Supplementary Information

Synthesis of a novel 1,2-dithianenucleoside via Pummerer-like reaction, followed by Vorbruggen glycosylation between 1,2-dithiane derivative and uracil

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**General Methods.** Physical data were measured as follows: Melting points are uncorrected. $^1$H and $^{13}$C NMR spectra were recorded at 400 or 500 MHz and 100 or 125 MHz instruments (Bruker AV500 or AV400) in CDCl$_3$ or DMSO-$d_6$ as the solvent with tetramethylsilane as an internal standard. Chemical shifts are reported in parts per million (ppm), and signals are expressed as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), or br (broad). All exchangeable protons were detected by addition of D$_2$O. Mass spectra were measured by Waters Micromass LTC PREMIER. X-ray crystallographic analysis was performed with a Rigaku RAXIS-RAPID instrument (Rigaku Corporation). A software, "CrystalStructure 3.6.0 (Rigaku Corporation)" was used for solving the data. TLC was done on Merck Kieselgel F254 precoated plates. Silica gel used for column chromatography was Merck silica gel 60 (70–230 mesh).

![Scheme S1](image)

**cis-4,5-Diacetoxy-1,2-dithiane (3)**. A solution of 1 (1.5 g, 9.7 mmol) in 10% aq. KOH–MeOH (36 mL, 1:5) was stirred for 48 h under O$_2$ atmosphere. After being cooled to 0 °C, the reaction mixture was neutralized with saturated aq. NH$_4$Cl, and the reaction mixture was concentrated *in vacuo*. The residue was coevaporated with toluene, and then MeOH was added to the residue. The resulting insoluble materials were filtered off, and the filtrate was concentrated *in vacuo* to give crude 2. To a solution of the resulting 2 in dry CH$_3$CN (97 mL) were added Et$_3$N...
(6.7 mL, 48.6 mmol), acetic anhydride (4.6 mL, 48.6 mmol), and DMAP (200 mg, 1.9 mmol), and the whole was stirred for 2 h at room temperature. The reaction was quenched by addition of MeOH and the solvent was removed in vacuo. The residue was partitioned between AcOEt and H$_2$O, and the separated organic layer was further washed with saturated aqueous NaHCO$_3$, followed by brine. The organic layer was dried (Na$_2$SO$_4$) and concentrated in vacuo. The residue was purified by a silica gel column, eluted with hexane/AcOEt (4:1–2:1), to give 3 (1.75 g, 76% as a yellow solid): $^1$H NMR (CDCl$_3$); δ 5.17 (m, 2 H), 3.23–2.66 (m, 4 H), 2.09 (s, 6 H).

(4$S$, 5$R$)-4,5-Diacetoxy-1-oxo-1,2-dithiane (4). To a solution of 3 (1.74 g, 7.4 mmol) in CH$_2$Cl$_2$ (20 mL) was added a solution of mCPBA (2.0 g, 8.1 mmol) in CH$_2$Cl$_2$ (5 mL) dropwise at −78 °C. After being stirred at the same temperature, the reaction was quenched by addition of saturated aqueous NaHCO$_3$. The reaction mixture was partitioned between AcOEt and H$_2$O, and the separated organic layer was further washed with H$_2$O, followed by brine. The organic layer was dried (Na$_2$SO$_4$) and concentrated in vacuo. The residue was purified by a silica gel column, eluted with hexane/AcOEt (2:1–1:2), to give 4 as a 7:1 mixture of diastereomers (1.64 g, 88% as a white solid). As analytical samples, each diastereomer was purified by a silica gel column.

NMR spectrum of diastereomer A; $^1$H NMR (CDCl$_3$); δ 5.75 (m, 1 H), 5.43 (m, 1 H), 3.97 (m, 1 H), 3.43–3.30 (m, 3 H), 2.17 (s, 3 H), 2.05 (s, 3 H).

NMR spectrum of diastereomer B; $^1$H NMR (CDCl$_3$); δ 5.46 (m, 1 H), 5.26 (ddd, 1 H, J = 2.7, 3.3 and 11.3 Hz), 4.02 (dd, 1 H, J = 11.3 and 13.6 Hz), 4.00 (dd, 1 H, J = 5.0 and 13.6 Hz), 3.23 (dd, 1 H, J = 2.7 and 12.5 Hz), 2.84 (dd, 1 H, J = 3.3 and 12.5 Hz), 2.16 (s, 3 H), 2.10 (s, 3 H).

