Supporting Information

for

Synthesis of protected precursors of chitin oligosaccharides by electrochemical polyglycosylation of thioglycosides

Md Azadur Rahman, Kana Kuroda, Hirofumi Endo, Norihiko Sasaki, Tomoaki Hamada, Hiraku Sakai and Toshiki Nokami

*Beilstein J. Org. Chem.* **2022**, *18*, 1133–1139. doi:10.3762/bjoc.18.117

Additional experimental details and compound characterization data
## Contents

1. General .......................................................... S2  
2. Synthesis of oligosaccharides by electrochemical polyglycosylation S2  
3. Optimization of electricity and electrolyte ........................................... S13  
4. Influence of reaction parameters ..................................................... S14  
5. Measurement of oxidation potential of oligosaccharides ......................... S16  
6. Electrochemical dimerization of tetrasaccharide ................................... S17  
7. Protocol modification of electrochemical polyglycosylation ..................... S18  
8. References ................................................................ S19  
9. $^1$H and $^{13}$C NMR, H,H-COSY, and HMQC spectra of oligosaccharides ...... S20
1. General

All reactions were carried out under argon atmosphere except where otherwise noted. $^1$H NMR and $^{13}$C NMR spectra were recorded on Bruker AVANCE II 600 (600 MHz for $^1$H and 150 MHz for $^{13}$C) and JEOL JNM-ECZ600 spectrometers (600 MHz for $^1$H and 150 MHz for $^{13}$C). ESI-MS spectra were recorded on a Thermo Scientific Exacti ve spectrometer. MALDI-TOF MS spectra were recorded on a Bruker Ultraflextreme spectrometer. Optical rotation data was recorded on a JASCO DIP-370 digital polarimeter. Merck TLC plates (silica gel 60 F$_{254}$) were employed for TLC analysis. Gel permeation chromatography (GPC) was used with JAI Labo Ace LC-5060 recycling preparative HPLC (eluent: CHCl$_3$). Kanto silica gel (spherical, neutral, 63–210 μm) and Sephadex LH-20 were used for silica gel chromatography and gel filtration chromatography, respectively. Rotating disk electrode voltammetry was carried out using a BAS 700c analyzer and a RRDE-3 rotating ring disk electrode. Measurements of oxidation potential of substrates ($c = 4.0$ mM) were carried out in 0.1 M Bu$_4$NTOF/CH$_2$Cl$_2$ using a glassy carbon disk working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) as a reference electrode, with a sweep rate of 10 mV/s at 2000 rpm. Compounds 1a [1], 1b [2], 1c [1], and 1d [1] were synthesized according to the reported procedures. Unless otherwise mentioned, all reagents were obtained from commercial suppliers and used without extra purification.

2. Synthesis of oligosaccharides by electrochemical polyglycosylation

The electrochemical polymerization synthesis of linear oligosaccharides (2a–7a) was carried out in an H-type divided cell (4G glass filter). The cell had a carbon felt anode (Nippon Carbon JF-20-P7) and platinum square plate (20 mm × 20 mm). Building block 1a (0.39 mmol, 218 mg), Bu$_4$NTOF (1.00 mmol, 393 mg), and CH$_2$Cl$_2$ (20 mL) were added to the anodic chamber. Trifluoromethanesulfonic acid (0.4 mmol, 35 μL), Bu$_4$NTOF (1.00 mmol, 393 mg), and CH$_2$Cl$_2$ (20 mL) were added to the cathodic chamber. The constant current (8 mA (current density: 2.0 mA/cm$^2$), 45 V (electrode distance: 4.5 cm)) was employed at −80 °C with magnetic stirring until 0.52 F/mol of the electricity was consumed. After the electrolysis, the reaction was kept stirring at −50 °C for 1 h. After that, triethylamine (0.3 mL) was added to both chambers. The solution in both chambers was collected in an “eggplant” flask, and the solvent was removed under reduced pressure. The mixture was dissolved in EtOAc and washed with water (3 × ) and brine, respectively. The solution was dried over Na$_2$SO$_4$, and the solvent was removed under reduced pressure. The crude product was purified with preparative GPC to afford linear oligosaccharides 2a ($n = 2$, 53 μmol, 52.0 mg, 27%), 3a ($n = 3$, 25 μmol, 34.7
mg, 19%), 4a (n = 4, 11 μmol, 19.3 mg, 11%), 5a (n = 5, 2.2 μmol, 5.0 mg, 3%), 6a (n = 6, 0.90 μmol, 2.4 mg, 1%), and 7a (n = 7, trace) as white solids. Recovered yield of building block 1a was 27% (58.2 mg, 106 μmol).

4-Fluorophenyl (3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (2a); TLC (Hexane:EtOAc 1:2): Rf 0.57. [α]D = −7.88 (c = 1.0, CHCl3, 26 °C). Eox = 1.76 V vs. SCE; 1H NMR (CDCl3, 600 MHz) δ 7.86–7.77 (m, 4 H), 7.76–7.72 (m, 2 H), 7.71–7.67 (m, 2 H), 7.35–7.32 (m, 6 H), 7.31–7.26 (m, 4 H), 7.22 (d, J = 7.0 Hz, 2 H), 6.82 (pseudo-t, J = 8.6 Hz, 2 H), 5.67 (dd, J = 9.9, 8.9 Hz, 1 H), 5.57 (dd, J = 10.6, 8.9 Hz, 1 H), 5.50 (d, J = 10.5 Hz, 1 H), 5.45 (d, J = 8.3 Hz, 1 H), 4.54 (d, J = 11.8 Hz, 1 H), 4.49 (d, J = 11.8 Hz, 1 H), 4.37 (d, J = 11.8 Hz, 1 H), 4.31 (d, J = 11.9 Hz, 1 H), 4.15 (pseudo-t, J = 10.3 Hz, 1 H), 4.11 (dd, J = 10.7, 8.3 Hz, 1 H), 4.03 (pseudo-t, J = 9.2 Hz, 1 H), 3.81 (td, J = 9.2, 3.2 Hz, 1 H), 3.75 (dd, J = 10.0, 4.0 Hz, 1 H), 3.66 (dd, J = 10.0, 4.9 Hz, 1 H), 3.52 (dd, J = 9.8, 2.3 Hz, 2 H), 3.49–3.43 (m, 2 H), 2.96 (d, J = 2.8 Hz, 1 H), 1.88 (s, 3 H), 1.82 (s, 3 H); 13C NMR (CDCl3, 150 MHz) δ 171.0, 170.0, 167.8, 167.3, 163.0 (d, J = 247.5 Hz), 138.2, 137.4, 136.1 (d, J = 9.0 Hz), 134.4, 134.3, 143.2, 131.7, 131.4, 131.2, 128.5, 128.3, 128.0, 127.7, 127.5, 127.4, 125.8 (d, J = 3.0 Hz), 123.7, 123.5, 115.9 (d, J = 22.5 Hz), 97.2, 82.6, 78.5, 74.1, 73.6, 73.4, 73.2, 72.7, 72.4, 71.4, 70.0, 67.8, 54.9, 53.8, 20.63, 20.61; HRMS (ESI) m/z calculated for C52H47FKN2O14S [M+K]+, 1013.2364; found, 1013.2322.

4-Fluorophenyl (3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (3a); TLC (Hexane:EtOAc 1:2): Rf 0.50. [α]D = −15.8 (c = 1.0, CHCl3, 26 °C). Eox = 1.74 V vs. SCE; 1H NMR (CDCl3, 600 MHz) δ 7.88–7.77 (m, 6 H), 7.76–7.67 (m, 6 H), 7.35–7.31 (m, 4 H), 7.30–7.26 (m, 5 H), 7.25–7.20 (m, 5 H), 7.14 (pseudo-t, J = 7.8 Hz, 2 H), 6.82 (pseudo-t, J = 8.6 Hz, 2 H), 5.58 (pseudo-t, J = 9.4 Hz, 1 H), 5.54 (td, J = 10.6, 1.6 Hz, 1 H), 5.51 (td, J = 10.6, 1.6 Hz, 1 H), 5.46 (d, J = 10.5 Hz, 1 H), 5.38 (d, J = 8.3 Hz, 1 H), 5.27 (d, J = 8.4 Hz, 1 H), 4.52 (d, J = 11.7 Hz, 1 H), 4.47 (d, J = 11.8 Hz, 1 H), 4.43 (d, J = 11.8 Hz, 1 H), 4.42 (d, J = 11.6 Hz, 1 H), 4.38 (d, J = 11.8 Hz, 1 H), 4.31 (d, J = 11.6 Hz, 1 H), 4.14 (dd, J = 9.4, 5.5 Hz, 1 H), 4.12 (dd, J = 9.4, 4.4 Hz, 1 H), 4.07 (dd, J = 10.7, 8.3 Hz, 1 H), 4.02 (dd, J = 10.4, 8.2 Hz, 1 H), 3.99 (pseudo-t, J = 9.4 Hz, 1 H), 3.79 (td, J = 9.2, 3.2 Hz, 1 H), 3.72 (dd, J = 9.9, 4.0 Hz, 1 H), 3.63 (dd, J = 9.9, 4.9 Hz, 1 H), 3.54 (d, J = 10.4 Hz, 1 H), 3.46 (dd, J = 10.7, 3.7 Hz, 1 H), 3.42 (d, J = 10.9 Hz, 2 H), 3.30 (dd, J = 11.2, 3.5 Hz, 1 H), 3.27 (dd, J = 9.2, 4.4 Hz, 1 H), 3.10 (d, J = 8.8 Hz, 1 H), 2.88 (d, J = 3.3 Hz, 1 H), 1.80 (s, 3 H), 1.71 (s, 3 H), 1.63 (s, 3 H); 13C NMR (CDCl3, 150 MHz) δ 171.0, 170.2, 170.1, 168.1, 167.8, 167.2 163.0 (d, J = 247.5 Hz), 138.2, 138.1, 137.4, 136.0 (d, J = 9.0 Hz), 134.4, 134.3, 134.1, 131.7, 131.2, 128.5, 128.2, 128.1, 127.9, 127.6,
HRMS (ESI) m/z calculated for C_{75}H_{68}FN_{12}O_{21}S [M+K]^+; 1436.3682; found, 1436.3613.

