DOI: 10.1002/ejoc.201000726

Modular Synthesis of 5-Substituted Furan-2-yl *C*-2′-Deoxyribonucleosides and Biaryl Covalent Base-Pair Analogues

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Keywords: Alkylation / Cross-coupling / C-glycosides / DNA structures / Nucleosides

A modular and efficient synthesis of 5-(hetero)arylfuran *C*-2′-deoxyribonucleosides was developed. Friedel–Crafts C-glycosidation of 2-bromofuran with toluoyl-protected methyl 2′-deoxyribofuranoside in the presence of $BF_3{\cdot}Et_2O$ gave 5-bromofuran C-nucleosides, which were used as key intermediates for Stille or Suzuki coupling with (hetero)arylstannanes or boronic acids to afford a series of 5-(hetero)arylfuran C-nucleosides. 5-Boronofuran C-nucleoside was prepared by the Suzuki coupling of bromofuran with bis(pinacolatodiboron) or by Ir-catalyzed C–H borylation of furan and was used for cross-coupling with 5-bromoheteroaryl C-nucleosides to furnish novel covalent analogues of nucleoside pairs. The title 5-arylfuran C-nucleosides possess interesting fluorescence properties that may be applicable for fluorescent labeling of biomolecules.

Introduction

C-Nucleosides are an important nucleoside sub-class that are characterized by replacement of the nucleosidic bond by a chemically stable C–C bond.[1] They possess a wide range of biological activities and are extensively applied in chemical biology.[1] Some (hetero)aryl-*C*-2′-deoxyribonucleosides are promising candidates for the development of novel base-pairs in the quest to extend the genetic alphabet[2] due to formation of selective hydrophobic pairs in DNA duplexes.[3] Some of the artificial base-pairs have already been efficiently replicated by DNA polymerases[4] and the most successful pairs[5] were even used in the first successful PCR with a 6-letter genetic alphabet.[6] Biaryl C-nucleosides are of particular interest because of the extended stacking that occurs, which results in the formation of very stable duplexes.[7] A donor- and acceptor-modified biphenyl C-nucleoside-containing oligonucleotide was employed to recognize a complementary hydrophobic modification in the opposite strand or a bulge or single-strand region.[8] Oligonucleotide arrays of several α-aryl- or α-oligoaryl-*C*-deoxyribonucleoside units in a DNA-like chain were developed as "oligodeoxyfluorosides" (ODFs)[9] to tune the emission maxima of fluorescence depending on the sequence, and were successfully employed for fluorescence staining of cells and zebra fish embryos.[10]

Most of the current approaches[1,11] to the synthesis of *C*-nucleosides are not general and some suffer from low efficiency and stereoselectivity. Therefore, we have been developing a modular approach[12,13] based on the synthesis of halo(hetero)aryl-*C*-nucleoside intermediates and their subsequent functionalization by cross-coupling, amination and other reactions, to afford a series of derivatives from each intermediate. In our synthesis of aryl-thionyl-*C*-nucleosides, we found[13] that all of the products were fluorescent and that the emission maxima can be finely tuned by changing the attached aryl group. To further explore this type of fluorescent nucleoside, we decided to develop the synthesis and to study the properties of 5-aryl-substituted furan-*C*-2′-deoxyribonucleosides.

Furan-C-nucleosides of the *ribo* series were the focus of most of the previous studies. Furanfurin is an antitumor compound[14] and many other derivatives have been prepared, usually by Friedel–Crafts glycosidation of furan derivatives by peracetylated ribose in the presence of Lewis acids,[15,16] where some β-selectivity has been observed due to neighboring group participation, or alternatively by addition of lithiofuran to tribenzylribose followed by cyclization under Mitsunobu conditions.[17] Double arylation of the ribose moiety was observed as a side reaction in some Friedel–Crafts glycosidations of furans, causing dramatic decreases in yields.[16] Furan[18] and 5-methylfuran[19] *C*-2′-deoxyribonucleosides (the only two known examples in the 2′-deoxyribo series) were prepared by addition of lithiated furans to protected deoxyribose followed by cyclization. The latter derivative was used as a moderately successful candidate in an extension of the genetic alphabet.[19]

Results and Discussion

Our selected approach to the synthesis of a series of 5-substituted furan-2-yl-*C*-nucleosides was based on the syn-

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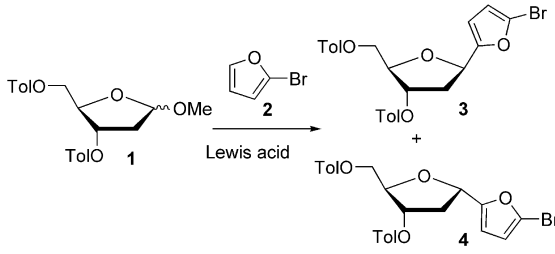
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201000726.

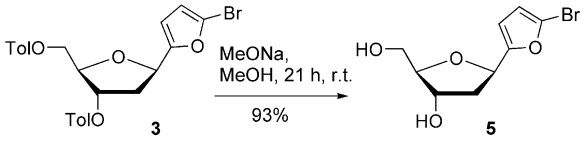
thesis of protected or unprotected 5-bromothiophen-2-yl-*C*-nucleoside key intermediates, followed by further synthetic transformations. Our previous synthesis[13] of a related 5-bromothiophen-2-yl-*C*-nucleoside intermediate involved the use of Friedel–Crafts type *C*-glycosidation of 2-bromothiophene with toluoyl-protected 2′-deoxyribose *O*-Me-glycoside (**1**), which gave the desired *C*-nucleoside very efficiently and with good β-selectivity (despite the use of an anomeric mixture of **1**). Therefore, we focused on analogous Friedel–Crafts reactions of 2-bromofuran (**2**) and applied the most efficient conditions developed from the previous work.[13] The reactions of toluoyl-protected glycoside **1** with bromofuran (**2**) were performed in the presence of a range of Lewis acids under different conditions (Scheme 1, Table 1). Reactions in the presence of $SnCl_4$ did not give any C-glycosidation, whereas when the same reaction was performed in the presence of $AgOCOCF_3$ as co-activator, complex mixtures of products with very low yields of the desired β- (**3**) and undesired α- (**4**) C-nucleoside anomers was generated (Table 1, entries 1–4). The use of TMSOTf gave similarly low yields (Table 1, entry 5). Furthermore, isolation of C-nucleosides and the separation of **3** and **4** by column chromatography was extremely difficult (large silica gel column and very slow elution with slow gradient of ethyl acetate in hexanes was necessary for efficient separation). Both bromofuran nucleosides **3** and **4** were found to be of limited stability in air and when exposed to light (both turned dark over several days) and therefore must be stored in a freezer under argon. We screened a wide range of Lewis acids ($ZnCl_2$, $AlCl_3$, $TiCl_4$, $SnCl_2$–$AgClO_4$, Cp_2ZrCl_2–$AgClO_4$, and Cp_2HfCl_2–$AgClO_4$) without any improvement in reactivity (data not shown).



Scheme 1. Preparation of the key intermediate by C-glycosidation of 2-bromofuran.

Finally, $BF_3{\cdot}Et_2O$ was found to be the best Lewis acid for this reaction. When the reaction was performed for 3 h, an encouraging increase in the yield of **3** to 13% (Table 1, entry 6) was observed; these conditions also somewhat suppressed formation of the α-anomer **4** (6%). Shortening of the reaction time to 15 min. (Table 1, entry 7) resulted in a dramatic increase in the yield, and gave the desired β-anomeric nucleoside **3** in 39% yield accompanied by only 17% formation of **4**. The use of $AgOCOCF_3$ as co-activator (Table 1, entry 7) did not bring about any improvement and, moreover, complicated the separation (Table 1, entry 8). Use of the pure β-anomer of **1** gave almost the same yield and selectivity as those obtained with the anomeric mixture (Table 1, entry 9), indicating that the configuration of the starting glycoside does not have any influence on the outcome of the reaction. The best procedure (Table 1, entry 10) involved the use of $BF_3{\cdot}Et_2O$ and a very short reaction time (5 min.), to afford the desired β-*C*-nucleoside **3** in good yield (45%) even when the reaction was performed on a multigram scale. When stored under argon at –10 °C, the compound was stable for several months. The undesired α-anomer **4** was epimerized by reaction with $BF_3{\cdot}Et_2O$ in dichloromethane at room temp. for 30 min, to give a mixture of **3** (70%) and **4** (30%). In this way, the total yield of the intermediate **3** can be increased to an acceptable 58%.

Deprotection of the toluoylated bromofuran-*C*-nucleoside intermediate **3** under Zemplén conditions (NaOMe/MeOH) gave the free 2′-deoxyribonucleoside **5**, which is a potential intermediate for aqueous-phase cross-coupling reactions, in 93% yield (Scheme 2).



Scheme 2. Deprotection of the nucleoside intermediate.

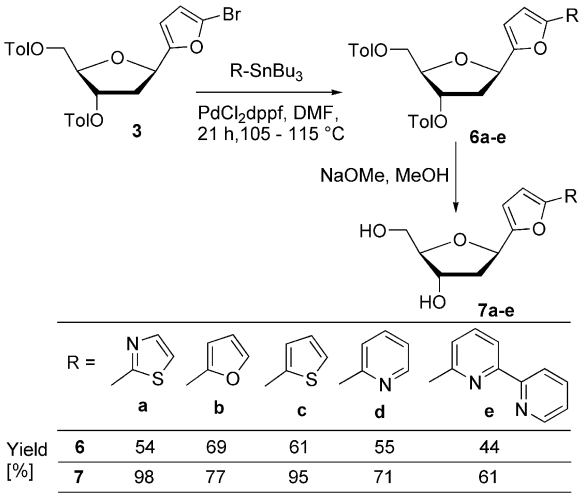
Having the optimized multigram-scale procedures for the synthesis of 5-bromofuran-2-yl-*C*-nucleosides **3** and **5** at hand, we then studied further functional group transformations. Initially, we introduced aryl and heteroaryl groups by using the Stille cross-coupling reactions of toluoyl-pro-

Table 1. Friedel–Crafts alkylation of methylglycoside **1** with 2-bromofuran (**2**).[a]

Entry	Lewis acid [equiv.]	Temp. [°C]	Time [min]	**3** [%]	**4** [%]
1	$SnCl_4$ (1)	room temp.	18	0	0
2	$SnCl_4$ (1)	0	13	0	0
3[b]	$SnCl_4$ (1.5), $AgOCOCF_3$ (0.6)	–20	30	2	2
4[b]	$SnCl_4$ (1.5), $AgOCOCF_3$ (0.6)	–20	10	9	4
5	TMSOTf (1)	room temp.	10	3	2
6	$BF_3{\cdot}Et_2O$ (3.8)	–30 to room temp.	3 h	13	6
7	$BF_3{\cdot}Et_2O$ (3.8)	room temp.	15	39	17
8	$BF_3{\cdot}Et_2O$ (3.8), $AgOCOCF_3$ (0.6)	room temp.	15	40	18
9[c]	$BF_3{\cdot}Et_2O$ (3.8)	room temp.	15	42	20
10	$BF_3{\cdot}Et_2O$ (3.8)	room temp.	5	45	18

[a] Unless otherwise stated, **2** (2 equiv.) and an anomeric mixture (ca. 1:1) of **1** were used in all experiments. [b] 2-Bromofuran (**2**; 3 equiv.) was used. [c] Pure β-anomer of methyl glycoside **1** was used.

tected β-C-deoxribonucleoside **3** with aryl stannanes. The reactions were performed in the presence of [$PdCl_2$dppf] in *N*,*N*-dimethylformamide (DMF) at 105–115 °C for 21 h. (Scheme 3). In all cases, the reactions proceeded smoothly to give the target protected biaryl β-C-nucleosides **6a**–**e** in acceptable yields of 54–69% (accompanied by some degradation products). Only the reaction of strongly chelating bipyridyl-stannane gave a lower yield of 44%, which was probably due to coordination of the Pd-catalyst. Deprotection of toluoylated nucleosides **6a**–**e** by using sodium methoxide in methanol gave the free β-biaryl C-deoxyribonucleosides **7a**–**e** in good yields (Scheme 3).

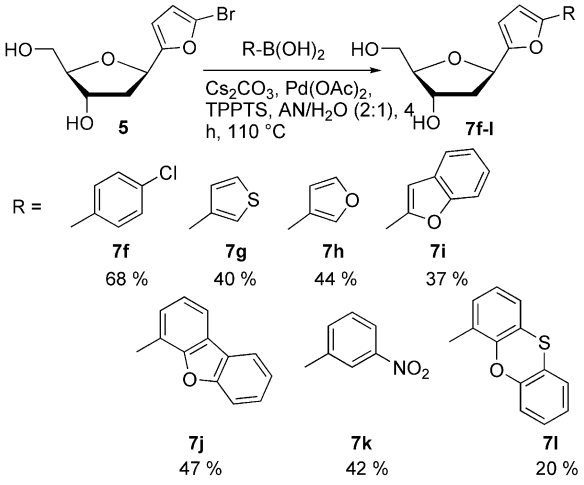


Yield [%]	**6**	54	69	61	55	44
	7	98	77	95	71	61

Scheme 3. The Stille cross-coupling and deprotection of 5-bromofuran-C-nucleoside.

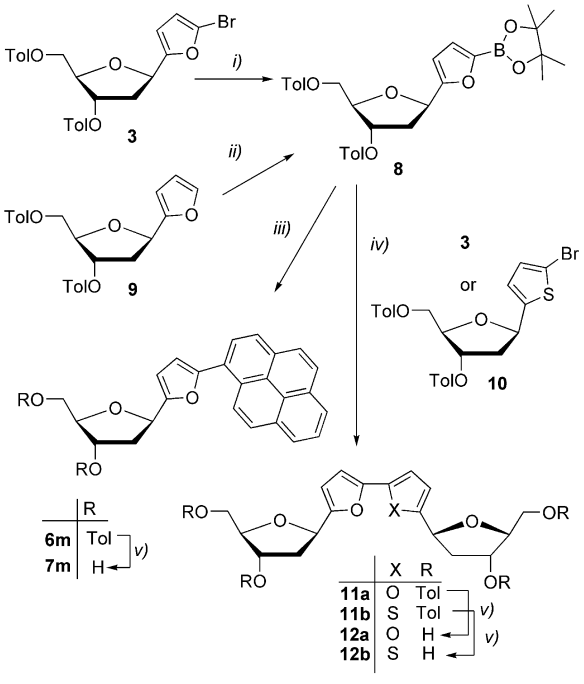
The unprotected 5-bromofuran-*C*-nucleoside **5** was used in aqueous-phase cross-coupling reactions. The Suzuki–Miyaura cross-coupling reactions of **5** with a variety of arylboronic acids were performed in the presence of Pd-$(OAc)_2$, sodium triphenylphosphane trisulfonate (TPPTS) ligand, and Cs_2CO_3 as base in a mixture of acetonitrile/water (2:1) for 4 h at 120 °C, to give biaryl β-*C*-nucleosides **7f**–**l** in moderate yields (Scheme 4). The yields were lowered by partial decomposition of the unstable starting compound **3** under the elevated temperature of the reaction. Despite the lower yields, this approach afforded the desired biaryl C-nucleosides in one step from the intermediate **5**, thus saving time and avoiding the need for an additional reaction and separation of the Stille coupling/deprotection products.

Further efforts focused on the transformation of bromofuran nucleoside **3** into the corresponding furylboronate derivative **8**, which could be a useful nucleophilic component for other cross-coupling reactions. The standard Miyaura reaction[20] of bromofuran with bis(pinacolato)diboron in the presence of [$PdCl_2$dppf] [dppf: 1,1′-bis(diphenylphosphanyl)ferrocene] and potassium acetate gave the desired boronate **8** in 68% yield, accompanied by minor side-products: debrominated nucleoside **9** (17%) and bis(furan) **11a** (traces) as a product of cross-coupling of **8** with **3**



Scheme 4. The Suzuki–Miyaura reaction of nucleoside **5**.

