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Synthesis of *C*-Aryl-Nucleosides and *O*-Aryl-Glycosides via Cuprate Glycosylation

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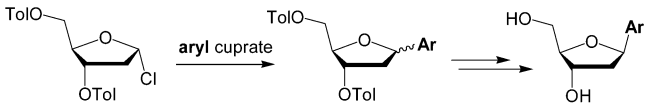

2′-Deoxy-*C*-aryl-nucleosides have found increasing importance in studying DNA−DNA and DNA−protein interactions, as unnatural DNA-base pairs, and as oligonucleotide based fluorophores. Access to the required *C*-aryl-nucleosides is provided by several glycosylation methods. Though useful in many cases, these methods often have drawbacks such as low yields or low economic efficiency. The necessity for intensive optimization of the reaction conditions and/or the use of hazardous and toxic reagents can render *C*-glycosylation reactions cumbersome. Herein we describe a robust and highly efficient *C*-glycosylation method. It is shown that aryl cuprates of the Normant-type reliably react with Hoffer's chlorosugar to deliver *C*-aryl-nucleosides in up to 93% yield. This method may substitute for the previously employed coupling with organocadmium or -zinc species. Peculiar reactivities are reported for *C*-glycosylation of Gilman-type aryl cuprates which required substantial arene-specific optimization. Interestingly, the glycosylation of Gilman cuprates was found to provide access not only to *C*-aryl-nucleosides but also to *O*-aryl-glycosides. The reactions of Gilman cuprates with Hoffer's chlorosugar **1** in the presence of oxygen provided the coresponding *O*-aryl-2′-deoxyribosides in up to 87% yield without concomitant *C*-glycosylation.

Introduction

Aromatic analogues of DNA nucleobases have become valuable tools in studies of DNA−DNA and DNA−protein interactions.[1] Designed *C*-aryl-nucleosides have been incorporated as base surrogates into DNA to study base stacking interactions,[2] to enable new base pairing modes,[3,4] and to probe the reaction mechanisms of DNA-polymerases[5] and DNA-repair enzymes.[6] We have used *C*-glycosidically linked bulky arenes in studies of the base flipping mechanism of DNA-methyltransferases.[7,8] Synthetic access of the *C*-aryl-nucleosides is provided by a variety of methods, which differ in the coupling chemistry used to achieve the critical coupling of the aryl moiety with the 2-deoxyribose backbone.[9] Though useful in many cases, these methods often have drawbacks such as low yields or economic efficiency, the necessity for intensive optimization of the reaction conditions, and/or the use of hazardous and environmentally toxic reagents. For example, the coupling of lithium organyls to ribonolactons is a widely applicable method but it requires the use of an expensive glycosyldonor to improve the typically low yields.[10−12] Costly glycosyl donors and time-consuming arene-specific optimizitation are required in β-selec-

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tive coupling chemistries which draw upon reactions of arylpalladium species with a glycal[13,3e] and of organoaluminium reagents with an 1,2-anhydrosugar.[14] Rapid and cost-efficient access to *C*-nucleosides is provided by Friedel−Crafts-alkylation.[15] However, this method is limited to electron-rich arenes. The most frequently applied general route to *C*-aryl-nucleosides involves the use of Hoffer's chlorosugar[16] **1** (1,2-dideoxy-3,5-di-*O*-(*p*-toluoyl)-α-1-chloro-D-ribofuranose) and an aryl metal species. The direct use of aryl Grignard[17] and aryl lithium reagents is plagued by concomitant elimination at the glycosyl donor. Transmetalation to cadmium is a commonly applied means to reduce the basicity of the aryl nucleophile.[7,18,19] Cadmium organyls are highly toxic and exhibit relatively modest reactivity. Our group and the Carell group have reported preliminary studies on the *C*-ribosylation of aryl cuprates.[4a,8] However, these studies were focused on the properties of base-modified oligonucleotides rather than on synthesis. Neither has the cuprate type, which is known to critically affect their reactivity,[20] been varied, nor have scope and limitations of cuprate glycosylation been investigated. In pursuit of providing robust and efficient access to *C*-aryl-nucleosides we became interested in exploring the utility of different cuprate reagents. Specifically, we investigated the reactivity of lithium- and magnesium-based aryl cuprates in *C*-glycosylations with Hoffer's chlorosugar **1**. We herein provide full experimental details and demonstrate that Normant-type aryl cuprates allow for both highly reliable and highly efficient syntheses of polycyclic *C*-aryl-nucleosides (Figure 1). To our surprise we noticed that minor changes of the reaction conditions enable efficient access of *O*-aryl-glycosides which are more difficult to synthesize by using conventional Lewis acid-mediated glycosylation reactions.

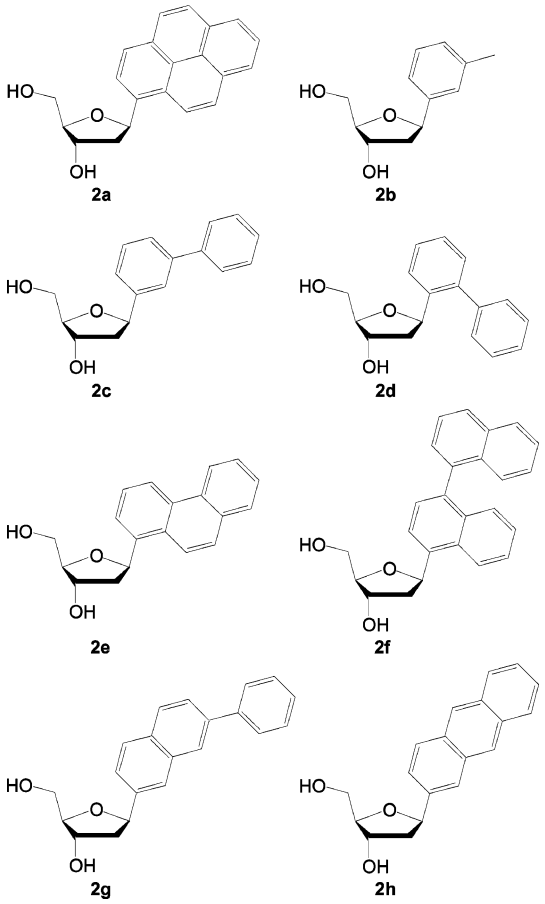

FIGURE 1. Structure of *C*-aryl-nucleosides synthesized by glycosylation of aryl cuprates.

Results and Discussion

Glycosylation. The usefulness of copper-based reagents for the synthesis of *C*-glycosides has been demonstrated first by Bihovsky, who reported the coupling of methyl- and phenyl-Gilman cuprates with α-glycopyranosylbromides.[21] Subsequently, anomeric pyranosyl esters[22] and 1,2-anhydropyranoses[23] have been shown to react with aromatic and aliphatic cuprates. Surprisingly, prior to our preliminary report[8] cuprates have not been used for the synthesis of *C*-linked furanosides such as 2-deoxy-*C*-aryl-nucleosides. Our first attempt in subjecting aryl cuprates to *C*-glycosylation reactions with chlorosugar **1** was

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TABLE 1. Reagents, Conditions, and Yields of Several Cuprate Reactions

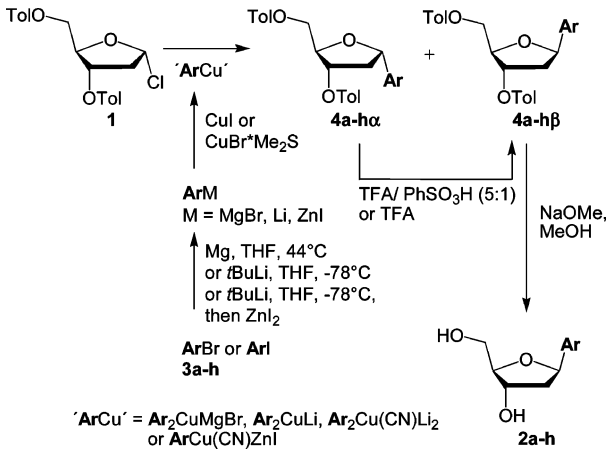
entry	product	cuprate	arene	conditions	anomeric selectivity α:β	yield, %
1	**4a**	$Ar_2CuMgBr$	1-bromopyrene	1 h; −10 °C to rt	4:1	75
2	**4a**	$Ar_2CuMgBr$	1-bromopyrene	1 h; 40 °C	3:1	93
3	**4a**	$Ar_2CuMgBr$	1-bromopyrene	1 h; 60 °C	2.3:1	86
4	**4b**	$Ar_2CuMgBr$	3-bromotoluene	1 h; 40 °C	1.5:1	87
5	**4b**	Ar_2CuLi	3-bromotoluene	18 h, −18 °C to rt	4:1	63
6	**4b**	Ar_2CuLi	3-bromotoluene	18 h, −40 °C	4:1	40
7	**4a**	Ar_2CuLi	1-bromopyrene	18 h; −18 °C to rt	>20:1	22
8	**4a**	Ar_2CuLi	1-bromopyrene	18 h; −78 °C to rt	>20:1	69
9	**4a**	$Ar_2Cu(CN)Li_2$	1-bromopyrene	18 h; 0 °C to rt	>20:1	63
10	**4a**	$ArCu(CN)ZnI$	1-bromopyrene	18 h; 0 °C to rt	>20:1	39
11	**4c**	$Ar_2CuMgBr$	2-bromobiphenyl	1 h; 40 °C	1:1.3	83
12	**4d**	$Ar_2CuMgBr$	3-bromobiphenyl	1 h; 40 °C	1.6:1	73
13	**4e**	$Ar_2CuMgBr$	1-bromophenanthrene	1 h; 40 °C	3:1	80
14	**4f**	$Ar_2CuMgBr$	4-bromo[1,1′]binaphthyl	1 h; 40 °C	3:1	75
15	**4g**	$Ar_2CuMgBr$	2-bromo(7-phenyl)naphthalene	1 h; 40 °C	1:1.5	76
16	**4h**	Ar_2CuLi	2-iodoanthracene	18 h, −25 °C	>20:1	47

based on the use of Normant cuprates which were prepared from the aryl Grignard reagents via treatment with 0.5 equiv of copper iodide. A subsequent report from Carell and co-workers suggested the usefulness of Gilman cuprates.[4a] We therefore decided to explore the reactivity of both Normant and Gilman cuprates in the synthesis of *C*-aryl-nucleosides.

