EurJOC European Journal of Organic Chemistry

FULL PAPER

DOI: 10.1002/ejoc.201200819

Synthesis of Substituted Benzyl Homo-*C*-Ribonucleosides and -Nucleotides as Carba Analogues of Phosphoribosylanthranilate

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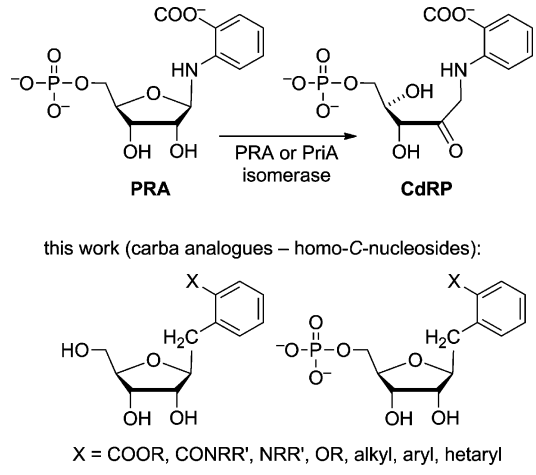
Keywords: Nucleosides / Nucleotides / Cross-coupling / Phosphoribosylanthranilate / Amides

New 2-substituted benzyl *C*-ribonucleosides and -nucleotides were designed as carba analogues of phosphoribosylanthranilate, a key intermediate in tryptophan biosynthesis. The synthesis was based on the preparation of TBS-protected 2-bromobenzyl *C*-ribonucleoside **4a** by addition of (2-bromobenzyl)magnesium bromide to ribonolactone followed by reduction and subsequent functional group transformations. Pd-catalyzed hydrogenation, cross-couplings, amination or hydroxylation, as well as lithiation followed by reaction with CO_2 and amidations, gave a large series of 2-alkyl-, 2-(het)-aryl, 2-amino, 2-hydroxy, 2-carboxy and 2-carbamoyl derivatives that were deprotected to afford free homo-*C*-ribonucleosides. Some of the title nucleosides were converted to 5′-*O*-phosphates.

Introduction

Phosphoribosylanthranilate (**PRA**) is an important intermediate in the biosynthesis of the essential amino acid tryptophan.[1] It is transformed by PRA isomerase to 1-(2-carboxyphenylamino)-1′-deoxyribulose-5′-phosphate (**CdRP**, Scheme 1). Since tryptophan biosynthesis does not occur in humans but is crucial for prokaryotes, targeting of this enzyme might constitute a viable approach to selective antibiotics. There is a clear evolutionary relationship[2] between PRA isomerase and ProFAR isomerase involved in biosynthesis of histidine. In mycobacteria (i.e. *Mycobacterium tuberculosis*) the enzyme PriA isomerase catalyzes both transformations carried out by PRA and ProFAR isomerases; this enzyme also is a potential target for antimycobacterial therapy. The mechanism consists of protonation of the furanose oxygen atom followed by ring opening to form a Schiff base, which – after isomerization to enolamine and further tautomerization – gives **CdRP**. Therefore, we have designed carba analogues of **PRA** based on homo-*C*-nucleosides as potential inhibitors of these enzymes.

C-Nucleosides[3] are an important class of nucleoside analogues characterized by replacement of the chemically and enzymatically labile nucleosidic C–N bond by the more stable C–C bond. Many hetaryl and aryl-*C*-nucleoside derivatives have been reported to possess important biological activities, and others have been used in chemical biology studies such as in the use of novel base-pairs for extending the genetic alphabet[4] and as model substrates for studying of mechanisms of polymerases.[5] There are many approaches[3] to the synthesis of *C*-nucleosides, but some of them suffer from poor stereoselectivities or low transformation efficiencies, and none of them is truly general. In our laboratory, we have developed a modular approach[6] consisting of the synthesis of a central halo-(het)aryl *C*-nucleoside intermediate followed by further functional group transformations such as Pd-catalyzed C–C or C–X couplings. Here we report the first application of this modular approach for the synthesis of 2-substituted benzyl *C*-nucleosides as carba analogues of **PRA**.



Scheme 1. Biotransformation catalyzed by PRA isomerase or PriA isomerase and the design of carba analogues of the substrate (**PRA**).

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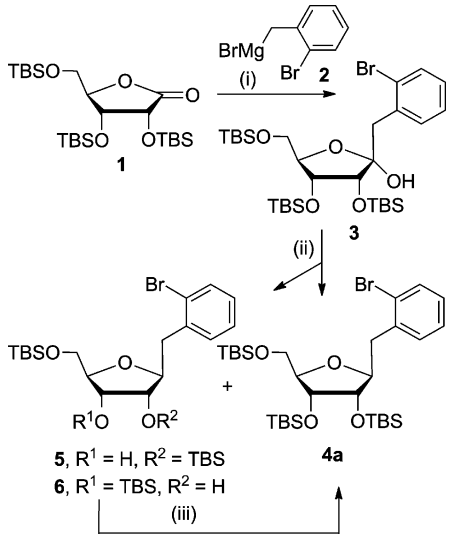
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201200819.

Results and Discussion

Our synthetic strategy for the preparation of the target benzyl *C*-nucleosides was based on the synthesis of 2-bromobenzyl *C*-ribonucleoside key intermediate and follow-up functional group transformations. For the synthesis of this intermediate, we decided to use nucleophilic addition of commercially available (2-bromobenzyl)magnesium bromide (**2**) to protected ribonolactone **1**. More reactive organolithium species are typically used for such additions, which proceed with β-stereoselectivity,[3] but only one example of an addition of arylmagnesium bromide has been reported in the literature.[7]

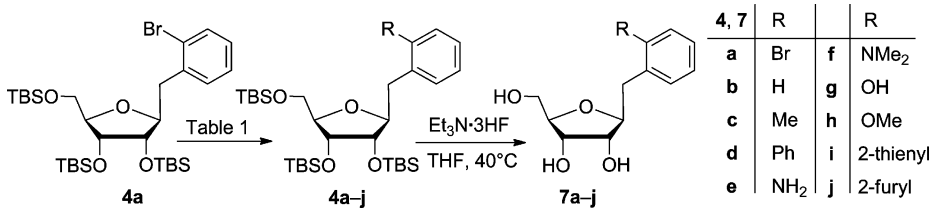
Starting ribonolactone[8] is easily available in two steps from D-ribose in multigram scale in very good overall yield (79%). The addition of the Grigard reagent **2** to lactone **1** proceeded very smoothly and stereoselectively to give desired hemiketal **3** in excellent 88% yield exclusively as the β-anomer (Scheme 2). The reaction was very facile and was performed at room temperature under air in multigram scale (up to 10 g). Reduction of the hemiketal **3** by Et_3SiH in the presence of $BF_3{\cdot}Et_2O$ gave the desired TBS-protected 2-bromobenzyl *C*-ribonucleoside key intermediate **4a** only in 36% yield accompanied by a mixture of two inseparable by-products lacking one of the TBS groups at 3′- or 2′-position (**5** and **6**, respectively) in 40% yield. However, the mixture of **5** and **6** was easily converted into the desired fully silylated nucleoside **4a** by further silylation. Therefore, the combined overall yield of **4a** was an acceptable 72% after reduction and re-silylation. Two-dimensional ROESY NMR spectra of compound **4a** confirmed the desired β-configuration.



Scheme 2. Reagents and conditions: (i) **2**, THF, room temp., 1 h; (ii) Et_3SiH, $BF_3{\cdot}Et_2O$, DCM, 0 °C, 10 min; (iii) TBSCl, imidazole, DMF, 24 h.

Having key intermediate **4a** in hand, we performed a systematic study of functional group transformations (hydrogenation, cross-coupling, amination and hydroxylation) to generate a series of 2-substituted benzyl *C*-nucleoside derivatives (Scheme 3, Table 1).

Catalytic hydrogenation of **4a** was performed at atmospheric pressure in the presence of palladium on carbon in a mixture of ethanol, THF, water, and Et_3N. The hydrogenation proceeded smoothly to give the 2-unsubstituted benzyl *C*-ribonucleoside **4b** in very good 85% yield



Scheme 3. Synthesis of 2-substituted benzyl *C*-ribonucleosides.

Table 1. Functional group transformations of 2-bromobenzyl *C*-ribonucleoside **4a** followed by deprotection.

Entry	Reagent	Catalyst	Ligand/base	Solvent	Conditions [h, °C]	Reaction (yield [%])	Deprotection (yield [%])
1							**7a** (80)
2	H_2	Pd/C	Et_3N	EtOH/THF/H_2O	12, r.t.	**4b** (85)	**7b** (80)
3	Me_3Al	$Pd(PPh_3)_4$		THF	24, 70	**4c** (91)	**7c** (70)
4	$PhB(OH)_2$	$Pd(PPh_3)_4$	K_2CO_3	toluene	12, 90	**4d** (87)	**7d** (82)
5	$KN(SiMe_3)_2$, Ph_3SiNH_2	Pd_2dba_3	CyJohnPhos[a]	toluene	18, 100	**4e** (37)	**7e** (74)
6	Me_2NH_2	Pd_2dba_3	JohnPhos[b]	THF/toluene	24, 60	**4f** (85)	**7f** (75)
7	KOH	Pd_2dba_3	*t*ButylXPhos[c]	dioxane/H_2O	2, 100	**4g** (80)	**7g** (82)
8	1. KOH, 2. MeI	Pd_2dba_3	*t*ButylXPhos[c]	dioxane/H_2O	2, 100	**4h** (84)	**7h** (82)
9	2-Bu_3Sn-Th[d]	$PdCl_2$	JohnPhos[b]	toluene	24, 130	**4i** (80)	**7i** (85)
10	2-Bu_3Sn-Fur[e]	$Pd(PPh_3)_2Cl_2$		DMF	24, 130	**4j** (86)	**7j** (88)

[a] CyJohnPhos = (biphenyl-2-yl)dicyclohexylphosphane. [b] JohnPhos = (biphenyl-2-yl)di-*tert*-butylphosphane. [c] *t*ButylXPhos = (2′,4′,6′-triisopropylbiphenyl-2-yl)di-*tert*-butylphosphane. [d] 2-Bu_3Sn-Th = 2-(tributylstannyl)thiophene. [e] 2-Bu_3Sn-Fur = 2-(tributylstannyl)furan.

(Table 1, Entry 2). The cross-coupling reaction of **4a** with trimethylaluminum was used for the introduction of a methyl group. Under standard conditions in the presence of $Pd(PPh_3)_4$ in THF, the desired protected 2-methylbenzyl *C*-nucleoside **4c** was obtained in excellent 91% yield (Table 1, Entry 3). 2-Phenylbenzyl *C*-ribonucleoside **4d** was prepared by the Suzuki–Miyaura cross-coupling of **4a** with phenylboronic acid in toluene in the presence of K_2CO_3 and $Pd(PPh_3)_4$ at 90 °C in 87% yield (Table 1, Entry 4).

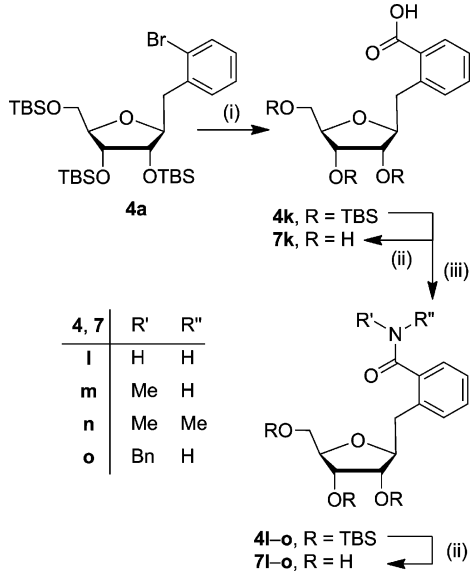
Hartwig-Buchwald reactions were employed for the introduction of *N*-substituents. We tried to prepare unsubstituted 2-aminobenzyl derivative **4e** using potassium bis(trimethylsilyl)amide in the presence of Pd_2dba_3 and Buchwald-type ligand (biphenyl-2-yl)dicyclohexylphosphane (CyJohnPhos).[9] However, we observed only traces of the desired product, even after prolonged reaction time and at elevated temperature. For the amination of *ortho*-substituted aryl halides, Buchwald had developed[10] a procedure using aminotriphenylsilane. By this approach, we were able to prepare the 2-aminobenzyl derivative **4e** in a moderate but acceptable 37% yield (Table 1, Entry 5). For introduction of the dimethylamino group, we used the Buchwald reaction of **4a** with dimethylamine.[11] The reaction was performed under standard conditions using Pd_2dba_3 and (biphenyl-2-yl)di-*tert*-butylphosphane (JohnPhos) to give 2-(dimethylamino)benzyl C-ribonucleoside **4f** in very good 85% yield.

The recently developed[12] palladium-catalyzed hydroxylation using KOH, Pd_2dba_3 and Buchwald-type ligand (2′,4′,6′-triisopropylbiphenyl-2-yl)di-*tert*-butylphosphane (*t*ButylXPhos) was used for the synthesis of hydroxybenzyl *C*-ribonucleoside **4g**. The reaction proceeded in a mixture of 1,4-dioxane/water (1:1) at 100 °C within 2 h to furnish the desired phenol nucleoside **4g** in excellent 80% yield. In order to introduce a methyl ether group, we performed a one-pot palladium-catalyzed hydroxylation followed by treatment with methyl iodide in the presence of phase-transfer catalyst Aliquat[12] to afford 2-methoxybenzyl derivative **4h** in 84% yield (Table 1, Entry 8).

For the synthesis of hetaryl-substituted derivatives, the Stille cross-coupling reaction was used. Reaction of **4a** with tributyl(2-furyl)stannane (Table 1, Entry 10) in the presence of $Pd(PPh_3)Cl_2$ in DMF was very slow and required a higher temperature (130 °C) and a longer reaction time (24 h) to reach complete conversion and to give the desired 2-(2-furyl)benzyl *C*-ribonucleoside **4j** in very good 86% yield. When we applied the same conditions to the reaction of **4a** with tributyl(2-thienyl)stannane, only an inseparable mixture of starting material and product was isolated. The desired 2-(2-thienyl)benzyl *C*-ribonucleoside **4j** was then prepared using $PdCl_2$ and JohnPhos in toluene at 130 °C for 24 h in 80% yield.

For the final deprotection of silylated nucleosides **4a**–**j**, treatment with triethylamine trihydrofluoride in tetrahydrofuran was used.[13] Stirring of the reaction mixture at 40 °C for 2 d followed by treatment with $NaHCO_3$ resulted in the formation of the desired free nucleosides **7a**–**j**. Chromatographic purification by silica flash chromatography gave pure nucleosides **7a**–**j** in good yields (70–88%, Table 1, Entries 1–10).

In order to prepare a series of diversely substituted carboxamides, we attempted to use a recently developed methodology for Pd-catalyzed aminocarbonylations.[14] However, in the case of *ortho*-substituted aryl halides, this methodology was found to be inefficient. Pd-catalyzed aminocarbonylations of **4a** at atmospheric pressure of CO and amines suffered from very low yields, and the reactions were not reproducible. Therefore, we changed our synthetic strategy and decided to prepare carboxylic acid **4k** and to attempt conversion to amides (Scheme 4). Carboxylic acid **4k** was prepared in a one-pot two-step sequence consisting of lithiation of **4a** with BuLi in THF at –78 °C followed by a reaction with dry ice. These reactions proceeded very well to afford **4k** in good 70% yield on a 3 g scale. Starting from carboxylic acid **4k**, a series of amides **4l**–**o** was prepared (Scheme 4, Table 2). The procedure involved activation of **4k** by peptide synthesis activators HOBt and EDC in DCM followed by reactions with NH_4Cl, amines or amine hydrochlorides. The desired unsubstituted or *N*-substituted carboxamides **4l**–**o** were obtained in excellent yields (88–97%). Deprotection of acid **4k** and amides **4l**–**o** was performed using a mixture of trifluoroacetic acid/water (9:1). Free acid **7k** and amides **7l**–**o** were obtained in ca. 80% yield (Table 2) after purification by silica gel flash chromatography.

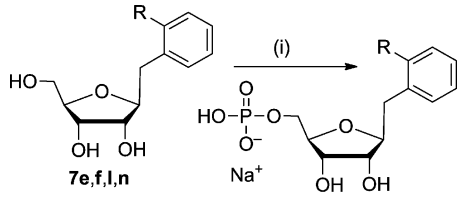


Scheme 4. Reagents and conditions: (i) 1. BuLi, THF, –78 °C, 60 min; 2. CO_2, –78 °C 60 min; (ii) TFA, H_2O, room temp., 4 h; (iii) 1. HOBt, EDC, DCM, room temp., 60 min; 2. amine, Et_3N, room temp., 30 min.

Table 2. Synthesis of carboxamides (Scheme 4).

Entry	Amine	Reaction (yield [%])	Deprotection (yield [%])
1	NH_4Cl	**4l** (94)	**7l** (74)
2	$MeNH_2$·HCl	**4m** (91)	**7m** (79)
3	Me_2NH·HCl	**4n** (88)	**7n** (76)
4	$BnNH_2$	**4o** (97)	**7o** (76)

Since the substrate for PRA isomerase is a 5′-phosphate (nucleotide), we decided to convert selected examples of nucleosides (amino derivatives **7e** and **7f** and amides **7l** and **7n**) to their corresponding 5′-phosphates to assess for enzyme inhibition (Scheme 4). The reaction of **7e**,**f**,**l** and **n** with $POCl_3$ in $PO(OMe)_3$ at 0 °C followed by conversion to the corresponding sodium salts afforded a series of 5′-monophosphate 2-substituted benzyl *C*-ribonucleosides **8e**,**f**,**l**,**n** in ca. 40% isolated yields. In the case of the preparation of 5′-monophosphate from primary amide **7l** using $POCl_3$, dehydration was found to lead to nitrile by-product **8p** isolated in 12% yield from the reaction mixture. (Scheme 5).



R	Compound (yield)		
NH_2	**8e** (46 %)		
NMe_2	**8f** (33 %)		
$CONH_2$	**8l** (29 %)	+ CN	**8p** (12 %)
$CONMe_2$	**8n** (49 %)		

Scheme 5. Synthesis 5′-monophosphates. Reagents and conditions: (i) 1. $POCl_3$, $PO(OMe)_3$, 0 °C, 3 h; 2. DOWEX Na^+.

All nucleosides **7a**–**l** and nucleotides **8e**,**f**,**l**,**n**,**p** were tested for the inhibition of PriA isomerase from *Mycobacterium tuberculosis*.[15] None of the compounds evaluated showed any significant enzyme inhibition up to concentrations of 0.5 mM, although there still could be some potential use in testing of these compounds with PRA isomerases from other prokaryotic pathogens. Since compounds **7** and **8** were designed as carba analogues of the substrate, we envision future PriA inhibitors that will serve as transition-state analogs or that will emulate intermediates of this biotransformation.

