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<Supporting Information>

Ring Opening of 4′, 5′-Epoxynucleosides: A Novel Stereoselective Entry to 4′-*C*-Branched Nucleosides

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General: Melting points are uncorrected. ^{1}H NMR was measured at 400 MHz or 500 MHz. Chemical shifts are reported relative to Me_4Si for ^{1}H NMR. Mass spectra (MS) were taken in FAB mode (*m*-nitrobenzyl alcohol as a matrix). Column chromatography was carried out on silica gel (Silica Gel 60, Merck). Thin layer chromatography (TLC) was performed on silica gel (pre-coated silica gel plate F_{254}, Merck). HPLC was carried out on a Shimadzu LC-6AD with a shim-pack PREP-SIL(H) · KIT column(2×25 cm).

1-[3-*O*-(*t*-Butyldimethylsilyl)-2,5-dideoxy-β-D-*glycero*-pent-4-enofuranosyl]thymine (3)

To an CH_3CN (150 mL) solution of 3′-*O*-acetyl-5′-deoxy-5′-iodothymidine[1] (11.9 g, 30.19 mmol) was added DBN (11.2 mL, 90.57 mmol) at 0 °C under an Ar atmosphere, and the reaction mixture was stirred at rt overnight. After neutralization with AcOH, the reaction mixture was evaporated to dryness and the residue was partitioned between $CHCl_3$/sat. $NaHCO_3$ (200 mL x 3/50 mL). Column chromatography (hexane/ AcOEt = 5/1-1/2) of the organic layer gave 1-(3-*O*-acetyl-2,5-dideoxy-β-D-*glycero*-pent-4-enofuranosyl)thymine (6.98 g, 87%) as a foam. The product (6.90 g, 25.92 mmol) was treated with sat. NH_3 in MeOH (350 mL) at 0 °C overnight. The reaction mixture was evaporated to dryness and dried overnight in vacuo. To a DMF (60 mL) solution of the residue were added imidazole (5.29 g, 77.75 mmol) and TBDMSCl (7.81 g, 51.83 mmol) at 0 °C under an Ar atmosphere, and the mixture was stirred at rt overnight. The reaction mixture was partitioned between AcOEt/H_2O (300 mL/100 mL x 5). Column chromatography (hexane/AcOEt = 10/1-3/1) of the organic layer gave 3 (7.87 g, 90%) as a foam: UV(MeOH) λ_{max} 264 nm (ε 11100), λ_{min} 234 nm (ε 4900);

^{1}H NMR ($CDCl_3$) δ 0.13 (6H, s), 0.91 (9H, s), 1.94 (3H, d, $J_{6,Me} = 1.2$ Hz), 2.13-2.20 (1H, m), 2.40 (1H, ddd, $J_{gem} = 13.6$, $J_{2'b,3'} = 3.4$ and $J_{1',2'b} = 6.2$ Hz), 4.24 (1H, d, $J_{gem} = 2.0$ Hz), 4.54 (1H, d, $J_{gem} = 2.0$ Hz), 4.75 (1H, dd, $J_{2'a,3'} = 6.0$ and $J_{2'b,3'} = 3.4$ Hz), 6.49 (1H, t, $J_{1',2'a} = J_{1',2'b} = 6.2$ Hz), 6.98 (1H, d, $J_{6,CH_3} = 1.2$ Hz), 8.47 (1H, br); FAB-MS (*m/z*) 339 (M^++H). *Anal.* Calcd for $C_{16}H_{26}N_2O_4Si$: C, 56.78; H, 7.74; N, 8.28. Found: C, 57.04; H, 7.99; N, 8.14.

1) Verheyden, J. P. H.; Moffatt, J. G. *J. Org. Chem.* 1974, *39*, 3573-3579.

3′-*O*-(*t*-Butyldimethylsilyl)thymidine 4′,5′-epoxide (4)

To a CH_2Cl_2 (3 mL) solution of **3** (20 mg, 0.059 mmol) was added DMDO (0.072 M in acetone, 1.2 mL, 0.089 mmol) at −30 °C under an Ar atmosphere, and the reaction mixture was stirred for 30 min. Evaporation of the solvents gave **4** as a solid: ^{1}H NMR ($CDCl_3$) δ 0.09, 0.10 (6H, each as s), 0.90 (9H, s), 1.95 (3H, d, $J_{6,Me} = 1.3$ Hz), 2.25 (1H, ddd, $J_{gem} = 14.0$, $J_{2'a,3'} = 4.9$ and $J_{1',2'a} = 7.1$ Hz), 2.52 (1H, ddd, $J_{gem} = 14.0$, $J_{2'b,3'} = 1.6$ and $J_{1',2'b} = 6.2$ Hz), 3.07 (1H, d, $J_{gem} = 3.3$ Hz), 3.36 (1H, d, $J_{gem} = 3.3$ Hz), 4.26 (1H, dd, $J_{2'a,3'} = 4.9$ and $J_{2'b,3'} = 1.6$ Hz), 6.12 (1H, dd, $J_{1',2'a} = 7.1$ and $J_{1',2'b} = 6.2$ Hz), 7.27 (1H, d, $J_{6,CH_3} = 1.3$ Hz), 9.06 (1H, br); FAB-MS (*m/z*) 355 (M^++H).

3′-*O*-(*t*-Butyldimethylsilyl)-4′-α-methylthymidine (5) and 3′-*O*-(*t*-Butyldimethylsilyl)-4′-β-methylthymidine (6)

To a CH_2Cl_2 (5 mL) solution of **3** (80 mg, 0.24 mmol) was added DMDO (0.067 M in acetone, 5.3 mL, 0.36 mmol) at −30 °C under an Ar atmosphere, and the reaction mixture was stirred for 30 min. The solvents were evaporated and the residue was dried in vacuo for 1 h to give **4**. To a CH_2Cl_2 (5 mL) solution of **4** was added Me_3Al (0.98 M in hexane, 0.72 mL, 0.71 mmol) at −30 °C under an Ar atmosphere, and the mixture was stirred for 2 h. After being quenched with sat. NH_4Cl, the reaction mixture was filtered through celite pad. The filtrate was partitioned between $CHCl_3$/sat. NH_4Cl (60 mL x 3/20 mL). Purification of the organic layer by column chromatography (hexane/AcOEt = 2/3) followed by HPLC (hexane/ AcOEt = 2/3) separation gave **5** ($t_R = 19.8$ min, 4.2 mg, 5%, syrup) and **6** ($t_R = 20.6$ min, 56 mg, 64%, foam).

