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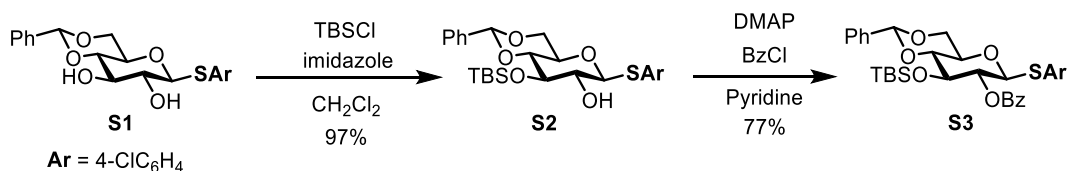
### 1. General

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker AVANCE II 600 (<sup>1</sup>H 600 MHz, <sup>13</sup>C 150 MHz). ESI-MS and MALDI-TOF-MS were recorded on Thermo Scientific Exactive spectrometer and Bruker ultrafleXtreme, respectively. Measurements of oxidation potentials of monosaccharides (conc. 4.0 mM) were carried out in 0.1 M of electrolyte in CH<sub>2</sub>Cl<sub>2</sub> 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 rpm. Preparative recycling gel permeation chromatography (PR-GPC) was performed on Japan Analytical Industry LC-5060. Kanto silica gel 60 N (spherical, neutral, 63-210 μm) was used for silica gel column chromatography. The automated synthesizer is consisting of the commercially available instruments such as the chiller with a cooling bath (UCR-150, Techno Sigma), the power supply for constant current electrolysis (PMC 350-0.2 A, KIKUSUI), the syringe pump (PHD 2000 infusion, Harvard apparatus), and the system controller (LabVIEW, National Instruments). Merck TLC (silica gel 60 F254) was used for TLC analysis. Starting material **S1** was prepared by the conventional method and characterized according to the reported method.<sup>1</sup> Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification.

## 2. Preparation of building blocks

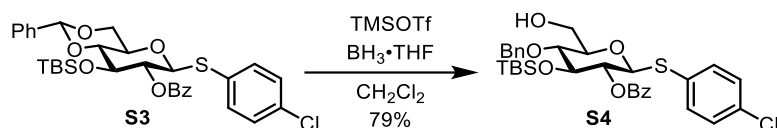
### 2-1. Preparation of 4-Chlorophenyl 2-*O*-benzoyl-4,6-*O*-dibenzyl-1-thio- $\beta$ -D-glucopyranoside (**6**)

#### 2-1-1. 4-Chlorophenyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-1-thio- $\beta$ -D-glucopyranoside (**S3**)



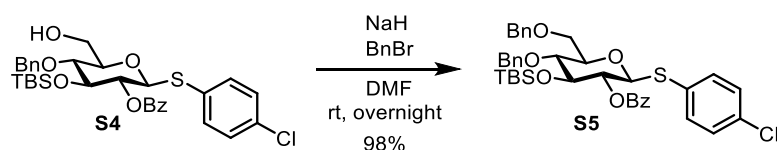
To the solution of **S1** (25.05 mmol, 9.89 g) in CH<sub>2</sub>Cl<sub>2</sub> (48 mL), *tert*-butyldimethylsilyl chloride (30.1 mmol, 4.53 g) and imidazole (35.1 mmol, 2.39 g) were sequentially added at 0°C and the reaction mixture was stirred at room temperature overnight. After the completion of the reaction determined by TLC (Hexane/EtOAc 1:1), the reaction mixture was quenched with MeOH. The mixture was washed with sat. aqueous NaHCO<sub>3</sub> for three times and H<sub>2</sub>O and extracted with EtOAc. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The crude product was purified with silica gel chromatography to obtain **S2** in 97% yield (24.3 mmol, 12.4 g). To the solution of **S2** (8.02 mmol, 3.89 g) and DMAP (0.802 mmol, 99.2 mg) in pyridine (64 mL), benzoyl chloride (16.04 mmol, 1.85 mL) was added, and the reaction mixture was stirred at 55°C overnight. The reaction was quenched by 1 N aqueous solution of hydrochloric acid and washed with deionized water three times. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under the reduced pressure. Thus obtained crude product was purified by silica gel chromatography (eluent: Hexane/EtOAc 7:3) to afford **S3** (6.15 mmol, 3.62 g) in 77% yield. TLC (Hexane/EtOAc 5:1) R<sub>f</sub> = 0.70; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)  $\delta$  8.06 (dd, *J* = 8.4, 1.2 Hz, 2 H), 7.58 (td, *J* = 7.2, 1.2 Hz, 1 H), 7.46 (td, *J* = 7.8, 1.8 Hz, 4 H), 7.39–7.34 (m, 5 H), 7.25 (td, *J* = 8.4, 2.4 Hz, 2 H), 5.53 (s, 1 H), 5.21 (*pseudo-t*, *J* = 9.6 Hz, 1 H), 4.80 (d, *J* = 10.2 Hz, 1 H), 4.39 (dd, *J* = 10.8, 4.8 Hz, 1 H), 4.03 (*pseudo-t*, *J* = 9.0 Hz, 1 H), 3.79 (*pseudo-t*, *J* = 9.0 Hz, 1 H), 3.61–3.55 (m, 2 H), 0.67 (s, 9 H), -0.07 (s, 3 H), -0.15 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz)  $\delta$  165.1, 136.9, 134.5, 133.2, 130.5, 129.9, 129.8, 129.1, 129.0, 128.4, 128.1, 126.3, 101.9, 86.7, 81.1, 74.3, 73.4, 70.8, 68.5, 25.5, 17.9, -4.2, -4.9; HRMS (ESI) *m/z* calculated for C<sub>32</sub>H<sub>37</sub>ClKO<sub>6</sub>SSi; [M+K]<sup>+</sup> 651.1400; found 651.1402.

2-1-2. 4-Chlorophenyl 2-*O*-benzoyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-1-thio- $\beta$ -D-glucopyranoside (**S4**)



To the mixture of **S3** (2.60 mmol, 1.60 g) and MS4A (855 mg) in  $\text{CH}_2\text{Cl}_2$  (13 mL),  $\text{BH}_3\cdot\text{THF}$  (1 M) (13 mmol, 13 mL) was added and the reaction mixture was stirred at  $0^\circ\text{C}$  for 10 min. Then TMSOTf (0.39 mmol, 0.07 mL) was added and the reaction mixture was stirred at room temperature overnight. After the completion of the reaction determined by TLC (Hexane/EtOAc 5:1), the reaction mixture was diluted with  $\text{CH}_2\text{Cl}_2$  and quenched with sat. aqueous  $\text{NaHCO}_3$ . The mixture was washed with  $\text{H}_2\text{O}$  for three times and dried over  $\text{Na}_2\text{SO}_4$ . After filtration and removal of solvent under reduced pressure, the crude product was purified with silica gel chromatography to obtain **S4** in 79% yield (2.06 mmol, 1.27 g). TLC (Hexane/EtOAc 5:1)  $R_f = 0.34$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  8.06–8.03 (m, 2 H), 7.59 (*pseudo-t*,  $J = 6.0$  Hz, 1 H), 7.47 (*pseudo-t*,  $J = 6.0$  Hz, 2 H), 7.36–7.29 (m, 7 H), 7.24–7.23 (m, 2 H), 5.16 (*pseudo-t*,  $J = 9.6$  Hz, 1 H), 4.85 (d,  $J = 11.4$  Hz, 1 H), 4.74 (d,  $J = 10.2$  Hz, 1 H), 4.63 (d,  $J = 12.0$  Hz, 1 H), 3.95 (*pseudo-t*,  $J = 9.0$  Hz, 1 H), 3.86 (ddd,  $J = 12.0, 6.0, 2.4$  Hz, 1 H), 3.69–3.64 (m, 1 H), 3.55 (*pseudo-t*,  $J = 9.0$  Hz, 1 H), 3.47 (ddd,  $J = 9.6, 4.8, 2.4$  Hz, 1 H), 1.80 (dd,  $J = 7.8, 6.0$  Hz, 1 H), 0.77 (s, 9 H), 0.004 (s, 3 H), -0.17 (s, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  165.4, 137.8, 134.3, 133.9, 133.3, 133.1, 130.04, 129.93, 129.1, 128.5, 127.8, 127.6, 86.3, 79.7, 78.1, 76.5, 75.1, 73.1, 62.0, 25.6, 17.8, -4.0, -4.3; HRMS (ESI)  $m/z$  calculated for  $\text{C}_{32}\text{H}_{39}\text{ClKO}_6\text{SSi}$ ;  $[\text{M}+\text{K}]^+$ , 653.1557; found 653.1556.

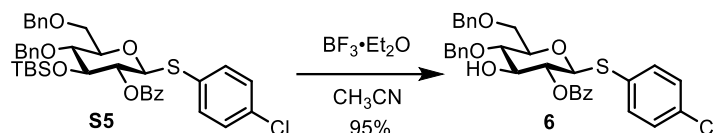
2-1-3. 4-Chlorophenyl 2-*O*-benzoyl-4,6-*O*-dibenzyl-3-*O*-*tert*-butyldimethylsilyl-1-thio- $\beta$ -D-glucopyranoside (**S5**)



To the mixture of **S4** (2.06 mmol, 1.27 g) and DMF (10 mL), benzyl bromide (7.4 mmol, 0.18 g) was added at  $0^\circ\text{C}$ . NaH 60% in mineral oil (7.42 mmol, 298 mg) was dissolved in DMF (10 mL) and added to the reaction mixture in five portions (2.0 mL). After the completion of the reaction confirmed by TLC (Hexane/EtOAc 5:1), the reaction mixture was quenched with MeOH. The mixture was washed with  $\text{H}_2\text{O}$  for three times and dried over  $\text{Na}_2\text{SO}_4$ . After filtration and removal of solvent under reduced pressure, the crude product was purified with silica gel chromatography to obtain **S5** in 98%

yield (2.01 mmol, 1.42 g). TLC (Hexane/EtOAc 5:1)  $R_f = 0.67$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  8.04 (d,  $J = 7.2$  Hz, 2 H), 7.58 (*pseudo-t*,  $J = 7.2$  Hz, 1 H), 7.46 (*pseudo-t*,  $J = 7.8$  Hz, 2 H), 7.40 (d,  $J = 8.4$  Hz, 2 H), 7.41–7.34 (m, 8 H), 7.33–7.27 (m, 2 H), 7.14 (td,  $J = 9.0, 2.4$  Hz, 2 H), 5.16 (*pseudo-t*,  $J = 9.0$  Hz, 1 H), 4.81 (d,  $J = 11.4$  Hz, 1 H), 4.69 (d,  $J = 10.2$  Hz, 1 H), 4.59 (d,  $J = 11.4$  Hz, 1 H), 4.55 (d,  $J = 12.0$  Hz, 1 H), 4.52 (d,  $J = 12.0$  Hz, 1 H), 3.95–3.91 (m, 1 H), 3.75 (d,  $J = 10.2$  Hz, 1 H), 3.68 (dd,  $J = 10.8, 3.6$  Hz, 1 H), 3.58 (d,  $J = 6.0$  Hz, 2 H), 0.76 (s, 9 H), -0.02 (s, 3 H), -0.18 (s, 3 H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  165.3, 138.1, 138.0, 134.0, 133.2, 131.3, 130.1, 129.9, 128.9, 128.8, 128.41, 128.35, 127.7, 127.6, 127.5, 86.0, 79.4, 78.6, 76.8, 75.0, 73.4, 73.0, 69.0, 25.6, 17.7, -4.0, -4.3; HRMS (ESI)  $m/z$  calculated for  $\text{C}_{39}\text{H}_{45}\text{ClNaO}_6\text{SSi}$ ;  $[\text{M}+\text{Na}]^+$ , 727.2287; found 727.2271.

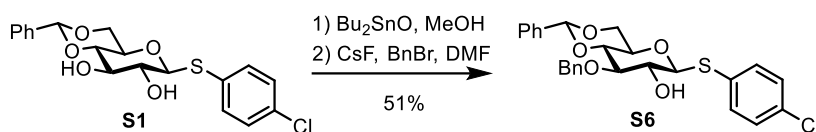
#### 2-1-4. 4-Chlorophenyl 2-*O*-benzoyl-4,6-*O*-dibenzyl-1-thio- $\beta$ -D-glucopyranoside (**6**)



To the solution of **S5** (3.88 mmol, 2.74 g) in  $\text{CH}_3\text{CN}$  (50 mL),  $\text{BF}_3/\text{Et}_2\text{O}$  (5.82 mmol, 0.736 mL) was added, and the reaction mixture was stirred at  $0^\circ\text{C}$  for 30 min. After the completion of the reaction determined by TLC (hexane/EtOAc 9:1), the reaction mixture was quenched with 1 N HCl. The mixture was washed with  $\text{H}_2\text{O}$  for three times and dried over  $\text{Na}_2\text{SO}_4$ . After filtration and removal of solvent under reduced pressure, the crude product was purified with silica gel chromatography to obtain **6** in 96% yield (3.71 mmol, 2.19 g). TLC (Hexane/EtOAc 9:1)  $R_f$  0.086;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  8.06 (d,  $J = 7.2$  Hz, 2 H), 7.56 (*pseudo-t*,  $J = 7.8$  Hz, 1 H), 7.45–7.23 (m, 14 H), 7.13 (d,  $J = 8.4$  Hz, 2 H), 5.01 (*pseudo-t*,  $J = 7.8$  Hz, 1 H), 4.78 (d,  $J = 11.4$  Hz, 1 H), 4.72 (d,  $J = 9.6$  Hz, 1 H), 4.62 (d,  $J = 11.4$  Hz, 1 H), 4.59 (d,  $J = 11.4$  Hz, 1 H), 4.44 (d,  $J = 12.0$  Hz, 1 H), 3.91–3.88 (m, 1 H), 3.80 (d,  $J = 10.8$  Hz, 1 H), 3.72 (dd,  $J = 10.8, 4.2$  Hz, 1 H), 3.59–3.56 (m, 2 H), 2.73 (s, 1 H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  166.2, 138.14, 138.05, 134.4, 133.6, 130.7, 130.1, 129.5, 129.1, 128.62, 128.56, 128.51, 128.12, 128.06, 127.82, 127.79, 85.3, 79.2, 77.9, 77.2, 75.0, 73.5, 73.2, 69.0; HRMS (ESI)  $m/z$  calculated for  $\text{C}_{33}\text{H}_{31}\text{ClKO}_6\text{S}$ ;  $[\text{M}+\text{K}]^+$ , 629.1161; found 629.1168.

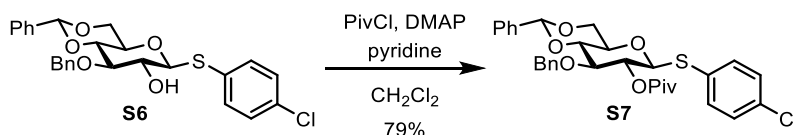
## 2-2. Preparation of 4-Chlorophenyl 3,4-*O*-dibenzyl-6-*O*-*tert*-butyldiphenylsilyl-2-*O*-pivaloyl-1-thio- $\beta$ -D-glucopyranoside (**7a**)

### 2-2-1. 4-Chlorophenyl 3-*O*-benzyl-4,6-*O*-benzylidene-1-thio- $\beta$ -D-glucopyranoside (**S6**)



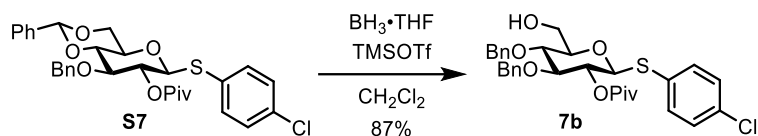
To the solution of **S1** (8.17 mmol, 3.23 g) in MeOH (33 mL), and dibutyltin oxide (10.2 mmol, 2.54 g) was added at room temperature and the reaction mixture was stirred at 80°C for 6 h. After removal of solvent under reduced pressure, DMF (63 mL), CsF (10.22 mmol, 1.55 g) and BnBr (10.2 mmol, 1.22 mL) were added, and the reaction mixture was stirred at room temperature for 16 h. After the completion of the reaction determined by TLC (Hexane/EtOAc 1:1). The reaction mixture was washed with H<sub>2</sub>O for three times and dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration and removal of solvent under reduced pressure, the crude product was purified with silica gel chromatography to obtain **S6** in 51% yield (4.15 mmol, 2.01 mg). TLC (Hexane/EtOAc 1:1) R<sub>f</sub> = 0.89; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ 7.48–7.46 (m, 4 H), 7.39–7.28 (m, 10 H), 5.56 (s, 1 H), 4.95 (d, *J* = 12.0 Hz, 1 H), 4.77 (d, *J* = 12.0 Hz, 1 H), 4.59 (d, *J* = 9.6 Hz, 1 H), 4.36 (dd, *J* = 10.2, 4.8 Hz, 1 H), 3.78 (*pseudo-t*, *J* = 10.8 Hz, 1 H), 3.68 (*pseudo-t*, *J* = 9.0 Hz, 1 H), 3.64 (*pseudo-t*, *J* = 9.0 Hz, 1 H), 3.51 (dd, *J* = 9.6, 4.8 Hz, 1 H), 3.47 (*pseudo-t*, *J* = 9.0 Hz, 1 H), 2.56 (s, 1 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ 138.1, 137.2, 134.8, 134.7, 129.2, 129.1, 128.5, 128.3, 128.1, 128.0, 126.0, 101.3, 88.1, 81.6, 81.1, 74.8, 72.1, 70.8, 68.6, 29.7.

#### 2-2-2. 4-Chlorophenyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-pivaloyl-1-thio-β-D-glucopyranoside (**S7**)



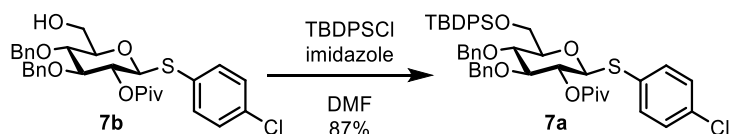
To the solution of **S6** (2.13 mmol, 1.00 g) in CH<sub>2</sub>Cl<sub>2</sub> (6.81 mL), DMAP (3.20 mmol, 391 mg), pyridine (10.7 mmol, 0.860 mL) and pivaloyl chloride (3.20 mmol, 0.395 mL) were added and the reaction mixture was stirred at 50°C overnight. After the completion of the reaction determined by TLC (Hexane/EtOAc 4:1), the reaction mixture was quenched with 1 N HCl. The mixture was washed with H<sub>2</sub>O for three times and dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration and removal of solvent under reduced pressure, the crude product was purified with silica gel chromatography to obtain **S7** in 79% yield (1.68 mmol, 928 mg). TLC (Hexane/EtOAc 4:1) R<sub>f</sub> = 0.68; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ 7.47–7.46 (m, 2 H), 7.41 (dt, *J* = 9.0, 2.4 Hz, 2 H), 7.39–7.36 (m, 3 H), 7.29–7.24 (m, 7 H), 5.56 (s, 1 H), 5.08–5.00 (m, 1 H), 4.86 (dd, *J* = 11.4, 3.0 Hz, 1 H), 4.68 (d, *J* = 11.4 Hz, 1 H), 4.64 (d, *J* = 11.4 Hz, 1 H), 4.38 (dd, *J* = 10.8, 4.8 Hz, 1 H), 3.82–3.77 (m, 2 H), 3.73 (*pseudo-t*, *J* = 9.6 Hz, 1 H), 3.52 (td, *J* = 9.6, 5.4 Hz, 1 H), 1.23 (s, 9 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ 176.5, 138.0, 137.1, 134.7, 134.5, 130.4, 129.13, 129.07, 128.3, 127.6, 127.5, 126.0, 101.3, 86.7, 81.2, 80.4, 74.6, 70.9, 70.6, 68.5, 38.8, 27.2; HRMS (ESI) *m/z* calculated for C<sub>31</sub>H<sub>33</sub>ClKO<sub>6</sub>S [M+K]<sup>+</sup> 607.1318; found 607.1328.

2-2-3. 4-Chlorophenyl 3,4-*O*-dibenzyl-2-*O*-pivaloyl-1-thio-β-D-glucopyranoside (**7b**)



To the solution of **7b** in  $\text{CH}_2\text{Cl}_2$  (8.12 mL),  $\text{BH}_3\cdot\text{THF}$  (8.16 mmol, 9.06 mL) was added at  $0^\circ\text{C}$  and the reaction mixture was stirred at  $0^\circ\text{C}$  for 10 min. Then trimethylsilyl triflate (0.245 mmol, 0.0451 mL) was added at  $0^\circ\text{C}$  and the reaction mixture was stirred at room temperature for 2.5 h. After the completion of the reaction determined by TLC (eluent: Hexane/EtOAc 4:1), the reaction mixture was quenched with sat. aqueous  $\text{NaHCO}_3$ . The mixture was washed with  $\text{H}_2\text{O}$  for three times and dried over  $\text{Na}_2\text{SO}_4$ . After filtration and removal of solvent under reduced pressure, the crude product was purified with silica gel chromatography to obtain **7b** in 87% yield (1.43 mmol, 815 mg). TLC (Hexane/EtOAc 4:1)  $R_f=0.36$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  7.39 (dt,  $J=8.4, 1.8$  Hz, 2 H), 7.33–7.24 (m, 12 H), 5.04 (*pseudo-t*,  $J=9.6$  Hz, 1 H), 4.79 (d,  $J=11.4$  Hz, 1 H), 4.78 (d,  $J=10.8$  Hz, 1 H), 4.70 (d,  $J=11.4$  Hz, 1 H), 4.62 (dd,  $J=13.2, 10.8$  Hz, 2 H), 3.88 (ddd,  $J=12.0, 6.0, 2.4$  Hz, 1 H), 3.74 (*pseudo-t*,  $J=9.0$  Hz, 1 H), 3.73–3.68 (m, 1 H), 3.63 (*pseudo-t*,  $J=9.6$  Hz, 1 H), 3.44 (ddd,  $J=9.6, 4.8, 3.0$  Hz, 1 H), 2.47 (s, 1 H), 1.23 (s, 9 H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  176.8, 138.11, 138.07, 138.05, 137.94, 137.89, 134.3, 133.7, 131.5, 129.3, 128.6, 128.5, 128.1, 128.0, 127.8, 127.4, 86.4, 84.5, 79.90, 79.85, 75.3, 75.2, 71.6, 61.9, 38.9, 27.3; HRMS (ESI)  $m/z$  calculated for  $\text{C}_{31}\text{H}_{35}\text{ClKO}_6\text{S}$   $[\text{M}+\text{K}]^+$  609.1474; found 609.1480.

