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SUPPLEMENTARY INFORMATION

Photo-Induced Glycosylation Using Reusable Organophotoacids

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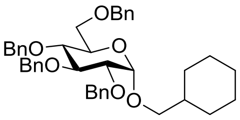
General experimental methods

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) spectrometer. ^{1}H NMR data are reported as follows; chemical shift in parts par million (ppm) downfield or upfield from tetramethylsilane (δ 0.00), $CDCl_3$ (δ 7.26) or acetone-d_6 (δ 2.05) integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet 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 29.8). For ^{1}H NMR analysis, prime number was used for assigning number to sugar carbon. 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.

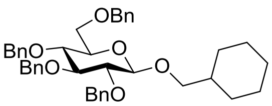
General procedure for glycosylations by using organophotoacids

To a stirred solution of glycosyl donor (0.1 mmol) and glycosyl acceptor (0.2~0.3 mmol) in Et_2O (0.5 M) was added organophotoacid **2** (0.03 mmol) or **5** (0.01 mmol). After stirring for 4 h under the photoirradiation using a UV lamp (365 nm, 12 mW/cm^2), the mixture was concentrated in vacuo. The purification of the residue by flash column chromatography gave the corresponding glycoside, and **2** or **5** was recovered.



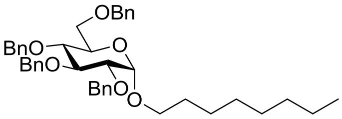
9α

Cyclohexylmethyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (9α)[1]: Colorless syrup; R_f 0.35 (4/1 *n*-hexane/EtOAc); $[\alpha]^{27}_D$ +41.1° (*c* 0.99, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85-1.00 (2H, m), 1.09-1.33 (3H, m), 1.60-1.88 (6H, m), 3.20 (1H, dd, *J* = 9.5 and 6.0 Hz, OCH_2), 3.42 (1H, dd, *J* = 9.5 and 7.5 Hz, OCH_2), 3.55 (1H, dd, *J* = 9.5 and 3.5 Hz, H-2), 3.58-3.82 (4H, m), 3.97 (1H, dd, *J* = 9.5 and 9.5 Hz, H-3), 4.47 and 4.61 (2H, ABq, *J* = 12.5 Hz, $ArCH_2$), 4.47 and 4.83 (2H, ABq, *J* = 11.0 Hz, $ArCH_2$), 4.64 and 4.76 (2H, ABq, *J* = 12.0 Hz, $ArCH_2$), 4.73 (1H, d, *J* = 3.5 Hz, H-1), 4.81 and 4.99 (2H, ABq, *J* = 10.5 Hz, $ArCH_2$), 7.11-7.16 (2H, m, ArH), 7.22-7.40 (18H, m, ArH); ^{13}C NMR (500 MHz, $CDCl_3$) δ 25.7, 25.8, 26.6, 30.0×2, 37.6, 68.5, 70.0, 73.0, 73.4, 73.9, 75.1, 75.6, 77.8, 80.3, 82.1, 97.1, 127.6, 127.7×2, 127.9×2, 128.0, 128.3, 128.4×2, 138.0, 138.3, 138.4, 139.0; HRMS (ESI-TOF) *m/z* 659.3329 (659.3349 calcd for $C_{41}H_{48}O_6Na$ $[M+Na]^+$).



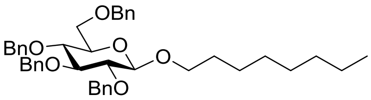
9β

Cyclohexylmethyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (9β)[1]: White solid; R_f 0.40 (4/1 *n*-hexane/EtOAc); $[\alpha]^{27}_D$ +4.2° (*c* 0.99, $CHCl_3$); mp 98.0-99.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90-1.06 (2H, m), 1.08-1.34 (3H, m), 1.58-1.92 (6H, m), 3.32 (1H, dd, *J* = 9.5 and 7.0 Hz, OCH_2), 3.40-3.49 (2H, m), 3.53-3.77 (4H, m), 3.79 (1H, dd, *J* = 9.5 and 6.0 Hz, OCH_2), 4.37 (1H, d, *J* = 7.5 Hz, H-1), 4.52 and 4.81 (2H, ABq, *J* = 11.0 Hz, $ArCH_2$), 4.56 and 4.62 (2H, ABq, *J* = 12.0 Hz, $ArCH_2$), 4.71 and 4.96 (2H, ABq, *J* = 11.0 Hz, $ArCH_2$), 4.78 and 4.92 (2H, ABq, *J* = 10.5 Hz, $ArCH_2$), 7.13-7.18 (2H, m, ArH), 7.22-7.38 (18H, m, ArH); ^{13}C NMR (500 MHz, $CDCl_3$) δ 25.8×2, 26.5, 29.9, 30.1, 38.1, 69.0, 73.4, 74.8, 74.9, 75.0, 75.7×2, 78.0, 82.3, 84.7, 103.8, 127.6, 127.7, 127.8, 128.1, 128.2, 128.3, 128.4, 138.1, 138.2, 138.5, 138.6; HRMS (ESI-TOF) *m/z* 659.3316 (659.3349 calcd for $C_{41}H_{48}O_6Na$ $[M+Na]^+$).



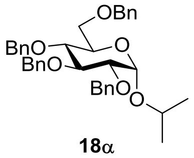
17α

***n*-Octyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (17α)[1]:** Colorless syrup; R_f 0.45 (6/1 *n*-hexane/EtOAc); $[\alpha]^{33}_{D}$ +37.6° (*c* 1.10, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.83-0.92 (3H, m), 1.20-1.40 (10H, m), 1.58-1.67 (2H, m), 3.41 (1H, dt, *J* = 10.0 and 6.5 Hz, OCH_2), 3.55 (1H, dd, *J* = 9.5 and 4.0 Hz, H-2), 3.58-3.68 (1H, m), 3.62 (1H, dd, *J* = 10.0 and 4.0 Hz, H-6), 3.63 (1H, dd, *J* = 9.5 and 4.5 Hz, H-4), 3.72 (1H, dd, *J* = 10.0 and 4.0 Hz, H-6), 3.78 (1H, ddd, *J* = 10.0, 5.0 and 4.0 Hz, H-5), 3.98 (1H, dd, *J* = 9.5 and 9.5 Hz, H-3), 4.47 and 4.61 (2H, ABq, *J* = 12.0 Hz, $ArCH_2$), 4.47 and 4.83 (2H, ABq, *J* = 10.5 Hz, $ArCH_2$), 4.65 and 4.78 (2H, ABq, *J* = 12.5 Hz, $ArCH_2$), 4.75 (1H, d, *J* = 3.5 Hz, H-1), 4.81 and 4.99 (2H, d, *J* = 11.0 Hz, $ArCH_2$), 7.10-7.16 (2H, m, ArH), 7.22-7.39 (18H, m, ArH); ^{13}C NMR (500 MHz, $CDCl_3$) δ 14.1, 22.7, 26.2, 29.2, 29.4, 31.8, 68.2, 68.5, 70.0, 73.1, 73.4, 75.1, 75.7, 77.8, 80.1, 82.1, 96.9, 127.5, 127.6, 127.7, 127.8, 127.9×2, 128.0, 128.4×2, 138.0, 138.3, 138.4, 138.9; HRMS (ESI-TOF) *m/z* 675.3634 (675.3662 calcd for $C_{42}H_{52}O_6Na$ $[M+Na]^+$).



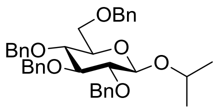
17β

***n*-Octyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (17β)[1]:** White solid; R_f 0.50 (6/1 *n*-hexane/EtOAc); $[\alpha]^{33}_{D}$ +7.0° (*c* 0.46, $CHCl_3$); mp 33.5-34.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.82-0.93 (3H, m), 1.19-1.46 (10H, m), 1.58-1.74 (2H, m), 3.44 (1H, dd, *J* = 9.0 and 7.5 Hz, H-2), 3.42-3.55 (2H, m), 3.57 (1H, dd, *J* = 9.0 and 9.0 Hz, H-3), 3.63-3.71 (1H, m), 3.64 (1H, dd, *J* = 9.0 and 9.0 Hz, H-4), 3.75 (1H, dd, *J* = 10.5 and 2.0 Hz, H-6), 3.96 (1H, dt, *J* = 9.5 and 6.0 Hz, OCH_2), 4.38 (1H, d, *J* = 8.0 Hz, H-1), 4.52 and 4.81 (2H, ABq, *J* = 10.5 Hz, $ArCH_2$), 4.56 and 4.61 (2H, ABq, *J* = 12.0 Hz, $ArCH_2$), 4.71 and 4.96 (2H, ABq, *J* = 11.5 Hz, $ArCH_2$), 4.78 and 4.93 (2H, ABq, *J* = 11.0 Hz, $ArCH_2$), 7.13-7.18 (2H, m, ArH), 7.23-7.38 (18H, m, ArH); ^{13}C NMR (500 MHz, $CDCl_3$) δ 14.1, 22.7, 26.2, 29.3, 29.4, 29.8, 31.8, 69.0, 70.2, 73.4, 74.8×2, 75.0, 75.7, 77.9, 82.3, 84.7, 103.6, 127.6×2, 127.7, 127.9, 128.0, 128.1, 128.3, 128.4×2, 138.1, 138.2, 138.5, 138.6; HRMS (ESI-TOF) *m/z* 675.3640 (675.3662 calcd for $C_{42}H_{52}O_6Na$ $[M+Na]^+$).



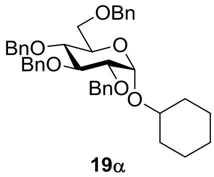
18α

Isopropyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (18α)[1]: Colorless syrup; R_f 0.60 (60/1 chloroform/EtOAc); $[\alpha]^{27}_{D}$ +37.2° (*c* 1.38, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.17 and 1.22 (each 3H, d, *J* = 6.0 Hz, CH_3), 3.55 (1H, dd, *J* = 10.0 and 3.5 Hz, H-2), 3.61 (1H, dd, *J* = 10.0 and 2.0 Hz, H-6), 3.64 (1H, dd, *J* = 9.8 and 8.5 Hz, H-4), 3.73 (1H, dd, *J* = 10.5 and 3.5 Hz, H-6), 3.84 (1H, ddd, *J* = 10.0, 3.5 and 1.5 Hz, H-5), 3.89 (1H, qq, *J* = 6.0 Hz, OCH), 3.99 (1H, dd, *J* = 9.0 and 9.0 Hz, H-3), 4.46 and 4.61 (2H, ABq, *J* = 12.0 Hz, $ArCH_2$), 4.47 and 4.83 (2H, ABq, *J* = 10.5 Hz, $ArCH_2$), 4.65 and 4.77 (2H, ABq, *J* = 12.0 Hz, $ArCH_2$), 4.81 and 5.00 (2H, ABq, *J* = 10.5 Hz, $ArCH_2$), 7.10-7.16 (2H, m, ArH), 7.22-7.41 (18H, m, ArH); ^{13}C NMR (500 MHz, $CDCl_3$) δ 21.1, 23.2, 68.5, 69.0, 70.0, 73.1, 73.4, 75.1, 75.7, 77.9, 79.9, 82.1, 94.8, 127.5, 127.6, 127.7, 127.8, 127.9×2, 128.0, 128.2, 128.3, 128.4×2, 138.0, 138.2, 138.3, 139.0; HRMS (ESI-TOF) 605.2849 (605.2879 calcd for $C_{37}H_{42}O_6Na$ $[M+Na]^+$).



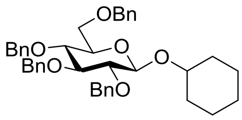
18β

Isopropyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (18β)[1]: White solid; R_f 0.46 (5/1 *n*-hexane/EtOAc); $[\alpha]^{27}_{D}$ +10.3° (*c* 0.64, $CHCl_3$); mp 109.5-110.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.24 and 1.32 (each 3H, d, *J* = 6.0 Hz, CH_3), 3.43 (1H, dd, *J* = 9.0 and 7.5 Hz, H-4), 3.44 (1H, ddd, *J* = 9.0, 4.0 and 2.0 Hz, H-5), 3.54 (1H, dd, *J* = 9.0 and 9.0 Hz, H-3), 3.63 (1H, dd, *J* = 9.0 and 7.5 Hz, H-2), 3.65 (1H, dd, *J* = 10.0 and 4.0 Hz, H-6), 3.74 (1H, dd, *J* = 11.0 and 2.0 Hz, H-6), 4.02 (1H, qq, *J* = 6.0 Hz, OCH), 4.46 (1H, d, *J* = 7.5 Hz, H-1), 4.53 and 4.82 (2H, ABq, *J* = 11.0 Hz, $ArCH_2$), 4.58 and 4.61(2H, ABq, *J* = 12.5 Hz, $ArCH_2$), 4.70 and 4.97 (2H, ABq, *J* = 11.0 Hz, $ArCH_2$), 4.78 and 4.92 (2H, ABq, *J* = 11.0 Hz, $ArCH_2$), 7.14-7.19 (2H, m, ArH), 7.23-7.39 (18H, m, ArH); ^{13}C NMR (500 MHz, $CDCl_3$) δ 22.2, 23.7, 69.2, 72.4, 73.4, 74.8, 75.0, 75.7, 78.0, 82.3, 84.8, 102.2, 127.5, 127.6×2, 127.7×2, 127.9, 128.0, 128.2, 128.3, 128.4, 138.1, 138.3, 138.5, 138.7; HRMS (ESI-TOF) 605.2907 (605.2879 calcd for $C_{37}H_{42}O_6Na$ $[M+Na]^+$).



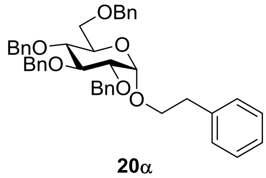
19α

Cyclohexyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (19α)[1]: Colorless syrup; R_f 0.64 (60/1 chloroform/EtOAc); $[\alpha]^{27}_{D}$ +51.0° (*c* 1.71, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.12-1.60 (6H, m), 1.69-1.96 (4H, m), 3.51-3.68 (1H, m), 3.55 (1H, dd, *J* = 10.0 and 3.5 Hz, H-2), 3.62 (1H, dd, *J* = 11.0 and 2.0 Hz, H-6), 3.63 (1H, dd, *J* = 10.0 and 9.5 Hz, H-4), 3.74 (1H, dd, *J* = 10.5 and 4.0 Hz, H-6), 3.88 (1H, ddd, *J* = 10.0, 4.0 and 2.0 Hz, H-5), 4.00 (1H, dd, *J* = 9.0 and 9.0 Hz, H-3), 4.46 and 4.61 (2H, ABq, *J* = 12.0 Hz, $ArCH_2$), 4.46 and 4.83 (2H, ABq, *J* = 10.5 Hz, $ArCH_2$), 4.66 and 4.74 (2H, ABq, *J* = 12.0 Hz, $ArCH_2$), 4.81 and 5.00 (2H, ABq, *J* = 10.5 Hz, $ArCH_2$), 4.95 (1H, d, *J* = 3.5 Hz, H-1), 7.11-7.16 (2H, m, ArH), 7.22-7.38 (18H, m, ArH); ^{13}C NMR (500 MHz, $CDCl_3$) δ 24.1, 24.4, 25.6, 31.4, 33.3, 68.6, 70.0, 72.9, 73.4, 75.1, 75.3, 75.6, 77.3, 77.9, 80.0, 82.1, 94.7, 127.5, 127.6, 127.7, 127.8×2, 127.9, 128.0, 128.1, 128.3×2, 138.0, 138.2, 138.3, 139.0; HRMS (ESI-TOF) 645.3193 (645.3192 calcd for $C_{40}H_{46}O_6Na$ $[M+Na]^+$).