(Scheme 5). As an alternative, the boronate **8** was also prepared by an Ir-catalyzed C–H borylation[21] of the furan *C*-nucleoside **9** with [B_2pin_2] in the presence of [IrCl(COD)]$_2$ and 4,4′-di-*tert*-butyl-2,2′-bipyridyl (dtbpy) in 39% yield after two days reaction time. The conversion of this reaction was only ca. 80%, probably due to the limited solubility of the reaction components in toluene.



Scheme 5. *Reagents and conditions:* (i) **3** (1 equiv.), B_2pin_2 (4 equiv.), AcOK (6 equiv.), [$PdCl_2$dppf] (15%), dioxane, 105 °C, 70 min; yield of **8**: 68%. (ii) **9** (1 equiv.), B_2pin_2 (1.2 equiv.), [IrCl(COD)]$_2$ (5%), dtbpy (15%), toluene, 2 d, 105 °C; yield **8**: 39%. (iii) 1-bromopyrene (1.1 equiv.), [$Pd(PPh_3)_4$] (5%), K_2CO_3 (4 equiv.), DMF, 19 h, 105 °C. (iv) **3** or **10** (1.1 equiv.), **8** (1 equiv.), [$PdCl_2$dppf] (5%), K_2CO_3 (4 equiv.), DMF, 17 h, 105 °C. (v) MeONa (1 M in MeOH, 2 equiv.), room temp., 15 h. Yields: **6m**, 78%; **11a**, 90%; **11b**, 76%; **7m**, 53%; **12a**, 91%; **12b**, 71%.

The Suzuki–Miyaura reaction of boronofuran *C*-nucleoside **8** with 1-bromopyrene under the standard conditions in DMF in the presence of $[Pd(PPh_3)_4]$ and K_2CO_3 proceeded smoothly to give the pyrenyl-furan *C*-nucleoside in 78% yield. Its deprotection under the standard Zemplén conditions gave the free nucleoside **7m** in 53%. The reaction of boronate **8** with bromofuran *C*-nucleoside **3** was performed in DMF in the presence of $[PdCl_2dppf]$ and K_2CO_3 to give the 2,2′-bifuran bis-nucleoside **11a** in an excellent yield of 90%. Its standard deprotection gave the biaryl bis-nucleoside **12a** in 91% yield. An analogous hetero-cross-coupling of **8** with 5-bromothiophene *C*-nucleoside **10** also proceeded smoothly with almost quantitative conversion but gave the desired thienylfuran bis-nucleoside **11b** as a complex mixture with the corresponding bifuran **11a** (8%) and bithiophene **11c** (13%), resulting from homo-coupling of **8** and **10**. The composition of this inseparable mixture was determined from NMR analysis to be a 10:1:1.8 ratio of **11b/11a/11c** (yield of **11b**: 76%). The whole mixture was deprotected under standard conditions and the free nucleosides were successfully separated by column chromatography to give the desired thienylfuran bis-nucleoside **12b** in 54% overall yield (ca. 71% yield for deprotection and separation) from **8** (the minor bis-nucleoside byproducts were not isolated). The novel biaryl bis-nucleosides **12** are an interesting new type of covalently linked nucleoside-pair analogues[22] that could be used for construction of permanent cross-links in DNA duplexes. The crystal structure of symmetrical dimer **12a** was determined by X-ray diffraction analysis (Figure 1).

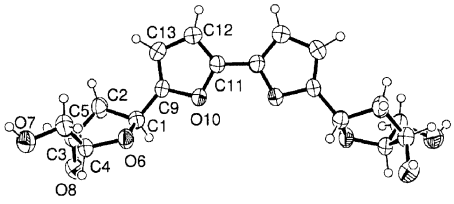


Figure 1. ORTEP drawing of **12a** with the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

UV/Vis and fluorescence spectroscopy was used to study all the title 5-arylfuran *C*-nucleosides **7a**–**m** and biaryl *C*-nucleoside dyads **12a** and **12b** (Table 2). The absorption maxima varied from 279 to 324 nm for most of the compounds, with the exception of the pyrenyl derivative **7m**, which exerted the longest wavelength maximum at 360 nm. All the compounds showed luminescence, with emission maxima varying from 324 to 411 nm. Similar to previous studies on substituted thiophene *C*-nucleosides,[13,23] the emission maxima could be finely tuned by changing the attached aryl groups. Pyridyl, benzofuryl and pyrenyl derivatives **7d**, **7i**, and **7m** showed high quantum yields of over 0.5, whereas the dibenzofuryl derivative **7j** exerted the brightest fluorescence, with a quantum yield of 0.96. In combination with other types of fluorescent nucleosides,[9,10,13,23] the title furan *C*-nucleosides clearly have the potential for applications in ODF arrays for fluorescent labeling of biomolecules.[9,10]

Table 2. UV/Vis and fluorescence spectroscopic data.

	Absorption λ_{max} [nm] (ε, $L\,mol^{-1}\,cm^{-1}$)	Emission λ_{max} [nm]	ϕ
7a	308 (20380)	362	0.03
7b	280 (21000), 286 (22200), 301 (13200)	324	0.18
7c	302 (19800)	351	0.06
7d	277 (14000), 304(18000)	360	0.55
7e	237 (22000), 279 (28000)	410	0.15
7f	290 (25600)	337	0.24
7g	229 (8200), 282 (11000)	341	0.03
7h	259 (12200), 264 (12400)	345	0.01
7i	307 (15400), 324 (11800)	330, 347	0.61
7j	254 (21200), 286 (18800), 328 (10200)	356	0.96
7k	273 (16000), 287 (16600)	342	0.01
7l	227 (9800), 288 (7600)	399	0.04
7m	232 (24400), 277 (15400), 360 (17000)	411	0.73
12a	286 (27000), 293 (28000), 308 (17800)	334	0.20
12b	310 (18800)	362	0.14

Conclusions

An efficient procedure for the synthesis of toluoyl-protected 5-bromofuran *C*-nucleoside **3** was developed based on Friedel–Crafts type C-glycosidation of 2-bromofuran with methyl glycoside **1** in the presence of $BF_3{\cdot}Et_2O$. A very short reaction time of 5 min was crucial to avoid side reactions. The separation of anomers **3** and **4** was quite difficult and required careful column chromatography using a very slow gradient of ethyl acetate in hexanes. The protected bromofuran nucleoside **3** was used directly for the Stille cross-couplings with (hetero)arylstannanes, whereas the unprotected nucleoside **5** was efficiently used for the Suzuki couplings with (hetero)arylboronic acids to afford a series of 5-(hetero)arylfuran *C*-nucleoside **7**. 5-Boronofuran *C*-nucleoside **8** was prepared for the first time either by the Suzuki coupling of bromofuran **3** with bis(pinacolatodiboron) or by Ir-catalyzed C–H borylation of furan **9**. The boronate **8** was used either for cross-coupling with aryl halides to make other arylfuran *C*-nucleosides, or with 5-bromoheteroaryl C-nucleosides to afford novel, interesting covalent analogues of nucleoside pairs **12a** and **12b**. Final 5-arylfuran *C*-nucleosides possess interesting fluorescence properties that may be applicable in the construction of ODF arrays for fluorescent labeling.

Experimental Section

General Methods: Melting points were determined with a Kofler block. Optical rotations, $[\alpha]_D$ were measured at 20 °C, values are given in units of $10^{-1}\,cm^2\,g^{-1}$. NMR spectra were measured at 500 MHz for ^1H and 125.8 MHz for ^{13}C; samples were recorded in $[D_6]$acetone for protected nucleosides and $[D_6]$DMSO for deprotected products (TMS was used as internal standard, referenced to the residual solvent signal). Chemical shifts are given in ppm (δ scale) and coupling constants (J) in Hz. Complete assignment of all NMR signals was performed by using a combination of H,H-COSY, H,H-ROESY, H,C-HSQC, and H,C-HMBC experiments. Mass spectra were measured by using ESI or EI (electron energy 70 eV). All solvents used for reactions were anhydrous, degassed in vacuo and stored over molecular sieves under an atmosphere of argon.

1β-(5-Bromofuran-2-yl)-1,2-dideoxy-3,5-di-*O*-toluoyl-D-ribofuranose (3): $BF_3{\cdot}Et_2O$ (3.7 mL, 29.7 mmol) was added dropwise by syringe to a dried flask covered with an aluminum foil containing methyl glycoside **1** (3 g, 7.8 mmol) and 2-bromofuran (**2**; 1.4 mL, 15.6 mmol) in anhydrous dichloromethane (50 mL) and the mixture was stirred for 5 min at room temp. The reaction was quenched by addition of satd. aqueous $NaHCO_3$ (40 mL) and the mixture was diluted with a satd. aqueous $NaHCO_3$ (100 mL), extracted with EtOAc (3×40 mL) and washed with satd. aqueous NaCl (100 mL). The collected organic layers were dried with Na_2SO_4 and the solvents were evaporated. Products were isolated by slow column chromatography on silica gel, eluent gradient from hexane to hexane/EtOAc (19.7:0.3) to give the desired product **3** (1.75 g, 45%) followed by the *α*-anomer **4** (0.7 g, 18%) as colorless oils. Compound **3**: HRMS (ESI): calcd. for $C_{25}H_{23}BrO_6Na$ [M + Na] 521.0570; found 521.0571. ^{1}H NMR (500 MHz, [D$_6$]acetone): δ = 2.41 and 2.42 (2×s, 2×3 H, CH_3-Tol), 2.68 (ddd, J_{gem} = 13.8, $J_{2'a,1'}$ = 5.4, $J_{2'a,3'}$ = 1.4 Hz, 1 H, 2′a-H), 2.68 (ddd, J_{gem} = 13.8, $J_{2'b,1'}$ = 10.7, $J_{2'b,3'}$ = 6.1 Hz, 1 H, 2′b-H), 4.48 (br. td, $J_{4',5'a}$ = $J_{4',5'b}$ = 4.2, $J_{4',3'}$ = 2.0 Hz, 1 H, 4′-H), 4.51 (dd, J_{gem} = 11.4, $J_{5'a,4'}$ = 4.3 Hz, 1 H, 5′a-H), 4.57 (dd, J_{gem} = 11.4, $J_{5'b,4'}$ = 4.0 Hz, 1 H, 5′b-H), 5.26 (dd, $J_{1',2b}$ = 10.7, $J_{1',2'a}$ = 5.4 Hz, 1 H, 1′-H), 5.65 (br. dtd, $J_{3',2'b}$ = 6.1, $J_{3',4'}$ = $J_{3',2'a}$ = 1.7, $J_{3',1'}$ = 0.4 Hz, 1 H, 3′-H), 6.44 (dd, $J_{4,3}$ = 3.3 Hz, 1 H, 4-H), 6.53 (dd, $J_{3,4}$ = 3.3, $J_{3,1'}$ = 0.4 Hz, 1 H, 3-H), 7.30–7.33 (m, 4 H, *o*-Tol-H), 7.96–8.02 (m, 4 H, *o*-Tol-H) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]acetone): δ = 21.58 (CH_3-Tol), 37.55 (CH_2-2′), 65.26 (CH_2-5′), 74.39 (CH-1′), 77.66 (CH-3′), 83.65 (CH-4′), 112.03 (CH-3), 113.17 (CH-4), 122.44 (C-5), 128.19 and 128.30 (C-*i*-Tol), 130.06 and 130.10 (CH-*o*-Tol), 130.47 (CH-*o*-Tol), 144.69 and 144.96 (C-*p*-Tol), 156.26 (C-2), 166.42 and 166.59 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 3390, 3304, 2893, 1501, 1131, 1045, 1032, 997, 792, 782 cm^{-1}. Compound **4**: HRMS (ESI): calcd. for $C_{25}H_{23}BrO_6Na$ [M + Na]: 521.0570; found 521.0572. ^{1}H NMR (500 MHz, [D$_6$]acetone): δ = 2.40 and 2.41 (2×s, 2×3 H, CH_3-Tol), 2.51 (ddd, J_{gem} = 14.0, $J_{2'a,1'}$ = 5.2, $J_{2'a,3'}$ = 3.4 Hz, 1 H, 2′a-H), 2.94 (ddd, J_{gem} = 14.0, $J_{2'b,1'}$ = 8.0, $J_{2'b,3'}$ = 7.1 Hz, 1 H, 2′b-H), 4.50–4.60 (m, 3 H, 4′,5′-H), 5.36 (ddd, $J_{1',2b}$ = 8.0, $J_{1',2'a}$ = 5.2, $J_{1',3}$ = 0.7 Hz, 1 H 1′-H), 5.64 (br. dt, $J_{3',2'b}$ = 7.0, $J_{3',4'}$ = $J_{3',2'a}$ = 3.3 Hz, 1 H, 3′-H), 6.45 (d, $J_{4,3}$ = 3.3 Hz, 1 H, 4-H), 6.52 (dd, $J_{3,4}$ = 3.3, $J_{3,1'}$ = 0.7 Hz, 1 H, 3-H), 7.32 and 7.33 (2×m, 2×2 H, *o*-Tol-H), 7.91 and 7.93 (2×m, 2×2 H, *o*-Tol-H) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]acetone): δ = 21.57 and 21.58 (CH_3-Tol), 37.10 (CH_2-2′), 65.19 (CH_2-5′), 74.41 (CH-1′), 76.83 (CH-3′), 82.87 (CH-4′), 111.22 (CH-3), 113.13 (CH-4), 122.03 (C-5), 128.12 and 128.24 (C-*i*-Tol), 130.04 and 130.09 (CH-*o*-Tol), 130.39 and 130.49 (CH-*o*-Tol), 144.75 and 144.90 (C-*p*-Tol), 157.87 (C-2), 166.49 and 166.59 (CO) ppm. IR (CCl_4): $\tilde{\nu}$ = 2925, 1726, 1613, 1268, 1178, 1106, 800 cm^{-1}.

General Procedure for the Stille Cross-Coupling Reaction: Heteroaryl(tributyl)stannane (1.2 equiv.) was added dropwise under argon to a stirred solution of **3** (1 equiv.) and [$PdCl_2$dppf] (10 mol.%) in DMF (10 mL). The mixture was stirred at 105–115 °C for 21 h. The crude reaction mixture was diluted with EtOAc (15 mL), filtered through Celite, and washed with 2 M HCl and brine. The aqueous layers were extracted with EtOAc (3×20 mL), the collected organic layers were dried with $MgSO_4$, and the solvents were evaporated under vacuum. The crude product was purified by chromatography on silica gel, eluent gradient from hexane to hexane/EtOAc (9.7:0.3).

