### **Supporting Information**

### [bmim][OTf] as co-solvent/promoter in room temperature reactivity-based One Pot glycosylation reactions

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#### **Experimental Procedures**

General. Chemicals were purchased from Aldrich and Fluka and used without further purification. Preactivated molecular sieves kept in an oven at 150 °C were activated in a standard Microwave (800 W) for 3 minutes (3 x 1 minute) and cooled under vacuum. Dry solvents, where necessary, where obtained by distillation using standard procedures or by passage through a column of anhydrous alumina using equipment from Anhydrous Engineering (University of Bristol) based on the Grubbs' design. Reactions requiring anhydrous conditions were performed under an atmosphere of dry nitrogen; glassware, syringes and needles were either flame dried immediately prior to use or placed in an oven (150 °C) for at least 2 hours and allowed to cool either in a desiccators or under an atmosphere of dry nitrogen; liquid reagents, solutions or solvents were added via syringe or cannula through rubber septa; solid reagents were added via Schlenk type adapters. Typical reactions were carried out in 40-50 mg scale. Reactions were monitored by TLC on Kieselgel 60 F254 (Merck). Detection was by examination under UV light (254 nm) and by charring with 10% sulfuric acid in methanol. Flash chromatography was performed using silica gel [Merck, 230-400 mesh (40-63 µm)], the crude material was applied to the column as a solution in CH<sub>2</sub>Cl<sub>2</sub> or by pre-adsorption onto silica, as appropriate. Extracts were concentrated under reduced pressure using both a Büchi rotary evaporator (bath temperatures up to 40 °C) at a pressure of either 15 mmHg (diaphragm pump) or 0.1 mmHg (oil pump), as appropriate, and a high vacuum line at room temperature. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured in the solvent stated at Varian *INOVA* 400 or 500 instruments, respectively. Chemical shifts quoted in parts per million from SiMe<sub>4</sub> and coupling constants (J) given in hertz. Multiplicities are abbreviated as: b (broad), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) or combinations thereof. Positive ion Matrix Assisted Laser Desorption Ionization Time-Of-Flight (MALDI-TOF) mass spectra were recorded using an HP-MALDI instrument using gentisic acid matrix.

*Phenyl 4,6-di-O-acetyl-2,3-di-O-benzyl-1-thio-β-D-glucopyranoside* (2f). A suspension of 2g (96 mg, 0.18 mmol) in glacial acetic acid (0.9 mL) and water (0.1 mL) was heated to 90 °C and stirred for 2 hours before the reaction was neutralised then concentrated *in vacuo*, azeotroping with toluene. The residue was dissolved in pyridine (1 mL) then 4-(dimethylamino) pyridine (1 mg, 0.05 equiv.) was added. After cooling to 0 °C, acetic anhydride (0.05 mL, 0.53 mmol, 3.0 equiv.) was added dropwise then the reaction was stirred at room temperature for 21 hours. The reaction mixture was concentrated *in vacuo*, azeotroping with toluene, and the residue purified by flash silica gel chromatography (gradient hexane/ethyl acetate, 7/3, v/v) to yield a white crystalline solid, **2f** (48 mg, 50 %); <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>) δ (ppm): 7.54-7.61 (m, 2H, Ph), 7.21-7.45 (m, 13H, Ph), 5.04 (dd, 1H,  $J_{4,3}$ =9.0 Hz,  $J_{4,5}$ =10.0 Hz, H-4), 4.90 (d, 1H,  $J_{=10.0}$  Hz,  $CH_2$ Ph), 4.72 (d, 1H, J=10.0 Hz,  $CH_2$ Ph), 4.67 (d, 1H,  $J_{1,2}$ =10.0 Hz, H-1), 4.65 (d, 1H, J=11.5 Hz,

