EurJOC European Journal of Organic Chemistry

FULL PAPER

DOI: 10.1002/ejoc.201402387

Fragmentation of Carbohydrate Anomeric Alkoxyl Radicals: Synthesis of Chiral Polyhydroxylated β-Iodo- and Alkenylorganophosphorus(V) Compounds

Daniel Hernández-Guerra,[a] María S. Rodríguez,*[a] and Ernesto Suárez*[a]

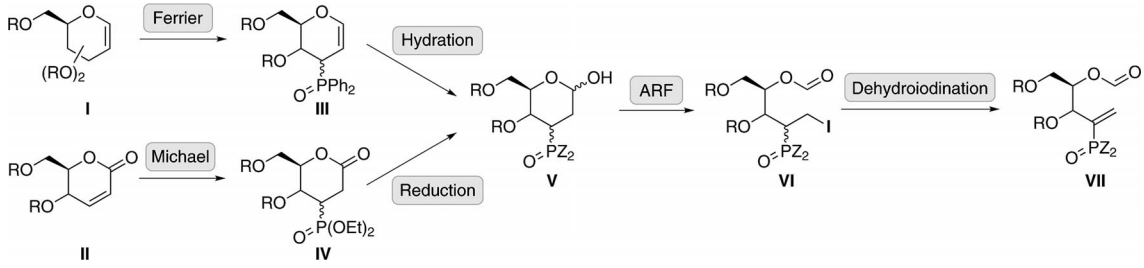
Keywords: Synthetic methods / Carbohydrates / Radicals / Phosphorus / Cyclization

A direct approach to β-iodophosphonates and β-iodophosphine oxides from 2,3-dideoxy-3-phosphoryl carbohydrate derivatives has been achieved by using the anomeric alkoxyl radical 1,2-fragmentation protocol. The reaction has been conducted on carbohydrate derivatives under mild conditions with (diacetoxyiodo)benzene and molecular iodine. Subsequent dehydroiodination afforded the corresponding vinylphosphonates and vinylphosphine oxides.

Introduction

The chemistry of vinylphosphonates[1] and vinylphosphine oxides[2] has attracted a great deal of attention because they constitute an important group of organic reagents and useful synthetic intermediates with a wide range of biological activities. These alkenylphosphorus compounds are used as key starting materials in Michael addition and subsequent Horner–Wadsworth–Emmons olefination of carbonyl compounds, 1,3-cycloadditions, Diels–Alder, Stetter, metathesis reactions, and for the preparation of phosphine ligands, among others. Of special interest is the Michael addition of amines to vinyl phosphonates and vinyl phosphinates in the preparation of β-aminophosphonic or β-aminophosphinic acids as bioisosteres of β-amino carboxylic acids.[1a,1e,1j] However, there is a paucity of information in the literature on radical additions to these electrophilic double bonds. All the examples we have been able to find correspond to the simplest members of the series, almost exclusively to dialkyl vinylphosphonates or diphenyl(vinyl)phosphine oxide.[3] Studies on the synthesis and chemical reactivity of β-iodoorganophosphorus(V) compounds are rare. 2-Iodoethylphosphine oxides appear to be practically unknown, with only one of the simplest members of the family, (2-iodoethyl)(diphenyl)phosphine oxide, having been synthesized.[4] 2-Iodoethylphosphonates are also relatively rare compounds and the reported examples that we were able to uncover correspond almost exclusively to diethyl 2-iodoethylphosphonate or simple alkyl-branched derivatives.

Such compounds have been prepared by halogen or OTs/I exchange under Finkelstein conditions[5] or by metallo-phosphorylation of zirconocene-alkene complexes with chlorophosphate using iodine as electrophile.[6] Studies on the chemical reactivity of these compounds have largely been limited to diethyl 2-iodoethylphosphonate.[5a,5c,7] In the context of carbohydrate-containing phosphorus compounds, a point of interest is the preparation of analogues in which the anomeric carbon has been replaced by an atom of phosphorus,[8] the so-called cyclic phostones[8o] or, more correctly, 1-phospha sugars.[8p] They have been accorded some attention from synthetic chemists as a consequence of



Scheme 1. Alkoxyl radical β-fragmentation of 2,3-dideoxy-3-phosphoryl-hexopyranoses and hexofuranoses. ARF = alkoxyl radical β-fragmentation reaction; Z = Ph (phosphine oxides), Z = OEt (phosphonates).

[a] Síntesis de Productos Naturales, Instituto de Productos Naturales y Agrobiología del CSIC,
Carretera de La Esperanza 3, 38206 La Laguna, Tenerife, Spain
E-mail: mrodriguez@ipna.csic.es
esuarez@ipna.csic.es
https://www.ipna.csic.es/dept/spn/sipn/

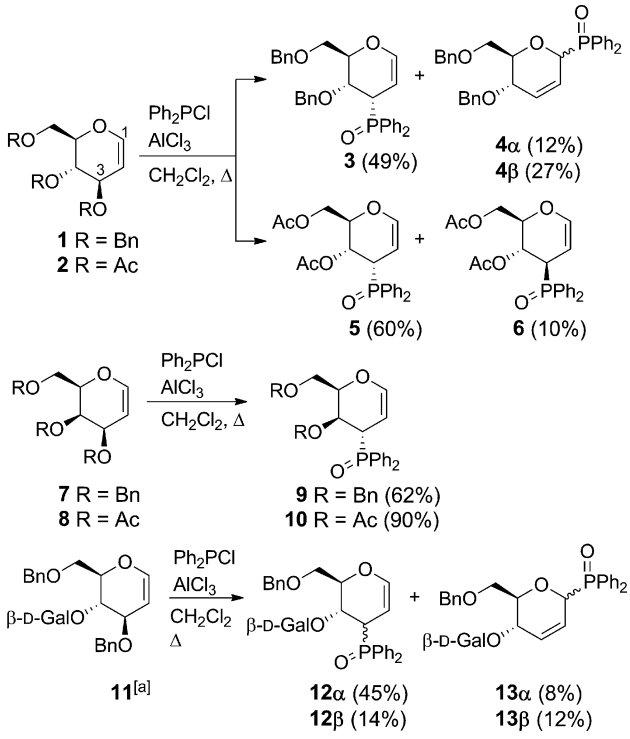
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201402387.

their potential biological activity as glycosidase inhibitors and anticancer agents.[9] In previous papers from this laboratory, we have described the anomeric alkoxyl radical β-fragmentation reaction (ARF) by treatment of carbohydrate free anomeric alcohols with hypervalent iodine(III) in the presence of molecular iodine.[10] This reaction permits the realization of remarkable transformations in the carbohydrate skeleton and the preparation of iminosugars,[11] 1,1,1-trihaloalditols,[12] and polyhydroxylated 2*H*-azirines,[13] among other alditol derivatives. The ready accessibility of the starting material, operational simplicity, and possible further synthetic transformations of the fragmentation products are noteworthy and merit further exploitation of these results. In demonstration of such a utility, we set out to develop a new method for the synthesis of chiral vinylphosphine oxides and vinylphosphonates of generalized structure **VII** (Scheme 1). We have described the preliminary results in a short communication and now report full details of this methodology and its extension to other saccharide models.[14]

Results and Discussion

Regioselective introduction of the C–P bond into the carbohydrate skeleton was accomplished by using two different strategies. 3-Phosphinyl derivatives **III** were prepared from glycals **I** through an anomalous Ferrier reaction,[15] whereas a phospha-Michael addition to readily available hex-2-enono-1,4-lactones **II** was used for the synthesis of 3-phosphonylated sugars **IV** (Scheme 1).[16] The required γ-hydroxyphosphinylated **V** (Z = Ph) or γ-hydroxyphosphonylated compounds **V** (Z = OEt) were then obtained, respectively, by hydration of glycals **III** or by reduction of lactones **IV**. The 3-hydroxyphosphorus compounds **V** were then submitted to the ARF reaction to give β-iodophosphorus compounds **VI**, which, by base dehydroiodination, provided the desired vinylorganophosphorus **VII**.

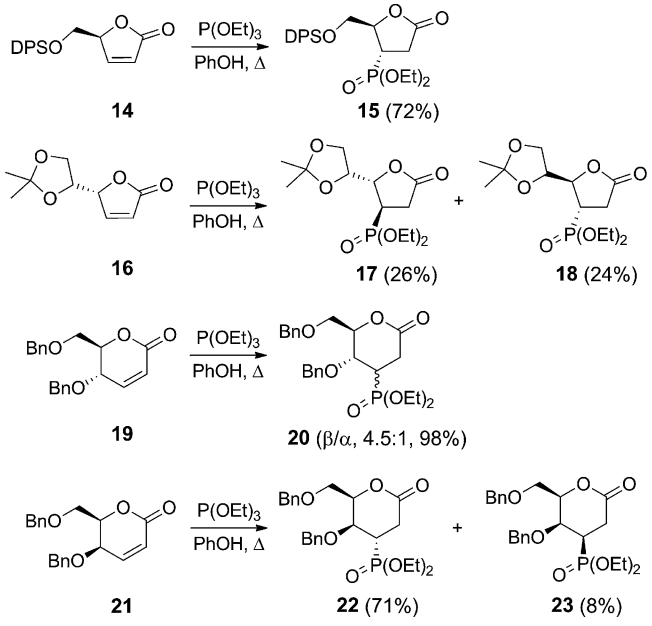
The Ferrier reaction of D-glucals **1** and **2**, D-galactals **7** and **8**, and D-lactal **11** (Scheme 2) was achieved with chlorodiphenylphosphine and aluminum chloride by a modification of the procedure reported by Yamamoto et al.[17] In contrast to hard O-nucleophiles, which attack almost exclusively at C1,[15] the Ferrier addition of softer N- and S-nucleophiles tends to lead preferentially to 3-substituted glycals under equilibrium conditions.[18] Consequently, carried out the reactions with the diphenylphosphenium cation intermediate under thermodynamic control. Indeed, reflux temperatures and prolonged reaction times afforded the preponderant formation of 3-phosphinyl glycal derivatives in moderate to good yields and, in some cases, with excellent regio- and stereoselectivity as shown in Scheme 2.[19] These conditions produced substantially different results, with respect to regioisomeric composition and yield of the Ferrier products, from those used by Yamamoto with **1**, **2** and **8** glycals, which gave principally the C1 kinetic compounds. Especially remarkable are the cases of D-galactal derivatives **7** and **8**, for which formation of C1 adducts is completely prevented and only 3-phosphinyl-D-gulal products **9** and **10** are obtained. The reaction of triacetyl D-glucal **2** deserves a brief comment. The glucal stereochemistry previously assigned to **5** is erroneous.[17] Based on a careful NMR study and comparison of spectroscopic data with true glucal derivative **6**, the allal stereochemistry shown in Scheme 2 is preferred. The coupling constant $^3J_{P,H4}$ that is dihedral angle-dependent, can be analyzed in terms of a generalized Karplus-type equation and proved to be diagnostic in distinguishing between these two isomers.[20] The observed value of 20.9 Hz for $^3J_{P\alpha,H4\beta}$ (calcd. 22.1 Hz) in compound **5** is notably higher than that measured in **6** ($^3J_{P\beta,H4\beta}$ = 9.1 Hz, calcd. 5.1 Hz).[21]



Scheme 2. Synthesis of 3-diphenylphosphoryl-hex-1-enitol precursors. [a] β-D-Gal refers to the perbenzylated moiety of β-D-galactose.

Preliminary attempts to prepare 3-phosphonylated glycals by using the Ferrier rearrangement mentioned above upon reaction of perbenzylated D-glucal with $(EtO)_2PCl/AlCl_3$ instead of $Ph_2PCl/AlCl_3$ proved to be unsuccessful; therefore, an alternative route was sought. The phospha-Michael addition of triethyl phosphite to readily accessible pent-2-enono-1,4-lactones **14**[22] and **16**[23] and hex-2-enono-1,5-lactones **19**[24] and **21**[25] under the conditions described by Kofoed and Pedersen,[26] using phenol as protonating agent, afforded the 3-phosphonylated γ-lactones **15**, **17**, and **18** and δ-lactones **20**, **22**, and **23** (Scheme 3). The reaction proceeded, in all cases, with excellent diastereoselectivity under steric control, with the 1,4-addition taking place preferentially *anti* to the vicinal substituent at the C4 position.

It is worthwhile to note that a mixture of isomers **17** and **18** was unexpectedly formed during the phosphorylation of



Scheme 3. Synthesis of 3-diethoxyphosphoryl-pentono-1,4-lactone and 3-diethoxyphosphoryl-hexono-1,5-lactone precursors.

lactone **16**, presumably through acid-catalyzed enolization of the lactone, which led to epimerization at C4 prior to the P-addition. The stereochemistry of the newly introduced contiguous stereocenters could not be determined unambiguously at this stage by NMR spectroscopy. The complete stereochemical characterization of both compounds by Mosher analysis of the C3 alcohol obtained by hydrolysis of related compound **60** (Table 2) is discussed below.

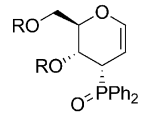
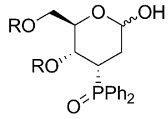
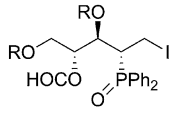
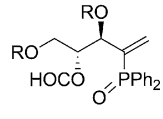
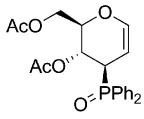
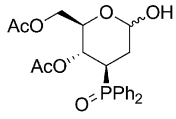
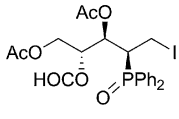
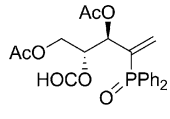
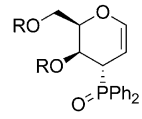
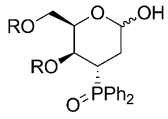
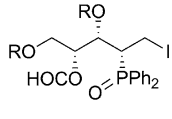
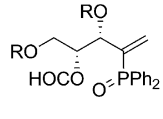
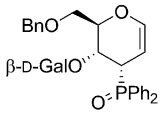
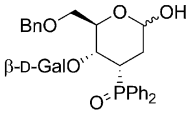
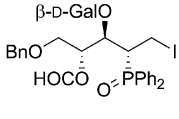
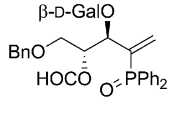
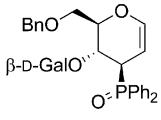
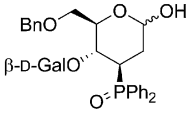
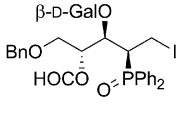
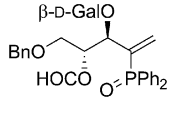
Precedents for such an isomerization of 4-substituted furanones are documented in the literature under mild basic catalytic conditions.[27] Curiously, the phosphorylation process under conditions similar to those of analogous lactone **14** does not appear to be accompanied by a concurrent epimerization step at C4 (see below).

Hydration of glycals **3**, **5**, **6**, **9**, **10**, and **12** by a modification of the procedure of Falck et al.,[28] was accomplished by using water as nucleophile. Reaction with catalytic amounts of $Ph_3P{\cdot}HBr$ in tetrahydrofuran (THF)/H_2O heated to reflux gave 2,3-dideoxy-hexopyranose compounds **24**–**30** in high yields (Table 1). The phosphoryl group stereochemistry is probably better studied at this stage with the pyranose ring in a more stable $^4C_1$ conformation. The involved vicinal coupling constants $^3J_{H,H}$ and $^3J_{P,H}$ in the major α-isomer can now be more accurately read or extracted through a full-lineshape fit of the calculated spectrum.[29] In compounds **24**–**30** the dihedral angle dependence of the $^3J_{P,H}$ coupling constants is clearly observed between the atom of phosphorus and hydrogen atoms at C2 and C4.[30] In some cases, the C3 stereochemistry was confirmed by 2D NOESY and $^1H\{^{31}P\}$ NMR decoupled spectra. The ARF reactions were performed under the conditions summarized in Table 1, with (diacetoxyiodo)benzene (DIB) and iodine in CH_2Cl_2. The reaction, which proceeded smoothly, appears to be very little affected by the sugar stereochemistry and the β-iodo phosphine oxides **31**–**36**, and **38** were obtained in good yields. No products coming from radical epimerization at the neighboring chiral centers could be detected in these reactions. However, in the fragmentation of **29**, a side reaction was observed, with the formation of iodide **36** being accompanied by a small amount (15%) of oxidized hexono-1,5-lactone **37** (not shown, see experimental section).

These β-iodo phosphine oxides were sufficiently stable to be purified by silica gel chromatography and could be stored under nitrogen in a freezer for an extended period of time. The dehydroiodination of these compounds was effectively accomplished with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in benzene to afford vinylphosphine oxides **39**–**44** in high yields. The reaction temperature was kept as low as possible 9–10 °C, just above the freezing point of benzene, to prevent hydrolysis of the formate group. In the elimination of iodides **32** and **36**, partial hydrolysis of the formate group occurred and small amounts of dehydroiodinated alcohols **41** (12%) and **45** (13%) (not shown in Table 1, see experimental section) were also formed. The presence in the ^1H NMR spectra of two doublets at 6.22–6.37 ($^3J_{P,Htrans} \approx 40$ Hz) and 5.58–5.75 ppm ($^3J_{P,Hcis} \approx 20$ Hz) corresponding to the vinylic protons and the ^{31}P NMR chemical shifts (29.2–33.0 ppm) are the most representative spectroscopic characteristics of these compounds and are in good agreement with those previously observed for other simpler analogues of diphenylvinylphosphine oxides prepared by hydrophosphination of terminal alkynes.[31] To assess the scope of this methodology on the phosphonylated series, a variety of 2,3-dideoxy-pentofuranose, -hexofuranose and -hexopyranose carbohydrates were obtained. The alcohols required by the ARF were prepared by diisobutylaluminum hydride (DIBAL-H) mediated reduction of the carboxylate group of 3-phosphonylated γ-lactones **15**, **17**, and **18**, and δ-lactones **20** and **22** (Table 2). Separation of 2-deoxy-D-glucose **49** and 2-deoxy-D-allose **50** derivatives was chromatographically accomplished at this step and the reaction sequence was continued with both compounds separately. The ARF reaction proceeds analogously to the diphenylphosphine oxide series, and β-iodophosphonates **52**–**57** were obtained in good to excellent yields. These compounds exhibit a similar stability to those of the β-iododiphenylphosphine oxide counterparts and can be stored at –20 °C for a long time and handled at room temperature without any apparent deterioration. The only exceptions are iodides **53** and **54**, which were partially dehydroiodinated under silica gel chromatographic conditions and could not be isolated in pure form. Finally, DBU-mediated elimination of iodide derivatives proceeded smoothly to give vinylphosphonates **58**–**62**. In the ^1H NMR spectra, two doublets at 6.24–6.35 ($^3J_{P,Hcis} \approx 22$ Hz) and 6.10–6.21 ppm ($^3J_{P,Htrans} \approx 45$ Hz) corresponding to the vinylic protons and the ^{31}P NMR chemical shifts (15.0–16.4 ppm) are now observed for these vinylphosphonates.

The absolute stereochemistry at C3 of compound **60** was determined by using Mosher ester analysis (Table 2, entry 3).[32] The alcohol obtained after formate hydrolysis was

Table 1. Synthesis of β-iodo- and vinyl-phosphine oxides derived from carbohydrates.

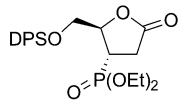
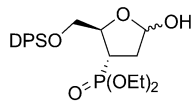
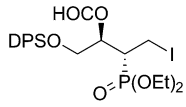
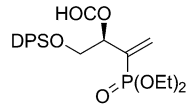
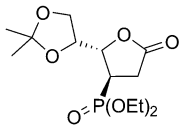
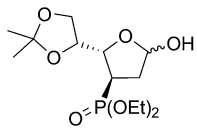
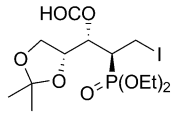
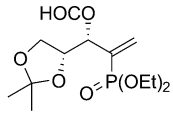
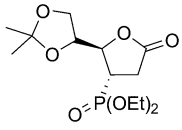
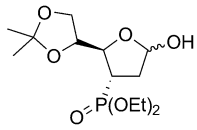
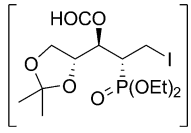
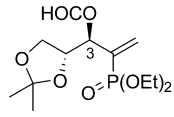
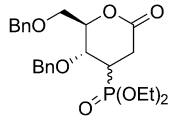
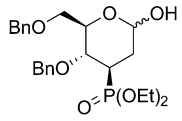
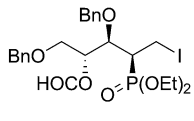
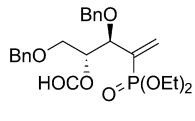
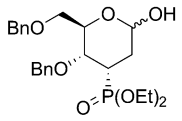
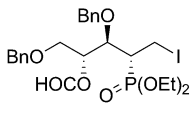
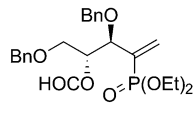
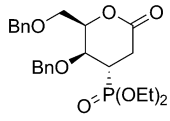
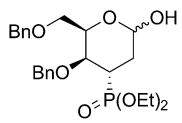
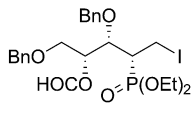
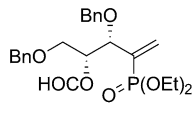
Entry	Substrate[a]	Time [h]	γ-Hydroxy-phosphorus [%][b]	Time [h]	β-Iodo-phosphorus [%][c]	Time [h]	Vinyl-phosphorus [%]
							
1	**3** R = Bn	1.5	**24** R = Bn (90)	2.5	**31** R = Bn (79)	0.5	**39** R = Bn (89)
2	**5** R = Ac	8	**25** R = Ac (55)	4.5	**32** R = Ac (85)	0.33	**40** R = Ac (75)[d]
							
3	**6**	13	**26** (59)	4	**33** (75)	1.75	**40** (85)
							
4	**9** R = Bn	3.75	**27** R = Bn (92)	2	**34** R = Bn (78)	1	**42** R = Bn (91)
5	**10** R = Ac	7.5	**28** R = Ac (73)	2.2	**35** R = Ac (80)	1	**43** R = Ac (97)
							
6	**12α**[e]	6	**29** (76)	0.5	**36** (67)[f]	12	**44** (83)[g]
							
7	**12β**	1.5	**30** (74)	0.67	**38** (70)	15	**44** (60)[h]

[a] Reagents and conditions per mmol of substrate: $Ph_3P{\cdot}HBr$ (0.12–0.46 mmol), H_2O (0.43 mL), THF (21.5 mL), reflux. [b] Reagents and conditions per mmol of substrate: DIB (1.1–1.5 mmol), I_2 (0.6–1.1 mmol), CH_2Cl_2 (25 mL). [c] Reagents and conditions per mmol of substrate: DBU (1.1–2.6 mmol), benzene (25 mL), 9–10 °C. [d] 12% hydrolyzed compound **41** (not shown, see experimental section) was also obtained, the global yield of the vinylphosphine oxide was 87%. [e] For clarity, β-D-Gal refers to the perbenzylated moiety of β-D-galactose. [f] 15% oxidized lactone **37** (not shown, see experimental section) was also obtained. [g] 13% hydrolyzed compound **45** (not shown, see experimental section) was also obtained, the global yield of the vinylphosphine oxide was 96%. [h] 32% hydrolyzed compound **45** (not shown, see experimental section) was also obtained, the global yield of the vinylphosphine oxide was 92%.

esterified with (*R*)- and (*S*)-MPA acids to form the respective 3-O-esters. Inspection of ^{1}H NMR spectra revealed that 3-*O*-(*R*)-MPA ester exhibited, with respect to ^{1}H NMR shift of 3-*O*-(*S*)-MPA ester, upfield shift of $\Delta\delta_{R,S}$ = –0.72 ppm for H1$_{trans}$ and $\Delta\delta_{R,S}$ = –0.31 ppm for H1$_{cis}$ and downfield of $\Delta\delta_{R,S}$ = 0.16 ppm for H5a and $\Delta\delta_{R,S}$ = 0.26 ppm for H5b. Hence, the absolute configuration at C3 was established as *R* and consequently a structure of D-*erythro*-pent-1-enitol was assigned to **60**. This means that compound **18** possesses a 2,3-dideoxy-3-diethoxyphosphoryl-5,6-*O*-isopropylidene-D-*ribo*-hexono-1,4-lactone structure and that it is the inverted isomer of the enolization equilibrium observed during the phosphorylation of lactone **16**. Consequently, a structure of 2,3-dideoxy-3-diethoxy phosphoryl-5,6-*O*-isopropylidene-D-*lyxo*-hexono-1,4-lactone (**17**) should be assigned to the other isomer. This equilibrium does not seem to be operative during the phosphorylation of lactone **14**, which would otherwise lead to racemization of vinylphosphonate **58** (Table 2, entry 1). The optical purity of compound **58** was determined by hydrolysis and conversion of the resulting alcohol into the Mosher ester, confirming by ^{1}H NMR analysis that no partial racemization occurs during the phosphorylation reaction.

Finally, to demonstrate the preparative utility of this methodology, we performed the ARF reaction starting from alcohol **26** on a 9.3 mmol scale to generate **33** (3.9 g, 7.1 mmol, 76%) and **40** (2.7 g, 6.2 mmol, 87%) (see Table 1, entry 3). Analogously, the phosphonate series was scaled-up by fragmentation of alcohol **49** (8.3 mmol) to afford **55** (4.3 g, 7.3 mmol, 88%) and **61** (3.4 g, 7.3 mmol, 100%) (see Table 2, entry 4). The synthetic versatility of these polyhydroxylated phosphorus compounds has been evaluated and the results are summarized in Schemes 4, 5, and 6. The formation of O–C-cyclic compounds is exemplified by the formate hydrolysis of β-iodo phosphine oxide **33** and subsequent silver triflate-assisted cyclization (Scheme 4). The 1,4-

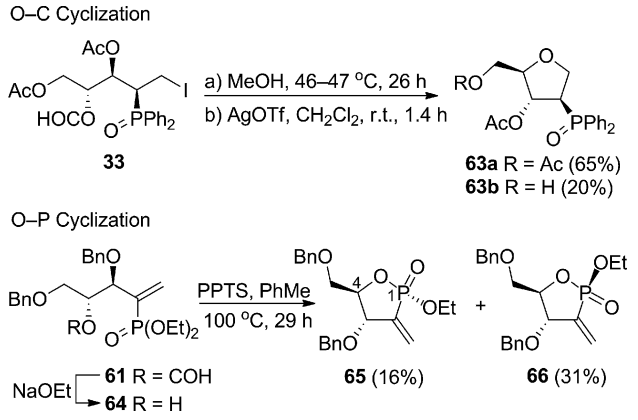
Table 2. Synthesis of β-iodo- and vinyl-phosphonates derived from carbohydrates.

