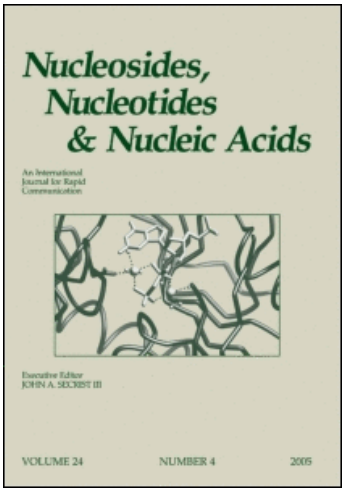

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ABSTRACT

A tunicaminyluracil derivative, which is a key component of the tunicamycin nucleoside antibiotics, was synthesized using a samarium diiodide (SmI_2) mediated aldol reaction and intramolecular Pummerer reaction as the key steps. The α-phenylthio ketone **11**, the precursor of the samarium enolate, was prepared from D-galactose. Treatment of **11** with SmI_2 at $-40°C$ resulted in complete conversion to the corresponding samarium enolate, and subsequent addition of uridine 5′-aldehyde **12** afforded the desired aldol products **13a**,**b**. Compound **13a** was converted to the sulfoxide **15** by a sequential diastereoselective reduction of the ketone and an oxidation with *m*CPBA. Activation of **15** with Tf_2O provided the desired cyclized compound **17**. In this reaction, the aldol product **13a** was also obtained as a consequence of a competitive intramolecular version of DMSO-oxidation via a 7-membered ring intermediate. Compound **18** or **19** are ready for use as a glycosyl donor

[†]In honor and celebration of the 70th birthday of Professor Leroy B. Townsend.
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in glycosylations to provide a range of analogues as potential glycosyltransferase inhibitors as well as related natural products.

Key Words: Tumicamycins; Tunicaminyluracil; Antibiotics; Samarium diiodide; Aldol reaction; Pummerer reaction.

INTRODUCTION

Tunicamycins[1–6] (**1**, Figure 1), isolated from the fermentation broths of *Streptomces lysosuperficus* in 1971, are nucleoside antibiotics composed of uridine, *N*-acetylglucosamine (GlcNAc), an aminoundecose which is a unique higher carbon sugar called tunicamine, and an amide-linked fatty acyl side chain.[3–5] They exhibit a variety of biological properties including antibacterial, antiviral, antifungal, and antitumor activities.[7–10] Treatment of eukaryotic cells with tunicamycins results in the complete truncation of the oligosaccharides from *N*-linked glycopeptides. Therefore, tunicamycins are also utilized as a biological tool to reveal functions of the oligosaccharides in the *N*-linked glycopeptides. Tunicamycins strongly and reversibly inhibits UDP-GlcNAc:polyprenol phosphate GlcNAc-1-P translocase, the enzyme which is responsible for the first *N*-acetylglucosamination of the *N*-linked glycopeptide in endothelial reticulum (ER). It is suggested that the structure of tunicamycins closely resemble the transition state of the transfer reaction of UDP-GlcNAc onto a dolicol monophosphate in the ER membrane catalyzed by the translocase (Figure 1). In particular, the C7′–C11′ moiety of the tunicamycin structure forming a galactopyranoside can be considered as a mimic of the structure of a divalent metal chelated diphosphate. This structural mimicry has been utilized to design inhibitors of glycosyltransferases, which are responsible for oligosaccharide biosynthesis.[11,12] Thus, tunicaminyluracil (**2**), which lacks the GlcNAc moiety and the fatty acyl chain of the tunicamycins, would be expected to be a versatile synthetic intermediate for the synthesis of various glycosyltransferase inhibitors (for a recent review associated with glycosyltransferase inhibitors: Ref. [13]).

Their structural complexity also renders them worthy targets in organic synthesis. The total synthesis of tunicamycins has been accomplished by the groups of Suami's[14,15]

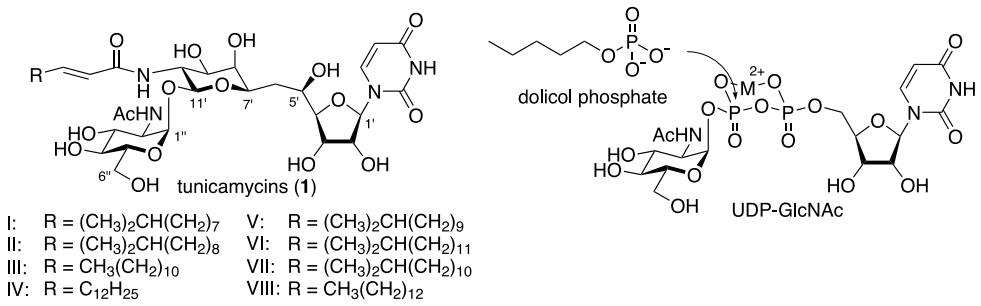

Figure 1. Structure of tunicamycins (**1**) and UDP-NacG1c.

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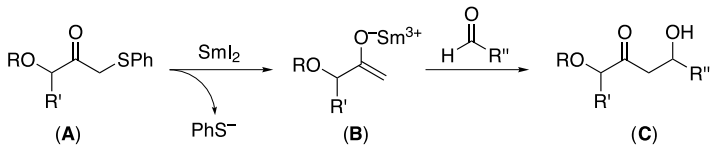
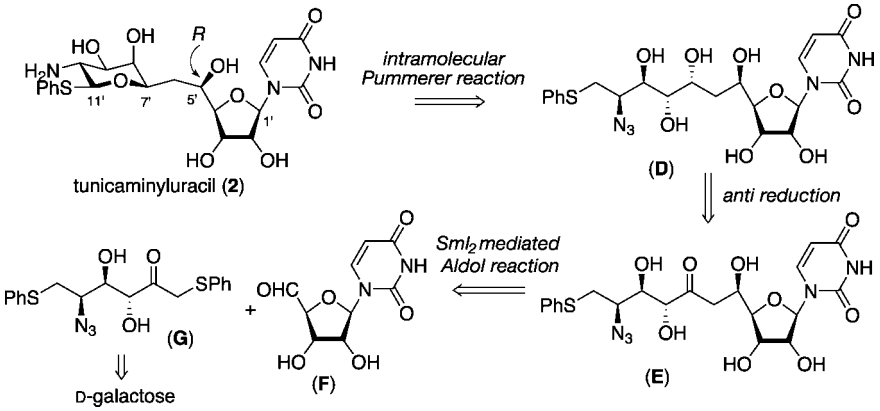


Scheme 1. Samarium diiodide (SmI_2)-mediated aldol reaction.

and Myers,[16,17] and other synthetic studies of related compounds have also been reported.[18–23]

Previously, we applied the samarium diiodide (SmI_2) mediated C–C bond formation reaction to nucleoside chemistry[24,25] and developed a novel aldol reaction via the samarium enolate (**B**) generated by two electron reductions of the α-phenylthio ketone (**A**) (Scheme 1).[26] The neutral and mild reaction conditions and the reactivity of the regioselectively generated samarium enolate (**B**) are suitable for the carbon-chain elongation to a base-labile nucleoside 5′-aldehyde derivative. This reaction was successfully applied to the total synthesis of the nucleoside antibiotic, herbicidin B.[27] This SmI_2-mediated aldol reaction could also be applied to the synthesis of tunicaminyluracil (**2**), the structure of which is a 5′-carbon-branched uridine derivative (Scheme 2). Here we describe the synthesis of tunicaminyluracil (**2**) as an extension of our SmI_2-mediated aldol reaction.

