

## SUPPLEMENTARY INFORMATION

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### Chemoselective glycosylations using 2,3-unsaturated-4-keto glycosyl donors

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**General Methods for Chemical Synthesis.** Melting points were determined on a micro hot-stage (Yanako MP-S3) and were uncorrected. Optical rotations were measured on a JASCO DIP-370 photo-electric polarimeter. <sup>1</sup>H-NMR spectra were recorded on a Varian MVX-300 (300 MHz) spectrometer using trimethylsilane as internal standard unless otherwise noted. ESI-TOF Mass spectra were measured on a Waters LCT Premier XE. Silica gel TLC and column chromatography were performed on Merck TLC 60F-254 (0.25 mm) and Silica Gel 60 N (spherical, neutral) (Kanto Chemical Co., Inc.), respectively. Air- and/or moisture-sensitive reactions were carried out under an atmosphere of argon using oven-dried glassware. In general, organic solvents were purified and dried using an appropriate procedure, and evaporation and concentration were carried out under reduced pressure below 30 °C, unless otherwise noted. The configurations at the anomeric positions of the 2,3-unsaturated glycosides were determined by the <sup>1</sup>H-NMR analyses of the corresponding 2,3-dideoxy glycosides which were obtained by standard hydrogenations of the double bond in the 2,3-unsaturated glycosides using H<sub>2</sub> and 10% Pd/C. On the other hand, the configurations at the anomeric positions of the 2,3-unsaturated-4-keto glycosides were determined by the <sup>1</sup>H-NMR analyses of the corresponding 2,3-dideoxy glycosides which were obtained by standard

hydrogenations of the double bond in the 2,3-unsaturated-4-keto glycosides using H<sub>2</sub> and 10% Pd/C, followed by stereoselective reductions of the ketone group in the resulting 2,3-dideoxy-4-keto glycosides using NaBH<sub>4</sub>.<sup>1</sup>

### General glycosylation procedure in Table 1.

A suspension of glycosyl donor (2,3-unsaturated glycosyl acetate **1**<sup>2</sup> (0.05 mmol) or 2,3-unsaturated-4-keto glycosyl acetate **2**<sup>3</sup> (0.05 mmol)), methyl 2,3,4-tri-*O*-benzyl- $\alpha$ -D-glucopyranoside (**3**) (0.05 mmol) and MS 5A (100 wt% to glycosyl donor) in dry CH<sub>2</sub>Cl<sub>2</sub> (40  $\mu$ L/mg to glycosyl donor) was stirred for 30 minutes at 25 °C, and then to the suspension was added an activator as listed in Table 1. After the suspension was stirred at the temperature and for the period as shown in Table 1, pyridine was added to the reaction mixture to quench the reaction. The resulting mixture was poured into water, and extracted with ethyl acetate. The extracts were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in *vacuo*. Purification of the residue by preparative TLC (hexane/ether=1/1) (for the glycosylation using **1**) or flash silica-gel column chromatography (hexane/ethyl acetate=1/1) (for the glycosylation using **2**) afforded disaccharide **4** and recovered **1** or disaccharide **5** and recovered **2** as indicated in Table 1. The  $\alpha$ : $\beta$  ratios were determined by <sup>1</sup>H-NMR analysis.

**Disaccharide 4- $\alpha$ .** Colorless syrup; *R*<sub>f</sub> 0.73 (1/1 *n*-hexane/EtOAc); [ $\alpha$ ]<sub>D</sub><sup>30</sup> +84.1° (*c* 1.57, CHCl<sub>3</sub>); NMR: <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS)  $\delta$  8.02-7.95 (4H, m, ArH), 7.66-7.52 (2H, m, ArH), 7.52-7.22 (19H, m, ArH), 6.02 (1H, ddd,  $J_{2',3'}=10.2$  Hz,  $J_{1',3'}=0.9$  Hz,  $J_{3',4'}=0.9$  Hz, H-3'), 5.91 (1H, ddd,  $J_{2',3'}=10.2$  Hz,  $J_{1',2'}=2.4$  Hz,  $J_{2',4'}=2.1$  Hz, H-2'), 5.68 (1H, ddd,  $J_{4',5'}=7.2$  Hz,  $J_{2',4'}=2.1$  Hz,  $J_{3',4'}=0.9$  Hz, H-4'), 5.16 (1H, dd,  $J_{1',2'}=2.4$  Hz,  $J_{1',3'}=0.9$  Hz, H-1'), 4.99 & 4.80 (2H, ABq,  $J=10.8$  Hz, ArCH<sub>2</sub>), 4.91 & 4.64 (2H, ABq,  $J=11.4$  Hz, ArCH<sub>2</sub>), 4.78 & 4.67 (2H, ABq,  $J=12.0$  Hz, ArCH<sub>2</sub>), 4.61 (1H, d,  $J_{1,2}=3.6$  Hz, H-1), 4.46 (1H, dd,  $J_{6',6''}=8.7$  Hz,  $J_{5',6'}=4.5$  Hz, H-6'), 4.37 (1H, ddd,  $J_{4',5'}=7.2$  Hz,  $J_{5',6'}=5.1$  Hz,  $J_{5',6''}=4.5$  Hz, H-5'), 4.34 (1H, dd,  $J_{6',6''}=8.7$  Hz,  $J_{5',6'}=5.1$  Hz, H-6'), 4.01 (1H, dd,

$J_{6,6}=11.4$  Hz,  $J_{5,6}=4.8$  Hz, H-6), 4.00 (1H, dd,  $J_{2,3}=J_{3,4}=9.3$  Hz, H-3), 3.82-3.72 (2H, m, H-5 & H-6), 3.53 (1H, dd,  $J_{3,4}=J_{4,5}=9.3$  Hz, H-4), 3.49 (1H, dd,  $J_{2,3}=9.3$  Hz,  $J_{1,2}=3.6$  Hz, H-2), 3.38 (3H, s, OMe); Anal. Calcd for  $C_{48}H_{48}O_{11}$ : C, 71.98; H, 6.04. Found: C, 71.83; H, 5.90.

**Disaccharide 4- $\beta$ .** Colorless syrup;  $R_f$  0.73 (1/1 *n*-hexane/EtOAc);  $[\alpha]^{30}_D +104.5^\circ$  (*c* 1.95,  $CHCl_3$ ); NMR:  $^1H$ -NMR ( $CDCl_3$ , TMS)  $\delta$  8.04-7.96 (4H, m, ArH), 7.61-7.46 (2H, m, ArH), 7.46-7.22 (19H, m, ArH), 6.10 (1H, ddd,  $J_{2',3'}=10.2$  Hz,  $J_{3',4'}=3.6$  Hz,  $J_{1',3'}=1.5$  Hz, H-3'), 5.92 (1H, ddd,  $J_{2',3'}=10.2$  Hz,  $J_{1',2'}=1.5$  Hz,  $J_{2',4'}=1.5$  Hz, H-2'), 5.55 (1H, ddd,  $J_{4',5'}=11.4$  Hz,  $J_{3',4'}=3.6$  Hz,  $J_{2',4'}=1.5$  Hz, H-4'), 5.16 (1H, dd,  $J_{1',2'}=1.5$  Hz,  $J_{1',3'}=1.5$  Hz, H-1'), 4.98 & 4.80 (2H, ABq,  $J=11.1$  Hz, ArCH<sub>2</sub>), 4.87 & 4.61 (2H, ABq,  $J=11.1$  Hz, ArCH<sub>2</sub>), 4.78 & 4.66 (2H, ABq,  $J=12.0$  Hz, ArCH<sub>2</sub>), 4.59 (1H, d,  $J_{1,2}=3.6$  Hz, H-1), 4.54 (1H, dd,  $J_{6',6'}=11.7$  Hz,  $J_{5',6'}=6.0$  Hz, H-6'), 4.49 (1H, dd,  $J_{6',6'}=11.7$  Hz,  $J_{5',6'}=5.4$  Hz, H-6'), 4.31 (1H, ddd,  $J_{4',5'}=11.4$  Hz,  $J_{5',6'}=6.0$  Hz,  $J_{5',6'}=5.4$  Hz, H-5'), 4.08-4.01 (1H, m, H-6), 3.97 (1H, dd,  $J_{2,3}=J_{3,4}=9.3$  Hz, H-3), 3.79-3.71 (2H, m, H-5 & H-6), 3.57 (1H, dd,  $J_{3,4}=J_{4,5}=9.3$  Hz, H-4), 3.53 (1H, dd,  $J_{2,3}=9.3$  Hz,  $J_{1,2}=3.6$  Hz, H-2), 3.30 (3H, s, OMe); Anal. Calcd for  $C_{48}H_{48}O_{11}$ : C, 71.98; H, 6.04. Found: C, 71.71; H, 6.15.

**Disaccharide 5- $\alpha$ .** Colorless syrup;  $R_f$  0.36 (50/1 chloroform/acetone);  $[\alpha]^{32}_D -19.9^\circ$  (*c* 1.14,  $CHCl_3$ ); NMR:  $^1H$ -NMR ( $CDCl_3$ , TMS)  $\delta$  7.96 (2H, dd,  $J_{o,m}=8.1$  Hz,  $J_{o,p}=1.2$  Hz, H<sub>o</sub> of Bz), 7.53 (1H, tt,  $J_{m,p}=7.2$  Hz,  $J_{o,p}=1.2$  Hz, H<sub>p</sub> of Bz), 7.41-7.24 (17H, m, H<sub>m</sub> of Bz & ArH of Bz), 6.90 (1H, dd,  $J_{2',3'}=10.2$  Hz,  $J_{1',2'}=3.3$  Hz, H-2'), 6.15 (1H, d,  $J_{2',3'}=10.2$  Hz, H-3'), 5.34 (1H, d,  $J_{1',2'}=3.3$  Hz, H-1'), 4.99 & 4.80 (2H, ABq,  $J=10.8$  Hz, ArCH<sub>2</sub>), 4.91 & 4.55 (2H, ABq,  $J=11.1$  Hz, ArCH<sub>2</sub>), 4.78 & 4.66 (2H, ABq,  $J=12.3$  Hz, ArCH<sub>2</sub>), 4.68 (1H, dd,  $J_{6',6'}=9.9$  Hz,  $J_{5',6'}=2.1$  Hz, H-6'), 4.61 (1H, dd,  $J_{6',6'}=9.9$  Hz,  $J_{5',6'}=3.9$  Hz, H-6'), 4.58 (1H, d,  $J_{1,2}=3.3$  Hz, H-1), 4.57 (1H, dd,  $J_{5',6'}=3.9$  Hz,  $J_{5',6'}=2.1$  Hz, H-5'), 4.00 (1H, dd,  $J_{6,6}=12.0$  Hz,  $J_{5,6}=5.4$  Hz, H-6), 3.99 (1H, dd,  $J_{2,3}=J_{3,4}=9.0$  Hz, H-3), 3.80 (1H, dd,  $J_{6,6}=12.0$  Hz,  $J_{5,6}=1.8$  Hz, H-6), 3.79 (1H, ddd,  $J_{4,5}=9.0$  Hz,  $J_{5,6}=5.4$  Hz,  $J_{5,6}=1.8$  Hz, H-5), 3.47 (1H, dd,  $J_{2,3}=9.0$  Hz,  $J_{1,2}=3.3$  Hz, H-2), 3.47 (1H, dd,  $J_{3,4}=J_{4,5}=9.0$  Hz, H-4), 3.35

(3H, s, OMe); Anal. Calcd for C<sub>41</sub>H<sub>42</sub>O<sub>10</sub>: C, 70.88; H, 6.09. Found: C, 70.67; H, 6.22; HRMS (ESI-TOF) *m/z* 717.2659 (717.2676 calcd for C<sub>41</sub>H<sub>42</sub>O<sub>10</sub>Na, [M+Na]<sup>+</sup>).

