



Supporting Information

for

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

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Additional experimental details and compound characterization data

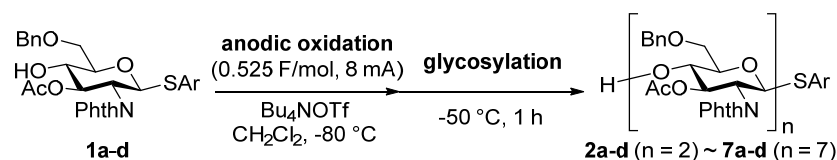
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1. General

All reactions were carried out under argon atmosphere except where otherwise noted. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE II 600 (600 MHz for ^1H and 150 MHz for ^{13}C) and JEOL JNM-ECZ600 spectrometers (600 MHz for ^1H and 150 MHz for ^{13}C). ESI-MS spectra were recorded on a Thermo Scientific Exactive 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 F₂₅₄) 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 ($c = 4.0 \text{ mM}$) were carried out in 0.1 M $\text{Bu}_4\text{NOTf}/\text{CH}_2\text{Cl}_2$ 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 $\times$ 20 mm). Building block **1a** (0.39 mmol, 218 mg), Bu_4NOTf (1.00 mmol, 393 mg), and CH_2Cl_2 (20 mL) were added to the anodic chamber. Trifluoromethanesulfonic acid (0.4 mmol, 35 μL), Bu_4NOTf (1.00 mmol, 393 mg), and CH_2Cl_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 $-80\text{ }^\circ\text{C}$ with magnetic stirring until 0.52 F/mol of the electricity was consumed. After the electrolysis, the reaction was kept stirring at $-50\text{ }^\circ\text{C}$ 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 $\times$) and brine, respectively. The solution was dried over Na_2SO_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 μ mol, 19.3 mg, 11%), **5a** ($n = 5$, 2.2 μ mol, 5.0 mg, 3%), **6a** ($n = 6$, 0.90 μ mol, 2.4 mg, 1%), and **7a** ($n = 7$, trace) as white solids. Recovered yield of buliding block **1a** was 27% (58.2 mg, 106 μ mol).

4-Fluorophenyl (3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio- β -D-glucopyranoside (2a); TLC (Hexane:EtOAc 1:2): R_f 0.57. $[\alpha]_D = -7.88$ ($c = 1.0$, CHCl₃, 26 °C). $E_{ox} = 1.76$ 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 C₅₂H₄₇FN₂O₁₄S [M+K]⁺, 1013.2364; found, 1013.2322.

4-Fluorophenyl (3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio- β -D-glucopyranoside (3a); TLC (Hexane:EtOAc 1:2): R_f 0.50. $[\alpha]_D = -15.8$ ($c = 1.0$, CHCl₃, 26 °C). $E_{ox} = 1.74$ 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,

127.4, 127.36, 127.26, 127.1 125.9 (d, $J = 3.3$ Hz), 123.6, 123.5, 115.9 (d, $J = 22.5$ Hz), 96.6, 96.5, 82.6, 78.5, 74.0, 73.6, 72.6, 72.3, 71.7, 71.4, 71.2, 70.0, 67.9, 67.3 55.3, 54.9, 53.8, 20.61, 20.57, 20.46; HRMS (ESI) m/z calculated for $C_{75}H_{68}FKN_3O_{21}S$ $[M+K]^+$, 1436.3682; found, 1436.3613.

4-Fluorophenyl (3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio- β -D-glucopyranoside (4a); TLC (Hexane:EtOAc 1:2): R_f 0.37. $[\alpha]_D = -22.9$ ($c = 1.1$, $CHCl_3$, 24 °C). 1H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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 $C_{98}H_{89}FN_4NaO_{28}S$ $[M+Na]^+$, 1843.5260; found, 1843.5217.

4-Fluorophenyl (3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio- β -D-glucopyranoside (5a); TLC (Hexane:EtOAc 1:2): R_f 0.28. $[\alpha]_D = -27.0$ ($c = 1.2$, $CHCl_3$, 25 °C); 1H NMR ($CDCl_3$, 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 (td, $J = 9.6$, 3.6

Hz, 1 H), 3.69 (dd, $J = 9.6, 3.6$ Hz, 1 H), 3.61 (dd, $J = 9.6, 4.8$ Hz, 1 H), 3.51 (d, $J = 9.6$ Hz, 1 H), 3.46–3.33 (m, 4 H), 3.23–3.12 (m, 4 H), 2.97 (d, $J = 9.0$ Hz, 1 H), 2.89 (d, $J = 3.6$ Hz, 1 H), 2.71 (d, $J = 9.0$ Hz, 1 H), 2.65 (d, $J = 8.4$ Hz, 1 H), 1.85 (s, 3 H), 1.77 (s, 3 H), 1.72 (s, 3 H), 1.69 (s, 3 H), 1.62 (s, 3 H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 170.9, 170.33, 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 $\text{C}_{121}\text{H}_{110}\text{FN}_5\text{NaO}_{35}\text{S}$ $[\text{M}+\text{Na}]^+$, 2266.6578; found, 2266.6513.

4-Fluorophenyl (3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio- β -D-glucopyranoside (6a); TLC (Hexane:EtOAc 1:2): R_f 0.20. $[\alpha]_D = -28.9$ ($c = 0.9$, CHCl_3 , 28 $^\circ\text{C}$); ^1H NMR (CDCl_3 , 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); ^{13}C NMR (CDCl_3 , 150 MHz) δ 171.2, 170.34, 170.30, 170.2, 170.1, 168.01, 167.97, 167.7, 167.2, 167.1, 162.9 (d, $J = 247.2$ Hz), 138.2, 138.15, 138.11, 138.08, 137.3, 135.9 (d, $J = 7.7$ Hz), 134.3, 134.1, 131.60, 131.56, 131.4, 131.1, 128.5, 128.2, 128.0, 127.90, 127.85, 127.80, 127.6, 127.42, 127.35, 127.26, 127.18, 127.14, 127.05, 126.82, 126.79, 125.9 (d, $J = 3.3$ Hz), 123.66, 123.54, 123.49, 123.38, 115.8 (d, $J = 21.9$ Hz), 96.49, 96.41, 95.89, 95.74, 82.7, 78.4, 73.8, 73.6, 73.5, 73.3, 73.1, 73.0, 72.5, 72.2, 71.9, 71.7, 71.3, 71.2, 70.73, 70.70, 70.6, 69.9, 67.8, 67.5, 67.4, 55.27, 55.14, 55.11, 55.08, 54.8, 53.7, 20.58, 20.55, 20.44; HRMS (ESI) m/z calculated for $\text{C}_{144}\text{H}_{131}\text{FN}_6\text{NaO}_{42}\text{S}$ $[\text{M}+\text{Na}]^+$, 2689.7896; found, 2689.7849.

4-Fluorophenyl (3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio- β -D-glucopyranoside (7a); TLC (Hexane:EtOAc 1:2): R_f 0.17. $[\alpha]_D = -28.9$ ($c = 0.64$, CHCl_3 , 28 °C); ^1H NMR (CDCl_3 , 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); ^{13}C NMR (CDCl_3 , 150 MHz) δ 171.0, 170.43, 170.41, 170.38, 170.30, 170.2, 168.05, 167.99, 167.8, 167.3, 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, 127.18, 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 $\text{C}_{167}\text{H}_{152}\text{FKN}_7\text{O}_{49}\text{S}$ $[\text{M}+\text{K}]^+$, 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 $\rightarrow$ 4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio- β -D-glucopyranoside (2b); TLC (Hexane:EtOAc 1:2): R_f 0.63. $[\alpha]_D = -8.62$ ($c = 1.3$, CHCl_3 , 27 °C); ^1H NMR (CDCl_3 , 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); ^{13}C NMR (CDCl_3 , 150 MHz) δ 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, 129.4, 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 $\text{C}_{52}\text{H}_{47}\text{ClN}_2\text{NaO}_{14}\text{S}$ $[\text{M}+\text{Na}]^+$, 1013.2329; found, 1013.2300.

4-Chlorophenyl (3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio- β -D-glucopyranoside (3b); TLC (Hexane:EtOAc 1:2): R_f 0.57. $[\alpha]_D = -17.5$ ($c = 1.3$, CHCl_3 , 27 $^\circ\text{C}$); ^1H NMR (CDCl_3 , 600 MHz) δ 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), 5.52 (dd, $J = 10.8, 9.0$ Hz, 1 H), 5.50 (d, $J = 10.8$ Hz, 1 H), 5.38 (d, $J = 8.4$ Hz, 1 H), 5.27 (d, $J = 8.4$ Hz, 1 H), 4.53 (d, $J = 11.4$ 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); ^{13}C NMR (CDCl_3 , 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, 123.4, 96.6, 96.5, 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 $\text{C}_{75}\text{H}_{68}\text{ClN}_3\text{NaO}_{21}\text{S}$ $[\text{M}+\text{Na}]^+$, 1436.3647; found, 1436.3621.

4-Chlorophenyl (3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio- β -D-glucopyranoside (4b); TLC (Hexane:EtOAc 1:2): R_f 0.50. $[\alpha]_D = -32.9$ ($c = 0.7$, CHCl_3 , 27 $^\circ\text{C}$); ^1H NMR (CDCl_3 , 600 MHz) δ 7.90–7.65 (m, 16 H), 7.36–7.32 (m, 2 H), 7.30–7.26 (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, $J = 8.4$ 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); ^{13}C NMR (CDCl_3 , 150 MHz) δ 171.9, 170.3, 170.2, 170.1, 168.1, 167.7, 167.23, 167.18, 138.20, 138.11, 138.09, 137.4, 134.58, 134.47, 134.37, 134.29, 134.17, 134.12, 131.6, 131.5, 131.4, 131.1, 129.6, 128.9, 128.5, 128.2, 128.1, 127.95, 127.92, 127.6, 127.4, 127.21, 127.18, 127.07, 126.97, 123.7, 123.54, 123.51, 123.36, 123.31, 96.52, 96.46, 95.9, 82.4, 78.5, 73.9, 73.7, 73.6, 73.3, 73.13, 73.07, 72.9, 72.5, 72.3, 72.2, 72.0, 71.6, 71.4, 71.2, 70.7, 69.9, 67.8, 67.4, 55.3, 55.2, 54.8, 53.7, 20.60, 20.57, 20.45; HRMS (ESI) m/z calculated for $\text{C}_{98}\text{H}_{89}\text{ClN}_4\text{NaO}_{28}\text{S}$ $[\text{M}+\text{Na}]^+$, 1859.4965; found, 1859.4932.

Buliding 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 buliding 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 $\rightarrow$ 4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio- β -D-glucopyranoside (2c); TLC (Hexane:EtOAc 1:2): R_f 0.50. $[\alpha]_D = -6.37$ ($c = 1.6$, CHCl_3 , 27 $^\circ\text{C}$); ^1H NMR (CDCl_3 , 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).; ^{13}C NMR (CDCl_3 , 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, 123.5, 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 $\text{C}_{53}\text{H}_{50}\text{N}_2\text{NaO}_{14}\text{S}$ $[\text{M}+\text{Na}]^+$, 993.2875; found, 993.2875.

4-Methylphenyl (3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio- β -D-glucopyranoside (3c); TLC (Hexane:EtOAc 1:2): R_f 0.57. $[\alpha]_D = -17.9$ ($c = 1.7$, CHCl_3 , 27 °C); ^1H NMR (CDCl_3 , 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); ^{13}C NMR (CDCl_3 , 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, 128.2, 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 $\text{C}_{76}\text{H}_{71}\text{N}_3\text{NaO}_{21}\text{S}$ $[\text{M}+\text{Na}]^+$, 1416.4193; found, 1416.4163.

4-Methylphenyl (3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio- β -D-glucopyranoside (4c); TLC (Hexane:EtOAc 1:2): R_f 0.48. $[\alpha]_D = -24.3$ ($c = 0.6$, CHCl_3 , 27 °C); ^1H NMR (CDCl_3 , 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); ^{13}C NMR (CDCl_3 , 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,

127.38, 127.2, 127.10, 127.08, 126.94, 123.67, 123.63, 123.60, 123.57, 123.51, 123.48, 123.39, 123.30, 96.51, 96.48, 95.9, 82.9, 78.6, 73.9, 73.7, 73.6, 73.3, 73.14, 73.13, 72.9, 72.5, 72.26, 72.24, 72.0, 71.8, 71.4, 70.7, 70.0, 67.9, 67.5, 55.3, 55.2, 54.9, 53.9, 21.1, 20.60, 20.57, 20.48, 20.45; HRMS (ESI) m/z calculated for $C_{99}H_{92}KN_4O_{28}S [M+K]^+$, 1855.5250; found, 1855.5226.

Buliding block **1d** (0.2 mmol, 114 mg) afforded oligosaccharides **2d** ($n = 2$, 23 μ mol, 22.8 mg, 23%), **3d** ($n = 3$, 6.7 μ mol, 9.5 mg, 10%), **4d** ($n = 4$, 4.3 μ mol, 8.0 mg, 9%), and **5d** ($n = 5$, 2.6 μ mol, 5.8 mg, 6%) as white solids. Recovered yield of buliding block **1d** was 37% (42 mg, 74 μ mol).

2,4-Difluorophenyl (3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio- β -D-glucopyranoside (2d); TLC (Hexane:EtOAc 1:2): R_f 0.60. $[\alpha]_D = -4.06$ ($c = 1.4$, $CHCl_3$, 27 $^{\circ}C$); 1H NMR ($CDCl_3$, 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), 4.54 (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).; ^{13}C NMR ($CDCl_3$, 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 (t, $J = 26.3$ Hz), 97.3, 82.0, 78.6, 74.0, 73.6, 73.5, 73.2, 72.8, 72.3, 71.2, 69.9, 67.8, 54.9, 53.8, 20.60, 20.58; HRMS (ESI) m/z calculated for $C_{52}H_{46}F_2KN_2O_{14}S [M+K]^+$, 1031.2269; found, 1031.2269.

2,4-Difluorophenyl (3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio- β -D-glucopyranoside (3d); TLC (Hexane:EtOAc 1:2): R_f 0.55. $[\alpha]_D = -18.1$ ($c = 1.7$, $CHCl_3$, 27 $^{\circ}C$); 1H NMR ($CDCl_3$, 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, $J = 10.2$, 8.4 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) δ 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, 127.64, 127.40, 127.31, 127.25, 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 $\text{C}_{75}\text{H}_{67}\text{F}_2\text{KN}_3\text{O}_{21}\text{S}$ $[\text{M}+\text{K}]^+$, 1454.3587; found, 1454.3563.

2,4-Difluorophenyl (3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio- β -D-glucopyranoside (4d); TLC (Hexane:EtOAc 1:2): R_f 0.47. $[\alpha]_D = -5.00$ ($c = 1.4$, CHCl_3 , 27 °C); ^1H NMR (CDCl_3 , 600 MHz) δ 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) δ 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, 134.1, 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, 123.61, 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 $\text{C}_{98}\text{H}_{88}\text{F}_2\text{N}_4\text{NaO}_{28}\text{S}$ $[\text{M}+\text{Na}]^+$, 1861.5166; found, 1861.5137.

2,4-Difluorophenyl (3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio- β -D-glucopyranoside (5d**);** TLC (Hexane:EtOAc 1:2): R_f 0.40. $[\alpha]_D = -27.1$ ($c = 1.0$, CHCl_3 , 30°C); ^1H NMR (CDCl_3 , 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); ^{13}C NMR (CDCl_3 , 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 $\text{C}_{121}\text{H}_{109}\text{F}_2\text{KN}_5\text{O}_{35}\text{S}$ $[\text{M}+\text{K}]^+$, 2300.6223; found, 2300.6287.

3. Optimization of electricity and electrolyte

Table S1. Optimization of electricity of electrochemical polyglycosylation.

$\text{1a (Ar = 4-FC}_6\text{H}_4\text{)}$
 $\xrightarrow[\text{CH}_2\text{Cl}_2, -80\text{ }^\circ\text{C}]{\text{anodic oxidation (X F/mol, 8 mA), Bu}_4\text{NOTf}}$
 $\xrightarrow[\text{-50 }^\circ\text{C, 1 h}]{\text{glycosylation}}$
 $\text{2a (n = 2) ~ 7a (n = 7)}$

entry	electricity (F/mol)	yield of oligosaccharides 2a (<i>n</i> = 2)– 7a (<i>n</i> = 7)							total
		2a	3a	4a	5a	6a	7a	Conv.	
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.

$\text{1a (Ar = 4-FC}_6\text{H}_4\text{)}$
 $\xrightarrow[\text{electrolyte CH}_2\text{Cl}_2, -80\text{ }^\circ\text{C}]{\text{anodic oxidation (0.525 F/mol, 8 mA)}}$
 $\xrightarrow[\text{-50 }^\circ\text{C, 1 h}]{\text{glycosylation}}$
 $\text{2a (n = 2) ~ 7a (n = 7)}$

entry	electrolyte	yield of oligosaccharides 2a (<i>n</i> = 2)– 7a (<i>n</i> = 7)							total
		2a	3a	4a	5a	6a	7a	conv.	
1	Bu ₄ NOTf	27%	19%	10%	3%	1%	trace	73%	61%
2	Et ₄ NOTf	41%	14%	4%	trace	—	—	79%	59%
3	[BMPy]OTf	33%	14%	6%	1%	—	—	79%	54%

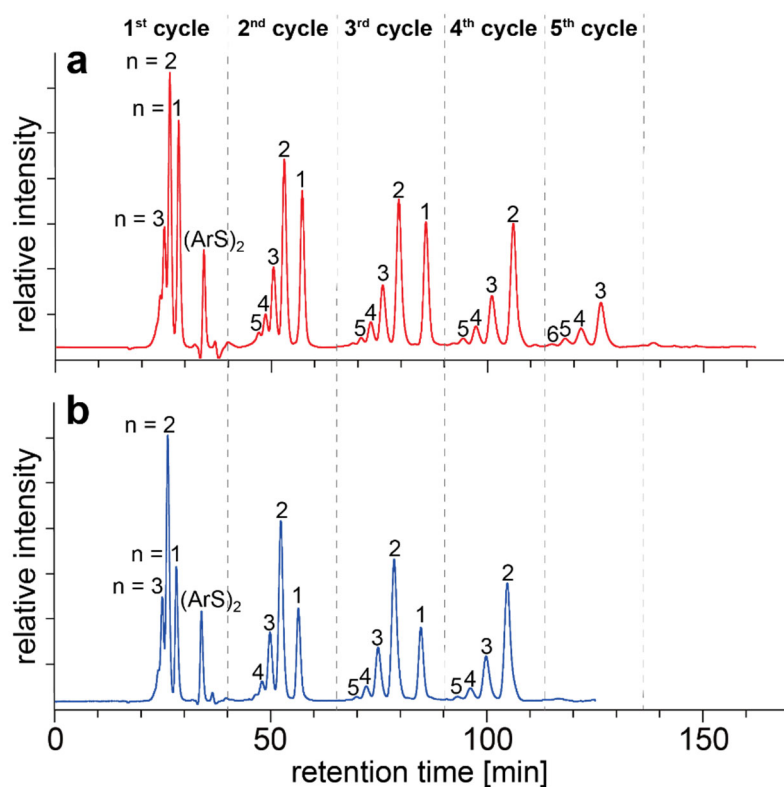


Figure S1. Preparative recycling GPC traces of protected oligosaccharides **2a** ($n = 2$)–**6a** ($n = 6$). (a) Bu_4NOTf as electrolyte (Table S2, entry 1). (b) Et_4NOTf as electrolyte (Table S2, entry 2).

4. Influence of reaction parameters

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

$ \begin{array}{c} \text{BnO} \\ \\ \text{HO} \text{---} \text{C} \text{---} \text{O} \text{---} \text{SAr} \\ \quad \quad \\ \text{AcO} \quad \text{PhthN} \\ \text{1a-d} \\ \text{Ar} = 4\text{-XC}_6\text{H}_4 \text{ or } 2,4\text{-F}_2\text{C}_6\text{H}_3 \end{array} \xrightarrow[\text{CH}_2\text{Cl}_2, -80^\circ\text{C}]{\text{anodic oxidation (0.525 F/mol, 8 mA), Bu}_4\text{NOTf}} \xrightarrow[\text{-50}^\circ\text{C, 1 h}]{\text{glycosylation}} \begin{array}{c} \left[\text{BnO} \text{---} \text{C} \text{---} \text{O} \text{---} \text{SAr} \right]_n \\ \quad \quad \\ \text{AcO} \quad \text{PhthN} \\ \text{2a-d (n = 2) ~ 7a-7d (n = 7)} \end{array} $										
entry	X	oxidation potential	yield of oligosaccharides 2a ($n = 2$)– 7a ($n = 7$)							total
			2a	3a	4a	5a	6a	7a	conv.	
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).

1a
Ar = 4-FC₆H₄

anodic oxidation
(0.525 F/mol, 8 mA)
Bu₄NOTf
CH₂Cl₂, -80 °C

glycosylation
T₂, 1 h

2a (n = 2) ~ **8a** (n = 8)

entry	T ₂	yield of oligosaccharides 2a (n = 2)– 7a (n = 7)						conv.	total
		2a	3a	4a	5a	6a	7a		
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).

1a
Ar = 4-FC₆H₄

anodic oxidation
(0.525 F/mol, 8 mA)
Bu₄NOTf
CH₂Cl₂, T₁

glycosylation
T₂, 1 h

2a (n = 2) ~ **8a** (n = 8)

entry	T ₁	T ₂	yield of oligosaccharides 2a (n = 2)– 7a (n = 7)						conv.	total
			2a	3a	4a	5a	6a	7a		
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).

Ar = 4-FC₆H₄

entry	cycles	yield of oligosaccharides 2a (<i>n</i> = 2)– 8a (<i>n</i> = 8)							total
		2a	3a	4a	5a	6a	7a	8a	
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

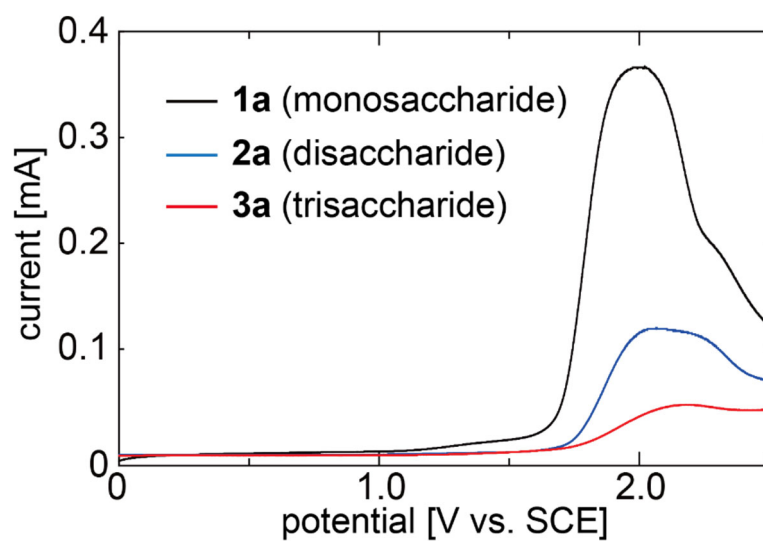
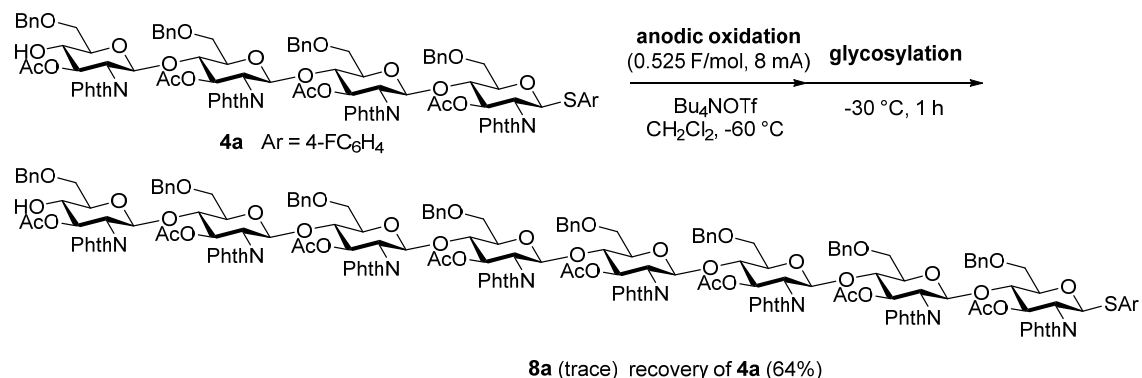


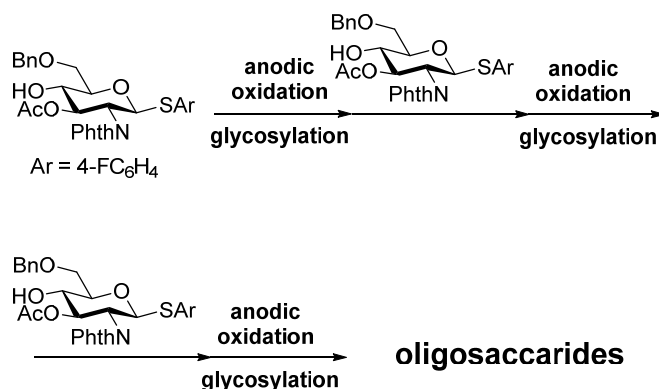
Figure S2. Linear sweep voltammetry of monosaccharide **1a** and oligosaccharides **2a** and **3a** measured by rotating disk electrode.