4,5-O-(1-Methylethylidene)-1,2-dithiane (6). In the same manner as described above, compound 1 (5.0 g, 32.8 mmol) was converted into the 1,2-dithiane derivarive 2. Then, the resulting crude 2 was dissolved in acetone (110 mL), and 2,2-dimethoxypropane (29 mL, 200 mmol) and p-TsOH (1.25 g, 6.6 mmol) were added to the solution. After being stirred for 10 min at room temperature, the reaction was quenched by addition of saturated aqueous NaHCO$_3$ at 0 °C, and the solvent was removed in vacuo. The residue was partitioned between AcOEt and H$_2$O, and
the separated organic layer was further washed with H₂O, followed by brine. The organic layer was dried (Na₂SO₄) and concentrated in vacuo. The residue was purified by a silica gel column, eluted with hexane/AcOEt (3:1–2:1), to give 3 (1.75 g, 97% as a white solid). Analytical sample was crystalized from Hexane to give 3 as white crystals: mp 48.5–49 °C; ESIMS-LR m/z = 215 (MNa⁺); ¹H NMR (CDCl₃) δ 4.20 (m, 2 H), 3.16 (m, 4 H), 1.55 and 1.38 (each s, each 3 H). ¹³C NMR (CDCl₃): δ 108.33, 70.73, 35.71, 28.30, 26.64. Anal. Calcd for C₇H₁₂O₂S₂: C, 43.72; H, 6.29. Found: C, 43.42; H, 6.11.

(4S, 5R)- 4,5-O-(1-Methylethylidene)-1-oxo-1,2-dithiane (7). In the same manner as described for 4, 6 (880 mg, 4.6 mmol) in CH₂Cl₂ (12 mL) was treated with mCPBA (1.24 g, 5.0 mmol) at −78 °C afforded 7 (789 mg, 83% as a white solid). As analytical samples, each diastereomer was purified by a silica gel column. ESIMS-LR m/z = 231 (MNa⁺).

Physical data of diastereomer A: mp 100–101 °C (crystallized from hexane/AcOEt); ESIMS-LR m/z = 231 (MNa⁺); ¹H NMR (CDCl₃): δ 4.47 (m, 1 H), 4.19 (ddd, 1 H, J = 4.0, 6.0, and 10.5 Hz), 3.78 (dd, 1 H, J = 3.8 and 13.3 Hz), 3.58 (dd, 1 H, J = 6.0 and 14.3 Hz), 3.23 (dd, 1 H, J = 10.5 and 14.3 Hz), 3.13 (dd, 1 H, J = 9.8 and 13.3 Hz), 1.51 and 1.36 (each s, each 3 H); ¹³C NMR (CDCl₃): δ 24.84, 25.59, 28.12, 55.17, 70.93, 72.41, 110.06. Anal. Calcd for C₁₇H₂₃O₃S₂: C, 40.36; H, 5.81. Found: C, 40.18; H, 5.74.

Physical data of diastereomer B: mp 73–74 °C (crystallized from hexane/AcOEt); ESIMS-LR m/z = 231 (MNa⁺); ¹H NMR (CDCl₃): δ 4.76 (ddd, 1 H, J = 5.3, 6.3, and 9.3 Hz), 4.60 (ddd, 1H, J = 3.3, 6.3, and 7.3 Hz), 3.71 (dd, 1 H, J = 5.3 and 13.3 Hz), 3.58 (dd, 1 H, J = 3.3 and 3.8 Hz), 3.12 (dd, 1 H, J = 7.3 and 13.8 Hz), 3.10 (dd, 1 H, J = 9.3 and 13.3 Hz), 1.50 and 1.39 (each s, each 3 H); ¹³C NMR (CDCl₃): δ 25.88, 27.71, 28.79, 51.95, 68.05, 70.70, 109.23. Anal. Calcd for C₁₇H₂₃O₃S₂: C, 40.36; H, 5.81. Found: C, 40.21; H, 5.64.