Entry	Substrate[a]	Time [h]	γ-Hydroxy-phosphorus [%][b]	Time [h]	β-Iodo-phosphorus [%][c]	Time [h]	Vinyl-phosphorus [%]
1	 **15**	1.3	 **46** (70)	0.75	 **52** (95)	0.25	 **58** (94)
2	 **17**	2.5	 **47** (61)	1.5	 **53** (70)	0.5	 **59** (87)
3	 **18**	2.5	 **48** (64)	1.5	 **54**[d]	0.17	 **60** (71)
4	 **20**	1	 **49** (49)	1	 **55** (82)	0.25	 **61** (99)
			 **50** (5)	1	 **56** (58)	0.67	 **61** (90)
5	 **22**	1.5	 **51** (77)	1.5	 **57** (73)	1	 **62** (90)

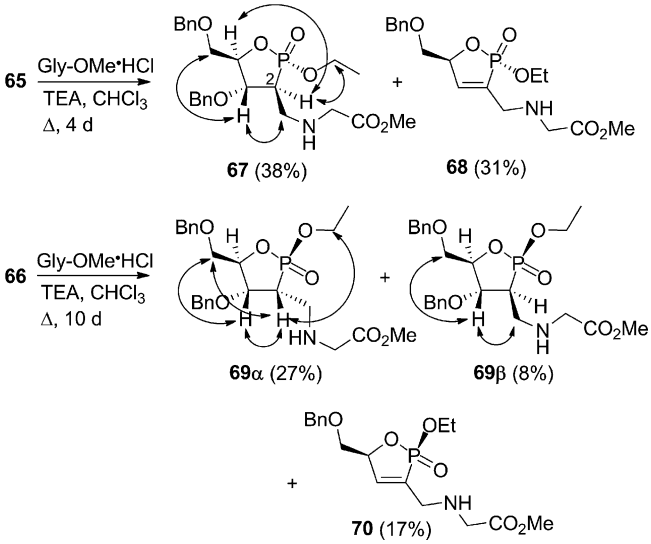
[a] Reagents and conditions per mmol of substrate: DIBAL (4 mmol), $PhCH_3$ (33 mL), –78 °C. [b] Reagents and conditions per mmol of substrate: DIB (1.1–1.5 mmol), I_2 (0.6–1.1 mmol), CH_2Cl_2 (25 mL). [c] Reagents and conditions per mmol of substrate: DBU (1.1–2.6 mmol), benzene (25 mL), 9–10 °C. [d] Unstable, could not be characterized.

anhydro-2-deoxy-2-diphenylphosphoryl-D-arabinitol derivative **63a** and its partially hydrolyzed alcohol **63b** were thus obtained in good overall yield. A 2D-NMR study of **63b**, in particular the HMBC correlation of H1 to C4, confirmed the presence of the five-membered furane ring and discarded the alternative pyranoid cyclization. Curiously, the three possible $^3J_{P,H}$ coupling constants have very similar experimental values (ca. 13–15 Hz), which appears to indicate a very specific conformation for the flexible furane ring. The conformation was studied by pseudorotational analysis using the experimental $^3J_{H,H}$ ring coupling constants calculated by iterative simulation.[33] Two envelope conformers were obtained with phase angles (*P*; north- and south-type, P_N and P_S, respectively) and populations, as indicated: E_2 (P_N = 335°, 66%) and E_1 (P_S = 133°, 34%). The weighted average for the coupling constants $^3J_{P,H}$ are in reasonable agreement with the observed values. The 1,4-anhydro-2-deoxy-2-phosphoryl-alditol derivatives may be of interest for the design and synthesis of new phosphorus ligands in asymmetric catalysis.[34] Our approach should also be applicable to the syntheses of 2-methylene-1-phospha-pentofuranoses (3-methylene-1,2-oxaphospholanes) by O–P-cyclization (Scheme 4). These compounds (e.g., **65** and **66**), also known as α-methylene-γ-phostones, are functional surrogates of α-methylene-γ-butyrolactones. 2-Deoxy-2-methylene-D-*erythro*-pentono-1,4-lactone, the *C*-isoster of **65** and **66**, has been prepared.[35] α-Methylene-γ-butyrolactone constitutes the core motif of widely encountered naturally occurring compounds with a variety of biologically interesting properties including anticancer, antimalarial, antiviral, antibacterial, antifungal, anti-inflammatory activities.[36] The information on the synthesis of 3-methylene-1,2-oxaphospholane derivatives is scant in the literature, and only a methodology based on a Reformatsky-like condensa-

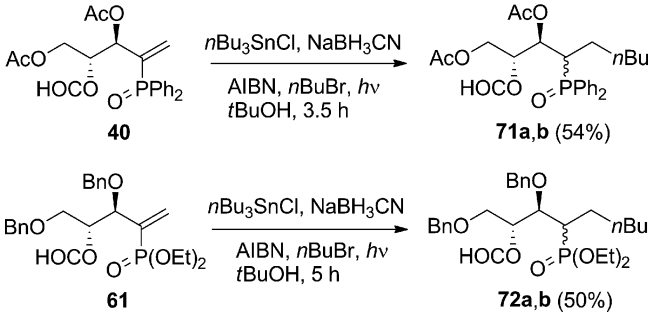
tion of diethyl 1-(bromomethyl)vinylphosphonate with aldehydes and ketones has been described.[37]



Scheme 4. Synthesis of 1,4-anhydro-2-deoxy-2-diphenylphosphoryl-D-arabinitol and 2-methylene-phospha-1-oxo-pentofuranoses by intramolecular cyclization.



Scheme 5. Use of 2-methylene-phospha-1-oxo-pentofuranoses as scaffolds. Michael addition products with glycine methyl ester. Principal NOESY correlations shown by arrows.



Scheme 6. Radical additions to vinylphosphine oxides and vinylphosphonates.

The preparation of 2-methylene-1-phospha-pentofuranoses **65** and **66** was accomplished starting from the vinylphosphonate **61**. Basic hydrolysis of the formate ester afforded alcohol **64**, which was subsequently submitted to intramolecular transesterification conditions employing PPTS. The P-diastereomeric mixture of **65** (R_P) and **66** (S_P) was separated by chromatography. The phosphorus stereochemistry was tentatively assigned on the basis of the small but significant deshielding effect of the P=O bond on all *syn* related protons (e.g., **65/66** $\Delta\delta$ 0.2 ppm for H3β and –0.15 ppm for H4α).[37c,38] The value of the NMR ring coupling constants ($^3J_{P,H3}$, $^3J_{P,H4}$, and $^3J_{H3,H4}$) differ markedly in both isomers. Because all of them depend on the dihedral angle in a Karplus-type relationship, these differences are attributable to different conformations of the ring.[20] Indeed, molecular mechanics models indicate that in **65** the 1,2-oxaphospholane ring preferentially adopts an envelope E_4 conformation with phase angle P = 52°, whereas **66** shows a preference for an E_3 (P = 204°).[37c,38b,39]

The use of these vinylphosphonates as scaffolds was exemplified by the synthesis of β-aminophosphonates **67** and **69** by Michael addition of the amino acid Gly-OMe·HCl to **65** and **66** (Scheme 5). The reaction stereochemistry could be ascribed to steric hindrance by the two vicinal ether groups. In the reaction of **65**, 1,4-conjugate addition on the β-side of the molecule was observed to give exclusively **67** as a single stereoisomer, whereas the sterically less demanding substrate **66** afforded a mixture of α- and β-isomers **69**. The stereochemistry at C-2 was assigned by NOESY experiments, with some of the observed interactions also confirming the phosphorus stereochemistry assigned previously for **65** and **66**. In both cases, conjugate elimination of the vicinal benzyl ether was observed as a side reaction, leading to the formation of **68** and **70**.

Finally, photoinduced addition of *n*BuBr to diphenyl vinylphosphine oxide **40** or vinylphosphonate **61**, in the presence of catalytic amounts of tri-*n*-butyltin chloride and an excess of sodium cyanoborohydride, was chosen as representative examples of the reaction of these compounds under radical conditions (Scheme 6). The reactions proceeded in moderate yield to give the addition products **71** and **72** as a diastereomeric mixture of isomers. Chromatographic separation of the isomer pairs was possible but, as expected, the stereochemistry of the D-ribitol and D-arabinitol epimers could not be assigned by spectroscopic methods.

Conclusions

The methodology described here for the synthesis of polyhydroxylated 1-alkylvinylphosphonate and -phosphine oxide chiral synthons employs a simple set of reactions, inexpensive starting carbohydrates, and mild reaction conditions. The key ARF reaction is smoothly promoted at low temperature (10–40 °C) and demonstrated high efficiency on a broad substrate scope and excellent compatibility with the presence of sensitive functional groups. The fragmentation has been tested by using a wide variety of 2,3-dideoxy-3-phosphoryl carbohydrate derivatives in pento- and hexofuranose, hexopyranose, and disaccharide structures, gen-

erally giving good to excellent yields. A significant advantage of this methodology is that the relative position of the readily hydrolyzable formyl group depends only on the pyranose or furanose form of the starting carbohydrate and this may be very convenient when further transformations are required. The pairs of *threo* (**59** and **62**) and *erythro* (**60** and **61**) isomers of pent-1-enitols illustrate this point (Table 2). Although the results reported in Table 1 and Table 2 were based on milligram-scale reactions, gram-scale reactions of selected examples also afforded the corresponding products in similar yields.

The ease with which these relatively complex 1-(iodomethyl)alkylphosphonate and -phosphine oxide intermediates can be prepared on a large scale adds significant value to this method, because the chemical reactivity of these systems has been little studied to date.

The synthetic usefulness and reactivity of these compounds has been preliminarily assessed, and the results are summarized in Scheme 4, Scheme 5, and Scheme 6. Examples of intramolecular O–C-cyclization and P–O-cyclization for the preparation of 1,4-anhydro-2-deoxy-2-diphenylphosphoryl-D-arabinitol **63** and 1-phospha sugars **65** and **66**, respectively, are illustrated in Scheme 4. The Michael addition of glycine to vinylphosphonates **65** and **66** and the use of these compounds for the synthesis of β-amino carboxylic acids are shown in Scheme 5. The activated carbon–carbon double bond of conjugated vinylphosphonates and vinylphosphine oxides have also been utilized as radical traps in intermolecular additions of alkyl radicals (Scheme 6).

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 a NaCl plate, $CHCl_3$, or CCl_4 solutions as stated. NMR spectra were determined at 500 or 400 MHz for ^1H, 125.7 or 100.6 MHz for ^{13}C, and 161.9 MHz for ^{31}P in $CDCl_3$ or C_6D_6 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-COSY, HSQC, NOESY, and HMBC experiments were performed routinely for all new compounds. When necessary, $J_{P,H}$ coupling constants were determined by using $^1H\{^{31}P\}$ NMR decoupled spectra. Low- and high-resolution mass spectra were recorded by using electron impact (EI) or electrospray (ESI^+) and TOF analyzer as specified. Merck silica gel 60 PF (0.063–0.2 mm) was used for column chromatography. Circular layers of 1 mm of Merck silica gel 60 PF_{254} were used on a Chromatotron for centrifugally-assisted radial chromatography. Commercially available reagents and solvents were analytical grade or were purified by standard procedures prior to use. The spray reagents for TLC analysis were composed of 0.5% vanillin in H_2SO_4/EtOH (4:1) or alternatively Hanessian' stain[40] and further heating until development of color.

General Procedure for the Introduction of the 3-Diphenylphosphoryl Group (Ferrier Reaction): To a stirred solution of $AlCl_3$ (2 equiv.) in CH_2Cl_2 (1.8 mL), at 0 °C under nitrogen was added dropwise a solution of Ph_2PCl (2 equiv.) in CH_2Cl_2 (1.8 mL) and stirring was continued over 1 h at room temperature. The glycal (1 equiv.) in CH_2Cl_2 (1.4 mL) was then added and stirring was continued at reflux temperature for the specified time. The reaction mixture was then poured into water and extracted with CH_2Cl_2. The combined extracts were washed with brine, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography (hexanes/EtOAc).

1,5-Anhydro-4,6-di-*O*-benzyl-2,3-dideoxy-3-diphenylphosphoryl-D-*ribo*-hex-1-enitol (3), (1*R*)-1,5-Anhydro-4,6-di-*O*-benzyl-2,3-dideoxy-1-diphenylphosphoryl-D-*erythro*-hex-2-enitol (4α) and (1*S*)-1,5-Anhydro-4,6-di-*O*-benzyl-2,3-dideoxy-1-diphenylphosphoryl-D-*erythro*-hex-2-enitol (4β):[17] From 3,4,6-tri-*O*-benzyl-D-glucal (**1**; 50 mg, 0.12 mmol) following the general procedure by stirring at reflux temperature for 3 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 55:45) gave **3** (30 mg, 0.059 mmol, 49%), **4α** (7.5 mg, 0.015 mmol, 12%), and **4β** (16.5 mg, 0.032 mmol, 27%).

Compound 3: White oil; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.57 (dddd, $^2J_{P,H}$ = 10.1, J = 6.4, 4.7, 1.9 Hz, 1 H), 3.66 (dd, J = 10.9, 2.9 Hz, 1 H), 3.77 (dd, J = 10.9, 3.7 Hz, 1 H), 4.13 (d, J = 11.4 Hz, 1 H), 4.22 (ddd, $^3J_{P,H}$ = 18.8, J = 8.2, 6.1 Hz, 1 H), 4.26 (d, J = 11.1 Hz, 1 H), 4.28 (ddd, $^3J_{P,H}$ = 4.2, J = 6.1, 4.2 Hz, 1 H), 4.44 (d, J = 11.9 Hz, 1 H), 4.50 (d, J = 12.2 Hz, 1 H), 4.82 (ddd, J = 7.4, 3.2, 3.2 Hz, 1 H), 6.47 (ddd, $^4J_{P,H}$ = 4.0, J = 5.8, 1.6 Hz, 1 H), 6.76–6.78 (m, 2 H), 7.09–7.16 (m, 3 H), 7.21–7.47 (m, 11 H), 7.76–7.85 (m, 4 H) ppm.

4,6-Di-*O*-acetyl-1,5-anhydro-2,3-dideoxy-3-diphenylphosphoryl-D-*ribo*-hex-1-enitol (5)[15] **and 4,6-Di-*O*-acetyl-1,5-anhydro-2,3-dideoxy-3-diphenylphosphoryl-D-*arabino*-hex-1-enitol (6):** From 3,4,6-tri-*O*-acetyl-D-glucal (**2**; 100 mg, 0.367 mmol) following the general procedure by stirring at reflux temperature for 14 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 3:7) gave **5** (91 mg, 0.219 mmol, 60%) and **6** (15.2 mg, 0.037 mmol, 10%).

Compound 5: Crystalline solid; m.p. 149–151 °C (*n*-hexane/EtOAc); $[\alpha]_D$ = +308.7 (c = 1.2, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.14 (s, 3 H), 2.01 (s, 3 H), 3.72 (dddd, $^2J_{P,H}$ = 5.8, J = 5.8, 5.8, 1.9 Hz, 1 H), 4.19 (ddd, $^3J_{P,H}$ = 3.2, J = 5.6, 5.6 Hz, 1 H), 4.22 (dd, J = 12.3, 1.9 Hz, 1 H), 4.40 (dd, J = 12.2, 3.7 Hz, 1 H), 5.14 (ddd, J = 10.1, 3.8, 2.1 Hz, 1 H), 5.32 (ddd, $^3J_{P,H}$ = 20.9, J = 10.1, 6.6 Hz, 1 H), 6.51 (ddd, $^4J_{P,H}$ = 4.5, J = 6.1, 1.6 Hz, 1 H), 7.44–7.52 (m, 6 H), 7.71–7.76 (m, 2 H), 7.85–7.87 (m, 2 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 19.4 (CH_3), 20.6 (CH_3), 35.2 (d, $^1J_{P,C}$ = 69.9 Hz, CH), 61.9 (CH_2), 66.6 (d, $^2J_{P,C}$ = 7.4 Hz, CH), 71.8 (CH), 92.4 (d, $^2J_{P,C}$ = 7.4 Hz, CH), 128.7 (d, $^3J_{P,C}$ = 11.7 Hz, 2× CH), 128.9 (d, $^3J_{P,C}$ = 11.7 Hz, 2× CH), 130.5 (d, $^2J_{P,C}$ = 8.5 Hz, 2× CH), 130.7 (d, $^2J_{P,C}$ = 8.5 Hz, 2× CH), 131.5 (d, $^4J_{P,C}$ = 2.1 Hz, 2× CH), 131.6 (d, $^4J_{P,C}$ = 2.1 Hz, 2× CH), 132.8 (d, $^1J_{P,C}$ = 100.7 Hz, 2× CH), 133.5 (d, $^1J_{P,C}$ = 95.4 Hz, 2× CH), 146.3 (d, $^3J_{P,C}$ = 9.5 Hz, CH), 170.2 (C), 170.6 (C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 25.8 (s, 1 P) ppm. IR (film): $\tilde{\nu}$ = 1740 cm^{-1}. MS (ESI^+): m/z (%) = 437 (100) $[M + Na]^+$. HRMS (ESI^+): m/z calcd. for $C_{22}H_{23}NaO_6P$ $[M + Na]^+$ 437.11301; found 437.1136.

Compound 6: Crystalline solid; m.p. 159.7–160.8 °C (*n*-hexane/EtOAc); $[\alpha]_D$ = –32.9 (c = 0.27, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.52 (s, 3 H), 2.04 (s, 3 H), 3.59 (dddd, $^2J_{P,H}$ = 8.7, J = 11.0, 2.5, 2.4 Hz, 1 H), 3.95 (ddd, J = 8.8, 5.1, 2.8 Hz, 1 H), 4.16 (dd, J = 12.3, 2.8 Hz, 1 H), 4.22 (dd, J = 12.5, 5.2 Hz, 1 H), 4.59

(ddd, $^3J_{P,H}$ = 8.7, J = 6.2, 2.2 Hz, 1 H), 5.53 (ddd, $^3J_{P,H}$ = 9.1, J = 11.1, 9.1 Hz, 1 H), 6.48 (ddd, $^4J_{P,H}$ = 2.9, J = 5.9, 2.9 Hz, 1 H), 7.48–7.60 (m, 6 H), 7.68–7.74 (m, 2 H), 7.81–7.87 (m, 2 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 20.1 (CH_3), 20.7 (CH_3), 39.4 (d, $^1J_{P,C}$ = 69.9 Hz, CH), 61.9 (CH_2), 63.4 (CH), 74.6 (d, $^3J_{P,C}$ = 8.2 Hz, CH), 94.6 (d, $^2J_{P,C}$ = 5.5 Hz, CH), 128.6 (d, $^3J_{P,C}$ = 11.8 Hz, 2× CH), 128.7 (d, $^3J_{P,C}$ = 10.9 Hz, 2× CH), 130.6 (d, $^1J_{P,C}$ = 99.0 Hz, C), 131.43 (d, $^2J_{P,C}$ = 9.1 Hz, 2× CH), 131.44 (d, $^2J_{P,C}$ = 8.2 Hz, 2× CH), 131.45 (d, $^1J_{P,C}$ = 97.2 Hz, C), 131.9 (d, $^4J_{P,C}$ = 2.7 Hz, CH), 132.1 (d, $^4J_{P,C}$ = 2.7 Hz, CH), 146.0 (d, $^3J_{P,C}$ = 9.1 Hz, CH), 170.0 (C), 170.7 (C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 28.8 (s, 1 P) ppm. IR (film): $\tilde{\nu}$ = 1743 cm^{-1}. MS (EI, 70 eV): m/z (%) = 415 (1) [M + H]$^+$, 287 (294), 201 (100). HRMS (EI, 70 eV): m/z calcd. for $C_{22}H_{24}O_6P$ [M + H]$^+$ 415.4311; found 415.4311. $C_{22}H_{23}O_6P$ (414.39): calcd. C 63.75, H 5.60; found C 63.60, H 5.42.

1,5-Anhydro-4,6-di-*O*-benzyl-2,3-dideoxy-3-diphenylphosphoryl-D-*xylo*-hex-1-enitol (9): From 3,4,6-tri-*O*-benzyl-D-galactal (**7**; 271.4 mg, 0.652 mmol) following the general procedure by stirring at reflux temperature for 5 h. Silica gel column chromatography of the reaction residue (hexanes/EtOAc, 1:1) gave **9** (205 mg, 0.402 mmol, 62%) as a crystalline solid: m.p. 109.9–111.0 °C (*n*-hexane/EtOAc); $[\alpha]_D$ = +60 (c = 0.14, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.27 (ddddd, $^2J_{P,H}$ = 12.6, J = 4.6, 1.5, 1.5, 1.5 Hz, 1 H), 3.49 (dd, J = 10.1, 6.6 Hz, 1 H), 3.67 (dd, J = 10.1, 6.6 Hz, 1 H), 3.95 (dddd, $^3J_{P,H}$ = 8.6, J = 1.6, 1.6, 1.6 Hz, 1 H), 4.23 (d, J = 12.2 Hz, 1 H), 4.37 (d, J = 11.9 Hz, 1 H), 4.42 (dddd, $^3J_{P,H}$ = 3.4, J = 6.4, 5.0, 1.9 Hz, 1 H), 4.45 (d, J = 12.2 Hz, 1 H), 4.47 (ddd, J = 6.4, 6.4, 1.6 Hz, 1 H), 4.49 (d, J = 12.2 Hz, 1 H), 6.64 (ddd, $^4J_{P,H}$ = 4.0, J = 6.2, 1.7 Hz, 1 H), 6.97 (m, 2 H), 7.25 (m, 8 H), 7.51 (m, 6 H), 7.80 (m, 4 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 37.3 (d, $^1J_{P,C}$ = 67.2 Hz, CH), 68.6 (CH_2), 69.1 (CH), 71.7 (CH_2), 72.9 (CH_2), 74.2 (CH), 92.3 (d, $^2J_{P,C}$ = 7.3 Hz, CH), 127.4 (CH), 127.5 (2× CH), 127.8 (CH), 128.1 (2× CH), 128.2 (2× CH), 128.3 (2× CH), 128.7 (d, $^3J_{P,C}$ = 11.8 Hz, 2× CH), 128.9 (d, $^3J_{P,C}$ = 10.9 Hz, 2× CH), 131.0 (d, $^1J_{P,C}$ = 98.1 Hz, C), 131.2 (d, $^2J_{P,C}$ = 9.1 Hz, 2× CH), 131.3 (d, $^2J_{P,C}$ = 9.1 Hz, 2× CH), 131.5 (d, $^1J_{P,C}$ = 95.4 Hz, C), 131.9 (d, $^4J_{P,C}$ = 2.7 Hz, CH), 132.0 (d, $^4J_{P,C}$ = 2.7 Hz, CH), 137.5 (C), 138.2 (C), 146.8 (d, $^3J_{P,C}$ = 9.1 Hz, CH) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 26.5 (s, 1 P) ppm. IR (film): $\tilde{\nu}$ = 1095 cm^{-1}. MS (EI, 70 eV): m/z (%) = 511 (< 1) [M + H]$^+$, 311 (92), 201 (72), 91 (100). HRMS (EI, 70 eV): m/z calcd. for $C_{32}H_{32}O_4P$ [M + H]$^+$ 511.2038; found 511.2047. $C_{32}H_{31}O_4P$ (510.57): calcd. C 75.28, H 6.12; found C 75.55, H 5.88.

4,6-Di-*O*-acetyl-1,5-anhydro-2,3-dideoxy-3-diphenylphosphoryl-D-*xylo*-hex-1-enitol (10):[15] From 3,4,6-tri-*O*-acetyl-D-galactal (**8**; 150 mg, 0.551 mmol) following the general procedure by stirring at reflux temperature for 20.5 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 4:6) gave **10** (207 mg, 0.498 mmol, 90%) as an oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.01 (s, 3 H), 2.04 (s, 3 H), 3.33 (ddddd, $^2J_{P,H}$ = 11.8, J = 4.8, 1.6, 1.5, 1.4 Hz, 1 H), 4.15 (dd, J = 11.5, 5.2 Hz, 1 H), 4.19 (dd, J = 11.5, 7.2 Hz, 1 H), 4.32 (dddd, $^3J_{P,H}$ = 3.0, J = 6.3, 4.8, 1.9 Hz, 1 H), 4.81 (ddddd, $^4J_{P,H}$ = 1.6, J = 7.2, 5.2, 1.6, 1.2 Hz, 1 H), 5.08 (dddd, $^3J_{P,H}$ = 7.9, J = 1.9, 1.4, 1.2 Hz, 1 H), 6.64 (ddd, $^4J_{P,H}$ = 4.3, J = 6.3, 1.5 Hz, 1 H), 7.46–7.58 (m, 6 H), 7.76–7.81 (m, 2 H), 7.93–7.98 (m, 2 H) ppm. The data for hydrogen atoms at C1–C6 shown here have been calculated by iterative simulation using program DAISY as implemented in Bruker Topspin v. 2.1.

1,5-Anhydro-6-*O*-benzyl-2,3-dideoxy-3-diphenylphosphoryl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-D-*ribo*-hex-1-enitol (12α), 1,5-Anhydro-6-*O*-benzyl-2,3-dideoxy-3-diphenylphosphoryl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-D-*arabino*-hex-1-enitol (12β), (1*R*)-1,5-Anhydro-6-*O*-benzyl-2,3-dideoxy-1-diphenylphosphoryl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-D-*erythro*-hex-2-enitol (13α), and (1*S*)-1,5-Anhydro-6-*O*-benzyl-2,3-dideoxy-1-diphenylphosphoryl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-D-*erythro*-hex-2-enitol (13β): From hexa-*O*-benzyl-D-lactal (**11**;[41] 1.227 g, 1.45 mmol) following the general procedure by stirring at reflux temperature for 22 h. Silica gel column chromatography (hexanes/EtOAc, 7:3) gave **12α** (616.8 mg, 0.655 mmol, 45%), **12β** (194.8 mg, 0.207 mmol, 14%), **13α** (103 mg, 0.109 mmol, 7.5%), and **13β** (174 mg, 0.185 mmol, 12%) all as colorless oils.

Compound 12α: $[\alpha]_D$ = +246.4 (c = 0.11, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.64 (dd, J = 9.9, 7.8 Hz, 1 H), 3.18 (dd, J = 9.8, 2.9 Hz, 1 H), 3.31 (ddd, J = 7.3, 5.8, 0.9 Hz, 1 H), 3.57 (dddd, $^2J_{P,H}$ = 5.8, J = 5.8, 5.8, 1.6 Hz, 1 H), 3.61–3.65 (m, 2 H), 3.72–3.78 (m, 2 H), 3.79 (dd, J = 2.9, 1.1 Hz, 1 H), 4.05 (dddd, $^3J_{P,H}$ = 5.6, J = 5.6, 5.6, 2.9 Hz, 1 H), 4.16 (d, J = 11.4 Hz, 1 H), 4.27 (d, J = 8.0 Hz, 1 H), 4.30 (d, J = 4.2 Hz, 1 H), 4.33 (d, J = 4.8 Hz, 1 H), 4.45–4.56 (m, 3 H), 4.59 (d, J = 11.9 Hz, 1 H), 4.65 (d, J = 12.2 Hz, 1 H), 4.71 (d, J = 11.9 Hz, 1 H), 4.89 (d, J = 10.3 Hz, 1 H), 5.05 (ddd, J = 9.8, 2.1, 2.1 Hz, 1 H), 6.49 (ddd, $^4J_{P,H}$ = 4.6, J = 6.0, 1.3 Hz, 1 H), 7.00 (m, 4 H), 7.19–7.41 (m, 27 H), 7.67 (m, 2 H), 7.83 (m, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 38.1 (d, $^1J_{P,C}$ = 69.9 Hz, CH), 68.1 (CH_2), 68.6 (CH_2), 71.4 ($^2J_{P,C}$ = 7.8 Hz, CH), 73.0 (CH_2), 73.1 (CH), 73.2 (CH_2), 73.4 (CH_2), 74.7 (2× CH), 74.9 (CH_2), 75.3 (CH_2), 78.5 (CH), 81.8 (CH), 92.7 (d, $^2J_{P,C}$ = 7.8 Hz, CH), 103.6 (CH), 127.2–128.7 (Ar, complex), 130.6–135.2 (Ar, complex), 138.0 (C), 138.2 (C), 138.7 (C), 138.8 (C), 139.1 (C), 146.5 (d, $^3J_{P,C}$ = 9.9 Hz, CH) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 28.2 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1076 cm^{-1}. MS (ESI$^+$): m/z (%) = 965 (100) [M + Na]$^+$. HRMS (ESI$^+$): m/z calcd. for $C_{59}H_{59}NaO_9P$ [M + Na]$^+$ 965.3794; found 965.3813. $C_{59}H_{59}O_9P$ (943.09): calcd. C 75.14, H 6.31; found C 75.07, H 6.19.

Compound 12β: $[\alpha]_D$ = –9.3 (c = 0.27, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.35 (m, 1 H), 3.37 (dd, J = 9.8, 3.2 Hz, 1 H), 3.41 (dd, J = 8.8, 5.1 Hz, 1 H), 3.49 (dd, J = 8.8, 7.9 Hz, 1 H), 3.61–3.63 (m, 1 H), 3.66 (dd, J = 9.8, 7.9 Hz, 1 H), 3.79 (dd, J = 9.9, 6.2 Hz, 1 H), 3.84 (d, J = 2.5 Hz, 1 H), 4.10 (dd, J = 10.1, 6.9 Hz, 1 H), 4.27 (d, J = 7.6 Hz, 1 H), 4.29–4.32 (m, 1 H), 4.38–4.40 (m, 1 H), 4.41 (d, J = 12.0 Hz, 1 H), 4.444 (d, J = 12.0 Hz, 1 H), 4.445–4.48 (m, 1 H), 4.49 (d, J = 12.0 Hz, 1 H), 4.58 (d, J = 11.4 Hz, 1 H), 4.62 (d, J = 12.0 Hz, 1 H), 4.66 (d, J = 12.0 Hz, 1 H), 4.67 (d, J = 10.7 Hz, 1 H), 4.71 (d, J = 11.7 Hz, 1 H), 4.86 (d, J = 11.0 Hz, 1 H), 4.92 (d, J = 11.4 Hz, 1 H), 6.50 (ddd, $^4J_{P,H}$ = 3.6, J = 6.2, 2.5 Hz, 1 H), 7.18–7.36 (m, 27 H), 7.37 (m, 4 H), 7.80–7.85 (m, 4 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 39.1 (d, $^1J_{P,C}$ = 68.1 Hz, CH), 67.2 (CH_2), 68.2 (CH_2), 71.6 (CH), 72.8 (CH_2), 73.03 (CH_2), 73.05 (CH), 73.4 (CH_2), 73.6 (CH), 74.7 (CH_2), 75.2 (CH_2), 75.4 (d, $^3J_{P,C}$ = 1.8 Hz, CH), 78.9 (CH), 82.1 (CH), 92.6 (d, $^2J_{P,C}$ = 6.4 Hz, CH), 103.5 (CH), 127.3–128.6 (Ar, complex), 130.8–132.4 (Ar, complex), 137.8 (C), 138.43 (C), 138.46 (C), 138.5 (C), 138.7 (C), 144.9 (d, $^3J_{P,C}$ = 10.0 Hz, CH) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 28.6 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1096 cm^{-1}. MS (ESI$^+$): m/z (%) = 965 (100) [M + Na]$^+$. HRMS (ESI$^+$): m/z calcd. for $C_{59}H_{59}NaO_9P$ [M + Na]$^+$ 965.3794; found 965.3794. $C_{59}H_{59}O_9P$ (943.09): calcd. C 75.14, H 6.31; found C 74.99, H 6.17.

