### **Supporting Information**

for

## Benzyne arylation of oxathiane glycosyl donors

Martin A. Fascione and W. Bruce Turnbull\*

School of Chemistry, University of Leeds, Leeds, LS2 9JT, UK.

\* Corresponding author

E-mail: W. Bruce Turnbull – <u>w.b.turnbull@leeds.ac.uk</u>

Experimental data for the synthesis of compounds 16-19, 22, 23 and 25.

#### **Experimental**

General Methods: All solvents were dried prior to use, according to standard methods [1]. Where appropriate anhydrous quality material was purchased. All solvents used for flash chromatography were GPR grade, except hexane and ethyl acetate, when HPLC grade was used. All concentrations were performed in vacuo, unless otherwise stated. All reactions were performed in oven dried glassware under a N<sub>2</sub>(g) atmosphere, unless otherwise stated. <sup>1</sup>H NMR spectra were recorded at 500 MHz on a Bruker avance 500 instrument or at 300 MHz on a Bruker avance 300 instrument. <sup>13</sup>C NMR spectra were recorded at 75 MHz on a Bruker avance 300 instrument. Chemical shifts are given in parts per million downfield from tetramethylsilane. The following abbreviations are used in <sup>1</sup>H NMR analysis: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doubledoublet, dt = double triplet, td = triple doublet, ddd = double doublet doublet. Electrospray (ES+) ionisation mass spectra were obtained on a Micromass LCT-KA111 mass spectrometer, and high resolution ES+ were performed on a Bruker Daltonics MicroTOF mass spectrometer. Melting points were obtained on a Reichert hot-stage apparatus and are uncorrected. Optical rotations were measured at the sodium D-line with an Optical Activity AA-1000 polarimeter.  $[\alpha]_D$  values are given in units of 10<sup>-1</sup> deg cm<sup>2</sup> g<sup>-1</sup>. Analytical T.L.C. was performed on silica gel 60-F<sup>254</sup> (Merck) with detection by fluorescence and/or charring following immersion in a 5% H<sub>2</sub>SO<sub>4</sub>/methanol solution, unless otherwise stated.

#### 2-(S)-Phenyl-(1,2-dideoxy-β-D-glucopyranoso)[1,2-e]-1,4-oxathiane (16)

TMSOTf (2.56 mL, 14.2 mmol) was added dropwise to a solution of 2-methoxy-2-(*S*)-phenyl-(1,2dideoxy- $\beta$ -D-glucopyranoso)[1,2-*e*]-1,4-oxathiane **13** (3.11 g, 9.4 mmol) in C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> (30 mL) at 0 °C, followed by addition of triethylsilane (2.29 mL, 14.2 mmol). After 1 h 25 min the reaction mixture was quenched with methanol (5 mL), and neutralised with triethylamine. The reaction mixture was concentrated to leave a colourless foam. The crude foam was purified by flash column chromatography (silica; 96:4 (v/v) CH<sub>2</sub>Cl<sub>2</sub>-methanol $\rightarrow$ 9:1 (v/v) CH<sub>2</sub>Cl<sub>2</sub>-methanol) to afford **16** (2.5 g, 89%) as a colourless foam; [ $\alpha$ ]<sub>D</sub><sup>23</sup>+68.3 (*c* 1.2, CHCl<sub>3</sub>); *R<sub>F</sub>* 0.28 (9:1 (v/v) CH<sub>2</sub>Cl<sub>2</sub>-methanol); IR (v<sub>max</sub>/cm<sup>-1</sup>): 3374 (OH); <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>); 7.38-7.32 (m, 5H, ArH), 4.69 (dd, 1H, *J*<sub>PhCH,SCHax</sub> 10.8 Hz, *J*<sub>PhCH,SCHeq</sub> 1.6 Hz, PhCH), 4.47 (d, 1H, *J*<sub>1,2</sub> 8.9 Hz, H-1), 3.94 (dd, 1H, *J*<sub>6,6</sub> 12.0 Hz, *J*<sub>5,6</sub> 3.3 Hz, H-6), 3.83 (dd, 1H, *J*<sub>6,6</sub> 12.0 Hz, *J*<sub>5,6</sub> 4.9 Hz, H-6'), 3.73 (dd, 1H, *J*<sub>2,3</sub> 9.2 Hz, *J*<sub>3,4</sub> 9.0 Hz, H-3), 3.67 (dd, 1H, *J*<sub>3,4</sub> 9.0 Hz, *J*<sub>4,5</sub> 8.9 Hz, H-4), 3.55 (m, 1H, H-5), 3.53 (dd, 1H, *J*<sub>2,3</sub> 9.2 Hz, *J*<sub>1,2</sub> 8.9 Hz, H-2), 3.06 (dd, 1H, *J*<sub>SCHax-eq</sub> 14.1 Hz, *J*<sub>PhCH,SCHax</sub> 10.8 Hz, SCH<sub>ax</sub>), 2.82 (br s, 1H, OH), 2.75 (dd, 1H, *J*<sub>SCHax-eq</sub> 14.1 Hz, *J*<sub>PhCH,SCHeq</sub>), 2.09 (br s, 1H, OH), 1.59 (br s, 1H, OH); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>); 140.1, 128.8, 128.6, 126.0 (ArC), 83.3 (C-2), 80.4 (C-5), 80.2 (PhCH), 75.5 (C-1), 75.4 (C-3), 70.6 (C-4), 62.3 (C-6), 35.4 (SCH<sub>2</sub>); HRMS: Found [M+Na]<sup>+</sup> 321.0772, C<sub>14</sub>H<sub>18</sub>O<sub>5</sub>SNa requires 321.0767.