1β-[5-(Thiazol-2-yl)furan-2-yl]-1,2-dideoxy-3,5-di-*O*-toluoyl-D-ribofuranose (6a): Prepared from **3** (271 mg, 0.54 mmol) and 2-(tributylstannyl)thiazole (210 μL, 0.65 mmol) by the general procedure (105 °C, 21 h). **6a** (273 mg, 54%) was obtained as a yellow oil. HRMS (ESI): calcd. for $C_{28}H_{25}O_6NSNa$ [M + Na] 526.1295; found 526.1293. ^{1}H NMR (500 MHz, [D$_6$]acetone): δ = 2.40 and 2.42 (2×s, 2×3 H, CH_3-Tol), 2.60 (ddd, J_{gem} = 13.7, $J_{2'a,1'}$ = 5.4, $J_{2'a,3'}$ = 1.4 Hz, 1 H, 2′a-H), 2.76 (ddd, J_{gem} = 13.7, $J_{2'b,1'}$ = 10.6, $J_{2'b,3'}$ = 6.0 Hz, 1 H, 2′b-H), 4.53 (ddd, $J_{4',5'b}$ = 4.7, $J_{4',5'a}$ = 4.2, $J_{4',3'}$ = 2.1 Hz, 1 H, 4′-H), 4.57 (dd, J_{gem} = 11.6, $J_{5'a,4'}$ = 4.1 Hz, 1 H, 5′a-H), 4.60 (dd, J_{gem} = 11.6, $J_{5'b,4'}$ = 4.8 Hz, 1 H, 5′b-H), 5.37 (dd, $J_{1',2b}$ = 10.6, $J_{1',2'a}$ = 5.4 Hz, 1 H, 1′-H), 5.72 (dddd, $J_{3',2'b}$ = 6.0, $J_{3',4'}$ = 2.0, $J_{3',2'a}$ = 1.4, $J_{3',1'}$ = 0.5 Hz, 1 H, 3′-H), 6.67 (br. d, $J_{3,4}$ = 3.4 Hz, 1 H, 3-H), 6.99 (d, $J_{4,3}$ = 3.4 Hz, 1 H, 4-H), 7.32 and 7.35 (2×m, 2×2 H, *o*-Tol-H), 7.59 (d, $J_{5,4}$ = 3.2 Hz, 1 H, thiazyl-5-H), 7.85 (d, $J_{4,5}$ = 3.2 Hz, 1 H, thiazyl-4-H), 7.98 and 8.00 (2×m, 2×2 H, *o*Tol-H) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]acetone): δ = 21.58 (CH_3-Tol), 37.83 (CH_2-2′), 65.22 (CH_2-5′), 74.43 (CH-1′), 77.60 (CH-3′), 83.69 (CH-4′), 109.96 (CH-4), 111.38 (CH-3), 119.66 (CH-5-thiazyl), 128.15 and 128.25 (C-*i*-Tol), 130.06 and 130.09 (CH-*o*-Tol), 130.44 and 130.47 (CH-*o*-Tol), 144.66 (CH-4-thiazyl), 144.70 and 144.95 (C-*p*-Tol), 150.01 (C-5), 155.38 (C-2), 158.22 (C-2-thiazyl), 166.43 and 166.56 (CO) ppm. IR (CCl_4): $\tilde{\nu}$ = 3039, 2982, 2925, 1726, 1613, 1443, 1268, 1178, 1103, 715 cm^{-1}.

1β-[5-(Furan-2-yl)furan-2-yl]-1,2-dideoxy-3,5-di-*O*-toluoyl-D-ribofuranose (6b): Compound **6b** was prepared from **3** (434 mg, 0.87 mmol) and 2-(tributylstannyl)furan (330 μL, 1.04 mmol), by the general procedure (115 °C, 21 h). **6b** was obtained (290 mg, 69%) as a colorless oil. HRMS (ESI): calcd. for $C_{29}H_{26}O_7Na$ [M + Na] 509.1571; found 509.1568. ^{1}H NMR (500 MHz, [D$_6$]acetone): δ = 2.41, 2.42 (2×s, 2×3 H, CH_3), 2.53 (ddd, J_{gem} = 13.8, $J_{2'a,1'}$ = 5.4, $J_{2'a,3'}$ = 1.3 Hz, 1 H, 2′a-H), 2.75 (ddd, J_{gem} = 13.8, $J_{2'b,1'}$ = 10.7, $J_{2'b,3'}$ = 6.0 Hz, 1 H, 2′b-H), 4.50 (td, $J_{4',5'a}$ = $J_{4',5'b}$ = 4.4, $J_{4',3'}$ = 2.0 Hz, 1 H, 4′-H), 4.54 (dd, J_{gem} = 11.6, $J_{5'a,4'}$ = 4.3 Hz, 1 H, 5′a-H), 4.60 (dd, J_{gem} = 11.6, $J_{5'b,4'}$ = 4.5 Hz, 1 H, 5′b-H), 5.32 (ddd, $J_{1',2b}$ = 10.7, $J_{1',2'a}$ = 5.4, $J_{1',3'}$ = 0.6 Hz, 1 H, 1′-H), 5.71 (dddd, $J_{3',2'b}$ = 6.0, $J_{3',4'}$ = 2.0, $J_{3',2'a}$ = 1.3, $J_{3',1'}$ = 0.6 Hz, 1 H, 3′-H), 6.46 (dd, $J_{6,7}$ = 3.4, $J_{6,8}$ = 0.8 Hz, 1 H, 6-H), 6.51 (dd, $J_{7,6}$ = 3.4, $J_{7,8}$ = 1.9 Hz, 1 H, 7-H), 6.57 (s, 2 H, 2-H, 3-H), 7.31–7.37 (m, 4 H, 4×3′′-H), 7.58 (dd, $J_{8,7}$ = 1.8, $J_{8,6}$ = 0.8 Hz, 1 H, 8-H), 7.97–8.01 (m, 4 H, 4×2′′-H) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]acetone): δ = 21.57 (2×CH_3), 37.72 (CH_2-2′), 65.26 (CH_2-5′), 74.50 (CH-1′), 77.72 (CH-3′), 83.55 (CH-4′), 106.29 (CH-6), 106.56 (CH-3), 110.87 (CH-2), 112.28 (CH-7), 128.18, 128.29 (2×C-1′′), 130.06, 130.09 (2×CH-3′′), 130.43, 130.46 (2×CH-2′′), 143.27 (CH-8), 144.72, 144.94 (2×C-4′′), 147.04 (C-4, C-5), 153.37 (C-1), 166.44, 166.54 (2×CO) ppm. IR (CCl_4): $\tilde{\nu}$ = 2925, 1725, 1613, 1269, 1178, 1103, 730 cm^{-1}.

1β-[5-(Thiophen-2-yl)furan-2-yl]-1,2-dideoxy-3,5-di-*O*-toluoyl-D-ribofuranose (6c): Prepared from **3** (358 mg, 0.72 mmol) and 2-(tributylstannyl)thiophene (270 μL, 0.86 mmol), by the general procedure (110 °C, 21 h). Compound **6c** (220 mg, 61%) was obtained as a colorless oil. HRMS (ESI): calcd. for $C_{29}H_{26}O_6SNa$ [M + Na] 525.1342; found 525.1340. ^{1}H NMR (500 MHz, [D$_6$]acetone): δ = 2.41 and 2.42 (2×s, 2×3 H, CH_3-Tol), 2.54 (ddd, J_{gem} = 13.7, $J_{2'a,1'}$ = 5.4, $J_{2'a,3'}$ = 1.3 Hz, 1 H, 2′a-H), 2.76 (ddd, J_{gem} = 13.7, $J_{2'b,1'}$ = 10.7, $J_{2'b,3'}$ = 6.0 Hz, 1 H, 2′b-H), 4.50 (td, $J_{4',5'a}$ = $J_{4',5'b}$ = 4.4, $J_{4',3'}$ = 2.0 Hz, 1 H, 4′-H), 4.54 (dd, J_{gem} = 11.6, $J_{5'a,4'}$ = 4.3 Hz, 1 H, 5′a-H), 4.61 (dd, J_{gem} = 11.6, $J_{5'b,4'}$ = 4.6 Hz, 1 H, 5′b-H), 5.32 (dd, $J_{1',2b}$ = 10.7, $J_{1',2'a}$ = 5.4 Hz, 1 H, 1′-H), 5.72 (dddd, $J_{3',2'b}$ = 6.0, $J_{3',4'}$ = 2.0, $J_{3',2'a}$ = 1.3, $J_{3',1'}$ = 0.6 Hz, 1 H, 3′-H), 6.55 (dd, $J_{3,4}$ = 3.4, $J_{3,1'}$ = 0.4 Hz, 1 H, 3-H), 6.60 (d, $J_{4,3}$ = 3.4 Hz, 1 H, 4-H), 7.05 (dd, $J_{4,5}$ = 5.1, $J_{4,3}$ = 3.6 Hz, 1 H, thienyl-4-H), 7.22 (br. dd, $J_{3,4}$ = 3.6, $J_{3,5}$ = 1.2 Hz, 1 H, thienyl-3-H), 7.33 and 7.36 (2×m, 2×2 H, *o*-Tol-H), 7.41 (dd, $J_{5,4}$ = 5.1, $J_{5,3}$ = 1.2 Hz, 1 H, thienyl-5-H), 7.97–8.01 (m, 4 H, *o*-Tol-H) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]acetone): δ = 21.58 (CH_3-Tol), 37.71 (CH_2-

2′), 65.25 (CH_2-5′), 74.50 (CH-1′), 77.69 (CH-3′), 83.54 (CH-4′), 106.55 (CH-4), 111.23 (CH-3), 123.81 (CH-3-thienyl), 125.55 (CH-5-thienyl), 128.20 and 128.30 (C-*i*-Tol), 128.63 (CH-4-thienyl), 130.06 and 130.10 (CH-*o*-Tol), 130.44 and 130.47 (CH-*o*-Tol), 134.11 (C-2-thienyl), 144.70 and 144.94 (C-*p*-Tol), 150.29 (C-5), 153.12 (C-2), 166.45 and 166.55 (CO) ppm. IR (CCl_4): $\tilde{\nu}$ = 2926, 1725, 1613, 1268, 1178, 1103, 1021, 693 cm^{-1}.

1β-[5-(Pyridin-2-yl)furan-2-yl]-1,2-dideoxy-3,5-di-*O*-toluoyl-D-ribofuranose (6d): Prepared from **3** (409 mg, 0.82 mmol) and 2-(tributylstannyl)pyridine (270 μL, 0.98 mmol), by the general procedure (115 °C, 21 h). **6d** (223 mg, 55%) was obtained as a yellow oil. HRMS (ESI): calcd. for $C_{30}H_{27}NO_6Na$ [M + Na] 520.1731; found 520.1727. ^{1}H NMR (500 MHz, [D$_6$]acetone): δ = 2.41 and 2.42 (2 × s, 2 × 3 H, CH_3-Tol), 2.57 (ddd, J_{gem} = 13.7, $J_{2'a,1'}$ = 5.4, $J_{2'a,3'}$ = 1.3 Hz, 1 H, 2′a-H), 2.82 (ddd, J_{gem} = 13.7, $J_{2'b,1'}$ = 10.7, $J_{2'b,3'}$ = 6.0 Hz, 1 H, 2′b-H), 4.52 (td, $J_{4',5'a}$ = $J_{4',5'b}$ = 4.2, $J_{4',3'}$ = 2.0 Hz, 1 H, 4′-H), 4.55 (dd, J_{gem} = 11.5, $J_{5'a,4'}$ = 4.2 Hz, 1 H, 5′a-H), 4.65 (dd, J_{gem} = 11.5, $J_{5'b,4'}$ = 4.3 Hz, 1 H, 5′b-H), 5.37 (dd, $J_{1',2b}$ = 10.7, $J_{1',2'a}$ = 5.4 Hz, 1 H, 1′-H), 5.74 (dddd, $J_{3',2'b}$ = 6.0, $J_{3',4'}$ = 2.0, $J_{3',2'a}$ = 1.3, $J_{3',1'}$ = 0.5 Hz, 1 H, 3′-H), 6.63 (dd, $J_{3,4}$ = 3.4, $J_{3,1'}$ = 0.4 Hz, 1 H, 3-H), 7.04 (d, $J_{4,3}$ = 3.4 Hz, 1 H, 4-H), 7.23 (ddd, $J_{5,4}$ = 7.5, $J_{5,6}$ = 4.8, $J_{5,3}$ = 1.2 Hz, 1 H, py-5-H), 7.34 and 7.36 (2 × m, 2 × 2 H, *o*-Tol-H), 7.56 (dt, $J_{3,4}$ = 8.0, $J_{3,5}$ = $J_{3,6}$ = 1.1 Hz, 1 H, py-3-H), 7.71 (ddd, $J_{4,3}$ = 8.0, $J_{4,5}$ = 7.6, $J_{4,6}$ = 1.8 Hz, 1 H, py-4-H), 7.98–8.03 (m, 4 H, *o*-Tol-H), 8.54 (ddd, $J_{6,5}$ = 4.8, $J_{6,4}$ = 1.8, $J_{6,3}$ = 1.0 Hz, 1 H, py-6-H) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]acetone): δ = 21.58 (CH_3-Tol), 37.84 (CH_2-2′), 65.26 (CH_2-5′), 74.66 (CH-1′), 77.75 (CH-3′), 83.61 (CH-4′), 109.96 (CH-4), 111.53 (CH-3), 118.85 (CH-3-py), 123.05 (CH-5-py), 128.19 and 128.29 (C-*i*-Tol), 130.07 and 130.12 (CH-*o*-Tol), 130.44 and 130.47 (CH-*o*-Tol), 137.53 (CH-4-py), 144.74 and 144.97 (C-*p*-Tol), 149.92 (C-2-py), 150.53 (CH-6-py), 154.66 and 154.74 (C-2,5), 166.48 and 166.55 (CO) ppm. IR (CCl_4): $\tilde{\nu}$ = 2925, 1725, 1613, 1269, 1178, 1103, 1021 cm^{-1}.

