



Supporting Information

for

Synthesis of cyclic β -1,6-oligosaccharides from glucosamine monomers by electrochemical polyglycosylation

Md Azadur Rahman, Hirofumi Endo, Takashi Yamamoto, Shoma Okushiba,
Norihiro Sasaki and Toshiki Nokami

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Synthetic details, DFT calculations, and compound characterization data

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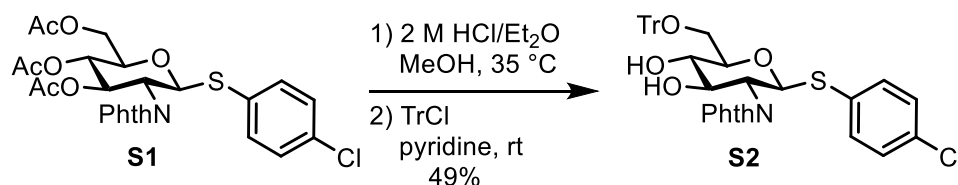
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1. General

All reactions were conducted under argon atmosphere except when otherwise noted. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE II 600 (600 MHz for ^1H and 150 MHz for ^{13}C) and a JEOL JNM-ECZ 600 (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 Bruker Ultraflextreme spectrometer. Merck TLC (silica gel 60 F₂₅₄) was used 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) was used. Starting materials **S1**,¹ **S4**,² **S5**,² and **S11**³ were prepared according to the reported procedures. All reagents were purchased from commercial suppliers and used without extra purification. Products **7a**,⁴ **7b**,⁵ **7c**,⁶ and **8a**⁷ are known compounds, and NMR spectra of these compounds were compared with reported values.

2. Preparation of building blocks

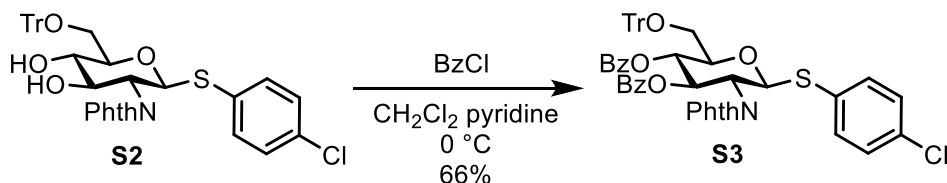
Preparation of 4-chlorophenyl-2-deoxy-2-phthalimido-1-thio-6-*O*-trityl- β -D-glucopyranoside (**S2**)



To a stirred solution of **S1**¹ (4.64 mmol, 2.61 g) in methanol (50 mL) at 35 °C was added 2 M HCl/Et₂O (10 mL). After 2 hours, the progress of the reaction was checked by TLC analysis, and the solution was concentrated under reduced pressure to afford deacetylated sugar. Then, the crude product and trityl chloride (TrCl) (6.96 mmol, 1.94 g, 1.5 equiv) were dissolved in pyridine (20 mL). The reaction mixture was kept stirred overnight, at which point the TLC analysis indicated consumption of the starting material. The reaction was quenched with excessive methanol, and the solvent was removed under reduced pressure. The crude product was purified with silica gel chromatography (hexane/EtOAc 3:2) to obtain **S2** (2.29 mmol, 1.55 g, 49%) as a white solid.

4-Chlorophenyl-2-deoxy-2-phthalimido-1-thio-6-*O*-trityl- β -D-glucopyranoside (**S2**): TLC (eluent: hexane/EtOAc 1:1) R_f = 0.22; ^1H NMR (CDCl_3 , 600 MHz) δ 7.92–7.82 (m, 2 H), 7.78–7.74 (m, 2 H), 7.49–7.45 (m, 6 H), 7.42–7.39 (m, 2 H), 7.36–7.32 (m, 6 H), 7.30–7.27 (m, 3 H), 7.21–7.18 (m, 2 H), 5.56 (d, J = 10.3 Hz, 1 H), 4.30 (ddd, J = 12.7, 8.6, 4.1 Hz, 1 H), 4.20 (*pseudo-t*, J = 10.3 Hz, 1 H), 3.62 (td, J = 8.8, 3.2 Hz, 1 H), 3.59–3.54 (m, 1 H), 3.53 (dd, J = 10.0, 4.0 Hz, 1 H), 3.45 (dd, J = 10.0, 4.5 Hz, 1 H), 2.50 (d, J = 3.2 Hz, 1 H), 2.36 (d, J = 4.3 Hz, 1 H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 143.6, 134.4, 134.3, 130.3, 129.1, 128.6, 128.0, 127.3, 87.1, 83.2, 78.3, 72.9, 72.7, 63.6, 56.2; HRMS (ESI) m/z calcd for $\text{C}_{39}\text{H}_{32}\text{ClKNO}_6\text{S}$; $[\text{M}+\text{K}]^+$, 716.1271, found 716.1211.

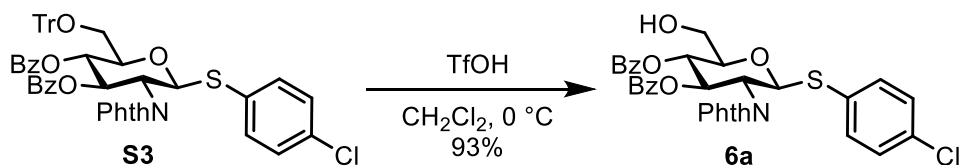
Preparation of 4-chlorophenyl-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-6-*O*-trityl-1-thio- β -D-glucopyranoside (**S3**)



To a stirred solution of **S2** (2.19 mmol, 1.48 g) in CH_2Cl_2 (25 mL) and pyridine (5.0 mL) was added benzyl chloride (BzCl) (11.0 mmol, 0.890 mL, 5.0 equiv) dropwise. The reaction was kept stirring over a period of 4 hours at 0 °C, and the progress of the reaction was checked by TLC analysis. The solution was concentrated under the reduced pressure. The mixture was diluted with in EtOAc (100 mL) and washed with 1 M HCl aqueous solution (50 mL \times 2), saturated aqueous NaHCO_3 solution (50 mL \times 2), and brine (50 mL). The organic layer was dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure to give the crude product. The crude product was purified with silica gel chromatography (hexane/EtOAc 3:1) to afford **S3** (1.45 mmol, 1.28 g, 66%) as a white solid.

4-Chlorophenyl-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-6-*O*-trityl-1-thio- β -D-glucopyranoside (**S3**): TLC (eluent: hexane/EtOAc 2:1) R_f = 0.55; ^1H NMR (CDCl_3 , 600 MHz) δ 7.92–7.88 (m, 2 H), 7.77–7.65 (m, 7 H), 7.55–7.52 (m, 2 H), 7.50–7.46 (m, 1 H), 7.44–7.40 (m, 6 H), 7.30–7.27 (m, 4 H), 7.24–7.22 (m, 2 H), 7.20–7.15 (m, 6 H), 7.14–7.12 (m, 3 H); 6.14 (dd, J = 10.3, 9.3 Hz, 1 H), 5.84 (d, J = 10.5 Hz, 1 H), 5.58 (*pseudo*-t, J = 9.8 Hz, 1 H), 4.61 (*pseudo*-t, J = 6.7 Hz, 1 H), 3.98 (ddd, J = 10.1, 5.3, 2.3 Hz, 1 H), 3.35 (dd, J = 11.0, 2.2 Hz, 1 H), 3.30 (dd, J = 10.6, 7.6 Hz, 1 H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 168.1, 167.0, 165.8, 164.8, 143.6, 134.9, 134.8, 134.4, 134.3, 133.3, 133.1, 131.7, 129.8, 129.8, 129.7, 129.2, 129.0, 128.6, 128.6, 128.3, 128.2, 127.8, 127.0, 123.8, 123.7, 86.8, 83.2, 78.2, 72.4, 69.4, 62.4, 54.0; HRMS (ESI) m/z calcd for $\text{C}_{53}\text{H}_{40}\text{ClKNO}_8\text{S}$; $[\text{M}+\text{K}]^+$, 924.1795, found 924.1733.

Preparation of 4-chlorophenyl-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-1-thio- β -D-glucopyranoside (**6a**)

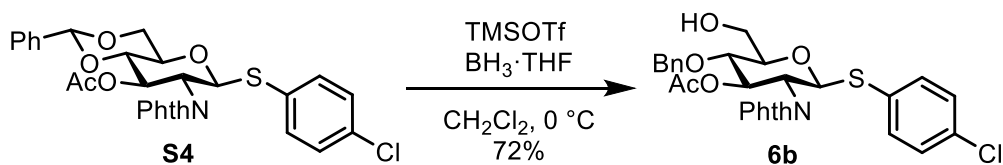


To a stirred solution of **S3** (1.49 mmol, 1.32 g) in CH_2Cl_2 (20 mL) was added trifluoromethanesulfonic acid (TfOH) dropwise (1.63 mmol, 143 μL , 1.1 equiv) at 0 °C. The reaction was kept stirring until the reaction complete (*ca.* 3 hours). The reaction was quenched with saturated aqueous NaHCO_3 solution, and the solvent was removed under the reduced pressure. The reaction mixture was dissolved in EtOAc

(50 mL) and washed with H₂O (50 mL × 3). The organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure to obtain the crude product. The crude product was purified with silica gel chromatography (hexane/EtOAc 3:1) to afford **6a** (1.38 mmol, 889 mg, 93%) as a white solid.

4-Chlorophenyl-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (**6a**): TLC (eluent: hexane/EtOAc 1:1) R_f = 0.54; ¹H NMR (CDCl₃, 600 MHz) δ 7.95–7.92 (m, 2 H), 7.92–7.87 (m, 1 H), 7.76–7.72 (m, 4 H), 7.72–7.67 (m, 1 H), 7.54–7.49 (m, 1 H), 7.45–7.35 (m, 5 H), 7.32–7.27 (m, 3 H), 7.26–7.24 (m, 1 H), 6.32 (*pseudo*-t, *J* = 9.8 Hz, 1 H), 5.85 (d, *J* = 10.7 Hz, 1 H), 5.49 (*pseudo*-t, *J* = 9.6 Hz, 1 H), 4.56 (*pseudo*-t, *J* = 10.2 Hz, 1 H) 3.95–3.85 (m, 2 H), 3.73 (dd, *J* = 8.0, 4.6 Hz, 1 H); 2.51 (*pseudo*-t, *J* = 7.9 Hz, 1 H); ¹³C NMR (CDCl₃, 150 MHz) δ 168.1, 166.9, 166.0, 165.7, 135.0, 134.8, 134.5, 134.3, 133.7, 133.4, 131.5, 131.1, 130.0, 129.7, 129.3, 129.3, 128.5, 128.5, 128.5, 128.4, 123.8, 83.1, 78.8, 71.7, 69.7, 61.5, 53.9; HRMS (ESI) *m/z* calcd for C₃₄H₂₆ClKNO₈S; [M+K]⁺, 682.0700, found 682.0688.

Preparation of 4-chlorophenyl-3-*O*-acetyl-4-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (**6b**)

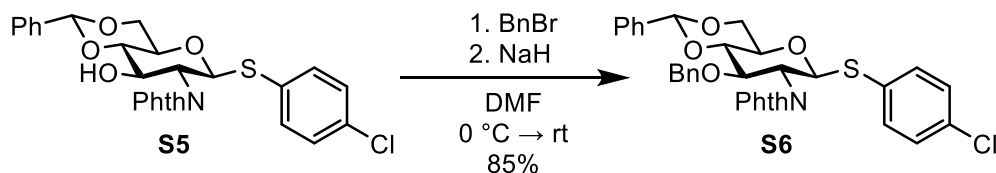


To a stirred solution of **S4**² (5.51 mmol, 3.12 g) in CH₂Cl₂ (24 mL) was added BH₃·THF (6.0 mL) at 0 °C. Then, trimethylsilyl trimethylsilyl trifluoromethanesulfonate (TMSOTf) (7.69 mmol, 1.39 mL, 1.4 equiv) was added dropwise. After 3 hours, the completion of the reaction was checked TLC analysis, and the reaction was quenched with saturated aqueous NaHCO₃ solution. Then, the solvent was removed under reduced pressure. The mixture was dissolved in EtOAc (100 mL) and washed with H₂O (100 mL × 3). The organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure to give the crude product. The crude product was purified with silica gel chromatography (hexane/EtOAc 1:1) to obtain **6b** (3.97 mmol, 2.26 g, 72%) as a white solid.

4-Chlorophenyl-3-*O*-acetyl-4-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (**6b**): TLC (eluent: hexane/EtOAc 1:1) R_f = 0.48; ¹H NMR (CDCl₃, 600 MHz) δ 7.90–7.83 (m, 2 H), 7.77–7.73 (m, 2 H), 7.35–7.31 (m, 4 H), 7.29–7.27 (m, 3 H), 7.25–7.23 (m, 2 H), 5.79 (*pseudo*-t, *J* = 9.5 Hz, 1 H), 5.74 (d, *J* = 5.3 Hz, 1 H), 4.67 (d, *J* = 11.4 Hz, 1 H), 4.64 (d, *J* = 11.5 Hz, 1 H), 4.21 (*pseudo*-t, *J* = 10.2 Hz, 1 H), 3.95 (dd, *J* = 11.6, 3.5 Hz, 1 H), 3.80–3.76 (m, 1 H), 3.76 (*pseudo*-t, *J* = 8.0 Hz, 1 H) 3.65 (m, 1 H), 1.83 (dd, *J* = 8.5, 5.5 Hz, 1 H), 1.76 (s, 3 H); ¹³C NMR (CDCl₃, 150 MHz) δ 170.1, 167.8, 167.3, 137.6, 134.7, 134.5, 134.4, 134.2, 131.6,

131.1, 129.6, 129.2, 128.5, 123.0, 127.8, 123.7, 123.6, 82.8, 79.5, 75.9, 74.8, 73.9, 61.7, 54.1, 20.5;
HRMS (ESI) m/z calcd for $C_{29}H_{26}ClKNO_7S$; $[M+K]^+$, 606.0751, found 606.0741.

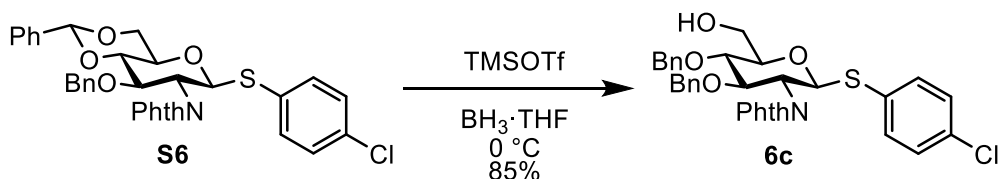
Preparation of 4-chlorophenyl-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-1-thio- β -D-glucopyranoside (**S6**)



To a stirred solution of **S5**² (1.33 mmol, 0.696 g) in DMF (15 mL) was added benzyl bromide (BnBr) (4.00 mmol, 476 μ L) at 0 °C. Then, 60% sodium hydride (NaH) (160 mg, 4.00 mmol) in DMF (4 mL) was added dropwise. The reaction was kept stirring overnight and the progress of the reaction was checked by TLC analysis. The reaction was quenched with saturated aqueous $NaHCO_3$ solution, and the solution was diluted with in EtOAc (50 mL) and washed with 1 M HCl aqueous solution (50 mL \times 2), saturated aqueous $NaHCO_3$ solution (50 mL \times 2), and brine (50 mL). The organic layer was dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure to give the crude product. The crude product was purified with silica gel chromatography (hexane/EtOAc 5:1) to afford **S6** (1.13 mmol, 0.690 g, 85%) as a white solid.

4-Chlorophenyl-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-1-thio- β -D-glucopyranoside (**S6**): TLC (eluent: hexane/EtOAc 5:1) R_f = 0.39; 1H NMR (600 MHz, $CDCl_3$) δ 7.89–7.84 (m, 1 H), 7.77–7.70 (m, 2 H), 7.66–7.60 (m, 1 H), 7.53–7.48 (m, 2 H), 7.44–7.36 (m, 3 H), 7.33–7.28 (m, 2 H), 7.24–7.20 (m, 2 H), 6.98–6.95 (m, 2 H), 6.93–6.88 (m, 1 H), 6.87–6.84 (m, 2 H), 5.63 (s, 1 H), 5.60 (d, J = 10.6 Hz, 1 H), 4.75 (d, J = 12.3 Hz, 1 H), 4.48 (d, J = 12.4 Hz, 1 H), 4.42 (dd, J = 10.5, 4.9 Hz, 1 H), 4.40 (*pseudo-t*, J = 9.3 Hz, 1 H), 4.24 (*pseudo-t*, J = 10.3 Hz, 1 H), 3.83 (*pseudo-t*, J = 10.3 Hz, 1 H), 3.77 (*pseudo-t*, J = 9.1 Hz, 1 H), 3.70 (td, J = 9.7, 4.9 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.8, 167.2, 137.7, 137.3, 134.7, 134.6, 134.1, 134.0, 131.5, 129.7, 129.1, 128.3, 128.2, 128.1, 127.5, 126.1, 123.6, 123.4, 101.4, 83.8, 82.8, 75.4, 74.3, 70.4, 68.6, 54.7; HRMS (ESI) m/z calcd for $C_{34}H_{28}ClKNO_6S$ $[M+Na]^+$, 652.0958; found, 652.0943.

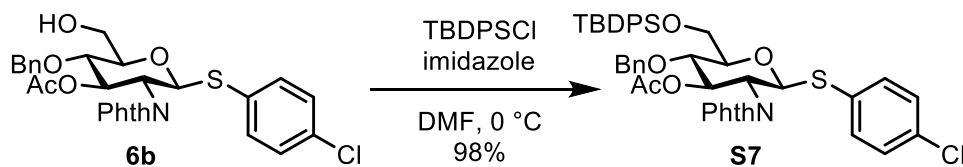
Preparation of 4-chlorophenyl-3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-*D*-glucopyranoside (**6c**)



To a stirred solution of **S6** (1.38 mmol, .849 mg) and $\text{BH}_3 \cdot \text{THF}$ (7.0 mL), TMSOTf (0.70 mL) was added dropwise at 0 °C. Then, the mixture was stirred for 4 hours at room temperature. The reaction was quenched with saturated aqueous NaHCO_3 solution, and the solution was diluted in EtOAc. The mixture was washed with saturated aqueous NaHCO_3 solution (3 times), H_2O (3 times) and brine respectively. The organic layer was dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The crude product was purified with silica gel chromatography (hexane/EtOAc 3:1) to give **6c** (1.17 mmol, 730 mg, 85%) as a white solid.

4-Chlorophenyl-3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-*D*-glucopyranoside (**6c**): TLC (eluent: hexane/EtOAc 2:1) $R_f = 0.50$; ^1H NMR (600 MHz, CDCl_3) δ 7.81–7.60 (m, 4 H), 7.37–7.32 (m, 4 H), 7.31–7.25 (m, 3 H), 7.20–7.18 (m, 2 H), 6.99–6.97 (m, 2 H), 6.89–6.82 (m, 3 H), 5.54 (d, $J = 10.5$ Hz, 1 H), 4.87 (d, $J = 10.8$ Hz, 1 H), 4.79 (d, $J = 12.3$ Hz, 1 H), 4.72 (d, $J = 10.8$ Hz, 1 H), 4.44 (d, $J = 12.3$ Hz, 1 H), 4.37 (dd, $J = 10.2, 9.0$ Hz, 1 H), 4.19 (*pseudo-t*, $J = 10.5$ Hz, 1 H), 3.93 (dd, $J = 12.3, 2.4$ Hz, 1 H), 3.76 (dd, $J = 12.3, 4.5$ Hz, 1 H), 3.72–3.68 (m, 1 H), 3.59 (dd, $J = 9.9, 2.4$ Hz, 1 H), 2.16–2.04 (m, 1 H); ^{13}C NMR (150 MHz, CDCl_3) δ 168.2, 167.5, 138.0, 137.9, 134.3, 134.2, 134.1, 133.9, 131.7, 131.5, 130.6, 129.2, 128.7, 128.3, 128.2, 128.1, 127.6, 123.6, 123.6, 83.4, 80.2, 80.0, 79.3, 77.7, 77.5, 77.3, 75.2, 75.1, 61.8, 55.1; HRMS (ESI) m/z calcd for $\text{C}_{34}\text{H}_{30}\text{ClNNaO}_6\text{S}$ $[\text{M}+\text{Na}]^+$, 638.1375; found, 638.1357.

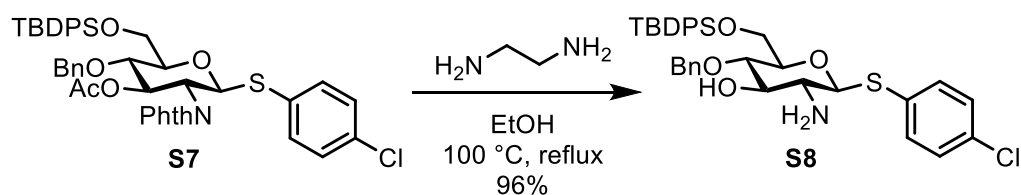
Preparation of 4-chlorophenyl-3-*O*-acetyl-4-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-1-thio-β-*D*-glucopyranoside (**S7**)



To a stirred solution of **6b** (3.61 mmol, 2.05 g) and imidazole (14.4 mmol, 1.06 g, 4.0 equiv) in DMF (15 mL) was added *tert*-butyldiphenylsilyl chloride (TBDPSCI) (10.8 mmol, 3.16 mL, 3.0 equiv) dropwise at 0 °C. The completion of the reaction was monitored by TLC analysis, and the reaction was quenched with saturated aqueous NaHCO_3 solution. The mixture was dissolved in EtOAc (100 mL) and washed with 1 M HCl aqueous solution (100 mL \times 2), saturated aqueous NaHCO_3 solution (50 mL \times 2), and brine (50 mL). The organic layer was dried over anhydrous Na_2SO_4 , filtered and

concentrated under reduced pressure to give the crude product. The crude product was purified with silica gel chromatography (hexane/EtOAc 5:1) to afford **S7** (3.52 mmol, 2.84 g, 98%) as a white solid. 4-Chlorophenyl-3-*O*-acetyl-4-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-1-thio- β -D-glucopyranoside (**S7**): TLC (eluent: hexane/EtOAc 3:1) R_f = 0.47; ^1H NMR (CDCl_3 , 600 MHz) δ 7.90–7.85 (m, 2 H), 7.80–7.77 (m, 2 H), 7.76–7.74 (m, 2 H), 7.72–7.69 (m, 2 H), 7.46–7.43 (m, 2 H), 7.40–7.35 (m, 6 H), 7.26–7.23 (m, 3 H), 7.15–7.10 (m, 4 H), 5.80 (*pseudo*-t, J = 9.5 Hz, 1 H), 5.71 (d, J = 10.4 Hz, 1 H), 4.68 (d, J = 11.6 Hz, 1 H), 4.63 (d, J = 11.6 Hz, 1 H), 4.26 (*pseudo*-t, J = 10.3 Hz, 1 H), 4.05–4.01 (m, 1 H), 3.97 (dd, J = 11.7, 2.8 Hz, 1 H), 3.93 (*pseudo*-t, J = 9.5 Hz, 1 H), 3.65 (dd, J = 10.1, 1.3 Hz, 1 H), 1.76 (s, 3 H), 1.12 (s, 9 H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 170.2, 167.9, 167.4, 137.9, 135.9, 135.6, 134.5, 134.4, 134.3, 134.2, 133.3, 132.8, 131.8, 131.2, 130.0, 129.8, 129.1, 128.5, 127.83, 127.79, 127.76, 127.5, 123.7, 123.6, 82.7, 80.1, 76.2, 74.9, 74.2, 62.5, 54.2, 26.9, 20.6, 19.4; HRMS (ESI) m/z calcd for $\text{C}_{45}\text{H}_{44}\text{ClKNO}_7\text{SSi}$; $[\text{M}+\text{K}]^+$, 844.1928, found 844.1914.

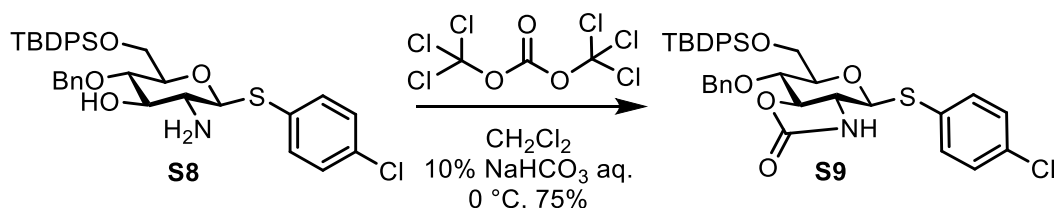
Preparation of 4-chlorophenyl-2-amino-4-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-1-thio- β -D-glucopyranoside (**S8**)



To a stirred solution of **S7** (3.82 mmol, 3.07 g) in ethanol (30 mL) was added ethylenediamine anhydrous (6.4 mL) at room temperature. The reaction temperature was gradually raised from room temperature to 100 °C and kept stirring. The progress of the reaction was checked by TLC analysis, and heating was halted in 3 hours. The solvent was removed under the reduced pressure, and the mixture was purified with silica gel chromatography (hexane/EtOAc 1:3 + 1% Et_3N) to obtain **S8** (3.65 mmol, 2.31 g, 96%) as a white solid.

4-Chlorophenyl-2-amino-4-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-1-thio- β -D-glucopyranoside (**S8**): TLC (eluent: hexane/EtOAc 1:3) R_f = 0.38; ^1H NMR (CDCl_3 , 600 MHz) δ 7.79–7.76 (m, 2 H), 7.73–7.70 (m, 2 H), 7.51–7.48 (m, 2 H), 7.45–7.40 (m, 2 H), 7.37–7.33 (m, 4 H), 7.32–7.27 (m, 3 H), 7.25–7.22 (m, 2 H), 7.17–7.13 (m, 2 H), 4.80 (d, J = 11.2 Hz, 1 H), 4.71 (d, J = 11.2 Hz, 1 H), 4.40 (d, J = 9.9 Hz, 1 H), 4.03–3.99 (m, 1 H), 3.95 (dd, J = 11.2, 3.9 Hz, 1 H), 3.64 (*pseudo*-t, J = 9.3 Hz, 1 H), 3.48 (*pseudo*-t, J = 9.2 Hz, 1 H), 3.41 (dd, J = 9.8, 2.5 Hz, 1 H), 2.69 (*pseudo*-t, J = 9.6 Hz, 1 H), 1.10 (s, 9 H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 138.3, 135.9, 135.6, 134.0, 133.6, 133.4, 133.0, 131.2, 129.8, 129.7, 129.1, 128.6, 127.9, 127.9, 127.8, 127.7, 89.3, 80.0, 78.3, 77.5, 74.8, 62.9, 56.1, 26.9, 19.4; HRMS (ESI) m/z calcd for $\text{C}_{35}\text{H}_{40}\text{ClINNaO}_4\text{SSi}$; $[\text{M}+\text{Na}]^+$, 656.2029, found 656.2006.

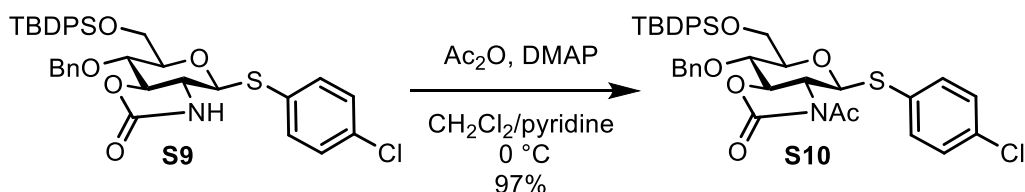
Preparation of 4-chlorophenyl-4-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-2,3-*N,O*-carbonyl-2-deoxy-1-thio- β -D-glucopyranoside (**S9**)



To a stirred solution of **S8** (3.59 mmol, 2.28 g) in CH_2Cl_2 (50 mL) and 10% aqueous NaHCO_3 solution was added triphosgene (1.38 mmol, 408 mg, 0.383 equiv) at room temperature. The reaction was kept stirring for overnight. The completion of the reaction was checked by TLC analysis, then the solution was extracted with CH_2Cl_2 (50 mL \times 3). The organic layer was dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure. The crude product was purified with silica gel chromatography (hexane/EtOAc = 5:1) to obtain **S9** (2.69 mmol, 1.78 g, 75%) as a white solid.

4-Chlorophenyl-4-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-2,3-*N,O*-carbonyl-2-deoxy-1-thio- β -D-glucopyranoside (**S9**): TLC (eluent: hexane/EtOAc 3:1) R_f = 0.46; ^1H NMR (CDCl_3 , 600 MHz) δ 7.75–7.72 (m, 2 H), 7.71–7.68 (m, 2 H), 7.50–7.47 (m, 2 H), 7.45–7.42 (m, 2 H), 7.38–7.33 (m, 4 H), 7.30–7.28 (m, 3 H), 7.25–7.18 (m, 4 H), 5.00 (s, 1 H), 4.88 (d, J = 10.5 Hz, 1 H), 4.73 (d, J = 11.2 Hz, 1 H), 4.57 (d, J = 11.0 Hz, 1 H), 4.28 (*pseudo*-t, J = 10.4 Hz, 1 H), 4.04 (*pseudo*-t, J = 9.4 Hz, 1 H), 4.00–3.7 (m, 2 H), 3.56 (dd, J = 8.7, 3.0 Hz, 1 H), 3.44 (*pseudo*-t, J = 10.6 Hz, 1 H) 1.07 (s, 9 H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 159.0, 137.2, 135.7, 135.6, 135.1, 134.6, 133.2, 133.0, 129.8, 129.4, 129.1, 128.5, 128.0, 128.0, 127.8, 127.8, 85.4, 84.2, 81.3, 73.5, 73.2, 62.4, 58.5, 26.8, 19.4; HRMS (ESI) m/z calcd for $\text{C}_{36}\text{H}_{38}\text{ClKNO}_5\text{SSi}$; $[\text{M}+\text{K}]^+$, 698.1561, found 698.1538.

