-1-phospha-D-Ara*p* structure via direct introduction of the phosphorus at the reducing unit on a disaccharide framework.[28]

Synthesis of 5-Phosphasugars. The second approach was first tested with compound **21**, which possesses a tethered 5-phosphonate monoester functionality on a D-ribofuranose

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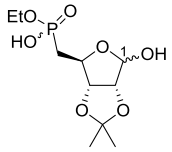
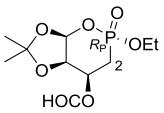
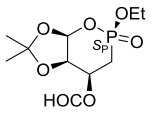
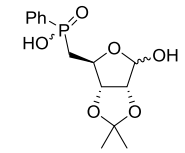
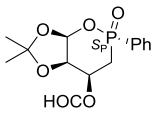
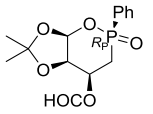
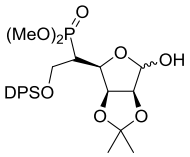
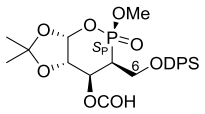
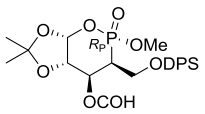
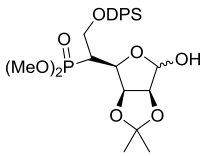
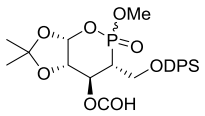
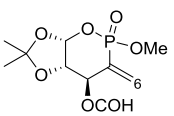
Table 2. Synthesis of 5-Phosphasugars[abc]

entry	substrate	time (h)	products (yield)	
1	 **21**[a]	2.5	 **46** (32)	 **47** (15)
2	 **24**[b]	3.5	 **48** (29)	 **49** (51)
3	 **31**[c]	2	 **50** (26)[d]	 **51** (42)[d]
4	 **32**[c]	5.5	 **52** (n.d.)	 **53** (13)[d]

[a]Reagents and conditions per mmol of substrate: DIB (2.0 mmol), I_2 (1.1 mmol), $CHCl_3$, rt. [b]DIB (2.2 mmol), I_2 (1.1 mmol), CH_2Cl_2, rt, $h\nu$. [c](i) NaOH/MeOH (2 M, 5.3 mL), 40−43 °C, 30 h; (ii) DIB (2.1−2.2 mmol), I_2 (1.0−1.1 mmol), CH_2Cl_2, rt, $h\nu$. [d]Two-step overall yield. n.d. = not detected.

skeleton. The reaction with $PhI(OAc)_2$ and iodine triggers the alkoxyl radical fragmentation and the intramolecular cyclization via a nucleophilic radical-polar crossover mechanism. In consequence, a 2-ethoxy-1,2-oxaphosphinane 2-oxide ring system was formed and isolated as a chromatographically separable mixture of *P*-diastereomers **46** and **47** (Table 2, entry 1). The 6-*exo* cyclization is highly stereoselective; only one isomer at C5 is formed leaving the isopropilidene in cis disposition. *P*-Stereochemistries were assigned by NOESY analyses, and the rings adopt predominantly very similar E_3 conformations. The calculated vicinal coupling constants in these E_3 minimized structures agreed reasonably well with the experimental values (Figures and Tables S11 and S12 in the SI). The ^{1}H NMR spectrum of **46** shows a ^4J_w coupling (0.7 Hz, calcd 1.2 Hz)[29] between H2α and H4 hydrogens, which also supports the previously mentioned conformation.

Curiously, in the ^{1}H NMR spectra of both isomers, the formyl hydrogen signal appears splitting as a doublet of doublets with two long-range couplings: ^4J_w with the H3 (ca. 1 Hz) and $^5J_{PH}$ with the atom of phosphorus (ca. 2.8 Hz), as determined by selective spin decoupling and $^1H\{^{31}P\}$ NMR spectroscopy, respectively.

The cyclized 2-phenyl-1,2-oxaphosphinanes **48** and **49** were prepared analogously from the free phosphinic acid **24** (Table 2, entry 2). The stereochemical assignment of these examples rests on spectroscopic evidences and on a single-crystal X-ray crystallographic analysis of **48** (Figure S17 in the SI). The solution conformation of the 1,2-oxaphosphinane ring, elucidated from the experimental homo- and heteronuclear ^3J coupling constants of the ring protons, was practically identical to the slightly distorted $B_{3,O}$ boat conformation (Cremer-Pople parameters: φ = 188.9°, θ = 79.5°, Q = 0.636 Å) observed in the crystalline structure of **48** (Figure and Table S13 in the SI). The ^4J_w coupling (0.9 Hz, calcd 1.2 Hz)[29] between H2α and H4 hydrogens provides additional support for this conformation. Interestingly, the ring of the R_P isomer **49** seems to adopt in solution a conformation closer to a $^4C_1$ chair than to the $B_{3,O}$ boat (Figure and Table S14 in the SI). The most significant difference was observed in the heteronuclear $^3J_{POCH_3}$ coupling constant [**48** (19.0 Hz, calcd 21.1 Hz, TA = −161.5°, $B_{3,O}$); **49** (0.7 Hz, calcd 1.5 Hz, TA = −89.6°, $^4C_1$)] in full agreement with the Karplus equation and the geometry of the rings.[30]

An example with the phosphorous on a secondary carbon of the sugar side chain has also been accomplished. The 5-dimethoxyphosphoryl-L-gulofuranose derivative (**31**) was partially hydrolyzed to the monoester and immediately subjected to the ARF reaction (Table 2, entry 3). The *P*-configuration of the two 1,2-oxaphosphinane derivatives obtained **50** and **51** was determined on the basis of NOE interactions of the P−OMe with protons in close spatial proximity to the β- and α-side of the ring, respectively (Figures S15 and S16 in the SI). The $^3J_{H2\alpha,H3}$ coupling constant and the NOE interaction of the H2 with the endo methyl group of the isopropylidene established the stereochemistry at C2 and, consequently, confirmed that of compounds **28**−**32**. Both epimeric compounds appear to exist in solution predominantly in a ^3E conformation (Tables S15 and S16 in the SI).

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However, the cyclization completely failed with the minor isomeric 5-dimethoxyphosphoryl-D-mannofuranose derivative (**32**) (Table 2, entry 4). The reaction is slower, and the expected 5-phosphasugar **52** could not be detected in the complex mixture of products obtained. Instead, a compound eventually identified as the cyclized olefin **53** was obtained by chromatography in a low yield. A hypothesis that can rationalize this result is based on unfavorable steric interactions between the large side chain and the crowded α-side of the molecule that may hinder the cyclization step. The formation of **53** may be explained by cyclization after desilylation and subsequent elimination of the alcohol. The 3-methylene-1,2-oxaphosphinane structure of **53** was characterized by spectroscopic means. Most significantly, $^{3}J_{PH6cis}$ = 23.6 Hz and $^{3}J_{PH6trans}$ = 43.8 Hz coupling constants of the methylene protons are observed in the ^{1}H NMR spectrum.[31]

Assignment of *P*-Stereochemistry. Phosphorous stereochemistry in cyclic phosphonates or phosphinates was determined by studying one-dimensional (1D) and two-dimensional (2D) NOE experiments on minimized structures with the established conformation for the five- or six-membered rings. In some cases, other ^{1}H and ^{31}P NMR supporting data have also been taken into account. In general, it has been observed that in hexopyranoses possessing a 2-methoxy-1,2-oxaphosphinane 2-oxide ring system, the signal of the ^{31}P{^{1}H} NMR for the axial α-P−OMe is 2−4 ppm upfield from the corresponding equatorial β-P−OMe.[4b,c,f,9b] This trend has also been detected in our 2-deoxy compounds, although the observed difference is smaller (ca. 1 ppm) [compare ^{31}P-chemical shift displacements of compounds **36**−**37** (1 ppm), **44**−**45** (1 ppm), and **47**−**46** (1.6 ppm)]. In some previous cases, this decrease has been attributed to conformational changes in the chair ring, and this may be the reason for the small difference observed in our compounds.[4c] Five- or six-membered cyclic phosphinates show a greater difference in the ^{31}P NMR chemical shifts displacement between both *P*-isomers [i.e., **38**−**39** (3.3 ppm), **42**−**43** (4.0 ppm), and **49**−**48** (3.2 ppm)]. This trend, which the small number of examples does not allow us to generalize, however coincides with that observed for another pair of this type of compounds described in the literature.[4h] The $^{2}J_{PH2}$ coupling constant has also been used for the determination of the configuration at phosphorus in the glucopyranose series. This constant is considerably smaller in the α-P−OMe (2−5 Hz) than in the β-P−OMe compounds (6−10 Hz).[4f] As one might expect this correlation of $^{2}J_{PH2}$ with phosphorus, stereochemistry does not seem to be applicable to our 2-deoxy compounds, in which the $^{2}J_{PH2\alpha}$ and $^{2}J_{PH2\beta}$ are in general very similar and considerably higher (ca. 16−20 Hz).

■ CONCLUSIONS

In summary, we have successfully applied the anomeric ARF reaction for the synthesis of 1-phosphahexopyranose, 1-phosphahexofuranose, and 5-phosphapentopyranose sugars. The process initiated by the 1-*O*-yl radical is strongly influenced by the polarity of the C2 substituent. In the presence of an EWG at C2, rapid β-fragmentation affords a stabilized C2 radical, which is trapped by the iodine atoms present in the medium. The acyclic iodide can be readily transformed into 1-phosphasugars using a three-step sequence: Arbuzov reaction, selective hydrolysis, and intramolecular cyclization. Cyclic phosphonates and phosphinates with 2-oxo-1,2-oxaphosphinane and 2-oxo-1,2-oxaphospholane ring systems can be obtained using this methodology. The 1-phosphasugar ring has the same number of atoms and stereochemistry as the original carbohydrate. This sequence has also been applied to D-lactose for the synthesis of β-D-Gal*p*-(1 → 4)-1-phospha-D-Ara*p* with a disaccharide structure. Nevertheless, if the C2 substituent is an EDG, the C2 radical intermediate undergoes one-electron oxidation causing a crossover from the radical to an oxocarbenium ion that can be trapped intramolecularly by tethered *P*-nucleophiles strategically located in the carbohydrate skeleton. This methodology using the same sequence of reactions, although in a different order, provides access to ring-expanded phosphinates and phosphonates with a hitherto unknown 5-phosphapentopyranose skeleton. The five- and six-membered cyclic phosphinates and phosphonates prepared herein present a wide variety of solution conformations that have been studied using ^{3}J homo- and heteronuclear coupling constants.

■ EXPERIMENTAL SECTION

General Methods. Melting points were determined with a hot-stage apparatus. Optical rotations were measured at the sodium line at ambient temperature in $CHCl_3$ solutions. IR spectra were measured as thin films on $CHCl_3$ solutions. NMR spectra were determined at 500 MHz for ^{1}H, 125.7 MHz for ^{13}C{^{1}H}, and 162 or 202.5 MHz for ^{31}P{^{1}H} in $CDCl_3$ as stated. The chemical shifts are given in parts per million (ppm) relative to TMS at δ 0.00 ppm or to residual $CDCl_3$ at δ 7.26 ppm for proton spectra, relative to $CDCl_3$ at δ 77.00 ppm for carbon spectra, and relative to external phosphoric acid at δ 0.00 ppm for phosphorus spectra. ^{13}C DEPT-90, −135 and 2D correlation spectroscopy (COSY), heteronuclear single-quantum coherence (HSQC), NOESY, and heteronuclear multiple bond correlation (HMBC) experiments were performed routinely for all new compounds. When necessary, J_{PH} coupling constants have been determined using ^{1}H{^{31}P} NMR decoupled spectra. The DAISY program as implemented in the TopSpin 4.0.6 software package was used for the simulation of ^{1}H NMR spectra. Low- and high-resolution mass spectra were recorded using electrospray ionization (ESI^+) and time-of-flight (TOF) analyzer. Merck silica gel 60 PF (0.063−0.2 mm) was used for column chromatography. Circular layers of 1 and 2 mm of Merck silica gel 60 PF_{254} were used on a Chromatotron for centrifugally assisted chromatography. HPLC separations were undertaken using a semipreparative (10 mm × 250 mm) Ascentis Si normal-phase column. Commercially available reagents and solvents were of analytical grade or were purified by standard procedures prior to use. The spray reagents for TLC analysis were used with 0.5% vanillin in H_2SO_4−EtOH (4:1), with Hanessian's stain,[32] or alternatively with ninhydrin and further heating until development of color.

6-O-tert-Butyldiphenylsilyl-2-deoxy-3,4-O-isopropylidene-D-lyxo-hexopyranose (2).[33] A solution of glycal **1**[34] (228.0 mg, 0.537 mmol) in THF (11.7 mL) containing water (233 μL, 12.9 mmol) and Ph_3P·HBr (29.5 mg, 0.086 mmol) was stirred at room temperature for 24 h. The reaction mixture was then poured into a saturated solution of $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic extracts were washed with a saturated solution of $NaHCO_3$, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexanes−EtOAc, 70:30) to give **2** (237.1 mg, 0.536 mmol, 100%, anomeric mixture, α/β, 3.7:1) as a colorless oil: IR ($CHCl_3$) 3592, 2932, 1427, 1112 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, major isomer) δ_H 1.08 (9H, s), 1.33 (3H, s), 1.42 (3H, s), 1.70 (1H, ddd, J = 15.0, 6.8, 3.8 Hz, H2a), 2.23 (1H, ddd, J = 15.1, 5.0, 4.2 Hz, H2b), 3.83 (1H, dd, J = 10.1, 6.6 Hz, H6a), 3.90 (1H, dd, J = 10.1, 6.3 Hz, H6b), 3.99 (1H, ddd, J = 6.6, 6.6, 1.9 Hz, H5), 4.24 (1H, dd, J = 7.3, 1.9 Hz, H4), 4.51 (1H, ddd, J = 7.3, 4.2, 4.2 Hz, H3), 5.33 (1H, dd, J = 6.9, 5.0 Hz, H1), 7.36−7.43 (6H, m), 7.69−7.74 (4H, m); ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$,

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major isomer) δ_C 19.3 (C), 25.2 (CH_3), 26.6 (CH_3), 26.8 (3 × CH_3), 31.4 (CH_2, C2), 63.0 (CH_2, C6), 69.7 (CH, C5), 70.3 (CH, C3), 72.3 (CH, C4), 90.5 (CH, C1), 108.8 (C), 127.55 (2 × CH), 127.60 (2 × CH), 129.6 (2 × CH), 133.6 (C), 133.7 (C), 135.6 (2 × CH), 135.7 (2 × CH); MS (ESI^+-TOF) *m/z* (%) 465 [$(M + Na)^+$, 100]; HRMS (ESI^+-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{25}H_{34}NaO_5Si$ 465.2073; found 465.2072. Anal. calcd for $C_{25}H_{34}O_5Si$: C, 67.84; H, 7.74. Found: C, 67.85; H, 8.07.

*1-O-tert-Butyldiphenylsilyl-5-deoxy-2-O-formyl-3,4-O-isopropylidene-5-iodo-D-arabinitol (**3**).* A solution of alcohol **2** (101.5 mg, 0.229 mmol) in CH_2Cl_2 (5.8 mL) containing $PhI(OAc)_2$ (81.2 mg, 0.252 mmol) and I_2 (64 mg, 0.252 mmol) under nitrogen was stirred at room temperature for 1 h. The reaction mixture was then poured into 10% aqueous $Na_2S_2O_3$, extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated. The residue was purified by Chromatotron chromatography (hexanes−EtOAc, 80:20) to give compound **3** (130.1 mg, 0.229 mmol, 100%) as a yellowish oil: $[\alpha]_D$ −1.4 (*c*, 0.98, $CHCl_3$); IR ($CHCl_3$) 2934, 1726, 1428, 1181, 1113 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 1.10 (9H, s), 1.40 (3H, s), 1.52 (3H, s), 3.13 (1H, dd, *J* = 10.2, 5.4 Hz, H2a), 3.23 (1H, dd, *J* = 9.8, 8.0 Hz, H2b), 3.80 (1H, dd, *J* = 10.6, 6.1 Hz, H6a), 3.85 (1H, dd, *J* = 10.6, 6.1 Hz, H6b), 4.43−4.48 (2H, m, H3, H4), 5.29−5.33 (1H, m, H5), 7.41−7.50 (6H, m), 7.69−7.73 (4H, m), 8.08 (1H, s, CHO); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ_C 2.4 (CH_2, C2), 19.0 (C), 25.5 (CH_3), 26.7 (3 × CH_3), 27.2 (CH_3), 62.5 (CH_2, C6), 70.7 (CH, C5), 75.3 (CH, C4), 77.4 (CH, C3), 109.2 (C), 127.76 (2 × CH), 127.78 (2 × CH), 129.9 (2 × CH), 132.57 (C), 132.64 (C), 135.4 (2 × CH), 135.5 (2 × CH), 160.0 (CH, CHO); MS (ESI^+-TOF) *m/z* (%) 591 [$(M + Na)^+$, 100]; HRMS (ESI^+-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{25}H_{33}INaO_5Si$ 591.1040; found 591.1037. Anal. calcd for $C_{25}H_{33}IO_5Si$: C, 52.82; H, 5.85. Found: C, 52.96; H, 6.18.

*1-O-tert-Butyldiphenylsilyl-5-deoxy-5-diethoxyphosphoryl-2-O-formyl-3,4-O-isopropylidene-D-arabinitol (**4**).* A solution of **3** (114 mg, 0.2 mmol) in $(EtO)_3P$ (1.82 mL, 10.6 mmol) was stirred at reflux temperature for 3.5 h. The reaction mixture was concentrated under high vacuum, and the residue was purified by Chromatotron chromatography (hexanes−EtOAc, 50:50) to give compound **4** (81.7 mg, 0.141 mmol, 71%) as a colorless oil: $[\alpha]_D$ −13.1 (*c*, 0.49, $CHCl_3$); IR ($CHCl_3$) 2993, 1724, 1383, 1253, 1183, 1029 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 1.05 (9H, s), 1.325 (3H, t, *J* = 7.1 Hz), 1.327 (3H, t, *J* = 7.1 Hz), 1.36 (3H, s), 1.48 (3H, s), 1.97 (1H, ddd, $^2J_{PH}$ = 19.6 Hz, *J* = 15.1, 5.7 Hz, H2a), 2.11 (1H, ddd, $^2J_{PH}$ = 18.9 Hz, *J* = 14.8, 8.2 Hz, H2b), 3.77 (1H, dd, *J* = 10.7, 5.7 Hz, H6a), 3.81 (1H, dd, *J* = 10.7, 6.6 Hz, H6b), 4.08−4.16 (4H, m), 4.37 (1H, dd, *J* = 6.3, 3.5 Hz, H4), 4.58 (1H, dddd, $^3J_{PH}$ = 8.4 Hz, *J* = 8.4, 6.0, 6.0 Hz, H3), 5.26 (1H, ddd, *J* = 5.8, 5.8, 3.8 Hz, H5), 7.37−7.45 (6H, m), 7.64−7.68 (4H, m), 8.07 (1H, s, CHO); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ_C 16.3 (CH_3, d, $^3J_{PC}$ = 6.4 Hz), 16.4 (CH_3, d, $^3J_{PC}$ = 5.3 Hz), 19.1 (C), 25.6 (CH_3), 26.7 (3 × CH_3), 26.8 (CH_3), 27.1 (CH_2, d, $^1J_{PC}$ = 143.1 Hz, C2), 61.7 (CH_2, d, $^2J_{PC}$ = 6.4 Hz), 62.1 (CH_2, d, $^2J_{PC}$ = 6.4 Hz), 62.8 (CH_2, C6), 71.6 (CH, C5), 71.7 (CH, d, $^2J_{PC}$ = 3.2 Hz, C3), 75.4 (CH, d, $^3J_{PC}$ = 10.6 Hz, C4), 108.9 (C), 127.73 (2 × CH), 127.74 (2 × CH), 129.80 (2 × CH), 132.89 (C), 132.91 (C), 135.5 (2 × CH), 135.6 (2 × CH), 160.2 (CH, CHO); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ_P 27.5 (P); MS (ESI^+-TOF) *m/z* (%) 601 [$(M + Na)^+$, 100]; HRMS (ESI^+-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{29}H_{43}NaO_8PSi$ 601.2363; found 601.2363. Anal. calcd for $C_{29}H_{43}O_8PSi$: C, 60.19; H, 7.49. Found: C, 60.47; H, 7.46.

