DOI: 10.1002/ejoc.200701168

A Modular Methodology for the Synthesis of 4- and 3-Substituted Benzene and Aniline C-Ribonucleosides

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Keywords: Nucleosides / Cross-coupling / Amination / Arene

A modular, efficient, and practical methodology for the preparation of 4- and 3-substituted benzene and aniline C-ribonucleosides was developed. Addition of 4- or 3-bromophenyllithium (**2** or **12**) to TBDMS-protected ribonolactone **3** gave hemiacetal adducts **4** or **13** as pure β-anomers. Their reduction with Et_3SiH and $BF_3{\cdot}Et_2O$ afforded the desired protected 4- or 3-bromophenyl-C-ribonucleosides **6** or **15** in 66 and 75 %, respectively, over two steps from **3**. Bromophenyl intermediates **6** and **15** were subjected to a series of palladium-catalyzed cross-coupling, alkoxylation, and amination reactions to give a series of protected 1β-(3- and 4-substituted phenyl)ribonuleosides **9** and **18**. Deprotection of silylated nucleosides **9** or **18** by $Et_3N{\cdot}3HF$ afforded a series of free C-ribonucleosides **10** or **19** (20 examples).

Introduction

C-Nucleosides bearing hydrophobic aryl groups as nucleobase are interesting compounds with a wide range of applications in chemical biology, in particular in the extension of the genetic alphabet.[1] If incorporated to oligonucleotide duplexes, they usually selectively pair with the same type of hydrophobic nucleobase as a owing to increased packing interactions and favorable desolvation energy in comparison to canonical hydrophilic nucleobases.[2] Triphosphates of some of the C-nucleosides are efficiently incorporated into DNA by DNA polymerase.[3] Most studies were performed on 2′-deoxyribonucleosides and addressed the stability of DNA duplexes and the specificity of incorporation by DNA polymerases. Much less work has been done on C-ribonucleosides, which represents the second step in the extension of the genetic alphabet − the transcription. Some C-ribonucleosides that have been prepared have been used for studying the stability of modified RNA,[4] RNA interference,[5] or active sites of ribozymes;[6] some others have been studied as potential antitumor or antiviral agents.[7] C-nucleoside analogues of nicotinamide riboside were studied as IMP dehydrogenase inhibitors.[8]

Biaryl C-nucleosides are of particular interest because of largely extended stacking and formation of very stable duplexes.[9] Both theoretical calculations[10] and experimental (NMR spectroscopic structure) results[11] confirmed that they form a stacked-pair within the B-DNA duplex. In contrast, incorporation of bulky biaryl C-nucleosides into a duplex opposite to a purine or pyrimidine nucleobase causes local disruption of the stacking.[12] Very recently, donor- and acceptor-modified biphenyl C-nucleoside-containing oligonucleotide was used[13] for recognition of another hydrophobic modification in the opposite strand or even of a bulge position. Moreover, oligoaryl C-nucleosides have been used by Kool at al.[14] for the construction of fluorescent oligonucleotide probes.

There are several synthetic approaches to C-nucleosides: (i) addition reactions of organometallics to ribono- or 2-deoxyribonolactones,[3,9,15] (ii) coupling of a halogenose with organometallics,[16] (iii) electrophilic substitution reactions of electron-rich aromatics with sugars under Lewis acid catalysis,[17] or (iv) Heck-type coupling of aryl iodides with glycals.[18] However, none of them is truly general, and many of them suffer from poor selectivity and low yields.

We are currently involved in development of modular methodologies based on larger-scale syntheses of a versatile C-nucleoside intermediates and their further use for the generation of a series of diverse derivatives. We have already developed modular syntheses of 3- and 4-substituted benzene,[19] 6-substituted pyridin-2-yl,[20] and 6-substituted pyridin-3-yl[21] C-2′-deoxyribonucleosides by the preparation of a general halogenated C-arylnucleoside intermediate, following by displacement of the bromine atom by alkyl, aryl, or amino substituents by cross-coupling reactions. An analogous modular approach was also used by Leumann[22] to prepare some biaryl C-2′-deoxyribonucleosides. However, so far no application in the synthesis of C-ribonucleosides has been published. Therefore, we report here on an efficient and modular synthesis of diverse 4- or 3-substituted benzene C-ribonucleosides.

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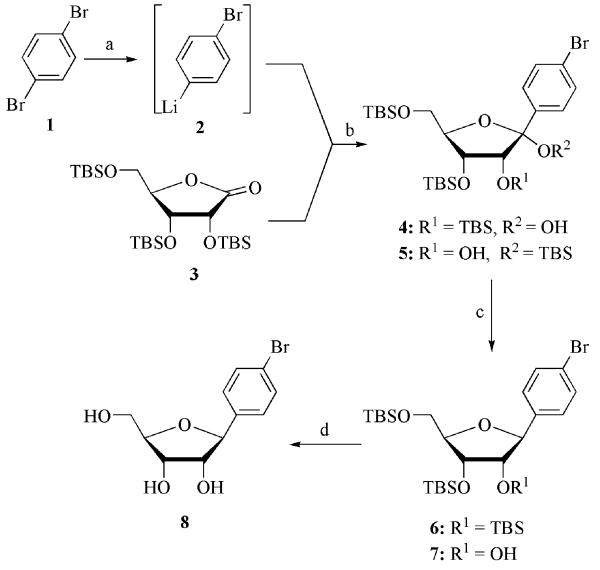
Results and Discussion

Our selected approach for the synthesis of a series of 4- and 3-substituted benzene C-nucleosides was based on the synthesis of a suitably protected 4- or 3-halophenyl C-nucleoside intermediate and on its further transformation (cross-coupling, amination, alkoxylation). Therefore, our first efforts were focused on the preparation of the protected bromophenyl nucleoside intermediate. As a starting material, we chose TBS-protected ribonolactone **3**,[23] which is easily available in two steps from D-ribose. First, oxidation of D-ribose by aqueous bromine generates the corresponding D-ribonolactone and subsequent reaction of this crude product with TBSCl and imidazole produces the TBS-protected ribonolactone in very good overall yield (75%) on a multigram scale. The first addition reaction was performed in analogy to a related literature example in the 2′-deoxy-ribo series.[22] Thus, 4-bromophenyllithium (**2**) was generated from 1,4-dibromobenzene (**1**) by its initial treatment with *n*BuLi, followed by its reaction with lactone **3** at –78 °C for 1 h. This reaction gave desired hemiketal **4** (51%) and side product **5** (34%), which was identified as a product resulting from the migration of the TBS group from the hydroxy group in the 2-position of the sugar moiety to the hemiketal hydroxy group (Scheme 1). The addition reactions proceeded stereoselectively – exclusive formation of the β-anomers of hemiketals **4** and **5** was observed and proved by ROESY spectra. In addition, the structure of side product **5** was determined by X-ray diffraction (Figure 1). Shortening of the reaction time to 30 min after the addition of bromophenyllithium resulted in a decrease in the formation of side product **5** (17%) and desired product **4** was isolated in 77% yield.



Scheme 1. Synthesis of 4-bromophenyl C-nucleosides. Reagents and conditions: (a) BuLi, THF, –78 °C, 30 min; (b) **3** (addition over 30 min), THF, –78 °C, 30 min, **4** (77%) and **5** (17%); (c) Et_3SiH, $BF_3{\cdot}Et_2O$, CH_2Cl_2, –10 °C, 5 min, **6** (85% from **4**), **7** (89% from **5**); (d) $Et_3N{\cdot}3HF$, THF, 40 °C, 2 d, **8** (85% from **6**).

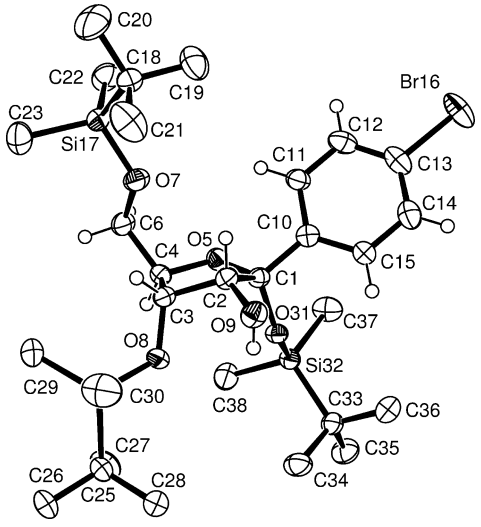
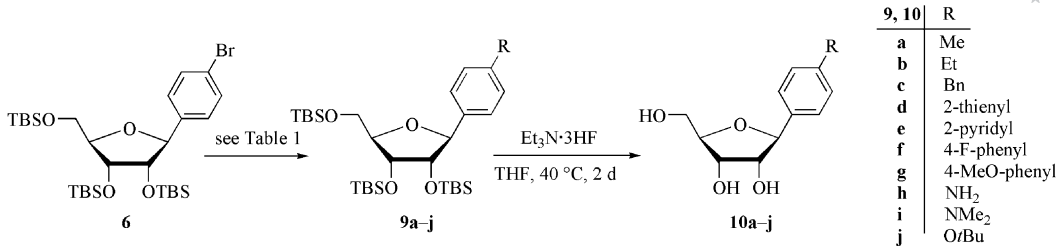


Figure 1. ORTEP drawing of **5** with the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms on the TBS groups are omitted for clarity.

Reduction of hemiketal **4** was then performed with $Et_3SiH/BF_3{\cdot}Et_2O$ in analogy to the literature procedures.[20,22] Here we found that the use of Et_3SiH (3.3 equiv.) and $BF_3{\cdot}Et_2O$ (1.2 equiv.) in CH_2Cl_2 at –10 °C for just 5 min is sufficient for total conversion of starting hemiketal **4** to desired C-nucleoside **6** in 85% yield. We then tried the analogous reduction of 1′-*O*-TBS derivative **5** under the same conditions. This silyl acetal reacted in the same way to give 2′-unprotected C-nucleoside **7** in 89% yield. The very short reaction time was crucial for the selectivity, as prolongation of the reaction time resulted in partial cleavage of the TBS protecting groups and degradation of the desired product. In both cases, β-anomeric nucleosides **6** and **7** were isolated as the only products. Treatment of silylated nucleoside **6** with $Et_3N{\cdot}3HF$ gave the free bromophenyl-C-nucleoside **8** in 85% yield (for discussion of the deprotection protocol vide infra).

The TBS-protected 4-bromophenyl-C-nucleoside key intermediate **6** was then subjected to a series of Pd-catalyzed cross-coupling, amination, and alkoxylation reactions at the 4-position (Scheme 2). Cross-coupling reactions with organoaluminum or organozinc reagents were used for the introduction of sp^3 (alkyl and benzyl) substituents. The reactions of **6** with trimethylaluminum, triethylaluminum, and benzylzinc bromide were performed under standard conditions[19] in the presence of $Pd(PPh_3)_4$ in THF at 55 °C without any optimization (Table 1, Entries 1-3). In all cases, desired nucleosides **9a**–**c** were obtained in good-to-excellent yields (67–90%; Table 1, Entries 1–3).

In order to introduce hetaryl-substituents, Stille cross-coupling reactions were used. The reactions were carried out in DMF by using $PdCl_2(PPh_3)_2$ as a catalyst. Reaction of **6** with 2-thienyl(tributyl)stannane (Table 1, Entry 4) proceeded very smoothly within 10 min at 100 °C to give desired 4-(2-thienyl)benzene-C-nucleoside **9d** in 79% yield. In contrast, reaction of **6** with 2-pyridyl(tributyl)stannane required a longer time to reach complete conversion, and



Scheme 2. Cross-coupling, amination, and alkoxylation reactions of intermediate **6** and deprotection.

Table 1. Cross-coupling, amination, and alkoxylation reactions of intermediate **6** and deprotection.

Entry	Reagent	Catalyst	Ligand/base	Solvent	Other conditions	Product (yield, %)[g]	Product (yield, %)[h]
1	Me_3Al	$Pd(PPh_3)_4$		THF	48 h, 55 °C	**9a** (90)	**10a** (95)
2	Et_3Al	$Pd(PPh_3)_4$		THF	48 h, 55 °C	**9b** (77)	**10b** (85)
3	BnZnBr	$Pd(PPh_3)_4$		THF	48 h, 55 °C	**9c** (67)	**10c** (84)
4	2-Bu_3Sn-thiophene[a]	$Pd(PPh_3)_2Cl_2$		DMF	10 min, 100 °C	**9d** (79)	**10d** (95)
5	2-Bu_3Sn-pyridine[b]	$Pd(PPh_3)_2Cl_2$		DMF	32 h, 100 °C	**9e** (56)	**10e** (86)
6	4-F-C_6H_4-boronic acid[c]	$Pd(PPh_3)_4$	K_2CO_3	toluene	10 min, 110 °C	**9f** (85)	**10f** (95)
7	4-MeO-C_6H_4-boronic acid[d]	$Pd(PPh_3)_4$	K_2CO_3	toluene	3.5 h, 110 °C	**9g** (72)	**10g** (95)
8	$LiN(SiMe_3)_2$	Pd_2dba_3	bdCyp[e],	THF	48 h, 60 °C	**9h** (84)	**10h** (68)
9	Me_2NH·HCl	Pd_2dba_3	bdtbp,[f] *t*BuONa	toluene	72 h, 37 °C	**9i** (82)	**10i** (86)
10	*t*BuONa	Pd_2dba_3	bdtbp[f]	toluene	8 h, 90 °C	**9j** (69)	**10j** (95)

[a] 2-Bu_3Sn-thiophene = 2-(tributylstannyl)thiophene. [b] 2-Bu_3Sn-pyridine = 2-(tributylstannyl)pyridine. [c] 4-F-Ph-boronic acid = 4-fluorophenylboronic acid. [d] 4-MeO-Ph-boronic acid = 4-methoxyphenylboronic acid. [e] bdCyp = (2-biphenyl)dicyclohexylphosphane. [f] bdtbp = (2-biphenyl)di-*tert*-butylphosphane. [g] Cross-coupling/amination product. [h] Deprotection product.

moreover, formation of some byproducts were observed. The extraction and column chromatography isolation of resulting nucleoside **9e** from lipophilic tin-containing side products was more complicated, which is reflected in the lower isolated yield of 56% (Table 1, Entry 5).

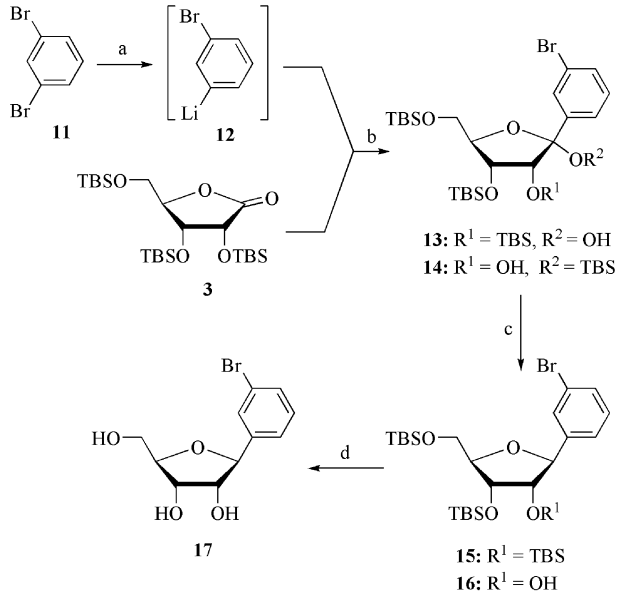
Substituted biphenyl-C-nucleosides were prepared by the Suzuki–Miyaura cross coupling of **6** with the corresponding substituted phenylboronic acid in toluene in the presence of K_2CO_3 and $Pd(PPh_3)_4$ as a catalyst. In both cases, the reaction proceeded very smoothly. In the case of 4-fluorophenylboronic acid (Table 1, Entry 6), the reaction was complete within 10 min and yielded desired nucleoside **9f** in 85% yield. The reaction with 4-methoxyphenylboronic acid required a somewhat longer time and more difficult isolation to afford target nucleoside **9g** in 72% yield (Table 1, Entry 7).

Hartwig–Buchwald reactions[24] were used to introduce the N-substituents. Unsubstituted aminophenyl derivative **9h** was prepared by the reaction of **6** with lithium bis(trimethylsilyl)amide in the presence of Pd_2dba_3 and P(*t*Bu)$_3$ [generated in situ from P(*t*Bu)$_3$·HBF$_4$] in a low yield of only 24%. The use of Buchwald-type ligand (2-biphenyl)dicyclohexylphosphane (bdCyp)[25] under the same conditions gave desired aniline nucleoside **9h** in a very good yield of 84% (Table 1, Entry 8). The Buchwald reaction was also used for the introduction of the dimethylamino group. The reaction of **6** with dimethylamine hydrochloride (Me_2NH·HCl) was performed under standard conditions by using Pd_2dba_3, 2-(di-*tert*-butylphosphanyl)biphenyl (bdtbp), and *t*BuONa as a base at 37 °C for 3 d to give target dimethylaniline C-nucleoside **9i** in 82% yield (Table 1, Entry 9). When this reaction was performed at 80 °C, formation of 4-(*tert*-butoxy)phenyl C-nucleoside **9j** was observed as a side product in 7%. In order to obtain this compound on a preparative scale, we performed the reaction of **6** with *t*BuONa in toluene by using Pd_2dba_3 and dbtbp (virtually the same conditions as above but in the absence of dimethylamine). The 4-(*tert*-butoxy)phenyl derivative **9j** was obtained in this way in 63% yield (Table 1, Entry 10).

After successful preparation of the whole series of TBS-protected C-ribonucleosides, we turned our attention to the final deprotection step. Trying to find a general deprotection protocol for all the synthesized C-ribonucleosides was not easy. Three reagents known to cleave *O*-TBS groups under mild conditions were tried. TBAF (tetrabutylammonium fluoride) in THF worked perfectly for bromo derivative **6**, but in the case of **9b**, we were unable to separate TBAF from the final free nucleoside. Next, we tried TFA (trifluoroacetic acid) in water (TFA/H_2O, 9:1). Deprotection again proceeded smoothly and was complete at room temperature within 30 min. This method was successfully used for compounds **9a**–**c**, but we encountered serious problems with compound **9j**, where epimerization and decomposition was observed. Finally, we turned to Et_3N·3HF, which is a favorite reagent for deprotection of TBS-protected nucleosides.[26] The reactions required 6 d to go to completion when they were carried out in THF at room temperature. However, the reactions were clean and no degradation or epimerization was observed. Only in case of the amino derivative **9h** was formation of a complex between Et_3N·3HF and the amino group observed, but this could be easily cleaved by treatment with $NaHCO_3$. This treatment was then also used for all other compounds to make the isolation of the products easier and more efficient.

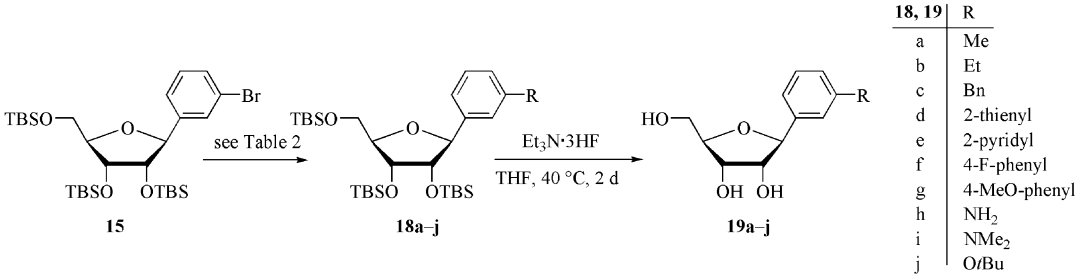
The last problem to be overcome was the unacceptably long reaction time required for deprotection. An increase in the concentration of $Et_3N{\cdot}3HF$ in the reaction mixture also brought no improvement. However, simple heating of the reaction mixture to 40 °C resulted in a decrease in the reaction time to an acceptable 2 d, during which time there was no influence on the purity of the prepared free C-ribonucleosides. Finally, deprotection under these general conditions yielded free C-nucleosides **10a**–**j** in good-to-excellent yields (Table 1, Entries 1–10; last column).

After finishing the first series of 4-substituted benzene C-ribonucleosides, we turned our attention to the preparation of analogous 3-substituted benzene nucleosides. Again, the key protected 3-bromophenyl C-nucleoside intermediate **15** must have been prepared very efficiently. For its preparation, we adopted analogous conditions to those used in the first series. The addition of 3-bromophenyllithium (**12**, generated from **11**) to lactone **3** was performed as described above (Scheme 3) to give desired hemiketal **13** in excellent 89% yield. In this case, 1′-*O*-TBS side product **14** was formed in only very low yield of 4%. Again, the addition was stereoselective and gave both products **13** and **14** as pure β-anomers. Also, the subsequent reduction was accomplished under the same conditions as those used in the first series, which included the use of $Et_3SiH/BF_3{\cdot}Et_2O$ as a reducing system, to result in formation of desired key intermediate **15** in 84% yield (Scheme 3). Reduction of **14** was accomplished under the same conditions, which resulted in the smooth formation of nucleoside **16** in 73% yield. Deprotection of **15** with $Et_3N{\cdot}3HF$ gave free nucleoside **17** in 88% yield.



Scheme 3. Synthesis of 3-bromophenyl C-nucleosides. Reagents and conditions: (a) BuLi, THF, –78 °C, 30 min; (b) **3** (addition over 30 min), THF, –78 °C, 30 min, **13** (89%) and **14** (4%); (c) Et_3SiH, $BF_3{\cdot}Et_2O$, CH_2Cl_2, –10 °C, 5 min, **15** (84% from **13**), **16** (73% from **14**); (d) $Et_3N{\cdot}3HF$, THF, 40 °C, 2 d, **17** (88% from **15**).

With key intermediate **15** in hand, we performed a series of cross-coupling, amination, and alkoxylation reactions in analogy to the first series (Scheme 4, Table 2). Generally, we used analogous conditions (i.e., catalyst type and loading, ligands, solvents etc., with only slight modifications to the



Scheme 4. Cross-coupling, amination, and alkoxylation reactions of intermediate **15** and deprotection.

Table 2. Cross-coupling, amination, and alkoxylation reactions of intermediate **15** and deprotection.

