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General and Modular Synthesis of Isomeric 5-Substituted Pyridin-2-yl and 6-Substituted Pyridin-3-yl *C*-Ribonucleosides Bearing Diverse Alkyl, Aryl, Hetaryl, Amino, Carbamoyl, and Hydroxy Groups

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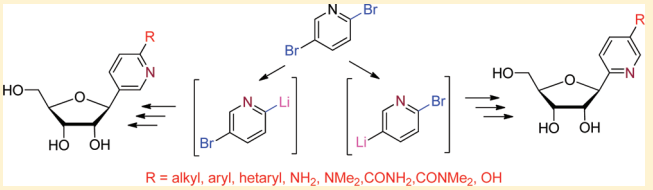
Supporting Information

ABSTRACT: A general modular and practical methodology for preparation of diverse 5-substituted pyridin-2-yl and 6-substituted pyridin-3-yl *C*-ribonucleosides was developed. Regioselective lithiation of 2,5-dibromopyridine proceeded at position 5 or 2 depending on the solvent, and the resulting bromopyridyl lithium species underwent additions to TBS-protected ribonolactone and follow-up transformations to corresponding acetylated hemiketal intermediates **7** and **10** that were diastereoselectively reduced to give either 5-bromopyridin-2-yl or 6-bromopyridin-3-yl silyl-protected *C*-ribonucleosides **8** or **11** in 68% and 77% overall yields as pure β-anomers. These bromopyridyl *C*-nucleoside intermediates were then subjected to a series of palladium-catalyzed cross-coupling reactions, aminations, aminocarbonylations, and hydroxylations to give a series of protected 1β-(5-alkyl-, 5-aryl-, 5-amino-, 5-carbamoyl-, and 5-hydroxypyridin-2-yl)-*C*-ribonucleosides **13a**−**i** and β-(6-alkyl-, 6-aryl-, 6-amino-, 6-carbamoyl-, and 6-hydroxypyridin-3-yl)-*C*-ribonucleosides **15a**−**i**. Deprotection of silylated nucleosides by $Et_3N \cdot 3HF$, TBAF, or TFA gave a series of free *C*-nucleosides **14a**−**i** and **16a**−**i**.



INTRODUCTION

The syntheses, as well as the importance, biological activities, and other applications of *C*-nucleosides as hydrolytically stable analogues of natural N-nucleosides were thoroughly discussed and summarized in several recent reviews.[1] Our group is interested in development of general and modular methods of synthesis of diverse substituted (het)aryl-*C*-nucleosides. Our approach is based on synthesis of halo(het)aryl-*C*-nucleoside intermediates and their follow-up derivatizations by means of cross-coupling reactions, Hartwig−Buchwald aminations, aminocarbonylations,[2] and hydroxylations.[3] In this way, we have prepared 3- and 4-substituted benzene,[4] 6-substituted pyridin-2-yl[5] and pyridin-3-yl,[6] 5-substituted thiophen-2-yl,[7] 5-substituted furan-2-yl,[8] and 2,4-disubstituted pyrimidin-5-yl[9] *C*-2′-deoxyribonucleosides some of which were used for chemical biology studies on DNA polymerases and primases.[10] In the ribonucleoside series, we reported only the synthesis of benzene[11,2,3] and 6-substituted pyridin-2-yl[12] derivatives so far (Chart 1).

Some other types of pyridine *C*-ribonucleosides have been reported and applied in diverse areas (Chart 1). 2-Aminopyridin-5-yl *C*-ribonucleosides were prepared[13] as deletion analogues of cytidine for probing the function of cytosine in ribozymes, and the corresponding 2′-deoxyribonucleosides were used[14] for synthesis of triplex-forming oligonucleotides (ONs). 2-Oxopyridin-5-yl *C*-ribonucleosides served[15] as deletion analogues of uridine for prospective RNA studies. 2-Oxopyridin-3-yl *C*-ribonucleosides[16] selectively pair with 6-substituted-2-aminopurines[17] and were used in extension of the genetic alphabet for transcription to synthetize modified RNA[18] and to construct proteins containing unnatural amino acids.[19] 5-Carbamoylpyridin-2-yl *C*-ribonucleoside was prepared[20] as a nicotinamide ribonucleoside analogue. Isomeric 6-substituted pyridin-3-yl *C*-ribonucleosides occur[21] only very scarcely in the literature. In all the above-mentioned cases, each single

Chart 1. Selected Known *C*-Ribonucleosides

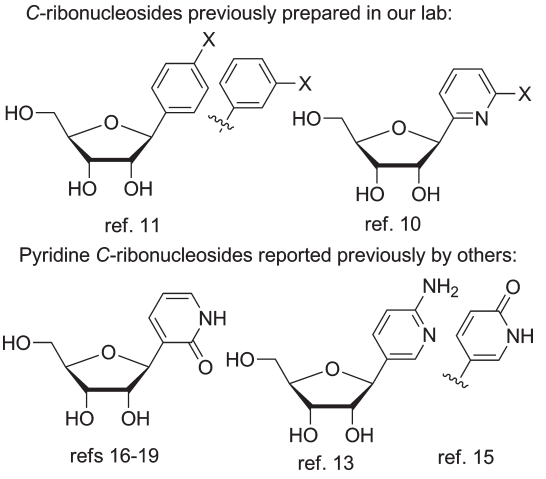


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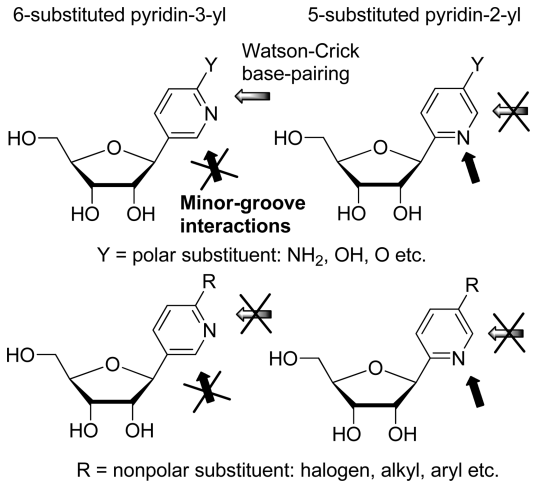
Chart 2. Pyridine *C*-Nucleosides from This Work and Their Possible H-Bonding Interactions



derivative was prepared by a specific multistep sequence involving *C*-glycosidation reaction with a protected functionalized pyridine organometallic reagent.

To complement the series of isomeric pyridine *C*-ribonucleosides, we report here on a general synthesis of two important underexplored types of analogues: 5-substituted pyridin-2-yl and 6-substituted pyridin-3-yl *C*-ribonucleosides (Chart 2). The former type bearing polar substituents (NH_2, O) should retain H-bonding ability to form Watson−Crick pairs but lacks functionality for minor-groove interactions, whereas the derivatives bearing nonpolar substituents (halogen, methyl, etc.) are shape mimetics of the natural pyrimidines lacking any H-donors. The latter type contains an H-acceptor in the minor groove but the H-bonding at the Watson−Crick is altered. Therefore, these compounds have great potential in studying mechanism of incorporation by RNA polymerases and as building blocks for construction of modified RNAs.

RESULTS AND DISCUSSION

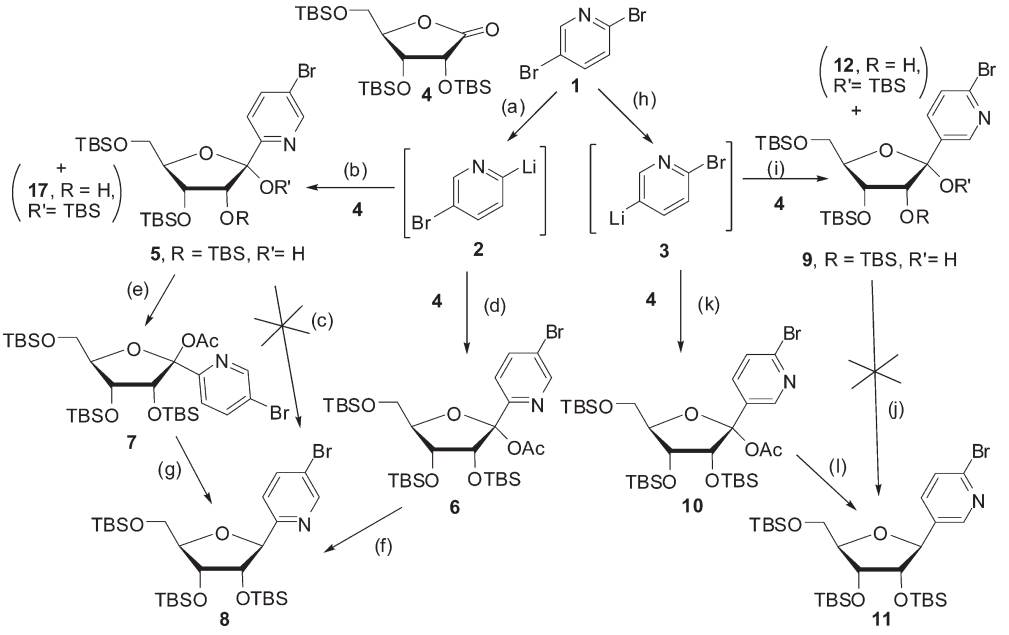
The key intermediates for the two classes of target *C*-nucleosides were the corresponding suitably protected 5-bromopyridin-2-yl and 6-bromopyridin-3-yl *C*-ribonucleosides. The synthesis of both of them was based on known[22] dichotomy in regioselective lithiation of 2,5-dibromopyridine **1**. In toluene, a debromolithiation proceeds[22] at position 2 leading to 5-bromo-2-lithiopyridine **2**, whereas in Et_2O at position 5 to furnish 2-bromo-5-lithiopyridine **3** (Scheme 1). Thus, the lithiation of **1** with *n*BuLi in toluene for 30 min at −78 °C selectively formed **2** which was immediately reacted with TBS-protected lactone **4** (0.5 equiv) for 10 min to afford the corresponding hemiketal **5** as a pure α-anomer in poor 24% yield accompanied by a side-product **17** (12%) formed by a migration of TBS group from 2′-OH to the hemiketal OH. In order to achieve complete conversion of the starting lactone **4** and suppress formation of the undesired **17**, an extensive optimization was required. The optimized conditions used 6 equiv of **1** (for lithiation to **2**), resulting in complete conversion of lactone **4** within 10 min Subsequent quenching with MeOH at −78 °C and aqueous workup gave the desired hemiketal **5** in very good 73% yield as a pure α-anomer (**17** was formed in less than 2%). Then we turned our attention to reduction of **5** under standard conditions using $Et_3SiH/BF_3\cdot Et_2O$, but all attempts to perform this reduction failed and only unreacted starting material was isolated. Therefore, in analogy to previous works of others[15,23] and us,[12] we tried to convert the hemiketal **5** to its *O*-acetate **6** which should be more reactive toward the reduction. Thus, the hemiketal alkoxide, generated by addition of monolithiated pyridine **2** to lactone **4** was directly in situ acylated on treatment with Ac_2O to give the hemiketal-acetate **6** in low yield of 18% accompanied by hemiketal **5** (51%).

As an alternative, we focused on acetylations of isolated pure hemiketal **5**. Its acylations with Ac_2O or AcCl in the presence of catalytic amount of DMAP in pyridine were tested, but only very low conversions (∼5%) to **6** were observed. However, the treatment of **5** with LiHMDS at room temperature followed by addition of Ac_2O led to the formation of unexpected opposite β-anomer hemiketal-acetate **7** in 30%. It seems that α-alkoxide **X**, generated by deprotonation of α-hemiacetal **5**, is at room temperature transformed to thermodynamically more stable β-anomer **Y** which upon quenching with Ac_2O gives acetal **7** (Scheme 2). In order to increase the yield of **7**, an optimized protocol using 4.5 equiv of the LiHMDS, added to **5** in three portions, was developed. Addition of each portion was followed by quenching with Ac_2O (1.5 equiv). This methodology was efficient even on a large-scale synthesis, yielding acylated hemiketal **7** in 84% yield. The reductive deacetylation of α-acetal **6** under standard conditions (3 equiv of Et_3SiH and 1.5 equiv of $BF_3\cdot Et_2O$ at 0 °C) gave the desired 5-bromopyridin-2-yl *C*-ribonucleoside **8** in 79% yield as a pure β-anomer. Interestingly, the reduction of the epimeric β-acetal **7** under the same conditions proceeded with inversion of configurayion at *C*-1′ to furnish **8** in 81% yield as a single diastereomer. The stereochemistry of all nucleosides **5**−**8** was verified by ROESY spectra.

For the synthesis of 6-substituted pyridin-3-yl *C*-ribonucleosides, we adopted an analogous synthetic strategy using the lithiation of 2,5-dibromopyridine **1** at position 5 (Scheme 1, h−j). Thus, the lithiation of **1** in diethyl ether at −78 °C using *n*BuLi resulted in selective formation of 2-bromo-5-lithiopyridine **3** which upon coupling with lactone **4** furnished hemiketal **9** in 51% yield (only the α-anomer was formed) and side-product **12** (12% yield) formed by migration of TBS-protecting group from 2′-OH to hemiketal. In order to achieve complete consumption of lactone **4**, 5 equiv of pyridine **1** had to be used. Structure of compound **12** was proved by X-ray structure analysis (Figure 1). To suppress the formation of undesired **12**, quenching of the reaction mixture with MeOH at −78 °C was found to be very efficient giving the desired hemiketal **9** in very good 75% yield with only a trace amount of **12** (>2%).

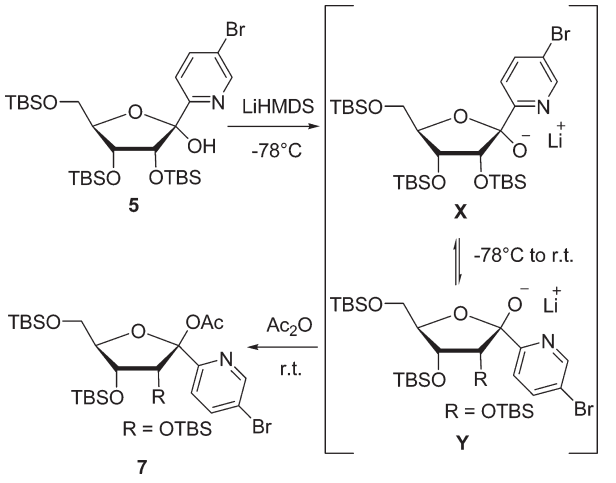
Reduction of **9** under standard conditions (3 equiv of Et_3SiH, 1.5 equiv of $BF_3\cdot Et_2O$ at 0 °C) failed similarly to the reduction of **5**. Again, we relied on acetylation of the hemiketal to increase the reactivity toward the reduction. Thus, the addition of 5-lithio-2-bromopyridine **3** to lactone **4** at −78 °C followed by direct in situ quenching with Ac_2O gave a mixture of acylated ketal **10** and hemiketal **9** in 54% and 11% yield, respectively. Unreacted hemiketal **9** could be transformed to **10** upon reaction with LiHMDS at −78 °C followed by quenching with A_2O in 80% yield. It is noteworthy to mention that in this case, no inversion of anomeric configuration was observed at −78 °C (in contrast to analogous acetylation of **5**, vide supra). Subsequent reduction of

Scheme 1[a]



[a] Reagents and conditions: (a) **1**, *n*BuLi, toluene, −78 °C, 30 min; (b) **4**, −78 °C, 10 min then MeOH gives **5** (73% based on **4**); (c) Et_3SiH, $BF_3 \cdot Et_2O$, DCM, 0 °C, 10 min, 0%; (d) **4**, −78 °C, 10 min then Ac_2O, −78 °C→ r.t. gives **6** (18% based on **4**); (e) LiHMDS then Ac_2O, toluene, r.t. gives **7** (84% from **4**); (f) Et_3SiH, $BF_3 \cdot Et_2O$, DCM, 0 °C, 10 min gives **8** (81% from **7**); (g) Et_3SiH, $BF_3 \cdot Et_2O$, DCM, 0 °C, 10 min gives **8** (79% from **6**); (h) **1**, Et_2O, *n*BuLi, −78 °C, 30 min; (i) **4**, −78°C, 10 min then MeOH gives **9** (75% based on **4**); (j) Et_3SiH, $BF_3 \cdot Et_2O$, DCM, 0 °C, 10 min 0%; (k) **4**, −78°C, 10 min then Ac_2O followed by LiHMDS, then Ac_2O gives **10** (77% based on **4**); (l) Et_3SiH, $BF_3 \cdot Et_2O$, DCM, −10 °C, 5 min gives **11** (71% from **10**).

Scheme 2. Synthesis of Acylated Hemiketal 7: Proposed Mechanism of Inversion at the Anomeric Carbon



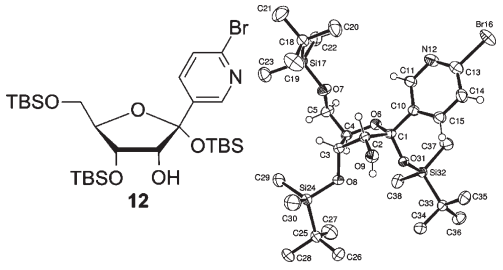


Figure 1. Chemical and X-ray structure of the side-product **12**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms on TBS groups were omitted for clarity.

10 by Et_3SiH (3 equiv) in the presence of $BF_3 \cdot Et_2O$ (1.5 equiv) at −10 °C furnished the desired TBS-protected 6-bromopyridin-3-yl *C*-ribonucleoside **11** in 71% yield as a pure β-anomer.

This stepwise synthetic sequence was quite laborious, requiring isolation of each intermediate, and gave the desired *C*-ribonucleoside intermediate **11** in 54% overall yield based on lactone **4**. In order to increase the overall yield and simplify the isolation process we have further optimized the whole synthetic sequence. Thus, the lithiation of pyridine **1** (5 equiv to **4**) followed by coupling with lactone **4** and quenching with Ac_2O gave a crude mixture of compounds **9** and **10**. Subsequent addition of LiHMDS to the crude reaction mixture at −78 °C followed by quenching with another portion of Ac_2O and workup afforded crude hemiketal **10.** This was directly, without purification, used in final reduction step, yielding after silica gel column chromatography the desired bromopyridine *C*-ribonucleoside **11** as a pure β-anomer in very good 77% overall yield based on lactone **4**.

With the key intermediates **8** and **11** in hand, we turned our attention to palladium-catalyzed cross-couplings, aminations, aminocarbonylations, and hydroxylations (Scheme 3, Table 1, Scheme 4, Table 2). Coupling of **8** with trimethylaluminium under standard conditions using $Pd(PPh_3)_4$ in THF at 65 °C gives 5-methylpyridin-2-yl *C*-ribonucleoside **13a** in 90% yield (Scheme 2, Table 1, entry 1). 5-Phenylpyridin-2-yl *C*-ribonucleoside **13b** was prepared by Suzuki−Miyaura cross-coupling of phenylboronic with **8** in toluene at 100 °C under catalysis of $Pd(PPh_3)_4$ and K_2CO_3 in 89% yield (entry 2). In order to introduce hetaryl substituents, the Stille cross-coupling reactions using $PdCl_2(PPh_3)_2$ in DMF were used. Reactions of **8** with

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Scheme 3. Synthesis of a Series of 5-Substituted Pyridin-2-yl *C*-Ribonucleosides

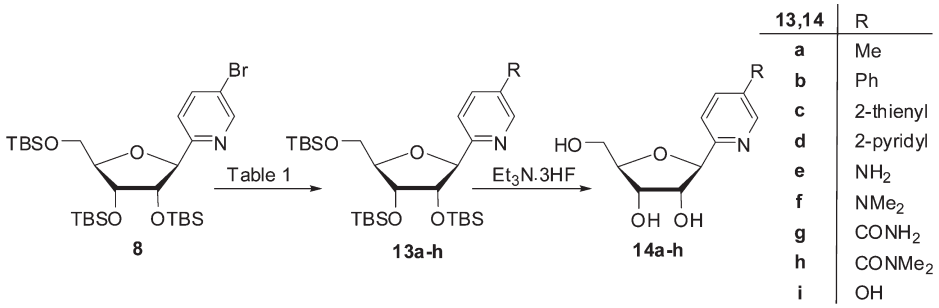

Table 1. Functional Group Transformations of 8 Followed by Deprotection

entry	reagent	catalyst	ligand/Base	solvent	other conditions	reaction (yield)	deprotection (yield)
1	Me_3Al	$Pd(PPh_3)_4$		THF	12 h, 65 °C	**13a** (90%)	**14a** (83%)
2	$PhB(OH)_2$[a]	$Pd(PPh_3)_4$	K_2CO_3	toluene	3 h, 100 °C	**13b** (89%)	**14b** (80%)
3	2-Bu_3Sn- thiophene [b]	$Pd(PPh_3)_2Cl_2$		DMF	2 h, 100 °C	**13c** (84%)	**14c** (83%)
4	2-Bu_3Sn- Pyridine [c]	$Pd(PPh_3)_2Cl_2$		DMF	1.5 h, 100 °C	**13d** (63%)	**14d** (83%)
5	$LiN(SiMe_3)_2$	Pd_2dba_3	$P^tBu_3 \cdot HBF_4$	THF	11 h 50 °C	**13e** (63%)	**14e** (75%)
6	Me_2NH [d]	Pd_2dba_3	JohnPhos [e]/*t*BuONa	toluene	3 h 60 °C	**13f** (70%)	**14f** (76%)
7	NH_3[f] $CO_{(1\ atm)}$	$Pd(OAc)_2$	Xantphos [g]/ K_3PO_4	toluene	6 h, 80 °C	**13g** (74%)	**14g** (75%)
8	$Me_2NH \cdot HCl$ $CO_{(1\ atm)}$	$Pd(OAc)_2$	Xantphos [g]/ K_3PO_4	toluene	1.5 h, 80 °C	**13h** (80%)	**14h** (81%)
9	KOH	Pd_2dba_3	L[h]	dioxane/H_2O	1.5 h 80 °C	**13i** (73%)	**14i** (74%)

[a] $PhB(OH)_2$ = phenylboronic acid . [b] 2-Bu_3Sn-thiophene = 2-(tributylstannyl)thiophene. [c] 2-Bu_3Sn-pyridine = 2-(tributylstannyl)pyridine. [d] 2 M solution in THF. [e] JohnPhos = (2-biphenyl)di-*tert*-butylphosphane. [f] 0.5 M in 1,4-dioxane. [g] Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene. [h] L = di-*tert*-butylphosphino-3,4,5,6-tetramethyl-2′,4′,6′-triisopropylbiphenyl.

2-thienyl(tributyl)stannane proceeded very smoothly within 2 h at 100 °C to give the desired 5-(2-thienyl)pyridine **13c** in 84% yield (entry 3). Reaction of **8** with 2-pyridyl(tributyl)stannane (entry 4) required only 1.5 h to reach complete conversion and the target 5,2′-bipyridine-2-yl *C*-ribonucleoside **13d** was isolated in 63% yield (entry 4). Palladium-catalyzed amination reactions (Hartwig−Buchwald)[24] were used for the synthesis of primary and tertiary amines. Primary aminopyridine derivate **13e** was prepared by reaction of **8** with lithium bis(trimethylsilyl)amide (LiHMDS) in the presence of Pd_2dba_3 and Buchwald-type biaryl-ligand. When (2-biphenyl)dicyclohexylphosphane (cHex JohnPhos)[25,26] was employed as a ligand, no reaction occurred even after long reaction time of 48 h at 50 °C. Only the use of tri-*tert*-butylphosphane (generated in situ from tri-*tert*-butylphosphonium tetrafluoroborate) gave the target 5-aminopyridine C-ribonucleoside **13e** in acceptable 63% yield after prolonged reaction time (11 h) at 50 °C (entry 5). The dimethylamino group was introduced by the reaction of **8** with dimethylamine (2 M solution in THF) in a sealed tube in the presence of Pd_2dba_3, 2-(di-*tert*-butylphosphanyl)biphenyl (JohnPhos), and *t*BuONa. A short reaction time of 3 h (60 °C) was sufficient to give dimethylaminopyridine *C*-ribonucleoside **13f** in very good 70% yield (entry 6).