4-Fluorophenyl (3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (4a); TLC (Hexane:EtOAc 1:2): Rf 0.37. [α]_{D}^{22} = –22.9 (c = 1.1, CHCl₃, 24 °C). [1H NMR (CDCl₃, 600 MHz) δ 7.89–7.65 (m, 16 H), 7.35–7.26 (m, 9 H), 7.25–7.17 (m, 7 H), 7.10 (pseudo-t, J = 7.8 Hz, 2 H), 6.99 (pseudo-t, J = 7.8 Hz, 2 H), 6.94 (pseudo-t, J = 7.2 Hz, 1 H), 6.82 (pseudo-t, J = 8.4 Hz, 2 H), 6.69 (pseudo-t, J = 7.2 Hz, 1 H), 5.57 (dd, J = 10.2, 9.0 Hz, 1 H), 5.49 (dd, J = 10.8, 9.0 Hz, 1 H), 5.48–5.44 (m, 3 H), 5.34 (d, J = 8.4 Hz, 1 H), 5.21 (d, J = 8.4 Hz, 1 H), 5.18 (d, J = 8.4 Hz, 1 H), 4.52 (d, J = 11.4 Hz, 1 H), 4.47 (d, J = 11.4 Hz, 1 H), 4.45–4.33 (m, 5 H), 4.32 (d, J = 11.4 Hz, 1 H), 4.14 (d, J = 10.8 Hz, 1 H), 4.10 (d, J = 9.0 Hz, 1 H), 4.09–3.95 (m, 5 H), 3.77 (pseudo-t, J = 9.6 Hz, 1 H), 3.71 (dd, J = 10.2, 4.2 Hz, 1 H), 3.62 (dd, J = 9.6, 4.8 Hz, 1 H), 3.53 (d, J = 9.6 Hz, 1 H), 3.47–3.43 (m, 2 H), 3.41–3.37 (m, 2 H), 3.26–3.20 (m, 3 H), 3.01 (dd, J = 9.6, 1.8 Hz, 1 H), 2.86 (s, 1 H), 2.79 (d, J = 9.0 Hz, 1 H), 1.87 (s, 3 H), 1.79 (s, 3 H), 1.73 (s, 3 H), 1.67 (s, 3 H); 13C NMR (CDCl₃, 150 MHz) δ 171.0, 170.4, 170.3, 170.2, 168.2, 167.8, 167.3, 163.0 (d, J = 247.2 Hz), 138.3, 138.19, 138.17, 137.5, 136.0 (d, J = 8.7 Hz), 134.5, 134.4, 134.3, 134.2, 131.7, 131.5, 131.2, 128.6, 128.3, 128.11, 128.03, 127.97, 127.7, 127.5, 127.3, 127.2, 127.0, 126.0 (d, J = 3.3 Hz), 123.7, 123.63, 123.58, 123.45, 123.39, 115.9 (d, J = 20.9 Hz), 96.60, 96.56, 96.0, 82.7, 78.5, 73.9, 73.8, 73.6, 73.38, 73.33, 73.1, 73.0, 72.6, 72.33, 72.30, 72.1, 71.8, 71.3, 70.8, 69.9, 67.9, 67.5, 55.4, 55.2, 55.0, 53.8, 20.67, 20.65, 20.53; HRMS (ESI) m/z calculated for C_{88}H_{69}FNaNO_{23}S [M+Na]^+; 1843.5260; found, 1843.5217.