**2-(S)-Phenyl-(3,4,6-tri-***O***-acetyl-1,2-dideoxy-β-D-glucopyranoso)[1,2-***e***]-1,4-oxathiane (17) Acetic anhydride (1.05 mL, 11.07 mmol) was added to a solution of 2-(***S***)-phenyl-(1,2-dideoxy-β-D-glucopyranoso)[1,2-***e***]-1,4-oxathiane <b>16** (1 g, 3.35 mmol) in pyridine (10 mL), at 0 °C. The reaction mixture was stirred, allowing the temperature to rise to r.t. After 14 h 30 min, the reaction mixture was concentrated. The residue was redissolved in CH<sub>2</sub>Cl<sub>2</sub> (25 mL) and washed with 1M HCl (25 mL), aq. NaHCO<sub>3</sub> (25 mL) and aq. NaCl (25 mL). The organic phase was dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated to afford an orange foam. The crude foam was recrystallised from methanol to afford **17** (1.01 g, 72%) as colourless needles, m.p. 128.8-132.3 °C;  $[\alpha]_D^{25}$  –24.0 (*c* 0.45, CHCl<sub>3</sub>); *R<sub>F</sub>* 0.47 (1:1 (v/v) hexane-ethyl acetate); IR (v<sub>max</sub>/cm<sup>-1</sup>): 1747 (C=O); <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>); 7.36-7.26 (m, 5H, ArH), 5.28 (dd, 1H, *J*<sub>2,3</sub> 9.5 Hz, *J*<sub>3,4</sub> 9.5 Hz, H-3), 5.15 (dd, 1H, *J*<sub>3,4</sub> 9.5 Hz, *J*<sub>4,5</sub> 9.7 Hz, H-4), 4.70 (dd, 1H, *J*<sub>5,6</sub> 5.0 Hz, H-6'), 4.15 (dd, 1H, *J*<sub>6,6</sub> 12.5 Hz, *J*<sub>5,6</sub> 5.0 Hz, H-6'), 4.15 (dd, 1H, *J*<sub>1,2</sub> 9.0 Hz, *J*<sub>2,3</sub> 9.5 Hz, H-2), 2.98 (dd, 1H, *J*<sub>4,5</sub> 9.7 Hz, *J*<sub>5,6</sub> 5.0 Hz, *J*<sub>5,6</sub> 2.1 Hz, H-5), 3.75 (dd, 1H, *J*<sub>3,2</sub> 9.5 Hz, *J*<sub>2,3</sub> 9.5 Hz, H-2), 2.98 (dd, 1H, *J*<sub>3,5</sub> 9.7 Hz, *J*<sub>5,6</sub> 5.0 Hz, *J*<sub>5,6</sub> 5.0 Hz, NCH<sub>av</sub>), 2.82 (dd, 1H, *J*<sub>5,2</sub> 2.1 Hz, H-2), 2.98 (dd, 1H, *J*<sub>5,2</sub> 9.7 Hz, *J*<sub>5,6</sub> 5.0 Hz, *J*<sub>5,6</sub> 5.0 Hz, SCH<sub>av</sub>), 2.82 (dd, 1H, *J*<sub>5,2</sub> 2.1 Hz, H-2), 2.98 (dd, 1H, *J*<sub>5,2</sub> 9.7 Hz, *J*<sub>5,6</sub> 5.0 Hz, *J*<sub>5,6</sub> 5.0 Hz, SCH<sub>av</sub>), 2.82 (dd, 1H, *J*<sub>5,2</sub> 9.7 Hz, *J*<sub>5,6</sub> 5.0 Hz, SCH<sub>av</sub>), 2.82 (dd, 1H, *J*<sub>5,2</sub> 9.7 Hz, *J*<sub>5,6</sub> 5.0 Hz, H-2), 2.98 (dd, 1H, *J*<sub>5,2</sub> 9.7 Hz, *J*<sub>5,6</sub> 5.0 Hz, *J*<sub>5,6</sub> 5.0 Hz, SCH<sub>av</sub>), 2.82 (dd, 1H, *J*<sub>5,2</sub> 9.7 Hz, *J*<sub>5,6</sub> 5.0 Hz, SCH<sub>av</sub>), 2.82 (dd, 1H, *J*<sub>5,2</sub> 9.7 Hz, *J*<sub>5,6</sub> 5.0 Hz, 5.0 Hz, SCH<sub>av</sub>), 2.82 (dd, 1H, *J*<sub>5,2</sub> 9.7 Hz, *J*<sub>5,6</sub> 5.0 Hz, SCH<sub>av</sub>), 2.82 (dd, 1H, *J*<sub>5,2</sub> 9.7 Hz, *J*<sub>5,6</sub> 14.1 Hz, *J*<sub>5,6</sub> 5.0 Hz, SCH<sub>av</sub>), 2. 2.10 (s, 3H, C(O)CH<sub>3</sub>), 2.05 (s, 3H, C(O)CH<sub>3</sub>), 2.00 (s, 3H, C(O)CH<sub>3</sub>); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>); 169.5 (C=O), 139.5, 128.5, 127.9, 125.3 (ArC), 81.0 (C-2), 79.5 (PhCH), 76.6 (C-1), 75.8 (C-5), 72.9 (C-3), 68.5 (C-4), 62.1 (C-6), 35.6 (SCH<sub>2</sub>), 20.8, 20.7, 20.7 (C(O)<u>C</u>H<sub>3</sub>); HRMS: Found [M+Na]<sup>+</sup> 447.1069, C<sub>20</sub>H<sub>24</sub>O<sub>8</sub>SNa requires 447.1084.