*(S_P)-6-O-tert-Butyldiphenylsilyl-1,2-dideoxy-1-ethoxy-3,4-O-isopropylidene-1-phospha-1-oxo-D-lyxo-hexopyranose (**36**) and (R_P)-6-O-tert-Butyldiphenylsilyl-1,2-dideoxy-1-ethoxy-3,4-O-isopropylidene-1-phospha-1-oxo-D-lyxo-hexopyranose (**37**).* A solution of **4** (44.4 mg, 0.077 mmol) in NaOEt/EtOH 0.01 M (0.67 mL, 0.0067 mmol) was stirred at room temperature for 102 h. The reaction mixture was concentrated under reduced pressure, and the residue was purified by Chromatotron chromatography (hexanes−EtOAc, 50:50) to give an inseparable mixture of isomers **36** and **37** (34.9 mg, 0.069 mmol, 90%, **36**:**37**, 1:3) as a colorless oil. The mixture was then separated by HPLC (hexanes−EtOAc, 40:60; Φ = 3 mL/min) to give compound **36**: $[\alpha]_D$ −12.7 (*c*, 0.52, $CHCl_3$); IR ($CHCl_3$) 2931, 1251, 1228, 1113, 1020 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, simulated coupling constants using DAISY) δ_H 1.06 (9H, s), 1.33 (3H, t, *J* = 6.9 Hz), 1.36 (3H, s), 1.46 (3H, s), 2.17 (1H, ddd, $^2J_{PH}$ = 16.3 Hz, *J* = 15.9, 4.7 Hz, H2*α*), 2.31 (1H, ddd, $^2J_{PH}$ = 17.6 Hz, *J* = 15.9, 4.9 Hz, H2*β*), 3.90 (1H, dd, *J* = 9.8, 5.9 Hz, H6a), 3.97 (1H, ddd, $^4J_{PH}$ = 0.7 Hz, *J* = 9.8, 8.0 Hz, H6b), 4.12−4.22 (2H, m), 4.44 (1H, ddd, $^4J_{PH}$ = 0.9 Hz, *J* = 6.7, 1.8 Hz, H4), 4.47 (1H, dddd, $^3J_{PH}$ = 4.7 Hz, *J* = 8.0, 5.9, 1.8 Hz, H5), 4.73 (1H, dddd, $^3J_{PH}$ = 26.4 Hz, *J* = 6.7, 4.9, 4.7 Hz, H3), 7.37−7.46 (6H, m), 7.67−7.72 (4H, m); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ_C 16.5 (CH_3, d, $^3J_{PC}$ = 5.3 Hz), 19.2 (C), 24.9 (CH_3), 25.5 (CH_2, d, $^1J_{PC}$ = 126.1 Hz, C2), 26.5 (CH_3), 26.7 (3 × CH_3), 62.4 (CH_2, d, $^3J_{PC}$ = 10.6 Hz, C6), 62.6 (CH_2, d, $^2J_{PC}$ = 5.3 Hz), 71.5 (CH, d, $^2J_{PC}$ = 6.4 Hz, C3), 72.2 (CH, d, $^3J_{PC}$ = 5.3 Hz, C4), 75.4 (CH, d, $^2J_{PC}$ = 3.2 Hz, C5), 109.0 (C), 127.65 (2 × CH), 127.74 (2 × CH), 129.7 (CH), 129.8 (CH), 133.0 (C), 133.1 (C), 135.56 (2 × CH), 135.63 (2 × CH); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ_P 25.0 (P); MS (ESI^+-TOF) *m/z* (%) 527 [$(M + Na)^+$, 100]; HRMS (ESI^+-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{26}H_{37}NaO_6PSi$ 527.1995; found 527.1995. Anal. calcd for $C_{26}H_{37}O_6PSi$: C, 61.88; H, 7.39. Found: C, 61.97; H, 7.55. Compound **37**: $[\alpha]_D$ +7.7 (*c*, 0.48, $CHCl_3$); IR ($CHCl_3$) 2932, 1272, 1227, 1113, 1031 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, simulated coupling constants using DAISY) δ_H 1.07 (9H, s), 1.31 (3H, t, *J* = 6.9 Hz), 1.33 (3H, s), 1.50 (3H, s), 2.11 (1H, ddd, $^2J_{PH}$ = 16.4 Hz, *J* = 15.8, 4.6 Hz, H2*α*), 2.33 (1H, ddd, $^2J_{PH}$ = 18.9 Hz, *J* = 15.8, 5.8 Hz, H2*β*), 3.93 (1H, dd, *J* = 10.5, 7.0 Hz, H6a), 3.96 (1H, ddd, $^4J_{PH}$ = 2.0 Hz, *J* = 10.5, 5.8 Hz, H6b), 4.06−4.17 (2H, m), 4.19 (1H, dddd, $^3J_{PH}$ = 4.7 Hz, *J* = 7.0, 5.8, 1.9 Hz, H5), 4.25 (1H, ddd, $^4J_{PH}$ = 1.0 Hz, *J* = 6.1, 1.9 Hz, H4), 4.62 (1H, dddd, $^3J_{PH}$ = 23.2 Hz, *J* = 6.1, 5.8, 4.6 Hz, H3), 7.38−7.47 (6H, m), 7.68−7.71 (4H, m); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ_C 16.4 (CH_3, d, $^3J_{PC}$ = 6.4 Hz), 19.2 (C), 25.4 (CH_3), 25.5 (CH_2, d, $^1J_{PC}$ = 128.2 Hz, C2), 26.8 (3 × CH_3), 26.9 (CH_3), 61.0 (CH_2, d, $^2J_{PC}$ = 6.4 Hz), 63.0 (CH_2, d, $^3J_{PC}$ = 9.5 Hz, C6), 72.0 (CH, d, $^2J_{PC}$ = 6.4 Hz, C3), 72.5 (CH, d, $^3J_{PC}$ = 5.3 Hz, C4), 76.8 (CH, d, $^2J_{PC}$ = 5.5 Hz, C5), 109.6 (C), 127.7 (2 × CH), 127.8 (2 × CH), 129.8 (2 × CH), 133.0 (C), 133.1 (C), 135.6 (4 × CH); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ_P 24.0 (P); MS (ESI^+-TOF) *m/z* (%) 527 [$(M + Na)^+$, 100]; HRMS (ESI^+-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{26}H_{37}NaO_6PSi$ 527.1995; found 527.2007. Anal. calcd for $C_{26}H_{37}O_6PSi$: C, 61.88; H, 7.39. Found: C, 61.86; H, 7.49.

*(S_P)-1-O-tert-Butyldiphenylsilyl-5-deoxy-5-ethoxyphenylphosphoryl-2-O-formyl-3,4-O-isopropylidene-D-arabinitol (**5**) and (R_P)-1-O-tert-Butyldiphenylsilyl-5-deoxy-5-ethoxyphenylphosphoryl-2-O-formyl-3,4-O-isopropylidene-D-arabinitol (**6**).* A solution of **3** (71 mg, 0.125 mmol) in $PhP(OEt)_2$ (140 *μ*L, 0.73 mmol) was stirred at 160 °C under nitrogen for 6 h. The reaction mixture was concentrated under high vacuum, and the residue was purified by Chromatotron chromatography (hexanes−EtOAc, 70:30) to give starting material **3** (7.4 mg, 0.013 mmol, 10%) and a mixture of compounds **5** and **6** (66.3 mg, 0.109 mmol, 87%, **5**/**6**, 1:1.1) as a colorless oil. The mixture was separated by HPLC (hexanes−EtOAc, 50:50; Φ = 3 mL/min). Compound **5**: $[\alpha]_D$ −25.5 (*c*, 0.2, $CHCl_3$); IR ($CHCl_3$) 1722, 1185, 1113 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 1.02 (9H, s), 1.31 (3H, t, *J* = 7.3 Hz), 1.32 (3H, s), 1.42 (3H, s), 2.03 (1H, ddd, $^2J_{PH}$ = 13.6 Hz, *J* = 15.1, 5.7 Hz, H2a), 2.30 (1H, ddd, $^2J_{PH}$ = 15.1 Hz, *J* = 15.1, 8.2 Hz, H2b), 3.66 (1H, dd, *J* = 10.7, 5.0 Hz, H6a), 3.74 (1H, dd, *J* = 10.7, 6.9 Hz, H6b), 3.94 (1H, ddddd, $^2J_{PH}$ = 7.2 Hz, *J* = 10.1, 7.2, 7.2, 7.2 Hz), 4.09−4.19 (1H, m), 4.26 (1H, dd, *J* = 6.0, 3.8 Hz, H4), 4.60 (1H, dddd, $^3J_{PH}$ = 8.2 Hz, *J* = 8.2, 5.7, 5.7 Hz, H3), 5.11 (1H, m, H5), 7.35−7.44 (6H, m), 7.46−7.51 (2H, m), 7.54−7.58 (1H, m), 7.61−7.64 (4H, m), 7.78−7.85 (2H, m), 8.04 (1H, s, CHO); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, the C-*ipso* was not observed) δ_C 16.5 (CH_3, d, $^3J_{PC}$ = 6.4 Hz), 19.1 (C), 25.6 (CH_3), 26.7 (3 × CH_3), 26.8 (CH_3), 31.3 (CH_2, d, $^1J_{PC}$ = 99.6 Hz, C2), 61.0 (CH_2, d, $^2J_{PC}$ = 5.3 Hz), 62.8 (CH_2, C6), 71.2 (CH, d, $^2J_{PC}$ = 3.2 Hz, C3), 71.7 (CH, C5), 75.5 (CH, d, $^3J_{PC}$ = 9.5 Hz, C4), 108.9 (C), 127.72 (2 × CH), 127.74 (2 × CH), 128.7 (2 × CH, d, $^3J_{PC}$ = 12.7 Hz), 129.80 (CH), 128.82 (CH), 131.6 (2 × CH, d, $^2J_{PC}$ = 10.6 Hz), 132.5 (CH, d, $^4J_{PC}$ = 2.1 Hz), 132.9 (2 × C), 135.5 (2 × CH), 135.6 (2 × CH), 160.4 (CH, CHO); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ_P 40.1 (P); MS (ESI^+-TOF) *m/z* (%) 633 [$(M + Na)^+$, 100]; HRMS (ESI^+-TOF) *m/*

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z: $[M + Na]^+$ calcd for $C_{33}H_{43}NaO_7PSi$ 633.2413; found 633.2404. Anal. calcd for $C_{33}H_{43}O_7SiP$: C, 64.90; H, 7.10. Found: C, 64.76; H, 7.45. Compound **6**: $[\alpha]_D$ −2.7 (*c*, 0.15, $CHCl_3$); IR ($CHCl_3$) 1729, 1374, 1249 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 1.06 (9H, s), 1.19 (3H, s), 1.25 (3H, s), 1.27 (3H, t, *J* = 6.9 Hz), 2.15−2.31 (2H, m, H2a, H2b) 3.76 (1H, dd, *J* = 10.7, 5.0 Hz, H6a), 3.82 (1H, dd, *J* = 10.7, 6.9 Hz, H6b), 3.83−3.88 (1H, m), 4.03−4.11 (1H, m), 4.36 (1H, dd, *J* = 5.8, 3.6 Hz, H4), 4.63 (1H, dddd, $^3J_{PH}$ = 6.8 Hz, *J* = 6.8, 6.8, 6.8 Hz, H3), 5.40 (1H, ddd, *J* = 6.9, 5.7, 4.1 Hz, H5), 7.38−7.46 (6H, m), 7.48−7.51 (2H, m), 7.55−7.58 (1H, m), 7.65−7.69 (4H, m), 7.80−7.84 (2H, m), 8.07 (1H, s, CHO); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, the C-*ipso* was not observed) δ_C 16.4 (CH_3, d, $^3J_{PC}$ = 7.4 Hz), 19.1 (C), 25.5 (CH_3), 26.4 (CH_3), 26.7 (3 × CH_3), 30.8 (CH_2, d, $^1J_{PC}$ = 100.7 Hz, C2), 60.8 (CH_2, d, $^2J_{PC}$ = 6.4 Hz), 62.9 (CH_2, C6), 71.4 (CH, C3), 71.6 (CH, C5), 75.4 (CH, d, $^3J_{PC}$ = 8.5 Hz, C4), 108.7 (C), 127.75 (2 × CH), 127.78 (2 × CH), 128.5 (2 × CH, d, $^3J_{PC}$ = 12.7 Hz), 129.8 (2 × CH), 131.9 (2 × CH, d, $^2J_{PC}$ = 10.6 Hz), 132.4 (CH, d, $^4J_{PC}$ = 2.1 Hz), 132.9 (2 × C), 135.5 (2 × CH), 135.6 (2 × CH), 160.5 (CH, CHO); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ_P 41.1 (P); MS (ESI^+-TOF) *m*/*z* (%) 633 [$(M + Na)^+$, 100]; HRMS (ESI^+-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{33}H_{43}NaO_7PSi$ 633.2413; found 633.2400. Anal. calcd for $C_{33}H_{43}O_7PSi$: C, 64.90; H, 7.10. Found: C, 65.11; H, 7.32.

*(R_P)-6-O-tert-Butyldiphenylsilyl-1,2-dideoxy-3,4-O-isopropylidene-1-phenyl-1-phospha-1-oxo-D-lyxo-hexopyranose (**38**).* A solution of **5** (8.5 mg, 0.014 mmol) in NaOEt/EtOH 0.01 M (0.12 mL, 1.2×10^{-3} mmol) was stirred at room temperature under nitrogen for 24 h. The reaction mixture was concentrated under reduced pressure, and the residue was purified by Chromatotron chromatography (hexanes−EtOAc, 40:60) to give compound **38** (5.2 mg, 0.01 mmol, 70%) as a crystalline solid: mp 134.4−135.6 °C (from *n*-hexane−EtOAc); $[\alpha]_D$ +11.9 (*c*, 0.27, $CHCl_3$); IR ($CHCl_3$) 2996, 1428, 1243, 1229, 1113 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, simulated coupling constants using DAISY) δ_H 1.07 (9H, s), 1.37 (3H, s), 1.39 (3H, s), 2.36 (1H, ddd, $^2J_{PH}$ = 17.8 Hz, *J* = 16.3, 4.5 Hz, H2α), 2.59 (1H, ddd, $^2J_{PH}$ = 7.9 Hz, *J* = 16.3, 4.5 Hz, H2β), 3.96 (1H, dd, *J* = 9.8, 6.0 Hz, H6a), 4.05 (1H, dd, *J* = 9.8, 7.6 Hz, H6b), 4.52 (1H, ddd, $^3J_{PH}$ = 0.8 Hz, *J* = 6.9, 1.9 Hz, H4), 4.72 (1H, dddd, $^3J_{PH}$ = 6.3 Hz, *J* = 7.6, 6.0, 1.9 Hz, H5), 4.81 (1H, dddd, $^3J_{PH}$ = 24.6 Hz, *J* = 6.9, 4.5, 4.5 Hz, H3), 7.34−7.47 (8H, m), 7.53−7.56 (1H, m), 7.67−7.70 (2H, m), 7.72−7.75 (2H, m), 7.90−7.95 (2H, m); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ_C 19.2 (C), 24.6 (CH_3), 26.2 (CH_3), 26.7 (3 × CH_3), 28.1 (CH_2, d, $^1J_{PC}$ = 85.8 Hz, C2), 62.6 (CH_2, d, $^3J_{PC}$ = 9.5 Hz, C6), 70.8 (CH, d, $^2J_{PC}$ = 6.4 Hz, C3), 72.1 (CH, d, $^3J_{PC}$ = 4.2 Hz, C4), 73.7 (CH, d, $^2J_{PC}$ = 5.3 Hz, C5), 108.8 (C), 127.6 (2 × CH), 127.7 (2 × CH), 128.3 (2 × CH, d, $^3J_{PC}$ = 13.8 Hz), 129.7 (CH), 129.73 (CH), 130.7 (C, d, $^1J_{PC}$ = 142.0 Hz), 131.6 (2 × CH, d, $^2J_{PC}$ = 10.6 Hz), 132.5 (CH, d, $^4J_{PC}$ = 3.2 Hz), 133.0 (C), 133.2 (C), 135.6 (2 × CH), 135.7 (2 × CH); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ_P 37.2 (P); MS (ESI^+-TOF) *m*/*z* (%) 559 [$(M + Na)^+$, 100]; HRMS (ESI^+-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{30}H_{37}NaO_5PSi$ 559.2046; found 559.2057. Anal. calcd for $C_{30}H_{37}O_5PSi$: C, 67.14; H, 6.95. Found: C, 67.32; H, 6.92.

*(S_P)-6-O-tert-Butyldiphenylsilyl-1,2-dideoxy-3,4-O-isopropylidene-1-phenyl-1-phospha-1-oxo-D-lyxo-hexopyranose (**39**).* A solution of **6** (4.8 mg, 0.0079 mmol) in NaOEt/EtOH 0.01 M (0.07 mL, 0.7×10^{-3} mmol) was stirred at room temperature under nitrogen for 24 h. The reaction mixture was concentrated under reduced pressure, and the residue was purified by Chromatoron chromatography (hexanes−EtOAc, 40:60) to give **39** (3.2 mg, 6.0×10^3 mmol, 75%) as a crystalline solid: mp 171.8−173.2 °C (from *n*-hexane−EtOAc); $[\alpha]_D$ +10.8 (*c*, 0.12, $CHCl_3$); IR ($CHCl_3$) 2997, 1229, 1113 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, simulated coupling constants using DAISY) δ_H 1.08 (9H, s), 1.35 (3H, s), 1.63 (3H, s), 2.11 (1H, ddd, $^2J_{PH}$ = 6.6 Hz, *J* = 15.9, 4.0 Hz, H2α), 2.62 (1H, ddd, $^2J_{PH}$ = 14.8 Hz, *J* = 15.9, 4.1 Hz, H2β), 3.99 (1H, ddd, $^4J_{PH}$ = 2.3 Hz, *J* = 10.7, 5.5 Hz, H6a), 4.07 (1H, dd, *J* = 10.7, 6.8 Hz, H6b), 4.19 (1H, dddd, $^3J_{PH}$ = 3.3 Hz, *J* = 6.8, 5.5, 1.5 Hz, H5), 4.35 (1H, ddd, $^3J_{PH}$ = 0.9 Hz, *J* = 7.2, 1.5 Hz, H4), 4.78 (1H, dddd, $^3J_{PH}$ = 24.2 Hz, *J* = 7.2, 4.0, 4.1 Hz, H3), 7.37−7.41 (4H, m), 7.43−7.47 (4H, m), 7.53−7.57 (1H, m), 7.68−7.71 (4H, m), 7.76−7.80 (2H, m); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, the C-*ipso* was not observed) δ_C 19.2 (C), 24.8 (CH_3), 26.2 (CH_3), 26.8 (3 × CH_3), 27.5 (CH_2, d, $^1J_{PC}$ = 85.8 Hz, C2), 63.6 (CH_2, d, $^3J_{PC}$ = 9.5 Hz, C6), 71.4 (CH, d, $^2J_{PC}$ = 7.4 Hz, C3), 72.4 (CH, d, $^3J_{PC}$ = 6.4 Hz, C4), 77.7 (CH, d, $^2J_{PC}$ = 6.4 Hz, C5), 110.0 (C), 127.7 (2 × CH), 127.8 (2 × CH), 128.79 (2 × CH, d, $^3J_{PC}$ = 13.8 Hz), 129.82 (2 × CH), 130.2 (2 × CH, d, $^2J_{PC}$ = 9.5 Hz), 132.2 (CH, d, $^4J_{PC}$ = 2.1 Hz), 132.9 (C), 133.0 (C), 135.6 (4 × CH); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ_P 33.9 (P); MS (ESI^+-TOF) *m*/*z* (%) 559 [$(M + Na)^+$, 100]; HRMS (ESI^+-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{30}H_{37}NaO_5PSi$ 559.2046; found 559.2043. Anal. calcd for $C_{30}H_{37}O_5PSi$: C, 67.14; H, 6.95. Found: C, 67.03; H, 6.96.

*2-Deoxy-5,6-O-isopropylidene-3-O-methyl-D-arabino-hexofuranose (**8**).* To 1,4-anhydro-2-deoxy-3-*O*-methyl-5,6-*O*-isopropylidene-D-*arabino*-hex-1-enitol 7[35] (4 g, 20 mmol) in THF (56 mL) and water (40 mL), $Hg(OAc)_2$ (7 g, 22 mmol) was added at room temperature. The reaction mixture was stirred at this temperature for 1 h, and afterward, the solution was kept at 0 °C for 15 min. To this reaction mixture, an aqueous solution of KI (15.9 g, 96 mmol in 18 mL of water) was added and the mixture was stirred for another 30 min. To the resulting reaction mixture at 0 °C, an aqueous solution of $NaBH_4$ (831 mg, 22 mmol in 40 mL of water) was added dropwise and stirred for 1.5 h at this temperature. The insoluble part was removed by filtration through a bed of Celite and washed with EtOAc. The filtrate was separated, and the organic layer was extracted with EtOAc, dried over Na_2SO_4, and concentrated under reduced pressure to give a residue (5 g), which was purified by column chromatography (hexanes−EtOAc, 60:40) to obtain **8** (1.63 g, 7.48 mmol, 37%) as a crystalline mixture of anomeric isomers (6:4); IR ($CHCl_3$) 3597, 3398, 2938, 1228, 1069 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, minor isomer) δ 1.37 (3H, s), 1.43 (3H, s), 2.00 (1H, ddd, *J* = 14.2, 5.7, 3.5 Hz, H2a), 2.26 (1H, ddd, *J* = 14.3, 5.6, 1.5 Hz, H2b), 3.33 (3H, s), 3.94 (1H, dd, *J* = 8.8, 6.1 Hz, H6a), 4.02 (1H, m, H3), 4.05 (1H, dd, *J* = 8.6, 6.4 Hz, H6b), 4.19 (1H, dd, *J* = 6.6, 4.1 Hz, H4), 4.32 (1H, ddd, *J* = 6.3, 6.3, 6.3 Hz, H5), 5.64 (1H, ddd, *J* = 5.6, 3.0, 3.0 Hz, H1); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, minor isomer) δ 25.3 (CH_3), 26.6 (CH_3), 39.7 (CH_2, C2), 57.2 (CH_3), 66.6 (CH_2, C6), 73.3 (CH, C5), 80.6 (CH, C3), 80.9 (CH, C4), 98.0 (CH, C1) 108.7 (C); ^1H NMR (500 MHz, $CDCl_3$, major isomer) δ 1.37 (3H, s), 1.42 (3H, s), 1.97 (1H, ddd, *J* = 13.9, 5.0, 4.1 Hz, H2a), 2.25 (1H, br d, *J* = 13.9 Hz, H2b), 3.45 (3H, s), 3.71 (1H, d, *J* = 11.3 Hz, OH), 3.85 (1H, dd, *J* = 7.7, 3.6 Hz, H4), 3.96 (1H, m, H3), 4.02 (1H, m, H6a), 4.13 (1H, dd, *J* = 8.7, 6.1 Hz, H6b), 4.37 (1H, ddd, *J* = 7.9, 5.8, 5.8 Hz, H5), 5.36 (1H, dd, *J* = 11.3, 5.0 Hz, H1); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, major isomer) δ 25.4 (CH_3), 26.8 (CH_3), 38.6 (CH_2, C2), 57.8 (CH_3), 67.2 (CH_2, C6), 73.8 (CH, C5), 80.1 (CH, C3), 83.8 (CH, C4), 99.0 (CH, C1), 108.9 (C); MS (ESI^+-TOF) *m*/*z* (%) 241 [$(M + Na)^+$, 100]; HRMS (ESI^+-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{10}H_{18}NaO_5$ 241.1052; found 241.1051. Anal. calcd for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 54.93; H, 8.24.

