

*Supplementary Information*

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**Regio- and stereoselective  $\beta$ -mannosylation using a boronic acid catalyst and its application to the synthesis of a tetrasaccharide repeating unit of lipopolysaccharide derived from *E. coli* O75**

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## General experimental methods

NMR spectra were recorded on a JEOL ECA-500 (500 MHz for  $^1\text{H}$ , 125 MHz for  $^{13}\text{C}$ ) spectrometer.  $^1\text{H}$  NMR data are reported as follows; chemical shift in parts per million (ppm) downfield or upfield from  $\text{CDCl}_3$  ( $\delta$  7.26), acetone- $d_6$  ( $\delta$  2.05), or tetramethyl silane ( $\delta$  0.00) integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet and m = multiplet), and coupling constants (Hz).  $^{13}\text{C}$  NMR chemical shifts are reported in ppm downfield or upfield from  $\text{CDCl}_3$  ( $\delta$  77.0), acetone- $d_6$  ( $\delta$  29.8). ESI-TOF Mass spectra were measured on a Waters LCT premier XE. Melting points were determined on a micro hot-stage (Yanako MP-S3). Optical rotations were measured on a JASCO P-2200 polarimeter. Silica gel TLC, column chromatography and flash column chromatography were performed using Merck TLC 60F-254, Silica Gel 60N (spherical, neutral, 63-210  $\mu\text{m}$ ) (Kanto Chemical Co., Inc.) and Silica Gel 60 N (spherical, neutral, 40-50  $\mu\text{m}$ ) (Kanto Chemical Co., Inc.), respectively. Reverse phase column chromatography separations were performed using Wakosil 25C18 (Wako pure chemical industries, Ltd.). Air- and/or moisture-sensitive reactions were carried out under an argon atmosphere using oven-dried glassware.

## General procedure A for glycosylation of **5** and **9** using glycosyl acceptor-derived boronic ester catalysts **10a-d**

To a solution of glucoside **9**<sup>1)</sup> (0.01-0.04 mmol, 1.0 equiv.) in dry toluene (0.3 M to glycosyl acceptor) was added **8a-d** (2-8  $\mu\text{mol}$ , 0.2 equiv.) at room temperature under Ar atmosphere. After stirring under reflux conditions for 3 h, the reaction mixture was concentrated in *vacuo*. The residue was diluted with dry solvent under Ar atmosphere, and then the resulting mixture was cooled to the temperature indicated. To the mixture was slowly added a solution of **5** (0.03-0.16 mmol, 3.0 equiv.) in dry solvent (50 mM final conc. of **5**). After the reaction mixture was stirred for the reaction time indicated, the reaction was quenched by addition of 50 mM  $\text{NaBO}_3$  aq. (4.4-17.6  $\mu\text{mol}$ , 2.2 equiv.). The resultant mixture was added sat.  $\text{NH}_4\text{Cl}$  aq. (2 mL) and extracted with EtOAc (3 mL $\times$ 3), and then the extracts were washed with brine (6 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated in *vacuo*. Purification of the residue by preparative TLC or column chromatography gave the corresponding glycosides.

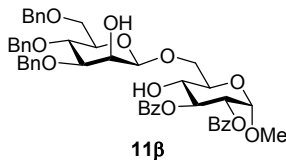
## General procedure B for glycosylation of **5** and glycosyl acceptors using boronic acid catalyst **8d**

To a solution of 4-nitrophenylboronic acid (**8d**) (2-8  $\mu\text{mol}$ , 0.2 equiv.) and glycosyl acceptor (0.01-0.04 mmol, 1.0 equiv.) in dry MeCN was added a solution of **5** (0.03-0.12 mmol, 3.0 equiv.) in dry MeCN (10-50 mM final conc. of **5**) at the temperature indicated under Ar atmosphere. After the reaction mixture was

stirred for reaction time indicated, the reaction was quenched by addition of 50 mM NaBO<sub>3</sub> aq. (4.4-17.6 μmol, 2.2 equiv.). The resultant mixture was added sat. NH<sub>4</sub>Cl aq. (2 mL) and extracted with EtOAc (3 mL×3), and then the extracts were washed with brine (6 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated in *vacuo*. Purification of the residue by preparative TLC gave the corresponding glycosides.

## Synthesis of $\beta$ -mannosides **11** and **17-20**

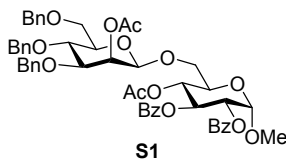
### Compound **11 $\beta$**



Compound **11 $\beta$**  was synthesized in 90% yield according to the general procedure A from glucoside **9**, **5** (50 mM final conc.), and **10d**.

Data for **11 $\beta$** : White solid;  $R_f$  0.60 (2/1 toluene/acetone);  $[\alpha]^{26}_D +68.1^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ ); mp 65-67 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.40 (3H, s), 3.45-3.48 (1H, m), 3.57 (1H, dd,  $J = 3.0$  and 9.0 Hz), 3.69 (1H, dd,  $J = 6.0$  and 11.0 Hz), 3.75 (1H, dd,  $J = 2.0$  and 11.0 Hz), 3.82-3.88 (2H, m), 3.92 (1H, dd,  $J = 5.5$  and 11.0 Hz), 4.00-4.03 (1H, m), 4.15 (1H, d,  $J = 3.0$  Hz), 4.24 (1H, dd,  $J = 3.5$  and 11.0 Hz), 4.54 (1H, br-s), 4.35 and 4.59 (2H, ABq,  $J = 12.0$  Hz), 4.65 and 4.75 (2H, ABq,  $J = 11.5$  Hz), 4.52 and 4.86 (2H, ABq,  $J = 11.0$  Hz), 5.09 (1H, d,  $J = 4.0$  Hz), 5.23 (1H, dd,  $J = 4.0$  and 10.0 Hz), 5.75 (1H, dd,  $J = 10.0$  and 11.5 Hz), 7.18-7.20 (2H, m), 7.24-7.37 (17H, m), 7.46-7.51 (2H, m), 7.96-7.99 (4H, m);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  55.3, 68.0, 68.9, 69.1, 70.5, 70.6, 71.4, 73.4, 74.0, 74.1, 75.1, 75.2, 81.3, 96.9, 100.1 ( $^1J_{\text{CH}} = 158$  Hz), 127.6, 127.7, 128.0, 128.3 $\times$ 2, 128.4, 129.1, 129.3, 129.8 $\times$ 2, 133.3, 138.0, 138.1, 165.9, 167.2; HRMS (ESI-TOF)  $m/z$  835.3342 (835.3330 calcd for  $\text{C}_{48}\text{H}_{51}\text{O}_{13}$   $[\text{M}+\text{H}]^+$ ).

### Compound **S1**

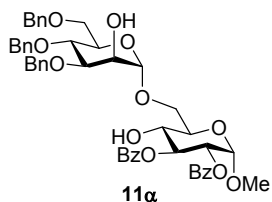


To a solution of **11 $\beta$**  (6.6 mg, 7.90  $\mu\text{mol}$ ) in pyridine (0.158 mL, 50 mM) were added  $\text{Ac}_2\text{O}$  (6.1  $\mu\text{L}$ , 0.0632 mmol) and DMAP (1.0 mg, 7.90  $\mu\text{mol}$ ) at 0 °C. After the reaction mixture was stirred for 2 h at room temperature, the reaction was quenched by addition of water (2 mL). The resultant mixture was extracted with EtOAc (2 mL $\times$ 3), and then the extracts were washed with brine (2 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated in *vacuo*. The residue was subjected to silica gel column chromatography (2/1 *n*-hexane/EtOAc) to give **S1** (6.4 mg, 6.97  $\mu\text{mol}$ , 85% yield).

Data for **S1**: Colorless syrup;  $R_f$  0.26 (10/1 toluene/acetone);  $[\alpha]^{26}_D +44.8^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.91 (3H, s), 2.20 (3H, s), 3.41 (3H, s), 3.46-3.50 (1H, m), 3.61 (1H, dd,  $J = 7.5$  and 11.0 Hz), 3.66-3.69 (1H, dd,  $J = 3.0$  and 9.5 Hz), 3.78-3.83 (3H, m), 3.92 (1H, dd,  $J = 2.0$  and 11.0 Hz),

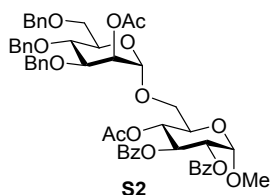
4.08-4.13 (1H, m), 4.48-4.53 (3H, m), 4.58 (1H, br-s), 4.65 (1H, d,  $J = 12.0$  Hz), 4.76 (1H, d,  $J = 11.0$  Hz), 4.87 (1H, d,  $J = 11.0$  Hz), 5.13-5.18 (3H, m), 5.71 (1H, br-d,  $J = 3.0$  Hz), 5.95 (1H, dd,  $J = 9.5$  and  $9.5$  Hz), 7.14-7.18 (2H, m), 7.23-7.42 (17H, m), 7.48-7.53 (2H, m), 7.93-7.98 (4H, m);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  20.6, 21.1, 55.1, 67.8, 68.5, 68.9, 69.0, 69.1, 70.6, 71.5, 72.0, 73.5, 74.2, 75.2, 75.5, 80.2, 96.5, 99.5, 127.6, 127.7, 127.9 $\times 2$ , 128.2, 128.3, 128.4 $\times 2$ , 129.0, 129.2, 129.7, 129.9, 133.2, 133.3, 137.5, 138.1, 138.2, 165.7, 165.8, 169.9, 170.4; HRMS (ESI-TOF)  $m/z$  957.3116 (957.3100 calcd for  $\text{C}_{52}\text{H}_{54}\text{O}_{15}\text{K}$   $[\text{M}+\text{K}]^+$ ).

### Compound **11 $\alpha$**



Data for isomer **11 $\alpha$**  : Colorless syrup ;  $R_f$  0.59 (2/1 toluene/acetone)  $[\alpha]_D^{25} +114.4^\circ$  ( $c$  0.99,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.40 (3H, s), 3.60 (1H, dd,  $J = 6.0$  and  $10.5$  Hz), 3.68-3.71 (1H, m), 3.75 (1H, dd,  $J = 9.5$  and  $9.5$  Hz), 3.82 (1H, dd,  $J = 2.0$  and  $11.0$  Hz), 3.85-3.97 (4H, m), 4.16-4.20 (2H, m), 4.46 and 4.79 (2H, ABq,  $J = 11.0$  Hz), 4.49 and 4.52 (2H, ABq,  $J = 12.5$  Hz), 4.72 and 4.75 (2H, ABq,  $J = 11.5$  Hz), 4.97 (1H, br-s), 5.13 (1H, d,  $J = 4.0$  Hz), 5.23 (1H, dd,  $J = 4.0$  and  $10.5$  Hz), 5.75 (1H, dd,  $J = 9.0$  and  $10.5$  Hz), 7.10-7.14 (2H, m), 7.19-7.39 (15H, m), 7.48-7.53 (2H, m), 7.96-8.03 (4H, m);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  55.4, 65.6, 68.4, 68.6, 68.7, 70.6, 71.5, 72.2, 73.3, 73.8, 74.4, 75.2, 80.2, 97.2, 99.5 ( $^1J_{\text{CH}} = 168$  Hz), 127.7, 127.8, 128.0, 128.1, 128.3 $\times 2$ , 128.4 $\times 2$ , 128.6, 129.2, 129.5, 129.9 $\times 2$ , 133.2, 133.3, 137.5, 137.8, 137.9, 166.0, 167.0; HRMS (ESI-TOF)  $m/z$  857.3135 (857.3149 calcd for  $\text{C}_{48}\text{H}_{50}\text{O}_{13}\text{Na}$   $[\text{M}+\text{Na}]^+$ ).

### Compound **S2**

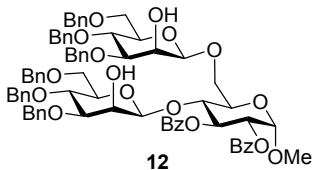


To a solution of **11 $\alpha$**  (20.8 mg, 24.9  $\mu\text{mol}$ ) in pyridine (0.498 mL, 50 mM) were added  $\text{Ac}_2\text{O}$  (9.6  $\mu\text{L}$ , 0.0996 mmol) and DMAP (3.0 mg, 24.9  $\mu\text{mol}$ ) at  $0^\circ\text{C}$ . After the reaction mixture was stirred for 0.5 h at

room temperature, the reaction was quenched by addition of water (2 mL). The resultant mixture was extracted with EtOAc (2 mL×3), and then the extracts were washed with brine (2 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated in *vacuo*. The residue was subjected to silica gel column chromatography (1/1 *n*-hexane/EtOAc) to give **S2** (16.5 mg, 17.9 μmol, 72% yield).

Data for **S2**: Colorless syrup ; R<sub>f</sub> 0.64 (1/1 *n*-hexane/EtOAc) [ $\alpha$ ]<sup>25</sup><sub>D</sub> +111.3° (*c* 0.81, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  1.92 (3H, s), 2.16 (3H, s), 3.35 (3H, s), 3.58 (1H, dd, *J* = 2.0 and 11.0 Hz), 3.69 (1H, br-d, *J* = 11.0 Hz), 3.76-3.84 (3H, m), 3.90 (1H, dd, *J* = 9.5 and 9.5 Hz), 3.99 (1H, dd, *J* = 3.5 and 9.5 Hz), 4.03-4.08 (1H, m), 4.49 and 4.87 (2H, ABq, *J* = 10.5 Hz), 4.51 and 4.67 (2H, ABq, *J* = 12.5 Hz), 4.58 and 4.73 (2H, ABq, *J* = 11.0 Hz), 4.91 (1H, d, *J* = 2.0 Hz), 5.13 (1H, d, *J* = 3.5 Hz), 5.17 (1H, dd, *J* = 3.5 and 10.0 Hz), 5.26 (1H, dd, *J* = 10.0 and 10.0 Hz), 5.39 (1H, dd, *J* = 2.0 and 3.5 Hz), 5.93 (1H, dd, *J* = 10.0 and 10.0 Hz), 7.16-7.18 (2H, m), 7.25-7.40 (17H, m), 7.47-7.53 (2H, m), 7.93-7.98 (4H, m); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  20.6, 21.1, 55.4, 65.9, 68.0, 68.7, 68.8, 68.9, 70.7, 71.6, 71.8, 71.9, 73.4, 74.1, 75.0, 77.7, 96.7, 97.7, 127.5, 127.6, 127.7, 127.8, 128.1, 128.3×2, 129.1, 129.2, 129.7, 129.9, 133.2, 133.3, 137.9, 138.2, 138.5, 165.8×2, 169.5, 170.4; HRMS (ESI-TOF) *m/z* 941.3353 (941.3360 calcd for C<sub>52</sub>H<sub>54</sub>O<sub>15</sub>Na [M+Na]<sup>+</sup>).

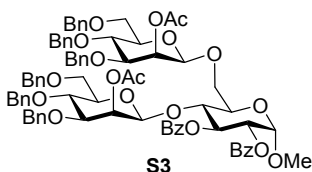
#### Compound 12



Data for **12**: Colorless syrup; R<sub>f</sub> 0.65 (2/1 toluene/acetone); [ $\alpha$ ]<sup>26</sup><sub>D</sub> +43.0° (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  2.52 (1H, br-s), 2.73 (1H, dd, *J* = 6.5 and 10.5 Hz), 2.80 (1H, br-s), 3.22-3.25 (1H, m), 3.31 (1H, dd, *J* = 2.0 and 10.5 Hz), 3.36 (3H, s), 3.41-3.50 (3H, m), 3.54 (1H, dd, *J* = 3.0 and 9.0 Hz), 3.70 (1H, dd, *J* = 5.0 and 11.0 Hz), 3.73-3.78 (2H, m), 3.83 (1H, dd, *J* = 9.0 and 9.0 Hz), 4.05-4.18 (5H, m), 4.18 and 4.25 (2H, ABq, *J* = 12.0 Hz), 4.35 and 4.80 (2H, ABq, *J* = 11.0 Hz), 4.47 (1H, br-s), 4.48 (1H, br-s), 4.49 and 4.85 (2H, ABq, *J* = 11.0 Hz), 4.51 and 4.60 (2H, ABq, *J* = 12.5 Hz), 4.59 and 4.74 (2H, ABq, *J* = 12.0 Hz), 5.07 (1H, d, *J* = 4.0 Hz), 5.25 (1H, dd, *J* = 4.0 and 10.5 Hz), 5.90 (1H, dd, *J* = 8.5 and 10.5 Hz), 7.09-7.11 (2H, m), 7.16-7.19 (2H, m), 7.22-7.38 (30H, m), 7.43-7.52 (2H, m), 7.95-7.99 (4H, m); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  55.3, 67.9, 68.1, 68.3, 69.1, 69.3, 71.0, 71.2, 71.4×2, 73.0, 73.4, 74.1, 74.3, 74.8, 75.1×2, 75.4, 75.5, 81.3, 81.6, 96.7, 98.3 (<sup>1</sup>J<sub>CH</sub> = 159 Hz), 100.2 (<sup>1</sup>J<sub>CH</sub> = 160 Hz), 127.5, 127.6, 127.7 ×2, 127.8, 127.9×2, 128.0, 128.2, 128.3, 128.4×2, 128.5, 129.2, 129.8, 129.9,

130.3, 132.9, 133.3, 137.7, 138.0, 138.1, 138.2, 138.4, 165.9, 167.0; HRMS (ESI-TOF)  $m/z$  1284.5527 (1284.5532 calcd for  $C_{75}H_{82}NO_{18} [M+NH_4]^+$ ).

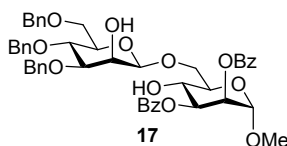
### Compound **S3**



To a solution of **12** (4.9 mg, 3.87  $\mu$ mol) in pyridine (0.077 mL, 50 mM) were added  $Ac_2O$  (3.0  $\mu$ L, 0.0310 mmol) and DMAP (0.5 mg, 3.87  $\mu$ mol) at 0 °C. After the reaction mixture was stirred for 2 h at room temperature, the reaction was quenched by addition of water (2 mL). The resultant mixture was extracted with EtOAc (2 mL $\times$ 3), and then the extracts were washed with brine (2 mL), dried over anhydrous  $Na_2SO_4$ , and concentrated in *vacuo*. The residue was subjected to silica gel column chromatography (2/1 *n*-hexane/EtOAc) to give **S3** (4.9 mg, 3.64  $\mu$ mol, 94% yield).

Data for **S3**: Colorless syrup;  $R_f$  0.60 (8/1 toluene/acetone);  $[\alpha]^{27}_D +23.1^\circ$  ( $c$  0.48,  $CHCl_3$ );  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  2.14 (3H, s), 2.27 (3H, s), 2.89-2.92 (2H, m), 3.24 (1H, dd,  $J = 4.0$  and 14.0 Hz), 3.36 (3H, s), 3.57-3.60 (1H, m), 3.71-3.88 (7H, m), 3.95-4.00 (1H, m), 4.06 (1H, dd,  $J = 12.5$  and 12.5 Hz), 4.13 (1H, br-d,  $J = 12.5$  Hz), 4.25 and 4.53 (2H, ABq,  $J = 15.5$  Hz), 4.37 and 4.57 (2H, ABq,  $J = 14.0$  Hz), 4.38 and 4.68 (2H, ABq,  $J = 13.5$  Hz), 4.48 and 4.76 (2H, ABq,  $J = 13.5$  Hz), 4.52 and 4.85 (2H, ABq,  $J = 14.0$  Hz), 4.61 (2H, s), 4.67 (1H, br-s), 4.72 (1H, br-s), 5.00-5.05 (1H, m), 5.11 (1H, d,  $J = 4.5$  Hz), 5.71 (1H, br-s), 5.82 (1H, d,  $J = 2.5$  Hz), 6.03 (1H, dd,  $J = 12.0$  and 12.0 Hz), 7.02-7.13 (4H, m), 7.15-7.38 (30H, m), 7.42-7.51 (2H, m), 7.94-8.00 (4H, m);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  21.1, 21.3, 55.2, 67.7, 67.9, 68.1, 68.4, 68.6, 69.5, 71.4, 71.7, 71.8, 72.4, 73.3, 73.5, 73.6, 74.5, 75.0, 75.1, 75.6, 75.7, 76.1, 80.5, 96.8, 98.5, 100.4, 127.3, 127.5, 127.6 $\times$ 2, 127.7 $\times$ 2, 127.8, 127.9 $\times$ 2, 128.1, 128.2, 128.3, 128.4, 129.1, 129.6, 129.9, 133.0, 133.2, 137.4, 137.6, 138.1, 138.3, 138.4, 138.5, 164.9, 166.0, 171.1, 171.2; HRMS (ESI-TOF)  $m/z$  695.2557 (695.2552 calcd for  $C_{75}H_{82}O_{18}K [M+H+K]^{2+}$ ).

### Compound **17**

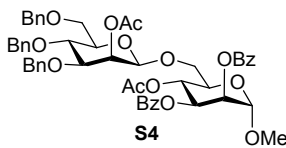


Compound **17** was synthesized in 81% yield according to the general procedure B from mannoside

**13**<sup>2</sup>) and **5** (50 mM final conc.).

Data for **17**: Colorless syrup;  $R_f$  0.55 (1/1 *n*-hexane/acetone);  $[\alpha]^{26}_D$  -38.8° (*c* 0.73, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  2.46 (1H, br-s), 2.97 (1H, d,  $J$  = 5.5 Hz), 3.43-3.48 (4H, m), 3.55 (1H, dd,  $J$  = 4.0 and 11.5 Hz), 3.93 (1H, dd,  $J$  = 7.0 and 13.5 Hz), 3.75 (1H, dd,  $J$  = 2.5 and 13.5 Hz), 3.84 (1H, dd,  $J$  = 11.5 and 11.5 Hz), 3.93 (1H, dd,  $J$  = 7.0 and 13.5 Hz), 3.98-4.02 (1H, m), 4.13-4.19 (2H, m), 4.31 (1H, dd,  $J$  = 3.5 and 13.5 Hz), 4.50-4.60 (4H, m), 4.65 and 4.74 (2H, ABq,  $J$  = 15.0 Hz), 4.85-4.87 (2H, m), 5.53-5.56 (2H, m), 7.18-7.19 (2H, m), 7.24-7.36 (15H, m), 7.43-7.52 (3H, m), 7.57 (1H, m), 7.89 (2H, d,  $J$  = 9.0 Hz), 8.05 (2H, d,  $J$  = 9.0 Hz); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  55.2, 67.8, 68.2, 69.2, 69.3, 70.5, 71.5, 71.6, 72.9, 73.5, 74.2, 75.1, 75.3, 81.4, 98.5, 100.1 ( $^1J_{CH}$  = 157 Hz), 127.6, 127.8 $\times$ 2, 127.9 $\times$ 2, 128.1, 128.3, 128.4 $\times$ 2, 128.5, 128.6, 129.4, 129.5, 129.8, 129.9, 133.3, 133.4, 137.8, 138.1 $\times$ 2, 165.4, 166.8; HRMS (ESI-TOF)  $m/z$  835.3326 (835.3330 calcd for C<sub>48</sub>H<sub>51</sub>O<sub>13</sub> [M+H]<sup>+</sup>).

#### Compound **S4**

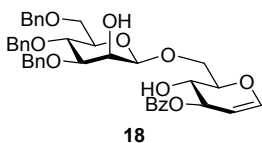


To a solution of **17** (15.4 mg, 18.4  $\mu$ mol) in pyridine (0.368 mL, 50 mM) were added Ac<sub>2</sub>O (13.9  $\mu$ L, 0.147 mmol) and DMAP (2.2 mg, 18.4  $\mu$ mol) at 0 °C. After the reaction mixture was stirred for 3 h at room temperature, the reaction was quenched by addition of water (2 mL). The resultant mixture was extracted with EtOAc (2 mL $\times$ 3), and then the extracts were washed with brine (2 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated in *vacuo*. The residue was subjected to silica gel column chromatography (11/1 toluene/acetone) to give **S4** (15.4 mg, 16.7  $\mu$ mol, 91% yield).

Data for **S4**: Colorless syrup;  $R_f$  0.72 (4/1 toluene/acetone);  $[\alpha]^{27}_D$  -76.3° (*c* 0.65, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  1.92 (3H, s), 2.16 (3H, s), 3.45-3.49 (4H, m), 3.65-3.70 (2H, m), 3.74-3.80 (3H, m), 4.07-4.13 (2H, m), 4.47-4.53 (3H, m), 4.59 (1H, br-s), 4.64 (1H, d,  $J$  = 11.0 Hz), 4.75 (1H, d,  $J$  = 11.0 Hz), 4.86 (1H, d,  $J$  = 11.0 Hz), 4.89 (1H, d,  $J$  = 2.0 Hz), 5.44 (1H, dd,  $J$  = 10.5 and 10.5 Hz), 5.59 (1H, dd,  $J$  = 2.0 and 3.5 Hz), 5.66 (1H, dd,  $J$  = 3.5 and 10.5 Hz), 5.71 (1H, br-d,  $J$  = 3.0 Hz), 7.14-7.16 (2H, m), 7.26-7.35 (15H, m), 7.46-7.51 (3H, m), 7.60 (1H, t,  $J$  = 7.5 Hz), 7.93 (2H, d,  $J$  = 7.0 Hz), 8.04 (2H, d,  $J$  = 7.5 Hz); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  20.7, 21.0, 55.1, 66.8, 67.8, 69.1, 69.2, 69.5, 70.0, 70.4, 71.5, 73.5, 74.2, 75.2, 75.5, 80.2, 98.2, 99.6, 127.6, 127.7, 127.9, 128.2, 128.3, 128.4, 128.4, 128.6, 129.2, 129.3, 129.7, 129.9, 133.2, 133.4, 137.5, 138.1, 165.3, 165.5, 170.1, 170.3; HRMS (ESI-TOF)  $m/z$  936.3810 (936.3806 calcd for C<sub>52</sub>H<sub>58</sub>NO<sub>15</sub> [M+NH<sub>4</sub>]<sup>+</sup>).



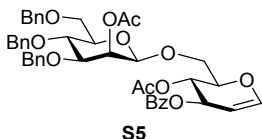
### Compound **18**



Compound **18** was synthesized in 91% yield according to the general procedure B from glucal **14**<sup>3)</sup> and **5** (50 mM final conc.).

Data for **18**: White solid;  $R_f$  0.60 (2/1 toluene/acetone);  $[\alpha]^{26}_D$   $-43.5^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ ); mp 39-41  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.43-3.47 (1H, m), 4.18 (1H, dd,  $J = 2.5$  and 9.0 Hz), 3.69 (1H, dd,  $J = 5.5$  and 10.5 Hz), 3.76 (1H, dd,  $J = 2.0$  and 10.5 Hz), 3.86 (1H, dd,  $J = 9.0$  and 9.0 Hz), 3.96 (1H, dd,  $J = 5.5$  and 11.0 Hz), 4.05 (1H, dd,  $J = 6.5$  and 9.5 Hz), 4.10-4.12 (1H, m), 4.18 (1H, d,  $J = 2.5$  Hz), 4.32 (1H, dd,  $J = 3.0$  and 11.0 Hz), 4.54 (1H, br-s), 4.55 and 4.60 (2H, ABq,  $J = 12.0$  Hz), 4.66 and 4.75 (2H, ABq,  $J = 11.5$  Hz), 4.53 and 4.87 (2H, ABq,  $J = 11.0$  Hz), 4.83 (1H, dd,  $J = 2.0$  and 6.5 Hz), 5.71 (1H, m), 6.50 (1H, dd,  $J = 2.0$  and 5.0 Hz), 7.19-7.20 (2H, m), 7.24-7.37 (13H, m), 7.47 (2H, t,  $J = 7.5$  Hz), 7.58 (1H, t,  $J = 7.5$  Hz), 8.05 (2H, d,  $J = 7.5$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  68.0, 68.2, 69.1, 71.4, 73.5, 74.0, 74.1, 75.1, 75.3, 77.5, 81.4, 99.0, 100.1 ( $^1J_{\text{CH}} = 157$  Hz), 127.6, 127.7, 127.9 $\times$ 2, 128.1, 128.4, 128.4, 128.5, 129.6, 129.8, 133.4, 137.7, 138.0, 138.1, 146.4, 167.9; HRMS (ESI-TOF)  $m/z$  700.3143 (700.3122 calcd for  $\text{C}_{40}\text{H}_{46}\text{NO}_{10}$  [ $\text{M}+\text{NH}_4$ ] $^+$ ).

### Compound **S5**

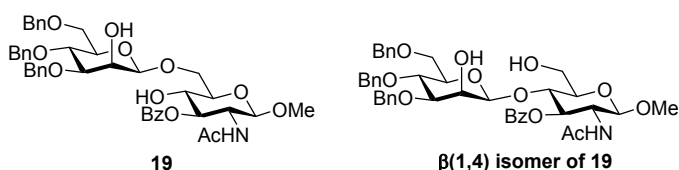


To a solution of **18** (13.1 mg, 19.2  $\mu\text{mol}$ ) in pyridine (0.384 mL, 50 mM) were added  $\text{Ac}_2\text{O}$  (14.4  $\mu\text{L}$ , 0.154 mmol) and DMAP (2.34 mg, 19.2  $\mu\text{mol}$ ) at 0  $^\circ\text{C}$ . After the reaction mixture was stirred for 2 h at room temperature, the reaction was quenched by addition of water (2 mL). The resultant mixture was extracted with EtOAc (2 mL $\times$ 3), and then the extracts were washed with brine (2 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated in *vacuo*. The residue was subjected to preparative TLC (2/1 *n*-hexane/acetone) to give **S5** (10.1 mg, 13.2  $\mu\text{mol}$ , 69% yield).

Data for **S5**: Colorless syrup;  $R_f$  0.45 (2/1 *n*-hexane/acetone);  $[\alpha]^{27}_D$   $-88.5^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.06 (3H, s), 2.14 (3H, s), 3.45-3.48 (1H, m), 3.67 (1H, dd,  $J = 3.0$  and 9.0 Hz), 3.45 (2H, d,  $J = 3.5$  Hz), 3.80 (1H, dd,  $J = 9.0$  and 9.5 Hz), 3.87 (1H, dd,  $J = 7.5$  and 11.5 Hz), 4.11 (1H, dd,  $J$

= 3.0 and 11.5 Hz), 4.37-4.40 (1H, m), 4.48-4.52 (3H, m), 4.61 (1H, br-s), 4.62 (1H, d,  $J = 13.5$  Hz), 4.77 (1H, d,  $J = 10.5$  Hz), 4.88 (1H, d,  $J = 11.0$  Hz), 5.00 (1H, dd,  $J = 6.5$  and  $4.0$  Hz), 5.33 (1H, dd,  $J = 6.0$  and  $6.0$  Hz), 5.46 (1H, m), 5.70 (1H, br-d,  $J = 3.0$  Hz), 6.49 (1H, d,  $J = 6.5$  Hz), 7.19-7.20 (2H, m), 7.22-7.34 (13H, m), 7.41 (2H, t,  $J = 7.5$  Hz), 7.52 (1H, m), 8.01 (2H, d,  $J = 8.5$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  20.8, 21.1, 67.2, 67.4, 67.6, 67.7, 69.0, 71.5, 73.5, 74.1, 75.1 $\times$ 2, 75.6, 80.3, 98.4, 99.3, 127.6, 127.7, 127.8, 127.9, 128.2, 128.3 $\times$ 2, 128.4 $\times$ 2, 129.6, 129.8, 133.2, 137.5, 138.1, 138.2, 145.7, 165.8, 169.6, 170.5; HRMS (ESI-TOF)  $m/z$  789.2896 (789.2887 calcd for  $\text{C}_{44}\text{H}_{46}\text{O}_{12}\text{Na}[\text{M}+\text{Na}]^+$ ).

### Compound 19



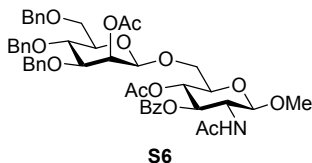
Compound **19** and  **$\beta$ (1,4) isomer of 19** were synthesized in 78% and 4% yield, respectively, according to the general procedure B from glucosaminide **15**<sup>4)</sup> and **5** (50 mM final conc.).

Data for **19**: Colorless syrup;  $R_f$  0.64 (1/2 toluene/acetone);  $[\alpha]_{\text{D}}^{27} -17.3^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.85 (3H, s), 3.42-3.50 (5H, m), 3.54 (1H, dd,  $J = 3.0$  and  $9.0$  Hz), 3.64-3.78 (4H, m), 3.81 (1H, dd,  $J = 9.0$  and  $9.0$  Hz), 3.93 (1H, dd,  $J = 5.5$  and  $11.5$  Hz), 4.10-4.17 (2H, m), 4.22 (1H, dd,  $J = 2.0$  and  $11.5$  Hz), 4.45-4.57 (5H, m), 4.64 and 4.72 (2H, ABq,  $J = 12.0$  Hz), 4.83 (1H, d,  $J = 11.0$  Hz), 5.28 (1H, dd,  $J = 10.5$  and  $10.5$  Hz), 5.64 (1H, d,  $J = 9.5$  Hz), 7.16-7.17 (2H, m), 7.22-7.36 (13H, m), 7.41 (2H, t,  $J = 7.5$  Hz), 7.55 (1H, t,  $J = 7.5$  Hz), 8.01 (2H, d,  $J = 8.0$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  23.3, 53.8, 56.6, 68.0, 69.0, 69.8, 71.2, 71.5, 73.4, 74.1, 74.7, 75.0, 75.1, 76.4, 81.2, 100.2 ( $^1J_{\text{CH}} = 159$  Hz), 101.9, 127.6, 127.7, 127.8, 127.9, 128.0, 128.4, 128.5 $\times$ 2, 129.2, 129.9, 133.5, 137.7, 138.0, 138.1, 167.6, 170.3; HRMS (ESI-TOF)  $m/z$  772.3337 (772.3333 calcd for  $\text{C}_{43}\text{H}_{50}\text{NO}_{12}[\text{M}+\text{H}]^+$ ).

Data for  **$\beta$ (1,4) isomer of 19**: Colorless syrup;  $R_f$  0.51 (1/2 toluene/acetone);  $[\alpha]_{\text{D}}^{26} -6.85^\circ$  ( $c$  0.44,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.86 (3H, s), 3.10 (1H, dd,  $J = 5.0$  and  $10.5$  Hz), 3.18-3.24 (2H, m), 3.46 (1H, dd,  $J = 3.0$  and  $9.0$  Hz), 3.51 (3H, s), 3.58-3.62 (1H, m), 3.65 (1H, dd,  $J = 9.0$  and  $9.0$  Hz), 3.78 (1H, dd,  $J = 4.0$  and  $12.0$  Hz), 3.92 (1H, dd,  $J = 2.0$  and  $12.0$  Hz), 4.02 (1H, br-d,  $J = 3.0$  Hz), 4.12-4.21 (2H, m), 4.24 and 4.30 (2H, ABq,  $J = 12.0$  Hz), 4.39 and 4.77 (2H, ABq,  $J = 11.0$  Hz), 4.50 (1H, d,  $J = 8.0$  Hz), 4.55 (1H, br-s), 4.60 and 4.70 (2H, ABq,  $J = 12.0$  Hz), 5.46 (1H, dd,  $J = 9.0$  and  $10.5$  Hz), 5.67 (1H, d,  $J = 9.0$  Hz), 7.08-7.12 (2H, m), 7.22-7.39 (15H, m), 7.52 (1H, t,  $J = 8.0$  Hz), 8.02 (1H, d,  $J = 7.5$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  23.3, 53.8, 56.8, 61.7, 68.2, 68.7, 71.4, 73.0, 73.9, 74.0, 74.8, 75.0, 75.1, 75.2, 81.5, 99.5 ( $^1J_{\text{CH}} = 160$  Hz), 102.1, 127.5, 127.7, 127.8, 127.8, 127.9, 128.3 $\times$ 2, 128.4,

128.5, 129.7, 129.9, 133.3, 137.8, 138.1, 167.1, 170.3; HRMS (ESI-TOF)  $m/z$  772.3364 (772.3333 calcd for  $C_{43}H_{50}NO_{12}$   $[M+H]^+$ ).

