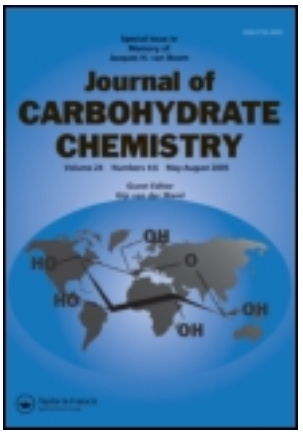

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5-AMINO-5-DEOXY-1-THIOGLUCOPYRANOSIDES – SYNTHESIS OF THIOGLYCOSIDE DERIVATIVES OF NOJIRIMYCIN

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ABSTRACT

N-Benzyloxycarbonyl-protected 5-amino-5-deoxyglucofuranose derivative **1** could be readily transformed into 6-*O*, *N*-carbonylidene nojirimycin **3** which afforded the corresponding piperidinosyl trichloroacetimidate **6**. This compound turned out to be a versatile piperidinosyl donor. Reaction with various mercaptans as acceptors in the presence of TMSOTf as catalyst gave 5-aza-1-thioglucopyranosides **7a-c**, **9**, and **13** which were successfully deprotected.

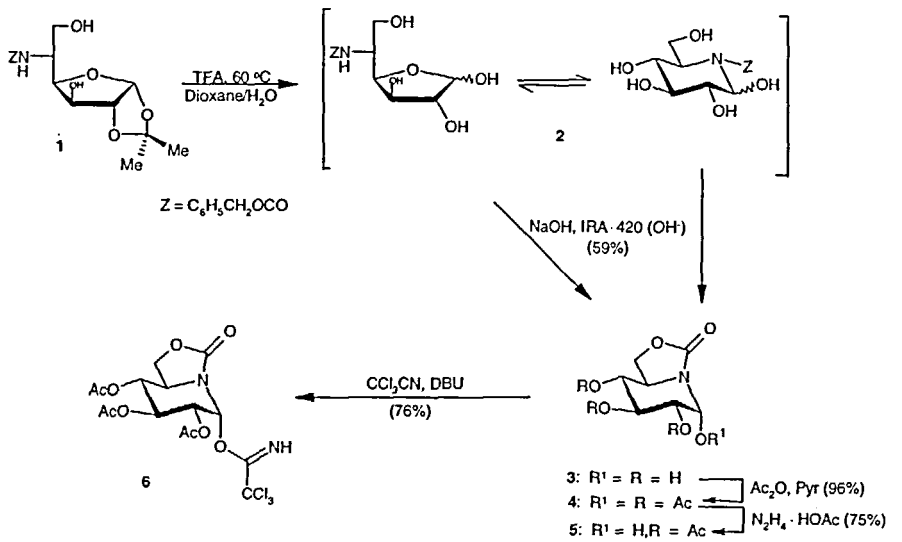
INTRODUCTION

The synthesis of thioglycosides has gained wide interest. Thioglycosides have been extensively used as glycosyl donors;[1,2] however, thioglycosides are also substrates for glycosidases, yet cleavage generally occurs at a much lower rate than the cleavage of the corresponding *O*-glycosides.[3] This may reflect not only the difference in stability of *O,S*

vs *O,O*-acetals but also the different conformer populations which are due to different bond lengths and bond angles.[4] Glycosidase cleavage, or better, inhibition of cleavage is a particularly interesting aspect of aza-sugars (5-amino-5-deoxy- or 4-amino-4-deoxysugars, which are piperidine and pyrrolidine derivatives, respectively); they are also found in nature as glycosidase inhibitors and nojirimycin (5-amino-5-deoxy-glucopyranose) is the most prominent example.[5-7] In this paper,[8] we describe the combination of the two structural moieties, i.e., the synthesis of novel nojirimycin-1-thioglycosides, which have a 6-*O,N*-carbonylidene group for stabilization of the glycosidic linkage. As leaving group of the required piperidinosyl donor the trichloroacetimidate group[2] was selected.

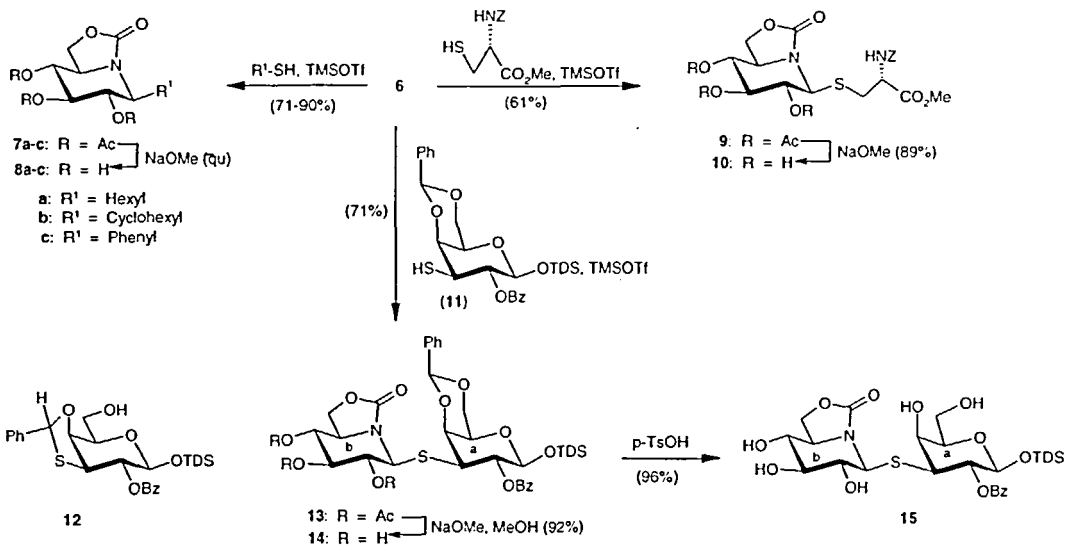
RESULTS AND DISCUSSION

The synthesis of a 5-azapyranosyl disaccharide with a thioglycosidic linkage (*N,S*-acetal with *N* in the ring and *S* in the bridge) has been already reported.[9] This compound was only stable at low pH; above pH 5 it hydrolyzed rapidly.[9,10] However, *N-tert*-butoxycarbonyl protected intermediates were stable.[9] Therefore, in order to obtain stable compounds electron-withdrawing groups at the nitrogen or at the ring are required. Hence, a cyclic urethane moiety including the ring nitrogen of nojirimycin and the 6-hydroxy group should provide interesting target molecules.