*1-Deoxy-3-O-formyl-1-iodo-4,5-O-isopropylidene-2-O-methyl-D-arabinitol (**9**).* To a solution of **8** (52 mg, 0.24 mmol) in dry CH_2Cl_2 (3.3 mL) were added $PhI(OAc)_2$ (93.4 mg, 0.29 mmol) and I_2 (61 mg, 0.24 mmol). The reaction mixture was stirred at room temperature for 1.25 h, poured into an aqueous solution of $Na_2S_2O_3$ (10%), and extracted with CH_2Cl_2. The organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by Chromatotron chromatography (hexanes−EtOAc, 8:2) to give **9** (70 mg, 0.20 mmol, 85%) as a colorless oil: $[\alpha]_D$ +11.7 (*c*, 0.97, $CHCl_3$); IR ($CHCl_3$) 1733, 1372, 1226, 1164, 1077 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.36 (3H, s), 1.43 (3H, s), 3.07 (1H, dd, *J* = 10.4, 8.2 Hz, H6a), 3.29 (1H, dd, *J* = 10.4, 5.7 Hz, H6b), 3.52 (3H, s), 3.72 (1H, ddd, *J* = 8.0, 5.6, 2.5 Hz, H3), 3.85 (1H, dd, *J* = 8.8, 5.7 Hz, H2a), 4.02 (1H, dd, *J* = 8.8, 6.0 Hz, H2b), 4.27 (1H, ddd, *J* = 7.6, 6.0, 6.0 Hz, H5), 5.35 (1H, dd, *J* = 7.3, 2.5 Hz, H4), 8.14 (1H, s, CHO); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ 1.6 (CH_2, C2), 25.4 (CH_3), 26.7 (CH_3), 59.3 (CH_3), 66.3 (CH_2, C6), 72.9 (CH, C4), 74.1 (CH, C5), 79.8 (CH, C3), 109.6 (C), 160.1 (CH, CHO); MS (ESI^+-TOF) *m*/*z* (%) 367 [$(M + Na)^+$, 100]; HRMS (ESI^+-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{10}H_{17}INaO_5$

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367.0018; found 367.0018. Anal. calcd for $C_{10}H_{17}IO_5$: C, 34.90; H, 4.98. Found: C, 34.88; H, 5.21.

*1-Deoxy-1-diethoxyphosphoryl-3-O-formyl-4,5-O-isopropylidene-2-O-methyl-D-arabinitol (**10**).* A solution of **9** (311 mg, 0.90 mmol) in $(EtO)_3P$ (8.2 mL, 48 mmol) was stirred at reflux temperature for 3 h. The mixture was concentrated under high vacuum, and the residue was purified by Chromatotron chromatography (hexanes−EtOAc, 3:7 → 2:8) to give compound **10** (248 mg, 0.7 mmol, 78%). Small quantities of alcohol **33** (14 mg, 0.043 mmol, 5%) and cyclized compounds **40** (13 mg, 0.046 mmol, 5%) and **41** (15 mg, 0.054 mmol, 6%) were also obtained (vide infra). Compound **10**: colorless oil, $[\alpha]_D$ +1.6 (*c*, 0.87, $CHCl_3$); IR ($CHCl_3$) 2995, 1733, 1375, 1236, 1167, 1027 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.306 (3H, t, *J* = 6.9 Hz), 1.308 (3H, t, *J* = 6.9 Hz), 1.33 (3H, s), 1.38 (3H, s), 1.91 (1H, ddd, $^2J_{PH}$ = 18.6 Hz, *J* = 15.4, 6.6 Hz, H2a), 2.02 (1H, ddd, $^2J_{PH}$ = 19.2 Hz, *J* = 16.1, 6.3 Hz, H2b), 3.46 (3H, s), 3.83 (1H, dd, *J* = 8.7, 6.1 Hz, H6a), 3.92 (1H, dddd, $^3J_{PH}$ = 9.5 Hz, *J* = 6.6, 6.6, 2.2 Hz, H3), 3.99 (1H, dd, *J* = 8.8, 6.3 Hz, H6b), 4.08 (4H, m), 4.26 (1H, ddd, *J* = 6.2, 6.2, 6.2 Hz, H5), 5.12 (1H, dd, *J* = 6.5, 2.0 Hz, H4), 8.13 (1H, s, CHO); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ 16.30 (CH_3, d, $^3J_{PC}$ = 6.4 Hz), 16.32 (CH_3, d, $^3J_{PC}$ = 6.4 Hz), 25.4 (CH_3), 26.5 (CH_3), 27.6 (CH_2, d, $^1J_{PC}$ = 140.9 Hz, C2), 58.7 (CH_3), 61.7 (CH_2, d, $^2J_{PC}$ = 6.4 Hz), 61.9 (CH_2, d, $^2J_{PC}$ = 6.4 Hz), 66.3 (CH_2, C6), 74.0 (CH, C5), 74.8 (CH, C4), 74.9 (CH, d, $^2J_{PC}$ = 9.5 Hz, C3), 109.3 (C), 160.3 (CH, CHO); $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$) δ 27.5 (P); MS (ESI$^+$-TOF) *m*/*z* (%) 377 [(M + Na)$^+$, 100]; HRMS (ESI$^+$-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{27}NaO_8P$ 377.1341; found 377.1344. Anal. calcd for $C_{14}H_{27}O_8P$: C, 47.44; H, 7.68. Found: C, 47.23; H, 7.40.

*1-Deoxy-1-diethoxyphosphoryl-4,5-O-isopropylidene-2-O-methyl-D-arabinitol (**33**).* A solution of **10** (48 mg, 0.135 mmol) in NaOEt/EtOH 0.011 M (1.1 mL, 0.012 mmol) was stirred at room temperature under nitrogen for 1.25 h. The mixture was concentrated under reduced pressure, and the residue was purified by Chromatotron chromatography (hexanes−EtOAc, 2:98) to give alcohol **33** (34 mg, 0.104 mmol, 77%). Small quantities of cyclized compounds **40** (2.8 mg, 0.01 mmol, 7%) and **41** (1.5 mg, 0.0054 mmol, 4%) were also obtained (vide infra). Compound **33**: colorless oil, $[\alpha]_D$ −21.3 (*c*, 0.92, $CHCl_3$); IR ($CHCl_3$) 3389, 2986, 1373, 1231, 1160, 1072, 1032 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.33 (6H, t, *J* = 7.2 Hz), 1.34 (3H, s), 1.39 (3H, s), 2.14 (1H, ddd, $^2J_{HP}$ = 19.8 Hz, *J* = 15.5, 5.3 Hz, H2a), 2.23 (1H, ddd, $^2J_{HP}$ = 18.3 Hz, *J* = 15.4, 7.6 Hz, H2b), 2.91 (1H, br d, *J* = 8.0 Hz, OH), 3.44 (3H, s), 3.56 (1H, ddd, *J* = 7.8, 7.8, 1.6 Hz, H4), 3.83 (1H, dddd, $^3J_{HP}$ = 12.0 Hz, *J* = 7.5, 5.3, 1.6 Hz, H3), 4.09 (7H, m); ^1H NMR (500 MHz, C_6H_6) δ 1.03 (3H, t, *J* = 6.9 Hz), 1.06 (3H, t, *J* = 6.9 Hz), 1.31 (3H, s), 1.44 (3H, s), 2.12 (1H, ddd, $^2J_{HP}$ = 19.9 Hz, *J* = 15.1, 5.0 Hz, H2a), 2.33 (1H, ddd, $^2J_{HP}$ = 17.8 Hz, *J* = 15.3, 7.9 Hz, H2b), 2.42 (1H, m, OH), 3.26 (3H, s), 3.81 (1H, br dd, *J* = 7.0, 7.0 Hz, H4), 3.90 (4H, m), 3.98 (1H, m, H3), 4.10 (1H, dd, *J* = 8.2, 6.0 Hz, H6a), 4.23 (2H, m, H5 and H6b); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ 16.3 (2 × CH_3, d, $^3J_{PC}$ = 6.4 Hz), 25.4 (CH_3), 26.81 (CH_3), 27.2 (CH_2, d, $^1J_{PC}$ = 137.8 Hz, C2), 58.1 (CH_3), 61.7 (CH_2, d, $^2J_{PC}$ = 7.4 Hz), 61.8 (CH_2, d, $^2J_{PC}$ = 6.4 Hz), 67.3 (CH_2, C6), 74.2 (CH, d, $^2J_{PC}$ = 6.4 Hz, C4), 75.2 (CH, C3), 75.4 (CH, C5), 109.1 (C); $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6) δ 16.4 (2 × CH_3, d, $^3J_{PC}$ = 6.4 Hz), 25.7 (CH_3), 27.2 (CH_3), 27.6 (CH_2, d, *J* = 137.8 Hz, C2), 57.8 (CH_3), 61.5 (CH_2, d, $^2J_{PC}$ = 6.4 Hz), 61.6 (CH_2, d, $^2J_{PC}$ = 6.4 Hz), 68.0 (CH_2, C6), 74.7 (CH, d, $^2J_{PC}$ = 5.3 Hz, C4), 76.0 (CH, C5), 76.1 (CH, C3), 109.3 (C); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 29.16 (1P, s); $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ 42.91 (1P, s); MS (ESI$^+$-TOF) *m*/*z* (%) 349 [(M + Na)$^+$, 100]; HRMS (ESI$^+$-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{27}NaO_7P$ 349.1392; found 349.1395. Anal. calcd for $C_{13}H_{27}O_7P$: C, 47.85; H, 8.34. Found: C, 47.98; H, 7.96.

*(S_P)-1,2-Dideoxy-1-ethoxy-5,6-O-isopropylidene-3-O-methyl-1-oxo-1-phospha-D-arabino-hexofuranose (**40**) and (R_P)-1,2-Dideoxy-1-ethoxy-5,6-O-isopropylidene-3-O-methyl-1-oxo-1-phospha-D-arabino-hexofuranose (**41**).* A solution of **33** (29 mg, 0.089 mmol) and pyridinium *p*-toluenesulfonate (PPTS) (45 mg, 0.18 mmol) in dry $CHCl_3$ (0.8 mL), containing molecular sieves (4 Å powder, 30 mg), was stirred at reflux temperature under nitrogen for 86.5 h. The mixture was poured into brine and extracted with $CHCl_3$, and the residue was purified by Chromatotron chromatography ($CHCl_3$−EtOAc, 30:70) to give the cyclized compounds **40** (1.8 mg, 0.0064 mmol, 7%, 9% brsm) and **41** (10.4 mg, 0.037 mmol, 41%, 52% brsm) while the starting material **33** (6 mg, 0.018 mmol, 20%) was recovered. Compound **40**: colorless oil, $[\alpha]_D$ = −26.8 (*c*, 0.96, $CHCl_3$); IR ($CHCl_3$) 2935, 1373, 1250, 1221, 1077, 1044, 1013 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.33 (3H, t, *J* = 7.1 Hz), 1.36 (3H, s), 1.42 (3H, s), 1.95 (1H, ddd, $^2J_{PH}$ = 15.9 Hz, *J* = 15.9, 5.3 Hz, H2α), 2.24 (1H, ddd, $^2J_{PH}$ = 11.8 Hz, *J* = 15.7, 1.2 Hz, H2β), 3.38 (3H, s), 4.08 (4H, m), 4.18 (2H, m), 4.46 (1H, ddd, *J* = 7.3, 6.3, 5.0 Hz); ^1H NMR (500 MHz, C_6D_6, simulated coupling constants using DAISY) δ 1.02 (3H, t, *J* = 7.0 Hz), 1.22 (3H, s), 1.32 (1H, ddd, $^2J_{PH}$ = 15.9 Hz, *J* = 15.7, 5.7 Hz, H2α), 1.36 (3H, s), 1.80 (1H, ddd, $^2J_{PH}$ = 11.7 Hz, *J* = 15.7, 1.2 Hz, H2β), 2.83 (3H, s), 3.45 (1H, dddd, $^3J_{PH}$ = 28.7 Hz, *J* = 5.7, 3.3, 1.2 Hz, H3), 3.83 (1H, dd, *J* = 7.3, 3.3 Hz, H4), 3.92 (1H, dd, *J* = 9.0, 6.5 Hz, H6a), 3.97 (2H, m), 4.07 (1H, dd, *J* = 9.0, 5.1 Hz, H6b), 4.42 (1H, ddd, *J* = 7.3, 6.5, 5.1 Hz, H5); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ 16.4 (CH_3, d, $^3J_{PC}$ = 5.3 Hz), 25.3 (CH_3), 26.3 (CH_2, d, $^1J_{PC}$ = 124.0 Hz, C2), 26.9 (CH_3), 57.2 (CH_3), 62.4 (CH_2, d, $^2J_{PC}$ = 6.4 Hz), 66.6 (CH_2, C6), 73.1 (CH, d, $^3J_{PC}$ = 11.7 Hz, C5), 77.6 (CH, C3), 81.6 (CH, d, $^2J_{PC}$ = 7.4 Hz, C4), 109.4 (C); $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6) δ 16.5 (CH_3, d, $^3J_{PC}$ = 5.3 Hz), 25.3 (CH_3), 26.2 (CH_2, d, $^1J_{PC}$ = 122.9 Hz, C2), 27.0 (CH_3), 56.6 (CH_3), 61.9 (CH_2, d, $^2J_{PC}$ = 6.4 Hz), 66.9 (CH_2, C6), 73.6 (CH, d, $^3J_{PC}$ = 11.7 Hz, C5), 77.9 (CH, C3), 81.7 (CH, d, $^2J_{PC}$ = 7.4 Hz, C4), 109.2 (C); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 45.02 (1P, s); $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ 57.0 (1P, s); MS (ESI$^+$-TOF) *m*/*z* (%) 303 [(M + Na)$^+$, 100]; HRMS (ESI$^+$-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{21}NaO_6P$ 303.0973; found 303.0970. Anal. calcd for $C_{11}H_{21}O_6P$: C, 47.14; H, 7.55. Found: C, 47.16; H, 7.24. Compound **41**: colorless oil, $[\alpha]_D$ = −49.5 (*c*, 0.98, $CHCl_3$); IR ($CHCl_3$) 2934, 1375, 1252, 1160, 1077, 1046, 1013 cm^{-1}; ^1H NMR (500 MHz, C_6D_6, simulated coupling constants using DAISY) δ 1.01 (3H, t, *J* = 7.1 Hz), 1.23 (3H, s), 1.36 (3H, s), 1.53 (1H, ddd, $^2J_{PH}$ = 16.7 Hz, *J* = 16.0, 5.3 Hz, H2α), 1.67 (1H, ddd, $^2J_{PH}$ = 10.6 Hz, *J* = 16.0, 0.9 Hz, H2β), 2.79 (3H, s), 3.40 (1H, dddd, $^3J_{PH}$ = 30.7 Hz, *J* = 5.3, 4.1, 0.9 Hz, H3), 3.93 (1H, dd, *J* = 8.8, 6.9 Hz, H6a), 3.97 (2H, m, CH_2-P), 3.97 (1H, dd, *J* = 7.0, 4.1 Hz, H4), 4.04 (1H, dd, *J* = 8.8, 5.3 Hz, H6b), 4.32 (1H, ddd, *J* = 7.0, 6.9, 5.3 Hz, H5); $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6) δ 16.5 (CH_3, d, $^3J_{PC}$ = 5.3 Hz), 25.4 (CH_3), 26.1 (CH_2, d, $^1J_{PC}$ = 121.9 Hz, C2), 27.0 (CH_3), 56.6 (CH_3), 62.5 (CH_2, d, $^2J_{PC}$ = 6.4 Hz), 66.9 (CH_2, C6), 73.6 (CH, d, $^3J_{PC}$ = 10.6 Hz, C5), 78.3 (CH, C3), 82.1 (CH, d, $^2J_{PC}$ = 8.5 Hz, C4), 109.3 (C); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 45.4 (1P, s); $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ 57.3 (1P, s); MS (ESI$^+$-TOF) *m*/*z* (%) 303 [(M + Na)$^+$, 100]; HRMS (ESI$^+$-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{21}NaO_6P$ 303.0973; found 303.0981. Anal. calcd for $C_{11}H_{21}O_6P$: C, 47.14; H, 7.55. Found: C, 47.20; H, 7.38.

*(S_P)-1-Deoxy-1-ethoxyphenylphosphoryl-3-O-formyl-4,5-O-isopropylidene-2-O-methyl-D-arabinitol (**11**) and (R_P)-1-Deoxy-1-ethoxyphenylphosphoryl-3-O-formyl-4,5-O-isopropylidene-2-O-methyl-D-arabinitol (**12**).* A solution of **9** (61 mg, 0.177 mmol) in $PhP(OEt)_2$ (360 μL, 1.87 mmol) was stirred at 150 °C for 6 h under nitrogen. The mixture was concentrated under high vacuum, and the residue was purified by Chromatotron chromatography (toluene−EtOAc, 30:70) to give a mixture of *P*-isomers (49.6 mg, 0.128 mmol, 1:1, 72%), which was separated by HPLC: Nucleosil 100-5 chiral-3, 250 mm × 4 mm, *n*-hexane−EtOAc, 40:60, 0.65 mL/min, **12** at 25 min (22 mg, 0.057 mmol, 32%), **11** at 31 min (23.5 mg, 0.061 mmol, 34%). Compound **12**: colorless oil, $[\alpha]_D$ = +24.9 (*c*, 0.94, $CHCl_3$); IR ($CHCl_3$) 3017, 1730, 1228, 1170, 1123, 1075, 1036 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.28 (3H, t, *J* = 6.9 Hz), 1.35 (3H, s), 1.41 (3H, s), 2.15 (2H, dd, $^2J_{PH}$ = 14.8 Hz, *J* = 6.6 Hz, H2), 3.29 (3H, s), 3.80 (1H, m), 3.85 (1H, dd, *J* = 8.7, 6.1 Hz, H6a), 4.01 (1H, dd, *J* = 8.7, 6.1 Hz, H6b), 4.06 (2H, m), 4.27 (1H, ddd, *J* = 6.5, 6.5, 6.5 Hz, H5), 5.19 (1H, dd, *J* = 6.6, 2.2 Hz, H4), 7.50 (2H, m), 7.56 (1H, m), 7.78 (2H, m), 8.17 (1H, s, CHO); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ 16.4 (CH_3, d, $^3J_{PC}$ = 7.4 Hz), 25.4 (CH_3), 26.54 (CH_3), 31.7 (CH_2, d,