4-Fluorophenyl (3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (5a); TLC (Hexane:EtOAc 1:2): Rf 0.28. [α]_{D}^{22} = –27.0 (c = 1.2, CHCl₃, 25 °C); [1H NMR (CDCl₃, 600 MHz) δ 7.89–7.64 (m, 20 H), 7.34–7.25 (m, 10 H), 7.23–7.14 (m, 9 H), 7.07 (pseudo-t, J = 7.8 Hz, 2 H), 6.92 (pseudo-t, J = 7.8 Hz, 2 H), 6.90 (pseudo-t, J = 7.8 Hz, 2 H), 6.81 (pseudo-t, J = 9.0 Hz, 2 H), 6.61 (pseudo-t, J = 7.2 Hz, 1 H), 6.55 (pseudo-t, J = 7.2 Hz, 1 H), 5.55 (dd, J = 10.2, 9.6 Hz, 1 H), 5.50–5.40 (m, 4 H), 5.36 (dd, J = 10.2, 9.0 Hz, 1 H), 5.31 (d, J = 8.4 Hz, 1 H), 5.18 (d, J = 8.4 Hz, 1 H), 5.12 (d, J = 8.4 Hz, 1 H), 5.10 (d, J = 8.4 Hz, 1 H), 4.50 (d, J = 11.4 Hz, 1 H), 4.46 (d, J = 11.4 Hz, 1 H), 4.44–4.28 (m, 8 H), 4.13–3.90 (m, 10 H), 3.75 (dd, J = 9.6, 3.6
4-Fluorophenyl (3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (6a); TLC (Hexane:EtOAc 1:2): Rf 0.20. [α]D = –28.9 (c = 0.9, CHCl3, 28 °C); 1H NMR (CDCl3, 600 MHz) δ 7.90–7.64 (m, 24 H), 7.34–7.26 (m, 9 H), 7.23–7.15 (m, 12 H), 7.08 (pseudo-t, J = 7.8 Hz, 2 H), 6.94 (pseudo-t, J = 7.8 Hz, 2 H), 6.93–6.85 (m, 4 H), 6.82 (pseudo-t, J = 8.4 Hz, 2 H), 6.61 (pseudo-t, J = 7.2 Hz, 1 H), 6.53 (pseudo-t, J = 7.8 Hz, 1 H), 6.49 (pseudo-t, J = 7.2 Hz, 1 H), 5.56 (dd, J = 10.2, 9.0 Hz, 1 H), 5.48 (dd, J = 10.8, 9.0 Hz, 1 H), 5.46–5.41 (m, 3 H), 5.38–5.31 (m, 3 H), 5.18 (d, J = 8.4 Hz, 1 H), 5.12 (d, J = 8.4 Hz, 1 H), 5.10 (d, J = 8.4 Hz, 1 H), 5.06 (d, J = 8.4 Hz, 1 H), 4.51 (d, J = 11.4 Hz, 1 H), 4.46 (d, J = 11.4 Hz, 1 H), 4.44–4.29 (m, 10 H), 4.14–3.89 (m, 12 H), 3.76 (td, J = 9.6, 3.6 Hz, 1 H), 3.70 (dd, J = 9.6, 3.6 Hz, 1 H), 3.62 (dd, J = 9.6, 4.8 Hz, 1 H), 3.52 (d, J = 10.2 Hz, 1 H), 3.45–3.35 (m, 5 H), 3.23–3.16 (m, 3 H), 3.14–3.09 (m, 2 H), 2.98 (d, J = 9.0 Hz, 1 H), 2.89 (d, J = 3.6 Hz, 1 H), 2.70 (d, J = 9.6 Hz, 1 H), 2.64 (d, J = 9.0 Hz, 1 H), 2.59 (d, J = 9.6 Hz, 1 H), 1.86 (s, 3 H), 1.78 (s, 3 H), 1.73 (s, 3 H), 1.71 (s, 3 H), 1.69 (s, 3 H), 1.65 (s, 3 H); 13C NMR (CDCl3, 150 MHz) δ 171.2, 170.34, 170.30, 170.2, 170.1, 168.0, 167.7, 167.20, 167.16, 162.9 (d, J = 247.2 Hz), 138.22, 138.13, 138.12, 138.08, 137.4, 135.9 (d, J = 7.7 Hz), 134.4, 134.29, 134.23, 134.16, 134.1, 131.6, 131.5, 131.3, 131.1, 128.5, 128.26, 128.20, 128.12, 128.0, 127.89, 127.87, 127.6, 127.42, 127.38, 127.36, 127.19, 127.15, 127.06, 126.90, 126.85, 125.9 (d, J = 3.3 Hz), 123.63, 123.54, 123.49, 123.39, 123.33, 115.8 (d, J = 21.9 Hz), 96.5, 96.4, 95.9, 95.8, 82.7, 73.8, 73.6, 73.3, 73.2, 73.0, 72.9, 72.5, 72.2, 72.0, 71.9, 71.7, 71.3, 71.2, 70.7, 70.6, 69.9, 67.8, 67.5, 67.4, 55.3, 55.2, 55.1, 54.8, 53.7, 20.58, 20.55, 20.44; HRMS (ESI) m/z calculated for C121H110FN5NaO35S [M+Na]+, 2266.6578; found, 2266.6513.
4-Fluorophenyl (3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (7a); TLC (Hexane:EtOAc 1:2): Rf 0.17.\[\alpha\]D = −28.9 (c = 0.64, CHCl3, 28°C); 1H NMR (CDCl3, 600 MHz) δ 7.89–7.66 (m, 28 H), 7.35–7.27 (m, 10 H), 7.24–7.13 (m, 13 H), 7.08 (pseudo-t, J = 7.8 Hz, 2 H), 6.94 (pseudo-t, J = 7.8 Hz, 2 H), 6.92–6.84 (m, 6 H), 6.82 (pseudo-t, J = 7.8 Hz, 2 H), 6.61 (pseudo-t, J = 7.8 Hz, 1 H), 6.52 (pseudo-t, J = 7.2 Hz, 1 H), 6.48 (pseudo-t, J = 7.8 Hz, 1 H), 6.46 (pseudo-t, J = 7.8 Hz, 1 H), 5.56 (dd, J = 10.2, 9.0 Hz, 1 H), 5.48 (dd, J = 10.8, 9.0 Hz, 1 H), 5.46–5.40 (m, 3 H), 5.37–5.30 (m, 4 H), 5.18 (d, J = 8.4 Hz, 1 H), 5.11 (d, J = 9.0 Hz, 1 H), 5.09 (d, J = 8.4 Hz, 1 H), 5.048 (d, J = 8.4 Hz, 1 H), 5.046 (d, J = 8.4 Hz, 1 H), 4.51 (d, J = 11.4 Hz, 1 H), 4.46 (d, J = 11.4 Hz, 1 H), 4.44–4.37 (m, 6 H), 4.36–4.28 (m, 6 H), 4.14–3.88 (m, 16 H), 3.79–3.74 (m, 1 H), 3.70 (dd, J = 9.6, 3.6 Hz, 1 H), 3.61 (dd, J = 10.2, 4.8 Hz, 1 H), 3.52 (d, J = 10.2 Hz, 1 H), 3.45–3.35 (m, 6 H), 3.23–3.16 (m, 3 H), 3.13–3.07 (m, 2 H), 2.97 (d, J = 9.6 Hz, 1 H), 2.87 (s, 1 H), 2.70 (d, J = 10.2 Hz, 1 H), 2.63 (d, J = 9.0 Hz, 1 H), 2.58–2.55 (m, 1 H), 1.86 (s, 3 H), 1.77 (s, 3 H), 1.73 (s, 3 H), 1.71 (s, 3 H), 1.70 (s, 3 H), 1.68 (s, 3 H), 1.64 (s, 3 H); 13C NMR (CDCl3, 150 MHz) δ 170.30, 170.43, 170.41, 170.38, 170.30, 170.2, 167.05, 167.99, 167.8, 167.73, 167.23, 167.18, 167.17, 163.0 (d, J = 247.5 Hz), 138.2, 138.11, 138.08, 138.04, 138.0, 137.4, 136.0 (d, J = 8.3 Hz), 134.39, 134.32, 134.25, 134.17, 131.6, 131.5, 131.4, 131.3, 131.1, 128.5, 128.2, 128.0, 127.91, 127.88, 127.87, 127.81, 127.6, 127.40, 127.37, 127.23, 127.21, 127.15, 127.0, 126.9, 126.84, 126.80, 125.9 (d, J = 2.9 Hz), 123.69, 123.66, 123.58, 123.52, 123.4, 115.8 (d, J = 21.9 Hz), 96.5, 96.4, 95.9, 95.7, 82.7, 78.4, 77.3, 77.0, 76.8, 73.8, 73.57, 73.53, 73.47, 73.32, 73.27, 73.0, 72.8, 72.5, 72.2, 71.9, 71.7, 71.2, 71.1, 70.72, 70.69, 70.61, 69.8, 67.8, 67.5, 67.4, 55.3, 55.12, 55.08, 54.9, 53.7, 20.59, 20.56, 20.45, 20.43; HRMS (ESI) m/z calculated for C16H152FKN+O40S [M+K]+, 3128.8954; found, 3128.8948.

Buliding block 1b (0.40 mmol, 220 mg) afforded oligosaccharides 2b (n = 2, 60 μmol, 60 mg, 30%), 3b (n = 3, 27 μmol, 40 mg, 20%), and 4b (n = 4, 14 μmol, 26 mg, 14%) as white solids. Recovered yield of buliding block 1b was 21% (47 mg, 83 μmol).

4-Chlorophenyl (3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (2b); TLC (Hexane:EtOAc 1:2): Rf 0.63. [α]D = −8.62 (c = 1.3, CHCl3, 27°C); 1H NMR (CDCl3, 600 MHz) δ 7.86–7.78 (m, 4 H), 7.76–7.68 (m, 4 H), 7.35–7.26 (m, 10 H), 7.23–7.21 (m, 2 H), 7.10–7.07 (m, 2 H), 5.68 (dd, J = 10.2, 9.0 Hz, 1 H), 5.57 (dd, J = 10.8, 9.0 Hz, 1 H), 5.54 (d, J = 10.2 Hz, 1 H), 5.49
(d, J = 8.4 Hz, 1 H), 4.55 (d, J = 12.0 Hz, 1 H), 4.49 (d, J = 12.0 Hz, 1 H), 4.37 (d, J = 12.0 Hz, 1 H), 4.31 (d, J = 11.4 Hz, 1 H), 4.18 (pseudo-t, J = 10.2 Hz, 1 H), 4.11 (dd, J = 10.8, 8.4 Hz, 1 H), 4.04 (pseudo-t, J = 8.4 Hz, 1 H), 3.84–3.79 (m, 1 H), 3.76 (dd, J = 10.2, 4.2 Hz, 1 H), 3.66 (dd, J = 9.6, 4.8 Hz, 1 H), 3.56–3.51 (m, 2 H), 3.50–3.43 (m, 2 H), 2.95 (d, J = 3.6 Hz, 1 H), 1.89 (s, 3 H), 1.82 (s, 3 H); 13C NMR (CDCl3, 150 MHz) $\delta$ 171.0, 170.0, 167.8, 167.2, 138.1, 137.3, 134.7, 134.6, 134.4, 134.3, 134.2, 131.7, 131.42, 131.39, 131.2, 129.0, 128.5, 128.3, 127.9, 127.7, 127.5, 127.3, 123.7, 123.5, 97.2, 82.4, 78.5, 74.1, 73.6, 73.5, 73.2, 72.8, 72.3, 71.3, 69.9, 67.8, 54.9, 53.9, 20.61, 20.58; HRMS (ESI) m/z calculated for C52H47ClN2NaO14S [M+Na]+, 1013.2329; found, 1013.2300.