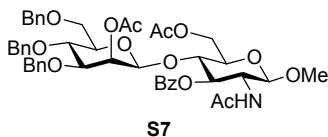
#### Compound S6



To a solution of **19** (6.3 mg, 8.16  $\mu$ mol) in pyridine (0.163 mL, 50 mM) were added  $Ac_2O$  (6.2  $\mu$ L, 0.0656 mmol) and DMAP (1.0 mg, 8.16  $\mu$ mol) at 0 °C. After the reaction mixture was stirred for 4 h at room temperature, the reaction was quenched by addition of water (2 mL). The resultant mixture was extracted with EtOAc (2 mL $\times$ 3), and then the extracts were washed with brine (2 mL), dried over anhydrous  $Na_2SO_4$ , and concentrated in *vacuo*. The residue was subjected to preparative TLC (2/1 *n*-hexane/acetone) to give **S6** (6.9 mg, 8.06  $\mu$ mol, 99% yield).

Data for **S6**: Colorless syrup;  $R_f$  0.84 (1/2 toluene/acetone);  $[\alpha]^{27}_D$  -33.5° (*c* 0.62,  $CHCl_3$ );  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  1.86 (3H, s), 1.88 (3H, s), 2.20 (3H, s), 3.42-3.49 (1H, m), 3.50 (3H, s), 3.62-3.68 (2H, m), 3.74-3.81 (4H, m), 3.96 (1H, dd,  $J$  = 2.0 and 11.5 Hz), 4.02-4.08 (1H, m), 4.47-4.55 (4H, m), 4.59 (1H, br-s), 4.66 (1H, d,  $J$  = 12.0 Hz), 4.74 (1H, d,  $J$  = 11.0 Hz), 4.85 (1H, d,  $J$  = 10.5 Hz), 5.06 (1H, dd,  $J$  = 9.5 and 9.5 Hz), 5.41 (1H, dd,  $J$  = 11.0 and 9.5 Hz), 5.49 (1H, d,  $J$  = 8.0 Hz), 5.65 (1H, br-d,  $J$  = 3.0 Hz), 7.14-7.16 (2H, m), 7.26-7.35 (13H, m), 7.43 (2H, t,  $J$  = 8.0 Hz), 7.57 (1H, t,  $J$  = 7.0 Hz), 7.97 (2H, d,  $J$  = 7.5 Hz);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  20.6, 21.2, 23.4, 54.6, 56.8, 67.9, 69.0, 69.2 $\times$ 2, 71.5, 73.1, 73.5, 73.6, 74.2, 75.2, 75.4, 80.3, 99.7, 101.8, 127.6, 127.7, 127.8, 127.9, 128.2, 128.3, 128.4, 128.6, 128.8, 129.9, 133.6, 137.5, 138.2, 166.7, 169.7, 170.2, 170.5; HRMS (ESI-TOF)  $m/z$  856.3529 (856.3544 calcd for  $C_{47}H_{54}NO_{14}$   $[M+H]^+$ ).

#### Compound S7

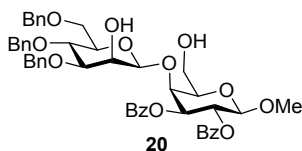


To a solution of  **$\beta$ (1,4) isomer of 19** (7.4 mg, 9.59  $\mu$ mol) in pyridine (0.192 mL, 50 mM) were added  $Ac_2O$  (7.2  $\mu$ L, 0.0767 mmol) and DMAP (1.2 mg, 9.59  $\mu$ mol) at 0 °C. After the reaction mixture was stirred for 7 h at room temperature, the reaction was quenched by addition of sat.  $NaHCO_3$  aq. (2 mL). The resultant mixture was extracted with EtOAc (2 mL $\times$ 3), and then the extracts were washed with brine (2

mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated in *vacuo*. The residue was subjected to preparative TLC (2/1 toluene/acetone) to give **S7** (6.8 mg, 7.94 μmol, 83% yield).

Data for **S7**: Colorless syrup; *R<sub>f</sub>* 0.38 (2/1 toluene/acetone); [α]<sup>27</sup><sub>D</sub> -40.2° (*c* 0.62, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.85 (3H, s), 1.98 (3H, s), 2.09 (3H, s), 3.17-3.21 (1H, m), 3.33 (1H, br-d, *J* = 10.5 Hz), 3.44 (1H, dd, *J* = 4.5 and 10.5 Hz), 3.48 (3H, s), 3.57 (1H, dd, *J* = 3.5 and 9.5 Hz), 3.65 (1H, dd, *J* = 9.5 and 9.5 Hz), 3.72-3.75 (1H, m), 4.09-4.18 (2H, m), 4.34-4.45 (5H, m), 4.52 (1H, d, *J* = 12.0 Hz), 4.55 (1H, br-s), 4.68 (1H, d, *J* = 11.5 Hz), 4.78 (1H, d, *J* = 11.0 Hz), 5.39 (1H, dd, *J* = 9.0 and 10.0 Hz), 5.53 (1H, d, *J* = 2.5 Hz), 5.61 (1H, d, *J* = 9.5 Hz), 7.11-7.14 (2H, m), 7.26-7.38 (15H, m), 7.52 (1H, m), 8.04 (2H, m); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 20.7, 20.9, 23.3, 53.8, 56.7, 62.6, 67.8, 68.5, 71.5, 72.7, 73.0, 73.3, 73.9, 74.1, 75.1, 75.5, 80.1, 98.1, 102.0, 127.6, 127.7, 127.9×2, 128.1, 128.3, 128.4, 128.4×2, 129.4, 130.0, 133.4, 137.4, 138.1, 138.3, 166.6, 170.2, 170.7; HRMS (ESI-TOF) *m/z* 878.3386 (878.3364 calcd for C<sub>47</sub>H<sub>53</sub>NO<sub>14</sub>Na [M+Na]<sup>+</sup>).

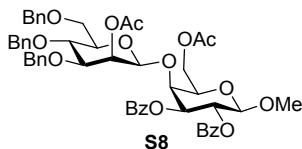
#### Compound **20**



Compound **20** was synthesized in 86% yield according to the general procedure B from galactoside **16**<sup>5)</sup> and **5** (50 mM final conc.).

Data for **20**: White solid; *R<sub>f</sub>* 0.59 (2/1 toluene/acetone); [α]<sup>26</sup><sub>D</sub> +26.5° (*c* 1.0, CHCl<sub>3</sub>); mp 153-155 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 3.24 (1H, dd, *J* = 3.0 and 9.0 Hz), 3.29 (1H, m), 3.44 (1H, dd, *J* = 8.0 and 10.0 Hz), 3.53 (3H, s), 3.59-3.61 (2H, m), 3.72 (1H, dd, *J* = 10.5 and 5.0 Hz), 3.77 (1H, m), 4.03 (1H, dd, *J* = 10.5 and 10.5 Hz), 4.27 (1H, br-d, *J* = 3.0 Hz), 4.29 (1H, br-s), 4.39-4.45 (3H, m), 4.50 (1H, br-d, *J* = 3.0 Hz), 4.55 (1H, d, *J* = 12.0 Hz), 4.60 (1H, d, *J* = 8.0 Hz), 4.72 (1H, d, *J* = 12.0 Hz), 4.80 (1H, d, *J* = 11.0 Hz), 5.41 (1H, dd, *J* = 3.0 and 10.0 Hz), 5.69 (1H, dd, *J* = 8.0 and 10.0 Hz), 7.05-7.09 (2H, m), 7.24-7.40 (17H, m), 7.50 (2H, m), 7.87 (2H, d, *J* = 7.0 Hz), 7.98 (2H, d, *J* = 7.5 Hz); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 57.2, 59.0, 67.6, 69.1, 70.0, 70.8, 73.3, 73.5, 73.8, 74.1, 74.2, 75.2, 80.9, 100.8 (<sup>1</sup>*J*<sub>CH</sub> = 157 Hz), 102.3, 127.9×2, 128.1, 128.2, 128.3, 128.4×2, 128.5, 128.6, 128.8, 129.5, 129.6, 129.8, 133.2, 133.7, 137.3, 137.5, 137.7, 165.4, 165.5; HRMS (ESI-TOF) *m/z* 857.3147 (857.3149 calcd for C<sub>48</sub>H<sub>50</sub>O<sub>13</sub>Na [M+Na]<sup>+</sup>).

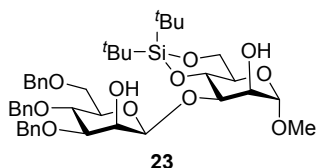
#### Compound **S8**



To a solution of **20** (17.5 mg, 21.0  $\mu\text{mol}$ ) in pyridine (0.420 mL, 50 mM) were added  $\text{Ac}_2\text{O}$  (15.7  $\mu\text{L}$ , 0.166 mmol) and DMAP (2.6 mg, 21.3  $\mu\text{mol}$ ) at 0  $^\circ\text{C}$ . After the reaction mixture was stirred for 3 h at room temperature, the reaction was quenched by addition of water (2 mL). The resultant mixture was extracted with EtOAc (2 mL $\times$ 3), and then the extracts were washed with brine (2 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated in *vacuo*. The residue was subjected to silica gel column chromatography (11/1 toluene/acetone) to give **S8** (17.9 mg, 19.5  $\mu\text{mol}$ , 93% yield).

Data for **S8**: White solid;  $R_f$  0.42 (10/1 toluene/acetone);  $[\alpha]^{26}_D +30.2^\circ$  ( $c$  0.92,  $\text{CHCl}_3$ ); mp 53-55  $^\circ\text{C}$ ;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.05 (3H, s), 2.23 (3H, s), 3.12 (1H, dd,  $J = 4.5$  and 10.0 Hz), 3.32 (1H, dd,  $J = 3.0$  and 9.5 Hz), 3.52 (3H, s), 3.62 (1H, d,  $J = 11.0$  Hz), 3.69-3.75 (2H, m), 3.91 (1H, dd,  $J = 5.0$  and 6.0 Hz), 4.26 and 4.67 (2H, ABq,  $J = 11.0$  Hz), 4.36-4.38 (2H, m), 4.43 (1H, br-d,  $J = 3.0$  Hz), 4.46 and 4.77 (2H, ABq,  $J = 11.0$  Hz), 4.51 and 4.64 (2H, ABq,  $J = 12.0$  Hz), 4.52 (1H, br-s), 4.60 (1H, d,  $J = 8.0$  Hz), 5.41 (1H, dd,  $J = 3.0$  and 10.5 Hz), 5.69-5.72 (2H, m), 7.11-7.13 (2H, m), 7.24-7.38 (17H, m), 7.50 (2H, t,  $J = 7.5$  Hz), 7.97-8.01 (4H, m);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  20.8, 21.0, 56.2, 63.6, 67.5, 69.0, 69.2, 71.2, 72.2, 73.1, 73.5, 73.9, 74.0, 75.2, 75.7, 80.2, 99.0, 101.7, 127.5 $\times$ 2, 127.7, 127.9, 128.0, 128.2, 128.3 $\times$ 2, 128.4, 128.6, 128.8, 129.6, 129.7, 129.8, 133.0, 133.8, 137.5, 138.1, 138.5, 165.1, 165.7, 170.2, 170.6; HRMS (ESI-TOF)  $m/z$  941.3359 (941.3360 calcd for  $\text{C}_{52}\text{H}_{54}\text{O}_{15}\text{Na}$  [ $\text{M}+\text{Na}$ ] $^+$ ).

### Compound **23**

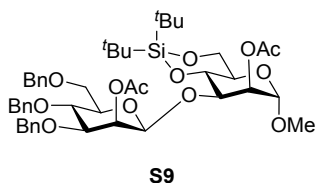


Compound **23** was synthesized in 75% yield according to the general procedure B from mannoside **21**<sup>(6)</sup> and **5** (25 mM final conc.).

Data for **23**: Colorless syrup;  $R_f$  0.43 (4/1 toluene/acetone);  $[\alpha]^{24}_D +14.2^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.00 (9H, s), 1.01 (9H, s), 2.90 (1H, br-s), 3.36 (3H, s), 3.49 (1H, ddd,  $J = 2.5$ , 6.0 and 9.5 Hz), 3.55 (1H, dd,  $J = 2.5$  and 9.5 Hz), 3.64-3.76 (4H, m), 3.87 (1H, dd,  $J = 9.5$  and 9.5 Hz), 3.99 (1H, dd,  $J = 10.0$  and 10.5 Hz), 4.03 (1H, br-s), 4.11 (1H, dd,  $J = 5.0$  and 10.0 Hz), 4.16 (1H, d,  $J = 2.5$  Hz), 4.25 (1H, dd,  $J = 2.5$  and 9.5 Hz), 4.36 (1H, dd,  $J = 9.5$  and 9.5 Hz), 4.52 and 4.87 (2H, ABq,  $J = 10.0$  Hz),

4.52 and 4.60 (2H, ABq,  $J = 12.0$  Hz), 4.66 and 4.74 (2H, ABq,  $J = 11.5$  Hz), 4.66 (1H, d,  $J = 1.0$  Hz), 4.84 (1H, br-s), 7.19 (2H, m), 7.26-7.37 (13H, m);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  19.9, 22.6, 27.0, 27.5, 55.2, 66.7, 67.8, 68.6, 68.9, 70.5, 71.4, 71.5, 73.5, 73.9, 75.3, 77.1, 81.5, 95.9 ( $^1J_{\text{CH}} = 160.0$  Hz), 101.4, 127.6, 127.9 $\times$ 2, 128.2, 128.3, 128.4, 128.5, 137.7, 138.0; HRMS (ESI-TOF)  $m/z$  789.3621 (789.3646 calcd for  $\text{C}_{42}\text{H}_{58}\text{O}_{11}\text{NaSi}$   $[\text{M}+\text{Na}]^+$ ).

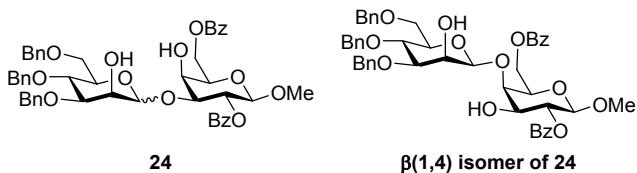
### Compound S9



To a solution of **23** (16.2 mg, 21.1  $\mu\text{mol}$ ) in pyridine (0.156 mL, 50 mM) were added  $\text{Ac}_2\text{O}$  (16.0  $\mu\text{L}$ , 169 mmol) and DMAP (2.6 mg, 21.1  $\mu\text{mol}$ ) at 0  $^\circ\text{C}$ . After the reaction mixture was stirred for 0.5 h at room temperature, the reactions was quenched by addition of water (2 mL). The resultant mixture was extracted with  $\text{EtOAc}$  (2 mL $\times$ 3), and then the extracts were washed with brine (2 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated in *vacuo*. The residue was subjected to silica gel column chromatography (10/1 toluene/acetone) to give **S9** (18.0 mg, 21.1  $\mu\text{mol}$ , quant.).

Data for **S9**: Colorless syrup;  $R_f$  0.68 (8/1 toluene/acetone);  $[\alpha]^{24}_{\text{D}} -30.5^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.95 (9H, s), 1.02 (9H, s), 2.12 (3H, s), 2.17 (3H, s), 3.37 (3H, s), 3.45 (1H, ddd,  $J = 2.0$ , 4.0 and 10.0 Hz), 3.68 (1H, dd,  $J = 3.0$  and 9.0 Hz), 3.69-3.75 (1H, m), 3.79 (1H, dd,  $J = 2.0$  and 11.5 Hz), 3.85 (1H, dd,  $J = 9.0$  and 10.0 Hz), 3.86 (1H, dd,  $J = 4.0$  and 11.5 Hz), 3.96 (1H, dd,  $J = 10.5$  and 10.5 Hz), 4.01-4.05 (2H, m), 4.11 (1H, dd,  $J = 5.0$  and 10.0 Hz), 4.50-4.57 (3H, m), 4.60 (1H, d,  $J = 2.0$  Hz), 4.67 (1H, br-s), 4.72 (1H, d,  $J = 12.0$  Hz), 4.73 (1H, d,  $J = 11.5$  Hz), 4.85 (1H, d,  $J = 11.0$  Hz), 5.27 (1H, dd,  $J = 2.0$  and 3.0 Hz), 5.50 (1H, br-d,  $J = 3.0$  Hz), 7.14-7.36 (15H, m);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  19.9, 20.9, 21.0, 22.6, 27.0, 27.4, 55.2, 66.7, 67.4, 67.6, 68.4, 69.4, 71.4, 72.9, 73.9 $\times$ 2, 74.3, 75.2, 76.2, 80.2, 96.0, 99.5, 127.4, 127.6, 127.8 $\times$ 2, 128.0, 128.2 $\times$ 2, 128.3, 128.4, 137.7, 138.4, 138.6, 170.5, 170.7; HRMS (ESI-TOF)  $m/z$  873.3892 (873.3857 calcd for  $\text{C}_{46}\text{H}_{62}\text{O}_{13}\text{NaSi}$   $[\text{M}+\text{Na}]^+$ ).

### Compound 24

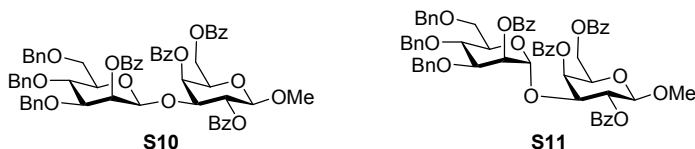


Compound **24** and  **$\beta(1,4)$  isomer of 24** were synthesized in 71% yield ( $\beta/\alpha = 92/8$ ) and 21% yield, respectively, according to the general procedure B from galactoside **22**<sup>7</sup>) and **5** (10 mM final conc.). The  $\beta/\alpha$  ratio was determined by <sup>1</sup>H NMR analysis.

Data for **24** ( $\beta$  anomer is only shown): Colorless syrup;  $R_f$  0.45 (2/1 toluene/acetone); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  3.32 (1H, dd,  $J = 3.0$  and  $9.0$  Hz), 3.99-3.43 (1H, m), 3.46 (3H, s), 3.65 (2H, br-d,  $J = 4.0$  Hz), 3.76 (1H, dd,  $J = 9.0$  and  $9.0$  Hz), 3.87-3.92 (2H, m), 3.95 (1H, dd,  $J = 3.0$  and  $10.0$  Hz), 4.26 (1H, br-s), 4.39 (1H, d,  $J = 11.5$  Hz), 4.45-4.56 (6H, m), 4.59-4.68 (2H, m), 4.81 (1H, d,  $J = 11.0$  Hz), 5.54 (1H, dd,  $J = 8.0$  and  $10.0$  Hz), 7.14-7.18 (2H, m), 7.22-7.34 (13H, m), 7.40-7.48 (4H, m), 7.54-7.62 (2H, m), 8.01-8.06 (4H, m); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  56.5, 63.6, 67.7, 68.5, 69.2, 71.1, 71.4, 72.2, 73.4, 73.9, 75.1, 75.2, 80.3, 80.7, 100.6, 101.8, 127.7, 127.8 $\times$ 2, 128.1, 128.4 $\times$ 2, 128.5, 129.7, 129.8, 129.9, 133.1, 133.2, 137.5, 137.9 $\times$ 2, 165.2, 166.4.

Data for  **$\beta(1,4)$  isomer of 24**: Colorless syrup;  $R_f$  0.63 (2/1 toluene/acetone);  $[\alpha]^{26}_D -23.4^\circ$  ( $c$  1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  2.54 (1H, br-d,  $J = 2.0$  Hz), 3.21 (1H, d,  $J = 6.5$  Hz), 3.47 (1H, m), 3.51 (3H, s), 3.58 (1H, dd,  $J = 3.0$  and  $9.0$  Hz), 3.71 (2H, br-d,  $J = 3.5$  Hz), 3.86-3.92 (3H, m), 4.29 (1H, br-d,  $J = 3.0$  Hz), 4.30-4.33 (1H, m), 4.47 and 4.55 (2H, ABq,  $J = 12.0$  Hz), 4.51 (1H, d,  $J = 8.0$  Hz), 4.55 and 4.87 (2H, ABq,  $J = 11.0$  Hz), 4.59 (1H, dd,  $J = 7.5$  and  $12.0$  Hz), 4.66 and 4.81 (2H, ABq,  $J = 12.0$  Hz), 4.78 (1H, dd,  $J = 4.5$  and  $12.0$  Hz), 4.82 (1H, br-s), 5.23 (1H, dd,  $J = 8.0$  and  $10.0$  Hz), 7.18-7.35 (13H, m), 7.38-7.49 (6H, m), 7.54-7.62 (2H, m), 8.04-8.08 (4H, m); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  56.9, 64.2, 67.9, 69.6, 71.3, 72.4, 73.4 $\times$ 2, 74.1, 74.2, 75.1, 75.3 $\times$ 2, 81.2, 100.4 (<sup>1</sup> $J_{CH} = 161$  Hz), 101.7, 127.4, 127.7, 127.8, 127.9, 128.1, 128.3, 128.4, 128.5 $\times$ 2, 129.4, 129.6, 130.0, 130.1, 133.1, 133.5, 137.9, 138.2, 166.3, 167.4; HRMS (ESI-TOF)  $m/z$  857.3123 (857.3149 calcd for C<sub>48</sub>H<sub>50</sub>O<sub>13</sub>Na [M+Na]<sup>+</sup>).

### Compound **S10** and **S11**



To a solution of **24** (11.2 mg, 0.0134 mmol) in pyridine (268  $\mu$ L) was added BzCl (6.2  $\mu$ L, 0.0536 mmol) at 0  $^\circ$ C. After the reaction mixture was stirred for 1 h at room temperature, the reaction was

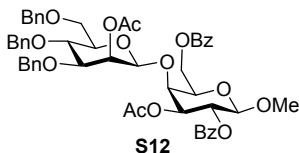
quenched by addition of water (2 mL). The resultant mixture was extracted with EtOAc (2 mL×3), and then the extracts were washed with brine (2 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The residue was subjected to preparative TLC (9/1 toluene/acetone) to give **S10** (12.0 mg, 11.5 μmol, 86% yield) and **S11** (1.1 mg, 1.05 μmol, 8% yield).

Data for **S10**: Colorless syrup; *R<sub>f</sub>* 0.58 (8/1 toluene/acetone); [α]<sup>23</sup><sub>D</sub> +34.4° (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 3.40 (1H, dd, *J* = 3.0 and 9.5 Hz), 3.44-3.48 (1H, m), 3.49 (3H, s), 3.76-3.82 (2H, m), 3.89 (1H, dd, *J* = 5.0 and 11.5 Hz), 4.07 (1H, br-t, *J* = 6.5 Hz), 4.17 and 4.55 (2H, ABq, *J* = 11.5 Hz), 4.25 (1H, dd, *J* = 3.5 and 10.0 Hz), 4.44 (2H, br-d, *J* = 6.5 Hz), 4.47 and 4.73 (2H, ABq, *J* = 10.5 Hz), 4.56 (1H, d, *J* = 8.0 Hz), 4.61 and 4.84 (2H, ABq, *J* = 12.0 Hz), 4.66 (1H, br-s), 5.45 (1H, br-d, *J* = 3.0 Hz), 5.57 (1H, dd, *J* = 8.0 and 11.0 Hz), 5.83 (1H, br-d, *J* = 3.0 Hz), 7.06-7.17 (11H, m), 7.24-7.29 (4H, m), 7.33-7.36 (6H, m), 7.40-7.41 (2H, m), 7.47-7.53 (3H, m), 7.59-7.62 (1H, m), 7.68-7.69 (4H, m), 8.00-8.01 (2H, m), 8.09-8.10 (2H, m); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 56.8, 62.9, 67.5, 69.3, 70.2, 70.9, 71.8, 71.9, 73.6, 73.9, 75.3, 76.1, 80.0, 99.6 (<sup>1</sup>*J*<sub>CH</sub> = 155 Hz), 102.1, 127.2, 127.3, 127.6, 127.7, 127.9, 128.0, 128.1, 128.2, 128.3×2, 128.6, 128.9, 129.0, 129.4, 129.7×2, 129.8, 132.3, 132.7, 133.1, 133.3, 137.4, 138.1, 138.8, 164.8, 165.0, 165.4, 166.1; HRMS (ESI-TOF) *m/z* 1065.3689 (1065.3673 calcd for C<sub>62</sub>H<sub>58</sub>O<sub>15</sub>Na [M+Na]<sup>+</sup>).

Data for **S11**: Colorless syrup; *R<sub>f</sub>* 0.70 (8/1 toluene/acetone); [α]<sup>23</sup><sub>D</sub> +50.3° (*c* 0.65, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 3.38-3.43 (2H, m), 3.56 (3H, s), 3.60-3.66 (2H, m), 3.78 (1H, dd, *J* = 9.5 and 9.5 Hz), 4.11-4.13 (2H, m), 4.20 and 4.54 (2H, ABq, *J* = 11.5 Hz), 4.28 (1H, dd, *J* = 3.5 and 10.0 Hz), 4.36-4.41 (2H, m), 4.49 (1H, d, *J* = 10.5 Hz), 4.57-4.61 (2H, m), 4.70 (1H, dd, *J* = 6.0 and 11.0 Hz), 5.31 (1H, d, *J* = 2.0 Hz), 5.42 (1H, dd, *J* = 2.0 and 2.5 Hz), 5.53 (1H, dd, *J* = 8.0 and 10.0 Hz), 5.85 (1H, br-d, *J* = 3.5 Hz), 6.78-6.80 (2H, m), 7.03-7.05 (2H, m), 7.09-7.14 (3H, m), 7.15-7.20 (2H, m), 7.22-7.32 (10H, m), 7.39-7.44 (3H, m), 7.49-7.57 (4H, m), 7.61-7.64 (1H, m), 7.96-8.03 (6H, m), 8.25-8.26 (2H, m); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 57.1, 62.1, 66.3, 68.2, 68.8, 70.4, 71.0, 71.3, 72.0, 73.3, 73.5, 73.8, 74.2, 77.8, 95.5 (<sup>1</sup>*J*<sub>CH</sub> = 170 Hz), 102.4, 127.0, 127.2, 127.3, 127.4, 127.9, 128.1×2, 128.2, 128.3, 128.5, 128.7, 129.2, 129.4, 129.5, 129.8, 130.0×2, 130.2, 132.9, 133.1, 133.3, 133.6, 137.8, 138.5, 138.7, 165.0×2, 165.8, 166.1; HRMS (ESI-TOF) *m/z* 1065.3708 (1065.3673 calcd for C<sub>62</sub>H<sub>58</sub>O<sub>15</sub>Na [M+Na]<sup>+</sup>).

## Compound **S12**

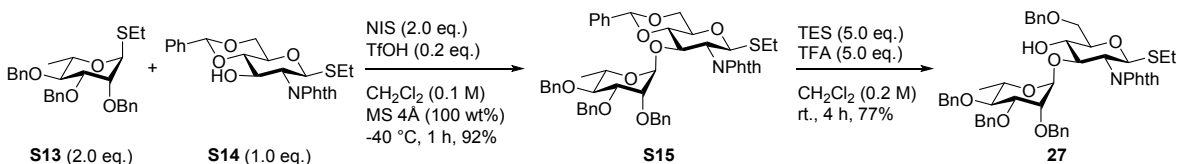




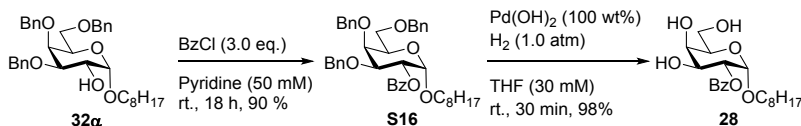
To a solution of  **$\beta$ (1,4) isomer of 24** (6.5 mg, 7.79  $\mu$ mol) in pyridine (0.156 mL, 50 mM) were added Ac<sub>2</sub>O (6.0  $\mu$ L, 0.062 mmol) and DMAP (0.95 mg, 7.79  $\mu$ mol) at 0 °C. After the reaction mixture was stirred for 0.5 h at room temperature, the reaction was quenched by addition of water (2 mL). The resultant mixture was extracted with EtOAc (2 mL $\times$ 3), and then the extracts were washed with brine (2 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated in *vacuo*. The residue was subjected to silica gel column chromatography (9/1 toluene/acetone) to give **S12** (7.0 mg, 7.62  $\mu$ mol, 98% yield).

Data for **S12**: Colorless syrup; *R<sub>f</sub>* 0.53 (8/1 toluene/acetone); [ $\alpha$ ]<sub>D</sub><sup>24</sup> -11.2° (*c* 0.95, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  1.93 (3H, s), 2.24 (3H, s), 3.39 (1H, ddd, *J* = 2.5, 4.5 and 9.5 Hz), 3.48 (3H, s), 3.64 (1H, dd, *J* = 3.0 and 9.5 Hz), 3.69-3.71 (2H, m), 3.73 (1H, dd, *J* = 9.5 and 9.5 Hz), 3.98-4.01 (1H, m), 4.39 (1H, br-d, *J* = 3.0 Hz), 4.43 (1H, d, *J* = 12.0 Hz), 4.50-4.57 (5H, m), 4.61 (1H, dd, *J* = 5.0 and 7.0 Hz), 4.73 (1H, br-s), 4.82 (1H, d, *J* = 11.5 Hz), 4.87 (1H, d, *J* = 11.0 Hz), 5.28 (1H, dd, *J* = 3.0 and 10.0 Hz), 5.52 (1H, dd, *J* = 7.5 and 10.0 Hz), 5.76 (1H, br-d, *J* = 3.0 Hz), 7.16-7.20 (2H, m), 7.23-7.33 (11H, m), 7.35-7.37 (2H, m), 7.41-7.47 (4H, m), 7.54-7.60 (2H, m), 8.00-8.08 (4H, m); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  20.8, 21.0, 56.1, 64.0, 67.5, 69.4, 69.5, 71.4, 72.0, 72.5, 73.0, 73.4, 74.3, 75.3, 75.9, 80.2, 98.3, 101.8, 127.5, 127.6, 127.7, 127.8, 128.0, 128.3 $\times$ 2, 128.4 $\times$ 3, 129.6, 129.7, 129.8, 130.0, 133.1, 133.2, 137.5, 138.1, 138.3, 165.2, 166.2, 170.0, 170.2; HRMS (ESI-TOF) *m/z* 941.3395 (941.3360 calcd for C<sub>52</sub>H<sub>54</sub>O<sub>15</sub>Na [M+Na]<sup>+</sup>).

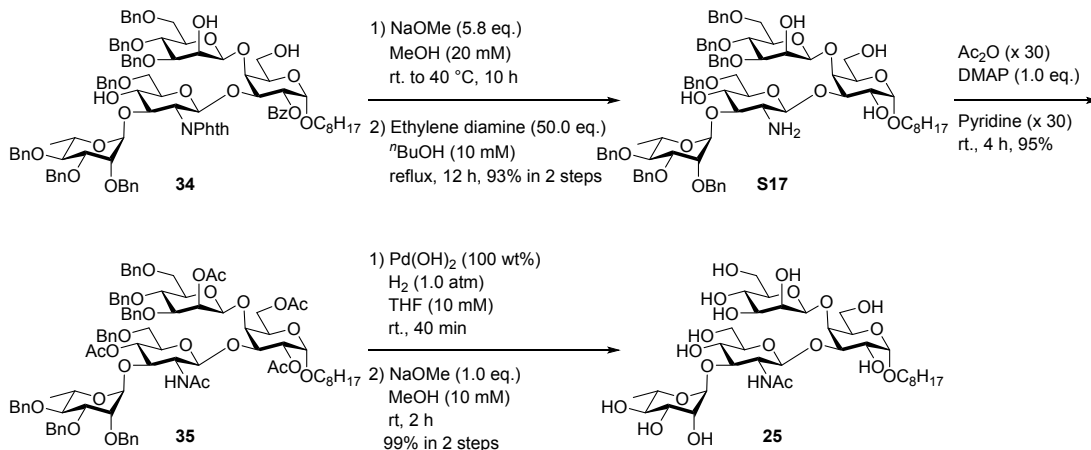
### Synthetic schemes of compounds 27, 28 and 25



**Scheme S1** Synthetic scheme of **27**



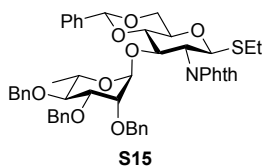
### Scheme S2 Synthetic scheme of 28



### Scheme S3 Synthetic scheme of 25

#### Synthesis of the tetrasaccharide 25

##### Compound S15

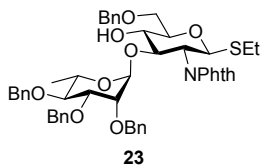


To a solution of compound **S13**<sup>8)</sup> (1.12 g, 2.33 mmol) and **S14**<sup>9)</sup> (515 mg, 1.17 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (11.7 mL, 0.10 M) was added MS 4 Å and the reaction mixture was stirred under Ar at room temperature for 30 min. The reaction mixture was cooled to -40 °C, and then NIS (524 mg, 2.33 mmol) and TfOH (23.3 μL, 0.23 mmol) were added to the reaction mixture. After the reaction mixture was stirred at same temperature for 1 h, NEt<sub>3</sub> (5.0 mL) was added to the reaction mixture. To the resulting mixture were added 10% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> aq. (15 mL) and sat. NaHCO<sub>3</sub> aq. (15 mL), and then the mixture was extracted with CHCl<sub>3</sub> (30 mL). And then the extracts were washed with brine (30 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated in *vacuo*. Purification of the residue by column chromatography (4/1 to 2/1 *n*-hexane/EtOAc) gave **S15** (920 mg, 1.07 mmol, 92% yield).

Data for **S15**: White foam; R<sub>f</sub> 0.54 (2/1 *n*-hexane/EtOAc); [α]<sub>D</sub><sup>25</sup> -5.3° (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 0.81 (3H, d, *J* = 6.5 Hz), 1.20 (3H, t, *J* = 7.5 Hz), 2.68 (2H, m), 3.37 (1H, dd, *J* = 9.5 and 9.5 Hz), 3.44 (1H, dd, *J* = 2.0 and 3.0 Hz), 3.64 (1H, dd, *J* = 9.0 and 9.5 Hz), 3.72-3.77 (2H, m), 3.80 (1H, t, *J* = 10.0 Hz), 3.88 (2H, m), 3.94 and 3.98 (2H, ABq, *J* = 12.0 Hz), 4.35 (1H, dd, *J* = 10.0 and 10.5 Hz),

4.41 and 4.49 (2H, ABq,  $J = 12.0$  Hz), 4.48 and 4.79 (2H, ABq,  $J = 11.5$  Hz), 4.66 (2H, m), 5.42 (1H, d,  $J = 10.5$  Hz), 5.54 (1H, s), 6.91 (2H, m), 7.11-7.21 (4H, m), 7.24-7.32 (12H, m), 7.49 (2H, m), 7.73 (2H, m), 7.86 (2H, br-t,  $J = 7.5$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  14.8, 17.2, 24.1, 55.5, 68.1, 68.4, 70.7, 71.6, 72.2, 74.8 $\times$ 2, 76.0, 77.2, 79.4, 80.0, 80.3, 81.6, 98.1, 101.6, 123.6, 126.2, 127.0, 127.2 $\times$ 2, 127.3, 127.6, 127.9 $\times$ 2, 128.0, 128.1, 128.9, 131.1, 134.4, 134.5, 136.8, 137.7, 138.4, 138.6, 167.1, 167.8; HRMS (ESI-TOF)  $m/z$  858.3345 (858.3312 calcd for  $\text{C}_{50}\text{H}_{52}\text{NO}_{10}\text{S}$   $[\text{M}+\text{H}]^+$ ).