1β-[5-(2,2′-Bipyridin-6-yl)furan-2-yl]-1,2-dideoxy-3,5-di-*O*-toluoyl-D-ribofuranose (6e): *n*BuLi (1.75 mL, 1.6 M in hexane, 2.8 mmol) was added dropwise into a solution of 6-bromo-2,2′-bipyridine (460 mg, 1.96 mmol) in THF (15 mL) under argon at –72 °C during 5 min, and the mixture was stirred for 2 min followed by addition of Bu_3SnCl (530 μL, 1.96 mmol). After stirring for 20 min at –72 °C, the reaction was warmed to room temp., and the solvent was carefully evaporated under vacuum. The crude 6-(tributylstannyl)-2,2′-bipyridine was dissolved in DMF (5 mL) and added through septum to a flask containing **3** (700 mg, 1.4 mmol) and [$PdCl_2$dppf] (103 mg, 0.14 mmol) under argon. The reaction mixture was stirred at 100 °C for 21 h. Chromatography on silica gel, eluent gradient from hexane to hexane/EtOAc (9.7:0.3) gave **6e** (355 mg, 44%) as a yellow oil. HRMS (ESI): for $C_{35}H_{30}N_2O_6Na$ [M + Na] 597.1996; found 597.1993. ^{1}H NMR (500 MHz, [D$_6$]-acetone): δ = 2.41 and 2.43 (2 × s, 2 × 3 H, CH_3-Tol), 2.60 (ddd, J_{gem} = 13.7, $J_{2'a,1'}$ = 5.5, $J_{2'a,3'}$ = 1.5 Hz, 1 H, 2′a-H), 2.85 (ddd, J_{gem} = 13.7, $J_{2'b,1'}$ = 10.6, $J_{2'b,3'}$ = 6.0 Hz, 1 H, 2′b-H), 4.54 (td, $J_{4',5'a}$ = $J_{4',5'b}$ = 4.1, $J_{4',3'}$ = 2.0 Hz, 1 H, 4′-H), 4.57 (dd, J_{gem} = 11.3, $J_{5'a,4'}$ = 4.2 Hz, 1 H, 5′a-H), 4.68 (dd, J_{gem} = 11.3, $J_{5'b,4'}$ = 4.1 Hz, 1 H, 5′b-H), 5.40 (dd, $J_{1',2b}$ = 10.6, $J_{1',2'a}$ = 5.5 Hz, 1 H, 1′-H), 5.78 (br. dt, $J_{3',2'b}$ = 5.9, $J_{3',2'a}$ = $J_{3',4'}$ = 1.7 Hz, 1 H, 3′-H), 6.68 (br. d, $J_{3,4}$ = 3.4 Hz, 1 H, 3-H), 7.23 (d, $J_{4,3}$ = 3.3 Hz, 1 H, 4-H), 7.34 and 7.37 (2 × m, 2 × 2 H, *o*-Tol-H), 7.43 (ddd, $J_{5',4'}$ = 7.5, $J_{5',6'}$ = 4.7, $J_{5',3'}$ = 1.2 Hz, 1 H, bipy-5′-H), 7.61 (dd, $J_{5,4}$ = 7.8, $J_{5,3}$ = 1.0 Hz, 1 H, bipy-5-H), 7.87 (t, $J_{4,3}$ = $J_{4,5}$ = 7.9 Hz, 1 H, bipy-4-H), 7.93 (ddd, $J_{4',3'}$ = 7.9, $J_{4',5'}$ = 7.5, $J_{4',6'}$ = 1.8 Hz, 1 H, bipy-4′-H), 7.99–8.03 (m, 4 H, *o*-Tol-H), 8.36 (dd, $J_{3,4}$ = 7.8, $J_{3,5}$ = 1.0 Hz, 1 H, -bipy-3-H), 8.59 (dt, $J_{3',4'}$ = 8.0, $J_{3',5'}$ = $J_{3',6'}$ = 1.1 Hz, 1 H, bipy-3′-H), 8.68 (ddd, $J_{6',5'}$ = 4.7, $J_{6',4'}$ = 1.8, $J_{6',3'}$ = 0.9 Hz, 1 H, bipy-6′-′H) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]acetone): δ = 21.59 (CH_3-Tol), 37.86 (CH_2-2′), 65.26 (CH_2-5′), 74.68 (CH-1′), 77.75 (CH-3′), 83.61 (CH-4′), 110.26 (CH-4), 111.54 (CH-3), 119.01 (CH-5-bipy), 119.84 (CH-3-bipy), 121.58 (CH-3′-bipy), 124.97 (CH-5′-bipy), 128.21 and 128.30 (C-*i*-Tol), 130.08 and 130.14 (CH-*o*-Tol), 130.45 and 130.48 (CH-*o*-Tol), 137.81 (CH-4′-bipy), 138.64 (CH-4-bipy), 144.75 and 144.97 (C-*p*-Tol), 149.35 (C-6-bipy), 150.06 (CH-6′-bipy), 154.71 (C-5), 154.90 (C-2), 156.44 (C-2′-bipy), 156.60 (C-2-bipy), 166.48 and 166.55 (CO) ppm. IR (CCl_4): $\tilde{\nu}$ = 3039, 2955, 2926, 1725, 1613, 1428, 1268, 1178, 1103, 1021, 690 cm^{-1}.

General Procedure for the Zemplén Deprotection: NaOMe (1 M in MeOH, 0.32 mL, 0.32 mmol) was added to a solution of toluoyl-protected *C*-nucleoside **3**, **6a**–**e**, **6m**, or **11a**–**b** (0.16 mmol) in MeOH (30 mL) and the resulting solution was stirred at r.t. overnight. The solvent was evaporated and the products were isolated by column chromatography on silica gel, eluent gradient from chloroform to chloroform/MeOH (19.5:0.5). Compounds were re-purified by flash chromatography on reverse-phase C18 column (with linear gradient of H_2O to MeOH).

1β-(5-Bromofuran-2-yl)-1,2-dideoxy-D-ribofuranose (5): Compound **5** was prepared from **3** (1.10 g, 2.22 mmol) according to the general procedure in 93% yield as a colorless oil. After coevaporation with EtOAc the oil furnished a white powder, which was stored under argon in the freezer; m.p. 101–102 °C. HRMS (ESI): calcd. for $C_9H_{11}O_4BrNa$ [M + Na] 284.9733; found 284.9734. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 1.95 (ddd, J_{gem} = 12.8, $J_{2'a,1'}$ = 5.8, $J_{2'a,3'}$ = 2.0 Hz, 1 H, 2′a-H), 2.12 (ddd, J_{gem} = 12.8, $J_{2'b,1'}$ = 10.2, $J_{2'b,3'}$ = 5.7 Hz, 1 H, 2′b-H), 3.32 (dd, J_{gem} = 11.4, $J_{5'a,4'}$ = 6.0 Hz, 1 H, 5′a-H), 3.36 (dd, J_{gem} = 11.4, $J_{5'b,4'}$ = 5.4 Hz, 1 H, 5′b-H), 3.70 (ddd, $J_{4',5'a}$ = 6.0, $J_{4',5'b}$ = 5.4, $J_{4',3'}$ = 2.5 Hz, 1 H, 4′-H), 4.17 (br. dt, $J_{3',2'b}$ = 5.7, $J_{3',2'a}$ = $J_{3',4'}$ = 2.2 Hz, 1 H, 3′-H), 4.94 (dd, $J_{1',2b}$ = 10.2, $J_{1',2'a}$ = 5.8 Hz, 1 H, 1′-H), 6.49 (br. d, $J_{3,4}$ = 3.3 Hz, 1 H, 3-H), 6.51 (d, $J_{4,3}$ = 3.3 Hz, 1 H, 4-H) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ = 38.70 (CH_2-2′), 62.43 (CH_2-5′), 71.97 (CH-3′), 72.12 (CH-1′), 87.88 (CH-4′), 110.74 (CH-3), 112.47 (CH-4), 121.09 (C-5), 156.64 (C-2) ppm. $C_9H_{11}BrO_4$ (263.1): calcd. C 41.09, H 4.21, Br 30.37; found C 41.30, H 4.26, Br 30.78. IR (KBr): $\tilde{\nu}$ = 3390, 3304, 1501, 1045, 1032, 792, 782, 605 cm^{-1}. $[\alpha]_D^{20}$ = +10.9 (*c* = 0.27, MeOH).

1β-[5-(Thiazol-2-yl)furan-2-yl]-1,2-dideoxy-D-ribofuranose (7a): Compound **6a** was prepared (80 mg, 0.47 mmol) by the general procedure. **7a** (41 mg, 98%) was obtained as a yellow oil, which was crystallized from 2-propanol/heptane to give gray crystals. HRMS (ESI): calcd. for $C_{12}H_{13}O_4NSNa$ [M + Na] 290.0460; found 290.0457. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 2.05 (ddd, J_{gem} = 12.8, $J_{2'a,1'}$ = 6.0, $J_{2'a,3'}$ = 2.2 Hz, 1 H, 2′a-H), 2.21 (ddd, J_{gem} = 12.8, $J_{2'b,1'}$ = 9.9, $J_{2'b,3'}$ = 5.7 Hz, 1 H, 2′b-H), 3.40 (m, 2 H, 5′-H), 4.76 (td, $J_{4',5'b}$ = $J_{4',5'a}$ = 5.7, $J_{4',3'}$ = 2.5 Hz, 1 H, 4′-H), 4.23 (m, 1 H, 3′-H), 4.76 (t, $J_{OH,5'a}$ = $J_{OH,5'b}$ = 5.7 Hz, OH-5′), 5.06 (dd, $J_{1',2b}$ = 9.9, $J_{1',2'a}$ = 6.0 Hz, 1 H, 1′-H), 5.13 (d, $J_{OH,3'}$ = 4.1 Hz, OH-3′), 6.30 (dd, $J_{3,4}$ = 3.4, $J_{3,1'}$ = 0.5 Hz, 1 H, 3-H), 7.01 (d, $J_{4,3}$ = 3.4 Hz, 1 H, 4-H), 7.75 (d, $J_{5,4}$ = 3.2 Hz, 1 H, thiazyl-5-H), 7.88 (d, $J_{4,5}$ = 3.2 Hz, 1 H, thiazyl-4-H) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ = 39.00 (CH_2-2′), 62.44 (CH_2-5′), 72.03 (CH-3′), 72.21 (CH-1′), 87.95 (CH-4′), 109.75 (CH-4), 110.14 (CH-3), 119.77 (CH-5-thiazyl), 143.93 (CH-4-thiazyl), 148.03 (C-5), 156.13 (C-2), 157.13 (C-2-thiazyl) ppm. IR (KBr): $\tilde{\nu}$ = 3410, 3110, 2913, 1603, 1338, 1255, 1215, 1057, 1033, 998, 793, 652 cm^{-1}. $[\alpha]_D^{20}$ = –15.0 (*c* = 0.25, MeOH).

1β-[5-(Furan-2-yl)furan-2-yl]-1,2-dideoxy-D-ribofuranose (7b): Compound **7b** was prepared from **6b** (365 mg, 0.75 mmol) by the general

procedure. **7b** (145 mg, 77%) was obtained as a white powder; m.p. 102–104 °C. HRMS (ESI): calcd. for $C_{13}H_{14}O_5Na$ [M + Na] 273.0734; found 273.0733. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 2.00 (ddd, J_{gem} = 12.8, $J_{2'a,1'}$ = 5.9, $J_{2'a,3'}$ = 2.1 Hz, 1 H, 2′a-H), 2.19 (ddd, J_{gem} = 12.8, $J_{2'b,1'}$ = 10.1, $J_{2'b,3'}$ = 5.8 Hz, 1 H, 2′b-H), 3.36 (dd, J_{gem} = 11.4, $J_{5'a,4'}$ = 6.0 Hz, 1 H, 5′a-H), 3.39 (dd, J_{gem} = 11.4, $J_{5'b,4'}$ = 5.4 Hz, 1 H, 5′b-H), 3.73 (ddd, $J_{4',5'a}$ = 5.9, $J_{4',5'b}$ = 5.5, $J_{4',3'}$ = 2.5 Hz, 1 H, 4′-H), 4.21 (br. dt, $J_{3',2'b}$ = 5.8, $J_{3',2'a}$ = $J_{3',4'}$ = 2.3 Hz, 1 H, 3′-H), 4.73 (br. s, 1 H, OH-5′), 5.01 (dd, $J_{1',2b}$ = 10.0, $J_{1',2'a}$ = 5.9 Hz, 1 H, 1′-H), 5.10 (br. s, 1 H, OH-3′), 6.52 (dd, $J_{3,4}$ = 3.4, $J_{3,1'}$ = 0.6 Hz, 1 H, 3-H), 6.59 (dd, $J_{4,3}$ = 3.4, $J_{4,5}$ = 1.8 Hz, 1 H, furyl-4-H), 6.61 (d, $J_{4,3}$ = 3.4 Hz, 1 H, 4-H), 6.66 (dd, $J_{3,4}$ = 3.4, $J_{3,5}$ = 0.9 Hz, 1 H, furyl-3-H), 7.72 (dd, $J_{5,4}$ = 1.8, $J_{5,3}$ = 0.8 Hz, 1 H, furyl-5-H) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]-DMSO): δ = 38.94 (CH$_2$-2′), 62.48 (CH$_2$-5′), 72.04 (CH-3′), 72.24 (CH-1′), 87.87 (CH-4′), 105.77 (CH-3-furyl), 106.23 (CH-4), 109.48 (CH-3), 111.94 (CH-4-furyl), 142.98 (CH-5-furyl), 145.38 and 145.67 (C-2-furyl, C-5), 154.07 (C-2) ppm. IR (KBr): $\tilde{\nu}$ = 3401, 3131, 2919, 1337, 1211, 1061, 1008, 790, 747 cm^{-1}. $[\alpha]_D^{20}$ = –10.7 (*c* = 2.52, DMSO).

1β-[5-(Thiophen-2-yl)furan-2-yl]-1,2-dideoxy-D-ribofuranose (7c): Compound **7c** was prepared from **6c** (480 mg, 0.96 mmol) by the general procedure. **7c** (240 mg, 95%) was obtained as a white powder; m.p. 98–102 °C. HRMS (ESI): calcd. for $C_{13}H_{14}O_4SNa$ [M + Na] 289.0506; found 289.0505. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 2.00 (ddd, J_{gem} = 12.8, $J_{2'a,1'}$ = 5.8, $J_{2'a,3'}$ = 2.1 Hz, 1 H, 2′a-H), 2.20 (ddd, J_{gem} = 12.8, $J_{2'b,1'}$ = 10.1, $J_{2'b,3'}$ = 5.7 Hz, 1 H, 2′b-H), 3.34–3.43 (m, 2 H, 5′a-H, 5′b-H), 3.76 (ddd, $J_{4',5'a}$ = 6.1, $J_{4',5'b}$ = 5.5, $J_{4',3'}$ = 2.4 Hz, 1 H, 4′-H), 4.21 (br. dt, $J_{3',2'b}$ = 5.6, $J_{3',2'a}$ = $J_{3',4'}$ = 2.3 Hz, 1 H, 3′-H), 4.75 (br. s, 1 H, OH-5′), 5.01 (br. dd, $J_{1',2b}$ = 10.1, $J_{1',2'a}$ = 5.8 Hz, 1 H, 1′-H), 5.12 (br. s, 1 H, OH-3′), 6.50 (dd, $J_{3,4}$ = 3.3, $J_{3,1'}$ = 0.6 Hz, 1 H, 3-H), 6.67 (d, $J_{4,3}$ = 3.4 Hz, 1 H, 4-H), 7.10 (dd, $J_{4,5}$ = 5.1, $J_{4,3}$ = 3.6 Hz, 1 H, thienyl-4-H), 7.34 (dd, $J_{3,4}$ = 3.5, $J_{3,5}$ = 1.2 Hz, 1 H, thienyl-3-H), 7.52 (dd, $J_{5,4}$ = 5.1, $J_{5,3}$ = 1.2 Hz, 1 H, Thienyl-5-H) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ = 38.87 (CH$_2$-2′), 62.53 (CH$_2$-5′), 72.08 (CH-3′), 72.26 (CH-1′), 87.86 (CH-4′), 106.16 (CH-4), 109.90 (CH-3), 123.18 (CH-3-thienyl), 125.41 (CH-5-thienyl), 128.31 (CH-4-thienyl), 132.99 (C-2-thienyl), 148.53 (C-5), 153.76 (C-2) ppm. IR (KBr): $\tilde{\nu}$ = 3388, 2919, 1328, 1203, 1068, 1006, 947, 790, 687 cm^{-1}. $[\alpha]_D^{20}$ = –13.7 (*c* = 0.28, DMSO).

