A Pd-Catalyzed Approach for (1→6)-Linked *C*-Glycosides

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Supporting Information

Table of Contents

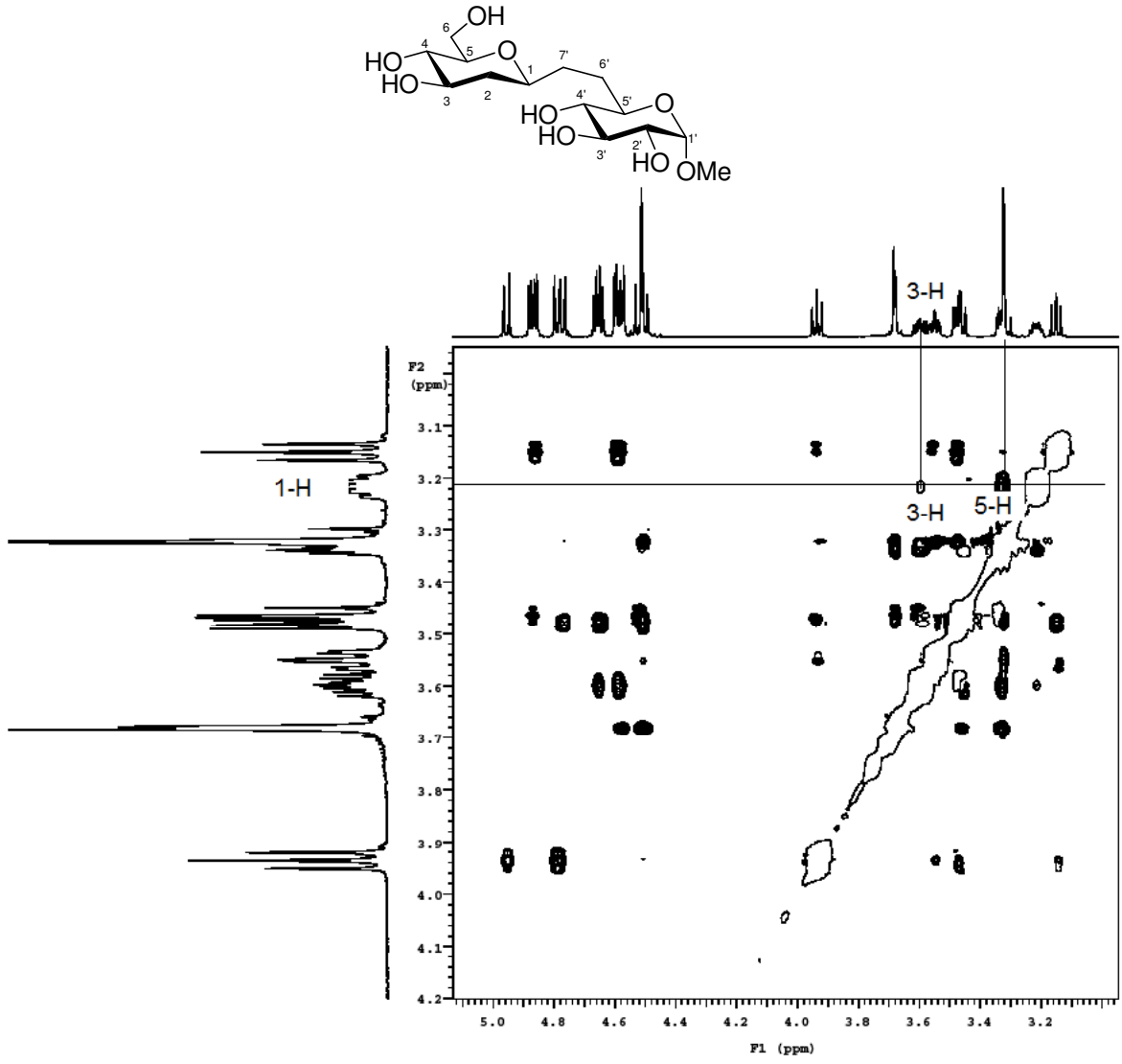
General Experimental

All solvents were distilled before use unless otherwise stated. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium/benzophenone under a nitrogen atmosphere. Dichloromethane (CH_2Cl_2) and toluene were distilled from $CaCl_2$ under a nitrogen atmosphere. Air and moisture sensitive reactions were carried out in oven-dried or flame-dried glassware, septum-capped under atmospheric pressure of argon. Commercially available compounds were used without further purification unless otherwise stated. A microwave oven with adjustable power in the range of 0-400 W has been used to apply microwave irradiation. The exact reaction conditions are given in the respective procedure. Proton (^1H) and carbon (^{13}C) NMR spectra were recorded on a 300, 500 or 600 MHz instrument using