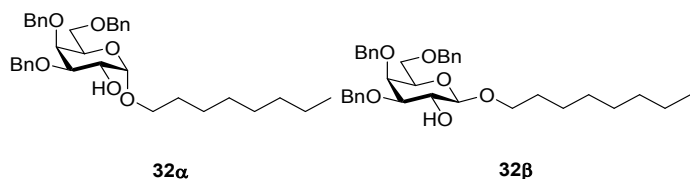
### Compound 27



To a solution of compound **S15** (302 mg, 353  $\mu\text{mol}$ ) in dry  $\text{CH}_2\text{Cl}_2$  (1.8 mL, 0.20 M) was added TES (281  $\mu\text{L}$ , 1.77 mmol) and TFA (135  $\mu\text{L}$ , 1.77 mmol) at 0  $^\circ\text{C}$ . After the reaction mixture was stirred under Ar at room temperature for 4 h, sat.  $\text{NaHCO}_3$  aq. (5 mL) was added to the reaction mixture. The resultant mixture was extracted with EtOAc (10 mL), washed with brine (10 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated in *vacuo*. Purification of the residue by column chromatography (20/1 to 10/1 toluene/acetone) of the residue gave **27** (234 mg, 272  $\mu\text{mol}$ , 77% yield).

Data for **27**: White foam;  $R_f$  0.48 (2/1 *n*-hexane/EtOAc);  $[\alpha]_D^{25} +23.5^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.22 (3H, t,  $J = 5.0$  Hz), 1.30 (3H, d,  $J = 6.5$  Hz), 2.68 (2H, m), 3.23 (1H, br-s), 3.51 (1H, dd,  $J = 8.0$  and 8.0 Hz), 3.57 (1H, dd,  $J = 7.0$  and 9.5 Hz), 3.65 (1H, m), 3.68 (1H, dd,  $J = 2.5$  and 8.0 Hz), 3.76 (1H, dd,  $J = 5.5$  and 10.5 Hz), 3.86-3.93 (2H, m), 4.19 and 4.32 (2H, ABq,  $J = 12.0$  Hz), 4.20-4.31 (4H, m), 4.52 and 4.79 (2H, ABq,  $J = 11.0$  Hz), 4.61 and 4.65 (2H, ABq,  $J = 12.0$  Hz), 4.73 (1H, d,  $J = 2.0$  Hz), 5.27 (1H, d,  $J = 9.5$  Hz), 7.02 (2H, br-d,  $J = 7.5$  Hz), 7.12-7.20 (4H, m), 7.22-7.37 (14H, m), 7.68-7.75 (2H, m), 7.78-7.80 (2H, m);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  14.9, 18.0, 24.0, 54.1, 69.6 $\times$ 2, 70.6, 71.8, 72.4, 73.4, 74.8, 74.9, 78.9, 79.4, 79.6, 80.9, 83.8, 99.9, 123.4, 127.4 $\times$ 2, 127.5, 127.6, 127.7, 128.2, 128.2, 131.3, 131.4, 134.2, 137.5, 138.1, 138.2, 138.3, 167.2, 167.9; HRMS (ESI-TOF)  $m/z$  882.3292 (882.3288 calcd for  $\text{C}_{50}\text{H}_{53}\text{NO}_{10}\text{NaS}$   $[\text{M}+\text{Na}]^+$ ).

### Compound 32

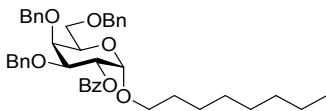


To a solution of a borinic acid **30** (2.76 mg, 12.6  $\mu\text{mol}$ ) and **31** (10.0  $\mu\text{L}$ , 63.2  $\mu\text{mol}$ ) in dry THF (500  $\mu\text{L}$ , 126 mM to glycosyl acceptor) was added a solution of **29**<sup>10</sup> (54.5 mg, 126  $\mu\text{mol}$ ) in dry THF (2.03 mL, 62.1 mM to glycosyl donor) at 0 °C under Ar atmosphere. After the reaction mixture was stirred at same temperature for 24 h, 50 mM NaBO<sub>3</sub> aq. (598  $\mu\text{L}$ , 29.9  $\mu\text{mol}$ ) and sat. NH<sub>4</sub>Cl aq. (2 mL) were added to the reaction mixture. The resultant mixture was extracted with EtOAc (3 mL $\times$ 3), washed with brine (6 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated in *vacuo*. Purification of the residue by preparative TLC (0.25 mm silica gel plate) gave **32 $\alpha$**  (26.5 mg, 47.1  $\mu\text{mol}$ , 74% yield) and a trace amount of **32 $\beta$**  ( $\alpha/\beta = > 95/5$ ).

Data for **32 $\alpha$** : White solid; R<sub>f</sub> 0.61 (8/1 toluene/acetone); [ $\alpha$ ]<sub>D</sub><sup>25</sup> +95.7° (*c* 1.0, CHCl<sub>3</sub>); mp 69-70 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  0.88 (3H, t, *J* = 7.0 Hz), 1.22-1.35 (10H, m), 1.60 (2H, m), 2.09 (1H, d, *J* = 8.5 Hz), 3.45 (1H, dt, *J* = 6.5 and 10.0 Hz), 3.55 (1H, dd, *J* = 6.5 and 9.5 Hz), 3.60 (1H, dd, *J* = 7.0 and 9.5 Hz), 3.68 (1H, dt, *J* = 4.0 and 10.0 Hz), 3.68 (1H, dt, *J* = 2.0 and 12.5 Hz), 3.93 (1H, dd, *J* = 6.5 and 7.0 Hz), 3.99 (1H, d, *J* = 2.0 Hz), 4.15 (1H, ddd, *J* = 4.0, 8.5 and 12.5 Hz), 4.43 and 4.51 (2H, ABq, *J* = 12.0 Hz), 4.57 and 4.90 (2H, ABq, *J* = 11.5 Hz), 4.74 (2H, s), 4.93 (1H, d, *J* = 4.0 Hz), 7.22-7.40 (15H, m), <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  14.0, 22.5, 26.0, 29.1, 29.2, 29.3, 31.7, 68.2, 68.8, 69.0, 69.5, 72.3, 73.3, 74.0, 74.5, 79.7, 98.5, 127.4, 127.5, 127.6 $\times$ 2, 128.0, 128.1, 128.2, 128.3, 137.8, 138.2, 138.4; HRMS (ESI-TOF) *m/z* 585.3212 (585.3192 calcd for C<sub>35</sub>H<sub>46</sub>O<sub>6</sub>Na [M+Na]<sup>+</sup>).

Data for **32 $\beta$** : White solid; R<sub>f</sub> 0.68 (8/1 toluene/acetone); [ $\alpha$ ]<sub>D</sub><sup>20</sup> -10.0° (*c* 1.0, CHCl<sub>3</sub>); mp 81-82 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  0.87 (3H, t, *J* = 7.0 Hz), 1.22-1.34 (10H, m), 1.56-1.64 (2H, m), 2.35 (1H, br-s), 3.43 (1H, dd, *J* = 2.5 and 9.5 Hz), 3.47 (1H, dt, *J* = 7.0 and 9.5 Hz), 3.55-3.65 (3H, m), 3.87 (1H, dt, *J* = 7.0 and 9.5 Hz), 3.92 (1H, br-d, *J* = 2.5 Hz), 3.92-3.97 (1H, m), 4.22 (1H, d, *J* = 7.5 Hz), 4.43 and 4.47 (2H, ABq, *J* = 11.5 Hz), 4.60 and 4.89 (2H, ABq, *J* = 12.0 Hz), 4.68 and 4.73 (2H, ABq, *J* = 12.0 Hz), 7.22-7.39 (15H, m); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  14.1, 22.6, 25.9, 29.2, 29.4, 29.5, 31.8, 68.7, 70.0, 71.4, 72.4, 72.9, 73.5, 73.7, 74.5, 81.9, 103.2, 127.5, 127.6, 127.7, 127.8, 127.9, 128.1, 128.2, 128.4, 128.5, 137.9, 138.1, 138.5; HRMS (ESI-TOF) *m/z* 585.3217 (585.3192 calcd for C<sub>35</sub>H<sub>46</sub>O<sub>6</sub>Na [M+Na]<sup>+</sup>).

## Compound S16

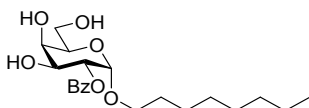


**S16**

To a solution of **32** (23.9 mg, 42.5  $\mu\text{mol}$ ) in dry pyridine (850  $\mu\text{L}$ , 50 mM) was added BzCl (14.9  $\mu\text{L}$ , 128  $\mu\text{mol}$ ) at 0  $^{\circ}\text{C}$  under Ar atmosphere. After the reaction mixture was stirred for 18 h at room temperature, H<sub>2</sub>O (3 mL) was added to the reaction mixture. The resulting mixture was extracted with EtOAc (5 mL $\times$ 3), washed with brine (5 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated in *vacuo*. Purification of the residue by column chromatography (6/1 *n*-hexane/EtOAc) gave **S16** (25.4 mg, 38.1  $\mu\text{mol}$ , 90% yield).

Data for **S16**: White solid; R<sub>f</sub> 0.61 (6/1 *n*-hexane/EtOAc);  $[\alpha]^{24}_{\text{D}} +104.6^{\circ}$  (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  0.84 (3H, t, *J* = 9.0 Hz), 1.09-1.28 (10H, m), 1.49 (2H, m), 3.36 (1H, dt, *J* = 8.0 and 12.5 Hz), 3.55-3.68 (3H, m), 4.03 (1H, dd, *J* = 8.0 and 8.5 Hz), 4.06 (1H, br-s), 4.11 (1H, dd, *J* = 3.5 and 13.0 Hz), 4.43 and 4.51 (2H, ABq, *J* = 15.0 Hz), 4.60 and 4.96 (2H, ABq, *J* = 14.5 Hz), 4.71 (2H, s), 5.19 (1H, d, *J* = 5.0 Hz), 5.53 (1H, dd, *J* = 5.0 and 13.0 Hz), 7.24-7.37 (15H, m), 7.43 (2H, t, *J* = 7.5 Hz), 7.56 (1H, br-t, *J* = 7.5 Hz), 8.05 (2H, m); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  14.0, 22.6, 26.0, 29.1, 29.2, 29.3, 31.7, 68.2, 68.8, 69.2, 71.8, 72.5, 73.4, 74.5, 74.7, 76.8, 96.3, 127.4, 127.5 $\times$ 2, 127.7 $\times$ 2, 128.2 $\times$ 4, 128.3, 129.7, 130.1, 132.9, 137.9, 138.2, 138.4, 166.0; HRMS (ESI-TOF) *m/z* 689.3459 (689.3454 calcd for C<sub>42</sub>H<sub>50</sub>O<sub>7</sub>Na [M+Na]<sup>+</sup>).

**Compound 28**



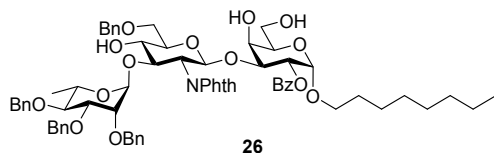
**28**

To a solution of **S16** (25.4 mg, 38.1  $\mu\text{mol}$ ) in anhydrous THF (1.27 mL, 30 mM) was added 100 wt% Pd/(OH)<sub>2</sub>/C (25.4 mg) under H<sub>2</sub> atmosphere (balloon) at room temperature. After the reaction mixture was stirred for 30 min, the reaction mixture was filtrated through celite pad, and then the filtrate was concentrated in *vacuo*. Purification of the residue by column chromatography (1/1 toluene/acetone) gave **28** (14.8 mg, 37.3  $\mu\text{mol}$ , 98% yield).

Data for **28**: Colorless syrup; R<sub>f</sub> 0.55 (1/1 toluene/acetone);  $[\alpha]^{25}_{\text{D}} +194.7^{\circ}$  (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>)  $\delta$  0.84 (3H, t, *J* = 7.5 Hz), 1.13-1.36 (10H, m), 1.53 (1H, m), 3.37 (1H, dt, *J* = 6.5 and 10.0 Hz), 3.72 (1H, dt, *J* = 6.5 and 10.0 Hz), 3.79 (3H, m), 3.91 (1H, dd, *J* = 5.0 and 5.5 Hz), 4.02 (1H,

br-s), 4.10 (1H, br-s), 4.16 (1H, dd,  $J = 3.0$  and  $10.0$  Hz), 4.25 (1H, br-s), 5.08 (1H, d,  $J = 4.0$  Hz), 5.21 (1H, dd,  $J = 4.0$  and  $10.0$  Hz), 7.52 (2H, m), 7.65 (1H, tt,  $J = 1.5$  and  $8.5$  Hz), 8.05-8.08 (2H, m);  $^{13}\text{C}$  NMR (125 MHz, acetone- $d_6$ )  $\delta$  14.3, 23.2, 26.8, 29.9, 30.0, 30.1, 32.4, 62.4, 68.2, 68.6, 70.8, 71.7, 73.4, 97.0, 129.2, 130.3, 131.2, 133.8, 166.8; HRMS (ESI-TOF)  $m/z$  419.2051 (419.2046 calcd for  $\text{C}_{21}\text{H}_{32}\text{O}_7\text{Na}$   $[\text{M}+\text{Na}]^+$ ).

### Compound 26

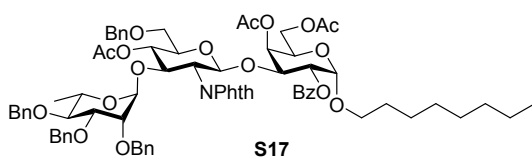


To a solution of **28** (42.2 mg, 106  $\mu\text{mol}$ ) in dry acetone (1.0 mL, 106 mM) was added boronic acid **8a** (17.8 mg, 117  $\mu\text{mol}$ ) at room temperature under Ar atmosphere. After the reaction mixture was stirred under reflux condition for 3 h, the reaction mixture was concentrated in *vacuo*. To a solution of the residue in dry toluene (2.12 mL, 50 mM to glycosyl acceptor) were added MS 4 Å (42.2 mg, 100 wt% to glycosyl acceptor) and a solution of **27** (183 mg, 213  $\mu\text{mol}$ ) in dry 1,2-dichloroethane (2.12 mL, 100 mM to glycosyl acceptor) at room temperature under Ar atmosphere. After the reaction mixture was stirred for 30 min, the reaction mixture was cooled to  $-30$  °C. And then NIS (57.5 mg, 256  $\mu\text{mol}$ ) and TfOH (2.1  $\mu\text{L}$ , 21.3  $\mu\text{mol}$ ) were added to the reaction mixture. After the reaction mixture was stirred at same temperature for 3 h,  $\text{NEt}_3$  (5 mL) was added to the reaction mixture. To the resulting mixture were added 10%  $\text{Na}_2\text{S}_2\text{O}_3$  aq. (3 mL) and sat.  $\text{NaHCO}_3$  aq. (3 mL), and then the mixture was extracted with EtOAc (15 mL), washed with brine (15 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated in *vacuo*. To a solution of the residue in MeCN (1.0 mL) was added 0.25 M  $\text{NaBO}_3$  aq. (1.0 mL, 257  $\mu\text{mol}$ ). After the resulting mixture was stirred for 30 min at room temperature, the mixture was extracted with EtOAc (3.0 mL $\times$ 3), washed with brine (3.0 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated in *vacuo*. Purification of the residue by flash silica gel column chromatography (10/1 to 4/1 toluene/acetone) gave **26** (122.7 mg, 103  $\mu\text{mol}$ , 96% yield).

Data for **26**: White foam;  $R_f$  0.29 (4/1 toluene/acetone);  $[\alpha]^{24}_{\text{D}} +70.0^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.83 (3H, t,  $J = 7.0$  Hz), 1.03-1.24 (10H, m), 1.27 (3H, t,  $J = 7.0$  Hz), 1.45 (2H, m), 2.32 (1H, br-d,  $J = 9.5$  Hz), 2.95 (1H, s), 3.11 (1H, dd,  $J = 2.5$  and  $2.5$  Hz), 3.28 (1H, dt,  $J = 7.0$  and  $10.5$  Hz), 3.50 (1H, dd,  $J = 9.0$  and  $9.0$  Hz), 3.50 (1H, dd,  $J = 9.0$  and  $9.0$  Hz), 3.57 (1H, dd,  $J = 2.5$  and  $9.0$  Hz), 3.62 (1H, dt,  $J = 7.0$  and  $10.5$  Hz), 3.75-3.74 (3H, m), 3.82 (1H, dd,  $J = 7.0$  and  $9.0$  Hz), 3.84-3.93 (3H, m), 4.07 and 4.21 (2H, ABq,  $J = 11.5$  Hz), 4.14 (1H, dd,  $J = 3.5$  and  $10.0$  Hz), 4.15-4.24 (4H, m), 4.31 (2H, m), 4.48 and 4.75 (2H, ABq,  $J = 10.5$  Hz), 4.58 and 4.62 (2H, ABq,  $J = 12.0$  Hz), 4.64 (1H, d,  $J =$

2.5 Hz), 5.00 (1H, d,  $J = 4.0$  Hz), 5.28 (1H, dd,  $J = 4.0$  and  $10.0$  Hz), 5.33 (1H, br-d,  $J = 8.5$  Hz), 6.97 (2H, br-d,  $J = 7.0$  Hz), 7.08-7.34 (17H, m), 7.35-7.46 (8H, m), 7.64 (2H, dd,  $J = 1.5$  and  $8.0$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  14.1, 18.0, 22.6, 26.0, 29.1, 29.2, 31.7, 54.7, 63.0, 68.2, 68.6, 69.5, 69.7, 69.8, 70.2, 70.8, 71.7, 72.5, 73.5, 74.8, 74.9, 75.2, 77.7, 78.6, 79.5, 82.6, 96.1, 99.0, 100.1, 127.4, 127.6 $\times$ 2, 127.8, 128.0, 128.2, 128.3 $\times$ 2, 128.5, 129.2, 129.5, 132.6, 133.8, 137.5, 138.0 $\times$ 2, 138.2, 165.2; HRMS (ESI-TOF)  $m/z$  1216.5206 (1216.5246 calcd for  $\text{C}_{69}\text{H}_{79}\text{NO}_{17}\text{Na}$   $[\text{M}+\text{Na}]^+$ ).

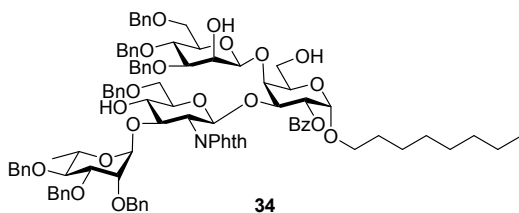
### Compound **S17**



To a solution of **26** (8.3 mg, 6.95  $\mu\text{mol}$ ) in dry pyridine (400  $\mu\text{L}$ , 17 mM) were added  $\text{Ac}_2\text{O}$  (400  $\mu\text{L}$ , 4.23 mmol) and DMAP (2.0 mg, 1.64  $\mu\text{mol}$ ) at  $0^\circ\text{C}$ . After the reaction mixture was stirred for 3 h at room temperature,  $\text{H}_2\text{O}$  (1.0 mL) was added to the reaction mixture at  $0^\circ\text{C}$ . The resulting mixture was extracted with EtOAc (2 mL), washed with brine (2 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated *in vacuo*. Purification of the residue by column chromatography (2/1 *n*-hexane/EtOAc) gave **S17** (9.0 mg, 6.81  $\mu\text{mol}$ , 98% yield).

Data for **S17**: Colorless syrup;  $R_f$  0.30 (2/1 *n*-hexane/EtOAc);  $[\alpha]_D^{24} +82.2^\circ$  ( $c$  0.90,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.84 (3H, t,  $J = 7.0$  Hz), 1.05-1.28 (10H, m), 1.15 (3H, d,  $J = 6.5$  Hz), 1.41-1.50 (2H, m), 1.97 (3H, s), 2.00 (3H, s), 2.17 (3H, s), 3.10 (1H, dd,  $J = 2.5$  and  $2.5$  Hz), 3.29 (1H, dt,  $J = 6.5$  and  $10.0$  Hz), 3.35 (1H, dd,  $J = 9.5$  and  $9.5$  Hz), 3.52 (1H, dd,  $J = 2.5$  and  $9.5$  Hz), 3.55-3.70 (4H, m), 3.76 (1H, ddd,  $J = 3.5$ ,  $6.5$  and  $10.0$  Hz), 3.88 and 4.11 (2H, ABq,  $J = 11.5$  Hz), 4.00 (1H, m), 4.06-4.14 (3H, m), 4.16 and 4.22 (2H, ABq,  $J = 12.5$  Hz), 4.29 (1H, dd,  $J = 3.5$  and  $10.0$  Hz), 4.48 (1H, dd,  $J = 10.0$  Hz), 4.49 and 4.77 (2H, ABq,  $J = 11.0$  Hz), 4.58 (1H, s), 4.59 and 4.65 (2H, ABq,  $J = 11.5$  Hz), 4.96 (1H, dd,  $J = 10.0$  and  $10.0$  Hz), 4.99 (1H, d,  $J = 3.5$  Hz), 5.11 (1H, dd,  $J = 3.5$  and  $10.0$  Hz), 5.30 (1H, d,  $J = 8.5$  Hz), 5.56 (1H, d,  $J = 3.5$  Hz), 6.99 (2H, m), 7.05 (2H, m), 7.12-7.31 (16H, m), 7.35-7.40 (6H, m), 7.58 (1H, m), 7.72 (2H, m);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  14.1, 17.7, 20.7, 21.2, 22.6, 26.0, 29.1, 29.2 $\times$ 2, 29.7, 31.7, 55.8, 62.9, 66.8, 68.4, 69.2, 70.1, 70.3, 70.5, 71.5, 71.6, 72.3, 73.3, 73.6, 73.7, 74.8, 75.3, 79.7, 79.8, 95.9, 98.7, 99.9, 127.2, 127.3, 127.4, 127.6 $\times$ 2, 128.2 $\times$ 2, 128.4, 129.0, 129.8, 133.0, 133.8, 137.9, 138.1, 138.2, 138.7, 165.3, 169.8, 170.1, 170.4; HRMS (ESI-TOF)  $m/z$  1342.5618 (1342.5563 calcd for  $\text{C}_{75}\text{H}_{85}\text{NO}_{20}\text{Na}$   $[\text{M}+\text{Na}]^+$ ).

### Compound **34**

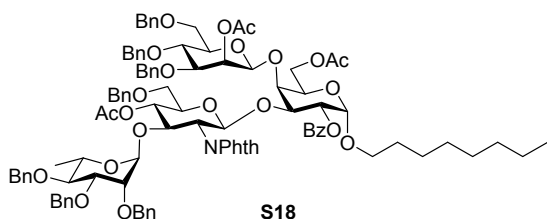


Compound **34** was synthesized in 91% yield according to the general procedure B from glycoside **26** and **5** (50 mM final conc.).

Data for **34**: White foam;  $R_f$  0.38 (4/1 toluene/acetone);  $[\alpha]^{25}_D +36.8^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.84 (3H, t,  $J = 7.0$  Hz), 1.02-1.26 (10H, m), 1.30 (3H, d,  $J = 6.0$  Hz), 1.43 (2H, m), 2.30 (1H, br-s), 3.16 (1H, dd,  $J = 3.0$  and 3.0 Hz), 3.25 (1H, dt,  $J = 6.5$  and 10.0 Hz), 3.47 (2H, m), 3.52-3.65 (7H, m), 3.68-3.77 (3H, m), 3.80 (1H, dd,  $J = 3.0$  and 9.0 Hz), 3.86-3.93 (4H, m), 3.98 (1H, dd,  $J = 8.5$  and 11.0 Hz), 4.06 and 4.15 (2H, ABq,  $J = 11.5$  Hz), 4.20 and 4.24 (2H, ABq,  $J = 12.5$  Hz), 4.29-4.34 (2H, m), 4.43 and 4.48 (2H, ABq,  $J = 12.5$  Hz), 4.45 and 4.88 (2H, ABq,  $J = 11.5$  Hz), 4.46 and 4.75 (2H, ABq,  $J = 11.5$  Hz), 4.44-4.50 (2H, m), 4.54 and 4.57 (2H, ABq,  $J = 12.0$  Hz), 4.69 (1H, d,  $J = 3.0$  Hz), 4.84 and 5.01 (2H, ABq,  $J = 11.5$  Hz), 4.92 (1H, d,  $J = 3.5$  Hz), 4.92 (1H, br-s), 5.12 (1H, dd,  $J = 3.5$  and 10.5 Hz), 5.26 (1H, d,  $J = 8.5$  Hz), 6.89 (1H, d,  $J = 7.0$  Hz), 6.96-7.02 (4H, m), 7.06-7.16 (8H, m), 7.18-7.22 (4H, m), 7.24-7.33 (17H, m), 7.37-7.42 (3H, m), 7.49 (2H, br-d,  $J = 7.0$  Hz), 7.53 (1H, br-t,  $J = 7.5$  Hz), 7.57-7.62 (2H, m), 7.75-7.78 (2H, m);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  14.0, 17.9, 22.5, 25.9, 29.0, 29.2, 31.7, 55.2, 59.4, 67.2, 68.2, 68.8, 69.2, 69.3, 69.6, 70.5, 70.8, 71.7, 72.3, 73.2, 73.5, 74.2 $\times$ 2, 74.7, 74.8, 75.0 $\times$ 2, 75.3, 75.9, 78.5, 79.6, 81.6, 81.8, 95.9 ( $^1J_{\text{CH}} = 169$  Hz), 99.1 ( $^1J_{\text{CH}} = 164$  Hz), 99.8 ( $^1J_{\text{CH}} = 169$  Hz), 100.8 ( $^1J_{\text{CH}} = 161$  Hz), 122.8, 123.0, 127.4, 127.5, 127.6, 127.7, 128.0, 128.1, 128.2, 128.3 $\times$ 2, 128.9, 129.2, 129.7, 130.6, 130.8, 132.9, 133.7, 133.8, 137.4, 137.6, 138.1, 138.2 $\times$ 2, 165.3, 167.2, 167.5; HRMS (ESI-TOF)  $m/z$  832.8460 (832.8495 calcd for  $\text{C}_{96}\text{H}_{108}\text{NO}_{22}\text{K}$  [ $\text{M}+\text{H}+\text{K}$ ] $^{2+}$ ).

### Compound **S18**

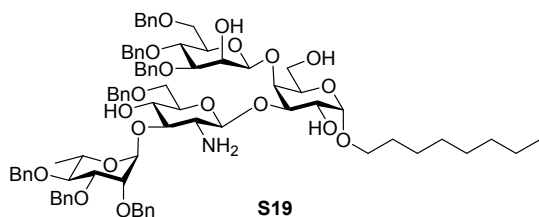




To a solution of **34** (14.8 mg, 9.10  $\mu\text{mol}$ ) in dry pyridine (400  $\mu\text{L}$ , 23 mM) were added  $\text{Ac}_2\text{O}$  (400  $\mu\text{L}$ , 4.23 mmol) and DMAP (2.0 mg, 1.64  $\mu\text{mol}$ ) at 0  $^\circ\text{C}$ . After the reaction mixture was stirred for 3 h at room temperature,  $\text{H}_2\text{O}$  (1.0 mL) was added to the reaction mixture at 0  $^\circ\text{C}$ . The resulting mixture was extracted with EtOAc (2 mL), washed with brine (2 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated *in vacuo*. Purification of the residue by column chromatography (2/1 *n*-hexane/EtOAc) gave **S18** (15.5 mg, 8.83  $\mu\text{mol}$ , 97% yield).

Data for **S18**: Colorless syrup;  $R_f$  0.30 (2/1 *n*-hexane/EtOAc);  $[\alpha]_D^{24} +42.3^\circ$  ( $c$  0.96,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.84 (3H, t,  $J = 7.5$  Hz), 1.02-1.28 (10H, m), 1.17 (3H, d,  $J = 6.0$  Hz), 1.44 (2H, m), 1.97 (3H, s), 2.01 (3H, s), 2.12 (3H, s), 3.16 (1H, dd,  $J = 2.5$  and 2.5 Hz), 3.28 (1H, dt,  $J = 7.0$  and 10.0 Hz), 3.37 (1H, dd,  $J = 9.5$  and 9.5 Hz), 3.51-3.70 (6H, m), 3.71-3.84 (4H, m), 3.85 and 4.05 (2H, ABq,  $J = 11.5$  Hz), 3.99 (1H, dd,  $J = 3.0$  and 8.0 Hz), 4.01-4.05 (1H, m), 4.07 (1H, dd,  $J = 8.5$  and 11.0 Hz), 4.19 and 4.22 (2H, ABq,  $J = 12.0$  Hz), 4.21 (1H, m), 4.25-4.29 (2H, m), 4.33 (1H, dd,  $J = 3.5$  and 12.0 Hz), 4.47 and 4.52 (2H, ABq,  $J = 12.0$  Hz), 4.49 and 4.78 (2H, ABq,  $J = 10.5$  Hz), 4.54 and 4.69 (2H, ABq,  $J = 12.0$  Hz), 4.57 and 4.90 (2H, ABq,  $J = 11.0$  Hz), 4.61 (1H, dd,  $J = 9.5$  and 11.0 Hz), 4.64 (1H, br-s), 4.76 and 5.01 (2H, ABq,  $J = 10.5$  Hz), 4.98 (1H, d,  $J = 3.5$  Hz), 5.00 (2H, m), 5.05 (1H, dd,  $J = 3.5$  and 10.0 Hz), 5.26 (1H, d,  $J = 8.5$  Hz), 5.74 (1H, d,  $J = 3.0$  Hz), 6.79 (1H, m), 6.95-7.00 (4H, m), 7.09-7.37 (30H, m), 7.40-7.52 (5H, m), 7.61-7.65 (2H, m), 7.79 (2H, br-d,  $J = 7.5$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  14.1, 17.7, 20.8, 21.0, 21.2, 22.6, 26.0, 29.1, 29.2 $\times$ 2, 29.7, 31.7, 56.1, 64.6, 67.9, 68.0, 68.1, 69.2, 69.7, 69.9, 70.7, 71.4, 71.6 $\times$ 2, 72.3, 73.4, 73.5, 73.6, 74.5, 74.9 $\times$ 2, 75.0 $\times$ 2, 75.2, 75.6, 76.3, 79.7, 80.7, 95.8, 98.6, 98.9, 99.9, 129.4, 129.9, 130.5, 130.9, 132.9, 133.9, 134.1, 137.8, 137.9, 138.1, 138.3, 138.6, 138.7 $\times$ 2, 165.0, 167.1, 167.6, 169.8, 170.3, 170.6; HRMS (ESI-TOF)  $m/z$  895.8638 (895.8653 calcd for  $\text{C}_{102}\text{H}_{114}\text{NO}_{25}\text{K}$   $[\text{M}+\text{H}+\text{K}]^{2+}$ ).

Compound **S19**

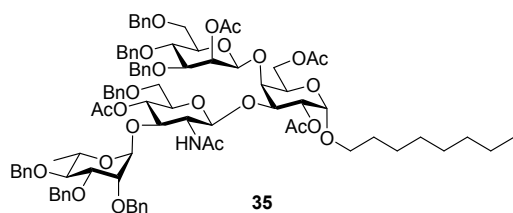


To a solution of **34** (20.2 mg, 12.0  $\mu\text{mol}$ ) in dry MeOH (600  $\mu\text{L}$ , 20 mM) was added 28% NaOMe in MeOH (14.5  $\mu\text{L}$ , 69.6  $\mu\text{mol}$ ) at 0  $^{\circ}\text{C}$ . The reaction mixture was stirred for 4 h at room temperature, and then the reaction temperature was raised to 40  $^{\circ}\text{C}$ . After the reaction mixture was stirred for 6 h, the reaction mixture was neutralized with Dowex 50W-4X, filtered, and concentrated in *vacuo*.

To a solution of the above residue in *n*-BuOH (1.24 mL, 10 mM) was added ethylene diamine (60  $\mu\text{L}$ , 0.60 mmol). After the reaction mixture was stirred under reflux condition for 12 h, the reaction mixture was concentrated in *vacuo*. Purification of the residue by column chromatography (20/1  $\text{CHCl}_3/\text{MeOH}$ ) gave **S19** (16.1 mg, 11.2  $\mu\text{mol}$ , 93% yield in 2 steps).

Data for **S19**: Colorless syrup;  $R_f$  0.75 (20/1  $\text{CHCl}_3/\text{MeOH}$ );  $[\alpha]_D^{23} +10.9^{\circ}$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.89 (3H, t,  $J = 7.0$  Hz), 1.24-1.34 (10H, m), 1.35 (3H, d,  $J = 6.0$  Hz), 1.58 (2H, m), 2.31 (1H, br-s), 2.67 (1H, dd,  $J = 8.5$  and 8.5 Hz), 3.16 (1H, dd,  $J = 7.5$  and 9.5 Hz), 3.34-3.50 (5H, m), 3.50-3.62 (4H, m), 3.62-3.84 (9H, m), 3.86-3.94 (3H, m), 4.19 (1H, br-d,  $J = 2.5$  Hz), 4.34 (1H, d,  $J = 8.0$  Hz), 4.36-4.38 (2H, br-s), 4.42 and 4.48 (2H, ABq,  $J = 12.5$  Hz), 4.20 and 4.47 (2H, ABq,  $J = 12.0$  Hz), 4.46 and 4.84 (2H, ABq,  $J = 11.0$  Hz), 4.57 and 4.72 (2H, ABq,  $J = 11.5$  Hz), 4.60 and 4.48 (2H, ABq,  $J = 12.0$  Hz), 4.63 and 4.90 (2H, ABq,  $J = 11.0$  Hz), 4.67 and 4.73 (2H, ABq,  $J = 12.0$  Hz), 4.86 (1H, br-s), 4.87 (1H, d,  $J = 3.5$  Hz), 4.92 (1H, br-s), 7.12-7.35 (35H, m);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  13.8, 14.0, 17.9, 18.8, 22.6, 26.1, 29.1, 29.3, 29.4, 31.7, 34.8, 56.2, 59.4, 62.4, 67.8, 68.4 $\times$ 2, 68.8, 69.1, 69.3, 69.4, 69.7, 71.1, 72.6, 72.8, 73.2, 74.0, 74.5, 74.9, 75.1, 75.3, 75.5, 78.4, 80.0, 81.5, 81.8, 89.2, 98.5, 100.1, 100.3, 105.8, 127.4 $\times$ 2, 127.6 $\times$ 3, 127.7, 127.8 $\times$ 2, 127.9, 128.0 $\times$ 2, 128.2, 128.3 $\times$ 4, 128.4, 137.5, 137.7, 137.9, 138.1 $\times$ 2, 138.2; HRMS (ESI-TOF)  $m/z$  707.8462 (707.8466 calcd for  $\text{C}_{81}\text{H}_{102}\text{NO}_{19}\text{Na}$   $[\text{M}+\text{H}+\text{Na}]^{2+}$ ).