1-[(3R,4R,5S)-4,5-O-(1-Methylethylidene)-1,2-dithianyl]uracil (8) and 1-[(3S,4R,5S)-4,5-O-(1-methylethylidene)-1,2-dithianyl]uracil (9). To a suspension of uracil (112 mg, 1.0 mmol) in dry toluene (2 mL) were added triethylamine (280 μL, 2.0 mmol) and
TMSOTf (723 μL, 4.0 mmol), and the mixture was stirred at room temperature until giving two-phase clear solution. Dry CH₃CN (3.0 mL) was added to the above solution, which gave an one-phase clear solution, and the whole was added to a solution of 7 (104 mg, 0.5 mmol) in dry CH₃CN (3.0 mL) dropwise over 10 min via a cannula. An additional triethylamine (280 μL, 2.0 mmol) in dry toluene (1.5 mL) was added dropwise to the reaction mixture at 0 °C. After being stirred for 10 min at the same temperature, the reaction was quenched by addition of saturated aqueous NaHCO₃ at 0 °C, and the reaction mixture was partitioned between AcOEt and H₂O. The separated organic layer was washed with saturated aqueous NaHCO₃, followed by brine. The organic layer was dried (Na₂SO₄) and concentrated in vacuo. The residue was purified by a silica gel column, eluted with MeOH in CHCl₃ (0%–5%), to give 8 (49 mg, 32% as a white solid) and 9 (26 mg, 17% as a colorless glass).

Physical data of 8: mp 212–214 °C (dec.) (crystallized from MeOH); ESIMS-LR m/z = 325 (MNa⁺); ¹H NMR (CDCl₃); δ 8.24 (brs, 1 H), 7.17 (d, 1 H, J = 8.0 Hz), 5.76 (dd, 1 H, J = 1.8 and 8.0 Hz), 5.60 (d, 1 H, J = 9.8 Hz), 4.65 (m, 1 H), 4.40 (dd, 1 H, J = 4.5 and 9.8 Hz), 3.49 (dd, 1 H, J = 3.3 and 15.1 Hz), 3.27 (dd, 1 H, J = 3.0 and 15.1 Hz), 1.62 and 1.40 (each s, each 3 H); ¹³C NMR (CDCl₃); δ 162.13, 149.94, 140.92, 109.81, 103.56, 74.51, 74.39, 36.93, 28.17, 26.63; Anal. Calcd for C₁₁H₁₄N₂O₄S₂•1/2 H₂O: C, 42.43 ; H, 4.86 ; N, 9.00. Found: C, 42.50 ; H, 4.52 ; N, 8.93.

Physical data of 9: ESIMS-LR m/z = 325 (MNa⁺); ESIMS-HR (MNa⁺) calcd for C₁₁H₁₄N₂O₄NaS₂ 325.0293, found 325.0280; ¹H NMR (CDCl₃); δ 9.25 (brs, 1 H ), 7.66 (d, 1 H, J = 8.0 Hz), 6.29 (d, 1 H, J = 2.5 Hz), 5.73 (d, 1 H, J = 8.0 Hz), 4.40 (dd, 1 H, J = 2.5 and 4.3 Hz), 4.36 (ddd, 1 H, J = 4.3, 5.8, and 10.3 Hz), 2.95 (dd, 1 H, J = 10.3 and 14.0 Hz), 2.83 (dd, 1 H, J = 5.8 and 14.0 Hz), 1.59 and 1.36 (each s, each 3 H); ¹³C NMR (CDCl₃); δ 162.42, 150.02, 142.58, 110.74, 102.73, 75.50, 73.86, 58.40, 34.09, 28.61, 27.12.
To a solution of 2,3,5-Tri-O-p-methoxybenzyl-D-ribitol\(^\text{18}\) (27.9 g, 54.5 mmol) in dry pyridine (145 mL) was added MsCl (14.8 mL, 0.19 mol) and the whole mixture was stirred for 30 min at 0 °C. The reaction was quenched by addition of ice, and the reaction mixture concentrated \textit{in vacuo}. The residue was partitioned between AcOEt and H\(_2\)O, and the separated organic layer was further washed with saturated aqueous NaHCO\(_3\), followed by brine. The organic layer was dried (Na\(_2\)SO\(_4\)) and concentrated \textit{in vacuo}, and the residue was coevaporated with toluene to give the crude dimesylate as a yellow oil. The resulting dimesylate in methyl ethyl ketone (130 mL) containing lithium
bromide (45.5 g, 0.52 mol) was heated for 5 h under reflux. The residue was partitioned between AcOEt and H₂O, and the separated organic layer was further washed with saturated aqueous NaHCO₃, followed by brine. The reaction mixture was allowed to cool to room temperature and concentrated in vacuo. The residue was partitioned between AcOEt and H₂O, and the separated organic layer was further washed with H₂O, followed by brine. The organic layer was dried (Na₂SO₄) and concentrated in vacuo. The residue was purified by a silica gel column, eluted with hexane/AcOEt (7:1–3:1), to give 10 (20.9 g, 62% as a yellow oil): ¹H NMR (CDCl₃); δ 7.21 (m, 6 H), 6.86 (m, 6 H), 4.68–4.46 (m, 6 H), 4.40 (m, 1 H), 3.79 (s, 9 H), 3.89 (m, 1 H), 3.76–3.69 (m, 4 H), 3.64 (m, 1 H).

