Supporting Information
for DOI: 10.1055/s-0028-1087913
© Georg Thieme Verlag KG Stuttgart · New York 2008
Supporting information for Synlett

Tandem One-pot Acetalation–Acetylation for Direct Access of Differentially Protected Thioglycosides and O-Glycosides with p-Toluenesulfonic Acid

Kwok-Kong Tony Mong,* Chin-Sheng Chao, Min-Chun Chen, Chun-Wei Lin

Department of Applied Chemistry, National Chiao Tung University
1001, Ta-Hsueh Road, Hsinchu, Taiwan, 300, ROC

Email: tmong@mail.nctu.edu.tw
Table of contents --------------------------------------------------------------1–2
Preparation of (6-chlorohexyl) β-D-galactopyranoside 3------------------------3
Preparation of (2-methyl-5-t-butyl-phenyl) 2-(2,2,2-trichloroethoxycarbamyl)-
2-deoxy-1-thio-β-D-glucopyranoside 11-----------------------------------------4
Table S1: Amounts of reagents in one-pot acetalation–acetylation of carbohydrate
substrates 3–12-----------------------------------------------------------------5
Spectroscopic data for compounds 2, 13–20---------------------------------------6–8
Spectroscopic data for compounds 21–24-----------------------------------------8–9
1H and 13C NMR spectra of methyl 2,3-di-O-acetyl-4,6-O-benzylidene
1-α-D-glucopyranoside (2)------------------------------------------------------10–11
1H and 13C NMR spectra of (6-chlorohexyl) 2,3,4,6-tetra-O-acetyl
β-D-galactopyranoside s3-------------------------------------------------------12–13
1H and 13C NMR spectra of 6-chlorohexyl 2,3-di-O-acetyl-4,6-O-
benzylidene-1-β-D-galactopyranoside (13)---------------------------------------14–15
1H and 13C NMR spectra of methyl 2-acetamido-3-O-acetyl-
4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (14)---------------------------16–17
1H and 13C NMR spectra of p-tolyl 2,3-di-O-acetyl-4,6-O-benzylidene-
1-thio-β-D-galactopyranoside (15)---------------------------------------------18–19
1H and 13C NMR spectra of p-tolyl 2,3-di-O-acetyl-4,6-O-benzylidene-
1-thio-β-D-glucopyranoside (16)-----------------------------------------------20–21
1H and 13C NMR spectra of p-tolyl 2,3-di-O-acetyl-4,6-O-
benzylidene-1-thio-α-D-mannopyranoside (17)--------------------------------22–23
1H and 13C NMR spectra of p-tolyl 2,3,6-tri-O-acetyl-4-O-(2’,3’-di-O-acetyl-4’,6’-O-
benzylidene-β-D-galactopyranosyl)-1-thio-β-D-glucopyranoside (18)-----------24–25
1H and 13C NMR spectra of p-tolyl 3-O-acetyl-4,6-O-benzylidene-
2-(2,2,2-trichloroethoxycarbamyl)-2-deoxy-1-thio-β-D-glucopyranoside (19) --26–27
1H and 13C NMR spectra of (2-methyl-5-t-butyl-phenyl) 3,4,6-tri-O-acetyl-
2-(2,2,2-trichloroethoxycarbamyl)-2-deoxy-1-thio-β-D-glucopyranoside (s11) --28–29
$^1$H and $^{13}$C NMR spectra of (2-methyl-5-t-butyl-phenyl) 3-0-acetyl-4,6-0-
benzyldene-2-(2,2,2-trichloroethoxycarbonyl)-2-deoxy-1-thio-$\beta$-D-gluco-
pyranoside (20) ------------------------------------------------------------------------------------------------------30–31

$^1$H and $^{13}$C NMR spectra of $p$-tolyl 2,6-di-0-acetyl-3,4-0-isopropylidene-
1-thio-$\beta$-D-galactopyranoside (21) ------------------------------------------------------------------------------------------------------32–33

$^1$H and $^{13}$C NMR spectra of $p$-tolyl 2,3-di-0-acetyl-4,6-0-isopropylidene-
1-thio-$\beta$-D-glucopyranoside (22) ------------------------------------------------------------------------------------------------------34–35

$^1$H and $^{13}$C NMR spectra of $p$-tolyl 4-0-acetyl-2,3-0-isopropylidene-
1-thio-$\alpha$-L-rhamnopyranoside (23) ------------------------------------------------------------------------------------------------------36–37

$^1$H and $^{13}$C NMR spectra of methyl 5-acetamido-4,7-di-0-acetyl-3,5-dideoxy-
8,9-O-isopropylidene-$\beta$-D-glycero-D-galacto-2-nonulopyranosonate (24) -------38–39

H-H COSY spectrum of methyl 5-acetamido-4,7-di-0-acetyl-3,5-dideoxy-
8,9-O-isopropylidene-$\beta$-D-glycero-D-galacto-2-nonulopyranosonate (24) ----------40