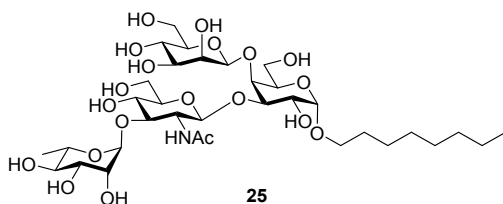
### Compound 35



To a solution of **S19** (16.1 mg, 11.6  $\mu\text{mol}$ ) in dry pyridine (480  $\mu\text{L}$ , 24 mM) were added  $\text{Ac}_2\text{O}$  (480  $\mu\text{L}$ , 5.08 mmol) and DMAP (1.4 mg, 11.6  $\mu\text{mol}$ ) at 0  $^\circ\text{C}$ . After the reaction mixture was stirred for 4 h at room temperature,  $\text{H}_2\text{O}$  (1.0 mL) was added to the reaction mixture at 0  $^\circ\text{C}$ . The resulting mixture was extracted with EtOAc (2 mL), washed with brine (2 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated in *vacuo*. Purification of the residue by column chromatography (8/1 toluene/acetone) gave **35** (17.5 mg, 10.9  $\mu\text{mol}$ , 95% yield).

Data for **35**: White foam;  $R_f$  0.55 (4/1 toluene/acetone);  $[\alpha]_D^{25} +14.0^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.88 (3H, t,  $J = 7.0$  Hz), 1.22-1.31 (13H, m), 1.52-1.58 (2H, m), 1.79 (3H, s), 1.95 (3H, s), 1.99 (3H, s), 2.12 (3H, s), 2.22 (3H, s), 3.10-3.17 (1H, m), 3.35-3.42 (2H, m), 3.48-3.57 (3H, m), 3.58-3.62 (2H, m), 3.65 (1H, br-dd,  $J = 2.0$  and 2.0 Hz), 3.67-3.75 (6H, m), 3.94 (1H, dd,  $J = 6.0$  and 6.0 Hz), 4.08 (1H, d,  $J = 3.0$  Hz), 4.13 (1H, dd,  $J = 3.0$  and 10.0 Hz), 4.27 (1H, dd,  $J = 6.0$  and 11.5 Hz), 4.36 (1H, dd,  $J = 6.0$  and 11.5 Hz), 4.38 and 4.43 (2H, ABq,  $J = 12.0$  Hz), 4.47 (2H, s), 4.50 and 4.63 (2H, ABq,  $J = 12.0$  Hz), 4.52 and 4.85 (2H, ABq,  $J = 11.0$  Hz), 4.56 and 4.77 (2H, ABq,  $J = 11.5$  Hz), 4.58 and 4.87 (2H, ABq,  $J = 11.0$  Hz), 4.59 (1H, m), 4.64 (1H, br-s), 4.64 and 4.68 (2H, ABq,  $J = 12.0$  Hz) 4.92 (1H, t,  $J = 10.0$  Hz), 4.95 (1H, d,  $J = 7.5$  Hz), 4.96 (1H, d,  $J = 4.0$  Hz), 4.98 (1H, br-d,  $J = 2.0$  Hz), 5.02 (1H, dd,  $J = 4.0$  and 10.0 Hz), 5.65 (1H, s), 6.20 (1H, d,  $J = 7.0$  Hz), 7.17-7.35 (35H, m);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  14.1, 17.9, 20.8, 21.1, 21.2, 22.6, 23.4, 26.1, 29.2, 29.3 $\times$ 2, 31.8, 58.8, 60.4, 63.7, 67.6, 68.3, 68.5, 68.9, 69.4, 69.5, 70.9, 71.0, 71.6, 72.1, 72.5, 72.9, 73.4, 73.5, 74.2, 74.9, 75.0, 75.4, 75.5, 76.2, 79.7, 80.1, 95.8, 99.0, 99.2, 100.8, 127.3, 127.4 $\times$ 2, 127.5, 127.6 $\times$ 2, 127.7 $\times$ 2, 127.8 $\times$ 2, 128.1, 128.2 $\times$ 2, 128.3 $\times$ 2, 128.4, 128.5, 137.7 $\times$ 2, 138.3, 138.4, 138.5 $\times$ 2, 138.8, 169.9, 170.4, 170.9, 171.2; HRMS (ESI-TOF)  $m/z$  820.8563 (820.8600 calcd for  $\text{C}_{91}\text{H}_{112}\text{NO}_{24}\text{K} [\text{M}+\text{H}+\text{K}]^{2+}$ ).

#### Compound 25



To a solution of **35** (17.5 mg, 10.9  $\mu\text{mol}$ ) in dry THF (1.09 mL, 10 mM) was added 100 wt% Pd/(OH) $_2$ /C (17.5 mg) under  $\text{H}_2$  atmosphere (balloon) at room temperature. After stirring for 40 min, the reaction was filtrated through celite pad, and the filtrate was concentrated in *vacuo*.

To a solution of the above residue in dry MeOH (1.09 mL, 10 mM) was added 28% NaOMe in MeOH (2.0  $\mu\text{L}$ , 10.9  $\mu\text{mol}$ ) at 0  $^\circ\text{C}$ . After the reaction mixture was stirred for 2 h at room temperature, the reaction

miture was neutralized with Dowex 50W-4X, filtered, and concentrated in *vacuo*. Purification of the residue by reverse-phase column chromatography eluted with 30% MeOH/H<sub>2</sub>O gave **25** (8.7 mg, 10.8 μmol, 99% yield in 2 steps).

Data for **25**: White solid; *R<sub>f</sub>* 0.20 (1/1 CHCl<sub>3</sub>/MeOH); [α]<sup>23</sup><sub>D</sub> +8.04° (*c* 1.0, H<sub>2</sub>O); mp 154-155 °C; <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O) δ 0.93 (3H, t, *J* = 7.0 Hz), 1.30 (3H, d, *J* = 6.5 Hz), 1.32-1.48 (10H, m), 1.69 (2H, m), 2.13 (3H, s), 3.42 (1H, m), 3.49 (1H, dd, *J* = 9.5 and 9.5 Hz), 3.52-3.63 (4H, m), 3.67 (1H, dd, *J* = 10.0 and 10.0 Hz), 3.70 (1H, dd, *J* = 3.0 and 10.0 Hz), 3.74-3.91 (8H, m), 3.97-4.01 (5H, m), 4.08 (1H, d, *J* = 3.0 Hz), 4.12 (1H, dd, *J* = 2.5 and 10.5 Hz), 4.42 (1H, br-s), 4.88 (1H, d, *J* = 9.0 Hz), 4.93 (1H, br-s), 4.97 (1H, d, *J* = 4.0 Hz), 5.02 (1H, br-s); <sup>13</sup>C NMR (125 MHz, D<sub>2</sub>O) δ 14.1, 17.1, 22.7, 22.8, 26.1, 29.1, 29.2, 29.3, 31.8, 56.5, 61.3, 61.5, 61.8, 67.7, 68.8, 69.2, 69.3, 69.5, 70.8×2, 71.2, 71.4, 72.5, 73.6, 76.6, 76.7, 78.1, 82.0, 99.3, 100.9, 102.0, 174.9; HRMS (ESI-TOF) *m/z* 826.3647 (826.3685 calcd for C<sub>34</sub>H<sub>61</sub>NO<sub>20</sub>Na [M+Na]<sup>+</sup>).

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**$^1\text{H}$  and  $^{13}\text{C}$  NMR  
spectrum charts**