6. Electrochemical dimerization of tetrasaccharide



The electrochemical dimerization of tetrasaccharide **4a** was carried out 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). 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 an 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

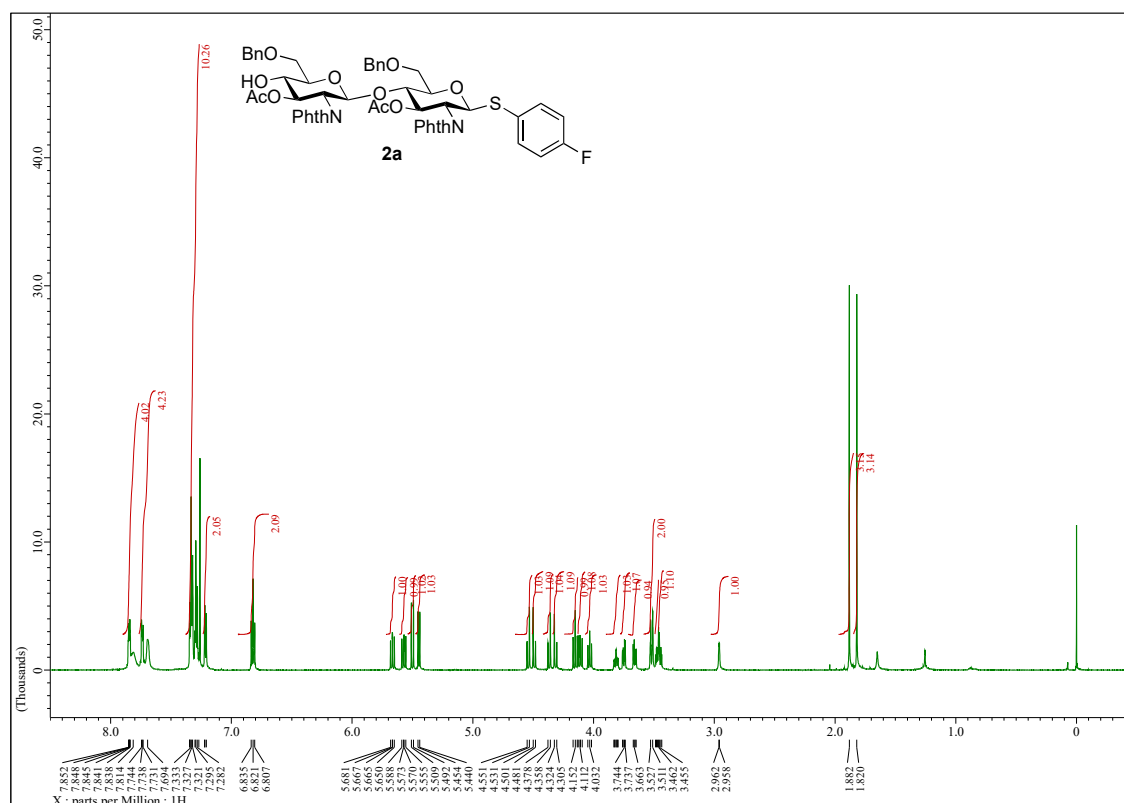


The electrochemical polymerization synthesis of linear oligosaccharides (**2a–8a**) was carried out in an H-type divided cell (4G glass filter). The cell had a carbon felt anode (Nippon Carbon JF-20-P7) and platinum square plate (20 mm × 20 mm). Building block **1a** (0.200 mmol, 109 mg), Bu₄NOTf (1.00 mmol, 393 mg), and CH₂Cl₂ (10 mL) were added to the anodic chamber. Trifluoromethanesulfonic acid (0.200 mmol, 18 μL), Bu₄NOTf (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 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio- β -D-glucopyranoside (8a); TLC (Hexane:EtOAc 1:2): R_f 0.13. $[\alpha]_D = -25.8$ ($c = 0.9$, 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 C₁₉₀H₁₇₃FN₈O₅₆S [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.

¹H NMR

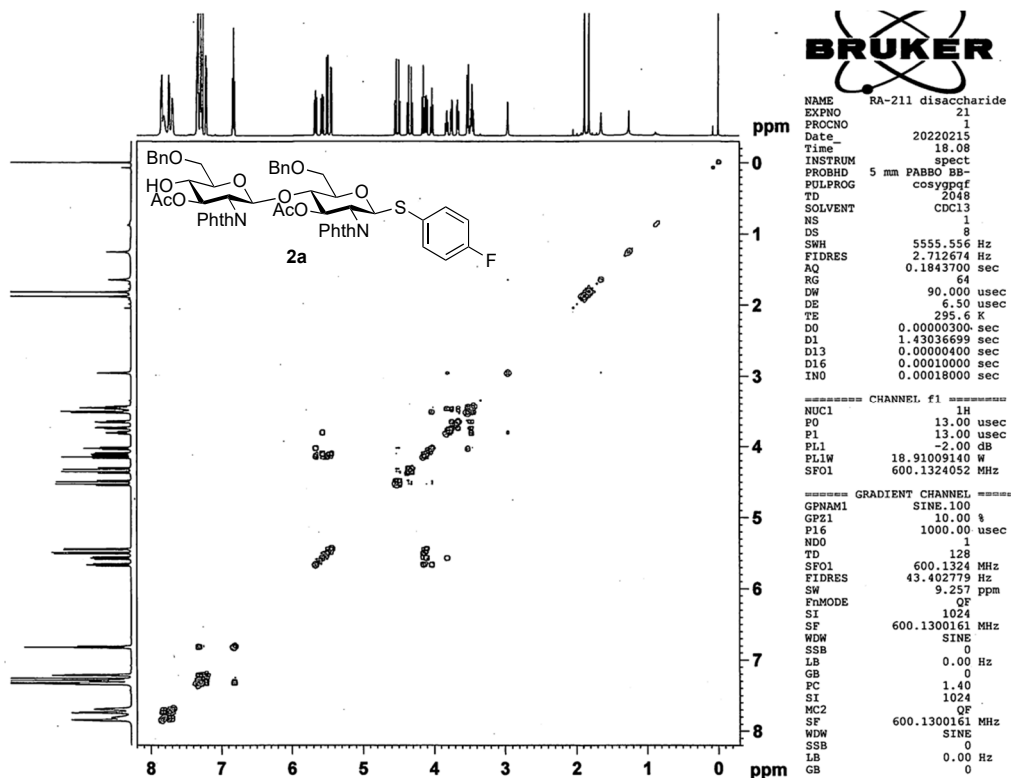
2a

(Thousands)

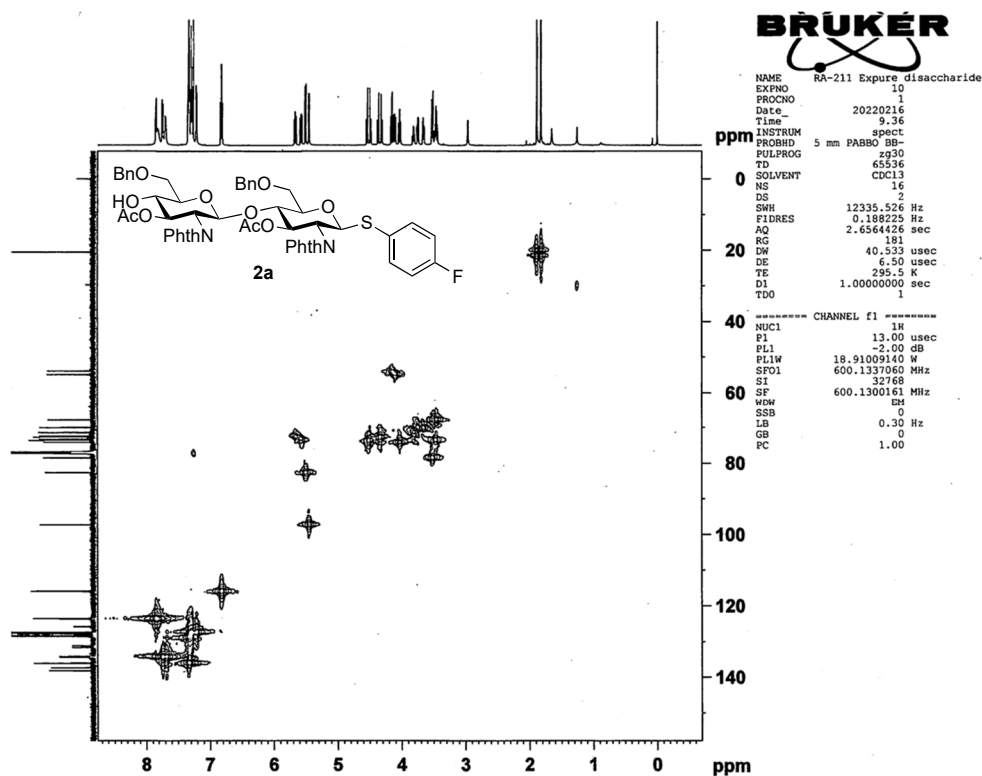
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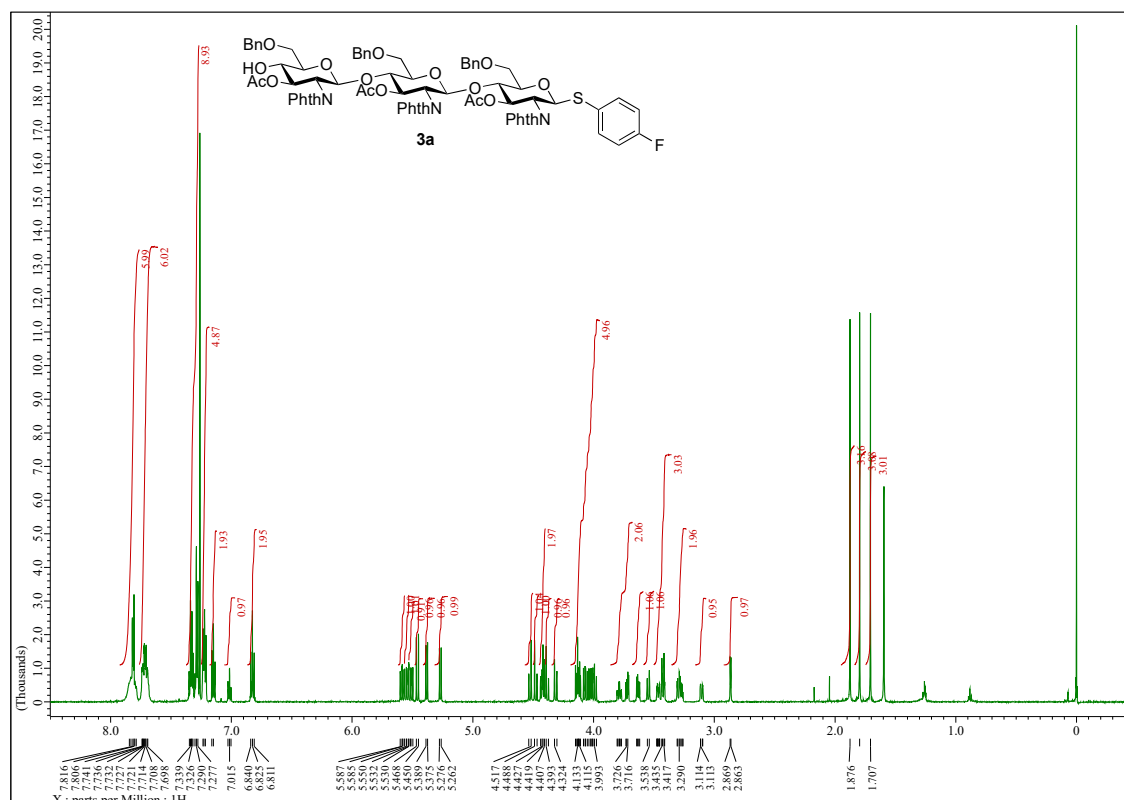
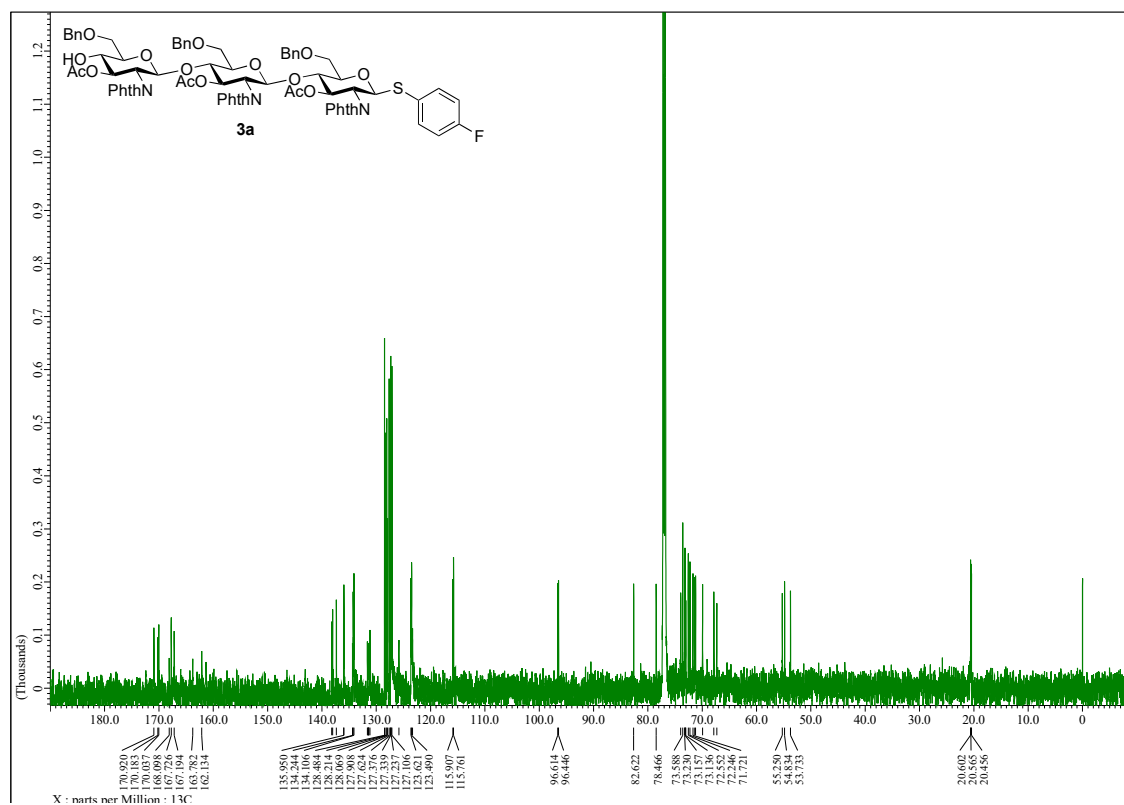
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H,H-COSY

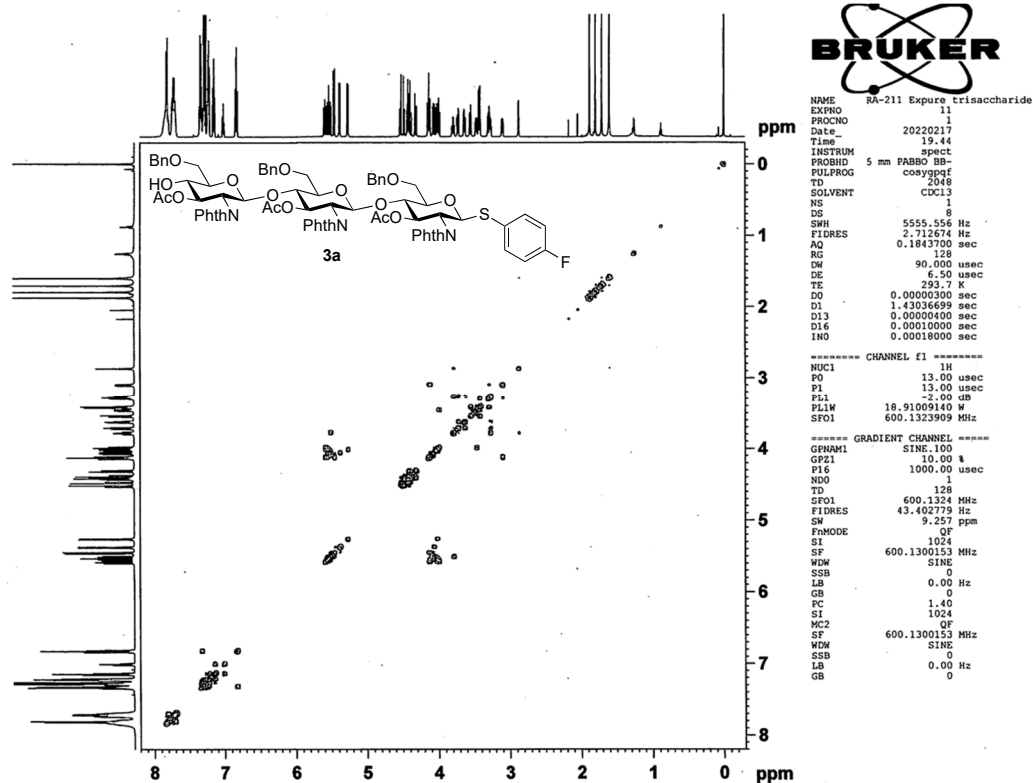


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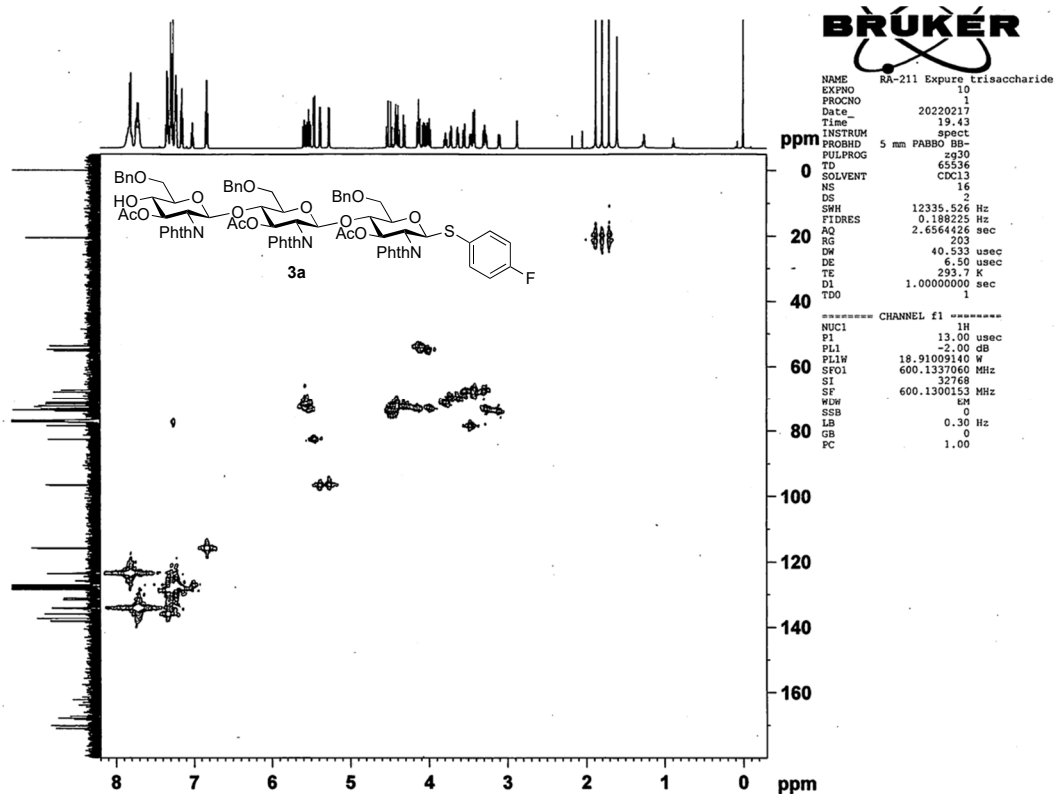


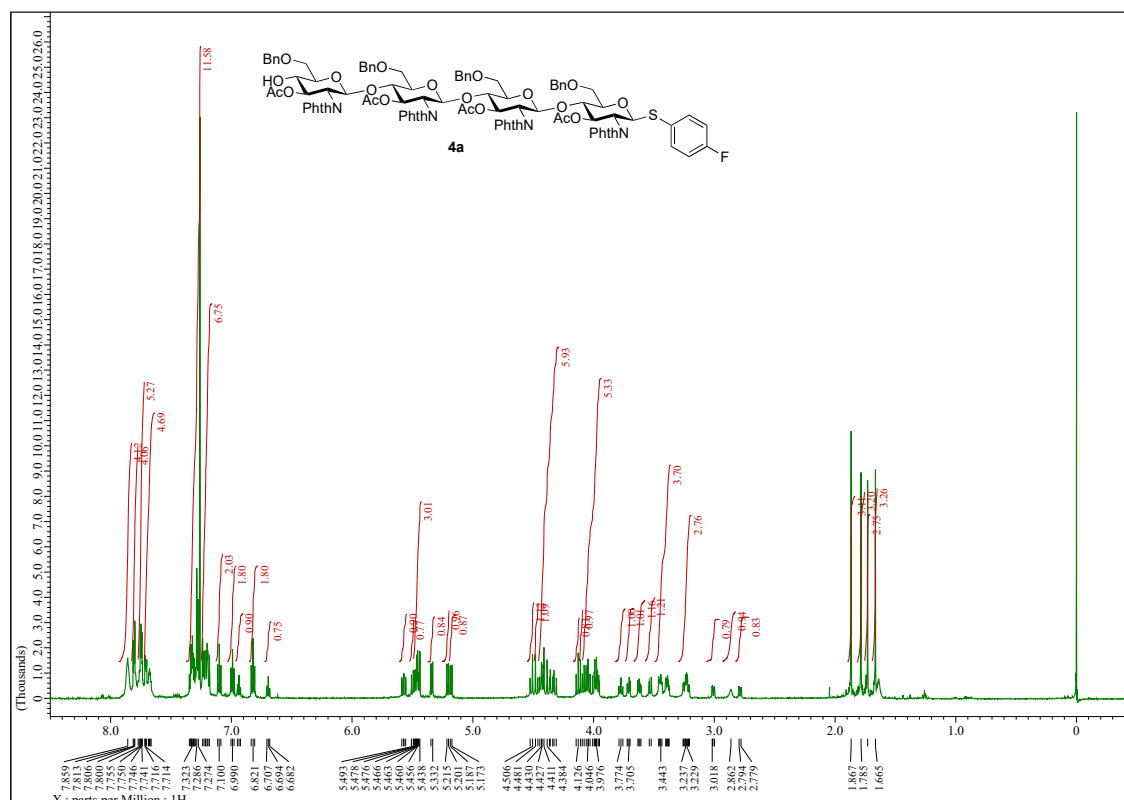
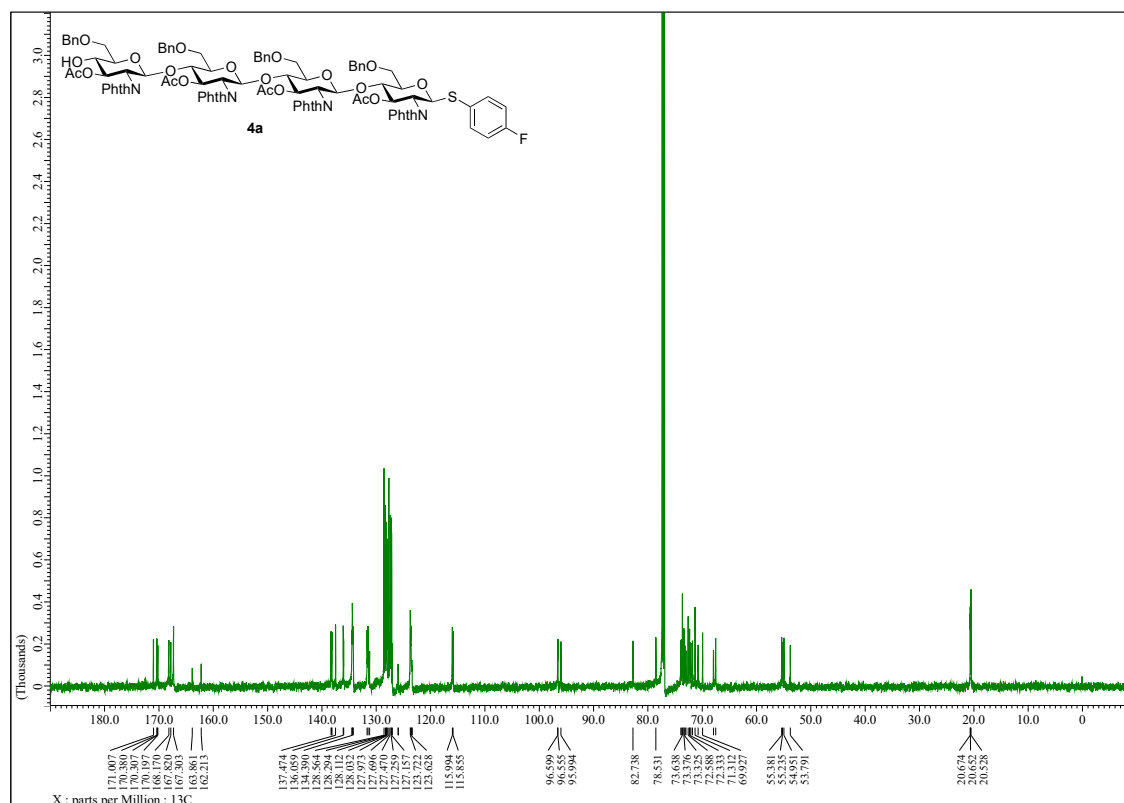
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H,H-COSY