Our strategy includes the regioselective generation of a samarium enolate from the α-phenylthio ketone (**G**), aldol reaction with the uridine 5′-aldehyde (**F**) to assemble the undecose system (**E**). After stereoselective reduction of the 7′-keto group in **E**, cyclization of the resulting 7′-hydroxyl group in **D** to the carbon atom at the 11′-position by an intramolecular Pummerer reaction can be expected to give **2**. If such a cyclization occurs effectively, further introduction of certain carbohydrates using the resulting phenylthio pyranoside **2** as a versatile intermediate could be realized.



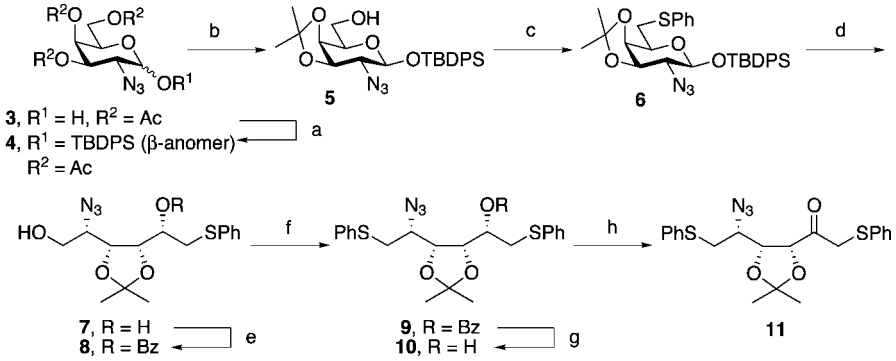
Scheme 2. Retro-synthetic analysis of tunicaminyluracil.

Therefore, this approach would provide a ready access to a range of sugar analogues for the development of glycosyltransferase inhibitors.

RESULTS AND DISCUSSION

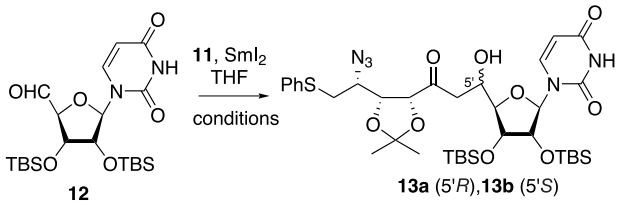
The synthesis of the key α-phenylthio ketone **11** is summarized in Scheme 3. Protection of 2-azido-2-deoxy-3,4,6-tri-*O*-acetylgalactose **3**[28] with a TBDPS group gave only the β-galactoside **4**, and successive removal of the acetyl groups followed by protection of the resulting secondary alcohols with an isopropylidene group under thermodynamic conditions provided **5**. Introduction of a phenylthio group at the 6-position, which would become a leaving group when the samarium enolate is generated, was conducted by activation of the hydroxyl group as its triflate, followed by displacement with thiophenol to afford **6** in 93% yield in 2 steps. After deprotection of the TBDPS group of **6** with tetrabutylammonium fluoride (TBAF), followed by reductive ring opening of the resulting pyranose by $NaBH_4$, the desired diol **7** was obtained in 86% yield. Subsequent protecting group manipulations afforded the monobenzoate **8** (83% yield for 3 steps) at the 5 position, and the remaining primary alcohol at position 1 was further converted to a phenylthio group in 90% yield as in the procedure for the preparation of **6**. It should be noted that selective activation of the primary alcohol of **7** with Tf_2O followed by substitution with thiophenol was unsuccessful and gave a tetrahydropyran derivative as a result of ring closure of the triflate intermediate. Deprotection of the benzoyl group followed by Dess–Martin periodinane oxidation afforded the α-phenylthio ketone **11** without oxidizing either of the phenylthio groups in quantitative yield.

The key SmI_2-mediated aldol reaction was conducted (Scheme 4) and the results are summarized in Table 1. Our previous study revealed that the two-electron reduction



[*]***Reagents and conditions***; a. TBDPSCl, imidazole, DMF, 73%. b. i) NaOMe, MeOH. ii) 2,2'-dimethoxypropane, *p*-TsOH, acetone, 69% for 2 steps. c. i) Tf_2O, pyridine, CH_2Cl_2. ii) PhSH, Et_3N, CH_2Cl_2 93% for 2 steps. d. i) TBAF, THF. ii) $NaBH_4$, MeOH, 86% for 2 steps. e. i) TBSCl, imidazole, DMF. ii) BzCl, pyridine. iii) TBAF, THF, 83% for 3 steps. f. i) Tf_2O, pyridine, CH_2Cl_2. ii) PhSH, Et_3N, CH_2Cl_2 90% for 2 steps. g. NaOMe, MeOH, 90%.h. Dess-Martin periodinane, CH_2Cl_2, 99%.

Scheme 3. Preparation of α-phenylthio ketone.



Scheme 4. SmI_2-mediated aldol reaction.

by SmI_2 to generate a samarium enolate from a 1-phenylthio-2-ulose derivative occurred at −78°C. However, the treatment of α-phenylthio ketone **11** with 2.2 equiv of SmI_2 followed by addition of 1.0 equiv of the aldehyde **12**[a] at −78°C gave the desired aldol products **13a**,**b** in 13% yield (Table 1, entry 1, 5′*R*/5′*S* = 64/36). The low yield of the products and the large amount of the unreacted **11** observed in the reaction mixture indicated that the α-phenylthio ketone **11** without a hetero atom adjacent to the phenylthio group is less reactive to the two-electron reduction than that with an oxygen atom.[26,27] After several attempts to optimize the reaction temperature, the reaction at −40°C gave complete consumption of **11**. Addition of the aldehyde **12** at −78°C after generation of the samarium enolate provided **13a**,**b** in 71% (entry 3, 5′*R*/5′*S* = 66/34), although the addition at 0°C resulted in inverted selectivity (entry 2, 5′*R*/5′*S* = 28/72). It is known that SmI_2 can reduce an azido group to the corresponding amino group. However, no such reduction of the azido group in **13** was detected, and therefore the two-electron reduction was chemoselectively accomplished.