Conclusions

We have developed a facile approach for the synthesis of diverse 2-substituted derivatives of benzyl *C*-ribonucleosides and -nucleotides. The key intermediate **4a** was prepared by addition of (2-bromobenzyl)magnesium bromide to TBS-protected ribonolactone followed by reduction and re-silylation. Pd-catalyzed hydrogenation, cross-couplings, aminations and hydroxylation gave corresponding 2-unsubstituted or 2-alkyl-, 2-aryl-, 2-hetaryl-, 2-amino and 2-hydroxy derivatives **4b**–**j** that were deprotected to free nucleosides **7a**–**j**. Lithiation of **4a** followed by reaction with CO_2 gave carboxylic acid **4k**, which was transformed into carboxamides **4l**–**o**, which were also deprotected to free nucleosides **7k**–**o**. This general methodology has the potential for further applications in the synthesis of other types of homo-*C*-nucleosides relevant to medicinal chemistry or chemical biology.

Experimental Section

General: All cross-coupling reactions were carried out in evacuated flame-dried glassware with magnetic stirring under argon. THF, toluene, and hexanes were dried and distilled from sodium/benzophenone. Other reagents were purchased from commercial suppliers and used as received. NMR spectra were recorded with a 400 MHz spectrometer (^{1}H at 400 MHz, ^{13}C at 100.6 MHz), 500 MHz spectrometer (^{1}H at 500 MHz, ^{13}C at 125.8 MHz), and/or 600 MHz spectrometer (^{1}H at 600 MHz, ^{13}C at 151 MHz). The samples were measured in $CDCl_3$ using TMS as an internal standard or in [D_6]DMSO referenced to the residual solvent signal (^{1}H NMR: δ = 2.50 ppm; ^{13}C NMR: δ = 39.7 ppm). Chemical shifts are given in ppm (δ scale), coupling constants (J) in Hz. Complete assignment of all NMR signals was performed using a combination of 2D NMR (H,H-COSY, H,C-HSQC, and H,C-HMBC) experiments, and configurations were established by two-dimensional ROESY spectra. Testing of PriA isomerase inhibitor candidates was performed according to a literature procedure.[15]

1β-(2-Bromobenzyl)-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (3): (2-Bromobenzyl)magnesium bromide solution (**2**) (24 mL, 6.0 mmol, 2 equiv., 0.25 M in Et_2O) was added to a flask containing ribonolactone **1** (1.5 g, 3.0 mmol, 1 equiv.), and the resulting reaction mixture was stirred at room temp. for 60 min. Then a saturated solution of $NaHCO_3$ was added (200 mL), and the mixture was extracted with diethyl ether (3× 150 mL), solvents were removed, and the product was filtered through silica gel to give the crude hemiketal **3** in 88% yield as colorless oil. The crude product was used without further purification in the next step. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.05, 0.08, 0.090, 0.092, 0.10 and 0.11 (6× s, 6× 3 H, CH_3Si); 0.89, 0.93 and 0.94 [3× s, 3× 9 H, $(CH_3)_3C$]; 2.99 (dd, J_{gem} = 14.0, $J_{CH2a,OH}$ = 1.1 Hz, 1 H, CH_2a); 3.32 (d, J_{gem} = 14.0 Hz, 1 H, CH_2b); 3.62 (dd, J_{gem} = 11.1, $J_{5'a,4'}$ = 4.2 Hz, 1 H, 5′-Ha); 3.66 (dd, J_{gem} = 11.1, $J_{5'b,4'}$ = 3.1 Hz, 1 H, 5′-Hb); 3.96 (d, $J_{2',3'}$ = 4.6 Hz, 1 H, 2′-H); 4.04 (dt, $J_{4',5'a}$ = 4.2, $J_{4',3'}$ = $J_{4',5'b}$ = 3.1 Hz, 1 H, 4′-H); 4.18 (dd, $J_{3',2'}$ = 4.6, $J_{3',4'}$ = 3.0 Hz, 1 H, 3′-H); 4.45 (d, $J_{OH,CH2a}$ = 1.1 Hz, 1 H, O1′-H); 7.05 (td, $J_{4,3}$ = $J_{4,5}$ = 7.7, $J_{4,6}$ = 1.8 Hz, 1 H, 4-H); 7.23 (td, $J_{5,4}$ = $J_{5,6}$ = 7.5, $J_{5,3}$ = 1.3 Hz, 1 H, 5-H); 7.53 (dd, $J_{3,4}$ = 8.0, $J_{3,5}$ = 1.3 Hz, 1 H, 3-H), 7.63 (dd, $J_{6,5}$ = 7.7, $J_{6,4}$ = 1.8 Hz, 1 H, 6-H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.5, –5.3, –4.9, –4.5, –4.5 and –4.0 (CH_3Si); 17.9, 18.1 and 18.4 [$(CH_3)_3$**C**]; 25.86, 25.89 and 26.0 [**C**$(CH_3)_3$C]; 42.8 (CH_2); 62.7 (CH_2-5′); 73.2 (CH-3′); 75.0 (CH-2′); 83.4 (CH-4′); 103.7 (C-1′); 125.7 (C-2); 126.9 (CH-5); 127.9 (CH-4); 132.5 (CH-3); 132.8 (CH-6); 136.3 (C-1) ppm. HRMS (ESI) for $C_{30}H_{57}BrO_5Si_3$: $[M + Na]^+$ calcd. 683.2589, found 683.2588.

1β-(2-Bromobenzyl)-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-1-deoxy-D-ribofuranose (4a): Et_3SiH (4.5 mL, 28.4 mmol, 3 equiv.) was added in one portion to a stirred solution of hemiketal **3** (6.27 g, 9.45 mmol) in dry DCM (40 mL) under argon at 0 °C (ice bath). After 5 min, $BF_3{\cdot}Et_2O$ (1.34 mL, 11.3 mmol, 1.2 equiv.) was slowly added in one portion, and the resulting mixture was stirred for an additional 5 min. Subsequently, Et_3N (30 mL) was added, and the reaction mixture was concentrated under reduced pressure. The crude product was directly chromatographed on silica gel eluting with a gradient of hexanes to 7% EtOAc in hexanes to give **4a**

(2.1 g, 36%) as a colorless oil and inseparable mixture of compounds **5** and **6** (1.9 g, 40%) as a colorless oil.

Compound 4a: ^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.07, –0.02, 0.087, 0.089, 0.093 and 0.10 (6× s, 6× 3 H, CH_3Si); 0.88, 0.90 and 0.94 [3× s, 3× 9 H, $(CH_3)_3C$]; 2.80 (dd, J_{gem} = 14.1, $J_{CH2a,1'}$ = 8.0 Hz, 1 H, CH_2a); 3.05 (dd, J_{gem} = 14.1, $J_{CH2b,1'}$ = 5.8 Hz, 1 H, CH_2b); 3.65 (dd, J_{gem} = 11.2, $J_{5'a,4'}$ = 3.1 Hz, 1 H, 5′-Ha); 3.73 (dd, J_{gem} = 11.2, $J_{5'b,4'}$ = 3.4 Hz, 1 H, 5′-Hb); 3.88 (t, $J_{2',1'}$ = $J_{2',3'}$ = 4.3 Hz, 1 H, 2′-H); 3.83 (dt, $J_{4',3'}$ = 5.2, $J_{4',5'a}$ = $J_{4',5'b}$ = 3.2 Hz, 1 H, 4′-H); 4.13 (ddd, $J_{1',CH2a}$ = 8.0, $J_{1',CH2b}$ = 5.8, $J_{1',2'}$ = 4.3 Hz, 1 H, 1′-H); 4.14 (t, $J_{3',2'}$ = $J_{3',4'}$ = 4.7 Hz, 1 H, 3′-H); 7.07 (ddd, $J_{4,3}$ = 7.9, $J_{4,5}$ = 7.4, $J_{4,6}$ = 1.8 Hz, 1 H, 4-H); 7.25 (td, $J_{5,4}$ = $J_{5,6}$ = 7.5, $J_{5,3}$ = 1.3 Hz, 1 H, 5-H); 7.35 (dd, $J_{6,5}$ = 7.7, $J_{6,4}$ = 1.8 Hz, 1 H, 6-H); 7.54 (dd, $J_{3,4}$ = 8.0, $J_{3,5}$ = 1.3 Hz, 1 H, 3-H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.4, –5.2, –4.8, –4.6, –4.5 and –4.3 (CH_3Si); 18.0, 18.1 and 18.4 [$(CH_3)_3$**C**]; 25.85, 25.92 and 26.0 [(**C**$H_3)_3C$]; 40.2 (CH_2); 62.6 (CH_2-5′); 72.1 (CH-3′); 75.7 (CH-2′); 82.4 (CH-1′); 83.6 (CH-4′); 124.8 (C-2); 127.3 (CH-5); 128.0 (CH-4); 131.5 (CH-6); 132.8 (CH-3); 138.2 (C-1) ppm. HRMS (ESI) for $C_{30}H_{57}BrO_4Si_3$: $[M + Na]^+$ calcd. 667.2640, found 667.2639. IR (CCl_4): $\tilde{\nu}$ = 3069, 2956, 2897, 1593, 1568, 1472, 1463, 1440, 1406, 1390, 1362, 1255, 1276, 1219, 1128, 1118, 1088, 1048, 1032, 1021, 1003, 940, 838, 701, 680, 661, 540, 496 cm^{-1}.

1β-(2-Bromobenzyl)-2,5-di-*O*-(*tert*-butyldimethylsilyl)-1-deoxy-D-ribofuranose (5): Spectra taken from the mixture of **5** + **6**. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.05, 0.07, 0.09 and 0.11 (4× s, 4× 3 H, CH_3Si); 0.91 and 0.94 [2× s, 2× 9 H, $(CH_3)_3C$]; 2.61 (br. d, $J_{OH',3'}$ = 5.2 Hz, 1 H, O3′-H); 2.83 (dd, J_{gem} = 14.1, $J_{CH2a,1'}$ = 8.7 Hz, 1 H, CH_2a); 3.10 (dd, J_{gem} = 14.1, $J_{CH2b,1'}$ = 4.4 Hz, 1 H, CH_2b); 3.71 (dd, J_{gem} = 11.2, $J_{5'a,4'}$ = 3.1 Hz, 1 H, 5′-Ha); 3.78 (dd, J_{gem} = 11.2, $J_{5'b,4'}$ = 2.7 Hz, 1 H, 5′-Hb); 3.90 (dt, $J_{4',3'}$ = 4.3, $J_{4',5'a}$ = $J_{4',5'b}$ = 2.9 Hz, 1 H, 4′-H); 4.01 (t, $J_{2',1'}$ = $J_{2',3'}$ = 5.2 Hz, 1 H, 2′-H); 4.05 (m, 1 H, 3′-H); 4.10 (ddd, $J_{1',CH2a}$ = 8.6, $J_{1',2'}$ = 5.1, $J_{1',CH2b}$ = 4.5 Hz, 1 H, 1′-H); 7.08 (br. ddd, $J_{4,3}$ = 7.9, $J_{4,5}$ = 7.5, $J_{4,6}$ = 1.8 Hz, 1 H, 4-H); 7.24 (td, $J_{5,4}$ = $J_{5,6}$ = 7.5, $J_{5,3}$ = 1.3 Hz, 1 H, 5-H); 7.35 (dd, $J_{6,5}$ = 7.7, $J_{6,4}$ = 1.8 Hz, 1 H, 6-H); 7.53 (dd, $J_{3,4}$ = 8.0, $J_{3,5}$ = 1.3 Hz, 1 H, 3-H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.5, –5.3, –4.9 and –4.7 (CH_3Si); 18.0 and 18.4 [$(CH_3)_3$**C**]; 25.7 and 26.0 [(**C**$H_3)_3C$]; 39.9 (CH_2); 63.4 (CH_2-5′); 71.9 (CH-3′); 76.2 (CH-2′); 81.8 (CH-1′); 84.5 (CH-4′); 124.6 (C-2); 127.3 (CH-5); 128.1 (CH-4); 131.6 (CH-6); 132.7 (CH-3); 137.9 (C-1) ppm. HRMS (ESI) for $C_{24}H_{43}BrO_4Si_2$: $[M - H]^-$ calcd. 529.1811, found 529.1817.

1β-(2-Bromobenzyl)-3,5-di-*O*-(*tert*-butyldimethylsilyl)-1-deoxy-D-ribofuranose (6): Spectra taken from the mixture of **5** + **6**. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.07, 0.08, 0.12 and 0.13 (4× s, 4× 3 H, CH_3Si); 0.91 [s, 2× 9 H, $(CH_3)_3C$]; 2.59 (d, $J_{OH',2'}$ = 7.6 Hz, 1 H, O2′-H); 2.91 (dd, J_{gem} = 14.3, $J_{CH2a,1'}$ = 7.8 Hz, 1 H, CH_2a); 3.17 (dd, J_{gem} = 14.3, $J_{CH2b,1'}$ = 5.2 Hz, 1 H, CH_2b); 3.63 (dd, J_{gem} = 11.1, $J_{5'a,4'}$ = 4.1 Hz, 1 H, 5′-Ha); 3.66 (dd, J_{gem} = 11.1, $J_{5'b,4'}$ = 3.4 Hz, 1 H, 5′-Hb); 3.79 (br. dt, $J_{2',OH}$ = 7.6, $J_{2',1'}$ = $J_{2',3'}$ = 5.8 Hz, 1 H, 2′-H); 3.83 (q, $J_{4',5'a}$ = $J_{4',5'b}$ = $J_{4',3'}$ = 3.7 Hz, 1 H, 4′-H); 4.04 (ddd, $J_{1',CH2a}$ = 7.8, $J_{1',2'}$ = 6.0, $J_{1',CH2b}$ = 5.2 Hz, 1 H, 1′-H); 4.24 (dd, $J_{3',2'}$ = 5.5, $J_{3',4'}$ = 3.8 Hz, 1 H, 3′-H); 7.07 (br. ddd, $J_{4,3}$ = 8.0, $J_{4,5}$ = 7.5, $J_{4,6}$ = 1.8 Hz, 1 H, 4-H); 7.24 (td, $J_{5,4}$ = $J_{5,6}$ = 7.5, $J_{5,3}$ = 1.3 Hz, 1 H, 5-H); 7.34 (dd, $J_{6,5}$ = 7.7, $J_{6,4}$ = 1.8 Hz, 1 H, 6-H); 7.54 (dd, $J_{3,4}$ = 8.0, $J_{3,5}$ = 1.3 Hz, 1 H, 3-H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.5, –5.3, –4.9 and –4.5 (CH_3Si); 18.0 and 18.4 [$(CH_3)_3$**C**]; 25.8 and 26.0 [(**C**$H_3)_3C$]; 39.6 (CH_2); 62.7 (CH_2-5′); 72.5 (CH-3′); 74.8 (CH-2′); 82.1 (CH-1′); 84.4 (CH-4′); 124.8 (C-2); 127.2 (CH-5); 128.0 (CH-4); 131.5 (CH-6); 132.7 (CH-3); 137.8 (C-1) ppm. HRMS (ESI) for $C_{24}H_{43}BrO_4Si_2$: $[M - H]^-$ calcd. 529.1811, found 529.1817.

Procedure for the Re-Silylation of the Mixture of Compounds 5 and 6: Imidazole (486 mg, 7.14 mmol, 2 equiv.) and then TBDMSCl (1.08 g, 7.14 mmol, 2 equiv.) were added to a flame-dried flask containing a solution of the mixture of nucleosides **5** and **6** (1.9 g, 3.57 mmol) in dry DMF (50 mL) at 0 °C under argon, the solution was warmed to room temp. and stirred for 16 h. The reaction mixture was then poured into a saturated solution of NaCl (100 mL) and extracted with EtOAc (3× 30 mL). the collected organic fractions were washed with a saturated NaCl solution, dried with $MgSO_4$, and the solvents were evaporated under vacuum. The crude product was chromatographed on silica gel eluting with a gradient of hexanes to 7% EtOAc in hexanes to give the nucleoside **4a** (2.1 g, 91%) as a colorless oil.

1β-Benzyl-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-1-deoxy-D-ribofuranose (4b): 10% Pd/C (150 mg) was added to a solution of **4a** (400 mg, 0.69 mmol) in a mixture of THF (15 mL), EtOH (15 mL), H_2O (1.5 mL), and Et_3N (1.0 mL). The reaction flask was then sealed with a septum, evacuated, and filled with H_2 (101 kPa). After the reaction was completed (12 h), the Pd catalyst was filtered off, the filtrate was poured into H_2O, and crude product was extracted with EtOAc. Chromatography (silica gel, elution with a gradient of hexanes to 5% EtOAc in hexanes) gave **4b** (300 mg, 85%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.02, 0.02, 0.06, 0.08, 0.09 and 0.10 (6× s, 6× 3 H, CH_3Si); 0.900, 0.902 and 0.94 [3× s, 3× 9 H, $(CH_3)_3C$]; 2.70 (dd, J_{gem} = 13.8, $J_{CH2a,1'}$ = 8.2 Hz, 1 H, CH_2a); 2.85 (dd, J_{gem} = 13.8, $J_{CH2b,1'}$ = 4.9 Hz, 1 H, CH_2b); 3.62 (dd, J_{gem} = 11.1, $J_{5'a,4'}$ = 3.5 Hz, 1 H, 5′-Ha); 3.65 (dd, J_{gem} = 11.1, $J_{5'b,4'}$ = 3.6 Hz, 1 H, 5′-Hb); 3.79 (dd, $J_{2',1'}$ = 5.4, $J_{2',3'}$ = 4.4 Hz, 1 H, 2′-H); 3.88 (br. dt, $J_{4',3'}$ = 4.2, $J_{4',5'a}$ = $J_{4',5'b}$ = 3.5 Hz, 1 H, 4′-H); 4.02 (t, $J_{3',2'}$ = $J_{3',4'}$ = 4.3 Hz, 1 H, 3′-H); 4.06 (dt, $J_{1',CH2a}$ = 8.3, $J_{1',CH2b}$ = $J_{1',2'}$ = 5.1 Hz, 1 H, 1′-H); 7.21–7.32 (m, 5 H, 2,3,4-H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.4, –5.2, –4.7, –4.5, –4.4 and –4.3 (CH_3Si); 18.1 and 18.4 [$(CH_3)_3$**C**]; 25.88, 25.91 and 26.0 [(**C**$H_3)_3C$]; 40.4 (CH_2); 63.0 (CH_2-5′); 72.5 (CH-3′); 75.9 (CH-2′); 83.1 (CH-1′); 84.0 (CH-4′); 126.2 (CH-4); 128.3 (CH-3); 129.3 (CH-2); 139.0 (C-1) ppm. HRMS (ESI) for $C_{30}H_{58}O_4Si_3$: $[M + H]^+$ calcd. 567.3716, found 567.3717. IR (CCl_4): $\tilde{\nu}$ = 3099, 3066, 3030, 2955, 2896, 1605, 1586, 1496, 1472, 1463, 1455, 1406, 1390, 1362, 1255, 1311, 1090, 1079, 1023, 1004, 940, 838, 699, 680, 671 cm^{-1}.