Physical data of **5**: UV(MeOH) λ_{max} 267 nm (ε 9600), λ_{min} 234 nm (ε 1900); ^{1}H NMR ($CDCl_3$) δ 0.09 (6H, s), 0.90 (9H, s), 1.14 (3H, s), 1.92 (3H, s, $J_{6,Me} = 1.2$ Hz), 2.25-2.32 (1H, m), 2.40-2.47 (2H, m), 3.56 (1H, d, $J_{gem} = 11.5$ Hz), 3.70 (1H, d, $J_{gem} = 11.5$ Hz), 4.51 (1H, dd, $J_{2'a,3'} = 5.5$ and $J_{2'b,3'} = 7.0$ Hz), 6.07

(1H, t, $J_{1',2'a} = J_{1',2'b} = 6.5$ Hz), 7.39 (1H, d, $J_{6,CH_3} = 1.2$ Hz), 8.27 (1H, br); nOe experiment, H-1′/CH_3-4′ (4%) and CH_2-5′/H-3′ (4%); FAB-MS (*m/z*) 371 (M^++H). *Anal.* Calcd for $C_{17}H_{30}N_2O_5Si \cdot 1/10\ H_2O$: C, 54.84; H, 8.18; N, 7.52. Found: C, 54.64; H, 8.34; N, 7.29.

Physical data of 6: UV(MeOH) λ_{max} 266 nm (ε 12300), λ_{min} 235 nm (ε 5900); ^{1}H NMR ($CDCl_3$) δ 0.09, 0.09 (6H, each as s), 0.89 (9H, s), 1.34 (3H, s), 1.91 (3H, s), 2.26-2.33 (1H, m), 2.41-2.47 (1H, m), 2.54 (1H, br), 3.59 (1H, d, $J_{gem} = 11.9$ Hz), 3.75 (1H, d, $J_{gem} = 11.9$ Hz), 4.29 (1H, t, $J_{2'a,3'} = J_{2'b,3'} = 6.2$ Hz), 6.15 (1H, t, $J_{1',2'a} = J_{1',2'b} = 6.1$ Hz), 7.15 (1H, d, $J_{6,Me} = 1.1$ Hz), 9.58 (1H, br); nOe experiment Me-4′/H-6 (3%) and Me-4′/H-3′ (9%); FAB-MS (*m/z*) 371 (M^++H). *Anal.* Calcd for $C_{17}H_{30}N_2O_5Si \cdot 1/4H_2O$: C, 54.45; H, 8.20; N, 7.47. Found: C, 54.21; H, 8.19; N, 7.28.

4′-α-Allyl-3′-*O*-(*t*-butyldimethylsilyl)thymidine (8)

To a CH_2Cl_2 (5 mL) solution of 3 (80 mg, 0.24 mmol) was added DMDO (0.098 M in acetone, 3.6 mL, 0.36 mmol) at −30 °C under an Ar atmosphere, and the mixture was stirred for 30 min. The solvents were evaporated and the residue was dried in vacuo for 1 h to give 4. To a CH_2Cl_2 (5 mL) solution of 4 were added allyltrimethylsilane (0.11 mL, 0.71 mmol) and $SnCl_4$ (1 M in CH_2Cl_2, 0.71 mL, 0.71 mmol) at −30 °C under an Ar atmosphere, and the mixture was stirred for 4 h. After being quenched with sat. $NaHCO_3$, the reaction mixture was filtered through celite pad. The filtrate was partitioned between $CHCl_3$/sat. $NaHCO_3$ (60 mL x 3/20 mL). The organic layer was evaporated to dryness and the residue was treated with sat. NH_3 in MeOH (30 mL) at rt for 12 h. Evaporation followed by preparative TLC (hexane/EtOAc = 2/3) separation of the organic layer gave 8 (75 mg, 80%) as a foam: UV(MeOH) λ_{max} 267 nm (ε 12700), λ_{min} 235 nm (ε 5900); ^{1}H NMR ($CDCl_3$) δ 0.08, 0.08 (6H, each as s), 0.89 (9H, s), 1.87 (3H, d, $J_{6,Me} = 1.1$ Hz), 2.16 (1H, dd, $J_{gem} = 14.5$ and $J_{6'a,7'} = 8.1$ Hz), 2.27-2.39 (2H, m), 2.44 (1H, dd, $J_{gem} = 14.5$ and $J_{6'b,7'} = 6.3$ Hz), 2.94 (1H, br), 3.52 (1H, dd, $J_{gem} = 11.8$ and $J_{5',OH} = 6.1$ Hz), 3.73 (1H, dd, $J_{gem} = 11.8$ and $J_{5',OH} = 2.7$ Hz), 4.62 (1H, dd, $J_{2'a,3'} = 5.8$ and $J_{2'b,3'} = 7.0$ Hz), 5.07-5.13 (2H, m), 5.83-5.93 (1H, m), 6.11 (1H, dd, $J_{1',2'a} = 5.8$ and $J_{1',2'b} = 6.9$ Hz), 7.45 (1H, d, $J_{6,CH_3} = 1.1$ Hz), 9.40 (1H, br); nOe experiment, H-1′/$CH_2CH=CH_2$ (0.8%), CH_2-5′/H-3′ (5.3%), CH_2-5′/H-6 (0.6%), HO-5′/H-3′ (0.7%) and HO-5′/H-6 (1.2%); FAB-MS (*m/z*) 397 (M^++H). *Anal.* Calcd for $C_{19}H_{32}N_2O_5Si \cdot 1/3H_2O$: C, 56.69; H, 8.18; N, 6.96. Found: C, 56.46; H, 8.18; N, 6.87.

