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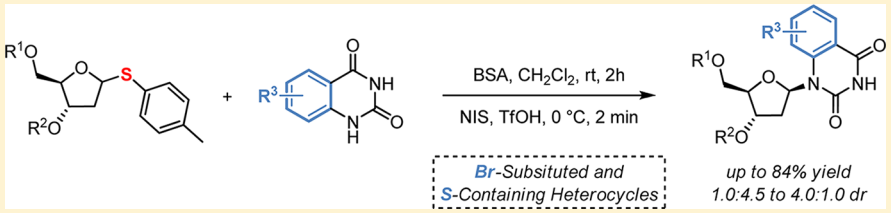
Stereoselective *N*-Glycosylation of 2-Deoxythioribosides for Fluorescent Nucleoside Synthesis

Guillaume Mata and Nathan W. Luedtke*

Institute of Organic Chemistry, University of Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

Supporting Information



ABSTRACT: An efficient method for the *N*-2-deoxyribosylation of modified nucleobases by 2-deoxythioriboside donors is reported. In the presence of an in situ silylated nucleobase, thioglycosides can be activated with NIS/HOTf to give nucleosides in high yields and with good β-selectivity. By tuning the protecting groups on the C3 and C5 hydroxyls, α/β ratios ranging from 1.0:4.0 to 4.5:1.0 can be obtained. This strategy is applicable to the synthesis of various nucleosides, including ring-expanded pyrimidine derivatives containing sulfur that have previously been reported in low yields. The utility of this approach is further demonstrated by the synthesis of fluorescent nucleosides analogues such as quinazoline and oxophenothiazine that should find broad utility in DNA-folding and recognition studies.

INTRODUCTION

Due to their broad spectrum of antiviral and antitumor activities, the synthesis of nucleoside analogues has been a key focus of medicinal chemistry for nearly 40 years.[1−3] More recently, modified nucleosides and nucleotides have emerged as tools for manipulating genetic processes,[4−6] as fluorescent probes for studying DNA folding and recognition,[7,8] and as metabolic labels for cellular DNA in vivo.[9,10] In many cases, these applications require synthetic nucleosides with ring-expanded nucleobases that exhibit unique photophysical and/or chemical reactivities.

Synthetic strategies that access 2′-β-deoxynucleosides typically involve *N*-glycosylation of ribofuranosyl derivatives. Stereoselectivity for the desired β-anomer can be achieved by using 1-*O*-acetylribofuranosyl derivatives that mediate a C2-*O*-ester neighboring group effect (Figure 1, route A). Using this approach, high stereoselectivity and good yields can be obtained, but subsequent 2′-deoxygenation procedures must be performed to obtain the desired 2′-D-deoxyribonucleosides. This requires two to four additional synthetic steps; therefore resulting in only low to moderate overall yields.[11−14] In addition, commonly used deoxygenation reactions that proceed via radical elimination are not compatible with haloheterocyclic derivatives.[15,16] An alternative approach for 2′-deoxygenation using a photosensitized electron-transfer reaction has recently been reported,[17,18] but this elegant strategy is incompatible with fluorescent nucleobases that act as electron acceptors.[19]

Glycosylation reactions that employ protected 2-deoxyribosides as glycosyl donors provide a more direct pathway to the synthesis of 2′-β-deoxynucleosides, but previously reported examples of *N*-2-deoxyribosylation suffer from modest yields and poor β-selectivity. The most commonly reported approach utilizes the commercially available 2-deoxy-3,5-di-*O*-*p*-toluoyl-α-D-*erythro*-pentofuranosyl chloride as the glycosyl donor (Figure 1, route B). Although it has been successfully used for the stereoselective glycosylation of purine analogues via an S_N2-type mechanism under basic conditions,[20,21] this donor suffers from a number of significant drawbacks for pyrimidine

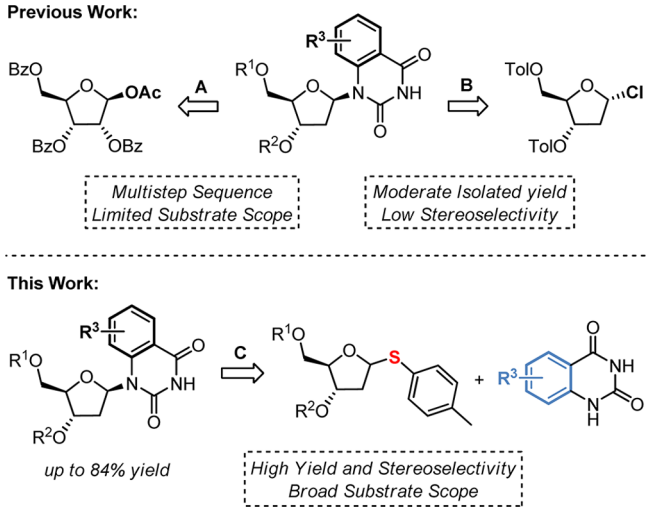


Figure 1. Strategies for stereoselective *N*-glycosylation of heterocyclic acceptors.

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derivatives under Lewis acidic conditions.[22,23] The long reaction times needed for weak nucleophiles can result in epimerization and the formation of α-nucleosides as the major product.[24,25] Its instability in solution can also result in low to moderate yields of the isolated coupling products, as well as inseparable α/β anomeric mixtures of nucleosides.[25−30] Moreover, direct modification of the C3 and C5 hydroxyl groups is not normally feasible due to the lability of the anomeric chloride. The development of new and efficient stereoselective reactions for constructing 2′-β-D-deoxyribonucleosidic linkages therefore remains an important goal.

In recent decades, extensive efforts in oligosaccharide chemistry have revealed a wide variety of efficient glycosylation reactions for the stereoselective synthesis of *O*-glycosidic bonds in complex carbohydrates. These include the utilization of classic glycosyl donors such as glycosyl bromides, chlorides, acetates, trichloroacetimidates, thioglycosides, and, more recently, the introduction of glycosyl sulfoxides, iodides, and phosphites.[31−35] Relatively few of these established methodologies have been applied for *N*-glycosylation reactions or in nucleoside synthesis. A small handful of 2-deoxyribose thioglycosides have been developed as glycosyl donors but have been used only for the *N*-glycosylation of natural pyrimidine nucleobases, which are known to exhibit facile reactions with a wide variety of glycosyl donors.[36−38] In contrast, unnatural nucleobase acceptors with extended surface areas are highly problematic *N*-glycosidic acceptors.[39]

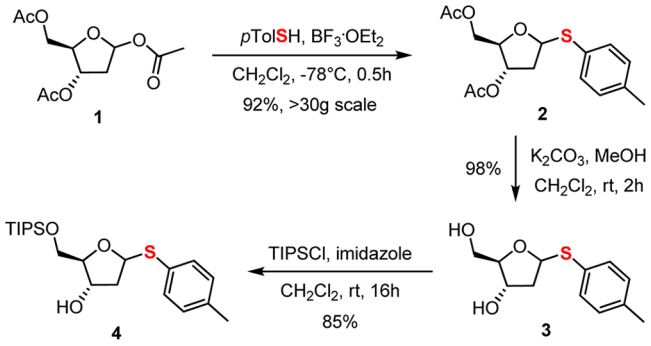
Given the growing importance of fluorescent 2′-deoxynucleosides,[7] we become interested in the development of a new 2-deoxyribose donor for robust β-selective *N*-glycosylation reactions in high yields. Here we report Vorbrüggen-type[40−42] *N*-2-deoxyribosilation of 2-deoxythioribosides by ring-expanded nucleobase analogues that exhibit limited solubility and poor nucleophilicity (Figure 1, route C). 6-Bromoquinazoline-2,4-(1*H*,3*H*)-dione was selected as an initial model for evaluating these *N*-glycosylation reactions, since quinazoline-2,4-(3*H*)-dione β-nucleosides are synthesized in low yield[25] and are of particular interest for further elaboration into fluorescent nucleoside analogs. Following optimization of the thioglycoside donor, a variety of other, highly challenging, nucleobases were glycosylated in moderate to high yields and good β-selectivity.

RESULTS

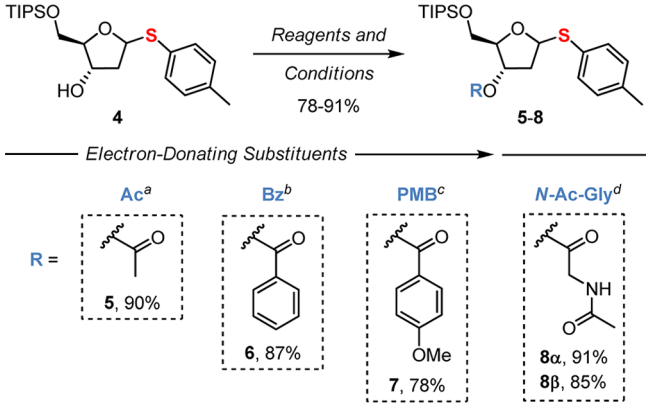
Synthesis of 2-Deoxythioriboside Donors. Our study started with the preparation of variable 2-deoxythioriboside donors by systematic variation of the functional groups at the C3 and C5 positions. Thioglycosides are especially amenable to this approach because of their high stability under a wide range of reaction conditions. To generate the thioether aglycon, commercially available 1,3,5-tri-*O*-acetyl-2-deoxy-D-ribose **1** was treated with 1.02 equiv of *p*-toluenethiol (*p*TolSH) and $BF_3{\cdot}Et_2O$ at −78 °C to afford thioglycoside donor **2** (Scheme 1). The resulting 2-deoxythioriboside was obtained in 92% yield on a 30 g scale as an anomeric mixture (α/β = 1.0:1.8). Deacetylation of **2** was then conducted using K_2CO_3 in a mixture of $MeOH/CH_2Cl_2$ to give diol **3** in 98% yield. Regioselective silylation of 5-OH with triisopropylsilyl chloride (TIPSCl) afforded compounds **4*β*** (56%) and **4*α*** (31%), which were readily separated using preparative scale silica gel chromatography.

Upon the basis of previous studies,[43] we anticipated that an ester group at C3 may provide anchimeric assistance, enhancing the β-selectivity of *N*-glycosylation. C3-*O*-Esterification reactions were therefore performed with the combined thioglycosides **4*β*** and **4*α*** to afford esters **5**−**7** (Scheme 2) that were obtained as anomeric mixtures (α/β = 1.0:1.8). Thioglycoside **5** was obtained in 90% yield by acetylation with Ac_2O, and thioglycosides **6** and **7** were obtained after treatment with benzoyl chloride (BzCl) or *p*-methoxybenzoyl chloride (PMBCl), in 87% and 78% yields, respectively. On the basis of previous studies by Zhang and co-workers,[44] we were interested in a possible neighboring group participation by an *N*-acetylglycine residue at the C3 position. Enantiopure thioglycosides **8*α*** and **8*β*** containing C3-*O*-*N*-acetylglycine were therefore prepared using *N*,*N*′-diisopropylcarbodiimide (DIC) as a coupling reagent.

Scheme 1. Formation of the Thioether Aglycon



Scheme 2. Synthesis of C3-Substituted 2-Deoxythioriboside Donors 5−8[a]



[a]Reagents and conditions: (a) Ac_2O, Et_3N, DMAP, MeCN, rt, 2 h; (b) BzCl, Et_3N, DMAP, pyridine, CH_2Cl_2, rt, 2 h; (c) PMBCl, Et_3N, DMAP, pyridine, CH_2Cl_2, rt, 16 h; (d) *N*-Ac-Gly-OH, DIC, DMAP, CH_2Cl_2, rt, 12 h.

On the basis of previous studies,[45] we also focused our attention on C3−5-*O*-silylated cyclic functional groups that can induce conformational restrictions and therefore influence stereoselectivity during glycosylation. C3−5-*O*-silylated thioglycosides **9** and **10** containing six- and eight-membered rings were therefore prepared from **3** in 83% and 93% yield, respectively (Scheme 3). Finally, in order to provide a direct comparison of differences in chemical reactivity between thioglycosides and the commonly used 2-deoxy-3,5-di-*O*-*p*-toluoyl-α-D-*erythro*-pentofuranosyl chloride, compound **11** was synthesized in 86% yield.

***N*-2-Deoxyribosilation of 2-Deoxythioriboside Donors.** With the 2-deoxythioriboside donors **2** and **5**−**11** in

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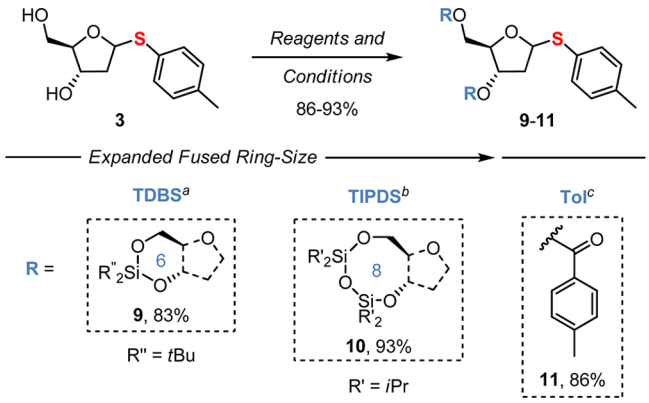
Scheme 3. Synthesis of C3,5-*O*-Silylated Six- and Eight-Membered Ring 2-Deoxythioriboside Donors 9−11[a]

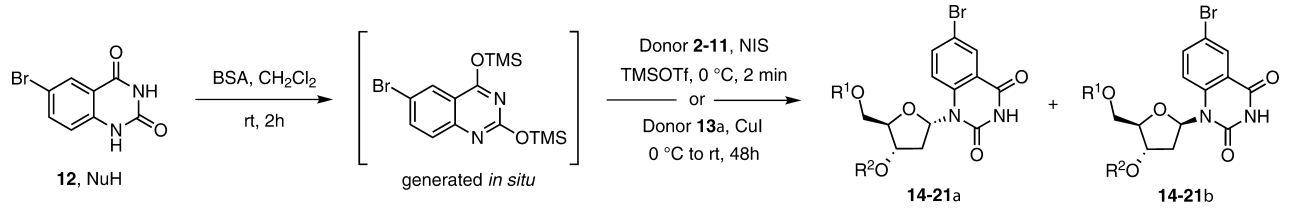


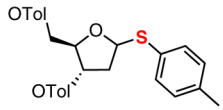
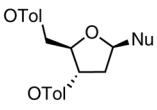
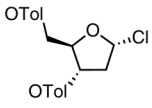
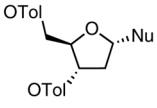
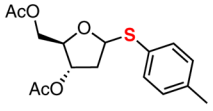
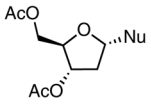
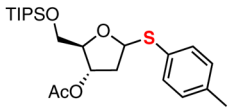
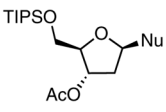
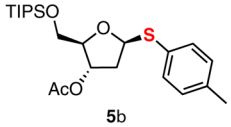
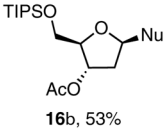
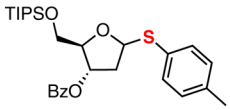
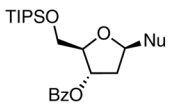
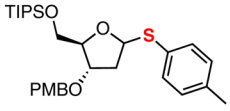
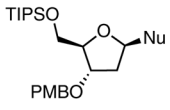
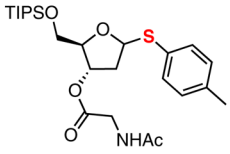
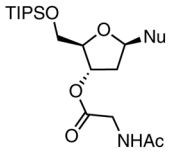
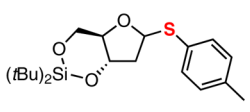
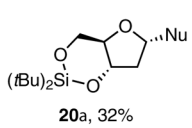
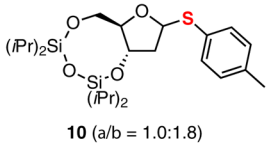
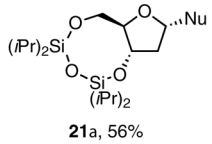
[a]Reagents and conditions: (a) tBu_2SiOTf_2, 2,6-lutidine, CH_2Cl_2/DMF, 0 °C to rt, 16 h; (b) TIPDSCl, pyridine, 0 °C to rt, 12 h; (c) *p*-toluoyl chloride, Et_3N, DMAP, pyridine, CH_2Cl_2, rt, 16 h.

hand, we investigated their reactivity in the *N*-glycosylation of 6-bromoquinazoline-2,4-(1*H*,3*H*)-dione (**12**, NuH). This reaction was carried out starting with in situ silylation of the acceptor nucleobase **12** (NuH, 1.2 equiv) with *N*,*O*-bis-(trimethylsilyl)acetamide (BSA, 2.5 equiv) in CH_2Cl_2 for 2 h, followed by addition of the 2-deoxythioriboside donor (**2**−**11**, 1.0 equiv) and sequential addition of *N*-iodosuccinimide (NIS, 1.2 equiv) and trimethylsilyl trifluoromethanesulfonate (TMSOTf, 0.6 equiv).[46] The isolated yields and α/β ratios (as determined by ^{1}H NMR of the crude reactions) of these reactions are summarized in Table 1.