Primary and tertiary carboxamides **13g** and **13h** were prepared by Pd-catalyzed aminocarbonylation[2] reactions in the presence of $Pd(OAc)_2$, Xantphos, and K_3PO_4. Reaction of ammonium chloride (NH_4Cl) with **8** in the presence of 5 mol % $Pd(OAc)_2$ and 10 mol % of Xantphos gives amide **13g** in 50% after a short reaction time (1.5 h) at 80 °C. When 0.5 M THF solution of ammonia was used instead of NH_4Cl, primary amide **13g** was isolated in improved 74% yield after somewhat longer (6 h) reaction time (entry 7). Reaction of **8** with dimethylamine hydrochloride resulted in formation of *N*,*N*-dimethyl carboxamide **13h** in 80% yield (entry 8). Recently developed[3] palladium-catalyzed hydroxylation using KOH, Pd_2dba_3, and di-*tert*-butylphosphino-3,4,5,6-tetramethyl-2′,4′,6′-triisopropylbiphenyl was applied for the conversion of **8** to corresponding hydroxypyridine **13i**. The reaction was performed in 1,4-dioxane−water (3:1) and proceeded smoothly at 80 °C in a short reaction time (1.5 h) to afford the desired hydroxypyridine *C*-ribonucleoside **13i** in very good 73% yield.

For final deprotection of the silylated nucleosides **13a**−**i**, reaction with $Et_3N \cdot 3HF$[27] was used. Heating at 40 °C for 2 days followed by treatment with $NaHCO_3$ resulted in complete cleavage of TBS-protecting groups. Chromatographic purification on reverse-phase flash chromatography and subsequent lyophilization/crystallization give free nucleosides **14a**−**d**,**f**,**h** in good yields (76−83%, Table 1, entries 1−4, 6, 8, last column). Due to strongly hydrophilic character of compounds **14e**,**g**,**i** highly polar impurities could not be removed by reverse-phase chromatography. Therefore, ion-exchange chromatography Dowex 50 in H^+ cycle was used to remove polar salts while the pyridine *C*-nucleosides were eluted after washing with 25% aqueous ammonia. Subsequent purification on reverse-phase flash chromatography and lyophilization give free nucleosides **14e**,**g**,**i** in good yields (74−75%, Table 1, entries 5, 7, 9, last column).

Analogously, we prepared a series of 6-substituted pyridin-3-yl *C*-ribonucleosides starting from intermediate **11** (Scheme 4, Table 2). Methyl, phenyl, 2-thienyl, and 2-pyridyl substituents

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Scheme 4. Synthesis of a Series of 6-Substituted Pyridin-3-yl *C*-Ribonucleosides

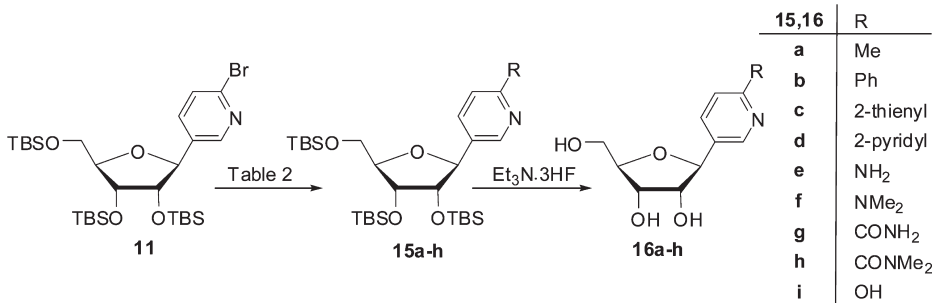

Table 2. Functional Group Transformations of 11 Followed by Deprotection

entry	reagent	catalyst	ligand/Base	solvent	other conditions	reaction (yield)	deprotection (yield)
1	Me_3Al	$Pd(PPh_3)_4$		THF	2 h, 70 °C	**15a** (93%)	**16a** (90%)
2	$PhB(OH)_2$[a]	$Pd(PPh_3)_4$	K_2CO_3	toluene	1.5 h, 110 °C	**15b** (95%)	**16b** (91%)
3	2-Bu_3Sn- thiophene [b]	$Pd(PPh_3)_2Cl_2$		DMF	1.5 h, 110 °C	**15c** (81%)	**16c** (89%)
4	2-Bu_3Sn- pyridine [c]	$Pd(PPh_3)_2Cl_2$		DMF	4.5 h, 80 °C	**15d** (51%)	**16d** (52%)
5	$LiN(SiMe)_2$	Pd_2dba_3	cHex JohPhos[d]	THF	5 h 50 °C	**15e** (88%)	**16e** (65%)[e]
6	Me_2NH [f]	Pd_2dba_3	JohnPhos [g]/*t*BuONa	toluene	4.5 h 65 °C	**15f** (89%)	**16f** (88%)
7	NH_3[h] $CO_{(1\ atm)}$	$Pd(OAc)_2$	Xantphos [i]/ K_3PO_4	toluene	2 h, 80 °C	**15g** (81%)	**16g** (85%)
8	Me_2NH [f] $CO_{(1\ atm)}$	$Pd(OAc)_2$	Xantphos [i]/ K_3PO_4	toluene	3 h, 80 °C	**15h** (76%)	**16h** (88%)
9	KOH	Pd_2dba_3	L[j]	dioxane/H_2O	4 h 80 °C	**15i** (79%)	**16i** (41%) [k]

[a] $PhB(OH)_2$ = phenylboronic acid. [b] 2-Bu_3Sn-thiophene = 2-(tributylstannyl)thiophene. [c] 2-Bu_3Sn-pyridine = 2-(tributylstannyl)pyridine. [d] CHex JohPhos = 2-(dicyclohexylphosphino)biphenyl. [e] TBAF was used for cleavage of TBS groups. [f] 2 M solution in THF. [g] JohnPhos = (2-biphenyl)di-*tert*-butylphosphane. [h] 0.5 M solution in 1,4-dioxane. [i] Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene. [j] L = di-*tert*-butylphosphino-3,4,5,6-tetramethyl-2′,4′,6′-triisopropylbiphenyl. [k] Trifluoroacetic acid was used for the cleavage of TBS groups.

were introduced using standard cross-couplings to give the protected alkyl, aryl, and hetaryl *C*-nucleosides **15a**−**d** in 93%, 95%, 81%, and 51%, respectively (entries 1−4). Reaction of **11** with LiHMDS in the presence of Pd_2dba_3 and cHex JohnPhos was very efficient, yielding target aminopyridine **15e** in 88% yield (entry 5). Dimethylaminopyridine **15f** was prepared in excellent 89% yield using the same conditions as in the previous series (entry 6). Palladium-catalyzed aminocarbonylation under atmospheric CO pressure was used for the synthesis of corresponding carboxamides. Thus, reaction of **11** with NH_3 (0.5 M in 1,4-dioxane) and $HNMe_2$ (2 M in THF) in the presence of $Pd(OAc)_2$, Xantphos, and K_3PO_4 at 80 °C produced target primary and tertiary amides **15g** and **15h** in 81% and 76% yield, respectively. Palladium-catalyzed hydroxylation using KOH, Pd_2dba_3 and di-*tert*-butylphosphino-3,4,5,6-tetramethyl-2′,4′,6′-triisopropylbiphenyl in 1,4-dioxane−water was used for the conversion of bromopyridine **11** to corresponding pyridone **15i** in 79% yield.

For the final cleavage of TBS-protecting groups, treatment with $Et_3N \cdot 3HF$ for 2 days at 40 °C followed by basic workup was successfully applied for compounds **15a**−**d**,**f**−**h**. Chromatographic purification by reverse-phase flash chromatography and subsequent lyophilization/crystallization give free nucleosides **16a**−**d**,**f**−**h** in good yields (52−91%, Table 2, entries 1−4, 6, 8, last column). For compound **15g**, ion-exchange chromatography (Dowex 50 in H^+ cycle, eluting with water and then 25% aqueous NH_3) had to be used prior to the reverse-phase flash chromatography purification, giving free **16g** in 85% yield. For the

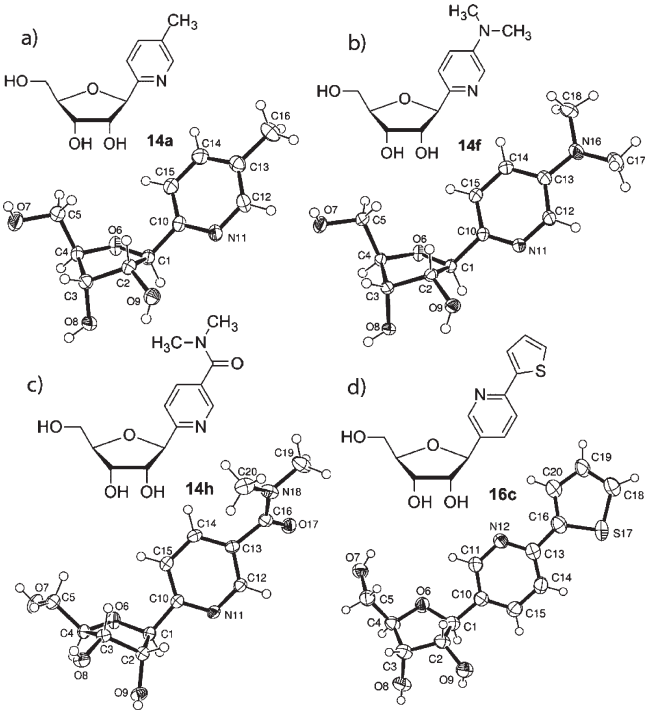

Figure 2. X-ray structures of compounds (a) **14a**, (b) **14f**, (c) **14h**, and (d) **16c**.

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Table 3. Conformational Analysis of the Sugar Part of Selected Nucleosides 14

compd	R	solvent	P_N	Φ_N	P_S	Φ_S	X_N:X_S	rms
14a	Me	DMSO-d_6	10	35	131	35	52:48	0.012
		$CDCl_3$	−29	35	146	35	40:60	0.000
14b	Ph	DMSO-d_6	4	35	127	35	49:51	0.004
		$CDCl_3$	−29	35	146	35	42:58	0.000
14c	2-thienyl	DMSO-d_6	10	35	132	35	51:49	0.011
		$CDCl_3$	−29	35	146	35	40:60	0.000
14d	2-py	DMSO-d_6	15	35	138	35	53:47	0.027
		$CDCl_3$	−34	35	144	35	40:60	0.000
14f	Me_2N	DMSO-d_6	10	35	133	35	49:51	0.010
		$CDCl_3$	−31	35	142	35	40:60	0.000
14h	$CONMe_2$	DMSO-d_6	11	35	139	35	50:50	0.011
		$CDCl_3$	−35	35	145	35	36:64	0.000

deprotection of aminopyridine *C*-nucleoside **15e**, TBAF was found as a reagent of choice. Subsequent ion-exchange chromatography (Dowex 50 in H^+ cycle) and reverse-phase chromatography furnished free *C*-nucleoside **16e** in 65% yield. Desilylation of compound **15i** was performed by treatment with TFA. Free nucleoside **16i** was purified by ion-exchange chromatography followed by reverse-phase chromatography, yielding **16i** in 41%.

Structures of several free *C*-ribonucleosides were determined by single-crystal X-ray diffraction (Figure 2). Surprisingly, the solid-state conformation of the sugar part in compounds **14a**, **14f**, and **16c** was found to be C2′-endo (S-type) typical for 2′-deoxyribonucleosides, whereas only amide **14h** adopted expected C3′-endo configuration (N-type). No intramolecular H-bonds from 5′-OH to pyridine nitrogen were observed (in contrast to previously reported[12] 6-substituted pyridin-2-yl *C*-ribonucleosides). Therefore, we have determined solution conformation of selected nucleosides by ^{1}H NMR in DMSO-d_6 and $CDCl_3$. The results (Table 3) indicate that in solution, the equilibrium of both conformers is ca. 1:1 in DMSO whereas in $CDCl_3$ the N-conformers slightly prevail.

In conclusion, a novel modular diversity-oriented synthesis of a large series of isomeric 5-substituted pyridin-2-yl and 6-substituted pyridin-3-yl *C*-ribonucleosides bearing diverse alkyl, aryl, hetaryl, amino, carbamoyl, and hydroxy groups was developed starting from 2,5-dibromopyridine. Its regioselective lithiation at position 2 (in toluene) or at position 5 (in Et_2O) gave the corresponding isomeric bromopyridyl lithium species that after addition to TBS-protected ribonolactone **4** and follow-up transformations gave the corresponding acylated hemiketals **7** and **10**. These readily underwent reductive deacetoxylation using $Et_3SiH/BF_3\cdot Et_2O$ to give a facile access to multigram amounts of key protected 5-bromypyridin-2-yl and 6-bromopyridin-3-yl *C*-ribonucleoside intermediates **8** and **11** in good overall yields (68% and 77%). These intermediates were good substrates for Pd-catalyzed cross-coupling reactions with alkylaluminum, arylboronic acids, and hetarylstannanes to give alkyl, aryl, or hetaryl derivatives. Primary and tertiary amines and carboxamines were easily prepared by Hartwig−Buchwald aminations and Pd-catalyzed aminocarbonylations. Recently developed Pd-catalyzed hydroxylation was used for the preparation of corresponding hydroxypyridine and pyridone *C*-nucleosides. Free nucleosides **14a**−**i** and **16a**−**i** were prepared by desilylation of the intermediates by $Et_3N\cdot 3HF$, TBAF, or TFA. They did not exert any considerable cytotoxicity, and therefore they are good candidates for conversion to nucleoside triphosphates as model compounds for studying specificity and fidelity of RNA polymerases and primases or could serve as building blocks for modification or construction of base-modified RNAs (artificial ribozymes, riboswitches, aptamers, etc.).

EXPERIMENTAL SECTION

All cross-coupling reactions were carried out in evacuated flame-dried glassware with magnetic stirring under argon atmosphere. THF, toluene, and hexanes were dried and distilled from sodium/benzophenone. Other reagents were purchased from commercial suppliers and used as received. NMR spectra were recorded on a 400 MHz spectrometer (^{1}H at 400 MHz, ^{13}C at 100.6 MHz), 500 MHz spectrometer (^{1}H at 500 and 125.8 MHz at ^{13}C), and/or 600 MHz spectrometer (^{1}H at 600 MHz, ^{13}C at 151 MHz). The samples were measured in $CDCl_3$ using TMS as an internal standard or in DMSO-d_6 referenced to the residual solvent signal (^{1}H NMR δ 2.50 ppm, ^{13}C NMR 39.7 ppm). Chemical shifts are given in ppm (δ scale), coupling constants (J) in hertz. Complete assignment of all NMR signals was performed using a combination of 2D-NMR (H,H-COSY, H,C-HSQC, and H,C-HMBC) experiments and configurations were established by two-dimensional ROESY spectra. Melting points were determined on a Kofler block and are uncorrected. Optical rotations were measured at 25 °C, $[\alpha]_D$ values are given in 10^{-1} deg·cm^2·g^{-1}. The X-ray diffraction experiment of single crystals was carried out on an X-ray diffractometer using $Cu_{K\alpha}$ radiation (λ = 1.54180 Å).

1β-(5-Bromopyridin-2-yl)-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (5). To a cooled (−78 °C) solution of 2,5-dibromopyridine **1** (11.3 g, 47.7 mmol, 6 equiv) in toluene (406 mL) was added *n*-BuLi (33 mL, 52.5 mmol, 6.6 equiv, 1.6 M in hexanes) dropwise over a period of 10 min. The resulting brown-yellow solution was stirred for a further 30 min at −78 °C, the solution of lactone **4** (3.9 g, 7.9 mmol) in toluene (42 mL) was added dropwise over 10 min, and the mixture was stirred for another 10 min. Subsequently absol MeOH (4.8 mL, 119 mmol, 15 equiv) was added, and the resulting orange-yellow solution was heated to ambient temperature. The reaction mixture was then poured into 2 M HCl (300 mL) and extracted into hexanes (2 × 900 mL). The combined organic layers were washed with 2 M HCl (300 mL), sat. aq $NaHCO_3$ (300 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was chromatographed on silica gel in gradient hexanes to 9% Et_2O in hexanes to give **5** (3.7 g, 73%) as a yellowish oil. HRMS (ESI) $C_{28}H_{55}NO_5Si_3Br$: [M + H] calculated 648.2566, found 648.2556. ^{1}H NMR (500 MHz, $CDCl_3$): −0.39, −0.10, 0.07, 0.09, 0.14, and 0.15 (6 × s, 6 × 3H, CH_3Si); 0.78, 0.92, and 0.95 (3 × s, 3 × 9H, $(CH_3)_3C$); 3.68 (dd, 1H, J_{gem} = 10.8 Hz, $J_{5'a,4'}$ = 7.1 Hz, H-5′a); 3.76 (dd, 1H, J_{gem} = 10.8 Hz, $J_{5'b,4'}$ = 3.9 Hz, H-5′b); 4.20 (ddd, 1H, $J_{4',5'a}$ = 7.0 Hz, $J_{4',5'b}$ = 3.9 Hz, $J_{4',3'}$ = 0.9 Hz, H-4′); 4.30 (dd, 1H, $J_{3',2'}$ = 4.5 Hz, $J_{3',4'}$ = 1.0 Hz, H-3′); 4.68 (d, 1H, $J_{2',3'}$ = 4.5 Hz, H-2′); 5.14 (s, 1H, OH-1′); 7.72 (dd, 1H, $J_{3,4}$ = 8.5 Hz, $J_{3,6}$ = 0.8 Hz, H-3); 7.79 (dd, 1H, $J_{4,3}$ = 8.5 Hz, $J_{4,6}$ = 2.4 Hz, H-4); 8.62 (dd, 1H, $J_{6,4}$ = 2.4 Hz, $J_{6,3}$ = 0.8 Hz, H-6). ^{13}C NMR (125.7 MHz, $CDCl_3$): −5.50, −5.47, −5.3, −4.9, −4.54, and −4.52 (CH_3Si); 17.9, 18.0, and 18.3 ($(CH_3)_3C$); 25.7, 25.8, and 25.9 ($(CH_3)_3C$); 63.2 (CH_2-5′); 74.7 (CH-3′); 75.0 (CH-2′); 85.1 (CH-4′); 103.3 (C-1′); 120.2 (C-5); 123.4 (CH-3); 138.7 (CH-4); 149.7 (CH-6); 157.2 (C-2). IR spectrum (CCl_4): 2957, 2929, 1858, 1471, 1463, 1259, 1116, 1009 cm^{-1}.

1β-(5-Bromopyridin-2-yl)-1,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (17). Isolated as a side-product in the synthesis of **5**. HRMS (ESI) $C_{28}H_{55}NO_5Si_3Br$: [M + H] calculated 648.2566, found 648.2556. ^{1}H NMR (500 MHz, $CDCl_3$): −0.25, 0.047, 0.052, 0.06, 0.12, and 0.13 (6 × s, 6 × 3H, CH_3Si); 0.86, 0.91, and 0.93 (3 × s, 3 × 9H, $(CH_3)_3C$); 3.06 (d, $J_{OH,2'}$ = 11.2 Hz, OH-2′); 3.76 − 3.82 (m, 2H, H-5′); 3.87 (dd, 1H, $J_{2',OH}$ = 11.2 Hz, $J_{2',3'}$ = 6.2 Hz, H-2′); 4.23 (dd,

1H, $J_{3',2'}$ = 6.2 Hz, $J_{3',4'}$ = 2.3 Hz, H-3′); 4.26 (bddd, 1H, $J_{4',5'a}$ = 4.4 Hz, $J_{4',5'b}$ = 3.5 Hz, $J_{4',3'}$ = 2.3 Hz, H-4′); 7.57 (dd, 1H, $J_{3,4}$ = 8.4 Hz, $J_{3,6}$ = 0.8 Hz, H-3); 7.75 (dd, 1H, $J_{4,3}$ = 8.4 Hz, $J_{4,6}$ = 2.4 Hz, H-4); 8.64 (dd, 1H, $J_{6,4}$ = 2.4 Hz, $J_{6,3}$ = 0.8 Hz, H-6). ^{13}C NMR (125.7 MHz, $CDCl_3$): −5.5, −5.4, −4.9, −4.7, −3.7, and −3.1 (CH_3Si); 18.1, 18.3, and 18.4 ((CH_3)$_3$C); 25.8, 25.9, and 26.0 ((CH_3)$_3$C); 63.4 (CH_2-5′); 72.9 (CH-3′); 77.6 (CH-2′); 86.1 (CH-4′); 103.7 (C-1′); 119.9 (C-5); 122.2 (CH-3); 138.6 (CH-4); 149.7 (CH-6); 160.0 (C-2).

1α-(5-Bromopyridin-2-yl)-1-*O*-acetyl-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (6). To a cooled (−78 °C) solution of 2,5-dibromopyridine **1** (267 mg, 1.13 mmol, 6 equiv) in toluene (14 mL) was added *n*-BuLi (0.7 mL, 1.13 mmol, 6 equiv, 1.6 M in hexanes) dropwise over a period of 10 min. The resulting brown-yellow solution was stirred for a further 30 min at −78 °C, a solution of lactone **4** (92 mg, 0.19 mmol) in toluene (1 mL) was added dropwise over a period of 1 min, and the stirring was continued for another 10 min. Subsequently, Ac_2O (130 μL, 1.35 mmol, 7.2 equiv) was added dropwise. and the resulting orange-yellow solution was allowed to warm to ambient temperature. The reaction mixture was then poured into sat. aq $NaHCO_3$ (20 mL), carefully neutralized, extracted to hexanes (2 × 80 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was chromatographed on silica gel in gradient hexanes to 5% Et_2O in hexanes to give **6** (23 mg, 18%) as a yellowish oil. HRMS (ESI) $C_{30}H_{56}NO_6Si_3BrNa$: [M + Na] calculated 712.2491, found 712.2493. ^{1}H NMR (500 MHz, $CDCl_3$): −0.38, −0.10, 0.06, 0.080, 0.088, and 0.090 (6 × s, 6 × 3H, CH_3Si); 0.87, 0.89, and 0.94 (3 × s, 3 × 9H, (CH_3)$_3$C); 2.09 (s, 3H, CH_3CO); 3.78 (dd, 1H, J_{gem} = 11.3 Hz, $J_{5'a,4'}$ = 2.1 Hz, H-5′a); 3.95 (dd, 1H, J_{gem} = 11.3 Hz, $J_{5'b,4'}$ = 2.9 Hz, H-5′b); 4.08 (d, 1H, $J_{2',3'}$ = 5.1 Hz, H-2′); 4.17 (dd, 1H, $J_{3',2'}$ = 5.1 Hz, $J_{3',4'}$ = 2.6 Hz, H-3′); 4.27 (m, 1H, H-4′); 7.59 (dd, 1H, $J_{3,4}$ = 8.5 Hz, $J_{3,6}$ = 0.7 Hz, H-3); 7.74 (dd, 1H, $J_{4,3}$ = 8.5 Hz, $J_{4,6}$ = 2.4 Hz, H-4); 8.55 (dd, 1H, $J_{6,4}$ = 2.4 Hz, $J_{6,3}$ = 0.7 Hz, H-6). ^{13}C NMR (125.7 MHz, $CDCl_3$): −5.62, −5.61, −5.5, −4.6, −4.40, and −4.37 (CH_3Si); 17.9, 18.1, and 18.3 ((CH_3)$_3$C); 21.9 (CH_3CO); 25.74, 25.79, and 25.9 ((CH_3)$_3$C); 62.6 (CH_2-5′); 72.1 (CH-3′); 79.6 (CH-2′); 87.3 (CH-4′); 105.6 (C-1′); 119.9 (C-5); 122.3 (CH-3); 138.8 (CH-4); 149.3 (CH-6); 157.3 (C-2); 169.8 (CO). IR spectrum (KBr): 2956, 2930, 1858, 1754, 1472, 1463, 1263, 1255, 1094, 1009, 839 cm^{-1}.