HMQC spectrum of methyl 5-acetamido-4,7-di-0-acetyl-3,5-dideoxy-
8,9-O-isopropylidene-$\beta$-D-glycero-D-galacto-2-nonulopyranosonate (24) ----------41
Preparation of (6-chlorohexyl) β-D-galactopyranoside (3). A suspension of penta-
O-acetyl-β-D-galactopyranosyl acetate (4.0 g, 10 mmol), 6-chlorohexanol (4.0 g, 4.0
mmol) and MS-AW300 (4.0 g) in dried CH₂Cl₂ (20 mL) was treated with BF₃·Et₂O
(6.4 mL, 52 mmol) at −5 °C under N₂. The reaction mixture was stirred from −5 °C
to rt for 18 h. Upon completion of reaction, Et₃N was added. The reaction crude was
diluted with CH₂Cl₂ (50 mL), filtered, and then sequentially washed with sat.NaHCO₃
(1 ×50 mL), H₂O (1 × 50 mL), brine (1 × 50 mL), then dried over MgSO₄,
concentrated for column chromatography over silica gel to afford (6-chlorohexyl)
2,3,4,6-penta-O-acetyl β-D-galactopyranoside s₃ as white glassy solid (2.8 g, 59%).
The prepared galactoside s₃ was then dissolved in a solution of 2:1 MeOH/CH₂Cl₂
(20 mL) with Na(s) (ca. 100 mg) at room temperature. Upon completion of
decaetylation, the reaction was neutralized with IR-120 H⁺ resin, filtered, and
concentrated to afford the crude compound 3 as white amorphous solid (1.32 g, 95%).
For (6-chlorohexyl) 2,3,4,6-penta-O-acetyl-β-D-galactopyranoside s₃. ¹H-NMR (300
MHz; CDCl₃): δ = 5.39 (dd, J = 0.75 and 3.45 Hz, 1 H), 5.20 (dd, J = 7.8 and 10.5 Hz,
1 H), 5.02 (dd, J = 3.6 and 10.5 Hz, 1 H), 4.46 (d, J = 8.1 Hz, 1 H, H-1), 4.22–4.10 (m,
2 H), 3.93–3.86 (m, 2H), , 3.56–3.45 (m, 3 H), 2.15 (s, 3 H), 2.06 (s, 3 H), 2.05 (s, 3
H), 1.99 (s, 3 H), 1.82–1.72 (m, 3 H), 1.66–1.55 (m, 2 H), 1.50–1.26 (m, 3 H). ¹³C-
NMR (75 MHz; CDCl₃): δ = 170.8, 170.7, 170.6, 169.8, 101.7, 71.3, 70.9, 70.4, 69.3,
67.5, 61.7, 45.4, 32.9, 29.6, 26.9, 25.5, 21.16, 21.07, 20.99. HRMS–ES m/z: [M +
Preparation of (2-methyl-5-\text{-}t\text{-}butyl-phenyl)\ 2\text{-}(2,2,2\text{-}trichloroethoxycarbamyl)\text{-}2\text{-}deoxy\text{-}1\text{-}thio\text{-}\beta\text{-}D\text{-}glucopyranoside (11)\text{.} \text{TsOH (5.4 mg, 0.28 mmol) was added into a stirring mixture of 2\text{-}(2,2,2\text{-}trichloroethoxycarbamyl)\text{-}2\text{-}deoxy\text{-}D\text{-}glucopyranose (1.0 g, 2.8 mmol), Ac}_2\text{O (1.28 mL, 13.6 mmol) in CH}_3\text{CN (1 mL) at r.t. under N}_2. \text{Upon completion of acetylation as assessed by TLC, the solvent was removed by co-evaporation with toluene (2 × 2 mL) by rotary evaporator to furnish the crude per-O-acetyl N-Troc glucosaminyl acetate. After then, BF}_3\text{.OEt}_2 (0.71 mL, 5.6 mmol) was added into a stirring CH}_2\text{Cl}_2 solution (6 mL) of crude per-O-acetyl N-Troc glucosaminyl acetate, 2-methyl-5-\text{-}t\text{-}butyl-thiophenol (0.78 mL, 0.42 mmol) at 0 \text{°C under N}_2. \text{After 15h, the reaction mixture was diluted with 30 mL CH}_2\text{Cl}_2, \text{washed with sat.NaHCO}_3 (1 × 20 mL), brine (1 × 20 mL), dried over MgSO}_4, \text{filtered, and concentrated for column chromatography over silica gel to afford thioglycoside s11 as white glassy solid (1.16 g, 71% over 2 steps). A piece of freshly cut Na(s) (ca. 50 mg) was then added in a stirring solution of the aforementioned crude thioglycoside s11 in 2:1 MeOH/CH}_2\text{Cl}_2 (20 mL) at 0 \text{°C for 2h. The resulting mixture was neutralized with IR-120 H\text{\textsuperscript{+}} resin at 0 \text{°C, filtered, and concentrated to afford the crude unprotected thioglycoside 11 as white glassy solid (860 mg, 96%). For thioglycoside s11: 1H-NMR (300 MHz; CDCl}_3): \delta = 7.55 (d, J = 1.65 Hz, 1 H), 7.22 (dd, J = 1.8 and 7.8 Hz, 1 H), 7.09 (dd, J = 1.75 and 7.75 Hz, 1 H), 5.87 (bs, J = 9.3 Hz, 1 H, N-H), 5.27 (t, J = 9.6 Hz, 1 H), 5.02 (t, J = 9.6 Hz, 1 H), 4.78–4.65 (m, 3H), 4.20 (dd, J = 4.0 and 9.6 Hz, 1 H), 4.09–4.05 (m, 1H), 3.81–3.69 (m, 2H), 2.33 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.86 (s, 3H), 1.27 (s, 9H). 13C-NMR (75 MHz; CDCl}_3): \delta = 171.3, 171.1, 169.9, 169.8, 155.5, 154.5, 152.1, 150.0, 137.9, 131.8, 131.2, 130.5, 127.9, 126.0, 124.0, 95.9, 87.8, 74.9, 69.3, 69.1, 62.9, 60.9, 55.4, 34.8, 31.7, 31.6, 21.1, 21.0, 21.0, 21.0, 21.0, \ldots)
20.8. MS–ES m/z: [M + Na]+ calcd. for C_{26}H_{34}Cl_{3}NO_{9}S, 664.1. Found, 664.1.