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$^1J_{PC}$ = 100.7 Hz, C2), 58.7 (CH_3), 60.9 (CH_2, d, $^2J_{PC}$ = 6.4 Hz), 66.3 (CH_2, C6), 74.0 (CH, C5), 74.5 (CH, C3), 75.5 (CH, d, $^3J_{PC}$ = 8.5 Hz, C4), 109.4 (C), 128.7 (2 × CH, $^3J_{PC}$ = 12.7 Hz, C-*meta*), 131.5 (2 × CH, d, $^2J_{PC}$ = 9.5 Hz, C-*ortho*), 132.4 (CH, d, $^4J_{PC}$ = 3.2 Hz, C-*para*), 160.5 (CH, CHO), (the C-*ipso* is not observed); ^{1}H NMR (500 MHz, C_6D_6) δ 0.96 (3H, t, J = 7.1 Hz), 1.24 (3H, s), 1.37 (3H, s), 2.08 (1H, ddd, $^2J_{PH}$ = 12.0 Hz, J = 15.4, 6.9 Hz, H2a), 2.21 (1H, ddd, $^2J_{PH}$ = 16.7 Hz, J = 15.1, 6.0 Hz, H2b), 3.10 (3H, s), 3.52 (1H, m), 3.79 (1H, dd, J = 8.7, 6.1 Hz, H6a), 3.84 (1H, m), 3.90 (1H, dd, J = 8.5, 6.0 Hz, H6b), 4.14 (1H, m, H3), 4.16 (1H, ddd, J = 6.3, 6.3, 6.3 Hz, H5), 5.37 (1H, dd, J = 6.5, 3.0 Hz, H4), 7.07 (3H, m), 7.68 (1H, s, CHO), 7.79 (2H, m); $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6) δ = 16.3 (CH_3, d, $^3J_{PC}$ = 6.4 Hz), 25.6 (CH_3), 26.7 (CH_3), 31.9 (CH_2, d, $^1J_{PC}$ = 102.8 Hz, C2), 58.2 (CH_3), 60.6 (CH_2, d, $^2J_{PC}$ = 6.4 Hz), 66.4 (CH_2, C6), 74.7 (CH, C3 or C5), 75.1 (CH, C5 or C3), 75.7 (CH, d, $^3J_{PC}$ = 8.5 Hz, C4), 109.3 (C), 128.6 (2 × CH, d, $^3J_{PC}$ = 11.7 Hz, C-*meta*), 131.9 (2 × CH, d, $^2J_{PC}$ = 9.5 Hz, C-*ortho*), 132.0 (CH, d, $^4J_{PC}$ = 2.1 Hz, C-*para*), 132.7 (C, d, $^1J_{PC}$ = 124.0 Hz, C-*ipso*), 160.5 (CH, CHO); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 40.9 (1P, s); $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ 52.5 (1P, s); MS (ESI$^+$-TOF) m/z (%) 409 [$(M + Na)^+$, 100]; HRMS (ESI$^+$-TOF) m/z $[M + Na]^+$ calcd for $C_{18}H_{27}NaO_7P$ 409.1392; found 409.1392. Anal. calcd for $C_{18}H_{27}O_7P$: C, 55.95; H, 7.04. Found: C, 55.71; H, 7.15. Compound **11**: colorless oil, $[\alpha]_D$ = −9.8 (*c*, 0.89, $CHCl_3$); IR ($CHCl_3$) 3024, 1729, 1439, 1373, 1228, 1203, 1172, 1035 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.30 (3H, t, J = 6.9 Hz), 1.33 (3H, s), 1.34 (3H, s), 2.04 (1H, ddd, $^2J_{PH}$ = 12.2 Hz, J = 15.4, 5.5 Hz, H2a), 2.25 (1H, ddd, $^2J_{PH}$ = 15.9 Hz, J = 15.9, 6.9 Hz, H2b), 3.47 (3H, s), 3.80 (1H, dd, J = 8.5, 6.3 Hz, H6a), 3.87 (1H, m), 3.99 (1H, dd, J = 8.8, 6.3 Hz, H6b), 4.01 (1H, m, H3), 4.09 (1H, m), 4.26 (1H, ddd, J = 6.3, 6.3, 6.3 Hz, H5), 5.00 (1H, dd, J = 6.5, 1.7 Hz, H4), 7.50 (2H, m), 7.57 (1H, m), 7.79 (2H, m), 8.05 (1H, s, CHO); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ 16.4 (CH_3, d, $^3J_{PC}$ = 7.4 Hz), 25.4 (CH_3), 26.5 (CH_3), 32.0 (CH_2, d, $^1J_{PC}$ = 100.7 Hz, C2), 58.7 (CH_3), 61.0 (CH_2, d, $^2J_{PC}$ = 6.4 Hz), 66.2 (CH_2, C6), 74.0 (CH, C5), 74.2 (CH, C3), 75.5 (CH, d, $^3J_{PC}$ = 8.5 Hz, C4), 109.3 (C), 128.8 (2 × CH, d, $^3J_{PC}$ = 12.7 Hz, C-*meta*), 131.5 (2 × CH, d, $^2J_{PC}$ = 10.6 Hz, C-*ortho*), 132.6 (CH, d, $^4J_{PC}$ = 3.2 Hz, C-*para*), 160.4 (CH, CHO) (the C-*ipso* is not observed); ^{1}H NMR (500 MHz, C_6D_6) δ 0.97 (3H, t, J = 7.3 Hz), 1.22 (3H, s), 1.29 (3H, s), 2.06 (1H, ddd, $^2J_{PH}$ = 11.7 Hz, J = 15.8, 5.7 Hz, H2a), 2.26 (1H, ddd, $^2J_{PH}$ = 16.1 Hz, J = 16.1, 6.3 Hz, H2b), 3.29 (3H, s), 3.57 (1H, m), 3.76 (1H, dd, J = 8.5, 6.6 Hz, H6a), 3.84 (1H, dd, J = 8.2, 6.6 Hz, H6b), 3.90 (1H, m), 4.05 (1H, m, H3), 4.15 (1H, ddd, J = 6.2, 6.2, 6.2 Hz, H5), 5.16 (1H, dd, J = 6.0, 2.5 Hz, H4), 7.07 (3H, m), 7.57 (1H, s, CHO), 7.78 (2H, m); ^{1}H NMR (500 MHz, C_6D_6, 60 °C, simulated coupling constants using DAISY) δ 1.01 (3H, t, J = 6.9 Hz), 1.23 (3H, s), 1.29 (3H, s), 2.10 (1H, ddd, $^2J_{PH}$ = 11.5 Hz, J = 15.3, 6.0 Hz, H2a), 2.25 (1H, ddd, $^2J_{PH}$ = 17.2 Hz, J = 15.3, 6.3 Hz, H2b), 3.30 (3H, s), 3.65 (1H, m), 3.79 (1H, dd, J = 8.6, 6.3 Hz, H6a), 3.83 (1H, dd, J = 8.6, 6.3 Hz, H6b), 3.92 (1H, m), 4.03 (1H, dddd, $^3J_{PH}$ = 11.1 Hz, J = 6.3, 6.0, 3.1 Hz, H3), 4.17 (1H, ddd, J = 6.3, 6.3, 6.2 Hz, H5), 5.15 (1H, dd, J = 6.3, 3.1 Hz, H4), 7.10 (3H, m), 7.64 (1H, s, CHO), 7.78 (2H, m); $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6) δ 16.4 (CH_3, d, $^3J_{PC}$ = 6.4 Hz), 25.6 (CH_3), 26.6 (CH_3), 32.1 (CH_2, d, $^1J_{PC}$ = 98.5 Hz, C2), 58.1 (CH_3), 60.6 (CH_2, d, $^2J_{PC}$ = 7.4 Hz), 66.4 (CH_2, C6), 74.7 (CH, C5), 74.8 (CH, C3), 75.7 (CH, d, $^3J_{PC}$ = 8.5 Hz, C4), 109.3 (C), 128.8 (2 × CH, d, $^3J_{PC}$ = 12.7 Hz, C-*meta*), 131.9 (2 × CH, d, $^2J_{PC}$ = 9.5 Hz, C-*ortho*), 132.2 (CH, br. s., C-*para*), 160.5 (CH, CHO), (the C-*ipso* is not observed); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 40.5 (1P, s); $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ 52.3 (1P, s); MS (ESI$^+$-TOF) m/z (%) 409 [$(M + Na)^+$, 100]; HRMS (ESI$^+$-TOF) m/z $[M + Na]^+$ calcd for $C_{18}H_{27}NaO_7P$ 409.1392; found 409.1399. Anal. calcd for $C_{18}H_{27}O_7P$: C, 55.95; H, 7.04. Found: C, 55.83; H, 7.15.

*(S_p)-1-Deoxy-1-ethoxyphenylphosphoryl-4,5-O-isopropylidene-2-O-methyl-D-arabinitol (**34**).* A solution of **11** (7.5 mg, 0.019 mmol) in NaOEt/EtOH 0.011 M (160 μL, 1.65 × 10^{-3} mmol) was stirred at room temperature under nitrogen for 1.25 h. The organic extracts were concentrated under reduced pressure, and the residue was purified by purified by Chromatotron chromatography ($CHCl_3$− EtOAc, 30:70) to give alcohol **34** (3.2 mg, 0.009 mmol, 46%), and a small amount of the cyclized compound **42** (0.5 mg, 0.0016 mmol, 8%) is also obtained (vide infra). Compound **34**: colorless oil, ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.30 (3H, t, J = 7.1 Hz), 1.34 (3H, s), 1.38 (3H, s), 2.33−2−38 (2H, m, H2), 3.29 (3H, s), 3.42 (1H, d, J = 6.9 Hz, OH), 3.56 (1H, ddd, J = 7.6, 7.6, 1.6 Hz, H4), 3.82−3.87 (1H, m), 3.87−3.93 (1H, m, H3), 3.96−4.01 (1H, m, H6a), 4.05−4.14 (3H, m, H5, H6b, P-O-CH_2), 7.45−7.53 (2H, m), 7.54−7.60 (1H, m), 7.77−7.85 (2H, m); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ 16.4 (CH_3, d, $^3J_{PC}$ = 6.4 Hz), 25.5 (CH_3), 26.9 (CH_3), 31.7 (CH_2, d, J = 98.5 Hz, C2), 57.9 (CH_3), 60.9 (CH_2, d, $^2J_{PC}$ = 6.4 Hz), 67.5 (CH_2, C6), 74.7 (CH, d, J = 4.2 Hz, C4), 75.3 (CH), 75.4 (CH), 109.1 (C), 128.7 (2 × CH, d, $^3J_{PC}$ = 12.7 Hz, C-*meta*), 131.6 (2 × CH, d, $^2J_{PC}$ = 9.5 Hz, C-*ortho*), 132.5 (CH, d, $^4J_{PC}$ = 4.2 Hz, C-*para*), (the C-*ipso* is not observed); ^{1}H NMR (500 MHz, C_6D_6) δ 0.96 (3H, t, J = 7.1 Hz), 1.31 (3H, s), 1.44 (3H, s), 2.22 (1H, ddd, $^2J_{PH}$ = 17.0 Hz, J = 15.4, 4.4 Hz, H2a), 2.32 (1H, ddd, $^2J_{PH}$ = 11.3 Hz, J = 15.4, 8.2 Hz, H2b), 3.08 (3H, s), 3.48−3.57 (1H, m), 3.75 (1H, br dd, J = 6.9, 6.9 Hz, H4), 3.82−3.88 (1H, m), 3.90 (1H, br d, J = 6.9 Hz, OH), 4.04 (1H, dddd, $^3J_{PH}$ = 12.6 Hz, J = 7.9, 4.4, 1.6 Hz, H3), 4.08 (1H, dd, J = 8.2, 6.0 Hz, H6a), 4.19 (1H, dd, J = 8.5, 5.0 Hz, H6b), 4.24 (1H, ddd, J = 8.4, 5.8, 5.8 Hz, H5), 6.98−7.09 (3H, m), 7.70−7.77 (2H, m); $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6) δ 16.3 (CH_3, d, $^3J_{PC}$ = 5.3 Hz), 25.6 (CH_3), 27.2 (CH_3), 31.8 (CH_2, d, $^1J_{PC}$ = 95.4 Hz, C2), 57.4 (CH_3), 60.5 (CH_2, d, $^2J_{PC}$ = 5.3 Hz), 68.0 (CH_2, C6), 75.3 (CH, d, $^3J_{PC}$ = 4.2 Hz, C4), 75.9 (CH), 76.0 (CH), 109.1 (C), 128.5 (2 × CH, d, $^3J_{PC}$ = 12.7 Hz, C-*meta*), 131.9 (2 × CH, d, $^2J_{PC}$ = 9.5 Hz, C-*ortho*), 132.0 (CH, d, $^4J_{PC}$ = 2.1 Hz, C-*para*), (the C-*ipso* is not observed); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 42.6 (1P, s); $^{31}P\{^1H\}$ NMR (202.5 MHz, C_6D_6) δ 54.9 (1P, s); MS (ESI$^+$-TOF) m/z (%) 381 [$(M + Na)^+$, 100]; HRMS (ESI$^+$-TOF) m/z $[M + Na]^+$ calcd for $C_{17}H_{27}NaO_6P$ 381.1443; found 381.1443.

*(R_p)-1-Deoxy-1-ethoxyphenylphosphoryl-4,5-O-isopropylidene-2-O-methyl-D-arabinitol (**35**).* A solution of **12** (6.8 mg, 0.018 mmol) in NaOEt/EtOH 0.011 M (150 μL, 1.65 × 10^{-3} mmol) was stirred at room temperature under nitrogen for 1.25 h. The organic extracts were concentrated under reduced pressure, and the residue was purified by Chromatotron chromatography (hexanes−EtOAc, 5:95) to give alcohol **35** (3.3 mg, 0.0092 mmol, 52%), and a small amount of the cyclized compound **43** (0.5 mg, 0.0016 mmol, 9%) is also obtained (vide infra). Compound **35**: colorless oil, ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.29 (3H, t, J = 7.1 Hz), 1.33 (3H, s), 1.35 (3H, s), 2.26 (1H, ddd, $^2J_{PH}$ = 12.5 Hz, J = 15.4, 5.5 Hz, H2a), 2.44 (1H, ddd, $^2J_{PH}$ = 17.5 Hz, J = 15.3, 7.6 Hz, H2b), 2.99 (1H, br d, J = 7.9 Hz, OH), 3.32 (3H, s), 3.58 (1H, br dd, J = 7.9, 7.9 Hz, H4), 3.84 (2H, m, H3, P-O-CH_2), 4.00 (1H, m, H6), 4.08 (3H, m, H6, P-O-CH_2, C5), 7.51 (2H, m), 7.57 (1H, m), 7.80 (2H, m); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ 16.4 (CH_3, d, $^3J_{PC}$ = 6.4 Hz), 25.5 (CH_3), 26.9 (CH_3), 31.4 (CH_2, d, $^1J_{PC}$ = 99.6 Hz, C2), 58.1 (CH_3), 60.8 (CH_2, d, $^2J_{PC}$ = 6.4 Hz), 67.4 (CH_2, C6), 74.6 (CH, d, $^3J_{PC}$ = 5.3 Hz, C4), 75.0 (CH, C3), 75.5 (CH, C5), 109.2 (C), 128.7 (2 × CH, d, $^3J_{PC}$ = 12.7 Hz, C-*meta*), 131.5 (2 × CH, d, $^2J_{PC}$ = 10.6 Hz, C-*ortho*), 132.4 (CH, d, $^4J_{PC}$ = 3.2 Hz, C-*para*) (the C-*ipso* is not observed); ^{1}H NMR (500 MHz, C_6D_6) δ 0.93 (3H, t, J = 7.1 Hz), 1.28 (3H, s), 1.40 (3H, s), 2.11 (1H, ddd, $^2J_{PH}$ = 12.3 Hz, J = 15.1, 5.0 Hz, H2a), 2.48 (1H, ddd, $^2J_{PH}$ = 17.8 Hz, J = 15.1, 8.0 Hz, H2b), 3.12 (3H, s), 3.40 (1H, br d, J = 7.3 Hz, OH), 3.56 (1H, ddq, $^2J_{PH}$ = 8.2 Hz, J = 10.1, 6.9, 6.9, 6.9 Hz), 3.79 (1H, br dd, J = 7.1, 7.1 Hz, H4), 3.85 (1H, ddq, $^2J_{PH}$ = 7.9 Hz, J = 10.1, 6.9, 6.9, 6.9 Hz), 3.94 (1H, dddd, $^3J_{PH}$ = 10.8 Hz, J = 7.9, 4.9, 1.9 Hz, H3), 4.04 (1H, dd, J = 8.0, 5.5 Hz, H6a), 4.16 (1H, ddd, J = 8.2, 5.4, 5.4 Hz, H5), 4.19 (1H, dd, J = 7.9, 4.7 Hz, H6b), 7.08 (3H, m), 7.76 (2H, m); $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6) δ = 16.4 (CH_3, d, $^3J_{PC}$ = 6.4 Hz), 25.7 (CH_3), 27.2 (CH_3), 31.6 (CH_2, d, $^1J_{PC}$ = 99.6 Hz, C2), 57.7 (CH_3), 60.6 (CH_2, d, $^2J_{PC}$ = 6.4 Hz), 68.0 (CH_2, C6), 75.1 (CH, d, $^3J_{PC}$ = 4.2 Hz, C4), 75.8 (CH), 76.0 (CH), 109.3 (C), 128.7 (2 × CH, d, $^3J_{PC}$ = 12.7 Hz, C-*meta*), 131.8 (2 × CH, d, $^2J_{PC}$ = 9.5 Hz, C-*ortho*), 132.1 (CH, d, $^4J_{PC}$ = 2.1 Hz, C-*para*) (the C-*ipso* is not observed); $^{31}P\{^1H\}$ NMR (162 MHz,

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$CDCl_3$) δ 42.0 (1P, s); $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ 54.1 (1P, s); MS (ESI$^+$-TOF) m/z (%) 381 [(M + Na)$^+$, 100]; HRMS (ESI$^+$-TOF) m/z [M + Na]$^+$ calcd for $C_{17}H_{27}NaO_6P$ 381.1443; found 381.1439.

*(R_P)-1,2-Dideoxy-1-phenyl-5,6-O-isopropylidene-3-O-methyl-1-oxo-1-phospha-D-arabino-hexofuranose (**42**).* To a solution of **34** (12.5 mg, 0.035 mmol) in dry $CHCl_3$ (0.4 mL) were added molecular sieves (4 Å powder, 10 mg) and PPTS (20 mg, 0.08 mmol) under nitrogen. The mixture was stirred at reflux temperature for 90 h and then filtered, poured into brine, and exhaustively extracted with $CHCl_3$. The organic extract was concentrated under reduced pressure, and the residue was purified by Chromatotron chromatography (hexanes−EtOAc, 5:95) to give the cyclized compounds **42** (10 mg, 0.032 mmol, 92%). Compound **42**: colorless oil, $[\alpha]_D$ = −44.3 (*c*, 0.98, $CHCl_3$); IR ($CHCl_3$) 2933, 1372, 1228, 1157, 1121, 1072, 1043, 1008 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, simulated coupling constants using DAISY) δ 1.38 (3H, s), 1.43 (3H, s), 2.33 (1H, ddd, $^2J_{PH}$ = 19.3 Hz, J = 16.4, 5.1 Hz, H2α), 2.46 (1H, ddd, $^2J_{PH}$ = 1.9 Hz, J = 16.4, 0.9 Hz, H2β), 3.38 (3H, s), 4.10 (1H, dd, J = 8.9, 4.3 Hz, H6a), 4.13 (1H, dd, J = 8.9, 6.1 Hz, H6b), 4.25 (1H, dddd, $^3J_{PH}$ = 27.3 Hz, J = 5.1, 2.8, 0.9 Hz, H3), 4.50 (1H, dd, J = 8.0, 2.8 Hz, H4), 4.52 (1H, ddd, J = 8.0, 6.1, 4.3 Hz, H5), 7.45−7.50 (2H, m), 7.54−7.59 (1H, m), 7.88−7.95 (2H, m); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ 25.4 (CH_3), 26.9 (CH_3), 32.7 (CH_2, d, $^1J_{PC}$ = 81.6 Hz, C2), 57.0 (CH_3), 67.1 (CH_2, C6), 72.8 (CH, d, J_{PC} = 11.7 Hz), 79.5 (CH, C3), 84.4 (CH, d, J_{PC} = 3.2 Hz), 109.6 (C), 128.4 (2 × CH, d, $^3J_{PC}$ = 14.8 Hz, C-*meta*), 129.8 (CH, d, $^1J_{PC}$ = 134.6 Hz, C-*ipso*), 132.4 (2 × CH, d, $^2J_{PC}$ = 11.7 Hz, C-*ortho*), 132.8 (CH, d, $^4J_{PC}$ = 3.2 Hz, C-*para*); ^1H NMR (500 MHz, C_6D_6) δ 1.23 (3H, s), 1.32 (3H, s), 1.87 (1H, ddd, $^2J_{PH}$ = 2.5 Hz, J = 16.1, 0.0 Hz, H2β), 1.93 (1H, ddd, $^2J_{PH}$ = 16.1 Hz, J = 16.1, 4.7 Hz, H2α), 2.78 (3H, s), 3.58 (1H, dddd, $^3J_{PH}$ = 25.5 Hz, J = 3.5, 3.5, 0.0, H3), 3.89 (1H, dd, J = 9.0, 6.1 Hz, H6a), 3.98 (1H, dd, J = 8.8, 5.0 Hz, H6b), 4.27 (1H, dd, J = 8.2, 2.8 Hz, H4), 4.41 (1H, ddd, J = 7.9, 5.7, 5.7 Hz, H5), 7.09 (4H, m), 8.15 (2H, m); $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6) δ 25.5 (CH_3), 27.0 (CH_3), 32.8 (CH_2, d, $^1J_{PC}$ = 80.5 Hz, C2), 56.5 (CH_3), 67.4 (CH_2, C6), 73.3 (CH, d, $^3J_{PC}$ = 12.7 Hz, C5), 79.9 (CH, C3), 84.5 (CH, d, $^2J_{PC}$ = 4.2 Hz, C4), 109.4 (C), 128.5 (2 × CH, d, $^3J_{PC}$ = 12.7 Hz, C-*meta*), 132.4 (CH, d, $^4J_{PC}$ = 3.2 Hz, C-*para*), 132.9 (2 × CH, d, $^2J_{PC}$ = 11.7 Hz, C-*ortho*), (the C-*ipso* is not observed); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 57.7 (1P, s); $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ 68.1 (1P, s); MS (ESI$^+$-TOF) m/z (%) 335 [(M + Na)$^+$, 100]; HRMS (ESI$^+$-TOF) m/z [M + Na]$^+$ calcd for $C_{15}H_{21}NaO_5P$ 335.1024; found 335.1018. Anal. calcd for $C_{15}H_{21}O_5P$: C, 57.69; H, 6.78. Found: C, 57.79; H, 6.95.

