Electronic Supplementary Information

Synthesis of Protected Precursors of Chitin Oligosaccharides by Electrochemical Polyglycosylation of Thioglycosides

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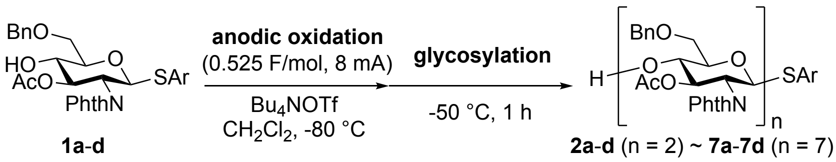
1. General

All reactions were carried out under argon atmosphere except notice. ^{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 (600 MHz for ^{1}H and 150 MHz for ^{13}C). ESI-MS spectra were recorded on Thermo Scientific Exactive spectrometer. MALDI-TOF MS spectra were recorded on Bruker Ultraflextreme spectrometer. Optical rotation data was recorded on JASCO DIP-370 digital polarimeter. Merck TLC (silica gel 60 F_{254}) was 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 BAS 700c analyzer and RRDE-3 rotating ring disk electrode. Measurements of oxidation potential of substrates (conc. 4.0 mM) were carried out in 0.1 M Bu_4NOTf/CH_2Cl_2 using a glassy carbon disk working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) as a reference electrode with sweep rate of 10 mV/s at 2000 r.p.m.. 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 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_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 °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 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, 0.053 mmol, 52.0 mg, 27%), **3a** (*n* = 3, 0.0248 mmol, 34.7 mg, 19%), **4a** (*n* = 4, 0.0106 mmol, 19.3 mg, 11%), **5a** (*n* = 5, 2.22 μmol, 5.0 mg, 3%), **6a** (*n* =

6, 0.090 μmol, 2.4 mg, 1%), and **7a** (n = 7, trace) as white solids. Recovered yield of buliding block **1a** was 27% (58.2 mg, 0.1055 mmol).

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): R_f 0.57. $[\alpha]_D$ = –7.88 (c = 1.0, $CHCl_3$, 26 °C). E_{ox} = 1.76 V vs. SCE; ^{1}H NMR ($CDCl_3$, 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).; ^{13}C NMR ($CDCl_3$, 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 $C_{52}H_{47}FKN_2O_{14}S$ $[M+K]^+$, 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-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): R_f 0.50. $[\alpha]_D$ = –15.8 (c = 1.0, $CHCl_3$, 26 °C). E_{ox} = 1.74 V vs. SCE; ^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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→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): 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→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 (**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 $C_{121}H_{110}FN_5NaO_{35}S$ $[M+Na]^+$, 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-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 °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 $C_{144}H_{131}FN_6NaO_{42}S$ $[M+Na]^+$, 2689.7896; found, 2689.7849.

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-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); ^{1}H 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 $C_{167}H_{152}FKN_7O_{49}S$ $[M+K]^+$, 3128.8954; found, 3128.8948.

Buliding block **1b** (0.40 mmol, 220 mg) afforded oligosaccharides **2b** (n = 2, 0.060 mmol, 60 mg, 30%), **3b** (n = 3, 0.027 mmol, 40 mg, 20%), and **4b** (n = 4, 0.014 mmol, 26 mg, 14%) as white solids. Recovered yield of buliding block **1b** was 21% (47 mg, 0.083 mmol).

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): R_f 0.63. $[\alpha]_D$ = –8.62 (c = 1.3, $CHCl_3$, 27 °C); ^{1}H 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 $C_{52}H_{47}ClN_2NaO_{14}S$ [M+Na]$^+$, 1013.2329; found, 1013.2300.

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-β-D-glucopyranosyl)-(1→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 °C).; ^{1}H 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 $C_{75}H_{68}ClN_3NaO_{21}S$ [M+Na]$^+$, 1436.3647; found, 1436.3621.

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-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 (**4b**); TLC (Hexane:EtOAc 1:2): R_f 0.50. $[\alpha]_D$ = –32.9 (*c* = 0.7, $CHCl_3$, 27 °C); ^{1}H 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 $C_{98}H_{89}ClN_4NaO_{28}S$ $[M+Na]^+$, 1859.4965; found, 1859.4932.

Buliding block **1c** (0.20 mmol, 110 mg) afforded oligosaccharides **2c** (*n* = 2, 0.017 mmol, 16 mg, 17%), **3c** (*n* = 3, 0.0060 mmol, 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, 0.0973 mmol).

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): R_f 0.50. $[\alpha]_D$ = –6.37 (*c* = 1.6, $CHCl_3$, 27 °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 $C_{53}H_{50}N_2NaO_{14}S$ $[M+Na]^+$, 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-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 $C_{76}H_{71}N_3NaO_{21}S$ $[M+Na]^+$, 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-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): R_f 0.48. $[\alpha]_D$ = –24.3 (*c* = 0.6, $CHCl_3$, 27 °C); ^{1}H 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, 0.023 mmol, 22.8 mg, 23%), **3d** (*n* = 3, 0.0067 mmol, 9.5 mg, 10%), **4d** (*n* = 4, 0.0043 mmol, 8.0 mg, 9%), and **5d** (*n* = 5, 0.0026 mmol, 5.8 mg, 6%) as white solids. Recovered yield of buliding block **1d** was 37% (42 mg, 0.074 mmol).

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-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 °C); ^{1}H 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.

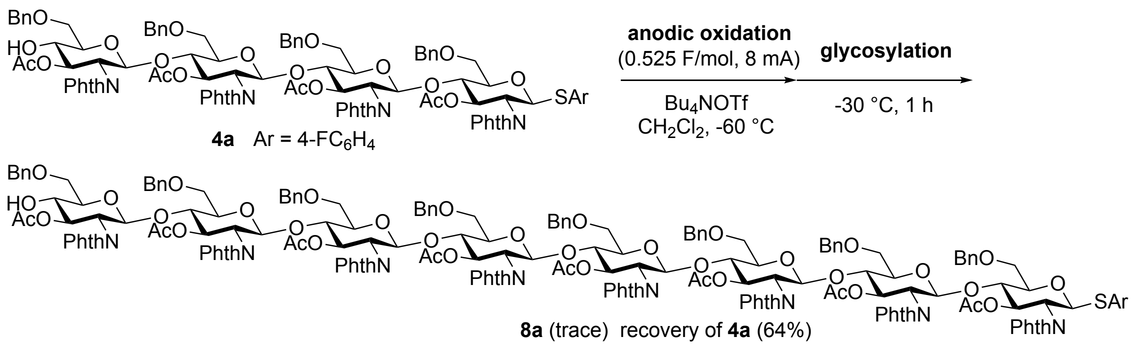
2,4-Difluorophenyl (3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (**3d**); TLC (Hexane:EtOAc 1:2): R_f 0.55. $[\alpha]_D$ = –18.1 (*c* = 1.7, $CHCl_3$, 27 °C); ^{1}H 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 $C_{75}H_{67}F_2KN_3O_{21}S$ $[M+K]^+$, 1454.3587; found, 1454.3563.

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-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); ^{1}H 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 $C_{98}H_{88}F_2N_4NaO_{28}S$ $[M+Na]^+$, 1861.5166; found, 1861.5137.

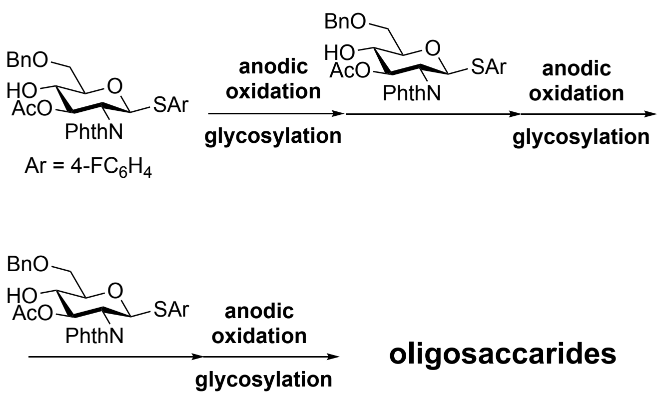
2,4-Difluorophenyl (3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (**5d**); TLC (Hexane:EtOAc 1:2): R_f 0.40. $[\alpha]_D$ = –27.1 (c = 1.0, $CHCl_3$, 30 °C); ^{1}H 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 $C_{121}H_{109}F_2KN_5O_{35}S$ $[M+K]^+$, 2300.6223; found, 2300.6287.

3. 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), Bu_4NOTf (0.5 mmol, 196 mg), and CH_2Cl_2 (5 mL) were added to the anodic chamber. Trifluoromethanesulfonic acid (0.1 mmol, 9 μL), Bu_4NOTf (0.5 mmol, 196 mg), and CH_2Cl_2 (5 mL) were added to the cathodic chamber. The constant current (6 mA (current density: 2.0 mA/cm^2), 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 Na_2SO_4, 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.

4. Protocol modification of electrochemical polyglycosylation



The electrochemical polymerization synthesis of linear oligosaccharides (**2a**~**8a**) 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). Building block **1a** (0.200 mmol, 109 mg), Bu_4NOTf (1.00

mmol, 393 mg), and CH_2Cl_2 (10 mL) were added to the anodic chamber. Trifluoromethanesulfonic acid (0.200 mmol, 18 μL), Bu_4NOTf (1.00 mmol, 393 mg), and CH_2Cl_2 (10 mL) were added to the cathodic chamber. The constant current (8 mA (current density: 2.0 mA/cm^2), 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 CH_2Cl_2 (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 eggplant flask, and the solvent was removed under reduced pressure. The reaction mixture was dissolved in EtOAc and washed with water (3 times) and brine, respectively. The solution was dried over Na_2SO_4, and solvent was removed under reduced pressure. The crude product was purified with preparative-GPC to afford linear oligosaccharides **2a** (*n* = 2, 0.065 mmol, 63 mg, 22%), **3a** (*n* = 3, 0.034 mmol, 47 mg, 17%), **4a** (*n* = 4, 0.017 mmol, 31 mg, 11%), **5a** (*n* = 5, 0.0094 mmol, 21 mg, 8%), **6a** (*n* = 6, 0.0056 mmol, 15 mg, 6%), **7a** (*n* = 7, 0.0042 mmol, 13 mg, 5%), and **8a** (*n* = 8, 0.0023 mmol, 7.6 mg, 3%) 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-1-thio-β-D-glucopyranoside (**8a**); TLC (Hexane:EtOAc 1:2): R_f 0.13. $[\alpha]_D$ = –25.8 (*c* = 0.9, $CHCl_3$, 32 °C); ^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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 $C_{190}H_{173}FKN_8O_{56}S$ $[M+K]^+$, 3552.0272; found, 3552.0203.

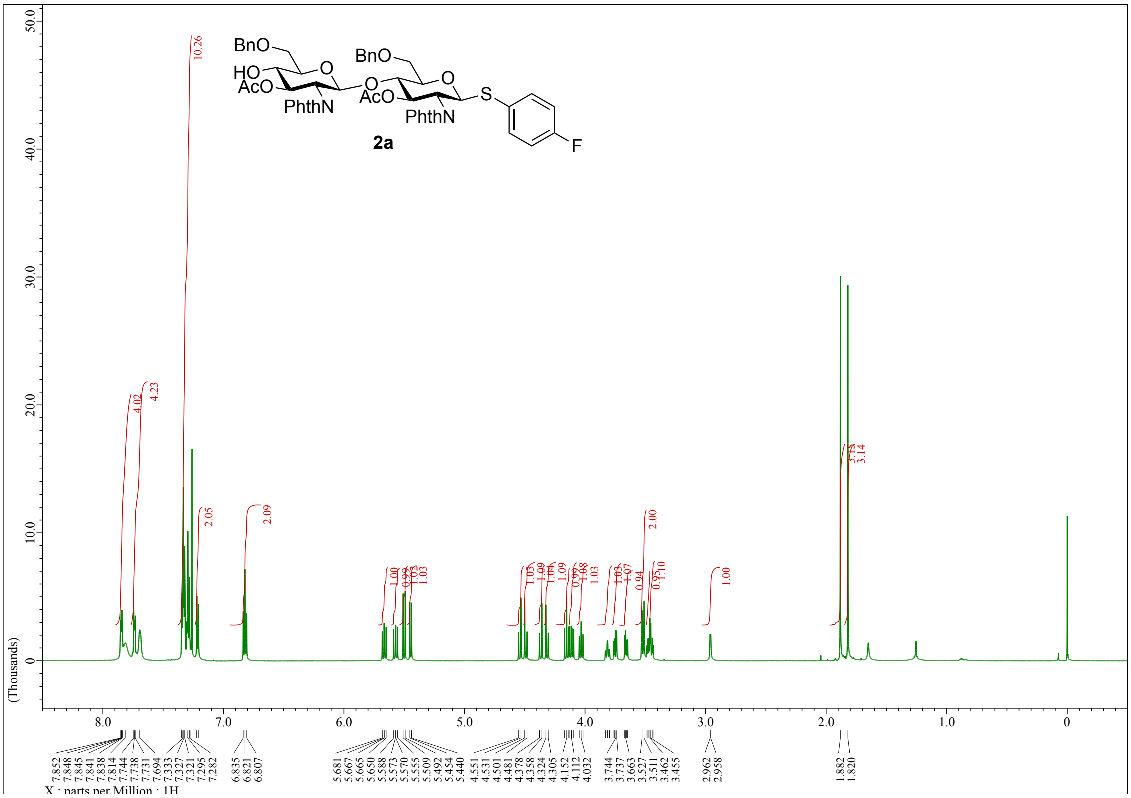
5. References

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.

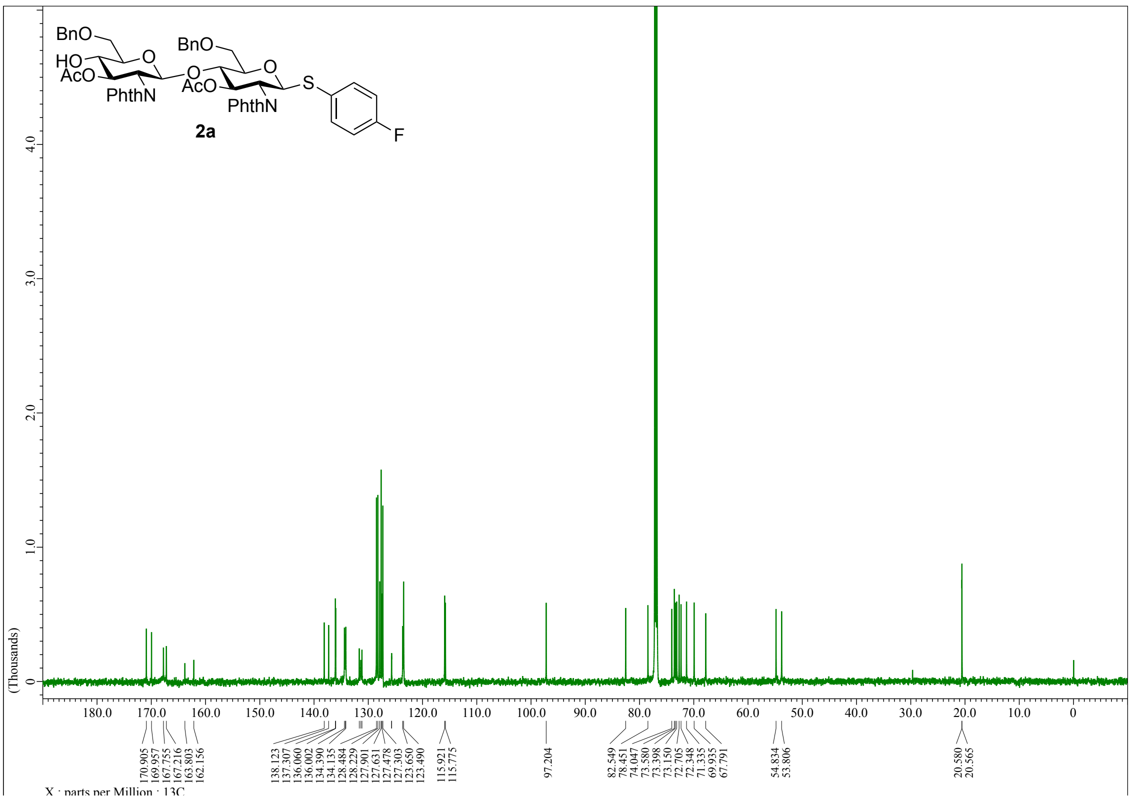
2 K. Yano, T. Itoh and T. Nokami, *Carbohydr. Res.*, **2020**, *492*, 108018.

6. ^{1}H, ^{13}C NMR, H-H COSY and HMQC spectra of oligosaccharides

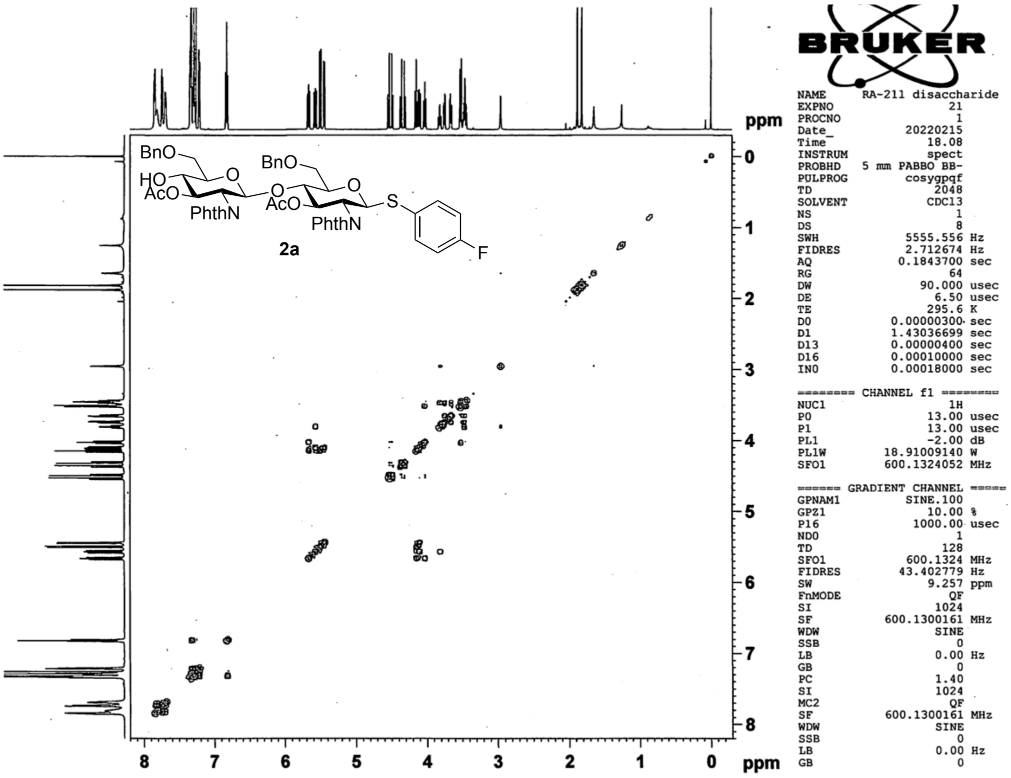
^{1}H NMR



^{13}C NMR



H-H cosy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AcO
PhthN
BnO
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AcO
PhthN
S
F
2a
ppm
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PROCNO 1
Date_ 20220215
Time 18.08
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TD 2048
SOLVENT CDCl3
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DS 8
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FIDRES 2.712674 Hz
AQ 0.1843700 sec
RG 64
DW 90.000 usec
DE 6.50 usec
TE 295.6 K
D0 0.00000300 sec
D1 1.43036699 sec
D13 0.00000400 sec
D16 0.00010000 sec
IN0 0.00018000 sec
======== CHANNEL f1 ========
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P0 13.00 usec
P1 13.00 usec
PL1 -2.00 dB
PL1W 18.91009140 W
SFO1 600.1324052 MHz
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GPZ1 10.00 %
P16 1000.00 usec
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SFO1 600.1324 MHz
FIDRES 43.402779 Hz
SW 9.257 ppm
FnMODE QF
SI 1024
SF 600.1300161 MHz
WDW SINE
SSB 0
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GB 0
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SI 1024
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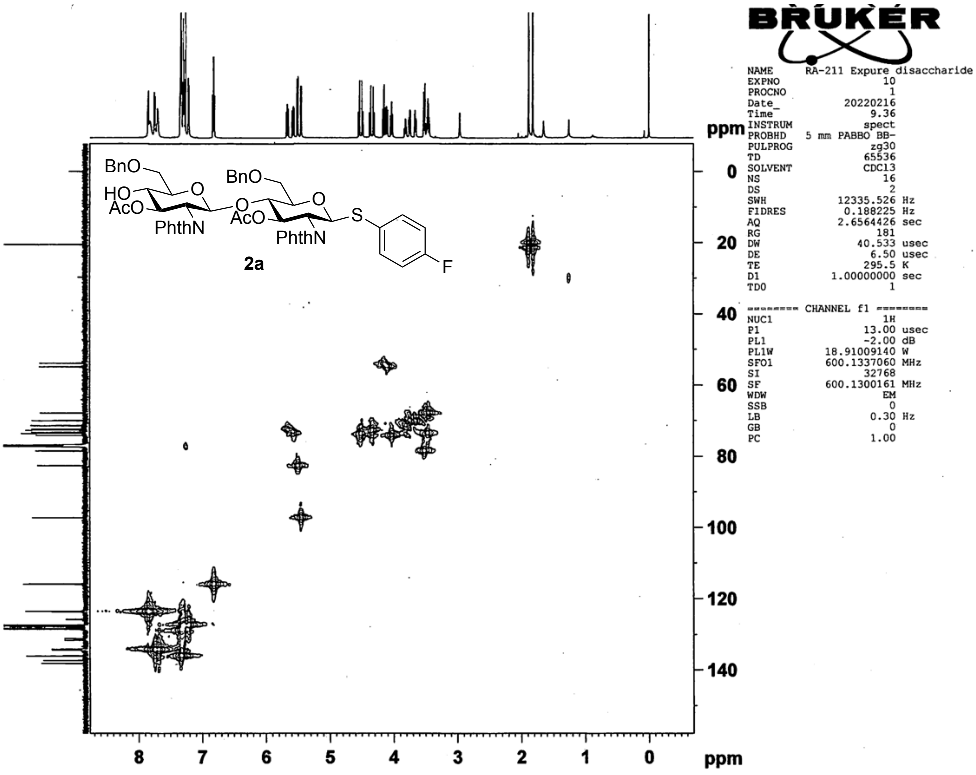
SF 600.1300161 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0