(2R,3S,4R)-2,5-Dithioacetyl-1,3,4-tris-p-methoxybenzyloxypentane (11). To a solution of 10 (20.8 g, 32.7 mmol) in dry DMF (32 mL) was added potassium thioacetate (26.0 g, 0.2 mol) and the whole mixture was stirred for 7 h at 100 °C. The reaction mixture was allowed to cool to room temperature and concentrated in vacuo. The residue was partitioned between AcOEt and H₂O, and the separated organic layer was further washed with H₂O, followed by brine. The organic layer was dried (Na₂SO₄) and concentrated in vacuo. The residue was purified by a silica gel column, eluted with hexane/AcOEt (6:1–3:1), to give 11 (7.6 g, 37% as a brown oil): ESIMS-LR m/z = 651 (MNa⁺); ESIMS-HR (MNa⁺) calc for C₃₃H₄₀O₈NaS₂ 651.2062, found 651.2078; ¹H NMR (CDCl₃); δ 7.22 (m, 6 H), 6.84 (m, 6 H), 4.53–4.39 (m, 6 H), 3.90 (m, 1 H), 3.84 (dd, 1 H, J = 4.8 and 5.5 Hz), 3.79 (s, 9 H), 3.63 (m, 2 H), 3.43 (dd, 1 H, J = 5.5 and 6.5 Hz), 3.33 (dd, 1 H, J = 4.3 and 14.1 Hz), 3.18 (dd, 1 H, J = 5.3 and 14.1 Hz), 2.35 (s, 3 H), 2.30 (s, 3 H); ¹³C NMR (CDCl₃); δ 196.07, 195.01, 159.64, 159.58, 130.39, 130.20, 129.99, 129.68, 114.09, 114.04, 78.66, 78.44, 73.43, 72.96, 71.83, 70.07, 55.63, 45.02, 31.07, 30.99, 30.01.

(3R,4S,5R)-4,5-Bis-p-methoxybenzyl-oxy-3-p-methoxybenzyloxymethyl-1,2-dithiane (12). A solution of 11 (7.6 g, 12.1 mmol) in 10% aq. KOH–MeOH (84 mL, 1:5) was stirred for 8 h under O₂ atmosphere. After being cooled to 0 °C, the reaction mixture was neutralized with saturated aq. NH₄Cl, and the reaction mixture was concentrated in vacuo. The residue was partitioned between AcOEt and H₂O, and the separated organic layer was further washed with H₂O,
followed by brine. The organic layer was dried (Na$_2$SO$_4$) and concentrated in vacuo. The residue was purified by a silica gel column, eluted with hexane/AcOEt (6:1–3:1), to give **12** (4.79 g, 73% as a brown oil): ESIMS-LR $m/z = 565$ (MNa$^+$); ESIMS-HR (MNa$^+$) calcd for C$_{29}$H$_{34}$O$_6$NaS$_2$ 565.1694, found 565.1650; $^1$H NMR (CDCl$_3$); δ 7.23 (m, 6 H), 6.86 (m, 6 H), 4.56–4.41 (m, 6 H), 3.89–3.75 (m, 4 H), 3.80 (s, 9 H), 3.50 (m, 1 H), 3.22 (m, 1 H), 2.78 (m, 1 H); $^{13}$C NMR (CDCl$_3$); δ 159.05, 129.48, 129.43, 129.18, 113.65, 113.62, 80.18, 78.94, 72.55, 71.27, 71.16, 68.19, 55.13, 46.99, 30.59.

**3R,4S,5R-4,5-Dihydroxy-3-hydroxymethyl-1,2-dithiane (13).** A solution of **12** (4.79 g, 8.83 mmol) in TFA–CH$_2$Cl$_2$ (20 mL, 1:4) was stirred for 5 h at room temperature. The reaction mixture was concentrated in vacuo, and the residue was coevaporated with MeOH several times. Then, the resulting precipitates were filtered off, washed with MeOH. The solvent was removed in vacuo, and the residue was purified by a silica gel column, eluted with CHCl$_3$/MeOH (19:1–17:3), to give **13** (1.35 g, 84% as a colorless oil): ESIMS-LR $m/z = 205$ (MNa$^+$); ESIMS-HR (MNa$^+$) calcd for C$_5$H$_{10}$O$_3$NaS$_2$ 204.9969, found 205.0009; $^1$H NMR (DMSO-d$_6$); δ 4.85 (br s, 3 H, exchangeable with D$_2$O), 3.86 (m, 1 H), 3.75–3.55 (m, 3 H), 3.16 (m, 1 H), 2.97 (m, 1 H), 2.75 (m, 1 H); $^{13}$C NMR (DMSO-d$_6$); δ 75.56, 73.89, 64.34, 52.18, 32.36.