Scheme 1

To this end we synthesized known 5-benzyloxycarbonylamino-5-deoxyglucose derivative **1** (Scheme 1, Z = benzyloxycarbonyl) which is readily available from glucose.[11,12] Treatment with trifluoroacetic acid (TFA) in aqueous dioxane led to de-*O*-isopropylidenation, thus presumably resulting in anomeric mixtures of the furanose and the pyranose form (**2**). Neutralization with sodium hydroxide and then treatment with amberlite IR-420 in the OH-form led to the desired cyclic urethane **3** of nojirimycin in good yield; only the α-anomer was detected. Obviously, a strong anomeric effect is operative in this type of *N*-acylpiperidinose. This can be explained both, on opposing strong dipole moments or, alternatively, on strong n-σ* interaction in this system. Standard transformations, i.e., per-*O*-acetylation of **3** (→ **4**), selective 1-*O*-deacetylation with hydrazinium acetate[13] (→ **5**), and then treatment with trichloroacetonitrile in the presence of 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) afforded trichloroacetimidate **6**. Again, only the α-anomers were observed in compounds **4-6**.



Scheme 2

With piperidinosyl donor **6** in hand, glycosylation of mercaptans could be investigated. Reaction of **6** with hexylmercaptan, cyclohexylmercaptan, and phenylmercaptan in the presence of trimethylsilyl trifluoromethanesulfonate at room temperature afforded the desired thioglycosides **7a-c** in high yields (Scheme 2); due to neighboring group participation only the β-anomers were obtained, as could be derived

from their NMR data ($^3J_{1,2} \approx 7$ Hz). Treatment of **7a-c** with sodium methanolate in methanol (Zemplén conditions)[14] afforded *O*-unprotected compounds **8a-c**. Similarly, reaction of **6** with Z-unprotected cysteine methyl ester[15] in the presence of TMSOTf as catalyst afforded β-thioglycoside **9** ($^3J_{1,2}$ = 7.2 Hz) which on treatment with sodium methanolate in methanol gave de-*O*-acylated derivative **10**. Also thiodisaccharide formation went smoothly, as exhibited in the reaction of known thiol **11**[16] with **6** in the presence of TMSOTf as catalyst affording β-linked thiodisaccharide **13** in 71% yield ($^3J_{1b,2b} \approx 7.2$ Hz). Due to the use of excess **11**, some benzylidene group migration leading to **12** as minor byproduct was detected; this assignment is in accordance with the shift differences of the benzylidene hydrogen in **11-13** (**11,13**: $\delta \approx 5.6$; **12**: δ 6.10). Treatment of **13** with sodium methanolate in methanol led even to regioselective de-*O*-acylation providing compound **14**. This is presumably due to the lower reactivity of the benzoyl group compared with the acetyl group in combination with the steric shielding exerted by the 1,1,2-trimethylpropyldimethylsilyl (= thexyldimethylsilyl, TDS) group. Acid treatment of **14** with *p*-toluenesulfonic acid (*p*-TsOH) led to clean debenzylidenation affording azathiodisaccharide **15**, thus exhibiting that various protective group manipulations are compatible with this novel glycoside derivative.

EXPERIMENTAL

Reagents and solvents were obtained from commercial suppliers. Solvents were purified by distillation and were dried as usual, except for distilled dichloromethane and toluene which were passed through columns of commercially available neutral aluminium oxide (ICN Alumina N, activity grade super I) as an alternative drying procedure. All nonhydrolytic reactions were conducted in oven-dried glassware and under dry argon. Analytical TLC was performed on silica gel Merck Kieselgel 60 F_{254} plates (0.2 mm). The plates were visualized by immersion in mostain [200 mL 10 % sulfuric acid, 10 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, 200 mg $Ce(SO_4)_2$] followed by heating (165 °C). Flash chromatography was carried out on Mallinckrodt-Baker 7024-02 silica gel 40 μ. FAB mass spectra were recorded on a modified Finnigan MAT 312/AMD 5000. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Brukerm AC 250 Cryospec and a Bruker DRX 600

instrument. Proton chemical shifts are reported in ppm relative to the corresponding solvent peak, as are carbon chemical shifts. Assignments of protons and carbons were carried out by the help of 600 MHz spectra: COSY, HMQC, DEPT. Measurements of optical rotations were performed on a Perkin-Elmer polarimeter 241 MC (1 dm cell).

6-*O,N*-Carbonylidene-5-deoxy-1,5-imino-α-D-glucopyranose (3). To a solution of **1**[12] (1.0 g, 2.83 mmol) in dioxane (7 mL) was added water (16 mL) and trifluoroacetic acid (0.69 mL, 8.49 mmol). The solution was heated to 60 °C and stirred for 14 h to give **2** (light yellow solution). After cooling to rt the solution was neutralized with aqueous sodium hydroxide (1.0 M, 8.5 mL) and concentrated in vacuo. The remaining oily residue was slowly passed through a column of strong basic ion exchange resin (Amberlite IRA-420 [OH^-], 8.0 g, pressure: 40 kPa) using water as solvent. Subsequently, the resin was washed with both water and water/dioxane (1:1 v/v). TLC monitoring (3:1 CH_2Cl_2/MeOH) indicated fractions containing **3**. The combined fractions were neutralized with acetic acid and subsequently concentrated to dryness. The residue was purified by flash chromatography (3:1 CH_2Cl_2/MeOH) to yield **3** (424 mg, 2.07 mmol, 59 %) as a colorless solid; TLC (3:1 CH_2Cl_2/MeOH): R_f = 0.38 (characteristic yellow spot); $[\alpha]_D$ + 87 (*c* 1.0, MeOH); mp 145 °C. ^1H NMR (250 MHz, MeOH-d_4) δ 3.29 (m, 1 H, H-4), 3.37 (dd, $^3J_{1,2}$ = 4.0 Hz, $^3J_{2,3}$ = 9.5 Hz, 1 H, H-2), 3.65 (dd, $^3J_{2,3}$ = $^3J_{3,4}$ = 9.5 Hz, 1 H, H-3), 3.85 (m, 1 H, H-5), 4.21 (dd, $^2J_{6,6'}$ = 8.6 Hz, $^3J_{5,6'}$ = 6.5 Hz, 1 H, H-6'), 4.52 (dd, $^2J_{6,6'}$ = $^3J_{5,6}$ = 8.6 Hz, 1 H, H-6), 4.84 (br. s, OH), 5.29 (d, $^3J_{1,2}$ = 4.0 Hz, 1 H, H-1). ^{13}C NMR (62.9 MHz, MeOH-d_4) δ 54.7 (1 C, C-5), 68.4 (1 C, C-6), 73.5, 74.4, 75.7, 76.4 (4 C, 1-, 2-, 3-, C-4), 158.2 [1 C, OC(O)N].

Anal. Calcd for $C_7H_{11}NO_6$ (205.17): C, 40.98; H, 5.40; N, 6.83. Found C, 40.82; H, 5.47; N, 6.84; MS (FAB, positive mode, matrix: 1:1 methanol/3-nitrobenzyl alcohol): *m/z* 228 [MNa^+], 206 [MH^+], 188 [$(MH-H_2O)^+$].

