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# Modular and Practical Synthesis of 6-Substituted Pyridin-3-yl C-Nucleosides

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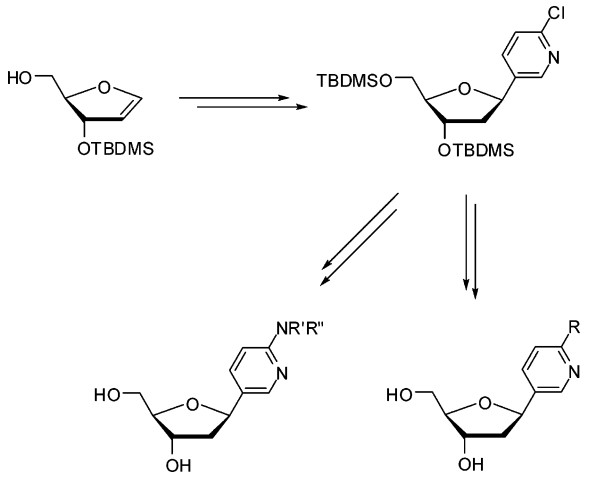


A novel modular and practical methodology for preparation of 6-substituted pyridin-3-yl C-nucleosides was developed. The Heck reaction of 2-chloro-5-iodopyridine with a 3′-TBDMS-protected glycal gave a 6-chloropyridin-3-yl nucleoside analogue, which was then desilylated, selectively reduced, and reprotected to give the TBDMS-protected 6-chloropyridin-3-yl C-2′-deoxyribonucleoside as a pure $\beta$-anomer in a total yield of 39% over four steps. This key intermediate was then subjected to a series of palladium-catalyzed cross-coupling reactions, aminations, and alkoxylations to give a series of protected 1$\beta$-(6-alkyl-, 6-aryl-, 6-hetaryl, 6-amino-, and 6-*tert*-butoxypyridin-3-yl)-2′-deoxyribonucleosides. 6-Unsubstituted pyridin-3-yl C-nucleoside was prepared by catalytic hydrogenation of the chloro derivative and 6-oxopyridine C-nucleoside by treatment of the 6-*tert*-butoxy derivative with TFA. Deprotection of all the silylated nucleosides by $Et_3N{\cdot}3HF$ gave a series of free C-nucleosides (10 examples).

## Introduction

C-Nucleosides are an important class of compounds characterized by replacement of a labile glycosidic C−N bond by a stable hardly degradable C−C bond. C-Nucleosides bearing hydrophobic aryl groups as nucleobase surrogates attract great attention due to their use in the extension of the genetic alphabet.[1] In oligonucleotide duplexes, they selectively pair with the same or other hydrophobic nucleobase due to increased packing and favorable desolvation energy as compared to canonical hydrophilic nucleobases.[2] Triphosphates of some of the C-nucleosides are efficiently incorporated to DNA by DNA polymerases;[3] however, further extension of the duplex is much more problematic. Recent studies show crucial importance of minor-groove interactions[4,5] of the artificial nucleobase with the enzyme. Therefore, the most promising candidates for efficient incorporation and extension are the triphosphates of hetaryl-C-nucleosides,[4,6] such as pyridine nucleosides, possessing equivocal nature between hydrophilic and hydrophobic species.

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There are several synthetic approaches[7] to C-nucleosides: (i) additions of organometallics to ribono- or 2-deoxyribonolactones;[3,8,9] (ii) coupling of a halogenose with organometallics (usually highly toxic diarylcadmium species[10] or arylcuprates[11]); (iii) electrophilic substitutions of electron-rich aromatics with sugars under Lewis acid catalysis;[12] (iv) Heck-type coupling of aryl iodides with glycals[9,13−15] or opening of glycal epoxides with arylaluminum reagents.[16] Most of these approaches suffer from rather poor yields and/or insufficient anomeric selectivity and necessity to optimize reaction and separation conditions for each particular C-nucleoside, which makes it very difficult to prepare larger series of derivatives. Often the target 2′-deoxyribo-C-nucleosides[17] must be prepared indirectly via additions to ribonolactones, followed by reduction and Barton deoxygenation at the 2′-position. Therefore, development of a general and also possibly modular approaches to the synthesis of these extremely important compounds is still of great interest.

We are currently involved in the development of modular methodologies based on larger scale syntheses of versatile C-nucleoside intermediates and their further use for a generation of a series of diverse derivatives. Recently, we have developed a modular approach consisting of the preparation of 3- and 4-bromophenyl C-nucleosides[18] or 6-bromopyridin-2-yl C-nucleoside,[19] followed by displacement of the bromine for alkyl, aryl, or amino substituents by cross-coupling reactions and Hartwig−Buchwald aminations. Other groups have recently also applied this approach[3a,20] for analogous C-nucleosides. Another modular methodology was based on construction of an aromatic ring on deoxyribose by cyclotrimerizations of 1-ethynyl-2-deoxyribose with α,ω-diynes.[21] As the pyridine C-nucleosides are important analogues of pyrimidine nucleosides and there are just a few rather scattered examples of syntheses of 3-pyridyl ribo-[22] and 2-deoxyribonucleosides,[9,13] we wish to report here on a modular and practical synthesis of diverse 6-substituted pyridin-3-yl C-nucleosides.

## Results and Discussion

Our selected approach of choice for the synthesis of a series of 6-substituted 3-pyridyl C-nucleosides was based on the synthesis of a suitably protected 6-halo 3-pyridyl C-nucleoside intermediate and on its further synthetic transformations (cross-coupling, amination, etc.). Therefore, our first efforts were devoted to the synthesis of the corresponding halopyridine nucleoside intermediate. Several reactions have been studied for this purpose, in analogy with the literature (Scheme 1). 2,5-Dibromopyridine **1a** was reported to be selectively lithiated in position 5[23] to give 5-lithio-2-bromopyridine **2a**, which should react with TBDMS-protected 2′-deoxyribonolactone **3**.[24] Unfortunately, in our hands, the lithiation did not proceed selectively and, even after attempted optimizing of the conditions, complex mixtures of products were obtained. In order to perform reactions selectively in the position 5 of the pyridine moiety, we tried lithiation of 2-chloro-5-iodopyridine **1b** or bis-PMB-protected 2-amino-5-bromopyridine **1c**,[25] followed by addition to lactone **3**. In all cases, complex mixtures of unseparable products were formed and/or dehalogenation of pyridine was observed. Similar reactivity was observed when we replaced lactone **3** with lactol **4** (easily obtained from lactone **3** in 92% yield, by reduction in presence of DIBALH in $Et_2O$ at −70 °C in 40 min).[26] For more details on the unsuccessful approaches, see Supporting Information.

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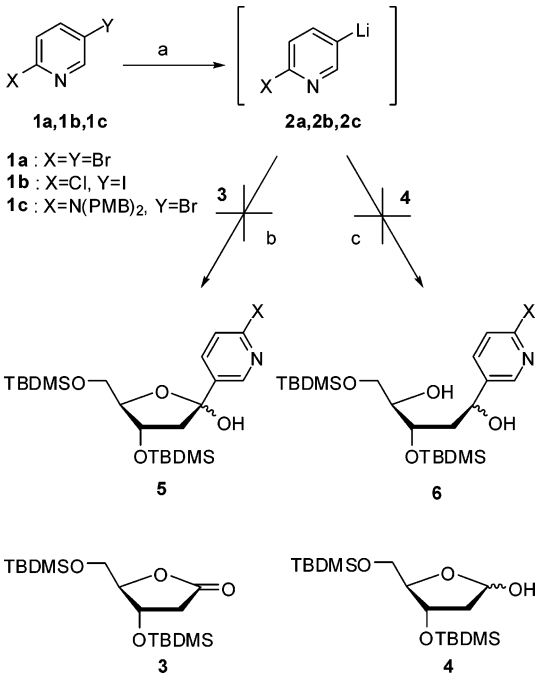
**TABLE 1. Optimization of the Heck Reaction**

| entry | glycal | Pd catalyst | ligand | solvent | base | *T* (°C) | time | product (yield) |
|---|---|---|---|---|---|---|---|---|
| 1 | **7a** | $Pd(OAc)_2$ | $AsPh_3$ | DMF | $(n\text{Bu})_3N$ | 70 | 1 day | degradation |
| 2 | **7a** | $Pd_2dba_3$ | $(PhF_5)_3P$ | $CH_3CN$ | $(i\text{Pr})_2\text{NEt}$ | 50 | 2 days | no reaction |
| 3 | **7b** | $Pd_2dba_3$ | bdtbp[a] | $CH_3CN$ | $(i\text{Pr})_2\text{NEt}$ | 60 | 4 days | no reaction |
| 4 | **7b** | $Pd_2dba_3$ | $(PhF_5)_3P$ | $CH_3CN$ | $(i\text{Pr})_2\text{NEt}$ | 60 | 2 days | degradation |
| 5 | **7b** | $Pd(OAc)_2$ | $AsPh_3$ | DMF | $K_2CO_3$ | 80 | 2 days | degradation |
| 6 | **7b** | $Pd(OAc)_2$ | bdtbp[a] | DMF | $Et_3N$ | 80 | 5 days | degradation |
| 7 | **7b** | $Pd_2dba_3$ | dppf[b] | $CH_3CN$ | $(n\text{Bu})_3N$ | 80 | 2 days | degradation |
| 8 | **7b** | $Pd(OAc)_2$ | $AsPh_3$ | DMF | $(n\text{Bu})_3N$ | 80 | 2 days | degradation |
| 9 | **7b** | $Pd(OAc)_2$ | $AsPh_3$ | $CHCl_3$ | $(n\text{Bu})_3N$ | 60 | 5 days | **8b** (14%) |
| 10 | **7b** | $Pd(OAc)_2$ | $AsPh_3$ | $CHCl_3$ | $(n\text{Bu})_3N + AgNO_3$ | 60 | 16 h | **8b** (40%) |
| 11 | **7b** | $Pd(OAc)_2$ | $AsPh_3$ | $CHCl_3$ | $Ag_2CO_3$ | 60 | 16 h | **8b** (65%) |
| 12 | **7b** | $Pd(OAc)_2$ | $AsPh_3$ | $C_2H_4Cl_2$ | $Ag_2CO_3$ | 60 | 16 h | **8b** (0%) |
| 13 | **7a** | $Pd(OAc)_2$ | $AsPh_3$ | $CHCl_3$ | $(n\text{Bu})_3N$ + AgNO3 | 60 | 16 h | **8a** (traces) |
| 14 | **7a** | $Pd(OAc)_2$ | $AsPh_3$ | $CHCl_3$ | $Ag_2CO_3$ | 60 | 16 h | **8a** (16%) |

[a] bdtbp = (2-biphenyl)di-*tert*-butylphosphine. [b] dppf = diphenylphosphinoferrocene.