2-2-4. 4-Chlorophenyl 3,4-*O*-dibenzyl-6-*O*-*tert*-butyldiphenylsilyl-2-*O*-pivaloyl-1-thio-β-D-glucopyranoside (**7a**)

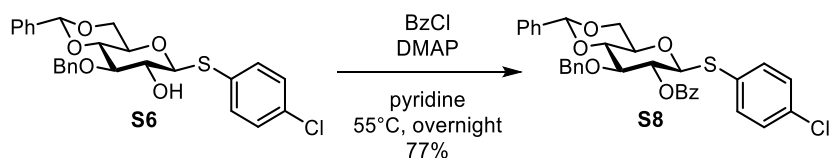


To the solution of **7b** (2.71 mmol, 1.55 g) in DMF (8.41 mL), imidazole (5.43 mmol, 370 mg) and *tert*-butylchlorodiphenylsilane (4.07 mmol, 1.05 mL) were added at  $0^\circ\text{C}$  and the reaction mixture was stirred at room temperature overnight. After the completion of the reaction determined by TLC (Hexane/EtOAc 4:1), the reaction mixture was quenched with sat. aqueous  $\text{NaHCO}_3$ . The mixture was washed with  $\text{H}_2\text{O}$  for three times and dried over  $\text{Na}_2\text{SO}_4$ . After filtration and removal of solvent under reduced pressure, the crude product was purified with silica gel chromatography to obtain **7a** in 67% yield (1.83 mmol, 1.48 g). TLC (Hexane/EtOAc 4:1)  $R_f=0.67$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  7.75 (dd,  $J=7.8, 1.2$  Hz, 2 H), 7.69 (dd,  $J=7.8, 1.2$  Hz, 2 H), 7.45 (d,  $J=9.0$  Hz, 2 H), 7.42 (td,  $J=7.2, 1.2$  Hz, 2 H), 7.36–7.24 (m, 12 H), 7.15 (dt,  $J=9.0, 2.4$  Hz, 2 H), 7.09 (dd,  $J=7.8, 3.6$  Hz, 2 H), 5.09

(*pseudo-t*,  $J = 9.6$  Hz, 1 H), 4.79 (d,  $J = 10.8$  Hz, 1 H), 4.78 (d,  $J = 10.8$  Hz, 1 H), 4.69 (d,  $J = 10.8$  Hz, 1 H), 4.61 (dd,  $J = 7.8$  Hz, 2 H), 3.98 (dd,  $J = 11.4, 1.2$  Hz, 1 H), 3.92 (dd,  $J = 11.4, 4.2$  Hz, 1 H), 3.80 (*pseudo-t*,  $J = 9.6$  Hz, 1 H), 3.73 (*pseudo-t*,  $J = 9.0$  Hz, 1 H), 3.44 (ddd,  $J = 9.6, 3.6, 1.2$  Hz, 1 H), 1.24 (s, 9 H), 1.07 (s, 9 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  176.7, 138.1, 138.0, 136.0, 135.7, 134.1, 133.8, 133.4, 133.0, 131.8, 129.9, 129.1, 128.5, 128.0, 127.9, 127.8, 127.5, 86.4, 84.9, 80.4, 75.5, 75.2, 71.7, 62.8, 38.9, 27.3, 27.0, 19.4; HRMS (ESI)  $m/z$  calculated for  $\text{C}_{47}\text{H}_{53}\text{ClKO}_6\text{SSi}$   $[\text{M}+\text{K}]^+$  847.2652; found 847.2664.

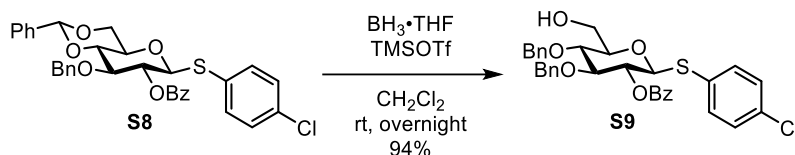
## 2-3. Preparation of 4-Chlorophenyl 2-*O*-benzoyl-3,4,6-*O*-tribenzyl-1-thio- $\beta$ -D-glucopyranoside (**9**)

### 2-3-1. 4-Chlorophenyl 2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio- $\beta$ -D-glucopyranoside (**S8**)



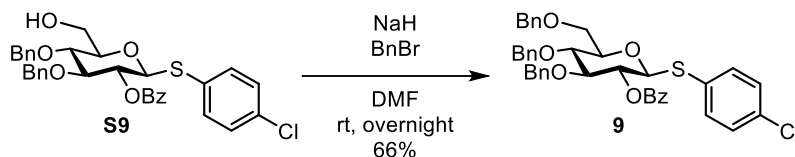
To the mixture of **S6** (8.02 mmol, 3.89 g) and DMAP (0.802 mmol, 97.98 mg) in pyridine (64 mL), benzoyl chloride (16.0 mmol, 1.86 mL) was added, and the reaction mixture was stirred at 55°C overnight. After the completion of the reaction determined by TLC (Hexane/EtOAc 7:3), the reaction mixture was quenched with 1N HCl. The mixture was diluted with  $\text{CH}_2\text{Cl}_2$ , washed with  $\text{H}_2\text{O}$  for three times and dried over  $\text{Na}_2\text{SO}_4$ . After filtration and removal of solvent under reduced pressure, the crude product was purified with silica gel chromatography to obtain **S8** in 77% yield (6.15 mmol, 3.62 g). TLC (Hexane/EtOAc 4:1)  $R_f = 0.67$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02–8.00 (m, 2 H), 7.62 (*pseudo-t*,  $J = 7.2$  Hz, 1 H), 7.51–7.46 (m, 4 H), 7.42–7.38 (m, 5 H), 7.25 (s, 2 H), 7.14–7.04 (m, 5 H), 5.61 (s, 1 H), 5.24 (dd,  $J = 10.2, 9.0$  Hz, 1 H), 4.80 (d,  $J = 12.0$  Hz, 1 H), 4.78 (d,  $J = 9.6$  Hz, 1 H), 4.66 (d,  $J = 12.0$  Hz, 1 H), 4.42 (dd,  $J = 10.2, 5.4$  Hz, 1 H), 3.88 (*pseudo-t*,  $J = 9.6$  Hz, 1 H), 3.83 (*pseudo-t*,  $J = 10.2$  Hz, 1 H), 3.79 (*pseudo-t*,  $J = 9.6$  Hz, 1 H), 3.56 (td,  $J = 9.6, 4.8$  Hz, 1 H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  164.9, 137.5, 137.0, 134.7, 133.3, 130.0, 129.0, 128.4, 128.2, 128.1, 128.0, 127.5, 125.9, 101.2, 86.4, 81.3, 79.1, 74.2, 71.8, 70.5, 68.4; HRMS (ESI)  $m/z$  calculated for  $\text{C}_{33}\text{H}_{29}\text{ClKO}_6\text{S}$   $[\text{M}+\text{K}]^+$  627.1005; found 627.1010.

### 2-3-2. 4-Chlorophenyl 2-*O*-benzoyl-3,4-*O*-dibenzyl-1-thio-β-D-glucopyranoside (**S9**)



To the mixture of **S8** (4.70 mmol, 2.77 g) and MS4A (1.5 g) in CH<sub>2</sub>Cl<sub>2</sub> (24 mL), BH<sub>3</sub>·THF (1.0 M, 24 mmol, 24 mL) and TMSOTf (0.703 mmol, 127 μL) were added at 0 °C and the reaction mixture was stirred at room temperature overnight. After the completion of the reaction determined by TLC (Hexane/EtOAc 7:3), the reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and quenched with sat. aqueous NaHCO<sub>3</sub>. The mixture was washed with H<sub>2</sub>O for three times and dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration and removal of solvent under reduced pressure, the crude product was purified with silica gel chromatography to obtain **S9** in 81% yield (3.81 mmol, 2.25 g). TLC (Hexane/EtOAc 5:1) R<sub>f</sub> = 0.20; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ 8.04–8.01 (m, 2 H), 7.62–7.59 (m, 1 H), 7.46 (*pseudo-t*, *J* = 7.8 Hz, 2 H), 7.38–7.29 (m, 8 H), 7.24 (s, 1 H), 7.14–7.09 (m, 5 H), 5.22 (*pseudo-t*, *J* = 9.0 Hz, 1 H), 4.84 (d, *J* = 10.8 Hz, 1 H), 4.76 (d, *J* = 9.6 Hz, 1 H), 4.74 (d, *J* = 11.4 Hz, 1 H), 4.66 (d, *J* = 10.8 Hz, 1 H), 4.65 (d, *J* = 10.8 Hz, 1 H), 4.62 (d, *J* = 10.8 Hz, 1 H), 3.91 (ddd, *J* = 12.0, 6.0, 3.0 Hz, 1 H), 3.86 (*pseudo-t*, *J* = 9.0 Hz, 1 H), 3.75–3.71 (m, 1 H), 3.68 (*pseudo-t*, *J* = 9.0 Hz, 1 H), 3.44 (ddd, *J* = 9.6, 4.8, 3.0 Hz, 1 H), 1.82 (dd, *J* = 7.8, 6.0 Hz, 1 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ 165.20, 137.83, 137.72, 137.57, 134.48, 134.14, 133.98, 133.40, 133.25, 130.74, 129.89, 129.69, 129.24, 129.15, 128.59, 128.54, 128.33, 128.21, 128.14, 128.10, 128.07, 127.78, 86.53, 85.95, 83.97, 79.77, 79.47, 77.42, 75.86, 75.61, 75.40, 75.22, 72.43, 62.00; HRMS (ESI) *m/z* calculated for C<sub>33</sub>H<sub>31</sub>ClKO<sub>6</sub>S [M+K]<sup>+</sup> 629.1161; found 629.1163.

### 2-3-3. 4-Chlorophenyl 2-*O*-benzoyl-3,4,6-*O*-tribenzyl-1-thio-β-D-glucopyranoside (**9**)



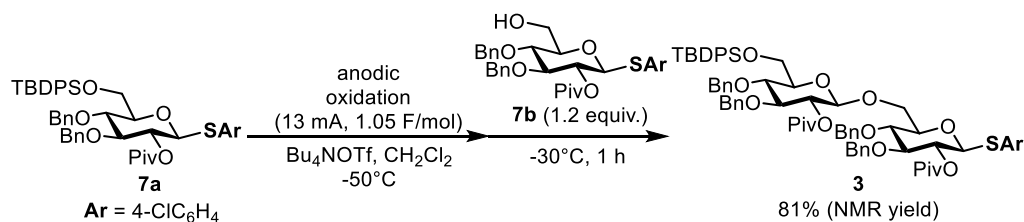
To the mixture of **S9** (3.81 mmol, 2.25 g) and DMF (30 mL), benzyl bromide (13.7 mmol, 1.63 mL) was added at 0°C. NaH 60% in mineral oil (13.7 mmol, 548 mg) was dissolved in DMF (10 mL) and added to the reaction mixture in five portions (2.0 mL×5). After the completion of the reaction determined by TLC (Hexane/EtOAc 4:1), the reaction mixture was quenched with MeOH, diluted with EtOAc. The mixture was washed with H<sub>2</sub>O for three times and dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration and removal of solvent under reduced pressure, the crude product was purified with silica gel



chromatography to obtain **9** in 60% yield (2.30 mmol, 1.57 g). TLC (Hexane/EtOAc 5:1)  $R_f = 0.25$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  8.03 (d,  $J = 7.8$  Hz, 2 H), 7.58 (*pseudo-t*,  $J = 7.8$  Hz, 1 H), 7.45 (*pseudo-t*,  $J = 7.8$  Hz, 2 H), 7.42 (d,  $J = 8.4$  Hz, 2 H), 7.38–7.28 (m, 8 H), 7.21 (d,  $J = 7.2$  Hz, 2 H), 7.15–7.07 (m, 7 H), 5.23 (*pseudo-t*,  $J = 9.6$  Hz, 1 H), 4.80 (d,  $J = 10.8$  Hz, 1 H), 4.72 (d,  $J = 10.2$  Hz, 2 H), 4.63 (d,  $J = 10.8$  Hz, 1 H), 4.60–4.53 (m, 3 H), 3.84 (d,  $J = 9.0$  Hz, 1 H), 3.83–3.79 (m, 1 H), 3.75–3.69 (m, 2 H), 3.62–3.58 (m, 1 H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  165.18, 138.15, 137.89, 137.64, 134.33, 134.26, 133.34, 130.85, 129.90, 129.81, 128.97, 128.62, 128.52, 128.48, 128.33, 128.07, 127.97, 127.77, 127.72, 85.67, 84.25, 79.45, 77.75, 75.43, 75.19, 73.52, 72.36, 68.95; HRMS (ESI)  $m/z$  calculated for  $\text{C}_{40}\text{H}_{37}\text{ClKO}_6\text{S}$   $[\text{M}+\text{K}]^+$  719.1631; found 719.1630.

### 3. Synthesis of disaccharide building blocks

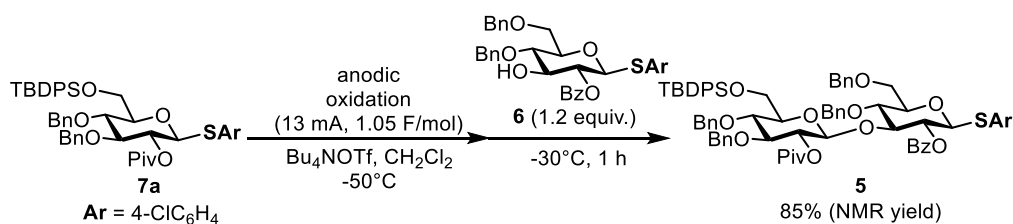
3-1. Preparation of 4-Chlorophenyl 3,4-*O*-dibenzyl-6-*O*-*tert*-butyldiphenylsilyl-2-*O*-pivaloyl- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 6)-3,4-*O*-dibenzyl-2-*O*-pivaloyl-1-thio- $\beta$ -D-glucopyranoside (**3**)



The automated synthesis of **3** was carried out in an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon JF-20-P7) and a platinum plate cathode (10 mm×20 mm). In the anodic chamber were placed terminal building block **7a** (0.601 mmol, 486 mg), Bu<sub>4</sub>NOTf (1.50 mmol, 588 mg) and CH<sub>2</sub>Cl<sub>2</sub> (15 mL). In the cathodic chamber were placed trifluoromethanesulfonic acid (0.65 mmol, 57  $\mu\text{L}$ ), Bu<sub>4</sub>NOTf (1.50 mmol, 588 mg) and CH<sub>2</sub>Cl<sub>2</sub> (15 mL). The constant current electrolysis (13.0 mA) was carried out at -50°C with magnetic stirring until 1.05 F/mol of electricity was consumed. After the electrolysis, building block **7b** (0.72 mmol, 418 mg) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL) was subsequently added by the syringe pump under an argon atmosphere at -30°C, and kept for 60 min. After the cycle, Et<sub>3</sub>N (0.50 mL) was added, and the mixture was filtered through a short column (4×3 cm) of silica gel to remove Bu<sub>4</sub>NOTf. After removal of the solvent under reduced pressure, the crude product was purified with silica gel chromatography to obtain **3** (241 mg). NMR yield was determined using tetrachloroethane as internal standard (0.487 mmol, 81% yield). TLC (Hexane/EtOAc 4:1)  $R_f$  0.66;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  7.74–7.70 (*m*, 2 H), 7.67 (dd,  $J = 7.8, 1.2$  Hz, 2 H), 7.42 (d,  $J = 8.4$  Hz, 2 H), 7.38 (d,  $J = 7.2$  Hz, 1 H), 7.34–7.22 (*m*, 21 H), 7.21 (d,  $J = 6.6$  Hz, 2 H), 7.18 (ddd,  $J = 5.4, 2.4, 1.2$  Hz, 2 H), 7.15 (dd,  $J = 6.0, 2.4$  Hz, 2 H), 5.09 (dd,  $J = 9.6, 8.4$  Hz,

1 H), 4.99 (*pseudo-t*,  $J = 10.2$  Hz, 1 H), 4.84–4.66 (m, 7 H), 4.54 (*pseudo-t*,  $J = 9.6$  Hz, 2 H), 4.48 (d,  $J = 7.8$  Hz, 1 H), 4.01 (d,  $J = 9.6$  Hz, 1 H), 3.86 (*pseudo-t*,  $J = 9.0$  Hz, 1 H), 3.71 (*pseudo-t*,  $J = 9.0$  Hz, 1 H), 3.67–3.61 (m, 3 H), 3.36–3.32 (m, 2 H), 1.22 (s, 9 H), 1.15 (s, 9 H), 1.04 (s, 9 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  176.8, 176.7, 138.23, 138.16, 137.95, 137.69, 135.9, 135.6, 134.3, 134.1, 133.6, 133.1, 131.4, 129.8, 129.3, 128.5, 128.1, 128.0, 127.84, 127.77, 127.73, 127.6, 127.4, 101.1, 86.3, 84.7, 83.4, 79.8, 78.0, 77.7, 76.2, 75.34, 75.27, 75.1, 75.0, 73.2, 71.5, 67.8, 62.7, 38.9, 38.8, 27.3, 19.4; HRMS (ESI)  $m/z$  calculated for  $\text{C}_{72}\text{H}_{83}\text{ClKO}_{12}\text{SSi}$   $[\text{M}+\text{K}]^+$  1273.4695; found 1273.4636.

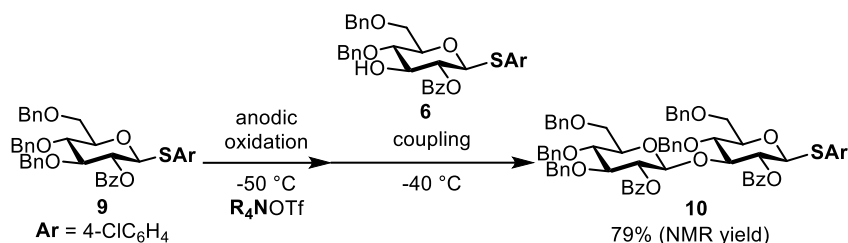
### 3-2. Preparation of 4-Chlorophenyl 3,4-*O*-dibenzyl-6-*O*-*tert*-butyldiphenylsilyl-2-*O*-pivaloyl- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 3)-2-*O*-benzoyl-4,6-*O*-dibenzyl-1-thio- $\beta$ -D-glucopyranoside (**5**)



The automated synthesis of **5** was carried out in an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon JF-20-P7) and a platinum plate cathode (10 mm×20 mm). In the anodic chamber were placed terminal building block **7a** (0.603 mmol, 489 mg),  $\text{Bu}_4\text{NOTf}$  (1.50 mmol, 595 mg) and  $\text{CH}_2\text{Cl}_2$  (15 mL). In the cathodic chamber were placed trifluoromethanesulfonic acid (0.67 mmol, 59  $\mu\text{L}$ ),  $\text{Bu}_4\text{NOTf}$  (1.50 mmol, 595 mg) and  $\text{CH}_2\text{Cl}_2$  (15 mL). The constant current electrolysis (13.0 mA) was carried out at  $-30$  °C with magnetic stirring until 1.05 F/mol of electricity was consumed. After the electrolysis, building block **6** (0.741 mmol, 438 mg) dissolved in  $\text{CH}_2\text{Cl}_2$  (2.0 mL) was subsequently added by the syringe pump under an argon atmosphere at  $-40$  °C, and kept for 60 min. After the cycle,  $\text{Et}_3\text{N}$  (0.50 mL) was added, and the mixture was filtered through a short column (4×3 cm) of silica gel to remove  $\text{Bu}_4\text{NOTf}$ . After removal of the solvent under reduced pressure, the crude product was purified with silica gel chromatography to obtain **5** (276 mg). NMR yield was determined using tetrachloroethane as internal standard (0.513 mmol, 85% yield). TLC (Hexane/EtOAc 4:1)  $R_f$  0.63;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  8.02 (dd,  $J = 8.4, 1.2$  Hz, 2 H), 7.74 (dd,  $J = 5.4, 2.4$  Hz, 2 H), 7.68 (dd,  $J = 7.8, 1.2$  Hz, 2 H), 7.60 (*pseudo-t*,  $J = 7.2$  Hz, 1 H), 7.45–7.20 (m, 28 H), 7.10 (dt,  $J = 9.0, 2.4$  Hz, 2 H), 7.05 (dd,  $J = 7.2, 1.2$  Hz, 2 H), 5.21 (*pseudo-t*,  $J = 9.0$  Hz, 1 H), 5.05 (dd,  $J = 9.6, 7.8$  Hz, 1 H), 4.96 (d,  $J = 12.0$  Hz, 1 H), 4.72 (d,  $J = 10.8$  Hz, 1 H), 4.68–4.56 (m, 6 H), 4.52 (d,  $J = 10.8$  Hz, 1 H), 4.50 (d,  $J = 10.8$  Hz, 1 H), 4.48 (d,  $J = 12.0$  Hz, 1 H), 3.92 (dd,  $J = 10.8, 1.2$  Hz, 1 H), 3.77 (dt,  $J = 11.4, 1.8$  Hz, 2 H), 3.69 (*pseudo-t*,  $J = 9.0$  Hz, 1 H), 3.60 (ddd,  $J = 9.6, 6.6, 1.8$  Hz, 1 H), 3.52–3.48 (m, 2 H), 3.44 (*pseudo-t*,  $J = 9.0$  Hz, 1 H), 3.19 (dd,  $J = 9.6, 3.6$  Hz, 1 H),

1.21 (s, 9 H), 1.02 (s, 9 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  177.3, 164.9, 138.3, 138.1, 137.8, 136.0, 135.7, 134.1, 133.8, 133.2, 133.1, 131.8, 129.8, 129.6, 129.0, 128.9, 128.8, 128.6, 128.5, 128.3, 128.2, 127.99, 127.95, 127.8, 127.63, 127.56, 98.8, 86.3, 83.2, 79.4, 78.2, 77.8, 76.7, 75.31, 75.25, 74.8, 74.0, 73.5, 69.6, 62.6, 39.0, 27.3, 26.9, 19.3; HRMS (ESI)  $m/z$  calculated for  $\text{C}_{74}\text{H}_{79}\text{ClKO}_{12}\text{SSi}$   $[\text{M}+\text{K}]^+$  1293.4382; found 1293.4398.