*(S_P)-1,2-Dideoxy-1-phenyl-5,6-O-isopropylidene-3-O-methyl-1-oxo-1-phospha-D-arabino-hexofuranose (**43**).* To a solution of **35** (13.7 mg, 0.038 mmol) in dry $CHCl_3$ (0.4 mL) were added molecular sieves (4 Å powder, 10 mg) and PPTS (22 mg, 0.088 mmol) under nitrogen. The mixture was stirred at reflux temperature for 94 h and then filtered, poured into brine, and exhaustively extracted with $CHCl_3$. The organic extract was concentrated under reduced pressure, and the residue was purified by Chromatotron chromatography (hexanes−EtOAc, 5:95) to give the cyclized compounds **43** (8.2 mg, 0.026 mmol, 69%). Compound **43**: colorless oil, $[\alpha]_D$ = −33.8 (*c*, 0.48, $CHCl_3$); IR ($CHCl_3$) 2929, 1373, 1230, 1122, 1074, 1012 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.39 (3H, s), 1.45 (3H, s), 2.01 (1H, ddd, $^2J_{PH}$ = 6.9 Hz, J = 15.5, 4.7 Hz, H2α), 2.60 (1H, ddd, $^2J_{PH}$ = 9.7 Hz, J = 15.4, 1.3 Hz, H2β), 3.48 (3H, s), 4.18 (2H, m), 4.23 (1H, m), 4.27 (1H, m), 4.64 (1H, ddd, J = 7.4, 5.4, 5.4 Hz), 7.50 (2H, m), 7.57 (1H, m), 7.76 (2H, m); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ 25.3 (CH_3), 26.9 (CH_3), 31.8 (CH_2, d, $^1J_{PC}$ = 83.7 Hz, C2), 57.5 (CH_3), 66.8 (CH_2, C6), 73.4 (CH, d, J_{PC} = 6.4 Hz), 77.5 (CH), 86.1 (CH, d, J = 3.2 Hz), 109.4 (C), 128.8 (2 × CH, d, $^3J_{PC}$ = 13.8 Hz, C-*meta*), 131.3 (2 × CH, d, $^2J_{PC}$ = 10.6 Hz, C-*ortho*), 132.7 (CH, d, $^4J_{PC}$ = 2.1 Hz, C-*para*), (the C-*ipso* is not observed); ^1H NMR (500 MHz, C_6D_6, simulated coupling constants using DAISY) δ 1.23 (1H, ddd, $^2J_{PH}$ = 6.5 Hz, J = 15.6, 4.9 Hz, H2α), 1.26 (3H, s), 1.42 (3H, s), 2.09 (1H, ddd, $^2J_{PH}$ = 9.5 Hz, J = 15.6, 1.4 Hz, H2β), 2.99 (3H, s), 3.60 (1H, dddd, $^3J_{PH}$ = 26.0 Hz, J = 4.9, 3.6, 1.4 Hz, H3), 3.97 (1H, dd, J = 9.0, 6.4 Hz, H6a), 4.03 (1H, ddd, $^3J_{PH}$ = 2.8 Hz, J = 7.1, 3.6 Hz, H4), 4.18 (1H, dd, J = 9.0, 5.2 Hz, H6b), 4.57 (1H, ddd, J = 7.1, 6.4, 5.2 Hz, H5), 7.05 (3H, m), 7.70 (2H, m); $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6) δ 25.2 (CH_3), 27.1 (CH_3), 31.1 (CH_2, d, $^1J_{PC}$ = 89.0 Hz, C2), 56.8 (CH_3), 67.0 (CH_2, C6), 73.9 (CH, d, J_{PC} = 6.4 Hz, C5), 77.8 (CH, C3), 86.2 (CH, d, J = 3.2 Hz, C4), 109.2 (C), 128.7 (2 × CH, d, $^3J_{PC}$ = 13.8 Hz, C-*meta*), 131.7 (2 × CH, d, $^2J_{PC}$ = 9.5 Hz, C-*ortho*), 132.2 (CH, d, $^4J_{PC}$ = 2.1 Hz, C-*para*), (the C-*ipso* is not observed); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 53.7 (1P, s); $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ 63.5 (1P, s); MS (ESI$^+$-TOF) m/z (%) 335 [(M + Na)$^+$, 100]; HRMS (ESI$^+$-TOF) m/z [M + Na]$^+$ calcd for $C_{15}H_{21}NaO_5P$ 335.1024; found 335.1026.

*(R_P)-1,2-Dideoxy-1-phenyl-5,6-O-isopropylidene-3-O-methyl-1-oxo-1-phospha-D-arabino-hexofuranose (**42**) and (S_P)-1,2-Dideoxy-1-phenyl-5,6-O-isopropylidene-3-O-methyl-1-oxo-1-phospha-D-arabino-hexofuranose (**43**).* A solution of iodine **9** (67 mg, 0.195 mmol) in $PhP(OEt)_2$ (225 μL, 1.17 mmol) was stirred at 120 °C for 68 h under nitrogen. The mixture was concentrated under high vacuum, and the residue was purified by Chromatotron chromatography (toluene−EtOAc, 20:80) to give a mixture of the cyclized compounds **42** and **43** (22.4 mg, 0.072 mmol, 60:40, 37%).

*3,6-Di-O-benzyl-2-deoxy-4-O-(2,3,4,6-tetra-O-benzyl-β-D-galactopyranosyl)-D-arabino-hexopyranose (**14**).*[36] A solution of lactal 13[37] (401 mg, 0.473 mmol) in THF (10.3 mL) containing water (206 μL, 11.4 mmol) and $Ph_3P{\cdot}HBr$ (43.8 mg, 0.127 mmol) was stirred at reflux temperature for 2 h. The reaction mixture was then poured into a saturated solution of $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic extracts were washed with a saturated solution of $NaHCO_3$, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexanes−EtOAc, 70:30) to give the anomeric mixture 14 (329 mg, 0.379 mmol, 80%) as a colorless oil.

*2,5-Di-O-benzyl-1-deoxy-4-O-formyl-1-iodo-3-O-(2,3,4,6-tetra-O-benzyl-β-D-galactopyranosyl)-D-arabinitol (**15**).* A solution of the alcohol **14** (329 mg, 0.38 mmol) in CH_2Cl_2 (9.5 mL) containing $PhI(OAc)_2$ (134.5 mg, 0.418 mmol) and I_2 (106 mg, 0.417 mmol) under nitrogen was irradiated with a 80 W tungsten-filament lamp at room temperature for 2 h. The reaction mixture was then poured into 10% aqueous $Na_2S_2O_3$, extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated. The residue was purified by Chromatotron chromatography (hexanes−EtOAc, 70:30) to give compound **15** (283 mg, 0.285 mmol, 75%) as a colorless oil: $[\alpha]_D$ −11.3 (*c*, 0.62, $CHCl_3$); IR ($CHCl_3$) 2870, 1725, 1098, 1070 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 3.34 (1H, dd, J = 10.0, 5.2 Hz, H2a), 3.39 (1H, dd, J = 9.8, 3.1 Hz, H3′), 3.43 (1H, ddd, J = 8.0, 5.2, 0.9 Hz, H5′), 3.62 (1H, dd, J = 9.8, 8.0 Hz, H2b), 3.64 (1H, dd, J = 11.2, 2.5 Hz, H6a), 3.65 (1H, dd, J = 8.1, 8.1 Hz, H6′a), 3.71 (1H, dd, J = 9.1, 5.4 Hz, H6′b), 3.78 (1H, dd, J = 9.8, 7.8 Hz, H2′), 3.83 (1H, dd, J = 11.2, 4.6 Hz, H6b), 3.85 (1H, ddd, J = 7.8, 5.2, 2.3 Hz, H3), 3.90 (1H, dd, J = 2.9, 0.9 Hz, H4′), 4.25 (1H, d, J = 12.0 Hz), 4.28 (1H, dd, J = 7.8, 2.2 Hz, H4), 4.32 (1H, d, J = 12.0 Hz), 4.36 (1H, d, J = 7.8 Hz, H1′), 4.41 (1H, d, J = 11.7 Hz), 4.44 (1H, d, J = 11.4 Hz), 4.45 (1H, d, J = 11.7 Hz), 4.57 (1H, d, J = 11.7 Hz), 4.65 (1H, d, J = 11.4 Hz), 4.69 (2H, s), 4.76 (1H, d, J = 11.2 Hz), 4.80 (1H, d, J = 11.4 Hz), 4.90 (1H, d, J = 11.7 Hz), 5.22 (1H, dddd, J = 7.5, 4.2, 2.3, 0.5 Hz, H5), 7.28 (30H, m), 7.84 (1H, d, J = 0.8 Hz, CHO); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ_C 4.5 (CH_2, C2), 67.6 (CH_2, C6), 68.4 (CH_2, C6′), 72.1 (CH, C5), 72.5 (CH_2), 72.7 (2 × CH_2), 73.2 (CH, C5′), 73.5 (CH_2), 73.6 (CH, C4′), 74.6 (CH_2), 75.2 (CH_2), 75.5 (CH, C4), 78.9 (CH, C3), 79.2 (CH, C2′), 82.5 (CH, C3′), 103.3 (CH, C1′), 127.4 (4 × CH), 127.51 (CH), 127.53 (CH), 127.6 (2 × CH), 127.7 (CH), 127.8 (CH), 127.87 (2 × CH), 127.89 (4 × CH), 128.14 (2 × CH), 128.16 (2 × CH), 128.25 (4 × CH), 128.29 (2 × CH), 128.3 (2 × CH), 128.4 (2 × CH), 137.5 (C), 137.9 (2 × C), 138.4 (C), 138.6 (C), 138.7 (C), 160.0 (CH, CHO); MS (ESI$^+$-TOF) m/z (%) 1015 [(M + Na)$^+$, 100]; HRMS (ESI$^+$-TOF) m/z: [M + Na]$^+$ calcd for $C_{54}H_{57}INaO_{10}$ 1015.2894; found 1015.2890. Anal. calcd for $C_{54}H_{57}IO_{10}$: C, 65.32; H, 5.79. Found: C, 65.42; H, 6.10.

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*2,5-Di-O-benzyl-1-deoxy-1-diethoxyphosphoryl-4-O-formyl-3-O-(2,3,4,6-tetra-O-benzyl-β-D-galactopyranosyl)-D-arabinitol (**16**).* A solution of **15** (139 mg, 0.14 mmol) in $(EtO)_3P$ (1.27 mL, 7.4 mmol) was stirred at reflux temperature under nitrogen for 6 h. The reaction mixture was concentrated under high vacuum, and the residue was purified by Chromatotron chromatography (hexanes−EtOAc, 50:50) to give compound **16** (115.5 mg, 0.115 mmol, 82%) as a colorless oil: $[\alpha]_D$ −12.9 (*c*, 0.89, $CHCl_3$); IR ($CHCl_3$) 2870, 1724, 1099, 1072 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 1.18 (3H, t, *J* = 7.3 Hz), 1.20 (3H, t, *J* = 7.3 Hz), 2.14 (1H, ddd, $^2J_{PH}$ = 18.6 Hz, *J* = 15.5, 6.6 Hz, H2a), 2.52 (1H, ddd, $^2J_{PH}$ = 18.3 Hz, *J* = 15.8, 5.4 Hz, H2b), 3.41 (1H, dd, *J* = 9.8, 2.8 Hz, H3′), 3.41−3.44 (1H, m, H5′), 3.57 (1H, dd, *J* = 8.8, 5.0 Hz, H6′a), 3.64 (1H, dd, *J* = 8.2, 8.2 Hz, H6′b), 3.66 (1H, dd, *J* = 11.0, 2.5 Hz, H6a), 3.77 (1H, dd, *J* = 9.5, 7.6 Hz, H2′), 3.84 (1H, dd, *J* = 11.0, 4.7 Hz, H6b), 3.90 (1H, dd, *J* = 2.8, 0.6 Hz, H4′), 3.99 (4H, m), 4.09 (1H, dddd, $^3J_{PH}$ = 12.0 Hz, *J* = 6.6, 5.4, 2.5 Hz, H3), 4.16 (1H, dd, *J* = 7.3, 2.5 Hz, H4), 4.24 (1H, d, *J* = 12.0 Hz), 4.31 (1H, d, *J* = 11.7 Hz), 4.41 (1H, d, *J* = 11.7 Hz), 4.43 (1H, d, *J* = 6.9 Hz, H1′), 4.45 (1H, d, *J* = 11.7 Hz), 4.46 (1H, d, *J* = 11.4 Hz), 4.56 (1H, d, *J* = 11.1 Hz), 4.65 (1H, d, *J* = 11.4 Hz), 4.71 (2H, s), 4.78 (1H, d, *J* = 11.0 Hz), 4.82 (1H, d, *J* = 11.0 Hz), 4.92 (1H, d, *J* = 11.7 Hz), 5.26 (1H, ddd, *J* = 7.3, 4.7, 2.5 Hz, H5), 7.28 (30H, m), 7.84 (1H, d, *J* = 0.8 Hz, CHO); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ_C 16.26 (CH_3, d, $^3J_{PC}$ = 6.4 Hz), 16.28 (CH_3, d, $^3J_{PC}$ = 6.4 Hz), 26.9 (CH_2, d, $^1J_{PC}$ = 138.8 Hz, C2), 61.3 (CH_2, d, J_{PC} = 6.4 Hz), 61.5 (CH_2, d, J_{PC} = 6.4 Hz), 68.0 (CH_2, C6), 68.1 (CH_2, C6′), 71.87 (CH_2), 71.94 (CH, C5), 72.70 (CH_2), 72.72 (CH_2), 73.1 (CH, C5′), 73.3 (CH, C3), 73.4 (CH_2), 73.6 (CH, C4′), 74.6 (CH_2), 75.2 (CH_2), 76.9 (CH, d, $^3J_{PC}$ = 10.6 Hz, C4), 79.2 (CH, C2′), 82.4 (CH, C3′), 103.2 (CH, C1′), 127.39 (CH), 127.41 (3 × CH), 127.48 (CH), 127.51 (2 × CH), 127.53 (2 × CH), 127.7 (3 × CH), 127.8 (2 × CH), 127.9 (2 × CH), 128.1 (2 × CH), 128.15 (6 × CH), 128.20 (2 × CH), 128.3 (2 × CH), 128.4 (2 × CH), 137.85 (2 × C), 137.91 (C), 138.3 (C), 138.6 (C), 138.7 (C), 160.1 (CH, CHO); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ_P 30.2 (P); MS (ESI^+-TOF) *m*/*z* (%) 1025 $[(M + Na)^+, 100]$; HRMS (ESI^+-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{58}H_{67}NaO_{13}P$ 1025.4217; found 1025.4203. Anal. calcd for $C_{58}H_{67}O_{13}P$: C, 69.45; H, 6.73. Found: C, 69.33; H, 6.74.

*(S_P)-3,6-Di-O-benzyl-1,2-dideoxy-1-ethoxy-1-phospha-1-oxo-3-O-(2,3,4,6-tetra-O-benzyl-β-D-galactopyranosyl)-D-arabino-hexopyranose (**44**) and (R_P)-3,6-Di-O-benzyl-1,2-dideoxy-1-ethoxy-1-phospha-1-oxo-3-O-(2,3,4,6-tetra-O-benzyl-β-D-galactopyranosyl)-D-arabino-hexopyranose (**45**).* A solution of **16** (107 mg, 0.107 mmol) in NaOEt/EtOH 0.01 M (0.94 mL, 9.4 × 10^{-3} mmol) was stirred at room temperature for 27 h. The reaction mixture was concentrated under reduced pressure, and the residue was purified by Chromatotron chromatography (hexanes−EtOAc, 50:50) to give compound **44** (20.2 mg, 0.022 mmol, 20%) and compound **45** (41.5 mg, 0.045 mmol, 42%) as colorless oils. Compound **44**: $[\alpha]_D$ +6.6 (*c*, 0.62, $CHCl_3$); IR ($CHCl_3$) 2868, 1249, 1230, 1094, 1028 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, simulated coupling constants of ring I using DAISY) δ_H 1.31 (3H, t, *J* = 6.9 Hz), 1.98 (1H, ddd, $^2J_{PH}$ = 17.5 Hz, *J* = 14.4, 9.8 Hz, H2*β*), 2.42 (1H, ddd, $^2J_{PH}$ = 18.2 Hz, *J* = 14.4, 5.1 Hz, H2*α*), 3.39 (1H, br dd, *J* = 6.0, 6.0 Hz, H5′), 3.41 (1H, dd, *J* = 9.5, 2.8 Hz, H3′), 3.44 (1H, dd, *J* = 9.1, 5.4 Hz, H6′a), 3.54 (1H, dd, *J* = 9.1, 7.9 Hz, H6′b), 3.64 (1H, dd, *J* = 11.0, 3.3 Hz, H6a), 3.78 (1H, dd, *J* = 9.5, 7.6 Hz, H2′), 3.88 (1H, br d, *J* = 2.5 Hz, H4′), 3.97 (1H, ddd, $^4J_{PH}$ = 3.7 Hz, *J* = 11.0, 2.6 Hz, H6b), 4.04 (1H, dd, *J* = 7.7, 7.2 Hz, H4), 4.06 (1H, dddd, $^3J_{PH}$ = 2.1 Hz, *J* = 9.8, 7.7, 5.1 Hz, H3), 4.14 (2H, m), 4.31 (1H, d, *J* = 11.7 Hz), 4.33 (1H, dddd, $^3J_{PH}$ = 3.4 Hz, *J* = 7.2, 3.3, 2.6 Hz, H5), 4.39 (1H, d, *J* = 12.0 Hz), 4.40 (1H, d, *J* = 12.0 Hz), 4.43 (1H, d, *J* = 7.6 Hz, H1′), 4.51 (1H, d, *J* = 12.0 Hz), 4.55 (1H, d, *J* = 11.4 Hz), 4.56 (1H, d, *J* = 11.7 Hz), 4.72 (2H, s), 4.75 (1H, d, *J* = 11.4 Hz), 4.78 (2H, s), 4.96 (1H, d, *J* = 11.4 Hz), 7.28 (30H, m); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ_C 16.4 (CH_3, d, $^3J_{PC}$ = 5.5 Hz), 27.3 (CH_2, d, $^1J_{PC}$ = 122.9 Hz, C2), 62.5 (CH_2, d, $^2J_{PC}$ = 6.4 Hz), 68.3 (CH_2, d, $^3J_{PC}$ = 8.5 Hz, C6), 68.5 (CH_2, C6′), 72.81 (CH_2), 72.83 (CH_2), 73.0 (CH_2), 73.4 (CH, C5′), 73.5 (CH_2), 73.65 (CH, C4′), 74.67 (CH_2), 75.4 (CH_2), 76.0 (CH, C3), 76.1 (CH, d, J_{PC} = 3.2 Hz, C4), 77.2 (CH, d, $^2J_{PC}$ = 4.2 Hz, C5), 79.5 (CH, C2′), 82.4 (CH, C3′), 103.0 (CH, C1′), 127.4 (CH), 127.45 (3 × CH), 127.53 (CH), 127.57 (CH), 127.60 (CH), 127.64 (2 × CH), 127.7 (CH), 127.8 (4 × CH), 127.9 (2 × CH), 128.08 (2 × CH), 128.13 (2 × CH), 128.18 (2 × CH), 128.25 (2 × CH), 128.3 (2 × CH), 128.4 (4 × CH), 137.99 (C), 138.06 (C), 138.3 (C), 138.4 (C), 138.5 (C), 138.8 (C); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ_P 24.3 (P); MS (ESI^+-TOF) *m*/*z* (%) 951 $[(M + Na)^+, 100]$; HRMS (ESI^+-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{55}H_{61}NaO_{11}P$ 951.3849; found 951.3843. Anal. calcd for $C_{55}H_{61}O_{11}P$: C, 71.10; H, 6.62. Found: C, 71.17; H, 6.90. Compound **45**: $[\alpha]_D$ +22.7 (*c*, 1.19, $CHCl_3$); IR ($CHCl_3$) 2868, 1275, 1230, 1094, 1028 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, simulated coupling constants of ring I using DAISY) δ_H 1.32 (3H, t, *J* = 7.3 Hz), 2.00 (1H, ddd, $^2J_{PH}$ = 18.0 Hz, *J* = 14.9, 10.4 Hz, H2*β*), 2.37 (1H, ddd, $^2J_{PH}$ = 18.1 Hz, *J* = 14.9, 4.6 Hz, H2*α*), 3.39 (1H, ddd, *J* = 6.3, 6.3 Hz, H5′), 3.42 (1H, dd, *J* = 8.5, 5.4 Hz, H6′a), 3.44 (1H, dd, *J* = 9.8, 2.8 Hz, H3′), 3.54 (1H, dd, *J* = 8.5, 7.6 Hz, H6′b), 3.68 (1H, dd, *J* = 10.9, 2.2 Hz, H6a), 3.77 (1H, dd, *J* = 9.8, 7.6 Hz, H2′), 3.83 (1H, dddd, $^3J_{PH}$ = 2.3 Hz, *J* = 10.4, 8.6, 4.6 Hz, H3), 3.89 (1H, ddd, $^4J_{PH}$ = 3.2 Hz, *J* = 10.9, 3.2 Hz, H6b), 3.91 (1H, br d, *J* = 2.5 Hz, H4′), 3.99 (1H, dd, *J* = 8.9, 8.6 Hz, H4), 3.99 (1H, dddd, $^3J_{PH}$ = 2.7 Hz, *J* = 8.9, 3.2, 2.2 Hz, H5), 4.13 (2H, m), 4.30 (1H, d, *J* = 12.0 Hz), 4.38 (1H, d, *J* = 11.8 Hz), 4.42 (1H, d, *J* = 12.0 Hz), 4.47 (1H, d, *J* = 7.6 Hz, H1′), 4.52 (1H, d, *J* = 12.3 Hz), 4.56 (1H, d, *J* = 11.4 Hz), 4.57 (1H, d, *J* = 11.4 Hz), 4.68 (1H, d, *J* = 12.0 Hz), 4.72 (1H, d, *J* = 12.0 Hz), 4.74 (1H, d, *J* = 11.4 Hz), 4.77 (1H, d, *J* = 11.4 Hz), 4.83 (1H, d, *J* = 11.0 Hz), 4.95 (1H, d, *J* = 11.4 Hz), 7.28 (30H, m); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ_C 16.4 (CH_3, d, $^3J_{PC}$ = 5.5 Hz), 27.7 (CH_2, d, $^1J_{PC}$ = 122.6 Hz, C2), 61.4 (CH_2, d, $^2J_{PC}$ = 6.5 Hz), 68.3 (CH_2, C6′), 68.6 (CH_2, d, $^3J_{PC}$ = 8.2 Hz, C6), 72.6 (CH_2), 72.7 (CH_2), 73.2 (CH_2), 73.3 (CH, C5′), 73.45 (CH_2), 73.50 (CH, C4′), 74.7 (CH_2), 75.2 (CH_2), 76.1 (CH, C3), 76.6 (CH, br s, C5), 77.5 (CH, d, $^3J_{PC}$ = 5.5 Hz, C4), 79.7 (CH, C2′), 82.6 (CH, C3′), 102.8 (CH, C1′), 127.36 (CH), 127.41 (CH), 127.45 (2 × CH), 127.46 (CH), 127.5 (CH), 127.6 (3 × CH), 127.7 (CH), 127.76 (4 × CH), 127.80 (2 × CH), 127.9 (2 × CH), 128.1 (2 × CH), 128.15 (2 × CH), 128.2 (2 × CH), 128.3 (2 × CH), 128.34 (2 × CH), 128.4 (2 × CH), 138.0 (C), 138.1 (C), 138.3 (2 × C), 138.6 (C), 138.8 (C); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ_P 23.3 (P); MS (ESI^+-TOF) *m*/*z* (%) 951 $[(M + Na)^+, 100]$; HRMS (ESI^+-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{55}H_{61}NaO_{11}P$ 951.3849; found 951.3849. Anal. calcd for $C_{55}H_{61}O_{11}P$: C, 71.10; H, 6.62. Found: C, 70.88; H, 6.88.

