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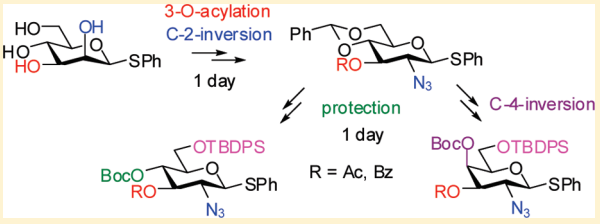
Rapid Transformation of D-Mannose into Orthogonally Protected D-Glucosamine and D-Galactosamine Thioglycosides

Madhu Emmadi and Suvarn S. Kulkarni*

Department of Chemistry, Indian Institute of Technology Bombay, Mumbai 400076, India

Supporting Information

ABSTRACT: An expedient protocol for synthesis of orthogonally protected 2-azido-2-deoxy-D-glucosamine and 2-azido-2-deoxy-D-galactosamine donors from D-mannose is described. Readily available phenyl β-D-thiomannoside is rapidly transformed into D-GlcN$_3$ thioglycosides via a highly regioselective 3-*O*-acylation followed by 4,6-*O*-benzylidenation and azide displacement of C2-OTf, which is further converted into D-GalN$_3$ thioglycosides through Lattrell−Dax inversion of the C4 hydroxy group and its Boc protection. The reaction sequence may be completed in 2 days and involves simple workups and minimal column chromatography.



Carbohydrates are involved in a plethora of important biological processes, such as viral and bacterial infections, cell growth and proliferation, cell−cell communication, and immune response.[1,2] 2-Amino-2-deoxysugars are ubiquitous in the most important classes of glycoconjugates and oligosaccharides. In particular, *N*-acetylated and *N*-sulfonated derivatives of D-glucosamine (D-GlcNH$_2$) and D-galactosamine (D-GalNH$_2$) form key structural components of biologically important *O*-glycoproteins, blood group antigens, *N*-glycoproteins, GPI anchors, glycosphingolipids, lipopolysaccharides, and antifreeze glycoproteins.

Owing to their biological importance and the difficulties associated with their procurement in acceptable purity and amounts from natural sources, the glycosamine-containing oligosaccharides and glycoconjugates have received immense attention from the synthetic chemists.[3−5] The challenging target molecules often contain branched structures with various sugars joined to the aminosugars at their 3-O, 4-O, as well as 6-O positions. The aminosugars are in turn connected at the reducing end with other glycosides or conjugates in a 1,2-*cis* or more frequently 1,2-*trans* manner. Of these, the installation of 1,2-*trans* linkages could be achieved by taking advantage of the neighboring group participation of the C2 functionality. On the other hand, a nonparticipating C2 azido group on the 2-azido-2-deoxyglycopyranosyl donor is often used to direct the formation of a more challenging 1,2-*cis* linkage. The azide functionality is stable under generally employed glycosylation conditions as well as protecting group manipulations, and it could be conveniently transformed into the requisite -NH$_2$ or -NHAc groups upon reduction or treatment with thioacetic acid, respectively. Consequently, several routes have been devised for the synthesis of appropriately protected 2-azido-2-deoxy-D-glucopyranose (D-GlcN$_3$) **1** and 2-azido-2-deoxy-D-galactopyranose (D-GalN$_3$) **2** donors (Figure 1) starting from either a glycosamine or by stereoselective introduction of an azido group at the C2 position of 1,6-anhydrosugar derivatives, glycals, or hexopyranoses.

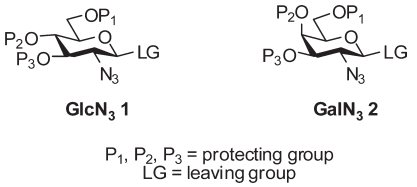


Figure 1. Regioselectively protected D-glucosamine and D-galactosamine donors.

The common methods of preparation for both (D-GlcN$_3$ **1**) and (D-GalN$_3$ **2**) derivatives include (1) Paulsen's azide opening of either 1,6,2,3-anhydro-manno[6]/talo[7] configured Černý epoxides[8,9] or the 2-deoxy-2-iodo-1,6-anhydrosugars[10] via transiently formed Černý epoxides and (2) Lemieux's azidonitration[11] or azidoselenation[12] and one-pot azidochlorination[13] of glycals. Danishefsky's sulfamidoglycosylation[14] and Gin's acetamidoglycosylation[15] protocols give direct access to the GlcNAc and GalNAc containing glycosides starting from glycals. The D-GlcN$_3$ derivatives have been also accessed by (1) azide displacement of the O2 triflate derivative of β-mannopyranoside,[16−20] 1,6-anhydro-β-mannopyranosides,[21] and their cyclic sulfates[22] and (2) direct conversion of glucosamine derivatives by diazo transfer using TfN$_3$[23] or imidazole-1-sulfonyl azide hydrochloride[24] or through 2-deoxy-2-hydrazinoglucopyranose.[25] Although the diazotransfer procedure is also applicable to GalNH$_2$, it is seldom[26] carried out because of its high cost. Instead, C4 epimerization of the easily available 2-acetamido-2-deoxyglucopyranose (D-GlcNAc)[27] or 2-pthalamido-2-deoxyglucopyranose derivatives (D-GlcNPhth)[28,29] is a preferred route. Syntheses of D-GalNH$_2$ starting from L-lyxose[30] or D-tagatose[31] have been also reported. Recently, a procedure for amination of