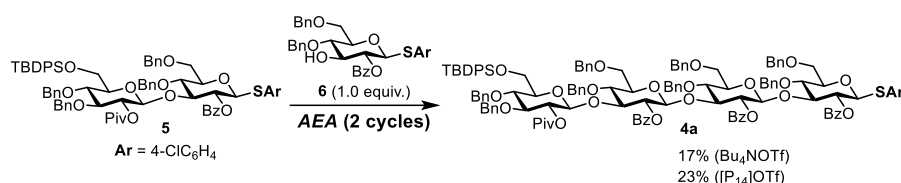
#### 4. Optimisation of electrolyte



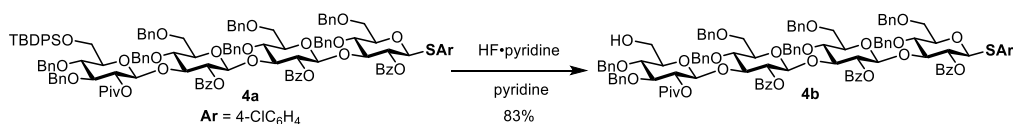
The automated synthesis of disaccharide **10** was carried out in an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon JF-20-P7) and a platinum plate cathode (10 mm×20 mm). In the anodic chamber were placed terminal building block **9** (0.101 mmol, 68.9 mg),  $\text{Bu}_4\text{NOTf}$  (0.5 mmol, 196 mg) and  $\text{CH}_2\text{Cl}_2$  (5.0 mL). In the cathodic chamber were placed trifluoromethanesulfonic acid (0.09 mmol, 8.0  $\mu\text{L}$ ),  $\text{Bu}_4\text{NOTf}$  (0.5 mmol, 196 mg) and  $\text{CH}_2\text{Cl}_2$  (5.0 mL). The constant current electrolysis (3.0 mA) was carried out at  $-50^\circ\text{C}$  with magnetic stirring until 1.2 F/mol of electricity was consumed. After the electrolysis, building block **6** (0.120 mmol, 71.2 mg) dissolved in  $\text{CH}_2\text{Cl}_2$  (0.60 mL) was subsequently added by the syringe pump under an argon atmosphere at  $-40^\circ\text{C}$ , and kept for 60 min. After the cycle,  $\text{Et}_3\text{N}$  (0.20 mL) was added, and the mixture was filtered through a short column (4×3 cm) of silica gel to remove  $\text{Bu}_4\text{NOTf}$ . After removal of the solvent under reduced pressure, NMR yield was determined using tetrachloroethane as internal standard (0.079 mmol, 79% yield). **4-Chlorophenyl 2-O-benzoyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-di-O-benzyl-1-thio-β-D-glucopyranoside (10)** TLC (Hexane/EtOAc 7:3)  $R_f = 0.53$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (dd,  $J = 7.2, 1.2$  Hz, 2 H), 7.80 (d,  $J = 7.2$  Hz, 2 H), 7.66 (*pseudo-t*,  $J = 7.2$  Hz, 1 H), 7.59 (*pseudo-t*,  $J = 7.2$  Hz, 1 H), 7.52 (*pseudo-t*,  $J = 7.8$  Hz, 2 H), 7.43–7.41 (m, 2 H), 7.35–7.33 (m, 2 H), 7.30–7.27 (m, 13 H), 7.22–7.21 (m, 4 H), 7.14–7.08 (m, 8 H), 7.00 (d,  $J = 6.6$  Hz, 2 H), 5.24 (dd,  $J = 9.6, 7.8$  Hz, 1 H), 5.16 (*pseudo-t*,  $J = 9.6$  Hz, 1 H), 5.06 (d,  $J = 11.4$  Hz, 1 H), 4.80 (d,  $J = 7.8$  Hz, 1 H), 4.73 (d,  $J = 10.8$  Hz, 1 H), 4.65 (d,  $J = 5.4$  Hz, 1 H), 4.55 (d,  $J = 12.0$  Hz, 2 H), 4.53–4.48 (m, 4 H), 4.44 (*pseudo-t*,  $J = 11.4$  Hz, 2 H), 4.28 (*pseudo-t*,  $J = 9.0$  Hz, 1 H), 3.82 (dd,  $J = 11.4, 1.8$  Hz, 1 H), 3.75 (dd,  $J = 10.8, 1.8$  Hz, 1 H), 3.62–3.57

(m, 5 H), 3.52 (ddd,  $J = 10.2, 6.0, 3.6$  Hz, 1 H), 3.44 (ddd,  $J = 10.8, 5.4, 1.8$  Hz, 1 H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  165.45, 164.60, 138.45, 138.42, 138.20, 137.71, 137.58, 133.73, 133.61, 133.18, 133.07, 132.16, 129.96, 129.90, 129.77, 129.56, 129.36, 128.93, 128.71, 128.60, 128.53, 128.45, 128.42, 128.41, 128.40, 128.27, 128.24, 128.16, 128.01, 128.00, 127.91, 127.84, 127.76, 127.69, 127.59, 127.54, 127.48, 127.31, 100.27, 86.23, 83.00, 80.41, 79.22, 78.14, 75.81, 75.69, 75.25, 75.15, 75.04, 74.00, 73.57, 73.50, 73.44, 73.01, 69.32, 69.12, 29.76; HRMS (ESI)  $m/z$  calculated for  $\text{C}_{67}\text{H}_{63}\text{ClKO}_{12}\text{S}$   $[\text{M}+\text{K}]^+$  1165.3360; found 1165.3311.

## 5. Synthesis of tetrasaccharide building block



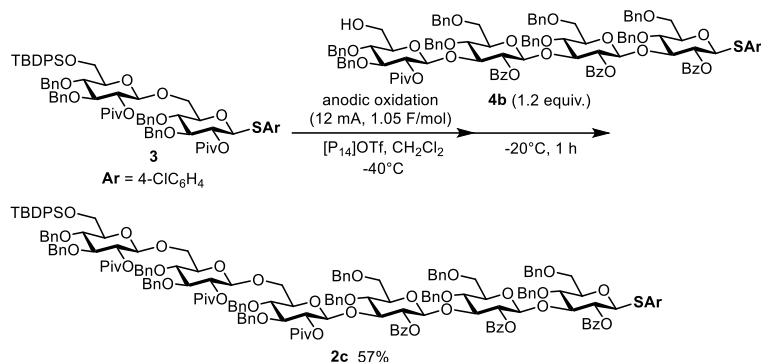
The automated synthesis of tetrasaccharide **4a** was carried out in an H-type divided cell equipped with a carbon felt anode and a platinum plate cathode (10 mm×10 mm). In the anodic chamber were placed disaccharide building block **5** (0.10 mmol, 126 mg),  $[\text{P}_{14}]\text{OTf}$  (0.50 mmol, 0.12 mL) and  $\text{CH}_2\text{Cl}_2$  (5 mL). In the cathodic chamber were placed trifluoromethanesulfonic acid (0.1 mmol, 9  $\mu\text{L}$ ),  $[\text{P}_{14}]\text{OTf}$  (0.50 mmol, 0.12 mL) and  $\text{CH}_2\text{Cl}_2$  (5 mL). The constant current electrolysis (3.0 mA) was carried out at  $-50^\circ\text{C}$  with stirring until 1.2 F/mol of electricity was consumed. After the electrolysis, building block **6** (0.10 mmol, 59 mg) dissolved in  $\text{CH}_2\text{Cl}_2$  (0.6 mL) was subsequently added by the syringe pump under an argon atmosphere at  $-50^\circ\text{C}$  and then  $-30^\circ\text{C}$  kept for 60 min. This process was repeated two cycles. After the second cycle,  $\text{Et}_3\text{N}$  (0.2 mL) was added, and the reaction mixture was filtered through a short column (4×3 cm) of silica gel to remove electrolyte. Removal of the solvent under reduced pressure and the crude product was purified with silica gel chromatography (eluent: Hexane/ $\text{EtOAc}$  4:1) and preparative recycling GPC (eluent:  $\text{CHCl}_3$ ). Target tetrasaccharide **4a** was obtained in 23% isolated yield (0.023 mmol, 49 mg). Thus obtained **4a** was used as a starting material for the next step without detailed structural characterization.



Tetrasaccharide **4a** (0.46 mmol, 0.98 g) was dissolved in pyridine (3.5 mL) and the solution was cooled to  $0^\circ\text{C}$ . 70%  $\text{HF}\cdot\text{pyridine}$  (0.35 mL) was added to the solution and the reaction mixture was

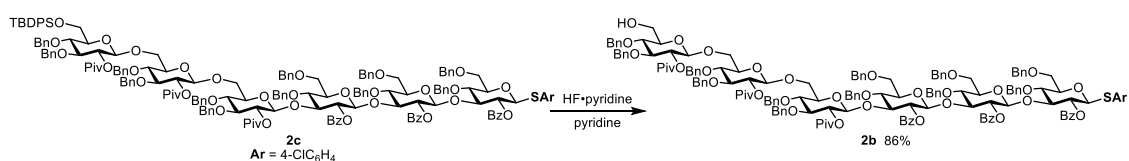
stirred at 0°C to room temperature for overnight. Conversion of **4a** was confirmed by TLC (Hexane/EtOAc 3:1) and aqueous sodium bicarbonate solution was added to quench the reaction. The aqueous solution was extracted with chloroform and the combined organic layer was washed with aqueous sodium bicarbonate solution and 1 N aqueous hydrochloric acid. The reaction mixture was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to obtain crude product (1.45 g). Thus-obtained crude product was purified by silica gel chromatography (eluent: Hexane/EtOAc 4:1) and tetrasaccharide **4b** (0.38 mmol, 723 mg) in 83% yield. **4-Chlorophenyl 3,4-di-O-benzyl-2-O-pivaloyl-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-di-O-benzyl-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-di-O-benzyl-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-di-O-benzyl-1-thio-β-D-glucopyranoside (4b)** TLC (Hexane/EtOAc 3:1) R<sub>f</sub> = 0.19; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.87 (dd, *J* = 8.4, 1.8 Hz, 2 H), 7.73 (dd, *J* = 8.4, 1.2 Hz, 2 H), 7.67–7.62 (m, 3 H), 7.61–7.57 (m, 1 H), 7.55–7.51 (m, 1 H), 7.46–7.43 (m, 2 H), 7.38–7.35 (m, 4 H), 7.34–7.18 (m, 40 H), 7.16–7.14 (m, 2 H), 7.07–7.04 (m, 2 H), 5.05 (dd, *J* = 9.0, 7.8 Hz, 1 H), 4.98–4.90 (m, 4 H), 4.89 (dd, *J* = 9.6, 7.8 Hz, 1 H), 4.81 (d, *J* = 10.8 Hz, 1 H), 4.71 (d, *J* = 7.8 Hz, 1 H), 4.67 (d, *J* = 10.8 Hz, 1 H), 4.59 (d, *J* = 10.8 Hz, 1 H), 4.57 (d, *J* = 7.8 Hz, 1 H), 4.55 (d, *J* = 9.6 Hz, 1 H), 4.51 (d, *J* = 10.2 Hz, 1 H), 4.47–4.38 (m, 10 H), 4.33 (d, *J* = 12.0 Hz, 1 H), 4.11 (*pseudo-t*, *J* = 9.0 Hz, 1 H), 3.90 (*pseudo-t*, *J* = 7.8 Hz, 1 H), 3.88 (*pseudo-t*, *J* = 9.0 Hz, 1 H), 3.73–3.62 (m, 4 H), 3.55–3.36 (m, 10 H), 3.30 (ddd, *J* = 9.6, 4.8, 1.8 Hz, 1 H), 3.27 (*pseudo-t*, *J* = 9.0 Hz, 1 H), 3.00 (ddd, *J* = 9.6, 4.8, 1.8 Hz, 1 H), 1.03 (s, 9 H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 177.1, 164.5, 164.4, 164.3, 138.49, 138.46, 138.31, 138.14, 137.8, 137.6, 133.6, 133.4, 133.2, 133.1, 132.1, 129.88, 123.83, 129.79, 129.76, 129.53, 129.37, 129.35, 128.79, 128.46, 128.38, 128.31, 128.25, 128.13, 128.05, 127.81, 127.65, 127.62, 127.45, 127.16, 100.3, 100.2, 99.5, 86.1, 82.7, 80.7, 79.6, 79.1, 78.1, 77.6, 76.1, 76.0, 75.8, 75.4, 75.3, 75.2, 75.0, 74.9, 74.8, 74.6, 74.2, 74.0, 73.39, 73.38, 73.31, 73.0, 72.9, 69.6, 69.2, 68.9, 61.4, 38.7, 27.0; HRMS (ESI) *m/z* calculated for C<sub>112</sub>H<sub>113</sub>ClKO<sub>24</sub>S [M+K]<sup>+</sup> 1947.6663; found 1947.6721.

## 6. Synthesis of semi-circular hexasaccharide



The automated synthesis of semi-circular hexasaccharide **2c** was carried out in an H-type divided cell equipped with a carbon felt anode and a platinum plate cathode (20 mm×20 mm). In the anodic chamber were placed disaccharide building block **3** (0.75 mmol, 930 mg), [P<sub>14</sub>]OTf (1.6 mmol, 0.63 g) and CH<sub>2</sub>Cl<sub>2</sub> (15 mL). In the cathodic chamber were placed trifluoromethanesulfonic acid (0.79 mmol, 70 μL), [P<sub>14</sub>]OTf (0.50 mmol, 0.12 mL) and CH<sub>2</sub>Cl<sub>2</sub> (15 mL). The constant current electrolysis (12 mA) was carried out at -40°C with stirring until 1.05 F/mol of electricity was consumed. After the electrolysis, tetrasaccharide building block **4b** (0.90 mmol, 1.71 g) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (3.5 mL) was subsequently added by the syringe pump under an argon atmosphere at -40°C and then -20°C kept for 60 min. Then Et<sub>3</sub>N (0.75 mL) was added, and solvent was removed under reduced pressure. The crude product was purified with silica gel chromatography (eluent: Hexane/EtOAc 5:1). Target semi-circular hexasaccharide **2c** was obtained in 57% isolated yield (0.423 mmol, 1.27 g). **4-Chlorophenyl 3,4-di-O-benzyl-6-O-tert-butylidiphenylsilyl-2-O-pivaloyl-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzyl-2-O-pivaloyl-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzyl-2-O-pivaloyl-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-di-O-benzyl-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-di-O-benzyl-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-di-O-benzyl-1-thio-β-D-glucopyranoside** (**2c**); (Hexane/EtOAc 3:1) R<sub>f</sub> = 0.50; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.82 (d, *J* = 7.2 Hz, 2 H), 7.78 (d, *J* = 7.2 Hz, 2 H), 7.70–7.69 (m, 2 H), 7.63 (d, *J* = 7.2 Hz, 2 H), 7.55–7.48 (m, 4 H), 7.37–7.08 (m, 75 H), 7.06 (d, *J* = 8.4 Hz, 2 H), 5.09–5.04 (m, 3 H), 4.94–4.85 (m, 5 H), 4.83 (d, *J* = 10.8 Hz, 1 H), 4.76–4.66 (m, 8 H), 4.64–4.51 (m, 10 H), 4.49–4.44 (m, 4 H), 4.41 (d, *J* = 12.6 Hz, 1 H), 4.38 (d, *J* = 11.4 Hz, 1 H), 4.34–4.29 (m, 3 H), 4.26 (d, *J* = 12.0 Hz, 1 H), 4.20 (d, *J* = 12.4 Hz, 1 H), 4.10 (*pseudo-t*, *J* = 9.0 Hz, 1 H), 4.07 (*pseudo-t*, *J* = 8.4 Hz, 1 H), 3.99 (d, *J* = 10.8 Hz, 1 H), 3.95–3.90 (m, 3 H), 3.85–3.79 (m, 2 H), 3.75 (*pseudo-t*, *J* = 9.0 Hz, 1 H), 3.71 (dd, *J* = 12.0, 5.4 Hz, 1 H), 3.67–3.64 (m, 4 H), 3.59 (d, *J* = 10.8 Hz, 1 H), 3.35–3.26 (m, 13 H), 3.21 (*pseudo-t*, *J* = 9.0 Hz, 1 H), 3.13 (ddd, *J* = 9.6, 3.6, 1.8 Hz, 1 H), 1.14 (s, 9 H), 1.13 (s, 9 H), 1.06 (s, 9 H), 1.00 (s, 9 H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 177.1, 176.64, 176.59, 164.51, 164.47, 164.45, 138.5, 138.4, 138.3, 138.2, 138.1, 138.0, 137.98,

137.91, 137.66, 135.8, 135.7, 135.5, 135.4, 133.54, 133.45, 133.26, 133.0, 132.9, 132.1, 129.77, 129.72, 129.64, 129.60, 129.45, 129.24, 129.16, 128.75, 128.42, 128.35, 128.27, 128.20, 128.13, 128.01, 127.91, 127.84, 127.62, 127.57, 127.51, 127.46, 127.41, 127.35, 127.30, 127.26, 126.9, 100.9, 100.3, 99.80, 99.77, 99.5, 86.0, 83.13, 83.11, 82.5, 80.3, 79.04, 78.98, 78.6, 78.2, 77.8, 77.4, 76.2, 76.1, 76.0, 75.8, 75.7, 75.14, 75.05, 74.89, 74.85, 74.79, 74.76, 74.73, 74.65, 74.55, 74.52, 74.46, 74.35, 74.03, 73.8, 73.3, 73.2, 73.1, 72.7, 72.6, 69.8, 69.2, 69.1, 67.5, 66.4, 62.5, 38.7, 38.6, 27.23, 27.18, 27.0, 26.7, 19.2; HRMS (ESI)  $m/z$  calculated for  $C_{178}H_{191}ClKO_36SSi$   $[M+K]^+$  3038.1925; found 3038.2100.

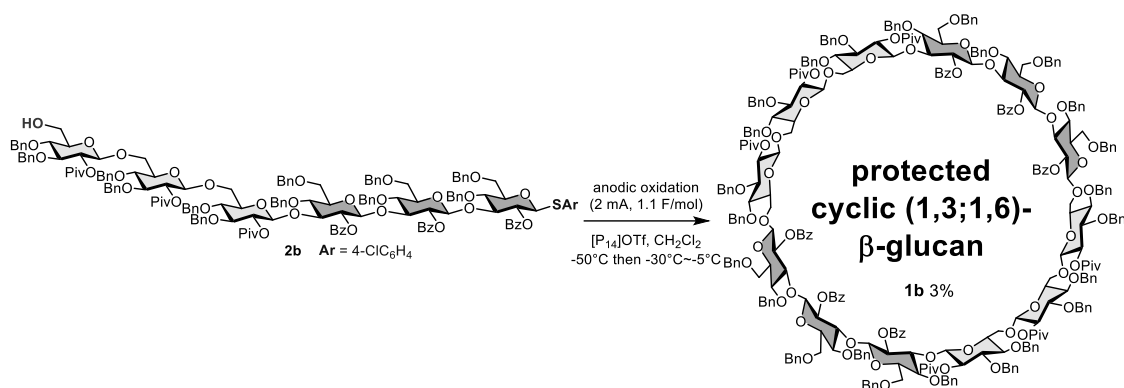


Semi-circular hexasaccharide **2c** (0.26 mmol, 790 mg) was dissolved in pyridine (2.0 mL) and the solution was cooled to 0°C. 70% HF·pyridine (0.35 mL) was added to the solution and the reaction mixture was stirred at 0°C to room temperature for 4 h. Conversion of **2c** was confirmed by TLC (Hexane/EtOAc 7:3) and aqueous sodium bicarbonate solution was added to quench the reaction. The aqueous solution was extracted with chloroform and the combined organic layer was washed with aqueous sodium bicarbonate solution and 1 N aqueous hydrochloric acid. The reaction mixture was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to obtain crude product. Thus-obtained crude product was purified by silica gel chromatography (eluent: Hexane/EtOAc 3:1) and semi-circular hexasaccharide **2b** (0.227 mmol, 628 mg) in 86% yield. **4-Chlorophenyl 3,4-di-O-benzyl-2-O-pivaloyl-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzyl-2-O-pivaloyl-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzyl-2-O-pivaloyl-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-di-O-benzyl-β-gluco-pyranosyl-(1→3)-2-O-benzoyl-4,6-di-O-benzyl-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-di-O-benzyl-1-thio-β-D-glucopyranoside (2b)**; TLC (Hexane/EtOAc 7:3)  $R_f$  = 0.50; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.83 (dd,  $J$  = 7.2, 4.2 Hz, 4 H), 7.55 (*pseudo-t*,  $J$  = 7.2 Hz, 1 H), 7.49 (*pseudo-t*,  $J$  = 7.2 Hz, 1 H), 7.45 (d,  $J$  = 7.8 Hz, 2 H), 7.38–7.14 (m, 63 H), 7.12–7.07 (m, 8 H), 5.12 (*pseudo-t*,  $J$  = 8.4 Hz, 1 H), 5.01–4.89 (m, 3 H), 4.88–4.70 (m, 7 H), 4.69–4.58 (m, 6 H), 4.58–4.44 (m, 11 H), 4.42 (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), 4.29–4.27 (m, 2 H), 4.24 (d,  $J$  = 12.0 Hz, 1 H), 4.21 (d,  $J$  = 12.0 Hz, 1 H), 4.12 (*pseudo-t*,  $J$  = 7.8 Hz, 1 H), 4.09 (*pseudo-t*,  $J$  = 9.0 Hz, 1 H), 3.93 (*pseudo-t*,  $J$  = 7.2 Hz, 1 H), 3.88 (d,  $J$  = 10.2 Hz, 1 H), 3.74–3.42 (m, 20 H), 3.37–3.31 (m, 5 H), 3.26 (ddd,  $J$  = 10.2, 4.8, 2.4 Hz, 1 H), 3.11 (*pseudo-t*,  $J$  = 9.0 Hz, 1 H), 2.15 (*pseudo-t*, 1 H), 1.18 (s, 9 H), 1.11 (s, 9 H), 1.09 (m, 9 H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 177.2, 176.6,

176.5, 164.53, 164.49, 138.52, 138.47, 138.26, 138.23, 138.20, 138.15, 138.09, 138.07, 138.02, 137.9, 137.8, 133.7, 133.6, 133.56, 133.32, 133.25, 133.0, 132.9, 132.1, 129.8, 129.7, 129.6, 129.5, 129.2, 129.1, 128.77, 128.65, 128.49, 128.36, 128.29, 128.24, 128.21, 128.19, 128.13, 128.08, 128.01, 127.95, 127.92, 127.78, 127.74, 127.64, 127.57, 127.47, 127.41, 127.38, 127.33, 127.28, 127.25, 127.22, 127.14, 127.04, 126.99, 101.4, 100.6, 99.71, 99.68, 99.63, 86.0, 83.0, 82.8, 82.4, 80.3, 79.1, 78.8, 78.7, 77.8, 77.7, 77.4, 76.2, 76.0, 75.7, 75.5, 75.1, 74.90, 74.78, 74.76, 74.62, 74.58, 74.55, 74.49, 74.37, 74.29, 73.8, 73.7, 73.3, 73.2, 73.1, 72.84, 72.79, 72.57, 70.0, 69.2, 68.5, 67.3, 61.8, 38.73, 38.69, 38.66, 27.25, 27.08, 27.00. 26.9; HRMS (ESI)  $m/z$  calculated for  $C_{162}H_{173}ClKO_{36}S [M+K]^+$  2800.0753; found 2800.0688.