Entry	Reagent	Catalyst	Ligand/base	Solvent	Other conditions	Product (yield,%)[g]	Product (yield,%)[h]
1	Me_3Al	$Pd(PPh_3)_4$		THF	48 h, 55 °C	**18a** (95%)	**19a** (72%)
2	Et_3Al	$Pd(PPh_3)_4$		THF	48 h, 55 °C	**18b** (73%)	**19b** (77%)
3	BnZnBr	$Pd(PPh_3)_4$		THF	48 h, 55 °C	**18c** (67%)	**19c** (80%)
4	2-Bu_3Sn-thiophene[a]	$Pd(PPh_3)_2Cl_2$		DMF	0.5 h, 100 °C	**18d** (73%)	**19d** (72%)
5	2-Bu_3Sn-pyridine[b]	$Pd(PPh_3)_2Cl_2$		DMF	17 h, 100 °C	**18e** (46%)	**19e** (68%)
6	4-F-C_6H_4-boronic acid[c]	$Pd(PPh_3)_4$	K_2CO_3	toluene	0.5 h, 100 °C	**18f** (69%)	**19f** (77%)
7	4-MeO-C_6H_4-boronic acid[d]	$Pd(PPh_3)_4$	K_2CO_3	toluene	2 h, 95 °C	**18g** (81%)	**19g** (73%)
8	$LiN(SiMe_3)_2$	Pd_2dba_3	bdCyp,[e] *t*BuONa	THF	48 h, 60 °C	**18h** (73%)	**19h** (84%)
9	$Me_2NH{\cdot}HCl$	Pd_2dba_3	bdtbp[f]	toluene	72 h, 40 °C	**18i** (77%)	**19i** (77%)
10	*t*BuONa	Pd_2dba_3	bdtbp[f]	toluene	8 h, 50 °C	**18j** (68%)	**19j** (78%)

[a] 2-Bu_3Sn-thiophene = 2-(tributylstannyl)thiophene. [b] 2-Bu_3Sn-pyridine = 2-(tributylstannyl)pyridine. [c] 4-F-Ph-boronic acid = 4-fluorophenylboronic acid. [d] 4-MeO-Ph-boronic acid = 4-methoxyphenylboronic acid. [e] bdCyp = (2-biphenyl)dicyclohexylphosphane. [f] bdtbp = (2-biphenyl)di-*tert*-butylphosphane. [g] Cross-coupling/amination product. [h] Deprotection product.

reaction temperatures and times) to get the series of TBS-protected 3-substituted benzene and aniline C-ribonucleosides **18a**–**j** in yields comparable to those obtained for the 4-substituted series. Desilylation of the TBS-protected C-ribonucleosides **18a**–**j** was performed by the general procedure on the basis of the reaction with $Et_3N{\cdot}3HF$, in THF for 2 d at 40 °C and subsequent treatment with $NaHCO_3$. This methodology was highly efficient and yielded free C-ribonucleosides **19a**–**j** in good yields (68–84%; Table 2, Entries 1–10).

All the final 4-substituted benzene and aniline C-ribonucleosides **10a**–**j** were crystalline compounds. The crystal structure of **10i** was determined by X-ray diffraction (Figure 2), and it provides evidence for the 3′-*exo* conformation of the sugar. In contrast, the 3-substituted benzene C-nucleosides **19a**–**j** were all oily compounds and all attempts to crystallize them failed (only in some cases solid precipitates were obtained). All the final nucleosides were tested for anti-HCV activity. None of them showed any considerable activity or cytotoxicity.

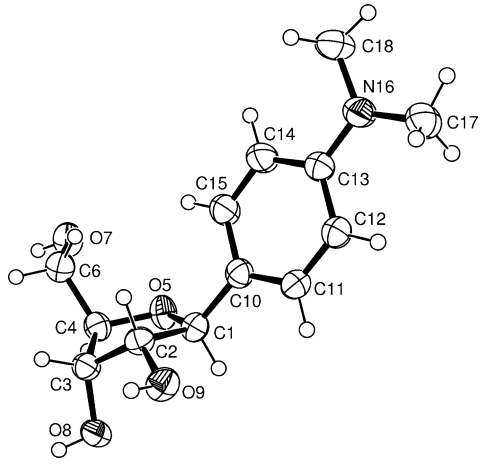


Figure 2. ORTEP drawing of **10i** with the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

Conclusions

A general modular methodology for the synthesis of 4- or 3-substitutred benzene C-ribonucleosides was developed. Key TBS-protected bromobenzene nucleoside intermediates **6** and **15** were efficiently and stereoselectively prepared from easily available ribonolactone in two steps. Pd-catalyzed cross-coupling and amination reactions proceeded well to give a series of protected benzene and aniline C-ribonucleosides. $Et_3N{\cdot}3HF$ was used for final deprotection of the whole series of C-nucleosides. As these nucleosides are not cytotoxic, they might be good candidates for conversion to triphosphates and tested as substrates for RNA polymerases.

Experimental Section

General Methods: Melting points were determined with a Kofler block. Optical rotations were measured at 25 °C, $[\alpha]_D^{20}$, and values are given in $10^{-1}\,°\,cm^2\,g^{-1}$. NMR spectra were measured at 400 MHz for ^1H and 100.6 MHz for ^{13}C nuclei, at 500 MHz for ^1H and 125.8 MHz for ^{13}C, or at 600 MHz for ^1H and 151 MHz for ^{13}C in $CDCl_3$, for protected nucleosides and $[D_6]$DMSO for deprotected ones. (TMS was used as internal standard), $[D_6]$DMSO (referenced to the residual solvent signal). Chemical shifts are given in ppm (δ scale) and coupling constants (J) in Hz. Complete assignment of all NMR signals was performed by using a combination of H, H-COSY, H,H-ROESY, H,C-HSQC, and H,C-HMBC experiments. Mass spectra were measured by using FAB (ionization by Xe, accelerating voltage 8 kV, glycerol +thioglycerol matrix) of EI (electron energy 70 eV). DMF was degassed in vacuo and stored over molecular sieves under an atmosphere of argon.

1β-(4-Bromophenyl)-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (4) and 1β-(4-Bromophenyl)-1,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (5): To a stirred solution of *p*-dibromobenzene (8.07 g, 0.034 mol, 1.7 equiv.) in dry THF (80 mL) at –72 °C was quickly added *n*BuLi (1.6 M *in* hexanes, 20.5 mL, 0.033 mol, 1.65 equiv.), and mixture was stirred for 30 min. Then, a solution of TBS protected ribonolactone **3** (10 g, 0.020 mol) in dry THF (80 mL) was slowly added over 30 min and stirred for an additional 30 min at –72 °C. The reaction mixture was than poured into a saturated NH_4Cl solution and extracted with AcOEt. The combined organic phase was washed with a saturated NH_4Cl solution, dried ($MgSO_4$), and concentrated under vacuum. Purification on silica gel (gradient hexane to hexane/toluene, 1:1 to toluene) gave desired hemiketal **4** (10.14 g, 77%) as a colorless oil and **5** (2.27 g, 17%) as a white solid, which was crystallized from MeOH, to obtain fine needles. Compound **4**: ^1H NMR (400 MHz, $CDCl_3$): δ = –0.53, –0.14, 0.12, 0.126, 0.13 and 0.133 (6 s, 6 × 3 H, CH_3Si), 0.83, 0.94 and 0.95 [3 s, 3 × 9 H, $(CH_3)_3C$], 3.80 (dd, J_{gem} = 11.0 Hz, $J_{5b,4}$ = 2.6 Hz, 1 H, 5′b-H), 3.84 (dd, J_{gem} = 11.0 Hz, $J_{5a,4}$ = 3.4 Hz, 1 H, 5′a-H), 4.00 (d, $J_{2',3'}$ = 4.7 Hz, 1 H, 2′-H), 4.17 (dd, $J_{3',2'}$ = 4.7 Hz, $J_{3',4'}$ = 0.8 Hz, 1 H, 3′-H), 4.20 (ddd, $J_{4',5'}$ = 3.4, 2.6 Hz, $J_{4',3'}$ = 0.8 Hz, 1 H, 4′-H), 5.07 (s, 1 H, OH), 7.43 (m, 2 H, 3,5-H), 7.53 (m, 2 H, 2,6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –5.82, –5.62, –5.47, –4.83, –4.57 and –4.53 (CH_3Si), 17.83, 17.90 and 18.29 [$C(CH_3)_3$], 25.74, 25.77 and 25.93 [$(CH_3)_3C$], 63.66 (CH_2-5′), 74.98 (CH-3′), 77.88 (CH-2′), 85.14 (CH-4′), 103.79 (C-1′), 122.21 (C-4), 128.79 (CH-2,6), 130.68 (CH-3,5), 140.13 (C-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 3507, 2955, 2930, 2897, 2859, 1590, 1472, 1362, 1257, 1171, 1149, 1106, 1096, 1012, 961 cm^{-1}. HRMS (FAB): calcd. for $C_{29}H_{55}O_5Si_3BrNa$ [M + Na] 669.2438; found 669.2400. Compound **5**: M.p. 82–84 °C. ^1H NMR (600 MHz, C_6D_6): δ = –0.20, –0.03, –0.02, 0.15, 0.17 and 0.25 (6 s, 6 × 3 H, CH_3Si), 0.83, 0.997 and 1.001 [3 s, 3 × 9 H, $(CH_3)_3C$], 3.18 (d, $J_{OH,2'}$ = 12.2 Hz, 1 H, OH), 3.60 (dd, J_{gem} = 10.9 Hz, $J_{5'b,4'}$ = 3.0 Hz, 1 H, 5′b-H), 3.63 (dd, J_{gem} = 10.9 Hz, $J_{5'a,4'}$ = 3.4 Hz, 1 H, 5′a-H), 3.90 (dd, $J_{2',OH}$ = 12.2 Hz, $J_{2',3'}$ = 6.4 Hz, 1 H, 2′-H), 4.26 (dd, $J_{3',2'}$ = 6.4 Hz, $J_{3',4'}$ = 2.0 Hz, 1 H, 3′-H), 4.29 (br. ddd, $J_{4',5'}$ = 3.4, 3.0 Hz, $J_{4',3'}$ = 2.0 Hz, 1 H, 4′-H), 7.37 (m, 2 H, 3,5-H), 7.65 (m, 2 H, 2,6-H) ppm. ^{13}C NMR (151 MHz, C_6D_6): δ = –5.66, –5.43, –4.84, –4.50, –3.48 and –2.58 (CH_3Si), 18.26, 18.31 and 18.59 [$C(CH_3)_3$], 25.84, 26.05 and 26.29 [$(CH_3)_3C$], 63.92 (CH_2-5′), 73.56 (CH-3′), 79.27 (CH-2′), 86.72 (CH-4′), 104.43 (C-1′), 122.43 (C-4), 128.05 (CH-2,6), 131.17 (CH-3,5), 143.45 (C-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 3554, 2955, 2927, 2894, 2857, 1594, 1471, 1256, 1132, 1088, 1048, 1021, 963, 929, 836 cm^{-1}. HRMS (FAB): calcd. for $C_{29}H_{55}O_5Si_3BrNa$ [M + Na] 669.2438; found 669.2465.

1β-(4-Bromophenyl)-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (6): Et_3SiH (3.4 mL, 21.1 mmol, 3.33 equiv.) was added in one portion to a stirred solution of hemiketal **4** (4.1 g, 6.33 mmol) in dry CH_2Cl_2 (23.3 mL) in an ice–brine bath (–10 °C)

under an atmosphere of argon. After 5 min, $BF_3{\cdot}Et_2O$ (0.9 mL, 7.59 mmol, 1.2 equiv.) was added over 1 min by syringe. The resulting mixture was stirred for an additional 5 min, then poured into saturated $NaHCO_3$, extracted with CH_2Cl_2, dried with $MgSO_4$, and concentrated under vacuum. The crude product was chromathographed on silica gel (hexane/toluene, 2:1 to toluene) to obtain **6** (3.4 g, 85%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.44, –0.12, 0.087, 0.09, 0.11 and 0.12 (6 s, 6×H, CH_3Si), 0.81, 0.93 and 0.94 [3 s, 3×9 H, $(CH_3)_3C$], 3.76 (dd, J_{gem} = 11.0 Hz, $J_{5'b,4'}$ = 2.9 Hz, 1 H, 5′b-H), 3.80 (dd, J_{gem} = 11.0 Hz, $J_{5'a,4'}$ = 3.7 Hz, 1 H, 5′a-H), 3.81 (dd, $J_{2',1'}$ = 7.8 Hz, $J_{2',3'}$ = 4.4 Hz, 1 H, 2′-H), 4.02 (ddd, $J_{4',5'}$ = 3.7, 2.9 Hz, $J_{4',3'}$ = 1.9 Hz, 1 H, 4′-H), 4.11 (ddd, $J_{3',2'}$ = 4.4 Hz, $J_{3',4'}$ = 1.9 Hz, $J_{3',1'}$ = 0.5 Hz, 1 H, 3′-H), 4.72 (d, $J_{1',2'}$ = 7.8 Hz, 1 H, 1′-H), 7.31 (m, 2 H, 2,6-H), 7.43 (m, 2 H, 3,5-H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.52, –5.43, –5.40, –4.48, –4.46 and –4.41 (CH_3Si), 17.92, 18.07 and 18.35 [$C(CH_3)_3$], 25.83, 25.88 and 25.98 [$C(CH_3)_3$], 63.63 (CH_2-5′), 73.89 (CH-3′), 79.57 (CH-2′), 82.28 (CH-1′), 86.13 (CH-4′), 121.36 (C-4), 128.59 (CH-2,6), 131.06 (CH-3,5), 139.88 (C-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 3084, 3049, 3032, 2897, 1595, 1577, 1492, 1488, 1472, 1463, 1408, 1389, 1362, 1308, 1254, 1220, 1188, 1071, 1012, 937, 838 cm^{-1}. HRMS (FAB): calcd. for $C_{29}H_{56}O_4Si_3Br$ [M + H] 631.2670; found 631.2680.

1β-(4-Bromophenyl)-1-deoxy-3,5-di-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (7): Et_3SiH (1 mL, 6.12 mmol, 3.33 equiv.) was added in one portion to a stirred solution of **5** (1.19 g, 1.84 mmol) in dry CH_2Cl_2 (6.7 mL) in an ice–brine bath (–10 °C) under an atmosphere of argon. After 5 min, $BF_3{\cdot}Et_2O$ (0.26 mL, 2.20 mmol, 1.2 equiv.) was added over 1 min by syringe. The resulting mixture was stirred for an additional 5 min, then poured into saturated $NaHCO_3$, extracted with CH_2Cl_2, dried with $MgSO_4$, and concentrated under vacuum. Purification on silica gel (hexane/toluene, 1:1) furnished **7** (853 mg, 89%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.093, 0.095, 0.14 and 0.15 (4 s, 4×3 H, CH_3Si), 0.91 and 0.95 [2 s, 2×9 H, $(CH_3)_3C$], 2.75 (d, $J_{OH,2'}$ = 8.3 Hz, 1 H, OH-2′), 3.77 (dd, J_{gem} = 11.1 Hz, $J_{5'b,4'}$ = 3.2 Hz, 1 H, 5′b-H), 3.79 (ddd, $J_{OH,2'}$ = 8.3 Hz, $J_{2',1'}$ = 6.8 Hz, $J_{2',3'}$ = 5.5 Hz, 1 H, 2′-H), 3.81 (dd, J_{gem} = 11.1 Hz, $J_{5'a,4'}$ = 3.9 Hz, 1 H, 5′a-H), 3.99 (ddd, $J_{4',5'}$ = 3.9, 3.2 Hz, $J_{4',3'}$ = 3.3 Hz, 1 H, 4′-H), 4.28 (ddd, $J_{3',2'}$ = 5.5 Hz, $J_{3',4'}$ = 3.3 Hz, $J_{3',1'}$ = 0.3 Hz, 1 H, 3′-H), 4.64 (d, $J_{1',2'}$ = 6.8 Hz, 1 H, 1′-H), 7.33 (m, 2 H, 2,6-H), 7.45 (m, 2 H, 3,5-H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.53, –5.39, –4.89 and –4.44 (CH_3Si), 18.04 and 18.34 [$C(CH_3)_3$], 25.75 and 25.91 [$C(CH_3)_3$], 62.82 (CH_2-5′), 72.77 (CH-3′), 77.74 (CH-2′), 83.73 (CH-1′), 84.94 (CH-4′), 121.39 (C-4), 127.69 (CH-2,6), 131.31 (CH-3,5), 139.57 (C-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 3624, 3543, 3084, 3049, 2898, 1596, 1576, 1489, 1472, 1463, 1407, 1390, 1362, 1310, 1295, 1255, 1220, 1186, 1118, 1088, 1088, 1073, 1012, 939 cm^{-1}. HRMS: calcd. for $C_{23}H_{42}BrO_4Si_2$ [M + H] 517.1727; found 517.1805.

1β-(4-Methylphenyl)-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (9a): Me_3Al (2 M in hexanes, 0.48 mL, 0.956 mmol, 2 equiv.) was added in one portion to a vigorously stirred solution of **6** (302 mg, 0.478 mmol) and $Pd(PPh_3)_4$ (5 mol-%, 28 mg, 0.024 mmol) in THF (10 mL) under an atmosphere of argon. The mixture was stirred at 55 °C for 48 h, then worked up by pouring into saturated NaH_2PO_4 and extracted with EtOAc. The crude product was chromatographed on silica gel (hexane/ethyl acetate, 40:1) to give **9a** (243 mg, 90%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.41, –0.13, 0.085, 0.088, 0.11 and 0.13 (6 s, 6×3 H, CH_3Si), 0.81, 0.93 and 0.95 [3 s, 3×9 H, $(CH_3)_3C$], 2.33 (s, 3 H, CH_3), 3.77 (dd, J_{gem} = 10.9 Hz, $J_{5'b,4'}$ = 3.2 Hz, 1 H, H-5′b), 3.80 (dd, J_{gem} = 10.9 Hz, $J_{5'a,4'}$ = 4.0 Hz, 1 H, H-5′a), 3.84 (dd, $J_{2',1'}$ = 7.3 Hz, $J_{2',3'}$ = 4.4 Hz, 1 H, H-2′), 4.01 (ddd, $J_{4',5'}$ = 4.0, 3.2 Hz, $J_{4',3'}$ = 2.3 Hz, 1 H, H-4′), 4.13 (ddd, $J_{3',2'}$ = 4.4 Hz, $J_{3',4'}$ = 2.3 Hz, $J_{3',1'}$ = 0.4 Hz, 1 H, H-3′), 4.74 (d, $J_{1',2'}$ = 7.3 Hz, 1 H, H-1′), 7.10 (m, 2 H, H-3,5), 7.29 (m, 2 H, H-2,6) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.50, –5.39, –5.31, –4.53 and –4.43 (CH_3Si), 17.97, 18.10 and 18.40 [$C(CH_3)_3$], 21.28 (CH_3), 25.88, 25.92 and 26.02 [$C(CH_3)_3$], 63.67 (CH_2-5′), 73.71 (CH-3′), 79.51 (CH-2′), 83.07 (CH-1′), 85.52 (CH-4′), 126.84 (CH-2,6), 128.63 (CH-3,5), 137.14 (C-4), 137.59 (C-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 3099, 3054, 3030, 3013, 2896, 1618, 1516, 1472, 1463, 1406, 1389, 1373, 1361, 1304, 1280, 1257, 1213, 1187, 1021, 937 cm^{-1}. HRMS (FAB): calcd. for $C_{30}H_{59}O_4Si_3$ [M + H] 567.3721; found 567.3713.

1β-(4-Ethylphenyl)-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (9b): Et_3Al (1 M in hexanes, 1.8 mmol, 2 equiv., 1.8 mL) was added in one portion to a vigorously stirred solution of **6** (566 mg, 0.895 mmol) and $Pd(PPh_3)_4$ (5 mol-%, 52 mg, 0.045 mmol) in THF (10 mL) under an atmosphere of argon. The mixture was stirred at 55 °C for 48 h and then worked up by pouring into saturated NaH_2PO_4 and extracting with EtOAc. The crude product was chromatographed on silica gel (hexane/EtOAc, 95:3) to give **9b** (398 mg, 77%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.42, –0.14, 0.089, 0.090, 0.11 and 0.13 (6 s, 6×3 H, CH_3Si), 0.79, 0.93 and 0.95 [3 s, 3×9 H, $(CH_3)_3C$], 1.20 (t, J_{vic} = 7.6 Hz, 3 H, CH_3CH_2), 2.62 (q, J_{vic} = 7.6 Hz, 2 H, CH_2CH_3), 3.77 (dd, J_{gem} = 10.9 Hz, $J_{5'b,4'}$ = 3.3 Hz, 1 H, 5′b-H), 3.80 (dd, J_{gem} = 10.9 Hz, $J_{5'a,4'}$ = 3.8 Hz, 1 H, 5′a-H), 3.85 (dd, $J_{2',1'}$ = 7.4 Hz, $J_{2',3'}$ = 4.4 Hz, 1 H, 2′-H), 4.01 (ddd, $J_{4',5'}$ = 3.9, 3.3 Hz, $J_{4',3'}$ = 2.3 Hz, 1 H, 4′-H), 4.13 (ddd, $J_{3',2'}$ = 4.4 Hz, $J_{3',4'}$ = 2.3 Hz, $J_{3',1'}$ = 0.5 Hz, 1 H, 3′-H), 4.74 (d, $J_{1',2'}$ = 7.4 Hz, 1 H, 1′-H), 7.12 (m, 2 H, 3,5-H), 7.32 (m, 2 H, 2,6-H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.50, –5.39, –4.55 and –4.43 (CH_3Si), 15.80 (CH_3CH_2), 17.99, 18.10 and 18.40 [$C(CH_3)_3$], 25.87, 25.92 and 26.02 [$C(CH_3)_3$], 28.65 (CH_2CH_3), 63.70 (CH_2-5′), 73.73 (CH-3′), 79.56 (CH-2′), 83.03 (CH-1′), 85.58 (CH-4′), 126.92 (CH-2,6), 127.46 (CH-3,5), 137.79 (C-1), 143.74 (C-4) ppm. IR (CCl_4): $\tilde{\nu}$ = 3095, 3037, 3017, 2896, 1617, 1515, 1472, 1423, 1406, 1389, 1374, 1362, 1308, 1282, 1263, 1257, 1213, 1187, 1020, 938 cm^{-1}. HRMS (FAB): calcd. for $C_{31}H_{61}O_4Si_3$ [M + H] 581.3878; found 581.3895.

1β-(4-Benzylphenyl)-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (9c): THF (4.3 mL) was added to a flame-dried and argon-purged flask containing **6** (143 mg, 0.226 mmol) and $Pd(PPh_3)_4$ (5 mol-%, 13 mg, 0.011 mmol), and the mixture was stirred until a clear solution was formed. The commercial solution of benzylzinc bromide (0.5 M solution in THF, 0.9 mL, 0.454 mmol, 2 equiv.) was added in one portion, and the mixture was stirred at 55 °C for 48 h. After workup, the crude product was chromatographed on silica gel (hexane/EtOAc, 50:1) to give **9c** (88 mg, 67%) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.43, –0.14, 0.09, 0.10 and 0.11 (5 s, 18 H, CH_3Si), 0.78, 0.931 and 0.934 (3 s, 3×9 H, $(CH_3)_3C$), 3.77 (d, $J_{5',4'}$ = 3.7 Hz, 2 H, 5′-H), 3.84 (dd, $J_{2',1'}$ = 7.7 Hz, $J_{2',3'}$ = 4.5 Hz, 1 H, 2′-H), 3.97 (s, 2 H, CH_2Ph), 4.01 (td, $J_{4',5'}$ = 3.7 Hz, $J_{4',3'}$ = 2.0 Hz, 1 H, 4′-H), 4.12 (ddd, $J_{3',2'}$ = 4.5 Hz, $J_{3',4'}$ = 2.0 Hz, $J_{3',1'}$ = 0.5 Hz, 1 H, 3′-H), 4.74 (d, $J_{1',2'}$ = 7.7 Hz, 1 H, 1′-H), 7.12 (m, 2 H, 3,5-H), 7.14 (m, 2 H, *o*-Ph-H), 7.18 (m, 1 H, *p*-Ph-H), 7.26 (m, 2 H, *m*-Ph-H), 7.33 (m, 2 H, 2,6-H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.51, –5.36, –4.51, –4.43 and –4.41 (CH_3Si), 17.99, 18.10 and 18.39 [$C(CH_3)_3$], 25.87, 25.92 and 26.01 [$C(CH_3)_3$], 41.60 (CH_2Ph), 63.76 (CH_2-5′), 73.86 (CH-3′), 79.61 (CH-2′), 82.83 (CH-1′), 85.82 (CH-4′), 125.90 (CH-*p*-Ph), 127.13 (CH-2,6), 128.29 (CH-*m*-Ph), 128.81 (CH-3,5), 128.84 (CH-*o*-Ph), 138.40 (C-1), 140.35 (C-4), 141.47 (C-*i*-Ph) ppm. IR (CCl_4): $\tilde{\nu}$ = 3087, 3064, 3029, 2897, 1604, 1514, 1495, 1482, 1463, 1454, 1422, 1406, 1389, 1362, 1309, 1286, 1257, 1187, 1031,

1020, 939 cm^{-1}. HRMS (FAB): calcd. for $C_{36}H_{63}O_4Si_3$ [M + H] 643.4034; found 643.4054.