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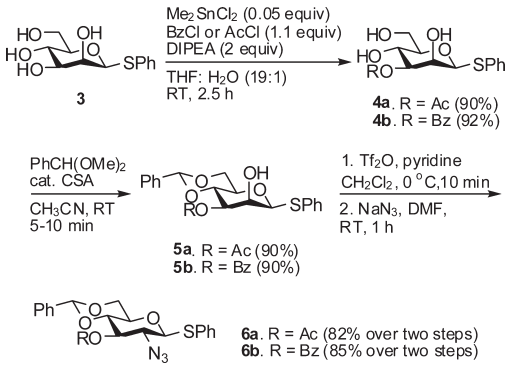
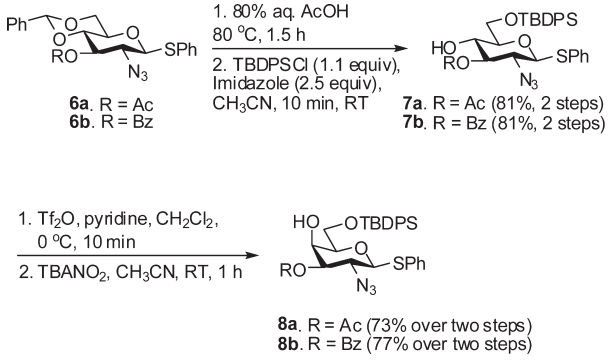
Scheme 1. Rapid and Efficient Transformation of β-D-Thiomannoside 3 into D-GlcN_3 Thioglycoside Donors



Scheme 2. Conversion of D-GalN_3 Derivatives into Regioselectively Protected D-GalN_3 Thioglycoside Donors



C2 of a β-galactopyranoside with retention of configuration by double inversion process, involving azide displacement of O2-imidazylate is reported.[32] In spite of the mammoth efforts, a short, efficient, and practical synthesis of orthogonally protected D-GlcN_3 and more importantly D-GalN_3 donors is elusive.

In the context of our ongoing project on the synthesis of mucin core oligosaccharides we require a ready access to large quantities of regioselectively protected D-GlcN_3 and D-GalN_3 donors. Herein, we describe an expeditious and convenient route for the preparation of orthogonally substituted D-GlcN_3 and D-GalN_3 donors from a readily available and inexpensive starting material derived from D-mannose.

van Boom and co-workers first observed that the C2-OTf group of a methyl β-D-mannoside undergoes a facile nucleophilic displacement by azide anions to afford the 2-azido-2-deoxyglucose compound in excellent yields, whereas the corresponding α-anomers do not react easily.[16] On the basis of this pioneering approach, a few reports on the conversion of β-D-mannoside to D-glucosamine building blocks have been published. Since the alkyl β-*O*-mannosides were difficult to prepare and to convert into glycosyl donors, Pavliak and Kovác employed 1,3,4,6-tetra-*O*-acetyl-β-D-mannopyranoside.[17] However, difficulties resulted as there were no methods to obtain the starting material efficiently.[18] To circumvent this problem, Pozsgay reported two methods using easily accessible β-D-thiomannopyranoside.[19,20] These improved methods still involve lengthy routes to obtain selectively protected D-GlcN_3 donors.

We envisioned that the readily available phenyl 1-thio-β-D-mannopyranoside **3**[33] could be regioselectively protected in a few steps such that all the hydroxyls are differentiated. A C2 inversion by azide displacement of 2-OTf followed by C4 epimerization would give a facile access to orthogonally protected D-GlcN_3 and D-GalN_3 donors, respectively.

A simple and straightforward preparation of regioselectively protected D-GlcN_3 donors, involving regioselective 3-*O*-acylation of mannoside **3**, as a key step, is shown in Scheme 1. Recently, a regioselective protection of various hexopyranosides catalyzed by dimethyltin dichloride (Me_2SnCl_2) is reported,[34] wherein the regioselectivity of monobenzoylation is conceived as an intrinsic character of the sugar dependent on the relative disposition of the free hydroxyl groups and also on the stereochemistry of the anomeric function. For example, the α and β isomers of methyl glucopyranoside have been shown to afford exclusively the 2-*O*- or 6-*O*-benzoylated products, respectively, whereas methyl α-mannopyranoside exhibited a preference for 3-*O*-acylation. Intriguingly, no studies have been reported for the β-mannosides as well as any thioglycosides. We tested this reaction on β thiomannoside **3** and found that it works very well to afford the corresponding 3-*O*-acylated products in excellent yields. Thus, compound **3** was treated successively with 0.05 equiv of Me_2SnCl_2, DIPEA (2 equiv), and 1.1 equiv of acetyl chloride or benzoyl chloride in THF/H_2O (19:1) at rt for 2.5 h to afford the corresponding 3-*O*-acetate or 3-*O*-benzoate mannosides **4a** and **4b**, in very good isolated yields (90% and 92%), respectively. Compound **4a**, upon treatment with benzaldehyde dimethyl acetal (1.3 equiv) in the presence of 10-camphorsulfonic acid (0.25 equiv) in CH_3CN at ambient temperature, rapidly afforded the 4,6-*O*-benzylidene acetal **5a** (90%), which upon triflation at O2 followed by nucleophilic displacement of the triflyloxy group by NaN_3 furnished the desired D-GlcN_3 building block **6a** in 82% yield over two steps. Under identical conditions, 4,6-*O*-bezylidenation of **4b** instantly generated 2-OH compound **5b** (90%), which upon similar triflation followed by azide displacement of C2 triflyloxy group furnished **6b** (85%, two steps). Since each reaction was essentially completed within a short time and no side products were encountered, it was realized that the crude products could be carried forward as such until the last step. Accordingly, the overall four-step sequence could be carried out on a 2 g scale in a day without any intermittent purification to obtain compound **6b** (1.6 g) in 44% overall yield after a single chromatographic purification.

With the successful preparation of selectively protected D-GlcN_3 building blocks we proceeded further to obtain the corresponding D-GalN_3 derivatives. Scheme 2 outlines the preparation of orthogonally substituted D-GalN_3 building blocks. Hydrolysis of the 4,6-*O*-benzylidene acetal of **6a** followed by selective TBDPS protection of the primary hydroxyl group of the so formed diol cleanly afforded the 4-OH compound **7a** (81%, two steps). It should be noted that switching the solvent from DMF[35] to acetonitrile resulted in remarkable acceleration of this reaction. The reaction was completed in only 10 min, and the use of acetonitrile in place of DMF also expedited the workup procedure. In a similar manner, benzoate **6b** was rapidly transformed into the 4-hydroxy derivative **7b** in excellent yield. With the requisite 4-OH D-GlcN_3 derivatives **7a** and **7b** in hand, the stage was set for C4 inversion. Of the various conditions attempted for the C4 epimerization of D-GlcN_3, the Lattrell–Dax reaction[36,37] involving