C<u>H</u><sub>2</sub>Ph), 4.22 (dd, 1H,  $J_{6a,5}$ =6.0 Hz,  $J_{6a,6b}$ =12.0 Hz, H-6a), 4.13 (dd, 1H,  $J_{6b,5}$ =2.5 Hz,  $J_{6b,6a}$ =12.0 Hz, H-6b), 3.68 (t, 1H,  $J_{3,2}$ = $J_{3,4}$ =9.0 Hz, H-3), 3.60 (ddd, 1H,  $J_{5,6b}$ =2.5 Hz,  $J_{5,6a}$ =6.0 Hz,  $J_{5,4}$ =10.0 Hz, H-5), 3.56 (dd, 1H,  $J_{2,3}$  = 9.0 Hz,  $J_{2,1}$ = 10.0 Hz, H-2), 2.08 and 1.92 (2s, 6H, C<u>H</u><sub>3</sub>C(O)). <sup>13</sup>C-NMR: (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 170.68 (CO), 169.59 (CO), 138.0, 137.7, 133.2, 132.3, 128.9, 128.5, 128.3, 128.0, 127.8, 127.8 (10×Ph), 87.6 (C-1), 83.8 (C-3), 80.6 (C-2), 75.9 (C-5), 75.6 (<u>C</u>H<sub>2</sub>Ph), 75.5 (<u>C</u>H<sub>2</sub>Ph), 69.7 (C-4), 62.7 (C-6), 20.8 (CH<sub>3</sub> *Ac*), 20.7 (CH<sub>3</sub> *Ac*). mp: 124-126 °C, HRMS (ESI) C<sub>30</sub>H<sub>32</sub>O<sub>7</sub>S: [M+Na]<sup>+</sup> required 717.1942, found 717.1970.



Scheme 1. i) Py, Ac<sub>2</sub>O; ii) Et<sub>3</sub>SiH, TFA

3-O-acetyl-4,6-O-benzylidene-2-deoxy-1-thio-2-(2,2,2-trichloroethoxycarbonyl-amino)- $\beta$ -D-Phenyl glucopyranoside (2h). To a solution of 10 (1.0 g, 1.9 mmol) in pyridine (10 mL) acetic anhydride (10 mL) was added. The reaction mixture was stirred at r.t. for 1 hr 30 mins, after which time the reaction mixture was diluted with H<sub>2</sub>O (40 mL) and extracted with EtOAc (40 mL). The organic phase was washed with aqueous HCl (1 M, 2×40 mL), dried (MgSO<sub>4</sub>), concentrated in vacuo and co-evaporated with toluene to yield **2h** (1.0 g, 91 %) as a colourless solid; <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.50-7.48 (m, 2H, Ph), 7.42 (m, 1H, Ph), 7.35-7.32 (m, 7H, Ph), 5.50 (s, 1H, CHPh), 5.37-5.27 (m, 2H, NH + H-3) 4.83 (d, 1H, J<sub>1,2</sub>=10.0 Hz, H-1), 4.81 (d, 1H, J=12.0 Hz, CH<sub>2</sub>CCl<sub>3</sub>), 4.73 (d, 1H, J=12.0 Hz, CH2CCl3), 4.39 (dd, 1H,  $J_{6b,5}$ = 5.0 Hz,  $J_{6b,6a}$  = 11.5 Hz H-6b), 3.80 (m, 1H, H-6a), 3.68 (t, 1H,  $J_{4,3}$ =  $J_{4,5}$ = 9.5 Hz, H-4), 3.54 (m, 1H, H-2), 3.38 (m, 1H, H-5), 2.05 (s, 3H,  $CH_3C(O)$ ). <sup>13</sup>C NMR: (100 MHz, CDCl<sub>3</sub>) δ (ppm): 170.8 (CO) 154.3 (CO, *Troc*), 136.8, 132.8, 132.3, 129.2, 129.1, 128.3, 126.2 (7×Ph) 101.4 (<u>CHPh</u>), 95.5 (CH<sub>2</sub><u>C</u>Cl<sub>3</sub>), 88.1 (C-1), 78.4 (C-5), 74.6 (<u>C</u>H<sub>2</sub>CCl<sub>3</sub>), 72.4 (C-3), 70.7 (C-4), 68.4 (C-6), 55.6 (C-2), 20.8 (COCH<sub>3</sub>). m.p. 223.5-225.0 °C, Found: C, 50.14; H, 4.39; N, 2.73; Cl, 18.67; S, 5.29. C<sub>24</sub>H<sub>24</sub>Cl<sub>3</sub>NO<sub>7</sub>S requires C, 49.97; H, 4.19; N, 2.43; Cl, 18.44; S, 5.56; HRMS (ESI)  $C_{24}H_{24}Cl_3NO_7S$  [M+Na]<sup>+</sup> required 598.0231, found 598.0232 (<sup>35</sup>Cl).