1β-(5-Bromopyridin-2-yl)-1-*O*-acetyl-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (7). To a solution of **5** (5.0 g, 7.7 mmol) in toluene (46 mL) was added LiHMDS (11.6 mL, 11.6 mmol, 1 M in THF, 1.5 equiv) at room temperature. The reaction mixture was stirred for 5 min, Ac_2O (1.1 mL, 11.6 mmol, 1.5 equiv) was added dropwise, and the stirring was continued for another 5 min (addition of 1.5 equiv of LiHMDS followed by Ac_2O (1.5 equiv) was repeated two more times). Then sat. aq $NaHCO_3$ (300 mL) was added, and the mixture was stirred for 10 min at room temperature, transferred to separatory funnel, and extracted with EtOAc (2 × 600 mL). The organic layers were dried over Na_2SO_4, concentrated under reduced pressure, and chromatographed on silica gel column eluting in gradient hexanes to 10% EtOAc in hexanes to give **7** (4.36 g, 84%) as a yellowish oil. HRMS (ESI) $C_{30}H_{56}NO_6Si_3BrNa$: [M + Na] calculated 712.2491, found 712.2492. ^{1}H NMR (500 MHz, DMSO-d_6): −0.64, −0.01, 0.03, 0.04, 0.11, and 0.15 (6 × s, 6 × 3H, CH_3Si); 0.62, 0.88, and 0.90 (3 × s, 3 × 9H, (CH_3)$_3$C); 1.92 (s, 3H, CH_3CO); 3.69 (dd, 1H, J_{gem} = 12.2 Hz, $J_{5'a,4'}$ = 3.2 Hz, H-5′a); 3.94 (dd, 1H, J_{gem} = 12.2 Hz, $J_{5'b,4'}$ = 2.3 Hz, H-5′b); 4.18 (bdt, 1H, $J_{4',3'}$ = 8.0 Hz, $J_{4',5'a}$ = $J_{4',5'b}$ = 2.7 Hz, H-4′); 4.24 (d, 1H, $J_{2',3'}$ = 3.5 Hz, H-2′); 4.55 (dd, 1H, $J_{3',4'}$ = 8.1 Hz, $J_{3',2'}$ = 3.5 Hz, H-3′); 7.50 (dd, 1H, $J_{3,4}$ = 8.5 Hz, $J_{3,6}$ = 0.8 Hz, H-3); 8.02 (dd, 1H, $J_{4,3}$ = 8.5 Hz, $J_{4,6}$ = 2.4 Hz, H-4); 8.60 (dd, 1H, $J_{6,4}$ = 2.4 Hz, $J_{6,3}$ = 0.8 Hz, H-6). ^{13}C NMR (125.7 MHz, DMSO-d_6): −5.4, −5.28, −5.27, −4.7, −4.4, and −3.8 (CH_3Si); 17.8, 18.1, and 18.4 ((CH_3)$_3$C); 21.9 (CH_3CO); 25.7, 26.1, and 26.2 ((CH_3)$_3$C); 61.1 (CH_2-5′); 70.9 (CH-3′); 78.6 (CH-2′); 83.9 (CH-4′); 107.9 (C-1′); 119.4 (C-5); 125.3 (CH-3); 138.5 (CH-4); 149.0 (CH-6); 156.1 (C-2); 167.5 (CO). IR spectrum (CCl_4): 2956, 2930, 2858, 1756, 1578, 1559, 1472, 1464, 1366, 1253, 1213, 1171, 1121, 1072, 988 cm^{-1}.

1β-(5-Bromopyridin-2-yl)-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (8). Et_3SiH (3.5 mL, 21.7 mmol, 3 equiv) was added in one portion to a stirred solution of acylated hemiketal **7** (5.0 g, 7.23 mmol) in dry dichloromethane (36 mL) on ice bath (0 °C) under argon. After 5 min, $BF_3 \cdot Et_2O$ (1.3 mL, 10.8 mmol, 1.5 equiv) was slowly added in one portion, and the resulting mixture was stirred for an additional 5 min. Subsequently, Et_3N (20 mL) was added, and the reaction mixture was evaporation under reduced pressure. The crude product was directly chromatographed on silica gel in gradient hexanes to 2% Et_2O in hexanes to give **8** (3.7 g, 81%) as a colorless oil. HRMS (ESI) $C_{28}H_{55}NO_4Si_3Br$: [M + H] calculated 632.2617, found 632.2617. ^{1}H NMR (500 MHz, $CDCl_3$): −0.17, −0.04, 0.06, 0.07, 0.10, and 0.11 (6 × s, 6 × 3H, CH_3Si); 0.84, 0.91, and 0.93 (3 × s, 3 × 9H, (CH_3)$_3$C); 3.76 (dd, 1H, J_{gem} = 11.1 Hz, $J_{5'a,4'}$ = 2.9 Hz, H-5′a); 3.87 (dd, 1H, J_{gem} = 11.1 Hz, $J_{5'b,4'}$ = 3.8 Hz, H-5′b); 4.07 (btd, 1H, $J_{4',3'}$ = $J_{4',5'b}$ = 4.0 Hz, $J_{4',5'a}$ = 2.9 Hz, H-4′); 4.10 (bt, 1H, $J_{3',2'}$ = $J_{3',4'}$ = 4.1 Hz, H-3′); 4.14 (dd, 1H, $J_{2',1'}$ = 5.4 Hz, $J_{2',3'}$ = 4.1 Hz, H-2′); 4.90 (d, 1H, $J_{1',2'}$ = 5.4 Hz, H-1′); 7.54 (bd, 1H, $J_{3,4}$ = 8.4 Hz, H-3); 7.77 (dd, 1H, $J_{4,3}$ = 8.4 Hz, $J_{4,6}$ = 2.4 Hz, H-4); 8.62 (bd, H, $J_{6,4}$ = 2.4 Hz, H-6). ^{13}C NMR (125.7 MHz, $CDCl_3$): −5.41, −5.39, −4.95, −4.61, −4.59, and −4.4 (CH_3Si); 18.00, 18.04, and 18.4 ((CH_3)$_3$C); 25.80, 25.85, and 26.0 ((CH_3)$_3$C); 62.8 (CH_2-5′); 72.5 (CH-3′); 78.5 (CH-2′); 84.4 (CH-1′); 84.7 (CH-4′); 119.4 (C-5); 123.0 (CH-3); 138.8 (CH-4); 149.9 (CH-6); 159.2 (C-2). IR spectrum (CCl_4): 2956, 1930, 1858, 1472, 1463, 1362, 1256, 1155, 1130, 1119, 1077, 1009 cm^{-1}.

1β-(6-Bromopyridin-3-yl)-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (9). To a cooled (−78 °C) solution of 2,5-dibromopyridine **1** (519 mg, 2.19 mmol, 5 equiv) in Et_2O (26 mL) was added *n*-BuLi (1.6 mL, 2.52 mmol, 5.75 equiv, 1.6 M in hexanes) dropwise over a period of 3 min. The resulting red solution was stirred for a further 30 min at −78 °C, a solution of lactone **4** (215 mg, 0.438 mmol) in Et_2O (3 mL) was added dropwise in 3 min, and stirring was continued for another 10 min. Subsequently, absol MeOH (0.18 mL, 4.38 mmol, 10 equiv) was added at −78 °C, and the resulting orange-yellow solution was allowed to warm to ambient temperature. The reaction mixture was then poured into 2 M HCl (30 mL) and extracted to Et_2O (2 × 70 mL). Combined organic layers were washed with 2 M HCl (30 mL) and sat. aq $NaHCO_3$ (30 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was chromatographed on silica gel in gradient hexanes to 2% Et_2O in hexanes to give **9** (213 mg, 75%) as a yellowish oil. HRMS (ESI) $C_{28}H_{55}NO_5Si_3Br$: [M + H] calculated 648.2566, found 648.2568. ^{1}H NMR (500 MHz, $CDCl_3$): −0.50, −0.10, 0.12, 0.127, and 0.134 (6 × s, 6 × 3H, CH_3Si); 0.84, 0.92, and 0.95 (3 × s, 3 × 9H, (CH_3)$_3$C); 3.80 (dd, 1H, J_{gem} = 11.1 Hz, $J_{5'a,4'}$ = 2.4 Hz, H-5′a); 3.84 (dd, 1H, J_{gem} = 11.1 Hz, $J_{5'b,4'}$ = 3.3 Hz, H-5′b); 4.01 (d, 1H, $J_{2',3'}$ = 4.6 Hz, H-2′); 4.18 (dd, 1H, $J_{3',2'}$ = 4.6 Hz, $J_{3',4'}$ = 0.7 Hz, H-3′); 4.23 (m, 1H, H-4′); 5.13 (s, 1H, OH-1′); 7.42 (dd, 1H, $J_{5,4}$ = 8.3 Hz, $J_{5,2}$ = 0.7 Hz, H-5); 7.80 (dd, 1H, $J_{4,5}$ = 8.3 Hz, $J_{4,2}$ = 2.5 Hz, H-4); 8.59 (dd, 1H, $J_{2,4}$ = 2.5 Hz, $J_{2,5}$ = 0.7 Hz, H-2). ^{13}C NMR (125.7 MHz, $CDCl_3$): −5.63, −5.62, −5.4, −4.8, −4.58, and −4.46 (CH_3Si); 17.81, 17.85, and 18.3 ((CH_3)$_3$C); 25.70, 25.74, and 25.9 ((CH_3)$_3$C); 63.5 (CH_2-5′); 74.9 (CH-3′); 77.7 (CH-2′); 85.5 (CH-4′); 102.8 (C-1′); 126.9 (CH-5); 136.1 (C-3); 137.4 (CH-4); 141.9 (C-6); 149.3 (CH-2). IR spectrum (CCl_4): 3499, 2956, 2931, 1585, 1472, 1462, 1363, 1257, 1103 cm^{-1}.

1β-(6-Bromopyridin-3-yl)-1,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (12). Isolated as a side-product in the synthesis of **9**. HRMS (ESI) $C_{28}H_{55}NO_5Si_3Br$: [M + H] calculated 648.2566, found 648.2566. ^{1}H NMR (500 MHz, $CDCl_3$): −0.32, 0.06, 0.07, 0.11, 0.12, and 0.13 (6 × s, 6 × 3H, CH_3Si); 0.84, 0.90, and 0.93 (3 × s, 3 × 9H, (CH_3)$_3$C); 2.99 (d, 1H, $J_{OH,2'}$ = 12.4 Hz, OH-2′); 3.70 (dd, 1H,

$J_{2',OH'}$ = 12.4 Hz, $J_{2',3'}$ = 6.4 Hz, H-2′); 3.77 (dd, 1H, J_{gem} = 11.0 Hz, $J_{5'a,4'}$ = 2.6 Hz, H-5′a); 3.83 (dd, 1H, J_{gem} = 11.0 Hz, $J_{5'b,4'}$ = 3.2 Hz, H-5′b); 4.20 (dd, 1H, $J_{3',2'}$ = 6.4 Hz, $J_{3',4'}$ = 1.7 Hz, H-3′); 4.24 (td, 1H, $J_{4',5'a} = J_{4',5'b}$ = 2.9 Hz, $J_{4',3'}$ = 1.7 Hz, H-4′); 7.40 (dd, 1H, $J_{5,4}$ = 8.3 Hz, $J_{5,2}$ = 0.8 Hz, H-5); 7.77 (dd, 1H, $J_{4,5}$ = 8.3 Hz, $J_{4,2}$ = 2.5 Hz, H-4); 8.55 (dd, 1H, $J_{2,4}$ = 2.5 Hz, $J_{2,5}$ = 0.8 Hz, H-2). ^{13}C NMR (125.7 MHz, $CDCl_3$): −5.7, −5.4, −4.9, −4.7, −3.6, and −2.9 (CH_3Si); 17.9, 18.2, and 18.4 ($(CH_3)_3C$); 25.8, 25.9, and 26.0 ($(CH_3)_3C$); 63.6 (CH_2-5′); 72.9 (CH-3′); 79.0 (CH-2′); 86.8 (CH-4′); 102.9 (C-1′); 127.0 (CH-5); 136.3 (CH-4); 138.9 (C-3); 141.4 (C-6); 147.9 (CH-2).

1β-(6-Bromopyridin-3-yl)-1-*O*-acetyl-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (10). To a cooled (−78 °C) solution of 2,5-dibromopyridine **1** (1.18 g, 5.0 mmol, 5 equiv) in Et_2O (60 mL) was added *n*-BuLi (3.6 mL, 5.73 mmol, 5.75 equiv, 1.6 M in hexanes) dropwise over a period of 3 min. The resulting red solution was stirred for a further 30 min at −78 °C, a solution of lactone **4** (489 mg, 1.00 mmol) in Et_2O (7.0 mL) was added dropwise over a period of 3 min, and the stirring was continued for another 10 min. Subsequently, Ac_2O (760 μL, 7.47 mmol, 7.5 equiv) was added dropwise, and the resulting yellow solution was allowed to warm to ambient temperature. Then the mixture was cooled to −78 °C, and LiHMDS (5.0 mL, 5.00 mmol, 5 equiv 1.0 M in THF) was added. The resulting yellow solution was stirred for a further 5 min, Ac_2O (470 μL, 5.0 mmol, 5 equiv) was added, and the reaction was allowed to warm to ambient temperature and quenched with sat. aq $NaHCO_3$ (200 mL). After additional stirring for a further 15 min, the mixture was extracted with Et_2O (2 × 300 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The resulting brown-orange solid was suspended in hexanes (500 mL), and the organic layer was filtered off and concentrated under reduced pressure to afford a yellowish oil. The crude product was chromatographed on silica gel in gradient hexanes to 6% EtOAc in hexanes to give **10** (528 mg, 77%) as a light yellow oil. HRMS (ESI) $C_{30}H_{57}NO_6Si_3Br$: [M + H] calculated 690.2672, found 690.2673. ^{1}H NMR (500 MHz, DMSO-d_6): −0.51, −0.09, 0.07, 0.09, 0.098, and 0.104 (6 × s, 6 × 3H, CH_3Si); 0.85, 0.86, and 0.92 (3 × s, 3 × 9H, $(CH_3)_3C$); 2.01 (s, 3H, CH_3CO); 3.79 (d, 1H, $J_{2',3'}$ = 5.3 Hz, H-2′); 3.80 (dd, 1H, J_{gem} = 11.5 Hz, $J_{5'a,4'}$ = 2.4 Hz, H-5′a); 3.88 (dd, 1H, J_{gem} = 11.5 Hz, $J_{5'b,4'}$ = 3.1 Hz, H-5′b); 4.10 (dd, 1H, $J_{3',2'}$ = 5.4 Hz, $J_{3',4'}$ = 1.2 Hz, H-3′); 4.21 (btd, 1H, $J_{4',5'a} = J_{4',5'b}$ = 2.7 Hz, $J_{4',3'}$ = 1.1 Hz, H-4′); 7.61 (dd, 1H, $J_{4,3}$ = 8.3 Hz, $J_{4,6}$ = 2.5 Hz, H-4); 7.67 (dd, 1H, $J_{3,4}$ = 8.3 Hz, $J_{3,6}$ = 0.8 Hz, H-3); 8.31 (bdd, 1H, $J_{6,4}$ = 2.4 Hz, $J_{6,3}$ = 0.8 Hz, H-6). ^{13}C NMR (125.7 MHz, DMSO-d_6): −5.8, −5.6, −5.4, −4.7, −4.5, and −4.2 (CH_3Si); 17.68, 17.72, and 18.0 ($(CH_3)_3C$); 21.8 (CH_3CO); 25.70, 25.73, and 25.9 ($(CH_3)_3C$); 63.0 (CH_2-5′); 72.0 (CH-3′); 80.2 (CH-2′); 88.0 (CH-4′); 104.5 (C-1′); 127.5 (CH-3); 135.8 (C-5); 136.4 (CH-4); 140.9 (C-2); 147.4 (CH-6); 168.4 (CO). IR spectrum (CCl_4):2955, 2931, 2859, 1758, 1242, 1365, 1119, 840 cm^{-1}.

1β-(6-Bromopyridin-3-yl)-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (11). Et_3SiH (630 μL, 3.9 mmol, 3 equiv) was added in one portion to a stirred solution of acylated hemiketal **10** (905 mg, 1.3 mmol) in dry dichloromethane (7 mL) cooled to −10 °C. After 5 min, $BF_3 \cdot Et_2O$ (234 μL, 2.0 mmol, 1.5 equiv) was slowly added, and the resulting mixture was stirred for an additional 5 min. Subsequently, Et_3N (20 mL) was added, and the reaction mixture was evaporation under reduced pressure. The crude product was directly chromatographed on silica gel in gradient hexanes to 2% Et_2O in hexanes to give **11** (588 mg, 71%) as a colorless oil. HRMS (ESI) $C_{28}H_{55}NO_4Si_3Br$: [M + H] calculated 632.2617, found 632.2614. ^{1}H NMR (600 MHz, $CDCl_3$): −0.44, −0.10, 0.08, 0.09, 0.10, and 0.11 (6 × s, 6 × 3H, CH_3Si); 0.81, 0.92, and 0.93 (3 × s, 3 × 9H, $(CH_3)_3C$); 3.75 (dd, 1H, J_{gem} = 11.1 Hz, $J_{5'a,4'}$ = 2.7 Hz, H-5′a); 3.78 (dd, 1H, J_{gem} = 11.1 Hz, $J_{5'b,4'}$ = 3.5 Hz, H-5′b); 3.83 (dd, $J_{2',1'}$ = 8.2 Hz, $J_{2',3'}$ = 4.4 Hz, H-2′); 4.04 (ddd, 1H, $J_{4',5'b}$ = 3.5 Hz, $J_{4',5'a}$ = 2.7 Hz, $J_{4',3'}$ = 1.4 Hz, H-4′); 4.11 (ddd, 1H, $J_{3',2'}$ = 4.4 Hz, $J_{3',4'}$ = 1.5 Hz, $J_{3',1'}$ = 0.5 Hz, H-3′); 4.75 (bd, 1H, $J_{1',2'}$ = 8.2 Hz, H-1′); 7.42 (bd, 1H, $J_{5,4}$ = 8.3 Hz, H-5); 7.67 (ddd, 1H, $J_{4,5}$ = 8.2 Hz, $J_{4,2}$ = 2.4 Hz, $J_{4,1'}$ = 0.6 Hz, H-4); 8.36 (dt, 1H, $J_{2,4}$ = 2.4 Hz, $J_{2,5} = J_{2,1'}$ = 0.6 Hz, H-2).^{13}C NMR (150.9 MHz, $CDCl_3$): −5.6, −5.4, −5.3, −4.50, −4.48, and −4.39 (CH_3Si); 17.8, 18.0, and 18.3 ($(CH_3)_3C$); 25.76, 25.83, and 25.9 ($(CH_3)_3C$); 63.6 (CH_2-5′); 74.0 (CH-3′); 79.5 (CH-2′); 79.8 (CH-1′); 86.7 (CH-4′); 127.5 (CH-5); 135.9 (C-3); 136.9 (CH-4); 141.2 (C-6); 148.9 (C-2). IR spectrum (CCl_4): 2956, 2930, 2859, 1585, 1564, 1472, 1463, 1257, 1153, 1113, 1089 cm^{-1}.

1β-(6-Bromopyridin-3-yl)-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (11): Optimized Procedure Starting from 1. To a cooled (−78 °C) solution of 2,5-dibromopyridine **1** (1.54 g, 6.47 mmol, 5 equiv) in Et_2O (78 mL) was added *n*-BuLi (4.7 mL, 7.45 mmol, 5.75 equiv, 1.6 M in hexanes) dropwise over a period of 3 min. The resulting red solution was stirred for a further 30 min at −78 °C, a solution of lactone **4** (636 mg, 1.29 mmol) in Et_2O (9.0 mL) was added dropwise over a period of 3 min, and the stirring was continued for another 10 min. Subsequently, Ac_2O (920 μL, 9.72 mmol, 7.5 equiv) was added dropwise, and resulting yellow solution was allowed to warm to ambient temperature. The mixture was then cooled to −78 °C, and LiHMDS (6.5 mL, 6.5 mmol, 5 equiv 1.0 M in THF) was added. The resulting yellow solution was stirred for a further 3 min, Ac_2O (613 μL, 6.47 mmol, 5 equiv) was added, and the reaction mixture was allowed to warm to ambient temperature and quenched with sat. aq $NaHCO_3$ (200 mL). After additional stirring for a further 20 min, the reaction mixture was extracted with Et_2O (2 × 300 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The resulting brown-orange solid was suspended in hexanes (500 mL), and the organic layer was filtered off and concentrated under reduced pressure to afford crude **10** as a yellowish oil (1.26 g). Crude **10** was dissolved in dry CH_2Cl_2 (9 mL) and cooled to −10 °C, Et_3SiH (871 μL, 5.47 mmol, 3 equiv) was added, and the resulting solution was stirred for a further 5 min. Subsequently, $BF_3 \cdot Et_2O$ (544 μL, 4.56 mmol, 2.5 equiv) was added dropwise. After 15 min, Et_3N (15 mL) was added, and the reaction mixture was warmed up to room temperature and concentrated under reduced pressure. The crude product was chromatographed on silica gel in gradient hexanes to 2.7% Et_2O in hexanes to give **11** (629 g, 77%, based on lactone **4**) as a colorless oil.