**3R,4S,5R-4,5-Dihydroxy-3-triisopropylsiloxymethyl-1,2-dithiane (14).** To a solution of **13** (1.2 g, 6.58 mmol) in dry DMF (32 mL) were added triisopropylsilyl chloride (1.5 mL, 7.24 mmol) and imidazole (0.99 g, 14.5 mmol), and the whole mixture was stirred for 5 h at room temperature. The reaction was quenched by addition of ice, and the solvent was removed in vacuo. The residue was partitioned between AcOEt and H$_2$O, and the separated organic layer was further washed with H$_2$O, followed by brine. The organic layer was dried (Na$_2$SO$_4$) and concentrated in vacuo. The residue was purified by a silica gel column, eluted with hexane/AcOEt (5:1–1:1), to give **14** (2.0 g, 91% as a brown oil): ESIMS-LR $m/z = 361$ (MNa$^+$); ESIMS-HR (MNa$^+$) calcd for C$_{14}$H$_{30}$O$_3$NaS$_2$Si 361.1303, found 361.1303; $^1$H NMR (DMSO-d$_6$); δ 4.85 (br s, 2 H, exchangeable with D$_2$O), 4.12 (m, 1 H), 3.92 (m, 1 H), 3.80 (m, 1 H), 3.61 (m, 1 H), 3.31 (m, 1 H), 3.16 (m, 1 H), 2.98 (m, 1 H), 2.79 (m, 1 H); $^{13}$C NMR (CDCl$_3$); δ 74.74, 67.07, 60.30, 48.19, 33.52, 17.78, 11.63.
(3R,4S,5R)-4,5-O-(1-Methylethylidene)-3-triisopropylsiloxymethyl-1,2-dithiane (15).

To a solution of 14 (2.0 g, 5.9 mmol) in acetone (20 mL) were added 2,2-dimethoxypropane (5.3 mL, 41 mmol) and pTsCl (0.22 g, 1.2 mmol), and the whole mixture was stirred for 10 min at room temperature. The reaction was quenched by addition of saturated aqueous NaHCO₃ at 0 °C, and the solvent was removed in vacuo. The residue was partitioned between AcOEt and H₂O, and the separated organic layer was further washed with H₂O, followed by brine. The organic layer was dried (Na₂SO₄) and concentrated in vacuo. The residue was purified by a silica gel column, eluted with hexane/AcOEt (49:1–24:1), to give 15 (1.98 g, 98% as a brown oil): ESIMS-LR m/z = 401 (MNa⁺); ESIMS-HR (MNa⁺) calcd for C₁₇H₃₄O₃NaS₂Si 401.1616, found 401.1655; ¹H NMR (CDCl₃); δ 4.33 (m, 1 H), 4.22 (dd, 1 H, J = 4.6 and 8.7 Hz), 4.11 (dd, 1 H, J = 4.5 and 10.4 Hz), 3.98 (dd, 1 H, J = 5.0 and 10.4 Hz), 3.31 (dd, 1 H, J = 3.7 and 14.6 Hz), 3.26 (m, 1 H), 3.18 (dd, 1 H, J = 4.5 and 14.6 Hz), 1.52 and 1.38 (each s, each 3 H), 1.07 (m, 21 H); ¹³C NMR (CDCl₃); δ 108.14, 72.73, 71.14, 62.96, 51.89, 36.58, 28.60, 26.86, 18.12, 12.04.

(3R,4S,5R)-4,5-O-(1-Methylethylidene)-1-oxo-3-triisopropylsiloxymethyl-1,2-dithiane (16). To a solution of 15 (1.9 g, 5.2 mmol) in dry CH₂Cl₂ (26 mL) was added a solution of mCPBA (1.42 g, 5.75 mmol) in CH₂Cl₂ (5 mL) dropwisely at −78 °C, and the whole mixture was stirred for 10 min at the same temperature. The reaction was quenched by addition of saturated aqueous NaHCO₃ at −78 °C. The reaction mixture was partitioned between AcOEt and H₂O, and the separated organic layer was further washed with H₂O, followed by brine. The organic layer was dried (Na₂SO₄) and concentrated in vacuo. The residue was purified by a silica gel column, eluted with hexane/AcOEt (7:1–4:1), to give 16 as a 4:1 mixture of diastereomers (1.78 g, 86% as a colorless oil). Analytical samples were purified by a silica gel column: ESIMS-LR m/z = 395 (MH⁺); ESIMS-HR (MH⁺) calcd for C₁₇H₃₄O₄NaS₂Si 417.1565, found 417.1602.