the residual signals from $CHCl_3$, δ 7.26 ppm and δ 77.0 ppm, DMSO, δ 2.54 ppm and δ 40.45 ppm, acetone, δ 2.09 ppm and δ 30.92 ppm, δ 207.07 ppm, and methanol, δ 4.87 ppm and δ 49.2 ppm, as internal references for ^1H and ^{13}C chemical shifts, respectively. Assignments of the respective signals were made by the combination of H,H-COSY, HSQC and HMBC experiments. ESI-HRMS mass spectrometry was carried out on a FTICR instrument. IR spectra were measured using a conventional spectrometer. UV spectra were measured with a common photometer. Optical rotations were measured at 20 °C using a common optical rotation instrument.

2D-NOE Experiments

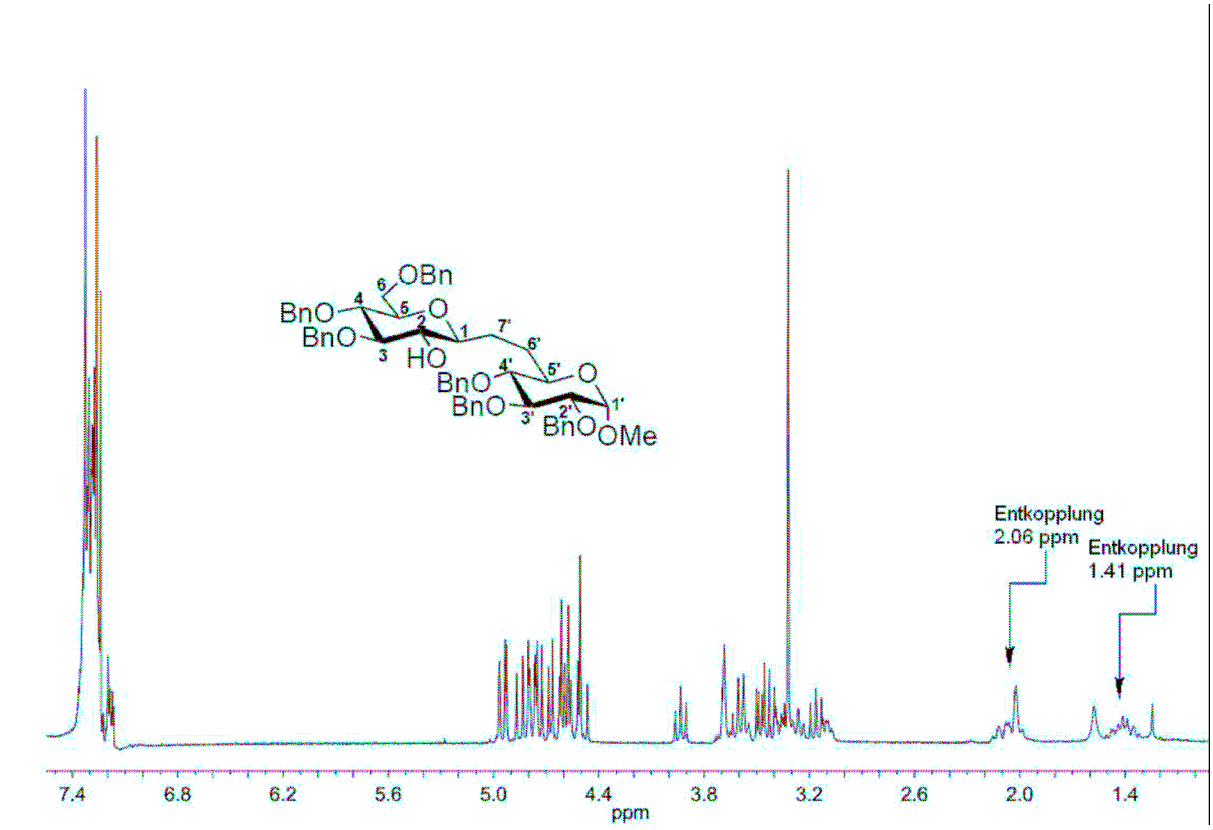
To assign all proton signals, 2D-NMR spectroscopy was performed. H-H-COSY, HSQC and HMBC as well as DEPT spectra were used to assign all sugar signals. Due to the difficult isolation of the NMR-signal of the 1-H a selective 1D-NOE was very difficult to accomplish, hence 2D-NOE had to be performed.