Stereoselective reduction of the ketone **13a** was required in the next step. Intramolecular hydride delivery from $NaBH(OAc)_3$ via a 6-membered transition state selectively afforded the desired 1,3-*anti*-diol **14** in quantitative yield. If the resulting hydroxyl group at the 7′ position cyclized with the carbon atom at the 11 position to form a hexopyranose via an intramolecular Pummerer reaction, the desired tunicaminyluracil derivative **17** could be obtained. There are several methods available to promote the Pummerer reaction including the direct activation of a sulfide or of the corresponding sulfoxide. Direct activation of the sulfide **14** by treatment with NIS in the presence of a catalytic amount of TfOH resulted in the iodo-etherification product **16** between the 5′-hydroxyl group and the 5,6-double bond within the uracil base, and the desired cyclization failed to occur. Next, the activation of the corresponding sulfoxide **15** was examined (Ref. [29] a review for intramolecular Pummerer reaction: Ref. [30]). Oxidation of **14** with *m*CPBA provided the corresponding sulfoxide **15** as a mixture of diastereomers. An initial effort to activate **15** with $(CF_3CO)_2O$ resulted in extensive trifluoroacetylation of the alcohols and only a trace amount of the desired product **17** was obtained. However, treatment of the sulfoxide **15** with Tf_2O in the presence of pyridine at −20°C provided the desired product **17** along with **13a** as an inseparable mixture in a ratio of 62:38. After the mixture was treated with $NaBH(OAc)_3$, compound **17** could be separated from the corresponding reduced

[a]The uridine 5′-aldehyde derivative **12** was prepared by Dess–Martin periodinane oxidation of 2′,3′-di-*O*-TBS uridine.

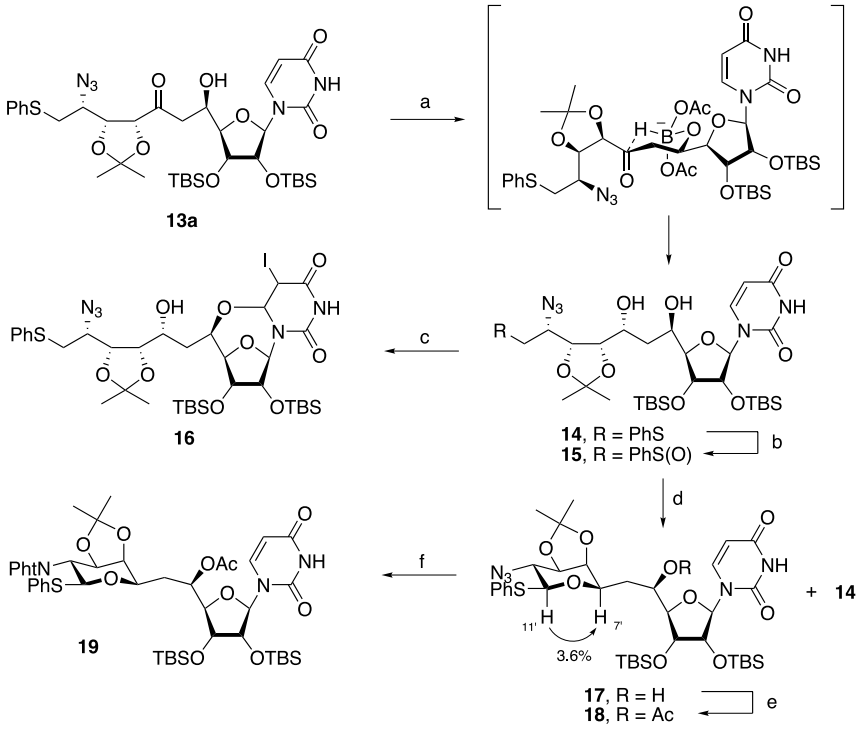
Table 1.

Entry	Temp. (°C)* A	Temp. (°C)* B	Yield (%)	Ratio (**13a/13b**)
1	−78	−78	13	64/36
2	−40	0	62	28/72
3	−40	−78	71	66/34

*A: temperature at the addition of **11**. B: temperature at the addition of **12**.

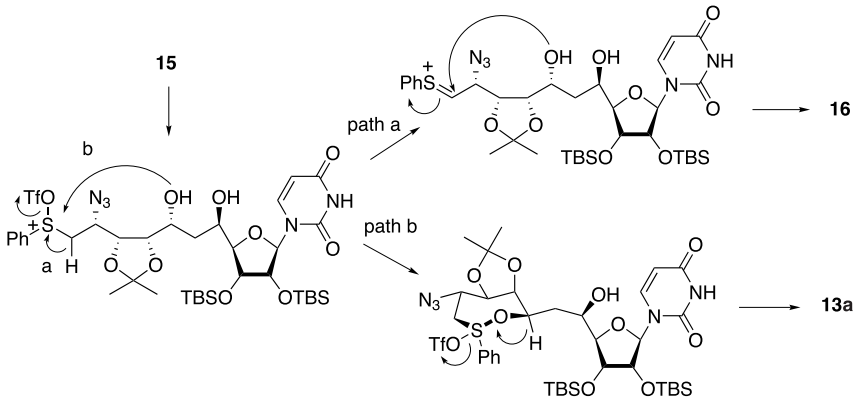
product **14** by the usual silica gel column chromatography. The phenylthio glycoside **17** was a single β-anomer. The stereochemistry of **17** was determined by an NOE (3.6%) between H7′ and H11′ (Scheme 5).

Sulfonylation of the sulfoxide with Tf_2O promotes β-elimination to give a thiocarbenium intermediate. Intramolecular nucleophilic attack of the 7′-hydroxyl group on the 11′-carbon atom affords the cyclized product **17** (Scheme 6, path a). We suppose



Reagents and conditions; a. $NaBH_4$, AcOH–CH_2Cl_2, 92%. b. *m*CPBA, CH_2Cl_2, 96%. c. with **14**. NIS, TfOH, CH_2Cl_2. d. i) Tf_2O, pyridine, CH_2Cl_2. ii) $NaBH_4$, AcOH–CH_2Cl_2, 53% for **17**, 36% for **14**. e. Ac_2O, DMAP, CH_2Cl_2, 96%. f. i) PhSeH, Et_3N. ii) phthaloyl dichloride, DBU, toluene, 92% for 2 steps.

Scheme 5. Synthesis of tunicaminyluracil derivative.



Scheme 6. Reaction pathways to give **16** and **13a.**

that the aldol product **13a** is produced through the nucleophilic attack of the 7′-hydroxyl group on the activated thionium cation with the formation of a 7-membered ring followed by hydrogen abstraction and elimination resulting in the oxidation of the alcohol, an intramolecular version of the DMSO-oxidation (Scheme 6, path b). The fact that the 5′-keto derivative or the sulfoxide of **13a**, which is also possible a product if this reaction proceeds in an intermolecular fashion, was not detected in the reaction mixture indicates that the mechanism of the oxidation involves the intramolecular pathway b. Following acetylation of the 5′-hydroxyl group of **17**, the 10'-azido group of the corresponding acetate **18** was reduced with PhSeH in the presence of Et_3N. The liberated amine was then protected with a phthaloyl group to afford **19**, a fully protected tunicaminyluracil.

In conclusion, the tumicaminyluracil derivative **19** has been synthesized by an aldol reaction via the samarium enolate generated from the α-phenylthio ketone **11** and the intramolecular Pummerer reaction as the key steps. The SmI_2-mediated aldol reaction was successfully applied to the carbon-chain elongation of the uridine 5′-aldehyde derivative **12**. Compound **18** or **19** would then be ready for use as glycosyl donor in glycosylations to provide a range of sugar analogues as well as related natural products.