4-Chlorophenyl (3-o-acetyl-6-o-benzyl-2-deoxy-2-phthalimido-\(\beta\)-D-glucopyranosyl)-(1→4)-(3-o-acetyl-6-o-benzyl-2-deoxy-2-phthalimido-\(\beta\)-D-glucopyranosyl)-(1→4)-3-o-acetyl-6-o-benzyl-2-deoxy-2-phthalimido-1-thio-\(\beta\)-D-glucopyranoside (3b); TLC (Hexane:EtOAc 1:2): Rf 0.57. $[\alpha]_D = -17.5$ (c = 1.3, CHCl3, 27 °C). 1H NMR (CDCl3, 600 MHz) $\delta$ 7.88–7.79 (m, 6 H), 7.76–7.67 (m, 6 H), 7.36–7.32 (m, 2 H), 7.31–7.26 (m, 7 H), 7.25–7.20 (m, 5 H), 7.15 (pseudo-t, J = 7.8 Hz, 2 H), 7.10–7.08 (m, 2 H), 7.01 (pseudo-t, J = 7.2 Hz, 1 H), 5.60 (dd, J = 10.2, 9.0 Hz, 1 H), 5.55 (dd, J = 10.2, 8.4 Hz, 1 H), 5.50 (d, J = 10.8 Hz, 1 H), 4.53 (d, J = 11.4 Hz, 1 H), 4.48 (d, J = 12.0 Hz, 1 H), 4.43 (d, J = 11.4 Hz, 1 H), 4.42 (d, J = 11.4 Hz, 1 H), 4.38 (d, J = 11.4 Hz, 1 H), 4.32 (d, J = 11.4 Hz, 1 H), 4.17 (pseudo-t, J = 10.2 Hz, 1 H), 4.13 (pseudo-t, J = 9.0 Hz, 1 H), 4.07 (dd, J = 10.8, 8.4 Hz, 1 H), 4.03 (dd, J = 10.8, 8.4 Hz, 1 H), 4.00 (pseudo-t, J = 9.0 Hz, 1 H), 3.79 (td, J = 9.6, 3.0 Hz, 1 H), 3.72 (dd, J = 10.2, 4.2 Hz, 1 H), 3.63 (dd, J = 10.2, 4.8 Hz, 1 H), 3.55 (d, J = 9.6 Hz, 1 H), 3.48 (ddd, J = 9.6, 3.6, 1.2 Hz, 1 H), 3.45–3.41 (m, 2 H), 3.31–3.25 (m, 2 H), 3.11 (dd, J = 10.2, 1.2 Hz, 1 H), 2.89 (d, J = 3.6 Hz, 1 H), 1.88 (s, 3 H), 1.80 (s, 3 H), 1.71 (s, 3 H); 13C NMR (CDCl3, 150 MHz) δ 170.9, 170.2, 170.1, 168.1, 167.7, 167.3, 167.2, 138.2, 138.0, 137.4, 134.6, 134.5, 134.4, 134.3, 134.1, 131.6, 131.5, 131.44, 131.38, 131.1, 129.5, 128.9, 128.5, 128.2, 128.1, 127.9, 127.6, 127.42, 127.39, 127.3, 127.1, 123.7, 123.5, 97.2, 82.4, 78.5, 74.0, 73.6, 73.26, 73.23, 73.1, 73.0, 72.6, 72.3, 71.1, 71.4, 71.2, 69.9, 67.9, 67.4, 55.3, 54.9, 53.8, 20.61, 20.57, 20.46; HRMS (ESI) m/z calculated for C75H68ClN3NaO21S [M+Na]+, 1436.3647; found, 1436.3621.

4-Chlorophenyl (3-o-acetyl-6-o-benzyl-2-deoxy-2-phthalimido-\(\beta\)-D-glucopyranosyl)-(1→4)-(3-o-acetyl-6-o-benzyl-2-deoxy-2-phthalimido-\(\beta\)-D-glucopyranosyl)-(1→4)-3-o-acetyl-6-o-benzyl-2-deoxy-2-phthalimido-1-thio-\(\beta\)-D-glucopyranoside (3b); TLC (Hexane:EtOAc 1:2): Rf 0.50. $[\alpha]_D = -32.9$ (c = 0.7, CHCl3, 27 °C). 1H NMR (CDCl3, 600 MHz) δ 7.90–7.65 (m, 16 H), 7.36–7.32 (m, 6 H), 7.25–7.18 (m, 8 H), 7.12–7.07 (m, 4 H), 6.99 (pseudo-t, J = 7.8 Hz, 2 H), 6.94 (pseudo-t, J = 7.8 Hz, 1 H), 6.70 (pseudo-t, J = 7.2 Hz, 1 H), 5.58 (dd, J = 10.2, 9.0 Hz, 1 H), 5.51–5.44 (m, 4
H), 5.34 (d, J = 8.4 Hz, 1 H), 5.21 (d, J = 8.4 Hz, 1 H), 5.18 (d, J = 11.4 Hz, 1 H), 4.52 (d, J = 12.0 Hz, 1 H), 4.47 (d, J = 11.4 Hz, 1 H), 4.45–4.37 (m, 4 H), 4.35 (d, J = 11.4 Hz, 1 H), 4.32 (d, J = 11.4 Hz, 1 H), 4.15 (pseudo-t, J = 10.2 Hz, 1 H), 4.09 (pseudo-t, J = 9.6 Hz, 1 H), 4.07–3.95 (m, 5 H), 3.77 (td, J = 9.0, 3.0 Hz, 1 H), 3.71 (dd, J = 10.2, 4.2 Hz, 1 H), 3.62 (dd, J = 10.2, 5.4 Hz, 1 H), 3.54 (d, J = 10.2 Hz, 1 H), 3.48–3.45 (m, 2 H), 3.41–3.38 (m, 2 H), 3.26–3.21 (m, 3 H), 3.01 (dd, J = 10.2, 1.8 Hz, 1 H), 2.86 (d, J = 3.0 Hz, 1 H), 2.79 (dd, J = 10.2, 1.2 Hz, 1 H), 1.87 (s, 3 H), 1.79 (s, 3 H), 1.73 (s, 3 H), 1.67 (s, 3 H); 13C NMR (CDCl3, 150 MHz) δ 171.9, 170.3, 170.2, 170.1, 168.1, 167.7, 167.2, 167.1, 138.2, 138.1, 138.0, 137.4, 134.6, 134.5, 134.4, 134.3, 134.2, 134.1, 131.6, 131.5, 131.4, 131.1, 129.6, 128.9, 128.5, 128.2, 128.1, 127.9, 127.6, 127.4, 127.2, 127.0, 126.9, 126.5, 124.3, 123.5, 123.3, 123.1, 96.5, 96.4, 95.9, 82.4, 78.5, 73.9, 73.7, 73.6, 73.3, 73.1, 73.0, 72.9, 72.5, 72.3, 72.2, 72.0, 71.6, 71.4, 71.2, 70.7, 69.9, 67.8, 64.7, 55.3, 52.5, 52.4, 52.3, 20.6, 20.5, 20.4; HRMS (ESI) m/z calculated for C98H89ClN4NaO28S [M+Na]+, 1859.4965; found, 1859.4932.

Building block 1c (0.20 mmol, 110 mg) afforded oligosaccharides 2c (n = 2, 17 μmol, 16 mg, 17%), 3c (n = 3, 6.0 μmol, 8.3 mg, 9%), and 4c (n = 4, 0.99 μmol, 1.8 mg, 2%) as white solids. Recovered yield of building block 1c was 49% (53.3 mg, 97 μmol).

4-Methylphenyl (3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (2c); TLC (Hexane:EtOAc 1:2): Rf 0.50. [α]D = −6.37 (c = 1.6, CHCl3, 27 °C); 1H NMR (CDCl3, 600 MHz) δ 7.87–7.71 (m, 4 H), 7.75–7.71 (m, 2 H), 7.71–7.66 (m, 2 H), 7.35–7.27 (m, 8 H), 7.23 (d, J = 7.8 Hz, 2 H), 7.21 (d, J = 8.4 Hz, 2 H), 6.94 (d, J = 7.8 Hz, 2 H), 5.68 (dd, J = 10.2, 9.0 Hz, 1 H), 5.57 (dd, J = 10.8, 9.0 Hz, 1 H), 5.52 (d, J = 10.8 Hz, 1 H), 5.45 (d, J = 8.4 Hz, 1 H), 4.54 (d, J = 12.0 Hz, 1 H), 4.49 (d, J = 12.0 Hz, 1 H), 4.37 (d, J = 12.0 Hz, 1 H), 4.32 (d, J = 12.0 Hz, 1 H), 4.18 (pseudo-t, J = 10.2 Hz, 1 H), 4.11 (dd, J = 10.8, 8.4 Hz, 1 H), 4.04 (pseudo-t, J = 9.0 Hz, 1 H), 3.84–3.78 (m, 1 H), 3.75 (dd, J = 9.6, 3.6 Hz, 1 H), 3.65 (dd, J = 10.2, 5.4 Hz, 1 H), 3.54–3.50 (m, 2 H), 3.48–3.43 (m, 2 H), 2.96 (d, J = 3.0 Hz, 1 H), 2.25 (s, 3 H), 1.88 (s, 3 H), 1.82 (s, 3 H); 13C NMR (CDCl3, 150 MHz) δ 170.9, 170.0, 167.8, 167.3, 138.4, 138.2, 137.4, 134.3, 134.2, 134.1, 133.8, 131.7, 131.4, 131.2, 129.5, 128.5, 128.2, 127.9, 127.7, 127.4, 127.1, 123.6, 97.2, 82.7, 78.6, 74.1, 73.6, 73.5, 73.2, 72.7, 72.5, 89.0, 127.3, 120.7, 114.1, 113.8, 109.2, 102.9, 101.6, 97.2, 82.7, 78.6, 74.1, 73.6, 73.5, 73.2, 72.7, 72.5, 71.3, 70.0, 67.8, 54.9, 54.0, 21.1, 20.6; HRMS (ESI) m/z calculated for C53H50N2NaO14S [M+Na]+, 993.2875; found, 993.2875.
4-Methylphenyl (3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3-O-acetyl-6-O-benzyl-1-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (3c); TLC (Hexane:EtOAc 1:2): Rf 0.57. [α]D