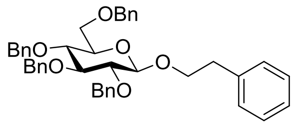
19β

Cyclohexyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (19β)[1]: White solid; R_f 0.48 (60/1 chloroform/EtOAc); $[\alpha]^{27}_{D}$ +8.7° (*c* 0.90, $CHCl_3$); mp 104-106 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.19-1.60 (6H, m), 1.70-1.81 (2H, m), 1.90-2.09 (2H, m), 3.44 (1H, dd, *J* = 9.5 and 9.5 Hz, H-3), 3.45 (1H, ddd, *J* = 9.0, 5.0 and 1.5 Hz, H-5), 3.51-3.79 (2H, m), 3.62 (1H, dd, *J* = 9.0 and 8.0 Hz, H-2), 3.75 (1H, dd, *J* = 11.0 and 2.0 Hz, H-6), 4.50 (1H, d, *J* = 8.0 Hz, H-1), 4.54 and 4.82 (2H, ABq, *J* = 11.5 Hz, $ArCH_2$), 4.56 and 4.61 (2H, ABq, *J* = 12.5 Hz, $ArCH_2$), 4.71 and 4.99 (2H, ABq, *J* = 10.5 Hz, $ArCH_2$), 4.78 and 4.92 (2H, ABq, *J* = 10.5 Hz, $ArCH_2$), 7.15-7.20 (2H, m, ArH), 7.24-7.38 (18H, m, ArH); ^{13}C NMR (500 MHz, $CDCl_3$) δ 24.0, 24.1, 25.6, 32.0, 33.8, 69.2, 73.4, 74.8×2, 75.0, 75.7, 77.8, 78.0, 82.3, 84.8, 101.9, 127.5×2, 127.6, 127.7×2, 127.9, 128.0, 128.2, 128.3×2, 128.4, 138.1, 138.3, 138.5, 138.7; HRMS (ESI-TOF) *m/z* 645.3163 (645.3192 calcd for $C_{38}H_{44}O_6Na$ $[M+Na]^+$).



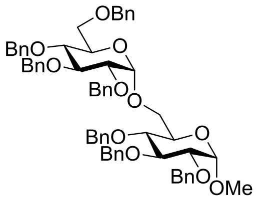
20α

2-Phenylethyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (20α): Colorless syrup; R_f 0.50 (3/1 *n*-hexane/EtOAc); $[\alpha]^{24}_{D}$ +45.3º (*c* 1.26, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 2.88-3.00 (2H, m), 3.50-3.71 (6H, m), 3.78-3.83 (1H, m), 3.97 (1H, dd, *J* = 9.5 and 9.5 Hz, H-3), 4.43 and 4.57 (2H, ABq, *J* = 12.5 Hz, $ArCH_2$), 4.45 and 4.81 (2H, ABq, *J* = 11.0 Hz, $ArCH_2$), 4.62 and 4.76 (2H, ABq, *J* = 12.0 Hz, $ArCH_2$), 4.77 (1H, d, *J* = 3.5 Hz, H-1), 4.82 and 4.98 (2H, ABq, *J* = 10.5 Hz, $ArCH_2$), 7.10-7.16 (2H, m, ArH), 7.16-7.40 (23H, m, ArH); ^{13}C NMR (500 MHz, $CDCl_3$) δ 36.0, 68.4, 68.7, 70.1, 73.2, 73.4, 74.9, 75.7, 77.6, 80.0, 82.0, 96.8, 126.3, 127.5, 127.6×2, 127.7, 127.8×2, 128.0×2, 128.3, 128.4×2, 129.0, 137.9, 138.3×2, 138.6, 138.8; HRMS (ESI-TOF) *m/z* 667.3035 (667.3036 calcd for $C_{42}H_{44}O_6Na$ $[M+Na]^+$).



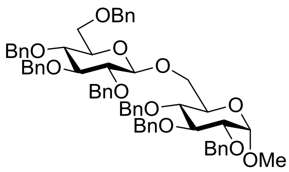
20β

2-Phenylethyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (20β): White solid; R_f 0.55 (3/1 *n*-hexane/EtOAc); $[\alpha]^{25}_{D}$ +12.3º (*c* 1.16, $CHCl_3$); mp 65.0-66.5 ºC; ^1H NMR (500 MHz, $CDCl_3$) δ 2.93-3.03 (2H, t, *J* = 7.0 Hz, $ArCH_2$), 3.40-3.49 (2H, m), 3.55-3.82 (5H, m), 4.21 (1H, m), 4.41 (1H, d, *J* = 8.0 Hz, H-1), 4.52 and 4.81 (2H, ABq, *J* = 11.0 Hz, $ArCH_2$), 4.54 and 4.61 (2H, ABq, *J* = 12.5 Hz, $ArCH_2$), 4.60 and 4.75 (2H, ABq, *J* = 11.5 Hz, $ArCH_2$), 4.77 and 4.91 (2H, ABq, *J* = 11.0 Hz, $ArCH_2$), 7.12-7.39 (25H, m, ArH); ^{13}C NMR (500 MHz, $CDCl_3$) δ 36.3, 68.9, 70.6, 73.5, 74.7, 74.8, 75.0, 75.7, 77.8, 82.2, 84.6, 103.6, 126.3, 127.6×2, 127.7, 127.8×2, 128.0, 128.1, 128.3×2, 128.4, 128.9, 138.1×2, 138.4, 138.6, 138.7; HRMS (ESI-TOF) *m/z* 667.3055 (667.3036 calcd for $C_{42}H_{44}O_6Na$ $[M+Na]^+$).



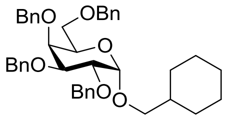
21α

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2',3',4',6'-tetra-*O*-benzyl-α-D-glucopyranosyl)-α-D-glucopyranoside (21α)[1]: White solid; R_f 0.35 (3/1 *n*-hexane/EtOAc); $[\alpha]^{28}_{D}$ +57.1^{o} (*c* 0.91, $CHCl_3$); mp 102.5-103.5 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.35 (3H, s, OMe), 3.44 (1H, dd, *J* = 9.5 and 3.5 Hz), 3.49-3.86 (9H, m), 3.90-4.03 (2H, m), 4.37-4.48 (2H, m), 4.53-4.67 (5H, m), 4.55 (1H, d, *J* = 3.5 Hz, H-1), 4.71 (1H, ABq, *J* = 12.0 Hz, $ArCH_2$), 4.77 (1H, ABq, *J* = 11.0 Hz, $ArCH_2$), 4.81 (1H, ABq, *J* = 10.5 Hz, $ArCH_2$), 4.82 (1H, ABq, *J* = 11.0 Hz, $ArCH_2$), 4.92 (1H, ABq, *J* = 11.5 Hz, $ArCH_2$), 4.93 (1H, ABq, *J* = 11.5 Hz, $ArCH_2$), 4.96 (1H, ABq, *J* = 11.5 Hz, $ArCH_2$), 4.98 (1H, d, *J* = 4.0 Hz, H-1'), 7.08-7.13 (2H, m, ArH), 7.20-7.36 (33H, m, ArH); ^{13}C NMR (500 MHz, $CDCl_3$) δ 55.1, 66.0, 68.4, 70.2, 70.3, 72.4, 73.4×2, 74.9×2, 75.5, 75.7, 77.6, 77.7, 79.9, 80.1, 81.7, 82.1, 97.2, 97.9, 127.5, 127.6, 127.7, 127.9×2, 128.0×2, 128.3×3, 128.4, 138.0, 138.2, 138.4×2, 138.8; HRMS (ESI-TOF) *m/z* 1009.4470 (1009.4503 calcd for $C_{62}H_{66}O_{11}Na$ $[M+Na]^+$).



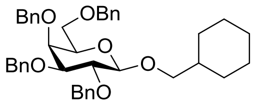
21β

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2',3',4',6'-tetra-*O*-benzyl-β-D-glucopyranosyl)-α-D-glucopyranoside (21β)[1]: White solid; R_f 0.35 (3/1 *n*-hexane/EtOAc); $[\alpha]^{27}_{D}$ +17.4^{o} (*c* 1.13, $CHCl_3$); mp 133-134 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.32 (3H, s, OMe), 3.40-3.75 (9H, m), 3.82 (1H, dd, *J* = 10.5 and 3.0 Hz), 3.99 (1H, dd, *J* = 9.5 and 9.5 Hz, H-3), 4.18 (1H, dd, *J* = 11.0 and 2.0 Hz), 4.34 (1H, d, *J* = 8.0 Hz, H-1'), 4.47-4.60 (5H, m), 4.61 (1H, d, *J* = 3.5 Hz, H-1), 4.65 (1H, ABq, *J* = 12.0 Hz, $ArCH_2$), 4.71 (1H, ABq, *J* = 11.0 Hz, $ArCH_2$), 4.74-4.82 (3H, m) 4.80 (1H, ABq, *J* = 11.0 Hz, $ArCH_2$), 4.90 (1H, ABq, *J* = 10.5 Hz, $ArCH_2$), 4.96 (1H, ABq, *J* = 11.0 Hz, $ArCH_2$), 4.97 (1H, ABq, *J* = 11.5 Hz, $ArCH_2$), 7.13-7.37 (35H, m, ArH); ^{13}C NMR (500 MHz, $CDCl_3$) δ 55.2, 68.5, 69.0, 69.8, 73.3, 73.4, 74.9, 75.0×2, 75.7×2, 77.9, 78.0, 79.8, 82.0×2, 84.8, 98.0, 103.8, 127.5, 127.6×2, 127.7, 127.9×3, 128.0×2, 128.2, 128.4×2, 128.5, 138.1×2, 138.2, 138.3×2, 138.6, 139.0; HRMS (ESI-TOF) *m/z* 1009.4460 (1009.4503calcd for $C_{62}H_{66}O_{11}Na$ $[M+Na]^+$).



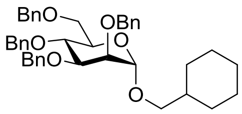
25α

Cyclohexylmethyl 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranoside (25α)[2]: Colorless syrup; R_f 0.67 (3/1 *n*-hexane/EtOAc); $[\alpha]^{28}_{D}$ +37.3° (*c* 0.49, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 0.82-1.00 (2H, m), 1.08-1.34 (3H, m), 1.58-1.87 (6H, m), 3.21 (1H, dd, *J* = 9.5 and 6.0 Hz, OCH_2), 3.42 (1H, dd, *J* = 9.5 and 7.5 Hz, OCH_2), 3.48-3.55 (2H, m), 3.90-4.00 (3H, m), 4.03 (1H, dd, *J* = 9.5 and 4.0 Hz), 4.39 and 4.48 (2H, ABq, *J* = 12.0 Hz, $ArCH_2$), 4.57 and 4.94 (2H, ABq, *J* = 11.5 Hz, $ArCH_2$), 4.66 and 4.81 (2H, ABq, *J* = 12.5 Hz, $ArCH_2$), 4.73 and 4.85 (2H, ABq, *J* = 12.0 Hz, $ArCH_2$), 4.79 (1H, d, *J* = 3.5 Hz, H-1), 7.21-7.42 (20H, m, ArH); ^{13}C NMR (500 MHz, $CDCl_3$) δ 25.7, 25.8, 26.6, 30.0, 30.2, 37.5, 69.1, 69.2, 73.2, 73.4, 73.8, 74.1, 75.1, 79.1, 97.6, 127.7, 127.9, 128.2×2, 128.3×2, 138.1, 138.7, 138.8, 138.9; HRMS (ESI-TOF) *m/z* 659.3348 (659.3349 calcd for $C_{41}H_{48}O_6Na$ $[M+Na]^+$).



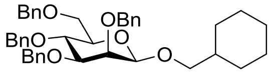
25β

Cyclohexylmethyl 2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranoside (25β)[2]: White solid; R_f 0.60 (3/1 *n*-hexane/EtOAc); $[\alpha]^{28}_{D}$ −7.2° (*c* 1.45, $CHCl_3$); mp 101.8-102.8 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 0.86-1.04 (2H, m), 1.06-1.33 (3H, m), 1.58-1.90 (6H, m), 3.27 (1H, dd, *J* = 9.5 and 7.5 Hz, OCH_2), 3.47-3.62 (4H, m), 3.75 (1H, dd, *J* = 9.0 and 5.0 Hz, OCH_2), 3.80 (1H, dd, *J* = 10.0 and 7.5 Hz, H-2), 3.88 (1H, br d, *J* = 2.5 Hz, H-4), 4.32 (1H, d, *J* = 7.5 Hz, H-1), 4.40 and 4.45 (2H, ABq, *J* = 11.5 Hz, $ArCH_2$), 4.62 and 4.93 (2H, ABq, *J* = 11.5 Hz, $ArCH_2$), 4.70 and 4.76 (2H, ABq, *J* = 12.0 Hz, $ArCH_2$), 4.75 and 4.93 (2H, ABq, *J* = 11.5 Hz, $ArCH_2$), 7.23-7.38 (20H, m, ArH); ^{13}C NMR (500 MHz, $CDCl_3$) δ 25.8×2, 29.8, 30.2, 68.9, 73.1, 73.4, 73.5, 74.4, 75.2, 75.6, 79.6, 82.3, 104.2, 127.5, 127.7, 127.9, 128.1, 128.2, 128.3×2, 128.4, 137.9, 138.6, 138.7×2; HRMS (ESI-TOF) *m/z* 659.3322 (659.3349 calcd for $C_{41}H_{48}O_6Na$ $[M+Na]^+$).



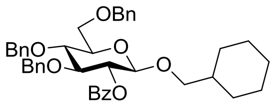
26α

Cyclohexylmethyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranoside (26α)[3]: Colorless syrup; R_f 0.60 (4/1 *n*-hexane/EtOAc); $[\alpha]^{25}_{D}$ +33.3° (*c* 0.56, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 0.80-1.74 (11H, m), 3.15 (1H, dd, *J* = 9.5 and 6.0 Hz, OCH_2), 3.45 (1H, dd, *J* = 9.0 and 7.0 Hz, OCH_2), 3.68-3.81 (4H, m), 3.86-4.01 (2H, m), 4.48-4.79 (7H, m, $ArCH_2$), 4.82 (1H, d, *J* = 1.5 Hz, H-1), 4.87 (1H, ABq, *J* = 11.0 Hz, $ArCH_2$), 7.14-7.39 (20H, m, ArH); ^{13}C NMR (500 MHz, $CDCl_3$) δ 25.7, 25.8, 26.5, 29.8, 30.0, 37.8, 69.3, 71.8, 72.2, 72.5, 73.1, 73.3, 74.9, 75.0, 75.2, 80.3, 97.9, 127.4, 127.5, 127.6, 127.7×2, 127.8, 128.1, 128.2, 128.3×2, 138.4, 138.5, 138.6; HRMS (ESI-TOF) *m/z* 659.3326 (659.3349 calcd for $C_{41}H_{48}O_6Na$ $[M+Na]^+$).



26β

Cyclohexylmethyl 2,3,4,6-tetra-*O*-benzyl-β-D-mannopyranoside (26β)[3]: White solid; R_f 0.60 (4/1 *n*-hexane/EtOAc); $[\alpha]^{25}_{D}$ –49.0° (*c* 0.92, $CHCl_3$); mp 64.5-66.0 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 0.83-1.87 (11H, m), 3.20 (1H, dd, *J* = 9.0 and 6.5 Hz, OCH_2), 3.44 (1H, ddd, *J* = 8.0, 6.5 and 4.0 Hz, H-5), 3.50 (1H, dd, *J* = 9.5 and 3.0 Hz, OCH_2), 3.71-3.92 (5H, m), 4.35 (1H, br s, H-1), 4.43 and 4.50 (2H, ABq, *J* = 12.0 Hz, $ArCH_2$), 4.53 and 4.91 (2H, ABq, *J* = 11.0 Hz, $ArCH_2$), 4.60 and 4.63 (2H, ABq, *J* = 12.0 Hz, $ArCH_2$), 4.87 and 5.00 (2H, ABq, *J* = 13.0 Hz, $ArCH_2$), 7.16-7.49 (20H, m, ArH); ^{13}C NMR (500 MHz, $CDCl_3$) δ 25.9×2, 26.6, 29.9, 30.1, 38.1, 69.7, 71.3, 73.4, 73.7, 75.0, 75.1, 75.8, 75.9, 82.4, 102.0, 127.3, 127.4, 127.5, 127.6, 128.1, 128.3×2, 128.4, 138.2, 138.3, 138.5, 138.8; HRMS (ESI-TOF) *m/z* 659.3380 (659.3349 calcd for $C_{41}H_{48}O_6Na$ $[M+Na]^+$).