**Disaccharide 5-β.** Colorless syrup; *R<sub>f</sub>* 0.31 (50/1 chloroform/acetone); [α]<sup>32</sup><sub>D</sub> +80.7° (*c* 0.24, CHCl<sub>3</sub>); NMR: <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS) δ 8.00 (2H, dd, *J*<sub>*o,m*</sub>=7.8 Hz, *J*<sub>*o,p*</sub>=1.2 Hz, H<sub>*o*</sub> of Bz), 7.53 (1H, tt, *J*<sub>*m,p*</sub>=7.5 Hz, *J*<sub>*o,p*</sub>=1.2 Hz, H<sub>*p*</sub> of Bz), 7.41-7.23 (17H, m, H<sub>*m*</sub> of Bz & ArH of Bz), 6.78 (1H, dd, *J*<sub>*2,3'*</sub>=10.2 Hz, *J*<sub>*1,2'*</sub>=1.8 Hz, H-2'), 6.18 (1H, dd, *J*<sub>*2,3'*</sub>=10.2 Hz, *J*<sub>*1,3'*</sub>=0.9 Hz, H-3'), 5.17 (1H, br-s, H-1'), 4.97 & 4.78 (2H, ABq, *J*=10.8 Hz, ArCH<sub>2</sub>), 4.85 & 4.57 (2H, ABq, *J*=11.1 Hz, ArCH<sub>2</sub>), 4.74 & 4.63 (2H, ABq, *J*=11.4 Hz, ArCH<sub>2</sub>), 4.71 (1H, dd, *J*<sub>*6',6'*</sub>=11.7 Hz, *J*<sub>*5',6'*</sub>=3.6 Hz, H-6'), 4.63 (1H, dd, *J*<sub>*6',6'*</sub>=11.7 Hz, *J*<sub>*5',6'*</sub>=6.6 Hz, H-6'), 4.54 (1H, d, *J*<sub>*1,2*</sub>=3.3 Hz, H-1), 4.50 (1H, dd, *J*<sub>*5',6'*</sub>=6.6 Hz, *J*<sub>*5',6'*</sub>=3.6 Hz, H-5'), 4.06 (1H, m, H-6), 3.95 (1H, dd, *J*<sub>*2,3*</sub>=*J*<sub>*3,4*</sub>=9.0 Hz, H-3), 3.74 (1H, dd, *J*<sub>*6,6*</sub>=10.5 Hz, *J*<sub>*5,6*</sub>=4.2 Hz, H-6), 3.71 (1H, m, H-5), 3.52 (1H, dd, *J*<sub>*3,4*</sub>=*J*<sub>*4,5*</sub>=9.0 Hz, H-4), 3.45 (1H, dd, *J*<sub>*2,3*</sub>=9.0 Hz, *J*<sub>*1,2*</sub>=3.3 Hz, H-2), 3.22 (3H, s, OMe); HRMS (ESI-TOF) *m/z* 717.2676 (717.2676 calcd for C<sub>41</sub>H<sub>42</sub>O<sub>10</sub>Na, [M+Na]<sup>+</sup>).

#### Chemoselective glycosylation using 1 and 6.

A suspension of 2,3-unsaturated glycosyl acetate **1** (23.2 mg, 0.059 mmol), 2,3-unsaturated-4-keto glycosyl acetate **6**<sup>4</sup> (22.0 mg, 0.118 mmol) and MS 5A (100 wt% to glycosyl donor) in dry CH<sub>2</sub>Cl<sub>2</sub> (40 μL/mg to glycosyl donor) was stirred for 30 minutes at 25 °C, and then to the suspension was added TMSOTf (3.2 μL 0.017 mmol) at -75 °C. After the suspension was stirred at -75 °C and for 30 minutes, pyridine was added to the reaction mixture to quench the reaction. The resulting mixture was poured into water, and extracted with ethyl acetate. The extracts were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in *vacuo*. Purification of the residue by preparative TLC (chloroform/ethyl acetate=9/1) afforded disaccharide **7** (27.9 mg, 91%, α/β=79/21). The α:β ratio was determined by <sup>1</sup>H-NMR analysis.

**Disaccharide 7-α.** Colorless syrup; *R<sub>f</sub>* 0.59 (9/1 chloroform/EtOAc); [α]<sup>32</sup><sub>D</sub> +12.1° (*c* 2.68,

CHCl<sub>3</sub>); NMR: <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS)  $\delta$  8.09-7.99 (4H, m, ArH), 7.60-7.49 (2H, m, ArH), 7.46-7.36 (4H, m, ArH), 6.91 (1H, dd,  $J_{2,3}$ =10.2 Hz,  $J_{1,2}$ =3.7 Hz, H-2), 6.56 (1H, d,  $J_{1,2}$ =3.7 Hz, H-1), 6.27 (1H, d,  $J_{2,3}$ =10.2 Hz, H-3), 6.05 (1H, br-d,  $J$ =10.5 Hz, H-3'), 5.90 (1H, ddd,  $J_{2',3'}$ =10.2 Hz,  $J_{2',4'}$ =2.0 Hz,  $J_{1',2'}$ =2.7 Hz, H-2'), 5.70 (1H, ddd,  $J_{4',5'}$ =9.5 Hz,  $J_{3',4'}$ =3.2 Hz,  $J_{2',4'}$ =2.0 Hz, H-4'), 5.13 (1H, br-s, H-1'), 4.68 (1H, dd,  $J_{5,6}$ =4.2 Hz,  $J_{5,6}$ =2.7 Hz, H-5), 4.65 (1H, dd,  $J_{6',6'}$ =10.5 Hz,  $J_{5',6'}$ =2.7 Hz, H-6'), 4.48 (1H, dd,  $J_{6',6'}$ =10.5 Hz,  $J_{5',6'}$ =5.4 Hz, H-6'), 4.40 (1H, m, H-5'), 4.38 (1H, dd,  $J_{6,6}$ =11.0 Hz,  $J_{5,6}$ =4.2 Hz, H-6), 3.90 (1H, dd,  $J_{6,6}$ =11.0 Hz,  $J_{5,6}$ =2.7 Hz, H-6), 2.14 (3H, s, OAc); Anal. Calcd for C<sub>28</sub>H<sub>26</sub>O<sub>10</sub>: C, 64.36; H, 5.02. Found: C, 64.59; H, 5.20; HRMS (ESI-TOF)  $m/z$  545.1406 (545.1424 calcd for C<sub>28</sub>H<sub>26</sub>O<sub>10</sub>Na, [M+Na]<sup>+</sup>).

**Disaccharide 7- $\beta$ .** Colorless syrup;  $R_f$  0.52 (9/1 chloroform/EtOAc);  $[\alpha]_D^{32} +57.5^\circ$  ( $c$  0.93, CHCl<sub>3</sub>); NMR: <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS)  $\delta$  8.06-8.01 (4H, m, ArH), 7.60-7.52 (2H, m, ArH), 7.45-7.40 (4H, m, ArH), 6.93 (1H, dd,  $J_{2,3}$ =10.2 Hz,  $J_{1,2}$ =3.7 Hz, H-2), 6.57 (1H, d,  $J_{1,2}$ =3.7 Hz, H-1), 6.21 (1H, d,  $J_{2,3}$ =10.2 Hz, H-3), 6.04 (1H, br-d, H-3'), 5.91 (1H, ddd,  $J_{2',3'}$ =10.2 Hz,  $J_{2',4'}$ =2.2 Hz,  $J_{1',3'}$ =1.2 Hz, H-2'), 5.70 (1H, ddd,  $J_{4',5'}$ =9.5 Hz,  $J_{3',4'}$ =3.8 Hz,  $J_{2',4'}$ =1.2 Hz, H-4'), 5.26 (1H, m, H-1'), 4.68 (1H, m, H-5), 4.65 (1H, dd,  $J_{6',6'}$ =11.0 Hz,  $J_{5',6'}$ =2.7 Hz, H-6'), 4.48 (1H, dd,  $J_{6',6'}$ =11.0 Hz,  $J_{5',6'}$ =5.4 Hz, H-6'), 4.40 (1H, m, H-5'), 4.38 (1H, dd,  $J_{6,6}$ =10.7 Hz,  $J_{5,6}$ =4.1 Hz, H-6), 3.90 (1H, dd,  $J_{6,6}$ =10.7 Hz,  $J_{5,6}$ =2.7 Hz, H-6), 2.10 (3H, s, OAc); HRMS (ESI-TOF)  $m/z$  545.1425 (545.1424 calcd for C<sub>28</sub>H<sub>26</sub>O<sub>10</sub>Na, [M+Na]<sup>+</sup>).

### Synthesis of trisaccharide 8 by glycosylation using 7- $\alpha$ and 3.

A suspension of disaccharide **7- $\alpha$**  (22.7 mg, 0.0434 mmol), methyl 2,3,4-tri-*O*-benzyl- $\alpha$ -D-glucopyranoside (**3**) (10.1 mg, 0.0217 mmol) and MS 5A (22.7 mg, 100 wt% to glycosyl donor) in dry toluene (0.908 mL, 40  $\mu$ L/mg to glycosyl donor) was stirred for 30 min at 25 °C, and then to the suspension was added TMSOTf (2.5  $\mu$ L 0.013 mmol) at -40 °C. After the suspension was stirred at -40 °C for 30 min, pyridine was added to the reaction mixture to

quench the reaction. The resulting mixture was poured into water, and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated in *vacuo*. Purification of the residue by flash silica-gel column chromatography (hexane/EtOAc = 1/1) afforded trisaccharide **8** (22.2 mg, 75%,  $\alpha:\beta = 79:21$ ). The  $\alpha:\beta$  ratio was determined by <sup>1</sup>H-NMR analysis.

**Trisaccharide 8- $\alpha$** : Colorless syrup; *R*<sub>f</sub> 0.70 (1/1 hexane/EtOAc); [ $\alpha$ ]<sup>32</sup><sub>D</sub> +28.3° (*c* 1.42, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS)  $\delta$  8.08-8.00 (4H, m, ArH), 7.59-7.23 (21H, m, ArH), 6.85 (1H, dd,  $J_{2',3'} = 10.2$  Hz,  $J_{1',2'} = 3.7$  Hz, H-2'), 6.11 (1H, d,  $J_{2',3'} = 10.2$  Hz, H-3'), 5.98 (1H, br-d,  $J_{2'',3''} = 10.0$  Hz,  $J_{3'',4''} = 2.7$  Hz, H-3''), 5.83 (1H, ddd,  $J_{2'',3''} = 10.0$  Hz,  $J_{1'',2''} = 2.7$  Hz,  $J_{2'',4''} = 2.2$  Hz, H-2''), 5.68 (1H, ddd,  $J_{4'',5''} = 8.9$  Hz,  $J_{3'',4''} = 2.7$  Hz,  $J_{2'',4''} = 2.2$  Hz, H-4''), 5.34 (1H, d,  $J_{1',2'} = 3.7$  Hz, H-1'), 5.07 (1H, d,  $J_{1'',2''} = 2.7$  Hz, H-1''), 5.00 & 4.80 (2H, ABq,  $J = 10.7$  Hz, ArCH<sub>2</sub>), 4.91 & 4.57 (2H, ABq,  $J = 11.0$  Hz, ArCH<sub>2</sub>), 4.79 & 4.66 (2H, ABq,  $J = 12.2$  Hz, ArCH<sub>2</sub>), 4.64 (1H, dd,  $J_{6'',6''} = 11.9$  Hz,  $J_{5'',6''} = 2.4$  Hz, H-6''), 4.59 (1H, d,  $J_{1,2} = 3.7$  Hz, H-1), 4.51 (1H, m, H-5'), 4.47 (1H, dd,  $J_{6'',6''} = 11.9$  Hz,  $J_{5'',6''} = 5.6$  Hz, H-6''), 4.36 (1H, m, H-5''), 4.30 (1H, dd,  $J_{6',6'} = 11.0$  Hz,  $J_{5',6'} = 3.9$  Hz, H-6'), 4.03 (1H, dd,  $J_{6,6} = 11.2$  Hz,  $J_{5,6} = 4.4$  Hz, H-6), 4.00 (1H, dd,  $J_{2,3} = J_{3,4} = 9.3$  Hz, H-3), 3.82 (1H, m, H-6), 3.79 (1H, m, H-5), 3.71 (1H, dd,  $J_{6',6'} = 11.0$  Hz,  $J_{5',6'} = 2.4$  Hz, H-6'), 3.53 (1H, dd,  $J_{3,4} = 9.5$  Hz,  $J_{4,5} = 6.8$  Hz, H-4), 3.51 (1H, dd,  $J_{2,3} = 9.3$  Hz,  $J_{1,2} = 3.7$  Hz, H-2), 3.35 (3H, s, OMe); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  193.69, 166.34, 165.78, 143.51, 138.62, 138.19, 138.08, 133.32, 132.88, 129.98, 129.75, 129.51, 128.45, 128.42, 128.39, 128.26, 128.03, 127.93, 127.83, 127.73, 127.63, 127.55, 127.47, 98.07, 94.09, 93.56, 81.98, 79.99, 77.67, 75.72, 74.88, 74.09, 73.33, 69.98, 67.61, 67.13, 66.13, 66.06, 63.66, 55.22; HRMS (ESI-TOF) *m/z* 949.3407 (949.3411 calcd for C<sub>54</sub>H<sub>54</sub>O<sub>14</sub>Na, [M+Na]<sup>+</sup>).

