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Electrophilic glycosidation employing 3,5-*O*-(di-*tert*-butylsilylene)-*erythro*-furanoid glycal leads to exclusive formation of the β-anomer: synthesis of 2′-deoxynucleosides and its 1′-branched analogues

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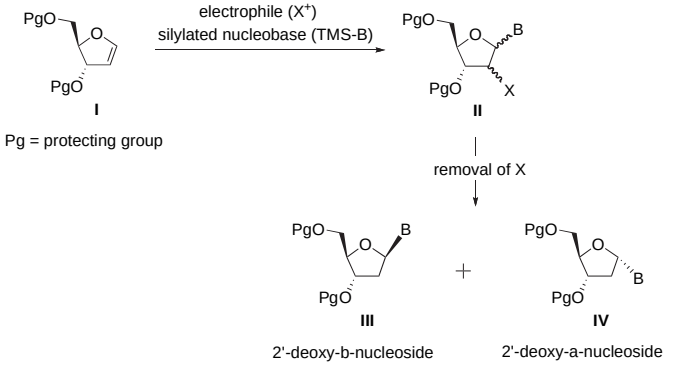
ABSTRACT

Stereoselectivity in *N*-iodosuccimide (NIS)-mediated electrophilic glycosidation was examined by employing 2,4-bis-*O*-(trimethylsilyl)thymine and three different silyl-protected *erythro*-furanoid glycals **12**, **16**, and **18**. As a result, it was found that 3,5-*O*-(di-*t*-butylsilylene)-protected **18** gave only the β-anomer (**21**). The remarkable stereoselectivity observed by employing **18** is discussed on the basis of its X-ray crystallographic analysis. 1-Substituted glycals gave the corresponding β-anomer, again exclusively, to provide access to 1′-branched 2′-deoxynucleosides.

1. Introduction

Electrophilic glycosidation between *erythro*-furanoid glycal (**I**) and a nucleobase followed by removal of the substituent X at the 2′-position of the resulting product (**II**) has been utilized for the synthesis of 2′-deoxynucleosides (Scheme 1).[1–3] However, this method usually gives a mixture of β- (**III**) and α- (**IV**) anomers. Efforts have been made to improve the β-selectivity by changing the protecting group of the hydroxyl groups at the 3- and 5-positions. To the best of our knowledge, the highest β-selectivity so far reported has been observed in the PhSeCl-mediated glycosidation using the 3-*O*-benzyl-5-*O*-(*tert*-butyldiphenylsilyl) derivative (**1**) and 2,4-bis-*O*-(trimethylsilyl)-uracil (bis-TMS-uracil): **2**/**3** plus **4**=77:23, combined yield 58% (Fig. 1).[3b]

We have previously reported the synthesis of 2′-deoxy-4′-thionucleosides by employing PhSeCl and 4-thiofuranoid glycals having three different 3,5-*O*-silyl– protecting groups (Fig. 2): bis-3,5-*O*-(*tert*-butyldimethylsilyl) (TBDMS) (**5**), 3,5-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl) (TIPDS) (**6**), and 3,5-*O*-(di-*tert*-butylsilylene) (DTBS) (**7**) groups.[4] The reaction of **5** with bis-TMS-uracil gave **8β** and **8α** in a ratio of 4:1 (combined yield 88%), while a higher β-selectivity was observed upon using **6**: **9β**/**9α**=18:1, combined yield 87%. In contrast to these two cases, the 3,5-*O*-DTBS-protected donor **7** gave the β-anomer **10** as the sole product in 88% yield.



Scheme 1. Electrophilic glycosidation between glycal **I** and silylated nucleobase leading to 2′-deoxynucleoside.

When the stable non-toxic electrophile NIS was used instead of PhSeCl in the reaction of **7**, again exclusive formation of the β-anomer **11** (73%) was observed.

Motivated by the above observations, we intended to optimize the β-selectivity of NIS-mediated electrophilic glycosidation between *erythro*-furanoid glycal and silylated nucleobase. In this paper, we describe the results of this glycosidation, which provide a remarkably stereo-defined entry to the β-anomer of

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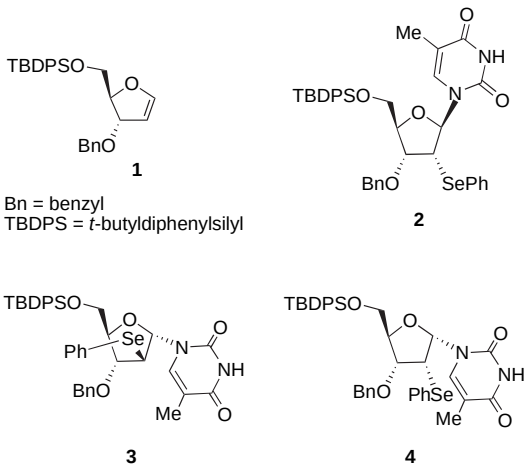


Figure 1. Compounds **1**–**4**.

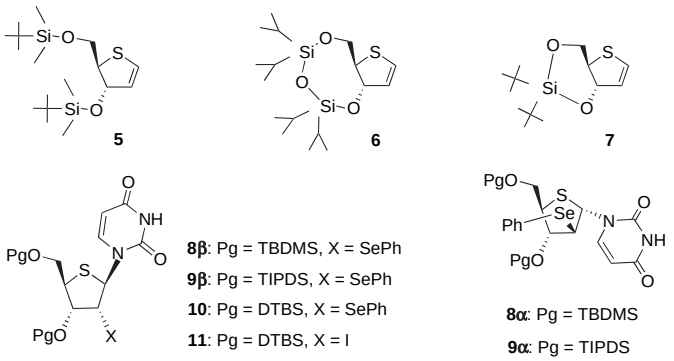


Figure 2. Compounds **5**–**11**.

2′-deoxynucleosides by combining subsequent radical-mediated removal of the 2′-iodo substituent. To investigate the applicability of this method, several 1-alkyl and 1-(ω-hydroxy)alkyl *erythro*-furanoid glycals were prepared based on lithiation chemistry. These compounds also gave the respective β-anomer exclusively, demonstrating the scope of the present glycosidation method.

2. Results and discussion

2.1. Preparation of the silyl-protected furanoid glycals (12, 16, and 18) and their use in electropilic glycosidation

The TBDMS-protected glycal **12** (Fig. 3) was prepared from 2-deoxy-D-ribonolactone by the published procedures.[5] For the preparation of the TIPDS- and DTBS-protected derivatives, sulfoxide *syn*-elimination of phenyl 2-deoxy-1-thio-D-*erythro*-pentofuranoside (**13**)[6] was employed because of its ready accessibility from 2-deoxy-D-ribose (Scheme 2). Thus, **13** was prepared in 97% yield by reacting 2-deoxy-D-ribose with $PhSH/H_2SO_4$ in DMF. Compound **13** was protected with TIPDS-group to give **14** (84%). The corresponding sulfoxide **15** was obtained in 96% yield simply by oxidation with *m*-CPBA. Upon heating in refluxing xylene in the presence of solid $NaHCO_3$, **15** underwent sulfoxide *syn*-elimination to furnish the desired glycal **16** in 84% yield.[7] Likewise, **13** was protected with the DTBS group to give **17** (93%), which was then converted to the 3,5-*O*-DTBS-protected glycal **18** in 83% yield through the above sulfoxide *syn*-elimination (overall yield of **18** from 2-deoxy-D-ribose, 75%). This is the first example for the efficient preparation of *erythro*-furanoid glycal by means of sulfoxide *syn*-elimination.

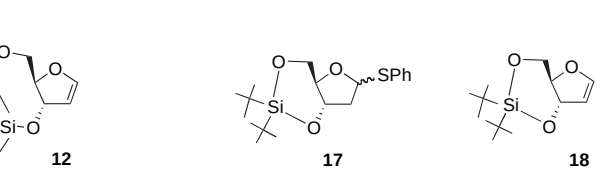
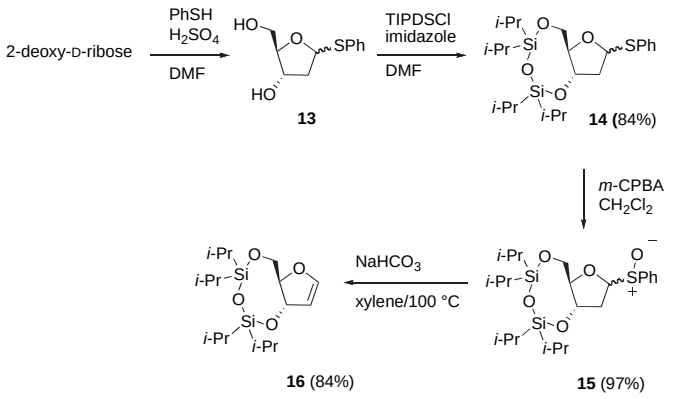
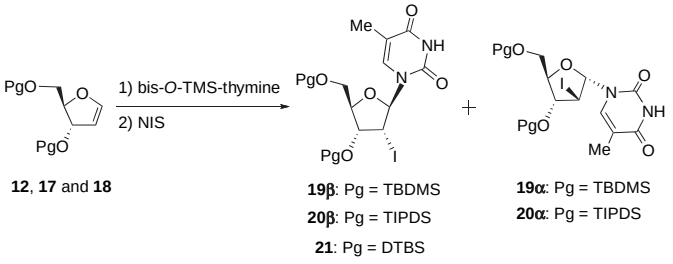


Figure 3. Compounds **12**, **17**, and **18**.



Scheme 2. Preparation of **16**.

With the requisite glycals **12**, **16**, and **18** in hand, NIS-mediated electrophilic glycosidation of silylated thymine was carried out (Scheme 3) and the results are summarized in Table 1. As shown in entry 1, when **12** was reacted with bis-TMS-thymine (3.0 equiv) in the presence of NIS (1.5 equiv) in CH_3CN/CH_2Cl_2 at rt for 12 h, formation of the α-anomer (**19α**, 62%) dominated over that of the β-anomer (**19β**, 15%). Their stereochemistry was determined by NOE experiments [**19α**, H-6/H-2′ (4.6%), H-6/H-4′ (2.6%), H-1′/H-3′ (1.6%), H-1′/H-5′ (0.5%), and H-2′/H-4′ (1.0%); **19β**, H-6/H-2′ (6.2%)]. Entry 2 shows that the TIPDS-protected glycal **16** gave equal amounts of the β- (**20β**) and α- (**20α**) anomers. On the other hand, the DTBS-glycal **18** showed remarkable stereoselectivity to furnish the β-anomer **21** exclusively in 76% yield (entry 3).



Scheme 3. NIS-mediated electrophilic glycosidation using glycals **12**, **17**, and **18**.

Table 1
NIS-initiated electrophilic glycosidation of silylated thymine by using **12**, **16**, and **18**[a]

Entry	Glycal	Product(s) (isolated yield)	Ratio of β-anomer/α-anomer
1	**12**	**19β** and **19α** (77%)	1:4
2	**16**	**20β** (35%) and **20α** (35%)	1:1
3	**18**	**21** (76%)	—

[a] All reactions were carried out in CH_3CN/CH_2Cl_2 at rt for 12 h by using 2,4-bis-*O*-TMS-thymine (3.0 equiv) and NIS (1.5 equiv).

The remarkable stereoselectivity observed by employing **18** can be explained in terms of steric strain between the hydrogen atom at the 3-position of **18** and the electrophile NIS. X-ray crystallographic analysis of **18** revealed that its H-3 is in a pseudo-axial disposition (Fig. 4), which is consistent with the $J_{3,4}$ value (11.5 Hz) measured in $CDCl_3$. Under such circumstances, if NIS is approaching from the β-face of the furanoid glycal, there would be severe steric repulsion due to the presence of the pseudo-axial H-3 (Fig. 5). As a consequence, formation of an iodonium intermediate will take place at the less constrained α-face, which is followed by nucleophilic attack by silylated thymine to lead to the observed exclusive formation of the β-anomer (**21**).

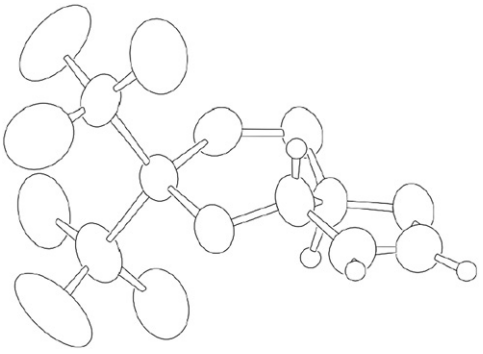


Figure 4. ORTEP drawing of compound **18**.

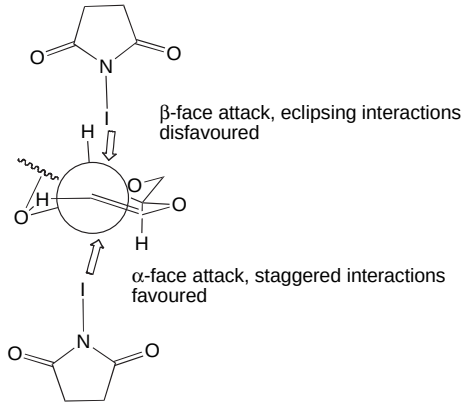


Figure 5. Rational illustration for exclusive formation of β-nucleoside.

Although we were unable to obtain X-ray crystallographic data of **12** and **16**, their $J_{3,4}$ values are considerably smaller (**12**, 2.7 Hz; **16**, 4.5 Hz) than that of **18**. Therefore, it would be reasonable to assume that the H-3 of **12** as well as **16** takes a pseudo-equatorial position, which allows NIS to approach from both α- and β-faces.

The electrophilic glycosidation employing the DTBS-glycal **18** also works well with silylated uracil and N^4-(acetyl)cytosine to give the respective β-anomer exclusively: **22**, 76%; **23**, 55% (Fig. 6). The use of silylated N^6-(benzoyl)adenine also follows the same stereochemical trend, but the yield of the desired N^9-glycoside **24** was only 26% due to the formation of the N^7- (**25**, 17%) and N^1- (**26**, 13%) isomers. The regiochemistry of **24**–**26** was determined on the basis of HMBC and NOE experiments: **24**, H-1′/C-4; **25**, H-1′/C-5; **26**, H-1′/C-2 and NOE correlation between H-1′/*ortho*-H-Ph. In the case of glycosidation of N^4-(acetyl)cytosine and N^6-(benzoyl)adenine, unidentified less polar products were formed.

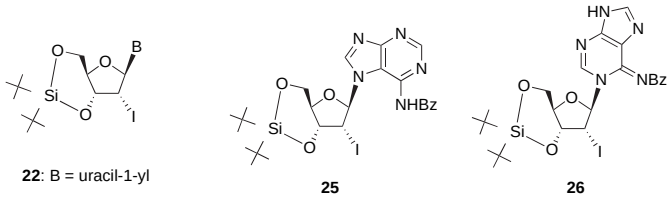


Figure 6. Compounds **22**–**26**.

The glycosidation products **21**–**24** were converted to the corresponding 2′-deoxynucleosides **27**–**30** in good yields by reacting with tributyltin radical (Scheme 4, yields are given in parentheses).

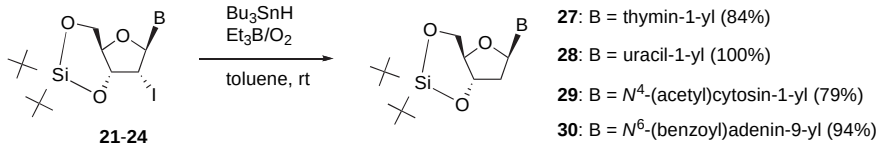
2.2. Preparation of 1-alkyl and 1-(ω-hydroxy)alkyl derivatives of the DTBS-protected glycal (18) and their use in electrophilic glycosidation

Stimulated by the discovery of a nucleoside antibiotic angustmycin C (1′-hydroxymethyladenosine),[8–10] a number of reports have been published for the synthesis of 1′-branched ribonucleosides either from carbohydrate precursors[11–15] or naturally occurring ribonucleosides.[16–18] On the other hand, 2′-deoxyribonucleosides branched at the 1′-position have recently been utilized as building blocks for modified oligodeoxyribonucleotides, which have been used as tools for studying damage and repair of nucleic acids[19] or in antigene technology.[20] However, few methods are available for the synthesis of 1′-branched 2′-deoxyribonucleosides.[16,21]

The above observation led us to introduce alkyl and (ω-hydroxy) alkyl groups to the 1-position of the DTBS-glycal **18**. Lithiation chemistry was employed for this purpose (Scheme 3).[22] The extent of C1-lithiation of **18** was examined by deuterium incorporation (Table 2). It was found that the lithiation could be effected by using LDA (entries 1 and 2). However, these D-incorporations and recoveries were insufficient. On the other hand, 87% D-incorporation (recovery of **18**, 92%) was observed upon using 2 equiv of *t*-BuLi (entry 3). Finally, when **18** was lithiated with *t*-BuLi (3 equiv), quantitative deuterium incorporation at the 1-position (recovery 96%) was observed as evidenced by ^1H NMR spectroscopy (entry 4).

The results obtained by reacting the above C1-lithiated species with carbon electrophiles (Scheme 5) are listed in Table 3. Methylation and benzylation were carried out in the presence of HMPA to give **31** and **32** in moderate yields (entries 1 and 2). It is important to note that no alkylation took place without adding HMPA in these reactions. Introduction of a hydroxymethyl group was carried by reaction with DMF followed by treatment with $NaBH_4$ to give **33** (entry 3). Although aromatic as well as aliphatic aldehydes reacted efficiently as exemplified by the preparation of **34** and **35** (entries 4 and 5), the reaction of acetone (entry 6) gave a low yield of product (**36**), presumably due to its ready formation of enolate ion. Cyclic ethers underwent BF_3-assisted ring opening (entries 7 and 8) to give moderate yields of products (**37** and **38**). In entries 1, 2, 7, and 8, unidentified by-products were formed. To obtain derivatives suitable for glycosidation, the above prepared 1-(ω-hydroxy)alkyl glycals **33**–**38** were converted to their *O*-triethylsilyl derivatives **39**–**44** (Scheme 5, yields are given in parentheses).

It was found that the NIS-initiated electrophilic glycosidation of these glycals (**31**, **32**, and **39**–**44**) under the reaction conditions used for the reaction of **18** results again in exclusive formation of their β-anomers as shown by the preparation of a series of 1′-branched 2′-iodothymidine derivatives **45**–**52** (Scheme 6, yields are given in parentheses). In the synthesis of **45**, **46**, **50**–**52**, unidentified non-nucleoside by-products were formed. These results clearly demonstrate the scope of the present method. Compounds **45**–**52** were transformed to the 1′-branched thymidines **53**–**60** in good yield (Scheme 6, yields are given in parentheses) by reacting with tributyltin radical.

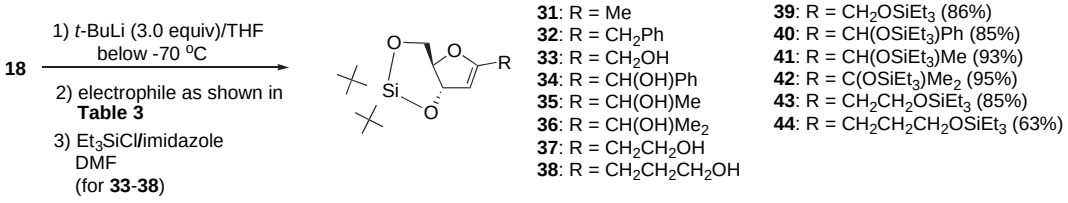


Scheme 4. Et_3B-mediated radical reduction of **21**–**24**.