Preparation of 4-chlorophenyl-2-acetamido-4-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-2,3-*N,O*-carbonyl-2-deoxy-1-thio- β -D-glucopyranoside (**S10**)

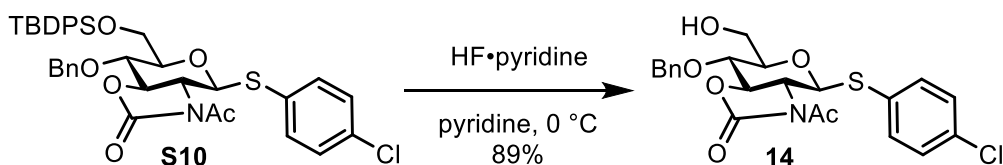


To a stirred solution of **S9** (2.54 mmol, 1.68 g) and 4-dimethylaminopyridine (DMAP) (1.27 mmol, 154 mg, 0.5 equiv) in CH_2Cl_2 (15 mL) and pyridine (3.0 mL) was added acetic anhydride (5.0 mL) at 0 °C. The reaction was monitored by TLC analysis and quenched with methanol after the completion (*ca.* 2 hours). The solvent was removed under reduced pressure. The mixture was diluted with in EtOAc (50 mL) and washed with 1 M HCl aqueous solution (50 mL \times 3), saturated aqueous NaHCO_3 solution (50 mL \times 3), and brine (50 mL). The organic layer was dried over anhydrous Na_2SO_4 , filtered

and concentrated under reduced pressure to give the purified product **S10** (2.46 mmol, 1.72 g, 97%) as a white solid.

4-Chlorophenyl-2-acetamido-4-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-2,3-*N,O*-carbonyl-2-deoxy-1-thio- β -D-glucopyranoside (**S10**): TLC (eluent: hexane/EtOAc 3:1) R_f = 0.67; ^1H NMR (CDCl_3 , 600 MHz) δ 7.75–7.70 (m, 2 H), 7.68–7.65 (m, 2H), 7.45–7.40 (m, 4 H), 7.39–7.34 (m, 4 H), 7.31–7.28 (m, 3 H), 7.25–7.20 (m, 2 H), 7.16–7.13 (m, 2 H), 4.88 (d, J = 11.2 Hz, 1 H), 4.82 (d, J = 8.5 Hz, 1 H), 4.60 (d, J = 11.5 Hz, 1 H), 4.27 (*pseudo*-t, J = 10.6 Hz, 1 H), 4.11–4.95 (m, 2 H), 3.92 (dd, J = 11.4, 4.2 Hz, 1 H), 3.88–3.84 (m, 1 H), 3.49 (dd, J = 8.2, 2.3 Hz, 1 H), 2.60 (s, 3 H), 1.05 (s, 9 H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 173.2, 154.0, 137.0, 135.8, 135.6, 134.1, 133.6, 133.2, 132.8, 132.7, 129.9, 129.8, 129.0, 128.5, 128.1, 128.0, 127.8, 127.8, 87.0, 82.8, 81.2, 74.0, 73.6, 62.5, 59.8, 26.9, 24.9, 19.3; HRMS (ESI) m/z calcd for $\text{C}_{38}\text{H}_{40}\text{ClKNO}_6\text{SSi}$; $[\text{M}+\text{K}]^+$, 740.1666, found 740.1654.

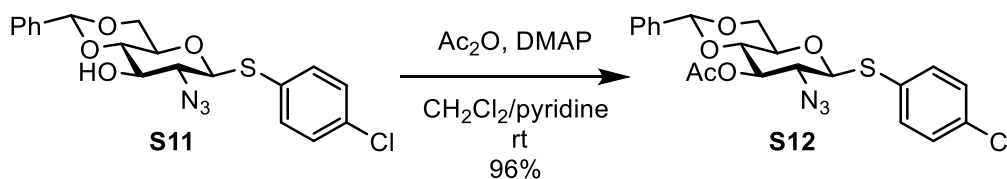
Preparation of 4-chlorophenyl-2-acetamido-4-*O*-benzyl-2,3-*N,O*-carbonyl-2-deoxy-1-thio- β -D-glucopyranoside (**14**)



To a stirred solution of **S10** (2.32 mmol, 1.63 g) in pyridine (20 mL) was added HF/pyridine (19.2 mmol, 2.53 mL, 8.3 equiv) dropwise at 0 °C. The reaction was monitored by TLC analysis and quenched with saturated aqueous NaHCO_3 solution when the reaction completed. The mixture was diluted with in EtOAc (50 mL) and washed with 1 M HCl aqueous solution (50 mL \times 3), saturated aqueous NaHCO_3 solution (50 mL \times 3), and brine (50 mL). The organic layer was dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure to obtain the crude product. The crude product was purified with silica gel chromatography to afford **14** (2.07 mmol, 963 mg, 89%) as a white solid.

4-Chlorophenyl-2-acetamido-4-*O*-benzyl-2,3-*N,O*-carbonyl-2-deoxy-1-thio- β -D-glucopyranoside (**14**): TLC (eluent: hexane/EtOAc 3:1) R_f = 0.36; ^1H NMR (CDCl_3 , 600 MHz) δ 7.43–7.40 (m, 2 H), 7.39–7.35 (m, 2 H), 7.35–7.30 (m, 3 H), 7.30–7.27 (m, 2 H), 4.894 (d, J = 11.0 Hz, 1 H), 4.892 (d, J = 8.6 Hz, 1 H), 4.63 (d, J = 11.4 Hz, 1 H), 4.38 (*pseudo*-t, J = 10.7 Hz, 1 H), 4.03 (dd, J = 11.3, 8.8 Hz, 1 H), 3.93 (*pseudo*-t, J = 9.3 Hz, 1 H), 3.82 (ddd, J = 11.5, 6.4, 2.2 Hz, 1 H), 3.72 (ddd, J = 13.7, 7.7, 4.5 Hz, 1 H), 3.52–3.46 (m, 1 H), 2.59 (s, 3 H), 1.84 (*pseudo*-t, J = 7.0 Hz, 1 H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 173.1, 153.7, 136.9, 134.4, 133.5, 132.1, 129.2, 128.6, 128.3, 128.1, 86.7, 82.5, 80.7, 73.7, 73.5, 61.5, 59.8, 24.8; HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{22}\text{ClKNO}_6\text{S}$; $[\text{M}+\text{K}]^+$, 502.0488, found 502.0474.

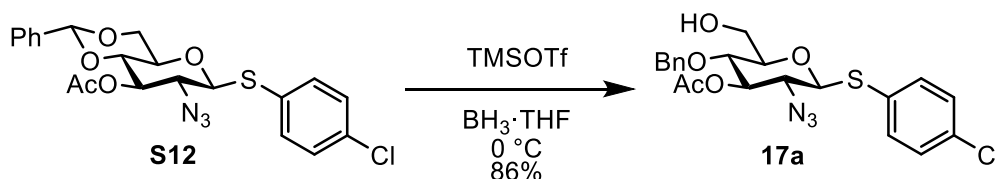
Preparation of 4-chlorophenyl-3-*O*-acetyl-2-azido-4,6-*O*-benzylidene-2-deoxy-1-thio-β-*D*-glucopyranoside (**S12**)



To a stirred solution of **S11**³ (6.45 mmol, 2.70 g) and DMAP (84 mg) in CH₂Cl₂ (24 mL) and pyridine (7.0 mL), acetic anhydride (4.0 mL) was added dropwise. Then, the mixture was stirred overnight at room temperature. The reaction was quenched with 1 M HCl aqueous solution, and the mixture was diluted in EtOAc, and the organic solution was washed with 1 M HCl aqueous solution (3 times), saturated aqueous NaHCO₃ solution (3 times), H₂O (3 times), and brine respectively. The organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified with silica gel chromatography (hexane/EtOAc 4:1) to afford **S12** (6.20 mmol, 2.89 g, 96%) as a white solid.

4-Chlorophenyl-3-*O*-acetyl-2-azido-4,6-*O*-benzylidene-2-deoxy-1-thio-β-*D*-glucopyranoside (**S12**): TLC (eluent: hexane/EtOAc 3:1) *R*_f = 0.50; ¹H NMR (600 MHz, CDCl₃) δ 7.50–7.48 (m, 2 H), 7.44–7.30 (m, 7 H), 5.45 (s, 1 H), 5.27 (*pseudo-t*, *J* = 9.6 Hz, 1 H), 4.55 (d, *J* = 10.2 Hz, 1 H), 4.32 (dd, *J* = 10.5, 4.8 Hz, 1 H), 3.72 (*pseudo-t*, *J* = 10.2 Hz, 1 H), 3.51 (*pseudo-t*, *J* = 9.6 Hz, 1 H), 3.46 (td, *J* = 9.6, 4.8, Hz, 1 H), 3.40 (*pseudo-t*, *J* = 9.9 Hz, 1 H), 2.10 (s, 3 H); ¹³C NMR (150 MHz, CDCl₃) δ 169.6, 137.0, 135.2, 135.2, 129.5, 129.3, 128.4, 126.3, 101.5, 86.6, 78.3, 77.7, 77.5, 77.3, 73.0, 70.7, 68.3, 63.6, 20.9; HRMS (ESI) *m/z* calcd for C₂₁H₂₀ClKN₃O₅S [M+K]⁺, 500.0444; found, 500.0425.

Preparation of 4-chlorophenyl-3-*O*-acetyl-2-azido-4-*O*-benzyl-2-deoxy-1-thio-β-*D*-glucopyranoside (**17a**)

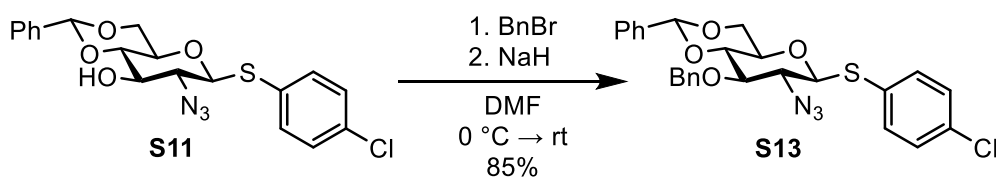


To a stirred solution of **S12** (1.37 mmol, 0.630 g), and BH₃·THF (7.0 mL), TMSOTf (0.70 mL) was added dropwise at 0 °C. Then, the mixture was stirred for 4 hours at room temperature. The reaction was quenched with saturated aqueous NaHCO₃ solution. The mixture was diluted in EtOAc, and the organic solution was washed with saturated aqueous NaHCO₃ solution (3 times), H₂O (3 times) and brine respectively. The organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified with silica gel chromatography (hexane/EtOAc 5:1) to afford **17a** (1.19 mmol, 0.550 g, 86%) as a white solid.

4-Chlorophenyl-3-*O*-acetyl-2-azido-4-*O*-benzyl-2-deoxy-1-thio-β-*D*-glucopyranoside (**17a**): TLC

(eluent: hexane/EtOAc 2:1) R_f = 0.47; ^1H NMR (600 MHz, CDCl_3) δ 7.49–7.46 (m, 2 H), 7.34–7.28 (m, 5 H), 7.26–7.24 (m, 2 H), 5.15 (*pseudo*-t, J = 9.6 Hz, 1 H), 4.61 (d, J = 11.4 Hz, 1 H), 4.56 (d, J = 11.4 Hz, 1 H), 4.49 (d, J = 10.2 Hz, 1 H), 3.89 (ddd, J = 12.3, 5.4, 2.4 Hz, 1 H), 3.74–3.70 (m, 1 H), 3.57 (*pseudo*-t, J = 9.6 Hz, 1 H), 3.41 (ddd, J = 9.9, 3.9, 2.7 Hz, 1 H), 3.26 (*pseudo*-t, J = 9.9 Hz, 1 H), 2.00 (s, 3 H), 1.88 (dd, J = 8.0, 5.2 Hz, 1 H); ^{13}C NMR (150 MHz, CDCl_3) δ 169.9, 137.4, 135.2, 135.0, 129.5, 129.4, 128.7, 128.2, 128.1, 86.1, 79.7, 77.3, 77.1, 76.9, 75.9, 75.1, 74.8, 63.4, 61.6, 20.9; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{22}\text{ClNaN}_3\text{O}_5\text{S}$ $[\text{M}+\text{Na}]^+$, 486.0861; found, 486.0842.

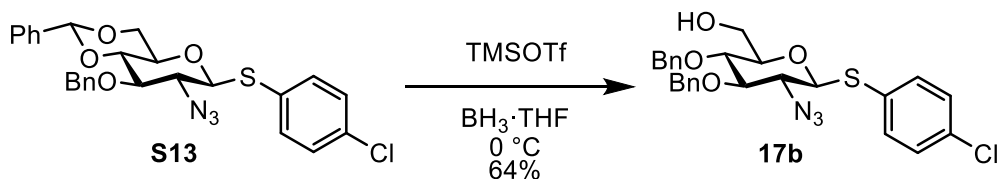
Preparation of 4-chlorophenyl-2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-1-thio- β -D-glucopyranoside (**S13**)



To a stirred solution of **S11**³ (2.40 mmol, 1.01 g) in DMF (20 mL) was added 60% NaH (4.80 mmol, 192 mg) at 0 °C. Then, BnBr (3.60 mmol, 450 μL) was added dropwise, and the reaction was kept stirring overnight. The progress of the reaction was monitored by TLC analysis, and the reaction was quenched with saturated aqueous NaHCO_3 solution. The solution was diluted with in EtOAc (100 mL) and washed with 1 M HCl aqueous solution (50 mL \times 2), saturated aqueous NaHCO_3 solution (50 mL \times 2), and brine (50 mL). The organic layer was dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure to give the crude product. The crude product was purified with silica gel chromatography (hexane/EtOAc 8:1) to afford **S13** (2.06 mmol, 1.05 g, 86%) as a white solid.

4-Chlorophenyl-2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-1-thio- β -D-glucopyranoside (**S13**): TLC (eluent: hexane/EtOAc 8:1) R_f = 0.46; ^1H NMR (600 MHz, CDCl_3) δ 7.51–7.46 (m, 4 H), 7.40–7.37 (m, 3 H), 7.36–7.29 (m, 7 H), 5.57 (s, 1 H), 4.91 (d, J = 11.0 Hz, 1 H), 4.78 (d, J = 11.0 Hz, 1 H), 4.44 (d, J = 10.1 Hz, 1 H), 4.38 (dd, J = 10.6, 5.0 Hz, 1 H), 3.77 (*pseudo*-t, J = 10.3 Hz, 1 H), 3.66 (*pseudo*-t, J = 9.1 Hz, 1 H), 3.63 (*pseudo*-t, J = 9.2 Hz, 1 H), 3.48–3.42 (m, 1 H), 3.33 (*pseudo*-t, J = 9.3 Hz, 1 H); ^{13}C NMR (150 MHz, CDCl_3) δ 137.5, 137.0, 135.4, 135.3, 129.4, 129.2, 129.0, 128.5, 128.4, 128.1, 126.0, 101.3, 86.5, 81.3, 80.9, 76.9, 75.2, 70.6, 68.5, 64.7; HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{24}\text{ClKN}_3\text{O}_6\text{S}$ $[\text{M}+\text{Na}]^+$, 548.0808; found, 548.0817.

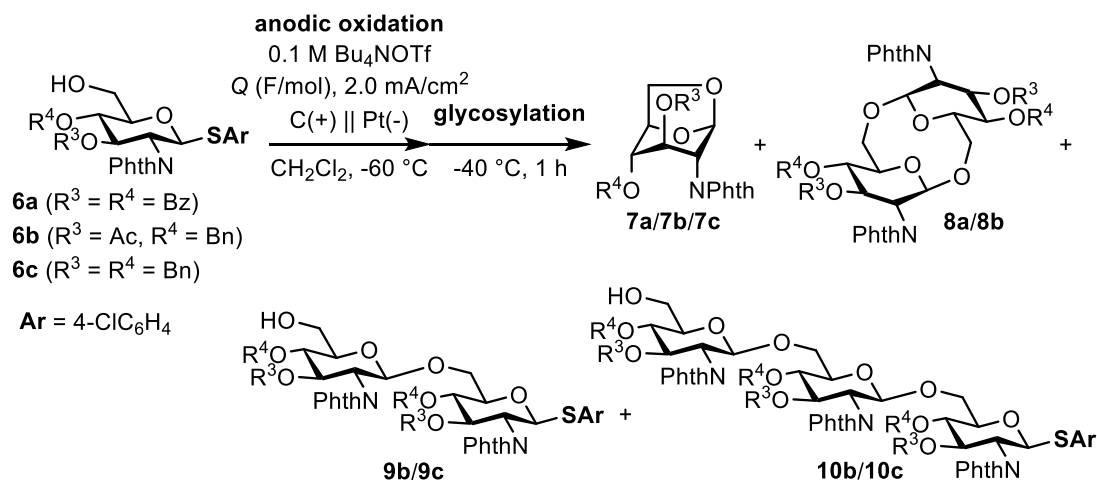
Preparation of 4-chlorophenyl-2-azido-3,4-di-*O*-benzyl-2-deoxy-1-thio-β-*D*-glucopyranoside (**17b**)



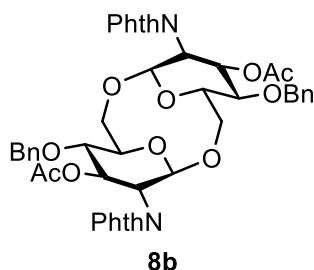
To a stirred solution of **S13** (2.31 mmol, 1.18 g), and $\text{BH}_3 \cdot \text{THF}$ (12 mL), TMSOTf (1.2 mL) was added dropwise at 0 °C. Then, the mixture was stirred for 6 hours at room temperature. The reaction was quenched with saturated aqueous NaHCO_3 solution, and the reaction mixture diluted with in EtOAc. The solution was washed with saturated aqueous NaHCO_3 solution (3 times), H_2O (3 times) and brine respectively. The organic layer was dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The crude product was purified with silica gel chromatography (hexane/EtOAc 5:1) to obtain **1d** (1.47 mmol, 0.750 g, 64%) as a white solid.

4-Chlorophenyl-2-azido-3,4-di-*O*-benzyl-2-deoxy-1-thio-β-*D*-glucopyranoside (**17b**): TLC (eluent: hexane/EtOAc 3:1) $R_f = 0.40$; ^1H NMR (600 MHz, CDCl_3) δ 7.48–7.46 (m, 2 H), 7.36–7.27 (m, 12 H), 4.87 (d, $J = 10.6$ Hz, 1 H), 4.86 (d, $J = 10.6$ Hz, 1 H), 4.84–4.82 (m, 1 H), 4.64 (d, $J = 11.1$ Hz, 1 H), 4.41 (d, $J = 10.2$ Hz, 1 H), 3.87 (dd, $J = 6.0, 2.7$ Hz, 1 H), 3.71–3.67 (m, 1 H), 3.55–3.50 (m, 2 H), 3.36 (dd, $J = 4.8, 2.7$ Hz, 1 H), 3.30 (ddd, $J = 10.2, 6.6, 2.7$ Hz, 1 H), 1.82 (*pseudo-t*, $J = 6.9$ Hz, 1 H); ^{13}C NMR (150 MHz, CDCl_3) δ 137.6, 137.5, 135.1, 134.9, 129.6, 129.4, 128.69, 128.65, 128.32, 128.21, 128.19, 128.12, 86.1, 84.9, 79.8, 76.0, 75.2, 65.3, 61.9; HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{26}\text{ClNaN}_3\text{O}_4\text{S} [\text{M}+\text{Na}]^+$, 534.1225; found, 534.1211.

3. General procedure for cyclic oligoglucosamine synthesis with phthalimide group

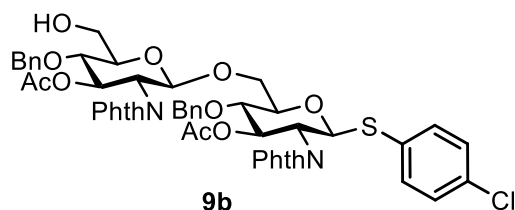


The electrochemical one-pot synthesis of cyclic oligosaccharides **8** and linear oligosaccharides **9** and **10** was conducted with an H-type divided cell (4G glass filter). The cell had a carbon felt anode (Nippon Carbon JF-20-p7) and platinum square plate (20 mm × 20 mm). Building block **6** (0.400 mmol), Bu₄NOTf (1.00 mmol), and CH₂Cl₂ (10 mL) were added to the anodic chamber. TfOH (0.400 mmol), Bu₄NOTf (1.00 mmol), and CH₂Cl₂ (10 mL) were added to the cathodic chamber. As the initiation phase of reaction, the constant current (8.0 mA (current density: 2.0 mA/cm²), (electrode distance: 4.5 cm)) was employed at -60 °C with magnetic stirring until electricity was consumed. After the electrolysis, the reaction temperature was raised from -60 °C to -40 °C as glycosylation phase. After glycosylation, Et₃N (0.5 mL) was added to both of the chambers. The mixture was collected, and the solvent was removed under reduced pressure. The mixture was dissolved in EtOAc and washed with H₂O to remove electrolyte. The solution was dried over anhydrous Na₂SO₄, filtered, and removed under reduced pressure. The crude product was purified with preparative GPC to afford 1,6-anhydrosugar **7**,⁴⁻⁶ cyclic oligosaccharides **8**⁷ and linear oligosaccharides **9** and **10**.

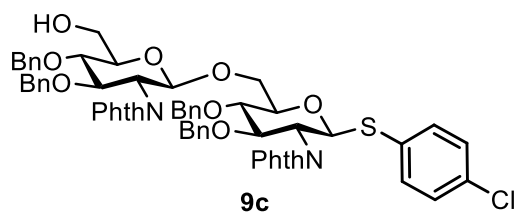


Building block **6b** (226 mg, 0.400 mmol) afforded **8b** as in 7% isolated yield (11 mg, 0.0130 mmol). Cyclobis[(1→6)-3-*O*-acetyl-4-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl] (**8b**): TLC (hexane/EtOAc 1:1) R_f = 0.25; ¹H NMR (600 MHz, CDCl₃) δ 7.87–7.86 (m, 2 H), 7.74–7.72 (m, 2 H), 7.39–7.38 (m, 1 H), 7.32–7.26 (m, 4 H), 5.70 (dd, *J* = 10.8, 8.7 Hz, 1 H), 4.93 (d, *J* = 1.8 Hz, 1 H),

4.78 (d, $J = 11.7$ Hz, 1 H), 4.70 (d, $J = 11.7$ Hz, 1 H), 4.48–4.45 (m, 2 H), 4.16–4.14 (m, 1 H), 3.88 (dd, $J = 12.0, 2.7$ Hz, 1 H), 3.80 (d, $J = 11.7$ Hz, 1 H), 1.90 (s, 3 H); ^{13}C NMR (150 MHz, CDCl_3) δ 170.5, 167.7, 138.3, 134.4, 131.7, 129.4, 128.5, 127.9, 123.7, 100.1, 77.4, 75.0, 73.4, 71.8, 68.3, 57.7, 20.9; HRMS (ESI) m/z calcd for $\text{C}_{46}\text{H}_{42}\text{KN}_2\text{O}_{14}$ $[\text{M}+\text{K}]^+$, 885.2268; found, 885.2217.

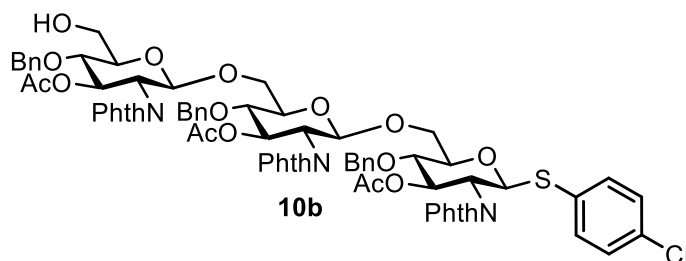


Building block **6b** (226 mg, 0.400 mmol) afforded **9b** as in 13% isolated yield (25 mg, 0.0253 mmol). 4-Chlorophenyl-(3-*O*-acetyl-4-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 \rightarrow 6)-3-*O*-acetyl-4-*O*-benzyl-2-deoxy-2-phthalimido-1-thio- β -D-glucopyranoside (**9b**): TLC (hexane/EtOAc 1:1) $R_f = 0.33$; ^1H NMR (600 MHz, CDCl_3) δ 7.81–7.70 (m, 7 H), 7.61–7.58 (m, 2 H), 7.34–7.30 (m, 3 H), 7.29–7.27 (m, 4 H), 7.25–7.20 (m, 4 H), 7.02–7.01 (m, 2 H), 5.79 (dd, $J = 10.5, 9.0$ Hz, 1 H), 5.66 (dd, $J = 10.2, 9.0$ Hz, 1 H), 5.56 (d, $J = 10.5$ Hz, 1 H), 5.53 (d, $J = 8.4$ Hz, 1 H), 4.69 (d, $J = 11.4$ Hz, 1 H), 4.61 (d, $J = 11.5$ Hz, 1 H), 4.36 (d, $J = 11.5$ Hz, 1 H), 4.32 (d, $J = 11.3$ Hz, 1 H), 4.28 (dd, $J = 10.8, 8.4$ Hz, 1 H), 4.10 (*pseudo-t*, $J = 10.5$ Hz, 1 H), 4.05 (dd, $J = 11.1, 1.5$ Hz, 1 H), 3.95 (dd, $J = 12.2, 2.6$ Hz, 1 H), 3.84–3.78 (m, 2 H), 3.76 (dd, $J = 11.2, 4.9$ Hz, 1 H), 3.67–3.62 (m, 2 H), 3.52 (*pseudo-t*, $J = 9.6$ Hz, 1 H), 2.12–2.05 (m, 1 H), 1.79 (s, 3 H), 1.66 (s, 3 H); ^{13}C NMR (150 MHz, CDCl_3) δ 170.3, 170.1, 167.8, 167.3, 137.8, 137.5, 134.6, 134.5, 134.4, 134.3, 131.7, 131.2, 129.8, 129.2, 128.6, 128.5, 128.1, 127.9, 127.9, 127.5, 123.8, 123.7, 123.6, 123.6, 107.4, 98.3, 82.6, 78.5, 77.3, 77.1, 76.9, 76.6, 76.4, 75.4, 74.8, 74.7, 73.9, 73.2, 68.5, 61.8, 55.2, 53.9, 29.8, 20.7, 20.5; HRMS (ESI) m/z calcd for $\text{C}_{52}\text{H}_{47}\text{ClKN}_2\text{O}_{14}\text{S}$ $[\text{M}+\text{K}]^+$, 1029.2068; found, 1029.2040.

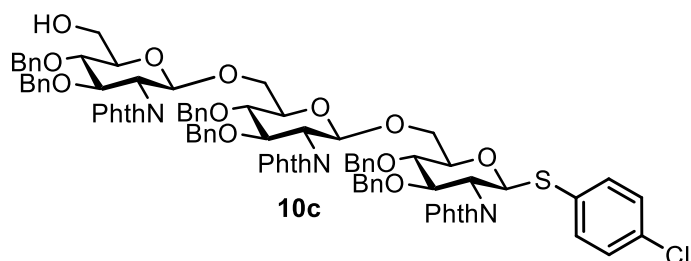


Building block **6c** (246 mg, 0.400 mmol) afforded **9c** in 4% isolated yield (8.0 mg, 6.84 μmol). 4-Chlorophenyl-(3,4-di-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 \rightarrow 6)-3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio- β -D-glucopyranoside (**9c**): TLC (hexane/EtOAc 2:1) $R_f = 0.23$. ^1H NMR (600 MHz, CDCl_3) δ 7.76–7.62 (m, 4H), 7.56–7.48 (m, 3H), 7.36–7.33 (m, 4H), 7.32–7.28

(m, 1H), 7.24–7.17 (m, 6H), 7.09–7.07 (m, 2H), 7.00–6.99 (m, 2 H), 6.89–6.84 (m, 5H), 6.84–6.78 (m, 5H), 5.31 (d, $J = 10.5$ Hz, 1 H), 5.28 (d, $J = 8.4$ Hz, 1 H), 4.89 (d, $J = 10.8$ Hz, 1 H), 4.81 (d, $J = 12.3$ Hz, 1 H), 4.74 (d, $J = 11.1$ Hz, 1 H), 4.64 (d, $J = 12.3$ Hz, 1 H), 4.52 (d, $J = 10.8$ Hz, 1 H), 4.45 (d, $J = 12.3$ Hz, 1 H), 4.37–4.33 (m, 2 H), 4.28 (d, $J = 12.3$ Hz, 1 H), 4.21 (dd, $J = 10.8, 8.7$ Hz, 2 H), 4.03 (*pseudo-t*, $J = 10.5$ Hz, 1 H), 3.99 (dd, $J = 10.8, 1.5$ Hz, 1 H), 3.91 (d, $J = 10.2$ Hz, 1 H), 3.78–3.72 (m, 2 H), 3.67 (dd, $J = 11.1, 5.1$ Hz, 1 H), 3.56–3.51 (m, 2 H), 3.44–3.40 (m, 1 H), 2.09–2.07 (m, 1 H); ^{13}C NMR (150 MHz, CDCl_3) δ 167.23, 167.21, 138.0, 137.9, 137.7, 137.5, 134.3, 134.0, 133.98, 133.97, 133.95, 133.9, 131.5, 131.49, 130.2, 129.1, 128.7, 128.6, 128.5, 128.4, 128.2, 128.15, 128.1, 128.07, 128.04, 128.01, 127.96, 127.5, 123.5, 123.48, 123.45, 123.4, 98.4, 82.9, 80.1, 79.6, 79.2, 79.1, 78.6, 75.5, 75.2, 75.0, 68.2, 62.0, 55.8, 54.6, 29.8; HRMS (ESI) m/z calcd for $\text{C}_{62}\text{H}_{55}\text{ClNaN}_2\text{O}_{12}\text{S}$ $[\text{M}+\text{Na}]^+$, 1109.3056; found, 1109.3041.



