Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

Light-Induced *O*-Glycosylation of Unprotected Deoxythioglycosyl Donors

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General experimental methods

Melting points were determined on a micro hot-stage (Yanako MP-S3). Optical rotations were measured on a JASCO P-2200 polarimeter. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECA-500 (500 MHz and 125 MHz) spectrometer. ^{1}H NMR data are reported as follows; chemical shift in parts par million (ppm) downfield or upfield from tetramethylsilane (δ 0.00), acetone-d_6 (δ 2.05), $CDCl_3$ (δ 7.26), integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, d = quartet, quint = quintet, and m = multiplet) and coupling constants (Hz). ^{13}C chemical shifts are reported in ppm downfield or upfield from $CDCl_3$ (δ 77.00) or acetone-d_6 (δ 29.80). 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, 40-50 μm) (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.

General procedure A for light-induced glycosylations using unprotected deoxythioglycosyl donors without a boronic acid.

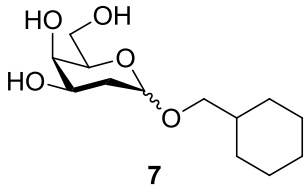
To a solution of unprotected deoxythioglycosyl donor (0.10 mmol) in dry acetonitrile (0.1 M) were added glycosyl acceptor (0.30 mmol) and DDQ (0.15 mmol) under Ar atmosphere at room temperature. After the mixture was stirred upon irradiation with a UV lamp (365 nm, 100 W, Blak-ray (B-100A), UVP Inc.) placed 5 cm from the reaction tube for 3 h at 38 ºC, the resulting mixture was concentrated in *vacuo*. Purification of the residue by silica-gel column chromatography gave the corresponding glycosides.

General procedure B for light-induced glycosylations using unprotected deoxythioglycosyl donors with a boronic acid.

To a solution of glycosyl donor (0.10 mmol) in a mixed solvent of dry toluene/acetone (1/1, 2.0 mL) was added a boronic acid (0.10 mmol) under Ar atmosphere at room temperature for 5 min, and then the resulting mixture was concentrated in *vacuo*. To a solution of the residue in dry acetonitrile (0.1 M) were added glycosyl acceptor (0.30 mmol) and DDQ (0.15 mmol) under Ar atmosphere at room temperature. After the mixture was stirred upon irradiation with a UV lamp (365 nm, 100 W) placed 5 cm from the reaction tube for 3 h at 38 ºC, 30% H_2O_2 aq. (20 μL) was added to the reaction mixture. After the resulting mixture was stirred for 1 h at room temperature, the reaction mixture was diluted with H_2O (7 mL). The resulting mixture was extracted with EtOAc (10 mL×6). The extracts were washed with brine, dried over anhydrous

Na_2SO_4, and concentrated in *vacuo*. Purification of the residue by silica-gel column chromatography gave the corresponding glycosides.

Cyclohexylmethyl 2-deoxy-α- and β-D-galactopyranosides (7)



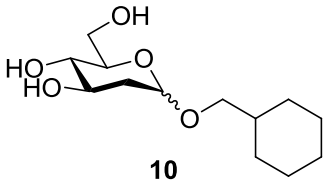
7

The title compounds were obtained according to the general procedure B with silica-gel column chromatography ($CHCl_3$/MeOH = 10/1), from phenylthio 2-deoxy-α-D-galactoside (**1**)[1] (0.10 mmol) and cyclohexylmetanol (**6**) (0.30 mmol) in 74% yield (α/β=76/24).

Date for **7α**: white solid; R_f 0.33 (10/1 $CHCl_3$/MeOH); mp 128-129 ºC; $[\alpha]^{24}_D$ +121.0° (*c* 1.0, CH_3OH); ^{1}H-NMR (500 MHz, acetone-d_6, TMS) δ 4.81 (1H, br d, *J* = 3.2 Hz, H-1), 3.92 (1H, m), 3.82 (1H, m), 3.73-3.69 (3H, m), 3.65 (1H, m), 3.62 (1H, d, *J* = 7.0 Hz), 3.51 (1H, d, *J* = 4.0 Hz), 3.45 (1H, dd, *J* = 6.9, 9.5 Hz), 3.13 (1H, dd, *J* = 6.0, 9.5 Hz), 1.88 (1H, ddd, *J* = 3.8, 12.3, 12.3 Hz), 1.78-1.69 (6H, m), 1.55 (1H, m), 1.30-1.13 (3H, m), 0.97 (2H, m); ^{13}C-NMR (125 MHz, acetone-d_6) δ 98.4, 73.2, 71.7, 69.4, 66.1, 63.1, 38.8, 33.9, 30.8, 30.7, 27.3, 26.6, 26.5; HRMS (ESI-TOF) *m*/*z* 283.1511 (283.1521 calcd for $C_{13}H_{24}O_5Na$, $[M+Na]^+$).

Date for **7β**: white solid; R_f 0.31 (10/1 $CHCl_3$/MeOH); mp 138-139 ºC; $[\alpha]^{26}_D$ −23.3° (*c* 1.1, CH_3OH); ^{1}H-NMR (500 MHz, acetone-d_6, TMS) δ 4.42 (1H, dd, *J* = 2.0, 9.8 Hz, H-1), 3.76-3.65 (6H, m), 3.67 (1H, dd, *J* = 6.6, 9.5 Hz), 3.45 (1H, d, *J* = 4.3 Hz), 3.38 (1H, dd, *J* = 5.6, 5.6 Hz), 3.22 (1H, dd, *J* = 6.6, 9.5 Hz), 1.81-1.63 (7H, m), 1.53 (1H, m), 1.29-1.12 (3H, m), 0.97 (2H, m); ^{13}C-NMR (125 MHz, acetone-d_6) δ 101.4, 76.3, 75.0, 69.4, 68.5, 62.7, 38.9, 36.0, 30.7, 30.6, 27.3, 26.5×2; HRMS (ESI-TOF) *m*/*z* 283.1521 (283.1521 calcd for $C_{13}H_{24}O_5Na$, $[M+Na]^+$).

Cyclohexylmethyl 2-deoxy-α- and β-D-glucopyranosides (10)



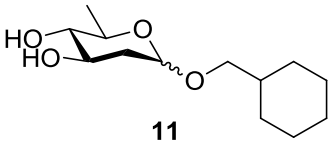
10

The title compounds were obtained according to the general procedure B with silica-gel column chromatography ($CHCl_3$/MeOH = 10/1), from phenylthio 2-deoxy-α-D-glucoside (**2**)[2] (0.10 mmol) and cyclohexylmetanol (**6**) (0.30 mmol) in 72% yield (α/β=54/46).

Date for **10α**: white solid; R_f 0.33 (10/1 $CHCl_3$/MeOH); mp 115-116 ºC; $[\alpha]^{25}_D$ +108.7° (*c* 1.0, CH_3OH); ^{1}H-NMR (500 MHz, acetone-d_6, TMS) δ 4.81 (1H, br d, *J* = 3.2 Hz, H-1), 4.09 (1H, d, *J* = 4.6 Hz), 3.89 (1H, d, *J* = 4.6 Hz), 3.84 (1H, m), 3.78 (1H, ddd, *J* = 3.1, 6.3, 11.5 Hz), 3.66 (1H, ddd, *J* = 5.5, 6.3, 11.5 Hz), 3.51 (1H, ddd, *J* = 3.1, 5.5, 9.3 Hz), 3.46 (1H, dd, *J* = 7.2, 9.5 Hz), 3.41 (1H, t, *J* = 6.3 Hz), 3.25 (1H, ddd, *J* = 4.6, 9.3, 9.3 Hz), 3.13 (1H, dd, *J* = 6.0, 9.5 Hz), 2.00 (1H, ddd, *J* = 1.2, 5.2, 12.9 Hz), 1.80-1.64 (5H, m), 1.57-1.52 (2H, m), 1.30-1.13 (3H, m), 0.97 (2H, m); ^{13}C-NMR (125 MHz, acetone-d_6) δ 98.1, 74.0, 73.4, 73.1, 69.7, 63.2, 38.8, 38.7, 30.8, 30.7, 27.3, 26.6, 26.5; HRMS (ESI-TOF) *m*/*z* 283.1527 (283.1521 calcd for $C_{13}H_{24}O_5Na$, $[M+Na]^+$).

Date for **10β**: white solid; R_f 0.31 (10/1 $CHCl_3$/MeOH); mp 140-141 ºC; $[\alpha]^{27}_D$ −32.8° (*c* 0.8, CH_3OH); ^{1}H-NMR (500 MHz, acetone-d_6, TMS) δ 4.52 (1H, dd, *J* = 2.0, 9.7 Hz, H-1), 4.10 (1H, m), 4.00 (1H, d, *J* = 4.6 Hz), 3.82 (1H, m), 3.68-3.64 (2H, m), 3.57 (1H, m), 3.47 (1H, t, *J* = 6.3 Hz), 3.22 (1H, dd, *J* = 6.6, 9.5 Hz), 3.19 (2H, m), 2.08 (1H, m), 1.79-1.64 (5H, m), 1.53 (1H, m), 1.43 (1H, ddd, *J* = 9.5, 12.0, 12.0 Hz), 1.29-1.15 (3H, m), 0.93 (2H, m); ^{13}C-NMR (125 MHz, acetone-d_6) δ 100.1, 76.6, 74.3, 73.0, 71.6, 62.5, 39.4, 38.1, 29.9, 29.8, 26.5, 25.7×2; HRMS (ESI-TOF) *m*/*z* 283.1518 (283.1521 calcd for $C_{13}H_{24}O_5Na$, $[M+Na]^+$).

Cyclohexylmethyl α- and β-D-olivosides (11)



11

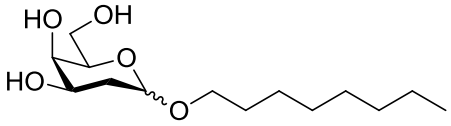
The title compounds were obtained according to the general procedure A with silica-gel column chromatography ($CHCl_3$/MeOH = 20/1), from phenylthio α-D-olivoside (**3**)[3] (0.10 mmol) and cyclohexylmetanol (**6**) (0.30 mmol) in 82% yield (α/β=73/27).

Date for **11α**: white solid; R_f 0.30 (20/1 CH_3Cl/MeOH); mp 92-93 ºC; $[\alpha]^{25}_D$ +103.6° (*c* 1.0, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$, TMS) δ 4.81 (1H, br d, *J* = 2.9 Hz, H-1), 3.93 (1H, m, H-3), 3.64 (1H, dq, *J* = 6.3, 9.2 Hz), 3.41 (1H, dd, *J* = 7.2, 9.2 Hz), 3.15 (1H, dd, *J* = 6.0, 9.2 Hz), 3.11 (1H, dd, *J* = 9.2, 9.2 Hz), 2.52-2.14 (2H, m), 2.13 (1H, m), 1.78-1.65 (6H, m), 1.56 (1H, m), 1.29 (3H, d, *J* = 6.3 Hz), 1.29-1.12 (3H, m), 0.94 (2H, m); ^{13}C-NMR (125 MHz, $CDCl_3$); δ 97.3, 78.2, 72.9, 69.4, 67.3, 37.9×2, 30.2, 30.0, 26.6, 25.9, 25.8, 17.7; Anal. Calcd for $C_{13}H_{24}O_4$: C, 63.91; H, 9.90. Found: C, 63.87; H, 9.80.

Date for **11β**: white solid; R_f 0.27 (20/1 $CHCl_3$/MeOH); mp 75-76 ºC; $[\alpha]^{24}_D$ −45.9° (*c* 0.8, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$, TMS) δ 4.44 (1H, br d, *J* = 9.5 Hz, H-1), 3.68 (1H, dd, *J* = 7.2, 9.5 Hz), 3.56 (1H, m), 3.41 (1H, m), 3.38 (1H, m), 3.24 (1H, m), 3.21 (1H, dd, *J* = 7.2, 9.5 Hz), 3.07 (1H, dd, *J* = 8.9, 8.9 Hz), 2.19 (1H, br dd, *J* = 4.9, 12.3 Hz), 1.79-1.65 (5H, m),

1.65-1.54 (2H, m), 1.32 (3H, d, J = 6.1 Hz), 1.28-1.12 (3H, m), 0.90 (2H, m); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 99.9, 77.5, 75.3, 71.7, 71.6, 39.0, 37.9, 30.0, 29.8, 26.5, 25.8×2, 17.7; Anal. Calcd for $C_{13}H_{24}O_4$: C, 63.90; H, 9.81. Found: C, 63.87; H, 9.80.

_n_-Octyl 2-deoxy-α- and β-D-galactopyranosides (17)



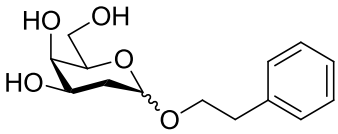
17

The title compounds were obtained according to the general procedure B with silica-gel column chromatography ($CHCl_3$/MeOH = 10/1), from phenylthio 2-deoxy-α-D-galactoside (**1**) (0.10 mmol) and *n*-octanol (**13**) (0.30 mmol) in 80% yield (α/β=75/25).

Date for **17α**: white solid; R_f 0.33 (10/1 $CHCl_3$/MeOH); mp 63-64 ºC; $[\alpha]^{24}_D$ +117.9° (*c* 1.0, CH_3OH); ^{1}H-NMR (500 MHz, acetone-d_6, TMS) δ 4.85 (1H, br d, J = 3.4 Hz, H-1), 3.93 (1H, m), 3.83 (1H, m), 3.71 (6H, m), 3.64 (1H, dt, J = 6.6, 9.5 Hz), 3.32 (1H, dt, J = 6.6, 9.5 Hz), 1.89 (1H, ddd, J = 3.4, 12.3, 12.3 Hz), 1.70 (1H, br dd, J = 4.9, 12.3 Hz), 1.55 (2H, m), 1.39-1.28 (10H, m), 0.88 (3H, t, J = 7.2 Hz); ^{13}C-NMR (125 MHz, acetone-d_6) δ 98.3, 71.7, 69.3, 67.6, 66.0, 63.0, 33.9, 32.5, 30.3, 30.0×2, 27.0, 23.3, 14.3; HRMS (ESI-TOF) *m*/*z* 299.1830 (299.1834 calcd for $C_{14}H_{28}O_5Na$, $[M+Na]^+$).

Date for **17β**: white solid; R_f 0.31 (10/1 $CHCl_3$/MeOH); mp 95-96 ºC; $[\alpha]^{25}_D$ −21.9° (*c* 0.9, CH_3OH); ^{1}H-NMR (500 MHz, acetone-d_6, TMS) δ 4.45 (1H, dd, J = 2.0, 9.5 Hz, H-1), 3.84 (1H, dt, J = 6.6, 9.5 Hz), 3.76-3.67 (6H, m), 3.47 (1H, m), 3.42 (1H, dt, J = 6.6, 9.5 Hz), 3.39 (1H, m), 1.72 (1H, m), 1.69 (1H, m), 1.54 (2H, m), 1.36-1.26 (10H, m), 0.88 (3H, t, J = 6.9 Hz); ^{13}C-NMR (125 MHz, acetone-d_6) δ 101.1, 76.3, 69.3×2, 68.4, 62.6, 36.0×2, 32.6, 30.5, 30.4, 26.9, 23.3, 14.3; HRMS (ESI-TOF) *m*/*z* 299.1830 (299.1834 calcd for $C_{14}H_{28}O_5Na$, $[M+Na]^+$).

2-Phenylethyl 2-deoxy-α- and β-D-galactopyranosides (18)



18

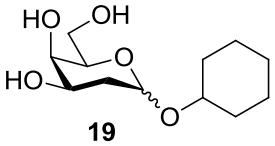
The title compounds were obtained according to the general procedure B with silica-gel column chromatography ($CHCl_3$/MeOH = 10/1), from phenylthio 2-deoxy-α-D-galactoside (**1**) (0.10 mmol) and phenethyl alcohol (**14**) (0.30 mmol) in 84% yield (α/β=81/19).

Date for **18α**: white solid; R_f 0.33 (10/1 $CHCl_3$/MeOH); mp 112-113 ºC; $[\alpha]^{24}_D$ +124.4° (*c* 1.0,

CH_3OH); ^{1}H-NMR (500 MHz, acetone-d_6, TMS) δ 7.29-7.25 (4H, m), 7.20-7.17 (1H, m), 4.87 (1H, br d, J = 3.5 Hz, H-1), 3.89 (1H, m), 3.84 (1H, dt, J = 7.2, 9.8 Hz), 3.79-3.74 (3H, m), 3.69-3,65 (3H, m), 3.58 (1H, dt, J = 7.2, 9.8 Hz), 3.56 (1H, m), 2.86 (2H, t, J = 7.2 Hz), 1.89 (1H, ddd, J = 3.8, 12.3, 12.3 Hz), 1.70 (1H, br dd, J = 5.2, 12.3 Hz); ^{13}C-NMR (125 MHz, acetone-d_6) δ 140.2, 129.7×2, 129.0×2, 126.8, 98.2, 71.6, 69.4, 68.3, 66.0, 63.1, 36.7, 33.7; HRMS (ESI-TOF) m/z 291.1196 (291.1208 calcd for $C_{14}H_{20}O_5Na$, $[M+Na]^+$).

Date for **18β**: white solid; R_f 0.31 (10/1 $CHCl_3$/MeOH); mp 131-132 ºC; $[\alpha]^{25}_D$ −23.5° (*c* 1.0, CH_3OH); ^{1}H-NMR (500 MHz, acetone-d_6, TMS) δ 7.29-7.23 (4H, m), 7.20-7.16 (1H, m), 4.49 (1H, dd, J = 2.0, 9.5 Hz, H-1), 4.05 (1H, dt, J = 7.2, 9.8 Hz), 3.78-3.70 (6H, m), 3.66 (1H, dt, J = 7.2, 9.8 Hz), 3.52 (1H, d, J = 4.3 Hz), 3.40 (1H, m), 2.86 (2H, t, J = 7.2 Hz), 1.79 (1H, m), 1.71 (1H, ddd, J = 9.5, 12.0 Hz); ^{13}C-NMR (125 MHz, acetone-d_6) δ 140.1, 129.8×2, 129.0×2, 126.8, 101.1, 71.3, 70.2, 69.3, 68.5, 62.7, 36.7, 33.7; HRMS (ESI-TOF) m/z 291.1199 (291.1208 calcd for $C_{14}H_{20}O_5Na$, $[M+Na]^+$).

Cyclohexyl 2-deoxy-α- and β-D-galactopyranosides (19)



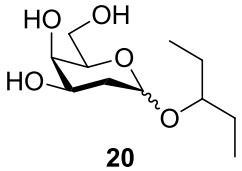
19

The title compounds were obtained according to the general procedure B with silica-gel column chromatography ($CHCl_3$/MeOH = 10/1), from phenylthio 2-deoxy-α-D-galactoside (**1**) (0.10 mmol) and cyclohexanol (**15**) (0.30 mmol) in 71% yield (α/β=86/14).

Date for **19α**: white solid; R_f 0.29 (10/1 $CHCl_3$/MeOH); mp 121-122 ºC; $[\alpha]^{26}_D$ +152.2° (*c* 1.0, CH_3OH); ^{1}H-NMR (500 MHz, acetone-d_6, TMS) δ 5.03 (1H, br d, J = 3.5 Hz, H-1), 3.94 (1H, m), 3.82 (1H, m), 3.79 (1H, m), 3.72-3.69 (2H, m), 3.67 (1H, m), 3.62 (1H, d, J = 4.0 Hz), 3.57 (1H, m), 3.52 (1H, d, J = 4.0 Hz), 1.90 (1H, ddd, J = 3.5, 12.4, 12.4 Hz), 1.84 (2H, m), 1.69 (2H, m), 1.65 (1H, br dd, J = 5.5, 12.4 Hz), 1.50 (1H, m), 1.38-1.18 (5H, m); ^{13}C-NMR (125 MHz, acetone-d_6) δ 96.1, 74.4, 71.8, 69.5, 66.1, 63.1, 34.4, 34.1, 32.2, 26.5, 24.8, 24.5; HRMS (ESI-TOF) m/z 269.1356 (269.1365 calcd for $C_{12}H_{22}O_5Na$, $[M+Na]^+$).