Table 2
Deuterium incorporation of glycal **18** with lithiating agent

Entry	Lithiating agent (equiv)	Deuterium incorporation (%)	Recovery of **18** (%)
1	LDA (2)	35	81
2	LDA (3)	72	80
3	*t*-BuLi (2)	87	92
4	*t*-BuLi (3)	100	96

Also carried out here are reactions of the glycal **39** with silylated N^4-(acetyl)cytosine and N^6-(benzoyl)adenine. The former reaction gave **61** in 84% yield (Fig. 7). The latter reaction gave the N^9-β-glycoside **62** (21%) and N^1-β-glycoside **63** (10%). This result is slightly different from that of **18** in that the corresponding N^7-glycoside was not observed. We assume that steric repulsion between the benzoylyamino group of the approaching nucleobase and the CH_2OSiEt_3 substituent at the 1-position of **39** prevented the expected N^7-glycoside formation. Compounds **61** and **62** were converted to **64** (95%) and **65** (74%), respectively.



Scheme 5. Preparation of 1-substituted glycals **31**–**44**.

Table 3
Preparation of 1-alkyl and 1-(ω-hydroxy)alkyl glycals based on lithiation of **18**[a]

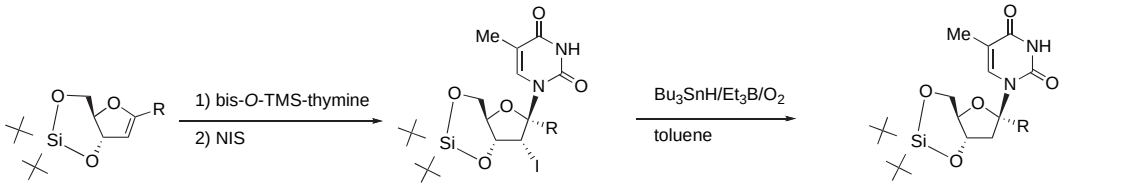
Entry	Electrophile (equiv)	R	Product (isolated yield)
1	MeI (10)/HMPA (5)	Me	**31** (56%)
2	$PhCH_2Br$ (5)/HMPA (10)[b]	CH_2Ph	**32** (56%)
3	DMF (5) then NaBH4 (1.5)	CH_2OH	**33** (82%)
4	PhCHO (3)	CH(OH)Ph	**34** (93%)[c]
5	MeCHO (5)	CH(OH)Me	**35** (90%)[c]
6	CH_3COCH_3 (5)	$C(OH)Me_2$	**36** (19%)[d]
7	Ethylene oxide (5) plus $BF_3{\cdot}OEt_2$ (5)	CH_2CH_2OH	**37** (62%)
8	Trimethylene oxide (5) plus $BF_3{\cdot}OEt_2$ (3)	$CH_2CH_2CH_2OH$	**38** (65%)

[a] After addition of the respective electrophile, the reaction mixture was stirred below −70 °C for 0.5 h, except entry 2.
[b] After addition of the electrophile, the reaction mixture was stirred at −40 °C for 11 h.
[c] The product was obtained as a mixture of diastereomers.
[d] The starting material (**18**) was recovered in 78% yield.

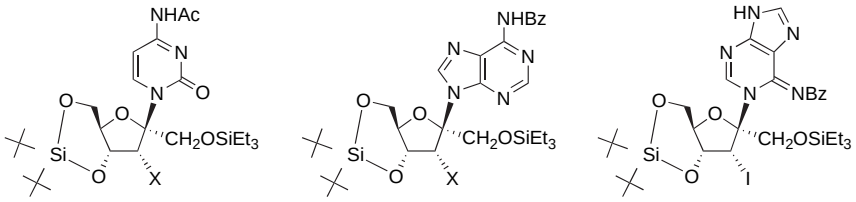
3. Conclusion

In conclusion, the present study has demonstrated that NIS-mediated electrophilic glycosidations of silylated thymine, uracil, N^4-(acetyl)cytosine, and N^6-(benzoyl)adenine by employing the 3,5-*O*-DTBS-*erythro*-furanoid glycal (**18**) all result in exclusive formation of the β-anomer. Since the introduced 2′-iodo substituent of the glycosidation products can readily be removed by radical reaction, the present reaction sequence provides a highly reliable access to 2′-deoxynucleosides. The glycal **18** can be prepared in 75% overall yield from 2-deoxy-D-ribose through sulfoxide *syn*-elimination.

For the synthesis of 1′-branched analogues of 2′-deoxynucleosides, lithiation of **18** was carried out to give glycals having a variety of alkyl and (ω-hydroxy)alkyl substituents at the 1-position. These glycals uniformly serve also as highly β-selective donors, demonstrating the scope of the present electrophilic glycosidation.



Scheme 6. NIS-initiated electrophilic glycosidation using 1′-substituted glycals and radical reduction of the glycosides **45**–**52**.



61: X = I
64: X = H
62: X = I
65: X = H
63

Figure 7. Compounds **61**–**65**.

4. Experimental

4.1. General methods

Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded either at 400 MHz or at 500 MHz. Chemical shifts are recorded relative to Me_4Si. Of the two protons at the 5′-position, the one that appears at a higher field is designated as H-5′a, and the other as H-5′b, throughout the text and Experimental section. The same applied to H-2′. Mass spectra (MS) were taken in FAB mode with *m*-nitrobenzyl alcohol as a matrix. Column chromatography was carried out on silica gel. Thin layer chromatography (TLC) was performed on silica gel. When necessary, analytical samples were purified by high performance liquid chromatography (HPLC). THF was distilled from benzophenone ketyl.

4.2. Phenyl 3,5-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-2-deoxy-1-thio-D-*erythro*-pentofuranoside (14)

To a DMF (10 mL) solution of **13** (1.00 g, 3.76 mmol) were added imidazole (1.02 g, 31.2 mmol) and 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (1.32 mL, 4.13 mmol) at 0 °C under Ar atmosphere and the mixture was stirred at rt overnight. The reaction mixture was partitioned between AcOEt and H_2O. Silica gel column chromatography (hexane/ethyl acetate=30:1) of the organic layer gave **14** (1.42 g, 84%, major isomer/minor isomer=6.7:1) as colorless oil; UV (MeOH): λ_{max} 249 nm (ε 7000), λ_{min} 232 nm (ε 3500); $[\alpha]_D^{20}$ +110.4 (*c* 1.14, $CHCl_3$); IR (neat, cm^{-1}): 3060, 2892, 2758, 2724, 1464, 1389, 1248, 1138, 1109, and 1036; ^{1}H NMR ($CDCl_3$) δ (major isomer) 1.00–1.10 (28H, m), 2.03 (1H, ddd, $J_{1,2a}$=6.6 Hz, $J_{2a,3}$=7.8 Hz and J_{gem}=13.4 Hz), 2.75 (1H, dt, $J_{1,2b}$=$J_{2b,3'}$=7.6 Hz and J_{gem}=13.4 Hz), 3.84–4.07 (2H, m), 4.32–4.38 (1H, m), 5.60 (1H, dd, $J_{1,2a}$=6.6 Hz and $J_{1,2b}$=7.6 Hz), 7.19–7.32 and 7.46–7.52 (5H, each as m, Ph); ^{1}H NMR ($CDCl_3$) δ (selected data for minor isomer) 2.34 (1H, ddd, *J*=3.9, 7.5, and 13.2 Hz), 2.46 (1H, dt, *J*=7.3 and 13.2 Hz), 3.84–3.90 (1H, m), 4.32–4.38 (1H, m), 4.50–4.55 (1H, m), 5.55 (1H, dd, *J*=4.0 and 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 12.9, 13.2, 13.5, 13.8, 17.3, 17.4, 17.5, 17.6, 17.7, 17.9, 40.7, 61.7, 71.0, 82.0, 85.5, 127.1, 129.1, 129.2, 130.9, 136.4. FABMS (*m*/*z*): 507 (M^++K). Anal. Calcd for $C_{23}H_{40}O_4SSi_2$: C, 58.93; H, 8.60. Found: C, 58.85; H, 8.63.

4.3. Phenyl 3,5-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-2-deoxy-1-thio-D-*erythro*-pentofuranose *S*-oxide (15)

To a CH_2Cl_2 (60 mL) solution of **14** (3.20 g, 6.83 mmol) was added a CH_2Cl_2 solution of *m*-CPBA (1.81 g, 6.83 mmol) at 0 °C and the mixture was stirred for 20 min. The reaction mixture was neutralized with Et_3N and partitioned between CH_2Cl_2 and saturated $NaHCO_3$. Silica gel column chromatography (hexane/ethyl acetate=4:1) of the organic layer gave **15** (3.21 g, 97%) as colorless syrup; UV (MeOH): λ_{max} 273 nm (ε 2700), λ_{min} 263 nm (ε 2500); $[\alpha]_D^{20}$ −9.51 (*c* 0.25, $CHCl_3$); IR (neat, cm^{-1}): 2945, 2893, 2868, 1248, 1142, 1070, and 1038; ^{1}H NMR ($CDCl_3$) δ (major isomer) 0.90–1.14 (28H, m), 2.08 (1H, ddd, $J_{1,2a}$=7.3 Hz, $J_{2a,3}$=7.8 Hz and J_{gem}=14.6 Hz), 2.67–2.79 (1H, m), 3.88–3.93 (3H, m), 4.36–4.45 (1H, m), 5.71 (1H, t, *J*=7.1 Hz), 7.46–7.61 (5H, m); ^{13}C NMR ($CDCl_3$) δ 12.5, 12.7, 12.8, 13.0, 13.4, 16.9, 17.5, 30.2, 60.5, 70.5, 85.1, 95.8, 124.2, 124.7, 125.6, 129.0, 129.1, 129.3, 131.0, 140.9; FABMS (*m*/*z*): 485 (M^++H). Anal. Calcd for $C_{23}H_{40}O_5SSi_2$: C, 56.98; H, 8.32. Found: C, 56.71; H, 8.36.

4.4. 1,4-Anhydro-2-deoxy-3,5-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-D-*erythro*-pent-1-entiol (16)

To a xylene (20 mL) solution of **15** was added *i*-Pr_2NEt (1.8 mL, 10.3 mmol) and the mixture was stirred under reflux for 1 h. The reaction mixture was partitioned between AcOEt and saturated $NaHCO_3$. Silica gel column chromatography (hexane/ethyl acetate=50:1) of the organic layer gave **16** (621 mg, 84%) as colorless syrup: $[\alpha]_D^{20}$ +29.3 (*c* 1.03, $CHCl_3$); IR (neat, cm^{-1}): 2945, 2895, 2868, 1618, 1466, 1387, 1250, 1228, 1147, 1090, and 1043; ^{1}H NMR ($CDCl_3$) δ 1.03–1.10 (28H, m), 3.59 (1H, t, $J_{4,5a}$=J_{gem}=11.5 Hz), 4.14 (1H, dd, $J_{4,5b}$=4.5 Hz and J_{gem}=11.5 Hz), 4.42 (1H, dt, $J_{3,4}$=$J_{4,5b}$=4.5 Hz and $J_{4,5a}$=11.5 Hz), 5.06 (1H, t, $J_{1,3}$=2.7 Hz), 5.25–5.28 (1H, m), 6.44 (1H, dd, $J_{1,2}$=1.5 Hz and $J_{1,3}$=2.7 Hz); ^{13}C NMR ($CDCl_3$) δ 13.1, 13.9, 14.3, 14.3, 17.5, 17.6, 17.7, 17.9, 18.1, 18.2, 18.3, 64.7, 78.4, 89.1, 103.3, 149.2, 163.8; FABMS (*m*/*z*): 396 (M^++K). Anal. Calcd for $C_{17}H_{34}O_4Si_2$: C, 56.94; H, 9.56. Found: C, 57.02; H, 9.56.

4.5. Phenyl 3,5-*O*-(di-*tert*-butylsilylene)-1-thio-D-*erythro*-pentofuranoside (17)

To a DMF (40 mL) solution of **13** (4.4 g, 12.0 mmol) was added imidazole (2.12 g, 31.2 mmol) and di-*tert*-butylsilyl bis(trifluoromethanesulfonate) (3.7 mL, 10.1 mmol) at 0 °C under Ar atmosphere and the mixture was stirred overnight at rt. The reaction mixture was partitioned between AcOEt and saturated $NaHCO_3$. Silica gel column chromatography (hexane/ethyl acetate=10:1) of the organic layer gave **17** (2.65 g, 93%, major isomer/minor isomer=6.7:1) as white colorless solid: mp 90–92 °C; UV (MeOH): λ_{max} 249 nm (ε 7300), λ_{min} 232 nm (ε 3600); $[\alpha]_D^{20}$ +212.2 (*c* 0.71, $CHCl_3$); IR (neat, cm^{-1}): 2933, 2887, 1128, 1105, 1068, and 1049; ^{1}H NMR ($CDCl_3$) δ (for major isomer) 1.00 and 1.05 (18H, each as s), 1.88 (1H, ddd, $J_{1,2a}$=$J_{2a,3}$=8.0 Hz and J_{gem}=12.7 Hz), 2.83 (1H, ddd, $J_{2b,3}$=7.1 Hz and J_{gem}=$J_{1,2}$=12.7 Hz), 3.84 (1H, ddd, $J_{4,5b}$=4.4 Hz, $J_{3,4}$=8.5 Hz and $J_{4,5a}$=10.2 Hz), 3.90 (1H, dd, J_{gem}=8.8 Hz and $J_{4,5a}$=10.2 Hz), 3.99–4.06 (1H, m), 4.39 (1H, dd, $J_{4,5b}$=4.4 Hz and J_{gem}=8.8 Hz), 5.59 (1H, dd, $J_{1,2b}$=7.1 Hz and $J_{1,2a}$=8.0 Hz), 7.12–7.32 and 7.48–7.51 (5H, each as m); ^{1}H NMR ($CDCl_3$) δ (selected data for minor isomer) 0.97 and 0.98 (18H, each as s), 2.36–2.42 (2H, m), 3.57–3.63 (1H, m), 3.80–3.82 (1H, m), 4.34 (1H, dd, *J*=5.1 and 9.3 Hz), 5.54 (1H, dd, *J*=3.5 and 7.9 Hz); ^{13}C NMR ($CDCl_3$) δ 20.8, 23.3, 27.8, 28.1, 39.8, 68.2, 75.8, 76.1, 85.8, 127.9, 129.6; ^{13}C NMR ($CDCl_3$) δ (selected data for minor isomer) 20.7, 23.2, 40.1, 68.7, 79.6, 85.0, 128.7, 129.6, 133.7, 135.9. FABMS (*m*/*z*): 383 (M^++H). Anal. Calcd for $C_{19}H_{30}O_4SSi$: C, 62.25; H, 8.25. Found: C, 62.47; H, 8.29.

4.6. 1,4-Anhydro-2-deoxy-3,5-*O*-(di-*tert*-butylsilylene)-D-*erythro*-pent-1-entiol (18)

To a CH_2Cl_2 (50 mL) solution of **17** (3.38 g, 9.22 mmol) was added a CH_2Cl_2 (50 mL) solution of *m*-CPBA (2.45 g, 9.22 mmol) at 0 °C and the mixture was stirred for 5 min. The reaction mixture was neutralized with Et_3N and partitioned between CH_2Cl_2 and saturated $NaHCO_3$. Silica gel column chromatograpy (hexane/ethyl acetate=4: 1) of the organic layer gave the *S*-oxides (3.52 g, 99% a mixture of diastereomers) as syrup. To a xylene solution (50 mL) of the *S*-oxides was added $NaHCO_3$ (4.2 g, 49.5 mmol) and the mixture was stirred under reflux for 1 h. The reaction mixture was partitioned between AcOEt and saturated $NaHCO_3$. Silica gel column chromatography (hexane/ethyl acetate=70:1) of the organic layer gave **18** (2.07 g, 83%) as colorless solid: mp 62–64 °C; $[\alpha]_D^{20}$ +41 (*c* 0.77, $CHCl_3$); IR (neat, cm^{-1}): 2968, 2897, 2860, 1583, 1473, 1365, 1352, 1149, 1105, and 1068; ^1H NMR ($CDCl_3$) δ 1.02 and 1.05 (9H, s), 4.06 (1H, ddd, $J_{4,5b}$=5.2 Hz and $J_{3,4}$=$J_{4,5a}$=11.5 Hz), 4.14 (1H, dd, J_{gem}=9.2 Hz and $J_{4,5}$=11.5 Hz), 4.47 (1H, dd, J_{gem}=9.2 Hz and $J_{4,5b}$=5.2 Hz), 5.16 (1H, dd, $J_{1,2}$=2.0 Hz and $J_{3,4}$=11.5 Hz), 5.41 (1H, s), 6.43 (1H, d, $J_{1,3}$=2.0 Hz); ^{13}C NMR ($CDCl_3$) δ 20.3, 22.5, 27.4, 27.6, 67.4, 80.3, 83.3, 107.6, 148.1; FABMS (*m*/*z*): 257 (M^++H). Anal. Calcd for $C_{13}H_{24}O_3Si$: C, 60.89; H, 9.43. Found: C, 60.89; H, 9.43.

4.7. 1-[3,5-Bis-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-2-iodo-β-D-ribofuranosyl]thymine (19β) and 1-[3,5-bis-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-2-iodo-α-D-ribofuranosyl] thymine (19α)

To a CH_3CN (0.6 mL) solution of bis-*O*-TMS-thymine, prepared from thymine (55 mg, 0.44 mmol) and *N*,*O*-bis-(trimethylsilyl) acetamide (BSA) (0.21 mL, 0.87 mmol), were added a CH_2Cl_2 (3 mL) solution of **12** (100 mg, 0.29 mmol), and *N*-iodosuccinimide (NIS) (98 mg, 0.44 mmol) at 0 °C under Ar atmosphere and the mixture was stirred 12 h. The reaction mixture was partitioned between AcOEt and saturated $NaHCO_3$/saturated $Na_2S_2O_3$. Silica gel column chromatography on silica gel (hexane/ethyl acetate=3:1) gave a mixture of **19β** and **19α** (134 mg, 77%, **19β**/**19α**=1:4) as pale yellow foam: $[\alpha]_D^{20}$ +11.3 (*c* 1.0, $CHCl_3$); IR (neat, cm^{-1}): 3186, 3055, 2954, 2929, 2885, 2858, 1697, 1259, and 1101; ^1H NMR (CD_3CN) (**19α**) δ 0.10–0.20 (12H, m), 0.88 and 0.93 (18H, each as s), 1.83 (3H, d, $J_{5\text{-Me},6}$=1.2 Hz), 3.85 (1H, dd, $J_{4',5'a}$=4.1 Hz and J_{gem}=11.2 Hz), 3.88 (1H, dd, $J_{4',5'b}$=4.4 Hz and J_{gem}=11.2 Hz), 4.20 (1H, t, $J_{3',4'}$=$J_{4',5'b}$=4.4 Hz), 4.26 (1H, t, $J_{2',3'}$=6.1 Hz), 4.69 (1H, dd, $J_{4',5'b}$=4.4 Hz and J_{gem}=11.2 Hz), 6.20 (1H, d, $J_{1',2'}$=6.1 Hz), 7.33 (1H, d, $J_{5\text{-Me},6}$=1.2 Hz), 8.96 (1H, br); selected data of **19β**: 3.77–3.83 (2H, m), 4.04–4.08 (2H, m), 4.39 (1H, dd, *J*=4.6 and 8.3 Hz), 6.26 (1H, d, *J*=8.0 Hz), 7.30 (1H, d, *J*=1.2 Hz); ^{13}C NMR ($CDCl_3$) δ 12.8, 20.6, 22.8, 27.1, 27.2, 30.2, 40.0, 66.6, 74.8, 76.9, 98.3, 110.5, 134.0, 149.8, 164.1; FABMS (*m*/*z*): 523 (M^+). FAB-HRMS (*m*/*z*): calcd for $C_{22}H_{41}IN_2O_5Si_2$: 523.2711, found: 523.2686 (M^+).