HMQC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HO
AcO
PhthN
BnO
O
AcO
PhthN
S
F
2a
ppm
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PROCNO 1
Date_ 20220216
Time 9.36
INSTRUM spect
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PULPROG zg30
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SOLVENT CDCl3
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DS 2
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FIDRES 0.188225 Hz
AQ 2.6564426 sec
RG 181
DW 40.533 usec
DE 6.50 usec
TE 295.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
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P1 13.00 usec
PL1 -2.00 dB
PL1W 18.91009140 W
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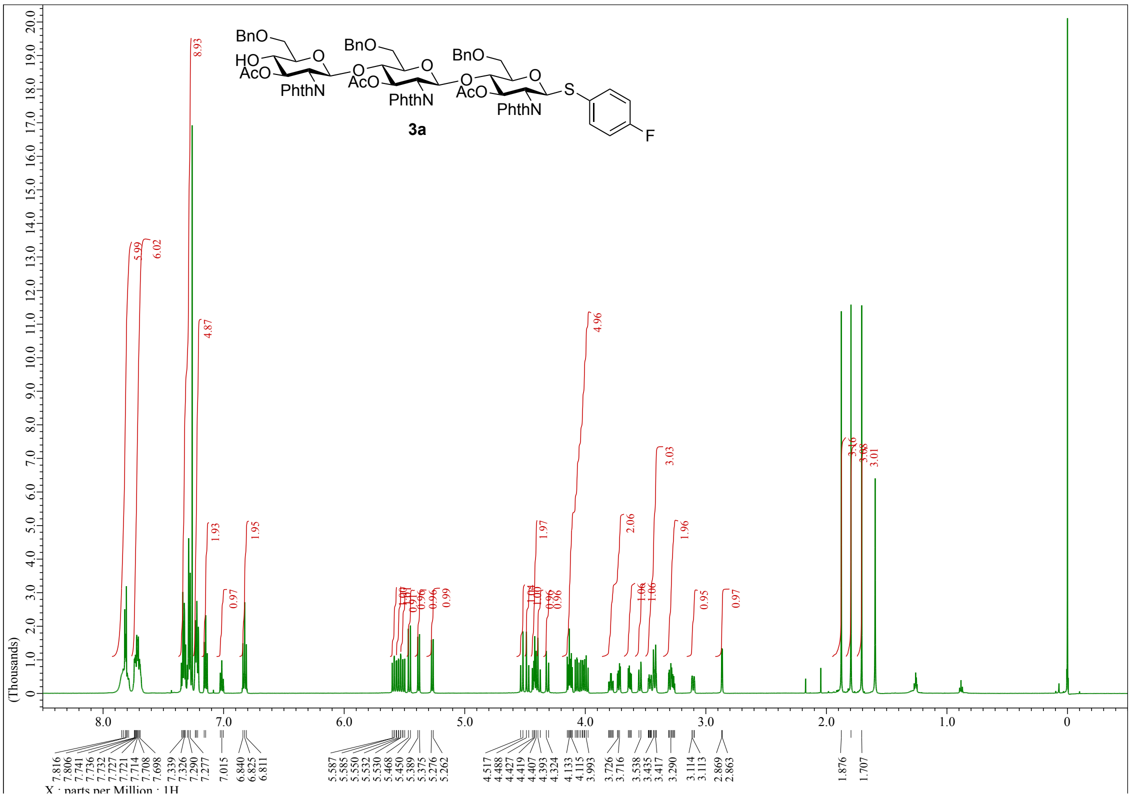
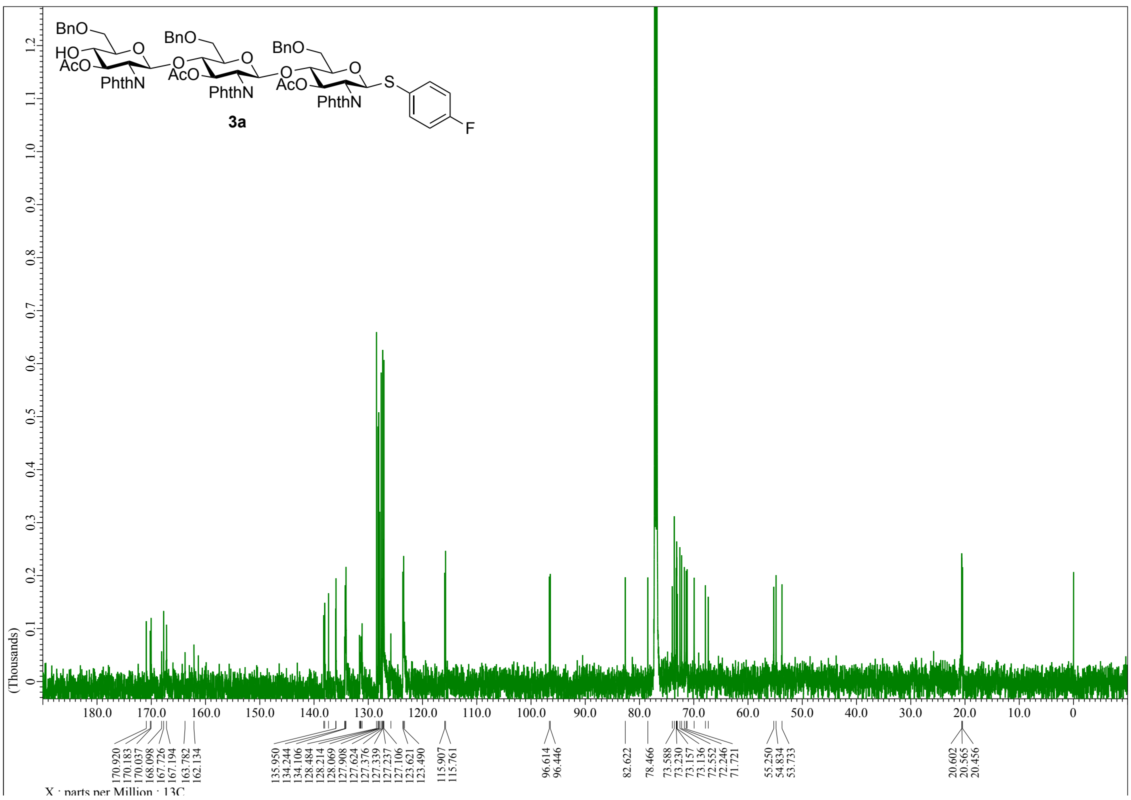
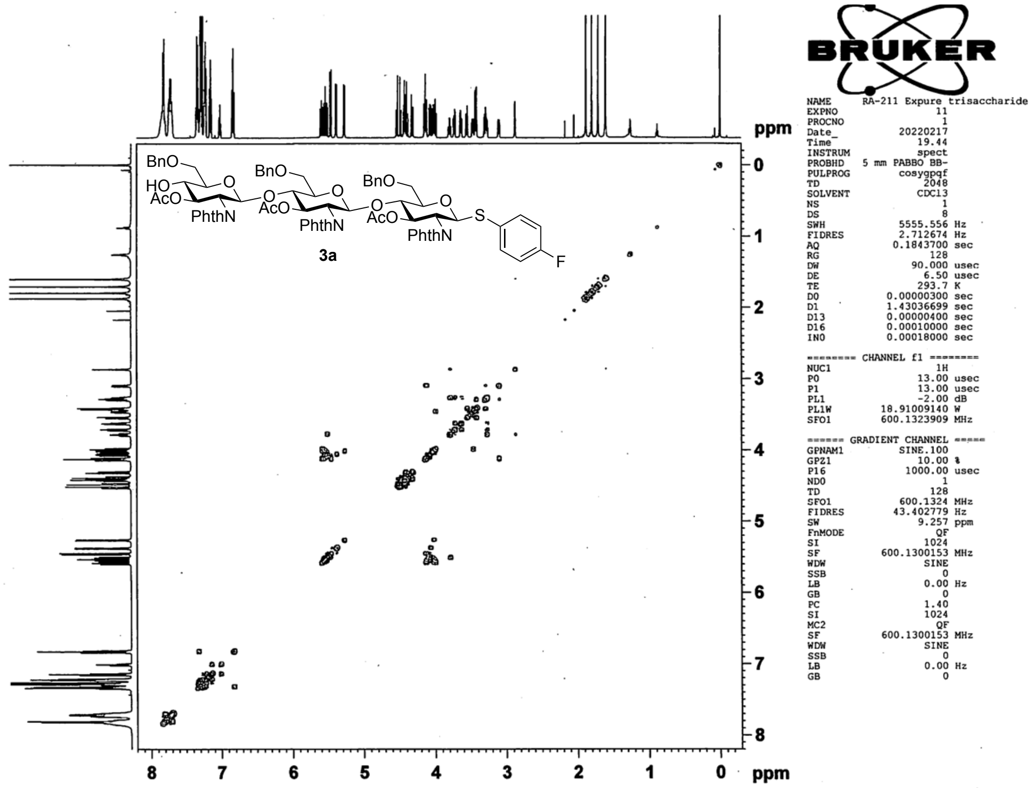
^{1}H NMR



^{13}C NMR



H-H cosy



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AcO
PhthN
BnO
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AcO
PhthN
BnO
O
AcO
PhthN
S
F
3a
ppm
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PROCNO 1
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Time 19.44
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TD 2048
SOLVENT CDCl3
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DS 8
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FIDRES 2.712674 Hz
AQ 0.1843700 sec
RG 128
DW 90.000 usec
DE 6.50 usec
TE 293.7 K
D0 0.00000300 sec
D1 1.43036699 sec
D13 0.00000400 sec
D16 0.00010000 sec
IN0 0.00018000 sec
======== CHANNEL f1 ========
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P1 13.00 usec
PL1 -2.00 dB
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P16 1000.00 usec
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SFO1 600.1324 MHz
FIDRES 43.402779 Hz
SW 9.257 ppm
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SI 1024
SF 600.1300153 MHz
WDW SINE
SSB 0
LB 0.00 Hz
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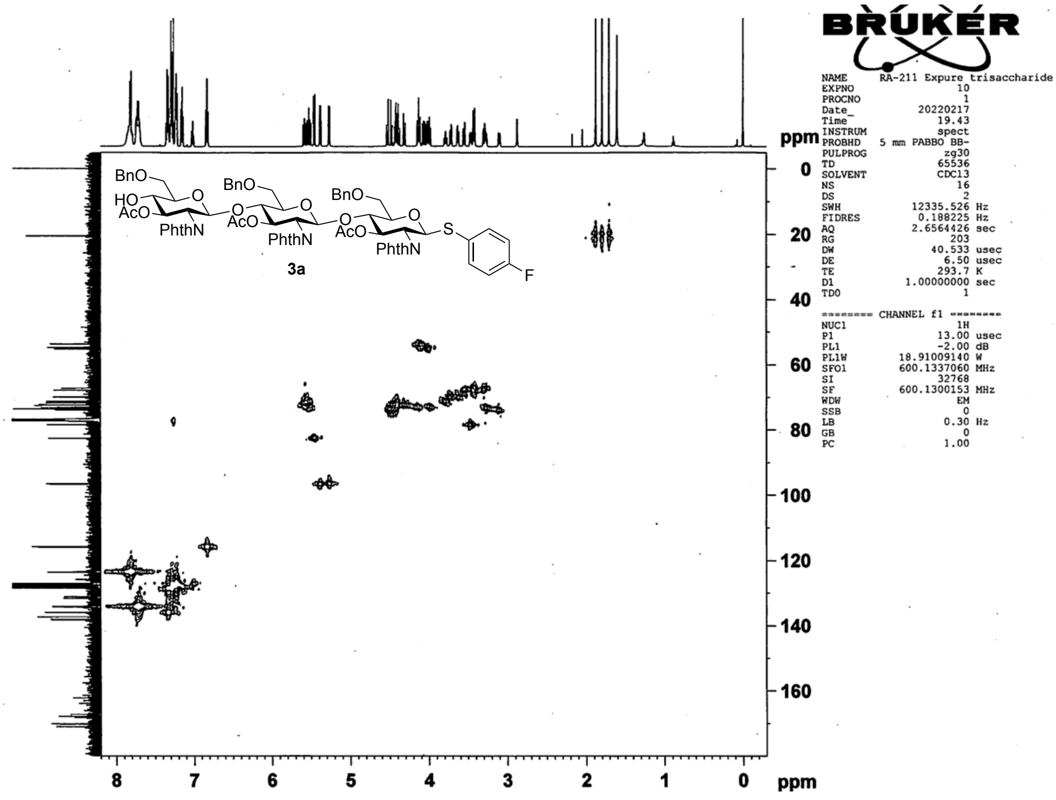
LB 0.00 Hz
GB 0

HMQC



BnO
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AcO
PhthN
BnO
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BnO
O
AcO
PhthN
S
F
3a
ppm
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PROCNO 1
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PULPROG zg30
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SOLVENT CDCl3
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DS 2
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FIDRES 0.188225 Hz
AQ 2.6564426 sec
RG 203
DW 40.533 usec
DE 6.50 usec
TE 293.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -2.00 dB
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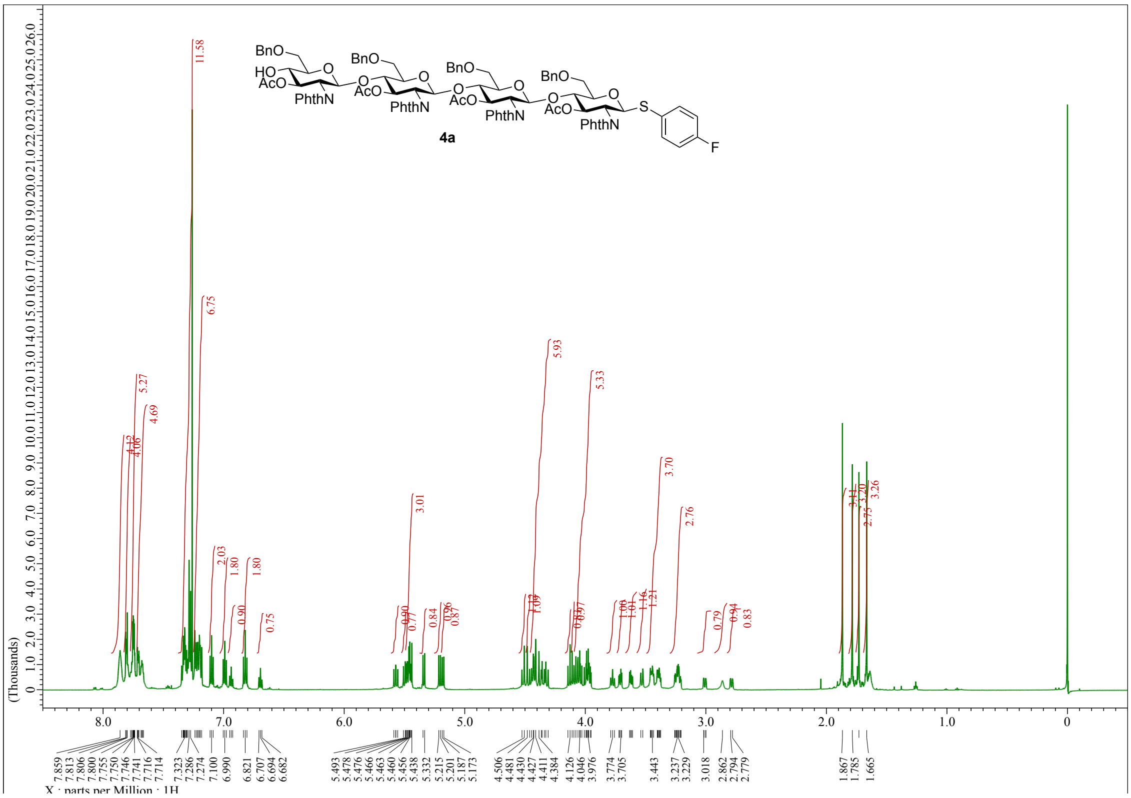
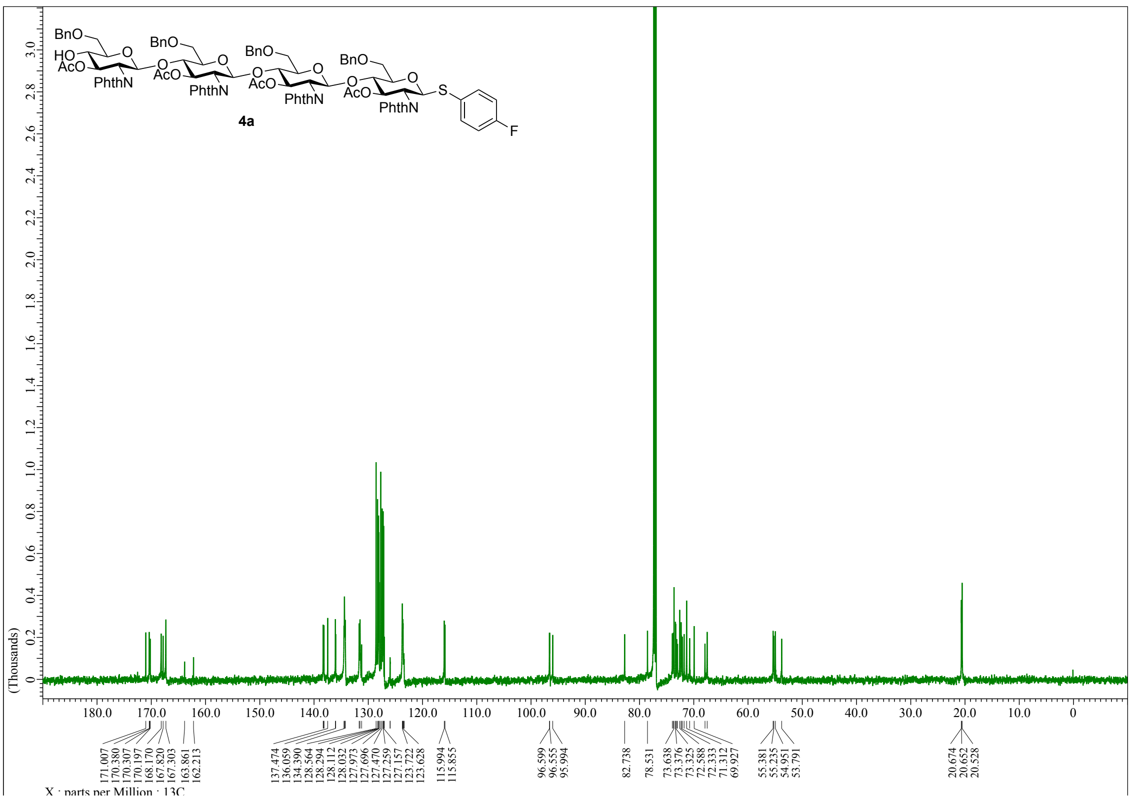
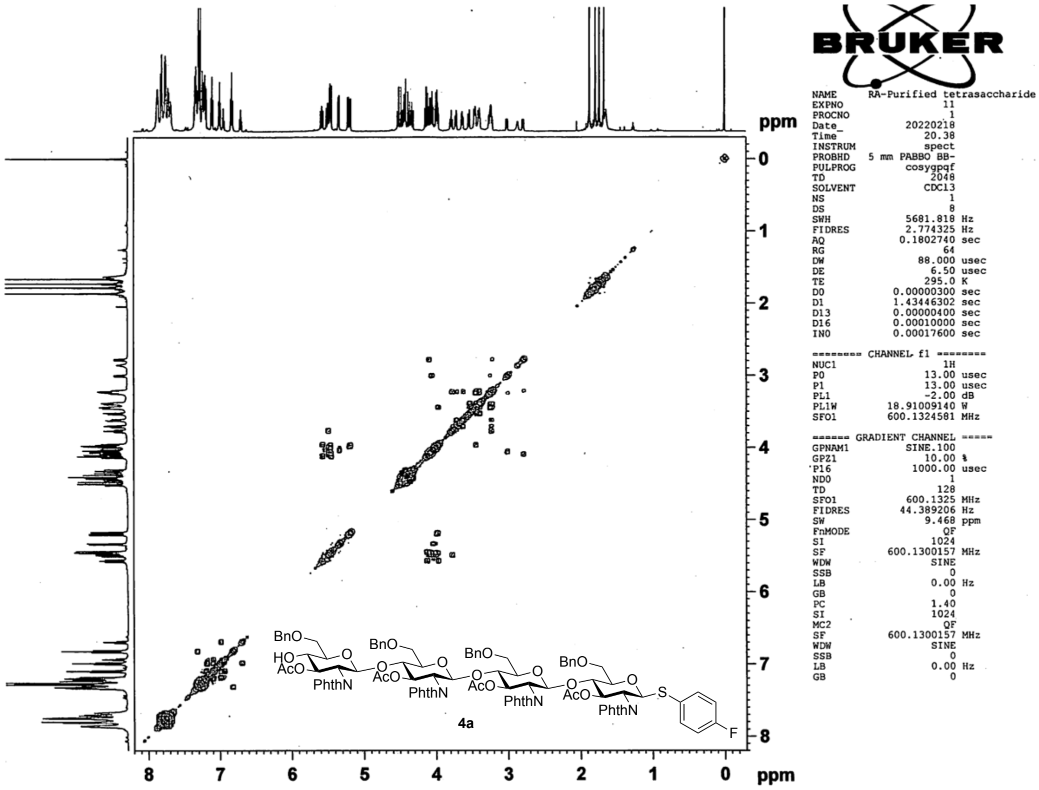
^{1}H NMR



^{13}C NMR



H-H cosy



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FIDRES 2.774325 Hz
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TE 295.0 K
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D1 1.43446302 sec
D13 0.00000400 sec
D16 0.00010000 sec
IN0 0.00017600 sec
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P1 13.00 usec
PL1 -2.00 dB
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SFO1 600.1324581 MHz
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P16 1000.00 usec
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FIDRES 44.389206 Hz
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SF 600.1300157 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
SI 1024
MC2 QF
SF 600.1300157 MHz
WDW SINE
SSB 0
LB 0.00 Hz
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4a
ppm
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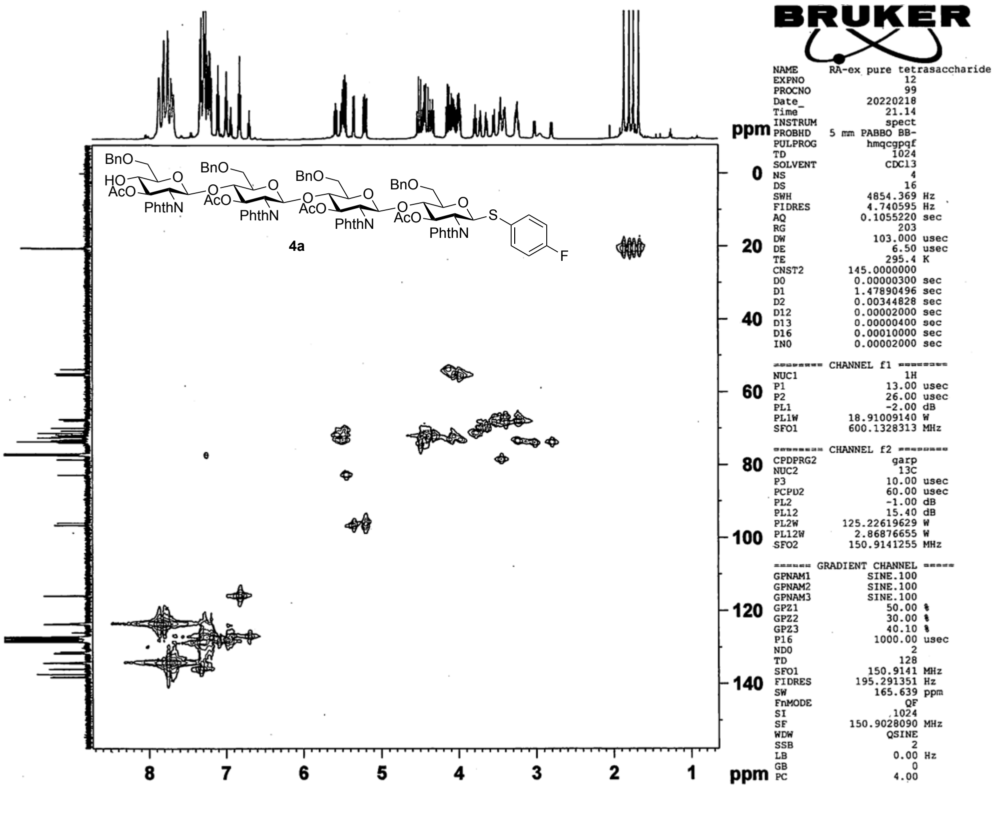
HMQC



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IN0 0.00002000 sec
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P2 26.00 usec
PL1 -2.00 dB
PL1W 18.91009140 W
SFO1 600.1328313 MHz
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PCPD2 60.00 usec
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PL12 15.40 dB
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PL12W 2.86876655 W
SFO2 150.9141255 MHz
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GPNAM2 SINE.100
GPNAM3 SINE.100
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GPZ2 30.00 %
GPZ3 40.10 %
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SW 165.639 ppm
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LB 0.00 Hz
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PC 4.00
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4a
ppm
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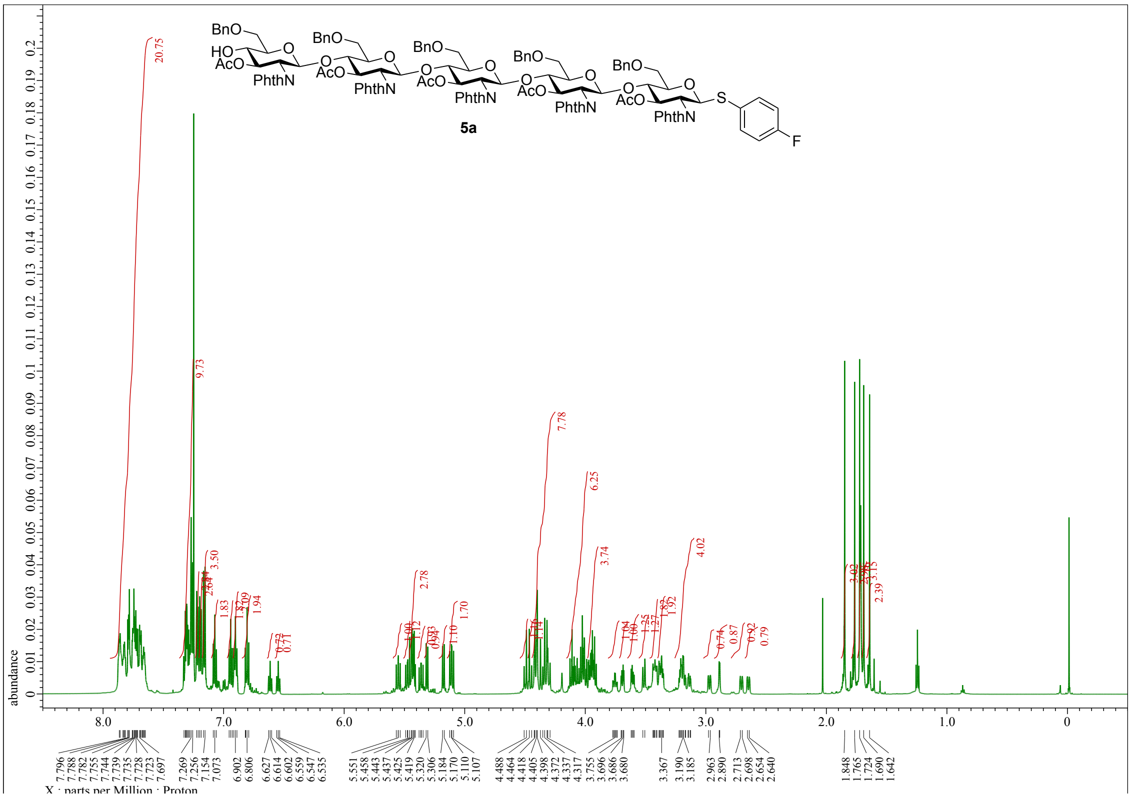
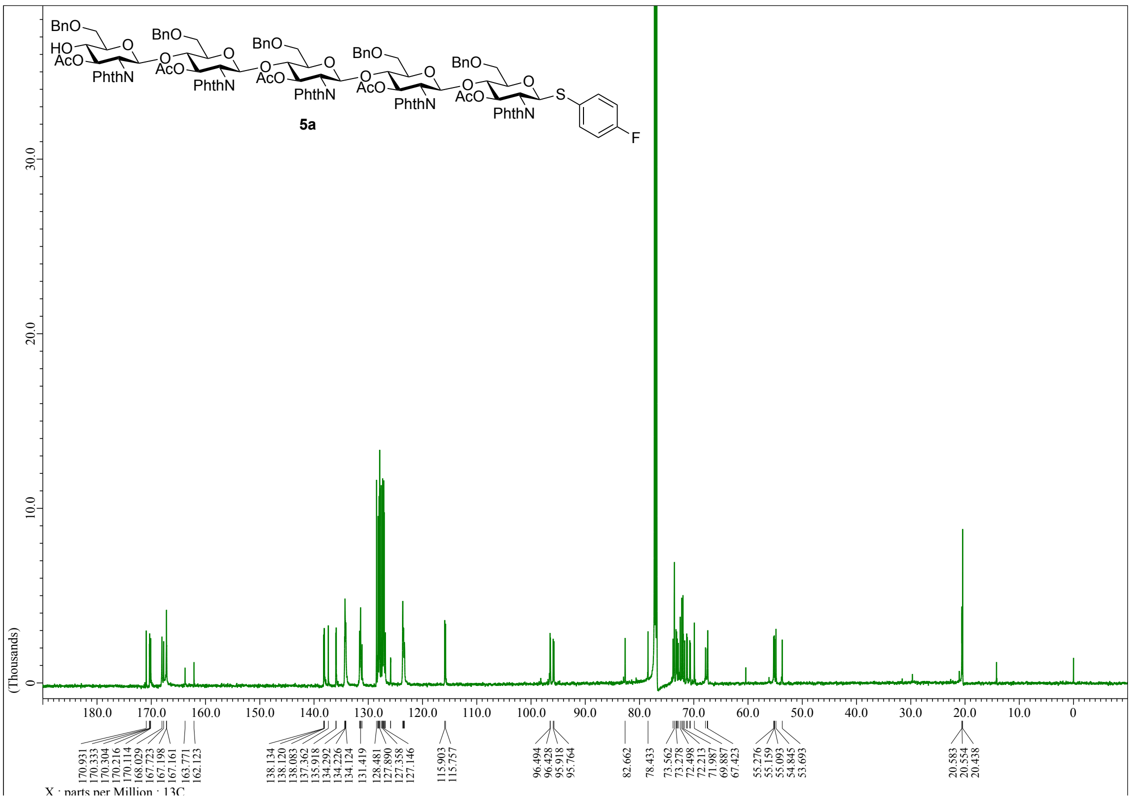
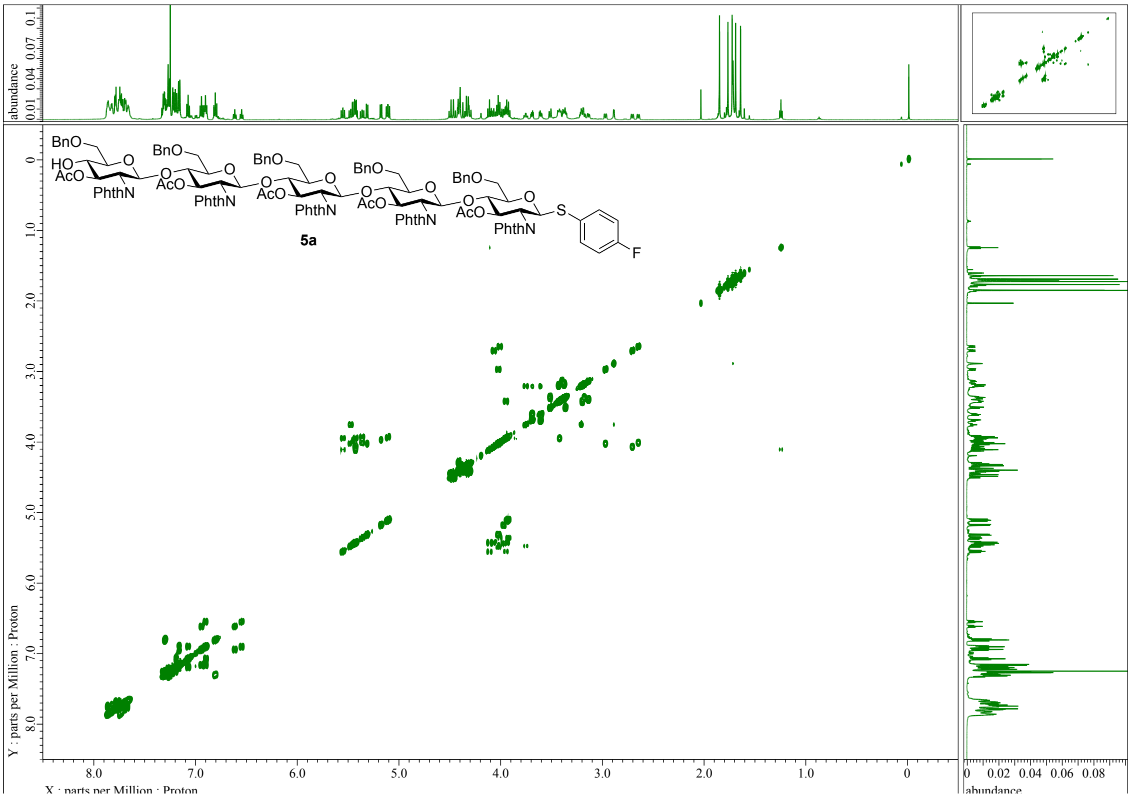
^{1}H NMR