#### 2-(S)-Phenyl-(3,4,6-tri-O-benzyl-1,2-dideoxy-β-D-glucopyranoso)[1,2-e]-1,4-oxathiane (18)

Sodium hydride (60% dispersion in oil, 560 mg, 14 mmol) was added in portions to a solution of 2-(S)-phenyl-(1,2-dideoxy- $\beta$ -D-glucopyranoso)[1,2-e]-1,4-oxathiane 16 (1.1 g, 3.69 mmol) in DMF (15 mL), at 0 °C. The reaction mixture was stirred for 5 min before benzyl bromide (1.67 mL, 14 mmol) was added dropwise. The reaction mixture was stirred, allowing the temperature to rise to r.t. After 14 h 30 min, the reaction mixture was guenched with methanol (10 mL) and concentrated. The residue was redissolved in CH<sub>2</sub>Cl<sub>2</sub> (30 mL), washed with aq. NaCl (2 x 30 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated to leave a yellow solid. The crude solid was purified by flash chromatography (silica; 3:1 hexane-ethyl acetate $\rightarrow$ 1:1 (v/v) hexane-ethyl acetate) to afford 18 as colourless needles (1.74 g, 83%), m.p. 102.9-104.5 (from 1:1 (v/v) hexane-ethyl acetate);  $[\alpha]_D^{23} + 33.6$  (c 1.14, CHCl<sub>3</sub>);  $R_F 0.71$  (1:1 (v/v) hexane-ethyl acetate); IR (v<sub>max</sub>/cm<sup>-1</sup>): 3029 (C-H), 1090 (C-OR); <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>); 7.40-7.15 (m, 20H, ArH), 4.92 (d, 1H, J 11.2 Hz, OCH<sub>2</sub>Ph), 4.86 (d, 1H, J 10.9 Hz, OCH2Ph), 4.75 (dd, 1H, JPhCH.SCHax 10.6 Hz, JPhCH.SCHeq 1.7 Hz, PhCH), 4.74 (d, 1H, J 11.2 Hz, OCH<sub>2</sub>Ph), 4.61 (d, 1H, J 12.1 Hz, OCH<sub>2</sub>Ph), 4.54 (d, 1H, J 10.9 Hz, OCH<sub>2</sub>Ph), 4.53 (d, 1H, J 12.1 Hz, OCH<sub>2</sub>Ph), 4.41 (d, 1H, J<sub>1,2</sub> 8.6 Hz, H-1), 3.79-3.70 (m, 5H, H-2, H-3, H-4, H-6, H-6'), 3.62 (m, 1H, H-5), 3.04 (dd, 1H, J<sub>SCHax-eq</sub> 14.0 Hz, J<sub>PhCH,SCHax</sub> 10.6 Hz, SCH<sub>ax</sub>), 2.79 (dd, 1H, J<sub>SCHax-eq</sub> 14.0 Hz, J<sub>PhCH.SCHea</sub> 1.7 Hz, SCH<sub>ea</sub>); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>); 140.6, 138.5, 138.1, 138.1, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.9, 127.8, 127.8, 127.0, 127.6, 125.7 (ArC), 84.8 (C-1), 83.7 (PhCH), 80.4, 80.4, 79.8, 75.6 (C-2, C-3, C-4, C-5), 75.6, 75.2, 73.6 (OCH<sub>2</sub>Ph), 68.8 (C-6), 35.5 (SCH<sub>2</sub>); HRMS: Found [M+Na]<sup>+</sup> 591.2165, C<sub>35</sub>H<sub>36</sub>O<sub>5</sub>SNa requires 591.2176.