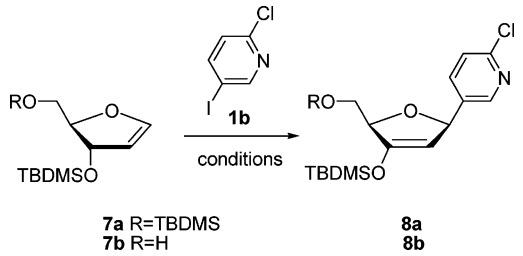
**SCHEME 1. Reactions of Lactone 3 and Lactol 4 with Organometallics[a]**




[a] Reagents and conditions: (a) BuLi, toluene, −100 to −70 °C, 10 min; with or without the following additive: (i) $ZnCl_2$; (ii) CuI (b) **3**, toluene, −100 to −70 °C, 10 min; (c) **4**, toluene, −100 to −70 °C, 10 min.

Having no encouraging results with the addition of lithiated pyridines to lactone **3** or lactol **4**, we focused our attention on the palladium-catalyzed Heck reaction[27] of iodopyridine **1b** with bis-TBDMS-protected glycal **7a** or mono-3′-TBDMS-protected glycal **7b**.[15] The starting bis-TBDMS-protected glycal **7a** was obtained by a one-pot mesylation−elimination sequence from lactol **4**, by treatment with MsCl and $Et_3N$ in $CH_2Cl_2$. Mono-TBDMS-3′-protected glycal **7b** was prepared via selective 5′-desilylation of **7a** in the presence of TBAF in THF at 0 °C in 60% yield.[28] First we have tried the Heck reaction of 2-chloro-5-iodopyridine with bis-TBDMS-protected glycal **7a** under conditions analogous to the literature.[29] Only degradation was observed when using the $AsPh_3$ ligand in DMF at 70 °C, while the use of $P(C_6F_5)_3$ in acetonitrile did not give any reaction (Scheme 2 and Table 1, entries 1 and 2). Therefore, we have further performed Heck reactions with mono-3′-TBDMS-protected glycal **7b** which was known[26,30] to have superior reactivity. Nevertheless, the first experiments under analogous conditions did not bring any improvement (entries 3−8). Only the use of $Pd(OAc)_2/AsPh_3$ in chloroform in the presence of $(n\text{-Bu})_3N$ afforded the desired compound **8b** in a low but encouraging yield (14% yield, entry 9). In order to improve the reactivity of the glycal in the Heck reaction, we decided to use some silver salts as additives.[31] When silver nitrate was added in addition to tributylamine, the yield reached 40% (entry 10). When silver carbonate was used as a base and additive (without tributylamine), the desired compound **8b** was obtained in good yield of 65% as a pure $\beta$-anomer (entry 11). This reaction is very sensitive to solvent—even the replacement of chloroform by dichloroethane led to degradation with no traces of the product (entry 12). Finally, application of the optimized conditions on bis-protected glycal **7a** gave the desired nucleoside **8a** in very low yields confirming that the 5′-TBDMS protecting group decreases the reactivity of the glycal (entries 14 and 15). Therefore, the preparative procedure involved the reaction of 2-chloro-5-iodopyridine (**1b**) with mono-TBDMS-protected glycal **7b** in the presence of $Pd(OAc)_2/AsPh_3$ and $Ag_2CO_3$ in chloroform to give the desired C-nucleoside precursor **8b** in acceptable 65% yield even on 10 mmol scale.

**SCHEME 2. Optimization of the Heck Reaction**

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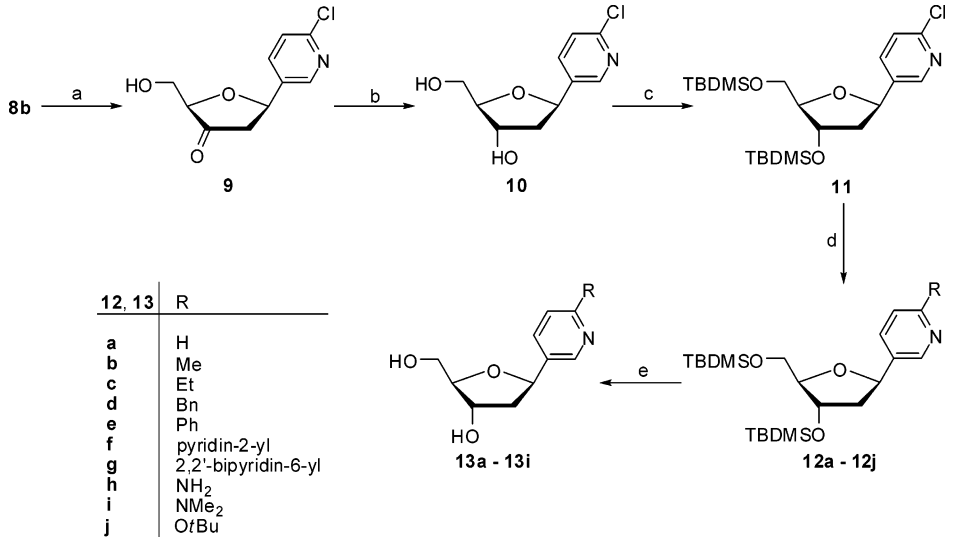
**SCHEME 3. Synthesis, Cross-Coupling, and Amination Reactions of Chloroderivative 11**[a]




[a] Reagents and conditions: (a) $Et_3N{\cdot}3HF$, THF, rt, 5 min; (b) $NaBH(OAc)_3$, $CH_3CN$, AcOH, 0 °C, 5 min, 70%, two steps; (c) TBDMSCl, imidazole, DMF, rt, 16h, 87%; (d) see Table 2 ; (e) $Et_3N{\cdot}3HF$, THF, rt, 16 h.

**TABLE 2. Reactions of Intermediate 11 and Deprotections**

| entry | reagent | catalyst | ligand/base | solvent | other conditions | product | yield (%) | deprotection product | yield (%) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $H_2$ | Pd/C | $Et_3N$ | THF, EtOH, $H_2O$ | rt, 101 kPa | **12a** | 82 | **13a** | 86 |
| 2 | $Me_3Al$ | $Pd(PPh_3)_4$ | | THF | 72 h, 70 °C | **12b** | 90 | **13b** | 90 |
| 3 | $Et_3Al$ | $Pd(PPh_3)_4$ | | THF | 18 h, 70 °C | **12c** | 81 | **13c** | 89 |
| 4 | BnZnBr | $Pd(PPh_3)_4$ | | THF | 20 h, 60 °C | **12d** | 76 | **13d** | 85 |
| 5 | $PhB(OH)_2$ | $Pd_2(dba)_3$ | KF, P(*t*-Bu)$_3{\cdot}HBF_4$ | THF | 72 h, 60 °C | **12e** | 60 | **13e** | 80 |
| 6 | 2-$Bu_3Sn$-Py[d] | $PdCl_2$dppf | | DMF | 18 h, 95 °C | **12f** | 65 | **13f** | 90 |
| 7 | 6-$Bu_3Sn$-[2,2′]-biPy[e] | $PdCl_2$dppf | | DMF | 18 h, 95 °C | **12g** | 49[f] | **13g** | 85 (42)[g] |
| 8 | $LiN(SiMe_3)_2$ | $Pd_2(dba)_3$ | bdCyp[a] | THF | 21 h, 60 °C | **12h** | 90 | **13h** | 90 |
| 9 | $Me_2NH.HCl$ | $Pd(OAc)_2$ | CyPF-*t*Bu,[b] *t*BuONa | DME | 60 h, 70 °C | **12i** | 60 | **13i** | 84 |
| 10 | *t*BuONa | $Pd_2(dba)_3$ | bdtbp[c] | toluene | 24 h, 90 °C | **12j** | 51 | | |

[a] bdCyp = (2-biphenyl)dicyclohexylphosphine. [b] CyPF-*t*Bu = Josiphos ligand. [c] bdtbp = (2-biphenyl)di-*tert*-butylphosphine. [d] Py = pyridine. [e] 6-$Bu_3Sn$-[2,2′]-biPy = 6-tributylstannyl-[2,2′]-bipyridine. [f] Estimated yield based on NMR purity (70%) of crude product. [g] isolated yield over two steps in parenthesis.

The subsequent step was the desilylation of **8b** (Scheme 3). The common use of TBAF in THF[32] for desilylation led in our case to an unseparable mixture of compounds, whereas the complex $Et_3N{\cdot}3HF$ in THF at 0 °C in 5 min gave us the desired ketone **9**, which was directly reduced in the following step using triacetoxyborohydride[33] in a mixture of acetonitrile and acetic acid. The reduction proceeded very well to give the final C-nucleoside **10** in a good yield of 70% for the two steps. In accord with the literature precedent,[15] the pathway via Heck reaction afforded **10** as a single diastereoisomer of desired *β-erythro*-configuration (confirmed by $^1H$ NMR ROESY spectroscopy). In order to facilitate further functional group transformations on the heterocycle ring, the nucleoside **10** was protected using TBDMSCl with imidazole in DMF to afford the fully protected key intermediate *β*-C-nucleoside **11** in 87% yield (39% overall yield in 10 mmol scale over four steps from glycal **7b**, Scheme 3).

Having a practical, reproducible, and scalable procedure for the preparation of the protected 6-chloropyridine C-nucleoside **11** in hand, we decided to submit it to various cross-coupling reactions and other transformations to prepare a series of new C-nucleosides (Scheme 3, Table 2). The first target derivative was the 6-unsubstituted pyridine nucleoside **12a**. We performed a catalytical hydrogenolysis of chlorine in nucleoside **11**, using $H_2$ over Pd/C for 3 h, in a mixture of EtOH, THF, and $H_2O$, in presence of $Et_3N$ (to neutralize HCl to avoid formation of byproducts and deprotection of silyl groups), to give the desired nucleoside **12a** in 86% yield (entry 1).