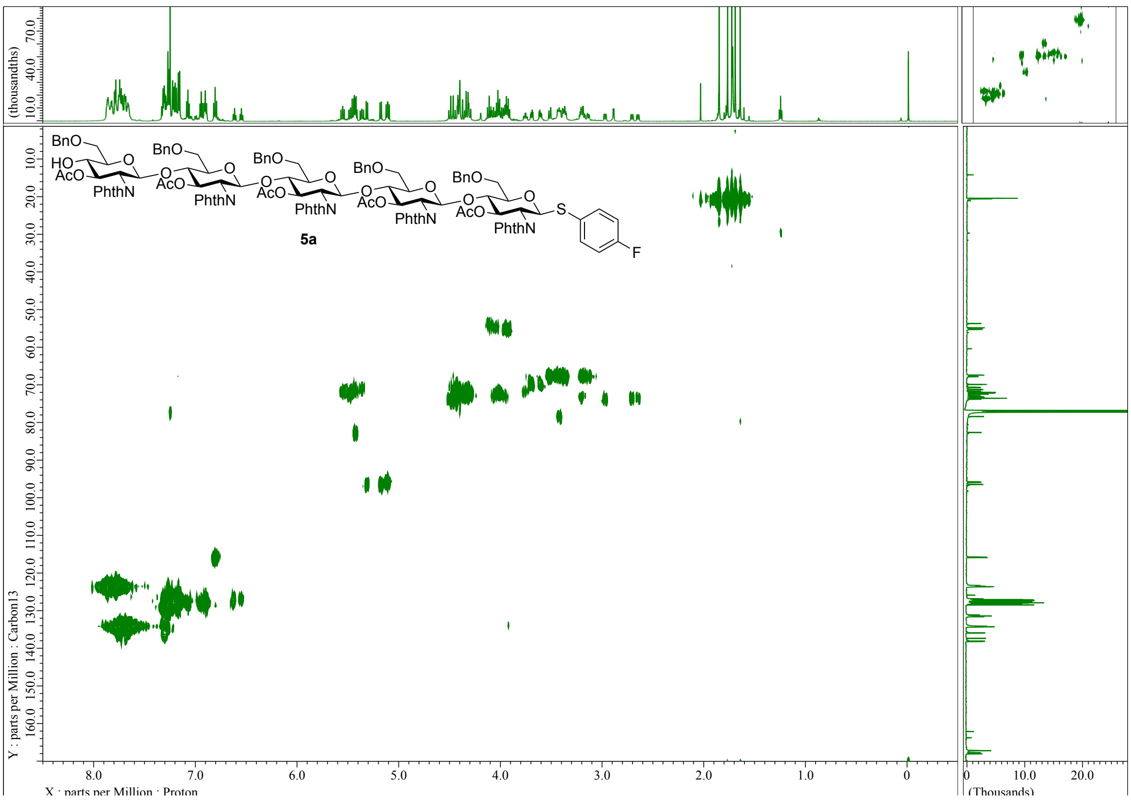
^{13}C NMR



H-H cosy



HMQC



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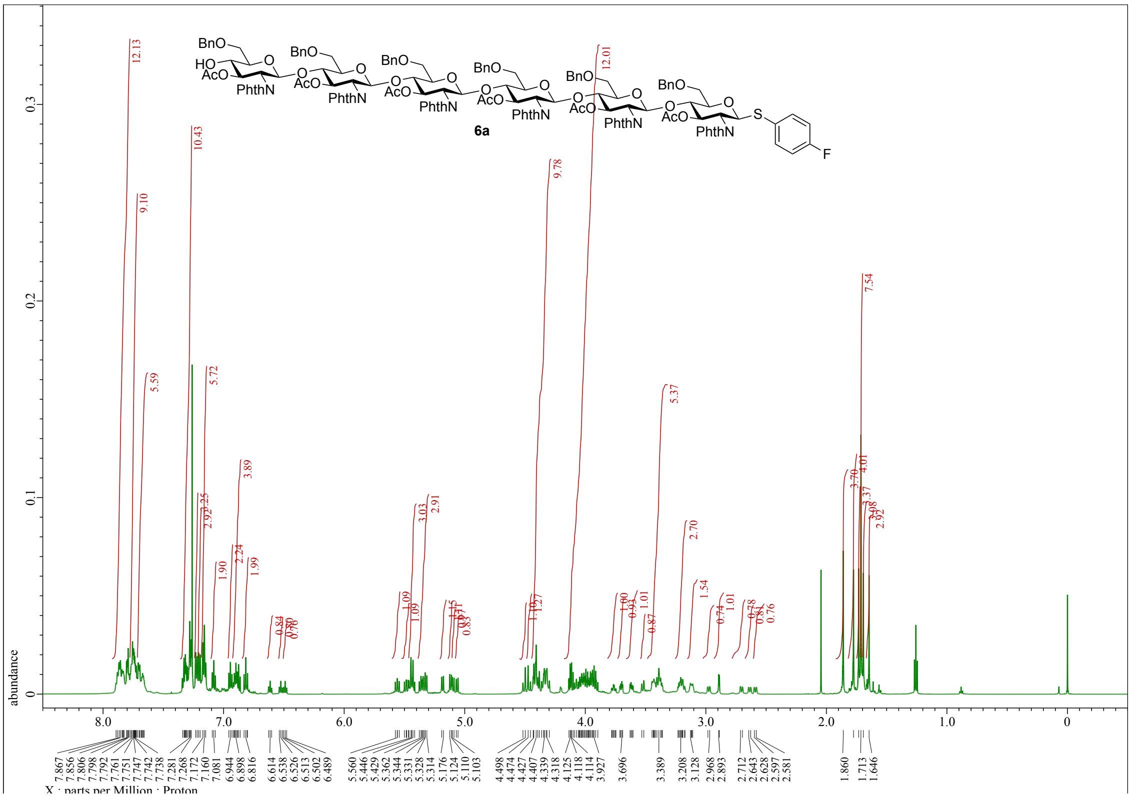
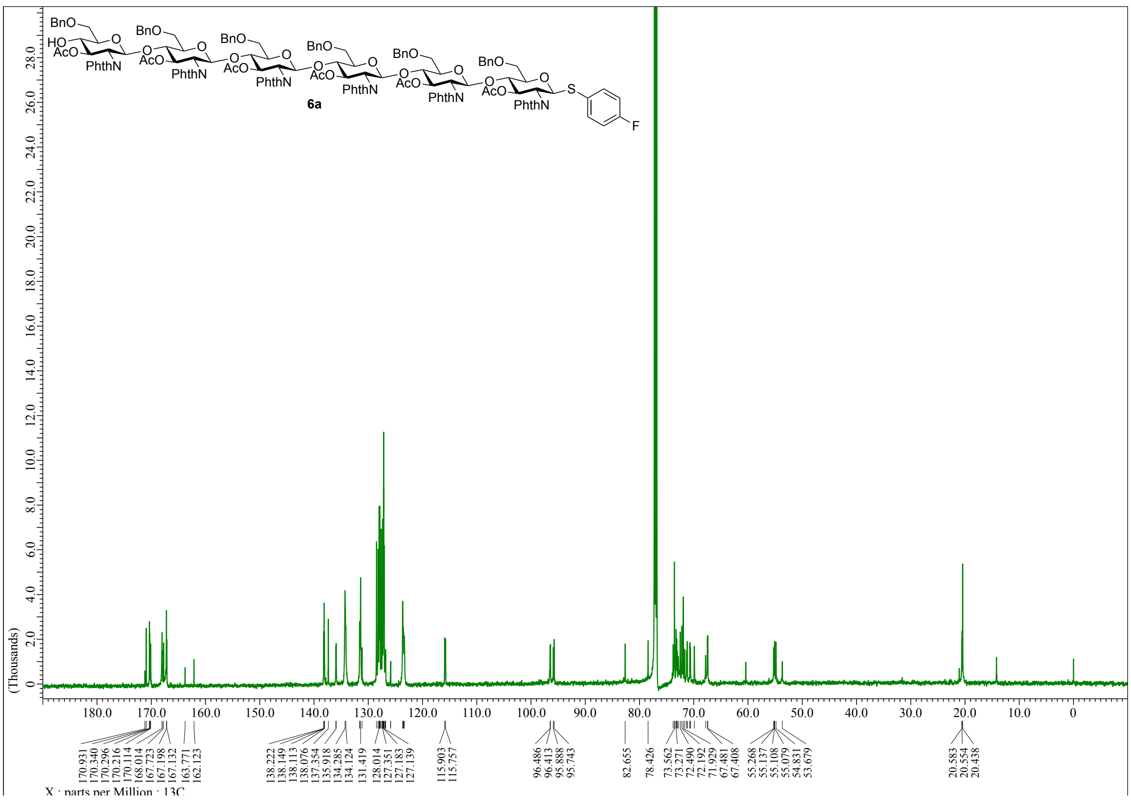
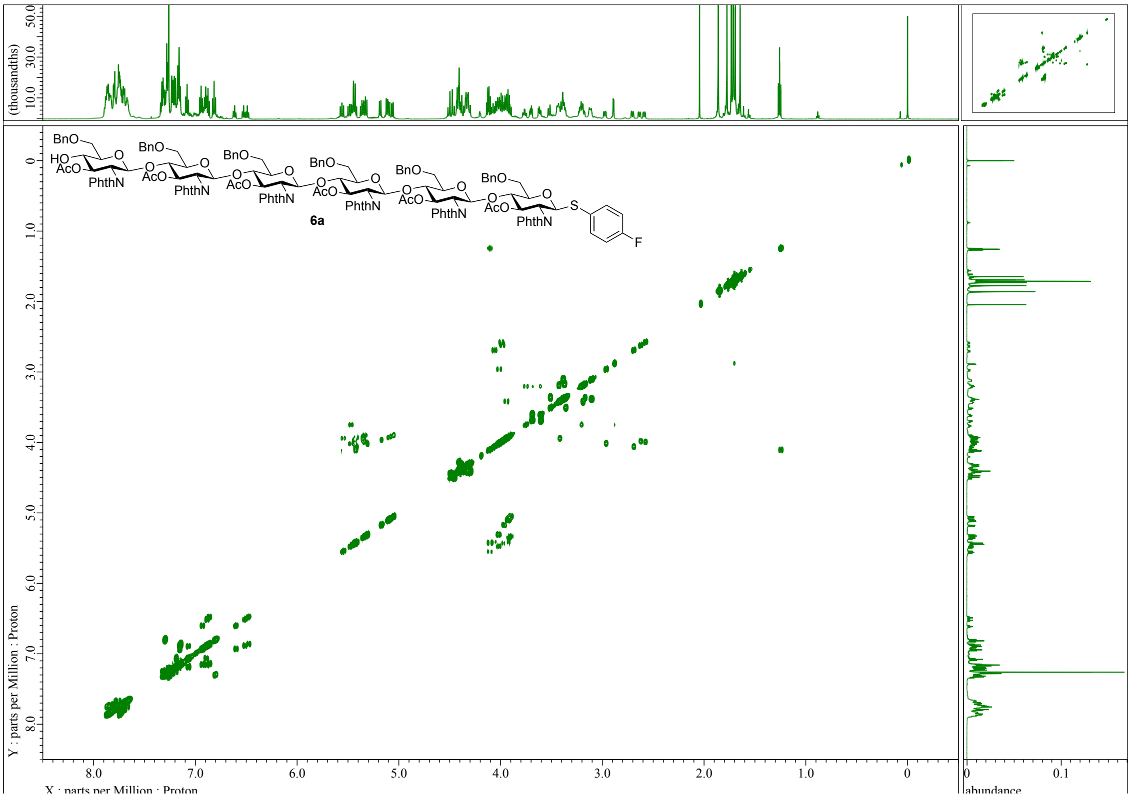


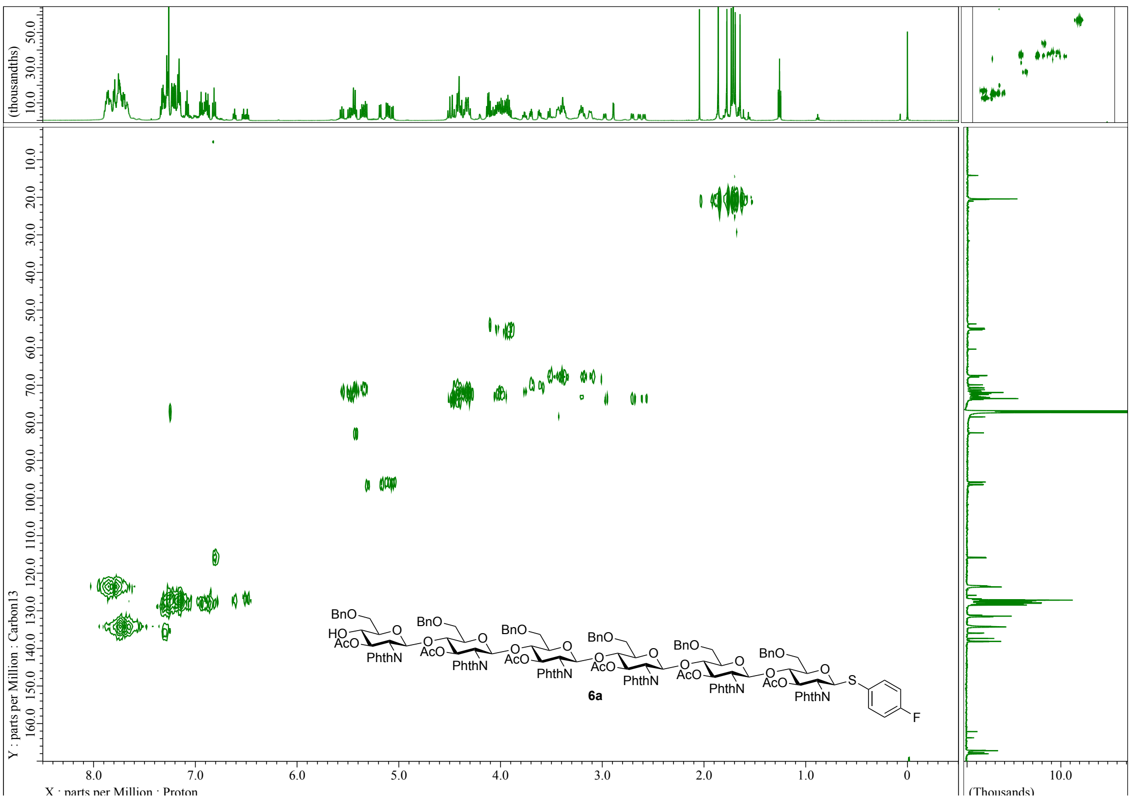
^{13}C NMR



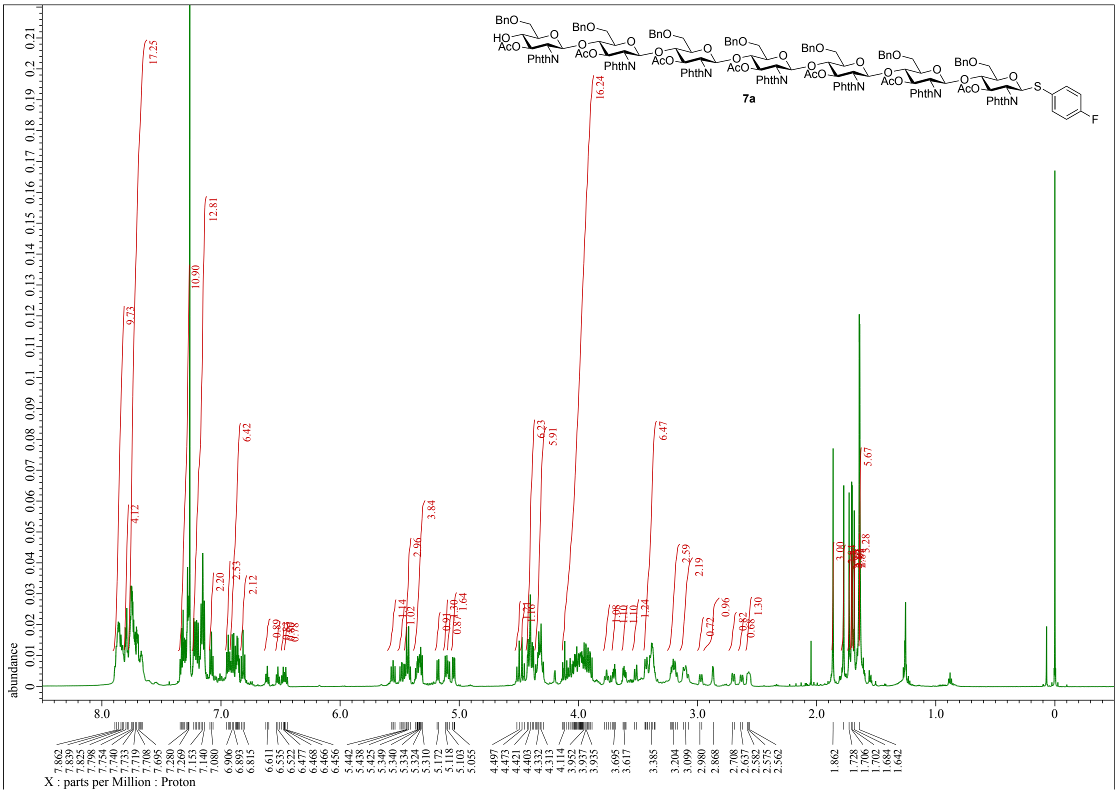
H-H cosy


(thousandths)
Y : parts per Million : Proton
X : parts per Million : Proton
abundance
6a

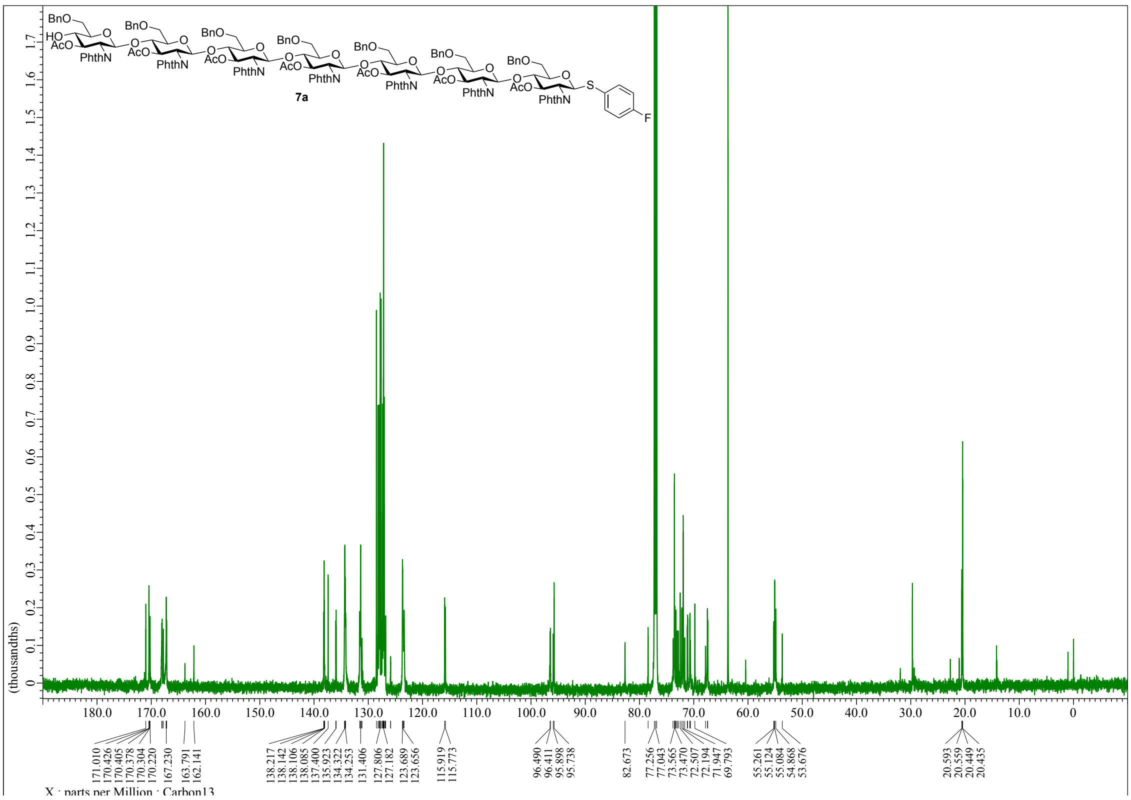
HMQC


(thousandths)
Y : parts per Million : Carbon13
X : parts per Million : Proton
(Thousands)
6a