### 1,3,4,6-Tetra-O-acetyl-2-O-[1-methoxy-1-(S)-phenyl-2-(phenylsulfanyl)-ethyl]-α-D-

### glucopyranose (19)

Lead tetraacetate (47 mg, 0.105 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (300  $\mu$ L) was added dropwise to a solution of 2methoxy-2-(S)-phenyl-(3,4,6-tri-O-acetyl-1,2-dideoxy-β-D-gluco-pyranoso)[1,2-e]-1,4-oxathiane 14 (40 mg, 88  $\mu$ mol) and 1-aminobenzotriazole (14 mg, 0.105 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (700  $\mu$ L), at -78 °C. After 30 min the temp was raised to -30 °C, and held for 35 min before raising to r.t. After a further 1h 50 min the reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (5 mL), washed with aq. NaHCO<sub>3</sub> (2 x 5 mL) and aq. NaCl (2 x 5 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated to afford a colourless syrup. The crude syrup was purified by flash chromatography (silica; 5:1 (v/v) hexane-ethyl acetate) to afford **19** (45 mg, 82%) as a colourless syrup;  $[\alpha]_D^{23}$ +81.5 (*c* 0.5, CHCl<sub>3</sub>);  $R_F$  0.66 (3:2 (v/v) hexaneethyl acetate); IR (v<sub>max</sub>/cm<sup>-1</sup>): 2918 (C-H), 1751 (C=O); <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>); 7.47-7.10 (m, 10H, ArH), 6.31 (d, 1H, J<sub>12</sub> 3.4 Hz, H-1), 5.46 (dd, 1H, J<sub>23</sub> 9.7 Hz, J<sub>34</sub> 9.7 Hz, H-3), 4.88 (dd, 1H, J<sub>3,4</sub>9.7 Hz, J<sub>4,5</sub>9.6 Hz, H-4), 4.20 (dd, 1H, J<sub>6,6'</sub> 12.4 Hz, J<sub>5,6</sub> 4.4 Hz, H-6), 3.97-3.93 (m, 2H, H-5, H-6'), 3.78 (d, 1H, J<sub>23</sub> 9.7 Hz, J<sub>12</sub> 3.4 Hz, H-2), 3.57 (d, 1H, J<sub>SCH2,SCH2'</sub> 13.1 Hz, SCH<sub>2</sub>), 3.39 (dd, 1H, J<sub>SCH2.SCH2'</sub> 13.1 Hz, SCH'<sub>2</sub>), 3.31 (s, 3H, OCH<sub>3</sub>), 2.22 (s, 3H, C(O)CH<sub>3</sub>), 2.04 (s, 3H, C(O)CH<sub>3</sub>), 2.03 (s, 3H, C(O)CH<sub>3</sub>), 2.00 (s, 3H, C(O)CH<sub>3</sub>); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>); 170.6, 170.1, 169.5, 169.2 (C=O), 137.7, 135.9, 129.8, 129.7, 128.9, 128.8, 128.7, 128.7, 128.2, 127.4, 126.2 (ArC), 104.2 (C-OMe), 91.0 (C-1), 70.9 (C-3), 69.8, 68.7, 68.4 (C-2, C-4, C-5), 61.7 (C-6), 50.2 (OCH<sub>3</sub>), 42.7 (SCH<sub>2</sub>), 21.1, 20.9, 20.6, 20.5 (C(O)<u>C</u>H<sub>3</sub>); HRMS: Found [M+Na]<sup>+</sup> 613.1706, C<sub>29</sub>H<sub>34</sub>O<sub>11</sub>SNa requires 613.1714.