Pd-catalyzed cross-coupling reactions were used for introduction of alkyl or aryl substituents. The reactions of **11** with trimethylaluminum, triethylaluminum, and benzylzinc bromide were performed under standard conditions in THF using standard catalysis of $Pd(PPh_3)_4$ and with no optimization. Though the lower reactivity of chlorine (in comparison of bromine)[17] made the reaction last 3 days to reach completion (TLC monitoring), in all of these reactions, the desired nucleosides, **12b**, **12c**, and **12d** respectively (entries 2−4), were obtained in good isolated yields (>75%). In the case of the Suzuki cross-coupling, specific conditions were used to overcome the low reactivity of chlorine.[34] Reaction of **11** with phenylboronic acid was performed in presence of $Pd_2(dba)_3$, KF, and P(*t*Bu)$_3{\cdot}HBF_4$ in THF (in analogy to literature[34] conditions), but the reaction was still very slow to give the desired nucleoside **12e** with a satisfactory yield of 60% only after 72 h at 60 °C (entry 5). The Stille cross-coupling reactions[35] of **11** with 2-$Bu_3Sn$-pyridine and 6-$Bu_3Sn$-2,2′-bipyridine in the

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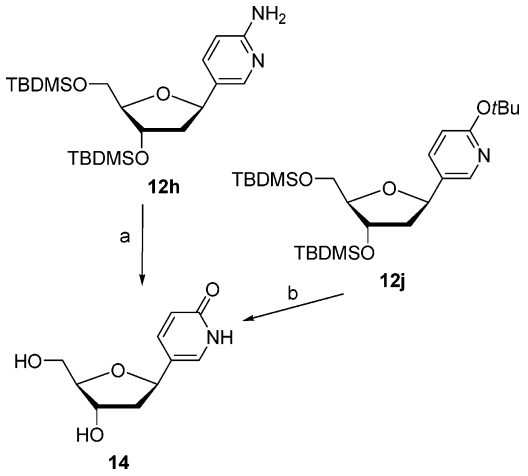
presence of $PdCl_2$dppf in DMF were used for the synthesis of 2,2′-bipyridin-5-yl and [2,2′;6′,2″]terpyridin-5-yl C-nucleosides **12f** and **12g** (entries 6 and 7), interesting metal-chelating C-nucleoside ligands. While, in the former case, the desired bipyridine product **12f** was isolated in acceptable yield of 65%, the terpyridine product **12g** was not fully purified even after repeated chromatography (entry 7) and was used in the subsequent deprotection step in crude form (ca. 70% NMR purity).

Hartwig−Buchwald aminations[36,37] were performed for introduction of N-substituents. Lithium bis(trimethylsilyl)amide ($LiN(SiMe_3)_2$) was used as an ammonia equivalent for introduction of amino group. In our first attempt, the reaction of $LiN(SiMe_3)_2$ with **11** was performed in the presence of $Pd_2(dba)_3$ and P(*t*Bu)$_3$ (generated in situ from P(*t*Bu)$_3$·$HBF_4$ using excess of the amide) in THF in analogy to our previous work[19] on bromopyridine nucleosides. This reaction gave only traces of the desired product, due to low reactivity of chlorine. Therefore, (2-biphenyl)dicyclohexylphosphine, known to be a superior ligand for amination of 2-chloropyridine,[38] was used under analogous conditions to give the desired aminopyridine nucleoside **12h** in good yield of 78% (entry 8). Hartwig−Buchwald[39] reactions were also used for introduction of a substituted amino group. We used conditions for aminations of chloropyridine recently developed by Hartwig.[40] The reaction of **11** with dimethylamine hydrochloride was performed in the presence of $Pd_2(dba)_3$, Josiphos ligand CyPF-*t*Bu, and excess of *t*BuONa as base to give the target substituted amine **12i** in 60% yield (entry 9). Analogous reaction of **11** with sodium *tert*-butoxide in the absence of an amine using $Pd_2(dba)_3$/(2-biphenyl)di-*tert*-butylphosphine catalytic system in toluene gave preparatively the 6-(*tert*-butoxy)pyridine C-nucleoside **12j** in 51% yield (entry 10).

All the silylated nucleosides **12a**−**i** were deprotected using $Et_3N$·3HF in THF[41] to give the free 6-substituted pyridine C-nucleosides **13a**−**i** in good yields (>80%). Even in case of the crude protected terpyridine nucleoside **12g** (containing unseparable impurities), the corresponding free terpyridine C-nucleoside **13g** was isolated in pure form after deprotection (preparative yield of 42% over two steps). This novel C-nucleoside is of particular interest due to metal chelating properties of the terpyridine unit.[42]

We were also interested in the synthesis of pyridin-2-one C-nucleoside, which is a "deletion-modified" analogue of uridine.[43] Diazotation of 2-aminopyridines using isoamyl nitrite in aqueous acetic acid is a classical approach[44] to pyridones successfully used recently for the 6-linked 2-pyridone C-nucleoside.[19] Unfortunately, in this case, treatment of aminopyridine C-nucleoside **12h** with isopentyl nitrite in 80% aqueous AcOH at 70 °C for 100 min afforded the desired 6-oxopyridin-3-yl C-nucleoside **14** accompanied by some unseparable impurities. Therefore, we have prepared the target pyridone by complete deprotection of the 6-(*tert*-butoxy)pyridine derivative **12j** on treatment with TFA for 20 min to give the desired free pyridone C-nucleoside **14** in 84% yield (Scheme 4).

**SCHEME 4. Preparation of 6-Oxopyridin-3-yl Nucleoside 14**[a]




[a] Reagents and conditions: (a) isopentyl nitrite, 80% AcOH in $H_2O$, 70 °C, 1 h 40, impure compound; (b) TFA, rt, 20 min, 84%.

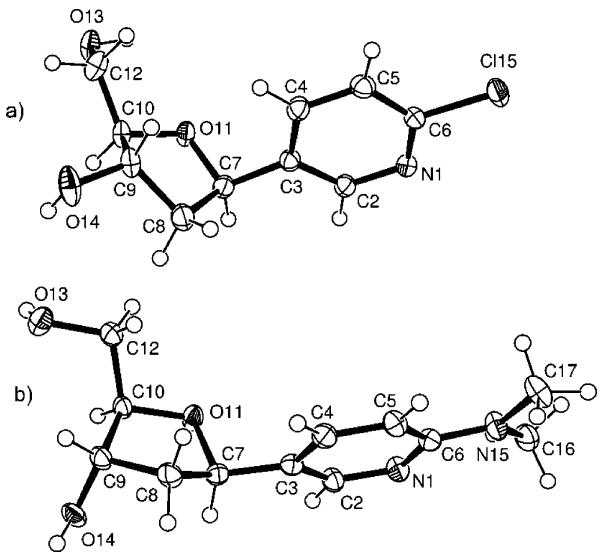



**FIGURE 1.** ORTEP drawing of **10** (a) and **13i** (b) with atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

All compounds were fully characterized, and the crystal structures of **10** and **13h** were also determined by X-ray diffraction (Figure 1). NMR conformation analysis (see Supporting Information) indicates that, in DMSO or methanol

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solution, the free nucleosides **10**, **13a**−**i**, and **14** occur preferentially in the C2′-*endo* conformer, in a C2′-*endo* versus C3′-*endo* conformer ratio dependent on the substituent effect. According to the X-ray diffraction, the C-nucleoside **13h** occurs in the solid state in the expected C2′-*endo* conformation; however, the chloropyridine nucleoside **10** occurs in the C3′-*endo* form in the solid state (in contrast to C2′-*endo* conformation prefered in solution). Both of these crystal structures reveal *anti*-conformation of the nucleobase due to intermolecular hydrogen bonds between the 5′-OH group and nitrogen atom in the pyridine of a neighbor molecule (see Figure S1 in Supporting Information).

In conclusion, a modular and reasonably practical methodology of the synthesis of 6-substituted pyridin-3-yl C-nucleosides was developed based on cross-coupling reactions and Hartwig−Buchwald aminations of 6-chloropyridin-3-yl C-nucleoside **11**, available in four steps (36%) from monosilylated glycal **7b** via a Heck reaction. The methodology enables the synthesis of a large series of pyridine C-nucleosides bearing diverse C (alkyl, aryl, or hetaryl), N (unsubstituted and dialkylamino), or O (alkoxy or oxo) groups from one common intermediate. These C-nucleosides are interesting building blocks for construction of modified nucleic acids (including metal chelating oligonucleotides and metallo base pairs) and potential candidates for extension of the genetic alphabet.

## Experimental Section

**1β-(6-Chloropyridin-3-yl)-1,2-dideoxy-2,3-didehydro-3-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (8b).** $CHCl_3$ (62 mL) was added to an argon-purged, dried flask containing $Pd(OAc)_2$ (302 mg, 1.4 mmol) and $AsPh_3$ (863 mg, 2.80 mmol), and the mixture was stirred at rt for 30 min. Then 2-chloro-5-iodopyridine (2.42 g, 9.90 mmol), a solution of glycal **7b** (1.52 g, 6.60 mmol) in $CHCl_3$ (62 mL), and $Ag_2CO_3$ (2.78 g, 9.90 mmol) were added, and the reaction mixture was stirred until the disappearance of glycal **7b** (typically 16 h, checked by TLC). The reaction mixture was then cooled, the solvents were removed in vacuum, and the crude product was chromatographed on silica gel in gradient hexane to hexane/EtOAc 8/2 to give the desired nucleoside **8b** (1.47 g, 65%) as a yellow oil: MS (FAB) *m*/*z* 342 (M + 1); HRMS (FAB) for $C_{16}H_{25}O_3SiCl$ [M + H] calcd 342.1292, found 342.1276; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.24 (s, 6H, $CH_3Si$), 0.96 (s, 9H, $(CH_3)_3C$), 3.74 (dd, 1H, $J_{gem}$ = 12.0 Hz, $J_{5'b,4'}$ = 3.7 Hz, H-5′b), 3.79 (ddd, 1H, $J_{gem}$ = 12.0 Hz, $J_{5'a,4'}$ = 3.0 Hz, $J_{5'a,2'}$ = 0.7 Hz, H-5′a), 4.63 (dq, 1H, $J_{4',1'}$ = 3.9 Hz, $J_{4',5'}$ = 3.7, 3.0 Hz, $J_{4',2'}$ = 1.9 Hz, H-4′), 4.81 (br t, 1H, $J_{2',4'}$ = 1.9 Hz, $J_{2',1'}$ = 1.6 Hz, H-2′), 5.75 (dd, 1H, $J_{1',4'}$ = 3.9 Hz, $J_{1',2'}$ = 1.6 Hz, H-1′), 7.32 (dd, 1H, $J_{3,4}$ = 8.2 Hz, $J_{3,6}$ = 0.7 Hz, H-3), 7.77 (dd, 1H, $J_{4,3}$ = 8.2 Hz, $J_{4,6}$ = 2.5 Hz, H-4), 8.38 (br d, 1H, $J_{6,4}$ = 2.5 Hz, H-6); $^{13}$C NMR (100.6 MHz, $CDCl_3$) $\delta$ −5.0 and −4.9 ($CH_3Si$), 18.0 ($\mathbf{C}(CH_3)_3$), 25.5 (($\mathbf{C}H_3)_3C$), 62.9 ($CH_2$-5′), 81.8 (CH-1′), 83.5 (CH-4′), 100.3 (CH-2′), 124.3 (CH-3), 137.0 (C-5), 137.9 (CH-4), 148.7 (CH-6), 151.2 (C-2), 152.3 (C-3′); IR spectrum ($CHCl_3$) 3605, 1766, 1709, 1662, 1604, 1589, 1570, 1485, 1463, 1441, 1395, 1367, 1287, 1259, 1137, 1110, 1089, 1048, 939, 838 cm$^{-1}$. Due to nonremovable traces of heterocycle, no more analyses were performed, and the product was used for the next step without any problem.