1β-(5-Methylpyridin-2-yl)-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (13a). Me_3Al (0.93 mL, 1.86 mmol, 2 equiv, 2 M in toluene) was added to a vigorously stirred solution of **8** (587 mg, 0.927 mmol) and $Pd(PPh_3)_4$ (54 mg, 0.043 mmol, 5 mol %) in THF (13 mL) under argon. The mixture was stirred at 65 °C for 12 h, quenched by pouring into saturated NaH_2PO_4 (50 mL), and extracted to EtOAc (3 × 50 mL). The crude product was chromatographed on silica gel in gradient hexanes to 3.5% EtOAc in hexanes to give **13a** (472 mg, 90%) as colorless oil. HRMS (ESI) $C_{29}H_{58}NO_4Si_3$: [M + H] calculated 568.3668, found 568.3671. ^{1}H NMR (500 MHz, DMSO-d_6): −0.25, −0.11, 0.05, 0.07, 0.08, and 0.09 (6 × s, 6 × 3H, CH_3Si); 0.77, 0.89, and 0.90 (3 × s, 3 × 9H, $(CH_3)_3C$); 2.28 (s, 3H, CH_3-5); 3.70 (dd, 1H, J_{gem} = 11.2 Hz, $J_{5'a,4'}$ = 3.4 Hz, H-5′a); 3.80 (dd, 1H, J_{gem} = 11.2 Hz, $J_{5'b,4'}$ = 4.2 Hz, H-5′b); 3.92 (bq, 1H, $J_{4',3'} = J_{4',5'a} = J_{4',5'b}$ = 3.7 Hz, H-4′); 4.10 (m, 1H, H-3′); 4.16 (dd, 1H, $J_{2',1'}$ = 5.9 Hz, $J_{2',3'}$ = 4.4 Hz, H-2′); 4.70 (d, 1H, $J_{1',2'}$ = 5.9 Hz, H-1′); 7.45 (bd, 1H, $J_{3,4}$ = 7.9 Hz, H-3); 7.57 (ddd, 1H, $J_{4,3}$ = 7.9 Hz, $J_{4,6}$ = 2.3 Hz, J_{LR} = 0.8 Hz, H-4); 8.35 (dt, 1H, $J_{6,4}$ = 2.3 Hz, $J_{6,3} = J_{LR}$ = 0.8 Hz, H-6). ^{13}C NMR (125.7 MHz, DMSO-d_6): −5.3, −5.1, and −4.6 (CH_3Si); 17.8 (CH_3-5); 17.88, 17.98, and 18.2 ($(CH_3)_3C$); 25.8, 25.9, and 26.0 ($(CH_3)_3C$); 62.9 (CH_2-5′); 72.8 (CH-3′); 78.1 (CH-2′); 84.3 and 84.4 (CH-1′,4′); 121.1 (CH-3); 132.3 (C-5); 136.9 (CH-4); 149.1 (CH-6); 157.1 (C-2). IR spectrum (CCl_4): 2956, 2929, 2858, 1602, 1574, 1472, 1463, 1389, 1362, 1254, 1155, 997, 838 cm^{-1}.

1β-(5-Phenylpyridin-2-yl)-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (13b). Compound **8** (504 mg, 0.796 mmol),

K_2CO_3 (243 mg, 1.75 mmol, 2.2 equiv), $Pd(PPh_3)_4$ (46 mg, 0.040 mmol, 5 mol %), and $PhB(OH)_2$ (194 mg, 1.59 mmol, 2 equiv) were dissolved in toluene (16 mL) under argon, and the mixture was stirred at 100 °C for 3 h. The reaction mixture was concentrated under reduced pressure, and crude product was chromatographed on silica gel in toluene to give **13b** (446 mg, 89%) as a colorless oil. HRMS (ESI) $C_{34}H_{60}NO_4Si_3$: [M + H] calculated 630.3825, found 630.3828. ^{1}H NMR (500 MHz, $CDCl_3$): −0.12, −0.01, 0.109, 0.112, 0.13, and 0.14 (6 × s, 6 × 3H, CH_3Si); 0.86, 0.95, and 0.96 (3 × s, 3 × 9H, $(CH_3)_3C$); 3.83 (dd, 1H, J_{gem} = 11.1 Hz, $J_{5'a,4'}$ = 3.5 Hz, H-5′a); 3.91 (dd, 1H, J_{gem} = 11.1 Hz, $J_{5'b,4'}$ = 4.5 Hz, H-5′b); 4.12 (td, $J_{4',3'} = J_{4',5'b}$ = 4.2 Hz, $J_{4',5'a}$ = 3.5 Hz, H-4′); 4.20 (bt, 1H, $J_{3',4'} = J_{3',2'}$ = 4.1 Hz, H-3′); 4.30 (dd, 1H, $J_{2',1'}$ = 5.7 Hz, $J_{2',3'}$ = 4.3 Hz, H-2′); 5.02 (d, 1H, $J_{1',2'}$ = 5.7 Hz, H-1′); 7.40 (m, 1H, H-*p*-Ph); 7.47 (m, 2H, H-*m*-Ph); 7.58 (m, 2H, H-*o*-Ph); 7.65 (bd, 1H, $J_{3,4}$ = 8.1 Hz, H-3); 7.86 (dd, 1H, $J_{4,3}$ = 8.1 Hz, $J_{4,6}$ = 2.4 Hz, H-4); 8.83 (dd, 1H, $J_{6,4}$ = 2.4 Hz, $J_{6,3}$ = 0.8 Hz, H-6). ^{13}C NMR (125.7 MHz, $CDCl_3$): −5.34, −5.31, −4.8, −4.48, −4.47, and −4.3 (CH_3Si); 18.10, 18.13, and 18.5 ($(CH_3)_3C$); 25.93, 25.97, and 26.1 ($(CH_3)_3C$); 63.4 (CH_2-5′); 73.1 (CH-3′); 78.6 (CH-2′); 84.5 (CH-1′); 85.1 (CH-4′); 121.9 (CH-3); 127.2 (CH-*o*-Ph); 128.1 (CH-*p*-Ph); 129.1 (CH-*m*-Ph); 135.0 (CH-4); 135.8 (C-5); 137.9 (C-*i*-Ph); 147.0 (C-6); 159.0 (C-2). IR spectrum (CCl_4): 2957, 2930, 2858, 1597, 1473, 1362, 1258, 1155, 1120, 1006 cm^{-1}.

1β-[5-(2-Thienyl)pyridin-2-yl]-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (13c). DMF (15 mL) was added to a flame-dried and argon-purged flask containing **8** (600 mg, 0.948 mmol) and $PdCl_2(PPh_3)_2$ (33 mg, 0.047 mmol, 5 mol %). After 5 min stirring at room temperature, tributyl(thiophen-2-yl)stannane (0.4 mL, 1.33 mmol, 1.4 equiv) was added, and reaction vessel was immersed to oil bath (100 °C) and stirred for 2 h. After cooling to room temperature, the crude reaction mixture was diluted with Et_2O (100 mL), washed with 2 M HCl (2 × 100 mL) and saturated $NaHCO_3$ (100 mL), and dried over $MgSO_4$. After evaporation of solvents under reduced pressure, crude product was chromatographed on silica gel in gradient hexanes to 2% EtOAc in hexanes to obtain **13c** (509 mg, 84%) as a colorless oil. HRMS (ESI) $C_{32}H_{58}NSO_4Si_3$: [M + H] calculated 636.3389, found 636.3395. ^{1}H NMR (500 MHz, $CDCl_3$): −0.10, 0.00, 0.101, 0.104, 0.13, and 0.14 (6 × s, 6 × 3H, CH_3Si); 0.87, 0.95, and 0.96 (3 × s, 3 × 9H, $(CH_3)_3C$); 3.81 (dd, 1H, J_{gem} = 11.1 Hz, $J_{5'a,4'}$ = 3.5 Hz, H-5′a); 3.90 (dd, 1H, J_{gem} = 11.1 Hz, $J_{5'b,4'}$ = 4.3 Hz, H-5′b); 4.11 (btd, 1H, $J_{4',5'b} = J_{4',3'}$ = 4.2 Hz, $J_{4',5'a}$ = 3.6 Hz, H-4′); 4.17 (t, 1H, $J_{3',2'} = J_{3',4'}$ = 4.3 Hz, H-3′); 4.29 (bdd, 1H, $J_{2',1'}$ = 5.4 Hz, $J_{2',3'}$ = 4.4 Hz, H-2′); 4.98 (d, 1H, $J_{1',2'}$ = 5.5 Hz, H-1′); 7.11 (dd, 1H, $J_{4,5}$ = 5.1 Hz, $J_{4,3}$ = 3.6 Hz, H-4-thienyl); 7.34 (bdd, 1H, $J_{5,4}$ = 5.0 Hz, $J_{5,3}$ = 1.2 Hz, H-5-thienyl); 7.35 (bdd, 1H, $J_{3,4}$ = 3.5 Hz, $J_{3,5}$ = 1.2 Hz, H-3-thienyl); 7.59 (bd, 1H, $J_{3,4}$ = 8.2 Hz, H-3); 7.83 (dd, 1H, $J_{4,3}$ = 8.1 Hz, $J_{4,6}$ = 2.3 Hz, H-4); 8.85 (bd, 1H, $J_{6,4}$ = 2.3 Hz, H-6). ^{13}C NMR (125.7 MHz, $CDCl_3$): −5.34, −5.30, −4.76, −4.50, 4.47, and −4.29 (CH_3Si); 18.09, 18.12, and 18.5 ($(CH_3)_3C$); 25.93, 25.97, and 26.1 ($(CH_3)_3C$); 63.3 (CH_2-5′); 73.0 (CH-3′); 78.5 (CH-2′); 84.7 (CH-1′); 84.9 (CH-4′); 121.9 (CH-3); 124.2 (CH-3-thienyl); 125.8 (CH-5-thienyl); 128.2 (CH-4-thienyl); 129.5 (C-5); 133.5 (CH-4); 140.6 (C-2-thienyl); 146.0 (C-6); 159.1 (C-2). IR spectrum (CCl_4): 2956, 2930, 2858, 1600, 1578, 1472, 1463, 1282, 1256, 1145, 1080 cm^{-1}.

1β-[5-(2-Pyridyl)pyridin-2-yl]-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (13d). DMF (5 mL) was added to a flame-dried and argon-purged flask containing **8** (189 mg, 0.30 mmol), and $PdCl_2(PPh_3)_2$ (11 mg, 0.015 mmol, 5 mol %). After 5 min stirring at room temperature, tributyl(pyridin-2-yl)stannane (0.15 mL, 0.45 mmol, 1.5 equiv) was added, and reaction vessel was immersed to oil bath preheated to 100 °C. After 1.5 h, the crude reaction mixture was diluted with Et_2O (300 mL), washed with 2 M HCl (2 × 100 mL) and saturated $NaHCO_3$ (100 mL), and dried over $MgSO_4$. After evaporation of solvents under reduced pressure, the crude product was chromatographed on silica gel in gradient hexanes to 10% EtOAc in hexanes to obtain **13d** (119 mg, 63%) as a colorless oil. HRMS (ESI) $C_{33}H_{59}N_2O_4Si_3$ [M + H] calculated 631.3777, found 631.3780. ^{1}H NMR (500 MHz, $CDCl_3$): −0.16, −0.04, 0.07, 0.08, 0.12, and 0.14 (6 × s, 6 × 3H, CH_3Si); 0.84, 0.92, and 0.95 (3 × s, 3 × 9H, $(CH_3)_3C$); 3.80 (dd, 1H, J_{gem} = 11.1 Hz, $J_{5'a,4'}$ = 3.2 Hz, H-5′a); 3.91 (dd, 1H, J_{gem} = 11.1 Hz, $J_{5'b,4'}$ = 4.1 Hz, H-5′b); 4.11 (td, $J_{4',3'} = J_{4',5'b}$ = 4.1 Hz, $J_{4',5'a}$ = 3.2 Hz, H-4′); 4.15 (t, 1H, $J_{3',4'} = J_{3',2'}$ = 4.2 Hz, H-3′); 4.22 (dd, 1H, $J_{2',1'}$ = 5.6 Hz, $J_{2',3'}$ = 4.2 Hz, H-2′); 5.01 (d, 1H, $J_{1',2'}$ = 5.6 Hz, H-1′); 7.29 (ddd, 1H, $J_{5,4}$ = 7.2 Hz, $J_{5,6}$ = 4.8 Hz, $J_{5,3}$ = 1.4 Hz, H-5-py); 7.72 (bd, 1H, $J_{3,4}$ = 8.1 Hz, H-3); 7.76 (dt, 1H, $J_{3,4}$ = 7.9 Hz, $J_{3,5} = J_{3,6}$ = 1.3 Hz, H-3-py); 7.79 (ddd, 1H, $J_{4,3}$ = 8.0 Hz, $J_{4,5}$ = 7.1 Hz, $J_{4,6}$ = 1.8 Hz, H-4-py); 8.31 (dd, 1H, $J_{4,3}$ = 8.2 Hz, $J_{4,6}$ = 2.3 Hz, H-4); 8.72 (ddd, 1H, $J_{6,5}$ = 4.8 Hz, $J_{6,4}$ = 1.8 Hz, $J_{6,3}$ = 1.0 Hz, H-6-py); 9.13 (dd, 1H, $J_{6,4}$ = 2.3 Hz, $J_{6,3}$ = 0.8 Hz, H-6). ^{13}C NMR (125.7 MHz, $CDCl_3$): −5.39, −5.33, −4.9, −4.6, and −4.4 (CH_3Si); 18.0, 18.1, and 18.5 ($(CH_3)_3C$); 25.85, 25.88, and 26.1 ($(CH_3)_3C$); 63.1 (CH_2-5′); 72.7 (CH-3′); 78.6 (CH-2′); 84.7 (CH-1′); 84.8 (CH-4′); 120.6 (CH-3-py); 121.6 (CH-3); 122.7 (CH-5-py); 133.7 (C-5); 134.8 (CH-4); 137.0 (CH-4-py); 147.2 (C-6); 150.0 (CH-6-py); 154.8 (C-2-py); 160.9 (C-2). IR spectrum (CCl_4): 2956, 2930, 2858, 1588, 1472, 1464, 1254, 1154, 1120, 1077, 968, 838 cm^{-1}.

1β-(5-Aminopyridin-2-yl)-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (13e). $LiN(SiMe_3)_2$ (0.58 mL, 0.575 mmol, 2 equiv 1 M solution in THF) was added to a flame-dried and argon-purged flask containing **8** (182 mg, 0.288 mmol), $Pd_2(dba)_3$, (13 mg, 0.014 mmol, 5 mol %), and tri-*tert*-butylphosphonium tetrafluoroborate (17 mg, 0.058 mmol, 20 mol %), and the mixture was stirred at 50 °C for 11 h. After cooling to room temperature, the reaction mixture was diluted with Et_2O (30 mL), washed with 2 M HCl (10 mL) and 1 M NaOH (15 mL), and dried over $MgSO_4$. The crude product was chromatographed on silica gel in gradient hexanes to 17% EtOAc in hexanes to give **13e** (103 mg, 63%) as a yellowish oil. HRMS (ESI) $C_{28}H_{57}N_2O_4Si_3$: [M + H] calculated 569.3621, found 569.3622. ^{1}H NMR (500 MHz, DMSO-d_6): −0.27, −0.13, 0.05, 0.068, 0.071, and 0.08 (6 × s, 6 × 3H, CH_3Si); 0.76, 0.89, and 0.90 (3 × s, 3 × 9H, $(CH_3)_3C$); 3.67 (dd, 1H, J_{gem} = 11.1 Hz, $J_{5'a,4'}$ = 3.6 Hz, H-5′a); 3.72 (dd, 1H, J_{gem} = 11.1 Hz, $J_{5'b,4'}$ = 4.6 Hz, H-5′b); 3.84 (m, 1H, H-4′); 4.09 (dd, 1H, $J_{3',2'}$ = 4.4 Hz, $J_{3',4'}$ = 3.1 Hz H-3′); 4.12 (dd, 1H, $J_{2',1'}$ = 6.4 Hz, $J_{2',3'}$ = 4.4 Hz, H-2′); 4.57 (d, 1H, $J_{1',2'}$ = 6.4 Hz, H-1′); 5.25 (s, 2H, NH_2); 6.86 (dd, 1H, $J_{4,3}$ = 8.4 Hz, $J_{4,6}$ = 2.7 Hz, H-4); 7.17 (d, 1H, $J_{3,4}$ = 8.4 Hz, H-3); 7.85 (d, 1H, $J_{6,4}$ = 2.7 Hz, H-6). ^{13}C NMR (125.7 MHz, DMSO-d_6): −5.34, −5.31, −4.84, −4.56, −4.48, and −4.41 (CH_3Si); 17.9, 18.0, and 18.2 ($(CH_3)_3C$); 25.87, 25.93, and 26.0 ($(CH_3)_3C$); 63.2 (CH_2-5′); 73.1 (CH-3′); 77.6 (CH-2′); 84.0 and 84.3 (CH-1′,4′); 120.1 (CH-4); 122.1 (CH-3); 135.3 (CH-6); 144.4 (C-5); 146.4 (C-2). IR spectrum (CCl_4): 3481, 3397, 2956, 2930, 2886, 2858, 1616, 1472, 1463, 1389, 1354, 1254, 1135, 1078, 838 cm^{-1}

1β-[5-(Dimethylamino)pyridin-2-yl]-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (13f). Toluene (0.5 mL) and Me_2NH (1.1 mL, 2.18 mmol, 6 equiv; 2 M solution in THF) were added to a flame-dried and argon-purged flask containing **8** (230 mg, 0.363 mmol), $Pd_2(dba)_3$ (17 mg, 0.018 mmol, 5 mol %), (2-biphenyl)-di-*tert*-butylphosphine (22 mg, 0.073 mmol, 20 mol %), and sodium *tert*-butoxide (35 mg, 0.363 mmol, 1 equiv). The resulting mixture was stirred at 60 °C for 3 h, diluted with Et_2O (50 mL), filtered through a plug of Celite, and concentrated under reduced pressure. The crude product was chromatographed on silica in gradient hexanes to 9% EtOAc in hexanes, to give **13f** (152 mg, 70%) as a colorless oil. HRMS (ESI) $C_{30}H_{61}N_2O_4Si3$: [M + H] calculated 597.3934, found 597.3935. ^{1}H NMR (500 MHz, $CDCl_3$): −0.22, −0.08, 0.067, 0.075, 0.09, and 0.10 (6 × s, 6 × 3H, CH_3Si); 0.80, 0.91, and 0.93 (3 × s, 3 × 9H, $(CH_3)_3C$); 2.95 (s, 6H,

$(CH_3)_2N$); 3.76 (dd, 1H, J_{gem} = 10.9 Hz, $J_{5'a,4'}$ = 3.7 Hz, H-5′a); 3.80 (dd, 1H, J_{gem} = 10.9 Hz, $J_{5'b,4'}$ = 5.0 Hz, H-5′b); 4.02 (dt, 1H, $J_{4',5'b}$ = 4.9 Hz, $J_{4',3'}$ = $J_{4',5'a}$ = 3.6 Hz, H-4′); 4.13 (dd, 1H, $J_{3',2'}$ = 4.4 Hz, $J_{3',4'}$ = 3.4 Hz, H-3′); 4.18 (dd, 1H, $J_{2',1'}$ = 6.1 Hz, $J_{2',3'}$ = 4.3 Hz, H-2′); 4.84 (d, 1H, $J_{1',2'}$ = 6.1 Hz, H-1′); 6.93 (dd, 1H, $J_{4,3}$ = 8.7 Hz, $J_{4,6}$ = 3.1 Hz, H-4); 7.33 (d, 1H, $J_{3,4}$ = 8.7 Hz, H-3); 8.10 (bd, H, $J_{6,4}$ = 3.1 Hz, H-6). ^{13}C NMR (125.7 MHz, $CDCl_3$): −5.41, −5.37, −4.95, −4.60, −4.55, and −4.46 (CH_3Si); 18.02, 18.06, and 18.4 ($(CH_3)_3C$); 25.84, 25.89, and 26.0 ($(CH_3)_3C$); 40.3 ($(CH_3)_2N$); 63.4 (CH_2-5′); 73.1 (CH-3′); 77.8 (CH-2′); 84.3 (CH-1′); 84.7 (CH-4′); 119.1 (CH-4); 122.1 (CH-3); 134.5 (CH-6); 145.6 (C-5); 147.4 (C-2). IR spectrum (CCl_4): 2956, 2929, 2857, 1595, 1592, 1500, 1463, 1361, 1253, 1155, 1140, 1079 cm^{-1}.

1β-[5-(Carbamoyl)pyridin-2-yl]-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (13g). A flame-dried septum-sealed flask (30 mL) containing **8** (478 mg, 0.755 mmol), $Pd(OAc)_2$ (17 mg, 0.076 mmol, 5 mol %), Xantphos (87 mg, 0.151 mmol, 10 mol %), and K_3PO_4 (481 mg, 2.27 mmol, 3 equiv) was evacuated and backfilled with $CO_{(g)}$. Then, toluene (3 mL) and NH_3 (6 mL, 3.02 mmol, 4 equiv; 0.5 M solution in dioxane) were added via syringe. The reaction mixture was stirred at room temperature for 5 min and then immersed into a preheated oil bath (80 °C) and vigorously stirred for 6 h. After cooling to the room temperature, Et_2O (15 mL) was added, and the reaction mixture was filtered through a plug of Celite (eluting with Et_2O) and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel in gradient hexanes to 25% EtOAc in hexanes to give **13g** (335 mg, 74%) as a white solid. HRMS (ESI) $C_{29}H_{57}N_2O_5Si_3$: [M + H] calculated 597.3570, found 597.3575. ^{1}H NMR (500 MHz, $CDCl_3$): −0.19, −0.05, 0.062, 0.063, 0.11, and 0.12 (6 × s, 6 × 3H, CH_3Si); 0.83, 0.91, and 0.93 (3 × s, 3 × 9H, $(CH_3)_3C$); 3.78 (dd, 1H, J_{gem} = 11.2 Hz, $J_{5'a,4'}$ = 2.7 Hz, H-5′a); 3.90 (dd, 1H, J_{gem} = 11.2 Hz, $J_{5'b,4'}$ = 3.5 Hz, H-5′b); 4.09 − 4.12 (m, 2H, H-3′,4′); 4.16 (dd, 1H, $J_{2',1'}$ = 5.6 Hz, $J_{2',3'}$ = 3.9 Hz, H-2′); 5.00 (d, 1H, $J_{1',2'}$ = 5.6 Hz, H-1′); 5.91 and 6.41 (2 × bs, 2 × 1H, NH_2); 7.76 (d, 1H, $J_{3,4}$ = 8.2 Hz, H-3); 8.16 (dd, 1H, $J_{4,3}$ = 8.2 Hz, $J_{4,6}$ = 2.3 Hz, H-4); 9.03 (bd, 1H, $J_{6,4}$ = 2.3 Hz, H-6). ^{13}C NMR (125.7 MHz, $CDCl_3$): −5.42, −5.38, −5.0, −4.6, and −4.4 (CH_3Si); 17.97, 18.03, and 18.4 ($(CH_3)_3C$); 25.79, 25.84, and 26.0 ($(CH_3)_3C$); 62.8 (CH_2-5′); 72.7 (CH-3′); 78.7 (CH-2′); 84.3 (CH-1′); 85.1 (CH-4′); 121.5 (CH-3); 128.0 (C-5); 136.5 (CH-4); 147.0 (CH-6); 164.1 (C-2); 167.1 (CO). IR spectrum (CCl_4):2956, 2930, 2858, 1687, 1598, 1472, 1463, 1390, 1362, 1254, 1155, 1119 cm^{-1}.