*Phenyl* 3-O-acetyl-6-O-benzyl-2-deoxy-1-thio-2-(2,2,2-trichloroethoxycarbonyl-amino)-β-Dglucopyranoside (12). To a cooled (0 °C) solution of 2h (130 mg, 0.226 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.2 mL) containing 4 Å molecular sieves was added triethylsilane (0.36 mL, 2.26 mmol, 10 equiv.). TFA (0.17 mL, 2.26 mmol, 10 equiv.) was then added dropwise over 5 mins. The reaction mixture was stirred at 0 °C under N<sub>2</sub> for 30 minutes, after which time the reaction mixture was slowly quenched with saturated NaHCO<sub>3</sub> (5 mL), diluted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL). After separating from aqueous layer, the chlorinated layer was washed with H<sub>2</sub>O (2×5 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo*. The residue was purified by flash column chromatography (gradient hexane/ethyl acetate, 4/1 to 3/1, v/v) to yield **12** (110 mg, 85%) as a colourless solid. <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.53-7.49 (m, 2H, Ph), 7.38-7.31 (m, 5H Ph), 7.30-7.25 (m, 3H, Ph) 5.48 (d, 1H,  $J_{NH,2}$ =10.0 Hz, N<u>H</u>) 5.06 (dd, 1H,  $J_{3,4}$ =9.5 Hz,  $J_{3,2}$ =10.0 Hz, H-3), 4.82 (d, 1H, J=12.0 Hz, C<u>H</u><sub>2</sub>Ph), 4.75 (d, 1H,  $J_{1,2}$ =10.0 Hz, H-1), 4.72 (d, 1H, J=12.0 Hz, C<u>H</u><sub>2</sub>Ph), 4.60 (d, 1H, J=12.0 Hz, C<u>H</u><sub>2</sub>CCl<sub>3</sub>), 4.57 (d, 1H, J=12.0 Hz, C<u>H</u><sub>2</sub>CCl<sub>3</sub>), 3.81 (m, 2H, H-6), 3.75 (q, 1H,  $J_{2,1} = J_{2,3} = J_{2,NH} = 10.0$  Hz, H-2), 3.72 (t, 1H,  $J_{4,3} = J_{4,5} = 9.5$  Hz, H-4), 3.58 (dt, 1H,  $J_{5,6a} = J_{5,6b} = 4.5$  Hz,  $J_{5,4} = 9.5$  Hz, H-5), 3.18 (bs, 1H, OH), 2.08 (C<u>H</u><sub>3</sub> Ac). <sup>13</sup>C NMR: (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 171.8 (CO) 154.2 (CO, *Troc*), 137.6, 132.2, 129.0, 128.9, 128.4, 128.2, 127.9, 127.8, 127.7, 125.3 (10×Ph), 95.5 (CH<sub>2</sub>CCl<sub>3</sub>), 87.0 (C-1), 78.3 (C-5), 76.2 (C-3), 74.5 (CH2CCl<sub>3</sub>), 73.7 (CH<sub>2</sub>Ph), 70.3 (C-4), 70.1 (C-6), 54.8 (C-2), 20.9 (COCH<sub>3</sub>). m.p. 128.0-128.5 °C; HRMS (ESI) C<sub>24</sub>H<sub>26</sub>Cl<sub>3</sub>NO<sub>7</sub>S [M+Na]<sup>+</sup> required 600.0388, found 600.0404 (<sup>35</sup>Cl).

#### General protocols for glycosylation reactions

#### Typical IL promoted glycosylation procedures:

A) For activated thiophenyl donors 2a, 2d and 2e with glycosyl acceptor 3. 1-butyl-3-methyl imidazolium triflate 1 (100  $\mu$ L) was added to a stirred suspension of thioglycoside donor (2 equiv.), glycosyl acceptor (1 equiv.) and NIS (2 equiv.) in dry dichloromethane (1 mL). The mixture was left stirring at r.t. for 3 hours. TLC (hexane/ethyl acetate, 1/1, v/v) indicated completion of the reaction. The mixture was neutralized with triethylamine (2 equiv.) and concentrated under reduced pressure. The syrup mixture was then washed with diethyl ether (4×30 mL) to extract the product from the ionic liquid, which was monitored by TLC to ensure all the product was in the ether phase. Interestingly, NIS shows preferential solubility in the ionic liquid phase for 1, thus it did not extract into the ether portion. The washes were then collected and after evaporation of the solvent, the residue was further purified by flash silica gel chromatography (gradient hexane/ethyl acetate, 3/1 to 1/1, v/v) to yield the corresponding oligosaccharides 4a, 4d, 4e, 6 and 9.