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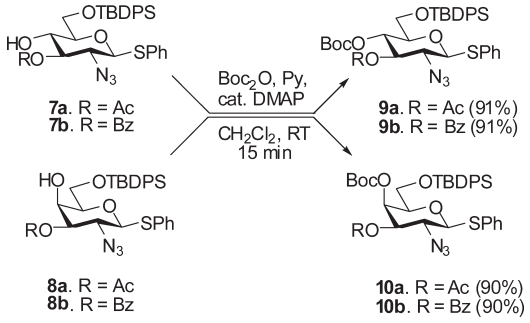
Scheme 3. Preparation of Orthogonally Protected D-GlcN$_3$ and D-GalN$_3$ Thioglycoside Donors



triflate displacement by nitrite ion under mild conditions worked the best. Accordingly, triflation of **7a** (Tf_2O, Py, CH_2Cl_2, 10 min) followed by nucleophilic displacement of the formed 4-triflyloxy group with 3 equiv of tetrabutylammonium nitrite ($TBANO_2$) in CH_3CN at rt for 1 h cleanly afforded the desired D-GalN$_3$ derivative **8a** in 73% yield over two steps. In similar fashion, 3-OBz derivative **7b** underwent a facile C4 epimerization to deliver **8b** in good yield (77%). No side products were obtained. Our results are in agreement with the observations made by Konradsson[29] and Ramström[38] in the D-gluco and other related systems, wherein the success of such nucleophilic displacements has been attributed to the presence of a neighboring equatorial ester group. The four-step sequence involving two brief workups and subsequent passing through silica gel column could be executed in a day in 58% overall yield.

Scheme 3 delineates protection of the free 4-OH groups of D-GlcN$_3$ and D-GlcN$_3$ building blocks to construct orthogonally protected building blocks. The D-GlcN$_3$ 4-OH compounds **7a** and **7b** and D-GalN$_3$ derivatives **8a** and **8b**, individually, upon treatment with Boc anhydride in the presence of cat. DMAP in pyridine and CH_2Cl_2 at rt instantly provided the fully protected building blocks **9a**, **9b**, **10a**, and **10b** in 91%, 91%, 90%, and 90% yields, respectively.

In conclusion, we have established a straightforward route to transform β-D-thiomannosides into selectively protected 2-azido-2-deoxyglucose and 2-azido-2-deoxygalactose thioglycoside donors. All the building blocks are new compounds which have been characterized thoroughly using NMR and other spectroscopic methods (see the Supporting Information). The protecting groups employed, Boc, TBDPS, Ac (or Bz), and N_3, being stable and orthogonal to each other, could be selectively deprotected, in any order, during chain elongation, allowing access to diverse building blocks for glycoside assembly. The amenability of the benzylidene acetals to their regioselective O4 or O6 reductive opening imparts extra flexibility to this class of donors, as demonstrated by Hung and co-workers in their efficient one-pot protection approach extended to 2-azidothioglucosides[39] and very recently to anomeric acetates.[40]

Thioglycosides have always been among the choicest of stable donors owing to their ease in handling and ability to be transformed into other types of donors.[41,42] Our method allows a rapid access to versatile thioglycoside donors. All the reactions are simple and clean and involve routine workup and minimal column chromatography. With the individual reaction time ranging from 5 min to 2 h, the entire sequence could be carried out in 2 days and is also amenable to scale-up. Most of the reactions are performed at rt or in an ice bath and do not require any special apparatus. The protocol is expected to accommodate various other acyl groups as well as substituted benzylidene acetals to further expand the scope. This method should find a wide application in synthesis of glycosamine-containing complex carbohydrates.

EXPERIMENTAL SECTION

General Methods. All reactions were conducted under a dry nitrogen atmosphere. Solvents (CH_2Cl_2 >99%, THF 99.5%, acetonitrile 99.8%, DMF 99.5%) were purchased in capped bottles and dried under sodium or CaH_2. All other solvents and reagents were used without further purification. All glassware was oven-dried before use. TLC was performed on precoated aluminum plates of silica gel 60 F254 (0.25 mm, E. Merck). Developed TLC plates were visualized under a short-wave UV lamp and by heating plates that were dipped in ammonium molybdate/cerium(IV) sulfate solution. Silica gel column chromatography was performed using silica gel (100−200 mesh) and employed a solvent polarity correlated with TLC mobility. NMR experiments were conducted on 400 MHz instrument using $CDCl_3$ (D, 99.8%) or $(CD_3)_2CO$ (D, 99.9%) as solvents. Chemical shifts are relative to the deuterated solvent peaks and are in parts per million (ppm). $^1H-^1H$ COSY was used to confirm proton assignments. Mass spectra were acquired in the ESI mode. Melting points were determined by capillary apparatus. Specific rotation experiments were measured at 589 nm (Na) and 25 °C. IR spectra were recorded on an FT-IR spectrometer using CsCl plates.

Phenyl 3-*O*-Acetyl-1-thio-β-D-mannopyranoside (4a). Me_2SnCl_2 (0.08 g, 0.37 mmol) and DIPEA (2.5 mL, 15.05 mmol) were added sequentially to a stirred solution of phenyl 1-thio-β-D-mannopyranoside **3**[33] (2.0 g, 7.52 mmol) in THF/H_2O (48 mL, 19:1). After 5 min, AcCl (0.6 mL, 8.28 mmol) was added, and the solution was stirred at rt for 2.5 h. After total consumption of the starting material, the reaction was quenched with 3% HCl (40 mL) and extracted against EtOAc (80 mL), and the aqueous layer was separated and washed with EtOAc (80 mL × 2). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (7:3 ethyl acetate/petroleum ether) to obtain **4a** as a white foam (2.12 g, 90%): $[\alpha]^{25}_D$ −100.2 (*c* 0.92, $CHCl_3$); IR ($CHCl_3$) ν 3398, 3019, 2975, 1736, 1522, 1219, 1047, 772, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42−7.39 (m, 2H, ArH), 7.23−7.19 (m, 3H, ArH), 4.94 (s, 1H, H-1), 4.83 (dd, *J* = 10.0, 3.0 Hz 1H, H-3), 4.30 (d, *J* = 3.0 Hz, 1H, H-2), 4.25 (t, *J* = 10.0 Hz, 1H, H-4), 3.93 (bs, 2H, H-6), 3.37−3.35 (m, 1H, H-5), 2.14 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 134.2, 131.0, 129.2, 127.6, 87.3, 80.3, 76.7, 71.0, 63.6, 61.2, 21.2; HRMS calcd for $C_{14}H_{18}O_6S$ $[M + Na]^+$ 337.0722, found 337.0711.