**Trisaccharide 8- $\beta$** : Colorless syrup; *R*<sub>f</sub> 0.67 (1/1 hexane/EtOAc); [ $\alpha$ ]<sup>32</sup><sub>D</sub> +110.6° (*c* 0.64, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS)  $\delta$  8.06-7.98 (4H, m, ArH), 7.59-7.22 (21H, m, ArH), 6.75 (1H, dd,  $J_{2',3'} =$

10.5 Hz,  $J_{1',2'} = 1.7$  Hz, H-2'), 6.12 (1H, dd,  $J_{2',3'} = 10.5$  Hz,  $J_{1',3'} = 1.4$  Hz, H-3'), 5.99 (1H, br-d,  $J_{2'',3''} = 10.2$  Hz, H-3''), 5.85 (1H, ddd,  $J_{2'',3''} = 10.0$  Hz,  $J_{1'',2''} = J_{2'',4''} = 2.2$  Hz, H-2''), 5.68 (1H, m, H-4''), 5.17 (1H, br-d,  $J_{1',2'} = 1.7$  Hz, H-1'), 5.10 (1H, m, H-1''), 4.99 & 4.80 (2H, ABq,  $J = 10.7$  Hz, ArCH<sub>2</sub>), 4.88 & 4.60 (2H, ABq,  $J = 11.2$  Hz, ArCH<sub>2</sub>), 4.76 & 4.64 (2H, ABq,  $J = 11.4$  Hz, ArCH<sub>2</sub>), 4.58-4.52 (1H, m, H-6''), 4.57 (1H, d,  $J_{1,2} = 3.6$  Hz, H-1), 4.48-4.39 (2H, m, H-5'' & H-6''), 4.27 (1H, m, H-5'), 4.21 (1H, dd,  $J_{6',6'} = 11.0$  Hz,  $J_{5',6'} = 4.9$  Hz, H-6'), 4.06 (1H, m, H-6), 3.99 (1H, dd,  $J_{2,3} = 9.5$  Hz,  $J_{3,4} = 9.0$  Hz, H-3), 3.96 (1H, dd,  $J_{6',6'} = 11.0$  Hz,  $J_{5',6'} = 3.2$  Hz, H-6'), 3.78-3.71 (2H, m, H-5 & H-6), 3.52 (1H, dd,  $J_{4,5} = 9.7$  Hz,  $J_{3,4} = 9.0$  Hz, H-4), 3.49 (1H, dd,  $J_{2,3} = 9.5$  Hz,  $J_{1,2} = 3.4$  Hz, H-2), 3.31 (3H, s, OMe); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  193.63, 166.32, 165.80, 146.68, 138.72, 138.38, 138.11, 133.39, 132.95, 129.94, 129.79, 129.54, 129.38, 128.98, 128.49, 128.42, 128.32, 128.11, 128.01, 127.95, 127.90, 127.85, 127.81, 127.65, 98.07, 95.90, 94.59, 82.15, 79.90, 78.24, 75.77, 74.80, 73.32, 69.70, 67.54, 67.35, 67.25, 66.16, 63.76, 55.21; HRMS (ESI-TOF)  $m/z$  949.3402 (949.3411 calcd for C<sub>54</sub>H<sub>54</sub>O<sub>14</sub>Na, [M+Na]<sup>+</sup>).

### General glycosylation procedure in Table 2.

A suspension of glycosyl donor (2,3-dideoxy glycosyl acetate **10** (0.05 mmol) or 2,3-unsaturated-4-keto glycosyl acetate **2** (0.05 mmol)), methyl 2,3,4-tri-*O*-benzyl- $\alpha$ -D-glucopyranoside (**3**) (0.05 mmol) and MS 5A (100 wt% to glycosyl donor) in dry CH<sub>2</sub>Cl<sub>2</sub> (40  $\mu$ L/mg to glycosyl donor) was stirred for 30 minutes at 25 °C, and then to the suspension was added an activator as listed in Table 2. After the suspension was stirred at the temperature and for the period as shown in Table 2, pyridine was added to the reaction mixture to quench the reaction. The resulting mixture was poured into water, and extracted with ethyl acetate. The extracts were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in *vacuo*. Purification of the residue by flash silica-gel column chromatography (hexane/ether=1/1 (for the glycosylation using **10**) or hexane/ethyl acetate=1/1 (for the glycosylation using **2**)) afforded

disaccharide **12** and recovered **10** or disaccharide **5** and recovered **2** as indicated in Table 2. The  $\alpha$ : $\beta$  ratios were determined by  $^1\text{H-NMR}$  analysis.

**Disaccharide 12- $\alpha$ .** Colorless syrup;  $R_f$  0.38 (9/1 toluene/EtOAc);  $[\alpha]_D^{32} +65.3^\circ$  ( $c$  3.63,  $\text{CHCl}_3$ ); NMR:  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , TMS)  $\delta$  7.95 (2H, dd,  $J_{o,m}=8.5$  Hz,  $J_{o,p}=1.2$  Hz,  $H_o$  of Bz), 7.52 (1H, tt,  $J_{m,p}=7.4$  Hz,  $J_{o,p}=1.2$  Hz,  $H_p$  of Bz), 7.39-7.19 (23H, m, ArH), 4.99 & 4.81 (2H, ABq,  $J=12.0$  Hz, ArCH<sub>2</sub>), 4.95 & 4.62 (2H, ABq,  $J=11.4$  Hz, ArCH<sub>2</sub>), 4.85 (1H, br-s, H-1'), 4.77 & 4.67 (2H, ABq,  $J=12.0$  Hz, ArCH<sub>2</sub>), 4.63 & 4.43 (2H, ABq,  $J=11.7$  Hz, ArCH<sub>2</sub>), 4.61 (1H, d,  $J_{1,2}=3.5$  Hz, H-1'), 4.48-4.37 (2H, m, H-6' $\times$ 2), 4.01 (1H, dd,  $J_{2,3}=J_{3,4}=9.0$  Hz, H-3), 3.99-3.94 (1H, m, H-5'), 3.89 (1H, dd,  $J_{6,6}=11.0$  Hz,  $J_{5,6}=5.0$  Hz, H-6), 3.77 (1H, ddd,  $J_{4,5}=9.0$  Hz,  $J_{5,6}=5.0$  Hz,  $J_{5,6}=1.5$  Hz, H-5), 3.62 (1H, dd,  $J_{6,6}=11.0$  Hz,  $J_{5,6}=1.5$  Hz, H-6), 3.52 (1H, dd,  $J_{3,4}=J_{4,5}=9.0$  Hz, H-4), 3.51 (1H, dd,  $J_{2,3}=9.0$  Hz,  $J_{1,2}=3.5$  Hz, H-2), 3.46 (1H, ddd,  $J_{3',4'}=J_{4',5'}=10.2$  Hz,  $J_{3',4'}=4.5$  Hz, H-4'), 3.37 (3H, s, OMe), 2.11-2.06 (1H, m, H-3'), 1.93-1.67 (3H, m, H-2' $\times$ 2 & H-3); Anal. Calcd for  $\text{C}_{48}\text{H}_{52}\text{O}_{10}$ : C, 73.08; H, 6.64. Found: C, 72.78; H, 6.69; HRMS (ESI-TOF)  $m/z$  811.3450 (811.3458 calcd for  $\text{C}_{48}\text{H}_{52}\text{O}_{10}\text{Na}$ ,  $[\text{M}+\text{Na}]^+$ ).

**Disaccharide 12- $\beta$ .** Colorless syrup;  $R_f$  0.27 (9/1 toluene/EtOAc);  $[\alpha]_D^{32} +30.1^\circ$  ( $c$  2.86,  $\text{CHCl}_3$ ); NMR:  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , TMS)  $\delta$  7.99 (2H, dd,  $J_{o,m}=8.3$  Hz,  $J_{o,p}=1.2$  Hz,  $H_o$  of Bz), 7.53 (1H, tt,  $J_{m,p}=7.3$  Hz,  $J_{o,p}=1.2$  Hz,  $H_p$  of Bz), 7.41-7.21 (23H, m, ArH), 4.97 & 4.79 (2H, ABq,  $J=11.0$  Hz, ArCH<sub>2</sub>), 4.85 & 4.55 (2H, ABq,  $J=11.2$  Hz, ArCH<sub>2</sub>), 4.78 & 4.64 (2H, ABq,  $J=11.9$  Hz, ArCH<sub>2</sub>), 4.60 & 4.43 (2H, ABq,  $J=11.5$  Hz, ArCH<sub>2</sub>), 4.59 (1H, d,  $J_{1,2}=3.7$  Hz, H-1), 4.59-4.53 (1H, m, H-6'), 4.47 (1H,  $J_{6',6'}=11.7$  Hz,  $J_{5',6'}=5.6$  Hz, H-6'), 4.35 (1H, dd,  $J_{1',2'}=9.3$  Hz,  $J_{1',2'}=2.1$  Hz, H-1'), 4.05 (1H, dd,  $J_{6',6'}=11.7$  Hz,  $J_{5',6'}=2.0$  Hz, H-6'), 4.00 (1H, dd,  $J_{2,3}=J_{3,4}=9.2$  Hz, H-3), 3.73 (1H, m, H-5), 3.68-3.57 (2H, m, H-6 & H-5'), 3.61 (1H, dd,  $J_{6,6}=10.5$  Hz,  $J_{5,6}=10.0$  Hz, H-6), 3.54 (1H, dd,  $J_{3,4}=J_{4,5}=9.0$  Hz, H-4), 3.52 (1H, dd,  $J_{2,3}=9.2$  Hz,  $J_{1,2}=3.7$  Hz, H-2), 3.41 (1H, ddd,  $J_{3',4'}=J_{4',5'}=9.2$  Hz,  $J_{3',4'}=5.3$  Hz, H-4'), 3.31 (3H, s, OMe), 2.29-2.24 (1H, m, H-3'), 1.83-1.42 (3H, m, H-2' $\times$ 2 &



H-3); HRMS (ESI-TOF)  $m/z$  811.3448 (811.3458 calcd for  $C_{48}H_{52}O_{10}Na$ ,  $[M+Na]^+$ ).

### Chemoselective glycosylation using **10** and **6**.

A suspension of 2,3-dideoxy glycosyl acetate **10** (41.3 mg, 0.107 mmol), 2,3-unsaturated-4-keto glycosyl acetate **6** (10.0 mg, 0.054 mmol) and MS 5A (100 wt% to glycosyl donor) in dry  $CH_2Cl_2$  (40  $\mu$ L/mg to glycosyl donor) was stirred for 30 minutes at 25 °C, and then to the suspension was added TMSOTf (3.1  $\mu$ L 0.016 mmol) at -50 °C. After the suspension was stirred at -50 °C and for 1 h, pyridine was added to the reaction mixture to quench the reaction. The resulting mixture was poured into water, and extracted with ethyl acetate. The extracts were washed with brine, dried over anhydrous  $Na_2SO_4$  and concentrated in *vacuo*. Purification of the residue by preparative TLC (hexane/ethyl acetate=1/1) afforded disaccharide **13** (24.1 mg, 88%,  $\alpha:\beta$  = 89/11). The  $\alpha:\beta$  ratio was determined by  $^1H$ -NMR analysis.