1,2,3,4- Tetra- *O*- acetyl-6 -*O,N*- carbonylidene -5-deoxy-1,5-imino-α-D-gluco-pyranose (4). Compound **3** (260 mg, 1.27 mmol) was dissolved in anhyd pyridine (15 mL) and acetic anhydride (12 mL) under dry Ar. The solution was stirred at rt for 20 h. Subsequently, the solution was concentrated in vacuo and coevaporated with toluene. The remaining white solid crystallized in chloroform providing colorless needles of **4** (455 mg, 1.22 mmol, 96 %); TLC (2:1 toluene/ethyl acetate): R_f = 0.19; $[\alpha]_D$ = + 61 (*c* 1.0,

$CHCl_3$); mp 151 °C. ^1H NMR (250 MHz, $CDCl_3$) δ 1.98, 2.02, 2.05, 2.12 (4 s, 12 H, 4 OAc), 4.02 (ddd, $^3J_{4,5}$ = 9.7 Hz, $^3J_{5,6}$ = 8.2 Hz, $^3J_{5,6'}$ = 8.8 Hz, 1 H, H-5), 4.25 (dd, $^3J_{5,6'}$ = $^2J_{6,6'}$ = 8.8 Hz, 1 H, H-6'), 4.42 (dd, $^3J_{5,6}$ = 8.2 Hz, $^2J_{6,6'}$ = 8.8 Hz, 1 H, H-6), 4.95 (dd, $^3J_{3,4}$ = $^3J_{4,5}$ = 9.7 Hz, 1 H, H-4), 5.05 (dd, $^3J_{1,2}$ = 3.9 Hz, $^3J_{2,3}$ = 9.7 Hz, 1 H, H-2), 5.47 (dd, $^3J_{2,3}$ = $^3J_{3,4}$ = 9.7 Hz, 1 H, H-3), 6.68 (d, $^3J_{1,2}$ = 3.9 Hz, 1 H, H-1).

Anal. Calcd for $C_{15}H_{19}NO_{10}\cdot 0.5\ H_2O$ (382.33): C, 47.12; H, 5.27; N, 3.66. Found C, 47.21; H, 5.20; N, 3.66.

2,3,4-Tri-*O*-acetyl-6-*O,N*-carbonylidene-5-deoxy-1,5-imino-α-D- glucopyranose (5). Compound **4** (200 mg, 536 μmol) was dissolved in anhyd *N,N*-dimethylformamide (9.0 mL). Subsequently, dry hydrazinium acetate (64 mg, 696 μmol) was added to the solution and stirring was continued for 3 h at room temp. After complete anomeric de-*O*-acetylation (TLC monitoring: 1:1 toluene/ethyl acetate) the solution was diluted with ethyl acetate (40 mL) and extracted with half-satd. brine (4 times, 20 mL each). The organic layer was dried with $MgSO_4$ and concentrated to dryness under high vaccum to give a colorless foam. Flash chromatography (amount of silica gel: 50 fold excess of the crude product; 30:1 CH_2Cl_2/MeOH) yielded pure **5** (133 mg, 402 μmol, 75 %) as an amorphous white solid; TLC (10:1 CH_2Cl_2/MeOH): R_f = 0.72 (characteristic yellow spot); $[\alpha]_D$ + 49 (*c* 1.0, MeOH). ^1H NMR (250 MHz, MeOH-d_4) δ 2.07, 2.08, 2.11 (3 s, 9 H, 3 OAc), 4.17 (ddd, $^3J_{4,5}$ = 9.5 Hz, $^3J_{5,6}$ = 8.3 Hz, $^3J_{5,6'}$ = 7.5 Hz, 1 H, H-5), 4.32 (dd, $^3J_{5,6'}$ = 7.5 Hz, $^2J_{6,6'}$ = 8.8 Hz, 1 H, H-6'), 4.53 (dd, $^3J_{5,6}$ = 8.3 Hz, $^2J_{6,6'}$ = 8.8 Hz, 1 H, H-6), 4.90 (dd, $^3J_{1,2}$ = 3.7 Hz, $^3J_{2,3}$ = 9.5 Hz, 1 H, H-2), 5.10 (dd, $^3J_{3,4}$ = $^3J_{4,5}$ = 9.5 Hz, 1 H, H-4), 5.59 (dd, $^3J_{2,3}$ = $^3J_{3,4}$ = 9.5 Hz, 1 H, H-3), 5.61 (d, $^3J_{1,2}$ = 3.7 Hz, 1 H, H-1).

Anal. Calcd for $C_{13}H_{17}NO_9$ (331.28): C, 47.13; H, 5.17; N, 4.23. Found C, 47.88; H, 5.35; N, 4.24.

2,3,4-Tri-*O*- acetyl-6-*O,N*- carbonylidene-5- deoxy-1,5- imino-α-D-glucopyranosyl Trichloroacetimidate (6). Compound **5** (136 mg, 411 μmol) was suspended in anhyd CH_2Cl_2 (0.6 mL) and trichloroacetonitrile (616 μL, 6.16 mmol) under dry Ar. After adding DBU (30 μL, 0.2 μmol) **5** was completely dissolved. Simultaneously, the reaction solution became dark brown. Stirring was continued for 3 h at rt. After the reaction was complete (TLC 1:1 toluene/ethyl acetate) the solution was concentrated to dryness under high vacuum. The dark brown residue was purified by flash chromatography (amount of

silica gel: 60 fold excess of the crude product, 5:1 toluene/ethyl acetate + 1 vol. % Et_3N) to afford **6** (148 mg, 312 µmol, 76 %) as a colorless oil; TLC (2:1 toluene/ethyl acetate): R_f = 0.34 (characteristic yellow spot); $[\alpha]_D$ + 89 (*c* 1.0, CH_2Cl_2). ^1H NMR (250 MHz, $CDCl_3$) δ 1.97, 2.03, 2.06 (3 s, 9 H, 3 OAc), 4.10 (ddd, $^3J_{4,5}$ = 9.6 Hz, $^3J_{5,6}$ = 8.1 Hz, $^3J_{5,6'}$ = 7.7 Hz, 1 H, H-5), 4.27 (dd, $^3J_{5,6'}$ = 7.7 Hz, $^2J_{6,6'}$ = 9.1 Hz, 1 H, H-6'), 4.45 (dd, $^3J_{5,6}$ = 8.1 Hz, $^2J_{6,6'}$ = 9.1 Hz, 1 H, H-6), 5.00 (dd, $^3J_{3,4}$ = $^3J_{4,5}$ = 9.6 Hz, 1 H, H-4), 5.12 (dd, $^3J_{1,2}$ = 3.8 Hz, $^3J_{2,3}$ = 9.6 Hz, 1 H, H-2), 5.59 (dd, $^3J_{2,3}$ = $^3J_{3,4}$ = 9.6 Hz, 1 H, H-3), 6.94 (d, $^3J_{1,2}$ = 3.8 Hz, 1 H, H-1). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 20.3, 20.4, 20.5 [3 C, 3 OC(O)*C*H_3], 52.5 (1 C, C-5), 66.8, 69.0, 69.5, 72.2 (4 C, 2-, 3-, 4-, C-6), 83.0 (1 C, C-1), 90.5 [1 C, OC(=NH)*C*Cl_3], 154.1 [1 C, O*C*(=NH)CCl_3], 160.7 [1 C, OC(O)N], 169.4, 169.5, 170.0 [3 C, 3 O*C*(O)CH_3].