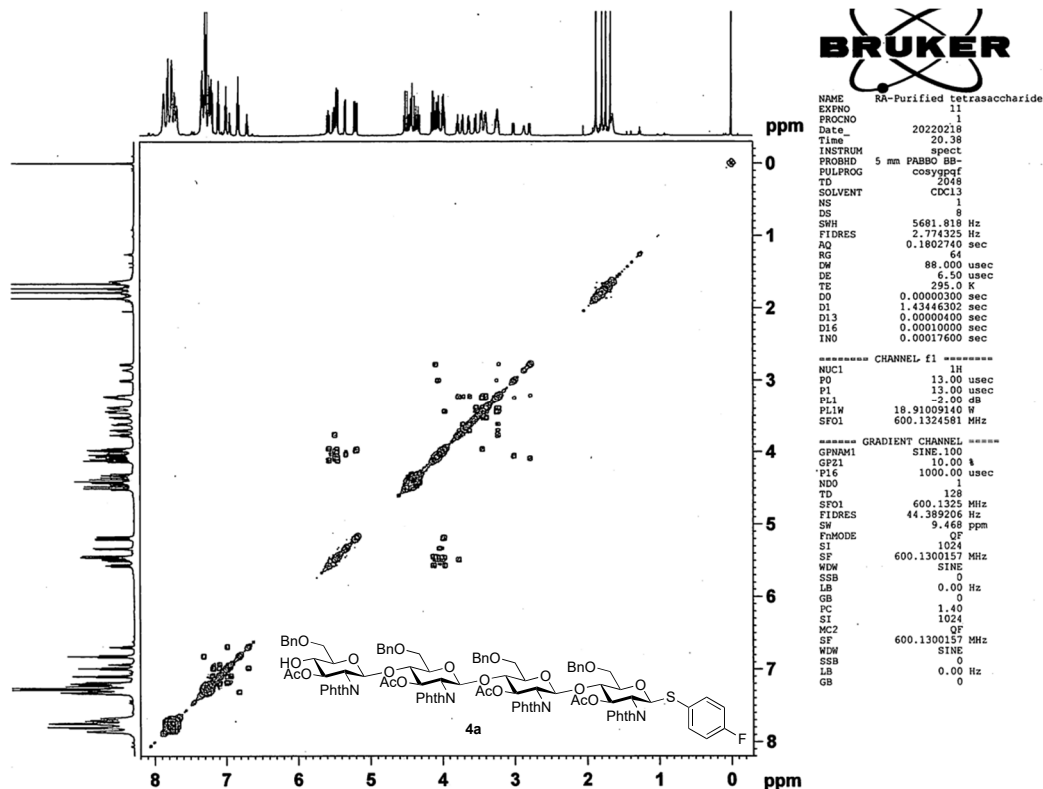


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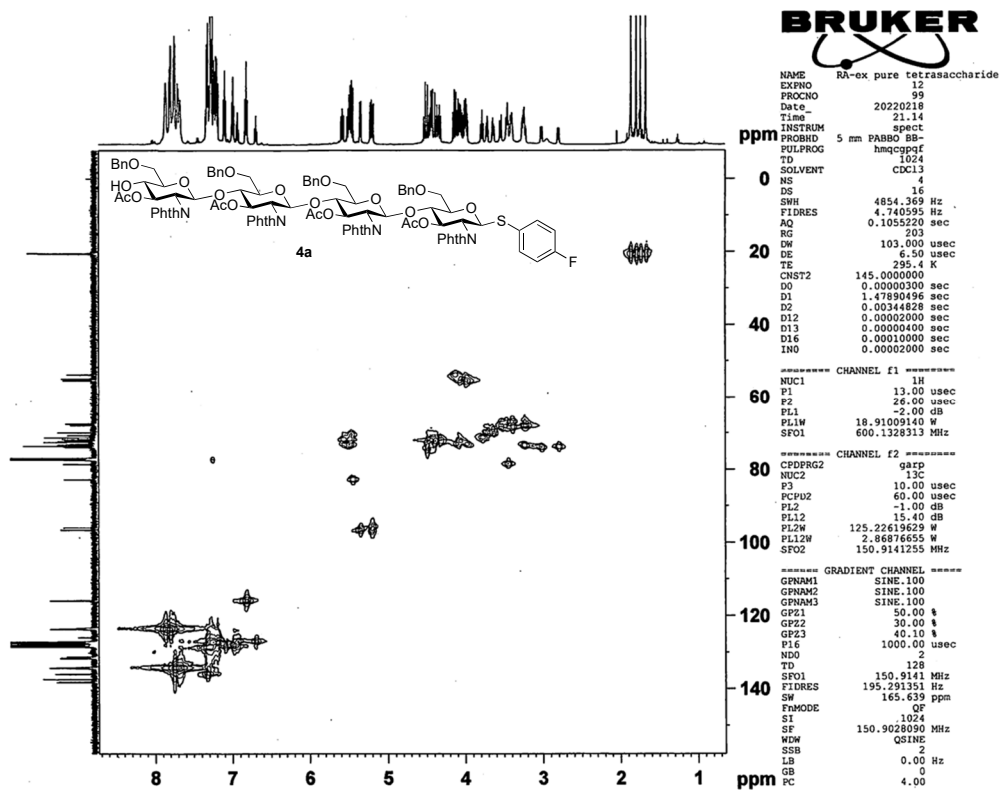


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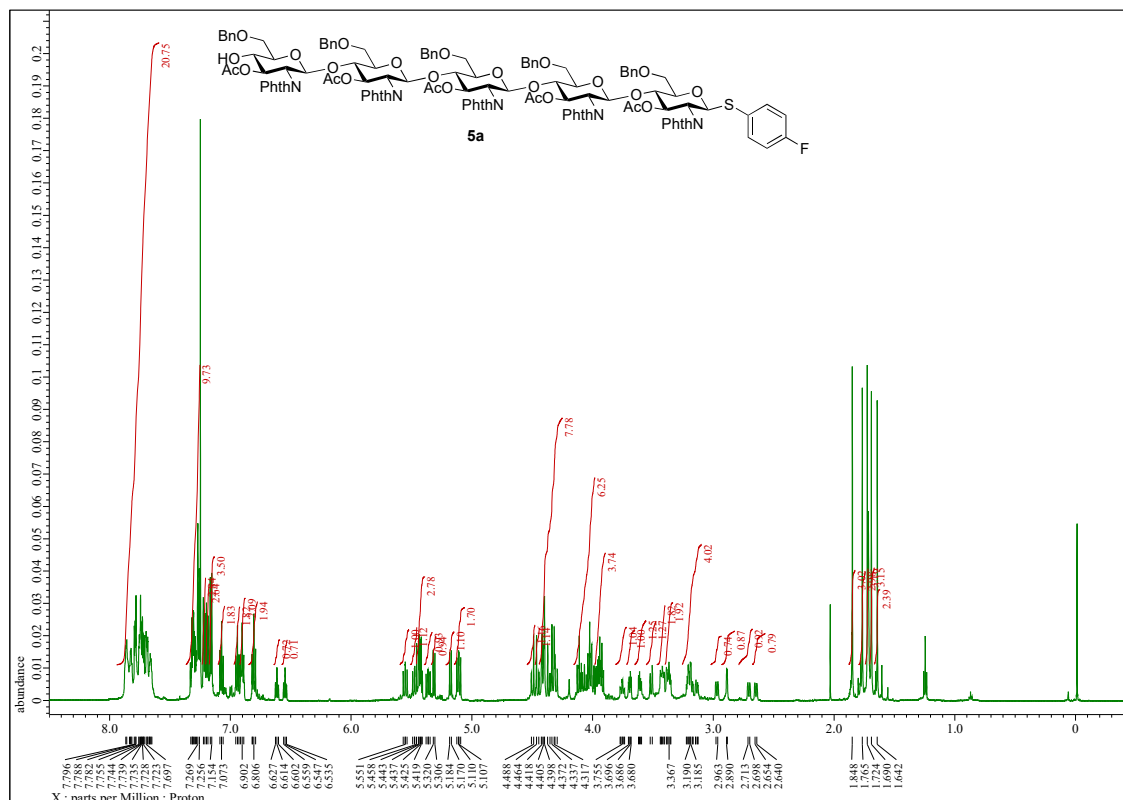
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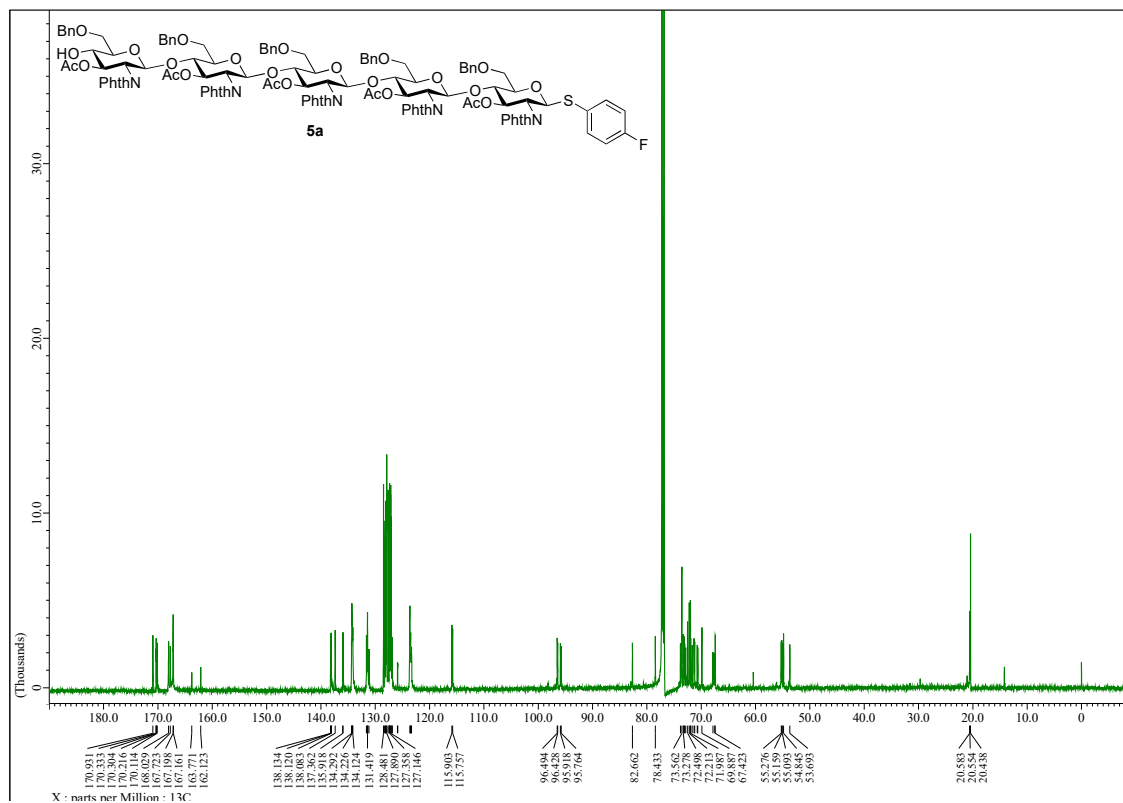
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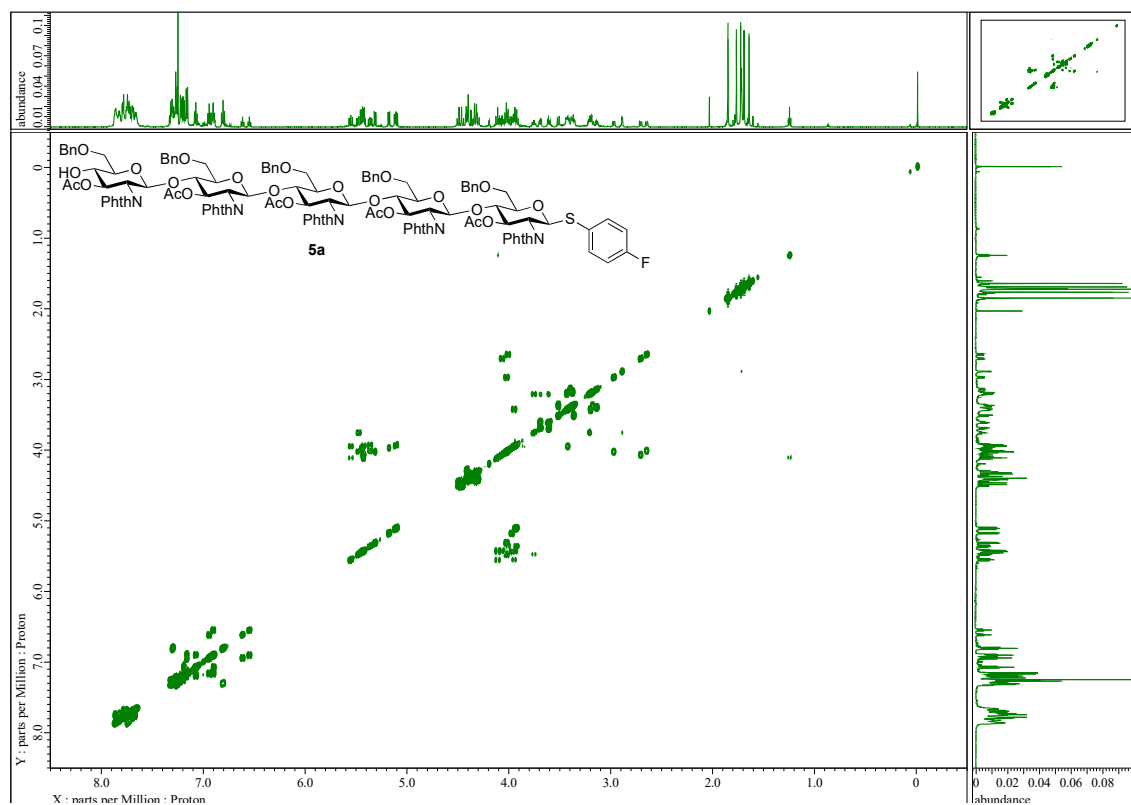
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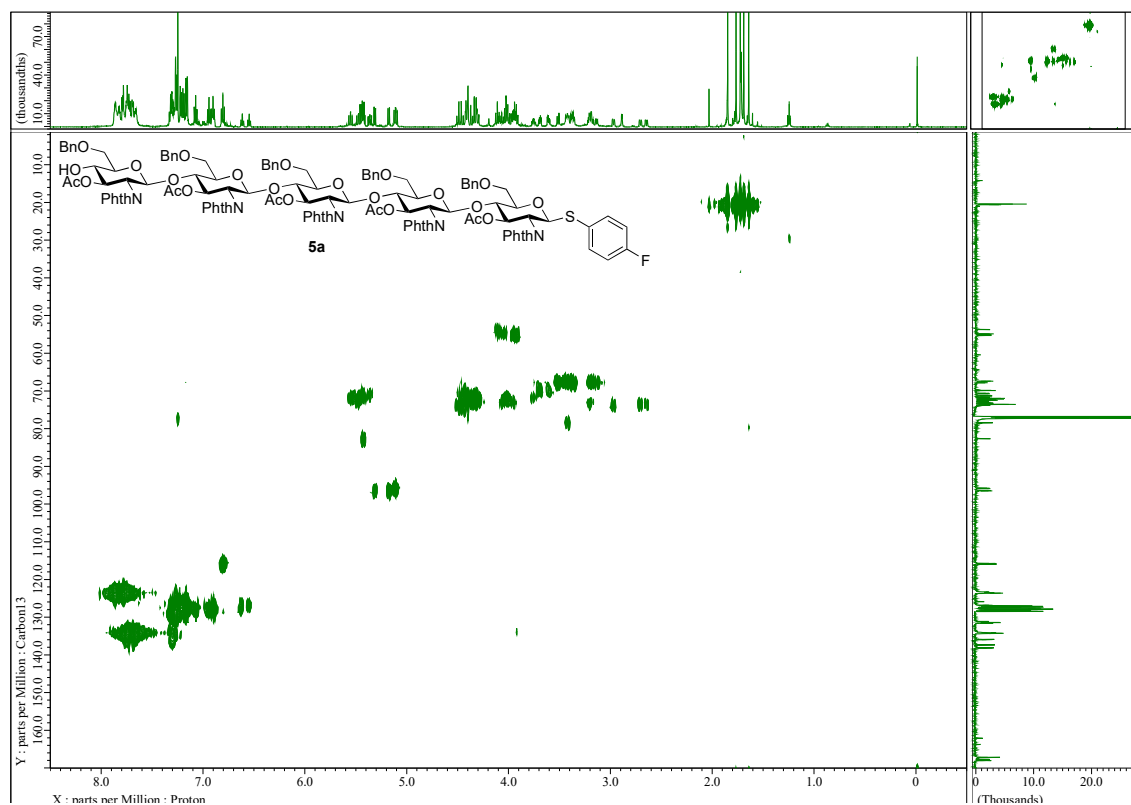
¹³C NMR



¹H,¹H-COSY



HMQC



Chemical structure of compound **6a** is shown above the spectrum. The structure is a linear oligomer of a protected disaccharide unit, with a terminal phenylthio group and a terminal phenyl group. The repeating unit consists of a glucose derivative linked to a mannose derivative, both protected with benzoyl and phenylthio groups. The terminal unit is a glucose derivative with a phenylthio group at C2 and a phenyl group at C6. The chemical structure is labeled **6a**.

¹H NMR spectrum (CDCl₃) of compound **6a**. The x-axis represents chemical shift in ppm, ranging from 0 to 10. The y-axis represents abundance. The spectrum shows several sharp peaks in the aromatic region (6.5-8.5 ppm) and a cluster of peaks in the aliphatic region (1.4-4.5 ppm). The chemical structure of **6a** is shown above the spectrum.

Chemical structure of compound **6a** is shown above the spectrum. The structure is a linear oligomer of a protected disaccharide unit, with a terminal phenylthio group and a terminal phenyl group. The repeating unit consists of a glucose derivative linked to a mannose derivative, both protected with benzoyl and phenylthio groups. The terminal unit is a glucose derivative with a phenylthio group at C2 and a phenyl group at C6. The chemical structure is labeled **6a**.

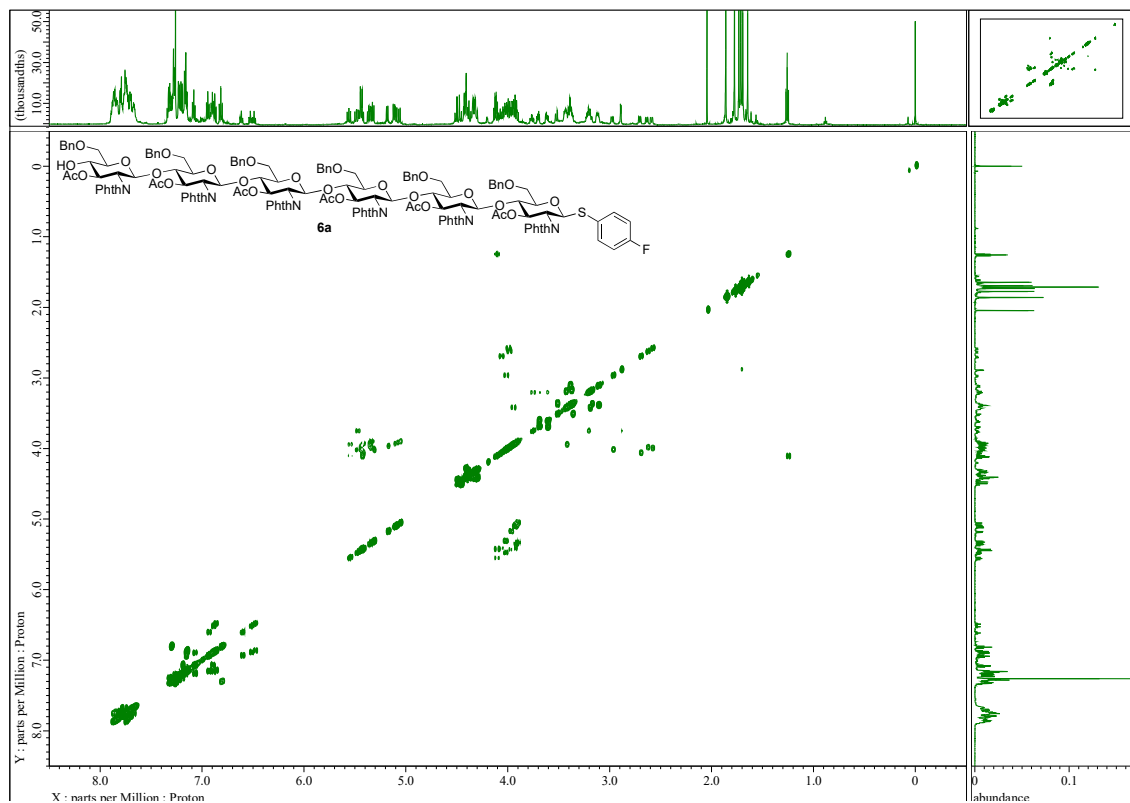
Chemical structure of compound **6a** is shown above the spectrum. The structure consists of a chain of five 2-acetate-3-benzyloxymethyl-4-benzoyl-5-phenylthio-2-deoxy-D-glucopyranoside units linked by 1,3-glycosidic bonds. The terminal unit on the right is a 4-fluorophenylthio group.

¹³C NMR spectrum (X = ppm) of compound **6a** is shown below. The spectrum displays numerous peaks corresponding to the various carbon environments in the molecule. The x-axis ranges from 0 to 180 ppm, and the y-axis represents intensity.

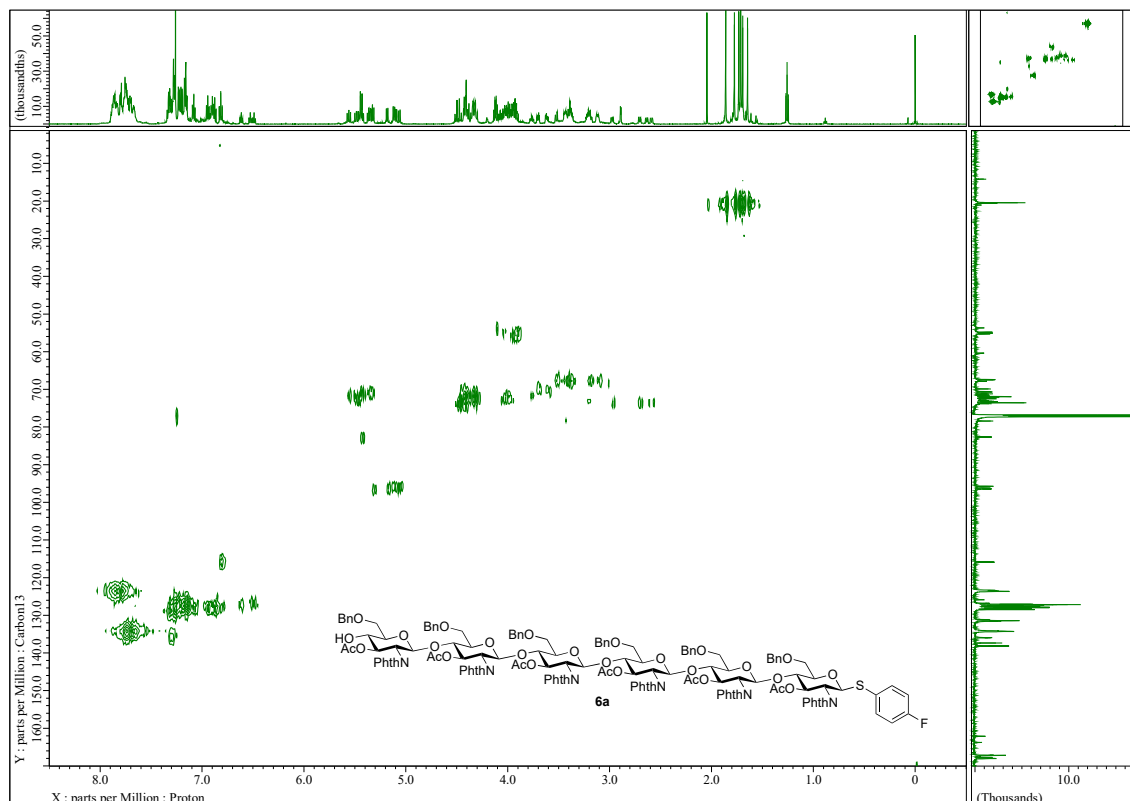
Chemical shift values (ppm) labeled on the spectrum:

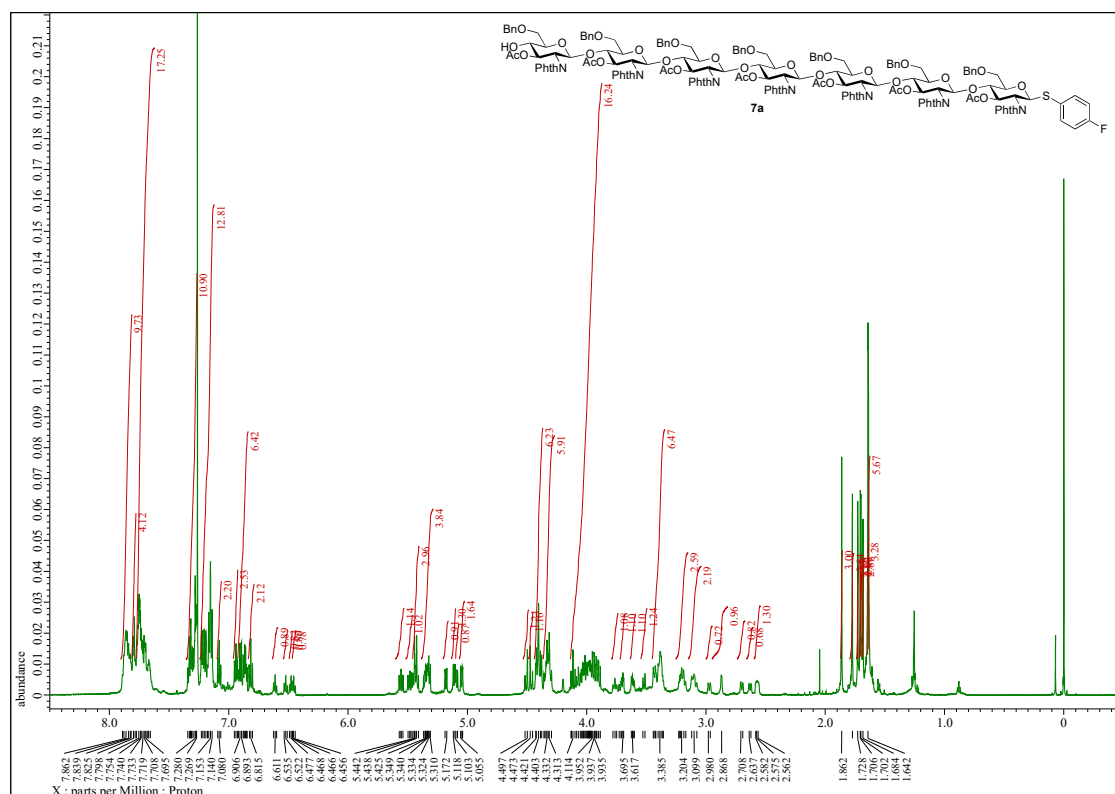
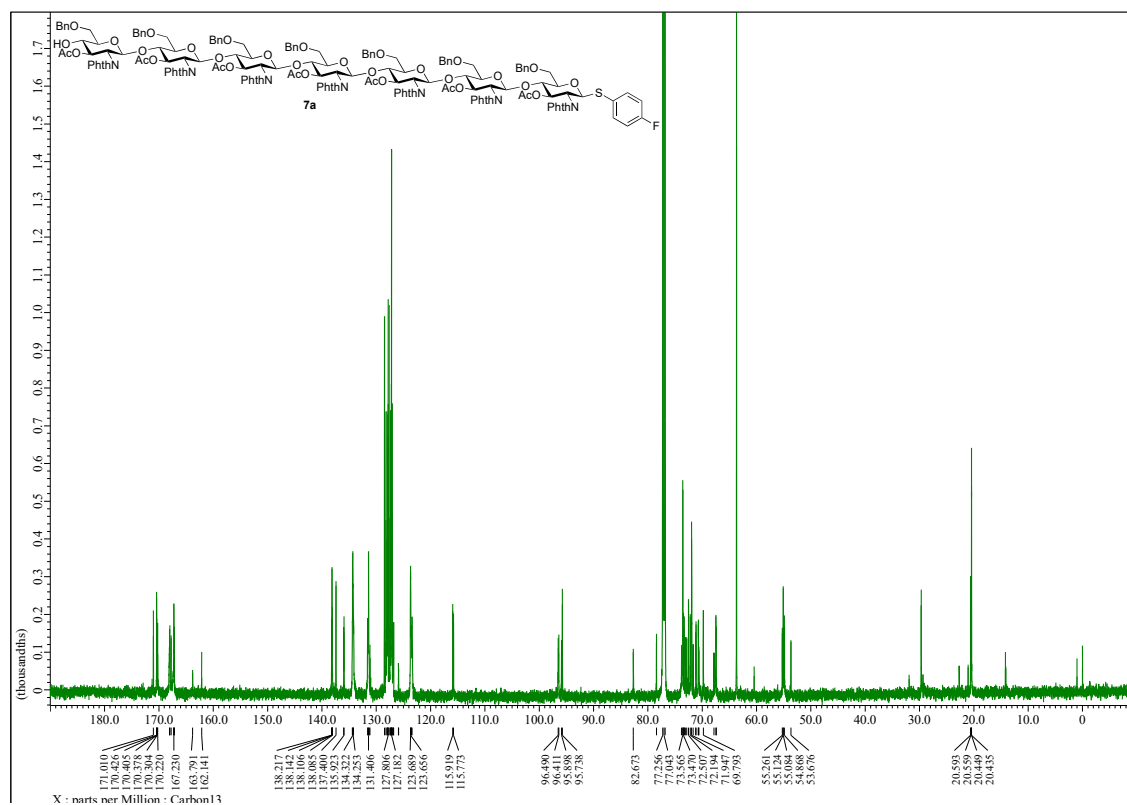
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- 115.903, 115.757
- 96.486, 96.413, 95.888, 95.743
- 82.655, 78.426, 73.521, 73.271, 72.490, 72.192, 71.977, 67.481, 67.408
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¹H,¹H-COSY

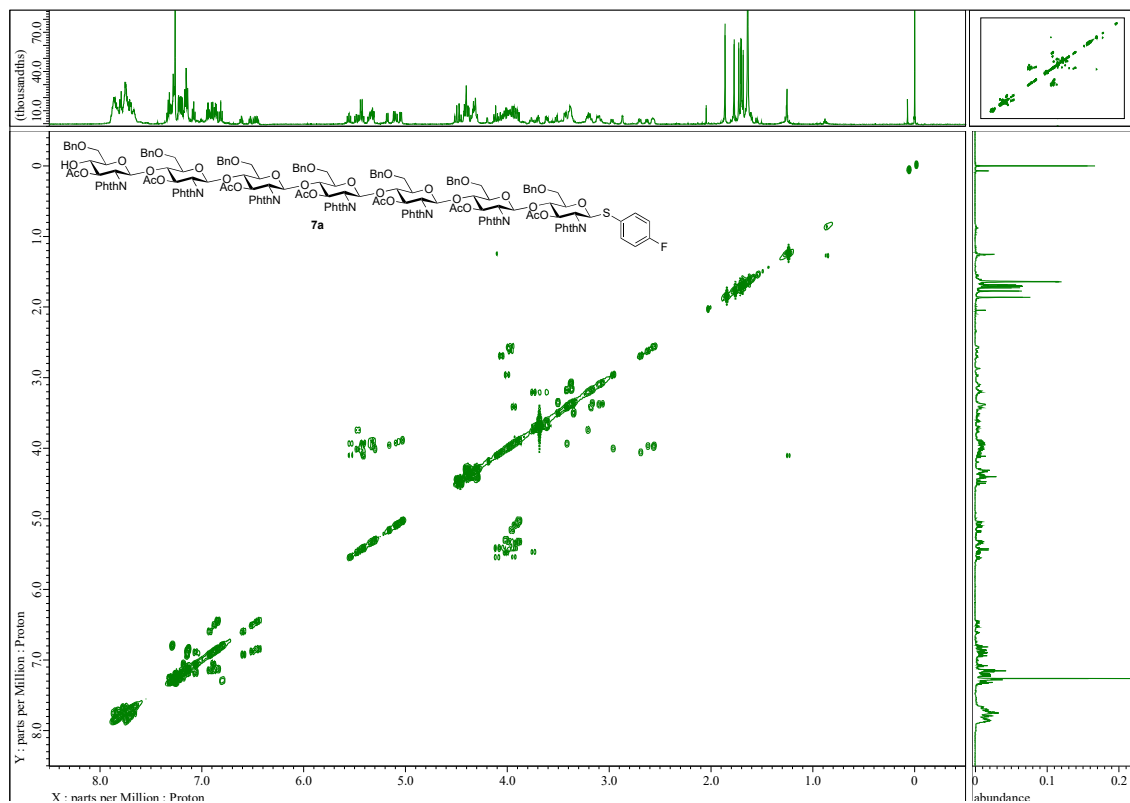


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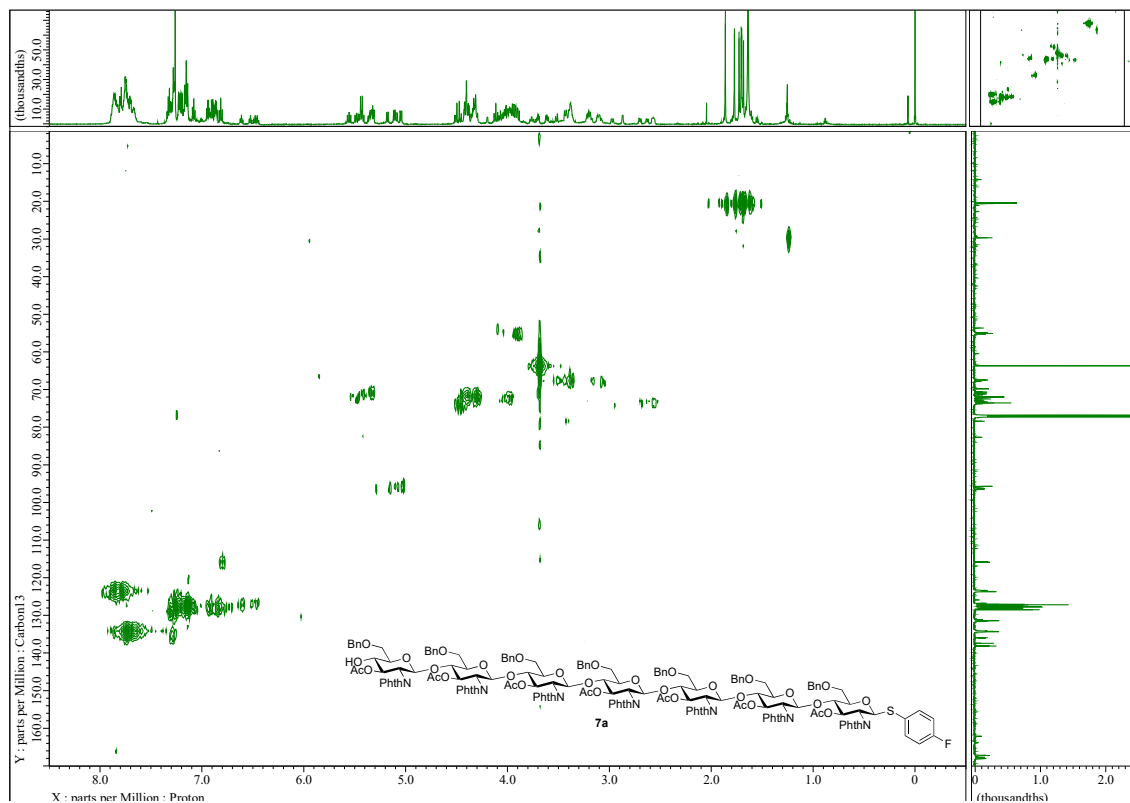


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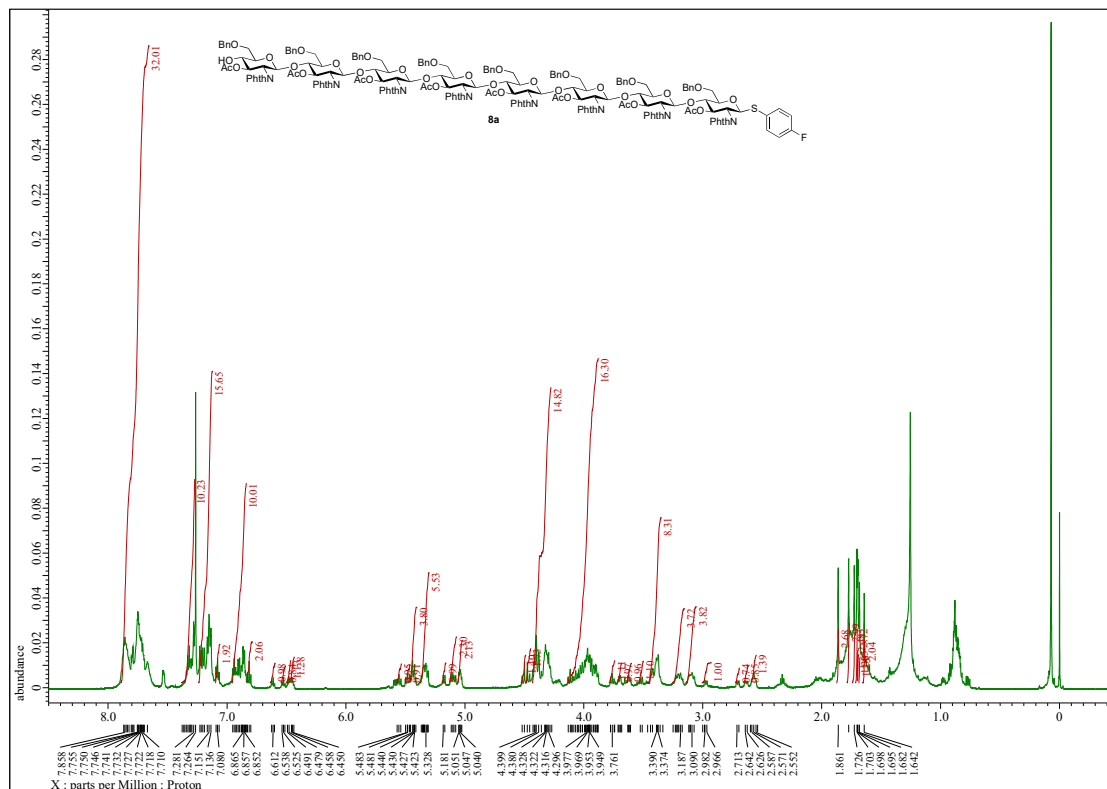
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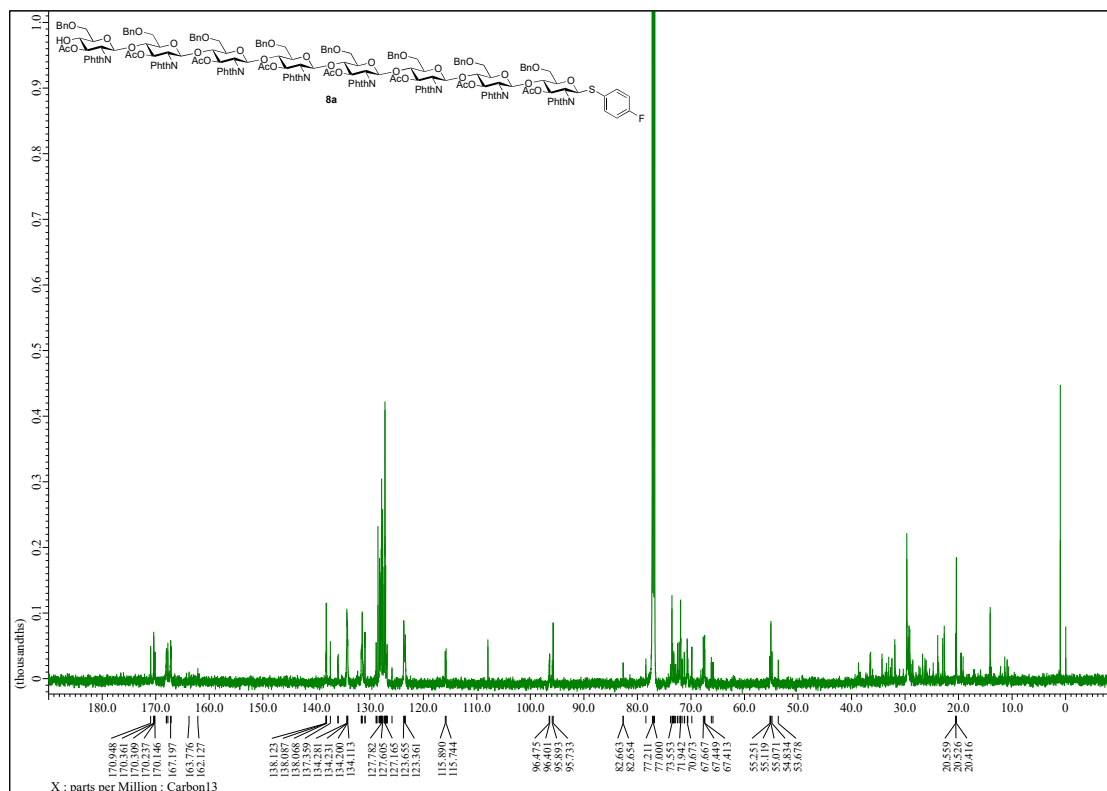
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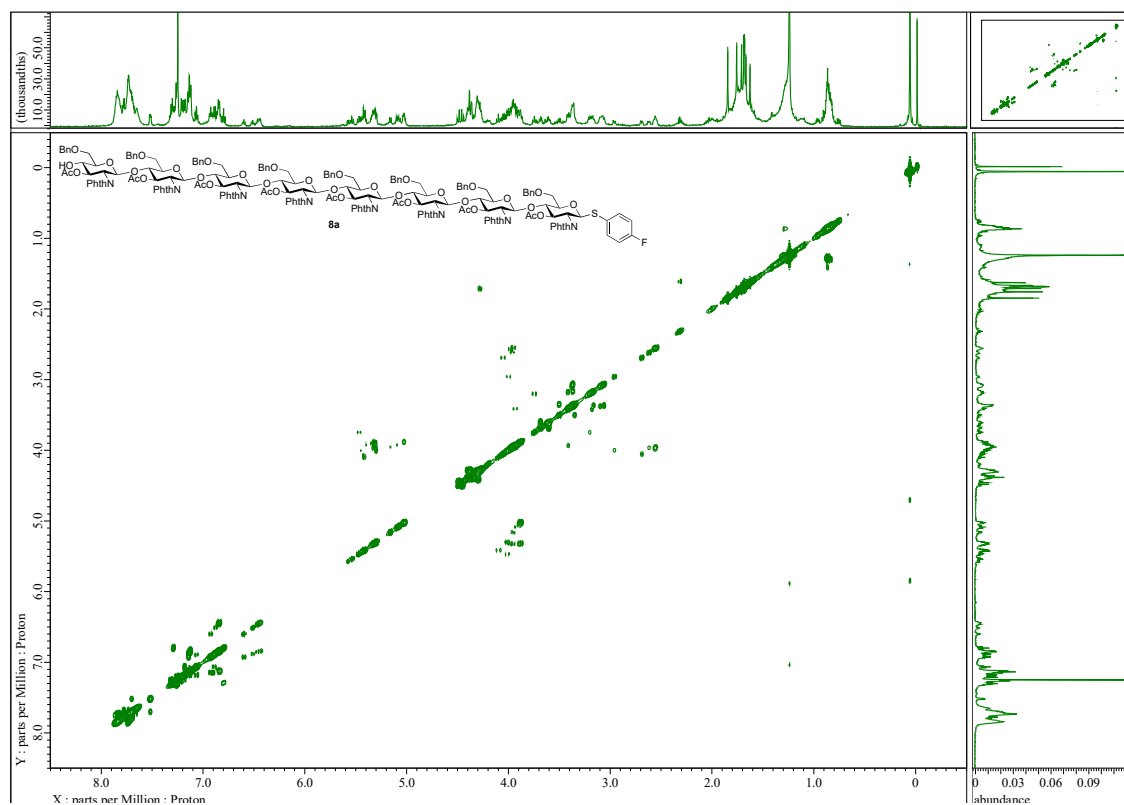
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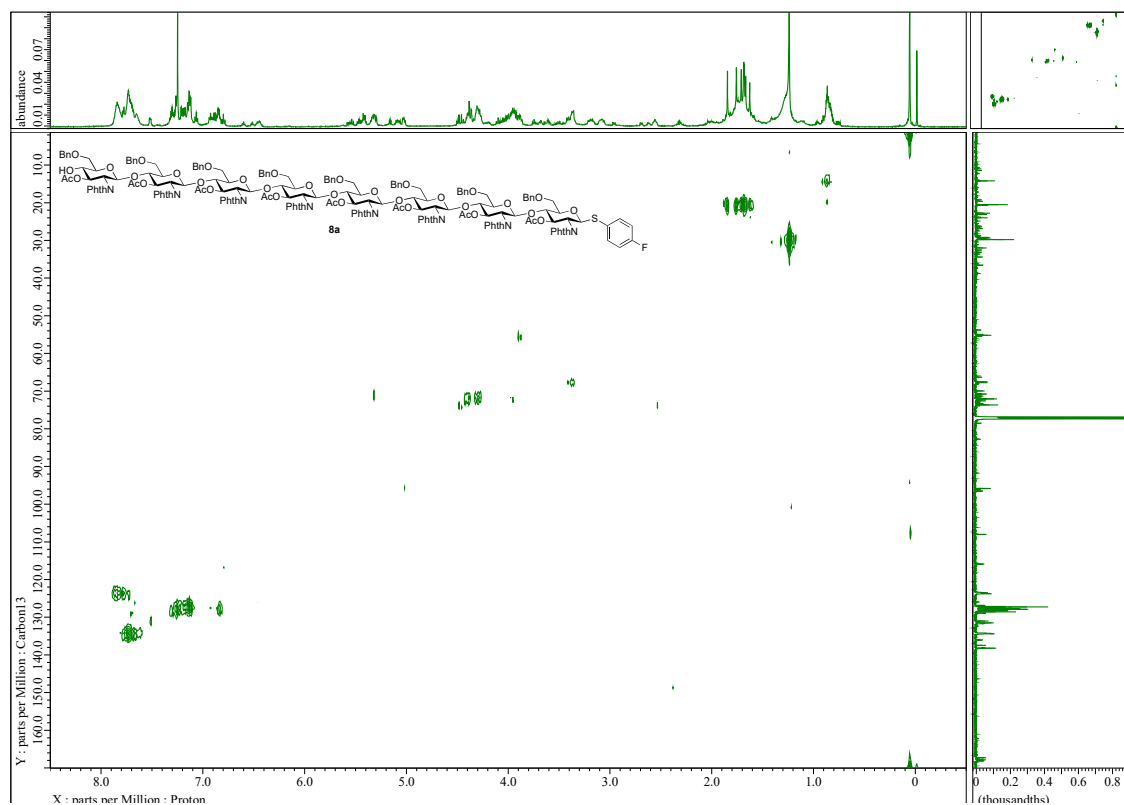
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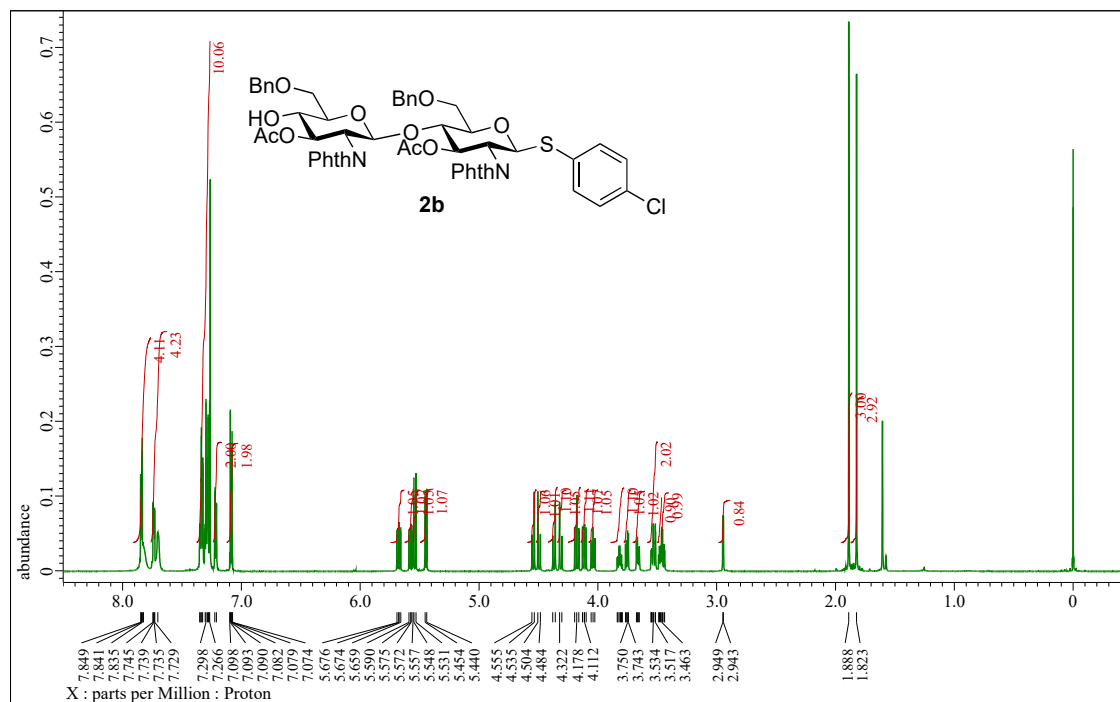
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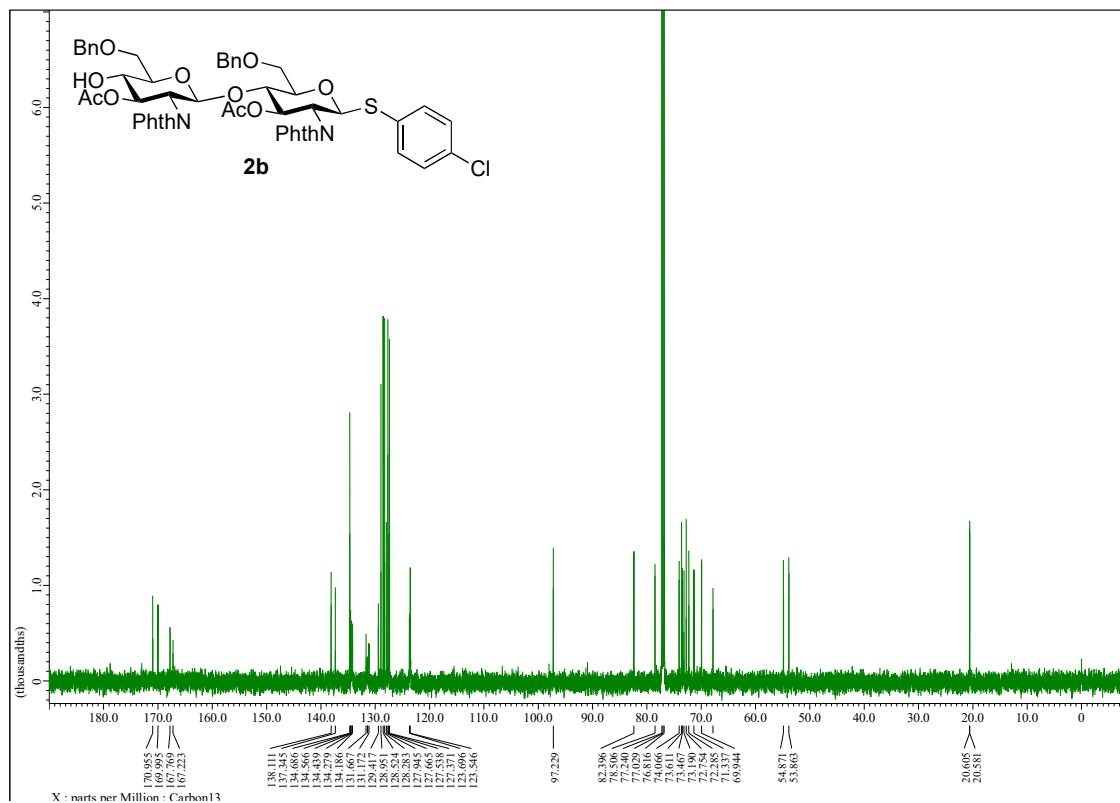
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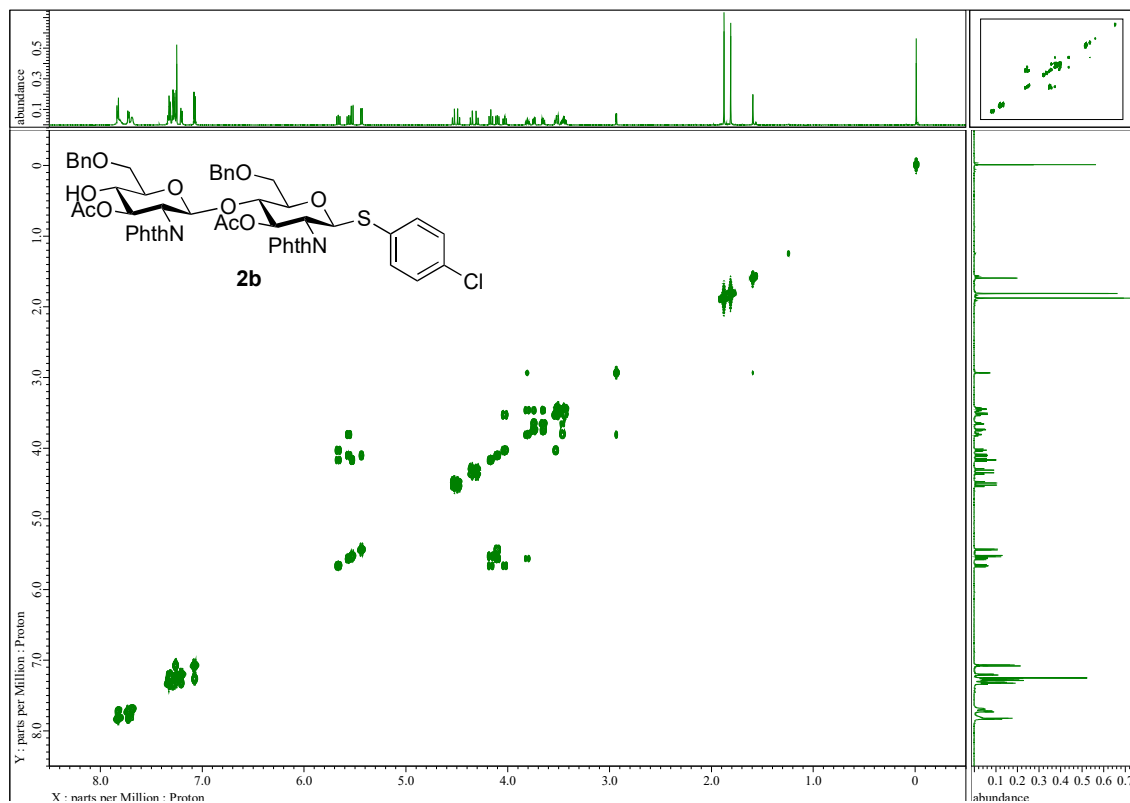
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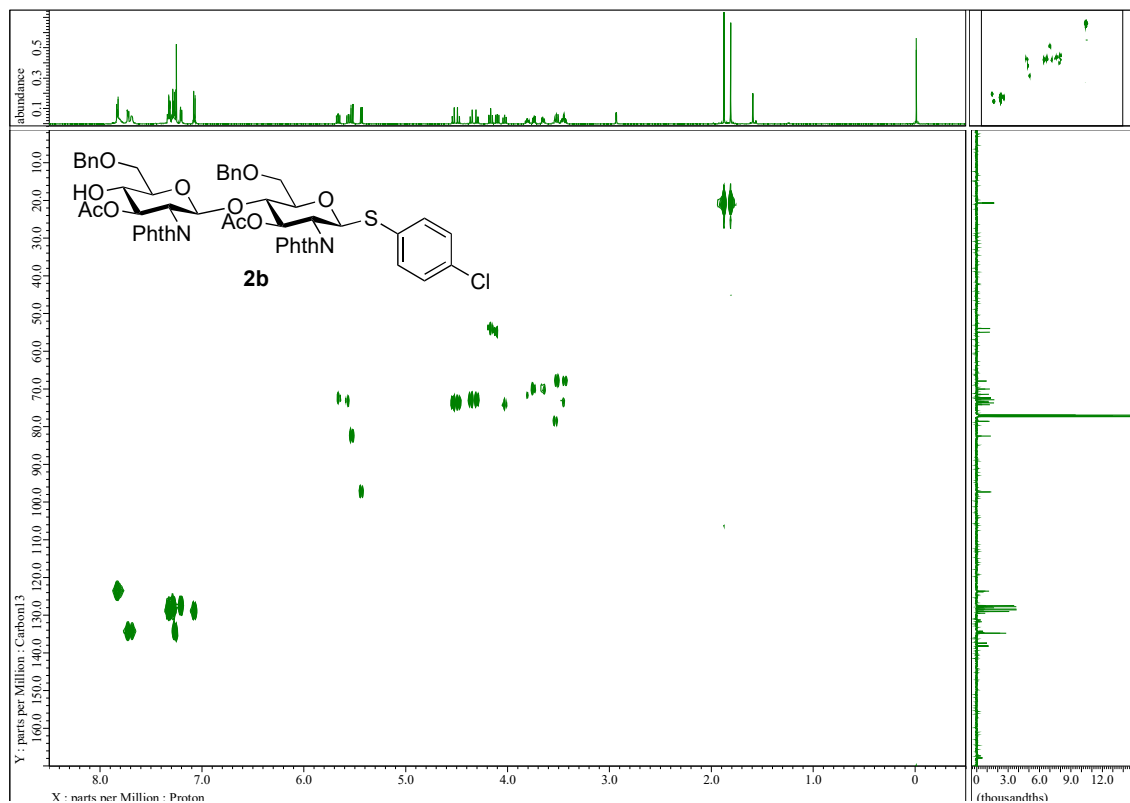
¹³C NMR