**Disaccharide 13- $\alpha$** . Colorless syrup;  $R_f$  0.40 (3/5/3 hexane/chloroform/ether);  $[\alpha]^{32}_D +2.7^\circ$  ( $c$  6.75,  $CHCl_3$ ); NMR:  $^1H$ -NMR ( $CDCl_3$ , TMS)  $\delta$  8.03 (2H, dd,  $J_{o,m}=8.3$  Hz,  $J_{o,p}=1.2$  Hz,  $H_o$  of Bz), 7.58 (1H, tt,  $J_{m,p}=7.3$  Hz,  $J_{o,p}=1.2$  Hz,  $H_p$  of Bz), 7.41 (2H, dd,  $J_{o,m}=8.3$  Hz,  $J_{m,p}=7.3$  Hz,  $H_m$  of Bz), 7.32-7.17 (5H, m, ArH), 6.96 (1H, dd,  $J_{2,3}=10.2$  Hz,  $J_{1,2}=3.7$  Hz, H-2), 6.57 (1H, d,  $J_{1,2}=3.7$  Hz, H-1), 6.26 (1H, d,  $J_{2,3}=10.2$  Hz, H-3), 4.82 (1H, br-s, H-1'), 4.64 (1H, dd,  $J_{5,6}=3.9$  Hz,  $J_{5,6}=2.7$  Hz, H-5), 4.63 & 4.46 (2H, ABq,  $J=11.9$  Hz,  $ArCH_2$ ), 4.61 (1H, dd,  $J_{6',6''}=11.7$  Hz,  $J_{5',6''}=2.5$  Hz, H-6'), 4.55 (1H, dd,  $J_{6',6''}=11.7$  Hz,  $J_{5',6''}=4.9$  Hz, H-6'), 4.23 (1H, dd,  $J_{6,6''}=11.0$  Hz,  $J_{5,6''}=3.9$  Hz, H-6), 4.00 (1H, ddd,  $J_{4',5'}=10.0$  Hz,  $J_{5',6''}=4.9$  Hz,  $J_{5',6''}=2.5$  Hz, H-5'), 3.76 (1H, dd,  $J_{6,6''}=11.0$  Hz,  $J_{5,6''}=2.7$  Hz, H-6), 3.47 (1H, ddd,  $J_{3',4'}=J_{4',5'}=10.0$  Hz,  $J_{3',4'}=4.4$  Hz, H-4'), 2.13 (3H, s, OAc), 2.10-2.03 (1H, m, H-3'), 1.91-1.85 (1H, m, H-2'), 1.77-1.68 (2H, m, H-2' & H-3'); Anal. Calcd for  $C_{28}H_{30}O_9$ : C, 65.87; H, 5.92. Found: C, 65.88; H, 6.09; HRMS (ESI-TOF)  $m/z$  533.1783 (533.1788 calcd for  $C_{28}H_{30}O_9Na$ ,  $[M+Na]^+$ ).

**Disaccharide 13- $\beta$** . Colorless syrup;  $R_f$  0.37 (3/5/3 hexane/chloroform/ether); NMR:  $^1H$ -NMR

(CDCl<sub>3</sub>, TMS)  $\delta$ 8.01 (2H, dd,  $J_{o,m}$ =8.3 Hz,  $J_{o,p}$ =1.5 Hz, H<sub>o</sub> of Bz), 7.55 (1H, tt,  $J_{m,p}$ =6.6 Hz,  $J_{o,p}$ =1.5 Hz, H<sub>p</sub> of Bz), 7.42 (2H, dd,  $J_{o,m}$ =8.3 Hz,  $J_{m,p}$ =6.6 Hz, H<sub>m</sub> of Bz), 7.29-7.19 (5H, m, ArH), 6.90 (1H, dd,  $J_{2,3}$ =10.2 Hz,  $J_{1,2}$ =3.7 Hz, H-2), 6.54 (1H, d,  $J_{1,2}$ =3.7 Hz, H-1), 6.19 (1H, d,  $J_{2,3}$ =10.2 Hz, H-3), 4.71 (1H, dd,  $J_{5,6}$ =5.6 Hz,  $J_{5,6'}$ =2.2 Hz, H-5), 4.66-4.53 (1H, m, H-6'), 4.61 & 4.45 (2H, ABq,  $J$ =11.5 Hz, ArCH<sub>2</sub>), 4.57 (1H, dd,  $J_{1,2}$ =9.2 Hz,  $J_{1,2'}$ =2.4 Hz, H-1'), 4.51-4.44 (1H, m, H-6'), 4.30 (1H, dd,  $J_{6,6}$ =11.7 Hz,  $J_{5,6}$ =2.2 Hz, H-6), 3.92 (1H, dd,  $J_{6,6}$ =11.7 Hz,  $J_{5,6}$ =5.6 Hz, H-6), 3.73 (1H, ddd,  $J_{4',5'}$ =9.0 Hz,  $J_{5',6'}$ =6.0 Hz,  $J_{5',6}$ =3.0 Hz, H-5'), 3.45 (1H, m, H-4'), 2.08 (3H, s, OAc), 2.35-2.25 (1H, m, H-3'), 1.95-1.91 (1H, m, H-2'), 1.65-1.51 (2H, m, H-2' & H-3'). This compound was found to be too unstable to precisely measure other data.

### Synthesis of trisaccharide 14 by glycosylation using 13- $\alpha$ and 3.

A suspension of disaccharide **13- $\alpha$**  (22.6 mg, 0.0443 mmol), methyl 2,3,4-tri-*O*-benzyl- $\alpha$ -D-glucopyranoside (**3**) (10.3 mg, 0.0222 mmol) and MS 5A (22.6 mg, 100 wt% to glycosyl donor) in dry toluene (0.904 mL, 40  $\mu$ L/mg to glycosyl donor) was stirred for 30 min at 25 °C, and then to the suspension was added TMSOTf (2.6  $\mu$ L 0.013 mmol) at -35 °C. After the suspension was stirred at -35 °C for 30 min, pyridine was added to the reaction mixture to quench the reaction. The resulting mixture was poured into water, and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated in *vacuo*. Purification of the residue by flash silica-gel column chromatography (hexane/EtOAc = 1/1) afforded trisaccharide **14** (16.4 mg, 81%,  $\alpha$ : $\beta$  = 78:22). The  $\alpha$ : $\beta$  ratio was determined by <sup>1</sup>H-NMR analysis.

**Trisaccharide 14- $\alpha$** : Colorless syrup;  $R_f$  0.43 (3/5/3 hexane/chloroform/ether);  $[\alpha]_D^{31}$  +28.6° (c 5.05, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS)  $\delta$ 8.02 (2H, dd,  $J_{o,m}$  = 8.3 Hz,  $J_{o,p}$  = 1.2 Hz, H<sub>o</sub> of Bz), 7.52 (1H, tt,  $J_{m,p}$  = 6.6 Hz,  $J_{o,p}$  = 1.2 Hz, H<sub>p</sub> of Bz), 7.39 (2H, dd,  $J_{o,m}$  = 8.3 Hz,  $J_{m,p}$  = 6.6 Hz, H<sub>m</sub> of Bz), 7.36-7.16 (20H, m, ArH), 6.84 (1H, dd,  $J_{2',3'}$  = 10.2 Hz,  $J_{1',2'}$  = 3.7 Hz, H-2'), 6.09 (1H, d,  $J_{2',3'}$  =

10.2 Hz, H-3'), 5.34 (1H, d,  $J_{1',2'} = 3.7$  Hz, H-1'), 4.98 & 4.80 (2H, ABq,  $J = 11.0$  Hz, ArCH<sub>2</sub>), 4.89 & 4.57 (2H, ABq,  $J = 11.2$  Hz, ArCH<sub>2</sub>), 4.79 & 4.66 (2H, ABq,  $J = 12.2$  Hz, ArCH<sub>2</sub>), 4.77 (1H, br-s, H-1''), 4.63-4.49 (3H, m, H-5', H-6'' × 2), 4.61 & 4.43 (2H, ABq,  $J = 11.9$  Hz, ArCH<sub>2</sub>), 4.59 (1H, br, H-1), 4.10 (1H, dd,  $J_{6',6'} = 10.7$  Hz,  $J_{5',6'} = 4.9$  Hz, H-6'), 4.05-4.00 (2H, m, H-6, H-5''), 4.00 (1H, dd,  $J_{2,3} = J_{3,4} = 9.8$  Hz, H-3), 3.82-3.75 (2H, m, H-5, H-6), 3.67 (1H, dd,  $J_{6',6'} = 10.7$  Hz,  $J_{5',6'} = 2.7$  Hz, H-6'), 3.52 (1H, dd,  $J_{3,4} = J_{4,5} = 9.8$  Hz, H-4), 3.51 (1H, dd,  $J_{2,3} = 9.8$  Hz,  $J_{1,2} = 3.4$  Hz, H-2), 3.43 (1H, ddd,  $J_{3'',4''} = J_{4'',5''} = 9.5$  Hz,  $J_{3'',4''} = 5.4$  Hz, H-4''), 3.34 (3H, s, OMe), 2.04-1.97 (1H, m, H-3''), 1.84-1.62 (3H, m, H-2'' × 2, H-3''); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  193.76, 166.40, 143.51, 138.60, 138.16, 138.05, 132.70, 130.31, 129.62, 128.41, 128.34, 128.31, 128.18, 127.98, 127.88, 127.76, 127.70, 127.65, 127.62, 127.57, 127.45, 97.97, 95.83, 93.40, 81.95, 79.88, 77.67, 75.67, 74.86, 73.92, 73.23, 72.61, 70.35, 70.17, 69.94, 67.44, 64.79, 64.28, 55.14, 28.69, 23.67; HRMS (ESI-TOF)  $m/z$  937.3779 (937.3775 calcd for C<sub>54</sub>H<sub>54</sub>O<sub>14</sub>Na, [M+Na]<sup>+</sup>).

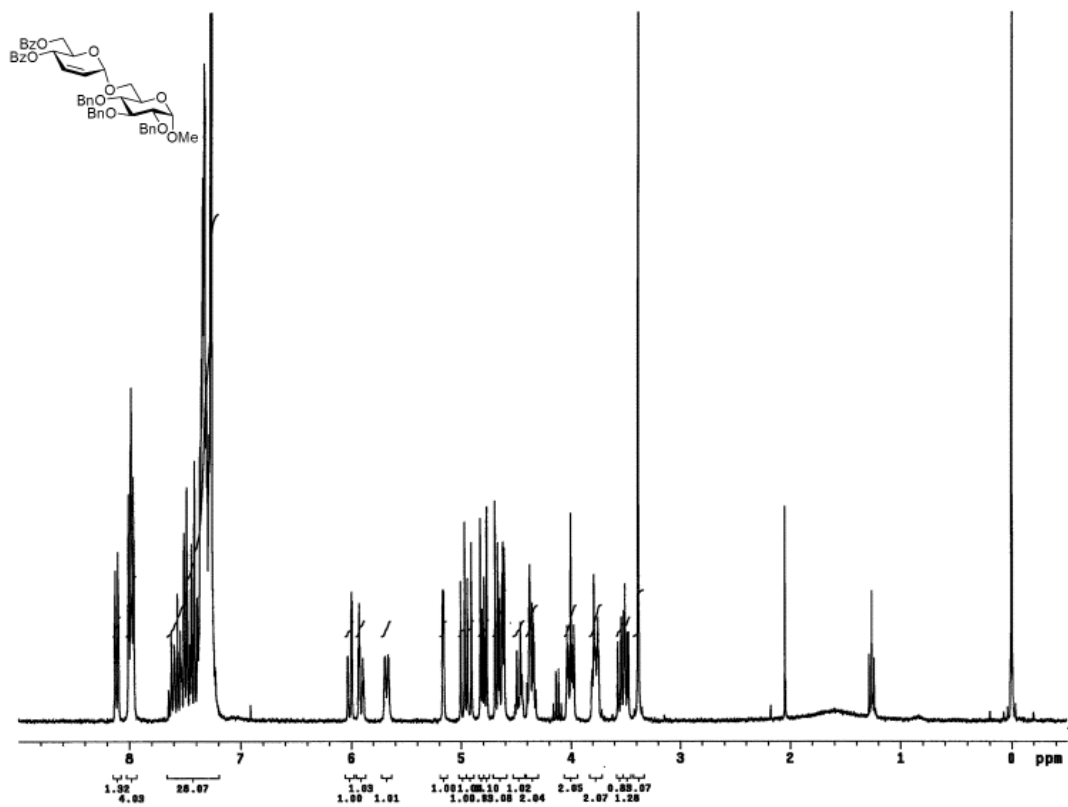
**Trisaccharide 14- $\beta$** : Colorless syrup;  $R_f$  0.38 (3/5/3 hexane/chloroform/ether);  $[\alpha]_D^{31} +86.6^\circ$  ( $c$  0.56, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS)  $\delta$  8.00 (2H, dd,  $J_{o,m} = 8.3$  Hz,  $J_{o,p} = 1.2$  Hz, H<sub>o</sub> of Bz), 7.53 (1H, tt,  $J_{m,p} = 7.3$  Hz,  $J_{o,p} = 1.2$  Hz, H<sub>p</sub> of Bz), 7.41 (2H, dd,  $J_{o,m} = 8.3$  Hz,  $J_{m,p} = 7.3$  Hz, H<sub>m</sub> of Bz), 7.36-7.19 (20H, m, ArH), 6.73 (1H, dd,  $J_{2',3'} = 10.5$  Hz,  $J_{1',2'} = 1.5$  Hz, H-2'), 6.11 (1H, dd,  $J_{2',3'} = 10.5$  Hz,  $J_{1',3'} = 1.5$  Hz, H-3'), 5.13 (1H, br-s, H-1'), 4.99 & 4.80 (2H, ABq,  $J = 10.7$  Hz, ArCH<sub>2</sub>), 4.88 & 4.60 (2H, ABq,  $J = 11.2$  Hz, ArCH<sub>2</sub>), 4.79 (1H, dd,  $J_{1'',2''} = 8.8$  Hz,  $J_{1'',2''} = 2.7$  Hz, H-1''), 4.76 & 4.64 (2H, ABq,  $J = 11.9$  Hz, ArCH<sub>2</sub>), 4.63-4.57 (1H, m, H-6'), 4.62 (1H, d,  $J_{1,2} = 3.4$  Hz, H-1), 4.60 & 4.22 (2H, ABq,  $J = 11.5$  Hz, ArCH<sub>2</sub>), 4.23 (1H, dd,  $J_{5'',6''} = 5.6$  Hz,  $J_{5'',6''} = 3.2$  Hz, H-5''), 4.07 (1H, dd,  $J_{6'',6''} = 11.0$  Hz,  $J_{5'',6''} = 5.6$  Hz, H-6''), 4.09-3.99 (2H, m, H-6 & H-5'), 3.99 (1H, dd,  $J_{2,3} = J_{3,4} = 9.2$  Hz, H-3), 3.82 (1H, dd,  $J_{6'',6''} = 11.0$  Hz,  $J_{5'',6''} = 3.2$  Hz, H-6''), 3.77-3.73 (2H, m, H-5, H-6), 3.55 (1H, dd,  $J_{3,4} = J_{4,5} = 9.2$  Hz, H-4), 3.51-3.41 (3H, m, H-2, H-4' & H-6'), 3.31 (3H, s, OMe), 2.02 (1H, m, H-3''), 1.88-1.63 (3H, m, H-2'' × 2 & H-3''); <sup>13</sup>C NMR (CDCl<sub>3</sub>)