*Benzyl 5-Deoxy-5-iodo-2,3-O-isopropylidene-β-D-ribofuranoside (**18**).* A solution of **17**[38] (100 mg, 0.35 mmol) in benzene (3.18 mL) containing iodine (180 mg, 0.71 mmol), Ph_3P (186 mg, 0.71 mmol), and imidazole (76 mg, 1.11 mmol) was stirred at 80 °C under nitrogen for 25 min. The mixture was concentrated under reduced pressure, and the residue was purified by Chromatotron chromatography (hexanes−EtOAc, 90:10) to give 18 (115.2 mg, 0.295 mmol, 85%) as a crystalline solid: mp 37.6−38.6 °C (from *n*-hexane−EtOAc); $[\alpha]_D$ −86.3 (c 1.12, $CHCl_3$); IR ($CHCl_3$) 2941, 1377, 1091, 1014 cm^{-1}; 1H NMR (500 MHz, $CDCl_3$) δ_H 1.34 (3H, s), 1.50 (3H, s), 3.23 (1H, dd, *J* = 9.8, 9.8 Hz, H5a), 3.34 (1H, dd, *J* = 10.1, 6.3 Hz, H5b), 4.50 (1H, dd, *J* = 9.8, 6.3 Hz, H4), 4.51 (1H, d, *J* = 11.7 Hz), 4.74 (1H, d, *J* = 6.0 Hz, H2), 4.78 (1H, d, J = 11.7 Hz), 4.79 (1H, d, *J* = 6.0 Hz, H3), 5.27 (1H, s, H1), 7.35 (5H, m); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ_C 6.8 (CH_2, C5), 24.9 (CH_3), 26.3 (CH_3), 69.6 (CH_2), 83.0 (CH, C3), 85.5 (CH, C2), 87.6 (CH, C4), 107.6 (CH, C1), 112.6 (C), 127.9 (CH), 128.0 (2 × CH), 128.5 (2 × CH), 136.8 (C); MS (ESI^+-TOF) *m*/*z* (%) 413 $[(M + Na)^+, 100]$; HRMS (ESI^+-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{15}H_{19}INaO_4$ 413.0215; found 413.0220. Anal. calcd for $C_{15}H_{19}IO_4$: C, 46.17; H, 4.91. Found: C, 46.41; H, 4.78.

*Benzyl 5-Deoxy-5-diethoxyphosphoryl-2,3-O-isopropylidene-β-D-ribofuranoside (**19**).* A solution of **18** (1 g, 2.56 mmol) in triethyl phosphite (23 mL) was heated at reflux temperature under nitrogen for 28 h. The mixture was concentrated under high vacuum, and the residue was purified by column chromatography (hexanes−EtOAc, 50:50 → 40:60) to give starting material **18** (271 mg, 0.69 mmol, 27%) and **19** (718 mg, 1.8 mmol, 70%, 96% brsm). Compound **19**: colorless oil, $[\alpha]_D$ −67.8 (*c* 0.91, $CHCl_3$); IR ($CHCl_3$) 2994, 1378,

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1241, 1026 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 1.28 (3H, s), 1.30 (3H, t, J = 6.9 Hz), 1.31 (3H, t, J = 6.9 Hz), 1.44 (3H, s), 2.12 (1H, ddd, $^2J_{PH}$ = 18.0 Hz, J = 15.1, 8.5 Hz, H5a), 2.21 (1H, ddd, $^2J_{PH}$ = 19.6 Hz, J = 15.5, 6.3 Hz, H5b), 4.11 (4H, m), 4.46 (1H, d, J = 11.7 Hz), 4.54 (1H, ddd, $^3J_{PH}$ = 7.9 Hz, J = 7.9, 6.3 Hz, H4), 4.69 (1H, d, J = 6.0 Hz, H2), 4.74 (1H, d, J = 11.7 Hz), 4.78 (1H, d, J = 6.0 Hz, H3), 5.13 (1H, d, $^5J_{PH}$ = 1.6 Hz, H1), 7.30 (5H, m); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ_C 16.3 (2 × CH_3, d, $^3J_{PC}$ = 5.3 Hz), 24.8 (CH_3), 26.3 (CH_3), 32.3 (CH_2, d, $^1J_{PC}$ = 137.8 Hz, C5), 61.74 (CH_2, d, $^2J_{PC}$ = 6.4 Hz), 61.71 (CH_2, d, $^2J_{PC}$ = 6.4 Hz), 69.1 (CH_2), 81.9 (CH, C4), 84.4 (CH, d, $^3J_{PC}$ = 8.5 Hz, C3), 85.4 (CH, C2), 107.7 (CH, C1), 112.3 (C), 127.7 (CH), 127.9 (2 × CH), 128.4 (2 × CH), 137.1 (C); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ_P 26.5 (P); MS (ESI$^+$-TOF) m/z (%) 423 [(M + Na)$^+$, 100]; HRMS (ESI$^+$-TOF) m/z: [M + Na]$^+$ calcd for $C_{19}H_{29}NaO_7P$ 423.1549; found 423.1559. Anal. calcd for $C_{19}H_{29}O_7P$: C, 56.99; H, 7.30. Found: C, 56.61; H, 7.67.

*5-Deoxy-5-diethoxyphosphoryl-2,3-O-isopropylidene-D-ribofuranose (**20**).* A solution of **19** (628 mg, 1.57 mmol) in EtOAc (18 mL) containing Pd/C 10% (605 mg) was stirred at room temperature under 1 atm of hydrogen (balloon) for 2.5 h. The mixture was then filtered over Celite and concentrated under reduced pressure. The residue was purified by Chromatotron chromatography (hexanes−EtOAc, 10:90) to give **20** as an amorphous solid (451 mg, 1.45 mmol, 92%, dr, 90:10): IR ($CHCl_3$) 2994, 1376, 1230, 1056, 1028 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, major isomer) δ_H 1.28 (3H, s), 1.29 (3H, t, J = 7.3 Hz), 1.31 (3H, t, J = 7.3 Hz), 1.43 (3H, s), 2.14 (1H, ddd, $^2J_{PH}$ = 19.2 Hz, J = 15.1, 6.3 Hz, H5a), 2.28 (1H, ddd, $^2J_{PH}$ = 18.6 Hz, J = 15.4, 8.8 Hz, H5b), 4.11 (4H, m), 4.43 (1H, m, H4), 4.63 (1H, d, J = 5.7 Hz, H2), 4.69 (1H, d, J = 6.0 Hz, H3), 5.42 (1H, s, H1); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, major isomer) δ_C 16.31 (CH_3, d, $^3J_{PC}$ = 6.4 Hz), 16.32 (CH_3, d, $^3J_{PC}$ = 6.4 Hz), 24.9 (CH_3), 26.4 (CH_3), 32.6 (CH_2, d, $^1J_{PC}$ = 139.9 Hz, C5), 61.7 (CH_2, d, $^2J_{PC}$ = 6.4 Hz), 62.4 (CH_2, d, $^2J_{PC}$ = 6.4 Hz), 81.2 (CH, d, $^2J_{PC}$ = 4.2 Hz, C4), 85.0 (CH, d, $^3J_{PC}$ = 14.8 Hz, C3), 86.2 (CH, C2), 103.4 (CH, C1), 112.4 (C); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, major isomer) δ_P 27.7 (P); MS (ESI$^+$-TOF) m/z (%) 333 [(M + Na)$^+$, 100]; HRMS (ESI$^+$-TOF) m/z: [M + Na]$^+$ calcd for $C_{12}H_{23}NaO_7P$ 333.1079; found 333.1079. Anal. calcd for $C_{12}H_{23}O_7P$: C, 46.45; H, 7.47. Found: C, 46.08; H, 7.80.

*5-Deoxy-5-ethoxyphosphoryl-2,3-O-isopropylidene-D-ribofuranose (**21**).* A solution of **20** (370 mg, 1.19 mmol) in EtOH (29.8 mL) was treated with aqueous 2 M NaOH (5.37 mL) and stirred at room temperature for 48 h. The mixture was neutralized with acid ion-exchange resin Amberlite IR120, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography ($CHCl_3$−MeOH, 60:40) to give **21** (258 mg, 0.91 mmol, 77%) as an amorphous solid: IR ($CHCl_3$) 3683, 3013, 2400, 1522, 1235 cm^{-1}; ^1H NMR (500 MHz, CD_3OD, major isomer) δ_H 1.27 (3H, t, J = 7.3 Hz), 1.31 (3H, s), 1.44 (3H, s), 2.05 (2H, m, H5), 3.97 (2H, m), 4.49 (1H, ddd, $^3J_{PH}$ = 7.9 Hz, J = 7.9, 7.9 Hz, H4), 4.62 (1H, d, J = 6.0 Hz, H2), 4.89 (1H, d, J = 6.0 Hz, H3), 5.34 (1H, s, H1); $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_3OD, major isomer) δ_C 17.1 (CH_3, d, $^3J_{PC}$ = 6.4 Hz), 25.2 (CH_3), 26.9 (CH_3), 34.9 (CH_2, d, $^1J_{PC}$ = 135.6 Hz, C5), 61.0 (CH_2, d, $^2J_{PC}$ = 5.3 Hz), 84.3 (CH, C4) 86.4 (CH, d, $^3J_{PC}$ = 8.4 Hz, C3), 87.6 (CH, C2), 104.5 (CH, C1), 113.2 (C); $^{31}P\{^1H\}$ NMR (162 MHz, CD_3OD, major isomer) δ_P 18.2 (P); MS (ESI$^+$-TOF) m/z (%) 281 [(M − H)$^+$, 100]; HRMS (ESI$^+$-TOF) m/z: [M − H]$^+$ calcd for $C_{10}H_{18}O_7P$ 281.0790; found 281.0783. Anal. calcd for $C_{10}H_{19}O_7P$: C, 42.56 H, 6.79. Found: C, 42.67; H, 6.79.

*(R_P)-4-Deoxy-5-ethoxy-3-O-formyl-1,2-O-isopropylidene-5-phospha-5-oxo-α-D-erythro-pentopyranose (**46**) and (S_P)-4-Deoxy-5-ethoxy-3-O-formyl-1,2-O-isopropylidene-5-phospha-5-oxo-α-D-erythro-pentopyranose (**47**).* A solution of the crude alcohol **21** (29.3 mg, 0.104 mmol) in $CHCl_3$ (2.1 mL) containing $PhI(OAc)_2$ (67 mg, 0.208 mmol) and I_2 (26.4 mg, 0.114 mmol) was stirred under nitrogen at room temperature for 2.5 h. The reaction mixture was then poured into 10% aqueous $Na_2S_2O_3$, extracted with $CHCl_3$, dried over Na_2SO_4, and concentrated. The residue was purified by Chromatotron chromatography (benzene−EtOAc, 50:50) to give compounds **46** (9.2 mg, 0.033 mmol, 32%) and **47** (4.4 mg, 0.016 mmol, 15%). Compound **46**: colorless oil, $[\alpha]_D$ +27.5 (c 1.11, $CHCl_3$); IR ($CHCl_3$) 3009, 1730, 1279, 1149, 1022 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, simulated coupling constants using DAISY) δ_H 1.38 (3H, t, J = 6.9 Hz), 1.45 (3H, s), 1.65 (3H, s), 2.29 (1H, dddd, $^2J_{PH}$ = 19.5 Hz, J = 14.0, 4.6, ^4J_w = 0.7 Hz, H2α), 2.43 (1H, ddd, $^2J_{PH}$ = 18.6 Hz, J = 14.0, 12.6 Hz, H2β), 4.20 (2H, m), 4.35 (1H, ddd, J = 2.8, 2.5 Hz, ^4J_w = 0.7, H4), 5.51 (1H, ddddd, $^3J_{PH}$ = 2.5 Hz, J = 12.6, 4.6, 2.8 Hz, ^4J_w = 1.1 Hz, H3), [Decoupling by selective irradiation at CHO (8.09 ppm) (1H, dddd, $^3J_{PH}$ = 2.5 Hz, J = 12.2, 4.3, 2.5 Hz, H3)], 5.64 (1H, dd, $^3J_{PH}$ = 3.9 Hz, J = 2.5 Hz, H5), 8.09 (1H, dd, $^5J_{PH}$ = 2.7 Hz, ^4J_w = 1.1 Hz, CHO) [Decoupling by selective irradiation at H3 (5.51 ppm) (1H, d, $^5J_{PH}$ = 3.0 Hz, CHO)]; $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ_C 16.4 (CH_3, d, $^4J_{PC}$ = 5.3 Hz), 23.2 (CH_2, d, $^1J_{PC}$ = 125.0 Hz, C2), 25.8 (CH_3), 27.4 (CH_3), 62.3 (CH_2, d, $^2J_{PC}$ = 6.4 Hz), 66.1 (CH, d, $^2J_{PC}$ = 5.3 Hz, C3), 75.2 (CH, d, $^3J_{PC}$ = 4.2 Hz, C4), 97.6 (CH, d, $^2J_{PC}$ = 4.2 Hz, C5), 113.7 (C), 159.5(CH, CHO); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ_P 18.0 (P); MS (ESI$^+$-TOF) m/z (%) 303 [(M + Na)$^+$, 100]; HRMS (ESI$^+$-TOF) m/z: [M + Na]$^+$ calcd for $C_{10}H_{17}NaO_7P$ 303.0610; found 303.0615. Anal. calcd for $C_{10}H_{17}O_7P$: C, 42.86; H, 6.12. Found: C, 42.90; H, 6.50. Compound **47**: colorless oil, $[\alpha]_D$ +1.7 (c 0.35, $CHCl_3$); IR ($CHCl_3$) 2931, 1731, 1242, 1147, 1021 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, simulated coupling constants using DAISY) δ_H 1.37 (3H, t, J = 6.9 Hz), 1.43 (3H, s), 1.62 (3H, s), 2.33 (1H, ddd, $^2J_{PH}$ = 20.1 Hz, J = 13.3, 4.5 Hz, H2α), 2.43 (1H, ddd, $^2J_{PH}$ = 18.2 Hz, J = 13.3, 12.9 Hz, H2β), 4.22 (2H, m), 4.44 (1H, dd, J = 3.0, 2.6 Hz, H4), 5.67 (1H, ddddd, $^3J_{PH}$ = 3.1 Hz, J = 12.9, 4.5, 2.6 Hz, ^4J_w = 0.8 Hz, H3) [Decoupling by selective irradiation at CHO (8.08 ppm) (1H, dddd, $^3J_{PH}$ = 3.0 Hz, J = 12.8, 5.4, 3.0 Hz, H3)], 5.82 (1H, dd, $^3J_{PH}$ = 8.5 Hz, J = 3.0 Hz, H5), 8.08 (1H, dd, $^5J_{PH}$ = 2.8 Hz, ^4J_w = 0.8 Hz, CHO); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ_C 16.4 (CH_3, d, $^4J_{PC}$ = 6.4 Hz), 23.7 (CH_2, d, $^1J_{PC}$ = 125.0 Hz, C2), 25.7 (CH_3), 27.0 (CH_3), 62.9 (CH_2, d, $^2J_{PC}$ = 6.4 Hz), 65.9 (CH, d, $^2J_{PC}$ = 7.4 Hz, C3), 75.3 (CH, d, $^3J_{PC}$ = 4.2 Hz, C4), 97.5 (CH, d, $^2J_{PC}$ = 3.2 Hz, C5), 113.1 (C), 159.2 (CH, CHO); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ_P 19.6 (P); MS (ESI$^+$-TOF) m/z (%) 303 [(M + Na)$^+$, 100]; HRMS (ESI$^+$-TOF) m/z: [M + Na]$^+$ calcd for $C_{10}H_{17}NaO_7P$ 303.0610; found 303.0612. Anal. calcd for $C_{10}H_{17}O_7P$: C, 42.86; H, 6.12. Found: C, 43.19; H, 5.89.

*Benzyl 5-Deoxy-5-ethoxyphenylphosphoryl-2,3-O-isopropylidene-β-D-ribofuranoside (**22**).* A solution of iodine **18** (1.2 g, 3.075 mmol) in $PhP(OEt)_2$ (5.9 mL) was heated at 160 °C under nitrogen for 28 h. The mixture was concentrated under high vacuum, and the residue was purified by column chromatography (hexanes−EtOAc, 70:30 → 60:40) to give starting material **18** (500 mg, 1.28 mmol, 41%) and **22** (396 mg, 0.917 mmol, 30%, 51% brsm, dr, 6:4): colorless oil, $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ_P 39.4 (P, minor), 39.8 (P, major); MS (ESI$^+$-TOF) m/z (%) 455 [(M + Na)$^+$, 100]; HRMS (ESI$^+$-TOF) m/z: [M + Na]$^+$ calcd for $C_{23}H_{29}NaO_6P$ 455.1599; found 455.1603. Anal. calcd for $C_{23}H_{29}O_6P$: C, 63.88; H, 6.76. Found: C, 63.66; H, 7.02.

*5-Deoxy-5-ethoxyphenylphosphoryl-2,3-O-isopropylidene-D-ribofuranose (**23**).* A solution of **22** (396 mg, 0.916 mmol) in EtOAc (10.5 mL) containing Pd/C 10% (353 mg) was stirred at room temperature under 1 atm of hydrogen (balloon) for 20 h. The mixture was then filtered over Celite and concentrated under reduced pressure. The residue was purified by Chromatotron chromatography (hexanes−EtOAc, 9:95) to give **23** (306 mg, 0.89 mmol, 97%) as a colorless oil. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ_P 40.9 (P, major), 42.4 (P, minor); MS (ESI$^+$-TOF) m/z (%) 365 [(M + Na)$^+$, 100]; HRMS (ESI$^+$-TOF) m/z: [M + Na]$^+$ calcd for $C_{16}H_{23}NaO_6P$ 365.1130; found 365.1138.