## 7. Synthesis of protected cyclic dodecasaccharide

### 7-1. One-pot dimerisation-cyclisation process

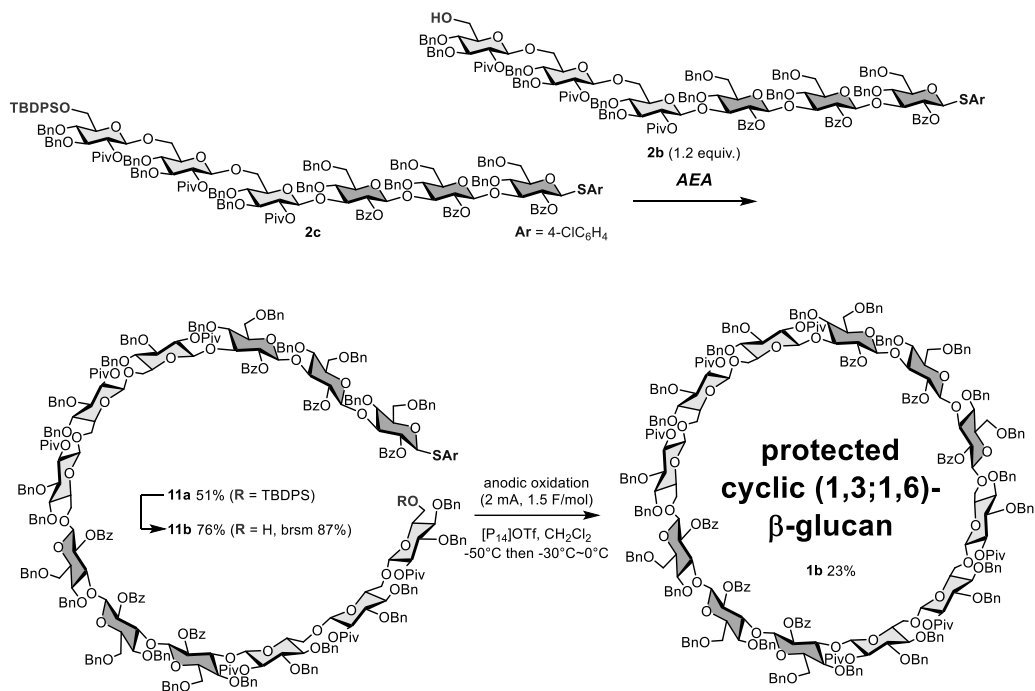


The dimerisation and cyclisation of linear dodecasaccharide **2b** was carried out in an H-type divided cell equipped with a carbon felt anode and a platinum plate cathode (10 mm×10 mm). In the anodic chamber were placed protected linear dodecasaccharide **2b** (0.135 mmol, 374 mg), [P<sub>14</sub>]OTf (0.63 mmol, 0.15 mL) and CH<sub>2</sub>Cl<sub>2</sub> (5.0 mL). In the cathodic chamber were placed trifluoromethanesulfonic acid (0.15 mmol, 13  $\mu$ L), [P<sub>14</sub>]OTf (0.50 mmol, 0.12 mL) and CH<sub>2</sub>Cl<sub>2</sub> (4.2 mL). The constant current electrolysis (2.0 mA) was carried out at -50°C with stirring until 1.1 F/mol of electricity was consumed and then -30°C kept for 60 min. After elevation of the reaction temperature to -50°C, Et<sub>3</sub>N (0.2 mL) was added to both chambers, and the reaction mixture was dissolved in CHCl<sub>3</sub> and washed with water to remove electrolyte [P<sub>14</sub>]OTf. Thus-obtained organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to obtain the crude product (479 mg). Silica gel chromatography (eluent: Hexane/EtOAc 4:1) and preparative recycling GPC (eluent: CHCl<sub>3</sub>) afforded target protected cyclic dodecasaccharide **1b** in 3% yield (2.3  $\mu$ mol, 12 mg). **Cyclobis-(1→6)-(3,4-di-**



***O*-benzyl-2-*O*-pivaloyl- $\beta$ -D-glucopyranosyl)-(1 $\rightarrow$ 6)-(3,4-di-*O*-benzyl-2-*O*-pivaloyl- $\beta$ -D-glucopyranosyl)-(1 $\rightarrow$ 6)-(3,4-di-*O*-benzyl-2-*O*-pivaloyl- $\beta$ -D-glucopyranosyl)-(1 $\rightarrow$ 3)-(2-*O*-benzoyl-4,6-di-*O*-benzyl- $\beta$ -D-glucopyranosyl)-(1 $\rightarrow$ 3)-(2-*O*-benzoyl-4,6-di-*O*-benzyl- $\beta$ -D-glucopyranosyl) (1b);** TLC (Hexane/EtOAc 3:1)  $R_f = 0.30$ ;  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (*pseudo-t*,  $J = 6.6$  Hz, 4 H), 7.79 (*pseudo-t*,  $J = 6.0$  Hz, 4 H), 7.67–7.62 (m, 4 H), 7.59 (d,  $J = 7.2$  Hz, 4 H), 7.46–7.43 (m, 6 H), 7.36–7.14 (m, 126 H), 7.05 (d,  $J = 6.0$  Hz, 2 H), 5.09–5.00 (m, 12 H), 4.96–4.88 (m, 6 H), 4.74 (d,  $J = 7.8$  Hz, 2 H), 4.70 (dd,  $J = 10.8, 3.0$  Hz, 2 H), 4.66–4.61 (m, 6 H), 4.56–4.42 (m, 26 H), 4.38–4.25 (m, 12 H), 4.15 (d,  $J = 7.8$  Hz, 2 H), 4.09 (*pseudo-t*,  $J = 9.0$  Hz, 2 H), 4.02 (*pseudo-t*,  $J = 9.0$  Hz, 2 H), 4.00–3.96 (m, 4 H), 3.79–3.74 (m, 4 H), 3.67–3.27 (m, 48 H), 3.21–3.15 (m, 4 H), 1.11 (s, 36 H), 1.08 (s, 18 H);  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  177.0, 176.5, 176.4, 164.7, 164.4, 163.8, 138.7, 138.6, 138.43, 138.38, 138.2, 138.1, 138.04, 137.95, 137.91, 133.30, 133.24, 133.20, 129.82, 129.75, 129.5, 129.4, 129.3, 128.8, 128.61, 128.56, 128.43, 128.35, 128.25, 128.20, 128.15, 128.10, 128.05, 128.01, 127.96, 127.7, 127.6, 127.45, 127.39, 127.35, 127.31, 127.26, 127.21, 127.13, 127.0, 126.9, 126.8, 100.7, 100.5, 100.43, 100.35, 100.14, 99.3, 83.0, 82.9, 82.8, 82.7, 79.75, 79.66, 78.3, 78.2, 78.1, 77.6, 77.5, 76.3, 76.1, 75.6, 75.3, 75.2, 75.1, 74.85, 74.80, 74.72, 74.59, 74.54, 74.48, 74.33, 74.21, 73.84, 73.76, 73.3, 73.2, 73.1, 72.9, 72.2, 69.7, 69.15, 69.07, 67.7, 66.9, 38.65, 38.63, 38.59, 27.3, 27.1, 26.9; MS (MALDI)  $m/z$  calculated for  $\text{C}_{312}\text{H}_{336}\text{KO}_{72}$   $[\text{M}+\text{K}]^+$  5273.22; found 5273.04.

## 7-2. Stepwise process via AEA



The automated synthesis of linear dodecasaccharide **11a** was carried out in an H-type divided cell equipped with a carbon felt anode and a platinum plate cathode (20 mm×20 mm). In the anodic chamber were placed hexasaccharide building block **2c** (0.135 mmol, 405 mg), [P<sub>14</sub>]OTf (0.76 mmol, 0.175 mL) and CH<sub>2</sub>Cl<sub>2</sub> (3.9 mL). In the cathodic chamber were placed trifluoromethanesulfonic acid (0.20 mmol, 18  $\mu$ L), [P<sub>14</sub>]OTf (0.50 mmol, 0.12 mL) and CH<sub>2</sub>Cl<sub>2</sub> (4.9 mL). The constant current electrolysis (2.0 mA) was carried out at -50°C with stirring until 1.1 F/mol of electricity was consumed. After the electrolysis, hexasaccharide building block **2b** (0.162 mmol, 450 mg) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (0.9 mL) was subsequently added by the syringe pump under an argon atmosphere at -50°C and then -30°C kept for 60 min. After elevation of the reaction temperature to -5°C, Et<sub>3</sub>N (0.4 mL) was added, and the reaction mixture was filtered through a short column (4×3 cm) of silica gel to remove electrolyte Bu<sub>4</sub>NOTf. Removal of the solvent under reduced pressure and the crude product was purified with silica gel chromatography (eluent: Hexane/EtOAc 3:1) and preparative recycling GPC (eluent: CHCl<sub>3</sub>). Target linear dodecasaccharide **11a** was obtained in 51% isolated yield (0.069 mmol, 389 mg). Thus obtained **11a** was used as a starting material for the next step without detailed structural characterization.

Linear dodecasaccharide **11a** (0.069 mmol, 389 mg) was dissolved in pyridine (0.53 mL) and the solution was cooled to 0°C. 70% HF•pyridine (0.10 mL) was added to the solution and the reaction mixture was stirred at 0°C to room temperature for 2 h. Conversion of **11a** was confirmed by TLC

(Hexane/EtOAc 7:3) and aqueous sodium bicarbonate solution was added to quench the reaction. The aqueous solution was extracted with chloroform and the combined organic layer was washed with aqueous sodium bicarbonate solution and 1 N aqueous hydrochloric acid. The reaction mixture was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to obtain crude product (430 mg). Thus-obtained crude product was purified by silica gel chromatography (eluent: Hexane/EtOAc 7:3) and **11b** (0.053 mmol, 284 mg) in 76% yield (87% conversion). **4-Chlorophenyl 3,4-di-O-benzyl-2-O-pivaloyl-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzyl-2-O-pivaloyl-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzyl-2-O-pivaloyl-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-di-O-benzyl-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-di-O-benzyl-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzyl-2-O-pivaloyl-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzyl-2-O-pivaloyl-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-di-O-benzyl-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-di-O-benzyl-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-di-O-benzyl-1-thio-β-D-glucopyranoside (11b)**; TLC (Hexane/EtOAc 7:3) R<sub>f</sub> = 0.20; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.80 (d, *J* = 7.2 Hz, 2 H), 7.76–7.73 (m, 5 H), 7.52–7.48 (m, 2 H), 7.45 (d, *J* = 7.2 Hz, 1 H), 7.41–7.39 (m, 2 H), 7.36–6.99 (m, 141 H), 6.89–6.86 (m, 1 H), 5.08–5.05 (m, 2 H), 4.99–4.80 (m, 16 H), 4.74–4.14 (m, 55 H), 4.10–4.00 (m, 6 H), 3.90–3.82 (m, 5 H), 3.71–3.62 (m, 6 H), 3.60–3.16 (m, 41 H), 3.04–3.00 (m, 1 H), 2.17 (*pseudo-t*, *J* = 6.0 Hz, 1 H), 1.10 (s, 18 H), 1.08 (s, 9 H), 1.06 (s, 9 H), 1.05 (s, 9 H), 1.04 (s, 9 H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 177.3, 177.2, 177.1, 176.7, 176.6, 176.5, 176.4, 164.52, 164.47, 163.9, 138.58, 138.54, 138.51, 138.45, 138.35, 138.31, 138.28, 138.21, 138.18, 138.15, 138.11, 138.07, 138.01, 137.96, 137.87, 137.8, 137.7, 133.6, 133.28, 133.25, 133.22, 133.14, 133.0, 132.93, 132.90, 132.1, 129.78, 129.72, 129.65, 129.55, 129.48, 129.45, 129.38, 129.32, 129.25, 129.18, 129.15, 128.8, 128.7, 128.6, 128.53, 128.46, 128.35, 128.29, 128.24, 128.21, 128.18, 128.14, 128.03, 127.97, 127.94, 127.92, 127.91, 127.76, 127.73, 127.69, 127.63, 127.60, 127.56, 127.43, 127.41, 127.37, 127.35, 127.31, 127.26, 127.22, 127.21, 127.1, 127.0, 126.9, 101.5, 100.8, 100.7, 100.6, 100.5, 100.2, 99.8, 99.6, 99.5, 86.0, 83.1, 82.99, 82.95, 82.93, 82.85, 82.5, 82.4, 80.4, 79.1, 79.0, 78.78, 78.60, 77.73, 77.65, 77.63, 77.43, 76.4, 76.3, 75.98, 75.93, 75.89, 75.87, 75.72, 75.59, 75.56, 75.44, 75.15, 75.11, 75.03, 74.85, 74.77, 74.65, 74.61, 74.51, 74.37, 74.34, 74.27, 74.15, 74.12, 74.02, 73.96, 73.87, 73.79, 73.30, 73.25, 73.17, 73.11, 73.09, 72.82, 72.80, 72.52, 72.44, 72.22, 69.9, 69.21, 69.17, 69.10, 67.6, 61.8, 38.68, 38.62, 38.58, 27.24, 27.19, 27.13, 27.09, 26.99, 26.80, 26.76; MS (MALDI) *m/z* calculated for C<sub>318</sub>H<sub>341</sub>ClKO<sub>72</sub>S [M+K]<sup>+</sup> 5417.21; found 5417.67.

The intramolecular glycosylation of linear dodecasaccharide **11b** was carried out in an H-type divided cell equipped with a carbon felt anode and a platinum plate cathode (10 mm×10 mm). In the anodic chamber were placed protected linear dodecasaccharide **11b** (0.028 mmol, 151 mg), [P<sub>14</sub>]OTf

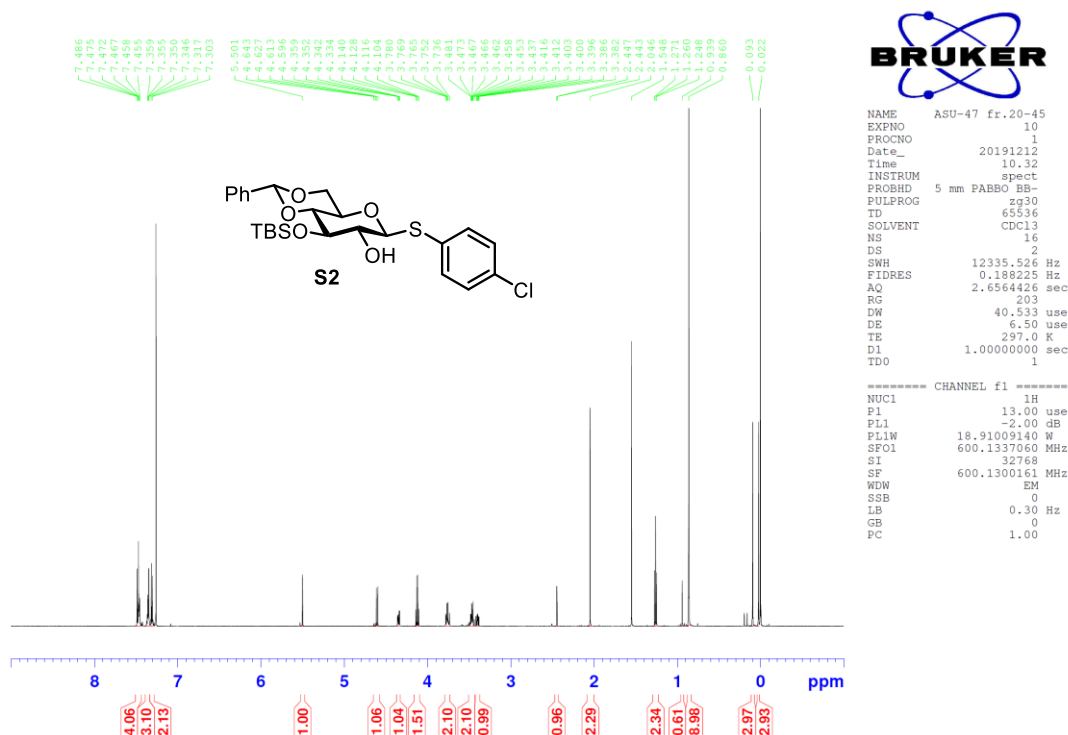
(0.74 mmol, 0.17 mL) and CH<sub>2</sub>Cl<sub>2</sub> (5.0 mL). In the cathodic chamber were placed trifluoromethanesulfonic acid (0.14 mmol, 12 μL), [P<sub>14</sub>]OTf (0.50 mmol, 0.12 mL) and CH<sub>2</sub>Cl<sub>2</sub> (5.1 mL). The constant current electrolysis (2.0 mA) was carried out at -50°C with stirring until 1.5 F/mol of electricity was consumed and then -30°C kept for 60 min. After elevation of the reaction temperature to -5°C, Et<sub>3</sub>N (0.1 mL) was added to both chambers, and the reaction mixture was dissolved in CHCl<sub>3</sub> and washed with water to remove electrolyte [P<sub>14</sub>]OTf. Thus-obtained organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to obtain the crude product (160 mg). Silica gel chromatography (eluent: Hexane/EtOAc 3:1) and preparative recycling GPC (eluent: CHCl<sub>3</sub>) afforded target protected cyclic dodecasaccharide **1b** in 23% yield (6.9 μmol, 36 mg).

## 8. Reference

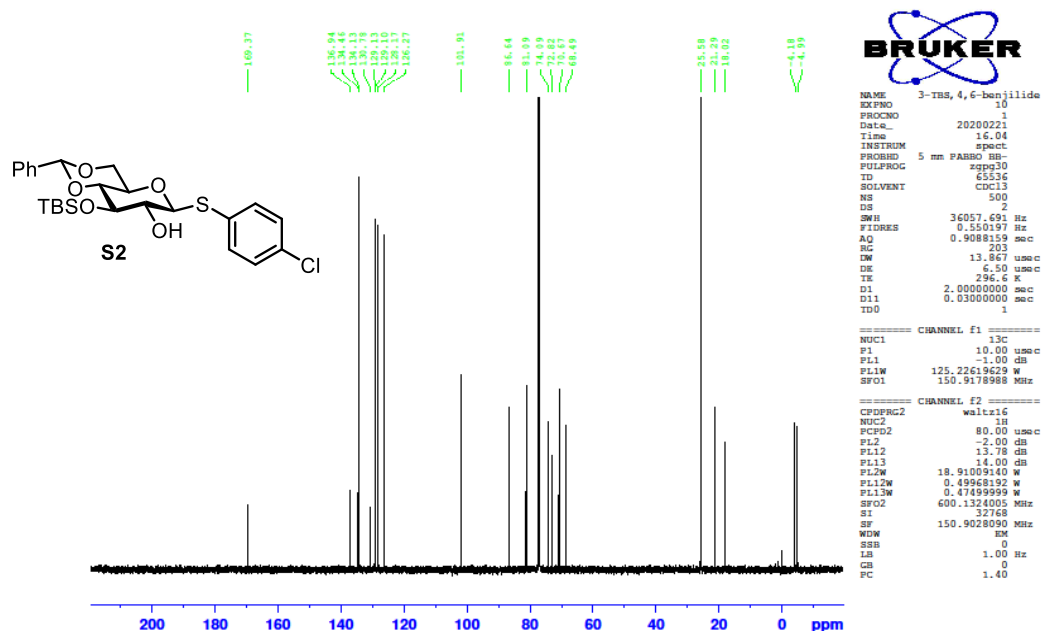
- 1) N. Basu, S. K. Maity, S. Roy, S. Singha and R. Ghosh, *Carbohydr. Res.*, 2011, **346**, 534.