Phenyl 3-*O*-Benzoyl-1-thio-β-D-mannopyranoside (4b). Me_2SnCl_2 (0.08 mg, 0.37 mmol) and DIPEA (2.6 mL, 15.13 mmol) were added sequentially to a stirred solution of **3** (2.0 g, 7.56 mmol) in THF/H_2O (48 mL, 19:1). After 5 min, BzCl (0.95 mL, 8.32 mmol) was added, and the solution was stirred at rt for 2.5 h. After total consumption of the starting material, the reaction was quenched with 3% HCl (40 mL) and extracted against EtOAc (80 mL), and the aqueous layer was separated and washed with EtOAc (80 mL × 2). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (1:1 ethyl acetate/petroleum ether) to obtain compound **4b** as a white solid (2.6 g, 92%): $[\alpha]^{25}_D$ −40.0 (*c* 0.56, $CHCl_3$); mp 158.5 °C; IR ($CHCl_3$) ν 3434, 3019, 1720, 1523, 1217, 928, 770, 669 cm^{-1}; ^1H NMR (400 MHz, $(CD_3)_2CO$) δ 8.08 (d, *J* = 7.0 Hz, 2H, ArH), 7.62 (t, *J* = 7.5 Hz, 1H, ArH), 7.52−7.48 (m, 4H, ArH), 7.31 (t, *J* = 7.5 Hz, 2H, ArH), 7.23

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(t, J = 7.5 Hz, 1H, ArH), 5.27 (s, 1H, H-1), 5.10 (dd, J = 9.8, 3.3 Hz, 1H, H-3), 4.43 (d, J = 3.3 Hz, 1H, H-2), 4.21 (t, J = 9.8 Hz, 1H, H-4), 3.92 (dd, J = 12.0, 2.5 Hz, 1H, H-6a), 3.81 (dd, J = 12.0, 5.1 Hz, 1H, H-6b), 3.60−3.56 (m, 1H, H-5); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 166.7, 137.0, 133.8, 131.3, 130.5, 130.3, 129.8, 129.2, 127.3, 87.7, 82.0, 79.0, 71.4, 65.3, 62.5; HRMS calcd for $C_{19}H_{20}O_6S$ $[M + Na]^+$ 399.0878, found 399.0880.

Phenyl 3-*O*-Acetyl-4,6-*O*-benzylidene-1-thio-*β*-D-manno-pyranoside (5a). 10-Camphorsulfonic acid (0.1 g, 0.46 mmol) was added to a solution of **4a** (0.578 g, 1.84 mmol) in acetonitrile (7 mL). To this solution was added benzaldehyde dimethyl acetal (0.33 mL, 2.2 mmol) dropwise under N_2 atmosphere and the mixture allowed to stir at rt. After 10 min, the reaction was quenched with Et_3N, solvents were evaporated on rotor, and the residue was chromatographed on silica gel (3:7 ethyl acetate/petroleum ether) to afford desired product **5a** as a white solid (0.66 g, 90%): $[\alpha]^{25}_D$ −69.6 (c 0.21, $CHCl_3$); mp 203 °C; IR ($CHCl_3$) ν 3020, 2925, 1740, 1523, 1217, 771, 669 cm^{-1}; ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.49−7.44 (m, 4H, ArH), 7.37−7.30 (m, 5H, ArH), 7.26−7.22 (m, 1H, ArH), 5.65 (s, 1H, benzylidene), 5.35 (s, 1H, H-1), 5.07 (dd, J = 10.0, 3.3 Hz 1H, H-3), 5.00 (dd, J = 5.7, 0.8 Hz, OH; exchangeable by D_2O), 4.43−4.38 (m, 1H, H-2), 4.27 (dd, J = 10.0, 5.0 Hz, 1H, H-6eq), 4.19 (t, J = 10.0 Hz, 1H, H-4), 3.84 (t, J = 10.0 Hz, 1H, H-6ax), 3.69 (dt, J = 10.0, 5.0 Hz, 1H, H-5), 2.03 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 170.8, 138.9, 136.7, 130.4, 129.8, 129.6, 128.8, 127.5, 127.2, 102.4, 88.46, 76.3, 74.3, 71.9, 71.4, 69.0, 20.9; HRMS calcd for $C_{21}H_{22}O_6S$ $[M + Na]^+$ 425.1035, found 425.1026.

Phenyl 3-*O*-Benzoyl-4,6-*O*-bezylidene-1-thio-*β*-D-manno-pyranoside (5b). 10-Camphorsulfonic acid (0.08 g, 0.345 mmol) was added to a solution of **4b** (0.52 g, 1.38 mmol) in acetonitrile (7 mL). To this solution was added benzaldehyde dimethyl acetal (0.25 mL, 1.65 mmol) dropwise under N_2 atmosphere and the mixture allowed to stir at rt. After 10 min, the reaction was quenched with Et_3N, solvents were evaporated on rotor, and the residue was chromatographed on silica gel (2:8 ethyl acetate/petroleum ether) to afford desired product **5b** as a white solid (0.576 g, 90%): $[\alpha]^{25}_D$ −57.0 (c 0.25, $CHCl_3$); mp 193 °C; IR ($CHCl_3$) ν 3019, 1719, 1522, 1216, 767, 669 cm^{-1}; ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.08 (d, J = 7.2 Hz, 2H, ArH), 7.62 (t, J = 7.5 Hz, 1H, ArH), 7.52−7.41 (m, 6H, ArH), 7.35−7.23 (m, 6H, ArH), 5.72 (s, 1H, benzylidene), 5.46 (s, 1H, H-1), 5.40 (dd, J = 10.0, 3.3 Hz 1H, H-3), 4.58 (d, J = 3.3 Hz, 1H, H-2), 4.39 (t, J = 10.0 Hz, 1H, H-4), 4.31 (dd, J = 10.0, 5.0 Hz, 1H, H-6eq), 3.90 (t, J = 10.0 Hz, 1H, H-6ax), 3.79 (dt, J = 10.0, 5.0 Hz, 1H, H-5); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 166.3, 138.9, 136.8, 134.0, 131.0 (2C), 130.5, 129.9, 129.6, 129.3, 128.8, 127.5, 127.1, 102.3, 88.67, 76.5, 75.0, 72.0, 71.6, 69.1; HRMS calcd for $C_{26}H_{24}O_6S$ $[M + Na]^+$ 487.1191, found 487.1171.