1β-[5-(Pyridin-2-yl)furan-2-yl]-1,2-dideoxy-D-ribofuranose (7d): Compound **7d** was prepared from **6d** (233 mg, 0.47 mmol) by the general procedure. **7d** (86 mg, 71%) was obtained as a yellow oil. HRMS (ESI): calcd. for $C_{14}H_{15}NO_4Na$ [M + Na] 284.0894; found 284.0893. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 2.04 (ddd, J_{gem} = 12.8, $J_{2'a,1'}$ = 5.9, $J_{2'a,3'}$ = 2.1 Hz, 1 H, H-2′a), 2.25 (ddd, J_{gem} = 12.8, $J_{2'b,1'}$ = 10.0, $J_{2'b,3'}$ = 5.7 Hz, 1 H, H-2′b), 3.36–3.45 (m, 2 H, H-5′a, H-5′b), 3.76 (ddd, $J_{4',5'a}$ = 6.0, $J_{4',5'b}$ = 5.5, $J_{4',3'}$ = 2.4 Hz, 1 H, H-4′), 4.24 (br. dt, $J_{3',2'b}$ = 5.7, $J_{3',2'a}$ = $J_{3',4'}$ = 2.3 Hz, 1 H, H-3′), 4.78 (br. s, 1 H, OH-5′), 5.07 (dd, $J_{1',2b}$ = 10.0, $J_{1',2'a}$ = 5.9 Hz, 1 H, H-1′), 5.15 (br. s, 1 H, OH-3′), 6.58 (dd, $J_{3,4}$ = 3.4, $J_{3,1'}$ = 0.4 Hz, 1 H, H-3), 7.03 (d, $J_{4,3}$ = 3.4 Hz, 1 H, H-4), 7.28 (ddd, $J_{5,4}$ = 7.6, $J_{5,6}$ = 4.8, $J_{5,3}$ = 1.1 Hz, 1 H, H-5-py), 7.69 (dt, $J_{3,4}$ = 8.0, $J_{3,5}$ = $J_{3,6}$ = 1.1 Hz, 1 H, H-3-py), 7.85 (ddd, $J_{4,3}$ = 7.9, $J_{4,5}$ = 7.6, $J_{4,6}$ = 1.8 Hz, 1 H, H-4-py), 8.56 (ddd, $J_{6,5}$ = 4.8, $J_{6,4}$ = 1.8, $J_{6,3}$ = 1.0 Hz, 1 H, H-6-py) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ = 39.04 (CH$_2$-2′), 62.54 (CH$_2$-5′), 72.14 (CH-3′), 72.46 (CH-1′), 87.92 (CH-4′), 109.57 (CH-4), 110.11 (CH-3), 118.33 (CH-3-py), 122.60 (CH-5-py), 137.36 (CH-4-py), 148.67 (C-2-py), 149.85 (CH-6-py), 152.79 (C-5), 155.57 (C-2) ppm. IR (KBr): $\tilde{\nu}$ = 3382, 2924, 2877, 1588, 1427, 1047, 778 cm^{-1}. $[\alpha]_D^{20}$ = –8.1 (*c* = 2.10, DMSO).

1β-[5-(2,2′-Bipyridin-6-yl)furan-2-yl]-1,2-dideoxy-D-ribofuranose (7e): Compound **7e** was prepared from **6e** (240 mg, 0.42 mmol) by the general procedure. **7e** (86 mg, 61%) was obtained as a yellow oil. HRMS (ESI): calcd. for $C_{19}H_{18}N_2O_4Na$ [M + Na] 361.1161; found 361.1159. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 2.07 (ddd, J_{gem} = 12.8, $J_{2'a,1'}$ = 5.9, $J_{2'a,3'}$ = 2.1 Hz, 1 H, H-2′a), 2.28 (ddd, J_{gem} = 12.8, $J_{2'b,1'}$ = 10.0, $J_{2'b,3'}$ = 5.7 Hz, 1 H, H-2′b), 3.39–3.47 (m, 2 H, H-5′a, H-5′b), 3.78 (ddd, $J_{4',5'a}$ = 5.9, $J_{4',5'b}$ = 5.5, $J_{4',3'}$ = 2.4 Hz, 1 H, H-4′), 4.26 (br. dt, $J_{3',2'b}$ = 5.6, $J_{3',2'a}$ = $J_{3',4'}$ = 2.3 Hz, 1 H, H-3′), 4.81 (br. s, 1 H, OH-5′), 5.10 (dd, $J_{1',2b}$ = 10.0, $J_{1',2'a}$ = 5.9 Hz, 1 H, H-1′), 5.16 (br. s, 1 H, OH-3′), 6.64 (dd, $J_{3,4}$ = 3.3, $J_{3,1'}$ = 0.5 Hz, 1 H, H-3), 7.22 (d, $J_{4,3}$ = 3.3 Hz, 1 H, H-4), 7.48 (ddd, $J_{5',4'}$ = 7.5, $J_{5',6'}$ = 4.7, $J_{5',3'}$ = 1.2 Hz, 1 H, H-5′-bipy), 7.75 (dd, $J_{5,4}$ = 7.8, $J_{5,3}$ = 1.0 Hz, 1 H, H-5-bipy), 7.99 (ddd, $J_{4',3'}$ = 7.9, $J_{4',5'}$ = 7.5, $J_{4',6'}$ = 1.8 Hz, 1 H, H-4′-bipy), 8.01 (t, $J_{4,3}$ = $J_{4,5}$ = 7.9 Hz, 1 H, H-4-bipy), 8.28 (dd, $J_{3,4}$ = 7.9, $J_{3,5}$ = 1.0 Hz, 1 H, H-3-bipy), 8.51 (dt, $J_{3',4'}$ = 7.9, $J_{3',5'}$ = $J_{3',6'}$ = 1.1 Hz, 1 H, H-3′-bipy), 8.70 (ddd, $J_{6',5'}$ = 4.8, $J_{6',4'}$ = 1.8, $J_{6',3'}$ = 0.9 Hz, 1 H, H-6′-bipy) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ = 39.07 (CH$_2$-2′), 62.56 (CH$_2$-5′), 72.16 (CH-3′), 72.48 (CH-1′), 87.95 (CH-4′), 110.01 (CH-4), 110.15 (CH-3), 118.56 (CH-5-bipy), 119.03 (CH-3-bipy), 120.87 (CH-3′-bipy), 124.65 (CH-5′-bipy), 137.61 (CH-4′-bipy), 138.58 (CH-4-bipy), 148.29 (C-6-bipy), 149.51 (CH-6′-bipy), 152.70 (C-5), 155.07 and 155.26 (C-2,2′-bipy), 155.79 (C-2) ppm. IR (KBr): $\tilde{\nu}$ = 3421, 2923, 2873, 1699, 1611, 1564, 1428, 1085, 1045, 993, 778 cm^{-1}. $[\alpha]_D^{20}$ = +12.0 (*c* = 0.27, MeOH).

General Procedure for the Suzuki Cross-Coupling: A mixture of H_2O/acetonitrile (2:1, 5 mL) was added to an argon-purged flask containing TPPTS (76 mg, 0.13 mmol) and [Pd(OAc)$_2$] (12 mg, 0.05 mmol), and the mixture was sonicated for 1 min. This solution was added into a mixture of **5** (280 mg, 1.06 mmol), boronic acid (1.6 mmol), and Na_2CO_3 (340 mg, 3.2 mmol) in H_2O/acetonitrile (2:1, 5 mL). The mixture was then stirred at 110 °C for 4 h. After evaporation, the crude product was purified by column chromatography on silica gel, eluent gradient from $CHCl_3$ to $CHCl_3$/MeOH (9.5:0.5).

1β-[5-(4-Chlorophenyl)furan-2-yl]-1,2-dideoxy-D-ribofuranose (7f): Compound **7f** was prepared from **5** and 4-chlorophenylboronic acid (250 mg, 1.6 mmol) by the general procedure (110 °C, 4 h). **7f** (212 mg, 68%) was obtained as a yellow solid, which was crystallized from 2-propanol/heptane to give yellow crystals; m.p. 120–124 °C. HRMS (ESI): calcd. for $C_{15}H_{15}ClO_4Na$ [M + Na] 317.0551; found 317.0551. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 2.01 (ddd, J_{gem} = 12.8, $J_{2'a,1'}$ = 5.9, $J_{2'a,3'}$ = 2.0 Hz, 1 H, H-2′a), 2.23 (ddd, J_{gem} = 12.8, $J_{2'b,1'}$ = 10.0, $J_{2'b,3'}$ = 5.7 Hz, 1 H, H-2′b), 3.34–3.44 (m, 2 H, H-5′a, H-5′b), 3.75 (ddd, $J_{4',5'a}$ = 6.0, $J_{4',5'b}$ = 5.5, $J_{4',3'}$ = 2.4 Hz, 1 H, H-4′), 4.23 (m, 1 H, H-3′), 4.77 (t, $J_{OH,5'}$ = 5.7 Hz, 1 H, OH-5′), 5.03 (dd, $J_{1',2b}$ = 10.0, $J_{1',2'a}$ = 5.9 Hz, 1 H, H-1′), 5.14 (d, $J_{OH,3'}$ = 4.0 Hz, 1 H, OH-3′), 6.53 (dd, $J_{3,4}$ = 3.4, $J_{3,1'}$ = 0.5 Hz, 1 H, H-3), 6.93 (d, $J_{4,3}$ = 3.3 Hz, 1 H, H-4), 7.48 (m, 2 H, H-*m*-C_6H_4Cl), 7.69 (m, 2 H, H-*o*-C_6H_4Cl) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ = 38.97 (CH$_2$-2′), 62.59 (CH$_2$-5′), 72.18 (CH-3′), 72.43 (CH-1′), 87.88 (CH-4′), 107.44 (CH-4), 110.18 (CH-3), 125.26 (CH-*o*-C_6H_4Cl), 129.21 (CH-*m*-C_6H_4Cl), 129.36 (C-*i*-C_6H_4Cl), 132.04 (C-*p*-C_6H_4Cl), 151.68 (C-5), 154.64 (C-2) ppm. IR (KBr): $\tilde{\nu}$ = 3408, 3343, 1483, 1086, 1044, 1035, 839, 793 cm^{-1}. Anal. calcd. $C_{15}H_{15}ClO_4$ (294.7): C 61.13, H 5.13, Cl 12.03; found C 61.01, H 4.99, Cl 12.11. $[\alpha]_D^{20}$ = +8.2 (*c* = 0.24, MeOH).

1β-[5-(Thiophen-3-yl)furan-2-yl]-1,2-dideoxy-D-ribofuranose (7g): Prepared from **5** and 3-thienylboronic acid (204 mg, 1.6 mmol) by

the general procedure (110 °C, 4 h). **7g** (112 mg, 40%) was obtained as a yellow oil, which was crystallized from 2-propanol/heptane to give grey crystals; m.p. 132–134 °C. HRMS (ESI): calcd. for $C_{13}H_{14}O_4SNa$ [M + Na] 289.0505; found 289.0506. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 1.99 (ddd, J_{gem} = 12.8, $J_{2'a,1'}$ = 5.8, $J_{2'a,3'}$ = 2.1 Hz, 1 H, H-2′a), 2.22 (ddd, J_{gem} = 12.8, $J_{2'b,1'}$ = 10.1, $J_{2'b,3'}$ = 5.7 Hz, 1 H, H-2′b), 3.34–3.43 (m, 2 H, H-5′a, H-5′b), 3.73 (ddd, $J_{4',5'a}$ = 5.9, $J_{4',5'b}$ = 5.5, $J_{4',3'}$ = 2.4 Hz, 1 H, H-4′), 4.21 (m, 1 H, H-3′), 4.75 (t, $J_{OH,5'}$ = 5.7 Hz, 1 H, OH-5′), 5.01 (dd, $J_{1',2b}$ = 10.1, $J_{1',2'a}$ = 5.8 Hz, 1 H, H-1′), 5.11 (d, $J_{OH,3'}$ = 4.0 Hz, 1 H, OH-3′), 6.47 (dd, $J_{3,4}$ = 3.3, $J_{3,1'}$ = 0.5 Hz, 1 H, H-3), 6.67 (d, $J_{4,3}$ = 3.3 Hz, 1 H, H-4), 7.40 (dd, $J_{4,5}$ = 5.0, $J_{4,2}$ = 1.3 Hz, 1 H, Thienyl-4-H), 7.62 (dd, $J_{5,4}$ = 5.0, $J_{5,2}$ = 3.0 Hz, 1 H, Thienyl-5-H), 7.67 (dd, $J_{2,5}$ = 3.0, $J_{2,4}$ = 1.3 Hz, 1 H, H-2-thienyl). ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ = 38.93 (CH$_2$-2′), 62.58 (CH$_2$-5′), 72.14 (CH-3′), 72.40 (CH-1′), 87.85 (CH-4′), 106.13 (CH-4), 109.52 (CH-3), 119.48 (CH-2-thienyl), 124.92 (CH-4-thienyl), 127.62 (CH-5-thienyl), 132.24 (C-3-thienyl), 150.20 (C-5), 153.38 (C-2) ppm. IR (KBr): $\tilde{\nu}$ = 3412, 3350, 2880, 1033, 785, 600 cm^{-1}. $C_{13}H_{14}O_4S$ (266.3): C 58.63, H 5.30, S 12.04; found C 58.37, H 5.37, S 12.51. $[\alpha]_D^{20}$ = +10.5 (*c* = 0.23, MeOH).

1β-[5-(Furan-3-yl)furan-2-yl]-1,2-dideoxy-D-ribofuranose (7h): Prepared from **5** and 3-furylboronic acid (179 mg, 1.6 mmol) by the general procedure (110 °C, 4 h). **7h** (120 mg, 44%) was obtained as a yellow oil and crystallized from 2-propanol/heptane to give orange crystals; m.p. 120–121 °C. HRMS (ESI): calcd. for $C_{13}H_{14}O_5Na$ [M + Na] 273.0733; found 273.0733. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 1.98 (ddd, J_{gem} = 12.8, $J_{2'a,1'}$ = 5.8, $J_{2'a,3'}$ = 2.0 Hz, 1 H, H-2′a), 2.19 (ddd, J_{gem} = 12.8, $J_{2'b,1'}$ = 10.2, $J_{2'b,3'}$ = 5.8 Hz, 1 H, H-2′b), 3.32–3.42 (m, 2 H, H-5′a, H-5′b), 3.72 (ddd, $J_{4',5'a}$ = 5.9, $J_{4',5'b}$ = 5.6, $J_{4',3'}$ = 2.4 Hz, 1 H, H-4′), 4.20 (ddt, $J_{3',2'b}$ = 6.0, $J_{3',OH}$ = 3.9, $J_{3',2'a}$ = $J_{3',4'}$ = 2.2 Hz, 1 H, H-3′), 4.73 (t, $J_{OH,5'}$ = 5.7 Hz, 1 H, OH-5′), 4.98 (dd, $J_{1',2b}$ = 10.2, $J_{1',2'a}$ = 5.7 Hz, 1 H, H-1′), 5.09 (d, $J_{OH,3'}$ = 4.1 Hz, 1 H, OH-3′), 6.45 (dd, $J_{3,4}$ = 3.3, $J_{3,1'}$ = 0.5 Hz, 1 H, H-3), 6.55 (d, $J_{4,3}$ = 3.4 Hz, 1 H, H-4), 6.79 (dd, $J_{4,5}$ = 1.9, $J_{4,2}$ = 0.8 Hz, 1 H, H-4-furyl), 7.73 (t, $J_{5,4}$ = $J_{5,2}$ = 1.7 Hz, 1 H, H-3-furyl), 8.00 (m, 1 H, H-2-furyl). ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ = 38.90 (CH$_2$-2′), 62.53 (CH$_2$-5′), 72.09 (CH-3′), 72.32 (CH-1′), 87.85 (CH-4′), 106.40 (CH-4), 108.05 (CH-4-furyl), 109.30 (CH-3), 117.63 (C-3-furyl), 138.52 (CH-2-furyl), 144.51 (CH-5-furyl), 147.06 (C-5), 153.29 (C-2) ppm. IR (KBr): $\tilde{\nu}$ = 3406, 3335, 2951, 1157, 1044, 1031, 787, 596 cm^{-1}. $[\alpha]_D^{20}$ = +3.1 (*c* = 0.29, MeOH).