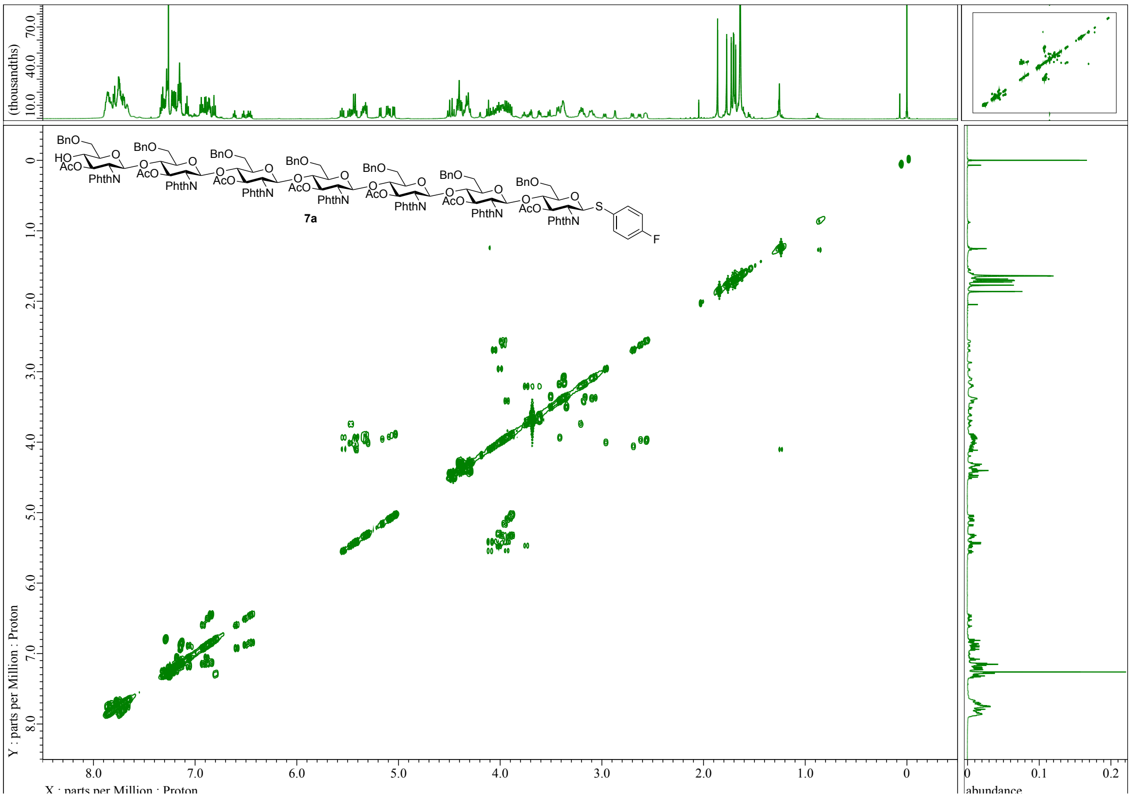
^{1}H NMR



^{13}C NMR



H-H cosy



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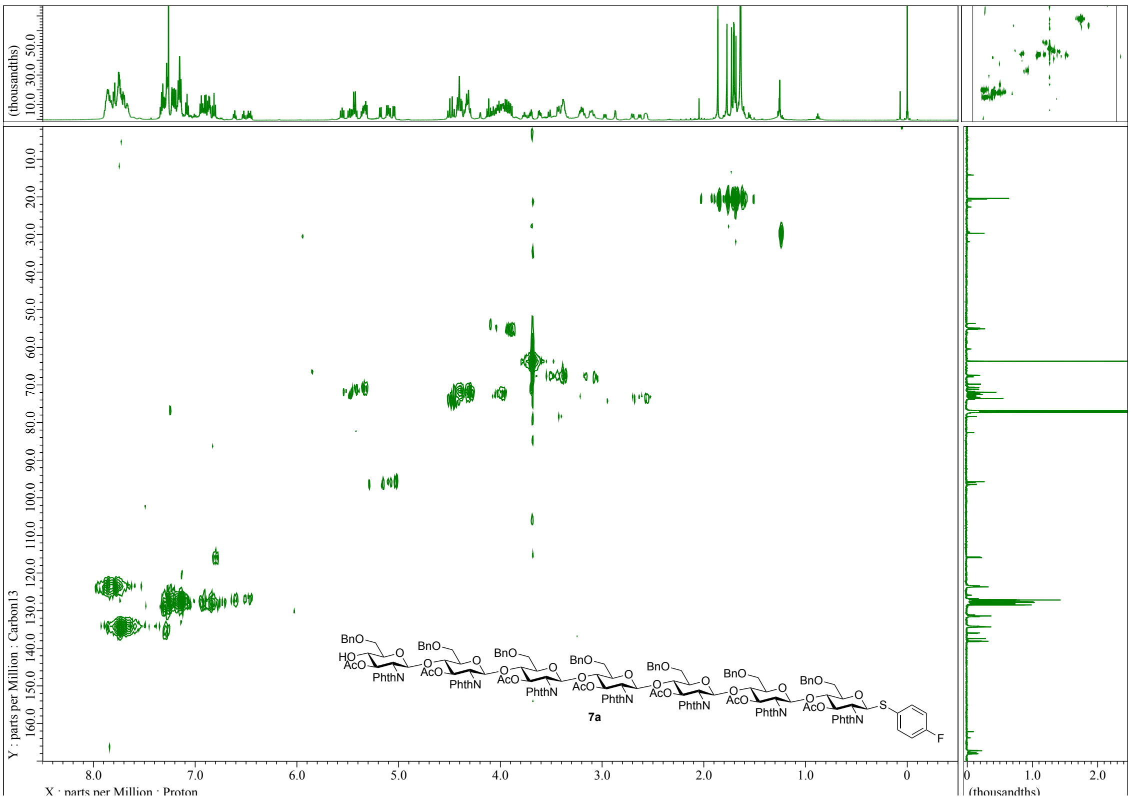
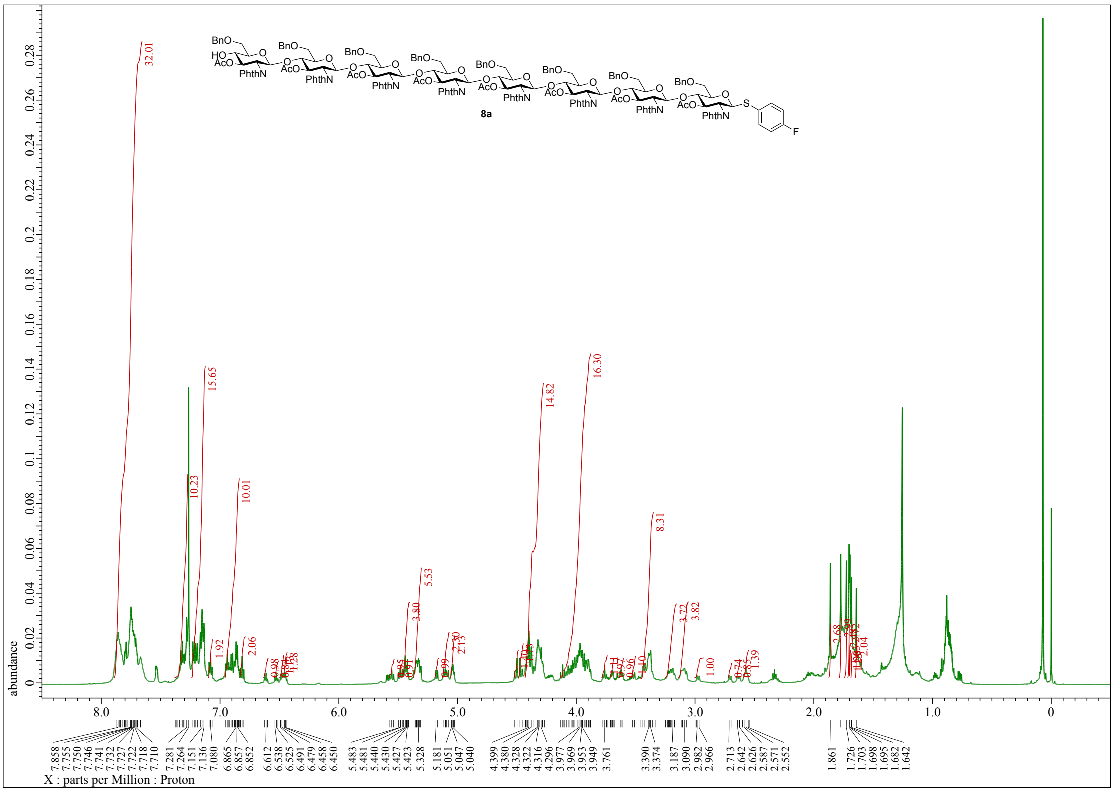
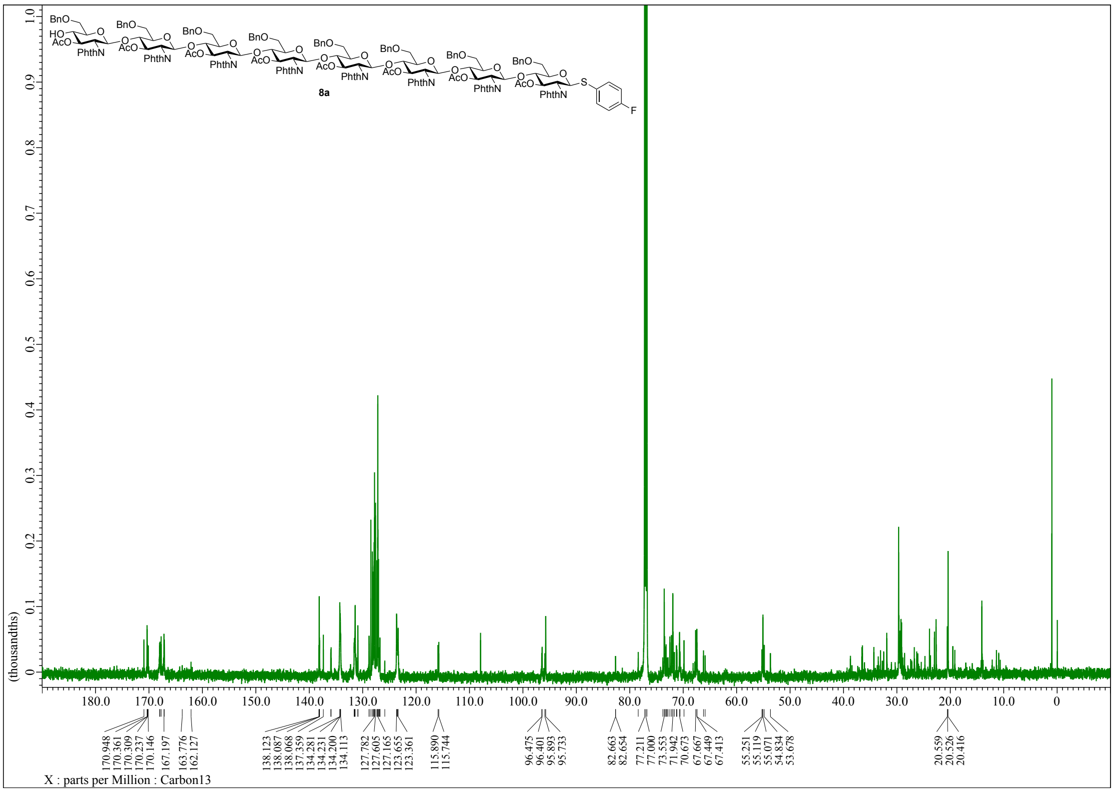


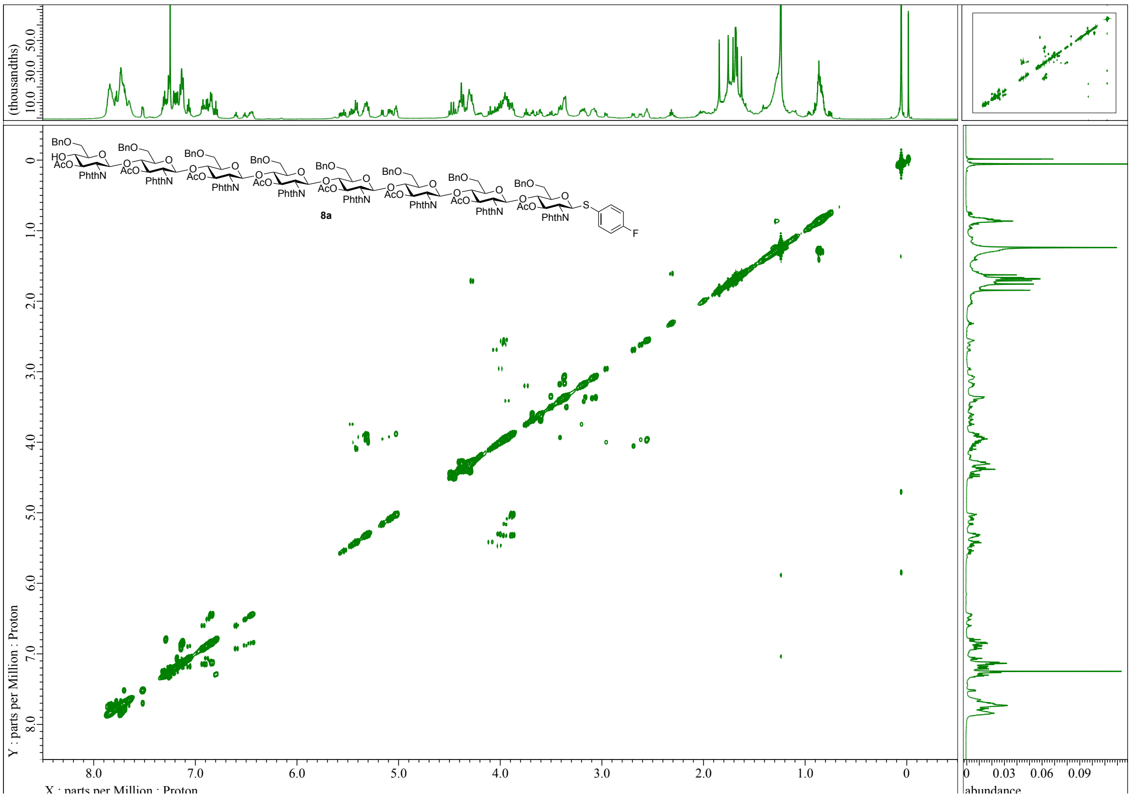
^{1}H NMR



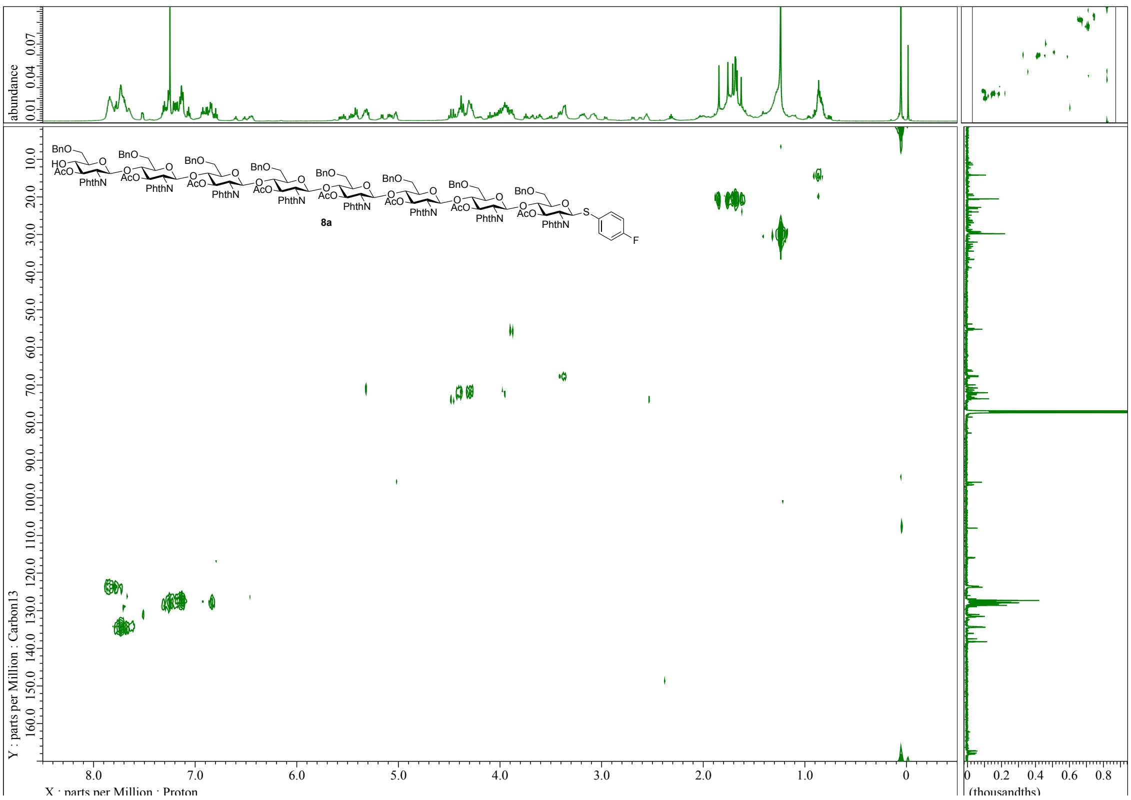
^{13}C NMR



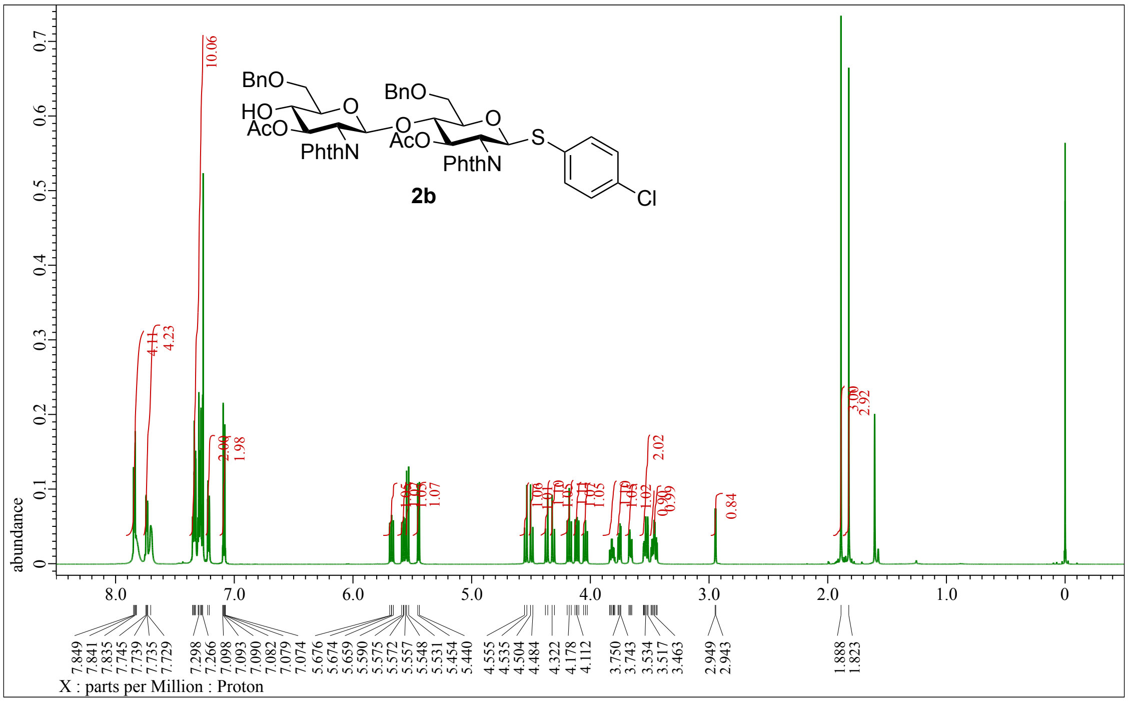
H-H cosy



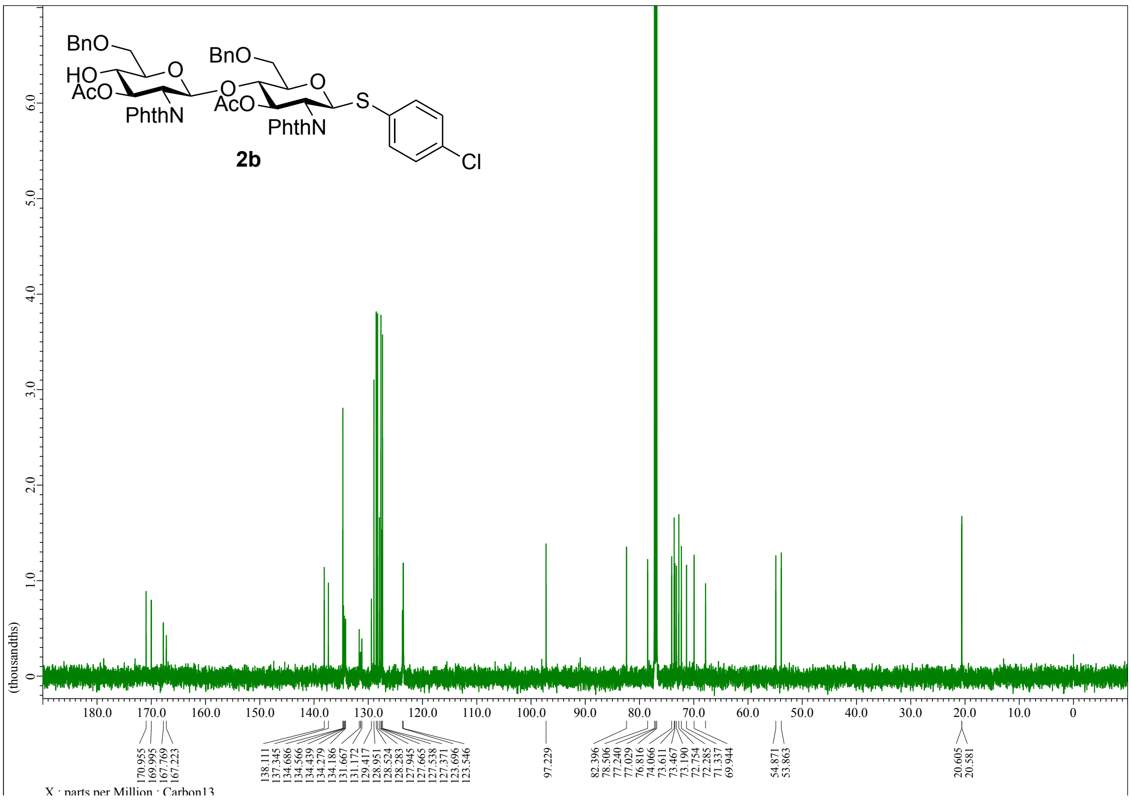
HMQC



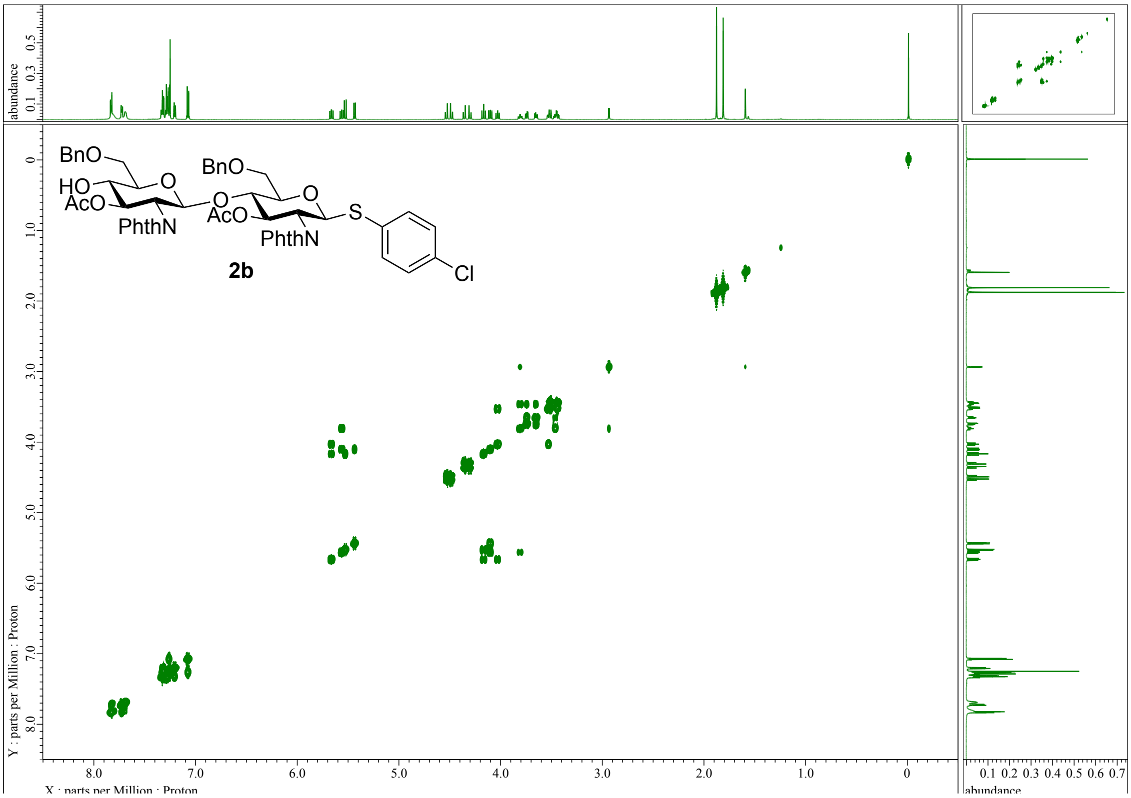
^{1}H NMR



^{13}C NMR

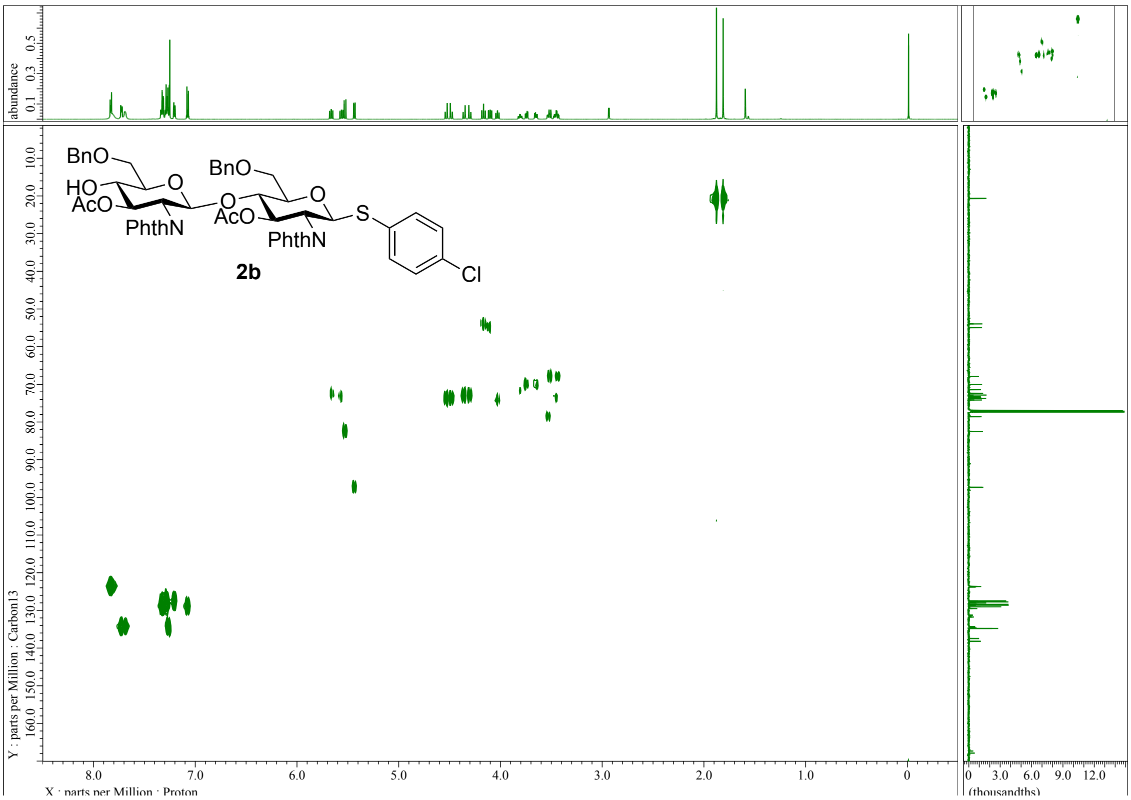


H-H cosy



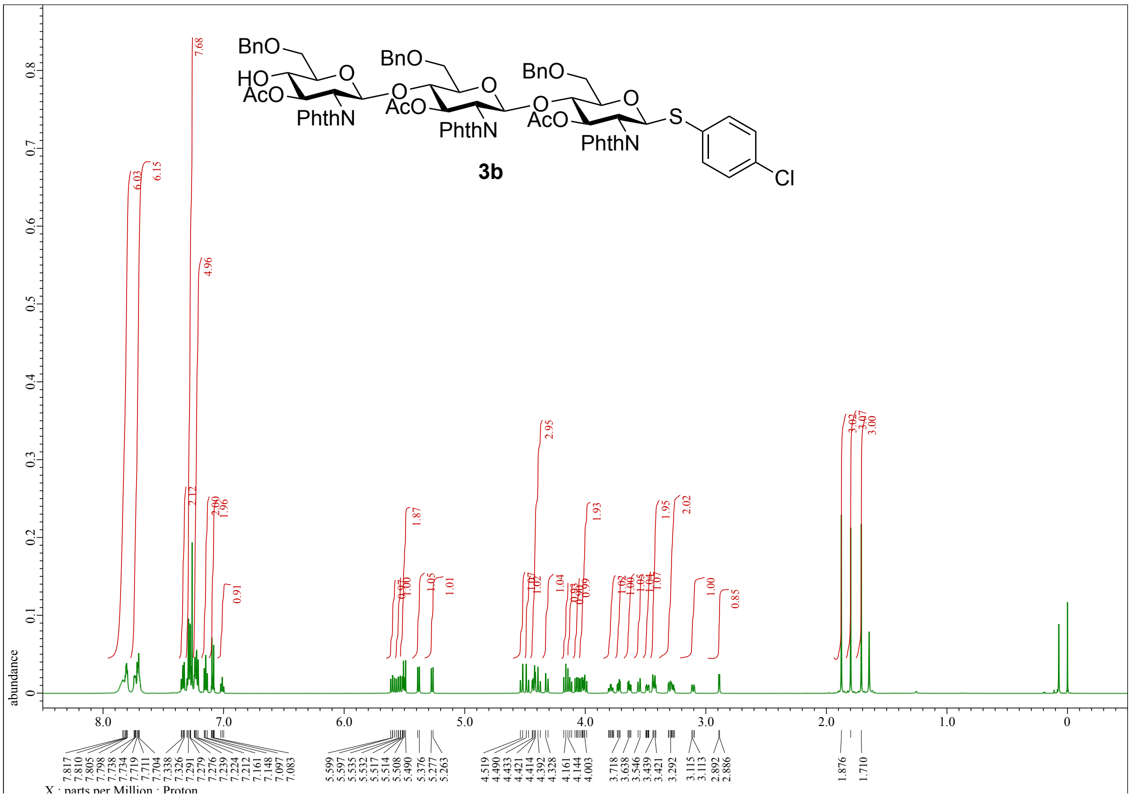
BnO
HO
AcO
O
PhthN
BnO
O
AcO
O
PhthN
S
Cl
2b
abundance
Y : parts per Million : Proton
X : parts per Million : Proton
abundance