Anal. Calcd for $C_{15}H_{17}Cl_3N_2O_9$ (475.67): C, 37.88; H, 3.60; N, 5.89. Found: C, 38.08; H, 3.49; N, 5.82.

General Procedure for the Synthesis of Thioglycosides. Trichloroacetimidate **6** was dissolved in dry dichloromethane and the appropriate thiol was added under dry argon. Subsequently, a catalytic amount (0.015 eq) of trimethylsilyl trifluoromethanesulfonate (0.1 M TMSOTf solution made from 37 µL TMSOTf and 2 mL dichloromethane) was added to the reaction solution and stirring was continued for 1 h up to 4 h at rt (TLC monitoring). Thereafter, the reaction mixture was diluted with dichloromethane and subsequently extracted with both satd. sodium hydrogen carbonate solution and brine. The combined organic layers were dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was purified by flash chromatography (toluene/ethyl acetate) to afford the corresponding thioglycosides as colorless oils.

Hexyl 2,3,4-Tri-*O*-acetyl-6-*O*,*N*-carbonylidene-5-deoxy-1,5-imino-1-thio-β-D-glucopyranoside (7a). The procedure for the synthesis of thioglycoside **7a** is described above (see General Procedure). Compound **6** (180 mg, 378 µmol), dissolved in dichloromethane (3 mL), hexylmercaptan (107 µL, 756 µmol), 57 µL 0.1 M TMSOTf solution, stirring for 3 h at rt, flash chromatography (amount of silica gel: 60 fold excess of crude product, 5:1 toluene/ethyl acetate), yield: colorless oil (**7a**, 116 mg, 269 µmol, 71 %); TLC (3:1 toluene/ethyl acetate): R_f = 0.32, $[a]_D$ + 41 (*c* 1.0, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ 0.83 (t, ^3J = 6.5 Hz, 3 H, CH_3-6a), 1.23 – 1.40, 1.42 – 1.63 (m, 8 H, H-

2a, -2a', -3a, -3a', -4a, -4a', -5a, -5a'), 1.99, 2.03, 2.05 (3 s, 9 H, 3 OAc), 2.38 – 2.61 (m, 2 H, H-1a, -1a'), 4.11 (m, 1 H, H-5), 4.25 (dd, $^3J_{5,6'}$ = 6.5 Hz, 1 H, H-6'), 4.42 (dd, $^3J_{5,6}$ = $^2J_{6,6'}$ = 9.1 Hz, 1 H, H-6), 4.89 (m, 2 H, 2-, H-4), 5.38 (dd, $^3J_{2,3}$ = $^3J_{3,4}$ = 9.8 Hz, 1 H, H-3), 5.63 (d, $^3J_{1,2}$ = 7.6 Hz, 1 H, H-1).

Anal. Calcd for $C_{19}H_{29}NO_8S$ (431.51). MS (FAB, positive mode, matrix 1:1 dichloromethane/3-nitrobenzyl alcohol, sodium iodide): *m/z* 604 [(M+NaI)Na$^+$], 454 [MNa$^+$].

Cyclohexyl 2,3,4-Tri-*O*-acetyl-6-*O,N*-carbonylidene-5-deoxy-1,5-imino-1-thio-β-D-glucopyranoside (7b). The procedure for the synthesis of thioglycoside **7b** is described above (see General Procedure). Compound **6** (75 mg, 157 µmol), dissolved in dichloromethane (1 mL), cyclohexylmercaptan (39 µL, 315 µmol), 24 µL 0.1 M TMSOTf solution, stirring for 1 h at rt, flash chromatography (amount of silica gel: 60 fold excess of crude product, 5:1 toluene/ethyl acetate), yield: colorless oil (**7b**, 49 mg, 114 µmol, 73 %); TLC (3:1 toluene/ethyl acetate): R_f = 0.35, $[\alpha]_D$ + 32 (*c* 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.24 – 1.39, 1.53 – 1.86 (2 m, 10 H, H-2a, -2a', -3a, -3a', -4a, -4a'), 2.00, 2.03, 2.06 (3 s, 9 H, 3 OAc), 2.74 (m, 1 H, H-1a), 4.17 (m, 1 H, H-5), 4.24 (dd, $^2J_{6,6'}$ = 8.5 Hz, $^3J_{5,6'}$ = 6.5 Hz, 1 H, H-6'), 4.43 (dd, $^2J_{6,6'}$ = $^3J_{5,6}$ = 8.5 Hz, 1 H, H-6), 4.89 (m, 2 H, 2-, H-4), 5.36 (dd, $^3J_{2,3}$ = $^3J_{3,4}$ = 9.8 Hz, 1 H, H-3), 5.69 (d, $^3J_{1,2}$ = 7.6 Hz, 1 H, H-1).

Anal. Calcd for $C_{19}H_{27}NO_8S$ (429.49); MS (FAB, positive mode, matrix 1:1 dichloromethane/3-nitrobenzyl alcohol, sodium iodide): *m/z* 602 [(M+NaI)Na$^+$], 452 [MNa$^+$].

Phenyl 2,3,4-Tri-*O*-acetyl-6-*O,N*-carbonylidene-5-deoxy-1,5-imino-1-thio-β-D-glucopyranoside (7c). The procedure for the synthesis of thioglycoside **7c** is described above (see General Procedure). Compound **6** (89 mg, 187 µmol), dissolved in dichloromethane (1 mL), phenylmercaptan (38 µL, 372 µmol), 19 µL 0.1 M TMSOTf solution, stirring for 3 h at rt, flash chromatography (amount of silica gel: 30 fold excess of crude product, 5:1 toluene/ethyl acetate), yield: colorless, amorphous solid (**7c**, 71 mg, 168 µmol, 90 %); TLC (3:1 toluene/ethyl acetate): R_f = 0.23, $[a]_D$ + 48 (*c* 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.02 – 2.11 (m, 9 H, 3 OAc), 4.11 (m, 1 H, H-6'), 4.17 (dd, $^2J_{6,6'}$ = 11.7 Hz, $^3J_{5,6'}$ = 6.0 Hz, 1 H, H-6), 4.29 (m, 1 H, H-5), 4.91 (dd, $^3J_{3,4}$ = $^3J_{4,5}$ = 9.6 Hz, 1 H, H-4), 5.02 (dd, $^3J_{1,2}$ = 6.9 Hz, $^3J_{2,3}$ = 9.6 Hz, 1 H, H-2), 5.58 (dd, $^3J_{2,3}$ = $^3J_{3,4}$ =

9.6 Hz, 1 H, H-3), 5.91 (d, $^3J_{1,2}$ = 6.9 Hz, 1 H, H-1), 7.26 – 7.31, 7.43 – 7.49 (2 m, 5 H, Ph).

Anal. Calcd for $C_{19}H_{21}NO_8S$ (423.45); MS (EI, T = 185 °C); *m/z* 423 [M^+], 314 [$(M\text{-}SPh)^+$].