#### **2-O**-Acetyl-3,4,6-tetra-O-benzyl-α-D-glucopyranose (22)[2]

Lead tetraacetate (71 mg, 0.161 mmol) in  $CH_2Cl_2$  (300 µL) was added dropwise to a solution of 2methoxy-2-(*S*)-phenyl-(3,4,6-tri-*O*-benzyl-1,2-dideoxy- $\beta$ -D-glucopyranoso)[1,2-*e*]-1,4-oxathiane **15** (80 mg, 0.134 mmol), 1-aminobenzotriazole (21.5 mg, 0.161 mmol) in  $CH_2Cl_2$  (700 µL), at -78 °C. The reaction mixture was allowed to warm to r.t and stirred for 1 h 30 min, and then quenched with aq. NaHCO<sub>3</sub> (5 mL), and diluted with CH<sub>2</sub>Cl<sub>2</sub> (5 mL). The organic layer was washed with aq. NaCl (5 mL), dried (MgSO<sub>4</sub>) and concentrated to afford a colourless oil. The crude oil was purified by flash chromatography (silica; 7:1 (v/v) hexane-ethyl acetate $\rightarrow$ 9:1 (v/v) CH<sub>2</sub>Cl<sub>2</sub>-methanol) to afford **22** (46 mg, 70%) as a colourless solid; m.p. 120-123 °C, lit.<sup>2</sup> m.p. 124-126 °C; [ $\alpha$ ]<sub>D</sub><sup>21</sup>+48.8 (*c* 0.8, CHCl<sub>3</sub>), lit.<sup>2</sup>[ $\alpha$ ]<sub>D</sub><sup>23</sup>+64 (*c* 1, CHCl<sub>3</sub>); *R<sub>F</sub>* 0.40 (2:1 (v/v) hexane-ethyl acetate); IR (v<sub>max</sub>/cm<sup>-1</sup>): 3478 (OH), 1748 (C=O); <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>); 7.35-7.14 (m, 15H, ArH), 5.39 (d, 1H, *J*<sub>1,2</sub> 3.6 Hz, H-1), 4.87 (dd, 1H, *J*<sub>2,3</sub> 10.0 Hz, *J*<sub>1,2</sub> 3.6 Hz, H-2), 4.83-4.48 (m, 6H, 3 x OCH<sub>2</sub>Ph), 4.09-4.03 (m, 2H, H-3, H-4), 3.71-3.59 (m, 3H, H-5, H-6, H-6'), 3.55-3.41 (br d, 1H, OH), 2.02 (s, 3H, C(O)CH<sub>3</sub>); m/z (ES+, %); 510.5 ([M+NH4]<sup>+</sup>);