27β

Cyclohexylmethyl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (27β): White solid; R_f 0.40 (4/1 *n*-hexane/EtOAc); $[\alpha]^{26}_{D}$ +19.9° (*c* 1.50, $CHCl_3$); mp 83.0-84.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.69-0.84 (2H, m), 0.90-1.12 (3H, m), 1.40-1.63 (6H, m), 3.22 (1H, dd, *J* = 9.7 and 6.9 Hz, OCH_2), 3.52-3.58 (1H, m), 3.66-3.85 (3H, m), 3.78 (1H, dd, *J* = 9.0 and 2.0 Hz, H-4), 3.81 (1H, dd, *J* = 9.2 and 9.2 Hz, H-3), 4.47 (1H, d, *J* = 8.0 Hz, H-1), 4.58 and 4.82 (2H, ABq, *J* = 10.6 Hz, $ArCH_2$), 4.59 and 4.65 (2H, ABq, *J* = 12.3 Hz, $ArCH_2$), 4.67 and 4.74 (2H, ABq, *J* = 11.2 Hz, $ArCH_2$), 5.27 (1H, dd, *J* = 9.5 and 8.0 Hz, H-2), 7.08-8.06 (20H, m); ^{13}C NMR (500 MHz, $CDCl_3$) δ 25.6, 26.4, 29.5, 29.6, 37.7, 68.8, 73.5, 73.9, 74.9, 75.0, 75.2, 75.5, 78.1, 82.7, 101.5, 127.6, 127.7, 127.8, 128.0×2, 128.2, 128.3×2, 128.4, 129.7, 130.1, 132.9, 137.8, 137.9, 138.1, 165.2; HRMS (ESI-TOF) *m/z* 673.3127 (673.3141 calcd for $C_{41}H_{46}O_7Na$ $[M+Na]^+$).