*5-Deoxy-5-phenylphosphoryl-2,3-O-isopropylidene-D-ribofuranose (**24**).* A solution of **23** (278 mg, 0.812 mmol) was treated with 2 M NaOH (3.65 mL) in EtOH and stirred at room temperature for 42 h. The mixture was neutralized with acid ion-exchange resin Amberlite IR120, filtered, and concentrated under reduced pressure. The residue was used in the next reaction without further purification **24** (250 mg, 0.80 mmol): $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$) δ_P 41.1 (P, major); MS (ESI$^+$-TOF) m/z (%) 455 [(M − H)$^+$, 100];

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HRMS (ESI$^+$-TOF) m/z: [M − H]$^+$ calcd for $C_{14}H_{18}O_6P$ 313.0841; found 313.0838. Anal. calcd for $C_{14}H_{18}O_6P$: C, 53.51; H, 6.09. Found: C, 53.27; H, 6.18.

*(S_P)-4-Deoxy-3-O-formyl-1,2-O-isopropylidene-5-phenyl-5-phospha-5-oxo-α-D-erythro-pentopyranose (**48**) and (R_P)-4-Deoxy-3-O-formyl-1,2-O-isopropylidene-5-phenyl-5-phospha-5-oxo-α-D-erythro-pentopyranose (**49**).* A solution of the crude alcohol **24** (42.4 mg, 0.135 mmol) in dry CH_2Cl_2 (7.4 mL) containing $PhI(OAc)_2$ (96.6 mg, 0.3 mmol) and I_2 (41.1 mg, 0.152 mmol) under nitrogen was stirred and irradiated with two 80 W tungsten-filament lamps at room temperature for 3.5 h. The reaction mixture was then poured into 10% aqueous $Na_2S_2O_3$, extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated. The residue was purified by Chromatotron chromatography (hexanes−EtOAc, 20:80) to give compounds **48** (12.2 mg, 0.039 mmol, 29%) and **49** (21.4 mg, 0.069 mmol, 51%). Compound **48**: crystalline solid, mp 166.2−167.4 °C (from *n*-hexane−EtOAc); IR ($CHCl_3$) 1729, 1229, 1139, 1036 cm^{-1}; $[\alpha]_D$ −12.7 (*c* 0.67, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, simulated coupling constants using DAISY) δ_H 1.46 (3H, s), 1.85 (3H, s), 2.58 (1H, dddd, $^2J_{PH}$ = 10.1 Hz, J = 14.6, 5.1, ^4J_w = 0.9 Hz, H2α), 2.79 (1H, ddd, $^2J_{PH}$ = 21.3 Hz, J = 14.6, 12.6 Hz, H2β), 4.54 (1H, ddd, J = 3.8, 1.8 Hz, ^4J_w = 0.9 Hz, H4), 5.39 (1H, ddddd, $^3J_{PH}$ = 2.0 Hz, J = 12.6, 5.1, 1.8 Hz, ^4J_w = 1.1 Hz, H3) [Decoupling by selective irradiation at CHO (8.08 ppm) (1H, dddd, $^3J_{PH}$ = 1.8 Hz, J = 12.2, 4.9, 1.8 Hz, H3)], 5.92 (1H, dd, $^3J_{PH}$ = 19.0 Hz, J = 3.8 Hz, H5), 7.48−7.55 (2H, m), 7.56−7.62 (1H, m), 7.73−7.80 (2H, m), 8.08 (1H, dd, $^5J_{PH}$ = 2.2 Hz, ^4J_w = 1.1 Hz, CHO) [Decoupling by selective irradiation at H3 (5.39 ppm) (1H, d, $^5J_{PH}$ = 2.2 Hz, H3)]; ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$) δ 26.0 (CH_3), 26.2 (CH_3), 26.9 (CH_2, d, ^1J = 80.5 Hz, C2), 66.3 (CH, d, ^2J = 4.2 Hz, C3), 75.1 (CH, d, ^3J = 5.3 Hz, C4), 99.4 (CH, d, ^2J = 10.6 Hz, C5), 114.2 (C), 128.9 (2 × CH, d, ^3J = 12.7 Hz), 130.3 (2 × CH, d, ^2J = 11.7 Hz), 131.6 (C, d, ^1J = 142.0 Hz), 132.8 (CH, d, ^4J = 2.1 Hz), 159.7 (C, C1); ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$) δ_P 30.9 (P); MS (ESI$^+$-TOF) m/z (%) 335 [(M + Na)$^+$, 100]; HRMS (ESI$^+$-TOF) m/z: [M + Na]$^+$ calcd for $C_{14}H_{17}NaO_6P$ 335.0660; found 335.0658. Anal. calcd for $C_{14}H_{17}O_6P$: C, 53.85; H, 5.49. Found: C, 53.69; H, 5.68. Compound **49**: colorless oil, $[\alpha]_D$ −30.2 (*c* 0.61, $CHCl_3$); IR ($CHCl_3$) 1731, 1243, 1229, 1146, 1032 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, simulated coupling constants using DAISY) δ_H 1.49 (3H, s), 1.70 (3H, s), 2.37 (1H, dddd, $^2J_{PH}$ = 12.9 Hz, J = 13.0, 4.2, ^4J_w = 0.7 Hz, H2α), 2.50 (1H, ddd, $^2J_{PH}$ = 10.0 Hz, J = 13.0, 12.8 Hz, H2β), 4.53 (1H, dd, J = 2.9, 2.3 Hz, ^4J_w = 0.7 Hz, H4), 6.02 (1H, ddddd, $^3J_{PH}$ = 3.3 Hz, J = 12.8, 4.2, 2.9 Hz, ^4J_w = 1.1 Hz, H3) [Decoupling by selective irradiation at CHO (8.10 ppm) (1H, dddd, $^3J_{PH}$ = 3.2 Hz, J = 12.9, 4.1, 3.2 Hz, H3)], 6.04 (1H, br d, $^3J_{PH}$ = 0.7 Hz, J = 2.3 Hz, H5), 7.50−7.55 (2H, m), 7.60−7.65 (1H, m), 7.80−7.86 (2H, m), 8.10 (1H, dd, $^5J_{PH}$ = 2.1 Hz, ^4J_w = 1.1 Hz, CHO) [Decoupling by selective irradiation at H3 (6.02 ppm) (1H, d, $^5J_{PH}$ = 2.2 Hz, CHO)]; ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$) δ 25.6 (CH_3), 26.4 (CH_2, d, $^1J_{PC}$ = 83.7 Hz, C2), 27.9 (CH_3), 65.3 (CH, d, $^2J_{PC}$ = 2.1 Hz, C3), 75.9 (CH, d, $^4J_{PC}$ = 3.2 Hz, C4), 97.5 (CH, d, $^2J_{PC}$ = 4.2 Hz, C5), 113.1 (C), 128.77 (2 × CH, d, $^3J_{PC}$ = 13.8 Hz), 128.84 (C, d, $^1J_{PC}$ = 143.1 Hz), 131.1 (2 × CH, d, $^2J_{PC}$ = 10.6 Hz), 133.3 (CH, d, $^4J_{PC}$ = 3.2 Hz), 159.3 (C, C1); ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$) δ_P 34.1 (P); MS (ESI$^+$-TOF) m/z (%) 335 [(M + Na)$^+$, 100]; HRMS (ESI$^+$-TOF) m/z: [M + Na]$^+$ calcd for $C_{14}H_{17}NaO_6P$ 335.0660; found 335.0656. Anal. calcd for $C_{14}H_{17}O_6P$: C, 53.85; H, 5.49. Found: C, 54.09; H, 5.76.

*1-O-Benzoyl-6-O-tert-butyldiphenylsilyl-2,3-O-isopropylidene-α-D-mannofuranose (**26**).* To a solution of 1-*O*-benzoyl-2,3-*O*-isopropylidene-α-D-mannofuranose **25**[39] (188 mg, 0.58 mmol) in dry DMF (2 mL) were added imidazole (79 mg, 1.16 mmol), DMAP (1 mg, 0.008 mmol), and TBDPSiCl (200 μL, 0.769 mmol) at room temperature under nitrogen. The mixture was then stirred for 2 h, poured into water, and extracted with CH_2Cl_2. The organic extracts were concentrated under reduced pressure, and the residue was purified by Chromatotron chromatography (hexanes−EtOAc, 85:15) to give **26** (300 mg, 0.532 mmol, 92%) as a colorless oil: $[\alpha]_D$ +8.1 (*c*, 1.54, $CHCl_3$); IR ($CHCl_3$) 3564, 2934, 2858, 1728, 1427, 1259, 1091 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 0.99 (9H, s), 1.39 (3H, s), 1.51 (3H, s), 2.79 (1H, d, J = 6.9 Hz, OH), 3.89 (2H, m, H6), 4.10 (1H, dddd, J = 7.4, 7.4, 3.7, 3.7 Hz, H5), 4.34 (1H, dd, J = 8.5, 3.5 Hz, H4), 4.88 (1H, d, J = 5.7 Hz, H2), 5.03 (1H, dd, J = 5.7, 3.5 Hz, H3), 6.43 (1H, s, H1), 7.31−7.46 (8H, m), 7.53−7.58 (1H, m), 7.59−7.69 (4H, m), 7.97−8.04 (2H, m); ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$) δ_C 19.2 (C), 24.8 (CH_3), 26.1 (CH_3), 26.7 (3 × CH_3), 64.9 (CH_2, C6), 69.4 (CH, C5), 79.9 (CH, C3), 81.0 (CH, C4), 85.0 (CH, C2), 101.4 (CH, C1), 113.2 (C), 127.7 (4 × CH), 128.4 (2 × CH), 129.5 (C), 129.7 (2 × CH), 129.8 (2 × CH), 132.7 (C), 133.0 (C), 133.4 (CH), 135.5 (2 × CH), 135.5 (2 × CH), 164.9 (C); MS (ESI$^+$-TOF) m/z (%) 585 [(M + Na)$^+$, 100]; HRMS (ESI$^+$-TOF) m/z [M + Na]$^+$ calcd for $C_{32}H_{38}NaO_7Si$ 585.2285; found 585.2290. Anal. calcd for $C_{32}H_{38}O_7Si$: C, 68.30; H, 6.81. Found: C, 68.21; H, 6.85.

*1-O-Benzoyl-6-O-tert-butyldiphenylsilyl-2,3-O-isopropylidene-α-D-lyxo-hexofuranos-5-ulose (**27**).* To a stirred solution of **26** (3 g, 5.3 mmol) in dry CH_2Cl_2 (160 mL) at room temperature were added MS 3 Å (5 g) and PCC (3 g, 13.9 mmol). After 9 h, isopropanol (2 mL) was added and the mixture diluted with Et_2O and filtered through Celite. The filtrated was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography (hexanes−EtOAc, 90:10 → 85:15) to give **27** (2.68 g, 4.8 mmol, 91%) as a colorless oil: $[\alpha]_D$ −18.8 (*c*, 1.22, $CHCl_3$); IR ($CHCl_3$) 2860, 1737, 1428, 1260, 1105 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.13 (9H, s), 1.31 (6H, s), 4.52 (2H, s, H6), 4.86 (1H, d, J = 5.7 Hz, H2), 4.99 (1H, d, J = 4.1 Hz, H4), 5.30 (1H, dd, J = 5.7, 4.1 Hz, H3), 6.48 (1H, s, H1), 7.36−7.48 (8H, m), 7.57−7.62 (1H, m), 7.65−7.73 (4H, m), 7.98−8.00 (2H, m); ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$) δ 19.3 (C), 24.6 (CH_3), 25.7 (CH_3), 26.8 (3 × CH_3), 69.0 (CH_2, C6), 80.3 (CH, C3), 84.3 (CH, C2), 86.1 (CH, C4), 101.1 (CH, C1), 113.7 (C), 127.77 (2 × CH), 127.8 (2 × CH), 128.5 (2 × CH), 129.2 (C), 129.7 (2 × CH), 129.86 (CH), 129.93 (CH), 132.5 (C), 132.6 (C), 133.6 (CH), 135.48 (2 × CH), 135.51 (2 × CH), 164.6 (C), 202.3 (C, C5); MS (ESI$^+$-TOF) m/z (%) 583 [(M + Na)$^+$, 100]; HRMS (ESI$^+$-TOF) m/z [M + Na]$^+$ calcd for $C_{32}H_{36}NaO_7Si$ 583.2128; found 583.2128. Anal. calcd for $C_{32}H_{36}O_7Si$: C, 68.55; H, 6.47. Found: C, 68.70; H, 6.45.

*1-O-Benzoyl-6-O-tert-butyldiphenylsilyl-5-C-dimethoxyphosphoryl-2,3-O-isopropylidene-α-D-mannofuranose (**28R**) and 1-O-Benzoyl-6-O-tert-butyldiphenylsilyl-5-C-dimethoxyphosphoryl-2,3-O-isopropylidene-β-L-gulofuranose (**28S**).* To a solution of **27** (314 mg, 0.56 mmol) in $(MeO)_2P(O)H$ (2.3 mL, 25.1 mmol) was added DBU (100 μL, 0.67 mmol) at 0 °C under nitrogen, and the mixture was stirred for 30 min at this temperature. An aqueous saturated solution of NH_4Cl (0.3 mL) was then added, and the stirring was continued for 4 h. The mixture was then extracted with $CHCl_3$, washed with water, and the organic extract was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexanes−EtOAc, 50:50) to give **28*R*** (42 mg, 0.063mmol, 11%) and **28*S*** (260 mg, 0.388 mmol, 69%). Compound **28*R***: Colorless oil, $[\alpha]_D$ +36.5 (*c*, 1.23, $CHCl_3$); IR ($CHCl_3$) 3469, 3001, 2959, 1729, 1428, 1260, 1059 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.11 (9H, s), 1.22 (3H, s), 1.45(3 H, s), 3.74 (3H, d, $^3J_{PH}$ = 10.7 Hz), 3.80 (3H, d, $^3J_{PH}$ = 10.7 Hz), 4.04 (1H, dd, $^3J_{PH}$ = 18.6 Hz, J = 10.7 Hz, H6a), 4.20 (1H, dd, $^3J_{PH}$ = 10.4 Hz, J = 10.4 Hz, H6b), 4.21 (1H, d, $^3J_{PH}$ = 20.8 Hz, OH), 4.65 (1H, dd, $^3J_{PH}$ = 3.6 Hz, J = 3.6 Hz, H4), 4.78 (1H, d, J = 6.0 Hz, H2), 4.86 (1H, dd, J = 5.7, 3.2 Hz, H3), 6.44 (1H, s, H1), 7.36−7.47 (8H, m), 7.57−7.60 (1H, s), 7.67−7.76 (4H, m), 7.99−8.01 (2H, m); ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$) δ 19.3 (C), 24.3 (CH_3), 25.8 (CH_3), 26.8 (3 × CH_3), 53.3 (CH_3, d, $^2J_{PC}$ = 7.4 Hz), 54.0 (CH_3, d, $^2J_{PC}$ = 7.4 Hz), 66.1 (CH_2, d, $^2J_{PC}$ = 2.1 Hz, C6), 76.7 (C, d, $^1J_{PC}$ = 167.4 Hz, C5), 80.1 (CH), 81.1 (CH, d, J_{PC} = 10.6 Hz, C3), 85.0 (CH, C2), 100.6 (CH, C1), 113.5 (C), 127.7 (4 × CH), 128.5 (2 × CH), 129.4 (C), 129.7 (2 × CH), 129.85 (CH), 129.87 (CH), 132.7 (C), 132.8 (C), 133.5 (CH), 135.7 (2 × CH), 135.8 (2 × CH), 164.9 (C); ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$) δ 22.7 (P); MS (ESI$^+$-TOF) m/z (%) 693 [(M + Na)$^+$, 100]; HRMS (ESI$^+$-TOF) m/z [M + Na]$^+$ calcd for $C_{34}H_{43}O_{10}NaPSi$ 693.2261; found 693.2264. Anal. calcd for $C_{34}H_{43}O_{10}PSi$: C, 60.88; H, 6.46. Found: C, 60.58; H, 6.54. Compound **28*S***: Crystalline solid, mp 140.2−141.3 °C (from CH_2Cl_2−*n*-hexane); $[\alpha]_D$ +16.6 (*c*, 1.23,

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$CHCl_3$); IR ($CHCl_3$) 3460, 3001, 2957, 1729, 1452, 1428, 1248, 1090 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.88 (9H, s), 1.40 (3H, s), 1.56 (3H, s), 3.78 (3H, d, $^3J_{PH}$ = 10.4 Hz), 3.84 (3H, d, $^3J_{PH}$ = 10.4 Hz), 3.88 (1H, dd, $^3J_{PH}$ = 10.1 Hz, J = 10.1 Hz, H6a), 4.03 (1H, dd, $^3J_{PH}$ = 30.3 Hz, J = 9.8 Hz, H6b), 4.61 (1H, br s, OH), 4.90 (1H, d, J = 2.8 Hz, H4), 4.97 (1H, d, J = 5.7 Hz, H2), 5.27 (1H, dd, J = 5.7, 2.8 Hz, H3), 6.55 (1H, d, $^5J_{PH}$ = 2.2 Hz, H1), 7.29−7.42 (8H, m), 7.47−7.53 (1H, m), 7.59−7.61 (2H, m), 7.70−7.74 (2H, m), 7.92−7.97 (2H, m); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ 19.0 (C), 24.7 (CH_3), 26.0 (CH_3), 26.4 (3 × CH_3), 53.3 (CH_3, d, $^2J_{PC}$ = 7.4 Hz), 53.7 (CH_3, d, $^2J_{PC}$ = 8.5 Hz), 64.3 (CH_2, d, $^2J_{PC}$ = 2.1 Hz, C6), 76.8 (C, d, $^1J_{PC}$ = 154.7 Hz, C5), 77.4 (CH, $^2J_{PC}$ = 21.8 Hz, C4), 82.0 (CH, C3), 86.2 (CH, C2), 100.7 (CH, C1), 113.7 (C), 127.55 (2 × CH), 127.63 (2 × CH), 128.3 (2 × CH), 129.3 (C), 129.57 (CH), 129.60 (CH), 129.8 (2 × CH), 132.4 (C), 132.8 (C), 133.3 (CH), 135.5 (2 × CH), 135.7 (2 × CH), 164.9 (C); $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$) δ 24.1 (P); MS (ESI$^+$-TOF) m/z (%) 693 [(M + Na)$^+$, 100]; HRMS (ESI$^+$-TOF) m/z [M + Na]$^+$ calcd for $C_{34}H_{43}O_{10}NaPSi$ 693.2261; found 693.2255. Anal. calcd for $C_{34}H_{43}O_{10}PSi$: C, 60.88; H, 6.46. Found: C, 60.85; H, 6.41.