2,3,5-Tri-*O*-(*tert*-butyldimethylsilyl)-1-deoxy-1β-(2-methylbenzyl)-D-ribofuranose (4c): Me_3Al (0.23 mL, 0.47 mmol, 1.5 equiv., 2 M in toluene) was added to a vigorously stirred solution of **4a** (200 mg, 0.31 mmol) and $Pd(PPh_3)_4$ (18 mg, 0.015 mmol, 5 mol-%) in THF (5 mL) under argon. The mixture was stirred at 70 °C for 24 h, quenched by pouring into saturated NaH_2PO_4 (50 mL), and extracted with EtOAc (3× 50 mL). The crude product was chromatographed on silica gel eluting with a gradient of hexanes to 1% EtOAc in hexanes to give **4c** (163 mg, 91%) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.04, 0.00, 0.075, 0.084, 0.09 and 0.10 (6× s, 6× 3 H, CH_3Si); 0.89, 0.90 and 0.94 [3× s, 3× 9 H, $(CH_3)_3C$]; 2.33 (s, 3 H, CH_3-2); 2.69 (dd, J_{gem} = 14.1, $J_{CH2a,1'}$ = 8.4 Hz, 1 H, CH_2a); 2.85 (dd, J_{gem} = 14.1, $J_{CH2b,1'}$ = 5.1 Hz, 1 H, CH_2b); 3.64 (dd, J_{gem} = 11.1, $J_{5'a,4'}$ = 3.2 Hz, 1 H, 5′-Ha); 3.67 (dd, J_{gem} = 11.1, $J_{5'b,4'}$ = 3.6 Hz, 1 H, 5′-Hb); 3.81 (dd, $J_{2',1'}$ = 5.5, $J_{2',3'}$ = 4.4 Hz, 1 H, 2′-H); 3.87 (br. q, $J_{4',3'}$ = $J_{4',5'a}$ = $J_{4',5'b}$ = 3.6 Hz, 1 H, 4′-H); 4.06 (dt, $J_{1',CH2a}$ = 8.5, $J_{1',CH2b}$ = $J_{1',2'}$ = 5.3 Hz, 1 H, 1′-H); 4.11 (t, $J_{3',2'}$ = $J_{3',4'}$ = 4.2 Hz, 1 H, 3′-H); 7.09–7.17 (m, 3 H, 3,4,5-H); 7.21 (m, 1 H, 6-H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.5, –5.3, –4.8, –4.5, –4.41 and –4.36 (CH_3Si); 18.00, 18.04 and 18.4 [$(CH_3)_3$**C**]; 19.7 (CH_3-2); 25.86, 25.90 and 26.0 [(**C**$H_3)_3C$]; 37.6 (CH_2); 63.0 (CH_2-5′); 72.5 (CH-3′); 76.1 (CH-2′); 82.2 (CH-1′); 84.2 (CH-4′); 125.9 (CH-5); 126.4 (CH-4); 129.9

(CH-6); 130.2 (CH-3); 136.3 and 137.3 (C-1,2) ppm. HRMS (ESI) for $C_{31}H_{60}O_4Si_3$: $[M + H]^+$ calcd. 581.3872, found 581.3874. IR (CCl_4): $\tilde{\nu}$ = 3065, 3019, 2955, 2897, 1606, 1584, 1509, 1472, 1463, 1406, 1389, 1380, 1362, 1277, 1254, 1087, 1041, 1003, 939, 865, 838, 819, 721, 696, 679, 671, 589, 542 cm^{-1}.

2,3,5-Tri-*O*-(*tert*-butyldimethylsilyl)-1-deoxy-1β-(2-phenylbenzyl)-D-ribofuranose (4d): K_2CO_3 (106 mg, 0.77 mmol), $Pd(PPh_3)_4$ (59 mg, 0.05 mmol, 10 mol-%), $PhB(OH)_2$ (125 mg, 1.02 mmol, 2 equiv.) and starting nucleoside **4a** (330 mg, 0.51 mmol) were dissolved in toluene (6 mL) under argon, and the mixture was stirred at 90 °C for 12 h. The reaction mixture was concentrated under reduced pressure, and the crude product was chromatographed on silica gel eluting with a gradient of hexanes to 1% EtOAc in hexanes to give **4d** (287 mg, 87%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.23, –0.10, –0.01, 0.00, 0.067 and 0.070 (6× s, 6× 3 H, CH_3Si); 0.78, 0.87 and 0.92 [3× s, 3× 9 H, $(CH_3)_3C$]; 2.69 (dd, J_{gem} = 14.3, $J_{CH2a,1'}$ = 8.0 Hz, 1 H, CH_2a); 2.92 (dd, J_{gem} = 14.3, $J_{CH2b,1'}$ = 5.5 Hz, 1 H, CH_2b); 3.56 (dd, $J_{2',1'}$ = 4.8, $J_{2',3'}$ = 3.8 Hz, 1 H, 2′-H); 3.57–3.65 (m, 2 H, 5′-H); 3.81–3.85 (m, 2 H,3′,4′-H); 3.96 (ddd, $J_{1',CH2a}$ = 8.0, $J_{1',CH2b}$ = 5.5, $J_{1',2'}$ = 4.8 Hz, 1 H, 1′-H); 7.22 (dd, $J_{3,4}$ = 7.4, $J_{3,5}$ = 1.7 Hz, 1 H, 3-H); 7.26 (td, $J_{4,3}$ = $J_{4,5}$ = 7.4, $J_{4,6}$ = 1.4 Hz, 1 H, 4-H); 7.30–7.36 (m, 4 H, 5-H,*o*,*p*-C_6H_5); 7.39 (m, 2 H, H-*m*-C_6H_5); 7.48 (dd, $J_{6,5}$ = 7.7, $J_{6,4}$ = 1.5 Hz, 1 H, 6-H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.4, –5.3, –5.0, –4.6, –4.5 and –4.3 (CH_3Si); 17.9, 18.0 and 18.4 [$(CH_3)_3$**C**]; 25.8, 25.9 and 26.0 [(**C**$H_3)_3$C]; 37.1 (CH_2); 62.7 (CH_2-5′); 72.0 (CH-3′); 75.8 (CH-2′); 83.4 (CH-1′); 83.6 (CH-4′); 126.1 (CH-4); 126.8 (CH–*p*-C_6H_5); 127.3 (CH-5); 128.2 (CH–*m*-C_6H_5); 129.5 (CH–*o*-C_6H_5); 130.1 (CH-3); 130.3 (CH-6); 136.2 (C-1); 141.7 (C-*i*-C_6H_5); 142.1 (C-2) ppm. HRMS (ESI) for $C_{36}H_{63}O_4Si_3$: $[M + H]^+$ calcd. 643.4029, found 643.4031. IR (CCl_4): $\tilde{\nu}$ = 3061, 3026, 2956, 2896, 1599, 1587, 1500, 1480, 1472, 1463, 1450, 1405, 1435, 1389, 1361, 1255, 1087, 1024, 1003, 940, 838, 702, 680, 671 cm^{-1}.

1β-(2-Aminobenzyl)-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-1-deoxy-D-ribofuranose (4e): $KN(SiMe_3)_2$ (4.05 mL, 2.02 mmol, 2.5 equiv. 0.5 M solution in toluene) was added to a flame-dried and argon-purged flask containing **4a** (519 mg, 0.81 mmol), Ph_3SiNH_2 (446 mg, 1.62 mmol), $Pd_2(dba)_3$, (43 mg, 0.041 mmol, 5 mol-%), and (biphenyl-2-yl)dicyclohexylphosphane (57 mg, 0.162 mmol, 20 mol-%), and the mixture was stirred at 100 °C for 18 h. After cooling to room temp., the reaction mixture was diluted with Et_2O (30 mL), washed with 2 M HCl (10 mL) and 1 M NaOH (15 mL). The crude product was chromatographed on silica gel eluting with a gradient of hexanes to 2% EtOAc in hexanes to give **4e** (173 mg, 37%) as a colorless oil. ^{1}H NMR (500 MHz, [D_6]acetone): δ = –0.04, 0.01, 0.11, 0.12, 0.128 and 0.132 (6× s, 6× 3 H, CH_3Si); 0.89, 0.92 and 0.95 [3× s, 3× 9 H, $(CH_3)_3C$]; 2.45 (dd, J_{gem} = 13.7, $J_{CH2a,1'}$ = 7.7 Hz, 1 H, CH_2a); 2.72 (dd, J_{gem} = 13.7, $J_{CH2b,1'}$ = 5.9 Hz, 1 H, CH_2b); 3.67 (dd, J_{gem} = 11.2, $J_{5'a,4'}$ = 3.3 Hz, 1 H, 5′-Ha); 3.74 (dd, J_{gem} = 11.2, $J_{5'b,4'}$ = 3.4 Hz, 1 H, 5′-Hb); 3.79 (dt, $J_{4',3'}$ = 5.0, $J_{4',5'a}$ = $J_{4',5'b}$ = 3.4 Hz, 1 H, 4′-H); 3.92 (ddd, $J_{1',CH2a}$ = 7.7, $J_{1',CH2b}$ = 6.0, $J_{1',2'}$ = 4.5 Hz, 1 H, 1′-H); 3.99 (t, $J_{2',1'}$ = $J_{2',3'}$ = 4.4 Hz, 1 H, 2′-H); 4.13 (br. t, $J_{3',4'}$ = $J_{3',2'}$ = 4.7 Hz, 1 H, 3′-H); 6.53 (dd, $J_{3,4}$ = 7.8, $J_{3,5}$ = 1.4 Hz, 1 H, 3-H); 6.97 (td, $J_{5,4}$ = $J_{5,6}$ = 7.5, $J_{5,3}$ = 1.4 Hz, 1 H, 5-H); 7.13 (td, $J_{4,3}$ = $J_{4,5}$ = 7.6, $J_{4,6}$ = 1.5 Hz, 1 H, 4-H); 7.28 (dd, $J_{6,5}$ = 7.6, $J_{6,4}$ = 1.5 Hz, 1 H, 6-H) ppm. ^{13}C NMR (125.7 MHz, [D_6]acetone): δ = –5.2, –5.00, –4.4, –4.2, –4.1 and –3.9 (CH_3Si); 18.6 and 19.0 [$(CH_3)_3$**C**]; 26.36 and 26.43 [(**C**$H_3)_3$C]; 36.4 (CH_2); 63.6 (CH_2-5′); 73.2 (CH-3′); 76.6 (CH-2′); 83.7 (CH-1′); 84.3 (CH-4′); 119.7 (CH-3); 123.7 (CH-5); 127.6 (CH-4); 129.2 (C-1); 131.6 (CH-6); 151.2 (C-2) ppm. HRMS (ESI) for $C_{30}H_{59}O_4NSi_3$: $[M + H]^+$ calcd. 582.3825, found 582.3826. IR (CCl_4): $\tilde{\nu}$ = 3447, 3354, 3071, 3053, 3026, 3005, 2956, 2897, 1624, 1606, 1586, 1499, 1472, 1462, 1406, 1390, 1362, 1313, 1277, 1256, 1188, 1090, 1080, 1053, 1005, 940, 928, 864, 838, 712, 678, 672, 529, 505 cm^{-1}.

2,3,5-Tri-*O*-(*tert*-butyldimethylsilyl)-1-deoxy-1β-[2-(dimethylamino)-benzyl]-D-ribofuranose (4f): Toluene (0.6 mL) and Me_2NH (1.2 mL, 2.32 mmol, 6 equiv; 2 M solution in THF) were added to a flame-dried and argon-purged flask containing **4a** (249 mg, 0.39 mmol), $Pd_2(dba)_3$ (18 mg, 0.019 mmol, 5 mol-%), (biphenyl-2-yl)di-*tert*-butylphosphane (23 mg, 0.077 mmol, 20 mol-%), and sodium *tert*-butoxide (37 mg, 0.39 mmol, 1 equiv.). The reaction mixture was stirred at 60 °C for 24 h, concentrated under reduced pressure, and the crude product was chromatographed on silica gel eluting with a gradient of hexanes to 1% EtOAc in hexanes, to give **4f** (200 mg, 85%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.16, –0.09, 0.08, 0.09, 0.10 and 0.11 (6× s, 6× 3 H, CH_3Si); 0.85, 0.90 and 0.94 [3× s, 3× 9 H, $(CH_3)_3C$]; 2.67 [s, 6 H, $(CH_3)_2N$]; 2.71 (dd, J_{gem} = 13.8, $J_{CH2a,1'}$ = 6.9 Hz, 1 H, CH_2a); 3.03 (dd, J_{gem} = 13.8, $J_{CH2b,1'}$ = 6.9 Hz, 1 H, CH_2b); 3.65 (dd, J_{gem} = 11.2, $J_{5'a,4'}$ = 3.1 Hz, 1 H, 5′-Ha); 3.76 (dd, J_{gem} = 11.2, $J_{5'b,4'}$ = 3.1 Hz, 1 H, 5′-Hb); 3.84 (br. t, $J_{2',1'}$ = $J_{2',3'}$ = 3.9 Hz, 1 H, 2′-H); 3.89 (dt, $J_{4',3'}$ = 6.1, $J_{4',5'a}$ = $J_{4',5'b}$ = 3.1 Hz, 1 H, 4′-H); 4.08 (td, $J_{1',CH2a}$ = $J_{1',CH2b}$ = 6.9, $J_{1',2'}$ = 3.5 Hz, 1 H, 1′-H); 4.11 (dd, $J_{3',4'}$ = 6.0, $J_{3',2'}$ = 4.3 Hz, 1 H, 3′-H); 7.02 (td, $J_{5,4}$ = $J_{5,6}$ = 7.4, $J_{5,3}$ = 1.4 Hz, 1 H, 5-H); 7.10 (dd, $J_{3,4}$ = 8.1, $J_{3,5}$ = 1.4 Hz, 1 H, 3-H); 7.18 (br. ddd, $J_{4,3}$ = 7.9, $J_{4,5}$ = 7.4, $J_{4,6}$ = 1.7 Hz, 1 H, 4-H); 7.31 (dd, $J_{6,5}$ = 7.5, $J_{6,4}$ = 1.7 Hz, 1 H, 6-H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.4, –5.2, –4.9, –4.64, –4.60 and –4.3 (CH_3Si); 18.0, 18.1 and 18.4 [$(CH_3)_3$**C**]; 25.8, 25.9 and 26.0 [(**C**$H_3)_3$C]; 35.3 (CH_2); 45.3 [$(CH_3)_2$N]; 62.4 (CH_2-5′); 71.8 (CH-3′); 75.6 (CH-2′); 82.9 (CH-4′); 84.5 (CH-1′); 119.4 (CH-3); 123.4 (CH-5); 127.1 (CH-4); 131.0 (CH-6); 133.7 (C-1); 152.9 (C-2) ppm. HRMS (ESI) for $C_{32}H_{64}O_4NSi_3$: $[M + H]^+$ calcd. 610.4138, found 610.4138. IR (CCl_4): $\tilde{\nu}$ = 3062, 3023, 2955, 2896, 2827, 2787, 1599, 1580, 1494, 1472, 1462, 1453, 1406, 1389, 1362, 1306, 1254, 1187, 1081, 1034, 946, 940, 838, 699, 680 cm^{-1}.

2,3,5-Tri-*O*-(*tert*-butyldimethylsilyl)-1-deoxy-1β-(2-hydroxybenzyl)-D-ribofuranose (4g): Water (1.0 mL) and 1,4-dioxane (1.0 mL) were added to a septum-sealed flask containing **4a** (430 mg, 0.67 mmol), Pd_2dba_3 (31 mg, 0.034 mmol, 5.0 mol-%), (2′,4′,6′-triisopropylbiphenyl-2-yl)di-*tert*-butylphosphane (57 mg, 0.13 mmol, 20 mol-%) and KOH (114 mg, 2.0 mmol, 3 equiv.) under argon. The reaction mixture was heated at 100 °C for 2 h, cooled to room temp., and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel eluting with a gradient of hexanes to 3% EtOAc in hexanes, furnishing **4g** (312 mg, 80%) as a colorless oil. ^{1}H NMR (500 MHz, [D_6]DMSO): δ = –0.20, 0.14, 0.056, 0.058, 0.064 and 0.07 (6× s, 6× 3 H, CH_3Si); 0.80, 0.87 and 0.89 [3× s, 3× 9 H, $(CH_3)_3C$]; 2.55 (dd, J_{gem} = 13.2, $J_{CH2a,1'}$ = 6.4 Hz, 1 H, CH_2a); 2.72 (dd, J_{gem} = 13.2, $J_{CH2b,1'}$ = 7.5 Hz, 1 H, CH_2b); 3.56 (dd, J_{gem} = 11.1, $J_{5'a,4'}$ = 4.2 Hz, 1 H, 5′-Ha); 3.68–3.74 (m, 2 H, 4′-H,5′-Hb); 3.90 (dd, $J_{2',3'}$ = 4.2, $J_{2',1'}$ = 2.6 Hz, 1 H, 2′-H); 3.92 (ddd, $J_{1',CH2a}$ = 7.5, $J_{1',CH2b}$ = 6.5, $J_{1',2'}$ = 2.6 Hz, 1 H, 1′-H); 4.08 (dd, $J_{3',4'}$ = 6.6, $J_{3',2'}$ = 4.1 Hz, 1 H, 3′-H); 6.70 (td, $J_{5,4}$ = $J_{5,6}$ = 7.4, $J_{5,3}$ = 1.2 Hz, 1 H, 5-H); 6.79 (dd, $J_{3,4}$ = 8.1, $J_{3,5}$ = 1.2 Hz, 1 H, 3-H); 7.01 (br. ddd, $J_{4,3}$ = 8.0, $J_{4,5}$ = 7.4, $J_{4,6}$ = 1.7 Hz, 1 H, 4-H); 7.05 (dd, $J_{6,5}$ = 7.5, $J_{6,4}$ = 1.8 Hz, 1 H, 6-H); 9.35 (s, 1 H, O2-H) ppm. ^{13}C NMR (125.7 MHz, [D_6]DMSO): δ = –5.3, –5.1, –4.77, –4.75, –4.7 and –4.3 (CH_3Si); 17.8, 17.9 and 18.2 [$(CH_3)_3$**C**]; 25.8, 25.96 and 26.00 [(**C**$H_3)_3$C]; 34.6 (CH_2); 62.2 (CH_2-5′); 71.3 (CH-3′); 75.0 (CH-2′); 81.7 (CH-4′); 83.5 (CH-1′); 115.1 (CH-3); 118.9 (CH-5); 124.4 (C-1); 127.5 (CH-4); 131.2 (CH-6); 155.4 (C-2) ppm. HRMS (ESI) for $C_{30}H_{58}O_5Si_3$: $[M + Na]^+$ calcd. 605.3484, found 605.3483. IR

(CCl_4): $\tilde{\nu}$ = 3610, 3348, 3069, 3035, 2955, 2897, 1616, 1585, 1507, 1472, 1463, 1444, 1405, 1390, 1362, 1255, 1240, 1160, 1111, 1100, 1089, 1006, 940, 838, 680 cm^{-1}.