**1β-(6-Chloropyridin-3-yl)-1,2-dideoxy-D-ribofuranose (10).** To a dried flask containing a solution of the nucleoside **8b** (346 mg, 1.01 mmol) in dry THF (2.6 mL) at 0 °C under argon was added $Et_3N{\cdot}HF$ (420 μL, 2.58 mmol). After disappearance of the nucleoside **8b** (typically 2 min, checked by TLC), the reaction mixture was filtered on a small pad of silica gel (1.5 cm) and eluted with EtOAc. The solvents were removed under vacuum, and the crude product was used without further purification in the next step. For analysis, a sample was chromatographed on silica gel in gradient hexane to hexane/EtOAc 3/7 to give the desired nucleoside **9** as a colorless oil (for characterization data, see Supporting Information). $NaBH(OAc)_3$ (322.0 mg, 1.52 mmol) was added to a dried flask containing a solution of the crude nucleoside **9** in a mixture of $AcOH/CH_3CN$ 2/1 (15 mL) at 0 °C under argon. After 5 min (disappearance of **9** observed by TLC), a solution of $EtOH/H_2O$ 1/1 (10 mL) was added to neutralize the solution. Then the solvents were evaporated in vacuum, and the crude product was chromatographed on silica gel in gradient EtOAc to EtOAc/MeOH 9/1. Crystallization from EtOAc/heptane gave the desired nucleoside **10** (161 mg, 70% for two steps) as colorless crystals (for characterization data, see Supporting Information).

**1β-(6-Chloropyridin-3-yl)-1,2-dideoxy-3,5-di-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (11).** To a dried flask containing a solution of the nucleoside **10** (486 mg, 2.12 mmol) in dry DMF (9.8 mL) at 0 °C under argon were added imidazole (576 mg, 8.46 mmol) and then TBDMSCl (797 mg, 5.29 mmol), and the solution was allowed to warm to rt and was stirred for 16 h. The reaction mixture was then poured into a saturated solution of NaCl (100 mL) and extracted with EtOAc (3 × 30 mL). Collected organic fractions were washed with a saturated NaCl solution, dried over $MgSO_4$, and the solvents were evaporated under vacuum. The crude product was chromatographed on silica gel in gradient hexane to hexane/EtOAc 9/1 to give the desired nucleoside **11** (169 mg, 73%) as a colorless oil: MS (FAB) *m*/*z* 458 (M + 1); HRMS (FAB) for $C_{22}H_{41}NO_3Si_2Cl$ [M + H] calcd 458.2314, found 458.2334; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 0.07, 0.08 and 0.10 (3 × s, 12H, $CH_3$−Si), 0.90 and 0.92 (2 × s, 2 × 9H, $(CH_3)_3C$), 1.87 (ddd, 1H, $J_{gem}$ = 12.6 Hz, $J_{2'b,1'}$ = 10.5 Hz, $J_{2'b,3'}$ = 5.3 Hz, H-2′b), 2.15 (ddd, 1H, $J_{gem}$ = 12.6 Hz, $J_{2'a,1'}$ = 5.4 Hz, $J_{2'a,3'}$ = 1.6 Hz, H-2′a), 3.64 (dd, 1H, $J_{gem}$ = 10.8 Hz, $J_{5'b,4'}$ = 5.2 Hz, H-5′b), 3.75 (dd, 1H, $J_{gem}$ = 10.8 Hz, $J_{5'a,4'}$ = 3.5 Hz, H-5′a), 3.98 (ddd, 1H, $J_{4',5'}$ = 5.2, 3.5 Hz, $J_{4',3'}$ = 1.9 Hz, H-4′), 4.39 (m, 1H, $J_{3',2'}$ = 5.3, 1.6 Hz, $J_{3',4'}$ = 1.9 Hz, $J_{3',1'}$ = 0.6 Hz, H-3′), 5.15 (m, 1H, $J_{1',2'}$ = 10.5, 5.4 Hz, $J_{1',3'} = J_{1',3} = J_{1',4} = J_{1',6}$ = 0.6 Hz, H-1′), 7.28 (dt, 1H, $J_{3,4}$ = 8.2 Hz, $J_{3,6}$ = 0.9 Hz, $J_{3,1'}$ = 0.6 Hz, H-3), 7.71 (ddd, 1H, $J_{4,3}$ = 8.3 Hz, $J_{4,6}$ = 2.5 Hz, $J_{4,1'}$ = 0.6 Hz, H-4), 8.36 (dt, 1H, $J_{6,4}$ = 2.5 Hz, $J_{6,3}$ = 0.9 Hz, $J_{6,1'}$ = 0.6 Hz, H-6); $^{13}$C NMR (125.7 MHz, $CDCl_3$) $\delta$ −5.2, −5.4, −4.72 and −4.67 ($CH_3$−Si), 18.0 and 18.3 ($\mathbf{C}(CH_3)_3$), 25.8 and 25.9 (($\mathbf{C}H_3)_3C$), 44.4 ($CH_2$-2′), 63.7 ($CH_2$-5′), 74.3 (CH-3′), 77.2 (CH-1′), 88.7 (CH-4′), 123.9 (CH-3), 136.7 (CH-4), 137.0 (C-5), 147.7 (CH-6), 150.4 (C-2); IR spectrum ($CHCl_3$): 3054, 2898, 1591, 1567, 1472, 1463, 1406, 1390, 1362, 1258, 1092, 940, 838, 681 cm$^{-1}$; $[\alpha]^{20}_D$ +16.0 (*c* 6.88, $CHCl_3$). Anal. Calcd for $C_{22}H_{40}ClNO_3Si_2$ (458.2): C, 57.67; H, 8.80; Cl, 7.74; N, 3.06. Found: C, 57.82; H, 9.01; Cl, 7.71; N, 3.00.

**1β-(Pyridin-3-yl)-1,2-dideoxy-3,5-di-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (12a).** To a solution of the nucleoside **11** (289 mg, 0.63 mmol) in a mixture of THF/EtOH/$H_2O$ 10/10/1 (23 mL) at rt were added 10% Pd/C (170 mg, 0.23 mmol) and $Et_3N$ (0.66 mL). The flask was evacuated and then filled with $H_2$ (100 kPa) and stirred at rt. After the reaction was completed (50 min, checked by TLC), the Pd was filtered off, and the filtrate was poured into water and extracted with EtOAc. Collected organic fractions were dried on $MgSO_4$, and solvents were evaporated under vacuum. The crude product was chromatographed on silica gel in gradient hexane to hexane/EtOAc 9/1 to give the desired nucleoside **12a** (220 mg, 82%) as a colorless oil (for characterization data, see Supporting Information).

**1β-(6-Methylpyridin-3-yl)-1,2-dideoxy-3,5-di-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (12b).** A solution of $Me_3Al$ (1.3 mmol) in THF was dropwise added to a vigorously stirred solution of **11** (300 mg, 0.65 mmol) and $Pd(PPh_3)_4$ (39 mg, 0.033 mmol) in THF (13 mL). The mixture was stirred at 60 °C for 72 h and then worked up. Crude product **12b** was chromatographed on silica gel in gradient hexane to hexane/EtOAc 9/1 to give **12b** (259 mg, 90%) as a colorless oil (for characterization data, see Supporting Information).

**1β-(6-Ethylpyridin-3-yl)-1,2-dideoxy-3,5-di-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (12c).** A solution of $Et_3Al$ (1.4 mmol) in THF was dropwise added to a vigorously stirred solution of **11** (325 mg, 0.7 mmol) and $Pd(PPh_3)_4$ (43 mg, 0.035 mmol) in THF (14 mL). The mixture was stirred at 70 °C for 48 h and then worked up. Crude product **12c** was chromatographed on silica gel in gradient hexane to hexane/EtOAc 9/1 to give **12c** (260 mg, 81%) as a colorless oil (for characterization data, see Supporting Information).

**1β-(6-Benzylpyridin-3-yl)-1,2-dideoxy-3,5-di-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (12d).** THF (9 mL) was added to a flame-dried and argon-purged flask containing **11** (214 mg, 0.47 mmol) and $Pd(PPh_3)_4$ (29 mg, 5 mol %), and the mixture was stirred until clear solution formed. Then commercial solution of benzylzinc bromide (0.94 mmol) in THF was added dropwise, and the mixture was stirred at 60 °C for 20 h. After the workup, the product was chromatographed on silica gel in gradient hexane to 10% EtOAc in hexane to give **12d** (182 mg, 76%) as a yellow oil (for characterization data, see Supporting Information).

**1β-(6-Phenylpyridin-3-yl)-1,2-dideoxy-3,5-di-O-(*tert*-butyldimethylsilyl)-D-ribofuranose (12e).** Compound **11** (91 mg, 0.20 mmol), KF (38 mg, 0.66 mmol), $Pd_2dba_3$ (10 mg, 0.01 mmol), $P(t\text{-}Bu)_3{\cdot}HBF_4$ (6 mg, 0.02 mmol), and $PhB(OH)_2$ (27 mg, 0.22 mmol) were dissolved in THF (0.4 mL), and the mixture was stirred at 60 °C for 72 h. The reaction mixture was worked up, and crude product **12e** was chromatographed on silica gel in gradient hexane to hexane/EtOAc 9/1 to give **12e** (60 mg, 60%) as a colorless oil (for characterization data, see Supporting Information).