1β-[4-(2-Thienyl)phenyl]-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (9d): DMF (3.5 mL) was added to a flame-dried and argon-purged flask containing **6** (480 mg, 0.760 mmol) and $PdCl_2(PPh_3)_2$ (5 mol-%, 27 mg, 0.038 mmol). After 5 min stirring at room temperature, tributyl(thiophen-2-yl)stannane (0.29 mL, 0.912 mmol, 1.2 equiv.) was added, and reaction vessel was immersed into an oil bath preheated to 100 °C. After 10 min, the reaction mixture became dark-brown and the reaction was finished (monitored by TLC; hexanes/EtOAc, 10:1). The crude reaction mixture was diluted with Et_2O, washed with saturated NaCl solution, and dried with $MgSO_4$. After evaporation of the solvents under reduced pressure, the crude product was chromatographed on silica gel (hexanes/EtOAc, 50:1) to obtain **9d** (381 mg, 79%) as a colorless oil. ^1H NMR (600 MHz, $CDCl_3$): δ = –0.41, –0.12, 0.10, 0.13 and 0.14 (5 s, 18 H, CH_3Si), 0.81, 0.94 and 0.95 [3 s, 3×9 H, $(CH_3)_3C$], 3.79 (dd, J_{gem} = 10.9 Hz, $J_{5'b,4'}$ = 3.0 Hz, 1 H, 5′b-H), 3.82 (dd, J_{gem} = 10.9 Hz, $J_{5'a,4'}$ = 3.9 Hz, 1 H, 5′a-H), 3.87 (dd, $J_{2',1'}$ = 7.7 Hz, $J_{2',3'}$ = 4.4 Hz, 1 H, 2′-H), 4.04 (ddd, $J_{4',5'}$ = 3.9, 3.0 Hz, $J_{4',3'}$ = 2.0 Hz, 1 H, 4′-H), 4.14 (dd, $J_{3',2'}$ = 4.4 Hz, $J_{3',4'}$ = 2.0 Hz, 1 H, 3′-H), 4.78 (d, $J_{1',2'}$ = 7.7 Hz, 1 H, 1′-H), 7.08 (dd, $J_{4,5}$ = 5.1 Hz, $J_{4,3}$ = 3.6 Hz, 1 H, 4-thienyl-H), 7.26 (dd, $J_{5,4}$ = 5.1 Hz, $J_{5,3}$ = 1.2 Hz, 1 H, 5-thienyl-H), 7.32 (dd, $J_{3,4}$ = 3.6 Hz, $J_{3,5}$ = 1.2 Hz, 1 H, 3-thienyl-H), 7.43 (m, 2 H, 2,6-H), 7.55 (m, 2 H, 3,5-H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = –5.51, –5.38, –5.32, –4.50, –4.45 and –4.43 (CH_3Si), 17.95, 18.09 and 18.38 [$C(CH_3)_3$], 25.85, 25.90 and 26.01 [$C(CH_3)_3$], 63.67 (CH_2-5′), 73.86 (CH-3′), 79.51 (CH-2′), 82.67 (CH-1′), 85.92 (CH-4′), 122.85 (CH-3-thienyl), 124.50 (CH-5-thienyl), 125.49 (CH-3,5), 127.42 (CH-2,6), 127.94 (CH-4-thienyl), 133.68 (C-4), 140.08 (C-1), 144.50 (C-2-thienyl) ppm. IR (CCl_4): $\tilde{\nu}$ = 3115, 3077, 3030, 2956, 2897, 1613, 1538, 1504, 1472, 1433, 1418, 1407, 1389, 1362, 1309, 1298, 1263, 1257, 1257, 1215, 1187, 1112, 1095, 1081, 1081, 1046, 1019, 971, 946, 938, 839 cm^{-1}. HRMS (FAB): calcd. for $C_{33}H_{58}O_4SSi_3Na$ [M + Na] 657.3261; found 657.3249.

1β-[4-(Pyridin-2-yl)phenyl]-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (9e): DMF (2 mL) was added to a flame-dried and argon-purged flask containing **6** (273 mg, 0.432 mmol) and $PdCl_2(PPh_3)_2$ (5 mol-%, 15 mg, 0.022 mmol). After 5 min stirring at room temperature, 2-(tributylstannyl)pyridine (0.17 mL, 0.605 mmol, 1.4 equiv.) was added in one portion, and the reaction vessel was immersed into an oil bath preheated at 100 °C. After 32 h, the reaction mixture was diluted with Et_2O and filtered trough Celite. The filtrate was washed with HCl (2 M) and saturated $NaHCO_3$ solution and then dried with $MgSO_4$. After evaporation of the solvent under reduced pressure, the crude product was chromatographed on silica gel (toluene/hexanes, 4:1 to hexanes/EtOAc, 13:1) to obtain **9e** (152 mg, 56%) as a colorless oil. ^1H NMR (600 MHz, $CDCl_3$): δ = –0.41, –0.12, 0.10, 0.13 and 0.15 (5 s, 18 H, CH_3Si), 0.82, 0.94 and 0.96 [3 s, 3×9 H, $(CH_3)_3C$], 3.80 (dd, J_{gem} = 10.9 Hz, $J_{5'b,4'}$ = 2.9 Hz, 1 H, 5′b-H), 3.84 (dd, J_{gem} = 10.9 Hz, $J_{5'a,4'}$ = 3.8 Hz, 1 H, 5′a-H), 3.91 (dd, $J_{2',1'}$ = 7.6 Hz, $J_{2',3'}$ = 4.4 Hz, 1 H, 2′-H), 4.06 (ddd, $J_{4',5'}$ = 3.8, 2.9 Hz, $J_{4',3'}$ = 2.0 Hz, 1 H, 4′-H), 4.16 (ddd, $J_{3',2'}$ = 4.4 Hz, $J_{3',4'}$ = 2.0 Hz, $J_{3',1'}$ = 0.4 Hz, 1 H, 3′-H), 4.84 (d, $J_{1',2'}$ = 7.6 Hz, 1 H, 1′-H), 7.22 (m, 1 H, 5-py-H), 7.54 (m, 2 H, 2,6-H), 7.72 –7.77 (m, 2 H, 3,4-py-H), 7.95 (m, 2 H, 3,5-H), 8.70 (ddd, $J_{6,5}$ = 4.8 Hz, $J_{6,4}$ = 1.7 Hz, $J_{6,3}$ = 1.3 Hz, 1 H, 6-py-H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = –5.51, –5.36, –5.27, –4.51, –4.45 and –4.42 (CH_3Si), 17.94, 18.09 and 18.39 [$C(CH_3)_3$], 25.87, 25.90 and 26.02 [$C(CH_3)_3$], 63.66 (CH_2-5′), 73.87 (CH-3′), 79.55 (CH-2′), 82.74 (CH-1′), 85.95 (CH-4′), 120.51 (CH-3-py), 121.97 (CH-5-py), 126.49 (CH-3,5), 127.31 (CH-2,6), 136.69 (CH-4-py), 138.64 (C-4), 141.68 (C-1), 149.61 (CH-6-py), 157.35 (C-2-py) ppm. IR (CCl_4): $\tilde{\nu}$ = 2896, 1611, 1588, 1579, 1564, 1468, 1468, 1436, 1414, 1408, 1389, 1362, 1308, 1295, 1256, 1220, 1187, 1095, 1080, 1074, 1016, 995, 939 cm^{-1}. HRMS: calcd. for $C_{34}H_{60}NO_4Si_3$ [M + H] 630.3830; found 630.3819.

1β-[4-(4-Fluorophenyl)phenyl]-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (9f): Toluene (4 mL) was added to a flame-dried and argon-purged flask containing **6** (344 mg, 0.545 mmol), $Pd(PPh_3)_4$ (2.5 mol-%, 16 mg, 0.014 mmol), K_2CO_3 (151 mg, 1.090 mmol, 2 equiv.), and 4-fluorophenylboronic acid (152 mg, 1.090 mmol, 2 equiv.), and the red mixture was stirred at 110 °C for 10 min. After the reaction was complete (monitored by TLC; hexanes/toluene, 2:1), the reaction mixture was evaporated under reduced pressure and chromatographed on silica gel (hexanes/toluene, 2:1) to give **9f** (301 mg, 85%) as a colorless oil. ^1H NMR (600 MHz, $CDCl_3$): δ = –0.42, –0.11, 0.10, 0.13 and 0.14 (5 s, 18 H, CH_3Si), 0.81, 0.94 and 0.95 [3 s, 3×9 H, $(CH_3)_3C$], 3.80 (dd, J_{gem} = 10.9 Hz, $J_{5'b,4'}$ = 2.9 Hz, 1 H, 5′b-H), 3.83 (dd, J_{gem} = 10.9 Hz, $J_{5'a,4'}$ = 3.9 Hz, 1 H, 5′a-H), 3.89 (dd, $J_{2',1'}$ = 7.6 Hz, $J_{2',3'}$ = 4.4 Hz, 1 H, 2′-H), 4.05 (ddd, $J_{4',5'}$ = 3.9, 2.9 Hz, $J_{4',3'}$ = 2.0 Hz, 1 H, 4′-H), 4.15 (ddd, $J_{3',2'}$ = 4.4 Hz, $J_{3',4'}$ = 2.0 Hz, $J_{3',1'}$ = 0.5 Hz, 1 H, 3′-H), 4.81 (d, $J_{1',2'}$ = 7.6 Hz, 1 H, 1′-H), 7.12 (m, 2 H, m-C_6H_4F-H), 7.49 (m, 4 H, 2,3,5,6-H), 7.54 (m, 2 H, o-C_6H_4F-H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = –5.51, –5.40, –5.39, –4.50, –4.44 and –4.42 (CH_3Si), 17.96, 18.09 and 18.38 [$C(CH_3)_3$], 25.85, 25.90 and 26.01 [$C(CH_3)_3$], 63.67 (CH_2-5′), 73.84 (CH-3′), 79.61 (CH-2′), 82.71 (CH-1′), 85.92 (CH-4′), 115.51 (d, $J_{C,F}$ = 21 Hz, CH-*m*-C_6H_4F), 126.57 (CH-3,5), 127.39 (CH-2,6), 128.58 (d, $J_{C,F}$ = 8 Hz, CH-*o*-C_6H_4F), 137.26 (d, $J_{C,F}$ = 3 Hz, C-*i*-C_6H_4F), 139.53 (C-4), 139.83 (C-1), 162.36 (d, $J_{C,F}$ = 246 Hz, C-*p*-C_6H_4F) ppm. ^{19}F NMR (470.3 MHz, $CDCl_3$): δ = –116.08 ppm. IR (CCl_4): $\tilde{\nu}$ = 3033, 2956, 2897, 1615, 1605, 1595, 1569, 1525, 1499, 1472, 1463, 1405, 1390, 1362, 1303, 1280, 1236, 1226, 1186, 1158, 1096, 1080, 1026, 1007, 945, 939 cm^{-1}. HRMS (FAB): calcd. for $C_{35}H_{59}FO_4Si_3Na$ [M + Na] 669.3603; found 669.3605.

1β-[4-(4-Methoxyphenyl)phenyl]-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (9g): Toluene (4 mL) was added to a flame-dried and argon-purged flask containing **6** (461 mg, 0.731 mmol), $Pd(PPh_3)_4$ (5 mol-%, 43 mg, 0.037 mmol), K_2CO_3 (202 mg, 1.461 mmol, 2 equiv.), and 4-methoxyphenylboronic acid (222 mg, 1.461 mmol, 2 equiv.), and the yellow mixture was stirred at 110 °C for 3.5 h. After the reaction was complete (monitored by TLC; hexanes/toluene, 2:1), the reaction mixture was filtered though Celite, evaporated under reduced pressure, and chromatographed on silica gel (gradient hexanes/toluene, 4:1 to 1:1) to give **9g** (350 mg, 72%) as a colorless oil. ^1H NMR (600 MHz, $CDCl_3$): δ = –0.41, –0.12, 0.10, 0.13 and 0.14 (5 s, 18 H, CH_3Si), 0.81, 0.94 and 0.95 [3 s, 3×9 H, $(CH_3)_3C$], 3.80 (dd, J_{gem} = 10.9 Hz, $J_{5'b,4'}$ = 3.0 Hz, 1 H, H-5′b), 3.83 (dd, J_{gem} = 10.9 Hz, $J_{5'a,4'}$ = 4.0 Hz, 1 H, H-5′a), 3.85 (s, 3 H, CH_3O), 3.89 (dd, $J_{2',1'}$ = 7.5 Hz, $J_{2',3'}$ = 4.4 Hz, 1 H, H-2′), 4.05 (ddd, $J_{4',5'}$ = 4.0, 3.0 Hz, $J_{4',3'}$ = 2.2 Hz, 1 H, H-4′), 4.15 (ddd, $J_{3',2'}$ = 4.4 Hz, $J_{3',4'}$ = 2.2 Hz, $J_{3',1'}$ = 0.4 Hz, 1 H, H-3′), 4.81 (d, $J_{1',2'}$ = 7.5 Hz, 1 H, H-1′), 6.97 (m, 2 H, H-*m*-C_6H_4OMe), 7.46 (m, 2 H, H-2,6), 7.49 (m, 2 H, H-3,5), 7.54 (m, 2 H, H-*o*-C_6H_4OMe) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = –5.50, –5.39, –5.37, –4.50 and –4.44 (CH_3Si), 17.97, 18.10 and 18.39 [$C(CH_3)_3$], 25.86, 25.91 and 26.01 [$C(CH_3)_3$], 55.36 (CH_3O), 63.66 (CH_2-5′), 73.79 (CH-3′), 79.58 (CH-2′), 82.84 (CH-1′), 85.78 (CH-4′), 114.12 (CH-*m*-C_6H_4OMe), 126.27 (CH-3,5), 127.29 (CH-2,6), 128.04 (CH-*o*-C_6H_4OMe), 133.72 (C-*i*-C_6H_4OMe), 139.13 (C-1), 140.07 (C-1), 159.01 (C-*p*-C_6H_4OMe) ppm. IR (CCl_4): $\tilde{\nu}$ = 3033, 3001, 2956, 2897, 2837, 1612, 1584, 1567, 1527, 1500, 1472, 1442, 1428, 1405, 1389, 1362, 1362, 1310, 1299, 1287, 1270, 1263, 1260,

1249, 1220, 1215, 1181, 1175, 1110, 1095, 1080, 1044, 1026, 1016, 949, 939 cm^{-1}. HRMS (FAB): calcd. for $C_{36}H_{63}O_5Si_3$ [M + H] 659.3983; found 659.3971.

1β-(4-Aminophenyl)-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (9h): $LiN(SiMe_3)_2$ (1 M solution in THF, 1.47 mL, 1.468 mmol, 1.3 equiv.) was added to a flame-dried and argon-purged flask containing **6** (714 mg, 1.129 mmol), (2-biphenyl)dicyclohexylphosphane (40 mg, 0.113 mmol), and $Pd_2(dba)_3$ (26 mg, 0.028 mmol), and the mixture was stirred at 60 °C for 48 h. After cooling to room temperature, the reaction mixture was diluted with Et_2O (5 mL) and HCl (2 M, 1 mL) was added. The resulting heterogeneous mixture was stirred for an additional 5 min then transferred into a saturated solution of $NaHCO_3$ and extracted with Et_2O. The crude product was chromatographed on silica gel (gradient hexane/EtOAc, 50:1 to 15:1) to gave **9h** (641 mg, 84%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.38, –0.13, 0.08, 0.10 and 0.12 (5 s, 18 H, CH_3Si), 0.80, 0.93 and 0.94 [3 s, 3 × 9 H, $(CH_3)_3C$], 3.60 (br. s, 2 H, NH_2), 3.75 (dd, J_{gem} = 10.9 Hz, $J_{5'b,4'}$ = 3.4 Hz, 1 H, H-5′b), 3.78 (dd, J_{gem} = 10.9 Hz, $J_{5'a,4'}$ = 3.8 Hz, 1 H, H-5′a), 3.82 (dd, $J_{2',1'}$ = 7.5 Hz, $J_{2',3'}$ = 4.5 Hz, 1 H, H-2′), 3.98 (ddd, $J_{4',5'}$ = 3.8, 3.4 Hz, $J_{4',3'}$ = 2.1 Hz, 1 H, H-4′), 4.12 (dd, $J_{3',2'}$ = 4.5 Hz, $J_{3',4'}$ = 2.1 Hz, 1 H, H-3′), 4.67 (d, $J_{1',2'}$ = 7.5 Hz, 1 H, H-1′), 6.63 (m, 2 H, H-3,5), 7.19 (m, 2 H, H-2,6) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.51, –5.40, –5.21, –4.50 and –4.44 (CH_3Si), 17.98, 18.10 and 18.39 [$C(CH_3)_3$], 25.89, 25.92 and 26.02 [$C(CH_3)_3$], 63.77 (CH_2-5′), 73.82 (CH-3′), 79.31 (CH-2′), 82.96 (CH-1′), 85.47 (CH-4′), 114.80 (CH-3,5), 126.13 (CH-2,6), 130.62 (C-1), 145.89 (C-4) ppm. IR (CCl_4): $\tilde{\nu}$ = 3479, 3395, 3026, 3010, 1956, 1896, 1623, 1588, 1519, 1472, 1406, 1389, 1362, 1331, 1297, 1274, 1263, 1257, 1219, 1175, 1096, 1083, 1013, 940, 928, 838 cm^{-1}. HRMS: calcd. for $C_{29}H_{58}NO_4Si_3$ [M + H] 568.3673; found 568.3681.

1β-(4-Dimethylaminophenyl)-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (9i): Toluene (2.0 mL) was added to a flame-dried and argon-purged flask containing **6** (482 mg, 0.763 mmol), $Pd_2(dba)_3$ (17 mg, 0.019 mmol), (2-biphenyl)-di-*tert*-butylphosphane (27 mg, 0.076 mmol), sodium *tert*-butoxide (440 mg, 4.58 mmol, 6 equiv.), and $Me_2NH{\cdot}HCl$ (311 mg, 3.815 mmol, 5 equiv.). The resulting mixture was stirred at 37 °C for 72 h and then diluted with Et_2O, poured into water, extracted with Et_2O, and dried with $MgSO_4$. After removal of the solvent under reduced pressure, the crude product was chromatographed on silica gel (gradient hexane/EtOAc, 250:1 to 63:1) to give **9i** (455 mg, 82%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.36, –0.12, 0.08, 0.09, 0.11 and 0.12 (6 s, 6 × 3 H, CH_3Si), 0.81, 0.93 and 0.95 [3 s, 3 × 9 H, $(CH_3)_3C$], 2.92 [s, 6 H, $(CH_3)_2N$], 3.76 (dd, J_{gem} = 10.9 Hz, $J_{5'b,4'}$ = 3.5 Hz, 1 H, 5′b-H), 3.79 (dd, J_{gem} = 10.9 Hz, $J_{5'a,4'}$ = 3.9 Hz, 1 H, 5′a-H), 3.85 (dd, $J_{2',1'}$ = 7.2 Hz, $J_{2',3'}$ = 4.5 Hz, 1 H, 2′-H), 3.99 (ddd, $J_{4',5'}$ = 3.9, 3.5 Hz, $J_{4',3'}$ = 2.5 Hz, 1 H, 4′-H), 4.13 (dd, $J_{3',2'}$ = 4.5 Hz, $J_{3',4'}$ = 2.5 Hz, 1 H, 3′-H), 4.70 (d, $J_{1',2'}$ = 7.2 Hz, 1 H, 1′-H), 6.68 (m, 2 H, 3,5-H), 7.25 (m, 2 H, 2,6-H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.49, –5.36, –5.12, –4.51, –4.46 and –4.41 (CH_3Si), 18.00, 18.11 and 18.43 [$C(CH_3)_3$], 25.90, 25.94 and 26.04 [$C(CH_3)_3$], 40.86 [$(CH_3)_2N$], 63.75 (CH_2-5′), 73.68 (CH-3′), 79.22 (CH-2′), 83.19 (CH-1′), 85.16 (CH-4′), 112.51 (CH-3,5), 127.84 (CH-2,6), 128.61 (C-1), 150.53 (C-4) ppm. IR (CCl_4): $\tilde{\nu}$ = 3076, 2896, 2803, 1617, 1572, 1524, 1472, 1463, 1444, 1406, 1389, 1361, 1349, 1318, 1286, 1257, 1252, 1188, 998, 948, 941, 838 cm^{-1}. HRMS (FAB): calcd. for $C_{31}H_{62}NO_4Si_3$ [M + H] 596.3987; found 596.3965.

1β-(4-*tert*-Butoxyphenyl)-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (9j): Toluene (1.8 mL) was added to a flame-dried and argon-purged flask containing **6** (387 mg, 0.614 mmol), Pd_2dba_3 (14 mg, 0.015 mmol), (2-biphenyl)-di-*tert*-butylphosphane (18 mg, 0.061 mmol), and sodium *tert*-butoxide (177 mg, 1.84 mmol, 3 equiv.), and the resulting brown-yellow solution was stirred at 90 °C for 8 h. After the reaction was complete (monitored by TLC; hexanes/EtOAc, 10:1), the reaction mixture was evaporated under reduced pressure and directly chromatographed on silica gel (gradient hexanes/toluene, 2:1 to toluene) to give **9j** (263 mg, 69%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = –0.48, –0.15, 0.09, 0.10, 0.11 and 0.13 (6 s, 6 × 3 H, CH_3Si), 0.77, 0.937 and 0.941 [3 s, 3 × 9 H, $(CH_3)_3CSi$], 1.31 [s, 9 H, $(CH_3)_3CO$], 3.78 (d, $J_{5',4'}$ = 3.5 Hz, 2 H, 5′-H), 3.84 (dd, $J_{2',1'}$ = 8.2 Hz, $J_{2',3'}$ = 4.5 Hz, 1 H, 2′-H), 4.01 (td, $J_{4',5'}$ = 3.5 Hz, $J_{4',3'}$ = 1.4 Hz, 1 H, 4′-H), 4.12 (ddd, $J_{3',2'}$ = 4.5 Hz, $J_{3',4'}$ = 1.4 Hz, $J_{3',1'}$ = 0.5 Hz, 1 H, 3′-H), 4.72 (d, $J_{1',2'}$ = 8.2 Hz, 1 H, 1′-H), 6.94 (m, 2 H, 3,5-H), 7.32 (m, 2 H, 2,6-H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = –5.55, –5.46, –5.44, –4.51, –4.49 and –4.41 (CH_3Si), 17.97, 18.09 and 18.34 [$SiC(CH_3)_3$], 25.84, 25.89 and 25.97 [$(CH_3)_3CSi$], 28.76 [$(CH_3)_3CO$], 63.88 (CH_2-5′), 74.18 (CH-3′), 78.40 [$OC(CH_3)_3$], 79.60 (CH-2′), 82.29 (CH-1′), 86.26 (CH-4′), 124.15 (CH-3,5), 127.58 (CH-2,6), 135.61 (C-1), 154.79 (C-4) ppm. IR (CCl_4): $\tilde{\nu}$ = 2955, 2930, 2896, 2858, 1609, 1508, 1473, 1463, 1389, 1364, 1257, 1158, 1112, 1045, 1006, 969, 938, 901, 837, 777 cm^{-1}. HRMS (FAB): calcd. for $C_{33}H_{65}O_5Si_3$ [M + H] 625.4140; found 625.4150.