2,3,5-Tri-*O*-(*tert*-butyldimethylsilyl)-1-deoxy-1β-(2-methoxybenzyl)-D-ribofuranose (4h): Water (0.5 mL) and 1,4-dioxane (0.5 mL) were added to a septum-sealed flask containing **4a** (147 mg, 0.23 mmol), Pd_2dba_3 (11 mg, 0.012 mmol, 5.0 mol-%), (2′,4′,6′-triisopropylbiphenyl-2-yl)di-*tert*-butylphosphane (20 mg, 0.046 mmol, 20 mol-%) and KOH (39 mg, 0.69 mmol, 3 equiv.) under argon. The reaction mixture was heated at 100 °C for 2 h. Then it was cooled to room temp., and tetrabutylammonium bromide (8 mg, 0.023 mmol), KOH (26 mg, 0.46 mmol) and methyl iodide (29 μL, 0.46 mol) were added, and reaction mixture was heated at 100 °C for an additional 2 h. After cooling to room temp., the reaction mixture was concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel eluting with a gradient of hexanes to 1% EtOAc in hexanes, furnishing **4h** (136 mg, 84%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.18, –0.09, 0.07, 0.08, 0.09 and 0.10 (6× s, 6× 3 H, CH_3Si); 0.84, 0.90 and 0.93 [3× s, 3× 9 H, $(CH_3)_3C$]; 2.72 (dd, J_{gem} = 13.5, $J_{CH2a,1'}$ = 6.8 Hz, 1 H, CH_2a); 2.85 (dd, J_{gem} = 13.5, $J_{CH2b,1'}$ = 7.3 Hz, 1 H, CH_2b); 3.63 (dd, J_{gem} = 11.3, $J_{5'a,4'}$ = 3.3 Hz, 1 H, 5′-Ha); 3.77 (dd, J_{gem} = 11.3, $J_{5'b,4'}$ = 2.8 Hz, 1 H, 5′-Hb); 3.81 (s, 3 H, CH_3O-2); 3.84 (dd, $J_{2',3'}$ = 4.3, $J_{2',1'}$ = 2.8 Hz, 1 H, 2′-H); 3.89 (br. dt, $J_{4',3'}$ = 6.7, $J_{4',5'a}$ = $J_{4',5'b}$ = 3.1 Hz, 1 H, 4′-H); 4.088 (dd, $J_{3',4'}$ = 6.7, $J_{3',2'}$ = 4.3 Hz, 1 H, 3′-H); 4.091 (td, $J_{1',CH2a}$ = $J_{1',CH2b}$ = 7.0, $J_{1',2'}$ = 2.8 Hz, 1 H, 1′-H); 6.84 (dd, $J_{3,4}$ = 8.7, $J_{3,5}$ = 1.1 Hz, 1 H, 3-H); 6.89 (td, $J_{5,4}$ = $J_{5,6}$ = 7.4, $J_{5,3}$ = 1.1 Hz, 1 H, 5-H); 7.16–7.22 (m, 2 H, 4,6-H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.4, –5.2, –4.9, –4.8, –4.7 and –4.3 (CH_3Si); 18.0, 18.1 and 18.5 [$(CH_3)_3$**C**]; 25.8, 25.9 and 26.1 [**C**$H_3)_3$C]; 34.8 (CH_2); 55.1 (CH_3O-2); 62.4 (CH_2-5′); 71.6 (CH-3′); 75.5 (CH-2′); 82.4 (CH-4′); 83.8 (CH-1′); 110.2 (CH-3); 120.4 (CH-5); 127.6 (C-1); 128.3 (CH-4); 131.2 (CH-6); 157.4 (C-2) ppm. HRMS (ESI) for $C_{31}H_{60}O_5Si_3$: $[M + Na]^+$ calcd. 619.3641, found 619.3638. IR (CCl_4): $\tilde{\nu}$ = 3067, 2956, 2929, 2897, 2857, 2838, 1603, 1588, 1494, 1472, 1463, 1439, 1405, 1389, 1362, 1251, 1242, 1081, 1037, 1003, 940, 838, 680 cm^{-1}.

2,3,5-Tri-*O*-(*tert*-butyldimethylsilyl)-1-deoxy-1β-[2-(2-thienyl)-benzyl]-D-ribofuranose (4i): Toluene (3 mL) was added to a flame-dried and argon-purged flask containing **4a** (287 mg, 0.45 mmol), $PdCl_2$ (8 mg, 0.045 mmol) and (biphenyl-2-yl)di-*tert*-butylphosphane (32 mg, 0.09 mmol). After 5 min of stirring at room temp., tributyl(thiophen-2-yl)stannane (220 μL, 0.68 mmol) was added, and the mixture was heated to 130 °C for 24 h. The crude reaction mixture was diluted with Et_2O (300 mL), washed with 2 M HCl (80 mL) and saturated $NaHCO_3$ (100 mL). After evaporation of the solvents under reduced pressure, the crude product was chromatographed on silica gel eluting with a gradient of hexanes to 1% EtOAc in hexanes to obtain **4i** (231 mg, 80%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.18, –0.07, 0.02, 0.03, 0.076 and 0.082 (6× s, 6× 3 H, CH_3Si); 0.81, 0.88 and 0.92 [3× s, 3× 9 H, $(CH_3)_3C$]; 2.79 (dd, J_{gem} = 14.2, $J_{CH2a,1'}$ = 8.1 Hz, 1 H, CH_2a); 3.08 (dd, J_{gem} = 14.2, $J_{CH2b,1'}$ = 5.4 Hz, 1 H, CH_2b); 3.61 (dd, J_{gem} = 11.2, $J_{5'a,4'}$ = 3.2 Hz, 1 H, 5′-Ha); 3.66 (dd, J_{gem} = 11.2, $J_{5'b,4'}$ = 3.6 Hz, 1 H, 5′-Hb); 3.67 (br. dd, $J_{2',1'}$ = 5.0, $J_{2',3'}$ = 4.4 Hz, 1 H, 2′-H); 3.85 (dt, $J_{4',3'}$ = 4.6, $J_{4',5'a}$ = $J_{4',5'b}$ = 3.4 Hz, 1 H, 4′-H); 3.93 (t, $J_{3',2'}$ = $J_{3',4'}$ = 4.5 Hz, 1 H, 3′-H); 4.03 (dt, $J_{1',CH2a}$ = 8.0, $J_{1',CH2b}$ = $J_{1',2'}$ = 5.2 Hz, 1 H, 1′-H); 7.05 (br. dd, $J_{3,4}$ = 3.5, $J_{3,5}$ = 1.5 Hz, 1 H, 3-H-thienyl); 7.06 (br. dd, $J_{4,5}$ = 4.9, $J_{4,3}$ = 3.5 Hz, 1 H, 4-H-thienyl); 7.23 (td, $J_{4,5}$ = $J_{4,3}$ = 7.5, $J_{4,6}$ = 1.5 Hz, 1 H, 4-H); 7.31 (td, $J_{5,4}$ = $J_{5,6}$ = 7.4, $J_{5,3}$ = 1.5 Hz, 1 H, 5-H); 7.32 (dd, $J_{5,4}$ = 4.9, $J_{5,3}$ = 1.5 Hz, 1 H, 5-H-thienyl); 7.37 (dd, $J_{3,4}$ = 7.6, $J_{3,5}$ = 1.5 Hz, 1 H, 3-H); 7.45 (dd, $J_{6,5}$ = 7.7, $J_{6,4}$ = 1.5 Hz, 1 H, 6-H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.4, –5.3, –4.9, –4.6, –4.5 and –4.3 (CH_3Si); 17.9, 18.0 and 18.4 [$(CH_3)_3$**C**]; 25.8, 25.9 and 26.0 [(**C**$H_3)_3$C]; 37.3 (CH_2); 62.8 (CH_2-5′); 72.2 (CH-3′); 75.9 (CH-2′); 83.1 (CH-1′); 83.8 (CH-4′); 125.3 (CH-5-thienyl); 126.2 (CH-4); 126.8 (CH-3-thienyl); 127.1 (CH-4-thienyl); 128.0 (CH-5); 130.6 (CH-6); 131.2 (CH-3); 134.2 (C-2); 137.3 (C-1); 142.6 (C-2-thienyl) ppm. HRMS (ESI) for $C_{34}H_{60}O_4SSi_3$: $[M + H]^+$ calcd. 649.3593, found 649.3595. IR (CCl_4): $\tilde{\nu}$ = 3066, 3021, 2956, 2897, 1602, 1484, 1472, 1463, 1448, 1431, 1406, 1389, 1362, 1255, 1220, 1086, 1023, 1004, 940, 853, 838, 696, 679, 591, 498 cm^{-1}.

2,3,5-Tri-*O*-(*tert*-butyldimethylsilyl)-1-deoxy-1β-[2-(2-furyl)benzyl]-D-ribofuranose (4j): DMF (3.0 mL) was added to a flame-dried and argon-purged flask, containing **4a** (306 mg, 0.48 mmol), and $PdCl_2(PPh_3)_2$ (17 mg, 0.024 mmol, 5 mol-%). After 5 min of stirring at room temp., tributyl(2-furyl)stannane (0.23 mL, 0.72 mmol, 1.5 equiv.) was added, and mixture was heated to 130 °C for 24 h. The crude reaction mixture was diluted with Et_2O (300 mL), washed with 2 M HCl (80 mL) and saturated $NaHCO_3$ (100 mL). After evaporation of the solvents under reduced pressure, the crude product was chromatographed on silica gel eluting with a gradient of hexanes to 2% EtOAc in hexanes to obtain **4i** (258 mg, 86%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.12, –0.04, 0.046, 0.049, 0.09 and 0.10 (6× s, 6× 3 H, CH_3Si); 0.85, 0.88 and 0.94 [3× s, 3× 9 H, $(CH_3)_3C$]; 2.89 (dd, J_{gem} = 14.1, $J_{CH2a,1'}$ = 8.1 Hz, 1 H, CH_2a); 3.15 (dd, J_{gem} = 14.1, $J_{CH2b,1'}$ = 5.3 Hz, 1 H, CH_2b); 3.63 (dd, J_{gem} = 11.2, $J_{5'a,4'}$ = 3.2 Hz, 1 H, 5′-Ha); 3.69 (dd, J_{gem} = 11.2, $J_{5'b,4'}$ = 3.6 Hz, 1 H, 5′-Hb); 3.76 (br. dd, $J_{2',1'}$ = 5.0, $J_{2',3'}$ = 4.4 Hz, 1 H, 2′-H); 3.87 (dt, $J_{4',3'}$ = 4.4, $J_{4',5'a}$ = $J_{4',5'b}$ = 3.4 Hz, 1 H, 4′-H); 4.03 (t, $J_{3',2'}$ = $J_{3',4'}$ = 4.4 Hz, 1 H, 3′-H); 4.10 (dt, $J_{1',CH2a}$ = 8.1, $J_{1',CH2b}$ = $J_{1',2'}$ = 5.2 Hz, 1 H, 1′-H); 6.46 (dd, $J_{4,3}$ = 3.3, $J_{4,5}$ = 1.8 Hz, 1 H, 4-H-furyl); 6.59 (br. dd, $J_{3,4}$ = 3.3, $J_{3,5}$ = 0.8 Hz, 1 H, 3-H-furyl); 7.24–7.28 (m, 2 H, 5,4-H); 7.37 (m, 1 H, 6-H); 7.49 (dd, $J_{5,4}$ = 1.8, $J_{5,4}$ = 0.8 Hz, 1 H, 5-H-furyl); 7.59 (m, 1 H, 3-H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.4, –5.3, –4.9, –4.5 and –4.4 (CH_3Si); 17.98, 18.01 and 18.4 [$(CH_3)_3$**C**]; 25.8, 25.9 and 26.0 [(**C**$H_3)_3$C]; 38.0 (CH_2); 62.8 (CH_2-5′); 72.3 (CH-3′); 76.0 (CH-2′); 82.4 (CH-1′); 83.9 (CH-4′); 108.7 (CH-3-furyl); 111.3 (CH-4-furyl); 126.5 (CH-4); 127.8 (CH-5); 128.3 (CH-3); 130.5 (C-2); 131.2 (CH-6); 136.0 (C-1); 141.9 (CH-5-furyl); 153.5 (C-2-furyl) ppm. HRMS (ESI) for $C_{34}H_{60}O_5Si_3$: $[M + H]^+$ calcd. 633.3821, found 633.3824. IR (CCl_4): $\tilde{\nu}$ = 3120, 3065, 3020, 2956, 2896, 1605, 1594, 1505, 1485, 1472, 1463, 1440, 1406, 1389, 1377, 1362, 1285, 1253, 1217, 1156, 1085, 1022, 1005, 940, 884, 838, 733, 680, 596, 510 cm^{-1}.

General Procedure for the Deprotection of the TBS Group. Method A: $Et_3N{\cdot}3HF$ (400 μL, 2.4 mmol, 6 equiv.) was added to the solution of silylated compound **4a**–**j** (0.40 mmol) in THF (2.00 mL), and the resulting mixture was stirred at 40 °C for 2 d. After the reaction was finished (monitored by TLC eluting with $CHCl_3$/MeOH, 10:1), the solvent was removed under reduced pressure, the crude product was dissolved in water, and solid $NaHCO_3$ was added until pH = 8. The solvents were removed under reduced pressure, and the crude product was chromatographed on silica gel (20 g) eluting with a gradient of $CHCl_3$ to 15% MeOH in $CHCl_3$ to give free *C*-ribonucleosides **7a**–**j**.

1β-(2-Bromobenzyl)-1-deoxy-D-ribofuranose (7a): Compound **7a** was prepared from **4a** (200 mg, 0.31 mmol) according to the general procedure (method A) in 80% yield as a white solid. ^{1}H NMR (500 MHz, CD_3OD): δ = 2.95 (dd, J_{gem} = 14.3, $J_{CH2a,1'}$ = 7.9 Hz, 1 H, CH_2a); 3.11 (dd, J_{gem} = 14.3, $J_{CH2b,1'}$ = 5.2 Hz, 1 H, CH_2b); 3.58 (dd, J_{gem} = 11.9, $J_{5'a,4'}$ = 4.8 Hz, 1 H, 5′-Ha); 3.67 (dd, J_{gem} = 11.9, $J_{5'b,4'}$ = 3.6 Hz, 1 H, 5′-Hb); 3.79 (br. td, $J_{4',5'a}$ = $J_{4',3'}$ =

5.1, $J_{4',5'b}$ = 3.6 Hz, 1 H, 4′-H); 3.84 (t, $J_{2',1'} = J_{2',3'}$ = 5.5 Hz, 1 H, 2′-H); 3.97 (t, $J_{3',2'} = J_{3',4'}$ = 5.5 Hz, 1 H, 3′-H); 4.08 (dt, $J_{1',CH2a}$ = 7.9, $J_{1',CH2b} = J_{1',2'}$ = 5.3 Hz, 1 H, 1′-H); 7.11 (ddd, $J_{4,3}$ = 8.0, $J_{4,5}$ = 7.4, $J_{4,6}$ = 1.8 Hz, 1 H, 4-H); 7.27 (td, $J_{5,4} = J_{5,6}$ = 7.5, $J_{5,3}$ = 1.3 Hz, 1 H, 5-H); 7.42 (br. dd, $J_{6,5}$ = 7.7, $J_{6,4}$ = 1.8 Hz, 1 H, 6-H); 7.54 (dd, $J_{3,4}$ = 8.0, $J_{3,5}$ = 1.3 Hz, 1 H, 3-H) ppm. ^{13}C NMR (125.7 MHz, CD_3OD): δ = 40.8 (CH_2); 63.5 (CH_2-5′); 72.6 (CH-3′); 75.9 (CH-2′); 83.5 (CH-1′); 85.4 (CH-4′); 125.6 (C-2); 128.5 (CH-5); 129.2 (CH-4); 133.0 (CH-6); 133.7 (CH-3); 139.2 (C-1) ppm. HRMS (ESI) for $C_{12}H_{15}BrO_4$: $[M - H]^-$ calcd. 301.0081, found 301.0083. IR (KBr): $\tilde{\nu}$ = 3425, 3392, 3269, 1567, 1472, 1460, 1205, 1160, 1122, 1111, 1071, 1057, 1045, 1029, 941, 862, 771, 748, 659, 595, 536, 447 cm^{-1}.

1β-(2-Benzyl)-1-deoxy-D-ribofuranose (7b): Compound **7b** was prepared from **4b** (255 mg, 0.45 mmol) according to the general procedure (method A) in 80% yield as a white gum. ^{1}H NMR (500 MHz, CD_3OD): δ = 2.80 (dd, J_{gem} = 14.2, $J_{CH2a,1'}$ = 7.4 Hz, 1 H, CH_2a); 2.94 (dd, J_{gem} = 14.2, $J_{CH2b,1'}$ = 4.6 Hz, 1 H, CH_2b); 3.53 (dd, J_{gem} = 11.9, $J_{5'a,4'}$ = 5.0 Hz, 1 H, 5′-Ha); 3.60 (dd, J_{gem} = 11.9, $J_{5'b,4'}$ = 3.8 Hz, 1 H, 5′-Hb); 3.73 (t, $J_{2',1'} = J_{2',3'}$ = 5.7 Hz, 1 H, 2′-H); 3.77 (dt, $J_{4',3'} = J_{4',5'a}$ = 5.0, $J_{4',5'b}$ = 3.7 Hz, 1 H, 4′-H); 3.82 (br. t, $J_{3',2'} = J_{3',4'}$ = 5.3 Hz, 1 H, 3′-H); 3.98 (ddd, $J_{1',CH2a}$ = 7.4, $J_{1',2'}$ = 5.9, $J_{1',CH2b}$ = 4.6 Hz, 1 H, 1′-H); 7.15–7.20 (m, 1 H, 4-H); 7.23–7.29 (m, 4 H, 2,3-H) ppm. ^{13}C NMR (125.7 MHz, CD_3OD): δ = 40.5 (CH_2); 63.7 (CH_2-5′); 72.7 (CH-3′); 75.5 (CH-2′); 84.8 (CH-1′); 85.6 (CH-4′); 127.2 (CH-4); 129.2 (CH-3); 130.6 (CH-2); 139.8 (C-1) ppm. HRMS (ESI) for $C_{12}H_{16}O_4$: $[M + Na]^+$ calcd. 247.0941, found 247.0941. IR (KBr): $\tilde{\nu}$ = 3435, 3410, 3253, 3087, 3064, 3030, 3004, 1603, 1584, 1496, 1455, 1308, 1201, 1112, 1098, 1070, 1057, 1030, 904, 842, 762, 744, 704, 531 cm^{-1}.