HMQC

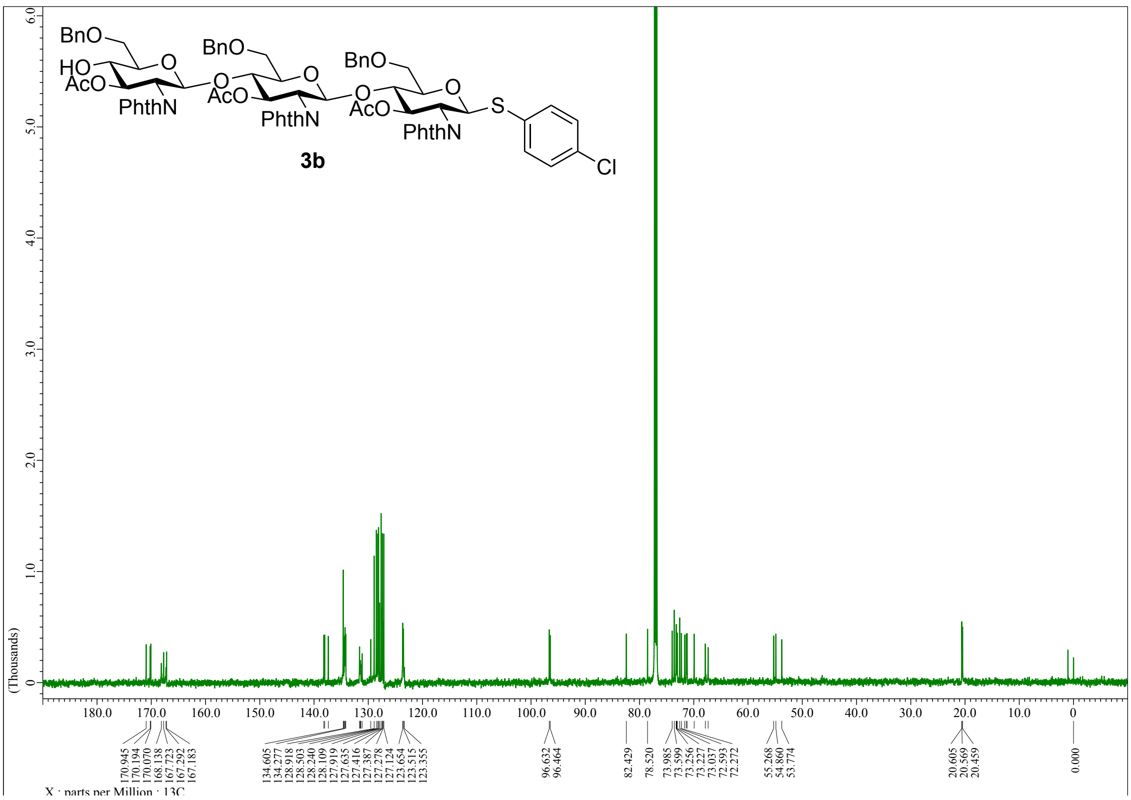


BnO
HO
AcO
O
PhthN
BnO
O
AcO
O
PhthN
S
Cl
2b
abundance
Y : parts per Million : Carbon13
X : parts per Million : Proton
(thousandths)

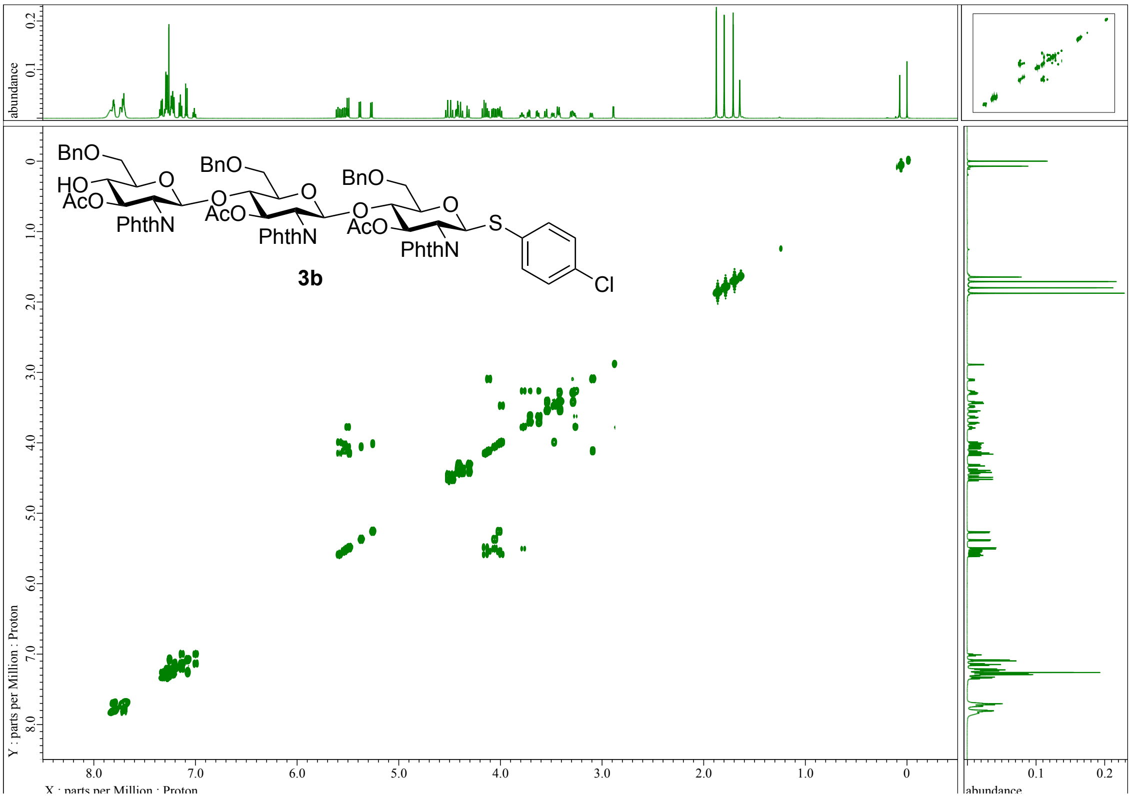
^{1}H NMR



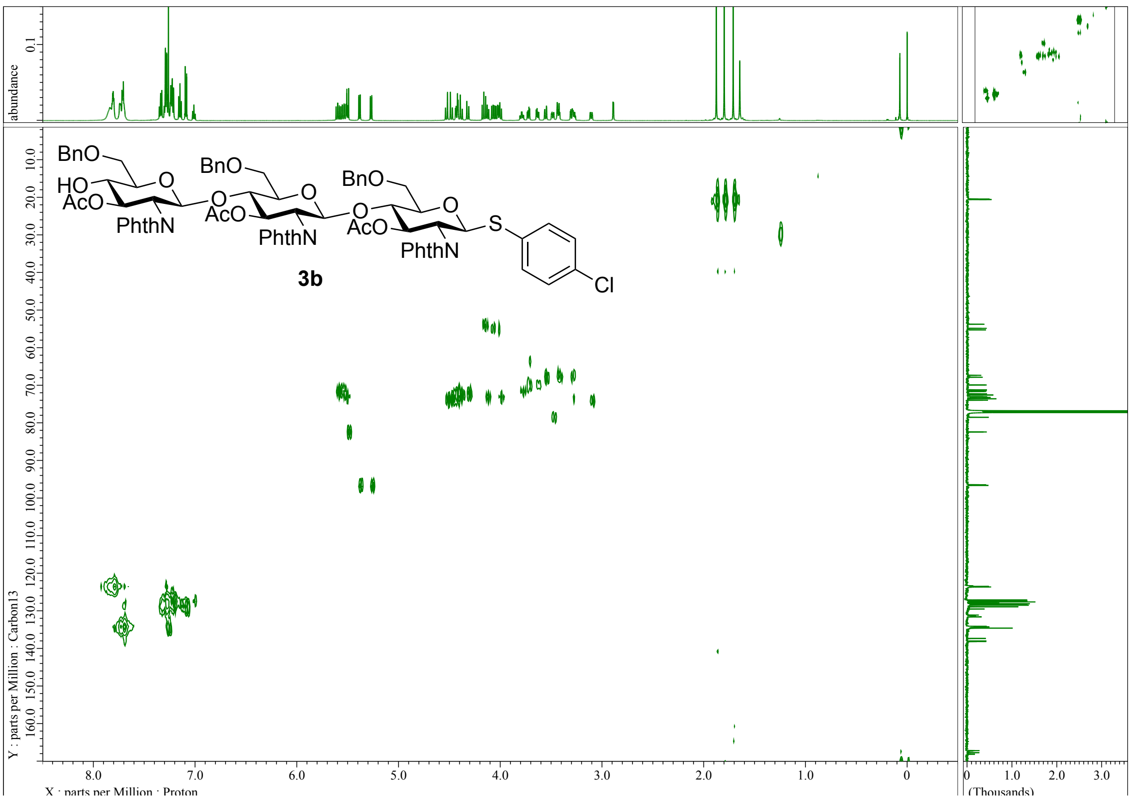
^{13}C NMR



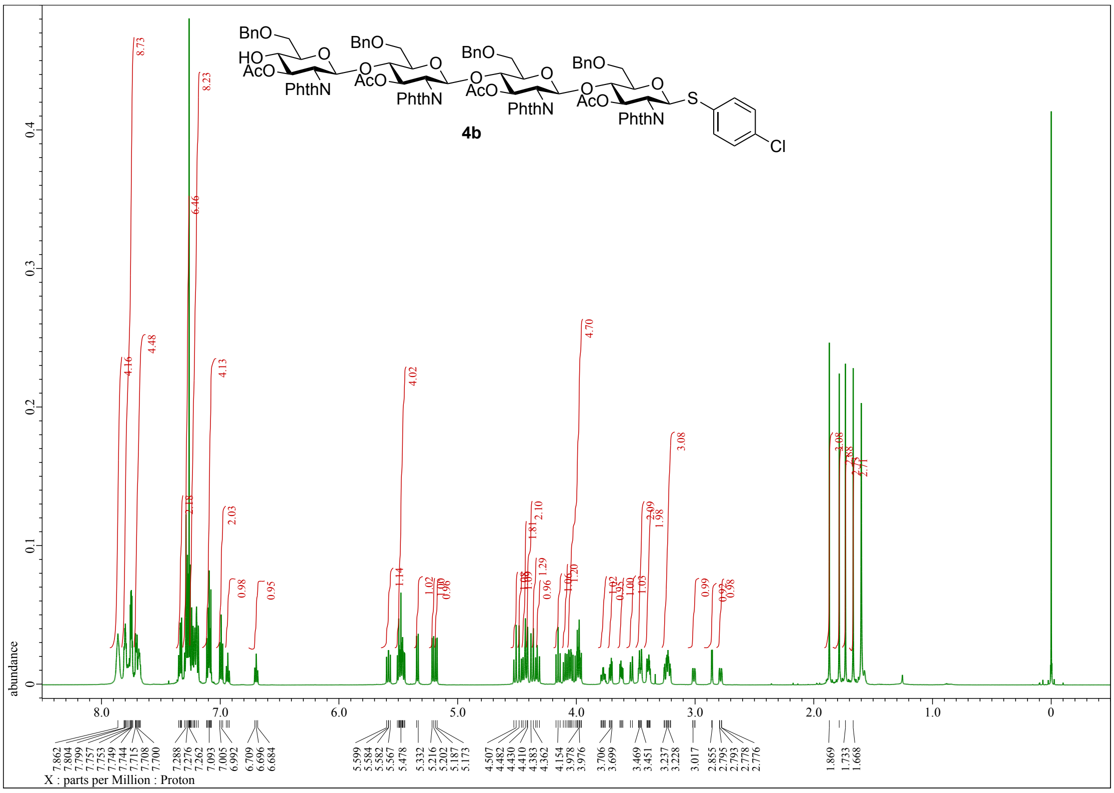
H-H cosy


BnO
HO
AcO
PhthN
O
BnO
O
AcO
PhthN
O
BnO
O
AcO
PhthN
O
S
Cl
3b
abundance
X : parts per Million : Proton
Y : parts per Million : Proton

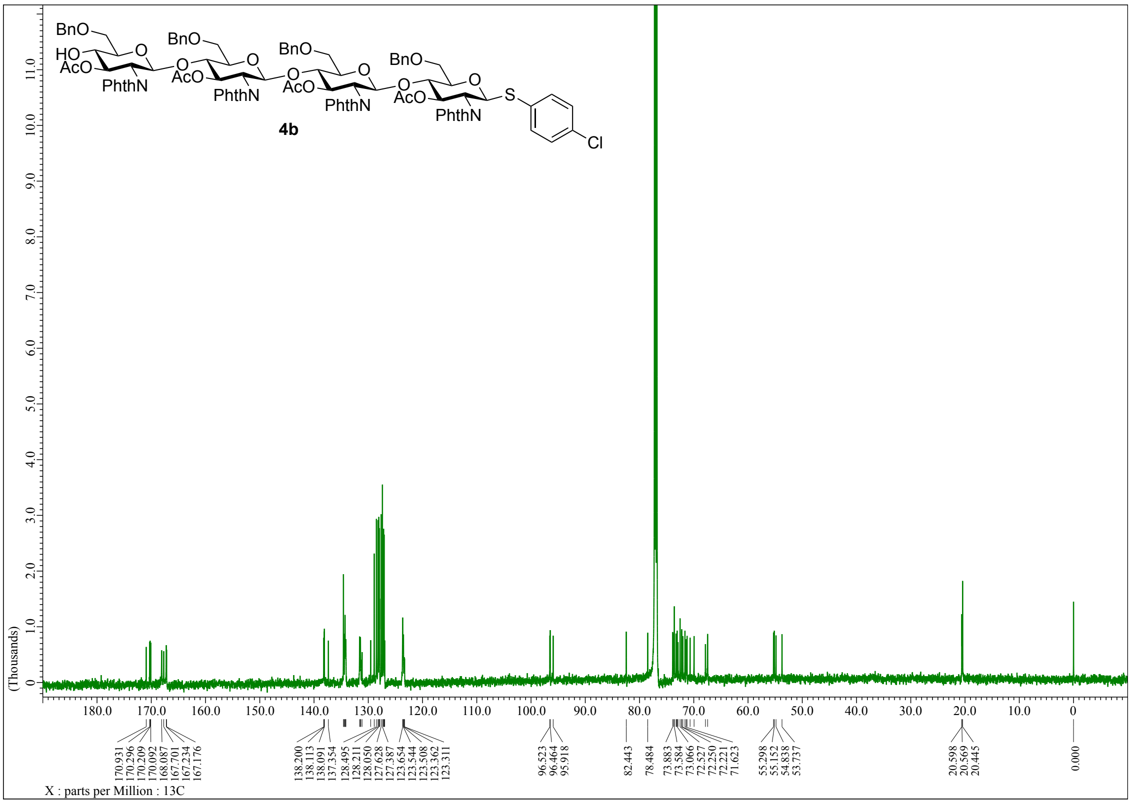
HMQC


BnO
HO
AcO
PhthN
O
BnO
O
AcO
PhthN
O
BnO
O
AcO
PhthN
O
S
Cl
3b
abundance
X : parts per Million : Proton
Y : parts per Million : Carbon13
(Thousands)

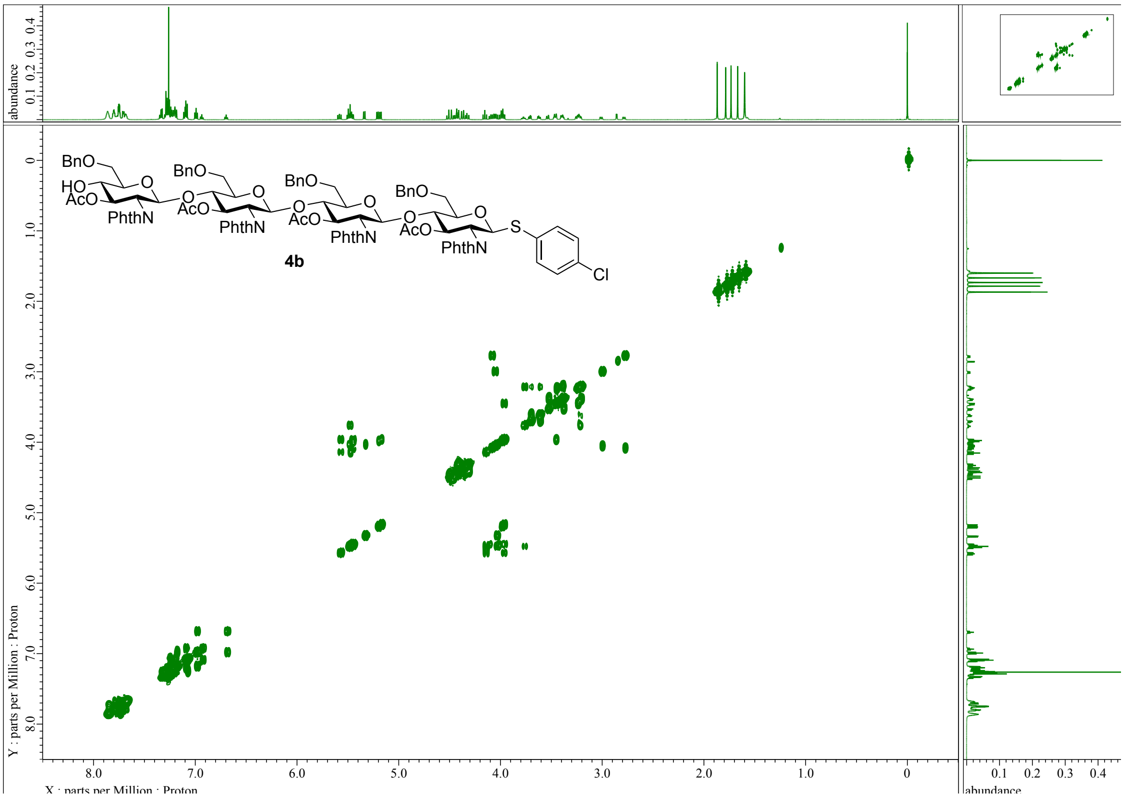
[1]H NMR



[13]C NMR

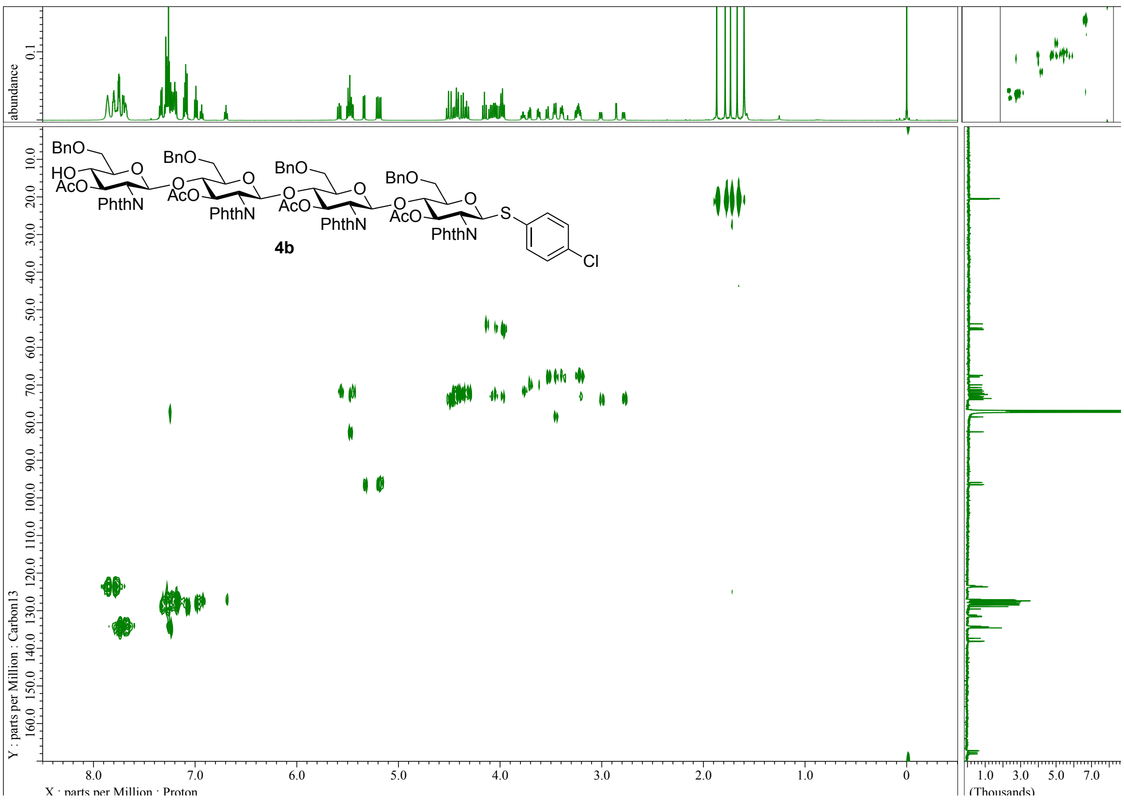


H-H cosy



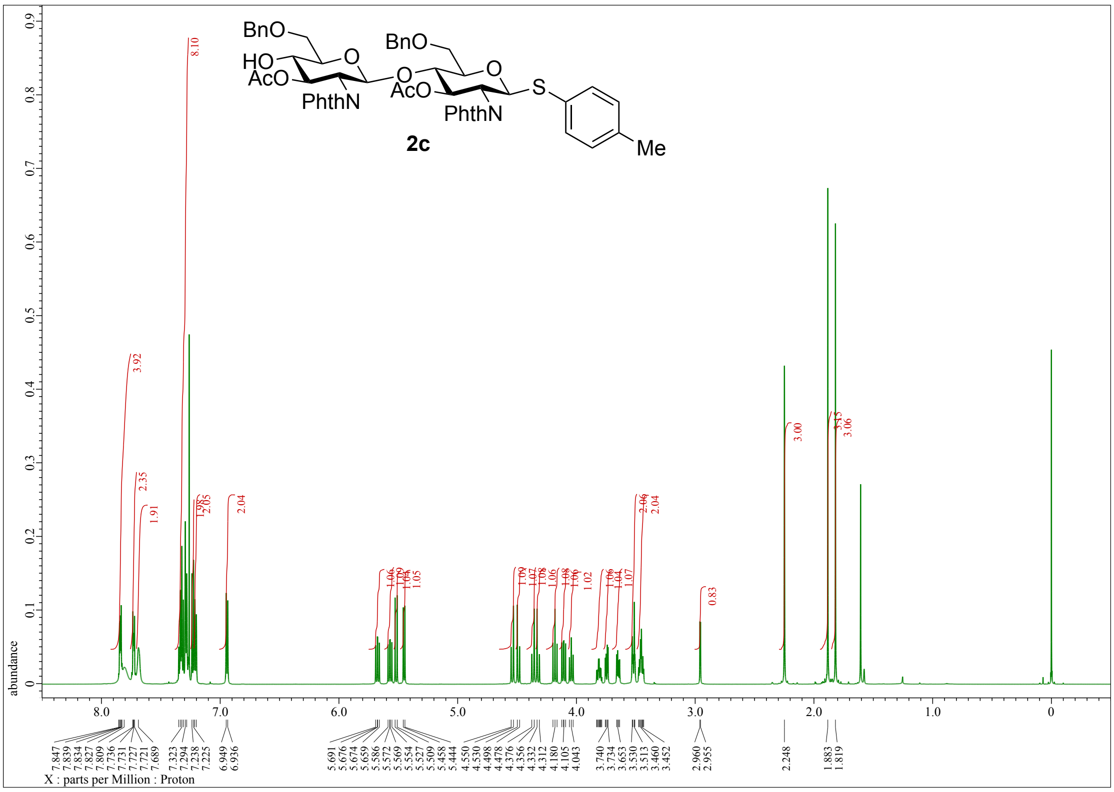
4b
X : parts per Million : Proton
Y : parts per Million : Proton
abundance