= −17.9 (c = 1.7, CHCl3, 27 °C); 1H NMR (CDCl3, 600 MHz) δ 7.89–7.77 (m, 6 H), 7.76–7.66 (m, 6 H), 7.36–7.32 (m, 2 H), 7.31–7.27 (m, 5 H), 7.24–7.20 (m, 7 H), 7.13 (pseudo-t, J = 7.8 Hz, 2 H), 6.99 (pseudo-t, J = 7.2 Hz, 1 H), 6.94 (d, J = 7.8 Hz, 2 H), 5.60 (dd, J = 10.2, 9.0 Hz, 1 H), 5.55 (dd, J = 10.8, 9.0 Hz, 1 H), 5.51 (dd, J = 10.2, 8.4 Hz, 1 H), 5.48 (d, J = 10.8 Hz, 1 H), 5.38 (d, J = 8.4 Hz, 1 H), 5.27 (d, J = 7.8 Hz, 1 H), 4.53 (d, J = 11.4 Hz, 1 H), 4.48 (d, J = 12.0 Hz, 1 H), 4.44–4.38 (m, 3 H), 4.32 (d, J = 11.4 Hz, 1 H), 4.17 (pseudo-t, J = 10.8 Hz, 1 H), 4.12 (pseudo-t, J = 9.0 Hz, 1 H), 4.07 (dd, J = 10.8, 8.4 Hz, 1 H), 4.03–3.99 (m, 2 H), 3.79 (td, J = 9.0, 3.0 Hz, 1 H), 3.72 (dd, J = 10.2, 4.2 Hz, 1 H), 3.63 (dd, J = 9.6, 4.8 Hz, 1 H), 3.55 (d, J = 10.2 Hz, 1 H), 3.46 (dd, J = 10.2, 3.6 Hz, 1 H), 3.44–3.39 (m, 2 H), 3.31–3.25 (m, 2 H), 3.09 (dd, J = 10.2, 1.2 Hz, 1 H), 2.88 (d, J = 3.6 Hz, 1 H), 2.24 (s, 3 H), 1.88 (s, 3 H), 1.80 (s, 3 H), 1.70 (s, 3 H); 13C NMR (CDCl3, 150 MHz) δ 171.0, 170.2, 170.1, 168.1, 167.7, 167.32, 167.26, 138.3, 138.1, 137.4, 134.3, 134.09, 134.05, 133.7, 131.7, 131.54, 131.45, 131.3, 129.5, 128.5, 128.0, 127.9, 127.6, 127.41, 127.39, 127.3, 127.1, 123.60, 123.55, 123.47, 123.3, 96.6, 96.5, 82.9, 78.6, 74.0, 73.6, 73.26, 73.21, 73.16, 73.09, 72.6, 72.3, 71.9, 71.4, 71.3, 69.9, 67.9, 67.3, 55.3, 54.9, 53.9, 21.1, 20.61, 20.58, 20.49; HRMS (ESI) m/z calculated for C76H71N3NaO21S [M+Na]+, 1416.4193; found, 1416.4163.

4-Methylphenyl (3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (4c); TLC (Hexane:EtOAc 1:2): Rf 0.48. [α]D

= −24.3 (c = 0.6, CHCl3, 27 °C); 1H NMR (CDCl3, 600 MHz) δ 7.90–7.84 (m, 4 H), 7.83–7.74 (m, 8 H), 7.73–7.65 (m, 4 H), 7.37–7.26 (m, 8 H), 7.25–7.18 (m, 8 H), 7.09 (d, J = 6.0 Hz, 1 H), 7.08 (d, J = 7.8 Hz, 1 H), 6.99 (pseudo-t, J = 7.8 Hz, 2 H), 6.95–6.89 (m, 3 H), 6.69 (pseudo-t, J = 7.2 Hz, 1 H), 5.58 (pseudo-t, J = 9.6 Hz, 1 H), 5.52–5.48 (m, 2 H), 5.45 (d, J = 7.8 Hz, 2 H), 5.34 (d, J = 8.4 Hz, 1 H), 5.21 (d, J = 8.4 Hz, 1 H), 5.18 (d, J = 8.4 Hz, 1 H), 4.52 (d, J = 12.0 Hz, 1 H), 4.47 (d, J = 11.4 Hz, 1 H), 4.43 (d, J = 11.4 Hz, 1 H), 4.42 (d, J = 11.4 Hz, 1 H), 4.41–4.38 (m, 2 H), 4.35 (d, J = 11.4 Hz, 1 H), 4.32 (d, J = 11.4 Hz, 1 H), 4.16 (pseudo-t, J = 10.2 Hz, 1 H), 4.12–4.02 (m, 3 H), 4.01–3.95 (m, 3 H), 3.77 (pseudo-t, J = 9.0 Hz, 1 H), 3.75–3.69 (m, 1 H), 3.62 (dd, J = 9.6, 4.8 Hz, 1 H), 3.54 (d, J = 10.8 Hz, 1 H), 3.46–3.42 (m, 2 H), 3.41–3.37 (m, 2 H), 3.26–3.19 (m, 3 H), 2.99 (d, J = 10.2 Hz, 1 H), 2.87 (s, 1 H), 2.78 (d, J = 9.6 Hz, 1 H), 2.24 (s, 3 H), 1.87 (s, 3 H), 1.79 (s, 3 H), 1.73 (s, 3 H), 1.67 (s, 3 H); 13C NMR (CDCl3, 150 MHz) δ 171.0, 170.3, 170.2, 170.1, 168.1, 167.7, 167.3, 138.4, 138.3, 138.2, 138.1, 137.4, 134.29, 134.27, 134.23, 134.19, 134.17, 134.0, 133.7, 131.7, 131.6, 131.5, 131.49, 131.46, 131.42, 131.39, 131.27, 129.5, 128.5, 128.2, 127.99, 127.96, 127.92, 127.6, 127.41, 127.38.
Buliding block 1d (0.2 mmol, 114 mg) afforded oligosaccharides 2d (n = 2, 23 μmol, 22.8 mg, 23%), 3d (n = 3, 6.7 μmol, 9.5 mg, 10%), 4d (n = 4, 4.3 μmol, 8.0 mg, 9%), and 5d (n = 5, 2.6 μmol, 5.8 mg, 6%) as white solids. Recovered yield of buliding block 1d was 37% (42 mg, 74 μmol).

2,4-Difluorophenyl (3-O-acetyl-6-O-benzyl-2-deoxy-2-thalimido-β-D-glucopyranosyl)-(1→4)-3-O-acetyl-6-O-benzyl-2-deoxy-2-thalimido-1-thio-β-D-glucopyranoside (2d); TLC (Hexane:EtOAc 1:2): Rf 0.60. [α]D = –4.06 (c = 1.4, CHCl3, 27 °C); 1H NMR (CDCl3, 600 MHz) δ 7.86–7.67 (m, 8 H), 7.46 (td, J = 8.4, 6.0 Hz, 1 H), 7.36–7.28 (m, 8 H), 7.20 (d, J = 8.4 Hz, 2 H), 6.70 (td, J = 8.4, 2.4 Hz, 1 H), 6.64 (td, J = 8.4, 2.4 Hz, 1 H), 5.66 (pseudo-t, J = 9.6 Hz, 1 H), 5.57 (dd, J = 10.8, 9.6 Hz, 1 H), 5.52 (d, J = 10.2 Hz, 1 H), 5.45 (d, J = 8.4 Hz, 1 H), 5.40 (d, J = 12.0 Hz, 1 H), 4.49 (d, J = 11.4 Hz, 1 H), 4.35 (d, J = 12.0 Hz, 1 H), 4.32 (d, J = 11.4 Hz, 1 H), 4.14–4.08 (m, 2 H), 4.03 (pseudo-t, J = 9.0 Hz, 1 H), 3.82 (td, J = 10.8, 3.6 Hz, 1 H), 3.75 (dd, J = 9.6, 3.6 Hz, 1 H), 3.66 (dd, J = 10.2, 5.4 Hz, 1 H), 3.53–3.50 (m, 2 H), 3.48 (dd, J = 9.6, 4.8 Hz, 1 H), 3.45 (dd, J = 11.4, 3.6 Hz, 1 H), 2.96 (d, J = 3.0 Hz, 1 H), 1.88 (s, 3 H), 1.82 (s, 3 H); 13C NMR (CDCl3, 150 MHz) δ 171.0, 170.0, 167.8, 167.3, 163.6 (dd, J = 250.7, 11.4 Hz), 162.8 (dd, J = 248.6, 12.3 Hz), 138.2, 137.8 (d, J = 9.3 Hz), 137.4, 134.4, 134.25, 134.17, 131.6, 131.4, 131.2, 128.5, 128.2, 127.9, 127.7, 127.5, 127.3, 123.7, 123.5, 112.9 (dd, J = 18.5, 4.1 Hz), 111.9 (dd, J = 21.3, 3.6 Hz), 104.4 (tt, J = 26.3 Hz, 97.3), 82.0, 78.6, 74.0, 73.6, 73.5, 73.2, 72.8, 70.0, 67.8, 54.9, 53.8, 26.0, 25.8; HRMS (ESI) m/z calculated for C52H46F2KN2O14S [M+K]+, 1031.2269; found, 1031.2269.

