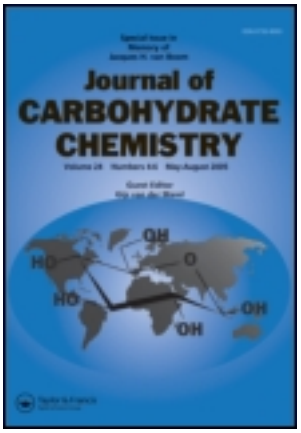

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A Facile and Efficient Method for the One-Pot Synthesis of Per-O-acetylated Thioglycosides from Unprotected Sugars

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A Facile and Efficient Method for the One-Pot Synthesis of Per-*O*-acetylated Thioglycosides from Unprotected Sugars

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An efficient, convenient protocol for the preparation of per-*O*-acetylated *p*-tolylthio glycosides is described. Treatment of various unprotected sugars, including 2-deoxy-2-amino sugars, sialic acid, lactose, and maltose, with acetic anhydride using $SnCl_4$ as a catalyst, and subsequently with *p*-tolylthiol, furnished the corresponding thioglycosides in 71%–90% yield under solvent-free conditions.

Keywords Acetylation; Thioglycosides; One-pot synthesis; Unprotected sugars; $SnCl_4$

INTRODUCTION

The rapid development of glycobiology reveals that oligosaccharides play important roles in a wide array of biological processes such as cell–cell interaction, cell–cell adhesion, bacterial attachment, viral infection, and substrate–receptor recognition.[1] Therefore, highly efficient and practical methodologies for the synthesis of oligosaccharides employing thioglycosides as glycosyl donors have attracted considerable interest, because thioglycosides enable new synthetic strategies such as armed–disarmed glycosylation,[2] orthogonal glycosylation,[3] sequential iterative glycosylation,[4] reactivity-based

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one-pot glycosylation,[5] and automated solid-phase oligosaccharide synthesis.[6]

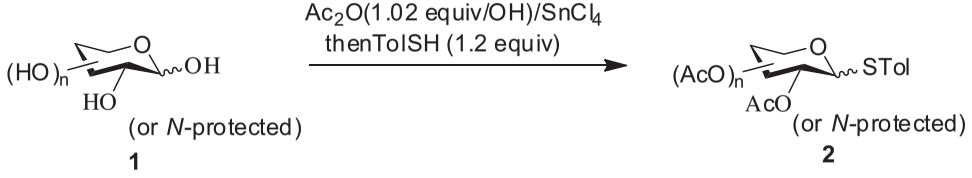
In practice, per-*O*-acetylated thioglycosides are valuable building blocks for the synthesis of carbohydrate derivatives[7] due to their unique characteristics. Not only could they be activated as glycosyl donors under particular conditions to take part in glycosylation, but also they have the capability to survive various reaction conditions to make complex building blocks or transform to other glycosyl donors. Conventionally, the preparation of per-*O*-acetylated thioglycosides is achieved by a two-step sequence involving acetylation of free sugar with an excess of acetic anhydride in pyridine, followed by the displacement of the anomeric acetate group by a thiol in the presence of a Lewis acid. Recently, two-step one-pot and three-step one-pot strategies for the preparation of per-*O*-acetylated thioglycosides from unprotected reducing sugars have been developed with catalyst systems including $Cu(OTf)_2/BF_3{\cdot}OEt_2$,[9] $La(OTf)_3/BF_3{\cdot}OEt_2$,[10] $LiClO_4$/ $BF_3{\cdot}OEt_2$,[11] TsOH/ $BF_3{\cdot}OEt_2$,[12] simple $BF_3{\cdot}OEt_2$,[13] I_2/I_2-Al,[14] I_2/I_2-HMDS,[15] and HBr-AcOH/TBAHS-$NaHCO_3$.[16] However, most of the existing methods have pitfalls such as being time-consuming,[9,11,12] requiring solvent removal before thioglycosidation,[10,12] and having a limited substrate scope.[9,14]