When thioglycoside **11** (α/β = 1.0:1.8) was activated by a combination of NIS and TMSOTf, the desired coupling products **14*α*** and **14*β*** were isolated in 72% yield with the *β*-anomer as the major product (α/β = 1.0:1.6). While this diastereoisomeric mixture was not separable using chromatographic methods, the major *β*-nucleoside **14*β*** could be isolated via precipitation from EtOAc. The relative regio- and stereochemistry of **14*β*** was confirmed by 2D ^{1}H−^{13}C HMBC and ^{1}H−^{1}H ROESY experiments. Upon the basis of the α/β ratio and total isolated yield, the desired *β*-nucleoside **14*β*** was obtained in 43% yield. In comparison, the commonly used *α*-glycoside chloride **13*α*** was activated under standard conditions by CuI in a 48 h reaction to afford 58% yield of the expected

Table 1. *N*-2-Deoxyribosilation of 6-Bromoquinazoline-2,4-(1*H*,3*H*)-dione (12, NuH) by 2-Deoxythioriboside Donors



Entry	Donor	Major Product	Yield[a]	a/b[b]
1	 **11** (a/b = 1.0:1.8)	 **14b**, 43%	72%	1.0:1.6
2	 **13a**	 **14a**, 45%	58%	3.5:1.0
3	 **2** (a/b = 1.0:1.8)	 **15a**, 42%	76%	1.2:1.0
4	 **5** (a/b = 1.0:1.8)	 **16b**, 54%	84%	1.0:1.8
5	 **5b**	 **16b**, 53%	82%	1.0:1.8
6	 **6** (a/b = 1.0:1.8)	 **17b**, 51%	83%	1.0:1.6
7	 **7** (a/b = 1.0:1.8)	 **18b**, 50%	80%	1.0:1.7
8	 **8a** or **8b**	 **19b**, 41%	51%	1.0:4.0
9	 **9** (a/b = 1.0:1.8)	 **20a**, 32%	50%	1.8:1.0
10	 **10** (a/b = 1.0:1.8)	 **21a**, 56%	68%	4.5:1.0

[a]Isolated yield for both anomers. [b]Ratio determined by ^{1}H NMR analysis of the crude mixture.

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product, but in a highly α-selective fashion (α/β = 3.5:1.0). This is consistent with previous reports on *N*-glycosylation of quinazoline-2,4-(3*H*)-dione by **13α**,[25] where the β-nucleoside was obtained in only 13% yield. Similar poor yields for *N*-glycosylation of other nucleobase acceptors by **13α** have also been reported.[27,30]

The use of thioglycoside **2** (entry 3) afforded the coupling products **15α** and **15β** in a similar overall yield (76%) as thioglycoside **11**, but the β-selectivity was lost (α/β = 1.2:1.0). As compared to **2**, thioglycoside **5** exhibited enhanced β-selectivity (α/β = 1.0:1.8) and a slightly higher isolated yield of 84%. The introduction of a C5-*O*-TIPS group into thioglycoside **5** also enabled facile and quantitative separation of the α/β anomeric mixture from multigram reactions using silica gel chromatography (TLC ΔR_f = 0.2) to afford 54% isolated yield of the β-nucleoside **16β**, after only a 2 min reaction time. Consistent with an S_N1 pathway involving an oxocarbenium ion intermediate, enantiopure thioglycoside **5β** was submitted to the same reaction conditions and afforded the exact same anomeric ratio of nucleoside as thioglycoside **5** (α/β = 1.0:1.8).

The modest differences in yield and stereoselectivity exhibited by donor **5** versus **2** can be explained by the armed−disarmed concept, where the electron-withdrawing C5-*O*-acetyl group present in donor **2** is replaced by the electron-donating C5-*O*-TIPS group.[47] This change can "arm" the glycosyl donor by stabilizing the formation of the oxocarbenium ion intermediate (Figure 2). To further evaluate this

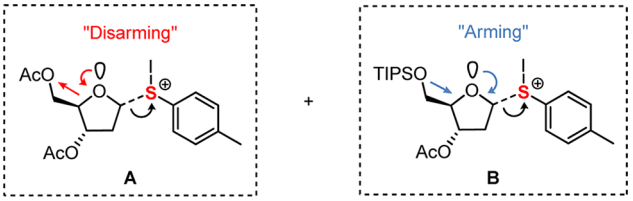

Figure 2. Arming and disarming effect in thioglycosides **2** and **5**.

concept in the context of 2′-deoxyribonucleoside synthesis, a competition experiment was conducted where a mixture of thioglycosides **2** (1 equiv) and **5** (1 equiv) competed in the same reaction mixture with a limited amount of the nucleobase (**12**, 1 equiv) and using an excess of activator (NIS, 3 equiv). Consistent with faster oxocarbenium ion formation by thioglycoside **5**, a 2-fold difference in product ratio was observed in the crude product mixture (**15**/**16** = 1.0:2.0).

Use of thioglycosides **6** and **7** furnished the expected products in high yields, 83% and 80%, respectively (entry 6 and 7). Contrary to our expectations,[43] a constant β-selectivity was observed for the benzoyl ester as well as for the more electron-donating *p*-methoxybenzoyl ester at the C3 position. These results suggest that simple C3-*O*-ester groups do not act as directing groups in these reactions. However, donors **8α** and **8β**, containing *N*-acetylglycine groups,[44] exhibited highly stereoselective formation of the β-anomer (α/β = 1.0:4.0), albeit with lower overall isolated yield of 51% under these reaction conditions.

In contrast to **8**, thioglycoside **9** containing the C3−5-*O*-silylated six-membered ring was found to be α-selective (α/β = 1.8:1.0, entry 9). In this reaction, the coupling products **20α** and **20β** were obtained in 50% yield, and unreacted starting material was recovered. More importantly, thioglycoside **10** containing the C3−5-*O*-silylated eight-membered ring gave the corresponding nucleosides **21α** and **21β** in 68% yield in a highly α-selective fashion (α/β = 4.5:1.0).

Scope of the *N*-2-Deoxyribosylation of Ring-Expanded Pyrimidine Nucleobases. Having indentified thioglycoside **5** as an excellent donor for high-yielding, β-selective *N*-2-deoxyribosylation of 6-bromoquinazoline-2,4-(1*H*,3*H*)-dione, we explored the scope of this reaction in constructing 2′-β-D-deoxyribonucleosidic linkages known to be highly challenging. *N*-Heterocyclic nucleobases **25**−**28** were therefore synthesized according to known procedures from their corresponding starting materials **34**−**37**. The corresponding β-nucleosides **31β**−**33β** have been shown to exhibit useful fluorescent properties upon incorporation into DNA.[48] However, all previous syntheses of these nucleosides have been achieved in low yields by using the α-glycoside chloride method for **31β** (isolated after three steps in 9%[24] and 3%[26,27]), the 2′-deoxygenation method for **32β** (isolated after five steps in 16%),[13] or the sodium salt method for **33β** (isolated after 2 steps in 14%).[30,39]

Table 2 summarizes our results for *N*-2-deoxyribosylation using thioglycoside donor **5**. Reactions with quinazoline-2,4-(1*H*,3*H*)-dione **24** and 5-methoxyquinazoline-2,4-(1*H*,3*H*)-dione **25** furnished the expected nucleosides in high yield, 83% and 80%, respectively, and with good β-selectivity (**29α**/**29β** = 1.0:1.8 and **30α**/**30β** = 1.0:1.7). Optimal yields were obtained by increasing the solubility of the heterocyclic nucleobase **26**−**28** by presilylation with hexamethyldisilazane (HMDS) at 110 °C before being subjected to the standard reaction conditions. Benzo[*g*]quinazoline-2,4-(1*H*,3*H*)-dione **26**, containing an even larger aromatic surface, gave the desired products (**31α**/**31β** = 1.0:1.8) in 70% yield.

Given the use of NIS for thioglycoside activation in these reactions, cross-reactivity with sulfur-containing groups was a particular concern. However, thieno[3,2-*d*]pyrimidine-2,4-dione **27** containing a thiophene group furnished the desired nucleosides in 73% yield and in good β-selectivity (**32α**/**32β** = 1.0:2.0). Furthermore, when thioether **28** was subjected to glycosylation with **5**, the desired nucleosides were obtained in 46% yield with the β-anomer as the major product (**33α**/**33β** = 1.0:2.5). The structure of **33β** was confirmed by 2D ^{1}H−^{1}H ROESY, where correlations between $H_{1'}$ and $H_{4'}$, $H_{1'}$ and $H_{2\alpha'}$, H_6 and $H_{1'}$, H_6 and $H_{2\beta'}$, as well as H_6 and $H_{5'}$, were observed (see Supporting Information).

DISCUSSION

Mechanistic Considerations. During 2-deoxyribosylation reactions involving thioglycoside donors, an oxocarbenium intermediate is formed by elimination of the activated thioether aglycon. Evidence for an S_N1 pathway is provided by the enantiopure thioglycoside **5β** (entry 5, Table 1), which gives the exact same anomeric ratio of nucleoside products as the 1.0:1.8 (α/β) mixture of thioglycoside **5** (entry 4, Table 1). The presence of an oxocarbenium intermediate is further supported by the scope of the glycosylation reaction described in Table 2, where thioglycoside **5** afforded roughly the same α/β mixtures, independent of the nucleobase structure. Reactions utilizing the common α-glycosyl chloride donor **13α**, in contrast, proceed via S_N2-type pathways, where competing anomerization reactions to the β-glycosyl chloride can result in α-nucleosides as the major product.[24]

In SN_1 reactions involving an 2-deoxyribofuranoside oxocarbenium intermediate, two conformations are possible, where C3 is situated either above or below the C2−C1−O−C4

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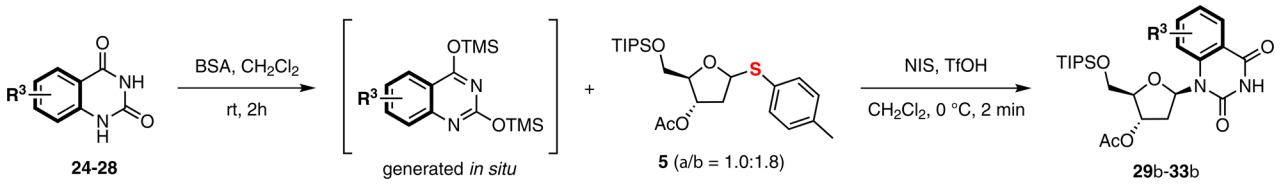
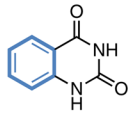
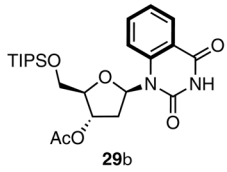
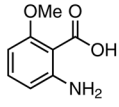
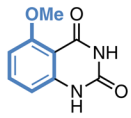
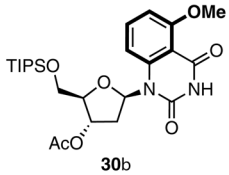
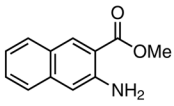
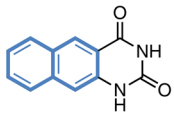
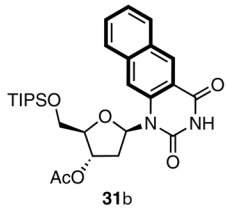
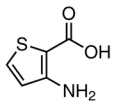
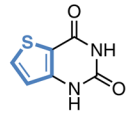
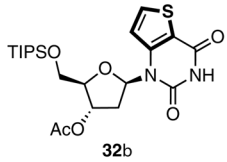
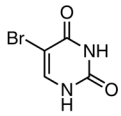
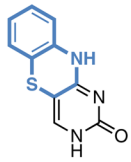
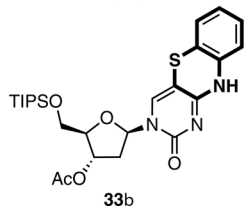
Table 2. Scope of the *N*-2-Deoxyribosylation of 2-Deoxythioriboside 5 with Ring-Expanded Pyrimidine Nucleobases



Entry	Precursor	Acceptor	Major Product	Yield[a]	a/b[b]	b-Yield
1	/	 **24**	 **29b**	83%	1.0:1.8	53%
2	 **34**	 **25** (1 step, 90%)	 **30b**	80%	1.0:1.7	50%[c]
3	 **35**	 **26**[d] (1 step, 82%)	 **31b**	70%	1.0:1.8	45%
4	 **36**	 **27**[d] (1 step, 70%)	 **32b**	73%	1.0:2.0	49%[c]
5	 **37**	 **28**[d] (2 steps, 22%)	 **33b**	46%	1.0:2.5	33%

[a]Isolated yield of the combined anomers. [b]Ratio determined by ^{1}H NMR analysis of the crude mixture. [c]The direct separation of the anomers was not realized. The yield was calculated from the isolated yield of the mixture and the α/β selectivity of the reaction. [d]The nucleobase was first presilylated in HMDS at 110 °C for 10 h (See the general procedure in the Experimental Section).

plane, to give the ^{3}E or E_3 conformer, respectively.[49,50] The group at C3 principally governs the lowest energy conformer, adopting a pseudoaxial orientation in the case of an alkoxy group. A useful model to explain diastereoselective reactions on such five-membered rings was proposed by Woerpel et al,[49,50] where a nucleophile preferentially attacks from the inside face of the oxocarbenium envelope to give the α-product. In contrast to this model, the NIS/TMSOTf promoted *N*-glycosylation of thioglycoside donors provides primarily the β-anomer. This can be observed with thioglycosides **5**−**7** but in particular with thioglycoside **8**, whose enhanced stereoselectivity is supported by a C1−3-anchimeric participation mechanism (Figure 3, intermediate A).[44] It is possible that, under our reaction conditions, a counterion occupies the inside face of the oxocarbenium envelope and/or the large steric bulk of the silylated nucleobase causes a change in preference from "inside" to "outside" attack of the nucleophile.