1β-[5-(Dimethylcarbamoyl)pyridin-2-yl]-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (13h). A flame-dried septum-sealed flask containing **8** (551 mg, 0.871 mmol), $Pd(OAc)_2$ (9.8 mg, 0.044 mmol, 5 mol %), Xantphos (50 mg, 0.087 mmol, 10 mol %), K_3PO_4 (1109 mg, 5.22 mmol, 6 equiv), and $Me_2NH\cdot HCl$ (213 mg, 2.61 mmol, 3 equiv) was evacuated and backfilled with $CO_{(g)}$. Then, toluene (3.5 mL) was added, and the reaction mixture was stirred at room temperature for 5 min, immersed into a preheated oil bath (80 °C), and vigorously stirred for 1.5 h under CO atmosphere (baloon). After the completion of the reaction (monitored by TLC, Hexanes/EtOAc 8:2), the mixture was cooled to room temperature, diluted with Et_2O (20 mL), filtered through a plug of Celite (eluting with Et_2O), and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel in gradient hexanes to 17% ethyl acetate in hexanes, furnishing **13h** (435 mg, 80%) as a colorless oil. HRMS (ESI) $C_{31}H_{61}N_2O_5Si_3$: [M + H] calculated 625.3883, found 625.3880. ^{1}H NMR (500 MHz, $CDCl_3$): −0.15, −0.04, 0.059, 0.063, 0.11, and 0.12 (6 × s, 6 × 3H, CH_3Si); 0.83, 0.91, and 0.93 (3 × s, 3 × 9H, $(CH_3)_3C$); 3.00 and 3.12 (2 × s, 2 × 3H, $(CH_3)_2N$); 3.78 (dd, 1H, J_{gem} = 11.2 Hz, $J_{5'a,4'}$ = 2.9 Hz, H-5′a); 3.90 (dd, 1H, J_{gem} = 11.2 Hz, $J_{5'b,4'}$ = 3.7 Hz, H-5′b); 4.06 − 4.12 (m, 2H, H-3′,4′); 4.16 (dd, 1H, $J_{2',1'}$ = 5.3 Hz, $J_{2',3'}$ = 3.8 Hz, H-2′); 4.97 (d, 1H, $J_{1',2'}$ = 5.2 Hz, H-1′); 7.70 (d, 1H, $J_{3,4}$ = 8.0 Hz, H-3); 7.74 (dd, 1H, $J_{4,3}$ = 8.0 Hz, $J_{4,6}$ = 2.0 Hz, H-4); 8.63 (bd, H, $J_{6,4}$ = 2.1 Hz, H-6). ^{13}C NMR (125.7 MHz, $CDCl_3$): −5.41, −5.39, −4.9, −4.62, −4.59, and −4.4 (CH_3Si); 18.00, 18.02, and 18.4 ($(CH_3)_3C$); 25.81, 25.84, and 26.0 ($(CH_3)_3C$); 35.47 and 39.54 ($(CH_3)_2N$); 62.8 (CH_2-5′); 72.4 (CH-3′); 78.6 (CH-2′); 84.7 (CH-1′,4′); 121.2 (CH-3); 130.9 (C-5); 135.7 (CH-4); 147.0 (CH-6); 161.8 (C-2); 169.1 (CO). IR spectrum (CCl_4): 2956, 2930, 22858, 1646, 4597, 1472, 1463, 1393, 1255, 1155, 1120, 1083, 878 cm^{-1}.

1β-(5-Hydroxypyridin-2-yl)-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (13i). A septum-sealed flask containing **8** (342 mg, 0.540 mmol), Pd_2bda_3 (12 mg, 0.014 mmol, 2.5 mol %), 2-di-*tert*-butylphosphino-3,4,5,6-tetramethyl-2′,4′,6′-triisopropylbiphenyl (26 mg, 0.054 mmol, 10 mol %) and KOH (91 mg, 1.62 mmol, 3 equiv) was evacuated and backfilled with argon. Then 1,4-dioxane (0.8 mL) and water (0.3 mL) were added. The resulting dark-brown reaction mixture was immersed into preheated oil bath (80 °C) and stirred for 1.5 h. After the completion of the reaction (monitored by TLC, hexanes/EtOAc 10:1), the mixture was cooled to room temperature, diluted with THF (10 mL), filtered through a plug of Celite (eluting with THF), and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel in gradient chloroform to 13% ethyl acetate in chloroform, furnishing **13i** (227 mg, 73%) as a white foam. HRMS (ESI) $C_{28}H_{56}NO_5Si_3$: [M + H] calculated 570.3461, found 570.3463. ^{1}H NMR (500 MHz, DMSO-d_6): −0.29, −0.13, 0.05, 0.07, and 0.08 (6 × s, 6 × 3H, CH_3Si); 0.76, 0.891, and 0.895 (3 × s, 3 × 9H, $(CH_3)_3C$); 3.68 (dd, 1H, J_{gem} = 11.2 Hz, $J_{5'a,4'}$ = 3.6 Hz, H-5′a); 3.74 (dd, 1H, J_{gem} = 11.2 Hz, $J_{5'b,4'}$ = 4.6 Hz, H-5′b); 3.88 (dt, 1H, $J_{4',5'b}$ = 4.6 Hz, $J_{4',5'a}$ = $J_{4',3'}$ = 3.3 Hz, H-4′); 4.09 (dd, 1H, $J_{3',2'}$ = 4.4 Hz, $J_{3',4'}$ = 3.1 Hz H-3′); 4.14 (dd, 1H, $J_{2',1'}$ = 6.5 Hz, $J_{2',3'}$ = 4.4 Hz, H-2′); 4.64 (d, 1H, $J_{1',2'}$ = 6.5 Hz, H-1′); 7.10 (dd, 1H, $J_{4,3}$ = 8.5 Hz, $J_{4,6}$ = 2.8 Hz, H-4); 7.35 (bd, 1H, $J_{3,4}$ = 8.5 Hz, H-3); 8.04 (dd, 1H, $J_{6,4}$ = 2.8 Hz, $J_{6,3}$ = 0.6 Hz, H-6); 9.85 (s, 1H, OH-5). ^{13}C NMR (125.7 MHz, DMSO-d_6): −5.32, −5.29, −4.95, −4.55, −4.47, and −4.40 (CH_3Si); 17.90, 17.99, and 18.2 ($(CH_3)_3C$); 25.85, 25.94, and 26.02 ($(CH_3)_3C$); 63.2 (CH_2-5′); 73.1 (CH-3′); 77.9 (CH-2′); 83.8 (CH-1′); 84.6 (CH-4′); 122.5 (CH-3,4); 136.9 (CH-6); 150.0 (C-2); 153.3 (C-5). IR spectrum (CCl_4): 2956, 2930, 2858, 1472, 1463, 1255, 1155, 1120, 1077, 838 cm^{-1}.

1β-(6-Methylpyridin-3-yl)-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (15a). Me_3Al (0.76 mL, 1.51 mmol, 2 equiv, 2 M in toluene) was added to a vigorously stirred solution of **11** (479 mg, 0.757 mmol) and $Pd(PPh_3)_4$ (44 mg, 0.038 mmol, 5 mol %) in THF (11 mL) under argon. The mixture was stirred at 70 °C for 2 h, quenched by pouring into saturated NaH_2PO_4 (50 mL), and extracted to EtOAc (3 × 50 mL). The crude product was chromatographed on silica gel in gradient hexanes to 7.5% EtOAc in hexanes to give **15a** (400 mg, 93%) as colorless oil. HRMS (ESI) $C_{29}H_{58}NO_4Si_3$: [M + H] calculated 568.3668, found 568.3666. ^{1}H NMR (500 MHz, $CDCl_3$): −0.44, −0.11, 0.09, 0.10, 0.11, and 0.12 (6 × s, 6 × 3H, CH_3Si); 0.81, 0.93, and 0.94 (3 × s, 3 × 9H, $(CH_3)_3C$); 2.56 (s, 3H, CH_3); 3.76 (dd, 1H, J_{gem} = 11.0 Hz, $J_{5'a,4'}$ = 3.2 Hz, H-5′a); 3.79 (dd, 1H, J_{gem} = 11.0 Hz, $J_{5'b,4'}$ = 3.6 Hz, H-5′b); 3.86 (dd, 1H, $J_{2',1'}$ = 8.0 Hz, $J_{2',3'}$ = 4.4 Hz, H-2′); 4.04 (td, 1H, $J_{4',5'a}$ = $J_{4',5'b}$ = 3.4 Hz, $J_{4',3'}$ = 1.7 Hz, H-4′); 4.13 (dd, 1H, $J_{3',2'}$ = 4.5 Hz, $J_{3',4'}$ = 1.7 Hz, H-3′); 4.77 (d, 1H, $J_{1',2'}$ = 8.0 Hz, H-1′); 7.12 (d,1H, $J_{3,4}$ = 8.0 Hz, H-3); 7.71 (bd, 1H, $J_{3,4}$ = 8.0 Hz, H-4); 8.47 (d, 1H, $J_{6,4}$ = 2.2 Hz, H-6). ^{13}C NMR (125.7 MHz, $CDCl_3$): −5.5, −5.4, −5.3, −4.49, −4.47, and −4.40 (CH_3Si); 17.9, 18.1, and 18.4 ($(CH_3)_3C$); 23.8 (CH_3); 25.8, 25.9, and 26.0 ($(CH_3)_3C$); 63.7 (CH_2-5′); 73.9 (CH-3′); 79.4 (CH-2′); 80.5 (CH-1′); 86.4 (CH-4′); 122.9 (CH-3); 133.2 (C-5); 135.1 (CH-4); 147.5 (CH-6); 157.6 (C-2). IR spectrum (CCl_4): 2956, 2858, 1605, 1472, 1463, 1257, 1153, 1113, 838 cm^{-1}.

1β-(6-Phenylpyridin-3-yl)-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (15b). Compound **11** (458 mg, 0.724 mmol),

K_2CO_3 (221 mg, 1.59 mmol, 2.2 equiv), $Pd(PPh_3)_4$ (42 mg, 0.036 mmol, 5 mol %), and $PhB(OH)_2$ (177 mg, 1.45 mmol, 2 equiv) were dissolved in toluene (15 mL) under argon, and the mixture was stirred at 110 °C for 1.5 h. The reaction mixture was filtered through a plug of Celite and concentrated under reduced pressure. The crude product was chromatographed on silica gel in gradient hexanes to 6% Et_2O in hexanes to give **15b** (437 mg, 95%) as a colorless oil. HRMS (ESI) $C_{34}H_{60}NO_4Si_3$: [M + H] calculated 630.3825, found 630.3823. ^{1}H NMR (500 MHz, $CDCl_3$): −0.40, −0.09, 0.110, 0.113, 0.13, and 0.15 (6 × s, 6 × 3H, CH_3Si); 0.82 and 0.95 (3 × s, 3 × 9H, $(CH_3)_3C$); 3.80 (dd, 1H, J_{gem} = 11.0 Hz, $J_{5'a,4'}$ = 3.2 Hz, H-5′a); 3.82 (dd, 1H, J_{gem} = 11.0 Hz, $J_{5'b,4'}$ = 3.8 Hz, H-5′b); 3.92 (dd, 1H, $J_{2',1'}$ = 7.8 Hz, $J_{2',3'}$ = 4.4 Hz, H-2′); 4.08 (td, 1H, $J_{4',5'a} = J_{4',5'b}$ = 3.5 Hz, $J_{4',3'}$ = 1.8 Hz, H-4′); 4.17 (dd, 1H, $J_{3',2'}$ = 4.4 Hz, $J_{3',4'}$ = 1.8 Hz, H-3′); 4.86 (d, 1H, $J_{1',2'}$ = 7.8 Hz, H-1′); 7.41 (m, 1H, H-*p*-Ph); 7.48 (m, 2H, H-*m*-Ph); 7.70 (d, 1H, $J_{3,4}$ = 8.2 Hz, H-3); 7.88 (m, 1H, H-4); 8.00 (m, 2H, H-*o*-Ph); 8.68 (d, 1H, $J_{6,4}$ = 2.2 Hz, H-6). ^{13}C NMR (125.7 MHz, $CDCl_3$): −5.5, −5.4, −5.2, −4.47, −4.45, and −4.40 (CH_3Si); 17.9, 18.1, and 18.4 ($(CH_3)_3C$); 25.8, 25.9, and 26.0 ($(CH_3)_3C$); 63.7 (CH_2-5′); 73.9 (CH-3′); 79.5 (CH-2′); 80.6 (CH-1′); 86.3 (CH-4′); 120.1 (CH-3); 127.0 (CH-*o*-Ph); 128.7 (CH-*m,p*-Ph); 134.7 (C-5); 135.3 (CH-4); 139.4 (C-*i*-Ph); 148.5 (CH-6); 156.9 (C-2). IR spectrum (CCl_4): 2956, 2930, 1599, 1565, 1473, 1257, 1153 cm^{-1}.

1β-[6-(2-Thienyl)pyridin-3-yl]-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (15c). DMF (12 mL) was added to a flame-dried and argon-purged flask containing **11** (453 mg, 0.716 mmol) and $PdCl_2(PPh_3)_2$ (25 mg, 0.036 mmol, 5 mol %). After 5 min stirring at room temperature, tributyl(thiophen-2-yl)stannane (320 μL, 1.00 mmol, 1.4 equiv) was added, and reaction vessel was immersed to oil bath (110 °C) and stirred for 1.5 h. After cooling to room temperature, the crude reaction mixture was diluted with Et_2O (100 mL), washed with 2 M HCl (2 × 100 mL) and saturated $NaHCO_3$ (100 mL), and dried over $MgSO_4$. After evaporation of solvents under reduced pressure, the crude product was chromatographed on silica gel in gradient hexanes to 6% Et_2O in hexanes to obtain **15c** (370 mg, 81%) as a colorless oil. HRMS (ESI) $C_{32}H_{58}NSO_4Si_3$: [M + H] calculated 636.3389, found 636.3387. ^{1}H NMR (500 MHz, $CDCl_3$): −0.38, −0.09, 0.103, 0.104, 0.12, and 0.14 (6 × s, 6 × 3H, CH_3Si); 0.83, 0.94, and 0.95 (3 × s, 3 × 9H, $(CH_3)_3C$); 3.79 (m, 2H, H-5′); 3.90 (dd, 1H, $J_{2',1'}$ = 7.7 Hz, $J_{2',3'}$ = 4.4 Hz, H-2′); 4.06 (td, 1H, $J_{4',5'a} = J_{4',5'b}$ = 3.5 Hz, $J_{4',3'}$ = 2.0 Hz, H-4′); 4.15 (dd, 1H, $J_{3',2'}$ = 4.4 Hz, $J_{3',4'}$ = 1.9 Hz, H-3′); 4.81 (d, 1H, $J_{1',2'}$ = 7.7 Hz, H-1′); 7.11 (dd, 1H, $J_{4,5}$ = 5.1 Hz $J_{4,3}$ = 3.7 Hz, H-4-thienyl); 7.38 (dd, 1H, $J_{5,4}$ = 5.1 Hz, $J_{5,3}$ = 1.2 Hz, H-5-thienyl); 7.59 (m, 1H, H-3-thienyl); 7.61 (bd, 1H, $J_{3,4}$ = 8.2 Hz, H-3); 7.87 (bd, 1H, $J_{3,4}$ = 8.2 Hz, H-4); 8.54 (d, 1H, $J_{6,4}$ = 2.2 Hz, H-6). ^{13}C NMR (125.7 MHz, $CDCl_3$): −5.5, −5.4, −5.1, −4.47, −4.45, and −4.42 (CH_3Si); 17.9, 18.1, and 18.4 ($(CH_3)_3C$); 25.8, 25.9, and 26.0 ($(CH_3)_3C$); 63.7 (CH_2-5′); 73.8 (CH-3′); 79.4 (CH-2′); 80.7 (CH-1′); 86.2 (CH-4′); 118.3 (CH-3); 124.4 (CH-3-thienyl); 127.3 (CH-5-thienyl); 128.0 (CH-4-thienyl); 134.6 (C-5); 135.1 (CH-4); 144.9 (C-2-thienyl); 148.3 (CH-6); 152.1 (C-2). IR spectrum (CCl_4): 2956, 2930, 2585, 1730, 1598, 1473, 1257, 1115 cm^{-1}.

1β-[6-(2-Pyridyl)pyridin-3-yl]-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (15d). DMF (6 mL) was added to a flame-dried and argon-purged flask containing **11** (366 mg, 0.578 mmol) and $PdCl_2(PPh_3)_2$ (20 mg, 0.029 mmol, 5 mol %). After 5 min stirring at room temperature, tributyl(pyridin-2-yl)stannane (280 μL, 0.867 mmol, 1.5 equiv) was added, and the reaction vessel was immersed to oil bath preheated to 80 °C. After 4.5 h, crude reaction mixture was diluted with Et_2O (300 mL), washed with 2 M HCl (2 × 100 mL) and sat. $NaHCO_3$ (100 mL), and dried over $MgSO_4$. After evaporation of solvents under reduced pressure, crude product was chromatographed on silica gel in gradient hexanes to 6% EtOAc in hexanes to obtain **15d** (186 mg, 51%) as a colorless oil. HRMS (ESI) $C_{33}H_{59}N_2O_4Si_3$ [M + H] calculated 631.3777, found 631.3775. ^{1}H NMR (500 MHz, DMSO-d_6): −0.49, −0.13, 0.10, 0.116, 0.122, and 0.14 (6 × s, 6 × 3H, CH_3Si); 0.77, 0.92, and 0.93 (3 × s, 3 × 9H, $(CH_3)_3C$); 3.78 (dd, 1H, J_{gem} = 11.2 Hz, $J_{5'a,4'}$ = 3.1 Hz, H-5′a); 3.83 (dd, 1H, J_{gem} = 11.2 Hz, $J_{5'b,4'}$ = 4.2 Hz, H-5′b); 3.99 (bddd, $J_{4',5'b}$ = 4.2 Hz, $J_{4',5'a}$ = 3.0 Hz, $J_{4',3'}$ = 1.4 Hz, H-4′); 4.00 (dd, 1H, $J_{2',1'}$ = 8.2 Hz, $J_{2',3'}$ = 4.4 Hz, H-2′); 4.14 (dd, 1H, $J_{3',2'}$ = 4.4 Hz, $J_{3',4'}$ = 1.4 Hz, H-3′); 4.74 (d, 1H, $J_{1',2'}$ = 8.2 Hz, H-1′); 7.45 (ddd, 1H, $J_{5,4}$ = 7.5 Hz, $J_{5,6}$ = 4.8 Hz, $J_{5,3}$ = 1.2 Hz, H-5-py); 7.94 (btd, 1H, $J_{4,3} = J_{4,5}$ = 7.7 Hz, $J_{4,6}$ = 1.9 Hz, H-4-py); 7.95 (bdd, 1H, $J_{4,3}$ = 8.2 Hz, $J_{4,6}$ = 2.2 Hz, H-4); 8.35 (dd, 1H, $J_{3,4}$ = 8.2 Hz, $J_{3,6}$ = 0.8 Hz, H-3); 8.38 (dt, 1H, $J_{3,4}$ = 8.0 Hz, $J_{3,5} = J_{3,6}$ = 1.1 Hz, H-3-py); 8.65 (bd, 1H, $J_{6,4}$ = 2.3 Hz, H-6); 8.68 (ddd, 1H, $J_{6,5}$ = 4.7 Hz, $J_{6,4}$ = 1.8 Hz, $J_{6,3}$ = 0.9 Hz, H-6-py). ^{13}C NMR (125.7 MHz, DMSO-d_6): −5.42, −5.34, −5.32, −4.50, −4.45, and −4.36 (CH_3Si); 17.7, 18.0, and 18.2 ($(CH_3)_3C$); 25.8, 25.9, and 26.0 ($(CH_3)_3C$); 63.5 (CH_2-5′); 74.1 (CH-3′); 79.1 (CH-2′); 80.1 (CH-1′); 86.2 (CH-4′); 120.0 (CH-3); 120.6 (CH-3-py); 124.4 (CH-5-py); 135.6 (CH-4); 136.4 (C-5); 137.5 (CH-4-py); 148.3 (CH-6); 149.5 (CH-6-py); 155.2 and 155.3 (C-2, C-2-py). IR spectrum (CCl_4): 2956, 2930, 2858, 1591, 1577, 1560, 1472, 1462, 1255, 1153, 1113 cm^{-1}.

1β-(6-Aminopyridin-3-yl)-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (15e). $LiN(SiMe_3)_2$ (1.1 mL, 1.1 mmol, 1.5 equiv 1 M solution in THF) was added to a flame-dried and argon-purged flask containing **11** (464 mg, 0.733 mmol), $Pd_2(dba)_3$, (17 mg, 0.018 mmol, 2.5 mol %), and tri-*tert*-butylphosphonium tetrafluoroborate (26 mg, 0.073 mmol, 10 mol %), and the mixture was stirred at 50 °C for 5 h. After cooling to room temperature, the reaction mixture was diluted with Et_2O (60 mL), washed with 2 M HCl (2 × 30 mL) and 1 M NaOH (30 mL), and dried over $MgSO_4$. The crude product was chromatographed on silica gel in gradient chloroform to 1.2% MeOH in chloroform to give **15e** (367 mg, 88%) as a yellowish oil. HRMS (ESI) $C_{28}H_{57}N_2O_4Si_3$: [M + H] calculated 569.3621, found 569.3620. ^{1}H NMR (500 MHz, $CDCl_3$): −0.36, −0.09, 0.087, 0.093, 0.10, and 0.11 (6 × s, 6 × 3H, CH_3Si); 0.81, 0.930, and 0.933 (3 × s, 3 × 9H, $(CH_3)_3C$); 3.71 − 3.79 (m, 2H, H-5′); 3.84 (dd, 1H, $J_{2',1'}$ = 8.1 Hz, $J_{2',3'}$ = 4.5 Hz, H-2′); 4.00 (td, 1H, $J_{4',5'a} = J_{4',5'b}$ = 3.4 Hz, $J_{4',3'}$ = 1.6 Hz, H-4′); 4.11 (dd, 1H, $J_{3',2'}$ = 4.5 Hz, $J_{3',4'}$ = 1.6 Hz, H-3′); 4.66 (d, 1H, $J_{1',2'}$ = 8.1 Hz, H-1′); 4.89 (bs, 2H, NH_2); 6.55 (dd, 1H, $J_{3,4}$ = 8.6 Hz, $J_{3,6}$ = 0.6 Hz, H-3); 7.61 (dd, 1H, $J_{4,3}$ = 8.6 Hz, $J_{4,6}$ = 2.3 Hz, H-4); 7.99 (bd, 1H, $J_{6,4}$ = 2.2 Hz, H-6). ^{13}C NMR (125.7 MHz, $CDCl_3$): −5.5, −5.4, −5.1, −4.48, −4.44, and −4.41 (CH_3Si); 17.9, 18.1, and 18.4 ($(CH_3)_3C$); 25.8, 25.9, and 26.0 ($(CH_3)_3C$); 63.8 (CH_2-5′); 74.0 (CH-3′); 79.0 (CH-2′); 80.4 (CH-1′); 86.2 (CH-4′); 109.1 (CH-3); 126.1 (C-5); 137.7 (CH-4); 144.6 (CH-6); 157.5 (C-2). IR spectrum (CCl_4): 34813509, 3408, 2956, 2930, 2858, 1616, 1500, 1257, 1154 cm^{-1}

1β-[6-(Dimethylamino)pyridin-3-yl]-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (15f). Me_2NH (1.6 mL, 3.13 mmol, 7 equiv; 2 M solution in THF) was added to a flame-dried and argon-purged flask containing **11** (283 mg, 0.447 mmol), $Pd_2(dba)_3$ (10 mg, 0.011 mmol, 2.5 mol %), (2-biphenyl)-di-*tert*-butylphosphine (14 mg, 0.045 mmol, 10 mol %), and sodium *tert*-butoxide (43 mg, 0.447 mmol, 1 equiv). The resulting mixture was stirred at 65 °C for 4.5 h, diluted with Et_2O (75 mL), filtered through a plug of Celite, and concentrated under reduced pressure. The crude product was chromatographed on silica in gradient hexanes to 6% EtOAc in hexanes to give **15f** (237 mg, 89%) as colorless oil. HRMS (ESI) $C_{30}H_{61}N_2O_4Si_3$: [M + H] calculated 597.3934, found 597.3933.^{1}H NMR (500 MHz, DMSO-d_6): −0.41, −0.14, 0.08, 0.09, and 0.10 (6 × s, 6 × 3H, CH_3Si); 0.76, 0.906, and 0.909 (3 × s, 3 × 9H, $(CH_3)_3C$); 2.99 (s, 6H, $(CH_3)_2N$); 3.70 (dd, 1H, J_{gem} = 11.0 Hz, $J_{5'a,4'}$ = 3.5 Hz, H-5′a); 3.73 (dd, 1H, J_{gem} = 11.1

Hz, $J_{5'b,4'}$ = 4.2 Hz, H-5′b); 3.86 (btd, 1H, $J_{4',5'a} = J_{4',5'b}$ = 3.8 Hz, $J_{4',3'}$ = 1.6 Hz, H-4′); 3.91 (dd, 1H, $J_{2',1'}$ = 8.1 Hz, $J_{2',3'}$ = 4.5 Hz, H-2′); 4.09 (dd, 1H, $J_{3',2'}$ = 4.5 Hz, $J_{3',4'}$ = 1.6 Hz, H-3′); 4.49 (d, 1H, $J_{1',2'}$ = 8.1 Hz, H-1′); 6.59 (d, 1H, $J_{3,4}$ = 8.8 Hz, H-3); 7.49 (dd, 1H, $J_{4,3}$ = 8.8 Hz, $J_{4,6}$ = 2.4 Hz, H-4); 7.99 (d, 1H, $J_{6,4}$ = 2.4 Hz, H-6). ^{13}C NMR (125.7 MHz, DMSO-d_6): −5.4, −5.3, −5.0, −4.46, −4.44, and −4.40 (CH_3Si); 17.8, 18.0, and 18.2 ($(CH_3)_3C$); 25.82, 25.95, and 25.99 ($(CH_3)_3C$); 37.9 ($(CH_3)_2N$) 63.6 (CH_2-5′); 73.9 (CH-3′); 78.3 (CH-2′); 80.5 (CH-1′); 85.4 (CH-4′); 105.4 (CH-3); 122.5 (C-5); 136.1 (CH-4); 146.9 (CH-6); 159.3 (C-2). IR spectrum (CCl_4): 2955, 2930, 1922, 1611, 1563, 1514, 1472, 1463, 1256, 1151 cm^{-1}.