$\delta$ 193.71, 166.45, 146.60, 138.70, 138.39, 138.09, 132.76, 130.30, 129.71, 128.93, 128.45, 128.37, 128.24, 128.11, 128.01, 127.88, 127.76, 127.68, 127.63, 98.01, 96.16, 95.87, 82.17, 79.80, 78.12, 77.15, 75.75, 74.76, 73.27, 72.59, 70.37, 70.26, 69.60, 67.26, 66.00, 64.32, 55.19, 28.72, 23.70; HRMS (ESI-TOF)  $m/z$  937.3763 (937.3775 calcd for  $C_{54}H_{54}O_{14}Na$ ,  $[M+Na]^+$ ).

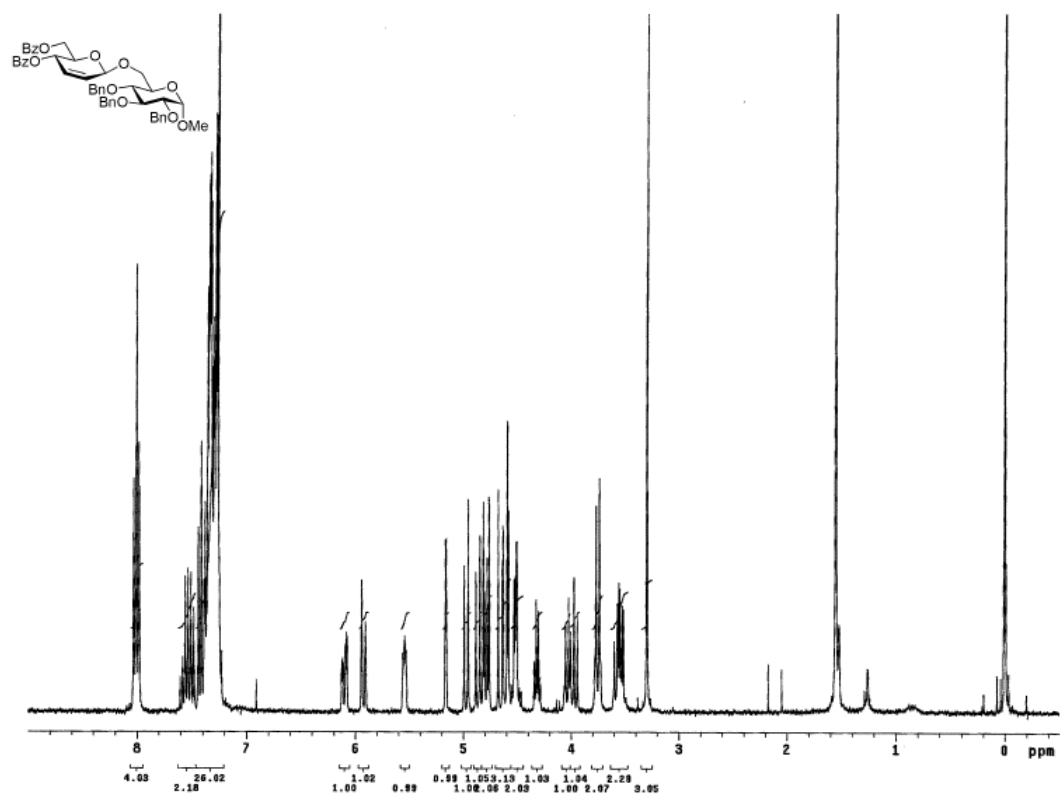
## References

- 1 R. S. Babu, M. Zhou and G. A. O'Doherty, *J. Am. Chem. Soc.* 2004, **126**, 3428.
- 2 K. Sasaki, S. Matsumura and K. Toshima, *Tetrahedron Lett.*, 2006, **47**, 9039.
- 3 The 2,3-unsaturated-4-keto glycosyl donor **2** was prepared from *p*-methoxyphenyl  $\alpha$ -D-erythro-hex-2-enopyranoside in four steps including 1) selective benzylation of the C6 hydroxy group, 2) PDC oxidation of the C4 hydroxy group, 3) deprotection of MP group at the C1 position, and 4) acetylation of the C1 hydroxy group.
- 4 The 2,3-unsaturated-4-keto glycosyl acceptor **6** was prepared from *p*-methoxyphenyl  $\alpha$ -D-erythro-hex-2-enopyranoside in five steps including 1) selective *t*-butyldiphenylsilylation of the C6 hydroxy group, 2) PDC oxidation of the C4 hydroxy group, 3) deprotection of MP group at the C1 position, 4) acetylation of the C1 hydroxy group, and 5) deprotection of TBDPS group at the C6 position.

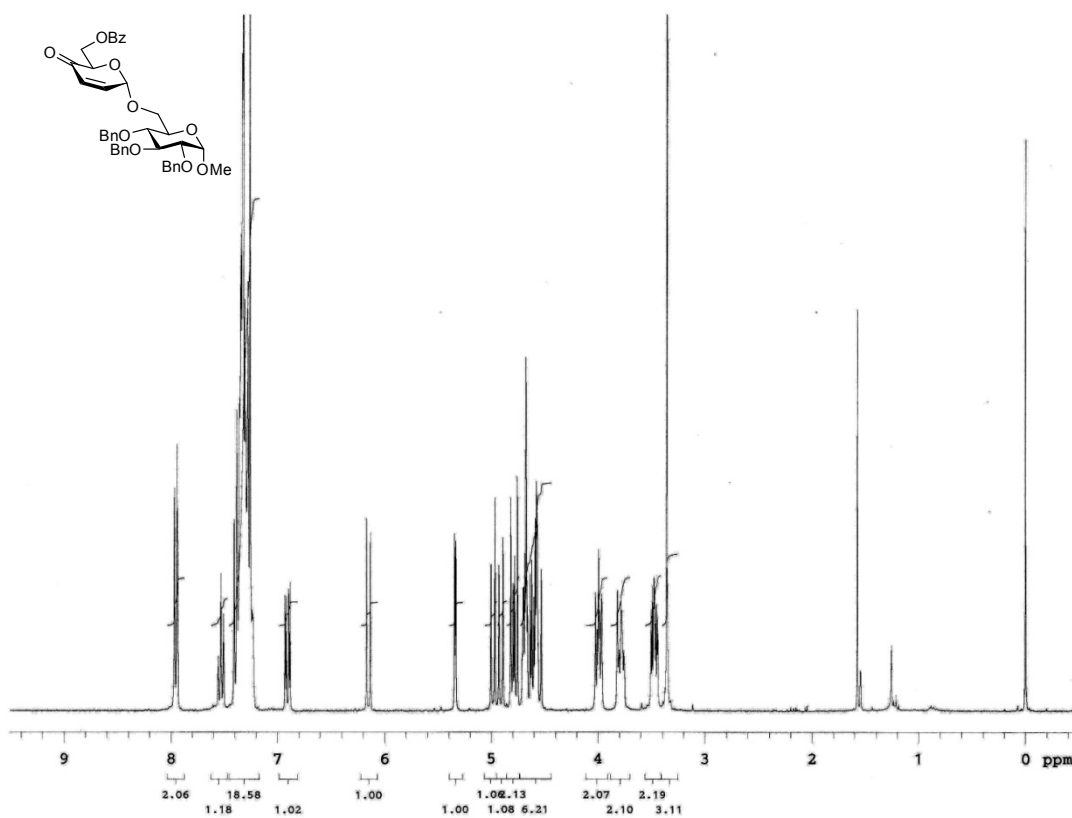
## **$^1\text{H}$ - and $^{13}\text{C}$ -NMR spectrum charts**



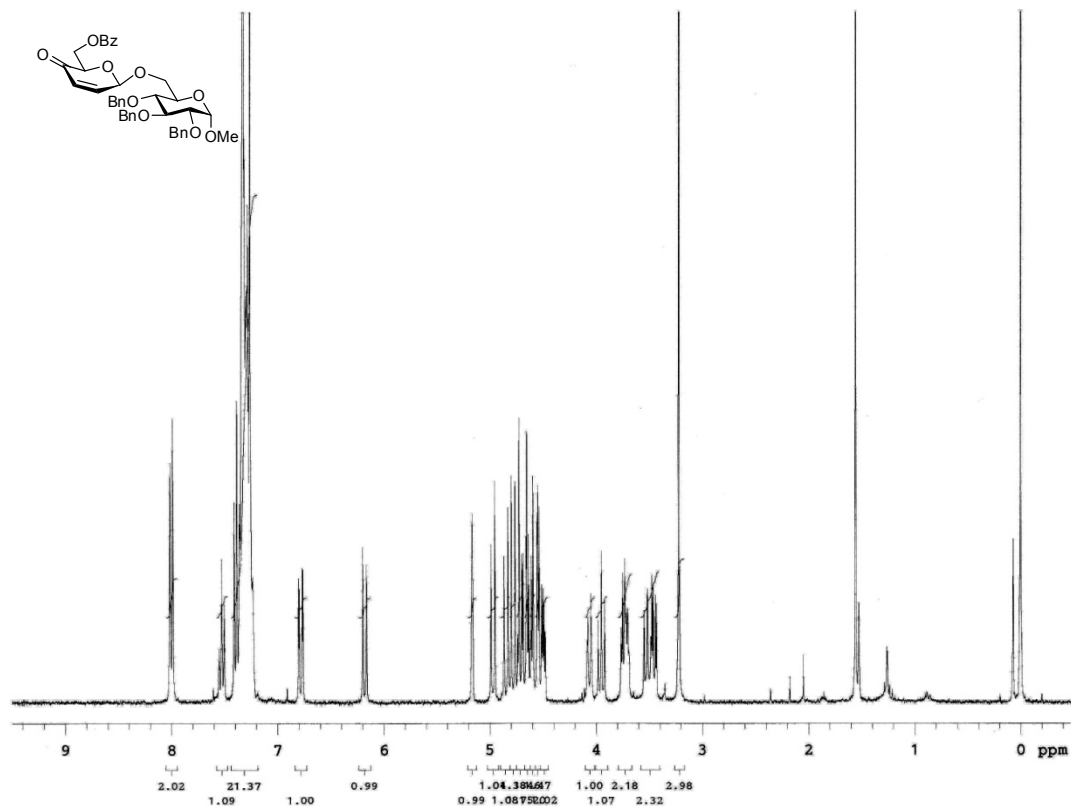
<sup>1</sup>H NMR spectrum of 4- $\alpha$