Our first aim was to optimize the coupling of Normant cuprates with Hoffer's chlorosugar **1**. The pyrene nucleoside **2a**[18] was chosen as a representative example. The Grignard reagent 1-pyrenylmagnesium bromide was prepared in THF from 1-bromopyrene **3a** and subjected to transmetallation with copper iodide. The *C*-glycosylation was commenced upon addition of chlorosugar **1**. The bis-toluoyl-protected nucleoside **4a** was obtained as a mixture of β-epimer **4a**β and α-epimer **4a**α in 74% yield when the reaction was performed for 1 h at −10 °C (entry 1, Table 1). Increases of the reaction temperature to 40 °C resulted in significant increases of coupling yield (93%) and changes of the α/β-anomer ratio from 4:1 to 3:1 (entry 2, Table 1). The reaction still proceeded remarkably well at 60 °C furnishing **4a** in slightly reduced 86% yield and higher content of the β-anomer (α:β = 2.3:1). Other alterations of the reaction conditions such as the use of cosolvents like 1,4-dioxane, dichloromethane, and toluene or the exclusion of iodide ions by omitting iodine etching of magnesium and using copper bromide−dimethyl sulfide instead of copper iodide had little effect on reaction yields or selectivities (data not shown). The optimized conditions were further evaluated in the synthesis of 3-tolyl nucleoside **4b**.[10] The use of Normant cuprate $(3\text{-tolyl})_2CuMgBr$, synthesized from 3-bromotoluene **3b**, provided for a smooth reaction and delivered **4b** in 87% yield. Notably, the yields furnished by the cuprate method are higher than the yields reported for the reactions of the corresponding aryl cadmium (**4a**, 72%)[8] and aryl lithium derivatives (**4b**, 35%)[10] with chlorosugar and ribonolactone, respectively.

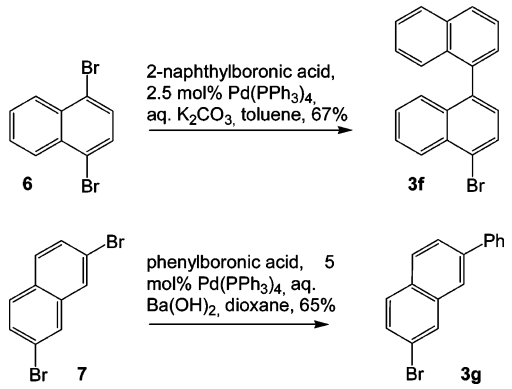
We next studied cuprates that were synthesized from lithium organyls via transmetallation with copper iodide. The 3-tolyl-based Gilman cuprate was allowed to react with chlorosugar **1**. In the optimization process, we noticed that the reactions proceeded more slowly, requiring lower reaction temperatures and longer reaction times of up to 18 h than the *C*-glycosylation reactions of Normant cuprates. In addition, rather peculiar reactivities were observed. The highest yield (63%) was obtained when the reaction was performed at −18 °C in THF (entry 5, Table 1). The reduction of reaction temperature to −40 °C resulted in the formation of the *O*-glycoside **5a** (vide infra). The use of carefully degassed THF solved the problem of *O*-glycoside formation; however, it reduced the efficiency of *C*-glycosylation to 40% synthesis yield (entry 6, Table 1). The attempt to synthesize the 1-pyrenyl-*C*-nucleoside **4a** by using the Gilman cuprate and applying the reaction conditions optimized for the synthesis of 3-tolyl-*C*-nucleoside **4b** failed to provide useful synthesis yields (entry 7, Table 1). In this case it proved necessary to reduce the reaction temperature to −78 °C (entry 8, Table 1). Under these conditions **4a** was obtained in 69% yield with high α-selectivity (α:β = >20:1). The use of the higher order cyanocuprate $(1\text{-pyrenyl})_2Cu(CN)Li_2$ or the zinc copper reagent (1-pyrenyl)Cu(CN)ZnI did not result in enhancements of reaction yields (entries 9 and 10, Table 1). In these reactions the formation of the α-epimer was highly favored.

SCHEME 1. Synthesis of *C*-Aryl-Nucleosides



The results discussed above suggested that the use of Normant-type aryl cuprates provides for higher robustness and synthesis yields than the use of Gilman-type aryl cuprates. For further exploration the *C*-glycosylation of cuprates was tested in the synthesis of additional *C*-aryl-nucleosides which were required in an ongoing project toward mechanistical studies of base flipping DNA-methyltransferases. Precursors for the 2-bromobiphenyl nucleoside **2c** and the 3-bromobiphenyl nucleoside **2d**, 2-bromobiphenyl **3c** and 3-bromobiphenyl **3c**, were commercially available. The "aglycon units" of *C*-aryl-nucleosides **2e** and **2h**, 1-bromophenanthrene **3e** and 2-iodoanthracene **3h**,

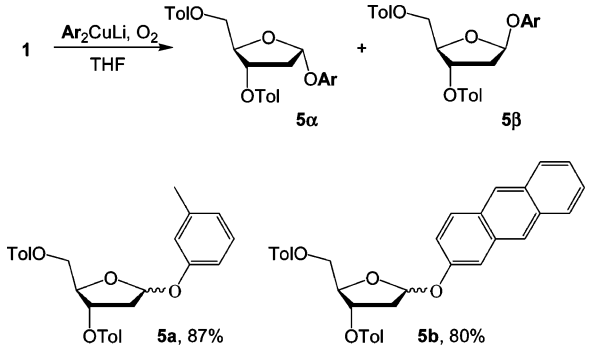
SCHEME 2. Synthesis of 4-Bromo[1,1′]binaphthyl 3f and 2-Bromo(7-phenyl)naphthalene 3g



were synthesized according to literature procedures.[24,25] The naphthyl-based aryl-nucleosides **2f** and **2g** were prepared by glycosylation of cuprates from aryl bromides **3f** and **3g**. The latter were assessed by coupling 1-naphthylboronic acid with 1,4-dibromonaphthalene[26] **6** or phenylboronic acid with 2,7-dibromonaphthalene[27] **7** at Suzuki coupling conditions[28,29] (Scheme 2).

The aryl bromides **3c**−**e**, **3f**, and **3g** were converted to Normant cuprates and used in *C*-glycosylation reactions with chlorosugar **1** at conditions which were identified during the optimization of the coupling of pyrene cuprates. The reaction delivered the desired products in reliable 73−86% yield after purification (entries 11−15, Table 1). We note that these yields were obtained at the first attempt without further arene-specific optimization, which attests to the robustness of Normant cuprate-mediated *C*-glycosylation. The anomers were usually separated at the *O*-protected stage via flash chromatography. However, the α- and *β*-form of 2-biphenyl nucleoside **4c** exhibited identical R_f-values. In this case, the anomers were separated after deacylation. For the synthesis of 2-anthracenyl-*C*-nucleoside[30] **4h** we resumed the use of Gilman cuprates since the 2-iodoanthracene **3h** is not amenable to Grignard reaction. Thus, lithiation had to be employed to provide access to a cuprate. The coupling of **3h** with chlorosugar **1** again required substantial optimization to deliver purified **4h** in 47% yield. During the optimization process we noticed the formation of an additional product that coeluted in flash chromatography with the *C*-nucleoside but showed additional signals in the NMR spectra. The new product was the sole product when the reaction of the Gilman cuprate with **1** was performed at temperatures below −40 °C in not perfectly degassed THF. NMR spectroscopy and high-resolution mass spectrometry revealed the *O*-aryl-glycoside structure **5**. After the identification of the new product, the cuprate-mediated glycosylation was carried out under air instead of an argon atmosphere by using 3-bromotoluene and 2-iodoanthracene precursors. The reactions proceeded smoothly and

SCHEME 3. Synthesis of *O*-Aryl-Glycosides



delivered the 3-tolyloxy-2′-deoxyriboside **5a** (α:*β* = 2.5:1, 87%) and the 2-anthracenyloxy-2′-deoxyriboside **5b** (α:*β* = 4:1; 80%) in surprisingly high yields after purification. *O*-aryl-glycoside structures are found in several natural products like vancomycin, chromomycin, and olivomycin.[31] Their synthesis is usually a quite demanding task that requires careful optimization of the reaction conditions.[32] A typical problem in the most commonly applied Lewis acid-promoted *O*-glycosylation of arylalcohols is the concurrent formation of *C*-linked aryl-glycosides. In contrast, glycosylation of Gilman cuprates with **1** under aerobic conditions at low temperatures (≤−40 °C) provided the *O*-aryl-nucleosides **5** without concomitant *C*-glycosylation.