## 9. <sup>1</sup>H and <sup>13</sup>C NMR spectra of synthetic intermediates and monosaccharide building blocks

### <sup>1</sup>H NMR

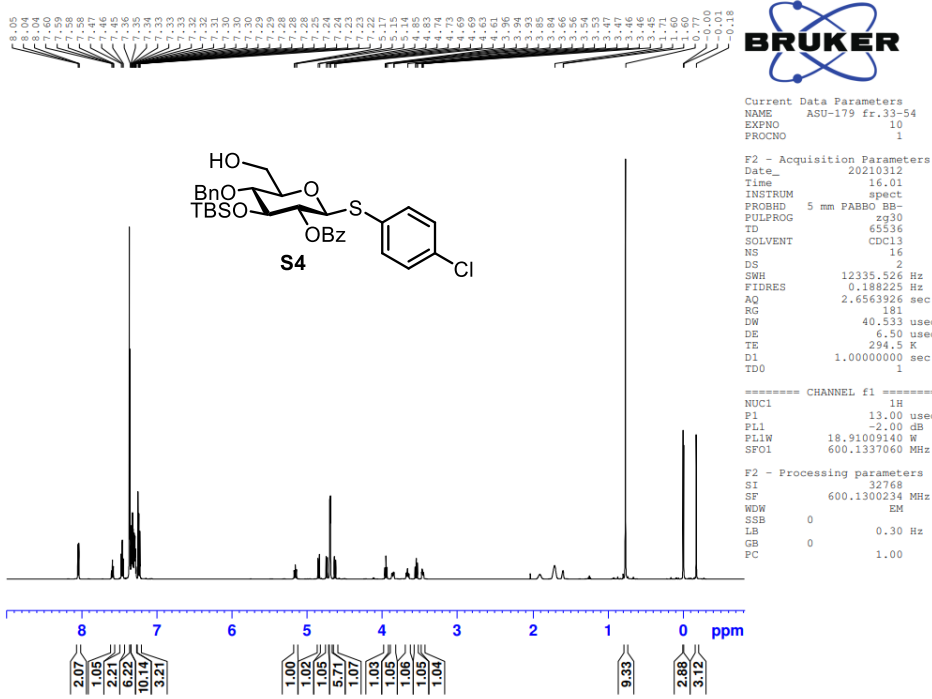


### <sup>13</sup>C NMR

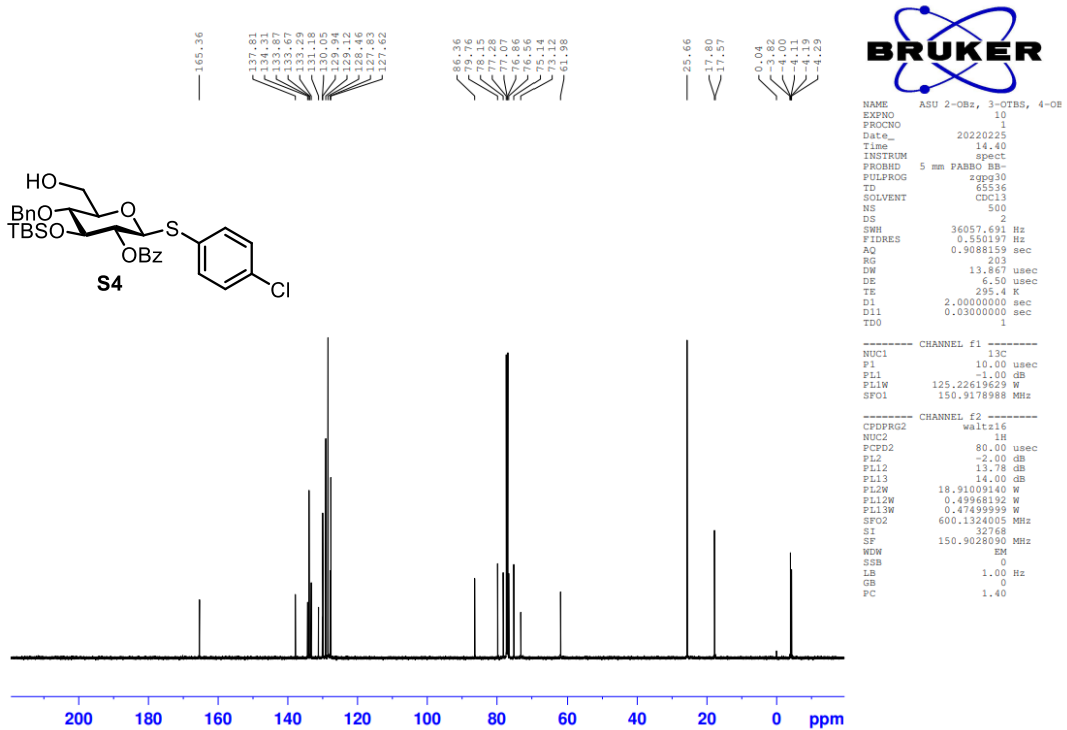




<sup>1</sup>H NMR



<sup>13</sup>C NMR

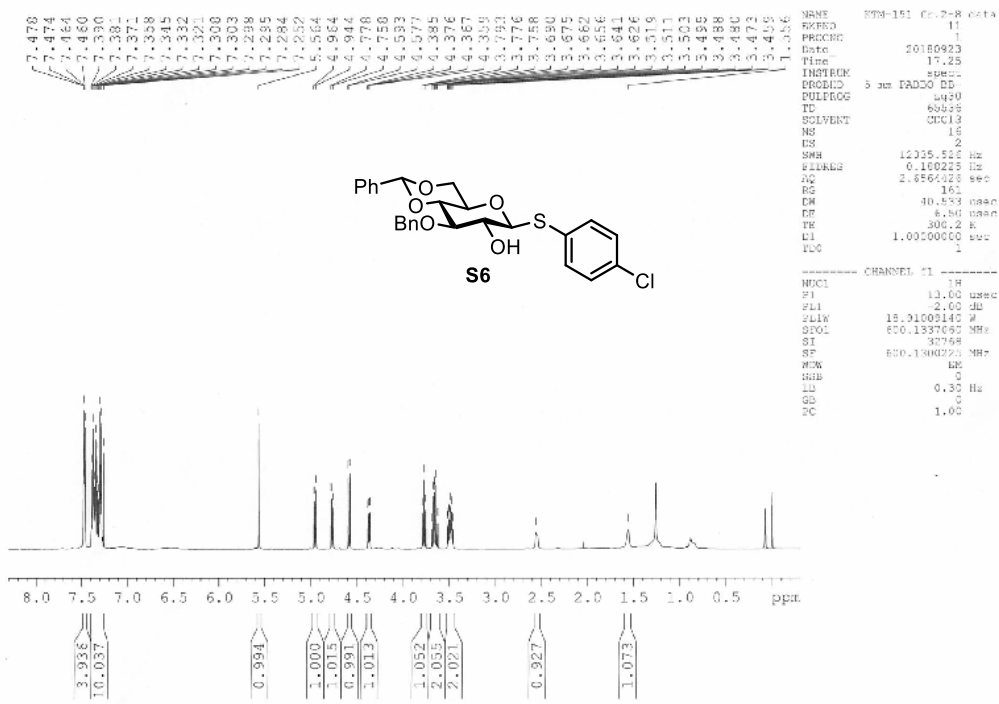




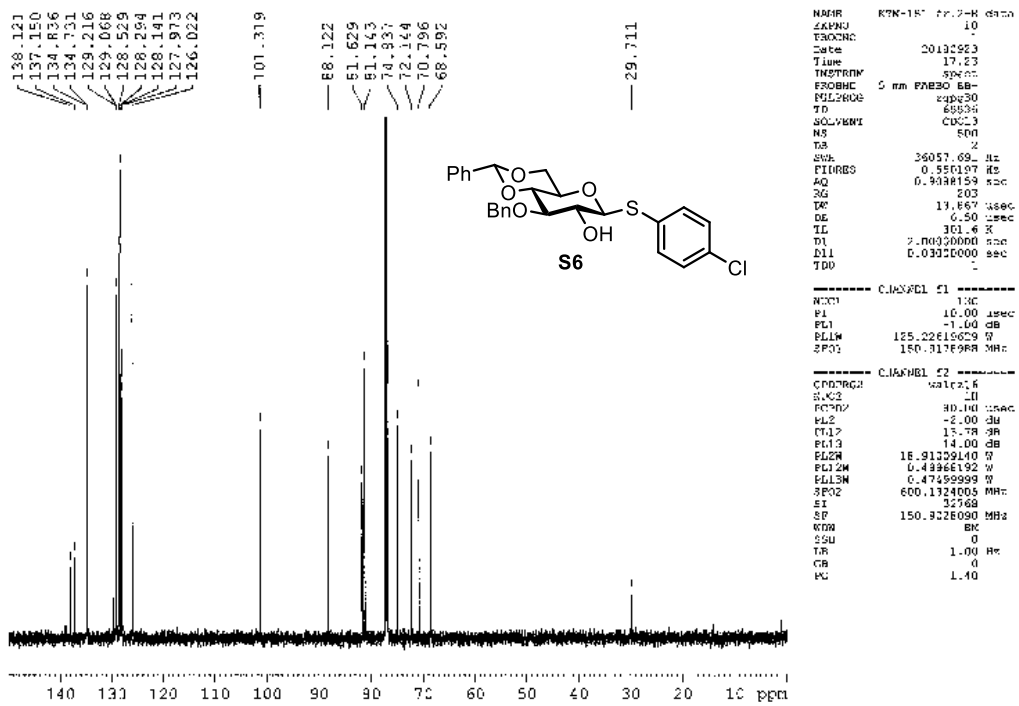




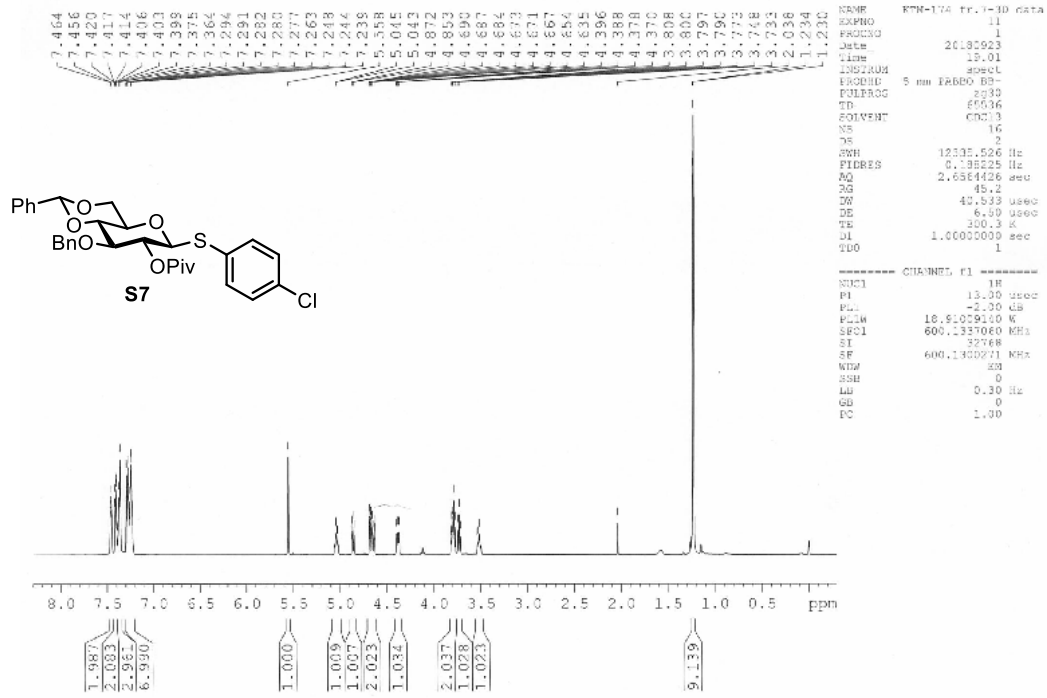
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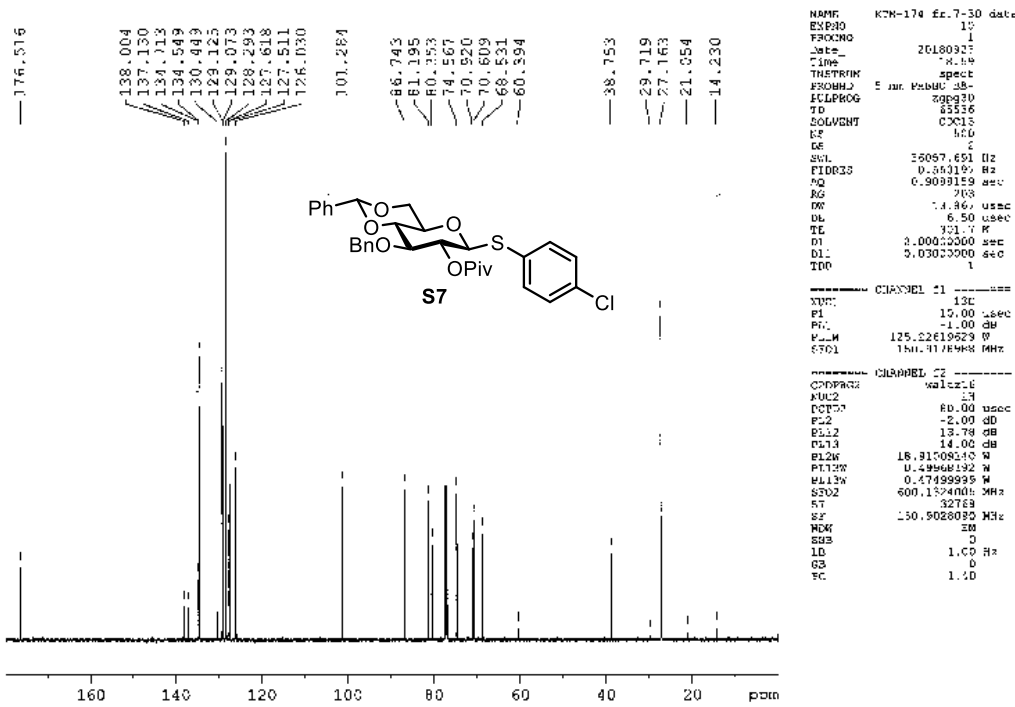
<sup>13</sup>C NMR



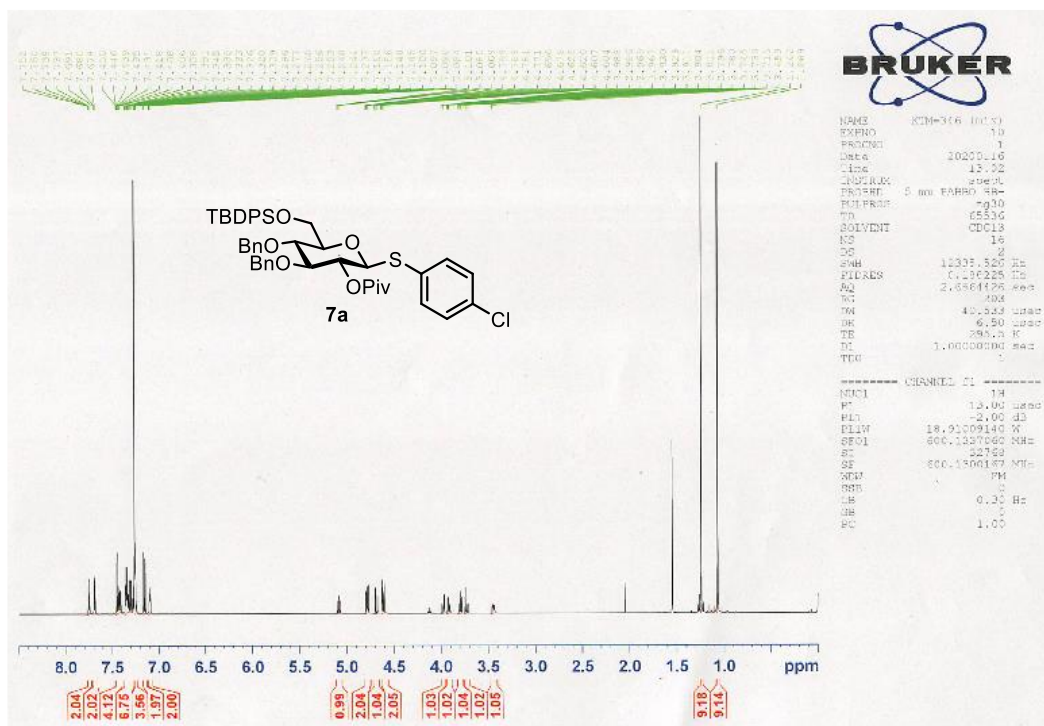
<sup>1</sup>H NMR



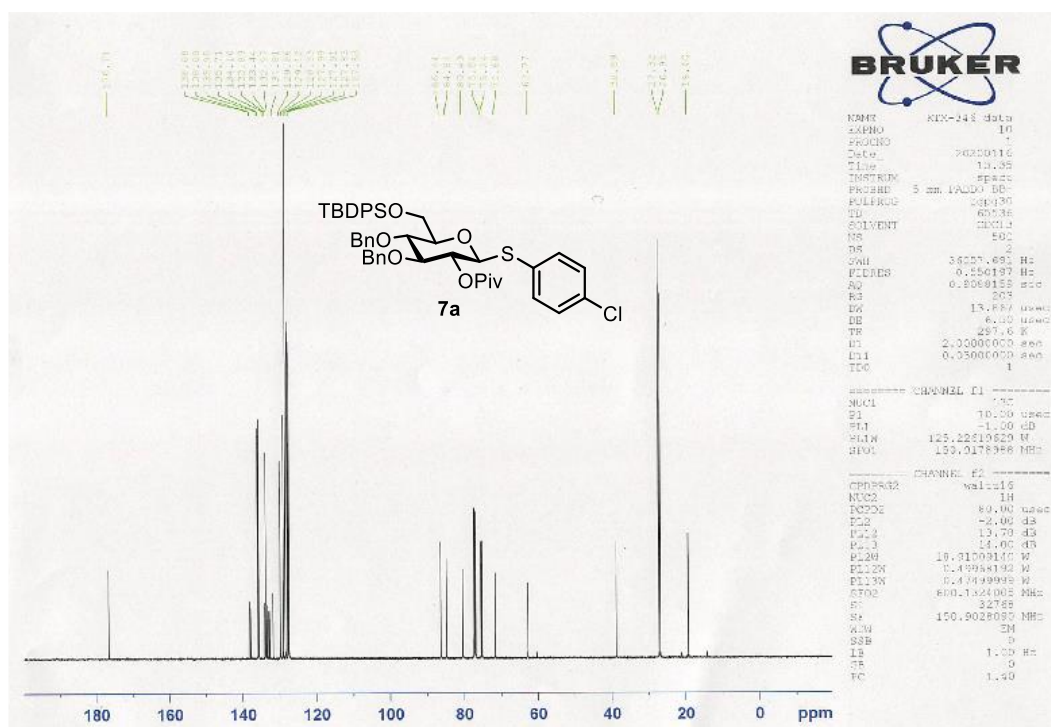
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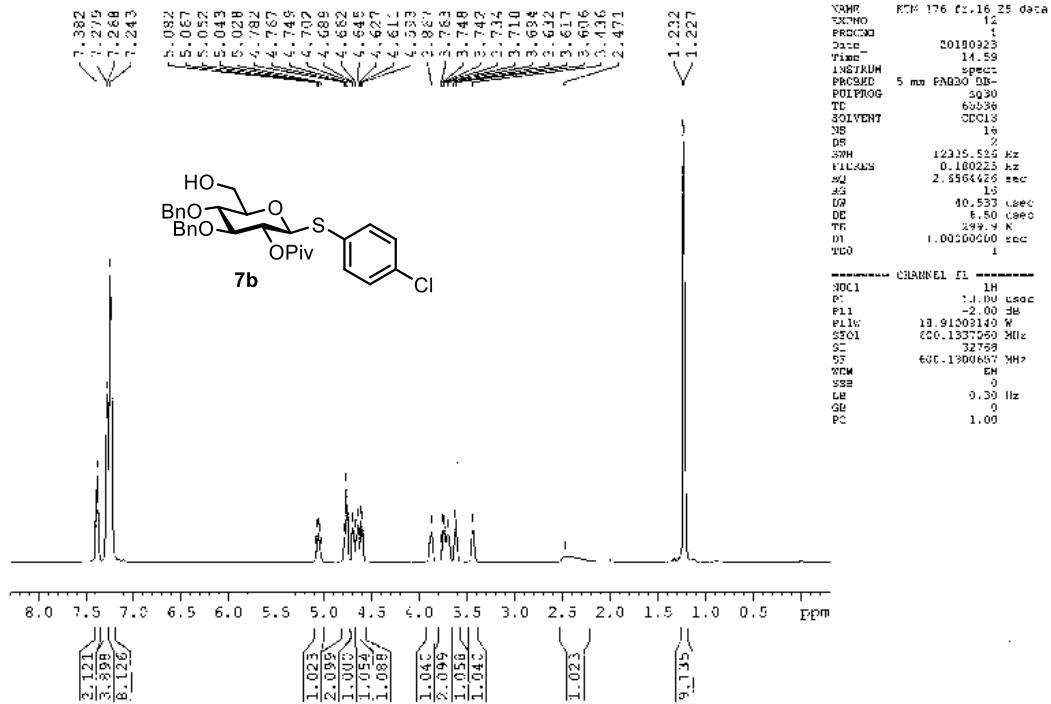
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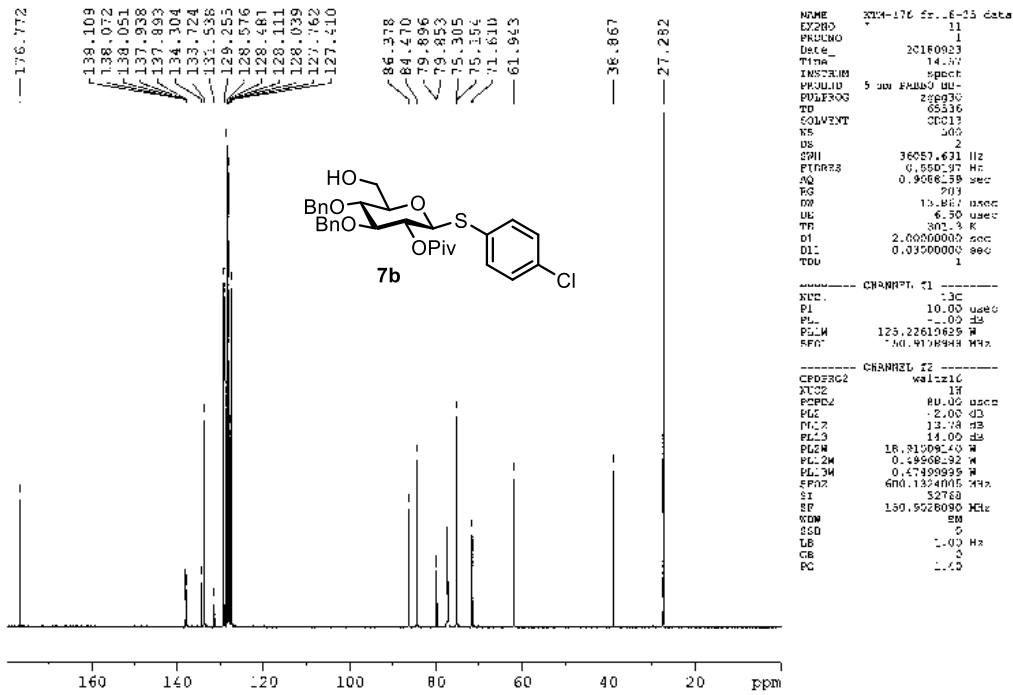
# <sup>13</sup>C NMR



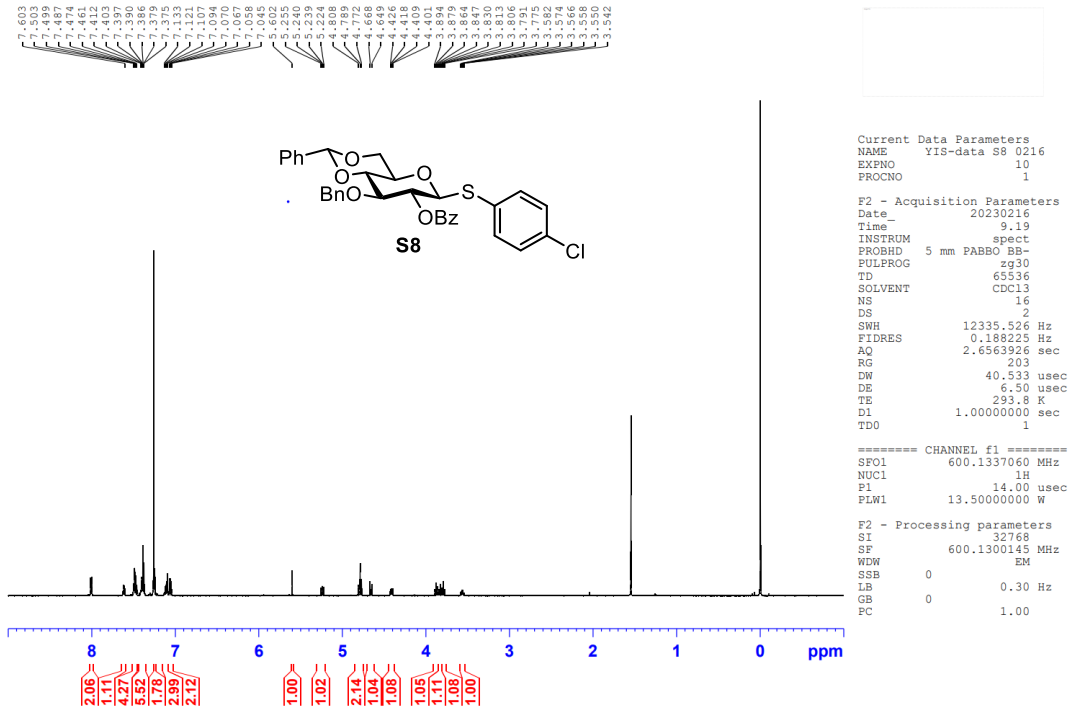
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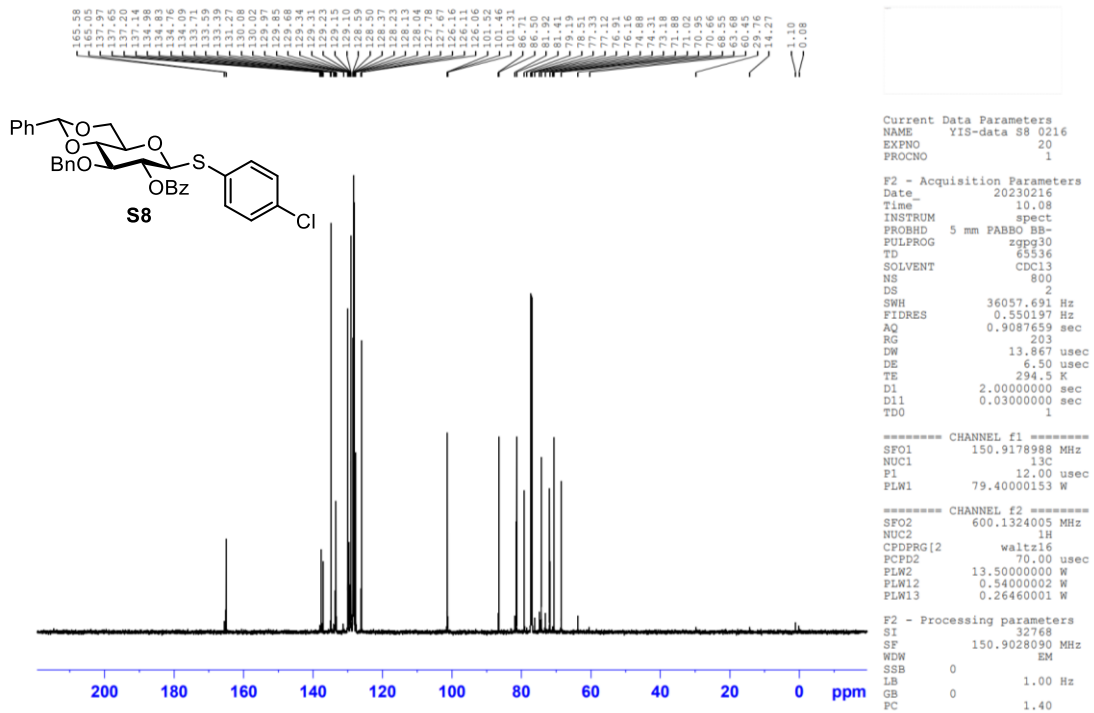
<sup>13</sup>C NMR