Building block **6b** (226 mg, 0.400 mmol) afforded **10b** in 6% isolated yield (11 mg, 7.80 μmol). 4-Chlorophenyl-(3-*O*-acetyl-4-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 \rightarrow 6)-(3-*O*-acetyl-4-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 \rightarrow 6)-(3-*O*-acetyl-4-*O*-benzyl-2-deoxy-2-phthalimido-1-thio- β -D-glucopyranoside (**10b**): TLC (hexane/EtOAc 1:1) $R_f = 0.23$; ^1H NMR (600 MHz, CDCl_3) δ 7.85–7.80 (m, 2 H), 7.76–7.68 (m, 6 H), 7.62–7.57 (m, 4 H), 7.31–7.26 (m, 7 H), 7.24–7.22 (m, 2 H), 7.21–7.18 (m, 6 H), 7.02–6.96 (m, 4 H), 5.78 (dd, $J = 10.8, 9.0$ Hz, 1 H), 5.66–5.62 (m, 2 H), 5.55 (d, $J = 8.4$ Hz, 1 H), 5.54 (d, $J = 10.5$ Hz, 1 H), 5.45 (d, $J = 8.4$ Hz, 1 H), 4.67 (d, $J = 11.7$ Hz, 1 H), 4.61 (d, $J = 11.7$ Hz, 1 H), 4.36–4.30 (m, 3 H), 4.28 (d, $J = 11.2$ Hz, 1 H), 4.24 (d, $J = 11.3$ Hz, 1 H), 4.21 (dd, $J = 10.7, 8.5$ Hz, 1 H), 4.13–4.09 (m, 1 H), 4.06–4.01 (m, 2 H), 3.96 (ddd, $J = 12.1, 4.9, 2.2$ Hz, 1 H), 3.87 (dd, $J = 11.4, 4.2$ Hz, 1 H), 3.80–3.75 (m, 2 H), 3.70 (dd, $J = 11.4, 4.8$ Hz, 1 H), 3.67–3.64 (m, 2 H), 3.63–3.57 (m, 2 H), 3.45 (*pseudo-t*, $J = 9.6$ Hz, 1 H), 2.32 (dd, $J = 8.5, 5.2$ Hz, 1 H), 1.76 (s, 3 H), 1.70 (s, 3 H), 1.62 (s, 3 H); ^{13}C NMR (150 MHz, CDCl_3) δ 170.3, 170.1, 167.9, 167.3, 137.9, 137.6, 134.9, 134.7, 134.5, 134.3, 134.2, 134.1, 131.8, 131.2, 129.3, 128.6, 128.5, 128.4, 128.4, 127.9, 127.8, 127.6, 127.5, 123.8, 123.7, 123.6, 98.2, 82.0, 78.3, 76.7, 76.5, 76.4, 75.5, 74.8, 74.7, 74.66, 74.65, 73.8, 73.3, 73.25, 73.2, 68.2, 68.16, 61.6, 60.5, 55.3, 55.0, 31.7, 22.7, 21.2, 20.7, 20.6, 20.5, 14.3, 14.2; HRMS (ESI) m/z calculated for $\text{C}_{75}\text{H}_{68}\text{ClNaN}_3\text{O}_{21}\text{S}$ $[\text{M}+\text{Na}]^+$, 1436.3647; found, 1436.3628.

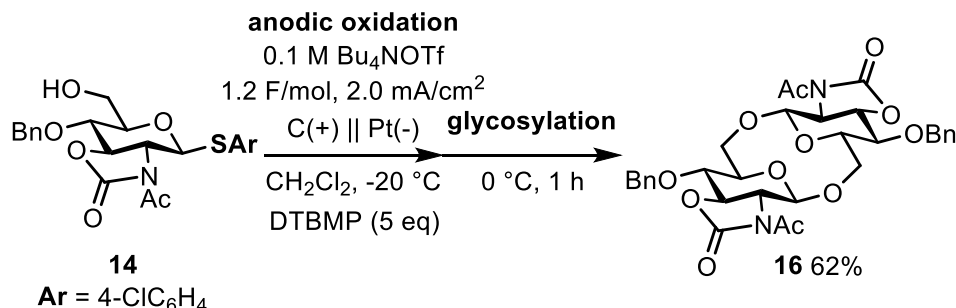


Building block **6c** (246 mg, 0.40 mmol) afforded **10c** in 2% isolated yield (5.0 mg, 3.21 μ mol).

4-Chlorophenyl-(3,4-di-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 \rightarrow 6)-(3,4-di-*O*-benzyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-(1 \rightarrow 6)-3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio- β -D-glucopyranoside (**10c**): TLC (hexane/EtOAc 1:1) R_f = 0.50; ^1H NMR (600 MHz, CDCl_3) δ 7.78–7.74 (m, 1 H), 7.72–7.62 (m, 5 H), 7.56–7.54 (m, 1 H), 7.53–7.48 (m, 2 H), 7.34–7.32 (m, 4 H), 7.30–7.26 (m, 4 H), 7.23–7.20 (m, 6 H), 7.20–7.17 (m, 4 H), 7.10–7.08 (m, 2 H), 7.07–7.04 (m, 2 H), 6.97–6.95 (m, 2 H), 6.87–6.85 (m, 2 H), 6.93–6.90 (m, 2 H), 6.97–6.77 (m, 9 H), 5.32 (d, J = 8.4 Hz, 1 H), 5.25 (d, J = 10.4 Hz, 1 H), 5.16 (d, J = 8.2 Hz, 1 H), 4.85 (d, J = 10.9 Hz, 1 H), 4.77 (d, J = 12.1 Hz, 1 H), 4.72 (d, J = 11.0 Hz, 1 H), 4.66 (d, J = 12.2 Hz, 1 H), 4.59 (d, J = 12.1 Hz, 1 H), 4.47 (d, J = 10.6 Hz, 1 H), 4.44–4.38 (m, 2 H), 4.37 (d, J = 12.0 Hz, 1 H), 4.35 (dd, J = 10.7, 8.6 Hz, 1 H), 4.33–4.30 (m, 2 H), 4.28–4.24 (m, 3 H), 4.21–4.12 (m, 4 H), 4.06 (dd, J = 10.9, 1.5 Hz, 1 H), 3.98–3.91 (m, 3 H), 3.78 (dd, J = 11.3, 4.5 Hz, 1 H), 3.72 (*pseudo*-t, J = 9.1 Hz, 1 H), 3.60–3.55 (m, 2 H), 3.50 (dd, J = 10.0, 3.8 Hz, 1 H), 3.42 (dd, J = 10.3, 3.1 Hz, 1 H), 3.37 (*pseudo*-t, J = 9.6 Hz, 1 H), 2.45–2.37 (m, 1 H); ^{13}C NMR (150 MHz, CDCl_3) δ 168.2, 168.0, 137.6, 137.4, 134.8, 134.6, 134.3, 134.2, 133.9, 131.8, 131.4, 129.2, 129.14, 129.1, 128.8, 128.7, 128.6, 128.59, 128.57, 128.5, 128.4, 128.3, 128.25, 128.2, 128.15, 128.13, 128.10, 128.09, 128.05, 128.04, 128.02, 127.99, 127.93, 127.91, 127.9, 127.6, 127.4, 127.36, 123.9, 123.6, 123.4, 102.2, 101.1, 85.4, 79.0, 76.5, 75.1, 74.8, 72.5, 71.8, 70.4, 70.3, 68.8, 68.2, 64.7, 57.8, 51.9, 29.8, 26.5; HRMS (ESI) m/z calcd for $\text{C}_{90}\text{H}_{80}\text{ClKN}_3\text{O}_{18}\text{S}$ $[\text{M}+\text{K}]^+$, 1596.4478; found, 1596.4441.

4. General procedure for cyclic oligoglucosamine with a 2,3-oxazolidinone group

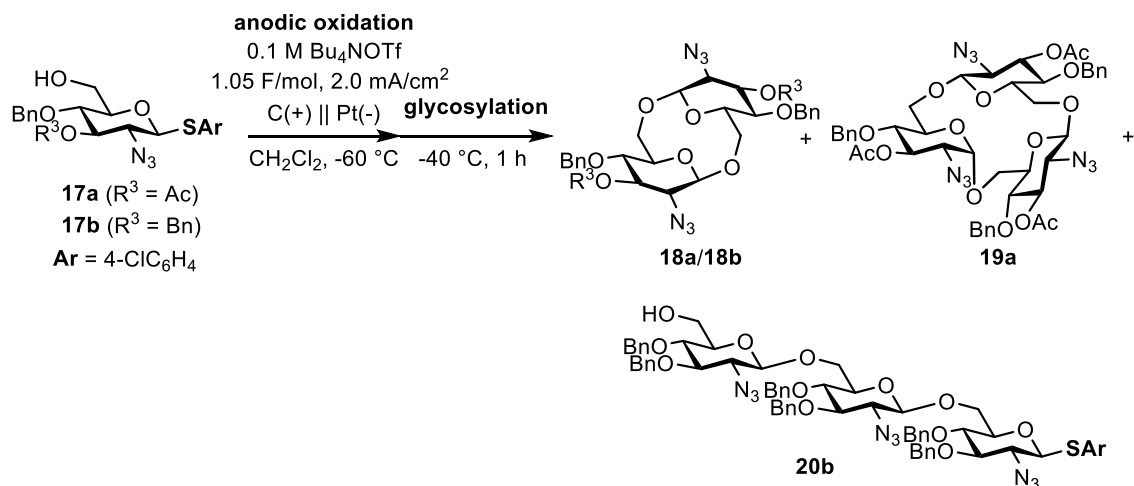
Synthesis of cyclobis[(1→6)-2-acetamido-4-*O*-benzyl-2,3-*N,O*-carbonyl-2-deoxy-β-*D*-glucopyranosyl] (**16**)



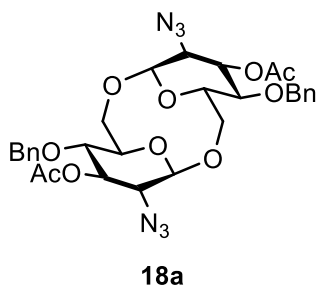
The electrochemical one-pot synthesis of cyclic disaccharide **16** was conducted with an H-type divided cell (4G glass filter). The cell had a carbon felt anode (Nippon Carbon JF-20-p7) and platinum square plate (20 mm × 20 mm). Building block **14** (0.400 mmol, 186 mg), Bu₄NOTf (1.00 mmol, 392 mg), 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) (2.0 mmol, 411 mg), and CH₂Cl₂ (10 mL) were added to the anodic chamber. TfOH (0.400 mmol, 35.2 μL), Bu₄NOTf (1.00 mmol, 392 mg), and CH₂Cl₂ (10 mL) were added to the cathodic chamber. As the initiation phase of reaction, the constant current (8.0 mA (current density: 2.0 mA/cm²), 18~22 V (electrode distance: 4.5 cm)) was employed at -20 °C with magnetic stirring until 1.2 F/mol of electricity was consumed. After the electrolysis, the reaction temperature was raised from -20 °C to 0 °C as glycosylation phase. After glycosylation, Et₃N (0.5 mL) was added to both of the chambers. The solution was collected, and the solvent was removed under reduced pressure. The mixture was dissolved in EtOAc and washed with H₂O to remove electrolyte. It was further washed with 1 N HCl (aq) to remove excessive DTBMP. The solution was dried over anhydrous Na₂SO₄, and the solvent was removed under reduced pressure. The crude product was purified with preparative GPC to afford cyclic oligosaccharide **16** (0.125 mmol, 79.7 mg, 62%) as a white solid.

Cyclobis[(1→6)-2-acetamido-4-*O*-benzyl-2,3-*N,O*-carbonyl-2-deoxy-β-*D*-glucopyranosyl] (**16**): TLC (eluent: hexane/EtOAc 2:1) R_f = 0.31; ¹H NMR (CDCl₃, 600 MHz) δ 7.38–7.35 (m, 4 H), 7.33–7.30 (m, 1 H), 5.24 (d, *J* = 5.7 Hz, 1 H), 4.89 (d, *J* = 11.4 Hz, 1 H), 4.62 (d, *J* = 11.2 Hz, 1 H), 4.31 (dd, *J* = 12.5, 6.6 Hz, 1 H), 4.18 (dd, *J* = 9.7, 4.3 Hz, 1 H), 4.16–4.13 (m, 1 H), 4.01 (dd, *J* = 10.9, 2.5 Hz, 1 H), 3.94 (dd, *J* = 12.5, 5.8 Hz, 1 H), 3.59 (dd, *J* = 11.0, 1.5 Hz, 1H), 2.53 (s, 3 H); ¹³C NMR (CDCl₃, 150 MHz) δ 170.6, 153.7, 137.3, 128.5, 128.0, 127.9, 97.0, 81.7, 73.1, 63.8, 62.0, 24.5; HRMS (ESI) *m/z* calcd for C₃₂H₃₄KN₂O₁₂; [M+K]⁺, 677.1744, found 677.1735.

5. General procedure for cyclic oligoglucosamines with an azido group



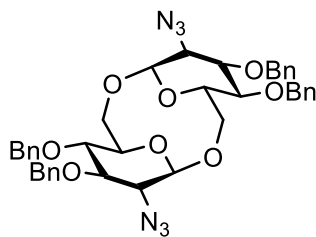
The electrochemical polymerization synthesis of cyclic oligosaccharides **18** and **19** and linear oligosaccharide **20** was carried out by an H-type divided cell (4G glass filter). The cell had a carbon felt anode (Nippon Carbon JF-20-P7) and platinum square plate (20 mm × 20 mm). Building block **17** (0.40 mmol), Bu₄NOTf (1.00 mmol), and CH₂Cl₂ (10 mL) were added to the anodic chamber. TfOH (0.4 mmol), Bu₄NOTf (1.00 mmol), and CH₂Cl₂ (10 mL) were added to the cathodic chamber. The constant current (8 mA (current density: 2.0 mA/cm²), (electrode distance: 4.5 cm)) was employed at -60 °C with magnetic stirring until the electricity was consumed. After the electrolysis, the reaction was kept stirring at -40 °C for 1 h. After that, Et₃N (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 H₂O to remove electrolyte. The solution was dried over anhydrous Na₂SO₄, filtered, and the solution was removed under reduced pressure. The crude product was purified with preparative GPC to afford cyclic oligosaccharides **18** and **19** and linear trisaccharide **20b**.



Building block **17a** (185 mg, 0.40 mmol) afforded **18a** in 49% isolated yield (63 mg, 0.987mmol).

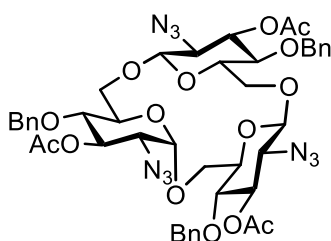
Cyclobis[(1→6)-3-*O*-acetyl-2-azido-4-*O*-benzyl-2-deoxy-2-β-D-glucopyranosyl] (**18a**): TLC (hexane/EtOAc 3:1) R_f = 0.28; ¹H NMR (600 MHz, CDCl₃) δ 7.35–7.29 (m, 5 H), 5.05 (dd, *J* = 9.0,

3.6 Hz, 1 H), 4.72 (d, $J = 1.8$ Hz, 1 H), 4.69 (d, $J = 11.6$ Hz, 1 H), 4.61 (d, $J = 11.5$ Hz, 1 H), 4.44 (dd, $J = 10.2, 9.6$ Hz, 1 H), 4.11 (dd, $J = 12.3, 1.2$ Hz, 1 H), 3.82–3.79 (m, 1 H), 3.71 (dd, $J = 12.6, 1.2$ Hz, 1 H), 3.65 (dd, $J = 3.6, 1.8$ Hz, 1 H), 1.96 (s, 3 H); ^{13}C NMR (150 MHz, CDCl_3) δ 170.2, 138.1, 128.6, 128.2, 128.0, 100.3, 75.7, 74.7, 74.5, 73.7, 70.9, 65.3, 21.0; HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{34}\text{KN}_6\text{O}_{10}$ $[\text{M}+\text{K}]^+$, 677.1968; found, 677.1933.



18b

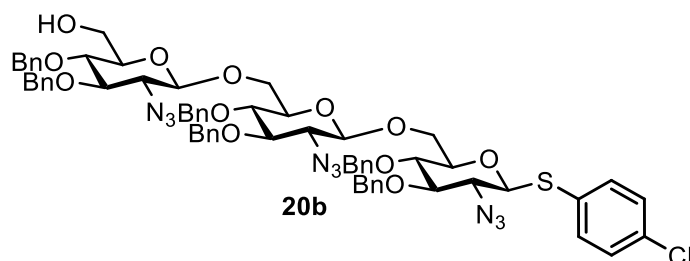
Building block **17b** (205 mg, 0.40 mmol) afforded **18b** in 14% isolated yield (21 mg, 0.0281 mmol).
 Cyclobis[(1→6)-2-azido-3,4-di-*O*-benzyl-2-deoxy-2-β-D-glucopyranosyl] (**18b**): TLC (hexane/EtOAc 3:1) $R_f = 0.63$; ^1H NMR (600 MHz, CDCl_3) δ 7.36–7.28 (m, 10 H), 4.86 (d, $J = 11.3$ Hz, 1 H), 4.84 (d, $J = 11.0$ Hz, 1 H), 4.78 (d, $J = 11.1$ Hz, 1 H), 4.67 (d, $J = 11.4$ Hz, 1 H), 4.58–4.57 (m, 1 H), 4.20 (*pseudo-t*, $J = 9.6$ Hz, 1 H), 3.92 (dd, $J = 12.0, 2.4$ Hz, 1 H), 3.76 (dd, $J = 9.6, 1.8$ Hz, 1 H), 3.67–3.62 (m, 2 H), 3.50 (dd, $J = 6.6, 1.2$ Hz, 1 H), 1.43 (dd, $J = 15.0, 7.5$ Hz, 2 H); ^{13}C NMR (150 MHz, CDCl_3) δ 138.2, 137.8, 128.54, 128.49, 128.13, 128.09, 127.98, 127.97, 100.9, 81.7, 77.0, 75.0, 74.5, 74.2, 69.2, 67.7, 58.9, 24.0, 19.7, 13.7; HRMS (ESI) m/z calcd for $\text{C}_{40}\text{H}_{42}\text{KN}_6\text{O}_8$ $[\text{M}+\text{K}]^+$, 773.2696; found, 773.2650.



19a

Building block **17a** (185 mg, 0.40 mmol) afforded **19a** in 16% isolated yield (19 mg, 0.0208 mmol).
 Cyclotris[(1→6)-3-*O*-acetyl-2-azido-4-*O*-benzyl-2-deoxy-2-α,β,β-D-glucopyranosyl] (**19a**): TLC (hexane/EtOAc 2:1) $R_f = 0.32$; ^1H NMR (600 MHz, CDCl_3) δ 7.37–7.28 (m, 10 H), 7.28–7.25 (m, 2 H), 7.22–7.21 (m, 3 H), 5.61 (dd, $J = 10.8, 9.0$ Hz, 1 H), 5.10 (dd, $J = 10.8, 9.6$ Hz, 1 H), 4.95 (*pseudo-t*, $J = 10.2$ Hz, 1 H), 4.80 (d, $J = 3.6$ Hz, 1 H), 4.72 (d, $J = 11.4$ Hz, 1 H), 4.63 (d, $J = 11.4$ Hz, 1 H), 4.61 (d, $J = 11.4$ Hz, 2 H), 4.53 (d, $J = 12.0$ Hz, 1 H), 4.52 (d, $J = 7.8$ Hz, 1 H), 4.51 (d, $J = 11.4$ Hz, 1 H), 4.33 (dd, $J = 12.6, 1.8$ Hz, 1 H), 4.22 (d, $J = 7.8$ Hz, 1 H), 4.03 (dd, $J = 12.6, 8.4$ Hz, 1 H), 3.91–

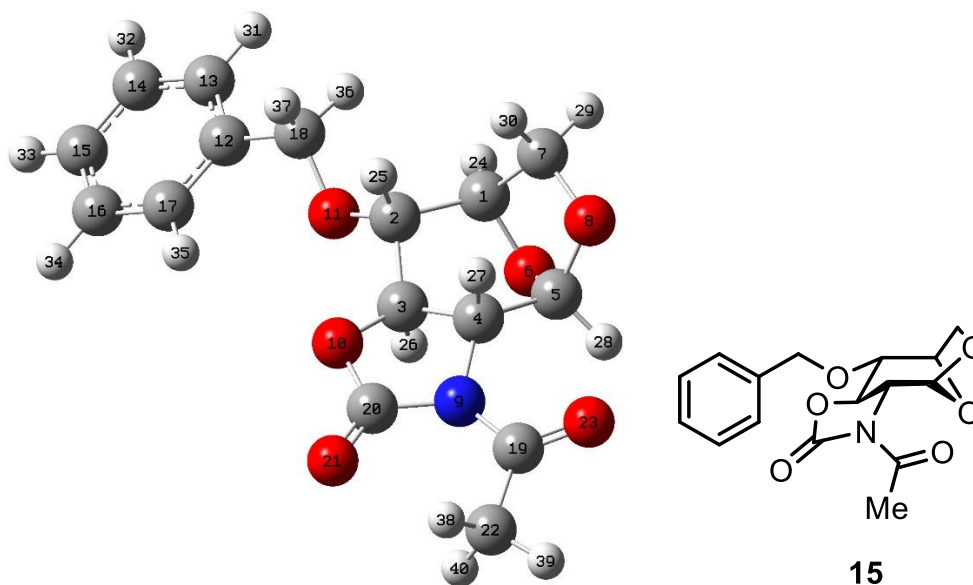
3.89 (m, 1 H), 3.81–3.77 (m, 3 H), 3.75 (*pseudo*-t, $J = 9.6$ Hz, 1 H), 3.70 (ddd, $J = 9.0, 6.6, 1.2$ Hz, 1 H), 3.45 (dd, $J = 10.2, 7.8$ Hz, 1 H), 3.44 (dd, $J = 10.3, 6.0$ Hz, 1H), 3.29 (*pseudo*-t, $J = 9.6$ Hz, 1H), 3.18–3.15 (m, 1 H), 3.15 (*pseudo*-t, $J = 9.6$ Hz, 1 H), 3.06 (dd, $J = 10.8, 3.6$ Hz, 1 H), 2.08 (s, 3 H), 2.06 (s, 3 H), 1.96 (s, 3 H); ^{13}C NMR (150 MHz, CDCl_3) δ 170.0, 169.7, 137.9, 137.2, 137.15, 128.8, 128.7, 128.5, 128.48, 128.3, 128.0, 127.9, 127.74, 127.7, 105.7, 101.3, 97.9, 77.7, 76.4, 75.3, 75.28, 74.9, 74.3, 74.2, 74.0, 73.9, 73.5, 71.8, 71.6, 69.6, 68.8, 64.9, 63.7, 61.2, 21.1, 21.0, 20.96, 14.3; HRMS (ESI) m/z calcd for $\text{C}_{45}\text{H}_{51}\text{KN}_9\text{O}_{15}$ $[\text{M}+\text{K}]^+$, 996.3136; found, 996.3195.



Building block **17b** (205 mg, 0.40 mmol) afforded **20b** in 13% isolated yield (21 mg, 0.0171 mmol). 4-Chlorophenyl-(2-azido-2-deoxy-3,4-di-*O*-benzyl- β -D-glucopyranosyl)-(1 \rightarrow 6)-(2-azido-2-deoxy-3,4-di-*O*-benzyl- β -D-glucopyranosyl)-(1 \rightarrow 6)-2-azido-2-deoxy-3,4-di-*O*-benzyl-1-thio- β -D-glucopyranoside (**20b**): TLC (hexane/EtOAc 2:1) $R_f = 0.40$; ^1H NMR (600 MHz, CDCl_3) δ 7.55–7.53 (m, 2 H), 7.37–7.34 (m, 5 H), 7.33–7.30 (m, 15 H), 7.29–7.26 (m, 12 H), 4.64–4.61 (m, 3 H), 4.42 (d, $J = 10.2$ Hz, 1 H), 4.29–4.26 (m, 2 H), 4.16 (dd, $J = 11.4, 1.8$ Hz, 1 H), 4.04 (dd, $J = 11.4, 1.5$ Hz, 1 H), 3.79 (dd, $J = 11.4, 5.1$ Hz, 1 H), 3.66–3.62 (m, 2 H), 3.54–3.45 (m, 4 H), 3.43–3.40 (m, 1 H), 3.38–3.36 (m, 1 H), 3.31 (dd, $J = 10.2, 9.3$ Hz, 1 H), 3.21 (*pseudo*-t, $J = 8.7$ Hz, 4 H), 1.90 (dd, $J = 7.7, 6.0$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 137.9, 137.82, 137.79, 137.6, 135.0, 129.3, 128.82, 128.77, 128.66, 128.62, 128.61, 128.54, 128.49, 128.3, 128.21, 128.19, 128.18, 128.15, 128.13, 128.09, 128.08, 128.05, 128.02, 127.99, 127.98, 129.92, 127.9, 127.7, 102.6, 102.4, 86.0, 85.0, 83.2, 82.9, 78.9, 77.8, 77.6, 75.9, 75.8, 75.5, 75.4, 75.13, 75.10, 75.09, 74.8, 66.5, 66.4, 65.1, 61.7, 58.9, 24.0, 19.8, 13.7; HRMS (ESI) m/z calcd for $\text{C}_{66}\text{H}_{68}\text{ClNaN}_9\text{O}_{12}\text{S}$ $[\text{M}+\text{Na}]^+$, 1268.4289; found, 1268.4249.