HMQC

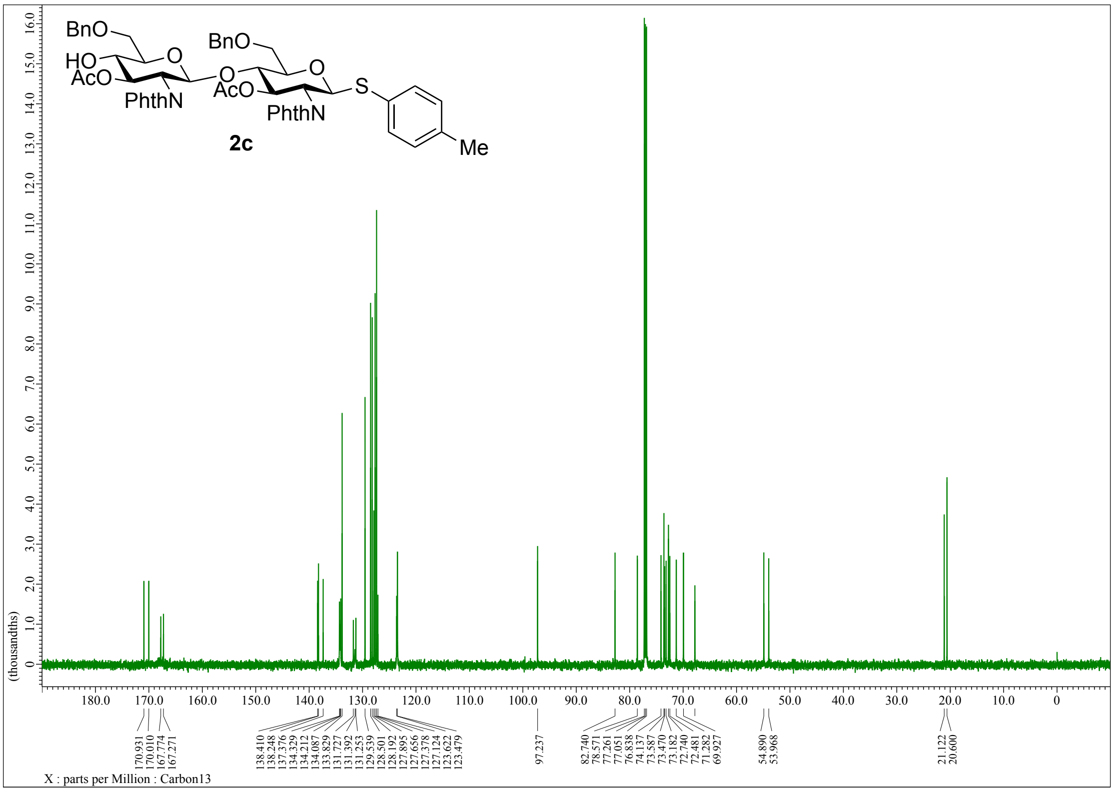


4b
X : parts per Million : Proton
Y : parts per Million : Carbon13
abundance
(Thousands)

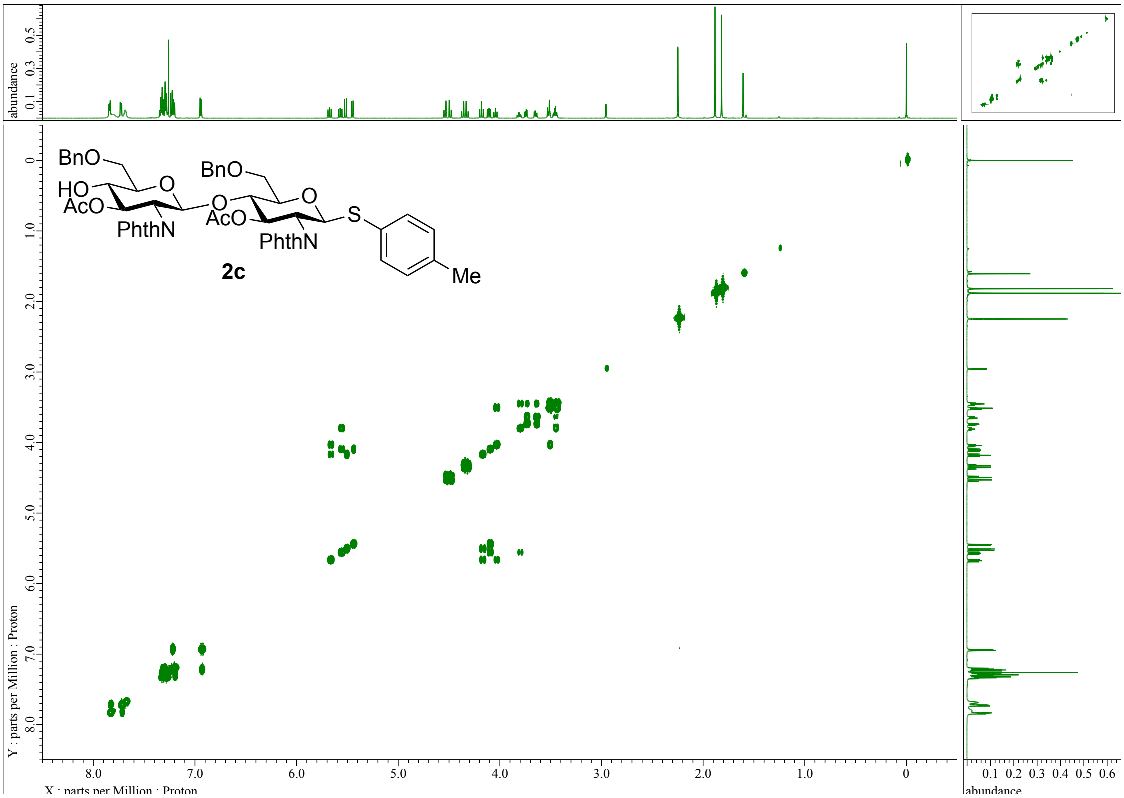
^{1}H NMR



^{13}C NMR

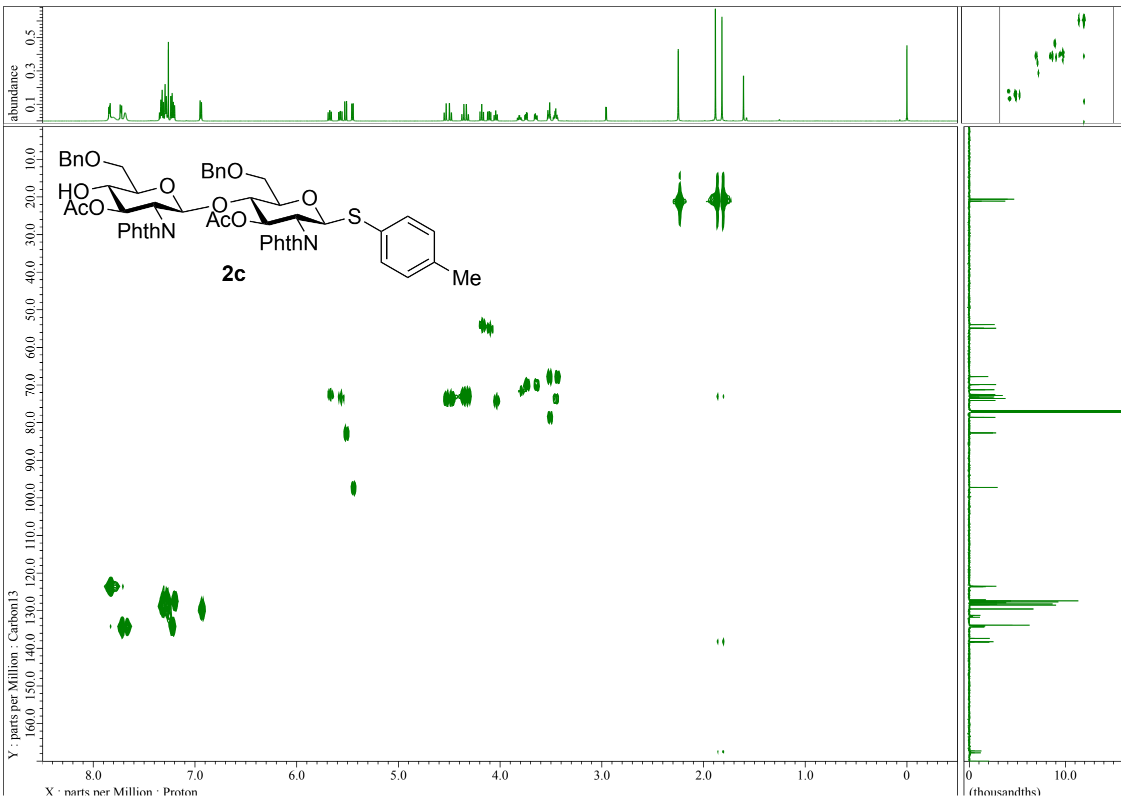


H-H cosy



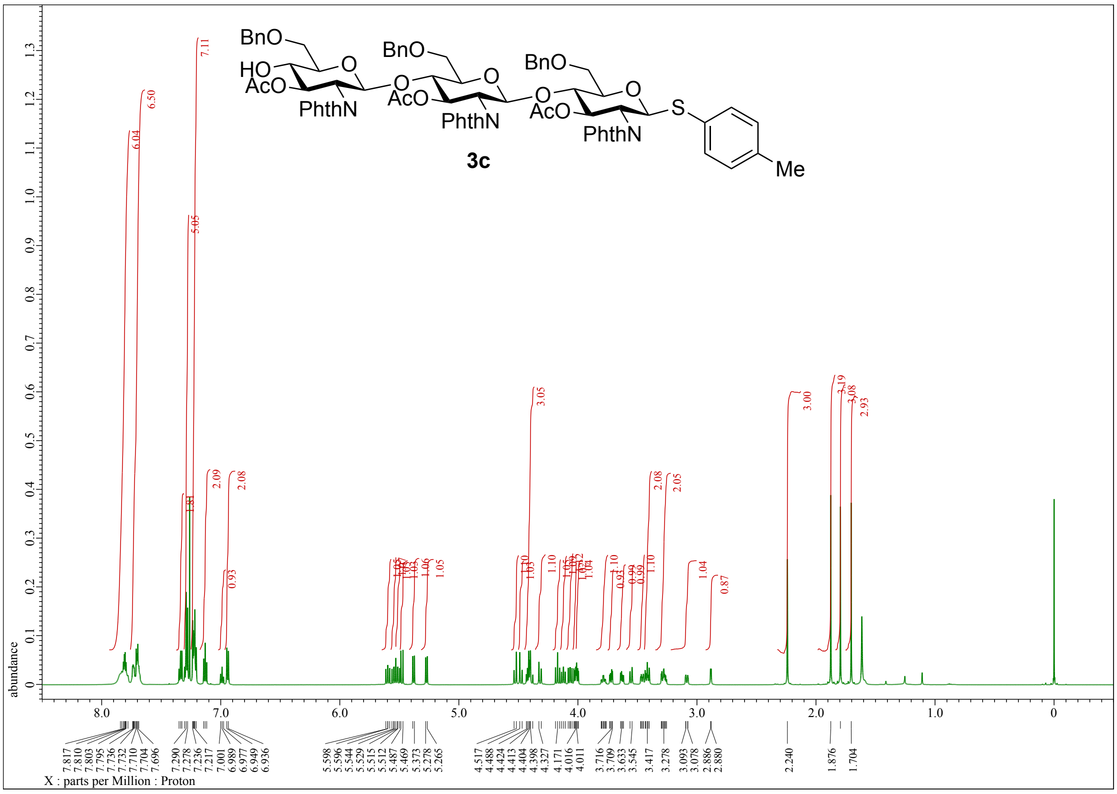
abundance
Y : parts per Million : Proton
X : parts per Million : Proton
BnO
HO
AcO
O
PhthN
BnO
O
AcO
O
PhthN
S
Me
2c
abundance

HMQC

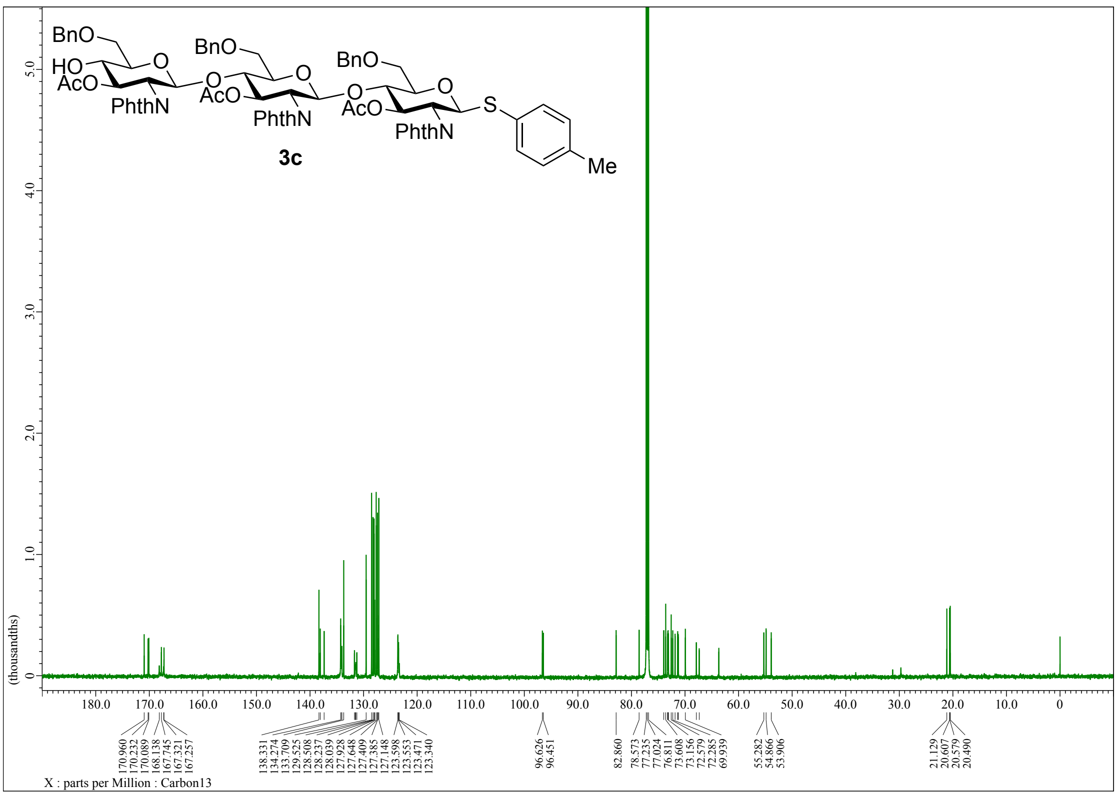


abundance
Y : parts per Million : Carbon13
X : parts per Million : Proton
BnO
HO
AcO
O
PhthN
BnO
O
AcO
O
PhthN
S
Me
2c
(thousandths)

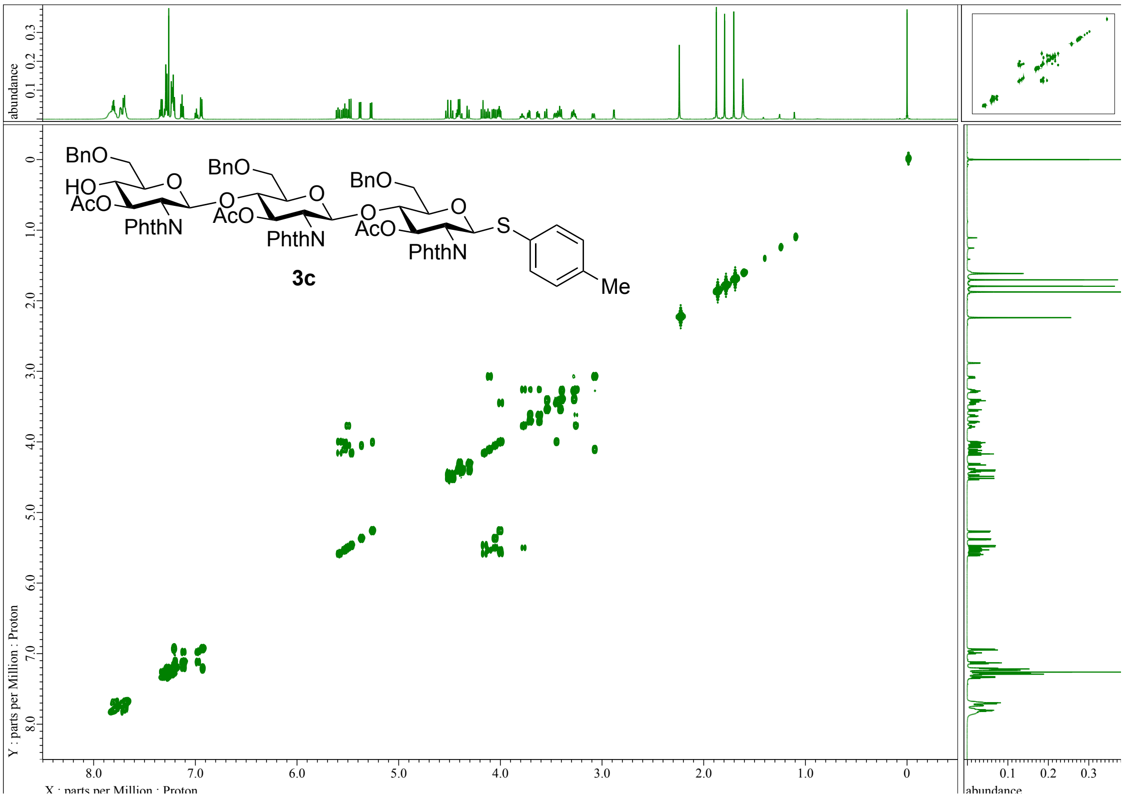
[1]H NMR



[13]C NMR

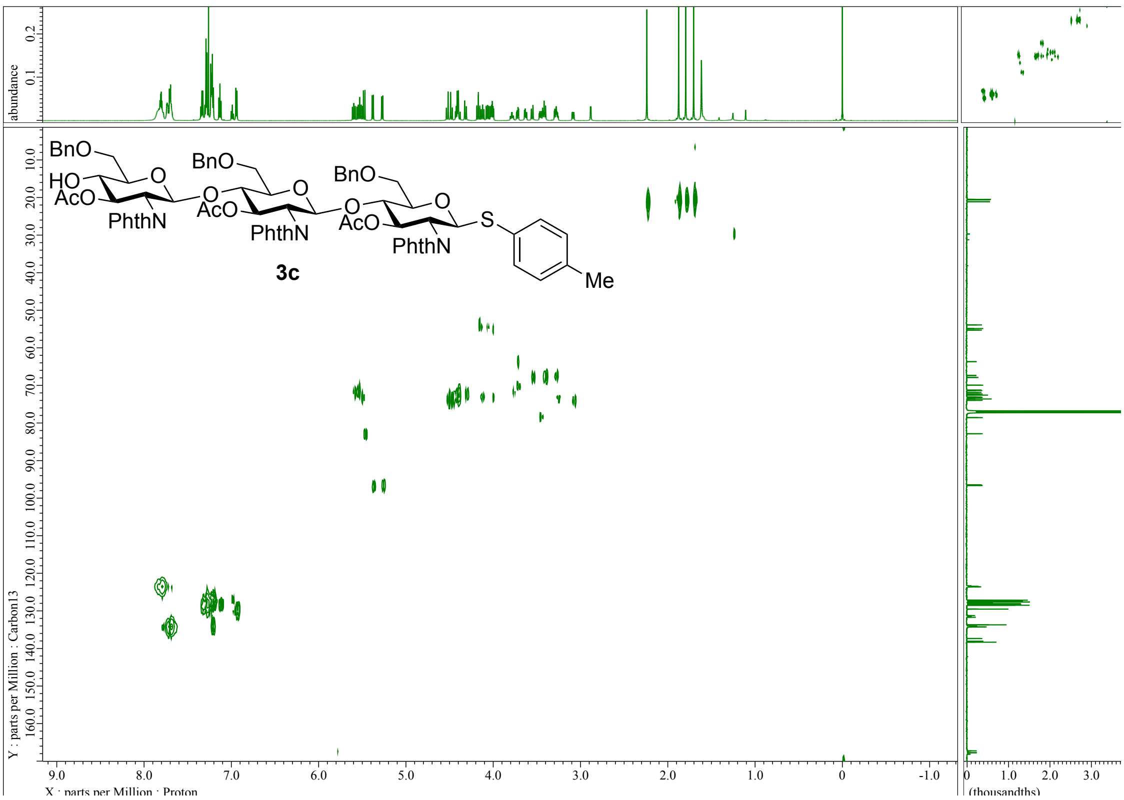


H-H cosy



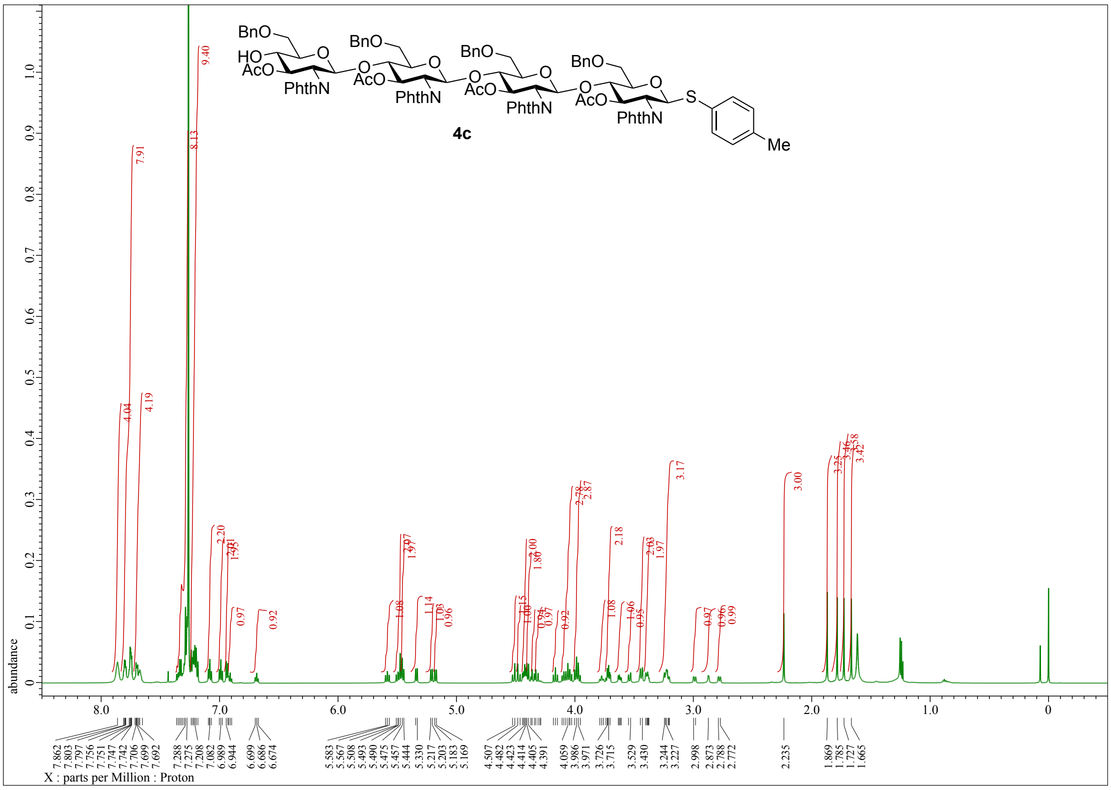
BnO
HO
AcO
PhthN
O
BnO
AcO
PhthN
O
BnO
AcO
PhthN
S
Me
3c
abundance
Y : parts per Million : Proton
X : parts per Million : Proton

HMQC

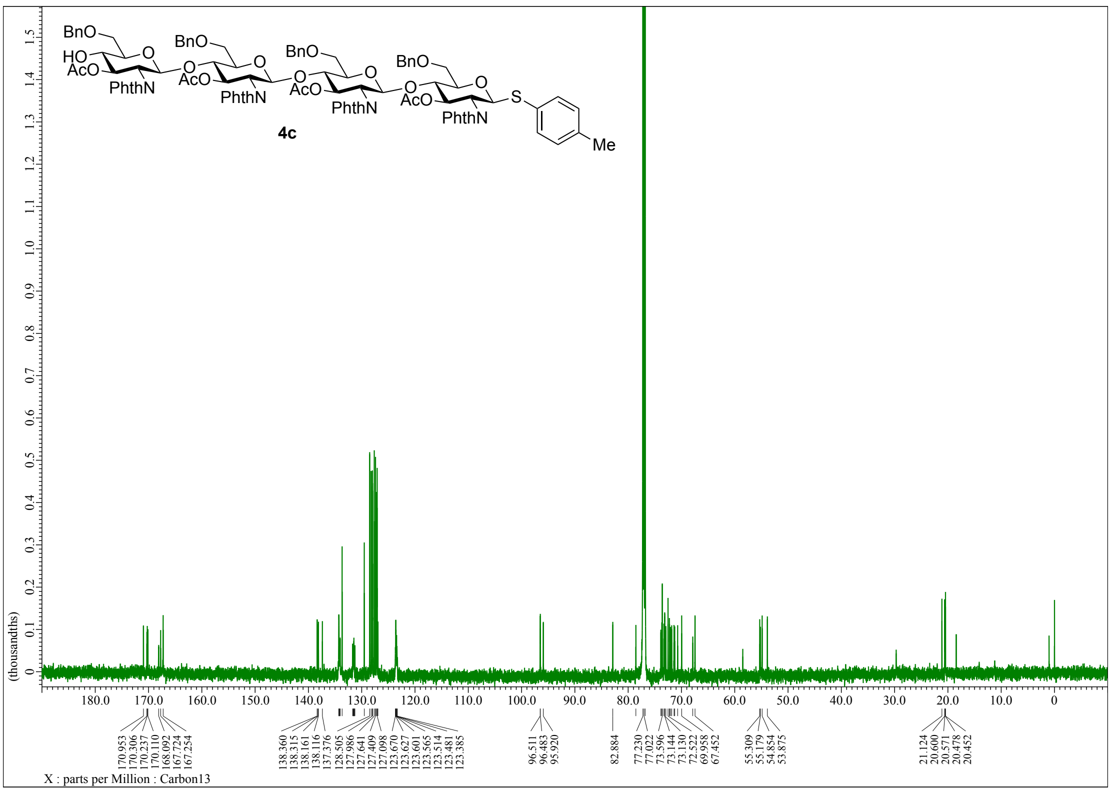


BnO
HO
AcO
PhthN
O
BnO
AcO
PhthN
O
BnO
AcO
PhthN
S
Me
3c
abundance
Y : parts per Million : Carbon13
X : parts per Million : Proton
(thousandths)