Compound 13α: $[\alpha]_D$ = +23 (c = 0.20, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.39–3.43 (m, 2 H), 3.49–3.56 (m, 4 H), 3.67–3.71 (m, 2 H), 3.85 (d, J = 2.8 Hz, 1 H), 4.05 (m, 1 H), 4.23 (d, J = 7.6 Hz, 1 H), 4.32 (d, J = 12.0 Hz, 1 H), 4.38–4.40 (m, 3 H), 4.60 (d, J = 11.7 Hz, 2 H), 4.63 (d, J = 11.0 Hz, 1 H), 4.68 (d, J = 11.7 Hz, 1

H), 4.72 (d, J = 12.0 Hz, 1 H), 4.92 (d, J = 11.7 Hz, 1 H), 5.09 (dddd, $^2J_{P,H}$ = 11.2, J = 2.7, 2.7, 2.7 Hz, 1 H), 6.12 (dddd, J = 10.5, 2.4, 2.4, 2.4 Hz, 1 H), 6.20 (dddd, J = 10.4, 2.5, 2.5, 2.5 Hz, 1 H), 7.21–7.57 (m, 31 H), 7.77 (m, 2 H), 7.99 (m, 2 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 68.7 (CH_2), 68.8 (CH_2), 70.5 (CH), 73.01 (CH_2), 73.03 (CH_2), 73.28 (d, $^1J_{P,C}$ = 77.2 Hz, CH), 73.34 (CH), 73.46 (CH), 73.48 (CH_2), 73.59 (CH), 74.60 (CH_2), 75.1 (CH_2), 79.3 (CH), 82.2 (CH), 104.2 (CH), 122.7 (d, $^2J_{P,C}$ = 1.8 Hz, CH), 127.5–128.6 (Ar, complex), 130.84 (d, $^1J_{P,C}$ = 94.5 Hz, C), 130.87 (d, $^3J_{P,C}$ = 10.0 Hz, CH), 130.9 (d, $^1J_{P,C}$ = 94.5 Hz, C), 131.8–132.4 (Ar, complex), 137.9 (C), 138.3 (C), 138.47 (C), 138.56 (C), 138.6 (C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 28.0 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1100 cm^{-1}. MS (ESI$^+$): m/z (%) = 965 (100) [M + Na]$^+$. HRMS (ESI$^+$): m/z calcd. for $C_{59}H_{59}NaO_9P$ [M + Na]$^+$ 965.3794; found 965.3794. $C_{59}H_{59}O_9P$ (943.09): calcd. C 75.14, H 6.31; found C 75.36, H 6.13.

Compound 13β: $[\alpha]_D$ = +44.7 (c = 0.19, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.44–3.47 (m, 2 H), 3.49–3.55 (m, 2 H), 3.58 (dd, J = 10.4. 5.4 Hz, 1 H), 3.65 (m, 1 H), 3.69 (d, J = 10.4 Hz, 1 H), 3.76 (dd, J = 9.6, 7.7 Hz, 1 H), 3.86 (d, J = 2.8 Hz, 1 H), 3.91–3.93 (m, 1 H), 4.28 (d, J = 12.0 Hz, 1 H), 4.30 (d, J = 7.6 Hz, 1 H), 4.35 (d, J = 12.0 Hz, 1 H), 4.38 (s, 2 H), 4.58 (d, J = 11.7 Hz, 1 H), 4.70 (s, 2 H), 4.78 (s, 2 H), 4.90 (d, J = 11.7 Hz, 1 H), 5.11 (br. d, $^2J_{P,H}$ = 12.3 Hz, 1 H), 6.08 (br. d, J = 11.0 Hz, 1 H), 6.14 (br. d, J = 11.7 Hz, 1 H), 7.17–7.33 (m, 27 H), 7.41–7.45 (m, 3 H), 7.51–7.54 (m, 1 H), 7.83–7.87 (m, 2 H), 7.91–7.95 (m, 2 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 68.8 (CH_2), 69.3 (CH_2), 71.8 (d, $^4J_{P,C}$ = 1.8 Hz, CH), 72.9 (CH_2), 73.0 (CH_2), 73.4 (CH), 73.5 (CH_2), 73.5 (CH), 74.5 (CH_2), 74.8 (d, $^1J_{P,C}$ = 92.7 Hz, CH), 75.3 (CH_2), 76.8 (d, $^3J_{P,C}$ = 7.3 Hz, CH), 79.3 (CH), 82.4 (CH), 104.6 (CH), 123.1 (d, $^2J_{P,C}$ = 4.5 Hz, CH), 127.4–128.4 (Ar, complex), 131.3 (d, $^3J_{P,C}$ = 9.1 Hz, CH), 131.7–132.4 (Ar, complex), 137.8 (C), 138.3 (C), 138.52 (C), 138.57 (C), 138.6 (C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 28.3 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1097 cm^{-1}. MS (ESI$^+$): m/z (%) = 965 (100) [M + Na]$^+$. HRMS (ESI$^+$): m/z calcd. for $C_{59}H_{59}NaO_9P$ [M + Na]$^+$ 965.3794; found 965.3794. $C_{59}H_{59}O_9P$ (943.09): calcd. C 75.14, H 6.31; found C 75.13, H 6.15.

General Procedure for the Introduction of the 3-Diethoxyphosphoryl Group (phospha-Michael Addition): To a solution of the α,β-unsaturated lactone (1 equiv.) in phenol (4.2 mL) was added dropwise triethyl phosphite (5 equiv.) at room temperature under nitrogen. The mixture was stirred at 100 °C for the specified time and the solvent was evaporated under reduced pressure. The residue was purified by Chromatotron chromatography (hexanes/EtOAc).

5-*O*-(*tert*-Butyldiphenylsilyl)-2,3-dideoxy-3-diethoxyphosphoryl-D-ribono-1,4-lactone (15):[26] From 5-*O*-(*tert*-butyldiphenylsilyl)-2,3-dideoxy-D-*glycero*-pent-2-enono-1,4-lactone (**14**;[22] 130.5 mg, 0.370 mmol) following the general procedure by stirring at 100 °C for 6 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 6:4) gave **15** (130.8 mg, 0.266 mmol, 72%) as a colorless oil: $[\alpha]_D$ = +25.6 (c = 0.39, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.05 (s, 9 H), 1.30 (t, J = 6.9 Hz, 3 H), 1.32 (t, J = 7.3 Hz, 3 H), 2.75–3.02 (m, 3 H), 3.71 (dd, J = 11.7, 2.5 Hz, 1 H), 4.01 (dd, J = 11.7, 2.2 Hz, 1 H), 4.08–4.16 (m, 4 H), 4.73 (dddd, $^3J_{P,H}$ = 15.7, J = 5.2, 2.6, 2.4 Hz, 1 H), 7.37–7.45 (m, 6 H), 7.62–7.65 (m, 4 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 16.4 (d, $^3J_{P,C}$ = 5.4 Hz, 2× CH_3), 19.2 (C), 26.8 (3× CH_3), 30.2 (d, $^2J_{P,C}$ = 4.5 Hz, CH_2), 32.9 (d, $^1J_{P,C}$ = 151.6 Hz, CH), 62.6 (d, $^2J_{P,C}$ = 7.3 Hz, CH_2), 62.7 (d, $^2J_{P,C}$ = 7.3 Hz, CH_2), 64.5 (d, $^3J_{P,C}$ = 7.3 Hz, CH_2), 79.6 (CH), 127.9 (4× CH), 130.02 (CH), 130.03 (CH), 132.2 (C), 132.8 (C), 135.5 (2× CH), 135.7 (2× CH), 174.7 (d, $^3J_{P,C}$ = 10 Hz, C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 26.8 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1783, 1216 cm^{-1}. MS (ESI$^+$): m/z (%) = 513 (100) [M + Na]$^+$. HRMS (ESI$^+$): m/z calcd. for $C_{25}H_{35}NaO_6PSi$ [M + Na]$^+$ 513.1838; found 513.1847. $C_{25}H_{35}O_6PSi$ (490.61): calcd. C 61.20, H 7.19; found C 61.52, H 7.30.

2,3-Dideoxy-3-diethoxyphosphoryl-5,6-*O*-isopropylidene-D-*lyxo*-hexono-1,4-lactone (17) and 2,3-Dideoxy-3-diethoxyphosphoryl-5,6-*O*-isopropylidene-D-*ribo*-hexono-1,4-lactone (18): From **16**[23] (164 mg, 0.89 mmol) following the general procedure by stirring at 100 °C for 8 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 4:6) gave **17** (72.5 mg, 0.225 mmol, 25%) and **18** (72.5 mg, 0.225 mmol, 25%).

Compound 17: Crystalline solid; m.p. 46.3–47.1 °C (*n*-hexane/EtOAc); $[\alpha]_D$ = –20.5 (c = 0.39, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.33 (t, J = 7.1 Hz, 3 H), 1.34 (t, J = 7.1 Hz, 3 H), 1.36 (s, 3 H), 1.37 (s, 3 H), 2.66–2.76 (m, 1 H), 2.83–2.92 (m, 2 H), 3.98 (dd, J = 8.5, 6.9 Hz, 1 H), 4.08 (dd, J = 8.4, 6.8 Hz, 1 H), 4.11–4.18 (m, 4 H), 4.22 (ddd, J = 6.9, 6.9, 1.3 Hz, 1 H), 4.66 ppm (ddd, $^3J_{P,H}$ = 16.4, J = 4.7, 1.6 Hz, 1 H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 16.39 (d, $^3J_{P,C}$ = 5.3 Hz, CH_3), 16.41 (d, $^3J_{P,C}$ = 5.7 Hz, CH_3), 25.6 (CH_3), 25.7 (CH_3), 29.5 (d, $^2J_{P,C}$ = 5.3 Hz, CH_2), 34.5 (d, $^1J_{P,C}$ = 151.5 Hz, CH), 62.7 (d, $^2J_{P,C}$ = 7.4 Hz, CH_2), 62.8 (d, $^2J_{P,C}$ = 7.4 Hz, CH_2), 65.4 (CH_2), 77.0 (d, $^3J_{P,C}$ = 8.2 Hz, CH), 77.1 (CH), 110.2 (C), 174.6 (d, $^3J_{P,C}$ = 7.4 Hz, C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 26.4 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2995, 1786, 1224, 1025 cm^{-1}. MS (ESI$^+$): m/z (%) = 345 (100) [M + Na]$^+$. HRMS (ESI$^+$): m/z calcd. for $C_{13}H_{23}NaO_7P$ [M + Na]$^+$ 345.1079; found 345.1081. $C_{13}H_{23}O_7P$ (322.30): calcd. C 48.45, H 7.19; found C 48.43, H 6.99.

Compound 18: Colorless oil; $[\alpha]_D$ = –20.0 (c = 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (t, J = 7.2 Hz, 6 H), 1.32 (s, 3 H), 1.44 (s, 3 H), 2.65–2.90 (m, 3 H), 3.86 (dd, J = 9.1, 4.9 Hz, 1 H), 4.09 (dd, J = 9.3, 7.2 Hz, 1 H), 4.12–4.18 (m, 4 H), 4.28 (ddd, J = 7.2, 4.8, 4.8 Hz, 1 H), 4.64 (ddd, $^3J_{P,H}$ = 17.2, J = 4.8, 2.9 Hz, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.33 (d, $^3J_{P,C}$ = 6.4 Hz, CH_3), 16.34 (d, $^3J_{P,C}$ = 5.6 Hz, CH_3), 24.4 (CH_3), 26.2 (CH_3), 29.0 (d, $^2J_{P,C}$ = 5.0 Hz, CH_2), 32.2 (d, $^1J_{P,C}$ = 150.4 Hz, CH), 62.7 (d, $^2J_{P,C}$ = 7.1 Hz, CH_2), 62.8 (d, $^2J_{P,C}$ = 7.1 Hz, CH_2), 65.2 (CH_2), 75.9 (d, $^3J_{P,C}$ = 10.0 Hz, CH), 79.2 ($^2J_{P,C}$ = 2.1 Hz, CH), 110.4 (C), 174.4 ppm (d, $^3J_{P,C}$ = 3.5 Hz, C). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ_P = 27.3 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2995, 1784, 1216, 1026 cm^{-1}. MS (ESI$^+$): m/z (%) = 345 (100) [M + Na]$^+$. HRMS (ESI$^+$): m/z calcd. for $C_{13}H_{23}NaO_7P$ [M + Na]$^+$ 345.1079; found 345.1078. $C_{13}H_{23}O_7P$ (322.30): calcd. C 48.45, H 7.19; found C 48.34, H 6.94.

4,6-Di-*O*-benzyl-2,3-dideoxy-3-diethoxyphosphoryl-D-*arabino*-hexono-1,5-lactone (20β) and 4,6-Di-*O*-benzyl-2,3-dideoxy-3-diethoxyphosphoryl-D-*ribo*-hexono-1,5-lactone (20α): From 4,6-di-*O*-benzyl-2,3-dideoxy-D-*erythro*-hex-2-enono-1,5-lactone (**19**;[24] 280 mg, 0.863 mmol) following the general procedure by stirring at 100 °C for 4.5 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 4:6) gave the irresoluble mixture **20α,β** (392 mg, 0.848 mmol, β/α, 4.5:1, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100.6 MHz, $CDCl_3$) exhibit complex resonance patterns. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 25.9 (s, 1 P), 27.1 (s, 1 P) ppm. IR (CCl_4): $\tilde{\nu}$ = 2985, 1751, 1241, 1026 cm^{-1}. MS (ESI$^+$): m/z (%) = 485 (100) [M + Na]$^+$. HRMS (ESI$^+$): m/z calcd. for $C_{24}H_{31}NaO_7P$ [M + Na]$^+$ 485.1705; found 485.1707. $C_{24}H_{31}O_7P$ (462.48): calcd. C 62.33, H 6.76; found C 62.34, H 6.67.

4,6-Di-*O*-benzyl-2,3-dideoxy-3-diethoxyphosphoryl-D-*xylo*-hexono-1,5-lactone (22) and 4,6-Di-*O*-benzyl-2,3-dideoxy-3-diethoxyphosphoryl-D-*lyxo*-hexono-1,5-lactone (23): From 4,6-di-*O*-benzyl-2,3-

dideoxy-D-*threo*-hex-2-enono-1,5-lactone (**21**;[25] 100 mg, 0.308 mmol) following the general procedure by stirring at 100 °C for 1.5 h. Chromatotron chromatography (hexanes/EtOAc, 4:6) gave **22** (101.3 mg, 0.219 mmol, 71%) and **23** (12 mg, 0.026 mmol, 8.4%).

Compound 22: Colorless oil; $[\alpha]_D$ = +21.3 (c = 0.47, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.32 (t, J = 7.2 Hz, 3 H), 1.33 (t, J = 6.9 Hz, 3 H), 2.58 (dddd, $^2J_{P,H}$ = 20.7, J = 8.0, 8.0, 2.7 Hz, 1 H), 2.61–2.71 (m, 1 H), 2.75–2.83 (m, 1 H), 3.70 (dd, J = 9.9, 6.5 Hz, 1 H), 3.74 (dd, J = 9.9, 5.9 Hz, 1 H), 4.08–4.18 (m, 5 H), 4.44 (d, J = 11.7 Hz, 1 H), 4.47 (d, J = 11.4 Hz, 1 H), 4.54 (d, J = 11.9 Hz, 1 H), 4.543 (ddd, J = 6.1, 6.1, 2.1 Hz, 1 H), 4.66 (d, J = 11.9 Hz, 1 H), 7.24–7.33 (m, 10 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.4 (2× CH_3), 27.4 (CH_2), 34.7 (d, $^1J_{P,C}$ = 142.0 Hz, CH), 62.66 (d, $^2J_{P,C}$ = 12.7 Hz, CH_2), 62.68 (d, $^2J_{P,C}$ = 11.3 Hz, CH_2), 68.0 (CH_2), 70.0 (CH), 71.5 (CH_2), 73.5 (CH_2), 78.4 (CH), 127.69 (2× CH), 127.74 (CH), 127.84 (2× CH), 127.95 (CH), 128.35 (2× CH), 128.4 (2× CH), 137.1 (C), 137.6 (C), 169.1 (d, $^3J_{P,C}$ = 12.0 Hz, C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 26.7 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3009, 1747, 1241, 1026 cm^{-1}. MS (ESI^+): m/z (%) = 485 (100) $[M + Na]^+$. HRMS (ESI^+): m/z calcd. for $C_{24}H_{31}NaO_7P$ $[M + Na]^+$ 485.1705; found 485.1707. $C_{24}H_{31}O_7P$ (462.48): calcd. C 62.33, H 6.76; found C 62.34, H 6.67.

Compound 23: Colorless oil; $[\alpha]_D$ = –15.0 (c = 0.12, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.21 (t, J = 6.9 Hz, 3 H), 1.33 (t, J = 7.3 Hz, 3 H), 2.44 (dddd, $^2J_{P,H}$ = 19.6, J = 13.2, 6.0, 1.3 Hz, 1 H), 2.76 (ddd, $^3J_{P,H}$ = 2.2, J = 18.3, 6.0 Hz, 1 H), 3.05 (ddd, $^3J_{P,H}$ = 13.3, J = 18.3, 13.3 Hz, 1 H), 3.63 (dd, J = 9.8, 6.0 Hz, 1 H), 3.70 (dd, J = 9.5, 9.5 Hz, 1 H), 4.00–4.16 (m, 4 H), 4.39 (br. d, $^3J_{P,H}$ = 7.3 Hz, 1 H), 4.47–4.50 (m, 1 H), 4.47 (d, J = 11.7 Hz, 1 H), 4.52 (d, J = 11.7 Hz, 1 H), 4.66 (d, J = 11.4 Hz, 1 H), 4.91 (d, J = 11.0 Hz, 1 H), 7.26–7.36 (m, 10 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 16.3 (d, $^3J_{P,C}$ = 5.4 Hz, CH_3), 16.5 (d, $^3J_{P,C}$ = 5.4 Hz, CH_3), 26.4 (d, $^2J_{P,C}$ = 2.7 Hz, CH_2), 35.9 (d, $^1J_{P,C}$ = 150.8 Hz, CH), 62.2 (d, $^2J_{P,C}$ = 6.4 Hz, CH_2), 62.4 (d, $^2J_{P,C}$ = 6.4 Hz, CH_2), 67.8 (d, $^4J_{P,C}$ = 3.6 Hz, CH_2), 69.2 (d, $^2J_{P,C}$ = 6.4 Hz, CH), 73.7 (CH_2), 74.3 (CH_2), 81.9 (d, $^3J_{P,C}$ = 16.3 Hz, CH), 127.4 (2× CH), 127.7 (CH), 127.9 (2× CH), 128.0 (CH), 128.3 (2× CH), 128.5 (2× CH), 137.3 (C), 137.8 (C), 167.9 (d, $^3J_{P,C}$ = 19.1 Hz, C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 25.1 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3019, 1740, 1216, 1028 cm^{-1}. MS (ESI^+): m/z (%) = 485 (100) $[M + Na]^+$. HRMS (ESI^+): m/z calcd. for $C_{24}H_{31}NaO_7P$ $[M + Na]^+$ 485.1705; found 485.1707. $C_{24}H_{31}O_7P$ (462.48): calcd. C 62.33, H 6.76; found C 62.56, H 6.84.

General Procedure for the Hydration Reaction: A stirred 0.045 M solution of lactal (1 equiv.) in THF containing water (24 equiv.) and $Ph_3P{\cdot}HBr$[28] (0.12–0.46 equiv.) was heated at reflux temperature for the specified time. The reaction mixture was then poured into a saturated aqueous solution of $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic extracts were washed with a saturated aqueous solution of $NaHCO_3$, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by Chromatotron chromatography (hexanes/EtOAc).

4,6-Di-*O*-benzyl-2,3-dideoxy-3-diphenylphosphoryl-D-*ribo*-hexopyranose (24): From 1,5-anhydro-4,6-di-*O*-benzyl-2,3-dideoxy-3-diphenylphosphoryl-D-*ribo*-hex-1-enitol (**3**;[17] 25 mg, 0.049 mmol) in THF/H_2O containing $Ph_3P{\cdot}HBr$ (2 mg, 5.8×10^{-3} mmol) following the general procedure by heating at reflux for 1.5 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 4:6) gave **24** (23 mg, 0.044 mmol, 90%, anomeric mixture, α/β, 4.5:1) as a crystalline solid: m.p. 151.7–152.7 °C (*n*-hexane/EtOAc); $[\alpha]_D$ = –141.4 (c = 0.07, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ (major isomer) = 1.98 (dddd, $^3J_{P,H}$ = 9.9, J = 14.5, 2.4, 2.2 Hz, 1 H), 2.25 (dddd, $^3J_{P,H}$ = 30.1, J = 14.7, 7.0, 4.3 Hz, 1 H), 3.24 (dddd, $^2J_{P,H}$ = 6.3, J = 6.3, 6.3, 2.8 Hz, 1 H), 3.62 (dd, J = 10.6, 2.4 Hz, 1 H), 3.75 (dd, J = 10.7, 2.8 Hz, 1 H), 4.09 (d, J = 11.4 Hz, 1 H), 4.15 (ddd, $^3J_{P,H}$ = 24.6, J = 9.1, 6.0 Hz, 1 H), 4.19 (d, J = 11.4 Hz, 1 H), 4.43 (d, J = 12.0 Hz, 1 H), 4.53 (d, J = 12.0 Hz, 1 H), 4.60 (ddd, J = 9.1, 2.5, 2.5 Hz, 1 H), 5.12 (br. d, J = 2.8 Hz, 1 H), 6.71 (m, 2 H), 7.10–7.27 (m, 10 H), 7.47 (m, 4 H), 7.78 (m, 4 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (major isomer) = 31.1 (CH_2), 35.6 (d, $^1J_{P,C}$ = 69.9 Hz, CH), 68.9 (d, $^3J_{P,C}$ = 1.8 Hz, CH), 69.3 (CH_2), 72.3 (CH_2), 73.5 (CH_2), 74.6 (d, $^2J_{P,C}$ = 6.4 Hz, CH), 90.1 (d, $^3J_{P,C}$ = 2.7 Hz, CH), 127.3–129.0 (Ar, complex), 130.6–132.0 (Ar, complex), 132.5 (C), 132.8 (C), 137.2 (C), 138.0 (C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 36.8 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3212 cm^{-1}. MS (EI, 70 eV): m/z (%) = 529 (2) $[M + H]^+$, 511 (5), 202 (36), 91 (100). HRMS (EI, 70 eV): m/z calcd. for $C_{32}H_{34}O_5P$ $[M + H]^+$ 529.2144; found 529.2130. $C_{32}H_{33}O_5P$ (528.58): calcd. C 72.71, H 6.29; found C 72.63, H 6.11.

4,6-Di-*O*-acetyl-2,3-dideoxy-3-diphenylphosphoryl-D-*ribo*-hexopyranose (25): From **5** (90.8 mg, 0.219 mmol) in THF/H_2O containing $Ph_3P{\cdot}HBr$ (25 mg, 0.073 mmol) following the general procedure by heating at reflux for 8 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 6:4→3:7) gave starting material **5** (20.7 mg, 0.05 mmol, 23%) and compound **25** (52 mg, 0.12 mmol, 55%, anomeric mixture, α/β, 10:1). Compound **25**: crystalline solid; m.p. (double): 174.9–175.8 °C (needles), 178.0–178.6 °C (prisms) (*n*-hexane/EtOAc); $[\alpha]_D$ = +26.8 (c = 0.13, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ (major isomer) = 1.10 (s, 3 H), 1.96 (dddd, $^3J_{P,H}$ = 10.2, J = 15.0, 1.3, 1.3 Hz, 1 H), 2.04 (s, 3 H), 2.37 (dddd, $^3J_{P,H}$ = 32.2, J = 15.1, 7.6, 4.0 Hz, 1 H), 3.43 (dddd, $^2J_{P,H}$ = 4.8, J = 7.7, 6.6, 1.4 Hz, 1 H), 4.03 (dd, J = 12.2, 2.1 Hz, 1 H), 4.43 (dd, J = 12.1, 3.8 Hz, 1 H), 4.81 (ddd, J = 10.6, 3.7, 2.1 Hz, 1 H), 5.13 (br. d, J = 3.4 Hz, 1 H), 5.17 (ddd, $^3J_{P,H}$ = 25.2, J = 10.5, 6.8 Hz, 1 H), 7.51 (m, 6 H), 7.79 (m, 2 H), 7.86 (m, 2 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (major isomer) = 19.4 (CH_3), 20.7 (CH_3), 30.9 (d, $^2J_{P,C}$ = 1.8 Hz, CH_2), 33.7 (d, $^1J_{P,C}$ = 69.0 Hz, CH), 62.8 (CH_2), 65.4 (CH), 68.0 (d, $^2J_{P,C}$ = 6.4 Hz, CH), 89.9 (CH), 129.0 (d, $^3J_{P,C}$ = 11.8 Hz, 2× CH), 129.1 (d, $^3J_{P,C}$ = 10.9 Hz, 2× CH), 130.3 (d, $^2J_{P,C}$ = 2.7 Hz, 2× CH), 130.4 (d, $^2J_{P,C}$ = 4.5 Hz, 2× CH), 131.3 (d, $^1J_{P,C}$ = 98.1 Hz, C), 131.7 (d, $^4J_{P,C}$ = 2.7 Hz, CH), 132.10 (d, $^1J_{P,C}$ = 99.9 Hz, C), 132.13 (d, $^4J_{P,C}$ = 2.7 Hz, CH), 170.3 (C), 170.7 (C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 35.5 (s, 1 P) ppm. IR (film): $\tilde{\nu}$ = 3178, 1738 cm^{-1}. MS (EI, 70 eV): m/z (%) = 433 (9) $[M + H]^+$, 287 (24), 202 (100). HRMS (EI, 70 eV): m/z calcd. for $C_{22}H_{26}O_7P$ $[M + H]^+$ 433.1416; found 433.1414. $C_{22}H_{25}O_7P$ (432.41): calcd. C 61.11, H 5.83; found C 61.21, H 5.74.