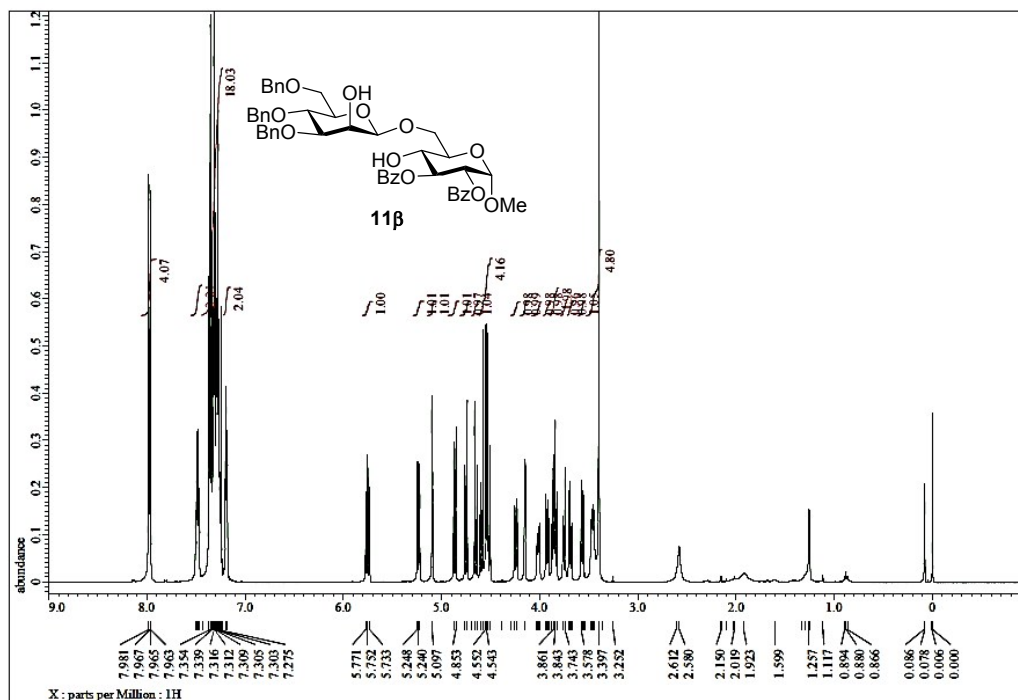


Figure S1 <sup>1</sup>H NMR spectrum of **11β**

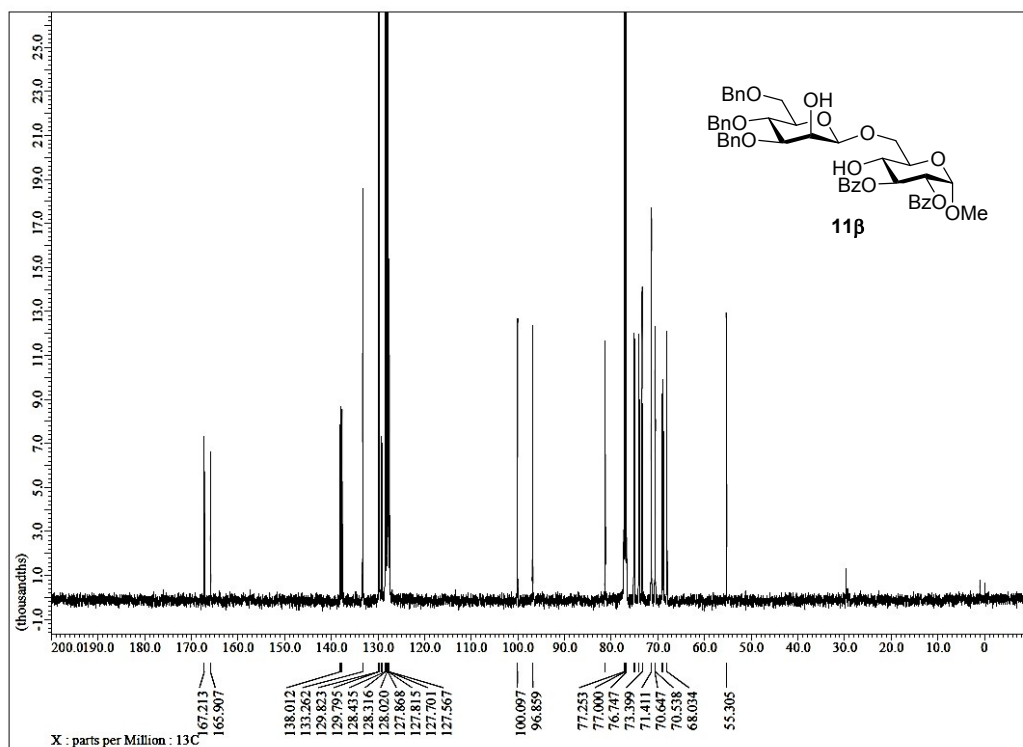


Figure S2 <sup>13</sup>C NMR spectrum of **11β**

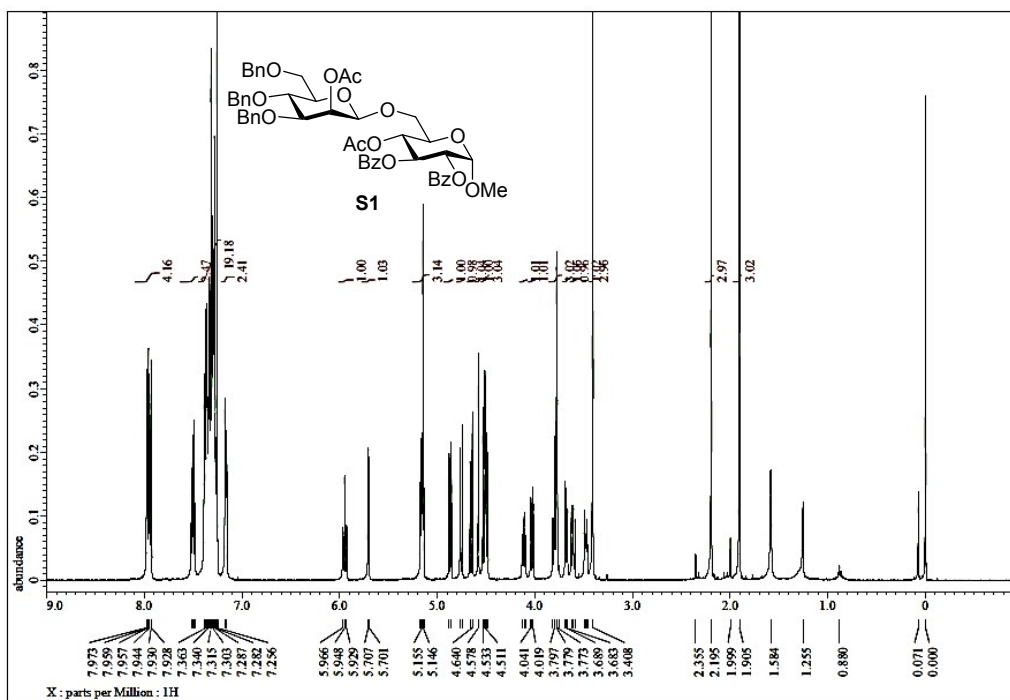


Figure S3 <sup>1</sup>H NMR spectrum of S1

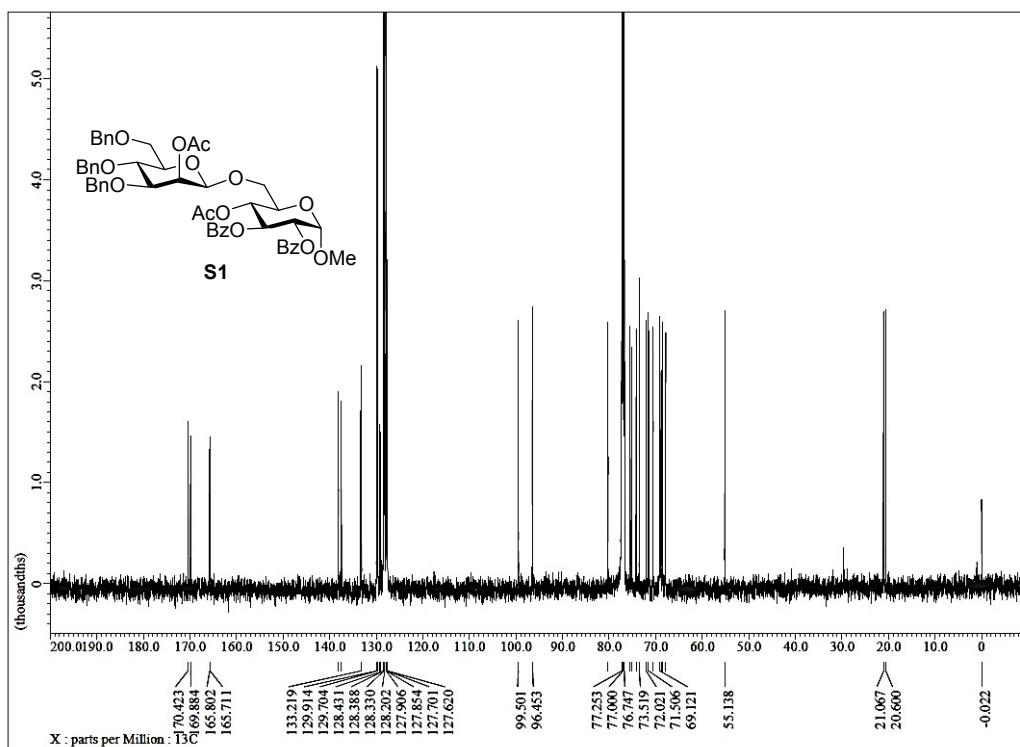


Figure S4 <sup>13</sup>C NMR spectrum of S1

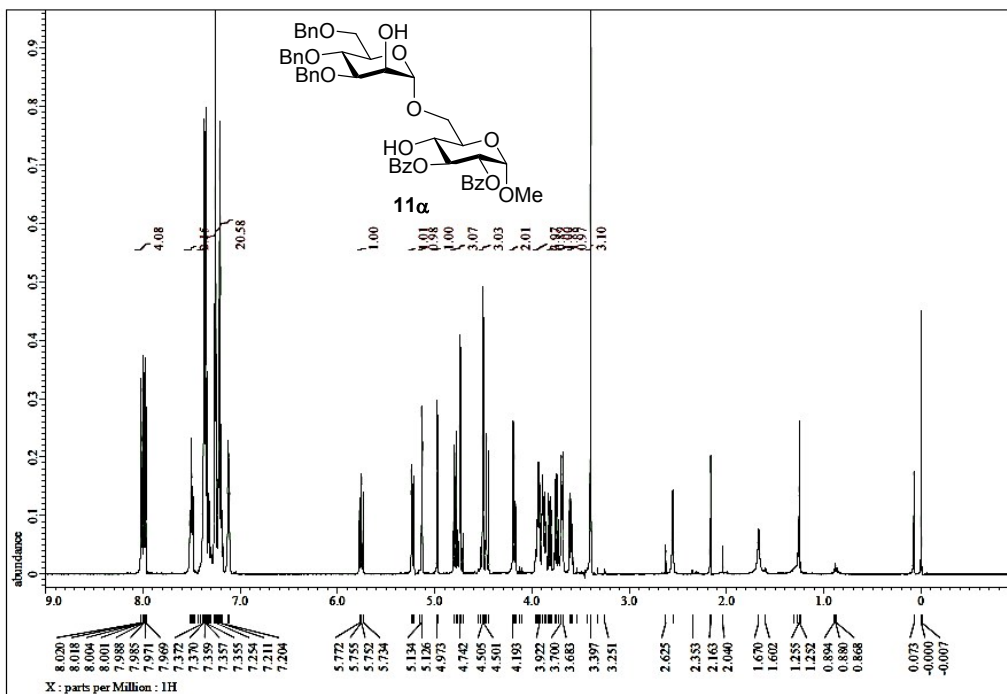


Figure S5 <sup>1</sup>H NMR spectrum of **11α**

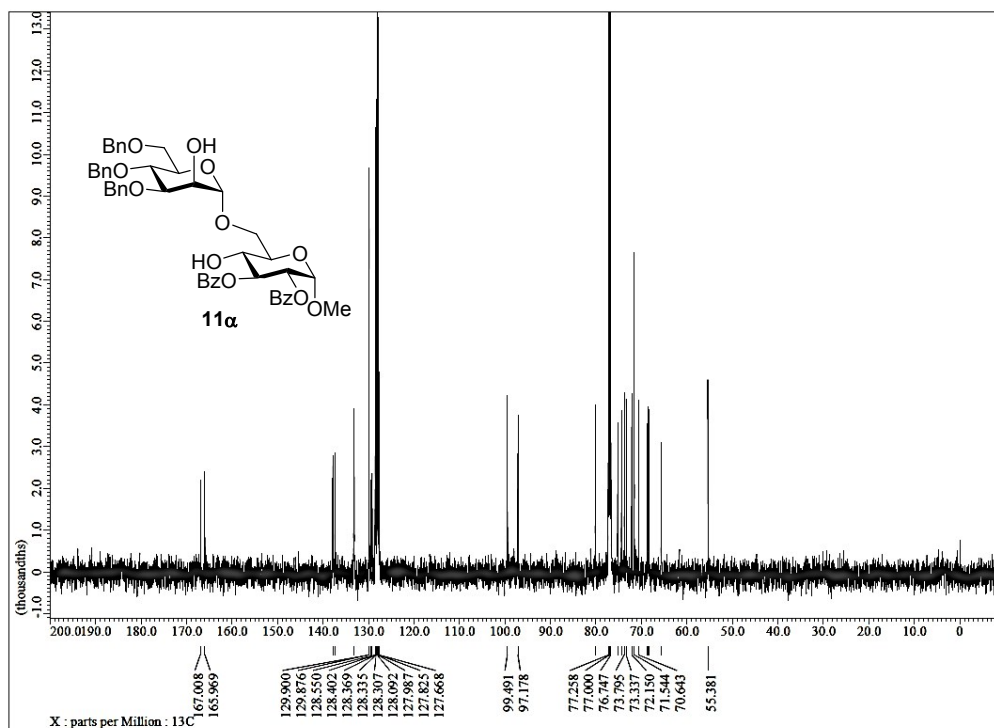


Figure S6 <sup>13</sup>C NMR spectrum of **11α**



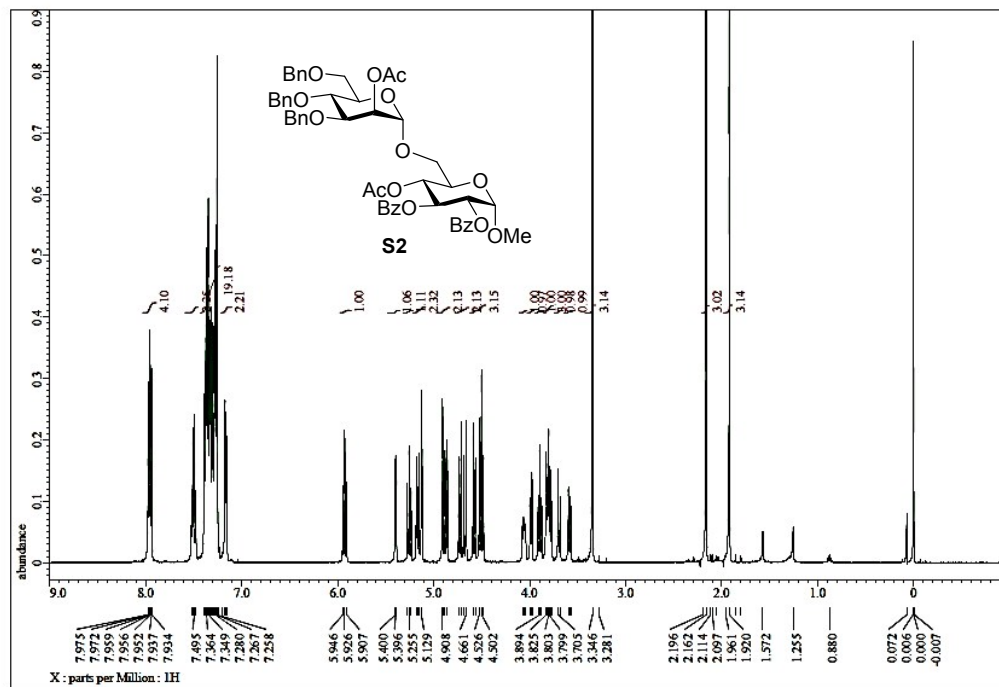


Figure S7 <sup>1</sup>H NMR spectrum of S2

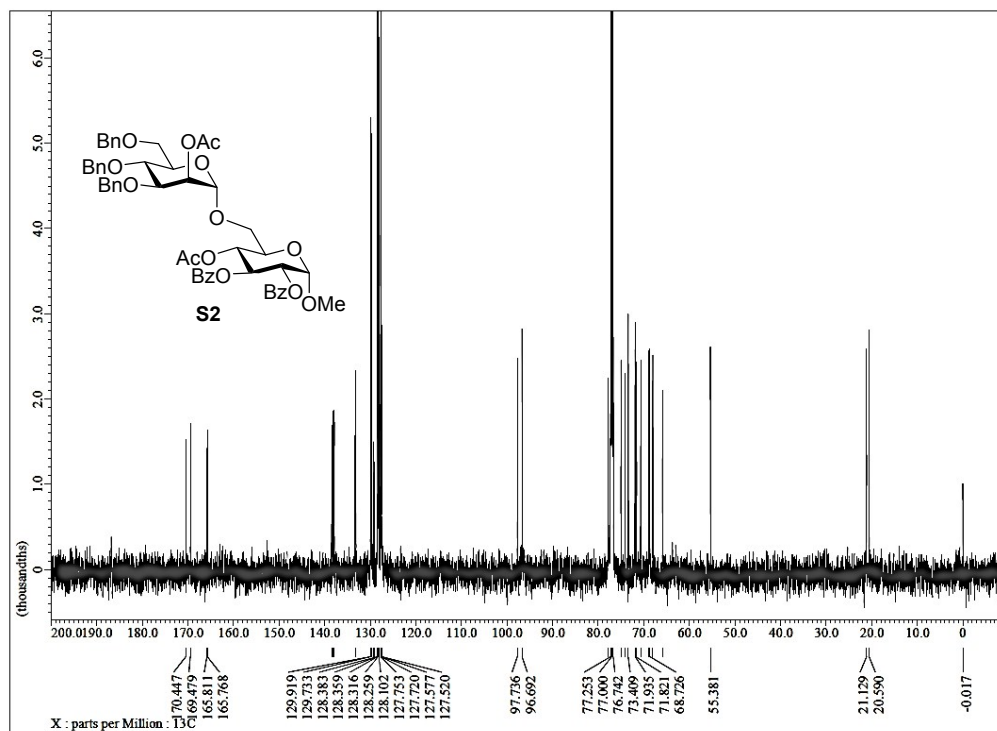


Figure S8 <sup>13</sup>C NMR spectrum of S2

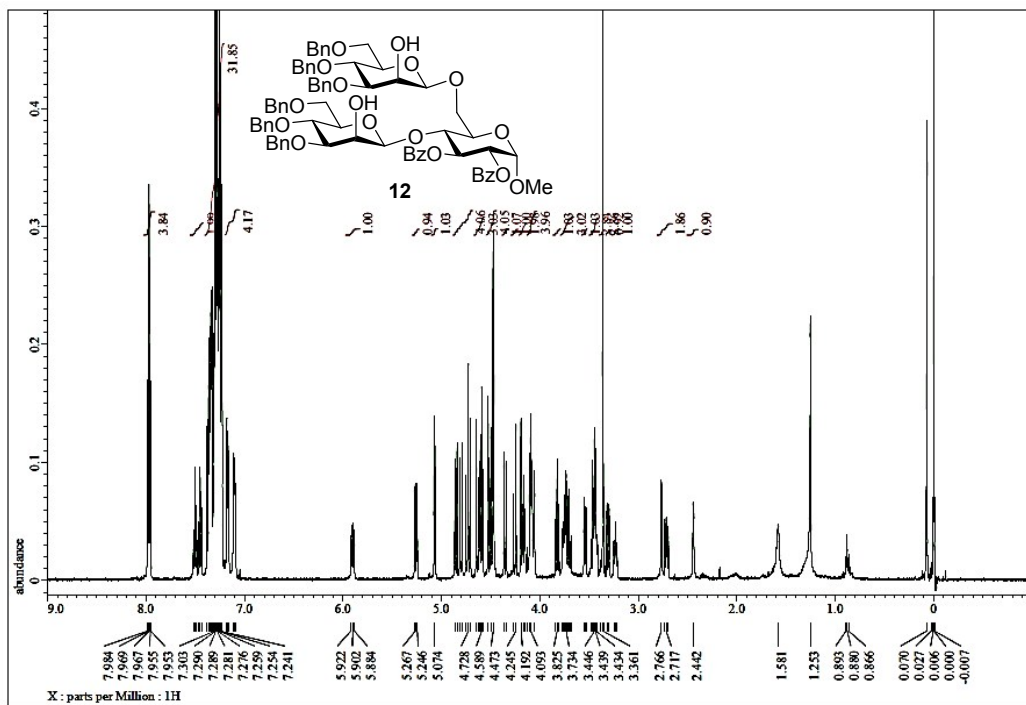


Figure S9 <sup>1</sup>H NMR spectrum of **12**

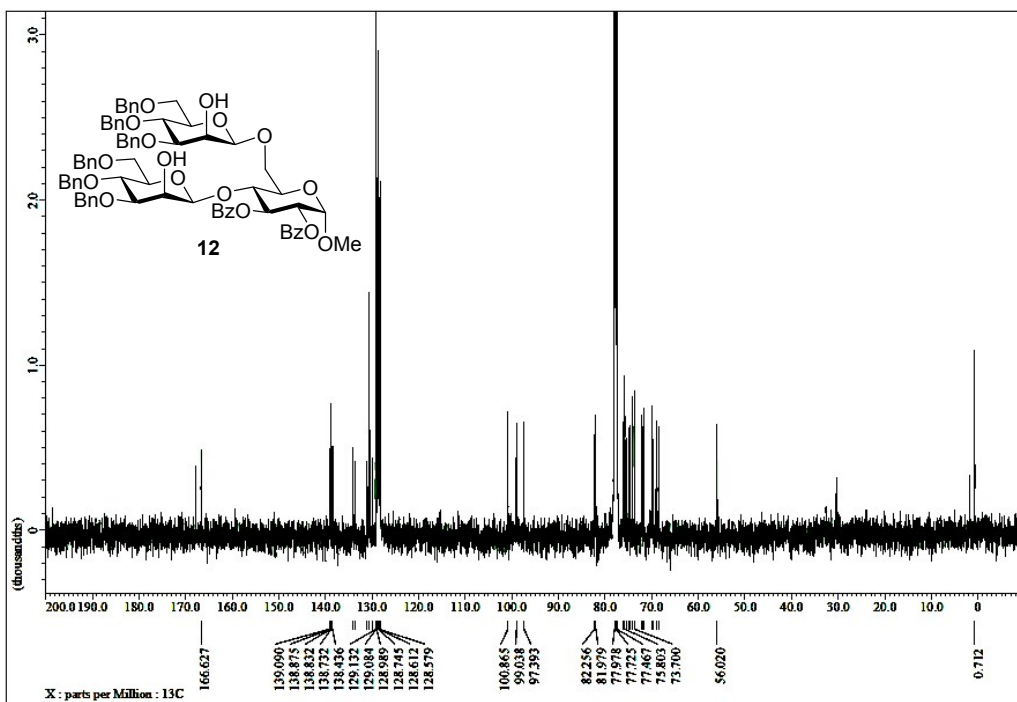


Figure S10  $^{13}\text{C}$  NMR spectrum of **12**

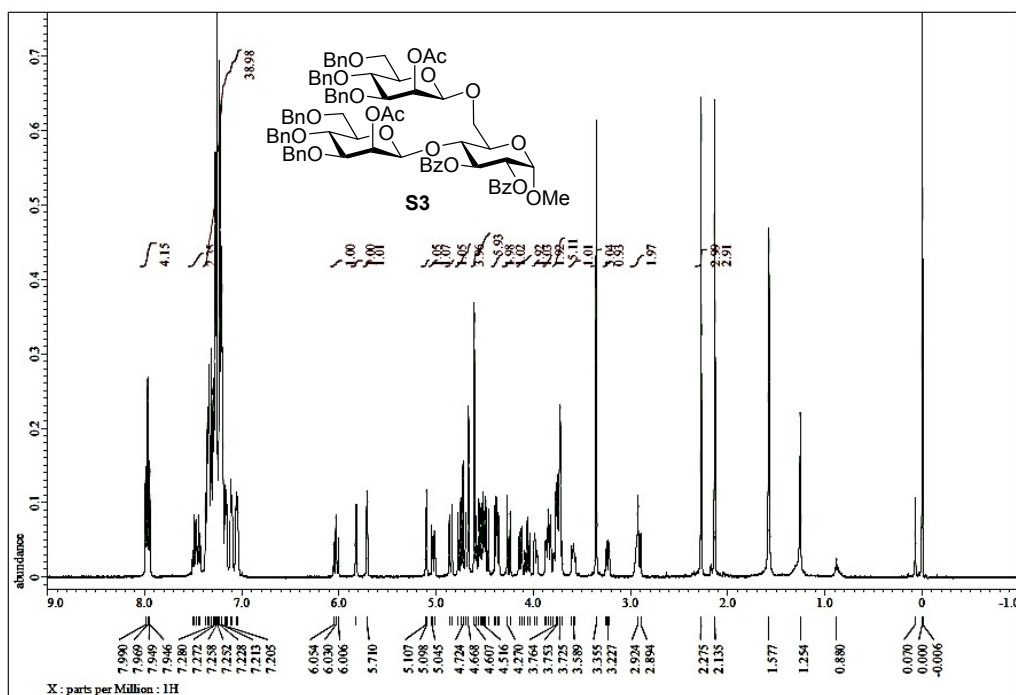


Figure S11  $^1\text{H}$  NMR spectrum of **S3**

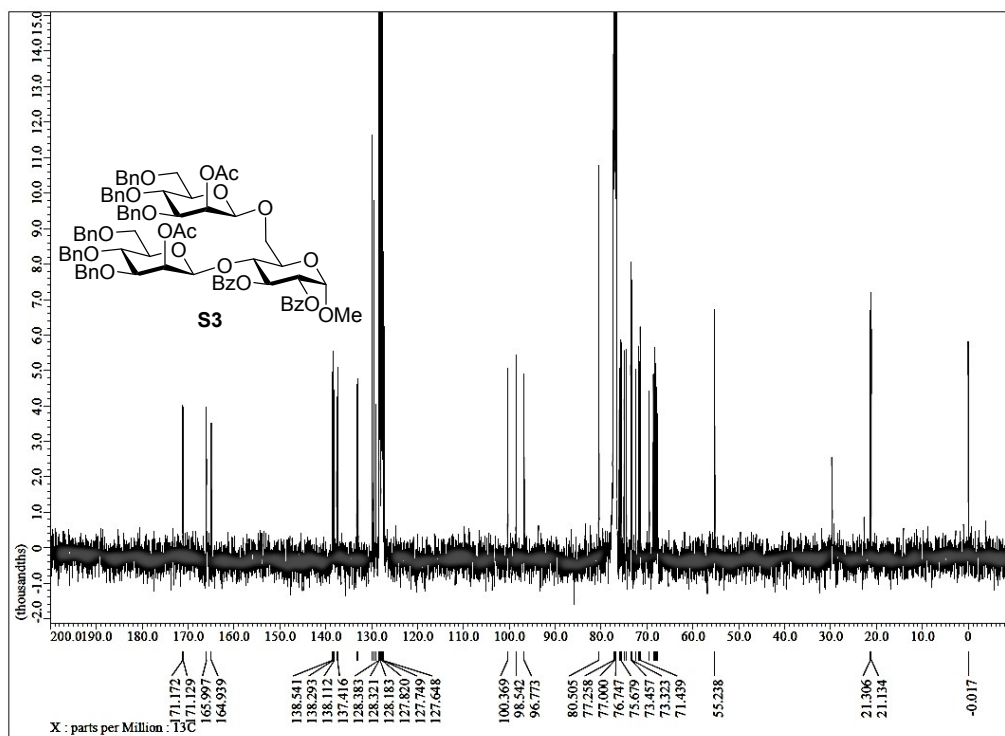


Figure S12 <sup>13</sup>C NMR spectrum of **S3**

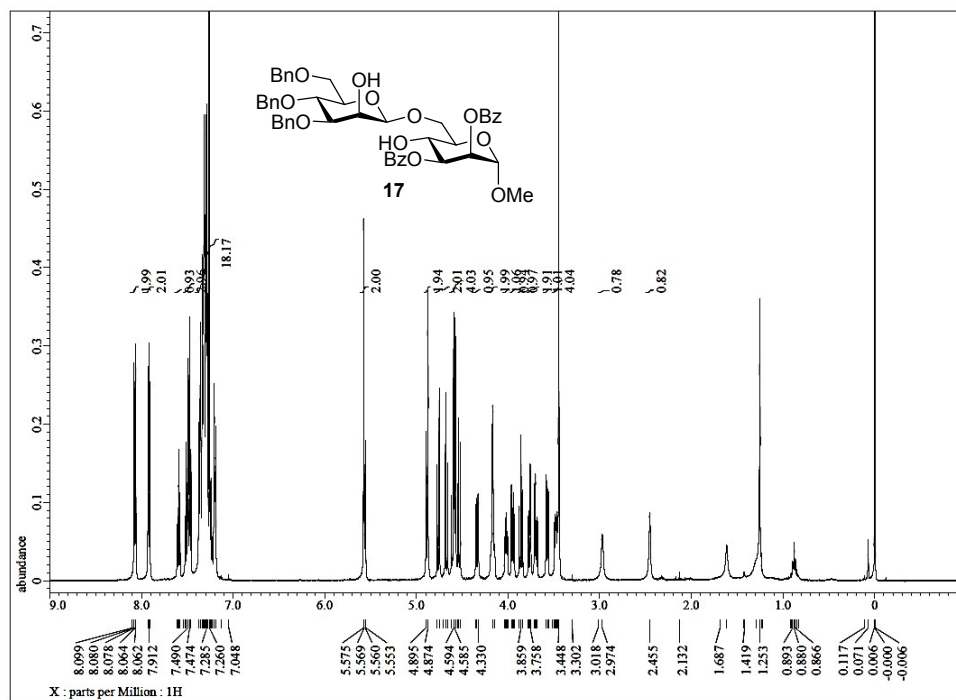


Figure S13 <sup>1</sup>H NMR spectrum of **17**

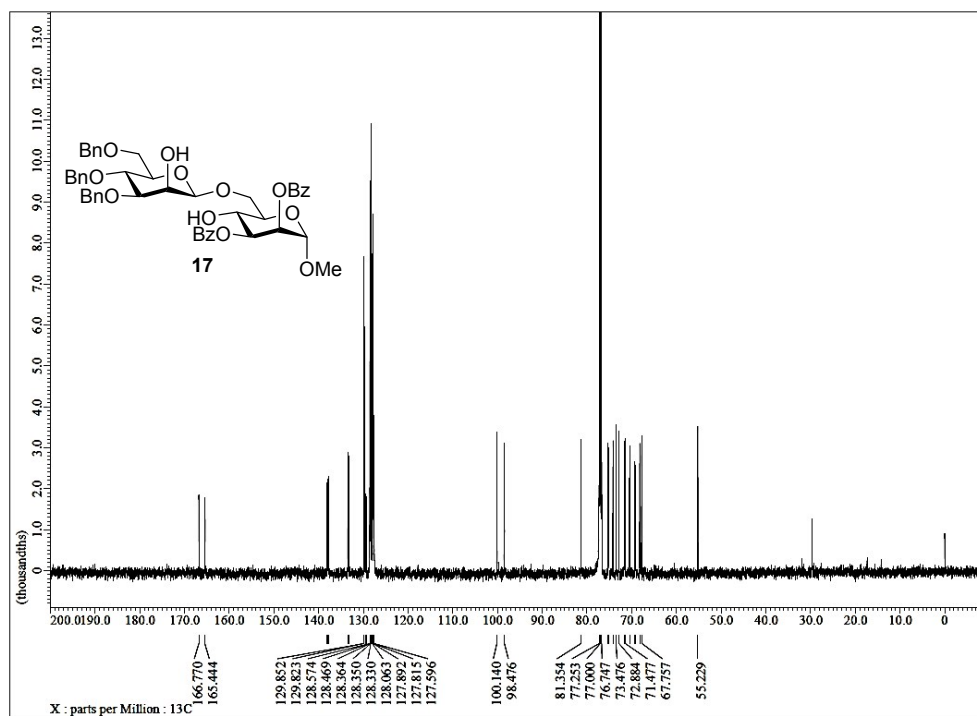


Figure S14  $^{13}\text{C}$  NMR spectrum of **17**

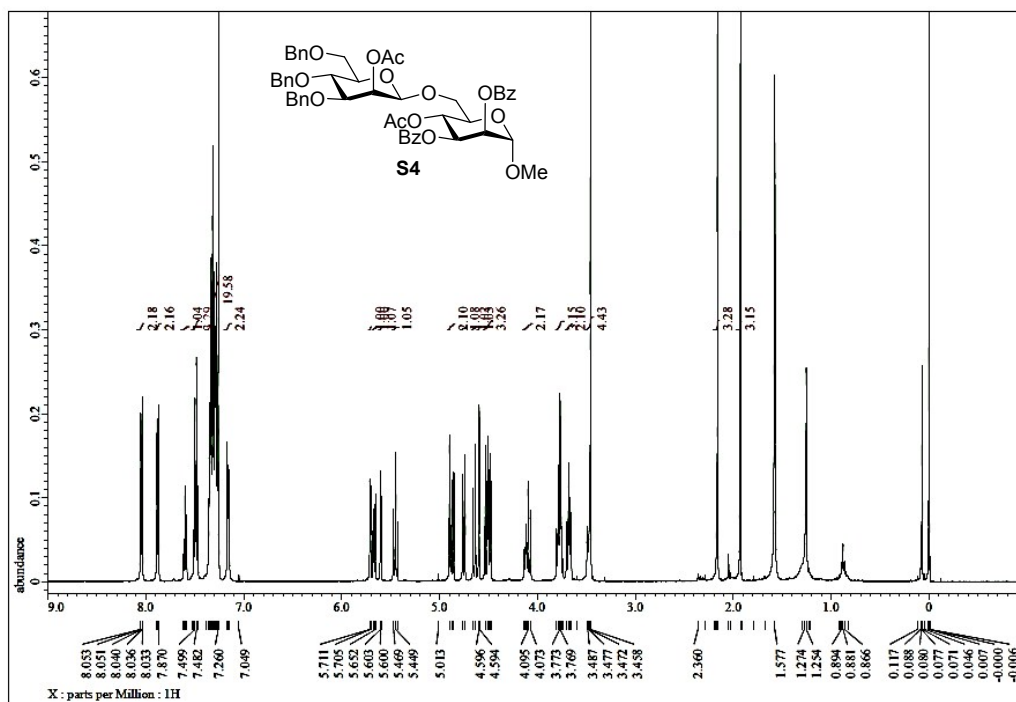


Figure S15  $^1\text{H}$  NMR spectrum of **S4**

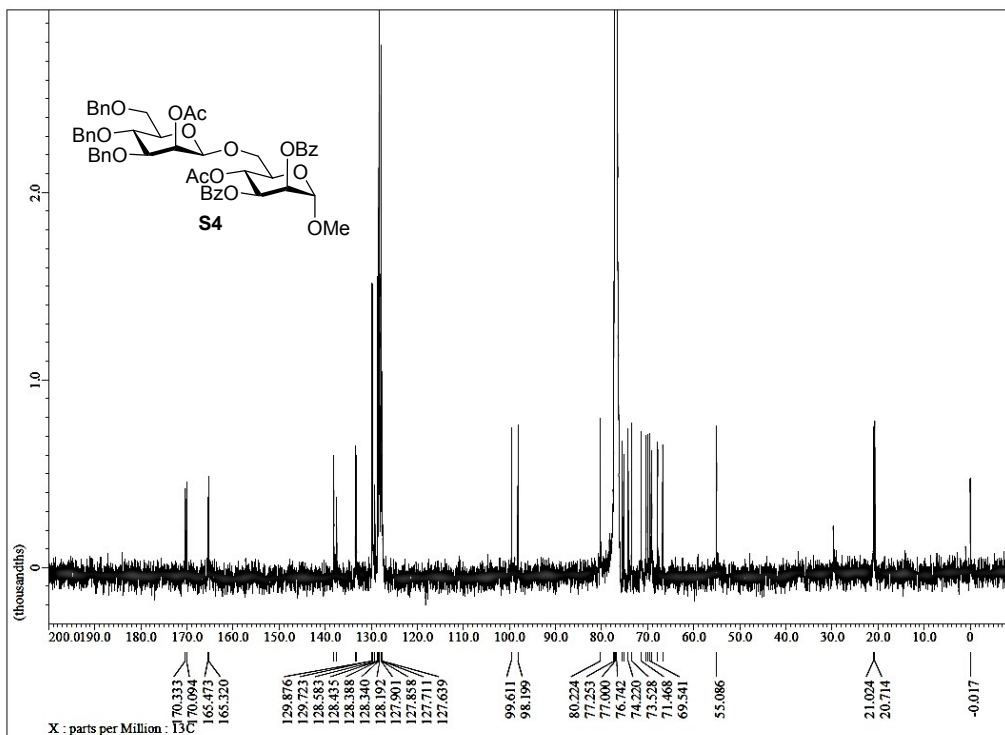


Figure S16 <sup>13</sup>C NMR spectrum of **17**

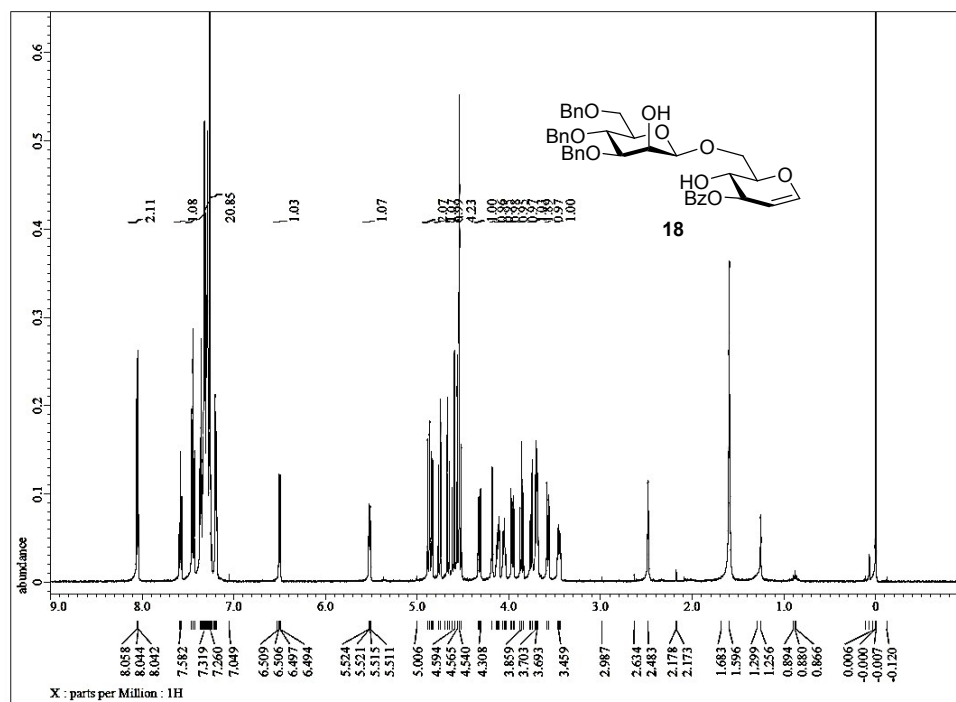


Figure S17 <sup>1</sup>H NMR spectrum of **18**

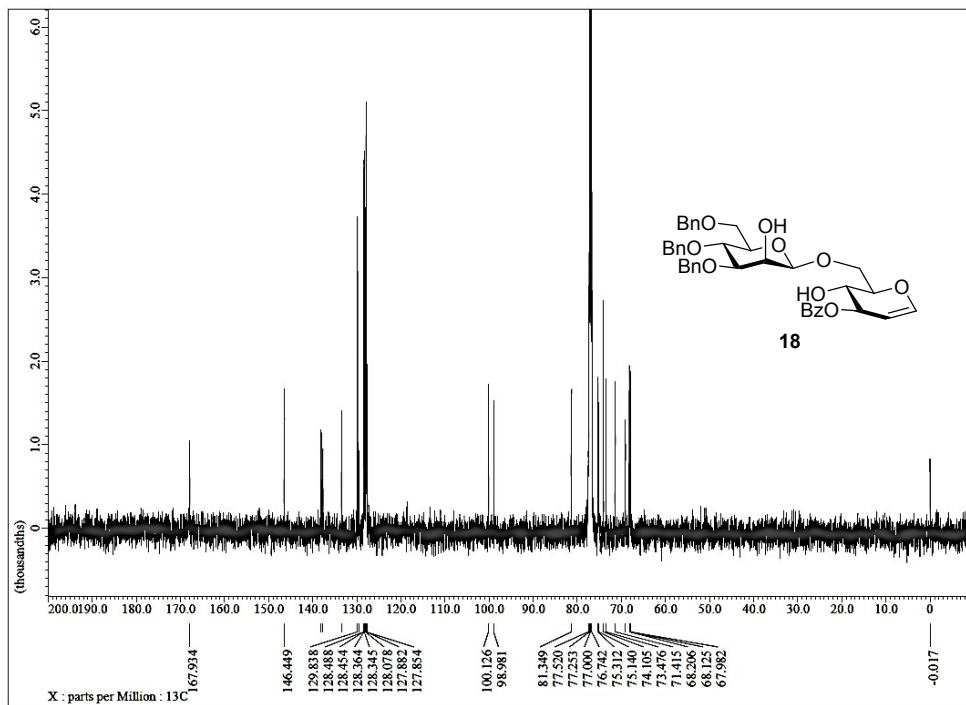


Figure S18  $^{13}\text{C}$  NMR spectrum of **18**

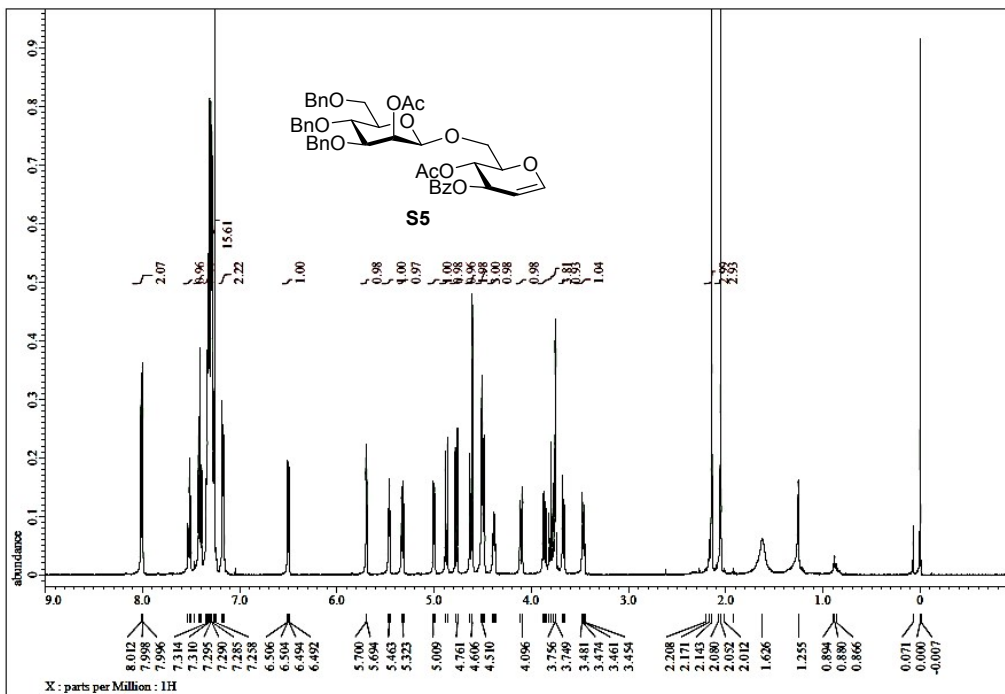


Figure S19  $^1\text{H}$  NMR spectrum of **S5**

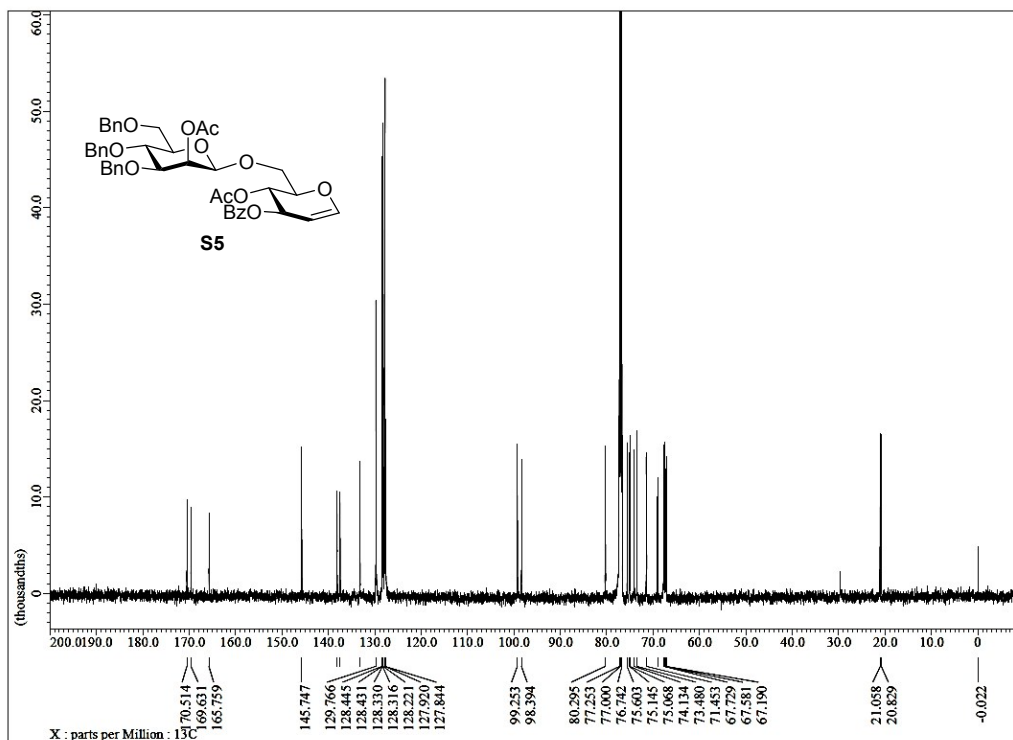