EXPERIMENTAL

General methods. Physical data were measured as follows: ^1H and ^{13}C NMR spectra were recorded at 500 MHz and 125 MHz instruments in $CDCl_3$ as the solvent with tetramethylsilane as an internal standard. Chemical shifts are reported in parts per million (δ), 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_2O. Assignment of ^1H signals was based on two-dimentional NMR and NOE experiments. Mass spectra were measured on JEOL JMS-D300 spectrometer. TLC was done on Merck Kieselgel F254 precoated plates. Silica gel used for column chromatography was Merck silica gel 5715.

***tert*-Butyldiphenylsilyl 2-Azido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranoside (4).** A mixture of **3** (2.50 g, 7.50 mmol), TBDPSCl (2.34 mL, 9.00 mmol), and imidazole (1.23 g, 18.0 mmol) in DMF (40 mL) was stirred for 3 h at 50°C. After MeOH (5 mL) was added, the mixture was partitioned between AcOEt (200 mL) and H_2O (200 mL), and the organic layer was washed with H_2O (200 mL), brine (100 mL), dried (Na_2SO_4), and evaporated under reduced pressure. The residue was purified by column chromatography (SiO_2, 25% AcOEt/hexane) to give **4** (3.10 g, 73% as a colorless syrup): $[\alpha]_D$ − 9.29° (*c* 0.96, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.73–7.36 (m, 10H), 5.23 (d, 1H, *J* = 3.0 Hz), 3.68 (dd, 1H, *J* = 3.3, 10.8 Hz), 4.46 (d, 1H, *J* = 7.7 Hz), 3.96 (dd, 1H, *J* = 6.6, 11.2 Hz), 3.89 (dd, 1H, *J* = 6.6, 11.2 Hz), 3.72 (dd, 1H, *J* = 7.6, 10.7 Hz), 3.53 (t, 1H, *J* = 6.6 Hz), 2.17 (s, 3H), 2.03 (s, 3H), 1.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.5, 170.3, 170.0, 136.1, 136.0, 133.1, 132.6, 130.3, 130.1, 127.9, 127.7, 97.2, 71.5, 70.8, 66.7, 63.7, 61.4, 27.0, 20.9, 20.8, 20.7, 19.4; MS (FAB) *m*/*z* 568 (MH^+); Exact MS (FAB) Calcd for $C_{28}H_{29}N_3O_8Si$: 570.2271, found: 570.2291.

***tert*-Butyldiphenylsilyl 2-Azido-2-deoxy-3,4-*O*-isopropylidene-β-D-galactopyranoside (5).** A mixture of **4** (2.84 g, 5.00 mmol) in MeOH (50 mL) containing NaOMe in MeOH (28%, 100 μL) was stirred for 2 h at room temperature. After neutralized by adding Dowex 50 (H^+), the resin was removed by filtration, and the filtrate was evaporated under reduced pressure. The residue was coevaporated with toluene (3 × 10 mL). The residue and anhydrous *p*-TsOH (85 mg, 0.5 mmol) in acetone (50 mL) was stirred for 5 h at room temperature. The mixture was neutralized with saturated aqueous $NaHCO_3$, and the mixture was concentrated under reduced pressure. The residue was partitioned between AcOEt (200 mL) and H_2O (200 mL), and the organic layer was washed with H_2O (200 mL), brine (100 mL), dried (Na_2SO_4), and evaporated under reduced pressure. The residue was purified by flush column chromatography (SiO_2, 25% AcOEt/hexane) to give **5** (3.10 g, 73% as a colorless syrup): $[\alpha]_D$ 52.8° (*c* 1.01, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.75–7.38 (m, 10H), 4.43 (d, 1H, *J* = 8.3 Hz), 3.91 (dd, 1H, *J* = 1.7, 5.2 Hz), 3.85 (dd, 1H, *J* = 5.4, 8.1 Hz), 3.66 (dd, 1H, *J* = 8.1, 11.9 Hz), 3.48 (dd, 1H, *J* = 5.6, 11.9 Hz), 3.43 (t, 1H, *J* = 8.1 Hz), 3.38 (ddd, 1H, *J* = 1.7, 5.6, 8.1 Hz), 1.56 (s, 3H), 1.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 137.4, 137.3, 135.2, 134.1, 131.7, 131.6, 129.4, 129.1, 112.3, 98.1, 79.2, 75.4, 74.5, 69.6, 63.7, 29.9, 28.4, 27.8, 20.6; MS (FAB) *m*/*z* 484 (MH^+); Exact MS (FAB) Calcd for $C_{25}H_{34}N_3O_5Si$: 484.2267, found: 484.2251. Anal. Calcd for $C_{25}H_{33}N_3O_5Si$: C, 62.09; H, 6.88; N, 8.69. Found: C, 62.05; H, 6.89; N, 8.73.

***tert*-Butyldiphenylsilyl 2-Azido-2-deoxy-3,4-*O*-isopropylidene-6-*S*-phenyl-6-thio-β-D-galactopyranoside (6).** A mixture of **5** (370 mg, 0.76 mmol) and Tf_2O (258 μL, 1.56 mmol) in CH_2Cl_2 (8 mL) containing pyridine (129 μL, 1.72 mmol) was stirred for 5 min at −20°C. The mixture was diluted with CH_2Cl_2 (20 mL), washed with H_2O (50 mL), saturated aqueous $NaHCO_3$ (30 mL), and brine (100 mL), dried (Na_2SO_4), and evaporated under reduced pressure. A solution of PhSH (117 μL, 1.17 mmol) and Et_3N (214 μL, 1.56 mmol) in CH_2Cl_2 (8 mL) was added to the above residue in CH_2Cl_2 (5 mL). The mixture was stirred for 1 h at room temperature, diluted with CH_2Cl_2 (20 mL), and washed with H_2O (50 mL). The organic layer was evaporated under reduced pressure. The residue was purified by column chromatography (SiO_2, 4%

AcOEt/hexane) to give **6** (406 mg, 93% as a colorless syrup): $[\alpha]_D$ 21.0° (*c* 1.11, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.73–7.16 (m, 15H), 4.27 (d, 1H, *J* = 8.2 Hz), 4.10 (dd, 1H, *J* = 2.1, 5.2 Hz), 3.78 (dd, 1H, *J* = 5.3, 8.1 Hz), 3.42 (t, 1H, *J* = 8.2 Hz), 3.34 (ddd, 1H, *J* = 2.1, 5.3, 8.8 Hz), 1.54 (s, 3H), 1.26 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 136.0, 135.9, 135.6, 133.1, 132.6, 130.8, 129.9, 129.8, 129.1, 129.0, 127.6, 127.4, 127.1, 126.2, 110.2, 96.4, 72.7, 71.8, 67.9, 33.2, 28.3, 26.8, 26.1, 19.1; MS (FAB) *m/z* 576 (MH^+); Exact MS (FAB) Calcd for $C_{31}H_{38}N_3O_4SSi$: 576.2352, found: 576.2330.