Structure Verification. The structures of the newly synthesized nucleosides were verified by ^{1}H NMR,^{13}C NMR, and ^{1}H−^{1}H NOESY-NMR spectroscopy and HRMS. The NOESY spectrum of the *β*-anomers **4c**−**e**, **4f**, and **2g** showed in all cases characteristic interactions between H1′ and H2′α and also H3′ and H2′*β*, which confirmed the anomeric configuration. In the case of the 2-biphenyl nucleoside **2b***β* the NMR signals of H2′α and H2′*β* overlap. Hence the NOESY spectrum of the unnaturally configured α-anomeric *C*-nucleoside **2b**α was used to confirm the structure of the nucleoside wherein H2′*β* shows predominant interactions with H1′ and H3′. The NMR spectra of the anomerically pure binaphthyl nucleoside **2f** exposed the existence of two different diastereomers. The [1,1′]binaphthyl group provides axial chirality. The energy barrier for rotation around the binaphthyl bond was, however, not sufficient to allow separation by reversed phase-HPLC at ambient temperature. The structures of the *O*-glycosides **5** were confirmed by HRMS, ^{1}H NMR, ^{1}H,^{1}H NOESY-NMR, and ^{13}C NMR. The low field shift of the anomeric carbon atoms (*δ* 102−103 ppm) indicated the presence of an *O*-glycoside structure rather than a *C*-glycoside (*δ* 78−81 ppm).

Epimerization and Deprotection. The cuprate-mediated glycosylation reactions provided the *C*-aryl-nucleosides as a mixture of anomers. Often the α-anomer was favored. Acid-mediated epimerization was used to enrich the thermodynamically slightly favored *β*-anomers. We applied conditions reported by Stivers and co-workers and employed trifluoroactic acid (TFA) or TFA/benzenesulfonic acid (5:1 v:w) in dichloromethane to promote epimerization.[33] In general, the more electron-rich arenes required smaller amounts of promotor. For example, **4a**, having an electron-rich 1-pyrenyl substructure, epimerized in the presence of a 1% solution of TFA. In contrast,

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TABLE 2. Reagents, Conditions, and Yields of Epimerization and Deprotection Reactions

entry	toluoyl ester	epimerization conditions[a]	starting ratio α:β	product ratio α:β	yield, % (isolated β-anomer)	deprotection product	yield, %
1	**4a**	1% TFA	3:1	1:2.3	57	**2a**	91
2	**4b**	10% TFA/$PhSO_3H$	1.5:1	1:2.4	52	**2b**	92
3	**4c**					**2c**	81
4	**4d**	18% TFA/$PhSO_3H$	1.6:1	1:2.6	59	**2d**	70
5	**4e**	6% TFA/$PhSO_3H$	3:1	1:2.1	58	**2e**	79
6	**4f**	6% TFA/ $PhSO_3H$	3:1	1:1.5	47	**2f**	70
7	**4g**	12% TFA/$PhSO_3H$	Pure α	1:3.9	46	**2g**	93
8	**4h**	5% TFA	>20:1	1:2.6	44	**2h**	57

[a] In dichloromethane at 40 °C.

the comparatively electron-poor meta-substituted nucleosides **4b** and **4d** required 10% and 18% solutions of a more effective TFA/benzensulfonic acid promotor (Table 2).[34] After two epimerization cycles the β-anomers were isolated in up to 70% yield. For the synthesis of the *O*-unprotected *C*-aryl-nucleosides **2**, the toluoyl protecting groups were removed by treatment of **4a**−**h**β with sodium methoxide in dry methanol by applying conditions known in literature.[18] After column chromatography the corresponding unprotected *C*-nucleosides **4a**−**h** were obtained in high yields. The 2-biphenyl nucleoside **4c**α/β was deprotected as the anomeric mixture and then separated by using preparative reversed phase-HPLC to yield the pure anomers **2c**α/β and **2c**α/β.

Many powerful methods have been developed to improve the critical *C*−*C*-coupling step in the synthesis of *C*-aryl-nucleosides. Most attractive methods use inexpensive, readily available starting materials and require little optimization and as few synthetic steps as possible. Unparalled rapid access to *C*-aryl-nucleosides (4 steps) is provided by the Friedel−Crafts-like glycosylation, but the limitation to electron-rich arenes restricts the general applicability of this method.[15] By contrast, the coupling of disiloxane-protected ribonolactone to aryllithiums is widely applicable.[10,11] The critical *C*−*C*-coupling has been reported to occur in up to 56% yield; however, a modest 17% yield has been reported for the *C*-glycosylation of sterically hindered 2-substituted arenes.[10] The described glycosylation of cuprates with Hoffer's chlorosugar combines general applicability with conciseness (6 steps) and high synthetic efficiency affording up to 93% *C*−*C*-coupling yield when Normant cuprates are used. Remarkably, coupling of sterically hindered arenes such as 2-bromobiphenyl **2c** still proceeded in 83% yield. Cuprate-mediated reactions occur under almost neutral conditions which is advantageous with regard to the general applicability. For example, one may envision new entries to the modular synthesis of multicyclic ring systems as described by Hocek and co-workers.[11,34] One drawback of the nonacidic reaction medium is the resulting bias to the formation of α-diastereomers. Nevertheless, the combined yields of *C*−*C*-coupling and subsequent epimerization still surpass those of most other methods. We wish to note that in the few cases where it is difficult to separate β- from α-anomers one may consider the use of strictly β-selective routes such as the palladium-catalyzed coupling of iodoarenes with glycals[13] or the *syn*-opening of 1,2-anhydroarabinose by arylaluminium reagents.[14] These methods typically require more steps and involve the use of expensive starting materials.

The coupling reactions between Hoffer's chlorosugar and magnesium organyls have been reported to proceed in 22−57% yield.[17] The use of the corresponding cadmium- and zinc organyls allowed 40−80% yield with electron-rich arylhalogenides providing higher yields than electron-poor precursors.[7,18,19] The results described in this study demonstrated the beneficial reactivity of organocuprates which reacted faster and delivered higher yields than previously used organometal compounds. Although several types of cuprates were effective, the most successful method relied on the use of Normant cuprates. The use of Gilman cuprates required careful optimization of reaction conditions. The cuprate method should also offer a versatile strategy for the synthesis of functionalized *C*-aryl-nucleosides. Carrell and co-worker have shown the cuprate-mediated synthesis of *C*-nucleosides featuring formyl and hydroxyl functional groups.[4] Recent work by Knochel allows access to a broad range of functionalized aryl magnesium compounds using isopropylmagnesium chloride for halogen/magnesium-exchange and their utility in copper-mediated reactions has been demonstrated.[35] *C*-Aryl-nucleosides bearing, for example, nitrile, ester, or amide functions or several heterocyclic *C*-aryl-nucleosides should be available after a halogen/magnesium-exchange and further transmetallation to Normant cuprates.

Interestingly, the glycosylation of Gilman cuprates was found to provide access not only to *C*-aryl-nucleosides but also to *O*-aryl-glycosides. There are only a few examples in which arylhalogenides have been used for the synthesis of *O*-aryl-2′-deoxyribosides. In one, an organozinc reagent has been shown to furnish the product of *O*-glycosylation in 19% yield.[36] The reactions of Gilman cuprates with Hoffer's chlorosugar **1** in the presence of oxygen provided the coresponding *O*-aryl-2′-deoxyribosides **5** in up to 87% yield, which expands the versatility of the cuprate glycosyation method.

Experimental Section

4-Bromo[1,1′]binaphthyl (12).[28] In an argon-flushed Schlenk flask 1.40 g (5.0 mmol) of 1,4-dibromonaphthalene **10** and 0.95 g (5.5 mmol) of 1-naphthylboronic acid were dissolved in 10 mL of degassed toluene. After the addition of 10 mL of degassed 2 M aq potassium carbonate solution and 143 mg (0.125 mmol) of Pd-$(PPh_3)_4$ the solution was stirred for 24 h at 100 °C. The reaction mixture was worked up after the addition of 10% aq NH_4Cl by extraction with 30 mL of CH_2Cl_2 (3×). The combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$ and brine and dried over anhydrous $MgSO_4$ and solvent was removed under reduced pressure. Flash chromatography (cyclohexane) yielded 1.12 g (67%) of a colorless solid. Mp 135−136 °C. MS(EI): *m*/*z* $C_{20}H_{13}Br^+$ calcd 332.0 (M), found 332.0. ^1H

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NMR (300 MHz, $CDCl_3$): δ 8.38 (d, J = 8.7, 1H), 8.01−7.97 (m, 2H), 7.94 (d, J = 8.1, 1H), 7.65−7.59 (m, 2H), 7.54−7.49 (m, 2H), 7.45−7.30 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.6, 137.5, 134.1, 133.5, 132.7, 131.9, 129.5, 128.2, 128.1, 127.9, 127.4, 127.3, 127.2, 126.8, 126.3, 126.2, 125.9, 125.4, 122.6. Anal. Calcd for $C_{20}H_{13}Br$: C, 72.09; H, 3.93; Br, 23.98. Found: C, 72.17; H, 4.26; Br, 23.22.