Date for **19β**: white solid; R_f 0.27 (10/1 $CHCl_3$/MeOH); mp 103-104 ºC; $[\alpha]^{26}_D$ −38.1° (*c* 1.0, CH_3OH); ^{1}H-NMR (500 MHz, acetone-d_6, TMS) δ 4.60 (1H, dd, J = 2.3, 9.5 Hz, H-1), 3.76-3.71 (5H, m), 3.70 (1H, m), 3.65 (1H, m), 3.45 (1H, d, J = 4.6 Hz), 3.39 (1H, t, J = 6.0 Hz), 1.86 (2H, m), 1.74-1.66 (4H, m), 1.50 (1H, m), 1.36-1.17 (5H, m); ^{13}C-NMR (125 MHz, acetone-d_6) δ 98.9, 76.2, 75.9, 69.4, 68.5, 62.7, 36.6, 34.5, 32.5, 26.4, 24.7, 24.5; HRMS (ESI-TOF) m/z 269.1356 (269.1365 calcd for $C_{12}H_{22}O_5Na$, $[M+Na]^+$).

3-Pentyl 2-deoxy-α- and β-D-galactopyranosides (20)



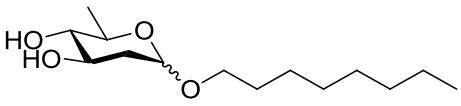
20

The title compounds were obtained according to the general procedure B with silica-gel column chromatography ($CHCl_3$/MeOH = 10/1), from phenylthio 2-deoxy-α-D-galactoside (**1**) (0.10 mmol) and 3-pentanol (**16**) (0.30 mmol) in 70% yield (α/β=85/15).

Date for **20α**: white solid; R_f 0.29 (10/1 $CHCl_3$/MeOH); mp 68-69 ºC; $[\alpha]^{24}_D$ +148.2° (*c* 1.0, CH_3OH); ^{1}H-NMR (500 MHz, acetone-d_6, TMS) δ 4.99 (1H, br d, *J* = 3.5 Hz, H-1), 3.94 (1H, m), 3.85-3.81 (2H, m), 3.72-3.70 (3H, m), 3.65 (1H, m), 3.55 (1H, d, *J* = 3.5 Hz), 3.49 (1H, quint, *J* = 5.7 Hz), 1.92 (1H, ddd, *J* = 3.5, 12.3, 12.3 Hz), 1.69 (1H, br dd, *J* = 4.9, 12.3 Hz), 1.50 (4H, m), 0.89 (3H, t, *J* = 7.7 Hz), 0.86 (3H, t, *J* = 7.7 Hz); ^{13}C-NMR (125 MHz, acetone-d_6) δ 96.8, 78.9, 71.9, 69.5, 66.2, 63.0, 32.2, 27.4, 25.6, 10.2, 9.3; HRMS (ESI-TOF) *m*/*z* 257.1357 (257.1365 calcd for $C_{11}H_{22}O_5Na$, $[M+Na]^+$).

Date for **20β**: white solid; R_f 0.27 (10/1 $CHCl_3$/MeOH); mp 68-69 ºC; $[\alpha]^{26}_D$ −18.3° (*c* 1.0, CH_3OH); ^{1}H-NMR (500 MHz, acetone-d_6, TMS) δ 4.53 (1H, dd, *J* = 2.3, 9.8 Hz, H-1), 3.78-3.70 (6H, m), 3.61 (1H, dd, *J* = 3.4, 6.9 Hz), 3.54 (1H, quint, *J* = 6.0 Hz), 3.46 (1H, d, *J* = 4.6 Hz), 3.38 (1H, t, *J* = 5.8 Hz), 1.80 (1H, m), 1.71 (1H, m), 1.48 (4H, m), 0.88 (3H, t, *J* = 7.5 Hz), 0.87 (3H, t, *J* = 7.5 Hz); ^{13}C-NMR (125 MHz, acetone-d_6) δ 100.4, 81.2, 76.1, 69.5, 68.4, 62.6, 36.4, 28.0, 26.8, 10.0, 9.66; HRMS (ESI-TOF) *m*/*z* 257.1355 (257.1365 calcd for $C_{11}H_{22}O_5Na$, $[M+Na]^+$).

***n*-Octyl α- and β-D-olivosides (21)**



21

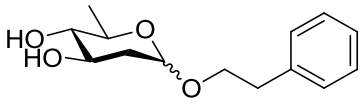
The title compounds were obtained according to the general procedure A with silica-gel column chromatography ($CHCl_3$/MeOH = 20/1), from phenylthio α-D-olivoside (**3**) (0.10 mmol) and *n*-octanol (**13**) (0.30 mmol) in 79% yield (α/β=76/24).

Date for **21α**: colorless syrup; R_f 0.30 (20/1 $CHCl_3$/MeOH); $[\alpha]^{24}_D$ +103.6° (*c* 1.0, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$, TMS) δ 4.83 (1H, br d, *J* = 3.2 Hz, H-1), 3.91 (1H, ddd, *J* = 4.9, 9.2, 11.8 Hz), 3.63 (1H, m), 3.60 (1H, dt, *J* = 6.9, 9.5 Hz), 3.34 (1H, dt, *J* = 6.9, 9.5 Hz), 3.09 (1H, dd, *J* = 9.2, 9.2 Hz), 2.99 (1H, br s), 2.92 (1H, br s), 2.12 (1H, br dd, *J* = 4.9, 12.6 Hz), 1.68 (1H, ddd, *J* = 3.2, 11.8, 11.8 Hz), 1.56 (2H, m), 1.29-1.28 (13H, m), 0.88 (3H, t, *J* = 7.2 Hz);

^{13}C-NMR (125 MHz, $CDCl_3$) δ 97.1, 78.0, 69.2, 67.4×2, 37.9, 31.8, 29.5, 29.4, 29.2, 26.2, 22.6, 17.7, 14.1; Anal. Calcd for $C_{14}H_{28}O_4$: C, 64.58; H, 10.84. Found: C, 64.48; H, 10.77.

Date for **21β**: colorless syrup; R_f 0.27 (20/1 $CHCl_3$/MeOH); mp 70-71 ºC; $[\alpha]^{26}_D$ −39.2° (*c* 1.0, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$, TMS) δ 4.48 (1H, dd, *J* = 1.4, 9.7 Hz, H-1), 3.86 (1H, dt, *J* =6.9, 9.2 Hz), 3.59 (1H, m), 3.43 (1H, dt, *J* = 7.2, 9.2 Hz), 3.27 (1H, dq, *J* = 6.3, 8.9 Hz), 3.09 (1H, dd, *J* = 8.9, 8.9 Hz, H-4), 2.92 (1H, br s), 2.85 (1H, br s), 2.20 (1H, br dd, *J* = 1.4, 12.4 Hz), 1.65-1.56 (3H, m), 1.34 (3H, d, *J* = 6.3 Hz), 1.31-1.20 (10H, m), 0.88 (3H, t, *J* = 6.9 Hz); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 99.5, 77.6, 71.7, 71.5, 69.6, 39.1, 31.8, 29.6, 29.4, 29.2, 26.0, 22.6, 17.7, 14.1; Anal. Calcd for $C_{14}H_{28}O_4$: C, 64.58; H, 10.84. Found: C, 64.64; H, 10.81.

2-Phenylethyl 2,6-dideoxy-α- and β-D-*arabino*-hexopyranosides (22)



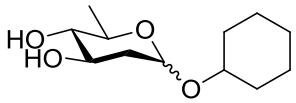
22

The title compounds were obtained according to the general procedure A with silica-gel column chromatography ($CHCl_3$/MeOH = 20/1), from phenylthio α-D-olivoside (**3**) (0.10 mmol) and phenethyl alcohol (**14**) (0.30 mmol) in 72% yield (α/β=70/30).

Date for **22α**: colorless syrup; R_f 0.30 (20/1 $CHCl_3$/MeOH); $[\alpha]^{26}_D$ +134.0° (*c* 1.0, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$, TMS) δ 7.23-7.24 (2H, m), 7.21-7.19 (3H, m), 4.82 (1H, br d, *J* = 3.0 Hz, H-1), 3.88-3.70 (3H, m), 3.82 (1H, dt, *J* = 7.0, 10.0 Hz), 3.60 (1H, dt, *J* = 7.0, 10.0 Hz), 3.43 (1H, dq, *J* = 6.5, 9.5 Hz), 3.03 (1H, dd, *J* = 9.5, 9.5 Hz), 2.87 (2H, dt, *J* = 2.0, 7.0 Hz), 2.11 (1H, br dd, *J* =4.6, 12.0 Hz), 1.64 (1H, ddd, *J* = 3.0, 12.0, 12.0 Hz), 1.22 (3H, d, *J* = 6.5 Hz); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 138.8, 128.8×2, 128.3×2, 126.2, 97.0, 77.8, 69.0, 68.0, 67.6, 37.7, 36.1, 17.7; Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.64; H, 7.92.

Date for **22β**: colorless syrup; R_f 0.27 (20/1 $CHCl_3$/MeOH); $[\alpha]^{24}_D$ −33.0° (*c* 1.0, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$, TMS) δ 7.30-7.26 (2H, m), 7.22-7.19 (3H, m), 4.46 (1H, dd, *J* = 2.0, 9.0 Hz, H-1), 4.09 (1H, dt, *J* = 7.0, 9.5 Hz), 3.65 (1H, dt, *J* = 7.0, 9.5 Hz), 3.56 (1H, m), 3.25 (1H, dq, *J* = 6.0, 9.0 Hz), 3.09 (1H, dd, *J* = 9.0, 9.0 Hz), 2.92 (2H, t, *J* = 7.0 Hz), 2.72 (1H, br s), 2.65 (1H, br s), 2.19 (1H, ddd, *J* = 2.0, 5.0, 12.6 Hz), 1.62 (1H, ddd, *J* = 9.0, 12.6, 12.6 Hz), 1.32 (3H, d, *J* = 6.0 Hz); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 138.4, 128.9×2, 128.3×2, 126.3, 99.6, 77.5, 71.6×2, 70.2, 39.0, 36.2, 17.7.; Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.59; H, 7.96.

Cyclohexyl α- and β -D-olivosides (23)



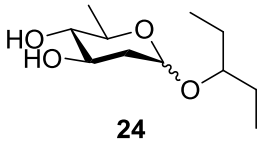
23

The title compounds were obtained according to the general procedure A with silica-gel column chromatography ($CHCl_3$/MeOH = 20/1), from phenylthio α-D-olivoside (**3**) (0.10 mmol) and cyclohexanol (**6**) (0.30 mmol) in 70% yield (α/β=71/29).

Date for **23α**: white solid; R_f 0.27 (20/1 CH_3Cl/MeOH); mp 128-129 ºC; $[\alpha]^{26}_D$ +134.1° (*c* 1.0, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$, TMS) δ 5.00 (1H, br d, *J* = 3.4 Hz, H-1), 3.94 (1H, m), 3.72 (1H, dq, *J* = 6.0, 9.2 Hz), 3.53 (1H, m), 3.09 (1H, dd, *J* = 9.2, 9.2 Hz), 3.04 (1H, br s), 2.94 (1H, br s), 2.07 (1H, ddd, *J* = 0.9, 4.9, 12.6 Hz), 1.85 (2H, m), 1.74-1.66 (3H, m), 1.53 (1H, m), 1.40-1.16 (8H, m); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 94.9, 78.2, 74.5, 69.3, 67.5, 38.3, 33.5, 31.5, 25.7, 24.3, 24.0, 17.7.; Anal. Calcd for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63. Found: C, 62.53; H, 9.56.

Date for **23β**: colorless syrup; R_f 0.24 (20/1 $CHCl_3$/MeOH); $[\alpha]^{24}_D$ −43.0° (*c* 1.0, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$, TMS) δ 4.61 (1H, dd, *J* = 1.4, 9.7 Hz, H-1), 3.64 (1H, m), 3.58 (1H, m), 3.33 (1H, br s, OH), 3.28 (1H, br s, OH), 3.26 (1H, dq, *J* = 6.0, 8.9 Hz), 3.08 (1H, dd, *J* = 8.9, 8.9 Hz), 2.15 (1H, ddd, *J* = 1.4, 4.9, 12.3 Hz), 1.96-1.87 (2H, m), 1.74 (2H, m), 1.64 (1H, ddd, *J* = 9.7, 12.3, 12.3 Hz), 1.53 (1H, m), 1.32 (3H, d, *J* = 6.0 Hz), 1.31-1.13(5H, m); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 97.3, 77.4, 76.6, 71.8, 71.5, 39.6, 33.6, 31.8, 25.6, 24.2, 24.1, 17.8.; Anal. Calcd for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63. Found: C, 62.66; H, 9.55.

3-Pentyl α- and β -D-olivosides (24)



24

The title compounds were obtained according to the general procedure A with silica-gel column chromatography ($CHCl_3$/MeOH = 20/1), from phenylthio α-D-olivoside (**3**) (0.10 mmol) and 3-pentanol (**16**) (0.30 mmol) in 70% yield (α/β=70/30).

Date for **24α**: white solid; R_f 0.27 (20/1 $CHCl_3$/MeOH); mp 88-89 ºC; $[\alpha]^{26}_D$ +133.2° (*c* 1.0, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$, TMS) δ 4.93 (1H, br d, *J* = 3.5 Hz, H-1), 4.28 (1H, br s), 4.22 (1H, br s), 3.90 (1H, m), 3.73 (1H, dq, *J* = 6.0, 9.2 Hz), 3.45 (1H, quint, *J* = 5.8 Hz), 3.05 (1H, ddd, *J* = 3.4, 9.2, 9.2 Hz), 2.09 (1H, br dd, *J* = 4.9, 12.6 Hz), 1.68 (1H, ddd, *J* = 3.5, 12.6, 12.6 Hz), 1.55-1.45 (4H, m), 1.26 (3H, d, *J* = 6.0 Hz), 0.91 (3H, t, *J* = 7.2 Hz), 0.86 (3H, t, *J* = 7.2 Hz); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 95.7 79.1, 78.1, 69.3, 67.7, 38.3, 26.8, 25.1, 17.6, 9.95,

9.10.; Anal. Calcd for $C_{11}H_{22}O_4$: C, 60.52; H, 10.16. Found: C, 60.56; H, 10.12.

Date for **24β**: colorless syrup; R_f 0.24 (20/1 $CHCl_3$/MeOH); $[\alpha]^{24}_D$ −27.0° (*c* 1.0, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$, TMS) δ 4.52 (1H, dd, *J* = 2.0, 9.8 Hz, H-1), 3.58 (1H, m), 3.49 (1H, quint, *J* = 6.1 Hz), 3.23 (1H, dq, *J* = 6.3, 8.9 Hz), 3.08 (1H, dd, *J* = 8.9, 8.9 Hz), 3.06-2.98 (2H, m), 2.18 (1H, ddd, *J* = 2.0, 5.2, 12.3 Hz), 1.63 (1H, ddd, *J* = 9.8, 12.3, 12.3 Hz), 1.60-1.43 (4H, m), 1.31 (3H, d, *J* = 6.3 Hz), 0.90 (3H, t, *J* = 7.4 Hz), 0.89 (3H, t, *J* = 7.4 Hz); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 98.8, 81.8, 77.6, 71.9, 71.5, 39.4, 27.2, 25.9, 17.7, 9.72, 9.39.; Anal. Calcd for $C_{11}H_{22}O_4$: C, 60.52; H, 10.16. Found: C, 60.49; H, 10.20.

^{1}H NMR assay using 2 and 4 (Figure S1)

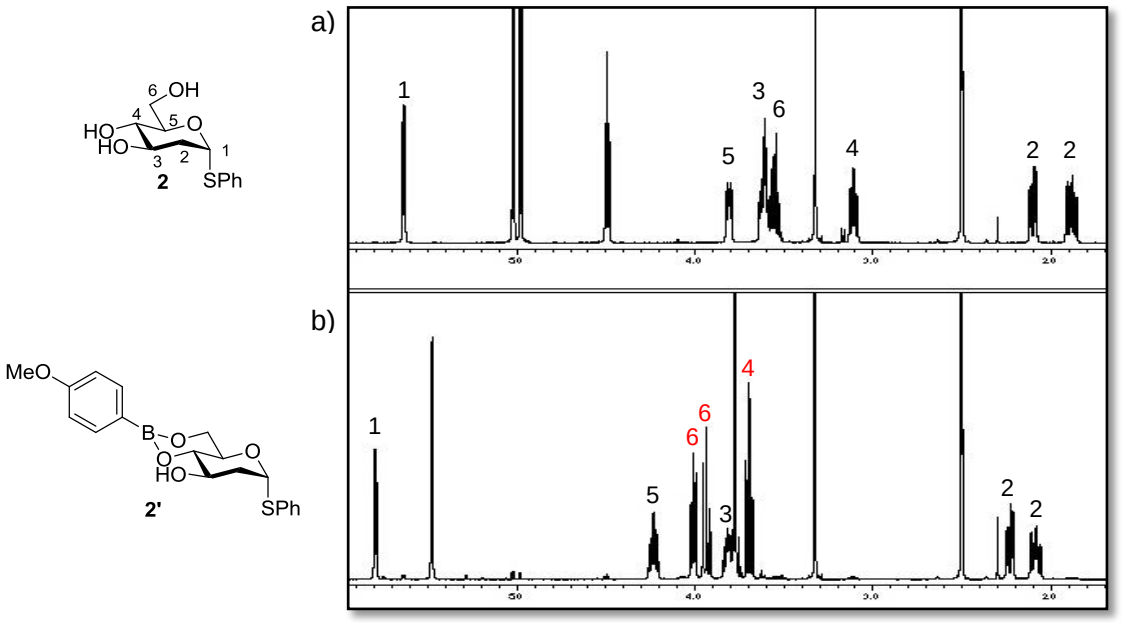


Figure S1. a) ^{1}H NMR spectrum of **2** (10 mM) in DMSO-d_6. b) ^{1}H NMR spectrum of complex **2'** resulted from **2** (10 mM) with **4** (10 mM) in DMSO-d_6.

^{1}H NMR assay using 3 and 4 (Figure S2)

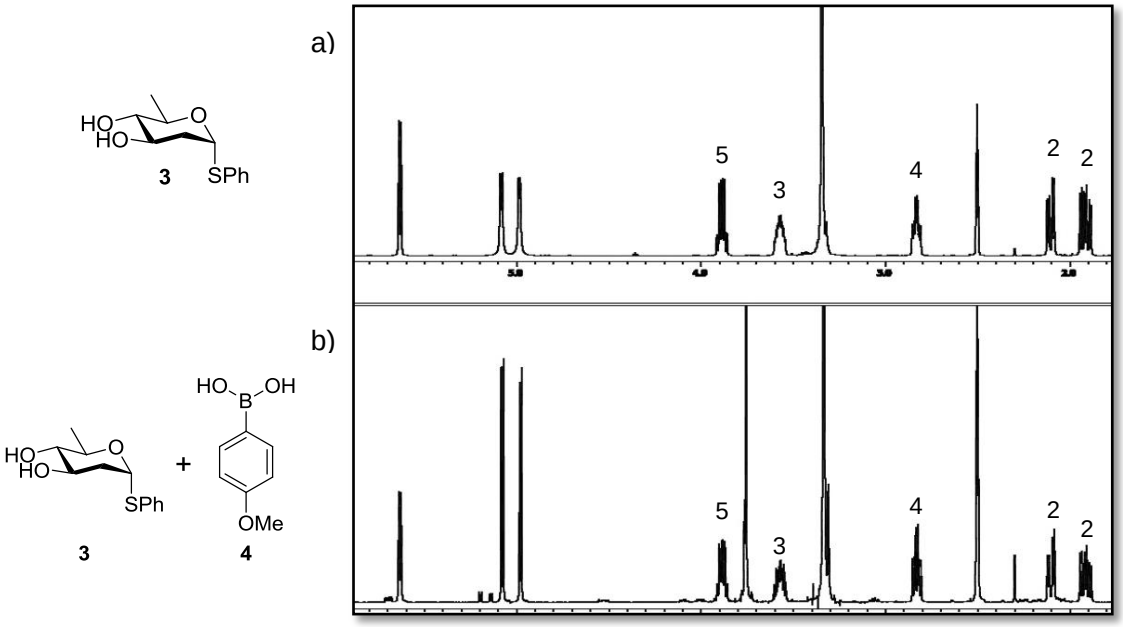


Figure S2. a) ^{1}H NMR spectrum of **3** (10 mM) in DMSO-d_6. b) ^{1}H NMR spectrum of **3** (10 mM) in the presence of **4** (10 mM) in DMSO-d_6.