4.8. 1-[3,5-*O*-(1,1,3,3-Tetraisopropyldisiloxane-1,3-diyl)-2-deoxy-2-iodo-β-D-ribofuranosyl]thymine (20β) and 1-[3,5-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-2-deoxy-2-iodo-α-D-ribofuranosyl]thymine (20α)

Compounds **20β** and **20α** were prepared as described above for **19** starting from a CH_3CN (3 mL) of thymine (263 mg, 2.09 mmol)/BSA (1.0 mL, 4.17 mmol), a CH_2Cl_2 (14 mL) solution of **16** (500 mg, 0.75 mmol), and NIS (468 mg, 2.09 mmol). Silica gel column chromatography on silica gel (hexane/ethyl acetate=3:1) of the crude mixture gave **20β** and **20α** (423 mg, 70%, **20β**/**20α**=1:1). HPLC separation (hexane/ethyl acetate=5:1) gave analytically pure sample of **20β** (211 mg, 35%, t_R=20.6 min) and **20α** (211 mg, 35%, t_R=22.2 min).

Physical data of **20β**: $[\alpha]_D^{20}$ −23.7 (*c* 1.7, $CHCl_3$); IR (neat, cm^{-1}): 3197, 3066, 2945, 2895, 2868, 1697, 1458, 1265, 1117, and 1039; ^1H NMR ($CDCl_3$) δ 0.94–1.74 (28H, m), 1.92 (3H, d, $J_{5\text{-Me},6}$=1.1 Hz), 3.57 (1H, dd, $J_{3',4'}$=6.0 Hz and $J_{2',3'}$=8.3 Hz), 4.00 (1H, dd, $J_{4',5'a}$=2.9 Hz, J_{gem}=13.7 Hz), 4.13–4.15 (1H, m), 4.23 (1H, d, J_{gem}=13.7 Hz), 4.46 (1H, d, $J_{2',3'}$=6.0 Hz, H-2′), 6.27 (1H, s), 7.56 (1H, d, $J_{5\text{-Me},6}$=1.1 Hz), 9.07 (1H, br); NOE experiment: H-6/H-2′ (0.6%) and H-5′/H-6 (4.7%); ^{13}C NMR ($CDCl_3$) δ 12.6, 12.7, 12.7, 12.9, 13.4, 16.9, 17.4, 35.0, 59.4, 66.6, 84.2, 92.6, 110.3, 134.5, 149.9, 163.8; FABMS (*m*/*z*): 611 (M^++H); FAB-HRMS (*m*/*z*): calcd for $C_{22}H_{39}IN_2O_6Si_2$: 611.1470, found: 611.1453 (M^++H).

Physical data of **20α**: $[\alpha]_D^{20}$ −46.2 (*c* 0.11, $CHCl_3$); IR (neat, cm^{-1}): 3197, 3064, 2945, 2895, 2868, 1684, 1458, 1273, 1144, and 1038; ^1H NMR ($CDCl_3$) δ 1.04–1.17 (28H, m), 1.95 (3H, d, $J_{5\text{-Me},6}$=1.1 Hz), 3.99 (1H, dd, $J_{4',5'a}$=5.2 Hz and J_{gem}=13.2 Hz), 4.02 (1H, dd, $J_{4',5'b}$=3.4 Hz and J_{gem}=13.2 Hz), 4.10–4.15 (1H, m), 4.57–4.62 (2H, m), 6.07 (1H, d, $J_{1',2'}$=6.3 Hz), 7.05 (1H, d, $J_{5\text{-Me},6}$=1.1 Hz), 9.03 (1H, br); NOE experiment: H-2′/H-6 (4.5%) and H-4′/H-6 (3.8%); ^{13}C NMR ($CDCl_3$) δ 12.4, 12.5, 12.6, 13.0, 14.0, 17.2, 17.3, 26.3, 61.3, 78.6, 83.7, 92.8, 111.7, 136.2, 150.1, 163.6; FABMS (*m*/*z*): 611 (M^++H). FAB-HRMS (*m*/*z*): calcd for $C_{22}H_{39}IN_2O_6Si_2$: 611.1470, found: 611.1453 (M^++H).

4.9. 1-[3,5-*O*-(Di-*tert*-butylsilylene)-2-deoxy-2-iodo-β-D-ribofuranosyl]thymine (21)

Compound **21** was prepared as described above for **19** starting from a CH_3CN (0.7 mL) solution of thymine (74 mg, 0.59 mmol)/BSA (0.3 mL, 1.17 mmol), a CH_2Cl_2 (4 mL) solution of **18** (100 mg, 0.39 mmol), and NIS (131 mg, 0.59 mmol). Silica gel column chromatography on silica gel (hexane/ethyl acetate=5:1) of the crude mixture gave **21** (150 mg, 76%) as pale yellow foam: $[\alpha]_D^{20}$ −46.3 (*c* 1.0, $CHCl_3$); IR (neat, cm^{-1}): 3197, 3055, 2933, 2893, 2860, 1672, 1473, 1458, 1263, 1117, and 1068; ^1H NMR ($CDCl_3$) δ 1.07 and 1.09 (18H, each as s), 1.94 (3H, d, $J_{5\text{-Me},6}$=1.2 Hz), 3.41 (1H, dd, $J_{2',3'}$=6.3 Hz and $J_{3',4'}$=8.6 Hz), 4.02 (1H, ddd, $J_{4',5'b}$=5.0 Hz, $J_{3',4'}$=8.6 Hz, and $J_{4',5'a}$=10.3 Hz), 4.10 (1H, t, $J_{4',5'a}$=10.3 Hz), 4.50 (1H, dd, $J_{4',5'b}$=5.0 Hz and J_{gem}=9.2 Hz), 4.66 (1H, dd, $J_{1',2'}$=1.2 Hz and $J_{2',3'}$=6.3 Hz), 6.32 (1H, s), 7.05 (1H, d, $J_{5\text{-Me},6}$=1.2 Hz), 8.89 (1H, br); NOE experiment: H-6/H-2′ (1.6%), H-6/H-5′ (0.9%), H-6/H-3′ (3.7%) and H-1′/H-4′ (2.8%); ^{13}C NMR ($CDCl_3$) δ 12.6, 20.6, 22.8, 27.1, 27.3, 33.6, 66.6, 74.2, 76.5, 95.4, 111.3, 135.1, 149.6, 163.4; FABMS (*m*/*z*): 509 (M^++H). FAB-HRMS (*m*/*z*): calcd for $C_{18}H_{29}IN_2O_5Si$: 509.0969, found: 509.0981 (M^++H).

4.10. 1-[3,5-*O*-(Di-*tert*-butylsilylene)-2-deoxy-2-iodo-β-D-ribofuranosyl]uracil (22)

Compound **22** was prepared as described above for **19** starting from a CH_3CN (3.5 mL) solution of uracil (84 mg, 0.75 mmol)/BSA (0.37 mL, 1.50 mmol), a CH_2Cl_2 (3 mL) solution of **18** (100 mg, 0.39 mmol), and NIS (131 mg, 0.59 mmol). Silica gel column chromatography (hexane/ethyl acetate=2:1) of the crude mixture gave **22** (146 mg, 76%) as pale yellow foam: UV (MeOH): λ_{max} 261 nm (ε 10,000), λ_{min} 232 nm (ε 3200); $[\alpha]_D^{20}$ −35.6 (*c* 0.5, $CHCl_3$); IR (neat, cm^{-1}): 3213, 3064, 2935, 2891, 2860, 1699, 1265, and 1068; ^1H NMR ($CDCl_3$) δ 1.06 and 1.09 (18H, each as s), 3.34 (1H, $J_{2',3'}$=6.3 Hz and $J_{3',4'}$=8.0 Hz), 4.03–4.14 (2H, m), 4.45 (1H, dd, $J_{4',5'b}$=3.9 Hz and $J_{5'a,5'b}$=8.0 Hz), 4.66 (1H, dd, $J_{1',2'}$=1.2 Hz and $J_{2',3'}$=6.2 Hz), 5.80 (1H, d, $J_{5,6}$=8.0 Hz), 6.35 (1H, s), 7.31 (1H, d, $J_{5,6}$=8.0 Hz), 10.05 (1H, br, NH); NOE experiment: H-6/H-2′ (0.7%) and H-6/H-3′ (2.5%); ^{13}C NMR ($CDCl_3$) δ 20.6, 22.8, 27.1, 27.3, 33.5, 66.6, 74.2, 76.7, 95.0, 102.6, 138.9, 149.5, 162.8; FABMS (*m*/*z*): 495 (M^++H). Anal. Calcd for $C_{17}H_{27}IN_2O_5Si$: C, 41.30; H, 5.50; N, 5.67. Found: C, 41.00; H, 5.31; N, 5.32.

4.11. N^4-Acetyl-1-[3,5-*O*-(di-*tert*-butylsilylene)-2-deoxy-2-iodo-β-D-ribofuranosyl]-cytosine (23)

Compound **23** was prepared as described above for **19** starting from a CH_3CN (3.5 mL) solution of N^4-Ac-cytosine (115 mg, 0.75 mmol)/BSA (0.37 mL, 1.50 mmol), a CH_2Cl_2 (3 mL) solution of **18** (100 mg, 0.39 mmol), and NIS (131 mg, 0.59 mmol). Silica gel column chromatography (hexane/ethyl acetate=2:1) of the crude mixture gave **23** (119 mg, 55%) as pale yellow foam: UV (MeOH): $\lambda_{shoulder}$ 301 nm (ε 10,000) and 269 (ε 8300), λ_{max} 249 nm (ε 9900), λ_{min} 227 nm (ε 7300); $[\alpha]_D^{20}$ −61.8 (*c* 0.1, $CHCl_3$); IR (neat, cm^{-1}): 2964, 2933, 2895, 2860, 1653, 1558, 1315, 1242, and 1074; ^1H NMR ($CDCl_3$) δ 1.04 and 1.09 (18H, each as s), 2.77 (3H, s), 3.14 (1H, dd, $J_{2',3'}$=9.2 Hz and $J_{3',4'}$=10.9 Hz), 4.14 (1H, t, $J_{4',5'a}$=J_{gem}=9.2 Hz), 4.22 (1H, ddd, $J_{4',5'b}$=4.8 Hz and $J_{4',5'a}$=$J_{3',4'}$=9.2 Hz), 4.57 (1H, dd, $J_{4',5'b}$=4.8 Hz and J_{gem}=9.2 Hz), 4.65 (1H, d, $J_{2',3'}$=5.7 Hz), 6.33 (1H, s), 7.49 (1H, d, $J_{5,6}$=8.0 Hz), 7.74 (1H, d, $J_{5,6}$=8.0 Hz), 9.81 (1H, br); NOE experiment: H-6/H-2′ (0.6%) and H-1′/H-4′ (0.9%); ^{13}C NMR ($CDCl_3$) δ 20.6, 22.8, 24.9, 27.1, 27.2, 33.5, 66.7, 74.0, 77.2, 95.0, 96.7, 142.5, 154.7, 162.9, 170.9; FABMS (*m*/*z*): 536 (M^++H). Anal. Calcd for $C_{19}H_{27}IN_2O_5Si$: C, 42.62; H, 5.65; N, 7.85. Found: C, 42.25; H, 5.50; N, 8.05.

4.12. N^6-Benzoyl-9-[3,5-*O*-(di-*tert*-butylsilylene)-2-deoxy-2-iodo-β-D-ribofuranosyl]adenine (24), N^6-benzoyl-7-[3,5-*O*-(di-*tert*-butylsilylene)-2-deoxy-2-iodo-β-D-ribofuranosyl]adenine (25), and N^6-benzoyl-1-[3,5-*O*-(di-*tert*-butylsilylene)-2-deoxy-2-iodo-β-D-ribofuranosyl]adenine (26)

Compounds **24**–**26** were prepared as described above for **19** starting from a CH_3CN (3.5 mL) solution of N^6-benzoyladenine (179 mg, 0.75 mmol)/BSA (0.19 mL, 0.75 mmol), a CH_2Cl_2 (3 mL) solution of **18** (128.2 mg, 0.50 mmol), and NIS (168.7 mg, 0.75 mmol). Preparative TLC (hexane/ethyl acetate=3:1) of the crude mixture gave **24** (80.8 mg, 26%, pale yellow foam), **25** (50.9 mg, 17%, pale yellow foam), and **26** (40.2 mg, 13%, pale yellow foam).

Physical data of **24**: λ_{max} 279 nm (ε 19,100), λ_{min} 246 nm (ε 11,600); $[\alpha]_D^{20}$ −109.6 (*c* 0.2, $CHCl_3$); IR (neat, cm^{-1}): 3099, 2935, 2891, 2860, 1699, 1246, 1136, and 1068; ^1H NMR ($CDCl_3$) δ 1.11 and 1.12 (18H, each as s), 4.10–4.20 (3H, m), 4.10–4.13 (2H, m, H-4), 4.48 (1H, dd, $J_{4,5'b}$=4.0 Hz and J_{gem}=8.0 Hz), 5.07 (1H, d, $J_{2',3'}$=5.7 Hz), 7.49–7.52 and 7.58–7.61 (5H, each as m), 8.01–8.02 (2H, m), 8.05 (1H, s), 8.73 (1H, s), 9.28 (1H, br); NOE experiment: H-2′/H-2 (0.1%), H-2′/H-8 (0.6%); HMBC: H-1′/C-4; ^{13}C NMR ($CDCl_3$) δ 20.5, 22.7, 27.1, 27.3, 33.2, 66.6, 74.0, 77.0, 93.4, 123.9, 127.9, 128.8, 132.8, 133.3, 141.3, 149.8, 150.8, 152.7, 164.7. FABMS (*m*/*z*): 622 (M^++H). Anal. Calcd for $C_{25}H_{32}IN_5O_4Si\cdot 1/4AcOEt$: C, 48.52; H, 5.32; N, 10.88. Found: C, 48.41; H, 5.29; N, 10.56.

Physical data of **25**: λ_{max} 329 nm (ε 11,000) and 279 nm (ε 9500), λ_{min} 304 nm (ε 5700) and 267 nm (ε 8900); $[\alpha]_D^{20}$ +135.7 (*c* 0.4, $CHCl_3$); IR (neat, cm^{-1}): 3141, 3057, 2935, 2893, 2860, 1635, 1558, 1396, 1315, 1284, and 1070; ^1H NMR ($CDCl_3$) δ 1.04 and 1.11 (18H, each as s), 3.32 (1H, dd, $J_{2,3'}$=5.4 Hz and $J_{3',4'}$=9.0 Hz), 4.33 (1H, t, $J_{4,5'a}$=$J_{4',5'a}$=10.8 Hz), 4.35–4.43 (1H, m), 4.48 (1H, dd, $J_{4,5'b}$=4.4 Hz and $J_{5'a,5'b}$=10.8 Hz), 4.79 (1H, d, $J_{2',3'}$=5.4 Hz), 7.19 (1H, s), 7.46–7.50, 7.52–7.59 and 8.45–8.48 (5H, each as m), 8.15 and 8.54 (2H, each as s), 12.39 (1H, br); NOE experiment: H-8/H-3 (4.2%), H-8/H-5′a (2.2%), and H-1′/H-4 (1.3%); HMBC: H-1′/C-5; ^{13}C NMR ($CDCl_3$) δ 20.7, 22.7, 27.1, 27.2, 34.6, 66.5, 73.9, 78.0, 95.3, 114.4, 128.0, 130.7, 132.5, 136.4, 141.4, 142.0, 148.4, 157.1, 176.0. FABMS (*m*/*z*): 622 (M^++H). Anal. Calcd for $C_{25}H_{32}IN_5O_4Si\cdot 1/4AcOEt$: C, 48.52; H, 5.32; N, 10.88. Found: C, 48.52; H, 5.31; N, 10.66.

Physical data of **26**: λ_{max} 331 nm (ε 14,800) and 226 nm (ε 14,900), $\lambda_{shoulder}$ 247 nm (ε 11,400), λ_{min} 293 nm (ε 4900); $[\alpha]_D^{20}$ +52.5 (*c* 0.4, $CHCl_3$); IR (neat, cm^{-1}): 3219, 2995, 2933, 2895, 2860, 2779, 1716, 1558, 1473, 1419, 1362, 1286, 1173, and 1070; ^1H NMR ($CDCl_3$) δ 1.06 and 1.11 (18H, each as s), 3.44–3.47 (1H, m), 4.26 (1H, t, $J_{4,5'a}$=$J_{5'a,5'b}$=10.0 Hz), 4.29–4.35 (1H, m), 4.61 (1H, dd, $J_{4,5'b}$=4.0 Hz and $J_{5'a,5'b}$=10.0 Hz), 4.66 (1H, d, $J_{2',3'}$=5.6 Hz), 7.45–7.49, 7.54–7.57 and 8.41–8.43 (5H, each as m), 7.79 (1H, s), 8.29 and 8.33 (2H, each as s); NOE experiment: H-1′/*ortho*-H-Ph (1.9%) and H-2′/H-2 (0.4%); HMBC: H-1′/C-2; ^{13}C NMR ($CDCl_3$) δ 20.7, 22.8, 27.1, 27.2, 34.8, 66.8, 74.1, 76.8, 93.5, 114.3, 128.0, 130.2, 132.5, 136.4, 142.3, 142.5, 150.5, 158.5, 180.1. FABMS (*m*/*z*): 622 (M^++H). Anal. Calcd for $C_{25}H_{32}IN_5O_4Si$: C, 48.31; H, 5.19; N, 11.27. Found: C, 48.52; H, 5.22; N, 11.26.

4.13. 1-[3,5-*O*-(Di-*tert*-butylsilylene)-2-deoxy-β-D-ribofuranosyl]thymine (27)

To a toluene (2 mL) solution of **21** (98 mg, 0.19 mmol) were added Bu_3SnH (0.08 mL, 0.29 mmol) and Et_3B (0.1 mL, 0.10 mmol) at rt under Ar atmosphere and the mixture was stirred for 10 min under O_2 atmosphere. Silica gel column chromatography (hexane/ethyl acetate=2:1) of the reaction mixture gave **27** (62 mg, 84%) as colorless foam: $[\alpha]_D^{20}$ −5.77 (*c* 0.4, $CHCl_3$); IR (neat, cm^{-1}): 3197, 3057, 2935, 2891, 2860, 1697, 1473, 1273, 1115, 1063, and 1012; ^1H NMR ($CDCl_3$) δ 1.02 and 1.08 (18H, each as s), 1.95 (3H, d, $J_{5\text{-}Me,6}$=1.2 Hz), 2.35–2.39 (2H, m), 3.65–3.71 (1H, m), 4.01 (1H, t, $J_{4',5'a}$=J_{gem}=10.0 Hz), 4.22 (1H, dd, $J_{4',5'b}$=9.0 Hz and J_{gem}=10.0 Hz), 4.45 (1H, dd, *J*=5.0 and 9.0 Hz), 6.21 (1H, dd, *J*=4.2 and 6.7 Hz), 7.03 (1H, d, $J_{5,6}$=1.2 Hz), 8.58 (1H, br); ^{13}C NMR ($CDCl_3$) δ 12.7, 20.1, 22.7, 27.1, 27.4, 38.4, 67.3, 74.9, 76.8, 83.8, 111.5, 135.1, 149.9, 163.2; FABMS (*m*/*z*): 383 (M^++H). FAB-HRMS (*m*/*z*): calcd for $C_{18}H_{30}N_2O_5Si$: 383.2002, found: 383.2022 (M^++H).