1β-[5-(Benzofuran-2-yl)furan-2-yl]-1,2-dideoxy-D-ribofuranose (7i): Prepared from **5** (120 mg, 0.46 mmol) and 2-benzofurylboronic acid (111 mg, 1.6 mmol) by the general procedure (110 °C, 4 h). Compound **7i** (137 mg, 37%) was obtained as a yellow oil, which was crystallized from 2-propanol/heptane to give orange crystals; m.p. 124–128 °C. HRMS (ESI): calcd. for $C_{17}H_{16}O_5Na$ [M + Na] 323.0892; found 323.0890. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 2.05 (ddd, J_{gem} = 12.8, $J_{2'a,1'}$ = 5.8, $J_{2'a,3'}$ = 2.1 Hz, 1 H, H-2′a), 2.24 (ddd, J_{gem} = 12.8, $J_{2'b,1'}$ = 10.0, $J_{2'b,3'}$ = 5.9 Hz, 1 H, H-2′b), 3.38–3.44 (m, 2 H, H-5′a, H-5′b), 3.76 (td, $J_{4',5'a}$ = $J_{4',5'b}$ = 5.7, $J_{4',3'}$ = 2.5 Hz, 1 H, H-4′), 4.24 (m, 1 H, H-3′), 4.75 (m, 1 H, OH-5′), 5.07 (dd, $J_{1',2b}$ = 10.0, $J_{1',2'a}$ = 5.8 Hz, 1 H, H-1′), 5.13 (br. s, 1 H, OH-3′), 6.63 (dd, $J_{3,4}$ = 3.4, $J_{3,1'}$ = 0.5 Hz, 1 H, H-3), 6.91 (d, $J_{4,3}$ = 3.4 Hz, 1 H, H-4), 7.12 (br. d, $J_{3,7}$ = 1.0 Hz, 1 H, H-3-C$_8$H$_5$O), 7.29 (td, $J_{5,4}$ = $J_{5,6}$ = 7.5, $J_{5,7}$ = 1.1 Hz, 1 H, H-5-C$_8$H$_5$O), 7.32 (ddd, $J_{6,7}$ = 8.2, $J_{6,5}$ = 7.3, $J_{6,4}$ = 1.4 Hz, 1 H, H-6-C$_8$H$_5$O), 7.61 (dq, $J_{7,6}$ = 8.2, $J_{7,5}$ = $J_{7,4}$ = $J_{7,3}$ = 1.0 Hz, 1 H, H-7-C$_8$H$_5$O), 7.66 (ddd, $J_{4,5}$ = 7.7, $J_{4,6}$ = 1.4, $J_{4,7}$ = 0.7 Hz, 1 H, H-4-C$_8$H$_5$O) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ = 39.03 (CH$_2$-2′), 62.45 (CH$_2$-5′), 72.05 (CH-3′), 72.27 (CH-1′), 87.96 (CH-4′), 101.51 (CH-3-C$_8$H$_5$O), 109.15 (CH-4), 109.84 (CH-3), 111.26 (CH-7-C$_8$H$_5$O), 121.46 (CH-4-C$_8$H$_5$O), 123.67 (CH-5-C$_8$H$_5$O), 124.94 (CH-6-C$_8$H$_5$O), 128.44 (C-9-C$_8$H$_5$O), 144.70 (C-5), 147.41 (C-2-C$_8$H$_5$O), 154.11 (C-8-C$_8$H$_5$O), 155.73 (C-2) ppm. IR (KBr): $\tilde{\nu}$ = 3439, 2924, 1629, 1446, 1253, 1045, 793, 755 cm^{-1}. $C_{17}H_{16}O_5$ (300.3): C 67.99, H 5.37; found C 67.83, H 5.75. $[\alpha]_D^{20}$ = –2.9 (*c* = 0.24, DMSO).

1β-[5-(Dibenzo[*b*,*d*]furan-4-yl)furan-2-yl]-1,2-dideoxy-D-ribofuranose (7j): Prepared from **5** and dibenzo[*b*,*d*]furan-4-ylboronic acid (339 mg, 1.6 mmol) by the general procedure (110 °C, 4 h). Compound **7j** (175 mg, 47%) was obtained as a yellow oil, which was crystallized from 2-propanol/heptane to give yellow crystals; m.p. 139–142 °C. HRMS (ESI): calcd. for $C_{21}H_{18}O_5Na$ [M + Na] 373.1046; found 373.1046. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 2.08 (ddd, J_{gem} = 12.8, $J_{2'a,1'}$ = 5.9, $J_{2'a,3'}$ = 2.1 Hz, 1 H, H-2′a), 2.31 (ddd, J_{gem} = 12.8, $J_{2'b,1'}$ = 10.0, $J_{2'b,3'}$ = 5.7 Hz, 1 H, H-2′b), 3.42–3.48 (m, 2 H, H-5′a, H-5′b), 3.79 (ddd, $J_{4',5'a}$ = 6.0, $J_{4',5'b}$ = 5.6, $J_{4',3'}$ = 2.4 Hz, 1 H, H-4′), 4.29 (br. ddt, $J_{3',2'b}$ = 5.8, $J_{3',OH}$ = 3.8, $J_{3',2'a}$ = $J_{3',4'}$ = 2.2 Hz, 1 H, H-3′), 4.79 (t, $J_{OH,5'a}$ = $J_{OH,5'b}$ = 5.7 Hz, 1 H, OH-5′), 5.13 (dd, $J_{1',2b}$ = 9.9, $J_{1',2'a}$ = 5.9 Hz, 1 H, H-1′), 5.15 (d, $J_{OH,3'}$ = 4.0 Hz, 1 H, OH-3′), 6.69 (d, $J_{3,4}$ = 3.4 Hz, 1 H, H-3), 7.26 (d, $J_{4,3}$ = 3.3 Hz, 1 H, H-4), 7.45 (td, $J_{8,7}$ = $J_{8,9}$ = 7.5, $J_{8,6}$ = 1.0 Hz, 1 H, H-8-C$_{12}$H$_7$O), 7.49 (t, $J_{2,1}$ = $J_{2,3}$ = 7.7 Hz, 1 H, H-2-C$_{12}$H$_7$O), 7.58 (ddd, $J_{7,6}$ = 8.4, $J_{7,8}$ = 7.3, $J_{7,9}$ = 1.4 Hz, 1 H, H-7-C$_{12}$H$_7$O), 7.82 (dt, $J_{6,7}$ = 8.3, $J_{6,8}$ = $J_{6,9}$ = 0.9 Hz, 1 H, H-6-C$_{12}$H$_7$O), 7.85 (dd, $J_{3,2}$ = 7.7, $J_{3,1}$ = 1.2 Hz, 1 H, H-3-C$_{12}$H$_7$O), 8.10 (dd, $J_{1,2}$ = 7.7, $J_{1,3}$ = 1.2 Hz, 1 H, H-1-C$_{12}$H$_7$O), 8.20 (ddd, $J_{9,8}$ = 7.7, $J_{9,7}$ = 1.4, $J_{9,6}$ = 0.7 Hz, 1 H, H-9-C$_{12}$H$_7$O) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ = 39.05 (CH$_2$-2′), 62.62 (CH$_2$-5′), 72.20 (CH-3′), 72.43 (CH-1′), 87.91 (CH-4′), 110.22 (CH-3), 110.89 (CH-4), 112.16 (CH-6-C$_{12}$H$_7$O), 115.35 (C-4-C$_{12}$H$_7$O), 120.29 (CH-1-C$_{12}$H$_7$O), 121.56 (CH-9-C$_{12}$H$_7$O), 122.23 (CH-3-C$_{12}$H$_7$O), 123.46 (C-9a-C$_{12}$H$_7$O), 123.71 and 123.78 (CH-2,8-C$_{12}$H$_7$O), 124.59 (C-9b-C$_{12}$H$_7$O), 128.14 (CH-7-C$_{12}$H$_7$O), 147.93 (C-5), 150.51 (C-4a-C$_{12}$H$_7$O), 154.62 (C-2), 155.73 (C-5a-C$_{12}$H$_7$O) ppm. IR (KBr): $\tilde{\nu}$ = 3399, 3326, 2927, 1450, 1193, 1060, 794, 750 cm^{-1}. $C_{21}H_{18}O_5$ (350.4): C 71.99, H 5.18; found C 71.73, H 5.30. $[\alpha]_D^{20}$ = +10.8 (*c* = 0.24, MeOH).

1β-[5-(3-Nitrophenyl)furan-2-yl]-1,2-dideoxy-D-ribofuranose (7k): Prepared from **5** and 3-nitrophenylboronic acid (267 mg, 1.6 mmol) by the general procedure (110 °C, 4 h). Compound **7k** (135 mg, 42%) was obtained as a yellow oil, which was crystallized from toluene/heptane to give yellow crystals; m.p. 146–149 °C. HRMS (ESI): calcd. for $C_{15}H_{15}NO_6Na$ [M + Na] 328.0792; found 328.0791. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 2.04 (ddd, J_{gem} = 12.8, $J_{2'a,1'}$ = 5.9, $J_{2'a,3'}$ = 2.1 Hz, 1 H, H-2′a), 2.25 (ddd, J_{gem} = 12.8, $J_{2'b,1'}$ = 10.0, $J_{2'b,3'}$ = 5.7 Hz, 1 H, H-2′b), 3.36–3.45 (m, 2 H, H-5′a, H-5′b), 3.76 (ddd, $J_{4',5'a}$ = 6.0, $J_{4',5'b}$ = 5.5, $J_{4',3'}$ = 2.4 Hz, 1 H, H-4′), 4.25 (ddm, $J_{3',2'b}$ = 5.8, $J_{3',OH}$ = 3.7 Hz, 1 H, H-3′), 4.77 (t, $J_{OH,5'a}$ = $J_{OH,5'b}$ = 5.7 Hz, 1 H, OH-5′), 5.07 (dd, $J_{1',2b}$ = 10.0, $J_{1',2'a}$ = 5.9 Hz, 1 H, H-1′), 5.14 (d, $J_{OH,3'}$ = 4.0 Hz, 1 H, OH-3′), 6.61 (br. d, $J_{3,4}$ = 3.4 Hz, 1 H, H-3), 7.20 (d, $J_{4,3}$ = 3.4 Hz, 1 H, H-4), 7.72 (t, $J_{5,4}$ = $J_{5,6}$ = 8.0 Hz, 1 H, H-5-C$_6$H$_4$NO$_2$), 8.11–8.14 (m, 2 H, H-4,6-C$_6$H$_4$NO$_2$), 8.42 (t, $J_{2,4}$ = $J_{2,6}$ = 2.0 Hz, 1 H, H-2-C$_6$H$_4$NO$_2$) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ = 38.99 (CH$_2$-2′), 62.50 (CH$_2$-5′), 72.11 (CH-3′), 72.36 (CH-1′), 87.93 (CH-4′), 109.26 (CH-4), 110.30 (CH-3), 117.62 (CH-2-C$_6$H$_4$NO$_2$), 122.04, 129.62 (CH-4,6-C$_6$H$_4$NO$_2$), 130.84 (CH-5-C$_6$H$_4$NO$_2$), 131.90 (C-1-C$_6$H$_4$NO$_2$), 148.65 (C-3-C$_6$H$_4$NO$_2$), 150.47 (C-5), 155.61 (C-2) ppm. IR (KBr): $\tilde{\nu}$ = 3531, 3378, 1525, 1354, 1081, 802, 741 cm^{-1}. $C_{15}H_{15}NO_6$ (305.3): C 59.01, H 4.95, N 4.59; found C 58.70, H 4.86, N 4.34. $[\alpha]_D^{20}$ = +12.2 (*c* = 0.26, MeOH).

1β-[5-(Phenoxathiin-4-yl)furan-2-yl]-1,2-dideoxy-D-ribofuranose (7l): Prepared from **5** and phenoxathiin-4-ylboronic acid (390 mg, 1.6 mmol) by the general procedure (110 °C, 4 h). Compound **7l** (80 mg, 20%) was obtained as an orange oil, which was crystallized from 2-propanol/heptane to give orange crystals; m.p. 71–75 °C. HRMS (ESI): calcd. for $C_{21}H_{18}O_5SNa$ [M + Na] 405.0767; found 405.0766. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 2.04 (ddd, J_{gem} = 12.8, $J_{2'a,1'}$ = 5.9, $J_{2'a,3'}$ = 2.1 Hz, 1 H, H-2′a), 2.27 (ddd, J_{gem} = 12.8, $J_{2'b,1'}$ = 10.0, $J_{2'b,3'}$ = 5.7 Hz, 1 H, H-2′b), 3.36–3.46 (m, 2 H, H-5′a, H-5′b), 3.77 (ddd, $J_{4',5'a}$ = 6.0, $J_{4',5'b}$ = 5.5, $J_{4',3'}$ = 2.4 Hz, 1 H, H-4′), 4.25 (ddm, $J_{3',2'b}$ = 5.8, $J_{3',OH}$ = 3.8 Hz, 1 H, H-3′), 4.77 (t, $J_{OH,5'a}$ = $J_{OH,5'b}$ = 5.7 Hz, 1 H, OH-5′), 5.09 (dd, $J_{1',2b}$ = 10.0, $J_{1',2'a}$ = 5.9 Hz, 1 H, H-1′), 5.13 (d, $J_{OH,3'}$ = 4.0 Hz, 1 H, OH-3′), 6.62 (d, $J_{3,4}$ = 3.3 Hz, 1 H, H-3), 7.16 (td, $J_{8,7}$ = $J_{8,9}$ = 7.5, $J_{8,6}$ = 1.5 Hz, 1 H, H-8-$C_{12}H_7SO$), 7.20 (t, $J_{2,1}$ = $J_{2,3}$ = 7.6 Hz, 1 H, H-2-$C_{12}H_7SO$), 7.23 (dd, $J_{3,2}$ = 7.7, $J_{3,1}$ = 2.0 Hz, 1 H, H-3-$C_{12}H_7SO$), 7.23 (d, $J_{4,3}$ = 3.3 Hz, 1 H, H-4), 7.27 (ddd, $J_{7,6}$ = 8.3, $J_{7,8}$ = 7.3, $J_{7,9}$ = 1.5 Hz, 1 H, H-7-$C_{12}H_7SO$), 7.32–7.35 (m, 2 H, H-6,9-$C_{12}H_7SO$), 7.63 (dd, $J_{1,2}$ = 7.5, $J_{1,3}$ = 2.0 Hz, 1 H, H-1-$C_{12}H_7SO$) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ = 39.04 (CH_2-2′), 62.56 (CH_2-5′), 72.16 (CH-3′), 72.38 (CH-1′), 87.88 (CH-4′), 110.31 (CH-3), 112.25 (CH-4), 118.45 (CH-6-$C_{12}H_7SO$), 119.97 (C-9a-$C_{12}H_7SO$), 120.27 (C-10a-$C_{12}H_7SO$), 121.03 (C-4-$C_{12}H_7SO$), 124.49 (CH-1-$C_{12}H_7SO$), 125.31 (CH-2-$C_{12}H_7SO$), 125.79 (CH-8-$C_{12}H_7SO$), 126.09 (CH-3-$C_{12}H_7SO$), 127.33 (CH-9-$C_{12}H_7SO$), 128.64 (CH-7-$C_{12}H_7SO$), 147.27 (C-4a-$C_{12}H_7SO$), 147.52 (C-5), 151.62 (C-5a-$C_{12}H_7SO$), 154.36 (C-2) ppm. IR (KBr): $\tilde{\nu}$ = 3401, 1715, 1454, 1435, 1223, 1027, 780, 752 cm^{-1}. $[\alpha]_D^{20}$ = +7.4 (*c* = 0.20, MeOH).

1β-[5-(Pinacolatoboryl)furan-2-yl]-1,2-dideoxy-3,5-di-*O*-toluoyl-D-ribofuranose (8). Method A: A solution of **3** (1.42 g, 2.84 mmol) in anhydrous dioxane (10 mL) under argon was added dropwise in five portions (each portion: 2 mL/3.5 min then 2 min pause) to a stirred solution of bis(pinacolato)diboron (2.9 g, 11.4 mmol), AcOK (1.67 g, 17 mmol) and [PdCl$_2$dppf] (312 mg, 0.43 mmol) under argon in anhydrous dioxane (11 mL) at 105 °C. The mixture was then stirred at 105 °C for 40 min. The crude reaction mixture was filtered through Celite, diluted with EtOAc (20 mL) and solvents were evaporated under vacuum. The crude product was purified by chromatography on silica gel, eluent gradient from hexane to hexane/EtOAc (9.7:0.3) to give the desired product **8** (1.06 g, 68%), followed by **9** (0.20 g, 17%) as colorless oils.