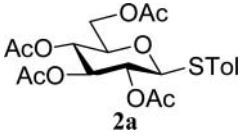
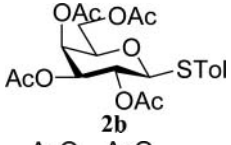
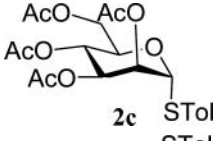
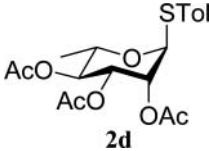
Tin tetrachloride ($SnCl_4$) has been extensively used as a Lewis acid in organic synthesis.[17] Recently, $SnCl_4$ supported on silica gel has been documented as a catalyst for the conversion of aldehydes into their corresponding acylals with an excess of acetic anhydride.[18] Meanwhile, it is well known that $SnCl_4$ is able to promote glycosidation of peracetylated sugars with thiol and alcohols.[19] Inspired by these results, we envisioned that the use of a stoichiometric quantity of acetic anhydride in the presence of $SnCl_4$ followed by the addition of a thiol would result in a one-pot strategy for the preparation of per-*O*-acetylated thioglycosides. Herein, we describe our findings along this line.

RESULTS AND DISCUSSION

To the best of our knowledge, $SnCl_4$-promoted acetylation of free sugars with stoichiometric acetic anhydride followed by subsequent glycosylation with thiol in a one-pot manner has not been explored. Thus, we commenced with D-glucose for the standardization of reaction conditions. After screening various conditions, the optimized procedure was found to be treatment of D-glucose **1a** (1.0 mmol) with acetic anhydride (5.1 mmol) at rt followed by slow addition of $SnCl_4$ (2.0 mmol) to result in an immediate exothermic reaction and a clean solution within a few minutes. After per-*O*-acetylated D-glucose was formed with the complete consumption of glucose as indicated by TLC, *p*-thiocresol (1.2 equiv.) was added to the reaction mixture, with the resulting solution being stirred for an extensive 12 h. After usual workup, the reaction gave rise to the desired thioglycoside **2a** in 74% yield (entry 1, Table 1).

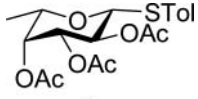
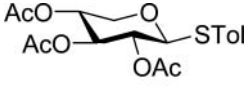
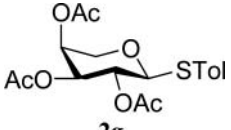
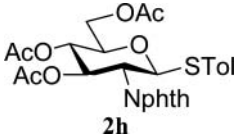
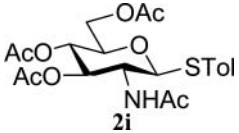
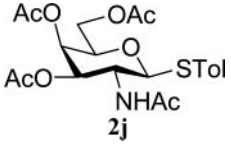
Table 1: One-pot synthesis of per-*O*-acetylated thioglycosides

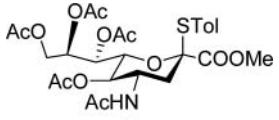
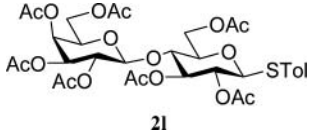
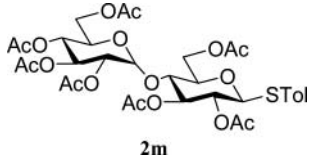


Entry	Substrate	Product	Time 1[a] (min)	Time 2[b] (h)	Yield[f] (%)	Ref.
1	D-Glucose **1a**	 **2a**	10	12.0[c]	74	12
2	D-Galactose **1b**	 **2b**	10	12.0[c]	75	12
3	D-Mannose **1c**	 **2c**	10	12.0[c]	71	12
4	L-Rhamnose. H_2O **1d**	 **2d**	3	1.0[d]	90[g]	12

(Continued on next page)

Table 1: One-pot synthesis of per-*O*-acetylated thioglycosides *(Continued)*

Entry	Substrate	Product	Time 1[a] (min)	Time 2[b] (h)	Yield[f] (%)	Ref.
5	L-Fucose **1e**	 **2e**	3	1.0[d]	87	12
6	D-Xylose **1f**	 **2f**	5	1.0[d]	81	—
7	L-Arabinose **1g**	 **2g**	5	1.0[d]	78	14
8	2-Phthalimdo-2-deoxy-D-glucopyranose **1h**	 **2h**	10	6.0[c]	83	20
9	2-Acetamido-2-deoxy-D-glucopyranose **1i**	 **2i**	5	8.0[c,e]	84	12
10	2-Acetamido-2-deoxy-D-galacopyranose **1j**	 **2j**	5	8.0[c,e]	89	21