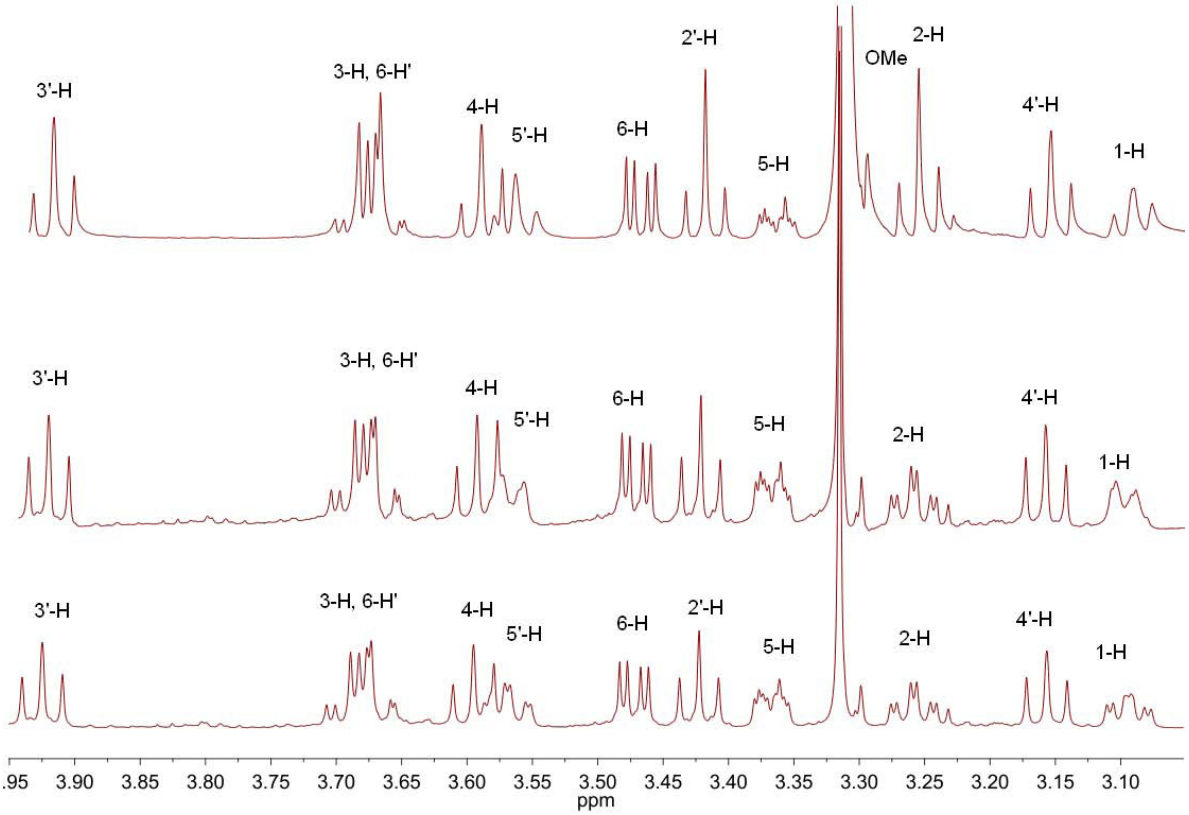
As can be seen in the spectrum the anomeric proton (1-H) shows a cross-peak in the 2D-NOE spectrum with 3-H and 5-H. Therefore one can conclude that the anomeric proton is in the axial position. The sugar has to be β-configured.