B) For deactivated thiophenyl donors 10 and 12 with glycosyl acceptor 7. Trimethylsilyl triflate (0.8 equiv.) was added to a stirred suspension of 1-butyl-3-methyl imidazolium triflate 1, thioglycoside donor (2 equiv.), glycosyl acceptor (1 equiv.), molecular sieves 4 Å (100-300 mg) and NIS (2 equiv.) in dry dichloromethane (1–4 mL). The mixture was left stirring at r.t. for 6 hours. TLC (hexane/ethyl acetate, 1/1, v/v) indicated completion of the reaction. The mixture was neutralized with triethylamine (2 equiv.) and concentrated under reduced pressure. The syrup mixture was then washed with diethyl ether (4×30 mL) to extract the product from the ionic liquid, which was monitored by TLC to ensure all the product was in the ether phase. Interestingly, NIS showed preferential solubility in the [bmim][OTf] phase and it did not extract into the ether portion. The

washes were then collected and after evaporation of the solvent, the residue was further purified by flash silica gel chromatography (gradient hexane/ethyl acetate, 3/1 to 1/1, v/v) to yield the corresponding oligosaccharides **11** and **13**.

#### Characterization data for disaccharides synthesized:

*1,2:3,4-di-O-Isopropylidene-6-O-(2,3,4,6-tetra-O-benzyl-\alpha/\beta-D-glucopyranosyl)-\alpha-D-galactopyranose (4a).* Prepared following procedure A. Spectroscopic data in agreement with literature data.<sup>1</sup>

*6-O-(2-O-Acetyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl)- 1,2:3,4-di-O-isopropylidene-α-D-galactopyranose* (4d). Prepared following procedures A. Spectroscopic data in agreement with literature data.<sup>2</sup>

6-O-(6-O-Acetyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl)-1,2:3,4-di-O-isopropylidene-α-D-

*galactopyranose* (4e). Prepared following procedure A. Spectroscopic data in agreement with literature data.<sup>3</sup>

Methyl 2,3-di-O-benzyl-6-O-(2,3,4,6-tetra-O-benzyl-α/β-D-glucopyranosyl)-α-D-glucopyranoside
(6). Prepared following procedure A. Spectroscopic data in agreement with literature data.<sup>4,5</sup>
Methyl 2,3,4-tri-O-benzyl-6-O-(3,4,6-tri-O-benzyl-α/β-D-glucopyranosyl)-α-D-glucopyranoside (9).
Prepared following procedure A. Spectroscopic data in agreement with literature data.<sup>6</sup>

*Methyl* 2,3,4-tri-O-benzyl-6-O-(4,6-O-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonyl-amino)-β-D-glucopyranosyl)-α-D-glucopyranoside (11). Prepared following procedure B. <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>) δ (ppm): 7.47-7.19 (m, 20H, Ph), 5.46 (s, 1H, C<u>H</u>Ph), 5.11 (bs, 1H, N<u>H</u>Troc), 4.92 (d, 1H, *J*=11.0 Hz, C<u>H</u><sub>2</sub>Ph), 4.81 (d, 1H, *J*=11.3 Hz, C<u>H</u><sub>2</sub>Ph), 4.72 (d, 1H, *J*=12.0 Hz, C<u>H</u><sub>2</sub>CCl<sub>3</sub>), 4.71 (d, 1H, C<u>H</u><sub>2</sub>CCl<sub>3</sub>), 4.58 (d, 1H, *J*=12.2 Hz, C<u>H</u><sub>2</sub>Ph), 4.57 (d, 1H, *J*=12.0 Hz, C<u>H</u><sub>2</sub>Ph), 4.53 (d, 1H, *J*=12.0 Hz, C<u>H</u><sub>2</sub>Ph), 4.50 (d, 1H, J<sub>1,2</sub>=3.9 Hz, H-1), 4.48 (d, 1H, J<sub>1,2</sub>=8.3 Hz, H-1'), 4.24 (dd, 1H, J<sub>6b',5'</sub>=4.9 Hz, J<sub>6b',6a'</sub>=10.5 Hz, H-6b'), 4.03 (dd, 1H, J<sub>6b,5</sub>=2.0 Hz, J<sub>6b,6a</sub>=10.5 Hz, H-6b), 3.92 (t, 1H, J<sub>3,2</sub>=J<sub>3,4</sub>=9.3 Hz, H-3), 3.73-3.66 (m, 3H, H-6a', H-5, H-4'), 3.66 (dd, 1H, J<sub>6a',5'</sub>=4.2 Hz, H-6a'), 3.49 (t, 1H, J<sub>3',2'</sub>=J<sub>3',4'</sub>=8.8 Hz, H-3'), 3.40 (m, 2H, H-5', H-2'), 3.47-3.42 (m, 2H, H-4, H-2), 3.30 (s, 3H, OC<u>H</u><sub>3</sub>). <sup>13</sup>C NMR: (101 MHz, CDCl<sub>3</sub>) δ (ppm): 141.9-127.4 (4×Ph), 101.9 (CHPh), 100.7 (C-1'), 98.1 (C-1), 82.0, 81.2, 76.61, 76.3, 75.8 (CH<sub>2</sub>Ph), 74.8 (CH<sub>2</sub>Ph), 74.6 (CH<sub>2</sub>CCl<sub>3</sub>), 73.40 (CH<sub>2</sub>Ph), 69.4, 68.5 (C-6'), 68.4 (C-6), 66.2, 58.8, 55.3, 29.5 (CH<sub>3</sub>CO). HRMS (ESI) C<sub>44</sub>H<sub>48</sub>Cl<sub>3</sub>NO<sub>12</sub> [M+H]<sup>+</sup> requires 888.2320, found 888.2315.