1β-(3-Bromophenyl)-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (13) and 1β-(3-Bromophenyl)-1,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (14): To a stirred solution of *m*-dibromobenzene (4.05 mL, 8.07 g, 0.034 mol, 1.7 equiv.) in dry THF (80 mL) cooled to –72 °C was added *n*BuLi (1.6 M in hexanes, 20.5 mL, 0.033 mol, 1.65 equiv.), and the mixture was stirred for 30 min. Then, a solution of TBS-protected ribonolactone **3** (10 g, 0.020 mol) in dry THF (80 mL) was slowly added over 30 min, and the resulting yellow solution was stirred for additional 30 min at –72 °C and then quenched with a saturated NH_4Cl solution. After extraction with AcOEt, the combined organic phase was washed with saturated NH_4Cl solution, dried ($MgSO_4$), and concentrated under vacuum to obtain 14.3 g of colorless oil. Purification on silica gel (gradient hexane to hexane/toluene, 1:1 to toluene) gave desired hemiketal **13** (11.8 g, 89%) as colorless oil and **14** (0.5 g, 4%) as a white solid, which was crystallized from MeOH. Compound **13**: ^{1}H NMR (600 MHz, $CDCl_3$): δ = –0.54, –0.14, 0.128, 0.132, 0.133 and 0.157 (6 s, 6 × 3 H, CH_3Si), 0.84, 0.94 and 0.95 [3 s, 3 × 9 H, $(CH_3)_3C$], 3.81 (dd, J_{gem} = 11.0 Hz, $J_{5'b,4'}$ = 2.4 Hz, 1 H, 5′b-H), 3.86 (dd, J_{gem} = 11.0 Hz, $J_{5'a,4'}$ = 3.3 Hz, 1 H, 5′a-H), 4.00 (d, $J_{2',3'}$ = 4.7 Hz, 1 H, 2′-H), 4.17 (dd, $J_{3',2'}$ = 4.7 Hz, $J_{3',4'}$ = 0.6 Hz, 1 H, 3′-H), 4.23 (ddd, $J_{4',5'}$ = 3.3, 2.4 Hz, $J_{4',3'}$ = 0.6 Hz, 1 H, 4′-H), 5.11 (s, 1 H, OH), 7.18 (t, $J_{5,4}$ = 7.9 Hz, $J_{5,6}$ = 7.8 Hz, 1 H, 5-H), 7.41 (ddd, $J_{4,5}$ = 7.9 Hz, $J_{4,2}$ = 2.1 Hz, $J_{4,6}$ = 1.1 Hz, 1 H, 4-H), 7.58 (ddd, $J_{6,5}$ = 7.8 Hz, $J_{6,2}$ = 1.6 Hz, $J_{6,4}$ = 1.1 Hz, 1 H, 6-H), 7.80 (t, $J_{2,4}$ = 2.1 Hz, $J_{2,6}$ = 1.6 Hz, 1 H, 2-H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = –5.98, –5.64, –5.43, –4.86, –4.58 and –4.53 (**C**H_3Si), 17.82, 17.90 and 18.27 [$C(CH_3)_3$], 25.72, 25.76 and 25.95 [$C(CH_3)_3$], 63.60 (CH_2-5′), 75.01 (CH-3′), 77.85 (CH-2′), 85.35 (CH-4′), 103.51 (CH-1′), 121.85 (C-3), 125.51 (CH-6), 129.21 (CH-5), 130.07 (CH-2), 131.08 (CH-4), 143.20 (C-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 3605, 3503, 3071, 2956, 2930, 2859, 1600, 1582, 1571, 1472, 1463, 1362, 1259, 1170, 1150, 1106, 1005, 962, 839 cm^{-1}. HRMS (FAB): calcd. for $C_{29}H_{55}BrO_5Si_3Na$ [M + Na] 669.2438; found 669.2434. Compound **14**: White crystals, m.p. 59–60 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = –0.33, –0.08, 0.09, 0.11 and 0.12 (5 s, 12 H, CH_3Si), 0.86, 0.92 and 0.93 [3 s, 3 × 9 H, $(CH_3)_3C$], 3.01 (d, $J_{OH,2'}$ = 12.2 Hz, 1 H, OH-2′), 3.70 (dd, $J_{2',OH}$ = 12.2 Hz, $J_{2',3'}$ = 6.4 Hz, 1 H, 2′-H), 3.78 (dd, J_{gem} = 11.0 Hz, $J_{5'b,4'}$ = 2.7 Hz, 1 H, 5′b-H),

3.85 (dd, J_{gem} = 11.0 Hz, $J_{5'a,4'}$ = 3.1 Hz, 1 H, 5′a-H), 4.11 (dd, $J_{3',2'}$ = 6.4 Hz, $J_{3',4'}$ = 1.9 Hz, 1 H, 3′-H), 4.22 (ddd, $J_{4',5'}$ = 3.1, 2.7 Hz, $J_{4',3'}$ = 1.9 Hz, 1 H, 4′-H), 7.16 (ddd, $J_{5,4}$ = 7.9 Hz, $J_{5,6}$ = 7.8 Hz, $J_{5,2}$ = 0.3 Hz, 1 H, 5-H), 7.39 (ddd, $J_{4,5}$ = 7.9 Hz, $J_{4,2}$ = 2.1 Hz, $J_{4,6}$ = 1.1 Hz, 1 H, 4-H), 7.52 (ddd, $J_{6,5}$ = 7.8 Hz, $J_{6,2}$ = 1.6 Hz, $J_{6,4}$ = 1.1 Hz, 1 H, 6-H), 7.75 (ddd, $J_{2,4}$ = 2.1 Hz, $J_{2,6}$ = 1.6 Hz, $J_{2,5}$ = 0.3 Hz, 1 H, 2-H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = –5.67, –5.43, –4.92, –4.71, –3.79 and –2.90 (CH_3Si), 18.01, 18.25 and 18.36 [$C(CH_3)_3$], 25.82, 25.86 and 26.06 [$C(CH_3)_3$], 63.63 (CH_2-5′), 72.98 (CH-3′), 78.88 (CH-2′), 86.44 (CH-4′), 103.63 (CH-1′), 121.82 (C-3), 124.50 (CH-6), 128.68 (CH-2), 129.24 (CH-5), 130.66 (CH-4), 146.08 (C-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 2955, 2930, 2896, 2858, 1609, 1508, 1473, 1463, 1389, 1364, 1257, 1158, 1112, 969, 938 cm^{-1}. HRMS (FAB): calcd. for $C_{29}H_{55}BrO_5Si_3Na$ [M + Na] 669.2438; found 669.2434. HRMS: calcd. for $C_{29}H_{56}BrO_5Si_3$ [M + H] 647.2619; found 647.2602.

1β-(3-Bromophenyl)-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (15): Et_3SiH (9.7 mL, 0.061 mol, 3.33 equiv.) was added in one portion to a solution of hemiketal **13** (11.8 g, 0.018 mol) in dry CH_2Cl_2 (70 mL) in an ice–brine bath (–10 °C) under an atmosphere of argon. After 5 min, $BF_3{\cdot}Et_2O$ (2.6 mL, 0.022 mol, 1.2 equiv.) was added over 1 min by syringe, and the solution was stirred for an additional 5 min. The mixture was then quenched with saturated $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic layer was washed with saturated NH_4Cl solution, dried with $MgSO_4$, and concentrated under reduced pressure. The crude product was chromatographed on silica gel (gradient hexane/toluene, 2:1 to toluene) to give **15** (9.7 g, 84%) as a colorless oil, which crystallized on standing. ^{1}H NMR (600 MHz, $CDCl_3$): δ = –0.47, –0.12, 0.09, 0.10, 0.12 and 0.14 (6 s, 6×3 H, CH_3Si), 0.81, 0.937 and 0.941 [3 s, 3×9 H, $(CH_3)_3C$], 3.77 (dd, J_{gem} = 11.0 Hz, $J_{5'b,4'}$ = 2.8 Hz, 1 H, 5′b-H), 3.80 (dd, J_{gem} = 11.0 Hz, $J_{5'a,4'}$ = 3.6 Hz, 1 H, 5′a-H), 3.82 (dd, $J_{2',1'}$ = 8.3 Hz, $J_{2',3'}$ = 4.4 Hz, 1 H, 2′-H), 4.03 (ddd, $J_{4',5'}$ = 3.6, 2.8 Hz, $J_{4',3'}$ = 1.3 Hz, 1 H, 4′-H), 4.11 (ddd, $J_{3',2'}$ = 4.4 Hz, $J_{3',4'}$ = 1.3 Hz, $J_{3',1'}$ = 0.5 Hz, 1 H, 3′-H), 4.72 (d, $J_{1',2'}$ = 8.3 Hz, 1 H, 1′-H), 7.16 (dd, $J_{5,4}$ = 7.9 Hz, $J_{5,6}$ = 7.7 Hz, 1 H, 5-H), 7.34 (dddd, $J_{6,5}$ = 7.7 Hz, $J_{6,2}$ = 1.5 Hz, $J_{6,4}$ = 1.1 Hz, $J_{6,1'}$ = 0.6 Hz, 1 H, 6-H), 7.38 (ddd, $J_{4,5}$ = 7.9 Hz, $J_{4,2}$ = 2.1 Hz, $J_{4,6}$ = 1.1 Hz, 1 H, 4-H), 7.59 (ddt, $J_{2,4}$ = 2.1 Hz, $J_{2,6}$ = 1.5 Hz, $J_{2,5}$ = $J_{2,1'}$ = 0.5 Hz, 1 H, 2-H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = –5.61, –5.55, –5.41, –4.50 and –4.38 (CH_3Si), 17.91, 18.06 and 18.34 [$C(CH_3)_3$], 25.81, 25.87 and 26.00 [$C(CH_3)_3$], 63.74 (CH_2-5′), 74.20 (CH-3′), 79.60 (CH-2′), 81.86 (CH-1′), 86.59 (CH-4′), 122.27 (C-3), 125.54 (CH-6), 129.52 (CH-5), 129.67 (CH-2), 130.68 (CH-4), 143.17 (C-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 3066, 2897, 1599, 1572, 1472, 1463, 1430, 1407, 1389, 1361, 1256, 1093, 1079, 997, 940 cm^{-1}. MS (FAB): *m*/*z* = 631 [M + H]. HRMS (FAB): calcd. for $C_{29}H_{56}O_4Si_3Br$ [M + H] 631.2670; found 631.2661.

1β-(3-Bromophenyl)-1-deoxy-3,5-di-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (16): Et_3SiH (123 μL, 0.772 mol, 3.33 equiv.) was added in one portion to a solution of hemiketal **14** (83 mg, 0.129 mmol) in dry CH_2Cl_2 (0.5 mL) in an ice–brine bath (–10 °C) under an atmosphere of argon. After 5 min, $BF_3{\cdot}Et_2O$ (18 μL, 0.148 mol, 1.2 equiv.) was added over 1 min by syringe, and the solution was stirred for an additional 5 min. The mixture was then quenched with saturated $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic layer was washed with saturated NH_4Cl solution, dried with $MgSO_4$, and concentrated under reduced pressure. The crude product was chromatographed on silica gel (gradient hexane/toluene, 2:1 to toluene) to give **16** (67 mg, 73%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.108, 0.113, 0.15 and 0.16 (4 s, 4×3 H, CH_3Si), 0.92 and 0.95 [2 s, 2×9 H, $(CH_3)_3C$], 2.76 (d, $J_{OH,2'}$ = 8.7 Hz, 1 H, OH-2′), 3.78 (dd, J_{gem} = 11.1 Hz, $J_{5'b,4'}$ = 3.1 Hz, 1 H, 5′b-H), 3.82 (dd, J_{gem} = 11.1 Hz, $J_{5'a,4'}$ = 3.8 Hz, 1 H, 5′a-H), 3.83 (ddd, $J_{OH,2'}$ = 8.7 Hz, $J_{2',1'}$ = 7.0 Hz, $J_{2',3'}$ = 5.5 Hz, 1 H, 2′-H), 4.00 (ddd, $J_{4',5'}$ = 3.8, 3.1 Hz, $J_{4',3'}$ = 3.0 Hz, 1 H, 4′-H), 4.28 (dd, $J_{3',2'}$ = 5.5 Hz, $J_{3',4'}$ = 3.0 Hz, 1 H, 3′-H), 4.63 (d, $J_{1',2'}$ = 7.0 Hz, 1 H, 1′-H), 7.20 (t, $J_{5,4}$ = $J_{5,6}$ = 7.8 Hz, 1 H, 5-H), 7.37 (dddd, $J_{6,5}$ = 7.8 Hz, $J_{6,2}$ = 1.6 Hz, $J_{6,4}$ = 1.0 Hz, $J_{6,1'}$ = 0.6 Hz, 1 H, 6-H), 7.40 (ddd, $J_{4,5}$ = 7.8 Hz, $J_{4,2}$ = 2.0 Hz, $J_{4,6}$ = 1.0 Hz, 1 H, 4-H), 7.61 (dd, $J_{2,4}$ = 2.0 Hz, $J_{2,6}$ = 1.6 Hz, 1 H, 2-H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = –5.53, –5.37, –4.89 and –4.42 (CH_3Si), 18.05 and 18.36 [$C(CH_3)_3$], 25.76 and 25.94 [$C(CH_3)_3$], 62.90 (CH_2-5′), 72.98 (CH-3′), 77.75 (CH-2′), 83.61 (CH-1′), 85.17 (CH-4′), 122.53 (C-3), 124.72 (CH-6), 128.85 (CH-2), 129.79 (CH-5), 130.67 (CH-4), 142.82 (C-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 3541, 2956, 2930, 2898, 2858, 1729, 1598, 1570, 1472, 1463, 1389, 1258, 1115, 1090, 1057, 1024, 822 cm^{-1}. HRMS (FAB): calcd. for $C_{23}H_{42}O_4Si_2Br$ [M + H] 517.1805; found 517.1799.

1β-(3-Methylphenyl)-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (18a): Compound 1**8a** was prepared according to the procedure outlined for **9a** starting from **15** (560 mg, 0.887 mmol). C-nucleoside **18a** was prepared in 95% yield as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = –0.48, –0.14, 0.09, 0.10, 0.12 and 0.13 (6 s, 6×3 H, CH_3Si), 0.79, 0.94 and 0.95 [3 s, 3×9 H, $(CH_3)_3C$], 2.32 (s, 3 H, CH_3), 3.78 (dd, J_{gem} = 10.9, $J_{5'b,4'}$ = 3.1 Hz, 1 H, 5′b-H), 3.80 (dd, J_{gem} = 10.9 Hz, $J_{5'a,4'}$ = 3.9 Hz, 1 H, 5′a-H), 3.83 (dd, $J_{2',1'}$ = 7.9 Hz, $J_{2',3'}$ = 4.7 Hz, 1 H, 2′-H), 4.02 (ddd, $J_{4',5'}$ = 3.9, 3.1 Hz, $J_{4',3'}$ = 1.7 Hz, 1 H, 4′-H), 4.12 (dd, $J_{3',2'}$ = 4.7 Hz, $J_{3',4'}$ = 1.7 Hz, 1 H, 3′-H), 4.73 (d, $J_{1',2'}$ = 7.9 Hz, 1 H, 1′-H), 7.06 (ddd, $J_{4,5}$ = 7.4 Hz, $J_{4,2}$ = 1.7 Hz, $J_{4,6}$ = 0.8 Hz, 1 H, 4-H), 7.18 (dd, $J_{5,6}$ = 8.1 Hz, $J_{5,4}$ = 7.4 Hz, 1 H, 5-H), 7.20 –7.22 (m, 2 H, 2-H and 6-H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = –5.59, –5.53, –5.42, –4.53, –4.47 and –4.42 (CH_3Si), 17.94, 18.08 and 18.35 [$C(CH_3)_3$], 21.33 (CH_3), 25.82, 25.90 and 25.99 [$C(CH_3)_3$], 63.78 (CH_2-5′), 74.03 (CH-3′), 79.50 (CH-2′), 82.73 (CH-1′), 86.05 (CH-4′), 124.02 (CH-6), 127.50 (CH-2), 127.86 (CH-5), 128.33 (CH-4), 137.40 (C-3), 140.38 (C-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 3107, 3029, 2897, 1661, 1596, 1490, 1472, 1463, 1406, 1389, 1377, 1362, 1281, 1254, 1166, 1094, 1082, 939, 837 cm^{-1}. HRMS (FAB): calcd. for $C_{30}H_{58}O_4Si_3Na$ [M + Na] 589.3541; found 589.3548.

1β-(3-Ethylphenyl)-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (18b): Compound **18b** was prepared according to the procedure outlined for **9b** starting from **15** (584 mg, 0.924 mmol). Corresponding C-nucleoside **18b** was prepared in 73% yield (394 mg) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = –0.48, –0.15, 0.09, 0.10, 0.12 and 0.13 (6 s, 6×3 H, CH_3Si), 0.78, 0.94 and 0.95 [3 s, 3×9 H, $(CH_3)_3C$], 1.21 (t, J_{vic} = 7.6 Hz, 3 H, CH_3CH_2), 2.62 (q, J_{vic} = 7.6 Hz, 2 H, CH_2CH_3), 3.78 (dd, J_{gem} = 10.9 Hz, $J_{5'b,4'}$ = 3.2 Hz, 1 H, 5′b-H), 3.80 (dd, J_{gem} = 10.9 Hz, $J_{5'a,4'}$ = 3.9 Hz, 1 H, 5′a-H), 3.85 (dd, $J_{2',1'}$ = 8.0 Hz, $J_{2',3'}$ = 4.5 Hz, 1 H, 2′-H), 4.02 (ddd, $J_{4',5'}$ = 3.9, 3.2 Hz, $J_{4',3'}$ = 1.7 Hz, 1 H, 4′-H), 4.12 (dd, $J_{3',2'}$ = 4.5 Hz, $J_{3',4'}$ = 1.7 Hz, 1 H, 3′-H), 4.73 (d, $J_{1',2'}$ = 8.0 Hz, 1 H, 1′-H), 7.09 (dt, $J_{4,5}$ = 7.4 Hz, $J_{4,2}$ = $J_{4,6}$ = 1.7 Hz, 1 H, 4-H), 7.19 –7.25 (m, 3 H, 2-H, 5-H and 6-H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = –5.56, –5.52, –5.42, –4.56, –4.47 and –4.41 (CH_3Si), 15.78 (CH_3CH_2), 17.95, 18.09 and 18.36 [$C(CH_3)_3$], 25.85, 25.90 and 25.99 [$C(CH_3)_3$], 28.88 (CH_2CH_3), 63.81 (CH_2-5′), 74.03 (CH-3′), 79.53 (CH-2′), 82.83 (CH-1′), 86.09 (CH-4′), 124.39 (CH-6), 126.56 (CH-2), 127.19 (CH-4), 127.96 (CH-5), 140.35 (C-1), 143.90 (C-3) ppm. IR (CCl_4): $\tilde{\nu}$ = 3105, 3062, 3031, 2896, 1610, 1592, 1487, 1472, 1463, 1406, 1389, 1374, 1362, 1256, 1098, 1083, 972, 940, 837 cm^{-1}. HRMS (FAB): calcd. for $C_{31}H_{60}O_4Si_3Na$ [M + Na] 603.3697; found 603.3686.

1β-(3-Benzylphenyl)-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose) (18c): Compound **18c** was prepared according to the procedure outlined for **9c** starting from **15** (652 mg, 1.03 mmol). Corresponding C-nucleoside **18c** was prepared in 67% yield as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = –0.50, –0.16, 0.085, 0.087, 0.10 and 0.11 (6 s, 6×3 H, CH_3Si), 0.77, 0.929 and 0.931 [3 s, 3×9 H, $(CH_3)_3C$], 3.76 (d, $J_{5',4'}$ = 3.6 Hz, 2 H, 5′-H), 3.84 (dd, $J_{2',1'}$ = 8.0 Hz, $J_{2',3'}$ = 4.5 Hz, 1 H, 2′-H), 3.96 (s, 2 H, CH_2Ph), 4.01 (td, $J_{4',5'}$ = 3.6 Hz, $J_{4',3'}$ = 1.7 Hz, 1 H, 4′-H), 4.11 (dd, $J_{3',2'}$ = 4.5 Hz, $J_{3',4'}$ = 1.7 Hz, 1 H, 3′-H), 4.73 (d, $J_{1',2'}$ = 8.0 Hz, 1 H, 1′-H), 7.05 (ddd, $J_{4,5}$ = 7.6 Hz, $J_{4,2}$ = 1.7 Hz, $J_{4,6}$ = 1.3 Hz, 1 H, 4-H), 7.16 (m, 2 H, *o*-Ph-H), 7.18 (m, 1 H, *p*-Ph-H), 7.21 (t, $J_{5,4}$ = $J_{5,3}$ = 7.6 Hz, 1 H, 5-H), 7.23–7.29 (m, 4 H, 2-H, 6-H and *m*-Ph-H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = –5.53, –5.47, –5.42, –4.55, –4.47 and –4.42 (CH_3Si), 17.92, 18.08 and 18.35 [$C(CH_3)_3$], 25.83, 25.89 and 25.98 [$C(CH_3)_3$], 41.84 (CH_2Ph), 63.79 (CH_2-5′), 74.02 (CH-3′), 79.49 (CH-2′), 82.76 (CH-1′), 86.08 (CH-4′), 124.90 (CH-6), 125.93 (CH-*p*-Ph), 127.61 (CH-2), 128.14 (CH-5), 128.33 (CH-*m*-Ph), 128.42 (CH-4), 128.94 (CH-*o*-Ph), 140.63 and 140.67 (C-1 and C-3), 141.16 (C-*i*-Ph) ppm. IR (CCl_4): $\tilde{\nu}$ = 2897, 1612, 1603, 1593, 1593, 1495, 1488, 1472, 1463, 1455, 1406, 1389, 1362, 1257, 1187, 1092, 1081, 1006, 939, 837 cm^{-1}. HRMS (FAB): calcd. for $C_{36}H_{62}O_4Si_3Na$ [M + Na] 665.3854; found 665.3845.