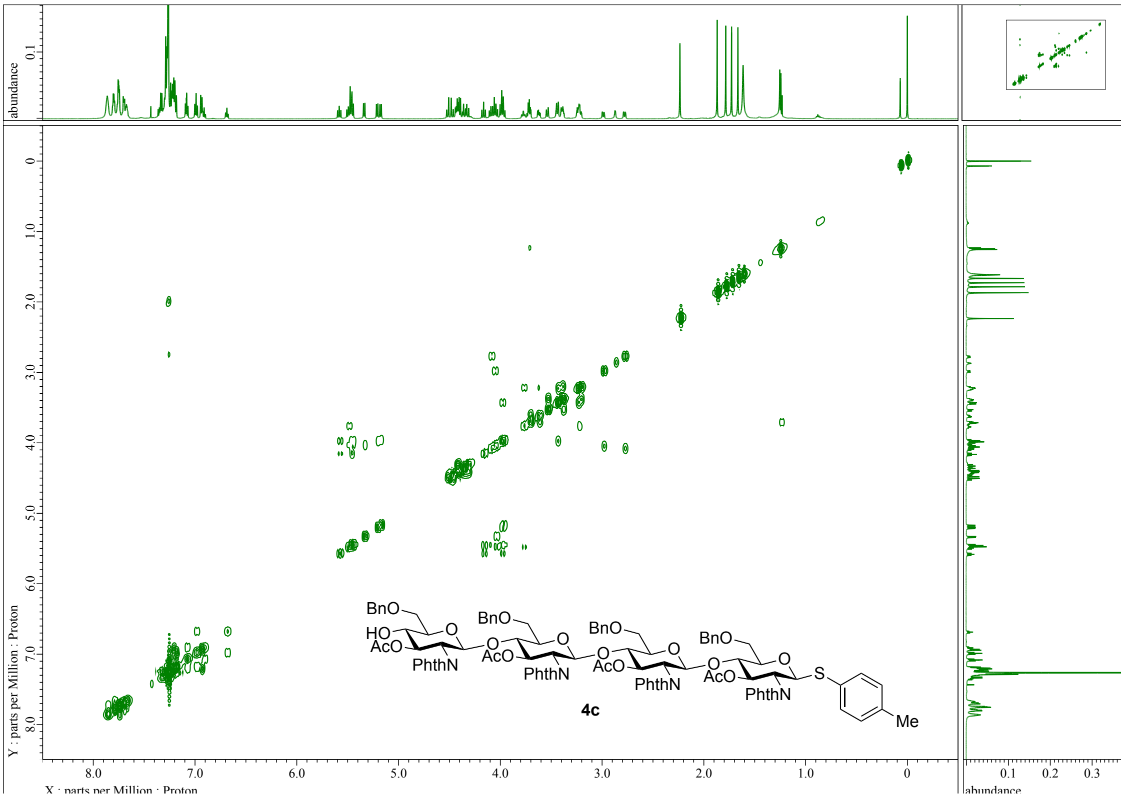
[1]H NMR



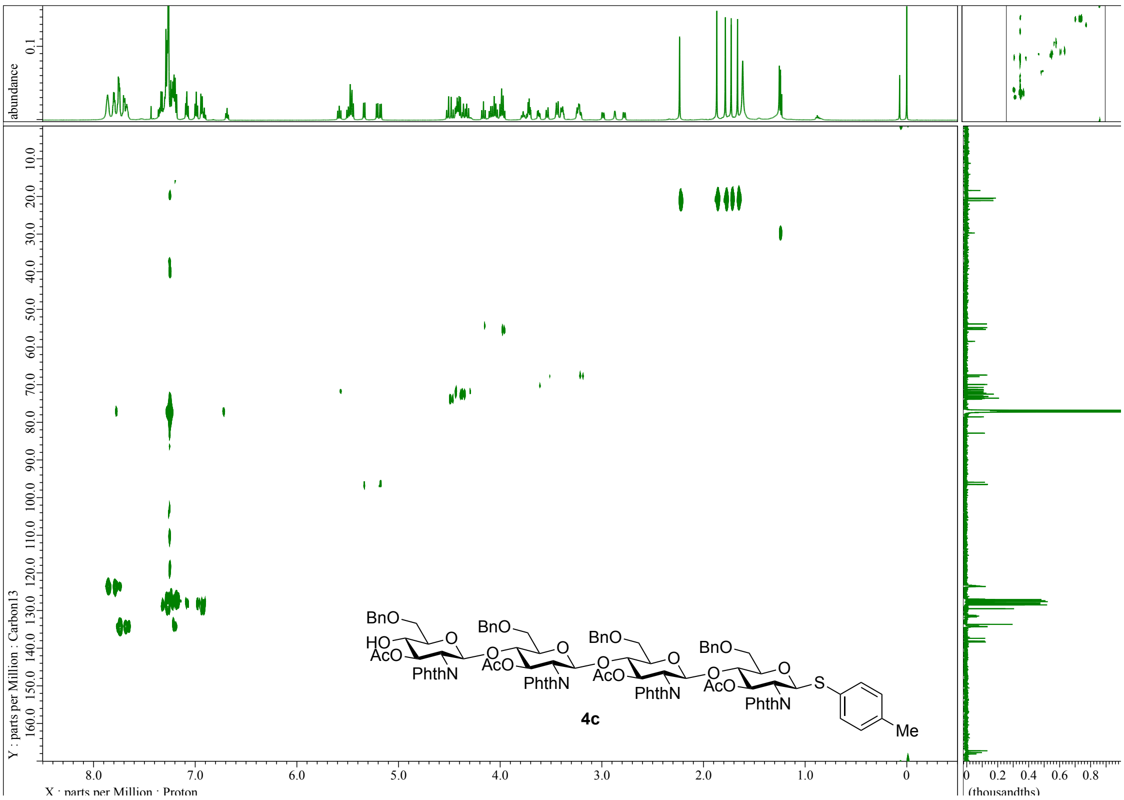
[13]C NMR



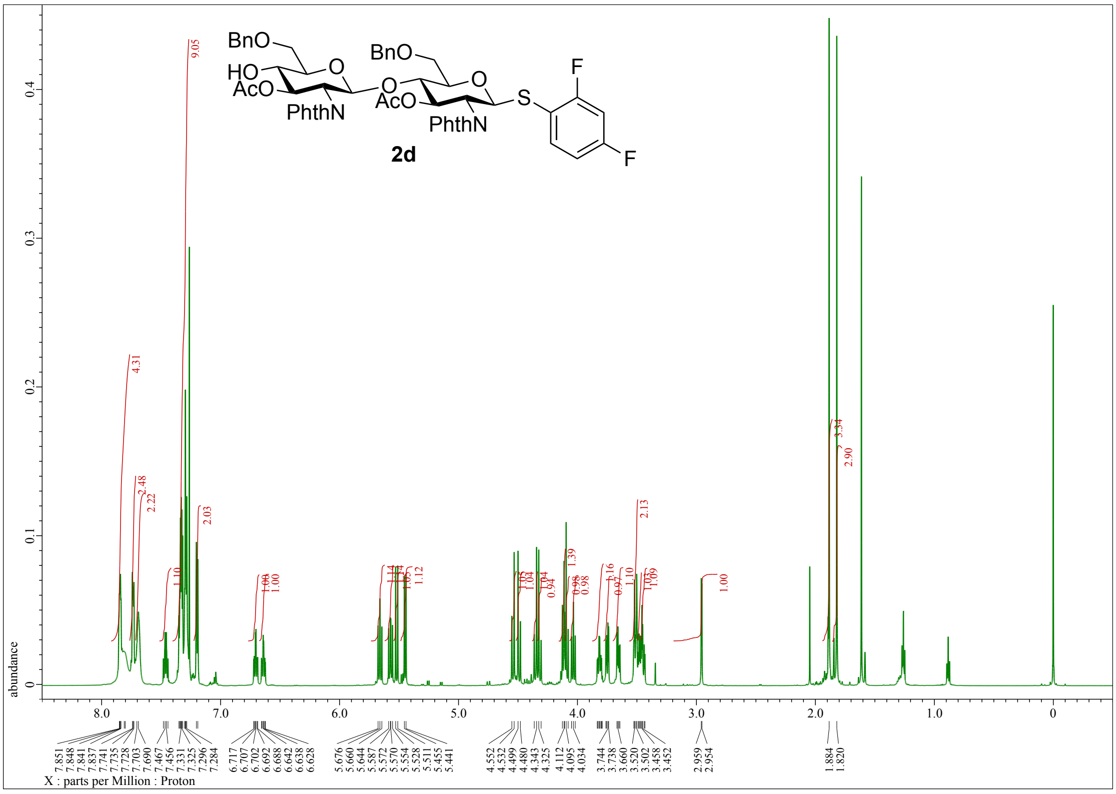
H-H cosy


abundance
0.1
Y : parts per Million : Proton
X : parts per Million : Proton
abundance
BnO
HO
AcO
PhthN
O
AcO
S
Me
4c

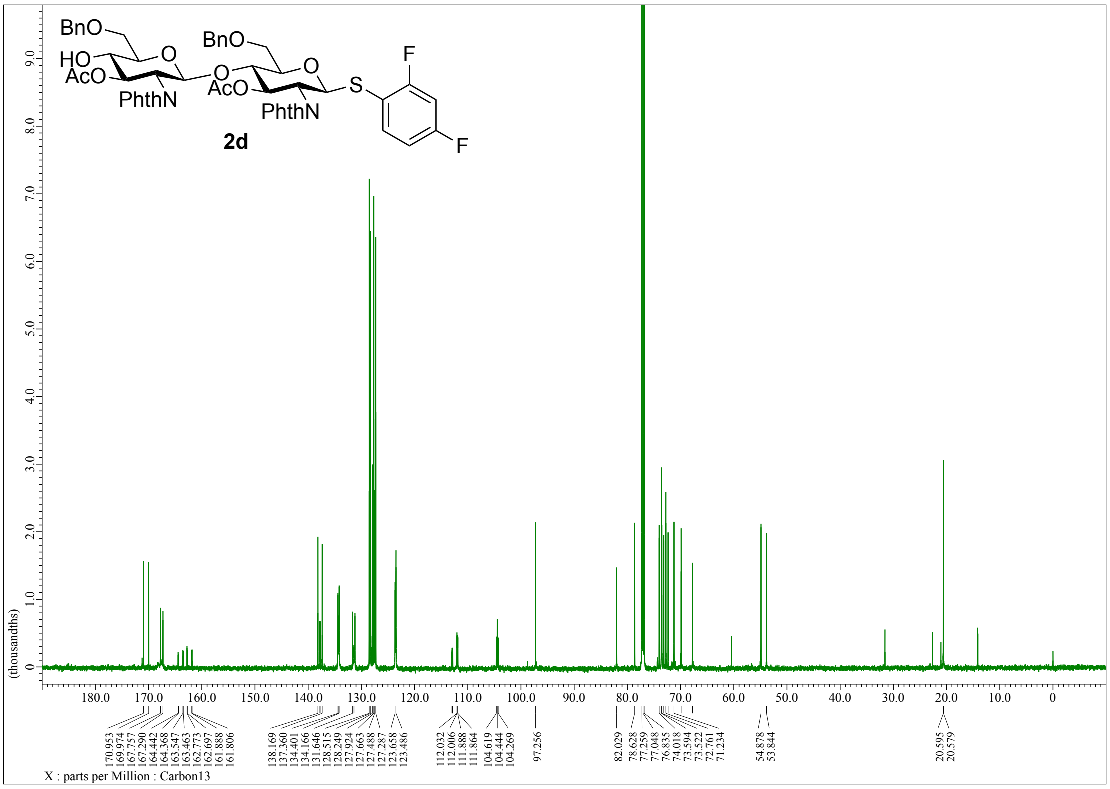
HMQC


abundance
0.1
Y : parts per Million : Carbon13
X : parts per Million : Proton
(thousandths)
BnO
HO
AcO
PhthN
O
AcO
S
Me
4c

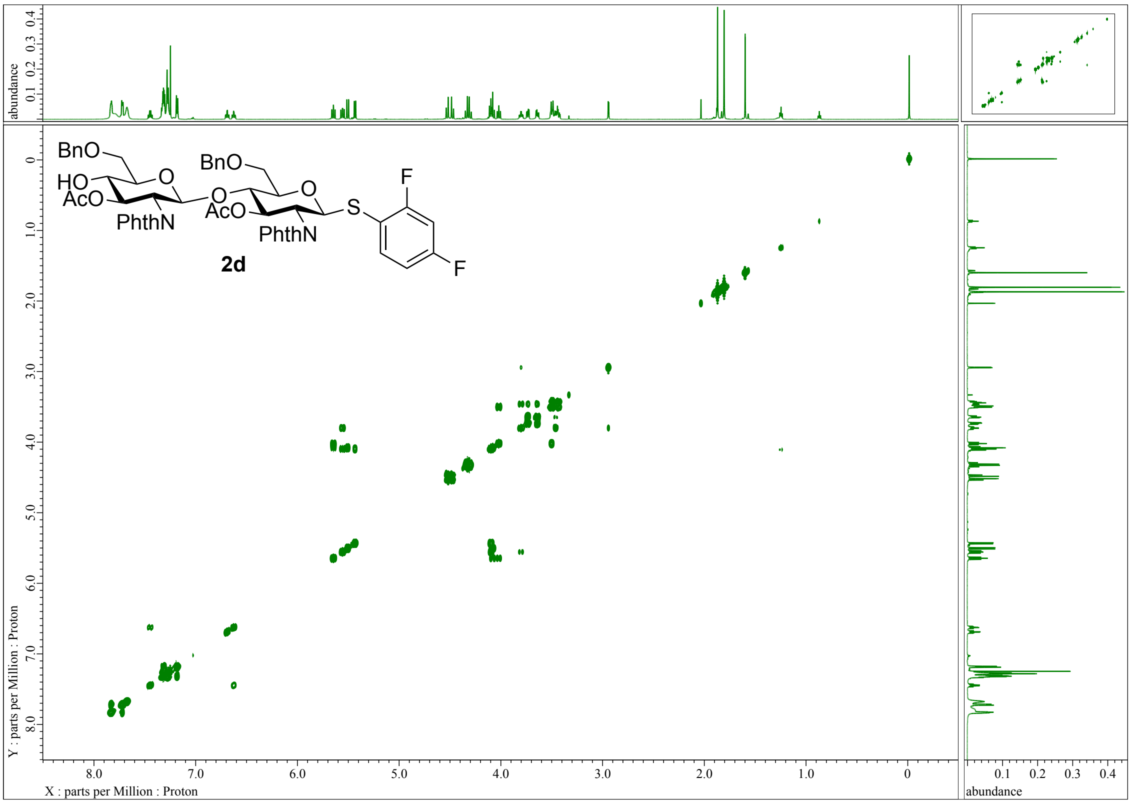
^{1}H NMR



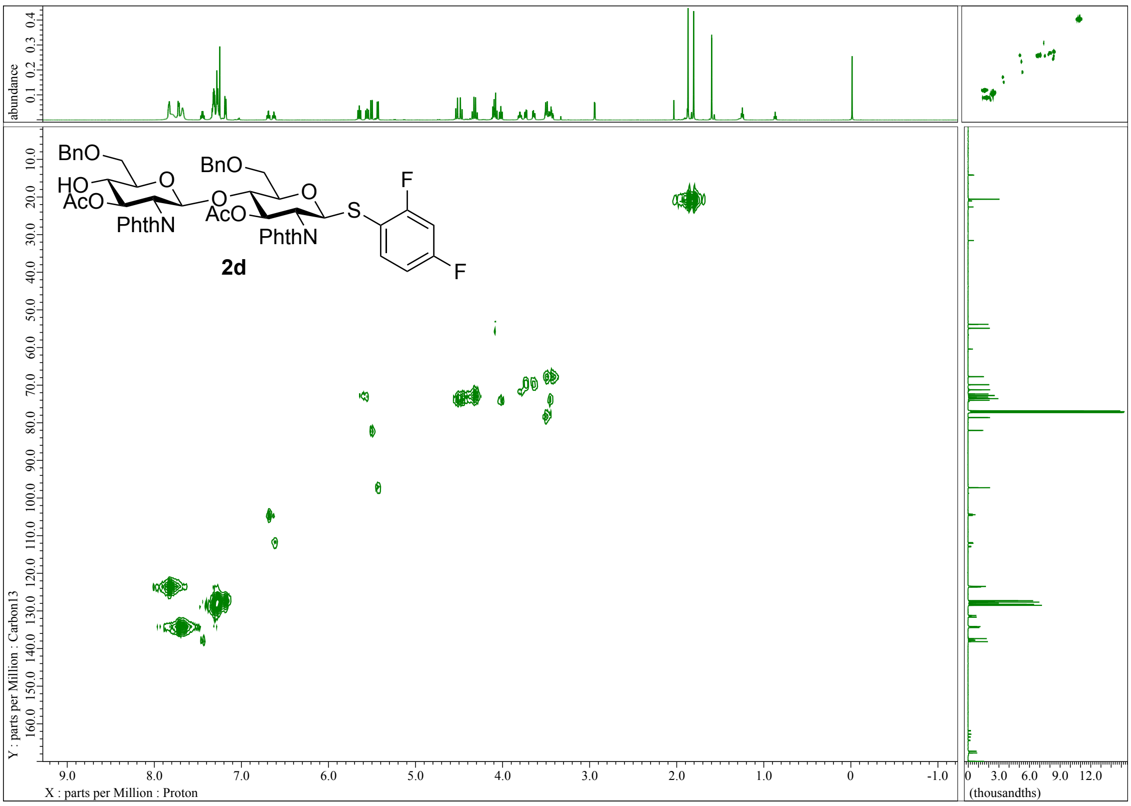
^{13}C NMR



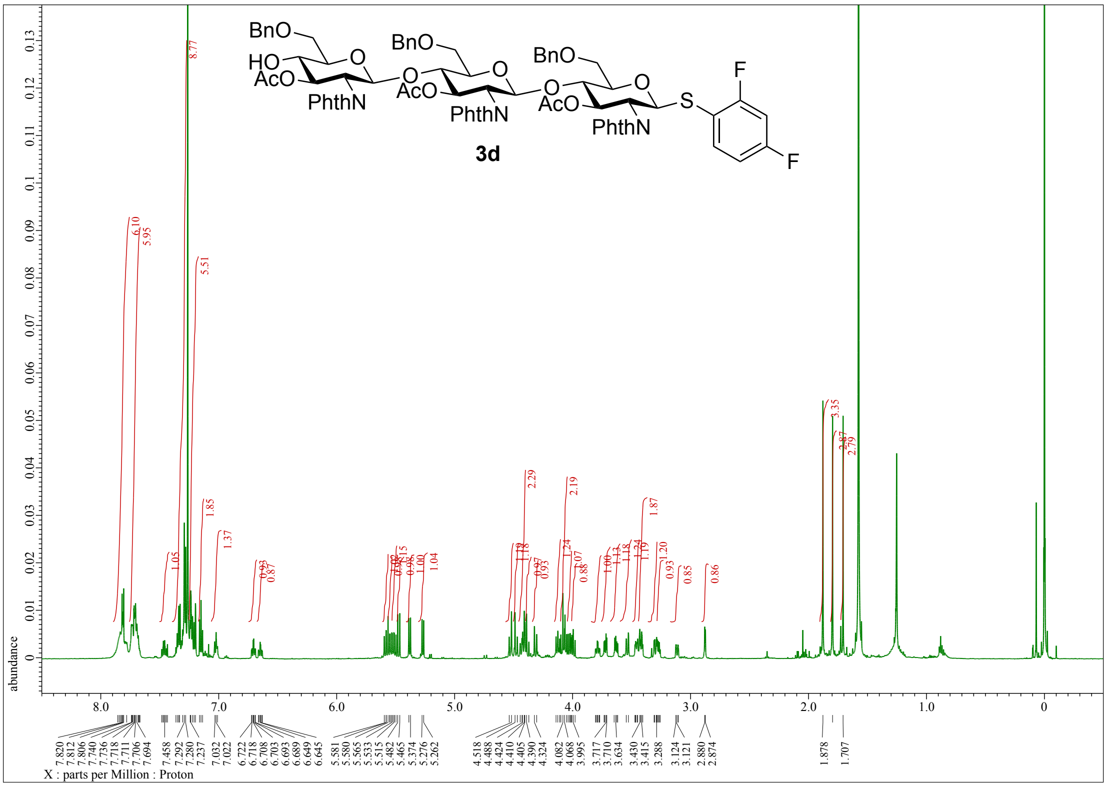
H-H cosy


BnO
HO
AcO
O
PhthN
BnO
O
AcO
O
PhthN
S
F
F
2d
abundance
Y : parts per Million : Proton
X : parts per Million : Proton

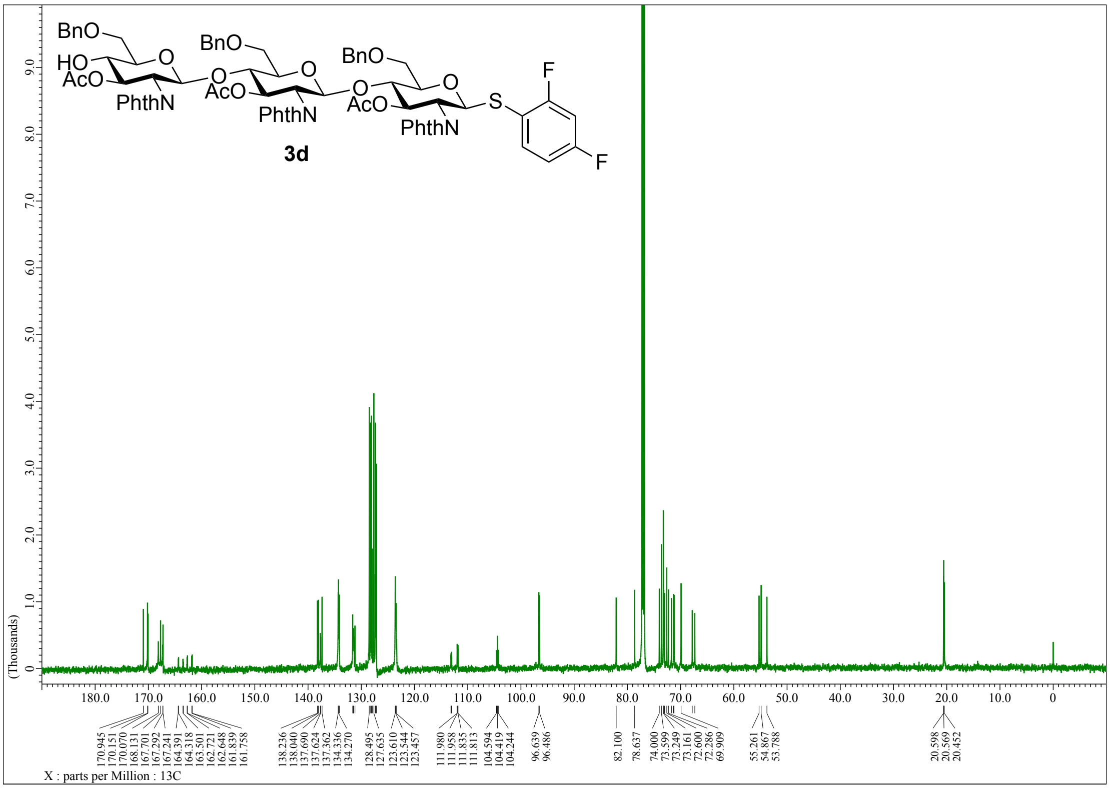
HMQC


BnO
HO
AcO
O
PhthN
BnO
O
AcO
O
PhthN
S
F
F
2d
abundance
(thousandths)
Y : parts per Million : Carbon13
X : parts per Million : Proton