¹H,¹H-COSY



HMQC



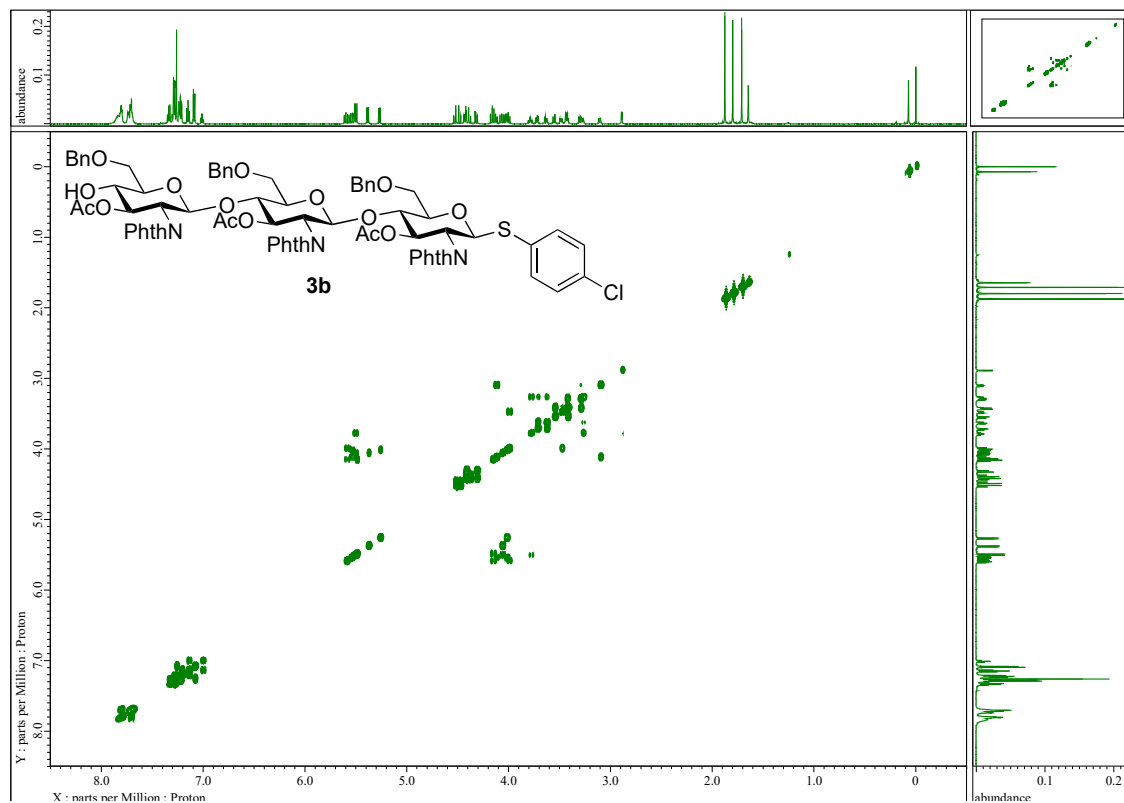
3b

Chemical structure of **3b** is shown above the spectrum. It is a trimeric sugar derivative, specifically a 1,3:2,6-di-O-isopropylidene- α -D-glucopyranoside derivative, substituted with benzoyl (BnO) and phthalimide (PhthN) groups, and a terminal 4-chlorophenylthio group.

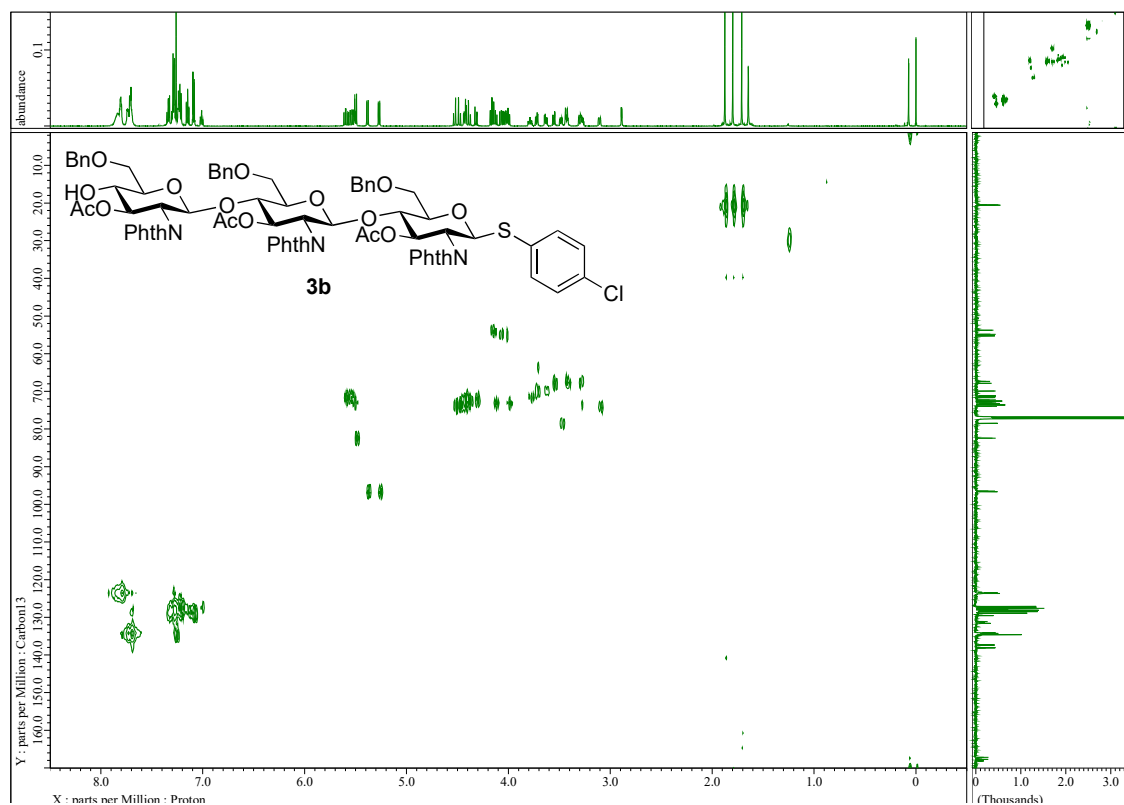
The ^1H NMR spectrum (CDCl₃) shows the following chemical shifts (ppm):

- 7.68, 7.66, 7.65, 7.64, 7.63, 7.62, 7.61, 7.60, 7.59, 7.58, 7.57, 7.56, 7.55, 7.54, 7.53, 7.52, 7.51, 7.50, 7.49, 7.48, 7.47, 7.46, 7.45, 7.44, 7.43, 7.42, 7.41, 7.40, 7.39, 7.38, 7.37, 7.36, 7.35, 7.34, 7.33, 7.32, 7.31, 7.30, 7.29, 7.28, 7.27, 7.26, 7.25, 7.24, 7.23, 7.22, 7.21, 7.20, 7.19, 7.18, 7.17, 7.16, 7.15, 7.14, 7.13, 7.12, 7.11, 7.10, 7.09, 7.08, 7.07, 7.06, 7.05, 7.04, 7.03, 7.02, 7.01, 7.00, 6.99, 6.98, 6.97, 6.96, 6.95, 6.94, 6.93, 6.92, 6.91, 6.90, 6.89, 6.88, 6.87, 6.86, 6.85, 6.84, 6.83, 6.82, 6.81, 6.80, 6.79, 6.78, 6.77, 6.76, 6.75, 6.74, 6.73, 6.72, 6.71, 6.70, 6.69, 6.68, 6.67, 6.66, 6.65, 6.64, 6.63, 6.62, 6.61, 6.60, 6.59, 6.58, 6.57, 6.56, 6.55, 6.54, 6.53, 6.52, 6.51, 6.50, 6.49, 6.48, 6.47, 6.46, 6.45, 6.44, 6.43, 6.42, 6.41, 6.40, 6.39, 6.38, 6.37, 6.36, 6.35, 6.34, 6.33, 6.32, 6.31, 6.30, 6.29, 6.28, 6.27, 6.26, 6.25, 6.24, 6.23, 6.22, 6.21, 6.20, 6.19, 6.18, 6.17, 6.16, 6.15, 6.14, 6.13, 6.12, 6.11, 6.10, 6.09, 6.08, 6.07, 6.06, 6.05, 6.04, 6.03, 6.02, 6.01, 6.00, 5.99, 5.98, 5.97, 5.96, 5.95, 5.94, 5.93, 5.92, 5.91, 5.90, 5.89, 5.88, 5.87, 5.86, 5.85, 5.84, 5.83, 5.82, 5.81, 5.80, 5.79, 5.78, 5.77, 5.76, 5.75, 5.74, 5.73, 5.72, 5.71, 5.70, 5.69, 5.68, 5.67, 5.66, 5.65, 5.64, 5.63, 5.62, 5.61, 5.60, 5.59, 5.58, 5.57, 5.56, 5.55, 5.54, 5.53, 5.52, 5.51, 5.50, 5.49, 5.48, 5.47, 5.46, 5.45, 5.44, 5.43, 5.42, 5.41, 5.40, 5.39, 5.38, 5.37, 5.36, 5.35, 5.34, 5.33, 5.32, 5.31, 5.30, 5.29, 5.28, 5.27, 5.26, 5.25, 5.24, 5.23, 5.22, 5.21, 5.20, 5.19, 5.18, 5.17, 5.16, 5.15, 5.14, 5.13, 5.12, 5.11, 5.10, 5.09, 5.08, 5.07, 5.06, 5.05, 5.04, 5.03, 5.02, 5.01, 5.00, 4.99, 4.98, 4.97, 4.96, 4.95, 4.94, 4.93, 4.92, 4.91, 4.90, 4.89, 4.88, 4.87, 4.86, 4.85, 4.84, 4.83, 4.82, 4.81, 4.80, 4.79, 4.78, 4.77, 4.76, 4.75, 4.74, 4.73, 4.72, 4.71, 4.70, 4.69, 4.68, 4.67, 4.66, 4.65, 4.64, 4.63, 4.62, 4.61, 4.60, 4.59, 4.58, 4.57, 4.56, 4.55, 4.54, 4.53, 4.52, 4.51, 4.50, 4.49, 4.48, 4.47, 4.46, 4.45, 4.44, 4.43, 4.42, 4.41, 4.40, 4.39, 4.38, 4.37, 4.36, 4.35, 4.34, 4.33, 4.32, 4.31, 4.30, 4.29, 4.28, 4.27, 4.26, 4.25, 4.24, 4.23, 4.22, 4.21, 4.20, 4.19, 4.18, 4.17, 4.16, 4.15, 4.14, 4.13, 4.12, 4.11, 4.10, 4.09, 4.08, 4.07, 4.06, 4.05, 4.04, 4.03, 4.02, 4.01, 4.00, 3.99, 3.98, 3.97, 3.96, 3.95, 3.94, 3.93, 3.92, 3.91, 3.90, 3.89, 3.88, 3.87, 3.86, 3.85, 3.84, 3.83, 3.82, 3.81, 3.80, 3.79, 3.78, 3.77, 3.76, 3.75, 3.74, 3.73, 3.72, 3.71, 3.70, 3.69, 3.68, 3.67, 3.66, 3.65, 3.64, 3.63, 3.62, 3.61, 3.60, 3.59, 3.58, 3.57, 3.56, 3.55, 3.54, 3.53, 3.52, 3.51, 3.50, 3.49, 3.48, 3.47, 3.46, 3.45, 3.44, 3.43, 3.42, 3.41, 3.40, 3.39, 3.38, 3.37, 3.36, 3.35, 3.34, 3.33, 3.32, 3.31, 3.30, 3.29, 3.28, 3.27, 3.26, 3.25, 3.24, 3.23, 3.22, 3.21, 3.20, 3.19, 3.18, 3.17, 3.16, 3.15, 3.14, 3.13, 3.12, 3.11, 3.10, 3.09, 3.08, 3.07, 3.06, 3.05, 3.04, 3.03, 3.02, 3.01, 3.00, 2.99, 2.98, 2.97, 2.96, 2.95, 2.94, 2.93, 2.92, 2.91, 2.90, 2.89, 2.88, 2.87, 2.86, 2.85, 2.84, 2.83, 2.82, 2.81, 2.80, 2.79, 2.78, 2.77, 2.76, 2.75, 2.74, 2.73, 2.72, 2.71, 2.70, 2.69, 2.68, 2.67, 2.66, 2.65, 2.64, 2.63, 2.62, 2.61, 2.60, 2.59, 2.58, 2.57, 2.56, 2.55, 2.54, 2.53, 2.52, 2.51, 2.50, 2.49, 2.48, 2.47, 2.46, 2.45, 2.44, 2.43, 2.42, 2.41, 2.40, 2.39, 2.38, 2.37, 2.36, 2.35, 2.34, 2.33, 2.32, 2.31, 2.30, 2.29, 2.28, 2.27, 2.26, 2.25, 2.24, 2.23, 2.22, 2.21, 2.20, 2.19, 2.18, 2.17, 2.16, 2.15, 2.14, 2.13, 2.12, 2.11, 2.10, 2.09, 2.08, 2.07, 2.06, 2.05, 2.04, 2.03, 2.02, 2.01, 2.00, 1.99, 1.98, 1.97, 1.96, 1.95, 1.94, 1.93, 1.92, 1.91, 1.90, 1.89, 1.88, 1.87, 1.86, 1.85, 1.84, 1.83, 1.82, 1.81, 1.80, 1.79, 1.78, 1.77, 1.76, 1.75, 1.74, 1.73, 1.72, 1.71, 1.70, 1.69, 1.68, 1.67, 1.66, 1.65, 1.64, 1.63, 1.62, 1.61, 1.60, 1.59, 1.58, 1.57, 1.56, 1.55, 1.54, 1.53, 1.52, 1.51, 1.50, 1.49, 1.48, 1.47, 1.46, 1.45, 1.44, 1.43, 1.42, 1.41, 1.40, 1.39, 1.38, 1.37, 1.36, 1.35, 1.34, 1.33, 1.32, 1.31, 1.30, 1.29, 1.28, 1