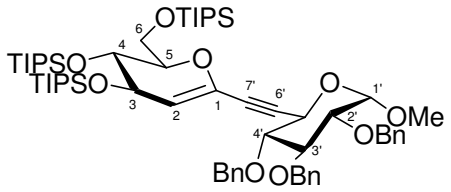
HOMOnuclear Decoupling Experiments

To get an idea whether the compound is the α- or the β-derivative one has to know the coupling constant of 1-H to 2-H. If the coupling constant is large, one can assume a β-configuration due to the axial-axial coupling (Karplus equation). In the case of a small coupling constant an α-configuration can be concluded, due to the axial-equatorial coupling. 1-H should show three different coupling constants, one to the 2-H and two to the diastereotopic 7'-H protons. Due to the diastereotopicity they should show different coupling constants. Moreover they are anisochronic and resonate in the multiplets at δ = 1.24-1.57 ppm and δ = 2.02-2.12 ppm, respectively. The resulting pattern of the NMR signal of 1-H in the ^{1}H-NMR is a doublet of doublet of doublet, which is nearly a doublet of triplet, due to two similar coupling constants. A homonuclear decoupling at 1.41 ppm leads to a doublet of doublet with one large and one small coupling constant indicating a large coupling constant from 1-H to 7'-H has been decoupled. The homonuclear decoupling at 2.06 ppm leads to a triplet (theoretically a doublet of doublet with two large coupling constants), which indicates a small coupling constant to the other diastereotopic 7'-H. In summary, one can conclude that a large coupling constant remains for the coupling of 1-H with 2-H. This fact indicates the presence of a β-configured linkage.


OBn
BnO
BnO
HO
BnO
BnO
BnO
OMe
Entkopplung
2.06 ppm
Entkopplung
1.41 ppm
7.4
6.8
6.2
5.6
5.0
4.4
3.8
3.2
2.6
2.0
1.4
ppm


3'-H
3-H, 6-H'
4-H
5'-H
6-H
2'-H
5-H
OMe
2-H
4'-H
1-H
3'-H
3-H, 6-H'
4-H
5'-H
6-H
5-H
2-H
4'-H
1-H
3'-H
3-H, 6-H'
4-H
5'-H
6-H
2'-H
5-H
2-H
4'-H
1-H
.95
3.90
3.85
3.80
3.75
3.70
3.65
3.60
3.55
3.50
3.45
3.40
3.35
3.30
3.25
3.20
3.15
3.10
ppm

Enyne *pseudo*-Disaccharide **5**

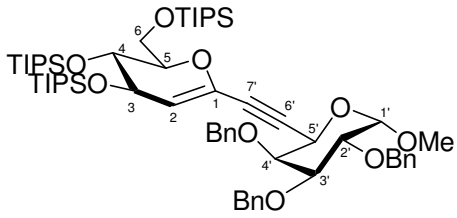


$C_{62}H_{98}O_9Si_3$ (1071.69)

Iodoglucal **1** (405.5 mg, 0.547 mmol, 1.0 eq) and alkyne **2** (276 mg, 0.602 mmol, 1.1 eq) were dissolved in NEt_3 (16 mL). $Pd(PPh_3)_2Cl_2$ (19.0 mg, 27 µmol, 0.05 eq) and CuI (10.4 mg, 55 µmol, 0.1 eq) were added simultaneously. The reaction mixture was stirred over night at room temperature. After evaporation of the solvents a silica flash column chromatography (Pentane:EtOAc = 12:1) furnished 586 mg (99%) of the desired *C*-glycoside **5**.