11	*N*-Acetyl neuraminic acid methyl ester **1k**	 **2k**	30	6.0[c]	85	12
12	D-Lactose **1l**	 **2l**	30	10.0[c]	86	12
13	D-Maltose.H_2O **1m**	 **2m**	30	10.0[c]	88	11

[a] Before thiol addition.
[b] After thiol addition.
[c] 2 equiv. of $SnCl_4$ was used for thioglycosidation.
[d] 1 equiv. of $SnCl_4$ was used for thioglycosidation.
[e] Heated at 50°C.
[f] Isolated yields.
[g] $\alpha/\beta = 5/1$.

When D-galactose **1b** and D-mannose **1c** were exposed to the reaction conditions, the corresponding thioglycosides **2b** and **2c** were obtained in 75% and 71% yields, respectively (entries 2 and 3, Table 1). For 6-deoxy sugars including L-rhamnose **1d** and L-fucose **1e,** as well as pentoses like L-arabinose **1g** and D-xylose **1f**, it should be noted that 1.0 equivalent of $SnCl_4$ enabled the preparation of thioglycosides **2d**–**2g** in a shorter time (1.0 h) in good to excellent yield of 78%–90% (Entry 4–7, Table 1), which might be ascribed to the higher reactivity of deoxysugars and pentoses compared with the common sugars. Moreover, we further extended the substrates to amino sugars, frequently occurring in natural oligosaccharides,[22] which did not work well with some of the documented catalysts.[9,14] To our delight, our protocol was well applicable to 2-phthalimdo-2-deoxy-D-glucopyranose **1h,** 2-acetamido-2-deoxy-D-glucopyranose **1i**, and 2-acetamido-2-deoxy-D-galacopyranose **1j**, which afforded the thioglycoside **2h**–**2j** in 83%–89% yields (entries 8–10, Table 1). It is noteworthy that *N*-acetyl sialic acid methyl ester **1k** could be stereoselectively converted into β-thioglycoside **2k** in 85% yield in 6 h according to our procedure (entry 11, Table 1), which is a valuable glycosyl donor in carbohydrate chemistry.[23] In addition, despite sluggish acetylation compared to monosaccharides, D-lactose **1l** and D-maltose **1m**, functioning as disaccharide units of many naturally occurring glycoconjugates and polysaccarides with α- and β-glycosidic bonds, respectively, were subjected to our protocol, leading to thioglycosides **2l** and **2m** in 86% and 88% yields with the original glycosidic bonds unaffected. In most of the cases, the 1,2-trans-thioglycoside was obtained, which is attributed to the neighboring group participation of the acetyl group at C-2, except for L-rhamnose monohydrate, which afforded an α/β-mixture in a ratio of 5/1. ^{1}H NMR, ^{13}C NMR, and MS spectra data of the thioglycosides listed in Table 1 are identical with those in the references.

In summary, a one-pot, efficient, and convenient protocol for the preparation of per-*O*-acetylated *p*-tolylthioglycosides from free sugars was developed, making use of acetylation with stoichiometric acetic anhydride and subsequent thioglycosidation with thiocresol mediated by $SnCl_4$. The reaction was fast, high yielding, and devoid of glycosidic bond cleavage. Given *p*-tolylthioglycosides as popular glycosyl donors in carbohydrate chemistry, the present method should find a wide application in oligosaccharide and glycoconjugate synthesis.

EXPERIMENTAL

General Methods

^{1}H and ^{13}C NMR spectra were recorded with a Bruker DPX400 spectrometer in $CDCl_3$ solutions. Internal references: TMS (δ 0.00 ppm for ^{1}H), $CDCl_3$

(δ 77.00 ppm for ^{13}C). Electrospray-ionization mass spectra (ESIMS) was performed by the Fudan University. Thin-layer chromatography (TLC) was performed on silica gel HF with detection by charring with 5% (v/v) H_2SO_4 in MeOH or by UV detection. Column chromatography was conducted by elution of a column of silica gel (200–300 mesh) with EtOAc/petroleum ether (bp 60–90°C) as the eluent. Solutions were concentrated at a temperature <60°C under diminished pressure.