#### 1,3,4,6-Tetra-O-acetyl-2-O-[1-(S)-phenyl-2-(phenylsulfanyl)-ethyl]-α-D-glucopyranose (23)[3]

Lead tetraacetate (125 mg, 0.28 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (500 µL) was added dropwise to a solution of 2-(*S*)-phenyl-(3,4,6-tri-*O*-acetyl-1,2-dideoxy- $\beta$ -D-glucopyranoso)[1,2-*e*]-1,4-oxathiane **17** (100 mg, 0.24 mmol), 1-aminobenzotriazole (38 mg, 0.28 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.5 mL), at -78 °C. After 10 min the reaction mixture was quenched with aq. NaHCO<sub>3</sub> (5 mL), warmed to r.t. and diluted with CH<sub>2</sub>Cl<sub>2</sub> (5 mL). The organic layer was washed with aq. NaCl (2 x 5 mL), dried (MgSO<sub>4</sub>) and concentrated to afford a colourless oil. The crude oil was purified by flash chromatography (silica; 3:2 (v/v) hexane-ethyl acetate) to afford **23** (82 mg, 62%) as a colourless syrup;  $[\alpha]_D^{23}$ +70.6 (*c* 2, CHCl<sub>3</sub>), lit.<sup>3</sup>  $[\alpha]_D^{20}$ +124.6 (*c* 0.6, CHCl<sub>3</sub>); *R<sub>F</sub>* 0.39 (2:1 (v/v) hexane-ethyl acetate); IR (v<sub>max</sub>/cm<sup>-1</sup>): 2925 (C-H), 1754 (C=O); <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>); 7.35-7.16 (m, 10H, ArH), 6.47 (d, 1H, *J*<sub>1,2</sub> 3.5 Hz, H-1), 5.39 (dd, 1H, *J*<sub>2,3</sub> 9.7 Hz, *J*<sub>3,4</sub> 9.7 Hz, H-3), 4.90 (dd, 1H, *J*<sub>3,4</sub> 9.7 Hz, *J*<sub>4,5</sub> 9.7 Hz, H-4), 4.47 (dd, 1H, *J*<sub>4,5</sub> 9.7 Hz, *J*<sub>5,6</sub> 3.7 Hz, *J*<sub>5,6</sub> 2.1 Hz, H-5), 3.99 (dd, 1H, *J*<sub>6,6</sub>· 12.4 Hz, *J*<sub>5,6</sub> 2.1 Hz, H-6), 3.58 (dd, 1H, *J*<sub>2,3</sub> 9.7 Hz, *J*<sub>1,2</sub> 3.5 Hz, H-2), 3.22 (dd, 1H, *J*<sub>SCH2,SCH2</sub>· 14.1 Hz, *J*<sub>PhCH,SCH2</sub> 8.4 Hz, SCH<sub>2</sub>), 3.04 (dd, 1H, *J*<sub>5CH2,SCH2</sub>· 14.1 Hz, *J*<sub>PhCH,SCH2</sub>· 4.5 Hz, SCH<sub>2</sub>), 2.19 (s, 3H, C(O)CH<sub>3</sub>), 2.03 (s, 3H, C(O)CH<sub>3</sub>), 1.98 (s, 3H, C(O)CH<sub>3</sub>), 1.82 (s, 3H, C(O)CH<sub>3</sub>); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>); 170.5, 170.0, 169.5, 169.2 (C=O), 139.7, 136.3, 129.2, 129.0, 128.6, 126.9, 126.1 (ArC), 88.6 (C-1), 81.4 (C-2), 74.6 (Ph<u>C</u>H), 71.1 (C-5), 69.3 (C-3), 68.0 (C-4), 61.5 (C-6), 41.5 (SCH<sub>2</sub>), 21.1, 20.6, 20.6, 20.5 (C(O)<u>C</u>H<sub>3</sub>); m/z (ES+, %); 578.2 ([M+NH<sub>4</sub>]<sup>+</sup>, 5).