1-Deoxy-1β-(2-methylbenzyl)-D-ribofuranose (7c): Compound **7c** was prepared from **4c** (160 mg, 0.28 mmol) according to the general procedure (method A) in 70% yield as a white solid. ^{1}H NMR (500 MHz, CD_3OD): δ = 2.34 (s, 3 H, CH_3-2); 2.83 (dd, J_{gem} = 14.4, $J_{CH2a,1'}$ = 7.6 Hz, 1 H, CH_2a); 2.95 (dd, J_{gem} = 14.4, $J_{CH2b,1'}$ = 4.9 Hz, 1 H, CH_2b); 3.55 (dd, J_{gem} = 11.9, $J_{5'a,4'}$ = 4.9 Hz, 1 H, 5′-Ha); 3.61 (dd, J_{gem} = 11.9, $J_{5'b,4'}$ = 3.9 Hz, 1 H, 5′-Hb); 3.77 (td, $J_{4',3'} = J_{4',5'a}$ = 4.9, $J_{4',5'b}$ = 3.9 Hz, 1 H, 4′-H); 3.77 (t, $J_{2',1'} = J_{2',3'}$ = 5.8 Hz, 1 H, 2′-H); 3.92 (br. dd, $J_{3',2'}$ = 5.5, $J_{3',4'}$ = 5.0 Hz, 1 H, 3′-H); 3.99 (ddd, $J_{1',CH2a}$ = 7.6, $J_{1',2'}$ = 6.0, $J_{1',CH2b}$ = 4.8 Hz, 1 H, 1′-H); 7.07–7.10 (m, 2 H, 4,5-H); 7.11 (m, 1 H, 3-H); 7.23 (m, 1 H, 6-H) ppm. ^{13}C NMR (125.7 MHz, CD_3OD): δ = 19.9 (CH_3-2); 37.7 (CH_2); 63.6 (CH_2-5′); 72.7 (CH-3′); 75.8 (CH-2′); 84.2 (CH-1′); 85.6 (CH-4′); 126.8 (CH-5); 127.4 (CH-4); 131.0 and 131.1 (CH-3,6); 137.7 and 138.1 (C-1,2) ppm. HRMS (ESI) for $C_{13}H_{18}O_4$: $[M + Na]^+$ calcd. 261.1097, found 261.1098. IR (KBr): $\tilde{\nu}$ = 3402, 3065, 3021, 1606, 1583, 1494, 1461, 1379, 1126, 1111, 1074, 1055, 771, 743, 698 cm^{-1}.

1-Deoxy-1β-(2-phenylbenzyl)-D-ribofuranose (7d): Compound **7d** was prepared from **4d** (280 mg, 0.44 mmol) according to the general procedure (method A) in 82% yield as a white solid. ^{1}H NMR (500 MHz, CD_3OD): δ = 2.84 (dd, J_{gem} = 14, $J_{CH2a,1'}$ = 7.8 Hz, 1 H, CH_2a); 2.89 (dd, J_{gem} = 14.5, $J_{CH2b,1'}$ = 5.5 Hz, 1 H, CH_2b); 3.50 (dd, J_{gem} = 11.8, $J_{5'a,4'}$ = 5.1 Hz, 1 H, 5′-Ha); 3.60 (dd, J_{gem} = 11.8, $J_{5'b,4'}$ = 3.6 Hz, 1 H, 5′-Hb); 3.61 (br. t, $J_{2',1'} = J_{2',3'}$ = 5.4 Hz, 1 H, 2′-H); 3.71 (ddd, $J_{4',3'}$ = 5.4, $J_{4',5'a}$ = 5.1, $J_{4',5'b}$ = 3.5 Hz, 1 H, 4′-H); 3.76 (t, $J_{3',2'} = J_{3',4'}$ = 5.5 Hz, 1 H, 3′-H); 3.90 (dt, $J_{1',CH2a} = J_{1',CH2b} = J_{1',2'}$ = 5.4 Hz, 1 H, 1′-H); 7.16 (dd, $J_{3,4}$ = 7.5, $J_{3,5}$ = 1.6 Hz, 1 H, 3-H); 7.24 (td, $J_{4,3} = J_{4,5}$ = 7.5, $J_{4,6}$ = 1.5 Hz, 1 H, 4-H); 7.29 (td, $J_{5,4} = J_{5,6}$ = 7.4, $J_{5,3}$ = 1.6 Hz, 1 H, 5-H); 7.30–7.35 (m, 3 H, H-*o*,*p*-C_6H_5); 7.40 (m, 2 H, H-*m*-C_6H_5); 7.46 (dd, $J_{6,5}$ = 7.7, $J_{6,4}$ = 1.5 Hz, 1 H, 6-H) ppm. ^{13}C NMR (125.7 MHz, CD_3OD): δ = 37.9 (CH_2); 63.6 (CH_2-5′); 72.5 (CH-3′); 75.8 (CH-2′); 84.9 (CH-1′); 85.2 (CH-4′); 127.2 (CH-4); 127.9 (CH-*p*-C_6H_5); 128.3 (CH-5); 129.2 (CH–*m*-C_6H_5); 130.6 (CH–*o*-C_6H_5); 131.0 (CH-3); 131.2 (CH-6); 137.1 (C-1); 143.2 (C-*i*-C_6H_5); 143.8 (C-2) ppm. HRMS (ESI) for $C_{18}H_{20}O_4$: $[M + Na]^+$ calcd. 323.1254, found 323.1254. IR (KBr): $\tilde{\nu}$ = 3414, 3059, 3024, 2599, 2579, 2568, 1500, 1480, 1450, 1438, 1313, 1202, 1101, 1118, 1073, 1050, 907, 774, 751, 723, 704, 617 cm^{-1}.

1β-(2-Aminobenzyl)-1-deoxy-D-ribofuranose (7e): Compound **7e** was prepared from **4e** (215 mg, 0.37 mmol) according to the general procedure (method A) in 74% yield as a yellow solid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 2.53 (dd, J_{gem} = 14.6, $J_{CH2a,1'}$ = 8.1 Hz, 1 H, CH_2a); 2.70 (dd, J_{gem} = 14.6, $J_{CH2b,1'}$ = 3.7 Hz, 1 H, CH_2b); 3.37 (m, 2 H, 5′-H); 3.60 (br. q, $J_{2',1'} = J_{2',OH} = J_{2',3'}$ = 5.8 Hz, 1 H, 2′-H); 3.61 (br. q, $J_{4',3'} = J_{4',5'a} = J_{4',5'b}$ = 4.6 Hz, 1 H, 4′-H); 3. 74 (br. td, $J_{3',2'} = J_{3',OH}$ = 5.4, $J_{3',4'}$ = 4.5 Hz, 1 H, 3′-H); 3.81 (ddd, $J_{1',CH2a}$ = 8.1, $J_{1',2'}$ = 6.1, $J_{1',CH2b}$ = 3.7 Hz, 1 H, 1′-H); 4.64 (t, $J_{OH,5'a} = J_{OH,5'b}$ = 5.6 Hz, 1 H, O5′-H); 4.71 (d, $J_{OH,3'}$ = 5.3 Hz, 1 H, O3′-H); 4.76 (br. d, $J_{OH,2'}$ = 6.1 Hz, 1 H, O2′-H); 4.78 (br. s, 2 H, NH_2); 6.50 (td, $J_{5,4} = J_{5,6}$ = 7.3, $J_{5,3}$ = 1.3 Hz, 1 H, 5-H); 6.61 (dd, $J_{3,4}$ = 7.9, $J_{3,5}$ = 1.3 Hz, 1 H, 3-H); 6.89 (br. td, $J_{4,3} = J_{4,5}$ = 7.6, $J_{4,6}$ = 1.6 Hz, 1 H, 4-H); 6.94 (dd, $J_{6,5}$ = 7.5, $J_{6,4}$ = 1.6 Hz, 1 H, 6-H) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ = 35.1 (CH_2); 62.1 (CH_2-5′); 71.1 (CH-3′); 74.4 (CH-2′); 82.6 (CH-1′); 84.6 (CH-4′); 115.3 (CH-3); 116.7 (CH-5); 123.4 (C-1); 126.9 (CH-4); 130.5 (CH-6); 146.8 (C-2) ppm. HRMS (ESI) for $C_{12}H_{17}NO_4$: $[M + Na]^+$ calcd. 262.1050, found 262.1049. IR (KBr): $\tilde{\nu}$ = 3060, 3425, 3346, 3310, 3240, 3024, 1625, 1610, 1583, 1498, 1458, 1259, 1118, 1102, 1063, 1010, 755, 656, 603 cm^{-1}.

1-Deoxy-1β-[2-(dimethylamino)benzyl]-D-ribofuranose (7f): Compound **7f** was prepared from **4f** (210 mg, 0.34 mmol) according to the general procedure (method A) in 75% yield as a white gum. ^{1}H NMR (500 MHz, CD_3OD): δ = 2.65 [s, 6 H, $(CH_3)_2$N]; 2.92 (dd, J_{gem} = 14.2, $J_{CH2a,1'}$ = 7.9 Hz, 1 H, CH_2a); 2.97 (dd, J_{gem} = 14.2, $J_{CH2b,1'}$ = 5.2 Hz, 1 H, CH_2b); 3.57 (dd, J_{gem} = 12.0, $J_{5'a,4'}$ = 4.4 Hz, 1 H, 5′-Ha); 3.68 (dd, J_{gem} = 12.0, $J_{5'b,4'}$ = 3.3 Hz, 1 H, 5′-Hb); 3.79 (ddd, $J_{4',3'}$ = 6.0, $J_{4',5'a}$ = 4.4, $J_{4',5'b}$ = 3.3 Hz, 1 H, 4′-H); 3.83 (dd, $J_{2',3'}$ = 5.4, $J_{2',1'}$ = 4.4 Hz, 1 H, 2′-H); 4.00 (t, $J_{3',4'} = J_{3',2'}$ = 5.7 Hz, 1 H, 3′-H); 4.09 (br. ddd, $J_{1',CH2a}$ = 7.9, $J_{1',CH2b}$ = 5.2, $J_{1',2'}$ = 4.5 Hz, 1 H, 1′-H); 7.02 (m, 1 H, 5-H); 7.15–7.19 (m, 2 H, 3,4-H); 7.32 (dm, $J_{6,5}$ = 7.7 Hz, 1 H, 6-H) ppm. ^{13}C NMR (125.7 MHz, CD_3OD): δ = 35.9 (CH_2); 45.8 [$(CH_3)_2$N]; 63.3 (CH_2-5′); 72.4 (CH-3′); 76.2 (CH-2′); 85.1 (CH-4′); 85.7 (CH-1′); 120.8 (CH-3); 125.0 (CH-5); 128.3 (CH-4); 131.8 (CH-6); 135.0 (C-1); 154.3 (C-2) ppm. HRMS (ESI) for $C_{14}H_{21}NO_4$: $[M + H]^+$ calcd. 268.1543, found 268.1544. IR (KBr): $\tilde{\nu}$ = 3380, 3061, 3025, 2828, 2786, 1598, 1580, 1494, 1477, 1452, 1406, 1304, 1187, 1156, 1100, 1049, 1036, 947, 827, 767, 703, 529 cm^{-1}.

1-Deoxy-1β-(2-hydroxybenzyl)-D-ribofuranose (7g): Compound **7g** was prepared from **4g** (300 mg, 0.51 mmol) according to the general procedure (method A) in 82% yield as a white solid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 2.60 (dd, J_{gem} = 14.0, $J_{CH2a,1'}$ = 7.7 Hz, 1 H, CH_2a); 2.76 (dd, J_{gem} = 14.0, $J_{CH2b,1'}$ = 5.4 Hz, 1 H, CH_2b); 3.36 (dd, J_{gem} = 11.6, $J_{5'a,OH}$ = 6.1, $J_{5'a,4'}$ = 5.1 Hz, 1 H, 5′-Ha); 3.46 (dd, J_{gem} = 11.6, $J_{5'b,OH}$ = 5.3, $J_{5'b,4'}$ = 3.8 Hz, 1 H, 5′-Hb); 3.59 (br. td, $J_{4',3'} = J_{4',5'a}$ = 5.4, $J_{4',5'b}$ = 3.8 Hz, 1 H, 4′-H); 3.63 (br. q, $J_{2',3'} = J_{2',1'} = J_{2',OH}$ = 5.2 Hz, 1 H, 2′-H); 3.76 (br. q, $J_{3',4'} = J_{3',2'} = J_{3',OH}$ = 5.7 Hz, 1 H, 3′-H); 3.87 (br. dt, $J_{1',CH2a}$ = 7.7, $J_{1',2'} = J_{1',CH2b}$ = 5.1 Hz, 1 H, 1′-H); 4.59 (br. t, $J_{OH,5'a} = J_{OH,5'b}$ = 5.7 Hz, 1 H, O5′-H); 4.63 (d, $J_{OH,2'}$ = 5.5 Hz, 1 H, O2′-H); 4.67 (d, $J_{OH,3'}$ = 5.9 Hz, 1 H, O3′-H); 6.70 (td, $J_{5,4} = J_{5,6}$ = 7.4, $J_{5,3}$ = 1.3 Hz, 1 H, 5-H); 6.76 (dd, $J_{3,4}$ = 8.1, $J_{3,5}$ =

1.3 Hz, 1 H, 3-H); 7.00 (br. td, $J_{4,3} = J_{4,5} = 7.7$, $J_{4,6} = 1.8$ Hz, 1 H, 4-H); 7.11 (dd, $J_{6,5} = 7.5$, $J_{6,4} = 1.8$ Hz, 1 H, 6-H); 9.18 (s, 1 H, O2-H) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ = 34.3 (CH_2); 62.2 (CH_2-5′); 71.1 (CH-3′); 74.3 (CH-2′); 82.5 (CH-1′); 83.8 (CH-4′); 115.0 (CH-3); 118.9 (CH-5); 125.2 (C-1); 127.2 (CH-4); 131.1 (CH-6); 155.4 (C-2) ppm. HRMS (ESI) for $C_{12}H_{16}O_5$: $[M + Na]^+$ calcd. 263.0890, found 263.0890. IR (KBr): $\tilde{\nu}$ = 3416, 3065, 3035, 1612, 1595, 1586, 1506, 1491, 1457, 1242, 1154, 1103, 1043, 906, 828, 752 cm^{-1}.

1-Deoxy-1β-(2-methoxybenzyl)-D-ribofuranose (7h): Compound **7h** was prepared from **4h** (190 mg, 0.32 mmol) according to the general procedure (method A) in 82% yield as a white solid. ^{1}H NMR (500 MHz, CD_3OD): δ = 2.83 (dd, $J_{gem} = 13.8$, $J_{CH2a,1'} = 7.1$ Hz, 1 H, CH_2a); 2.89 (dd, $J_{gem} = 13.8$, $J_{CH2b,1'} = 6.2$ Hz, 1 H, CH_2b); 3.55 (dd, $J_{gem} = 11.9$, $J_{5'a,4'} = 5.0$ Hz, 1 H, 5′-Ha); 3.66 (dd, $J_{gem} = 11.9$, $J_{5'b,4'} = 3.4$ Hz, 1 H, 5′-Hb); 3.77 (ddd, $J_{4',3'} = 6.2$, $J_{4',5'a} = 5.0$, $J_{4',5'b} = 3.4$ Hz, 1 H, 4′-H); 3.81 (dd, $J_{2',3'} = 5.5$, $J_{2',1'} = 4.4$ Hz, 1 H, 2′-H); 3.82 (s, 3 H, CH_3O); 3.90 (br. dd, $J_{3',4'} = 6.1$, $J_{3',2'} = 5.5$ Hz, 1 H, 3′-H); 4.07 (ddd, $J_{1',CH2a} = 7.1$, $J_{1',CH2b} = 6.1$, $J_{1',2'} = 4.4$ Hz, 1 H, 1′-H); 6.86 (td, $J_{5,4} = J_{5,6} = 7.4$, $J_{5,3} = 1.2$ Hz, 1 H, 5-H); 6.92 (dd, $J_{3,4} = 8.2$, $J_{3,5} = 1.2$ Hz, 1 H, 3-H); 7.18 (ddd, $J_{4,3} = 8.2$, $J_{4,5} = 7.5$, $J_{4,6} = 1.8$ Hz, 1 H, 4-H); 7.21 (dd, $J_{6,5} = 7.4$, $J_{6,4} = 1.8$ Hz, 1 H, 6-H) ppm. ^{13}C NMR (125.7 MHz, CD_3OD): δ = 35.3 (CH_2); 55.8 (CH_3O); 63.6 (CH_2-5′); 72.6 (CH-3′); 75.8 (CH-2′); 84.6 (CH-1′); 84.1 (CH-4′); 111.4 (CH-3); 121.4 (CH-5); 127.6 (C-1); 128.7 (CH-4); 132.2 (CH-6); 159.0 (C-2) ppm. HRMS (ESI) for $C_{13}H_{18}O_5$: $[M + Na]^+$ calcd. 277.1046, found 277.1045. IR (KBr): $\tilde{\nu}$ = 3076, 3034, 2961, 2933, 2845, 1600, 1587, 1496, 1466, 1446, 1247, 1118, 1035.933, 756, 608 cm^{-1}.

1-Deoxy-1β-[2-(2-thienyl)benzyl]-D-ribofuranose (7i): Compound **7i** was prepared from **4i** (210 mg, 0.32 mmol) according to the general procedure (method A) in 85% yield as an orange solid. ^{1}H NMR (500 MHz, CD_3OD): δ = 2.97 (dd, $J_{gem} = 14.4$, $J_{CH2a,1'} = 8.0$ Hz, 1 H, CH_2a); 3.06 (dd, $J_{gem} = 14.5$, $J_{CH2b,1'} = 5.2$ Hz, 1 H, CH_2b); 3.54 (dd, $J_{gem} = 11.9$, $J_{5'a,4'} = 5.0$ Hz, 1 H, 5′-Ha); 3.64 (dd, $J_{gem} = 11.9$, $J_{5'b,4'} = 3.7$ Hz, 1 H, 5′-Hb); 3.71 (t, $J_{2',1'} = J_{2',3'} = 5.5$ Hz, 1 H, 2′-H); 3.75 (td, $J_{4',3'} = J_{4',5'a} = 5.2$, $J_{4',5'b} = 3.8$ Hz, 1 H, 4′-H); 3.85 (t, $J_{3',2'} = J_{3',4'} = 5.5$ Hz, 1 H, 3′-H); 3.96 (dt, $J_{1',CH2a} = 8.0$, $J_{1',CH2b} = J_{1',2'} = 5.3$ Hz, 1 H, 1′-H); 7.09 (dd, $J_{4,5} = 5.0$, $J_{4,3} = 3.5$ Hz, 1 H, 4-H-thienyl); 7.10 (dd, $J_{3,4} = 3.5$, $J_{3,5} = 1.3$ Hz, 1 H, 3-H-thienyl); 7.23 (td, $J_{4,5} = J_{4,3} = 7.5$, $J_{4,6} = 1.5$ Hz, 1 H, 4-H); 7.30 (td, $J_{5,6} = J_{5,4} = 7.6$, $J_{5,3} = 1.6$ Hz, 1 H, 5-H); 7.33 (dd, $J_{3,4} = 7.5$, $J_{3,5} = 1.6$ Hz, 1 H, 3-H); 7.42 (dd, $J_{5,4} = 5.0$, $J_{5,3} = 1.4$ Hz, 1 H, 5-H-thienyl); 7.47 (dd, $J_{6,5} = 7.7$, $J_{6,4} = 1.6$ Hz, 1 H, 6-H) ppm. ^{13}C NMR (125.7 MHz, CD_3OD): δ = 38.2 (CH_2); 63.6 (CH_2-5′); 72.6 (CH-3′); 75.9 (CH-2′); 84.8 (CH-1′); 85.3 (CH-4′); 126.4 (CH-5-thienyl); 127.3 (CH-4); 127.17 and 127.18 (CH-3,4-thienyl); 129.0 (CH-5); 131.7 (CH-6); 132.1 (CH-3); 135.8 (C-2); 138.3 (C-1); 143.8 (C-2-furyl) ppm. HRMS (ESI) for $C_{16}H_{18}O_4S$: $[M + Na]^+$ calcd. 329.0818, found 329.0817. IR (KBr): $\tilde{\nu}$ = 3106, 3090, 3065, 1601, 1585, 1531, 1484, 1457, 1427, 1350, 1247, 1112, 1048, 1030, 849, 775, 687, 610 cm^{-1}.