Analytical data of **5**: R_f: 0.30 (Hexane/EtOAc = 5:1). $[\alpha]_D^{20}$ = +12.1° (c = 0.47, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.88–1.05 (m, 63 H, TIPS), 3.40 (s, 3 H, OMe), 3.47–3.62 (m, 2 H, 2'-H, 4'-H), 3.85–3.95 (m, 3 H, 6-H, 3'-H), 3.99–4.04 (m, 1 H, 3-H), 4.10–4.13 (m, 1 H, 4-H), 4.27–4.33 (m, 1 H, 5-H), 4.47–4.61 (m, 2 H, 1'-H, 5'-H), 4.61–4.65 (m, 1 H, CH_2Bn), 4.75–4.97 (m, 5 H, CH_2Bn), 5.26 (d, *J* = 5.6 Hz, 1 H, 2-H), 7.24–7.37 (m, 15 H, Bn). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 11.9 (TIPS), 12.2 (TIPS), 12.4 (TIPS), 17.9 (TIPS), 18.0 (TIPS), 55.6 (OMe), 61.4 (C-6), 61.9 (C-5'), 65.7 (C-3), 69.2 (C-4), 73.5 (CH_2Bn), 75.5 (CH_2Bn), 75.9 (CH_2Bn), 77.0 (C-7'), 79.1 (C-4'), 80.8 (C-3'), 81.3 (C-5), 81.9 (C-2'), 84.5 (C-6'), 98.4 (C-1'), 107.4 (C-2), 127.5, 127.6, 127.9, 128.1, 128.2, 128.3, 128.4 (C_{Ar}-Bn), 135.5 (C-1), 137.8, 138.0, 138.7 (C_q-Bn). IR (Film): $\tilde{\nu}$ (cm^{-1}) = 3170, 2757, 2626, 2560, 2243, 2082, 1947, 1874, 1807. UV (CH_3CN): λ_{max} (lg ε) [nm] = 239.5 (4.11). MS (ESI): *m/z* (%) = 1094.0 (100) $[M+Na]^+$. $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 1093.64163, found: 1093.64143.

Enyne *pseudo*-Disaccharide **6**



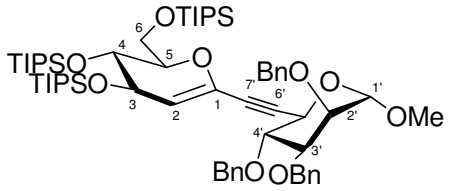
$C_{62}H_{98}O_9Si_3$ (1071.69)

Iodoglucal **1** (748 mg, 1.01 mmol, 1.0 eq) and alkyne **3** (480 mg, 1.04 mmol, 1.0 eq) were dissolved in NEt_3 (25 mL) and THF (9 mL). $Pd(PPh_3)_2Cl_2$ (35.4 mg, 50 µmol, 0.05 eq) and CuI (19.1 mg, 100 µmol, 0.1 eq) were added simultaneously. The reaction mixture was stirred over night at room temperature. After evaporation of the solvents a silica flash column chromatography (Pentane:EtOAc = 7:1) furnished 508 mg (47%) of the desired *C*-glycoside **6**.