General Procedure for the De-*O*-acetylation. Thioglycosides were dissolved in anhyd methanol at rt. Subsequently, 0.173 M NaOMe solution in methanol was added (0.05 eq) and stirring was continued for 3 h. After the reaction was complete (TLC monitoring), freshly washed acidic ion exchange resin Amberlite IR-120 [H^+] was added and stirring was continued for additional 10 min (pH neutral). After diluting with methanol, the reaction mixture was filtered and concentrated to dryness. If necessary, the remaining residue was purified by flash chromatography (dichloro-methane/methanol) to afford the de-*O*-acetylated thioglycosides as colorless, amorphous solids.

Hexyl 6-*O,N*-Carbonylidene-5-deoxy-1,5-imino-1-thio-β-D-glucopyranoside (8a). The procedure for the de-*O*-acetylation of thioglycoside **8a** is described above (see General Procedure). Thioglycoside **7a** (90 mg, 209 µmol), dissolved in MeOH (2 mL), 0.173 M NaOMe (63 µL, 11 µmol), Amberlite IR-120 [H^+] (15 mg), yield: pure **8a** (64 mg, 209 µmol, quant.) could be obtained without flash chromatography; TLC (10:1 dichloromethane/methanol): R_f = 0.38, $[\alpha]_D$ + 29 (*c* 1.0, MeOH). ^{1}H NMR (250 MHz, MeOH-d_4): δ 0.94 (t, 3 H, CH_3-6a), 1.31 – 1.48, 1.56 – 1.71 (2 m, 8 H, H-2a, -2a', -3a, -3a', -4a, -4a', -5a, -5a'), 2.49 – 2.68 (m, 2 H, H-1a, -1a'), 3.38 (m, 1 H, H-4), 3.56 (dd, $^3J_{2,3} = {}^3J_{3,4}$ = 9.2 Hz, 1 H, H-3), 3.70 (dd, $^3J_{1,2}$ = 6.9 Hz, $^3J_{2,3}$ = 9.2 Hz, 1 H, H-2), 3.97 (m, 1 H, H-5), 4.32 (dd, $^2J_{6,6'}$ = 10.0 Hz, $^3J_{5,6'}$ = 5.6 Hz, 1 H, H-6'), 4.62 (dd, $^2J_{6,6'} = {}^3J_{5,6}$ = 10.0 Hz, 1 H, H-6), 4.91 (br. s, OH), 5.30 (d, $^3J_{1,2}$ = 6.9 Hz, 1 H, H-1).

Anal. Calcd for $C_{13}H_{23}NO_5S \cdot 0.5\ H_2O$ (314.41): C, 49.66; H, 7.37; N, 4.45. Found: C, 49.95; H, 7.48; N, 4.34; MS (FAB, positive mode, matrix 1:1 methanol/3-nitrobenzyl alcohol, sodium iodide): *m/z* 328 [MNa^+], 306 [MH^+].

Cyclohexyl 6-*O,N*-Carbonylidene-5-deoxy-1,5-imino-1-thio-β-D-gluco-pyranoside (8b). The procedure for the de-*O*-acetylation of thioglycoside **8b** is described above (see General Procedure). Thioglycoside **7b** (46 mg, 107 µmol), dissolved in MeOH (1 mL), 0.173 M NaOMe (31 µL, 5 µmol), Amberlite IR-120 [H^+] (10 mg), flash chromatography (15:1 dichloromethane/ methanol), yield: **8b** (30 mg, 98 µmol, 91 %);

TLC (10:1 dichloromethane/methanol): R_f = 0.41, $[a]_D$ + 32 (*c* 1.0, MeOH). ^{1}H NMR (250 MHz, MeOH-d_4) δ 1.29 – 1.46, 1.56 – 1.93, 2.11 – 2.18 (3 m, 10 H, H-2a, -3a, -4a), 2.74 (m, 1 H, H-1a), 3.31 (m, 1 H, H-4), 3.50 (dd, $^3J_{2,3} = {}^3J_{3,4}$ = 9.1 Hz, 1 H, H-3), 3.62 (dd, $^3J_{1,2}$ = 6.9 Hz, $^3J_{2,3}$ = 9.1 Hz, 1 H, H-2), 3.92 (m, 1 H, H-5), 4.27 (dd, $^2J_{6,6'}$ = 8.7 Hz, $^3J_{5,6'}$ = 6.5 Hz, 1 H, H-6'), 4.55 (dd, $^2J_{6,6'} = {}^3J_{5,6}$ = 8.7 Hz, 1 H, H-6), 4.88 (br. s, OH), 5.31 (d, $^3J_{1,2}$ = 6.9 Hz, 1 H, H-1).

Anal. Calcd for $C_{13}H_{21}NO_5S \cdot 0.5\ H_2O$ (312.38): C, 49.98; H, 7.09; N, 4.48. Found: C, 49.95; H, 6.78; N, 4.47; MS (FAB, positive mode, matrix 1:1 methanol / 3-nitrobenzyl alcohol, sodium iodide): *m/z* 326 [MNa^+], 188 [$(M-H_2O)H^+$].

Phenyl 6-*O,N*-Carbonylidene-5-deoxy-1,5-imino-1-thio-β-D-glucopyranoside (8c). The procedure for the de-*O*-acetylation of thioglycoside **8c** is described above (see General Procedure). Thioglycoside **7c** (40 mg, 95 μmol), dissolved in MeOH (1 mL), 0.173 M NaOMe (16 μL, 3 μmol), Amberlite IR-120 [H^+] (8 mg), flash chromatography (20:1 dichloromethane/methanol), yield: **8c** (26 mg, 94 μmol, quant.); TLC (10:1 dichloromethane/methanol): R_f = 0.17, $[a]_D$ + 35 (*c* 1.0, MeOH). ^{1}H NMR (250 MHz, MeOH-d_4) δ 3.39 (m, 1 H, H-4), 3.71 (dd, $^3J_{2,3} = {}^3J_{3,4}$ = 9.6 Hz, 1 H, H-3), 3.79 (dd, $^3J_{1,2}$ = 6.8 Hz, $^3J_{2,3}$ = 9.6 Hz, 1 H, H-2), 4.03 (m, 1 H, H-5), 4.27 (dd, $^2J_{6,6'}$ = 9.0 Hz, $^3J_{5,6'}$ = 5.4 Hz, 1 H, H-6'), 4.43 (dd, $^2J_{6,6'} = {}^3J_{5,6'}$ = 9.0 Hz, 1 H, H-6), 4.93 (br. s, OH), 5.59 (d, $^3J_{1,2}$ = 6.8 Hz, 1 H, H-1), 7.33 – 7.38, 7.53 – 7.57 (2 m, $^3J_{1,2}$ = 6.8 Hz, 5 H, Ph).