Table S1. Stoichiometric and exact amounts of reagents used in one-pot acetalation–acetylation of carbohydrate substrates 3–12

![Diagrams of carbohydrate substrates 3–12]

<table>
<thead>
<tr>
<th>corresponding entry in Table 1</th>
<th>1 g carbohydrate substrate (mmol)</th>
<th>product</th>
<th>solvent (mL)</th>
<th>TsOH (mg, M)</th>
<th>Ac&quot;O (mL, mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>methyl α-D-Glc (5.0)</td>
<td>2</td>
<td>CH₃CN, 10</td>
<td>96, 0.049</td>
<td>2.8, 30</td>
</tr>
<tr>
<td>1</td>
<td>3 (3.4)</td>
<td>13</td>
<td>CH₃CN, 10</td>
<td>65, 0.031</td>
<td>1.9, 20</td>
</tr>
<tr>
<td>2</td>
<td>4 (4.3)</td>
<td>14</td>
<td>CH₃CN, 10</td>
<td>81, 0.041</td>
<td>2.4, 26</td>
</tr>
<tr>
<td>3</td>
<td>5 (3.5)</td>
<td>15</td>
<td>CH₃CN, 10</td>
<td>67, 0.032</td>
<td>2.0, 21</td>
</tr>
<tr>
<td>4</td>
<td>6 (3.5)</td>
<td>16</td>
<td>CH₃CN, 10</td>
<td>67, 0.032</td>
<td>2.0, 21</td>
</tr>
<tr>
<td>5</td>
<td>7 (3.5)</td>
<td>17</td>
<td>CH₃CN, 35</td>
<td>67, 0.010</td>
<td>2.0, 21</td>
</tr>
<tr>
<td>6</td>
<td>8 (2.2)</td>
<td>18</td>
<td>CH₃CN, 15</td>
<td>42, 0.014</td>
<td>2.2, 23</td>
</tr>
<tr>
<td>7</td>
<td>10 (2.2)</td>
<td>19</td>
<td>CH₃CN, 35</td>
<td>133, 0.019</td>
<td>1.2, 13</td>
</tr>
<tr>
<td>8</td>
<td>11 (1.9)*</td>
<td>20</td>
<td>CH₃CN, 7</td>
<td>37, 0.027</td>
<td>1.1, 12</td>
</tr>
<tr>
<td>9</td>
<td>5 (3.5)</td>
<td>21</td>
<td>acetone, 13</td>
<td>67, 0.023</td>
<td>2.0, 21</td>
</tr>
<tr>
<td>10</td>
<td>6 (3.5)</td>
<td>22</td>
<td>acetone, 13</td>
<td>67, 0.023</td>
<td>2.0, 21</td>
</tr>
<tr>
<td>11</td>
<td>9 (3.7)</td>
<td>23</td>
<td>acetone, 10</td>
<td>67, 0.018</td>
<td>2.1, 22</td>
</tr>
<tr>
<td>12</td>
<td>12 (3.1)</td>
<td>24</td>
<td>acetone, 15</td>
<td>59, 0.021</td>
<td>1.8, 19</td>
</tr>
</tbody>
</table>