Phenyl 3-*O*-Acetyl-2-azido-2-deoxy-4,6-*O*-bezylidene-1-thio-*β*-D-glucopyranoside (6a). Trifluoromethanesulfonic anhydride (0.53 mL, 3.12 mmol) was added dropwise at 0 °C to a stirred solution of **5a** (0.63 g, 1.56 mmol) in CH_2Cl_2 (9 mL). After 2 min, pyridine (0.25 mL, 3.12 mmol) was added to this stirred solution at the same temperature. After 10 min, the reaction mixture was diluted with CH_2Cl_2 (40 mL) and washed successively with aq $NaHCO_3$ (10 mL) and water (10 mL). The separated organic layer was dried over Na_2SO_4 and concentrated in vacuo. The crude product was used for the next step without purification.

The crude product which was obtained in the above step was dissolved in DMF (3.5 mL), and to this NaN_3 (0.2 g, 3.12 mmol) was added. This reaction mixture was stirred at rt for 1 h, and then the reaction mixture was diluted with EtOAc (40 mL) and washed with water. The separated aqueous layer was washed with EtOAc (40 mL × 2). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography on silica gel by using 1:9 ethyl acetate/ petroleum ether as eluent to obtain **6a** as a white solid (0.61 g, 82%): $[\alpha]^{25}_D$ −106.5 (c 0.62, $CHCl_3$); mp 111 °C; IR ($CHCl_3$) ν 3067, 2881, 2112, 1754, 1479,1370, 1217, 1100, 909, 739, 650 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59−7.55 (m, 2H, ArH), 7.42−7.33 (m, 8H, ArH), 5.48 (s, 1H, benzylidene), 5.24 (t, J = 10.0 Hz, 1H, H-3), 4.61 (d, J = 10.0 Hz, 1H, H-1), 4.39 (dd, J = 11.2, 4.4 Hz, 1H, H-6eq), 3.78 (t, J = 10.0 Hz, 1H, H-4), 3.55−4.52 (m, 2H, H-6a, H-5), 3.41 (t, J = 10.0 Hz, 1H, H-2), 2.11 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 136.8, 134.0, 130.7, 129.39, 129.33, 129.03, 128.4, 126.2, 101.6, 87.1, 78.4, 73.1, 70.8, 68.5, 63.7, 20.9; HRMS calcd for $C_{21}H_{21}O_5SN_3$ $[M + Na]^+$ 450.1100, found 450.1079.

Phenyl 2-Azido-2-deoxy-3-*O*-benzoyl-4,6-*O*-benzylidene-1-thio-*β*-D-glucopyranoside (6b). Trifluoromethanesulfonic anhydride (0.24 mL, 1.42 mmol) was added dropwise at 0 °C to a stirred solution of **5b** (0.33 g, 0.71 mmol) in CH_2Cl_2 (6 mL). After 2 min, pyridine (0.12 mL, 1.42 mmol) was added to the stirred solution at the same temperature. After 10 min, the reaction mixture was diluted with CH_2Cl_2 (30 mL) and washed successively with aq. $NaHCO_3$ (10 mL) and water (10 mL). The separated organic layer was dried over Na_2SO_4 and concentrated in vacuo. The crude product was used for the next step without purification.

The crude product which was obtained in the above step was dissolved in DMF (2.5 mL), and to this NaN_3 (0.09 mg, 1.42 mmol) was added. This reaction mixture was stirred at rt for 1 h, and then the reaction mixture was diluted with EtOAc (40 mL) and washed with water. The separated aqueous layer was washed with EtOAc (40 mL × 2). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The desired product was purified by column chromatography on silica gel (1:9 ethyl acetate/petroleum ether) as eluent to obtain **6b** as a white solid (0.3 g, 85%): $[\alpha]^{25}_D$ −75.5 (c 0.81, $CHCl_3$); mp 118 °C; IR ($CHCl_3$) ν 3020, 2114, 1732, 1521, 1261, 1220, 1101, 928, 765, 669 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.2 Hz, 2H, ArH), 7.62−7.56 (m, 3H, ArH), 7.40−7.27 (m, 10H, ArH), 5.50 (t, J = 9.6 Hz, 1H, H-3), 5.47 (s, 1H, benzylidene), 4.69 (d, J = 9.6 Hz, 1H, H-1), 4.39 (dd, J = 9.6, 5.0 Hz 1H, H-6eq), 3.80 (t, J = 9.6 Hz, 1H, H-6ax), 3.71 (t, J = 9.6 Hz, 1H, H-4), 3.63 (dt, J = 9.6, 4.4 Hz 1H, H-5), 3.58 (t, J = 9.6 Hz, 1H, H-2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 136.7, 133.8, 133.5, 130.8, 130.0, 129.4, 129.3, 129.1, 128.9, 128.5, 128.3, 126.2, 101.5, 87.3, 78.5, 73.6, 70.9, 68.5, 64.1; HRMS calcd for $C_{26}H_{23}O_5SN_3$ $[M + Na]^+$ 512.1256, found 512.1264.