1β-[3-(2-Thienyl)phenyl]-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (18d): Compound **18d** was prepared according to procedure outlined for **9d** starting from **15** (503 mg, 0.796 mmol). The reaction was carried out at 100 °C for 30 min, which resulted in the formation of nucleoside **18d** in 73% yield as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = –0.45, –0.13, 0.01, 0.11, 0.12 and 0.13 (6 s, 6×3 H, CH_3Si), 0.79, 0.94 and 0.95 [3 s, 3×9 H, $(CH_3)_3C$], 3.80 (dd, J_{gem} = 10.9 Hz, $J_{5'b,4'}$ = 3.4 Hz, 1 H, 5′b-H), 3.82 (dd, J_{gem} = 10.9 Hz, $J_{5'a,4'}$ = 3.8 Hz, 1 H, 5′a-H), 3.88 (dd, $J_{2',1'}$ = 8.0 Hz, $J_{2',3'}$ = 4.5 Hz, 1 H, 2′-H), 4.05 (ddd, $J_{4',5'}$ = 3.8, 3.4 Hz, $J_{4',3'}$ = 1.6 Hz, 1 H, 4′-H), 4.14 (ddd, $J_{3',2'}$ = 4.5 Hz, $J_{3',4'}$ = 1.6 Hz, $J_{3',1'}$ = 0.5 Hz, 1 H, 3′-H), 4.80 (d, $J_{1',2'}$ = 8.0 Hz, 1 H, 1′-H), 7.02 (dd, $J_{4,5}$ = 5.1 Hz, $J_{4,3}$ = 3.6 Hz, 1 H, 4-thienyl-H), 7.26 (dd, $J_{5,4}$ = 5.1 Hz, $J_{5,3}$ = 1.1 Hz, 1 H, 5-thienyl-H), 7.30 (dd, $J_{3,4}$ = 3.6 Hz, $J_{3,5}$ = 1.1 Hz, 1 H, 3-thienyl-H), 7.32 (t, $J_{5,4}$ = $J_{5,6}$ = 7.6 Hz, 1 H, 5-H), 7.14 (dddd, $J_{6,5}$ = 7.6 Hz, $J_{6,2}$ = 1.7 Hz, $J_{6,4}$ = 1.1 Hz, $J_{6,1'}$ = 0.5 Hz, 1 H, 6-H), 6.90 (ddd, $J_{4,5}$ = 7.6 Hz, $J_{4,2}$ = 1.9 Hz, $J_{4,6}$ = 1.1 Hz, 1 H, 4-H), 7.59 (ddt, $J_{2,4}$ = 1.9 Hz, $J_{2,6}$ = 1.7 Hz, $J_{2,5}$ = $J_{2,1'}$ = 0.5 Hz, 1 H, 2-H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = –5.50, –5.48, –5.39, –4.54, –4.46 and –4.40 (CH_3Si), 17.93, 18.10 and 18.37 [$C(CH_3)_3$], 25.84, 25.91 and 25.99 [$C(CH_3)_3$], 63.81 (CH_2-5′), 74.05 (CH-3′), 79.53 (CH-2′), 82.53 (CH-1′), 86.29 (CH-4′), 123.01 (CH-3-thienyl), 124.58 (CH-5-thienyl), 124.62 (CH-2), 125.36 (CH-4), 125.93 (CH-6), 127.83 (CH-4-thienyl), 128.64 (CH-5), 134.02 (C-3), 141.28 (C-1), 144.54 (C-2-thienyl) ppm. IR (CCl_4): $\tilde{\nu}$ = 2956, 2930, 2887, 2858, 1607, 1472, 1463, 1389, 1362, 1256, 1219, 1152, 1113, 1081, 1005, 966, 940, 873 cm^{-1}. HRMS (FAB): calcd. for $C_{33}H_{59}O_4SSi_3$ [M + H] 635.3442; found 635.3447.

1β-[3-(Pyridin-2-yl)phenyl]-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (18e): Compound **18e** was prepared according to the procedure outlined for **9e** starting from **15** (537 mg, 0.850 mmol). The reaction was carried out at 100 °C for 17 h, which resulted in the formation of nucleoside **18e** in 46% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.47, –0.14, 0.105, 0.107, 0.12 and 0.13 (6 s, 6×3 H, CH_3Si), 0.77, 0.93 and 0.95 [3 s, 3×9 H, $(CH_3)_3C$], 3.81 (dd, J_{gem} = 10.9 Hz, $J_{5'b,4'}$ = 3.2 Hz, 1 H, 5′b-H), 3.84 (dd, J_{gem} = 10.9 Hz, $J_{5'a,4'}$ = 3.9 Hz, 1 H, 5′a-H), 3.90 (dd, $J_{2',1'}$ = 8.1 Hz, $J_{2',3'}$ = 4.4 Hz, 1 H, 2′-H), 4.06 (ddd, $J_{4',5'}$ = 3.9, 3.2 Hz, $J_{4',3'}$ = 1.6 Hz, 1 H, 4′-H), 4.15 (dd, $J_{3',2'}$ = 4.4 Hz, $J_{3',4'}$ = 1.6 Hz, 1 H, 3′-H), 4.87 (d, $J_{1',2'}$ = 8.1 Hz, 1 H, 1′-H), 7.21 (m, 1 H, 5-py-H), 7.43 (m, 1 H, 5-H), 7.14 (ddd, $J_{6,5}$ = 7.6 Hz, $J_{6,4}$ = 1.3 Hz, $J_{6,2}$ = 1.2 Hz, 1 H, 6-H), 7.70–7.74 (m, 2 H, 3,4-py-H), 7.95 (ddd, $J_{4,5}$ = 6.4 Hz, $J_{4,2}$ = 1.8 Hz, $J_{4,6}$ = 1.3 Hz, 1 H, 4-H), 7.96 (dd, $J_{2,4}$ = 1.8 Hz, $J_{2,6}$ = 1.2 Hz, 1 H, 2-H), 8.68 (dt, $J_{6,5}$ = 4.7 Hz, $J_{6,4}$ = $J_{6,3}$ = 1.5 Hz, 1 H, 6-py-H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.51, –5.46, –5.43, –4.52, –4.47 and –4.36 (CH_3Si), 17.92, 18.09 and 18.37 [$C(CH_3)_3$], 25.82, 25.91 and 25.99 [$C(CH_3)_3$], 63.86 (CH_2-5′), 74.11 (CH-3′), 79.59 (CH-2′), 82.61 (CH-1′), 86.30 (CH-4′), 120.48 (CH-3-py), 121.94 (CH-5-py), 125.52 (CH-2), 126.37 (CH-4), 127.39 (CH-6), 128.58 (CH-5), 136.54 (CH-4-py), 139.06 (C-3), 141.03 (C-1), 149.57 (CH-6-py), 157.47 (C-2-py) ppm. IR (CCl_4): $\tilde{\nu}$ = 2897, 1607, 1587, 1587, 1567, 1494, 1472, 1463, 1437, 1407, 1390, 1362, 1288, 1257, 1080, 1050, 994, 940, 837 cm^{-1}. HRMS (FAB): calcd. for $C_{34}H_{60}NO_4Si_3$ [M + H] 630.3830; found 630.3810.

1β-[3-(4-Fluorophenyl)phenyl]-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (18f): Compound **18f** was prepared according to the procedure outlined for **9f** starting from **15** (520 mg, 0.822 mmol). The reaction was carried out at 100 °C for 30 min, which resulted in the formation of nucleoside **18f** in 69% yield as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = –0.48, –0.14, 0.100, 0.102, 0.103 and 0.106 (6 s, 6×3 H, CH_3Si), 0.77, 0.91 and 0.95 [3 s, 3×9 H, $(CH_3)_3C$], 3.79 (dd, J_{gem} = 10.9 Hz, $J_{5'b,4'}$ = 3.0 Hz, 1 H, 5′b-H), 3.82 (dd, J_{gem} = 10.9 Hz, $J_{5'a,4'}$ = 3.8 Hz, 1 H, 5′a-H), 3.89 (dd, $J_{2',1'}$ = 8.2 Hz $J_{2',3'}$ = 4.5 Hz, 1 H, 2′-H), 4.05 (ddd, $J_{4',5'}$ = 3.8 Hz, 3.0, $J_{4',3'}$ = 1.6 Hz, 1 H, 4′-H), 4.14 (ddd, $J_{3',2'}$ = 4.5 Hz, $J_{3',4'}$ = 1.6 Hz, $J_{3',1'}$ = 0.5 Hz, 1 H, 3′-H), 4.82 (d, $J_{1',2'}$ = 8.2 Hz, 1 H, 1′-H), 7.10 (m, 2 H, *m*-C_6H_4F-H), 7.36 (t, $J_{5,4}$ = $J_{5,6}$ = 7.6 Hz, 1 H, 5-H), 7.41–7.44 (m, 2 H, 4,6-H), 7.53 (m, 2 H, *o*-C_6H_4F-H), 7.56 (tt, $J_{2,4}$ = $J_{2,6}$ = 1.8 Hz $J_{2,5}$ = $J_{2,1'}$ = 0.5 Hz 1 H, 2-H) ppm.^{13}C NMR (151 MHz, $CDCl_3$): δ = –5.53, –5.52, –5.45, –4.52, –4.47 and –4.38 (CH_3Si), 17.93, 18.09 and 18.34 [$C(CH_3)_3$], 25.80, 25.90 and 25.96 [$(CH_3)_3C$], 63.82 (CH_2-5′), 74.08 (CH-3′, 79.65 (CH-2′, 82.64 (CH-1′), 86.36 (CH-4′), 115.42 (d, $J_{C,F}$ = 21 Hz, CH-*m*-C_6H_4F), 125.68 (CH-2), 125.97 (CH-6), 126.42 (CH-4), 128.50 (CH-5), 128.68 (d, $J_{C,F}$ = 8 Hz, CH-*o*-C_6H_4F), 137.47 (d, $J_{C,F}$ = 3 Hz, C-*i*-C_6H_4F), 139.99 (C-3), 141.11 (C-1), 162.35 (d, $J_{C,F}$ = 246 Hz C-*p*-C_6H_4F) ppm. IR (CCl_4): $\tilde{\nu}$ = 2956, 2930, 2897, 2858, 1610, 1515, 1472, 1389, 1362, 1256, 1236, 1157, 1112, 1006, 966, 875, 838 cm^{-1}. HRMS (FAB): calcd. for $C_{35}H_{60}FO_4Si_3$ [M + H] 647.3783; found 647.3778.

1β-[3-(4-Methoxyphenyl)phenyl]-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (18g): Compound **18g** was prepared according to the procedure outlined for **9g** starting from **15** (119 mg, 0.188 mmol). The reaction was carried out at 95 °C for 2 h, which resulted in the formation of nucleoside **18g** in 81% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.45, –0.14, 0.103, 0.105 and 0.109 (5 s, 18 H, CH_3Si), 0.78, 0.93 and 0.95 [3 s, 3×9 H, $(CH_3)_3C$], 3.79 (dd, J_{gem} = 10.9 Hz, $J_{5'b,4'}$ = 3.3 Hz, 1 H, 5′b-H), 3.82 (dd, J_{gem} = 10.9 Hz, $J_{5'a,4'}$ = 3.8 Hz, 1 H, 5′a-H), 3.85 (s, 3 H, CH_3O), 3.90 (dd, $J_{2',1'}$ = 8.0 Hz, $J_{2',3'}$ = 4.5 Hz, 1 H, 2′-H), 4.05 (ddd, $J_{4',5'}$ = 3.8, 3.3 Hz, $J_{4',3'}$ = 1.7 Hz, 1 H, 4′-H), 4.15 (dd, $J_{3',2'}$ = 4.5 Hz, $J_{3',4'}$ = 1.7 Hz, 1 H, 3′-H), 4.81 (d, $J_{1',2'}$ = 8.0 Hz, 1 H, 1′-H), 6.95 (m, 2 H, *m*-C_6H_4OMe-H), 7.35 (dd, $J_{5,6}$ = 7.8 Hz, $J_{5,4}$ = 7.5 Hz, 1 H, 5-H), 7.39 (dt, $J_{6,5}$ = 7.8 Hz, $J_{6,2}$ = $J_{6,4}$ = 1.7 Hz, 1 H, 6-H), 7.44 (dt, $J_{4,5}$ = 7.5 Hz, $J_{4,2}$ = $J_{4,6}$ = 1.7 Hz, 1 H, 4-H), 7.52 (m, 2 H, *o*-C_6H_4OMe-H), 7.59 (t, $J_{2,4}$ = $J_{2,6}$ = 1.7 Hz, 1 H, 2-H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.45, –5.41, –4.54, –4.45 and –4.39 (CH_3Si), 17.95, 18.09 and 18.37 [$C(CH_3)_3$], 25.83, 25.91 and 25.99 [$C(CH_3)_3$], 55.34 (CH_3O), 63.84 (CH_2-5′), 74.03 (CH-3′), 79.62 (CH-2′), 82.84 (CH-1′), 86.18 (CH-4′), 114.03 (CH-*m*-C_6H_4OMe), 125.36 (CH-6), 125.41 (CH-2), 126.14 (CH-4),

128.13 (CH-*o*-C_6H_4OMe), 128.42 (CH-5), 133.91 (C-*i*-C_6H_4OMe), 140.50 (C-3), 140.92 (C-1), 158.99 (C-*p*-C_6H_4OMe) ppm. IR (CCl_4): $\tilde{\nu}$ = 2897, 2838, 1611, 1611, 1591, 1576, 1517, 1482, 1472, 1441, 1407, 1389, 1299, 1262, 1249, 1179, 1092, 1081, 1044, 940, 836 cm^{-1}. HRMS (FAB): calcd. for $C_{36}H_{63}O_5Si_3$ [M + H] 659.3983; found 659.3969.

1β-(3-Aminophenyl)-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (18h): Compound **18h** was prepared according to the procedure outlined for **9h** starting from **15** (686 mg, 1.086 mmol). Corresponding C-nucleoside **18h** was prepared in 73% yield as a yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ = –0.38, –0.12, 0.09, 0.11 and 0.13 (5 s, 18 H, CH_3Si), 0.82, 0.93 and 0.94 [3 s, 3×9 H, $(CH_3)_3C$], 3.58 (br. s, 2 H, NH_2), 3.78 (d, $J_{5',4'}$ = 3.7 Hz, 2 H, 5′-H), 3.82 (dd, $J_{2',1'}$ = 7.7 Hz, $J_{2',3'}$ = 4.4 Hz, 1 H, 2′-H), 4.01 (td, $J_{4',5'}$ = 3.7 Hz, $J_{4',3'}$ = 2.0 Hz, 1 H, 4′-H), 4.11 (dd, $J_{3',2'}$ = 4.4 Hz, $J_{3',4'}$ = 2.0 Hz, 1 H, 3′-H), 4.68 (d, $J_{1',2'}$ = 7.7 Hz, 1 H, 1′-H), 6.58 (ddd, $J_{4,5}$ = 7.9 Hz, $J_{4,2}$ = 2.5 Hz, $J_{4,6}$ = 1.1 Hz, 1 H, 4-H), 6.74 (dd, $J_{2,4}$ = 2.5 Hz, $J_{2,6}$ = 1.7 Hz, 1 H, 2-H), 6.82 (ddd, $J_{6,5}$ = 7.6 Hz, $J_{6,2}$ = 1.7 Hz, $J_{6,4}$ = 1.1 Hz, 1 H, 6-H), 7.07 (dd, $J_{5,4}$ = 7.9 Hz, $J_{5,6}$ = 7.6 Hz, 1 H, 5-H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.48, –5.40, –5.38, –4.53, –4.45 and –4.43 (CH_3Si), 17.99, 18.08 and 18.38 [$C(CH_3)_3$], 25.87, 25.90 and 25.99 [$C(CH_3)_3$], 63.76 (CH_2-5′), 73.90 (CH-3′), 79.37 (CH-2′), 82.86 (CH-1′), 85.74 (CH-4′), 113.49 (CH-2), 114.47 (CH-4), 117.40 (CH-6), 128.89 (CH-5), 141.80 (C-1), 146.09 (C-3) ppm. IR (CCl_4): $\tilde{\nu}$ = 2897, 2804, 1606, 1583, 1500, 1472, 1463, 1440, 1406, 1389, 1361, 1332, 1313, 1289, 1258, 1114, 1081, 997, 940, 837 cm^{-1}. HRMS (FAB): calcd. for $C_{29}H_{58}NO_4Si_3$ [M + H] 568.3674; found 568.3683.

1β-[3-(Dimethylamino)phenyl]-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (18i): Compound **18i** was prepared according to the procedure outlined for **9i** starting from **15** (580 mg, 0.918 mmol). Corresponding C-nucleoside **18i** was prepared in 77% yield as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$): δ = –0.38, –0.12, 0.09, 0.11 and 0.12 (5 s, 18 H, CH_3Si), 0.81, 0.937 and 0.938 [3 s, 3×9 H, $(CH_3)_3C$], 2.93 (s, 6 H, CH_3N), 3.79 (d, $J_{5',4'}$ = 3.8 Hz, 2 H, 5′-H), 3.87 (dd, $J_{2',1'}$ = 7.5 Hz, $J_{2',3'}$ = 4.5 Hz, 1 H, 2′-H), 4.02 (td, $J_{4',5'}$ = 3.8 Hz, $J_{4',3'}$ = 2.2 Hz, 1 H, 4′-H), 4.12 (dd, $J_{3',2'}$ = 4.5 Hz, $J_{3',4'}$ = 2.2 Hz, 1 H, 3′-H), 4.72 (d, $J_{1',2'}$ = 7.5 Hz, 1 H, 1′-H), 6.66 (br. s, 1 H, 4-H), 6.74 (br. s, 1 H, 2-H), 6.85 (br. s, 1 H, 6-H), 7.17 (br. t, $J_{5,4}$ = $J_{5,6}$ = 8.0 Hz, 1 H, 5-H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –5.47, –5.39, –5.32, –4.56, –4.44 and –4.42 (CH_3Si), 17.99, 18.10 and 18.41 [$SiC(CH_3)_3$], 25.90, 25.93 and 26.02 [$C(CH_3)_3$], 40.84 (CH_3N), 63.82 (CH_2-5′), 73.80 (CH-3′), 79.41 (CH-2′), 83.56 (CH-1′), 85.62 (CH-4′), 111.78 (CH-2), 112.33 (CH-4), 115.46 (CH-6), 128.74 (CH-5), 141.26 (C-1), 150.58 (C-3) ppm. IR (CCl_4): $\tilde{\nu}$ = 2897, 2804, 1606, 1583, 1500, 1472, 1463, 1440, 1406, 1389, 1361, 1332, 1313, 1289, 1258, 1114, 1081, 997, 940, 837 cm^{-1}. HRMS (FAB): calcd. for $C_{31}H_{62}NO_4Si_3$ [M + H] 596.3987; found 596.3971.

1β-(3-*tert*-Butoxyphenyl)-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (18j): Compound **18j** was prepared according to the procedure outlined for **9j** starting from **15** (541 mg, 0.856 mmol). The reaction was carried out at 50 °C for 8 h, which resulted in the formation of nucleoside **18j** in 68% yield as a colorless oil. ^1H NMR (600 MHz, $CDCl_3$): δ = –0.42, –0.14, 0.09, 0.11 and 0.13 (5 s, 18 H, CH_3Si), 0.81, 0.935 and 0.943 [3 s, 3×9 H, $(CH_3)_3CSi$], 1.33 [s, 9 H, $(CH_3)_3CO$], 3.77 (dd, J_{gem} = 10.8 Hz, $J_{5'b,4'}$ = 4.1 Hz, 1 H, 5′b-H), 3.79 (dd, J_{gem} = 10.8 Hz, $J_{5'a,4'}$ = 3.4 Hz, 1 H, 5′a-H), 3.84 (dd, $J_{2',1'}$ = 7.8 Hz, $J_{2',3'}$ = 4.4 Hz, 1 H, 2′-H), 4.02 (ddd, $J_{4',5'}$ = 4.1, 3.4 Hz, $J_{4',3'}$ = 1.9 Hz, 1 H, 4′-H), 4.12 (dd, $J_{3',2'}$ = 4.4 Hz, $J_{3',4'}$ = 1.9 Hz, 1 H, 3′-H), 4.73 (d, $J_{1',2'}$ = 7.7 Hz, 1 H, 1′-H), 6.90 (ddd, $J_{4,5}$ = 7.9 Hz, $J_{4,2}$ = 2.5 Hz, $J_{4,6}$ = 1.2 Hz, 1 H, 4-H), 7.03 (dd, $J_{2,4}$ = 2.5 Hz, $J_{2,6}$ = 1.7 Hz, 1 H, 2-H), 7.14 (ddd, $J_{6,5}$ = 7.7 Hz, $J_{6,2}$ = 1.7 Hz, $J_{6,4}$ = 1.2 Hz, 1 H, 6-H), 7.19 (dd, $J_{5,4}$ = 7.9 Hz, $J_{5,6}$ = 7.7 Hz, 1 H, 5-H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = –5.50, –5.40, –5.32, –4.57, –4.47 and –4.43 (CH_3Si), 17.95, 18.08 and 18.40 [$SiC(CH_3)_3$], 25.87, 25.89 and 26.02 [$(CH_3)_3CSi$], 28.90 [$(CH_3)_3CO$], 63.81 (CH_2-5′), 73.89 (CH-3′), 78.24 [$OC(CH_3)_3$], 79.46 (CH-2′), 82.66 (CH-1′), 85.88 (CH-4′), 122.20 (CH-6), 122.59 (CH-2), 123.37 (CH-4), 128.33 (CH-5), 141.60 (C-1), 155.28 (C-3) ppm. IR (CCl_4): $\tilde{\nu}$ = 3102, 3069, 3032, 2980, 2897, 1604, 1587, 1485, 1472, 1463, 1440, 1406, 1390, 1364, 1308, 1257, 1180, 1163, 939 cm^{-1}. HRMS (FAB): calcd. for $C_{33}H_{65}O_5Si_3$ [M + H] 625.4140; found 625.4128.

General Procedure for the Deprotection of the TBDMS-Protecting Group: $Et_3N{\cdot}3HF$ (163 μL, 1.00 mmol, 10 equiv.) was added to the solution of compounds **6**, **9a**–**j**, **15**, or **18a**–**j** (0.10 mmol) in THF (1.00 mL), and the resulting mixture was stirred at 40 °C for 2 d. After the reaction was complete (TLC in $CHCl_3$/MeOH, 8:1), the solvents were removed under reduced pressure, and the crude product was dissolved in water/MeOH (8:2). Solid $NaHCO_3$ was added until basic pH was obtained. The solvents were then evaporated under reduced pressure, and the crude product was dissolved in MeOH, adsorbed on silica gel, and chromatographed on silica gel ($CHCl_3$/MeOH, 10:1) to obtain free C-ribonucleosides **8**, **10a**–**j**, **17**, or **19a**–**j**.