4.14. 1-[3,5-*O*-(Di-*tert*-butylsilylene)-2-deoxy-β-D-ribofuranosyl]uracil (28)

Compound **28** was prepared as described above for **27** starting from a toluene (3.5 mL) solution of **22** (98 mg, 0.19 mmol), Bu_3SnH (1.0 M solution in cyclohexane) (0.26 mL, 0.26 mmol), and Et_3B (1.0 M solution in THF) (0.087 mL, 0.087 mmol). Silica gel column chromatography (hexane/ethyl acetate=2:1) of the crude mixture gave **28** (64 mg, 100%) as colorless foam: λ_{max} 260 nm (ε 9400) and λ_{min} 230 nm (ε 2100); $[\alpha]_D^{20}$ +4.51 (*c* 0.3, $CHCl_3$); IR (neat, cm^{-1}): 3109, 3049, 2935, 2893, 2860, 1697, 1471, 1392, 1363, 1321, 1261, 1115, 1070, and 1047; ^1H NMR ($CDCl_3$) δ 1.01 and 1.07 (18H, each as s), 2.37–2.41 (1H, m), 3.70 (1H, $J_{3',4'}$=9.2 Hz, $J_{4',5'a}$=10.0 Hz, and $J_{4',5'b}$=5.2 Hz), 4.00 (1H, dd, $J_{4',5'a}$=10.0 Hz and $J_{5'a,5'b}$=9.6 Hz), 4.15–4.22 (1H, m), 4.55 (1H, dd, $J_{4',5'b}$=5.2 Hz and $J_{5'a,5'b}$=9.6 Hz), 5.78 (1H, dd, $J_{5,6}$=8.4 Hz and $J_{5,NH}$=2.0 Hz), 6.19 (1H, dd, *J*=3.8 and 6.8 Hz), 7.27 (1H, d, $J_{5,6}$=8.4 Hz), 8.38 (1H, br); ^{13}C NMR ($CDCl_3$) δ 20.1, 22.6, 27.1, 27.4, 38.7, 67.3, 74.6, 78.1, 84.1, 102.9, 139.3, 150.1, 163.0; FABMS (*m*/*z*): 369 (M^++H). Anal. Calcd for $C_{17}H_{28}IN_2O_5Si$: C, 55.14; H, 7.66; N, 7.60. Found: C, 55.45; H, 7.74; N, 7.23.

4.15. N^4-Acetyl-1-[3,5-*O*-(di-*tert*-butylsilylene)-2-deoxy-β-D-ribofuranosyl]-cytosine (29)

Compound **29** was prepared as described above for **27** starting from a toluene (3 mL) solution of **23** (117 mg, 0.22 mmol), Bu_3SnH (0.09 mL, 0.33 mmol), and Et_3B (0.11 mL, 0.11 mmol). Silica gel column chromatography (3% MeOH in CH_2Cl_2) of the crude mixture gave **29** (70 mg, 79%) as colorless foam: UV (MeOH): λ_{max} 271 nm (ε 7900) and 243 nm (ε 7900), λ_{min} 259 nm (ε 7300) and 228 nm (ε 7100); $[\alpha]_D^{20}$ +58.5 (*c* 0.23, $CHCl_3$); IR (neat, cm^{-1}): 3298, 3136, 2935, 2893, 2860, 1668, 1558, 1506, 1394, 1325, 1254, 1115, 1070, 1011, and 1000; ^1H NMR ($CDCl_3$) δ 1.01 and 1.05 (18H, each as s), 2.24 (3H, s), 2.42–2.47 (2H, m), 3.77–3.83 (1H, m), 4.04 (1H, dd, $J_{4',5'a}$=9.6 Hz and $J_{5'a,5'b}$=10.6 Hz), 4.08 (1H, dd, $J_{4',5'b}$=8.0 Hz and

$J_{5'a,5'b}$=10.6 Hz), 4.49–4.53 (1H, m), 6.15 (1H, dd, $J_{1',2'a}$=2.8 Hz and $J_{1',2'a}$=6.4 Hz), 7.44 (1H, d, $J_{5,6}$=7.6 Hz), 7.79 (1H, d, $J_{5,6}$=7.6 Hz), 8.75 (1H, br); ^{13}C NMR ($CDCl_3$) δ 20.1, 22.6, 24.9, 27.1, 27.4, 39.4, 67.4, 74.0, 78.5, 85.9, 96.7, 143.3, 154.8, 162.9, 171.1; FABMS (*m*/*z*): 410 (M^++H). FAB-HRMS (*m*/*z*): calcd for $C_{19}H_{32}N_3O_5Si$: 410.2111, found: 410.2135 (M^++H). Anal. Calcd for $C_{19}H_{31}N_3O_3Si$: C, 55.72; H, 7.63; N, 10.26. Found: C, 55.50; H, 7.65; N, 9.96.

4.16. N^6-Benzoyl-9-[3,5-*O*-(Di-*tert*-butylsilylene)-2-deoxy-β-D-ribofuranosyl]-adenine (30)

Compound **30** was prepared as described above for **27** starting from a toluene (3 mL) solution of **24** (43.6 mg, 0.07 mmol), Bu_3SnH (1.0 M solution in cyclohexane) (0.10 mL, 0.10 mmol), and Et_3B (0.035 mL, 0.035 mmol). Silica gel column chromatography (hexane/ethyl acetate=1:4) of the crude mixture gave **30** (32 mg, 94%) as colorless foam: $[\alpha]_D^{20}$ −37.1 (*c* 0.23, $CHCl_3$); IR (neat, cm^{-1}): 3064, 2935, 2889, 2860, 1699, 1614, 1456, 1255, 1119, 1070, and 1047; ^{1}H NMR ($CDCl_3$) δ 1.04 and 1.11 (18H, each as s), 2.56 (1H, ddd, $J_{1',2'a}$=8.2 Hz, $J_{2'a,3'}$=10.8 Hz and $J_{2'a,2'b}$=13.2 Hz), 2.85 (1H, ddd, $J_{1',2'b}$=1.6 Hz, $J_{2'b,3'}$=7.2 Hz, and $J_{2'a,2'b}$=13.2 Hz), 8.32 (1H, ddd, $J_{3',4'}$=10.5 Hz, $J_{4',5'a}$=9.6 Hz, and $J_{4',5'b}$=5.2 Hz), 4.05 (1H, dd, $J_{4',5'a}$=9.6 Hz and $J_{5'a,5'b}$=9.2 Hz), 4.45 (1H, dd, $J_{4',5'b}$=5.2 Hz and $J_{5'a,5'b}$=9.2 Hz), 4.75–4.82 (1H, m), 6.42 (1H, dd, $J_{1',2'a}$=8.2 Hz and $J_{1',2'b}$=1.6 Hz), 7.51–7.55, 7.60–7.64 and 8.02–8.04 (5H, each as m), 8.11 and 8.79 (2H, each as s), 9.00 (1H, br); ^{13}C NMR ($CDCl_3$) δ 20.1, 22.7, 27.1, 27.4, 38.6, 67.5, 74.5, 78.7, 83.1, 123.6, 127.9, 128.9, 132.8, 133.5, 141.1, 149.6, 151.2, 152.8, 164.5, 176.5; FABMS (*m*/*z*): 496 (M^++H). FAB-HRMS (*m*/*z*): calcd for $C_{25}H_{34}N_5O_4Si$: 496.2380, found: 496.2361 (M^++H).

4.17. 1,4-Anhydro-2-deoxy-3,5-bis-*O*-(di-*tert*-butylsilylene)-1-*C*-methyl-D-*erythro*-pent-1-enitol (31)

To a THF (16 mL) solution of **18** (300 mg, 1.17 mmol) was added *tert*-butyl lithium (pentane solution) (1.47 mL, 2.34 mmol) at −70 °C under Ar atmosphere and the mixture was stirred for 30 min. To the reaction mixture were added HMPA (1 mL, 5.85 mmol) and methyl iodide (0.73 mL, 11.7 mmol) and the reaction mixture was stirred for 30 min. The reaction mixture was partitioned between AcOEt and saturated NH_4Cl. Silica gel column chromatography (hexane/ethyl acetate=100:1) of the organic layer gave a mixture (209 mg) of **31** (56%, calculated on the basis of the integration in ^{1}H NMR) and **18** (11%, calculated on the basis of the integration in ^{1}H NMR): ^{1}H NMR ($CDCl_3$) δ 1.02 and 1.05 (18H, each as s), 1.82–1.82 (3H, m), 4.10–4.13 (2H, m), 4.42–4.45 (1H, m), 5.04 (1H, br), 5.12–5.14 (1H, m); ^{13}C NMR ($CDCl_3$) δ 14.4, 20.3, 27.3, 27.5, 67.5, 80.9, 83.6, 102.2, 107.6, 148.1, 157.6. FABMS (*m*/*z*): 269 (M^+−H). FAB-HRMS (*m*/*z*): calcd for $C_{14}H_{26}O_3Si$: 271.1729, found: 271.1736 (M^++H).

4.18. 1,4-Anhydro-1-*C*-benzyl-2-deoxy-3,5-di-*O*-(di-*tert*-butylsilylene)-D-*erythro*-pent-1-enitol (32)

Compound **32** was prepared as described above for **31** starting from a THF (4 mL) solution of **18** (100 mg, 0.39 mmol), *tert*-butyl lithium (pentane solution) (0.5 mL, 0.78 mmol), HMPA (0.7 mL, 3.90 mmol), and benzyl bromide (0.23 mL, 1.95 mmol). Silica gel column chromatography (hexane/ethyl acetate=100:1) of the crude mixture gave a mixture of **32** and **18**. HPLC separation (hexane/ethyl acetate=100:1) of the mixture gave **32** (t_R=8.1 min, 56%, colorless foam) and **18** (26%): $[\alpha]_D^{20}$ −33.0 (*c* 0.04, $CHCl_3$); IR (neat, cm^{-1}): 2933, 2858, 1068, and 1043; ^{1}H NMR ($CDCl_3$) δ 1.02 and 1.04 (18H, each as s), 3.41 and 3.45 (1H, d, *J*=16.0 Hz), 4.08–4.15 (2H, m), 4.43 (1H, dd, $J_{4,5b}$=2.3 Hz and J_{gem}=5.7 Hz), 5.01 (1H, s), 5.14 (1H, $J_{2,3}$=1.7 Hz and $J_{3,4}$=9.2 Hz), 7.23–7.25 and 7.29–7.32 (5H, each as m); ^{13}C NMR ($CDCl_3$) δ 20.3, 22.5, 27.4, 27.6, 35.3, 67.5, 80.6, 83.8, 103.3, 126.7, 128.4, 129.0, 136.4, 144.8, 160.1; FABMS (*m*/*z*): 385 (M^++K). Anal. Calcd for $C_{20}H_{30}O_3Si$: C, 69.32; H, 8.73. Found: C, 69.17; H, 9.03.

4.19. 1,4-Anhydro-2-deoxy-3,5-bis-*O*-(di-*tert*-butylsilylene)-1-*C*-hydroxymethyl-D-*erythro*-pent-1-enitol (33)

Compound **33** was prepared as described above for **31** starting from a THF (16 mL) solution of **18** (800 mg, 3.12 mmol), *tert*-butyl lithium (pentane solution) (3.9 mL, 6.24 mmol), and DMF (1.2 mL, 15.6 mmol). To a MeOH (35 mL) solution of the crude aldehyde was added $NaBH_4$ (177 mg, 4.68 mmol) at 0 °C under Ar atmosphere and the reaction mixture was stirred for 5 min. The reaction mixture was neutralized with AcOH and partitioned between AcOEt and saturated NH_4Cl. Silica gel column chromatography (hexane/ethyl acetate=10:1) of the organic layer gave **33** (732 mg, 82%) as colorless solid: mp 95–96 °C; $[\alpha]_D^{20}$ +40.0 (*c* 0.40, $CHCl_3$); IR (neat, cm^{-1}): 2933, 2860, 1653, 1473, 1458, 1365, 1348, 1215, 1188, 1090, 1043, and 1012; ^{1}H NMR ($CDCl_3$) δ 1.02 and 1.05 (9H, each as s), 4.13–4.19 (4H, m), 4.44 and 4.4.8 (1H, each as d, J_{gem}=12.1 Hz), 5.35 (1H, br); ^{13}C NMR ($CDCl_3$) δ 20.4, 22.5, 27.3, 27.5, 58.4, 67.2, 80.3, 83.8, 103.7, 158.9; FABMS (*m*/*z*): 285 (M^+−H). Anal. Calcd for $C_{14}H_{26}O_4Si\cdot 1/2H_2O$: C, 56.91; H, 9.21. Found: C, 56.93; H, 9.15.

4.20. 1,4-Anhydro-2-deoxy-3,5-di-*O*-(di-*tert*-butylsilylene)-1-*C*-(α-hydroxybenzyl)-D-*erythro*-pent-1-enitol (34a,b)

Compound **34** was prepared as described above for **31** starting from a THF (3.5 mL) solution of **18** (200 mg, 0.78 mmol), *tert*-butyl lithium (pentane solution) (1.0 mL, 1.56 mmol), and benzaldehyde (0.24 mL, 2.34 mmol). Silica gel column chromatography (hexane/ethyl acetate=5:1) of the crude mixture gave **34** (263 mg, 93%, ratio of isomer=1:1). HPLC separation (hexane/ethyl acetate=5:1) of the mixture gave less polar product **34a** (t_R=7.4 min, colorless foam) and more polar product **34b** (t_R=7.6 min, colorless foam).

Physical data of **34a**: $[\alpha]_D^{20}$ −28.1 (*c* 0.45, $CHCl_3$); IR (neat, cm^{-1}): 2935, 2891, 2860, 1734, 1637, 1473, 1363, 1267, 1117, 1068, and 1011; ^{1}H NMR ($CDCl_3$) δ 1.01 and 1.03 (18H, each as s), 2.64 (1H, d, *J*=4.0 Hz), 4.08–4.18 (2H, m), 4.39–4.44 (1H, m), 5.12–5.15 (1H, m), 5.19–5.20 (2H, m), 7.29–7.40 (5H, m); ^{13}C NMR ($CDCl_3$) δ 20.2, 22.5, 27.3, 27.5, 67.2, 70.5, 80.2, 84.0, 104.3, 126.7, 128.3, 128.4, 139.5, 160.8; FABMS (*m*/*z*): 361 (M^+−H). Anal. Calcd for $C_{20}H_{30}O_4Si\cdot 3/2H_2O$: C, 61.66; H, 8.15. Found: C, 61.94; H, 7.88.

Physical data of **34b**: $[\alpha]_D^{20}$ +33.9 (*c* 0.23, $CHCl_3$); IR (neat, cm^{-1}): 2935, 2891, 2860, 1734, 1637, 1473, 1456, 1387, 1365, 1217, 1117, 1088, and 1022; ^{1}H NMR ($CDCl_3$) δ 1.01 and 1.03 (18H, each as s), 2.64 (1H, d, *J*=4.3 Hz), 4.10–4.14 (2H, m), 4.41–4.43 (1H, m), 5.13–5.16 (1H, m), 5.22 (1H, d, *J*=4.3 Hz), 5.25 (1H, s), 7.29–7.41 (5H, m); ^{13}C NMR ($CDCl_3$) δ 20.2, 21.0, 27.3, 27.5, 67.2, 70.5, 80.2, 83.9, 104.1, 126.6, 128.3, 128.4, 139.6, 160.6; FABMS (*m*/*z*): 361 (M^+−H). Anal. Calcd for $C_{20}H_{30}O_4Si\cdot 3/2H_2O$: C, 61.66; H, 8.15. Found: C, 61.45; H, 7.78.

4.21. 1,4-Anhydro-2-deoxy-3,5-di-*O*-(di-*tert*-butylsilylene)-1-*C*-(α-hydroxyethyl)-D-*erythro*-pent-1-enitol (35)

Compound **35** was prepared as described above for **31** starting from a THF (3.5 mL) solution of **18** (500 mg, 1.95 mmol), *tert*-butyl lithium (pentane solution) (2.5 mL, 3.90 mmol), and acetaldehyde (0.6 mL, 9.75 mmol). Silica gel column chromatography (hexane/ethyl acetate=10:1) of the crude mixture gave **35** (525 mg, 90%: ratio of isomer=1:1): $[\alpha]_D^{20}$ −22.6 (*c* 0.26, $CHCl_3$); IR (neat, cm^{-1}): 2962, 2933, 2894, 2860, 1124, and 1068; ^{1}H NMR ($CDCl_3$) δ 1.03 and 1.06 (9H, each as s), 1.36 and 1.37 (3H, each as d, *J*=2.2 and 2.4 Hz), 1.85 and 1.92 (1H each as br), 4.09–4.19 (4H, m), 4.32–4.36 (1H, m), 4.43–4.50 (1H, m), 5.12–5.18 (1H, m), 5.29 (1H, s); ^{13}C NMR ($CDCl_3$)

δ 20.4, 20.6, 20.7, 22.9, 27.6, 27.9, 64.4, 64.5, 67.6, 80.7, 84.2, 84.2, 102.0, 102.0, 162.7, 162.8; FABMS (*m*/*z*): 301 (M^++H). Anal. Calcd for $C_{22}H_{44}O_4Si_2 \cdot 1/2H_2O$: C, 60.36; H, 10.36. Found: C, 60.60; H, 10.65.

4.22. 1,4-Anhydro-2-deoxy-3,5-di-*O*-(di-*tert*-butylsilylene)-1-*C*-(α-hydroxy-α-methylethyl)-D-*erythro*-pent-1-enitol (36)

Compound **36** was prepared as described above for **31** starting from a THF (80 mL) solution of **18** (2.86 g, 11.2 mmol), *tert*-butyl lithium (pentane solution) (21.2 mL, 33.45 mmol), and acetone (4.1 mL, 55.75 mmol). Silica gel column chromatography (hexane/ethyl acetate=10:1) of the crude mixture gave **36** (674 mg, 19%) as colorless foam: $[\alpha]_D^{20}$ +43.4 (*c* 0.81, $CHCl_3$); IR (neat, cm^{-1}): 3305, 2968, 2933, 2887, 2860, 1130, 1080, and 1041; ^1H NMR ($CDCl_3$) δ 1.03 and 1.06 (9H, each as s), 1.39 and 1.40 (3H, each as s), 4.11 (1H, dt, $J_{4,5b}$=4.6 Hz and $J_{3,4}$=$J_{4,5a}$=10.9 Hz), 4.16 (1H, dd, J_{gem}=8.6 Hz and $J_{4,5a}$=10.9 Hz), 4.46 (1H, dd, $J_{4,5b}$=5.2 Hz and J_{gem}=8.6 Hz), 5.14 (1H, dd, $J_{2,3}$=1.1 Hz and $J_{3,4}$=10.9 Hz), 5.23 (1H, br); ^{13}C NMR ($CDCl_3$) δ 20.2, 22.5, 27.2, 27.3, 27.5, 67.3, 68.7, 80.4, 84.0, 100.1, 165.0; FABMS (*m*/*z*): 313 (M^+−H). Anal. Calcd for $C_{13}H_{24}O_3Si$: C, 61.11; H, 9.61. Found: C, 61.26; H, 9.99.