4,6-Di-*O*-acetyl-2,3-dideoxy-3-diphenylphosphoryl-D-*arabino*-hexopyranose (26): From **6** (19.5 mg, 0.047 mmol) in THF/H_2O containing $Ph_3P{\cdot}HBr$ (6.5 mg, 0.019 mmol) following the general procedure by heating at reflux for 13 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 2:8) gave **26** (12 mg, 0.028 mmol, 59%, anomeric mixture, α/β, 10:1 in $CDCl_3$; 7:3 in CD_3OD) as a crystalline solid: m.p. 212–213.8 °C (*n*-hexane/$CHCl_3$); $[\alpha]_D$ = +27.2 (c = 0.614, $CHCl_3$). ^1H NMR (500 MHz, CD_3OD): δ (major isomer) = 1.12 (s, 3 H), 1.60 (dddd, $^3J_{P,H}$ = 5.7, J = 13.7, 3.6, 1.5 Hz, 1 H), 1.91 (dddd, $^3J_{P,H}$ = 7.0, J = 13.7, 13.6, 3.1 Hz, 1 H), 1.99 (s, 3 H), 3.55 (dddd, $^2J_{P,H}$ = 1.8, J = 13.6, 11.0, 3.6 Hz, 1 H), 3.93 (dd, J = 12.1, 2.9 Hz, 1 H), 4.05 (dd, J = 12.1, 4.7 Hz, 1 H), 4.18 (ddd, J = 9.9, 4.7, 2.9 Hz, 1 H), 5.22 (dd, J = 3.1, 1.5 Hz, 1 H), 5.36 (ddd, $^3J_{P,H}$ = 8.1, J = 11.0, 9.8 Hz, 1 H), 7.53 (m, 6 H), 7.81 (m, 2 H), 7.93 (m, 2 H) ppm. ^{13}C NMR (125.7 MHz, CD_3OD): δ (major isomer; note: one of the *ipso* carbons is not observed) = 19.8 (CH_3), 20.7 (CH_3), 30.8 (d, $^2J_{P,C}$ = 3.2 Hz, CH_2),

34.6 (d, $^1J_{P,C}$ = 73.1 Hz, CH), 64.2 (CH_2), 66.9 (d, $^2J_{P,C}$ = 6.4 Hz, CH), 69.4 (d, $^3J_{P,C}$ = 9.5 Hz, CH), 90.7 (d, $^3J_{P,C}$ = 12.7 Hz, CH), 129.9 (d, $^3J_{P,C}$ = 12.7 Hz, 2× CH), 130.1 (d, $^3J_{P,C}$ = 12.7 Hz, 2× CH), 131.7 (d, $^2J_{P,C}$ = 8.5 Hz, 2× CH), 132.0 (d, $^2J_{P,C}$ = 9.5 Hz, 2× CH), 133.1 (d, $^4J_{P,C}$ = 3.2 Hz, CH), 133.3 (d, $^4J_{P,C}$ = 2.1 Hz, CH), 133.7 (d, $^1J_{P,C}$ = 98.5 Hz, C), 170.8 (C), 172.5 (C) ppm. ^{31}P NMR (161.9 MHz, CD_3OD): δ = 32.6 (s, 1 P), 31.8 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3330, 1741 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 455 (100) [M + Na]$^+$. HRMS (ESI$^+$): *m*/*z* calcd. for $C_{22}H_{25}NaO_7P$ [M + Na]$^+$ 455.1236; found 455.1234. $C_{22}H_{25}O_7P$ (432.41): calcd. C 61.11, H 5.83; found C 60.87, H 5.86.

4,6-Di-*O*-benzyl-2,3-dideoxy-3-diphenylphosphoryl-D-*xylo*-hexopyranose (27): From **9** (75.4 mg, 0.148 mmol) in THF/H_2O containing Ph_3P·HBr (8.1 mg, 0.024 mmol) following the general procedure by heating at reflux for 3.75 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 6:4) gave starting material **9** (5.3 mg, 0.01 mmol, 7%) and **27** (72 mg, 0.136 mmol, 92%, anomeric mixture, α/β, 17:1) as a colorless amorphous solid: $[\alpha]_D$ = –38.3 (*c* = 0.12, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ (major isomer) = 1.78 (dddd, $^3J_{P,H}$ = 11.2, *J* = 14.4, 0.6, 0.0 Hz, 1 H), 2.59 (dddd, $^3J_{P,H}$ = 32.2, *J* = 14.8, 7.9, 4.4 Hz, 1 H), 2.80 (dddd, $^2J_{P,H}$ = 9.5, *J* = 8.5, 1.0, 1.0 Hz, 1 H), 3.55 (dd, *J* = 9.3, 5.5 Hz, 1 H), 3.58–3.61 (m, 2 H), 4.32 (d, *J* = 12.3 Hz, 1 H), 4.35 (d, *J* = 12.0 Hz, 1 H), 4.46 (d, *J* = 12.6 Hz, 1 H), 4.48 (d, *J* = 12.0 Hz, 1 H), 4.50 (dd, *J* = 8.7, 5.8 Hz, 1 H), 5.19 (d, *J* = 4.1 Hz, 1 H), 7.11 (m, 4 H), 7.28 (m, 6 H), 7.41 (m, 2 H), 7.49 (m, 2 H), 7.58 (m, 4 H), 7.69 (m, 2 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (major isomer) = 25.8 (d, $^2J_{P,C}$ = 2.1 Hz, CH_2), 35.5 (d, $^1J_{P,C}$ = 63.6 Hz, CH), 66.9 (CH), 68.7 (CH_2), 69.6 (d, $^2J_{P,C}$ = 5.3 Hz, CH), 72.6 (CH_2), 72.8 (CH_2), 89.7 (CH), 127.2 (2× CH), 127.3 (CH), 128.0 (CH), 128.13 (2× CH), 128.15 (2× CH), 128.5 (2× CH), 129.01 (d, $^3J_{P,C}$ = 11.7 Hz, 2× CH), 129.03 (d, $^1J_{P,C}$ = 99.6 Hz, C), 129.04 (d, $^3J_{P,C}$ = 11.7 Hz, 2× CH), 130.0 (d, $^1J_{P,C}$ = 99.6 Hz, C), 130.8 (d, $^2J_{P,C}$ = 8.5 Hz, 2× CH), 131.0 (d, $^2J_{P,C}$ = 8.5 Hz, 2× CH), 132.3 (d, $^4J_{P,C}$ = 2.1 Hz, CH), 132.4 (d, $^4J_{P,C}$ = 2.1 Hz, CH), 138.0 (C), 138.3 (C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 35.9 (s, 1 P) ppm. IR (film): $\tilde{\nu}$ = 3225 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 528 (< 1) [M]$^+$, 311 (25), 287 (25), 202 (81), 91 (100). HRMS (EI, 70 eV): *m*/*z* calcd. for $C_{32}H_{33}O_5P$ [M]$^+$ 528.2066; found 528.2079. $C_{32}H_{33}O_5P$ (528.58): calcd. C 72.71, H 6.29; found C 72.86, H 6.32.

4,6-Di-*O*-acetyl-2,3-dideoxy-3-diphenylphosphoryl-D-*xylo*-hexopyranose (28): From **10** (45.1 mg, 0.109 mmol) in THF/H_2O containing Ph_3P·HBr (16.3 mg, 0.05 mmol) following the general procedure by heating at reflux for 7.5 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 4:6) gave starting material **10** (8.2 mg, 0.02 mmol, 18%) and **28** (34.6 mg, 0.08 mmol, 73%, anomeric mixture, α/β, 25:1) as an oil: $[\alpha]_D$ = –19.2 (*c* = 0.36, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major isomer) = 1.86 (ddddd, $^3J_{P,H}$ = 10.7, *J* = 15.0, 0.8, 0.8, 0.8 Hz, 1 H), 1.91 (s, 3 H), 2.11 (s, 3 H), 2.44 (ddddd, $^3J_{P,H}$ = 31.5, *J* = 15.0, 8.0, 4.4 Hz, 1 H), 3.07 (dddd, $^2J_{P,H}$ = 11.1, *J* = 8.3, 1.5, 1.2 Hz, 1 H), 4.03 (dd, *J* = 11.3, 6.8 Hz, 1 H), 4.08 (dd, *J* = 11.3, 6.2 Hz, 1 H), 4.50 (ddd, *J* = 6.4, 6.4, 1.1 Hz, 1 H), 4.76 (br. d, $^3J_{P,H}$ = 6.4 Hz, 1 H), 5.23 (dd, *J* = 11.7, 4.0 Hz, 1 H), 7.56 (m, 6 H), 7.83 (m, 2 H), 8.02 (m, 2 H), 8.20 (d, *J* = 11.9 Hz, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (major isomer) = 20.5 (CH_3), 20.9 (CH_3), 25.1 (d, $^2J_{P,C}$ = 2.1 Hz, CH_2), 35.4 (d, $^1J_{P,C}$ = 63.6 Hz, CH), 62.9 (CH_2), 65.1 (CH), 65.9 (d, $^2J_{P,C}$ = 6.4 Hz, CH), 89.6 (CH), 127.9 (d, $^1J_{P,C}$ = 100.6 Hz, C), 129.0 (d, $^3J_{P,C}$ = 12.7 Hz, 2× CH), 129.1 (d, $^3J_{P,C}$ = 11.7 Hz, 2× CH), 129.9 (d, $^1J_{P,C}$ = 100.6 Hz, C), 130.8 (d, $^2J_{P,C}$ = 9.5 Hz, 2× CH), 131.4 (d, $^2J_{P,C}$ = 9.5 Hz, 2× CH), 132.5 (d, $^4J_{P,C}$ = 3.2 Hz, CH), 132.8 (d, $^4J_{P,C}$ = 2.1 Hz, CH), 170.4 (C), 170.7 (C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 35.8 (s, 1 P) ppm. IR (film): $\tilde{\nu}$ = 3215, 1732 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 433 (2) [M + H]$^+$, 415 (21), 202 (100), 201 (54). HRMS (EI, 70 eV): *m*/*z* calcd. for $C_{22}H_{26}O_7P$ [M + H]$^+$ 433.1416; found 433.1409. $C_{22}H_{25}O_7P$ (432.41): calcd. C 61.11, H 5.83; found C 61.34, H 5.91.

6-*O*-Benzyl-2,3-dideoxy-3-diphenylphosphoryl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-D-*ribo*-hexopyranose (29): From **12α** (240 mg, 0.254 mmol) in THF/H_2O containing Ph_3P·HBr (30 mg, 0.087 mmol) following the general procedure by heating at reflux for 6 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 6:4) gave starting material **12α** (34 mg, 0.036 mmol, 14%) and compound **29** (186 mg, 0.194 mmol, 76%, isomeric mixture, α/β, 25:1): crystalline solid; m.p. 173.3–174.1 °C (*n*-hexane/EtOAc); $[\alpha]_D$ = +71.5 (*c* = 0.17, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ (major isomer) = 1.23 (d, *J* = 6.3 Hz, 1 H), 1.86 (dd, $^3J_{P,H}$ = 10.3, *J* = 15.0 Hz, 1 H), 2.24 (dddd, $^2J_{P,H}$ = 32.6, *J* = 14.9, 7.5, 4.3 Hz, 1 H), 2.63 (dd, *J* = 8.8, 8.8 Hz, 1 H), 3.18 (dd, *J* = 9.8, 2.8 Hz, 1 H), 3.26 (ddd, $^3J_{P,H}$ = 6.2, *J* = 6.2, 6.2 Hz, 1 H), 3.35 (dd, *J* = 6.5, 6.5 Hz, 1 H), 3.46 (d, *J* = 10.7 Hz, 1 H), 3.66 (d, *J* = 10.1 Hz, 1 H), 3.67–3.69 (m, 1 H), 3.78 (dd, *J* = 8.2, 8.2 Hz, 1 H), 3.82 (d, *J* = 2.5 Hz, 1 H), 4.03 (s, 2 H), 4.23 (d, *J* = 7.9 Hz, 1 H), 4.30 (d, *J* = 12.0 Hz, 1 H), 4.36 (ddd, $^3J_{P,H}$ = 27.4, *J* = 10.2, 6.3 Hz, 1 H), 4.46 (d, *J* = 12.0 Hz, 1 H), 4.52 (d, *J* = 10.1 Hz, 1 H), 4.56 (d, *J* = 11.4 Hz, 1 H), 4.56 (d, *J* = 11.4 Hz, 1 H), 4.60 (d, *J* = 12.0 Hz, 1 H), 4.66 (d, *J* = 12.0 Hz, 1 H), 4.70 (d, *J* = 12.0 Hz, 1 H), 4.93 (d, *J* = 10.4 Hz, 1 H), 5.10 (d, *J* = 3.8 Hz, 1 H), 7.05–7.44 (m, 31 H), 7.73 (m, 2 H), 7.84 (m, 2 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (major isomer) = 31.4 (CH_2), 37.6 (d, $^1J_{P,C}$ = 68.9 Hz, CH), 68.3 (CH), 68.6 (CH_2), 68.7 (CH_2), 73.0 (CH_2), 73.1 (CH), 73.3 (CH_2), 73.4 (CH_2), 73.7 (d, $^2J_{P,C}$ = 5.3 Hz, CH), 74.7 (CH), 74.9 (CH_2), 75.3 (CH_2), 78.7 (CH), 81.7 (CH), 89.9 (CH), 104.0 (CH), 127.3–128.8 (Ar, complex), 130.5–133.2 (Ar, complex), 138.0 (C), 138.2 (C), 138.6 (C), 138.7 (C), 139.0 (C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 37.9 (s, 1 P) ppm. IR (film): $\tilde{\nu}$ = 3226, 1099 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 961 (< 1) [M + H]$^+$, 421 (2), 91 (100). HRMS (EI, 70 eV): *m*/*z* calcd. for $C_{59}H_{62}O_{10}P$ [M + H]$^+$ 961.4081; found 961.4055. $C_{59}H_{61}O_{10}P$ (961.10): calcd. C 73.73, H 6.40; found C 73.79, H 6.34.

6-*O*-Benzyl-2,3-dideoxy-3-diphenylphosphoryl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-D-*arabino*-hexopyranose (30): From **12β** (63 mg, 0.067 mmol) in THF/H_2O containing Ph_3P·HBr (3.8 mg, 0.011 mmol) following the general procedure by heating at reflux for 1.5 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 6:4) gave starting material **12β** (3.1 mg, 0.003 mmol, 5%) and compound **30** (47.6 mg, 0.049 mmol, 74%, isomeric mixture, α/β, 1:1): crystalline solid; m.p. 153.2–154.2 °C (*n*-hexane/EtOAc); $[\alpha]_D$ = +28.3 (*c* = 0.23, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125.7 MHz, $CDCl_3$) exhibit complex resonance patterns. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 31.0 (s, 1 P), 35.4 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3297, 1097 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 983 (100) [M + Na]$^+$. HRMS (ESI$^+$): *m*/*z* calcd. for $C_{59}H_{61}NaO_{10}P$ [M + Na]$^+$ 983.3900; found 983.3900. $C_{59}H_{61}O_{10}P$ (961.10): calcd. C 73.73, H 6.40; found C 75.72, H 6.29.

General Procedure for the β-Fragmentation Reaction: A 0.04 M solution of the alcohol (1 equiv.) in anhydrous CH_2Cl_2 (25 mL) containing $PhI(OAc)_2$ (1.1–1.5 equiv.) and I_2 (0.6–1.5 equiv.) under nitrogen was stirred for the temperature and time specified in each case. The reaction mixture was then poured into 10% aqueous $Na_2S_2O_3$, extracted with CH_2Cl_2, dried with Na_2SO_4, and concentrated. The residue was purified by Chromatotron chromatography (hexanes/EtOAc).

3,5-Di-*O*-benzyl-1,2-dideoxy-2-diphenylphosphoryl-4-*O*-formyl-1-iodo-D-ribitol (31): From **24** (20.2 mg, 0.038 mmol) in CH_2Cl_2

(1 mL) containing $PhI(OAc)_2$ (13.6 mg, 0.042 mmol) and I_2 (10.7 mg, 0.042 mmol) following the general procedure by stirring at room temperature for 2.5 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 6:4) gave **31** (19.7 mg, 0.03 mmol, 79%) as an oil: $[\alpha]_D$ = +12.5 (c = 0.24, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 3.21 (dddd, $^2J_{P,H}$ = 10.0, J = 9.1, 1.6, 1.6 Hz, 1 H), 3.40 (ddd, $^3J_{P,H}$ = 13.1, J = 10.9, 2.5 Hz, 1 H), 3.58 (dd, J = 11.0, 4.1 Hz, 1 H), 3.66 (ddd, $^3J_{P,H}$ = 5.7, J = 10.9, 9.0 Hz, 1 H), 3.76 (dd, J = 11.0, 2.5 Hz, 1 H), 4.31 (d, J = 12.0 Hz, 1 H), 4.35 (ddd, $^3J_{P,H}$ = 14.7, J = 8.6, 1.6 Hz, 1 H), 4.39 (d, J = 10.7 Hz, 1 H), 4.40 (d, J = 12.0 Hz, 1 H), 4.92 (d, J = 10.7 Hz, 1 H), 5.38 (ddd, J = 8.8, 3.2, 3.2 Hz, 1 H), 7.12 (m, 2 H), 7.26 (m, 8 H), 7.51 (m, 6 H), 7.86 (m, 4 H), 8.13 (s, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.8 (CH_2), 42.9 (d, $^1J_{P,C}$ = 62.5 Hz, CH), 67.9 (CH_2), 73.0 (2× CH_2), 73.3 (d, $^2J_{P,C}$ = 7.3 Hz, CH), 73.4 (CH), 127.4 (2× CH), 127.6 (CH), 127.7 (CH), 128.1 (2× CH), 128.2 (2× CH), 128.3 (2× CH), 128.9 (d, $^3J_{P,C}$ = 11.7 Hz, 2× CH), 129.0 (d, $^3J_{P,C}$ = 11.7 Hz, 2× CH), 131.0 (d, $^2J_{P,C}$ = 8.5 Hz, 2× CH), 131.1 (d, $^2J_{P,C}$ = 9.5 Hz, 2× CH), 131.3 (C), 131.7 (C), 132.1 (d, $^4J_{P,C}$ = 3.2 Hz, CH), 132.2 (d, $^4J_{P,C}$ = 2.1 Hz, CH), 137.6 (C), 137.7 (C), 160.2 (CH) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 34.2 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1729 cm^{-1}. MS (EI, 70 eV): m/z (%) = 655 (< 1) $[M + H]^+$, 329 (51), 202 (64), 91 (100). HRMS (EI, 70 eV): m/z calcd. for $C_{32}H_{33}IO_5P$ $[M + H]^+$ 655.1110; found 655.1120. $C_{32}H_{32}IO_5P$ (654.48): calcd. C 58.73, H 4.93; found C 58.79, H 5.12.

3,5-Di-*O*-acetyl-1,2-dideoxy-2-diphenylphosphoryl-4-*O*-formyl-1-iodo-D-ribitol (32): From **25** (44.8 mg, 0.104 mmol) in CH_2Cl_2 (2.6 mL) containing $PhI(OAc)_2$ (36.7 mg, 0.114 mmol) and I_2 (29 mg, 0.114 mmol) following the general procedure by stirring at room temperature for 4.5 h under irradiation with a 80 W tungsten-filament lamp. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 1:1) gave **32** (49.4 mg, 0.088 mmol, 85%) as an oil: $[\alpha]_D$ = +2.4 (c = 0.17, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.93 (s, 3 H), 1.94 (s, 3 H), 3.15 (dd, $^2J_{P,H}$ = 9.8, J = 9.8 Hz, 1 H), 3.40 (ddd, $^3J_{P,H}$ = 11.9, J = 11.9, 2.4 Hz, 1 H), 3.54 (ddd, $^3J_{P,H}$ = 5.0, J = 11.3, 9.2 Hz, 1 H), 4.08 (dd, J = 12.6, 4.4 Hz, 1 H), 4.37 (dd, J = 12.6, 2.5 Hz, 1 H), 5.63 (ddd, J = 7.8, 4.7, 2.8 Hz, 1 H), 5.70 (ddd, $^3J_{P,H}$ = 14.0, J = 8.4, 1.6 Hz, 1 H), 7.50–7.60 (m, 6 H), 7.55 (m, 6 H), 7.80 (m, 2 H), 7.86 (m, 2 H), 8.12 (s, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –6.6 (CH_2), 20.5 (CH_3), 20.6 (CH_3), 42.4 (d, $^1J_{P,C}$ = 60.4 Hz, CH), 61.1 (CH_2), 67.4 (CH), 70.2 (d, $^2J_{P,C}$ = 7.4 Hz, CH), 128.9 (d, $^3J_{P,C}$ = 11.7 Hz, 2× CH), 129.1 (d, $^3J_{P,C}$ = 11.7 Hz, 2× CH), 130.8 (d, $^2J_{P,C}$ = 8.5 Hz, 2× CH), 130.9 (d, $^1J_{P,C}$ = 97.5 Hz, 2× C), 131.0 (d, $^2J_{P,C}$ = 8.5 Hz, 2× CH), 132.2 (d, $^4J_{P,C}$ = 2.1 Hz, CH), 132.5 (d, $^4J_{P,C}$ = 2.1 Hz, CH), 159.4 (CH), 168.9 (C), 170.4 (C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 33.0 (s, 1 P) ppm. IR (film): $\tilde{\nu}$ = 1731 cm^{-1}. MS (EI, 70 eV): m/z (%) = 559 (1) $[M + H]^+$, 431 (27), 201 (100). HRMS (EI, 70 eV): m/z calcd. for $C_{22}H_{25}IO_7P$ $[M + H]^+$ 559.0383; found 559.0383. $C_{22}H_{24}IO_7P$ (558.31): calcd. C 47.33, H 4.33; found C 47.45, H 4.31.

3,5-Di-*O*-acetyl-1,2-dideoxy-2-diphenylphosphoryl-4-*O*-formyl-1-iodo-D-arabinitol (33): From **26** (1.53 g, 3.54 mmol) in CH_2Cl_2 (88 mL) containing $PhI(OAc)_2$ (1.254 g, 3.9 mmol) and I_2 (989 mg, 3.9 mmol) following the general procedure by stirring at room temperature for 4 h. Column chromatography of the reaction residue (hexanes/EtOAc, 4:6) gave **33** (1.486 g, 2.66 mmol, 75%) as a colorless oil: $[\alpha]_D$ = +63.6 (c = 1.07, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.94 (s, 3 H), 1.97 (s, 3 H), 3.27 (dddd, $^2J_{P,H}$ = 10.7, J = 10.7, 2.2, 2.2 Hz, 1 H), 3.34 (ddd, $^3J_{P,H}$ = 3.5, J = 10.7, 10.7 Hz, 1 H), 3.42 (ddd, $^3J_{P,H}$ = 10.7, J = 10.7, 2.5 Hz, 1 H), 4.08 (dd, J = 12.3, 4.1 Hz, 1 H), 4.16 (dd, J = 12.3, 2.5 Hz, 1 H), 5.31 (dddd, $^4J_{P,H}$ = 0.9, J = 8.8, 4.4, 2.5 Hz, 1 H), 5.53 (ddd, $^3J_{P,H}$ = 14.2, J = 8.8, 1.9 Hz, 1 H), 7.52 (m, 6 H), 7.82 (m, 4 H), 8.11 (br. s) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –0.7 (CH_2), 20.48 (CH_3), 20.54 (CH_3), 43.9 (d, $^1J_{P,C}$ = 59.3 Hz, CH), 61.6 (CH_2), 70.0 (CH), 70.6 (d, $^2J_{P,C}$ = 2.1 Hz, CH), 128.8 (d, $^3J_{P,C}$ = 11.7 Hz, 2× CH), 128.9 (d, $^3J_{P,C}$ = 11.7 Hz, 2× CH), 131.1 (d, $^2J_{P,C}$ = 8.5 Hz, 4× CH), 131.2 (d, $^1J_{P,C}$ = 99.6 Hz, C), 131.3 (d, $^1J_{P,C}$ = 98.6 Hz, C), 132.3 (d, $^4J_{P,C}$ = 3.2 Hz, CH), 132.4 (d, $^4J_{P,C}$ = 2.1 Hz, CH), 160.0 (CH), 169.9 (C), 170.3 (C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 29.6 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2993, 1736, 1231, 1167 cm^{-1}. MS (ESI^+): m/z (%) = 581 (100) $[M + Na]^+$. HRMS (ESI^+): m/z calcd. for $C_{22}H_{24}INaO_7P$ $[M + Na]^+$ 581.0202; found 581.0207. $C_{22}H_{24}IO_7P$ (558.31): calcd. C 47.33, H 4.33; found C 46.97, H 4.65.

3,5-Di-*O*-benzyl-1,2-dideoxy-2-diphenylphosphoryl-4-*O*-formyl-1-iodo-D-xylitol (34): From **27** (14.2 mg, 0.027 mmol) in CH_2Cl_2 (0.7 mL) containing $PhI(OAc)_2$ (9.5 mg, 0.03 mmol) and I_2 (4.1 mg, 0.016 mmol) following the general procedure by stirring at reflux temperature for 2 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 6:4) gave **34** (13.5 mg, 0.021 mmol, 78%) as a colorless oil: $[\alpha]_D$ = –11.9 (c = 0.18, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 3.11 (m, 2 H), 3.37 (m, 1 H), 3.70 (dd, J = 10.9, 4.6 Hz, 1 H), 3.78 (dd, J = 10.9, 3.9 Hz, 1 H), 4.41 (m, 1 H), 4.45 (d, J = 11.7 Hz, 1 H), 4.60 (d, J = 11.7 Hz, 1 H), 4.62 (d, J = 11.4 Hz, 1 H), 4.65 (d, J = 11.7 Hz, 1 H), 5.68 (ddd, J = 6.6, 4.4, 4.4 Hz, 1 H), 6.93 (m, 2 H), 7.20 (m, 3 H), 7.35 (m, 9 H), 7.47 (m, 2 H), 7.55 (m, 2 H), 7.66 (m, 2 H), 8.10 (s, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 1.4 (CH_2), 43.7 (d, $^1J_{P,C}$ = 62.9 Hz, CH), 68.7 (CH_2), 73.5 (CH_2), 74.9 (CH), 75.5 (CH_2), 79.3 (d, $^2J_{P,C}$ = 3.5 Hz, CH), 127.5 (CH), 127.87 (CH), 127.91 (2× CH), 128.1 (2× CH), 128.2 (2× CH), 128.3 (d, $^3J_{P,C}$ = 11.3 Hz, 2× CH), 128.4 (2× CH), 128.7 (d, $^3J_{P,C}$ = 12.0 Hz, 2× CH), 130.80 (d, $^2J_{P,C}$ = 9.2 Hz, 2× CH), 130.84 (d, $^1J_{P,C}$ = 96.8 Hz, C), 131.86 (d, $^4J_{P,C}$ = 7.8 Hz, CH), 131.88 (d, $^4J_{P,C}$ = 7.8 Hz, CH), 132.1 (d, $^2J_{P,C}$ = 9.2 Hz, 2× CH), 132.5 (d, $^1J_{P,C}$ = 98.9 Hz, C), 137.4 (C), 137.5 (C), 160.8 (CH) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 31.5 (s, 1 P) ppm. IR (film): $\tilde{\nu}$ = 1724 cm^{-1}. MS (EI, 70 eV): m/z (%) = 655 (< 1) $[M + H]^+$, 202 (60), 91 (100). HRMS (EI, 70 eV): m/z calcd. for $C_{32}H_{33}IO_5P$ $[M + H]^+$ 655.1110; found 655.1110. $C_{32}H_{32}IO_5P$ (654.48): calcd. C 58.73, H 4.93; found C 58.74, H 4.95.

3,5-Di-*O*-acetyl-1,2-dideoxy-2-diphenylphosphoryl-4-*O*-formyl-1-iodo-D-xylitol (35): From **28** (90 mg, 0.208 mmol) in CH_2Cl_2 (5.2 mL) containing $PhI(OAc)_2$ (74 mg, 0.23 mmol) and I_2 (58 mg, 0.23 mmol) following the general procedure by stirring at reflux temperature for 2.2 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 1:1) gave **35** (93.2 mg, 0.167 mmol, 80%) and **43** (12.1 mg, 0.028 mmol, 13%). Compound **35**: colorless oil; $[\alpha]_D$ = –39.0 (c = 0.25, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.75 (s, 3 H), 2.06 (s, 3 H), 3.23 (ddd, $^3J_{P,H}$ = 4.1, J = 10.1, 10.1 Hz, 1 H), 3.30 (dddd, $^2J_{P,H}$ = 13.1, J = 9.8, 2.7, 2.7 Hz, 1 H), 3.42 (ddd, $^3J_{P,H}$ = 12.6, J = 10.4, 2.4 Hz, 1 H), 4.34 (dd, J = 12.5, 4.3 Hz, 1 H), 4.37 (dd, J = 12.5, 4.6 Hz, 1 H), 5.67 (ddd, $^3J_{P,H}$ = 15.1, J = 6.5, 3.0 Hz, 1 H), 5.77 (ddd, J = 6.6, 4.4, 4.4 Hz, 1 H), 7.53 (m, 4 H), 7.59 (m, 2 H), 7.82 (m, 4 H), 8.03 (s, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –1.6 (CH_2), 20.2 (CH_3), 20.8 (CH_3), 43.8 (d, $^1J_{P,C}$ = 60.8 Hz, CH), 62.0 (CH_2), 71.3 (d, $^2J_{P,C}$ = 2.1 Hz, CH), 71.7 (CH), 128.7 (d, $^3J_{P,C}$ = 12.0 Hz, 2× CH), 129.1 (d, $^3J_{P,C}$ = 12.0 Hz, 2× CH), 130.5 (d, $^1J_{P,C}$ = 98.9 Hz, C), 130.8 (d, $^2J_{P,C}$ = 9.2 Hz, 2× CH), 131.5 (d, $^1J_{P,C}$ = 98.9 Hz, C), 131.6 (d, $^2J_{P,C}$ = 9.2 Hz, 2× CH), 132.3 (d, $^4J_{P,C}$ = 2.8 Hz, CH), 132.5 (d, $^4J_{P,C}$ = 2.1 Hz, CH), 159.7 (CH), 169.9 (C), 170.4 (C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 30.3 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1742, 1217 cm^{-1}. MS (ESI^+): m/z (%) = 581 (100) $[M + Na]^+$.