# 1-*O*-Acetyl-3,4,6-tetra-*O*-benzyl-2-*O*-[1-(*S*)-phenyl-2-(phenylsulfanyl)-ethyl]-α-Dglucopyranose (25)

Lead tetraacetate (70 mg, 0.16 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (300 µL) was added dropwise to a solution of 2-(S)-phenyl-(3,4,6-tri-O-benzyl-1,2-dideoxy- $\beta$ -D-glucopyranoso)[1,2-e]-1,4-oxathiane 18 (75 mg, 0.13 mmol), 1-aminobenzotriazole (21 mg, 0.16 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (700 µL), at -78 °C. After 10 min the reaction mixture was quenched with aq. NaHCO<sub>3</sub> (5 mL), warmed to r.t. and diluted with CH<sub>2</sub>Cl<sub>2</sub> (5 mL). The organic layer was washed with aq. NaCl (2 x 5 mL), dried (MgSO<sub>4</sub>) and concentrated to afford a colourless oil. The crude oil was purified by flash chromatography (silica; 7:1 (v/v) hexane-ethyl acetate) to afford 25 (53 mg, 57%,  $\alpha$ : $\beta$ : 96:4) as a colourless syrup; IR (v<sub>max</sub>/cm<sup>-1</sup>): 2921 (C-H), 1750 (C=O); <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>); 7.35-7.06 (m, 25H, ArH), 6.44 (d, 1H, *J*<sub>1,2</sub> 3.2 Hz, H-1), 4.96 (d, 1H, *J* 11.1 Hz, OCH<sub>2</sub>Ph), 4.79 (d, 1H, *J* 11.1 Hz, OCH<sub>2</sub>Ph), 4.75 (d, 1H, J 10.4 Hz, OCH<sub>2</sub>Ph), 4.66 (dd, 1H, J<sub>PhCH.SCH2</sub> 8.1 Hz, J<sub>PhCH.SCH2</sub> 4.6 Hz, PhCH), 4.55 (d, 1H, J 12.2 Hz, OCH2Ph), 4.43 (d, 1H, J 12.2 Hz, OCH2Ph), 4.41 (d, 1H, J 10.4 Hz, OCH2Ph), 3.93 (dd, 1H, J<sub>3,4</sub> 9.6 Hz, J<sub>4,5</sub> 9.6 Hz, H-4), 3.82 (dd, 1H, J<sub>2,3</sub> 10.6 Hz, J<sub>1,2</sub> 3.2 Hz, H-2), 3.70 (dd, 1H, J<sub>6,6</sub>, 11 Hz, J<sub>5,6</sub> 3.1 Hz, H-6), 3.63-3.56 (m, 3H, H-3, H-5, H-6'), 3.27 (dd, 1H, J<sub>SCH2,SCH2'</sub> 13.6 Hz, J<sub>PhCH,SCH2</sub> 8.1 Hz, SCH<sub>2</sub>), 3.09 (dd, 1H, J<sub>SCH2,SCH2</sub> 13.6 Hz, J<sub>PhCH,SCH2</sub> 4.6 Hz, SCH<sub>2</sub>), 2.18 (s, 3H, C(O)CH<sub>3</sub>); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>); 170.0 (C=O), 139.7, 139.3, 138.5, 138.2, 137.5, 129.8, 129.3, 129.0, 128.8, 128.7, 128.4, 128.3, 128.1, 128.0, 127.8, 127.6, 126.4 (ArC), 89.4 (C-1), 81.5 (PhCH), 79.9 (C-4), 77.3 (C-3), 76.1 (C-2), 75.9, 75.6, 74.0 (OCH<sub>2</sub>Ph), 73.1 (C-5), 68.5 (C-6), 42.6 (SCH<sub>2</sub>), 21.7 (C(O)<u>C</u>H<sub>3</sub>); HRMS: Found [M+Na]<sup>+</sup> 727.2679, C<sub>43</sub>H<sub>44</sub>O<sub>7</sub>SNa requires 727.2700.

### References

- Armarego, W. L. F.; Perrin, D. D. Purification of Laboratory Chemicals. 4th ed.; Butterworth-Heinemann, 1996.
- Schmidt, R. R.; Effenberger, G. Carbohydr. Res. 1987, 171, 59–79. doi:<u>10.1016/S0008-6215(00)90879-6</u>
- Kim, J. H.; Yang, H.; Park, J.; Boons, G. J. J. Am. Chem. Soc. 2005, 127, 12090–12097. doi:<u>10.1021/ja052548h</u>