2-Bromo(7-phenyl)naphthalene (13).[29] In an argon-flushed Schlenk flask 784 mg (2.74 mmol) of 2,7-dibromonaphthalene **11** and 419 mg (3.0 mmol) of phenylboronic acid were dissolved in 10 mL of degassed 1,4-dioxane. After the addition of 10 mL of degassed 2 M aq $Ba(OH)_2$ solution and 156 mg (0.137 mmol) of $Pd(PPh_3)_4$ the solution was stirred for 24 h at 80 °C. The reaction mixture was worked up after the addition of 10% aq NH_4Cl by extraction against 30 mL of CH_2Cl_2 (3×). The combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$ and brine and dried over anhydrous $MgSO_4$ and solvent was removed under reduced pressure. Flash chromatography (cyclohexane) yielded 500 mg (65%) of a colorless solid. Mp 100−101 °C. HRMS(EI): m/z $C_{16}H_{11}Br^+$ calcd 282.0044 (M), found 282.0043. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95 (s, 1H), 7.83 (s, 1H), 7.77 (d, J = 9.0, 1H), 7.66−7.57 (m, 4H), 7.46−7.30 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.6, 139.7, 134.8, 131.0, 130.2, 129.8, 129.5, 129.4, 129.3, 129.0, 128.4, 127.7, 127.5, 126.1, 124.8, 120.3.

Typical Procedure for Normant-Cuprate Mediated Synthesis of *C*-Aryl-Nucleosides: Synthesis of 4dα/β. For the preparation of aryl Grignard from 3-bromobiphenyl, magnesium (106 mg, 4.36 mmol) was activated for 1 h by iodine etching in a Schlenk tube while stirring without solvent. Then 25 mL of THF and 715 μL of 3-bromobiphenyl (4.29 mmol) were added to the magnesium and the mixture was stirred at 44 °C until consumption of magnesium. The resulting solution was cooled to 0 °C before 425 mg (2.23 mmol) of copper iodide was added. The reaction mixture was allowed to warm to 20 °C and stirred for 30 min until the copper iodide had dissolved. The solution was heated to 40 °C and the α-chlorosugar **1** (730 mg; 1.87 mmol) was added. The mixture was stirred for 1 h at 40 °C. Workup was commenced by the addition of a 10% aqueous solution of NH_4Cl followed by extraction with 30 mL of CH_2Cl_2 (3×). The combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$ (3×) and brine then dried over anhydrous $MgSO_4$ and solvent was removed under reduced pressure. The product was purified on a silica gel column with cyclohexane:ethyl acetate (19:1) to yield 726 mg (73%) of **4d**α/β (α:β = 1.6:1) as a colorless oil.

α-1′,2′-Dideoxy-3′,5′-di-*O*-toluoyl-1′-(3-biphenyl)ribofuranose (4dα). HRMS(ESI): m/z $C_{33}H_{30}O_5Na^+$ calcd 529.1985 (M + Na^+), found 529.1985. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.98 (d, J = 8.3, 2H), 7.67 (s, 1H), 7.67 (d, J = 8.3, 2H), 7.60−7.56 (m, 2H), 7.45−7.34 (m, 5H), 7.23 (d, J = 7.5, 2H), 7.08 (d, J = 7.9, 2H), 5.63 (ddd, J = 6.4, 3.8, 3.0, 1H, H3′), 5.43 (dd, $J_{H1',H2'\beta}$ = 7.3, $J_{H1',H2'\alpha}$ = 5.8, 1H, H1′), 4.72 (td, $J_{H4',H5'}$ = 4.8, $J_{H3',H4'}$ = 2.9, 1H, H4′), 4.59 (m, 2H, H5′), 2.98 (ddd, $J_{H2'\alpha,H2'\beta}$ = 13.9, $J_{H1',H2'\beta}$ = 7.5, $J_{H3',H2'\beta}$ = 6.7, 1H, H2′β), 2.40 (s, 3H), 2.36 (s, 3H), 2.40−2.36 (m, 1H, H2′α). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5, 166.2, 143.9, 143.9, 143.0, 141.5, 141.2, 129.8, 129.7, 129.2, 129.0, 128.8, 128.7, 127.3, 127.3, 127.1, 126.8, 126.3, 124.7, 124.5, 82.3, 80.3, 76.4, 64.6, 40.4, 21.7, 21.7.

α-1′,2′-Dideoxy-3′,5′-di-*O*-toluoyl-1′-(3-tolyl)ribofuranose (4bα). Compound **4b**α/β (641 mg; 87%) was synthesized from **1** (645 mg; 1.667 mmol) as a colorless oil. HRMS(EI): m/z $C_{28}H_{28}O_5^+$ calcd 444.1937 (M), found 444.1936. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01 (d, J = 8.2, 2 H), 7.76 (d, J = 8.2, 2 H), 7.31−7.20 (m, 7H), 7.15−7.11 (m, 1H), 5.64 (ddd, 1H, J = 6.8, 3.9, 3.0, H3′, 1H), 5.37 (dd, $J_{H1',H2'\beta}$ = 6.8, $J_{H1',H2'\alpha}$ = 6.8, 1H, H1′), 4.74 (td, 1H, $J_{H4',H5'}$ = 4.7, $J_{H3',H4'}$ = 2.9, H4′), 4.67−4.56 (m, 2H, H5′), 2.97 (ddd, $J_{H2'\alpha,H2'\beta}$ = 14.1, $J_{H1',H2'\beta}$ = 7.2, $J_{H3',H2'\beta}$ = 7.2, 1H, H2′β), 2.44 (s, 3H), 2.42 (s, 3H), 2.39 (s, 3H), 2.38−2.31 (m, 1H, H2′). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.3, 166.1, 143.9, 143.7, 142.2, 138.0, 129.7, 129.6, 129.1, 129.0, 128.3, 128.1, 127.0, 126.8, 126.2, 122.7, 82.1, 80.3, 77.4, 64.8, 40.3, 21.7, 21.5.

α,β-1′,2′-Dideoxy-3′,5′-di-*O*-toluoyl-1′-(2-biphenyl)ribofuranose (4cα/β). Compound **4c**α/β (609 mg; 83%; α:β = 1:1.3) was synthesized from **1** (563 mg; 1.45 mmol) as a colorless oil. HRMS-(EI): m/z $C_{33}H_{30}O_5^+$ calcd 506.2093 (M), found 506.2093. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99−7.16 (m, 17H), 5.53−5.45 (m, 1H, H3′), 5.36 (dd, $J_{H1',H2'\alpha}$ = 7.4, $J_{H1',H2'\beta}$ = 7.4, H1′(α-epimer)), 5.36 (dd, $J_{H1',H2'\alpha}$ = 10.9, $J_{H1',H2'\beta}$ = 6.0, 1H, H1′(β-epimer)), 4.75−4.71 (m, H4′(α-epimer)), 4.70−4.59 (m, H5′(β-epimer)), 4.52−4.41 (m, H5′(α-epimer)), 4.35 (td, $J_{H4',H5'}$ = 3.9, $J_{H3',H4'}$ = 2.5, H4′(β-epimer)), 2.70 (ddd, $J_{H2'\beta,H2'\alpha}$ = 14.1, $J_{H1',H2'\beta}$ = 7.2, $J_{H3',H2'\beta}$ = 7.2, H2′β (β-epimer)), 2.44 (s, 6H), 2.31−2.11 (m, H2′). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.4, 166.2, 166.0, 144.0, 143.8, 143.7, 141.0, 140.8, 140.8, 140.7, 139.5, 138.0, 130.0, 129.8, 129.7, 129.3, 129.2, 129.1, 128.3, 128.1, 128.0, 127.8, 127.5, 127.3, 127.2, 125.8, 125.7, 83.4, 82.0, 81.0, 77.7, 77.6, 64.9, 64.9, 41.9, 40.8, 21.7.

α-1′,2′-Dideoxy-3′,5′-ditoluoyl-1′-(1-phenanthrenyl)ribofuranose (4eα). Compound **4d**α/β (436 mg; 80%; α:β = 3:1) was synthesized from **1** (400 mg; 1.03 mmol) as a colorless oil. HRMS-(EI): m/z $C_{35}H_{30}O_5^+$ calcd 530.2093 (M), found 530.2093. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.75−8.70 (m, 2H), 8.09 (m, 2H), 7.94−7.62 (m, 9H), 7.30 (d, J = 8.5 Hz, 2H), 7.15 (d, J = 8.5 Hz, 2H), 6.17 (t, J = 5.7 Hz, 1H), 5.74−5.70 (m, 1H), 4.93−4.89 (m, 1H), 4.72−4.65 (m, 2H), 3.30−3.21 (m, 1H), 2.49−2.45 (m, 4H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.4, 166.0, 143.9, 138.8, 131.4, 130.6, 129.8, 129.7, 129.2, 129.0, 128.5, 128.3, 127.1, 126.8, 126.7, 126.6, 126.1, 123.0, 122.9, 122.1, 121.6, 82.5, 78.2, 77.2, 64.7, 40.0, 21.7, 21.6.

α-1″,2″-Dideoxy-3″,5″-ditoluoyl-1″-(*R*,*S*-[1,1′]binaphthylen-4-yl)ribofuranose (4fα). Compound **4f**α/β (314 mg; 75%; α:β = 3:1) was synthesized from **1** (270 mg; 0.70 mmol) as a colorless oil. HRMS(EI): m/z $C_{41}H_{34}O_5^+$ calcd 606.2406 (M), found 606.2403. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03−7.92 (m, 6H), 7.77 (d, J = 8.0, 1H), 7.73 (d, J = 8.0, 1H), 7.68−7.27 (m, 11H), 7.18 (d, J = 7.8, 1H), 7.09 (d, J = 8.0, 1H), 6.23−6.17 (m, 1H, H1′), 5.78−5.73 (m, 1H, H3′), 4.98−4.91 (m, 1H, H4′), 4.77−4.64 (m, 2H, H5′), 3.32−3.22 (m, 1H, H2′β), 2.63−2. 49 (m, 1H, H2′α), 2.44 (s, 3H), 2.40 (s, 1.3H), 2.30 (s, 1.7H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5, 166.1, 166.1, 144.0, 144.0, 143.9, 138.5, 138.2, 138.1, 137.8, 133.5, 133.5, 133.1, 132.9, 132.9, 130.2, 129.9, 129.8, 129.8, 129.6, 129.2, 129.2, 129.1, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.4, 127.3, 127.1, 126.8, 126.8, 126.6, 126.1, 126.0, 126.0, 125.9, 125.7, 125.6, 125.6, 125.5, 125.3, 123.3, 123.3, 82.8, 82.4, 78.4, 78.1, 64.8, 64.8, 39.9, 39.8, 21.7, 21.7, 21.6.