1β-[6-(Carbamoyl)pyridin-3-yl]-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (15g). A flame-dried septum-sealed flask (30 mL) containing **11** (304 mg, 0.480 mmol), $Pd(OAc)_2$ (5.4 mg, 0.024 mmol, 5 mol %), Xantphos (28 mg, 0.048 mmol, 10 mol %), and K_3PO_4 (306 mg, 1.44 mmol, 3 equiv) was evacuated and backfilled with CO(g). Then, toluene (0.5 mL) and NH_3 (3.8 mL, 1.92 mmol, 4 equiv; 0.5 M solution in 1,4-dioxane) were added via syringe. The reaction mixture was stirred at room temperature for 5 min, immersed into a preheated oil bath (80 °C), and vigorously stirred for 2 h. After cooling to the room temperature, Et_2O (20 mL) was added, and the reaction mixture was filtered through a plug of Celite (eluting with Et_2O) and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel in gradient chloroform to 7.4% EtOAc in chloroform to give **15g** (233 mg, 81%) as a white foam. HRMS (ESI) $C_{29}H_{57}N_2O_5Si_3$: [M + H] calculated 597.3570, found 597.3573. ^{1}H NMR (500 MHz, $CDCl_3$): −0.49, −0.10, 0.10, 0.11, 0.12, and 0.13 (6 × s, 6 × 3H, CH_3Si); 0.81, 0.93, and 0.94 (3 × s, 3 × 9H, $(CH_3)3C$); 3.78 (dd, 1H, J_{gem} = 11.1 Hz, $J_{5'a,4'}$ = 2.7 Hz, H-5′a); 3.82 (dd, 1H, J_{gem} = 11.1 Hz, $J_{5'b,4'}$ = 3.6 Hz, H-5′b); 3.88 (dd, 1H, $J_{2',1'}$ = 8.2 Hz, $J_{2',3'}$ = 4.4 Hz, H-2′); 4.08 (ddd, 1H, $J_{4',5'b}$ = 3.6 Hz, $J_{4',5'a}$ = 2.7 Hz, $J_{4',3'}$ = 1.4 Hz, H-4′); 4.14 (dd, 1H, $J_{3',2'}$ = 4.4 Hz, $J_{3',4'}$ = 1.5 Hz, H-3′); 4.87 (d, 1H, $J_{1',2'}$ = 8.2 Hz, H-1′); 5.62 and 7.97 (2 × m, 2 × 1H, NH_2); 8.00 (bdd, 1H, $J_{4,3}$ = 8.0 Hz, $J_{4,6}$ = 2.2 Hz, H-4); 8.19 (dd, 1H, $J_{3,4}$ = 8.0 Hz, $J_{3,6}$ = 0.8 Hz, H-3); 8.59 (bd, 1H, $J_{6,4}$ = 2.3 Hz, H-6). ^{13}C NMR (125.7 MHz, $CDCl_3$): −5.54, −5.43, −5.35, −4.47, −4.46, and −4.35 (CH_3Si); 17.86, 18.05, and 18.34 ($(CH_3)_3C$); 25.77, 25.85, and 25.97 ($(CH3)_3C$); 63.6 (CH2−5′); 74.1 (CH-3′); 79.7 (CH-2′); 80.3 (CH-1′); 86.9 (CH-4′); 122.3 (CH-3); 135.8 (CH-4); 140.2 (C-5); 146.7 (CH-6); 148.6 (C-2); 166.4 (CO). IR spectrum (CCl_4): 3528, 3458, 3401, 3277, 3199, 3148, 1700, 1597, 1575, 1556, 1409, 1257, 1153, 1113 cm^{-1}.

1β-[5-(Dimethylcarbamoyl)pyridin-2-yl]-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (15h). A flame-dried septum-sealed flask containing **11** (350 mg, 0.553 mmol), $Pd(OAc)_2$ (6.2 mg, 0.028 mmol, 5 mol %), Xantphos (32 mg, 0.055 mmol, 10 mol %), K_3PO_4 (352 mg, 1.66 mmol, 3 equiv), and $Me_2NH\cdot HCl$ (1.1 mL, 2.21 mmol, 4 equiv) was evacuated and backfilled with $CO_{(g)}$. Then, toluene (4.4 mL) was added, and the reaction mixture was stirred at room temperature for 5 min, immersed into a preheated oil bath (80 °C), and vigorously stirred for 3 h under CO atmosphere (balloon). After the completion of the reaction (monitored by TLC, hexanes/EtOAc 8:2), the mixture was cooled to room temperature, diluted with Et_2O (20 mL), filtered through a plug of Celite (eluting with Et_2O), and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel in gradient chloroform to 14% ethyl acetate in chloroform furnishing **15h** (728 mg, 76%) as colorless oil. HRMS (ESI) $C_{31}H_{61}N_2O_5Si_3$: [M + H] calculated 625.3883, found 625.3883. ^{1}H NMR (500 MHz, $CDCl_3$): −0.43, −0.09, 0.097, 0.102, 0.11, and 0.12 (6 × s, 6 × 3H, CH_3Si); 0.81, 0.92, and 0.94 (3 × s, 3 × 9H, $(CH_3)_3C$); 3.06 and 3.13 (2 × s, 2 × 3H, $(CH_3)_2N$); 3.77 (dd, 1H, J_{gem} = 11.0 Hz, $J_{5'a,4'}$ = 2.8 Hz, H-5′a); 3.81 (dd, 1H, J_{gem} = 11.0 Hz, $J_{5'b,4'}$ = 3.7 Hz, H-5′b); 3.88 (dd, 1H, $J_{2',1'}$ = 8.0 Hz, $J_{2',3'}$ = 4.4 Hz, H-2′); 4.07 (ddd, 1H, $J_{4',5'b}$ = 3.7 Hz, $J_{4',5'a}$ = 2.8 Hz, $J_{4',3'}$ = 1.6 Hz, H-4′); 4.14 (dd, 1H, $J_{3',2'}$ = 4.4 Hz, $J_{3',4'}$ = 1.6 Hz, H-3′); 4.85 (d, 1H, $J_{1',2'}$ = 8.0 Hz, H-1′); 7.64 (dd, 1H, $J_{3,4}$ = 8.0 Hz, $J_{3,6}$ = 0.9 Hz, H-3); 7.95 (dd, 1H, $J_{4,3}$ = 8.1 Hz, $J_{4,6}$ = 2.2 Hz, H-4); 8.60 (bd, 1H, $J_{6,4}$ = 2.3 Hz, H-6). ^{13}C NMR (125.7 MHz, $CDCl_3$): −5.54, −5.43, −5.26, −4.47, −4.45, and −4.36 (CH_3Si); 17.89, 18.04, and 18.33 ($(CH_3)_3C$); 25.78, 25.85, and 25.97 ($(CH_3)_3C$); 35.8 and 39.0 ($(CH_3)_2N$); 63.6 (CH_2-5′); 74.0 (CH-3′); 79.6 (CH-2′); 80.3 (CH-1′); 86.7 (CH-4′); 123.4 (CH-3); 135.9 (CH-4); 137.8 (C-5); 146.2 (CH-6); 153.2 (C-2); 168.3 (CO). IR spectrum (CCl_4): 2955, 2930, 2858, 1642, 1505, 1472, 1463, 1407, 1257, 1153 cm^{-1}.

1β-(6-Oxo-1*H*-pyridin-3-yl)-1-deoxy-2,3,5-tri-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (15i). Septum-sealed flask containing **11** (430 mg, 0.679 mmol), Pd_2dba_3 (16 mg, 0.017 mmol, 2.5 mol %), 2-di-*tert*-butylphosphino-3,4,5,6-tetramethyl-2′,4′,6′-*tri*isopropylbiphenyl (33 mg, 0.068 mmol, 10 mol %), and KOH (114 mg, 2.03 mmol, 3 equiv) was evacuated and backfilled with argon. Then 1,4-dioxane (1 mL) and water (0.3 mL) were added. The resulting dark-brown reaction mixture was immersed into preheated oil bath (80 °C) and stirred for 4 h. After the completion of the reaction (monitored by TLC, hexanes/EtOAc 10:1), the mixture was cooled to room temperature, diluted with THF (20 mL), filtered through a plug of Celite (eluting with THF), and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel in gradient chloroform to 36% ethyl acetate in chloroform furnishing **15i** (306 mg, 79%) as a white foam. HRMS (ESI) $C_{28}H_{56}NO_5Si_3$: [M + H] calculated 570.3461, found 570.3460. ^{1}H NMR (500 MHz, $CDCl_3$): −0.27, −0.07, 0.075, 0.080, 0.095, and 0.104 (6 × s, 6 × 3H, CH_3Si); 0.81, 0.91, and 0.92 (3 × s, 3 × 9H, $(CH_3)_3C$); 3.69 (dd, 1H, J_{gem} = 11.0 Hz, $J_{5'a,4'}$ = 4.0 Hz, H-5′a); 3.72 (dd, 1H, J_{gem} = 11.0 Hz, $J_{5'b,4'}$ = 3.0 Hz, H-5′b); 3.82 (dd, 1H, $J_{2',1'}$ = 8.1 Hz, $J_{2',3'}$ = 4.4 Hz, H-2′); 3.97 (bddd, 1H, $J_{4',5'a}$ = 4.0 Hz, $J_{4',5'b}$ = 3.0 Hz, $J_{4',3'}$ = 1.4 Hz, H-4′); 4.09 (dd, 1H, $J_{3',2'}$ = 4.5 Hz, $J_{3',4'}$ = 1.4 Hz, H-3′); 4.53 (d, 1H, $J_{1',2'}$ = 8.1 Hz, H-1′); 6.55 (d, 1H, $J_{3,4}$ = 9.4 Hz, H-3); 7.35 (bd, 1H, $J_{6,4}$ = 2.5 Hz, H-6), 7.61 (dd, 1H, $J_{4,3}$ = 9.4 Hz, $J_{4,6}$ = 2.5 Hz, H-4). ^{13}C NMR (125.7 MHz, $CDCl_3$): −5.55, −5.47, −4.97, −4.53, −4.41, and −4.39 (CH_3Si); 17.9, 18.0, and 18.3 ($(CH_3)_3C$); 25.78, 25.83, and 25.9 ($(CH_3)_3C$); 63.8 (CH_2-5′); 74.0 (CH-3′); 78.2 (CH-2′); 79.8 (CH-1′); 86.2 (CH-4′); 119.4 (C-5); 120.0 (CH-3); 132.7 (CH-6); 140.8 (CH-4); 165.4 (C-2). IR spectrum (CCl_4): 2956, 2930, 1665, 1631, 1554, 1472, 1257, 838 cm^{-1}.

General Procedure for the Deprotection of TBS Group. Method A. $Et_3N\cdot 3HF$ (98 μL, 1.00 mmol, 6 equiv) was added to the solution of silylated compound **13a**−**h**, **15a**−**d**,**f**,**h** (0.10 mmol) in THF (1.00 mL), and the resulting mixture was stirred at 40 °C for 2 days. After the reaction was complete (monitored by TLC eluted in $CHCl_3$/MeOH 8:2), solvent was removed under reduced pressure, the crude product was dissolved in water, and solid $NaHCO_3$ was added until pH 8. Solvents were removed under reduced pressure, and the crude product purified by reversed-phase chromatography (H_2O/MeOH as an eluent) to obtain free C-ribonucleosides **14a**−**h**, **16a**−**d**,**f**,**h**.

General Procedure for the Deprotection of TBS Group. Method B. $Et_3N\cdot 3HF$ (98 μL, 1.00 mmol, 6 equiv) was added to the solution of silylated compound **13i**, **16g** (0.10 mmol) in THF (1.00 mL), and the resulting mixture was stirred at 40 °C for 2 days. After the reaction was complete (monitored by TLC eluted in $CHCl_3$/MeOH 8:2), solvent was removed under reduced pressure, the crude product was dissolved in water, and solid $NaHCO_3$ was added until pH 8. The solution was then passed through a column packed with Dowex 50 in H^+ cycle, and the column was washed with 250 mL of water followed by 100 mL of 25% aqueous ammonia. The resulting ammonia fraction was concentrated under reduced pressure, and crude product was purified by reversed-phase chromatography (H_2O/MeOH) to obtain free C-ribonucleosides **14i.**

1β-(5-Methylpyridin-2-yl)-1-deoxy-D-ribofuranose (14a). Compound **14a** was prepared from **13a** (420 mg, 0.739 mmol) according to general procedure (Method A), in 83% yield as a white solid. Crystallization from EtOAc/MeOH furnished colorless crystals: mp 141−142 °C. HRMS (ESI) $C_{11}H_{16}NO_4$: [M + H] calculated 226.1074, found 226.1074. ^{1}H NMR (500 MHz, DMSO-d_6): 2.28 (s, 3H, CH_3-5); 3.51 (ddd, 1H, J_{gem} = 11.8 Hz, $J_{5'a,OH}$ = 6.3 Hz, $J_{5'a,4'}$ = 4.3 Hz, H-5′a); 3.64 (ddd, 1H, J_{gem} = 11.8 Hz, $J_{5'b,OH}$ = 5.0 Hz, $J_{5'b,4'}$ = 3.6 Hz, H-5′b); 3.84 (bddd, 1H, $J_{4',3'}$ = 5.6 Hz, $J_{4',5'a}$ = 4.2 Hz, $J_{4',5'b}$ = 3.6 Hz, H-4′); 3.88 (q, 1H, $J_{3',2'} = J_{3',4'} = J_{3',OH}$ = 5.3 Hz H-3′); 3.97 (dt, 1H, $J_{2',OH}$ = 5.7 Hz, $J_{2',1'} = J_{2',3'}$ = 4.9 Hz, H-2′); 4.68 (d, 1H, $J_{1',2'}$ = 4.7 Hz, H-1′); 4.83 (d, 1H, $J_{OH,3'}$ = 5.6 Hz, OH-3′); 4.96 (dd, 1H, $J_{OH,5'a}$ = 6.3 Hz, $J_{OH,5'b}$ = 5.0 Hz, OH-5′); 5.01 (d, 1H, $J_{OH,2'}$ = 5.7 Hz, OH-2′); 7.42 (d, 1H, $J_{3,4}$ = 7.9 Hz, H-3); 7.58 (bdd, 1H, $J_{4,3}$ = 7.9 Hz, $J_{4,6}$ = 2.3 Hz, H-4); 8.34 (bd, 1H, $J_{6,4}$ = 2.3 Hz, H-6). ^{13}C NMR (125.7 MHz, DMSO-d_6): 17.7 (CH_3-5); 62.0 (CH_2-5′); 71.2 (CH-3′); 76.7 (CH-2′); 84.4 (CH-4′); 85.3 (CH-1′); 121.0 (CH-3); 132.0 (C-5); 137.2 (CH-4); 149.0 (CH-6); 157.8 (C-2). IR spectrum (KBr): 2927, 2874, 1607, 1577, 1493, 1384, 1115, 1052, 830 cm^{-1}. $[\alpha]^{20}_D$ = −31.4 (*c* 2.26, MeOH). Anal. Calcd for $C_{11}H_{15}NO_4$: C, 58.66; H, 6.71; N, 6.22. Found: C, 58.52; H, 6.67; N, 6.09.

1β-(5-Phenylpyridin-2-yl)-1-deoxy-D-ribofuranose (14b). Compound **14b** was prepared from **13b** (416 mg, 0.660 mmol) according to general procedure (Method A), in 80% yield as a white solid which crystallized from EtOAc/MeOH as a white cotton-like solid: mp 132−134 °C. HRMS (ESI) $C_{16}H_{18}NO_4$: [M + H] calculated 288.1230, found 288.1230. ^{1}H NMR (500 MHz, DMSO-d_6): 3.55 (bdt, 1H, J_{gem} = 11.8 Hz, $J_{5'a,4'} = J_{5'a,OH}$ = 4.5 Hz, H-5′a); 3.67 (bdt, 1H, J_{gem} = 11.8 Hz, $J_{5'b,4'} = J_{5'b,OH}$ = 3.5 Hz, H-5′b); 3.88 (bddd, $J_{4',3'}$ = 5.5 Hz, $J_{4',5'a}$ = 4.2 Hz, $J_{4',5'b}$ = 3.7 Hz, H-4′); 3.93 (bt, 1H, $J_{3',4'} = J_{3',2'}$ = 5.2 Hz, H-3′); 4.05 (m, 1H, H-2′); 4.77 (d, 1H, $J_{1',2'}$ = 4.9 Hz, H-1′); 4.88 (m, 1H, OH-3′); 4.95 (m, 1H, OH-5′); 5.09 (m, 1H, OH-2′); 7.42 (m, 1H, H-*p*-Ph); 7.50 (m, 2H, H-*m*-Ph); 7.65 (bd, 1H, $J_{3,4}$ = 8.2 Hz, H-3); 7.73 (m, 2H, H-*o*-Ph); 8.06 (dd, 1H, $J_{4,3}$ = 8.2 Hz, $J_{4,6}$ = 2.4 Hz, H-4); 8.83 (dd, 1H, $J_{6,4}$ = 2.4 Hz, $J_{6,3}$ = 0.9 Hz, H-6). ^{13}C NMR (125.7 MHz, DMSO-d_6): 61.9 (CH_2-5′); 71.2 (CH-3′); 76.8 (CH-2′); 84.6 (CH-4′); 85.3 (CH-1′); 121.5 (CH-3); 127.0 (CH-*o*-Ph); 128.2 (CH-*p*-Ph); 129.3 (CH-*m*-Ph); 134.7 (C-5); 134.9 (CH-4); 137.2 (C-*i*-Ph); 146.9 (C-6); 159.8 (C-2). IR spectrum (KBr): 3369, 2926, 2872, 1603, 1482, 1454, 1372, 1355, 1312, 1207, 1109, 1056 cm^{-1}. $[\alpha]^{20}_D$ = −38.7 (*c* 2.40, MeOH). Anal. Calcd for $C_{16}H_{17}NO_4$: C, 66.89; H, 5.96; N, 4.88. Found: C, 66.79; H, 5.84; N, 4.78.

1β-[5-(2-Thienyl)pyridin-2-yl]-1-deoxy-D-ribofuranose (14c). Compound **14c** was prepared from **13c** (450 mg, 0.707 mmol) according to general procedure (Method A), in 83% yield, as a white solid, which after lyophilization furnished a white hygroscopic powder. Crystallization from EtOAc/MeOH yielded a white cotton-like solid: mp 155−156 °C. HRMS (ESI) $C_{14}H_{16}NO_4S$: [M + H] calculated 294.0795, found 294.0795. ^{1}H NMR (500 MHz, DMSO-d_6): 3.54 (ddd, 1H, J_{gem} = 11.8 Hz, $J_{5'a,OH}$ = 6.1 Hz, $J_{5'a,4'}$ = 4.3 Hz, H-5′a); 3.66 (ddd, 1H, J_{gem} = 11.8 Hz, $J_{5'b,OH}$ = 5.2 Hz, $J_{5'b,4'}$ = 3.5 Hz, H-5′b); 3.87 (bddd, 1H, $J_{4',3'}$ = 5.5 Hz, $J_{4',5'a}$ = 4.2 Hz, $J_{4',5'b}$ = 3.6 Hz, H-4′); 3.91 (bq, 1H, $J_{3',2'} = J_{3',4'} = J_{3',OH}$ = 5.3 Hz, H-3′); 4.02 (bdt, 1H, $J_{2',3'} = J_{2',OH}$ = 5.5 Hz, $J_{2',1'}$ = 4.9 Hz, H-2′); 4.74 (d, 1H, $J_{1',2'}$ = 4.8 Hz, H-1′); 4.88 (d, 1H, $J_{OH,3'}$ = 5.5 Hz, OH-3′); 4.92 (t, 1H, $J_{OH,5'a} = J_{OH,5'b}$ = 5.6 Hz, OH-5′); 5.09 (d, 1H, $J_{OH,2'}$ = 5.7 Hz, OH-2′); 7.19 (dd, 1H, $J_{4,5}$ = 5.0 Hz, $J_{4,3}$ = 3.7 Hz, H-4-thienyl); 7.61 (bd, 1H, $J_{3,4}$ = 8.2 Hz, H-3); 7.63 (dd, 1H, $J_{3,4}$ = 3.7 Hz, $J_{3,5}$ = 1.1 Hz, H-3-thienyl); 7.64 (dd, 1H, $J_{5,4}$ = 5.0 Hz, $J_{5,3}$ = 1.1 Hz, H-5-thienyl); 8.03 (dd, 1H, $J_{4,3}$ = 8.2 Hz, $J_{4,6}$ = 2.4 Hz, H-4); 8.83 (dd, 1H, $J_{6,4}$ = 2.4 Hz, $J_{6,3}$ = 0.9 Hz, H-6). ^{13}C NMR (125.7 MHz, DMSO-d_6): 61.9 (CH_2-5′); 71.2 (CH-3′); 76.8 (CH-2′); 84.5 (CH-4′); 85.3 (CH-1′); 121.7 (CH-3); 125.1 (CH-3-thienyl); 126.9 (CH-5-thienyl); 128.9 (CH-4-thienyl); 133.5 (CH-4); 139.7 (C-5); 140.7 (C-2-thienyl); 145.5 (C-6); 159.8 (C-2). IR spectrum (KBr): 3341, 2914, 1633, 1482, 1389, 1121, 1088, 1061 cm^{-1}. $[\alpha]^{20}_D$ = −34.3 (*c* 3.21, MeOH). Anal. Calcd for $C_{14}H_{15}NO_4S \cdot {}^1/_4H_2O$: C, 56.46; H, 5.25; N, 4.70. Found: C, 56.67; H, 5.01; N, 4.68.