(2*S*,3*R*,4*S*,5*R*)-2-Azido-3,4-(dimethylmethylenedioxy)-6-phenylthio-1,5-hexanediol (7). A mixture of **6** (3.60 g, 6.26 mmol) and TBAF (1 M, 6.89 mL, 6.89 mmol) in THF (60 mL) was stirred for 30 min at −20°C and evaporated under reduced pressure. Sodium borohydride (950 mg, 25.0 mmol) was added to the above residue in MeOH (60 mL) at −20°C, and the mixture was stirred for 30 min. The mixture was evaporated under reduced pressure, and then the residue was coevaporated with MeOH (3 × 10 mL). The residue was partitioned between AcOEt (200 mL) and H_2O (200 mL), and the organic layer was washed with H_2O (200 mL) and brine (100 mL), dried (Na_2SO_4), and evaporated under reduced pressure. The residue was purified by column chromatography (SiO_2, 33% AcOEt/hexane) to give **7** (1.83 g, 86% as a colorless syrup): $[\alpha]_D$ − 29.8° (*c* 0.99, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.38 (d, 2H, *J* = 7.7 Hz), 7.29 (t, 2H, *J* = 7.5 Hz), 7.21 (t, 1H, *J* = 7.4 Hz), 4.31 (dd, 1H, *J* = 1.8, 6.8 Hz), 4.27 (t, 1H, *J* = 6.5 Hz), 3.80 (m, 2H), 3.65 (m, 2H), 3.17 (dd, 1H, *J* = 6.5, 13.7 Hz), 3.06 (dd, 1H, *J* = 6.8, 13.7 Hz), 2.83 (d, 1H, *J* = 6.7 Hz, exchanged with D_2O), 2.27 (t, 1H, *J* = 5.7 Hz, exchanged with D_2O), 1.56 (s, 3H), 1.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 135.2, 129.8, 129.3, 129.2, 128.6, 126.7, 126.5, 126.1, 108.9, 68.0, 63.0, 61.7, 38.2, 26.5; MS (FAB) *m/z* 340 (MH^+); Exact MS (FAB) Calcd for $C_{15}H_{22}N_3O_4S$: 340.1331, found: 340.1339.

(2*S*,3*R*,4*S*,5*R*)-2-Azido-5-benzoyloxy-3,4-(dimethylmethylenedioxy)-6-phenylthio-1-hexanol (8). A mixture of **7** (500 mg, 1.47 mmol), TBSCl (243 mg, 1.67 mmol), and imidazole (220 mg, 3.23 mmol) in DMF (20 mL) was stirred for 1 h at 0°C. After MeOH (5 mL) was added, the mixture was partitioned between AcOEt (100 mL) and H_2O (100 mL), and the organic layer was washed with H_2O (100 mL) and brine (50 mL), dried (Na_2SO_4), and evaporated under reduced pressure. BzCl (256 μL, 2.21 mmol) was added to the residue in pyridine (20 mL), and the mixture was stirred for 12 h at room temperature. After MeOH (1 mL) was added, the mixture was evaporated under reduced pressure. The residue was partitioned between AcOEt (100 mL) and H_2O (100 mL), and the organic layer was washed with H_2O (100 mL) and brine (50 mL), dried (Na_2SO_4), and evaporated under reduced pressure. A mixture of the residue and TBAF (1 M, 1.67 mL, 1.67 mmol) in THF (20 mL) was stirred for 2 h at 0°C. The mixture was evaporated under reduced pressure, and the residue was purified by column chromatography (SiO_2, 10% AcOEt/hexane) to give **8** (534 mg, 83% as a colorless syrup): $[\alpha]_D$ − 52.7° (*c* 1.04, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 8.12–7.18 (m, 10H), 5.22 (ddd, 1H, *J* = 1.6, 5.2, 8.8 Hz), 4.70 (dd, 1H, *J* = 1.6, 6.4 Hz), 4.39 (m, 1H), 3.53 (m, 2H), 3.47 (dd, 1H, *J* = 5.2, 13.7 Hz), 3.26 (dd, 1H, *J* = 8.8, 13.7 Hz), 1.96 (t, 1H, *J* = 5.2 Hz, exchanged with D_2O), 1.67 (s, 3H), 1.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.7, 135.2, 133.7, 130.1, 130.0, 129.6, 129.3, 128.8,

126.7, 109.5, 75.1, 72.1, 62.9, 61.6, 33.8, 26.8, 25.6; MS (FAB) *m/z* 444 (MH^+); Exact MS (FAB) Calcd for $C_{22}H_{26}N_3O_5S$: 444.1593, found: 444.1580.

(2*S*,3*R*,4*S*,5*R*)-2-Azido-5-benzoyloxy-3,4-(dimethylmethylenedioxy)-1,6-di(phenylthio)hexane (9). A mixture of **8** (570 mg, 1.28 mmol) and Tf_2O (261 μL, 1.53 mmol) in CH_2Cl_2 (15 mL) containing pyridine (129 μL, 1.72 mmol) was stirred for 5 min at −20°C, and diluted with CH_2Cl_2 (20 mL). The mixture was washed with H_2O (50 mL), saturated aqueous $NaHCO_3$ (30 mL), and brine (100 mL), dried (Na_2SO_4), and evaporated under reduced pressure. A mixture of the residue in CH_2Cl_2 (15 mL), PhSH (394 μL, 3.84 mmol), and Et_3N (720 μL, 5.12 mmol) was stirred for 1 h at room temperature, diluted with CH_2Cl_2 (20 mL), and washed with H_2O (50 mL). The organic layer was evaporated under reduced pressure. The residue was purified by column chromatography (SiO_2, 4% AcOEt/hexane) to give **9** (614 mg, 90% as a colorless syrup): $[\alpha]_D$ 23.9° (*c* 1.02, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 8.03–7.12 (m, 15H), 5.07 (ddd, 1H, *J* = 3.0, 4.8, 8.3 Hz), 4.62 (dd, 1H, *J* = 3.0, 6.5 Hz), 4.41 (t, 1H, *J* = 6.8 Hz), 3.45 (dd, 1H, *J* = 6.8, 12.3 Hz), 3.41 (dd, 1H, *J* = 4.9, 13.8 Hz), 3.17 (dd, 1H, *J* = 8.4, 13.8 Hz), 2.97 (dd, 1H, *J* = 5.3, 13.8 Hz), 2.92 (dd, 1H, *J* = 7.0, 13.7 Hz), 1.61 (s, 3H), 1.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.2, 135.0, 134.5, 133.5, 131.2, 130.1, 129.9, 129.8, 129.5, 129.4, 128.7, 127.6, 126.9, 109.7, 78.3, 75.1, 71.7, 59.5, 36.9, 33.8, 25.7, 25.4; MS (FAB) *m/z* 536 (MH^+); Exact MS (FAB) Calcd for $C_{28}H_{30}N_3O_4S_2$: 536.1677, found: 536.1670.