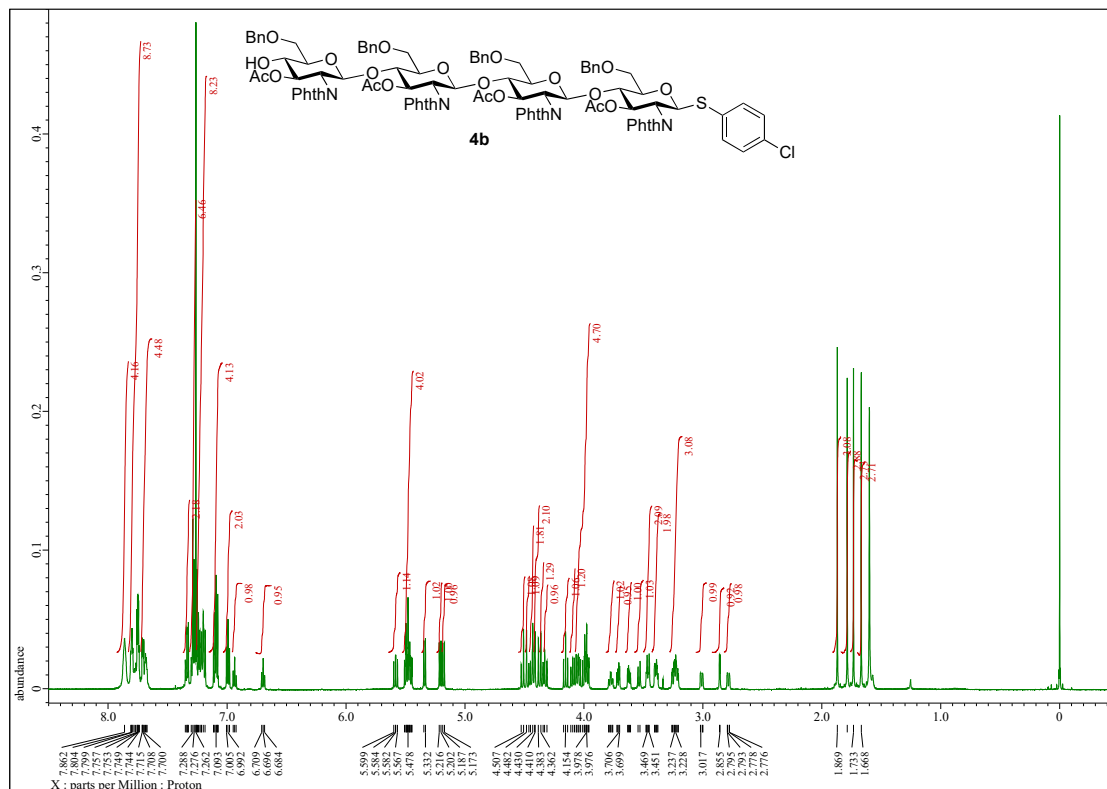
¹H,¹H-COSY



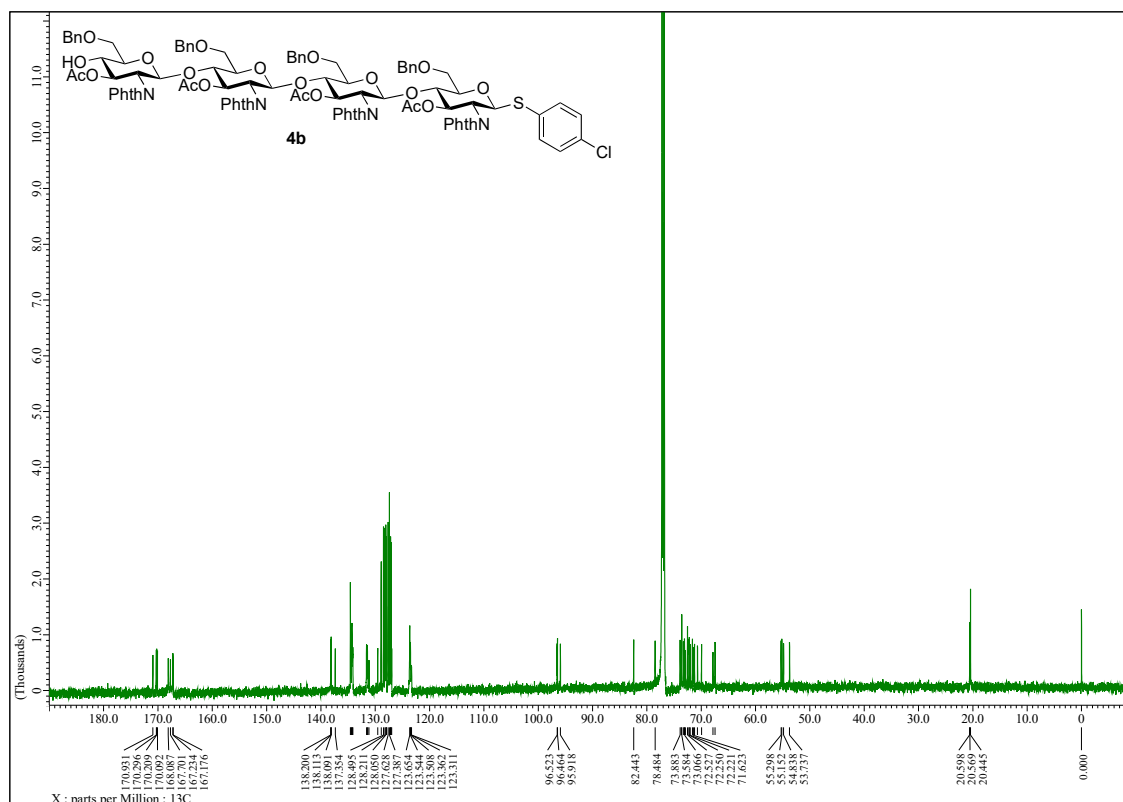
HMQC



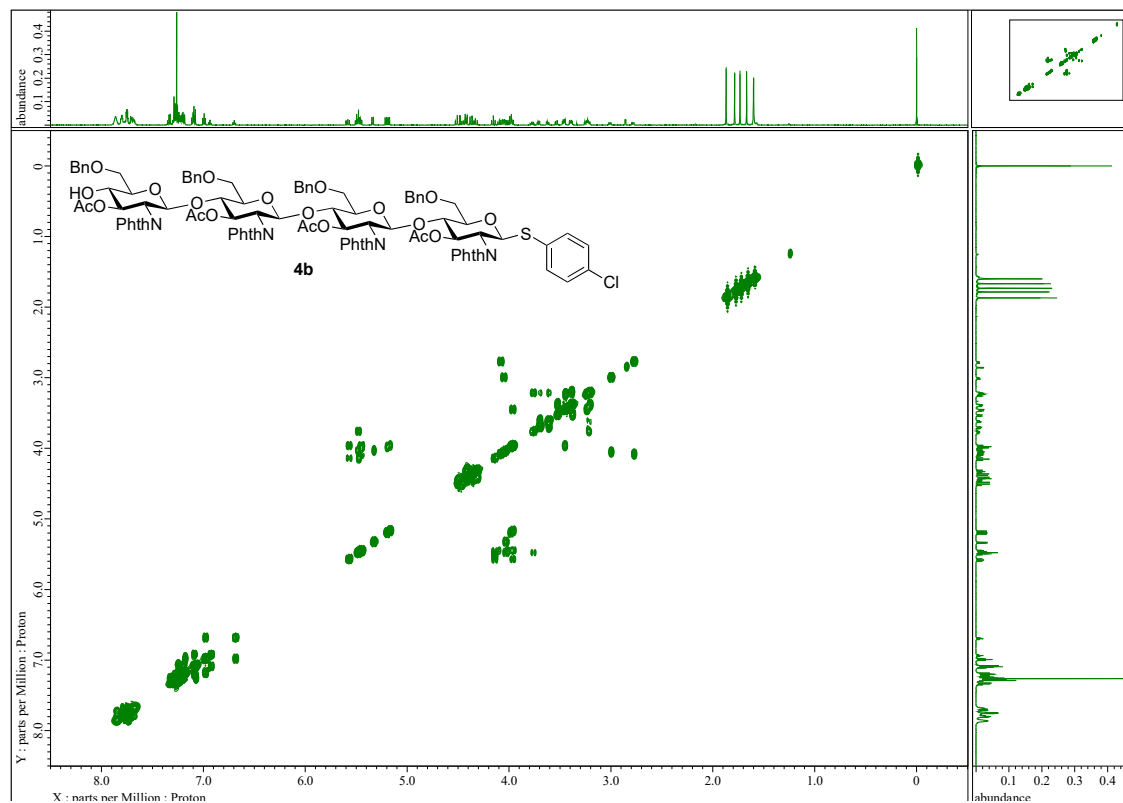
¹H NMR



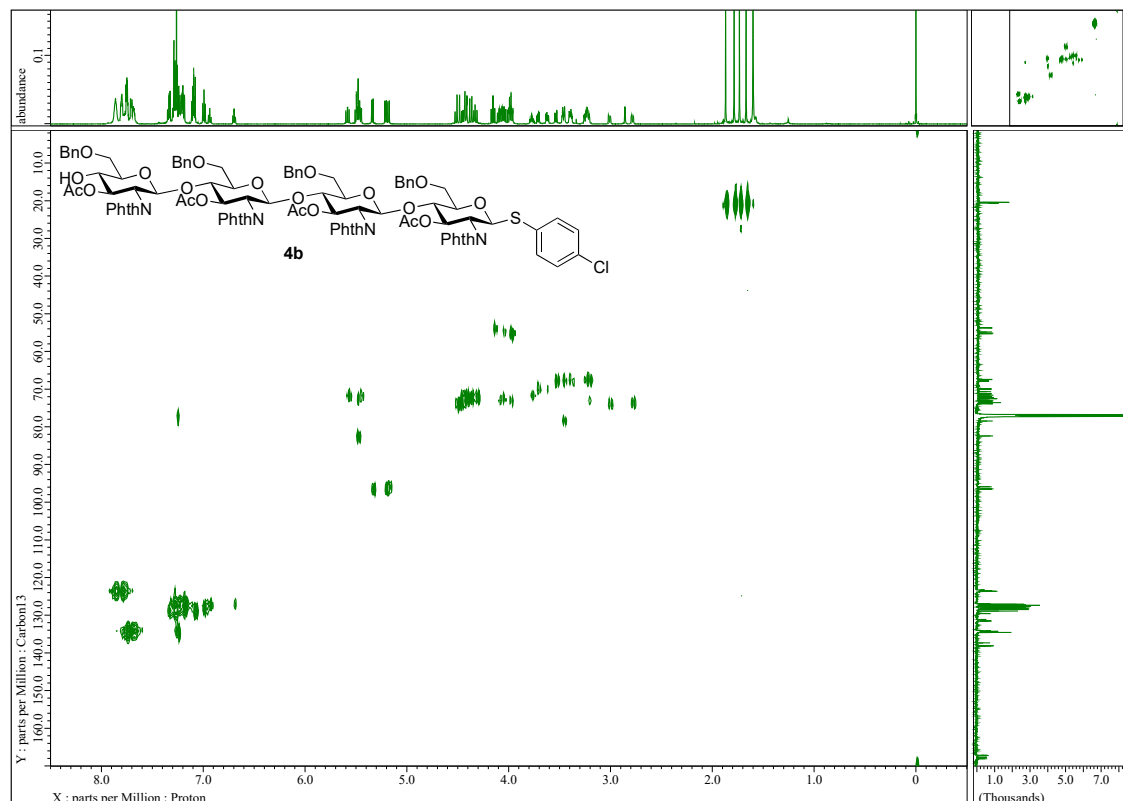
¹³C NMR



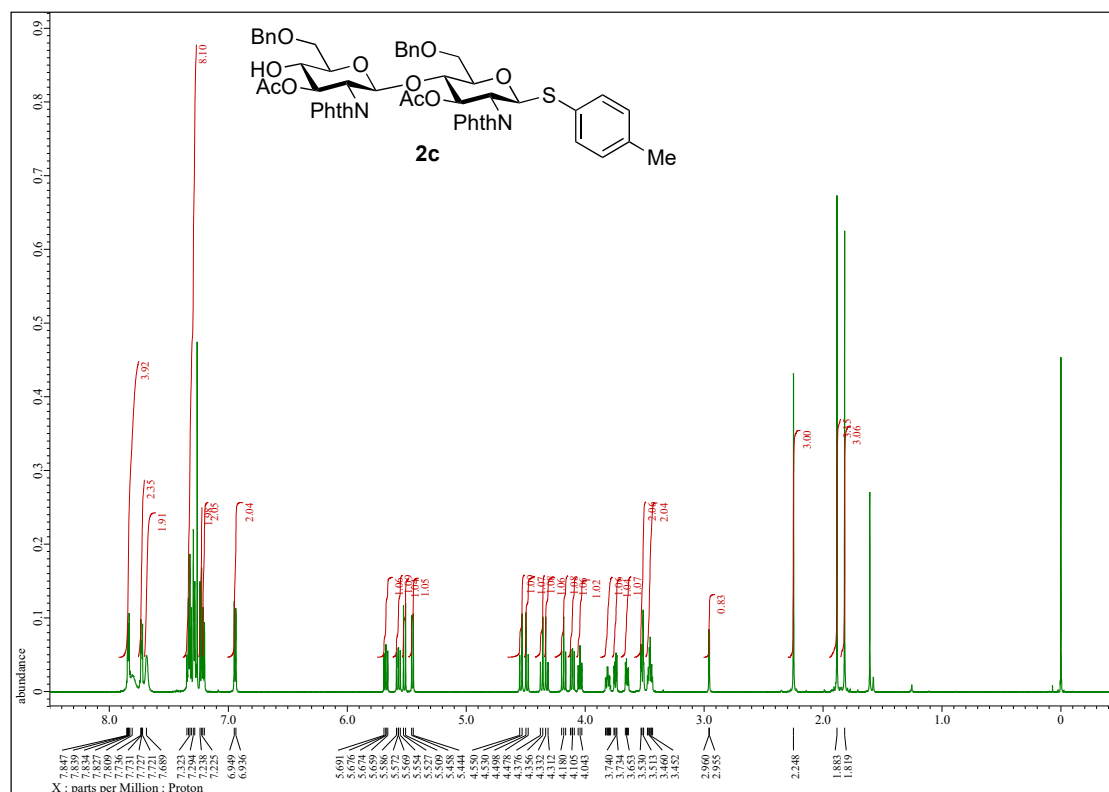
H,H-COSY



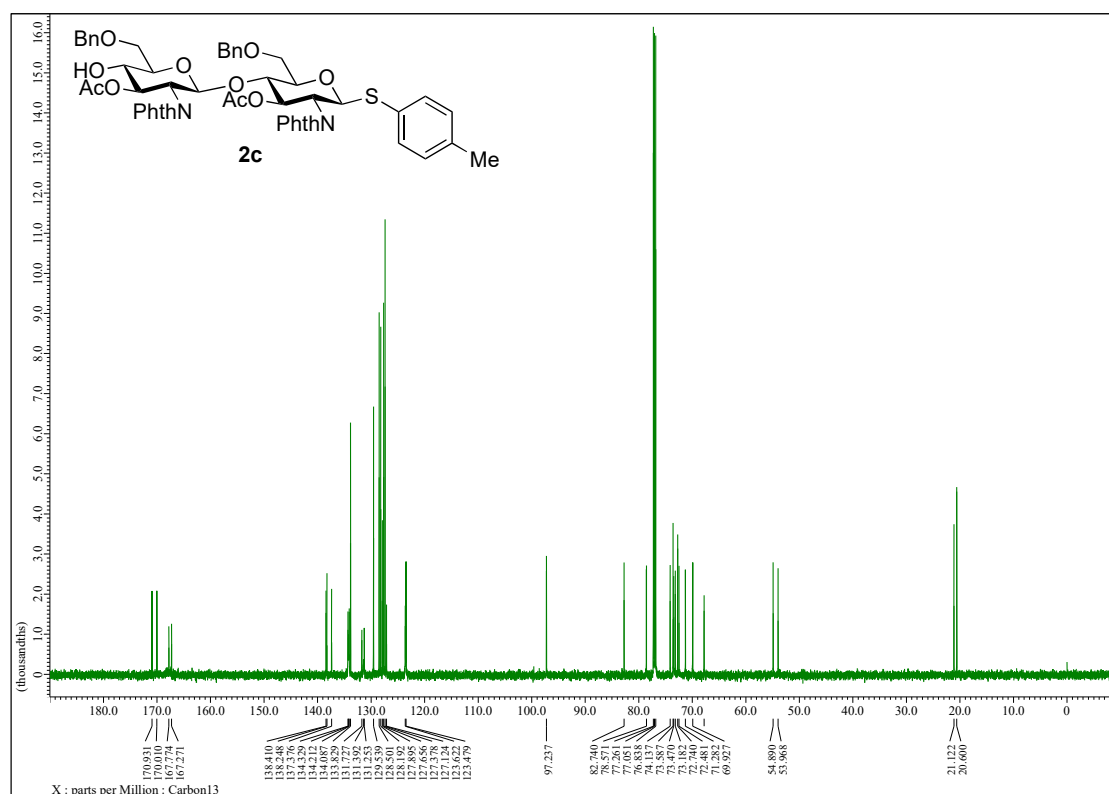
HMQC



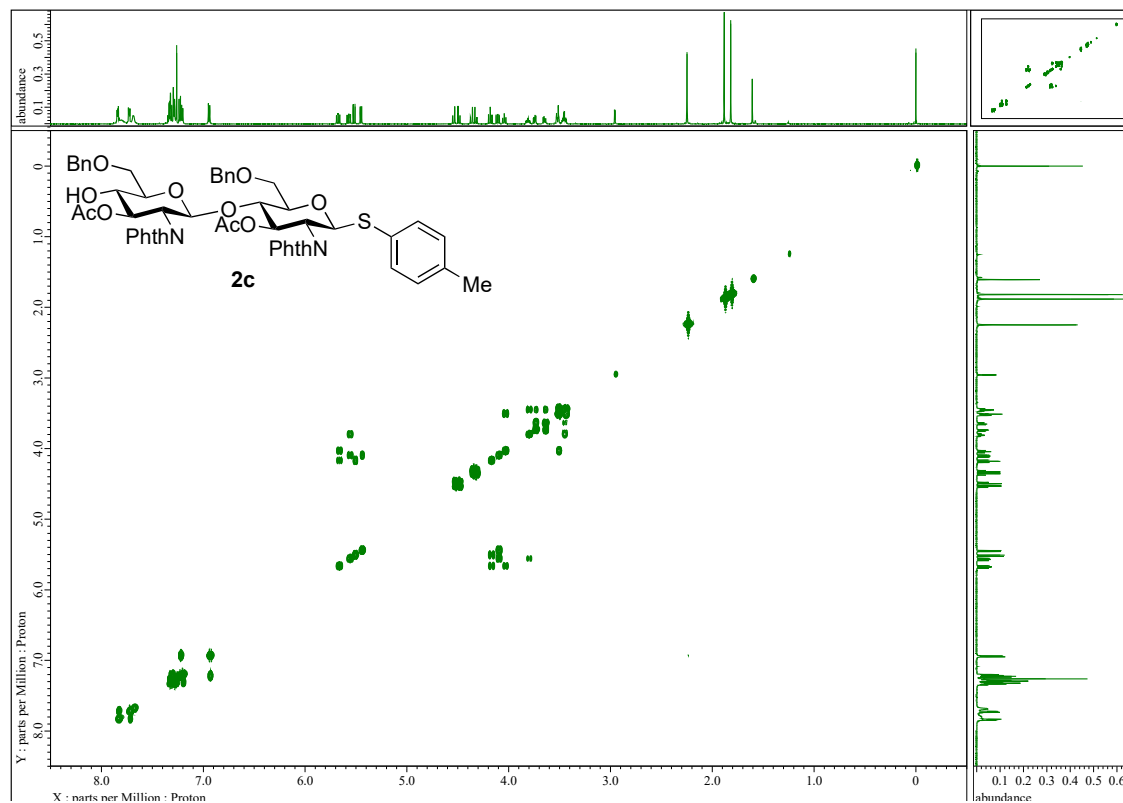
¹H NMR



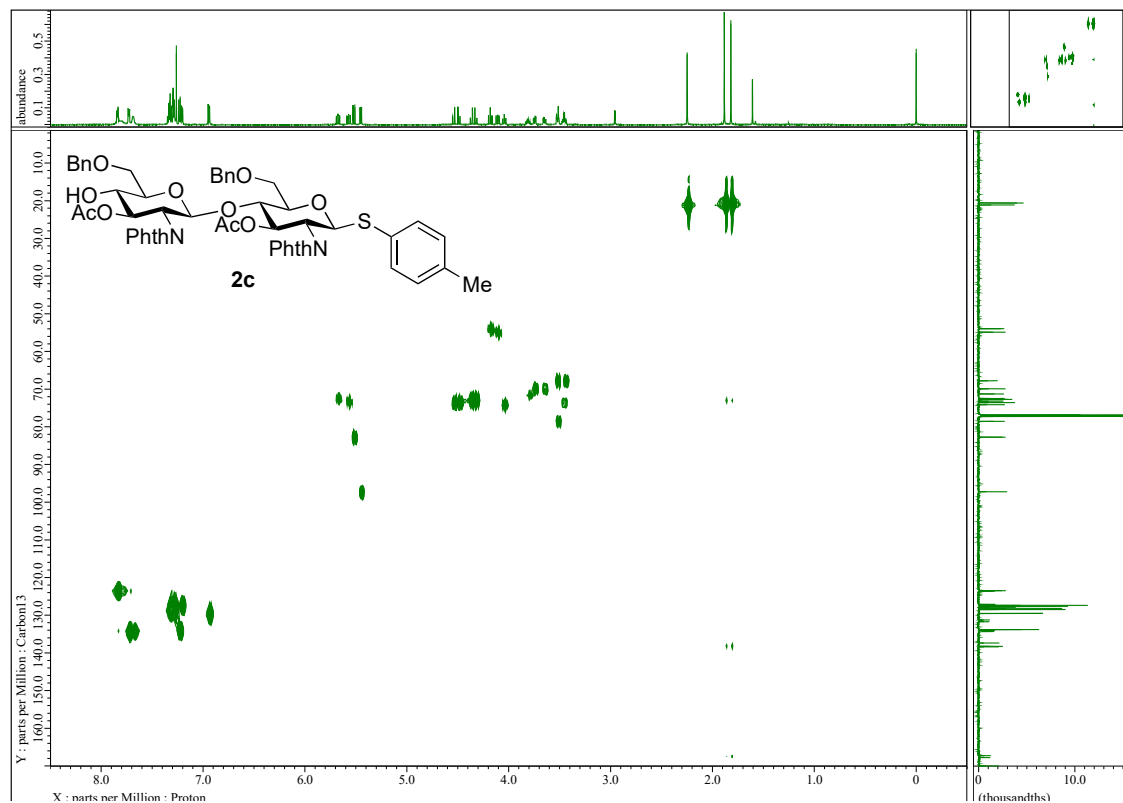
¹³C NMR



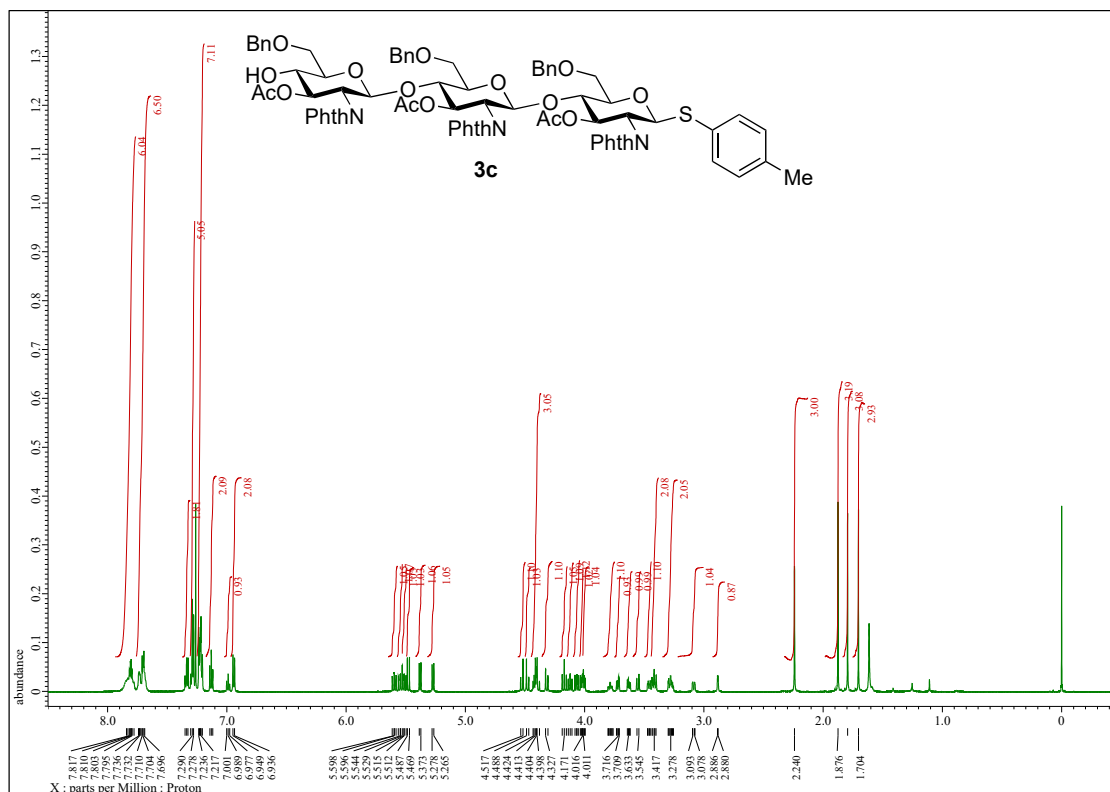
H,H-COSY



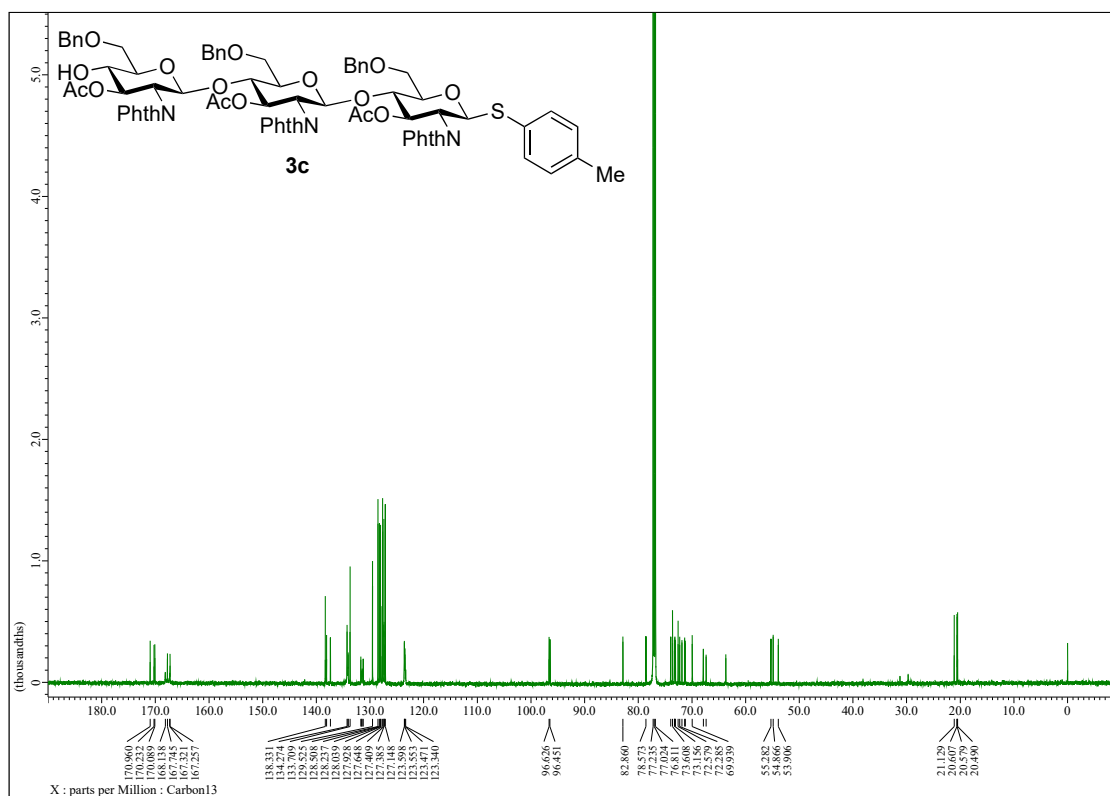
HMQC



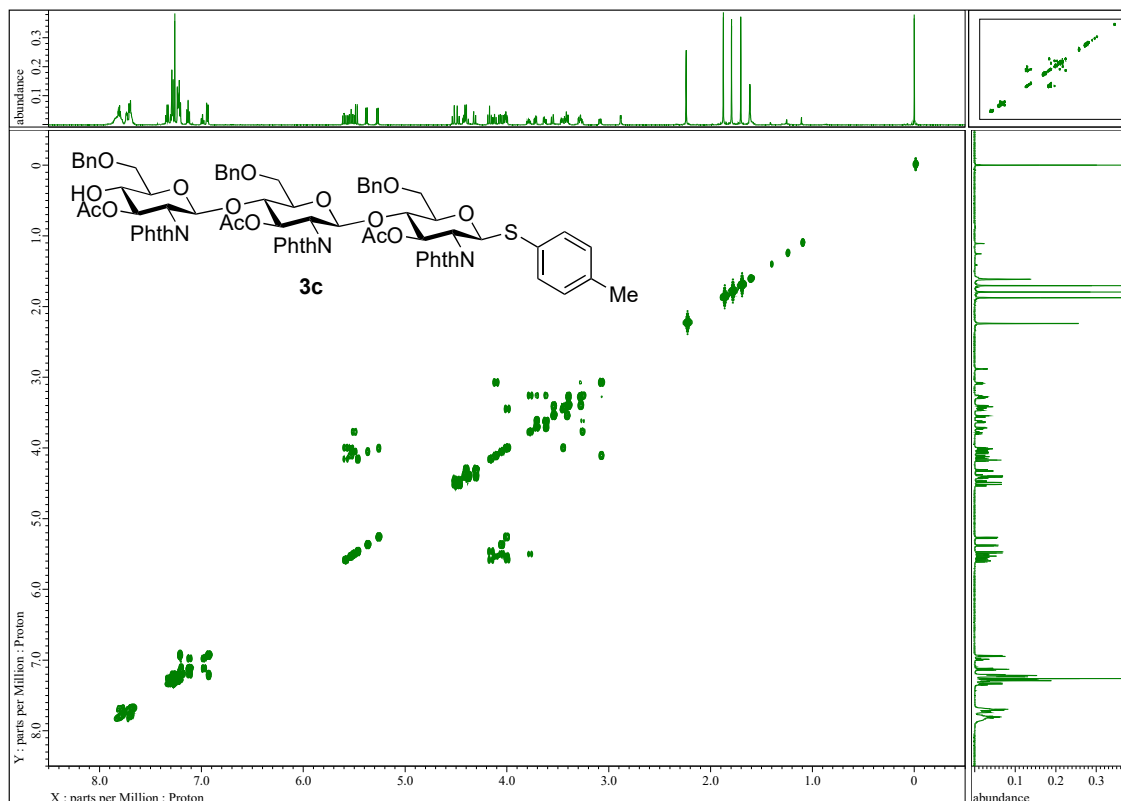
¹H NMR



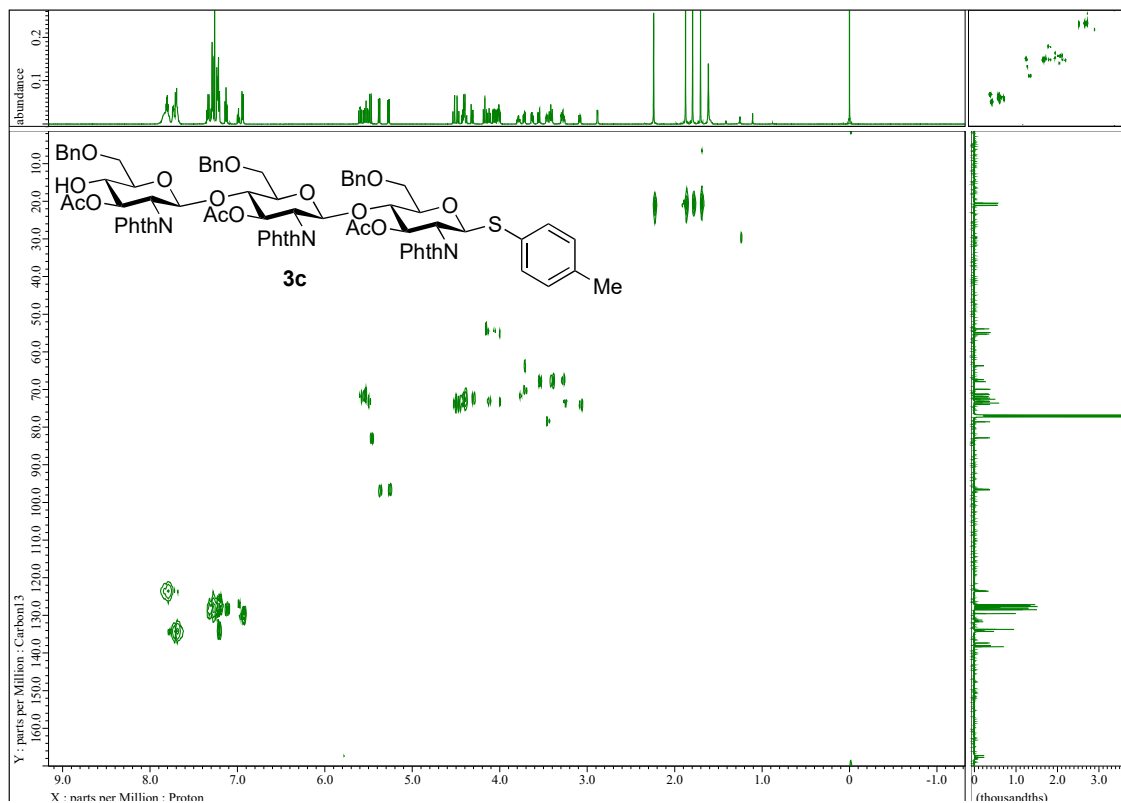
¹³C NMR



H,H-COSY



HMQC



Chemical structure of compound **4c** is shown above the spectrum. It is a tetramer of a substituted sugar derivative linked by (1 $\rightarrow$ 3)-glycosidic bonds. Each sugar unit has a benzoyl (BnO) group at C2, an acetate (AcO) group at C4, and a phenylthio (PhthN) group at C1. The terminal unit on the right is linked to a 4-methylphenyl group via a thioether bond.