1β-[5-(2-Pyridyl)pyridin-2-yl]-1-deoxy-D-ribofuranose (14d). Compound **14d** was prepared from **13d** (227 mg, 0.360 mmol) according to general procedure (Method A), in 83% yield, as a white solid, which after lyophilization furnished a white hygroscopic powder. HRMS (ESI) $C_{15}H_{17}N_2O_4$: [M + H] calculated 289.1183, found 289.1183. ^{1}H NMR (500 MHz, DMSO-d_6): 3.55 (ddd, 1H, J_{gem} = 11.8 Hz, $J_{5'a,OH}$ = 5.8 Hz, $J_{5'a,4'}$ = 4.3 Hz, H-5′a); 3.68 (ddd, 1H, J_{gem} = 11.8 Hz, $J_{5'a,OH}$ = 4.9 Hz, $J_{5'b,4'}$ = 3.5 Hz, H-5′b); 3.89 (ddd, $J_{4',3'}$ = 5.6 Hz, $J_{4',5'a}$ = 4.3 Hz, $J_{4',5'b}$ = 3.5 Hz, H-4′); 3.92 (bq, 1H, $J_{3',4'} = J_{3',2'} = J_{3',OH}$ = 4.2 Hz, H-3′); 4.04 (dd, 1H, $J_{2',OH}$ = 5.8 Hz, $J_{2',1'} = J_{2',3'}$ = 4.8 Hz, H-2′); 4.79 (d, 1H, $J_{1',2'}$ = 4.8 Hz, H-1′); 4.89 (d, 1H, $J_{OH,3'}$ = 5.5 Hz, OH-3′); 4.95 (t, 1H, $J_{OH,5'a} = J_{OH,5'b}$ = 5.5 Hz, OH-5′); 5.12 (d, 1H, $J_{OH,2'}$ = 5.8 Hz, OH-2′); 7.41 (ddd, 1H, $J_{5,4}$ = 7.5 Hz, $J_{5,6}$ = 4.8 Hz, $J_{5,3}$ = 1.1 Hz, H-5-py); 7.69 (bd, 1H, $J_{3,4}$ = 8.2 Hz, H-3); 7.93 (bddd, 1H, $J_{4,3}$ = 7.8 Hz, $J_{4,5}$ = 7.6 Hz, $J_{4,6}$ = 1.8 Hz, H-4-py); 8.05 (dt, 1H, $J_{3,4}$ = 8.0 Hz, $J_{3,5} = J_{3,6}$ = 1.1 Hz, H-3-py); 8.42 (dd, 1H, $J_{4,3}$ = 8.2 Hz, $J_{4,6}$ = 2.3 Hz, H-4); 8.70 (ddd, 1H, $J_{6,5}$ = 4.8 Hz, $J_{6,4}$ = 1.9 Hz, $J_{6,3}$ = 1.0 Hz, H-6-py); 9.19 (dd, 1H, $J_{6,4}$ = 2.3 Hz, $J_{6,3}$ = 0.9 Hz, H-6). ^{13}C NMR (125.7 MHz, DMSO-d_6): 61.9 (CH_2-5′); 71.2 (CH-3′); 76.9 (CH-2′); 84.5 (CH-4′); 85.4 (CH-1′); 120.8 (CH-3-py); 121.3 (CH-3); 123.3 (CH-5-py); 133.2 (C-5); 134.7 (CH-4); 137.6 (CH-4-py); 147.1 (C-6); 150.0 (CH-6-py); 153.9 (C-2-py); 161.3 (C-2). $[\alpha]^{20}_D$ = −35.4 (*c* 1.78, MeOH). Anal. Calcd for $C_{15}H_{16}N_2O_4 \cdot {}^1/_4H_2O$: C, 61.53; H, 5.68; N, 9.57. Found: C, 61.28; H, 5.44; N, 9.48.

1β-(5-Aminopyridin-2-yl)-1-deoxy-D-ribofuranose (14e). Compound **14e** was prepared from **13e** (500 mg, 0.880 mmol) according to general procedure (Method A), in 75% yield, as a yellowish oil, which after lyophilization furnished a yellow hygroscopic solid. HRMS (ESI) $C_{10}H_{15}N_2O_4$: [M + H] calculated 227.1026, found 227.1026. ^{1}H NMR (500 MHz, DMSO-d_6): 3.47 (bdm, 1H, J_{gem} = 11.7 Hz, H-5′a); 3.59 (dd, 1H, J_{gem} = 11.7 Hz, $J_{5'b,4'}$ = 3.7 Hz, H-5′b); 3.78 (bddd, 1H, $J_{4',3'}$ = 5.3 Hz, $J_{4',5'a}$ = 4.2 Hz, $J_{4',5'b}$ = 3.7 Hz, H-4′); 3.89 (t, 1H, $J_{3',2'} = J_{3',4'}$ = 5.2 Hz H-3′); 3.96 (t, 1H, $J_{2',1'} = J_{2',3'}$ = 5.1 Hz, H-2′); 4.53 (d, 1H, $J_{1',2'}$ = 5.0 Hz, H-1′); 4.78 − 5.10 (m, 3H, OH-2′,3′,5′); 5.26 (s, 2H, NH_2-5); 6.88 (dd, 1H, $J_{4,3}$ = 8.3 Hz, $J_{4,6}$ = 2.7 Hz, H-4); 7.11 (bd, 1H, $J_{3,4}$ = 8.4 Hz, H-3); 7.86 (dd, 1H, $J_{6,4}$ = 2.7 Hz, $J_{6,3}$ = 0.7 Hz, H-6). ^{13}C NMR (125.7 MHz, DMSO-d_6): 62.3 (CH_2-5′); 71.4 (CH-3′); 76.3 (CH-2′); 84.4 (CH-4′); 85.3 (CH-1′); 120.4 (CH-4); 122.1 (CH-3); 135.3 (CH-6); 144.35 (C-5); 147.3 (C-2). IR spectrum (KBr): 3421, 1630, 1498, 1307, 1114, 1052, 1024 cm^{-1}. $[\alpha]^{20}_D$ = −35.4 (*c* 2.85, MeOH).

1β-[5-(Dimethylamino)pyridin-2-yl]-1-deoxy-D-ribofuranose (14f). Compound **14f** was prepared from **13f** (450 mg, 0.754 mmol) according to general procedure (Method A), in 76% yield, as a yellowish solid. Crystallization from EtOAc/MeOH yielded yellowish crystals: mp 158−161 °C. HRMS (ESI) $C_{12}H_{19}N_2O_4$: [M + H] calculated 255.1339, found 255.1340. ^{1}H NMR (500 MHz, DMSO-d_6): 2.91 (s, 6H, $(CH_3)_2$N); 3.48 (dd, 1H, J_{gem} = 11.7 Hz, $J_{5'a,4'}$ = 4.4 Hz, H-5′a); 3.61 (dd, 1H, J_{gem} = 11.7 Hz, $J_{5'b,4'}$ = 3.7 Hz, H-5′b); 3.81 (dt, 1H, $J_{4',3'}$ = 5.2 Hz, $J_{4',5'a} = J_{4',5'b}$ = 4.0 Hz, H-4′); 3.90 (q, 1H, $J_{3',2'} = J_{3',4'} = J_{3',OH}$ = 5.2 Hz H-3′); 3.99 (q, 1H, $J_{2',OH} = J_{2',1'} = J_{2',3'}$ = 5.2 Hz, H-2′); 4.61 (d, 1H, $J_{1',2'}$ = 5.0 Hz, H-1′); 4.78 (d, 1H, $J_{OH,3'}$ = 5.5 Hz, OH-3′); 4.90 (d, 1H, $J_{OH,2'}$ = 5.7 Hz, OH-2′); 5.03 (bs, 1H, OH-5′); 7.08 (dd, 1H, $J_{4,3}$ = 8.7 Hz, $J_{4,6}$ = 3.1 Hz, H-4); 7.27 (d, 1H, $J_{3,4}$ = 8.6 Hz, H-3); 8.03 (bd, 1H, $J_{6,4}$ = 3.0 Hz, H-6). ^{13}C NMR (125.7 MHz, DMSO-d_6): 40.0 ($(CH_3)_2$N); 62.3 (CH_2-5′); 71.4 (CH-3′); 76.4 (CH-2′); 84.4 (CH-4′); 85.1 (CH-1′); 119.3 (CH-4); 121.8 (CH-3); 133.8 (CH-6); 145.7 (C-5); 147.6 (C-2). IR spectrum (KBr): 2812, 1362, 1226, 1170, 1128 cm^{-1}. $[\alpha]^{20}_D$ = −40.0 (*c* 3.87, MeOH). Anal. Calcd for $C_{12}H_{18}N_2O_4 \cdot {}^1/_4H_2O$: C, 55.69; H, 7.21; N, 10.82. Found: C, 55.72; H, 7.07; N, 10.63.

1β-[5-(Carbamoyl)pyridin-2-yl]-1-deoxy-D-ribofuranose (14g). Compound **14g** was prepared from **13g** (300 mg, 0.503 mmol)

according to general procedure (Method A), in 75% yield, as a colorless oil, which after lyophilization furnished a white hygroscopic cotton-like solid. HRMS (ESI) $C_{11}H_{15}N_2O_5$: [M + H] calculated 255.0976, found 255.0976. ^{1}H NMR (500 MHz, DMSO-d_6): 3.53 (dm, 1H, J_{gem} = 11.8 Hz, H-5′a); 3.65 (dm, 1H, J_{gem} = 11.8 Hz, H-5′b); 3.85 − 3.90 (m, 2H, H-3′,4′); 3.98 (bq, 1H, $J_{2',1'} = J_{2',3'} = J_{2',OH}$ = 4.8 Hz, H-2′); 4.77 (d, 1H, $J_{1',2'}$ = 4.7 Hz, H-1′); 4.89 (d, 1H, $J_{OH,3'}$ = 5.1 Hz, OH-3′); 4.92 (t, 1H, $J_{OH,5'a} = J_{OH,5'b}$ = 5.5 Hz, OH-5′); 5.13 (d, 1H, $J_{OH,2'}$ = 5.7 Hz, OH-2′); 7.56 (bs, 1H, NHa); 7.66 (bd, 1H, $J_{3,4}$ = 8.1 Hz, H-3); 8.13 (bs, 1H, NHb); 8.18 (dd, 1H, $J_{4,3}$ = 8.2 Hz, $J_{4,6}$ = 2.3 Hz, H-4); 8.96 (dd, 1H, $J_{6,4}$ = 2.3 Hz, $J_{6,3}$ = 0.8 Hz, H-6). ^{13}C NMR (125.7 MHz, DMSO-d_6): 61.7 (CH_2-5′); 71.0 (CH-3′); 76.9 (CH-2′); 84.5 (CH-4′); 85.4 (CH-1′); 120.7 (CH-3); 128.7 (C-5); 135.9 (CH-4); 148.1 (CH-6); 163.6 (C-2); 166.5 (CO). IR spectrum (KBr): 1670, 1615, 1407, 1112, 1051, 860 cm^{-1}. $[\alpha]^{20}_D$ = −32.2 (*c* 2.02, MeOH). Anal. Calcd for $C_{11}H_{14}N_2O_5 \cdot H_2O$: C, 48.53; H, 5.92; N, 10.29. Found: C, 48.41; H, 5.55; N, 10.00.

1β-[5-(Dimethylcarbamoyl)pyridin-2-yl]-1-deoxy-D-ribofuranose (14h). Compound **14h** was prepared from **13h** (440 mg, 0.704 mmol) according to general procedure (Method A), in 81% yield, as a colorless oil, which after lyophilization furnished a white hygroscopic powder. Crystallization from EtOAc/MeOH yielded white crystals: mp 142−143 °C. HRMS (ESI) $C_{13}H_{19}N_2O_5$: [M + H] calculated 283.1289, found 283.1288. ^{1}H NMR (500 MHz, DMSO-d_6): 2.93 and 3.00 (2 × s, 2 × 3H, $(CH_3)_2$N); 3.53 (ddd, 1H, J_{gem} = 11.9 Hz, $J_{5'a,OH}$ = 6.0 Hz, $J_{5'a,4'}$ = 4.2 Hz, H-5′a); 3.65 (ddd, 1H, J_{gem} = 11.9 Hz, $J_{5'b,OH}$ = 5.2 Hz, $J_{5'b,4'}$ = 3.5 Hz, H-5′b); 3.87 (m, 1H, H-4′); 3.89 (bq, 1H, $J_{3',2'} = J_{3',4'} = J_{3',OH}$ = 5.1 Hz, H-3′); 4.00 (q, 1H, $J_{2',1'} = J_{2',3'} = J_{2',OH}$ = 5.0 Hz, H-2′); 4.74 (d, 1H, $J_{1',2'}$ = 4.9 Hz, H-1′); 4.90 (d, 1H, $J_{OH,3'}$ = 5.1 Hz, OH-3′); 4.91 (t, 1H, $J_{OH,5'a} = J_{OH,5'b}$ = 5.6 Hz, OH-5′); 5.12 (d, 1H, $J_{OH,2'}$ = 5.6 Hz, OH-2′); 7.63 (bd, 1H, $J_{3,4}$ = 8.0 Hz, H-3); 7.83 (dd, 1H, $J_{4,3}$ = 8.0 Hz, $J_{4,6}$ = 2.2 Hz, H-4); 8.55 (dd, 1H, $J_{6,4}$ = 2.2 Hz, $J_{6,3}$ = 0.9 Hz, H-6). ^{13}C NMR (125.7 MHz, DMSO-d_6): 35.0 ($(CH_3)_2$N); 61.9 (CH_2-5′); 71.2 (CH-3′); 76.8 (CH-2′); 84.6 (CH-4′); 85.3 (CH-1′); 120.9 (CH-3); 131.3 (C-5); 135.6 (CH-4); 147.1 (CH-6); 161.7 (C-2); 168.1 (CO). IR spectrum (KBr): 3371, 2929, 2971, 1625, 1511, 1481, 1454, 1403, 1267, 1202, 1094, 1052 cm^{-1}. $[\alpha]^{20}_D$ = −37.1 (*c* 2.25, MeOH). Anal. Calcd for $C_{13}H_{18}N_2O_5$: C, 55.31; H, 6.43; N, 9.92. Found: C, 55.24; H, 6.56; N, 9.90.

1β-[5-Hydroxypyridin-2-yl]-1-deoxy-D-ribofuranose (14i). Compound **14i** was prepared from **13i** (652 mg, 1.14 mmol) according to general procedure (Method B), in 74% yield, as a colorless oil, which after lyophilization furnished a white hygroscopic powder. HRMS (ESI) $C_{10}H_{14}NO_5$: [M + H] calculated 228.0867, found 228.0866. ^{1}H NMR (500 MHz, DMSO-d_6): 3.48 (bd, 1H, J_{gem} = 11.9 Hz, H-5′a); 3.60 (bd, 1H, J_{gem} = 11.9 Hz, H-5′b); 3.80 (bddd, 1H, $J_{4',3'}$ = 5.3 Hz, $J_{4',5'a}$ = 4.5 Hz, $J_{4',5'b}$ = 3.8 Hz, H-4′); 3.88 (q, 1H, $J_{3',2'} = J_{3',4'} = J_{3',OH}$ = 5.3 Hz H-3′); 3.96 (bdt, 1H, $J_{2',OH}$ = 5.7 Hz, $J_{2',1'} = J_{2',3'}$ = 5.2 Hz, H-2′); 4.61 (d, 1H, $J_{1',2'}$ = 5.1 Hz, H-1′); 4.80 (d, 1H, $J_{OH,3'}$ = 5.6 Hz, OH-3′); 4.93 (bs, 1H, OH-5′); 4.93 (d, 1H, $J_{OH,2'}$ = 5.8 Hz, OH-2′); 7.13 (dd, 1H, $J_{4,3}$ = 8.4 Hz, $J_{4,6}$ = 2.9 Hz, H-4); 7.32 (bd, 1H, $J_{3,4}$ = 8.4 Hz, H-3); 8.05 (dd, 1H, $J_{6,4}$ = 2.8 Hz, $J_{6,3}$ = 0.7 Hz, H-6); 9.84 (s, 1H, OH-5). ^{13}C NMR (125.7 MHz, DMSO-d_6): 62.1 (CH_2-5′); 71.3 (CH-3′); 76.4 (CH-2′); 84.5 (CH-4′); 85.0 (CH-1′); 122.4 (CH-3); 122.7 (CH-4); 136.9 (CH-6); 150.9 (C-2); 153.1 (C-5). IR spectrum (KBr): 3430, 1583, 1495, 1275, 1249, 1106, 1051 cm^{-1}. $[\alpha]^{20}_D$ = −30.4 (*c* 2.04, MeOH). Anal. Calcd for $C_{10}H_{13}NO_5 \cdot {}^3/_2H_2O$: C 47.24; H, 6.34; N, 5.51., Found: C 47.34; H, 6.19; N, 5.48.

β-(6-Methylpyridin-3-yl)-1-deoxy-D-ribofuranose (16a). Compound **16a** was prepared from **15a** (374 mg, 0.658 mmol) according to general procedure (Method A), in 90% yield as a white solid, which after lyophilization furnished a white hygroscopic powder. HRMS (ESI) $C_{11}H_{16}NO_4$: [M + H] calculated 226.1074, found 226.1074. ^{1}H NMR (500 MHz, DMSO-d_6): 2.44 (s, 3H, CH_3); 3.49 − 3.59 (m, 2H, H-5′); 3.70 (m, 1H, H-2′); 3.82 (td, 1H, $J_{4',5'a} = J_{4',5'b}$ = 4.4 Hz, $J_{4',3'}$ = 3.2 Hz, H-4′); 3.91 (m, 1H, H-3′); 4.56 (d, 1H, $J_{1',2'}$ = 7.4 Hz, H-1′); 4.83 (t, 1H, $J_{OH,5'a} = J_{OH,5'b}$ = 5.6 Hz, OH-5′); 4.94 (d, 1H, $J_{OH,3'}$ = 4.6 Hz, OH-3′); 5.01 (d, 1H, $J_{OH,2'}$ = 7.0 Hz, OH-2′); 7.21 (bd, 1H, $J_{3,4}$ = 8.0 Hz, H-3); 7.67 (bdd, 1H, $J_{4,3}$ = 8.1 Hz, $J_{4,6}$ = 2.3 Hz, H-4); 8.42 (bd, 1H, $J_{6,4}$ = 2.2 Hz, H-6).^{13}C NMR (125.7 MHz, DMSO-d_6): 23.9 (CH_3); 62.2 (CH_2-5′); 71.7 (CH-3′); 77.8 (CH-2′); 80.9 (CH-1′); 85.6 (CH-4′); 122.8 (CH-3); 133.8 (C-5); 134.4 (CH-4); 147.3 (CH-6); 157.1 (C-2). IR spectrum (KBr): 3421, 2922, 1610, 1497, 1118, 1032 cm^{-1}. $[\alpha]^{20}_D$ = −26.4 (*c* 1.94, MeOH). Anal. Calcd for $C_{11}H_{15}NO_4 \cdot 0.6\,H_2O$: C, 55.97; H, 6.92; N, 5.93. Found: C, 56.28; H, 6.67; N, 5.52.

1β-(6-Phenylpyridin-3-yl)-1-deoxy-D-ribofuranose (16b). Compound **16b** was prepared from **15b** (395 mg, 0.627 mmol) according to general procedure (Method A), in 91% yield as a white solid, which after lyophilization furnished a white hygroscopic powder. HRMS (ESI) $C_{16}H_{18}NO_4$: [M + H] calculated 288.1230, found 288.1230. ^{1}H NMR (500 MHz, DMSO-d_6): 3.57 (ddd, 1H, J_{gem} = 11.7 Hz, $J_{5'a,OH}$ = 5.4 Hz, $J_{5'a,4'}$ = 4.4 Hz, H-5′a); 3.60 (ddd, 1H, J_{gem} = 11.7 Hz, $J_{5'b,OH}$ = 5.5 Hz, $J_{5'b,4'}$ = 4.4 Hz, H-5′b); 3.78 (td, 1H, $J_{2',1'} = J_{2',OH}$ = 7.2 Hz, $J_{2',3'}$ = 5.2 Hz, H-2′); 3.87 (td, 1H, $J_{4',5'a} = J_{4',5'b}$ = 4.4 Hz, $J_{4',3'}$ = 3.1 Hz, H-4′); 3.96 (btd, 1H, $J_{3',2'} = J_{3',OH}$ = 4.7 Hz, $J_{3',4'}$ = 3.2 Hz, H-3′); 4.67 (d, 1H, $J_{1',2'}$ = 7.5 Hz, H-1′); 4.88 (t, 1H, $J_{OH,5'a} = J_{OH,5'b}$ = 5.5 Hz, OH-5′); 4.99 (d, 1H, $J_{OH,3'}$ = 4.6 Hz, OH-3′); 5.10 (d, 1H, $J_{OH,2'}$ = 7.1 Hz, OH-2′); 7.43 (m, 1H, H-*p*-Ph); 7.49 (m, 2H, H-*m*-Ph); 7.89 (ddd, 1H, $J_{4,3}$ = 8.2 Hz, $J_{4,6}$ = 2.2 Hz, $J_{4,1'}$ = 0.6 Hz, H-4); 7.94 (dd, 1H, $J_{3,4}$ = 8.2 Hz, $J_{3,6}$ = 0.9 Hz, H-3); 8.08 (m, 2H, H-*o*-Ph); 8.67 (dt, 1H, $J_{6,4}$ = 2.2 Hz, $J_{6,3} = J_{6,1'}$ = 0.7 Hz, H-6). ^{13}C NMR (125.7 MHz, DMSO-d_6): 62.2 (CH_2-5′); 71.8 (CH-3′); 77.9 (CH-2′); 80.8 (CH-1′); 85.8 (CH-4′); 119.9 (CH-3); 126.6 (CH-*o*-Ph); 128.9 (CH-*m*-Ph); 129.1 (CH-*p*-Ph); 135.2 (CH-4); 135.7 (C-5); 138.8 (C-*i*-Ph); 148.0 (CH-6); 155.5 (C-2). IR spectrum (KBr): 3410, 2925, 1601, 1565, 1479, 1120 cm^{-1}. $[\alpha]^{20}_D$ = −37.3 (*c* 2.2, MeOH). Anal. Calcd for $C_{16}H_{17}NO_4 \cdot H_2O$: C, 64.65; H, 6.12; N, 4.73. Found: C, 64.81; H, 6.13; N, 4.65.