1-[2,3-Bis-*O*-(*t*-butyldimethylsilyl)-5-deoxy-β-D-*erythro*-pent-4-enofuranosyl]uracil (9)

To a dioxane (500 mL) suspension of uridine (30.0 g, 122.8 mmol) were added pyridine (19.9 mL, 245.7 mmol), PPh$_3$ (48.3 g, 184.3 mmol) and iodine (46.8 g, 184.3 mmol) under an Ar atmosphere, and the mixture was stirred at rt for 7 h. The reaction mixture was quenched with MeOH and sat. Na$_2$S$_2$O$_3$, and evaporated to dryness. The residue was dissolved with pyridine (300 mL) and reacted with Ac$_2$O (58 mL, 614.2 mmol) at rt overnight. The reaction mixture was evaporated dryness, and the residue was partitioned between CHCl$_3$/0.5 M HCl (500 mL x 2/300 mL). Column chromatography (CHCl$_3$/MeOH = 25/1) of the organic layer gave 2′, 3′-di-*O*-acetyl-5′-deoxy-5′-iodouridine.14) This compound was dissolved in CH$_3$CN (200 mL) and treated with DBN (3.8 mL, 273.9 mmol) at 0 °C under an Ar atmosphere and then was stirred at rt overnight. After neutralization with AcOH, the reaction mixture was evaporated to dryness and the residue was partitioned between CHCl$_3$/sat. NaHCO$_3$ (500 mL x 3/200 mL). Column chromatography (hexane/ AcOEt = 1/1) of the organic layer gave 1-(2,3-di-*O*-acetyl-5-deoxy-β-D-*erythro*-pent-4-enofuranosyl)uracil, which was treated with sat. NH$_3$ in MeOH (350 mL) at rt for 2 h. The reaction mixture was evaporated to dryness and solid precipitated was collected by suction filtration to give 1-(5-deoxy-β-D-*erythro*-pent-4-enofuranosyl)uracil (9.2 g, 33%). To a DMF (40 mL) solution of the product (4.5 g, 19.9 mmol) were added imidazole (6.8 g, 99.51 mmol) and TBDMSCl (12.0 g, 79.6 mmol) at 0 °C under an Ar atmosphere, and the mixture was stirred at rt overnight. The reaction mixture was partitioned between AcOEt/H$_2$O (300 mL/100 mLx4). Column chromatography (hexane/AcOEt = 10/1) of the organic layer gave **9** (8.19 g, 91%) as a solid: mp 164-166 °C; UV(MeOH) λ_{max} 260 nm (ε 11300), λ_{min} 232 nm (ε 5400); ^{1}H NMR (CDCl$_3$) δ 0.03, 0.06, 0.12 and 0.13 (12H, each as s), 0.87 and 0.92 (18H, each as s), 4.20 (1H, dd, $J_{1',2'}$ = 5.5 and $J_{2',3'}$ = 4.2 Hz), 4.26 (1H, d, J_{gem} = 2.5 Hz), 4.35 (1H, d, $J_{2',3'}$ = 4.2 Hz), 4.54 (1H, d, J_{gem} = 2.5 Hz), 5.79 (1H, d, $J_{5,6}$ = 8.2 Hz), 6.08 (1H, d, $J_{1',2'}$ = 5.5 Hz), 7.18 (1H, d, $J_{5,6}$ = 8.2 Hz), 8.26(1H, br); FAB-MS (*m/z*) 455 (M$^+$+H). *Anal.* Calcd for C$_{21}$H$_{38}$N$_2$O$_5$Si$_2$: C, 55.47; H, 8.42; N, 6.16. Found: C, 55.53; H, 8.73; N, 6.06.

4′-α-Allyl-2′, 3′-bis-*O*-(*t*-butyldimethylsilyl)uridine (11)

To a CH$_2$Cl$_2$ (5 mL) solution of 9 (50 mg, 0.11 mmol) was added DMDO (0.098 M in acetone, 1.7 mL, 0.17 mmol) at −30 °C under an Ar atmosphere, and the reaction mixture was stirred for 30 min. After evaporation of the solvents, the residue was dried in vacuo for 1 h to give the corresponding 4′,5′-epoxide 15. To a CH_2Cl_2 (5 mL) solution of 15 were added allyltrimethylsilane (52 μL, 0.33 mmol) and $SnCl_4$ (1 M in CH_2Cl_2, 0.33 mL, 0.33 mmol) at –30 °C under an Ar atmosphere, and the mixture was stirred at 0 °C for 5 h. After being quenched with sat. $NaHCO_3$, the reaction mixture was filtered through celite pad. The filtrate was partitioned between $CHCl_3$/sat. $NaHCO_3$ (60 mL x 3/20 mL). The organic layer was evaporated to dryness and the residue was treated with sat. NH_3 in MeOH (30 mL) at rt overnight. Evaporation followed by preparative TLC (hexane/EtOAc = 1/1) purification of the organic layer gave 11 (50.6 mg, 90%) as a solid: mp 166-168 °C; UV (MeOH) λ_{max} 262 nm (ε 13200), λ_{min} 232 nm (ε 6300); ^{1}H NMR ($CDCl_3$) δ 0.05, 0.08, 0.12 and 0.12 (12H, each as s), 0.91 and 0.94 (18H, each as s), 2.14 (1H, dd, J_{gem} = 14.9, $J_{6'a,7'}$ = 8.4 Hz), 2.63 (1H, br), 2.83-2.89 (1H, m), 3.49 (1H, d, J_{gem} = 11.9 Hz), 3.82 (1H, d, J_{gem} = 11.9 Hz), 4.36 (1H, d, $J_{2',3'}$ = 5.3 Hz), 4.52 (1H, dd, $J_{1',2'}$ = 4.1 and $J_{2',3'}$ = 5.3 Hz), 5.04-5.08 (2H, m), 5.55 (1H, d, $J_{1',2'}$ = 4.1 Hz), 5.73 (1H, d, $J_{5,6}$ = 8.1 Hz), 5.82-5.93 (1H, m), 7.63 (1H, d, $J_{5,6}$ = 8.1 Hz), 8.88(1H, br); nOe experiment, H-1′/C*H*$_2$CH=CH$_2$ (1.6%), CH$_2$-5′/H-3′ (4.2%), HO-5′/H-3′ (3.7%), HO-5′/H-2′ (5.1%) and HO-5′/H-6 (2.8%); FAB-MS (*m/z*) 551 (M$^+$+K) and 513 (M$^+$+H). *Anal.* Calcd for $C_{24}H_{44}N_2O_6Si_2$: C, 56.21; H, 8.65; N, 5.46. Found: C, 56.59; H, 8.97; N, 5.43.