Analytical data of **6**: R_f: 0.45 (Pentane/EtOAc = 4:1). $[\alpha]_D^{20}$ = +23.4° (c = 1.06, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.94–1.09 (m, 54 H, TIPS), 2.14 (s, 9 H, TIPS), 3.37 (s, 3 H, OMe), 3.82 (dd, *J* = 3.2, 10.0 Hz, 1 H, 2'-H), 3.86–4.05 (m, 6 H, 3-H, 4-H, 6-H, 3'-H, 4'-H), 4.25–4.31 (m, 1 H, 5-H), 4.56–4.90 (m, 8 H, CH_2Bn, 1'-H, 5'-H), 5.24–5.28 (m, 1 H, 2-H), 7.14–7.43 (m, 15 H, Bn).

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 18.0 (TIPS), 30.9 (TIPS), 55.8 (OMe), 61.5 (C-6), 62.1 (C-5'), 65.7 (C-3), 69.3 (C-4), 72.9 (CH_2Bn), 73.6 (CH_2Bn), 75.1 (CH_2Bn), 75.5 (C-4'*), 75.7 (C-3'*), 77.0 (C-2'*), 81.2 (C-7'), 81.3 (C-5), 83.3 (C-6'), 99.1 (C-1'), 107.6 (C-2), 127.3, 127.4, 127.6, 127.9, 128.0, 128.2, 128.3 (C_{Ar}-Bn), 135.3 (C-1), 138.1, 138.3, 138.5 (C_q-Bn). IR (Film): $\tilde{\nu}$ (cm^{-1}) = 3031, 2943, 2866, 1637, 1496, 1463, 1387. UV (CH_3CN): λ_{max} (lg ε) = 230.5 nm (4.03). MS (ESI): *m/z* (%) = 1093.6 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 1093.6411, found: 1093.6420.

Enyne *pseudo*-Disaccharide **7**

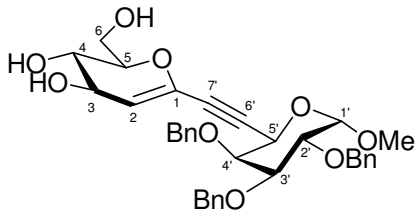


$C_{62}H_{98}O_9Si_3$ (1071.69)

Iodglucal **1** (561 mg, 0.757 mmol, 1.0 eq) and alkyne **4** (347 mg, 0.757 mmol, 1.0 eq) were dissolved in NEt_3 (24 mL). $Pd(PPh_3)_2Cl_2$ (26.5 mg, 38 µmol, 0.05 eq) and CuI (14.4 mg, 75 µmol, 0.1 eq) were added simultaneously. The reaction mixture was stirred over night at room temperature. After evaporation of the solvents a silica flash column chromatography (Pentane:EtOAc = 12:1) furnished 600 mg (74%) of the desired *C*-glycoside **7**.

Analytical data of **7**: R_f: 0.40 (Pentane/EtOAc = 6:1). $[\alpha]_D^{20}$ = +30.2° (c = 0.55, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 0.90–1.07 (m, 63 H, TIPS), 3.31 (s, 3 H, OMe), 3.68–3.77 (m, 2 H, 2'-H, 4'-H), 3.87–4.17 (m, 5 H, 3-H, 4-H, 6-H, 3'-H), 4.26–4.32 (m, 1 H, 5-H), 4.39–4.96 (m, 7 H, CH_2Bn, 1'-H), 5.25–5.28 (m, 1 H, 2-H), 7.22–7.38 (m, 15 H, Bn). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 12.3 (TIPS), 18.1 (TIPS), 55.2 (OMe), 60.4 (C-6), 63.2 (C-5'), 65.8 (C-3*), 69.3 (C-4*), 72.7 (CH_2Bn), 72.9 (CH_2Bn), 74.8 (C-4'*), 75.5 (CH_2Bn), 78.5 (C-3'*), 78.9 (C-2'*), 80.9 (C-7'), 81.2 (C-5), 84.8 (C-6'), 99.3 (C-1'), 107.2 (C-2), 127.4, 127.5, 127.8, 128.1, 128.2, 128.3 (C_{Ar}-Bn), 135.6 (C-1), 138.1, 138.5 (C_q-Bn). IR (film): $\tilde{\nu}$ (cm^{-1}) = 2944, 1728, 1464, 1265, 1065. UV (CH_3CN): λ_{max} (lg ε) [nm] = 235.0 (4.06). MS (ESI): *m/z* (%) = 1093.6 (100). $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 1093.64109, found: 1093.64083.