References

1. H. Nagai, K. Sasaki, S. Matsumura and K. Toshima, *Carbohydr. Res.*, 2005, **340**, 337.

2. T. Iimori, T. Shibazaki and S. Ikegami, *Tetrahedron Lett*., 1996, **37**, 2267.

3. K. Toshima, H. Nagai, K. Kasumi, K. Kawahara and S. Matsumura, *Tetrahedron*, 2004, **60**, 5331.

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

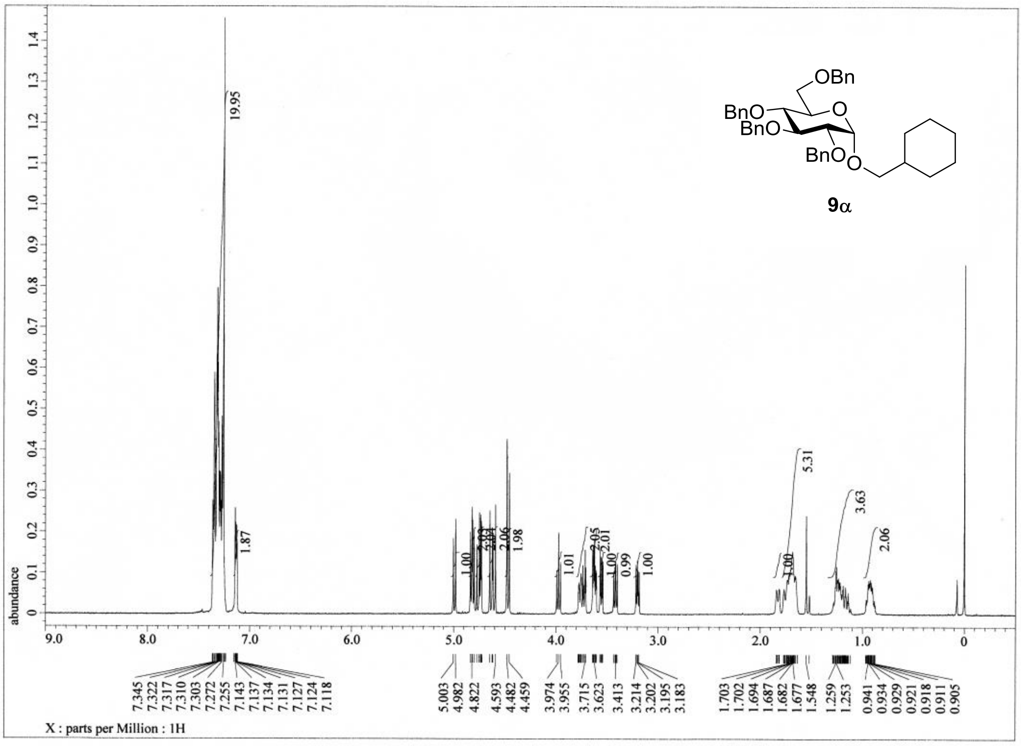


Figure S1 ^{1}H NMR spectrum of **9α**

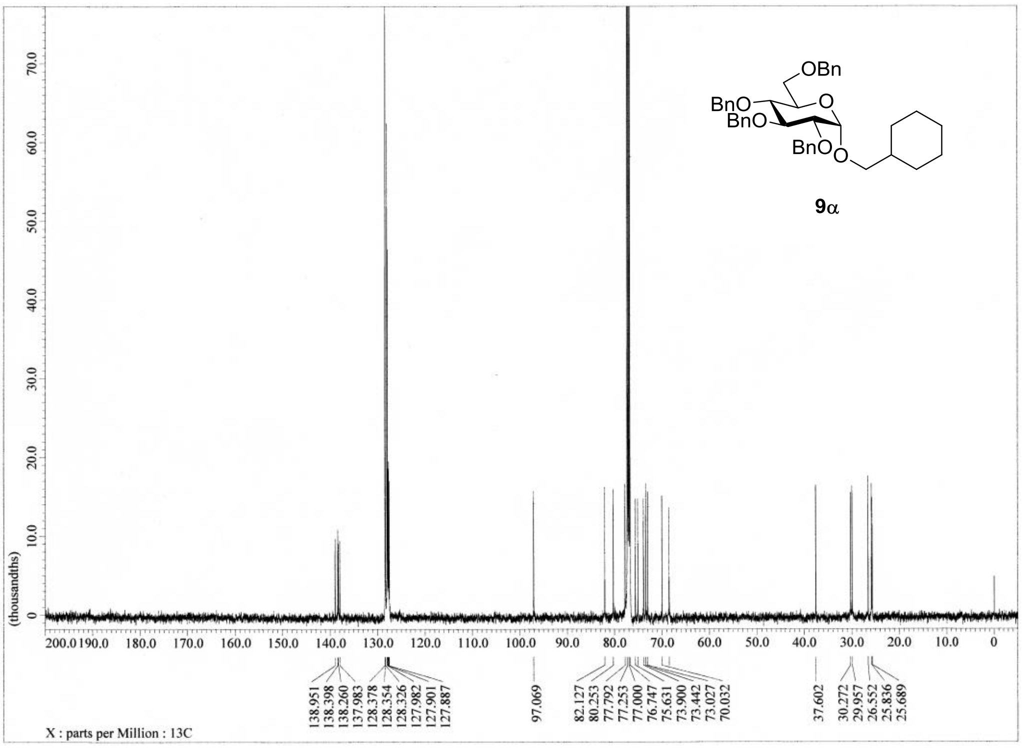


Figure S2 ^{13}C NMR spectrum of 9**α**

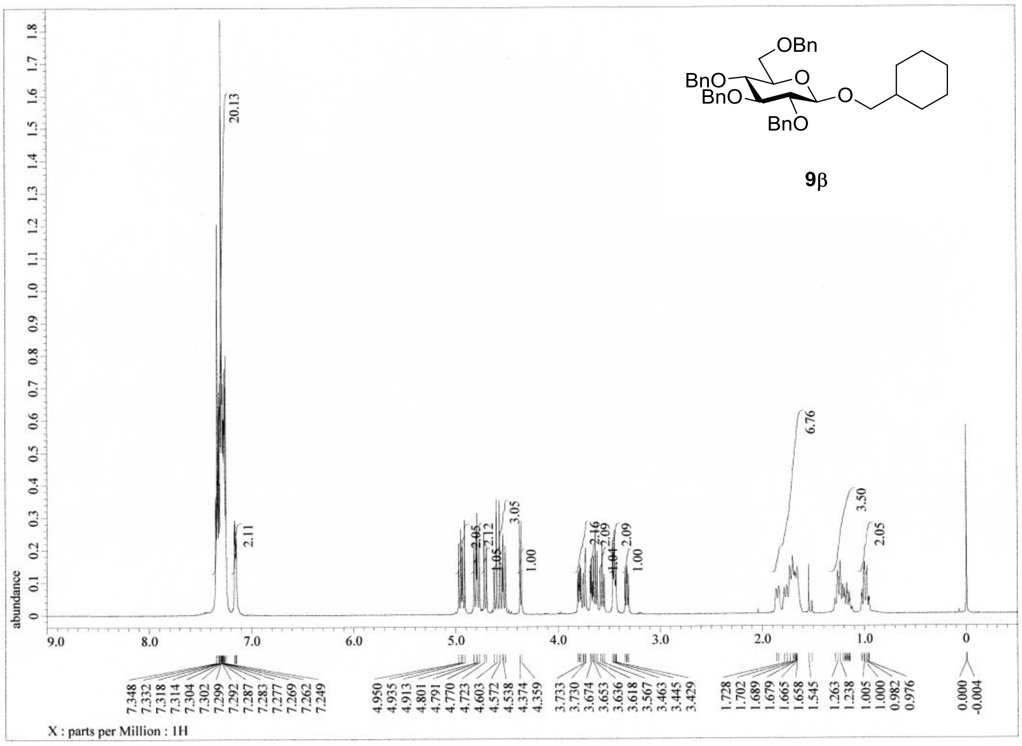


Figure S3 ^{1}H NMR spectrum of **9β**

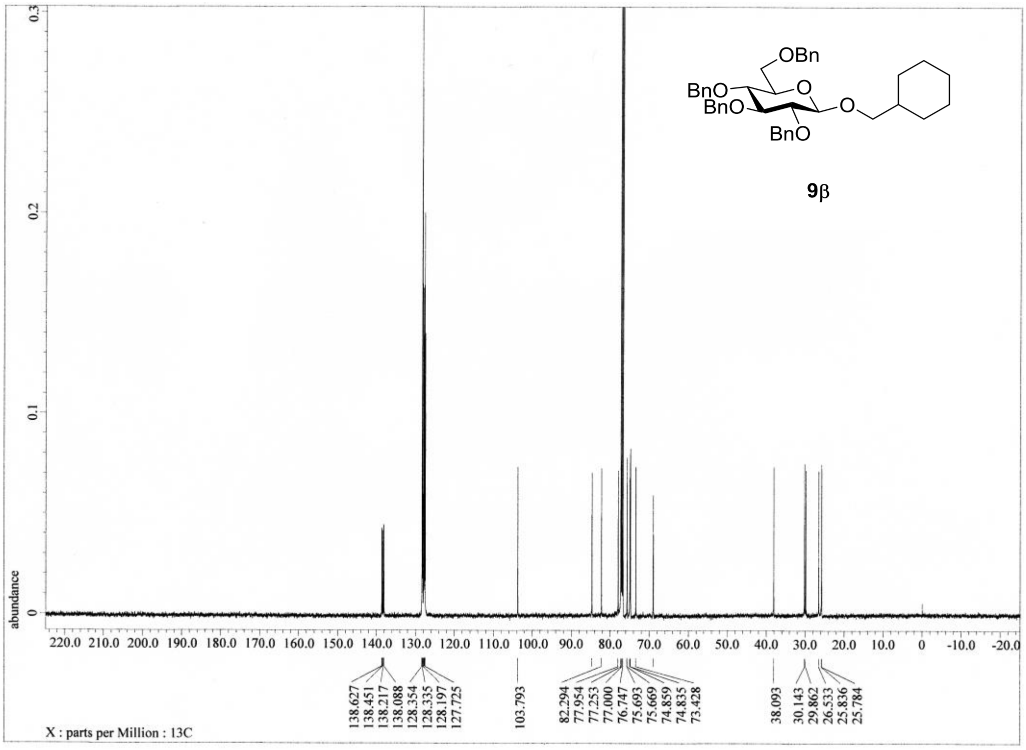


Figure S4 ^{13}C NMR spectrum of **9β**

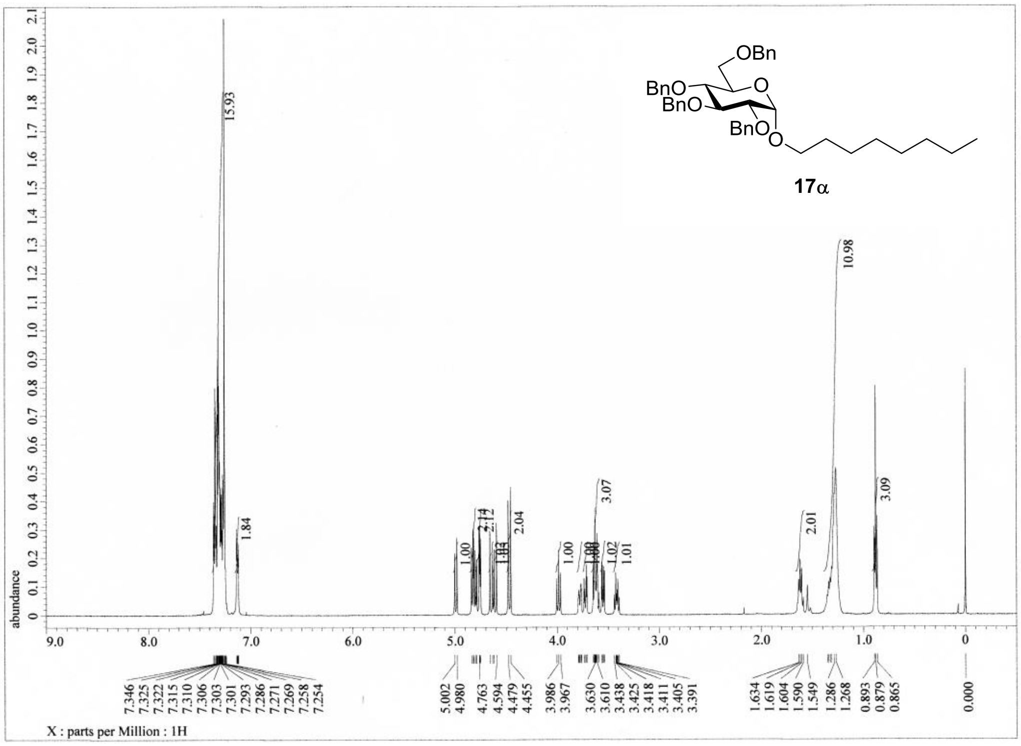