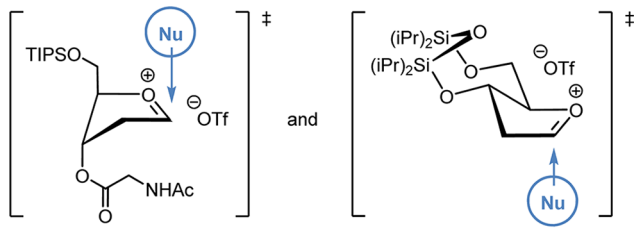


Figure 3. Plausible oxocarbenium ions for the preferred formation of α- and β-nucleosides.

Woerpel's and Ito's groups have reported that conformational perturbations present in fused rings can also mediate stereoelectronic effects.[45,51] For example, when C3−C4 are tethered, only a diequatorial oxocarbenium ion should be accessible (Figure 3, intermediate B).[51] The resulting ^{3}E

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conformer gives the opposite stereoselectivity of *N*-glycosylation as compared to the unconstrained thioglycosides, where **9** and **10** give α-anomers as primary products. These results suggest that the selectivity of the reaction is governed by the conformation of the oxocarbenium as well as anchimeric effects.

CONCLUSIONS

Here we report an efficient method for *N*-2-deoxyribosylation of challenging heterocyclic nucleobases. Thioglycosides provide a highly attractive alternative to the commonly used α-glycoside chloride for stereoselective synthesis of β-nucleosides. Thioglycoside donors can be activated in the presence of an in situ silylated nucleobase using NIS/HOTf as promoters. By tuning the protecting groups at the C3 and C5 hydroxyls, α/β ratios ranging from 1.0:4.0 to 4.5:1.0 were obtained. This method is compatible with highly challenging expanded nucleobases that were converted into 2′-deoxynucleosides in good yields and β-selectivity. 2-Deoxythioriboside coupling reactions tolerate a wide variety of functional groups in the nucleobase structure, including thiophene and thioether groups. Interestingly, all the coupling products where obtained after only 2 min reaction times with nearly the same α/β selectivity, suggesting a common, highly reactive oxocarbenium intermediate. As compared to other more commonly used methodologies, this approach can provide enhanced yields, β-selectivity, shorter reaction times, and a broader scope of nucleobase substrates. Thioglycosides therefore provide a powerful means for the synthesis of nucleoside analogues as new fluorescent probes and drug candidates that can expand our current understanding of DNA biology.

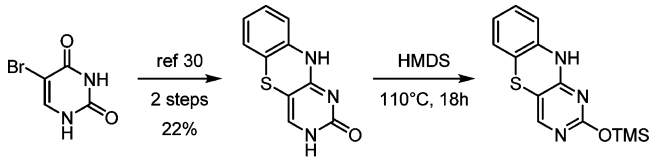
EXPERIMENTAL SECTION

General Information. Starting materials were obtained in the highest commercial grades and used without further purification. Commercially available 1,3,5-tri-*O*-acetyl-2-deoxy-D-ribose **1** was purified by flash column chromatography on silica gel (hexane/EtOAc, 6:4) prior to use. All reactions sensitive to moisture and/or air were carried out under an atmosphere of argon in dry, freshly distilled solvents under anhydrous conditions using oven-dried glassware. Commercially available dichloromethane (CH_2Cl_2) and acetonitrile (MeCN) were purified by a solvent purification system under an atmosphere of argon immediately prior to use. Commercially available anhydrous pyridine was used directly without further drying. Analytical thin-layer chromatography was performed on precoated 250 μm layer thickness silica gel 60 F_{254} plates. Visualization was performed by ultraviolet light and staining with a 15% H_2SO_4 solution in EtOH/H_2O. Flash column chromatography was performed using 40−63 μm silica gel using compressed air. ^{1}H NMR spectra were recorded on 400 and 500 MHz spectrometers; residual solvent peaks were used as internal standards: DMSO (quint, δ^H = 2.50 ppm), $CHCl_3$ (s, δ^H = 7.26 ppm). ^{13}C NMR spectra were recorded on 400 and 500 MHz spectrometers, with δ relative to DMSO (δ 40.5 ppm) or $CHCl_3$ (δ 77.23 ppm). Coupling constants (J) are reported in hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, m = multiplet, dd = doublet−doublet, ddd = doublet−doublet−doublet, dt = doublet−triplet, dq = doublet−quartet, br = broad. Mass spectra were obtained on a quadrupole ion trap instrument equipped with a atmospheric pressure ion (API) source. High-resolution electrospray mass spectra (HR-ESI MS) were recorded on a QTOF-MS instrument. Infrared spectra were recorded on a FTIR spectrometer.

General Procedure for the One-Pot BSA/NIS/TMSOTf-Mediated *N*-2-Deoxyribosylation of Thioglycoside Donor with Heterocyclic Acceptor (A). To a suspension of the heterocyclic acceptor (1.2 equiv) in CH_2Cl_2 (0.06 M) with activated molecular sieves (MS 4 Å, 2-fold mass excess as compared to the donor) was added BSA (2.5 equiv) dropwise over a 5 min period. The solution was stirred at room temperature for 2 h (complete dissolution was observed after 0.5 h). This solution was then cooled to 0 °C and the thioglycoside donor (1.0 equiv) in CH_2Cl_2 was added via cannula. After 5 min, NIS (1.2 equiv) and TMSOTf (0.6 equiv) or TfOH (0.4 equiv) were added (a deep red solution was formed) and the reaction mixture was stirred for 2 min at 0 °C. The reaction was then quenched with aq sat. $Na_2S_2O_3$ and extracted with aq sat. $NaHCO_3$ and CH_2Cl_2 (three times each). The combined organic layers were dried over $MgSO_4$, filtered, and evaporated in vacuo and subjected to column chromatography using silica gel (hexane/EtOAc). Prior to glycosylation of heterocyclic acceptors **26**−**28** (1.2 equiv), each nucleobase was first heated in HMDS (4 mL) with a catalytic amount of $(NH_4)_2SO_4$ at 110 °C for 10 h. The mixture was then evaporated and dried under vacuum and the residue used immediately.

Preparation of the Heterocyclic Acceptors. Following literature procedures, 5-methoxyquinazolin-2,4-(1*H*,3*H*)-dione[52] **25**, benzo[*g*]quinazoline-2,4-(1*H*,3*H*)-dione[26] **26**, and thieno[3,2-*d*]-pyrimidine-2,4-(1*H*,3*H*)-dione[12] **27** were prepared. 1,3-Diaza-2-oxophenothiazine **28** was also prepared according to a literature procedure[30] and was converted to the corresponding silylated compound **38** for full spectroscopic characterization (Scheme 4).

Scheme 4. Synthesis of the Silylated 1,3-Diaza-2-oxophenothiazine 38



37 28 38

1,3-Diaza-2-*O*-trimethylsilylphenothiazine (38). 1,3-Diaza-2-oxophenothiazine **28** (0.119 g, 0.547 mmol) was suspended in HMDS (4 mL) and stirred at 110 °C for 18 h. The solvent was evaporated and the residue was dried under vacuum to give compound **38** as a yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.14 (s, 1H), 6.99 (t, J_1 = 7.3 Hz, 1H), 6.93−6.85 (m, 2H), 6.58 (d, J_1 = 7.6 Hz, 1H), 0.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 160.3, 152.6, 137.8, 127.7, 126.8, 124.5, 117.4, 116.1, 104.2, 0.4; IR (neat) ν 3238, 1557, 1408, 1249, 1019, 848, 757 cm^{-1}. **28**: HR-ESI MS (m/z) [M + H]$^+$ calcd for $C_{10}H_8N_3OS$ 218.038 80, found 218.038 24.

p*-Tolyl-3,5-di-*O*-acetyl-1-thio-2-deoxy-α,β-D-ribofuranoside (2).** To a stirring solution of 1,3,5-tri-*O*-acetyl-2-deoxy-α,β-D-ribose **1** (30.34 g, 116.58 mmol) at −78 °C in CH_2Cl_2 (420 mL) was added *p*-TolSH (14.77 g, 118.91 mmol). After 5 min, $BF_3{\cdot}OEt_2$ (50.36 mL, 408.03 mmol) was added dropwise. The reaction mixture was stirred for 20 min and then quenched with aq sat. $NaHCO_3$. The resulting solution was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and evaporated in vacuo. The crude material was subjected to column chromatography on silica gel (hexane/EtOAc, 8:2) to give an inseparable isomer mixture of thioglycoside **2** (α/β = 1.0:1.8, 34.78 g, 92%) as a colorless oil: R_f (hexane/EtOAc, 7:3) 0.36; ^{1}H NMR (2D COSY, 500 MHz, $CDCl_3$) **2*α, δ 7.36−7.33 (m, 2H), 7.07−7.05 (m, 2H), 5.43 (dd, J_1 = 8.9 Hz, J_2 = 5.9 Hz, 1H, H_1), 5.09 (dt, J_1 = 6.1 Hz, J_2 = 1.7 Hz, 1H, H_3), 4.20−4.06 (m, 3H, H_5, H_5 and H_4), 2.31 (ddd, J_1 = 14.3, J_2 = 6.0 Hz, J_3 = 1.9 Hz, 1H, H_2), 2.27 (s, 3H), 2.20−2.14 (m, 1H, H_2), 2.00 (s, 3H), 1.98 (s, 3H); **2*β***, δ 7.36−7.33 (m, 2H), 7.07−7.05 (m, 2H), 5.60 (dd, J_1 = 7.8 Hz, J_2 = 3.0 Hz, 1H, H_1), 5.00 (ddd, J_1 = 7.6 Hz, J_2 = 4.4 Hz, J_3 = 3.0 Hz, 1H, H_3), 4.41 (q, J_1 = 4.5 Hz, 1H, H_4), 4.25 (dd, J_1 = 12.0 Hz, J_2 = 3.6 Hz, 1H, H_5), 4.20−4.14 (m, 1H, H_5), 2.73 (dt, J_1 = 15.5 Hz, J_2 = 7.8 Hz, 1H, H_2), 2.26 (s, 3H), 2.08−2.04 (m, 1H, H_2), 2.04 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 170.3, 170.2, 170.1, 137.6, 137.0, 132.7, 131.5, 131.3, 129.4, 87.5, 86.0, 82.8, 80.1, 75.3, 73.7, 63.7, 63.2, 39.0, 37.9, 20.91, 20.88, 20.77, 20.74, 20.61, 20.56; IR (neat) ν 2952, 1737, 1493, 1366, 1222, 1048, 1018,

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809 cm^{-1}; HR-ESI MS (m/z) [M + Na]$^+$ calcd for $C_{16}H_{20}O_5SNa$ 347.092 91, found 347.092 45.

***p*-Tolyl-1-thio-2-deoxy-α,β-D-ribofuranoside (3).** To a stirring solution of thioglycoside **2** (α/β = 1.0:1.8, 20.0 g, 61.65 mmol) in a mixture of MeOH/CH_2Cl_2 (202.5 mL, 4:1) was added K_2CO_3 (18.74 g, 135.64 mmol). The reaction mixture was stirred at room temperature for 2 h and then quenched with a solution of HCl (500 mL, 1 N). The mixture was extracted with $CHCl_3$ (3 × 400 mL), dried, filtered, and evaporated in vacuo. The crude material was subjected to column chromatography on silica gel (CH_2Cl_2/MeOH, 95:5) to give an inseparable isomer mixture of thioglycoside **3** (α/β = 1.0:1.8, 14.46 g, 98%) as a colorless oil: R_f (CH_2Cl_2/MeOH, 94:6) 0.25; ^{1}H NMR (2D COSY, 400 MHz, $CDCl_3$) **3α**, δ 7.41−7.39 (m, 2H), 7.14−7.12 (m, 2H), 5.64−5.61 (m, 1H, H_1), 4.40−4.37 (m, 1H, H_3), 4.00 (q, J_1 = 4.0 Hz, 1H, H_4), 3.70−3.68 (m, 1H, H_5), 3.60 (dd, J_1 = 12.0 Hz, J_2 = 4.3 Hz, 1H, H_5), 2.37−2.34 (m, 1H, H_2), 2.29 (s, 3H), 2.30 (s, 2H), 2.40−2.17 (m, 1H, H_2); **3β**, δ 7.41−7.39 (m, 2H), 7.14−7.12 (m, 2H), 5.63 (dd, J_1 = 7.4 Hz, J_2 = 3.4 Hz, 1H, H_1), 4.27 (ddd, J_1 = 7.5 Hz, J_2 = 4.6 Hz, J_3 = 3.8 Hz, 1H, H_3), 4.16 (q, J_1 = 4.0 Hz, 1H, H_4), 3.78 (dd, J_1 = 12.0 Hz, J_2 = 3.7 Hz, 1H, H_5), 3.70 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H, H_5), 2.64 (dt, J_1 = 14.2 Hz, J_2 = 7.4 Hz, 1H, H_2), 2.33 (s, 3H), 2.30 (s, 2H), 2.04 (dt, J_1 = 13.8 Hz, J_2 = 3.5 Hz, 1H, H_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 132.6, 132.3, 130.9, 130.0, 129.9, 88.3, 87.3, 86.5, 85.6, 72.8, 72.3, 62.9, 62.4, 42.1, 41.9, 21.32, 21.29; IR (neat) ν 3386, 2921, 2872, 1492, 1079, 1038, 808, 500 cm^{-1}; HR-ESI MS (m/z) [M + Na]$^+$ calcd for $C_{12}H_{16}O_3SNa$ 263.071 79, found 263.071 25.

***p*-Tolyl-1-thio-5-*O*-triisopropylsilyl-2-deoxy-α-D-ribofuranoside (4α) and *p*-Tolyl-1-thio-5-*O*-triisopropylsilyl-2-deoxy-β-D-ribofuranoside (4β).** To a stirring solution of thioglycoside **3** (α/β = 1.0:1.8, 14.0 g, 58.26 mmol) in CH_2Cl_2 (320 mL) were added TIPSCl (14.96 mL, 69.91 mmol) and imidazole (4.82 g, 69.91 mmol). The reaction mixture was stirred at room temperature for 16 h and then quenched with H_2O (400 mL). The resulting solution was extracted with CH_2Cl_2 (2 × 300 mL), and the combined organic layers were dried, filtered, and evaporated in vacuo. The crude material was subjected to column chromatography on silica gel (CH_2Cl_2/MeOH, 99:1) to give the separable isomers of thioglycoside **4α** and **4β** (19.64 g, 85%) as colorless oils. **4α**: R_f (CH_2Cl_2/MeOH, 96:4) 0.63; ^{1}H NMR (2D COSY, 400 MHz, $CDCl_3$) δ 7.39 (d, J_1 = 8.0 Hz, 2H), 7.10 (d, J_1 = 7.8 Hz, 2H), 5.55 (t, J_1 = 7.0 Hz, 1H, H_1), 4.39 (quint, J_1 = 3.4 Hz, 1H, H_3), 3.95−3.01 (m, 1H, H_4), 3.85 (dd, J_1 = 9.9 Hz, J_2 = 4.7 Hz, 1H, H_5), 3.50 (t, J_1 = 9.3 Hz, 1H, H_5), 2.30 (s, 3H), 2.35−2.29 (m, 1H, H_2), 2.23−2.16 (m, 1H, H_2), 2.07 (s, br, 1H), 1.10−1.05 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 132.7, 130.5, 129.7, 87.4, 86.1, 74.0, 64.7, 40.5, 21.2, 18.13, 18.11, 12.0; IR (neat) ν 3419, 2940, 2923, 2864, 1492, 1461, 1129, 1066, 996, 881, 807, 773, 680, 503 cm^{-1}; HR-ESI MS (m/z) [M + Na]$^+$ calcd for $C_{21}H_{36}O_3SSiNa$ 419.205 21, found 419.204 93. **4β**: R_f (CH_2Cl_2/MeOH, 96:4) 0.44; ^{1}H NMR (2D COSY, 400 MHz, $CDCl_3$) δ 7.40 (d, J_1 = 7.4 Hz, 2H), 7.11 (d, J_1 = 7.7 Hz, 2H), 5.64 (dd, J_1 = 7.3 Hz, J_2 = 3.4 Hz, 1H, H_1), 4.34−4.31 (m, 1H, H_3), 4.16 (q, J_1 = 4.2 Hz, 1H, H_4), 3.93 (dd, J_1 = 10.1 Hz, J_2 = 3.5 Hz, 1H, H_5), 3.70 (dd, J_1 = 10.1 Hz, J_2 = 5.8 Hz, 1H, H_5), 2.73−2.65 (m, 1H, H_2), 2.33 (s, br, 1H), 2.33 (s, 3H), 2.05 (dt, J_1 = 13.9 Hz, J_2 = 3.3 Hz, 1H, H_2), 1.08−1.05 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 132.2, 131.3, 129.8, 87.1, 85.8, 73.9, 64.4, 41.6, 21.3, 18.15, 18.12, 12.08, 12.06; IR (neat) ν 3419, 2940, 2923, 2864, 1492, 1461, 1127, 1062, 881, 806, 773, 681, 501 cm^{-1}; HR-ESI MS (m/z) [M + Na]$^+$ calcd for $C_{21}H_{36}O_3SSiNa$ 419.205 21, found 419.204 42.