(2*S*,3*R*,4*S*,5*R*)-2-Azido-3,4-(dimethylmethylenedioxy)-1,6-di(phenylthio)hexane (10). A mixture of **9** (4.70 g, 8.74 mmol) in MeOH (90 mL) containing NaOMe in MeOH (28%, 0.8 mL) was stirred for 1 h at room temperature. After neutralized by adding Dowex 50 (H^+), the resin was removed by filtration, and the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography (SiO_2, 4% AcOEt/hexane) to give **10** (3.40 g, 90% as a colorless syrup): $[\alpha]_D$ − 14.5° (*c* 1.11, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.37–7.20 (m, 15H), 4.32 (dd, 1H, *J* = 4.8, 6.9 Hz), 4.26 (dd, 1H, *J* = 2.8, 6.9 Hz), 3.68 (ddd, 1H, *J* = 2.9, 6.4, 9.1 Hz), 3.57 (dd, 1H, *J* = 6.4, 11.5 Hz), 3.06 (m, 3H), 2.98 (dd, 1H, *J* = 6.5, 13.7 Hz), 1.51 (d, 1H, *J* = 5.8 Hz, exchanged with D_2O), 1.54 (s, 3H), 1.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 135.3, 134.7, 131.2, 130.1, 129.5, 129.4, 127.6, 127.0, 126.3, 109.3, 68.1, 60.6, 59.6, 38.5, 36.9, 26.6, 25.0, 21.3; MS (FAB) *m/z* 432 (MH^+); Exact MS (FAB) Calcd for $C_{21}H_{26}N_3O_3S_2$: 432.1415, found: 432.1422.

(3*R*,4*R*,5*S*)-5-Azido-3,4-(dimethylmethylenedioxy)-1,6-di(phenylthio)-2-hexanone (11). A mixture of **10** (1.20 g, 2.79 mmol) and Dess–Martin periodinane (1.79 g, 4.19 mmol) in CH_2Cl_2 (30 mL) was stirred for 30 min at room temperature. After a mixture of saturated aqueous $NaHCO_3$ and saturated aqueous $Na_2S_2O_3$ (5:1, 50 mL) was added, the mixture was vigorously stirred until the organic layer turned to be clear. The organic layer was washed with H_2O (50 mL) and brine (50 mL), dried (Na_2SO_4), and evaporated under reduced pressure. The residue was purified by column chromatography (SiO_2, 8% hexane/AcOEt) to give **11** (1.20 g, 99%. as a colorless syrup): $[\alpha]_D$ 23.9° (*c* 1.17, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.40–7.19 (m, 15H), 4.69 (dd, 1H, *J* = 1.1, 8.7 Hz), 4.62 (d, 1H, *J* = 8.7 Hz), 4.19 (d, 1H, *J* = 15.7 Hz), 3.93 (d, 1H, *J* = 15.7 Hz), 3.34 (t, 1H, *J* = 6.6 Hz),3.27 (s, 2H), 1.60 (s, 3H), 1.32

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(s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 204.4, 135.0, 134.4, 130.5, 130.2, 129.3, 129.0, 127.2, 126.9, 110.5, 79.7, 78.7, 57.7, 42.1, 34.8, 25.9, 23.8; MS (FAB) *m/z* 430 (MH^+); Exact MS (FAB) Calcd for $C_{21}H_{24}N_3O_3S_2$: 430.1259, found: 430.1254.

1-[10-Azido-2,3-di-*O*-(*tert*-butyldimethylsilyl)-6,10,11-trideoxy-8,9-*O*-isopropylidene-11-*S*-phenyl-11-thio-L-*lyxo*-D-*allo*-undeculofuranosyl-(1,4)]uracil (13a) and 1-[10-Azido-2,3-di-*O*-(*tert*-butyldimethylsilyl)-6,10,11-trideoxy-8,9-*O*-isopropylidene-11-*S*-phenyl-11-thio-L-*lyxo*-L-*talo*-undeculofuranosyl-(1,4)]uracil (13b). Compound **11** (85 mg, 0.2 mmol) in THF (2 mL) was added dropwise to a THF solution of SmI_2 (0.1 M, 4.4 mL, 0.44 mmol) at −40°C. After the TLC analysis indicated the disappearance of **11**, oxygen gas was passed through the mixture. Then, **12** (94 mg, 0.2 mmol) in THF (2 mL) was added dropwise, and the mixture was stirred for 15 min at −78°C. After the mixture was allowed to warm to room temperature, saturated aqueous NH_4Cl was added. The mixture was filtrated through a Celite pad, and the filtrate was partitioned between AcOEt (50 mL) and H_2O (50 mL), and the organic layer was washed with saturated aqueous $NaHCO_3$ (20 mL) and brine (20 mL), dried (Na_2SO_4), and evaporated under reduced pressure. The residue was purified by flush column chromatography (SiO_2, 33% AcOEt/hexane) to give **13a** (74 mg, 47% as a white foam, fast moving) and **13b** (38 mg, 24% as a white foam, slow moving).

For **13a**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.95 (br s, 1H, exchanged with D_2O), 8.04 (d, 1H, *J* = 8.2 Hz), 7.43 (d, 2H, *J* = 7.7 Hz), 7.53 (t, 2H, *J* = 7.8 Hz), 7.26 (d, 1H, *J* = 7.7 Hz), 5.83 (d, 1H, *J* = 4.6 Hz), 5.69 (dd, 1H, *J* = 1.8, 8.1 Hz), 4.72 (d, 1H, *J* = 8.8 Hz), 4.48 (d, 1H, *J* = 8.8 Hz), 4.31 (t, 1H, *J* = 4.5 Hz), 4.26 (d, 1H, *J* = 10.2 Hz), 3.93 (d, 1H, *J* = 4.2 Hz), 3.43 (d, 1H, *J* = 2.1 Hz), 3.33 (m, 3H), 3.29 (dd, 1H, *J* = 10.1, 19.3 Hz), 2.88 (dd, 1H, *J* = 1.9, 19.3 Hz), 1.62 (s, 3H), 1.31 (s, 3H), 0.92 (s, 9H), 0.90 (s, 9H), 0.11 (s, 6H), 0.07 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 212.4, 163.6, 150.7, 141.4, 134.6, 130.7, 129.5, 127.5, 110.8, 102.3, 90.0, 87.1, 80.6, 79.2, 75.4, 72.4, 65.5, 57.9, 44.4, 35.2, 26.2, 26.1, 26.0, 24.0, 18.3, 18.2, −4.2, −4.4, −4.5, −4.6; MS (FAB) *m/z* 792 (MH^+); Exact MS (FAB) Calcd for $C_{36}H_{58}N_5O_9SSi_2$: 792.3493, found: 792.3521.