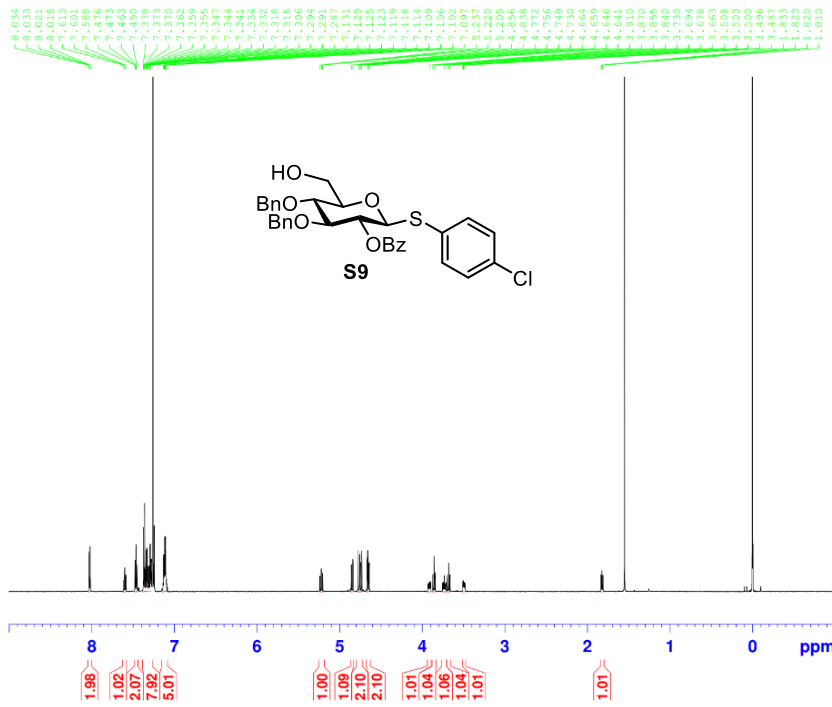
<sup>1</sup>H NMR



<sup>13</sup>C NMR



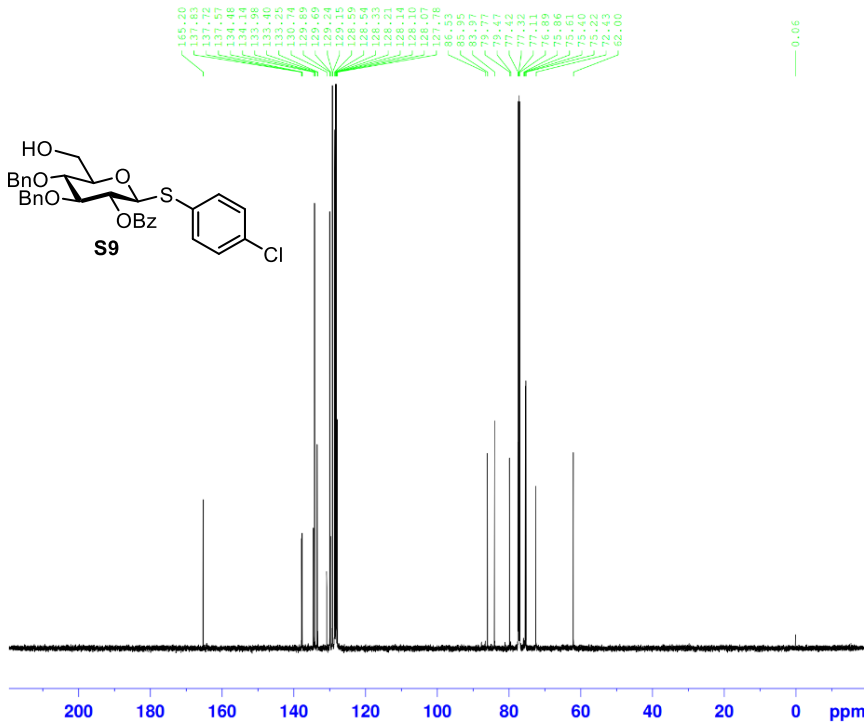
<sup>1</sup>H NMR



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PROCNO    1
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PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         16
DS         2
SWH        12335.526 Hz
FIDRES     0.18225 Hz
AQ         2.6564426 sec
RG         203
DW         40.533 usec
DE         4.50 usec
TE         295.4 K
D1         1.0000000 sec
TD0        1
----- CHANNEL f1 -----
NUC1       1H
P1          13.00 usec
PL1         -2.00 dB
PL12        18.91009140 dB
SFO1        600.137060 MHz
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WDW         EM
SSB         0 Hz
LB          0 Hz
GB          0 Hz
PC          1.00
    
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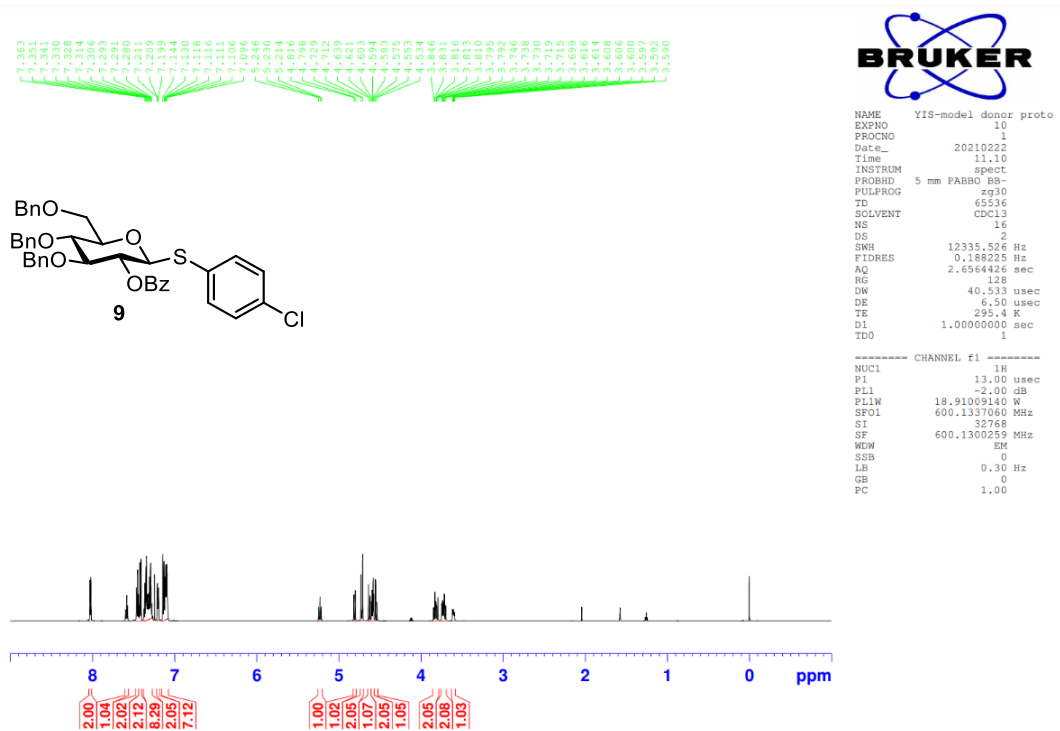
<sup>13</sup>C NMR



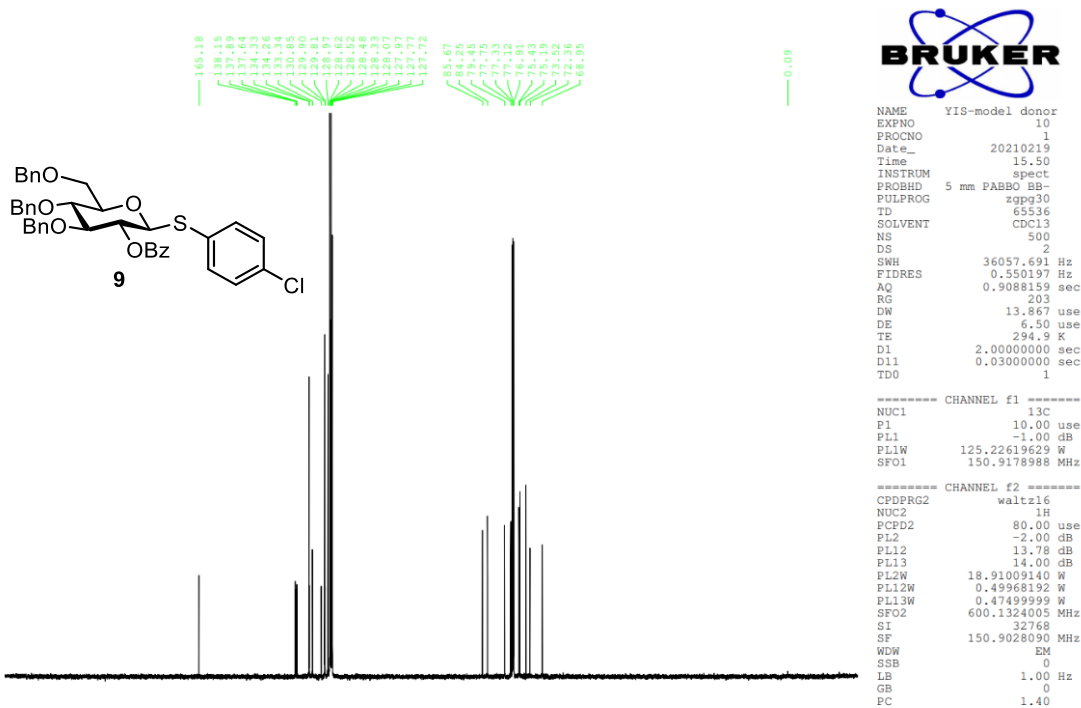
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PROCNO    1
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PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         16
DS         2
SWH        36057.691 Hz
FIDRES     0.250197 Hz
AQ         0.9088159 sec
RG         203
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DE         6.50 usec
TE         296.4 K
D1         2.0000000 sec
D11        0.3300000 sec
TD0        1
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NUC1       13C
P1          10.00 usec
PL1         -1.00 dB
PL12        125.22619629 dB
SFO1        125.9178988 MHz
----- CHANNEL f2 -----
CPDPRG2   waltz16
NUC2       1H
PCTP2      80.00 usec
PL2         -2.00 dB
PL12       13.78 dB
PL13       14.00 dB
PL14       14.00 dB
PL15       18.91009140 dB
PL16       0.49988192 dB
PL17       0.47439859 dB
SFO2        600.1324005 MHz
SI          32768
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WDW         EM
SSB         1.00 Hz
LB          0 Hz
GB          0 Hz
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<sup>1</sup>H NMR