Anal. Calcd for $C_{13}H_{15}NO_5S \cdot 0.4\ H_2O$ (304.54): C, 51.27; H, 5.23; N, 4.60. Found: C, 51.23; H, 5.24; N, 4.64.

***N*-Phenylmethyloxycarbonyl-*S*- (2,3,4- tri-*O*- acetyl- 6-*O,N*- carbonylidene-5-deoxy-1,5-imino-β-D-glucopyranosyl)-L-cysteine Methyl Ester (9).** The procedure for the synthesis of thioglycoside **9** is described above (see General Procedure). Compound **6** (80 mg, 168 μmol), dissolved in dichloromethane (1 mL), *N*-phenyl-methyloxycarbonyl-L-cysteine methyl ester[15] (91 mg, 336 μmol), 25 μL 0.1 M TMSOTf solution, stirring for 4 h at rt, flash chromatography (3:1 toluene/ethyl acetate), yield: colorless oil (**9**, 60 mg, 103 μmol, 61 %); TLC (2:1 toluene/ethyl acetate): R_f = 0.20, $[\alpha]_D$ + 64 (*c* 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.00, 2.03, 2.05 (3 s, 9 H, 3 OAc), 3.04 (m, 2 H, b, H-b'), 3.75 (s, 3 H, CO_2Me), 4.12 (m, 1 H, H-5), 4.22 (dd, $^2J_{6,6'}$ = 9.1 Hz, $^3J_{5,6'}$ = 6.3 Hz, 1 H, H-6'), 4.42 (dd, $^2J_{6,6'} = {}^3J_{5,6}$ = 9.1 Hz, 1 H, H-6), 4.58 (br. m, 1 H, a-H), 4.89 (dd, $^3J_{3,4} = {}^3J_{4,5}$ =

9.4 Hz, 1 H, H-4), 4.90 (dd, $^3J_{1,2}$ = 7.2 Hz, $^3J_{2,3}$ = 9.4 Hz, 1 H, H-2), 5.12 (br. s, 2 H, CH_2 [Cbz]), 5.32 (dd, $^3J_{2,3}$ = $^3J_{3,4}$ = 9.4 Hz, 1 H, H-3), 5.67 (br. m, 2 H, NH, H-1), 7.28 – 7.35 (m, 5 H, Ph). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 20.5 (3 C, OC(O)CH_3), 32.9, 51.2, 52.8, 54.2, 58.9, 66.3, 67.2, 69.4, 69.9, 72.3 (10 C, C-1, -2, -3, -4, -5, -6, -a, -b, CH_2 [Cbz], CO_2CH_3), 128.0 – 128.2, 136.1 (6 C, Ph), 155.6, 155.8 [2 C, 2 OC(O)N], 169.5, 169.9, 170.5 [3 C, OC(O)CH_3], 173.1 [1 C, C(O)CH_3].

Anal. Calcd for $C_{25}H_{30}N_2O_{12}S$ (582.58); MS (FAB, positive mode, matrix 1:1 methanol / 3-nitrobenzyl alcohol): *m/z* 715 [MCs$^+$], 605 [MNa$^+$], 583 [MH$^+$], 539 [(M-CO_2)H$^+$], 314 [{M-$SCH_2CH(NHCbz)CO_2Me$}H$^+$], 254 [(314-AcOH)H$^+$].

***N*-Phenylmethyloxycarbonyl-*S*-(6-*O*,*N*-carbonylidene-5-deoxy-1,5-imino-β-D-glucopyranosyl)-L-cysteine Methyl Ester (10).** The procedure for the de-*O*-acetylation of thioglycoside **9** is described above (see General Procedure). Thioglycoside **9** (78 mg, 134 μmol), dissolved in MeOH (1.5 mL), 0.173 M NaOMe (23 μL, 4 μmol), Amberlite IR-120 [H$^+$] (10 mg), yield: pure **10** (54 mg, 119 μmol, 89 %) could be obtained without flash chromatography after freeze-drying (H_2O); TLC (10:1 dichloromethane/methanol): R_f = 0.34, $[\alpha]_D$ + 52 (*c* 1.0, MeOH). ^{1}H NMR (600 MHz, MeOH-d_4) δ 2.88 (dd, $^2J_{b,b'}$ = 12.0 Hz, $^3J_{a,b'}$ = 8.8 Hz, 1 H, H-b'), 2.94 (dd, $^2J_{b,b'}$ = 12.0 Hz, $^3J_{a,b}$ = 4.9 Hz, 1 H, H-b), 3.22 (dd, $^3J_{3,4}$ = $^3J_{4,5}$ = 9.3 Hz, 1 H, H-4), 3.40 (dd, $^3J_{2,3}$ = $^3J_{3,4}$ = 9.3 Hz, 1 H, H-3), 3.56 (dd, $^3J_{1,2}$ = 6.9 Hz, $^3J_{2,3}$ = 9.3 Hz, 1 H, H-2), 3.66 (br.s, 3 H, CO_2Me), 3.81 (m, 1 H, H-5), 4.17 (dd, $^2J_{6,6'}$ = 8.7 Hz, $^3J_{5,6'}$ = 5.4 Hz, 1 H, H-6), 4.35 (dd, $^3J_{a,b}$ = 4.9 Hz, $^3J_{a,b'}$ = 8.8 Hz, 1 H, H-a), 4.43 (dd, $^2J_{6,6'}$ = $^3J_{5,6}$ = 8.7 Hz, 1 H, H-6), 4.78 (br. s, OH), 5.04 (br. s, 2 H, CH_2 [Cbz]), 5.24 (d, $^3J_{1,2}$ = 6.9 Hz, 1 H, H-1), 7.21 – 7.30 (m, 5 H, Ph). ^{13}C NMR (150.8 MHz, MeOH-d_4): δ 33.7 (1 C, β-C), 53.0 (1 C, CO_2CH_3), 54.6 (1 C, C-5), 55.9 (1 C, C-a), 64.2 (1 C, C-1), 67.8 (1 C, CH_2 [Cbz]), 68.2 (1 C, C-6), 72.5 (1 C, C-2), 75.1 (1 C, C-3), 75.4 (1 C, C-4), 128.8 – 129.5, 138.1 (6 C, Ph), 158.5 [2 C, 2 OC(O)N], 172.7 (1 C, CO_2Me).

Anal. Calcd for $C_{19}H_{24}N_2O_9S \cdot 0.5\ H_2O$ (465.47): C, 49.03; H, 5.41; N, 6.02. Found: C, 49.15; H, 5.35; N, 5.95; MS (FAB, positive mode, matrix 1:1 dichloromethane/3-nitrobenzyl alcohol, sodium iodide): *m/z* 479 [MNa$^+$], 329 [(M- C_7H_7-CO_2-Me)Na$^+$].