Typical procedure for the synthesis of per-*O*-acetylated thioglycosides

To a suspension of unprotected sugar (5.0 mmol) in Ac_2O (1.02 mmol/OH) was slowly added $SnCl_4$ (1.15 mL, 10.0 mmol). After completion of the reaction (as indicated by TLC), thiocresol (0.74 g, 6.0 mmol) was added and the reaction mixture was allowed to stir for the appropriate time in Table 1. Then the reaction mixture was poured into ice water and extracted with CH_2Cl_2. The organic layer was washed with saturated aqueous $NaHCO_3$ and brine and dried over anhydrous Na_2SO_4, and the solids filtered off. The filtrate was concentrated under reduced pressure and the remains were purified by column chromatography using hexane–EtOAc or recrystallization using EtOH to furnish the pure product.

p-Tolyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (2a)

^1H NMR (400 MHz, $CDCl_3$) δ: 7.38 (d, J = 7.8 Hz, 2H, ArH), 7.12 (d, J = 7.8 Hz, 2H, ArH), 5.20 (t, J = 9.4 Hz, 1H, H-3), 5.02 (t, J = 9.8 Hz, 1H, H-4), 4.93 (t, J = 9.8 Hz, 1H, H-2), 4.63 (d, J = 10.2 Hz, 1H, H-1), 4.23–4.15 (m, 2H, H-6), 3.69 (ddd, J = 2.3, 4.3, 7.4 Hz, 1H, H-5), 2.34 (s, 3H, STol-CH_3), 2.09 (s, 3H, Ac), 2.08 (s, 3H, Ac), 2.01 (s, 3H, Ac), 1.98 (s, 3H, Ac); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.56, 170.17, 169.36, 169.22, 138.76, 133.79, 129.64, 127.47, 85.77, 75.68, 73.96, 69.84, 68.12, 62.07, 21.15, 20.74, 20.70, 20.57.

p-Tolyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside (2b)

^1H NMR (400 MHz, $CDCl_3$) δ: 7.41 (d, J = 8.3 Hz, 2H, ArH), 7.12 (d, J = 7.9 Hz, 2H, ArH), 5.40 (d, J = 3.2 Hz, 1H, H-4), 5.21 (t, J = 9.9, 10.3 Hz, 1H, H-2), 5.03 (dd, J = 3.1, 9.9 Hz, H-3), 4.64 (d, J = 9.9 Hz, H-1), 4.18 (dd, J = 7.1, 11.4 Hz, 1H, H-6a), 4.10 (dd, J = 6.3, 11.4 Hz, H-6b), 3.90 (t, J = 6.7 Hz, H-5), 2.34 (s, 3H, STol-CH_3), 2.11 (s, 3H, Ac), 2.09 (s, 3H, Ac), 2.04 (s, 3H, Ac), 1.97 (s, 3H, Ac); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.36, 170.19, 170.06, 169.42, 138.44, 133.10, 129.60, 128.57, 86.92, 74.29, 71.98, 67.23, 67.16, 61.54, 21.12, 20.83, 20.64, 20.60, 20.56.

p-Tolyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranoside (2c)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37 (d, J = 8.2 Hz, 2H, ArH), 7.12 (d, J = 8.2 Hz, 2H, ArH), 5.48 (d, J = 1.6 Hz, 1H, H-2), 5.40 (d, J = 1.2 Hz, 1H, H-1), 5.35–5.29 (m, 2H, H-3, H-4), 4.55 (ddd, J = 2.4, 5.9, 9.8 Hz, 1H, H-5), 4.29 (dd, J = 5.8, 12.1 Hz, 1H, H-6a), 4.10 (dd, J = 2.1, 12.5 Hz, 1H, H-6b), 2.34 (s, 3H, STol-CH_3), 2.14 (s, 3H, Ac), 2.07 (s, 3H, Ac), 2.06 (s, 3H, Ac), 2.01 (s, 3H, Ac); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.51, 169.88, 169.77, 169.71, 138.40, 132.55, 129.89, 128.68, 85.95, 70.79, 69.32, 69.28, 66.31, 62.42, 21.07, 20.82, 20.66, 20.64, 20.59.