¹H NMR spectrum (CDCl₃) of compound **4c**. The x-axis represents the chemical shift (δ) in ppm, ranging from 0 to 10. The y-axis represents the abundance. The spectrum shows several sharp peaks in the aromatic region (6.5–8.5 ppm) and a cluster of peaks in the aliphatic region (1.6–4.6 ppm). Integration values are provided below the peaks.

Chemical shift values (ppm) and integration values (from left to right):

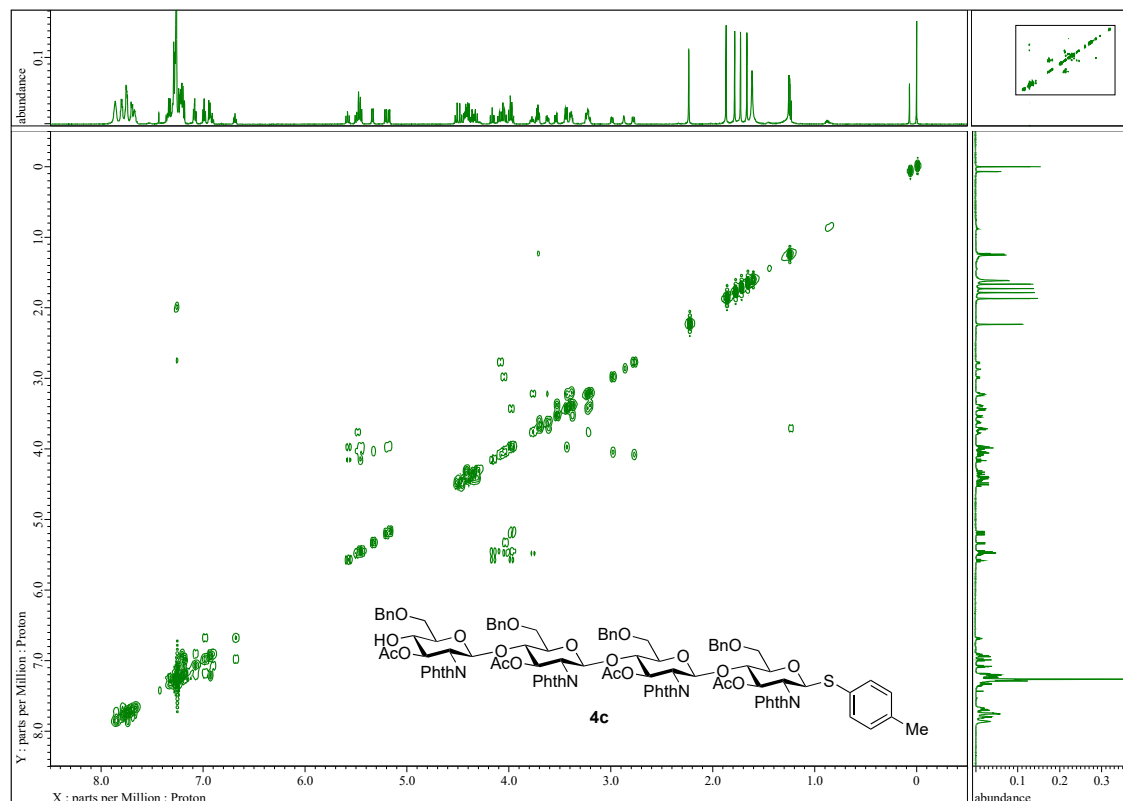
- 8.02, 7.982, 7.977, 7.956, 7.756, 7.741, 7.74, 7.697, 7.692, 7.686, 7.674 (integration: 4.04, 4.19)
- 7.288, 7.275, 7.208, 6.988, 6.944 (integration: 2.20, 1.99)
- 6.699, 6.686, 6.674 (integration: 0.97, 0.92)
- 5.983, 5.978, 5.973, 5.909, 5.493, 5.490, 5.457, 5.444, 5.330, 5.311, 5.203, 5.183, 5.169 (integration: 1.977, 1.96, 1.14, 0.96)
- 4.507, 4.482, 4.461, 4.414, 4.405, 4.391 (integration: 1.9815, 1.9815, 1.97, 1.97)
- 4.059, 4.046, 3.977, 3.971 (integration: 0.92, 2.97, 2.97)
- 3.726, 3.715, 3.711, 3.706, 3.696, 3.686, 3.676, 3.666, 3.656, 3.646, 3.636, 3.626, 3.616, 3.606, 3.596, 3.586, 3.576, 3.566, 3.556, 3.546, 3.536, 3.526, 3.516, 3.506, 3.496, 3.486, 3.476, 3.466, 3.456, 3.446, 3.436, 3.426, 3.416, 3.406, 3.396, 3.386, 3.376, 3.366, 3.356, 3.346, 3.336, 3.326, 3.316, 3.306, 3.296, 3.286, 3.276, 3.266, 3.256, 3.246, 3.236, 3.226, 3.216, 3.206, 3.196, 3.186, 3.176, 3.166, 3.156, 3.146, 3.136, 3.126, 3.116, 3.106, 3.096, 3.086, 3.076, 3.066, 3.056, 3.046, 3.036, 3.026, 3.016, 3.006, 3.000, 2.996, 2.986, 2.976, 2.966, 2.956, 2.946, 2.936, 2.926, 2.916, 2.906, 2.896, 2.886, 2.876, 2.866, 2.856, 2.846, 2.836, 2.826, 2.816, 2.806, 2.796, 2.786, 2.776, 2.766, 2.756, 2.746, 2.736, 2.726, 2.716, 2.706, 2.696, 2.686, 2.676, 2.666, 2.656, 2.646, 2.636, 2.626, 2.616, 2.606, 2.596, 2.586, 2.576, 2.566, 2.556, 2.546, 2.536, 2.526, 2.516, 2.506, 2.496, 2.486, 2.476, 2.466, 2.456, 2.446, 2.436, 2.426, 2.416, 2.406, 2.396, 2.386, 2.376, 2.366, 2.356, 2.346, 2.336, 2.326, 2.316, 2.306, 2.296, 2.286, 2.276, 2.266, 2.256, 2.246, 2.236 (integration: 1.08, 1.46, 1.97, 3.17, 3.00, 3.34, 3.34, 3.42)
- 1.669, 1.665 (integration: 1.669, 1.665)

Chemical structure of compound **4c** is shown above the spectrum. The structure is a linear tetramer of 2,3,6-tri-O-benzoyl-4-O-(4-methylphenylthio)- α -D-glucopyranoside units.

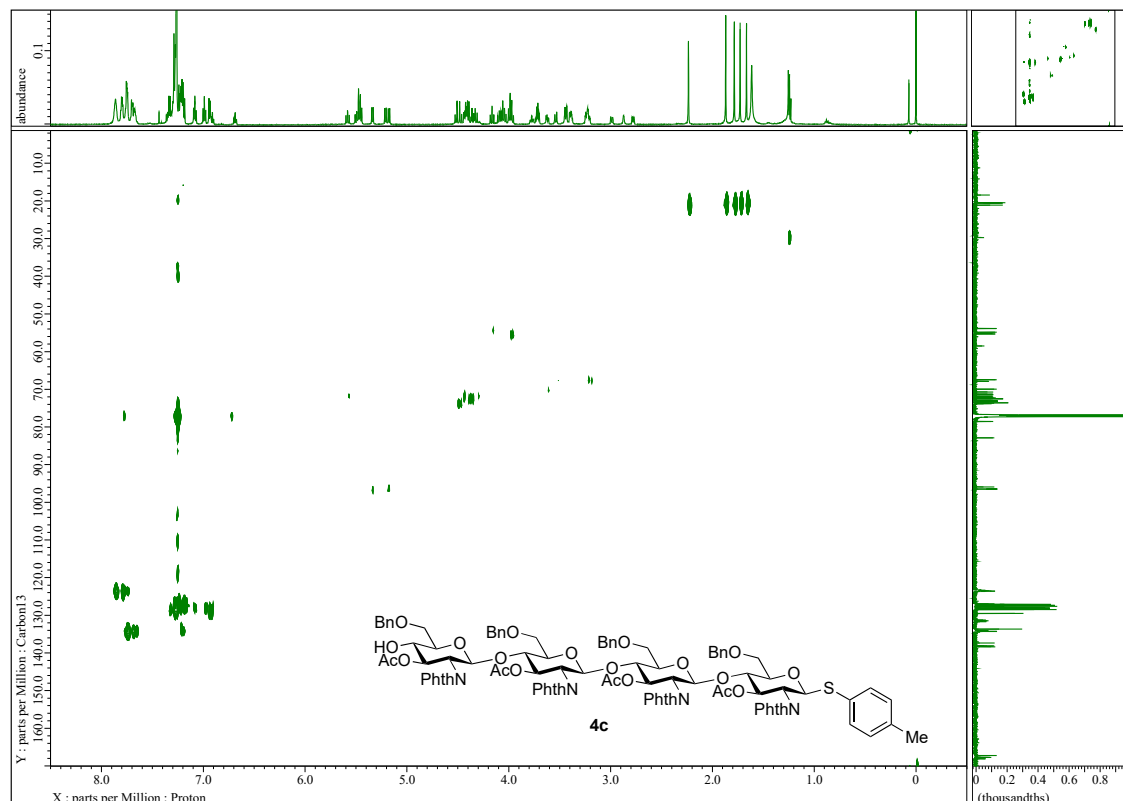
¹³C NMR spectrum (CDCl₃) of compound 4c:

Chemical shift (ppm): 170.953, 170.337, 170.110, 167.254, 167.254, 138.360, 138.215, 138.116, 137.276, 137.256, 127.986, 127.641, 127.608, 123.670, 123.627, 123.514, 123.505, 123.485, 96.511, 95.920, 82.884, 77.250, 77.022, 73.596, 73.114, 73.100, 72.522, 69.958, 67.252, 55.399, 55.179, 54.854, 53.875, 21.124, 20.600, 20.571, 20.478, 20.552.

¹H,¹H-COSY



HMQC



Chemical structure of **2d** is shown above the spectrum. It is a dimeric compound consisting of two 2-acetoxy-3-benzyloxy-4-phthalimidyl-5-O-(2,4-difluorophenylthio)-D-glucopyranoside units linked by a 1,4-glycosidic bond.

¹H NMR spectrum (CDCl₃) of compound **2d**. The x-axis represents chemical shift (δ) in ppm, ranging from 0 to 10. The y-axis represents abundance, ranging from 0 to 0.4. The spectrum shows several peaks with integration values (in red) and chemical shift values (in black) listed below the peaks.

Chemical shift values (ppm) listed below the spectrum:

- 8.851, 8.841, 8.837, 8.833, 8.829, 8.825, 8.821, 8.817, 8.813, 8.809, 8.805, 8.801, 8.797, 8.793, 8.789, 8.785, 8.781, 8.777, 8.773, 8.769, 8.765, 8.761, 8.757, 8.753, 8.749, 8.745, 8.741, 8.737, 8.733, 8.729, 8.725, 8.721, 8.717, 8.713, 8.709, 8.705, 8.701, 8.697, 8.693, 8.689, 8.685, 8.681, 8.677, 8.673, 8.669, 8.665, 8.661, 8.657, 8.653, 8.649, 8.645, 8.641, 8.637, 8.633, 8.629, 8.625, 8.621, 8.617, 8.613, 8.609, 8.605, 8.601, 8.597, 8.593, 8.589, 8.585, 8.581, 8.577, 8.573, 8.569, 8.565, 8.561, 8.557, 8.553, 8.549, 8.545, 8.541, 8.537, 8.533, 8.529, 8.525, 8.521, 8.517, 8.513, 8.509, 8.505, 8.501, 8.497, 8.493, 8.489, 8.485, 8.481, 8.477, 8.473, 8.469, 8.465, 8.461, 8.457, 8.453, 8.449, 8.445, 8.441, 8.437, 8.433, 8.429, 8.425, 8.421, 8.417, 8.413, 8.409, 8.405, 8.401, 8.397, 8.393, 8.389, 8.385, 8.381, 8.377, 8.373, 8.369, 8.365, 8.361, 8.357, 8.353, 8.349, 8.345, 8.341, 8.337, 8.333, 8.329, 8.325, 8.321, 8.317, 8.313, 8.309, 8.305, 8.301, 8.297, 8.293, 8.289, 8.285, 8.281, 8.277, 8.273, 8.269, 8.265, 8.261, 8.257, 8.253, 8.249, 8.245, 8.241, 8.237, 8.233, 8.229, 8.225, 8.221, 8.217, 8.213, 8.209, 8.205, 8.201, 8.197, 8.193, 8.189, 8.185, 8.181, 8.177, 8.173, 8.169, 8.165, 8.161, 8.157, 8.153, 8.149, 8.145, 8.141, 8.137, 8.133, 8.129, 8.125, 8.121, 8.117, 8.113, 8.109, 8.105, 8.101, 8.097, 8.093, 8.089, 8.085, 8.081, 8.077, 8.073, 8.069, 8.065, 8.061, 8.057, 8.053, 8.049, 8.045, 8.041, 8.037, 8.033, 8.029, 8.025, 8.021, 8.017, 8.013, 8.009, 8.005, 8.001, 7.997, 7.993, 7.989, 7.985, 7.981, 7.977, 7.973, 7.969, 7.965, 7.961, 7.957, 7.953, 7.949, 7.945, 7.941, 7.937, 7.933, 7.929, 7.925, 7.921, 7.917, 7.913, 7.909, 7.905, 7.901, 7.897, 7.893, 7.889, 7.885, 7.881, 7.877, 7.873, 7.869, 7.865, 7.861, 7.857, 7.853, 7.849, 7.845, 7.841, 7.837, 7.833, 7.829, 7.825, 7.821, 7.817, 7.813, 7.809, 7.805, 7.801, 7.797, 7.793, 7.789, 7.785, 7.781, 7.777, 7.773, 7.769, 7.765, 7.761, 7.757, 7.753, 7.749, 7.745, 7.741, 7.737, 7.733, 7.729, 7.725, 7.721, 7.717, 7.713, 7.709, 7.705, 7.701, 7.697, 7.693, 7.689, 7.685, 7.681, 7.677, 7.673, 7.669, 7.665, 7.661, 7.657, 7.653, 7.649, 7.645, 7.641, 7.637, 7.633, 7.629, 7.625, 7.621, 7.617, 7.613, 7.609, 7.605, 7.601, 7.597, 7.593, 7.589, 7.585, 7.581, 7.577, 7.573, 7.569, 7.565, 7.561, 7.557, 7.553, 7.549, 7.545, 7.541, 7.537, 7.533, 7.529, 7.525, 7.521, 7.517, 7.513, 7.509, 7.505, 7.501, 7.497, 7.493, 7.489, 7.485, 7.481, 7.477, 7.473, 7.469, 7.465, 7.461, 7.457, 7.453, 7.449, 7.445, 7.441, 7.437, 7.433, 7.429, 7.425, 7.421, 7.417, 7.413, 7.409, 7.405, 7.401, 7.397, 7.393, 7.389, 7.385, 7.381, 7.377, 7.373, 7.369, 7.365, 7.361, 7.357, 7.353, 7.349, 7.345, 7.341, 7.337, 7.333, 7.329, 7.325, 7.321, 7.317, 7.313, 7.309, 7.305, 7.301, 7.297, 7.293, 7.289, 7.285, 7.281, 7.277, 7.273, 7.269, 7.265, 7.261, 7.257, 7.253, 7.249, 7.245, 7.241, 7.237, 7.233, 7.229, 7.225, 7.221, 7.217, 7.213, 7.209, 7.205, 7.201, 7.197, 7.193, 7.189, 7.185, 7.181, 7.177, 7.173, 7.169, 7.165, 7.161, 7.157, 7.153, 7.149, 7.145, 7.141, 7.137, 7.133, 7.129, 7.125, 7.121, 7.117, 7.113, 7.109, 7.105, 7.101, 7.097, 7.093, 7.089, 7.085, 7.081, 7.077, 7.073, 7.069, 7.065, 7.061, 7.057, 7.053, 7.049, 7.045, 7.041, 7.037, 7.033, 7.029, 7.025, 7.021, 7.017, 7.013, 7.009, 7.005, 7.001, 6.997, 6.993, 6.989, 6.985, 6.981, 6.977, 6.973, 6.969, 6.965, 6.961, 6.957, 6.953, 6.949, 6.945, 6.941, 6.937, 6.933, 6.929, 6.925, 6.921, 6.917, 6.913, 6.909, 6.905, 6.901, 6.897, 6.893, 6.889, 6.885, 6.881, 6.877, 6.873, 6.869, 6.865, 6.861, 6.857, 6.853, 6.849, 6.845, 6.841, 6.837, 6.833, 6.829, 6.825, 6.821, 6.817, 6.813, 6.809, 6.805, 6.801, 6.797, 6.793, 6.789, 6.785, 6.781, 6.777, 6.773, 6.769, 6.765, 6.761, 6.757, 6.753, 6.749, 6.745, 6.741, 6.737, 6.733, 6.729, 6.725, 6.721, 6.717, 6.713, 6.709, 6.705, 6.701, 6.697, 6.693, 6.689, 6.685, 6.681, 6.677, 6.673, 6.669, 6.6

2d

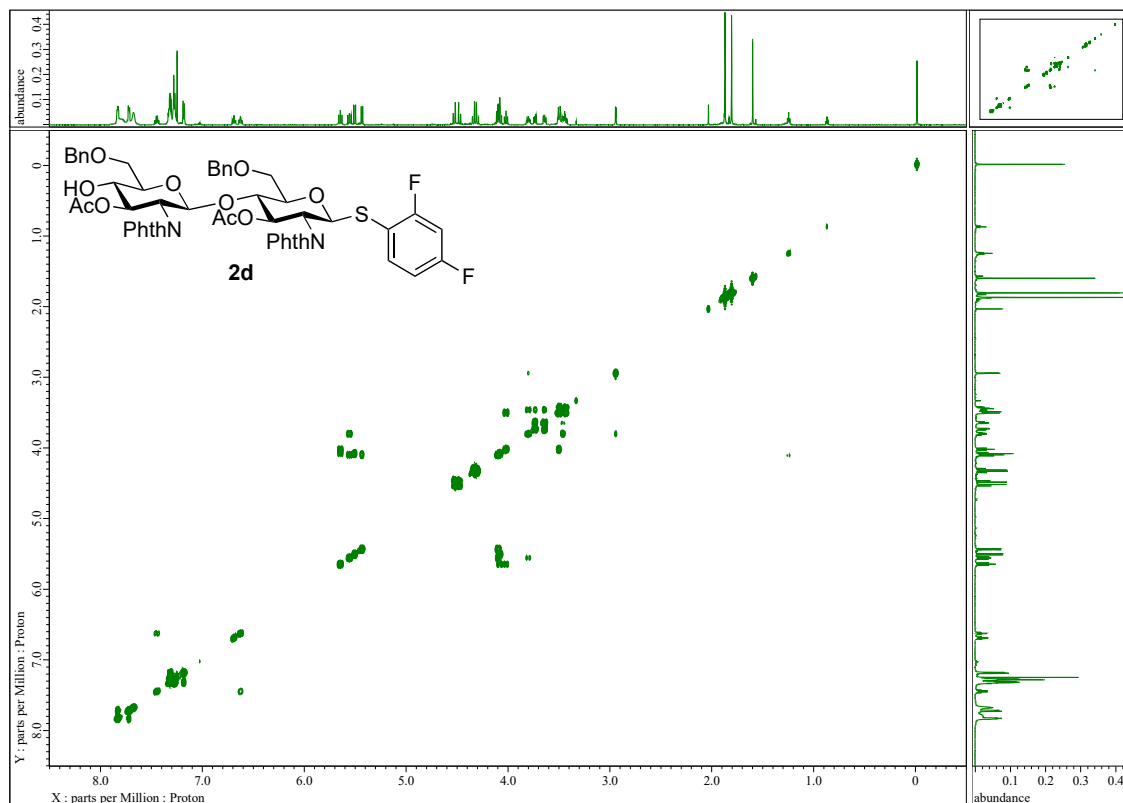
Chemical structure of compound **2d** is shown above the spectrum. The structure is a disaccharide derivative, specifically a 4,6-O-benzylidene-2-O-acetyl-beta-D-glucopyranosyl unit linked to a 2-O-acetyl-4-O-(4-fluorophenylthio)-D-glucopyranosyl unit.

The ^{13}C NMR spectrum (X : parts per Million : Carbon13) displays peaks corresponding to the carbon atoms in the molecule. The x-axis ranges from 180.0 to 0.0 ppm, and the y-axis represents intensity in thousands. The spectrum shows a complex pattern of peaks, with the most intense signals clustered between 60 and 80 ppm, characteristic of anomeric carbons and sugar ring carbons. Other significant peaks are observed in the 100-140 ppm range, likely corresponding to the acetyl and benzylidene groups.