1β-(4-Bromophenyl)-1-deoxy-D-ribofuranose (8): Compound **8** was prepared from **6** according to the general procedure in 85% yield. Crystallization from $CHCl_3$ yielded white needles. M.p. 97 –98 °C. $[\alpha]_D^{20}$ = –12.0 (*c* = 3.10, MeOH). ^1H NMR (600 MHz, [D$_6$]DMSO): δ = 3.52 (ddd, J_{gem} = 11.7 Hz, $J_{5'b,OH}$ = 5.5 Hz, $J_{5'b,4'}$ = 4.5 Hz, 1 H, 5′b-H), 3.55 (ddd, J_{gem} = 11.7 Hz, $J_{5'a,OH}$ = 5.6 Hz, $J_{5'a,4'}$ = 4.4 Hz, 1 H, 5′a-H), 3.63 (ddd, $J_{2',1'}$ = 7.3 Hz, $J_{2',OH}$ = 7.1 Hz, $J_{2',3'}$ = 5.3 Hz, 1 H, 2′-H), 3.82 (ddd, $J_{4',5'}$ = 4.5, 4.4 Hz, $J_{4',3'}$ = 3.4 Hz, 1 H, 4′-H), 3.88 (ddd, $J_{3',2'}$ = 5.3 Hz, $J_{3',OH}$ = 4.8 Hz, $J_{3',4'}$ = 3.4 Hz, 1 H, 3′-H), 4.53 (d, $J_{1',2'}$ = 7.3 Hz, 1 H, 1′-H), 4.84 (dd, $J_{OH,5'}$ = 5.6, 5.5 Hz, 1 H, OH-5′), 4.95 (d, $J_{OH,3'}$ = 4.8 Hz, 1 H, OH-3′), 5.02 (d, $J_{OH,2'}$ = 7.1 Hz, 1 H, OH-2′), 7.35 (m, 2 H, 2,6-H), 7.52 (m, 2 H, 3,5-H) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 62.18 (CH_2-5′), 71.64 (CH-3′), 77.95 (CH-2′), 82.34 (CH-1′), 85.53 (CH-4′), 120.45 (C-4), 128.57 (CH-2,6), 131.09 (CH-3,5), 141.17 (C-1) ppm. IR (KBr): $\tilde{\nu}$ = 3569, 3408, 3271, 3064, 1593, 1575, 1489, 1400, 1299, 1208, 1189, 1105, 1072, 1059, 1041, 1031, 967, 938 cm^{-1}. $C_{11}H_{13}BrO_4$ (289.1): calcd. C 45.70, H 4.53; found C 45.50, H 4.52. HRMS (FAB): calcd. for $C_{11}H_{13}O_4BrNa$ [M + Na] 310.9895; found 310.9908.

1β-(4-Methylphenyl)-1-deoxy-D-ribofuranose (10a): Compound **10a** was prepared from **9a** according to the general procedure in 95% yield. The crude product was crystallized from $CHCl_3$ to obtain white needles. M.p. 102–103 °C. $[\alpha]_D^{20}$ = –34.5 (*c* = 1.19, MeOH). ^1H NMR (600 MHz, [D$_6$]DMSO): δ = 2.28 (s, 3 H, CH_3), 3.51 (ddd, J_{gem} = 11.6 Hz, $J_{5'b,OH}$ = 5.5 Hz, $J_{5'b,4'}$ = 4.8 Hz, 1 H, 5′b-H), 3.54 (ddd, J_{gem} = 11.6 Hz, $J_{5'a,OH}$ = 5.7 Hz, $J_{5'a,4'}$ = 4.5 Hz, 1 H, 5′a-H), 3.64 (ddd, $J_{2',1'}$ = 7.1 Hz, $J_{2',OH}$ = 6.9 Hz, $J_{2',3'}$ = 5.4 Hz, 1 H, 2′-H), 3.78 (ddd, $J_{4',5'}$ = 4.8, 4.5 Hz, $J_{4',3'}$ = 3.7 Hz, 1 H, 4′-H), 3.86 (dddd, $J_{3',2'}$ = 5.4 Hz, $J_{3',OH}$ = 4.9 Hz, $J_{3',4'}$ = 3.7 Hz, $J_{3',1'}$ = 0.4 Hz, 1 H, 3′-H), 4.50 (d, $J_{1',2'}$ = 7.1 Hz, 1 H, 1′-H), 4.80 (dd, $J_{OH,5'}$ = 5.7, 5.5 Hz, 1 H, OH-5′), 4.88 (d, $J_{OH,3'}$ = 4.9 Hz, 1 H, OH-3′), 4.92 (d, $J_{OH,2'}$ = 6.9 Hz, 1 H, OH-2′), 7.12 (m, 2 H, 3,5-H), 7.26 (m, 2 H, 2,6-H) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 20.97 (CH_3), 62.30 (CH_2-5′), 71.62 (CH-3′), 77.79 (CH-2′), 83.17 (CH-1′), 85.17 (CH-4′), 126.44 (CH-2,6), 128.74 (CH-3,5), 136.50 (C-4), 138.59 (C-1) ppm. IR (KBr): $\tilde{\nu}$ = 3392, 3054, 3026, 3013, 2920, 1618, 1515, 1415, 1376, 1304, 1224, 1210, 1180, 1113,

1072, 1039, 1019, 942 cm^{-1}. HRMS (FAB): calcd. for $C_{12}H_{17}O_4$ [M + H] 225.1127; found 225.1118.

1β-(4-Ethylphenyl)-1-deoxy-D-ribofuranose (10b): Compound **10b** was prepared from **9b** according to the general procedure in 85% yield. The crude product was crystallized from EtOAc/heptane to obtain white needles. M.p. 100–101 °C. $[a]_D^{20}$ = –31.4 (c =3.04, MeOH). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 1.16 (t, J_{vic} = 7.6 Hz, 3 H, CH_3CH_2), 2.57 (q, J_{vic} = 7.6 Hz, 2 H, CH_2CH_3), 3.51 (ddd, J_{gem} = 11.6 Hz, $J_{5'b,OH}$ = 5.4 Hz, $J_{5'b,4'}$ = 4.8 Hz, 1 H, 5′b-H), 3.54 (ddd, J_{gem} = 11.6 Hz, $J_{5'a,OH}$ = 5.6 Hz, $J_{5'a,4'}$ = 4.5 Hz, 1 H, 5′a-H), 3.66 (ddd, $J_{2',1'}$ = 7.1 Hz, $J_{2',OH}$ = 6.9 Hz, $J_{2',3'}$ = 5.4 Hz, 1 H, 2′-H), 3.78 (ddd, $J_{4',5'}$ = 4.8, 4.5 Hz, $J_{4',3'}$ = 3.6 Hz, 1 H, 4′-H), 3.86 (ddd, $J_{3',2'}$ = 5.4 Hz, $J_{3',OH}$ = 4.8 Hz, $J_{3',4'}$ = 3.6 Hz, 1 H, 3′-H), 4.51 (d, $J_{1',2'}$ = 7.1 Hz, 1 H, 1′-H), 4.82 (dd, $J_{OH,5'}$ = 5.6, 5.4 Hz, 1 H, OH-5′), 4.89 (d, $J_{OH,3'}$ = 4.8 Hz, 1 H, OH-3′), 4.94 (d, $J_{OH,2'}$ = 6.9 Hz, 1 H, OH-2′), 7.15 (m, 2 H, 3,5-H), 7.28 (m, 2 H, 2,6-H) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 16.06 (CH_3CH_2), 28.19 (CH_2CH_3), 62.37 (CH_2-5′), 71.72 (CH-3′), 77.80 (CH-2′), 83.20 (CH-1′), 85.23 (CH-4′), 126.58 (CH-2,6), 127.64 (CH-3,5), 138.87 (C-1), 143.03 (C-4) ppm. IR (KBr): $\tilde{\nu}$ = 3227, 3414, 3084, 3060, 3024, 1603, 1586, 1514, 1494, 1452, 1433, 1415, 1342, 1333, 1309, 1205, 1181, 1114, 1073, 1052, 1039, 1012, 967, 789, 640, 525, 457 cm^{-1}. HRMS (FAB): calcd. for $C_{13}H_{18}O_4Na$ [M + Na] 261.1103; found 261.1110.

1β-(4-Benzylphenyl)-1-deoxy-D-ribofuranose (10c): Compound **10c** was prepared from **9c** according to the general procedure in 84% yield. The crude product was crystallized from $CHCl_3$ to obtain white needles. M.p. 129–130 °C. $[a]_D^{20}$ = –16.25 (c =2.45, MeOH). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 3.50 (ddd, J_{gem} = 11.7 Hz, $J_{5'b,OH}$ = 5.6 Hz, $J_{5'b,4'}$ = 4.8 Hz, 1 H, 5′b-H), 3.53 (ddd, J_{gem} = 11.7 Hz, $J_{5'a,OH}$ = 5.6 Hz $J_{5'a,4'}$ = 4.5 Hz, 1 H, 5′a-H), 3.65 (ddd, $J_{2',1'}$ = 7.1 Hz $J_{2',OH}$ = 7.0 Hz, $J_{2',3'}$ = 5.5 Hz, 1 H, 2′-H), 3.78 (ddd, $J_{4',5'}$ = 4.8, 4.5 Hz, $J_{4',3'}$ = 3.6 Hz 1 H, 4′-H), 3.85 (ddd, $J_{3',2'}$ = 5.5 Hz, $J_{3',OH}$ = 4.8 Hz, $J_{3',4'}$ = 3.6 Hz, 1 H, 3′-H), 3.91 (CH_2Ph), 4.50 (d, $J_{1',2'}$ = 7.1 Hz, 1 H, 1′-H), 4.77 (t, $J_{OH,5'}$ = 5.6 Hz, 1 H, OH-5′), 4.85 (d, $J_{OH,3'}$ = 4.8 Hz, 1 H, OH-3′), 4.92 (d, $J_{OH,2'}$= 7.0 Hz, 1 H, OH-2′), 7.17 (m, 1 H, p-Ph-H), 7 .18 (m, 2 H, H-3,5), 7.22 (m, 2 H, o-Ph-H), 7.27 (m, 2 H, m-Ph-H), 7.29 (m, 2 H, 2,6-H) ppm.^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ = 2.27 (CH_2-5′), 71.65 (CH-3′), 77.66 (CH-2′), 83.03 (CH-1′), 85.20 (CH-4′), 126.11 (CH-p-Ph), 126.60 (CH-2,6), 128.49 (CH-3,5), 128.59 (CH-m-Ph), 128.84 (CH-o-Ph), 139.21 (C-1), 140.46 (C-4), 141.60 (C-i-Ph) ppm. IR (KBr): $\tilde{\nu}$ = 3414, 3084, 3060, 3024, 1627, 1603, 1586, 1514, 1494, 1452, 1433, 1415, 1342, 1333, 1309, 1205, 1205, 1181, 1181, 1114, 1073, 1052, 1039, 1012, 967, 900, 842 cm^{-1}. HRMS (FAB): calcd. for $C_{18}H_{20}O_4Na$ [M + Na] 323.1259; found 323.1258.

1β-[4-(2-Thienyl)phenyl]-1-deoxy-D-ribofuranose (10d): Compound **10d** was prepared from **9d** according to the general procedure in 95% yield. The crude product was crystallized from $CHCl_3$ to obtain **10d** as white needles. M.p. 147–149 °C. $[a]_D^{20}$ = –19.4 (c =1.95, MeOH).^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 3.54 (ddd, J_{gem} = 11.6 Hz, $J_{5'b,OH}$ = 5.5 Hz, $J_{5'b,4'}$ = 4.7 Hz, 1 H, 5′b-H), 3.57 (ddd, J_{gem} = 11.6 Hz, $J_{5'a,OH}$ = 5.7 Hz, $J_{5'a,4'}$ = 4.5 Hz, 1 H, 5′a-H), 3.69 (ddd, $J_{2',1'}$ = 7.1 Hz, $J_{2',OH}$ = 6.9 Hz, $J_{2',3'}$ = 5.2 Hz, 1 H, 2′-H), 3.82 (ddd, $J_{4',5'}$ = 4.7, 4.5 Hz, $J_{4',3'}$ = 3.6 Hz, 1 H, 4′-H), 3.90 (ddd, $J_{3',2'}$ = 5.2 Hz, $J_{3',OH}$ = 4.7 Hz, $J_{3',4'}$ = 3.6 Hz, 1 H, 3′-H), 4.57 (d, $J_{1',2'}$ = 7.1 Hz, 1 H, 1′-H), 4.84 (dd, $J_{OH,5'}$ = 5.7, 5.5 Hz, 1 H, OH-5′), 4.93 (d, $J_{OH,3'}$ = 4.7 Hz, 1 H, OH-3′), 5.02 (d, $J_{OH,2'}$ = 6.9 Hz, 1 H, OH-2′), 7.13 (dd, $J_{4,5}$ = 5.0 Hz, $J_{4,3}$ = 3.6 Hz, 1 H, 4-thienyl-H), 7.43 (m, 2 H, 2,6-H), 7.49 (dd, $J_{3,4}$ = 3.6 Hz, $J_{3,5}$ = 1.2 Hz, 1 H, 3-thienyl-H), 7.52 (dd, $J_{5,4}$ = 5.0 Hz, $J_{5,3}$ = 1.2 Hz, 1 H, 5-thienyl-H), 7.61 (m, 2 H, 3,5-H) ppm. ^{13}C NMR (151 MHz, [D$_6$]-DMSO): δ = 62.27 (CH_2-5′), 71.69 (CH-3′), 77.88 (CH-2′), 82.87 (CH-1′), 85.37 (CH-4′), 123.76 (CH-3-thienyl), 125.35 (CH-3,5), 125.70 (CH-5-thienyl), 127.18 (CH-2,6), 128.71 (CH-4-thienyl), 133.02 (C-4), 141.12 (C-1), 143.53 (C-2-thienyl) ppm. IR (KBr): $\tilde{\nu}$ = 293.0777, 3401, 3109, 3065, 3029, 1633, 1615, 1568, 1536, 1502, 1442, 1413, 1351, 1302, 1285, 1258, 1224, 1211, 1183, 1114, 1072, 1072, 1051, 1036, 1014, 902 cm^{-1}. $C_{15}H_{16}O_4S$ (292.3): calcd. C 61.62, H 5.52; found C 61.23, H 5.46. HRMS (FAB): calcd. for $C_{15}H_{17}O_4S$ [M + H] 293.0769; found 293.0777.

1β-[4-(Pyridin-2-yl)phenyl]-1-deoxy-D-ribofuranose (10e): Compound **10e** was prepared from **9e** according to the general procedure in 86% yield as a white powder. The crude product was crystallized from $CHCl_3$ to obtain peel transparent crystals. M.p. 125–129 °C. $[a]_D^{20}$ = –26.6 (c =3.15, MeOH). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 3.55 (ddd, J_{gem} = 11.6 Hz, $J_{5'b,OH}$ = 5.6 Hz, $J_{5'b,4'}$ = 4.7 Hz, 1 H, 5′b-H), 3.59 (ddd, J_{gem} = 11.6 Hz, $J_{5'a,OH}$ = 5.6 Hz, $J_{5'a,4'}$ = 4.5 Hz, 1 H, 5′a-H), 3.72 (ddd, $J_{2',1'}$ = 7.2 Hz, $J_{2',OH}$ = 7.0 Hz, $J_{2',3'}$ = 5.4 Hz, 1 H, 2′-H), 3.84 (ddd, $J_{4',5'}$ = 4.7, 4.5 Hz, $J_{4',3'}$ = 3.6 Hz, 1 H, 4′-H), 3.91 (ddd, $J_{3',2'}$ = 5.4 Hz, $J_{3',OH}$ = 4.8 Hz, $J_{3',4'}$ = 3.6 Hz, 1 H, 3′-H), 4.62 (d, $J_{1',2'}$ = 7.2 Hz, 1 H, 1′-H), 4.85 (t, $J_{OH,5'}$ = 5.6 Hz, 1 H, OH-5′), 4.95 (d, $J_{OH,3'}$ = 4.8 Hz, 1 H, OH-3′), 5.02 (d, $J_{OH,2'}$ = 7.0 Hz, 1 H, OH-2′), 7.34 (ddd, $J_{5,4}$ = 7.4 Hz, $J_{5,6}$ = 4.7 Hz, $J_{5,3}$ = 1.1 Hz, 1 H, 5-py-H), 7.51 (m, 2 H, 2,6-H), 7.87 (ddd, $J_{4,3}$ = 8.0 Hz, $J_{4,5}$ = 7.4 Hz, $J_{4,6}$ = 1.8 Hz, 1 H, 4-py-H), 7.95 (ddd, $J_{3,4}$ = 8.0 Hz, $J_{3,5}$ = 1.1 Hz, $J_{3,6}$ = 1.0 Hz, 1 H, 3-py-H), 8.04 (m, 2 H, 3,5-H), 8.66 (ddd, $J_{6,5}$ = 4.7 Hz, $J_{6,4}$ = 1.8 Hz, $J_{6,3}$ = 1.0 Hz, 1 H, 6-py-H) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 62.27 (CH_2-5′), 71.70 (CH-3′), 77.91 (CH-2′), 82.92 (CH-1′), 85.42 (CH-4′), 120.36 (CH-3-py), 122.70 (CH-5-py), 126.40 (CH-3,5), 126.77 (CH-2,6), 137.43 (CH-4-py), 137.94 (C-4), 142.63 (C-1), 149.73 (CH-6-py), 156.15 (C-2-py) ppm. IR (KBr): $\tilde{\nu}$ = 3400, 3275, 2902, 1632, 1611, 1585, 1578, 1562, 1515, 1467, 1437, 1409, 1309, 1294, 1269 1151, 1115, 1098, 1072, 1055, 1039, 1010, 905 cm^{-1}. HRMS (FAB): calcd. for $C_{16}H_{18}NO_4$ [M + H] 288.1236; found 288.1245.

1β-[4-(4-Fluorophenyl)phenyl]-1-deoxy-D-ribofuranose (10f): Compound **10f** was prepared from **9f** according to the general procedure in 95% yield. The crude product was crystallized from $CHCl_3$ to obtain a white solid. M.p. 153–157 °C. $[a]_D^{20}$ = –13.8 (c =2.78, MeOH).^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 3.54 (ddd, J_{gem} = 11.6 Hz, $J_{5'b,OH}$ = 5.5 Hz, $J_{5'b,4'}$ = 4.7 Hz, 1 H, 5′b-H), 3.57 (ddd, J_{gem} = 11.6 Hz, $J_{5'a,OH}$ = 5.6 Hz, $J_{5'a,4'}$ = 4.5 Hz, 1 H, 5′a-H), 3.71 (ddd, $J_{2',1'}$ = 7.3 Hz, $J_{2',OH}$ = 7.0 Hz, $J_{2',3'}$ = 5.3 Hz, 1 H, 2′-H), 3.83 (ddd, $J_{4',5'}$ = 4.7, 4.5 Hz, $J_{4',3'}$ = 3.5 Hz, 1 H, 4′-H), 3.91 (ddd, $J_{3',2'}$ = 5.3 Hz, $J_{3',OH}$ = 4.8 Hz, $J_{3',4'}$ = 3.5 Hz, 1 H, 3′-H), 4.60 (d, $J_{1',2'}$ = 7.3 Hz, 1 H, 1′-H), 4.84 (dd, $J_{OH,5'}$ = 5.6, 5.5 Hz, 1 H, OH-5′), 4.93 (d, $J_{OH,3'}$ = 4.8 Hz, 1 H, OH-3′), 5.01 (d, $J_{OH,2'}$ = 7.0 Hz, 1 H, OH-2′), 7.29 (m, 2 H, m-C_6H_4F-H), 7.47 (m, 2 H, 2,6-H), 7.60 (m, 2 H, 3,5-H), 7.69 (m, 2 H, o-C_6H_4F-H) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 62.29 (CH_2-5′), 71.73 (CH-3′), 77.93 (CH-2′), 82.83 (CH-1′), 85.39 (CH-4′), 115.92 (d, $J_{C,F}$ = 21 Hz, CH-m-C_6H_4F), 126.53 (CH-3,5), 127.04 (CH-2,6), 128.80 (d, $J_{C,F}$ = 8, CH-o-C_6H_4F), 136.79 (d, $J_{C,F}$ = 3, C-i-C_6H_4F), 138.37 (C-4), 140.91 (C-1), 162.02 (d, $J_{C,F}$ = 244, C-p-C_6H_4F) ppm. ^{19}F NMR (470.3 MHz, [D$_6$]DMSO): δ = –116.10 ppm. IR (KBr): $\tilde{\nu}$ = 3370, 3032, 1615, 1604, 1596, 1570, 1524, 1498, 1427, 1395, 1305, 1284, 1240, 1226, 1186, 1161, 1115, 1099, 1070, 1055, 1021, 1007, 941 cm^{-1}. $C_{17}H_{17}FO_4$ (304.3): calcd. C 67.10, H 5.63, F 6.26; found C 66.60, H 5.61, F 6.53. HRMS (FAB): calcd. for $C_{17}H_{17}FO_4Na$ [M + Na] 327.1008; found 327.1003.

1β-[4-(4-Methoxyphenyl)phenyl]-1-deoxy-D-ribofuranose (10g): Compound **10g** was prepared from **9g** according to the general

procedure in 95% yield. The crude product was crystallized from EtOAc/heptane to obtain a white solid. M.p. 176 °C. $[\alpha]_D^{20}$ = –8.1 (*c* =2.60, MeOH).^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 3.54 (ddd, J_{gem} = 11.6 Hz, $J_{5'b,OH}$ = 5.4 Hz, $J_{5'b,4'}$ = 4.7 Hz, 1 H, 5′b-H), 3.57 (ddd, J_{gem} = 11.6 Hz, $J_{5'a,OH}$ = 5.6 Hz, $J_{5'a,4'}$ = 4.5 Hz, 1 H, 5′a-H), 3.71 (ddd, $J_{2',1'}$ = 7.1 Hz, $J_{2',OH}$ = 7.0 Hz, $J_{2',3'}$ = 5.3 Hz, 1 H, 2′-H), 3.79 (s, 3 H, CH_3O), 3.82 (ddd, $J_{4',5'}$ = 4.7, 4.5 Hz, $J_{4',3'}$ = 3.5 Hz, 1 H, 4′-H), 3.90 (ddd, $J_{3',2'}$ = 5.3 Hz, $J_{3',OH}$ = 4.8 Hz, $J_{3',4'}$ = 3.5 Hz, 1 H, 3′-H), 4.58 (d, $J_{1',2'}$ = 7.1 Hz, 1 H, 1′-H), 4.83 (dd, $J_{OH,5'}$ = 5.6, 5.4 Hz, 1 H, OH-5′), 4.92 (d, $J_{OH,3'}$ = 4.8 Hz, 1 H, OH-3′), 5.00 (d, $J_{OH,2'}$ = 7.0 Hz, 1 H, OH-2′), 7.02 (m, 2 H, *m*-C_6H_4OMe-H), 7.44 (m, 2 H, 2,6-H), 7.56 (m, 2 H, 3,5-H), 7.59 (m, 2 H, *o*-C_6H_4OMe-H) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 55.38 (CH_3O), 62.31 (CH_2-5′), 71.72 (CH-3′), 77.88 (CH-2′), 82.93 (CH-1′), 85.33 (CH-4′), 114.55 (CH-*m*-C_6H_4OMe), 126.03 (CH-3,5), 126.99 (CH-2,6), 127.89 (CH-*o*-C_6H_4OMe), 132.67 (C-*i*-C_6H_4OMe), 139.08 (C-1), 140.11 (C-4), 159.02 (C-*p*-C_6H_4OMe) ppm. IR (KBr): $\tilde{\nu}$ = 3485, 3413, 3282, 3065, 3032, 3005, 2844, 1605, 1585, 1566, 1532, 1517, 1442, 1433, 1414, 1322, 1308, 1288, 1277, 1217, 1200, 1187, 1170, 1126, 1102, 1102, 1078, 1061, 1032, 1018, 1011, 1008, 951, 827 cm^{-1}. HRMS (FAB): calcd. for $C_{18}H_{20}O_5$ [M + H] 316.1311; found 316.1321.