p-Tolyl 2,3,4-tri-*O*-acetyl-1-thio-α-L-rhamnopyranoside (2d)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (d, J = 7.8 Hz, 2H, ArH), 7.11 (d, J = 8.2 Hz, 2H, ArH), 5.47 (dd, J = 1.6, 3.1 Hz, 1H, H-2), 5.31 (d, J = 1.2 Hz, 1H, H-1), 5.28 (dd, J = 3.2, 9.8 Hz, 1H, H-3), 5.12 (t, J = 9.9 Hz, 1H, H-4), 4.35 (m, 1H, H-5), 2.31 (s, 3H, STol-CH_3), 2.12 (s, 3H, Ac), 2.06 (s, 3H, Ac), 1.99 (s, 3H, Ac), 1.23 (d, J = 6.2 Hz, 3H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.94, 169.86, 138.14, 132.38, 129.89, 129.29, 85.94, 71.19, 71.08, 69.29, 67.59, 21.05, 20.85, 20.76, 20.63, 17.25.

p-Tolyl 2,3,4-tri-*O*-acetyl-1-thio-β-L-fucopyranoside (2e)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (d, J = 7.8 Hz, 2H, ArH), 7.12 (d, J = 7.8 Hz, 2H, ArH), 5.25 (d, J = 3.5 Hz, 1H, H-4), 5.19 (t, J = 9.9 Hz, 1H, H-2), 5.03 (dd, J = 3.5, 9.8 Hz, 1H, H-3), 4.63 (d, J = 9.8 Hz, 1H, H-1), 3.80 (q, J = 6.4 Hz, 1H, H-5), 2.33 (s, 3H, STol-CH_3), 2.14 (s, 3H, Ac), 2.10 (s, 3H, Ac), 1.98 (s, 3H, Ac), 1.24 (d, J = 6.7 Hz, 3H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.59, 170.11, 169.46, 138.15, 132.84, 129.67, 129.56, 129.00, 86.80, 73.04, 72.39, 70.27, 67.32, 21.09, 20.84, 20.62, 20.59, 16.40.

p-Tolyl 2,3,4-tri-*O*-acetyl-1-thio-β-D-xylopyranoside (2f)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (d, J = 7.8 Hz, 2H, ArH), 7.12 (d, J = 7.8 Hz, 2H, ArH), 5.16 (t, J = 8.5 Hz, 1H, H-2), 4.92–4.88 (m, 2H, H-3, H-4), 4.70 (d, J = 8.6 Hz, 1H, H-1), 4.24 (dd, J = 4.7, 11.7 Hz, 1H, H-5a), 3.38 (dd, J = 9.0, 11.7 Hz, 1H, H-5b), 2.33 (s, 3H, STol-CH_3), 2.07 (s, 3H, Ac), 2.03 (s, 3H, Ac), 2.02 (s, 3H, Ac); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.9, 169.7, 169.3, 138.5, 133.4, 129.7, 128.0, 86.3, 72.2, 69.7, 68.4, 65.3, 21.1, 20.7, 20.6; HRMS calcd for $C_{18}H_{22}O_7SNa$ $(M+Na)^+$: 405.0984, found: 405.0973.

p-Tolyl 2,3,4-tri-*O*-acetyl-1-thio-β-L-arabinopyranoside (2g)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 (d, J = 8.2 Hz, 2H, ArH), 7.11 (d, J = 7.8 Hz, 2H, ArH), 5.29–5.21 (m, 2H, H-2, H-4), 5.08 (dd, J = 3.1, 8.6 Hz, 1H,

H-3), 4.73 (d, J = 8.2 Hz, 1H, H-1), 4.13 (dd, J = 3.9, 12.9 Hz, 1H, H-5a), 3.63 (dd, J = 1.9, 12.9 Hz, 1H, H-5b), 2.31 (s, 3H, STol-CH_3), 2.08 (s, 3H, Ac), 2.07 (s, 3H, Ac), 2.03 (s, 3H, Ac); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.18, 169.91, 169.37, 138.21, 132.80, 132.70, 129.76, 129.67, 129.33, 87.17, 70.51, 68.36, 67.53, 65.31, 21.08, 20.83, 20.81, 20.70, 20.65.