Methyl $6-O-(3-O-acetyl-6-O-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonyl-amino)-\beta-D-glucopyranosyl)-2,3,4-tri-O-benzyl-a-D-glucopyranoside (13).Prepared following procedure B. <sup>1</sup>HNMR: (400 MHz, CDCl<sub>3</sub>) <math>\delta$  (ppm): 7.47–7.19 (m, 20H, Ph), 5.08 (m, 1H, NHTroc), 4.98 (d, 1H,

*J*=10.8 Hz, C<u>H</u><sub>2</sub>Ph), 4.84 (d, 1H, *J*=11.8 Hz, C<u>H</u><sub>2</sub>Ph), 4.79 (d, 1H, *J*=12.0 Hz, C<u>H</u><sub>2</sub>Ph), 4.78 (d, 1H, *J*=10.8 Hz, C<u>H</u><sub>2</sub>CCl<sub>3</sub>), 4.65 (d, 1H, *J*=11.8 Hz, C<u>H</u><sub>2</sub>Ph), 4.63 (d, 1H, *J*=12.0 Hz, C<u>H</u><sub>2</sub>Ph), 4.61 (d, 1H, C<u>H</u><sub>2</sub>CCl<sub>3</sub>), 4.59 (d, 1H, *J*=12.0 Hz, C<u>H</u><sub>2</sub>Ph), 4.57 (d, 1H, *J*=12.0 Hz, C<u>H</u><sub>2</sub>Ph), 4.54 (d, 1H, *J*=12.0 Hz, C<u>H</u><sub>2</sub>Ph), 4.62-4.58 (m, 1H, H-1), 4.46 (d, 1H, *J*=12.0 Hz, C<u>H</u><sub>2</sub>Ph), 4.25 (d, 1H, J<sub>1',2'</sub>=8.8 Hz, H-1'), 4.02 (dd, 1H, *J*<sub>6b',6a'</sub>=10.4 Hz, H-6b'), 3.98 (t, 1H, *J*<sub>3,2</sub> = *J*<sub>3,4</sub> = 9.3 Hz, H-3), 3.78 (dd, 1H, *J*<sub>6b,5</sub>=4.9 Hz, *J*<sub>6b,6a</sub>=10.0 Hz, H-6b), 3.76 (dd, 1H, H-6a), 3.70-3.63 (m, 4H, H-6a', H-5, H-3', H-4'), 3.68 (dd, 1H, *J*<sub>3',2'</sub>=9.3Hz, H-2'), 3.47-3.42 (m, 2H, H-4, H-2), 3.36 (s, 3H, OC<u>H</u><sub>3</sub>). <sup>13</sup>C NMR: (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 170.7 (CO), 140.2-126.5 (4×Ph), 101.3 (C-1'), 98.7 (C-1), 82.6 (C-3), 79.8, 77.3, 75.8 (<u>C</u>H<sub>2</sub>Ph), 74.4 (<u>C</u>H<sub>2</sub>Ph), 74.4 (<u>C</u>H<sub>2</sub>Ph), 73.9 (<u>C</u>H<sub>2</sub>CCl<sub>3</sub>), 73.9, 73.7 (<u>C</u>H<sub>2</sub>Ph), 60.0, 55.1 (O<u>C</u>H<sub>3</sub>), 70.6 (C-6), 67.8 (C6'), 21.9 (CH<sub>3</sub>, *Ac*). HRMS (ESI) C<sub>46</sub>H<sub>52</sub>Cl<sub>3</sub>NO<sub>13</sub>: [M+Na]<sup>+</sup> required 954.2401, found 954.2396.