HRMS (ESI$^+$): *m*/*z* calcd. for $C_{22}H_{24}INaO_7P$ [M + Na]$^+$ 581.0202; found 581.0214. $C_{22}H_{24}IO_7P$ (558.31): calcd. C 47.33, H 4.33; found C 47.19, H 4.32.

5-*O*-Benzyl-1,2-dideoxy-2-diphenylphosphoryl-4-*O*-formyl-1-iodo-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-D-ribitol (36) and 6-*O*-Benzyl-2,3-dideoxy-3-diphenylphosphoryl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-D-*ribo*-hexono-1,5-lactone (37): From **29** (343.3 mg, 0.357 mmol) in CH_2Cl_2 (9.0 mL) containing $PhI(OAc)_2$ (172.6 mg, 0.536 mmol) and I_2 (136.0 mg, 0.536 mmol) following the general procedure by stirring at reflux temperature for 30 min. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 6:4→1:1) gave **36** (261.5 mg, 0.241 mmol, 67%) and **37** (51.3 mg, 0.053 mmol, 15%).

Compound 36: Yellowish oil; $[\alpha]_D$ = –5.9 (*c* = 0.27, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.29 (dd, *J* = 9.8, 7.6 Hz, 1 H), 3.36 (dd, *J* = 10.1, 2.8 Hz, 1 H), 3.38 (m, 1 H), 3.42 (dd, *J* = 10.9, 4.3 Hz, 1 H), 3.53 (dd, *J* = 8.7, 4.9 Hz, 1 H), 3.56 (d, *J* = 2.2 Hz, 1 H), 3.58 (ddd, $^2J_{P,H}$ = 6.0, *J* = 6.0, 2.2 Hz, 1 H), 3.64 (ddd, $^3J_{P,H}$ = 11.0, *J* = 11.0, 2.8 Hz, 1 H), 3.79 (dd, *J* = 8.7, 4.9 Hz, 1 H), 3.84 (dd, *J* = 8.8, 8.8 Hz, 1 H), 3.87 (d, *J* = 11.7 Hz, 1 H), 3.98 (d, *J* = 2.5 Hz, 1 H), 4.18 (d, *J* = 12.0 Hz, 1 H), 4.27 (d, *J* = 11.4 Hz, 1 H), 4.28 (d, *J* = 12.0 Hz, 1 H), 4.30 (d, *J* = 7.6 Hz, 1 H), 4.54 (d, *J* = 11.7 Hz, 1 H), 4.57 (d, *J* = 11.7 Hz, 1 H), 4.64 (d, *J* = 11.0 Hz, 1 H), 4.67 (ddd, $^3J_{P,H}$ = 24.3, *J* = 9.2, 2.2 Hz, 1 H), 4.69 (d, *J* = 12.0 Hz, 1 H), 4.72 (d, *J* = 12.0 Hz, 1 H), 5.02 (d, *J* = 11.0 Hz, 1 H), 5.28 (ddd, *J* = 9.1, 3.9, 1.9 Hz, 1 H), 7.08 (m, 2 H), 7.16–7.38 (m, 24 H), 7.47 (m, 5 H), 7.79 (m, 2 H), 7.87 (m, 2 H), 8.13 (s, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 2.3 (CH_2), 46.2 (d, $^1J_{P,C}$ = 60.4 Hz, CH), 67.8 (CH_2), 68.1 (CH_2), 72.79 (2× CH_2), 72.83 (CH), 73.60 (CH_2), 73.63 (CH), 74.4 (d, $^3J_{P,C}$ = 4.2 Hz, CH), 74.8 (CH_2), 75.1 (CH_2), 77.5 (d, $^2J_{P,C}$ = 3.5 Hz, CH), 79.1 (CH), 81.8 (CH), 105.2 (CH), 127.4–132.0 (Ar, complex), 137.7 (C), 138.0 (C), 138.3 (C), 138.4 (C), 139.1 (C), 160.8 (CH) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 28.7 (s, 1 P) ppm. IR (film): $\tilde{\nu}$ = 1731 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 1109 (100) [M + Na]$^+$. HRMS (ESI$^+$): *m*/*z* calcd. for $C_{59}H_{60}INaO_{10}P$ [M + Na]$^+$ 1109.2867; found 1109.2902. $C_{59}H_{60}IO_{10}P$ (1087.00): calcd. C 65.19, H 5.56; found C 65.22, H 5.57.

Compound 37: Colorless oil; $[\alpha]_D$ = +49.6 (*c* = 0.23, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.62 (ddd, $^3J_{P,H}$ = 10.7, *J* = 17.8, 6.0 Hz, 1 H), 2.70 (ddd, $^3J_{P,H}$ = 11.0, *J* = 17.8, 9.5 Hz, 1 H), 3.27 (dd, *J* = 9.8, 7.9 Hz, 1 H), 3.37 (dd, *J* = 9.9, 3.0 Hz, 1 H), 3.42 (dd, *J* = 7.4, 5.8 Hz, 1 H), 3.49 (m, 1 H), 3.52 (dd, *J* = 9.1, 5.4 Hz, 1 H), 3.63 (dd, *J* = 10.7, 2.5 Hz, 1 H), 3.69 (m, 2 H), 3.90 (d, *J* = 2.8 Hz, 1 H), 4.23 (d, *J* = 11.0 Hz, 1 H), 4.26 (d, *J* = 10.7 Hz, 1 H), 4.33 (d, *J* = 7.6 Hz, 1 H), 4.39 (d, *J* = 11.4 Hz, 1 H), 4.48 (d, *J* = 11.7 Hz, 1 H), 4.49 (d, *J* = 11.4 Hz, 1 H), 4.51 (d, *J* = 11.7 Hz, 1 H), 4.59 (d, *J* = 10.7 Hz, 1 H), 4.63 (ddd, $^3J_{P,H}$ = 14.2, *J* = 4.1, 4.1 Hz, 1 H), 4.69 (d, *J* = 12.0 Hz, 1 H), 4.71 (d, *J* = 12.0 Hz, 1 H), 4.93 (m, 1 H), 4.98 (d, *J* = 10.7 Hz, 1 H), 7.14–7.18 (m, 4 H), 7.22–7.42 (m, 27 H), 7.70 (m, 4 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 27.6 (CH_2), 35.1 (d, $^1J_{P,C}$ = 71.8 Hz, CH), 68.3 (CH_2), 69.1 (CH_2), 69.4 (d, $^2J_{P,C}$ = 5.5 Hz, CH), 73.0 (CH_2), 73.2 (CH), 73.5 (CH_2), 73.8 (CH_2), 74.0 (CH), 75.2 (2× CH_2), 78.4 (d, $^3J_{P,C}$ = 7.3 Hz, CH), 78.5 (CH), 81.9 (CH), 101.3 (CH), 127.5–128.5 (Ar, complex), 131.57 (CH), 131.63 (CH), 137.4 (C), 137.9 (C), 138.2 (C), 138.4 (C), 138.8 (C), 168.2 (d, $^3J_{P,C}$ = 10.9 Hz, C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 31.3 (s, 1 P) ppm. IR (film): $\tilde{\nu}$ = 1736 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 981 (100) [M + Na]$^+$. HRMS (ESI$^+$): *m*/*z* calcd. for $C_{59}H_{59}NaO_{10}P$ [M + Na]$^+$ 981.3744; found 981.3744. $C_{59}H_{59}O_{10}P$ (959.09): calcd. C 73.89, H 6.20; found C 73.73, H 6.39.

5-*O*-Benzyl-1,2-dideoxy-2-diphenylphosphoryl-4-*O*-formyl-1-iodo-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-D-arabinitol (38): From **30** (47 mg, 0.049 mmol) in CH_2Cl_2 (1.2 mL) containing $PhI(OAc)_2$ (23.6 mg, 0.073 mmol) and I_2 (18.6 mg, 0.073 mmol) following the general procedure by stirring at reflux temperature for 40 min. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 6:4→1:1) gave **38** (36.9 mg, 0.034 mmol, 70%) as a yellowish oil: $[\alpha]_D$ = +31.4 (*c* = 0.35, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.16 (br. dd, *J* = 19.6, 10.7 Hz, 1 H), 3.23 (dd, *J* = 9.8, 7.6 Hz, 1 H), 3.28 (dd, *J* = 9.6, 2.7 Hz, 1 H), 3.36–3.40 (m, 2 H), 3.61–3.67 (m, 3 H), 3.73 (dd, *J* = 11.2, 3.9 Hz, 1 H), 3.81 (ddd, *J* = 12.1, 9.7, 2.8 Hz, 1 H), 3.87 (d, *J* = 2.5 Hz, 1 H), 4.20 (d, *J* = 7.6 Hz, 1 H), 4.23 (d, *J* = 12.0 Hz, 1 H), 4.36 (d, *J* = 12.0 Hz, 1 H), 4.45 (d, *J* = 11.7 Hz, 1 H), 4.49 (d, *J* = 11.0 Hz, 1 H), 4.50 (d, *J* = 12.0 Hz, 1 H), 4.55 (ddd, $^3J_{P,H}$ = 22.4, *J* = 9.8, 1.6 Hz, 1 H), 4.70 (s, 2 H), 4.90 (d, *J* = 10.7 Hz, 1 H), 5.64 (ddd, *J* = 9.5, 2.8, 2.8 Hz, 1 H), 7.14–7.41 (m, 30 H), 7.45–7.48 (m, 1 H), 7.65–7.69 (m, 2 H), 7.73–7.77 (m, 2 H), 8.17 (s, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 3.7 (d, $^2J_{P,C}$ = 2.8 Hz, CH_2), 45.9 (d, $^1J_{P,C}$ = 60.1 Hz, CH), 67.6 (CH_2), 67.9 (CH_2), 72.6 (CH_2), 72.79 (CH_2), 72.83 (CH), 73.56 (CH_2), 73.67 (CH), 74.1 (CH), 75.0 (CH_2), 75.3 (CH_2), 76.9 (d, $^2J_{P,C}$ = 4.2 Hz, CH), 78.8 (CH), 82.2 (CH), 103.1 (CH), 127.5–128.8 (Ar, complex), 130.4–133.1 (Ar, complex), 137.7 (C), 138.0 (C), 138.4 (C), 138.4 (C), 139.0 (C), 161.0 (CH) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 31.8 (s, 1 P) ppm. IR (film): $\tilde{\nu}$ = 1728 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 1109 (100) [M + Na]$^+$. HRMS (ESI$^+$): *m*/*z* calcd. for $C_{59}H_{60}INaO_{10}P$ [M + Na]$^+$ 1109.2867; found 1109.2867. $C_{59}H_{60}IO_{10}P$ (1087.00): calcd. C 65.19, H 5.56; found C 65.06, H 5.52.

General Procedure for the Dehydroiodination Reaction: To a solution of β-iodo-phosphorus compound (1 equiv.) in anhydrous benzene (25–35 mL) cooled to 9–10 °C, was added DBU (1.1–2.6 equiv.) and the mixture was stirred at this temperature for the specified time. The reaction mixture was then poured into a saturated aqueous solution of $NaHSO_4$ and extracted with EtOAc. The combined organic extracts were washed with brine, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by Chromatotron chromatography (hexanes/EtOAc).

3,5-Di-*O*-benzyl-1,2-dideoxy-2-diphenylphosphoryl-4-*O*-formyl-D-*erythro*-pent-1-enitol (39): From **31** (18.1 mg, 0.028 mmol) in anhydrous benzene (0.9 mL) containing DBU (10.5 μL, 0.07 mmol) following the general procedure by stirring at 9–10 °C for 30 min. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 1:1) gave **39** (13.4 mg, 0.025 mmol, 89%) as a colorless oil: $[\alpha]_D$ = +42.2 (*c* = 0.11, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.68 (dd, *J* = 11.0, 6.6 Hz, 1 H), 3.74 (dd, *J* = 11.0, 2.8 Hz, 1 H), 4.30 (d, *J* = 11.7 Hz, 1 H), 4.40 (d, *J* = 12.0 Hz, 1 H), 4.41 (d, *J* = 11.4 Hz, 1 H), 4.47 (d, *J* = 12.0 Hz, 1 H), 4.58 (dd, $^3J_{P,H}$ = 8.7, *J* = 6.2 Hz, 1 H), 5.45 (ddd, *J* = 6.3, 6.3, 2.8 Hz, 1 H), 5.76 (d, $^3J_{P,H}$ = 19.6 Hz, 1 H), 6.37 (d, $^3J_{P,H}$ = 41.3 Hz, 1 H), 7.09 (m, 2 H), 7.28 (m, 8 H), 7.46 (m, 4 H), 7.54 (m, 2 H), 7.69 (m, 2 H), 7.74 (m, 2 H), 7.84 (s, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 68.1 (CH_2), 72.0 (CH_2), 73.0 (CH_2), 74.3 (CH), 76.8 (d, $^2J_{P,C}$ = 12.7 Hz, CH), 127.56 (CH), 127.64 (2× CH), 127.7 (CH), 127.8 (2× CH), 128.2 (2× CH), 128.3 (2× CH), 128.5 (d, $^3J_{P,C}$ = 11.7 Hz, 2× CH), 128.6 (d, $^3J_{P,C}$ = 11.7 Hz, 2× CH), 130.7 (d, $^1J_{P,C}$ = 98.6 Hz, 2× C), 131.9 (d, $^2J_{P,C}$ = 6.4 Hz, 2× CH), 132.0 (d, $^2J_{P,C}$ = 6.4 Hz, 2× CH), 132.07 (d, $^4J_{P,C}$ = 3.2 Hz, CH), 132.11 (d, $^4J_{P,C}$ = 3.2 Hz, CH), 133.2 (d, $^2J_{P,C}$ = 8.5 Hz, CH_2), 137.3 (C), 137.9 (C), 142.1 (d, $^1J_{P,C}$ = 91.1 Hz, C), 160.6 (CH) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 33.0 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1725 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 527 (5) [M + H]$^+$, 257 (82), 201 (52), 91 (100). HRMS (EI, 70 eV): *m*/*z* calcd. for $C_{32}H_{32}O_5P$ [M + H]$^+$

527.1987; found 527.1998. $C_{32}H_{31}O_5P$ (526.57): calcd. C 72.99, H 5.93; found C 73.16, H 5.95.

3,5-Di-*O*-acetyl-1,2-dideoxy-2-diphenylphosphoryl-4-*O*-formyl-D-*erythro*-pent-1-enitol (40) and 3,5-Di-*O*-acetyl-1,2-dideoxy-2-diphenylphosphoryl-D-*erythro*-pent-1-enitol (41): From **32** (37.5 mg, 0.067 mmol) in anhydrous benzene (2.3 mL) containing DBU (11.1 μL, 0.074 mmol) following the general procedure by stirring at 9–10 °C for 20 min. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 45:55) gave **40** (21.6 mg, 0.05 mmol, 75%) and **41** (3.1 mg, 7.7×10^{-3} mmol, 12%).

Compound 40: Colorless oil; $[\alpha]_D$ = +61.4 (c = 0.22, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.65 (s, 3 H), 2.03 (s, 3 H), 4.30 (dd, J = 12.5, 6.2 Hz, 1 H), 4.37 (dd, J = 12.6, 2.5 Hz, 1 H), 5.61 (d, $^3J_{P,H}$ = 19.2 Hz, 1 H), 5.75 (dd, $^3J_{P,H}$ = 11.5, J = 6.8 Hz, 1 H), 5.87 (ddd, J = 6.5, 6.5, 2.5 Hz, 1 H), 6.22 (d, $^3J_{P,H}$ = 39.4 Hz, 1 H), 7.52 (m, 6 H), 7.66 (m, 2 H), 7.75 (m, 2 H), 8.04 (s, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 20.1 (CH_3), 20.7 (CH_3), 61.6 (CH_2), 71.6 (CH), 72.6 (d, $^2J_{P,C}$ = 11.7 Hz, CH), 128.6 (d, $^3J_{P,C}$ = 12.7 Hz, 2× CH), 128.7 (d, $^3J_{P,C}$ = 12.7 Hz, 2× CH), 130.7 (d, $^1J_{P,C}$ = 103.8 Hz, C), 130.9 (d, $^1J_{P,C}$ = 102.7 Hz, C), 131.7 (d, $^2J_{P,C}$ = 9.5 Hz, 2× CH), 131.9 (d, $^2J_{P,C}$ = 9.5 Hz, 2× CH), 132.2 (d, $^4J_{P,C}$ = 2.1 Hz, CH), 132.3 (d, $^4J_{P,C}$ = 3.2 Hz, CH), 134.0 (d, $^2J_{P,C}$ = 8.5 Hz, CH_2), 139.4 (d, $^1J_{P,C}$ = 93.3 Hz, C), 159.8 (CH), 169.2 (C), 170.5 (C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 29.2 (s, 1 P) ppm. IR (film): $\tilde{\nu}$ = 1731 cm^{-1}. MS (EI, 70 eV): m/z (%) = 431 (2) $[M + H]^+$, 283 (99), 257 (100), 201 (94). HRMS (EI, 70 eV): m/z calcd. for $C_{22}H_{24}O_7P$ $[M + H]^+$ 431.1260; found 431.1252. $C_{22}H_{23}O_7P$ (430.39): calcd. C 61.40, H 5.39; found C 61.34, H 5.57.

Compound 41: Colorless oil; $[\alpha]_D$ = +68.6 (c = 0.14, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.60 (s, 3 H), 2.07 (s, 3 H), 4.11 (dd, J = 13.0, 6.6 Hz, 1 H), 4.19 (m, 2 H), 5.53 (d, $^3J_{P,H}$ = 19.6 Hz, 1 H), 5.64 (dd, $^3J_{P,H}$ = 13.8, J = 5.6 Hz, 1 H), 6.24 (d, $^3J_{P,H}$ = 40.8 Hz, 1 H), 7.48–7.61 (m, 6 H), 7.66 (m, 2 H), 7.76 (m, 2 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 20.3 (CH_3), 20.9 (CH_3), 65.1 (CH_2), 70.3 (CH), 76.1 (d, $^2J_{P,C}$ = 10.0 Hz, CH), 128.7 (d, $^3J_{P,C}$ = 12.7 Hz, 2× CH), 128.7 (d, $^3J_{P,C}$ = 12.7 Hz, 2× CH), 129.85 (d, $^1J_{P,C}$ = 106.2 Hz, C), 129.90 (d, $^1J_{P,C}$ = 106.2 Hz, C), 131.7 (d, $^2J_{P,C}$ = 10.0 Hz, 2× CH), 132.1 (d, $^2J_{P,C}$ = 10.0 Hz, 2× CH), 132.4 (d, $^4J_{P,C}$ = 2.7 Hz, CH), 132.6 (d, $^4J_{P,C}$ = 2.7 Hz, CH), 135.0 (d, $^2J_{P,C}$ = 10.0 Hz, CH_2), 140.2 (d, $^1J_{P,C}$ = 90.8 Hz, C), 169.5 (C), 170.9 (C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 33.3 (s, 1 P) ppm. IR (film): $\tilde{\nu}$ = 3232, 1738 cm^{-1}. MS (EI, 70 eV): m/z (%) = 403 (14) $[M + H]^+$, 300 (99), 257 (100), 201 (100). HRMS (EI, 70 eV): m/z calcd. for $C_{21}H_{24}O_6P$ $[M + H]^+$ 403.1311; found 403.1311. $C_{21}H_{23}O_6P$ (402.38): calcd. C 62.67, H 5.76; found C 62.42, H 6.05.

3,5-Di-*O*-acetyl-1,2-dideoxy-2-diphenylphosphoryl-4-*O*-formyl-D-*erythro*-pent-1-enitol (40) from (33): From **33** (1.234 g, 2.21 mmol) in anhydrous benzene (75 mL) containing DBU (0.362 mL, 2.43 mmol) following the general procedure by stirring at 9–10 °C for 1.75 h. Column chromatography of the reaction residue (hexanes/EtOAc, 2:8) gave **40** (810 mg, 1.88 mmol, 85%) as a colorless oil with properties identical to that prepared previously.

3,5-Di-*O*-benzyl-1,2-dideoxy-2-diphenylphosphoryl-4-*O*-formyl-D-*threo*-pent-1-enitol (42): From **34** (15.3 mg, 0.023 mmol) in anhydrous benzene (0.8 mL) containing DBU (8.9 μL, 0.06 mmol) following the general procedure by stirring at 9–10 °C for 1 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 6:4) gave **42** (11 mg, 0.021 mmol, 91%) as a colorless oil: $[\alpha]_D$ = –27.3 (c = 0.07, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 3.56 (dd, J = 10.6, 4.9 Hz, 1 H), 3.68 (dd, J = 10.6, 7.1 Hz, 1 H), 4.12 (d, J = 11.7 Hz, 1 H), 4.41 (s, 2 H), 4.45 (d, J = 11.7 Hz, 1 H), 4.55 (dd, $^3J_{P,H}$ = 7.1, J = 3.0 Hz, 1 H), 5.46 (ddd, J = 7.3, 4.7, 3.0 Hz, 1 H), 5.70 (d, $^3J_{P,H}$ = 19.9 Hz, 1 H), 6.37 (d, $^3J_{P,H}$ = 41.6 Hz, 1 H), 7.02 (m, 2 H), 7.27 (m, 8 H), 7.46 (m, 2 H), 7.53 (m, 3 H), 7.61 (m, 1 H), 7.70 (m, 2 H), 7.76 (m, 2 H), 8.05 (s, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 68.7 (CH_2), 71.5 (CH_2), 72.9 (CH_2), 73.5 (CH), 75.4 (d, $^2J_{P,C}$ = 14.8 Hz, CH), 127.6 (CH), 127.7 (2× CH), 127.9 (CH), 128.1 (2× CH), 128.3 (4× CH), 128.6 (d, $^3J_{P,C}$ = 12.7 Hz, 2× CH), 128.7 (d, $^3J_{P,C}$ = 11.7 Hz, 2× CH), 130.4 (d, $^1J_{P,C}$ = 101.7 Hz, C), 130.5 (d, $^1J_{P,C}$ = 104.9 Hz, C), 132.0 (d, $^2J_{P,C}$ = 10.6 Hz, 2× CH), 132.1 (d, $^2J_{P,C}$ = 10.6 Hz, 2× CH), 132.2 (CH_2), 132.3 (d, $^4J_{P,C}$ = 3.2 Hz, 2× CH), 137.0 (C), 137.8 (C), 141.0 (d, $^1J_{P,C}$ = 91.1 Hz, C), 160.7 (CH) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 29.7 (s, 1 P) ppm. IR (film): $\tilde{\nu}$ = 1731 cm^{-1}. MS (EI, 70 eV): m/z (%) = 527 (< 1) $[M + H]^+$, 257 (35), 201 (25), 91 (100). HRMS (EI, 70 eV): m/z calcd. for $C_{32}H_{32}O_5P$ $[M + H]^+$ 527.1987; found 527.1974. $C_{32}H_{31}O_5P$ (526.57): calcd. C 72.99, H 5.93; found C 73.03, H 5.93.

3,5-Di-*O*-acetyl-1,2-dideoxy-2-diphenylphosphoryl-4-*O*-formyl-D-*threo*-pent-1-enitol (43): From **35** (93.2 mg, 0.167 mmol) in anhydrous benzene (5.6 mL) containing DBU (27.5 μL, 0.184 mmol) following the general procedure by stirring at 9–10 °C for 1 h. The residue was purified by Chromatotron chromatography (hexanes/EtOAc, 4:6) to give **43** (70 mg, 0.163 mmol, 97%): colorless oil; $[\alpha]_D$ = –42.0 (c = 0.32, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.69 (s, 3 H), 2.04 (s, 3 H), 4.21 (dd, J = 12.2, 5.8 Hz, 1 H), 4.39 (dd, J = 12.2, 4.0 Hz, 1 H), 5.58 (d, $^3J_{P,H}$ = 19.3 Hz, 1 H), 5.82 (dd, $^3J_{P,H}$ = 11.4, J = 5.6 Hz, 1 H), 5.89 (ddd, J = 5.5, 5.5, 4.1 Hz, 1 H), 6.22 (dd, $^3J_{P,H}$ = 39.3, J = 0.7 Hz, 1 H), 7.50 (m, 4 H), 7.58 (m, 2 H), 7.70 (m, 4 H), 8.07 (s, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 20.1 (CH_3), 20.6 (CH_3), 62.3 (CH_2), 71.7 (CH), 73.3 (d, $^2J_{P,C}$ = 11.7 Hz, CH), 128.62 (d, $^3J_{P,C}$ = 11.7 Hz, 2× CH), 128.64 (d, $^3J_{P,C}$ = 12.7 Hz, 2× CH), 130.78 (d, $^1J_{P,C}$ = 104.9 Hz, C), 130.83 (d, $^1J_{P,C}$ = 104.9 Hz, C), 131.7 (d, $^2J_{P,C}$ = 9.5 Hz, 2× CH), 131.9 (d, $^2J_{P,C}$ = 9.5 Hz, 2× CH), 132.2 (d, $^4J_{P,C}$ = 2.1 Hz, CH), 132.3 (d, $^4J_{P,C}$ = 3.2 Hz, CH), 133.8 (d, $^2J_{P,C}$ = 7.4 Hz, CH_2), 139.4 (d, $^1J_{P,C}$ = 93.3 Hz, C), 160.0 (CH), 169.4 (C), 170.2 (C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 29.4 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1744, 1227 cm^{-1}. MS (ESI^+): m/z (%) = 453 (100), 425 (66) $[M + Na]^+$. HRMS (ESI^+): m/z calcd. for $C_{22}H_{23}NaO_7P$ $[M + Na]^+$ 453.1079; found 453.1071. $C_{22}H_{23}O_7P$ (430.39): calcd. C 61.40, H 5.39; found C 61.49, H 5.58.

5-*O*-Benzyl-1,2-dideoxy-2-diphenylphosphoryl-4-*O*-formyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosy)-D-*erythro*-pent-1-enitol (44) and 5-*O*-Benzyl-1,2-dideoxy-2-diphenylphosphoryl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-D-*erythro*-pent-1-enitol (45): From **36** (38 mg, 0.035 mmol) in anhydrous benzene (1.2 mL) containing DBU (7.85 μL, 0.052 mmol) following the general procedure by stirring at 9–10 °C for 12 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 6:4) gave **44** (28.2 mg, 0.029 mmol, 83%) and **45** (4.2 mg, 4.5×10^{-3} mmol, 13%) as colorless oils.

Compound 44: $[\alpha]_D$ +2.8 (c = 0.18, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 3.37–3.46 (m, 3 H), 3.54 (d, J = 7.6 Hz, 1 H), 3.56 (m, 1 H), 3.69 (d, J = 4.7 Hz, 1 H), 3.69 (d, J = 4.7 Hz, 1 H), 3.87 (d, J = 2.8 Hz, 1 H), 4.27 (d, J = 12.0 Hz, 1 H), 4.37 (d, J = 12.0 Hz, 1 H), 4.38 (d, J = 7.6 Hz, 1 H), 4.42 (s, 2 H), 4.57 (d, J = 11.4 Hz, 1 H), 4.64 (d, J = 11.0 Hz, 1 H), 4.68 (d, J = 11.7 Hz, 1 H), 4.72 (d, J = 11.7 Hz, 1 H), 4.73 (d, J = 11.0 Hz, 1 H), 4.79 (dd, $^3J_{P,H}$ = 9.6, J = 5.8 Hz, 1 H), 4.93 (d, J = 11.4 Hz, 1 H), 5.54 (ddd, J = 4.8, 4.8, 4.8 Hz, 1 H), 5.59 (d, $^3J_{P,H}$ = 20.2 Hz, 1 H), 6.32 (d, $^3J_{P,H}$ = 40.7 Hz, 1 H), 7.19 (m, 2 H), 7.22–7.34 (m, 27 H), 7.38 (m, 1 H), 7.42 (m, 1 H), 7.67 (m, 4 H), 7.86 (s, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 67.6 (CH_2), 68.4 (CH_2), 72.7 (CH_2), 73.0

(CH_2), 73.3 (CH), 73.5 (CH_2), 73.9 (CH), 74.5 (CH), 74.9 (CH_2), 75.0 (CH_2), 78.0 (d, $^2J_{P,C}$ = 14.8 Hz, CH), 79.1 (CH), 82.1 (CH), 104.4 (CH), 127.4–128.5 (Ar, complex), 131.1–131.4 (Ar, complex), 134.0 (d, $^2J_{P,C}$ = 8.5 Hz, CH_2), 137.8 (C), 138.0 (C), 138.4 (C), 138.6 (C), 138.8 (C), 141.0 (d, $^1J_{P,C}$ = 92.2 Hz, C), 160.8 (CH) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 30.5 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1727, 1099 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 958 (< 1) $[M]^+$, 555 (3), 91 (100). HRMS (EI, 70 eV): *m*/*z* calcd. for $C_{59}H_{59}O_{10}P$ $[M]^+$ 958.3846; found 958.3842. $C_{59}H_{59}O_{10}P$ (959.09): calcd. C 73.89, H 6.20; found C 73.80, H 6.22.