p-Tolyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (2h)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (dd, J = 3.2, 5.5 Hz, 2H, ArH), 7.77 (dd, J = 2.8, 5.2 Hz, 2H, ArH), 7.31 (d, J = 7.9 Hz, 2H, ArH), 7.08 (d, J = 7.9 Hz, 2H, ArH), 5.78 (t, J = 9.1, 10.3 Hz, 1H, H-3), 5.66 (d, J = 10.7 Hz, 1H, H-1), 5.13 (t, J = 9.5, 9.9 Hz, 1H, H-4), 4.32 (t, J = 10.3, 10.7 Hz, 1H, H-2), 4.31–4.19 (m, 2 H, H-6), 3.93–3.84 (m, 1 H, H-5), 2.33 (s, 3 H, STol-CH_3), 2.11 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 1.84 (s, 3 H, Ac); ^{13}C NMR (100MHz, $CDCl_3$) δ: 170.64, 170.10, 169.44, 167.82, 166.93, 138.75, 134.43, 133.91, 129.62, 126.90, 123.67, 83.08, 75.80, 71.62, 68.65, 62.16, 53.55, 21.15, 20.75, 20.60, 20.39.

p-Tolyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-1-thio-β-D-glucopyranoside (2i)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 (d, J = 7.8 Hz, 2H, ArH), 7.11 (d, J = 7.4 Hz, 2H, ArH), 5.66 (d, J = 8.6 Hz, 1H, NH), 5.20 (t, J = 9.8 Hz, 1H, H-3), 5.03 (t, J = 9.4, 9.8 Hz, 1H, H-4), 4.79 (d, J = 10.2 Hz, 1H, H-1), 4.23–4.14 (m, 2H, H-6, H-6), 3.98 (q, J = 9.8 Hz, 1H, H-2), 3.70 (m, 1H, H-5), 2.34 (s, 3H, STol-CH_3), 2.08 (s, 3H, Ac), 2.01 (s, 3H, Ac), 2.00 (s, 3H, Ac), 1.99 (s, 3H, Ac); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.00, 170.63, 170.00, 169.32, 138.40, 133.22, 129.63, 128.31, 86.71, 75.67, 73.73, 68.36, 62.32, 53.22, 23.29, 21.12, 20.71, 20.65, 20.55.

p-Tolyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-1-thio-β-D-galactopyranoside (2j)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (d, J = 8.2 Hz, 2H, ArH), 7.10 (d, J = 8.2 Hz, 2H, ArH), 5.62 (d, J = 9.4 Hz, 1H, NH), 5.36 (d, J = 3.1 Hz, 1H, H-4), 5.18 (dd, J = 3.1, 10.8 Hz, 1H, H-3), 4.84 (d, J = 10.2 Hz, 1H, H-1), 4.21–4.08 (m, 3H, H-2, H-6a, H-6b), 3.90 (t, J = 6.4 Hz, 1H, H-5), 2.32 (s, 3H, STol-CH_3), 2.12 (s, 3H, Ac), 2.02 (s, 3H, Ac), 1.98 (s, 3H, Ac), 1.97 (s, 3H, Ac); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.57, 170.41, 170.26, 170.24, 138.09, 132.63, 129.59, 129.16, 87.48, 74.30, 71.09, 66.88, 61.78, 49.69, 23.40, 21.09, 20.66.