4.23. 1,4-Anhydro-2-deoxy-3,5-bis-*O*-(di-*tert*-butylsilylene)-1-*C*-hydroxyethyl-D-*erythro*-pent-1-enitol (37)

Compound **37** was prepared as described above for **31** starting from a THF (4 mL) solution of **18** (100 mg, 0.39 mmol), *tert*-butyl lithium (pentane solution) (0.74 mL, 1.17 mmol), ethylene oxide (THF solution) (1.8 mL, 1.95 mmol), and $BF_3 \cdot OEt_2$ (0.24 mL, 1.95 mmol). Silica gel column chromatography (hexane/ethyl acetate=3:1) of the crude mixture gave **37** (73 mg, 62%) as colorless syrup: $[\alpha]_D^{20}$ +48.0 (*c* 0.53, $CHCl_3$); IR (neat, cm^{-1}): 3390, 2935, 1649, 1473, 1389, 1346, 1288, 1211, 1190, 1157, 1117, and 1043; ^1H NMR (CD_2Cl_2) δ 1.01 and 1.04 (9H, each as s), 1.79 (1H, br), 2.38 (2H, t, *J*=6.3 Hz), 2.38 (2H, br), 4.08 (1H, dt, $J_{4,5b}$=4.6 Hz and $J_{3,4}$=$J_{4,5a}$=10.9 Hz), 4.12 (1H, dd, J_{gem}=8.3 Hz and $J_{4,5a}$=10.9 Hz), 4.42 (1H, dd, $J_{4,5b}$=4.6 Hz and J_{gem}=8.3 Hz), 5.13–5.16 (2H, m); ^{13}C NMR (CD_2Cl_2) δ 20.5, 22.8, 27.5, 27.7, 32.6, 60.1, 67.8, 80.9, 84.0, 103.6, 159.0; FABMS (*m*/*z*): 301 (M^++H). Anal. Calcd for $C_{15}H_{28}O_4Si$: C, 59.96; H, 9.39. Found: C, 59.94; H, 9.79.

4.24. 1,4-Anhydro-2-deoxy-3,5-bis-*O*-(di-*tert*-butylsilylene)-1-hydroxypropyl-D-*erythro*-pent-1-enitol (38)

Compound **38** was prepared as described above for **31** starting from a THF (20 mL) solution of **18** (1.00 g, 3.90 mmol), *tert*-butyl lithium (pentane solution) (3.7 mL, 5.85 mmol), trimethylene oxide (0.6 mL, 9.75 mmol), and $BF_3 \cdot OEt_2$ (1.2 mL, 9.75 mmol). Silica gel column chromatography (hexane/ethyl acetate=3:1) of the crude mixture gave **38** (765 mg, 65%) as colorless syrup: $[\alpha]_D^{20}$ +38.0 (*c* 0.43, $CHCl_3$); IR (neat, cm^{-1}): 3446, 2935, 2889, 2860, 1473, 1458, 1088, 1043, and 1024; ^1H NMR ($CDCl_3$) δ 1.03 and 1.05 (9H, each as s), 1.43–1.45 (1H, m), 1.73–1.80 (2H, m), 2.24 (2H, t, *J*=6.6 Hz), 3.65–3.70 (2H, m), 4.08 (1H, dt, $J_{4,5b}$=5.2 Hz and $J_{3,4}$=$J_{4,5a}$=11.7 Hz), 4.13 (1H, dd, J_{gem}=8.3 Hz and $J_{4,5a}$=11.2 Hz), 4.44 (1H, dd, $J_{4,5b}$=4.6 Hz and J_{gem}=8.3 Hz), 5.09 (1H, br), 5.11–5.14 (1H, m); ^{13}C NMR ($CDCl_3$) δ 20.3, 20.4, 22.9, 24.1, 24.8, 27.38, 27.41, 27.6, 37.7, 38.0, 42.6, 42.9, 67.7, 68.3, 68.5, 76.3, 76.4, 78.0, 96.5, 113.5, 113.6; FABMS (*m*/*z*): 313 (M^+−H) and 315 (M^++H). Anal. Calcd for $C_{16}H_{30}O_4Si$: C, 61.11; H, 9.61. Found: C, 61.17; H, 9.93.

4.25. 1,4-Anhydro-2-deoxy-3,5-di-*O*-(di-*tert*-butylsilylene)-1-*C*-(triethylsilyloxy-methyl)-D-*erythro*-pent-1-entiol (39)

To a DMF (18 mL) solution of **33** (100 mg, 0.32 mmol) were added imidazole (596 mg, 8.75 mmol) and chlorotriethylsilane (0.4 mL, 2.28 mmol) at 0 °C under Ar atmosphere and the mixture was stirred for 10 min. The reaction mixture was partitioned between AcOEt and saturated $NaHCO_3$. Silica gel column chromatography (hexane/ethyl acetate=100:1) of the organic layer gave **39** (675 mg, 96%) as colorless syrup: $[\alpha]_D^{20}$ −9.90 (*c* 0.77, $CHCl_3$); IR (neat, cm^{-1}): 3421, 2935, 1734, 1635, 1473, 1417, 1389, 1365, 1236, 1068, and 1010; ^1H NMR ($CDCl_3$) δ 0.63 (6H, q), 0.96 (9H, t), 1.02 and 1.05 (18H, each as s), 4.10–4.20 (4H, m), 4.45 (1H, dd, *J*=11.7 and 17.2 Hz), 5.12–5.18 (1H, m), 5.33 (1H, m); ^{13}C NMR ($CDCl_3$) δ 4.3, 6.7, 20.3, 22.5, 27.3, 27.5, 58.7, 67.4, 80.4, 83.8, 102.9, 159.7.; FABMS (*m*/*z*): 399 (M^+−H). Anal. Calcd for $C_{25}H_{35}IN_2O_5Si \cdot 1.2H_2O$: C, 56.88; H, 10.12. Found: C, 56.64; H, 9.79.

4.26. 1,4-Anhydro-2-deoxy-3,5-di-*O*-(di-*tert*-butylsilylene)-1-*C*-(α-triethylsilyloxybenzyl)-D-*erythro*-pent-1-enitol (40)

Compound **40** was prepared as described above for **39** starting from a DMF (60 mL) solution of **34** (2.42 g, 6.68 mmol), imidazole (682 mg, 10.0 mmol), and chlorotriethylsilane (1.46 mL, 8.68 mmol). Silica gel column chromatography (hexane/ethyl acetate=100:1) of the crude mixture gave **40** (2.72 g, 85%) as colorless syrup: $[\alpha]_D^{20}$ +8.75 (*c* 1.22, $CHCl_3$); IR (neat, cm^{-1}): 2956, 2877, 2860, 1645, 1473, 1225, 1084, 1047, and 1020; ^1H NMR ($CDCl_3$) δ 0.54–0.66 (12H, m), 0.91 (18H, t, *J*=7.8 Hz), 1.00, 1.01, 1.03 and 1.04 (36H, each as s), 4.01–4.14 (4H, m), 4.36–4.40 (2H, m), 5.07–5.18 (4H, m), 5.29 (2H, s), 5.31 (2H, s), 7.20–7.40 (10H, m); ^{13}C NMR ($CDCl_3$) δ 4.69, 4.72, 6.68, 6.70, 20.2, 22.5, 27.3, 27.4, 27.6, 67.3, 67.4, 70.9, 80.3, 80.4, 83.9, 84.1, 103.0, 103.1, 126.5, 126.6, 127.68, 127.71, 128.1, 140.8, 140.9, 162.0, 162.1; FABMS (*m*/*z*): 477 (M^++H). FAB-HRMS (*m*/*z*): calcd for $C_{26}H_{44}O_4Si_2$: 477.2856, found: 477.2847 (M^++H).

4.27. 1,4-Anhydro-2-deoxy-3,5-di-*O*-(di-*tert*-butylsilylene)-1-*C*-(α-triethylsilyloxyethyl)-D-*erythro*-pent-1-enitol (41)

Compound **41** was prepared as described above for **39** starting from a DMF (8 mL) solution of **35** (242 mg, 0.81 mmol), imidazole (83 mg, 1.05 mmol), and chlorotriethylsilane (0.18 mL, 1.05 mmol). Silica gel column chromatography (hexane/ethyl acetate=100:1) of the crude mixture gave **41** (313 mg, 93%) as colorless syrup: $[\alpha]_D^{20}$ −4.79 (*c* 0.39, $CHCl_3$); IR (neat, cm^{-1}): 2962, 1699, 1261, and 1043; ^1H NMR ($CDCl_3$) δ 0.58–0.65 (12H, m), 0.91–0.98 (18H, m), 1.02, 1.02 and 1.05 (27H, each as s), 1.28 (3H, d, *J*=6.5 Hz), 1.32 (3H, d, *J*=6.3 Hz), 4.06–4.17 (4H, m), 4.26–4.35 (2H, m), 4.41–4.47 (2H, m), 5.10–5.14 (2H, m), 5.26–5.27 (2H, m); ^{13}C NMR ($CDCl_3$) δ 4.67, 4.70, 6.7, 6.8, 6.9, 20.3, 21.8, 21.9, 22.5, 27.4, 27.6, 64.6, 64.7, 67.37, 67.44, 80.46, 80.48, 83.8, 83.9, 101.2, 163.4, 163.5; FABMS (*m*/*z*): 411 (M^++H). FAB-HRMS (*m*/*z*): calcd for $C_{22}H_{39}IN_2O_6Si_2$: 411.1470, found: 411.1453 (M^++H).

4.28. 1,4-Anhydro-2-deoxy-3,5-di-*O*-(di-*tert*-butylsilylene)-1-*C*-(α-triethylsilyloxy-α-methylethyl)-D-*erythro*-pent-1-enitol (42)

Compound **42** was prepared as described above for **39** starting from a DMF (3.2 mL) solution of **36** (100 mg, 0.32 mmol), imidazole (33 mg, 0.48 mmol), and chlorotriethylsilane (0.07 mL, 0.42 mmol). Silica gel column chromatography (hexane/ethyl acetate=100:1) of the crude mixture gave **42** (133 mg, 95%) as colorless syrup: $[\alpha]_D^{20}$ +30.3 (*c* 0.86, $CHCl_3$); IR (neat, cm^{-1}): 2935, 2877, 2862, 1647, 1473, 1363, 1251, 1184, 1167, 1132, 1117, 1078, 1043, and 1024; ^1H NMR ($CDCl_3$) δ 0.59 (6H, q, *J*=8.0 Hz), 0.94 (9H, t, *J*=8.0 Hz), 1.03, 1.05 (9H, each as s), 1.35 and 1.37 (3H, each as s), 4.08 (1H, dt, $J_{4,5b}$=5.2 Hz and $J_{3,4}$=$J_{4,5a}$=10.9 Hz), 4.14 (1H, dd, J_{gem}=8.6 Hz and $J_{4,5a}$=10.9 Hz), 4.46 (1H, dd, $J_{4,5b}$=5.2 Hz and J_{gem}=8.6 Hz), 5.11 (1H, dd, $J_{2,3}$=1.7 Hz and $J_{3,4}$=10.9 Hz), 5.23 (1H, d, $J_{2,3}$=1.7 Hz); ^{13}C NMR ($CDCl_3$) δ 6.5, 7.0, 20.3, 22.5, 27.4, 27.6, 28.5, 28.7, 67.5, 71.1, 80.7, 83.9, 99.9, 166.2;

FABMS (*m*/*z*): 427 (M^+−H). Anal. Calcd for $C_{13}H_{24}O_3Si$: C, 61.63; H, 10.34. Found: C, 61.76; H, 10.69.

4.29. 1,4-Anhydro-2-deoxy-3,5-bis-*O*-(di-*tert*-butylsilylene)-1-*C*-(triethylsilyloxyethyl)-D-*erythro*-pent-1-enitol (43)

Compound **43** was prepared as described above for **39** starting from a DMF (9 mL) solution of **37** (272 mg, 0.91 mmol), imidazole (310 mg, 4.55 mmol), and chlorotriethylsilane (0.2 mL, 1.18 mmol). Silica gel column chromatography (hexane/ethyl acetate=100:1) of the crude mixture gave **43** (318 mg, 85%) as colorless syrup: $[\alpha]_D^{20}$ +21.6 (*c* 0.99, $CHCl_3$); IR (neat, cm^{-1}): 2956, 2935, 2877, 2860, 1473, 1088, 1055, 1022; ^1H NMR ($CDCl_3$) δ 0.60 (6H, q, *J*=8.0 Hz), 0.95 (9H, t, *J*=8.0 Hz), 1.02 and 1.05 (9H, each as s), 2.37 (2H, t, *J*=7.1 Hz), 3.74 (2H, t, *J*=7.1 Hz), 4.07 (1H, dt, $J_{4,5b}$=4.4 Hz and $J_{3,4}$=$J_{4,5a}$=11.0 Hz), 4.11 (1H, dd, J_{gem}=6.6 Hz and $J_{4,5a}$=11.0 Hz), 4.42–4.45 (1H, m), 5.12 (1H, m), 5.12 (1H, s), 5.15 (1H, dt, $J_{2,3}$=1.7 Hz and *J*=11.0 Hz); ^{13}C NMR ($CDCl_3$) δ 4.7, 7.1, 20.6, 22.9, 27.7, 28.0, 32.9, 60.1, 67.9, 81.1, 83.7, 103.4, 158.8; FABMS (*m*/*z*): 415 (M^++H); FAB-HRMS (*m*/*z*): calcd for $C_{21}H_{42}O_4Si_2$: 415.2700, found: 415.2705 (M^++H).

4.30. 1,4-Anhydro-2-deoxy-3,5-di-*O*-(di-*tert*-butylsilylene)-1-*C*-(triethylsilyloxypropyl)-D-*erythro*-pent-1-enitol (44)

Compound **44** was prepared as described above for **39** starting from a DMF (20 mL) solution of **38** (615 mg, 1.96 mmol), imidazole (667 mg, 9.80 mmol), and chlorotriethylsilane (0.4 mL, 2.55 mmol). Silica gel column chromatography (hexane/ethyl acetate=100:1) of the crude mixture gave **44** (523 mg, 63%) as colorless syrup: $[\alpha]_D^{20}$ −9.24 (*c* 0.68, $CHCl_3$); IR (neat, cm^{-1}): 2956, 1734, 1716, 1699, 1591, 1473, 1363, and 1068; ^1H NMR ($CDCl_3$) δ 0.59 (6H, q, *J*=8.0 Hz), 0.95 (9H, t, *J*=8.0 Hz), 1.03 and 1.05 (18H, each as s), 1.69–1.76 (2H, m), 2.19 (2H, t, *J*=7.5 Hz), 3.63 (2H, t, *J*=6.5 Hz), 4.07 (1H, ddd, $J_{4,5b}$=4.5 Hz, $J_{3,4}$=10.7 Hz and $J_{4,5a}$=11.2 Hz), 4.12 (1H, t, $J_{4,5a}$=J_{gem}=7.6 Hz), 4.44 (1H, dd, $J_{4,5b}$=4.5 Hz and J_{gem}=7.6 Hz), 5.05 (1H, br), 5.13 (1H, dd, $J_{2,3}$=1.7 Hz and $J_{3,4}$=10.7 Hz); ^{13}C NMR ($CDCl_3$) δ 4.4, 6.8, 20.3, 22.5, 25.1, 27.4, 27.6, 29.2, 61.9, 67.5, 80.7, 83.4, 101.5, 161.2; FABMS (*m*/*z*): 427 (M^+−H). Anal. Calcd for $C_{22}H_{44}O_4Si_2\cdot 1/2H_2O$: C, 60.36; H, 10.36. Found: C, 60.60; H, 10.65.

4.31. 1-[3,5-*O*-(Di-*tert*-butylsilylene)-2-deoxy-2-iodo-1-*C*-methyl-β-D-ribofuranosyl]thymine (45)

Compound **45** was prepared as described above for **19** starting from a CH_3CN (1.5 mL) solution of thymine (142 mg, 0.75 mmol)/BSA (0.6 mL, 2.25 mmol), CH_2Cl_2 (5 mL) solution of **31** (202 mg, 0.75 mmol, contaminated with **18**), and NIS (253 mg, 1.13 mmol). Silica gel column chromatography on silica gel (hexane/ethyl acetate=5:1) gave the crude mixture of **45** and **21** (**44**/**21**=1:0.03). HPLC separation (hexane/ethyl acetate=2.5:1) of the mixture gave **45** (187.0 mg, t_R=8.6 min, 57%) as pale yellow foam: λ_{max} 269 nm (ε 11,900) and λ_{min} 235 nm (ε 2700); $[\alpha]_D^{20}$ −89.5 (*c* 0.14, $CHCl_3$); IR (neat, cm^{-1}): 3197, 3055, 2933, 2895, 2860, 1699, 1290, 1244, 1192, 1147, 1130, 1088, 1055, and 1014; ^1H NMR ($CDCl_3$) δ 1.02 and 1.09 (18H, each as s), 1.94 (3H, d, $J_{5\text{-Me},6}$=1.2 Hz), 2.06 (3H, s), 3.17 (1H, dd, $J_{2',3'}$=5.2 Hz and $J_{3',4'}$=9.2 Hz), 4.02 (1H, dd, J_{gem}=9.2 Hz and $J_{4',5'a}$=10.3 Hz), 4.18 (1H, dt, $J_{4',5'b}$=5.2 Hz and $J_{4',5'a}$=$J_{3',4'}$=10.3 Hz), 4.51 (1H, dd, $J_{4',5'b}$=5.2 Hz and J_{gem}=9.2 Hz), 5.60 (1H, d, $J_{2',3'}$=5.2 Hz), 7.49 (1H, d, $J_{5\text{-Me},6}$=1.2 Hz), 9.04 (1H, br); NOE experiment: H-6/H-5′a (6.2%), H-6/H-2′(0.2%) and H-4′/CH_3-1′(0.6%); ^{13}C NMR ($CDCl_3$) δ 12.8, 20.6, 22.8, 27.1, 27.2, 30.2, 40.0, 66.6, 74.8, 76.9, 98.3, 110.5, 134.0, 149.8, 164.1; FABMS (*m*/*z*): 523 (M^+). Anal. Calcd for $C_{19}H_{31}IN_2O_5Si\cdot 1/2AcOEt$: C, 44.52; H, 6.23; N, 4.94. Found: C, 44.41; H, 6.12; N, 5.05.