^{1}H NMR assay using 1, 4 and 5 (Figure S3)

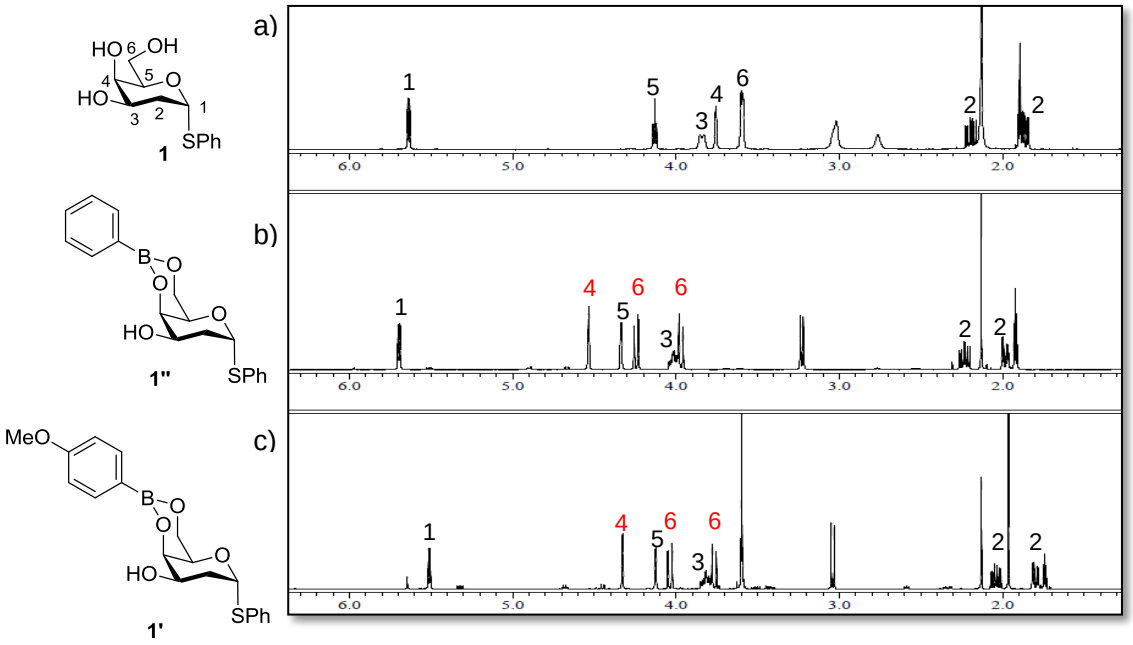


Figure S3. a) ^{1}H NMR spectrum of **1** (10 mM) in MeCN-d_3. b) ^{1}H NMR spectrum of complex **1"** resulted from **1** (10 mM) with **5** (10 mM) in MeCN-d_3. c) ^{1}H NMR spectrum of complex **1'** resulted from **1** (10 mM) with **4** (10 mM) in MeCN-d_3.

References

[1] K. Sakurai and D. Kahne, *Tetrahedron Lett*., 2010, **51**, 3724.

[2] W. D. Hitz, P. J. Card and K. G. Ripp, *J. Biol. Chem.*, 1986, **261**, 11986.

[3] H. Tanaka, A. Yoshizawa and T. Takahashi, *Angew. Chem. Int. Ed.*, 2007, **46**, 2505.