Figure S5 ^{1}H NMR spectrum of **17α**

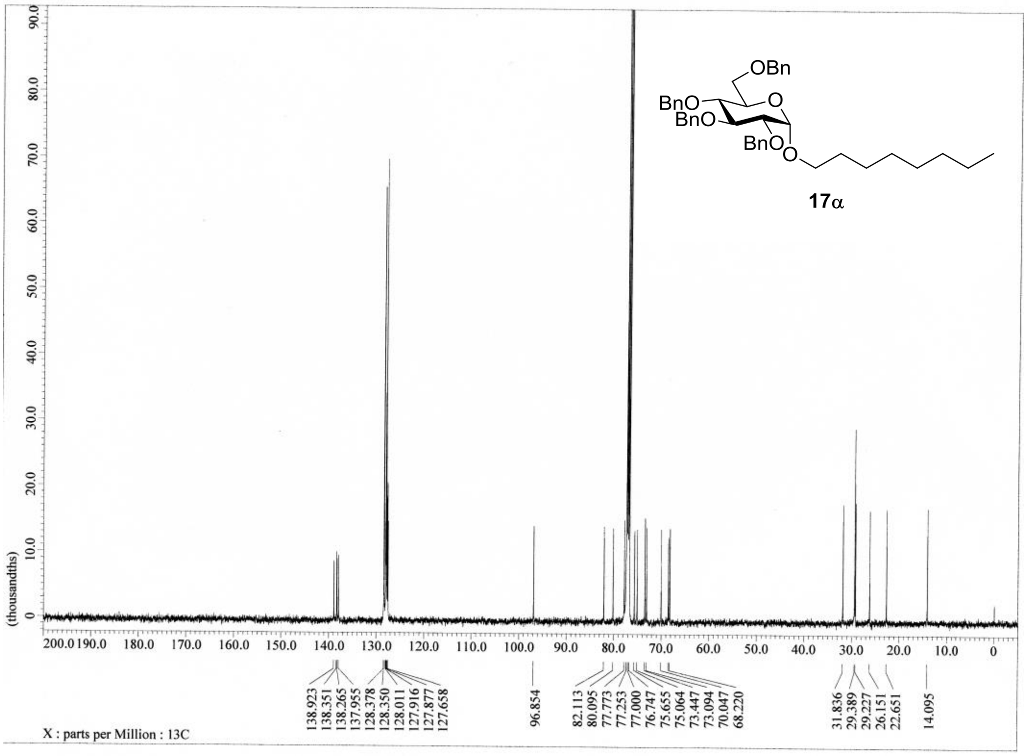


Figure S6 ^{13}C NMR spectrum of **17α**

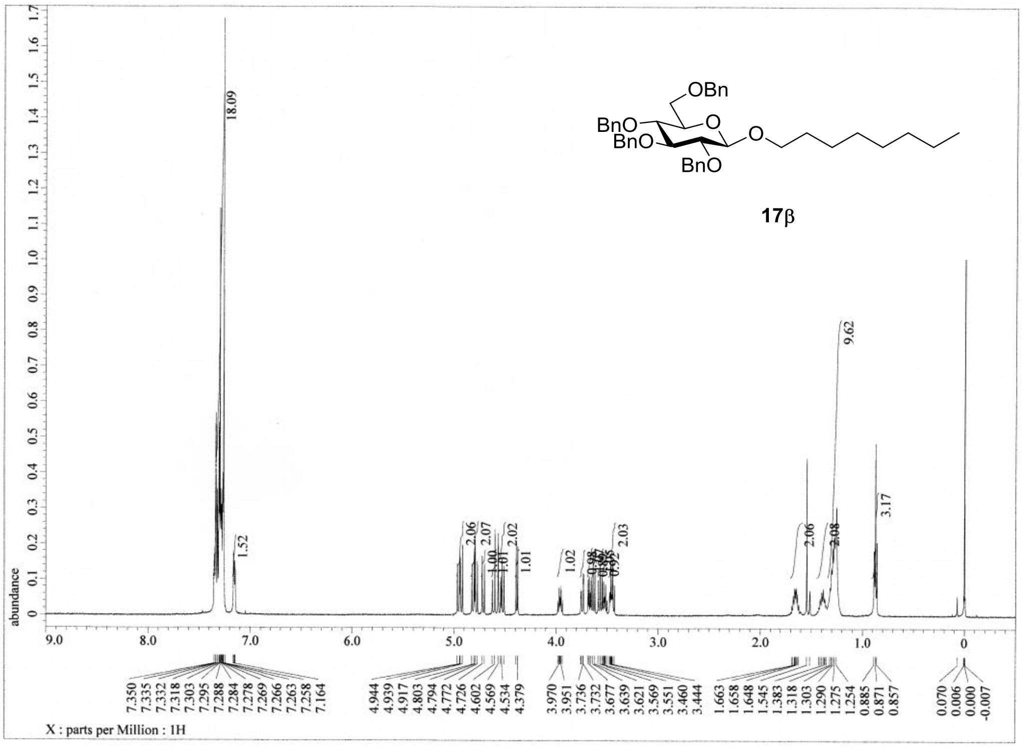


Figure S7 ^{1}H NMR spectrum of **17β**

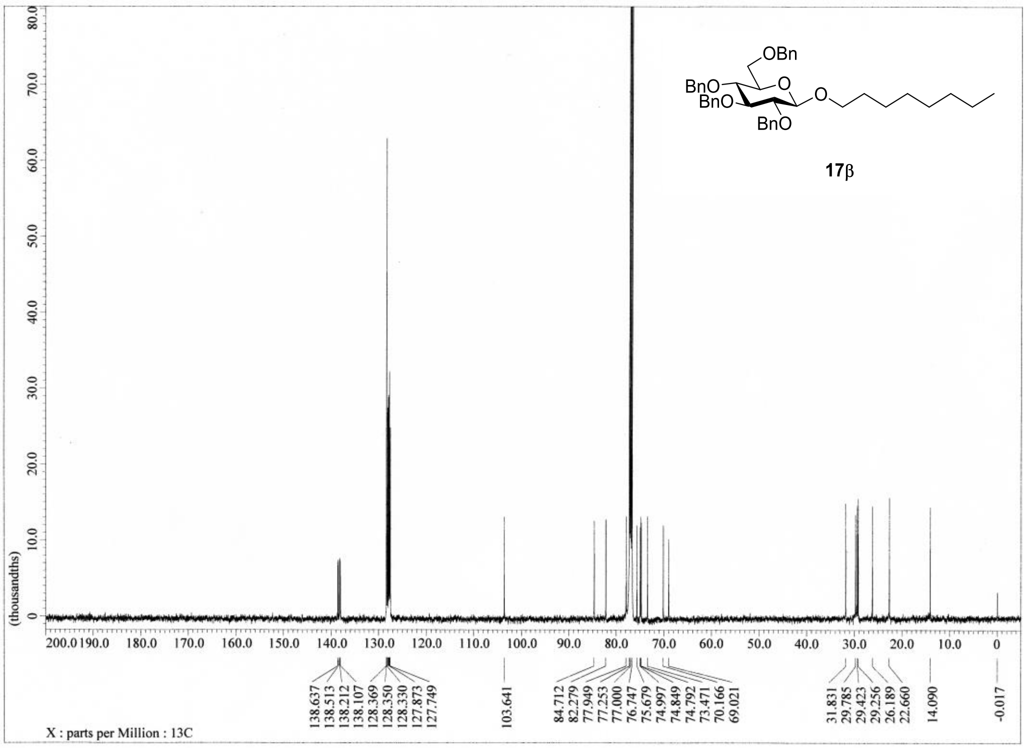


Figure S8 ^{13}C NMR spectrum of **17β**

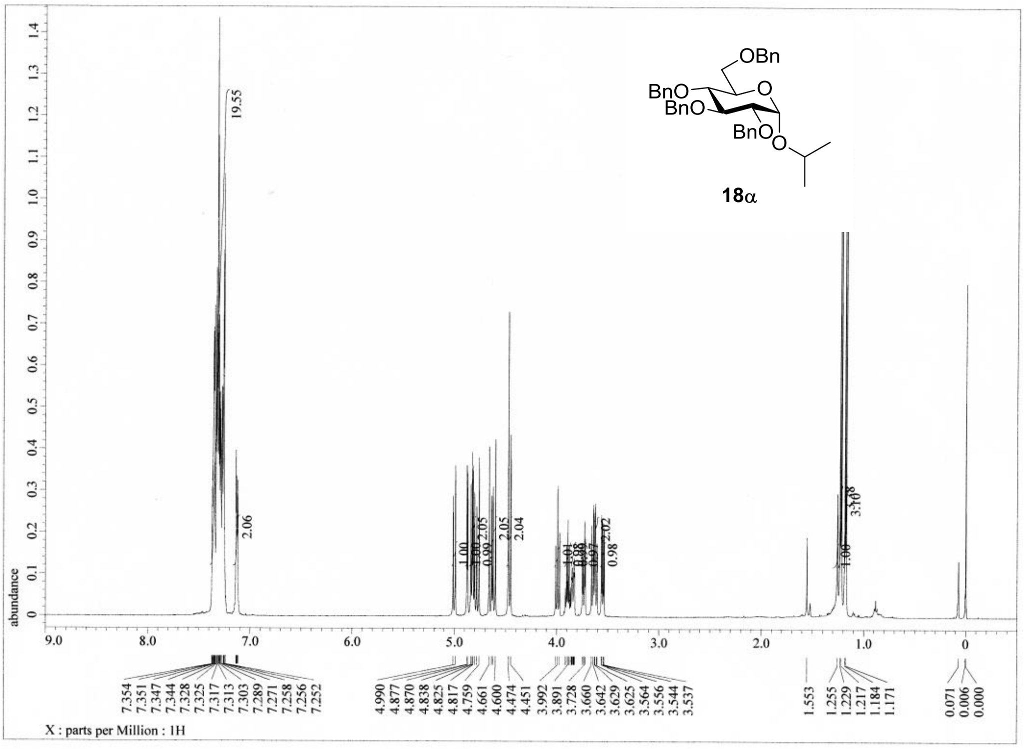


Figure S9 ^{1}H NMR spectrum of **18α**

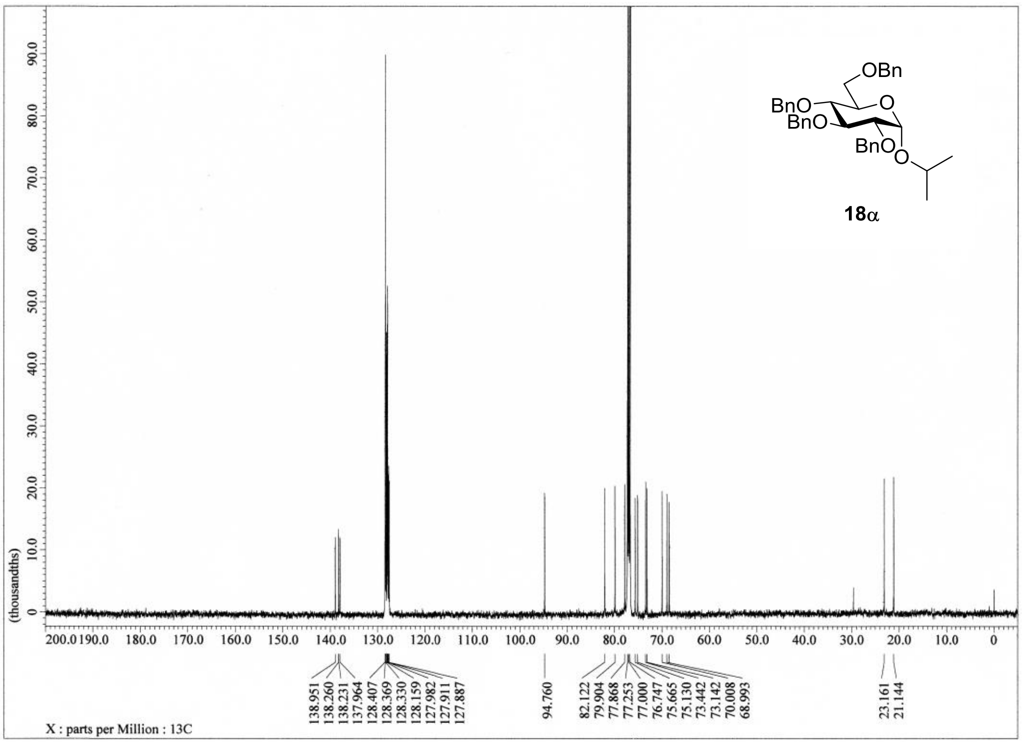


Figure S10 ^{13}C NMR spectrum of **18α**

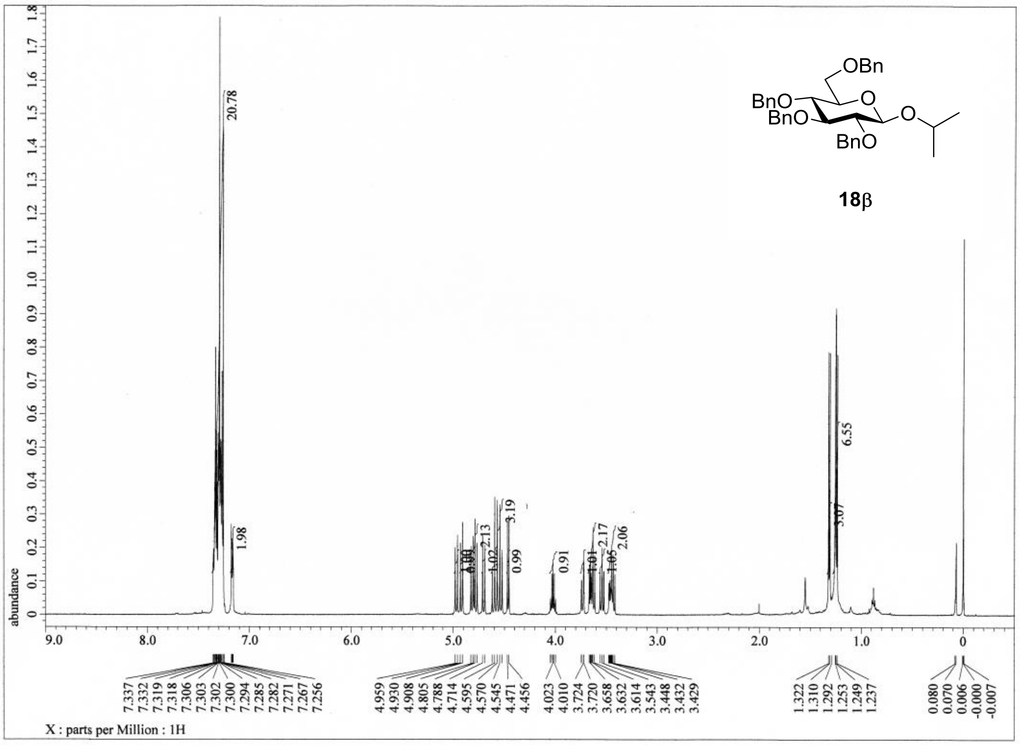


Figure S11 ^{1}H NMR spectrum of **18β**

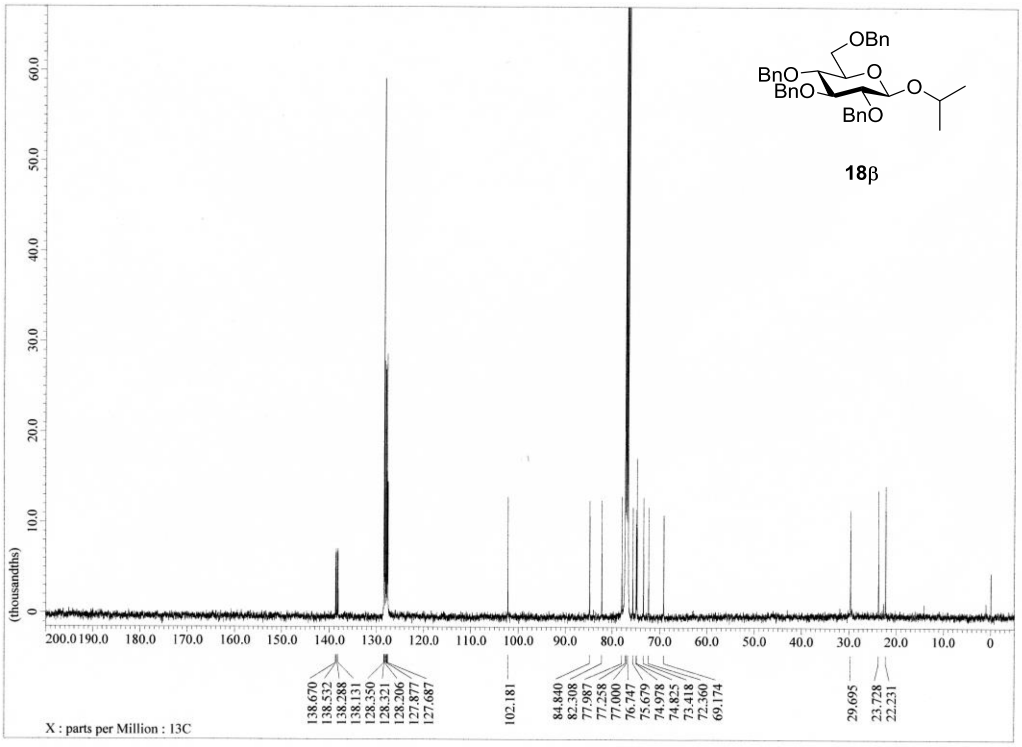


Figure S12 ^{13}C NMR spectrum of **18β**

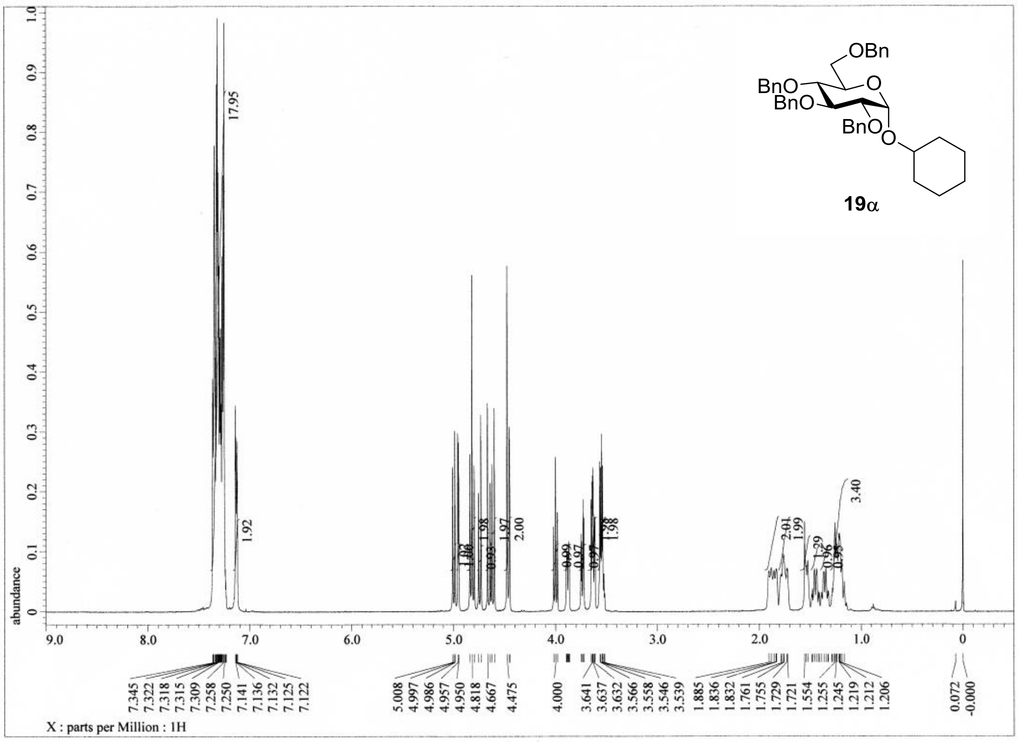


Figure S13 ^{1}H NMR spectrum of **19α**

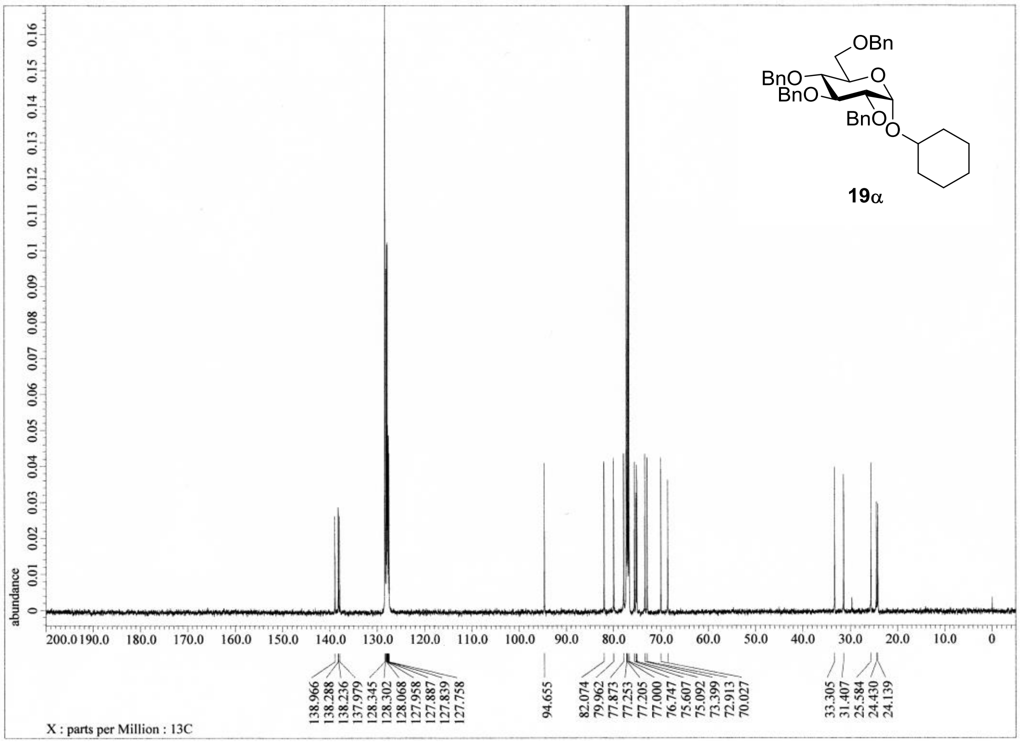