**1β-(2,2′-Bipyridin-5-yl)-1,2-dideoxy-3,5-di-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (12f).** 2-Tributylstannylpyridine (1.20 mL, 4.37 mmol) was added dropwise under argon to a stirred solution of **11** (200 mg, 0.44 mmol) and $PdCl_2$dppf (16 mg, 0.02 mmol) in DMF (2.0 mL). The mixture was stirred at 95 °C for 18 h and then worked up. Crude product **12f** was chromatographed two times on silica gel in gradient hexane to hexane/EtOAc 1/1 to give **12f** (142 mg, 65%) as a colorless oil (for characterization data, see Supporting Information).

**1β-([2,2′;6′,2″]-Terpyridin-5-yl)-1,2-dideoxy-3,5-di-O-(*tert*-butyldimethylsilyl)-D-ribofuranose (12g).** *n*-BuLi (1.44 mL, solution 1.6 M in hexane) was added to a solution of 6-bromo[2,2′]bipyridine (440 mg, 1.90 mmol) in THF (14.4 mL) under argon at −72 °C, and the mixture was stirred for 2 min followed by addition of $Bu_3SnCl$ (660 μL, 2.43 mmol). After being stirred for 20 min at −72 °C, the reaction was allowed to warm to rt, and the solvent was evaporated under vaccum. The crude 6-stannyl[2,2′]bipyridine was dissolved in DMF (2.3 mL) and added through septum to a flask containing **11** (320 mg, 0.7 mmol) and $PdCl_2$dppf (26 mg, 0.04 mmol) sealed under argon. The reaction mixture was stirred at 95 °C for 18 h and then worked up. Crude product **12g** was chromatographed two times on silica gel in gradient hexane to hexane/EtOAc 1/1 to give **12g** (284 mg) as a pale yellow oil (for characterization data, see Supporting Information), which contained some unseparable impurities (purity ca. 70% estimated from NMR; yield calculated on content of pure **12g** is ca. 49%). This compound was directly used in the next step of deprotection.

**1β-(6-Aminopyridin-3-yl)-1,2-dideoxy-3,5-di-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (12h).** $LiN(SiMe_3)_2$ (2.16 mL, 1 M solution in THF, 2.16 mmol) was added to a flame-dried argon-purged flask containing **11** (500 mg, 1.08 mmol), 2-(dicyclohexylphosphino)biphenyl (77 mg, 0.22 mol), and $Pd_2(dba)_3$ (100 mg, 0.11 mol), and the mixture was stirred at 60 °C for 21 h. The reaction was quenched by the addition of $Et_2O$ and 4 drops of 2 M aqueous solution of HCl and worked up. Chromatography on silica gel with gradient $CHCl_3$ to 10% MeOH in $CHCl_3$ gave **12h** (459 mg, 90%) as a yellow oil (for characterization data, see Supporting Information).

**1β-(6-Dimethylaminopyridin-3-yl)-1,2-dideoxy-3,5-di-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (12i).** A solution of $Pd(OAc)_2$ (9.2 mg, 1 mol %) and (2-biphenyl)-di-*tert*-butylphosphine (12 mg, 2 mol %) in DME (1.5 mL) was added to an argon-purged dry flask containing **11** (275 mg, 0.6 mmol), sodium *tert*-butoxide (159 mg, 1.5 mmol), and $Me_2NH{\cdot}HCl$ (150 mg, 1.5 mmol). The mixture was stirred at 70 °C for 60 h. Then the mixture was worked up, and crude product **12i** was chromatographed on silica gel in gradient hexane to 10% EtOAc in hexane to give **12i** (167 mg, 60%) as a yellow oil (for characterization data, see Supporting Information).

**1β-[6-(*tert*-Butyloxy)pyridin-3-yl]-1,2-dideoxy-3,5-di-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranose (12j).** A solution of **11** (300 mg, 0.65 mmol) in toluene (1.5 mL) was added to an argon-purged dry flask containing $Pd_2dba_3$ (30 mg, 5 mol %), (2-biphenyl)-di-*tert*-butylphosphine (10 mg, 5 mol %), and sodium *tert*-butoxide (193 mg, 2 mmol). The mixture was stirred at 90 °C for 17 h. Then the mixture was worked up, and crude product **12j** was chromatographed on silica gel in gradient hexane to 5% EtOAc in hexane to give **12j** (164 mg, 51%) as a colorless oil (for characterization data, see Supporting Information).

**General Procedure for the Deprotection of TBDMS Group.** $Et_3N{\cdot}3HF$ (320 μL, 1.95 mmol) was added to a solution of compounds **12a**−**i** (0.4 mmol) in THF (2 mL), and the mixture was stirred at room temperature for 14 h. After the reaction was completed (TLC in hexane/EtOAc 9/1), solvents were removed under reduced pressure. Then the crude product was dissolved in MeOH (2 mL), and a 1 M aqueous solution of sodium hydroxide (8 mL) was added to neutralize the mixture. Then the solvents were removed under reduced pressure, and the crude product was chromatographed on silica gel eluted with gradient $CHCl_3$−20% MeOH in $CHCl_3$ to give products **13a**−**i**.

**1β-(Pyridin-3-yl)-1,2-dideoxy-D-ribofuranose[45] (13a).** Compound **13a** was prepared from **12a** (178 mg, 0.42 mmol) by the general procedure. Crystallization from EtOAc/heptane gave **13a** (70 mg, 86%) as colorless crystals: mp 52−54 °C; MS (FAB) *m*/*z* 196 (M + 1); HRMS (FAB) for $C_{10}H_{14}NO_3$ [M + H] calcd 196.0974, found 196.0978; $^1$H NMR (500 MHz, $CD_3OD$) $\delta$ 1.96 (ddd, 1H, $J_{gem}$ = 13.1 Hz, $J_{2'b,1'}$ = 10.5 Hz, $J_{2'b,3'}$ = 5.9 Hz, H-2′b), 2.27 (ddd, 1H, $J_{gem}$ = 13.1 Hz, $J_{2'a,1'}$ = 5.5 Hz, $J_{2'a,3'}$ = 1.7 Hz, H-2′a), 3.69 (d, 2H, $J_{5',4'}$ = 4.8 Hz, H-5′), 3.97 (td, 1H, $J_{4',5'}$ = 4.8 Hz, $J_{4',3'}$ = 2.4 Hz, H-4′), 4.35 (dddd, 1H, $J_{3',2'}$ = 5.9, 1.7 Hz, $J_{3',4'}$ = 2.4 Hz, $J_{3',1'}$ = 0.6 Hz, H-3′), 5.18 (dd, 1H, $J_{1',2'}$ = 10.5, 5.5 Hz, H-1′), 7.42 (ddd, 1H, $J_{5,4}$ = 7.9 Hz, $J_{5,6}$ = 5.0 Hz, $J_{5,2}$ = 0.6 Hz, H-5), 7.91 (dddd, 1H, $J_{4,5}$ = 7.9 Hz, $J_{4,2}$ = 2.2 Hz, $J_{4,6}$ = 1.6 Hz, $J_{4,1'}$ = 0.6 Hz, H-4), 8.44 (dd, 1H, $J_{6,5}$ = 5.0 Hz, $J_{6,4}$ = 1.6 Hz, H-6), 8.58 (dt, 1H, $J_{2,4}$ = 2.2 Hz, $J_{2,5}$ = $J_{2,1'}$ = 0.6 Hz, H-2); $^{13}$C NMR (125.7 MHz, $CD_3OD$) $\delta$ 44.9 ($CH_2$-2′), 63.9 ($CH_2$-5′), 74.4 (CH-3′), 79.1 (CH-1′), 89.5 (CH-4′), 125.1 (CH-5), 136.1 (CH-4), 140.0 (C-3), 148.2 (CH-2), 149.2 (CH-6); IR spectrum (KBr) 3401, 1723, 1690, 1635, 1594, 1582, 1481, 1426, 1196, 1029, 1001, 808, 713, 632 cm$^{-1}$; $[\alpha]^{20}_D$ +25.5 (*c* 2.65, MeOH).

**1β-(6-Methylpyridin-3-yl)-1,2-dideoxy-D-ribofuranose (13b).** Compound **13b** was prepared from **12b** (223 mg, 0.51 mmol) by the general procedure. Crystallization from EtOAc/heptane gave **13b** (96 mg, 90%) as colorless crystals: mp 118−120 °C; MS (FAB) *m*/*z* 210 (M + 1); HRMS (FAB) for $C_{11}H_{16}NO_3$ [M + H] calcd 210.1130, found 210.1136; $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ 1.79 (ddd, 1H, $J_{gem}$ = 12.7 Hz, $J_{2'b,1'}$ = 10.5 Hz, $J_{2'b,3'}$ = 5.6 Hz, H-2′b), 2.07 (ddd, 1H, $J_{gem}$ = 12.7 Hz, $J_{2'a,1'}$ = 5.4 Hz, $J_{2'a,3'}$ = 1.6 Hz, H-2′a), 2.44 (s, 3H, $CH_3$), 3.42 (br dt, 1H, $J_{gem}$ = 11.4 Hz, $J_{5'b,4'}$ = 5.5 Hz, $J_{5'b,OH}$ = 5.0 Hz, H-5′b), 3.49 (br dt, 1H, $J_{gem}$ = 11.4 Hz, $J_{5'a,OH}$ = 5.0 Hz, $J_{5'a,4'}$ = 4.9 Hz, H-5′a), 3.78 (ddd, 1H, $J_{4',5'}$ = 5.5, 4.9 Hz, $J_{4',3'}$ = 2.1 Hz, H-4′), 4.20 (m, 1H, $J_{3',2'}$ = 5.6, 1.6 Hz, $J_{3',OH}$ = 3.8 Hz, $J_{3',4'}$ = 2.1 Hz, H-3′), 4.79 (br t, 1H, $J_{OH,5'}$ = 5.0 Hz, OH-5′), 5.01 (dd, 1H, $J_{1',2'}$ = 10.5, 5.4 Hz, H-1′), 5.09 (d, 1H, $J_{OH,3'}$ = 3.8 Hz, OH-3′), 7.20 (d, 1H, $J_{3,4}$ = 8.0 Hz, H-3), 7.66 (dd, 1H, $J_{4,3}$ = 8.0 Hz, $J_{4,6}$ = 2.3 Hz, H-4), 8.41 (d, 1H, $J_{6,4}$ = 2.3 Hz, H-6); $^{13}$C NMR (151 MHz, DMSO-$d_6$) $\delta$ 23.9 ($CH_3$), 43.6 ($CH_2$-2′), 62.6 ($CH_2$-5′), 72.7 (CH-3′), 77.3 (CH-1′), 88.1

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(CH-4′), 122.9 (CH-3), 134.4 (CH-4), 135.1 (C-5), 147.1 (CH-6), 157.0 (C-2); IR spectrum (KBr) 3300, 3116, 2970, 1607, 1573, 1496, 1429, 1395, 1381, 1299, 1258, 1088, 1054, 1036, 1009, 734, 723 $cm^{-1}$; $[\alpha]^{20}_D$ +74.2 (*c* 2.53, MeOH). Anal. Calcd for $C_{11}H_{15}NO_3$ (209.3): C, 63.14; H, 7.23; N, 6.69. Found: C, 63.34; H, 7.18; N, 6.53.