6. Molecular orbital calculations for the anhydrosugar **15**

The molecular orbital calculations were carried out with 1,6-anhydro-2-acetamido-4-*O*-benzyl-2,3-*N,O*-carbonyl-2-deoxy- β -D-glucopyranoside (**15**) at the B3LYP/6-31G(d) level using the Gaussian 16, Revision C.02.⁸ Geometries were fully optimized. All the optimized structures were local minima according to the vibration analysis. Cartesian coordinates of computationally characterized species are as follows:



(white H, black C, blue N, red O)

center	atomic	atomic	coordinates (Å)		
number	number	type	X	Y	Z
1	6	0	-0.16492	2.131337	0.2187
2	6	0	0.274667	0.754509	-0.42251
3	6	0	-0.7847	-0.2157	0.051899
4	6	0	-2.17365	0.346913	-0.18699
5	6	0	-2.30435	1.679611	0.613134
6	8	0	-1.08166	1.900996	1.306095
7	6	0	-1.02417	3.036293	-0.6985
8	8	0	-2.37958	2.739594	-0.32505
9	7	0	-2.93857	-0.87696	0.077304
10	8	0	-0.86217	-1.52716	-0.54015
11	8	0	1.526591	0.308336	0.050603
12	6	0	3.895483	0.079124	-0.22469
13	6	0	5.10813	0.755448	-0.05983
14	6	0	6.269702	0.058067	0.277473

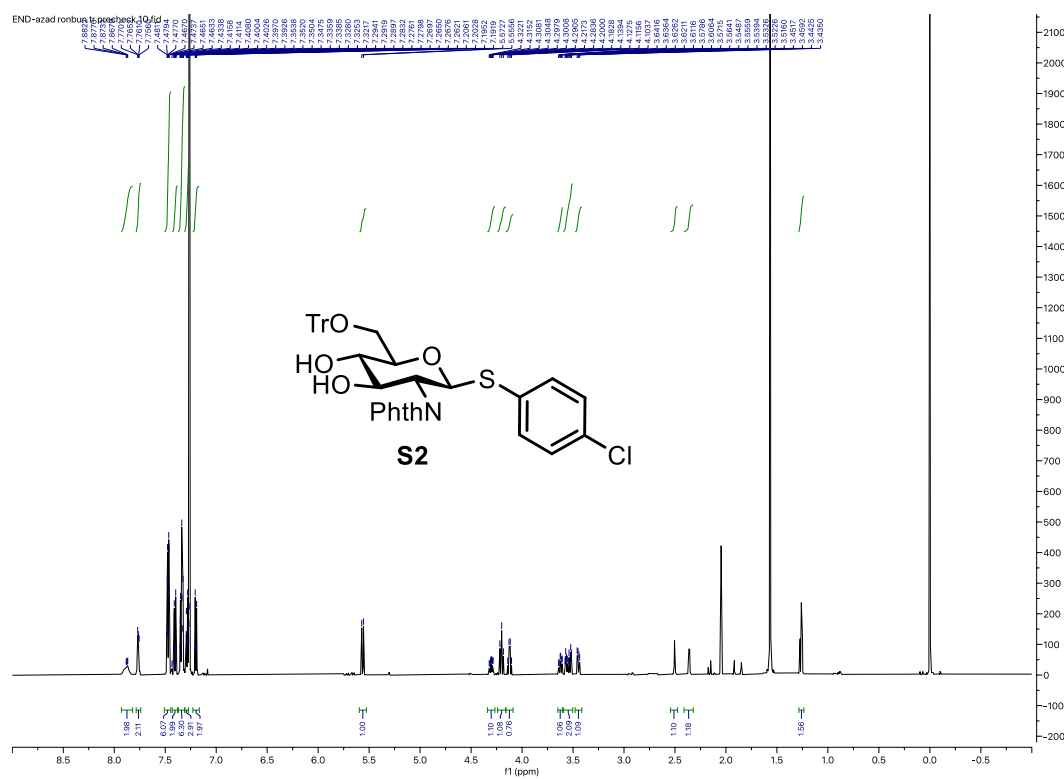
15	6	0	6.224147	-1.32373	0.464531
16	6	0	5.013341	-2.00364	0.310461
17	6	0	3.855851	-1.30808	-0.03621
18	6	0	2.654427	0.828476	-0.64793
19	6	0	-4.33893	-0.85859	0.207606
20	6	0	-2.13822	-1.97578	-0.3258
21	8	0	-2.47812	-3.11809	-0.48533
22	6	0	-5.05385	-2.18061	0.34572
23	8	0	-4.90638	0.219384	0.233441
24	1	0	0.711775	2.634626	0.628949
25	1	0	0.285138	0.831605	-1.52156
26	1	0	-0.63025	-0.35481	1.125877
27	1	0	-2.31666	0.608144	-1.2439
28	1	0	-3.14116	1.728496	1.304974
29	1	0	-0.83681	4.09738	-0.5056
30	1	0	-0.86848	2.837402	-1.76574
31	1	0	5.146116	1.834702	-0.19313
32	1	0	7.205483	0.596154	0.403168
33	1	0	7.125442	-1.86806	0.733453
34	1	0	4.970403	-3.07924	0.460004
35	1	0	2.911867	-1.83238	-0.14819
36	1	0	2.778026	1.905583	-0.45278
37	1	0	2.487933	0.714053	-1.73309
38	1	0	-4.98025	-2.75917	-0.57938
39	1	0	-6.09876	-1.96667	0.57474
40	1	0	-4.60718	-2.79555	1.131953

7. References

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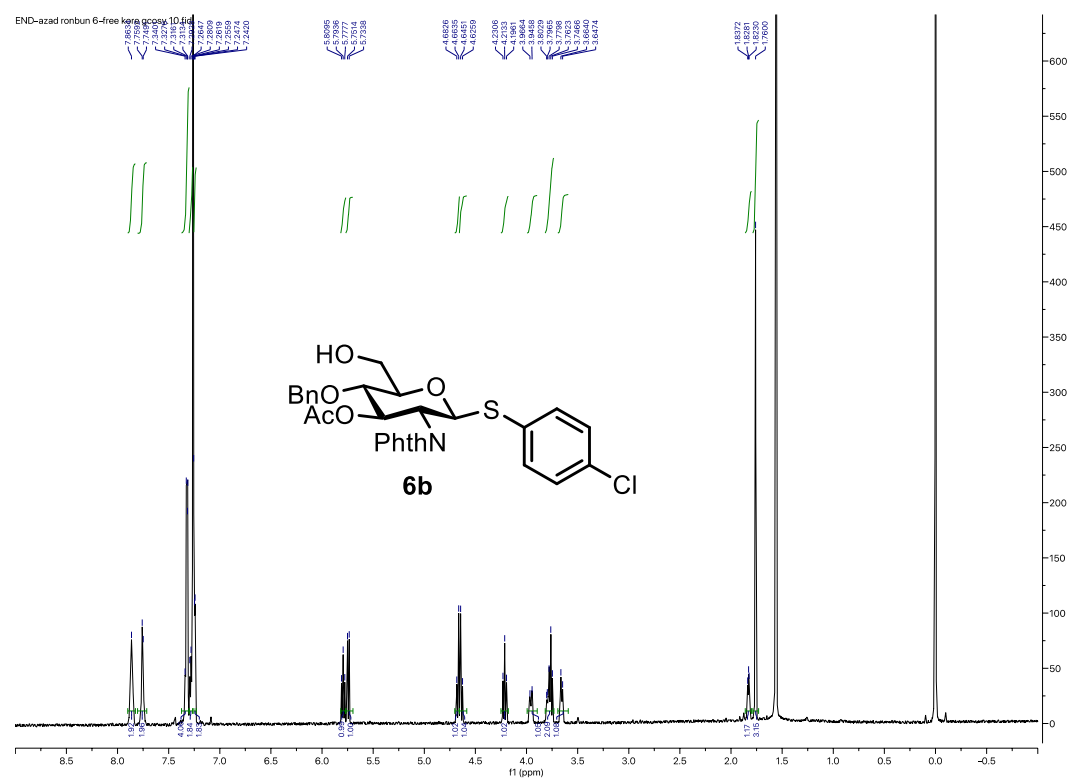
8. ^1H and ^{13}C NMR spectra of monosaccharides and oligosaccharides

^1H NMR



[illegible]

¹H NMR



Chemical structure of **S6** is shown above the spectrum. The structure is a 1,2:3,5-di-O-isopropylidene-4-O-(4-chlorophenylthio)-D-glucopyranose derivative.

¹H NMR spectrum (CDCl₃) of **S6** is shown below the structure. The x-axis represents the chemical shift in ppm (δ), ranging from 0 to 8.5. The y-axis represents the intensity of the signal.

Key peaks and integrations are labeled:

- Aromatic protons (Ph): 7.26 (m, 1H), 7.24 (m, 1H), 7.22 (m, 1H), 7.20 (m, 1H), 7.18 (m, 1H), 7.16 (m, 1H), 7.14 (m, 1H), 7.12 (m, 1H), 7.10 (m, 1H), 7.08 (m, 1H), 7.06 (m, 1H), 7.04 (m, 1H), 7.02 (m, 1H), 7.00 (m, 1H), 6.98 (m, 1H), 6.96 (m, 1H), 6.94 (m, 1H), 6.92 (m, 1H), 6.90 (m, 1H), 6.88 (m, 1H), 6.86 (m, 1H), 6.84 (m, 1H), 6.82 (m, 1H), 6.80 (m, 1H), 6.78 (m, 1H), 6.76 (m, 1H), 6.74 (m, 1H), 6.72 (m, 1H), 6.70 (m, 1H), 6.68 (m, 1H), 6.66 (m, 1H), 6.64 (m, 1H), 6.62 (m, 1H), 6.60 (m, 1H), 6.58 (m, 1H), 6.56 (m, 1H), 6.54 (m, 1H), 6.52 (m, 1H), 6.50 (m, 1H), 6.48 (m, 1H), 6.46 (m, 1H), 6.44 (m, 1H), 6.42 (m, 1H), 6.40 (m, 1H), 6.38 (m, 1H), 6.36 (m, 1H), 6.34 (m, 1H), 6.32 (m, 1H), 6.30 (m, 1H), 6.28 (m, 1H), 6.26 (m, 1H), 6.24 (m, 1H), 6.22 (m, 1H), 6.20 (m, 1H), 6.18 (m, 1H), 6.16 (m, 1H), 6.14 (m, 1H), 6.12 (m, 1H), 6.10 (m, 1H), 6.08 (m, 1H), 6.06 (m, 1H), 6.04 (m, 1H), 6.02 (m, 1H), 6.00 (m, 1H), 5.98 (m, 1H), 5.96 (m, 1H), 5.94 (m, 1H), 5.92 (m, 1H), 5.90 (m, 1H), 5.88 (m, 1H), 5.86 (m, 1H), 5.84 (m, 1H), 5.82 (m, 1H), 5.80 (m, 1H), 5.78 (m, 1H), 5.76 (m, 1H), 5.74 (m, 1H), 5.72 (m, 1H), 5.70 (m, 1H), 5.68 (m, 1H), 5.66 (m, 1H), 5.64 (m, 1H), 5.62 (m, 1H), 5.60 (m, 1H), 5.58 (m, 1H), 5.56 (m, 1H), 5.54 (m, 1H), 5.52 (m, 1H), 5.50 (m, 1H), 5.48 (m, 1H), 5.46 (m, 1H), 5.44 (m, 1H), 5.42 (m, 1H), 5.40 (m, 1H), 5.38 (m, 1H), 5.36 (m, 1H), 5.34 (m, 1H), 5.32 (m, 1H), 5.30 (m, 1H), 5.28 (m, 1H), 5.26 (m, 1H), 5.24 (m, 1H), 5.22 (m, 1H), 5.20 (m, 1H), 5.18 (m, 1H), 5.16 (m, 1H), 5.14 (m, 1H), 5.12 (m, 1H), 5.10 (m, 1H), 5.08 (m, 1H), 5.06 (m, 1H), 5.04 (m, 1H), 5.02 (m, 1H), 5.00 (m, 1H), 4.98 (m, 1H), 4.96 (m, 1H), 4.94 (m, 1H), 4.92 (m, 1H), 4.90 (m, 1H), 4.88 (m, 1H), 4.86 (m, 1H), 4.84 (m, 1H), 4.82 (m, 1H), 4.80 (m, 1H), 4.78 (m, 1H), 4.76 (m, 1H), 4.74 (m, 1H), 4.72 (m, 1H), 4.70 (m, 1H), 4.68 (m, 1H), 4.66 (m, 1H), 4.64 (m, 1H), 4.62 (m, 1H), 4.60 (m, 1H), 4.58 (m, 1H), 4.56 (m, 1H), 4.54 (m, 1H), 4.52 (m, 1H), 4.50 (m, 1H), 4.48 (m, 1H), 4.46 (m, 1H), 4.44 (m, 1H), 4.42 (m, 1H), 4.40 (m, 1H), 4.38 (m, 1H), 4.36 (m, 1H), 4.34 (m, 1H), 4.32 (m, 1H), 4.30 (m, 1H), 4.28 (m, 1H), 4.26 (m, 1H), 4.24 (m, 1H), 4.22 (m, 1H), 4.20 (m, 1H), 4.18 (m, 1H), 4.16 (m, 1H), 4.14 (m, 1H), 4.12 (m, 1H), 4.10 (m, 1H), 4.08 (m, 1H), 4.06 (m, 1H), 4.04 (m, 1H), 4.02 (m, 1H), 4.00 (m, 1H), 3.98 (m, 1H), 3.96 (m, 1H), 3.94 (m, 1H), 3.92 (m, 1H), 3.90 (m, 1H), 3.88 (m, 1H), 3.86 (m, 1H), 3.84 (m, 1H), 3.82 (m, 1H), 3.80 (m, 1H), 3.78 (m, 1H), 3.76 (m, 1H), 3.74 (m, 1H), 3.72 (m, 1H), 3.70 (m, 1H), 3.68 (m, 1H), 3.66 (m, 1H), 3.64 (m, 1H), 3.62 (m, 1H), 3.60 (m, 1H), 3.58 (m, 1H), 3.56 (m, 1H), 3.54 (m, 1H), 3.52 (m, 1H), 3.50 (m, 1H), 3.48 (m, 1H), 3.46 (m, 1H), 3.44 (m, 1H), 3.42 (m, 1H), 3.40 (m, 1H), 3.38 (m, 1H), 3.36 (m, 1H), 3.34 (m, 1H), 3.32 (m, 1H), 3.30 (m, 1H), 3.28 (m, 1H), 3.26 (m, 1H), 3.24 (m, 1H), 3.22 (m, 1H), 3.20 (m, 1H), 3.18 (m, 1H), 3.16 (m, 1H), 3.14 (m, 1H), 3.12 (m, 1H), 3.10 (m, 1H), 3.08 (m, 1H), 3.06 (m, 1H), 3.04 (m, 1H), 3.02 (m, 1H), 3.00 (m, 1H), 2.98 (m, 1H), 2.96 (m, 1H), 2.94 (m, 1H), 2.92 (m, 1H), 2.90 (m, 1H), 2.88 (m, 1H), 2.86 (m, 1H), 2.84 (m, 1H), 2.82 (m, 1H), 2.80 (m, 1H), 2.78 (m, 1H), 2.76 (m, 1H), 2.74 (m, 1H), 2.72 (m, 1H), 2.70 (m, 1H), 2.68 (m, 1H), 2.66 (m, 1H), 2.64 (m, 1H), 2.62 (m, 1H), 2.60 (m, 1H), 2.58 (m, 1H), 2.56 (m, 1H), 2.54 (m, 1H), 2.52 (m, 1H), 2.50 (m, 1H), 2.48 (m, 1H), 2.46 (m, 1H), 2.44 (m, 1H), 2.42 (m, 1H), 2.40 (m, 1H), 2.38 (m, 1H), 2.36 (m, 1H), 2.34 (m, 1H), 2.32 (m, 1H), 2.30 (m, 1H), 2.28 (m, 1H), 2.26 (m, 1H), 2.24 (m, 1H), 2.22 (m, 1H), 2.20 (m, 1H), 2.18 (m, 1H), 2.16 (m, 1H), 2.14 (m, 1H), 2.12 (m, 1H), 2.10 (m, 1H), 2.08 (m, 1H), 2.06 (m, 1H), 2.04 (m, 1H), 2.02 (m, 1H), 2.00 (m, 1H), 1.98 (m, 1H), 1.96 (m, 1H), 1.94 (m, 1H), 1.92 (m, 1H), 1.90 (m, 1H), 1.88 (m, 1H), 1.86 (m, 1H), 1.84 (m, 1H), 1.82 (m, 1H), 1.80 (m, 1H), 1.78 (m, 1H), 1.76 (m, 1H), 1.74 (m, 1H), 1.72 (m, 1H), 1.70 (m, 1H), 1.68 (m, 1H), 1.66 (m, 1H), 1.64 (m, 1H), 1.62 (m, 1H), 1.60 (m, 1H), 1.58 (m, 1H), 1.56 (m, 1H), 1.54 (m, 1H), 1.52 (m, 1H), 1.50 (m, 1H), 1.48 (m, 1H), 1.46 (m, 1H), 1.44 (m, 1H), 1.42 (m, 1H), 1.40 (m, 1H), 1.38 (m, 1H), 1.36 (m, 1H), 1.34 (m, 1H), 1.32 (m, 1H), 1.30 (m, 1H), 1.28 (m, 1H), 1.26 (m, 1H), 1.24 (m, 1H), 1.22 (m, 1H), 1.20 (m, 1H), 1.18 (m, 1H), 1.16 (m, 1H), 1.14 (m, 1H), 1.12 (m, 1H), 1.10 (m, 1H), 1.08 (m, 1H), 1.06 (m, 1H), 1.04 (m, 1H), 1.02 (m, 1H), 1.00 (m, 1H), 0.98

END-737 13C.20.fid

Chemical structure of S6: CC1(C)OC2C(C1OC3C(C2)OC(C3)SC4=CC=C(C=C4)Cl)OC(C5=CC=CC=C5)OC6=CC=CC=C6

S6

13C NMR peaks (ppm):

- 167.7992
- 167.2115
- 137.6565
- 136.2613
- 134.9761
- 134.6911
- 133.9670
- 133.9602
- 129.9522
- 128.9522
- 128.9503
- 126.0775
- 123.4583
- 101.3633
- 78.7672
- 78.7769
- 76.3776
- 74.2523
- 70.4498
- 68.6275
- 54.7214

6c

O[C@H]1[C@@H](OC(=O)c2ccccc2)[C@H](OC(=O)c3ccccc3)[C@@H](O)[C@H]1SCc4ccc(Cl)cc4

¹H NMR spectrum of compound **6c** in CDCl₃. The spectrum shows peaks from 0 to 8.5 ppm. Key features include a broad peak at ~7.2 ppm (NH), aromatic signals between 6.5-7.5 ppm, a multiplet at ~4.5 ppm, a doublet at ~3.8 ppm, and a singlet at ~2.1 ppm. Integration values are provided below the baseline. The chemical structure of **6c** is shown as an inset.

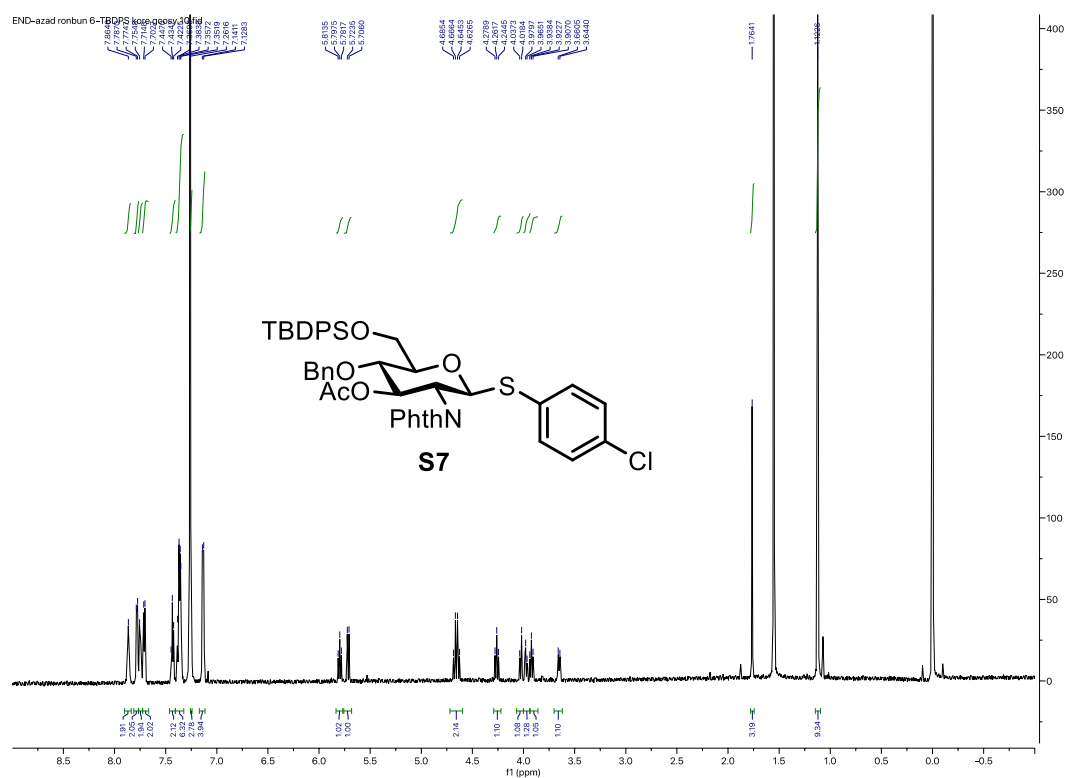
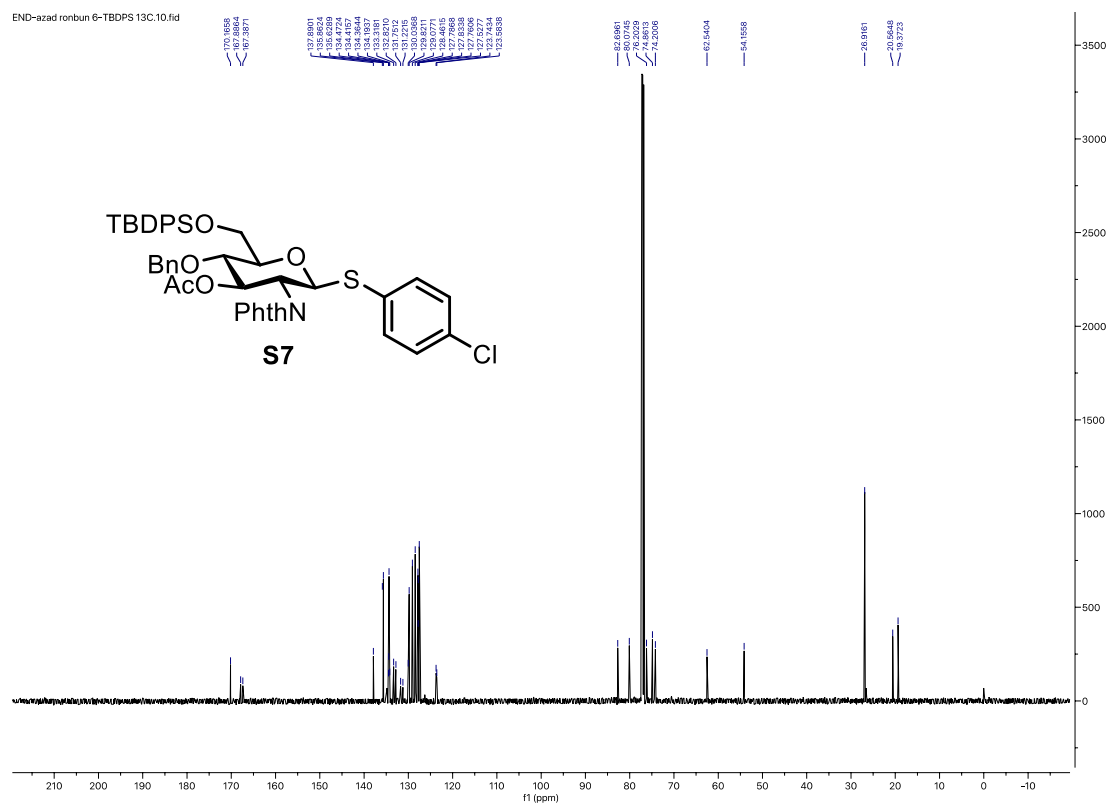
RA-PhthNOBnOBN 13C

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127.5605
123.5821
78.3525
78.1722
78.0905
77.8088
77.6291
77.4507
61.8457
55.5513

Chemical structure of **6c** is shown, featuring a substituted tetrahydropyran ring with a phthalimide group, a benzoyl group, a hydroxyl group, and a 4-chlorophenylthio group.

6c

f1 (ppm)

¹H NMR¹³C NMR

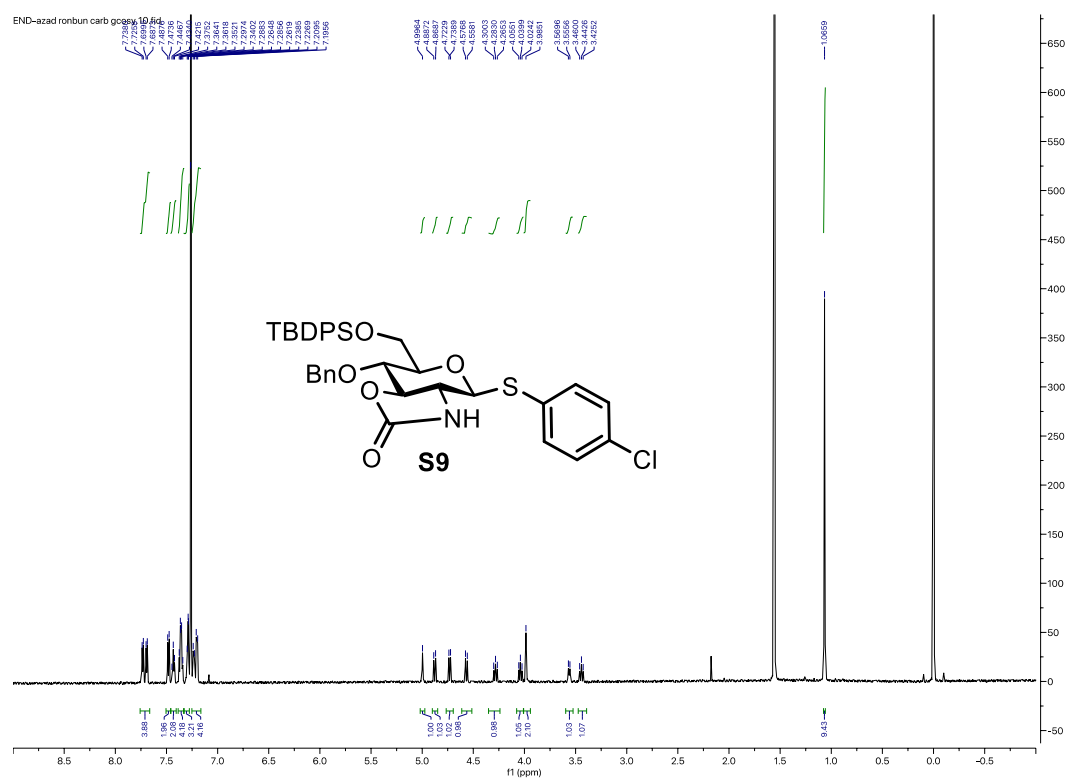
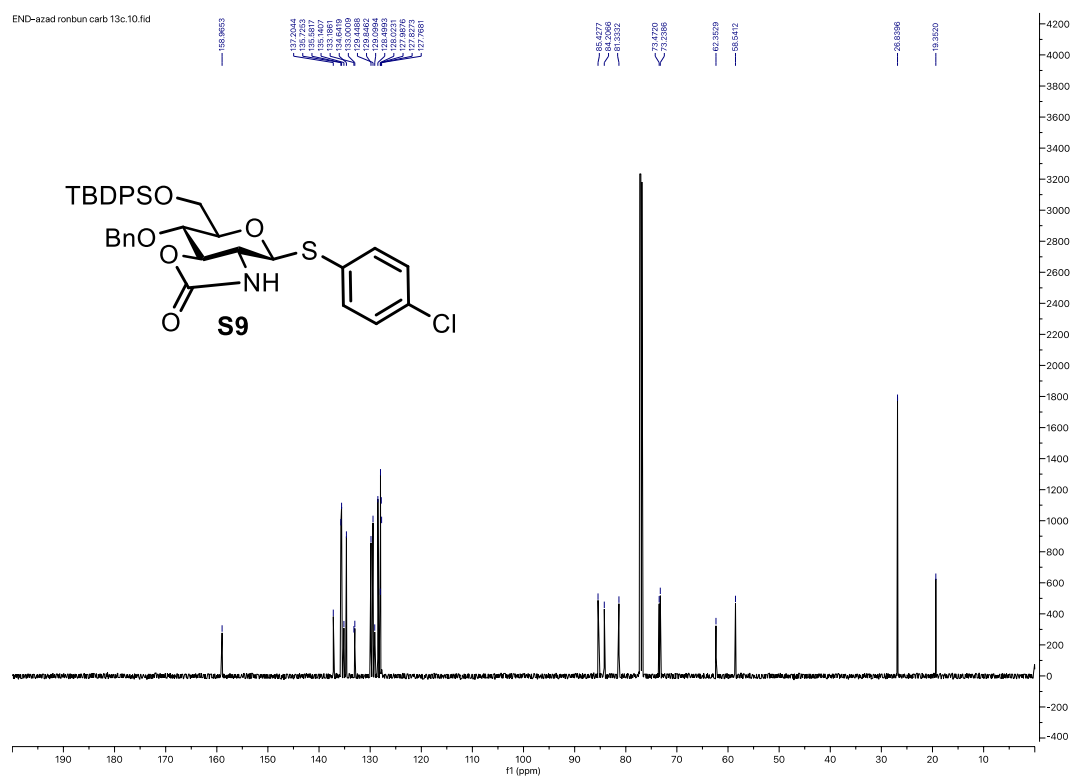
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END-azad ronbun NH2 dep 13C.10.fid

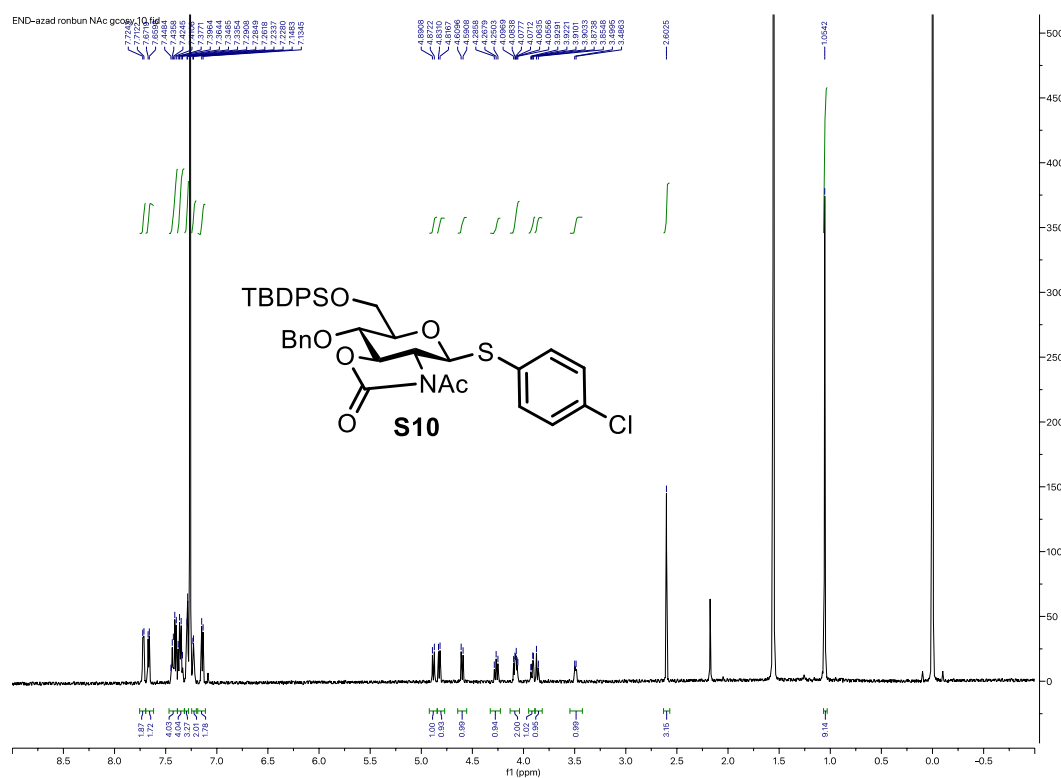
Chemical structure of S8 is shown above the spectrum. The structure is a sugar derivative with a TBDPSO group, a BnO group, a hydroxyl group, an amino group, and a 4-chlorophenylthio group.

Peak list (ppm):

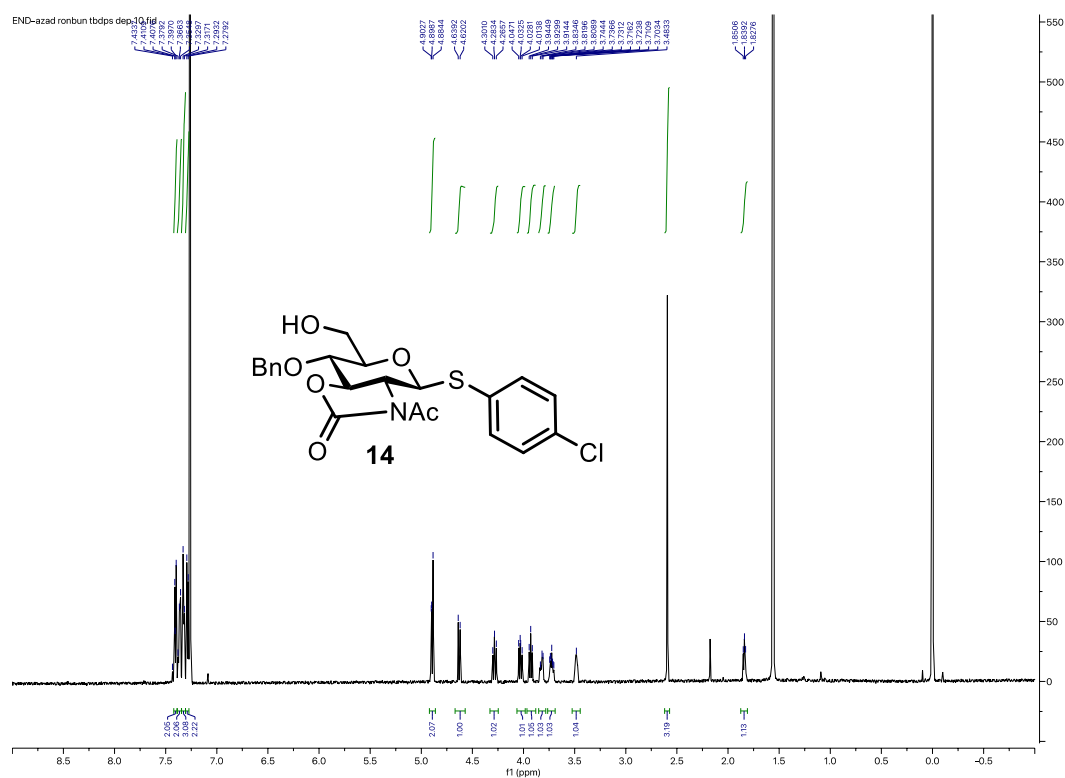
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- 129.6968
- 127.8028
- 127.7909
- 127.7158
- 89.2523
- 79.98533
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- 77.9853
- 74.77863
- 62.9154
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- 19.9562

¹H NMR¹³C NMR

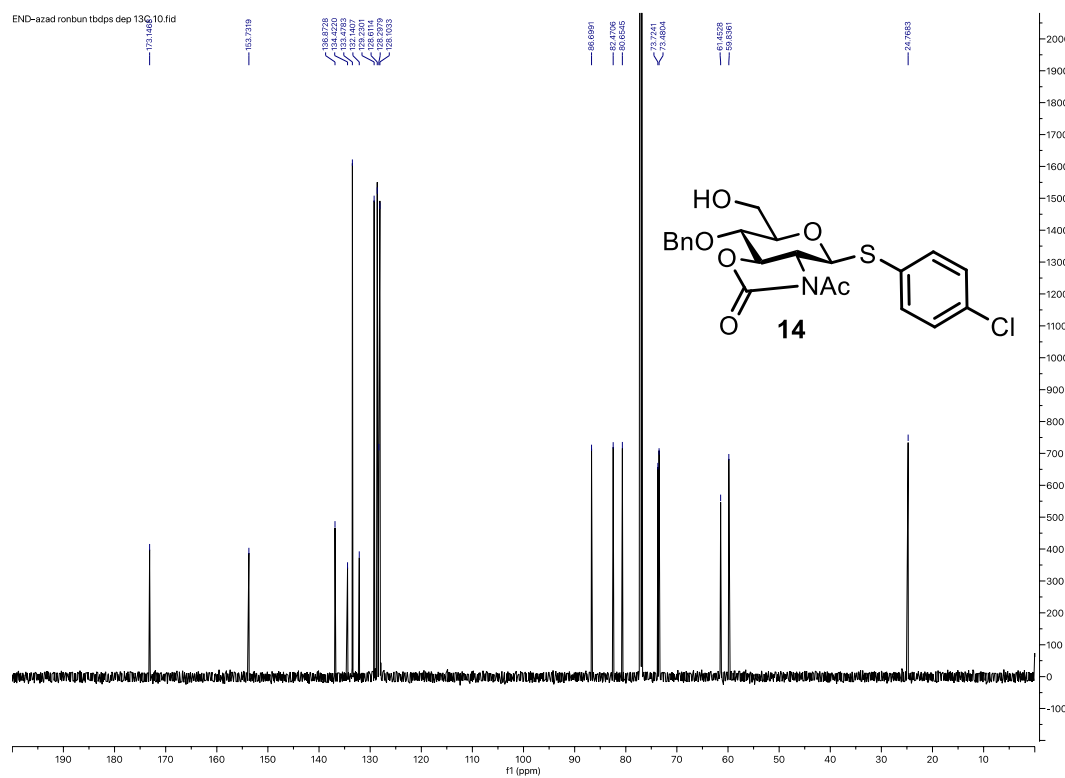
¹H NMR

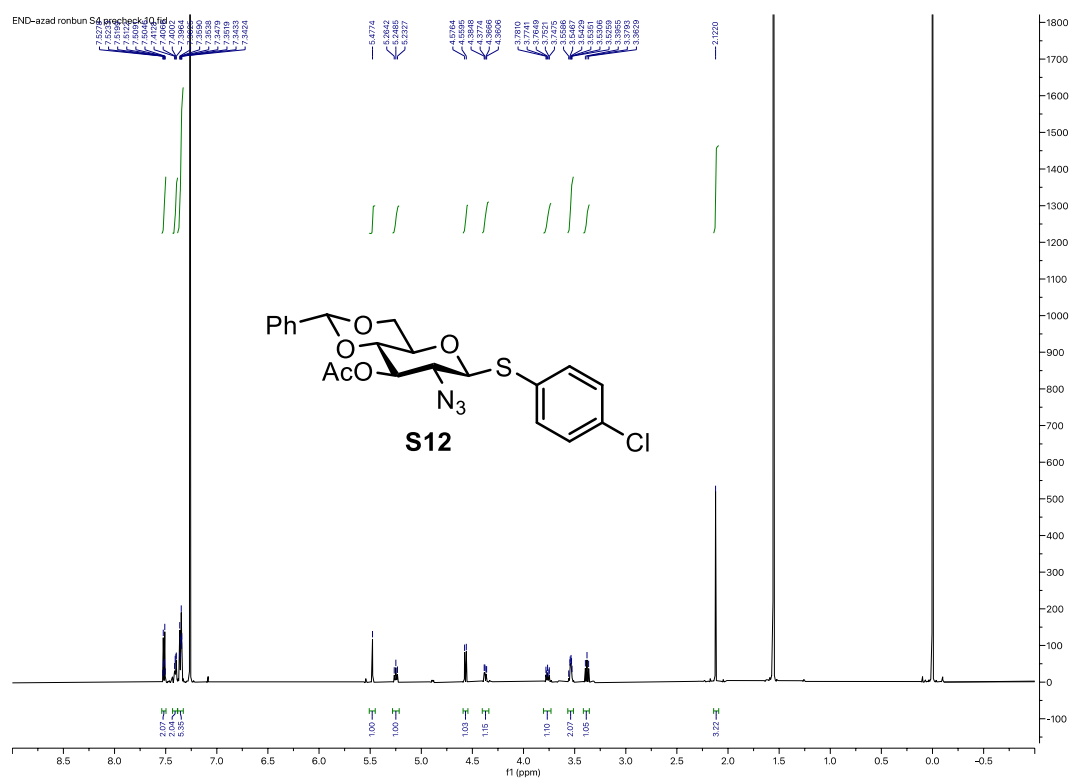
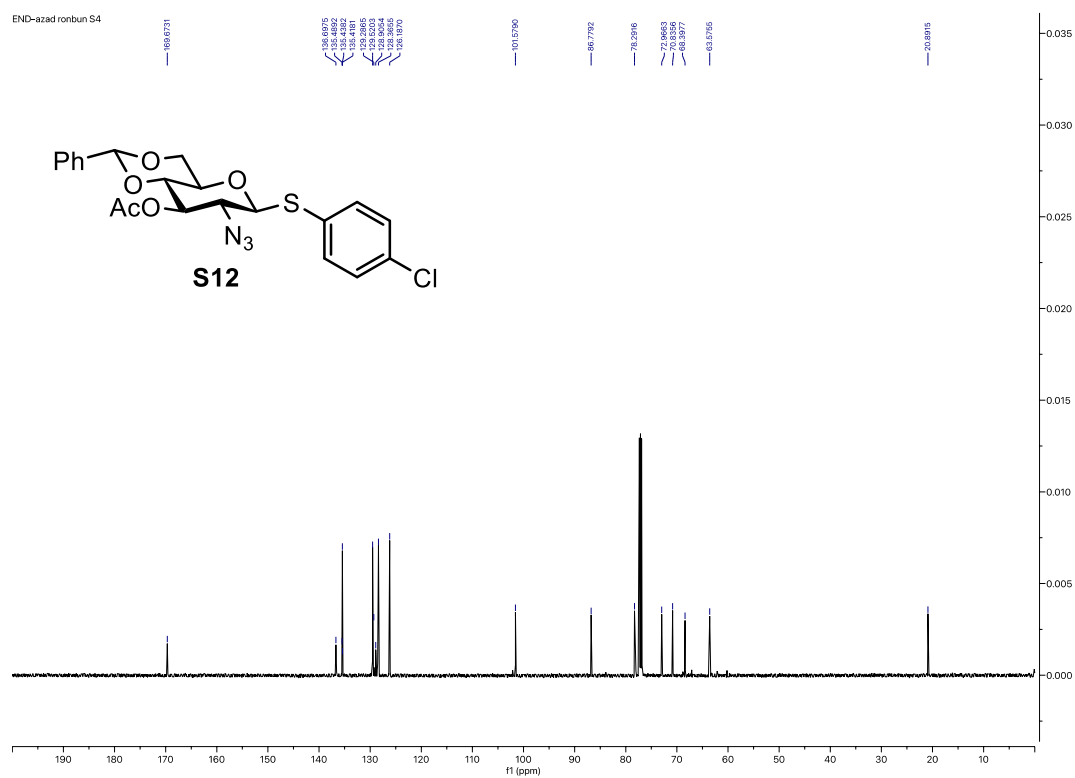


¹H NMR

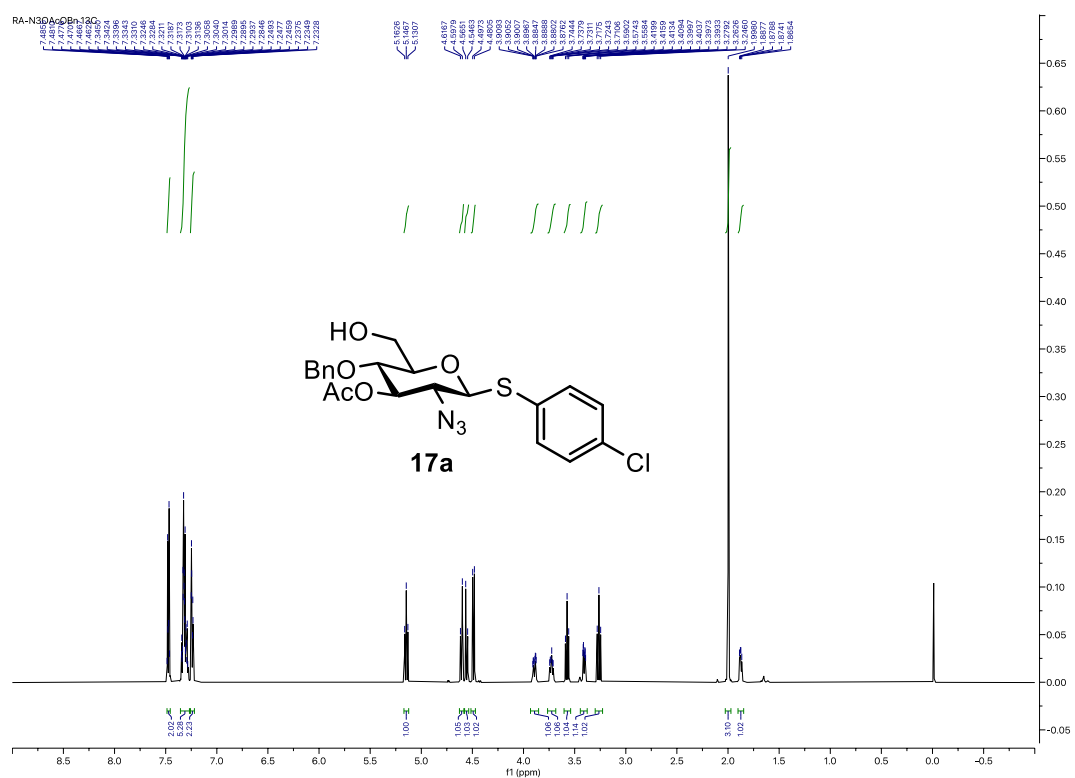


¹³C NMR

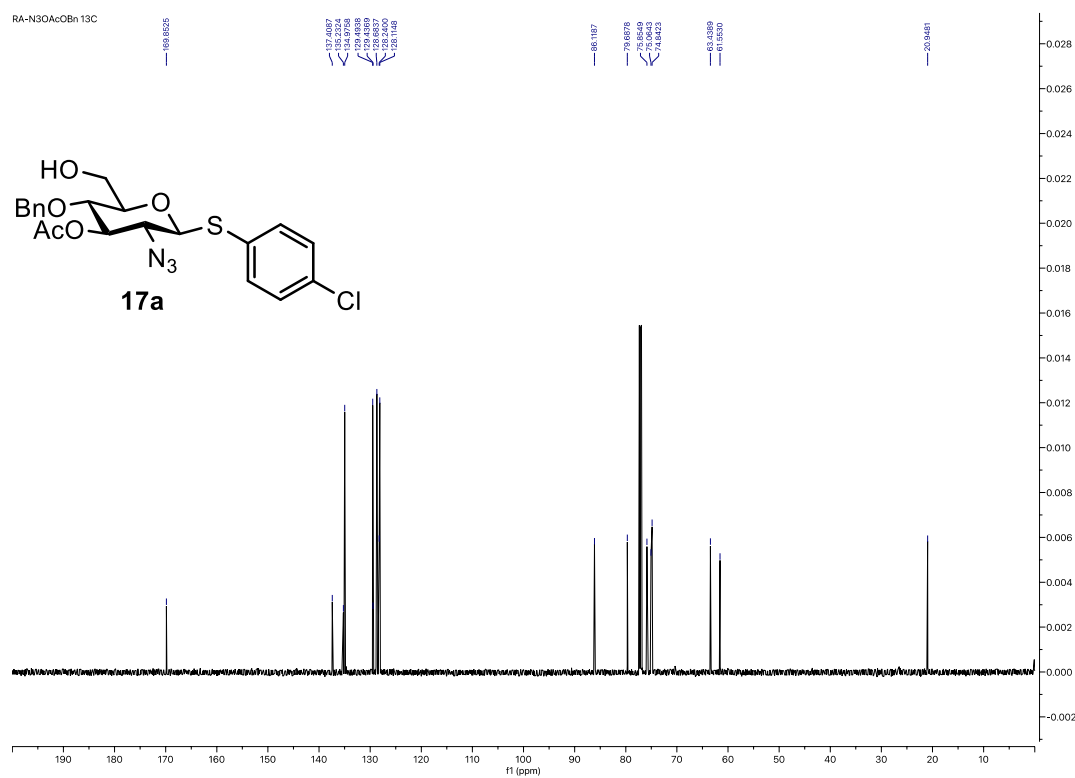


¹H NMR¹³C NMR

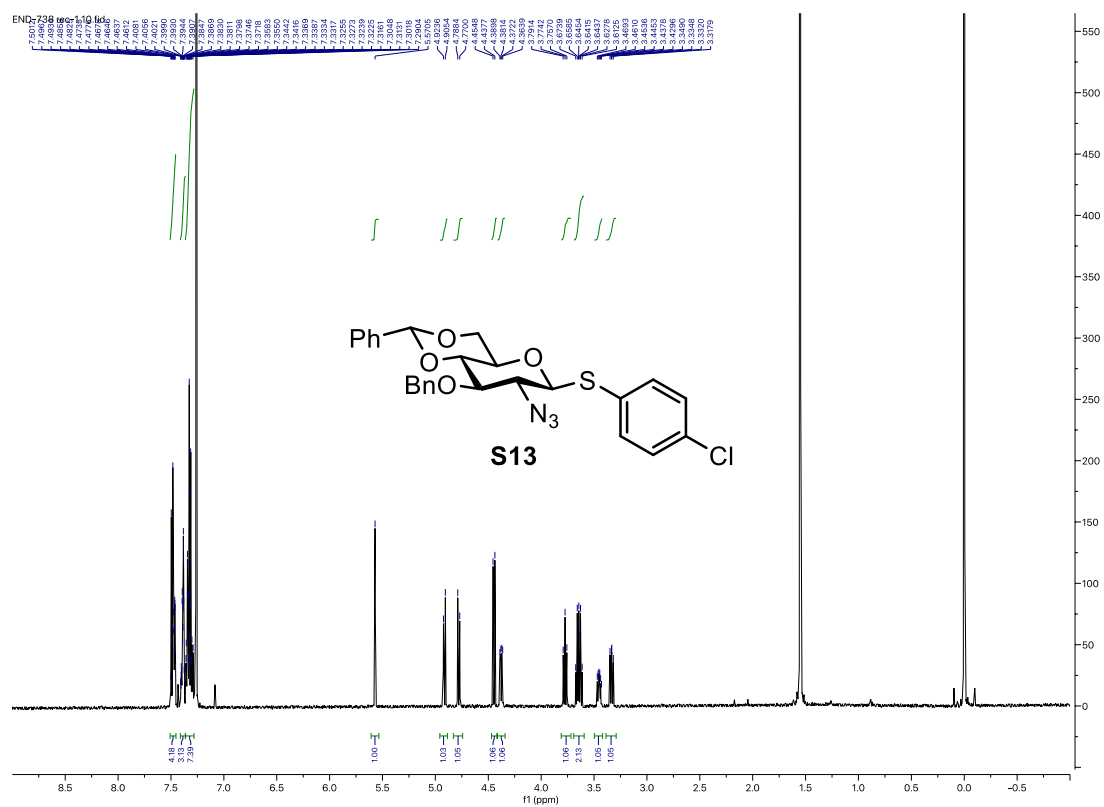
¹H NMR



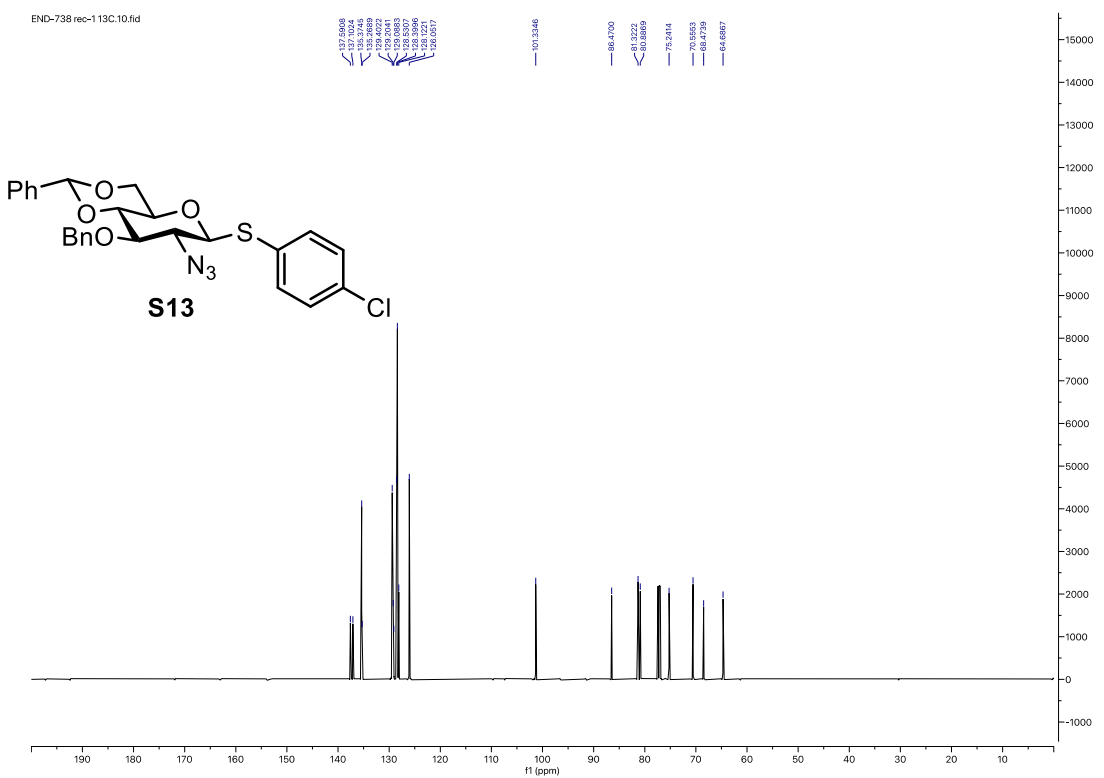
¹³C NMR

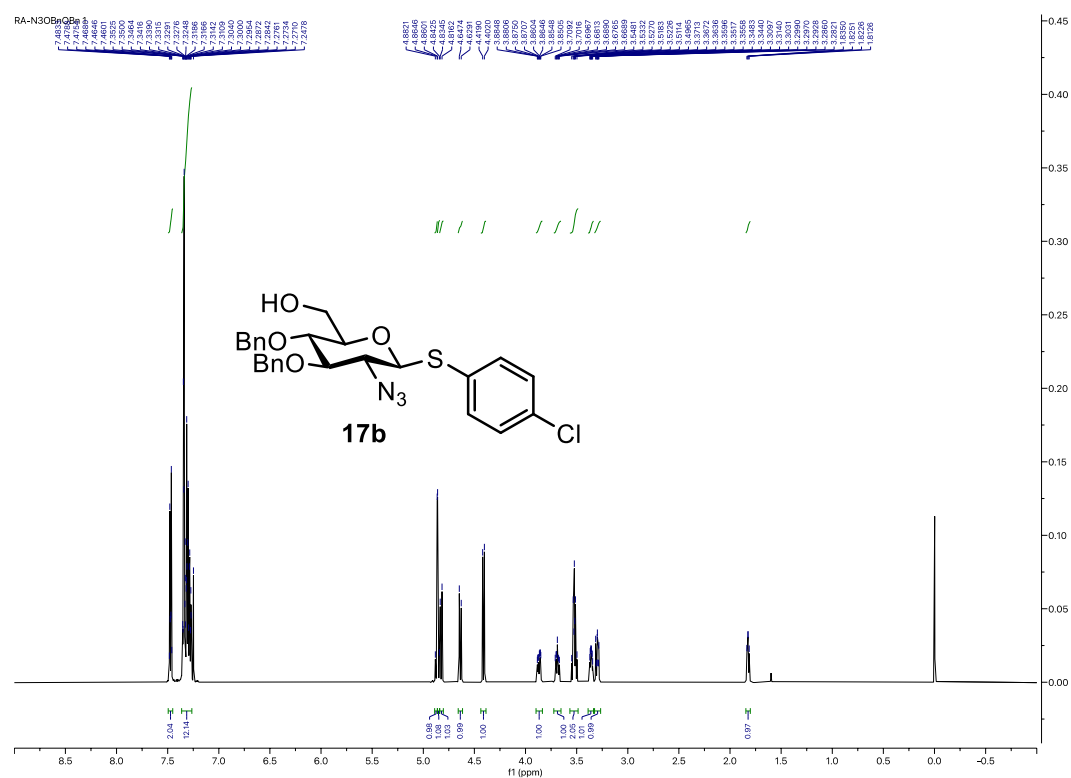
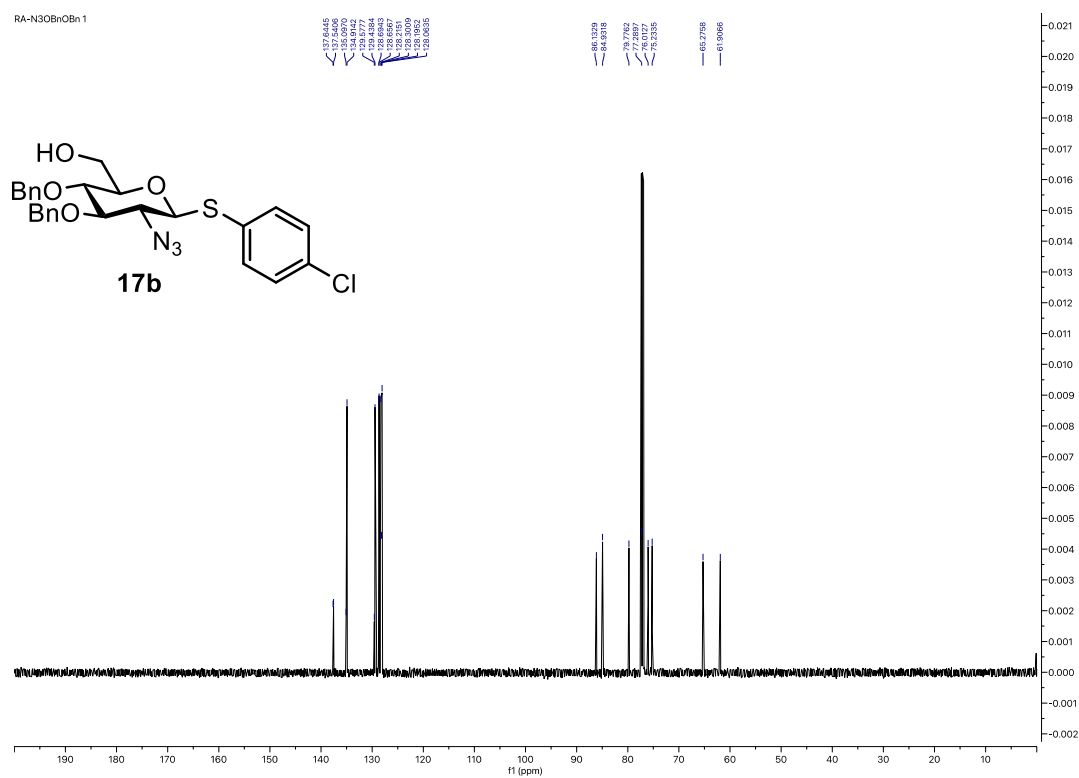


¹H NMR



¹³C NMR



¹H NMR¹³C NMR

RA-266 f1-6

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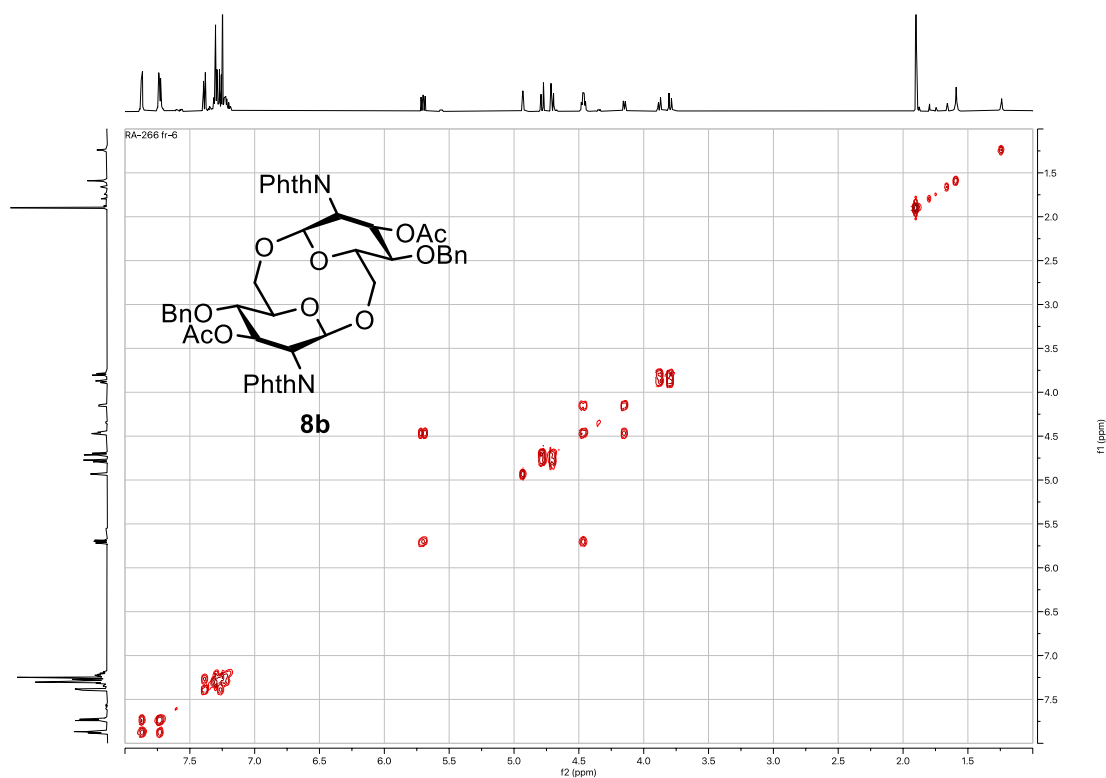
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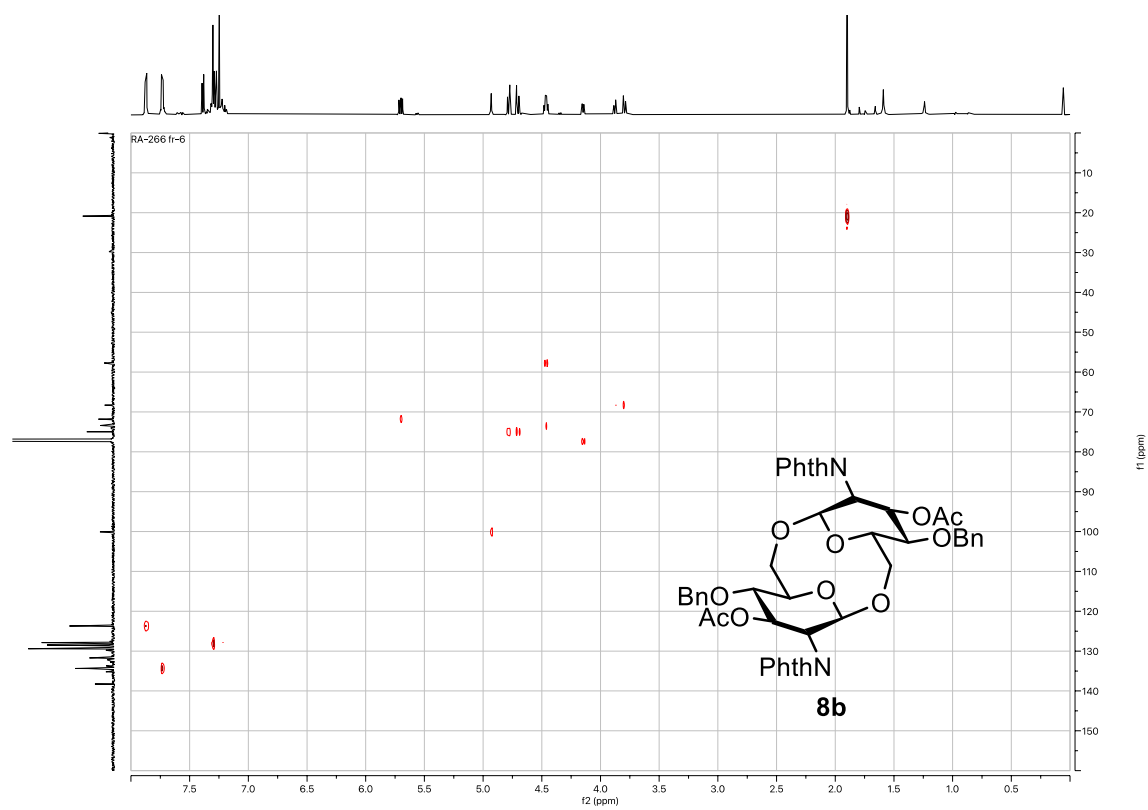
Chemical structure of compound **8b** is shown as an inset. The structure is a dimeric molecule with two phthalimide (PhthN) groups, two benzoyloxy (OBn) groups, and two acetoxy (OAc) groups.

¹H NMR spectrum (CDCl₃) of compound **8b** is shown. The x-axis is labeled f1 (ppm) and ranges from 190 to 10. The y-axis represents intensity from -0.00 to 0.012. Key peaks are labeled with their chemical shifts: 170.5397, 167.6949, 138.2550, 137.2977, 136.3974, 133.2625, 129.3974, 128.3974, 127.8168, 127.8625, 123.1047, 100.0860, 77.7777, 77.4942, 77.2114, 76.9286, 76.6458, 76.3630, 57.7022, and 20.8637.

^1H , ^1H -COSY



HMQC



9b

Chemical structure of **9b** is shown above the spectrum. The structure is a dimer of a substituted sugar derivative. It consists of two pyranose rings linked by a (1->3) glycosidic bond. The left ring has a PhthN group at C2, a BnO group at C3, and an AcO group at C4. The right ring has a PhthN group at C2, a BnO group at C3, and an AcO group at C4. The right ring is also linked to a 4-chlorophenyl group via a sulfur atom at C1.

¹H NMR spectrum (CDCl₃) of compound **9b**. The x-axis represents the chemical shift in ppm (f1), ranging from 0 to 8.5. The y-axis represents the intensity. The spectrum shows several peaks corresponding to the structure of **9b**.

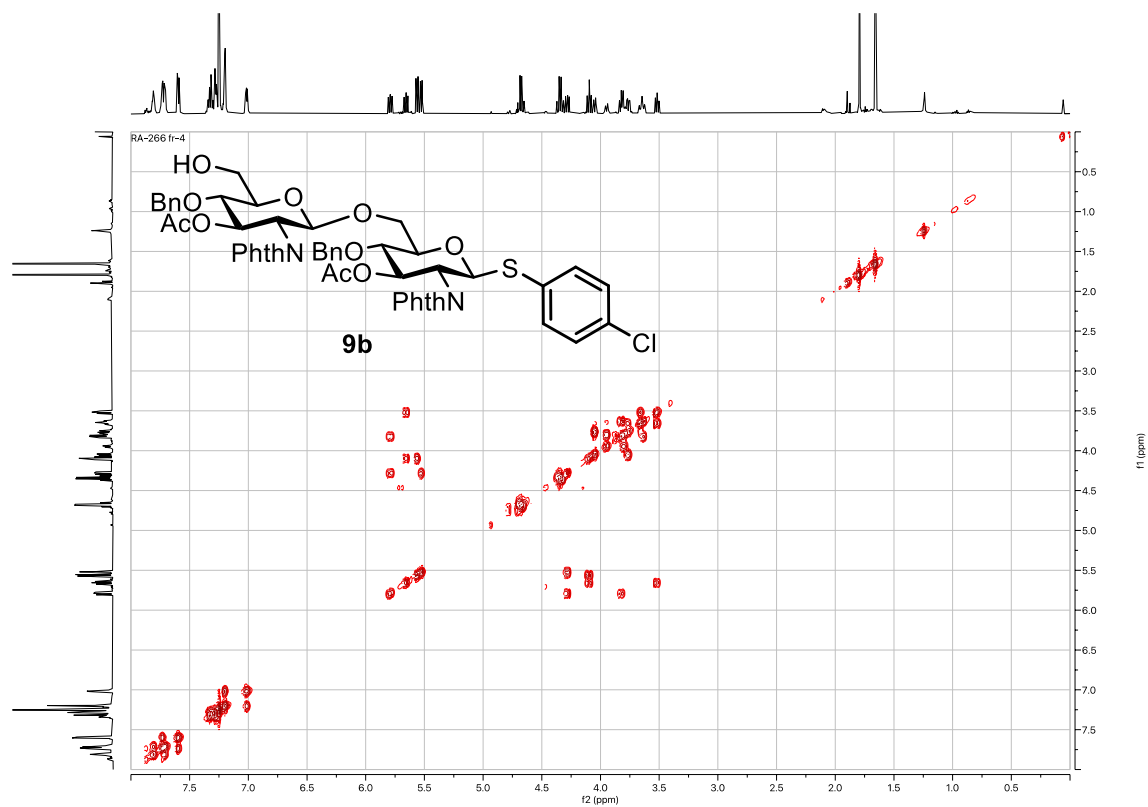
Key peaks and assignments:

- Aromatic protons (PhthN and 4-chlorophenyl): 7.0 - 7.8 ppm.
- Anomeric protons: 4.5 - 5.5 ppm.
- Sugar protons: 3.5 - 4.5 ppm.
- Aliphatic protons (BnO and AcO): 1.5 - 2.5 ppm.
- Solvent peak (CDCl₃): 7.26 ppm.

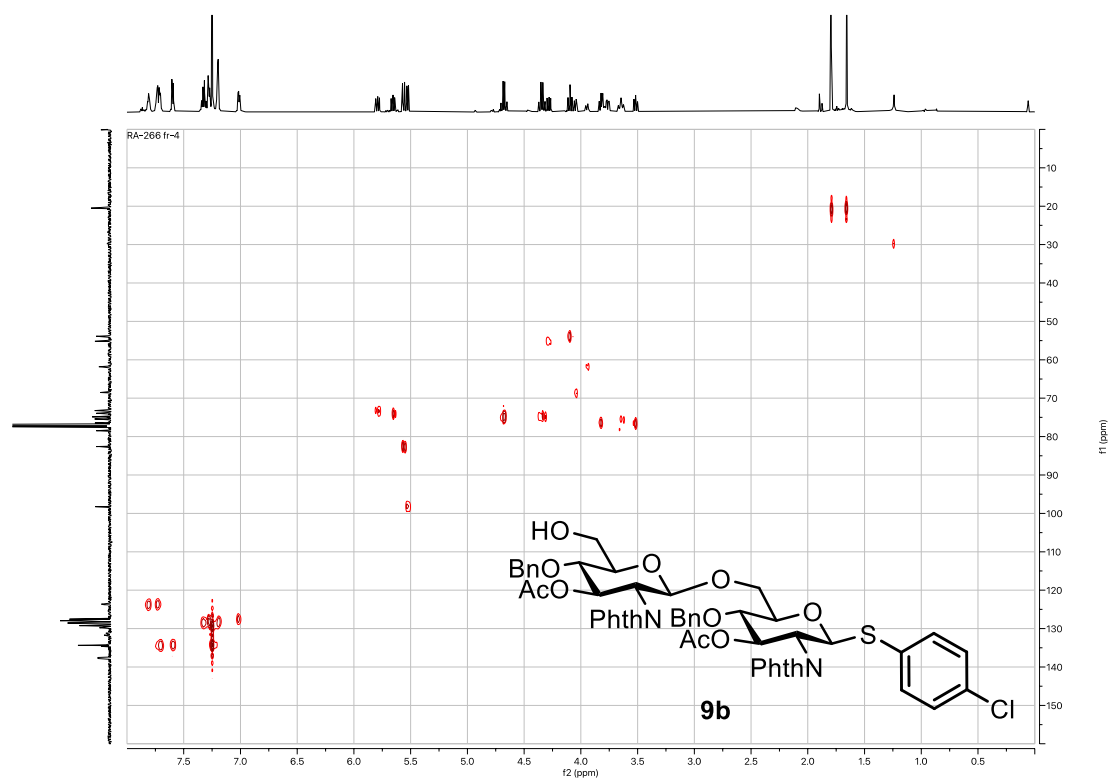
Integration values are provided below the baseline:

- 2.19, 4.78, 2.14, 2.89, 3.90, 4.10, 2.15
- 1.00, 1.00, 1.10, 1.10, 1.05
- 1.00, 1.00, 1.05, 1.05, 1.09, 2.27, 2.23, 1.07
- 0.05, 2.80, 3.04

^1H , ^1H -COSY



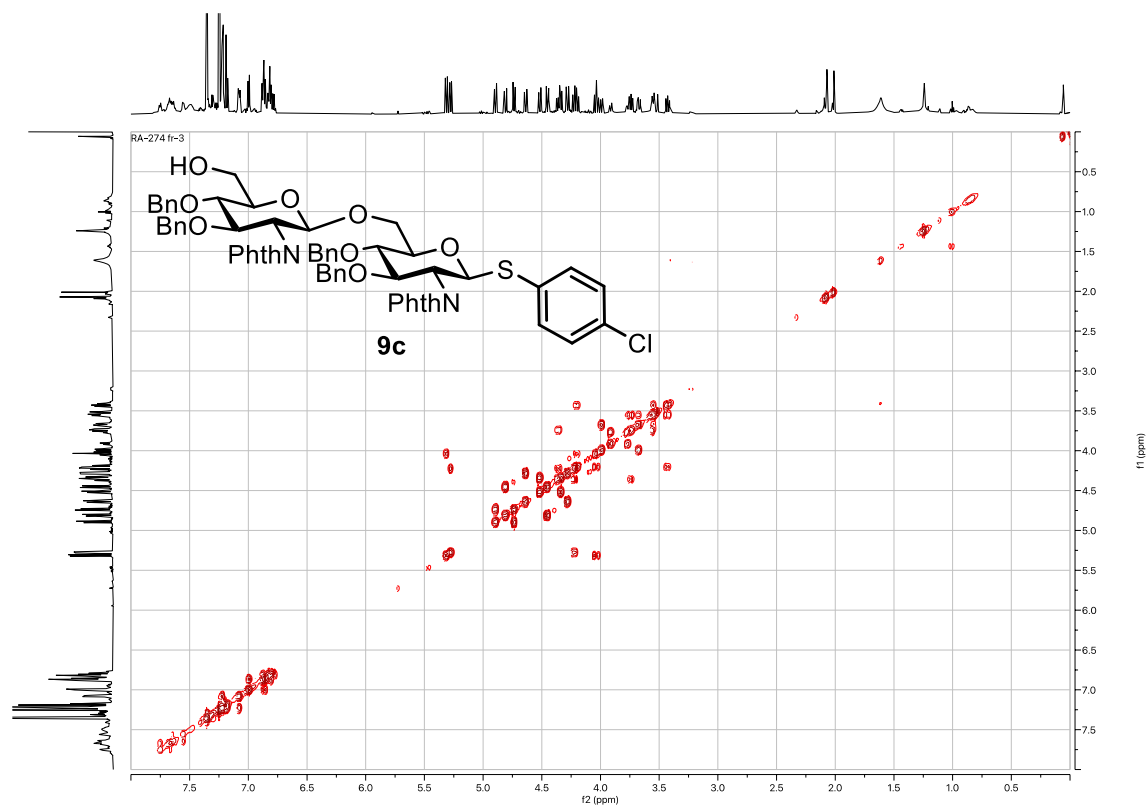
HMQC



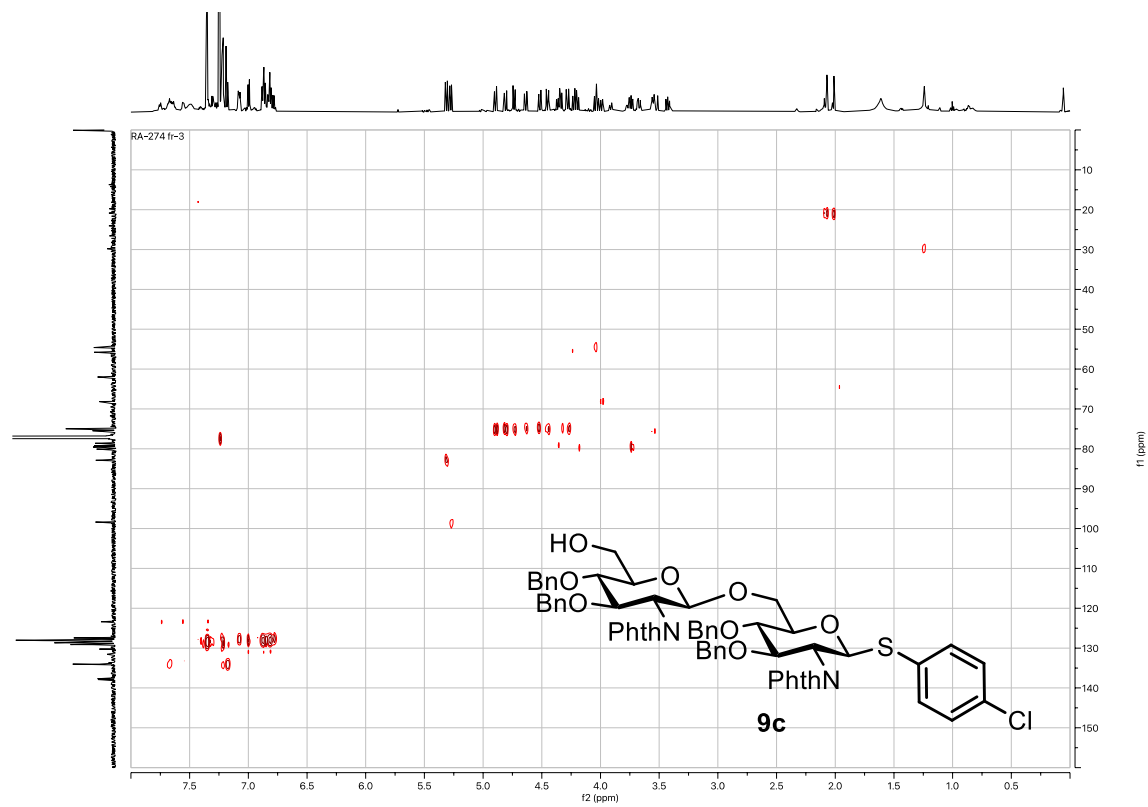
Chemical structure of compound **9c** is shown above the spectrum. The structure is a dimeric molecule consisting of two 2,3,6-tri-O-benzoyl-4-O-(4-chlorophenylthio)- α -D-glucopyranoside units linked by a 1,4-glycosidic bond. The left sugar has a PhthN group at C1, and the right sugar has a PhthN group at C1 and a 4-chlorophenylthio group at C4.

[illegible]

^1H , ^1H -COSY



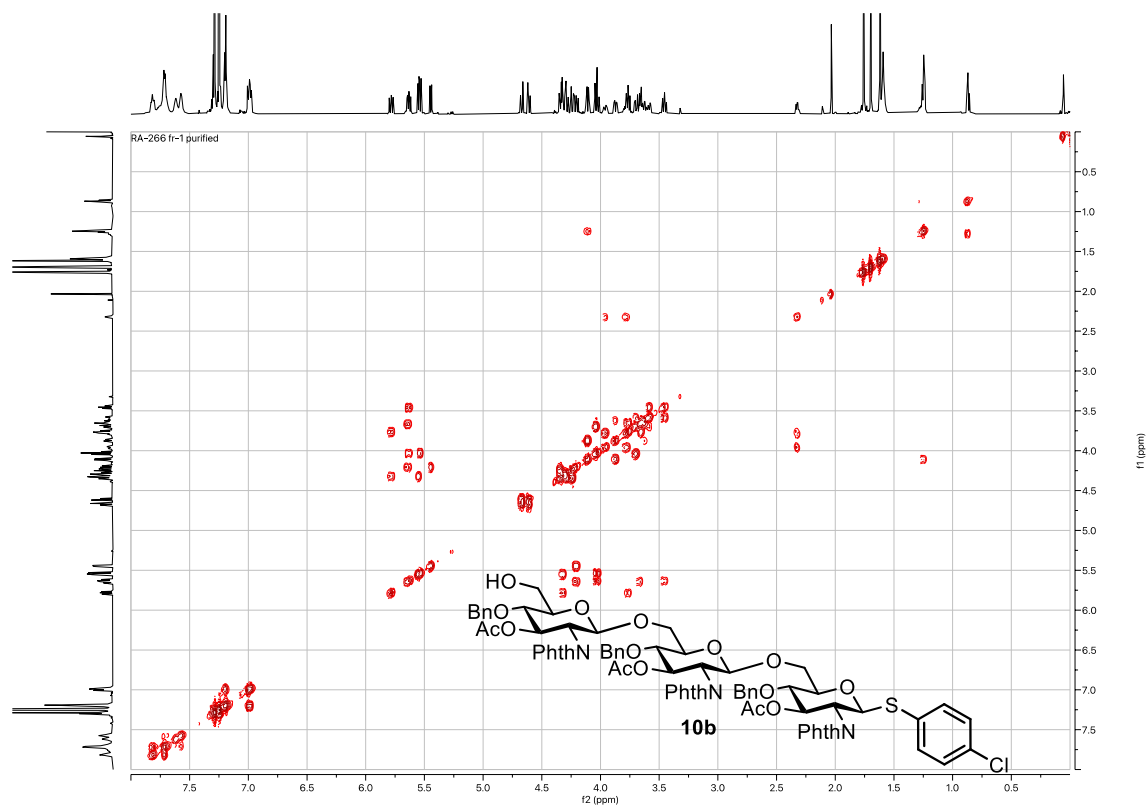
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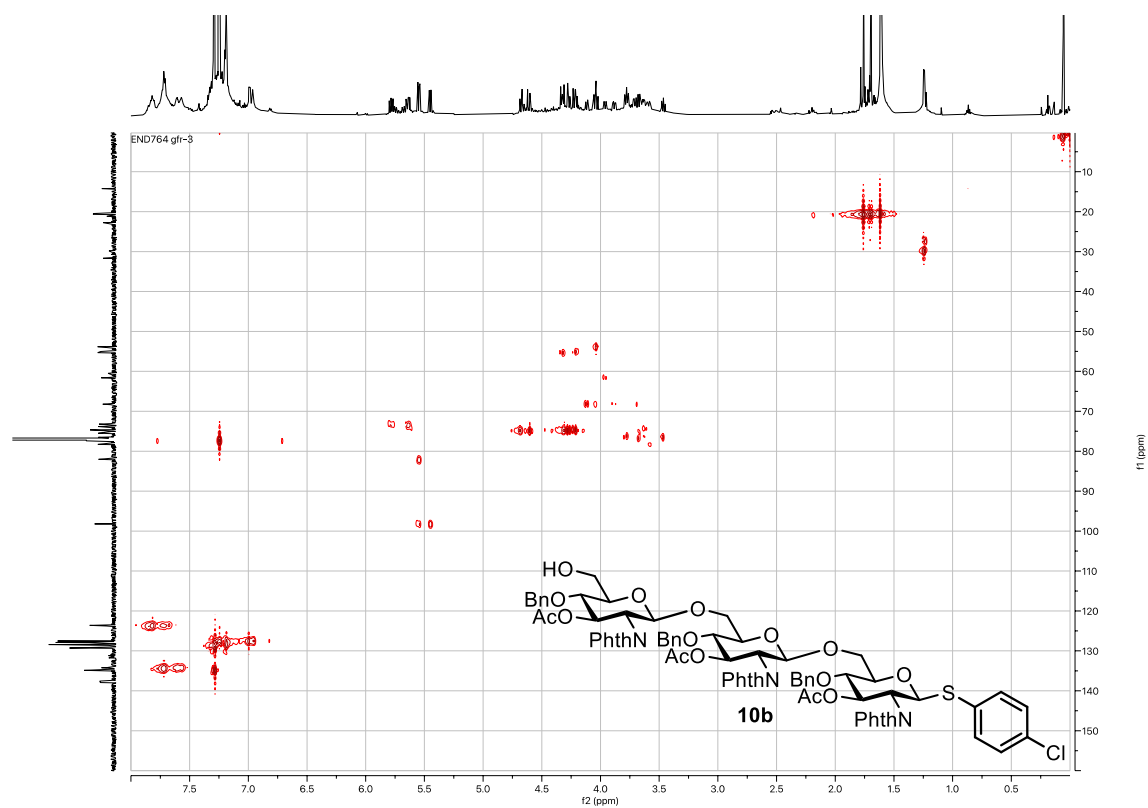
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RA-266 fr-1 purified

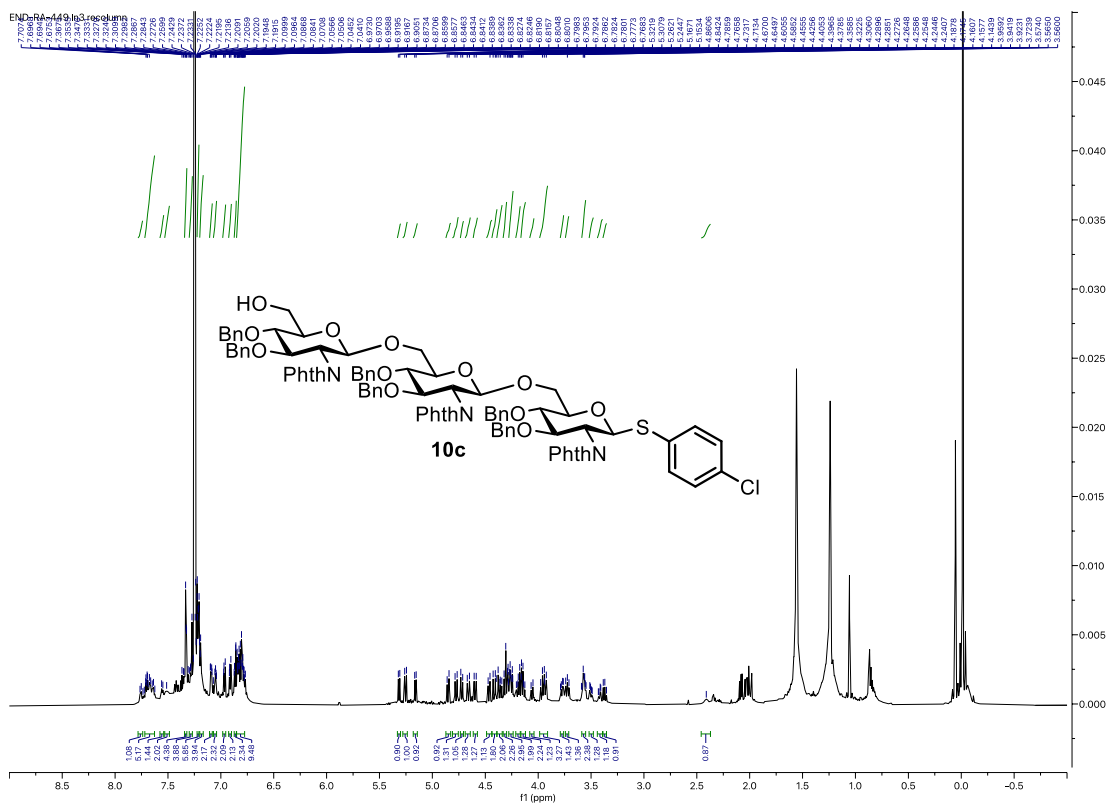
^1H , ^1H -COSY



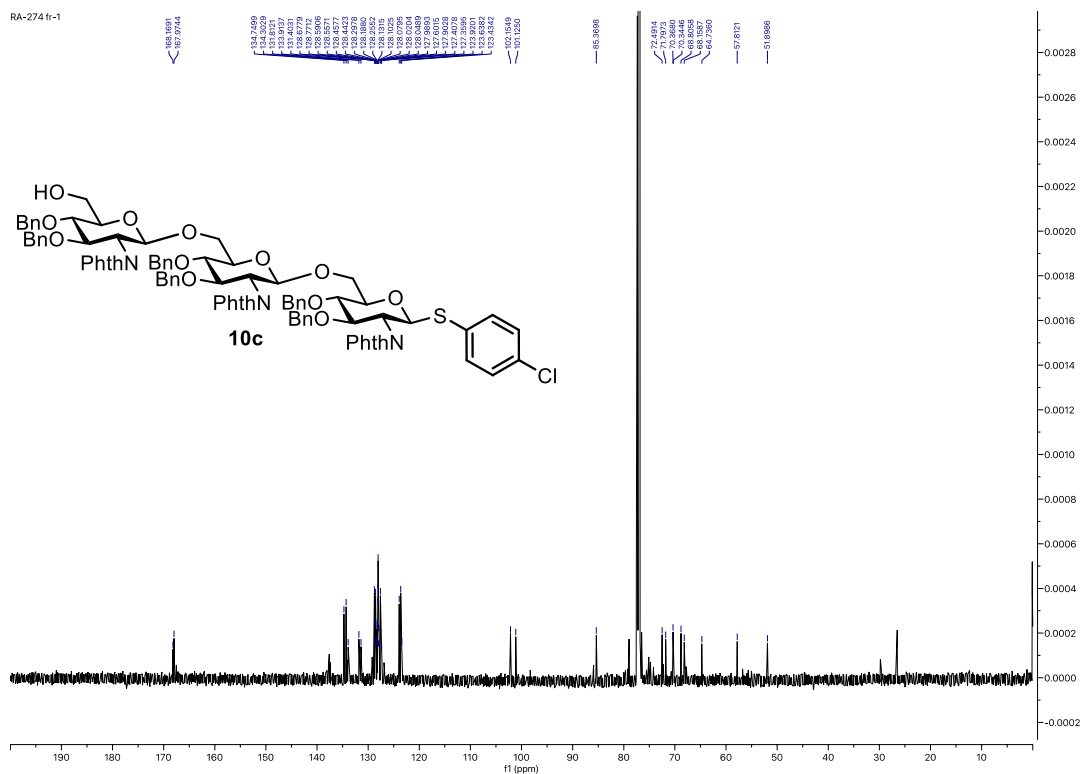
HMQC



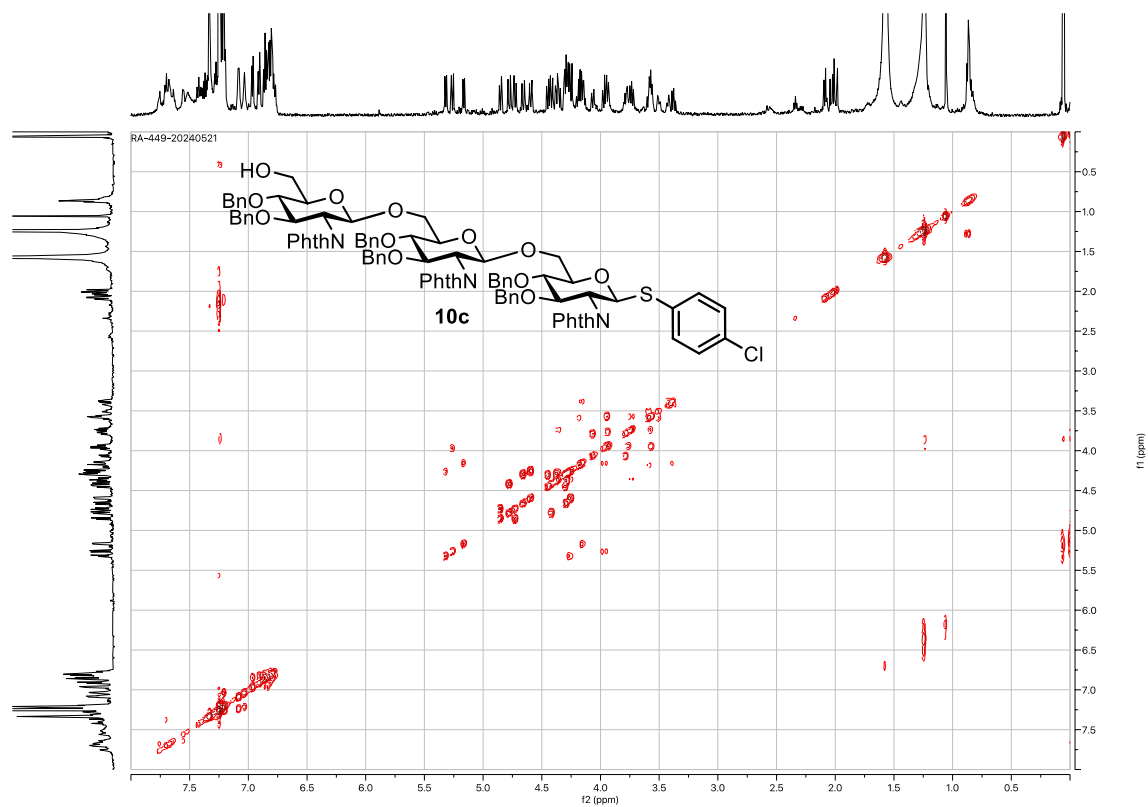
¹H NMR



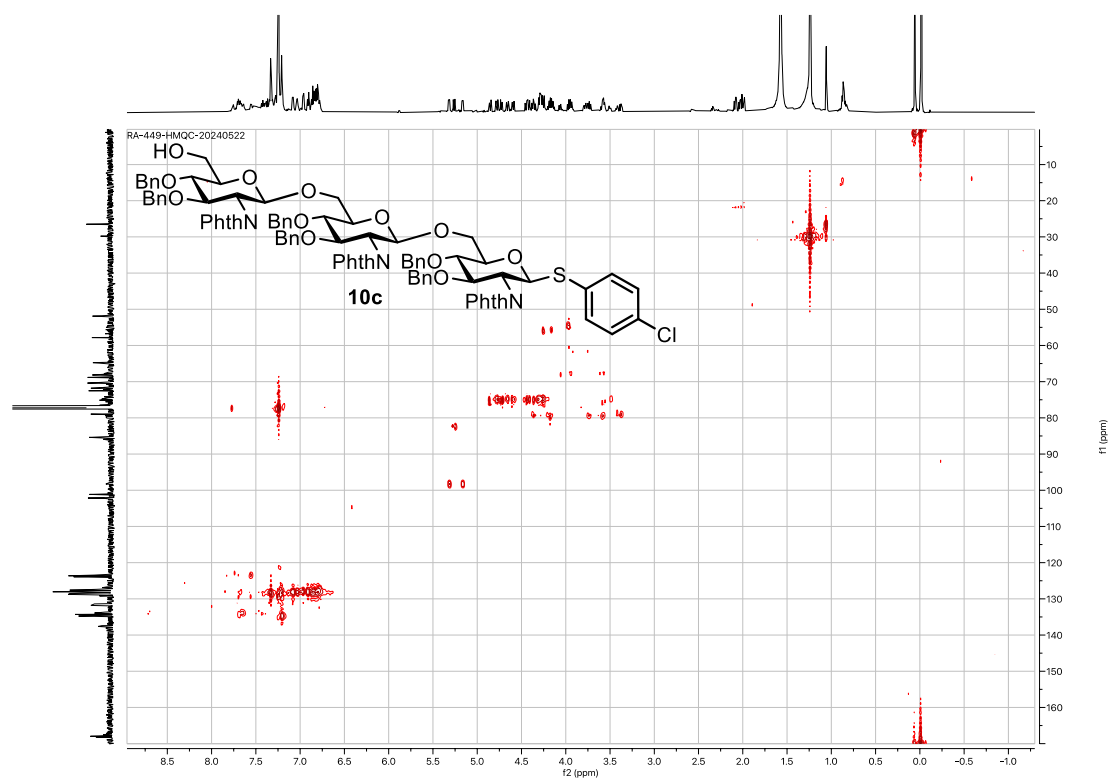
¹³C NMR

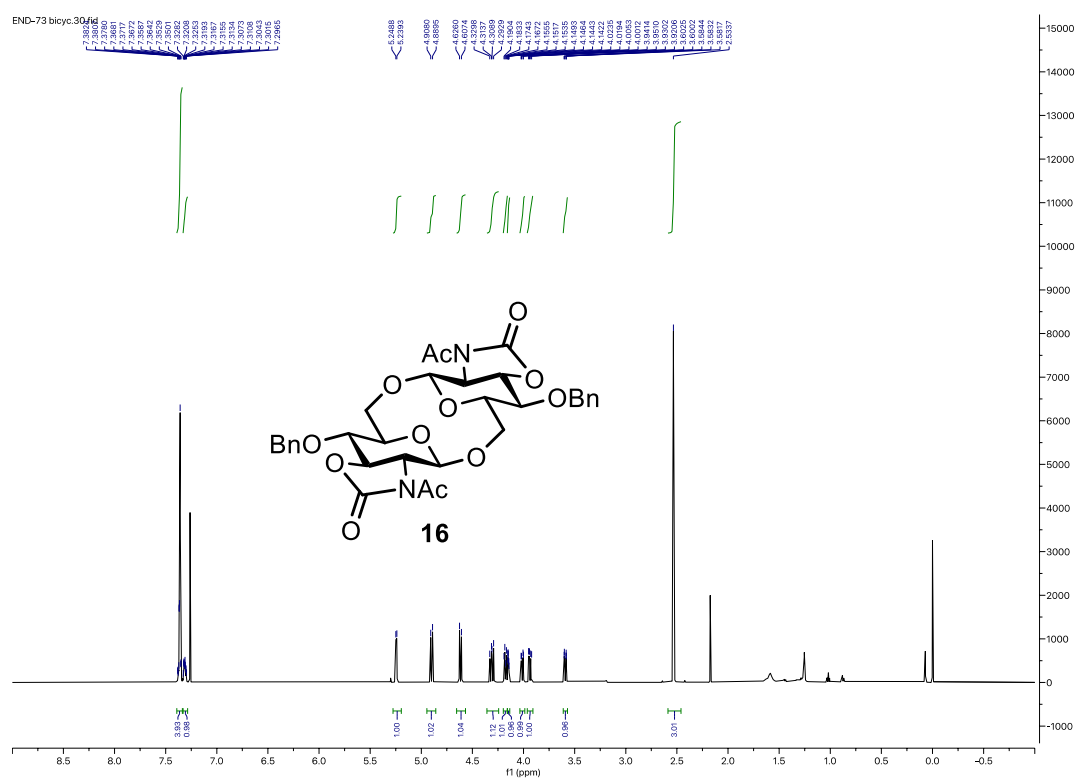
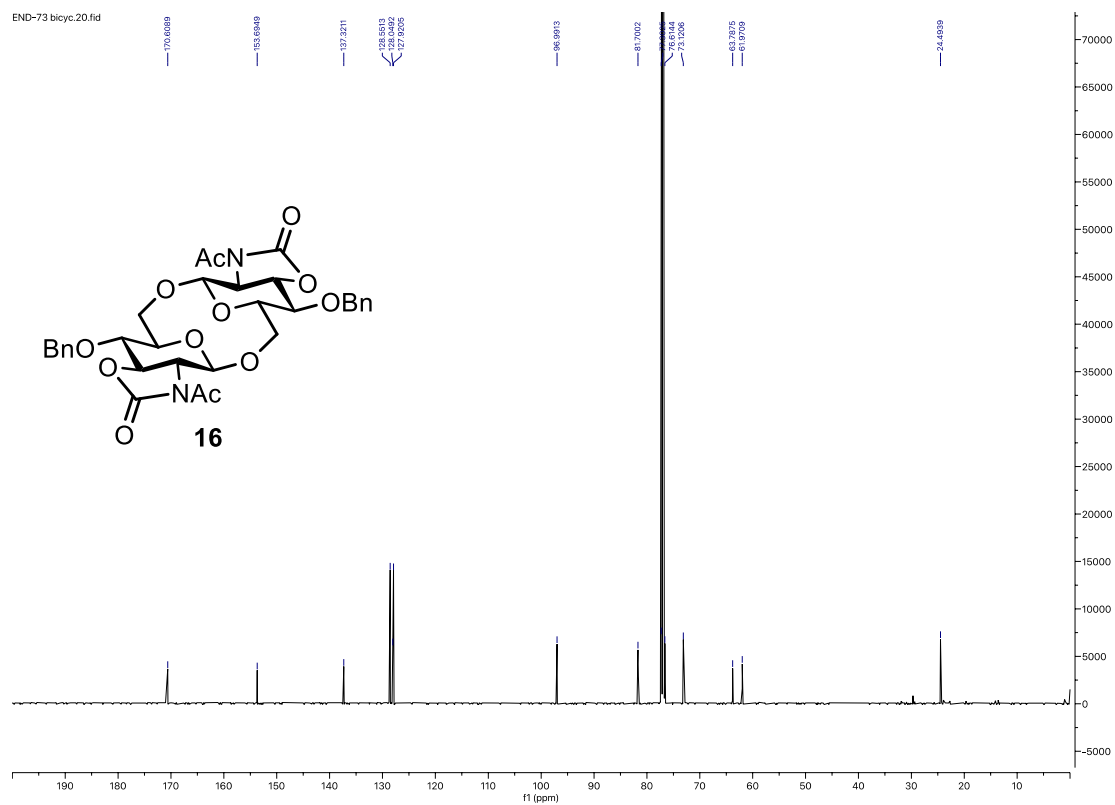