2,4-Difluorophenyl (3-O-acetyl-6-O-benzyl-2-deoxy-2-thalimido-β-D-glucopyranosyl)-(1→4)-3-O-acetyl-6-O-benzyl-2-deoxy-2-thalimido-1-thio-β-D-glucopyranoside (3d); TLC (Hexane:EtOAc 1:2): Rf 0.55. [α]D = –18.1 (c = 1.7, CHCl3, 27 °C); 1H NMR (CDCl3, 600 MHz) δ 7.88–7.67 (m, 12 H), 7.46 (td, J = 8.4, 6.6 Hz, 1 H), 7.37–7.19 (m, 12 H), 7.15 (pseudo-t, J = 7.8 Hz, 2 H), 7.02 (pseudo-t, J = 7.2 Hz, 1 H), 6.71 (td, J = 8.4, 2.4 Hz, 1 H), 6.65 (td, J = 8.4, 2.4 Hz, 1 H), 5.58 (dd, J = 9.6, 9.0 Hz, 1 H), 5.55 (dd, J = 10.8, 9.0 Hz, 1 H), 5.51 (dd, J = 10.8, 9.0 Hz, 1 H), 5.47 (d, J = 10.2 Hz, 1 H), 5.38 (d, J = 8.4 Hz, 1 H), 5.27 (d, J = 8.4 Hz, 1 H), 4.53 (d, J = 12.0 Hz, 1 H), 4.48 (d, J = 11.4 Hz, 1 H), 4.45–4.40 (m, 2 H), 4.38 (d, J = 11.4 Hz, 1 H), 4.31 (d, J = 12.0 Hz, 1 H), 4.13 (pseudo-t, J = 9.6 Hz, 1 H), 4.11–4.05 (m, 2 H), 4.02 (dd, J = 10.8, 8.4 Hz, 1 H), 4.00 (pseudo-t, J = 9.6 Hz, 1 H), 3.79 (td, J = 9.0, 3.0 Hz, 1 H), 3.72 (dd, J = 10.2, 4.2 Hz, 1 H), 3.63 (dd, J = 10.2, 4.8 Hz, 1 H), 3.54 (d, J =
10.8 Hz, 1 H), 3.48–3.40 (m, 3 H), 3.33–3.25 (m, 2 H), 3.11 (dd, \( J = 9.6, 1.2 \) Hz, 1 H), 2.88 (d, \( J = 3.6 \) Hz, 1 H), 1.88 (s, 3 H), 1.80 (s, 3 H), 1.71 (s, 3 H); \(^{13}\)C NMR (CDCl\(_3\), 150 MHz) \( \delta \) 170.9, 170.15, 170.07, 168.1, 167.7, 167.29, 167.24, 163.5 (dd, \( J = 250.5, 11.0 \) Hz), 162.6 (dd, \( J = 248.3, 12.2 \) Hz), 138.2, 138.0, 137.7 (d, \( J = 9.9 \) Hz), 137.4, 134.34, 134.27, 134.12, 131.61, 131.52, 131.44, 131.38, 131.18, 128.5, 128.24, 128.09, 127.92, 127.74, 127.5, 127.14, 123.61, 123.54, 123.46, 123.35, 113.1 (dd, \( J = 17.6, 3.3 \) Hz), 111.9 (dd, \( J = 21.8, 3.3 \) Hz), 104.4 (t, \( J = 26.3 \) Hz), 96.6, 96.5, 82.1, 78.6, 74.0, 73.6, 73.2, 73.0, 72.6, 72.3, 71.7, 71.3, 71.2, 69.9, 67.8, 67.3, 55.3, 54.9, 53.8, 20.60, 20.57, 20.45; HRMS (ESI) \( m/z \) calculated for C\(_{75}\)H\(_{67}\)F\(_2\)KN\(_3\)O\(_{21}\)S [M+K]\(^+\), 1454.3587; found, 1454.3563.

2,4-Difluorophenyl (3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-\( \beta \)-D-glucopyranosyl)-(1 - 4)-(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-\( \beta \)-D-glucopyranosyl)-(1 - 4)-(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-1-thio-\( \beta \)-D-glucopyranoside (4d)); TLC (Hexane:EtOAc 1:2): R\(_f\) 0.47. \([\alpha]\)\(_D\) = –5.00 (c = 1.4, CHCl\(_3\), 27 \(^\circ\)C); \(^1\)H NMR (CDCl\(_3\), 600 MHz) \( \delta \) 7.89–7.65 (m, 16 H), 7.46 (td, \( J = 7.8, 6.6 \) Hz, 1 H), 7.38–7.18 (m, 15 H), 7.10 (pseudo-t, \( J = 7.8 \) Hz, 1 H), 6.99 (pseudo-t, \( J = 7.8 \) Hz, 2 H), 6.95 (pseudo-t, \( J = 7.2 \) Hz, 1 H), 6.72–6.68 (m, 2 H), 6.65 (td, \( J = 8.4, 2.4 \) Hz, 1 H), 5.57 (pseudo-t, \( J = 10.2 \) Hz, 1 H), 5.51–5.43 (m, 4 H), 5.34 (d, \( J = 7.8 \) Hz, 1 H), 5.21 (d, \( J = 8.4 \) Hz, 1 H), 5.18 (d, \( J = 8.4 \) Hz, 1 H), 4.52 (d, \( J = 12.0 \) Hz, 1 H), 4.47 (d, \( J = 11.4 \) Hz, 1 H), 4.44–4.34 (m, 5 H), 4.32 (d, \( J = 11.4 \) Hz, 1 H), 4.13–3.95 (m, 7 H), 3.77 (td, \( J = 9.6, 3.0 \) Hz, 1 H), 3.71 (dd, \( J = 9.6, 3.6 \) Hz, 1 H), 3.62 (dd, \( J = 10.2, 4.8 \) Hz, 1 H), 3.52 (d, \( J = 10.2 \) Hz, 1 H), 3.49–3.35 (m, 4 H), 3.29–3.19 (m, 3 H), 3.02 (d, \( J = 10.2 \) Hz, 1 H), 2.87 (d, \( J = 3.0 \) Hz, 1 H), 2.79 (d, \( J = 10.2 \) Hz, 1 H), 1.87 (s, 3 H), 1.79 (s, 3 H), 1.73 (s, 3 H), 1.67 (s, 3 H); \(^{13}\)C NMR (CDCl\(_3\), 150 MHz) \( \delta \) 170.9, 170.3, 170.2, 168.1, 167.7, 167.2, 163.5 (dd, \( J = 249.3, 9.8 \) Hz), 162.6 (dd, \( J = 248.4, 12.2 \) Hz), 138.2, 138.11, 138.09, 137.6 (d, \( J = 8.7 \) Hz), 137.4, 134.4, 134.3, 134.2, 131.6, 131.44, 131.35, 131.2, 128.5, 128.2, 128.03, 127.96, 127.91, 127.6, 127.4, 127.3, 127.2, 127.1, 127.0, 126.31, 123.57, 123.45, 123.36, 113.1 (dd, \( J = 18.6, 4.4 \) Hz), 111.9 (dd, \( J = 21.9, 4.4 \) Hz), 104.4 (t, \( J = 26.3 \) Hz), 96.54, 96.46, 95.9, 82.1, 78.6, 73.9, 73.7, 73.6, 73.3, 73.2, 73.0, 72.9, 72.5, 72.2, 72.0, 71.7, 71.4, 71.2, 70.7, 69.9, 67.79, 67.45, 67.43, 55.3, 55.1, 54.9, 53.7, 20.60, 20.56, 20.44; HRMS (ESI) \( m/z \) calculated for C\(_{98}\)H\(_{88}\)F\(_2\)Na\(_2\)O\(_{28}\)S [M+Na]\(^+\), 1861.5166; found, 1861.5137.
2,4-Difluorophenyl (3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (5d); TLC (Hexane:EtOAc 1:2): Rf 0.40. [α]D = –27.1 (c = 1.0, CHCl3, 30 °C);