^{1}H and ^{13}C NMR spectra

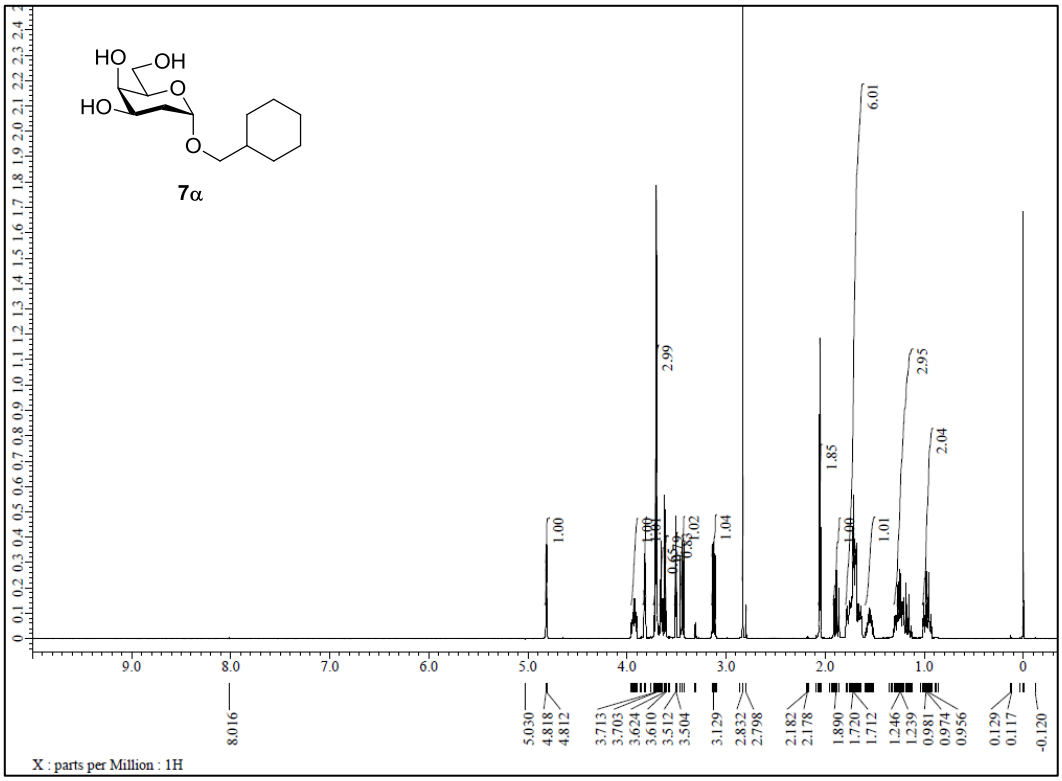


Figure S4 ^{1}H NMR spectrum of **7α**

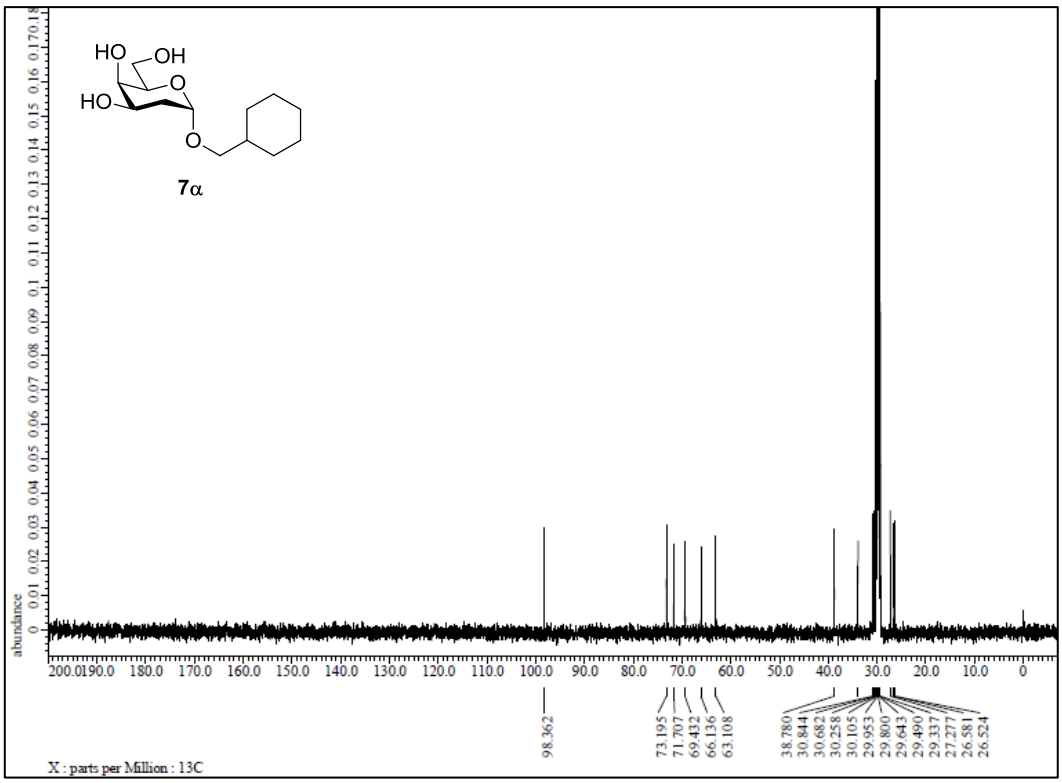


Figure S5 ^{13}C NMR spectrum of **7α**

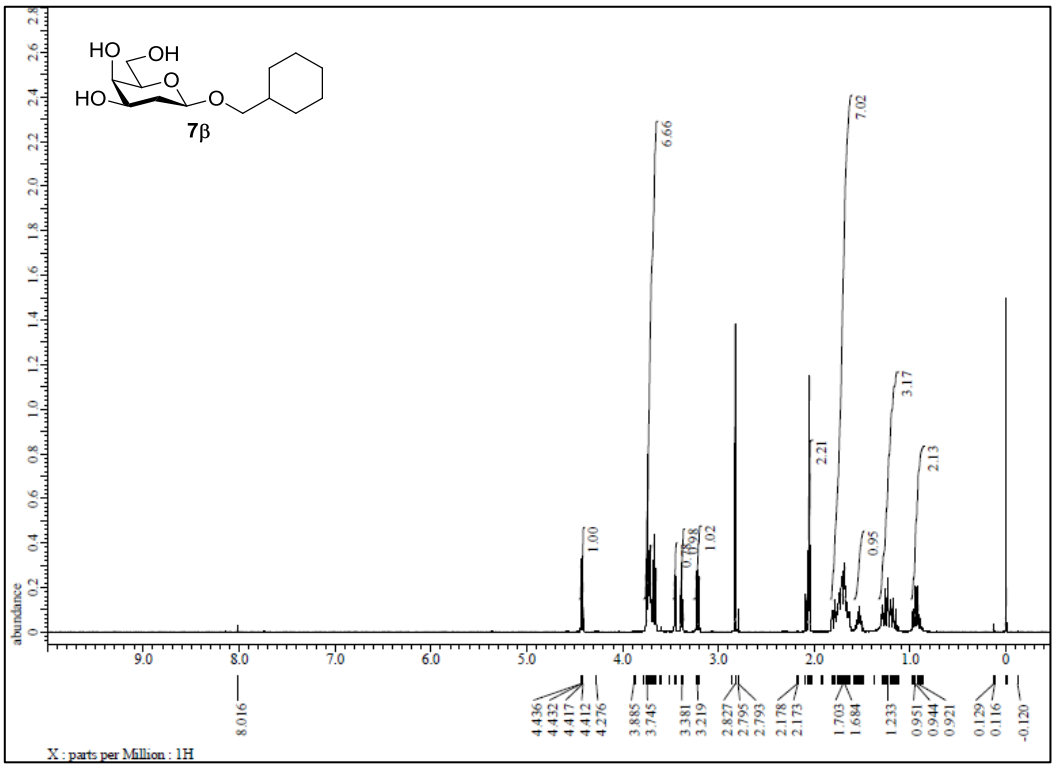


Figure S6 ^{1}H NMR spectrum of **7β**

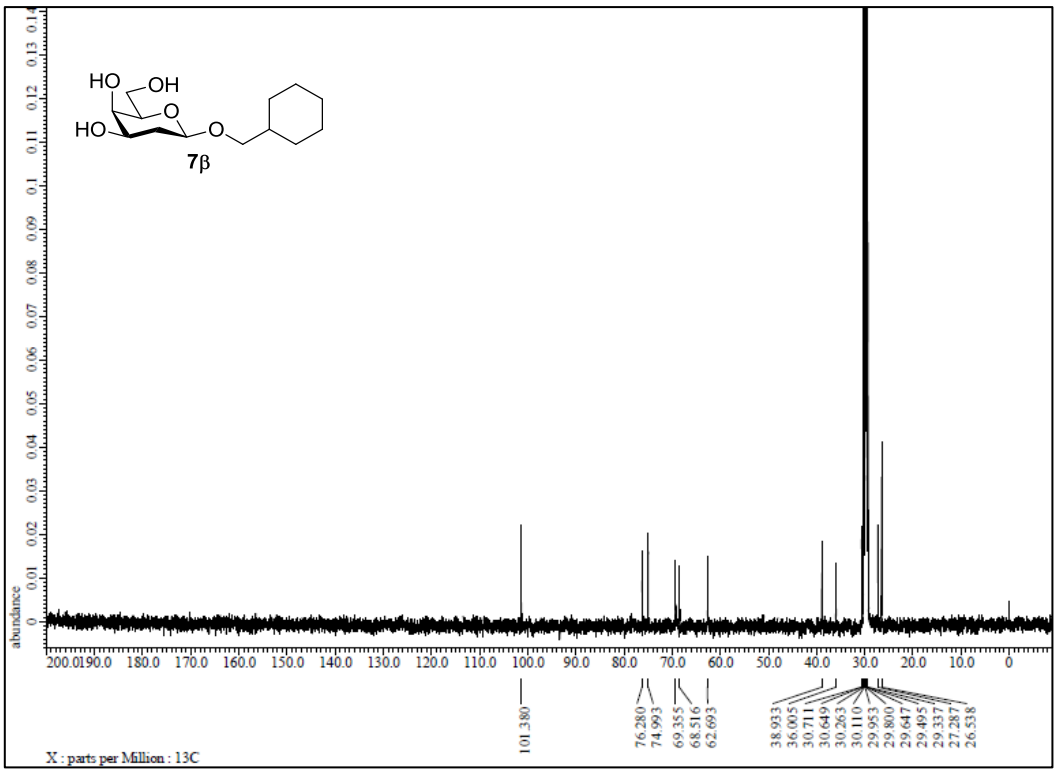


Figure S7 ^{13}C NMR spectrum of **7β**

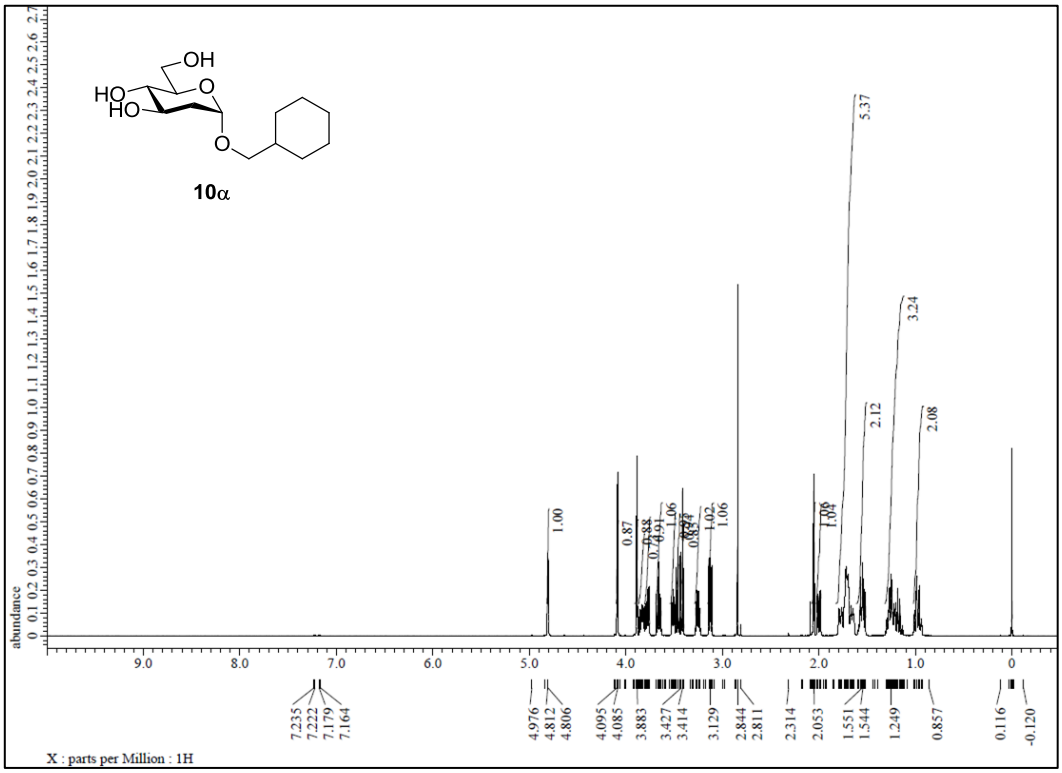


Figure S8 ^{1}H NMR spectrum of **10α**

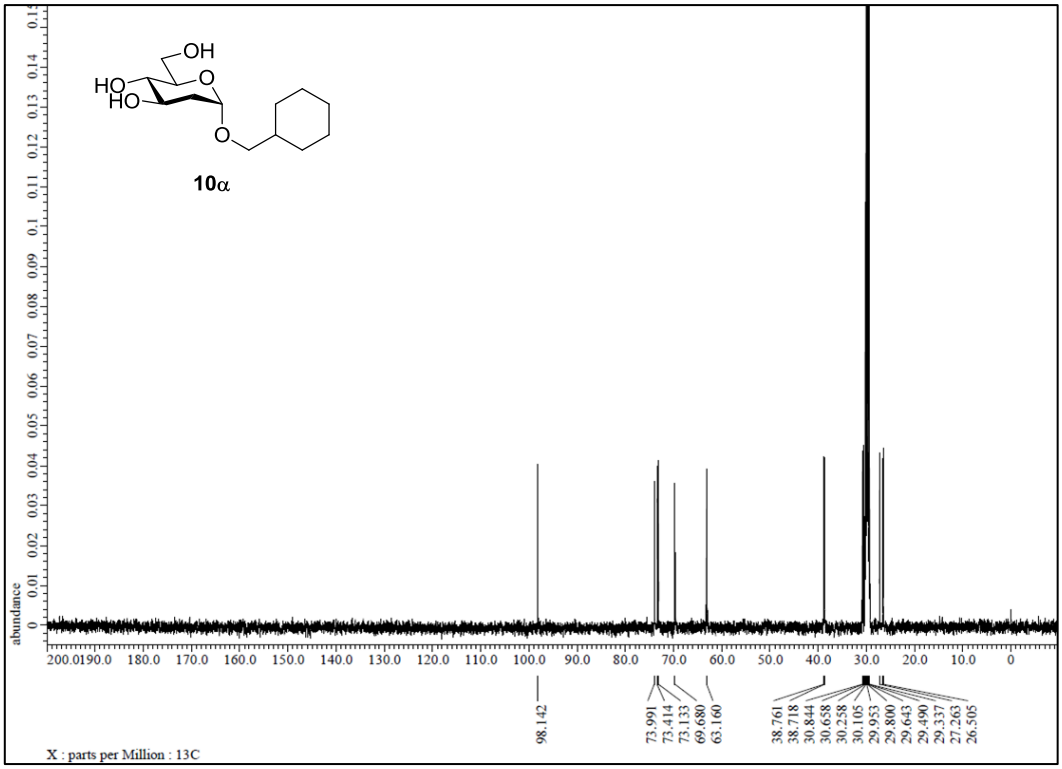


Figure S9 ^{13}C NMR spectrum of **10α**

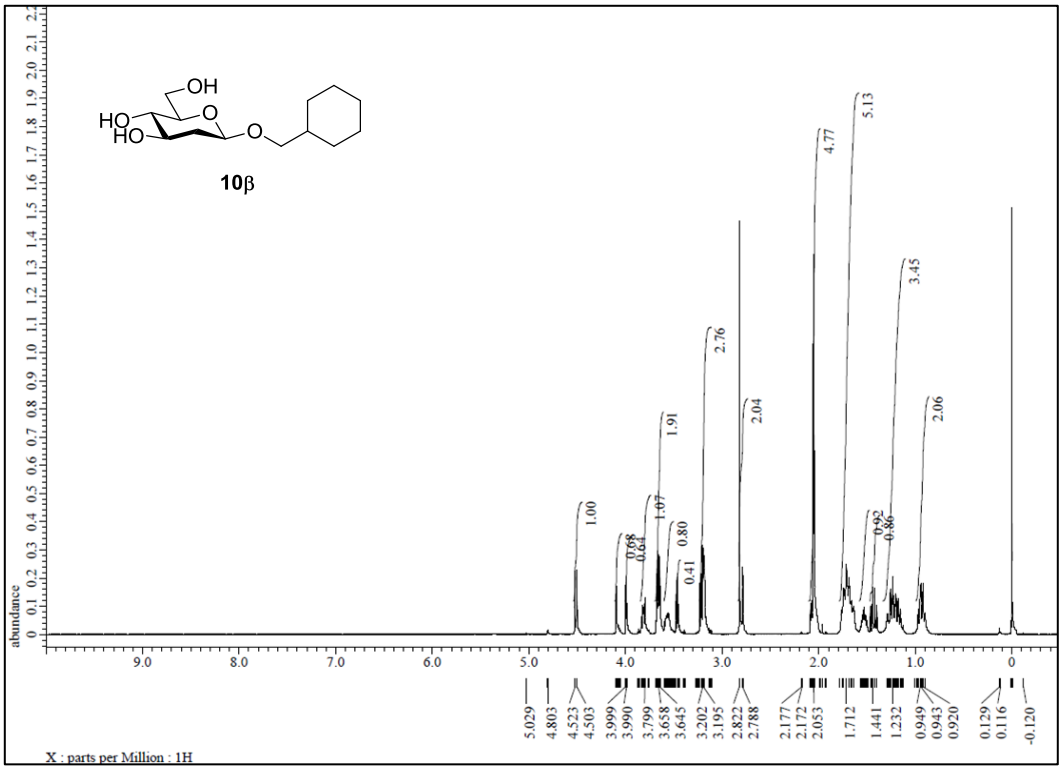


Figure S10 ^{1}H NMR spectrum of **10β**

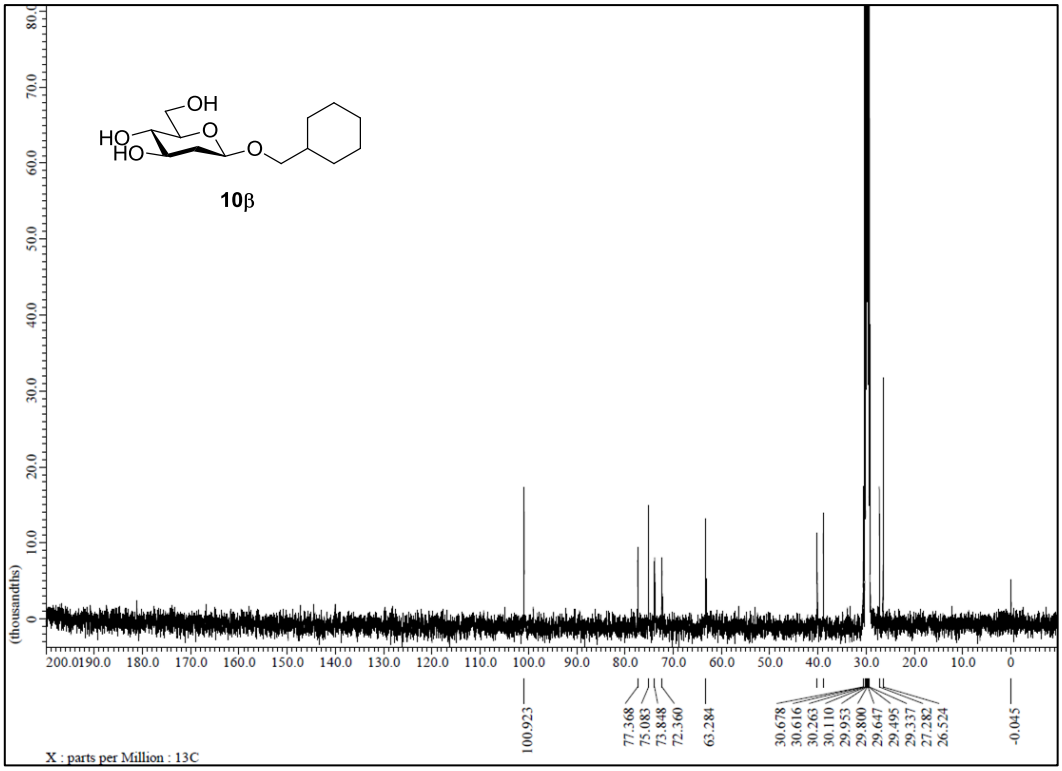


Figure S11 ^{13}C NMR spectrum of **10β**

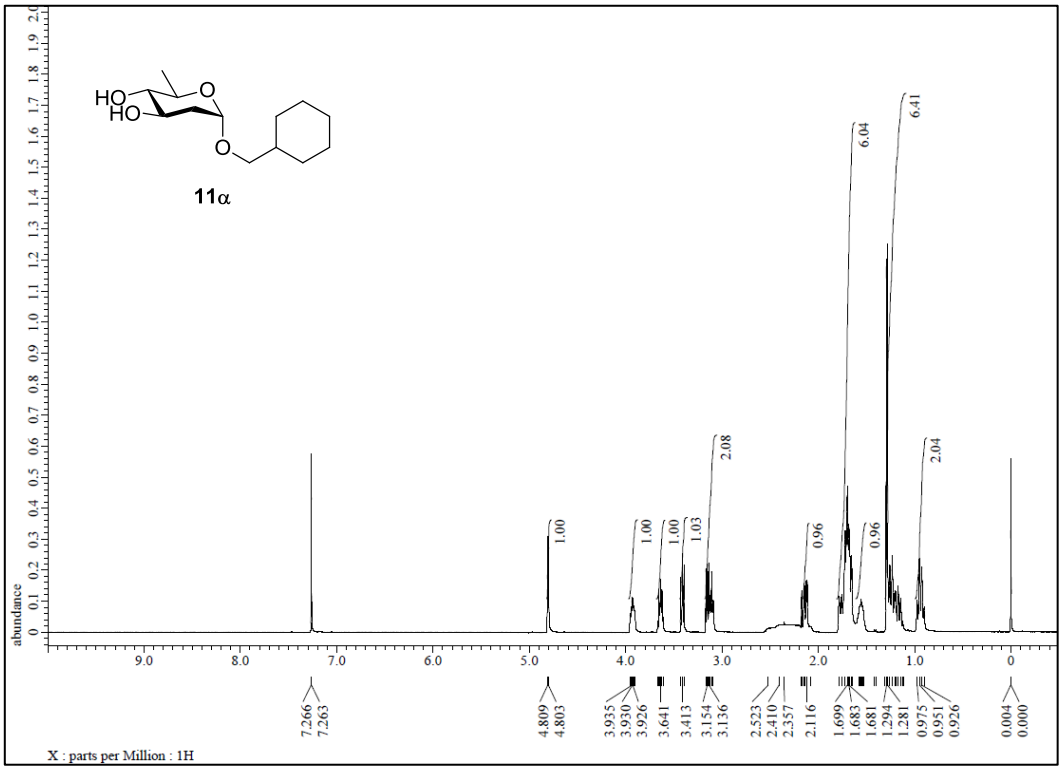