Figure S20  $^{13}\text{C}$  NMR spectrum of **S5**

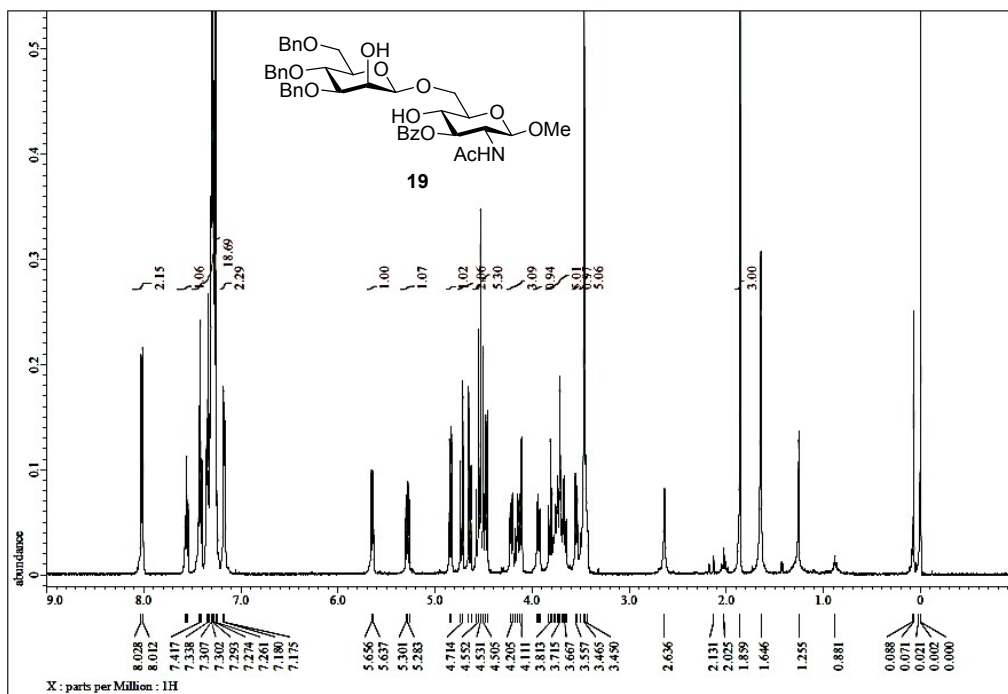


Figure S21  $^1\text{H}$  NMR spectrum of **19**



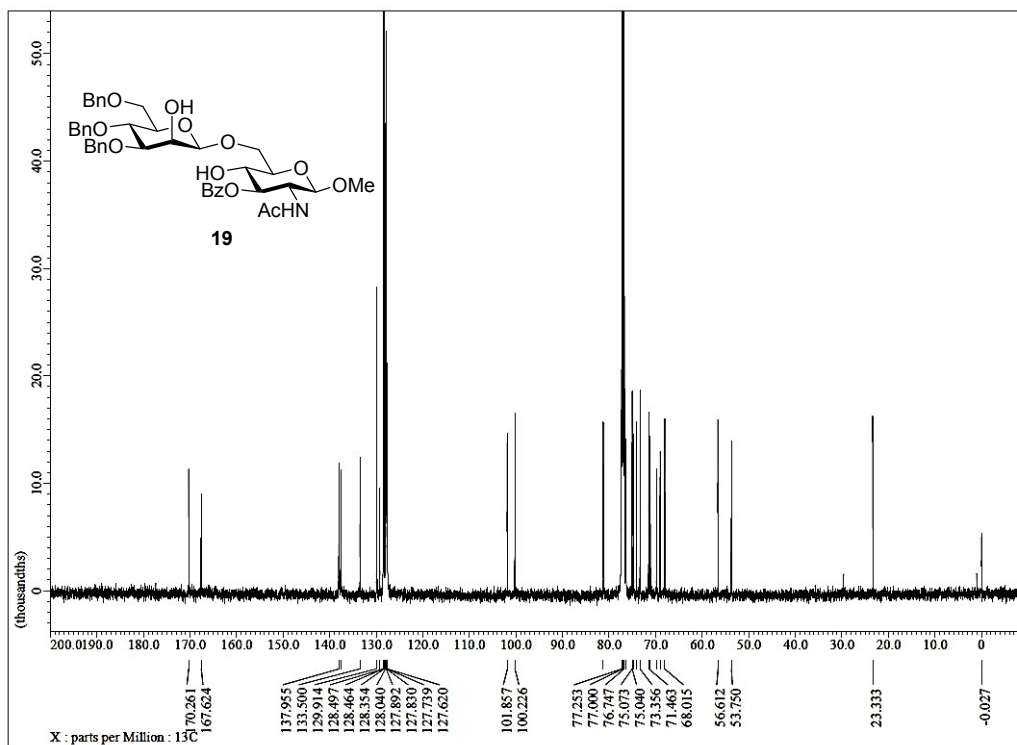


Figure S22 <sup>13</sup>C NMR spectrum of **19**

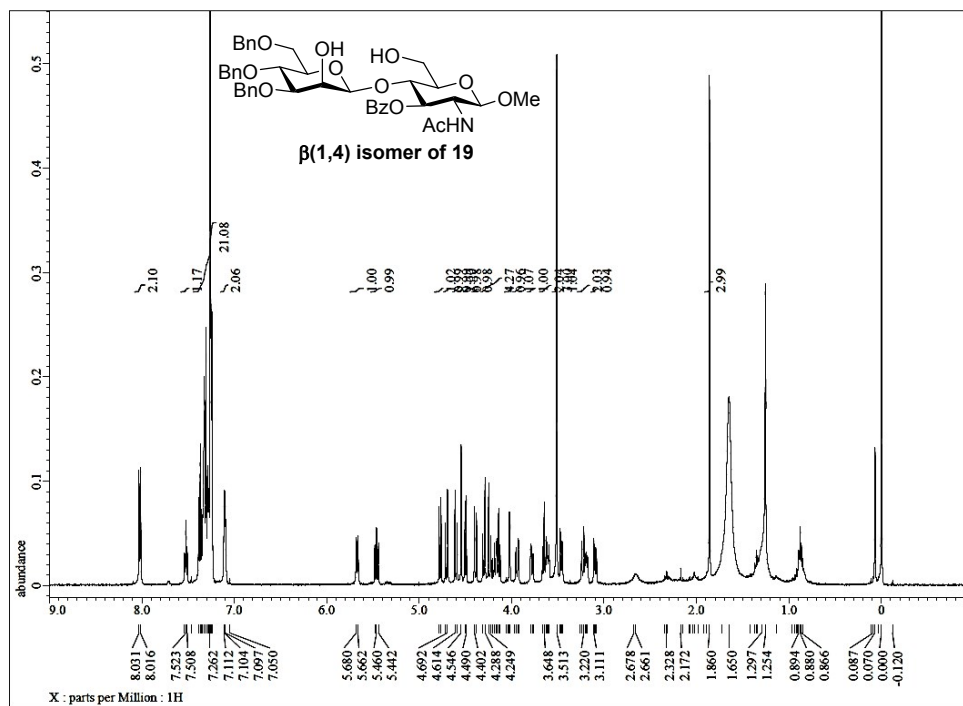


Figure S23 <sup>1</sup>H NMR spectrum of **β(1,4) isomer of 19**

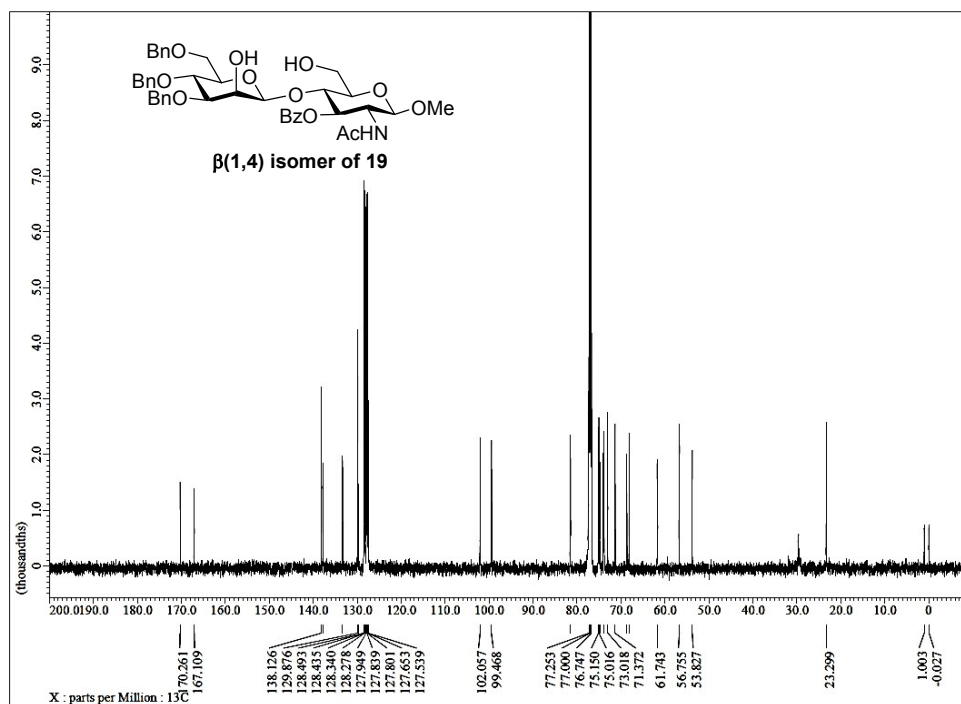


Figure S24  $^{13}\text{C}$  NMR spectrum of  $\beta(1,4)$  isomer of 19

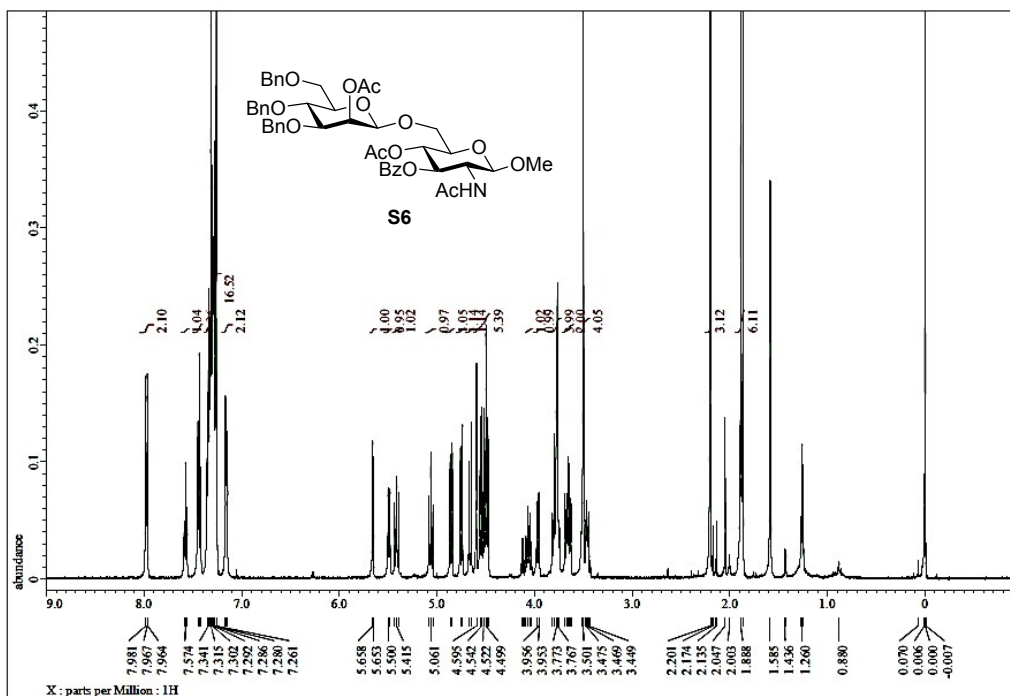


Figure S25  $^1\text{H}$  NMR spectrum of S6

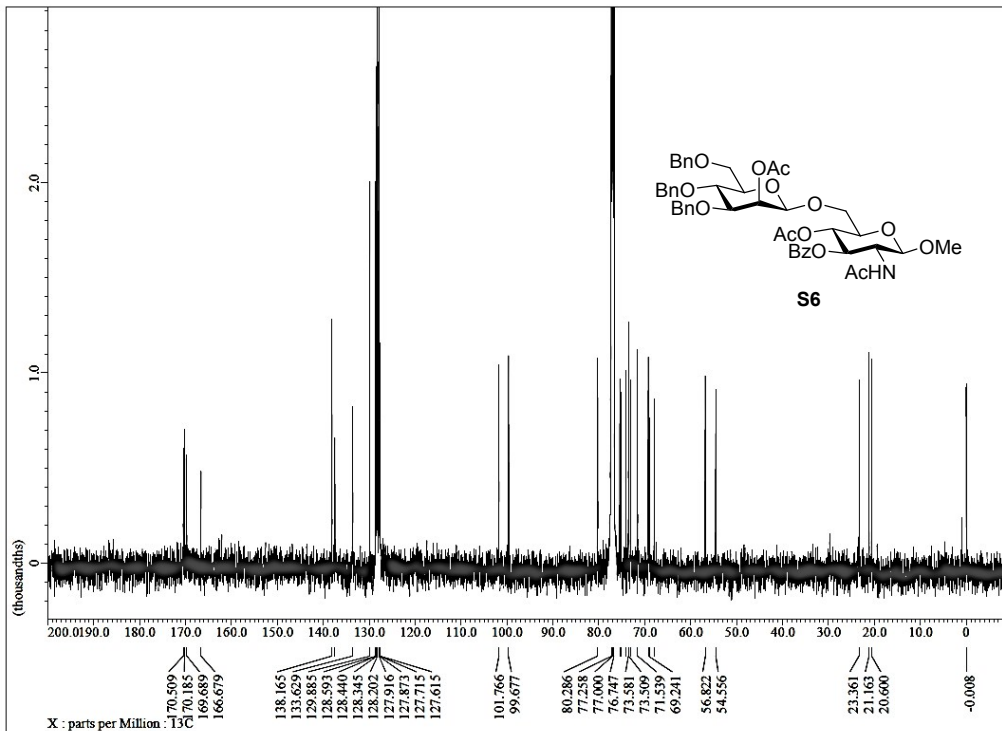


Figure S26  $^{13}\text{C}$  NMR spectrum of S6

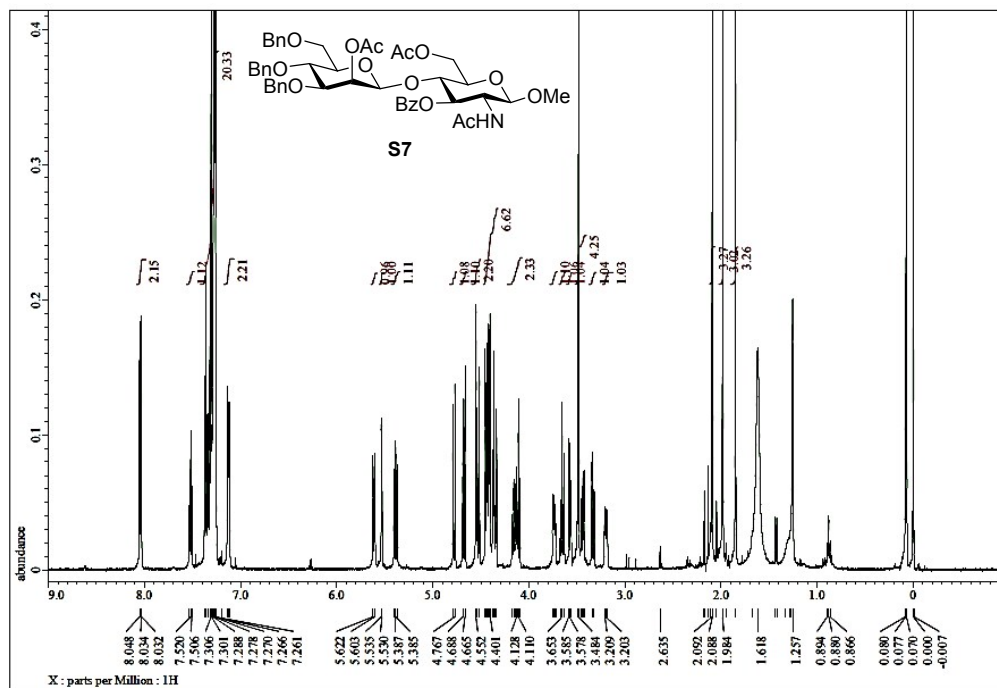


Figure S27  $^1\text{H}$  NMR spectrum of S7

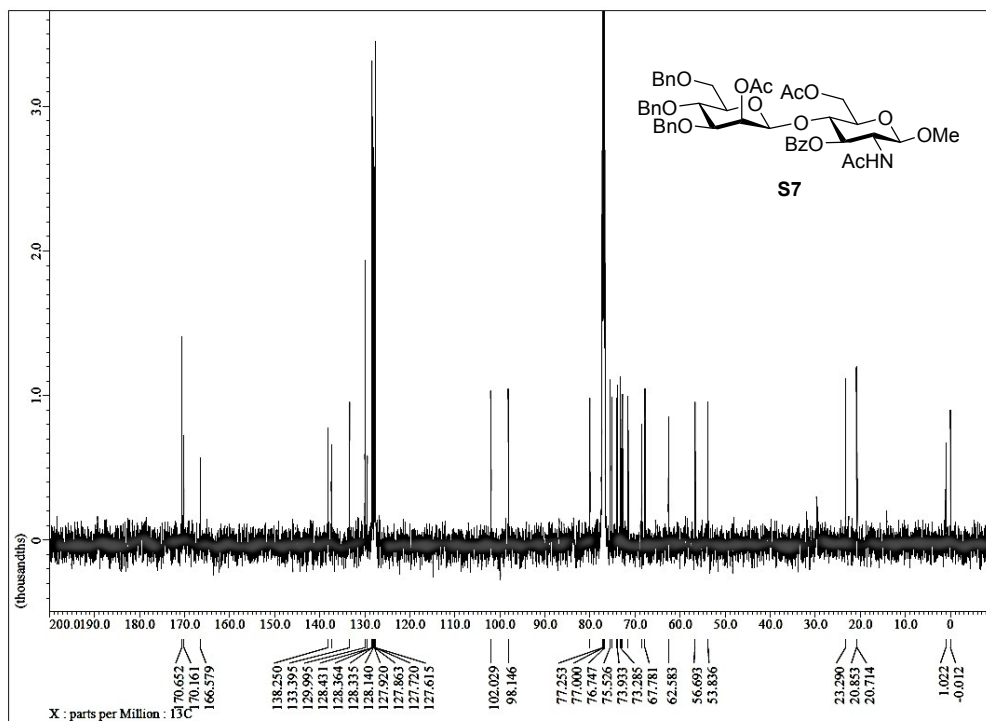


Figure S28  $^{13}\text{C}$  NMR spectrum of **S7**

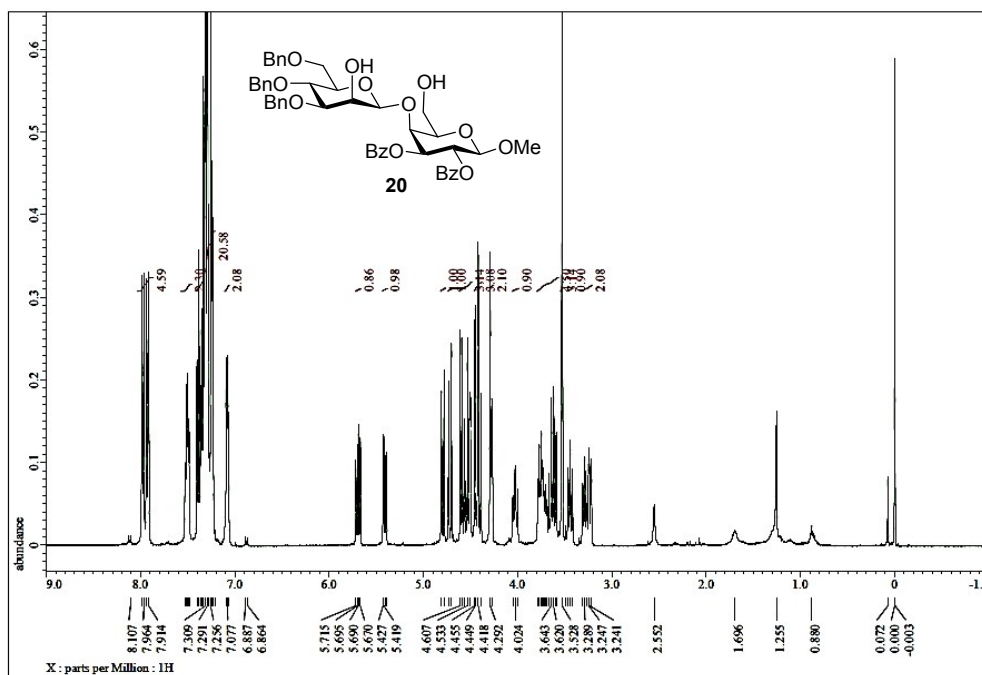


Figure S29  $^1\text{H}$  NMR spectrum of **20**

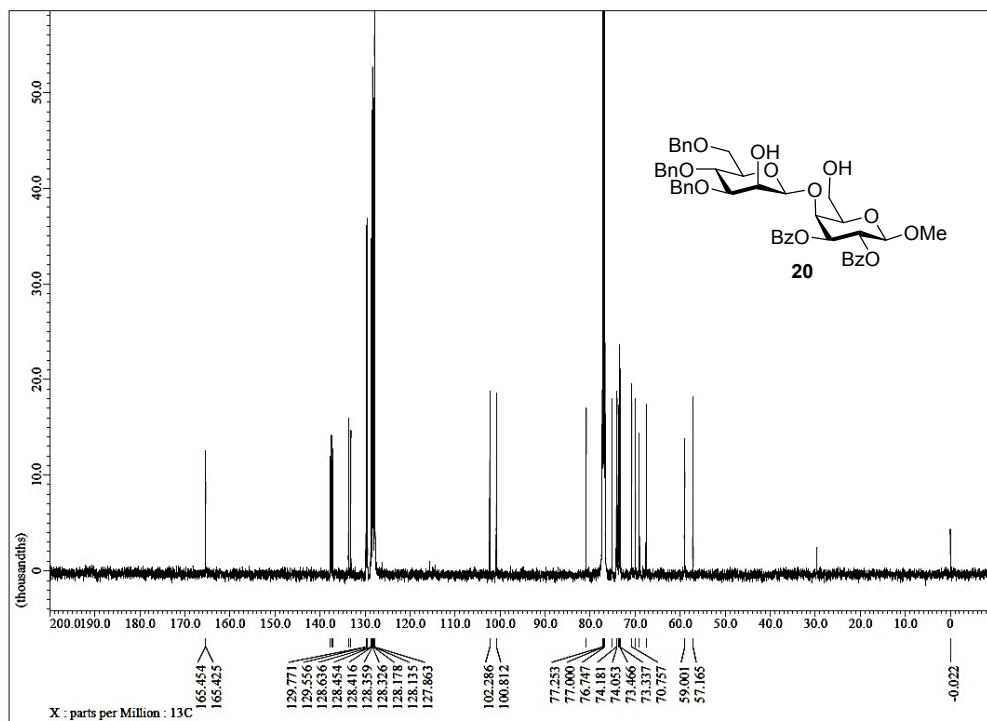


Figure S30  $^{13}\text{C}$  NMR spectrum of **20**

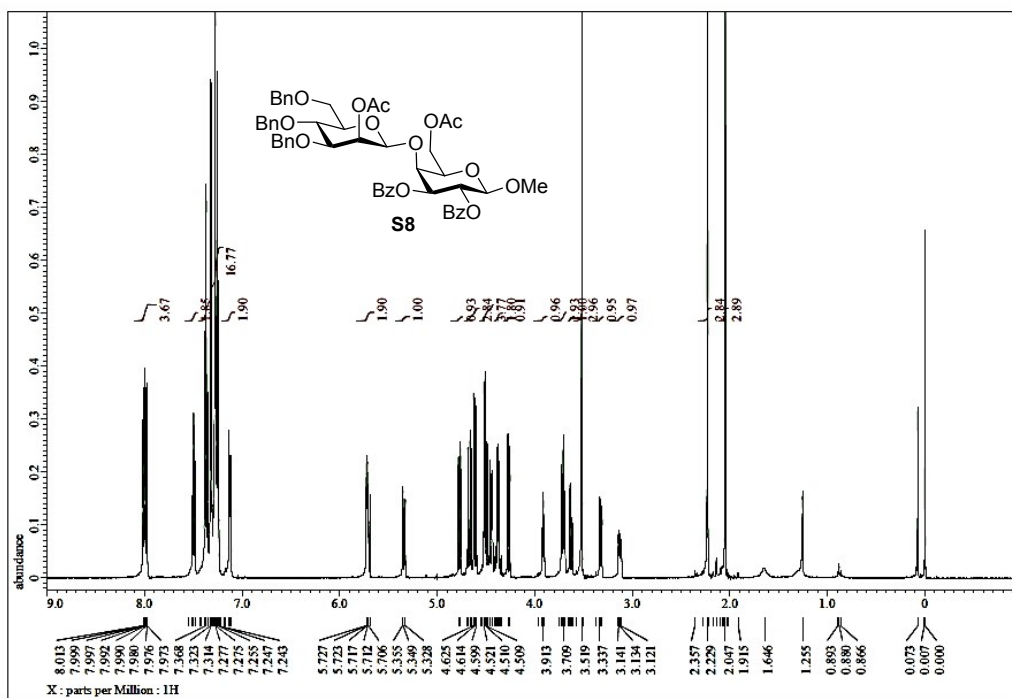


Figure S31  $^1\text{H}$  NMR spectrum of **S8**

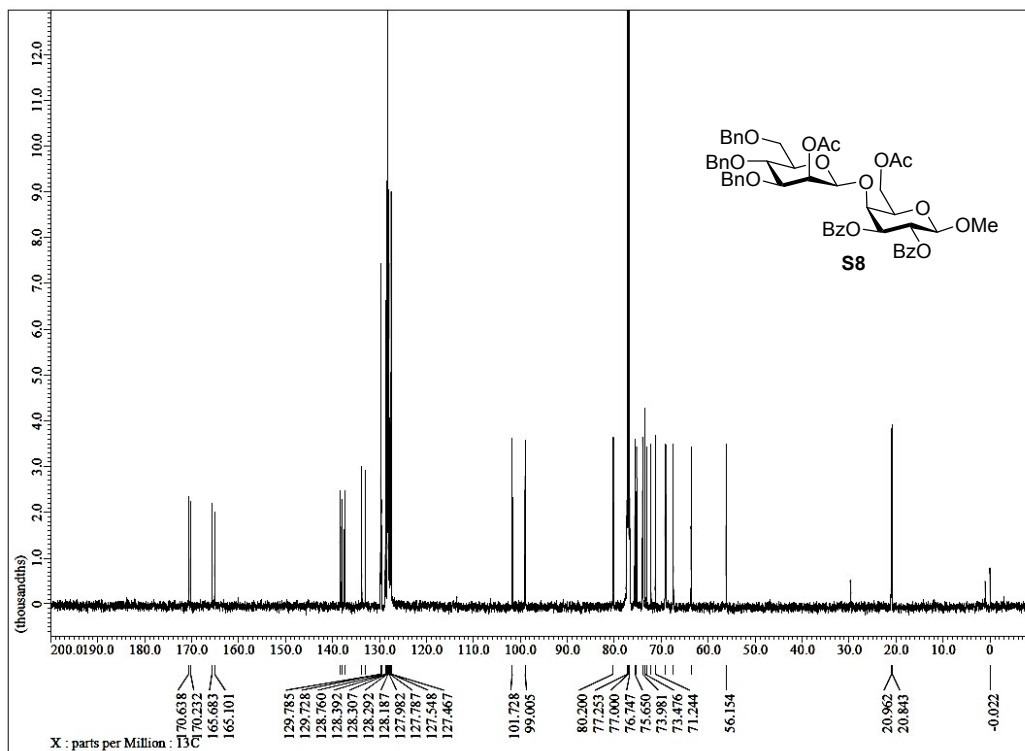


Figure S32  $^{13}\text{C}$  NMR spectrum of **S8**

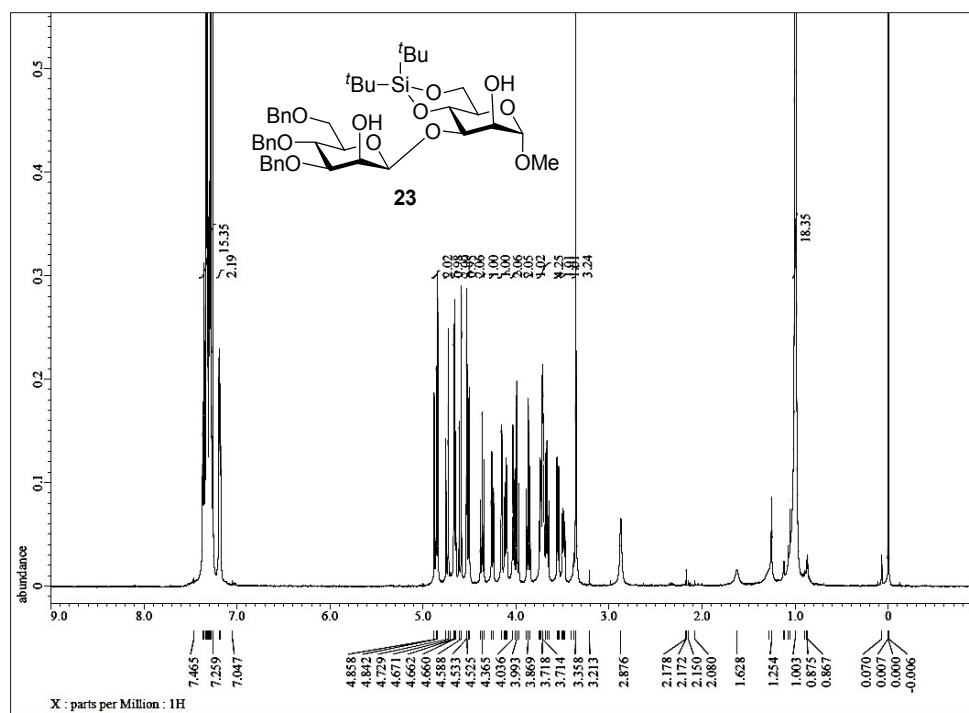


Figure S33  $^1\text{H}$  NMR spectrum of **23**

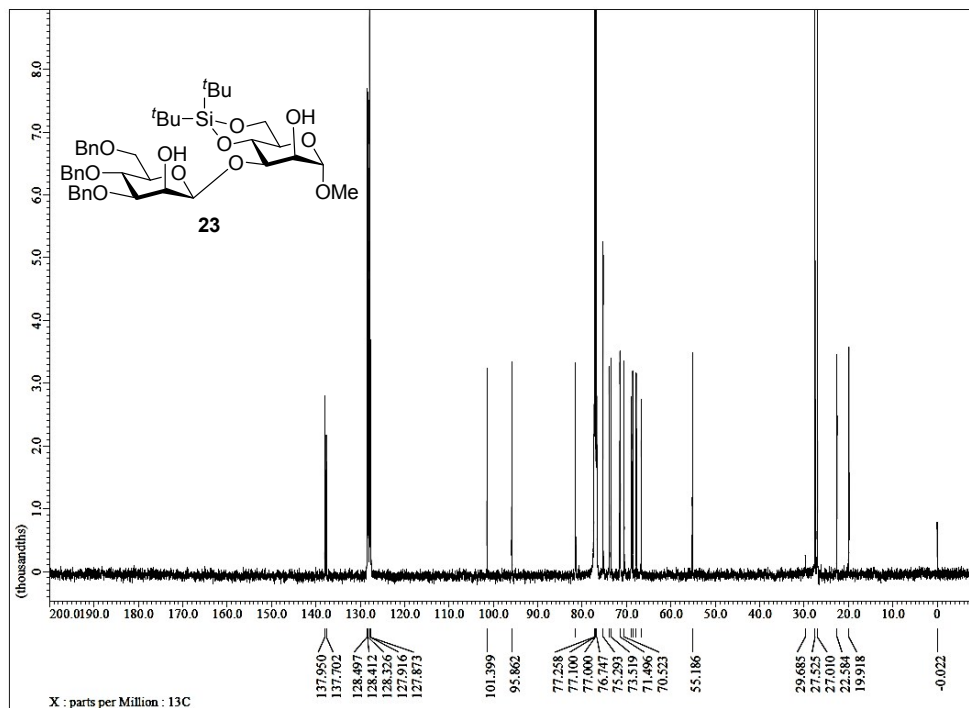


Figure S34  $^{13}\text{C}$  NMR spectrum of **23**

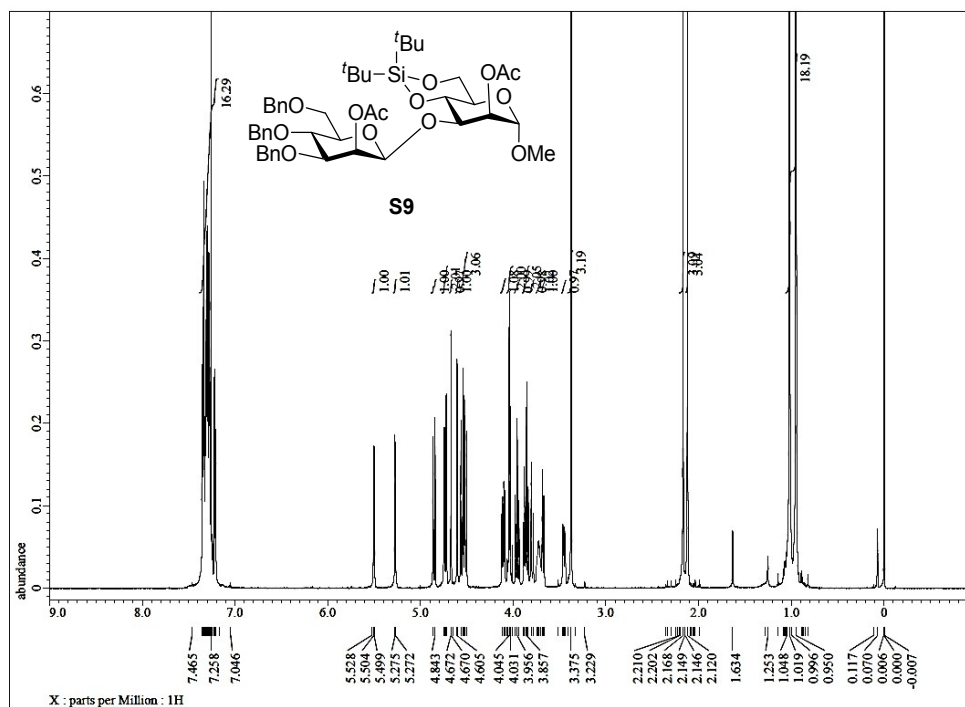


Figure S35 <sup>1</sup>H NMR spectrum of **S9**

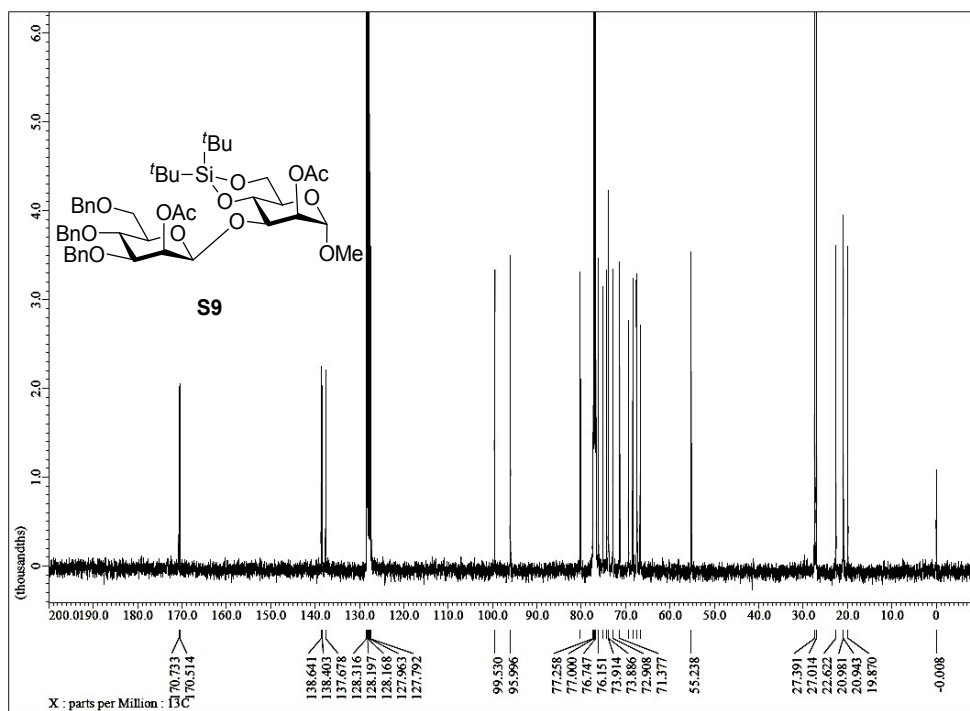


Figure S36 <sup>1</sup>H NMR spectrum of **S9**

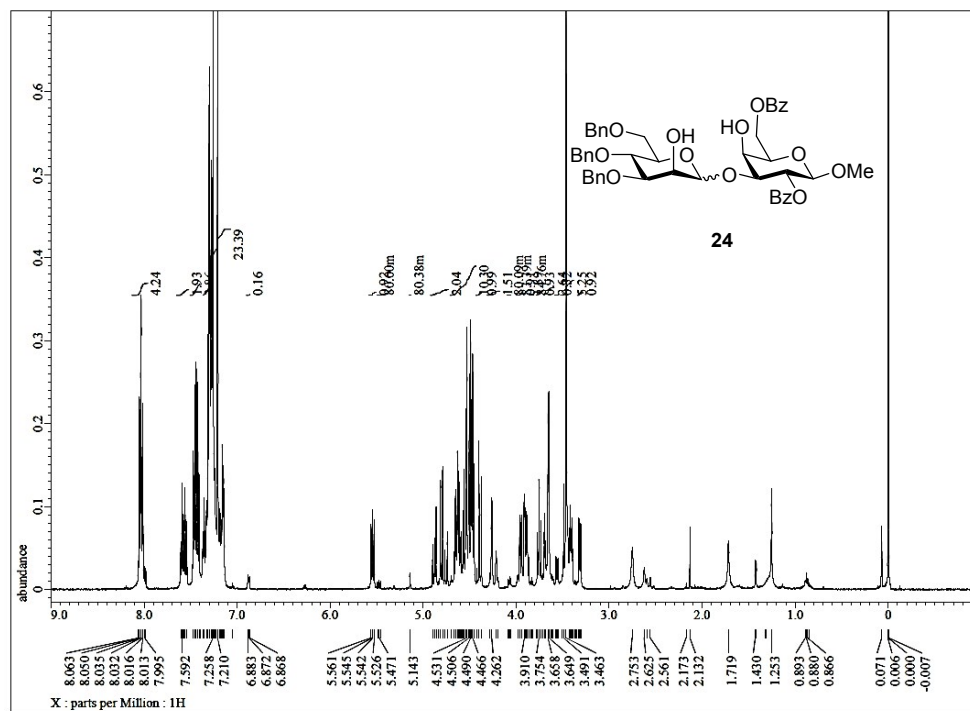




Figure S37 <sup>1</sup>H NMR spectrum of **24** ( $\beta/\alpha = 92/8$ )

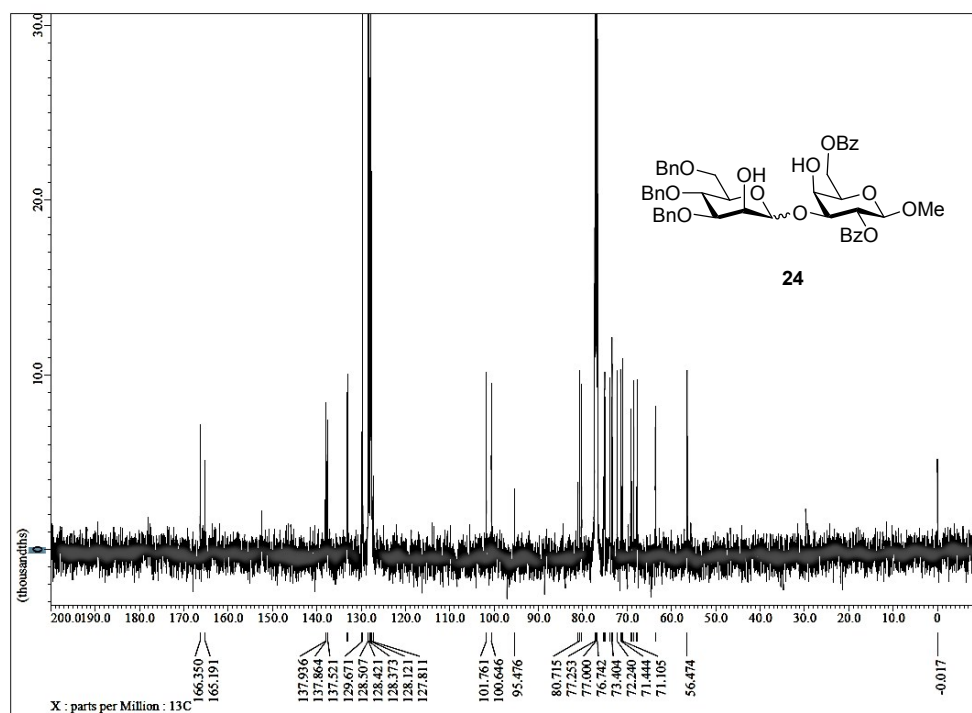


Figure S38 <sup>13</sup>C NMR spectrum of **24** ( $\beta/\alpha = 92/8$ )