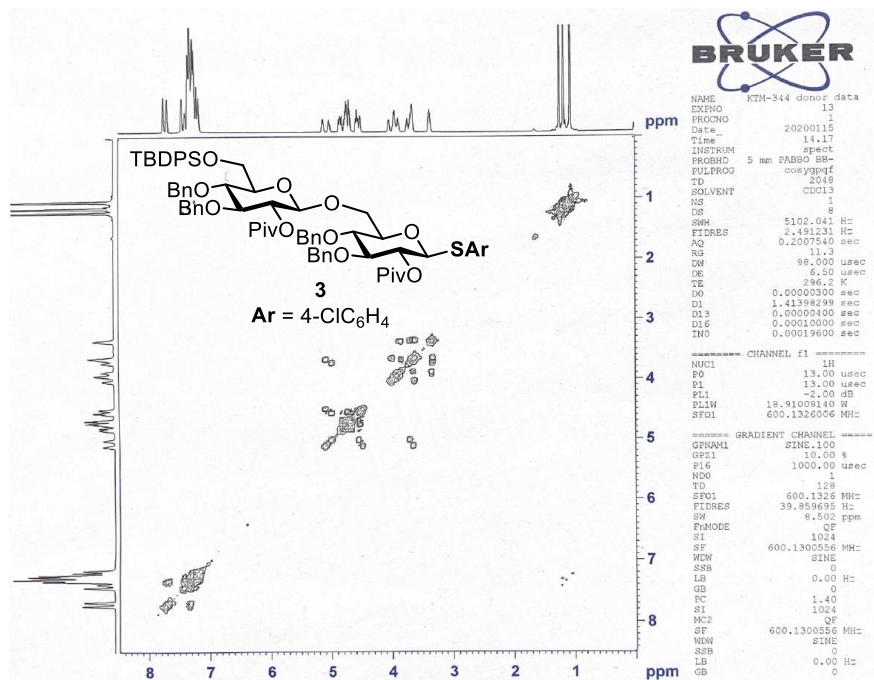
<sup>13</sup>C NMR



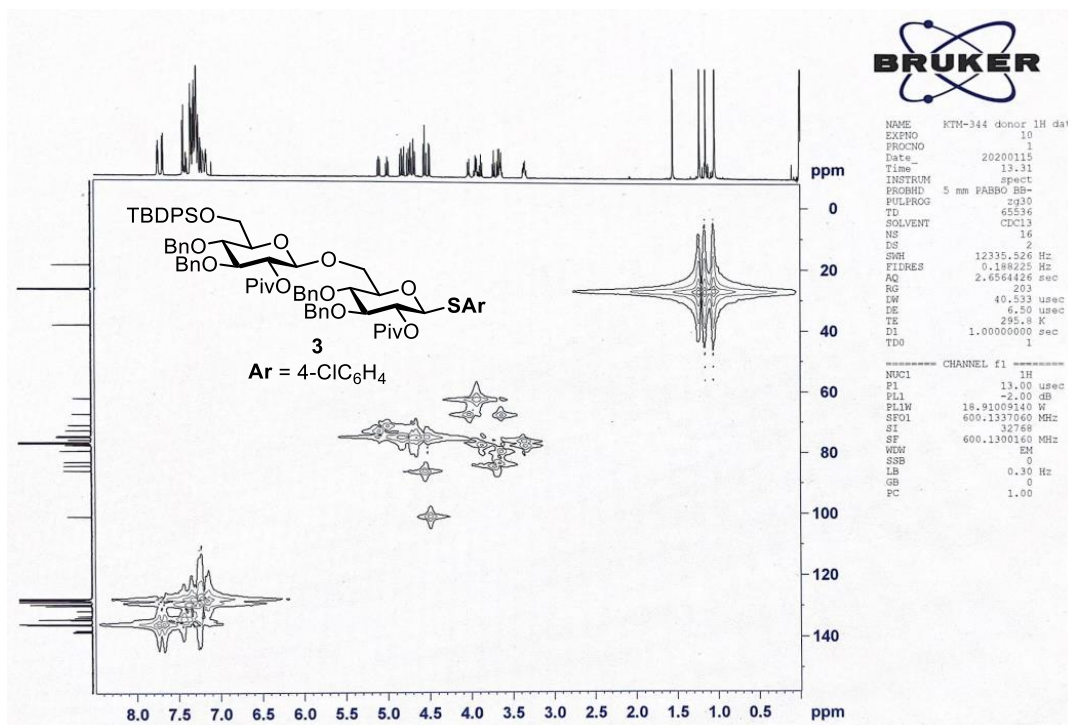




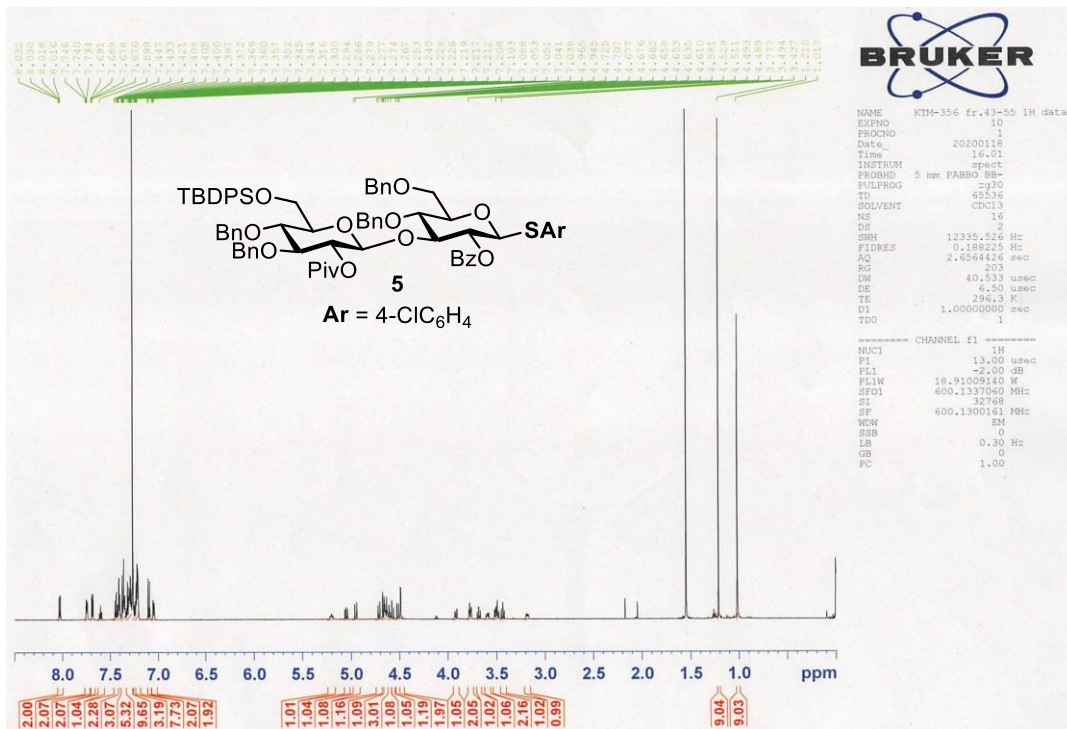
H-H cosy



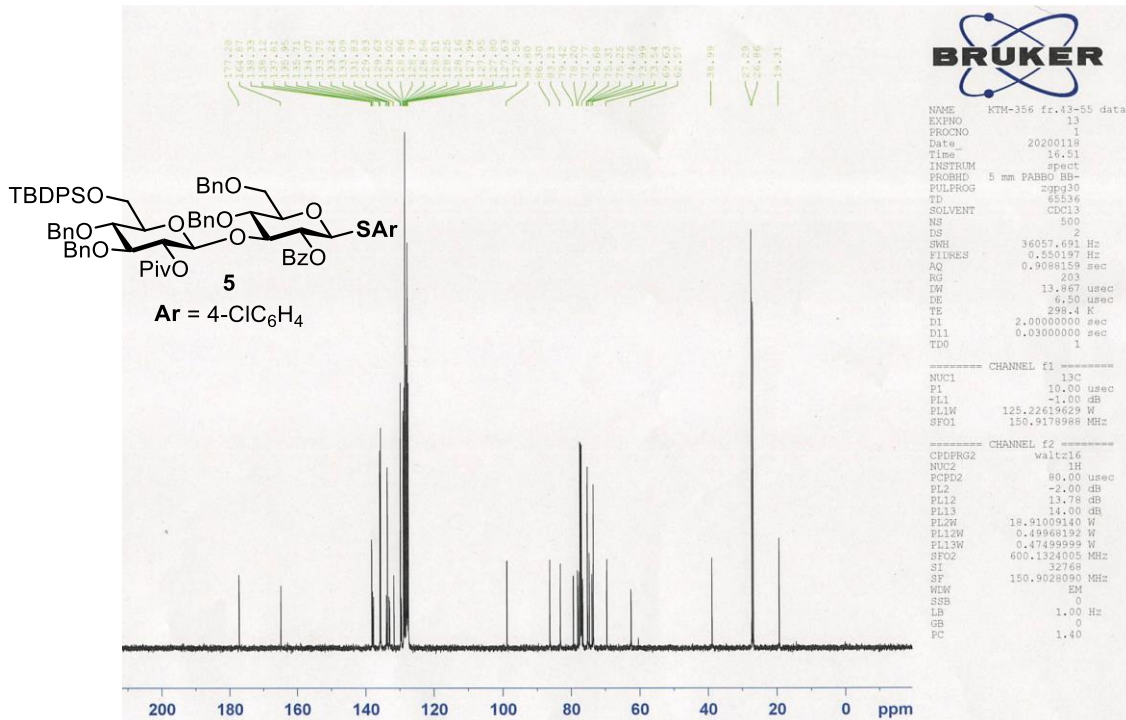
HMQC



<sup>1</sup>H NMR

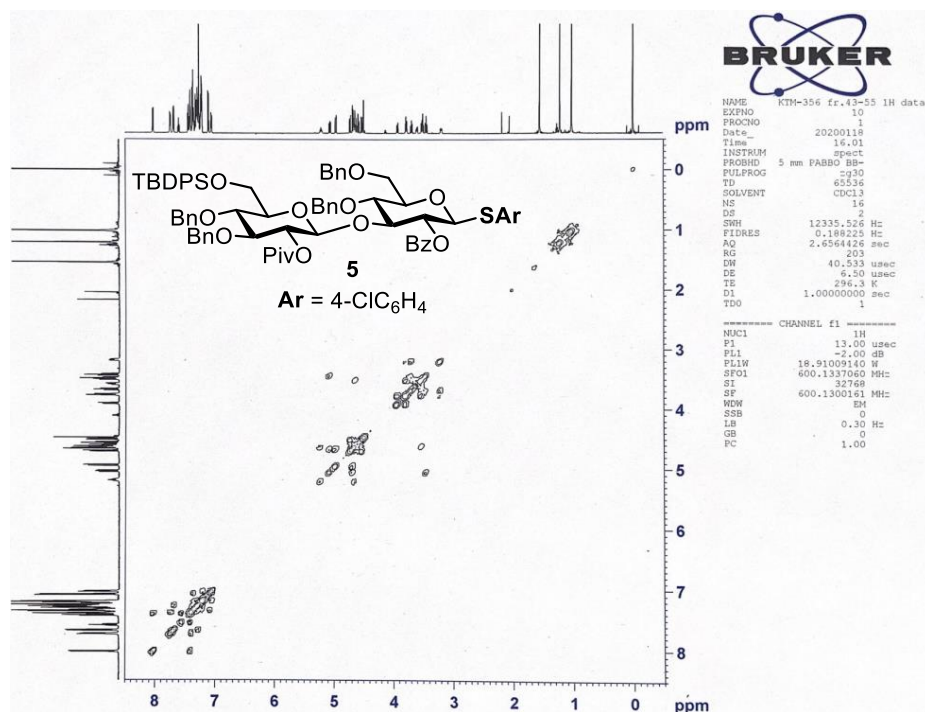


<sup>13</sup>C NMR

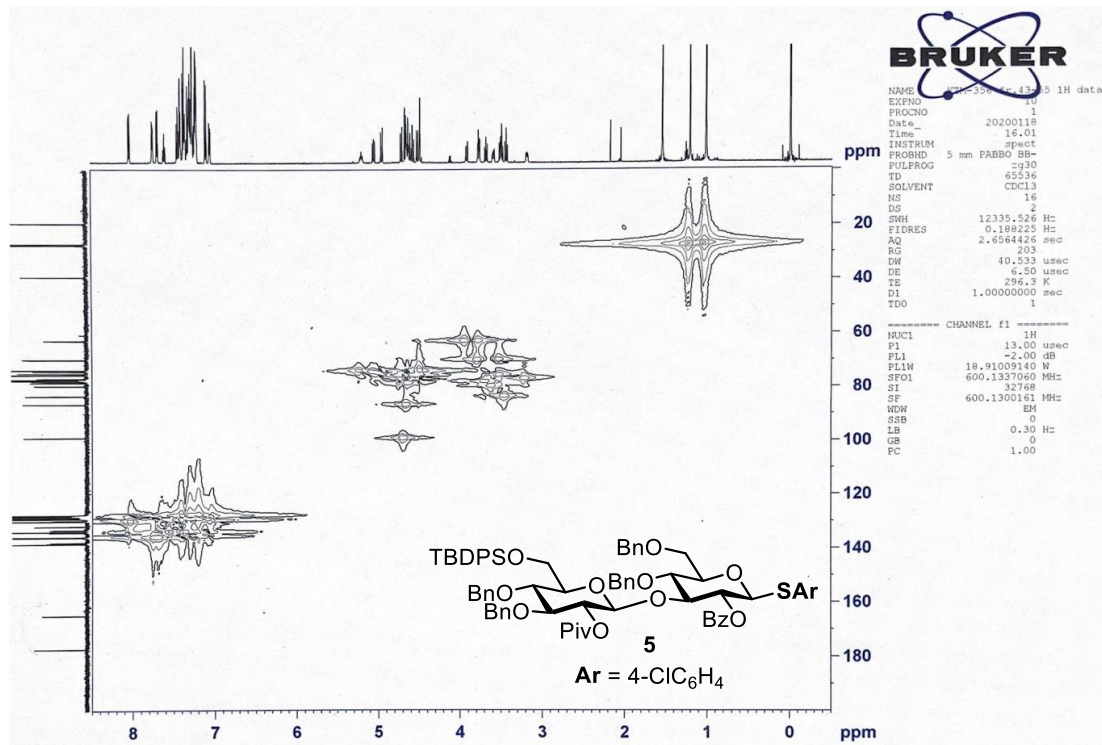




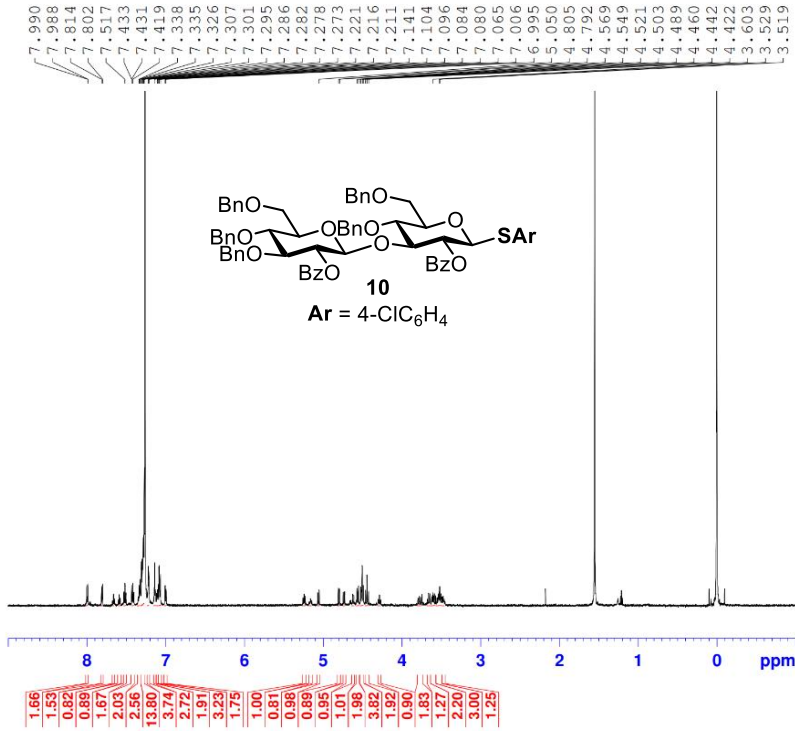
H-H cosy



HMQC



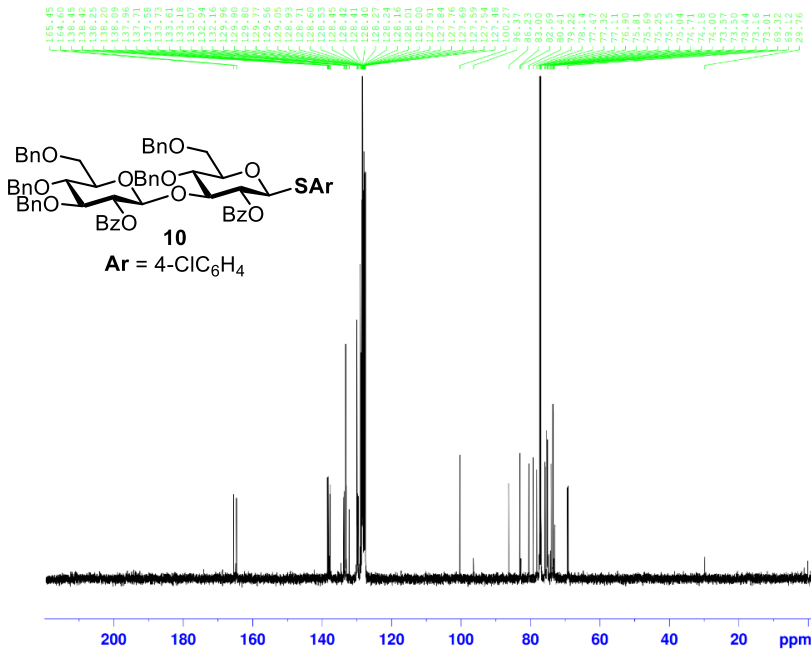
<sup>1</sup>H NMR



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EXPNO 10
PROCNO 1
Date_ 20210224
Time 17:29
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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2
DS 2
SSB 12335.526 Hz
FIDRES 0.188225 Hz
AQ 2.0564426 sec
RG 203
DE 6.50 usec
TE 304.3 K
D1 1.00000000 sec
TDD 1
===== CHANNEL f1 =====
NUC1 13C
P1 13.00 usec
PL1 0.00 dB
PL12 18.91009140 dB
SFO1 600.1337060 MHz
SI 32768
SF 600.1300154 MHz
WDW BM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
    
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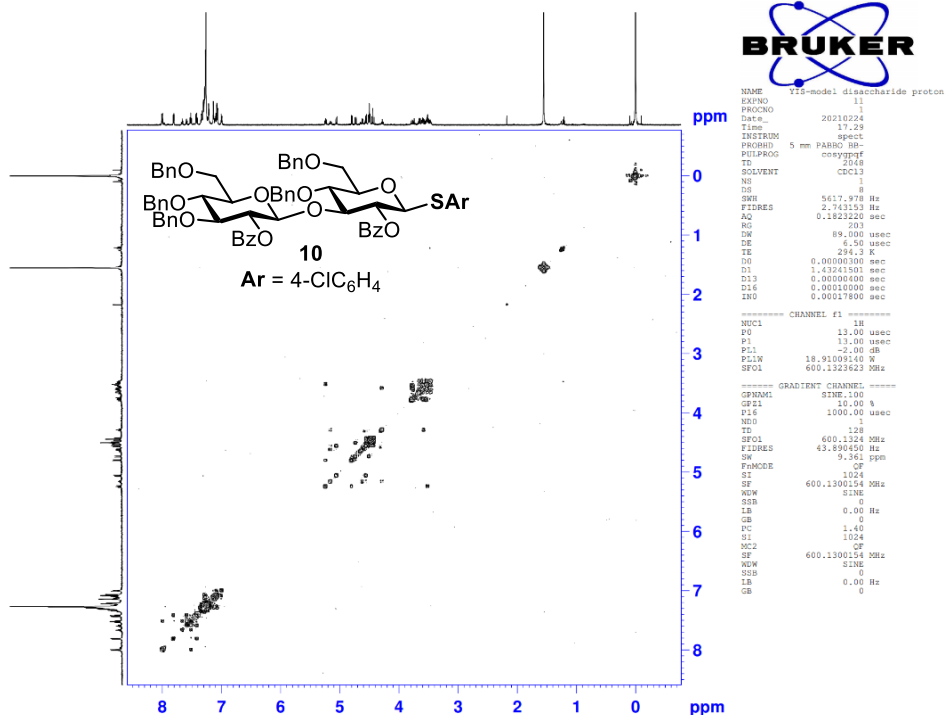
<sup>13</sup>C NMR



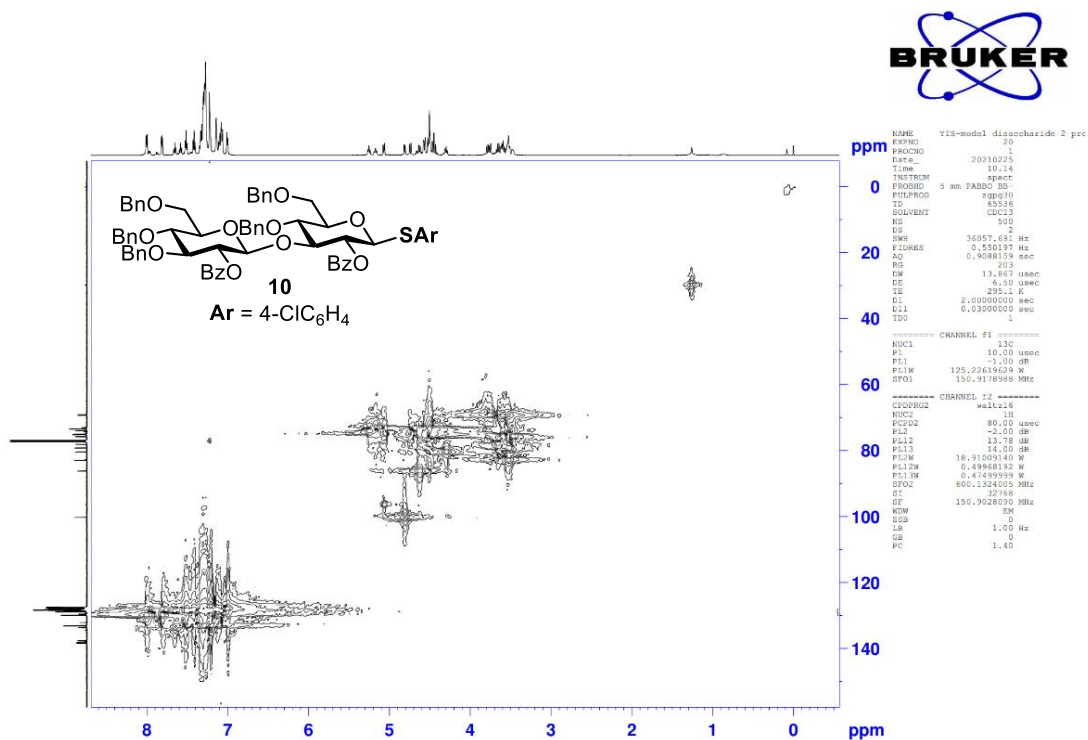
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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
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DS 2
SSB 36057.691 Hz
FIDRES 0.1550179 Hz
AQ 0.3088129 sec
RG 203
DE 6.50 usec
TE 304.3 K
D1 2.00000000 sec
D11 0.10000000 sec
TDD 1
===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PL1 0.00 dB
PL12 18.91009140 dB
SFO1 150.8178988 MHz
===== CHANNEL f2 =====
CHPROG2 waltz16
NUC2 13C
PULPR2 80.00 usec
PL2 2.00 dB
PL12 13.78 dB
PL13 14.00 dB
PL14 14.00 dB
PL15 14.00 dB
PL16 14.00 dB
PL17 14.00 dB
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H-H cosy