Figure S12 ^{1}H NMR spectrum of **11α**

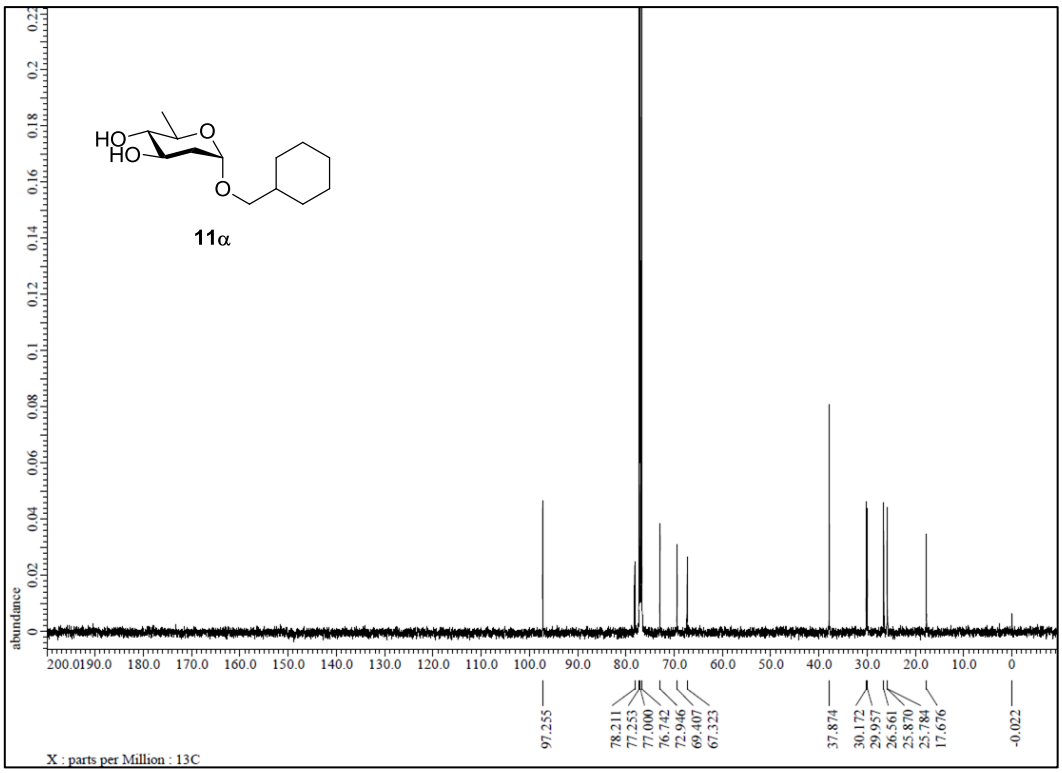


Figure S13 ^{13}C NMR spectrum of **11α**

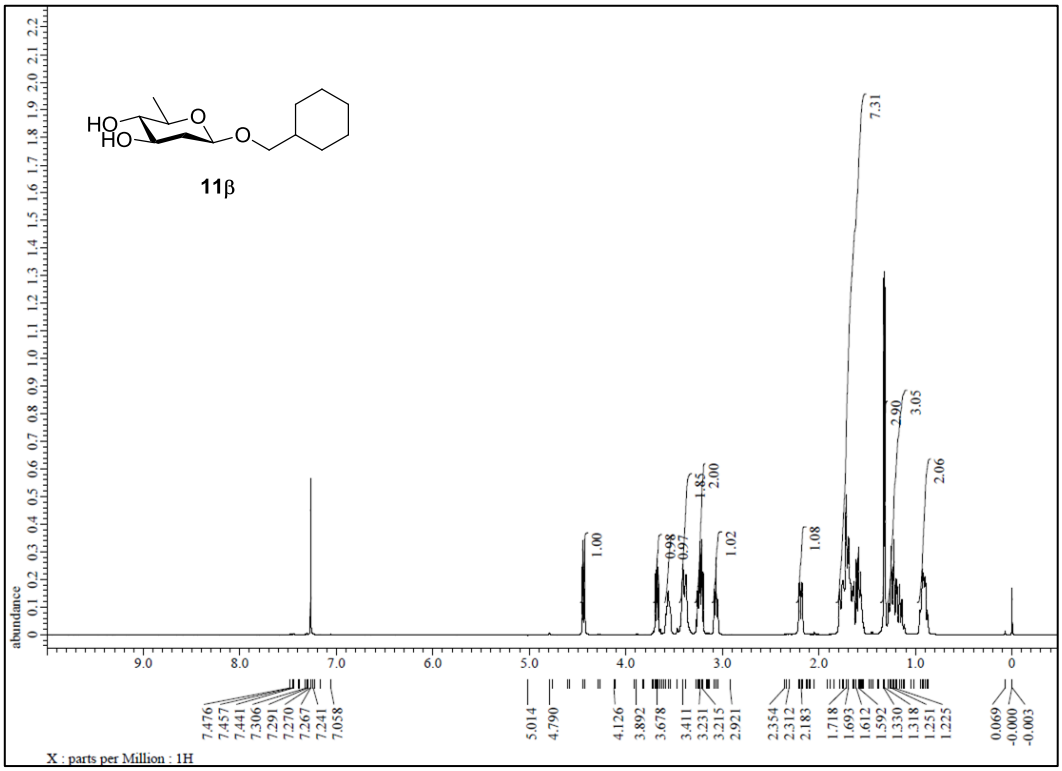


Figure S14 ^{1}H NMR spectrum of **11β**

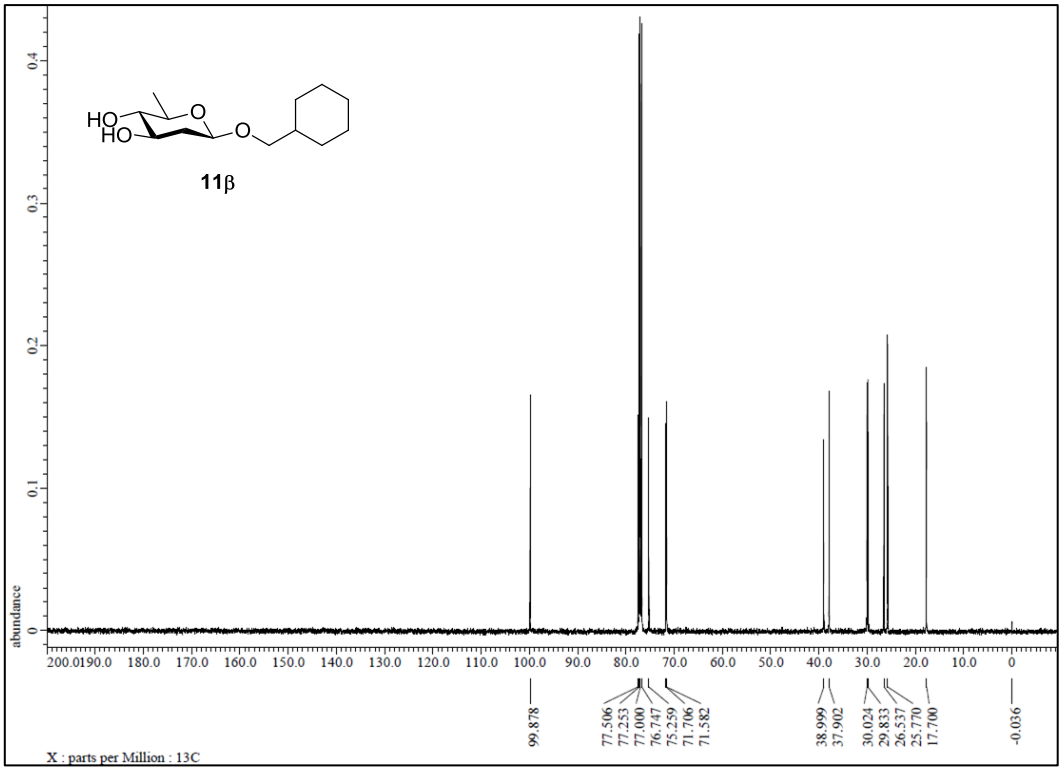


Figure S15 ^{13}C NMR spectrum of **11β**

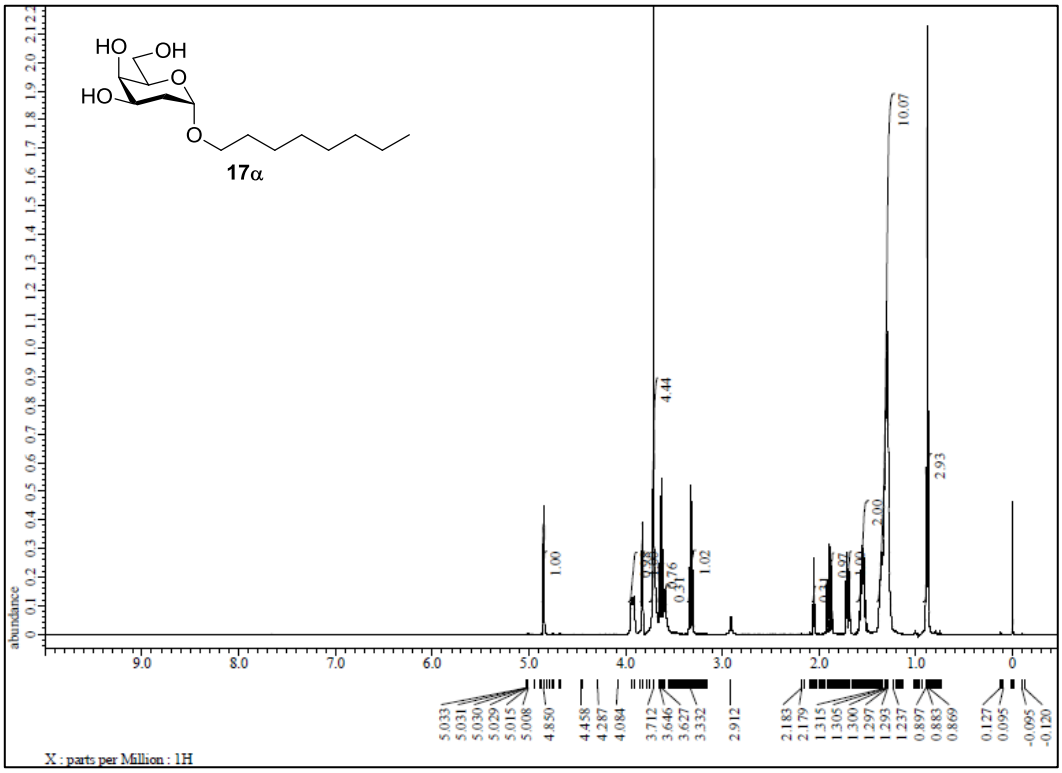


Figure S16 ^{1}H NMR spectrum of **17α**

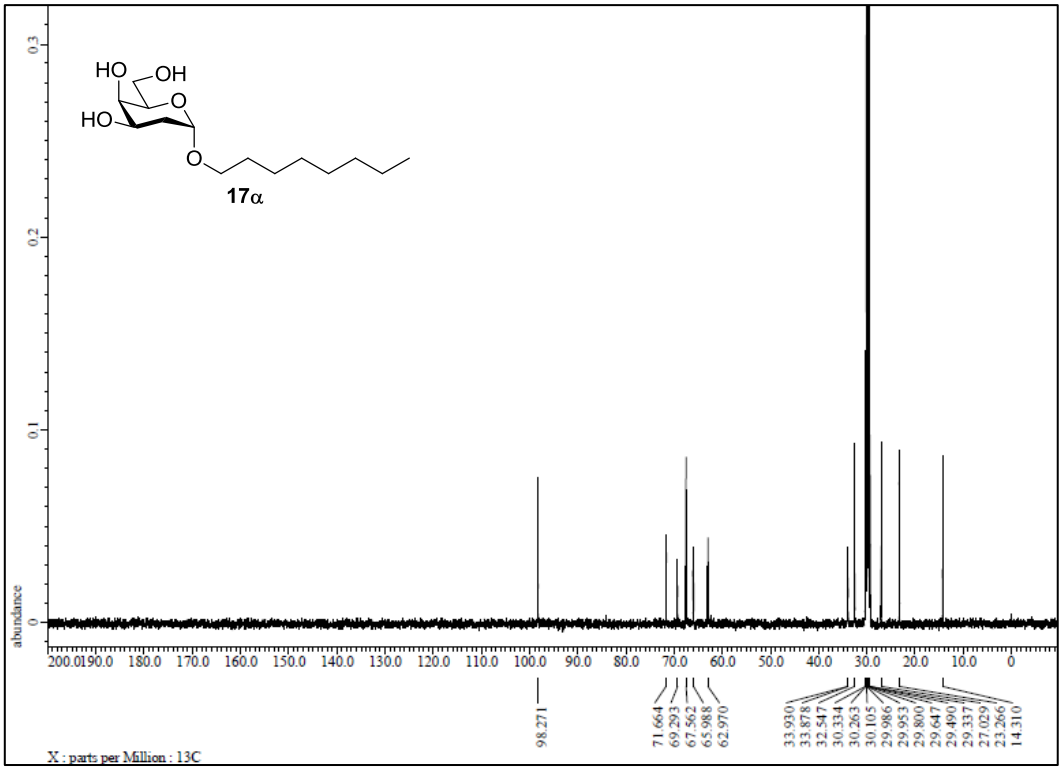


Figure S17 ^{13}C NMR spectrum of **17α**

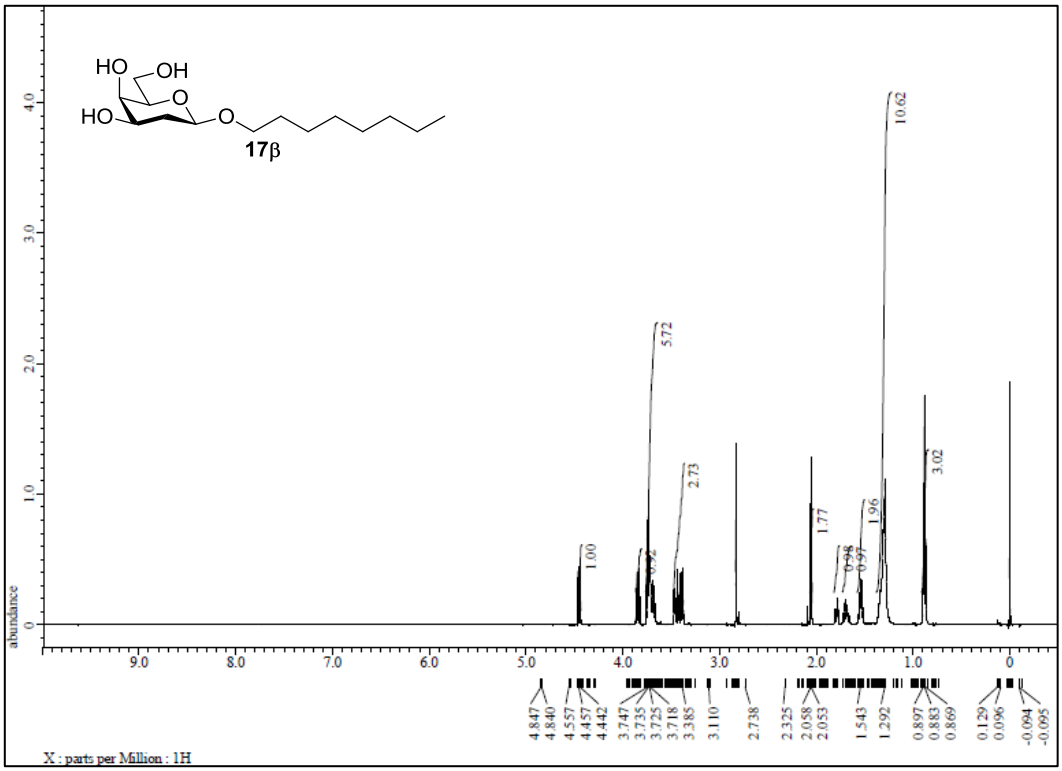


Figure S18 ^{1}H NMR spectrum of **17β**

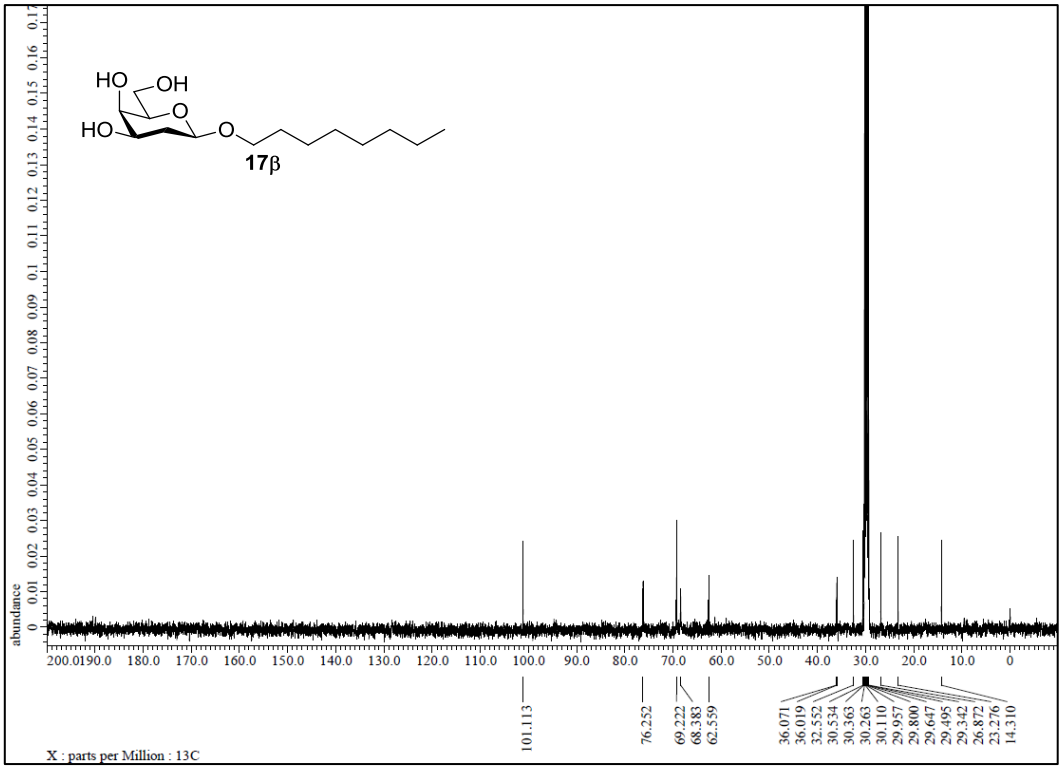


Figure S19 ^{1}H NMR spectrum of **17β**

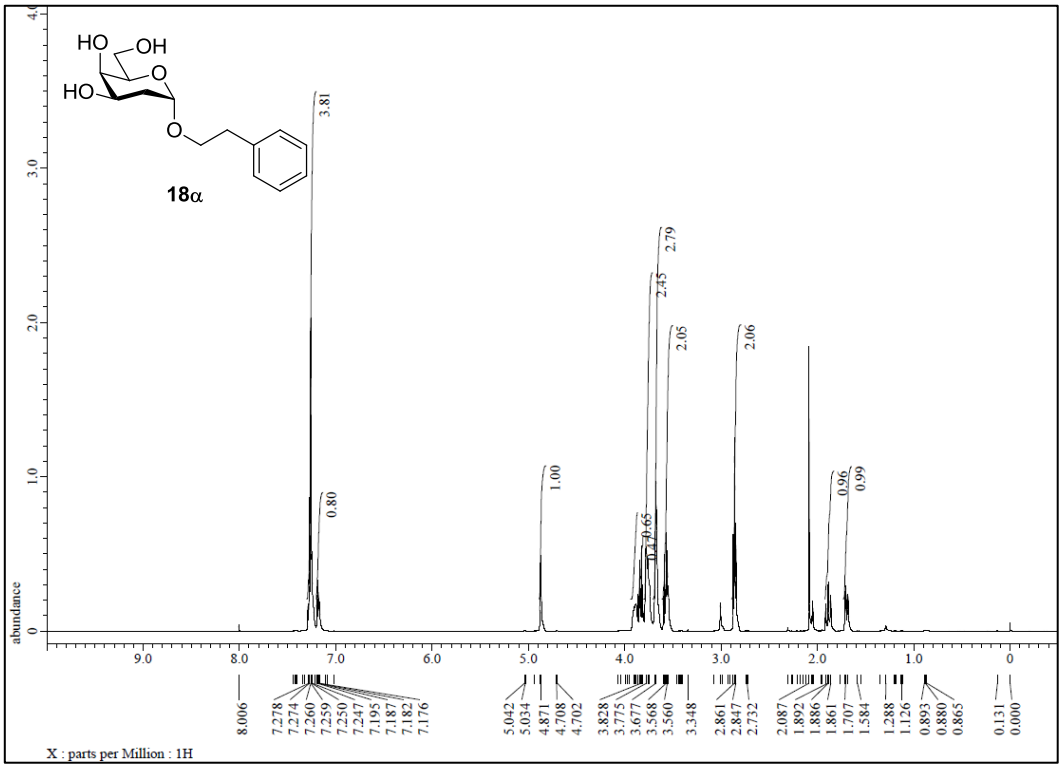


Figure S20 ^{1}H NMR spectrum of **18α**

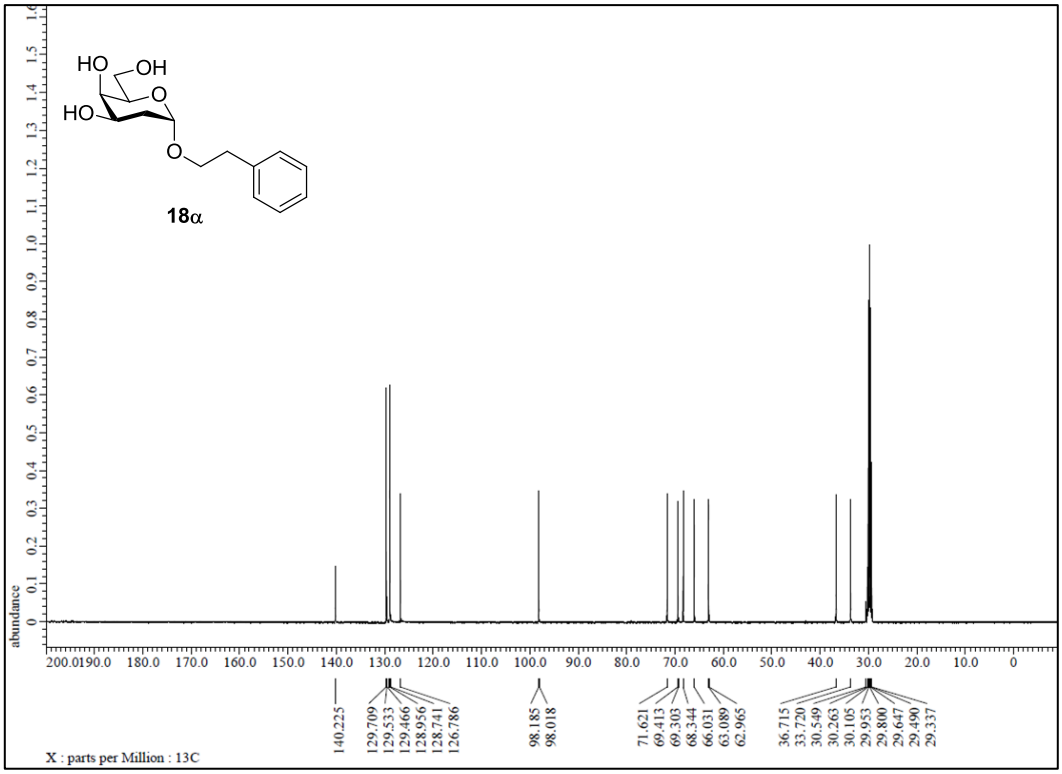