1β-(4-Aminophenyl)-1-deoxy-D-ribofuranose (10h):[6b] Compound **10h** was prepared from **9h** according to the general procedure in 68% yield as a white solid. M.p. 99–100 °C. $[\alpha]_D^{20}$ = –22.1 (*c* =2.22, DMSO). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 3.48 and 3.51 (2 br. dt, J_{gem} = 11.6 Hz, $J_{5',4'}$ = $J_{5',OH}$ = 5.1 Hz, 1 H, 5′-H), 3.65 (br. m, 1 H, 2′-H), 3.71 (td, $J_{4',5'}$ = 5.1 Hz, $J_{4',3'}$ = 3.1 Hz, 1 H, 4′-H), 3.83 (br. m, 1 H, 3′-H), 4.35 (d, $J_{1',2'}$ = 7.0 Hz, 1 H, 1′-H), 4.72 (br. t, $J_{OH,5'}$ = 5.1 Hz, 1 H, OH-5′), 4.76 (br. s, 2 H, OH-2′,3′), 4.94 (br. s, 2 H, NH_2), 6.50 (m, 2 H, 3,5-H), 7.00 (m, 2 H, 2,6-H) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ = 62.42 (CH_2-5′), 71.58 (CH-3′), 77.14 (CH-2′), 83.73 (CH-1′), 84.77 (CH-4′), 113.63 (CH-3,5), 127.57 (CH-2,6), 128.21 (C-1), 148.13 (C-4) ppm. IR (KBr): $\tilde{\nu}$ = 3408, 3385, 3371, 3300, 1631, 1615, 1587, 1519, 1325, 1291, 1218, 1179, 1107, 1078, 1054, 1020, 832 cm^{-1}. HRMS (FAB): calcd. for $C_{11}H_{16}NO_4$ [M + H] 226.1079; found 226.1073.

1β-[4-(Dimethylamino)phenyl]-1-deoxy-D-ribofuranose (10i): Compound **10i** was prepared from **9i** according to the general procedure in 86% yield. The crude product was crystallized from EtOAc/heptane to obtain white crystals. M.p. 101–103 °C. $[\alpha]_D^{20}$ = –33.5 (*c* =2.99, MeOH). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 2.86 [s, 6 H, $(CH_3)_2$N], 3.49 (br. dd, J_{gem} = 11.5 Hz, $J_{5'b,4'}$ = 4.9 Hz, 1 H, 5′b-H), 3.53 (br. dd, J_{gem} = 11.6 Hz, $J_{5'a,4'}$ = 4.6 Hz, 1 H, 5′a-H), 3.66 (br. dd, $J_{2',1'}$ = 7.0 Hz, $J_{2',3'}$ = 5.3 Hz, 1 H, 2′-H), 3.74 (ddd, $J_{4',5'}$ = 4.9, 4.6 Hz, $J_{4',3'}$ = 3.8 Hz, 1 H, 4′-H), 3.85 (br. dd, $J_{3',2'}$ = 5.3 Hz, $J_{3',4'}$ = 3.8 Hz, 1 H, 3′-H), 4.43 (d, $J_{1',2'}$ = 7.0 Hz, 1 H, 1′-H), 4.74 (br. s, 1 H, OH-5′), 4.82 (br. s, 2 H, OH-2′,3′), 6.68 (m, 2 H, 3,5-H), 7.17 (m, 2 H, 2,6-H) ppm. ^{13}C NMR (151 MHz, [D$_6$]-DMSO): δ = 40.53 [$(CH_3)_2$N], 62.41 (CH_2-5′), 71.64 (CH-3′), 77.41 (CH-2′), 83.39 (CH-1′), 84.90 (CH-4′), 112.30 (CH-3,5), 127.51 (CH-2,6), 128.87 (C-1), 150.19 (C-4) ppm. IR (KBr): $\tilde{\nu}$ = 3401, 2803, 1617, 1568, 1525, 1444, 1413, 1355, 1315, 1298, 1233, 1188, 1164, 1115, 1072, 1051, 1035, 950, 811 cm^{-1}. $C_{13}H_{19}NO_4$ (253.3): calcd. C 61.64, H 7.56, N 5.53; found C 61.60, H 7.56, N 5.39. HRMS (FAB): calcd. for $C_{13}H_{20}NO_4$ [M + H] 254.1392; found 254.1397.

1β-[(4-*tert*-Butoxy)phenyl]-1-deoxy-D-ribofuranose (10j): Compound **10j** was prepared from **9j** according to the general procedure in 95% yield. The crude product was crystallized from $CHCl_3$ to obtain peel transparent crystals. M.p. 108–109 °C. $[\alpha]_D^{20}$ = –33.6 (*c* =2.60, DMSO). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 1.28 [s, 9 H, $(CH_3)_3$C], 3.51 (ddd, J_{gem} = 11.6 Hz, $J_{5'b,OH}$ = 5.5 Hz, $J_{5'b,4'}$ = 4.7 Hz, 1 H, 5′b-H), 3.54 (ddd, J_{gem} = 11.6 Hz, $J_{5'a,OH}$ = 5.7 Hz, $J_{5'a,4'}$ = 4.6 Hz, 1 H, 5′a-H), 3.68 (ddd, $J_{2',1'}$ = 7.3 Hz, $J_{2',OH}$ = 7.0 Hz, $J_{2',3'}$ = 5.4 Hz, 1 H, 2′-H), 3.78 (ddd, $J_{4',5'}$ = 4.7, 4.6 Hz, $J_{4',3'}$ = 3.5 Hz, 1 H, 4′-H), 3.88 (dddd, $J_{3',2'}$ = 5.4 Hz, $J_{3',OH}$ = 4.8 Hz, $J_{3',4'}$ = 3.5 Hz, $J_{3',1'}$ = 0.3 Hz, 1 H, 3′-H), 4.50 (d, $J_{1',2'}$ = 7.3 Hz, 1 H, 1′-H), 4.80 (dd, $J_{OH,5'}$ = 5.7, 5.5 Hz, 1 H, OH-5′), 4.89 (d, $J_{OH,3'}$ = 4.8 Hz, 1 H, OH-3′), 4.93 (d, $J_{OH,2'}$ = 7.0 Hz, 1 H, OH-2′), 6.92 (m, 2 H, 3,5-H), 7.29 (m, 2 H, 2,6-H) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 28.77 [$C(CH_3)_3$], 62.32 (CH_2-5′), 71.69 (CH-3′), 77.60 (CH-2′), 78.00 [$C(CH_3)_3$], 82.90 (CH-1′), 85.28 (CH-4′), 123.48 (CH-3,5), 127.30 (CH-2,6), 136.08 (C-1), 154.46 (C-4) ppm. IR (KBr): $\tilde{\nu}$ = 3355, 3305, 3234, 3071, 3039, 2977, 1608, 1576, 1509, 1492, 1478, 1447, 1418, 1390, 1369, 1295, 1238, 1209, 1174, 1163, 1126, 1115, 1099, 1074, 1059, 1018, 952 cm^{-1}. HRMS (FAB): calcd. for $C_{15}H_{23}O_4$ [M + H] 283.1545; found 283.1553.

1β-(3-Bromophenyl)-1-deoxy-D-ribofuranose (17): Compound **17** was prepared from **15** according to the general procedure in 88% yield. Crystallization from $CHCl_3$ yielded white needles. M.p. 79–81 °C. $[\alpha]_D^{20}$ = –13.8 (*c* =2.54, MeOH). ^{1}H NMR (600 MHz, [D$_6$]-DMSO): δ = 3.52 (ddd, J_{gem} = 11.6 Hz, $J_{5'b,OH}$ = 5.6 Hz, $J_{5'b,4'}$ = 4.4 Hz, 1 H, 5′b-H), 3.56 (ddd, J_{gem} = 11.6 Hz, $J_{5'a,OH}$ = 5.6 Hz, $J_{5'a,4'}$ = 4.3 Hz, 1 H, 5′a-H), 3.65 (ddd, $J_{2',1'}$ = 7.4 Hz, $J_{2',OH}$ = 7.3 Hz, $J_{2',3'}$ = 5.4 Hz, 1 H, 2′-H), 3.82 (ddd, $J_{4',5'}$ = 4.4, 4.3 Hz, $J_{4',3'}$ = 3.3 Hz, 1 H, 4′-H), 3.89 (ddd, $J_{3',2'}$ = 5.4 Hz, $J_{3',OH}$ = 4.7 Hz, $J_{3',4'}$ = 3.3 Hz, 1 H, 3′-H), 4.54 (d, $J_{1',2'}$ = 7.4 Hz, 1 H, 1′-H), 4.88 (t, $J_{OH,5'}$ = 5.6 Hz, 1 H, OH-5′), 4.97 (d, $J_{OH,3'}$ = 4.7 Hz, 1 H, OH-3′), 5.06 (d, $J_{OH,2'}$ = 7.3 Hz, 1 H, OH-2′), 7.29 (dd, $J_{5,4}$ = 7.9 Hz, $J_{5,6}$ = 7.7 Hz, 1 H, 5-H), 7.39 (dddd, $J_{6,5}$ = 7.7 Hz, $J_{6,2}$ = 1.6 Hz, $J_{6,4}$ = 1.1 Hz, $J_{6,1'}$ = 0.6 Hz, 1 H, 6-H), 7.46 (ddd, $J_{4,5}$ = 7.9 Hz, $J_{4,2}$ = 2.1 Hz, $J_{4,6}$ = 1.1 Hz, 1 H, 4-H), 7.58 (ddt, $J_{2,4}$ = 2.1 Hz, $J_{2,6}$ = 1.6 Hz, $J_{2,5}$ = $J_{2,1'}$ = 0.5 Hz, 1 H, 2-H) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 62.12 (CH_2-5′), 71.62 (CH-3′), 78.01 (CH-2′), 82.22 (CH-1′), 85.64 (CH-4′), 121.74 (C-3), 125.50 (CH-6), 128.88 (CH-2), 130.32 (CH-4), 130.49 (CH-5), 144.61 (C-1) ppm. IR (KBr): $\tilde{\nu}$ = 3448, 3337, 3203, 3060, 1594, 1566, 1474, 1414, 1305, 1266, 1193, 1113, 1092, 1081, 1071, 1054, 845 cm^{-1}. HRMS (FAB): calcd. for $C_{11}H_{13}O_4BrNa$ [M + Na] 310.9895; found 310.9882.

1β-(3-Methylphenyl)-1-deoxy-D-ribofuranose (19a): Compound **19a** was prepared from **18a** (476 mg, 0.840 mmol) according to the general procedure in 72% yield as a colorless heavy oil, which after coevaporation with dry toluene and Et_2O furnished a white powder. M.p. 70–73 °C. $[\alpha]_D^{20}$ = –23.2 (*c* =3.10, MeOH). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 2.29 (s, 3 H, CH_3), 3.52 (ddd, J_{gem} = 11.6 Hz, $J_{5'b,OH}$ = 5.5 Hz, $J_{5'b,4'}$ = 4.8 Hz, 1 H, 5′b-H), 3.56 (ddd, J_{gem} = 11.6 Hz, $J_{5'a,OH}$ = 5.7 Hz, $J_{5'a,4'}$ = 4.4 Hz, 1 H, 5′a-H), 3.66 (ddd, $J_{2',1'}$ = 7.1 Hz, $J_{2',OH}$ = 7.0 Hz, $J_{2',3'}$ = 5.5 Hz, 1 H, 2′-H), 3.79 (ddd, $J_{4',5'}$ = 4.8, 4.4 Hz, $J_{4',3'}$ = 3.8 Hz, 1 H, 4′-H), 3.87 (ddd, $J_{3',2'}$ = 5.5 Hz, $J_{3',OH}$ = 4.9 Hz, $J_{3',4'}$ = 3.8 Hz, 1 H, 3′-H), 4.51 (d, $J_{1',2'}$ = 7.1 Hz, 1 H, 1′-H), 4.81 (dd, $J_{OH,5'}$ = 5.7, 5.5 Hz, 1 H, OH-5′), 4.89 (d, $J_{OH,3'}$ = 4.9 Hz, 1 H, OH-3′), 4.95 (d, $J_{OH,2'}$ = 7.0 Hz, 1 H, OH-2′), 7.39 (dddd, $J_{6,5}$ = 7.1 Hz, $J_{6,2}$ = 2.5 Hz, $J_{6,4}$ = 1.7 Hz, $J_{6,1'}$ = 0.5 Hz, 1 H, 6-H), 7.16–7.19 (m, 2 H, 2,4-H), 7.20 (dd, $J_{5,4}$ = 7.6 Hz, $J_{5,6}$ = 7.1 Hz, 1 H, 5-H) ppm. ^{13}C NMR (151 MHz, [D$_6$] DMSO): δ = 21.33 (CH_3), 62.29 (CH_2-5′), 71.62 (CH-3′), 77.76 (CH-2′), 83.31 (CH-1′), 85.24 (CH-4′), 123.62 (CH-4), 127.10 (CH-2), 128.09 (CH-6), 128.11 (CH-5), 137.19 (C-3), 141.55 (C-1) ppm. IR (KBr): $\tilde{\nu}$ = 3392, 3272, 3064, 3026, 1611, 1592, 1490, 1465, 1382, 1284, 1263, 1237, 1163, 1091 cm^{-1}. HRMS (FAB): calcd. for $C_{12}H_{16}O_4Na$ [M + Na] 247.0946; found 247.0943.

1β-(3-Ethylphenyl)-1-deoxy-D-ribofuranose (19b): Compound **19b** was prepared from **18b** (394 mg, 0.679 mmol) according to the general procedure in 77% yield as a colorless oil, which after coevaporation with dry toluene and Et_2O furnished a white solid. M.p. 61–62 °C. $[a]_D^{20}$ = –23.2 (*c* =3.10, MeOH). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 1.17 (t, J_{vic} = 7.6 Hz, 3 H, CH_3CH_2), 2.59 (q, J_{vic} = 7.6 Hz, 2 H, CH_2CH_3), 3.52 (ddd, J_{gem} = 11.7 Hz, $J_{5'b,OH}$ = 5.5 Hz, $J_{5'b,4'}$ = 4.8 Hz, 1 H, 5′b-H), 3.56 (ddd, J_{gem} = 11.7 Hz, $J_{5'a,OH}$ = 5.7 Hz, $J_{5'a,4'}$ = 4.5 Hz, 1 H, 5′a-H), 3.67 (ddd, $J_{2',1'}$ = 7.0 Hz, $J_{2',OH}$ = 6.9 Hz, $J_{2',3'}$ = 5.4 Hz, 1 H, 2′-H), 3.79 (ddd, $J_{4',5'}$ = 4.8, 4.5 Hz, $J_{4',3'}$ = 3.7 Hz, 1 H, 4′-H), 3.87 (ddd, $J_{3',2'}$ = 5.4 Hz, $J_{3',OH}$ = 4.9 Hz, $J_{3',4'}$ = 3.7 Hz, 1 H, 3′-H), 4.52 (d, $J_{1',2'}$ = 7.0 Hz, 1 H, 1′-H), 4.82 (dd, $J_{OH,5'}$ = 5.7, 5.5 Hz, 1 H, OH-5′), 4.89 (d, $J_{OH,3'}$ = 4.9 Hz, 1 H, OH-3′), 4.95 (d, $J_{OH,2'}$ = 6.9 Hz, 1 H, OH-2′), 7.10 (m, 1 H, 4-H), 7.39 (dtd, $J_{6,5}$ = 7.5 Hz, $J_{6,2}$ = $J_{6,4}$ = 1.7 Hz, $J_{6,1'}$ = 0.5 Hz, 1 H, 6-H), 7.22 (m, 1 H, 2-H), 7.23 (td, $J_{5,4}$ = $J_{5,6}$ = 7.5 Hz, $J_{5,2}$ = 0.4 Hz, 1 H, 5-H) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 15.91 (CH_3CH_2), 28.44 (CH_2CH_3), 62.28 (CH_2-5′), 71.60 (CH-3′), 77.74 (CH-2′), 83.42 (CH-1′), 85.20 (CH-4′), 123.89 (CH-6), 125.92 (CH-2), 126.89 (CH-4), 128.18 (CH-5), 141.58 (C-1), 143.59 (C-3) ppm. IR (KBr): $\tilde{\nu}$ = 3413, 3275, 3061, 3032, 1608, 1591, 1485, 1465, 1380, 1289, 1263, 1236, 1160, 1118, 1072, 1049 cm^{-1}. HRMS (FAB): calcd. for $C_{13}H_{18}O_4$ [M + H] 238.1205; found 238.1194.

1β-(3-Benzylphenyl)-1-deoxy-D-ribofuranose (19c): Compound **19c** was prepared from **18c** (442 mg, 0.700 mmol) according to the general procedure in 80% yield as a colorless oil, which after coevaporation with dry toluene and Et_2O furnished a white solid. M.p. 71–72 °C. $[a]_D^{20}$ = –22.7 (*c* =2.51, MeOH).^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 3.51 (dd, J_{gem} = 11.6 Hz, $J_{5'b,4'}$ = 4.8 Hz, 1 H, 5′b-H), 3.55 (dd, J_{gem} = 11.6 Hz, $J_{5'a,4'}$ = 4.5 Hz, 1 H, 5′a-H), 3.67 (dd, $J_{2',1'}$ = 7.0 Hz, $J_{2',3'}$ = 5.5 Hz, 1 H, 2′-H), 3.78 (ddd, $J_{4',5'}$ = 4.8, 4.5 Hz, $J_{4',3'}$ = 3.8 Hz, 1 H, 4′-H), 3.86 (dd, $J_{3',2'}$ = 5.5 Hz, $J_{3',4'}$ = 3.8 Hz, 1 H, 3′-H), 3.92 (s, 2 H, CH_2Ph), 4.51 (d, $J_{1',2'}$ = 7.0 Hz, 1 H, 1′-H), 4.82 (br. s, 1 H, OH-5′), 4.94 (br. s, 2 H, OH-2′,3′), 7.10 (dt, $J_{4,5}$ = 6.8 Hz, $J_{4,2}$ = $J_{4,6}$ = 1.9 Hz, 1 H, 4-H), 7.18 (m, 1 H, *p*-Ph-H), 7.20-7.25 (m, 4 H, 5,6-H and *o*-Ph-H), 7.26–7.30 (m, 3 H, 2-H and *m*-Ph-H) ppm. ^{13}C NMR (151 MHz, [D$_6$]-DMSO): δ = 41.37 (CH_2Ph), 62.26 (CH_2-5′), 71.59 (CH-3′), 77.72 (CH-2′), 83.34 (CH-1′), 85.21 (CH-4′), 124.20 (CH-6), 126.18 (CH-*p*-Ph), 126.89 (CH-2), 127.88 (CH-4), 128.33 (CH-5), 128.65 (CH-*m*-Ph), 128.90 (CH-*o*-Ph), 141.11 (C-3), 141.51 (C-*i*-Ph), 141.77 (C-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 3392, 1632, 1609, 1602, 1590, 1590, 1494, 1488, 1465, 1453, 1237, 1156, 1119, 1090, 1072, 1047 cm^{-1}. HRMS (FAB): calcd. for $C_{18}H_{21}O_4$ [M + H] 301.1440; found 301.1431.

1β-[3-(2-Thienyl)phenyl]-1-deoxy-D-ribofuranose (19d): Compound **19d** was prepared from **18d** (367 mg, 0.580 mmol) according to the general procedure in 72% yield as a colorless heavy oil, which after coevaporation with dry toluene and Et_2O furnished a white solid. M.p. 111 °C. $[a]_D^{20}$ = –49.7 (*c* =2.75, DMSO). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 3.56 (ddd, J_{gem} = 11.6 Hz, $J_{5'b,OH}$ = 5.4 Hz, $J_{5'b,4'}$ = 4.5 Hz, 1 H, 5′b-H), 3.59 (ddd, J_{gem} = 11.6 Hz, $J_{5'a,OH}$ = 5.6 Hz, $J_{5'a,4'}$ = 4.5 Hz, 1 H, 5′a-H), 3.72 (ddd, $J_{2',1'}$ = 7.0 Hz, $J_{2',OH}$ = 6.9 Hz, $J_{2',3'}$ = 5.3 Hz, 1 H, 2′-H), 3.84 (td, $J_{4',5'}$ = 4.5 Hz, $J_{4',3'}$ = 3.5 Hz, 1 H, 4′-H), 3.92 (ddd, $J_{3',2'}$ = 5.3 Hz, $J_{3',OH}$ = 4.9 Hz, $J_{3',4'}$ = 3.5 Hz, 1 H, 3′-H), 4.61 (d, $J_{1',2'}$ = 7.0 Hz, 1 H, 1′-H), 4.87 (dd, $J_{OH,5'}$ = 5.6, 5.4 Hz, 1 H, OH-5′), 4.94 (d, $J_{OH,3'}$ = 4.9 Hz, 1 H, OH-3′), 5.05 (d, $J_{OH,2'}$ = 6.9 Hz, 1 H, OH-2′), 7.14 (dd, $J_{4,5}$ = 5.1 Hz, $J_{4,3}$ = 3.6 Hz, 1 H, 4-thienyl-H), 7.34 (dtd, $J_{6,5}$ = 7.6 Hz, $J_{6,2}$ = $J_{6,4}$ = 1.5 Hz, $J_{6,1'}$ = 0.5 Hz, 1 H, 6-H), 7.37 (td, $J_{5,4}$ = $J_{5,6}$ = 7.6 Hz, $J_{5,2}$ = 0.5 Hz, 1 H, 5-H), 7.49 (dd, $J_{3,4}$ = 3.6 Hz, $J_{3,5}$ = 1.2 Hz, 1 H, 3-thienyl-H), 7.54 (dd, $J_{5,4}$ = 5.1 Hz, $J_{5,3}$ = 1.2 Hz, 1 H, 5-thienyl-H), 7.55 (dt, $J_{4,5}$ = 7.6 Hz, $J_{4,2}$ = $J_{4,6}$ = 1.5 Hz, 1 H, 4-H), 7.67 (tt, $J_{2,4}$ = $J_{2,6}$ = 1.5 Hz, $J_{2,5}$ = $J_{2,1'}$ = 0.5 Hz, 1 H, 2-H) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 62.18 (CH_2-5′), 71.59 (CH-3′), 77.89 (CH-2′), 82.99 (CH-1′), 85.34 (CH-4′), 123.47 (CH-2), 123.89 (CH-3-thienyl), 124.61 (CH-5-thienyl), 125.65 (CH-6), 125.87 (CH-4), 128.69 (CH-4-thienyl), 129.08 (CH-5), 133.70 (C-3), 142.69 (C-1), 143.69 (C-2-thienyl) ppm. IR (KBr): $\tilde{\nu}$ = 3340, 3306, 3240, 1632, 1604, 1585, 1537, 1481, 1446, 1386, 1341, 1277, 1177, 1123, 1092, 1073, 1057, 999, 868, 858, 852, 790, 695, 562, 521, 451 cm^{-1}. HRMS (FAB): calcd. for $C_{15}H_{16}O_4SNa$ [M + Na] 315.0667; found 315.0652.