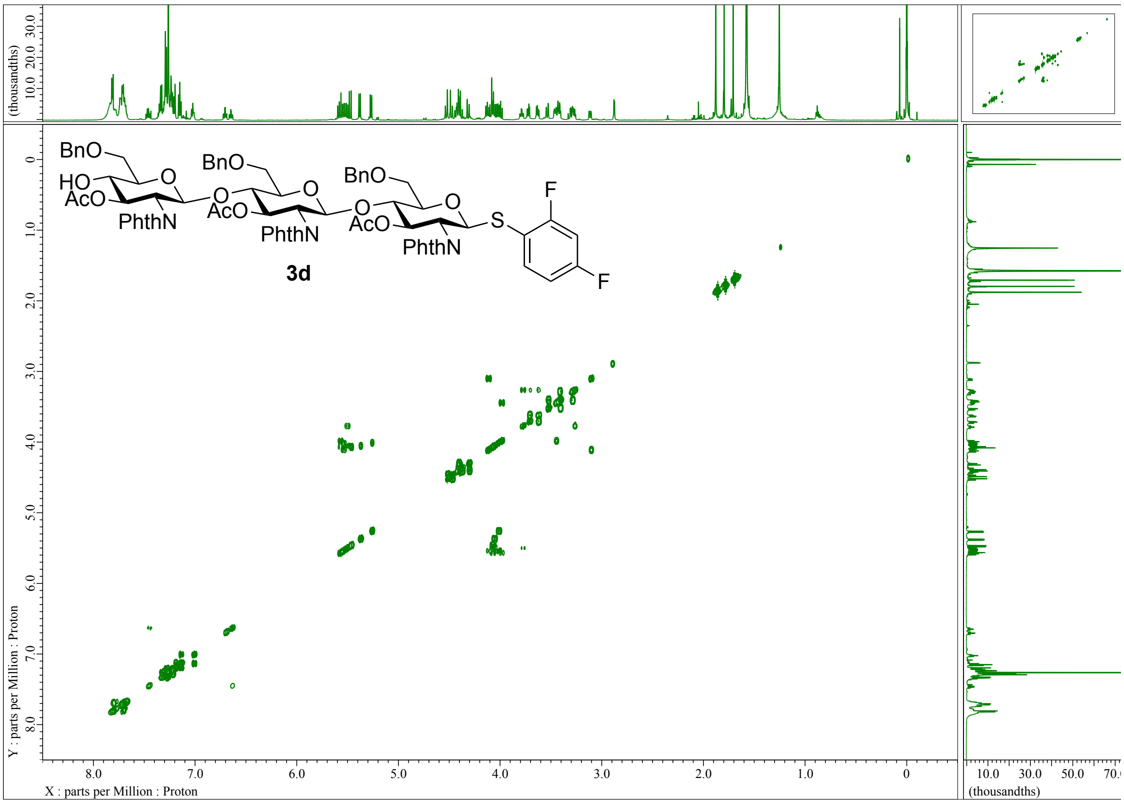
^{1}H NMR



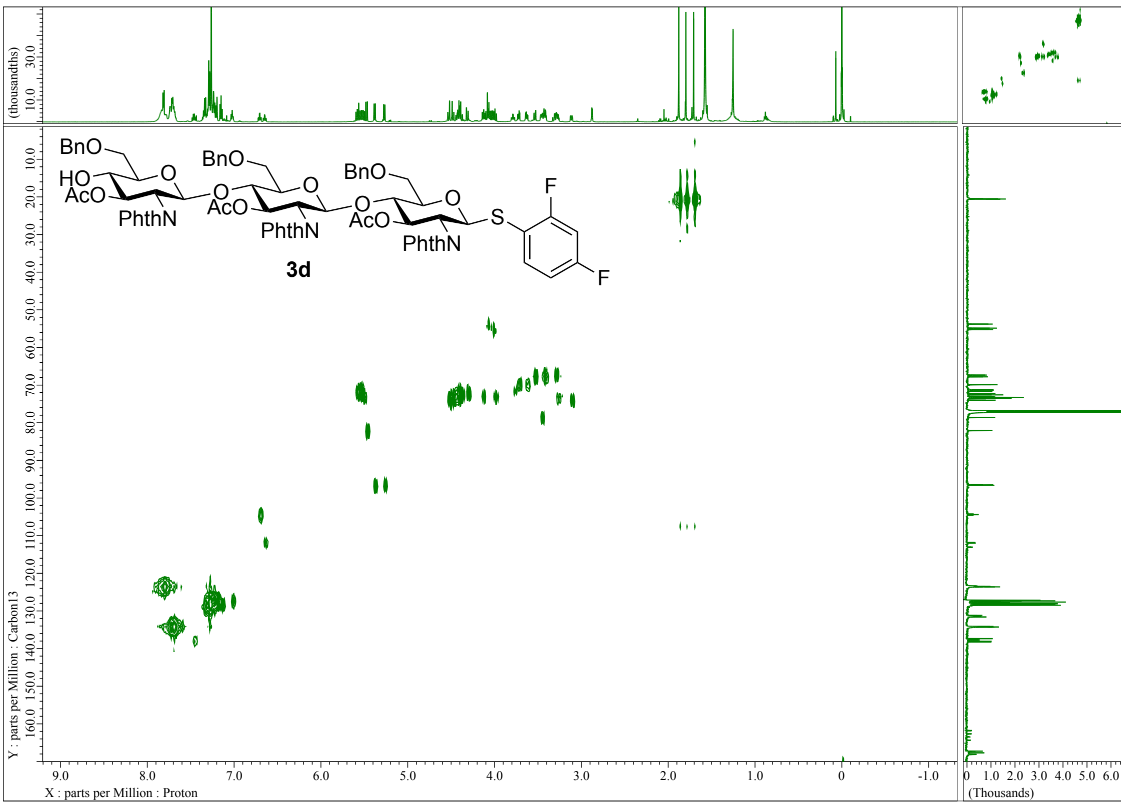
^{13}C NMR



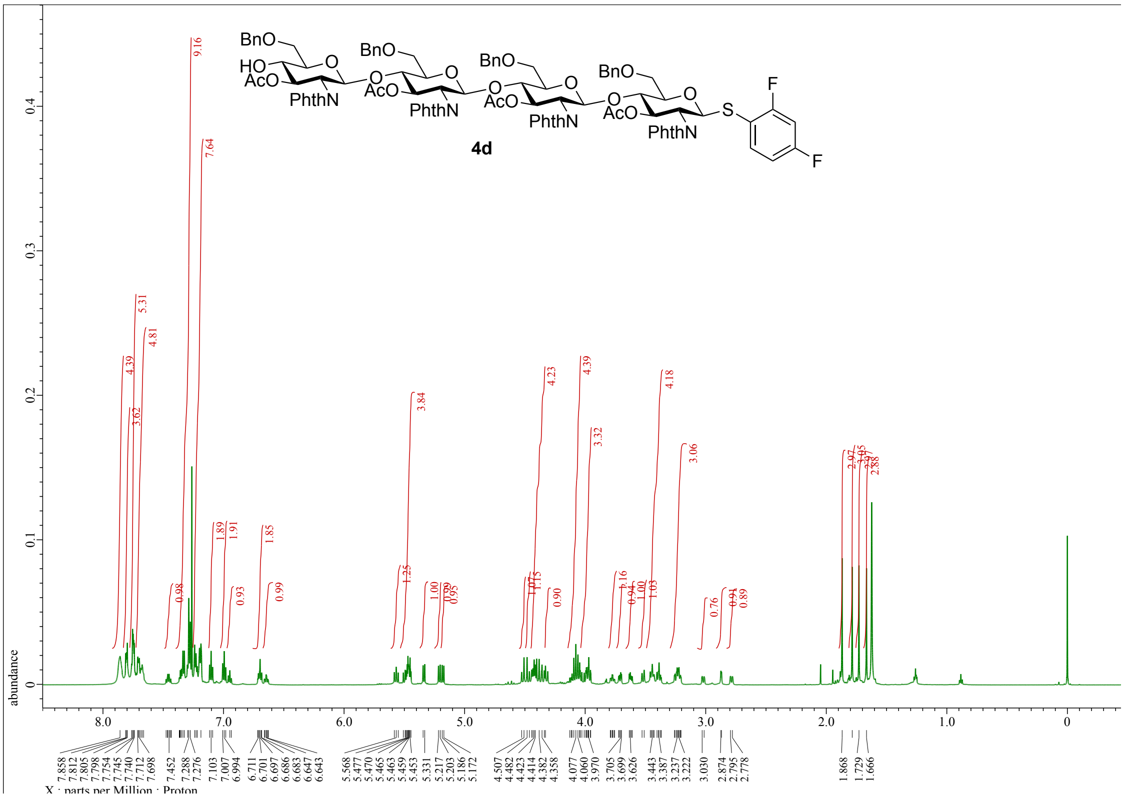
H-H cosy



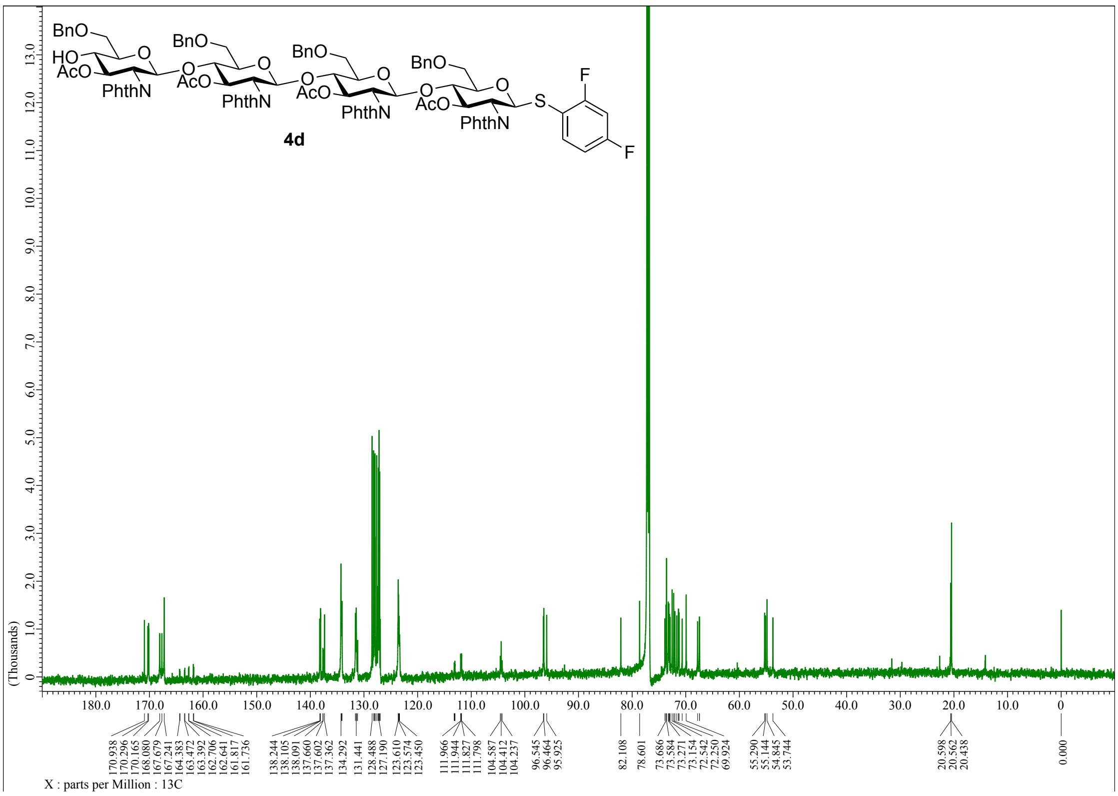
HMQC



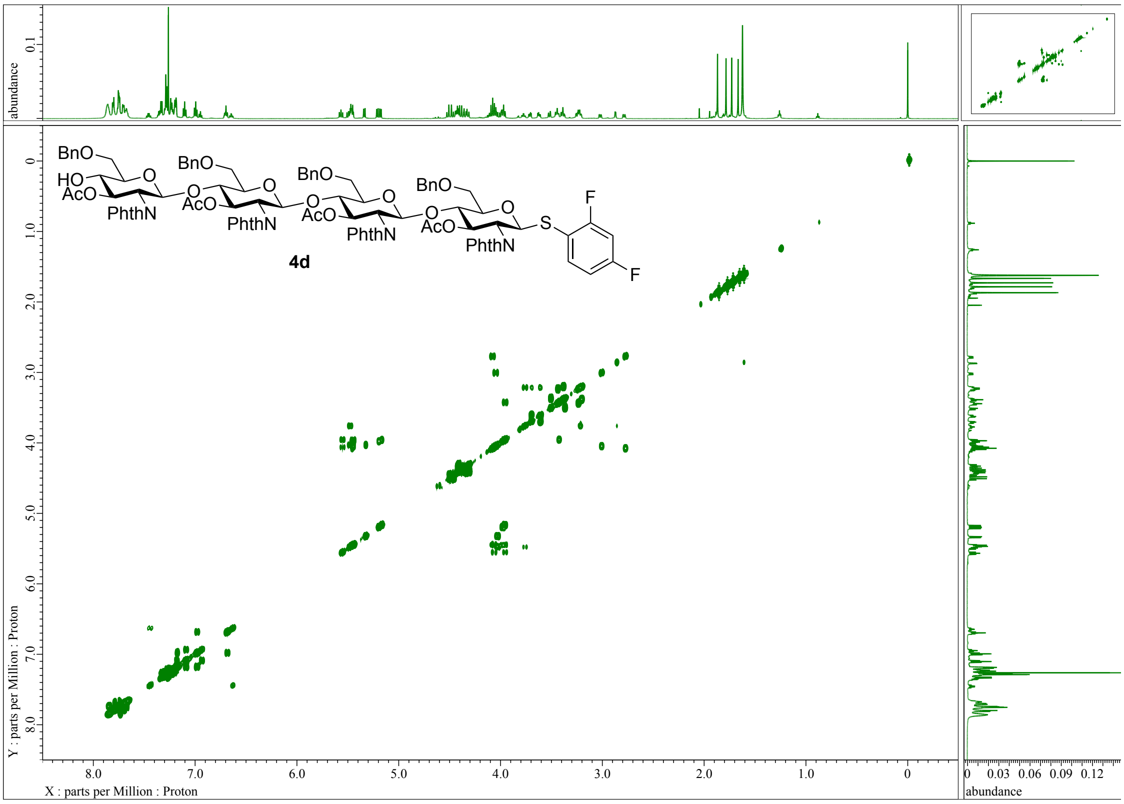
^{1}H NMR



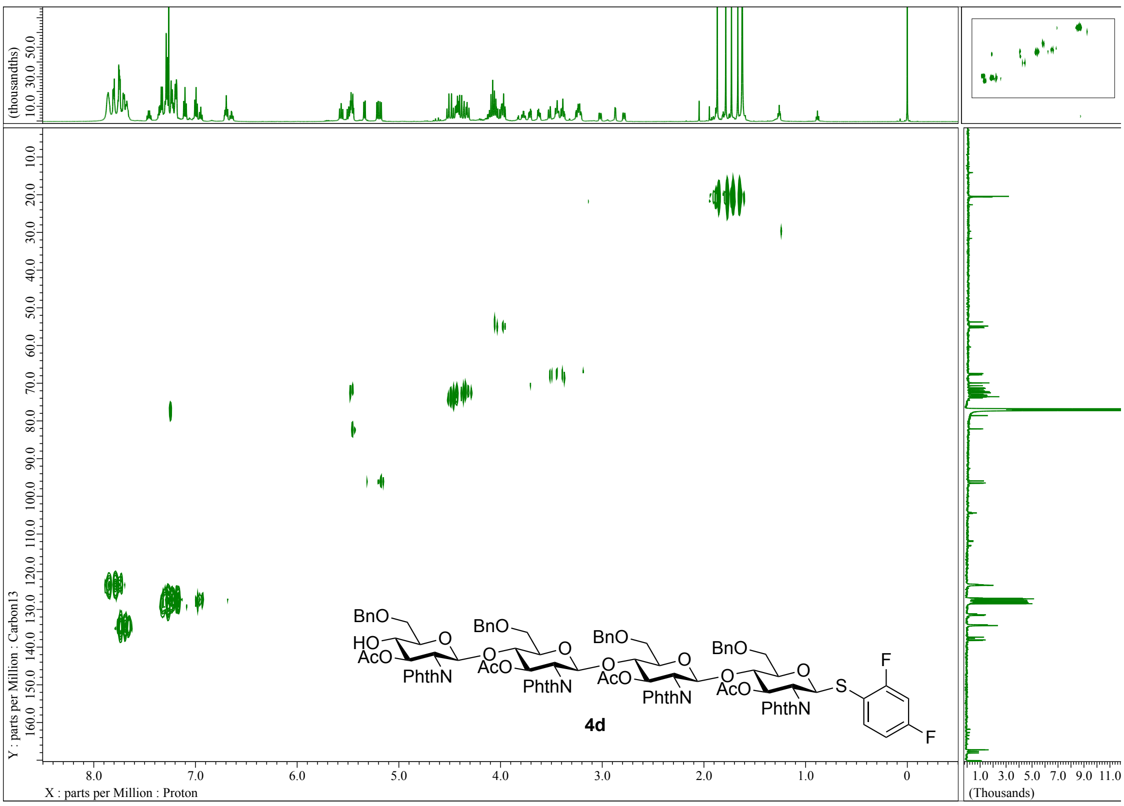
^{13}C NMR



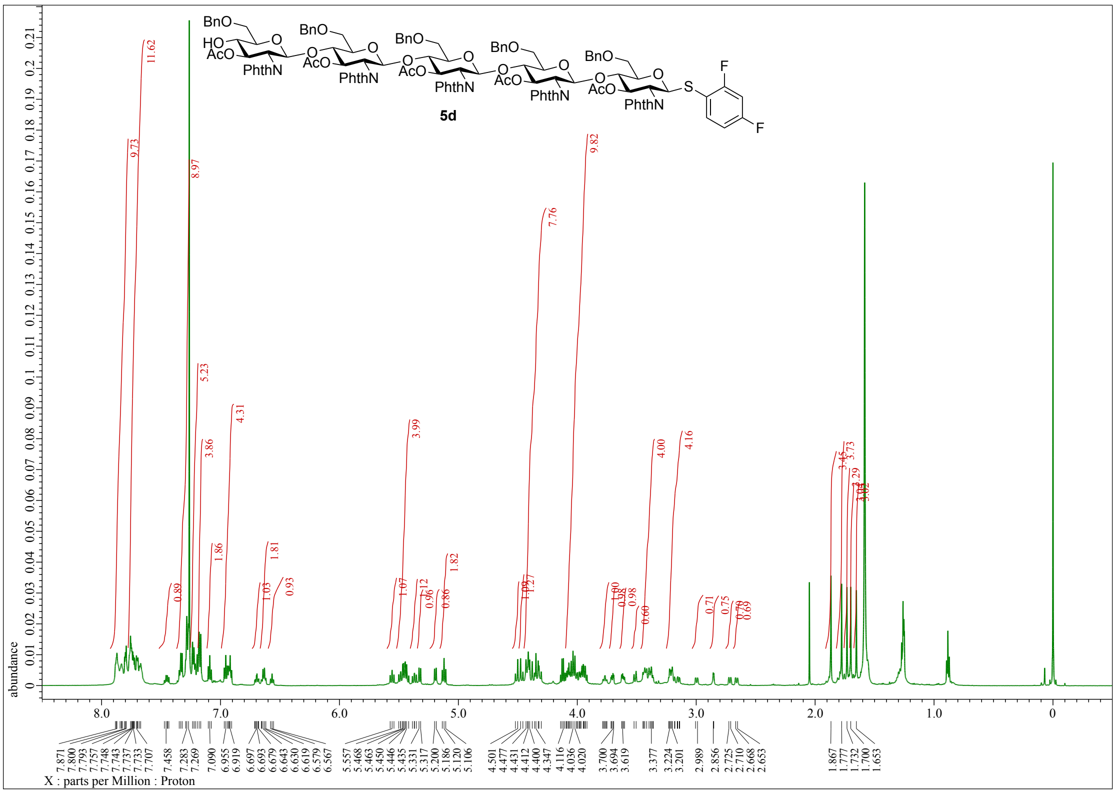
H-H cosy



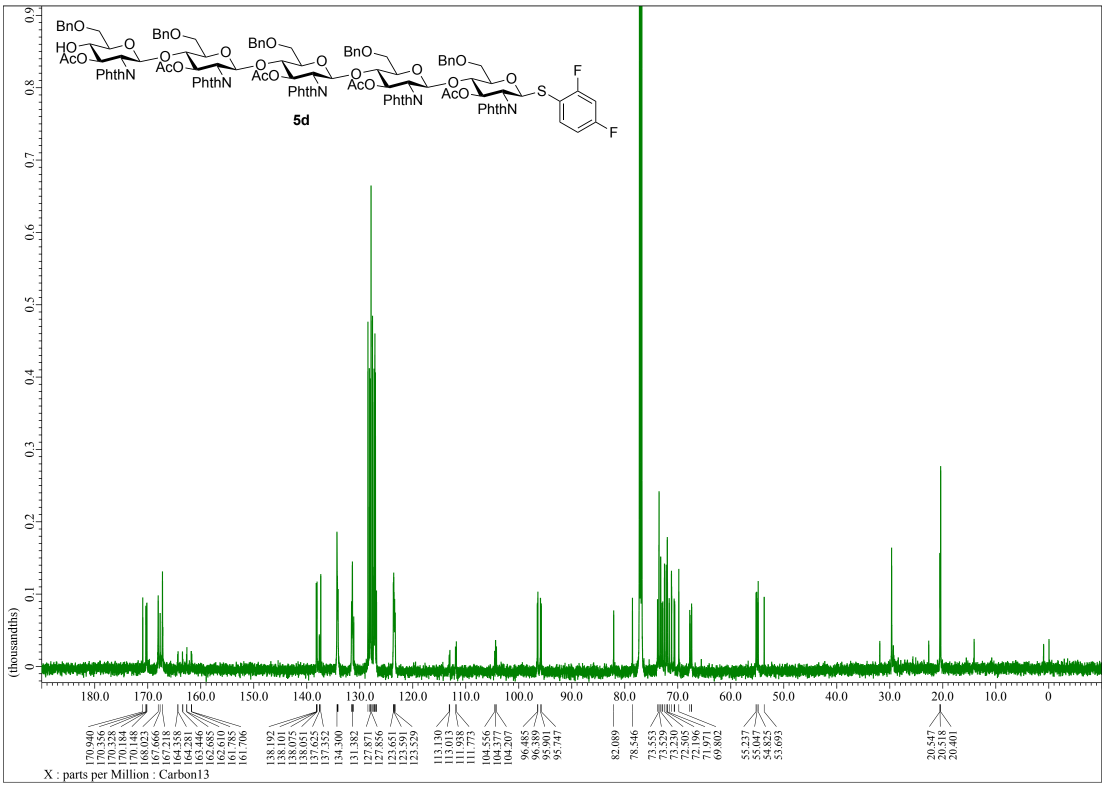
HMQC



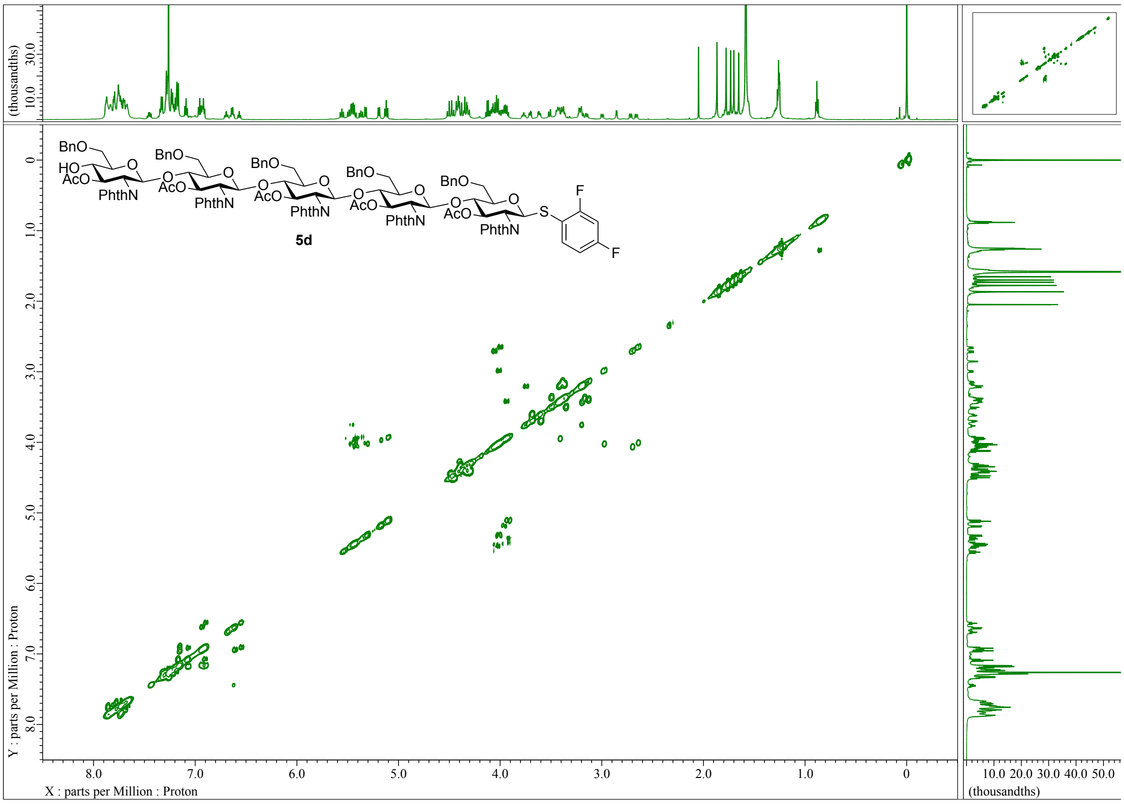
^{1}H NMR



^{13}C NMR

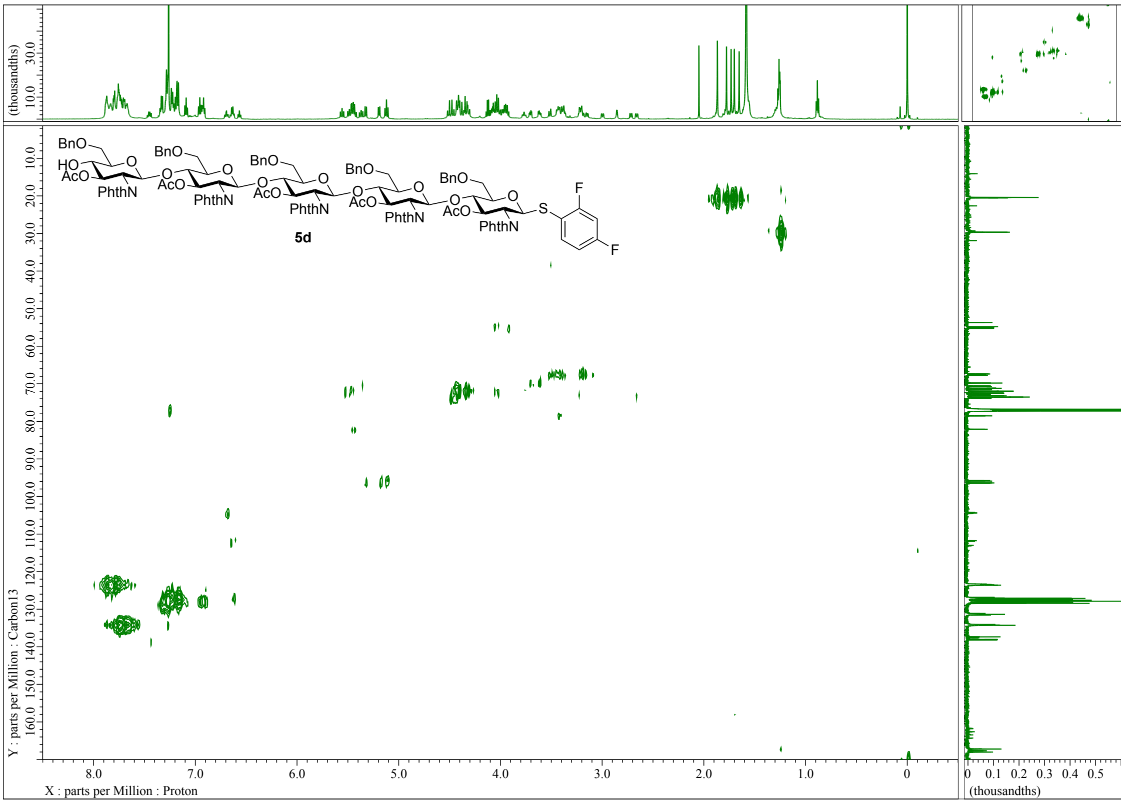


H-H cosy



5d
X : parts per Million : Proton
Y : parts per Million : Proton
(thousandths)

HMQC



5d
X : parts per Million : Proton
Y : parts per Million : Carbon13
(thousandths)