^1H , ^1H -COSY

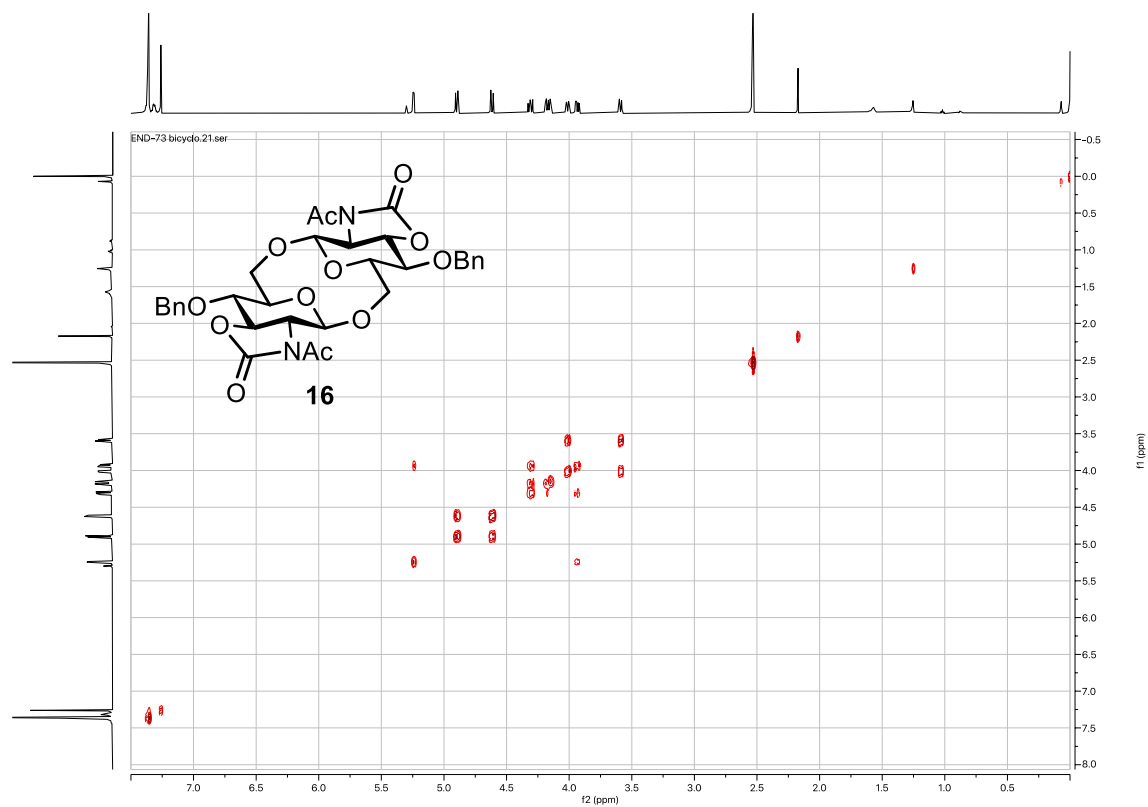


HMQC

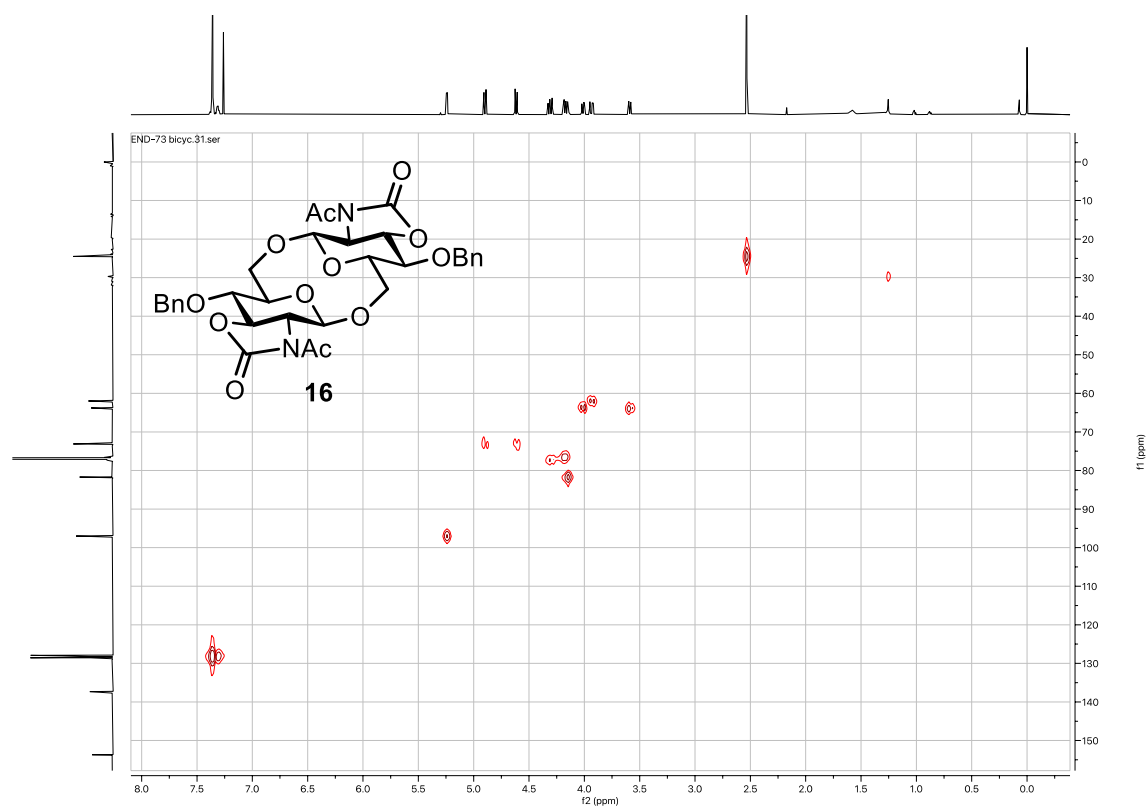


¹H NMR¹³C NMR

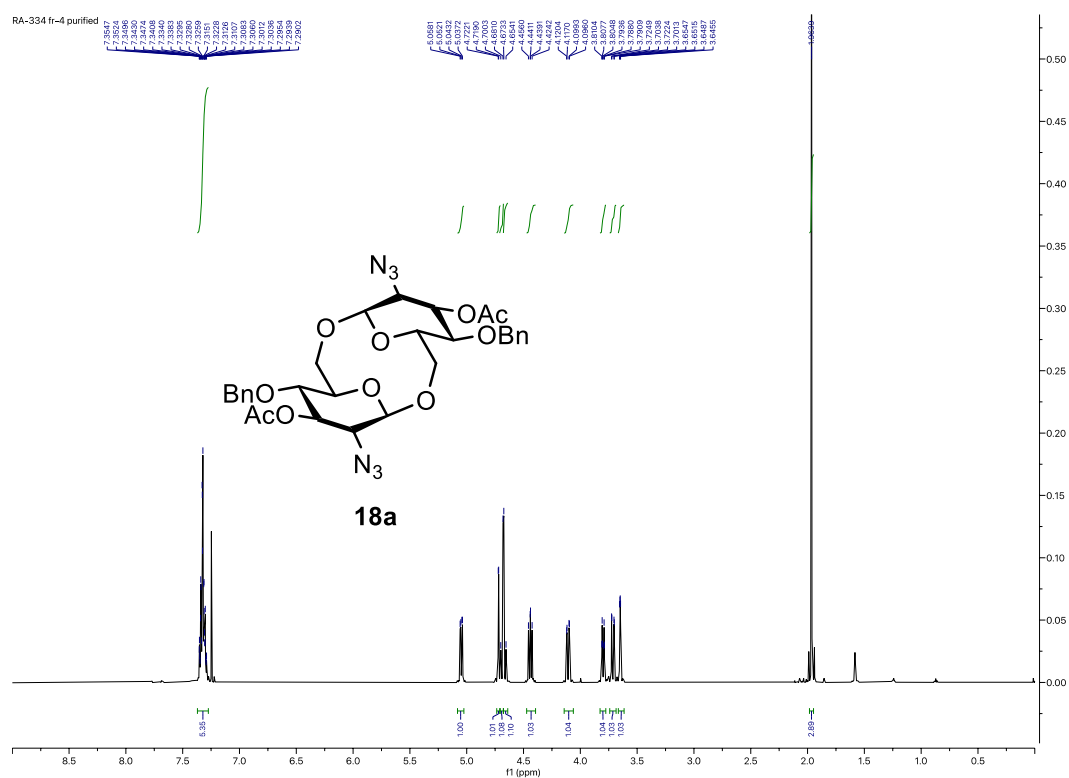
^1H , ^1H -COSY



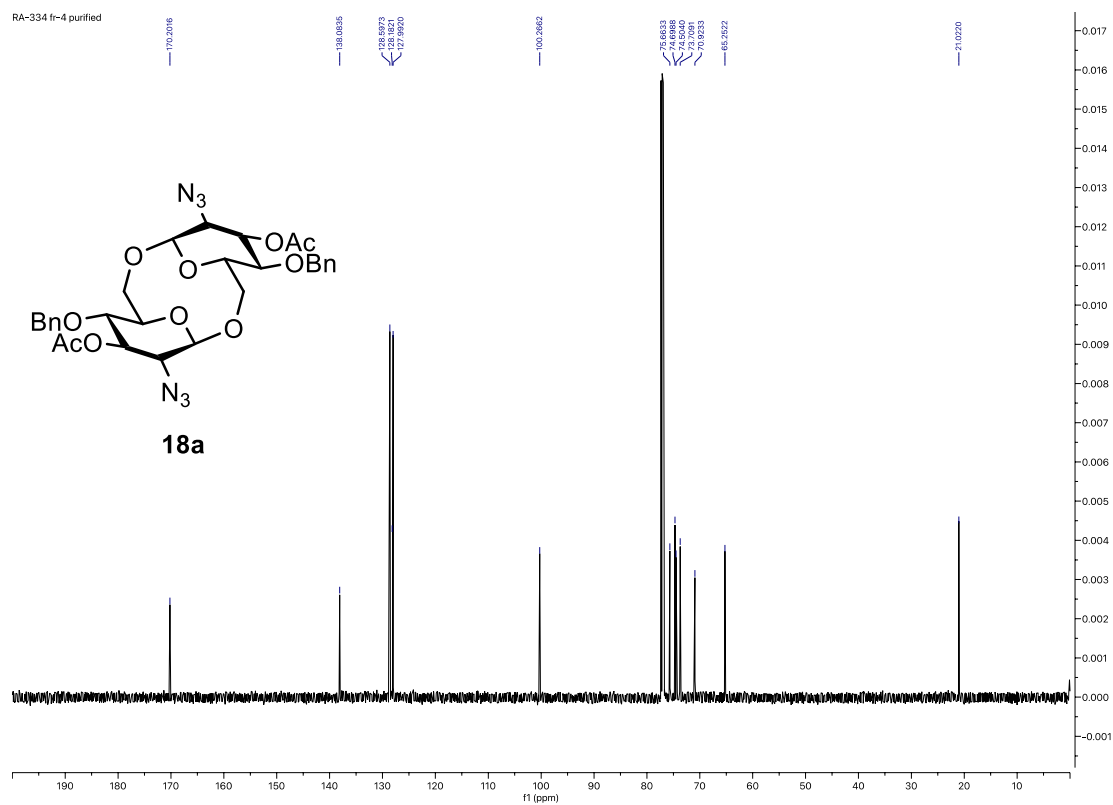
^{13}C NMR



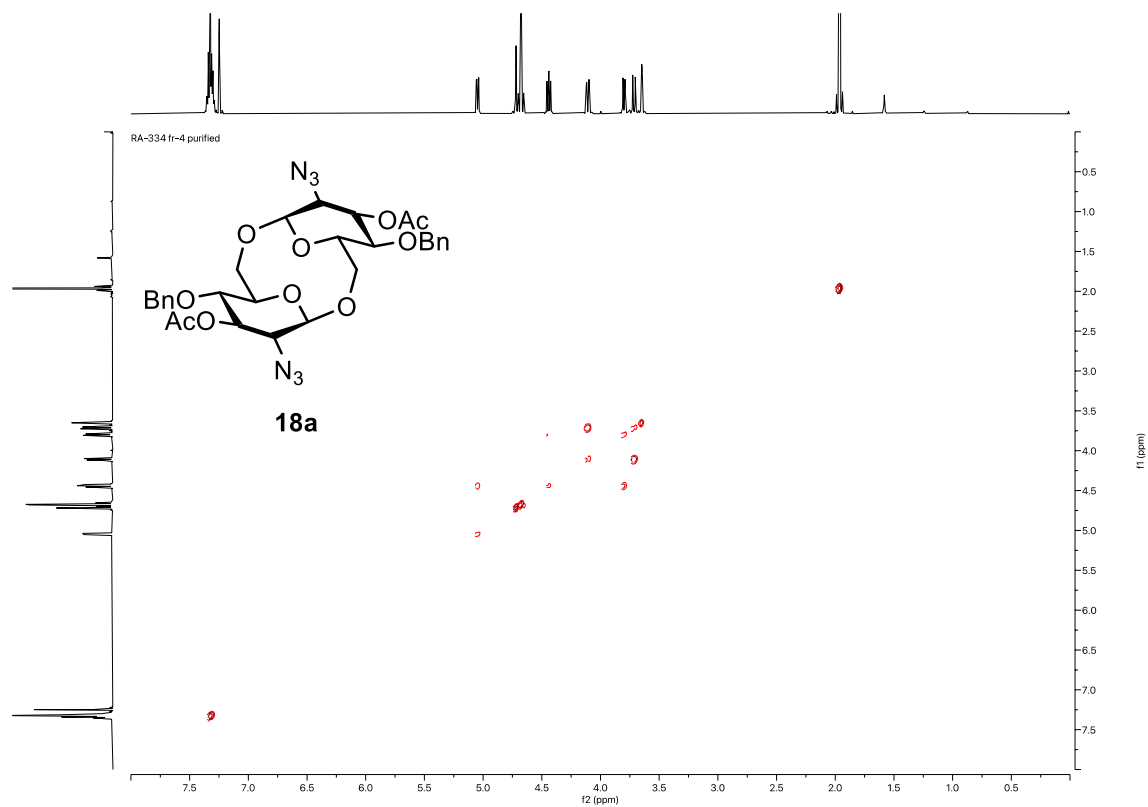
¹H NMR



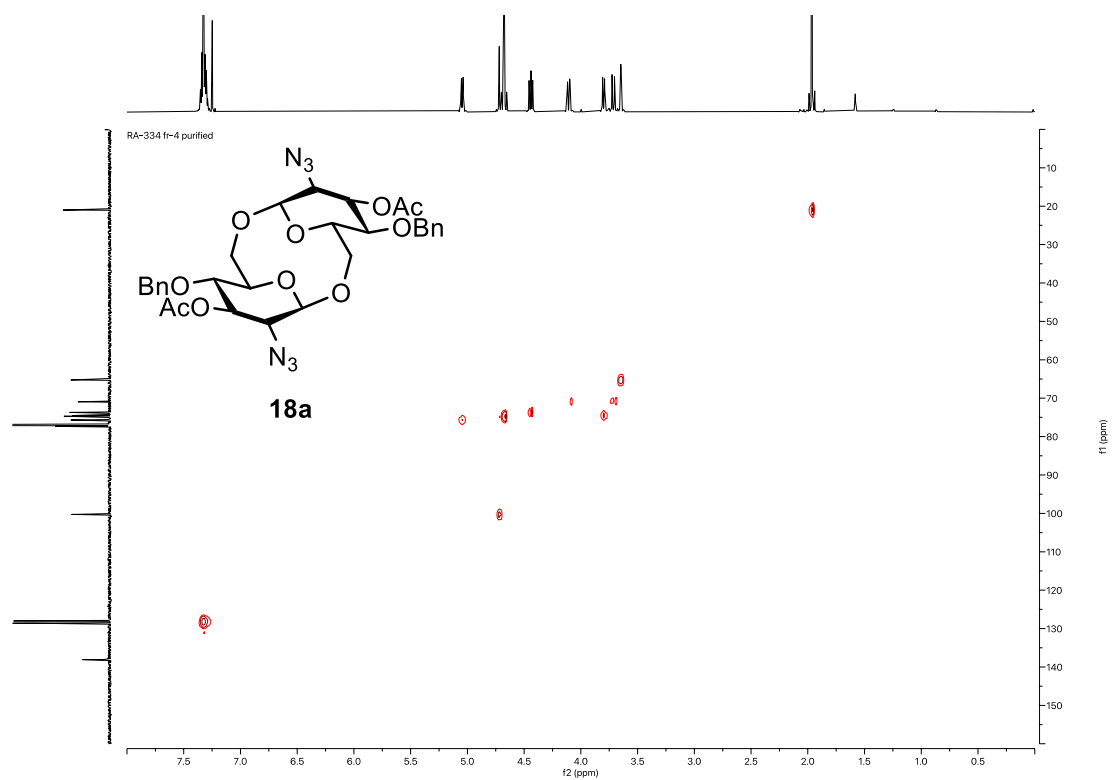
¹³C NMR



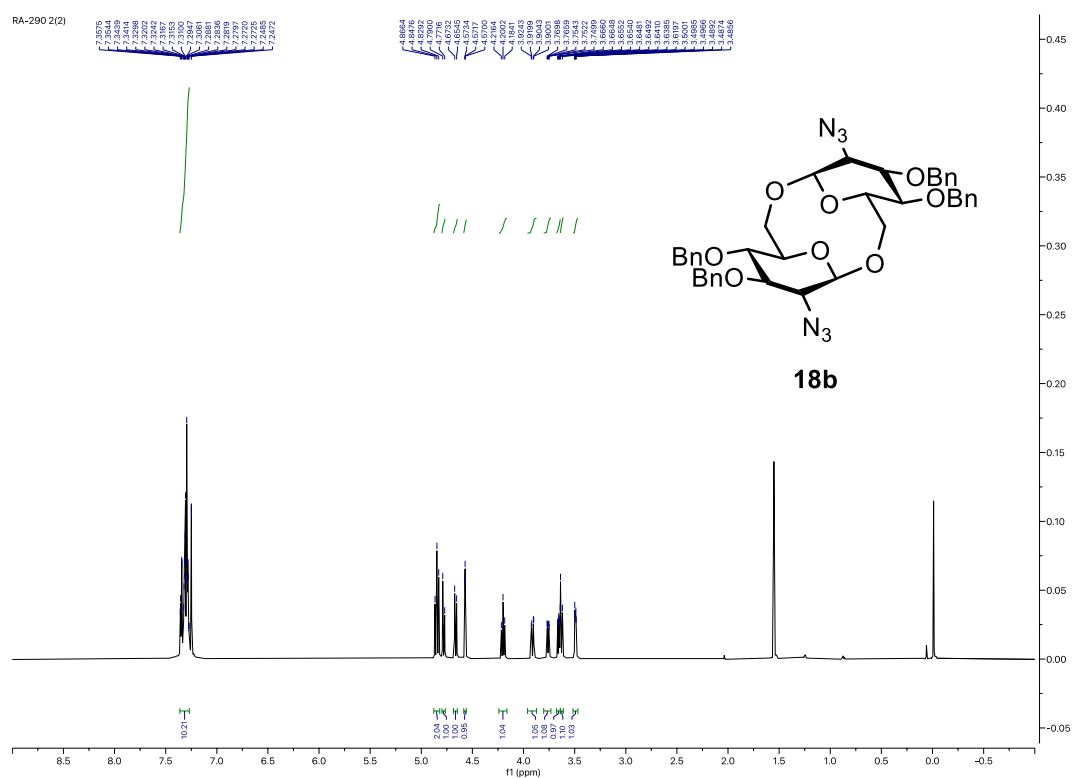
^1H , ^1H -COSY



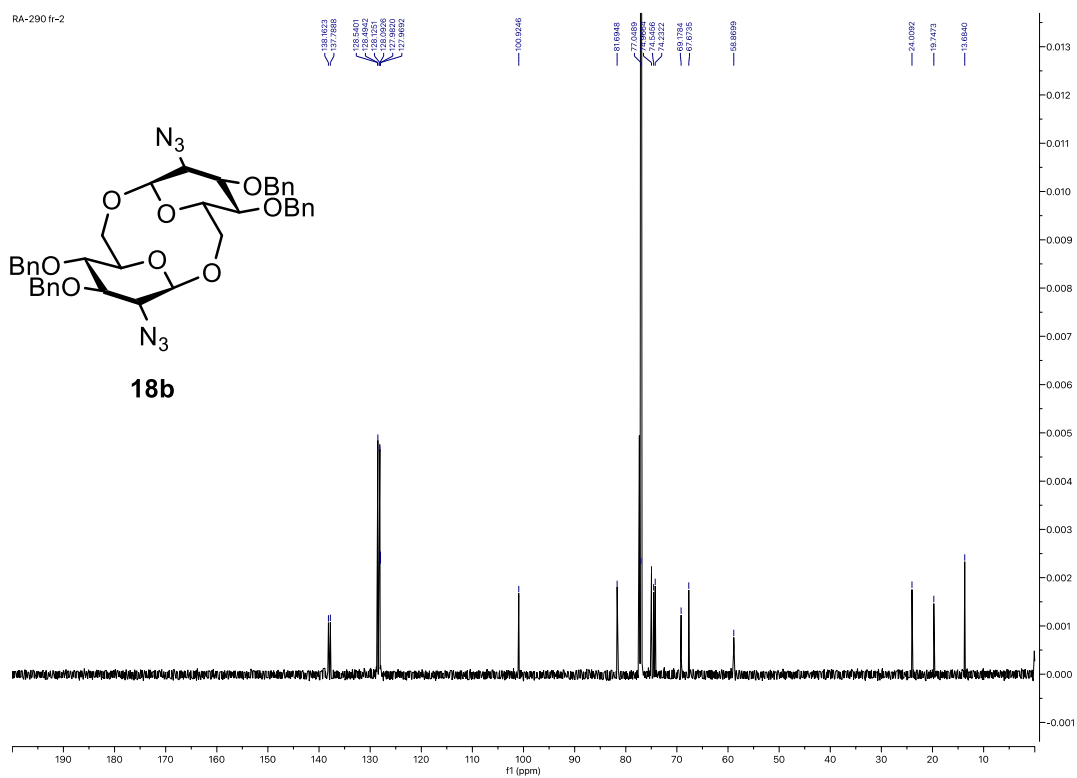
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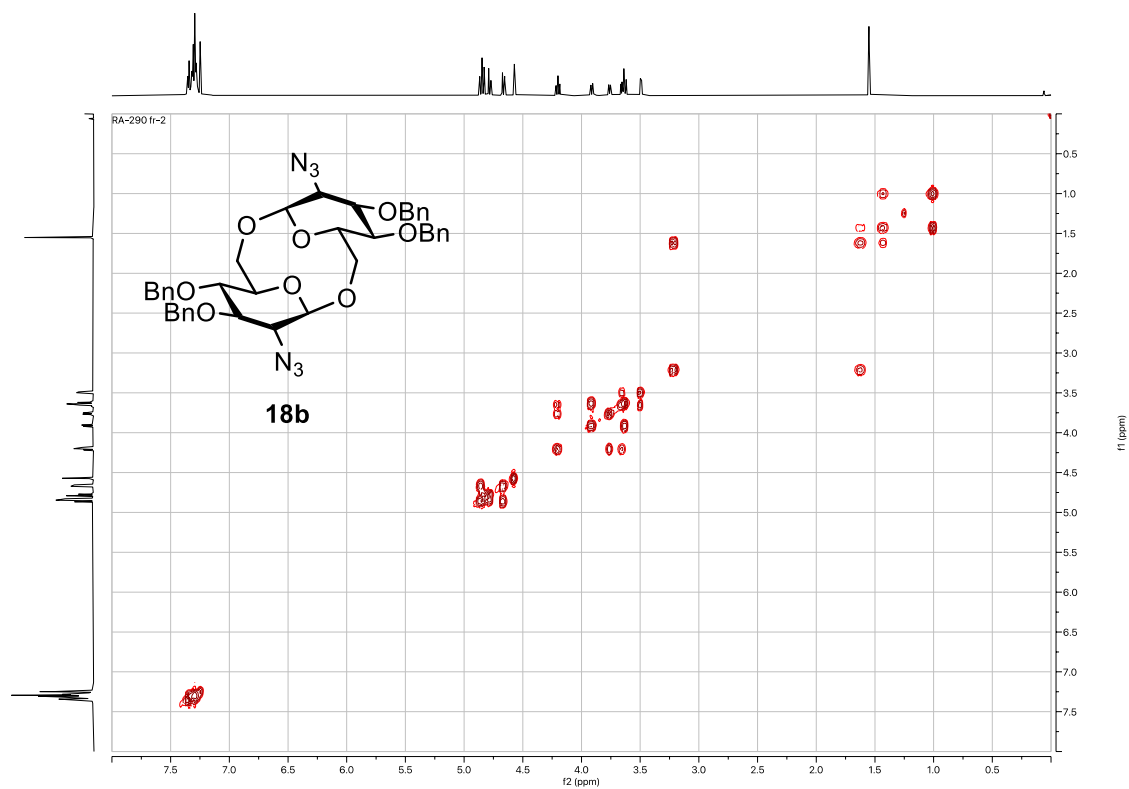
¹H NMR



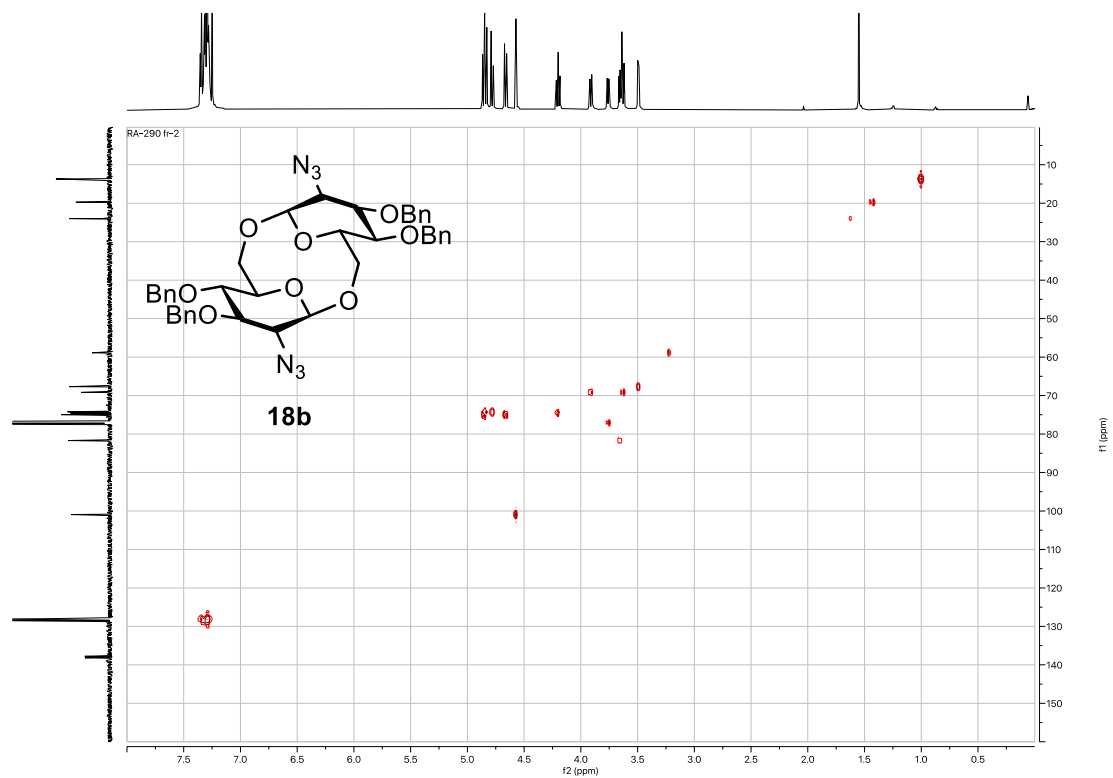
¹³C NMR



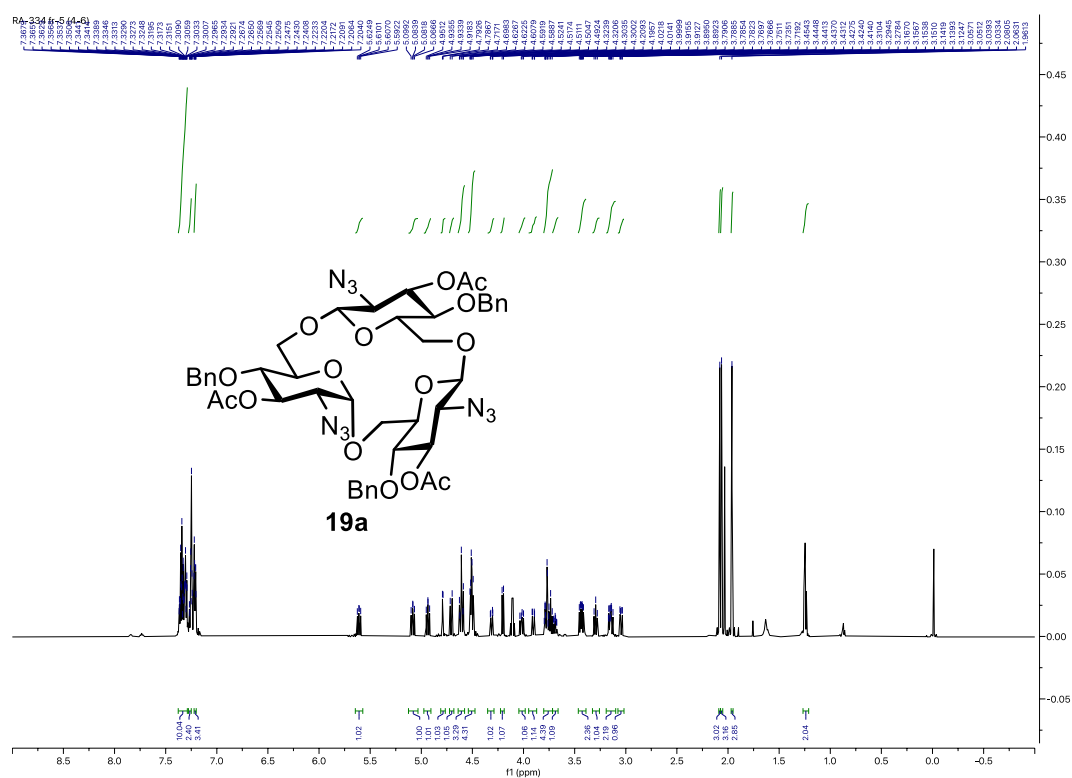
^1H , ^1H -COSY



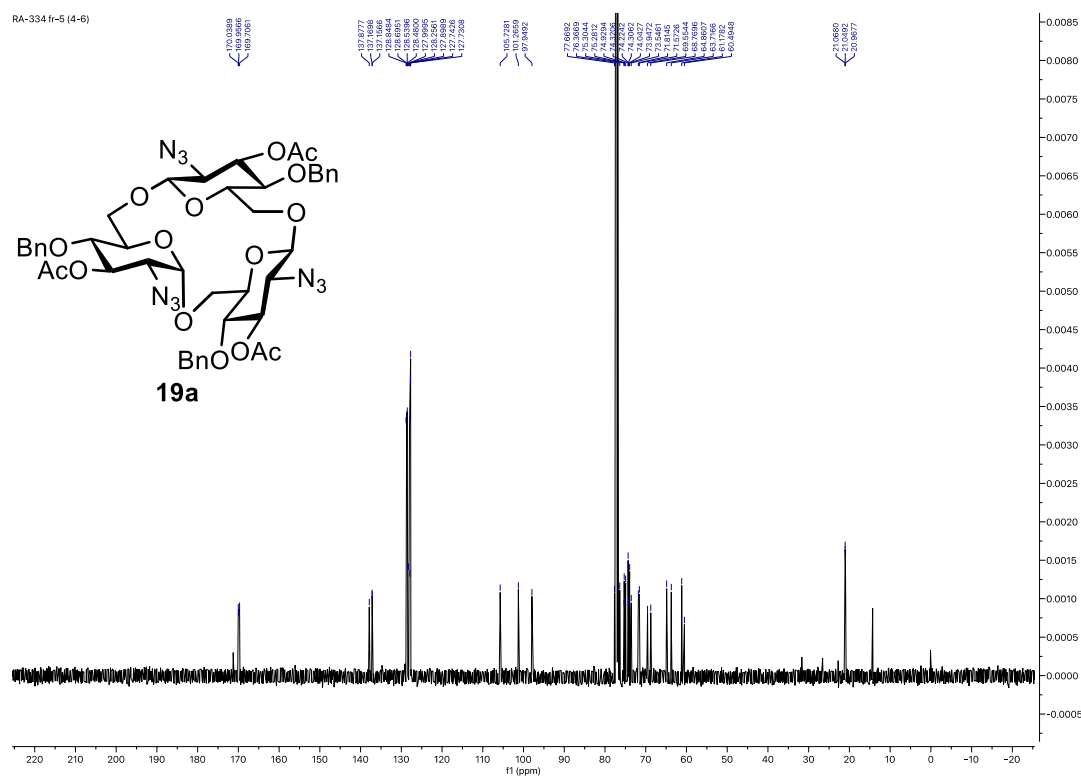
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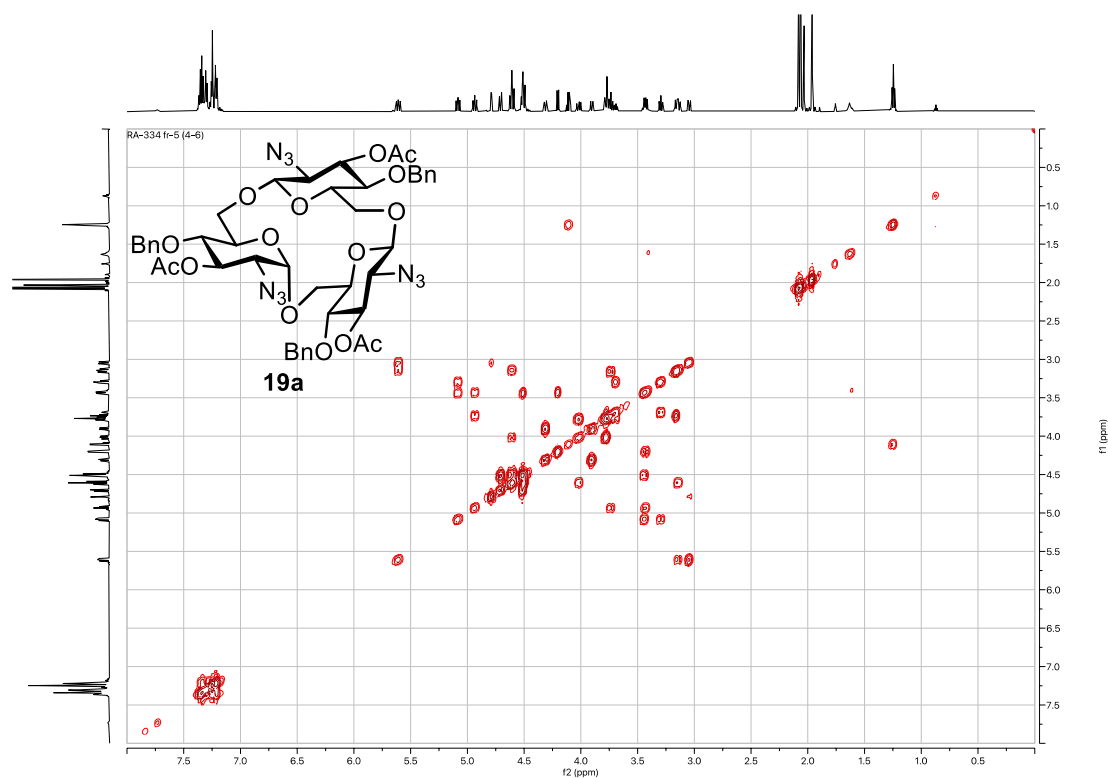
¹H NMR



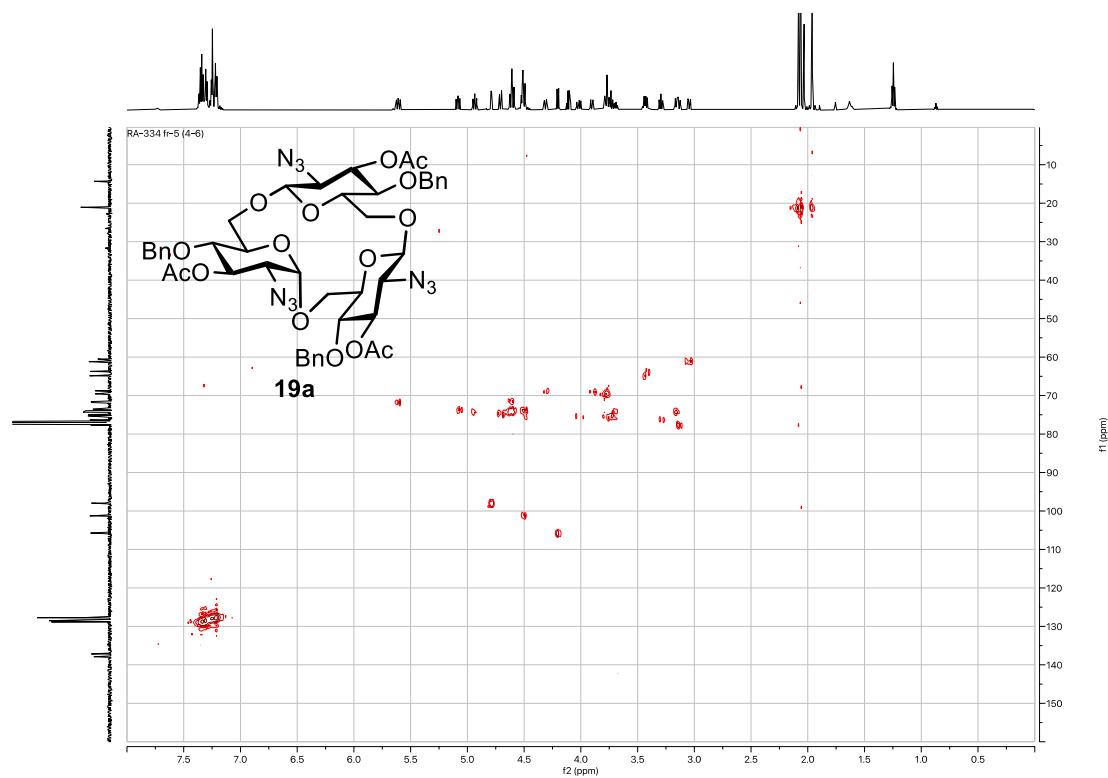
¹³C NMR

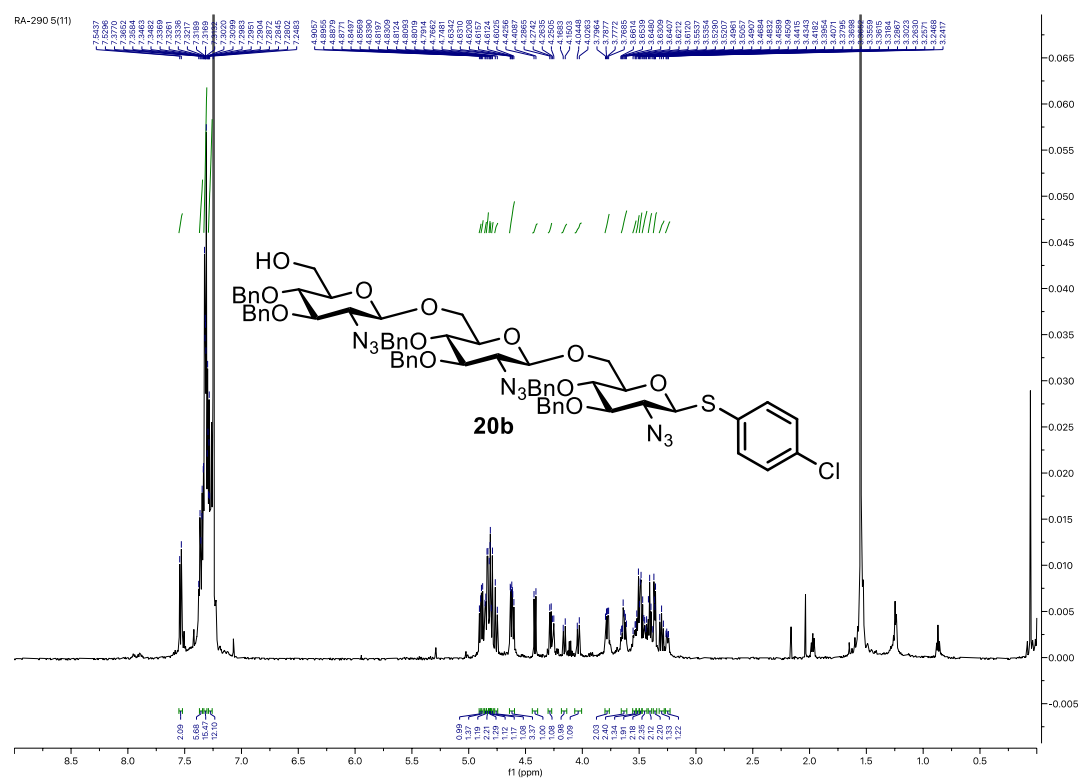
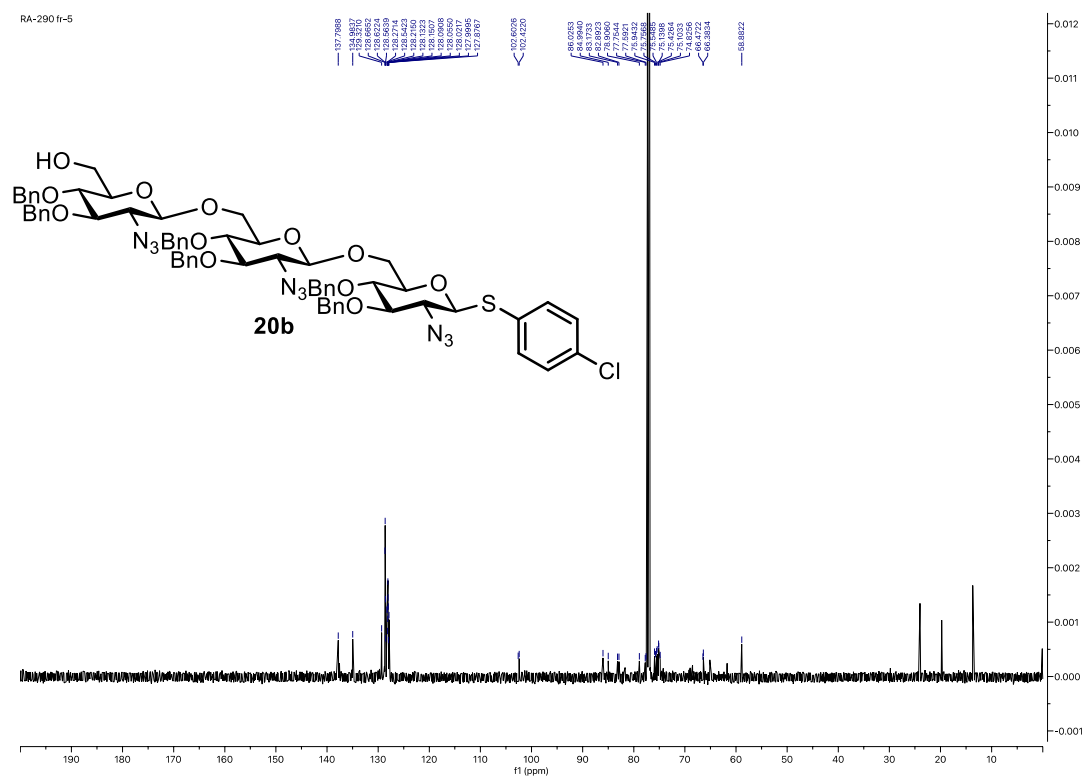


^1H , ^1H -COSY

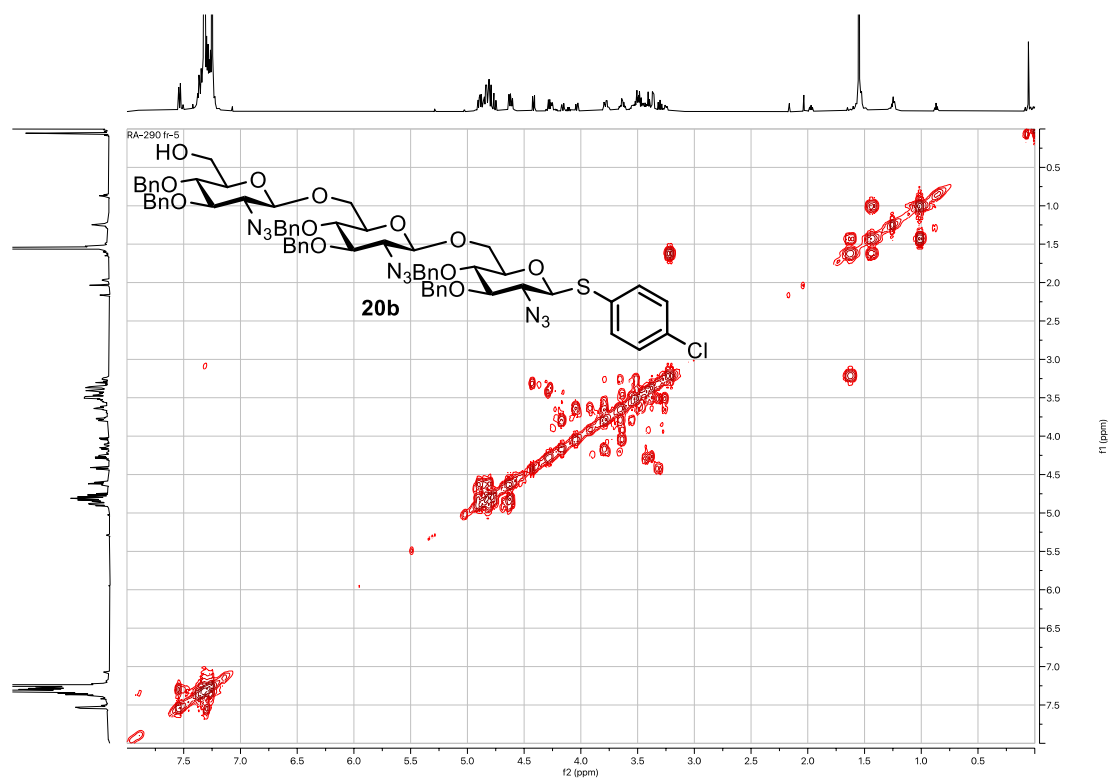


HMQC



¹H NMR¹³C NMR

^1H , ^1H -COSY



HMQC