*0.5 g of unprotected thioglycoside was used.
Methyl 2,3-di-O-acetyl-4,6-O-benzylidene-1-α-D-glucopyranoside (2). Yield: white glassy solid, 1.69 g, 90%. $^1$H-NMR (300 MHz; CDCl$_3$): $\delta = 7.48$–$7.43$ (m, 2 H), 7.39–7.34 (m, 3 H), 5.60 (t, $J = 9.0$ Hz, 1 H), 5.52 (s, 1 H), 4.97–4.90 (m, 2 H), 4.32 (dd, $J = 3.0$ and $9.0$ Hz, 2 H), 3.99–3.90 (m, 1 H), 3.79 (t, $J = 10$ Hz, 1 H), 3.67 (t, $J = 10$ Hz, 1 H), 3.43 (s, 3 H), 2.08 (s, 3 H), 2.06 (s, 3 H). $^{13}$C-NMR (75 MHz; CDCl$_3$): $\delta = 170.8$, 170.2, 137.3, 129.5, 128.6, 126.6, 101.9, 98.0, 79.6, 72.0, 69.4, 69.3, 62.7, 55.8, 21.2, 21.1.

6-Chlorohexyl 2,3-di-O-acetyl-4,6-O-benzylidene-1-β-D-galactopyranoside (13) (Table 1, entry 1). Yield: white amorphous solid, 1.28 g, 81%. $^1$H-NMR (300 MHz; CDCl$_3$): $\delta = 7.55$–$7.52$ (m, 2 H), 7.43–7.37 (m, 3 H), 5.52 (s, 1 H), 5.39 (dd, $J = 8.1$ and $10.5$ Hz, 1 H,), 4.97 (dd, $J = 3.6$ and $10.5$ Hz, 1 H), 4.50 (d, $J = 8.1$ Hz, 1 H, H-1), 4.39–4.32 (m, 2 H), 4.08 (dd, $J = 1.5$ and $12.3$ Hz, 1 H), 3.96–3.90 (m, 1 H), 3.56–3.44 (m, 4 H), 2.09 (s, 3 H), 2.07 (s, 3 H), 1.87–1.73 (m, 2 H), 1.53–1.69 (m, 2 H), 1.51–1.30 (m, 4 H). $^{13}$C-NMR (75 MHz; CDCl$_3$): $\delta = 171.3$, 169.8, 130.9, 130.9, 129.5, 128.6, 101.5, 101.4, 73.8, 72.5, 69.5, 69.3, 69.0, 66.7, 45.5, 32.9, 29.7, 26.9, 25.6, 21.3, 21.2. HRMS–FAB ($m/z$): [M]$^+$ calcd. for C$_{23}$H$_{31}$ClO$_8$, 470.1707; found, 470.1731.

Methyl 2-acetamido-3-O-acetyl-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (14) (Table 1, entry 2). Yield: white amorphous solid, 1.18 g, 76%. $^1$H-NMR (300 MHz; CDCl$_3$): $\delta = 7.86$–$7.45$ (m, 2 H), 7.39–7.36 (m, 3 H), 5.83 (d, $J = 9.6$ Hz, 1 H), 5.55 (s, 1 H), 5.32 (t, $J = 10.0$ Hz, 1 H), 4.74 (d, $J = 3.6$ Hz, 1 H), 3.90–3.70 (m, 3 H), 3.43 (s, 3 H), 2.08 (s, 3 H), 1.99 (s, 3 H). $^{13}$C-NMR (75 MHz; CDCl$_3$): $\delta = 171.9$, 170.5, 137.4, 129.5, 128.6, 126.6, 102.0, 99.4, 79.4, 70.7, 69.3, 63.2, 55.7, 53.0, 23.7, 21.3. HRMS–FAB ($m/z$): [M + H]$^+$ calcd. for C$_{19}$H$_{23}$NO$_7$ = 366.1547; found, 366.1541.

p-Tolyl 2,3-di-O-acetyl-4,6-O-benzylidene-1-thio-β-D-galactopyranoside (15) (Table 1, entry 3). Yield: white amorphous solid, 1.24 g, 77%. $^1$H-NMR (300 MHz; CDCl$_3$): $\delta = 7.52$ (d, $J = 8.1$ Hz, 2 H), 7.42–7.36 (m, 5 H), 7.09 (d, $J = 8.1$ Hz, 2 H), 5.48 (s, 1 H), 5.31 (t, $J = 9.9$ Hz, 1 H), 5.00 (dd, $J = 3.3$ and 9.9 Hz, 1 H), 4.67 (d, $J =$
9.6 Hz, 1 H, H-1), 4.41–4.37 (m, 2 H), 4.03 (d, J = 1.5 and 12.6 Hz, 1 H), 3.60 (d, J =
1.2 Hz, 1 H), 2.36 (s, 3 H), 2.11 (s, 3 H), 2.04 (s, 3 H). 13C-NMR (75 MHz; CDCl3): δ =
171.2, 169.5, 138.8, 137.9, 134.7, 130.0, 129.6, 128.5, 127.5, 101.6, 85.6, 73.8, 73.6, 70.0, 69.5, 67.2, 21.7, 21.34, 21.3. HRMS–FAB (m/z): [M + H]⁺ calcd. for
C24H26O7S, 459.1472; found, 459.1473.