NMR spectrum of diastereomer A: ¹H NMR (CDCl₃); δ 4.58 (ddd, 1 H, J = 3.5, 5.5 and 7.8 Hz), 4.30 (dd, 1 H, J = 4.3 and 10.5 Hz), 4.26 (dd, 1 H, J = 5.5 and 9.5 Hz), 4.13 (t, 1 H, J = 10.5 Hz), 3.55 (dd, 1 H, J = 3.5 and 13.6 Hz), 3.16 (dd, 1 H, J = 7.8 and 13.6 Hz), 3.06 (ddd, 1 H, J = 4.3, 9.5 and 10.5 Hz), 1.50 and 1.37 (each s, each 3 H), 1.07 (m, 21 H, TIPS); ¹³C NMR (CDCl₃) δ
NMR spectra of diastereomer B: $^1$H NMR (CDCl$_3$); $\delta$ 4.71 (dd, 1 H, $J$ = 6.0 and 10.3 Hz), 4.38 (dd, 1 H, $J$ = 2.3 and 10.5 Hz), 4.20 (ddd, 1 H, $J$ = 4.0, 6.0 and 10.3 Hz), 4.09 (dd, 1 H, $J$ = 2.8 and 10.5 Hz), 3.84 (dd, 1 H, $J$ = 4.0 and 13.3 Hz), 3.80 (m, 1 H), 2.98 (dd, 1 H, $J$ = 10.3 and 13.3 Hz), 1.49 and 1.36 (each s, each 3 H), 1.07 (m, 21 H); $^{13}$C NMR (CDCl$_3$) $\delta$ 109.76, 72.85, 71.66, 62.25, 55.31, 43.29, 27.87, 25.32, 17.79, 11.73.

(4$R$,6$S$,6$R$)-3-Acetoxy-4,5-O-(1-methylethylidene)-6-triisopropylsiloxymethyl-1,2-dithiane (17). A solution of 16 (1.75 g, 4.4 mmol) in acetic anhydride (22 mL) was heated for 33 h under reflux. After being cooled to room temperature, the reaction mixture was poured into saturated aqueous NaHCO$_3$ at 0 °C. Then, the whole was partitioned between AcOEt and H$_2$O, and the separated organic layer was further washed with saturated aqueous NaHCO$_3$, followed by brine. The organic layer was dried (Na$_2$SO$_4$) and concentrated in vacuo. The residue was purified by a silica gel column, eluted with hexane/AcOEt (30:1–20:1), to give 17 as a 1:1 mixture of diastereomers (0.37 g, 19% as a orange oil). Analytical samples were purified by a silica gel column: ESIMS-LR $m$/z = 459 (MNa$^+$); ESIMS-HR calcd for C$_{19}$H$_{36}$O$_5$NaS$_2$Si 459.1671, found 459.1633.

NMR spectra of diastereomer A: $^1$H NMR (CDCl$_3$); $\delta$ 6.01 (d, 1 H, $J$ = 4.8 Hz), 4.48 (dd, 1 H, $J$ = 4.8 and 7.5 Hz), 4.16 (t, 1 H, $J$ = 4.8 Hz), 4.14 (dd, 1 H, $J$ = 5.5 and 10.5 Hz), 4.00 (dd, 1 H, $J$ = 5.5 and 10.5 Hz), 3.26 (dt, 1 H, $J$ = 5.5 and 7.5 Hz), 2.16 (s, 3 H), 1.52 and 1.36 (each s, each 3 H), 1.07 (m, 21 H); $^{13}$C NMR (CDCl$_3$); $\delta$ 169.15, 108.50, 74.60, 74.45, 73.56, 62.88, 50.27, 28.38, 26.73, 21.15, 18.08, 12.01.