Enyne *pseudo*-Disaccharide **6a**

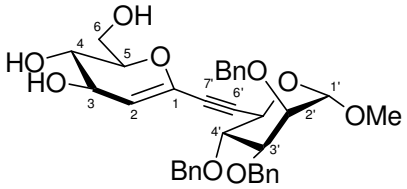


$C_{35}H_{38}O_9$ (602.67)

A solution of TBAF (662 mg, 2.10 mmol, 4.5 eq) in THF (4 mL) was added to a solution of carbohydrate **6** (500 mg, 0.47 mmol, 1.0 eq) in THF (17 mL) at room temperature. The mixture was allowed to stir over night, concentrated and the residue was purified by silica flash column chromatography (CH_2Cl_2/MeOH = 12:1) to afford 226 mg (80%) of *C*-glycoside **6a**.

Analytical data of **6a**: R_f: 0.35 (CH_2Cl_2/MeOH = 12:1). $[\alpha]_D^{20}$ = +65.7° (c = 0.35, MeOH). ^{1}H-NMR (600 MHz, CD_3OD): δ =3.36 (s, 3 H, OMe), 3.57–3.60 (m, 1 H, 4-H), 3.77–3.81 (m, 2 H, 5-H, 6-H), 3.85–3.88 (m, 2 H, 3'-H, 6-H), 3.94 (dd, *J* = 3.5, 10.0 Hz, 1 H, 2'-H), 4.05–4.06 (m, 1 H, 4'-H), 4.15 (dd, *J* = 3.0, 7.0 Hz, 1 H, 3-H), 4.58 (bs, 1 H, OH), 4.64–7.40 (m, 4 H, CH_2Bn), 4.72–4.74 (m, 3 H, 1'-H, CH_2Bn), 5.11 (d, *J* = 2.7 Hz, 1 H, 2-H), 7.24–7.42 (m, 15 H, Bn). ^{13}C-NMR (125 MHz, CD_3OD): δ = 56.1 (OMe), 62.0 (C-6), 63.3 (C-5'), 70.1 (C-4), 70.8 (C-3), 73.6, 74.4, 76.4 (CH_2Bn), 77.0 (C-2'), 78.6 (C-3', C-4'), 81.0 (C-7'), 81.3 (C-5), 85.9 (C-6'), 100.2 (C-1'), 111.9 (C-2), 128.5, 128.7, 129.1, 129.3 (C_{Ar}-Bn), 138.0 (C-1), 139.6, 139.7 (C_q-Bn). IR (Film): $\tilde{\nu}$ (cm^{-1}) = 3386, 3056, 2929, 1642, 1496, 1454, 1352, 1265. UV (CH_3CN): λ_{max} (lg ε) = 205.5 nm (4.42), 241.0 (4.05). MS (ESI): *m/z* (%) = 625.2 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 625.2408, found: 625.2398.

Enyne *pseudo*-Disaccharide **7a**

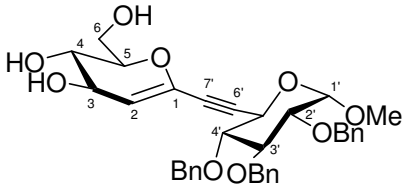


$C_{35}H_{38}O_9$ (602.67)

A solution of TBAF (795 mg, 2.50 mmol, 4.5 eq) in THF (4.8 mL) was added to a solution of carbohydrate **7** (596 mg, 0.56 mmol, 1.0 eq) in THF (20 mL) at room temperature. The mixture was allowed to stir over night, concentrated and the residue was purified by silica flash column chromatography (CH_2Cl_2/MeOH = 12:1) to afford 290 mg (86%) *C*-glycoside **7a**.