*p*-Tolyl 2,3-di-O-acetyl-4,6-O-benzylidene-1-thio-α-D-glucopyranoside (16) (Table
1, entry 4). Yield: white glassy solid, 1.20 g, 75%. 1H-NMR (300 MHz; CDCl3):
δ = 7.44–7.33 (m, 7 H), 7.15 (d, J = 7.8 Hz, 2 H), 5.49 (s, 1 H), 5.33 (t, J = 9 Hz, 1
H), 4.97 (dd, J = 9.0 and 9.9 Hz, 1 H), 4.74 (d, J = 10.2 Hz, 1 H), 4.38 (dd, J = 4.7
and 10.4 Hz, 1 H), 3.78 (t, J = 10.1 Hz, 1 H), 3.64 (t, J = 9.5 Hz, 1 H), 3.59–3.51 (m, 1
H), 2.36 (s, 3 H), 2.11 (s, 3 H), 2.03 (s, 3 H). 13C-NMR (75 MHz; CDCl3): δ =
170.5, 169.9, 137.2, 134.1, 130.2, 129.5, 128.6, 128.1, 126.5, 101.9, 87.2, 78.5, 73.4, 71.2, 71.0, 68.9, 21.6, 21.2, 21.1.

*p*-Tolyl 2,3-di-O-acetyl-4,6-O-benzylidene-1-thio-α-D-mannopyranoside (17)
(Table 1, entry 5). Yield: white amorphous solid, 1.12 g, 70%. 1H-NMR (300 MHz; CDCl3):
δ = 7.52–7.49 (m, 2 H), 7.43–7.38 (m, 5 H), 7.15 (d, J = 8.1 Hz, 2 H), 5.63 (dd, J = 1.35 and 3.5 Hz, 1 H), 5.61 (s, 1 H), 4.53–4.47 (m, 1 H), 4.27 (dd, J = 4.8 and
10.2 Hz, 1 H), 4.15 (t, J = 10.0 Hz, 1 H), 3.88 (t, J = 10.2 Hz, 1 H), 2.35 (s, 3 H), 2.17 (s, 3 H), 2.05 (s, 3 H). 13C-NMR (75 MHz; CDCl3): δ =

*p*-Tolyl 2,3,6-tri-O-acetyl-4-O-(2',3'-di-O-acetyl-4',6'-O-benzylidene-β-D-galactopyranosyl)-1-thio-β-D-glucopyranoside (18) (Table 1, entry 6). Yield:
white amorphous solid, 1.36 g, 82%. 1H-NMR (300 MHz; CDCl3): δ = 7.48–7.37 (m, 7 H), 7.12 (d, J = 7.12 Hz, 2 H), 5.47 (s, 1 H), 5.30–5.22 (m, 2 H), 4.93–4.87 (m, 2
H), 4.64–4.56 (m, 2 H), 4.46 (bs, 1 H), 4.36–4.26 (m, 2 H), 4.14–4.01 (m, 2 H), 3.73 (t, J = 9.36 Hz, 1 H), 3.66–3.60 (m, 1 H), 3.46 (s, 1 H), 2.35 (s, 3 H), 2.12 (s, 3 H), 2.09 (s, 3 H), 2.04 (m, 9 H). 13C-NMR (75 MHz; CDCl3): δ = 171.1, 170.7, 170.6,
HRMS–FAB (m/z): [M + H]\(^+\) calcd. for C\(_{36}\)H\(_{42}\)O\(_{15}\)S, 747.2317; found, 747.2336.

\(\text{p-Toly}-3\)-O-acetyl-4,6-O-benzylidene-2-(2,2,2-trichloroethoxycarbamyl)-2-deoxy-1-thio-\(\beta\)-D-glucopyranoside (19) (Table 1, entry 7). \(^6\) Yield: white glassy solid, 0.9 g, 70%. \(^1\)H-NMR (300 MHz; CDCl\(_3\)): \(\delta = 7.46\)–7.35 (m, 7 H), 7.16 (d, \(J = 7.8\) Hz, 2 H), 5.52 (s, 1 H), 5.37–5.28 (m, 2 H), 4.87–4.74 (m, 3 H), 4.37 (dd, \(J = 4.8\) and 10.5 Hz, 1 H), 3.82 (t, \(J = 10.4\) Hz, 2 H), 3.69 (t, \(J = 9.3\) Hz, 1 H). 13\(^C\)-NMR (75 MHz; CDCl\(_3\)): \(\delta = 171.2, 154.6, 139.1, 137.2, 133.9, 130.3, 129.6, 128.7, 126.6, 101.9, 95.8, 88.7, 78.8, 75.0, 72.8, 71.1, 68.9, 56.0, 21.6, 21.2.