α-1′,2′-Ditoluoyl-1′-(2-(7-phenyl)naphthyl)ribofuranose (4gα). Compound **4g**α/β was synthesized from **1** (300 mg; 0.77 mmol). The fractions were separated to yield 129 mg (30%) of compound **4g**α and 197 mg (46%) of compound **4g**β. HRMS(EI): m/z $C_{37}H_{32}O_5^+$ calcd 556.2250 (M), found 556.2250. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03−7.98 (m, 4H), 7.93 (d, J = 8.6, 1H), 7.89 (d, J = 8.50, 1H), 7.79−7.71 (m, 3H), 7.64 (d, J = 8.2, 2H), 7.56−7.48 (m, 3H), 7.44−7.38 (m, 1H), 7.27 (d, J = 8.0, 2H), 7.03 (d, J = 8.0, 2H), 5.68 (ddd, J = 6.5, 3.4, 3.4, 1H, H3′), 5.59 (dd, $J_{H1',H2'\alpha}$ = 7.5, $J_{H1',H2'\beta}$ = 5.6, 1H, H1′), 4.81 (td, 1H, $J_{H4',H5'}$ = 4.8, $J_{H3',H4'}$ = 2.8, H4′), 4.69−4.59 (m, 2H, H5′), 3.04 (ddd, $J_{H2'\alpha,H2'\beta}$ = 14.2, $J_{H1',H2'\beta}$ = 7.6, $J_{H3',H2'\beta}$ = 6.8, 1H, H2′β), 2.49−2.41 (m, 1H, H2′α), 2.44 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5, 166.1, 144.0, 143.9, 141.1, 140.4, 138.9, 133.5, 132.0, 129.8, 129.7, 129.2, 129.0, 128.9, 128.2, 128.0, 127.4, 127.1, 126.7, 125.9, 125.6, 124.7, 124.0, 82.5, 80.5, 76.5, 64.7, 40.3, 21.7, 21.6.

Typical Procedure for Gilman-Cuprate Mediated Synthesis of *C*-Aryl-nucleosides: Synthesis of 4hα. In a dry argon-flushed flask 2-iodoanthracene (1.8 g; 5.9 mmol.) was added to 20 mL of dry THF and cooled to −78 °C. With use of a glass syringe, *t*-BuLi in pentane (7.9 mL; 1.5 M; 11.8 mmol) was added dropwise and the solution was stirred for 15 min. After addition of copper iodide (562 mg; 2.95 mmol) the solution was allowed to warm while the

CuI dissolved. After cooling to −25 °C the chlorosugar **1** (730 mg; 1.87 mmol) was subsequently added and the mixture was stirred for 18 h at this temperature. For workup a 10% aqueous solution of NH_4Cl was added followed by extraction with 30 mL of CH_2Cl_2 (3×). The organic layers were washed with a saturated aqueous solution of $NaHCO_3$ (3×) and brine and dried over anhydrous $MgSO_4$ and solvent was removed under reduced pressure. The product was purified on a silica gel column with cyclohexane: ethylacetate (19:1) to yield 473 mg (47%) of **4h**α as a yellowish oil.

α-1′,2′-Dideoxy-3′,5′-di-*O*-toluoyl-1′-(2-anthracenyl)ribofuranose (4hα). HRMS(EI): *m*/*z* $C_{35}H_{30}O_5^+$ calcd 530.2093 (M), found 530.2093. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.49 (s, 1H), 8.46 (s, 1H), 8.07 (d, *J* = 8.1, 2H), 8.03−7.97 (m, 3H), 7.79 (d, *J* = 6.9, 1H), 7.70 (d, *J* = 8.1, 2H), 7.52−7.47 (m, 3H), 7.30 (d, *J* = 8.0, 2H), 7.16 (d, *J* = 8.0, 2H), 6.23 (dd, $J_{H1',H2'\alpha}$ = 7.3, $J_{H1',H2'\beta}$ = 6.1, 1H, H1′), 5.75 (ddd, *J* = 6.6, 3.4, 3.4, 1H, H3′), 4.92 (td, 1H, $J_{H4',H5'}$ = 4.7, $J_{H3',H4'}$ = 2.9, H4′), 4.79−4.69 (m, 2H, H5′), 3.32 (ddd, $J_{H2'\alpha,H2'\beta}$ = 14.4, $J_{H1',H2'\beta}$ = 7.3, $J_{H3',H2'\beta}$ = 7.3, 1H, H2′β), 2.53 (ddd, $J_{H2'\alpha,H2'\beta}$ = 13.6, $J_{H1',H2'\alpha}$ = 5.6, $J_{H3',H2'\alpha}$ =3.6, 1H, H2′α), 2.46 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5, 166.1, 144.0, 137.8, 132.0, 131.6, 131.3, 129.9, 129.7, 129.2, 129.0, 128.7, 128.5, 128.2, 127.9, 127.3, 127.2, 126.8, 125.7, 124.8, 121.9, 121.7, 82.4, 78.2, 76.5, 64.8, 39.7, 21.7, 21.7.

Representative Epimerization Procedure: Epimerization of 4dαβ. To a solution of the bistoluoylated nucleoside **4d**αβ (658 mg; 1.3 mmol) in 16 mL of CH_2Cl_2 trifluoroacetic acid (3 mL) was added 500 mg of benzensulfonic acid. After 18 h of stirring at 40 °C the solution was cooled to 0 °C and triethylamine (10 mL) was slowly added. The solvent was evaporated and the anomers were separated on a silica gel column with cyclohexane/ethyl acetate (19:1) to yield 385 mg of **4d**β as a colorless foam and 146 mg of **4d**α as a colorless oil.

β-1′,2′-Dideoxy-3′,5′-di-*O*-toluoyl-1′-(3-biphenyl)ribofuranose (4dβ). HRMS(ESI): *m*/*z* $C_{33}H_{30}O_5Na^+$ calcd 529.1985 (M + Na^+), found 529.1985. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.3, 2H), 7.93 (d, *J* = 7.9, 2H), 7.64 (s, 1H), 7.54−7.47 (m, 3H), 7.40−7.31 (m, 5H), 7.27 (d, *J* = 8.0, 2H), 7.15 (d, *J* = 7.9, 2H), 5.64 (d, *J* = 5.7, 1H, H3′), 5.32 (dd, $J_{H1',H2'\beta}$ = 11.1, $J_{H1',H2'\alpha}$ = 5.1, 1H, H1′), 4.74 −4.64 (m, 2H, H5′), 4.58 −4.54 (m, 1H, H4′), 2.58 (dd, $J_{H2'\alpha,H2'\beta}$ = 13.9, $J_{H1',H2'\alpha}$ = 4.9, 1H, H2′α), 2.44 (s, 3H), 2.37 (s, 3H), 2.30 (ddd, $J_{H2'\beta,H2'\alpha}$ = 13.9, $J_{H1',H2'\beta}$ = 11.3, $J_{H3',H2'\beta}$ = 6.0, 1H, H2′β). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.4, 166.2, 144.2, 143.8, 141.6, 141.2, 140.9, 129.8, 129.7, 129.2, 129.2, 129.0, 128.7, 127.3, 127.2, 127.0, 126.8, 125.0, 124.7, 83.2, 81.0, 77.4, 64.8, 42.0, 21.8, 21.7.

β-1′,2′-Dideoxy-3′,5′-ditoluoyl-1′-(1-phenanthrenyl)ribofuranose (4eβ). Epimerization of **4e**α/β (173 mg; 0.33 mmol) yielded 100 mg of **4d**β (58%) as a colorless foam and 49 mg of mixed fractions of **4e**α/β (28%). HRMS(EI): *m*/*z* $C_{35}H_{30}O_5^+$ calcd 530.2093 (M), found 530.2093. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.74−8.69 (m, 2H), 8.09 (d, *J* = 8.2, 2H), 8.00−7.90 (m, 5H), 7.80−7.62 (m, 4H), 7.34 (d, *J* = 7.9, 2H), 7.22 (d, *J* = 7.9, 2H), 6.07 (dd, $J_{H1',H2'\beta}$ = 10.7 Hz, $J_{H1',H2'\alpha}$ = 5.1 Hz, 1H), 5.73−5.71 (m, 1H, H3′), 4.80−4.78 (m, 2H, H5′), 4.72−4.70 (m, 1H, H4′), 2.90−2.84 (m, 1H, H2′α), 2.49 (s, 3H), 2.41 (s, 3H), 2.40−2.32 (m, 1H, H2′β). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.4, 166.2, 144.2, 143.8, 137.2, 131.4, 130.6, 130.4, 129.8, 129.7, 129.1, 128.7, 128.5, 127.2, 127.1, 127.0, 126.8, 126.6, 126.4, 123.0, 122.9, 122.4, 121.5, 82.7, 78.0, 77.2, 64.7, 41.0, 21.7, 21.6.