Thexyldimethylsilyl 2-*O*-Benzoyl-3,4-(*S*,*O*)-benzylidene-3-thio-β-D-galacto-pyranoside (12). Minor byproduct of the synthesis of thiodisaccharide **13** (see below).

After chromatographic separation from **13** (6:1 toluene/ethyl acetate) and freeze-drying (dioxane), **12** could be obtained as a colorless, amorphous solid (14 mg, 27 µmol, 11 %); TLC (2:1 toluene/ethyl acetate): $R_f = 0.33$, $[\alpha]_D + 32$ (*c* 1.0, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$) δ 0.05, 0.15 (2 s, 6 H, 2 $SiCH_3$), 0.7 (br.s, 12 H, 4 CH_3), 1.41 – 1.52 (m, 1 H, CH), 2.02 (br.s, 1 H, OH-6), 3.77 (dd, $^3J_{2,3} = 9.6$ Hz, $^3J_{3,4} = 4.2$ Hz, 1 H, H-3), 3.81 (br.m, 1 H, H-6'), 3.94 – 4.04 (m, 2 H, 5-, H-6), 4.14 (dd, $^3J_{3,4} = 4.2$ Hz, $^3J_{4,5} < 1$ Hz, 1 H, H-4), 4.86 (d, $^3J_{1,2} = 8.3$ Hz, 1 H, H-1), 5.40 (dd, $^3J_{1,2} = 8.3$ Hz, $^3J_{2,3} = 10.0$ Hz, 1 H, H-2), 6.10 (s, 1 H, C*H*Ph), 7.33 – 7.46, 7.52 – 7.61, 7.98 – 8.02 [3 m, 10 H, C(O)Ph, CH*Ph*].

Anal. Calcd for $C_{28}H_{38}O_6SSi$ (530.75); MS (FAB, positive mode, matrix 1:1 chloroform/3-nitrobenzyl alcohol, sodium iodide): *m/z* 569 [MK^+], 553 [MNa^+].

Thexyldimethylsilyl 3-*S*-(2,3,4-Tri-*O*-acetyl-6-*O*,*N*-carbonylidene-5-deoxy-1,5-imino- β-D- glucopyranosyl) -2-*O*-benzoyl-4,6-*O*-benzylidene-3-thio-β-D-galacto-pyranoside (13). The procedure for the synthesis of thioglycoside **13** is described above (see General Procedure). Compound **6** (70 mg, 147 µmol), dissolved in dichloromethane (1.3 mL), thiol **11**[16] (126 mg, 237 µmol), 16 µL 0.1 M TMSOTf solution (0.01 eq), stirring for 1 h at rt, flash chromatography (6:1 toluene/ethyl acetate) and freeze-drying (dioxane) afforded **13** as a colorless, amorphous solid (88 mg, 104 µmol, 71 %); TLC (2:1 toluene/ethyl acetate): $R_f = 0.46$, $[\alpha]_D + 16$ (*c* 1.0, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$) δ 0.04, 0.13 (2 s, 6 H, 2 $SiCH_3$), 0.65, 0.66, 0.67, 0.68 (4 s, 12 H, 4 CH_3), 1.43 (m, 1 H, CH), 1.80, 1.91, 1.95 (3 s, 9 H, 3 OAc), 3.46 (dd, $^3J_{2a,3a} = 9.7$ Hz, $^3J_{3a,4a} = 3.1$ Hz, 1 H, H-3a), 3.51 – 3.54 (m, 1 H, 5a-H), 3.59 – 3.70 (m, 2 H, H-5b, -6b'), 3.98 (m, 1 H, H-6b), 4.08 (dd, $^2J_{6a,6a'} = 11.0$ Hz, $^3J_{5,6a'} = 1.4$ Hz, 1 H, H-6a'), 4.16 (dd, $^3J_{3a,4a} = 3.1$ Hz, $^3J_{4a,5a} < 1$ Hz, 1 H, H-4a), 4.25 (dd, $^2J_{6a,6a'} = 11.0$ Hz, $^3J_{5a,6a} < 1$ Hz, 1 H, H-6a), 4.67 (m, 2 H, 2b-, H-4b), 4.81 (d, $^3J_{1a,2a} = 8.3$ Hz, 1 H, H-1a), 5.12 (dd, $^3J_{2b,3b} = {}^3J_{3b,4b} = 9.8$ Hz, 1 H, H-3b), 5.19 (dd, $^3J_{1a,2a} = 8.3$ Hz, $^3J_{2a,3a} = 9.7$ Hz, 1 H, H-2a), 5.53 (s, 1 H, CHPh), 5.89 (d, $^3J_{1b,2b} = 7.6$ Hz, 1 H, H-1b), 7.32 – 7.60, 8.03 – 8.07 [2 m, 10 H, Ph, C(O)Ph]. ^{13}C NMR (62.9 MHz, $CDCl_3$) δ (-) 3.1, (-) 1.7 (2 C, 2 $SiCH_3$), 18.4 [3 C, $OC(O)CH_3$], 19.8 – 20.5 [4 C, $SiC(CH_3)_2CH(CH_3)_2$], 24.7 [1 C, $SiC(CH_3)_2CH(CH_3)_2$], 33.8 [1 C, $SiC(CH_3)_2CH(CH_3)_2$], 51.0 (1 C, C-3a), 49.1, 57.6, 66.4, 68.5, 69.2, 69.4, 70.5, 71.4, 72.5, 74.2 (10 C, C-2a, -4a, -5a, -6a, -1b, -2b, -3b, -4b, -5b, -6b), 97.4 (1 C, C-1a), 101.4 (1 C, *C*HPh), 126.3 – 137.8 [12 C, C(O)*Ph*, CH*Ph*], 156.0 [1 C, OC(O)N], 165.0 [1 C, *C*(O)Ph], 169.1, 169.9, 170.0 [3 C, 3 O*C*(O)CH_3].

Anal. Calcd for $C_{41}H_{54}NO_{14}SSi \cdot H_2O$ (863.04): C, 57.06; H, 6.53; N, 1.62. Found: C, 56.89; H, 6.22; N, 1.46.