NMR spectra of diastereomer B: $^1$H NMR (CDCl$_3$); $\delta$ 6.16 (d, 1 H, $J$ = 3.0 Hz), 4.46 (dd, 1 H, $J$ = 5.0 and 9.0 Hz), 4.41 (dd, 1 H, $J$ = 3.0 and 5.0 Hz), 4.12 (dd, 1 H, $J$ = 4.3 and 10.5 Hz), 4.01 (dd, 1 H, $J$ = 4.3 and 10.5 Hz), 3.25 (dt, 1 H, $J$ = 4.3 and 9.0 Hz), 2.16 (s, 3 H), 1.54 and 1.39(each s, each 3 H), 1.07 (m, 21 H); $^{13}$C NMR (CDCl$_3$); $\delta$ 169.34, 109.86, 74.60, 74.45, 73.56, 62.41, 51.78, 27.93, 26.56, 21.19, 18.08, 12.01.
1-[(3\textit{R},4\textit{R},5\textit{S},6\textit{R})-4,5-\textit{O}-(1-Methylethylidene)-6-triisopropylsiloxymethyl-1,2-Dithianyl]uracil (18) and
1-[(3\textit{S},4\textit{R},5\textit{S},6\textit{R})-4,5-\textit{O}-(1-methylethylidene)-6-triisopropylsiloxymethyl-1,2-Dithianyl]uracil (19). To a suspension of 17 (233 mg, 0.53 mmol) and uracil (120 mg, 1.07 mmol) in dry CH\textsubscript{3}CN (3 mL) was added \textit{N},\textit{O}-bis(trimethylsilyl)acetamide (0.52 mL, 2.14 mmol), and TMSOTf (0.24 mL, 1.3 mmol) was added to the resulting clear solution at 0 °C. Then, the whole mixture was heated for 5 h under reflux. After being cooled to room temperature, the reaction mixture was quenched by addition of saturated aqueous NaHCO\textsubscript{3} at 0 °C. Then, the whole was partitioned between AcOEt and H\textsubscript{2}O, and the separated organic layer was further washed with saturated aqueous NaHCO\textsubscript{3}, followed by brine. The organic layer was dried (Na\textsubscript{2}SO\textsubscript{4}) and concentrated in vacuo. The residue was purified by a silica gel column, eluted with hexane/AcOEt (9:1–3:2), to give 18 (95 mg, 37% as a brown oil) and 19 (40 mg, 15% as a brown form).

Physical data of 18: ESIMS-LR \textit{m/z} = 511 (MNa\textsuperscript{+}); ESIMS-HR (MNa\textsuperscript{+}) calcd for C\textsubscript{21}H\textsubscript{36}N\textsubscript{2}O\textsubscript{2}Na\textsubscript{2}Si 511.1733, found 511.1706; \textit{\textsuperscript{1}H} NMR (CDCl\textsubscript{3}); \textit{\delta} 8.18 (br s, 1 H, exchangable with D\textsubscript{2}O), 7.39 (d, 1 H, \textit{J} = 8.2 Hz), 5.78 (d, 1 H, \textit{J} = 7.6 Hz), 5.75 (d, 1 H, \textit{J} = 8.2 Hz), 4.80 (t, 1 H, \textit{J} = 4.7 Hz), 4.38 (dd, 1 H, \textit{J} = 4.7 and 7.6 Hz), 4.17 (dd, 1 H, \textit{J} = 6.9 and 10.4 Hz), 4.14 (dd, 1 H, \textit{J} = 5.4 and 10.4 Hz), 3.33 (ddd, 1 H, \textit{J}_{6',5'} = 4.7, 5.4, and 6.9 Hz), 1.57 and 1.37 (each s, each 3 H), 1.07 (m, 21 H); \textit{\textsuperscript{13}C} NMR (CDCl\textsubscript{3}); \textit{\delta} 163.01, 150.15, 140.77, 108.92, 103.15, 74.20, 73.87, 63.09, 60.05, 49.55, 28.15, 26.53, 18.08, 11.98.