Compound 45: $[\alpha]_D$ +20.6 (*c* = 0.32, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.36 (dd, *J* = 9.8, 3.2 Hz, 1 H), 3.38–3.41 (m, 2 H), 3.44 (dd, *J* = 9.8, 7.6 Hz, 1 H), 3.53 (dd, *J* = 10.1, 4.1 Hz, 1 H), 3.57–3.59 (m, 1 H), 3.62 (dd, *J* = 10.1, 5.0 Hz, 1 H), 3.85 (d, *J* = 2.8 Hz, 1 H), 4.03 (ddd, *J* = 6.5, 4.6, 4.4 Hz, 1 H), 4.32 (d, *J* = 7.6 Hz, 1 H), 4.39 (d, *J* = 12.0 Hz, 1 H), 4.43–4.47 (m, 4 H), 4.57 (d, *J* = 11.0 Hz, 1 H), 4.58 (d, *J* = 11.0 Hz, 1 H), 4.66 (d, *J* = 11.7 Hz, 1 H), 4.69 (dd, $^3J_{P,H}$ = 12.9, *J* = 6.6 Hz, 1 H), 4.70 (d, *J* = 11.7 Hz, 1 H), 4.94 (d, *J* = 11.4 Hz, 1 H), 5.42 (d, $^3J_{P,H}$ = 20.2 Hz, 1 H), 6.23 (d, $^3J_{P,H}$ = 41.9 Hz, 1 H), 7.19–7.38 (m, 30 H), 7.44–7.47 (m, 1 H), 7.63–7.68 (m, 2 H), 7.70–7.74 (m, 2 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 68.5 (CH_2), 70.7 (CH_2), 72.3 (CH), 73.03 (CH_2), 73.06 (CH), 73.08 (CH_2), 73.4 (CH_2), 74.0 (CH), 74.8 (CH_2), 74.9 (CH_2), 79.1 (CH), 81.1 (d, $^2J_{P,C}$ = 10.6 Hz, CH), 82.1 (CH), 103.9 (CH), 127.3–128.5 (Ar, complex), 130.9 (d, $^1J_{P,C}$ = 105.9 Hz, C), 131.2 (d, $^1J_{P,C}$ = 104.9 Hz, C), 131.8–132.3 (Ar, complex), 134.3 (d, $^2J_{P,C}$ = 8.5 Hz, CH_2), 137.9 (C), 138.46 (C), 138.49 (C), 138.6 (C), 138.9 (C), 141.8 (d, $^1J_{P,C}$ = 91.1 Hz, C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 33.9 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3291, 1095 cm^{-1}. MS (ESI^+): *m*/*z* (%) = 953 (100) $[M + Na]^+$. HRMS (ESI^+): *m*/*z* calcd. for $C_{58}H_{59}NaO_9P$ $[M + Na]^+$ 953.3794; found 953.3794. $C_{58}H_{59}O_9P$ (931.07): calcd. C 74.82, H 6.39; found C 74.91, H 6.42.

5-*O*-Benzyl-1,2-dideoxy-2-diphenylphosphoryl-4-*O*-formyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosy)-D-*erythro*-pent-1-enitol (44) and 5-*O*-Benzyl-1,2-dideoxy-2-diphenylphosphoryl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-D-*erythro*-pent-1-enitol (45) from 38: From **38** (25.6 mg, 0.024 mmol) in anhydrous benzene (0.8 mL) containing DBU (3.9 μL, 0.026 mmol) following the general procedure by stirring at 9–10 °C for 15 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 6:4) gave **44** (13.6 mg, 0.014 mmol, 60%) and **45** (7 mg, 7.5×10^{-3} mmol, 32%).

General Procedure for the DIBAL-H Mediated Reduction of Lactones: To a solution of lactone (1 equiv.) in anhydrous toluene (33 mL), was added dropwise DIBAL-H (1 M in toluene, 4 mL, 4 equiv.) at –78 °C under nitrogen and the mixture was stirred for the specified time. EtOH (11 mL) was added at this temperature and the solution was allowed to warm to 0 °C. A saturated solution of NH_4Cl was then added and the mixture was extracted with EtOAc. The organic layer was washed with brine, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography (hexanes/EtOAc).

5-*O*-(*tert*-Butyldiphenylsilyl)-2,3-dideoxy-3-diethoxyphosphoryl-D-ribofuranose (46): From **15** (118 mg, 0.24 mmol) containing a 1 M solution of DIBAL-H (0.96 mL, 0.96 mmol) at –78 °C 1.3 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 1:1) gave **46** (83 mg, 0.168 mmol, α/β, 1:1, 70%) as a colorless oil: $[\alpha]_D$ = +18.2 (*c* = 0.6, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06 (s, 9 H), 1.09 (s, 9 H), 1.25 (t, *J* = 7.2 Hz, 6 H), 1.29 (t, *J* = 7.2 Hz, 3 H), 1.35 (t, *J* = 7.0 Hz, 3 H), 2.13–2.24 (m, 3 H), 2.42 (dddd, *J* = 29.2, 13.5, 11.1, 5.2 Hz, 1 H), 2.68 (dddd, *J* = 15.7, 11.2, 4.2, 2.4 Hz, 1 H), 2.83–2.93 (m, 1 H), 3.60–3.67 (m, 2 H), 3.74 (dd, *J* = 10.9, 4.2 Hz, 1 H), 3.91 (dd, *J* = 11.1, 2.1 Hz, 1 H), 4.00–4.21 (m, 8 H), 4.42 (dddd, *J* = 14.2, 8.6, 2.4, 2.4 Hz, 1 H), 4.54 (dddd, *J* = 17.8, 4.0, 4.0, 4.0 Hz, 1 H), 5.47 (d, *J* = 2.9 Hz, 1 H), 5.50 (d, *J* = 5.0 Hz, 1 H), 7.33–7.47 (m, 12 H), 7.64–7.72 (m, 8 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): complex resonance pattern. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 30.3 (s, 1 P), 34.2 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3385, 1213, 783, 746 cm^{-1}. MS (ESI^+): *m*/*z* (%) = 515 (100) $[M + Na]^+$. HRMS (ESI^+): *m*/*z* calcd. for $C_{25}H_{37}NaO_6PSi$ $[M + Na]^+$ 515.1995; found 515.1992. $C_{25}H_{37}O_6PSi$ (492.62): calcd. C 60.95, H 7.57; found C 60.86, H 7.80.

2,3-Dideoxy-3-diethoxyphosphoryl-5,6-*O*-isopropylidene-D-*lyxo*-hexofuranose (47): From **17** (60.5 mg, 0.188 mmol) containing a 1 M solution of DIBAL-H (0.75 mL, 0.75 mmol) following the general procedure by stirring at –78 °C for 2.5 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 2:8) gave **47** (37 mg, 0.114 mmol, 2:1, 61%) as a colorless oil: $[\alpha]_D$ = –25.4 (*c* = 0.67, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) and ^{3}C NMR (125.7 MHz, $CDCl_3$) exhibit complex resonance patterns. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 29.0 (s, 1 P), 33.4 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3399, 2992 cm^{-1}. MS (ESI^+): *m*/*z* (%) = 347 (100) $[M + Na]^+$. HRMS (ESI^+): *m*/*z* calcd. for $C_{13}H_{25}NaO_7P$ $[M + Na]^+$ 347.1236; found 347.1235. $C_{13}H_{25}O_7P$ (324.31): calcd. C 48.15, H 7.77; found C 48.10, H 7.66.

2,3-Dideoxy-3-diethoxyphosphoryl-5,6-*O*-isopropylidene-D-*ribo*-hexofuranose (48): From **18** (68 mg, 0.211 mmol) containing a 1 M solution of DIBAL-H (0.84 mL, 0.84 mmol) following the general procedure by stirring at –78 °C for 2.5 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 2:8) gave **48** (44 mg, 0.136 mmol, 1:1, 64%) as a colorless oil: Crystalline solid; m.p. 80.2–81.9 °C (*n*-hexane/EtOAc); $[\alpha]_D$ +18.7 (*c* = 0.75, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125.7 MHz, $CDCl_3$) exhibit complex resonance patterns. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 29.8 (s, 1 P), 33.9 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3341, 2992, 1026 cm^{-1}. MS (ESI^+): *m*/*z* (%) = 347 (100) $[M + Na]^+$. HRMS (ESI^+): *m*/*z* calcd. for $C_{13}H_{25}NaO_7P$ $[M + Na]^+$ 347.1236; found 347.1234. $C_{13}H_{25}O_7P$ (324.31): calcd. C 48.15, H 7.77; found C 48.35, H 7.47.

4,6-Di-*O*-benzyl-2,3-dideoxy-3-diethoxyphosphoryl-D-*arabino*-hexopyranose (49) and 4,6-Di-*O*-benzyl-2,3-dideoxy-3-diethoxyphosphoryl-D-*ribo*-hexopyranose (50): From **20** (378 mg, 0.817 mmol) containing DIBAL-H (1.0 M in toluene, 3.27 mL, 3.27 mmol) following the general procedure by stirring at –78 °C for 1 h. The residue was purified by column chromatography (hexanes/EtOAc, 1:1→3:7) to give **49** (185 mg, 0.398 mmol, 1.6:1, 49%) and **50** (17.5 mg, 0.038 mmol, 2.7:1, 4.6%) both as colorless oils.

Compound 49: ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (125.7 MHz, $CDCl_3$) exhibit complex resonance patterns. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 29.9 (s, 1 P), 32.7 (s, 1 P) ppm. IR (CCl_4): $\tilde{\nu}$ = 3316, 2985, 1026 cm^{-1}. MS (ESI^+): *m*/*z* (%) = 487 (100) $[M + Na]^+$. HRMS (ESI^+): *m*/*z* calcd. for $C_{24}H_{33}NaO_7P$ $[M + Na]^+$ 487.1862; found 487.1868. $C_{24}H_{33}O_7P$ (464.50): calcd. C 62.06, H 7.16; found C 62.19, H 6.94.

Compound 50: ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (125.7 MHz, $CDCl_3$) exhibit complex resonance patterns. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 28.3 (s, 1 P), 29.9 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3385, 3017, 1229 cm^{-1}. MS (ESI^+): *m*/*z* (%) = 487 (100) $[M + Na]^+$. HRMS (ESI^+): *m*/*z* calcd. for $C_{24}H_{33}NaO_7P$ $[M + Na]^+$ 487.1862; found 487.1861. $C_{24}H_{33}O_7P$ (464.50): calcd. C 62.06, H 7.16; found C 61.90, H 7.19.

4,6-Di-*O*-benzyl-2,3-dideoxy-3-diethoxyphosphoryl-D-*xylo*-hexopyranose (51): From **22** (101.3 mg, 0.22 mmol) containing a 1 M solution of DIBAL-H (0.88 mL, 0.88 mmol) following the general procedure by stirring at –78 °C. The residue was purified by Cromatotron chromatography (hexanes/EtOAc, 4:6), to give **51** (78.5 mg, 0.17 mmol, α/β, 3:1, 77%) as a colorless oil: $[\alpha]_D$ = –3.9 (*c* = 0.59, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ (major isomer) = 1.26 (t, *J* = 7.0 Hz, 3 H), 1.33 (t, *J* = 7.0 Hz, 3 H), 1.87–1.93 (m, 1 H), 2.37–2.53 (m, 2 H), 3.57 (dd, *J* = 9.3, 5.6 Hz, 1 H), 3.65 (dd, *J* = 9.3, 7.7 Hz, 1 H), 3.83 (d, *J* = 5.8 Hz, 1 H), 4.00–4.19 (m, 4 H), 4.37 (ddd, *J* = 7.5, 5.8, 1.3 Hz, 1 H), 4.44 (d, *J* = 12.2 Hz, 1 H), 4.50 (d, *J* = 12.7 Hz, 1 H), 4.58 (dd, *J* = 12.5, 12.5 Hz, 2 H), 5.19 (d, *J* = 3.7 Hz, 1 H), 7.24–7.33 (m, 10 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$) exhibits complex resonance pattern. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 28.9 (s, 1 P), 32.5 (s, 1 P) ppm. IR ($CHCl_3$): ṽ = 3340, 3016, 1216, 1047 cm^{-1}. MS (ESI^+): *m*/*z* (%) = 487 (100) $[M + Na]^+$. HRMS (ESI^+): *m*/*z* calcd. for $C_{24}H_{33}NaO_7P$ $[M + Na]^+$ 487.1862; found 487.1863. $C_{24}H_{33}O_7P$ (464.50): calcd. C 62.06, H 7.16; found C 62.37, H 7.09.

4-*O*-(*tert*-Butyldiphenylsilyl)-1,2-dideoxy-2-diethoxyphosphoryl-3-*O*-formyl-1-iodo-D-erythritol (52): From **46** (81 mg, 0.164 mmol) containing $PhI(OAc)_2$ (58.2 mg, 0.18 mmol) and I_2 (46 mg, 0.18 mmol) following the general procedure by stirring at room temperature for 0.75 h under irradiation with a 80 W tungsten-filament lamp. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 1:1) gave **52** (96.4 mg, 0.155 mmol, 95%) as an oil: $[\alpha]_D$ = –12.0 (*c* = 0.65, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.05 (s, 9 H), 1.26 (t, *J* = 7.1 Hz, 3 H), 1.28 (t, *J* = 7.1 Hz, 3 H), 2.68 (ddd, $^2J_{P,H}$ = 22.7, *J* = 10.4, 5.7 Hz, 1 H), 3.38 (ddd, $^3J_{P,H}$ = 6.3, *J* = 10.7, 10.7 Hz, 1 H), 3.49 (ddd, $^3J_{P,H}$ = 21.0, *J* = 10.7, 4.6 Hz, 1 H), 3.91 (dd, *J* = 11.4, 4.7 Hz, 1 H), 3.95 (dd, *J* = 11.4, 6.3 Hz, 1 H), 4.05–4.12 (m, 4 H), 5.43 (ddd, $^3J_{P,H}$ = 19.0, *J* = 5.4, 5.2 Hz, 1 H), 7.36–7.44 (m, 6 H), 7.63–7.67 (m, 4 H), 7.99 (s, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –3.8 (d, $^2J_{P,C}$ = 3.2 Hz, CH_2), 16.28 (d, $^3J_{P,C}$ = 5.3 Hz, CH_3), 16.33 (d, $^3J_{P,C}$ = 5.3 Hz, CH_3), 19.1 (C), 26.8 (3× CH_3), 39.7 (d, $^1J_{P,C}$ = 138.8 Hz, CH), 62.4 (d, $^2J_{P,C}$ = 6.4 Hz, CH_2), 62.5 (d, $^2J_{P,C}$ = 7.4 Hz, CH_2), 62.9 (d, $^3J_{P,C}$ = 6.4 Hz, CH_2), 73.0 (CH), 127.7 (4× CH), 129.8 (CH), 129.9 (CH), 132.8 (2× C), 135.5 (2× CH), 135.6 (2× CH), 160.0 (CH) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 24.3 (s, 1 P) ppm. IR ($CHCl_3$): ṽ = 3006, 1729, 1026 cm^{-1}. MS (ESI^+): *m*/*z* (%) = 641 (100) $[M + Na]^+$. HRMS (ESI^+): *m*/*z* calcd. for $C_{25}H_{36}INaO_6PSi$ $[M + Na]^+$ 641.0961; found 641.0964. $C_{25}H_{36}IO_6PSi$ (618.52): calcd. C 48.55, H 5.87; found C 48.58, H 5.87.

1,2-Dideoxy-2-diethoxyphosphoryl-3-*O*-formyl-1-iodo-4,5-*O*-isopropylidene-D-lyxitol (53): From **47** (30.8 mg, 0.095 mmol) containing $PhI(OAc)_2$ (33.6 mg, 0.1 mmol) and I_2 (26.5 mg, 0.1 mmol) following the general procedure by stirring at reflux temperature for 1.5 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 1:1) gave **53** (29.9 mg, 0.066 mmol, 70%) as an unstable oil, dehydroiodination occurs easily and therefore the compound could not be fully characterized: ^1H NMR (500 MHz, $CDCl_3$ note: The data of hydrogens at C1–C5 shown below have been calculated by iterative simulation using program DAISY as implemented in Bruker Topspin v. 2.1): δ = 1.345 (s, 3 H), 1.345 (t, *J* = 7.3 Hz, 3 H), 1.352 (t, *J* = 6.9 Hz, 3 H), 1.43 (s, 3 H), 2.54 (dddd, $^2J_{P,H}$ = 23.6, *J* = 5.7, 5.2, 4.7 Hz, 1 H), 3.47 (ddd, $^3J_{P,H}$ = 17.2, *J* = 10.8, 4.7 Hz, 1 H), 3.48 (ddd, $^3J_{P,H}$ = 14.9, *J* = 10.8, 5.2 Hz, 1 H), 3.77 (dd, *J* = 8.9, 5.5 Hz, 1 H), 4.11 (dd, *J* = 8.9, 6.7 Hz, 1 H), 4.14–4.20 (m, 4 H), 4.66 (ddd, *J* = 6.7, 5.5, 5.2 Hz, 1 H), 5.44 (ddd, $^3J_{P,H}$ = 10.5, *J* = 5.7, 5.2 Hz, 1 H), 8.16 (s, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –4.1 (d, $^2J_{P,C}$ = 3.5 Hz, CH_2), 16.3 (d, $^3J_{P,C}$ = 6.4 Hz, CH_3), 16.4 (d, $^3J_{P,C}$ = 6.4 Hz, CH_3), 25.3 (CH_3), 26.2 (CH_3), 41.0 (d, $^1J_{P,C}$ = 137.0 Hz, CH), 62.7–62.8 (m, 2× CH_2), 65.6 (CH_2), 71.5 (CH), 75.3 (d, $^3J_{P,C}$ = 8.5 Hz, CH), 110.0 (C), 160.0 (CH) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 23.9 (s, 1 P) ppm. MS (ESI^+): *m*/*z* (%) = 473 (100) $[M + Na]^+$, 345 (31) $[M + Na – HI]^+$. HRMS (ESI^+): *m*/*z* calcd. for $C_{13}H_{24}INaO_7P$ $[M + Na]^+$ 473.0202; found 473.0199; calcd. for $C_{13}H_{23}NaO_7P$ $[M + Na]^+$ 345.1079; found 345.1092.

3,5-Di-*O*-benzyl-1,2-dideoxy-2-diethoxyphosphoryl-4-*O*-formyl-1-iodo-D-arabinitol (55): From **49** (185 mg, 0.398 mmol) containing $PhI(OAc)_2$ (141 mg, 0.438 mmol) and I_2 (111 mg, 0.438 mmol) following the general procedure by stirring at room temperature for 1 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 1:1) gave **55** (193.3 mg, 0.327 mmol, 82%) as an oil: $[\alpha]_D$ = +21.0 (*c* = 1.03, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.25 (t, *J* = 7.2 Hz, 3 H), 1.28 (t, *J* = 7.2 Hz, 3 H), 2.44 (dddd, $^2J_{P,H}$ = 23.8, *J* = 6.1, 5.0, 5.0 Hz, 1 H), 3.47 (ddd, $^3J_{P,H}$ = 11.9, *J* = 10.4, 6.1 Hz, 1 H), 3.50 (ddd, $^3J_{P,H}$ = 20.2, *J* = 10.4, 4.7 Hz, 1 H), 3.69 (dd, *J* = 11.4, 5.8 Hz, 1 H), 3.75 (dd, *J* = 10.9, 3.4 Hz, 1 H), 4.07–4.21 (m, 4 H), 4.26 (ddd, $^3J_{P,H}$ = 13.4, *J* = 6.2, 4.5 Hz, 1 H), 4.43 (d, *J* = 12.2 Hz, 1 H), 4.50 (d, *J* = 11.9 Hz, 1 H), 4.64 (d, *J* = 10.9 Hz, 1 H), 4.72 (d, *J* = 11.1 Hz, 1 H), 5.47 (ddd, *J* = 5.4, 5.4, 3.4 Hz, 1 H), 7.26–7.34 (m, 10 H), 8.08 (s, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –2.8 (d, $^2J_{P,C}$ = 2.8 Hz, CH_2), 16.2 (d, $^3J_{P,C}$ = 5.7 Hz, CH_3), 16.3 (d, $^3J_{P,C}$ = 5.7 Hz, CH_3), 41.4 (d, $^1J_{P,C}$ = 137.0 Hz, CH), 62.3 (m, 2× CH_2), 67.8 (CH_2), 73.0 (d, $^3J_{P,C}$ = 7.8 Hz, CH), 73.1 (CH_2), 74.0 (CH_2), 76.2 (CH), 127.58 (2× CH), 127.60 (CH), 127.68 (CH), 127.72 (2× CH), 128.22 (2× CH), 128.25 (2× CH), 137.6 (2× C), 160.0 (CH) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 25.7 (s, 1 P) ppm. IR (CCl_4): ṽ = 2981, 1735, 1026 cm^{-1}. MS (ESI^+): *m*/*z* (%) = 613 (100) $[M + Na]^+$. HRMS (ESI^+): *m*/*z* calcd. for $C_{24}H_{32}INaO_7P$ $[M + Na]^+$ 613.0828; found 613.0829. $C_{24}H_{32}IO_7P$ (590.39): calcd. C 48.83, H 5.46; found C 48.73, H 5.64.

3,5-Di-*O*-benzyl-1,2-dideoxy-2-diethoxyphosphoryl-4-*O*-formyl-1-iodo-D-ribitol (56): From **50** (17.5 mg, 0.038 mmol) containing $PhI(OAc)_2$ (13.4 mg, 0.041 mmol) and I_2 (10.5 mg, 0.041 mmol) following the general procedure by stirring at room temperature for 1 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 1:1) gave **56** (13.1 mg, 0.022 mmol, 58%) as an oil: $[\alpha]_D$ = –19.5 (*c* = 0.21, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.16 (t, *J* = 7.1 Hz, 3 H), 1.25 (t, *J* = 7.1 Hz, 3 H), 2.49 (dddd, $^2J_{P,H}$ = 23.1, *J* = 11.2, 3.5, 2.2 Hz, 1 H), 3.28 (ddd, $^3J_{P,H}$ = 5.7, *J* = 10.9, 10.9 Hz, 1 H), 3.66 (ddd, $^3J_{P,H}$ = 9.1, *J* = 10.4, 3.5 Hz, 1 H), 3.78 (dd, *J* = 11.0, 4.4 Hz, 1 H), 3.86 (dd, *J* = 11.0, 2.8 Hz, 1 H), 3.89–4.09 (m, 4 H), 4.36 (ddd, $^3J_{P,H}$ = 29.5, *J* = 8.5, 2.4 Hz, 1 H), 4.51 (d, *J* = 12.0 Hz, 1 H), 4.60 (d, *J* = 12.0 Hz, 1 H), 4.69 (s, 2 H), 5.54 (ddd, *J* = 7.8, 3.8, 3.8 Hz, 1 H), 7.27–7.33 (m, 10 H), 8.11 (s, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 2.6 (CH_2), 16.2 (d, $^3J_{P,C}$ = 6.4 Hz, CH_3), 16.3 (d, $^3J_{P,C}$ = 6.4 Hz, CH_3), 43.3 (d, $^1J_{P,C}$ = 131.4 Hz, CH), 61.9 (d, $^2J_{P,C}$ = 6.4 Hz, CH_2), 62.2 (d, $^2J_{P,C}$ = 6.4 Hz, CH_2), 68.2 (CH_2), 73.4 (CH_2), 73.7 (CH), 75.5 (CH_2), 77.2 (d, $^2J_{P,C}$ = 5.5 Hz, CH), 127.8 (3× CH), 127.97 (CH), 128.1 (2× CH), 128.39 (2× CH), 128.43 (2× CH), 137.6 (C), 137.7 (C), 160.6 (CH) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 21.9 (s, 1 P) ppm. IR ($CHCl_3$): ṽ = 3018, 1726, 1026 cm^{-1}. MS (ESI^+): *m*/*z* (%) = 613 (100) $[M + Na]^+$. HRMS (ESI^+): *m*/*z* calcd. for $C_{24}H_{32}INaO_7P$ $[M + Na]^+$ 613.0828; found 613.0834. $C_{24}H_{32}IO_7P$ (590.39): calcd. C 48.83, H 5.46; found C 48.66, H 5.59.

3,5-Di-*O*-benzyl-1,2-dideoxy-2-diethoxyphosphoryl-4-*O*-formyl-1-iodo-D-xylitol (57): From **51** (76.6 mg, 0.165 mmol) containing $PhI(OAc)_2$ (58.4 mg, 0.18 mmol) and I_2 (46.1 mg, 0.18 mmol) following the general procedure by stirring at room temperature for

1.5 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 1:1), gave **57** (71.2 mg, 0.121 mmol, 73%) as an oil: $[a]_D$ = +15.4 (*c* = 0.65, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.07 (t, *J* = 7.0 Hz, 3 H), 1.22 (t, *J* = 7.2 Hz, 3 H), 2.30 (dddd, $^2J_{P,H}$ = 21.8, *J* = 10.8, 3.2, 2.9 Hz, 1 H), 3.33 (ddd, $^3J_{P,H}$ = 5.3, *J* = 10.7, 10.7 Hz, 1 H), 3.58 (ddd, $^3J_{P,H}$ = 8.9, *J* = 10.4, 3.4 Hz, 1 H), 3.67 (dd, *J* = 11.3, 3.3 Hz, 1 H), 3.71 (dd, *J* = 11.7, 3.7 Hz, 1 H), 3.82–4.05 (m, 4 H), 4.36 (ddd, $^3J_{P,H}$ = 30.8, *J* = 8.0, 2.5 Hz, 1 H), 4.46 (d, *J* = 12.2 Hz, 1 H), 4.62 (d, *J* = 11.9 Hz, 1 H), 4.70 (d, *J* = 11.1 Hz, 1 H), 4.82 (d, *J* = 11.1 Hz, 1 H), 5.82 (ddd, *J* = 7.7, 3.7, 3.3 Hz, 1 H), 7.27–7.40 (m, 10 H), 8.13 (s, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 2.5 (CH_2), 16.0 (d, $^3J_{P,C}$ = 6.4 Hz, CH_3), 16.2 (d, $^3J_{P,C}$ = 6.4 Hz, CH_3), 42.6 (d, $^1J_{P,C}$ = 131.4 Hz, CH), 61.6 (d, $^2J_{P,C}$ = 6.4 Hz, CH_2), 62.6 (d, $^2J_{P,C}$ = 5.3 Hz, CH_2), 68.7 (CH_2), 73.4 (CH_2), 75.7 (CH), 76.7 (CH_2), 78.7 (d, $^2J_{P,C}$ = 5.3 Hz, CH), 127.79 (CH), 127.84 (CH), 128.0 (2× CH), 128.1 (2× CH), 128.3 (4× CH), 137.3 (C), 137.8 (C), 160.7 (CH) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 21.8 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3007, 1725, 1216, 1028 cm^{-1}. MS (ESI^+): *m*/*z* (%) = 613 (100) $[M + Na]^+$. HRMS (ESI^+): *m*/*z* calcd. for $C_{24}H_{32}INaO_7P$ $[M + Na]^+$ 613.0828; found 613.0815. $C_{24}H_{32}IO_7P$ (590.39): calcd. C 48.83, H 5.46; found C 49.04, H 5.07.