***p*-Tolyl-3-*O*-acetyl-1-thio-5-*O*-triisopropylsilyl-2-deoxy-α,β-D-ribofuranoside (5).** To a stirring solution of thioglycosides **4α** and **4β** (α/β = 1.0:1.8, 2.05 g, 5.17 mmol) in MeCN (35 mL) were added Et_3N (0.86 mL, 6.20 mmol), Ac_2O (0.58 mL, 6.20 mmol), and DMAP (0.063 g, 0.52 mmol). The reaction mixture was stirred at room temperature for 2 h and then quenched with H_2O (50 mL). The resulting solution was extracted with CH_2Cl_2 (2 × 50 mL), and the combined organic layers were dried, filtered, and evaporated in vacuo. The crude material was subjected to column chromatography on silica gel (hexane/EtOAc, 93:7) to give an inseparable isomer mixture of thioglycoside **5** (α/β = 1.0:1.8, 2.04 g, 90%) as a colorless oil: R_f (hexane/EtOAc, 9:1) 0.38; ^{1}H NMR (2D COSY, 500 MHz, $CDCl_3$) **5α**, δ 7.41−7.39 (m, 2H), 7.12−7.10 (m, 2H), 5.47 (dd, J_1 = 7.7, J_2 = 3.5 Hz, 1H, H_1), 5.31−5.29 (m, 1H, H_3), 4.08 (t, J_1 = 5.1 Hz, 1H, H_4), 3.84−3.81 (m, 1H, H_5), 3.58 (dd, J_1 = 10.5 Hz, J_2 = 6.6 Hz, 1H, H_5), 2.33−2.31 (m, 1H, H_2), 2.32 (s, 3H), 2.26−2.21 (m, 1H, H_2), 2.04 (s, 3H), 1.07−1.04 (m, 21H); **5β**, δ 7.41−7.39 (m, 2H), 7.12−7.10 (m, 2H), 5.68 (dd, J_1 = 7.7 Hz, J_2 = 3.0 Hz, 1H, H_1), 5.24−5.22 (m, 1H, H_3), 4.32 (q, J_1 = 3.3 Hz, 1H, H_4), 3.93 (dd, J_1 = 10.8 Hz, J_2 = 3.3 Hz, 1H, H_5), 3.83 (dd, J_1 = 14.4 Hz, J_2 = 3.7 Hz, 1H, H_5), 2.81−2.77 (m, 1H, H_2), 2.32 (s, 3H), 2.11−2.09 (m, 1H, H_2), 2.09 (s, 3H), 1.07−1.04 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 170.3, 137.6, 136.9, 132.7, 132.3, 131.5, 130.5, 129.7, 129.6, 88.1, 86.4, 86.0, 84.4, 76.0, 74.9, 63.99, 63.91, 39.9, 38.4, 21.20, 21.16, 21.14, 18.10, 18.09, 18.05, 18.03, 12.0; IR (neat) ν 2942, 2892, 2866, 1741, 1240, 1065, 1017, 882, 773 cm^{-1}; HR-ESI MS (m/z) [M + Na]$^+$ calcd for $C_{23}H_{38}O_4SSiNa$ 461.215 78, found 461.215 09.

***p*-Tolyl-3-*O*-benzoyl-1-thio-5-*O*-triisopropylsilyl-2-deoxy-α,β-D-ribofuranoside (6).** To a stirring solution of thioglycoside **4** (α/β = 1.0:1.8, 0.405 g, 1.02 mmol) in CH_2Cl_2 (7.3 mL) were added pyridine (0.80 mL), Et_3N (0.20 mL, 1.43 mmol), BzCl (0.14 mL, 1.23 mmol), and DMAP (0.012 g, 0.10 mmol). The reaction mixture was stirred at room temperature for 2 h and then quenched with a solution of HCl (30 mL, 1 N). The resulting solution was extracted with CH_2Cl_2 (2 × 30 mL), and the combined organic layers were dried, filtered, and evaporated in vacuo. The crude material was subjected to column chromatography on silica gel (hexane/EtOAc, 95:5) to give an inseparable isomer mixture of thioglycoside **6** (α/β = 1.0:1.8, 0.445 g, 87%) as a colorless oil: R_f (hexane/EtOAc, 9:1) 0.50; ^{1}H NMR (2D COSY, 500 MHz, $CDCl_3$) **6α**, δ 8.02 (d, J_1 = 8.0 Hz, 2H), 7.59−7.54 (m, 1H), 7.47−7.43 (m, 4H), 7.13−7.10 (m, 2H), 5.57−5.53 (m, 2H, H_1 and H_3), 4.26 (t, J_1 = 5.7 Hz, 1H, H_4), 3.92−3.90 (m, 1H, H_5), 3.67 (dd, J_1 = 10.1 Hz, J_2 = 6.4 Hz, 1H, H_5), 2.47 (dd, J_1 = 14.2 Hz, J_2 = 5.7 Hz, 1H, H_2), 2.41−2.37 (m, 1H, H_2), 2.34 (s, 3H), 1.08−1.05 (m, 21H); **6β**, δ 8.12 (d, J_1 = 18.0 Hz, 2H), 7.59−7.54 (m, 1H), 7.47−7.43 (m, 4H), 7.13−7.10 (m, 2H), 5.78 (d, J_1 = 5.8 Hz, 1H, H_1), 5.57−5.53 (m, 1H, H_3), 4.49 (d, J_1 = 2.9 Hz, 1H, H_4), 4.03 (dd, J_1 = 10.9 Hz, J_2 = 3.0 Hz, 1H, H_5), 3.91 (dd, J_1 = 11.1 Hz, J_2 = 2.4 Hz, 1H, H_5), 2.90−2.84 (m, 1H, H_2), 2.32 (s, 3H), 2.32−2.30 (m, 1H, H_2), 1.08−1.05 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 166.0, 137.8, 137.1, 133.34, 133.32, 132.9, 132.5, 131.7, 130.6, 130.2, 130.1, 130.0, 129.84, 129.82, 129.81, 129.80, 128.6, 128.5, 88.7, 86.7, 86.2, 85.1, 76.7, 75.7, 64.15, 64.14, 40.2, 38.8, 21.3, 21.2, 18.22, 18.21, 18.16, 18.14, 12.1; IR (neat) ν 2942, 2892, 2866, 1719, 1271, 1110, 1066, 882, 773, 711 cm^{-1}; HR-ESI MS (m/z) [M + Na]$^+$ calcd for $C_{28}H_{40}O_4SSiNa$ 523.231 43, found 523.230 68.

***p*-Tolyl-3-*O*-*p*-methoxybenzoyl-1-thio-5-*O*-triisopropylsilyl-2-deoxy-α,β-D-ribofuranoside (7).** To a stirring solution of thioglycoside **4** (α/β = 1.0:1.8, 0.30 g, 0.76 mmol) in CH_2Cl_2 (4.0 mL) were added pyridine (0.4 mL), Et_3N (157 μL, 1.13 mmol), *p*-anisoyl chloride (PMBCl, 0.193 g, 1.13 mmol), and DMAP (0.018 g, 0.151 mmol). The reaction mixture was stirred at room temperature for 16 h and then quenched with a solution of HCl (20 mL, 0.5 N). The resulting solution was extracted with CH_2Cl_2 (2 × 20 mL), and the combined organic layers were dried, filtered, and evaporated in vacuo. The crude material was subjected to column chromatography on silica gel (hexane/EtOAc, 9:1) to give an inseparable isomer mixture of thioglycoside **7** (α/β = 1.0:1.8, 0.313 g, 78%) as a colorless oil: R_f (hexane/EtOAc, 9:1) 0.35; ^{1}H NMR (2D COSY, 400 MHz, $CDCl_3$) **7α**, δ 7.98 (d, J_1 = 9.0 Hz, 2H), 7.46 (d, J_1 = 8.0 Hz, 2H), 7.14−7.10 (m, 2H), 6.92−6.89 (m, 2H), 5.57 (dd, J_1 = 9.5 Hz, J_2 = 5.7 Hz, 1H, H_1), 5.52−5.49 (m, 1H, H_3), 4.27−4.25 (m, 1H, H_4), 3.93−3.88 (m, 1H, H_5), 3.84 (s, 3H), 3.68 (dd, J_1 = 10.5 Hz, J_2 = 6.2 Hz, 1H, H_5), 2.49 (dd, J_1 = 14.2 Hz, J_2 = 5.7 Hz, 1H, H_2), 2.39 (dd, J_1 = 9.5 Hz, J_2 = 5.8 Hz, 1H, H_2), 2.32 (s, 3H), 1.10−1.05 (m, 21H); **7β**, δ 8.08 (d, J_1 = 8.5 Hz, 2H), 7.45 (d, J_1 = 7.8 Hz, 2H), 7.11 (d, J_1 = 7.8 Hz, 2H), 6.94 (d, J_1 = 8.5 Hz, 2H), 5.78 (dd, J_1 = 7.7 Hz, J_2 = 2.2 Hz, 1H, H_1), 5.51 (d, J_1 = 7.1 Hz, 1H, H_3), 4.48 (d, J_1 = 2.9 Hz, 1H, H_4), 4.03 (dd, J_1 = 10.9 Hz, J_2 = 3.1 Hz, 1H, H_5), 3.91 (dd, J_1 = 10.9 Hz, J_2 = 3.1 Hz, 1H, H_5), 3.86 (s, 3H), 2.86 (quint, J_1 = 7.2 Hz, 1H, H_2), 2.32 (s, 3H),

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2.30−2.27 (m, 1H, H_2), 1.10−1.05 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.7, 163.6, 137.7, 136.9, 132.8, 132.5, 132.0, 131.8, 131.5, 130.6, 129.75, 129.72, 122.5, 122.4, 113.8, 113.7, 88.7, 86.6, 86.2, 85.2, 76.3, 75.3, 64.12, 64.10, 55.5, 40.2, 38.7, 21.25, 21.21, 18.17, 18.15, 18.11, 18.08, 12.0; IR (neat) ν 2937, 2865, 1712, 1605, 1273, 1254, 1166, 1098, 881, 769 cm^{-1}; HR-ESI MS (m/z) [M + Na]$^+$ calcd for $C_{29}H_{42}O_5SSiNa$ 553.241 99, found 553.240 99.

***p*-Tolyl-3-*O*-(*N*-acetyl)-glycyl-1-thio-5-*O*-triisopropylsilyl-2-deoxy-α-D-ribofuranoside (8α).** To a stirring solution of thioglycoside **4α** (0.50 g, 1.26 mmol) in CH_2Cl_2 (8.0 mL) were added *N*-acetylglycine (0.177 g, 1.51 mmol), DCI (0.24 mL, 1.51 mmol), and DMAP (0.01 g, 0.078 mmol). The reaction mixture was stirred at room temperature for 12 h and then quenched with aq sat. $NaHCO_3$ (40 mL). The resulting solution was extracted with CH_2Cl_2 (2 × 40 mL) and the combined organic layers were dried, filtered, and evaporated in vacuo. The residue was taken up in a mixture of hexane/EtOAc (5 mL, 10:1) and the precipitate was filtered off through cotton in a glass pipet. The resulting solution was evaporated and the crude material was subjected to column chromatography on silica gel (hexane/EtOAc, 1:1) to give thioglycoside **8α** (0.565 g, 91%) as a colorless oil: R_f (hexane/EtOAc, 1:1) 0.23; ^{1}H NMR (2D COSY, 400 MHz, $CDCl_3$) δ 7.37 (d, J_1 = 8.2 Hz, 2H), 7.09 (d, J_1 = 7.9 Hz, 2H), 6.29 (t, br, 1H), 5.43 (dd, J_1 = 9.4 Hz, J_2 = 5.8 Hz, 1H, H_1), 5.35 (d, J_1 = 5.6 Hz, 1H, H_3), 4.08−4.03 (m, 1H, H_4), 3.97 (ddd, AB system, J_1 = 27.5 Hz, J_2 = 18.3 Hz, J_3 = 5.2 Hz, 2H), 3.79 (dd, J_1 = 10.6 Hz, J_2 = 4.2 Hz, 1H, H_5), 3.53 (dd, J_1 = 10.6 Hz, J_2 = 6.6 Hz, 1H, H_5), 2.36−2.32 (m, 1H, H_2), 2.29 (s, 3H), 2.26−2.19 (m, 1H, H_2), 1.99 (s, 3H), 1.05−1.03 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 169.6, 137.8, 132.8, 130.1, 129.7, 86.3, 85.7, 77.4, 63.7, 41.5, 38.2, 23.5, 22.9, 18.07, 18.06, 11.9; IR (neat) ν 3333, 2941, 2891, 2865, 1750, 1656, 1541, 1463, 1381, 1193, 1064, 882, 683 cm^{-1}; HR-ESI MS (m/z) [M + Na]$^+$ calcd for $C_{25}H_{41}NO_5SSiNa$ 518.237 24, found 518.236 53.