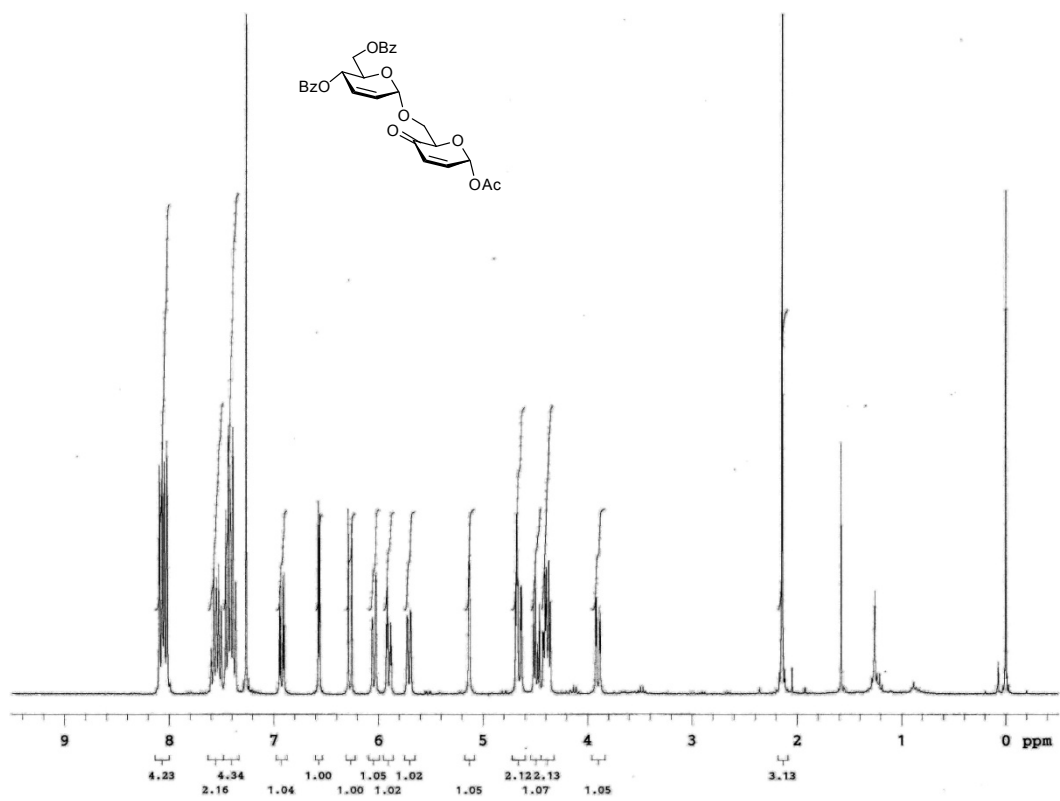
<sup>1</sup>H NMR spectrum of 4- $\beta$