#### **One pot reactions:**

# Methyl 2,3-di-O-benzyl-4-O-(2,3,4,6-tetra-O-acetyl- $\beta$ -D-glucopyranosyl)-6-O-(2,3,4,6-tetra-O-benzyl- $\alpha/\beta$ -D-glucopyranosyl)- $\alpha$ -D-glucopyranoside (14).

C) Step-wise addition of glycoside donors. 1-butyl-3-methyl imidazolium triflate 1 (100 µL) was added drop wise to a stirred suspension of activated thioglycoside donor 2a (164 mg, 0.26 mmol), glycosyl acceptor 5 (49 mg, 0.13 mmol), molecular sieves 4 Å (100 mg) and NIS (30 mg, 0.26 mmol) in dry dichloromethane (2 mL). The mixture was left stirring at r.t. for 3 hours. TLC (hexane/ethyl acetate, 1/1, v/v) indicated formation of disaccharide intermediate. Deactivated thioglycoside donor 13 (172 mg, 0.39 mmol), NIS (30 mg, 0.26 mmol) and trimethylsilyl trifluoromethanesulfonate (24 µL, 0.13 mmol) were then added to the mixture and reaction was left stirring for another 3 h until TLC showed completion of the reaction. The mixture was then neutralized with triethylamine (3 equiv.) and concentrated under reduced pressure. The syrup mixture was then washed with diethyl ether and hexane (4×30 mL) to extract the product from the ionic liquid, which was monitored by TLC to ensure all the product was in the ether phase. Interestingly, NIS shows preferential solubility in the ionic liquid phase for 1, thus it did not extract into the ether portion. The washes were then collected and after evaporation of the solvent, the residue was further purified by flash silica gel chromatography (gradient hexane/ethyl acetate, 3/1 to 1/1, v/v) to yield the corresponding oligosaccharides 14 (46 mg, 29%) as an inseparable  $\alpha/\beta$  mixture (0.45/1) colourless solid.

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>) δ (ppm): 7.47-7.19 (m, 30H, Ph), 5.14 (t, 1H, J<sub>3'',4''</sub>=9.5 Hz, H-4''), 5.06 (t, 1H, J<sub>3'',2''</sub>=9.8 Hz, H-3''), 5.03 (d, 1H, *J*=11.3 Hz, C<u>H</u><sub>2</sub>Ph), 5.00 (d, 1H, *J*=10.9 Hz, C<u>H</u><sub>2</sub>Ph), 4.96 (d, 1H, *J*=11.9 Hz, C<u>H</u><sub>2</sub>Ph), 4.91 (d, 1H, *J*=11.0 Hz, C<u>H</u><sub>2</sub>Ph), 4.85-4.67 (m, 1H, H-2''), 4.81 (d, 1H, *J*=11.9 Hz, C<u>H</u><sub>2</sub>Ph), 4.80 (m, 1H, α': H-1'), 4.75 (d, 1H, *J*=11.3 Hz, C<u>H</u><sub>2</sub>Ph), 4.72 (d, 1H, *J*=11.9