1-Deoxy-1β-[2-(2-furyl)benzyl]-D-ribofuranose (7j): Compound **7j** was prepared from **4j** (330 mg, 0.52 mmol) according to the general procedure (method A) in 88% yield as a yellow solid. ^{1}H NMR (500 MHz, CD_3OD): δ = 3.05 (dd, $J_{gem} = 14.3$, $J_{CH2a,1'} = 7.7$ Hz, 1 H, CH_2a); 3.17 (dd, $J_{gem} = 14.3$, $J_{CH2b,1'} = 5.3$ Hz, 1 H, CH_2b); 3.57 (dd, $J_{gem} = 11.9$, $J_{5'a,4'} = 4.8$ Hz, 1 H, 5′-Ha); 3.67 (dd, $J_{gem} = 11.9$, $J_{5'b,4'} = 3.6$ Hz, 1 H, 5′-Hb); 3.76 (br. ddd, $J_{4',3'} = 5.3$, $J_{4',5'a} = 5.0$, $J_{4',5'b} = 3.6$ Hz, 1 H, 4′-H); 3.80 (t, $J_{2',1'} = J_{2',3'} = 5.5$ Hz, 1 H, 2′-H); 3.93 (t, $J_{3',2'} = J_{3',4'} = 5.5$ Hz, 1 H, 3′-H); 4.01 (dt, $J_{1',CH2a} = 7.7$, $J_{1',CH2b} = J_{1',2'} = 5.3$ Hz, 1 H, 1′-H); 6.52 (dd, $J_{4,3} = 3.4$, $J_{4,5} = 1.9$ Hz, 1 H, 4-H-furyl); 6.66 (dd, $J_{3,4} = 3.4$, $J_{3,5} = 0.9$ Hz, 1 H, 3-H-furyl); 7.23–7.28 (m, 2 H, 5,4-H); 7.42 (m, 1 H, 6-H); 7.57 (m, 1 H, 3-H); 7.59 (dd, $J_{5,4} = 1.9$, $J_{5,4} = 0.8$ Hz, 1 H, 5-H-furyl) ppm. ^{13}C NMR (125.7 MHz, CD_3OD): δ = 39.0 (CH_2); 63.6 (CH_2-5′); 72.6 (CH-3′); 76.0 (CH-2′); 84.5 (CH-1′); 85.3 (CH-4′); 109.7 (CH-3-furyl); 112.3 (CH-4-furyl); 127.5 (CH-4); 128.8 (CH-5); 129.1 (CH-3); 131.9 (C-2); 132.5 (CH-6); 136.9 (C-1); 143.3 (CH-5-furyl); 154.9 (C-2-furyl) ppm. HRMS (ESI) for $C_{16}H_{18}O_5$: $[M - H]^-$ calcd. 289.1082, found 289.1082. IR (KBr): $\tilde{\nu}$ = 3411, 3120, 3065, 3028, 1604, 1573, 1504, 1485, 1464, 1407, 1283, 1215, 1156, 1103, 1051, 1010, 886, 763, 596 cm^{-1}.

2,3,5-Tri-*O*-(*tert*-butyldimethylsilyl)-1β-(2-carboxybenzyl)-1-deoxy-D-ribofuranose (4k): *n*BuLi (2.62 mL, 4.2 mmol, 1.6 M solution in hexane, 1.5 equiv.) was added to a vigorously stirred solution of compound **4a** (3.0 g, 2.79 mmol) in dry THF (26 mL) under argon at –78 °C and stirred at –78 °C for 60 min. Dry ice was placed in a the flame-dried flask (sealed with a septum) and introduced into the reaction mixture through cannula for 60 min. The resulting mixture was slowly warmed up to room temp., quenched by pouring into a solution of NH_4Cl in water (150 mL) and extracted with Et_2O (3× 250 mL). After evaporation of the solvents and chromatography eluting with a gradient of hexanes to 16% EtOAc in hexanes, compound **4k** (1.99 g, 70%) was obtained as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.05, 0.075, 0 078, 0.09 and 0.11 (6× s, 6× 3 H, CH_3Si); 0.88, 0.92 and 0.93 [3× s, 3× 9 H, $(CH_3)_3C$]; 2.96 (dd, $J_{gem} = 13.9$, $J_{CH2a,1'} = 9.8$ Hz, 1 H, CH_2a); 3.22 (dd, $J_{gem} = 13.9$, $J_{CH2b,1'} = 3.5$ Hz, 1 H, CH_2b); 3.61 (dd, $J_{gem} = 11.2$, $J_{5'a,4'} = 4.0$ Hz, 1 H, 5′-Ha); 3.64 (dd, $J_{gem} = 11.2$, $J_{5'b,4'} = 3.5$ Hz, 1 H, 5′-Hb); 3.89 (dd, $J_{2',1'} = 7.2$, $J_{2',3'} = 4.5$ Hz, 1 H, 2′-H); 3.94 (td, $J_{4',5'a} = J_{4',5'b} = 3.8$, $J_{4',3'} = 2.6$ Hz, 1 H, 4′-H); 4.07 (dd, $J_{3',2'} = 4.5$, $J_{3',4'} = 2.6$ Hz, 1 H, 3′-H); 4.12 (dd, $J_{1',CH2a} = 9.8$, $J_{1',2'} = 7.2$, $J_{1',CH2b} = 3.5$ Hz, 1 H, 1′-H); 7.30–7.35 (m, 2 H, 4,6-H); 7.48 (td, $J_{5,4} = J_{5,6} = 7.5$, $J_{5,3} = 1.5$ Hz, 1 H, 5-H); 7.85 (dd, $J_{3,4} = 8.1$, $J_{3,5} = 1.5$ Hz, 1 H, 5-H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.7, –5.4, –4.7, –4.5, –4.4 and –4.1 (CH_3Si); 18.0, 18.1 and 18.4 [$(CH_3)_3$**C**]; 25.8, 25.9 and 26.0 [**C**H_3)$_3$C]; 37.4 (CH_2); 62.7 (CH_2-5′); 73.2 (CH-3′); 75.9 (CH-2′); 83.0 (CH-1′); 86.2 (CH-4′); 126.9 (CH-4); 130.9 (CH-6); 131.0 (CH-3); 132.0 (CH-5); 132.3 (C-2); 137.8 (C-1); 170.3 (CO) ppm. HRMS (ESI) for $C_{31}H_{58}O_6Si_3$: $[M + H]^+$ calcd. 611.3614, found 611.3614. IR (CCl_4): $\tilde{\nu}$ = 3535, 3075, 3028, 2956, 2897, 1738, 1694, 1603, 1576, 1491, 1472, 1463, 1448, 1405, 1390, 1362, 1303, 1256, 1188, 1084, 1022, 940, 838, 717, 707, 680, 463 cm^{-1}.

General Procedure for Amide Synthesis: Hydroxybenzotriazole (95 mg, 0.71 mmol, 1.5 equiv.), 1-ethyl-3-[3-(dimethylamino)propyl]-carbodiimide (136 mg, 0.71 mmol, 1.5 equiv.) and starting nucleoside **4k** (285 mg, 0.47 mmol, 1.0 equiv.) were dissolved in DCM (4 mL), and the mixture was stirred at room temp. for 60 min. Then a solution of the amine source (0.94 mmol, 2.0 equiv.) and Et_3N (0.5 mL) in dry DCM (2 mL) were added, and the reaction mixture was stirred for another 30 min. The reaction mixture was then quenched by pouring into a solution of $NaHCO_3$ (50 mL), extracting with DCM (3× 50 mL) and drying with Na_2SO_4. After evaporation of the solvents, the crude product was chromatographed on silica gel eluting with a gradient of hexanes to 20% EtOAc in hexanes to give free *C*-ribonucleosides **4l**–**o**.

2,3,5-Tri-*O*-(*tert*-butyldimethylsilyl)-1β-(2-carbamoylbenzyl)-1-deoxy-D-ribofuranose (4l): Compound **4l** was prepared from **4k** (350 mg, 0.57 mmol) and ammonium chloride (61 mg, 1.14 mmol) according to the general procedure for amide synthesis in 94% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.03, 0.07, 0.08, 0.10 and 0.12 (6× s, 6× 3 H, CH_3Si); 0.89, 0.92 and 0.95

[3 × s, 3 × 9 H, $(CH_3)_3C$]; 2.97–3.07 (m, 2 H, CH_2); 3.54–3.61 (m, 2 H, 5′-H); 3.80 (dd, $J_{2',1'}$ = 8.3, $J_{2',3'}$ = 4.8 Hz, 1 H, 2′-H); 3.86 (td, $J_{4',5'a}$ = $J_{4',5'b}$ = 3.3, $J_{4',3'}$ = 1.7 Hz, 1 H, 4′-H); 3.98 (dd, $J_{3',4'}$ = 4.8, $J_{3',4'}$ = 1.7 Hz, 1 H, 3′-H); 4.12 (br. td, $J_{1',2'}$ = $J_{1',CH2}$ = 8.6, $J_{1',CH2}$ = 4.4 Hz, 1 H, 1′-H); 5.71 (br. s, 1 H, NH_2a); 7.28 (m, 1 H, 4-H); 7.30 (br. d, $J_{6,5}$ = 7.4 Hz, 1 H, 6-H); 7.42 (m, 1 H, 5-H); 7.67 (m, 1 H, 3-H); 7.99 (br. s, 1 H, NH_2b) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.5, –5.4, –4.6, –4.5, –4.3 and –4.0 (CH_3Si); 18.0; 18.1 and 18.3 [$(CH_3)_3$**C**]; 25.8, 25.9 and 26.0 [(**C**$H_3)_3$C]; 36.6 (CH_2); 63.3 (CH_2-5′); 73.5 (CH-3′); 76.5 (CH-2′); 83.0 (CH-1′); 86.7 (CH-4′); 126.7 (CH-4); 129.2 (CH-3); 130.0 (CH-6); 130.5 (CH-5); 136.0 and 136.1 (C-1, 2); 171.6 (CO) ppm. HRMS (ESI) for $C_{31}H_{59}NO_5Si_3$: $[M + H]^+$ calcd. 610.3774, found 610.3775. IR (CCl_4): ṽ = 3532, 3485, 3411, 3380, 3334, 3180, 3074, 3022, 2955, 2897, 1678, 1604, 1578, 1490, 1472, 1463, 1450, 1408, 1389, 1362, 1256, 1152, 1124, 1086, 1015, 1006, 940, 882, 839, 680 cm^{-1}.

2,3,5-Tri-*O*-(*tert*-butyldimethylsilyl)-1-deoxy-1β-[2-(*N*-methylcarbamoyl)benzyl]-D-ribofuranose (4m): Compound **4m** was prepared from **4k** (285 mg, 0.47 mmol) and methylamine hydrochloride (64 mg, 0.94 mmol) according to the general procedure for amide synthesis in 91% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.04, 0.07, 0.078, 0.080, 0.09 and 0.10 (6 × s, 6 × 3 H, CH_3Si); 0.89, 0.92 and 0.94 [3 × s, 3 × 9 H, $(CH_3)_3$C]; 2.79 (dd, J_{gem} = 13.9, $J_{CH2a,1'}$ = 10.0 Hz, 1 H, CH_2a); 2.93 (d, $J_{CH3,NH}$ = 4.7 Hz, 3 H, C**H**$_3$NH); 3.01 (dd, J_{gem} = 13.9, $J_{CH2b,1'}$ = 2.7 Hz, 1 H, CH_2b); 3.55 (dd, J_{gem} = 11.0, $J_{5'a,4'}$ = 4.4 Hz, 1 H, 5′-Ha); 3.60 (dd, J_{gem} = 11.0, $J_{5'b,4'}$ = 4.1 Hz, 1 H, 5′-Hb); 3.76 (dd, $J_{2',1'}$ = 8.0, $J_{2',3'}$ = 4.6 Hz, 1 H, 2′-H); 3.87 (td, $J_{4',5'a}$ = $J_{4',5'b}$ = 4.3, $J_{4',3'}$ = 1.9 Hz, 1 H, 4′-H); 3.98 (dd, $J_{3',4'}$ = 4.6, $J_{3',4'}$ = 1.9 Hz, 1 H, 3′-H); 4.09 (ddd, $J_{1',CH2a}$ = 10.0, $J_{1',2'}$ = 8.0, $J_{1',CH2b}$ = 2.6 Hz, 1 H, 1′-H); 7.26 (m, 1 H, 4-H); 7.27 (m, 1 H, 6-H); 7.37 (m, 1 H, 5-H); 7.48 (br. s, 1 H, NH); 7.56 (m, 1 H, 3-H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.5, –5.3, –4.7, –4.5, –4.4 and –4.0 (CH_3Si); 18.0; 18.1 and 18.4 [$(CH_3)_3$**C**]; 25.8, 25.9 and 26.0 [(**C**$H_3)_3$C]; 26.3 (CH_3NH); 36.5 (CH_2); 63.8 (CH_2-5′); 73.2 (CH-3′); 76.1 (CH-2′); 83.2 (CH-1′); 86.1 (CH-4′); 126.6 (CH-4); 128.8 (CH-3); 129.8 (CH-5); 130.1 (CH-6); 135.7 (C-1); 137.5 (C-2); 170.1 (CO) ppm. HRMS (ESI) for $C_{32}H_{61}NO_5Si_3$: $[M + H]^+$ calcd. 624.3930, found 624.3931. IR (CCl_4): ṽ = 3463, 3351, 3069, 3021, 2956, 2897, 1663, 1676, 1603, 1580, 1552, 1513, 1483, 1472, 1463, 1412, 1390, 1362, 1280, 1257, 1154, 1126, 1105, 1088, 1005, 940, 883, 838, 680 cm^{-1}.

2,3,5-Tri-*O*-(*tert*-butyldimethylsilyl)-1-deoxy-1β-[2-(*N*,*N*-dimethylcarbamoyl)benzyl]-D-ribofuranose (4n): Compound **4n** was prepared from **4k** (180 mg, 0.30 mmol) and dimethylamine hydrochloride (50 mg, 0.60 mmol) according to the general procedure for amide synthesis in 88% yield as a colorless oil. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = –0.09, –0.04, 0.06, 0.07 and 0.09 (6 × s, 6 × 3 H, CH_3Si); 0.84, 0.87 and 0.90 [3 × s, 3 × 9 H, $(CH_3)_3$C]; 2.50–2.75 (m, 2 H, CH_2); 2.72 and2.98 [2s, 2 × 3 H, $(CH_3)_2$N]; 3.58 (dd, J_{gem} = 11.3, $J_{5'a,4'}$ = 3.5 Hz, 1 H, 5′-Ha); 3.65 (dd, J_{gem} = 11.3, $J_{5'b,4'}$ = 3.6 Hz, 1 H, 5′-Hb); 3.72 (dt, $J_{4',3'}$ = 4.7, $J_{4',5'a}$ = $J_{4',5'b}$ = 3.5 Hz, 1 H, 4′-H); 3.87 (m, 1 H, 1′-H); 3.91 (br. t, $J_{2',1'}$ = $J_{2',3'}$ = 4.3 Hz, 1 H, 2′-H); 4.03 (br. t, $J_{3',4'}$ = $J_{3',2'}$ = 4.3 Hz, 1 H, 3′-H); 7.15 (br. dd, $J_{3,5}$ = 7.5, $J_{3,5}$ = 1.5 Hz, 1 H, 3-H); 7.26 (td, $J_{4,5}$ = $J_{4,3}$ = 7.5, $J_{4,6}$ = 1.5 Hz, 1 H, 4-H); 7.32 (td, $J_{5,6}$ = $J_{5,4}$ = 7.4, $J_{5,3}$ = 1.5 Hz, 1 H, 5-H); 7.36 (dd, $J_{6,5}$ = 7.7, $J_{6,4}$ = 1.5 Hz, 1 H, 6-H) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ = –5.5, –5.4, –4.84, –4.76, –4.6 and –4.5 (CH_3Si); 17.6, 17.7 and 18.0 [$(CH_3)_3$**C**]; 25.75, 25.77 and 25.8 [(**C**$H_3)_3$C]; 34.0 and 38.1 [$(CH_3)_2$N]; 36.8 (CH_2); 62.5 (CH_2-5′); 71.9 (CH-3′); 75.3 (CH-2′); 82.4 (CH-1′); 83.2 (CH-4′); 125.8 (CH-3); 126.2 (CH-4); 128.3 (CH-5); 130.4 (CH-6); 134.9 (C-1); 137.0 (C-2), 169.9 (CO) ppm. HRMS (ESI) for $C_{33}H_{63}NO_5Si_3$: $[M + H]^+$ calcd. 638.4087, found 638.4087. IR (CCl_4): ṽ = 3065, 3022, 2955, 2896, 1645, 1602, 1578, 1503, 1485, 1472, 1463, 1447, 1405, 1393, 1361, 1253, 1188, 1079, 1023, 1004, 940, 838, 702, 681, 655 cm^{-1}.