Physical data of 19: ESIMS-LR \textit{m/z} = 511 (MNa\textsuperscript{+}); ESIMS-HR (MNa\textsuperscript{+}) calcd for C\textsubscript{21}H\textsubscript{36}N\textsubscript{2}O\textsubscript{2}Na\textsubscript{2}Si 511.1733, found 511.1738; \textit{\textsuperscript{1}H} NMR (CDCl\textsubscript{3}); \textit{\delta} 8.35 (brs, 1 H, exchangable with D\textsubscript{2}O), 7.65 (d, 1 H, \textit{J} = 8.2 Hz), 6.25 (d, 1 H, \textit{J} = 2.7 Hz), 5.70 (d, 1 H, \textit{J} = 2.2 and 8.2 Hz), 4.44 (dd, 1 H, \textit{J} = 2.7 and 4.4 Hz), 4.36 (dd, 1 H, \textit{J} = 4.4 and 10.4 Hz), 4.11 (dd, 1 H, \textit{J} = 3.2 and 10.4 Hz), 3.98 (dd, 1 H, \textit{J} = 4.4 and 10.4 Hz), 3.18 (ddd, 1 H, \textit{J} = 3.2, 4.4, and 10.4 Hz), 1.54 and 1.35 (each s, each 3 H), 1.00 (m, 21 H); \textit{\textsuperscript{13}C} NMR (CDCl\textsubscript{3}); \textit{\delta} 163.03, 150.29, 142.84, 110.26,
1,2-dithianyl|uracil (20). A solution of 18 (73 mg, 0.15 mmol) in trifluoroacetic acid-CH₂Cl₂ (2 mL, 1:1) was stirred for 25 h at room temperature. The solvent was removed in vacuo, and the residue was coevaporated with MeOH, and then toluene. The residue was purified by a silica gel column, eluted with MeOH in CHCl₃ (15%–25%), to give 20 (40 mg, 91% as a brown solid). Analytical sample was crystalized from MeOH to give 20 as white crystals: mp 204–206 °C (dec.) (crystallized from MeOH); ESIMS-LR m/z = 315 (MNa⁺); ¹H NMR (DMSO-d₆, 70 °C) δ 7.63 (dd, 1 H, J = 4.0 and 8.2 Hz), 5.72 (d, 1 H, J = 9.8 Hz), 5.62 (dd, 1 H, J = 1.6 and 8.2 Hz), 5.34 (br s, 2 H, exchangeable with D₂O), 5.06 (br s, 1 H, exchangeable with D₂O), 4.28 (dd, 1 H, J = 2.2 and 3.5 Hz), 4.09 (dd, 1 H, J = 2.2 and 9.8 Hz), 3.92 (dd, 1 H, J = 3.8 and 11.3 Hz), 3.91 (dd, 1 H, J = 6.9 and 11.3 Hz), 3.10 (dddd, 1 H, J = 3.5, 3.8 and 6.9 Hz); ¹³C NMR (CDCl₃); δ 164.02, 151.13, 142.10, 102.56, 71.78, 67.70, 59.59, 55.55, 49.16; Anal. Calcd for C₉H₁₂N₂O₅S₂: C, 36.98; H, 4.14; N, 9.58. Found: C, 36.88; H, 4.28; N, 9.53.

![Scheme S3](image)

2, 3-⁰-(1-Methylethyldene)-5-⁰-triisopropylsilyl-1, 4-dithio-D-ribofuranoside (23). To a solution of 18 (24 mg, 0.05 mmol) in dry CH₂Cl₂ (2.0 mL) was added dithiothreitol (30 mg, 0.2 mmol) and Et₃N (14μL, 0.1 mmol), and the whole mixture was stirred for 4 h at room temperature. The solvent was removed in vacuo, and the residue was purified by a silica gel column, eluted with AcOEt in hexane (5%) and then MeOH in CHCl₃ (15–20%), to give 23 as a 1:1 mixture of
diastereomers (12 mg, 63% as a colorless oil) and uracil (2.7 mg, 49% as a white solid): ESIMS-LR m/z = 401 (MNa⁺); ESIMS-HR calcd for C₁₇H₃₄O₃NaS₂Si 401.1616, found 401.1646.

NMR spectra of diastereomer A: ¹H NMR (CDCl₃); δ 4.88 (m, 1 H), 4.65 (m, 2 H), 3.98 (dd, 1 H, J = 3.8 and 10.3 Hz), 3.77 (dd, 1 H, J = 5.3 and 10.3 Hz), 3.31 (m, 1 H), 2.28 (d, 1 H, J = 10.8 Hz), 1.56 and 1.37 (each s, each 3 H), 1.07 (m, 21 H); ¹³C NMR (CDCl₃); δ

NMR spectra of diastereomer B: ¹H NMR (CDCl₃); δ 4.96 (dd, 1 H, J = 2.0 and 5.5 Hz), 4.72 (dd, 1 H, J = 2.7 and 6.0 Hz), 4.48 (dd, 1 H, J = 2.7 and 5.5 Hz), 4.01 (dd, 1 H, J = 8.8 and 10.3 Hz), 3.84 (dd, 1 H, J = 6.0 and 10.3 Hz), 3.54 (ddd, 1 H, J = 2.0, 6.0 and 8.8 Hz), 2.44 (d, 1 H, J = 6.0 Hz), 1.52 and 1.32 (each s, each 3 H), 1.07 (m, 21 H); ¹³C NMR (CDCl₃); δ