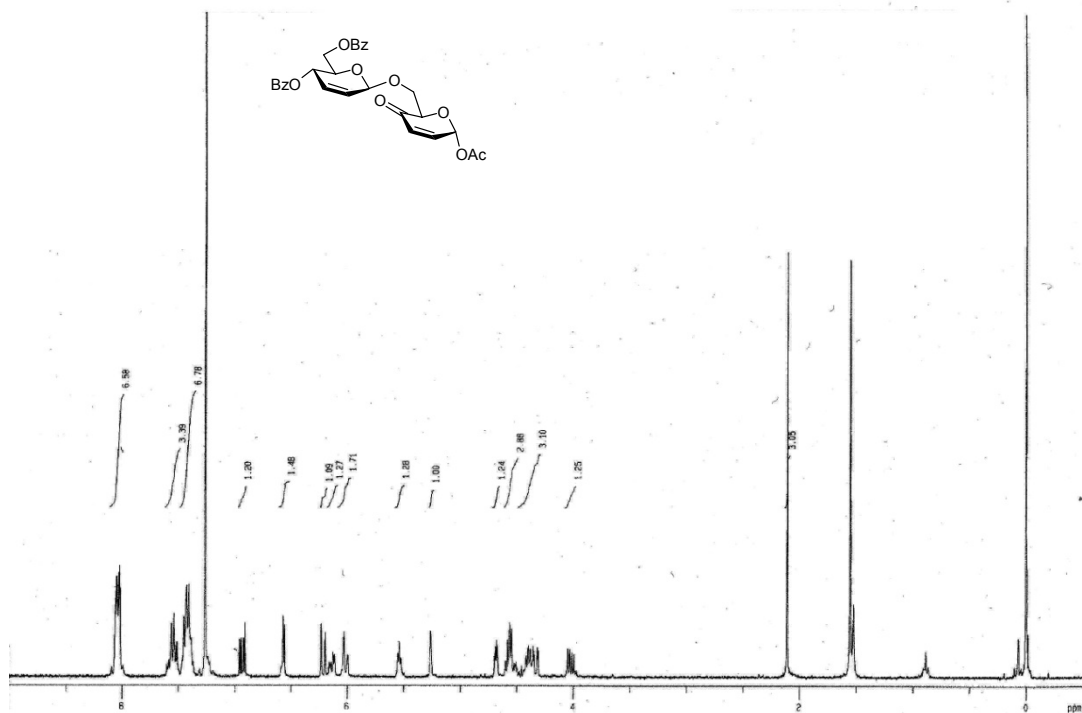
<sup>1</sup>H NMR spectrum of 5-α



<sup>1</sup>H NMR spectrum of 5-β

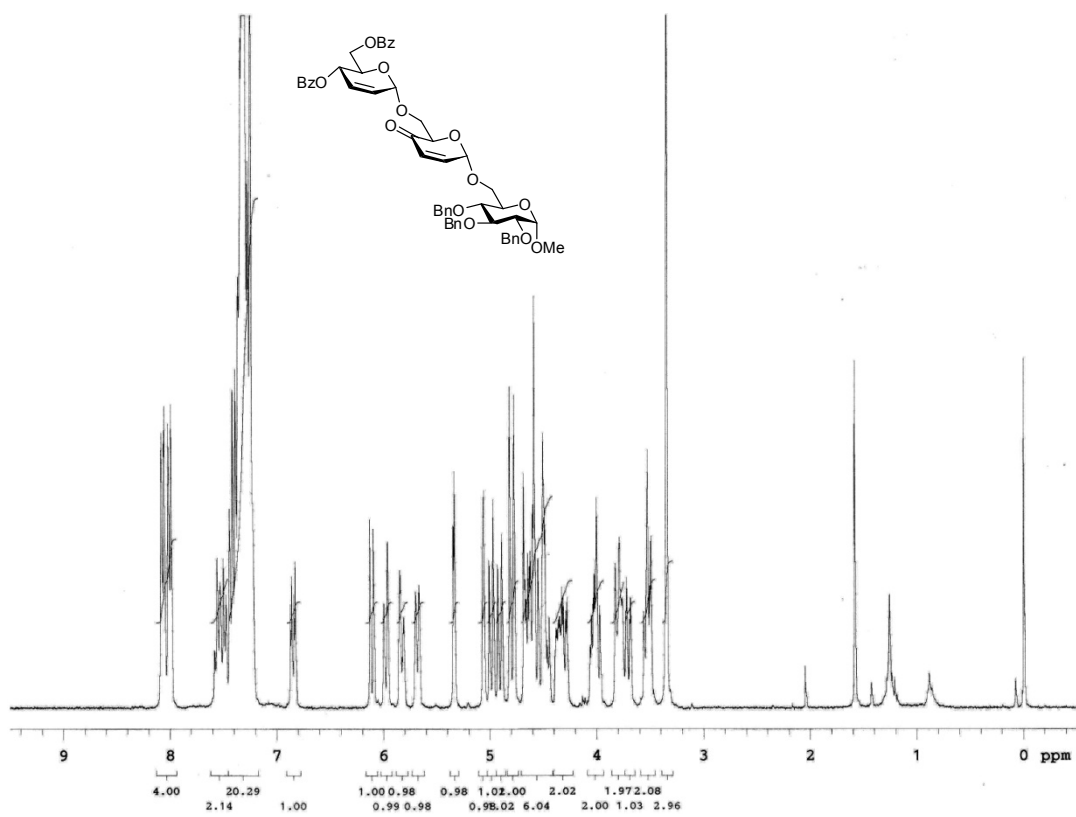


<sup>1</sup>H NMR spectrum of 7-α

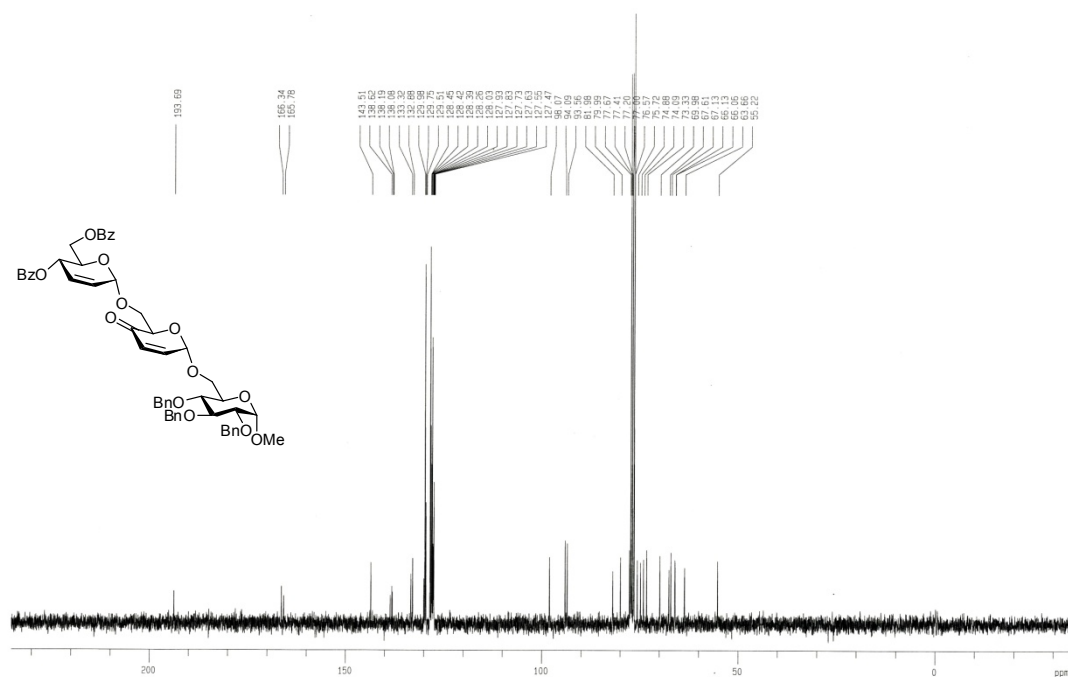


<sup>1</sup>H NMR spectrum of 7-β

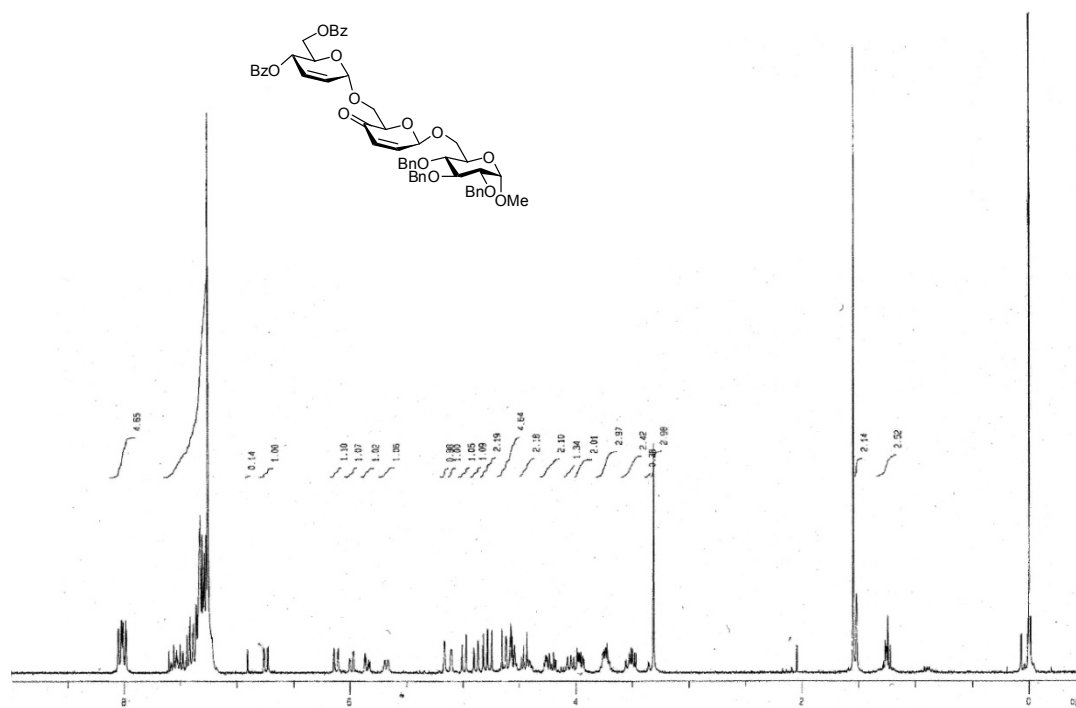




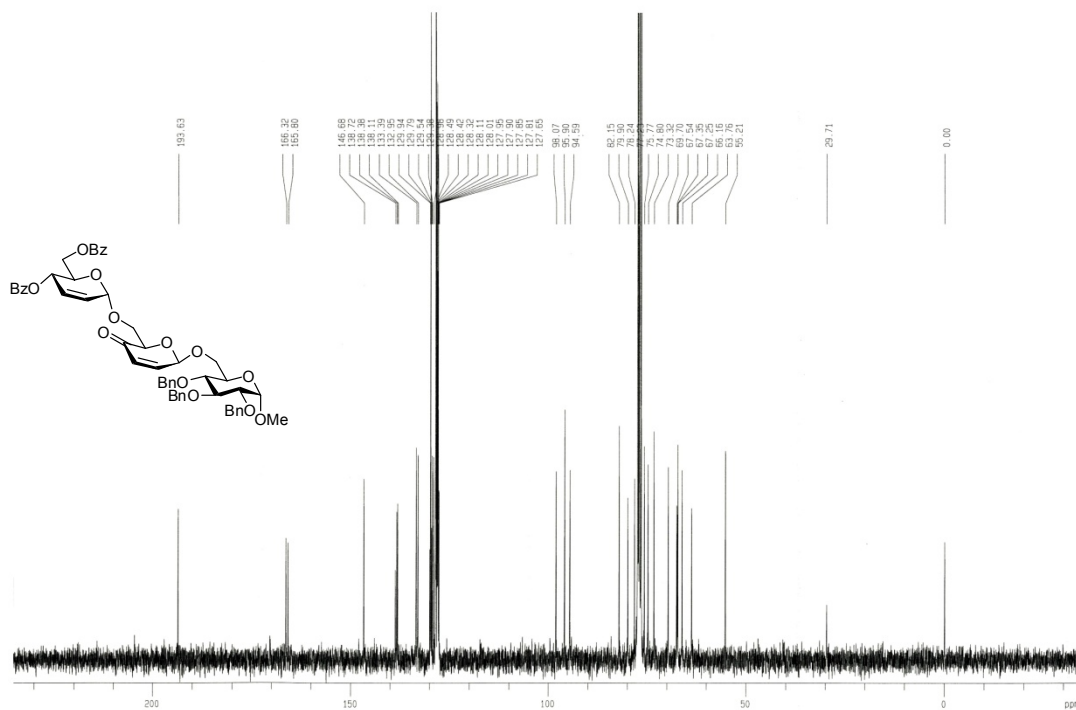
$^1\text{H NMR}$  spectrum of  $8\text{-}\alpha$



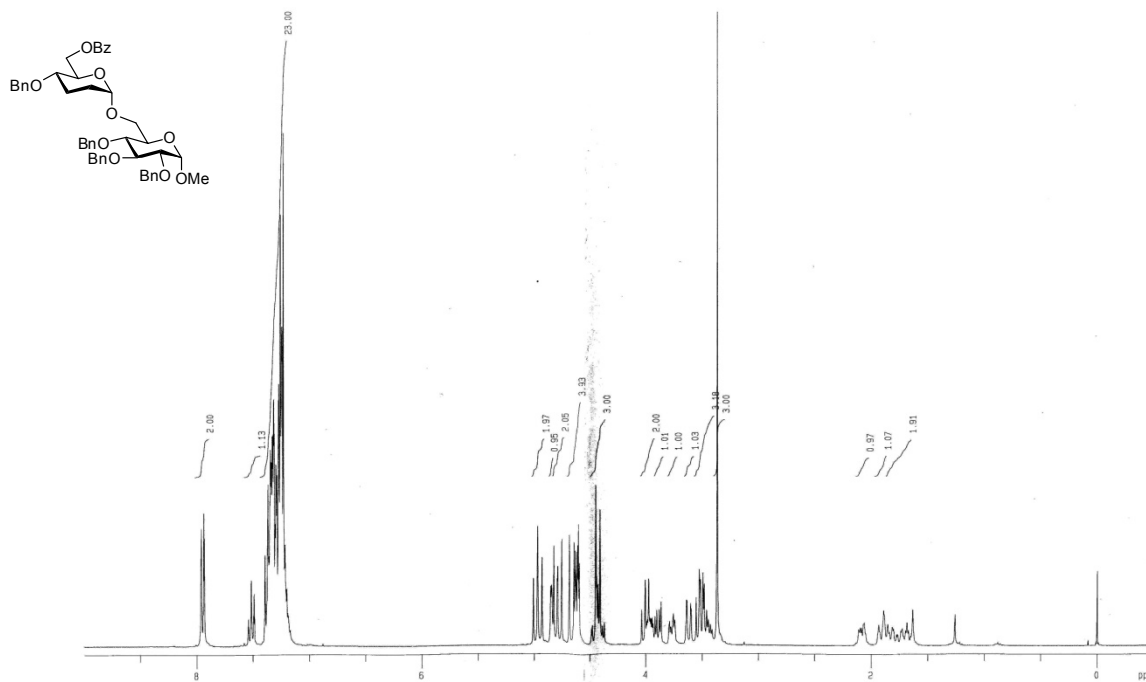
$^{13}\text{C NMR}$  spectrum of  $8\text{-}\alpha$



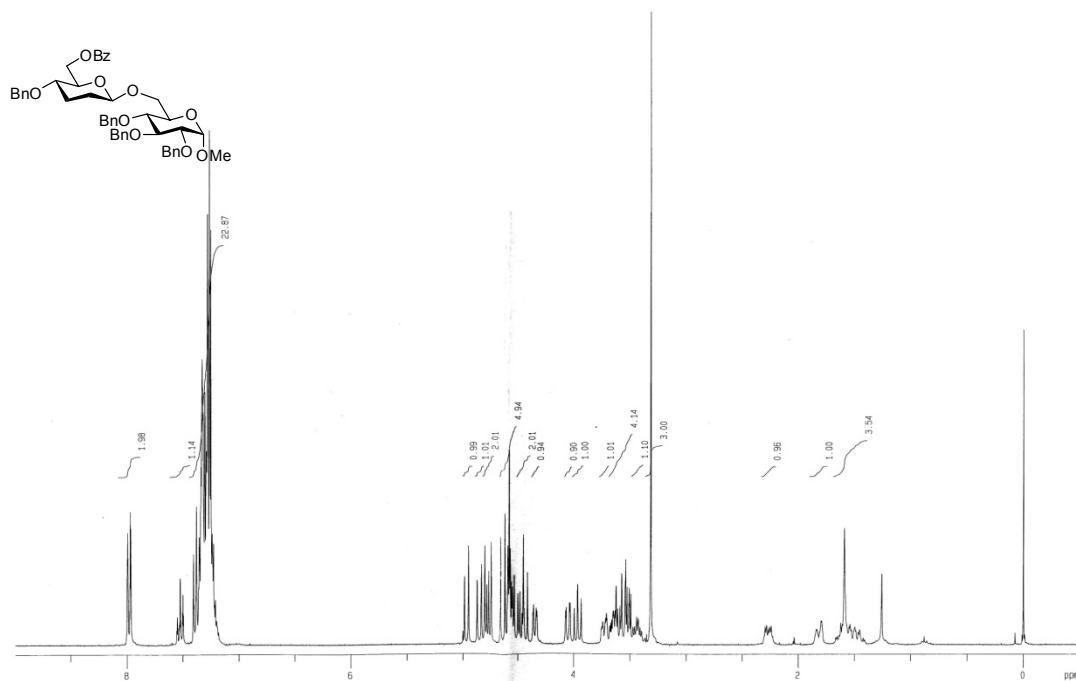
$^1\text{H}$  NMR spectrum of **8- $\beta$**



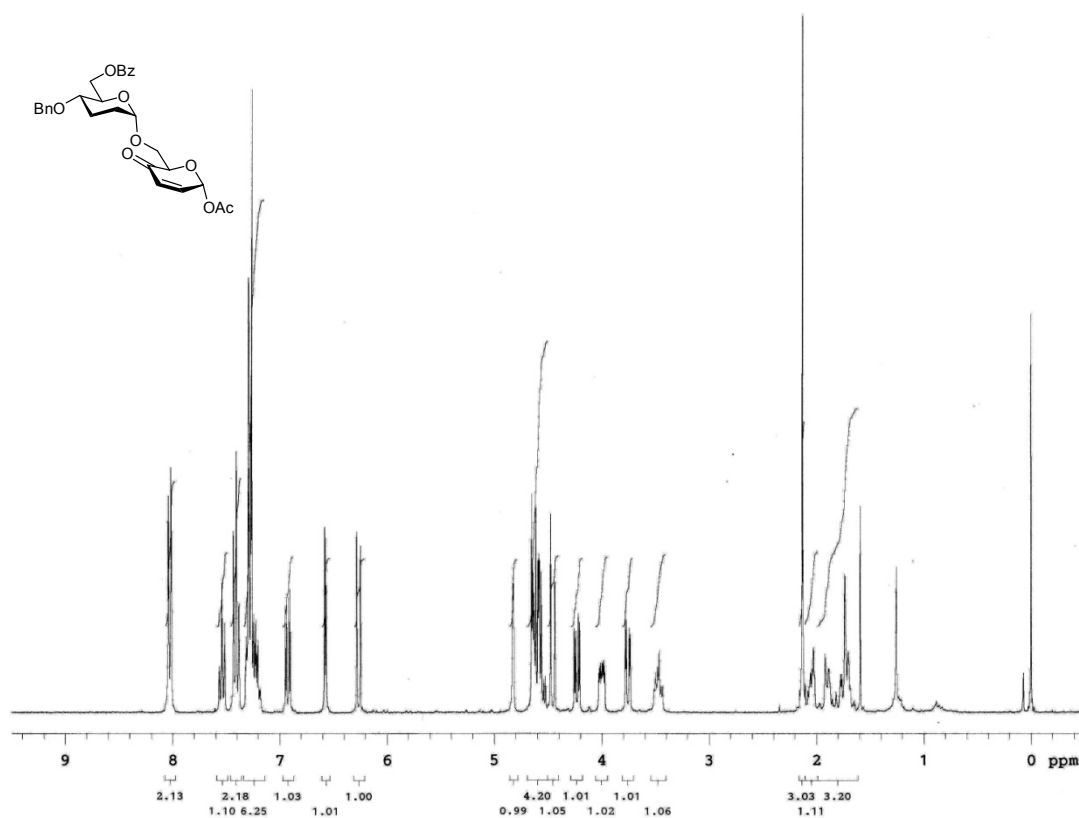
$^{13}\text{C}$  NMR spectrum of **8- $\beta$**