Hz, C<u>H</u><sub>2</sub>Ph), 4.72 (d, 1H, J<sub>1'',2''</sub>=6.6 Hz, H-1''), 4.64 (d, 1H, J=10.9 Hz, C<u>H</u><sub>2</sub>Ph), 4.62 (d, 1H, J<sub>1,2</sub>=3.4 Hz, H-1), 4.61 (d, 1H, J=12.2 Hz, C<u>H</u><sub>2</sub>Ph), 4.58 (d, 1H, J=10.9 Hz, C<u>H</u><sub>2</sub>Ph), 4.63 (d, 1H, J=12.0 Hz, C<u>H</u><sub>2</sub>Ph), 4.53 (d, 1H, J=11.0 Hz, C<u>H</u><sub>2</sub>Ph), 4.47 (d, 1H, J<sub>1',2'</sub>=7.8 Hz, β':H-1'), 4.13 (dd, 1H, J<sub>6b,5</sub>=2.2 Hz, J<sub>6b,6a</sub>=10.7 Hz, H-6b), 4.19 (dd, 1H, H-6a), 3.85-3.71 (m, 3H, H-2', H-3, H-4'), 3.81 (dd, 1H, H-6b'), 3.77 (m, 1H, H-5''), 3.70-3.54 (m, 3H, H-2, H-3' and H-5), 3.63 (dd, 1H, J<sub>6b'',6a''</sub>=10.0 Hz, H-6b''), 3.57 (dd, 1H, J<sub>6b'',5''</sub>=2.0 Hz, H-6a''), 3.51-3.45 (m, 2H, H-6a', H-2), 3.29 (s, 3H, α': OC<u>H</u><sub>3</sub>), 3.26 (s, 3H, β': OC<u>H</u><sub>3</sub>), 2.02, 2.01 1.95, and 1.92 (4s, 12H, C<u>H</u><sub>3</sub>CO). <sup>13</sup>C NMR: (101 MHz, CDCl<sub>3</sub>) δ (ppm): 170.8-168.6 (4× CH<sub>3</sub>CO), 126.6-127.4 (6×Ph), 103.9 (β: C-1'), 98.5 (C-1), 97.9 (C1''), 85.9 (α: C1'), 81.9, 79.9, 75.9 (CH<sub>2</sub>Ph), 75.8, 75.8, 75.3 (CH<sub>2</sub>Ph), 75.2, 75.3, 75.2 (CH<sub>2</sub>Ph), 70.6, 73.8 (C-3''), 73.9 (CH<sub>2</sub>Ph), 73.2 (CH<sub>2</sub>Ph), 71.2, 68.6 (C-4''), 69.7, 69.2 (C-6'), 68.6 (C-6''), 62.6 (C-6), 55.2 (OCH<sub>3</sub>), 20.0-21.0 (4xCH<sub>3</sub>CO) ppm. HRMS (ESI) C<sub>69</sub>H<sub>78</sub>O<sub>20</sub>: [M+Na]<sup>+</sup> required 1249.4984, found 1249.4981.

# Methyl 2,3,4-tri-O-benzyl-6-O-(3,4,6-tri-O-benzyl-2-O-(2,3,4,6-tetra-O-acetyl- $\beta$ -D-glucopyranosyl)- $\alpha/\beta$ -D-glucopyranosyl)- $\alpha$ -D-glucopyranoside (15).

C) Step-wise addition of glycoside donors. 1-butyl-3-methyl imidazolium triflate 1 (100 µL) was added drop wise to a stirred suspension of activated thioglycoside donor 8 (117 mg, 0.216 mmol.), glycosyl acceptor 7 (50 mg, 0.108 mmol), molecular sieves 4 Å (100 mg) and NIS (48.6 mg, 0.216 mmol) in dry dichloromethane (2 mL). The mixture was left stirring at r.t. for 3 hours. TLC (hexane/ethyl acetate, 1/1, v/v) indicated formation of disaccharide intermediate. Deactivated thioglycoside donor **2b** (142.6 mg, 0.324 mmol), NIS (48.6 mg, 0.216 mmol) and trimethylsilyl trifluoromethanesulfonate (20 µL, 0.108 mmol) were then added to the mixture and reaction was left stirring for another 3 h until TLC showed completion of the reaction. The mixture was then neutralized with triethylamine (50 µL) and concentrated under reduced pressure. The syrup mixture was then washed with diethyl ether and hexane  $(4 \times 30 \text{ mL})$  to extract the product from the ionic liquid, which was monitored by TLC to ensure all the product was in the ether phase. Interestingly, NIS shows preferential solubility in the ionic liquid phase for 1, thus it did not extract into the ether portion. The washes were then collected and after evaporation of the solvent, the residue was further purified by flash silica gel chromatography (gradient hexane/ethyl acetate, 3/1 to 1/1, v/v) to yield the corresponding oligosaccharides 15 (54 mg, 41%) as an inseparable  $\alpha/\beta$  mixture (0.3/1) white solid.

**D)** One Pot addition. 1-butyl-3-methyl imidazolium triflate 1 (100  $\mu$ L) was added drop wise to a stirred suspension of activated thioglycoside donor **8** (107 mg, 0.2 mmol), deactivated thioglycoside donor **2b** (131 mg, 0.3 mmol), glycosyl acceptor **7** (46 mg, 0.1 mmol) and NIS (44.6 mg, 0.2 mmol)

in dry dichloromethane (2 mL). The mixture was left stirring at RT for 3 hours. TLC (hexane/ethyl acetate, 1/1, v/v) indicated formation of disaccharide intermediate. NIS (44.6 mg, 0.2 mmol) and trimethylsilyl trifluoromethanesulfonate (18  $\mu$ L, 0.1 mmol) were then added to the mixture and reaction was left stirring for another 3 h until TLC showed completion of the reaction. The mixture was then neutralized with triethylamine (50  $\mu$ L) and concentrated under reduced pressure. The syrup mixture was then washed with diethyl ether and hexanes (4×30 mL) to extract the product from the ionic liquid, which was monitored by TLC to ensure all of the product was in the ether phase. The washes were then collected and after evaporation of the solvent, the residue was further purified by flash silica gel chromatography (gradient hexane/ethyl acetate, 3/1 to 1/1, v/v) to yield the corresponding oligosaccharide **15** (58 mg, 44%) as an inseparable  $\alpha/\beta$  mixture (0.3/1) white solid.