**1β-(6-Ethylpyridin-3-yl)-1,2-dideoxy-D-ribofuranose (13c).** Compound **13c** was prepared from **12c** (221 mg, 0.49 mmol) by the general procedure. Crystallization from EtOAc/heptane gave **13c** (98 mg, 89%) as colorless crystals: mp 82−84 °C; MS (FAB) *m*/*z* 224 (M + 1); HRMS (FAB) for $C_{12}H_{18}NO_3$ [M + H] calcd 224.1287, found 224.1289; $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 1.20 (t, 3H, $J_{vic}$ = 7.6 Hz, $CH_3CH_2$), 1.81 (ddd, 1H, $J_{gem}$ = 12.7 Hz, $J_{2'b,1'}$ = 10.5 Hz, $J_{2'b,3'}$ = 5.6 Hz, H-2′b), 2.08 (ddd, 1H, $J_{gem}$ = 12.7 Hz, $J_{2'a,1'}$ = 5.3 Hz, $J_{2'a,3'}$ = 1.4 Hz, H-2′a), 2.71 (q, 2H, $J_{vic}$ = 7.6 Hz, $CH_2CH_3$), 3.43 and 3.48 (2 × dt, 2H, $J_{gem}$ = 11.4 Hz, $J_{5',OH}$ = 5.6 Hz, $J_{5',4'}$ = 5.3 Hz, H-5′), 3.80 (td, 1H, $J_{4',5'}$ = 5.3 Hz, $J_{4',3'}$ = 2.0 Hz, H-4′), 4.21 (m, 1H, $J_{3',2'}$ = 5.6, 1.4 Hz, $J_{3',OH}$ = 3.8 Hz, $J_{3',4'}$ = 2.0 Hz, H-3′), 4.79 (t, 1H, $J_{OH,5'}$ = 5.6 Hz, OH-5′), 5.02 (dd, 1H, $J_{1',2'}$ = 10.5, 5.3 Hz, H-1′), 5.10 (d, 1H, $J_{OH,3'}$ = 3.8 Hz, OH-3′), 7.20 (d, 1H, $J_{3,4}$ = 8.0 Hz, H-3), 7.67 (dd, 1H, $J_{4,3}$ = 8.0 Hz, $J_{4,6}$ = 2.2 Hz, H-4), 8.45 (d, 1H, $J_{6,4}$ = 2.2 Hz, H-6); $^{13}$C NMR (125.7 MHz, DMSO-$d_6$) $\delta$ 14.1 ($CH_3CH_2$), 30.5 ($CH_2CH_3$), 43.5 ($CH_2$-2′), 62.6 ($CH_2$-5′), 72.7 (CH-3′), 77.3 (CH-1′), 88.1 (CH-4′), 121.7 (CH-3), 134.5 (CH-4), 135.3 (C-5), 147.3 (CH-6), 162.1 (C-2); IR spectrum (KBr) 3401, 1607, 1571, 1494, 1458, 1434, 1408, 1374, 1310, 1259, 1136, 1036, 999, 842 $cm^{-1}$; $[\alpha]^{20}_D$ +56.8 (*c* 2.68, MeOH).

**1β-(6-Benzylpyridin-3-yl)-1,2-dideoxy-D-ribofuranose (13d).** Compound **13d** was prepared from **12d** (104 mg, 0.20 mmol) by the general procedure to yield **13d** (49 mg, 85%) as a white gum: MS (FAB) *m*/*z* 286 (M + 1); HRMS (FAB) for $C_{17}H_{19}NO_3$ [M + 1] calcd 286.1443, found 286.1452; $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ 1.80 (ddd, 1H, $J_{gem}$ = 12.7 Hz, $J_{2'b,1'}$ = 10.5 Hz, $J_{2'b,3'}$ = 5.5 Hz, H-2′b), 2.07 (ddd, 1H, $J_{gem}$ = 12.7 Hz, $J_{2'a,1'}$ = 5.4 Hz, $J_{2'a,3'}$ = 1.5 Hz, H-2′a), 3.41 (dt, 1H, $J_{gem}$ = 11.4 Hz, $J_{5'b,OH}$ = $J_{5'b,4'}$ = 5.5 Hz, H-5′b), 3.47 (ddd, 1H, $J_{gem}$ = 11.4 Hz, $J_{5'a,OH}$ = 5.5 Hz, $J_{5'a,4'}$ = 4.8 Hz, H-5′a), 3.78 (ddd, 1H, $J_{4',5'}$ = 5.5, 4.8 Hz, $J_{4',3'}$ = 2.0 Hz, H-4′), 4.05 (s, 2H, $CH_2$Ph), 4.20 (m, 1H, $J_{3',2'}$ = 5.5, 1.5 Hz, $J_{3',OH}$ = 3.8 Hz, $J_{3',4'}$ = 2.0 Hz, $J_{3',1'}$ = 0.5 Hz, H-3′), 4.77 (br t, 1H, $J_{OH,5'}$ = 5.5 Hz, OH-5′), 5.01 (dd, 1H, $J_{1',2'}$ = 10.5, 5.4 Hz, H-1′), 5.09 (d, 1H, $J_{OH,3'}$ = 3.8 Hz, OH-3′), 7.18 (m, 1H, H-*p*-Ph), 7.23 (dd, 1H, $J_{3,4}$ = 8.0 Hz, $J_{3,6}$ = 0.6 Hz, H-3), 7.25−7.29 (m, 4H, H-*o*,*m*-Ph), 7.68 (ddd, 1H, $J_{4,3}$ = 8.0 Hz, $J_{4,6}$ = 2.3 Hz, $J_{4,1'}$ = 0.4 Hz, H-4), 8.46 (dt, 1H, $J_{6,4}$ = 2.3 Hz, $J_{6,3}$ = $J_{6,1'}$ = 0.6 Hz, H-6); $^{13}$C NMR (151 MHz, DMSO-$d_6$) $\delta$ 43.4 ($CH_2$-2′), 43.7 ($CH_2$Ph), 62.6 ($CH_2$-5′), 72.7 (CH-3′), 77.3 (CH-1′), 88.1 (CH-4′), 122.7 (CH-3), 126.3 (CH-*p*-Ph), 128.6 (CH-*m*-Ph), 129.1 (CH-*m*-Ph), 134.7 (CH-4), 135.6 (C-5), 140.2 (C-*i*-Ph), 147.5 (CH-6), 159.9 (C-2); IR spectrum (KBr) 3428, 3028, 1629, 1608, 1571, 1494, 1453, 1091, 1075, 1052, 742, 700, 580 $cm^{-1}$; $[\alpha]^{20}_D$ +57.2 (*c* 2.55, MeOH).

**1β-(6-Phenylpyridin-3-yl)-1,2-dideoxy-D-ribofuranose (13e).** Compound **13e** was prepared from **12e** (101 mg, 0.20 mmol) by the general procedure. Crystallization from *i*PrOH/heptane gave **13e** (44 mg, 80%) as colorless crystals: mp 78−80 °C; MS (FAB) *m*/*z* 272 (M + 1); HRMS (FAB) for $C_{16}H_{18}NO_3$ [M + H] calcd 272.1287, found 272.1278; $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ 1.87 (ddd, 1H, $J_{gem}$ = 12.8 Hz, $J_{2'b,1'}$ = 10.5 Hz, $J_{2'b,3'}$ = 5.5 Hz, H-2′b), 2.15 (ddd, 1H, $J_{gem}$ = 12.8 Hz, $J_{2'a,1'}$ = 5.5 Hz, $J_{2'a,3'}$ = 1.6 Hz, H-2′a), 3.47 (dt, 1H, $J_{gem}$ = 11.4 Hz, $J_{5'b,OH}$ = 5.7 Hz, $J_{5'b,4'}$ = 5.4 Hz, H-5′b), 3.52 (ddd, 1H, $J_{gem}$ = 11.4 Hz, $J_{5'a,OH}$ = 5.7 Hz, $J_{5'a,4'}$ = 4.9 Hz, H-5′a), 3.84 (td, 1H, $J_{4',5'}$ = 5.4, 4.9 Hz, $J_{4',3'}$ = 2.0 Hz, H-4′), 4.25 (m, 1H, $J_{3',2'}$ = 5.5, 1.6 Hz, $J_{3',OH}$ = 3.8 Hz, $J_{3',4'}$ = 2.0 Hz, H-3′), 4.83 (br t, 1H, $J_{OH,5'}$ = 5.7 Hz, OH-5′), 5.12 (dd, 1H, $J_{1',2'}$ = 10.5, 5.5 Hz, H-1′), 5.14 (d, 1H, $J_{OH,3'}$ = 3.8 Hz, OH-3′), 7.42 (m, 1H, H-*p*-Ph), 7.48 (m, 2H, H-*m*-Ph), 7.87 (ddd, 1H, $J_{4,3}$ = 8.2 Hz, $J_{4,6}$ = 2.3 Hz, $J_{4,1'}$ = 0.5 Hz, H-4), 7.92 (dd, 1H, $J_{3,4}$ = 8.2 Hz, $J_{3,6}$ = 0.8 Hz, H-3), 8.07 (m, 2H, H-*o*-Ph), 8.67 (dt, 1H, $J_{6,4}$ = 2.3 Hz, $J_{6,3}$ = 0.8 Hz, $J_{6,1'}$ = 0.5 Hz, H-6); $^{13}$C NMR (151 MHz, DMSO-$d_6$) $\delta$ 43.6 ($CH_2$-2′), 62.6 ($CH_2$-5′), 72.7 (CH-3′), 77.3 (CH-1′), 88.2 (CH-4′), 120.0 (CH-3), 126.7 (CH-*o*-Ph), 129.0 (CH-*m*-Ph), 129.1 (CH-*p*-Ph), 135.2 (CH-4), 137.0 (C-5), 138.8 (C-*i*-Ph), 147.9 (CH-6), 155.4 (C-2); IR spectrum (KBr) 3421, 3275, 3088, 3062, 3029, 1598, 1586, 1560, 1500, 1476, 1447, 1399, 1317, 1291, 1157, 1096, 1090, 1075, 1064, 1053, 1019, 980, 781, 738, 691, 616, 544 $cm^{-1}$; $[\alpha]^{20}_D$ +69.1 (*c* 2.58, MeOH). Anal. Calcd for $C_{16}H_{17}NO_3$ (271.3): C, 70.83; H, 6.32; N, 5.16. Found: C, 70.85; H, 6.34; N 5.10.