Method B: A solution of **4** (260 mg, 0.62 mmol), bis(pinacolato)-diboron (188 mg, 0.74 mmol), [IrCl(COD)]$_2$ (21 mg, 0.03 mmol) and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (22 mg, 0.08 mmol) under argon in anhydrous toluene (7 mL) was stirred at 105 °C for 2 d. The crude reaction mixture was filtered through Celite, diluted with EtOAc (20 mL) and the solvents were evaporated under vacuum. The crude product was purified by chromatography on silica gel, eluent gradient from hexane to hexane/EtOAc (9.7:0.3) to give the desired product **8** (130 mg, 39%), followed by **9** (50 mg) as colorless oils. Compound **8**: HRMS (ESI): calcd. for $C_{31}H_{35}O_8BNa$ [M + Na] 569.2317; found 569.2320. ^{1}H NMR (500 MHz, [D$_6$]acetone): δ = 1.31 and 1.32 [2 × s, 2 × 6 H, C(CH_3)$_2$], 2.41 and 2.42 (2 × s, 2 × 3 H, CH_3-Tol), 2.54 (ddd, J_{gem} = 13.7, $J_{2'a,1'}$ = 5.4, $J_{2'a,3'}$ = 1.4 Hz, 1 H, H-2′a), 2.67 (ddd, J_{gem} = 13.7, $J_{2'b,1'}$ = 10.7, $J_{2'b,3'}$ = 6.1 Hz, 1 H, H-2′b), 4.49 (td, $J_{4',5'a}$ = $J_{4',5'b}$ = 4.3, $J_{4',3'}$ = 2.2 Hz, 1 H, H-4′), 4.51 (dd, J_{gem} = 11.1, $J_{5'a,4'}$ = 4.4 Hz, 1 H, H-5′a), 4.58 (dd, J_{gem} = 11.1, $J_{5'b,4'}$ = 4.1 Hz, 1 H, H-5′b), 5.33 (br. dd, $J_{1',2b}$ = 10.8, $J_{1',2'a}$ = 5.4 Hz, 1 H, H-1′), 5.65 (dddd, $J_{3',2'b}$ = 6.1, $J_{3',4'}$ = 2.1, $J_{3',2'a}$ = 1.4, $J_{3',1'}$ = 0.5 Hz, 1 H, H-3′), 6.51 (dd, $J_{3,4}$ = 3.3, $J_{3,1'}$ = 0.5 Hz, 1 H, H-3), 6.99 (br. d, $J_{4,3}$ = 3.3 Hz, 1 H, H-4), 7.34 and 7.35 (2 × m, 2 × 2 H, H-*o*-Tol), 7.97 and 7.99 (2 × m, 2 × 2 H, H-*o*-Tol) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]acetone): δ = 21.57 and 21.59 (CH_3-Tol), 25.05 and 25.08 [(CH_3)$_2$C], 38.05 (CH_2-2′), 65.35 (CH_2-5′), 74.77 (CH-1′), 77.68 (CH-3′), 83.69 (CH-4′), 84.77 [(CH_3)$_2$*C*], 109.30 (CH-3), 125.01 (CH-4), 128.23 and 128.31 (C-*i*-Tol), 130.07 and 130.10 (CH-*o*-Tol), 130.45 and 130.49 (CH-*o*-Tol), 144.60 and 144.94 (C-*p*-Tol), 159.16 (C-2), 166.45 and 166.59 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 3429, 2927, 1721, 1613, 1346, 1271, 1106, 754 cm^{-1}. Compound **9**: HRMS (ESI): calcd. for $C_{25}H_{24}O_6Na$ [M + Na] 443.1465; found 443.1465. ^{1}H NMR (500 MHz, [D$_6$]acetone): δ = 2.41 and 2.42 (2 × s, 2 × 3 H, CH_3-Tol), 2.48 (ddd, J_{gem} = 13.8, $J_{2'a,1'}$ = 5.5, $J_{2'a,3'}$ = 1.5 Hz, 1 H, H-2′a), 2.69 (ddd, J_{gem} = 13.8, $J_{2'b,1'}$ = 10.7, $J_{2'b,3'}$ = 6.1 Hz, 1 H, H-2′b), 4.47 (ddd, $J_{4',5'b}$ = 5.0, $J_{4',5'a}$ = 4.2, $J_{4',3'}$ = 2.1 Hz, 1 H, H-4′), 4.49–4.56 (m, 2 H, H-5′), 5.29 (br. dd, $J_{1',2b}$ = 10.7, $J_{1',2'a}$ = 5.5 Hz, 1 H, H-1′), 5.66 (dddd, $J_{3',2'b}$ = 6.1, $J_{3',4'}$ = 2.1, $J_{3',2'a}$ = 1.5, $J_{3',1'}$ = 0.6 Hz, 1 H, H-3′), 6.39 (dd, $J_{4,3}$ = 3.3, $J_{4,5}$ = 1.8 Hz, 1 H, H-4), 6.46 (ddd, $J_{3,4}$ = 3.2, $J_{3,5}$ = 0.9, $J_{3,1'}$ = 0.5 Hz, 1 H, H-3), 7.33 and 7.35 (2 × m, 2 × 2 H, H-*o*-Tol), 7.52 (dd, $J_{5,4}$ = 1.8, $J_{5,3}$ = 0.9 Hz, 1 H, H-5), 7.96–8.00 (m, 4 H, H-*o*-Tol) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]acetone): δ = 21.57 and 21.58 (CH_3-Tol), 37.64 (CH_2-2′), 65.33 (CH_2-5′), 74.55 (CH-1′), 77.73 (CH-3′), 83.44 (CH-4′), 108.90 (CH-3), 111.16 (CH-4), 128.25 and 128.36 (C-*i*-Tol), 130.04 and 130.07 (CH-*o*-Tol), 130.43 and 130.47 (CH-*o*-Tol), 143.71 (CH-5), 144.68 and 144.93 (C-*p*-Tol), 154.00 (C-2), 166.44 and 166.58 (CO) ppm. IR (CCl_4): $\tilde{\nu}$ = 2926, 1725, 1613, 1269, 1178, 1104 cm^{-1}.

1β-[5-(Pyren-1-yl)furan-2-yl]-1,2-dideoxy-3,5-di-*O*-toluoyl-D-ribofuranose (6m): A solution of **8** (350 mg, 0.64 mmol), 1-bromopyrene (198 mg, 0.7 mmol), K_2CO_3 (354 mg, 2.56 mmol), and [PdCl$_2$dppf] (24 mg, 0.03 mmol) in anhydrous DMF (10 mL) under argon was stirred at 105 °C for 19 h. The mixture was diluted with satd. aqueous $NaHCO_3$ (50 mL) and extracted with EtOAc (3 × 10 mL) and washed with satd. aqueous NaCl (50 mL). The collected organic layers were dried with $MgSO_4$, and solvents were evaporated under vacuum. Products were isolated by column chromatography on silica gel, eluent gradient from hexane to hexane/EtOAc (19.5:0.5) to give **6m** (310 mg, 78%) as a yellow oil. HRMS (ESI): calcd. for $C_{41}H_{32}O_6Na$ [M + Na] 643.2091; found 643.2091. ^{1}H NMR (500 MHz, [D$_6$]acetone): δ = 2.10 and 2.43 (2 × s, 2 × 3 H, CH_3-Tol), 2.66 (ddd, J_{gem} = 13.8, $J_{2'a,1'}$ = 5.4, $J_{2'a,3'}$ = 1.4 Hz, 1 H, H-2′a), 2.95 (ddd, J_{gem} = 13.8, $J_{2'b,1'}$ = 10.6, $J_{2'b,3'}$ = 6.0 Hz, 1 H, H-2′b), 4.58 (br. ddd, $J_{4',5'b}$ = 4.4, $J_{4',5'a}$ = 3.9, $J_{4',3'}$ = 2.1 Hz, 1 H, H-4′), 4.63 (m, 2 H, H-5′), 5.50 (br. dd, $J_{1',2b}$ = 10.6, $J_{1',2'a}$ = 5.4 Hz, 1 H, H-1′), 5.77 (dddd, $J_{3',2'b}$ = 6.0, $J_{3',4'}$ = 2.1, $J_{3',2'a}$ = 1.4, $J_{3',1'}$ = 0.6 Hz, 1 H, H-3′), 6.79 (dd, $J_{3,4}$ = 3.3, $J_{3,1'}$ = 0.4 Hz, 1 H, H-3), 6.96 (m, 2 H, H-*o*-Tol), 6.99 (d, $J_{4,3}$ = 3.3 Hz, 1 H, H-4), 7.37 (m, 2 H, H-*o*-Tol), 7.89 and 8.03 (2 × m, 2 × 2 H, H-*o*-Tol), 8.09 (t, $J_{7,6}$ = $J_{7,8}$ = 7.6 Hz, 1 H, H-7-py), 8.17–8.23 (m, 3 H, H-4,5,9-py), 8.26–8.28 (m, 2 H, H-2,3-py), 8.27 and 8.31 (2 × dd, $J_{6,7}$ = 7.6, $J_{6,8}$ = 1.2, $J_{8,7}$ = 7.8, $J_{8,6}$ = 1.2 Hz, 2 H, H-6,8-py), 8.72 (d, $J_{10,9}$ = 9.3 Hz, 1 H, H-10-py) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]-acetone): δ = 21.30 and 21.61 (CH_3-Tol), 37.95 (CH_2-2′), 65.44 (CH_2-5′), 74.85 (CH-1′), 77.87 (CH-3′), 83.65 (CH-4′), 119.54 and 111.55 (CH-3, 4), 125.47 (C-10c-py), 125.61 (CH-10-py), 125.87 (C-10b-py), 125.89, 126.16 and 126.48 (CH-3,6,8-py), 126.49 (C-3a-py), 127.03 (CH-2-py), 127.29 (CH-7-py), 128.15 (C-*i*-Tol), 128.29 (CH-4 or 5 or 9-py), 128.29 (C-*i*-Tol), 128.46 (C-10a-py), 128.75 and 129.23 (CH-4 or 5 or 9-py), 129.80 and 130.10 (CH-*o*-Tol), 130.29 and 130.51 (CH-*o*-Tol), 131.82 (C-1-py), 132.05 and 132.44 (C-5a,8a-py), 144.37 and 144.97 (C-*p*-Tol), 154.45 (C-2), 154.85 (C-5), 166.53 and 166.66 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 3430, 1719, 1612, 1271, 1177, 1104, 752 cm^{-1}.

1β-[5-(Pyren-1-yl)furan-2-yl]-1,2-dideoxy-D-ribofuranose (7m): Prepared from **6m** (280 mg, 0.45 mmol) by the general procedure de-

scribed for the Zemplén deprotection. Careful reverse-phase flash chromatography (H_2O/MeOH) afforded **7m** (92 mg, 53%) as an orange powder; m.p. 166–170 °C. HRMS (ESI): calcd. for $C_{25}H_{20}O_4Na$ [M + Na] 407.1254; found 407.1254. ^1H NMR (500 MHz, [D$_6$]DMSO): δ = 2.13 (ddd, J_{gem} = 12.8, $J_{2'a,1'}$ = 5.9, $J_{2'a,3'}$ = 2.1 Hz, 1 H, H-2′a), 2.37 (ddd, J_{gem} = 12.8, $J_{2'b,1'}$ = 10.0, $J_{2'b,3'}$ = 5.7 Hz, 1 H, H-2′b), 3.48 (m, 2 H, H-5′), 3.83 (ddd, $J_{4',5'a}$ = 6.2, $J_{4',5'b}$ = 5.4, $J_{4',3'}$ = 2.4 Hz, 1 H, H-4′), 4.31 (m, 1 H, H-3), 4.80 (m, 1 H, OH-5′), 5.17 (m, 1 H, OH-3′), 5.20 (dd, $J_{1',2b}$ = 10.0, $J_{1',2'a}$ = 5.9 Hz, 1 H, H-1′), 6.73 (d, $J_{4,3}$ = 3.3 Hz, 1 H, H-4), 7.09 (d, $J_{3,4}$ = 3.3 Hz, 1 H, H-3), 8.11 (t, $J_{7,6}$ = $J_{7,8}$ = 7.6 Hz, 1 H, H-7-py), 8.19–8.24 (m, 2 H, H-4,5-py), 8.26 (d, $J_{9,10}$ = 9.4 Hz, 1 H, H-9-py), 8.28–8.37 (m, 4 H, H-2,3,6,8-py), 8.75 (d, $J_{10,9}$ = 9.4 Hz, 1 H, H-10-py) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ = 39.02 (CH_2-2′), 62.66 (CH_2-5′), 72.23 (CH-3′), 72.55 (CH-1′), 87.86 (CH-4′), 110.14 (CH-3), 111.12 (CH-4), 121.14 (C-10c-py), 124.59 (C-10b-py), 124.66 (CH-10-py), 125.14 (C-3a-py), 125.40, 125.42, 125.89 and 125.91 (CH-2,3,6,8-py), 126.61 (C-10a-py), 126.78 (CH-7-py), 127.53 and 127.93 (CH-4,5-py), 128.51 (CH-9-py), 130.50 (C-1-py), 130.64 and 131.20 (C-5a,8a-py), 152.89 (C-5), 155.15 (C-2) ppm. IR (KBr): $\tilde{\nu}$ = 3427, 1635, 1626, 1079, 1020, 843 cm^{-1}. $[\alpha]_D^{20}$ = –5.0 (*c* = 0.38, DMSO).

1β,1′β-(2,2′-Bifuran-5,5′-diyl)-bis(1,2-dideoxy-3,5-di-*O*-toluoyl-D-ribofuranose) (11a): A solution of **8** (330 mg, 0.60 mmol), **3** (332 mg, 0.66 mmol), K_2CO_3 (334 mg, 2.4 mmol), and [PdCl$_2$dppf] (22 mg, 0.03 mmol) in anhydrous DMF (10 mL) under argon was stirred at 105 °C for 17 h. The mixture was diluted with satd. aqueous $NaHCO_3$ (50 mL), extracted with EtOAc (3 × 10 mL) and washed with satd. aqueous NaCl (50 mL). The collected organic layers were dried with $MgSO_4$ and solvents were evaporated under vacuum. Products were isolated by column chromatography on silica gel, eluent gradient from hexane to hexane/EtOAc (19.5:0.5) to give the desired product **11a** (453 mg, 90%) as a colorless oil. HRMS (ESI): calcd. for $C_{50}H_{46}O_{12}Na$ [M + Na] 861.2881; found 861.2887. ^1H NMR (500 MHz, [D$_6$]acetone): δ = 2.40 and 2.42 (2 × s, 2 × 6 H, CH_3-Tol), 2.53 (ddd, J_{gem} = 13.8, $J_{2'a,1'}$ = 5.5, $J_{2'a,3'}$ = 1.4 Hz, 2 H, H-2′a), 2.75 (ddd, J_{gem} = 13.8, $J_{2'b,1'}$ = 10.6, $J_{2'b,3'}$ = 6.0 Hz, 2 H, H-2′b), 4.50 (td, $J_{4',5'a}$ = $J_{4',5'b}$ = 4.4, $J_{4',3'}$ = 1.9 Hz, 2 H, H-4′), 4.52 (dd, J_{gem} = 11.2, $J_{5'a,4'}$ = 4.4 Hz, 2 H, H-5′a), 4.60 (dd, J_{gem} = 11.2, $J_{5'b,4'}$ = 4.3 Hz, 2 H, H-5′b), 5.31 (br. dd, $J_{1',2b}$ = 10.5, $J_{1',2'a}$ = 5.4 Hz, 2 H, H-1′), 5.72 (br. dtd, $J_{3',2'b}$ = 6.0, $J_{3',2'a}$ = $J_{3',4'}$ = 1.7, $J_{3',1'}$ = 0.5 Hz, 2 H, H-3′), 6.40 (d, $J_{4,3}$ = 3.3 Hz, 2 H, H-4), 6.53 (dd, $J_{3,4}$ = 3.3, $J_{3,1'}$ = 0.4 Hz, 2 H, H-3), 7.31 and 7.35 (2 × m, 2 × 4 H, H-*o*-Tol), 7.97 and 7.99 (2 × m, 2 × 4 H, H-*o*-Tol) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]acetone): δ = 21.59 (CH_3-Tol), 37.74 (CH_2-2′), 65.28 (CH_2-5′), 74.51 (CH-1′), 77.73 (CH-3′), 83.54 (CH-4′), 106.88 (CH-4), 110.74 (CH-3), 128.25 and 128.32 (C-*i*-Tol), 130.08 and 130.09 (CH-*o*-Tol), 130.44 and 130.49 (CH-*o*-Tol), 144.71 and 144.95 (C-*p*-Tol), 147.02 (C-5), 153.71 (C-2), 166.45 and 166.56 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2925, 1725, 1613, 1269, 1178, 1103, 840 cm^{-1}.