***p*-Tolyl-3-*O*-(*N*-acetyl)-glycyl-1-thio-5-*O*-triisopropylsilyl-2-deoxy-β-D-ribofuranoside (8β).** To a stirring solution of **4β** (0.50 g, 1.26 mmol) in CH_2Cl_2 (8.0 mL) were added *N*-acetylglycine (0.177 g, 1.51 mmol), DCI (0.24 mL, 1.51 mmol), and DMAP (0.01 g, 0.078 mmol). The reaction mixture was stirred at room temperature for 12 h and then quenched with aq sat. $NaHCO_3$ (40 mL). The resulting solution was extracted with CH_2Cl_2 (2 × 40 mL), and the combined organic layers were dried, filtered, and evaporated in vacuo. The residue was taken up in a mixture of hexane/EtOAc (5 mL, 10:1) and the precipitate was filtered off through cotton in a glass pipet. The resulting solution was evaporated and the crude material was subjected to column chromatography on silica gel (hexane/EtOAc, 1:1) to give thioglycoside **8β** (0.53 g, 85%) as a colorless oil: R_f (hexane/EtOAc, 5:5) 0.25; ^{1}H NMR (2D COSY, 400 MHz, $CDCl_3$) δ 7.38 (d, J_1 = 8.2 Hz, 2H), 7.10 (d, J_1 = 8.0 Hz, 2H), 6.07 (s, br, 1H), 5.69 (dd, J_1 = 7.7 Hz, J_2 = 2.7 Hz, 1H, H_1), 5.33 (dt, J_1 = 6.8 Hz, J_2 = 2.2 Hz, 1H, H_3), 4.32 (q, J_1 = 3.1 Hz, 1H, H_4), 4.07 (dd, J_1 = 5.3 Hz, J_2 = 1.9 Hz, 2H), 3.92 (dd, J_1 = 10.9 Hz, J_2 = 3.2 Hz, 1H, H_5), 3.82 (dd, J_1 = 10.9 Hz, J_2 = 3.4 Hz, 1H, H_5), 2.77 (quint, J_1 = 7.5 Hz, 1H, H_2), 2.32 (s, 3H), 2.14 (dt, J_1 = 14.6 Hz, J_2 = 2.4 Hz, 1H, H_2), 2.04 (s, 3H), 1.07−1.04 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 169.8, 137.3, 131.9, 131.7, 129.8, 88.3, 84.7, 76.3, 63.8, 41.8, 39.8, 23.1, 21.2, 18.1, 18.0, 12.0; IR (neat) ν 3333, 2942, 2866, 1750, 1659, 1549, 1493, 1383, 1193, 1064, 882, 679 cm^{-1}; HR-ESI MS (m/z) [M + Na]$^+$ calcd for $C_{25}H_{41}NO_5SSiNa$ 518.237 24, found 518.236 81.

***p*-Tolyl-3,5-*O*-(di-*tert*-butylsilylene)-1-thio-2-deoxy-α,β-D-ribofuranoside (9).** To a stirring solution of thioglycoside **3** (α/β = 1.0:1.8, 0.150 g, 0.62 mmol) in a mixture of CH_2Cl_2/DMF (6 mL, 5:1) at 0 °C were added di-*tert*-butylsilylbistrifluoromethanesulfonate (tBu_2SiOTf_2, 0.24 mL, 0.75 mmol) and 2,6-lutidine (0.30 g, 2.81 mmol). The reaction mixture was stirred at room temperature for 16 h and then MeOH was added. The resulting solution was evaporated in vacuo and the residue was taken in CH_2Cl_2 (10 mL) and washed with H_2O and brine. The organic layer was dried, filtered, and evaporated in vacuo. The crude material was subjected to column chromatography on silica gel (hexane/EtOAc, 98:2) to give an inseparable isomer mixture of thioglycoside **9** (α/β = 1.0:1.8, 0.197 g, 83%) as a white solid: R_f (hexane/EtOAc, 98:2) 0.22; ^{1}H NMR (2D COSY, 400 MHz, $CDCl_3$) **9α**, δ 7.43−7.40 (m, 2H), 7.15−7.11 (m, 2H), 5.46 (dd, J_1 = 8.6 Hz, J_2 = 2.6 Hz, 1H, H_1), 4.33 (dd, J_1 = 9.3 Hz, J_2 = 4.8 Hz, 1H, H_4), 3.84−3.55 (m, 3H, H_3, H_5 and H_5), 2.42−2.34 (m, 2H, H_2 and H_2), 2.33 (s, 3H), 1.06 (s, 6H), 1.01 (s, 6H), 0.96 (s, 6H); **9β**, δ 7.43−7.40 (m, 2H), 7.15−7.11 (m, 2H), 5.51 (dd, J_1 = 8.0 Hz, J_2 = 7.1 Hz, 1H, H_1), 4.38 (dd, J_1 = 9.0 Hz, J_2 = 4.8 Hz, 1H, H_4), 4.04−3.98 (m, 1H, H_3), 3.92−3.82 (m, 2H, H_5 and H_5), 2.81 (dt, J_1 = 12.7 Hz, J_2 = 7.1 Hz, 1H, H_2), 2.32 (s, 3H), 1.87 (ddd, J_1 = 12.6 Hz, J_2 = 9.8 Hz, J_3 = 8.1 Hz, 1H, H_2), 1.06 (s, 6H), 1.01 (s, 6H), 0.96 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 137.6, 134.3, 131.9, 131.5, 129.84, 129.81, 129.0, 85.6, 84.7, 79.0, 75.7, 75.2, 74.9, 68.2, 67.7, 39.7, 39.2, 27.6, 27.5, 27.34, 27.33, 22.8, 22.6, 21.32, 21.28, 20.29, 20.20; IR (neat) ν 2962, 2933, 2887, 2859, 1473, 1127, 1065, 1050, 900, 827, 808, 753, 652, 418 cm^{-1}; HR-ESI MS (m/z) [M + Na]$^+$ calcd for $C_{20}H_{32}O_3SSiNa$ 403.173 91, found 403.173 38.

***p*-Tolyl-3,5-*O*-(tetraisopropylsiloxane-1,3-diyl)-1-thio-2-deoxy-α,β-D-ribofuranoside (10).** To a stirring solution of thioglycoside **3** (α/β = 1.0:1.8, 0.150 g, 0.62 mmol) in pyridine (0.8 mL) at 0 °C was added 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (TIPDSCl, 0.21 mL, 0.655 mmol). The reaction mixture was stirred at room temperature for 12 h and then MeOH was added. The resulting solution was diluted with CH_2Cl_2 (10 mL) and washed with H_2O and brine. The organic layer was dried, filtered, and evaporated in vacuo. The crude material was subjected to column chromatography on silica gel (hexane/EtOAc, 98:2) to give an inseparable isomer mixture of thioglycoside **10** (α/β = 1.0:1.8, 0.279 g, 93%) as a colorless oil: R_f (hexane/EtOAc, 96:4) 0.34; ^{1}H NMR (2D COSY, 400 MHz, $CDCl_3$) **10α**, δ 7.42−7.39 (m, 2H), 7.11−7.08 (m, 2H), 5.47 (dd, J_1 = 7.2 Hz, J_2 = 3.8 Hz, 1H, H_1), 4.41 (q, J_1 = 5.7 Hz, 1H, H_3), 4.07−3.90 (m, 2H, H_5 and H_5), 3.88−3.85 (m, 1H, H_4), 2.47−2.41 (m, 1H, H_2), 2.40−2.34 (m, 1H, H_2), 2.34 (s, 3H), 1.11−1.04 (s, 32H); **10β**, δ 7.42−7.39 (m, 2H), 7.11−7.08 (m, 2H), 5.53 (t, J_1 = 6.6 Hz, 1H, H_1), 4.31 (q, J_1 = 7.2 Hz, 1H, H_3), 4.00 (dd, J_1 = 11.8 Hz, J_2 = 2.8 Hz, 1H, H_5), 3.99−3.91 (m, 2H, H_4 and H_5), 2.74 (dt, J_1 = 15.4 Hz, J_2 = 7.6 Hz, 1H, H_2), 2.33 (s, 3H), 2.07−2.00 (m, 1H, H_2), 1.11−1.04 (s, 32H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 137.0, 133.1, 132.3, 131.53, 131.52, 130.2, 129.79, 129.70, 129.69, 85.9, 85.7, 85.5, 81.7, 74.3, 71.1, 65.4, 61.8, 42.0, 40.6, 21.27, 21.23, 17.74, 17.67, 17.65, 17.57, 17.56, 17.54, 17.55, 17.54, 17.50, 17.48, 17.46, 17.44, 17.32, 17.31, 17.22, 17.16, 17.15, 17.13, 13.6, 13.5, 13.3, 13.1; IR (neat) ν 2944, 2892, 2867, 1464, 1137, 1081, 1054, 1035, 999, 885, 776, 692 cm^{-1}; HR-ESI MS (m/z) [M + Na]$^+$ calcd for $C_{24}H_{42}O_4SSi_2Na$ 505.224 00, found 505.223 53.

***p*-Tolyl-3,5-di-*O*-*p*-toluoyl-1-thio-2-deoxy-α,β-D-ribofuranoside (11).** To a stirring solution of thioglycoside **3** (α/β = 1.0:1.8, 0.150 g, 0.62 mmol) in CH_2Cl_2 (4.5 mL) at 0 °C were added pyridine (0.5 mL), Et_3N (0.19 mL, 1.37 mmol), DMAP (0.031 g, 0.25 mmol), and *p*-toluoyl chloride (0.18 mL, 1.37 mmol). The reaction mixture was stirred at room temperature for 16 h and the color of the solution changed from orange to green. The resulting solution was diluted with CH_2Cl_2 (10 mL) and washed with HCl (10 mL, 1 N) and brine. The organic layer was dried, filtered, and evaporated in vacuo. The crude material was subjected to column chromatography on silica gel (hexane/EtOAc, 95:5 → 90:10) to give an inseparable isomer mixture of thioglycoside **11** (α/β = 1.0:1.8, 0.255 g, 86%) as a colorless oil: R_f (hexane/EtOAc, 9:1) 0.16; ^{1}H NMR (2D COSY, 400 MHz, $CDCl_3$) **11α**, δ 8.05−7.92 (m, 4H), 7.49−7.45 (m, 2H), 7.27−7.22 (m, 4H), 7.13−7.09 (m, 2H), 5.64 (dd, J_1 = 8.8 Hz, J_2 = 5.9 Hz, 1H, H_1), 5.53−5.49 (m, 1H, H_3), 4.56−4.48 (m, 3H, H_4, H_5 and H_5), 2.57−2.40 (m, 2H, H_2 and H_2), 2.42−2.40 (m, 6H), 2.29 (s, 3H); **10β**, δ 8.05−7.92 (m, 4H), 7.49−7.45 (m, 2H), 7.27−7.22 (m, 4H), 7.13−7.09 (m, 2H), 5.80 (dd, J_1 = 7.6 Hz, J_2 = 2.5 Hz, 1H, H_1), 5.53−5.49 (m, 1H, H_3), 4.79 (q, J_1 = 4.0 Hz, 1H, H_4), 4.65−4.61 (m, 2H, H_5 and H_5), 2.98−2.91 (m, 1H, H_2), 2.40−2.33 (m, 1H, H_2), 2.42−2.40 (m, 6H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 165.9, 144.2, 144.1, 143.8, 143.7, 138.0, 137.7, 137.4, 133.3, 132.23, 132.02, 132.01, 132.00, 131.7, 129.9, 129.87, 129.85, 129.84, 129.77, 129.76, 129.75, 129.4, 129.25, 129.23, 129.19, 129.17, 127.17, 127.15, 126.9, 126.8, 88.3, 86.4, 83.2, 81.3, 76.0, 74.80, 64.4, 64.0, 39.6, 38.5, 21.76, 21.74, 21.72, 21.16. IR (neat) ν 2358, 2338, 1716, 1608, 1268, 1177, 1104,

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906, 752, 726 cm^{-1}; HR-ESI MS (m/z) $[M + Na]^+$ calcd for $C_{28}H_{28}O_5SNa$ 499.155 52, found 499.154 90.

1′-(3′,5′-Di-*O*-*p*-toluoyl-2′-deoxy-α-D-ribofuranoside)-6-bromoquinazoline-2,4-(3*H*)-dione (14α) and 1′-(3′,5′-Di-*O*-*p*-toluoyl-2′-deoxy-β-D-ribofuranoside)-6-bromoquinazoline-2,4-(3*H*)-dione (14β). *Starting from Thioglycoside* ***11***. According to the general procedure A, the isomer mixture of nucleosides **14α** and **14β** (α/β = 1.0:1.6, 0.390 g, 72%) were obtained as off-white foams after column chromatography on silica gel (hexane/EtOAc, 6:4) using 6-bromoquinazoline-2,4-(1*H*,3*H*)-dione **12** (0.264 g, 1.10 mmol), BSA (0.56 mL, 2.28 mmol), thioglycoside **11** (α/β = 1.0:1.8, 0.435 g, 0.91 mmol), NIS (0.247 g, 1.10 mmol), and TMSOTf (100 μL, 0.55 mmol). The β-nucleoside **14β** was separated from **14α** via precipitation in EtOAc (two precipitations allowed complete removal of the α-nucleoside): R_f (hexane/EtOAc, 6:4) 0.26; ^{1}H NMR (2D COSY and ROESY, 500 MHz, $CDCl_3$) **14β**, δ 9.14 (s, 1H), 8.25 (d, J_1 = 2.5 Hz, 1H), 7.95 (d, J_1 = 1.5 Hz, 2H), 7.94 (d, J_1 = 1.5 Hz, 2H), 7.52 (d, J_1 = 9.0 Hz, 1H), 7.28−7.25 (m, 4H), 6.97 (dd, J_1 = 8.9 Hz, J_2 = 2.5 Hz, 1H), 6.86 (t, J_1 = 8.2 Hz, 1H, $H_{1'}$), 5.81 (ddd, J_1 = 8.2 Hz, J_2 = 4.8 Hz, J_3 = 3.2 Hz, 1H, $H_{3'}$), 4.91 (dd, J_1 = 12.2 Hz, J_2 = 2.9 Hz, 1H, $H_{5'}$), 4.66 (dd, J_1 = 12.3 Hz, J_2 = 4.0 Hz, 1H, $H_{5'}$), 4.45 (q, J_1 = 4.0 Hz, 1H, $H_{4'}$), 3.12 (dt, J_1 = 17.0 Hz, J_2 = 8.5 Hz, 1H, $H_{2'}$), 2.44 (s, 3H), 2.41 (s, 3H), 2.41−2.38 (m, 1H, $H_{2'}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 166.2, 160.5, 149.8, 144.6, 144.5, 138.5, 138.0, 131.3, 130.0, 129.9, 129.5, 129.4, 127.1, 126.5, 118.5, 118.2, 117.1, 84.4, 81.6, 73.5, 63.3, 34.4, 21.94, 21.92; IR (neat) ν 3218, 3073, 1703, 1603, 1483, 1465, 1311, 1266, 1177, 1093, 1019, 751, 729, 502 cm^{-1}; HR-ESI MS (m/z) $[M + Na]^+$ calcd for $C_{29}H_{25}BrN_2O_7Na$ 615.074 28, found 615.074 35.