**1β-(2,2′-Bipyridin-5-yl)-1,2-dideoxy-D-ribofuranose[8c,d] (13f).** Compound **13f** was prepared from **12f** (280 mg, 0.56 mmol) by the general procedure. Lyophilization from $H_2O$ gave **13f** (137 mg, 90%) as a pink gum: MS (FAB) *m*/*z* 273 (M + 1); HRMS (FAB) for $C_{15}H_{17}N_2O_3$ [M + H] calcd 273.1239, found 273.1236; $^1$H NMR (500 MHz, $CD_3OD$) $\delta$ 2.01 (ddd, 1H, $J_{gem}$ = 13.1 Hz, $J_{2'b,1'}$ = 10.5 Hz, $J_{2'b,3'}$ = 5.9 Hz, H-2′b), 2.30 (ddd, 1H, $J_{gem}$ = 13.1 Hz, $J_{2'a,1'}$ = 5.5 Hz, $J_{2'a,3'}$ = 1.7 Hz, H-2′a), 3.71 (d, 2H, $J_{5',4'}$ = 4.9 Hz, H-5′), 4.00 (td, 1H, $J_{4',5'}$ = 4.9 Hz, $J_{4',3'}$ = 2.4 Hz, H-4′), 4.38 (dddd, 1H, $J_{3',2'}$ = 5.9, 1.7 Hz, $J_{3',4'}$ = 2.4 Hz, $J_{3',1'}$ = 0.5 Hz, H-3′), 5.24 (dd, 1H, $J_{1',2'}$ = 10.5, 5.5 Hz, H-1′), 7.42 (ddd, 1H, $J_{5'',4''}$ = 7.5 Hz, $J_{5'',6''}$ = 4.9 Hz, $J_{5'',3''}$ = 1.2 Hz, H-5″), 7.92 (ddd, 1H, $J_{4'',3''}$ = 8.0 Hz, $J_{4'',5''}$ = 7.5 Hz, $J_{4'',6''}$ = 1.8 Hz, H-4″), 7.98 (ddd, 1H, $J_{4,3}$ = 8.2 Hz, $J_{4,6}$ = 2.2 Hz, $J_{4,1'}$ = 0.7 Hz, H-4), 8.27 (dd, 1H, $J_{3,4}$ = 8.2 Hz, $J_{3,6}$ = 0.9 Hz, H-3), 8.29 (dt, 1H, $J_{3'',4''}$ = 8.0 Hz, $J_{3'',5''}$ = 1.2 Hz, $J_{3'',6''}$ = 1.0 Hz, H-3″), 8.683 (ddd, 1H, $J_{6'',5''}$ = 4.9 Hz, $J_{6'',4''}$ = 1.8 Hz, $J_{6'',3''}$ = 1.0 Hz, H-6″), 8.67 (dt, 1H, $J_{6,4}$ = 2.2 Hz, $J_{6,3}$ = 0.9 Hz, $J_{6,1'}$ = 0.6 Hz, H-6); $^{13}$C NMR (125.7 MHz, $CD_3OD$) $\delta$ 44.8 ($CH_2$-2′), 63.9 ($CH_2$-5′), 74.4 (CH-3′), 79.1 (CH-1′), 89.5 (CH-4′), 122.3 (CH-3), 122.6 (CH-3″), 125.2 (CH-5″), 136.4 (CH-4), 138.7 (CH-4″), 139.7 (C-5), 148.4 (CH-6), 150.2 (CH-6″), 156.4 (C-2), 157.0 (C-2″); IR spectrum (KBr) 3409, 3056, 1628, 1590, 1575, 1558, 1490, 1462, 1436, 1255, 1148, 1092, 1065, 1051, 1026, 994, 797, 751, 640, 620, 400 $cm^{-1}$; $[\alpha]^{20}_D$ +49.3 (*c* 4.50, MeOH).

**1β-([2,2′;6′,2″]-Terpyridin-5-yl)-1,2-dideoxy-D-ribofuranose (13g).** Compound **13g** was prepared from crude **12g** (284 mg) by the general procedure. Lyophilization from $H_2O$ gave **13g** (102 mg, 85%; 42% isolated yield over two steps) as a white gum: MS (FAB) *m*/*z* 350 (M + 1); HRMS (FAB) for $C_{20}H_{20}N_3O_3$ [M + H] calcd 350.1505, found 350.1509; $^1$H NMR (500 MHz, $CD_3OD$) $\delta$ 2.03 (ddd, 1H, $J_{gem}$ = 13.1 Hz, $J_{2'b,1'}$ = 10.5 Hz, $J_{2'b,3'}$ = 5.9 Hz, H-2′b), 2.31 (ddd, 1H, $J_{gem}$ = 13.1 Hz, $J_{2'a,1'}$ = 5.5 Hz, $J_{2'a,3'}$ = 1.7 Hz, H-2′a), 3.73 (d, 2H, $J_{5',4'}$ = 4.9 Hz, H-5′), 4.01 (td, 1H, $J_{4',5'}$ = 4.9 Hz, $J_{4',3'}$ = 2.5 Hz, H-4′), 4.38 (dt, 1H, $J_{3',2'}$ = 5.9, 1.7 Hz, $J_{3',4'}$ = 2.5 Hz, H-3′), 5.25 (dd, 1H, $J_{1',2'}$ = 10.5, 5.5 Hz, H-1′), 7.43 (ddd, 1H, $J_{5''',4'''}$ = 7.5 Hz, $J_{5''',6'''}$ = 4.8 Hz, $J_{5''',3'''}$ = 1.2 Hz, H-5‴), 7.95 (ddd, 1H, $J_{4''',3'''}$ = 8.0 Hz, $J_{4''',5'''}$ = 7.5 Hz, $J_{4''',6'''}$ = 1.8 Hz, H-4‴), 7.99 (ddd, 1H, $J_{4,3}$ = 8.2 Hz, $J_{4,6}$ = 2.2 Hz, $J_{4,1'}$ = 0.6 Hz, H-4), 8.00 (t, 1H, $J_{4'',3''}$ = $J_{4'',5''}$ = 7.8 Hz, H-4″), 8.326 and 8.328 (2 × dd, 2 × 1H, $J_{3'',4''}$ = $J_{5'',4''}$ = 7.8 Hz, $J_{3'',5''}$ = 2.3 Hz, H-3″,5″), 8.54 (dd, 1H, $J_{3,4}$ = 8.2 Hz, $J_{3,6}$ = 0.8 Hz, H-3), 8.56 (dt, 1H, $J_{3''',4'''}$ = 8.0 Hz, $J_{3''',5'''}$ = 1.2 Hz, $J_{3''',6'''}$ = 0.9 Hz, H-3‴), 8.64 (ddd, 1H, $J_{6''',5'''}$ = 4.8 Hz, $J_{6''',4'''}$ = 1.8 Hz, $J_{6''',3'''}$ = 0.9 Hz, H-6‴), 8.67 (dt, 1H, $J_{6,4}$ = 2.2 Hz, $J_{6,3}$ = 0.8 Hz, $J_{6,1'}$ = 0.6 Hz, H-6); $^{13}$C NMR (125.7 MHz, $CD_3OD$) $\delta$ 44.8 ($CH_2$-2′), 64.0 ($CH_2$-5′), 74.4 (CH-3′), 79.2 (CH-1′), 89.5 (CH-4′), 122.05 and 122.07 (CH-3″ and CH-5″), 122.4 (CH-3), 122.8 (CH-3‴), 125.3 (CH-5‴), 136.4 (CH-4), 138.7 (CH-4‴), 139.2 (CH-4″), 139.7 (C-5), 148.2 (CH-6), 150.1 (CH-6‴), 156.4, 156.5 and 156.6 (C-2, C-2″ and C-6″), 157.2 (C-2‴); IR spectrum (KBr) 3421, 3062, 1630, 1598, 1584, 1561, 1492, 1475, 1454, 1431, 1414, 1263, 1148, 1102, 1093, 1080, 1051, 1027, 999, 991, 826, 787, 762, 640, 631, 619, 400 $cm^{-1}$; $[\alpha]^{20}_D$ +52.8 (*c* 2.03, MeOH).