For **13b**:^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.87 (br s, 1H, exchanged with D_2O), 7.75 (d, 1H, *J* = 8.1 Hz), 7.41 (d, 2H, *J* = 7.6 Hz), 7.32 (t, 2H, *J* = 7.4 Hz), 7.26 (d, 1H, *J* = 7.4 Hz), 5.85 (d, 1H, *J* = 6.6 Hz), 5.73 (dd, 1H, *J* = 1.7, 8.1 Hz), 4.71 (d, 1H, *J* = 8.8 Hz), 4.47 (d, 1H, *J* = 8.8 Hz), 4.36 (dd, 1H, *J* = 4.5, 6.5 Hz), 4.29 (d, 1H, *J* = 11.1 Hz), 4.19 (dd, 1H, *J* = 1.4, 4.2 Hz), 3.86 (br s, 1H), 3.65 (d, 1H, *J* = 2.0 Hz), 3.29 (br s, 3H), 3.07 (d, 1H, *J* = 7.7 Hz), 2.76 (dd, 1H, *J* = 10.6, 18.7 Hz), 1.59 (s, 3H), 1.31 (s, 3H), 0.93 (s, 9H), 0.86 (s, 9H), 0.12 (s, 3H), 0.11 (s, 3H), 0.03 (s, 3H), −0.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 212.1, 163.4, 150.6, 141.8, 134.6, 130.8, 130.7, 129.5, 127.5, 110.8, 102.7, 89.6, 88.4, 80.5, 79.2, 74.8, 71.8, 67.8, 57.7, 43.7, 35.1, 26.1, 26.0, 24.0, 23.9, 18.3, 18.2, −4.1, −4.2, −4.4, −4.6; MS (FAB) *m/z* 792 (MH^+); Exact MS (FAB) Calcd for $C_{36}H_{58}N_5O_9SSi_2$: 792.3493, found: 792.3486.

1-[10-Azido-2,3-di-*O*-(*tert*-butyldimethylsilyl)-6,10,11-trideoxy-8,9-*O*-isopropylidene-11-*S*-phenyl-11-thio-L-*galacto*-D-*allo*-undecofuranosyl-(1,4)]uracil (14). Sodium borohydride (7.1mg, 189 μmol) was added to a mixture of AcOH and CH_2Cl_2 (1:2, 1 mL) at −20°C, and then a solution of **13a** (50 mg, 63 μmol) in CH_2Cl_2 (0.5 mL) was added dropwise to the mixture. After being stirred for 30 min at −20°C, the mixture was evaporated under reduced pressure, and the residue was coevaporated with

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MeOH (3 × 1 mL). The residue was partitioned between AcOEt (30 mL) and H_2O (20 mL), and the organic layer was washed with saturated aqueous $NaHCO_3$ (20 mL) and brine (100 mL), dried (Na_2SO_4), and evaporated under reduced pressure. The residue was purified by column chromatography (SiO_2, 33% AcOEt/hexane) to give **14** (55 mg, quant. as a white foam): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.49 (br s, 1H, exchanged with D_2O), 7.61 (d, 1H, *J* = 8.0 Hz), 7.42 (d, 2H, *J* = 7.8 Hz), 7.29 (t, 2H, *J* = 7.8 Hz), 7.21 (d, 1H, *J* = 7.7 Hz), 5.69 (d, 1H, *J* = 8.0 Hz), 5.69 (d, 1H, *J* = 5.7 Hz), 4.60 (t, 1H, *J* = 5.1 Hz), 4.46 (dd, 1H, *J* = 2.2, 6.4 Hz), 4.24 (ddd, 1H, *J* = 6.3, 9.6, 12.6 Hz), 4.13 (d, 2H), 4.08 (dd, 1H, *J* = 6.7, 9.4 Hz), 3.91 (d, 1H, *J* = 2.4 Hz), 3.68 (dd, 1H, *J* = 2.0, 7.1 Hz), 3.43 (d, 1H, *J* = 6.2 Hz), 3.33 (dd, 1H, *J* = 7.1, 13.6Hz), 3.27 (dd, 1H, *J* = 4.3, 13.6 Hz), 2.09 (ddd, 1H, *J* = 3.3, 3.8, 13.8 Hz), 1.70 (ddd, 1H, *J* = 1.8, 6.5, 13.8 Hz), 1.49 (s, 3H), 1.31 (s, 3H), 0.90 (s, 9H), 0.87 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H) , 0.07 (s, 3H), 0.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.7, 150.8, 143.9, 135.2, 130.7, 129.3, 127.1, 109.3, 102.4, 94.8, 89.1, 78.7, 77.9, 73.2, 73.0, 67.7, 67.6, 58.6, 38.1, 36.5, 27.0, 26.1, 26.0, 25.1, 18.3, 18.2, −4.2, −4.4, −4.5, −4.7; MS (FAB) *m/z* 794 (MH^+); Exact MS (FAB) Calcd for $C_{36}H_{60}N_5O_9SSi_2$: 794.3650, found: 794.3666.

1-[10-Azido-2,3-di-*O*-(*tert*-butyldimethylsilyl)-6,10,11-trideoxy-8,9-*O*-isopropylidene-11-phenylsulfinyl-L-*galacto*-D-*allo*-undecofuranosyl]uracil (15). A mixture of **14** (30 mg, 26 μmol) and mCPBA (4.6 mg, 26 μmol) in CH_2Cl_2 (5 mL) was stirred for 30 min at 0°C. After a mixture of saturated aqueous $NaHCO_3$ and saturated aqous $Na_2S_2O_3$ (4:1, 5 mL) was added, the organic layer was washed with brine (5 mL), dried (Na_2SO_4), and evaporated under reduced pressure. The residue was purified by column chromatography (SiO_2, 66% AcOEt/hexane) to give a diastereomeric mixture of **15** (32 mg, quant. as a white foam): MS (FAB) *m/z* 810 (MH^+); Exact MS (FAB) Calcd for $C_{36}H_{60}N_5O_{10}SSi_2$: 810.3599, found: 810.3598.

Thioglycoside 17. A mixture of **15** (7.0 mg, 8.7 μmol) and Tf_2O (10.7 μL, 52 μmol) in CH_2Cl_2 (100 μL) containing pyridine (6.6 μL, 104 μmol) was stirred for 5 min at −20°C, and diluted with CH_2Cl_2 (5 mL). The mixture was washed with H_2O (3 mL), saturated aqueous $NaHCO_3$ (3 mL), and brine (3 mL), dried (Na_2SO_4), and evaporated under reduced pressure. The residue was purified by column chromatography (SiO_2, 33% AcOEt/hexane) to give an inseparable mixture of **17** and **13a** (5.7 mg, 89% as a glass, the ratio of **17** and **13a** was 62:38 by ^{1}H NMR). To isolate pure **17**, the next experiment was performed. $NaBH_4$ (9.4 mg, 189 μmol) was added to a mixture of AcOH and CH_2Cl_2 (1:2, 2 mL) at −20°C, and then the mixture of **17** and **13a** (50 mg, 63 μmol, the ratio of **17** and **13a** was 57:43) in CH_2Cl_2 (1 mL) was added dropwise to the above mixture. After being stirred for 30 min, the mixture was evaporated under reduced pressure, and the residue was coevaporated with MeOH (3 × 2 mL). The residue was partitioned between AcOEt (30 mL) and H_2O (20 mL), and the organic layer was washed with saturated aqueous $NaHCO_3$ (20 mL) and brine (10 mL), dried (Na_2SO_4), and evaporated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, 33% AcOEt/hexane) to give **17** (26 mg, 51.6% as a white foam, fast moving) and **14** (23 mg, 46% as a white foam, slow moving).