(2-methyl-5-tbutylphenyl) 3-O-acetyl-4,6-O-benzylidene-2-(2,2,2-trichloroethoxycarbamyl)-2-deoxy-1-thio-\(\beta\)-D-glucopyranoside (20) (Table 1, entry 8). Yield: white glassy solid, 940 mg, 75%. \(^1\)H-NMR (300 MHz; CDCl\(_3\)): \(\delta = 7.56\) (s, 1 H), 7.43 (d, \(J = 6.0\) Hz, 2 H), 7.36–7.23 (m, 4 H), 7.16 (d, \(J = 6.1\) Hz, 2 H), 5.58–5.50 (m, 2 H), 5.43–5.30 (dd, \(J = 3.1\) and 8.9 Hz, 1 H), 4.83 (d, \(J = 3.2\) Hz, 2 H), 4.72 (d, \(J = 8.2\) Hz, 1 H), 4.31–4.26 (m, 1 H), 3.93 (dd, \(J = 4.7\) and 10.5 Hz, 1 H), 3.79 (t, \(J = 10.2\) Hz, 2 H), 3.71 (t, \(J = 9.3\) Hz, 1 H), 3.56–3.48 (m, 1 H), 2.33 (s, 3 H), 2.07 (s, 3 H), 1.34 (s, 9 H). 13\(^C\)-NMR (75 MHz; CDCl\(_3\)): \(\delta = 171.4, 154.8, 150.1, 137.3, 137.2, 132.3, 130.5, 130.3, 130.1, 129.6, 129.0, 128.7, 126.5, 125.8, 101.7, 95.9, 88.9, 78.9, 75.0, 72.9, 70.8, 68.9, 56.0, 34.9, 31.7, 21.3, 20.7. HRMS–ES (m/z): [M + Na]\(^+\) calcd. for C\(_{29}\)H\(_{34}\)Cl\(_3\)NO\(_7\)S, 668.1014; found, 668.1070.

\(\text{p-Toly}-2,6\)-di-O-acetyl-3,4-O-isopropylidene-1-thio-\(\beta\)-D-galactopyranoside (21) (Table 1, entry 9). Yield: white amorphous solid, 1.0 g, 70%. \(^1\)H-NMR (300 MHz; CDCl\(_3\)): \(\delta = 7.42\) (d, \(J = 8.1\) Hz, 2 H), 7.11 (d, \(J = 7.9\) Hz, 2 H), 5.07–5.00 (m, 1 H), 4.54 (d, \(J = 10.1\) Hz, 1 H), 4.37 (d, \(J = 6.0\) Hz, 2 H), 4.23–4.20 (m, 2 H), 3.97 (dt, \(J = 1.5\) and 6.0 Hz, 1 H), 2.31 (s, 3 H), 2.15 (s, 3 H), 2.10 (s, 3 H), 1.53 (s, 3 H), 1.34 (s, 3 H). 13\(^C\)-NMR (75 MHz; CDCl\(_3\)): \(\delta = 171.2, 170.1, 138.4, 133.0, 130.0, 129.9, 111.3,
86.5, 74.5, 73.9, 71.8, 64.0, 28.0, 26.7, 21.5, 21.4, 21.2. HRMS−FAB (m/z): [M + H]+ calcd. for C_{20}H_{26}O_{7}S, 411.1472; found, 411.1477.

*p*-Tolyl 2,3-di-*O*-acetyl-4,6-*O*-isopropylidene-1-thio-*β*-D-glucopyranoside (22) (Table 1, entry 10). Yield: white amorphous solid, 740 mg, 52%. 1H-NMR (300 MHz; CDCl3): δ = 7.33 (d, J = 8.1 Hz, 2 H), 7.11 (d, J = 7.9 Hz, 2 H), 5.14 (td, J = 6.1 and 9.0 Hz, 1 H), 4.90 (dd, J = 6.3 and 9.1 Hz, 1 H), 4.67 (d, J = 9 Hz, 1 H), 3.96 (dd, J = 6.4 and 8.9 Hz, 1 H), 3.77 (dd, J = 6.2 and 9.9 Hz, 1 H), 3.67 (dd, J = 6.3 and 9.0 Hz, 1 H), 3.37 (td, J = 5.4 and 10.0 Hz, 1 H), 2.34 (s, 3 H), 2.08 (s, 3 H), 2.02 (s, 3 H), 1.44 (s, 3 H), 1.36 (s, 3 H). 13C-NMR (75 MHz; CDCl3): δ = 170.6, 169.9, 139.0, 133.9, 130.3, 128.0, 100.1, 87.0, 73.8, 72.0, 71.4, 71.3, 62.3, 29.3, 21.6, 21.22, 21.2, 19.3. HRMS−ES (m/z): [M + Na]+ calcd. for C_{20}H_{26}NaO_{7}S, 433.1291; found, 433.1288.