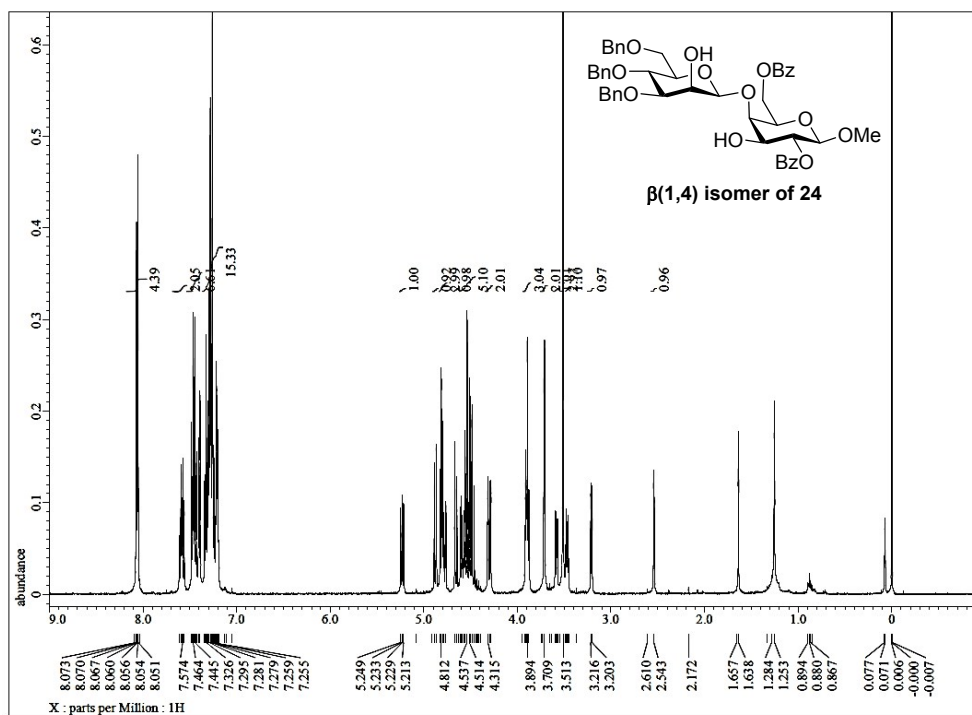


Figure S39  $^1\text{H}$  NMR spectrum of  $\beta(1,4)$  isomer of 24

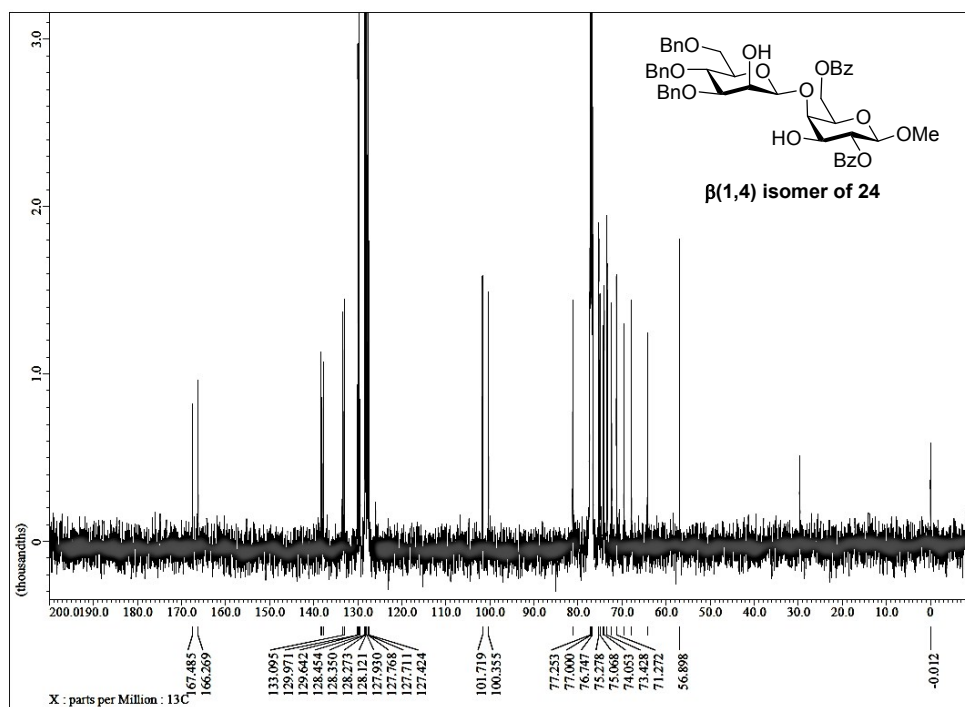


Figure S40  $^{13}\text{C}$  NMR spectrum of  $\beta(1,4)$  isomer of 24

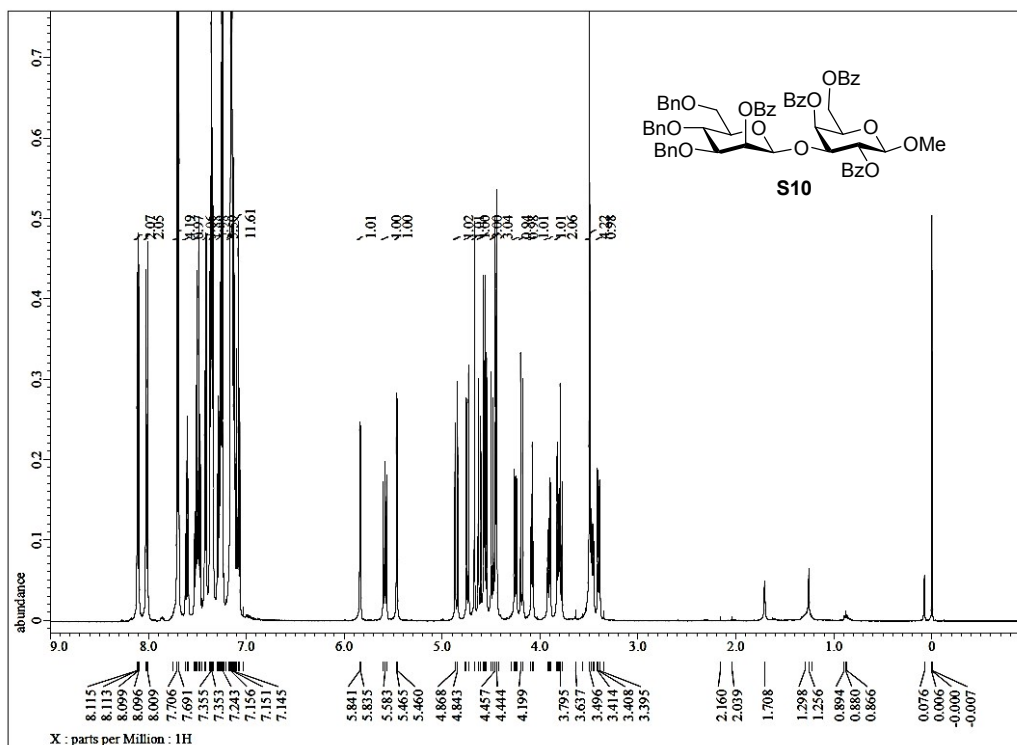


Figure S41 <sup>1</sup>H NMR spectrum of S10

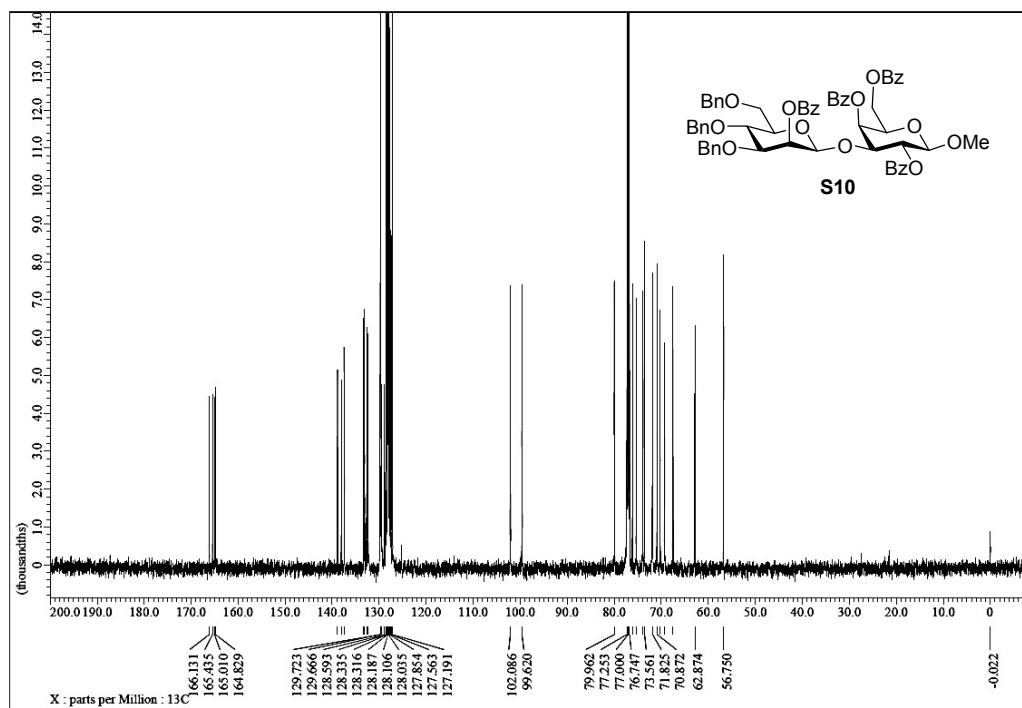


Figure S42 <sup>13</sup>C NMR spectrum of S10

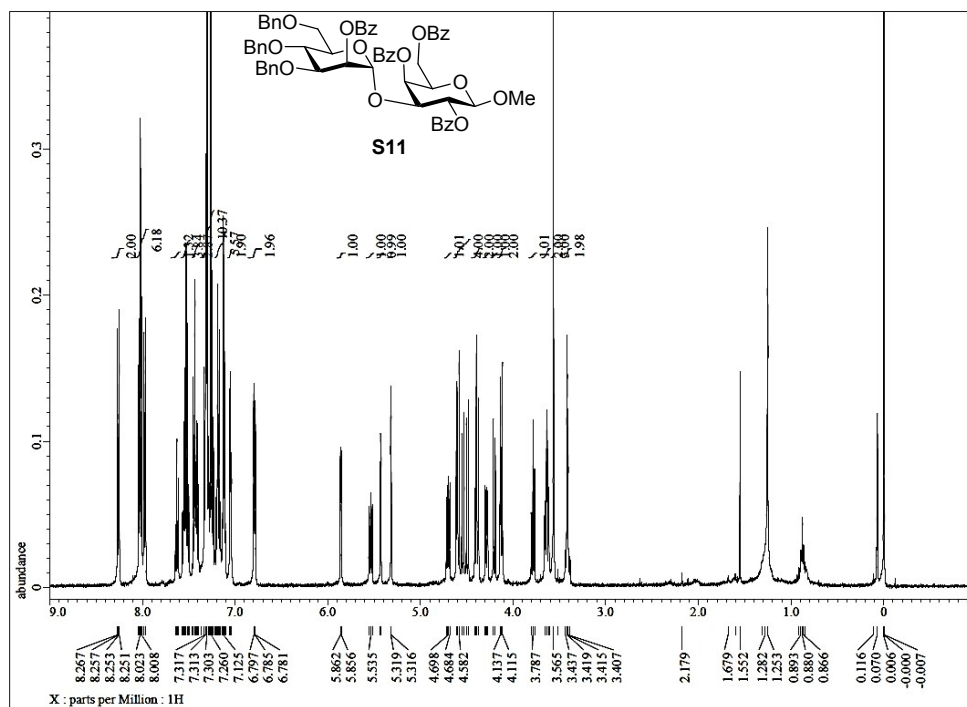


Figure S43 <sup>1</sup>H NMR spectrum of **S11**

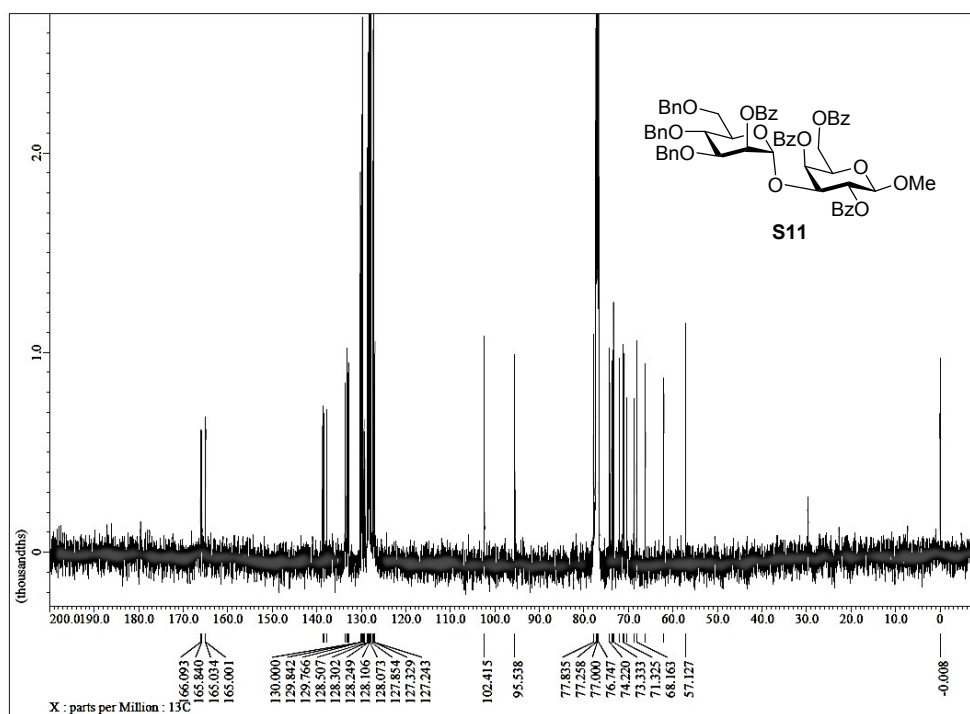


Figure S44 <sup>13</sup>C NMR spectrum of S11

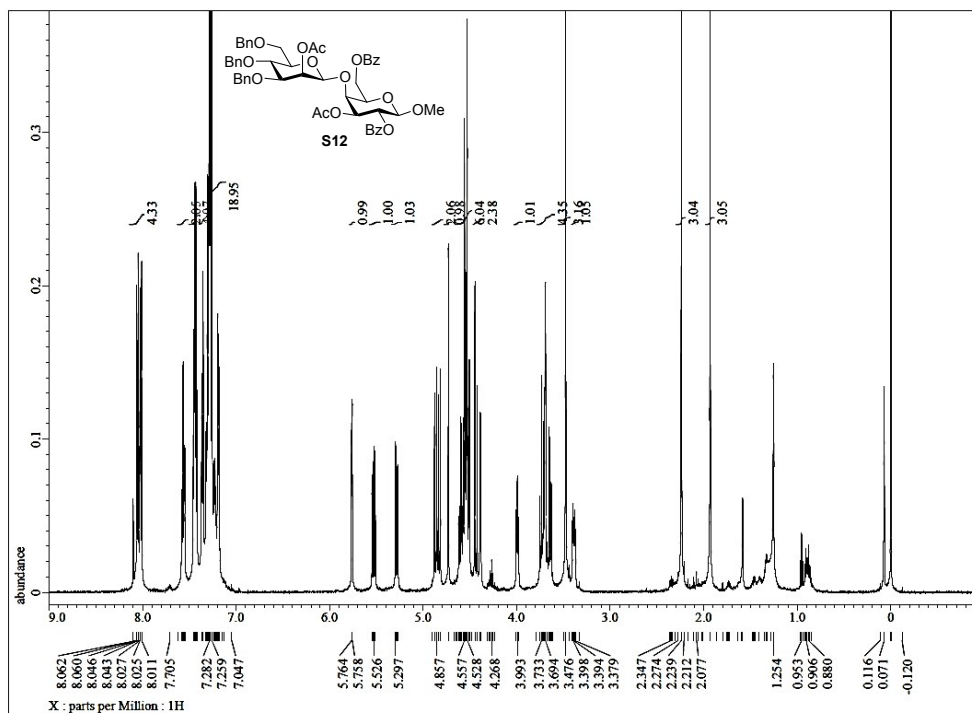


Figure S45 <sup>1</sup>H NMR spectrum of S12

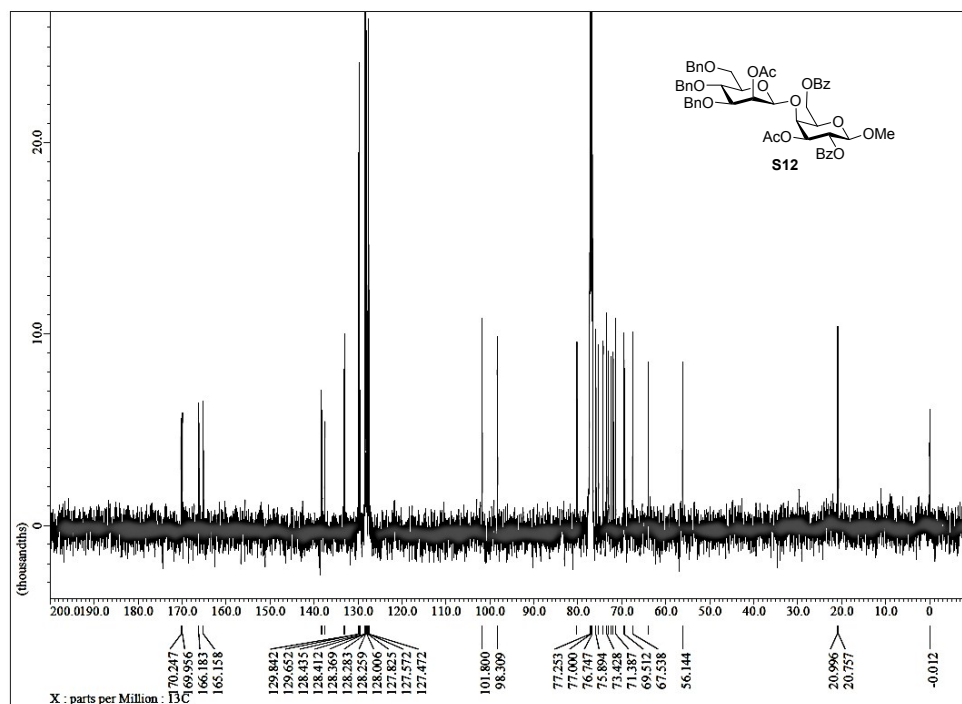


Figure S46  $^{13}\text{C}$  NMR spectrum of S12

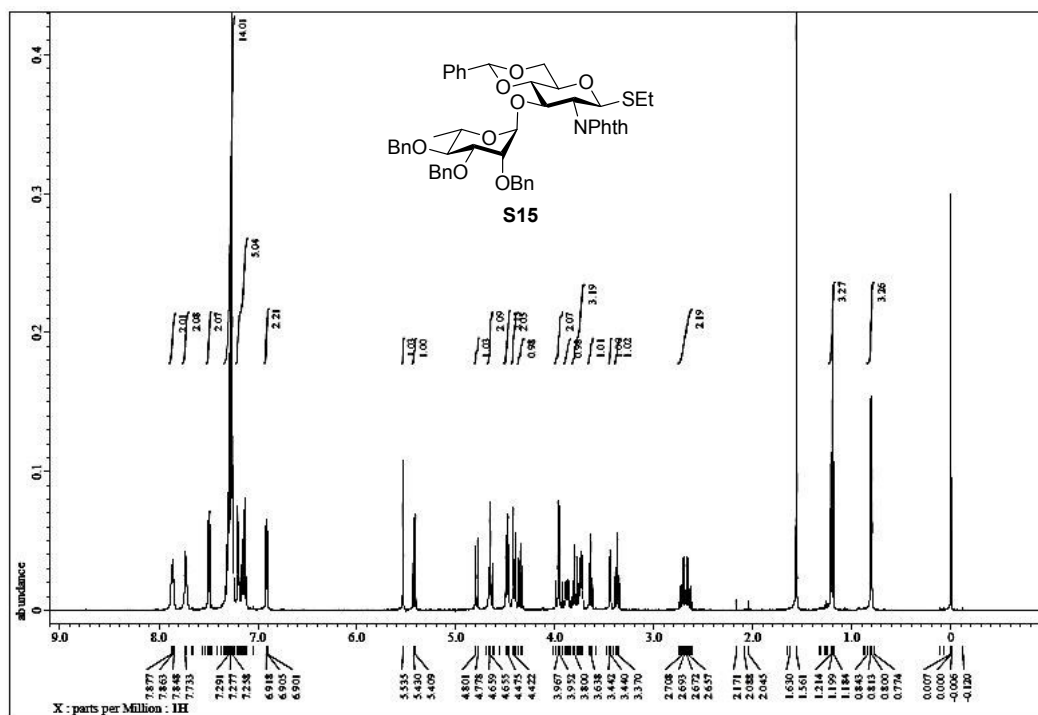


Figure S47  $^1\text{H}$  NMR spectrum of S15

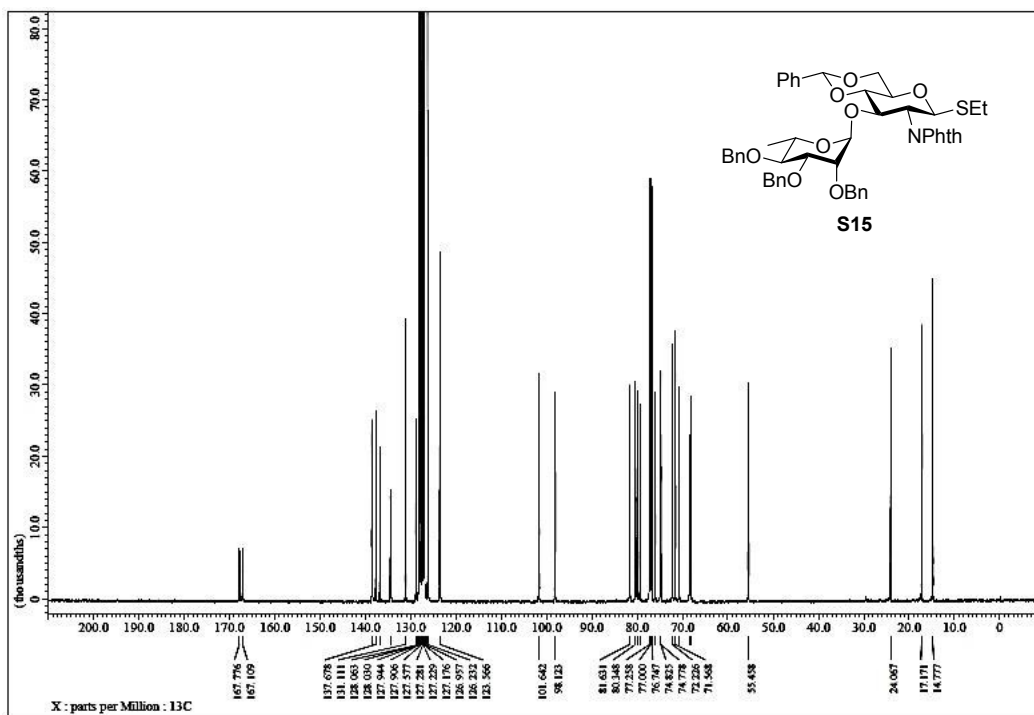


Figure S48  $^{13}\text{C}$  NMR spectrum of S15

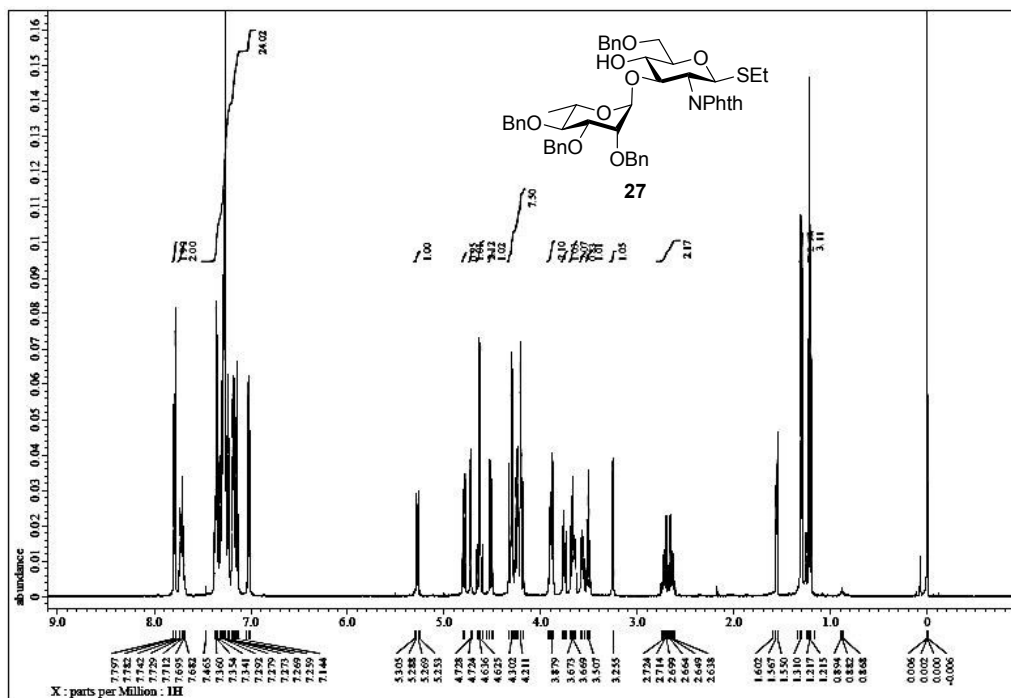


Figure S49  $^1\text{H}$  NMR spectrum of 27

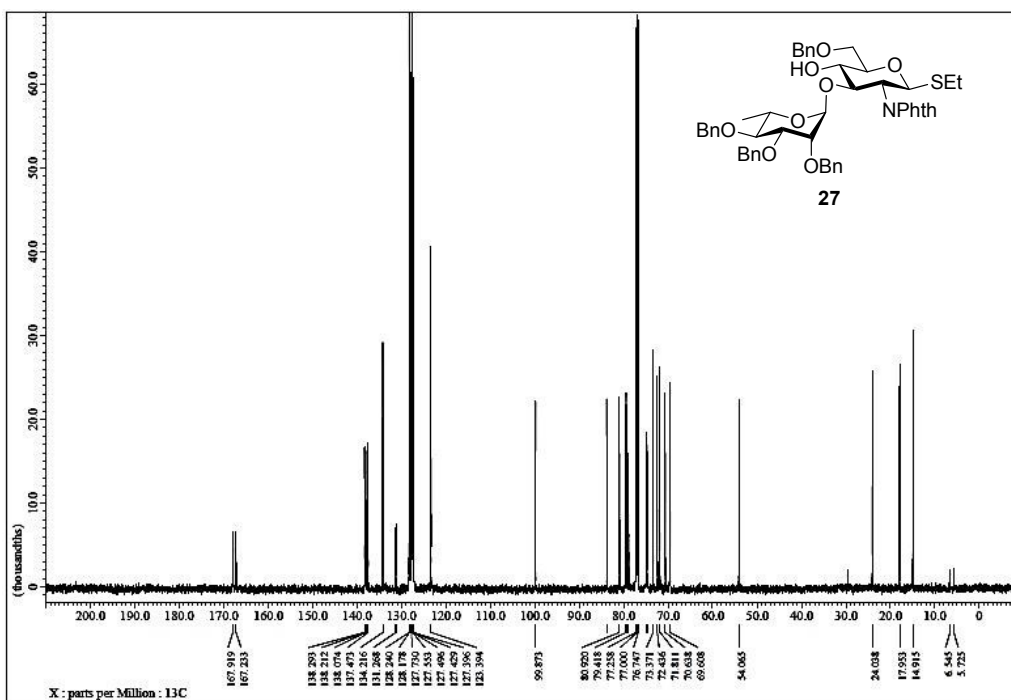


Figure S50  $^{13}\text{C}$  NMR spectrum of **27**

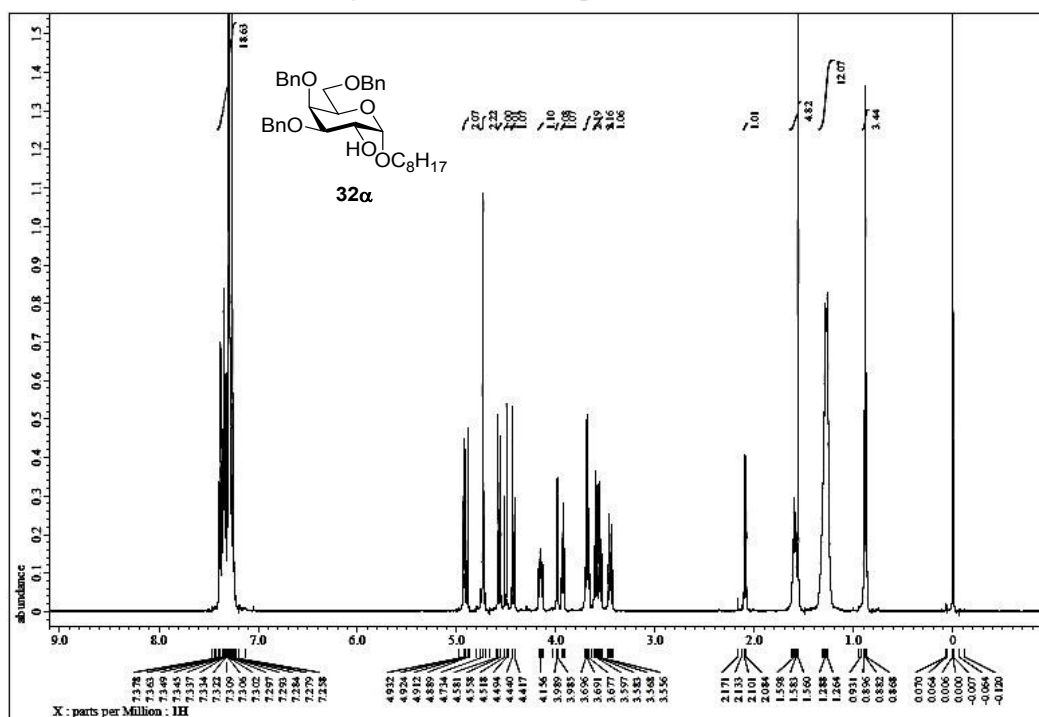


Figure S51  $^1\text{H}$  NMR spectrum of **32α**

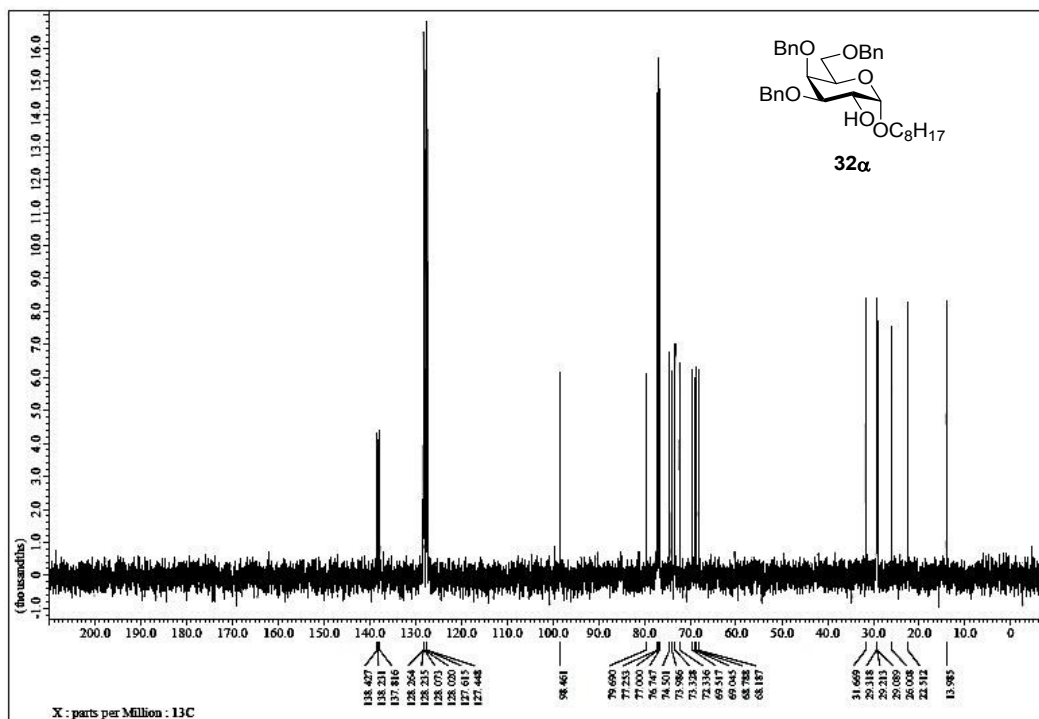




Figure S52  $^{13}\text{C}$  NMR spectrum of  $32\alpha$

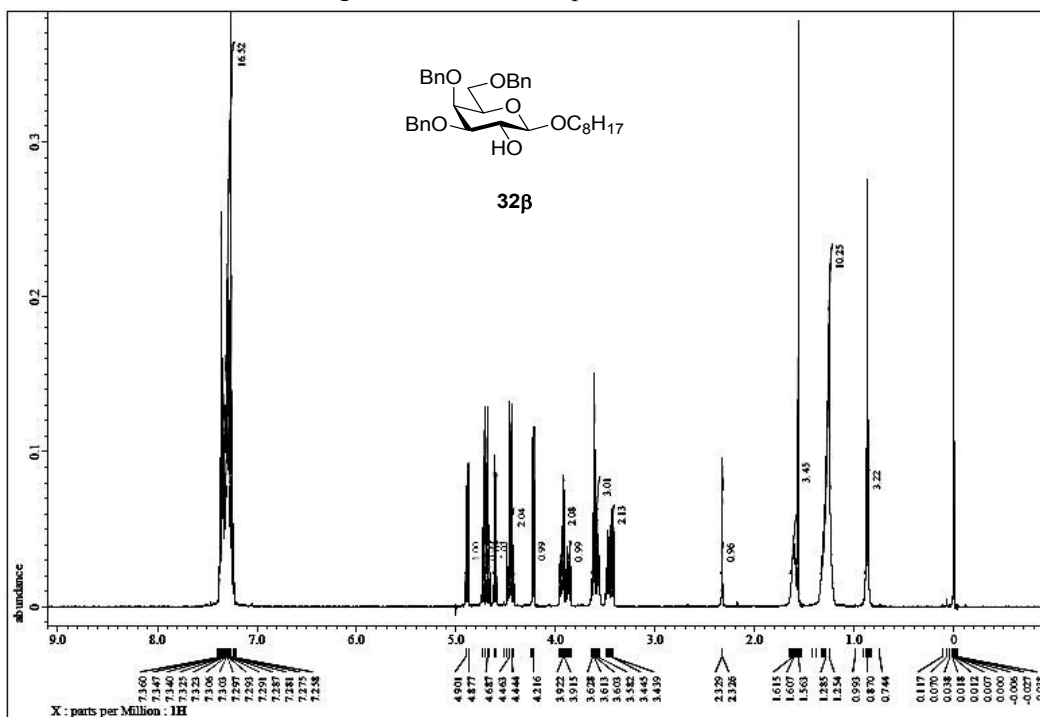


Figure S53  $^1\text{H}$  NMR spectrum of  $32\beta$

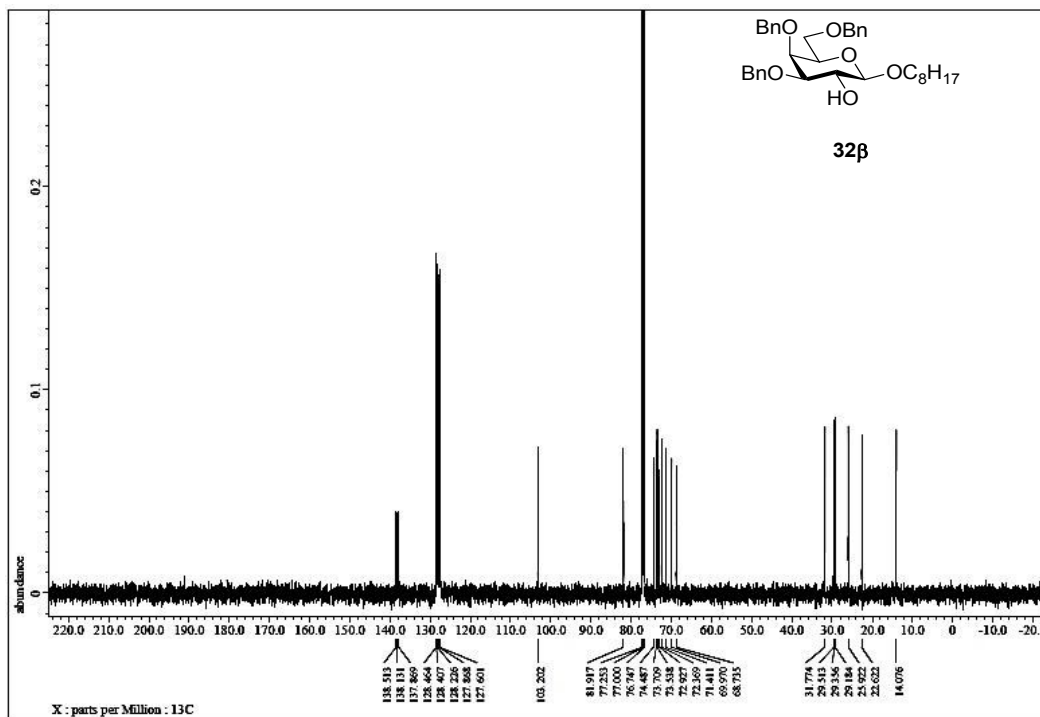


Figure S54  $^{13}\text{C}$  NMR spectrum of **32 $\beta$**

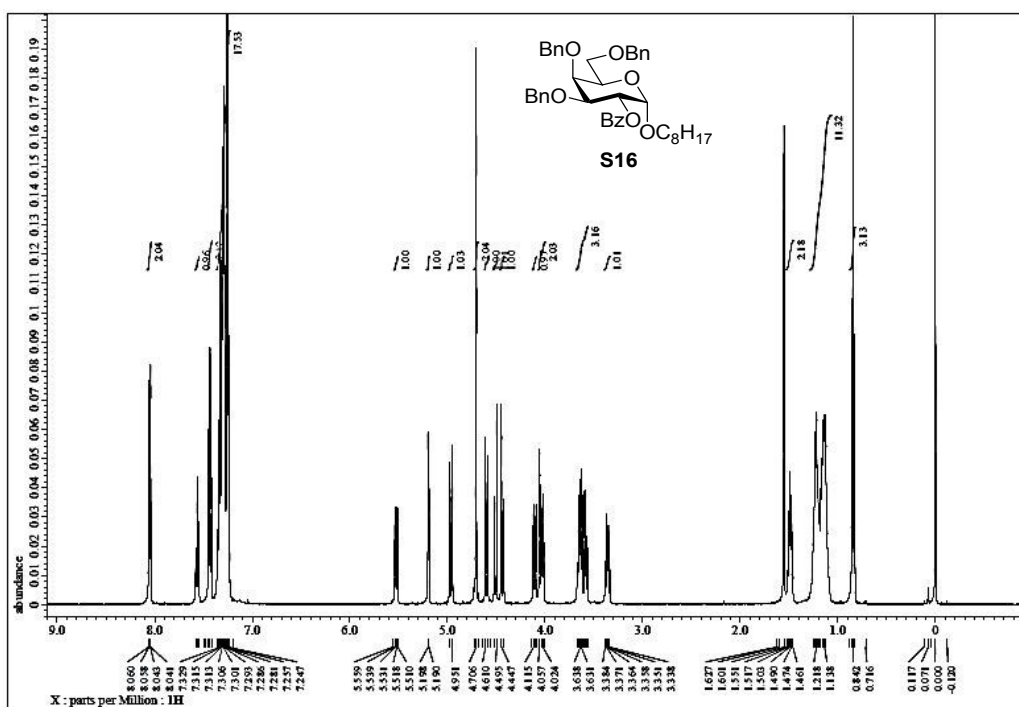