Figure S14 ^{13}C NMR spectrum of **19α**

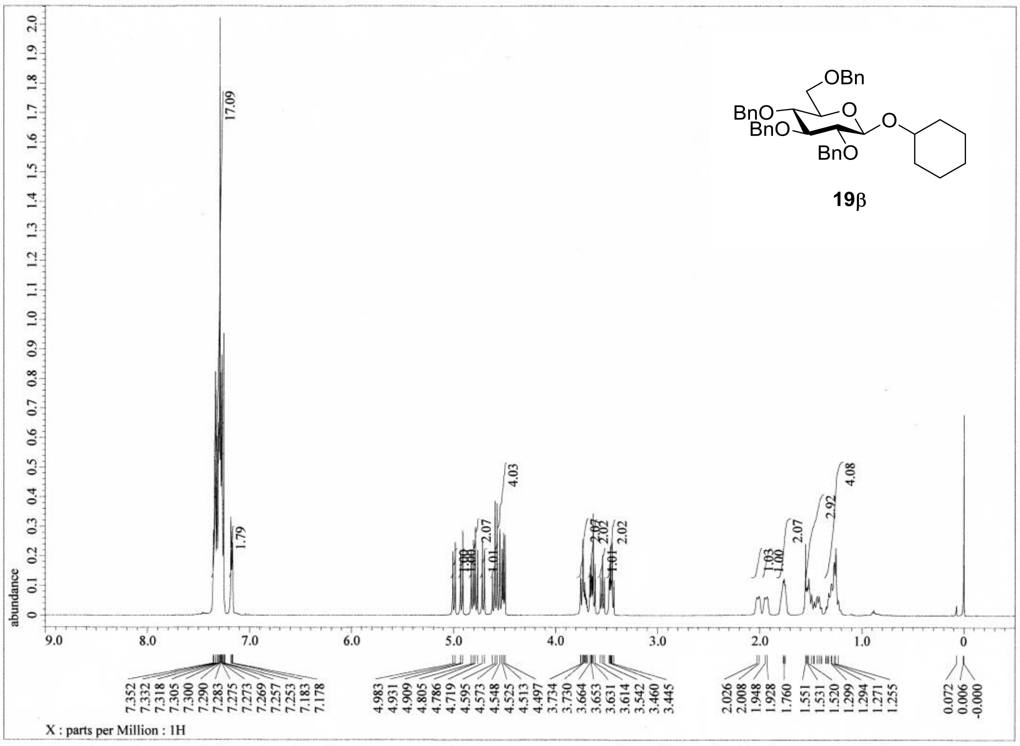


Figure S15 ^{1}H NMR spectrum of **19β**

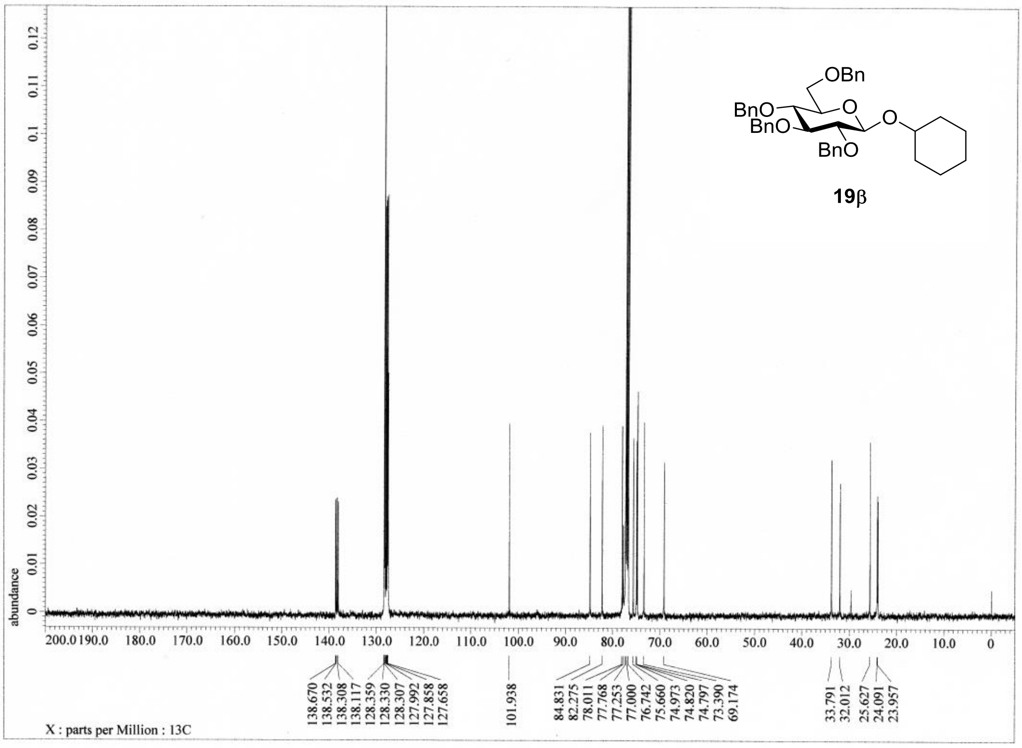


Figure S16 ^{13}C NMR spectrum of **19β**

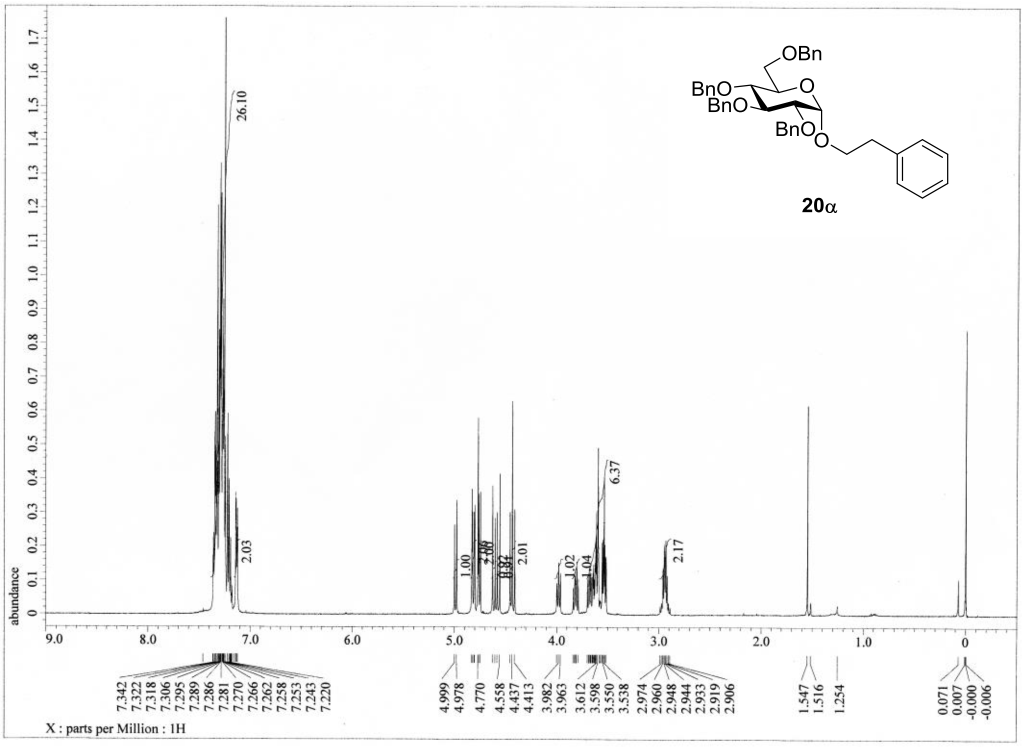


Figure S17 ^{1}H NMR spectrum of **20α**

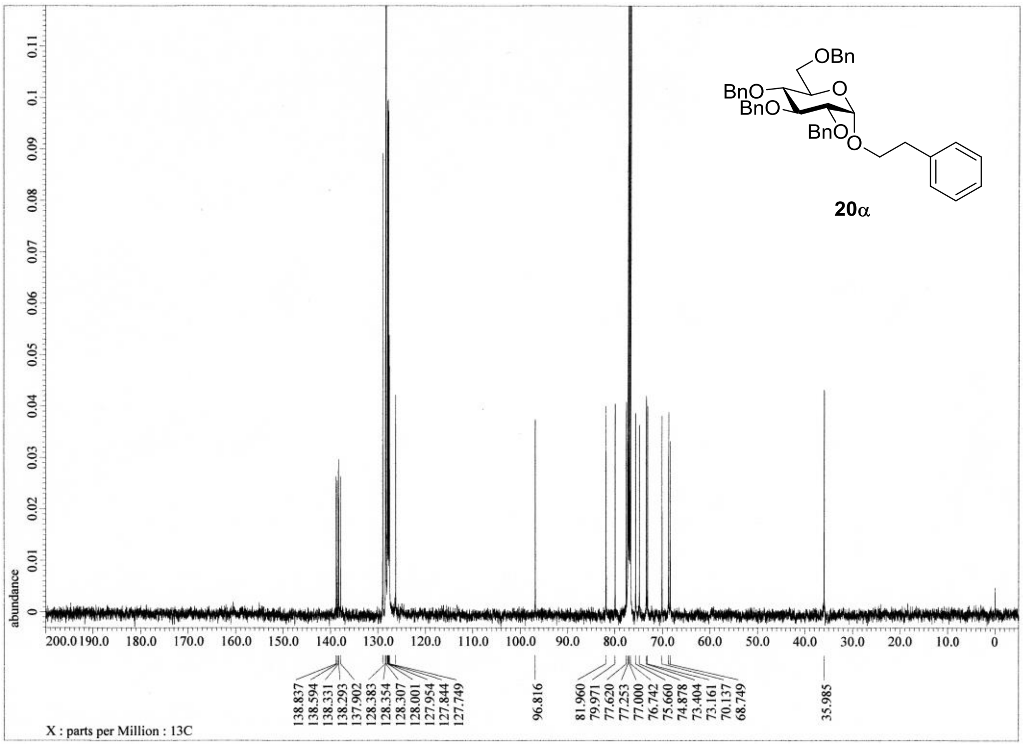


Figure S18 ^{13}C NMR spectrum of **20α**

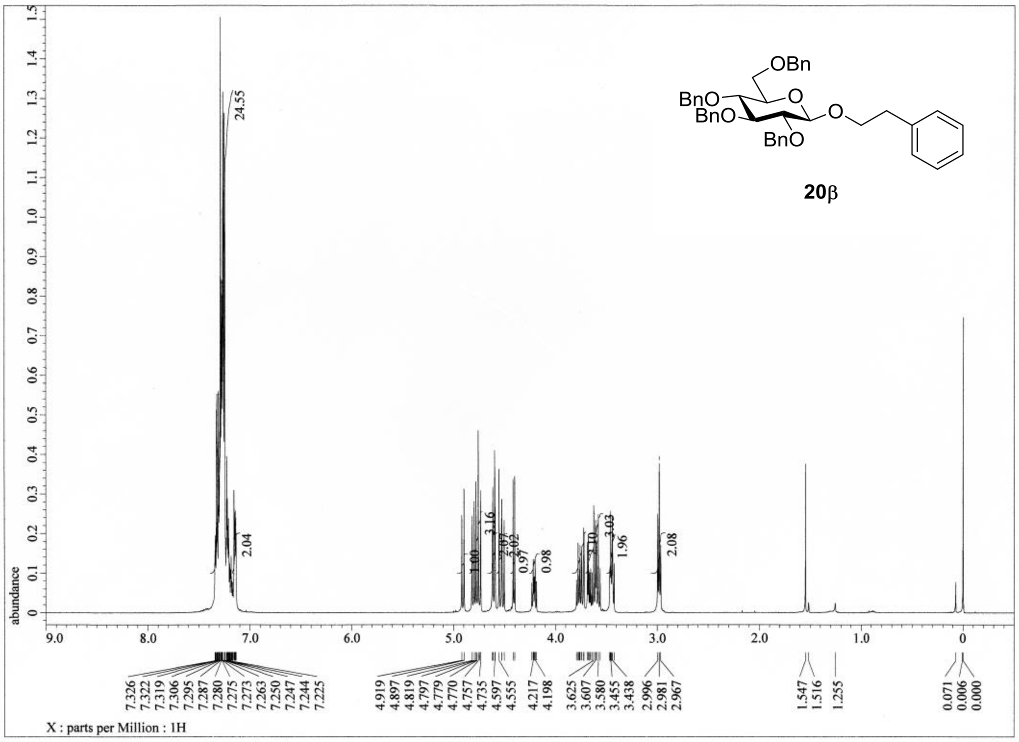


Figure S19 ^{1}H NMR spectrum of **20β**

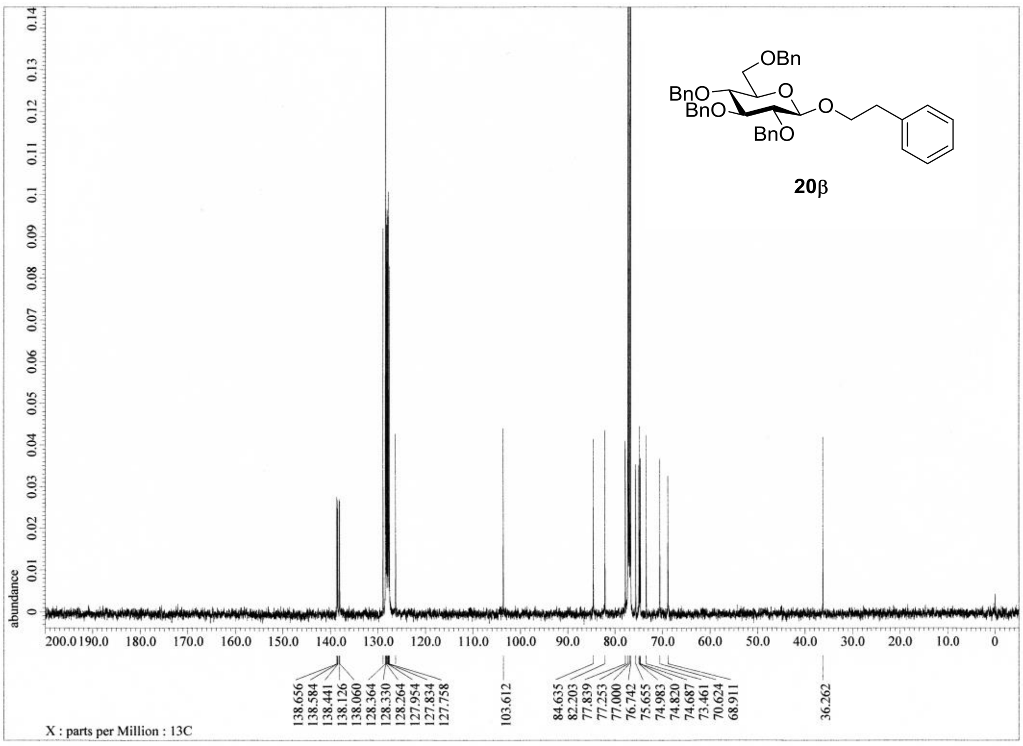


Figure S20 ^{13}C NMR spectrum of **20β**

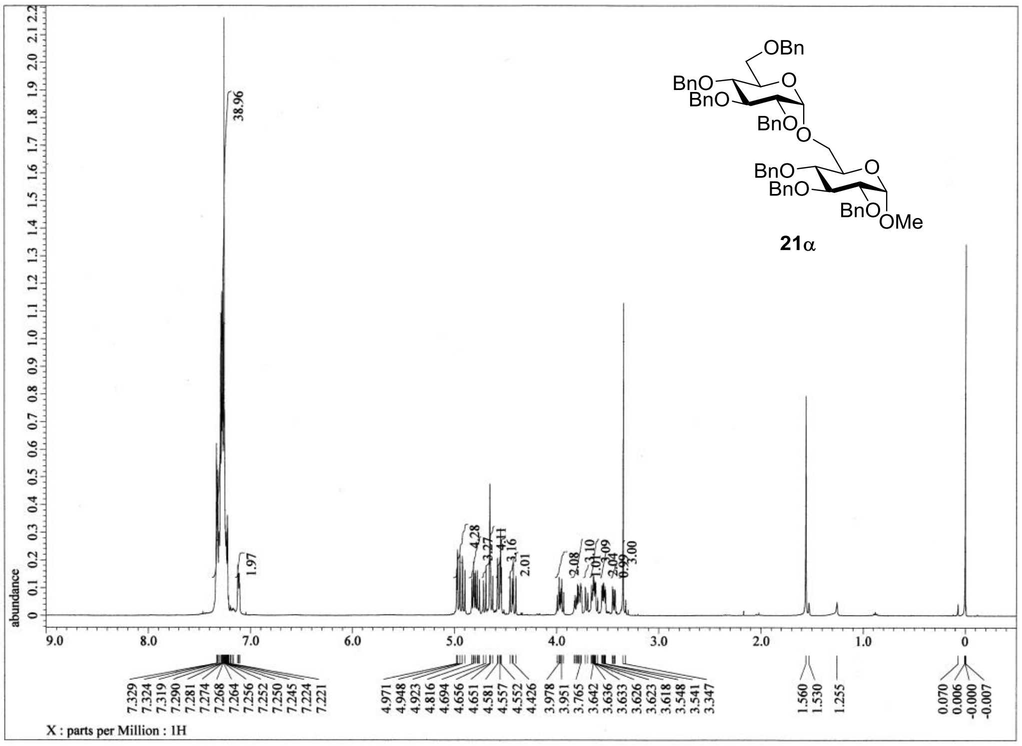


Figure S21 ^{1}H NMR spectrum of **21α**

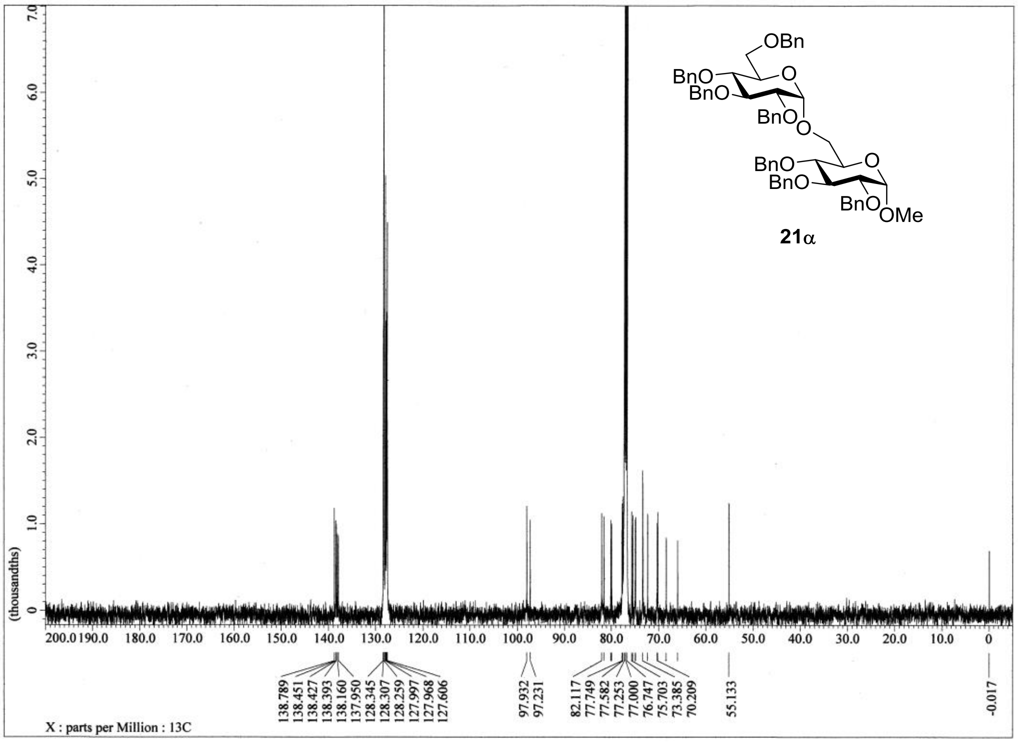


Figure S22 ^{13}C NMR spectrum of **21α**