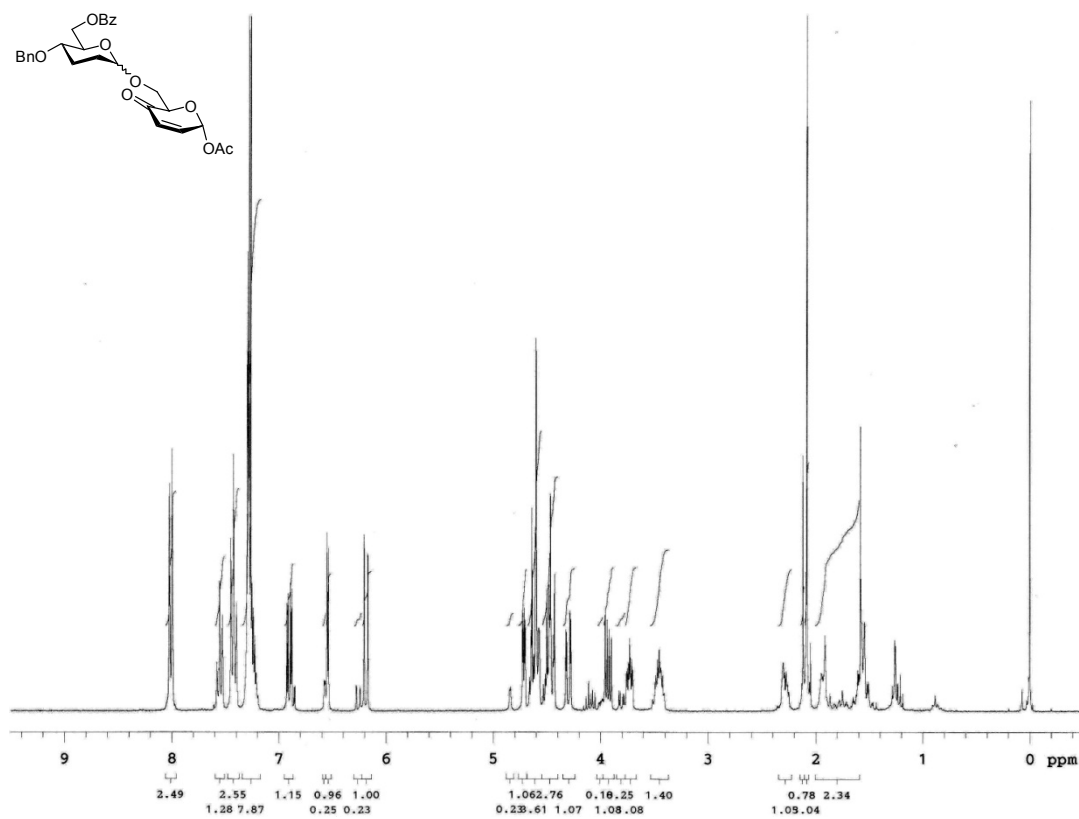
<sup>1</sup>H NMR spectrum of **12-α**



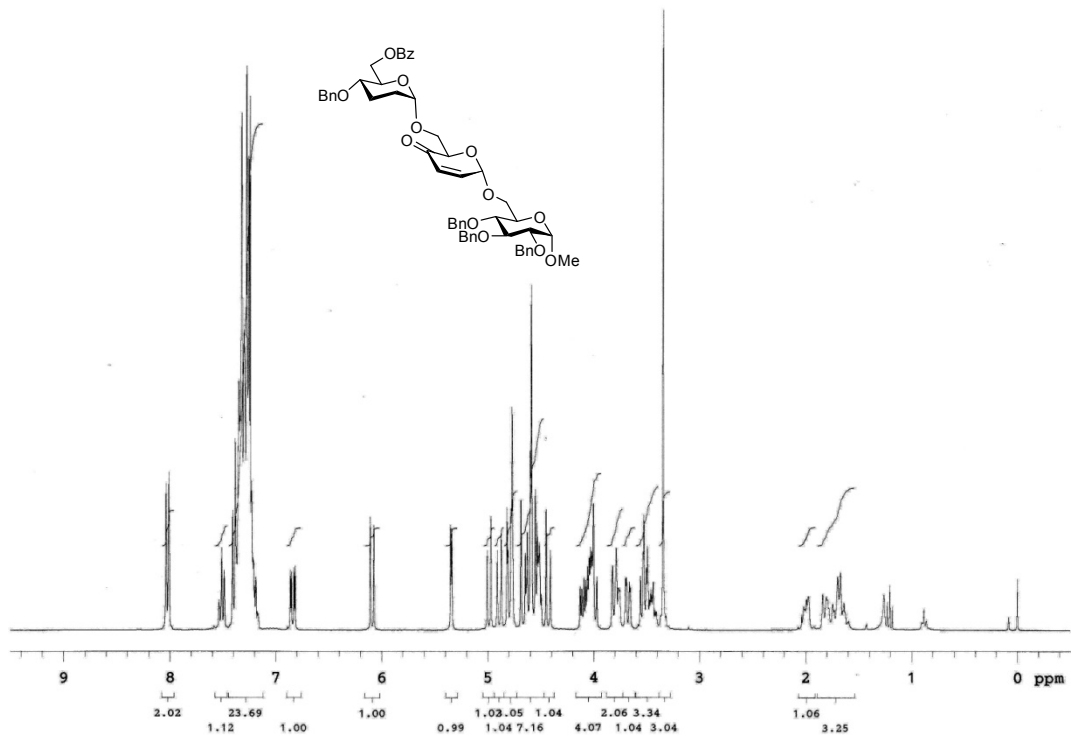
<sup>1</sup>H NMR spectrum of **12-β**



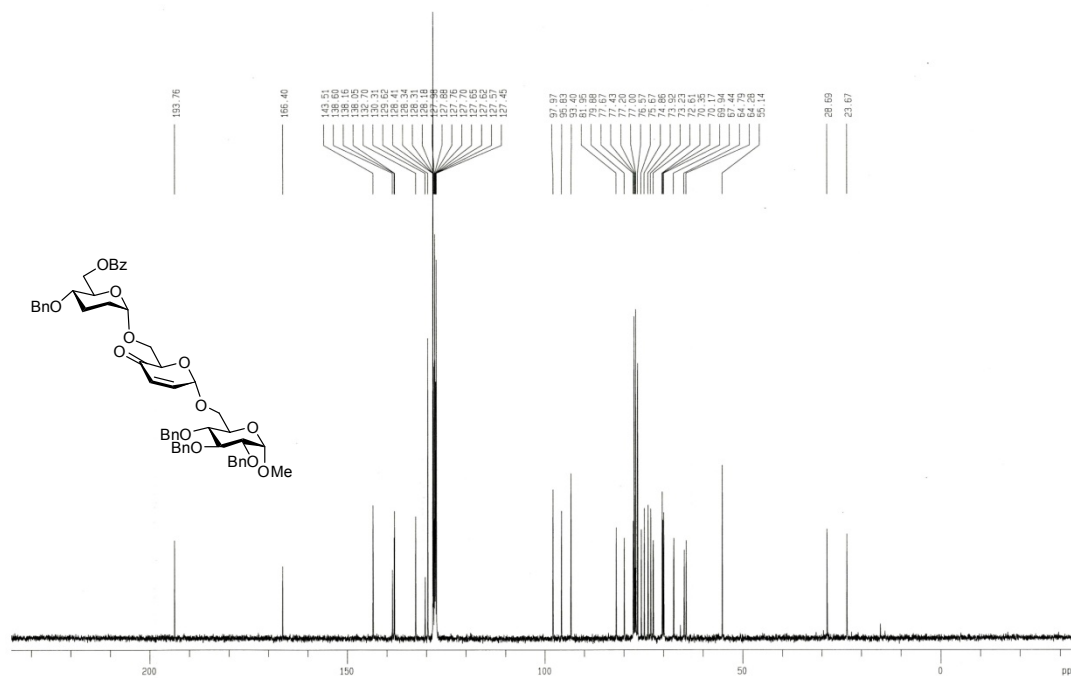
<sup>1</sup>H NMR spectrum of **13-α**



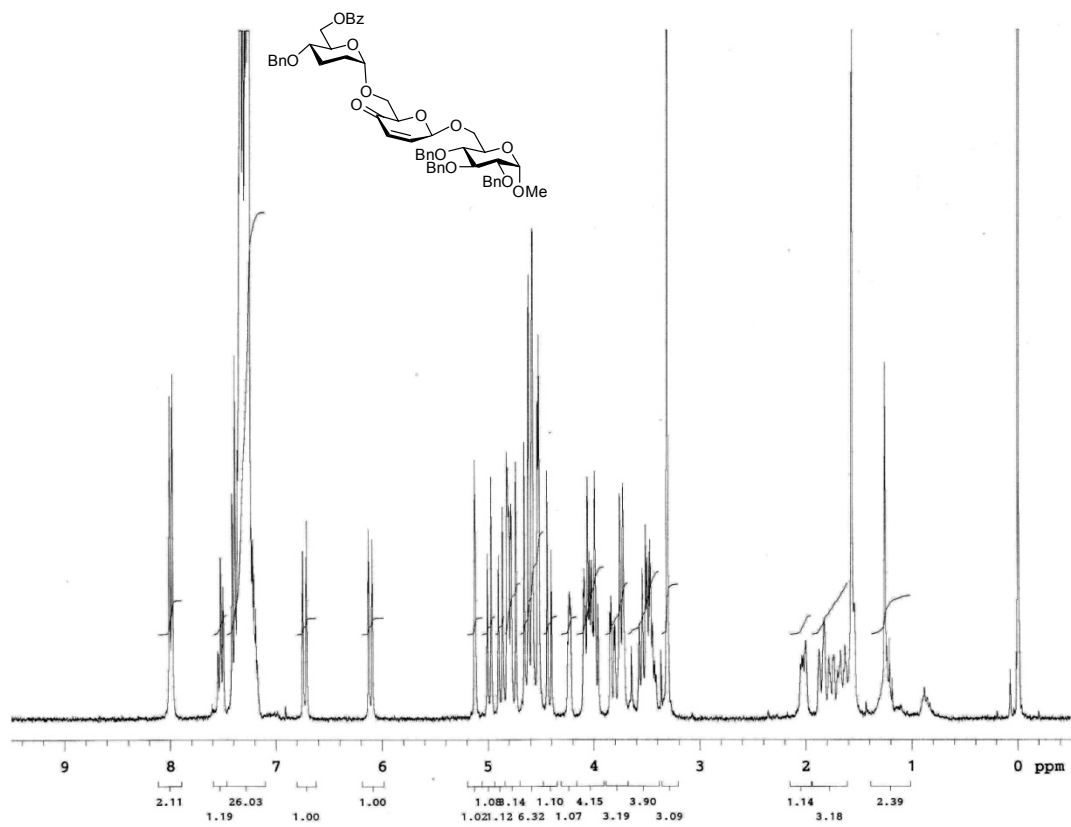
<sup>1</sup>H NMR spectrum of **13** ( $\alpha:\beta = 19:81$ )



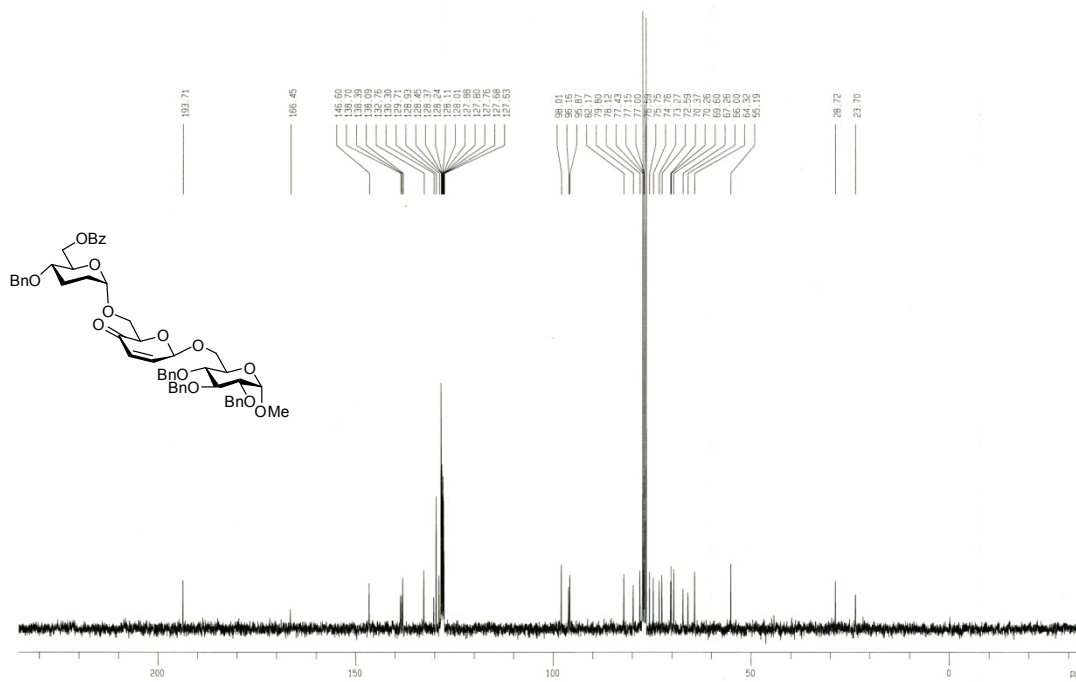
<sup>1</sup>H NMR spectrum of **14-α**



<sup>13</sup>C NMR spectrum of **14-α**



**$^1\text{H}$  NMR spectrum of 14- $\beta$**



**$^{13}\text{C}$  NMR spectrum of 14- $\beta$**