1β-[6-(2-Thienyl)pyridin-3-yl]-1-deoxy-D-ribofuranose (16c). Compound **16c** was prepared from **15c** (348 mg, 0.547 mmol) according to general procedure (Method A), in 89% yield, as a white solid, which after lyophilization furnished white hygroscopic powder. HRMS (ESI) $C_{14}H_{16}NO_4S$: [M + H] calculated 294.0795, found 294.0795. ^{1}H NMR (500 MHz, DMSO-d_6): 3.54 (ddd, 1H, J_{gem} = 11.7 Hz, $J_{5'a,OH}$ = 5.4 Hz, $J_{5'a,4'}$ = 4.4 Hz, H-5′a); 3.58 (ddd, 1H, J_{gem} = 11.8 Hz, $J_{5'b,OH}$ = 5.5 Hz, $J_{5'b,4'}$ = 4.3 Hz, H-5′b); 3.76 (m, 1H, H-2′); 3.85 (td, 1H, $J_{4',5'a} = J_{4',5'b}$ = 4.3 Hz, $J_{4',3'}$ = 3.1 Hz, H-4′); 3.94 (m, 1H, H-3′); 4.63 (d, 1H, $J_{1',2'}$ = 7.4 Hz, H-1′); 4.86 (t, 1H, $J_{OH,5'a} = J_{OH,5'b}$ = 5.5 Hz, OH-5′); 4.98 (d, 1H, $J_{OH,3'}$ = 4.0 Hz, OH-3′); 5.10 (d, 1H, $J_{OH,2'}$ = 5.8 Hz, OH-2′); 7.16 (dd,1H, $J_{4,5}$ = 5.0 Hz, $J_{4,3}$ = 3.7 Hz, H-4-thienyl); 7.61 (dd, 1H, $J_{5,4}$ = 5.0 Hz, $J_{5,3}$ = 1.2 Hz, H-5-thienyl); 7.78 (dd, 1H, $J_{3,4}$ = 3.7 Hz, $J_{3,5}$ = 1.2 Hz, H-3-thienyl); 7.83 (bdd, 1H, $J_{4,3}$ = 8.3 Hz, $J_{4,6}$ = 2.2 Hz, H-4); 7.88 (dd, 1H, $J_{3,4}$ = 8.2 Hz, $J_{3,6}$ = 0.9 Hz, H-3); 8.52 (bd, 1H, $J_{6,4}$ = 2.2 Hz, H-6). ^{13}C NMR (125.7 MHz, DMSO-d_6): 62.1 (CH_2-5′); 71.7 (CH-3′); 77.8 (CH-2′); 80.8 (CH-1′); 85.7 (CH-4′); 118.3 (CH-3); 125.2 (CH-3-thienyl); 128.3 (CH-5-thienyl); 128.6 (CH-4-thienyl); 135.1 (CH-4); 135.5 (C-5); 144.7 (C-2-thienyl); 147.7 (CH-6); 151.3 (C-2). IR spectrum (KBr): 3420, 2914, 1600, 1480, 1396, 1313, 1122, 2055, 1027, 818 cm^{-1}. $[\alpha]^{20}_D$ = −50.6 (*c* 1.9, DMSO). Anal. Calcd for $C_{14}H_{15}NO_4S$: C, 57.32; H, 5.17; N, 4.78. Found: C, 57.08; H, 5.00; N, 4.66.

1β-[6-(2-Pyridyl)pyridin-3-yl]-1-deoxy-D-ribofuranose (16d). Compound **16d** was prepared from **15d** (148 mg, 0.234 mmol) according to general procedure (Method A), in 52% yield, as a white solid, which after lyophilization furnished a white hygroscopic powder. HRMS (ESI) $C_{15}H_{17}N_2O_4$: [M + H] calculated 289.1183, found 289.1183. ^{1}H NMR (500 MHz, DMSO-d_6): 3.56 (bdt, 1H, J_{gem} = 11.7 Hz, $J_{5'a,OH} = J_{5'a,4'}$ = 4.8 Hz, H-5′a); 3.60 (bddd, 1H, J_{gem} = 11.7 Hz, $J_{5'a,OH}$ = 5.2 Hz, $J_{5'b,4'}$ = 4.5 Hz, H-5′b); 3.78 (m, 1H, H-2′); 3.88 (td, 1H, $J_{4',5'a} = J_{4',5'b}$ = 4.4 Hz,

$J_{4',3'}$ = 3.1 Hz, H-4′); 3.96 (m, 1H, H-3′); 4.69 (d, 1H, $J_{1',2'}$ = 7.5 Hz, H-1′); 4.88 (t, 1H, $J_{OH,5'a} = J_{OH,5'b}$ = 5.6 Hz, OH-5′); 5.01 (bm, 1H, OH-3′); 5.12 (bm, 1H, OH-2′); 7.44 (ddd, 1H, $J_{5,4}$ = 7.5 Hz, $J_{5,6}$ = 4.8 Hz, $J_{5,3}$ = 1.2 Hz, H-5-py); 7.94 (btd, 1H, $J_{4,3} = J_{4,5}$ = 7.7 Hz, $J_{4,6}$ = 1.8 Hz, H-4-py); 7.95 (bdd, 1H, $J_{4,3}$ = 8.2 Hz, $J_{4,6}$ = 2.1 Hz, H-4); 8.36 (dd, 1H, $J_{3,4}$ = 8.1 Hz, $J_{3,6}$ = 0.9 Hz, H-3); 8.38 (dt, 1H, $J_{3,4}$ = 7.9 Hz, $J_{3,5} = J_{3,6}$ = 1.1 Hz, H-3-py); 8.68 (ddd, 1H, $J_{6,5}$ = 4.8 Hz, $J_{6,4}$ = 1.9 Hz, $J_{6,3}$ = 1.0 Hz, H-6-py); 8.69 (dm, 1H, $J_{6,4}$ = 2.1 Hz, H-6).^{13}C NMR (125.7 MHz, DMSO-d_6): 62.2 (CH_2-5′); 71.8 (CH-3′); 77.9 (CH-2′); 80.8 (CH-1′); 85.9 (CH-4′); 120.1 (CH-3); 120.6 (CH-3-py); 124.3 (CH-5-py); 135.1 (CH-4); 137.5 (C-5); 137.5 (CH-4-py); 147.7 (CH-6); 149.5 (CH-6-py); 154.7 (C-2); 155.4 (C-2-py). IR spectrum (KBr): 3458, 3429, 3306, 1462, 1124, 1056, 1026 cm^{-1}. $[\alpha]^{20}_D$ = −60.0 (*c* 1.85, DMSO). Anal. Calcd for $C_{15}H_{16}N_2O_4 \cdot {}^1/_4H_2O$: C, 61.53; H, 5.68; N, 9.57. Found: C, 61.83; H, 5.70; N, 9.20.

1β-(6-Aminopyridin-3-yl)-1-deoxy-D-ribofuranose (16e). TBAF·3H_2O (886 mg, 2.81 mmol, 4 equiv) was added to a solution of **16e** (400 mg, 0.702 mmol) in THF (7 mL), and the resulting mixture was stirred for 3 h at room temperature. After evaporation of the solvent under reduced pressure, the resulting yellow oil was dissolved in water (30 mL) and filtered off. The filtrate was passed through column packed with Dowex 50 in H^+ cycle, and the column was washed with water (500 mL) and then eluted with 75 mL of 10% aqueous ammonia. The ammonia fraction was concentrated under reduced pressure and purified by reversed-phase chromatography (H_2O/MeOH as an eluent). Subsequent lyophilization furnished compound **16e** (103 mg, 65%) as a white hygroscopic powder. HRMS (ESI) $C_{10}H_{14}N_2O_4$: [M + H] calculated 227.1026, found 227.1026. ^{1}H NMR (500 MHz, DMSO-d_6): 3.47 (dd, 1H, J_{gem} = 11.6 Hz, $J_{5'a,4'}$ = 4.8 Hz, H-5′a); 3.51 (dd, 1H,, J_{gem} = 11.6 Hz, $J_{5'b,4'}$ = 4.4 Hz, H-5′b); 3.68 (bdd, 1H, $J_{2',1'}$ = 7.4 Hz, $J_{2',3'}$ = 5.5 Hz, H-2′); 3.73 (td, 1H, $J_{4',5'a} = J_{4',5'b}$ = 4.6 Hz, $J_{4',3'}$ = 3.4 Hz, H-4′); 3.87 (dd, 1H, $J_{3',2'}$ = 5.2 Hz, $J_{3',4'}$ = 3.4 Hz, H-3′); 4.37 (d, 1H, $J_{1',2'}$ = 7.4 Hz, H-1′); 4.62 - 5.02 (m, 3H, OH-2′, 3′, 5′); 5.86 (s, 2H, NH_2); 6.42 (d, 1H, $J_{3,4}$ = 8.5 Hz, H-3); 7.38 (dd, 1H, $J_{4,3}$ = 8.5 Hz, $J_{4,6}$ = 2.3 Hz, H-4); 7.85 (d, 1H, $J_{6,4}$ = 2.3 Hz, H-6). ^{13}C NMR (125.7 MHz, DMSO-d_6): 62.3 (CH_2-5′); 71.64 (CH-3′); 77.0 (CH-2′); 81.4 (CH-1′); 85.2 (CH-4′); 107.8 (CH-3); 124.0 (C-5); 135.9 (CH-4); 146.5 (CH-6); 159.6 (C-2). IR spectrum (KBr): 3480, 3379, 1636, 1569, 1511, 1130, 1018 cm^{-1}. $[\alpha]^{20}_D$ = −37.0 (*c* 1.6, MeOH).

1β-[6-(Dimethylamino)pyridin-3-yl]-1-deoxy-D-ribofuranose (16f). Compound **16f** was prepared from **15f** (434 mg, 0.727 mmol) according to general procedure (Method A), in 88% yield, as a yellowish solid. HRMS (ESI) $C_{12}H_{19}N_2O_4$: [M + H] calculated 255.1339, found 255.1339. ^{1}H NMR (500 MHz, DMSO-d_6): 3.00 (s, 6H, $(CH_3)_2$N); 3.46 − 3.56 (m, 2H, H-5′); 3.70 (td, 1H, $J_{2',OH} = J_{2',1'}$ = 7.0 Hz, $J_{2',3'}$ = 5.5 Hz, H-2′); 3.76 (td, 1H, $J_{4',5'a} = J_{4',5'b}$ = 4.5 Hz, $J_{4',3'}$ = 3.4 Hz, H-4′); 3.89 (m, 1H, H-3′); 4.43 (d, 1H, $J_{1',2'}$ = 7.4 Hz, H-1′); 4.77 (t, 1H, $J_{OH,5'a} = J_{OH,5'b}$ = 5.5 Hz, OH-5′); 4.84 (d, 1H, $J_{OH,3'}$ = 4.7 Hz, OH-3′); 4.86 (d, 1H, $J_{OH,2'}$ = 6.9 Hz, OH-2′); 6.61 (dd, 1H, $J_{3,4}$ = 8.8 Hz, $J_{3,6}$ = 0.6 Hz, H-3); 7.50 (bdd, 1H, $J_{4,3}$ = 8.8 Hz, $J_{4,6}$ = 2.4 Hz, H-4); 8.04 (dm, 1H, $J_{6,4}$ = 2.4 Hz, H-6). ^{13}C NMR (125.7 MHz, DMSO-d_6): 38.0 ($(CH_3)_2$N); 62.3 (CH_2-5′); 71.7 (CH-3′); 77.1 (CH-2′); 81.3 (CH-1′); 85.2 (CH-4′); 105.6 (CH-3); 123.7 (C-5); 135.9 (CH-4); 146.4 (CH-6); 159.1 (C-2). IR spectrum (KBr): 3410, 2918, 1617, 1524, 1404, 1115, 1054 cm^{-1}. $[\alpha]^{20}_D$ = −40.8 (*c* 2.0, MeOH). Anal. Calcd for $C_{12}H_{18}N_2O_4 \cdot 2/3\ H_2O$: C, 54.13; H, 7.32; N, 10.52. Found: C, 54.22; H, 7.16; N, 10.14.

1β-[6-(Carbamoyl)pyridin-3-yl]-1-deoxy-D-ribofuranose (16g). Compound **16g** was prepared from **15g** (216 mg, 0.361 mmol) according to general procedure (Method B), in 85% yield, as a colorless oil, which after lyophilization furnished a white hygroscopic solid. HRMS (ESI) $C_{11}H_{14}N_2O_5Na$: [M + Na] calculated 277.0795, found 277.0795. ^{1}H NMR (500 MHz, DMSO-d_6): 3.51 − 3.62 (m, 2H, H-5′); 3.74 (btd, 1H, $J_{2',OH} = J_{2',1'}$ = 7.2 Hz, $J_{2',3'}$ = 5.3 Hz, H-2′); 3.88 (td, 1H, $J_{4',5'a} = J_{4',5'b}$ = 4.3 Hz, $J_{4',3'}$ = 3.0 Hz, H-4′); 3.94 (m, 1H, H-3′); 4.71 (d, 1H, $J_{1',2'}$ = 7.5 Hz, H-1′); 4.87 (t, 1H, $J_{OH,5'a} = J_{OH,5'b}$ = 5.5 Hz, OH-5′); 5.01 (d, 1H, $J_{OH,3'}$ = 4.5 Hz, OH-3′); 5.14 (d, 1H, $J_{OH,2'}$ = 7.1 Hz, OH-2′); 7.61 (m, 1H, NH_2-a); 7.97 (ddd, 1H, $J_{4,3}$ = 8.0 Hz, $J_{4,6}$ = 2.1 Hz, $J_{4,1'}$ = 0.6 Hz, H-4); 8.01 (dd, 1H, $J_{3,4}$ = 8.0 Hz, $J_{3,6}$ = 0.9 Hz, H-3); 8.08 (m, 1H, NH_2-b); 8.63 (bdt, 1H, $J_{6,4}$ = 2.0 Hz, $J_{6,3} = J_{6,1'}$ = 0.7 Hz, H-6). ^{13}C NMR (125.7 MHz, DMSO-d_6): 62.1 (CH_2-5′); 71.7 (CH-3′); 78.0 (CH-2′); 80.6 (CH-1′); 85.9 (CH-4′); 121.7 (CH-3); 135.1 (CH-4); 140.0 (C-5); 146.7 (CH-6); 149.8 (C-2); 166.2 (CO). IR spectrum (KBr): 3411, 1683, 1574, 1418, 1059 cm^{-1}. $[\alpha]^{20}_D$ = −30.9 (*c* 2.08, MeOH).

1β-[6-(Dimethylcarbamoyl)pyridin-3-yl]-1-deoxy-D-ribofuranose (16h). Compound **16h** was prepared from **15h** (250 mg, 0.4 mmol) according to general procedure (Method A), in 88% yield, as a colorless oil, which after lyophilization furnished a white hygroscopic powder. HRMS (ESI) $C_{13}H_{18}N_2O_5Na$: [M + Na] calculated 305.1108, found 305.1107. ^{1}H NMR (500 MHz, DMSO-d_6): 2.94 and 3.00 (2 × s, 2 × 3H, $(CH_3)_2$N); 3.54 (ddd, 1H, J_{gem} = 11.7 Hz, $J_{5'a,OH}$ = 5.4 Hz, $J_{5'a,4'}$ = 4.4 Hz, H-5′a); 3.58 (ddd, 1H, J_{gem} = 11.8 Hz, $J_{5'b,OH}$ = 5.5 Hz, $J_{5'b,4'}$ = 4.3 Hz, H-5′b); 3.75 (td, 1H, $J_{2',1'} = J_{2',OH}$ = 7.3 Hz, $J_{2',3'}$ = 5.2 Hz, H-2′); 3.87 (td, 1H, $J_{4',5'a} = J_{4',5'b}$ = 4.3 Hz, $J_{4',3'}$ = 3.0 Hz, H-4′); 3.94 (m, 1H, H-3′); 4.66 (d, 1H, $J_{1',2'}$ = 7.6 Hz, H-1′); 4.86 (t, 1H, $J_{OH,5'a} = J_{OH,5'b}$ = 5.5 Hz, OH-5′); 5.01 (d, 1H, $J_{OH,3'}$ = 4.5 Hz, OH-3′); 5.11 (d, 1H, $J_{OH,2'}$ = 7.1 Hz, OH-2′); 7.53 (dd, 1H, $J_{3,4}$ = 8.0 Hz, $J_{3,6}$ = 0.9 Hz, H-3); 7.91 (ddd, 1H, $J_{4,3}$ = 8.0 Hz, $J_{4,6}$ = 2.1 Hz, $J_{4,1'}$ = 0.5 Hz, H-4); 8.58 (dm, 1H, $J_{6,4}$ = 2.1 Hz, H-6).^{13}C NMR (125.7 MHz, DMSO-d_6): 35.0 and 38.5 ($(CH_3)_2$N); 62.1 (CH_2-5′); 71.7 (CH-3′); 77.9 (CH-2′); 80.6 (CH-1′); 85.9 (CH-4′); 122.7 (CH-3); 135.0 (CH-4); 137.7 (C-5); 146.5 (CH-6); 153.8 (C-2); 168.2 (CO). IR spectrum (KBr): 3426, 2930, 1627, 1407, 1099 cm^{-1}. $[\alpha]^{20}_D$ = −34.0 (*c* 2.04, MeOH). Anal. Calcd for $C_{13}H_{18}N_2O_5 \cdot H_2O$: C, 51.99; H, 6.71; N, 9.33. Found: C, 52.22; H, 6.48; N, 8.97.

1β-(6-Oxo-1*H*-pyridin-3-yl)-1-deoxy-D-ribofuranose (16i). **15i** (207 mg, 0.363 mmol) was dissolved in TFA/H_2O (9:1, 1.1 mL) and stirred at room temperature for 2 h. The reaction mixture was then coevaporated with MeOH (3 × 100 mL), dissolved in water, and filtered off, and the filtrate was passed through column packed with DOWEX 50 in H^+ cycle. The column was washed with 250 mL of water followed by 75 mL of 25% NH_4OH. Ammonia solutions were concentrated under reduced pressure and purified by reversed-phase chromatography (H_2O/MeOH as an eluent). Subsequent lyophilization furnished compound **16i** (34 mg mg, 41%) as a white hygroscopic powder. HRMS (ESI) $C_{10}H_{12}NO_5$: [M − H] calculated 226.0721, found 226.0721. ^{1}H NMR (500 MHz, DMSO-d_6): 3.46 (ddd, 1H, J_{gem} = 11.7 Hz, $J_{5'a,OH}$ = 5.5 Hz, $J_{5'a,4'}$ = 4.4 Hz, H-5′a); 3.51 (ddd, 1H, J_{gem} = 11.7 Hz, $J_{5'b,OH}$ = 5.6 Hz, $J_{5'b,4'}$ = 4.3 Hz, H-5′b); 3.68 (btd, 1H, $J_{2',1'} = J_{2',OH}$ = 7.2 Hz, $J_{2',3'}$ = 5.3 Hz, H-2′); 3.74 (td, 1H, $J_{4',5'a} = J_{4',5'b}$ = 4.3 Hz, $J_{4',3'}$ = 3.1 Hz, H-4′); 3.87 (bddd, 1H, $J_{3',2'}$ = 5.2 Hz, $J_{3',OH}$ = 4.5 Hz, $J_{3',4'}$ = 3.1 Hz, H-3′); 4.31 (d, 1H, $J_{1',2'}$ = 7.5 Hz, H-1′); 4.80 (t, 1H, $J_{OH,5'a} = J_{OH,5'b}$ = 5.6 Hz, OH-5′); 4.86 (d, 1H, $J_{OH,3'}$ = 4.5 Hz, OH-3′); 4.90 (d, 1H, $J_{OH,2'}$ = 6.9 Hz, OH-2′); 6.32 (d, 1H, $J_{3,4}$ = 9.5 Hz, H-3); 7.29 (bd, 1H, $J_{6,4}$ = 2.6 Hz, H-6); 7.47 (dd, 1H, $J_{4,3}$ = 8.5 Hz, $J_{4,6}$ = 2.6 Hz, H-4); 11.47 (bs, 1H, NH).^{13}C NMR (125.7 MHz, DMSO-d_6): 62.1 (CH_2-5′); 71.6 (CH-3′); 76.3 (CH-2′); 80.2 (CH-1′); 85.3 (CH-4′); 117.6 (C-5); 120.0 (CH-3); 133.2 (CH-6); 140.1 (CH-4); 162.5 (C-2). IR spectrum (KBr): 3404, 3354, 1660, 1662, 1549, 1466, 1427, 1116, 1059, 1014 cm^{-1}. $[\alpha]^{20}_D$ = −45.2 (*c* 1.91, MeOH). Anal. Calcd for $C_{10}H_{13}NO_5 \cdot 1/3\ H_2O$ C, 51.50; H, 5.91; N, 6.01. Found: C, 51.66; H, 5.91; N, 6.02.

Conformational Analysis. A conformational analysis of the ribose ring was performed using program PSEUROT 6.3[28] used for description of five-membered ring conformation. Known parametrization for ribose, directly extracted vicinal proton−proton coupling constants, and procedure MANY were used as an input for nonlinear Newton−Raphson minimization implemented in PSEUROT. The results were postprocessed using program MULDER,[29] gaining values

for north and south conformers (phase angle P, puckering amplitude Φ, equilibrium ratio X).

Single Crystal X-ray Structure Analysis. The diffraction data of single crystals were collected on an X-ray diffractometer with $Cu_{K\alpha}$ (λ=1.54180 Å) at 150 K (**12**, **14a**, **14f**, **14h**) or at 170 K (**16c**). Both structures were solved by direct methods with SIR92[30] and refined by full-matrix least-squares on F with CRYSTALS.[31] All hydrogen atoms were located in a difference map, but those attached to carbon atoms were repositioned geometrically and then refined with riding constraints, while all other atoms were refined anisotropically in both cases.

Crystal data for ***12*** *(colorless, 0.08 × 0.32 × 0.75 mm).* $C_{28}H_{54}Br_1N_1O_5Si_3$, orthorhombic, space group $P2_12_12_1$, a = 8.32986(10) Å, b = 11.95103(15) Å, c = 35.3621(5) Å, V = 3520.31(8) Å^3, Z = 4, M = 648.90, 17910 reflections measured, 7383 independent reflections. Final R = 0.038, wR = 0.046, GoF = 0.928 for 6927 reflections with $I > 2\sigma(I)$ and 344 parameters. Flack parameter x = 0.048(14). CCDC 821676.

Crystal data for ***14a*** *(colorless, 0.04 × 0.44 × 0.69 mm).* $C_{11}H_{15}N_1O_4$, monoclinic, space group $P2_1$, a = 5.03627(13) Å, b = 10.7538(3) Å, c = 10.1690(3) Å, β = 97.824(2)°, V = 545.62(2) Å^3, Z = 2, M = 225.24, 4227 reflections measured, 2208 independent reflections. Final R = 0.040, wR = 0.047, GoF = 1.025 for 2110 reflections with $I > 2\sigma(I)$ and 146 parameters, Flack parameter x = 0.07(18). CCDC 821675.

Crystal data for ***14f*** *(colorless, 0.16 × 0.60 × 0.68 mm).* $C_{12}H_{18}N_2O_4$, monoclinic, space group $P2_1$, a = 4.99794(7) Å, b = 10.75451(16) Å, c = 11.36720(17) Å, β = 91.1917(13)°, V = 610.859(15) Å^3, Z = 2, M = 254.29, 4271 reflections measured, 2438 independent reflections. Final R = 0.030, wR = 0.033, GoF = 1.058 for 2421 reflections with $I > 2\sigma(I)$ and 165 parameters. Flack parameter x = 0.29(13). CCDC 821677.

Crystal data for ***14h*** *(colorless, 0.26 × 0.65 × 0.69 mm).* $C_{13}H_{18}N_2O_5$, monoclinic, space group $P2_1$, a = 6.8778(3) Å, b = 10.4003(5) Å, c = 9.7635(4) Å, β = 105.007(5)°, V = 674.58(5) Å^3, Z = 2, M = 282.30, 6885 reflections measured, 2616 independent reflections. Final R = 0.029, wR = 0.037, GoF = 0.933 for 2604 reflections with $I > 2\sigma(I)$ and 183 parameters. Flack parameter x = 0.09(11). CCDC 821678.

Crystal data for ***16c*** *(colorless, 0.07 × 0.17 × 0.51 mm).* $C_{14}H_{15}N_1O_4S_1$, monoclinic, space group $P2_1$, a = 4.9831(3) Å, b = 11.6287(8) Å, c = 11.8750(8) Å, β = 100.351(7)°, V = 676.92(8) Å^3, Z = 2, M = 293.34, 5444 reflections measured, 2758 independent reflections. Final R = 0.055, wR = 0.068, GoF = 1.071 for 2417 reflections with $I > 2\sigma(I)$ and 218 parameters. Flack parameter x = 0.05(4). The thienyl ring has been found to be disordered over two sites (57: 43). The disordered non-hydrogen atoms were refined anisotropically, but several restraints were used to regularize the geometry of the thienyl ring. CCDC 822843.

■ ASSOCIATED CONTENT

Supporting Information. CIF files for crystal structures and copies of the ^{1}H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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