Thexyldimethylsilyl 2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*S*-(6-*O*,*N*-carbonylidene-5-deoxy-1,5-imino-β-D-glucopyranosyl)-3-thio-β-D-galactopyranoside (14). The procedure for the de-*O*-acetylation of thioglycoside **13** is described above (see General Procedure). Thioglycoside **13** (61 mg, 72 μmol), dissolved in MeOH (0.75 mL), 0.173 M NaOMe (13 μL, 2 μmol), TLC monitoring (3:1 toluene/ethyl acetate), careful neutralization with Amberlite IR-120 [H^+] (6 mg), flash chromatography (20:1 dichloromethane/methanol) afforded **14** (48 mg, 66 μmol, 92 %) as colorless solid; TLC (10:1 dichloromethane/ methanol): R_f = 0.37, $[\alpha]_D$ + 11 (*c* 1.0, MeOH). ^{1}H NMR (600 MHz, MeOH-d_4) δ 0.03, 0.12 (2 s, 6 H, 2 SiMe), 0.62, 0.63, 0.64, 0.65 (4 s, 12 H, 4 CH_3), 1.42 (m, 1 H, CH), 3.07 (dd, $^3J_{3b,4b} = {}^3J_{4b,5b}$ = 9.1 Hz, 1 H, H-4b), 3.22 (dd, $^3J_{2b,3b} = {}^3J_{3b,4b}$ = 9.1 Hz, 1 H, H-3b), 3.39 (m, 1 H, H-5b), 3.44 (m, 1 H, H-3a), 3.51 (dd, $^3J_{1b,2b}$ = 6.9 Hz, $^3J_{2b,3b}$ = 9.1 Hz, 1 H, H-2b), 3.55 (dd, $^2J_{6b,6b'} = {}^3J_{5b,6b'}$ = 8.6 Hz, 1 H, H-6b'), 3.64 (m, 1 H, H-5a), 3.87 (dd, $^2J_{6b,6b'}$ = 8.6 Hz, $^3J_{5b,6b}$ = 6.3 Hz, 1 H, H-6b), 4.12 (m, 2 H, H-6a, -6a'), 4.35 (dd, $^3J_{3a,4a}$ = 2.9 Hz, $^3J_{4a,5a}$ < 1 Hz, 1 H, H-4a), 4.78 (br. s, OH), 4.89 (d, $^3J_{1a,2a}$ = 7.9 Hz, 1 H, H-1a), 5.14 (dd, $^3J_{1a,2a}$ = 7.9 Hz, $^3J_{2a,3a}$ = 9.8 Hz, 1 H, H-2a), 5.28 (d, $^3J_{1b,2b}$ = 6.9 Hz, 1 H, H-1b), 5.61 (s, 1 H, C*H*Ph), 7.29 – 7.31, 7.43 – 7.59, 7.98 – 8.00 (3 m, 10 H, C(O)Ph, Ph). ^{13}C NMR (150.8 MHz, MeOH-d_4): δ (-) 2.8, (-) 1.5 (2 C, 2 $SiCH_3$), 18.8, 18.9, 20.4, 20.5 (4 C, 4 CH_3 [TDS]), 25.7 [1 C, $SiC(CH_3)_2CH(CH_3)_2$], 35.1 [1 C, $SiC(CH_3)_2CH(CH_3)_2$], 50.6 (1 C, C-3a), 54.6 (1 C, C-5b), 64.0 (1 C, C-1b), 68.2 (1 C, C-6b), 70.1 (1 C, C-5a), 70.2 (1 C, C-6a), 72.3 (1 C, C-3b), 73.4 (1 C, C-1a), 74.8 (1 C, C-3b), 75.5 (1 C, C-4b), 76.8 (1 C, C-4a), 98.6 (1 C, C-1a), 102.6 (1 C, *C*HPh), 127.5 – 139.6 (10 C, C(O)PH, CH*Ph*), 158.5 [1 C, OC(O)N], 167.0 (1 C, O*C*(O)Ph).

Anal. Calcd for $C_{35}H_{47}NO_{11}SSi \cdot 0.66\ H_2O$ (729.79): C, 57.60; H, 6.67; N, 1.92. Found C, 57.51; H, 6.79; N, 1.84; MS (FAB, positive mode, matrix: 1:1 chloroform/3-nitrobenzyl alcohol, sodium iodide): *m/z* 890 [(M+NaI)Na^+], 756 [MK^+], 740 [MNa^+].

Thexyldimethylsilyl 2-*O*-Benzoyl-3-*S*-(6-*O*,*N*-carbonylidene-5-deoxy-1,5-imino-β-D-glucopyranosyl)-3-thio-β-D-galactopyranoside (15). Compound **14** (56 mg, 78 μmol) was dissolved in dichloromethane (2 mL). Subsequently, ethanthiol (35 μL, 234 μmol) and *p*-toluenesulfonic acid monohydrate (*p*-TsOH· H_2O, 2 mg) were added. Stirring

was continued for 2 h at rt. After complete deprotection (TLC monitoring: 10:1 dichloromethane/methanol) Et_3N (0.1 mL) was added and the solution was concentrated to dryness. The remaining residue was purified by flash chromatography (10:1 dichloromethane/methanol) to afford after freeze-drying (H_2O) **15** (47 mg, 75 µmol, 96 %) as a white powder; TLC (4:1 dichloromethane/methanol): R_f = 0.38, $[\alpha]_D$ + 9 (*c* 1.0, MeOH). ^{1}H NMR (600 MHz, MeOH-d_4) δ 0.0, 0.08 (2 s, 6 H, 2 $SiCH_3$), 0.61, 0.62, 0.63, 0.64 (4 s, 12 H, 4 CH_3), 1.40 (m, 1 H, CH), 3.09 (dd, $^3J_{3b,4b} = {}^3J_{4b,5b}$ = 9.8 Hz, 1 H, H-4b), 3.19 (dd, $^3J_{2b,3b} = {}^3J_{3b,4b}$ = 9.8 Hz, 1 H, H-3b), 3.28 (m, 1 H, H-3a), 3.39 (m, 1 H, H-5b), 3.53 (dd, $^3J_{1b,2b}$ = 6.9 Hz, $^3J_{2b,3b}$ = 9.8 Hz, 1 H, H-2b), 3.59 (m, 1 H, H-5a), 3.67 (dd, $^2J_{6a,6a'}$ = 11.1 Hz, $^3J_{5a,6a'}$ = 6.2 Hz, 1 H, 6a'-H), 3.72 (m, 2 H, 6a-, 6b'-H), 3.92 (dd, $^2J_{6b,6b'}$ = 8.6 Hz, $^3J_{5b,6b'}$ = 7.2 Hz, 1 H, H-6b), 4.04 (dd, $^3J_{3a,4a}$ = 2.1 Hz, $^3J_{4a,5a}$ < 1 Hz, 1 H, H-4a), 4.78 (br. s, OH), 4.79 (m, 1 H, H-1a), 5.06 (dd, $^3J_{1a,2a}$ = 7.8 Hz, $^3J_{2a,3a}$ = 9.8 Hz, 1 H, H-2a), 5.21 (d, $^3J_{1b,2b}$ = 6.9 Hz, 1 H, H-1b), 7.43 – 7.46, 7.56 – 7.58, 7.96 – 7.98 [3 m, 5 H, OC(O)Ph].

Anal. Calcd for $C_{28}H_{43}NO_{11}SSi \cdot H_2O$ (647.81): C, 51.91; H, 7.00; N, 2.16. Found C, 51.82; H, 6.97; N, 2.31; MS (FAB, positive mode, matrix: 1:1 methanol/3-nitrobenzyl alcohol, sodium iodide): *m/z* 802 [(M+NaI)Na$^+$], 652 [MNa$^+$].

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