For **17**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.68 (br s, 1H, exchanged with D_2O), 7.79 (d, 1H, *J* = 8.1 Hz), 7.51–7.30 (m, 5H), 5.70 (d, 1H, *J* = 8.1 Hz), 5.57 (d, 1H, *J* = 5.1

Hz), 5.16 (d, 1H, J = 7.5 Hz), 4.43 (t, 1H, J = 4.7 Hz), 4.17 (m, 3H), 4.07 (t, 1H, J = 4.2 Hz), 3.90 (m, 1H), 3.85 (m, 1H), 3.69 (t, 1H, J = 7.1 Hz), 3.22 (d, 1H, J = 6.5 Hz, exchanged with D_2O), 2.13 (m, 1H), 1.68 (m, 1H), 1.60 (s, 3H), 1.39 (s, 3H), 0.92 (s, 9H), 0.91 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H), 0.05 (s, 3H),0.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.2, 150.4, 142.6, 134.4, 131.4, 129.4, 127.9, 111.5, 102.3, 92.4, 88.2, 86.7, 76.2, 74.3, 72.6, 69.2, 66.6, 64.0, 38.4, 27.8, 26.1, 26.0, 25.7, 18.3, 18.2, −4.2, −4.4, −4.5, −4.6; MS (FAB) m/z 792 (MH^+); Exact MS (FAB) Calcd for $C_{36}H_{58}N_5O_9SSi_2$: 792.3493, found: 792.3496.

The physical data for **14** was in accordance with the compound obtained by reduction of **13a**.

Acetate 18. A mixture of **17** (20 mg, 25 μmol), Ac_2O (2.8 μL, 30 μmol), Et_3N (4.2 μL, 30 μmol), and DMAP (1 mg, 7.5 μmol) in CH_3CN (1 mL) was stirred for 12 h at room temperature. After MeOH (1 mL) was added to the mixture, the mixture was evaporated under reduced pressure. The residue was partitioned between AcOEt (30 mL) and H_2O (20 mL), and the organic layer was washed with saturated aqueous $NaHCO_3$ (20 mL) and brine (10 mL), dried (Na_2SO_4), and evaporated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, 33% AcOEt/hexane) to give **18** (21 mg, quant. as a white foam): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.49 (br s, 1H, exchanged with D_2O), 7.78 (d, 1H, J = 8.1 Hz), 7.54–7.27 (m, 5H), 5.88 (d, 1H, J = 4.2 Hz), 5.74 (dd, 1H, J = 1.1, 8.1 Hz), 5.27 (ddd, 1H, J = 3.0, 5.8, 8.2 Hz), 5.07 (d, 1H, J = 7.4 Hz), 4.18 (dd, 1H, J = 3.2, 4.7 Hz), 4.15 (t, 1H, J = 5.1 Hz), 4.13 (t, 1H, J = 4.4 Hz), 4.04 (m, 1H), 4.03 (t, 1H, J = 4.3 Hz), 3.90 (t, 1H, J = 4.5 Hz), 3.67 (t, 1H, J = 6.9 Hz), 2.17 (ddd, 1H, J = 5.1, 8.3, 14.3 Hz), 2.10 (s 3H), 2.04 (ddd, 1H, J = 3.3, 8.2, 14.3 Hz), 1.55 (s, 3H), 1.37 (s, 3H), 0.88 (s, 9H), 0.87 (s, 9H), 0.09 (s, 3H), 0.06 (s, 3H), 0.05 (s, 3H),0.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 181.3, 169.6, 169.3, 163.0, 139.7, 134.6, 132.0, 129.3, 128.1, 111.4, 102.4, 101.7, 100.1, 88.6, 87.2, 84.9, 76.4, 76.2, 75.9, 71.9, 69.5, 68.4, 63.8, 36.0, 30.3, 27.9, 26.0, 21.4, 20.9, −4.0, −4.2, −4.5, −4.8; MS (FAB) m/z 883 (MH^+); Exact MS (FAB) Calcd for $C_{38}H_{60}N_5O_{10}SSi_2$: 834.3599, found: 834.3578.

Protected tunicaminyluracil 19. A mixture of **18** (29 mg, 34 μmol) and PhSeH (10 μL, 101 μmol) in Et_3N (200 μL) was heated for 1 h at 60°C. Additional PhSeH (21 μL, 202 μmol) was added to the mixture, and the mixture was further stirred for 1 h to complete the reaction. The mixture was evaporated under reduced pressure. A mixture of the residue, phthalic chloride (15 μL, 101 μmol), and DBU (32 μL, 217 μmol) in toluene (1 mL) was heated for 3 h at 100°C. The mixture was allowed to cool to room temperature and evaporated under reduced pressure. The residue was partitioned between AcOEt (20 mL) and H_2O (10 mL), and the organic layer was washed with brine (10 mL), dried (Na_2SO_4), and evaporated under reduced pressure. The residue was purified by column chromatography (SiO_2, 33% AcOEt/hexane) to give **19** (31 mg, 98% as a pale yellow foam): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.04 (br s, 1H, exchanged with D_2O), 7.87–7.17 (m, 10H), 5.92 (d, 1H, J = 4.8 Hz), 5.87 (d, 1H, J = 10.3 Hz), 5.76 (d, 1H, J = 8.2 Hz), 5.27 (ddd, 1H, J = 3.2, 5.4, 8.2 Hz), 4.95 (dd, 1H, J = 6.9, 10.3 Hz), 4.41 (t, 1H, J = 10.4 Hz), 4.33 (t, 1H, J = 7.3 Hz), 4.17 (t, 1H, J = 3.8 Hz), 4.14 (dd, 1H, J = 4.5, 8.1 Hz), 3.98 (t, 1H, J = 4.6 Hz), 3.93 (t, 1H, J = 4.1 Hz), 2.22 (ddd, 1H, J = 4.4, 8.0, 14.1 Hz), 2.15 (s, 3H), 2.11 (ddd, 1H, J = 5.5, 8.9, 14.1 Hz),

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1.50 (s, 3H), 1.32 (s, 3H), 0.89 (s, 9H), 0.88 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H), 0.05 (s, 3H),0.03 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.5, 167.8, 162.6, 150.0, 139.5, 134.3, 131.7, 131.1, 128.9, 127.3, 132.6, 111.6, 102.4, 88.0, 85.2, 83.8, 75.7, 72.8, 72.0, 69.4, 68.8, 53.3, 36.0, 27.5, 25.8, 25.7, 21.2, 18.0, 17.9, −4.3, −4.5, −4.7, −4.9; MS (FAB) *m/z* 938 (MH^+); Exact MS (FAB) Calcd for $C_{46}H_{64}N_3O_{12}SSi_2$: 938.3749, found: 938.3724.

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