Starting from α-Glycosyl Chloride ***13α***. To a suspension of 6-bromoquinazoline-2,4-(1*H*,3*H*)-dione **12** (0.720 g, 0.175 mmol) in CH_2Cl_2 (12 mL) with activated molecular sieves (MS 4 Å, 2-fold mass excess as compared to the donor) was added BSA (0.37 mL, 1.50 mmol) dropwise over a 5 min period. The solution was stirring at room temperature for 2 h (the complete dissolution was observed after 0.5 h). This solution was then cooled to 0 °C and the α-glycoside chloride **13α** (0.233 g, 0.60 mmol) in CH_2Cl_2 was added. After 5 min, CuI (0.137 g, 0.72 mmol) was added and the reaction mixture was stirred for 48 h at room temperature. The solution was then filtered through Celite, washed with aq sat. NaCl and extracted with CH_2Cl_2 (three times). The combined organic layers were dried over $MgSO_4$, filtered, and evaporated in vacuo. The crude material was subjected to column chromatography on silica gel (CH_2Cl_2/MeOH, 98.5:1.5) to give the inseparable isomers of nucleosides **14α** and **14β** (α/β = 3.5:1.0, 0.206 g, 58%) as an off-white foam: R_f (hexane/EtOAc, 6:4) 0.28; ^{1}H NMR (2D COSY and ROESY, 400 MHz, $CDCl_3$) **14α**, δ 9.38 (s, br, 1H), 8.32 (d, J_1 = 2.2 Hz, 1H), 7.96−7.94 (m, 4H), 7.68−7.62 (m, 2H), 7.29−7.23 (m, 4H), 7.02 (t, J_1 = 7.8 Hz, 1H, $H_{1'}$), 5.62 (quint, J_1 = 4.5 Hz, 1H, $H_{3'}$), 4.91 (q, J_1 = 3.7 Hz, 1H, $H_{4'}$), 4.70 (dd, J_1 = 12.0 Hz, J_2 = 4.6 Hz, 1H, $H_{5'}$), 4.55 (dd, J_1 = 12.0 Hz, J_2 = 3.6 Hz, 1H, $H_{5'}$), 3.02 (dt, J_1 = 16.3 Hz, J_2 = 8.2 Hz, 1H, $H_{2'}$), 2.78 (ddd, J_1 = 14.5 Hz, J_2 = 7.6 Hz, J_3 = 4.6 Hz, 1H, $H_{2'}$), 2.44 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) **14α** and **14β**, δ 166.4, 166.3, 166.2, 160.6, 160.5, 149.9, 149.8, 144.8, 144.6, 144.5, 144.2, 138.4, 138.3, 137.9, 137.8, 131.5, 131.3, 130.0, 129.92, 129.91, 129.90, 129.89, 129.87, 129.8, 129.5, 129.46, 129.44, 129.35, 129.32, 129.30, 129.2, 127.1, 126.8, 126.5, 118.6, 118.4, 118.19, 118.18, 117.1, 117.0, 85.6, 84.4, 81.8, 81.5, 75.2, 73.4, 64.9, 63.3, 34.8, 34.4, 21.92, 21.90, 21.89, 21.85; IR (neat) ν 3208, 1705, 1604, 1483, 1465, 1362, 1310, 1267, 1177, 1094, 1020, 750, 503 cm^{-1}; HR-ESI MS (m/z) $[M + Na]^+$ calcd for $C_{29}H_{25}BrN_2O_7Na$ 615.074 28, found 615.074 44.

1′-(3′,5′-Di-*O*-acetyl-2′-deoxy-α,β-D-ribofuranoside)-6-bromoquinazoline-2,4-(3*H*)-dione (15α and 15β). According to the general procedure A, the inseparable isomer mixture of nucleosides **15α** and **15β** (α/β = 1.2:1.0, 0.207 g, 76%) was obtained as an off-white foam after column chromatography on silica gel (hexane/EtOAc, 1:1) using 6-bromo-quinazoline-2,4-(1*H*,3*H*)-dione **12** (0.178 g, 0.74 mmol), BSA (0.38 mL, 1.54 mmol), thioglycoside **2** (α/β = 1.0:1.8, 0.20 g, 0.62 mmol), NIS (0.166 g, 0.74 mmol), and TMSOTf (66 μL, 0.37 mmol): R_f (hexane/EtOAc, 4:6) 0.33; ^{1}H NMR (2D COSY and ROESY, 400 MHz, $CDCl_3$) **15α**, δ 9.67 (s, br, 1H), 8.32 (d, J_1 = 2.5 Hz, 1H), 7.67 (dd, J_1 = 9.0 Hz, J_2 = 2.5 Hz, 1H), 7.53 (d, J_1 = 9.0 Hz, 1H), 6.77 (t, J_1 = 7.8 Hz, 1H, $H_{1'}$), 5.31−5.27 (m, 1H, $H_{3'}$), 4.62 (q, J_1 = 4.6 Hz, 1H, $H_{4'}$), 4.32 (dd, J_1 = 12.0 Hz, J_2 = 3.4 Hz, 1H, $H_{5'}$), 4.25 (dd, J_1 = 12.1 Hz, J_2 = 5.1 Hz, 1H, $H_{5'}$), 2.88−2.81 (m, 1H, $H_{2'}$), 2.66−2.60 (m, 1H, $H_{2'}$), 2.14−2.11 (m, 6H); **15β**, δ 9.69 (s, br, 1H), 8.31 (d, J_1 = 2.5 Hz, 1H), 7.70 (dd, J_1 = 9.0 Hz, J_2 = 2.5 Hz, 1H), 7.50 (d, J_1 = 9.0 Hz, 1H), 6.68 (t, J_1 = 7.8 Hz, 1H, $H_{1'}$), 5.41−5.37 (m, 1H, $H_{3'}$), 4.46−4.38 (m, 2H, $H_{5'}$ and $H_{5'}$), 4.20 (q, J_1 = 3.8 Hz, 1H, $H_{4'}$), 3.03 (dt, J_1 = 16.4 Hz, J_2 = 8.3 Hz, 1H, $H_{2'}$), 2.24−2.19 (m, 1H, $H_{2'}$), 2.14−2.11 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.65, 170.63, 170.5, 160.8, 160.7, 150.0, 149.8, 138.8, 138.4, 137.77, 137.75, 131.55, 131.53, 118.5, 118.0, 117.9, 117.2, 117.1, 85.3, 84.6, 81.4, 81.1, 74.1, 73.3, 64.2, 63.6, 34.4, 34.3, 21.07, 21.06, 21.04, 21.02; IR (neat) ν 3005, 1733, 1715, 1699, 1220, 1050, 772 cm^{-1}; HR-ESI MS (m/z) $[M + Na]^+$ calcd for $C_{17}H_{17}BrN_2O_7Na$ 463.011 68, found 463.011 08.

1′-(3′-*O*-Acetyl-5′-*O*-triisopropylsilyl-2′-deoxy-α-D-ribofuranoside)-6-bromoquinazoline-2,4-(3*H*)-dione (16α) and 1′-(3′-*O*-Acetyl-5′-*O*-triisopropylsilyl-2′-deoxy-β-D-ribofuranoside)-6-bromoquinazoline-2,4-(3*H*)-dione (16β). According to the general procedure A, the separable isomer mixture of nucleosides **16α** (0.766 g, 30%) and **16β** (1.352 g, 54%) was obtained as off-white foams after column chromatography on silica gel (hexane/EtOAc, 8:2 → 6:4) using 6-bromo-quinazoline-2,4-(1*H*,3*H*)-dione **12** (1.312 g, 5.44 mmol), BSA (2.77 mL, 11.34 mmol), thioglycoside **5** (α/β = 1.0:1.8, 1.99 g, 4.54 mmol), NIS (1.22 g, 5.44 mmol), and TMSOTf (0.49 mL, 2.72 mmol). **16α**: R_f (hexane/EtOAc, 7:3) 0.28; ^{1}H NMR (2D COSY and ROESY, 500 MHz, $CDCl_3$) δ 9.75 (s, br, 1H), 8.32 (d, J_1 = 1.6 Hz, 1H), 7.68 (dd, J_1 = 9.1 Hz, J_2 = 1.6 Hz, 1H), 7.64 (d, J_1 = 9.1 Hz, 1H), 7.05 (t, J_1 = 7.8 Hz, 1H, $H_{1'}$), 5.52 (d, J_1 = 8.5 Hz, 1H, $H_{3'}$), 4.38 (s, 1H, $H_{4'}$), 4.00 (d, J_1 = 9.7 Hz, 1H, $H_{5'}$), 3.94 (dd, J_1 = 10.8 Hz, J_2 = 2.1 Hz, 1H, $H_{5'}$), 2.87−2.81 (m, 1H, $H_{2'}$), 2.43 (ddd, J_1 = 14.6 Hz, J_2 = 7.6 Hz, J_3 = 3.8 Hz, 1H, $H_{2'}$), 2.14 (s, 1H), 1.11−1.08 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 160.9, 150.0, 138.1, 137.3, 131.3, 118.6, 116.8, 86.2, 84.8, 75.7, 65.7, 35.2, 21.2, 18.13, 18.11, 12.0; IR (neat) ν 3191, 3072, 2941, 2865, 2360, 2341, 1741, 1706, 1691, 1603, 1483, 1462, 1360, 1311, 1229, 1015, 882, 681, 503 cm^{-1}; HR-ESI MS (m/z) $[M + Na]^+$ calcd for $C_{24}H_{35}BrN_2O_6SiNa$ 577.134 55, found 577.133 45. **16β**: R_f (hexane/EtOAc, 7:3) 0.14; ^{1}H NMR (2D COSY, 500 MHz, $CDCl_3$) δ 9.39 (s, br, 1H), 8.32 (d, J_1 = 2.5 Hz, 1H), 7.87 (d, J_1 = 9.1 Hz, 1H), 7.62 (dd, J_1 = 9.1 Hz, J_2 = 2.5 Hz, 1H), 6.82 (dd, J_1 = 9.5 Hz, J_2 = 6.2 Hz, 1H, $H_{1'}$), 5.52−5.50 (m, 1H, $H_{3'}$), 4.11−4.03 (m, 3H, $H_{4'}$, $H_{5'}$ and $H_{5'}$), 2.85−2.81 (m, 1H, $H_{2'}$), 2.16−2.14 (m, 1H, $H_{2'}$), 2.14 (s, 3H), 1.21−1.07 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 160.8, 150.3, 138.3, 137.8, 131.2, 119.4, 118.6, 117.17 84.2, 84.0, 72.7, 62.6, 33.9, 21.1, 18.14, 18.13, 12.0; IR (neat) ν 3196, 3064, 2942, 2865, 2360, 2341, 1739, 1698, 1603, 1483, 1465, 1361, 1318, 1236, 1015, 881, 680, 504 cm^{-1}; HR-ESI MS (m/z) $[M + Na]^+$ calcd for $C_{24}H_{35}BrN_2O_6SiNa$ 577.134 55, found 577.133 35.

1′-(3′-*O*-Benzoyl-5′-*O*-triisopropylsilyl-2′-deoxy-α-D-ribofuranoside)-6-bromoquinazoline-2,4-(3*H*)-dione (17α) and 1′-(3′-*O*-Benzoyl-5′-*O*-triisopropylsilyl-2′-deoxy-β-D-ribofuranoside)-6-bromoquinazoline-2,4-(3*H*)-dione (17β). According to the general procedure A, the separable isomer mixture of nucleosides **17α** (0.075 g, 32%) and **17β** (0.120 g, 51%) was obtained as off-white foams after column chromatography on silica gel (hexane/EtOAc, 8:2 → 7:3) using 6-bromo-quinazoline-2,4-(1*H*,3*H*)-dione **12** (0.110 g, 0.455 mmol), BSA (0.23 mL, 0.948 mmol), thioglycoside **6** (α/β = 1.0:1.8, 0.190 g, 0.379 mmol), NIS (0.102 g, 0.455 mmol), and TMSOTf (41 μL, 0.228 mmol). **17α**: R_f (hexane/EtOAc, 7:3) 0.40; ^{1}H NMR (2D COSY, 400 MHz, $CDCl_3$) δ 9.35 (s, br, 1H), 8.34 (d, J_1 = 2.3 Hz, 1H), 8.08 (d, J_1 = 7.8 Hz, 2H), 7.78 (d, J_1 = 9.1 Hz, 1H), 7.64 (t, J_1 = 7.5 Hz, 1H), 7.59 (dd, J_1 = 9.1 Hz, J_2 = 2.4 Hz, 1H), 7.52 (t, J_1 = 7.7 Hz, 2H), 7.19 (t, J_1 = 7.8 Hz, 1H, $H_{1'}$), 5.77 (d, J_1 = 7.9 Hz, 1H, $H_{3'}$), 4.56 (s, 1H, $H_{4'}$), 4.15 (d, J_1 = 9.3 Hz, 1H, $H_{5'}$), 4.03 (dd, J_1 = 10.6 Hz, J_2 = 2.0 Hz, 1H, $H_{5'}$), 3.03−2.95 (m, 1H, $H_{2'}$), 2.62 (ddd, J_1 = 15.8 Hz, J_2 = 7.3 Hz, J_3 = 3.2 Hz, 1H, $H_{2'}$), 1.15−1.13 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 160.7, 150.0, 138.1, 137.5, 133.8,

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131.4, 129.7, 129.6, 128.8, 118.8, 118.7, 116.9, 86.4, 85.2, 76.6, 66.1, 35.4, 18.2, 18.1, 12.0; IR (neat) ν 3186, 3071, 2942, 2865, 1716, 1692, 1603, 1483, 1463, 1314, 1269, 1248, 1095, 773, 710 cm^{-1}; HR-ESI MS (m/z) $[M + Na]^+$ calcd for $C_{29}H_{37}BrN_2O_6SiNa$ 639.150 20, found 639.149 05. **17β**: R_f (hexane/EtOAc, 7:3) 0.27; ^1H NMR (2D COSY, 400 MHz, $CDCl_3$) δ 9.79 (s, br, 1H), 8.33 (d, J_1 = 2.1 Hz, 1H), 8.06 (d, J_1 = 8.0 Hz, 2H), 7.91 (d, J_1 = 9.1 Hz, 1H), 7.65 (dd, J_1 = 8.7 Hz, J_2 = 2.0 Hz, 1H), 7.58 (t, J_1 = 7.6 Hz, 1H), 7.45 (t, J_1 = 7.6 Hz, 2H), 6.92 (dd, J_1 = 9.3 Hz, J_2 = 6.3 Hz, 1H, $H_{1'}$), 5.79−5.76 (m, 1H, $H_{3'}$), 4.22−4.11 (m, 3H, $H_{4'}$, $H_{5'}$ and $H_{5'}$), 3.02−2.94 (m, 1H, $H_{2'}$), 2.30 (dd, J_1 = 15.3 Hz, J_2 = 6.6 Hz, 1H, $H_{2'}$), 1.16−1.11 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 160.8, 150.2, 138.5, 137.8, 133.5, 131.2, 129.9, 129.6, 128.6, 119.4, 118.6, 117.1, 84.3, 84.2, 73.3, 62.8, 34.2, 18.19, 18.17, 12.1; IR (neat) ν 3187, 3066, 2943, 2865, 1713, 1603, 1485, 1467, 1316, 1270, 1105, 773, 711 cm^{-1}; HR-ESI MS (m/z) $[M + Na]^+$ calcd for $C_{29}H_{37}BrN_2O_6SiNa$ 639.150 20, found 639.149 48.