4-*O*-(*tert*-Butyldiphenylsilyl)-1,2-dideoxy-2-diethoxyphosphoryl-3-*O*-formyl-D-*glycero*-tetra-1-enitol (58): From **52** (92.4 mg, 0.149 mmol) in anhydrous benzene (3.8 mL) containing DBU (44.6 μL, 0.3 mmol) following the general procedure by stirring at 9–10 °C for 15 min. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 1:1) gave **58** (69 mg, 0.140 mmol, 94%) as a colorless oil: $[a]_D$ = +5.0 (*c* = 0.54, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.04 (s, 9 H), 1.20 (t, *J* = 7.3 Hz, 3 H), 1.29 (t, *J* = 6.9 Hz, 3 H), 3.79 (dd, *J* = 11.4, 7.3 Hz, 1 H), 3.94 (dd, *J* = 11.3, 3.2 Hz, 1 H), 3.97–4.10 (m, 4 H), 5.68 (ddd, $^3J_{P,H}$ = 10.0, *J* = 7.3, 3.2 Hz, 1 H), 6.11 (ddd, $^3J_{P,H}$ = 45.4, *J* = 1.3, 1.3 Hz, 1 H), 6.28 (dd, $^3J_{P,H}$ = 22.7, *J* = 1.3 Hz, 1 H), 7.37–7.46 (m, 6 H), 7.65–7.68 (m, 4 H), 8.10 (s, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.07 (d, $^3J_{P,C}$ = 3.5 Hz, CH_3), 16.14 (d, $^3J_{P,C}$ = 2.8 Hz, CH_3), 19.2 (C), 26.7 (3× CH_3), 62.1 (d, $^2J_{P,C}$ = 6.4 Hz, CH_2), 62.3 (d, $^2J_{P,C}$ = 5.7 Hz, CH_2), 64.7 (d, $^3J_{P,C}$ = 2.1 Hz, CH_2), 73.1 (d, $^2J_{P,C}$ = 18.4 Hz, CH), 127.7 (4× CH), 129.72 (CH), 129.75 (CH), 132.8 (d, $^2J_{P,C}$ = 6.4 Hz, CH_2), 133.05 (C), 133.08 (C), 135.3 (d, $^1J_{P,C}$ = 178.0 Hz, C), 135.50 (2× CH), 135.54 (2× CH), 159.8 (CH) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 15.6 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3003, 1728 cm^{-1}. MS (ESI^+): *m*/*z* (%) = 513 (100) $[M + Na]^+$. HRMS (ESI^+): *m*/*z* calcd. for $C_{25}H_{35}NaO_6PSi$ $[M + Na]^+$ 513.1838; found 513.1837. $C_{25}H_{35}O_6PSi$ (490.61): calcd. C 61.20, H 7.19; found C 61.12, H 7.33.

1,2-Dideoxy-2-diethoxyphosphoryl-3-*O*-formyl-4,5-*O*-isopropylidene-D-*threo*-pent-1-enitol (59): From **53** (13.2 mg, 0.029 mmol) in anhydrous benzene (0.73 mL) containing DBU (8.8 μL, 0.06 mmol) following the general procedure by stirring at 9–10 °C for 0.5 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 4:6) gave **59** (8.2 mg, 0.025 mmol, 87%) as a colorless oil: $[a]_D$ = –43.7 (*c* = 0.46, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.34 (t, *J* = 7.3 Hz, 6 H), 1.36 (s, 3 H), 1.45 (s, 3 H), 3.81 (dd, *J* = 8.8, 5.7 Hz, 1 H), 4.01 (dd, *J* = 8.8, 6.6 Hz, 1 H), 4.06–4.15 (m, 4 H), 4.54 (ddd, *J* = 6.5, 6.5, 6.5 Hz, 1 H), 5.55 (dd, $^3J_{P,H}$ = 14.8, *J* = 6.6 Hz, 1 H), 6.20 (d, $^3J_{P,H}$ = 44.5 Hz, 1 H), 6.32 (dd, $^3J_{P,H}$ = 21.8, *J* = 1.0 Hz, 1 H), 8.13 (s, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.2 (d, $^3J_{P,C}$ = 6.3 Hz, CH_3), 16.3 (d, $^3J_{P,C}$ = 6.3 Hz, CH_3), 25.3 (CH_3), 26.4 (CH_3), 62.44 (d, $^2J_{P,C}$ = 5.7 Hz, CH_2), 62.45 (d, $^2J_{P,C}$ = 5.7 Hz, CH_2), 65.8 (CH_2), 73.6 (d, $^2J_{P,C}$ = 15.5 Hz, CH), 75.7 (d, $^3J_{P,C}$ = 2.1 Hz, CH), 110.3 (C), 134.8 (d, $^2J_{P,C}$ = 7.1 Hz, CH_2), 135.4 (d, $^1J_{P,C}$ = 178.7 Hz, C), 159.7 (CH) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 15.0 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2294, 1729, 1025 cm^{-1}. MS (ESI^+): *m*/*z* (%) = 345 (100) $[M + Na]^+$. HRMS (ESI^+): *m*/*z* calcd. for $C_{13}H_{23}NaO_7P$ $[M + Na]^+$ 345.1079; found 345.1075. $C_{13}H_{23}O_7P$ (322.30): calcd. C 48.45, H 7.19; found C 48.29, H 7.16.

1,2-Dideoxy-2-diethoxyphosphoryl-3-*O*-formyl-4,5-*O*-isopropylidene-D-*erythro*-pent-1-enitol (60): From **48** (41 mg, 0.126 mmol) containing $PhI(OAc)_2$ (45 mg, 0.14 mmol) and I_2 (35.3 mg, 0.14 mmol) following the general procedure by stirring at reflux temperature for 1.2 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 1:1) gave impure **54** (37.2 mg) contaminated with **60**. To a solution of this mixture in anhydrous benzene (1.1 mL) cooled to 9–10 °C, was added DBU (12.6 μL, 0.08 mmol) and the mixture was stirred at this temperature for 0.17 h. The reaction mixture was then poured into a saturated aqueous solution of $NaHSO_4$ and extracted with EtOAc. The combined organic extracts were washed with brine, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by Chromatotron chromatography (hexanes/EtOAc, 4:6) to give **60** (29 mg, 0.09 mmol, two-step, 71%) as a colorless oil: $[a]_D$ = +10.0 (*c* = 0.41, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.33 (t, *J* = 6.6 Hz, 3 H), 1.33 (s, 3 H), 1.33 (t, *J* = 6.6 Hz, 3 H), 1.38 (s, 3 H), 3.89 (dd, *J* = 8.7, 6.2 Hz, 1 H), 3.95 (dd, *J* = 8.5, 6.9 Hz, 1 H), 4.05–4.14 (m, 4 H), 4.53 (ddd, *J* = 6.3, 6.3, 6.3 Hz, 1 H), 5.67 (dd, $^3J_{P,H}$ = 10.9, *J* = 4.6 Hz, 1 H), 6.10 (dd, $^3J_{P,H}$ = 44.8, *J* = 1.0 Hz, 1 H), 6.24 (d, $^3J_{P,H}$ = 22.4 Hz, 1 H), 8.10 (s, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.17 (d, $^3J_{P,C}$ = 5.3 Hz, CH_3), 16.22 (d, $^3J_{P,C}$ = 6.4 Hz, CH_3), 25.1 (CH_3), 26.3 (CH_3), 62.4 (d, $^2J_{P,C}$ = 5.3 Hz, CH_2), 62.5 (d, $^2J_{P,C}$ = 5.3 Hz, CH_2), 64.6 (CH_2), 71.9 (d, $^2J_{P,C}$ = 18.0 Hz, CH), 75.0 (CH), 110.0 (C), 132.8 (d, $^2J_{P,C}$ = 6.4 Hz, CH_2), 135.4 (d, $^1J_{P,C}$ = 178.0 Hz, C), 159.4 (CH) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 15.0 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2295, 1731, 1024 cm^{-1}. MS (ESI^+): *m*/*z* (%) = 345 (100) $[M + Na]^+$. HRMS (ESI^+): *m*/*z* calcd. for $C_{13}H_{23}NaO_7P$ $[M + Na]^+$ 345.1079; found 345.1078. $C_{13}H_{23}O_7P$ (322.30): calcd. C 48.45, H 7.19; found C 48.52, H 7.23.

3,5-Di-*O*-benzyl-1,2-dideoxy-2-diethoxyphosphoryl-4-*O*-formyl-D-*erythro*-pent-1-enitol (61): From **55** (175.2 mg, 0.297 mmol) in anhydrous benzene (7.4 mL) containing DBU (88.6 μL, 0.59 mmol) following the general procedure by stirring at 9–10 °C for 15 min. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 1:1) gave **61** (136 mg, 0.294 mmol, 99%) as a colorless oil: $[a]_D$ = +27.7 (*c* = 0.22, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.31 (t, *J* = 7.1 Hz, 6 H), 3.74 (dd, *J* = 11.0, 3.2 Hz, 1 H), 3.77 (dd, *J* = 11.0, 6.0 Hz, 1 H), 4.05–4.16 (m, 4 H), 4.36 (d, *J* = 11.7 Hz, 1 H), 4.39 (dd, $^3J_{P,H}$ = 12.9, *J* = 6.0 Hz, 1 H), 4.45 (d, *J* = 12.0 Hz, 1 H), 4.52 (d, *J* = 12.0 Hz, 1 H), 4.60 (d, *J* = 11.7 Hz, 1 H), 5.44 (ddd, *J* = 5.9, 5.9, 3.0 Hz, 1 H), 6.18 (d, $^3J_{P,H}$ = 46.0 Hz, 1 H), 6.35 (dd, $^3J_{P,H}$ = 22.2, *J* = 1.4 Hz, 1 H), 7.25–7.35 (m, 10 H), 8.06 (s, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 16.2 (d, $^3J_{P,C}$ = 6.4 Hz, CH_3), 16.3 (d, $^3J_{P,C}$ = 6.4 Hz, CH_3), 62.2 (d, $^2J_{P,C}$ = 6.4 Hz, CH_2), 62.3 (d, $^2J_{P,C}$ = 5.3 Hz, CH_2), 67.7 (CH_2), 71.6 (CH_2), 73.1 (CH_2), 73.4 (CH), 77.4 (d, $^2J_{P,C}$ = 14.8 Hz, CH), 127.60 (2× CH), 127.62 (CH), 127.81 (3× CH), 128.3 (4× CH), 133.6 (d, $^2J_{P,C}$ = 7.4 Hz, CH_2), 136.9 (d, $^1J_{P,C}$ = 175.9 Hz, C), 137.4 (C), 137.9 (C), 160.4 (CH) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 16.4 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2926, 1733, 1024 cm^{-1}. MS (ESI^+): *m*/*z* (%) = 485 (100) $[M + Na]^+$. HRMS (ESI^+): *m*/*z* $C_{24}H_{31}NaO_7P$ $[M + Na]^+$ 485.1705; found 485.1711. $C_{24}H_{31}O_7P$ (462.48): calcd. C 62.33, H 6.76; found C 62.19, H 6.96.

3,5-Di-*O*-benzyl-1,2-dideoxy-2-diethoxyphosphoryl-4-*O*-formyl-D-*erythro*-pent-1-enitol (61) from 56: From **56** (13 mg, 0.022 mmol) in

anhydrous benzene (0.55 mL) containing DBU (6.6 μL, 0.044 mmol) following the general procedure by stirring at 9–10 °C for 0.7 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 1:1) gave **61** (9.1 mg, 0.020 mmol, 90%) as a colorless oil with properties identical to those of the previously prepared compound.

3,5-Di-*O*-benzyl-1,2-dideoxy-2-diethoxyphosphoryl-4-*O*-formyl-D-*threo*-pent-1-enitol (62): From **57** (68.2 mg, 0.116 mmol) in anhydrous benzene (2.9 mL) containing DBU (34.5 μL, 0.23 mmol) following the general procedure by stirring at 9–10 °C for 1 h. Chromatotron chromatography of the reaction residue (hexanes/EtOAc, 6:4) gave **62** (48.1 mg, 0.010 mmol, 90%) as a colorless oil: $[\alpha]_D$ = –30.8 (*c* = 0.67, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.31 (t, *J* = 7.1 Hz, 3 H), 1.32 (t, *J* = 6.9 Hz, 3 H), 3.62 (dd, *J* = 10.4, 5.7 Hz, 1 H), 3.65 (dd, *J* = 10.4, 6.3 Hz, 1 H), 4.03–4.14 (m, 4 H), 4.29 (d, *J* = 11.7 Hz, 1 H), 4.44 (dd, $^3J_{P,H}$ = 10.7, *J* = 3.8 Hz, 1 H), 4.46 (br. s, 2 H), 4.60 (d, *J* = 11.7 Hz, 1 H), 5.43 (ddd, *J* = 6.0, 6.0, 3.8 Hz, 1 H), 6.21 (d, $^3J_{P,H}$ = 46.4 Hz, 1 H), 6.33 (dd, $^3J_{P,H}$ = 22.4, *J* = 1.6 Hz, 1 H), 7.25–7.33 (m, 10 H), 8.08 (s, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 16.2 (d, $^2J_{P,C}$ = 6.4 Hz, 2× CH_3), 62.0 (d, $^2J_{P,C}$ = 5.3 Hz, CH_2), 62.3 (d, $^2J_{P,C}$ = 6.4 Hz, CH_2), 68.2 (CH_2), 71.3 (CH_2), 72.4 (CH), 73.1 (CH_2), 75.9 (d, $^2J_{P,C}$ = 15.9 Hz, CH), 127.58 (2× CH), 127.61 (CH), 127.83 (CH), 128.0 (2× CH), 128.27 (2× CH), 128.31 (2× CH), 133.0 (d, $^2J_{P,C}$ = 6.4 Hz, CH_2), 136.1 (d, $^1J_{P,C}$ = 174.8 Hz, C), 137.3 (C), 137.7 (C), 160.3 (CH) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 16.4 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3004, 1727, 1027, 1180 cm^{-1}. MS (ESI^+): *m*/*z* (%) = 485 (100) $[M + Na]^+$. HRMS (ESI^+): *m*/*z* calcd. for $C_{24}H_{31}NaO_7P$ $[M + Na]^+$ 485.1705; found 485.1713. $C_{24}H_{31}O_7P$ (462.48): calcd. C 62.33, H 6.76; found C 62.44, H 6.69.

3,5-Di-*O*-acetyl-1,4-anhydro-2-deoxy-2-diphenylphosphoryl-D-arabinitol (63a) and 3-*O*-Acetyl-1,4-anhydro-2-deoxy-2-diphenylphosphoryl-D-arabinitol (63b): A solution of formate **33** (47 mg, 0.084 mmol) in MeOH (2.1 mL) was stirred at 46–47 °C for 26 h. The mixture was then concentrated in vacuo. To a solution of the residue in CH_2Cl_2 (2.8 mL) was added AgOTf (25.7 mg, 0.1 mmol) and the mixture was vigorously stirred at room temperature in the dark under nitrogen for 1.4 h. The reaction mixture was then poured into a saturated aqueous solution of $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatotron chromatography (hexanes/EtOAc, 1:9) to give **63a** (22 mg, 0.055 mmol, 65%) and the more polar alcohol **63b** (6 mg, 0.017 mmol, 20%), which was afterward eluted with chloroform/MeOH (95:5).

Compound 63a: Crystalline solid; m.p. 133.7–135.7 °C (*n*-hexane/CH_2Cl_2); $[\alpha]_D$ = +22.6 (*c* = 0.38, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.74 (s, 3 H), 2.07 (s, 3 H), 3.33 (dddd, $^2J_{P,H}$ = 3.5, *J* = 8.8, 8.8, 6.3 Hz, 1 H), 4.07 (ddd, *J* = 7.5, 4.0, 4.0 Hz, 1 H), 4.15–4.26 (m, 2 H), 4.18 (dd, *J* = 12.0, 7.3 Hz, 1 H), 4.29 (dd, *J* = 12.0, 3.8 Hz, 1 H), 5.46 (ddd, $^3J_{P,H}$ = 13.9, *J* = 6.3, 4.4 Hz, 1 H), 7.46–7.59 (m, 6 H), 7.75–7.83 (m, 4 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 20.2 (CH_3), 20.7 (CH_3), 44.5 (d, $^1J_{P,C}$ = 73.1 Hz, CH), 62.7 (CH_2), 66.7 (d, $^2J_{P,C}$ = 2.1 Hz, CH_2), 74.2 (CH), 82.8 (d, $^3J_{P,C}$ = 7.4 Hz, CH), 128.6 (d, $^3J_{P,C}$ = 12.7 Hz, 2× CH), 128.9 (d, $^3J_{P,C}$ = 11.7 Hz, 2× CH), 130.7 (d, $^2J_{P,C}$ = 8.5 Hz, 2× CH), 131.07 (d, $^1J_{P,C}$ = 100.7 Hz, C), 131.11 (d, $^2J_{P,C}$ = 9.5 Hz, 2× CH), 131.6 (d, $^1J_{P,C}$ = 99.6 Hz, C), 132.1 (d, $^4J_{P,C}$ = 2.1 Hz, CH), 132.3 (d, $^4J_{P,C}$ = 2.1 Hz, CH), 169.5 (C), 170.6 (C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 28.2 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2994, 1743, 1229 cm^{-1}. MS (ESI) *m*/*z* (%) = 425 (100) $[M + Na]^+$. HRMS (ESI): *m*/*z* calcd. for $C_{21}H_{23}NaO_6P$ $[M + Na]^+$ 425.1130; found 425.1129. $C_{21}H_{23}O_6P$ (402.38): calcd. C 62.68, H 5.76; found C 62.78, H 6.00.

Compound 63b: $[\alpha]_D$ = +10 (*c* = 0.6, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.87 (s, 3 H), 3.21 (dddd, $^2J_{P,H}$ = 3.7, *J* = 7.8, 5.6, 3.7 Hz, 1 H), 3.81 (dd, *J* = 12.6, 4.1 Hz, 1 H), 3.87 (dd, *J* = 12.3, 3.5 Hz, 1 H), 3.98 (ddd, *J* = 3.5, 3.5, 3.5 Hz, 1 H), 4.16 (ddd, $^3J_{P,H}$ = 15.8, *J* = 9.5, 7.9 Hz, 1 H), 4.28 (ddd, $^3J_{P,H}$ = 13.1, *J* = 9.5, 5.5 Hz, 1 H), 5.52 (ddd, $^3J_{P,H}$ = 13.7, *J* = 3.5, 3.5 Hz, 1 H), 7.47–7.60 (m, 6 H), 7.76–7.86 (m, 4 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 20.6 (CH_3), 45.4 (d, $^1J_{P,C}$ = 72.1 Hz, CH), 62.3 (CH_2), 67.0 (CH_2), 75.3 (d, $^2J_{P,C}$ = 3.2 Hz, CH), 86.7 (d, $^3J_{P,C}$ = 4.2 Hz, CH), 128.8 (d, $^3J_{P,C}$ = 11.7 Hz, 2× CH), 129.0 (d, $^3J_{P,C}$ = 12.7 Hz, 2× CH), 130.8 (d, $^2J_{P,C}$ = 9.5 Hz, 2× CH), 130.9 (d, $^1J_{P,C}$ = 100.7 Hz, C), 131.1 (d, $^2J_{P,C}$ = 9.5 Hz, 2× CH), 131.3 (d, $^1J_{P,C}$ = 100.7 Hz, C), 132.3 (d, $^3J_{P,C}$ = 3.2 Hz, CH), 132.4 (d, $^3J_{P,C}$ = 3.2 Hz, CH), 170.0 (C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 31.3 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3687, 3602, 3342, 3007, 1742, 1119 cm^{-1}. MS (ESI) *m*/*z* (%) = 383 (100) $[M + Na]^+$. HRMS (ESI): *m*/*z* calcd. for $C_{19}H_{21}NaO_5P$ $[M + Na]^+$ 383.1024; found 383.1034.

3,5-Di-*O*-benzyl-1,2-dideoxy-2-diethoxyphosphoryl-D-*erythro*-pent-1-enitol (64): A solution of **61** (200 mg, 0.432 mmol) in NaOEt/EtOH 0.01 M (3.8 mL, 0.038 mmol), was stirred at room temperature under nitrogen for 3 h. The mixture was then concentrated under reduced pressure and the residue was purified by Chromatotron chromatography (hexanes/EtOAc, 40:60) to give **64** (179.2 mg, 0.412 mmol, 95%) as a colorless oil: $[\alpha]_D$ = +34.0 (*c* = 1.05, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.29 (t, *J* = 7.3 Hz, 3 H), 1.32 (t, *J* = 7.3 Hz, 3 H), 3.62 (dd, *J* = 9.8, 5.0 Hz, 1 H), 3.64 (dd, *J* = 9.8, 3.8 Hz, 1 H), 4.04 (ddd, *J* = 6.9, 5.0, 3.8 Hz, 1 H), 4.06–4.17 (m, 4 H), 4.24 (dd, $^3J_{P,H}$ = 16.4, *J* = 6.9 Hz, 1 H), 4.33 (d, *J* = 11.3 Hz, 1 H), 4.50 (d, *J* = 12.0 Hz, 1 H), 4.54 (d, *J* = 12.0 Hz, 1 H), 4.57 (d, *J* = 11.3 Hz, 1 H), 6.11 (ddd, $^3J_{P,H}$ = 46.0, *J* = 1.0, 1.0 Hz, 1 H), 6.28 (dd, $^3J_{P,H}$ = 21.8, *J* = 1.6 Hz, 1 H), 7.24–7.33 (m, 10 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.16 (d, $^3J_{P,C}$ = 6.4 Hz, CH_3), 16.17 (d, $^3J_{P,C}$ = 6.4 Hz, CH_3), 62.2 (d, $^2J_{P,C}$ = 6.0 Hz, CH_2), 62.3 (d, $^2J_{P,C}$ = 6.0 Hz, CH_2), 70.6 (CH_2), 71.0 (CH_2), 72.1 (CH), 73.2 (CH_2), 80.0 (d, $^2J_{P,C}$ = 14.8 Hz, CH), 127.4 (CH), 127.57 (CH), 127.61 (2× CH), 127.7 (2× CH), 128.2 (4× CH), 132.9 (d, $^2J_{P,C}$ = 6.4 Hz, CH_2), 137.5 (d, $^1J_{P,C}$ = 173.8 Hz, C), 137.6 (C), 138.1 (C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 18.0 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3400, 3005, 1241, 1027, 973 cm^{-1}. MS (ESI^+): *m*/*z* (%) = 457 (100) $[M + Na]^+$. HRMS (ESI^+): *m*/*z* calcd. for $C_{23}H_{31}NaO_6P$ $[M + Na]^+$ 457.1756; found 457.1750. $C_{23}H_{31}O_6P$ (434.47): calcd. C 63.58, H 7.19; found C 63.74, H 7.22.

(R_P)-3,5-Di-*O*-benzyl-1,2-dideoxy-1-ethoxy-2-methylene-1-phospha-1-oxo-D-*erythro*-pentofuranose (65) and (S_P)-3,5-Di-*O*-benzyl-1,2-dideoxy-1-ethoxy-2-methylene-1-phospha-1-oxo-D-*erythro*-pentofuranose (66): To a solution of **64** (178 mg, 0.41 mmol) in toluene (2.0 mL), was added PPTS (205.9 mg, 0.819 mmol) and the mixture was stirred at 100 °C under nitrogen for 29 h. The solution was then poured into water and extracted with EtOAc. The organic layer was dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by Chromatotron chromatography (hexanes/EtOAc, 50:50) to give **65** (25.8 mg, 0.066 mmol, 16%) and **66** (48.6 mg, 0.125 mmol, 31%) as colorless oils.

Compound 65: $[\alpha]_D$ = +4.5 (*c* = 0.64, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.30 (t, *J* = 7.3 Hz, 3 H), 3.62 (ddd, $^4J_{P,H}$ = 2.2, *J* = 11.4, 3.8 Hz, 1 H), 3.69 (dd, *J* = 11.4, 3.8 Hz, 1 H), 4.10–4.21 (m, 2 H), 4.32 (dddd, $^3J_{P,H}$ = 6.6, *J* = 6.6, 3.8, 3.8 Hz, 1 H), 4.50 (d, *J* = 12.0 Hz, 1 H), 4.57 (d, *J* = 11.7 Hz, 1 H), 4.59 (d, *J* = 11.7 Hz, 1 H), 4.61 (dddd, $^3J_{P,H}$ = 8.2, *J* = 6.3, 2.2, 2.2 Hz, 1 H), 4.70 (d, *J*

= 11.7 Hz, 1 H), 6.03 (dd, $^3J_{P,H}$ = 46.7, J = 2.2 Hz, 1 H), 6.15 (dd, $^3J_{P,H}$ = 21.8, J = 2.5 Hz, 1 H), 7.29–7.37 (m, 10 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 16.4 (d, $^3J_{P,C}$ = 6.4 Hz, CH_3), 63.1 (d, $^2J_{P,C}$ = 6.4 Hz, CH_2), 68.5 (d, $^3J_{P,C}$ = 3.2 Hz, CH_2), 72.5 (CH_2), 73.4 (CH_2), 76.9 (d, $^2J_{P,C}$ = 32.9 Hz, CH), 80.9 (CH), 126.6 (d, $^2J_{P,C}$ = 7.4 Hz, CH_2), 127.6 (2× CH), 127.8 (CH), 127.9 (2× CH), 128.1 (CH), 128.4 (2× CH), 128.5 (2× CH), 136.8 (d, $^1J_{P,C}$ = 162.1 Hz, C), 137.2 (C), 137.6 (C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 24.7 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3008, 1259, 1227, 1036, 966 cm^{-1}. MS (ESI$^+$): m/z (%) = 411 (100) [M + Na]$^+$. HRMS (ESI$^+$): m/z calcd. for $C_{21}H_{25}NaO_5P$ [M + Na]$^+$ 411.1337; found 411.1338. $C_{21}H_{25}O_5P$ (388.40): calcd. C 64.94, H 6.49; found C 64.92, H 6.54.

Compound 66: $[\alpha]_D$ = +31.7 (c = 0.18, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.33 (t, J = 7.3 Hz, 3 H), 3.54 (dd, J = 10.7, 6.0 Hz, 1 H), 3.65 (ddd, $^4J_{P,H}$ = 0.9, J = 10.7, 4.7 Hz, 1 H), 4.17 (ddd, J = 7.3, 7.3, 7.3 Hz, 1 H), 4.18 (ddd, J = 6.9, 6.9, 6.9 Hz, 1 H), 4.42 (dddd, $^3J_{P,H}$ = 17.3, J = 2.8, 1.3, 1.3 Hz, 1 H), 4.47 (m, 1 H), 4.49 (d, J = 12.0 Hz, 1 H), 4.54 (d, J = 12.0 Hz, 1 H), 4.57 (d, J = 12.0 Hz, 1 H), 4.64 (d, J = 11.7 Hz, 1 H), 6.04 (dd, $^3J_{P,H}$ = 46.2, J = 1.2 Hz, 1 H), 6.26 (dd, $^3J_{P,H}$ = 20.8, J = 1.6 Hz, 1 H), 7.28–7.37 (m, 10 H) ppm. ^{1}H NMR (500 MHz, C_6D_6): δ = 1.03 (t, J = 6.9 Hz, 3 H), 3.35 (dd, J = 10.7, 5.7 Hz, 1 H), 3.38 (ddd, $^4J_{P,H}$ = 0.9, J = 10.7, 4.7 Hz, 1 H), 4.01 (m, 2 H), 4.12 (d, J = 11.7 Hz, 1 H), 4.19 (d, J = 12.0 Hz, 1 H), 4.26 (d, J = 12.3 Hz, 1 H), 4.27 (dddd, $^3J_{P,H}$ = 17.3, J = 3.2, 1.6, 1.6 Hz, 1 H), 4.31 (d, J = 11.7 Hz, 1 H), 4.42 (dddd, $^3J_{P,H}$ = 10.1, J = 5.7, 4.7, 3.2 Hz, 1 H), 5.53 (br. d, $^3J_{P,H}$ = 45.4 Hz, 1 H), 5.98 (dd, $^3J_{P,H}$ = 20.8, J = 1.3 Hz, 1 H), 7.05–7.20 (m, 10 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 16.3 (d, $^3J_{P,C}$ = 5.3 Hz, CH_3), 63.1 (d, $^2J_{P,C}$ = 6.4 Hz, CH_2), 69.3 (d, $^3J_{P,C}$ = 2.1 Hz, CH_2), 70.7 (CH_2), 73.6 (CH_2), 78.2 (d, $^2J_{P,C}$ = 27.6 Hz, CH), 81.3 (d, $^2J_{P,C}$ = 2.1 Hz, CH), 127.7 (2× CH), 127.8 (CH), 127.9 (2× CH), 128.0 (CH), 128.4 (2× CH), 128.5 (2× CH), 129.9 (d, $^2J_{P,C}$ = 9.5 Hz, CH_2), 135.2 (d, $^1J_{P,C}$ = 162.1 Hz, C), 137.0 (C), 137.5 (C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 26.3 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3442, 3012, 1260, 1094, 1010, 970 cm^{-1}. MS (ESI$^+$): m/z (%) = 411 (100) [M + Na]$^+$. HRMS (ESI$^+$): m/z calcd. for $C_{21}H_{25}NaO_5P$ [M + Na]$^+$ 411.1337; found 411.1340. $C_{21}H_{25}O_5P$ (388.40): calcd. C 64.94, H 6.49; found C 64.93, H 6.50.

(R_P)-2-[(2-Aza-3-methoxycarbonyl)propyl]-3,5-di-*O*-benzyl-1,2-dideoxy-1-ethoxy-1-phospha-1-oxo-D-*ribo*-pentofuranose (67) and (R_P)-2-[(2-Aza-3-methoxycarbonyl)propyl]-5-*O*-benzyl-1,2,3-trideoxy-1-ethoxy-1-phospha-1-oxo-D-*glycero*-pent-2-enofuranose (68): To a stirred solution of **65** (20 mg, 0.052 mmol) in $CHCl_3$ (1.7 mL) were added Et_3N (72 μL, 0.52 mmol) and glycine methyl ester hydrochloride (65.3 mg, 0.52 mmol). The reaction mixture was heated at reflux temperature under nitrogen for 4 days. The crude mixture was diluted with $CHCl_3$, washed twice with water and the aqueous phase was extracted twice with $CHCl_3$. The organic layer was dried with Na_2SO_4 and concentrated under reduced pressure to provide a yellow oil. The residue was purified by Chromatotron chromatography ($CHCl_3$/MeOH, 97:3) to give **65** (1.5 mg, 0.004 mmol, 7%), **67** (9.4 mg, 0.02 mmol, 38%) and **68** (6 mg, 0.016 mmol, 31%) as colorless oils.

Compound 67: $[\alpha]_D$ = –1.4 (c = 0.59, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.31 (t, J = 7.1 Hz, 3 H), 2.49 (dddd, $^2J_{P,H}$ = 20.3, J = 8.9, 8.9, 6.3 Hz, 1 H), 2.84 (ddd, $^3J_{P,H}$ = 12.3, J = 12.3, 8.8 Hz, 1 H), 3.06 (ddd, $^3J_{P,H}$ = 24.9, J = 11.7, 6.3 Hz, 1 H), 3.37 (d, J = 17.3 Hz, 1 H), 3.45 (d, J = 17.3 Hz, 1 H), 3.58 (ddd, $^4J_{P,H}$ = 1.6, J = 11.3, 4.1 Hz, 1 H), 3.68 (dd, J = 11.4, 3.1 Hz, 1 H), 3.73 (s, 3 H), 4.12 (ddd, $^3J_{P,H}$ = 2.2, J = 9.5, 7.6 Hz, 1 H), 4.18–4.27 (m, 3 H), 4.51 (d, J = 12.0 Hz, 1 H), 4.52 (d, J = 11.4 Hz, 1 H), 4.60 (d, J = 12.1 Hz, 1 H), 4.61 (d, J = 11.4 Hz, 1 H), 7.23–7.38 (m, 10 H). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 1.25 (t, J = 7.1 Hz, 3 H), 2.40 (dddd, $^2J_{P,H}$ = 19.9, J = 8.5, 8.5, 6.6 Hz, 1 H), 2.89 (ddd, $^3J_{P,H}$ = 11.8, J = 11.8, 8.6 Hz, 1 H), 3.06 (ddd, $^3J_{P,H}$ = 24.6, J = 11.6, 6.6 Hz, 1 H), 3.41 (d, J = 17.4 Hz, 1 H), 3.43 (d, J = 17.4 Hz, 1 H), 3.63 (ddd, $^4J_{P,H}$ = 1.2, J = 11.3, 4.8 Hz, 1 H), 3.67 (s, 3 H), 3.71 (dd, J = 11.3, 3.4 Hz, 1 H), 4.10–4.27 (m, 3 H), 4.22 (dddd, $^3J_{P,H}$ = 8.0, J = 7.2, 4.8, 3.2 Hz, 1 H), 4.54 (d, J = 12.0 Hz, 1 H), 4.57 (d, J = 10.8 Hz, 1 H), 4.60 (d, J = 11.6 Hz, 1 H), 4.71 (d, J = 11.6 Hz, 1 H), 7.27–7.39 (m, 10 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 16.5 (d, $^3J_{P,C}$ = 5.3 Hz, CH_3), 41.6 (d, $^1J_{P,C}$ = 119.7 Hz, CH), 46.4 (d, $^2J_{P,C}$ = 3.2 Hz, CH_2), 50.3 (CH_2), 51.8 (CH_3), 63.2 (d, $^2J_{P,C}$ = 6.4 Hz, CH_2), 68.7 (d, $^3J_{P,C}$ = 4.2 Hz, CH_2), 73.3 (2× CH_2), 78.9 (d, $^2J_{P,C}$ = 14.8 Hz, CH), 80.5 (CH), 127.7 (2× CH), 127.8 (CH), 127.96 (2× CH), 128.05 (CH), 128.4 (2× CH), 128.5 (2× CH), 137.4 (C), 137.7 (C), 172.5 (C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 39.6 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3034, 1735, 1258, 1034, 967 cm^{-1}. MS (ESI$^+$): m/z (%) = 500 (100) [M + Na]$^+$. HRMS (ESI$^+$): m/z calcd. for $C_{24}H_{32}NNaO_7P$ [M + Na]$^+$ 500.1814; found 500.1828. $C_{24}H_{32}NO_7P$ (477.49): calcd. C 60.37, H 6.75, N 2.93; found C 60.39, H 6.80, N 2.79.

Compound 68: $[\alpha]_D$ = –17.6 (c = 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.30 (t, J = 7.3 Hz, 3 H), 3.46 (s, 2 H), 3.61–3.68 (m, 4 H), 3.73 (s, 3 H), 4.17 (m, 2 H), 4.58 (s, 2 H), 4.99 (s, 1 H), 6.82 (br. d, $^3J_{P,H}$ = 44.1 Hz, 1 H), 7.28–7.37 (m, 5 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 16.5 (d, $^3J_{P,C}$ = 5.3 Hz, CH_3), 45.3 (d, $^2J_{P,C}$ = 15.9 Hz, CH_2), 49.7 (CH_2), 52.0 (CH_3), 63.4 (d, $^3J_{P,C}$ = 6.4 Hz, CH_2), 71.0 (CH_2), 73.6 (CH_2), 79.0 (d, $^2J_{P,C}$ = 10.6 Hz, CH), 127.7 (2× CH), 127.9 (CH), 128.4 (2× CH), 131.6 (d, $^1J_{P,C}$ = 155.8 Hz, C), 137.5 (C), 142.3 (d, $^2J_{P,C}$ = 23.3 Hz, CH), 172.2 (C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 38.7 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1740, 1118, 1023, 973 cm^{-1}. MS (ESI$^+$): m/z (%) = 392 (100) [M + Na]$^+$. HRMS (ESI$^+$): m/z calcd. for $C_{17}H_{24}NNaO_6P$ [M + Na]$^+$ 392.1239; found 392.1246.

(S_P)-2-[(2-Aza-3-methoxycarbonyl)propyl]-3,5-di-*O*-benzyl-1,2-dideoxy-1-ethoxy-1-phospha-1-oxo-D-*ribo*-pentofuranose (69α), (S_P)-2-[(2-Aza-3-methoxycarbonyl)propyl]-3,5-di-*O*-benzyl-1,2-dideoxy-1-ethoxy-1-phospha-1-oxo-D-*arabino*-pentofuranose (69β), and (S_P)-2-[(2-Aza-3-methoxycarbonyl)propyl]-5-*O*-benzyl-1,2,3-trideoxy-1-ethoxy-1-phospha-1-oxo-D-*glycero*-pent-2-enofuranose (70): To a stirred solution of **66** (24 mg, 0.062 mmol) in $CHCl_3$ (2.1 mL) were added Et_3N (86 μL, 0.62 mmol) and glycine methyl ester hydrochloride (77.8 mg, 0.62 mmol). The reaction mixture was heated at reflux temperature under nitrogen for 10 days. The crude mixture was diluted with $CHCl_3$, washed twice with water and the aqueous phase was extracted twice with $CHCl_3$. The organic layer was dried with Na_2SO_4 and concentrated under reduced pressure to provide a yellow oil. The residue was purified by Chromatotron chromatography ($CHCl_3$/MeOH, 99:1) to give **66** (4.4 mg, 0.0113 mmol, 18%), **69β** (2.5 mg, 0.0052 mmol, 8%), **69α** (8 mg, 0.0167 mmol, 27%), and **70** (3.8 mg, 0.0103 mmol, 17%) as colorless oils.

Compound 69α: $[\alpha]_D$ = +20.3 (c = 0.32, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.35 (t, J = 7.2 Hz, 3 H), 2.52 (dddd, $^2J_{P,H}$ = 18.9, J = 7.6, 7.6, 6.6 Hz, 1 H), 2.93 (ddd, $^3J_{P,H}$ = 12.0, J = 9.5, 7.6 Hz, 1 H), 3.05 (ddd, $^3J_{P,H}$ = 20.2, J = 12.3, 7.9 Hz, 1 H), 3.37 (d, J = 17.7 Hz, 1 H), 3.41 (d, J = 17.7 Hz, 1 H), 3.56 (ap. d, J = 4.8 Hz, 2 H), 3.71 (s, 3 H), 4.20 (ddd, $^3J_{P,H}$ = 26.2, J = 6.6, 2.5 Hz, 1 H), 4.24 (m, 2 H), 4.41 (dddd, $^3J_{P,H}$ = 11.4, J = 4.7, 4.7, 2.2 Hz, 1 H), 4.50 (d, J = 12.1 Hz, 1 H), 4.52 (d, J = 12.0 Hz, 1 H), 4.59 (d, J = 12.0 Hz, 1 H), 4.60 (d, J = 12.1 Hz, 1 H), 7.30 (m, 10 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 16.6 (d, $^3J_{P,C}$ = 5.3 Hz, CH_3), 37.2 (d, $^1J_{P,C}$ = 120.8 Hz, CH), 43.1 (CH_2), 50.6

(CH_2), 51.8 (CH_3), 63.4 (d, $^2J_{P,C}$ = 7.4 Hz, CH_2), 69.9 (d, $^3J_{P,C}$ = 2.1 Hz, CH_2), 72.0 (CH_2), 73.7 (CH_2), 77.2 (d, $^2J_{P,C}$ = 5.3 Hz, CH), 80.7 (d, $^2J_{P,C}$ = 6.4 Hz, CH), 127.8 (2× CH), 127.84 (CH), 127.9 (2× CH), 128.0 (CH), 128.5 (4× CH), 137.2 (C), 137.5 (C), 172.6 (C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 44.8 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3004, 2360, 1739, 1244, 1208, 1034, 824 cm^{-1}. MS (ESI^+): *m/z* (%) = 478 (100) $[M + H]^+$. HRMS (ESI^+): *m/z* calcd. for $C_{24}H_{33}NO_7P$ $[M + H]^+$ 478.1995; found 478.1992. $C_{24}H_{32}NO_7P$ (477.49): calcd. C 60.37, H 6.75, N 2.93; found C 60.35, H 6.80, N 2.79.

Compound 69β: $[\alpha]_D$ = +3.7 (*c* = 0.46, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 (t, *J* = 7.2 Hz, 3 H), 2.34 (dddd, $^2J_{P,H}$ = 19.0, *J* = 6.9, 6.9, 6.9 Hz, 1 H), 2.93 (m, 2 H), 3.36 (d, *J* = 17.5 Hz, 1 H), 3.40 (d, *J* = 17.4 Hz, 1 H), 3.62 (ddd, $^4J_{P,H}$ = 1.0, *J* = 11.0, 4.7 Hz, 1 H), 3.68 (dd, *J* = 11.5, 3.1 Hz, 1 H), 3.71 (s, 3 H), 4.11–4.23 (m, 4 H), 4.53 (d, *J* = 12.1 Hz, 1 H), 4.55 (d, *J* = 12.0 Hz, 1 H), 4.61 (d, *J* = 12.0 Hz, 1 H), 4.62 (d, *J* = 12.1 Hz, 1 H), 7.23–7.35 (m, 10 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 16.4 (d, $^3J_{P,C}$ = 5.3 Hz, CH_3), 40.7 (d, $^1J_{P,C}$ = 118.7 Hz, CH), 46.8 (CH_2), 50.62 (CH_2), 51.8 (CH_3), 62.7 (d, $^2J_{P,C}$ = 7.4 Hz, CH_2), 69.4 (d, $^3J_{P,C}$ = 7.4 Hz, CH_2), 72.9 (CH_2), 73.6 (CH_2), 79.3 (d, $^2J_{P,C}$ = 12.7 Hz, CH), 80.7 (d, $^2J_{P,C}$ = 3.2 Hz, CH), 127.8 (CH), 127.9 (2× CH), 128.0 (2× CH), 128.1 (CH), 128.4 (2× CH), 128.5 (2× CH), 137.4 (C), 137.7 (C), 172.3 (C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 41.9 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1740, 1015 cm^{-1}. MS (ESI^+): *m/z* (%) = 500 (100) $[M + Na]^+$. HRMS (ESI^+): *m/z* calcd. for $C_{24}H_{32}NNaO_7P$ $[M + Na]^+$ 500.1814; found 500.1826.

Compound 70: $[\alpha]_D$ = –38.6 (*c* = 0.66, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.34 (t, *J* = 6.9 Hz, 3 H), 3.44 (s, 2 H), 3.61 (m, 2 H), 3.61 (dd, *J* = 5.0, 10.4 Hz, 1 H), 3.68 (dd, *J* = 6.0, 10.4 Hz, 1 H), 3.73 (s, 3 H), 4.13–4.19 (m, 2 H), 4.58 (d, *J* = 12.0 Hz, 1 H), 4.61 (d, *J* = 12.0 Hz, 1 H), 4.94 (m, 1 H), 6.80 (br. d, $^3J_{P,H}$ = 44.5 Hz, 1 H), 7.27–7.37 (m, 5 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 16.5 (d, $^3J_{P,C}$ = 5.1 Hz, CH_3), 45.5 (d, $^2J_{P,C}$ = 15.9 Hz, CH_2), 49.9 (CH_2), 51.9 (CH_3), 63.2 (d, $^2J_{P,C}$ = 6.4 Hz, CH_2), 71.6 (CH_2), 73.8 (CH_2), 79.1 (d, $^2J_{P,C}$ = 10.6 Hz, CH), 127.8 (2× CH), 127.9 (CH), 128.5 (2× CH), 132.1 (d, $^1J_{P,C}$ = 154.7 Hz, C), 137.5 (C), 141.7 (d, $^2J_{P,C}$ = 22.3 Hz, CH), 172.49 (C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 38.4 (s, 1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1740, 1119, 1022, 971 cm^{-1}. MS (ESI^+): *m/z* (%) = 392 (100) $[M + Na]^+$. HRMS (ESI^+): *m/z* calcd. for $C_{17}H_{24}NNaO_6P$ $[M + Na]^+$ 392.1239; found 392.1247.

3,5-Di-*O*-acetyl-1,2-dideoxy-2-diphenylphosphoryl-4-*O*-formyl-1-*C*-butyl-D-ribitol and 3,5-Di-*O*-acetyl-1,2-dideoxy-2-diphenylphosphoryl-4-*O*-formyl-1-*C*-butyl-D-arabinitol (71ab): A solution of **40** (50 mg, 0.116 mmol) in freshly distilled *t*BuOH (4.2 mL) containing *n*Bu_3SnCl (141 μL, 0.52 mmol), sodium cyanoborohydride (164 mg, 2.6 mmol), AIBN (171.6 mg, 1.05 mmol), and *n*BuBr (187 μL, 1.74 mmol) was deoxygenated by saturation with argon bubbling for 10 min and irradiated through Pyrex-filtered light using a Hanovia 450 W medium-pressure mercury vapor lamp for 3.5 h. The mixture was concentrated under reduced pressure and the residue was dissolved in CH_2Cl_2 and washed with water. The solvent was evaporated and the residue was redissolved in MeCN and washed with *n*-hexane. Chromatotron chromatography (hexanes/EtOAc, 4:6) of the residue gave **71a** (16.8 mg, 0.034 mmol) and **71b** (13.7 mg, 0.028 mmol) in a 54% global yield.

Compound 71a: Colorless oil; $[\alpha]_D$ = +33.4 (*c* = 1.21, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.74 (t, *J* = 6.9 Hz, 3 H), 1.04–1.11 (m, 5 H), 1.27–1.32 (m, 1 H), 1.74–1.78 (m, 2 H), 1.90 (s, 3 H), 1.96 (s, 3 H), 2.59 (dddd, $^2J_{P,H}$ = 10.7, *J* = 5.6, 5.6, 2.9 Hz, 1 H), 4.06 (dd, *J* = 12.5, 6.1 Hz, 1 H), 4.33 (dd, *J* = 12.3, 2.5 Hz, 1 H), 5.42–5.48 (m, 1 H), 5.54 (ddd, $^3J_{P,H}$ = 13.9, *J* = 7.6, 2.8 Hz, 1 H), 7.45–7.56 (m, 6 H), 7.76–7.84 (m, 4 H), 8.10 (s, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 13.8 (CH_3), 20.6 (CH_3), 20.7 (CH_3), 22.0 (CH_2), 23.8 (CH_2), 29.3 (d, $J_{P,C}$ = 7.4 Hz, CH_2), 31.7 (CH_2), 39.0 (d, $^1J_{P,C}$ = 69.9 Hz, CH), 61.9 (CH_2), 68.4 (CH), 70.6 (d, $^3J_{P,C}$ = 8.5 Hz, CH), 128.67 (d, $^3J_{P,C}$ = 11.7 Hz, 2× CH), 128.72 (d, $^3J_{P,C}$ = 11.7 Hz, 2× CH), 131.0 (d, $^2J_{P,C}$ = 8.5 Hz, 4× CH), 131.8 (d, $^4J_{P,C}$ = 2.1 Hz, CH), 131.87 (d, $^4J_{P,C}$ = 2.1 Hz, CH), 131.90 (d, $^1J_{P,C}$ = 97.5 Hz, C), 132.1 (d, $^1J_{P,C}$ = 96.4 Hz, C), 159.6 (CH), 169.3 (C), 170.5 (C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 33.1 (1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2962, 1735, 1229, 1170 cm^{-1}. MS (ESI^+): *m/z* (%) = 511 (100) $[M + Na]^+$. HRMS (ESI^+): *m/z* calcd. for $C_{26}H_{33}NaO_7P$ $[M + Na]^+$ 511.1862; found 511.1873. $C_{26}H_{33}O_7P$ (488.52): calcd. C 63.92, H 6.81; found C 64.18, H 6.52.

Compound 71b: Colorless oil; $[\alpha]_D$ = +31.2 (*c* = 1.14, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.77 (t, *J* = 7.3 Hz, 3 H), 1.05–1.17 (m, 5 H), 1.34–1.41 (m, 1 H), 1.60–1.70 (m, 2 H), 1.83 (s, 3 H), 1.95 (s, 3 H), 2.87 (dddd, $^2J_{P,H}$ = 12.1, *J* = 8.0, 4.1, 4.1 Hz, 1 H), 4.12 (dd, *J* = 12.3, 5.4 Hz, 1 H), 4.25 (dd, *J* = 12.5, 2.4 Hz, 1 H), 5.40 (ddd, $^3J_{P,H}$ = 11.7, *J* = 8.2, 3.5 Hz, 1 H), 5.50 (dddd, *J* = 8.0, 5.5, 2.4, 0.8 Hz, 1 H), 7.44–7.53 (m, 6 H), 7.81–7.90 (m, 4 H), 8.13 (s, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 13.8 (CH_3), 20.50 (CH_3), 20.54 (CH_3), 22.1 (CH_2), 25.1 (CH_2), 28.0 (d, $J_{P,C}$ = 8.5 Hz, CH_2), 31.3 (CH_2), 39.7 (d, $^1J_{P,C}$ = 67.8 Hz, CH), 61.9 (CH_2), 69.8 (CH), 70.4 (CH), 128.6 (d, $^3J_{P,C}$ = 11.7 Hz, 2× CH), 128.6 (d, $^3J_{P,C}$ = 11.7 Hz, 2× CH), 131.0 (d, $^2J_{P,C}$ = 8.5 Hz, 2× CH), 131.1 (d, $^2J_{P,C}$ = 8.5 Hz, 2× CH), 131.6 (d, $^4J_{P,C}$ = 2.1 Hz, CH), 131.7 (d, $^4J_{P,C}$ = 2.1 Hz, CH), 132.87 (d, $^1J_{P,C}$ = 97.5 Hz, C), 132.85 (d, $^1J_{P,C}$ = 96.4 Hz, C), 160.2 (CH), 169.8 (C), 170.5 (C) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 30.7 (1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2962, 1737, 1232, 1166 cm^{-1}. MS (ESI^+): *m/z* (%) = 511 (100) $[M + Na]^+$. HRMS (ESI^+): *m/z* calcd. for $C_{26}H_{33}NaO_7P$ $[M + Na]^+$ 511.1862; found 511.1870. $C_{26}H_{33}O_7P$ (488.52): calcd. C 63.92, H 6.81; found C 64.21, H 6.93.

3,5-Di-*O*-benzyl-1,2-dideoxy-2-diethoxyphosphoryl-4-*O*-formyl-1-*C*-butyl-D-ribitol and 3,5-Di-*O*-benzyl-1,2-dideoxy-2-diethoxyphosphoryl-4-*O*-formyl-1-*C*-butyl-D-arabinitol (72ab): A solution of **61** (40.7 mg, 0.088 mmol) in freshly distilled *t*BuOH (4.4 mL) containing *n*Bu_3SnCl (110 μL, 0.4 mmol), sodium cyanoborohydride (124.4 mg, 1.98 mmol), AIBN (130 mg, 0.792 mmol), and *n*BuBr (140 μL, 1.32 mmol) was deoxygenated by saturation with argon bubbling for 10 min and irradiated through Pyrex-filtered light using a Hanovia 450 W medium-pressure mercury vapor lamp for 5 h. The mixture was concentrated under reduced pressure and the residue was dissolved in CH_2Cl_2 and washed with water. The solvent was evaporated and the residue was redissolved in MeCN and washed with *n*-hexane. The diastereomers were partially separated by careful Chromatotron chromatography (benzene/EtOAc, 9:1→6:4) of the residue to give **72a** (13.2 mg, 0.025 mmol, contaminated with ca. 19% of **72b**) and **72b** (9.8 mg, 0.019 mmol) in a 50% global yield.

Compound 72a: Colorless oil; $[\alpha]_D$ = +9.7 (*c* = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 7.1 Hz, 3 H), 1.19–1.33 (m, 4 H), 1.28 (t, *J* = 6.3 Hz, 3 H), 1.30 (t, *J* = 6.9 Hz, 3 H), 1.34–1.55 (m, 2 H), 1.66–1.82 (m, 2 H), 2.01 (dddd, $^2J_{P,H}$ = 22.7, *J* = 7.9, 5.0, 3.2 Hz, 1 H), 3.71 (dd, *J* = 11.0, 5.0 Hz, 1 H), 3.74 (dd, *J* = 11.0, 3.2 Hz, 1 H), 4.07–4.14 (m, 4 H), 4.25 (ddd, $^3J_{P,H}$ = 13.0, *J* = 7.3, 3.0 Hz, 1 H), 4.48 (d, *J* = 12.0 Hz, 1 H), 4.54 (d, *J* = 12.3 Hz, 1 H), 4.58 (d, *J* = 11.3 Hz, 1 H), 4.79 (d, *J* = 11.3 Hz, 1 H), 5.27 (ddd, *J* = 7.4, 4.9, 3.2 Hz, 1 H), 7.26–7.35 (m, 10 H), 8.11 (s, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 14.0 (CH_3), 16.36 (d, $^3J_{P,C}$ = 6.4 Hz, CH_3), 16.42 (d, $^3J_{P,C}$ = 5.3 Hz, CH_3), 22.4

(CH_2), 24.0 (d, $J_{P,C}$ = 3.2 Hz, CH_2), 28.5 (d, $J_{P,C}$ = 5.3 Hz, CH_2), 32.0 (CH_2), 38.2 (d, $^1J_{P,C}$ = 138.8 Hz, CH), 61.69 (d, $^2J_{P,C}$ = 7.4 Hz, CH_2), 61.73 (d, $^2J_{P,C}$ = 7.4 Hz, CH_2), 68.3 (CH_2), 72.9 ($^3J_{P,C}$ = 11.7 Hz, CH), 73.2 (CH_2), 73.8 (CH_2), 75.6 (CH), 127.56 (CH), 127.67 (2× CH), 127.70 (2× CH), 127.72 (CH), 128.2 (2× CH), 128.4 (2× CH), 137.7 (C), 138.2 (C), 160.2 (CH) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 32.3 (1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2931, 1726, 1179, 1053, 1029 cm^{-1}. MS (ESI^+): *m/z* (%) = 543 (100) [M + Na]$^+$. HRMS (ESI^+): *m/z* calcd. for $C_{28}H_{41}NaO_7P$ [M + Na]$^+$ 543.2488; found 543.2486. $C_{28}H_{41}O_7P$ (520.60): calcd. C 64.60, H 7.94; found C 64.79, H 7.64.

Compound 72b: Colorless oil; $[\alpha]_D$ = +2.3 (*c* = 0.47, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.1 Hz, 3 H), 1.23 (t, *J* = 7.1 Hz, 6 H), 1.25–1.34 (m, 4 H), 1.38–1.44 (m, 2 H), 1.56–1.68 (m, 1 H), 1.71–1.81 (m, 1 H), 2.15 (dddd, $^2J_{P,H}$ = 22.7, *J* = 7.3, 6.0, 3.2 Hz, 1 H), 3.76 (dd, *J* = 11.0, 5.0 Hz, 1 H), 3.80 (dd, *J* = 11.0, 2.8 Hz, 1 H), 3.96–4.08 (m, 5 H), 4.50 (d, *J* = 12.0 Hz, 1 H), 4.56 (d, *J* = 12.0 Hz, 1 H), 4.59 (d, *J* = 11.0 Hz, 1 H), 4.65 (d, *J* = 11.0 Hz, 1 H), 5.43 (ddd, *J* = 7.5, 4.8, 2.8 Hz, 1 H), 7.25–7.37 (m, 10 H), 8.11 (s, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 14.0 (CH_3), 16.43 (d, $^3J_{P,C}$ = 6.4 Hz, 2× CH_3), 22.4 (CH_2), 26.8 (d, $^2J_{P,C}$ = 3.2 Hz, CH_2), 27.8 (d, $^3J_{P,C}$ = 8.5 Hz, CH_2), 31.6 (CH_2), 39.4 (d, $^1J_{P,C}$ = 138.8 Hz, CH), 61.3 (d, $^2J_{P,C}$ = 6.4 Hz, CH_2), 61.6 (d, $^2J_{P,C}$ = 6.4 Hz, CH_2), 68.4 (CH_2), 73.3 (CH_2), 73.4 (CH), 74.4 (CH_2), 77.0 (d, $^2J_{P,C}$ = 3.6 Hz, CH), 127.7 (4× CH), 128.1 (2× CH), 128.3 (2× CH), 128.4 (2× CH), 137.87 (C), 137.83 (C), 160.7 (CH) ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 30.1 (1 P) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2931, 1726, 1179, 1054, 1029 cm^{-1}. MS (ESI^+): *m/z* (%) = 543 (100) [M + Na]$^+$. HRMS (ESI^+): *m/z* calcd. for $C_{28}H_{41}NaO_7P$ [M + Na]$^+$ 543.2488; found 543.2492. $C_{28}H_{41}O_7P$ (520.60): calcd. C 64.60, H 7.94; found C 64.65, H 7.88.

Supporting Information (see footnote on the first page of this article): Copies of ^{1}H, ^{13}C, and ^{31}P NMR spectra for all new compounds.

Acknowledgments

This work was supported by the Ministerio de Economía y Competitividad (Investigation Programs, grant numbers CTQ2010-18244 and CTQ2007-67492) and by the Gobierno de Canarias (grant numbers SolSub20081000192 and ProID20100088). D.H.-G. thanks the Ministerio de Economía y Competitividad for a fellowship.

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Received: April 10, 2014
Published Online: July 11, 2014