Phenyl 3-*O*-Acetyl-2-azido-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-1-thio-*β*-D-glucopyranoside (7a). Compound **6a** (90 mg, 0.21 mmol) was dissolved in 80% AcOH (4.5 mL) and kept for reflux at 85 °C for 90 min. Toluene (5 mL) was added, and the reaction mixture was concentrated in vacuo and subsequently coevaporated with toluene (3 × 5 mL). The crude product which was obtained after the removal of solvents was dissolved in CH_3CN (1.5 mL), and imidazole (40 mg, 0.526 mmol) was added. To this stirred solution was added TBDPSCl (65 μL, 0.252 mmol). After 10 min, the reaction mixture was concentrated in vacuo, and the crude product was purified by column chromatography using silica gel (1:9 ethyl acetate/petroleum ether) to afford product **7a** as a pale yellow viscous liquid (98 mg, 81%): $[\alpha]^{25}_D$ −30.2 (c 0.3, $CHCl_3$); IR ($CHCl_3$) ν 3446, 3019, 2976, 2113, 1746, 1521, 1426, 1391, 1219, 1046, 928, 767, 669, 625 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73−7.68 (m, 4H, ArH), 7.59−7.57 (m, 2H, ArH), 7.45−7.35 (m, 6H, ArH), 7.34−7.24 (m, 3H, ArH), 4.86 (t, J = 9.6 Hz, 1H, H-3), 4.42 (d, J = 9.6 Hz, 1H, H-1), 3.87 (d, J = 4.0 Hz, 2H, H-6), 3.63 (t, J = 9.6 Hz, 1H, H-4), 3.37−3.33 (m, 1H, H-5), 3.27 (t, J = 9.6 Hz, 1H, H-2), 2.08 (s, 3H, CH_3), 1.0 (s, 9H, $(CH_3)_3$CSi); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 135.9, 135.8, 135.7, 133.6, 133.0, 132.9 131.1, 130.0, 129.2, 128.6, 128.3, 128.0, 86.0, 79.8, 76.9, 69.9, 63.8, 62.7, 26.9, 21.1, 19.4; HRMS calcd for $C_{30}H_{35}O_5SN_3Si$ $[M + Na]^+$ 600.1964, found 600.1978.

Phenyl 2-Azido-2-deoxy-3-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-1-thio-*β*-D-glucopyranoside (7b). Compound **6b** (0.1 g, 0.24 mmol) was dissolved in 80% AcOH (5 mL) and kept for

reflux at 90 °C for 90 min. Toluene (5 mL) was added, and the reaction mixture was concentrated in vacuo and subsequently coevaporated with toluene (3 × 5 mL). The crude product which was obtained after the removal of solvents was dissolved in CH_3CN (1 mL), and imidazole (35 mg, 0.51 mmol) was added. To this stirred solution was added TBDPSCl (65 μL, 0.245 mmol). After 15 min, the reaction mixture was concentrated in vacuo, and the desired product was purified by column chromatography on silica gel by using 1:9 ethyl acetate/petroleum ether as eluent to afford the product **7b** as a white foam (103 mg, 81%): $[\alpha]^{25}_D$ +5.5 (*c* 0.98, $CHCl_3$); IR ($CHCl_3$) *ν* 3444, 3018, 2976, 2114, 1712, 1520, 1426, 1392, 1219, 1042, 928, 764, 669, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 8.07 (d, *J* = 7.2 Hz, 2H, ArH), 7.71 (t, *J* = 7.6 Hz, 4H, ArH), 7.63−7.28 (m, 14H, ArH), 5.17 (t, *J* = 9.6 Hz, 1H, H-3), 4.58 (d, *J* = 9.6 Hz, 1H, H-1), 3.99 (d, *J* = 4.0 Hz, 2H, H-6), 3.85 (t, *J* = 9.6 Hz, 1H, H-4), 3.54−3.49 (m, 2H, H-2 and H-5), 1.07 (s, 9H, $(CH_3)_3CSi$); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 167.1, 135.8, 135.7, 133.8, 133.5, 133.06, 133.0, 131.3, 130.1, 130.0, 129.2, 129.1, 128.7, 128.5, 127.9, 86.2, 80.0, 78.5, 69.9, 63.7, 63.1, 26.9, 19.4; HRMS calcd for $C_{35}H_{37}O_5SN_3Si$ $[M + Na]^+$ 662.2121, found 662.2136.

Phenyl 3-*O*-Acetyl-2-azido-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-1-thio-*β*-D-galactopyranoside (8a). Trifluoromethanesulfonic anhydride (0.1 mL, 0.54 mmol) was added dropwise at 0 °C to a stirred solution of **7a** (0.16 g, 0.27 mmol) in CH_2Cl_2 (2 mL). After 2 min, pyridine (50 μL, 0.54 mmol) was added to this stirred solution at the same temperature. After 10 min, the reaction mixture was diluted with CH_2Cl_2 (30 mL) and washed successively with 1 M HCl (10 mL), aq $NaHCO_3$ (10 mL), and water (10 mL). The separated organic layer was dried over Na_2SO_4 and concentrated, and this crude product was used for the next step without purification.

The crude product which was obtained after solvent removal was dissolved in acetonitrile (1.5 mL), $TBANO_2$ (0.23 mg, 0.81 mmol) was added, and this reaction was stirred at rt. After 1 h, the reaction mixture was diluted with EtOAc and washed with water. The separated aqueous layer was washed with EtOAc (30 mL × 2). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (1:9 ethyl acetate/petroleum ether) to obtain **8a** as a pale yellow viscous liquid (0.114 g, 73%): $[\alpha]^{25}_D$ +11.4 (*c* 0.12, $CHCl_3$); IR ($CHCl_3$) *ν* 3455, 3019, 2932, 2115, 1748, 1523, 1427, 1364, 1217, 928, 770, 669, 623 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.76−7.74 (m, 2H, ArH), 7.69−7.66 (m, 2H, ArH), 7.64−7.61 (m, 2H, ArH), 7.46−7.37 (m, 6H, ArH), 7.30−7.24 (m, 3H, ArH), 4.77 (dd, *J* = 10.0, 2.8 Hz, 1H, H-3), 4.47 (d, *J* = 10.0 Hz, 1H, H-1), 4.28 (d, *J* = 2.8 Hz, 1H, H-4), 4.02 (dd, *J* = 11.2, 4.0 Hz, 1H, H-6a), 3.92 (dd, *J* = 11.2, 4.0 Hz, 1H, H-6b), 3.85 (t, *J* = 10.0 Hz, 1H, H-2), 3.51 (t, *J* = 4.0 Hz, 1H, H-5), 2.16 (s, 3H, CH_3), 1.07 (s, 9H, $(CH_3)_3CSi$); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 170.3, 135.8, 135.6, 133.5, 132.4, 132.0, 131.2, 130.26, 130.23, 129.23, 128.5, 128.1, 128.0, 86.5, 77.5, 75.8, 68.4, 65.1, 59.2, 26.8, 21.1, 19.2; HRMS calcd for $C_{30}H_{35}O_5SN_3Si$ $[M + Na]^+$ 600.1964, found 600.1980.