Figure S55  $^1\text{H}$  NMR spectrum of **S16**

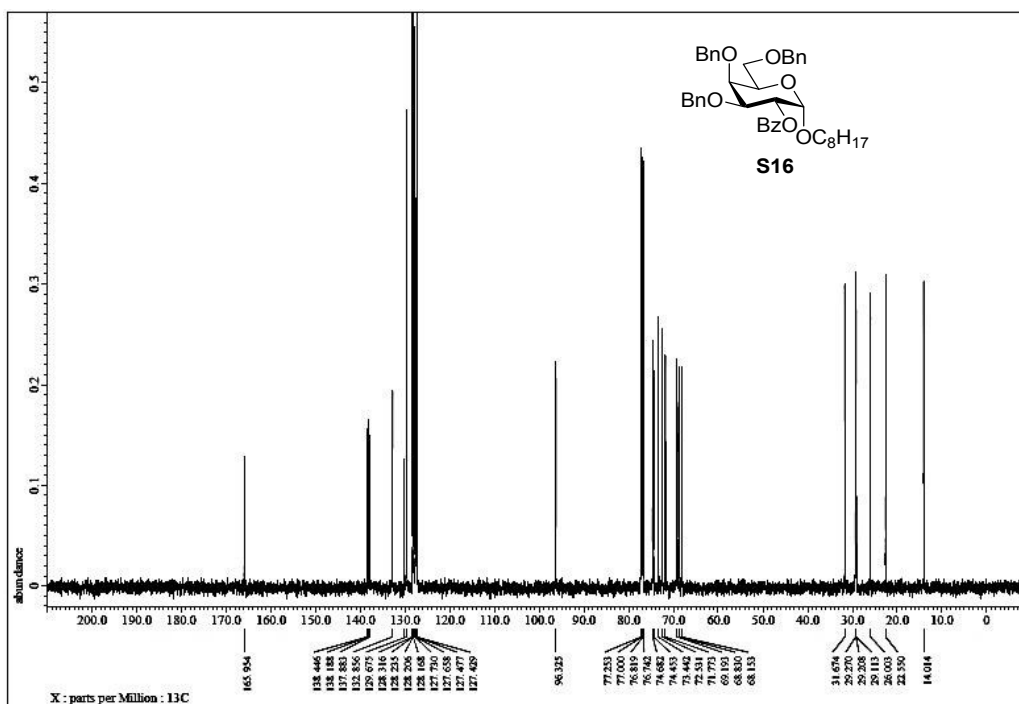


Figure S56  $^{13}\text{C}$  NMR spectrum of **S16**

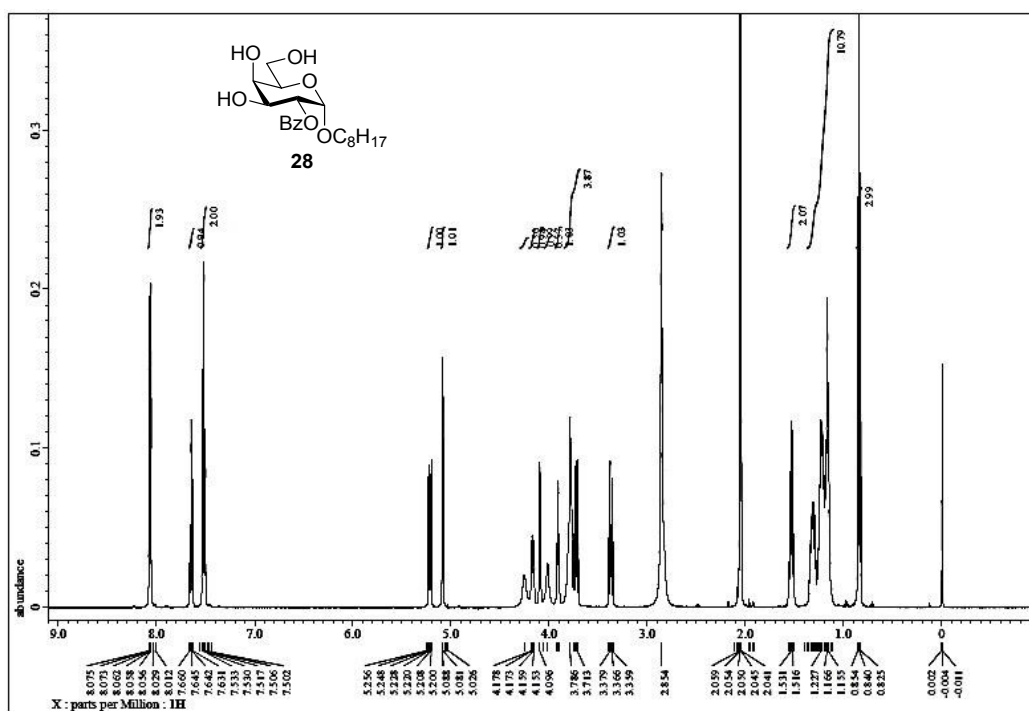


Figure S57  $^1\text{H}$  NMR spectrum of **28**

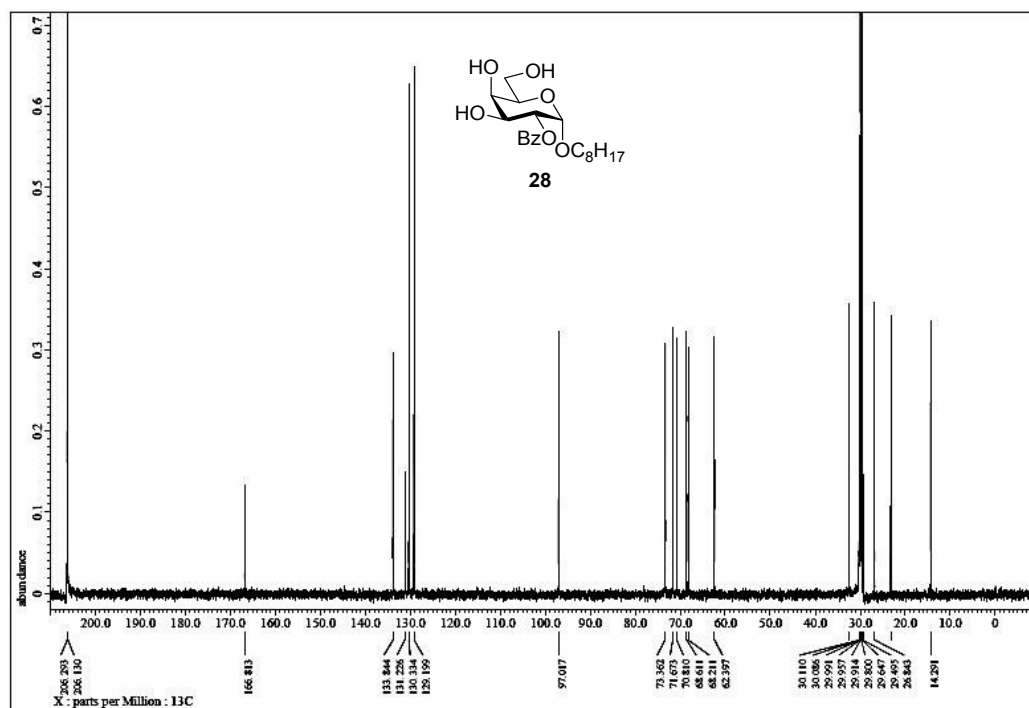


Figure S58 <sup>13</sup>C NMR spectrum of **28**

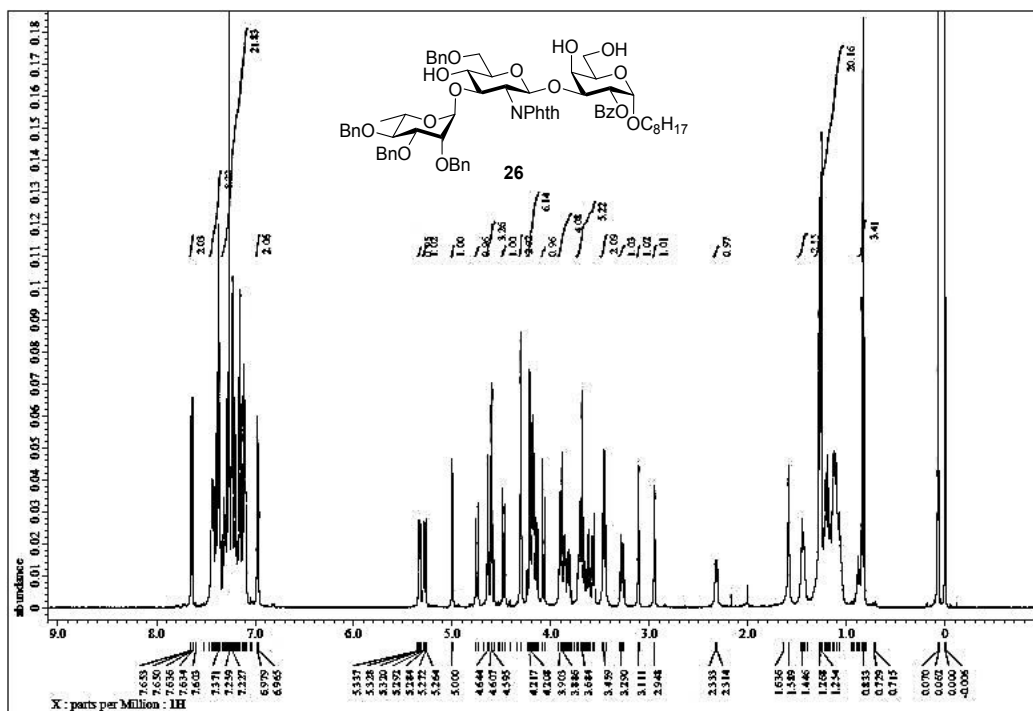


Figure S59 <sup>1</sup>H NMR spectrum of **26**

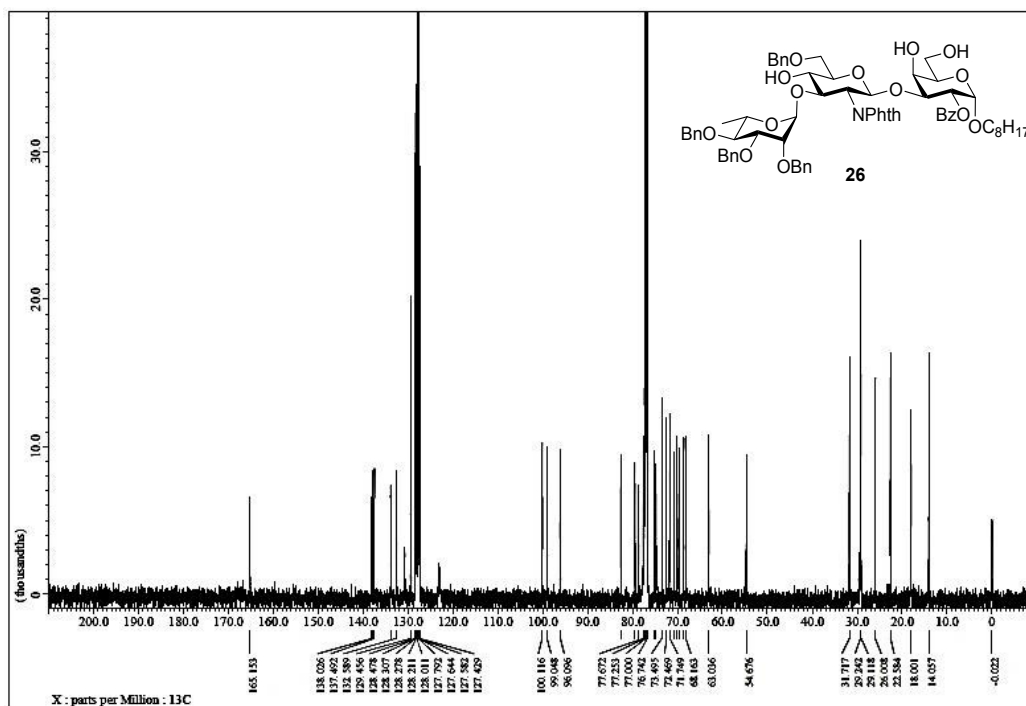


Figure S60  $^{13}\text{C}$  NMR spectrum of **26**

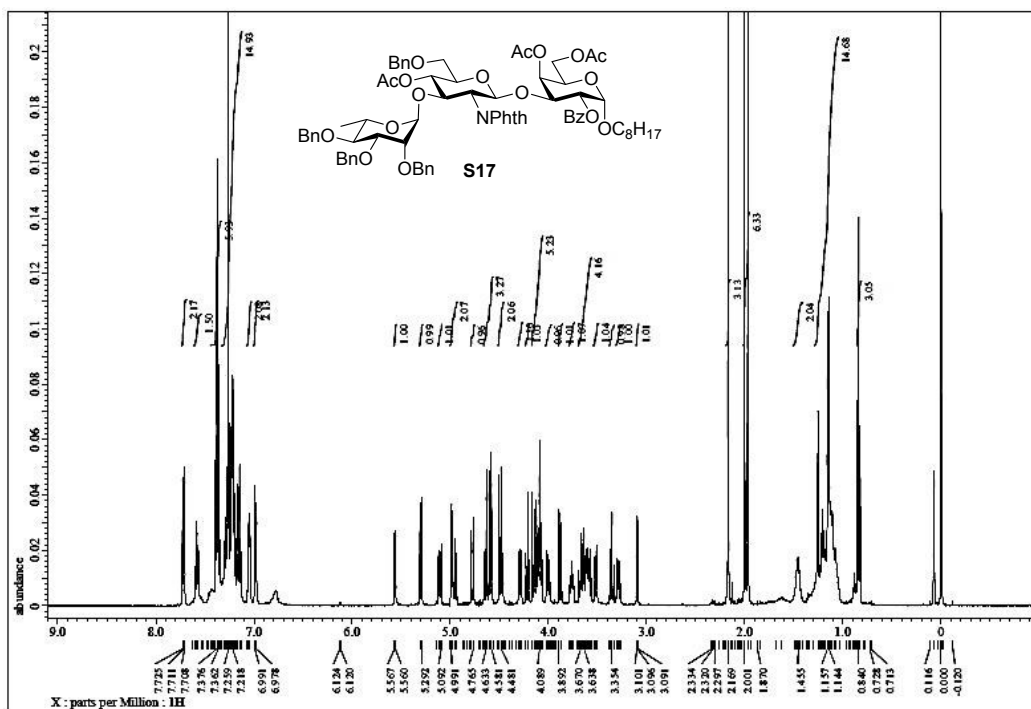


Figure S61  $^1\text{H}$  NMR spectrum of **S17**

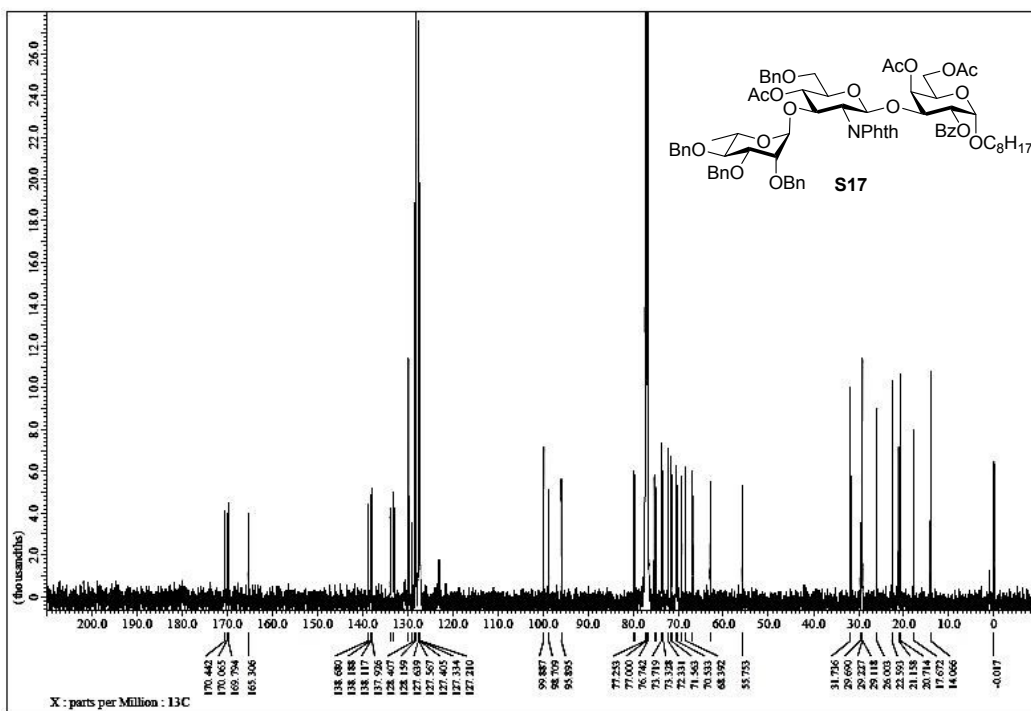


Figure S62  $^{13}\text{C}$  NMR spectrum of S17

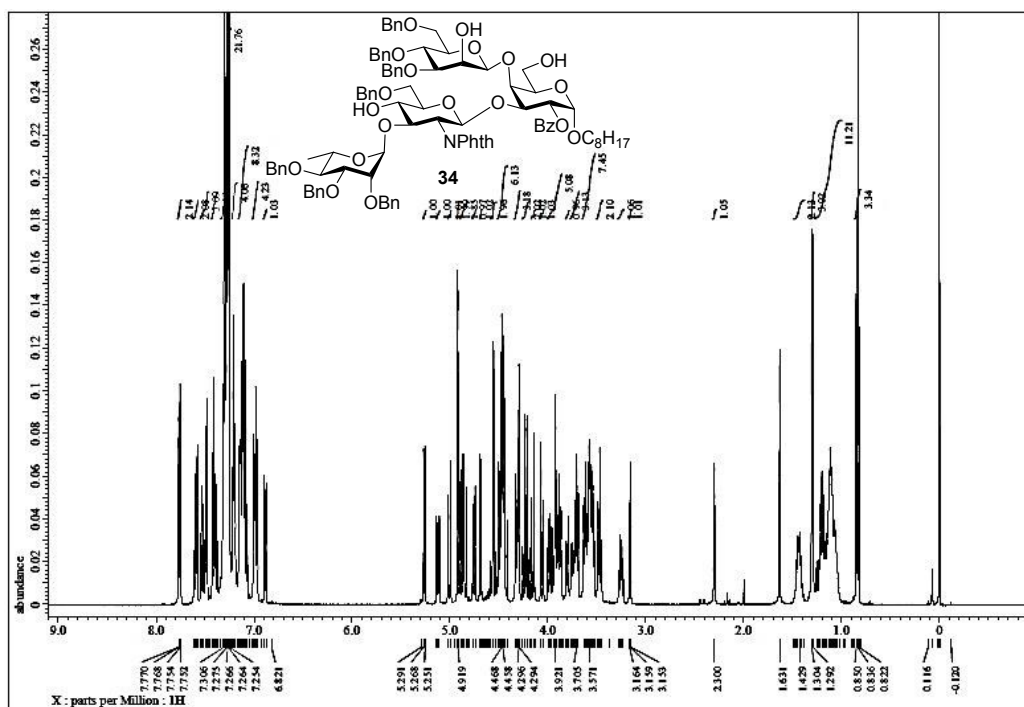


Figure S63  $^1\text{H}$  NMR spectrum of 34

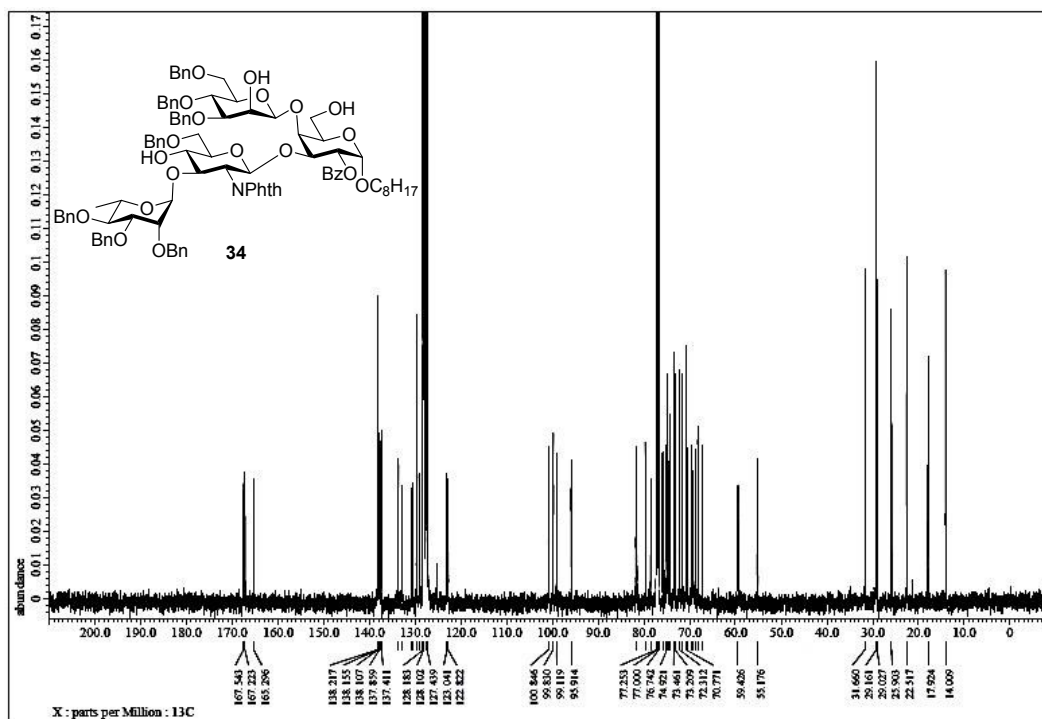


Figure S64  $^{13}\text{C}$  NMR spectrum of **34**

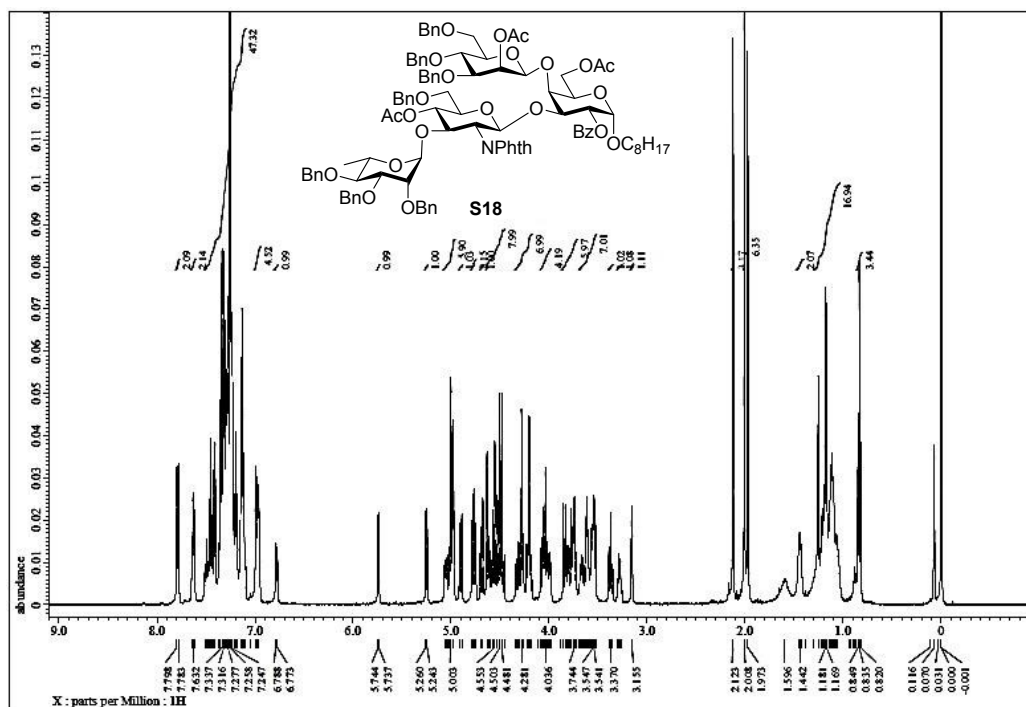


Figure S65  $^1\text{H}$  NMR spectrum of **S18**

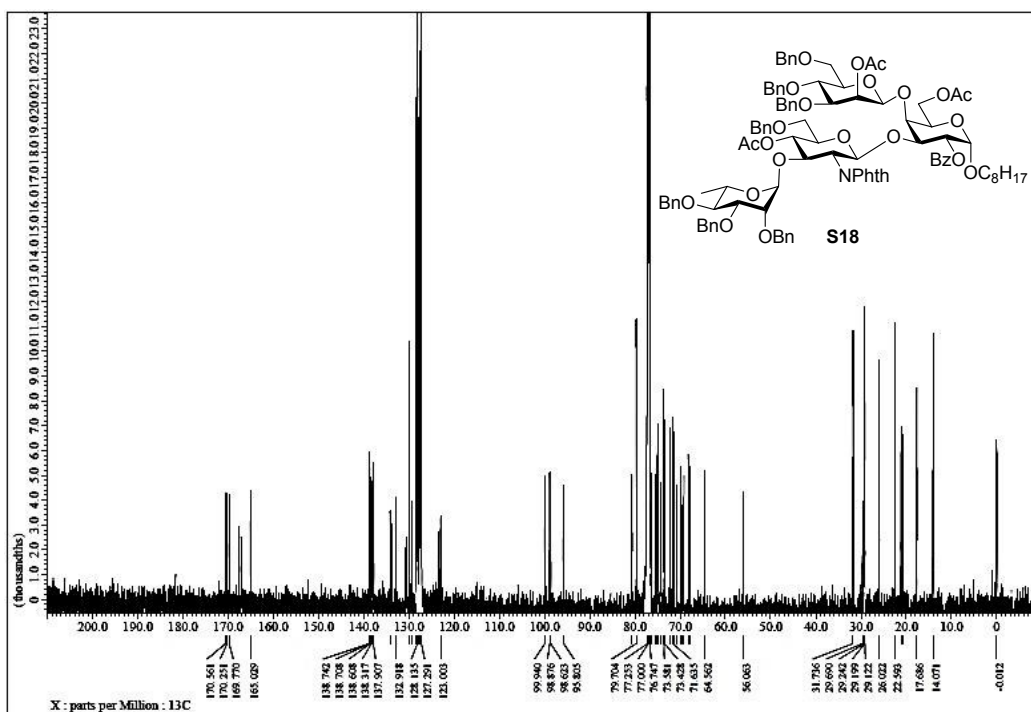


Figure S66  $^{13}\text{C}$  NMR spectrum of S18

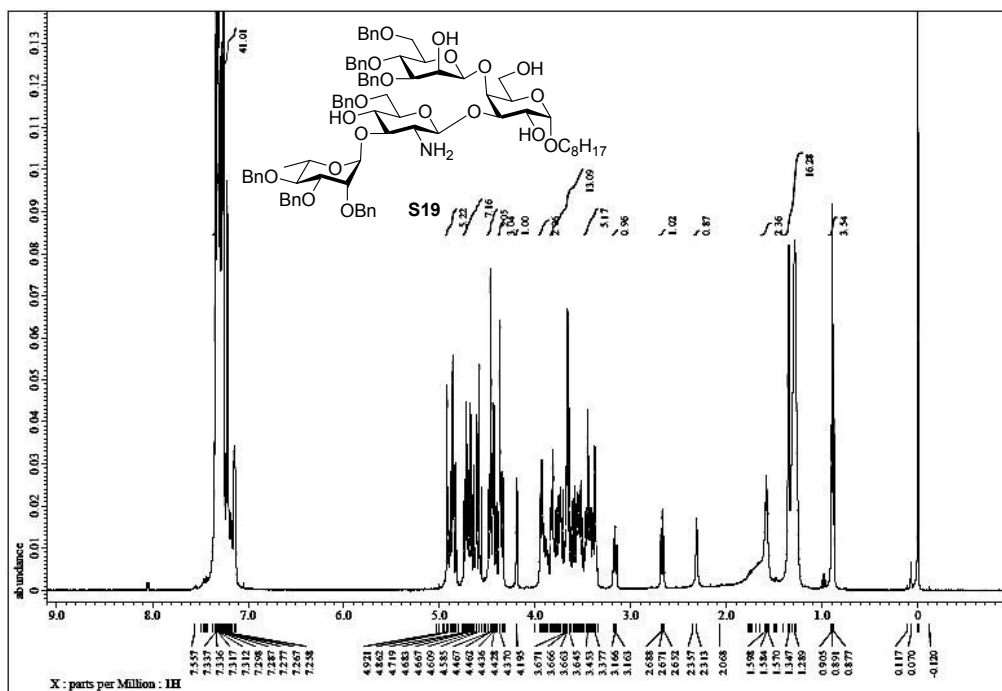


Figure S67  $^1\text{H}$  NMR spectrum of S19

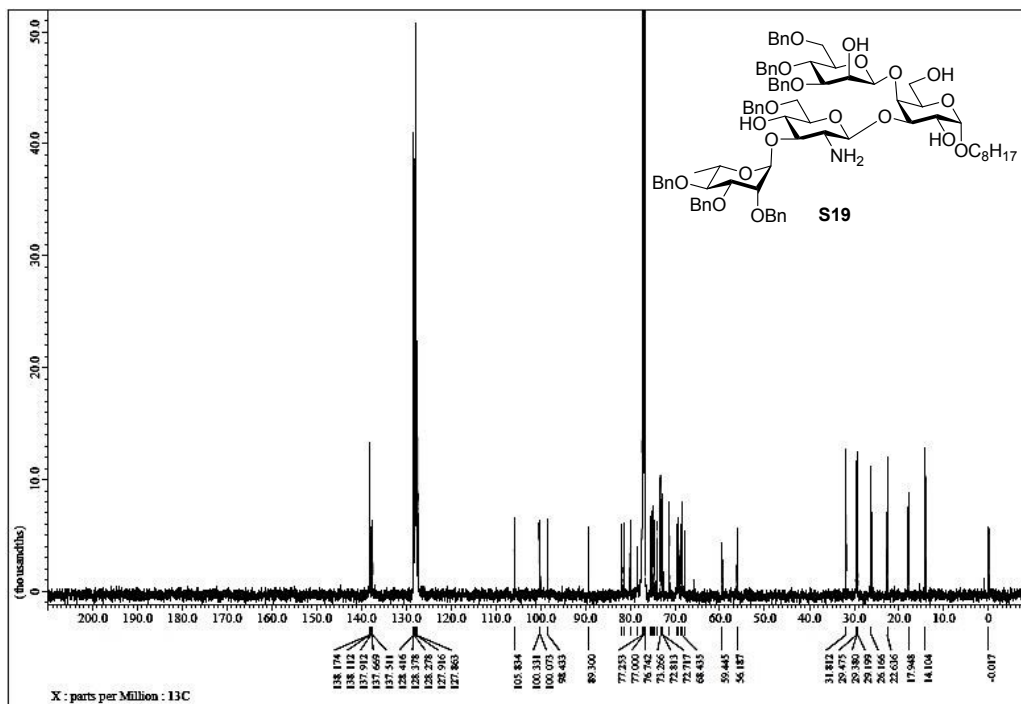




Figure S68 <sup>13</sup>C NMR spectrum of S19

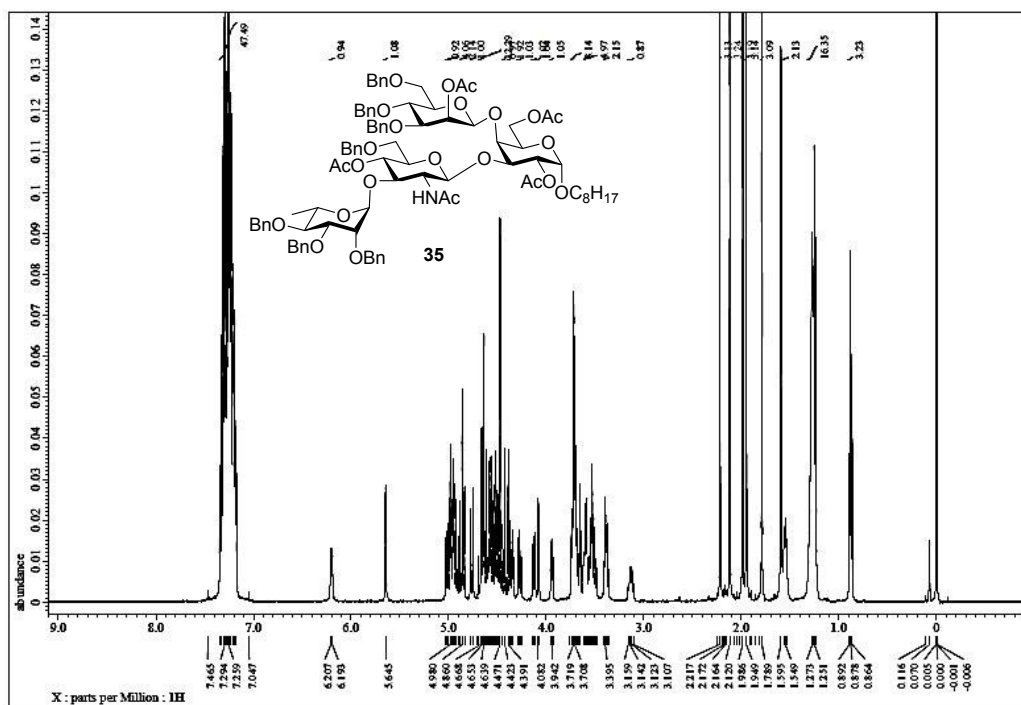


Figure S69 <sup>1</sup>H NMR spectrum of 35

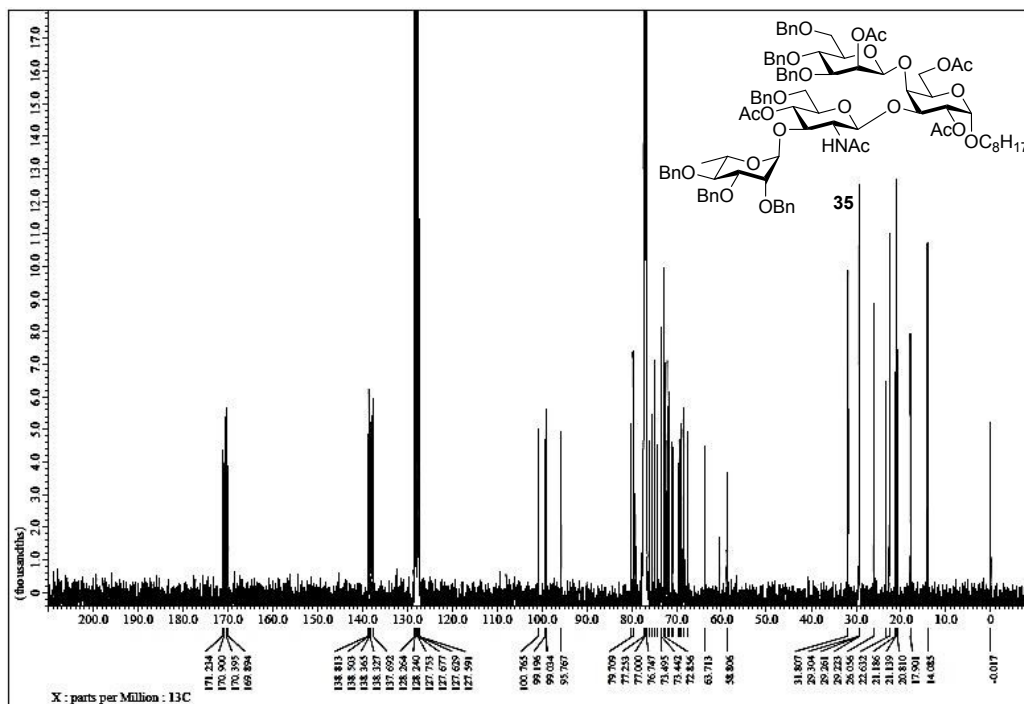


Figure S70  $^{13}\text{C}$  NMR spectrum of **35**

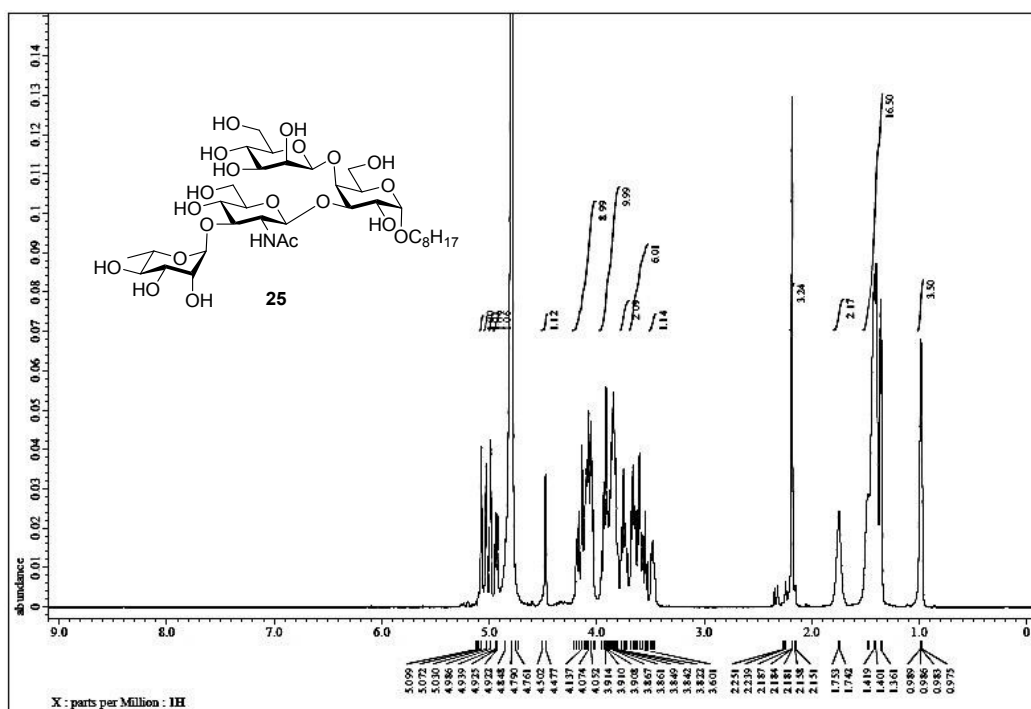


Figure S71  $^1\text{H}$  NMR spectrum of **25**

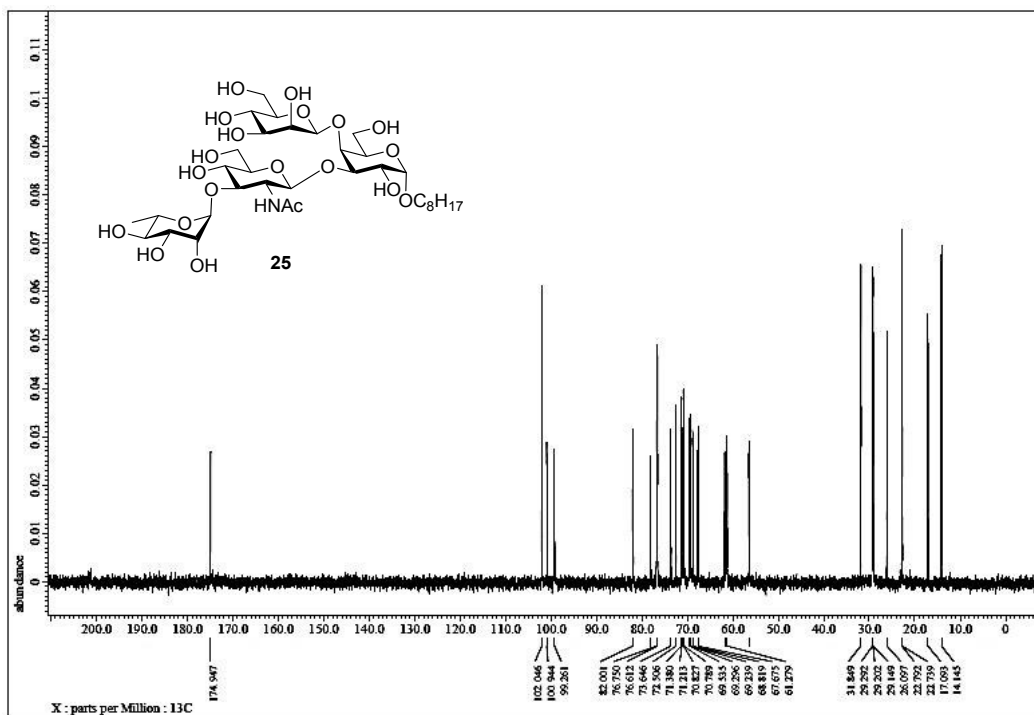


Figure S72  $^{13}\text{C}$  NMR spectrum of **25**