1β,1′β-(2,2′-Thienylfuran-5,5′-diyl)bis(1,2-dideoxy-3,5-di-*O*-toluoyl-D-ribofuranose) (11b): A solution of **8** (170 mg, 0.31 mmol), **10** (176 mg, 0.34 mmol), K_2CO_3 (172 mg, 1.24 mmol), and [PdCl$_2$dppf] (12 mg, 0.02 mmol) in anhydrous DMF (10 mL) under argon was stirred at 105 °C for 17 h. The mixture was diluted with satd. aqueous $NaHCO_3$ (50 mL), extracted with EtOAc (3 × 10 mL) and washed with satd. aqueous NaCl (50 mL). The collected organic layers were dried with $MgSO_4$ and the solvents were evaporated under vacuum. Products were isolated by column chromatography on silica gel, eluent gradient from hexane to hexane/EtOAc (19.5:0.5) to give an inseparable mixture of the desired product **11b** (76% by NMR analysis) accompanied by homo-coupling products **11a** (8%) and **11c** (13%). The crude mixture was used for the next deprotection step. Compound **11b** (spectra recorded from the mixture): HRMS (ESI): calcd. for $C_{50}H_{46}O_{11}NaS$ [M + Na] 877.2653; found 877.2655. ^1H NMR (500 MHz, [D$_6$]-acetone, assignment of sugar signals for furan part A and thiophene part B): δ = 2.38, 2.40, 2.42 and 2.43 (4 × s, 4 × 3 H, CH_3-Tol), 2.43 (ddd, J_{gem} = 13.8, $J_{2'a,1'}$ = 10.7, $J_{2'a,3'}$ = 6.1 Hz, 1 H, B-2′a-H), 2.53 (ddd, J_{gem} = 13.8, $J_{2'a,1'}$ = 5.4, $J_{2'a,3'}$ = 1.4 Hz, 1 H, A-2′a-H), 2.67 (ddd, J_{gem} = 13.8, $J_{2'b,1'}$ = 5.2, $J_{2'b,3'}$ = 1.4 Hz, 1 H, B-2′b-H), 2.73 (ddd, J_{gem} = 13.8, $J_{2'b,1'}$ = 10.7, $J_{2'b,3'}$ = 6.0 Hz, 1 H, A-2′b-H), 4.48–3.54 (m, 2 H, A,B-4′-H), 4.54–4.68 (m, 2 × 2 H, A,B-5′-H), 5.30 (dd, $J_{1',2b}$ = 10.7, $J_{1',2'a}$ = 5.3 Hz, 1 H, A-1′-H), 5.53 (br. dd, $J_{1',2a}$ = 10.7, $J_{1',2'b}$ = 5.2 Hz, 1 H, B-1′-H), 5.68 (br. dt, $J_{3',2'a}$ = 6.1, $J_{3',2'b}$ = $J_{3',4'}$ = 1.8 Hz, 1 H, B-3′-H), 5.70 (br. dt, $J_{3',2'b}$ = 6.0, $J_{3',2'a}$ = $J_{3',4'}$ = 1.8 Hz, 1 H, A-3′-H), 6.50 (d, $J_{4,3}$ = 3.4 Hz, 1 H, furyl-4-H), 6.53 (d, $J_{3,4}$ = 3.3 Hz, 1 H, furyl-3-H), 7.04 (dd, $J_{3,4}$ = 3.7, $J_{3,1'}$ = 0.8 Hz, 1 H, thienyl-3-H), 7.06 (d, $J_{4,3}$ = 3.6 Hz, 1 H, thienyl-4-H), 7.29–7.38 (m, 8 H, H-*o*-Tol), 7.95–8.01 (m, 8 H, H-*o*-Tol) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]acetone): δ = 21.60, 21.61 and 21.63 (CH_3-Tol), 37.78 (CH_2-2′-A), 42.49 (CH_2-2′-B), 65.26 (CH_2-5′-A, B), 74.54 (CH-1′-A), 77.57 (CH-1′-B), 77.70 (CH-3′-A), 77.99 (CH-3′-B), 83.58 and 83.94 (CH-4′-A, B), 106.62 (CH-4-furyl), 111.13 (CH-3-furyl), 123.23 (CH-4-thienyl), 126.26 (CH-3-thienyl), 128.22, 128.24, 128.32 and 128.33 (C-*i*-Tol), 130.05, 130.07, 130.08 and 130.10 (CH-*o*-Tol), 130.44, 130.47 and 130.49 (CH-*o*-Tol), 133.60 (C-5-thienyl), 144.68, 144.71, 144.90, 144.96 and 144.98 (C-*p*-Tol, C-2-thienyl), 150.13 (C-5-furyl), 153.33 (C-2-furyl), 166.45, 166.47, 166.55 and 166.59 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 3429, 1719, 1612, 1271, 1104, 752 cm^{-1}.

1β,1′β-(2,2′-Bifuran-5,5′-diyl)bis(1,2-dideoxy-D-ribofuranose) (12a): Prepared from **11a** (435 mg, 0.52 mmol) by the general procedure described for Zemplén deprotection. **12a** (173 mg, 91%) was obtained as a white powder, which was crystallized from 2-propanol/heptane to give white crystals; m.p. 145–147 °C. HRMS (ESI): calcd. for $C_{18}H_{22}O_8Na$ [M + Na] 389.1207; found 389.1205. ^1H NMR (500 MHz, [D$_6$]DMSO): δ = 2.00 (ddd, J_{gem} = 12.8, $J_{2'a,1'}$ = 5.8, $J_{2'a,3'}$ = 2.1 Hz, 2 × 1 H, 2′a-H), 2.19 (ddd, J_{gem} = 12.8, $J_{2'b,1'}$ = 10.1, $J_{2'b,3'}$ = 5.9 Hz, 2 × 1 H, 2′b-H), 3.38 (m, 2 × 2 H, 5′-H), 3.73 (td, $J_{4',5'a}$ = $J_{4',5'b}$ = 5.7, $J_{4',3'}$ = 2.6 Hz, 2 × 1 H, 4′-H), 4.20 (br. dt, $J_{3',2'b}$ = 5.9, $J_{3',2'a}$ = $J_{3',4'}$ = 2.3 Hz, 2 × 1 H, 3′-H), 4.73 (br. s, 2 × 1 H, OH-5′-H), 5.01 (dd, $J_{1',2b}$ = 10.0, $J_{1',2'a}$ = 5.9 Hz, 2 × 1 H, 1′-H), 5.10 (br. s, 2 × 1 H, OH-3′-H), 6.51 (br. d, $J_{3,4}$ = 3.4 Hz, 2 × 1 H, 3-H), 6.59 (d, $J_{4,3}$ = 3.3 Hz, 2 × 1 H, 4-H) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ = 38.96 (CH_2-2′), 62.45 (CH_2-5′), 72.02 (CH-3′), 72.23 (CH-1′), 87.88 (CH-4′), 106.32 (CH-4), 109.41 (CH-3), 145.23 (C-5), 154.18 (C-2) ppm. IR (KBr): $\tilde{\nu}$ = 3392, 2894, 1635, 1335, 1035, 857 cm^{-1}. $C_{18}H_{22}O_8$ (366.4): C 59.01, H 6.05; found C 59.18, H 6.26. $[\alpha]_D^{20}$ = –16.7 (*c* = 0.29, DMSO).

1β,1′β-(2,2′-Thienylfuran-5,5′-diyl)bis(1,2-dideoxy-D-ribofuranose) (12b): Prepared from the crude mixture **11b/11a/11c** (240 mg) by the general procedure described for the Zemplén deprotection. Careful reverse-phase flash chromatography (H_2O/MeOH) afforded pure **12b** (60 mg, 54% overall yield from **8**, ca. 71% yield for the deprotection step) as a white powder, which was recrystallized from 2-propanol/heptane to give white crystals; m.p. 133–136 °C. HRMS (ESI): calcd. for $C_{18}H_{22}O_7SNa$ [M + Na] 405.0978; found 405.0977. ^1H NMR (500 MHz, [D$_6$]DMSO, assignment of sugar signals for furan part A and thiophene part B): δ = 1.93 (ddd, J_{gem} = 12.8, $J_{2'a,1'}$ = 10.1, $J_{2'a,3'}$ = 5.6 Hz, 1 H, B-2′a-H), 2.00 (ddd, J_{gem} = 12.8, $J_{2'a,1'}$ = 5.9, $J_{2'a,3'}$ = 2.1 Hz, 1 H, A-2′a-H), 2.13 (ddd, J_{gem} = 12.8, $J_{2'b,1'}$ = 5.5, $J_{2'b,3'}$ = 1.8 Hz, 1 H, B-2′b-H), 2.19 (ddd, J_{gem} = 12.8, $J_{2'b,1'}$ = 10.0, $J_{2'b,3'}$ = 5.8 Hz, 1 H, A-2′b-

H), 3.34–3.47 (2×m, 2×2 H, A-5′-H, B), 3.73 (br. td, $J_{4',5'a}$ = $J_{4',5'b}$ = 5.7, $J_{4',3'}$ = 2.5 Hz, 1 H, A or B-4′-H), 3.76 (ddd, $J_{4',5'a}$ = 6.1, $J_{4',5'b}$ = 5.0, $J_{4',3'}$ = 2.2 Hz, 1 H, A or B-4′-H), 4.18–4.22 (m, 2 H, A,B-3′-H), 4.76 and 4.77 (2×t, $J_{OH,5'a}$ = $J_{OH,5'b}$ = 5.7, $J_{OH,5'a}$ = $J_{OH,5'b}$ = 5.6 Hz, 2×1 H, A,B-5′-OH), 4.99 (dd, $J_{1',2b}$ = 10.0, $J_{1',2'a}$ = 5.9 Hz, 1 H, A-1′-H), 5.09 and 5.12 (2×s, $J_{OH,3'}$ = 4.1, $J_{OH,3'}$ = 3.9 Hz, 2×1 H, A, B-3′-OH), 5.23 (br. dd, $J_{1',2a}$ = 10.1, $J_{1',2'b}$ = 5.5 Hz, 1 H, B-1′-H), 6.49 (br. d, $J_{3,4}$ = 3.3 Hz, 1 H, furyl-3-H), 6.62 (d, $J_{4,3}$ = 3.3 Hz, 1 H, furyl-4-H), 7.01 (dd, $J_{3,4}$ = 3.7, $J_{3,1'}$ = 0.9 Hz, 1 H, thienyl-3-H), 7.16 (d, $J_{4,3}$ = 3.6 Hz, 1 H, thienyl-4-H) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ = 38.87 (CH_2-2′-A), 43.71 (CH_2-2′-B), 62.49 and 62.62 (CH_2-5′-A, B), 72.04, 72.24 and 72.51 (CH-1′-A, CH-3′-A, B), 75.34 (CH-1′-B), 87.83 (CH-4′-A), 88.03 (CH-4′-B), 105.98 (CH-4-furyl), 109.86 (CH-3-furyl), 122.43 (CH-4-thienyl), 125.38 (CH-3-thienyl), 131.89 (C-5-thienyl), 145.56 (C-2-thienyl), 148.48 (C-5-furyl), 153.72 (C-2-furyl) ppm. IR (KBr): $\tilde{\nu}$ = 3388, 2905, 2505, 1628, 1067, 787 cm^{-1}. $C_{18}H_{22}O_7S$ (382.4): C 56.53, H 5.80, S 8.38; found C 56.84, H 5.96, S 8.78. $[\alpha]_D^{20}$ = –15.1 (c = 0.27, DMSO).

UV/Vis and Fluorescence Spectroscopy: UV/Vis spectra were measured with a Varian CARY 100 Bio Spectrophotometer (ε is the molar extinction coefficient in L mol^{-1} cm^{-1}) in MeOH. The fluorescence measurements (in MeOH) were performed with a spectrofluorometer Aminco Bowman series 2 with 220–850 nm range, xenon source, excitation and emission wavelength scans, spectral bandwidth 1–16 nm, PMT detector, scan rate 3–6000 nm/min, Saya-Namioka grating monochromator. We used the comparative method of Williams et al.[24] to record the fluorescence quantum yield of a sample Φ_{SA} [a 10 mM solution of quinine sulfate in 0.1 M H_2SO_4 (in H_2O) was chosen as a standard: Φ_{ST} = 0.54]. Thus, the fluorescence quantum yield of a sample Φ_{SA} was calculated by the formula given in Equation (1), where the subscripts ST and SA denote standard and sample, respectively, Φ is the fluorescent quantum yield, IFI the integrated fluorescence intensity, *Grad* the gradient from the plot of IFI vs. absorbance A, and η the refractive index of the solvent.

$$\Phi_{SA} = \Phi_{ST}\left(\frac{\eta_{SA}}{\eta_{ST}}\right)^2\left(\frac{Grad_{SA}}{Grad_{ST}}\right) \text{ where } Grad = \left(\frac{IFI}{A}\right)$$

Single-Crystal X-ray Structure Analysis: The diffraction data for single-crystals of **12a** (colorless, 0.04×0.08×0.59 mm) were collected with an Xcalibur X-ray diffractometer with Cu-K_α (λ = 1.54180 Å) at 293 K. The structure was solved by direct methods with SIR92[25] and refined by full-matrix, least-squares methods based on F with CRYSTALS.[26] The hydrogen atoms were located in a difference map; those attached to carbon atoms were repositioned geometrically and then refined with riding constraints. All other atoms were refined anisotropically in both cases.

X-ray Crystal Data for 12a: $C_{18}H_{22}O_8$; monoclinic; space group $C2$; a = 25.615(5) Å, b = 6.0607(12) Å, c = 5.5592(14) Å, β = 101.12(3)°; V = 846.9(3) Å^3; Z = 2; M = 183.18; 5028 reflections measured, 966 independent reflections. Final R = 0.052, wR = 0.055, GoF = 1.143 for 786 reflections with $I > 2\sigma(I)$ and 119 parameters.

CCDC-777665 contains 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.

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

Acknowledgments

This work was supported by the Academy of Sciences of the Czech Republic (Z4 055 905), by the Ministry of Education (LC 512), by the Grant Agency of the ASCR (IAA400550902) and by Gilead Sciences, Inc.

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Received: May 20, 2010
Published Online: August 16, 2010