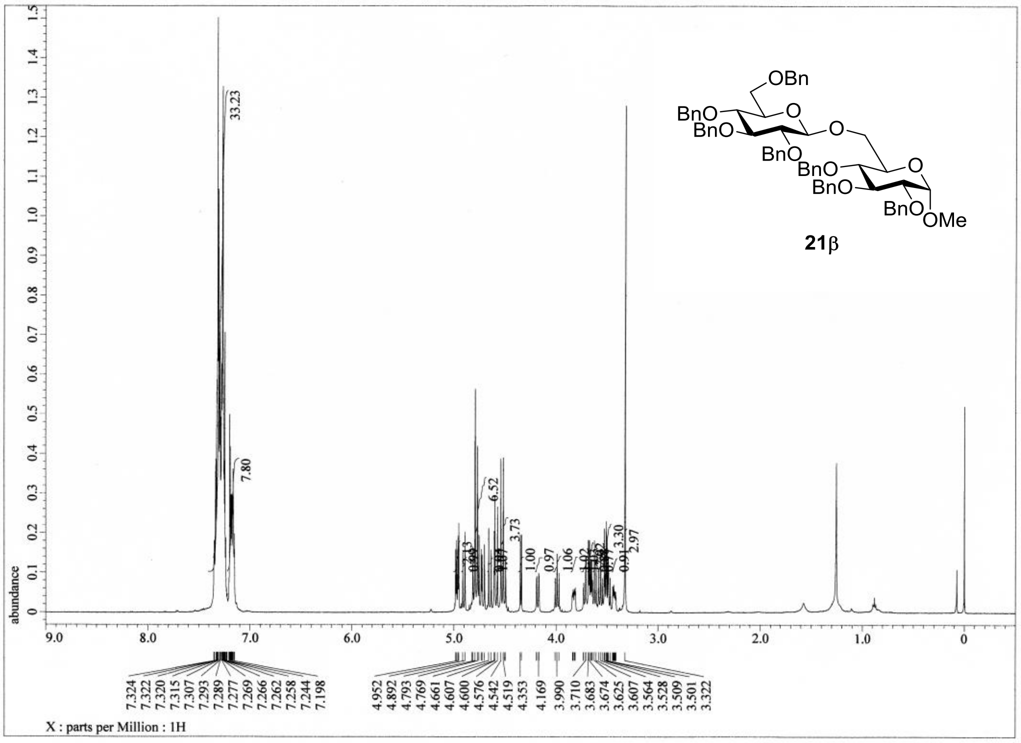


Figure S23 ^{1}H NMR spectrum of **21β**

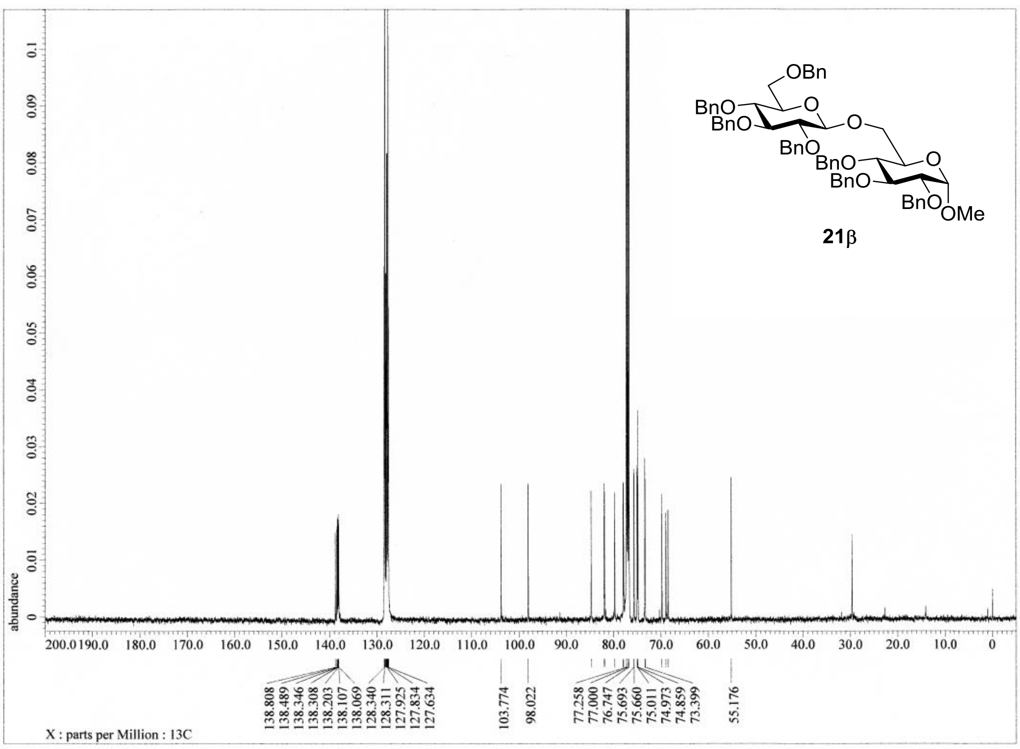


Figure S24 ^{13}C NMR spectrum of **21β**

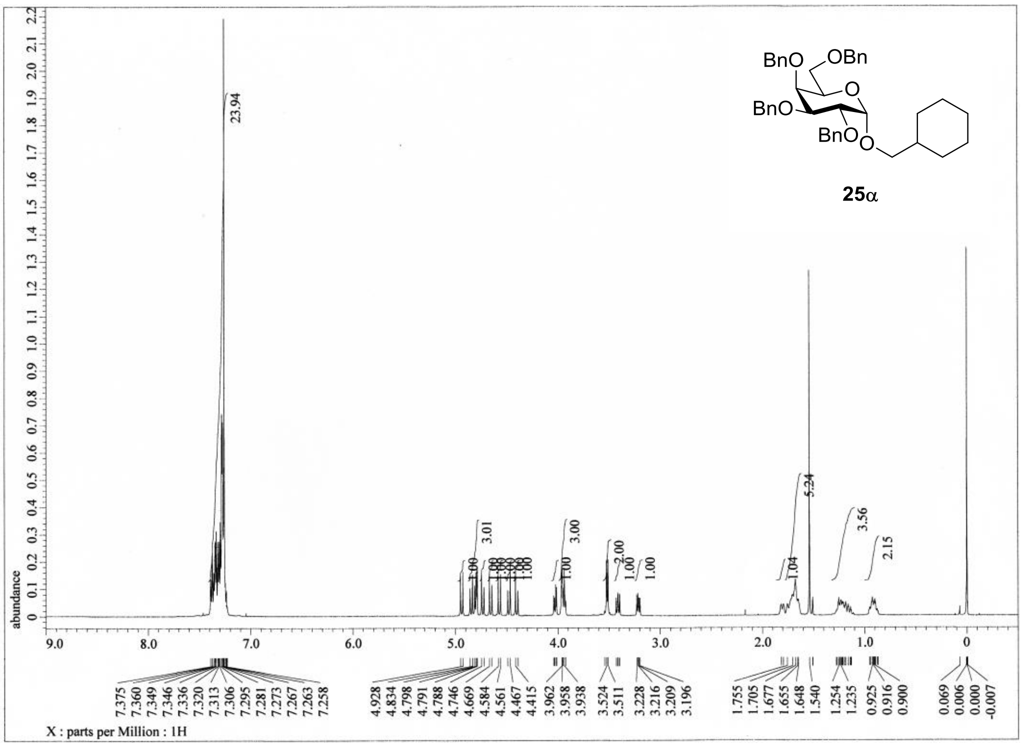


Figure S25 ^{1}H NMR spectrum of **25α**

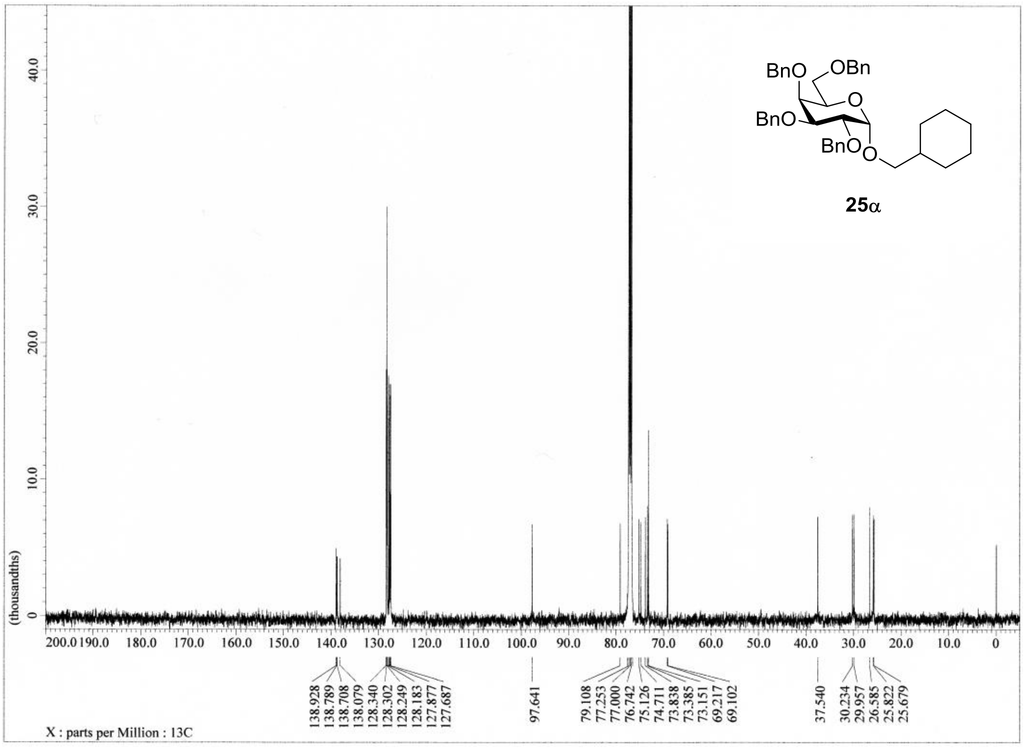


Figure S26 ^{13}C NMR spectrum of **25α**

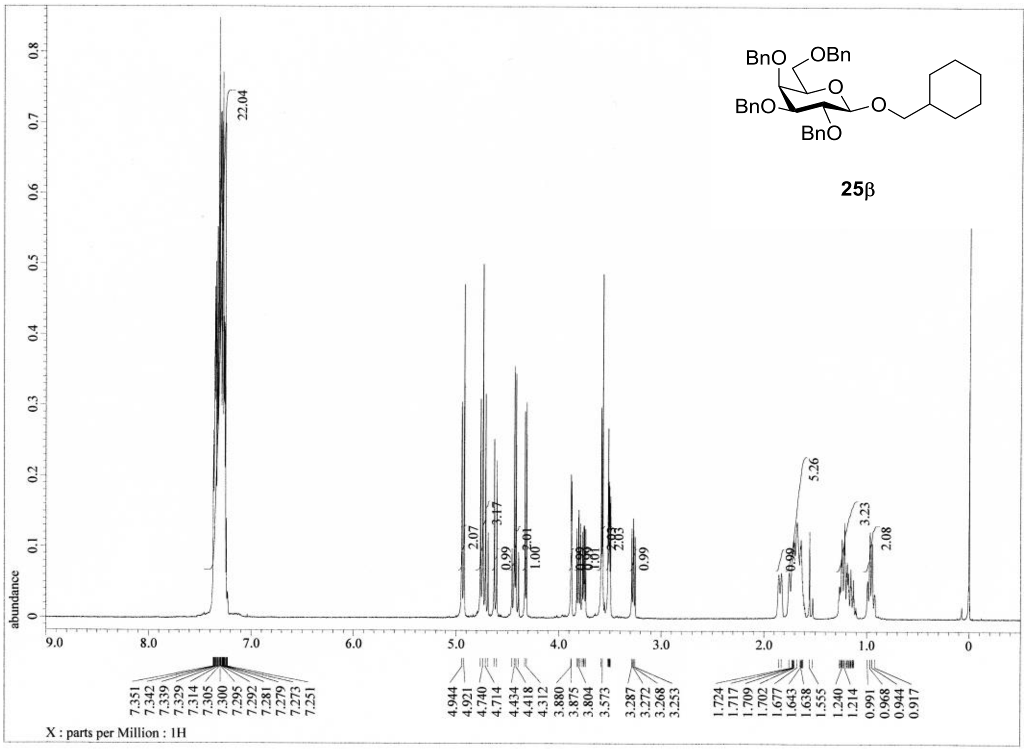


Figure S27 ^{1}H NMR spectrum of **25β**

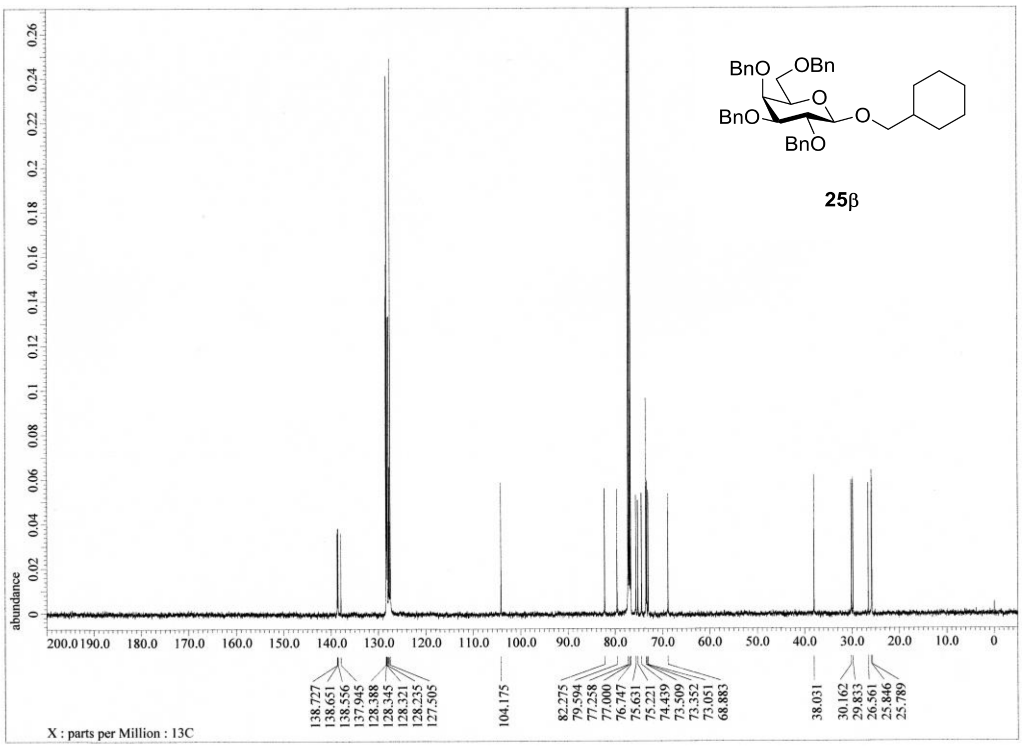


Figure S28 ^{13}C NMR spectrum of **25β**

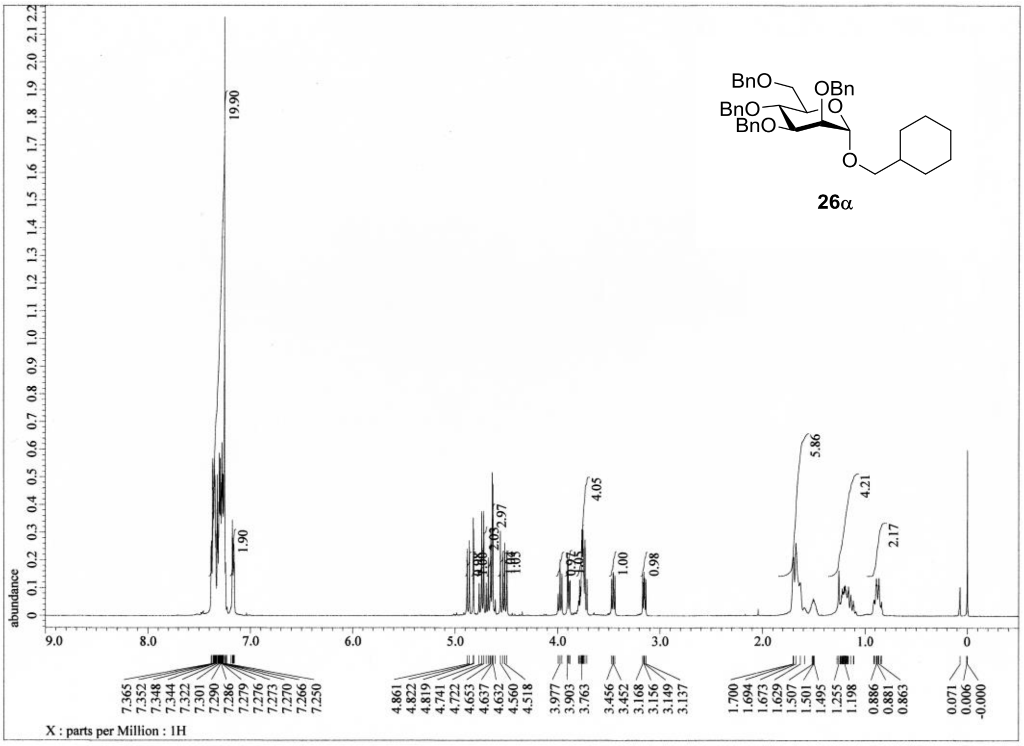


Figure S29 ^{1}H NMR spectrum of **26α**

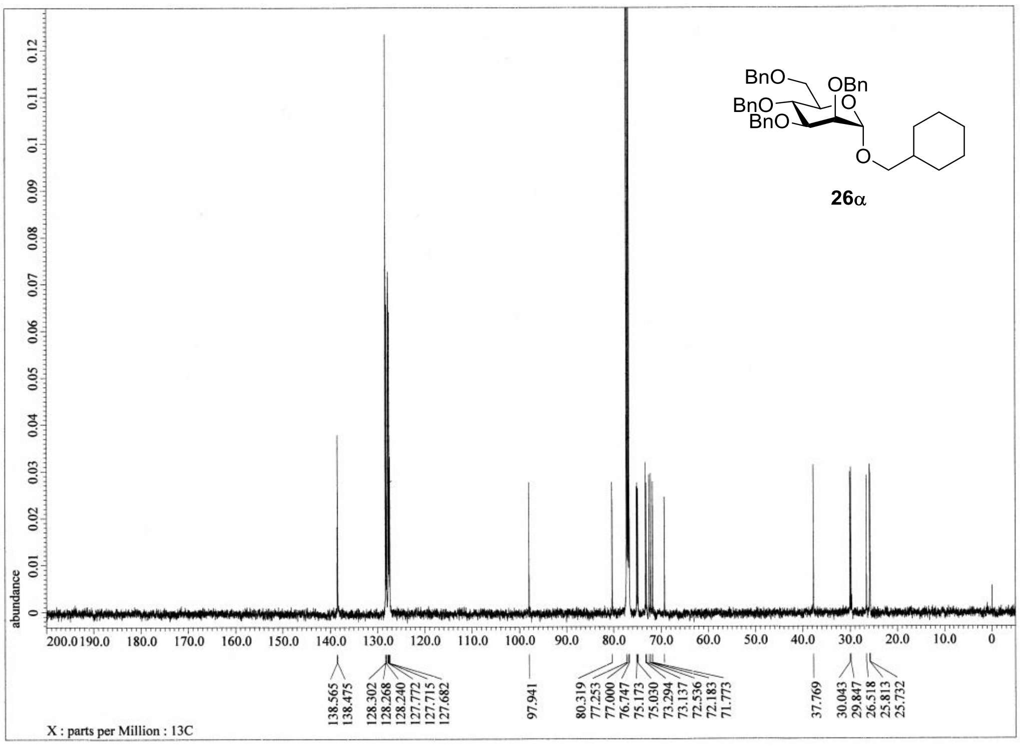


Figure S30 ^{13}C NMR spectrum of **26α**

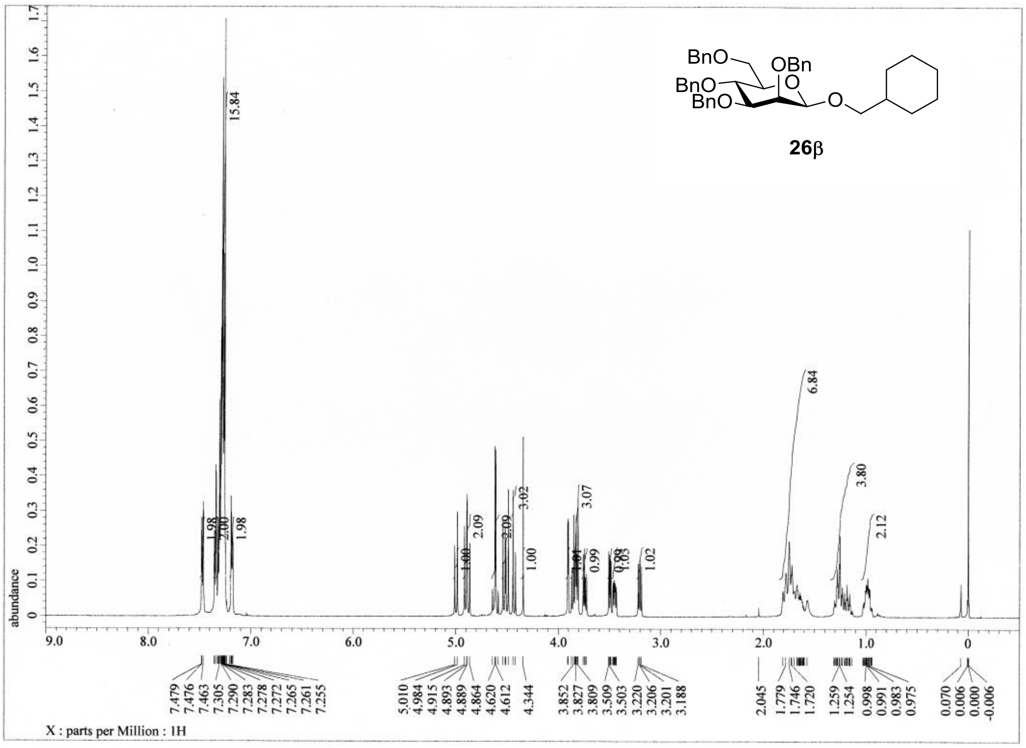