9-[2,3-Bis-*O*-(*t*-butyldimethylsilyl)-5-deoxy-β-D-*erythro*-pent-4-enofuranosyl]adenine (12)

To a DMF (150 mL) solution of 9-[5-deoxy-β-D-*erythro*-pento-4-enofuranosyl]adenine [2)] (4.84 g, 19.42 mmol) were added imidazole (6.61 g, 97.10 mmol) and TBDMSOTf (16.0 mL, 67.97 mmol) at 0 °C under an Ar atmosphere, and the reaction mixture was stirred at rt for 2 days. The reaction mixture was partitioned between AcOEt/H_2O (300 mL/100 mL x 4). Column chromatography (hexane/ AcOEt = 4/1-2/1) of the organic layer gave 12 (7.90 g, 85%) as a solid: mp 211-212 °C; UV(MeOH) λ_{max} 259 nm (ε 16200), λ_{min} 231 nm (ε 5800); ^{1}H NMR ($CDCl_3$) δ –0.30, –0.06 and 0.16 (12H, each as s), 0.76 and 0.95 (18H, each as s), 4.29 (1H, d, J_{gem} = 2.3 Hz), 4.53 (1H, d, J_{gem} = 2.3 Hz), 4.60 (1H, d, $J_{2',3'}$ = 4.2 Hz), 5.08 (1H, dd, $J_{1',2'}$ = 6.2 and $J_{2',3'}$ = 4.2 Hz), 5.68 (2H, br), 6.11 (1H, d, $J_{1',2'}$ = 6.2 Hz), 7.88 (1H, s), 8.37 (1H, s); FAB-MS (*m/z*) 478 (M$^+$+H). *Anal.* Calcd for $C_{22}H_{39}N_5O_5Si_2$: C, 55.31; H, 8.23; N, 14.66. Found: C, 55.66; H, 8.49; N, 14.40.

2) McCarthy, J. R. Jr.; Robins, R. K.; Robins, M. J. *J. Am. Chem. Soc.* 1968, *90*, 4993-4999.

9-[2,3-Bis-*O*-(*t*-butyldimethylsilyl)-5-deoxy-β-D-*erythro*-pent-4-enofuranosyl]-N^6-pivaloyladenine (13)

To a CH_2Cl_2 (5 mL) solution of 12 (110 mg, 0.23 mmol) was added *i*-Pr_2NEt (79 μL, 0.46 mmol) and *t*-BuCOCl (56 μL, 0.46 mmol) at 0 °C under an Ar atmosphere, and the mixture was stirred for 1.5 h. The reaction mixture was partitioned between $CHCl_3$/sat. $NaHCO_3$ (60 mL x 3/20 mL). Column chromatography (hexane/ AcOEt = 10/1-5/1) of the organic layer gave 13 (124 mg, 96%) as a foam: UV (MeOH) λ_{max} 272 nm (ε 19800), λ_{min} 234 nm (ε 7400); ^1H NMR ($CDCl_3$) δ −0.32, −0.06, 0.15 (12H, each as s), 0.76 and 0.95 (18H, each as s), 1.41 (9H s), 4.31 (1H, d, J_{gem} = 2.4 Hz), 4.54 (1H, d, J_{gem} = 2.4 Hz), 4.57 (1H, d, $J_{2',3'}$ = 4.1 Hz), 5.07 (1H, dd, $J_{1',2'}$ = 6.4 and $J_{2',3'}$ = 4.1 Hz), 6.17 (1H, d, $J_{1',2'}$ = 6.4 Hz), 8.05 (1H, s), 8.50 (1H, br), 8.78(1H, s); FAB-HR-MS (*m/z*): calcd for $C_{27}H_{48}N_5O_4Si_2$ 562.3245 [M^++H], found 562.3202. *Anal.* Calcd for $C_{27}H_{47}N_5O_4Si_2$: C, 57.72; H, 8.43; N, 12.46. Found: C, 57.47; H, 8.66; N, 12.37.