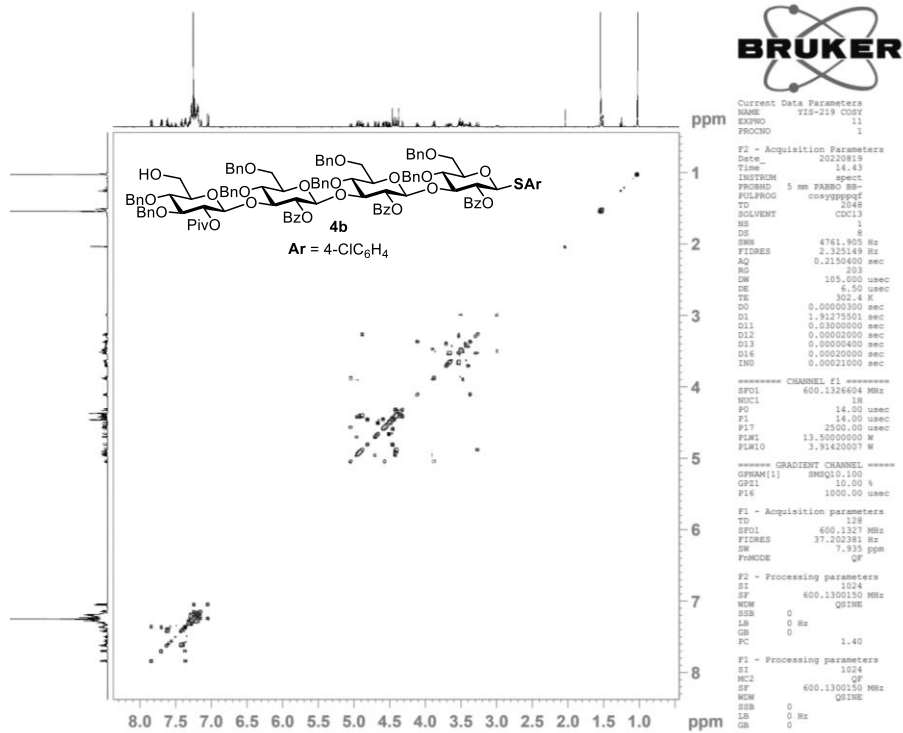


HMQC

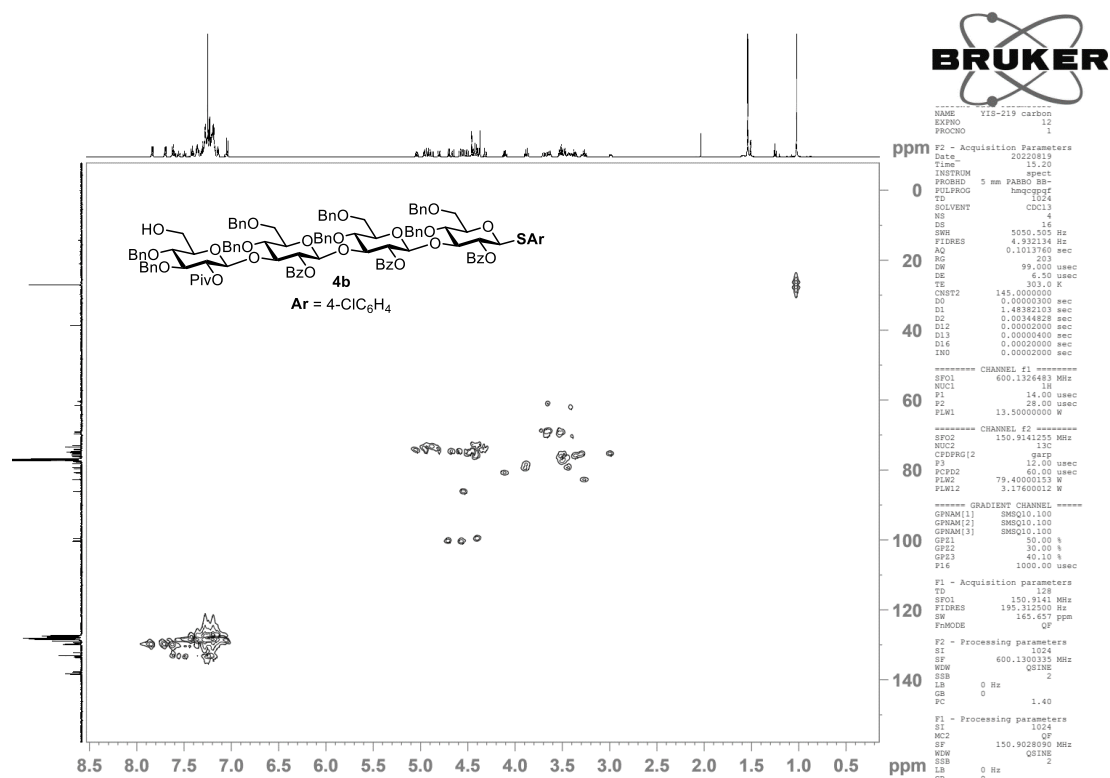




H-H cosy



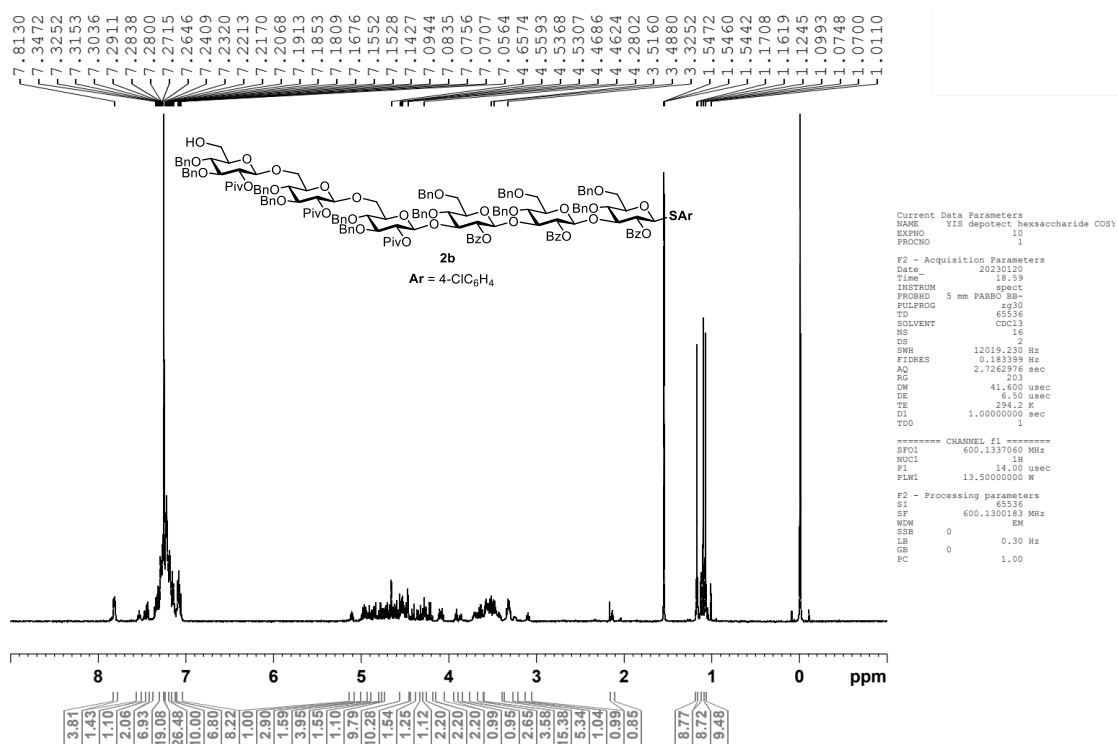
HMQC



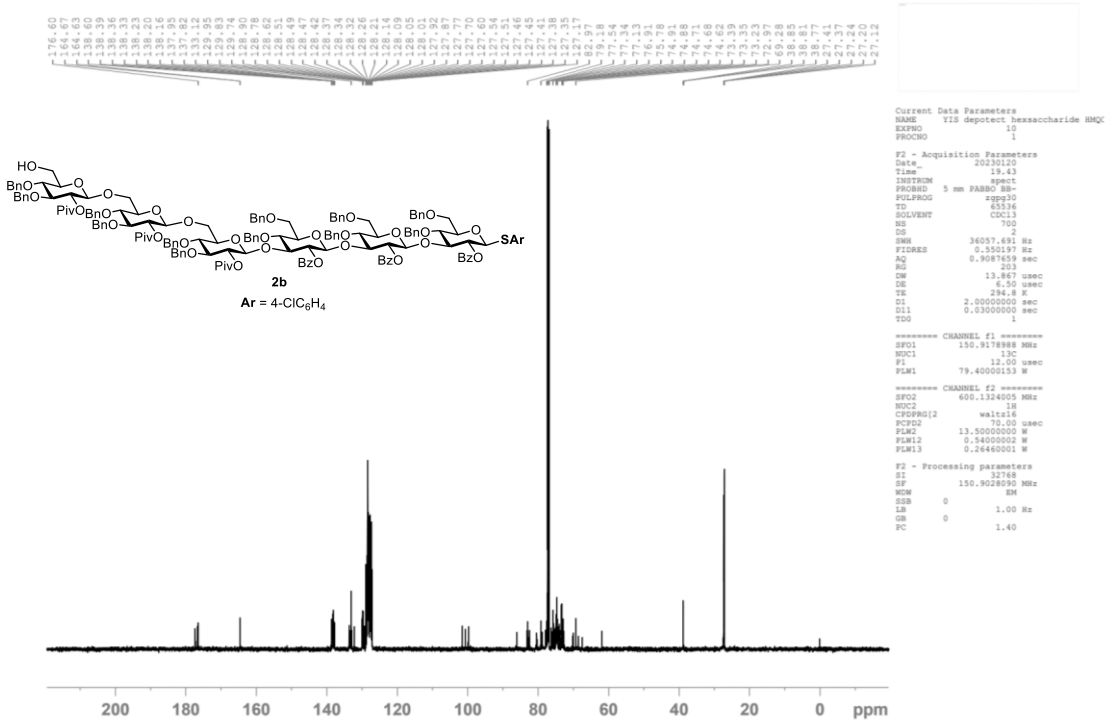


## 12. <sup>1</sup>H, <sup>13</sup>C NMR, H-H COSY and HMQC spectra of semi-circular hexasaccharide

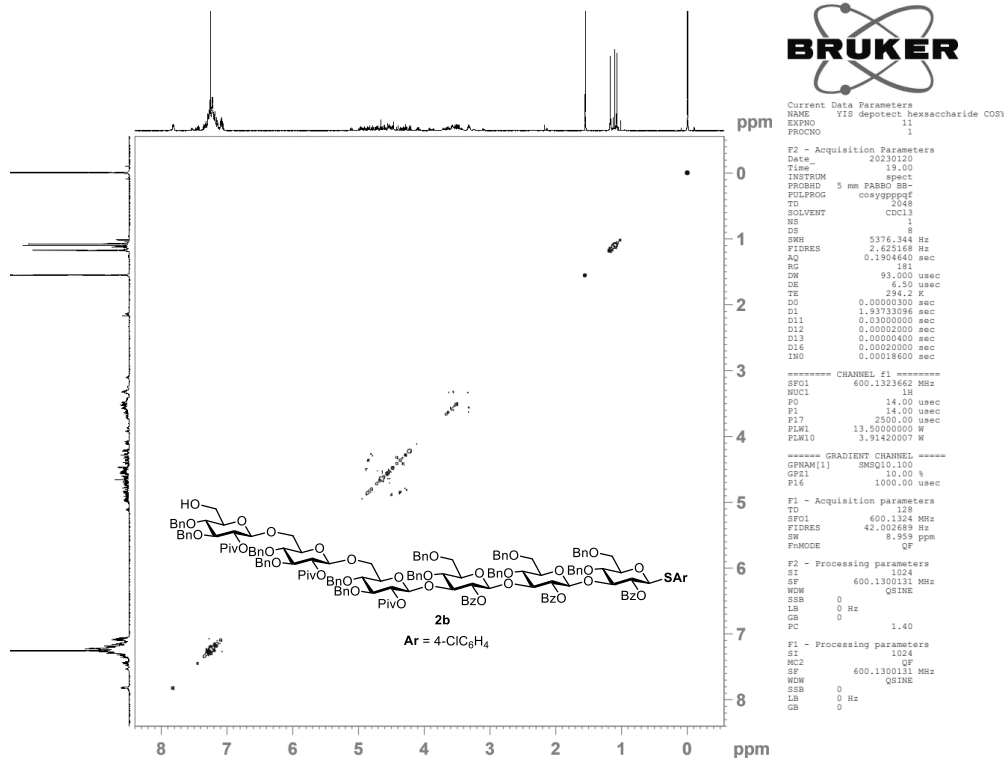
### <sup>1</sup>H NMR



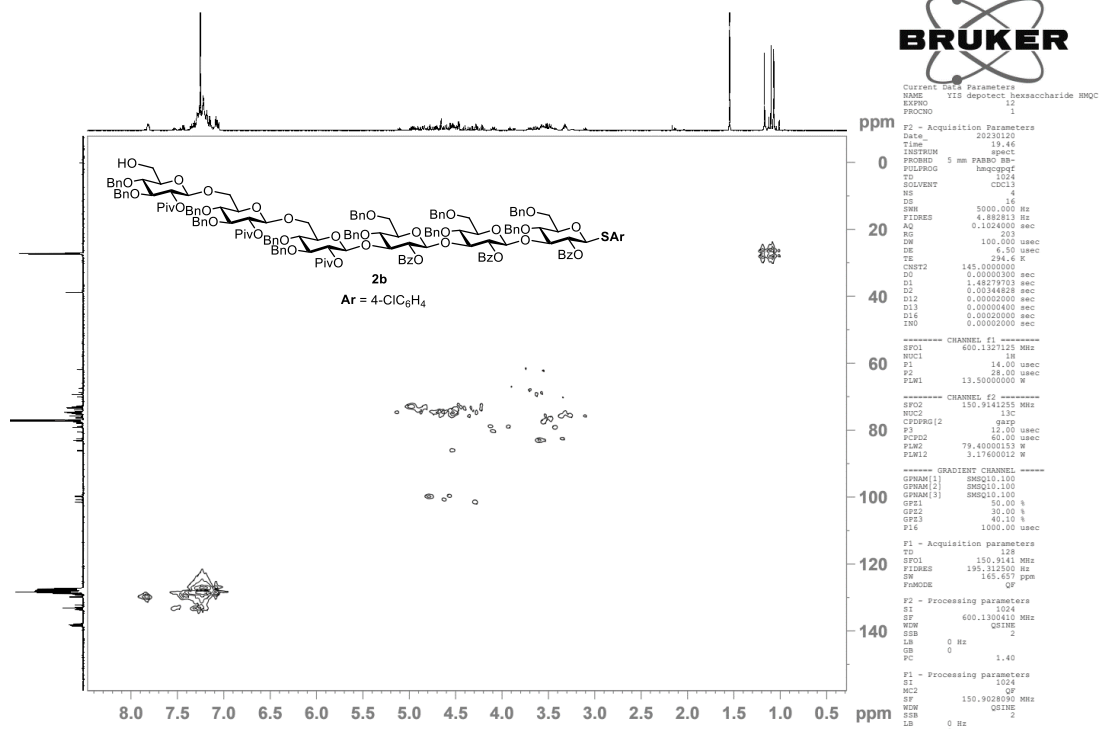
### <sup>13</sup>C NMR



H-H cosy

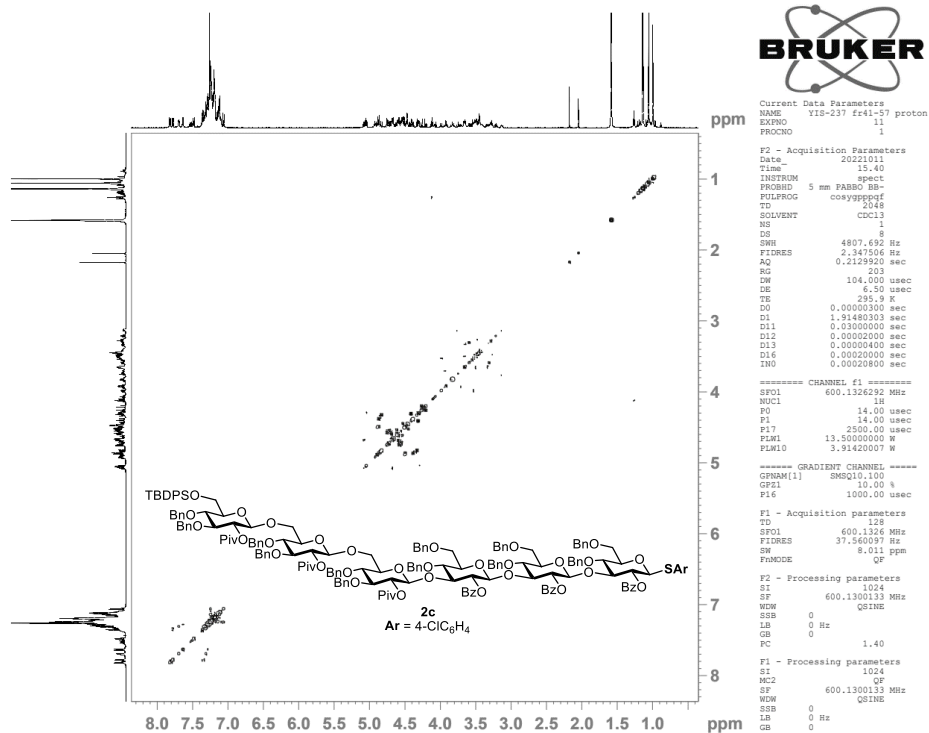


HMQC

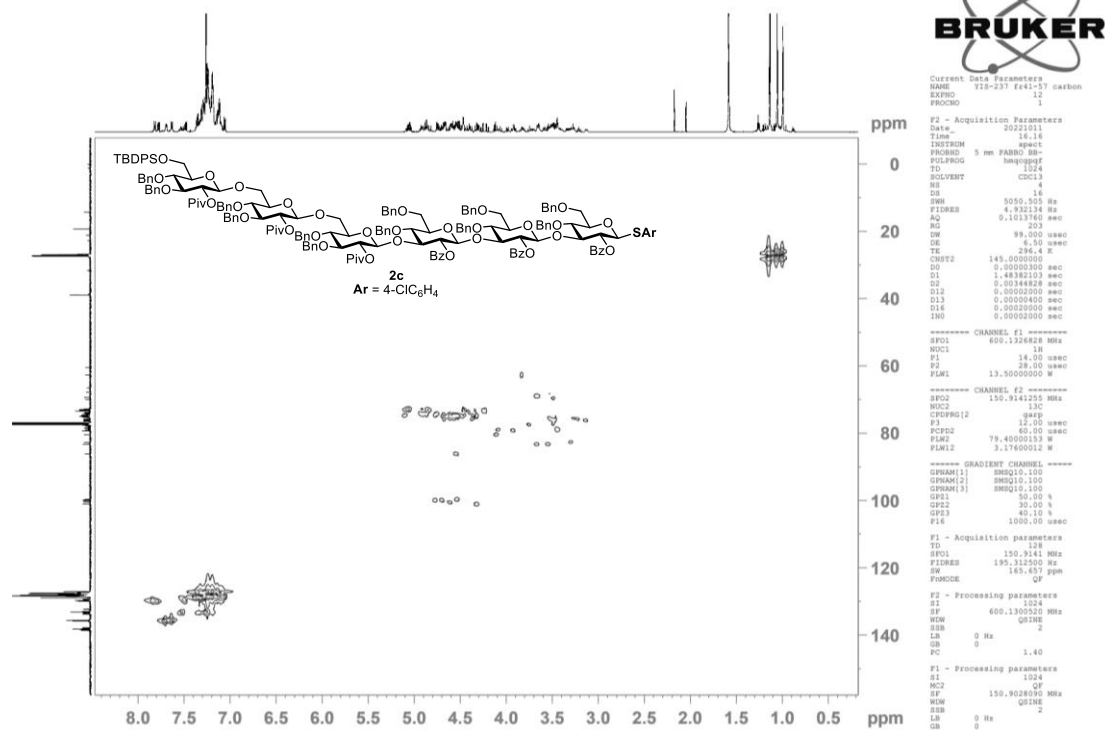




H-H cosy

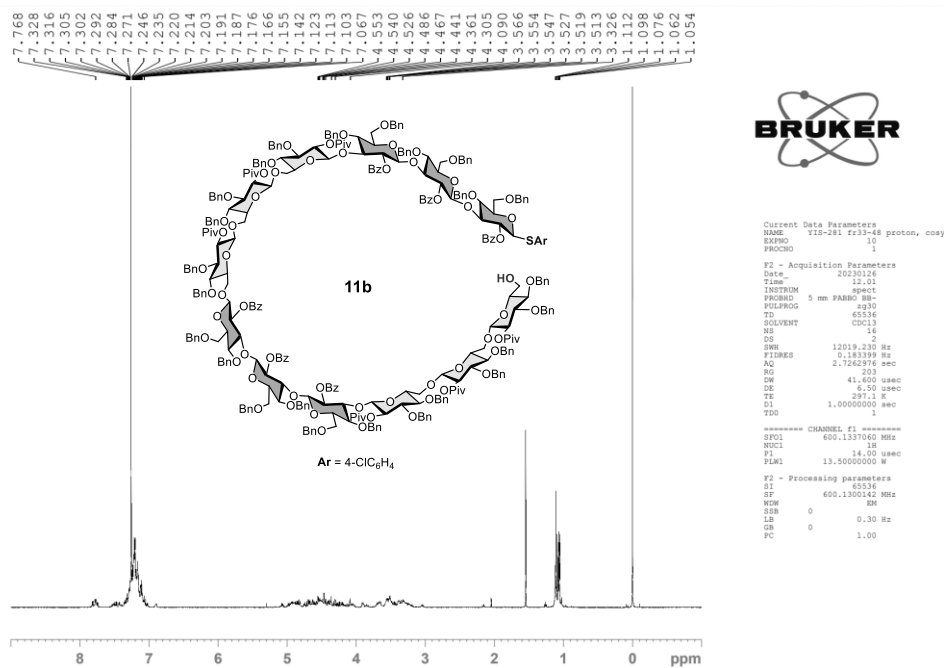


HMQC

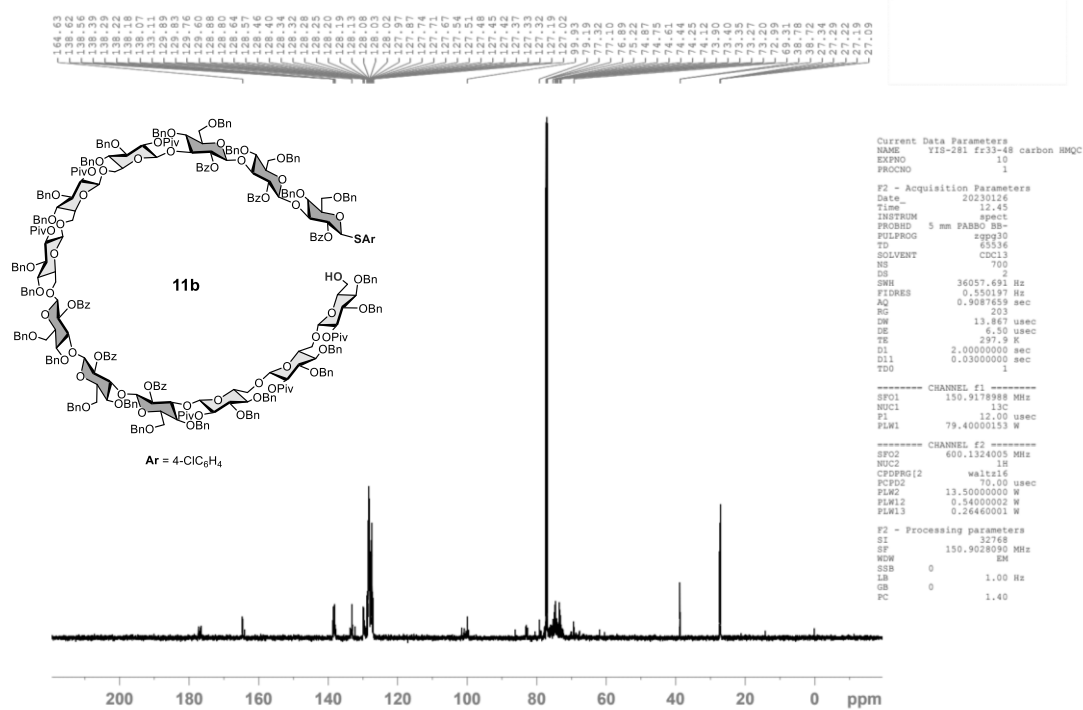


### 13. <sup>1</sup>H, <sup>13</sup>C NMR, H-H COSY and HMQC spectra of linear and cyclic dodecasaccharides

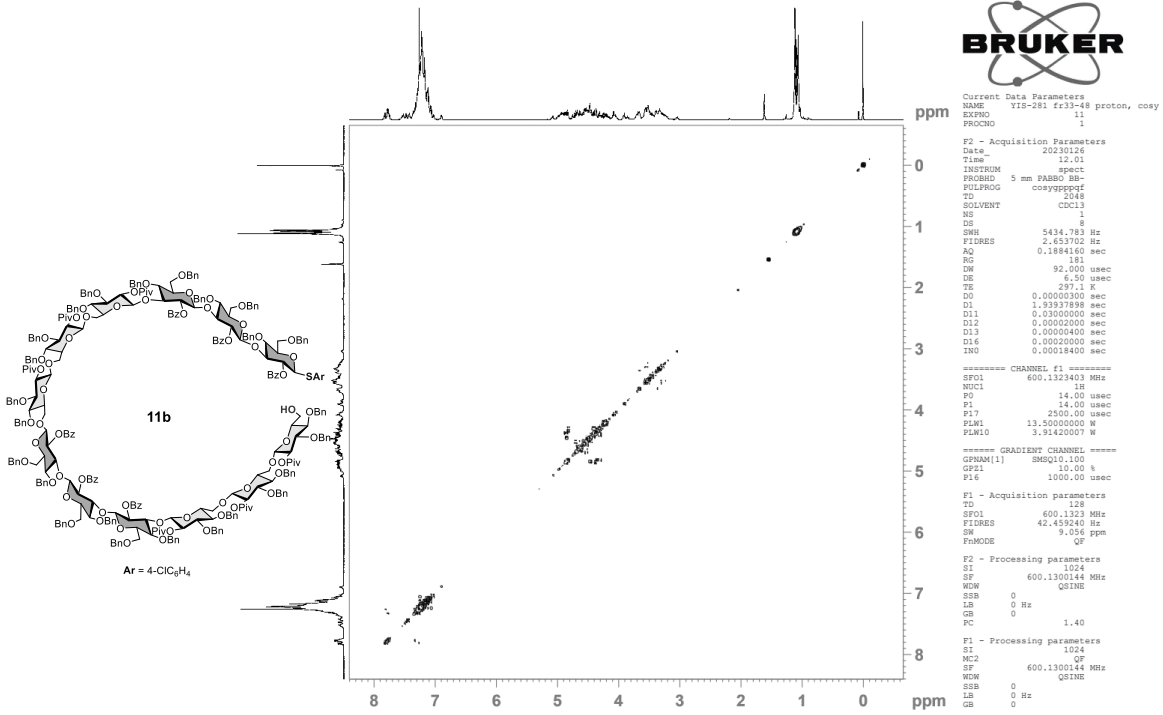
#### <sup>1</sup>H NMR



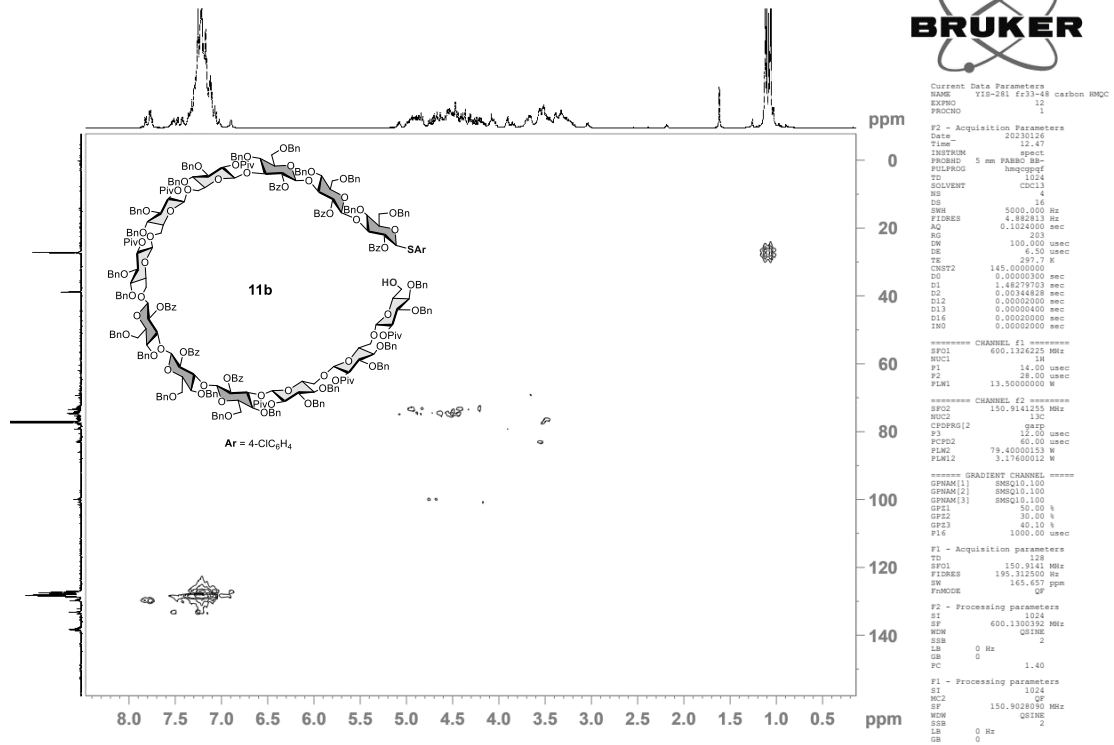
#### <sup>13</sup>C NMR



H-H cosy

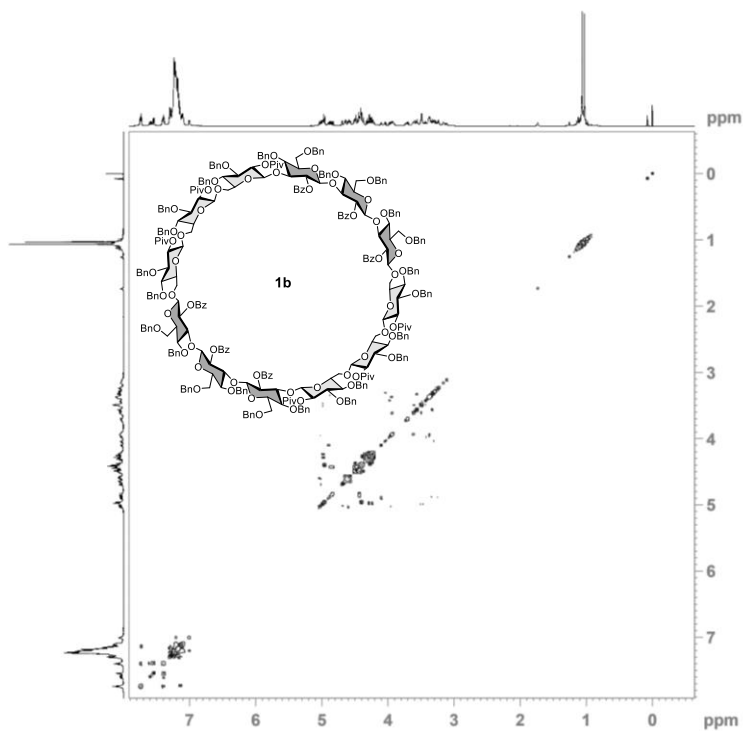


HMQC





H-H cosy



```

Current Data Parameters
NAME      IIS-cyclic12 0214
EXPNO    11
PROCNO   1
F2 - Acquisition Parameters
Date_    20230214
Time     15.23
INSTRUM  spect
PROBHD   5 mm PABBO BB-
PULPROG  coesypppgf
TD        2148
SOLVENT  CDCl3
NS        1
DS        8
SWH      5555.556 Hz
FIDRES   2.712674 Hz
AQ        0.1843200 sec
RG        36
DM        90.000 usec
DE        6.00 usec
TE        293.8 K
DQ        0.0000000 sec
D1        1.94347501 sec
D11       0.03000000 sec
D12       0.00020000 sec
D13       0.00000400 sec
D16       0.00020000 sec
IN0       0.00018000 sec

----- CHANNEL f1 -----
SFO1     600.1324234 MHz
NUC1     1H
P1        14.00 usec
P2        14.00 usec
P17       2500.00 usec
PL12     13.50000000 W
PL16     3.91420007 W

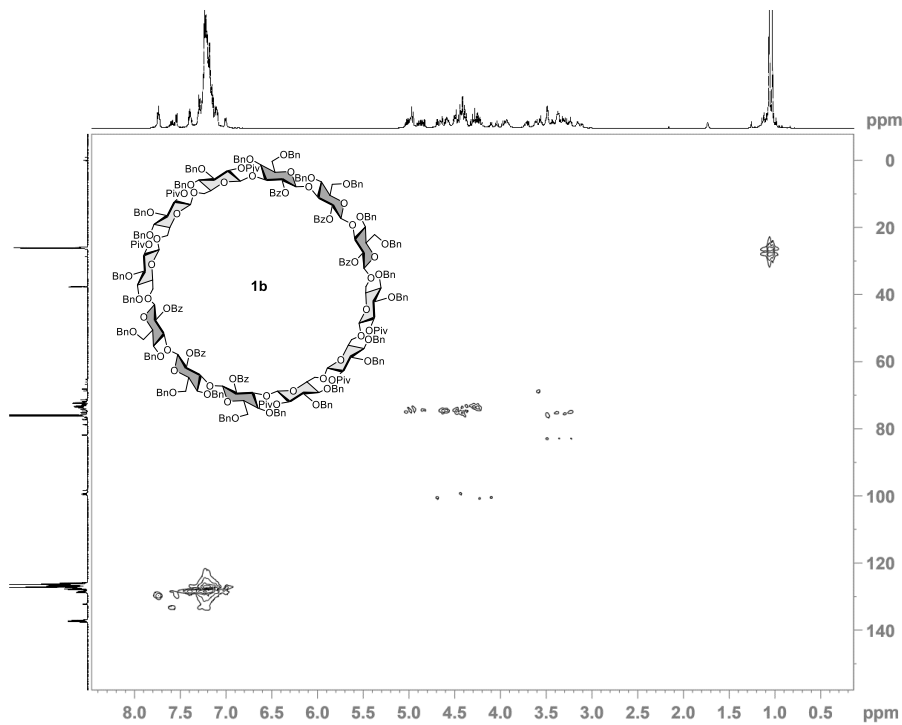
----- GRADIENT CHANNEL -----
GPRAM[1] SMSQ10.100
GPE1     10.00 %
P16      1000.00 usec

F1 - Acquisition parameters
TD        128
SFO1     600.1324 MHz
FIDRES   43.402779 Hz
DM        9.237 ppm
F0MODE   QF

F2 - Processing parameters
SI        1024
SF        600.1300377 MHz
WDW       0
SSB       0
LB        0 Hz
GB        0
PC        1.40

F1 - Processing parameters
SI        1024
SF        600.1300377 MHz
WDW       0
SSB       0
LB        0 Hz
GB        0
PC        0
    
```

HMQC



```

Current Data Parameters
NAME      IIS-cyclic12 0214
EXPNO    22
PROCNO   2
F2 - Acquisition Parameters
Date_    20230214
Time     17.15
INSTRUM  spect
PROBHD   5 mm PABBO BB-
PULPROG  hmqcpgf
TD        124
SOLVENT  CDCl3
NS        4
DS        16
SWH      5494.000 Hz
FIDRES   5.365779 Hz
AQ        0.0931840 sec
RG        253
DM        91.000 usec
DE        6.10 usec
TE        294.2 K
DQ        0.0000000 sec
D1        1.49201298 sec
D2        0.00344828 sec
D12       0.00020000 sec
D13       0.00000400 sec
D16       0.00020000 sec
IN0       0.00020000 sec

----- CHANNEL f1 -----
SFO1     600.1300377 MHz
NUC1     1H
P1        14.00 usec
P2        28.00 usec
PL12     13.50000000 W

----- CHANNEL f2 -----
SFO2     150.9141255 MHz
NUC2     13C
P1        13.00 usec
P2        60.00 usec
PL12     79.40000133 W
PL16     3.17600012 W

----- GRADIENT CHANNEL -----
GPRAM[1] SMSQ10.100
GPRAM[2] SMSQ10.100
GPRAM[3] SMSQ10.100
GPE1     50.00 %
GPE2     50.00 %
GPE3     40.10 %
P16      1000.00 usec

F1 - Acquisition parameters
TD        128
SFO1     150.9141 MHz
FIDRES   195.312500 Hz
DM        145.657 ppm
F0MODE   QF

F2 - Processing parameters
SI        1024
SF        600.1300298 MHz
WDW       0
SSB       0
LB        0 Hz
GB        0
PC        1.40

F1 - Processing parameters
SI        1024
SF        150.9028950 MHz
WDW       0
SSB       0
LB        0 Hz
GB        0
PC        2
    
```