*5-Deoxy-5-dimethoxyphosphoryl-1-O-benzoyl-6-O-tert-butyldiphenylsilyl-2,3-O-1-isopropylidene-β-L-gulofuranose (**29**) and 5-Deoxy-5-dimethoxyphosphoryl-1-O-benzoyl-6-O-tert-butyldiphenylsilyl-2,3-O-1-isopropylidene-α-D-mannofuranose (**30**).* Methyl oxalyl chloride (110 μL, 1.2 mmol) was added to a solution of **28S** (161 mg, 0.24 mmol) and DMAP (146.6 mg, 1.2 mmol) in dry MeCN (2 mL) at 0 °C, and the mixture was stirred at this temperature for 30 min under nitrogen. Additional amounts of MeCN (1 mL), methyl oxalyl chloride (55 μL, 0.6 mmol), and DMAP (73.3 mg, 0.6 mmol) were then added, and the stirring was continued for 30 min. Most of the solvent was distilled off in vacuo, and the residue was dissolved with $CHCl_3$. The organic layer was washed with water, saturated $NaHCO_3$ solution and brine, dried with Na_2SO_4, and evaporated under reduced pressure to give methoxalyl derivatives as a pale yellow syrup. The crude was coevaporated with dry toluene under reduced pressure. A solution of the residue in toluene (2 mL) was treated with tributyltin hydride (97 μL, 0.36 mmol) and AIBN (5.9 mg, 0.036 mmol), and the mixture was stirred at reflux temperature for 2 h under nitrogen. Additional AIBN (5.9 mg, 0.036 mmol) was added every 40 min. The mixture was then concentrated under reduced pressure, and the residue was partitioned between MeCN and hexane. The MeCN layer was extracted three times with hexane and then concentrated under reduced pressure. The residue was purified first by silica gel column chromatography (hexanes→hexanes−EtOAc, 6:4) and then by Chromatotron chromatography (hexanes−EtOAc, 70:30) to give **29** (110 mg, 0.168 mmol, 70%) and **30** (28 mg, 0.043 mmol, 18%). Compound **29**: colorless oil, $[\alpha]_D$ +40.6 (*c*, 1.18, $CHCl_3$); IR ($CHCl_3$) 2957, 2859, 1728, 1428, 1261, 1105, 1063 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ ppm 1.10 (9H, s), 1.21 (3H, s), 1.41 (3H, s), 2.63 (1H, dddd, $^2J_{PH}$ = 18.0 Hz, J = 10.1, 3.8, 3.8 Hz, H5), 3.70 (3H, d, $^3J_{PH}$ = 11.0 Hz), 3.73 (3H, d, $^3J_{PH}$ = 11.0 Hz), 4.01 (1 H, ddd, $^3J_{PH}$ = 26.8 Hz, J = 10.4, 3.8 Hz, H6a), 4.21 (1H, ddd, $^3J_{PH}$ = 11.0 Hz, J = 11.0, 3.9 Hz, H6b), 4.48 (1H, dd, J = 5.4, 3.5 Hz, H3), 4.61 (1 H, ddd, $^3J_{PH}$ = 6.7 Hz, J = 10.0, 3.2 Hz, H4), 4.71 (1 H, d, J = 5.7 Hz, H2), 6.37 (1H, s, H1), 7.35−7.48 (9 H, m), 7.67−7.74 (4 H, m), 7.99−8.01 (2H, m); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ 19.3 (C), 24.8 (CH_3), 26.0 (CH_3), 26.8 (3 × CH_3), 39.5 (CH, d, $^1J_{PC}$ = 143.1 Hz, C5), 52.4 (CH_3, d, $^2J_{PC}$ = 6.4 Hz), 52.9 (CH_3, d, $^2J_{PC}$ = 7.4 Hz), 61.1 (CH_2, d, $^2J_{PC}$ = 7.4 Hz, C6), 79.4 (CH, d, $^3J_{PC}$ = 11.7 Hz, C3), 79.8 (CH, d, $^2J_{PC}$ = 4.2 Hz, C4), 84.7 (CH, C2), 101.2 (CH, C1), 112.9 (C), 127.67 (2 × CH), 127.71 (2 × CH), 128.4 (2 × CH), 129.7 (2 × CH), 129.76 (CH), 129.77 (CH), 133.0 (2 × C), 133.4 (CH), 135.7 (4 × CH), 164.9 (C) (the benzoate *ipso* carbon is missing); $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$) δ 30.5 (P); MS (ESI$^+$-TOF) m/z (%) 677 [(M + Na)$^+$, 100]; HRMS (ESI$^+$-TOF) m/z [M + Na]$^+$ calcd for $C_{34}H_{43}NaO_9PSi$ 677.2312; found 677.2313. Anal. calcd for $C_{34}H_{43}O_9PSi$: C, 62.37; H, 6.62. Found: C, 62.23; H, 6.63. Compound **30**: colorless oil, $[\alpha]_D$ +20.9 (*c*, 1.13, $CHCl_3$); IR ($CHCl_3$) 2956, 2857, 1727, 1428, 1260, 1092 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, simulated coupling constants using DAISY) δ 0.87 (9H, s), 1.37 (3H, s), 1.47 (3H, s), 2.60 (1H, dddd, $^2J_{PH}$ = 20.0 Hz, J = 10.8, 3.3, 2.0 Hz, H5), 3.72 (3H, d, $^3J_{PH}$ = 10.7 Hz), 3.77 (3H, d, $^3J_{PH}$ = 11.0 Hz), 4.14 (1H, ddd, $^3J_{PH}$ = 34.5 Hz, J = 9.9, 3.3 Hz, H6a), 4.14 (1H, ddd, $^3J_{PH}$ = 11.3 Hz, J = 9.9, 2.0 Hz, H6b), 4.74 (1H, ddd, $^3J_{PH}$ = 4.3 Hz, J = 10.8, 2.9, Hz, H4), 4.84 (1H, d, J = 5.7 Hz, H2), 4.92 (1H, dd, J = 5.7, 2.9 Hz, H3), 6.36 (1H, br s, J = 0.4 Hz, H1), 7.23−7.35 (8H, m), 7.42−7.47 (1H, m), 7.54−7.59 (2H, m), 7.67−7.69 (2H, m), 7.89−7.93 (2H, m); ^1H NMR (500 MHz, C_6D_6, simulated coupling constants using DAISY) δ 1.06 (9H, s), 1.15 (3H, s), 1.31 (3H, s), 2.61 (1H, dddd, $^2J_{PH}$ = 20.0 Hz, J = 10.9, 3.1, 1.8 Hz, H5), 3.45 (3H, d, $^3J_{PH}$ = 10.7 Hz), 3.51 (3H, d, $^3J_{PH}$ = 11.0 Hz), 4.31 (1H, ddd, $^3J_{PH}$ = 34.7 Hz, J = 9.9, 3.1 Hz, H6a), 4.31 (1H, ddd, $^3J_{PH}$ = 10.8 Hz, J = 9.9, 1.8 Hz, H6b), 4.63 (1H, d, J = 5.7 Hz, H2), 4.92 (1H, dd, J = 5.7, 2.9 Hz, H3), 5.03 (1H, ddd, $^3J_{PH}$ = 4.2 Hz, J = 10.9, 2.9 Hz, H4), 6.73 (1H, br s, J = 0.9 Hz, H1), 6.95−7.02 (2H, m), 7.04−7.09 (1H, m), 7.18−7.25 (2H, m), 7.27−7.32 (2H, m), 7.36−7.39 (2H, m), 7.90 (2H, d, J = 6.9 Hz), 8.00 (2H, d, J = 6.9 Hz), 8.04 (2H, d, J = 7.6 Hz); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ 19.2 (C), 25.2 (CH_3), 26.3 (CH_3), 26.5 (3 × CH_3), 38.4 (CH, d, $^1J_{PC}$ = 137.8 Hz, C5), 52.2 (CH_3, d, $^2J_{PC}$ = 6.4 Hz), 52.6 (CH_3, d, $^2J_{PC}$ = 5.3 Hz), 60.0 (CH_2, d, $^2J_{PC}$ = 8.5 Hz, C6), 77.9 (CH, d, $^2J_{PC}$ = 8.5 Hz, C4), 80.3 (CH, C3), 85.8 (CH, C2), 100.9 (CH, C1), 112.8 (C), 127.6 (2 × CH), 127.6 (2 × CH), 128.3 (2 × CH), 129.49 (CH), 129.54 (CH), 129.8 (2 × CH), 132.8 (2 × C), 133.3 (CH), 135.6 (4 × CH), 165.1 (C) (the benzoate *ipso* carbon is missing); $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$) δ 30.0 (P); MS (ESI$^+$-TOF) m/z (%) 677 [(M + Na)$^+$, 100]; HRMS (ESI$^+$-TOF) m/z [M + Na]$^+$ calcd for $C_{34}H_{43}NaO_9PSi$ 677.2312; found 677.2310. Anal. calcd for $C_{34}H_{43}O_9PSi$: C, 62.37; H, 6.62. Found: C, 62.09; H, 6.84.

*5-Deoxy-5-dimethoxyphosphoryl-6-O-tert-butyldiphenylsilyl-2,3-O-1-isopropylidene-L-gulofuranose (**31**).* A solution of **29** (67 mg, 0.102 mmol) in dry MeOH (2.7 mL) containing NaOMe (11 mg, 0.204 mmol) was stirred at room temperature for 2 h. The mixture was neutralized with acid ion-exchange resin Amberlite IR120, filtered, and concentrated under reduced pressure. The residue was purified by Chromatotron chromatography (hexanes−EtOAc, 20:80) to give **31** (54 mg, 0.098 mmol, 96%, mixture of anomers, α−β, 92:8): colorless oil, major isomer, α-anomer: ^1H NMR (500 MHz, $CDCl_3$) δ 1.08 (9H, s), 1.19 (3H, s), 1.36 (3H, s), 2.58 (1H, dddd, $^2J_{PH}$ = 18.3 Hz, J = 10.5, 3.7, 3.7 Hz, H5), 3.72 (3H, d, $^3J_{PH}$ = 11.0 Hz), 3.75 (3H, d, $^3J_{PH}$ = 11.0 Hz), 3.94 (1H, ddd, $^3J_{PH}$ = 27.7 Hz, J = 10.7, 3.5 Hz, H6a), 4.10 (1H, ddd, $^3J_{PH}$ = 10.2 Hz, J = 10.2, 4.1 Hz, H6b), 4.41 (1H, dd, J = 5.4, 3.5 Hz, H3), 4.50 (1H, d, J = 5.7 Hz, H2), 4.56 (1H, ddd, $^3J_{PH}$ = 6.5 Hz, J = 10.2, 3.2 Hz, H4), 5.40 (1H, s, H1), 7.36−7.46 (6H, m), 7.68−7.71(4H, m); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ 19.2 (C), 24.8 (CH_3), 26.1 (CH_3), 26.8 (3 × CH_3), 39.6 (CH, d, $^1J_{PC}$ = 140.9 Hz, C5), 52.4 (CH_3, d, J = 7.4 Hz), 52.8 (CH_3, d, J = 6.4 Hz), 61.1 (CH_2, d, $^2J_{PC}$ = 6.4 Hz, C6), 77.0 (CH, d, $^2J_{PC}$ = 4.5 Hz, C4), 79.9 (CH, d, $^3J_{PC}$ = 12.7 Hz, C3), 85.4 (CH, C2), 100.9 (CH, C1), 112.0 (C), 127.6 (2 × CH), 127.7 (2 × CH), 129.68 (CH), 129.73 (CH), 133.1 (C), 133.2 (C), 135.7 (4 × CH); $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$) δ 32.2 (P, α-anomer), 31.3 (P, β-anomer); MS (ESI$^+$-TOF) m/z (%) 573 [(M + Na)$^+$, 100]; HRMS (ESI$^+$-TOF) m/z [M + Na]$^+$ calcd for $C_{27}H_{39}NaO_8PSi$ 573.2050; found 573.2048.

*5-Deoxy-5-dimethoxyphosphoryl-6-O-tert-butyldiphenylsilyl-2,3-O-1-isopropylidene-D-mannofuranose (**32**).* A solution of **30** (13.5 mg, 0.021 mmol) in dry MeOH (0.55 mL) containing NaOMe (2.3 mg, 0.042 mmol) was stirred at room temperature for 2 h. The mixture was neutralized with acid ion-exchange resin Amberlite IR120, filtered, and concentrated under reduced pressure. The residue was purified by Chromatotron chromatography (hexanes−EtOAc, 30:70) to give **32** (9.4 mg, 0.017 mmol, 81%, mixture of anomers, α−β, 92:8): colorless oil, major isomer, α-anomer: ^1H NMR (500 MHz, $CDCl_3$) δ 1.08 (9H, s), 1.31 (3H, s), 1.37 (3H, s), 1.63 (1H, br s), 2.57 (1H, dddd, $^2J_{PH}$ = 19.9 Hz, J = 10.4, 4.1, 2.5 Hz, H5), 3.74 (3H, d, J = 11.0 Hz), 3.76 (3H, d, J = 10.7 Hz), 4.15 (1H, ddd, $^3J_{PH}$ = 31.2 Hz, J = 9.8, 4.1 Hz, H6a), 4.26 (1H, ddd, $^3J_{PH}$ = 13.6 Hz, J = 10.2, 2.4 Hz, H6b), 4.57 (1H, d, J = 5.7 Hz, H2), 4.59 (1 H, ddd, $^3J_{PH}$ = 5.4 Hz, J = 10.4, 2.7, H4), 4.81 (1H, dd, J = 5.7, 2.8 Hz, H3), 5.16

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(1H, br s, H1), 7.35−7.44 (6H, m), 7.71−7.75 (4H, m); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ 19.4 (C), 25.1 (CH_3), 26.2 (CH_3), 26.7 (3 × CH_3), 38.3 (CH, d, $^1J_{PC}$ = 137.8 Hz, C5), 52.1 (CH_3, d, $^2J_{PC}$ = 7.4 Hz), 52.6 (CH_3, d, $^2J_{PC}$ = 6.4 Hz), 60.6 (CH_2, d, $^2J_{PC}$ = 9.5 Hz, C6), 75.6 (CH, d, J = 6.4 Hz, C4), 80.6 (CH, C3), 85.8 (CH, C2), 100.6 (CH, C1), 112.1 (C), 127.51 (2 × CH), 127.54 (2 × CH), 129.6 (2 × CH), 133.6 (C), 133.8 (C), 135.7 (2 × CH), 135.8 (2 × CH); $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$) δ 30.7 (P, α-anomer), 30.4 (P, β-anomer); MS (ESI$^+$-TOF) m/z (%) 573 [(M + Na)$^+$, 100]; HRMS (ESI$^+$-TOF) m/z [M + Na]$^+$ calcd for $C_{27}H_{39}NaO_8PSi$ 573.2050; found 573.2050.

*(S$_P$)-4-(tert-Butyldiphenylsilyloxy)methyl-4-deoxy-3-O-formyl-1,2-O-isopropylidene-5-methoxy-5-oxa-5-phospha-β-D-arabino-pyranose (**50**) and (R$_P$)-4-(tert-Butyldiphenylsilyloxy)methyl-4-deoxy-3-O-formyl-1,2-O-isopropylidene-5-methoxy-5-oxa-5-phospha-β-D-arabinopyranose (**51**).* A solution of **31** (18.6 mg, 0.034 mmol) in dry MeOH (0.18 mL) containing NaOH (15 mg, 0.375 mmol) was stirred at 40−43 °C for 30 h. The mixture was neutralized with acid ion-exchange resin Amberlite IR120, filtered, and concentrated under reduced pressure. The crude residue was used in the next reaction without further purification. To a solution of the residue (17.7 mg) in dry CH_2Cl_2 (1.6 mL) were added $PhI(OAc)_2$ (22.5 mg, 0.07 mmol) and I_2 (8.4 mg, 0.033 mmol). The mixture under nitrogen was stirred and irradiated with two 80 W tungsten-filament lamps at room temperature for 2 h. The solution was directly poured onto a Chromatotron chromatography plate and subsequently eluted (hexanes−EtOAc, 50:50) to give **50** (4.8 mg, 0.009 mmol, 26%) and **51** (7.6 mg, 0.014 mmol, 42%). Compound **50**: colorless oil, $[\alpha]_D$ +7.0 (*c*, 0.89, $CHCl_3$); IR ($CHCl_3$) 2958, 1732, 1472, 1428, 1387, 1273, 1114 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, simulated coupling constants using DAISY) δ 1.05 (9H, s), 1.42 (3H, s), 1.64 (3H, s), 2.84 (1H, dddd, $^2J_{PH}$ = 23.0 Hz, J = 10.6, 4.3, 4.1, Hz, H2), 3.68 (3H, d, $^3J_{PH}$ = 11.0 Hz), 3.77 (1H, ddd, $^3J_{PH}$ = 4.5 Hz, J = 10.6, 10.3 Hz, H6a), 4.15 (1H, ddd, $^3J_{PH}$ = 4.8 Hz, J = 10.3, 4.3 Hz, H6b), 4.21 (1H, dd, J = 3.3, 2.6 Hz, H4), 5.69 (1H, dd, $^3J_{PH}$ = 5.9 Hz, J = 2.6 Hz, H5), 6.01 (1H, ddd, $^3J_{PH}$ = 32.5 Hz, J = 4.1, 3.3 Hz, H3), 7.36−7.47 (6H, m), 7.60−7.62 (4H, m), 7.95 (1H, s); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ 19.1 (C), 25.8 (CH_3), 26.8 (3 × CH_3), 27.5 (CH_3), 35.9 (CH, d, $^1J_{PC}$ = 127.2 Hz, C2), 52.3 (CH_3, d, $^2J_{PC}$ = 7.4 Hz), 56.8 (CH_2, d, $^2J_{PC}$ = 5.3 Hz, C6), 66.4 (CH, d, $^2J_{PC}$ = 7.4 Hz, C3), 74.5 (CH, d, $^3J_{PC}$ = 7.4 Hz, C4), 99.2 (CH, d, $^2J_{PC}$ = 7.4 Hz, C5), 113.5 (C), 127.8 (2 × CH), 127.9 (2 × CH), 130.0 (2 × CH), 132.62 (C), 132.64 (C), 135.6 (2 × CH), 135.7 (2 × CH), 159.4 (CH); $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$) δ 17.3 (P); MS (ESI$^+$-TOF) m/z (%) 557 [(M + Na)$^+$, 100]; HRMS (ESI$^+$-TOF) m/z [M + Na]$^+$ calcd for $C_{26}H_{35}NaO_8PSi$ 557.1737; found 557.1724. Anal. calcd for $C_{26}H_{35}O_8PSi$: C, 58.41; H, 6.60. Found: C, 58.01; H, 6.99. Compound **51**: colorless oil, $[\alpha]_D$ +35.5 (*c*, 1.1, $CHCl_3$); IR ($CHCl_3$) 2958, 1731, 1472, 1428, 1387, 1250, 1113 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, simulated coupling constants using DAISY) δ 1.06 (9H, s), 1.41 (3H, s), 1.58 (3H, s), 2.66 (1H, dddd, $^2J_{PH}$ = 20.5 Hz, J = 9.9, 5.6, 3.6 Hz, H2), 3.66 (3H, d, $^2J_{PH}$ = 11.3 Hz), 3.93 (1H, ddd, $^3J_{PH}$ = 7.9 Hz, J = 10.7, 9.9 Hz, H6a), 4.04 (1H, ddd, $^3J_{PH}$ = 5.4 Hz, J = 10.7, 5.6 Hz, H6b), 4.30 (1H, dd, J = 3.8, 3.1 Hz, H4), 5.85 (1H, dd, $^3J_{PH}$ = 9.2 Hz, J = 3.1 Hz, H5), 5.98 (1H, ddd, $^3J_{PH}$ = 31.7 Hz, J = 3.8, 3.6 Hz, H3), 7.35−7.46 (6H, m), 7.62−7.65 (4H, m), 8.04 (1H, s); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ 19.1 (C), 25.7 (CH_3), 26.8 (3 × CH_3), 27.1 (CH_3), 35.2 (CH, d, $^1J_{PC}$ = 126.1 Hz, C2), 52.5 (CH_3, d, $^2J_{PC}$ = 6.4 Hz), 57.7 (CH_2, d, $^2J_{PC}$ = 5.3 Hz, C6), 66.8 (CH, d, $^2J_{PC}$ = 7.4 Hz, C3), 74.1 (CH, d, $^3J_{PC}$ = 7.4 Hz, C4), 99.0 (CH, d, $^2J_{PC}$ = 6.4 Hz, C5), 113.0 (C), 127.81 (2 × CH), 127.83 (2 × CH), 129.9 (CH), 130.0 (CH), 132.5 (C), 132.9 (C), 135.59 (2 × CH), 135.63 (2 × CH), 159.5 (CH); $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$) δ 18.0 (P); MS (ESI$^+$-TOF) m/z (%) 557 [(M + Na)$^+$, 100]; HRMS (ESI$^+$-TOF) m/z [M + Na]$^+$ calcd for $C_{26}H_{35}NaO_8PSi$ 557.1737; found 557.1737. Anal. calcd for $C_{26}H_{35}O_8PSi$: C, 58.41; H, 6.60. Found: C, 58.49; H, 6.99.

*4-Deoxy-3-O-formyl-1,2-O-isopropylidene-4-methylene-5-methoxy-5-oxa-5-phospha-β-D-threo-pentopyranose (**53**).* A solution of **32** (45.6 mg, 0.083 mmol) in dry MeOH (0.44 mL) containing NaOH (35 mg, 0.88 mmol) was stirred at 40−43 °C for 30 h. The mixture was neutralized with acid ion-exchange resin Amberlite IR120, filtered, and concentrated under reduced pressure. The crude residue was used in the next reaction without further purification. To a solution of the residue (41 mg) in dry CH_2Cl_2 (4 mL) were added $PhI(OAc)_2$ (60.2 mg, 0.187 mmol) and I_2 (22 mg, 0.087 mmol). The mixture was stirred under nitrogen and irradiated with two 80 W tungsten-filament lamps at room temperature for 5.5 h. The rather complex mixtures obtained were directly poured onto a Chromatotron chromatography plate and subsequently eluted (hexanes−EtOAc, 40:60 → 30:70) to give **53** (3 mg, 0.011 mmol, 13%) as the sole identifiable product. Compound **53**: colorless oil, IR ($CHCl_3$) 2929, 2858, 1732, 1600, 1462, 1373, 1117, 1044 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 1.42 (3H, s), 1.59 (3H, s), 3.74 (3H, d, $^3J_{PH}$ = 11.3 Hz), 4.19 (1H, dd, J = 2.5, 2.5 Hz, H4), 5.88 (1H, dd, J = 5.4, 2.5 Hz, H3), 5.95 (1H, dd, $^3J_{PH}$ = 23.6, J = 2.8 Hz, H5), 6.34 (1H, d, $^3J_{PH}$ = 43.8 Hz, P-H6*trans*), 6.51 (1H, d, $^3J_{PH}$ = 20.5 Hz, P-H6*cis*), 8.08 (1H, s); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ_C 25.9 (CH_3), 27.4 (CH_3), 52.4 (CH_3, d, $^2J_{PC}$ = 5.3 Hz), 71.6 (CH, d, $^2J_{PC}$ = 10.6 Hz, C5), 77.2 (CH, C4), 99.5 (CH, d, $^2J_{PC}$ = 6.4 Hz, C3), 113.6 (C), 138.3 (CH_2, d, $^2J_{PC}$ = 7.4 Hz, C6), 158.8 (C), (the C2 is not observed); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ_P 7.7 (P);MS (ESI$^+$-TOF) m/z (%) 301 [(M + Na)$^+$, 100]; HRMS (ESI$^+$-TOF) m/z: [M + Na]$^+$ calcd for $C_{10}H_{15}NaO_7P$ 301.0453; found 301.0444.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c00059.

X-ray crystallographic structure of compound **48** (CCDC 1973012); these data are provided free of charge by The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif X-ray compound 48 (CIF)

Ring conformations of 2-oxo-1,2-oxaphosphocyclanes **36**−**51**; copies of the ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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