*p*-Tolyl 4-*O*-acetyl-2,3-*O*-isopropylidene-1-thio-*α*-L-rhamnopyranoside (23) (Table 1, entry 11). Yield: white glassy solid, 980 mg, 75%. 1H-NMR (300 MHz; CDCl3): δ = 7.38 (d, J = 8.1 Hz, 2 H), 7.15 (d, J = 7.8 Hz, 2 H), 5.70 (s, 1 H), 4.90 (dd, J = 8.0 and 10.1 Hz, 1 H), 4.37 (dd, J = 0.5 and 5.3 Hz, 1 H), 4.25–4.18 (m, 2 H), 2.35 (s, 3 H), 2.14 (s, 3 H), 1.59 (s, 3 H), 1.38 (s, 3 H), 1.14 (d, J = 6.3 Hz, 3 H). 13C-NMR (75 MHz; CDCl3): δ = 170.5, 138.4, 132.9, 130.3, 129.7, 110.4, 84.4, 76.8, 75.9, 75.0, 65.9, 28.1, 26.9, 21.5, 21.4, 17.2.

Methyl 5-acetamido-4,7-*di*-*O*-acetyl-3,5-*dideoxy*-8,9-*O*-isopropylidene-*β*-D-glycero-2,3-*D*-galacto-2-nonulopyranosonate (24) (Table 1, entry 12). Yield: colorless oily liquid, 1.02 g, 74%. 1H-NMR (500 MHz; CDCl3): δ = 6.13 (d, J = 10.0 Hz, 1 H), 5.35–5.34 (m, 1 H, H-7), 5.22–5.18 (m, 1 H, H-4), 4.18 (dd, J = 2.0 and 11.0 Hz, 1 H, H-6), 4.13–4.10 (m, 1 H, H-8), 4.07–4.01 (m, 1 H, H-5), 3.91–3.88 (m, 3 H, H-9), 3.81–3.78 (m, 1 H, H-9), 3.76 (s, 3 H, OCH3), 2.15–2.09 (m, 2 H, H-3), 2.05 (s, 3 H), 1.95 (s, 3 H), 1.82 (s, 3 H), 1.24 (s, 6 H). 13C-NMR (125 MHz; CDCl3): δ = 171.1, 170.5, 170.3, 169.2, 108.3, 94.7, 75.3, 70.9, 69.3, 68.6, 65.3, 53.1, 49.2, 35.9, 26.2, 25.3, 22.8, 20.78, 20.76. HRMS−FAB (m/z): [M + H]+ calcd. for C_{19}H_{29}NO_{11}, 448.1813; found, 448.1821.
$^1$H NMR spectrum of methyl 2,3-di-\(O\)-acetyl-4,6-\(O\)-benzylidene-1-$\alpha$-D-gluco-pyranoside (2)
$^{13}$C NMR spectrum of methyl 2,3-di-$O$-acetyl-4,6-$O$-benzylidene-1-\(\alpha\)-D-glucopyranoside (2)
$^1$H NMR spectrum of (6-chlorohexyl) 2,3,4,6-tetra-O-acetyl 1-β-D-galactopyranoside s3
$^{13}$C NMR spectrum of (6-chlorohexyl) 2,3,4,6-tetra-$O$-acetyl 1-β-D-galactopyranoside $s3$
$^1$H NMR spectrum of 6-chlorohexyl 2,3-di-$O$-acetyl-4,6-$O$-benzylidene-1-\(\beta\)-\(D\)-galactopyranoside (13)
$^{13}$C NMR spectrum of 6-chlorohexyl 2,3-di-O-acetyl-4,6-O-benzylidene-1-β-D-galactopyranoside (13)
$^1$H NMR spectrum of methyl 2-acetamido-3-O-acetyl-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (14)
$^{13}$C NMR spectrum of methyl 2-acetamido-3-$O$-acetyl-4,6-$O$-benzylidene-2-deoxy-$\alpha$-$D$-glucopyranoside (14)
$^1$H NMR spectrum of $p$-tolyl 2,3-di-$O$-acetyl-4,6-$O$-benzylidene-1-thio-$\beta$-D-galactopyranoside (15)\textsuperscript{1}
$^{13}$C NMR spectrum of $p$-tolyl 2,3-di-O-acetyl-4,6-O-benzylidene-1-thio-β-D-galactopyranoside (15)
$^1$H NMR spectrum of $p$-tolyl 2,3-di-$O$-acetyl-4,6-$O$-benzylidene-1-thio-$\beta$-$D$-glucopyranoside (16)
$^{13}$C NMR spectrum of $p$-tolyl 2,3-di-$O$-acetyl-4,6-$O$-benzylidene-1-thio-$\beta$-$D$-glucopyranoside (16)$^3$
$^1$H NMR spectrum of p-tolyl 2,3-di-O-acetyl-4,6-O-benzylidene-1-thio-\(\alpha\)-D-mannopyranoside (17)