1′-(3′-*O*-*p*-Methoxybenzoyl-5′-*O*-triisopropylsilyl-2′-deoxy-α-D-ribofuranoside)-6-bromoquinazoline-2,4-(3*H*)-dione (18α) and 1′-(3′-*O*-*p*-Methoxybenzoyl-5′-*O*-triisopropylsilyl-2′-deoxy-β-D-ribofuranoside)-6-bromoquinazoline-2,4-(3*H*)-dione (18β). According to the general procedure A, the separable isomer mixture of nucleosides **18α** (0.072 g, 30%) and **18β** (0.123 g, 50%) was obtained as off-white foams after column chromatography on silica gel (hexane/EtOAc, 8:2 → 6:4) using 6-bromoquinazoline-2,4-(1*H*,3*H*)-dione **12** (0.109 g, 0.452 mmol), BSA (0.23 mL, 0.942 mmol), thioglycoside **7** (α/β = 1.0:1.8, 0.20 g, 0.377 mmol), NIS (0.102 g, 0.452 mmol), and TMSOTf (62 μL, 0.226 mmol). **18α**: R_f (hexane/EtOAc, 7:3) 0.38; ^1H NMR (2D COSY, 400 MHz, $CDCl_3$) δ 8.69 (s, br, 1H), 8.33 (d, J_1 = 2.3 Hz, 1H), 8.02 (d, J_1 = 8.8 Hz, 2H), 7.78 (d, J_1 = 9.1 Hz, 1H), 7.61 (dd, J_1 = 9.1 Hz, J_2 = 2.4 Hz, 1H), 7.17 (t, J_1 = 7.8 Hz, 1H, $H_{1'}$), 6.99 (d, J_1 = 8.8 Hz, 2H), 5.73 (d, J_1 = 7.9 Hz, 1H, $H_{3'}$), 4.54 (s, 1H, $H_{4'}$), 4.14 (dd, J_1 = 10.8 Hz, J_2 = 1.8 Hz, 1H, $H_{5'}$), 4.03 (dd, J_1 = 10.8 Hz, J_2 = 2.1 Hz, 1H, $H_{5'}$), 3.91 (s, 3H), 3.00−2.92 (m, 1H, $H_{2'}$), 2.59 (ddd, J_1 = 14.9 Hz, J_2 = 7.5 Hz, J_3 = 3.2 Hz, 1H, $H_{2'}$), 1.15−1.12 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 164.1, 160.4, 149.8, 138.1, 137.6, 131.8, 131.4, 121.9, 118.9, 118.7, 116.9, 114.1, 86.5, 85.3, 76.3, 66.2, 55.7, 35.5, 18.21, 18.19, 12.0; IR (neat) ν 2960, 2940, 2866, 1715, 1604, 1462, 1258, 1095, 772, 418 cm^{-1}; HR-ESI MS (m/z) $[M + Na]^+$ calcd for $C_{30}H_{39}BrN_2O_7SiNa$ 669.160 76, found 669.159 57. **18β**: R_f (hexane/EtOAc, 7:3) 0.23; ^1H NMR (2D COSY, 400 MHz, $CDCl_3$) δ 8.94 (s, br, 1H), 8.33 (d, J_1 = 2.3 Hz, 1H), 8.01 (d, J_1 = 8.8 Hz, 2H), 7.92 (d, J_1 = 9.1 Hz, 1H), 7.65 (dd, J_1 = 9.0 Hz, J_2 = 2.3 Hz, 1H), 6.93 (d, J_1 = 8.8 Hz, 1H), 6.89 (dd, J_1 = 9.8 Hz, J_2 = 6.5 Hz, 1H, $H_{1'}$), 5.75−5.72 (m, 1H, $H_{3'}$), 4.19−4.12 (m, 3H, $H_{4'}$, $H_{5'}$ and $H_{5'}$), 3.88 (s, 3H), 2.99−2.91 (m, 1H, $H_{2'}$), 2.27 (dd, J_1 = 14.1 Hz, J_2 = 6.4 Hz, 1H, $H_{2'}$), 1.20−1.11 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 163.9, 160.5, 149.9, 138.5, 137.9, 132.0, 131.3, 122.0, 119.5, 118.6, 117.2, 113.9, 84.5, 84.3, 73.0, 62.9, 55.6, 34.3, 18.23, 18.21, 12.1; IR (neat) ν 2960, 2940, 2866, 1715, 1605, 1257, 1218, 1065, 772, 417 cm^{-1}; HR-ESI MS (m/z) $[M + Na]^+$ calcd for $C_{30}H_{39}BrN_2O_7SiNa$ 669.160 76, found 669.159 68.

1′-(3′-*O*-(*N*-Acetyl)-glycyl-5′-*O*-triisopropylsilyl-2′-deoxy-β-D-ribofuranoside)-6-bromoquinazoline-2,4-(3*H*)-dione (19β). According to the general procedure A, nucleoside **19β** (0.150 g, 41%) was obtained as an off-white foam after column chromatography on silica gel (hexane/EtOAc, 1:9 → 0:1) using 6-bromoquinazoline-2,4-(1*H*,3*H*)-dione **12** (0.175 g, 0.726 mmol), BSA (0.37 mL, 1.513 mmol), thioglycoside **8α** or **8β** (0.30 g, 0.605 mmol), NIS (0.164 g, 0.726 mmol), and TMSOTf (66 μL, 0.363 mmol). **19β**: R_f (hexane/EtOAc, 1:9) 0.24; ^1H NMR (2D COSY, 400 MHz, $CDCl_3$) δ 10.06 (s, 1H), 8.19 (d, J_1 = 2.5 Hz, 1H), 7.80 (d, J_1 = 9.1 Hz, 1H), 7.59 (dd, J_1 = 9.1 Hz, J_2 = 2.5 Hz, 1H), 6.73 (dd, J_1 = 9.3 Hz, J_2 = 6.2 Hz, 1H, $H_{1'}$), 6.45 (t, J_1 = 5.3 Hz, 1H), 5.59−5.56 (m, 1H, $H_{3'}$), 4.08 (d, J_1 = 5.4 Hz, 2H), 4.06−4.01 (m, 3H, $H_{4'}$, $H_{5'}$ and $H_{5'}$), 2.90−2.82 (m, 1H, $H_{2'}$), 2.19 (ddd, J_1 = 14.1 Hz, J_2 = 6.2 Hz, J_3 = 2.1 Hz, 1H, $H_{2'}$), 2.05 (s, 3H), 1.16−1.07 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 169.9, 160.8, 150.2, 138.5, 137.7, 131.0, 119.2, 118.4, 117.0, 84.1, 84.0, 74.0, 62.7, 41.6, 33.9, 22.9, 18.11, 18.09, 12.0; IR (neat) ν 3225, 2943, 2866, 1706, 1603, 1484, 1467, 1187 cm^{-1}; HR-ESI MS (m/z) $[M + Na]^+$ calcd for $C_{26}H_{38}BrN_3O_7SiNa$ 634.156 01, found 634.155 05.

1′-(3′,5′-*O*-(Di-*tert*-butylsilylene)-2′-deoxy-α,β-D-ribofuranoside)-6-bromoquinazoline-2,4-(3*H*)-dione (20α and 20β). According to the general procedure A, the inseparable isomer mixture of nucleosides **20α** and **20β** (α/β = 1.8:1.0, 0.164 g, 50%) was obtained as a white solid after column chromatography on silica gel (hexane/EtOAc, 8:2) using 6-bromoquinazoline-2,4-(1*H*,3*H*)-dione **12** (0.190 g, 0.788 mmol), BSA (0.40 mL, 1.642 mmol), thioglycoside **9** (α/β = 1.0:1.8, 0.350 g, 0.657 mmol), NIS (0.177 g, 0.788 mmol), and TMSOTf (71 μL, 0.394 mmol): R_f (hexane/EtOAc, 8:2) 0.23; ^1H NMR (2D COSY, 400 MHz, $CDCl_3$) **20α**, δ 9.77 (s, br, 1H), 8.35 (d, J_1 = 2.5 Hz, 1H), 7.75 (d, J_1 = 2.5 Hz, 1H), 7.29 (d, J_1 = 9.2 Hz, 1H), 6.45 (dd, J_1 = 9.2 Hz, J_2 = 6.4 Hz, 1H, $H_{1'}$), 4.50−4.33 (m, 3H, $H_{3'}$, $H_{4'}$ and $H_{5'}$), 3.92 (dd, J_1 = 9.7 Hz, J_2 = 8.9 Hz, 1H, $H_{5'}$), 3.09−3.02 (m, 1H, $H_{2'}$), 2.53 (dt, J_1 = 12.8 Hz, J_2 = 6.5 Hz, 1H, $H_{2'}$), 1.13−1.06 (m, 18H); **20β**, δ 9.80 (s, br, 1H), 8.33 (d, J_1 = 2.5 Hz, 1H), 7.73 (d, J_1 = 2.5 Hz, 1H), 7.37 (d, J_1 = 9.1 Hz, 1H), 6.39 (dd, J_1 = 9.6 Hz, J_2 = 3.6 Hz, 1H, $H_{1'}$), 4.81 (q, J_1 = 8.8 Hz, 1H, $H_{3'}$), 4.50−3.37 (m, 1H, $H_{5'}$), 4.10 (t, J_1 = 10.4 Hz, 1H, $H_{5'}$), 3.71 (ddd, J_1 = 10.4 Hz, J_2 = 8.9 Hz, J_3 = 5.0 Hz, 1H, $H_{4'}$), 2.90 (ddd, J_1 = 6.5 Hz, J_2 = 3.5 Hz, J_3 = 2.1 Hz, 1H, $H_{2'}$), 2.32−2.28 (m, 1H, $H_{2'}$), 1.13−1.06 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 161.0, 149.6, 149.1, 139.9, 139.7, 138.18, 138.15, 131.7, 131.5, 118.3, 118.2, 117.1, 116.9, 116.3, 116.5, 84.9, 84.2, 78.4, 77.6, 76.2, 75.5, 68.2, 67.5, 35.8, 34.4, 27.7, 27.6, 27.4, 27.3, 22.85, 22.82, 20.4, 20.3; IR (neat) ν 2967, 2934, 2893, 2859, 1700, 1603, 1472, 1316, 1052, 826, 772, 749, 426 cm^{-1}; HR-ESI MS (m/z) $[M + Na]^+$ calcd for $C_{21}H_{29}BrN_2O_5SiNa$ 519.092 68, found 519.091 74.

1′-(3′,5′-*O*-(Tetraisopropylsiloxane-1,3-diyl)-2′-deoxy-α-D-ribofuranoside)-6-bromoquinazoline-2,4-(3*H*)-dione (21α). According to the general procedure A, the nucleosides **21α** (0.139 g, 56%) was obtained as an off-white foam after column chromatography on silica gel (hexane/EtOAc, 9:1 → 8:2) using 6-bromoquinazoline-2,4-(1*H*,3*H*)-dione **12** (0.120 g, 0.497 mmol), BSA (0.26 mL, 1.035 mmol), thioglycoside **21** (α/β = 1.0:1.8, 0.200 g, 0.414 mmol), NIS (0.112 g, 0.497 mmol), and TMSOTf (45 μL, 0.248 mmol). **21α**: R_f (hexane/EtOAc, 8:2) 0.23; ^1H NMR (2D COSY and ROESY, 500 MHz, $CDCl_3$) δ 9.53 (s, br, 1H), 8.34 (d, J_1 = 2.5 Hz, 1H), 7.75 (dd, J_1 = 9.1 Hz, J_2 = 2.5 Hz, 1H), 7.49 (d, J_1 = 9.1 Hz, 1H), 6.68 (dd, J_1 = 9.8 Hz, J_2 = 6.6 Hz, 1H, $H_{1'}$), 4.69 (q, J_1 = 7.5 Hz, 1H, $H_{3'}$), 4.29 (sext, J_1 = 3.6 Hz, 1H, $H_{4'}$), 4.02 (dd, J_1 = 12.1 Hz, J_2 = 3.6 Hz, 1H, $H_{5'}$), 3.88 (dd, J_1 = 12.1 Hz, J_2 = 7.0 Hz, 1H, $H_{5'}$), 2.86−2.79 (m, 1H, $H_{2'}$), 2.57−2.52 (m, 1H, $H_{2'}$), 1.11−1.04 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 150.1, 138.5, 137.9, 131.5, 118.6, 117.9, 117.0, 84.3, 84.1, 72.9, 63.5, 36.3, 17.7, 17.62, 17.60, 17.5, 17.4, 17.3, 17.2, 17.1, 13.6, 13.4, 13.1, 12.7, IR (neat) ν 2943, 2867, 1708, 1603, 1483, 1465, 1315, 1143, 1118, 1091, 885, 774, 705 cm^{-1}; HR-ESI MS (m/z) $[M + Na]^+$ calcd for $C_{25}H_{39}BrN_2O_6Si_2Na$ 621.142 77, found 621.142 73.

1′-(3′-*O*-Acetyl-5′-*O*-triisopropylsilyl-2′-deoxy-α-D-ribofuranoside)quinazoline-2,4-(3*H*)-dione (29α) and 1′-(3′-*O*-Acetyl-5′-*O*-triisopropylsilyl-2′-deoxy-β-D-ribofuranoside)-quinazoline-2,4-(3*H*)-dione (29β). According to the general procedure A, the separable isomer mixture of nucleosides **29α** (0.065 g, 30%) and **29β** (0.116 g, 53%) was obtained as off-white foams after column chromatography on silica gel (hexane/EtOAc, 8:2 → 6:4) using quinazoline-2,4-(1*H*,3*H*)-dione **24** (0.089 g, 0.547 mmol), BSA (0.28 mL, 1.14 mmol), thioglycoside **5** (α/β = 1.0:1.8, 0.20 g, 0.456 mmol), NIS (0.113 g, 0.502 mmol), and HOTf (16 μL, 0.182 mmol). **29α**: R_f (hexane/EtOAc, 7:3) 0.29; ^1H NMR (2D COSY and ROESY, 400 MHz, $CDCl_3$) δ 9.17 (s, br, 1H), 8.22 (dd, J_1 = 7.9 Hz, J_2 = 1.6 Hz, 1H), 7.73 (d, J_1 = 7.8 Hz, 1H), 7.64−7.60 (m, 1H), 7.29−7.25 (m, 1H), 7.05 (t, J_1 = 7.8 Hz, 1H, $H_{1'}$), 5.53 (ddd, J_1 = 8.5 Hz, J_2 = 4.0 Hz, J_3 = 2.5 Hz, 1H, $H_{3'}$), 4.42 (d, J_1 = 2.4 Hz, 1H, $H_{4'}$), 4.01 (dd, J_1 = 10.8 Hz, J_2 = 2.5 Hz, 1H, $H_{5'}$), 3.96 (dd, J_1 = 10.8 Hz, J_2 = 2.8 Hz, 1H, $H_{5'}$), 2.87−2.80 (m, 1H, $H_{2'}$), 2.54 (ddd, J_1 = 14.5 Hz, J_2 = 7.6 Hz, J_3 = 4.0 Hz, 1H, $H_{2'}$), 2.14 (s, 3H), 1.16−1.08 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 161.9, 150.2, 139.3, 134.6, 129.0, 123.7, 117.0, 116.7, 86.1, 84.6, 75.7, 65.6, 35.1, 21.2, 18.16, 18.14, 12.0; IR (neat) ν 3210, 3065, 2942, 2856, 2363, 2363, 1704, 1687, 1609, 1483, 1386, 1313, 1231, 772, 686 cm^{-1}; HR-ESI MS (m/z) $[M + Na]^+$ calcd for $C_{24}H_{36}N_2O_6SiNa$ 499.22403, found

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499.22307. **29β**: R_f (hexane/EtOAc, 7:3) 0.22; ^{1}H NMR (2D COSY and ROESY, 400 MHz, $CDCl_3$) δ 9.54 (s, br, 1H), 8.22 (dd, J_1 = 7.9 Hz, J_2 = 1.6 Hz, 1H), 7.95 (d, J_1 = 8.6 Hz, 1H), 7.60−7.56 (m, 1H), 7.28−7.25 (m, 1H), 6.85 (dd, J_1 = 9.5 Hz, J_2 = 6.7 Hz, 1H, $H_{1'}$), 5.54 (ddd, J_1 = 7.9 Hz, J_2 = 4.1 Hz, J_3 = 2.2 Hz, 1H, $H_{3'}$), 4.09−4.03 (m, 3H, $H_{4'}$, $H_{5'}$ and $H_{5''}$), 2.97−2.89 (m, 1H, $H_{2''}$), 2.14 (dd, J_1 = 6.3 Hz, J_2 = 2.2 Hz, 1H, $H_{2''}$), 2.10 (s, 3H), 1.12−1.09 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 161.9, 150.6, 139.5, 135.0, 128.8, 123.9, 117.5, 116.9, 84.2, 84.0, 72.9, 62.7, 33.9, 21.1, 18.17, 18.15, 12.1; IR (neat) ν 3210, 3066, 2942, 2865, 1740, 1690, 1609, 1483, 1386, 1314, 1239, 772, 686 cm^{-1}; HR-ESI MS (m/z) [M + Na]$^+$ calcd for $C_{24}H_{36}N_2O_6SiNa$ 499.224 03, found 499.223 39.