4′-α-Allyl-2′, 3′-bis-*O*-(*t*-butyldimethylsilyl)adenosine (14)

To a CH_2Cl_2 (5 mL) solution of 13 (120 mg, 0.21 mmol) was added DMDO (0.098 M in acetone, 3.3 mL, 0.32 mmol) at −30 °C under an Ar atmosphere, and the mixture was stirred for 1 h. The reaction mixture was evaporated to dryness and the residue was dried in vacuo for 1 h to give the corresponding 4′, 5′-epoxide. To a CH_2Cl_2 (5 mL) solution of the epoxide were added allyltrimethylsilane (0.1 mL, 0.64 mmol) and $SnCl_4$ (1 M in CH_2Cl_2, 0.64 mL, 0.64 mmol) at −30 °C under an Ar atmosphere, and the mixture was stirred for 20 h. After being quenched with sat. $NaHCO_3$, the reaction mixture was filtered through celite pad. The filtrate was partitioned between $CHCl_3$/sat. $NaHCO_3$ (60 mL x 3/20 mL). The organic layer was evaporated to dryness, and the residue was treated with sat. NH_3 in MeOH (30 mL) at rt overnight. Preparative TLC (hexane/EtOAc = 1/3) separation gave 14 (59.3 mg, 52%) as a solid: mp 201-202 °C; UV (MeOH) λ_{max} 260 nm (ε 17000), λ_{min} 229 nm (ε 5000); ^1H NMR ($CDCl_3$) δ −0.71, −0.14, 0.13 and 0.15 (12H, each as s), 0.79 and 0.99 (18H, each as s), 2.08 (1H, dd, J_{gem} = 14.6, $J_{6'a,7'}$ = 8.7 Hz), 2.76-2.81 (1H, m), 3.48 (1H, t, J_{gem} = $J_{5'a,OH}$ = 12.6 Hz), 3.88 (1H, d, J_{gem} = 12.6 Hz), 4.35 (1H, d, $J_{2',3'}$ = 4.6 Hz), 5.03-5.07 (2H, m), 5.27 (1H, dd, $J_{1',2'}$ = 7.8 and $J_{2',3'}$

= 4.6 Hz), 5.72 (1H, d, $J_{1',2'}$ = 7.8 Hz), 5.82-5.91 (1H, m), 6.03(2H, br), 6.70 (1H, m), 7.83 (1H, s), 8.32 (1H, s); nOe experiment, H-1′/$CH_2CH=CH_2$ (0.7%), CH_2-5′/H-3′ (5.4%), HO-5′/H-8 (2.9%). FAB-HR-MS (*m/z*) calcd for $C_{25}H_{46}N_5O_4Si_2$ 536.3088 [M^++H], found 536.3056. *Anal.* Calcd for $C_{25}H_{45}N_5O_4Si_2$: C, 56.04; H, 8.46; N, 13.07. Found: C, 56.10; H, 8.77; N, 12.97.

2′, 3′-Bis-*O*-(*t*-butyldimethylsilyl)-4′-β-chlorouridine (17) and 2′, 3′-Bis-*O*-(*t*-butyldimethylsilyl)-4′-α-chlorouridine (18)

To a CH_2Cl_2 (8 mL) solution of **9** (200 mg, 0.44 mmol) was added DMDO (0.098 M in acetone, 6.7 mL, 0.66 mmol) at −30 °C under an Ar atmosphere, and the mixture was stirred for 30 min. The reaction mixture was evaporated to dryness and the residue was dried in vacuo for 1 h to give 15. To a CH_2Cl_2 (8 mL) solution of 15 was added tin chloride (1 M in CH_2Cl_2, 1.32 mL, 1.32 mmol) at −30 °C under an Ar atmosphere and the mixture was stirred for 1 h. The reaction mixture was quenched with sat. $NaHCO_3$ and filtered through celite pad. The filtrate was partitioned between $CHCl_3$/sat. $NaHCO_3$ (60 mL x 3/20 mL). HPLC (hexane/EtOAc = 1/1) separation of the organic layer gave 17 (t_R = 8.6 min, 64.8 mg, 29%, solid) and 18 (t_R = 13.2 min, 39.6 mg, 18%, solid).

Spectral data of 17; mp 93-97 °C; ^1H NMR ($CDCl_3$) δ 0.03, 0.06, and 0.18 (12H, each as s), 0.89 and 0.95 (18H, each as s), 2.24 (1H, br), 3.87 (1H, d, J_{gem} = 12.3 Hz), 4.00 (1H, d, J_{gem} = 12.3 Hz), 4.43 (1H, d, $J_{2',3'}$ = 3.6 Hz), 4.79 (1H, dd, $J_{1',2'}$ = 7.1 and $J_{2',3'}$ = 3.6 Hz), 5.87 (1H, dd, $J_{5,6}$ = 8.2 and $J_{5,NH}$ = 2.0 Hz), 6.33 (1H, d, $J_{1',2'}$ = 7.1 Hz), 7.69 (1H, d, $J_{5,6}$ = 8.2 Hz), 8.56(1H, br); ^{13}C NMR($CDCl_3$) δ −4.80, −4.73, −4.37, −4.10, 18.15, 18.24, 25.80, 25.93, 64.96, 74.41, 79,11, 89.36, 103.89, 112.30, 139,98, 150.27, 162.65.; FAB-MS (*m/z*) 509 and 507 (M^++H); FAB-HR-MS (*m/z*): calcd for $C_{21}H_{40}N_2O_6Si_2Cl$ 507.2113 [M^++H], found 507.2114.

Spectral data of 18; mp 99-103 °C; ^1H NMR ($CDCl_3$) δ 0.02, 0.08, 0.12 and 0.16 (12H, each as s), 0.92 and 0.95 (18H, each as s), 2.18 (1H, br), 3.76 (1H, d, J_{gem} = 12.4 Hz), 4.01 (1H, d, J_{gem} = 12.4 Hz), 4.54 (1H, dd, $J_{1',2'}$ = 3.2 and $J_{2',3'}$ = 6.0 Hz), 4.67 (1H, d, $J_{2',3'}$ = 6.0 Hz), 5.54 (1H, d, $J_{1',2'}$ = 3.2 Hz), 5.76 (1H, dd, $J_{5,6}$ = 8.2 and $J_{5,NH}$ = 2.2 Hz), 7.30 (1H, d, $J_{5,6}$ = 8.2 Hz), 9.17(1H, br); ^{13}C NMR($CDCl_3$) δ −4.93, −4.65, −4.45, −3.94, 17.84, 18.09, 25.69, 25.80, 65.96, 71.33, 72.88, 97.60, 102.98, 108.63, 143.27, 149.88, 163.00.; nOe experiment, CH_2-5′/H-3′ (2.8%), HO-5′/H-3′ (1.0%).FAB-MS (*m/z*) 507 and 509 (M^++H). FAB-HR-MS (*m/z*): calcd for $C_{21}H_{40}N_2O_6Si_2Cl$ 507.2113 [M^++H], found

507.2068.