*Prepared following procedures C and D.* <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>) δ (ppm): 7.47-7.19 (m, 30H, Ph), 5.09 (t, 1H, J<sub>3",4"</sub>=9.3 Hz, H-4"), 5.08 (d, 1H, J=10.9 Hz, CH<sub>2</sub>Ph), 5.06 (d, 1H, J=10.9 Hz, CH<sub>2</sub>Ph), 5.03 (t, 1H, H-3''), 5.00 (d, 1H, J=11.3 Hz, CH<sub>2</sub>Ph), 4.97 (d, 1H, J=11.3 Hz, CH<sub>2</sub>Ph), 4.90-4.75 (m, 1H, H-2"), 4.86 (d, 1H, J=11.5 Hz, CH<sub>2</sub>Ph), 4.78 (d, 1H, J=11.5 Hz, CH<sub>2</sub>Ph), 4.65 (d, 1H, J=12.0 Hz, CH<sub>2</sub>Ph), 4.64 (d, 1H, J=11.5 Hz, CH<sub>2</sub>Ph), 4.62 (d, 1H, J=11.5 Hz, CH<sub>2</sub>Ph), 4.57 (d, 1H, J<sub>12</sub>=3.2 Hz, H-1), 4.55 (d, 1H, J=11.5 Hz, CH<sub>2</sub>Ph), 4.53 (d, 1H, J=11.5 Hz, CH<sub>2</sub>Ph), 4.37 (d, 1H,  $J_{1',2'}=7.8$  Hz, H-1'), 4.35 (d, 1H, J=11.5 Hz, CH<sub>2</sub>Ph), 4.20 (dd, 1H,  $J_{6b,5}=4.4$ ,  $J_{6b,5}=12.5$  Hz, H-6b), 4.13 (d, 1H, J<sub>1</sub>, 2, =7.1 Hz, H-1''), 4.09 (dd, 1H, J<sub>6b</sub>, 5, =3.2 Hz, J<sub>6b</sub>, 6a, =10.3 Hz, H-6b''), 4.06 (dd, 1H,  $J_{6b'',5''}=1.7$  Hz, H-6a''), 4.03-3.93 (m, 2H, H-2', H-3), 3.83 (d, 1H,  $J_{3',4'}=2.9$  Hz, H-4'), 3.71 (ddd, 1H, H-5''), 3.68 (m, 1H, H-6b'), 3.63 (dd, 1H, J<sub>6a.5</sub>=5.8 Hz, H-6a), 3.53 (m, 1H, H-6a'), 3.60-3.34 (m, 3H, H-2, H-3' and H-5), 3.38 (s, 3H, β: OCH<sub>3</sub>), 3.36 (s, 3H, α: OCH<sub>3</sub>), 2.01, 1.97, 1.96 and 1.88 (4s, 12H, CH<sub>3</sub>CO). <sup>13</sup>C NMR: (101 MHz, CDCl<sub>3</sub>) δ (ppm): 170.8-168.59 (4×CH<sub>3</sub>CO), 128.51-127.4 (6×Ph), 102.4 (C-1'), 101.0 (C-1''), 98.0 (C-1), 82.00, 81.89, 78.11, 75.73 (CH<sub>2</sub>Ph), 74.63 (CH<sub>2</sub>Ph), 74.83 (CH<sub>2</sub>Ph), 73.46 (CH<sub>2</sub>Ph), 73.29 (CH<sub>2</sub>Ph), 73.17 (CH<sub>2</sub>Ph), 73.39, 73.08, 72.18, 71.90, 70.12, 68.41, 55.34 (OCH<sub>3</sub>), 68.24 (C-6'), 68.14 (C-6), 62.01 (C-6''), 20.9-20.6 (4×CH<sub>3</sub>CO). HRMS (ESI)  $C_{69}H_{78}O_{20}$ : [M+Na]<sup>+</sup> required 1249.4984, found 1249.4979.

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