β-1″,2″-Dideoxy-3″,5″-ditoluoyl-1″-(*R*,*S*-[1,1′]binaphthylen-4-yl)ribofuranose (4fβ). Epimerization of **4f**α/β (220 mg; 0.36 mmol) yielded 105 mg of **4f**β (47%) as a colorless foam and 69 mg of of **2f**α (32%). HRMS(EI): *m*/*z* $C_{41}H_{34}O_5^+$ calcd 606.2406 (M), found 606.2403. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.15−7.18 (m, 21H), 6. 10 (dd, $J_{H1',H2'\alpha}$ = 10.2, $J_{H1',H2'\beta}$ = 4.8, 1H, H1′), 5.76−5.72 (m, 1H, H3′), 4.81−4.70 (m, 3H, H5′, H4′), 2.95−2.88 (m, 1H, H2′α), 2.46 (s, 3H), 2.56−2.44 (m, 1H, H2′β), 2.40 (s, 1.6H), 2.36 (s, 1.4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5, 166.3, 144.3, 143.9, 143.8, 138.4, 136.3, 136.3, 133.5, 133.0, 133.0, 132.9, 132.9, 130.5, 129.8, 129.8, 129.3, 129.2, 129.2, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.7, 127.5, 127.1, 127.0, 126.6, 126.6, 126.0, 125.9, 125.9, 125.8, 125.7, 125.4, 125.3, 123.2, 123.1, 122.0, 121.9, 82.7, 82.7, 78.2, 78.0, 64.7, 40.9, 40.8, 21.8, 21.7, 21.7.

β-1′,2′-Dideoxy-3′,5′-ditoluoyl-1′-(2-(7-phenyl)naphthyl)ribofuranose (4gβ). Epimerization of **4g**α/β (129 mg; 0.23 mmol) yielded 59 mg of **4g**β (46%) as a colorless foam and 15 mg of mixed fractions of **4g**α/β (12%). HRMS(EI): *m*/*z* $C_{37}H_{32}O_5^+$ calcd 556.2250 (M), found 556.2251. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.55 (s, 1H), 8.48 (s, 1H), 8.10 (d, *J* = 8.2, 2H), 8.04−7.95 (m, 5H), 7.80 (d, *J* = 6.9, 1H), 7.51−7.42 (m, 3H), 7.35 (d, *J* = 8.1, 2H), 7.21 (d, *J* = 8.1, 2H), 5.71 (d, 1H, *J* = 6.2, H3′), 5.47 (dd, $J_{H1',H2'\alpha}$ = 10.8, $J_{H1',H2'\beta}$ = 5.8, 1H, H1′), 4.84−4.67 (m, 2H, H5′), 4.65 (td, 1H, $J_{H4',H5'}$ = 3.6, $J_{H3',H4'}$ = 1.9, H4′), 2.65 (dd, $J_{H2'\alpha,H2'\beta}$ = 13.7, $J_{H1',H2'\alpha}$ = 5.2, $J_{H3',H2'\alpha}$ = 0.8, 1H, H2′α), 2.48 (s, 3H), 2.37 (s, 3H), 2.44−2.34 (m, 1H, H2′β). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5, 166.2, 144.2, 143.9, 141.0, 138.8, 138.8, 133.6, 132.3, 129.8, 129.8, 129.3, 128.9, 128.2, 128.1, 127.4, 127.1, 127.0, 125.9, 125.7, 125.1, 124.0, 83.2, 81.0, 77.4, 64.8, 42.0, 21.8, 21.6.

β-1′,2′-Dideoxy-3′,5′-di-*O*-toluoyl-1′-(3-tolyl)ribofuranose (4bβ). Epimerization of **4g**α/β (635 mg; 1.43 mmol) yielded 333 mg of **4g**β (52%) as a colorless foam and 128 mg of of **4g**α (20%). HRMS(ESI): *m*/*z* $C_{28}H_{28}O_5^+$ calcd 444.1937 (M), found 444.1936. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03−7.97 (m, 4H), 7.32−7.22 (m, 7H), 7.13−7.10 (m, 1H), 5.64 (d, 1H, *J* = 5.0, H3′, 1H), 5.24 (dd, $J_{H1',H2'\beta}$ = 11.1, $J_{H1',H2'\alpha}$ = 5.0, 1H, H1′), 4.64−4.54 (m, 2H, H5′), 4.45 (td, 1H, $J_{H4',H5'}$ = 3.7, $J_{H3',H4'}$ = 1.9, H4′), 2.36 (s, 3H), 2.32 (s, 3H), 2.46 (ddd, $J_{H2'\alpha,H2'\beta}$ = 13.8, $J_{H1',H2'\alpha}$ = 5.1, $J_{H3',H2'\alpha}$ = 0.9, 1H, H2′α), 2.20 (s, 3H), 2.22−2.15 (m, 1H, H2′β). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.4, 166.2, 144.1, 143.8, 140.6, 138.2, 129.8, 129.2, 129.2, 128.7, 128.4, 127.9, 127.1, 126.6, 123.1, 83.0, 81.0, 77.4, 64.8, 41.9, 21.7, 21.6, 21.4.

β-1′,2′-Dideoxy-3′,5′-di-O-toluoyl-1′-(2-anthracenyl)ribofuranose (4hβ). Epimerization of **4h**α (574 mg; 1.08 mmol) yielded 161 mg of **4h**β (28%) as a colorless foam and 283 mg of of **4h**α (49%). HRMS(EI): *m*/*z* $C_{35}H_{30}O_5^+$ calcd 530.2093 (M + Na^+), found 530.2093. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.39 (s, 1H), 8.30 (s, 1H), 8.04−7.95 (m, 8H), 7.49−7.44 (m, 3H), 7.30 (d, *J* = 8.0, 2H), 7.19 (d, *J* = 8.0, 2H), 5.69 (d, *J* = 6.2, 1H, H3′), 5.46 (dd, $J_{H1',H2'\alpha}$ = 10.7, $J_{H1',H2'\beta}$ = 5.2, 1H, H1′), 4.80−4.63 (m, 2H, H5′), 4.63 (td, $J_{H4',H5'}$ = 3.9, $J_{H3',H4'}$ = 2.1, 1H, H4′), 2.64 (ddd, $J_{H2'\alpha,H2'\beta}$ = 13.7, $J_{H1',H2'\alpha}$ = 5.2, $J_{H3',H2'\alpha}$ = 0.8, 1H, H2′α), 2.45 (s, 3H), 2.37 (s, 3H), 2.43−2.35 (m, 1H, H2′β). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5, 166.3, 144.2, 143.8, 136.6, 131.9, 131.6, 131.3, 129.8, 129.8, 129.3, 129.2, 128.5, 128.4, 127.9, 127.2, 125.6, 125.0, 121.7, 82.6, 78.0, 77.1, 64.7, 40.7, 21.7, 21.7.

General Deprotection Procedure: Synthesis of 2d. The bistoluoylated nucleoside **4d**β (312 mg; 0.45 mmol) was dissolved in 5 mL of dry methanol. Sodium methoxide (79 mg; 1.4 mmol) was subsequently added. The solution was stirred at room temperature for 4 h. For neutralization solid ammonium chloride was added until the reaction mixture was weakly basic. The mixture was poured into water and extracted with 20 mL ethyl acetate (3×). The combined organic layers were dried over anhydrous $MgSO_4$ and evaporated. The product was purified on silica gel flash chromatography with CH_2Cl_2:MeOH(0−3%) as eluent to yield 116 mg (70%) of deprotected product **2d** as a colorless oil.

β-1′,2′-Dideoxy-1′-(3-biphenyl)ribofuranose (2d). HRMS-(ESI): *m*/*z* $C_{17}H_{18}O_3Na^+$ calcd 293.1148 (M + Na^+), found 293.1151. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59−7.29 (m, 9H), 5.22 (dd, $J_{H1',H2'\beta}$ = 10.2, $J_{H1',H2'\alpha}$ = 5.7, 1H, H1′), 4.38 (ddd, 1H, $J_{H3',H2'\beta}$ = 6.4, $J_{H3',H4'}$ = 2.4, $J_{H3',H2'\alpha}$ = 2.4, H3′, 1H), 4.02 (td, 1H, $J_{H4',H5'}$ = 4.9, $J_{H3',H4'}$ = 3.0, H4′), 3.74 (m, 2H, H5′), 2.95 (br, 2H, −OH), 2.26 (ddd, $J_{H2'\alpha,H2'\beta}$ = 13.2, $J_{H1',H2'\alpha}$ = 5.7, $J_{H3',H2'\alpha}$ = 2.1, 1H, H2′α), 2.03 (ddd, $J_{H2'\alpha,H2'\beta}$ = 13.2, $J_{H1',H2'\beta}$ = 10.2, $J_{H3',H2'\beta}$ = 6.3, 1H, H2′β). ^{13}C NMR: (75 MHz, $CDCl_3$): δ 141.7, 141.5, 140.1, 129.0, 128.8, 127.4, 127.2, 126.7, 125.0, 87.4, 80.2, 73.6, 63.4, 43.7.