Allylation of 17.

To a CH_2Cl_2 (5 mL) solution of 17 (64.5 mg, 0.13 mmol) were added allyltrimethylsilane (61 μL, 0.38 mmol) and $SnCl_4$ (1 M in CH_2Cl_2, 0.38 mL, 0.38 mmol) at −30 °C under an Ar atmosphere, and the mixture was stirred at 0 °C for 5 h. After being quenched with sat. $NaHCO_3$, the reaction mixture was filtered through celite pad. The filtrate was partitioned between $CHCl_3$/sat. $NaHCO_3$ (60 mL x 3/20 mL). The organic layer was evaporated to dryness and the residue was treated with sat. NH_3 in MeOH (30 mL) at rt overnight. Preparative TLC (hexane/EtOAc = 1/1) purification of the organic layer gave 11 (52.7 mg, 81%) as a solid.

Allylation of 18.

To a CH_2Cl_2 (5 mL) solution of 18 (37.9 mg, 0.075 mmol) were added allyltrimethylsilane (36 μL, 0.22 mmol) and $SnCl_4$ (1 M in CH_2Cl_2, 0.22 mL, 0.22 mmol) at −30 °C under an Ar atmosphere, and the reaction mixture was stirred at 0 °C for 5 h. After being quenched with sat. $NaHCO_3$, the reaction mixture was filtered through celite pad. The filtrate was partitioned between $CHCl_3$/sat. $NaHCO_3$ (60 mL x 3/20 mL). The organic layer was evaporated to dryness and the residue was treated with sat. NH_3 in MeOH (30 mL) at rt overnight. Preparative TLC (hexane/EtOAc = 1/1) purification of the organic layer gave 11 (36.0 mg, 94%) as a solid.

Allylation of **9** in the presence of a catalytic amount of $SnCl_4$: Formation of **10**, **11**, **19a** and **19b**.

To a CH_2Cl_2 (7 mL) solution of **9** (100 mg, 0.22 mmol) was added DMDO (0.098 M in acetone, 3.4 mL, 0.33 mmol) at −30 °C under an Ar atmosphere, and the mixture was stirred for 30 min. The reaction mixture was evaporated to dryness and the residue was dried in vacuo for 1 h to give the corresponding 4′, 5′-epoxide **15**. To a CH_2Cl_2 (7 mL) solution of **15** were added allyltrimethylsilane (105 μL, 0.66 mmol) and $SnCl_4$ (1 M in CH_2Cl_2, 0.11 mL, 0.11 mmol) at −30 °C under an Ar atmosphere, and the reaction mixture was stirred for 6 h. After being quenched with sat. $NaHCO_3$, the reaction mixture was filtered through celite pad. The filtrate was partitioned between $CHCl_3$/sat. $NaHCO_3$ (60 mL x 3/20 mL). Preparative TLC (hexane/EtOAc = 3/2) separation of the organic layer gave a mixture of **19a** and **19b** (58.3 mg, 45%, foam), **10** (5.2 mg, 4%, syrup) and **11** (18.7 mg, 17%, solid).

Spectral data of **10**: UV (MeOH) λ_{max} 263 nm (ε 9900), λ_{min} 231 nm (ε 1700); ^{1}H NMR (CDCl$_3$) δ 0.09, 0.11, and 0.16 (12H, each as s), 0.16 (9H, s), 0.92 and 0.93 (18H, each as s), 2.16 (1H, dd, J_{gem} = 15.0, $J_{6'a,7'}$ = 8.5 Hz), 3.00 (1H, dd, J_{gem} = 15.0, $J_{6'b,7'}$ = 6.2 Hz), 3.44 (1H, d, J_{gem} = 11.3 Hz), 3.76 (1H, d, J_{gem} = 11.3 Hz), 4.19 (1H, dd, $J_{1',2'}$ = 2.6 and $J_{2',3'}$ = 4.9 Hz), 4.24 (1H, d, $J_{2',3'}$ = 4.9 Hz), 5.03-5.08 (2H, m), 5.65 (1H, d, $J_{5,6}$ = 8.1 and $J_{5,NH}$ = 1.7 Hz), 5.83-5.93 (1H, m), 5.86 (1H, d, $J_{1',2'}$ = 2.6 Hz), 8.17 (1H, d, $J_{5,6}$ = 8.1 Hz), 9.08 (1H, br); ^{13}C NMR(CDCl$_3$) δ −4.98, −4.92, −4.32, −3.79, -0.79, 18.05, 18.14, 25.95, 37.38, 64.02, 70.90, 77.37, 87.65, 89.75, 101.24, 117.72, 133.44, 140.80, 150.26, 163.47.; nOe experiment, CH$_2$-5'/H-3' (2.2%), CH$_2$-5'/H-6 (1.9%). FAB-HR-MS (*m/z*): calcd for $C_{27}H_{53}N_2O_6Si_3$ 585.3211 [M$^+$+H], found 585.3224.

Spectral data of **19a** and **19b**: UV (MeOH) λ_{max} 261 nm (ε 12000), λ_{min} 231 nm (ε 4600); ^{1}H NMR (CDCl$_3$) for **19a** δ 0.03 (9H, s), 0.10, 0.11, 0.12 and 0.17 (12H, each as s), 0.93 (18H, s), 0.97 (1H, dd, J_{gem} = 13.9, $J_{6'',7''a}$ = 9.9 Hz), 1.21 (1H, dd, J_{gem} = 13.9, $J_{6'',7''b}$ = 5.0 Hz), 1.55 (1H, dd, J_{gem} = 13.6, $J_{5''a,6''}$ = 8.6 Hz), 2.90 (1H, dd, J_{gem} = 13.6, $J_{5''b,6''}$ = 6.6 Hz), 3.63 (1H, d, J_{gem} = 10.1 Hz), 3.85-3.92 (1H, m), 3.88 (1H, d, $J_{2',3'}$ = 4.3 Hz), 4.04 (1H, d, J_{gem} = 10.1 Hz), 4.22 (1H, dd, $J_{1',2'}$ = 1.5 and $J_{2',3'}$ = 4.3 Hz), 5.49 (1H, d, $J_{1',2'}$ = 1.5 Hz), 5.74 (1H, dd, $J_{5,6}$ = 8.1 and $J_{5,NH}$ = 1.7 Hz), 7.27 (1H, d, $J_{5,6}$ = 8.1 Hz), 8.65(1H, br); ^{1}H NMR (CDCl$_3$) for **19b** δ 0.04 (9H, s), 0.09, 0.11, 0.12 and 0.12 (12H, each as s), 0.82 (1H, dd, J_{gem} = 13.9, $J_{6'',7''a}$ = 9.5 Hz), 0.91 and 0.93 (18H, each as s), 1.14 (1H, dd, J_{gem} = 13.9, $J_{6'',7''b}$ = 5.1 Hz), 1.93 (1H, dd, J_{gem} = 13.8 and $J_{5''a,6''}$ = 10.5 Hz), 2.09 (1H, dd, J_{gem} = 13.8, $J_{5''b,6''}$ = 5.0 Hz), 3.85 (1H, d, J_{gem} = 9.9 Hz), 3.91-3.95 (2H, m), 4.09-4.16 (1H, m), 4.26 (1H, dd, $J_{1',2'}$ = 2.9 and $J_{2',3'}$ = 4.0 Hz), 5.56 (1H, d, $J_{1',2'}$ = 2.9 Hz), 5.74 (1H, dd, $J_{5,6}$ = 8.2 and $J_{5,NH}$ = 1.9 Hz), 7.23 (1H, d, $J_{5,6}$ = 8.2 Hz), 8.47(1H, br); nOe experiment, CH$_{2a}$-5'/H-6 (3.3%), H-1'/H-5'' (2.3%); FAB-HR-MS (*m/z*): calcd for $C_{27}H_{53}N_2O_6Si_3$ 585.3211 [M$^+$+H], found 585.3198. *Anal.* Calcd for $C_{27}H_{52}N_2O_6Si_3$: C, 55.44; H, 8.96; N, 4.79. Found: C, 55.61; H, 9.33; N, 4.62.

4'-α-(2-Bromoallyl)-3'-*O*-(*t*-butyldimethylsilyl)thymidine (21)

To a CH$_2$Cl$_2$ (5 mL) solution of **3** (80 mg, 0.24 mmol) was added DMDO (0.098 M in acetone, 3.6 mL, 0.36 mmol) at −30 °C under an Ar atmosphere, and the mixture was stirred for 30 min. The reaction mixture was evaporated to dryness and the residue was dried in vacuo for 1 h to give **4**. To a CH$_2$Cl$_2$ (5 mL) solution of **4** were added (2-bromoallyl)trimethylsilane (0.12 mL, 0.71 mmol) and SnCl$_4$ (1 M in CH$_2$Cl$_2$, 0.71 mL, 0.71 mmol) at

–70 °C under an Ar atmosphere and the reaction mixture was stirred at 0 °C for 7 h. After being quenched with sat. $NaHCO_3$, the reaction mixture was filtered through celite pad. The filtrate was partitioned between $CHCl_3$/sat. $NaHCO_3$ (60 mL x 3/20 mL). The organic layer was evaporated to dryness and the residue was treated with sat. NH_3 in MeOH (30 mL) at rt for 12 h. Preparative TLC (hexane/EtOAc = 2/3) purification of the mixture gave 21 (53 mg, 47%) as a foam: UV(MeOH) λ_{max} 266 nm (ε 11200), λ_{min} 236 nm (ε 4200); ^1H NMR ($CDCl_3$) δ 0.10 and 0.11 (6H, each as s), 0.91 (9H, s), 1.90 (3H, d, J_{6,CH_3} = 1.0 Hz), 2.34-2.37 (2H, m), 2.58 (1H, d, J_{gem} = 15.6 Hz), 2.80 (1H, br), 2.95 (1H, d, J_{gem} = 15.6 Hz), 3.64 (1H, d, J_{gem} = 11.7 Hz), 3.99 (1H, d, J_{gem} = 11.7 Hz), 4.73 (1H, t, $J_{2'a,3'} = J_{2'b,3'}$ = 6.9 Hz), 5.64 (1H, d, J_{gem} = 1.1 Hz), 5.73 (1H, d, J_{gem} = 1.1 Hz), 6.21 (1H, t, $J_{1',2'a} = J_{1',2'b}$ = 6.2 Hz), 7.42 (1H, d, J_{6,CH_3} = 1.0 Hz), 9.07 (1H, br); nOe experiment, H-1′/CH_2CBr=CH_2 (1.0%), CH_2-5′/H-3′ (1.7%), and HO-5′/H-6 (1.8%); FAB-MS (*m/z*) 513, 515(M^++K) and 475, 477 (M^++H). *Anal.* Calcd for $C_{19}H_{31}BrN_2O_5Si$: C, 48.00; H, 6.57; N, 5.89. Found: C, 48.23; H, 6.65; N, 5.76.

3′-*O*-(*t*-Butyldimethylsilyl)-4′-α-(cyclopentenyl-3-yl)thymidine (22)

To a CH_2Cl_2 (5 mL) solution of 3 (50 mg, 0.15 mmol) was added DMDO (0.09 M in acetone, 2.5 mL, 0.22 mmol) at –30 °C under an Ar atmosphere, and the mixture was stirred for 30 min. The reaction mixture was evaporated to dryness and the residue was dried in vacuo for 1 h to give 4. To a CH_2Cl_2 (5 mL) solution of 4 were added 3-trimethylsilylcyclopentene (76 μL, 0.44 mmol) and $SnCl_4$ (1 M in CH_2Cl_2, 0.44 mL, 0.44 mmol) at –30 °C under an Ar atmosphere, and the mixture was stirred for 6 h. After being quenched with sat. $NaHCO_3$, the reaction mixture was filtered through celite pad. The filtrate was partitioned between $CHCl_3$/sat. $NaHCO_3$ (60 mL x 3/20 mL). The organic layer was evaporated to dryness and the residue was treated with sat. NH_3 in MeOH (30 mL) at rt overnight. Preparative TLC (hexane/EtOAc = 2/3) purification of of the mixture gave 22 [19.9 mg, 32%, a mixture of two isomers (74/26)] as a syrup: UV (MeOH) λ_{max} 267 nm (ε 11700), λ_{min} 235 nm (ε 4500); ^1H NMR ($CDCl_3$) (major isomer) δ 0.12 (6H, s), 0.92 (9H, s), 1.83-2.10 (4H, m), 1.91 (3H, d, J_{6,CH_3} = 1.1 Hz), 2.29-2.50 (3H, m), 3.23-3.28 (1H, m), 3.62 (1H, d, J_{gem} = 11.8 Hz), 3.74 (1H, d, J_{gem} = 11.8 Hz), 4.70 (1H, dd, $J_{2'a,3'}$ = 5.0 and $J_{2'b,3'}$ = 7.1 Hz), 5.61-5.84 (2H, m), 6.14 (1H, t, $J_{1',2'a} = J_{1',2'b}$ = 6.7 Hz), 7.45 (1H, d, J_{6,CH_3} = 1.1 Hz), 8.95 (1H, br); (minor isomer) δ 0.11 (6H, s), 0.92 (9H, s), 1.83-1.92 (3H, m), 1.94 (3H, d, $J_{6,\mathrm{CH3}}$ = 1.1 Hz), 2.24-2.29 (1H, m), 2.29-2.50 (3H, m), 2.97-3.02 (1H, m), 3.55 (1H, d, J_{gem} = 11.7 Hz), 3.78 (1H, d, J_{gem} = 11.7 Hz), 4.77 (1H, dd, $J_{2'\mathrm{a},3'}$ = 5.5 and $J_{2'\mathrm{b},3'}$ = 7.9 Hz), 5.84-5.92 (2H, m), 6.02 (1H, dd, $J_{1',2'\mathrm{a}}$ = 6.0 and $J_{1',2'\mathrm{b}}$ = 7.2 Hz), 7.41 (1H, d, $J_{6,\mathrm{CH3}}$ = 1.1 Hz), 8.95 (1H, br); nOe experiment (as its 5′-*O*-acetate), H-1′/C*H*-5″ (major isomer, 2.6%; minor isomer, 1.9%); FAB-MS (*m/z*) 461 (M^++K) and 423 (M^++H). *Anal.* Calcd for $C_{21}H_{34}N_2O_5Si \cdot 5/6\ H_2O$: C, 57.64; H, 8.22; N, 6.40. Found: C, 57.74; H, 8.11; N, 6.10.

3′-*O*-(*t*-Butyldimethylsilyl)-4′-α-cyanothymidine (23)

To a CH_2Cl_2 (5 mL) solution of 3 (50 mg, 0.24 mmol) was added DMDO (0.098 M in acetone, 2.3 mL, 0.22 mmol) at −30 °C under an Ar atmosphere, and the reaction mixture was stirred for 30 min. The reaction mixture was evaporated to dryness and the residue was dried in vacuo for 1 h to give 4. To a CH_2Cl_2 (5 mL) solution of 4 were added cyanotrimethylsilane (59 μL, 0.44 mmol) and $SnCl_4$ (1 M in CH_2Cl_2, 0.44 mL, 0.44 mmol) at −30 °C under an Ar atmosphere, and the mixture was stirred at rt for 15 h. After being quenched with sat. $NaHCO_3$, the reaction mixture was filtered through celite pad. The filtrate was partitioned between $CHCl_3$/sat. $NaHCO_3$ (60 mL x 3/20 mL). The organic layer was evaporated to dryness and the residue was treated with sat. NH_3 in MeOH (30 mL) at rt overnight. Preparative TLC (hexane/EtOAc = 1/2) purification of the mixture gave 23 (25.2 mg, 45%) as a foam: UV (MeOH) $\lambda_{\max}$ 263 nm (ε 10900), $\lambda_{\min}$ 234 nm (ε 4800); IR (neat) 2250 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.14 and 0.17 (6H, each as s), 0.94 (9H, s), 1.91 (3H, d, $J_{6,\mathrm{CH3}}$ = 1.1 Hz), 2.35-2.41 (1H, m), 2.65-2.72 (1H m), 3.53 (1H, br), 3.87 (1H, dd, J_{gem} = 12.1 and $J_{5',\mathrm{OH}}$ = 6.6 Hz), 4.03 (1H, d, J_{gem} = 12.1 Hz), 4.77 (1H, dd, $J_{2'\mathrm{a},3'}$ = 5.3 and $J_{2'\mathrm{b},3'}$ = 7.0 Hz), 6.07 (1H, t, $J_{1',2'\mathrm{a}} = J_{1',2'\mathrm{b}}$ = 6.8 Hz), 7.13 (1H, d, $J_{6,\mathrm{CH3}}$ = 1.1 Hz), 9.27 (1H, br); nOe experiment; CH_2-5′/H-3′ (1.4%), HO-5′/H-3′ (1.8%) and HO-5′/H-6 (0.2%); FAB-MS (*m/z*) 382 (M^++H). *Anal.* Calcd for $C_{17}H_{27}N_3O_5Si \cdot 1/4H_2O$: C, 52.90; H, 7.18; N, 10.89. Found: C, 53.16; H, 7.32; N, 10.59.