**1β-(6-Aminopyridin-3-yl)-1,2-dideoxy-D-ribofuranose (13h).** Compound **13h** was prepared from **12h** (159 mg, 0.36 mmol) by the general procedure. Lyophilization from $H_2O$ gave **13h** (69 mg, 90%) as a yellow oil: MS (FAB) *m*/*z* 211 (M + 1); HRMS (FAB) for $C_{10}H_{15}N_2O_3$ [M + 1] calcd 211.1083, found 211.1080; $^1$H NMR

(500 MHz, DMSO-$d_6$) $\delta$ 1.80 (ddd, 1H, $J_{gem}$ = 12.8 Hz, $J_{2'b,1'}$ = 10.5 Hz, $J_{2'b,3'}$ = 5.7 Hz, H-2′b), 1.92 (ddd, 1H, $J_{gem}$ = 12.8 Hz, $J_{2'a,1'}$ = 5.4 Hz, $J_{2'a,3'}$ = 1.6 Hz, H-2′a), 3.39 (br dd, 1H, $J_{gem}$ = 11.4 Hz, $J_{5'b,4'}$ = 5.5 Hz, H-5′b), 3.44 (br dd, 1H, $J_{gem}$ = 11.4 Hz, $J_{5'a,4'}$ = 4.8 Hz, H-5′a), 3.70 (ddd, 1H, $J_{4',5'}$ = 5.5, 4.8 Hz, $J_{4',3'}$ = 2.1 Hz, H-4′), 4.16 (br dt, 1H, $J_{3',2'}$ = 5.7, 1.6 Hz, $J_{3',4'}$ = 2.1 Hz, H-3′), 4.72 (br s, 1H, OH-5′), 4.82 (dd, 1H, $J_{1',2'}$ = 10.5, 5.4 Hz, H-1′), 5.00 (br s, 1H, OH-3′), 5.83 (br s, 2H, $NH_2$), 6.41 (d, 1H, $J_{3,4}$ = 8.8 Hz, H-3), 7.36 (dd, 1H, $J_{4,3}$ = 8.8 Hz, $J_{4,6}$ = 2.3 Hz, H-4), 7.84 (d, 1H, $J_{6,4}$ = 2.3 Hz, H-6); $^{13}$C NMR (125.7 MHz, DMSO-$d_6$) $\delta$ 42.99 ($CH_2$-2′), 62.72 ($CH_2$-5′), 72.72 (CH-3′), 77.56 (CH-1′), 87.69 (CH-4′), 107.89 (CH-3), 125.11 (C-5), 135.84 (CH-4), 146.33 (CH-6), 159.64 (C-2); IR spectrum (KBr) 3420, 2804, 2756, 2739, 2678, 2601, 2492, 1672, 1632, 1559, 1507, 1476, 1434, 1398, 1092, 1050 cm$^{-1}$; $[\alpha]^{20}_D$ +25.9 (*c* 2.32, MeOH).

**1$\beta$-(6-Dimethylaminopyridin-3-yl)-1,2-dideoxy-D-ribofuranose (13i).** Compound **13i** was prepared from **12i** (176 mg, 0.38 mmol) by the general procedure. Crystallization from EtOAc/heptane gave **13i** (75 mg, 84%) as colorless crystals: mp 104−106 °C; MS (FAB) *m*/*z* 238 (M + 1); HRMS (FAB) for $C_{12}H_{18}N_2O_3$ [M + H] calcd 238.1317, found 238.1324; $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ 1.82 (ddd, 1H, $J_{gem}$ = 12.8 Hz, $J_{2'b,1'}$ = 10.6 Hz, $J_{2'b,3'}$ = 5.6 Hz, H-2′b), 1.95 (ddd, 1H, $J_{gem}$ = 12.8 Hz, $J_{2'a,1'}$ = 5.3 Hz, $J_{2'a,3'}$ = 1.6 Hz, H-2′a), 3.00 (s, 6H, $(CH_3)_2$N), 3.40 (br dt, 1H, $J_{gem}$ = 11.3 Hz, $J_{5'b,4'}$ = 5.7 Hz, $J_{5'b,OH}$ = 5.4 Hz, H-5′b), 3.45 (br dt, 1H, $J_{gem}$ = 11.3 Hz, $J_{5'a,OH}$ = 5.4 Hz, $J_{5'a,4'}$ = 4.9 Hz, H-5′a), 3.72 (ddd, 1H, $J_{4',5'}$ = 5.7, 4.9 Hz, $J_{4',3'}$ = 2.1 Hz, H-4′), 4.18 (m, 1H, $J_{3',2'}$ = 5.6, 1.6 Hz, $J_{3',OH}$ = 3.8 Hz, $J_{3',4'}$ = 2.1 Hz, H-3′), 4.75 (br t, 1H, $J_{OH,5'}$ = 5.4 Hz, OH-5′), 4.89 (dd, 1H, $J_{1',2'}$ = 10.6, 5.3 Hz, H-1′), 5.03 (d, 1H, $J_{OH,3'}$ = 3.8 Hz, OH-3′), 6.63 (d, 1H, $J_{3,4}$ = 8.8 Hz, H-3), 7.52 (dd, 1H, $J_{4,3}$ = 8.8 Hz, $J_{4,6}$ = 2.4 Hz, H-4), 8.03 (dt, 1H, $J_{6,4}$ = 2.4 Hz, $J_{6,3}$ = $J_{6,1'}$ = 0.6 Hz, H-6); $^{13}$C NMR (151 MHz, DMSO-$d_6$) $\delta$ 38.03 ($(CH_3)_2$N), 43.09 ($CH_2$-2′), 62.71 ($CH_2$-5′), 72.73 (CH-3′), 77.35 (CH-1′), 87.75 (CH-4′), 106.01 (CH-3), 124.82 (C-5), 136.19 (CH-4), 145.60 (CH-6), 158.73 (C-2); IR spectrum (KBr) 3401, 3308, 2815, 1609, 1559, 1414, 1437, 1320, 1074, 1051, 1032, 1012, 995 cm$^{-1}$; $[\alpha]^{20}_D$ +40.3 (*c* 2.65, MeOH). Anal. Calcd for $C_{12}H_{18}N_2O_3$ (238.3): C, 60.49; H, 7.61; N, 11.76. Found: C, 60.76; H, 7.75; Cl, 7.71; N, 11.72.

**1$\beta$-(6-Oxopyridin-3-yl)-1,2-dideoxy-D-ribofuranose (14).** Compound **12j** (84 mg, 0.17 mmol) was dissolved in TFA (2 mL), and the solution was stirred until the reaction was completed (ca. 20 min, TLC). Then, TFA was evaporated and crude pyridone **14** was purified by chromatography on silica gel in gradient $CHCl_3$ to 50% MeOH in $CHCl_3$. Lyophilization from $H_2O$ gave **14** (30 mg, 84%) as colorless crystals: mp 157−159 °C; MS (FAB) *m*/*z* 212 (M + 1); HRMS (FAB) for $C_{10}H_{14}NO_4$ [M + H] calcd 212.0923, found 212.0920; $^1$H NMR (600 MHz, $CD_3OD$) $\delta$ 1.95 (ddd, 1H, $J_{gem}$ = 13.1 Hz, $J_{2'b,1'}$ = 10.5 Hz, $J_{2'b,3'}$ = 5.9 Hz, H-2′b), 2.11 (ddd, 1H, $J_{gem}$ = 13.1 Hz, $J_{2'a,1'}$ = 5.4 Hz, $J_{2'a,3'}$ = 1.7 Hz, H-2′a), 3.64 (dd, 1H, $J_{gem}$ = 11.7 Hz, $J_{5'b,4'}$ = 4.9 Hz, H-5′b), 3.66 (dd, 1H, $J_{gem}$ = 11.7 Hz, $J_{5'a,4'}$ = 4.6 Hz, H-5′a), 3.90 (td, 1H, $J_{4',5'}$ = 4.9, 4.6 Hz, $J_{4',3'}$ = 2.4 Hz, H-4′), 4.32 (dddd, 1H, $J_{3',2'}$ = 5.9, 1.7 Hz, $J_{3',4'}$ = 2.4 Hz, $J_{3',1'}$ = 0.6 Hz, H-3′), 4.94 (dd, 1H, $J_{1',2'}$ = 10.5, 5.4 Hz, H-1′), 6.56 (ddd, 1H, $J_{3,4}$ = 9.4 Hz, $J_{3,6}$ = 0.7 Hz, $J_{3,1'}$ = 0.4 Hz, H-3), 7.47 (dt, 1H, $J_{6,4}$ = 2.6 Hz, $J_{6,3}$ = $J_{6,1'}$ = 0.7 Hz, H-6), 7.71 (ddd, 1H, $J_{4,3}$ = 9.4 Hz, $J_{4,6}$ = 2.6 Hz, $J_{4,1'}$ = 0.3 Hz, H-4); $^{13}$C NMR (151 MHz, $CD_3OD$) $\delta$ 43.66 ($CH_2$-2′), 63.84 ($CH_2$-5′), 74.28 (CH-3′), 78.33 (CH-1′), 89.16 (CH-4′), 120.76 (CH-3), 122.69 (C-5), 133.44 (CH-4), 142.70 (CH-6), 165.53 (C-2); IR spectrum (KBr) 3428, 1687, 1659, 1618, 1551, 1207, 1183, 1091, 1050, 1004, 799, 722, 550 cm$^{-1}$; $[\alpha]^{20}_D$ +44.1 (*c* 1.71, MeOH).

**Single-Crystal X-ray Structure Analysis.** X-ray crystallographic analysis of single crystals of **10** (colorless, 0.14 × 0.47 × 0.53 mm) and **13i** (colorless, 0.07 × 0.16 × 0.46 mm) was performed with Xcalibur X-ray diffractometr with Cu K$\alpha$ ($\lambda$ = 1.54180 Å), data collected at 150 K. Both structures were solved by direct methods with SIR92[46] and refined by full-matrix least-squares on *F* with CRYSTALS.[47] The hydrogen atoms were all 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 **10**: CCDC642287; $C_{10}H_{12}Cl_1N_1O_3$, monoclinic, space group $P2_1$, $a$ = 7.1887(1) Å, $b$ = 7.5136(1) Å, $c$ = 9.5782(1) Å, $\beta$ = 96.1275(9)°, $V$ = 514.389(8) Å$^3$, $Z$ = 2, $M$ = 229.66, 9510 reflections measured, 2070 independent reflections. Final $R$ = 0.0288, $wR$ = 0.0328, GoF = 0.9217 for 2053 reflections with $I > 1.96\sigma(I)$ and 138 parameters.

Crystal data for **13i**: CCDC642288; $C_{12}H_{18}N_2O_3$, orthorhombic, space group $P2_12_12_1$, $a$ = 5.6723(1) Å, $b$ = 10.6767(1) Å, $c$ = 19.4350(1) Å, $V$ = 1177.01(2) Å$^3$, $Z$ = 4, $M$ = 238.28, 17723 reflections measured, 2401 independent reflections. Final $R$ = 0.0340, $wR$ = 0.0439, GoF = 1.0980 for 1947 reflections with $I > 1.96\sigma(I)$ and 156 parameters.

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**Supporting Information Available:** Detailed description of unsuccessful experiments, conformation analysis of nucleosides, general methods, synthesis, and characterization data of compounds **4**, **7a**,**b**, **12a**−**i**, cif files for **10** and **13i**, and copies of all NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC642287 and CCDC642288 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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