β-1′,2′-Dideoxy-1′-(3-tolyl)ribofuranose (2b). Compound **4b**β (333 mg; 0.75 mmol) was deprotected to yield **2b** (143 mg; 92%) as a colorless oil. HRMS(EI): *m*/*z* $C_{12}H_{15}O_3^+$ calcd 207.1018 (M), found 207.1018. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28−7.10 (m, 4H), 5.13 (dd, $J_{H1',H2'\beta}$ = 10.2, $J_{H1',H2'\alpha}$ = 5.6, 1H, H1′), 4.38 (ddd, 1H, $J_{H3',H2'\beta}$ = 6.4, $J_{H3',H4'}$ = 2.2, $J_{H3',H2'\alpha}$ = 2.2, H3′, 1H), 4.00 (td, 1H, $J_{H4',H5'}$ = 4.8, $J_{H3',H4'}$ = 3.0, H4′), 3.80−3.70 (m, 2H, H5′), 3.05 (br, 1H, −OH), 2.83 (br, 1H, −OH), 2.40 (s, 3H), 2.23 (ddd, $J_{H2'\alpha,H2'\beta}$ =13.3, $J_{H1',H2'\alpha}$ = 5.7, $J_{H3',H2'\alpha}$ = 2.0, 1H, H2′α), 2.02 (ddd, $J_{H2'\alpha,H2'\beta}$ =13.3, $J_{H1',H2'\beta}$ = 10.2, $J_{H3',H2'\beta}$ = 6.3, 1H, H2′β). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.0, 138.2, 128.6, 128.4, 126.8, 123.1, 87.3, 80.2, 73.6, 63.4, 43.6, 21.4.

β-1′,2′-Dideoxy-1′-(2-biphenyl)ribofuranose (2cβ). Compound **4c** (490 mg; 0.97 mmol) was deprotected to yield **2c**α**β** (211 mg; 81%) as a colorless oil. Separation with preparative HPLC afforded **2c**α**β** (100 mg) and **2c**α**β** (80 mg). HPLC: t_r = 23.2 min. HRMS-(ESI): *m*/*z* $C_{17}H_{18}O_3Na^+$ calcd 293.1148 (M + Na^+), found 293.1150. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 (dd, *J* = 6.2, 0.8, 1H), 7.38−7.19 (m, 9H), 5.13 (dd, $J_{H1',H2'\beta}$ = 8.0, $J_{H1',H2'\alpha}$ = 8.0, 1H, H1′), 4.21 (ddd, 1H, $J_{H3',H2'\beta}$= 4.4, $J_{H3',H2'\alpha}$ = 4.4, $J_{H3',H4'}$ = 4.0, H3′, 1H), 3.72 (td, 1H, $J_{H4',H5'}$ = 4.0, $J_{H3',H4'}$ = 4.0, H4′), 3.68−3.58 (m, 2H, H5′), 2.78 (br, 2H, −OH), 1.95−1.92 (m, 2H, H2′). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.2, 140.7, 138.6, 130.0, 129.2, 128.1, 127.8, 127.4, 127.2, 125.8, 86.6, 76.9, 73.4, 63.1, 44.0.

α-1′,2′-Dideoxy-1′-(*2*-biphenyl)ribofuranose (2cα). HPLC: t_r = 24.3 min. HRMS(ESI): *m*/*z* $C_{17}H_{18}O_3Na^+$ calcd 293.1148 (M + Na^+), found 293.1149. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 (dd, *J* = 6.2, 0.8, 1H), 7.39−7.16 (m, 8H), 5.01 (dd, *J* = 9.2, 6.4, 1H, H1′), 4.20 (ddd, 1H, *J* = 7.2, 7.2, 7.2, H3′, 1H), 3.98 (td, 1H, $J_{H4',H5'}$ = 4.4, $J_{H3',H4'}$ = 6.4, H4′), 3.66−3.52 (m, 2H, H5′), 2.60 (br, 2H, −OH), 2.36 (ddd, $J_{H2'\alpha,H2'\beta}$ =13.2, $J_{H1',H2'\alpha}$ = 6.5, $J_{H3',H2'\alpha}$ = 6.5, 1H, H2′α), 1.90 (ddd, $J_{H2'\alpha,H2'\beta}$ =12.4, $J_{H1',H2'\beta}$ = 9.6, $J_{H3',H2'\beta}$ = 8.0, 1H, H2′β). ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.8, 140.7, 139.9, 129.9, 129.2, 128.1, 127.9, 127.2, 127.1, 125.6, 84.9, 76.5, 72.6, 62.2, 43.6.

β-1′,2′-Dideoxy-1′-(1-phenanthrenyl)ribofuranose (2e). Compound **4e**β (224 mg; 0.42 mmol) was deprotected to yield **2e** (93 mg; 79%) as a colorless solid. Mp 163−165 °C. HRMS(ESI): *m*/*z* $C_{19}H_{18}O_3Na^+$ calcd 317.1144 (M + Na^+), found 317.1148. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.84 (d, *J* = 7.8, 1H), 8.78 (d, *J* = 8.3, 1H), 8.02−7.98 (m, 2H), 7.90 (d, *J* = 7.6, 1H), 7.87 (d, *J* = 5.7, 1H), 7.73−7.63 (m, 3H), 5.82 (dd, $J_{H1',H2'\beta}$ = 10.1, $J_{H1',H2'\alpha}$ = 5.5, 1H, H1′), 5.20 (d, *J* = 4.3, 1H, OH), 4.85 (t, *J* = 5.6, 1H, OH), 4.25 (m, 1H, H3′), 3.93 (td, 1H, $J_{H4',H5'}$ = 5.1, $J_{H3',H4'}$ = 2.6, H4′), 3.58 (m, 2H, H5′), 2.39 (ddd, $J_{H2'\alpha,H2'\beta}$ =12.7, $J_{H1',H2'\alpha}$ = 5.6, $J_{H3',H2'\alpha}$ = 1.9, 1H, H2′α), 2.11 (ddd, $J_{H2'\alpha,H2'\beta}$ =12.7, $J_{H1',H2'\beta}$ = 10.2, $J_{H3',H2'\beta}$ = 5.9, 1H, H2′β). ^{13}C NMR (75 MHz, DMSO-d_6): δ 139.7, 131.5, 130.5, 130.2, 128.8, 127.4, 127.3, 126.9, 123.6, 122.5, 122.4, 88.0, 76.6, 72.8, 62.8, 43.3.

β-1″,2″-Dideoxy-1″-(R,S-[1,1′]binaphthylen-4-yl)ribofuranose (2f). Compound **4f**β (173 mg; 0.34 mmol) was deprotected to yield **2f** (73 mg; 70%) as a white solid. Mp 164−166 °C. HRMS-(EI): *m*/*z* $C_{25}H_{22}O_3^+$ calcd 370.1568 (M), found 370.1568. ^{1}H NMR (300 MHz, MeOH-d_4): δ 8.11 (d, *J* = 8.4, 1H), 7.89−7.81 (m, 3H), 7.52−7.32 (m, 5H), 7.89−7.81 (m, 3H), 7.24−7.13 (m, 4H), 5.97−5.91 (m, 1H, H1″), 4.39−4.34 (ddd, *J* = 4.7, 4.7, 2.3, 1H, H3″), 4.08−4.04 (ddd, *J* = 5.2, 5.1, 2.9, 1H, H4″), 3.79−3.68 (m, 2H, H5″), 2.56−2.47 (m, 1H, H2″), 2.10−1.97 (m, 1H, H2″). ^{13}C NMR (75 MHz, MeOH-d_4): δ 139.9, 139.4, 139.1, 135.1, 134.2, 132.0, 129.3, 129.0, 128.9, 128.8, 128.5, 128.2, 127.4, 127.0, 126.9, 126.6, 126.4, 124.6, 122.8, 88.9, 78.3, 78.3, 74.4, 64.1, 44.1, 44.1.

β-1′,2′-Dideoxy-1′-(2-(7-phenyl)naphthyl)ribofuranose (2g). Compound **4g**β (190 mg, 0.34 mmol) was deprotected to yield **2g** (101 mg; 92%) as a white solid. Mp 125−127 °C. HRMS(ESI): *m*/*z* $C_{21}H_{20}O_3Na^+$ calcd 343.1305 (M + Na^+), found 343.1307. ^{1}H NMR (300 MHz, MeOH-d_4): δ 8.06 (s,1H), 7.94 (s,1H), 7.90 (d, *J* = 8.5, 1H), 7.85 (d, *J* = 8.4, 1H), 7.76−7.71 (m, 3H), 7.54−7.33 (m, 4H), 5.31 (dd, $J_{H1',H2'\beta}$ = 10.5, $J_{H1',H2'\alpha}$ = 5.4, 1H, H1′), 4.43 (m, H3′, 1H), 4.03 (td, 1H, $J_{H4',H5'}$ = 5.0, $J_{H3',H4'}$ = 2.4, H4′), 3.74 (m, 2H, H5′), 2.29 (dd, $J_{H2'\alpha,H2'\beta}$ = 13.1, $J_{H1',H2'\alpha}$ = 5.7, 1H, H2′α), 2.06 (ddd, $J_{H2'\alpha,H2'\beta}$ =12.9, $J_{H1',H2'\beta}$ = 10.6, $J_{H3',H2'\beta}$ = 6.1, 1H, H2′β). ^{13}C NMR (75 MHz, MeOH-d_4): δ 142.5, 141.3, 140.1, 135.1, 133.8, 130.0, 129.4, 128.9, 128.5, 128.4, 126.7, 126.5, 126.3, 125.5, 89.4, 81.9, 74.6, 64.2, 45.0.