1′-(3′-*O*-Acetyl-5′-*O*-triisopropylsilyl-2′-deoxy-α,β-D-ribofuranoside)-5-methoxyquinazoline-2,4-(3*H*)-dione (30β and 30α). According to the general procedure A, the inseparable isomer mixture of nucleosides **30α** and **30β** (α/β = 1.0:1.7, 0.184 g, 80%) was obtained as an off-white foam after column chromatography on silica gel (hexane/EtOAc, 4:6 → 3:7) using 5-methoxyquinazoline-2,4-(3*H*)-dione **25** (0.105 g, 0.547 mmol), BSA (0.28 mL, 1.14 mmol), thioglycoside **5** (α/β = 1.0:1.8, 0.20 g, 0.456 mmol), NIS (0.112 g, 0.502 mmol), and HOTf (16 μL, 0.182 mmol): R_f (hexane/EtOAc, 3:7) 0.25; ^{1}H NMR (2D COSY and ROESY, 500 MHz, $CDCl_3$) **30α**, δ 9.24 (s, 1H), 7.46 (t, J_1 = 8.6 Hz, 1H), 7.21 (d, J_1 = 8.7 Hz, 1H), 6.89 (t, J_1 = 7.9 Hz, 1H, $H_{1'}$), 6.74−6.70 (m, 1H), 5.47−5.45 (m, 1H, $H_{3'}$), 4.37−4.36 (m, 1H, $H_{4'}$), 4.00−3.90 (m, 2H, $H_{5'}$ and $H_{5''}$), 3.89 (s, 3H), 2.77−2.10 (m, 1H, $H_{2''}$), 2.54 (ddd, J_1 = 14.4 Hz, J_2 = 7.7 Hz, J_3 = 4.3 Hz, 1H, $H_{2''}$), 2.08 (s, 3H), 1.13−1.05 (s, 21H); **30β**, δ 9.36 (s, 1H), 7.44−7.42 (m, 2H), 6.74−6.70 (m, 2H, $H_{1'}$), 5.47−5.45 (m, 1H, $H_{3'}$), 4.00−3.90 (m, 3H, $H_{4'}$, $H_{5'}$, and $H_{5''}$), 3.89 (s, 3H), 2.95−2.89 (m, 1H, $H_{2''}$), 2.04 (s, 3H), 2.04−1.99 (m, 1H, $H_{2''}$), 1.13−1.05 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.6, 170.77, 170.75, 170.6, 161.6, 161.5, 160.4, 160.3, 150.3, 150.15, 150.14, 141.9, 141.7, 135.15, 135.12, 134.8, 109.4, 108.7, 86.3, 84.25, 84.24, 83.8, 75.3, 72.9, 65.2, 62.6, 56.4, 56.3, 34.7, 33.6, 21.0, 20.9, 17.99, 17.98, 11.9, 11.8; IR (neat) ν 3221, 2942, 2865, 1706, 1599, 1489, 1270, 772 cm^{-1}; HR-ESI MS (m/z) [M + Na]$^+$ calcd for $C_{25}H_{38}N_2O_7SiNa$ 529.234 60, found 529.233 82.

1′-(3′-*O*-Acetyl-5′-*O*-triisopropylsilyl-2′-deoxy-α-D-ribofuranoside)benzo[*g*]quinazoline-2,4-(3*H*)-dione (31α) and 1′-(3′-*O*-Acetyl-5′-*O*-triisopropylsilyl-2′-deoxy-β-D-ribofuranoside)benzo[*g*]quinazoline-2,4-(3*H*)-dione (31β). According to the general procedure A, the separable isomer mixture of nucleosides **31α** (0.060 g, 25%) and **31β** (0.107 g, 45%) was obtained as off-white foams after column chromatography on silica gel (hexane/EtOAc, 8:2 → 7:3) using benzo[*g*]quinazoline-2,4-(3*H*)-dione **26** (0.116 g, 0.547 mmol), BSA (0.28 mL, 1.14 mmol), thioglycoside **5** (α/β = 1.0:1.8, 0.20 g, 0.456 mmol), NIS (0.113 g, 0.502 mmol), and HOTf (16 μL, 0.182 mmol). **31α**: R_f (hexane/EtOAc, 7:3) 0.30; ^{1}H NMR (2D COSY, 400 MHz, $CDCl_3$) δ 8.98 (s, br, 1H), 8.83 (s, 1H), 8.07 (s, 1H), 7.96 (d, J_1 = 8.0 Hz, 1H), 7.82 (d, J_1 = 8.2 Hz, 1H), 7.61 (td, J_1 = 6.8 Hz, J_2 = 1.1 Hz, 1H), 7.49 (td, J_1 = 6.9 Hz, J_2 = 1.1 Hz, 1H), 7.17 (t, J_1 = 7.8 Hz, 1H, $H_{1'}$), 5.62 (ddd, J_1 = 8.6 Hz, J_2 = 3.6 Hz, J_3 = 2.3 Hz, 1H, $H_{3'}$), 4.55 (d, J_1 = 2.3 Hz, 1H, $H_{4'}$), 4.07 (dd, J_1 = 10.7 Hz, J_2 = 2.5 Hz, 1H, $H_{5'}$), 4.01 (dd, J_1 = 10.7 Hz, J_2 = 2.8 Hz, 1H, $H_{5''}$), 2.92−2.84 (m, 1H, $H_{2''}$), 2.65 (ddd, J_1 = 14.5 Hz, J_2 = 7.5 Hz, J_3 = 3.8 Hz, 1H, $H_{2''}$), 2.21 (s, 3H), 1.16−1.12 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 161.8, 150.1, 136.6, 134.1, 130.9, 129.7, 129.5, 129.1, 127.6, 126.2, 116.6, 114.0, 86.6, 84.9, 76.2, 65.9, 34.9, 21.5, 18.2, 18.1, 12.1; IR (neat) ν 3191, 3060, 2941, 2865, 1739, 1709, 1684, 1632, 1602, 1474, 1230, 1122, 1013, 880, 743 cm^{-1}; HR-ESI MS (m/z) [M + Na]$^+$ calcd for $C_{28}H_{38}N_2O_6SiNa$ 549.239 68, found 549.238 97. **31β**: R_f (hexane/EtOAc, 3:7) 0.20; ^{1}H NMR (2D COSY, 400 MHz, $CDCl_3$) δ 8.93 (s, br, 1H), 8.81 (s, 1H), 7.95 (d, J_1 = 8.2 Hz, 1H), 7.92 (s, 1H), 7.83 (d, J_1 = 8.2 Hz, 1H), 7.61 (td, J_1 = 6.9 Hz, J_2 = 1.2 Hz, 1H), 7.50 (td, J_1 = 6.9 Hz, J_2 = 1.1 Hz, 1H), 6.72 (t, J_1 = 7.4 Hz, 1H, $H_{1'}$), 5.57 (quint, J_1 = 3.9 Hz, 1H, $H_{3'}$), 4.20−4.16 (m, 1H, $H_{4'}$), 4.09−4.08 (m, 2H, $H_{5'}$ and $H_{5''}$), 3.32−3.24 (m, 1H, $H_{2''}$), 2.20 (ddd, J_1 = 14.2 Hz, J_2 = 7.4 Hz, J_3 = 3.7 Hz, 1H, $H_{2''}$), 2.12 (s, 3H), 1.15−1.05 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 161.9, 149.8, 136.7, 135.4, 131.0, 129.7, 129.4, 129.2, 127.9, 126.4, 116.3, 113.2, 85.2, 84.1, 74.1, 63.2, 34.5, 21.2, 18.1, 18.1, 12.1; IR (neat) ν 3192, 3055, 2942, 2864, 1737, 1691, 1632, 1602, 1476, 1384, 1234, 1065, 881, 731, 682 cm^{-1}; HR-ESI MS (m/z) [M + Na]$^+$ calcd for $C_{28}H_{38}N_2O_6SiNa$ 549.239 68, found 549.238 71.

1′-(3′-*O*-Acetyl-5′-*O*-triisopropylsilyl-2′-deoxy-α,β-D-ribofuranoside)thieno[3,2-*d*]pyrimidine-2,4-(3*H*)-dione (32α and 32β). According to the general procedure A, the inseparable isomer mixture of nucleosides **32α** and **32β** (α/β = 1.0:2.0, 0.16 g, 73%) was obtained as an off-white foam after column chromatography on silica gel (hexane/EtOAc, 7:3 → 6:4) using thieno[3,2-*d*]pyrimidine-2,4-(3*H*)-dione **27** (0.092 g, 0.547 mmol), BSA (0.28 mL, 1.14 mmol), thioglycoside **5** (α/β = 1.0:1.8, 0.20 g, 0.456 mmol), NIS (0.113 g, 0.502 mmol), and HOTf (16 μL, 0.182 mmol): R_f (hexane/EtOAc, 7:3) 0.16; ^{1}H NMR (2D COSY, 500 MHz, $CDCl_3$) **32α**, δ 9.45 (s, br, 1H), 7.73 (d, J_1 = 5.4 Hz, 1H), 7.39 (d, J_1 = 5.4 Hz, 1H), 6.87 (t, J_1 = 7.3 Hz, 1H, $H_{1'}$), 5.50−5.48 (m, 1H, $H_{3'}$), 4.37 (d, J_1 = 2.0 Hz, 1H, $H_{4'}$), 4.00 (dd, J_1 = 11.0 Hz, J_2 = 2.2 Hz, 1H, $H_{5'}$), 3.93 (dd, J_1 = 10.8 Hz, J_2 = 2.8 Hz, 1H, $H_{5''}$), 2.94−2.87 (m, 1H, $H_{2''}$), 2.34−2.28 (m, 1H, $H_{2''}$), 2.09 (s, 3H), 1.16−1.09 (m, 21H); **32β**, δ 9.60 (s, br, 1H), 7.81 (d, J_1 = 5.4 Hz, 1H), 7.62 (d, J_1 = 5.4 Hz, 1H), 6.72 (dd, J_1 = 10.0 Hz, J_2 = 5.4 Hz, 1H, $H_{1'}$), 5.50−5.48 (m, 1H, $H_{3'}$), 4.12 (dd, J_1 = 11.3 Hz, J_2 = 2.3 Hz, 1H, $H_{5'}$), 4.06−3.98 (m, 2H, $H_{4'}$ and H_5), 2.56 (ddd, J_1 = 17.8 Hz, J_2 = 10.0 Hz, J_3 = 7.8 Hz, 1H, $H_{2''}$), 2.21 (dd, J_1 = 13.9 Hz, J_2 = 5.7 Hz, 1H, $H_{2''}$), 2.10 (s, 3H), 1.16−1.09 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 170.7, 158.2, 158.0, 151.3, 151.0, 144.0, 134.7, 134.6, 120.2, 118.4, 115.6, 115.4, 86.6, 85.2, 84.8, 83.9, 75.6, 73.1, 65.6, 62.9, 36.7, 35.0, 21.2, 18.2, 18.1, 12.0; IR (neat) ν 3187, 3057, 2942, 2865, 1740, 1698, 1486, 1236, 1220, 772 cm^{-1}; HR-ESI MS (m/z) [M + Na]$^+$ calcd for $C_{22}H_{34}N_2O_6SSiNa$ 505.180 45, found 505.179 42.

1′-(3′-*O*-Acetyl-5′-*O*-triisopropylsilyl-2′-deoxy-α-D-ribofuranoside)-1,3-diaza-2-oxophenothiazine (33α) and 1′-(3′-*O*-Acetyl-5′-*O*-triisopropylsilyl-2′-deoxy-β-D-ribofuranoside)-1,3-diaza-2-oxophenothiazine (33β). According to the general procedure A, the separable isomer mixture of nucleosides **33α** (0.040 g, 13%) and **33β** (0.100 g, 33%) was obtained as yellow solids after column chromatography on silica gel (hexane/EtOAc, 4:6 → 0:1) using 1,3-diaza-2-oxophenothiazine **28** (0.148 g, 0.684 mmol), BSA (0.35 mL, 1.425 mmol), thioglycoside **5** (α/β = 1.0:1.8, 0.25 g, 0.570 mmol), NIS (0.141 g, 0.627 mmol), and HOTf (20 μL, 0.228 mmol). Compound **33α** was precipitated in a mixture of hexane/EtOAc. **33α**: R_f (hexane/EtOAc, 2:8) 0.33; ^{1}H NMR (2D COSY, 400 MHz, $CDCl_3$) δ 7.33 (s, 1H), 7.11−7.07 (m, 1H), 7.08−6.94 (m, 3H), 6.19 (d, J_1 = 6.4 Hz, 1H, $H_{1'}$), 5.32 (d, J_1 = 6.0 Hz, 1H, $H_{3'}$), 4.45 (t, J_1 = 2.8 Hz, 1H, $H_{4'}$), 3.92 (dd, J_1 = 11.0 Hz, J_2 = 2.6 Hz, 1H, $H_{5'}$), 3.84 (dd, J_1 = 11.0 Hz, J_2 = 3.4 Hz, 1H, $H_{5''}$), 2.88−2.81 (m, 1H, $H_{2''}$), 2.27 (d, J_1 = 15.3 Hz, 1H, $H_{2''}$), 2.02 (s, 3H), 1.09−1.05 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 158.2, 134.5, 134.2, 128.1, 126.3, 126.0, 118.6, 116.5, 96.0, 89.4, 88.9, 75.3, 64.3, 39.6, 21.2, 18.1, 12.0; IR (neat) ν 2942, 2865, 1741, 1655, 1470, 1444, 1415, 1254, 1129, 1094, 1013, 882, 751 cm^{-1}; HR-ESI MS (m/z) [M + Na]$^+$ calcd for $C_{26}H_{37}N_3O_5SSiNa$ 554.212 09, found 554.211 39. **33β**: R_f (hexane/EtOAc, 2:8) 0.20; ^{1}H NMR (2D COSY, 400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.24 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 1H), 7.08−7.04 (m, 1H), 6.95−6.88 (m, 2H), 6.34 (dd, J_1 = 8.8 Hz, J_2 = 5.3 Hz, 1H, $H_{1'}$), 5.32 (d, J_1 = 6.2 Hz, 1H, $H_{3'}$), 4.11 (d, J_1 = 1.7 Hz, 1H, $H_{4'}$), 3.99 (d, J_1 = 2.0 Hz, 2H, $H_{5'}$ and $H_{5''}$), 2.59 (dd, J_1 = 13.9 Hz, J_2 = 5.0 Hz, 1H, $H_{2''}$), 2.10−2.03 (m, 1H, $H_{2''}$), 2.07 (s, 3H), 1.20−1.10 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 160.8, 154.6, 135.9, 133.7, 127.7, 126.0, 124.6, 118.5, 116.7, 97.4, 86.5, 86.0, 75.5, 63.9, 39.1, 21.1, 18.2, 12.1; IR (neat) ν 2941, 2864, 1741, 1654, 1623, 1593, 1435, 1419, 1232, 1192, 1120, 1006, 759, 682 cm^{-1}; HR-ESI MS (m/z) [M + Na]$^+$ calcd for $C_{26}H_{37}N_3O_5SSiNa$ 554.212 09, found 554.211 59.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H NMR, ^{13}C NMR, 2D COSY, and 2D ROESY spectra of compounds **2**−**33**. This material is available free of charge via the Internet at http://pubs.acs.org.

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AUTHOR INFORMATION

Corresponding Author

*E-mail: luedtke@oci.uzh.ch

Notes

The authors declare no competing financial interest.

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