4.32. 1-[1-*C*-Benzyl-3,5-*O*-(di-*tert*-butylsilylene)-2-deoxy-2-iodo-β-D-ribofuranosyl]thymine (46)

Compound **46** was prepared as described above for **19** starting from a CH_3CN (1.0 mL) solution of thymine (76 mg, 0.60 mmol)/BSA (0.3 mL, 1.20 mmol), a CH_2Cl_2 (4 mL) solution of **32** (137 mg, 0.40 mmol), and NIS (135 mg, 0.60 mmol). Silica gel column chromatography (hexane/ethyl acetate=5:1) of the crude mixture gave **46** (131 mg, 55%) as pale yellow foam: UV (MeOH): λ_{max} 268 nm (ε 9700), λ_{min} 238 nm (ε 2500); $[\alpha]_D^{20}$ −113.6 (*c* 0.14, $CHCl_3$); IR (neat, cm^{-1}): 3230, 3064, 2933, 2893, 2860, 1685, 1697, 1288, 1240, 1194, 1151, 1124, 1093, 1068, 1052, and 1012; ^1H NMR ($CDCl_3$) δ 1.02 and 1.11 (18H, each as s), 1.58 (3H, d, $J_{5\text{-Me},6}$=1.2 Hz), 3.20 (1H, dd, $J_{2',3'}$=5.2 Hz, $J_{3',4'}$=9.2 Hz), 3.51 (1H, d, *J*=13.8 Hz), 3.85 (1H, d, *J*=13.8 Hz), 3.96 (1H, dd, J_{gem}=9.2 Hz and $J_{4',5'a}$=10.9 Hz), 4.30 (1H, dt, $J_{4',5'b}$=$J_{3',4'}$=5.2 Hz and $J_{4',5'a}$=10.9 Hz), 4.56 (1H, dd, $J_{4',5'b}$=5.2 Hz and J_{gem}=9.2 Hz), 5.76 (1H, d, $J_{2',3'}$=5.2 Hz), 6.75 (1H, d, $J_{5\text{-Me},6}$=1.2 Hz), 7.05–7.07 and 7.17–7.19 (5H, each as m), 8.62 (1H, br); NOE experiment: H-5′a/H-6 (5.4%) and H-2′/H-6 (1.3%); ^{13}C NMR ($CDCl_3$) δ 12.2, 20.6, 22.8, 27.1, 27.3, 40.6, 47.5, 66.8, 74.5, 77.3, 98.1, 109.1, 127.4, 128.3, 130.2, 134.6, 135.0, 149.9, 163.6; FABMS (*m*/*z*): 599 (M^++H). Anal. Calcd for $C_{25}H_{35}IN_2O_5Si\cdot 3/2H_2O$: C, 47.32; H, 5.88; N, 4.48. Found: C, 47.53; H, 5.69; N, 4.68.

4.33. 1-[3,5-*O*-(Di-*tert*-butylsilylene)-2-deoxy-2-iodo-1-*C*-(triethylsilyloxy-methyl)-β-D-ribofuranosyl]thymine (47)

Compound **47** was prepared as described above for **19** starting from a CH_3CN (1.0 mL) solution of thymine (95 mg, 0.75 mmol)/BSA (0.4 mL, 1.50 mmol), a CH_2Cl_2 (5 mL) solution of **39** (200 mg, 0.50 mmol), and NIS (168 mg, 0.75 mmol). Silica gel column chromatography (hexane/ethyl acetate=5:1) of the crude mixture gave **47** (230 mg, 71%) as pale yellow foam: λ_{max} 269 nm (ε 11,700), λ_{min} 235 nm (ε 2400); $[\alpha]_D^{20}$ −75.9 (*c* 0.87, $CHCl_3$); IR (neat, cm^{-1}): 3178, 3047, 2935, 1697, 1473, 1304, 1273, 1236, 1213, 1190, 1153, 1074, and 1012; ^1H NMR ($CDCl_3$) δ 0.46–0.59 (6H, m), 0.87 (9H, t, *J*=8.0 Hz), 1.03 and 1.08 (18H, each as s), 1.92 (3H, d, $J_{5\text{-Me},6}$=1.1 Hz), 3.22 (1H, dd, $J_{2',3'}$=5.2 Hz and $J_{3',4'}$=9.2 Hz), 4.00 (1H, d, *J*=10.9 Hz), 4.02 (1H, dd, J_{gem}=9.2 Hz and $J_{4',5'a}$=10.3 Hz), 4.12 (1H, ddd, $J_{4',5'b}$=5.2 Hz, $J_{3',4'}$=9.2 Hz, and $J_{4',5'a}$=10.3 Hz), 4.37 (1H, d, *J*=10.9 Hz), 4.54 (1H, dd, $J_{4',5'b}$=5.2 Hz and J_{gem}=9.2 Hz), 5.57 (1H, d, $J_{2',3'}$=5.2 Hz), 7.42 (1H, d, $J_{5\text{-Me},6}$=1.1 Hz), 8.69 (1H, br); NOE eperiment; H-6/H-2′(0.2%), H-6/H-3′ (1.1%) and H-6/H-5′(1.7%); ^{13}C NMR ($CDCl_3$) δ 4.2, 6.5, 12.6, 20.6, 22.7, 27.1, 27.3, 35.8, 66.9, 70.1, 74.3, 76.7, 96.4, 109.0, 136.7, 150.0, 164.0; FABMS (*m*/*z*): 653 (M^++H). Anal. Calcd for $C_{25}H_{45}IN_2O_6Si_2\cdot 1/2AcOEt$: C, 46.54; H, 7.09; N, 4.02. Found: C, 46.63; H, 7.10; N, 3.91.

4.34. 1-[3,5-*O*-(Di-*tert*-butylsilylene)-2-deoxy-2-iodo-1-*C*-(α-triethylsilyloxybenzyl)-β-D-ribofuranosyl]thymine (48a,b)

Compound **48** was prepared as described above for **19** starting from a CH_3CN (1.0 mL) solution of thymine (199 mg, 1.58 mmol)/BSA (0.8 mL, 3.15 mmol), a CH_2Cl_2 (11 mL) solution of **42** (500 mg, 1.05 mmol), and NIS (168 mg, 0.75 mmol). Silica gel column chromatography (hexane/ethyl acetate=5:1) of the crude mixture gave **48a** (348 mg, 45%, pale yellow foam) and **48b** (347 mg, 45%, pale yellow foam).

Physical data of **48a**: UV (MeOH): λ_{max} 273 nm (ε 10,400), λ_{min} 240 nm (ε 2900); $[\alpha]_D^{20}$ −106.9 (*c* 0.58, $CHCl_3$); IR (neat, cm^{-1}): 3197, 3064, 2935, 2875, 2862, 1699, 1685, 1652, 1473, 1456, 1288, 1236, 1194, 1149, 1128, 1107, 1072, and 1012; ^1H NMR ($CDCl_3$) δ 0.48–0.61 (6H, m), 0.85 (9H, t, *J*=8.0 Hz), 1.00 and 1.06 (18H, each as s), 1.59 (3H, d, $J_{5\text{-Me},6}$=1.2 Hz), 3.31 (1H, dd, $J_{2',3'}$=5.2 Hz and $J_{3',4'}$=9.2 Hz), 3.75 (1H, dd, J_{gem}=9.2 Hz and $J_{4',5'a}$=10.3 Hz), 4.22 (1H, ddd, $J_{4',5'b}$=5.2 Hz, $J_{3',4'}$=9.2 Hz and $J_{4',5'a}$=10.3 Hz), 4.36 (1H, dd, $J_{4',5'b}$=5.2 Hz and J_{gem}=9.2 Hz), 5.65 (1H, s), 6.38 (1H, d, $J_{5\text{-Me},6}$=1.2 Hz), 6.93 (1H, d, $J_{2',3'}$=5.2 Hz), 7.24–7.31 (5H, m), 8.31 (1H,

br); NOE experiment: H-6/H-2′ (0.2%) and H-3′/H-6 (13.4%); ^{13}C NMR ($CDCl_3$) δ 5.2, 6.7, 12.2, 20.6, 22.7, 27.2, 39.6, 67.1, 74.8, 78.1, 81.5, 99.9, 107.7, 127.4, 128.5, 129.6, 137.7, 149.9, 163.8; FABMS (*m*/*z*): 730 (M^++H). Anal. Calcd for $C_{31}H_{49}IN_2O_6Si$: C, 51.09; H, 6.78; N, 3.84. Found: C, 51.20; H, 6.87; N, 3.57.

Physical data of **48b**: UV (MeOH): λ_{max} 271 nm (ε 10,300), λ_{min} 239 nm (ε 2600); $[\alpha]_D^{20}$ −101.4 (*c* 0.72, $CHCl_3$); IR (neat, cm^{-1}): 3244, 3064, 2951, 2935, 2875, 2860, 1699, 1684, 1188, 1151, 1128, 1072, 1045, and 1011; ^{1}H NMR ($CDCl_3$) δ 0.44–0.56 (6H, m), 0.86 (9H, t, *J*=8.0 Hz), 1.04 and 1.12 (18H, each as s), 1.56 (3H, d, $J_{5\text{-Me},6}$=1.1 Hz), 3.21 (1H, dd, $J_{2',3'}$=6.9 Hz and $J_{3',4'}$=9.2 Hz), 3.99 (1H, dd, J_{gem}=9.2 Hz and $J_{4',5'a}$=10.2 Hz), 4.29 (1H, ddd, $J_{3',4'}$=9.2 Hz, $J_{4',5'b}$=4.2 Hz, and $J_{4',5'a}$=10.2 Hz), 4.59 (1H, dd, $J_{4',5'b}$=4.2 Hz and J_{gem}=9.2 Hz), 5.56 (1H, d, $J_{2',3'}$=6.9 Hz), 5.68 (1H, s), 6.88 (1H, d, $J_{5\text{-Me},6}$=1.1 Hz), 7.17–7.19 and 7.29–7.31 (5H, each as m), 8.44 (1H, br); NOE experiment; H-6/H-2′(0.2%), H-6/H-3′ (1.0%) and H-5′/H-6 (3.4%); ^{13}C NMR ($CDCl_3$) δ 5.3, 6.9, 12.2, 20.6, 22.7, 27.1, 27.3, 36.9, 67.2, 74.5, 77.4, 78.4, 97.2, 108.3, 127.6, 128.0, 128.8, 134.8, 149.9, 163.4; FABMS (*m*/*z*): 730 (M^++H). Anal. Calcd for $C_{31}H_{49}IN_2O_6Si$: C, 51.09; H, 6.78; N, 3.84. Found: C, 50.97; H, 6.80; N, 3.60.

4.35. 1-[3,5-*O*-(Di-*tert*-butylsilylene)-2-deoxy-2-iodo-1-*C*-(α-triethylsilyloxyethyl)-β-D-ribofuranosyl]thymine (49a,b)

Compound **49** was prepared as described above for **19** starting from a CH_3CN (1.0 mL) solution of thymine (115 mg, 0.92 mmol)/BSA (0.45 mL, 1.83 mmol), a CH_2Cl_2 (6 mL) solution of **41** (500 mg, 1.05 mmol), and NIS (207 mg, 0.92 mmol). Silica gel column chromatography on silica gel (hexane/ethyl acetate=3:1) of the crude mixture gave a mixture of **49a** and **49b**. HPLC separation (hexane/ethyl acetate=2.5:1) of the mixture gave **49a** (185 mg, 45%, pale yellow foam, t_R=5.8 min) and **49b** (185 mg, 45%, pale yellow foam, t_R=6.3 min).

Physical data of **49a**: UV (MeOH): λ_{max} 270 nm (ε 11,300), λ_{min} 237 nm (ε 2300); $[\alpha]_D^{20}$ −108.9 (*c* 0.15, $CHCl_3$); IR (neat, cm^{-1}): 3178, 3047, 2935, 2877, 2860, 1670, 1478, 1290, 1192, 1153, and 1070; ^{1}H NMR ($CDCl_3$) δ 0.45–0.56 (6H, m), 0.87 (9H, t, *J*=8.0 Hz), 1.03 and 1.07 (18H, each as s), 1.49 (3H, d, *J*=6.3 Hz), 1.92 (3H, br), 3.25 (1H, dd, $J_{2',3'}$=5.7 Hz and $J_{3',4'}$=8.6 Hz), 3.95–4.03 (2H, m), 4.53 (1H, dd, $J_{4',5'b}$=4.0 Hz and J_{gem}=8.6 Hz), 4.73 (1H, q, *J*=6.3 Hz), 5.73 (1H, d, $J_{2',3'}$=5.7 Hz), 7.40 (1H, br), 8.60 (1H, br); NOE experiment: H-6/H-2′ (0.3%), H-6/H-3′ (1.3%) and H-5′/H-6 (3.4%); ^{13}C NMR ($CDCl_3$) δ 5.0, 6.7, 12.6, 19.4, 20.6, 22.7, 27.1, 27.3, 36.5, 67.0, 73.2, 74.2, 77.4, 98.9, 108.7, 136.2, 150.1, 164.0; FABMS (*m*/*z*): 667 (M^++H). Anal. Calcd for $C_{26}H_{47}IN_2O_6Si$: C, 46.84; H, 7.11; N, 4.20. Found: C, 46.96; H, 7.19; N, 4.00.

Physical data of **49b**: UV (MeOH): λ_{max} 267 nm (ε 11,200), λ_{min} 235 nm (ε 2300); $[\alpha]_D^{20}$ −87.1 (*c* 0.67, $CHCl_3$); IR (neat, cm^{-1}): 3172, 3060, 2935, 1697, 1473, 1383, 1363, 1286, 1238, 1196, 1155, 1136, 1099, and 1057; ^{1}H NMR ($CDCl_3$) δ 0.61 (6H, q, *J*=8.0 Hz), 0.95 (9H, t, *J*=8.0 Hz), 1.01 and 1.08 (18H, each as s), 1.22 (3H, d, *J*=6.3 Hz), 1.90 (3H, br), 3.25 (1H, dd, $J_{2',3'}$=5.2 Hz and $J_{3',4'}$=10.9 Hz), 3.87 (1H, dd, J_{gem}=9.2 Hz and $J_{4',5'a}$=10.9 Hz), 4.19 (1H, dt, $J_{4',5'b}$=5.2 Hz, $J_{3',4'}$=$J_{4',5'a}$=10.9 Hz), 4.42 (1H, dd, $J_{4',5'b}$=5.2 Hz and J_{gem}=9.2 Hz), 4.61 (1H, q, *J*=6.3 Hz), 6.66 (1H, d, $J_{2',3'}$=5.2 Hz), 7.46 (1H, d, $J_{5\text{-Me},6}$=1.1 Hz), 9.12 (1H, br); NOE experiment: H-6/H-2′(0.3%), H-6/H-3′ (1.3%) and H-5′/H-6 (3.4%); ^{13}C NMR ($CDCl_3$) δ 4.9, 6.7, 12.5, 19.5, 20.6, 22.8, 27.2, 27.3, 36.7, 67.3, 75.1, 77.6, 77.8, 99.9, 108.3, 138.8, 150.6, 164.4; FABMS (*m*/*z*): 679 (M^++H). Anal. Calcd for $C_{26}H_{47}IN_2O_6Si$: C, 46.84; H, 7.11; N, 4.20. Found: C, 47.06; H, 7.23; N, 4.00.

4.36. 1-[3,5-*O*-(Di-*tert*-butylsilylene)-2-deoxy-2-iodo-1-*C*-(α-triethylsilyloxy-α-methylethyl)-β-D-ribofuranosyl]thymine (50)

Compound **50** was prepared as described above for **19** starting from a CH_3CN (2.0 mL) solution of thymine (204 mg, 1.62 mmol)/BSA (0.8 mL, 3.24 mmol), a CH_2Cl_2 (10 mL) solution of **42** (463 mg, 1.08 mmol), and NIS (364 mg, 1.62 mmol). Silica gel column chromatography (hexane/ethyl acetate=3:1) of the crude mixture gave **50** (248 mg, 34%) as pale yellow foam: UV (MeOH): λ_{max} 268 nm (ε 9900), λ_{min} 235 nm (ε 2500); $[\alpha]_D^{20}$ −79.3 (*c* 0.81, $CHCl_3$); IR (neat, cm^{-1}): 3176, 2931, 1697, 1471, 1388, 1365, 1319, 1286, 1192, and 1043; ^{1}H NMR ($CDCl_3$) δ 0.53 (6H, q, *J*=8.0 Hz), 0.88 (9H, t, *J*=8.0 Hz), 1.00 and 1.08 (18H, each as s), 1.52 and 1.73 (3H, each as s), 1.92 (3H, d, $J_{5\text{-Me},6}$=1.1 Hz), 3.18 (1H, dd, $J_{2',3'}$=5.2 Hz and $J_{3',4'}$=9.7 Hz), 3.89 (1H, J_{gem}=9.2 Hz and $J_{4',5'a}$=10.3 Hz), 4.12 (1H, ddd, $J_{4',5'b}$=5.2 Hz and $J_{3',4'}$=$J_{4',5'a}$=10.9 Hz), 4.47 (1H, dd, $J_{4',5'b}$=5.2 Hz and J_{gem}=9.2 Hz), 6.60 (1H, d, $J_{2',3'}$=5.2 Hz), 7.46 (1H, d, $J_{5\text{-Me},6}$=1.1 Hz), 8.93 (1H, br); NOE experiment: H-6/H-2′ (0.1%), H-5′ (1.4%), H-3′ (0.8%); ^{13}C NMR ($CDCl_3$) δ 6.4, 6.8, 12.7, 20.6, 22.8, 27.1, 27.2, 26.8, 28.4, 31.8, 67.1, 74.7, 77.4, 80.7, 102.9, 108.0, 138.8, 150.6, 164.1; FABMS (*m*/*z*): 680 (M^+). Anal. Calcd for $C_{27}H_{49}IN_2O_6Si_2$: C, 47.64; H, 7.25; N, 4.11. Found: C, 47.64; H, 7.40; N, 3.75.

4.37. 1-[3,5-*O*-(Di-*tert*-butylsilylene)-2-deoxy-2-iodo-1-*C*-(triethylsilyloxyethyl)-β-D-ribofuranosyl]thymine (51)

Compound **51** was prepared as described above for **19** starting from a CH_3CN (2.0 mL) solution of thymine (221 mg, 1.76 mmol)/BSA (0.9 mL, 3.51 mmol), a CH_2Cl_2 (12 mL) solution of **43** (486 mg, 1.17 mmol), and NIS (394 mg, 1.76 mmol). Silica gel column chromatography (hexane/ethyl acetate=3:1) of the crude mixture gave **51** (450 mg, 58%) as pale yellow foam: UV (MeOH): λ_{max} 271 nm (ε 11,000), λ_{min} 236 nm (ε 2200); $[\alpha]_D^{20}$ −49.0 (*c* 0.88, $CHCl_3$); IR (neat, cm^{-1}): 3195, 3047, 2935, 2877, 1697, 1473, 1300, 1244, 1192, 1153, 1095, 1057, and 1012; ^{1}H NMR ($CDCl_3$) δ 0.47 (6H, t, *J*=8.0 Hz), 0.87 (9H, t, *J*=8.0 Hz), 1.02 and 1.07 (18H, each as s), 1.93 (3H, s, br), 2.35 (1H, dt, *J*=4.0 and 14.9 Hz), 2.98 (1H, dt, *J*=6.9 and 14.9 Hz), 3.21 (1H, dd, $J_{2',3'}$=5.7 Hz and $J_{3',4'}$=10.3 Hz), 3.58 (2H, dd, *J*=4.0 and 6.9 Hz), 3.95 (1H, dd, J_{gem}=9.2 Hz and $J_{4',5'a}$=10.3 Hz), 4.13 (1H, dt, $J_{4',5'b}$=4.6 Hz and $J_{3',4}$=$J_{4',5'a}$=10.3 Hz), 4.51 (1H, dd, $J_{4',5'b}$=5.2 Hz and J_{gem}=9.2 Hz), 5.56 (1H, d, $J_{2',3'}$=5.7 Hz), 7.43 (1H, d, $J_{5\text{-Me},6}$=1.1 Hz), 8.72 (1H, br); NOE: H-6/H-2′ (0.2%), H-6/H-5′ (2.2%) and H-3′/H-6 (2.2%); ^{13}C NMR ($CDCl_3$) δ 4.1, 6.6, 12.8, 20.6, 22.8, 27.1, 27.2, 41.4, 43.4, 58.1, 66.7, 74.4, 76.7, 97.7, 109.6, 134.9, 150.0, 164.0; FABMS (*m*/*z*): 705 (M^++K). Anal. Calcd for $C_{31}H_{50}N_2O_6Si_2 \cdot 1/2AcOEt$: C, 47.31; H, 7.23; N, 3.94. Found: C, 47.42; H, 7.33; N, 3.60.