Figure S21 ^{13}C NMR spectrum of **18α**

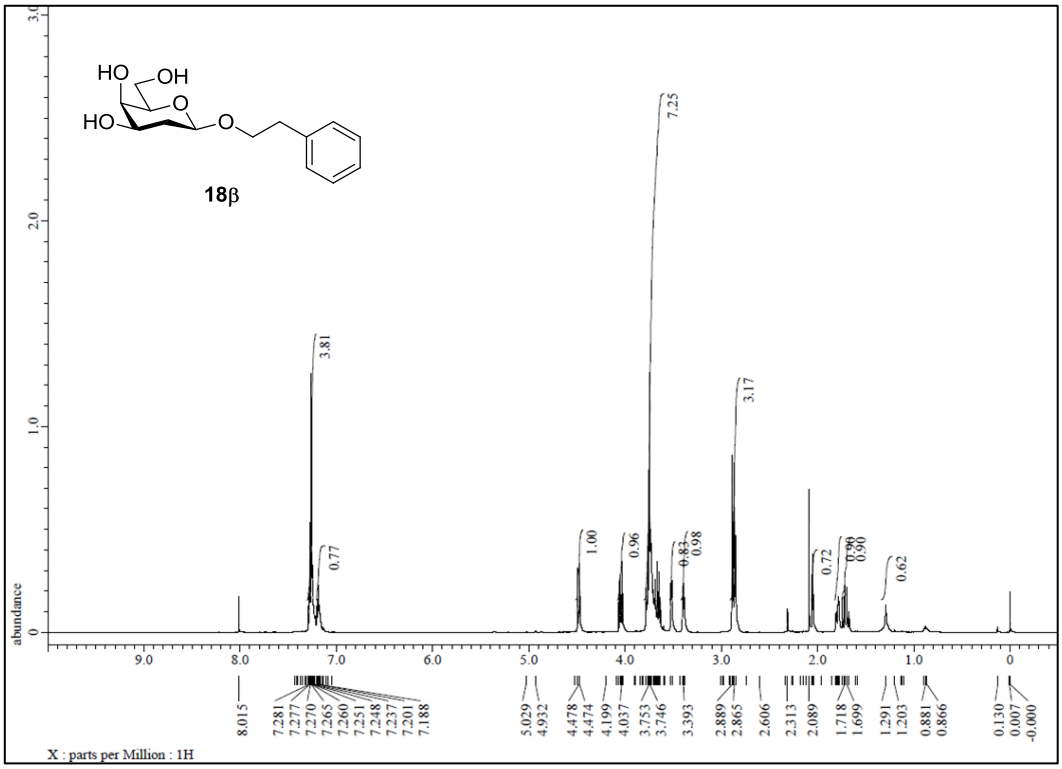


Figure S22 ^{1}H NMR spectrum of **18β**

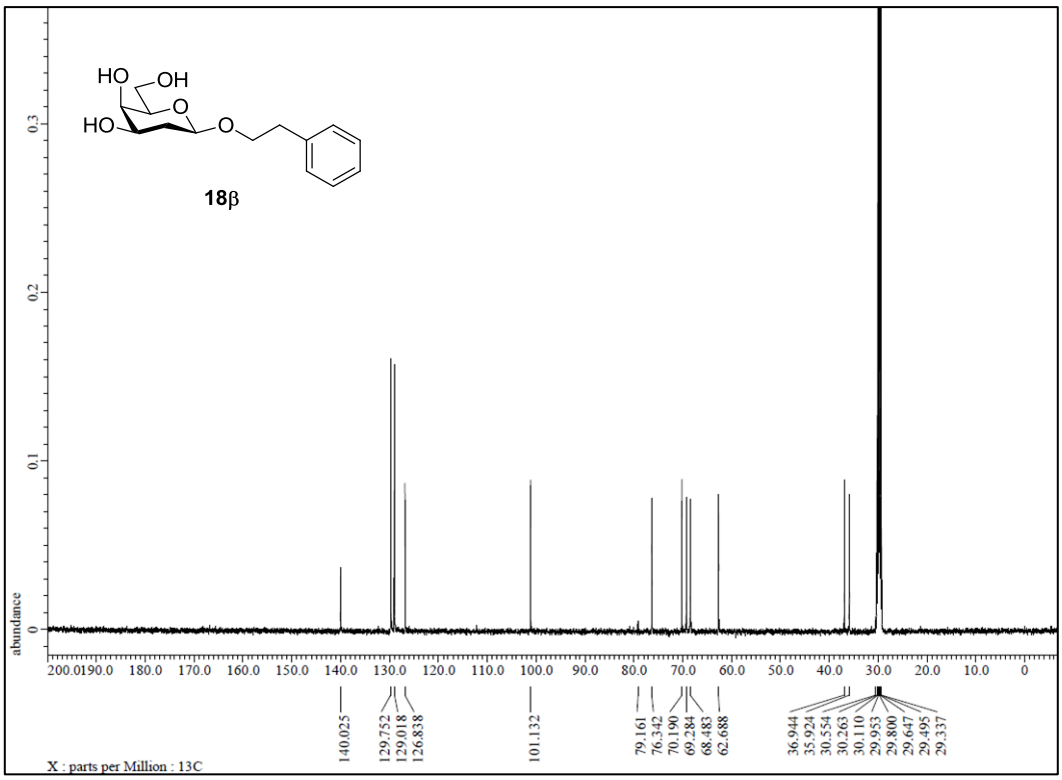


Figure S23 ^{13}C NMR spectrum of **18β**

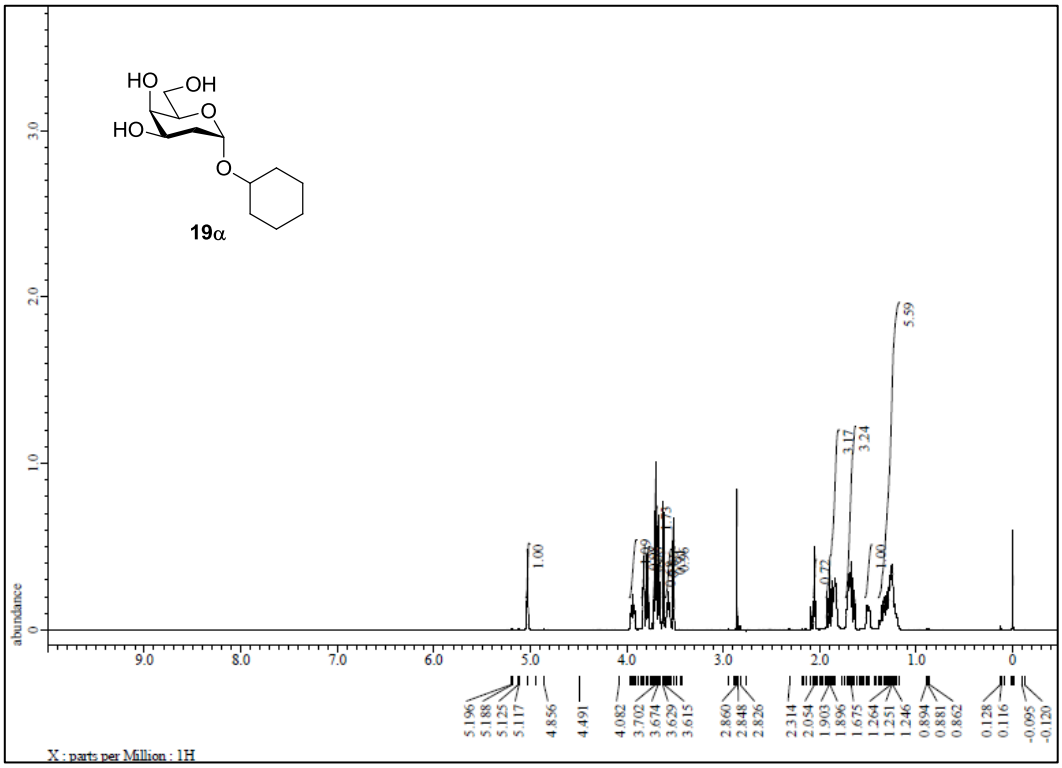


Figure S24 ^{1}H NMR spectrum of **19α**

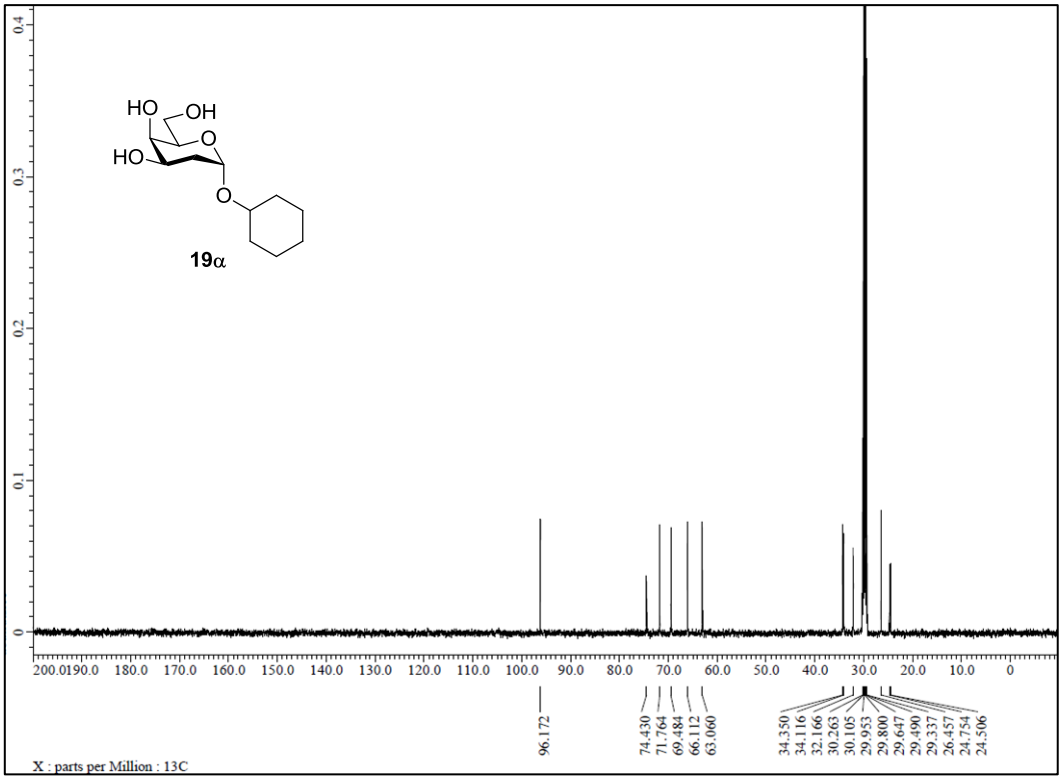


Figure S25 ^{13}C NMR spectrum of **19α**

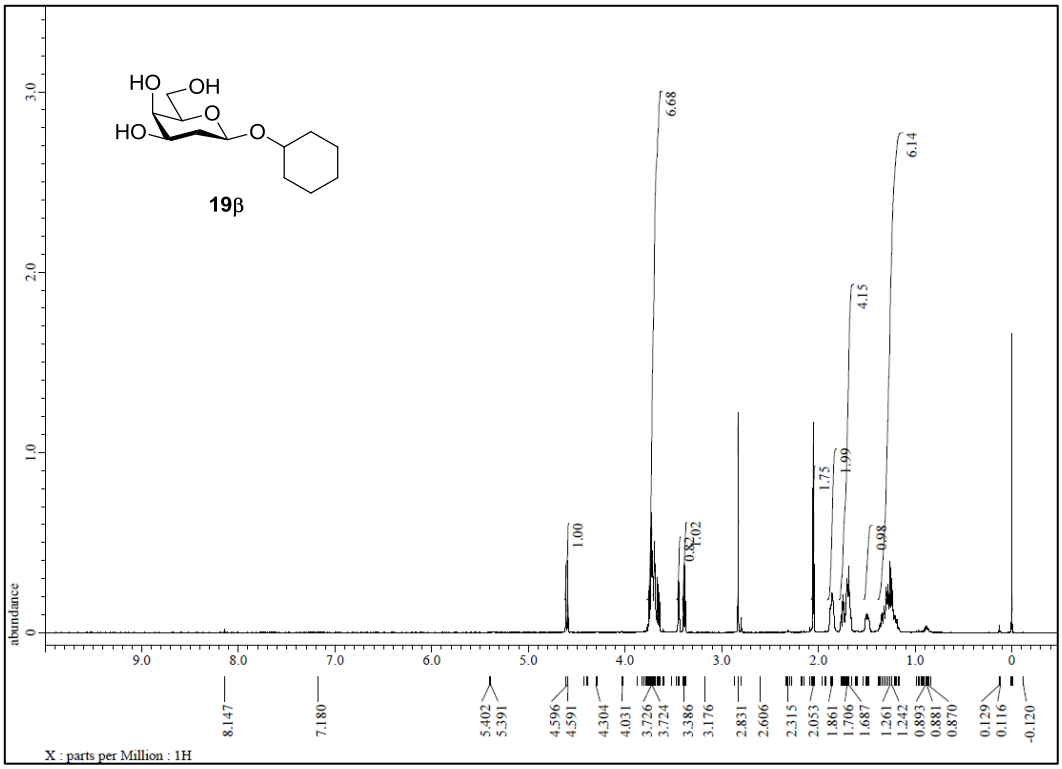


Figure S26 ^{1}H NMR spectrum of **19β**

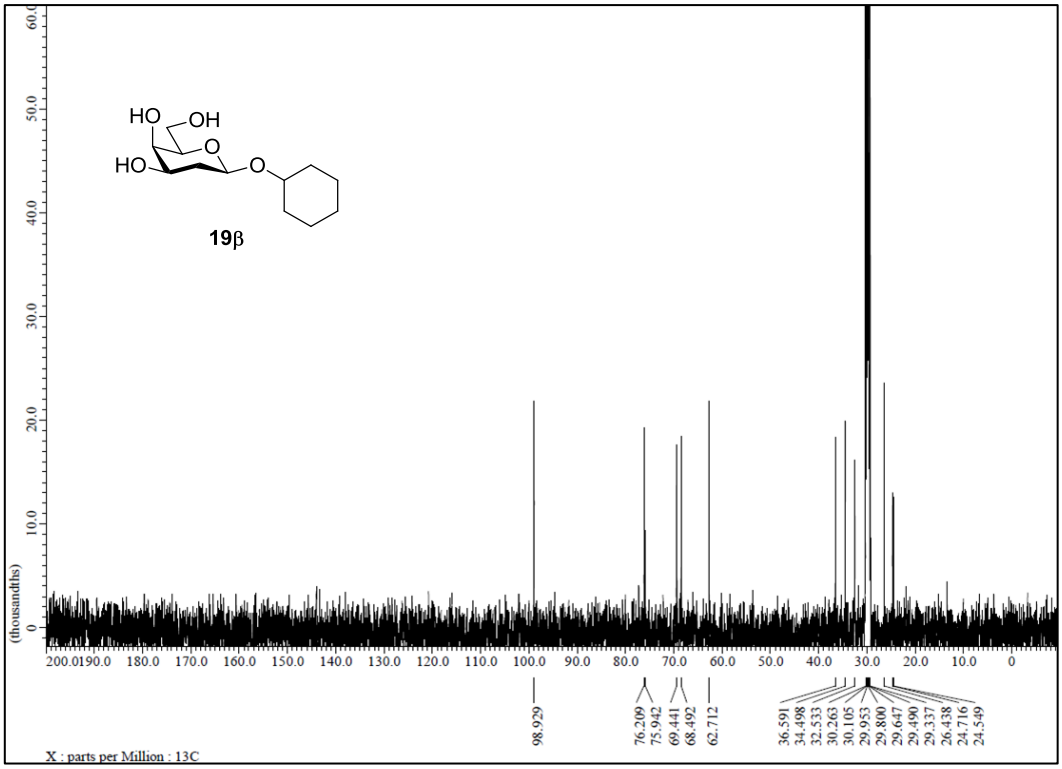


Figure S27 ^{13}C NMR spectrum of **19β**

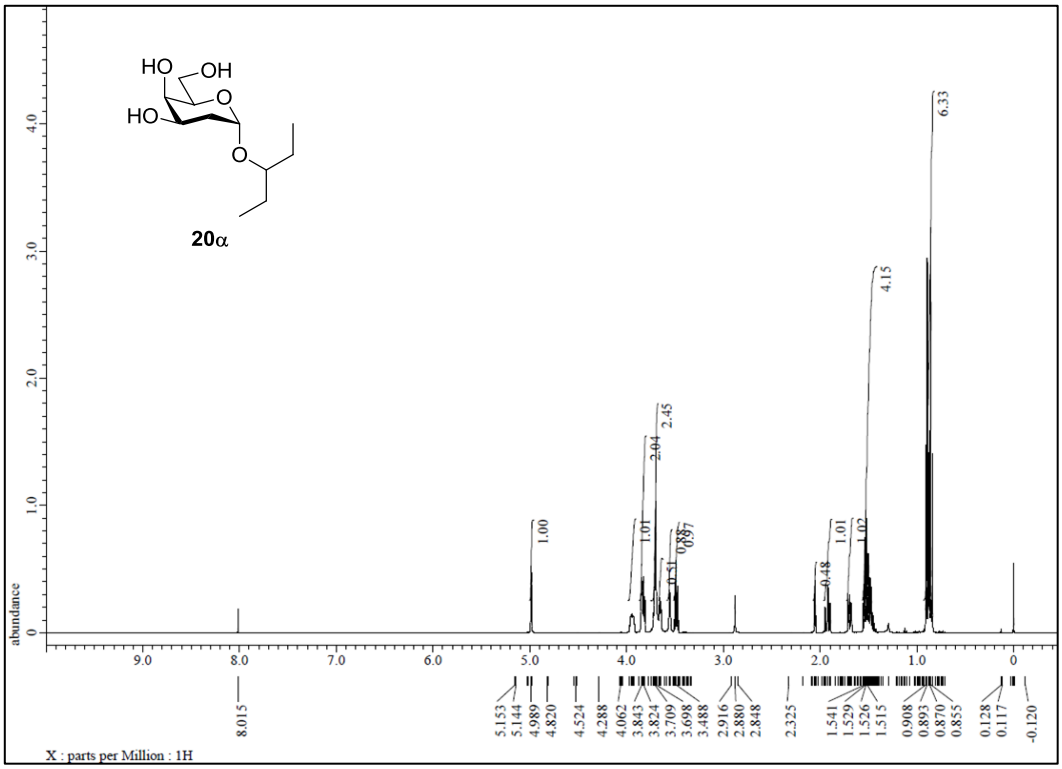


Figure S28 ^{1}H NMR spectrum of **20α**

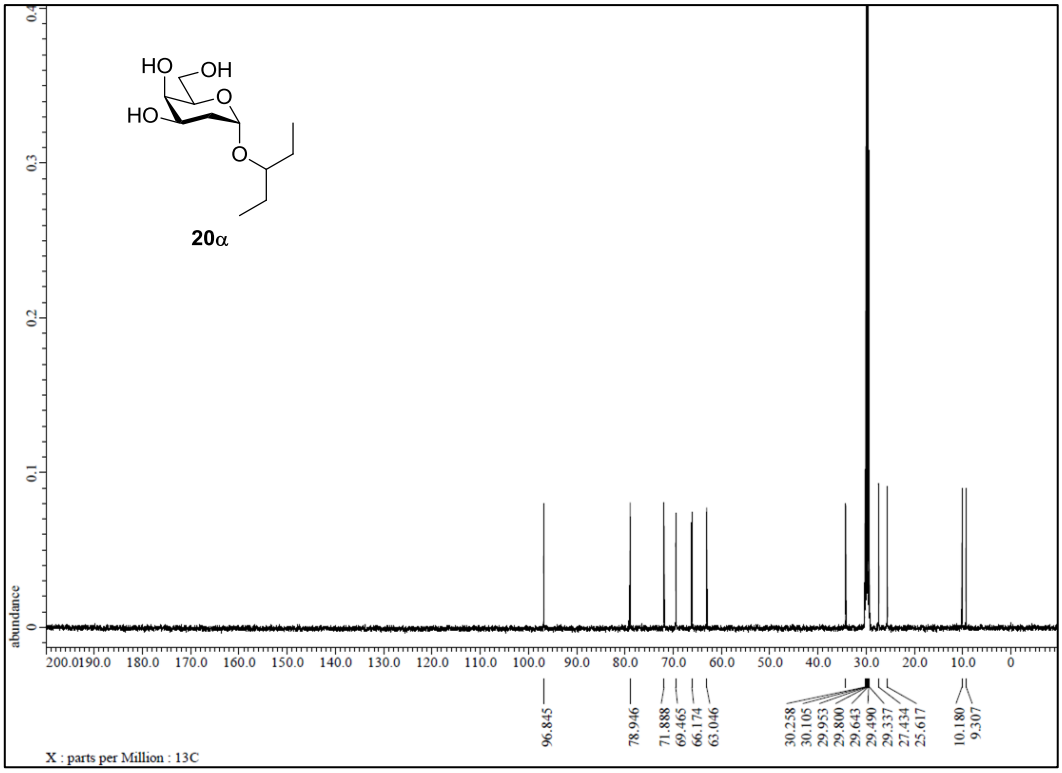


Figure S29 ^{13}C NMR spectrum of **20α**

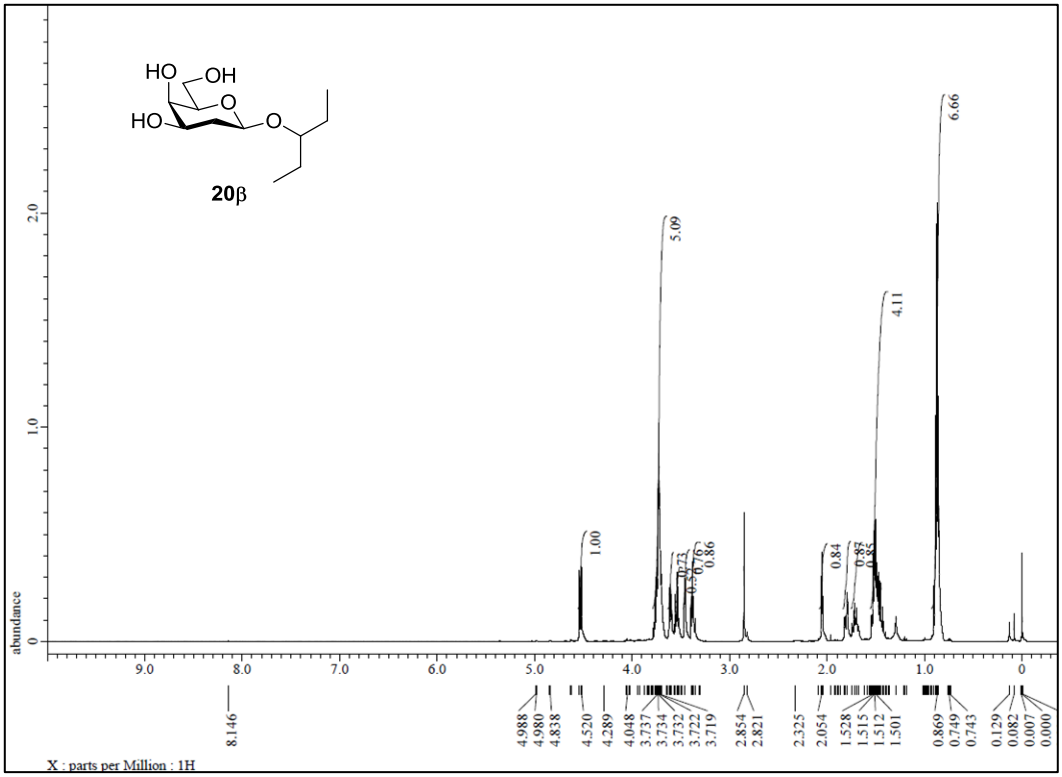