1β-[3-(Pyridin-2-yl)phenyl]-1-deoxy-D-ribofuranose (19e): Compound **19e** was prepared from **18e** (517 mg, 0.821 mmol) according to the general procedure in 68% yield as a colorless oil, which after coevaporation with dry toluene and Et_2O furnished a white solid. M.p. 137–139 °C. $[a]_D^{20}$ = –6.3 (*c* =3.19, MeOH). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 3.57 (ddd, J_{gem} = 11.6 Hz, $J_{5'b,OH}$ = 5.4 Hz, $J_{5'b,4'}$ = 4.7 Hz, 1 H, 5′b-H), 3.61 (ddd, J_{gem} = 11.6 Hz, $J_{5'a,OH}$ = 5.7 Hz, $J_{5'a,4'}$ = 4.4 Hz, 1 H, 5′a-H), 3.75 (ddd, $J_{2',1'}$ = 7.1 Hz, $J_{2',OH}$ = 6.9 Hz, $J_{2',3'}$ = 5.4 Hz, 1 H, 2′-H), 3.85 (ddd, $J_{4',5'}$ = 4.7, 4.4 Hz, $J_{4',3'}$ = 3.7 Hz, 1 H, 4′-H), 3.92 (ddd, $J_{3',2'}$ = 5.4 Hz, $J_{3',OH}$ = 4.9 Hz, $J_{3',4'}$ = 3.7 Hz, 1 H, 3′-H), 4.66 (d, $J_{1',2'}$ = 7.1 Hz, 1 H, 1′-H), 4.87 (dd, $J_{OH,5'}$ = 5.7, 5.4 Hz, 1 H, OH-5′), 4.94 (d, $J_{OH,3'}$ = 4.9 Hz, 1 H, OH-3′), 5.05 (d, $J_{OH,2'}$ = 6.9 Hz, 1 H, OH-2′), 7.35 (ddd, $J_{5,4}$ = 7.4 Hz, $J_{5,6}$ = 4.7 Hz, $J_{5,3}$ = 1.1 Hz, 1 H, 5-py-H), 7.45 (t, $J_{5,4}$ = $J_{5,6}$ = 7.6 Hz, 1 H, 5-H), 7.48 (dtd, $J_{6,5}$ = 7.6 Hz, $J_{6,2}$ = $J_{6,4}$ = 1.6 Hz, $J_{6,1'}$ = 0.5 Hz, 1 H, 6-H), 7.88 (ddd, $J_{4,3}$ = 8.0 Hz, $J_{4,5}$ = 7.4 Hz, $J_{4,6}$ = 1.7 Hz, 1 H, 4-py-H), 7.94 (ddd, $J_{3,4}$ = 8.0 Hz, $J_{3,5}$ = 1.1 Hz, $J_{3,6}$ = 1.0 Hz, 1 H, 3-py-H), 7.97 (dt, $J_{4,5}$ = 7.6 Hz, $J_{4,2}$ = $J_{4,6}$ = 1.6 Hz, 1 H, 4-H), 8.09 (tt, $J_{2,4}$ = $J_{2,6}$ = 1.6 Hz, $J_{2,5}$ = $J_{2,1'}$ = 0.6 Hz, 1 H, 2-H), 8.67 (ddd, $J_{6,5}$ = 4.7 Hz, $J_{6,4}$ = 1.7 Hz, $J_{6,3}$ = 1.0 Hz, 1 H, 6-py-H) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 62.24 (CH_2-5′), 71.57 (CH-3′), 77.85 (CH-2′), 83.27 (CH-1′), 85.38 (CH-4′), 120.52 (CH-3-py), 122.81 (CH-5-py), 124.63 (CH-2), 125.72 (CH-4), 127.12 (CH-6), 128.72 (CH-5), 137.45 (CH-4-py), 138.66 (C-3), 142.21 (C-1), 149.74 (CH-6-py), 156.31 (C-2-py) ppm. IR (KBr): $\tilde{\nu}$ = 3355, 3240, 3064, 2763, 1680, 1632, 1589, 1589, 1567, 1567, 1492, 1467, 1435, 1278, 1155, 1127, 1096, 1073, 1056, 1044, 1001 cm^{-1}. HRMS (FAB): calcd. for $C_{16}H_{18}NO_4$ [M + H] 288.1236; found 288.1244.

1β-[3-(4-Fluorophenyl)phenyl]-1-deoxy-D-ribofuranose (19f): Compound **19f** was prepared from **18f** (369 mg, 0.619 mmol) according to the general procedure in 77% yield as a colorless oil, which after coevaporation with dry toluene and Et_2O furnished a white solid. M.p. 119–122 °C. $[a]_D^{20}$ = –20.3 (*c* =2.66, MeOH). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 3.55 (ddd, J_{gem} = 11.6 Hz, $J_{5'b,OH}$ = 5.5 Hz, $J_{5'b,4'}$ = 4.6 Hz, 1 H, 5′b-H), 3.59 (ddd, J_{gem} = 11.6 Hz, $J_{5'a,OH}$ = 5.7 Hz, $J_{5'a,4'}$ = 4.4 Hz, 1 H, 5′a-H), 3.74 (ddd, $J_{2',1'}$ = 7.1 Hz, $J_{2',OH}$ = 6.9 Hz, $J_{2',3'}$ = 5.3 Hz, 1 H, 2′-H), 3.84 (ddd, $J_{4',5'}$ = 4.6, 4.4 Hz, $J_{4',3'}$ = 3.6 Hz, 1 H, 4′-H), 3.92 (ddd, $J_{3',2'}$ = 5.3 Hz, $J_{3',OH}$ = 4.8 Hz, $J_{3',4'}$ = 3.6 Hz, 1 H, 3′-H), 4.64 (d, $J_{1',2'}$ = 7.1 Hz, 1 H, 1′-H), 4.86 (dd, $J_{OH,5'}$ = 5.7, 5.5 Hz, 1 H, OH-5′), 4.93 (d, $J_{OH,3'}$ = 4.8 Hz, 1 H, OH-3′), 5.03 (d, $J_{OH,2'}$ = 6.9 Hz, 1 H, OH-2′), 7.29 (m, 2 H, *m*-C_6H_4F-H), 7.39 (dtd, $J_{6,5}$ = 7.6 Hz, $J_{6,2}$ = $J_{6,4}$ = 1.6 Hz, $J_{6,1'}$ = 0.5 Hz, 1 H, 6-H), 7.42 (ddd, $J_{5,6}$ = 7.6 Hz, $J_{5,4}$ = 7.3 Hz, $J_{5,2}$ = 0.6 Hz, 1 H, 5-H), 7.53 (dt, $J_{4,5}$ = 7.3 Hz, $J_{4,2}$ = $J_{4,6}$ = 1.6 Hz, 1 H, 4-H), 7.65 (tt, $J_{2,4}$ = $J_{2,6}$ = 1.6 Hz, $J_{2,5}$ = $J_{2,1'}$ = 0.6 Hz, 1 H, 2-H), 7.69 (m, 2 H, *o*-C_6H_4F-H) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 62.18 (CH_2-5′), 71.59 (CH-3′), 77.91 (CH-2′), 83.14 (CH-1′), 85.33 (CH-4′), 115.94 (d, $J_{C,F}$ = 21 Hz,CH-*m*-C_6H_4F), 124.69 (CH-2), 125.52 (CH-6), 125.82 (CH-4), 128.91 (d, $J_{C,F}$ = 8 Hz,CH-*o*-C_6H_4F), 128.92 (CH-5), 137.00 (d, $J_{C,F}$ = 3 Hz,C-*i*-C_6H_4F), 139.11 (C-3), 142.48 (C-1), 162.07 (d, $J_{C,F}$ = 244 Hz, C-*p*-C_6H_4F) ppm. ^{19}F NMR (MHz, [D$_6$]DMSO): δ =

–116.01 ppm. IR (KBr): $\tilde{\nu}$ = 3467, 3415, 3237, 1632, 1607, 1597, 1585, 1560, 1515, 1485, 1397, 1315, 1232, 1175, 1160, 1128, 1100, 1056, 1070, 1000, 877 cm^{-1}. HRMS (FAB): calcd. for $C_{17}H_{17}O_4FNa$ [M + Na] 327.1009; found 327.1018.

1β-[3-(4-Methoxyphenyl)phenyl]-1-deoxy-D-ribofuranose (19g): Compound **19g** was prepared from **18g** (479 mg, 0.727 mmol) according to the general procedure in 73% yield as a colorless oil, which after coevaporation with dry toluene and Et_2O furnished a white solid. M.p. 127–128 °C. $[\alpha]_D^{20}$ = –17.7 (*c* =3.29, MeOH). ^1H NMR (500 MHz, [D$_6$]DMSO): δ = 3.55 (ddd, J_{gem} = 11.6 Hz, $J_{5'b,OH}$ = 5.5 Hz, $J_{5'b,4'}$ = 4.6 Hz, 1 H, 5′b-H), 3.59 (ddd, J_{gem} = 11.6 Hz, $J_{5'a,OH}$ = 5.7 Hz, $J_{5'a,4'}$ = 4.4 Hz, 1 H, 5′a-H), 3.74 (td, $J_{2',1'}$ = $J_{2',OH}$ = 7.0 Hz, $J_{2',3'}$ = 5.3 Hz, 1 H, 2′-H), 3.79 (s, 3 H, CH_3O), 3.83 (ddd, $J_{4',5'}$ = 4.6, 4.4 Hz, $J_{4',3'}$ = 3.7 Hz, 1 H, 4′-H), 3.92 (ddd, $J_{3',2'}$ = 5.3 Hz, $J_{3',OH}$ = 4.8 Hz, $J_{3',4'}$ = 3.7 Hz, 1 H, 3′-H), 4.63 (d, $J_{1',2'}$ = 7.0 Hz, 1 H, 1′-H), 4.84 (dd, $J_{OH,5'}$ = 5.7, 5.5 Hz, 1 H, OH-5′), 4.90 (d, $J_{OH,3'}$ = 4.8 Hz, 1 H, OH-3′), 5.01 (d, $J_{OH,2'}$ = 7.0 Hz, 1 H, OH-2′), 7.03 (m, 2 H, *m*-C_6H_4OMe-H), 7.33 (dddd, $J_{6,5}$ = 7.6 Hz, $J_{6,2}$ = 1.9 Hz, $J_{6,4}$ = 1.3 Hz, $J_{6,1'}$ = 0.6 Hz, 1 H, 6-H), 7.38 (dd, $J_{5,6}$ = 7.6 Hz, $J_{5,4}$ = 7.5 Hz, 1 H, 5-H), 7.50 (ddd, $J_{4,5}$ = 7.5 Hz, $J_{4,2}$ = 1.9 Hz, $J_{4,6}$ = 1.3 Hz, 1 H, 4-H), 7.59 (m, 2 H, *o*-C_6H_4OMe-H), 7.62 (tt, $J_{2,4}$ = $J_{2,6}$ = 1.9 Hz, $J_{2,5}$ = $J_{2,1'}$ = 0.5 Hz, 1 H, 2-H) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]-DMSO): δ = 55.37 (CH_3O), 62.20 (CH_2-5′), 71.58 (CH-3′), 77.84 (CH-2′), 83.24 (CH-1′), 85.27 (CH-4′), 114.54 (CH-*m*-C_6H_4OMe), 124.24 (CH-2), 124.80 (CH-6), 125.31 (CH-4), 127.97 (CH-*o*-C_6H_4OMe), 128.76 (CH-5), 132.85 (C-*i*-C_6H_4OMe), 139.76 (C-3), 142.27 (C-1), 159.06 (C-*p*-C_6H_4OMe) ppm. IR (KBr): $\tilde{\nu}$ = 2837, 1607, 1607, 1589, 1573, 1517, 1482, 1453, 1439, 1302, 1265, 1247, 1180, 1116, 1103, 1085, 1065, 1053, 1035, 1022, 1003, 876, 839 cm^{-1}. HRMS (FAB): calcd. for $C_{18}H_{20}O_5Na$ [M + Na] 339.1208; found 339.1221.

1β-(3-Aminophenyl)-1-deoxy-D-ribofuranose (19h): Compound **19h** was prepared from **18h** (452 mg, 0.715 mmol) according to the general procedure in 84% yield as a colorless oil, which after coevaporation with dry toluene and Et_2O furnished a white solid. M.p. 113–115 °C. $[\alpha]_D^{20}$ = –26.6 (*c* =2.16, DMSO). ^1H NMR (600 MHz, [D$_6$]DMSO): δ = 3.51 (dt, J_{gem} = 11.6 Hz, $J_{5'b,OH}$ = $J_{5'b,4'}$ = 5.4 Hz, 1 H, 5′b-H), 3.53 (ddd, J_{gem} = 11.6 Hz, $J_{5'a,OH}$ = 5.7 Hz, $J_{5'a,4'}$ = 4.8 Hz, 1 H, 5′a-H), 3.64 (td, $J_{2',1'}$ = $J_{2',OH}$ = 6.8 Hz, $J_{2',3'}$ = 5.2 Hz, 1 H, 2′-H), 3.75 (ddd, $J_{4',5'}$ = 5.4, 4.8 Hz, $J_{4',3'}$ = 3.6 Hz, 1 H, 4′-H), 3.82 (ddd, $J_{3',2'}$ = 5.2 Hz, $J_{3',OH}$ = 5.1 Hz, $J_{3',4'}$ = 3.6 Hz, 1 H, 3′-H), 4.33 (d, $J_{1',2'}$ = 6.8 Hz, 1 H, 1′-H), 4.76 (dd, $J_{OH,5'}$ = 5.7, 5.4 Hz, 1 H, OH-5′), 4.84 (d, $J_{OH,3'}$ = 5.1 Hz, 1 H, OH-3′), 4.91 (d, $J_{OH,2'}$ = 6.8 Hz, 1 H, OH-2′), 4.97 (br. s, 2 H, NH_2), 6.44 (ddd, $J_{4,5}$ = 7.9 Hz, $J_{4,2}$ = 2.3 Hz, $J_{4,6}$ = 1.0 Hz, 1 H, 4-H), 6.53 (ddd, $J_{6,5}$ = 7.6 Hz, $J_{6,2}$ = 1.6 Hz, $J_{6,4}$ = 1.0 Hz, 1 H, 6-H), 6.57 (dd, $J_{2,4}$ = 2.3 Hz, $J_{2,6}$ = 1.6 Hz, 1 H, 2-H), 6.94 (dd, $J_{5,4}$ = 7.9 Hz, $J_{5,6}$ = 7.6 Hz, 1 H, 5-H) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 62.46 (CH_2-5′), 71.65 (CH-3′), 77.47 (CH-2′), 83.88 (CH-1′), 84.89 (CH-4′), 112.03 (CH-2), 113.11 (CH-4), 114.08 (CH-6), 128.64 (CH-5), 142.15 (C-1), 148.53 (C-3) ppm. IR (KBr): $\tilde{\nu}$ = 3412, 3374, 3306, 3223, 3052, 3041, 3028, 1631, 1631, 1609, 1609, 1599, 1494, 1463, 1305, 1168, 1121, 1113, 1072, 1050, 1032, 1001, 948 cm^{-1}. HRMS (FAB): calcd. for $C_{11}H_{16}NO_4$ [M + H] 226.1079; found 226.1071.

1β-[3-(Dimethylamino)phenyl]-1-deoxy-D-ribofuranose (19i): Compound **19i** was prepared from **18i** (579 mg, 0.971 mmol) according to the general procedure in 77% yield as a colorless oil, which after coevaporation with dry toluene and Et_2O furnished a white solid. M.p. 72–76 °C. $[\alpha]_D^{20}$ = –25.5 (*c* =3.15, MeOH). ^1H NMR (600 MHz, [D$_6$]DMSO): δ = 2.86 (s, 6 H, CH_3N), 3.52 (dt, J_{gem} = 11.7 Hz, $J_{5'b,OH}$ = $J_{5'b,4'}$ = 5.1 Hz, 1 H, 5′b-H), 3.57 (ddd, J_{gem} = 11.7 Hz, $J_{5'a,OH}$ = 5.7 Hz, $J_{5'a,4'}$ = 4.5 Hz, 1 H, 5′a-H), 3.66 (ddd, $J_{2',OH}$ = 6.6 Hz, $J_{2',1'}$ = 6.5 Hz, $J_{2',3'}$ = 5.0 Hz, 1 H, 2′-H), 3.78 (ddd, $J_{4',5'}$ = 5.1, 4.5 Hz, $J_{4',3'}$ = 3.7 Hz, 1 H, 4′-H), 3.87 (td, $J_{3',2'}$ = $J_{3',OH}$ = 5.0 Hz, $J_{3',4'}$ = 3.7 Hz, 1 H, 3′-H), 4.50 (d, $J_{1',2'}$ = 6.5 Hz, 1 H, 1′-H), 4.82 (dd, $J_{OH,5'}$ = 5.7, 5.1 Hz, 1 H, OH-5′), 4.85 (d, $J_{OH,3'}$ = 5.0 Hz, 1 H, OH-3′), 4.95 (d, $J_{OH,2'}$ = 6.6 Hz, 1 H, OH-2′), 6.60 (ddd, $J_{4,5}$ = 8.3 Hz, $J_{4,2}$ = 2.7 Hz, $J_{4,6}$ = 0.8 Hz, 1 H, 4-H), 6.67 (br. d, $J_{6,5}$ = 7.6 Hz, 1 H, 6-H), 6.77 (dd, $J_{2,4}$ = 2.7 Hz, $J_{2,6}$ = 1.3 Hz, 1 H, 2-H), 7.11 (dd, $J_{5,4}$ = 8.3 Hz, $J_{5,6}$ = 7.6 Hz, 1 H, 5-H) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 40.46 (CH_3N), 62.22 (CH_2-5′), 71.49 (CH-3′), 77.76 (CH-2′), 84.12 (CH-1′), 84.80 (CH-4′), 110.70 (CH-2), 111.67 (CH-4), 114.45 (CH-6), 128.78 (CH-5), 142.35 (C-1), 150.57 (C-3) ppm. IR (KBr): $\tilde{\nu}$ = 2800, 1609, 1585, 1501, 1456, 1440, 1317, 1286, 1100, 1047, 996 cm^{-1}. HRMS (FAB): calcd. for $C_{13}H_{20}NO_4$ [M + H] 254.1392; found 254.1402.

1β-[(3-*tert*-Butoxy)phenyl]-1-deoxy-D-ribofuranose (19j): Compound **19j** was prepared from **18j** (318 mg, 0.503 mmol) according to the general procedure in 78% yield as yellowish oil. $[\alpha]_D^{20}$ = –36.2 (*c* =4.27, DMSO). ^1H NMR (600 MHz, [D$_6$]DMSO): δ = 1.28 (s, 9 H, $(CH_3)_3C$), 3.51 (ddd, J_{gem} = 11.6 Hz, $J_{5'b,OH}$ = 5.5 Hz, $J_{5'b,4'}$ = 4.7 Hz, 1 H, 5′b-H), 3.54 (ddd, J_{gem} = 11.6 Hz, $J_{5'a,OH}$ = 5.6 Hz, $J_{5'a,4'}$ = 4.5 Hz, 1 H, 5′a-H), 3.66 (ddd, $J_{2',1'}$ = 7.0 Hz, $J_{2',OH}$ = 6.9 Hz, $J_{2',3'}$ = 5.3 Hz, 1 H, 2′-H), 3.80 (ddd, $J_{4',5'}$ = 4.7, 4.5 Hz, $J_{4',3'}$ = 3.6 Hz, 1 H, 4′-H), 3.87 (dddd, $J_{3',2'}$ = 5.3 Hz, $J_{3',OH}$ = 4.9 Hz, $J_{3',4'}$ = 3.6 Hz, $J_{3',1'}$ = 0.4 Hz, 1 H, 3′-H), 4.52 (d, $J_{1',2'}$ = 7.0 Hz, 1 H, 1′-H), 4.81 (dd, $J_{OH,5'}$ = 5.6, 5.5 Hz, 1 H, OH-5′), 4.89 (d, $J_{OH,3'}$ = 4.9 Hz, 1 H, OH-3′), 4.98 (d, $J_{OH,2'}$ = 6.9 Hz, 1 H, OH-2′), 6.85 (ddd, $J_{4,5}$ = 8.0 Hz, $J_{4,2}$ = 2.5 Hz, $J_{4,6}$ = 1.1 Hz, 1 H, 4-H), 7.00 (ddt, $J_{2,4}$ = 2.5 Hz, $J_{2,6}$ = 1.5 Hz, $J_{2,5}$ = $J_{2,1'}$ = 0.5 Hz, 1 H, 2-H), 7.07 (dddd, $J_{6,5}$ = 7.6 Hz, $J_{6,2}$ = 1.5 Hz, $J_{6,4}$ = 1.1 Hz, $J_{6,1'}$ = 0.7 Hz, 1 H, 6-H), 7.21 (dd, $J_{5,4}$ = 8.0 Hz, $J_{5,6}$ = 7.6 Hz, 1 H, 5-H) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 28.99 [$C(CH_3)_3$], 62.44 (CH_2-5′), 71.82 (CH-3′), 78.09 (CH-2′), 78.12 [$C(CH_3)_3$], 83.16 (CH-1′), 85.35 (CH-4′), 121.25 (CH-6), 121.64 (CH-2), 122.64 (CH-4), 128.89 (CH-5), 143.06 (C-1), 155.27 (C-3) ppm. IR (KBr): $\tilde{\nu}$ = 3414, 3070, 3032, 2977, 1604, 1586, 1486, 1440, 1391, 1367, 1314, 1262, 1177, 1165, 1112, 1075, 1049, 909, 862 cm^{-1}. HRMS (FAB): calcd. for $C_{15}H_{22}O_5Na$ [M + Na] 305.1368; found 305.1372.

Single Crystal X-ray Diffraction Analysis of 5 and 10i: X-ray diffraction analysis of single crystals of **5** (colorless, 0.21×0.31×0.63 mm) and **10i** (colorless, 0.08×0.27×0.60 mm) was performed with an Xcalibur X-ray diffractometer with Cu-K_α (λ = 1.54180 Å), data collected at 150 K (**5**) and at 295 K (**10i**). Both structures were solved by direct methods with SIR92[27] and refined by full-matrix least-squares on F with CRYSTALS.[28] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located in the difference map, but those attached to carbon atoms were repositioned geometrically and then refined with riding constraints. Crystal data for **5**: $C_{29}H_{55}BrO_5Si_3$, orthorhombic, space group $P2_12_12_1$, a = 8.4121(1) Å, b = 12.0094(1) Å, c = 35.3997(3) Å, V = 3576.23(6) Å^3, Z = 4, M = 647.90, 61159 reflections measured, 5970 independent reflections. Final R = 0.0275, wR = 0.0305, GoF = 1.0315 for 5397 reflections with $I > 2\sigma(I)$ and 344 parameters. Crystal data for **10i**: $C_{13}H_{19}NO_4$, orthorhombic, space group $P2_12_12_1$, a = 6.5896(1) Å, b = 7.0174(1) Å, c = 26.9375(2) Å, V = 1245.64(3) Å^3, Z = 4, M = 253.29, 19514 reflections measured, 2560 independent reflections. Final R = 0.0308, wR = 0.0392, GoF = 1.0508 for 2152 reflections with $I > 2\sigma(I)$ and 165 parameters.

CCDC-670179 (**5**) and -670180 (**10i**) contain the supplementary crystallographic data for this paper. These data can be obtained

free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This work was supported by the Centre of Biomolecules and Complex Molecular Systems (LC 512), by NIH, Fogarty International Center (Grant 1R03TW007372-01), and by Gilead Sciences Inc. as part of the research project Z04 055 905. Antiviral activity was studied by E. Mabery and Drs. I. Shih and R. Mackman (Gilead). The contribution of these scientists is gratefully acknowledged.

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Received: December 10, 2007
Published Online: February 12, 2008