Phenyl 2-Azido-2-deoxy-3-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-1-thio-*β*-D-galactopyranoside (8b). Trifluoromethanesulfonic anhydride (0.2 mL, 1.18 mmol) was added dropwise at 0 °C to a stirred solution of **7b** (0.38 g, 0.59 mmol) in CH_2Cl_2 (5 mL). After 2 min, pyridine (0.1 mL, 1.18 mmol) was added to this stirred solution at the same temperature. After 10 min, the reaction mixture was diluted with CH_2Cl_2 (40 mL) and washed successively with 1 M HCl (10 mL), aq $NaHCO_3$ (10 mL), and water (10 mL). The separated organic layer was dried over Na_2SO_4 and concentrated, and this crude product was used for the next step without purification.

The crude product which was obtained after solvent removal was dissolved in acetonitrile (4 mL),to this was added $TBANO_2$ (0.51 mg, 1.17 mmol), and the reaction mixture was stirred at rt. After 1 h, the reaction mixture was diluted with EtOAc (40 mL) and washed with water. The separated aqueous layer was washed with EtOAc (40 mL × 2). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The desired product was purified by column chromatography (1:9 ethyl acetate/petroleum ether) to obtain **8b** as a white foam (0.29 g, 77%): $[\alpha]^{25}_D$ +36.6 (*c* 0.61, $CHCl_3$); IR ($CHCl_3$) *ν* 3464, 3019, 2931, 2115, 1721, 1602, 1428, 1268, 1216, 1113, 929, 770, 669, 622, 505 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 8.08 (d, *J* = 6.8 Hz, 2H, ArH), 7.76−7.55 (m, 7H, ArH), 7.47−7.36 (m, 8H, ArH), 7.33−7.24 (m, 3H, ArH), 4.98 (dd, *J* = 10.0, 2.8 Hz, 1H, H-3), 4.55 (d, *J* = 10.0 Hz, 1H, H-1), 4.44 (d, *J* = 2.8 Hz, 1H, H-4), 4.05−3.93 (m, 3H, H-6a, 6b & H-2), 3.60 (t, *J* = 4.0 Hz, 1H, H-5), 3.33 (bs, 1H, OH) 1.06 (s, 9H, $(CH_3)_3CSi$); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 165.9, 135.8, 135.7, 133.7, 133.5, 132.5, 132.2, 131.5, 130.24, 130.21 130.1, 129.4, 129.2, 128.6, 128.5, 128.12, 128.09, 86.8, 77.5, 76.6, 68.2, 64.9, 59.7, 26.9, 19.2; HRMS calcd for $C_{35}H_{37}O_5SN_3Si$ $[M + Na]^+$ 662.2121, found 662.2112.

Phenyl 3-*O*-Acetyl-2-azido-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-4-*O*-*tert*-butyloxycarbonyl-1-thio-*β*-D-glucopyranoside (9a). Boc_2O (40 μL, 0.17 mmol) and DMAP (2 mg, 0.017 mmol) were added sequentially to a clear solution of **7a** (33 mg, 0.057 mmol) in CH_2Cl_2 (0.5 mL), and to this stirred solution was added pyridine (15 μL, 0.17 mmol). After 15 min, reaction was quenched with MeOH, diluted with CH_2Cl_2 (30 mL), and washed successively with $NaHCO_3$ (10 mL) and brine (10 mL). The separated organic layer was dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (1:12 ethyl acetate/petroleum ether) to obtain the desired product as a colorless viscous liquid **9a** (34.5 mg, 91%): $[\alpha]^{25}_D$ −23.1 (*c* 0.15, $CHCl_3$); IR ($CHCl_3$) *ν* 3020, 2932, 2114, 1756, 1524, 1275, 1258, 1216, 1112, 1045, 762, 669, 613, 505 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.78−7.75 (m, 2H, ArH), 7.69−7.66 (m, 2H, ArH), 7.64−7.61 (m, 2H, ArH), 7.44−7.24 (m, 9H, ArH), 5.12 (t, *J* = 10.0 Hz, 1H, H-3), 4.99 (t, *J* = 10.0 Hz, 1H, H-4), 4.49 (d, *J* = 10.0 Hz, 1H, H-1), 3.84 (d, *J* = 2.8 Hz, 2H, H-6), 3.56 (td, *J* = 4.0, 10.0 Hz, 1H, H-5), 3.45 (t, *J* = 10.0 Hz, 1H, H-2), 2.08 (s, 3H), 1.43 (s, 9H, $(CH_3)_3CO$) 1.05 (s, 9H, $(CH_3)_3CSi$); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 170.0, 152.4, 135.8, 135.7, 134.9, 134.1, 133.2, 132.9, 130.7, 129.9, 129.8, 129.3, 128.8, 127.9, 86.0, 83.0, 78.6, 75.3, 70.5, 62.8, 62.2, 27.7, 26.8, 20.9, 19.4; HRMS calcd for $C_{35}H_{43}O_7SN_3Si$ $[M + Na]^+$ 700.2489, found 700.2474.