Figure S30 ^{1}H NMR spectrum of **20β**

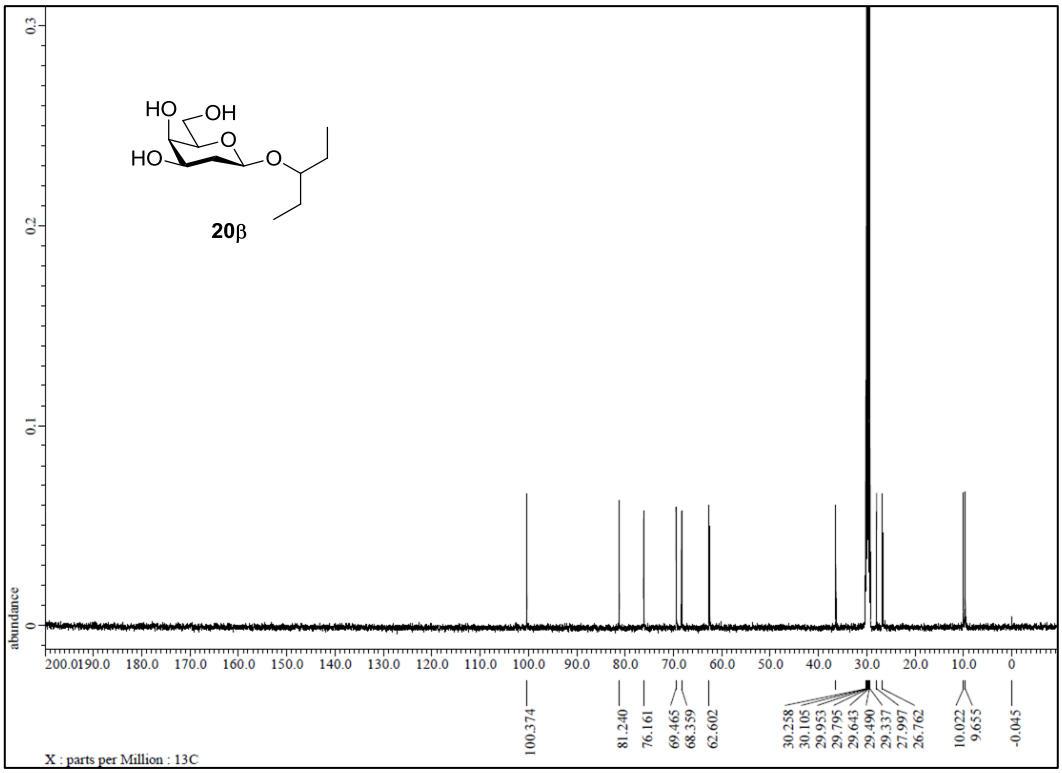


Figure S31 ^{13}C NMR spectrum of **20β**

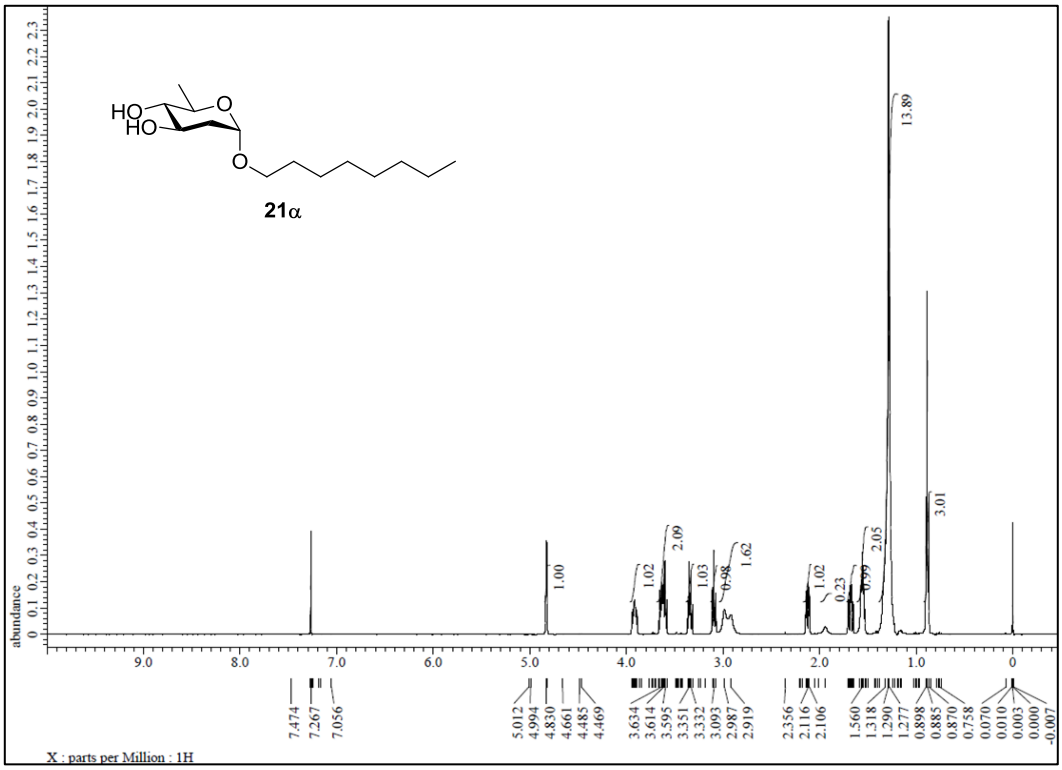


Figure S32 ^{1}H NMR spectrum of **21α**

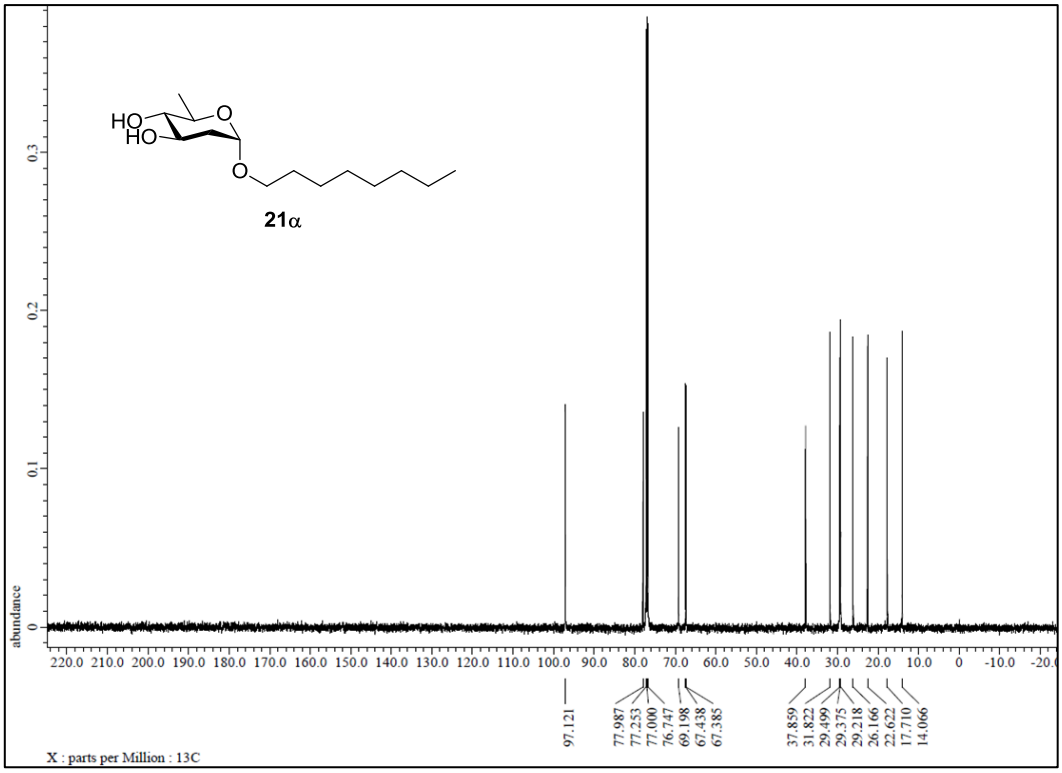


Figure S33 ^{13}C NMR spectrum of **21α**

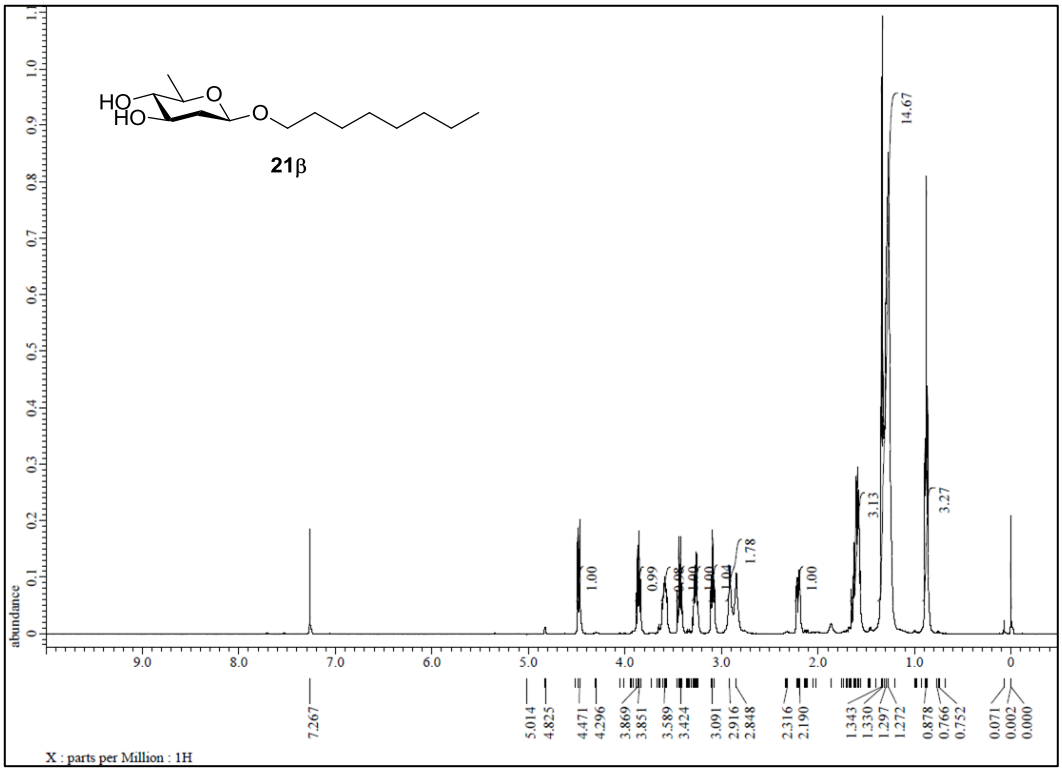


Figure S34 ^{1}H NMR spectrum of **21β**

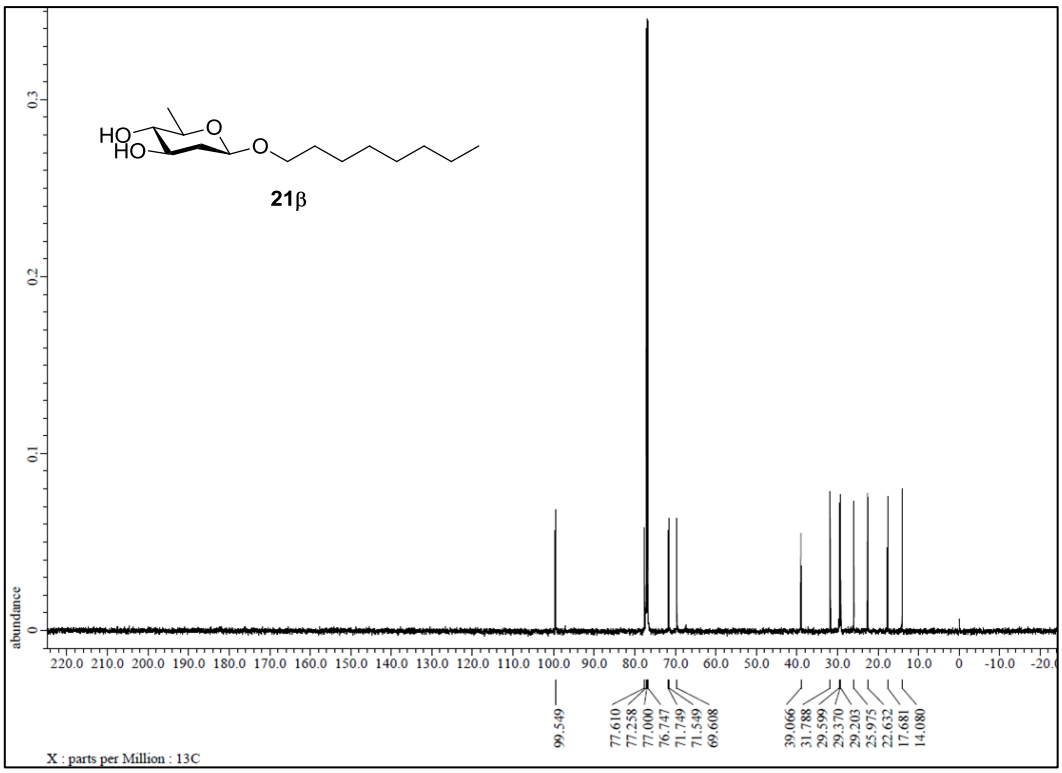


Figure S35 ^{13}C NMR spectrum of **21β**

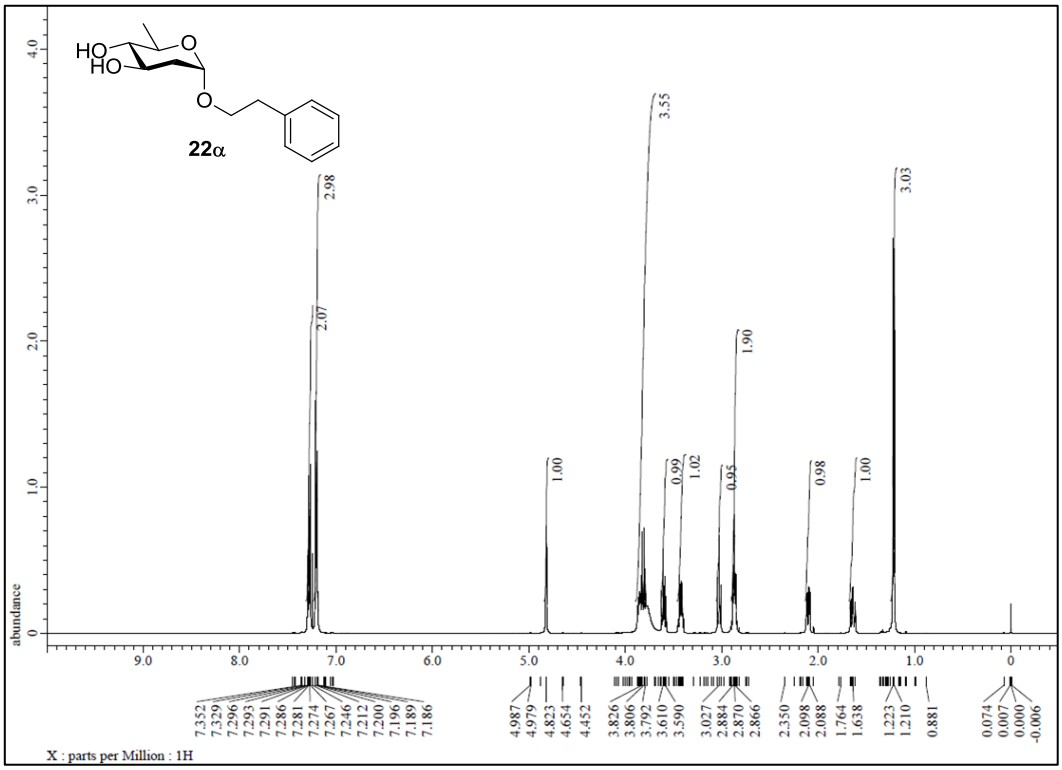


Figure S36 ^{1}H NMR spectrum of **22α**

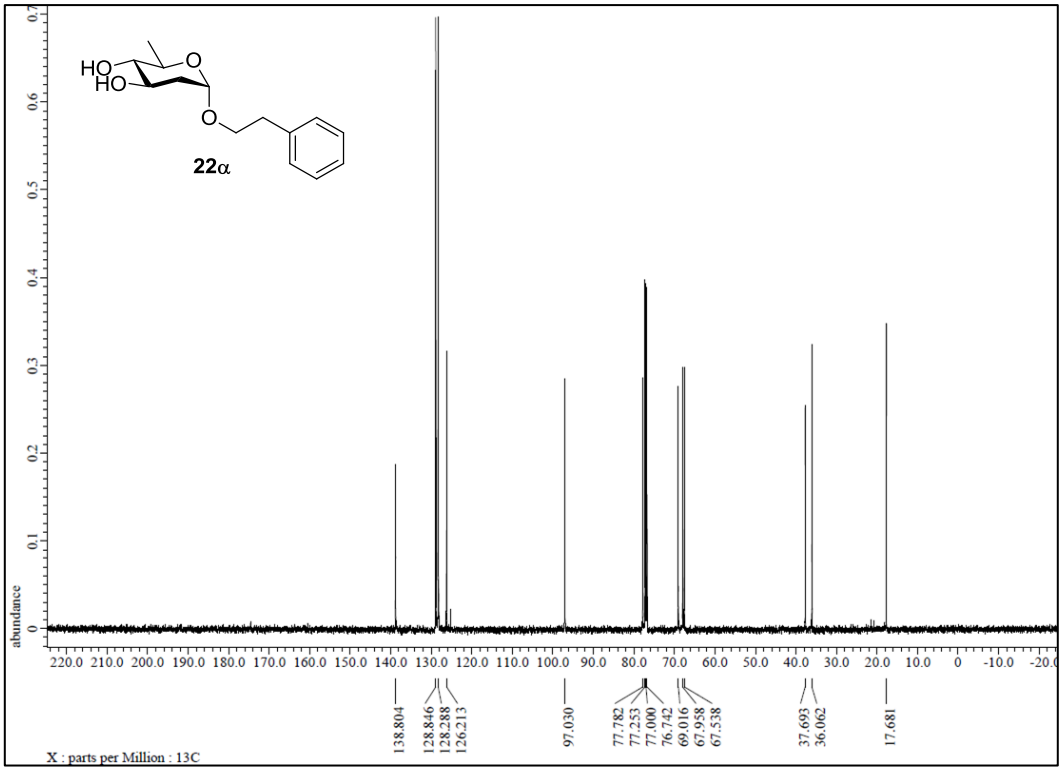


Figure S37 ^{13}C NMR spectrum of **22α**

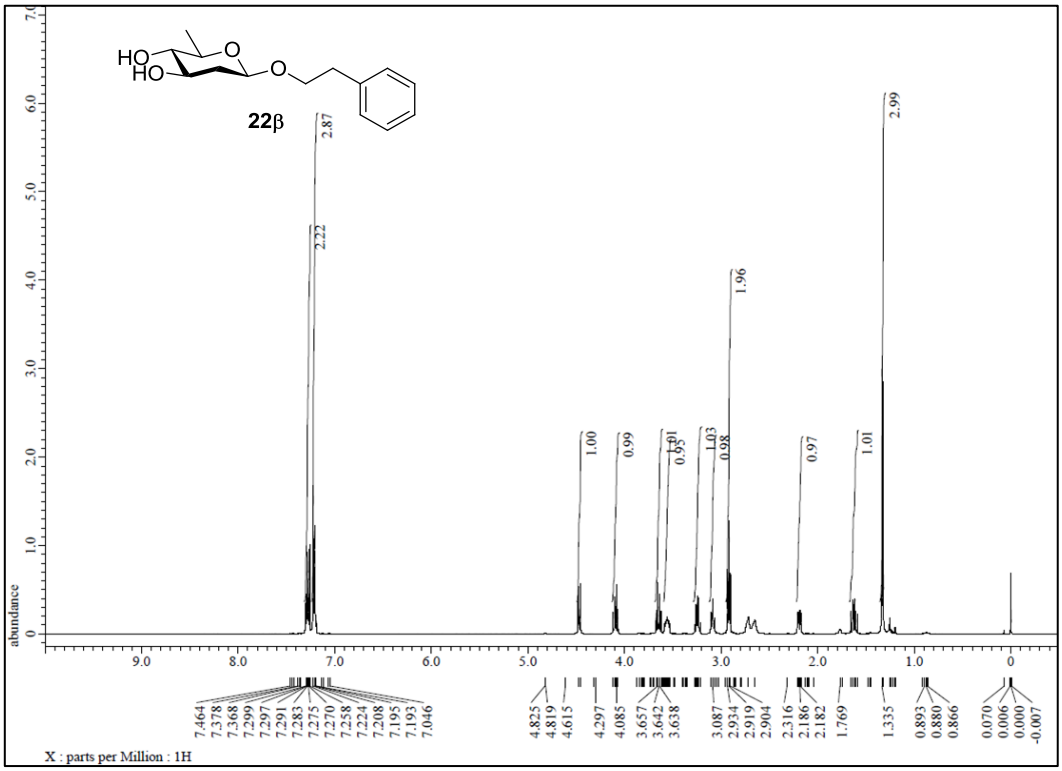


Figure S38 ^{1}H NMR spectrum of **22β**