1β-[2-(*N*-Benzylcarbamoyl)benzyl]-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-1-deoxy-D-ribofuranose (4o): Compound **4o** was prepared from **4k** (330 mg, 0.54 mmol) and benzylamine (118 μL, 1.08 mmol) according to the general procedure for amide synthesis in 97% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.00, 0.02, 0.03, 0.07, 0.076 and 0.079 (6 × s, 6 × 3 H, CH_3Si); 0.88, 0.89 and 0.94 [3 × s, 3 × 9 H, $(CH_3)_3$C]; 2.89 (dd, J_{gem} = 14.0, $J_{CH2a,1'}$ = 9.7 Hz, 1 H, CH_2a); 3.05 (dd, J_{gem} = 14.0, $J_{CH2b,1'}$ = 3.1 Hz, 1 H, CH_2b); 3.32 (dd, J_{gem} = 10.8, $J_{5'a,4'}$ = 5.5 Hz, 1 H, 5′-Ha); 3.42 (dd, J_{gem} = 10.8, $J_{5'b,4'}$ = 4.5 Hz, 1 H, 5′-Hb); 3.66 (dd, $J_{2',1'}$ = 7.8, $J_{2',3'}$ = 4.6 Hz, 1 H, 2′-H); 3.81 (ddd, $J_{4',5'a}$ = 5.5, $J_{4',5'b}$ = 4.5, $J_{4',3'}$ = 2.0 Hz, 1 H, 4′-H); 3.93 (dd, $J_{3',4'}$ = 4.6, $J_{3',4'}$ = 2.0 Hz, 1 H, 3′-H); 4.09 (ddd, $J_{1',CH2a}$ = 9.7, $J_{1',2'}$ = 7.8, $J_{1',CH2b}$ = 3.0 Hz, 1 H, 1′-H); 4.60 (dd, J_{gem} = 15.1, $J_{CH2a,NH}$ = 5.9 Hz, 1 H, CH_2a-Ph); 4.66 (dd, J_{gem} = 15.1, $J_{CH2b,NH}$ = 6.2 Hz, 1 H, CH_2b-Ph); 7.23–7.36 (m, 7 H, 4, 6-H, *o*,*m*,*p*-Ph); 7.38 (br. td, $J_{5,4'}$ = $J_{5,6}$ = 7.5, $J_{5,3}$ = 1.5 Hz, 1 H, 5-H); 7.58 (dd, $J_{3,4}$ = 7.7, $J_{3,5}$ = 1.5 Hz, 1 H, 3-H); 7.77 (br. t, $J_{NH,CH2a}$ = $J_{NH,CH2b}$ = 6.0 Hz, 1 H, NH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.41, –5.39, –4.7, –4.5, –4.3 and –4.0 (CH_3Si); 18.0, 18.1 and 18.3 [$(CH_3)_3$**C**]; 25.8, 25.9 and 26.0 [(**C**$H_3)_3$C]; 36.2 (CH_2); 43.4 (CH_2-Ph); 63.6 (CH_2-5′); 73.1 (CH-3′); 75.8 (CH-2′); 82.8 (CH-1′); 85.8 (CH-4′); 126.6 (CH-4); 127.2 (CH-*p*-Ph); 127.3 (CH-*o*-Ph); 128.6 (CH-*m*-Ph); 128.7 (CH-3); 129.9 (CH-5); 130.3 (CH-6); 135.9 (C-1); 137.2 (C-2); 138.9 (C-*i*-Ph); 169.5 (CO) ppm. HRMS (ESI) for $C_{38}H_{65}NO_5Si_3$: $[M + H]^+$ calcd. 700.4243, found 700.4245. IR (KBr): ṽ = 3089, 3067, 3031, 2955, 2896, 1603, 1587, 1577, 1543, 1500, 1482, 1472, 1463, 1455, 1406, 1389, 1361, 1275, 1256, 1089, 1025, 1005, 941, 839, 699, 680 cm^{-1}.

General Procedure for the Deprotection of the TBS Group. Method B: A mixture of CF_3COOH/H_2O (9:1) (2 mL) was added to silylated compounds **4k**–**o** (0.50 mmol), and the resulting homogeneous mixtures were stirred at room temp. for 4 h. After the reaction was complete (monitored by TLC eluting with $CHCl_3$/MeOH, 10:1), the solvents were removed under reduced pressure and the crude products co-evaporated with 3 × 50 mL of toluene. Subsequent purification by chromatography on silica gel (20 g) eluting with a gradient of $CHCl_3$ to 15% MeOH in $CHCl_3$ afforded the free *C*-ribonucleosides **7k**–**o**.

1β-(2-Carboxybenzyl)-1-deoxy-D-ribofuranose (7k): Compound **7k** was prepared from **4k** (250 mg, 0.41 mmol) according to the general procedure (method B) in 79% yield as a white solid. ^{1}H NMR (500 MHz, CD_3OD): δ = 3.21 (dd, J_{gem} = 13.9, $J_{CH2a,1'}$ = 7.5 Hz, 1 H, CH_2a); 3.39 (dd, J_{gem} = 13.8, $J_{CH2b,1'}$ = 5.0 Hz, 1 H, CH_2b); 3.53 (dd, J_{gem} = 12.0, $J_{5'a,4'}$ = 4.9 Hz, 1 H, 5′-Ha); 3.62 (dd, J_{gem} = 12.0, $J_{5'b,4'}$ = 3.6 Hz, 1 H, 5′-Hb); 3.76 (td, $J_{4',5'a}$ = $J_{4',3'}$ = 5.1, $J_{4',5'b}$ = 3.7 Hz, 1 H, 4′-H); 3.77 (t, $J_{2',3'}$ = $J_{2',1'}$ = 5.4 Hz, 1 H, 2′-H); 3. 89 (t, $J_{3',4'}$ = $J_{3',2'}$ = 5.4 Hz, 1 H, 3′-H); 4.04 (dt, $J_{1',CH2a}$ = 7.5, $J_{1',2'}$ = $J_{1',CH2b}$ = 5.2 Hz, 1 H, 1′-H); 7.28 (ddd, $J_{4,3}$ = 7.8, $J_{4,5}$ = 7.1, $J_{4,6}$ = 1.6 Hz, 1 H, 4-H); 7.40 (br. dd, $J_{6,5}$ = 7.7, $J_{6,4}$ = 1.6 Hz, 1 H, 6-H); 7.43 (ddd, $J_{5,6}$ = 7.7, $J_{5,4}$ = 7.1, $J_{5,3}$ = 1.5 Hz, 1 H, 5-H); 7.83 (dd, $J_{3,4}$ = 7.8, $J_{3,5}$ = 1.5 Hz, 1 H, 3-H) ppm. ^{13}C NMR (125.7 MHz, CD_3OD): δ = 38.4 (CH_2); 63.6 (CH_2-5′); 72.7 (CH-3′); 75.7 (CH-2′); 84.8 (CH-1′); 85.3 (CH-4′); 127.3 (CH-4); 131.3 (CH-3); 132.4 (CH-5); 133.0 (CH-6); 133.2 (C-2); 140.4 (C-1); 172.2 (CO) ppm. HRMS (ESI) for $C_{13}H_{16}O_6$: $[M - H]^-$ calcd. 267.0874, found 267.0874. IR (KBr): ṽ = 3419, 3392, 3335, 3280, 3240, 3079, 2660, 2573, 2542, 2521, 1728, 1600, 1578, 1498, 1445, 1435, 1314, 1304, 1117, 1076, 1051, 1039, 918, 783 cm^{-1}.

1β-(2-Carbamoylbenzyl)-1-deoxy-D-ribofuranose (7l): Compound **7l** was prepared from **4l** (275 mg, 0.45 mmol) according to the general procedure (method B) in 74% yield as a white solid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 2.85 (dd, J_{gem} = 14.1, $J_{CH2a,1'}$ = 8.3 Hz, 1 H, CH$_2$a); 3.05 (dd, J_{gem} = 14.1, $J_{CH2b,1'}$ = 4.6 Hz, 1 H, CH$_2$b); 3.33 (ddd, J_{gem} = 11.6, $J_{5'a,OH}$ = 6.0, $J_{5'a,4'}$ = 5.1 Hz, 1 H, 5′-Ha); 3.40 (ddd, J_{gem} = 11.6, $J_{5'b,OH}$ = 5.5, $J_{5'b,4'}$ = 4.2 Hz, 1 H, 5′-Hb); 3.59 (br. q, $J_{4',3'}$ = $J_{4',5'a}$ = $J_{4',5'b}$ = 4.6 Hz, 1 H, 4′-H); 3.61 (br. q, $J_{2',1'}$ = $J_{2',3'}$ = $J_{2',OH}$ = 5.7 Hz, 1 H, 2′-H); 3.75 (br. q, $J_{3',2'}$ = $J_{3',4'}$ = $J_{3',OH}$ = 5.2 Hz, 1 H, 3′-H); 3.87 (ddd, $J_{1',CH2a}$ = 8.3, $J_{1',2'}$ = 5.9, $J_{1',CH2b}$ = 4.6 Hz, 1 H, 1′-H); 4.59 (t, $J_{OH,5'a}$ = $J_{OH,5'b}$ = 5.7 Hz, 1 H, O5′-H); 4.71 (d, $J_{OH,3'}$ = 5.4 Hz, 1 H, O3′-H); 4.74 (d, $J_{OH,2'}$ = 5.8 Hz, 1 H, O2′-H); 7.23 (m, 1 H, 4-H); 7.30–7.36 (m, 4 H,3,5,6-H, NH$_2$a); 7.72 (br. s, 1 H, NH$_2$b) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ = 36.6 (CH$_2$); 62.2 (CH$_2$-5′); 71.2 (CH-3′); 74.4 (CH-2′); 82.7 (CH-1′); 84.4 (CH-4′); 125.9 (CH-4); 127.4 (CH-3); 129.2 (CH-5); 130.7 (CH-6); 136.4 (C-1); 137.7 (C-2); 171.4 (CO) ppm. HRMS (ESI) for $C_{13}H_{17}NO_5$: [M + Na]$^+$ calcd. 290.0999, found 290.0999. IR (KBr): $\tilde{\nu}$ = 3396, 3278, 3221, 3074, 3030, 1652, 1608, 1574, 1492, 1450, 1422, 1099, 1045, 761, 630, 599 cm^{-1}.

1-Deoxy-1β-[2-(*N*-methylcarbamoyl)benzyl]-D-ribofuranose (7m): Compound **7m** was prepared from **4m** (253 mg, 0.41 mmol) according to the general procedure (method B) in 79% yield as a white solid. ^{1}H NMR (500 MHz, CD$_3$OD): δ = 2.87 and 3.11 [2× s, 2× 3 H, (CH$_3$)$_2$N]; 2.60–3.10 (m, 2 H, CH$_2$); 3.52 (dd, J_{gem} = 11.9, $J_{5'a,4'}$ = 4.7 Hz, 1 H, 5′-Ha); 3.63 (dd, J_{gem} = 11.9, $J_{5'b,4'}$ = 3.7 Hz, 1 H, 5′-Hb); 3.71 (t, $J_{2',1'}$ = $J_{2',3'}$ = 5.9 Hz, 1 H, 2′-H); 3.75 (td, $J_{4',5'a}$ = $J_{4',3'}$ = 4.7, $J_{4',5'b}$ = 3.7 Hz, 1 H, 4′-H); 3.90 (dd, $J_{3',2'}$ = 5.7, $J_{3',4'}$ = 4.7 Hz, 1 H, 3′-H); 3.94 (br. q, $J_{1',CH2a}$ = $J_{1',2'}$ = $J_{1',CH2b}$ = 6.3 Hz, 1 H, 1′-H); 7.19 (dd, $J_{3,4}$ = 7.6, $J_{3,5}$ = 1.6 Hz, 1 H, 3-H); 7.29 (td, $J_{4,3}$ = $J_{4,5}$ = 7.5, $J_{4,6}$ = 1.3 Hz, 1 H, 4-H); 7.37 (td, $J_{5,6}$ = $J_{5,4}$ = 7.6, $J_{5,3}$ = 1.5 Hz, 1 H, 5-H); 7.46 (br. d, $J_{6,5}$ = 7.8 Hz, 1 H, 6-H) ppm. ^{13}C NMR (125.7 MHz, CD$_3$OD): δ = 35.1 and 39.5 [(CH$_3$)$_2$N]; 37.7 (CH$_2$); 63.5 (CH$_2$-5′); 72.6 (CH-3′); 76.0 (CH-2′); 84.4 (CH-1′); 85.9 (CH-4′); 127.2 (CH-3); 127.6 (CH-4); 130.3 (CH-5); 131.9 (CH-6); 136.8 (C-1); 137.8 (C-2); 173.9 (CO) ppm. HRMS (ESI) for $C_{14}H_{19}NO_5$: [M + Na]$^+$ calcd. 304.1155, found 304.1155. IR (KBr): $\tilde{\nu}$ = 3421, 3280, 3100, 3070, 3030, 1631, 1601, 1575, 1558, 1487, 1460, 1115, 1106, 1050, 763, 603 cm^{-1}.

1-Deoxy-1β-[2-(*N*,*N*-dimethylcarbamoyl)benzyl]-D-ribofuranose (7n): Compound **7n** was prepared from **4n** (270 mg, 0.42 mmol) according to the general procedure (method B) in 76% yield as a white solid. ^{1}H NMR (500 MHz, CD$_3$OD): δ = 2.87 and 3.11 [2× s, 2× 3 H, (CH$_3$)$_2$N]; 2.60–3.10 (m, 2 H, CH$_2$); 3.52 (dd, J_{gem} = 11.9, $J_{5'a,4'}$ = 4.7 Hz, 1 H, 5′-Ha); 3.63 (dd, J_{gem} = 11.9, $J_{5'b,4'}$ = 3.7 Hz, 1 H, 5′-Hb); 3.71 (t, $J_{2',1'}$ = $J_{2',3'}$ = 5.9 Hz, 1 H, 2′-H); 3.75 (td, $J_{4',5'a}$ = $J_{4',3'}$ = 4.7, $J_{4',5'b}$ = 3.7 Hz, 1 H, 4′-H); 3.90 (dd, $J_{3',2'}$ = 5.7, $J_{3',4'}$ = 4.7 Hz, 1 H, 3′-H); 3.94 (br. q, $J_{1',CH2a}$ = $J_{1',2'}$ = $J_{1',CH2b}$ = 6.3 Hz, 1 H, 1′-H); 7.19 (dd, $J_{3,4}$ = 7.6, $J_{3,5}$ = 1.6 Hz, 1 H, 3-H); 7.29 (td, $J_{4,3}$ = $J_{4,5}$ = 7.5, $J_{4,6}$ = 1.3 Hz, 1 H, 4-H); 7.37 (td, $J_{5,6}$ = $J_{5,4}$ = 7.6, $J_{5,3}$ = 1.5 Hz, 1 H, 5-H); 7.46 (br. d, $J_{6,5}$ = 7.8 Hz, 1 H, 6-H) ppm. ^{13}C NMR (125.7 MHz, CD$_3$OD): δ = 35.1 and 39.5 [(CH$_3$)$_2$N]; 37.7 (CH$_2$); 63.5 (CH$_2$-5′); 72.6 (CH-3′); 76.0 (CH-2′); 84.4 (CH-1′); 85.9 (CH-4′); 127.2 (CH-3); 127.6 (CH-4); 130.3 (CH-5); 131.9 (CH-6); 136.8 (C-1); 137.8 (C-2); 173.9 (CO) ppm. HRMS (ESI) for $C_{15}H_{21}NO_5$: [M + Na]$^+$ calcd. 318.1312, found 318.1311. IR (KBr): $\tilde{\nu}$ = 3431, 3072, 3025, 2923, 2869, 2860, 1624, 1600, 1580, 1509, 1482, 1458, 1444, 1400, 1120, 1101, 1045, 765, 597 cm^{-1}.

1β-[2-(*N*-Benzylcarbamoyl)benzyl]-1-deoxy-D-ribofuranose (7o): Compound **7o** was prepared from **4o** (303 mg, 0.43 mmol) according to the general procedure (method B) in 76% yield as a white solid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 2.82 (dd, J_{gem} = 14.1, $J_{CH2a,1'}$ = 8.5 Hz, 1 H, CH$_2$a); 3.03 (dd, J_{gem} = 14.1, $J_{CH2b,1'}$ = 4.5 Hz, 1 H, CH$_2$b); 3.31 (br. ddd, J_{gem} = 11.5, $J_{5'a,OH}$ = 5.7, $J_{5'a,4'}$ = 5.2 Hz, 1 H, 5′-Ha); 3.39 (ddd, J_{gem} = 11.5, $J_{5'b,OH}$ = 5.5, $J_{5'b,4'}$ = 4.1 Hz, 1 H, 5′-Hb); 3.57 (br. q, $J_{2',1'}$ = $J_{2',3'}$ = $J_{2',OH}$ = 5.8 Hz, 1 H, 2′-H); 3.58 (m, 1 H, 4′-H); 3.73 (br. q, $J_{3',2'}$ = $J_{3',4'}$ = $J_{3',OH}$ = 5.1 Hz, 1 H, 3′-H); 3.86 (ddd, $J_{1',CH2a}$ = 8.4, $J_{1',2'}$ = 6.0, $J_{1',CH2b}$ = 4.5 Hz, 1 H, 1′-H); 4.44 (d, $J_{CH2,NH}$ = 6.1 Hz, 2 H, CH$_2$-Ph); 4.62 (t, $J_{OH,5'a}$ = $J_{OH,5'b}$ = 5.6 Hz, 1 H, O5′-H); 4.72 (d, $J_{OH,3'}$ = 5.4 Hz, 1 H, O3′-H); 4.73 (d, $J_{OH,2'}$ = 5.9 Hz, 1 H, O2′-H); 7.22–7.29 (m, 2 H, 4-H, H-*p*-Ph); 7.32–7.39 (m, 3 H,3,5,6-H); 8.77 (t, $J_{NH,CH2}$ = 6.1 Hz, 1 H, NH) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ = 36.5 (CH$_2$); 42.6 (CH$_2$-Ph); 62.1 (CH$_2$-5′); 71.1 (CH-3′); 74.4 (CH-2′); 82.8 (CH-1′); 84.4 (CH-4′); 126.0 (CH-4); 126.9 (CH-*p*-Ph); 127.4 (CH-*o*-Ph); 127.5 (CH-3); 128.5 (CH-*m*-Ph); 129.3 (CH-5); 130.60 (CH-6); 136.59 (C-1); 137.5 (C-2); 139.8 (C-*i*-Ph); 169.4 (CO) ppm. HRMS (ESI) for $C_{20}H_{23}NO_5$: [M + Na]$^+$ calcd 380.1468, found 380.1467. IR (KBr): $\tilde{\nu}$ = 3450, 3283, 3087, 3064, 3061, 1640, 1629, 1597, 1578, 1541, 1496, 1487, 1453, 1284, 1209, 1105, 1030, 762, 698, 596 cm^{-1}.

General Procedure for the Synthesis of 5′-Monophosphates: Starting *C*-ribonucleoside (56 mg, 0.19 mmol) was placed in an argon-purged flask and dried at 80 °C for 2 h. Then PO(OMe)$_3$ (0.5 mL) and POCl$_3$ (27 μL, 0.28 mmol) were added successively at 0°C. The reaction mixture was stirred at 0 °C for 3 h and then quenched by addition of aqueous TEAB (triethylammonium bicarbonate, 2 M, 2 mL). The solvents were evaporated, and the residue was co-distilled with water several times. The product was isolated on a DEAE Sephadex column (300 mL) eluting with a gradient of 0–1.2 M TEAB, concentrated, co-distilled with water several times, converted into salt form (Dowex 50WX8 in Na$^+$ cycle) and lyophilized to give monophosphates **8e**,**f**,**l**,**n**,**p**.