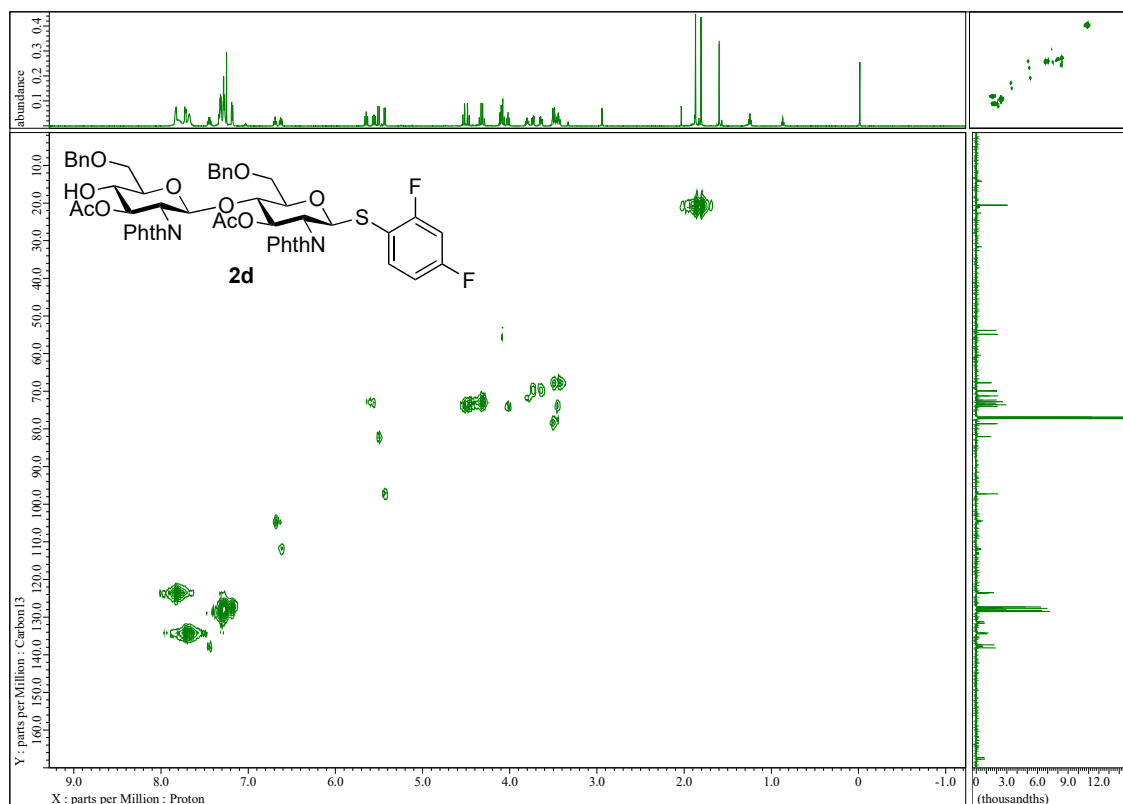
Key labeled peaks (ppm) include:

- 170.953, 169.747, 167.390, 164.442, 163.463, 163.547, 162.697, 161.886, 161.586
- 138.169, 137.560, 134.761, 134.166, 131.646, 128.515, 127.924, 127.663, 127.387, 123.658, 123.486
- 112.032, 111.666, 111.888, 111.864, 104.619, 104.244, 104.269, 97.256
- 82.029, 78.628, 77.044, 76.835, 74.018, 73.522, 73.522, 72.761, 71.234
- 54.878, 53.844
- 20.895, 20.579

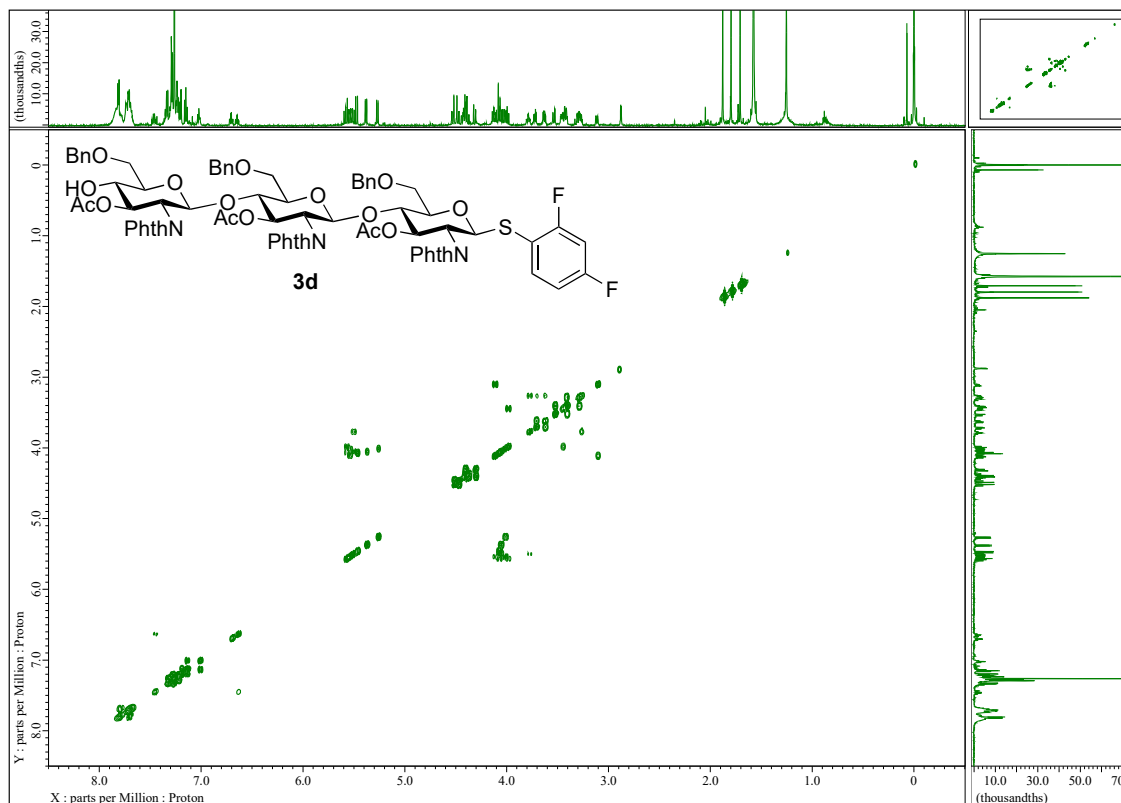
¹H,¹H-COSY



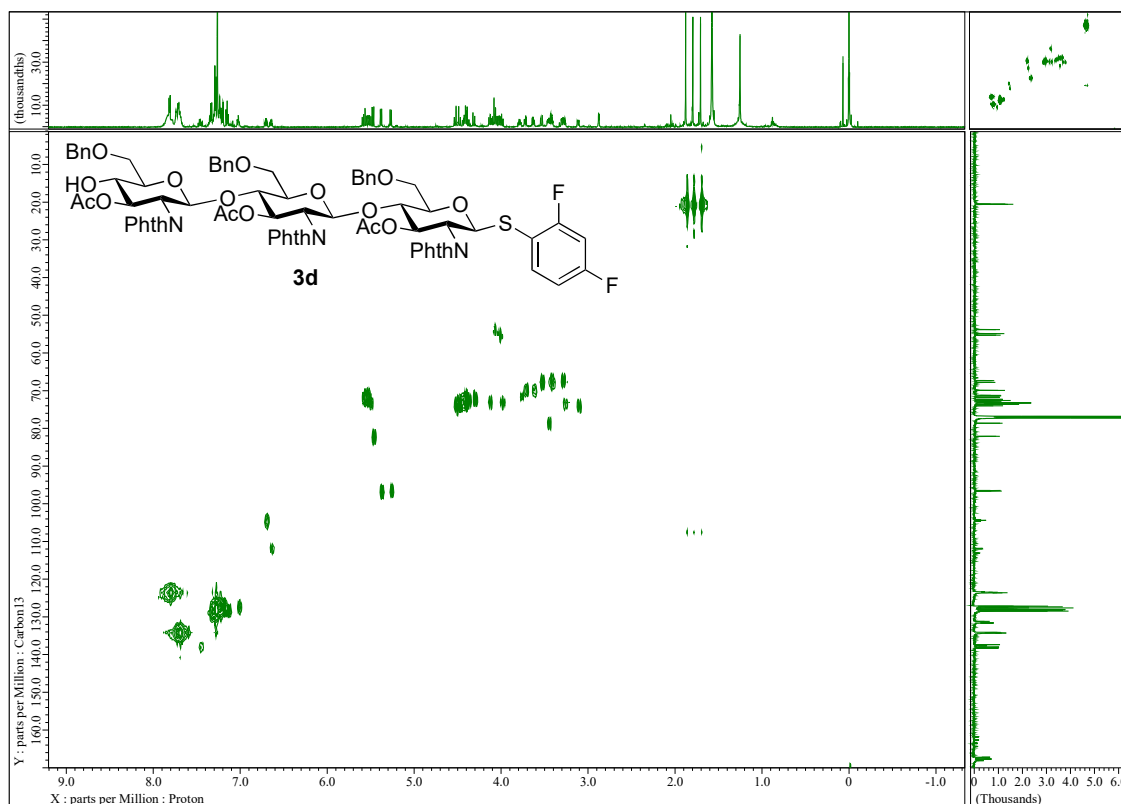
HMQC



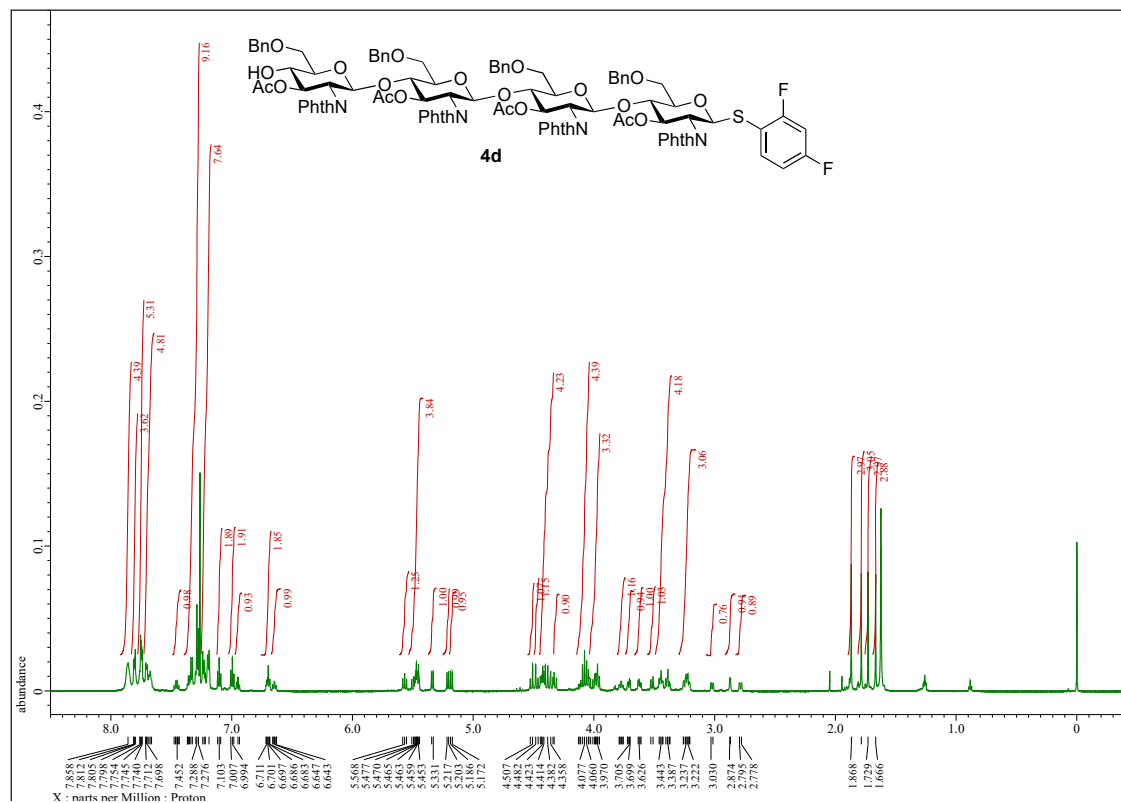
H,H-COSY



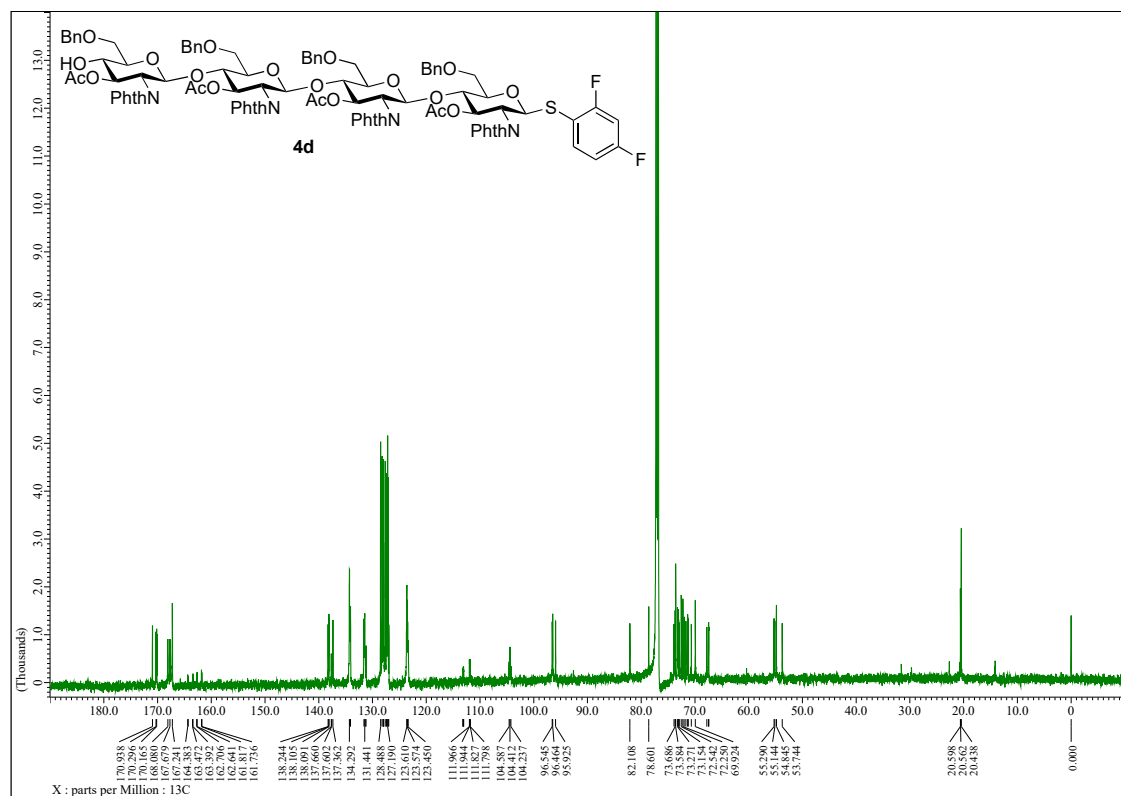
HMQC



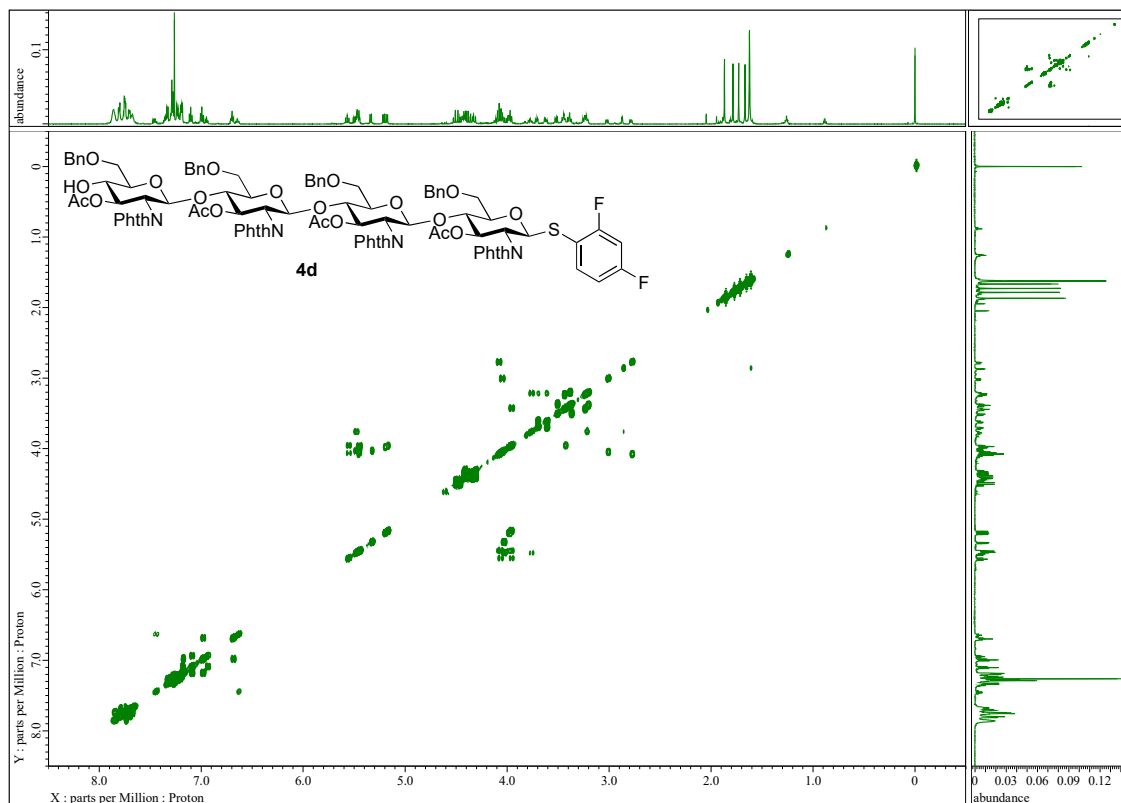
¹H NMR



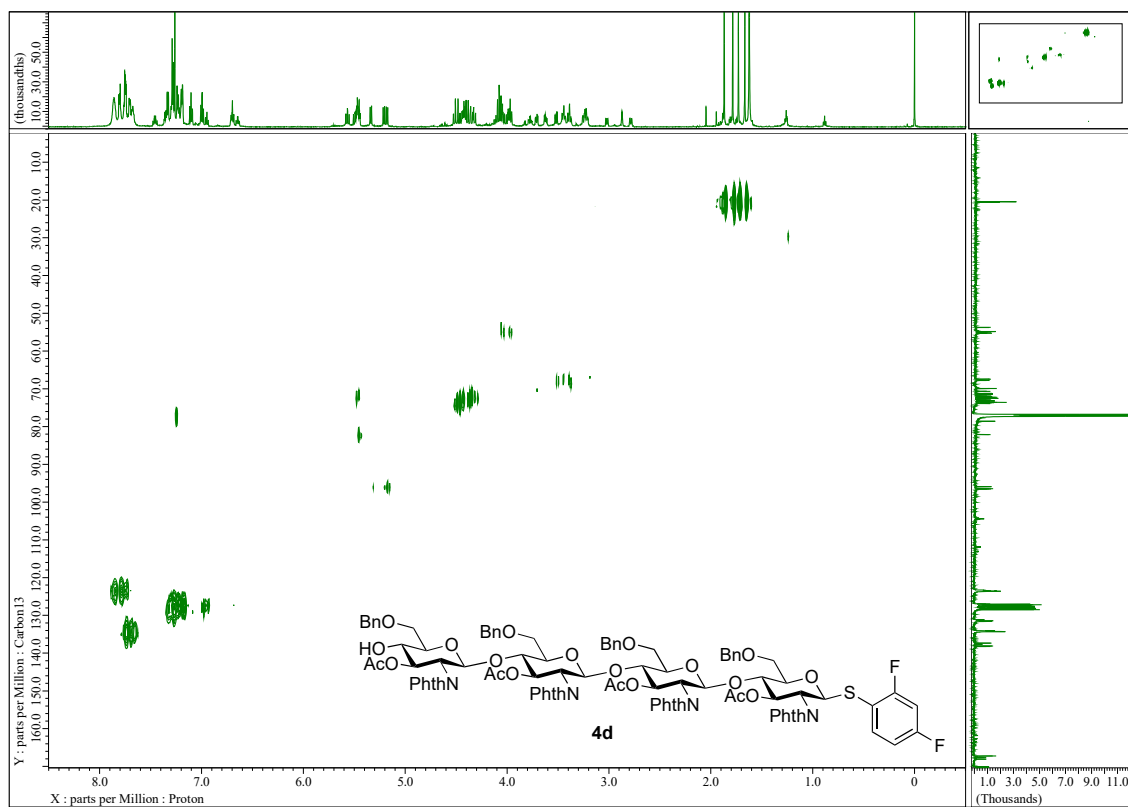
¹³C NMR



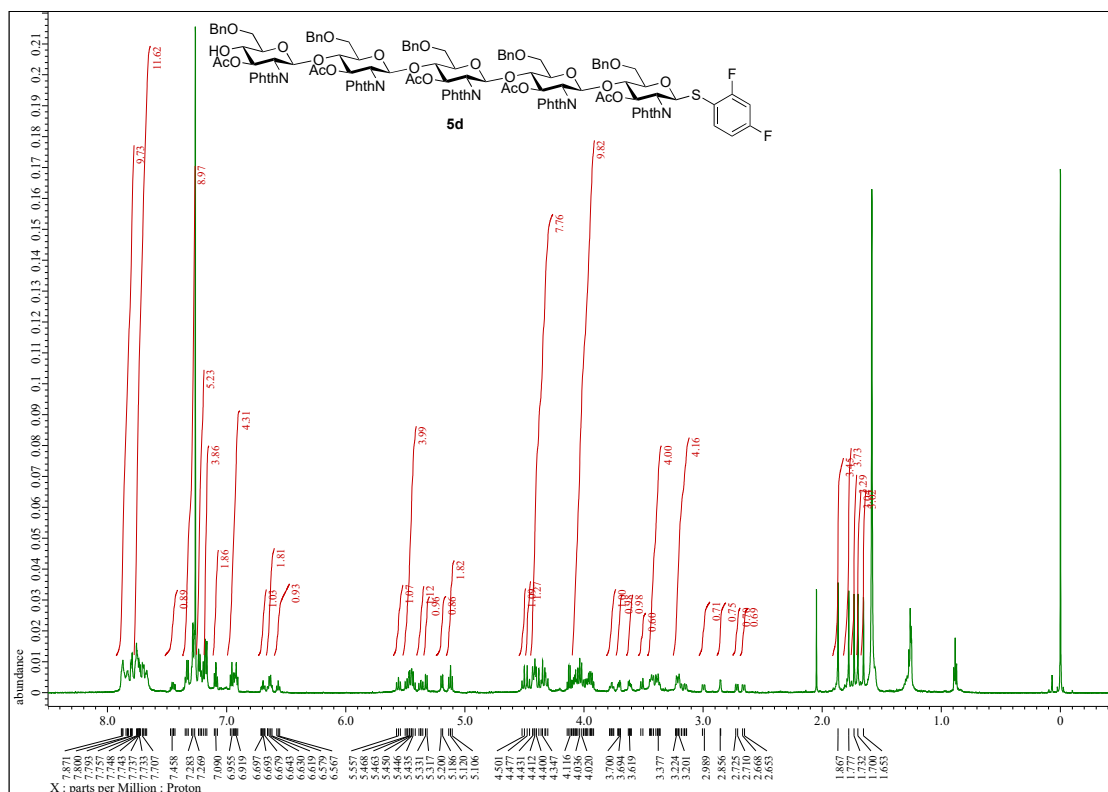
¹H,¹H-COSY



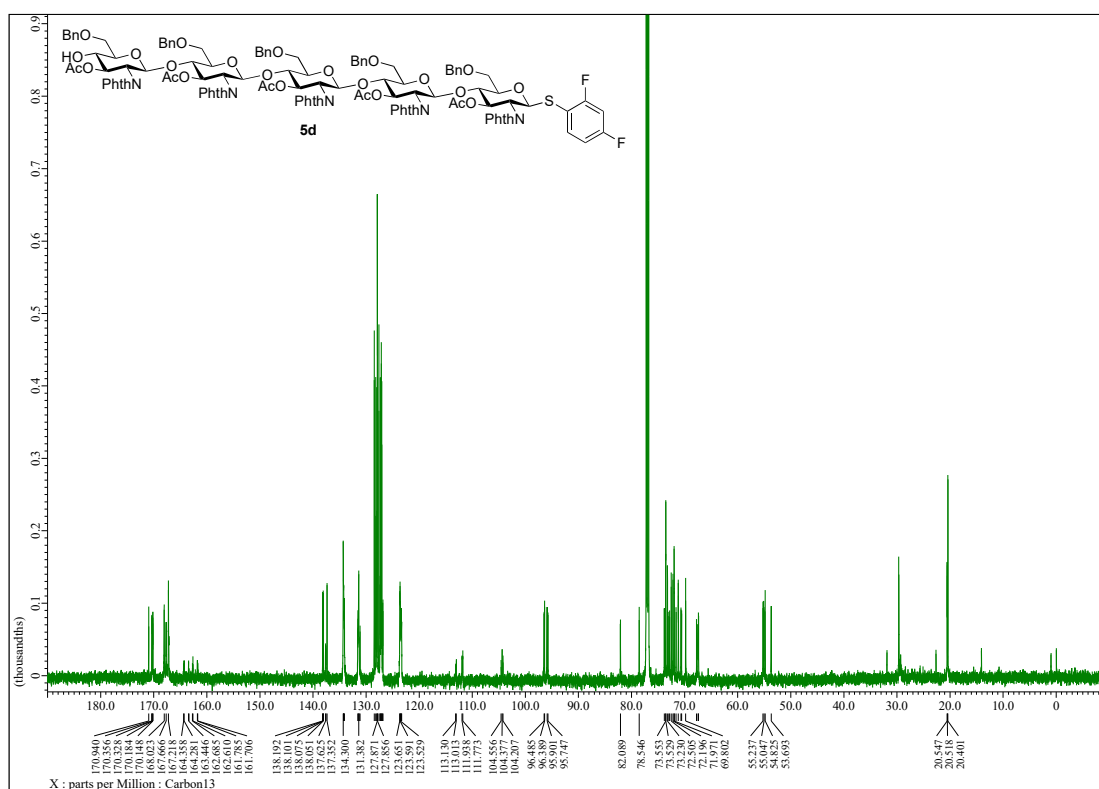
HMQC



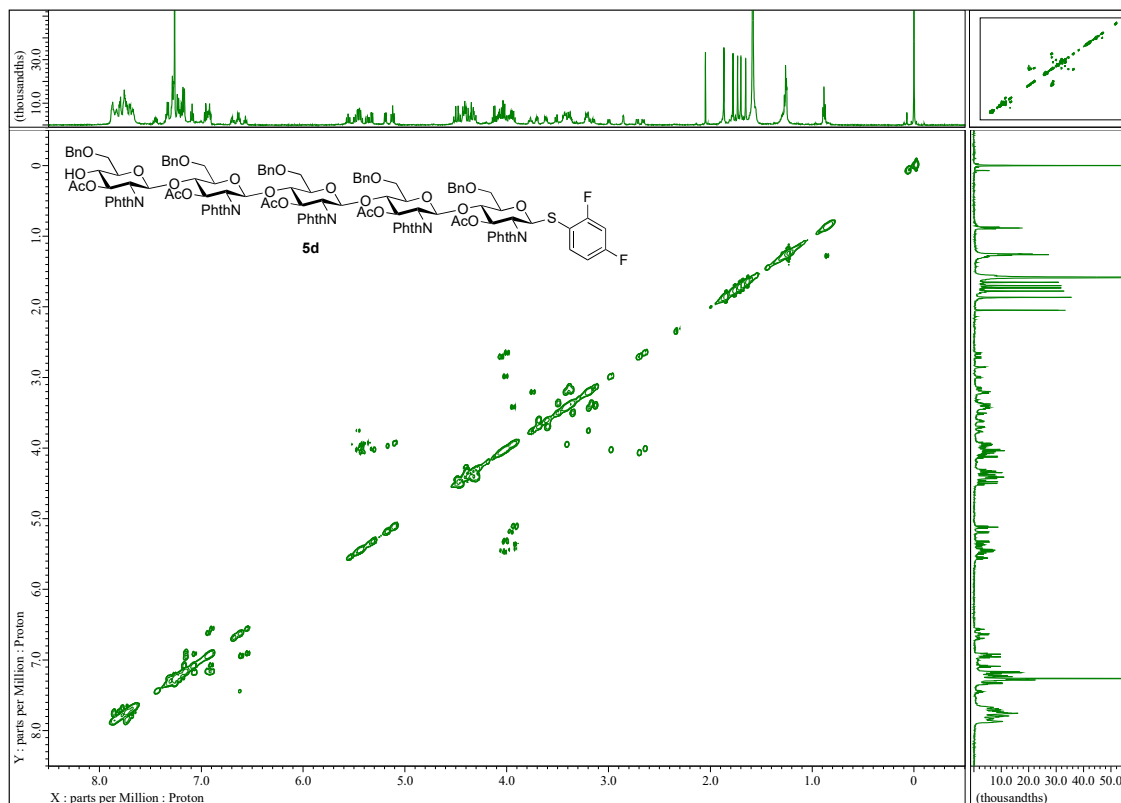
¹H NMR



¹³C NMR



H,H-COSY



HMQC