1H NMR (CDCl3, 600 MHz) δ 7.90–7.64 (m, 20 H), 7.45 (td, J = 7.8, 6.0 Hz, 1 H), 7.36–7.26 (m, 8 H), 7.25–7.15 (m, 9 H), 7.09 (pseudo-t, J = 7.2 Hz, 2 H), 6.97–6.90 (m, 4 H), 6.70 (td, J = 8.4, 2.4 Hz, 1 H), 6.66–6.61 (m, 2 H), 6.57 (pseudo-t, J = 7.8 Hz, 1 H), 5.57 (pseudo-t, J = 9.6 Hz, 1 H) 5.50–5.41 (m, 4 H), 5.37 (dd, J = 10.8, 9.6 Hz, 1 H), 5.32 (d, J = 8.4 Hz, 1 H), 5.19 (d, J = 8.4 Hz, 1 H), 5.12 (pseudo-t, J = 8.4 Hz, 2 H), 4.51 (d, J = 11.4 Hz, 1 H), 4.47 (d, J = 12.0 Hz, 1 H), 4.45–4.30 (m, 8 H), 4.10–3.91 (m, 10 H), 3.77 (td, J = 9.6, 3.6 Hz, 1 H), 3.71 (dd, J = 9.6, 3.6 Hz, 1 H), 3.62 (dd, J = 10.2, 4.8 Hz, 1 H), 3.51 (d, J = 10.8 Hz, 1 H), 3.46–3.36 (m, 4 H), 3.23–3.13 (m, 4 H), 3.00 (d, J = 10.2 Hz, 1 H), 2.85 (d, J = 2.4 Hz, 1 H), 2.72 (d, J = 9.0 Hz, 1 H), 2.61 (d, J = 9.0 Hz, 1 H), 1.88 (s, 3 H), 1.78 (s, 3 H), 1.73 (s, 3 H), 1.70 (s, 3 H), 1.65 (s, 3 H); 13C NMR (CDCl3, 150 MHz) δ 170.9, 170.35, 170.32, 170.18, 170.15, 168.0, 167.7, 167.22, 167.16, 163.5 (dd, J = 250.7, 11.3 Hz), 162.6 (dd, J = 249.1, 11.9 Hz), 138.2, 138.10, 138.08, 138.05, 137.6 (d, J = 9.0 Hz), 137.4, 134.3, 134.24, 134.22, 134.15, 134.09, 131.55, 131.48, 131.4, 131.3, 131.1, 128.46, 128.18, 128.00, 127.87, 127.86, 127.6, 127.4, 127.3, 127.19, 127.14, 127.04, 126.89, 126.84, 123.7, 123.6, 123.5, 123.4, 123.3, 113.1 (dd, J = 18.3, 3.6 Hz), 111.9 (dd, J = 22.4, 3.3 Hz), 104.3 (t, J = 25.5 Hz), 96.5, 96.4, 95.9, 95.7, 82.1, 78.5, 73.8, 73.55, 73.52, 73.2, 73.0, 72.8, 72.5, 72.2, 71.97, 71.95, 71.6, 71.2, 70.7, 70.6, 69.8, 67.7, 67.5, 67.4, 55.2, 55.0, 54.8, 53.7, 20.55, 20.52, 20.4; HRMS (ESI) m/z calculated for C121H109F2KN5O35S [M+K]+, 2300.6223; found, 2300.6287.
3. Optimization of electricity and electrolyte

**Table S1.** Optimization of electricity of electrochemical polyglycosylation.

| entry | electricity (F/mol) | yield of oligosaccharides 2a (n = 2)–7a (n = 7) |
|-------|---------------------|--------------------------------------------------|
| 1     | 0.3                 | 25% 3% trace — — — 53% 28%                       |
| 2     | 0.4                 | 32% 20% 2% — — — 63% 54%                        |
| 3     | 0.5                 | 31% 16% 7% 3% 2% — 70% 59%                      |
| 4     | 0.6                 | 33% 19% 8% — — — quant 60%                      |

**Table S2.** Optimization of electrolyte of electrochemical polyglycosylation.

| entry | electrolyte | yield of oligosaccharides 2a (n = 2)–7a (n = 7) |
|-------|-------------|--------------------------------------------------|
| 1     | Bu4N OTf    | 27% 19% 10% 3% 1% trace 73% 61%                 |
| 2     | Et4N OTf    | 41% 14% 4% trace — — 79% 59%                    |
| 3     | [BMPy] OTf  | 33% 14% 6% 1% — — 79% 54%                      |
Figure S1. Preparative recycling GPC traces of protected oligosaccharides 2a \((n = 2)\)–6a \((n = 6)\).
(a) Bu₄NOTf as electrolyte (Table S2, entry 1). (b) Et₄N OTf as electrolyte (Table S2, entry 2).

4. Influence of reaction parameters

Table S3. Effect of the anomeric leaving group on the yield of oligosaccharides (see Figure 2).

| entry | X     | oxidation potential | 2a | 3a | 4a | 5a | 6a | 7a | conv. | total |
|-------|-------|---------------------|----|----|----|----|----|----|------|-------|
| 1     | F     | 1.70 V              | 27%| 19%| 11%| 3% | 1% | trace | 73%  | 61%   |
| 2     | Cl    | 1.68 V              | 30%| 20%| 14%| —  | —  | —   | 79%  | 64%   |
| 3     | methyl| 1.47 V              | 17%| 9% | 2% | —  | —  | —   | 51%  | 28%   |
| 4     | difluoro| 1.73 V          | 23%| 10%| 7% | 6% | —  | —   | 63%  | 46%   |
Table S4. Influence of the glycosylation temperature on the yield of oligosaccharides (see Figure 3).

| entry | $T_2$  | yield of oligosaccharides | 2a | 3a | 4a | 5a | 6a | 7a | conv. | total |
|-------|--------|---------------------------|----|----|----|----|----|----|-------|-------|
| 1     | −30    |                           | 28%| 18%| 8% | 5% | 3% | 1% | 78%   | 63%   |
| 2     | −40    |                           | 26%| 16%| 9% | 7% | 4% | 1% | 84%   | 63%   |
| 3     | −50    |                           | 27%| 19%| 11%| 3% | 1% | trace| 77%   | 61%   |
| 4     | −60    |                           | 42%| 14%| 5% | 2% | 2% | —   | 79%   | 65%   |
| 5     | −80    |                           | 34%| 10%| 4% | 1% | —  | —   | 63    | 49%   |

Table S5. Influence of the temperature of anodic oxidation and glycosylation (see Figure 4).

| entry | $T_1$  | $T_2$  | yield of oligosaccharides | 2a | 3a | 4a | 5a | 6a | 7a | conv. | total |
|-------|--------|--------|---------------------------|----|----|----|----|----|----|-------|-------|
| 1     | −30    | −30    |                           | 17%| 12%| 11%| 6% | 4% | 1% | 71%   | 51%   |
| 2     | −60    | −30    |                           | 27%| 24%| 11%| 6% | 2% | —  | 82%   | 70%   |
| 3     | −60    | −60    |                           | 18%| 19%| 12%| 5% | 4% | 1% | 67%   | 59%   |
| 4     | −80    | −60    |                           | 42%| 14%| 5% | 2% | 2% | —  | 79%   | 65%   |
Table S6. Influence of the number of cycles on the yield of longer oligosaccharides (see Figure 9).

| entry | cycles | yield of oligosaccharides 2a (n = 2)–8a (n = 8) |
|-------|--------|---------------------------------|
|       |        | 2a | 3a | 4a | 5a | 6a | 7a | 8a | total |
| 1     | 1st    | 27% | 24% | 11% | 6% | 2% | —  | —  | 70%   |
| 2     | 2nd    | 29% | 20% | 11% | 7% | 5% | 3% | —  | 75%   |
| 3     | 3rd    | 22% | 17% | 11% | 8% | 6% | 5% | 3% | 72%   |

5. Measurement of oxidation potential of oligosaccharides

Figure S2. Linear sweep voltammetry of monosaccharide 1a and oligosaccharides 2a and 3a measured by rotating disk electrode.
6. Electrochemical dimerization of tetrasaccharide