1β-(2-Aminobenzyl)-1-deoxy-D-ribofuranose Monophosphate (8e): Compound **8e** was prepared from **7e** (80 mg, 0.33 mmol) according to the general procedure for 5′-monophosphate synthesis in 46% yield as a white powder. ^{1}H NMR (500 MHz, D$_2$O): δ = 2.83 (dd, J_{gem} = 14.7, $J_{CH2a,1'}$ = 8.2 Hz, 1 H, CH$_2$a); 2.94 (dd, J_{gem} = 14.7, $J_{CH2b,1'}$ = 4.1 Hz, 1 H, CH$_2$b); 3.84 (m, 2 H, 5′-H); 3.99 (br. q, $J_{4',3'}$ = $J_{4',5'a}$ = $J_{4',5'b}$ = 4.4 Hz, 1 H, 4′-H); 4.05 (br. t, $J_{2',1'}$ = $J_{2',3'}$ = 5.6 Hz, 1 H, 2′-H); 4.11 (ddd, $J_{1',CH2a}$ = 8.2, $J_{1',2'}$ = 5.8, $J_{1',CH2b}$ = 4.1 Hz, 1 H, 1′-H); 4.12 (br. t, $J_{3',2'}$ = $J_{3',4'}$ = 5.1 Hz, 1 H, 3′-H); 7.88–6.93 (m, 2 H, 5,3-H); 7.16 (br. td, $J_{4,3}$ = $J_{4,5}$ = 7.7, $J_{4,6}$ = 1.6 Hz, 1 H, 4-H); 7.22 (br. dd, $J_{6,5}$ = 7.9, $J_{6,4}$ = 1.6 Hz, 1 H, 6-H) ppm. ^{13}C NMR (125.7 MHz, D$_2$O): δ = 37.1 (CH$_2$); 66.8 [d, $J(C,P)$ = 4.8 Hz, CH$_2$-5′]; 73.9 (CH-3′); 76.8 (CH-2′); 85.3 (d, $J_{C,P}$ = 8.5 Hz, CH-4′); 86.0 (CH-1′); 120.4 (CH-3); 123.1 (CH-5); 127.5 (C-1); 130.7 (CH-4); 133.7 (CH-6); 146.8 (C-2) ppm. ^{31}P NMR (202.3 MHz, D$_2$O): δ = 3.33 ppm. HRMS (ESI) for $C_{12}H_{17}NNaO_7P$: [M – Na]$^-$ calcd. 318.0748, found 318.0750. IR (KBr): $\tilde{\nu}$ = 3430, 3252, 2707, 1628, 1603, 1586, 1498, 1458, 1137, 1107, 1072, 1046, 978, 916, 831, 753 cm^{-1}.

1β-[2-(Dimethylamino)benzyl]-1-deoxy-D-ribofuranose Monophosphate (8f): Compound **8f** was prepared from **7f** (39 mg, 0.15 mmol) according to the general procedure for 5′-monophosphate synthesis in 33% yield as a white powder. ^{1}H NMR (500 MHz, D$_2$O): δ = 2.85 [s, 6 H, (CH$_3$)$_2$N]; 3.04 (dd, J_{gem} = 14.9, $J_{CH2a,1'}$ = 8.8 Hz, 1 H, CH$_2$a); 3.10 (dd, J_{gem} = 14.9, $J_{CH2b,1'}$ = 4.3 Hz, 1 H, CH$_2$b); 3.86 (m, 2 H, 5′-H); 3.99 (q, $J_{4',3'}$ = $J_{4',5'a}$ = $J_{4',5'b}$ = 4.4 Hz, 1 H, 4′-H); 4.08 (br. t, $J_{2',1'}$ = $J_{2',3'}$ = 5.8 Hz, 1 H, 2′-H); 4.15 (ddd, $J_{1',CH2a}$ = 8.8, $J_{1',2'}$ = 6.1, $J_{1',CH2b}$ = 4.3 Hz, 1 H, 1′-H); 4.23 (br. t, $J_{3',2'}$ = $J_{3',4'}$ = 5.1 Hz, 1 H, 3′-H); 7.27 (td, $J_{5,4}$ = $J_{5,6}$ = 7.4, $J_{5,3}$

= 1.4 Hz, 1 H, 5-H); 7.39 (br. ddd, $J_{4,3}$ = 8.2, $J_{4,5}$ = 7.3, $J_{4,6}$ = 1.7 Hz, 1 H, 4-H); 7.44 (dd, $J_{3,4}$ = 8.2, $J_{3,5}$ = 1.3 Hz, 1 H, 3-H); 7.46 (dd, $J_{6,5}$ = 7.6, $J_{6,4}$ = 1.7 Hz, 1 H, 6-H) ppm. ^{13}C NMR (125.7 MHz, D_2O): δ = 36.8 (CH_2); 48.2 [$(CH_3)_2N$]; 66.4 (d, $J_{C,P}$ = 4.6 Hz, CH_2-5′); 73.9 (CH-3′); 77.1 (CH-2′); 85.6 (CH-1′); 85.8 (d, $J_{C,P}$ = 8.1 Hz, CH-4′); 122.69 (CH-3); 128.8 (CH-5); 130.9 (CH-4); 133.7 (CH-6); 134.7 (C-1); 152.2 (C-2) ppm. ^{31}P NMR (202 MHz, D_2O): δ = 4.43 ppm. HRMS (ESI) for $C_{14}H_{21}NNaO_7P$: [M – Na]$^-$ calcd. 346.1061, found 346.1060. IR (KBr): $\tilde{\nu}$ = 3435, 3060, 3000, 2824, 1782, 1695, 1599, 1579, 1570, 1494, 1453, 1305, 1188, 1134, 1099, 1050, 978, 945, 915, 767 cm^{-1}.

1β-(2-Carbamoylbenzyl)-1-deoxy-D-ribofuranose Monophosphate (8l): Compound **8l** was prepared from **7l** (56 mg, 0.21 mmol) according to the general procedure for 5′-monophosphate synthesis in 33% yield as a white powder, accompanied by **8p** in 12% yield as a white powder. ^{1}H NMR (500 MHz, D_2O): δ = 3.08 (dd, J_{gem} = 14.2, $J_{CH2a,1'}$ = 9.0 Hz, 1 H, CH_2a); 3.20 (dd, J_{gem} = 14.2, $J_{CH2b,1'}$ = 4.3 Hz, 1 H, CH_2b); 3.78 (m, 2 H, 5′-H); 3.95 (q, $J_{4',3'}$ = $J_{4',5'a}$ = $J_{4',5'b}$ = 4.7 Hz, 1 H, 4′-H); 4.03 (br. t, $J_{2',1'}$ = $J_{2',3'}$ = 5.8 Hz, 1 H, 2′-H); 4.09 (ddd, $J_{1',CH2a}$ = 9.0, $J_{1',2'}$ = 6.1, $J_{1',CH2b}$ = 4.3 Hz, 1 H, 1′-H); 4.15 (br. dd, $J_{3',2'}$ = 5.3, $J_{3',4'}$ = 4.9 Hz, 1 H, 3′-H); 7.38 (m, 1 H, 4-H); 7.46 (m, 1 H, 6-H); 7.49–7.54 (m, 2 H, 3,5-H) ppm. ^{13}C NMR (125.7 MHz, D_2O): δ = 38.7 (CH_2); 66.6 (d, $J_{C,P}$ = 4.5 Hz, CH_2-5′); 74.2 (CH-3′); 76.8 (CH-2′); 85.7 (d, $J_{C,P}$ = 8.5 Hz, CH-4′); 86.0 (CH-1′); 129.6 (CH-4); 130.3 (CH-3); 133.5 and 138.1 (CH-5, 6); 137.8 (C-1); 138.1 (C-2); 178.2 (CO) ppm. ^{31}P NMR (202 MHz, D_2O): δ = 4.61 ppm. HRMS (ESI) for $C_{13}H_{17}NNaO_8P$: [M – Na]$^-$ calcd. 346.0697, found 346.0697. IR (KBr): $\tilde{\nu}$ = 3428, 3197, 3067, 2690, 2580, 1663, 1617, 1573, 1493, 1452, 1397, 1301, 1130, 1098, 1046, 977, 916, 830, 764 cm^{-1}.

1β-(2-Cyanobenzyl)-1-deoxy-D-ribofuranose Monophosphate (8p): ^{1}H NMR (500 MHz, D_2O): δ = 3.12 (dd, J_{gem} = 14.2, $J_{CH2a,1'}$ = 8.3 Hz, 1 H, CH_2a); 3.25 (dd, J_{gem} = 14.2, $J_{CH2b,1'}$ = 4.8 Hz, 1 H, CH_2b); 3.81 (m, 2 H, 5′-H); 4.00 (q, $J_{4',3'}$ = $J_{4',5'a}$ = $J_{4',5'b}$ = 4.8 Hz, 1 H, 4′-H); 4.09 (br. t, $J_{2',1'}$ = $J_{2',3'}$ = 5.7 Hz, 1 H, 2′-H); 4.14 (ddd, $J_{1',CH2a}$ = 8.3, $J_{1',2'}$ = 6.0, $J_{1',CH2b}$ = 4.8 Hz, 1 H, 1′-H); 4.19 (br. t, $J_{3',2'}$ = $J_{3',4'}$ = 5.0 Hz, 1 H, 3′-H); 7.45 (td, $J_{4,3}$ = $J_{4,5}$ = 7.7, $J_{4,6}$ = 1.1 Hz, 1 H, 4-H); 7.58 (br. d, $J_{6,5}$ = 7.8 Hz, 1 H, 6-H); 7.68 (td, $J_{5,4}$ = $J_{5,6}$ = 7.7, $J_{5,3}$ = 1.4 Hz, 1 H, 5-H); 7.78 (dd, $J_{3,4}$ = 7.8, $J_{3,5}$ = 1.3 Hz, 1 H, 3-H) ppm. ^{13}C NMR (125.7 MHz, D_2O): δ = 40.4 (CH_2); 66.7 (d, $J_{C,P}$ = 4.8 Hz, CH_2-5′); 74.3 (CH-3′); 76.8 (CH-2′); 84.8 (CH-1′); 85.8 (d, $J_{C,P}$ = 8.3 Hz, CH-4′); 114.3 (C-2); 121.7 (CN); 130.1 (CH-4); 133.5 (CH-6); 135.9 (CH-3); 136.3 (CH-5); 144.4 (C-1) ppm. ^{31}P NMR (202 MHz, D_2O): δ = 4.62 ppm. HRMS (ESI) for $C_{13}H_{15}NNaO_7P$: [M – Na]$^-$ calcd. 328.0592, found 328.0591. IR (KBr): $\tilde{\nu}$ = 3435, 3072, 2800, 2700, 2570, 2226, 1602, 1578, 1489, 1450, 1303, 1213, 1180, 1136, 1097, 1046, 978, 916, 830, 761, 559 cm^{-1}.

1-Deoxy-1β-[2-(*N*,*N*-dimethylcarbamoyl)benzyl]-D-ribofuranose Monophosphate (8n): Compound **8n** was prepared from **7n** (56 mg, 0.19 mmol) according to the general procedure for 5′-monophosphate synthesis in 49% yield as a white powder. ^{1}H NMR (500 MHz, D_2O): δ = 2.83 (br. m, 1 H, CH_2a), 2.93 [s, 3 H, $(CH_3)_2N$]; 3.05 (m, 1 H, CH_2b); 3.15 [s, 3 H, $(CH_3)_2N$]; 3.88 (m, 2 H, 5′-H); 3.98 (br. q, $J_{4',5'a}$ = $J_{4',3'}$ = $J_{4',5'b}$ = 4.4 Hz, 1 H, 4′-H); 3.99 (t, $J_{2',1'}$ = $J_{2',3'}$ = 5.7 Hz, 1 H, 2′-H); 4.09 (br. m, 1 H, 1′-H); 4.18 (t, $J_{3',4'}$ = $J_{3',2'}$ = 4.9 Hz, 1 H, 3′-H); 7.28 (dd, $J_{3,4}$ = 7.6, $J_{3,5}$ = 1.4 Hz, 1 H, 3-H); 7.39 (td, $J_{4,3}$ = $J_{4,5}$ = 7.4, $J_{4,6}$ = 1.5 Hz, 1 H, 4-H); 7.48 (br. t, $J_{5,6}$ = $J_{5,4}$ = 7.5 Hz, 1 H, 5-H); 7.52 (br. d, $J_{6,5}$ = 7.5 Hz, 1 H, 6-H) ppm. ^{13}C NMR (125.7 MHz, D_2O): δ = 37.5 [$(CH_3)_2N$]; 39.0 (CH_2); 41.8 [$(CH_3)_2N$]; 67.3 (CH_2-5′); 74.0 (CH-3′); 77.1 (CH-2′); 85.3 (CH-1′,4′); 128.8 (CH-3); 129.7 (CH-4); 132.5 (CH-5); 134.1 (CH-6); 137.1 (C-1); 138.4 (C-2); 175.9 (CO) ppm. ^{31}P NMR (202 MHz, D_2O): δ = 2.51 ppm. HRMS (ESI) for $C_{15}H_{21}NaO_8P$: [M – Na]$^-$ calcd. 374.1010, found 374.1010. IR (KBr): $\tilde{\nu}$ = 3432, 3264, 3069, 1629, 1600, 1578, 1510, 1483, 1445, 1400, 1193, 1118, 1102, 1073, 1046, 978, 919 cm^{-1}.

Supporting Information (see footnote on the first page of this article): Copies of all NMR spectra.

Acknowledgments

This work was supported by the Academy of Sciences of the Czech Republic (ASCR) (RVO 61388963), the Czech Science Foundation (P207/11/0344 to M. H.), the Grant Agency of the ASCR (IAA400550902 to T. K.) and the Gilead Sciences, Inc.. The inhibition of PriA isomerase was studied by Dr. Jana Tatur and Prof. M. Wilmanns (EMBL Hamburg). The contribution of these scientists is gratefully appreciated.

[1] a) U. Hommel, M. Eberhard, K. Kirschner, *Biochemistry* **1995**, *34*, 5429–5439; b) W. M. Patrick, J. M. Blackburn, *FEBS J.* **2005**, *272*, 3684–3697.

[2] a) M. Hann-Sax, R. Thoma, S. Schmidt, M. Hennig, K. Kirschner, R. Sterner, *Biochemistry* **2002**, *41*, 12032–12042; b) J. Kuper, C. Doenges, M. Wilmanns, *EMBO Rep.* **2005**, *6*, 134–139; c) F. List, R. Sterner, M. Wilmanns, *ChemBioChem* **2011**, *12*, 1487–1494.

[3] Reviews: a) J. Štambaský, M. Hocek, P. Kočovský, *Chem. Rev.* **2009**, *109*, 6729–6764; b) M. F. A. Adamo, R. Pergoli, *Curr. Org. Chem.* **2008**, *12*, 1544–1569; c) Q. P. Wu, C. Simons, *Synthesis* **2004**, 1533–1553.

[4] Examples: a) D. Malyshev, Y. J. Seo, P. Ordoukhanian, F. E. Romesberg, *J. Am. Chem. Soc.* **2009**, *131*, 14620–14621; b) D. A. Malyshev, D. A. Pfaff, S. I. Ippoliti, G. T. Hwang, T. J. Dwyer, F. E. Romesberg, *Chem. Eur. J.* **2010**, *16*, 12650–12659; c) Y. J. Seo, D. A. Malyshev, T. Lavergne, P. Ordoukhanian, F. E. Romesberg, *J. Am. Chem. Soc.* **2011**, *133*, 19878–19888.

[5] a) M. Urban, N. Joubert, M. Hocek, R. E. Alexander, R. D. Kuchta, *Biochemistry* **2009**, *48*, 10866–10881; b) M. Urban, N. Joubert, B. Purse, M. Hocek, R. Kuchta, *Biochemistry* **2010**, *49*, 727–735; c) T. Lund, N. Cavanaugh, N. Joubert, M. Urban, J. Patro, M. Hocek, R. D. Kuchta, *Biochemistry* **2011**, *50*, 7243–7250.

[6] a) M. Hocek, R. Pohl, B. Klepetářová, *Eur. J. Org. Chem.* **2005**, 4525–4528; b) M. Urban, R. Pohl, B. Klepetářová, M. Hocek, *J. Org. Chem.* **2006**, *71*, 7322–7328; c) N. Joubert, R. Pohl, B. Klepetářová, M. Hocek, *J. Org. Chem.* **2007**, *72*, 6797–6805; d) M. Štefko, R. Pohl, B. Klepetářová, M. Hocek, *Eur. J. Org. Chem.* **2008**, 1689–1704; e) N. Joubert, M. Urban, R. Pohl, M. Hocek, *Synthesis* **2008**, 1918–1932; f) J. Bárta, R. Pohl, B. Klepetářová, N. P. Ernsting, M. Hocek, *J. Org. Chem.* **2008**, *73*, 3798–3806; g) T. Kubelka, L. Slavětínská, B. Klepetářová, M. Hocek, *Eur. J. Org. Chem.* **2010**, 2666–2669; h) M. Štefko, L. Slavětínská, B. Klepetářová, M. Hocek, *J. Org. Chem.* **2010**, *75*, 442–449; i) J. Bárta, L. Slavětínská, B. Klepetářová, M. Hocek, *Eur. J. Org. Chem.* **2010**, 5432–5443; j) M. Štefko, L. Slavětínská, B. Klepetářová, M. Hocek, *J. Org. Chem.* **2011**, *76*, 6619–6635; k) T. Kubelka, L. Slavětínská, M. Hocek, *Synthesis* **2012**, *44*, 953–965; l) H. Chapuis, N. Joubert, T. Kubelka, R. Pohl, M. Hocek, *Eur. J. Org. Chem.* **2012**, 1759–1767.

[7] L. F. Bonnac, G.-Y. Gao, L. Chen, S. E. Patterson, H. N. Jayaram, K. W. Pankiewicz, *Nucleosides, Nucleotides Nucleic Acids* **2007**, *26*, 1249–1253.

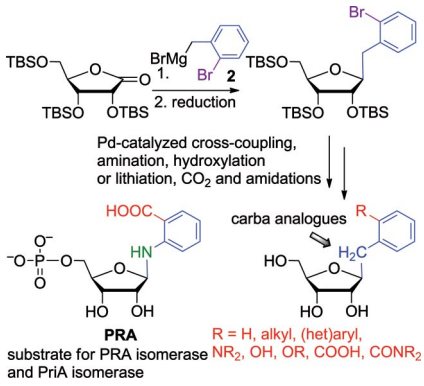
[8] A. G. M. Barrett, H. B. Broughton, S. V. Attwood, A. A. L. Gunatilaka, *J. Org. Chem.* **1986**, *51*, 495–503.

[9] J. P. Wolfe, H. Tomori, J. P. Sadighi, J. Yin, S. L. Buchwald, *J. Org. Chem.* **2000**, *65*, 1158–1174.
[10] X. Huang, S. L. Buchwald, *Org. Lett.* **2001**, *3*, 3417–3419.
[11] B. H. Yang, S. L. Buchwald, *J. Organomet. Chem.* **1999**, *576*, 125–146.
[12] a) K. W. Anderson, T. Ikawa, R. E. Tundel, S. L. Buchwald, *J. Am. Chem. Soc.* **2006**, *128*, 10694–10695; b) M. Štefko, M. Hocek, *Synthesis* **2010**, 4199–4206.
[13] P. Čapek, R. Pohl, M. Hocek, *J. Org. Chem.* **2005**, *70*, 8001–8008.
[14] M. Štefko, R. Pohl, M. Hocek, *Tetrahedron* **2009**, *65*, 4471–4483.
[15] A. V. Due, J. Kuper, A. Geerlof, J. P. von Kries, M. Wilmanns, *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 3554–3559.

Received: June 19, 2012
Published Online: ■

C-Nucleosides

Novel benzyl *C*-nucleosides were designed and prepared as carba analogues of phosphoribosylanthranilate, an important intermediate in the biosynthesis of tryptophan.



Keywords: Nucleosides / Nucleotides / Cross-coupling / Phosphoribosylanthranilate / Amides