Figure S31 ^{1}H NMR spectrum of **26β**

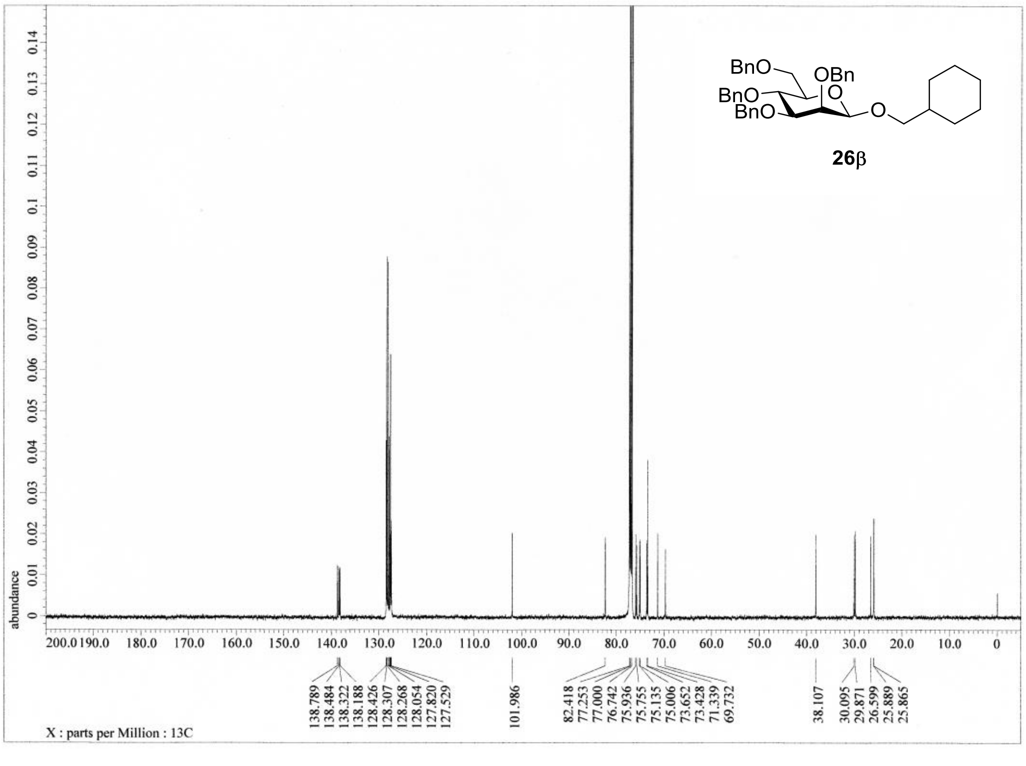


Figure S32 ^{13}C NMR spectrum of **26β**

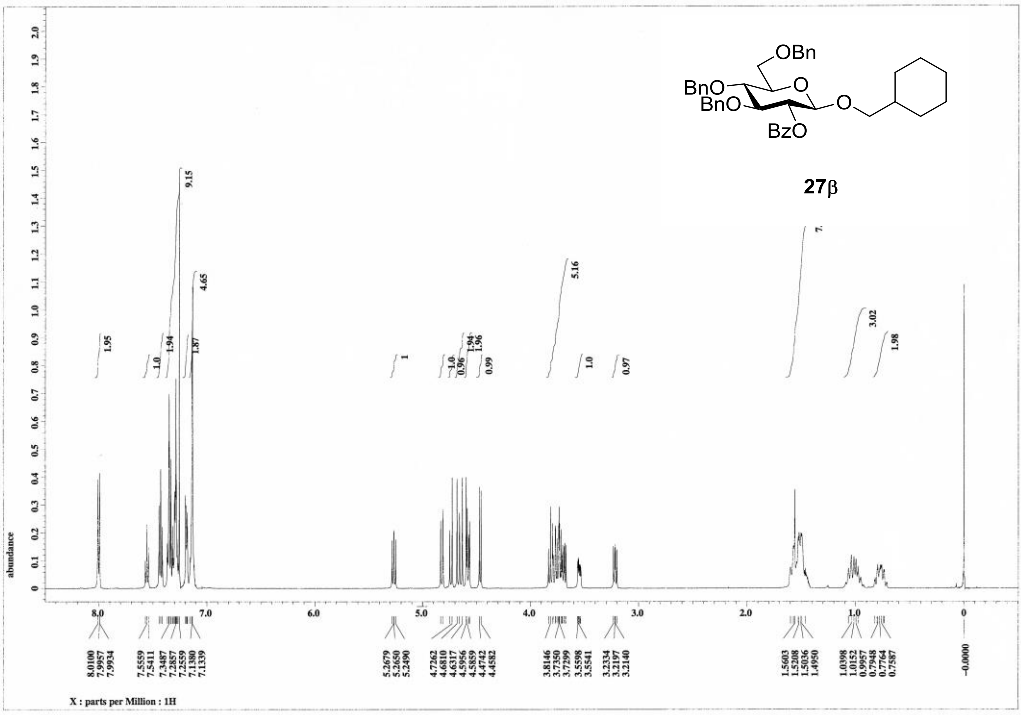


Figure S33 ^{1}H NMR spectrum of **27β**

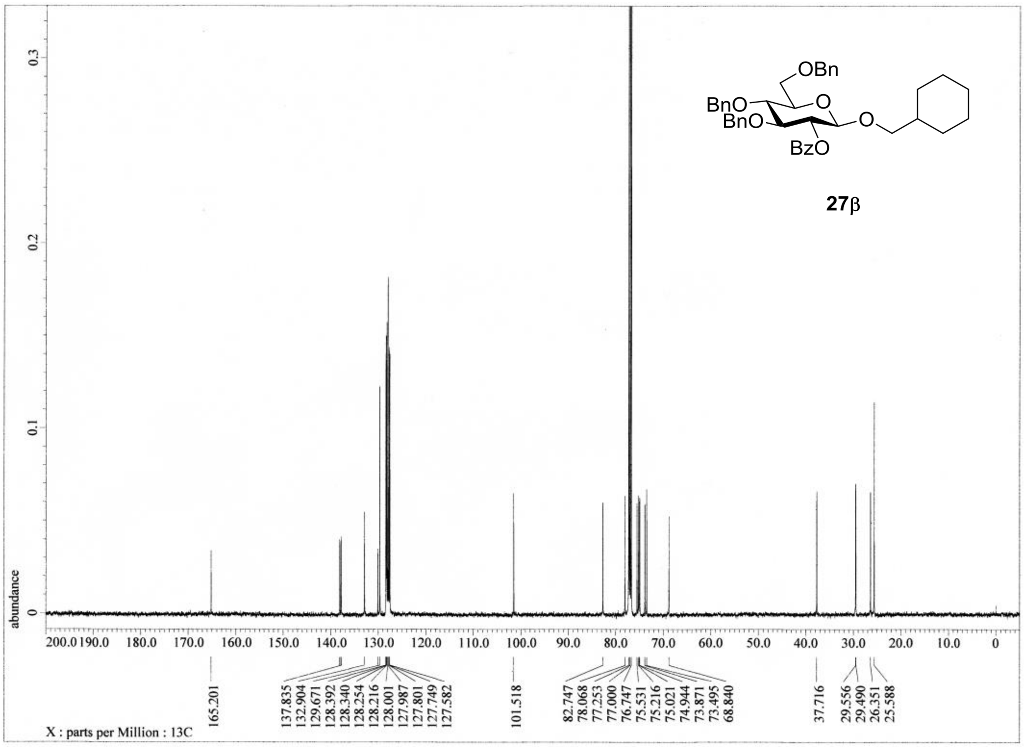


Figure S34 ^{13}C NMR spectrum of **27β**

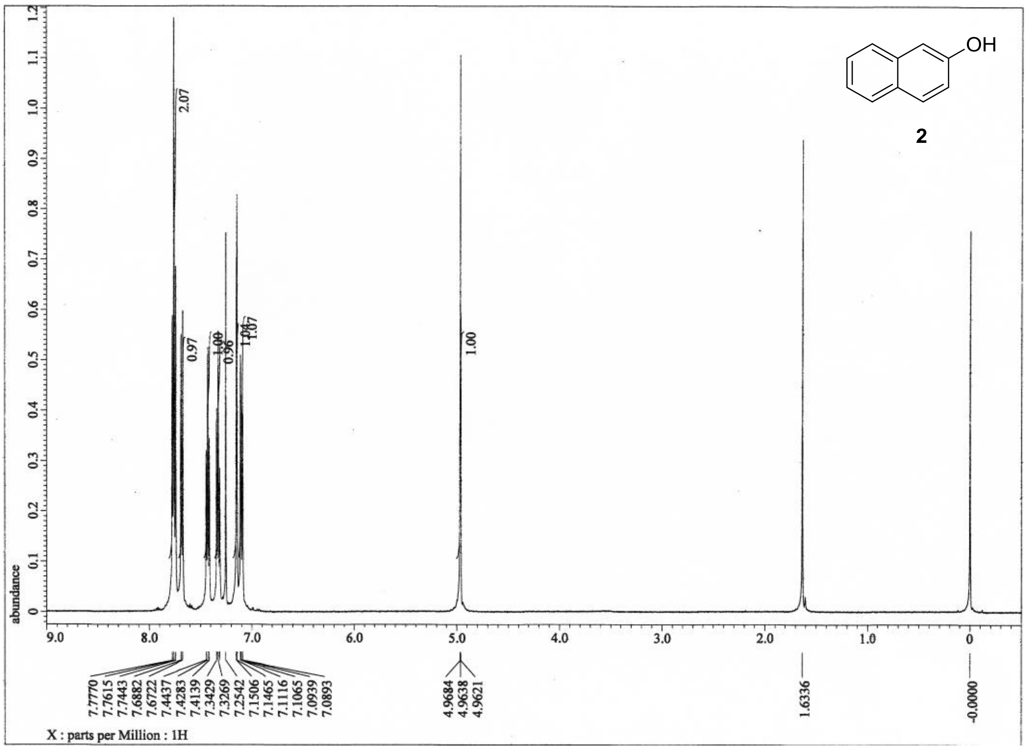


Figure S35 ^{1}H NMR spectrum of recovered **2** (500 MHz, $CDCl_3$)

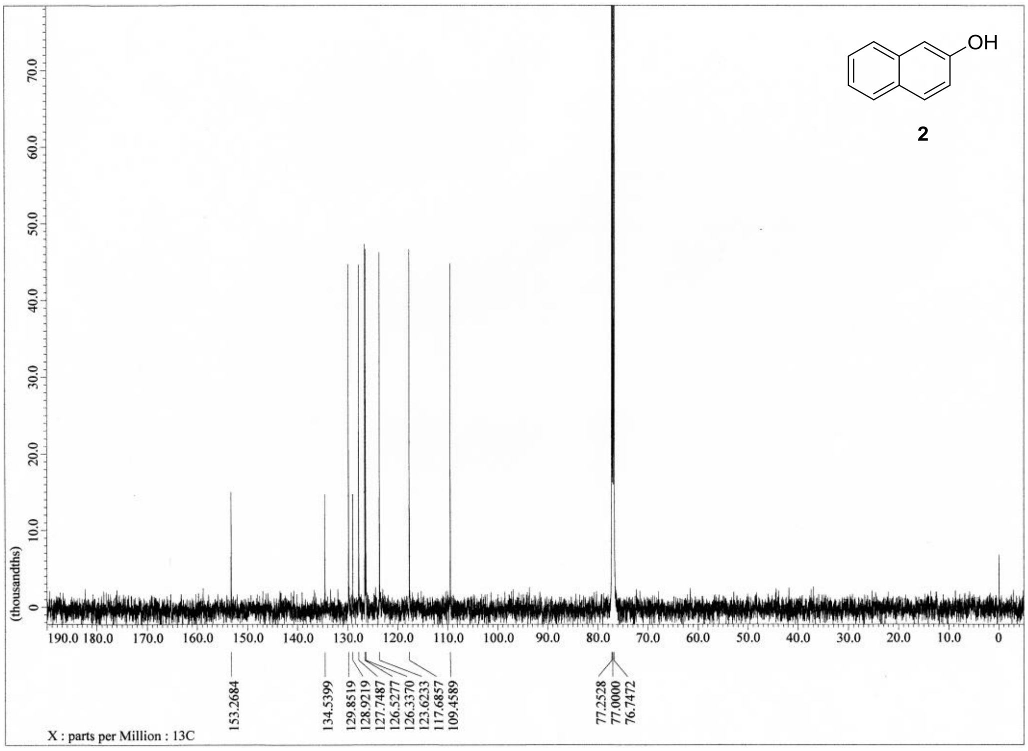


Figure S36 ^{13}C NMR spectrum of recovered **2** (500 MHz, $CDCl_3$)

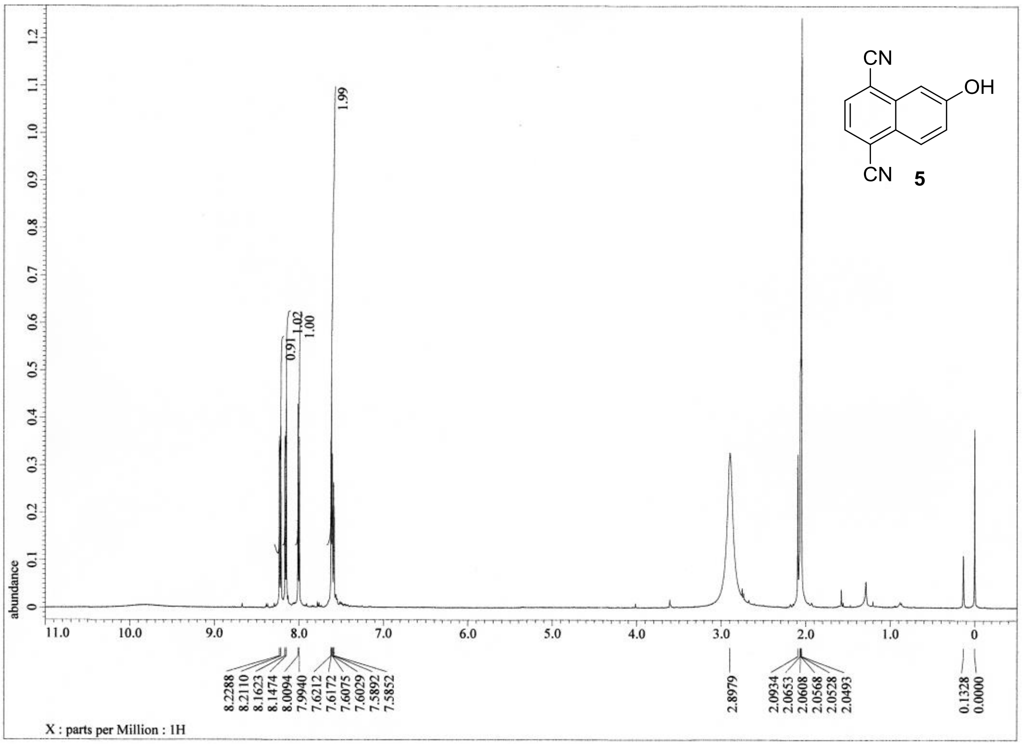


Figure S35 ^{1}H NMR spectrum of recovered **5** (500 MHz, acetone-d_6)

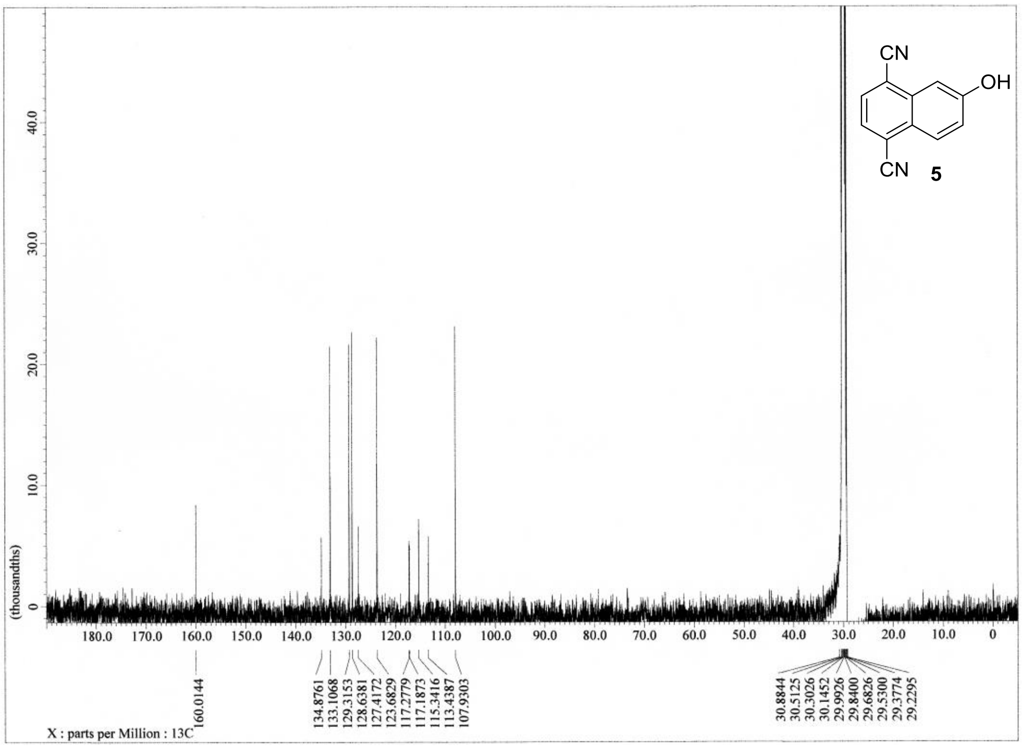


Figure S36 ^{13}C NMR spectrum of recovered **5** (500 MHz, acetone-d_6)