4.38. 1-[3,5-*O*-(Di-*tert*-butylsilylene)-2-deoxy-2-iodo-1-*C*-(triethylsilyloxypropyl)-β-D-ribofuranosyl]thymine (52)

Compound **52** was prepared as described above for **19** starting from a CH_3CN (2.0 mL) solution of thymine (89 mg, 0.71 mmol)/BSA (0.4 mL, 1.41 mmol), a CH_2Cl_2 (4.7 mL) solution of **44** (200 mg, 0.47 mmol), and NIS (158 mg, 0.71 mmol). Silica gel column chromatography (hexane/ethyl acetate=5:1) of the crude mixture gave **52** (154 mg, 48%) as pale yellow syrup: λ_{max} 268 nm (ε 11,700), λ_{min} 235 nm (ε 2500); $[\alpha]_D^{20}$ −58.5 (*c* 0.25, $CHCl_3$); IR (neat, cm^{-1}): 3197, 3064, 2951, 2875, 2862, 1699, 1473, 1458, 1286, 1236, 1194, 1151, 1128, 1093, and 1057; ^{1}H NMR ($CDCl_3$) δ 0.56–0.60 (6H, m), 0.93–0.96 (9H, m), 1.02 and 1.08 (18H, each as s), 1.00–1.08 (1H, m), 1.47–1.55 (1H, m), 1.94 (3H, d, $J_{5\text{-Me},6}$=1.1 Hz), 2.65–2.30 (1H, m), 2.65–2.73 (1H, m), 3.21 (1H, dd, $J_{2',3'}$=5.2 Hz and $J_{3',4'}$=9.2 Hz), 3.53–3.61 (2H, m), 4.02 (1H, dd, J_{gem}=9.2 Hz and $J_{4',5'a}$=10.3 Hz), 4.14 (1H, ddd, $J_{4',5'b}$=4.6 Hz, $J_{3',4}$=9.2 Hz, and $J_{4',5'a}$=10.3 Hz), 4.51 (1H, dd, $J_{4',5'b}$=4.6 Hz and J_{gem}=9.2 Hz), 5.56 (1H, d, $J_{2',3'}$=5.2 Hz), 7.41 (1H, d, $J_{5\text{-Me},6}$=1.1 Hz), 9.07 (1H, br); NOE experiment: H-5′/H-6 (7.4%), H-3′/H-6 (2.1%) and H-6/H-2′ (0.2%); ^{13}C NMR ($CDCl_3$) δ 4.3, 6.8, 12.8, 20.6, 22.8, 27.1, 27.2, 27.3, 38.2, 40.9, 61.9, 66.6, 74.5, 76.8, 99.0, 109.9, 134.8, 149.5, 164.0; FABMS (*m*/*z*): 679 (M^+−H). Anal. Calcd for $C_{27}H_{49}IN_2O_6Si_2 \cdot 1/2$ AcOEt: C, 48.06; H, 7.37; N, 3.86. Found: C, 48.15; H, 7.47; N, 3.58.

4.39. 1-[3,5-*O*-(Di-*tert*-butylsilylene)-2-deoxy-1-*C*-methyl-β-D-ribofuranosyl]-thymine (53)

Compound **53** was prepared as described above for **27** starting from a toluene (2 mL) solution of **45** (65 mg, 0.12 mmol), Bu_3SnH (0.05 mL, 0.18 mmol), and Et_3B (0.06 mL, 0.06 mmol). Silica gel column chromatography (hexane/ethyl acetate=3:1) of the crude mixture gave **53** (49 mg, 100%) as colorless foam: $[\alpha]_D^{20}$ +0.76 (*c* 0.77, $CHCl_3$); IR (neat, cm^{-1}): 3184, 3049, 2933, 2891, 2860, 1697, 1473, 1458, 1296, 1279, 1207, 1147, 1115, 1092, and 1060; ^1H NMR ($CDCl_3$) δ 1.00 and 1.03 (18H, each as s), 1.80 (3H, br), 1.93 (3H, s), 2.06 (1H, dd, $J_{2a',3'}$=11.2 Hz and J_{gem}=13.4 Hz), 3.36 (1H, dd, $J_{2b',3'}$=6.6 Hz and J_{gem}=13.4 Hz), 3.78–3.38 (1H, m), 3.91–3.97 (2H, m), 4.47 (1H, dd, $J_{4',5'b}$=4.9 Hz and J_{gem}=9.0 Hz), 7.56 (1H, br), 8.58 (1H, br); ^{13}C NMR ($CDCl_3$) δ 13.5, 20.7, 23.3, 27.8, 28.1, 44.2, 44.2, 68.1, 75.4, 78.5, 97.0, 110.3, 135.8, 150.4, 164.7; FABMS (*m*/*z*): 397 (M^++H); FAB-HRMS (*m*/*z*): calcd for $C_{19}H_{32}N_2O_5Si$: 397.2159, found: 397.2159 (M^++H).

4.40. 1-[1-*C*-Benzyl-3,5-*O*-(di-*tert*-butylsilylene)-2-deoxy-β-D-ribofuranosyl]-thymine (54)

Compound **54** was prepared as described above for **27** starting from a toluene (2 mL) solution of **46** (65 mg, 0.12 mmol), Bu_3SnH (0.05 mL, 0.18 mmol), and Et_3B (0.09 mL, 0.09 mmol). Silica gel column chromatography (hexane/ethyl acetate=3:1) of the crude mixture gave **54** (77 mg, 93%) as colorless foam: $[\alpha]_D^{20}$ −84.6 (*c* 0.23, $CHCl_3$); IR (neat, cm^{-1}): 3178, 3031, 2933, 2891, 2860, 1697, 1473, 1458, 1288, 1271, 1238, 1221, 1184, 1142, 1115, 1097, 1068, and 1051; ^1H NMR ($CDCl_3$) δ 1.00 and 1.01 (18H, each as s), 1.73 (3H, d, $J_{5\text{-}Me,6}$=1.1 Hz), 2.17 (1H, dd, $J_{2a',3'}$=10.3 Hz and J_{gem}=13.7 Hz), 3.30 (1H, d, *J*=14.0 Hz), 3.41 (1H, dd, $J_{2b',3'}$=6.9 Hz and J_{gem}=13.7 Hz), 3.54 (1H, d, *J*=14.0 Hz), 3.59 (1H, ddd, $J_{3',4'}$=5.2 Hz, $J_{2b',3'}$=6.9 Hz, and $J_{2a',3'}$=10.3 Hz), 3.88 (1H, dd, J_{gem}=9.2 Hz and $J_{4',5'a}$=10.3 Hz), 3.88–3.95 (1H, m), 4.45 (1H, dd, $J_{4',5'b}$=5.2 Hz and J_{gem}=9.2 Hz), 7.15–7.26 (6H, m), 8.56 (1H, br); ^{13}C NMR ($CDCl_3$) δ 12.4, 20.0, 22.5, 27.0, 27.3, 41.8, 44.2, 67.4, 74.3, 77.9, 97.3, 108.9, 127.3, 128.3, 134.4, 135.6, 149.8, 163.8; FABMS (*m*/*z*): 473 (M^++H); FAB-HRMS (*m*/*z*) calcd for $C_{25}H_{37}N_2O_5Si$: 473.2472, found: 473.2485 (M^++H).

4.41. 1-[3,5-*O*-(Di-*tert*-butylsilylene)-2-deoxy-1-(α-triethylsilyloxy-methyl)-β-D-ribofuranosyl]thymine (55)

Compound **55** was prepared as described above for **27** starting from a toluene (2 mL) solution of **47** (100 mg, 0.15 mmol), Bu_3SnH (0.06 mL, 0.23 mmol), and Et_3B (0.08 mL, 0.08 mmol). Silica gel column chromatography (hexane/ethyl acetate=3:1) of the crude mixture gave **55** (81 mg, 100%) as colorless foam: $[\alpha]_D^{20}$ −7.29 (*c* 0.78, $CHCl_3$); IR (neat, cm^{-1}): 3184, 3049, 2935, 1697, 1460, 1271, 1117, and 1011; ^1H NMR ($CDCl_3$) δ 0.54–0.60 (6H, m), 0.92 (9H, t, *J*=8.0 Hz), 1.00 and 1.94 (18H, each as s), 1.91 (3H, d, $J_{5\text{-}Me,6}$=1.1 Hz), 2.21 (1H, dd, $J_{2a',3'}$=11.0 Hz and J_{gem}=13.7 Hz), 2.75 (1H, dt, *J*=6.9 and 14.9 Hz), 3.24 (1H, dd, $J_{2b',3'}$=6.8 Hz and J_{gem}=13.7 Hz), 3.80–3.86 (1H, m), 3.90–4.01 (4H, m), 4.48 (1H, dd, $J_{4',5'b}$=4.6 Hz and J_{gem}=8.8 Hz), 7.53 (1H, d, $J_{5\text{-}Me,6}$=1.1 Hz), 8.70 (1H, br); ^{13}C NMR ($CDCl_3$) δ 4.9, 7.3, 13.3, 20.8, 23.3, 27.8, 28.1, 38.7, 65.9, 68.3, 75.2, 79.0, 97.7, 109.8, 137.2, 150.5, 164.7; FABMS (*m*/*z*): 527 (M^++H); FAB-HRMS (*m*/*z*) calcd for $C_{25}H_{46}N_2O_6Si_2$: 527.2973, found: 527.3005 (M^++H).

4.42. 1-[3,5-*O*-(Di-*tert*-butylsilylene)-2-deoxy-1-(α-triethylsilyloxybenzyl)-β-D-ribofuranosyl]thymine (56a)

Compound **56a** was prepared as described above for **27** starting from a toluene (4 mL) solution of **48a** (295 mg, 0.40 mmol), Bu_3SnH (0.16 mL, 0.60 mmol), and Et_3B (0.2 mL, 0.20 mmol). Silica gel column chromatography (hexane/ethyl acetate=3:1) of the crude mixture gave **56a** (227 mg, 94%) as colorless foam: $[\alpha]_D^{20}$ −51.9 (*c* 0.95, $CHCl_3$); IR (neat, cm^{-1}): 3184, 3049, 2956, 1697, 1456, 1292, 1238, 1188, 1068, and 1020; ^1H NMR ($CDCl_3$) δ 0.27–0.40 (6H, m), 7.0 (9H, s, Si-*t*-Bu), 0.71–0.74 (9H, m), 0.95 (9H, s), 1.96 (3H, d, $J_{5\text{-}Me,6}$=1.1 Hz), 2.00 (1H, dd, $J_{2a',3'}$=2.9 Hz and J_{gem}=13.5 Hz), 2.73–2.78 (1H, m), 3.34 (1H, dd, $J_{2b',3'}$=6.9 Hz and J_{gem}=13.5 Hz), 3.79 (1H, dd, J_{gem}=9.2 Hz and $J_{4',5'a}$=10.3 Hz), 3.82 (1H, ddd, $J_{4',5'b}$=5.2 Hz, $J_{3',4'}$=9.2 Hz, and $J_{4',5'a}$=10.3 Hz), 2.73–2.78 (1H, m), 4.30 (1H, dd, $J_{4',5'b}$=5.2 Hz and J_{gem}=9.2 Hz), 5.40 (1H, s), 7.29–7.51 (5H, m), 7.65 (1H, d, $J_{5\text{-}Me,6}$=1.1 Hz), 8.56 (1H, br); ^{13}C NMR ($CDCl_3$) δ 4.4, 6.4, 14.1, 19.8, 22.4, 26.8, 27.2, 38.6, 67.4, 74.0, 75.3, 78.5, 98.4, 108.5, 127.9, 128.5, 129.2, 137.9, 150.0, 164.0; FABMS (*m*/*z*): 603 (M^++H); FAB-HRMS (*m*/*z*) calcd for $C_{31}H_{50}N_2O_6Si_2$: 603.3286, found: 603.3298 (M^++H).

4.43. 1-[3,5-*O*-(Di-*tert*-butylsilylene)-2-deoxy-1-(α-triethylsiloxybenzyl)-β-D-ribofuranosyl]thymine (56b)

Compound **56b** was prepared as described above for **27** starting from a toluene (4 mL) solution of **48b** (257 mg, 0.35 mmol), Bu_3SnH (0.14 mL, 0.53 mmol), and Et_3B (0.2 mL, 0.20 mmol). Silica gel column chromatography (hexane/ethyl acetate=3:1) of the crude mixture gave **56b** (209 mg, 99%) as colorless foam: UV (MeOH): λ_{max} 270 nm (ε 9400), λ_{min} 238 nm (ε 2100); $[\alpha]_D^{20}$ −38.7 (*c* 0.83, $CHCl_3$); IR (neat, cm^{-1}): 3186, 3032, 2956, 2877, 1699, 1269, 1188, 1068, 1032, and 1010; ^1H NMR ($CDCl_3$) δ 0.45–0.57 (6H, m), 0.86–0.90 (9H, m), 1.03 and 1.04 (18H, each as s), 1.56 (3H, d, $J_{5\text{-}Me,6}$=1.1 Hz), 2.78 (1H, dd, $J_{2a',3'}$=10.9 Hz and J_{gem}=13.2 Hz), 3.35 (1H, dd, $J_{2b',3'}$=6.9 Hz and J_{gem}=13.2 Hz), 3.83 (1H, dd, J_{gem}=9.2 Hz and $J_{4',5'a}$=10.9 Hz), 3.91–3.97 (1H, m), 4.10–4.15 (1H, m), 4.53 (1H, dd, $J_{4',5'b}$=5.2 Hz and J_{gem}=9.2 Hz), 5.44 (1H, s), 6.72 (1H, d, $J_{5\text{-}Me,6}$=1.1 Hz), 7.18–7.19 (5H, m), 8.97 (1H, br); ^{13}C NMR ($CDCl_3$) δ 4.7, 6.7, 12.2, 20.1, 22.6, 27.1, 27.4, 38.7, 68.0, 74.6, 74.9, 79.5, 98.0, 108.7, 127.7, 127.9, 128.1, 138.2, 135.7, 150.1, 164.1; FABMS (*m*/*z*): 603 (M^++H). Anal. Calcd for $C_{31}H_{50}N_2O_6Si_2$: C, 61.76; H, 8.36; N, 4.65. Found: C, 61.56; H, 8.56; N, 4.37.

4.44. 1-[3,5-*O*-(Di-*tert*-butylsilylene)-2-deoxy-1-(α-triethylsilyloxyethyl)-β-D-ribofuranosyl]thymine (57a)

Compound **57a** was prepared as described above for **27** starting from a toluene (2 mL) solution of **49a** (130 mg, 0.19 mmol), Bu_3SnH (0.08 mL, 0.29 mmol), and Et_3B (0.1 mL, 0.10 mmol). Silica gel column chromatography (hexane/ethyl acetate=2:1) of the crude mixture gave **57a** (97 mg, 92%) as colorless foam: $[\alpha]_D^{20}$ −22.3 (*c* 0.71, $CHCl_3$); IR (neat, cm^{-1}): 3178, 3049, 2954, 1699, 1473, 1456, 1296, 1190, 1147, 1047, and 1011; ^1H NMR ($CDCl_3$) δ 0.40–0.58 (6H, m), 0.86 (9H, t, *J*=8.0 Hz), 1.00 and 1.03 (18H, each as s), 1.32 (3H, d, *J*=6.1 Hz), 1.91 (3H, d, $J_{5\text{-}Me,6}$=0.8 Hz), 2.10 (1H, dd, $J_{2a',3'}$=11.0 Hz and J_{gem}=13.7 Hz), 3.43 (1H, dd, $J_{2b',3'}$=6.6 Hz and J_{gem}=13.7 Hz), 3.77 (1H, ddd, $J_{4',5'b}$=4.9 Hz, $J_{3',4'}$=9.3 Hz, and $J_{4',5'a}$=10.2 Hz), 3.89 (1H, t, $J_{4',5'a}$=J_{gem}=9.0 Hz), 3.97 (1H, ddd, $J_{2'b,3'}$=6.6 Hz and $J_{3',4'}$=9.3 Hz and $J_{2a',3'}$=11.0 Hz), 4.53 (1H, dd, $J_{4',5'b}$=4.9 Hz and J_{gem}=9.0 Hz), 4.62 (1H, q, *J*=6.1 Hz), 7.52 (1H, d, $J_{5\text{-}Me,6}$=0.8 Hz), 8.44 (1H, br); ^{13}C NMR ($CDCl_3$) δ 4.7, 6.7, 12.6, 17.7, 20.1, 22.6, 27.1, 27.4, 38.2, 67.9, 69.4, 74.4, 79.8, 99.6, 108.7, 137.5, 149.8; FABMS (*m*/*z*): 541 (M^++H); FAB-HRMS (*m*/*z*) calcd for $C_{26}H_{48}N_2O_6Si_2$: 541.3130, found: 541.3203 (M^++H).

4.45. 1-[3,5-*O*-(Di-*tert*-butylsilylene)-2-deoxy-1-(α-triethylsilyloxyethyl)-β-D-ribofuranosyl]thymine (57b)

Compound **57b** was prepared as described above for **27** starting from a toluene (2 mL) solution of **49b** (127 mg, 0.19 mmol), Bu_3SnH (0.08 mL, 0.29 mmol), and Et_3B (0.1 mL, 0.10 mmol). Silica gel

column chromatography (hexane/ethyl acetate=3:1) of the crude mixture gave **57b** (97 mg, 94%) as colorless foam: $[\alpha]_D^{20}$ +22.8 (*c* 0.71, $CHCl_3$); IR (neat, cm^{-1}): 3178, 3099, 3049, 2935, 2877, 1699, 1295, 1271, 1115, 1072, and 1049; ^1H NMR ($CDCl_3$) δ 0.67 (6H, q, J=8.0 Hz), 0.67–1.02 (12H, m), 1.00 and 1.04 (18H, each as s), 1.93 (3H, d, $J_{5\text{-Me},6}$=1.1 Hz), 2.63 (1H, dd, $J_{2a',3'}$=10.7 Hz and J_{gem}=12.9 Hz), 3.12 (1H, dd, $J_{2b',3'}$=5.9 Hz and J_{gem}=12.9 Hz), 3.86–3.97 (3H, m), 4.49–4.55 (1H, m), 4.67 (1H, q, J=6.3 Hz), 7.49 (1H, d, $J_{5\text{-Me},6}$=1.1 Hz), 8.88 (1H, br); ^{13}C NMR ($CDCl_3$) δ 5.0, 6.9, 12.8, 16.3, 20.1, 22.6, 27.1, 27.4, 38.0, 67.8, 68.5, 74.8, 79.3, 98.7, 109.5, 135.7, 149.8; FABMS (*m*/*z*): 541 (M^++H); FAB-HRMS (*m*/*z*) calcd for $C_{26}H_{48}N_2O_6Si_2$: 541.3130, found: 541.3192 (M^++H).