The electrochemical dimerization of tetrasaccharide 4a was carried out an H-type divided cell (4G glass filter). The cell had a carbon felt anode (Nippon Carbon JF-20-P7) and platinum square plate (20 mm×20 mm). Tetrasaccharide 4a (0.1 mmol, 182 mg), Bu4NOTf (0.5 mmol, 196 mg), and CH2Cl2 (5 mL) were added to the anodic chamber. Trifluoromethanesulfonic acid (0.1 mmol, 9 µL), Bu4NOTf (0.5 mmol, 196 mg), and CH2Cl2 (5 mL) were added to the cathodic chamber. The constant current (6 mA (current density: 2.0 mA/cm²), 29 V (electrode distance: 4.5 cm)) was employed at −60 °C with magnetic stirring until 0.52 F/mol of the electricity was consumed. After the electrolysis, the reaction was kept stirring at −30 °C for 1 h. After that, triethylamine (0.2 mL) was added to both chambers. The solution in both chambers was collected in eggplant flask, and the solvent was removed under reduced pressure. The mixture was dissolved in EtOAc and washed with water (3 times) and brine, respectively. The solution was dried over Na2SO4, and the solvent was removed under reduced pressure. The crude product was purified with preparative-GPC to afford octasaccharides 8a (n = 8, trace), and recovered yield of tetrasaccharides 4a (n = 4, 0.6422 mmol, 117 mg, 64%) as white solids.
7. **Protocol modification of electrochemical polyglycosylation**

The electrochemical polymerization synthesis of linear oligosaccharides (2a–8a) was carried out in an H-type divided cell (4G glass filter). The cell had a carbon felt anode (Nippon Carbon JF-20-P7) and platinum square plate (20 mm × 20 mm). Building block 1a (0.200 mmol, 109 mg), Bu₄N OTf (1.00 mmol, 393 mg), and CH₂Cl₂ (10 mL) were added to the anodic chamber. Trifluoromethanesulfonic acid (0.200 mmol, 18 μL), Bu₄N OTf (1.00 mmol, 393 mg), and CH₂Cl₂ (10 mL) were added to the cathodic chamber. The constant current (8 mA (current density: 2.0 mA/cm²), 53 V (electrode distance: 4.5 cm)) was employed at −60 °C with magnetic stirring until 0.52 F/mol of the electricity was consumed. After the electrolysis, the reaction was kept stirring at −30 °C for 1 h. After that, building block 1a (0.400 mmol, 218 mg) dissolved in CH₂Cl₂ (2.0 mL) was subsequently added by the syringe (1.0 mL (0.200 mmol) for one cycle) at −30 °C. The reaction temperature was cooled down to −60 °C and the next cycle started. After the 2nd cycle, triethylamine (0.3 mL) was added to both chambers. The solution in both chambers was collected in an “eggplant” flask, and the solvent was removed under reduced pressure. The reaction mixture was dissolved in EtOAc and washed with water (3 ×) and brine, respectively. The solution was dried over Na₂SO₄, and the solvent was removed under reduced pressure. The crude product was purified with preparative GPC to afford linear oligosaccharides 2a (n = 2, 65 μmol, 63 mg), 3a (n = 3, 34 μmol, 47 mg), 4a (n = 4, 17 μmol, 31 mg), 5a (n = 5, 9.4 μmol, 21 mg), 6a (n = 6, 5.6 μmol, 15 mg), 7a (n = 7, 4.2 μmol, 13 mg), and 8a (n = 8, 2.3 μmol, 7.6 mg) as white solids.
4-Fluorophenyl (3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (8a); TLC (Hexane:EtOAc 1:2): Rf 0.13. [α]D = –25.8 (c = 0.9, CHCl3, 32 °C); 1H NMR (CDCl3, 600 MHz) δ 7.90–7.60 (m, 32 H), 7.36–7.25 (m, 10 H), 7.23–7.11 (m, 16 H), 7.08 (pseudo-t, J = 7.8 Hz, 2 H), 6.96–6.84 (m, 10 H), 6.81 (pseudo-t, J = 7.8 Hz, 2 H), 6.61 (pseudo-t, J = 7.2 Hz, 1 H), 6.52 (pseudo-t, J = 7.2 Hz, 1 H), 6.50–6.43 (m, 2 H), 5.56 (pseudo-t, J = 10.2 Hz, 1 H), 5.48 (dd, J = 10.2, 9.0 Hz, 1 H), 5.46–5.41 (m, 4 H), 5.38–5.30 (m, 5 H), 5.18 (d, J = 7.8 Hz, 1 H), 5.11 (d, J = 8.4 Hz, 1 H), 5.09 (d, J = 8.4 Hz, 1 H), 5.06–5.01 (m, 2 H), 4.51 (d, J = 11.4 Hz, 1 H), 4.47 (d, J = 11.4 Hz, 1 H), 4.44–4.27 (m, 14 H), 4.14–3.87 (m, 16 H), 3.76 (pseudo-t, J = 9.0 Hz, 1 H), 3.70 (dd, J = 9.6, 3.6 Hz, 1 H), 3.62 (dd, J = 9.6, 4.2 Hz, 1 H), 3.52 (d, J = 10.2 Hz, 1 H), 3.45–3.35 (m, 8 H), 3.24–3.16 (m, 4 H), 3.14–3.06 (m, 4 H), 2.97 (d, J = 9.6 Hz, 1 H), 2.70 (d, J = 10.2 Hz, 1 H), 2.63 (d, J = 9.6 Hz, 1 H), 2.60–2.54 (m, 1 H), 1.86 (s, 3 H), 1.77 (s, 3 H), 1.73 (s, 3 H), 1.703 (s, 3 H), 1.698 (s, 3 H), 1.695 (s, 3 H), 1.68 (s, 3 H), 1.64 (s, 3 H); 13C NMR (CDCl3, 150 MHz) δ 170.9, 170.4, 170.3, 170.2, 170.1, 168.0, 167.9, 167.2, 167.1, 163.0 (d, J = 247.4 Hz), 138.2, 138.12, 138.09, 138.07, 137.4, 135.9 (d, J = 8.3 Hz), 134.3, 134.23, 134.20, 134.1, 131.6, 131.55, 131.48, 131.40, 128.81, 128.78, 128.5, 128.2, 128.0, 127.89, 127.86, 127.84, 127.82, 127.78, 127.6, 127.35, 127.19, 127.17, 127.14, 127.05, 126.88, 126.82, 126.77, 126.76, 125.9, 123.66, 123.65, 123.64, 123.58, 123.54, 123.49, 123.48, 123.44, 123.36 115.8 (d, J = 21.9 Hz), 96.5, 96.4, 95.9, 95.7, 82.66, 82.65, 78.4, 73.8, 73.6, 73.5, 73.25, 73.20, 73.0, 72.8, 72.5, 72.2, 71.94, 71.91, 71.7, 71.25, 71.19, 70.7, 70.6, 69.8, 67.7, 67.45, 67.41, 66.2, 65.9, 55.25, 55.12, 55.07, 54.8, 20.56, 20.52, 20.4; HRMS (ESI) m/z calculated for C190H173FKN8O56S [M+K]+, 3552.0272; found, 3552.0203.

8. References
1 T. Nokami, Y. Isoda, N. Sasaki, A. Takaiso, S. Hayase, T. Itoh, R. Hayashi, A. Shimizu, and J. Yoshida, Org. Lett., 2015, 17, 1525-1528.
2 K. Yano, T. Itoh and T. Nokami, Carbohydr. Res., 2020, 492, 108018.
9. $^1$H and $^{13}$C NMR, H,H-COSY, and HMQC spectra of oligosaccharides

$^1$H NMR

$^{13}$C NMR
H,H-COSY

HMOCQ
$^1$H NMR

$^{13}$C NMR
H,H-COSY

HMOC
H,H-COSY

HMQCC

160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 (T housands)

10.0 30.0 50.0 (Thousandths)

X : parts per Million : Proton

Y : parts per Million : Carbon13

S29
H,H-COSY

HMQC
$^1$H NMR

$^{13}$C NMR
\textbf{\textsuperscript{1}H NMR}

\textbf{\textsuperscript{13}C NMR}
**1H NMR**

![1H NMR spectrum](image)

**13C NMR**

![13C NMR spectrum](image)
H,H-COSY

X: parts per Million : Proton
Y: parts per Million : Proton

abundance

0.1
0.2
0.3
0.4
0.5

abundance

0.1
0.2
0.3
0.4
0.5

0.6

HMQC

X: parts per Million : Carbon13
Y: parts per Million : Proton

abundance

0.1
0.2
0.3
0.4
0.5

abundance

0.1
0.2
0.3
0.4
0.5
$^1$H NMR

$^{13}$C NMR
$^1$H NMR

[Graph of $^1$H NMR spectrum]

$^{13}$C NMR

[Graph of $^{13}$C NMR spectrum]