Methyl (*p*-tolyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-D- glycero-β-D-*galacto*-non-2-ulopyranoside)-onate (2k)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 (d, J = 12.8 Hz, 2H, ArH), 7.12 (d, J = 7.9 Hz, 2H, ArH), 5.92 (br d, 1H, NH), 5.48 (s, 1H), 5.39 (td, J = 1.1, 4.2 Hz, 1H, H-4), 4.96 (d, J = 13.9 Hz, 1H), 4.64 (dd, J = 2.3, 10.5 Hz, 1H), 4.50 (dd, J = 1.9, 12.2 Hz, 1H), 4.13 (dd, J = 4.3, 13.4 Hz, 1H), 4.03 (dd, J = 8.7, 7.2 Hz, 1H), 3.59 (s, 3H, CH_3O), 2.64 (dd, J = 9.1, 4.7 Hz, 1H), 2.32 (s, 3H, STol-CH_3), 2.14 (s, 3H, Ac), 2.12 (s, 3H, Ac), 2.14–2.02 (m, 1H), 2.08 (s, 3H, Ac), 1.95 (s, 3H, Ac), 1.89 (s, 3H, Ac); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.23, 170.95, 170.35, 170.26, 168.27, 140.14, 136.19, 129.84, 125.09, 88.73, 73.13, 72.96, 69.03, 68.74, 62.63, 52.58, 49.32, 37.27, 23.14, 21.30, 21.09, 20.87, 20.72, 20.69.

p-Tolyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1$\rightarrow$4)-2,3,6-tri-*O*- acetyl-1-thio-β-D-glucopyranoside (2l)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (d, J = 7.8 Hz, 2H, ArH), 7.09 (d, J = 7.8 Hz, 2H, ArH), 5.32 (dd, J = 0.8, 2.3 Hz, 1H), 5.18 (t, J = 9.0 Hz, 1H), 5.08 (dd, J = 7.8 Hz, 1H), 4.92 (dd, J = 3.5, 10.6 Hz, 1H), 4.84 (t, J = 9.4, 9.8 Hz, 1H), 4.58 (d, J = 10.1 Hz, 1H), 4.51 (dd, J = 1.8, 12.1 Hz, 1H), 4.44 (d, J = 7.8 Hz, 1H), 4.11–4.02 (m, 3H), 3.84 (t, J = 6.6 Hz, 1H), 3.71 (t, J = 9.4, 9.8 Hz, 1H), 3.61 (m, 1H), 2.32 (s, 3H, STol-CH_3), 2.13 (s, 3H, Ac), 2.10 (s, 3H, Ac), 2.07 (s, 3H, Ac), 2.03 (s, 3H, Ac), 2.02 (s, 3H, Ac), 2.01 (s, 3H, Ac), 1.95 (s, 3H, Ac); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.27, 170.22, 170.09, 170.01, 169.68, 169.51, 168.98, 138.59, 133.67, 129.56, 127.60, 100.92, 85.55, 76.54, 76.01, 73.80, 70.88, 70.57, 70.13, 68.97, 66.50, 62.00, 60.69, 21.11, 20.78, 20.73, 20.72, 20.57, 20.54, 20.44.

p-Tolyl *O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-(1$\rightarrow$4)-2,3,6- tri-*O*-acetyl-1-thio-β-D-glucopyranoside (2m)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (d, J = 8.2 Hz, 2H, ArH), 7.11 (d, J = 8.2 Hz, 2H, ArH), 5.39–5.24 (m, 3H), 5.03 (t, J = 9.8, 10.1 Hz, 1H), 4.83 (dd, J = 4.0, 10.4 Hz, 1H), 4.75 (t, J = 9.4, 9.8 Hz, 1H), 4.64 (d, J = 9.8 Hz, 1H, H-1), 4.53 (dd, J = 2.7, 12.1 Hz, 1H), 4.25–4.17 (m, 2H), 4.03 (dd, J = 2.4, 12.5 Hz, 1H), 3.94–3.89 (m, 2H), 3.69 (m, 1H), 2.34 (s, 3H, STol-CH_3), 2.12 (s, 3H, Ac), 2.09 (s, 3H, Ac), 2.07 (s, 3H, Ac), 2.03 (s, 3H, Ac), 2.02 (s, 3H, Ac), 1.99 (s, 3H, Ac), 1.97 (s, 3H, Ac); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.49, 170.30, 170.13, 169.87, 169.49, 169.38, 138.78, 134.01, 129.59, 127.04, 95.44, 85.05, 76.45, 75.98, 72.25, 70.55, 69.89, 69.22, 68.40, 67.91, 62.70, 61.40, 21.13, 20.85, 20.76, 20.68, 20.62, 20.54, 20.52, 20.50.

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