4.46. 1-[3,5-*O*-(Di-*tert*-butylsilylene)-2-deoxy-1-(α-triethylsilyloxy-α-methylethyl)-β-D-ribofuranosyl]thymine (58)

Compound **58** was prepared as described above for **27** starting from a toluene (2 mL) solution of **50** (100 mg, 0.15 mmol), Bu_3SnH (0.06 mL, 0.23 mmol), and Et_3B (0.08 mL, 0.08 mmol). Silica gel column chromatography (hexane/ethyl acetate=3:1) of the crude mixture gave **58** (82 mg, 100%) as colorless foam: UV (MeOH): λ_{max} 266 nm (ε 8800), λ_{min} 235 nm (ε 1900); $[\alpha]_D^{20}$ −47.8 (*c* 2.69, $CHCl_3$); IR (neat, cm^{-1}): 3186, 3055, 2958, 2877, 2862, 1699, 1473, 1290, 1184, 1103, 1057, and 1011; ^1H NMR ($CDCl_3$) δ 0.86 (6H, q, J=8.0 Hz), 0.93 (9H, t, J=8.0 Hz), 1.00 and 1.03 (18H, each as s), 1.25, 1.34 and 1.91 (3H, each as s), 2.31 (1H, dd, $J_{2a',3'}$=11.5 Hz and J_{gem}=13.2 Hz), 3.76–3.81 (2H, m), 3.95–4.00 (1H, m), 4.30 (1H, dd, $J_{2b',3'}$=6.3 Hz and J_{gem}=13.2 Hz), 4.40 (1H, dd, $J_{4',5'b}$=11.2 Hz and J_{gem}=15.2 Hz), 7.55 (1H, d, $J_{5\text{-Me},6}$=1.1 Hz), 8.77 (1H, br); ^{13}C NMR ($CDCl_3$) δ 6.4, 6.9, 12.6, 20.1, 22.6, 25.3, 26.6, 27.1, 27.4, 35.3, 68.1, 74.9, 79.27, 79.30, 101.9, 108.3, 139.3, 150.3, 164.2; FABMS (*m*/*z*): 555 (M^++H). Anal. Calcd for $C_{27}H_{50}N_2O_6Si_2 \cdot 1/4AcOEt$: C, 58.30; H, 9.08; N, 4.86. Found: C, 58.34; H, 9.37; N, 4.51.

4.47. 1-[3,5-*O*-(Di-*tert*-butylsilylene)-2-deoxy-1-(α-triethylsilyloxyethyl)-β-D-ribofuranosyl]thymine (59)

Compound **59** was prepared as described above for **27** starting from a toluene (2 mL) solution of **51** (100 mg, 0.15 mmol), Bu_3SnH (0.06 mL, 0.23 mmol), and Et_3B (0.08 mL, 0.08 mmol). Silica gel column chromatography (hexane/ethyl acetate=3:1) of the crude mixture gave **59** (81 mg, 100%) as colorless foam: $[\alpha]_D^{20}$ −8.49 (*c* 0.87, $CHCl_3$); IR (neat, cm^{-1}): 3178, 3049, 2952, 2877, 1684, 1473, 1456, 1282, 1248, 1188, 1132, 1109, 1057, and 1012; ^1H NMR ($CDCl_3$) δ 0.50 (6H, t, J=8.0 Hz), 0.89 (9H, t, J=8.0 Hz), 1.91 and 1.92 (18H, each as s), 1.92 (3H, d, $J_{5\text{-Me},6}$=1.1 Hz), 2.09 (1H, dt, J=5.2 and 14.9 Hz), 2.17 (1H, dd, $J_{2a',3'}$=11.2 Hz and J_{gem}=13.4 Hz), 2.75 (1H, dt, J=6.9 and 14.9 Hz), 3.32 (1H, dd, $J_{2b',3'}$=6.6 Hz and J_{gem}=13.4 Hz), 3.66 (2H, J=5.2 and 6.3 Hz), 3.75–3.80 (1H, m), 3.91–3.96 (1H, m), 3.95 (1H, dd, J_{gem}=9.2 Hz and $J_{4',5'a}$=10.3 Hz), 4.48 (1H, dd, $J_{4',5'b}$=4.6 Hz and J_{gem}=9.2 Hz), 7.51 (1H, d, $J_{5\text{-Me},6}$=1.1 Hz), 8.76 (1H, br); ^{13}C NMR ($CDCl_3$) δ 4.1, 6.7, 12.8, 20.0, 22.6, 27.1, 27.4, 40.4, 43.3, 57.5, 67.5, 74.4, 77.9, 96.8, 109.0, 135.8, 150.0, 164.2; FABMS (*m*/*z*): 541 (M^++H); FAB-HRMS (*m*/*z*) calcd for $C_{25}H_{47}N_2O_6Si_2$: 541.3130, found: 541.3120 (M^++H).

4.48. 1-[3,5-*O*-(Di-*tert*-butylsilylene)-2-deoxy-1-(α-triethylsilyloxypropyl)-β-D-ribofuranosyl]thymine (60)

Compound **60** was prepared as described above for **27** starting from a toluene (1.1 mL) solution of **52** (78 mg, 0.11 mmol), Bu_3SnH (0.03 mL, 0.17 mmol), and Et_3B (0.06 mL, 0.06 mmol). Silica gel column chromatography (hexane/ethyl acetate=3:1) of the crude mixture gave **60** (50 mg, 78%) as colorless foam: $[\alpha]_D^{20}$ −10.5 (*c* 0.27, $CHCl_3$); IR (neat, cm^{-1}): 3184, 3049, 2935, 2877, 1697, 1473, 1458, 1362, 1290, 1238, 1219, 1184, 1109, 1065, and 1012; ^1H NMR ($CDCl_3$) δ 0.57 (6H, t, J=8.0 Hz), 0.94 (9H, t, J=8.0 Hz), 1.00 and 1.03 (18H, each as s),1.23 (2H, m), 1.92 (3H, d, $J_{5\text{-Me},6}$=1.1 Hz), 1.95–2.02 (1H, m), 2.17 (1H, dd, $J_{2a',3'}$=11.1 Hz and J_{gem}=13.5 Hz), 2.45–2.53 (1H, m), 3.32 (1H, dd, $J_{2b',3'}$=6.8 Hz and J_{gem}=13.5 Hz), 3.52–3.62 (2H, m), 3.76 (1H, ddd, $J_{4',5'b}$=4.9 Hz and $J_{4',5'a}$=10.5 Hz), 3.91–3.97 (2H, m), 4.47 (1H, dd, $J_{4',5'b}$=4.9 Hz and J_{gem}=9.3 Hz), 7.51 (1H, d, $J_{5\text{-Me},6}$=1.2 Hz), 9.01 (1H, br); ^{13}C NMR ($CDCl_3$) δ 5.0, 7.4, 13.5, 20.7, 23.2, 23.3, 27.5, 28.1, 35.7, 43.3, 62.8, 68.2, 75.1, 78.7, 98.7, 110.0, 136.4, 150.3, 164.9; FABMS (*m*/*z*): 555 (M^++H); FAB-HRMS (*m*/*z*) calcd for $C_{27}H_{50}N_2O_6Si_2$: 555.3286, found: 555.3267 (M^++H).

4.49. N^4-Acetyl-1-[3,5-*O*-(di-*tert*-butylsilylene)-2-deoxy-2-iodo-1-*C*-(triethyl-silyloxymethyl)-β-D-ribofuranosyl]cytosine (61)

Compound **61** was prepared as described above for **19** starting from a CH_3CN (2.0 mL) solution of *N*-Ac-cytosine (303 mg, 1.98 mmol)/BSA (0.97 mL, 3.96 mmol), a CH_2Cl_2 (13 mL) solution of **39** (200 mg, 1.98 mmol), and NIS (444 mg, 1.98 mmol). Silica gel column chromatography (hexane/ethyl acetate=2:1) of the crude mixture gave **61** (751 mg, 84%) as pale yellow syrup: UV (MeOH): λ_{max} 248 nm (ε16,100) and λ_{max} 301 nm (ε 7200), λ_{min} 229 nm (ε 6300) and λ_{min} 275 nm (ε 4000); $[\alpha]_D^{20}$ −94.4 (*c* 0.71, $CHCl_3$); IR (neat, cm^{-1}): 3221, 3122, 2935, 2877, 1718, 1668, 1620, 1558, 1718, 1668, 1491, 1367, 1333, 1274, 1236, 1194, 1151, 1068, and 1014; ^1H NMR ($CDCl_3$) δ 0.42–0.55 (6H, m), 0.84 (9H, t, J=7.7 Hz), 1.00 and 1.07 (18H, each as s), 2.29 (3H, s), 3.10 (1H, dd, $J_{2',3'}$=5.2 Hz and $J_{3',4'}$=9.2 Hz), 4.01 (1H, J_{gem}=9.2 Hz and $J_{4',5'a}$=10.3 Hz), 4.03 (1H, d, J=10.5 Hz), 4.15 (1H, dt, $J_{3',4'}$=9.2 Hz and $J_{4',5'a}$=$J_{4',5'b}$=10.3 Hz), 4.53 (1H, dd, J_{gem}=9.2 Hz and $J_{4',5'b}$=10.3 Hz), 5.69 (1H, d, $J_{2',3'}$=5.2 Hz), 7.41 (1H, d, $J_{5,6}$=7.8 Hz), 7.95 (1H, d, $J_{5,6}$=7.8 Hz), 10.1 (1H, br); NOE experiment: H-3′/H-6 (1.4%) and N^4-Ac/H-2′ (0.3%); ^{13}C NMR ($CDCl_3$) δ 4.2, 6.5, 20.6, 22.7, 24.9, 27.1, 27.2, 35.1, 66.9, 69.6, 73.4, 76.8, 96.0, 97.2, 145.5, 154.9, 163.0, 171.1; FABMS (*m*/*z*): 680 (M^+). Anal. Calcd for $C_{25}H_{35}IN_2O_5Si \cdot 1/2H_2O$: C, 45.34; H, 6.88; N, 6.10. Found: C, 45.48; H, 6.62; N, 5.83.

4.50. N^6-Benzoyl-9[3,5-*O*-(di-*tert*-butylsilylene)-2-deoxy-2-iodo-1-*C*-(triethy-lsilyloxymethyl)-β-D-ribofuranosyl]adenine (62) and N^6-benzoyl-1-[3,5-*O*-(di-*tert*-butylsilylene)-2-deoxy-2-iodo-1-*C*-(triethyl-silyloxymethyl)-β-D-ribofuranosyl] adenine (63)

Compounds **62** and **63** were prepared as described above for **19** starting from a CH_3CN (5.0 mL) solution of *N*-Bz-adenine (179 mg, 0.75 mmol)/BSA (0.22 mL, 0.90 mmol), a CH_2Cl_2 (5 mL) solution of **39** (202 mg, 0.50 mmol), and NIS (169 mg, 0.75 mmol). Preparative TLC (hexane/ethyl acetate=3:1) of the crude gave **62** (81.3 mg, 21%, pale yellow foam) and **63** (37 mg, 10%, pale yellow foam).

Physical data of **62**: UV (MeOH): λ_{max} 281 nm (ε19,500), λ_{min} 248 nm (ε 10,200); $[\alpha]_D^{20}$ −82.8 (*c* 0.13, $CHCl_3$); IR (neat, cm^{-1}): 2956, 2935, 2877, 2860, 1699, 1614, 1456, 1242, 1215, 1190, 1124, 1084, 1063, and 1004; ^1H NMR ($CDCl_3$) δ 0.26–0.40 (6H, m), 0.71 (9H, t, J=7.5 Hz), 0.97 and 1.09 (18H, each as s), 3.37 (1H, dd, $J_{2',3'}$=5.1 Hz and $J_{3',4'}$=9.5 Hz), 4.10 (1H, t, $J_{4',5'a}$=$J_{5'a,5'b}$=9.1 Hz), 4.26 and 4.30 (2H, each as d, J=11.1 Hz), 4.26–4.29 (1H, m), 4.59 (1H, dd, $J_{4',5'b}$=5.1 Hz and $J_{5'a,5'b}$=9.1 Hz), 6.04 (1H, d, $J_{2',3'}$=5.1 Hz), 7.51–7.54, 7.59–7.62 and 8.02–8.04 (5H, each as m), 8.18 and 8.80 (2H, each as s), 9.12 (1H, br); NOE experiment: H-8/H-2′ (0.2%), H-2/H-2′ (0.7%) and H-8/H-3′ (0.9%); ^{13}C NMR ($CDCl_3$) δ 4.0, 6.3, 20.6, 22.6, 27.1, 27.2, 35.0, 67.2, 71.0, 74.4, 77.1, 96.0, 123.8, 127.8, 128.8, 132.7, 133.6, 142.1, 149.4, 150.3, 152.3, 164.5; FABMS (*m*/*z*): 766 (M^++H). Anal. Calcd for $C_{32}H_{48}IN_5O_5Si_2$: C, 50.19; H, 6.32; N, 9.14. Found: C, 50.14; H, 6.38; N, 9.48.

Physical data of **63**: λ_{max} 330 nm (ε14,100) and 286 nm (ε10,300), λ_{min} 303 nm (ε 8700) and 270 nm (ε 8500); $[\alpha]_D^{20}$ −11.1 (*c* 0.69, $CHCl_3$); IR (neat, cm^{-1}): 3336, 2935, 2860, 1626, 1558, 1473,

1410, 1387, 1313, 1184, 1074, and 1012; ^{1}H NMR ($CDCl_3$) δ 0.28–0.45 (6H, m), 0.72 (9H, t, J=8.0 Hz), 0.92 and 1.06 (18H, each as s), 3.24 (1H, dd, $J_{2',3'}$=4.6 Hz and $J_{3',4'}$=9.2 Hz), 4.20 (1H, t, $J_{4',5'a}$=$J_{5'a,5'b}$=9.6 Hz), 4.39–4.46 (1H, m), 4.56 and 4.94 (2H, each as d, J=10.8 Hz), 4.61 (1H, dd, $J_{4',5'b}$=4.8 Hz and $J_{5'a,5'b}$=9.0 Hz), 6.05 (1H, d, $J_{2',3'}$=4.6 Hz), 7.47–7.51 and 7.53–7.61 (3H, each as m), 8.36–8.41 (3H, m), 8.51 (1H, s); NOE experiment; H-2/H-2′ (1.3%), H-2/H-3′ (1.2%) and H-2/H-5′a (0.9%); ^{13}C NMR ($CDCl_3$) δ 4.1, 6.3, 20.6, 22.7, 27.10, 27.13, 38.4, 66.7, 71.4, 74.3, 78.3, 99.0, 113.2, 127.8, 128.0, 128.8, 130.2, 132.3, 136.7, 142.0, 146.5, 151.0, 160.9, 180.7; FABMS (m/z): 765 (M^++H). Anal. Calcd for $C_{32}H_{48}IN_5O_5Si_2$: C, 50.19; H, 6.32; N, 9.14. Found: C, 50.50; H, 6.31; N, 8.74.

4.51. N^4-Acetyl-1-[3,5-*O*-(di-*tert*-butylsilylene)-2-deoxy-1-*C*-(triethylsilyloxy-methyl)-β-D-ribofuranosyl]cytosine (64)

Compound **64** was prepared as described above for **27** starting from a toluene (5.0 mL) solution of **61** (150 mg, 0.22 mmol), Bu_3SnH (1.0 M cyclohexane solution) (0.33 mL, 0.33 mmol), and Et_3B (0.11 mL, 0.11 mmol). Silica gel column chromatography (hexane/ethyl acetate=2:1) of the crude mixture gave **64** (115.4 mg, 95%) as colorless foam: UV (MeOH): $\lambda_{shoulder}$ 298 nm (ε 2500), λ_{max} 273 nm (ε 7300) and 243 nm (ε 9500), λ_{min} 265 nm (ε 7100); $[\alpha]_D^{20}$ −29.4 (c 0.33, $CHCl_3$); IR (neat, cm^{-1}): 3218, 3122, 3010, 2958, 2877, 1716, 1664, 1624, 1558, 1491, 1437, 1367, 1331, 1242, 1196, 1111, and 1012; ^{1}H NMR ($CDCl_3$) δ 0.50–0.62 (6H, m), 0.89 (9H, t, J=7.6 Hz), 1.00 and 1.01 (18H, each as s), 2.23 (1H, dd, $J_{2'a,3'}$=10.4 Hz and $J_{2'a,2'b}$=13.8 Hz), 2.24 (3H, s), 3.33 (1H, dd, $J_{2'b,3'}$=6.0 Hz and $J_{2'a,2'b}$=13.8 Hz), 3.84–3.93 (3H, m), 4.07 (2H, s), 4.47–4.50 (1H, m), 7.35 (1H, d, $J_{5,6}$=7.4 Hz), 8.09 (1H, d, $J_{5,6}$=7.4 Hz), 9.06 (1H, br); ^{13}C NMR ($CDCl_3$) δ 4.2, 6.6, 20.0, 22.5, 24.7, 27.0, 27.3, 37.1, 64.9, 67.6, 74.5, 78.4, 96.2, 97.8, 145.4, 154.7, 163.1, 171.4; FABMS (m/z): 554 (M^++H). Anal. Calcd for $C_{26}H_{47}N_3O_6Si_2$: C, 56.38; H, 8.55; N, 7.59. Found: C, 56.37; H, 8.59; N, 7.33.

4.52. N^6-Benzoyl-1-[3,5-*O*-(di-*tert*-butylsilylene)-2-deoxy-1-*C*-(triethylsilyloxy-methyl)-β-D-ribofuranosyl]adenine (65)

Compound **65** was prepared as described above for **27** starting from a toluene (3 mL) solution of **62** (66.8 mg, 0.09 mmol), Bu_3SnH (1.0 M cyclohexane solution) (0.14 mL, 0.14 mmol), and Et_3B (0.045 mL, 0.045 mmol). Silica gel column chromatography (hexane/ethyl acetate=4:1) of the crude mixture gave **65** (42.7 mg, 74%) as colorless foam: UV (MeOH): λ_{max} 280 nm (ε17,500), λ_{min} 248 nm (ε 9900); $[\alpha]_D^{20}$ −15.5 (c 0.21, $CHCl_3$); IR (neat, cm^{-1}): 2956, 2935, 2877, 2862, 1699, 1614, 1456, 1242, 1215, 1136, 1103, 1068, 1041, and 1028; ^{1}H NMR ($CDCl_3$) δ 0.48–0.58 (6H, m), 0.88 (9H, t, J=8.0 Hz), 1.00 and 1.02 (18H, each as s), 3.10 (1H, dd, $J_{2'a,3'}$=10.8 Hz and $J_{2'a,2'b}$=13.0 Hz), 3.42 (1H, dd, $J_{2'b,3'}$=6.4 Hz and $J_{2'a,2'b}$=13.0 Hz), 3.96 (1H, J_{gem}=10.8 Hz), 3.92–4.02 (2H, m), 4.07–4.14 (1H, m), 4.22 (1H, J_{gem}=10.8 Hz), 4.53–4.56 (1H, m), 7.51–7.55, 7.60–7.63 and 8.02–8.04 (5H, each as m), 8.23 and 8.79 (2H, each as s), 9.03 (1H, br); ^{13}C NMR ($CDCl_3$) δ 4.2, 6.5, 20.1, 22.6, 27.1, 27.4, 38.2, 66.3, 67.8, 74.8, 78.9, 96.4, 124.1, 127.8, 128.9, 132.8, 133.7, 141.6, 149.4, 150.5, 152.1, 164.5, 180.2; FABMS (m/z) (+KI): 678 (M^++K). Anal. Calcd for $C_{32}H_{49}N_5O_5Si_2$: C, 60.06; H, 7.72; N, 10.94. Found: C, 59.92; H, 7.79; N, 10.60.

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