$^{13}$C NMR spectrum of $p$-tolyl 2,3-di-$O$-acetyl-4,6-$O$-benzylidene-1-thio-$\alpha$-D-mannopyranoside (17)
\(^{1}\)H NMR spectrum of \(\text{p-tolyl 2,3,6-tri-O-acetyl-4-O-(2',3',6'-tri-O-acetyl-4',6'-O-benzylidene-\(\beta\)-D-galactopyranosyl)-1-thio-\(\beta\)-D-glucopyranoside (18)}\)
$^{13}$C NMR spectrum of $p$-tolyl 2,3,6-tri-$O$-acetyl-4-$O$-(2',3'-di-$O$-acetyl-4',6'-$O$-benzylidene-$\beta$-D-galactopyranosyl)-1-thio-$\beta$-D-glucopyranoside (18)\textsuperscript{5}
$^1$H NMR spectrum of $p$-tolyl 3-$O$-acetyl-4,6-$O$-benzylidene-2-(2,2,2-trichloroethoxy carbamyl)-2-deoxy-1-thio-$\beta$-$D$-glucopyranoside (19)
$^{13}$C NMR spectrum of $p$-tolyl 3-$O$-acetyl-4,6-$O$-benzylidene-2-(2,2,2-trichloroethoxycarbamyl)-2-deoxy-1-thio-$\beta$-D-glucopyranoside (19)
$^1$H NMR spectrum of (2-methyl-5-$t$-butyl-phenyl) 3,4,6-tri-$O$-acetyl-
2-(2,2,2-trichloroethoxycarbamyl)-2-deoxy-1-thio-$\beta$-D-glucopyranoside (s11)$^2$
$^{13}$C NMR spectrum of (2-methyl-5-$t$-butyl-phenyl) 3,4,6-tri-$O$-acetyl-2-(2,2,2-trichloroethoxycarbamyl)-2-deoxy-1-thio-$\beta$-D-glucopyranoside ($s11$)$^2$
$^1$H NMR spectrum of (2-methyl-5-t-buty-phenyl) 3-O-acetyl-4,6-O-benzylidene-2-(2,2,2-trichloroethoxycarbonyl)-2-deoxy-1-thio-β-D-glucopyranoside (20)$^6$
$^{13}$C NMR spectrum of (2-methyl-5-$t$-butyl-phenyl) 3-$O$-acetyl-4,6-$O$-benzylidene-2-(2,2,2-trichloroethoxycarbonyl)-2-deoxy-1-thio-$\beta$-D-glucopyranoside (20)$^6$
$^1$H NMR spectrum of $p$-tolyl 2,6-di-O-acetyl-3,4-O-isopropylidene-1-thio-β-D-galactopyranoside (21)
$^{13}$C NMR spectrum of $p$-tolyl 2,6-di-O-acetyl-3,4-O-isopropylidene-1-thio-$\beta$-D-galactopyranoside (21)
$^1$H NMR spectrum of $p$-tolyl 2,3-di-\textit{O}-acetyl-4,6-\textit{O}-isopropylidene-1-thio-\textit{\textbeta}-\text{D}-\text{glucopyranoside (22)}$
$^{13}$C NMR spectrum of $p$-tolyl 2,3-di-$O$-acetyl-4,6-$O$-isopropylidene-1-thio-$\beta$-$D$-glucopyranoside (22)
$^1$H NMR spectrum of $p$-tolyl 4-$O$-acetyl-2,3-$O$-isopropylidene-1-thio-$\alpha$-$L$-rhamnopyranoside (23)$^4$
$^{13}$C NMR spectrum of p-tolyl 4-O-acetyl-2,3-O-isopropylidene-1-thio-α-L-rhamnopyranoside (23)
'H NMR spectrum of methyl 5-acetamido-4,7-di-O-acetyl-3,5-dideoxy-8,9-O-isopropylidene-β-D-glycero-D-galacto-2-nonulopyranosonate (24)
$^{13}$C NMR spectrum of methyl 5-acetamido-4,7-di-$O$-acetyl-3,5-dideoxy-8,9-$O$-isopropylidene-$\beta$-D-glycero-D-galacto-2-nonulopyranosonate (24)$^7$
H-H COSY spectrum of methyl 5-acetamido-4,7-di-O-acetyl-3,5-dideoxy-8,9-O-isopropylidene-β-D-glycero-D-galacto-2-nonulopyranosonate (24)\textsuperscript{7}
HMQC spectrum of methyl 5-acetamido-4,7-di-O-acetyl-3,5-dideoxy-8,9-O-isopropylidene-β-D-glycero-D-galacto-2-nonulopyranosonate (24)\textsuperscript{7}
Reference:


