Synthesis of the *C*-Glycosidic Analogue of Adenophostin A and Its Uracil Congener as Potential IP_3 Receptor Ligands. Stereoselective Construction of the *C*-Glycosidic Structure by a Temporary Silicon-Tethered Radical Coupling Reaction†

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Synthesis of the *C*-glycosidic analogue **9** of adenophostin A, a very potent IP_3 receptor agonist, and its uracil congener **10** was achieved via a temporary silicon-tethered radical coupling reaction as the key step. Phenyl 3,4,6-tri-*O*-(*p*-methoxybenzyl)-1-seleno-β-D-glucopyranoside (**27**) and 3-deoxy-3-methylene-1,2-*O*-isopropylidene-α-D-*erythro*-pentofuranose (**30**) were connected by a dimethylsilyl tether to give the radical coupling reaction substrate **24**, which was successively treated with Bu_3-SnH/AIBN in benzene and TBAF in THF to give the coupling product **25** with the desired (3α,1′α)-configuration as the major product. From **25**, the targets **9** and **10** were synthesized via introduction of adenine or uracil base by Vorbrüggen's method and phosphorylation of the hydroxyls by the phosphoramidite method.

Introduction

Considerable attention has been focused on D-*myo*-inositol 1,4,5-trisphosphate (IP_3), an intracellular Ca^{2+}-mobilizing second messenger, because of its significant biological importance.[1,2] Therefore, analogues of IP_3 have been extensively studied to develop specific ligands for IP_3 receptors, which are very useful for proving the mechanism of IP_3-mediated Ca^{2+} signaling pathways.[3] However, none of these analogues has surpassed IP_3 itself either in binding affinity for the IP_3 receptor or in Ca^{2+}-mobilizing activity.[3]

Recently, Takahashi and co-workers isolated adenophostin A (**2**) and B (**3**) from *Penicillium brevicompactum* and found them to be very strong IP_3 receptor ligands. Compounds **2** and **3** are 10−100 times more potent than IP_3 with regard to both their affinity for the IP_3 receptor and their Ca^{2+}-mobilizing ability in cells.[4] Because of this interesting biological feature, adenophostins are considered attractive targets of total synthesis.[5] Their intriguing structural features have also prompted several groups including ours to perform synthetic studies of novel IP_3 receptor ligands.[6,7] Biological evaluations of these compounds, **4**, **5**, **6**, and **7**, the structures of which are shown in Figure 1, showed that (1) the α-D-glucopyranose structure is a good bioisostere of the *myo*-inositol backbone of IP_3; (2) the three-dimensional locations of the three phosphate groups of adenophostin A and its analogues are critical for their biological activity; and (3) the adenine moiety significantly enhances the activity.[6,7]

C-Glycosides, on the other hand, have been extensively studied since they are biologically stable mimics of the corresponding *O*-glycosides.[8] We designed the *C*-glycosidic analogue **9** of adenophostin A as a novel IP_3 receptor ligand. As described above, the three-dimensional locations of the phosphate groups of adenophostin A and B are critical for their biological activity. The conformation around the glycosyl linkages in carbohydrates, such as

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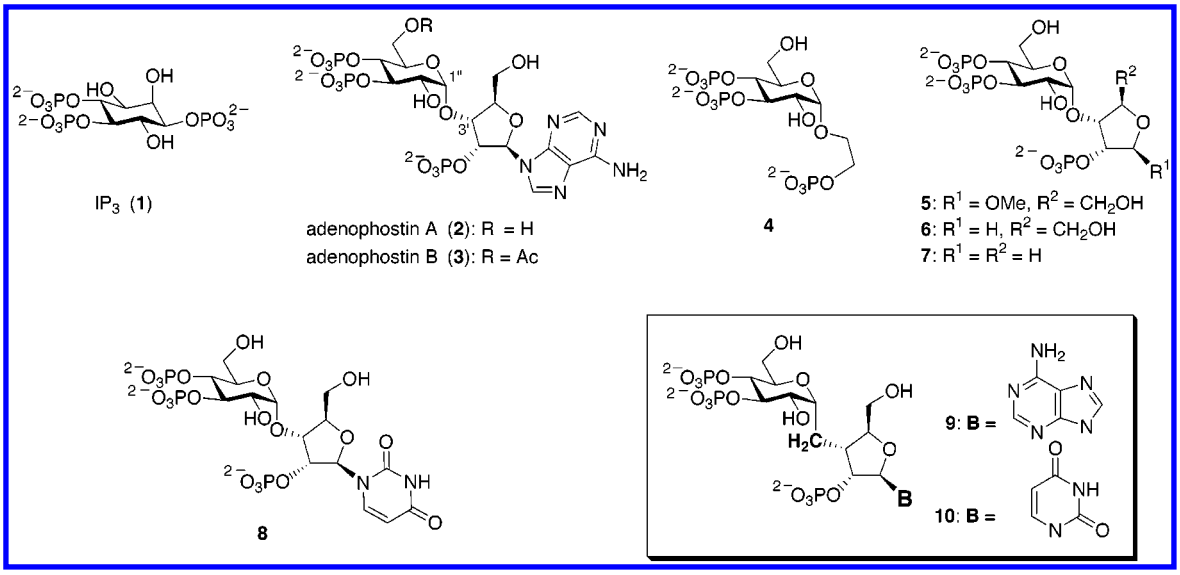


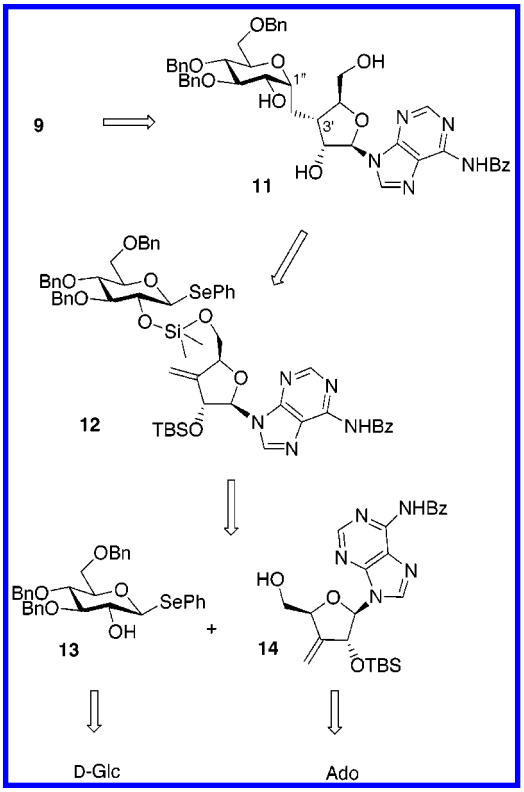
Figure 1.

adenophostins, which is known to be affected significantly by the anomeric effect of the sugar-ring oxygen, is an important determinant in the three-dimensional structure of these molecules.[9] Therefore, we were interested in investigating the biological activity and conformation of the *C*-glycoside **9** and in comparing these results with those of the parent *O*-glycoside, adenophostin A. This study may clarify the role of the glycosidic oxygen on the biological activity as well as the molecular conformation of adenophostin A.

The uracil congener **10** of *C*-glycosidic adenophostin was another of our synthetic targets, since the adenophostin analogue **8** having a uracil instead of an adenine as the base moiety was most recently identified as a very potent IP_3 receptor agonist.[10]

Synthetic Study with Silyl-Tethered Adenosine Derivative 12 as a Substrate for the Radical Coupling Reaction. In the synthesis of the target compound **9**, formation of the *C*-glycosidic linkage with the desired (3′α,1″α)-configuration is considered the key step. The use of radical reactions is an efficient methods for constructing *C*-glycosidic bonds.[8] Recently, a very efficient method for preparing *C*-glycosidic disaccharides by a temporary silicon-tethered reductive radical coupling reaction was reported.[11] We planned to use this type of radical coupling reaction as the key step for synthesizing the *C*-glycosidic analogue of adenophostin A.[12] Our synthetic plan is shown in Scheme 1. The key *C*-glycosidic linkage is constructed by a reductive radical coupling reaction of the silaketal-tethered substrate **12**, which can be prepared from the 1-phenylselenoglucose unit **13** and the 3′-exomethylene adenosine unit **14**. It is known that anomeric radicals of glucose derivatives adopt a $B_{2,5}$ boatlike conformation and that their addition reactions on alkenes selectively occur from the *axial* direction due to the anomeric effect to give the corresponding α-*C*-glycosides.[13] We therefore expected that radical reaction of **12** and subsequent removal of the silyl tether would give the desired *C*-glycosidic product **11** with the desired (3′α,1″α)-configuration. From **11**, the target compound **9** can be synthesized via introduction of the phosphate groups.

Scheme 1



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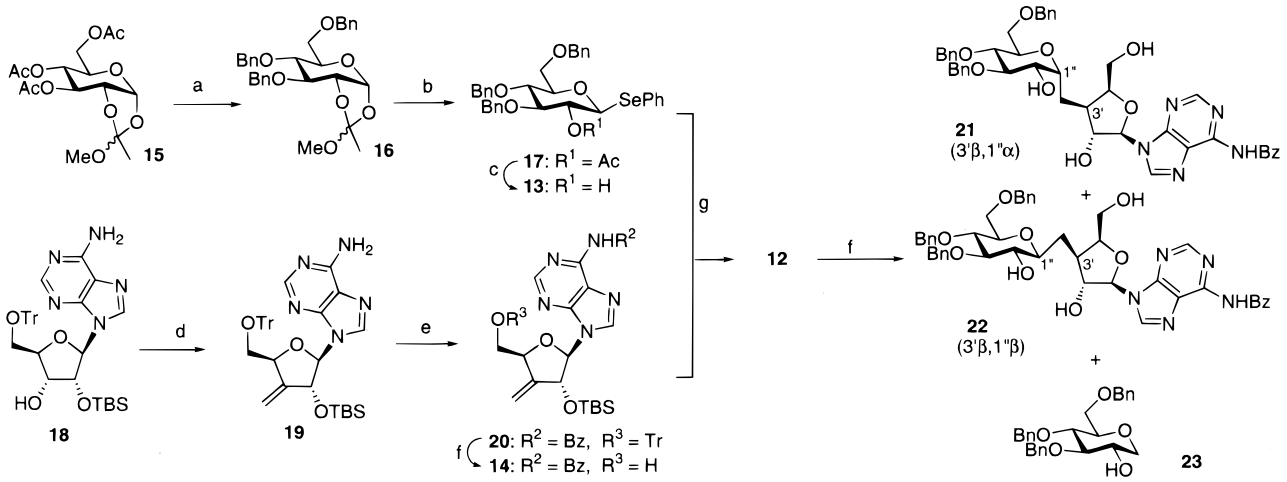
Scheme 2[a]



[a] Conditions: (a) (1) NaOMe, THF/MeOH, rt, (2) NaH, BnBr, HMPA/DMF, rt; (b) (1) PhSeH, molecular sieves 3A, $MeNO_2$, reflux; (c) NaOMe, THF/MeOH, rt, 59% (from **15**); (d) (1) CrO_3, Ac_2O, py, molecular sieves 4A, CH_2Cl_2, rt, (2) $NaOCMe_2Et$, Ph_3PMeBr, THF, rt, 72%; (e) (1) BzCl, DMAP, py, rt, (2) aqueous NH_3, 0 °C, 95%; (f) TFA, $CHCl_3$, rt, 84%; (g) (1) **13**, Me_2SiCl_2, BuLi, THF, −78 °C to rt, (2) **14**, Et_3N, THF, 0 °C to rt; (f) (1) Bu_3SnH, AIBN, benzene, reflux, (2) TBAF, THF, rt, **21** + **22** (35% from **13**, 28:72), **23** (25% from **13**).

The synthesis and radical reaction of the substrate **12** is summarized in Scheme 2. Removal of the acetyl groups of the known ortho ester **15**[14] and subsequent protection of the resulting hydroxyls with benzyl groups gave **16**. A PhSe group was introduced at the anomeric β-position by treating **16** with PhSeH/molecular sieves 3A,[15] and the resulting 2-*O*-acetyl group was removed to complete the synthesis of pyranose unit **13**. 2′-*O*-TBS-5′-*O*-Tr-adenosine (**18**) was successively treated with CrO_3/Ac_2O/pyridine/molecular sieves 4A in CH_2Cl_2, and $Ph_3P{=}CH_2$ in THF gave the 3′-methylene derivative **19**.[16] Protection of the N^6-amino function of **19** with a benzoyl group[17] and removal of the 5′-*O*-Tr group with TFA in $CHCl_3$ gave the adenosine unit **14**. Next, the units **13** and **14** were temporarily connected with a silaketal linkage. Thus, treatment of **13** with BuLi/Me_2SiCl_2 in THF yielded the corresponding 2-*O*-Si(Cl)Me_2 product, which was then treated with **14** in the presence of Et_3N to give the silaketal **12**, the substrate for the radical coupling reaction. The compound **12** was used directly for the next radical reaction without purification because of its instability.

The reductive coupling reaction of **12** was investigated with Bu_3SnH/AIBN under various conditions, and the products were purified by silica gel column chromatography after the radical reaction mixture was treated with TBAF in THF to remove the silyl tether. However, none of the desired (3′α,1″α)-*C*-glycoside **11** was obtained. For example, when a solution of Bu_3SnH (2.0 equiv) and AIBN (0.7 equiv) in benzene was added slowly over 1.2 h to a solution of **12** in benzene at 80 °C, a mixture of the undesired (3′β,1″α)-*C*-glycoside **21** and (3′β,1″β)-*C*-glycoside **22** resulted in 35% yield (**21**:**22** = 28:72), along with the direct reduction product **23** (25%), after desilylation. After the products were converted into the corresponding pentabenzoates **21′** and **22′**, their stereochemistries were confirmed by ^{1}H NMR spectra and NOE experiments, as shown in Figure 2.

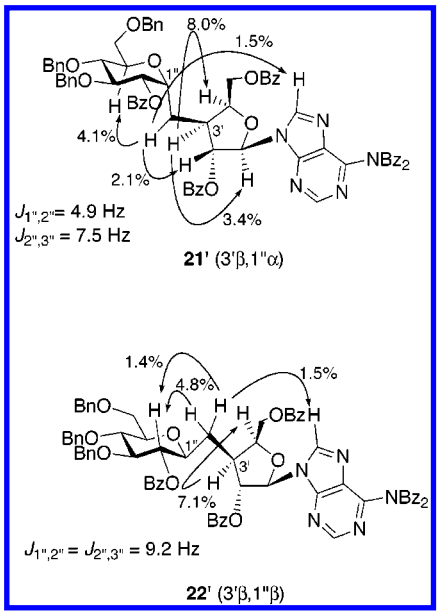


Figure 2.

These results suggested that in the anomeric radical intermediate (**I** or **II**), it would be difficult for the 3′-methylene moiety to approach the anomeric radical from the α-face, probably due to the steric repulsion between the bulky 2′-*O*-TBS group and the pyranose ring, to give the 1″β-product selectively, as shown in Scheme 3. Subsequent reduction of the resulting 3′-radical **III** by Bu_3SnH from the desired β-face was also disfavored, since the β-face of the ribose moiety of **III** was likely to be sterically very hindered due to the adenine base, and therefore would give the (3′β,1″β)-product **IV** as the major product (Scheme 3).

Synthetic Study with the Silyl-Tethered Ribose Derivative 24 as a Substrate for the Radical Cou-

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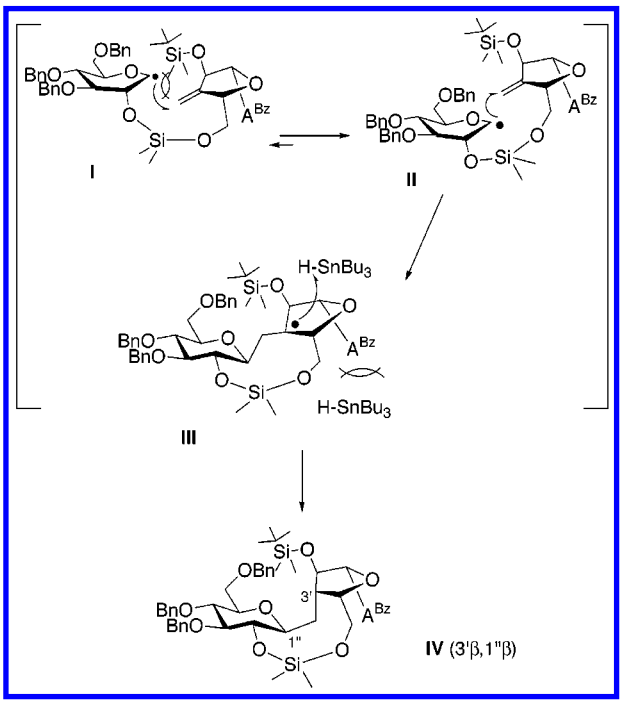
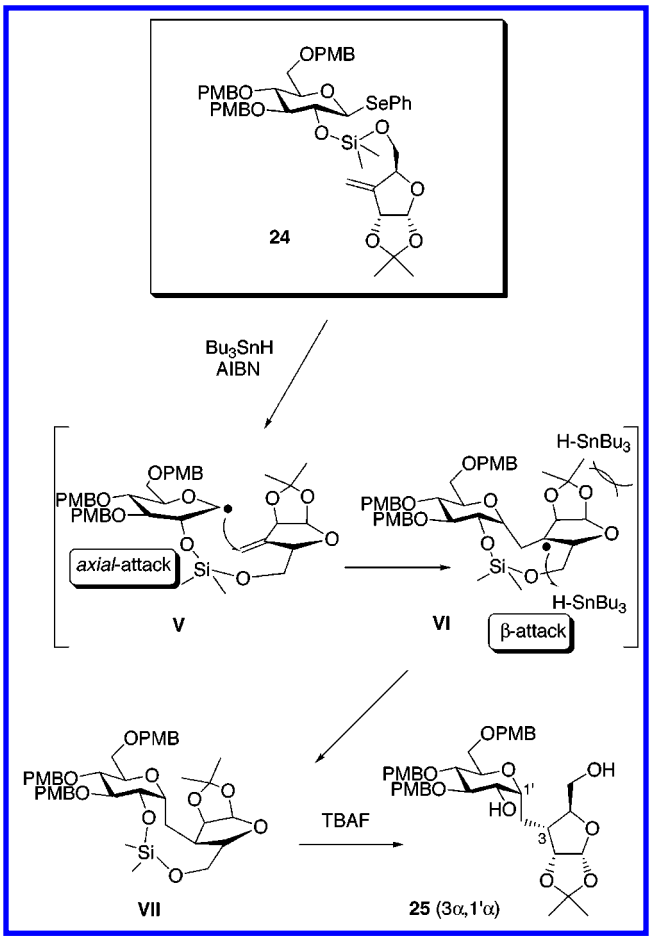
Scheme 3



Scheme 4



pling Reaction. Based on the above unsuccessful results, we designed an alternative substrate **24** (Scheme 4), in which 1,2-*O*-isopropylidene-3-methyleneribose derivative is connected with a glucose unit by a silyl tether, for the radical reaction. We assumed that the radical **V** derived from the substrate **24** would cyclize stereoselectively, due to the stereoelectronic effect[13] described above, to give the α-*C*-glycosidic radical **VI**. Subsequent reduction by Bu_3SnH would likely occur from the sterically unhindered *β*-face of the furanose ring, because of the steric repulsion of the isopropylidene group when Bu_3SnH attacked the 3-radical from the α-face. Accordingly, this radical reaction should proceed stereoselectively to give **VII**, and subsequent desilylation would give **25** with the desired (3α,1′α)-configuration (Scheme 4). From **25**, the target compounds **9** and **10** would be synthesized via the introduction of a nucleobase at the 1*β*-position by Vorbrüggen's procedure.[18]

The synthesis of the substrate **24** is shown in Scheme 5. The glucose unit **27** was synthesized from **15** by a method similar to the one for **13** described above. A Wittig reaction of a 3-keto sugar **28**,[19] prepared from D-xylose, with $Ph_3P{=}CH_2$ in THF gave the corresponding 3′-methylene product **29**, the 5-*O*-TBS group of which was removed with TBAF to give the furanose unit **30**. Next, the units **27** and **30** were temporarily connected with a silaketal linkage to give **24** in 67% yield.

The reductive coupling reaction of **24** was investigated with Bu_3SnH/AIBN under various conditions. When a solution of Bu_3SnH (2.0 equiv) and AIBN (0.5 equiv) in benzene was added slowly over 1.2 h to a solution of **24** in benzene at 80 °C, the best result was obtained. After the reaction mixture was treated with TBAF in THF and purified by silica gel flash chromatography, the desired (3α,1′α)-*C*-glycoside **25** was obtained as the major product (50%) along with the *C*-glycoside **31** having the (3α,1′*β*)-configuration (22%) and the directly reduced product **32** (25%). A similar radical reaction of **24** at 110 °C in toluene and subsequent desilylation also gave the desired **25**; however, the yield was poorer (**25** 22%, **31** 14%, **32** 36%). The stereochemistries of these *C*-glycosidic products were confirmed by ^1H NMR and gradient enhanced NOE (GOESY) spectra of the corresponding dibenzoates, as shown in Figure 3. One-pot conversion of **27** and **30** into the *C*-glycoside **25** was further investigated, since we noted that the silyl-tethered substrate **24** was rather unstable and likely to decompose partially during the workup. Thus, the tethered substrate **24**, without purification, was immediately treated under the same radical reaction conditions, followed by desilylation with TBAF, which successfully improved the yield of the desired *C*-glycoside **25** (50% from **27**).

Conversion of **25** into the targets **9** and **10** was performed as shown in Scheme 6. After protection of the two free hydroxyls of **25** with benzyl groups, the *p*-methoxybenzyl (PMB) groups and the isopropylidene group were removed with 90% TFA, and the resulting free hydroxyls were acetylated to give **34**. An adenine base was successfully introduced at the 1*β*-position of **34**, using the usual Vorbrüggen glycosylation procedure[18] with silylated N^6-benzoyladenine and $SnCl_4$ in MeCN to give adenyl *C*-disaccharide **35** in 78% yield. Similarly, the corresponding uracil derivative **36** was also synthesized using the Vorbrüggen reaction with silylated uracil. The four acetyl groups of **35** were removed simultaneously, and the 6″-primary hydroxyl was selectively protected with a trityl group to give **37**. Phosphate units

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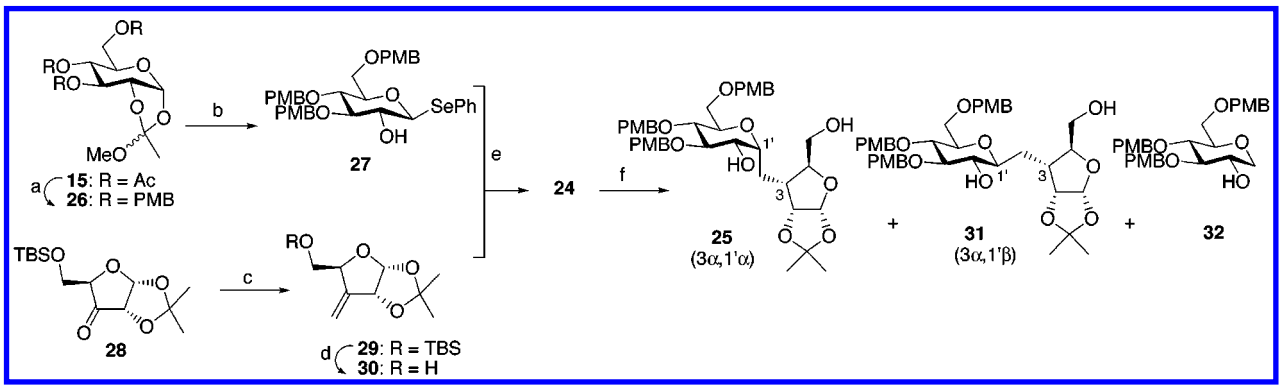
Scheme 5[a]



[a] Conditions: (a) (1) NaOMe, THF/MeOH, rt, (2) NaH, PMBCl, HMPA/DMF, rt, 77%; (b) (1) PhSeH, molecular sieves 3A, $MeNO_2$, reflux, (2) NaOMe, THF/MeOH, rt, 66%; (c) (1) $NaOCMe_2Et$, Ph_3PMeBr, THF, rt, 92%; (d) TBAF, THF, rt, 95%; (e) (1) **27**, Me_2SiCl_2, BuLi, THF, −78 °C to rt, (2) **30**, Et_3N, THF, 0 °C to rt; (f) (1) Bu_3SnH, AIBN, benzene, reflux, (2) TBAF, THF, **25** (50% from **27**), **31** (16% from **27**), **32** (11% from **27**).

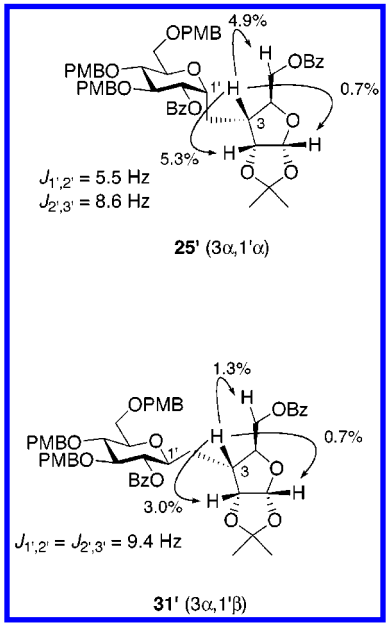


Figure 3.

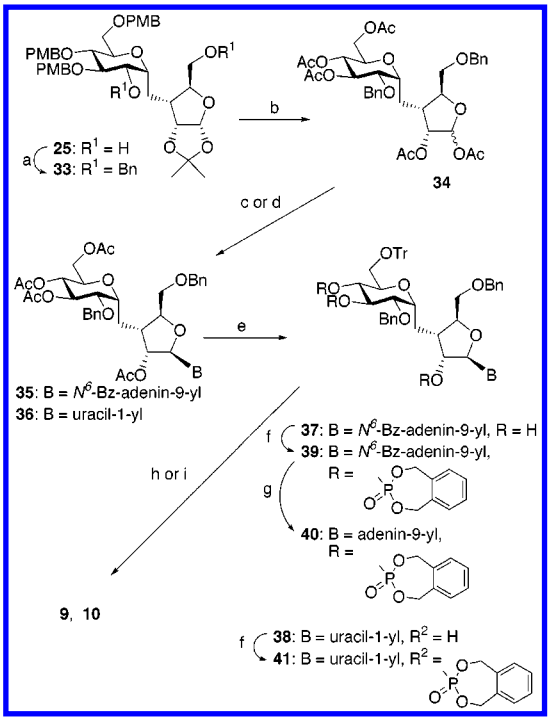
were introduced, using the phosphoramidite method with *o*-xylene *N*,*N*-diethylphosphoramidite (XEPA) developed by Watanabe and co-workers.[20] Thus, **37** was treated with XEPA and tetrazole in CH_2Cl_2, followed by oxidation with *m*-CPBA to give the desired 2′,3″,4″-trisphosphate derivative **39** in 92% yield. The N^6-benzoyl group was removed with NH_3 in aqueous dioxane. Finally, the trityl and benzyl protecting groups were all removed in one step by catalytic hydrogenation with Pd-black in aqueous MeOH to give the target compound **9** in 85% yield as a sodium salt, after treatment with ion-exchange resin. The uracil congener **10** was also successfully synthesized from **36** by a similar procedure as shown in Scheme 6.

In summary, we have successfully synthesized the *C*-glycosidic adenophostin A (**9**) and its uracil congener **10**, using a temporary silicon-tethered reductive coupling reaction as the key step. Biological evaluation is now in progress.

Experimental Section

^1H, ^{13}C, and ^{31}P NMR spectra were recorded at 270 and 500 MHz (^1H), at 100 and 125 MHz (^{13}C), and at 67.5 MHz (^{31}P), respectively. Chemical shifts are reported in ppm downfield from TMS (^1H and ^{13}C) or H_3PO_4 (^{31}P), and *J* values are given in hertz. The ^1H NMR assignments were in agreement with COSY spectra. Mass spectra were obtained by fast atom bombardment (FAB) methods. Thin-layer chromatography was done on Merck silica gel-coated plate $60F_{254}$. Silica gel chromatography was done on Merck silica gel 7734 or 9385. Reactions were carried out under an argon atmosphere.

Scheme 6[a]



[a] Conditions: (a) BnBr, NaH, HMPA/DMF/THF, 0 °C to rt, 71%; (b) (1) 90% TFA, 0 °C to rt, (2) NaOMe, MeOH, rt, (3) Ac_2O, Et_3N, DMAP, MeCN, 70%; (c) silylated N^6-benzoyladenine, $SnCl_4$, MeCN, 0 °C to rt, **35** (78%); (d) silylated uracil, TMSOTf, MeCN, 0 °C to rt, **36** (98%); (e) (1) NaOMe, MeOH, (2) TrCl, py, 0−50 °C, **37** (95%), **38** (92%); (f) XEPA, CH_2Cl_2, −40 °C, then *m*-CPBA, −40 °C to rt, **39** (92%), **41** (84%); (g) (1) NH_3, aqueous dioxane, rt, 89%; (h) H_2, Pd-black, aqueous MeOH, rt, 85%; (i) H_2, Pd−C, aqueous MeOH, rt, 85%.

Phenyl 3,4,6-Tri-*O*-benzyl-1-seleno-*β*-D-glucopyranoside (13). A mixture of **15**[14] (24.5 g, 67.6 mmol) and NaOMe (28% in MeOH, 2.7 mL) in MeOH/THF (30 mL/70 mL) was

(20) Watanabe, Y.; Komoda, Y.; Ebisuya, K.; Ozaki, S. *Tetrahedron Lett.* **1990**, *31*, 255−256.

stirred at room temperature for 1 h. The reaction mixture was evaporated and azeotroped with toluene (three times). A solution of the residue in DMF (150 mL) was added to a suspension of NaH (60%, 13.5 g, 338 mmol) in DMF/HMPA (300 mL/100 mL) at 0 °C, and the mixture was stirred at room temperature for 30 min. BnBr (32 mL, 270 mmol) was added to the reaction mixture at 0 °C, and the resulting mixture was stirred at room temperature for 10 h. After addition of MeOH (20 mL) at 0 °C, the mixture was partitioned between AcOEt (700 mL) and H_2O (500 mL), and the organic layer was washed with H_2O (500 mL, twice) and brine (300 mL), dried (Na_2SO_4), and evaporated. The residue was purified by column chromatography (SiO_2, hexane/AcOEt, 4:1) to give **16** (27.7 g). A mixture of the obtained **16**, PhSeH (8.5 mL, 54 mmol), and molecular sieves 3A powder (5.0 g) in CH_3NO_2 (75 mL) was heated under reflux for 6 h. The reaction mixture was partitioned between Et_2O (500 mL) and H_2O (400 mL), and the organic layer was washed with aqueous NaOH (1 M, 300 mL), H_2O (400 mL), aqueous NH_4Cl (saturated, 400 mL), and brine (300 mL), dried (Na_2SO_4), and evaporated to give crude **17**. A mixture of the crude **17** and NaOMe (28% in MeOH, 2.0 mL) in THF/MeOH (20 mL/40 mL) was stirred at room temperature for 3 h and then evaporated. The residue was purified by flash column chromatography (SiO_2, hexane/AcOEt, 10:1−8:1) to give **13** (39 g, 59% from **15** as an oil): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.69−7.65 (m, 2 H), 7.34−7.19 (m, 18 H), 4.89 (d, 1 H, J = 11.3), 4.83 (d, 1 H, J = 10.9), 4.81 (d, 1 H, J = 10.9), 4.72 (d, 1 H, J = 10.9), 4.60 (d, 1 H, J = 11.9 Hz), 4.56 (d, 1 H, J = 10.9), 4.53 (d, 1 H, J = 11.9), 3.78 (dd, 1 H, J = 2.0, 11.0), 3.74 (dd, 1 H, J = 4.1, 11.0), 3.6 (dd, 1 H, J = 8.7, 8.9), 3.56 (dd, 1 H, J = 8.7, 8.7), 3.51 (m, 1 H), 3.48 (dd, 1 H, J = 8.9, 10.9); ^{13}C NMR (125 MHz, $CDCl_3$) δ 129.03, 128.45, 128.35, 128.30, 127.94, 127.87, 127.73, 127.72, 127.58, 127.51, 126.63, 85.72, 84.70, 80.47, 77.28, 75.27, 75.01, 73.24, 69.93; FAB-LRMS *m/z* 591 (MH^+). Anal. Calcd for $C_{33}H_{34}O_5$-Se: C, 67.23; H, 5.81. Found: C, 67.21; H, 5.81.

9-(2-*O*-*tert*-Butyldimethylsilyl-5-*O*-trityl-β-D-ribofuranosyl)adenine (18). A suspension of $AgNO_3$ (19.6 g, 116 mmol), TBSCl (23 g, 154 mmol), and 5′-*O*-trityladenosine[21] (39.2 g, 77 mmol) in THF/pyridine (250 mL/220 mL)[22] was stirred at room temperature for 15 h. After addition of MeOH (6.2 mL), the mixture was filtered through Celite, evaporated, and crystallized from hexane/AcOEt to give **18** (22.6 g). The mother liquid was evaporated and dissolved in Et_3N/MeOH (5 mL/100 mL). The mixture was stirred at room temperature for 24 h, evaporated, and crystallized from hexane/AcOEt to give further **18** (11.0 g): total 36.6 g, 66% as a white solid; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 8.23 (s, 1 H), 7.98 (s, 1 H), 7.45−7.18 (m, 15 H), 5.99 (d, 1 H, J = 5.3), 5.54 (m, 2 H), 4.99 (dd, 1 H, J = 5.3, 5.3), 4.33 (m, 1 H), 4.24 (m, 1 H), 3. 51 (dd, 1 H, J = 3.3, 10.6), 3.37 (dd, 1 H, J = 4.0, 10.6), 2.69 (d, 1 H), 0.82 (s, 9 H), −0,03 (s, 3 H), −0.15 (s, 3 H); FAB-HRMS calcd for $C_{35}H_{42}$ N_5O_4Si 624.3006 (MH^+), found 624.2999.

9-(2-*O*-*tert*-Butyldimethylsilyl-3-deoxy-3-methylene-5-*O*-trityl-β-D-*erythro*-pentofuranosyl)adenine (19). CrO_3 (12.4 g, 124 mmol) was slowly added to a solution of pyridine (30 mL, 272 mmol) in CH_2Cl_2 (200 mL) containing molecular sieves 4A (30 g) at 0 °C, and the mixture was stirred at room temperature for 30 min. After addition of Ac_2O (11.7 mL, 124 mmol), the mixture was stirred at room temperature for 30 min. A solution of **18** (15.5 g, 24.8 mmol) in CH_2Cl_2 (150 mL) was slowly added to the mixture at 0 °C, and the resulting mixture was stirred at room temperature for 2 h. The mixture was partitioned between $CHCl_3$ (300 mL) and H_2O (400 mL), and the organic layer was washed with H_2O (400 mL) and brine (300 mL), dried (Na_2SO_4), and evaporated. The residue was purified by column chromatography (SiO_2, hexane/AcOEt, 1:2−1:10) to give 2′-*O*-TBS-5′-*O*-trityl-3′-ketoadenosine (16 g). After a mixture of $NaOCMe_2Et$ (95%, 8.94 g, 77 mmol) and Ph_3PMeBr (30.3 g, 84.8 mmol) in THF (350 mL) was stirred at room temperature for 2 h, a solution of the obtained 2′-*O*-TBS-5′-*O*-trityl-3′-ketoadenosine in THF (80 mL) was added at −78 °C, and the resulting mixture was warmed to 0 °C over 1 h and stirred at the same temperature for 48 h. After addition of aqueous NH_4Cl (saturated, 50 mL), the reaction mixture was partitioned between AcOEt (500 mL) and H_2O (300 mL), and the organic layer was washed with H_2O (300 mL) and brine (300 mL), dried (Na_2SO_4), and evaporated. The residue was purified by column chromatography (SiO_2, hexane/AcOEt, 1:1) to give **19** (9.2 g, 72% as a white solid): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 8.25 (s, 1 H), 7.98 (s, 1 H), 7.46−7.17 (m, 15 H), 5.85 (d, 1 H, J = 6.6), 5.53 (br s, 2 H), 5.36 (m, 1 H) 5.28 (m, 1 H), 5.12 (m, 1 H), 4.80 (m, 1 H), 3.45 (dd, 1 H, J = 5.3, 10.6) 3.35 (dd, 1 H, J = 3.3, 10.6), 0.78 (s, 9 H), −0.05 (s, 3 H), −0.38 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.46, 152.66, 151.80, 149.41, 146.73, 143.35, 141.31, 133.53, 132.47, 128.58, 128.46, 128.15, 127.69, 127.66, 127.02, 122.92, 109.14, 88.07, 86.92, 79.96, 77.22, 76.39, 66.20, 25.42, 17.79, −4.88, −5.28; FAB-HRMS calcd for $C_{36}H_{42}N_5O_3Si$ 620.3057 (MH^+), found 620.3043. Anal. Calcd for $C_{36}H_{41}N_5O_3Si$: C, 69.76; H, 6.67; N, 11.30. Found: C, 69.74; H, 6.69; N, 10.91.

***N*^{6}-Benzoyl-9-(2-*O*-*tert*-butyldimethylsilyl-3-deoxy-3-methylene-5-*O*-trityl-β-D-*erythro*-pentofuranosyl)adenine (20).** A mixture of **19** (7.74 g, 12.5 mmol), BzCl (5.8 mL, 50 mmol), and DMAP (150 mg, 1.2 mmol) in pyridine (70 mL) was stirred at room temperature for 2 h. After addition of aqueous NH_3 (25%, 20 mL), the mixture was stirred at 0 °C for 10 min and evaporated. The residue was purified by column chromatography (SiO_2, hexane/AcOEt, 3:2) to give **20** (8.56 g, 95% as a white amorphous solid): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 9.02 (br s, 1 H), 8.75 (s, 1 H), 8.21 (s, 1 H), 8.05−7.19 (m, 20 H), 6.08 (m, 1 H), 5.96 (d, 1 H, J = 2.3), 5.34 (dd, 1 H, J = 2.3, 2.3), 5.18 (dd, 1 H, J = 2.0, 2.0), 4.86 (m, 1 H), 3.50 (dd, 1 H, J = 4.6, 10.2), 3.41 (dd, 1 H, J = 3.3, 10.2), 0.80 (s, 9 H), −0.03 (s, 3 H), −0.39 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.56, 152.28, 150.50, 150.27, 146.37, 142.56, 133.34, 132.67, 128.62, 127.81, 123.95, 108.61, 91.35, 82.87, 74.71, 65.56, 25.44, 17.74, −4.90, −5.54; FAB-HRMS calcd for $C_{43}H_{46}N_5O_4Si$ 724.3319 (MH^+), found 724.3378. Anal. Calcd for $C_{43}H_{45}N_5O_4Si\cdot 1.5H_2O$: C, 68.77; H, 6.44; N, 9.33. Found: C, 68.90; H, 6.11; N, 9.45.

***N*^{6}-Benzoyl-9-(2-*O*-*tert*-butyldimethylsilyl-3-deoxy-3-methylene-β-D-*erythro*-pentofuranosyl)adenine (14).** To a solution of **20** (4.0 g, 6.45 mmol) in $CHCl_3$ (100 mL) was added aqueous TFA (80%, 10 mL) at 0 °C, and the resulting mixture was stirred at room temperature for 15 min. The reaction mixture was partitioned between $CHCl_3$ (150 mL) and H_2O (70 mL), and the organic layer was washed with H_2O (70 mL, twice), aqueous $NaHCO_3$ (saturated, 70 mL), and brine (70 mL), dried (Na_2SO_4), and evaporated. The residue was purified by column chromatography (SiO_2, hexane/AcOEt 1:3) to give **14** (2.6 g, 84% as a white amorphous solid): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 9.17 (br s, 1 H, NH), 8.85 (s, 1 H, H-2), 8.03 (s, 1 H, H-8), 8.06−7.46 (m, 5 H, Ar), 5.72 (m, 1 H, 5′-OH), 5.60 (d, 1 H, H-1′, J = 7.6), 5.45 (m, 1 H, H-2′), 5.34 (m, 1 H, =C*Ha*Hb), 5.28 (m, 1 H, =CHa*Hb*), 4.83 (m, 1 H, H-4′), 4.06 (m, 1 H, H-5′a), 3.72 (m, 1 H, H-5′b), 0.81 (s, 9 H, *t*Bu), −0.09 (s, 3 H, Me), −0.53 (s, 3 H, Me); FAB-HRMS calcd for $C_{24}H_{32}N_5O_4Si$ 482.2223 (MH^+), found 482.2209. Anal. Calcd for $C_{24}H_{31}N_5O_4Si$: C, 59.85; H, 6.49; N, 14.54. Found: C, 59.77; H, 6.55; N, 14.44.

***N*^{6}-Benzoyl-9-[3-deoxy-3-(4,5,7-tri-*O*-benzyl-2,6-anhydro-1-deoxy-D-*glycero*-D-*ido*-heptitol-1-yl)-β-D-*xylo*-pentofuranosyl]adenine (21), *N*^{6}-benzoyl-9-[3-deoxy-3-(4,5,7-tri-*O*-benzyl-2,6-anhydro-1-deoxy-D-*glycero*-D-*gulo*-heptitol-1-yl)-β-D-*xylo*-pentofuranosyl]adenine (22), and 1-Deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranose (23).** BuLi (1.50 M in hexane, 150 μL, 225 μmol) was slowly added to a solution of **13** (120 mg, 204 μmol) in THF (5 mL) at −78 °C, and after the resulting mixture was stirred at the same temperature for 5 min, Me_2SiCl_2 (173 μL, 1430 μmol) was added. The mixture was warmed to room temperature over 6 h, and the solvent was removed with argon stream. After the resulting oil was dried in vacuo at room temperature for 2 h, a solution of **14** (108 mg, 224 μmol) in THF (1 mL) and Et_3N (125 μL, 896

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(22) Hakimelahi, G. H.; Proba, Z. A.; Ogilvie, K. K. *Tetrahedron Lett*. **1981**, *22*, 4775−4778.

μmol) was added to a solution of the above residue in THF (4 mL) at 0 °C, and the mixture was stirred at room temperature for 1 h. The resulting mixture was partitioned between AcOEt (50 mL) and aqueous $NaHCO_3$ (saturated, 70 mL), and the organic layer was washed with aqueous $NaHCO_3$ (saturated, 70 mL) and brine (70 mL), dried (Na_2SO_4), and evaporated to give **12**, which was used for the next reaction without purification due to its instability. To a solution of the obtained **12** in benzene (19 mL) was added a solution of Bu_3SnH (71 μL, 266 μmol) and AIBN (15 mg, 93 μmol) in benzene (5 mL) at 80 °C slowly over 1.2 h, and then the resulting mixture was evaporated. A mixture of the resulting residue and TBAF (1 M in THF, 532 μL, 532 μmol) was stirred at room temperature for 1 h and then evaporated. The residue was purified by column chromatography (SiO_2, $CHCl_3$/MeOH, 50:1−10:1) to give **23** (14 mg, 25% as a white solid) and a mixture of **21** and **22** (57 mg, 35% as an oil, **21**/**22** = 28:72). For **21** (3′β,1″α): ^{1}H NMR (CD_3OD, 400 MHz) δ 8.68 (s, 1 H, H-2), 8.65 (s, 1 H, H-8), 8.08 (m, 2 H, Ar), 7.65 (m, 1 H, Ar), 7.55 (m, 2 H, Ar), 7.24 (m, 15 H, Ar), 5.91 (d, 1 H, H-1′, J = 7.0), 4.88 (m, 1 H, PhCH_2), 4.81 (dd, 1 H, H-2′, J = 7.0, 10.3), 4.73 (d, 1 H, PhCH_2, J = 4.7), 4.71 (d, 1 H, PhCH_2, J = 4.7), 4.47 (m, 3 H, PhCH_2), 4.37 (m, 1 H, H-4′), 4.05 (m, 1 H, H-1″), 3.83 (m, 4 H, H-2″, H-5″, H-5′a, H-5′b), 3.72 (dd, 1 H, H-4″, J = 7.9, 7.9), 3.63 (m, 2 H, H-6″a, H-6″b), 3.44 (dd, 1 H, H-3″, J = 7.9, 7.9), 2.69 (m, 1 H, H-3′), 2.34 (m, 1 H, 3′-C*Ha*Hb), 2.14 (m, 1 H, 3′-CHa*Hb*); FAB-HRMS calcd for $C_{45}H_{48}N_5O_9$ 802.3415 (MH^+), found 802.3397. For **22** (3′β,1″β): ^{1}H NMR (CD_3OD, 400 MHz) δ 8.66 (s, 2 H, H-2, H-8), 8.07−7.14 (m, 20 H, Ar), 5.89 (d, 1 H, H-1′, J = 7.0), 4.96 (d, 1 H, PhCH_2, J = 11.1), 4.79 (d, 1 H, PhCH_2, J = 11.1), 4.75 (d, 1 H, PhCH_2, J = 10.9), 4.73 (dd, 1 H, H-2′, J = 7.0, 10.6), 4.51 (d, 1 H, PhCH_2, J = 11.1), 4.44 (m, 3 H, H-4′, PhCH_2), 3.97 (d, 1 H, H-5′a, J = 11.0), 3.81 (d, 1 H, H-5′b, J = 11.0), 3.65 (d, 1 H, H-6″a, J = 9.7), 3.58 (dd, 1 H, H-6″b, J = 4.4, 10.6), 3.48 (m, 2 H, H-2″, H-5″), 3.41 (m, 1 H, H-1″), 3.36 (m, 2 H, H-3″, H-4″), 2.66 (m, 1 H, H-3′), 2.39 (dd, 1 H, 3′-C*Ha*Hb, J = 4.7, 14.4), 1.88 (m, 1 H, 3′-CHa*Hb*); FAB-HRMS calcd for $C_{45}H_{48}N_5O_9$ 802.3415 (MH^+), found 802.3384. For **23**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.37−7.16 (m, 15 H, Ar), 4.95 (m,1 H, PhCH_2), 4.77 (m, 2 H, PhCH_2), 4.61 (m, 1 H, PhCH_2), 4.53 (m, 2 H, PhCH_2), 4.01 (dd, 1 H, H-1a, J = 5.4, 11.2), 3.70 (m, 3 H, H-2, H-6a, H-6b), 3.59 (dd, 1 H, H-4, J = 9.2, 9.2), 3.45 (dd, 1 H, H-3, J = 9.2, 9.2), 3.41 (ddd, 1 H, H-5, J = 2.3, 3.9, 9.2), 3.21 (dd, 1 H, H-1b, J = 11.2, 11.2), 2.10 (d, 1 H, 2-OH, J = 3.2); FAB-HRMS calcd for $C_{27}H_{31}O_5$ 435.2171 (MH^+), found 435.2165.

***N*^{6}-Dibenzoyl-9-[2-*O*-benzoyl-3-deoxy-3-(3-*O*-benzoyl-4,5,7-tri-*O*-benzyl-2,6-anhydro-1-deoxy-D-*glycero*-D-*ido*-heptitol-1-yl-β-D-*xylo*-pentofuranosyl]adenine (21′).** A solution of **21** (24 mg, 30 μmol), BzCl (35 μL, 300 μmol), and DMAP (1 mg, 8 μmol) in pyridine (1 mL) was stirred at room temperature for 1 h. The resulting mixture was partitioned between AcOEt (8 mL) and aqueous $NaHCO_3$ (saturated, 6 mL), and the organic layer was washed with aqueous $NaHCO_3$ (saturated, 6 mL) and brine (7 mL), dried (Na_2SO_4), and evaporated. The residue was purified by column chromatography (SiO_2, hexane/AcOEt 2:1) to give **21′** (26 mg, 71% as a white solid): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.48 (s, 1 H, H-2), 8.30 (s, 1 H, H-8), 8.10−7.10 (m, 40 H, Ar), 6.31 (dd, 1 H, H-2′, J = 5.7, 7.7), 6.19 (d, 1 H, H-1′, J = 5.7), 5.28 (dd, 1 H, H-2″, J = 4.9, 7.5), 4.77 (m, 1 H, H-4′), 4.72 (d, 1 H, PhCH_2, J = 11.3), 4.67 (d, 1 H, PhCH_2, J = 11.3), 4.65 (d, 1 H, PhCH_2, J = 11.3), 4.62 (dd, 1 H, H-5′a, J = 3.3, 12.4), 4.52 (m, 2 H, H-1″, PhCH_2), 4.44 (m, 2 H, PhCH_2), 4.41 (dd, 1 H, H-5′b, J = 4.5, 12.4), 3.92 (dd, 1 H, H-3″, J = 7.5, 7.5), 3.82 (m, 1 H, H-5″), 3.75 (dd, 1 H, H-6″a, J = 5.6, 10.6), 3.65 (dd, 1 H, H-4″, J = 7.5, 7.5), 3.62 (dd, 1 H, H-6″b, J = 2.6, 10.6), 3.21 (m, 1 H, H-3′), 2.77 (m, 1 H, 3′-C*Ha*Hb), 2.00 (m, 1 H, 3′-CHa*Hb*); FAB-HRMS calcd for $C_{73}H_{63}N_5O_{13}Na$ 1240.4320 (MNa^+), found 1240.4340. NOE experiments were carried out in $CDCl_3$ at 400 MHz.

***N*^{6}-Dibenzoyl-9-[2-*O*-benzoyl-3-deoxy-3-(3-*O*-benzoyl-4,5,7-tri-*O*-benzyl-2,6-anhydro-1-deoxy-D-*glycero*-D-*gulo*-heptitol-1-yl)-β-D-*xylo*-pentofuranosyl]adenine (22′).** Compound **22′** was prepared from **22** (10 mg, 12 μmol) by the procedure described for the synthesis of **21′**. The resulting residue was purified by column chromatography (SiO_2, hexane/AcOEt 2:1) to give **22′** (13 mg, 89% as a white solid): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.32 (s, 1 H, H-2), 8.19 (s, 1 H, H-8), 7.98−7.06 (m, 40 H, Ar), 6.22 (m, 2 H, H-1′, H-2′), 5.20 (dd, 1 H, H-2″, J = 9.2, 9.2), 4.83 (m, 1 H, H-4′), 4.77 (d, 1 H, PhCH_2, J = 10.8), 4.73 (m, 2 H, H-5′a, PhCH_2), 4.65 (d, 1 H, PhCH_2, J = 11.3), 4.61 (d, 1 H, PhCH_2, J = 11.1), 4.54 (dd, 1 H, H-5′b, J = 5.6, 12.3), 4.51 (d, 1 H, PhCH_2, J = 10.8), 4.46 (s, 2 H, PhCH_2), 3.76 (dd, 1 H, H-3″, J = 9.2, 9.2), 3.72 (dd, 1 H, H-4″, J = 9.2, 9.2), 3.65 (m, 2 H, H-1″, H-6″a), 3.57 (dd, 1 H, H-6″b, J = 5.0, 10.6), 3.48 (m, 1 H, H-5″), 3.19 (m, 1 H, H-3′), 2.11 (m, 1 H, C*Ha*Hb), 1.96 (m, 1 H, CHa*Hb*); FAB-HRMS calcd for $C_{73}H_{63}N_5O_{13}Na$ 1240.4320 (MH^+), found 1240.4310. NOE experiments were carried out in $CDCl_3$ at 400 MHz.

3,4,6-Tri-*O*-*p*-methoxybenzyl-1,2-*O*-(1-methoxyethylidene)-α-D-glucopyranose (26). Compound **26** was prepared from **15**[14] (15.4 g, 42 mmol) by the procedure described for the synthesis of **16** with PMBCl (17.6 mL, 174 mmol) instead of BnBr. The resulting residue was purified by column chromatography (SiO_2, hexane/AcOEt, 4:1−2.5:1) to give **26** (19.3 g, 77% as an oil): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31−6.76 (m, 12 H), 6.60 (m, 1 H), 4.64−4.29 (m, 7 H), 3.84−3.56 (m, 14 H), 3.28 (m, 3 H), 2.04 (m, 3 H); FAB-HRMS calcd for $C_{33}H_{41}O_{10}$ 597.2699 (MH^+), found 597.2675.

Phenyl 3,4,6-Tri-*O*-*p*-methoxybenzyl-1-seleno-β-D-glucopyranoside (27). Compound **27** was prepared from **26** (4.28 g, 7.17 mmol) by the procedure described for the synthesis of **13**. The resulting residue was purified by column chromatography (SiO_2, hexane/AcOEt, 4:1−3:2) to give **27** (3.24 g, 66% as a white solid): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31−6.81 (m, 17 H, Ar), 4.80 (d, 1 H, PhCH_2, J = 11.0), 4.77 (d, 1 H, PhCH_2, J = 11.0), 4.72 (d, 1 H, PhCH_2, J = 11.3), 4.70 (m, 1 H, H-1), 4.54 (d, 1 H, PhCH_2, J = 11.3), 4.45 (m, 2 H, PhCH_2), 3.78 (m, 9 H, 3 x OCH_3), 3.72−3.45 (m, 6 H, H-2, H-3, H-4, H-5, H-6a, H-6b); ^{13}C NMR ($CDCl_3$ 100 MHz) δ 158.96, 158.94, 158.82, 134.80, 130.40, 130.11, 130.01, 129.40, 129.37, 129.11, 128.81, 127.97, 126.60, 113.72, 113.58, 113.53, 85.32, 84.56, 80.40, 76.95, 74.85, 74.57, 73.09, 72.94, 68.45, 55.20; FAB-HRMS calcd for $C_{36}H_{41}O_8Se$ 681.1966 (MH^+), found 681.1968. Anal. Calcd for $C_{36}H_{40}O_8Se$: C, 63.62; H, 5.93. Found: C, 63.46; H, 6.02.

5-*O*-*tert*-Butyldimethylsilyl-3-deoxy-3-methylene-1,2-*O*-(1-methylethylidene)-α-D-*erythro*-pentofuranose (29). After a mixture of $NaOCMe_2Et$ (95%, 2.72 g, 23.5 mmol) and Ph_3PMeBr (8.67 g, 24.3 mmol) in THF (150 mL) was stirred for 2 h, a solution of **28**[19] (2.37 g, 7.83 mmol) in THF (30 mL) was added at − 78 °C, and the reaction mixture was warmed to room temperature over 6 h and stirred for 3 h at the same temperature. After addition of aqueous NH_4Cl (saturated, 10 mL), the reaction mixture was partitioned between Et_2O (300 mL) and H_2O (200 mL), and the organic layer was washed with H_2O (200 mL) and brine (150 mL), dried (Na_2SO_4), and evaporated. The residue was purified by column chromatography (SiO_2, hexane/AcOEt, 5:1) to give **29** (2.16 g, 92% as an oil): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 5.83 (d, 1 H, J = 4.4), 5.40 (m, 1 H), 5.24 (m, 1 H), 4.86 (m, 1 H), 4.73 (m, 1 H), 3.73 (dd, 1 H, J = 4.0, 10.7), 3.65 (dd, 1 H, J = 4.0, 10.7), 1.48 (s, 3 H), 1.37 (s, 3 H), 0.86 (s, 9 H), 0.03 (s, 6 H); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 147.25, 112.12, 111.21, 104.69, 81.76, 80.63, 65.57, 27.51, 27.26, 25.80, −5.37, −5.43; FAB-LRMS *m/z* 301 ($C_{15}H_{29}O_4Si$); FAB-HRMS calcd for $C_{15}H_{29}O_4Si$ 301.1835 (MH^+), found 301.1847.

3-Deoxy-3-methylene-1,2-*O*-(1-methylethylidene)-α-D-*erythro*-pentofuranose (30). A mixture of **29** (15 g, 50 mmol) and TBAF (1 M in THF, 55 mL, 55 mmol) in THF (100 mL) was stirred at room temperature for 1 h and then evaporated. The resulting residue was purified by column chromatography (SiO_2, $CHCl_3$/EtOH, 30:1) to give **30** (8.84 g, 95% as an oil): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.87 (d, 1 H, H-1, J = 4.1), 5.48 (m, 1 H, =C*Ha*Hb), 5.19 (m, 1 H, =CHa*Hb*), 4.92 (dd, 1 H, H-2, J = 0.9, 4.1), 4.83 (m, 1 H, H-4), 3.88 (dd, 1 H, H-5a, J = 2.3, 12.0), 3.67 (dd, 1 H, H-5b, J = 4.7, 12.0), 1.52 (s, 3 H, CH_3), 1.39 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.27, 112.23, 111.85, 104.11, 81.74, 79.92, 63.30, 27.31, 27.04; FAB-

HRMS calcd for $C_9H_{13}O_4$ 185.0814, found 185.0815 [$(M - H)^+$]. Anal. Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 57.78; H, 7.50.

Dimethylsilyl-Tethered Substrate (24). BuLi (1.55 M in hexane, 4.33 mL, 6.71 mmol) was slowly added to a solution of **27** (5.73 g, 6.39 mmol) in THF (100 mL) at −78 °C, and after the resulting mixture was stirred at the same temperature for 5 min, Me_2SiCl_2 (5.43 mL, 44.8 mmol) was added. The mixture was warmed to room temperature over 6 h, and the solvent was removed with argon stream. After the resulting oil was dried in vacuo at room temperature for 5 h, a solution of **30** (1.43 g, 7.68 mmol) in THF (10 mL) and Et_3N (3.56 mL, 25.5 mmol) was added to a solution of the residue in THF (90 mL) at 0 °C, and the mixture was stirred at room temperature for 2 h. The resulting mixture was partitioned between Et_2O (400 mL) and aqueous $NaHCO_3$ (saturated, 300 mL), and the organic layer was washed with aqueous $NaHCO_3$ (saturated, 300 mL) and brine (200 mL), dried (Na_2SO_4), and evaporated. The resulting residue was purified by flash column chromatography (SiO_2, hexane/AcOEt, 3.5:1) to give **24** (3.95 g, 67% as an oil): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.66−6.77 (m, 17 H, Ar), 5.82 (d, 1 H, H-1, J = 4.1), 5.36 (m, 1 H, C*Ha*Hb), 5.16 (m, 1 H, CHa*Hb*), 4.81 (m, 5 H, H-2, H-4, H-1′, PhCH_2), 4.65−4.43 (m, 4 H, PhCH_2), 3.93 (dd, 1 H, H-5a, J = 3.8, 11.2), 3.80−3.73 (m, 10 H, H-5b, 3 x OCH_3), 3.71 (dd, 1 H, H-6′a, J = 1.8, 11.0), 3.66 (dd, 1 H, H-6′b, J = 4.5, 11.0), 3.59 (dd, 1 H, H-4′, J = 9.5, 9.5), 3.48 (m, 1 H, H-2′), 3.47 (dd, 1 H, H-3′, J = 9.5, 9.5), 3.42 (m, 1 H, H-5′), 1.47 (s, 3 H, CH_3), 1.37 (s, 3 H, CH_3), 0.49 (s, 3 H, $SiCH_3$), 0.13 (s, 3 H, $SiCH_3$); FAB-HRMS calcd for $C_{47}H_{58}O_{12}SeSiNa$ 945.2760 (MNa^+), found 945.2824. Anal. Calcd for $C_{47}H_{58}O_{12}SeSi$: C, 61.23; H, 6.34. Found: C, 61.08; H, 6.44.

3-Deoxy-3-(4,5,7-tri-*O*-*p*-methoxybenzyl-2,6-anhydro-1-deoxy-D-*glycero*-D-*ido*-heptitol-1-yl)-1,2-*O*-(1-methylethylidene)-α-D-*ribo*-pentofuranose (25) and 3-Deoxy-3-(4,5,7-tri-*O*-*p*-methoxybenzyl-2,6-anhydro-1-deoxy-D-*glycero*-D-*gulo*-heptitol-1-yl)-1,2-*O*-(1-methylethylidene)-α-D-*ribo*-pentofuranose (31), and 1-Deoxy-3,4,6-tri-*O*-*p*-methoxybenzyl-D-glucopyranose (32). To a solution of **24** (100 mg, 108 μmol) in benzene (15 mL) was added a solution of Bu_3SnH (58 μL, 216 μmol) and AIBN (9 mg, 55 μmol) in benzene (5 mL) slowly over 1.2 h at 80 °C, and then the resulting mixture was evaporated. A mixture of the resulting residue and TBAF (1 M in THF, 270 μL, 270 μmol) was stirred at room temperature for 1 h and evaporated. The residue was purified by column chromatography (SiO_2, $CHCl_3$/AcOEt, 2.5:1−1:4) to give **32** (14 mg, 25% as a solid) and a mixture of **25** and **31** (55 mg, 72% as an oil, **25**/**31** = 70:30). From the mixture, **25** (38 mg, 50%) and **31** (16 mg, 22%) were obtained in a pure form by flash column chromatography (SiO_2, hexane/AcOEt 5:1−2:1). For **25**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.28−6.81 (m, 12 H, Ar), 5.74 (d, 1 H, H-1, J = 3.6), 4.65 (dd, 1 H, H-2, J = 4.1, 4.1), 4.60 (d, 1 H, PhCH_2, J = 11.3), 5.69−4.40 (m, 5 H, PhCH_2), 4.04 (m, 1 H, H-1′), 3.93 (m, 1 H, H-5′), 3.89−3.83 (m, 3 H, H-4, H-6′a, H-6′b), 3.82 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3), 3.79 (s, 3 H, OCH_3), 3.69 (dd, 1 H, H-3′, J = 5.6, 5.6), 3.65 (m, 2 H, H-2′, H-5a), 3.50 (dd, 1 H, H-5b, J = 4.0, 10.4), 3.46 (dd, 1 H, H-4′, J = 5.6, 5.6), 2.93 (m, 1 H, 2′-OH), 2.16 (m, 1 H, H-3), 1.77 (m, 2 H, CH_2), 1.48 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.23, 159.18, 159.10, 129.96, 129.70, 129.55, 129.51, 129.28, 129.23, 113.84, 113.74, 113.68, 111.43, 104.89, 82.58, 82.38, 81.45, 81.27, 74.82, 73.28, 72.85, 72.73, 70.13, 69.95, 61.35, 55.45, 55.44, 55.40, 55.29, 55.25, 55.11, 39.88, 26.99, 26.91, 26.55, 23.46; FAB-HRMS calcd for $C_{39}H_{50}O_{12}Na$ 733.3200 (MNa^+), found 733.3187. Anal. Calcd for $C_{39}H_{50}O_{12}\cdot H_2O$: C, 64.27; H, 7.19. Found: C, 64.27; H, 7.21. For **31**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.29−6.81 (m, 12 H, Ar), 5.78 (d, 1 H, H-1, J = 3.2), 4.87 (m, 1 H, PhCH_2), 4.71 (m, 2 H, PhCH_2), 4.66 (dd, 1 H, H-4, J = 3.2, 3.2), 4.56−4.35 (m, 4 H, PhCH_2, H-5a), 3.84 (m, 3 H, H-2, H-5a, H-6′a), 3.78 (m, 9 H, 3 x OCH_3), 3.59 (m, 2 H, H-5′, H-6′a), 3.49 (m, 1 H, H-4′), 3.42 (m, 1 H, 2-OH), 3.41 (m, 1 H, H-3′), 3.29 (m, 1 H, H-2′), 3.24 (m, 1 H, H-1′), 2.29 (m, 1 H, H-3), 1.90 (m, 2 H, CH_2), 1.48 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3); FAB-HRMS calcd for $C_{39}H_{50}O_{12}Na$ 733.3200 (MNa^+), found 733.3245. For **32**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.29−6.81 (m, 12 H, Ar), 4.89 (m, 1 H, PhCH_2), 4.69 (m, 2 H, PhCH_2), 4.56 (m, 1 H, PhCH_2), 4.43 (m, 2 H, PhCH_2), 4.00 (dd, 1 H, H-1a, J = 5.3, 11.1), 3.80 (s, 3 H, OCH_3), 3.79 (s, 3 H, OCH_3), 3.78 (s, 3 H, OCH_3), 3.65 (m, 3 H, H-2, H-6a, H-6b), 3.52 (dd, 1 H, H-4, J = 9.3, 9.3), 3.39 (dd, 1 H, H-3, J = 9.3, 9.3), 3.36 (m, 1 H, H-5), 3.18 (dd, 1 H, H-1b, J = 11.1, 11.1), 2.07 (s, 1 H, 2-OH); FAB-HRMS calcd for $C_{30}H_{36}O_8Na$ 547.2308 (MNa^+), found 547.2287.

One-Pot Procedure for the Synthesis of 25 from 27 and 30. From **27** (800 mg, 1.34 mmol) and **30** (274 mg, 1.47 mmol) by the one-pot procedure described for the synthesis of **21** and **22**, **25** (472 mg, 50%), **31** (153 mg, 16%), and **32** (77 mg, 11%) were obtained, after purification by flash column chromatography (SiO_2, hexane/AcOEt 2.5:1−2:1−1:2).

5-*O*-Benzoyl-3-deoxy-3-(3-*O*-benzoyl-4,5,7-tri-*O*-*p*-methoxybenzyl-2,6-anhydro-1-deoxy-D-*glycero*-D-*ido*-heptitol-1-yl)-1,2-*O*-(1-methylethylidene)-α-D-*ribo*-pentofuranose (25′). A solution of **25** (206 mg, 290 μmol), Bz_2O (262 mg, 1.16 mmol), DMAP (3.5 mg, 29 μmol), and Et_3N (162 μL, 1.16 mmol) in CH_3CN (3 mL) was stirred at room temperature for 30 min. The resulting mixture was partitioned between AcOEt (25 mL) and aqueous $NaHCO_3$ (saturated, 20 mL), and the organic layer was washed with aqueous $NaHCO_3$ (saturated, 20 mL) and brine (20 mL), dried (Na_2SO_4), and evaporated. The residue was purified by column chromatography (SiO_2, hexane/AcOEt 2:1) to give **25′** (213 mg, 81% as a white solid): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.00 (m, 4 H, Ar), 7.60−7.32 (m, 6 H, Ar), 7.25−7.00 (m, 6 H, Ar), 6.90−6.70 (m, 6 H, Ar), 5.75 (d, 1 H, H-1, J = 3.7), 5.31 (dd, 1 H, H-2′, J = 5.5, 8.6), 4.67 (m, 4 H, H-2, PMB-CH_2), 4.51 (m, 1 H, H-5a), 4.50 (d, 1 H, PMB-CH_2, J = 11.3), 4.44 (m, 2 H, H-1′, H-5b), 4.37 (d, 1 H, PMB-CH_2, J = 10.6), 4.32 (d, 1 H, PMB-CH_2, J = 11.7), 4.09 (ddd, 1 H, H-4, J = 2.8, 4.5, 10.2), 3.88 (dd, 1 H, H-3′, J = 8.0, 8.0), 3.79 (s, 3 H, OCH_3), 3.77 (s, 3 H, OCH_3), 3.73 (s, 3 H, OCH_3), 3.67 (m, 2 H, H-4′, H-5′), 3.64 (m, 1 H, H-6′a), 3.48 (d, 1 H, H-6′b, J = 9.9), 2.14 (m, 1 H, H-3), 1.93 (m, 1 H, 3-C*Ha*Hb), 1.83 (m, 1 H, 3-CHa*Hb*), 1.21 (s, 3 H, CH_3), 1.15 (s, 3 H, CH_3); FAB-HRMS calcd for $C_{53}H_{58}O_{14}Na$ 941.3724 (MNa^+), found 941.3728. Anal. Calcd for $C_{53}H_{58}O_{14}$: C, 69.27; H, 6.36. Found: C, 69.07; H, 6.50. GOESY spectrum was measured in $CDCl_3$ at 400 MHz.

5-*O*-Benzoyl-3-deoxy-3-(3-*O*-benzoyl-4,5,7-tri-*O*-*p*-methoxybenzyl-2,6-anhydro-1-deoxy-D-*glycero*-D-*gulo*-heptitol-1-yl)-1,2-*O*-(1-methylethylidene)-α-D-*ribo*-pentofuranose (31′). Compound **31′** was prepared from **31** (202 mg, 284 μmol) by the procedure described for the synthesis of **25′**. The resulting residue was purified by column chromatography (SiO_2, hexane/AcOEt 2:1) to give **31′** (204 mg, 78% as a white solid): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.00 (m, 4 H, Ar), 7.55 (m, 2 H, Ar), 7.42 (m, 4 H, Ar), 7.22 (d, 2 H, Ar), 7.05 (m, 4 H, Ar), 6.84 (m, 4 H, Ar), 6.61 (m, 2 H, Ar), 5.75 (d, 1 H, H-1, J = 3.6), 5.13 (dd, 1 H, H-2′, J = 9.4, 9.4), 4.72 (dd, 1 H, H-2, J = 3.9, 3.9), 4.67 (m, 2 H, PMB-CH_2), 4.55 (dd, 1 H, H-5a, J = 2.0, 12.2), 4.53 (d, 1 H, PMB-CH_2, J = 10.9), 4.50−4.36 (m, 3 H, PMB-CH_2), 4.27 (dd, 1 H, H-5b, J = 5.3, 12.4), 4.11 (m, 1 H, H-4), 3.79 (s, 3 H, OCH_3), 3.78 (s, 3 H, OCH_3), 3.73 (m, 1 H, H-6′a), 3.72 (dd, 1 H, H-3′, J = 9.2, 9.2), 3.68 (s, 3 H, OCH_3), 3.63 (dd, 1 H, H-4′, J = 9.2, 9.2), 3.59 (m, 1 H, H-6′b), 3.55 (ddd, 1 H, H-1′, J = 3.0, 9.3, 9.3), 3.46 (m, 1 H, H-5′), 2.13 (m, 1 H, H-3), 2.03 (ddd, 1 H, 3-C*Ha*Hb J = 9.2, 9.2, 13.5), 1.72 (ddd, 1 H, 3-CHa*Hb*, J = 3.2, 3.2, 14.6), 1.38 (s, 3 H, CH_3), 1.23 (s, 3 H, CH_3); FAB-HRMS calcd for $C_{53}H_{58}O_{14}Na$ 941.3724 (MNa^+), found 941.3713. Anal. Calcd for $C_{53}H_{58}O_{14}$: C, 69.27; H, 6.36. Found: C, 69.21; H, 6.42. GOESY spectrum was measured in $CDCl_3$ at 400 MHz.

5-*O*-Benzyl-3-deoxy-3-(3-*O*-benzyl-4,5,7-tri-*O*-*p*-methoxybenzyl-2,6-anhydro-1-deoxy-D-*glycero*-D-*ido*-heptitol-1-yl)-1,2-*O*-(1-methylethylidene)-α-D-*ribo*-pentofuranose (33). A suspension of **25** (1.07 g, 1.5 mmol) and NaH (60%, 288 mg, 7.2 mmol) in THF/DMF/HMPA (7 mL/7 mL/1 mL) prepared at 0 °C was stirred at room temperature for 30 min. BnBr (568 μL, 4.8 mmol) was added to the mixture at 0 °C, and the resulting mixture was stirred at room temperature for 3 h. After addition of MeOH (500 μL) at 0 °C, the mixture

was partitioned between AcOEt (100 mL) and H_2O (70 mL), and the organic layer was washed with H_2O (70 mL, twice) and brine (70 mL), dried (Na_2SO_4), and evaporated. The residue was purified by column chromatography (SiO_2, hexane/AcOEt 2:1) to give **33** (958 mg, 71% as a white solid): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.35−7.18 (m, 15 H, Ar), 7.02 (m, 2 H, Ar), 6.87−6.80 (m, 5 H, Ar), 5.83 (d, 1 H, H-1, J = 3.7), 4.85−4.48 (m, 9 H, PhCH_2), 4.37 (m, 3 H, H-2, H-1′, PhCH_2), 4.00 (m, 1 H, H-4), 3.81 (s, 3 H, OCH_3), 3.78 (s, 3 H, OCH_3), 3.76 (s, 3 H, OCH_3), 3.75−3.46 (m, 8 H, H-5a, H-5b, H-2′, H-3′, H-4′, H-5′, H-6′a, H-6′b), 2.17 (m, 1 H, H-3), 1.93 (m, 1 H, 3-C*Ha*Hb), 1.75 (m, 1 H, 3-CHa*Hb*), 1.51 (s, 3 H, CH_3), 1.33 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.90, 158.88, 158.84, 137.84, 137.76, 130.76, 130.18, 129.68, 129.40, 129.29, 128.14, 127.85, 127.59, 127.41, 127.31, 113.50, 111.05, 104.95, 104.68, 82.06, 80.70, 80.48, 80.37, 80.06, 79.72, 79.59, 77.51, 75.20, 75.16, 74.74, 73.42, 73.33, 72.94, 72.79, 72.60, 71.56, 71.04, 69.08, 68.07, 55.45, 55.37, 55.30, 55.28, 55.20, 55.12, 55.04, 54.94, 40.32, 26.78, 26.69, 26.45, 26.40, 19.87; FAB-HRMS calcd for $C_{53}H_{62}O_{12}Na$ 913.4139 (MNa^+), found 913.4178. Anal. Calcd for $C_{53}H_{62}O_{12}$: C, 71.44; H, 7.01. Found: C, 71.46; H, 7.11.

5-*O*-Benzyl-1,2-di-*O*-acetyl-3-deoxy-3-(3-*O*-benzyl-4,5,7-tri-*O*-acetyl-2,6-anhydro-1-deoxy-D-*glycero*-D-*ido*-heptitol-1-yl)-α,*β*-D-*ribo*-pentofuranose (34). A solution of **33** (1.7 g, 1.9 mmol) in aqueous TFA (80%, 10 mL) was stirred at room temperature for 3 h and then evaporated. The residue was purified by column chromatography (SiO_2, $CHCl_3$/MeOH 50:1−4:1) to give an oil. A mixture of the oil obtained and NaOMe (28% in MeOH, 760 μL) in MeOH (10 mL) was stirred at room temperature for 30 min and then neutralized with Diaion WK 20 (H^+ form). The resin was filtered off, and the filtrate was evaporated. A solution of the resulting residue, Ac_2O (1.4 mL, 14.8 mmol), Et_3N (2.12 mL, 15 mmol), and DMAP (23 mg, 0.19 mmol) in MeCN (20 mL) was stirred at room temperature for 1 h. The reaction mixture was partitioned between AcOEt (200 mL) and aqueous $NaHCO_3$ (saturated, 150 mL), and the organic layer was washed with aqueous $NaHCO_3$ (saturated, 150 mL), H_2O (150 mL), and brine (100 mL), dried (Na_2SO_4), and evaporated. The residue was purified by column chromatography (SiO_2, hexane/AcOEt, 2:1) to give **34** (932 mg, 70% as a white solid): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.37−7.23 (m, 10 H, Ar), 6.36 (d, 0.26 H, H-1α, J = 4.0), 6.09 (s, 0.74 H, H-1β,), 5.40 (dd, 0.26 H, H-2, J = 4.0, 6.8), 5.32 (d, 0.74 H, H-2, J = 4.4), 5.25 (dd, 1 H, H-3′, J = 9.3, 9.3), 4.89 (m, 1 H, H-4′), 4.64−4.48 (m, 4 H, PhCH_2), 4.26−4.48 (m, 3 H, H-4, H-5a, H-1′), 3.94 (m, 1 H, H-5b), 3.77−3.57 (m, 3 H, H-2′, H-5′, H-6′a, H-6′b), 2.64−2.48 (m, 1 H, H-3), 2.07−1.78 (m, 17 H, 5 × Ac, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.28, 170,21, 169.99, 169.68, 169.56, 169.49, 169.16, 169.02, 155.26, 137.68, 137.59, 137.34, 132.72, 130.78, 129.60, 128.32, 127.85, 127.80, 127.64, 127.57, 127.50, 127.22, 113.42, 110.08, 98.98, 95.31, 82.73, 82.19, 77.20, 76.05, 73.53, 73.33, 72.58, 72.36, 72.29, 71.70, 71.45, 70.17, 68.84, 68.50, 68.21, 62.19, 55.11, 37.92, 34.90, 29.47, 21.39, 20.94, 20.76, 20.63, 20.47, 20.29, 20.22, 19.86; FAB-HRMS calcd for $C_{36}H_{44}O_{14}Na$ 723.2628 (MNa^+), found 723.2632. Anal. Calcd for $C_{36}H_{44}O_{14}$: C, 61.71; H, 6.33. Found: C, 61.66; H, 6.38.

***N*^{6}-Benzoyl-9-[5-*O*-benzyl-3-deoxy-3-(3-*O*-benzyl-4,5,7-tri-*O*-acetyl-2,6-anhydro-1-deoxy-D-*glycero*-D-*ido*-heptitol-1-yl)-*β*-D-*ribo*-pentofuranosyl]adenine (35).** A suspension of N^6-benzoyladenine (343 mg, 1.43 mmol) in HMDS/pyridine (4 mL/2 mL) was heated under reflux for 1 h. The resulting clear solution was evaporated and azeotroped with toluene (three times). To a mixture of the resulting residue and **34** (251 mg, 358 μmol) in CH_3CN (4 mL) was added $SnCl_4$ (209 μL, 1.79 mmol) at 0 °C, and the mixture was stirred at room temperature for 12 h. The resulting mixture was partitioned between AcOEt (60 mL) and aqueous HCl (1 M, 50 mL), and the organic layer was washed with aqueous HCl (1 M, 50 mL), H_2O (50 mL), aqueous $NaHCO_3$ (saturated, 50 mL), and brine (50 mL), dried (Na_2SO_4), and evaporated. The residue was purified by column chromatography (SiO_2, $CHCl_3$/EtOH, 60:1) to give **35** (265 mg, 78% as a white amorphous solid): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.07 (br s, 1 H, NH), 8.81 (s, 1 H, H-2), 8.51 (s, 1 H, H-8), 8.03 (d, 2 H, Ar, J = 7.6), 7.62−7.23 (m, 13 H, Ar), 6.23 (s, 1 H, H-1′), 5.73 (d, 1 H, H-2′, J = 4.6), 5.27 (dd, 1 H, H-3″, J = 9.1, 9.1), 4.86 (dd, 1 H, H-4″, J = 9.1, 9.1), 4.67−4.47 (m, 4 H, PhCH_2), 4.22 (m, 2 H, H-4′, H-1″), 4.14 (dd, 1 H, H-5′a, J = 4.5, 12.4), 3.94 (dd, 1 H, H-6″a, J = 1.9, 11.3), 3.81 (dd, 1H, H-5′b, J = 1.8, 12.4), 3.74 (m, 2 H, H-5″, H-6″b), 3.68 (dd, 1 H, H-2″, J = 5.8, 9.4), 2.99 (m, 1 H, H-3′), 2.04 (s, 3 H, Ac), 2.02 (s, 3 H, Ac), 2.00 (s, 3 H, Ac), 1.96 (s, 3 H, Ac), 1.89 (m, 1 H, 3′-C*Ha*Hb), 1.75 (m, 1 H, 3′-CHa*Hb*); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.05, 169.87, 169.18, 169.15, 164.27, 152.30, 150.68, 149.11, 140.87, 136.98, 136.70, 133.33, 132.31, 128.42, 128.36, 128.25, 128.15, 127.87, 127.69, 127.57, 127.51, 127.13, 122.96, 88.64, 83.19, 77.14, 77.05, 75.66, 73.59, 72.58, 71.37, 71.12, 68.60, 68.49, 67.93, 61.78, 36.14, 20.79, 20.65, 20.60, 20.50, 19.56; FAB-HRMS calcd for $C_{46}H_{50}N_5O_{13}$ 880.3404 (MH^+), found 880.3488. Anal. Calcd for $C_{46}H_{49}N_5O_{13}\cdot 0.5H_2O$: C, 62.15; H, 5.67; N, 7.88. Found: C, 62.17; H, 5.72; N, 7.81.

1-[5-*O*-Benzyl-3-deoxy-3-(3-*O*-benzyl-4,5,7-tri-*O*-acetyl-2,6-anhydro-1-deoxy-D-*glycero*-D-*ido*-heptitol-1-yl)-*β*-D-*ribo*-pentofuranosyl]uracil (36). A suspension of uracil (56 mg, 500 μmol) and $(NH_4)_2SO_4$ (2 mg, 15 μmol) in HMDS (3 mL) was heated under reflux for 30 min. The resulting clear solution was evaporated and azeotroped with toluene (three times). To a mixture of the resulting residue and **34** (50 mg, 71 μmol) in CH_3CN (2 mL) was added TMSOTf (90 μL, 497 μmol) at 0 °C, and the mixture was stirred at room temperature for 4 h. The reaction mixture was partitioned between AcOEt (40 mL) and aqueous HCl (1 M, 30 mL), and the organic layer was washed with aqueous HCl (1 M, 30 mL), H_2O (30 mL), aqueous $NaHCO_3$ (saturated, 30 mL), and brine (20 mL), dried (Na_2SO_4), and evaporated. The residue was purified by column chromatography (SiO_2, $CHCl_3$/AcOEt 1:1) to give **36** (52 mg, 98% as a white amorphous): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.12 (br s, 1 H, NH), 7.96 (d, 1 H, H-6, J = 8.2), 7.45−7.20 (m, 10 H, Ar), 5.82 (s, 1 H, H-1′), 5.49 (d, 1 H, H-2′, J = 4.7), 5.35 (dd, 1 H, H-5, J = 2.1, 8.2), 5.25 (dd, 1 H, H-3″, J = 8.8, 8.8), 4.86 (dd, 1 H, H-4″, J = 8.8, 8.8), 4.61−4.48 (m, 4 H, PhCH_2), 4.26 (m, 2 H, H-1″, H-6″a), 4.05 (m, 2 H, H-4′, H-6″b), 3.74 (m, 3 H, H-5′a, H-5′b, H-5″), 3.64 (dd, 1 H, H-2″, J = 5.6, 8.8), 2.56 (m, 1 H, H-3′), 2.05 (s, 3 H, Ac), 2.01 (s, 3 H, Ac), 1.94 (s, 3 H, Ac), 1.91 (s, 3 H, Ac), 1.79 (m, 1 H, 3′-C*Ha*Hb), 1.54 (m, 1 H, 3′-CHa*Hb*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.42, 170.39, 169.65, 169.22, 163.23, 149.94, 139.83, 137.41, 137.00, 139.83, 137.41, 137.00, 128.79, 128.52, 128.47, 128.00, 127.90, 127.58, 101.51, 89.88, 83.45, 76.96, 75.64, 73.98, 72.65, 71.16, 70.91, 69.00, 68.73, 67.82, 61.67, 60.39, 35.57, 35.57, 29.68, 20.85, 20.75, 20.60, 20.49, 19.83; FAB-HRMS calcd for $C_{38}H_{45}N_2O_{14}$ 753.2870 (MH^+), found 753.2866. Anal. Calcd for $C_{38}H_{44}N_2O_{14}$: C, 60.63; H, 5.89; N, 3.72. Found: C, 60.71; H, 6.06; N, 3.55.

***N*^{6}-Benzoyl-9-[5-*O*-benzyl-3-deoxy-3-(3-*O*-benzyl-7-*O*-trityl-2,6-anhydro-1-deoxy-D-*glycero*-D-*ido*-heptitol-1-yl)-*β*-D-*ribo*-pentofuranosyl]adenine (37).** A solution of **35** (224 mg, 255 μmol) and NaOMe (28% in MeOH, 102 μL, 510 μmol) in MeOH (2 mL) was stirred at 0 °C for 50 min and then neutralized with Diaion WK 20 (H^+ form). The resin was filtered off, and the filtrate was evaporated. A mixture of the resulting residue and TrCl (355 mg, 1.27 mmol) in pyridine (2 mL) was stirred at 50 °C for 1 h. The reaction mixture was partitioned between AcOEt (40 mL) and H_2O (30 mL), and the organic layer was washed with aqueous HCl (1 M, 30 mL), H_2O (30 mL), aqueous $NaHCO_3$ (saturated, 30 mL), and brine (20 mL), dried (Na_2SO_4), and evaporated. The residue was purified by column chromatography (SiO_2, $CHCl_3$/EtOH 30:1) to give **37** (235 mg, 97% as a white amorphous solid): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.03 (br s, 1 H), 8.76 (s, 1H), 8.50 (s, 1 H), 7.86 (d, 2 H, J = 7.6), 7.62−7.16 (m, 28 H), 6.14 (s, 1 H), 4.67 (m, 2 H), 4.53 (m, 3 H), 4.32 (d, 1 H, J = 10.0), 4.27 (m, 1 H), 3.87 (m, 1 H), 3.68 (dd, 1 H, J = 9.1, 9.1), 3.62 (dd, 1 H, J = 2.8, 11.0), 3.53 (m, 2 H), 3.45 (dd, 1 H, J = 9.1, 9.1), 3.22 (d, 2 H, J = 3.8), 2.61 (m, 1 H), 2.00 (m, 1 H), 1.72 (m, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.12, 151.69, 149.56, 149.07, 143.24, 140.79, 137.12, 137.03, 133.28, 132.36, 128.66, 128.40, 128.28, 128.13, 127.75, 127.62, 127.57, 127.43, 127.34, 126.72, 124.93, 122.79, 91.85, 86.46, 84.13, 78.57, 77.06, 73.12, 72.87,

72.20, 71.64, 71.51, 71.23, 67.98, 64.24, 37.11, 19.64; FAB-HRMS calcd for $C_{57}H_{56}N_5O_9$ 954.4077 (MH^+), found 954.4094. Anal. Calcd for $C_{57}H_{55}N_5O_9 \cdot H_2O$: C, 70.43; H, 5.91; N, 7.20. Found: C, 70.80; H, 6.00; N, 7.00.

1-[5-*O*-Benzyl-3-deoxy-3-(3-*O*-benzyl-7-*O*-trityl-2,6-anhydro-1-deoxy-D-*glycero*-D-*ido*-heptitol-1-yl)-*β*-D-*ribo*-pentofuranosyl]uracil (38). Compound **38** was prepared from **36** (47 mg, 71 μmol) by the procedure described for the synthesis of **37**. The resulting residue was purified by column chromatography (SiO_2, $CHCl_3$/EtOH 20:1) to give **38** (47 mg, 92% as a white solid): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 10.40 (br s, 1 H), 7.92 (d, 1 H, J = 8.1), 7.37−7.15 (m, 25 H), 5.77 (s, 1 H), 4.92 (d, 1 H, J = 8.1), 4.59 (m, 2 H), 4.44 (m, 2 H), 4.36 (m, 1 H), 4.34 (m, 1 H), 4.23 (d, 1 H, J = 10.9), 3.89 (m, 1 H), 3.69 (dd, 1 H, J = 8.9, 8.9), 3.57 (m, 4 H), 3.21 (d, 1 H, J = 2.6), 2.30 (m, 1 H), 1.97 (m, 1 H), 1.62 (m, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.87, 151.13, 143.93, 140.07, 137.88, 137.52, 137.16, 128.77, 128.71, 128.60, 128.27, 128.10, 127.78, 127.19, 101.38, 92.84, 86.56, 84.30, 79.08, 77.47, 76.39, 73.57, 73.49, 72.52, 71.91, 71.48, 71.03, 68.28, 63.87, 49.42, 49.25, 49.07, 36.75, 19.24; FAB-HRMS calcd for $C_{49}H_{50}N_2O_{10}Na$ 849.3363 (MNa^+), found 849.3387. Anal. Calcd for $C_{49}H_{50}N_2O_{10} \cdot H_2O$: C, 69.65; H, 6.20; N, 3.32. Found: C, 69.33; H, 6.30; N, 3.20.

***N*^{6}-Benzoyl-9-[5-*O*-benzyl-3-deoxy-3-[3-*O*-benzyl-7-*O*-trityl-4,5-bis-*O*-(*o*-xyloxyphosphoryl)-2,6-anhydro-1-deoxy-D-*glycero*-D-*ido*-heptitol-1-yl]-2-*O*-(*o*-xyloxyphosphoryl)-*β*-D-*ribo*-pentofuranosyl]adenine (39).** XEPA (239 μL, 1.11 mmol) was added to a mixture of **37** (235 mg, 246 μmol) and 1*H*-tetrazole (121 mg, 1.73 mmol) in CH_2Cl_2 (4 mL) at 0 °C, and the mixture was stirred at room temperature for 20 min. After addition of H_2O (40 μL), the mixture was stirred at room temperature for 10 min. The resulting mixture was cooled to −40 °C, and *m*-CPBA (299 mg, 1.73 mmol) was added. The mixture was warmed to room temperature over 20 min. The reaction mixture was partitioned between AcOEt (40 mL) and aqueous Na_2SO_3 (saturated, 30 mL), and the organic layer was washed with H_2O (30 mL), aqueous $NaHCO_3$ (saturated, 30 mL), and brine (20 mL), dried (Na_2SO_4), and evaporated. The residue was purified by column chromatography (SiO_2, $CHCl_3$/acetone 5:1) to give **39** (345 mg, 92% as a white amorphous): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.93 (br s, 1 H, NH), 8.60 (s, 1 H, H-2), 8.31 (s, 1 H, H-8), 7.99 (m, 2 H), 7.63−7.04 (m, 40 H), 6.44 (s, 1 H, H-1′), 5.51−3.21 (m, 27 H, 6 × XEP-CH_2, 2 × PhCH_2, H-2′, H-4′, H-5′a, H-5′b, H-1″, H-2″, H-3″, H-4″, H-5″, H-6″a, H-6″b), 2.90 (m, 1 H, H-3′), 2.01 (m, 2 H, 3′-CH_2); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.83, 152.26, 150.23, 148.84, 143.84, 143.04, 140.65, 137.27, 136.86, 135.04, 134.80, 134.70, 134.66, 134.55, 134.38, 133.47, 132.31, 129.12, 129.07, 128.94, 128.86, 128.52, 128.48, 128.41, 128.34, 128.27, 128.17, 128.13, 127.98, 127.42, 127.20, 127.15, 127.11, 126.49, 122.40, 88.60, 86.48, 82.95, 82.31, 82.24, 78.69, 77.11, 74.75, 73.19, 72.30, 70.77, 70.73, 70.51, 69.28, 68.78, 68.70, 68.59, 68.51, 68.45, 68.35, 68.28, 68.10, 68.01, 67.94, 67.63, 67.57, 62.29, 53.70, 39.02, 38.98, 37.12, 37.05, 31.64, 29.17, 19.74, 14.00, 13.98; ^{31}P NMR($CDCl_3$, 67.5 MHz) δ 0.57, −0.92, −1.13; FAB-HRMS calcd for $C_{81}H_{77}N_5O_{18}P_3$ 1500.4477 (MH^+), found 1500.4460. Anal. Calcd for $C_{81}H_{76}N_5O_{18}P_3 \cdot H_2O$: C, 64.07; H, 5.18; N, 4.61. Found: C, 63.88; H, 5.51; N, 4.62.

1-[5-*O*-Benzyl-3-deoxy-3-[3-*O*-benzyl-7-*O*-trityl-4,5-bis-*O*-(*o*-xyloxyphosphoryl)-2,6-anhydro-1-deoxy-D-*glycero*-D-*ido*-heptitol-1-yl]-2-*O*-(*o*-xyloxyphosphoryl)-*β*-D-*ribo*-pentofuranosyl]uracil (41). Compound **41** was prepared from **38** (28 mg, 34 μmol) by the procedure described for the synthesis of **39**. The resulting residue was purified by column chromatography (SiO_2, $CHCl_3$/EtOH 40:1) to give **41** (39 mg, 84% as a white solid): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.91 (br s, 1 H, NH), 7.63 (d, 1 H, H-6, J = 8.2), 7.49−7.12 (m, 37 H, Ar), 6.11 (s, 1 H, H-1′), 5.48−3.21 (m, 28 H, 6 × XEP-CH_2, 2 × PhCH_2, H-5, H-27, H-4′, H-5′a, H-5′b, H-1″, H-2″, H-3″, H-4″, H-5″, H-6″a, H-6″b), 2.50 (m, 1 H, H-3′), 1.98 (m, 2 H, 3′-CH_2); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 162.58, 149.96, 143.59, 139.25, 138.03, 137.27, 135.49, 135.27, 135.12, 135.07, 134.89, 134.87, 129.42, 129.15, 128.96, 128.88, 128.83, 128.78, 128.70, 128.64, 128.59, 128.54, 128.50, 128.36, 128.25, 128.01, 127.90, 127.73, 127.48, 127.41, 127.07, 101.78, 89.63, 86.69, 82.99, 82.11, 79.06, 77.65, 77.26, 75.32, 73.45, 72.34, 70.79, 70.27, 68.97, 68.92, 68.83, 68.78, 68.70, 68.50, 68.22, 68.17, 67.84, 62.39, 39.18, 36.91, 19.47, 14.05; ^{31}P NMR ($CDCl_3$, 67.5 MHz) δ -0.71, −1.03, 1.20; UV (MeOH) λ_{max} 280 nm; FAB-HRMS calcd for $C_{72}H_{72}N_2O_{19}P_3$ 1373.3942 (MH^+), found 1373.3860. Anal. Calcd for $C_{73}H_{71}N_2O_{19}P_3 \cdot H_2O$: C, 63.02; H, 5.29; N, 2.01. Found: C, 62.97; H, 5.48; N, 2.51.

9-[5-*O*-Benzyl-3-deoxy-3-[3-*O*-benzyl-7-*O*-trityl-4,5-bis-*O*-(*o*-xyloxyphosphoryl)-2,6-anhydro-1-deoxy-D-*glycero*-D-*ido*-heptitol-1-yl]-2-*O*-(*o*-xyloxyphosphoryl)-*β*-D-*ribo*-pentofuranosyl]adenine (40). A mixture of **39** (17 mg, 11 μmol) in aqueous NH_3 (25%)/dioxane (1 mL/1 mL) was stirred at room temperature for 7 h and then evaporated. The resulting residue was purified by column chromatography (SiO_2, $CHCl_3$/EtOH 30:1) to give **40** (14 mg, 89% as a white amorphous): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.07 (s, 1 H, H-2), 8.00 (s, 1 H, H-8), 7.82−7.03 (m, 37 H, Ar), 6.33 (s, 1 H, H-1′), 5.54 (br s, 2 H, NH_2), 5.50−3.24 (m, 27 H, 6 × XEP-CH_2, 2 × PhCH_2, H-2′, H-4′, H-5′a, H-5′b, H-1″, H-2″, H-3″, H-4″, H-5″, H-6″a, H-6″b), 3.00 (m, 1 H, H-3′), 2.03 (m, 2 H, 3′-CH_2); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.03, 155.02, 152.55, 148.80, 143.08, 138.23, 137.37, 137.12, 135.04, 134.75, 134.64, 134.61, 134.43, 133.14, 131.39, 129.01, 128.93, 128.80, 128.71, 128.57, 128.49, 128.41, 128.34, 128.28, 128.19, 128.10, 128.02, 127.93, 127.29, 127.24, 127.14, 127.05, 127.01, 126.52, 119.44, 88.83, 86.53, 82.80, 82.36, 82.31, 78.72, 77.32, 77.09, 74.94, 73.12, 72.20. 70.61, 68.70, 68.56, 68.50, 68.43, 68.36, 67.99, 67.92, 67.65, 67.58, 62.15, 39.03, 38.99, 37.80, 37.73, 19.91, 14.01, 13.98; ^{31}P NMR ($CDCl_3$, 67.5 MHz) δ 0.48, −0.77, −1.12; UV (MeOH) λ_{max} 261 nm; FAB-HRMS calcd for $C_{74}H_{73}N_5O_{17}P_3$ 1396.4214 (MH^+), found 1396.4290. Anal. Calcd for $C_{74}H_{72}N_5O_{17}P_3 \cdot H_2O$: C, 62.84; H, 5.27; N, 4.95. Found: C, 62.50; H, 5.42; N, 5.27.

9-[3-Deoxy-3-(4,5-di-*O*-phosphoryl-2,6-anhydro-1-deoxy-D-*glycero*-D-*ido*-heptitol-1-yl)-2-*O*-phosphoryl-*β*-D-*ribo*-pentofuranosyl]adenine Hexasodium Salt (9). A mixture of **40** (10 mg, 7.4 μmol) and Pd-black (2 mg) in aqueous MeOH (80%, 1 mL) was stirred under atmospheric pressure of hydrogen at room temperature for 72 h. After the catalysts were filtrated through a Celite pad, the filtrated was evaporated. A solution of the residue in H_2O (2 mL) was applied to Daiaion WK-20 (Na^+ form, developed with H_2O), and the fractions containing **9** were evaporated and dried in vacuo to give **9** (5.6 mg as a white solid, yield 85% based on quantitative UV analysis). This compound was hygroscopic, and therefore, the solvation status was measured by quantitative UV absorption at 260 nm. The content was 89% based on an molar absorption coefficient of 2′-AMP:[23] ^{1}H NMR (D_2O, 500 MHz) δ 8.29 (s, 1 H, H-2), 8.17 (s, 1 H, H-8), 6.35 (s, 1 H, H-1′), 5.00 (dd, 1 H, H-2′, J = 4.9, 7.6), 4.21 (m, 3 H, H-4′, H-1″, H-4″), 4.07 (dd, 1 H, H-6″a, J = 6.8, 12.9), 3.92 (ddd, 1 H, H-3″, J = 5.7, 5.7, 10.0), 3.82 (dd, 1 H, H-5′a, J = 1.4, 13.0), 3.79 (m, 2 H, H-2″, H-5″), 3.65 (dd, 1 H, H-5′b, J = 3.7, 13.0), 3.57 (dd, 1H, H-6″b, J = 3.2, 12.9), 2.71 (m, 1 H, H-3′), 2.02 (m, 1 H, 3′-C*Ha*Hb), 1.80 (m, 1 H, 3′-CHa*Hb*); ^{13}C NMR (D_2O, 125 MHz) δ 155.48, 152.47, 148.74, 140.25, 118.67, 89.32, 85.62, 77.64, 75.59, 68,41, 60.92, 59.69, 48.83, 37.78, 37.73, 23.24, 20.02; ^{31}P NMR(D_2O, 67.5 MHz) δ 4.68, 4.20, 4.14; UV (H_2O) λ_{max} 260 nm; FAB-HRMS (triethylammonium salt, negative) calcd for $C_{17}H_{27}N_5O_{17}P_3$ 666.0615 [$(M - H)^-$], found 666.0615.

1-[3-Deoxy-3-(4,5-di-*O*-phosphoryl-2,6-anhydro-1-deoxy-D-*glycero*-D-*ido*-heptitol-1-yl)-2-*O*-phosphoryl-*β*-D-*ribo*-pentofuranosyl]uracil Hexasodium Salt (10). Compound **10** (5 mg as white solid, yield 85% based on quantitative UV analysis) was prepared from **41** (10 mg, 2.2 μmol) by the procedure described for the synthesis of **9** with 10% Pd−C (4 mg) instead of Pd-black. This compound was hygroscopic, and therefore, the solvation status was measured by quantitative UV absorption at 260 nm: the content was 91% based on an molar absorption coefficient of 2′-UMP:[23] ^{1}H NMR (D_2O, 500 MHz) δ 7.59 (d, 1 H, H-6, J = 7.7), 6.02 (s, 1 H, H-1′), 5.72 (d,

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1 H, H-5, J = 7.7), 4.74 (m, 1 H, H-2′), 4.20 (m, 2 H, H-1″, H-4″), 4.07 (m, 2 H, H-4′, H-6″a), 3.93 (ddd, 1 H, H-3″, J = 5.0, 5.0, 10.8), 3.85 (m, 2 H, H-5′a, H-2″), 3.78 (dd, 1 H, H-5″, J = 3.5, 5.7), 3.68 (dd, 1 H, H-5′b, J = 4.5, 12.8), 3.61 (dd, 1 H, H-6″b, J = 3.5, 12.9), 2.35 (m, 1 H, H-3′), 2.00 (m, 1 H, 3′-C*Ha*Hb), 1.72 (m, 1 H, 3′-CHa*Hb*); ^{31}P NMR (D_2O, 67.5 MHz) δ 4.57, 4.09, 3.93; UV (H_2O) λ_{max} 262 nm; FAB-HRMS (triethylammonium salt, negative) calcd for $C_{16}H_{26}N_2O_{19}P_3$ 643.0343 [(M − H)$^-$], found 643.0359.

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Supporting Information Available: ^{1}H NMR spectral charts of **18**, **21**−**23**, **21′**, **22′**, **26**, **29**, **31**, **32**, **9**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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