β-1′,2′-Dideoxy-1′-(2-anthracenyl)ribofuranose (2h).[14] Compound **4h**β (316 mg; 0.57 mmol) was deprotected to yield **2h** (99 mg; 57%) as a yellow solid. Mp >170 °C dec. HRMS(EI): *m*/*z* $C_{19}H_{18}O_3^+$ calcd 294.1256 (M + Na^+), found 294.1256. ^{1}H NMR (300 MHz, $CDCl_3$/MeOH 3:1): δ 8.32 (s, 2H, 7.93−7.89 (m, 4H), 7.40−7.35 (m, 3H), 5.28 (dd, $J_{H1',H2'\beta}$ = 10.2, $J_{H1',H2'\alpha}$ = 5.6, 1H, H1′), 4.33 (ddd, 1H, $J_{H3',H2'\beta}$ = 5.5, $J_{H3',H4'}$ = 2.2, $J_{H3',H2'\alpha}$ = 2.2, H3′, 1H), 3.98 (td, 1H, $J_{H4',H5'}$ = 5.1, $J_{H3',H4'}$ = 2.8, H4′), 3.70 (m, 2H, H5′), 2.25 (ddd, $J_{H2'\alpha,H2'\beta}$ = 13.2, $J_{H1',H2'\alpha}$ = 5.7, $J_{H3',H2'\alpha}$ = 1.9, 1H, H2′α), 2.11 (ddd, $J_{H2'\alpha,\ H2'\beta}$ = 13.2, $J_{H1',H2'\beta}$ = 10.3, $J_{H3',H2'\beta}$ = 6.2, 1H, H2′β). ^{13}C NMR (75 MHz, $CDCl_3$/MeOH 6:1): δ 137.8, 131.6, 131.4, 131.0, 131.0, 128.3, 127.8, 127.7, 125.9, 125.7, 125.1, 125.0, 124.5, 123.5, 87.4, 80.2, 72.8, 62.7, 42.8.

Procedure for Gilman-Cuprate Mediated Synthesis of *O*-Aryl-glycosides: Synthesis of 5bα**β.** In a dry argon-flushed flask 2-iodoanthracene (240 mg; 0.79 mmol) was added to 10 mL of dry THF and the mixture was cooled to −78 °C. With use of a glass syringe, *t*-BuLi in pentane (1.05 mL; 1.5 M; 1.58 mmol) was added dropwise and the solution was stirred for 15 min. After addition of copper iodide (75 mg; 2.95 mmol) the solution was allowed to warm up while the CuI dissolved. After cooling to −40 °C **1** (730 mg; 1.87 mmol) was subsequently added. The argon was removed at reduced pressure and the flask was filled with air. The mixture was stirred for 18 h. For workup a 10% aqueous solution of NH_4Cl was added followed by extraction with 20 mL of CH_2Cl_2 (3×). The combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$ (3×) and brine and dried over anhydrous $MgSO_4$ and solvent was removed under reduced pressure. The product was purified on a silica gel column with cyclohexane:ethyl acetate (19:1) to yield 86 mg (64%) of **5b**α as a colorless oil and 22 mg (16%) of **5b**β as a colorless oil.

α-1′,2′-Dideoxy-1′-(2-anthracenyloxy)ribofuranose (5bα). HRMS(ESI): *m*/*z* $C_{35}H_{30}O_6Na^+$ calcd 569.1935 (M + Na^+), found 569.1935. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.38 (s, 1H), 8.33 (s, 1H), 8.06 (d, *J* = 8.2, 2H), 8.01−7.93 (m, 5H), 7.60 (d, *J* = 2.3, 1H), 7.50−7.40 (m, 2H), 7.33−7.22 (m, 6H), 6.22 (d, *J* = 4.7, 1H, H1′), 5.65 (ddd, *J* = 7.4, 2.9, 1.8, 1H, H3′), 4.80 (td, 1H, *J* = 6.9, 3.6, H4′), 4.73−4.61 (m, 2H, H5′), 2.81 (ddd, *J* = 14.4, 7.4, 5.2, 1H, H2′β), 2.67 (d, *J* = 14.7, 1H, H2′α), 2.47 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5, 166.3, 154.1, 144.1, 144.0, 132.5, 132.1, 130.6, 129.9, 129.9, 129.7, 129.2, 128.6, 128.2, 127.7, 127.0, 126.1, 125.5, 124.8, 124.8, 124.6, 120.7, 102.2, 82.7, 74.6, 64.3, 39.6, 21.7, 21.7.

β-1′,2′-Dideoxy-1′-(2-anthracenyloxy)ribofuranose (5bβ). HRMS(ESI): *m*/*z* $C_{35}H_{30}O_6Na^+$ calcd 569.1935 (M + Na^+), found 569.1934. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.34 (s, 1H), 8.28 (s, 1H), 8.01−7.82 (m, 6H), 7.58 (d, *J* = 2.3, 1H), 7.49−7.41 (m, 2H), 7.31−7.20 (m, 3H), 7.15 (dd, *J* = 9.1, 2.4, 1H), 7.06 (d, *J* = 7.9, 2H), 6.24 (dd, $J_{H1',H2'\alpha}$ = 5.6, $J_{H1',H2'\beta}$ = 2.5, 1H, H1′), 5.69 (ddd, *J* = 7.2, 4.5, 3.0, 1H, H3′), 4.75 (td, $J_{H4',H5'}$ = 5.6, $J_{H3',H4'}$ = 3.0, 1H, H4′), 4.67−4.50 (m, 2H, H5′), 2.98 (ddd, *J* = 14.4, 7.1, 2.5, 1H, H2′), 2.43−2.35 (ddd, *J* = 14.4, 5.6, 4.7, 1H, H2′), 2.46 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.2, 166.2, 154.1, 144.2, 143.6, 132.4, 132.1, 130.6, 129.8, 129.7, 129.2, 128.9, 128.6, 128.2, 127.7, 126.9, 126.8, 126.0, 125.5, 124.8, 124.6, 120.5, 102.7, 82.7, 75.3, 64.5, 39.6, 21.7, 21.6.

α-1′,2′-Dideoxy-3′,5′-di-*O*-toluoyl-1′-(3-tolyloxy)ribofuranose (5aα). Compound **5a**α was synthesized from **1** (100 mg; 0.26 mmol) to afford **5a**α (77 mg; 62%) as a colorless oil. HRMS-(ESI): *m*/*z* $C_{28}H_{28}O_6Na^+$ calcd 483.1778 (M + Na^+), found 483.1778. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.4, 2H), 7.94 (d, *J* = 8.1, 2H), 7.30−7.18 (m, 5H), 6.92 (s, 1H, H2), 6.91 (d, 1H), 6.85 (d, 1H), 6.01 (d, *J* = 4.5, 1H, H1′), 5.60−5.56 (m, 1H, H3′), 4.72−4.69 (m, 1H, H4′), 4.62−4.59 (m, 2H, H5′), 2.96

(ddd, $J_{H2'\alpha,H2'\beta}$ = 14.1, $J_{H1',H2'\beta}$ = 7.0, $J_{H3',H2'\beta}$ = 7.0, 1H, H2′β), 2.54 (ddd, $J_{H2'\beta,H2'\alpha}$= 14.1, J = 0.9, 1H, H2′ α), 2.45 (s, 3H), 2.44 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.2, 166.1, 156.9, 144.1, 143.6, 139.4, 129.8, 129.8, 129.2, 129.0, 127.1, 126.8, 122.9, 117.4, 113.6, 102.3, 82.5, 77.5, 64.6, 39.5, 21.7, 21.7, 21.5.

β-1′,2′-Dideoxy-3′,5′-di-*O*-toluoyl-1′-(3-tolyloxy)ribofuranose (5aβ). Compound **5a**β was synthesized from **1** (100 mg; 0.26 mmol) to afford **5a**β (31 mg; 25%) as a colorless oil. HRMS(ESI): *m*/*z* $C_{28}H_{28}O_6Na^+$ calcd 483.1778 (M + Na^+), found 483.1778. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 8.3, 2H), 7.88 (d, J = 8.0, 2H), 7.22 (d, J = 8.0, 2H), 7.17−7.10 (m, 3H), 6.83 (s, 1H, H2), 6.82 (d, J = 8.0, 1H, H6), 6.78 (d, J = 7.2, 1H, H5), 5.98 (dd, $J_{H1',H2'\alpha}$ = 6.4, $J_{H1',H2'\beta}$ = 3.2, 1H, H1′), 5.70 (ddd, J = 7.2, 4.4, 3.2, 1H, H3′), 4.65−4.60 (m, 1H, H4′), 4.56−4.43 (m, 2H, H5′), 2.82 (dd, $J_{H2'\alpha,H2'\beta}$ = 14.4, J = 6.8, $J_{H1',H2'\beta}$ = 2.4, 1H, H2′β), 2.54 (ddd, $J_{H2'\beta,H2'\alpha}$ = 14.4, $J_{H1',H2'\alpha}$ = 5.6, J = 4.4, 1H, H2′α), 2.40 (s, 3H), 2.37 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 156.7, 139.9, 139.8, 139.6, 131.2, 131.1, 129.4, 129.3, 128.9, 128.6, 128.1, 123.0, 117.2, 113.6, 112.3, 102.1, 82.2, 75.0, 64.5, 39.4, 21.5, 21.5, 21.4.

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Supporting Information Available: General procedures and NMR spectra, including the ^{1}H−^{1}H NOESY spectra of compounds **2b**β, **2c**β, **2c**α, **4d**β, **4f**β, **2g**, **6a**β, and **6b**α. This material is available free of charge via the Internet at http://pubs.acs.org.

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