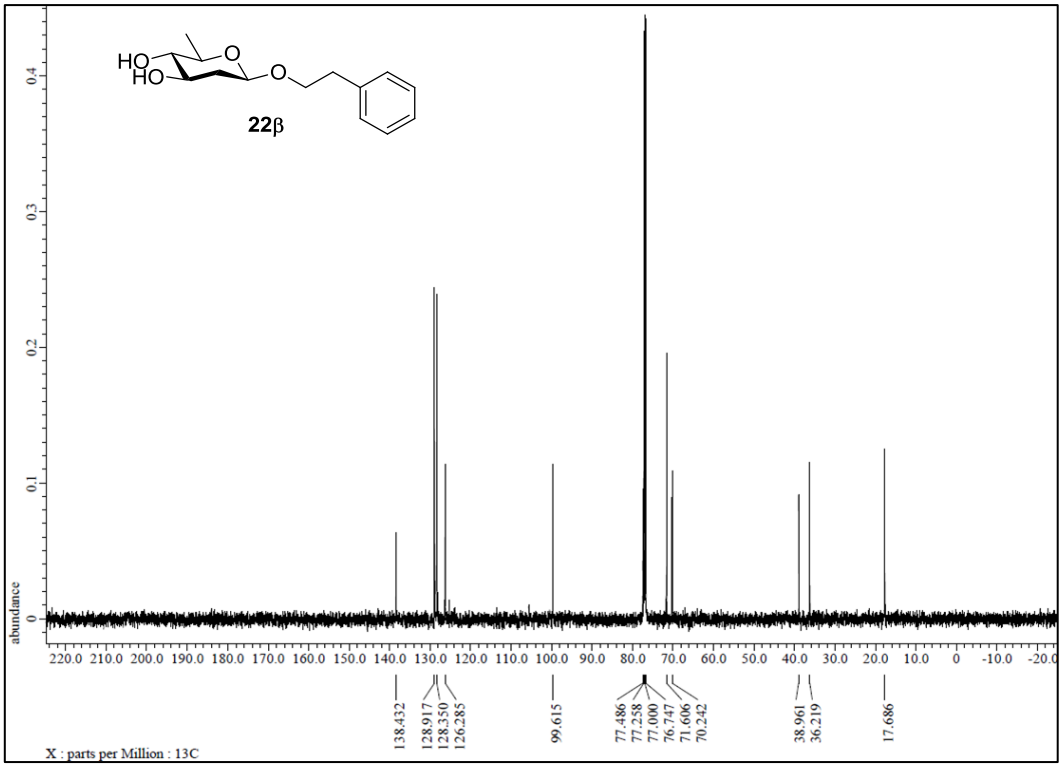


Figure S39 ^{13}C NMR spectrum of **22β**

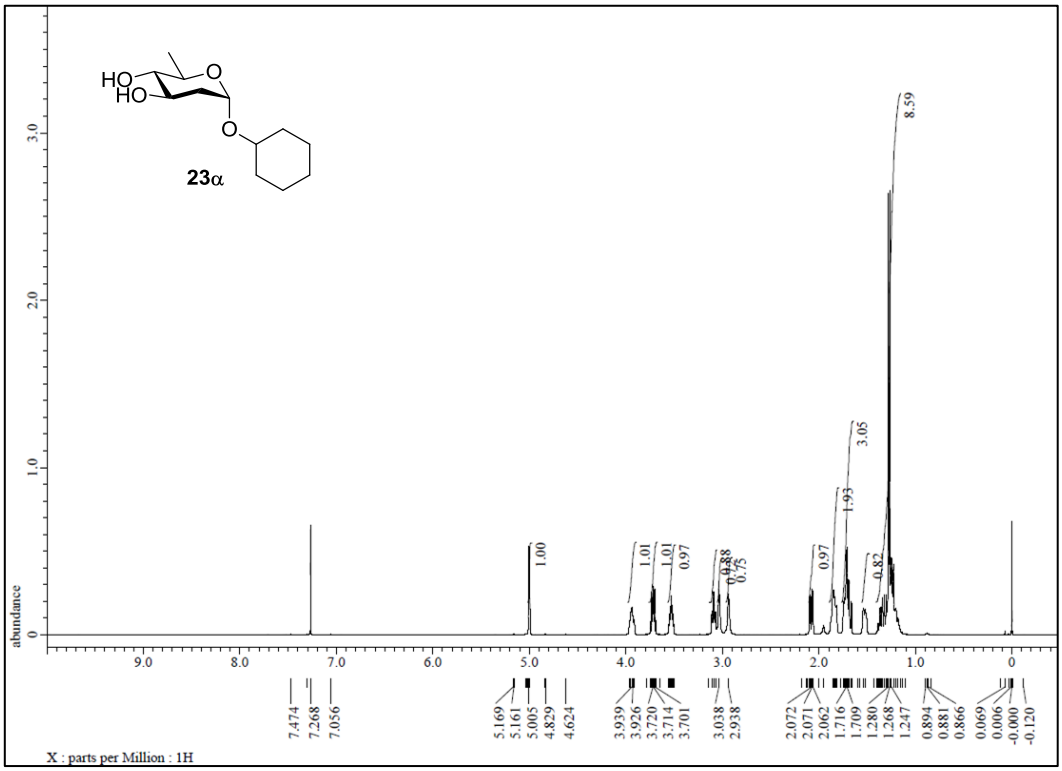


Figure S40 ^{1}H NMR spectrum of **23α**

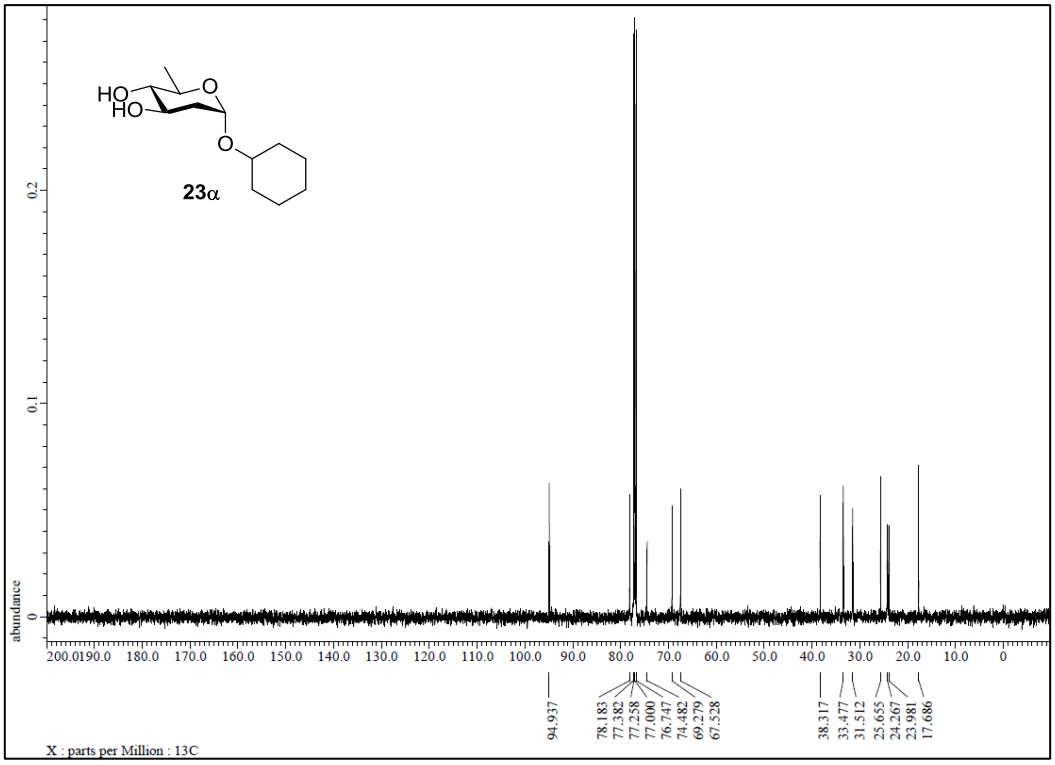


Figure S41 ^{13}C NMR spectrum of **23α**

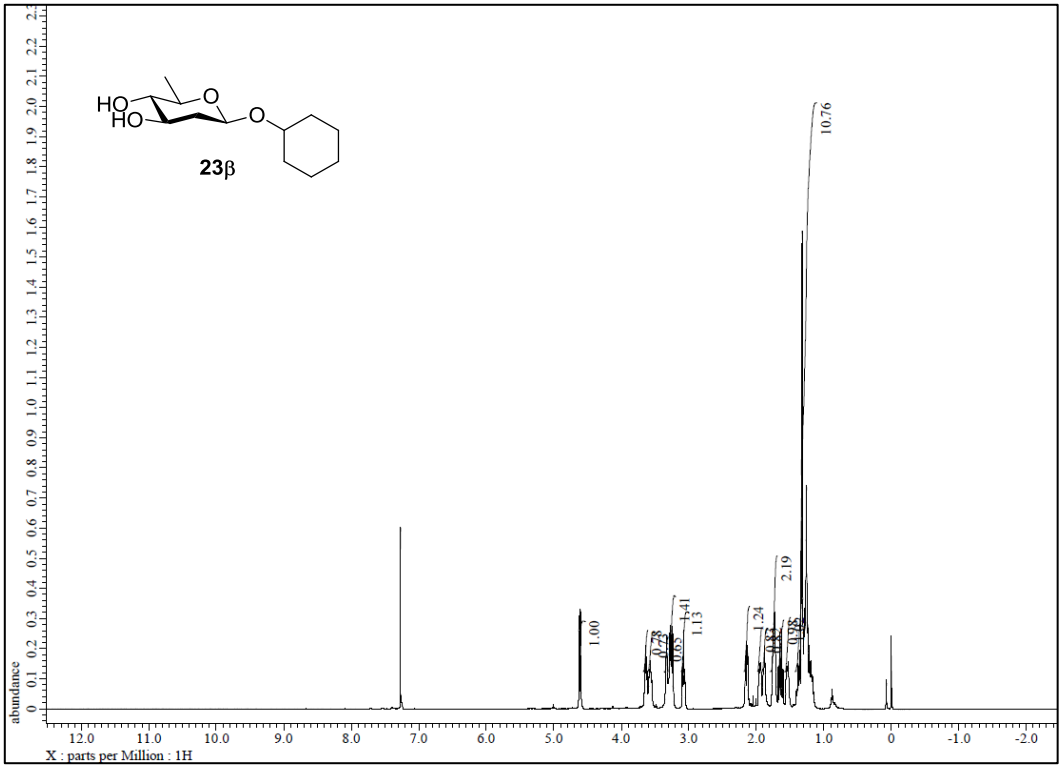


Figure S42 ^{1}H NMR spectrum of **23β**

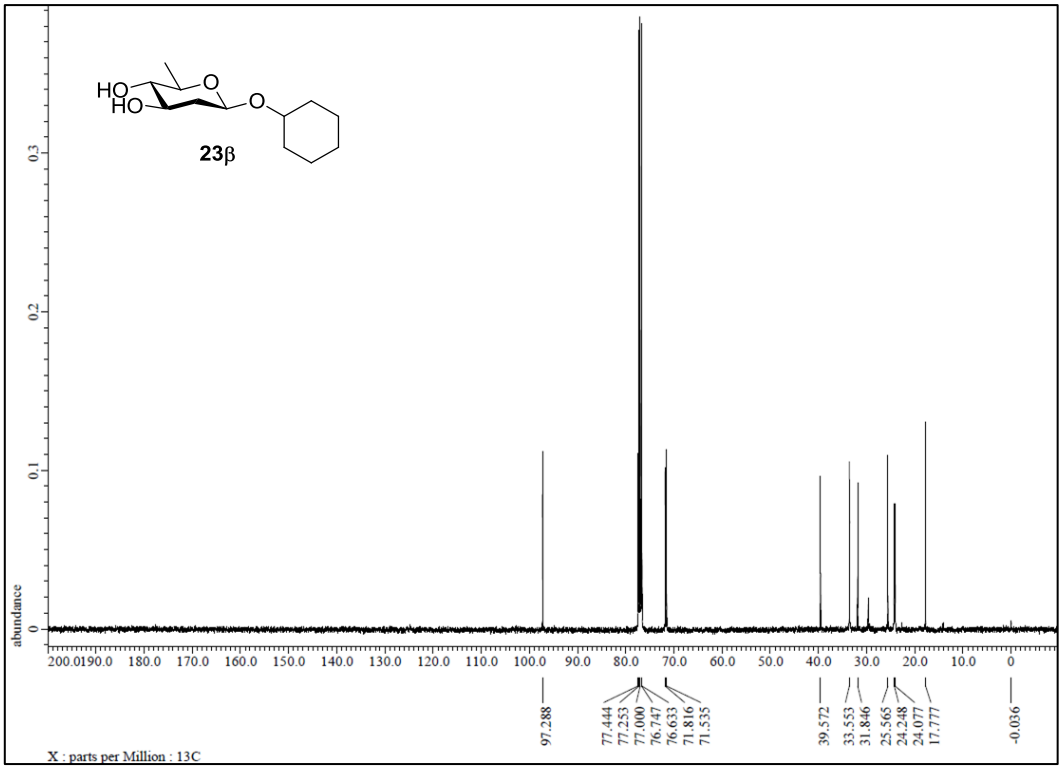


Figure S43 ^{13}C NMR spectrum of **23β**

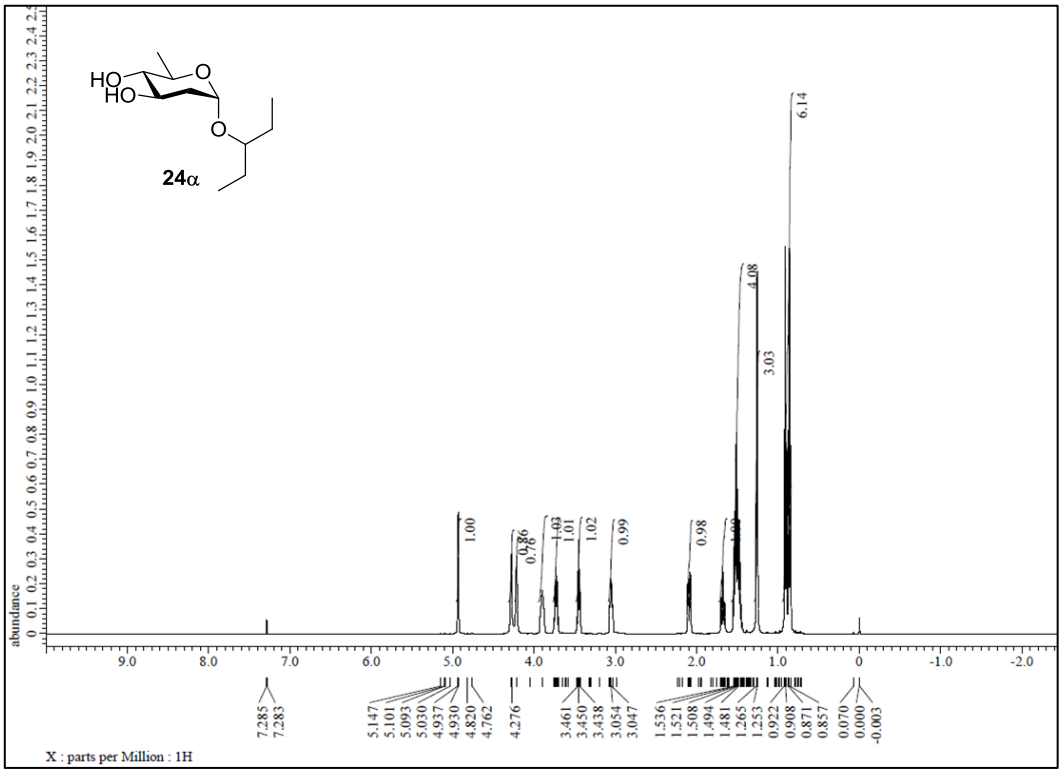


Figure S44 ^{1}H NMR spectrum of **24α**

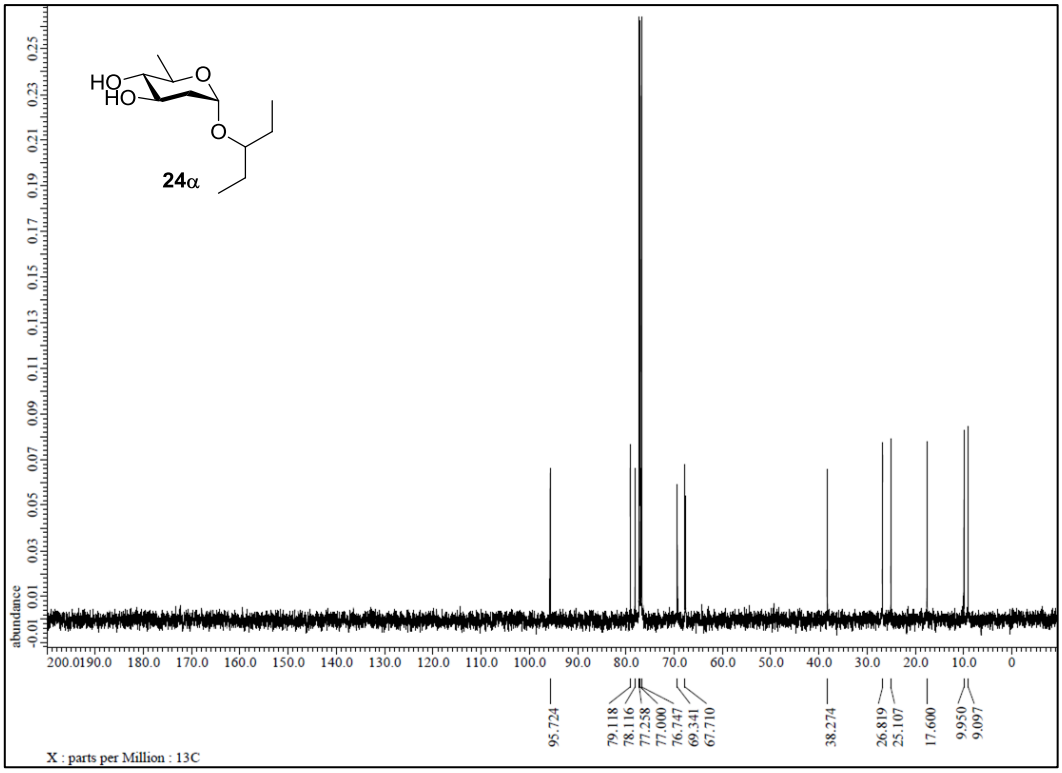


Figure S45 ^{13}C NMR spectrum of **24α**

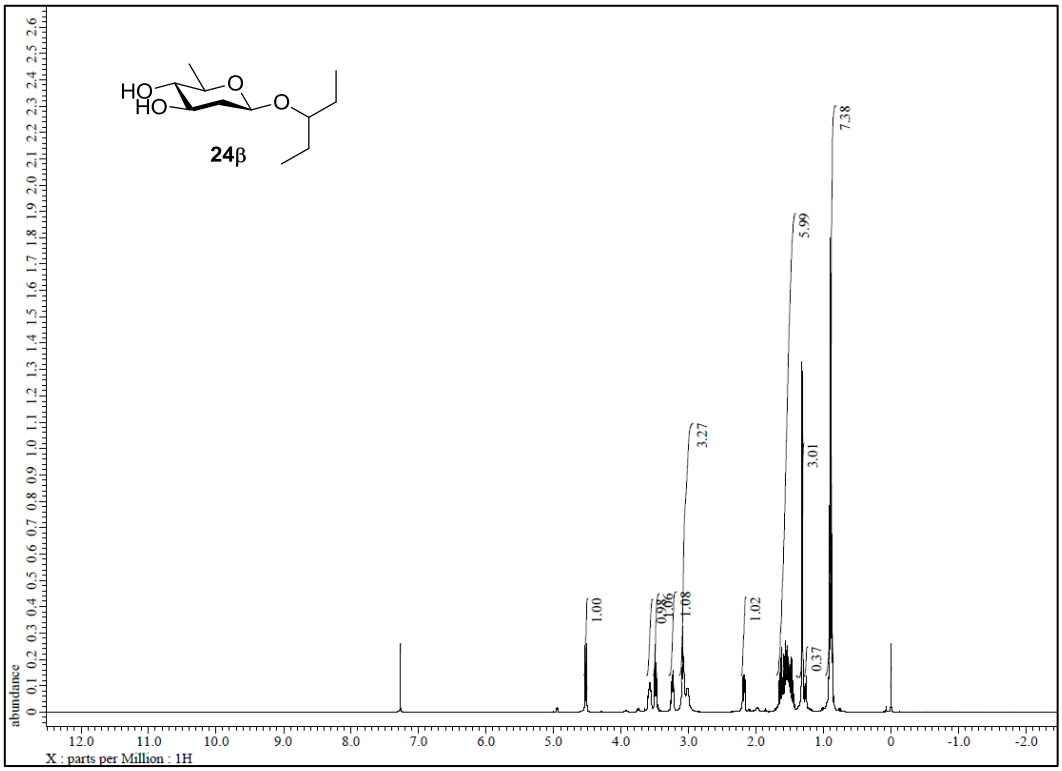


Figure S46 ^{1}H NMR spectrum of **24β**

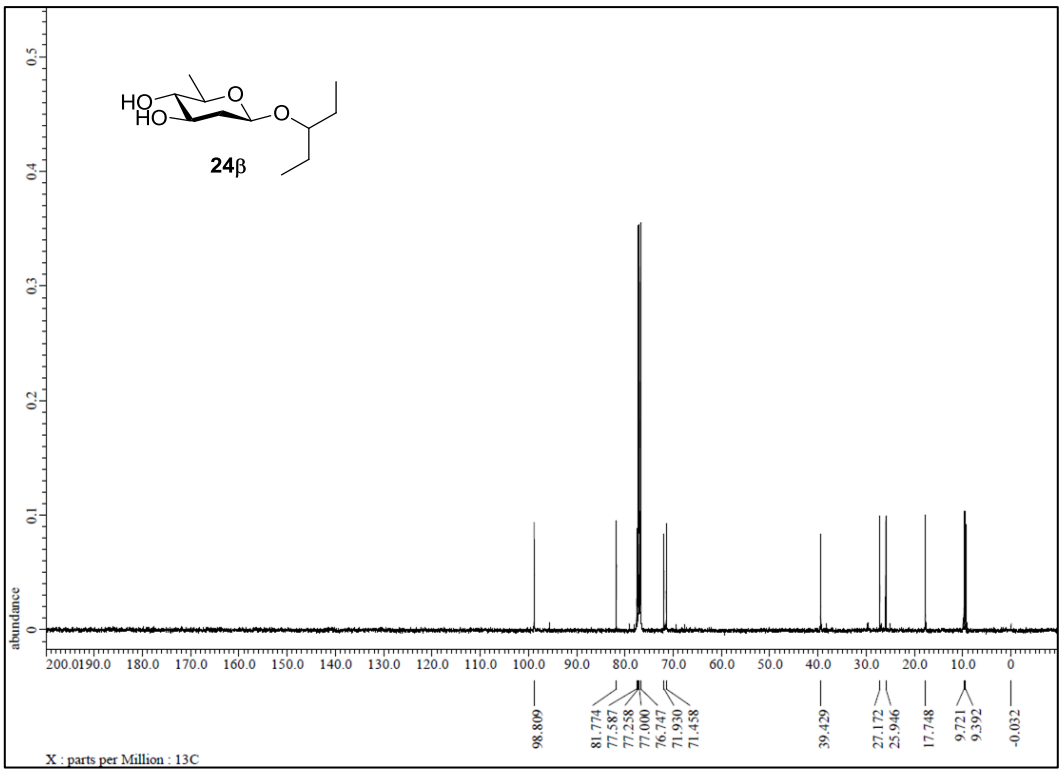


Figure S47 ^{13}C NMR spectrum of **24β**