Phenyl 2-Azido-2-deoxy-3-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-4-*O*-*tert*-butyloxycarbonyl-1-thio-*β*-D-glucopyranoside (9b). Boc_2O (0.23 mL, 0.98 mmol) and DMAP (0.012 g, 0.03 mmol) were added sequentially to a clear solution of **7b** (0.21 g, 0.33 mmol) in CH_2Cl_2 (2 mL), and to this stirred solution was added pyridine (80 μL, 0.98 mmol). After 15 min, the reaction was quenched with MeOH, diluted with CH_2Cl_2 (40 mL), and washed successively with $NaHCO_3$ (10 mL) and brine (10 mL). The separated organic layer was dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (1:12 ethyl acetate/petroleum ether) to obtain desired product **9b** as a white foam (0.223 g, 91%): $[\alpha]^{25}_D$ −26.0 (*c* 0.73, $CHCl_3$); IR ($CHCl_3$) *ν* 3019, 2976, 2114, 1750, 1523, 1427, 1219, 1046, 928, 759, 625, 505 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 8.08 (d, *J* = 6.8 Hz, 2H, ArH), 7.76−7.55 (m, 7H, ArH), 7.47−7.36 (m, 8H, ArH), 7.33−7.24 (m, 3H, ArH), 5.36 (t, *J* = 10.0 Hz, 1H, H-3), 5.15 (t, *J* = 10.0 Hz, 1H, H-4), 4.61 (d, *J* = 10.0 Hz, 1H, H-1), 3.87 (d, *J* = 2.8 Hz, 2H, H-6), 3.63 (td, *J* = 4.0, 10.0 Hz, 1H, H-5), 3.59 (t, *J* = 10.0 Hz, 1H, H-2), 1.21 (s, 9H, $(CH_3)_3CO$), 1.07 (s, 9H, $(CH_3)_3CSi$); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 165.7, 152.2, 135.8, 135.7, 134.9, 133.8, 133.5, 133.2, 133.0, 131.1, 130.2, 129.89, 129.83, 129.3, 128.7, 128.5, 127.92, 127.90, 86.4, 82.9, 78.7, 75.5, 70.4, 63.2, 62.3, 27.5, 26.8, 19.4; HRMS calcd for $C_{40}H_{45}O_7SN_3Si$ $[M + Na]^+$ 762.2645, found 762.2657.

Phenyl 3-*O*-Acetyl-2-azido-2-deoxy-6-*O*-*tert*-butyldiphenylsilyl-4-*O*-*tert*-butyloxycarbonyl-1-thio-*β*-D-galactopyranoside (10a). Boc_2O (52 μL, 0.22 mmol) and DMAP (0.003 g, 0.02 mmol)

were added sequentially to a clear solution of **8a** (0.043 g, 0.074 mmol) in CH_2Cl_2 (0.5 mL), and to this stirred solution was added pyridine (20 μL, 0.22 mmol). After 15 min, the reaction was quenched with MeOH, diluted with CH_2Cl_2 (30 mL), and washed successively with $NaHCO_3$ (10 mL) and brine (10 mL). The separated organic layer was dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (1:12 ethyl acetate/petroleum ether) to obtain product **10a** as a colorless viscous liquid (45 mg, 90%): $[\alpha]^{25}_D$ +10.0 (*c* 0.3, $CHCl_3$); IR ($CHCl_3$) ν 3019, 2929, 2115, 1750, 1520, 1273, 1254, 1214, 1114, 1043, 762, 669, 613, 505 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76−7.61 (m, 4H, ArH), 7.58−7.52 (m, 2H, ArH), 7.45−7.35 (m, 6H, ArH), 7.30−7.26 (m, 3H, ArH), 5.35 (d, *J* = 2.8 Hz, 1H, H-4), 4.89 (dd, *J* = 10.0, 2.8 Hz, 1H, H-3), 4.49 (d, *J* = 10.0 Hz, 1H, H-1), 3.80−3.71 (m, 4H, H-2, H-5, 6a and 6b), 2.06 (s, 3H, CH_3), 1.47 (s, 9H, $(CH_3)_3CO$), 1.01 (s, 9H, $(CH_3)_3CSi$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 153.2, 135.78, 135.72, 133.7, 133.1, 133.0, 132.8, 132.1, 130.0, 129.2, 129.1, 128.2, 127.9, 87.2, 82.6, 77.2, 73.6, 69.1, 61.5, 59.8, 27.8, 26.8, 20.9, 19.28; HRMS calcd for $C_{35}H_{43}O_7SN_3Si$ $[M + Na]^+$ 700.2489, found 700.2463.

Phenyl 2-Azido-2-deoxy-3-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-4-*O*-*t*-butyloxy carbonyl-1-thio-β-D-galactopyranoside (10b). Boc_2O (0.18 mL, 0.76 mmol) and DMAP (0.01 g, 0.076 mmol) were added sequentially to a clear solution of **8b** (0.164 g, 0.256 mmol) in CH_2Cl_2 (2 mL), and to this stirred solution was added pyridine (65 μL, 0.76 mmol). After 15 min, the reaction was quenched with MeOH, diluted with CH_2Cl_2, and washed successively with $NaHCO_3$ and brine. The separated organic layer was dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (1:12 ethyl acetate/petroleum ether) to obtain product **10b** as a white foam (0.17 g, 90%): $[\alpha]^{25}_D$ +51.0 (*c* 0.6, $CHCl_3$); IR ($CHCl_3$) ν 3019, 2932, 2116, 1746, 1523, 1286, 1218, 1142, 1112, 910, 772, 669, 504 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 6.8 Hz, 2H, ArH), 7.72−7.61 (m, 7H, ArH), 7.44−7.34 (m, 8H, ArH), 7.31−7.28 (m, 3H, ArH), 5.50 (d, *J* = 3.2 Hz, 1H, H-4), 5.16 (dd, *J* = 10.0, 3.2 Hz, 1H, H-3), 4.58 (d, *J* = 10.0 Hz, 1H, H-1), 3.94 (t, *J* = 10.0 Hz, 1H, H-2), 3.81- 3.78 (m, 3H, H-5, H-6a and 6b), 1.30 (s, 9H, $(CH_3)_3CO$); 1.02 (s, 9H, $(CH_3)_3CSi$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 152.8, 135.7, 134.9, 133.5, 133.1, 132.8, 132.2, 130.1, 130.0, 129.99, 129.81, 129.3, 129.2, 128.4, 128.2, 127.98, 127.95, 87.3, 82.7, 77.2, 74.1, 69.4, 61.7, 60.4, 27.6, 26.8, 19.2; HRMS calcd for $C_{40}H_{45}O_7SN_3Si$ $[M + Na]^+$ 762.2645, found 762.2651.

■ ASSOCIATED CONTENT

Supporting Information. ^1H and ^{13}C NMR spectra for all new compounds and $^1H-^1H$ COSY for compound **8a**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: suvarn@chem.iitb.ac.in.

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