Analytical data of **7a**: R_f: 0.27 (CH_2Cl_2/MeOH = 12:1). $[\alpha]_D^{20}$ = +90.7° (c = 1.4, MeOH). ^{1}H-NMR (300 MHz, CD_3OD): δ =3.39 (s, 3 H, OMe), 3.54–3.92 (m, 8 H, 4-H, 5-H, 6-H, 2'-H, 3'-H, 4'-H), 4.15 (dd, *J* = 2.8, 7.2 Hz, 1 H, 3-H), 4.34 (d, *J* = 9.4 Hz, 1 H, 5'-H), 4.55–4.87 (m, 7 H, CH_2Bn, 1'-H), 5.14 (d, *J* = 2.8 Hz, 1 H, 2-H), 7.19–7.39 (m, 15 H, Bn). ^{13}C-NMR (125 MHz, CD_3OD): δ = 58.2 (OMe), 64.5 (C-6), 66.7 (C-5'), 72.6 (C-4), 73.3 (C-3), 75.8 (CH_2Bn), 76.4 (CH_2Bn), 78.6 (CH_2Bn), 79.0 (C-7'), 82.1 (C-5), 82.4 (C-3'), 83.1 (C-4'), 83.8 (C-2'), 89.5 (C-6'), 103.1 (C-1'), 114.4 (C-2), 131.1, 131.2, 131.3, 131.6, 131.7, 131.8 (C_{Ar}-Bn), 140.5 (C-1), 141.9, 142.0 (C_q-Bn). IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3343, 2918, 1642, 1454, 1269, 1209. UV (MeOH): λ_{max} (lg ε) [nm] = 205.0 (4.46), 240.0 (4.07). MS (ESI): *m/z* (%) = 625.2 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 625.2408, found: 625.2421.

Enyne *pseudo*-Disaccharide **11**

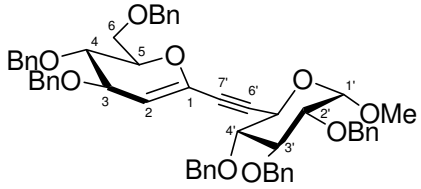


$C_{35}H_{38}O_9$ (602.67)

A solution of TBAF (173.2 mg, 0.546 mmol, 4.5 eq) in THF (1.1 mL) was added to a solution of carbohydrate **5** (130.0 mg, 0.121 mmol, 1.0 eq) in THF (4.4 mL) at room temperature. The mixture was allowed to stir over night, concentrated and the residue was purified by silica flash column chromatography (CH_2Cl_2/MeOH = 12:1) to afford 65.5 mg (90%) of *C*-glycoside **11**.

Analytical data of **11**: R_f: 0.16 (CH_2Cl_2/MeOH = 12:1). $[\alpha]_D^{20}$ = +16.0° (c = 0.20, $CHCl_3$). ^{1}H-NMR (300 MHz, CD_3OD): δ =3.38 (s, 3 H, OMe), 3.46–3.61 (m, 3 H, 4-H, 2'-H, 3'-H), 3.72–3.92 (m, 4 H, 5-H, 6-H, 4'-H), 4.13 (dd, *J* = 2.8, 7.2 Hz, 1 H, 3-H), 4.40 (d, *J* = 9.5 Hz, 1 H, 5'-H), 4.62–4.92 (m, 10 H, 1'-H, CH_2Bn, OH), 5.13 (d, *J* = 2.8 Hz, 1 H, 2-H), 7.22–7.36 (m, 15 H, Bn-H). ^{13}C-NMR (125 MHz, CD_3OD): δ =55.9 (C-Ome), 61.9 (C-6), 62.9 (C-5'), 7.0 (C-4), 70.7 (C-3), 74.1 (CH_2Bn), 76.4 (CH_2Bn), 76.6 (CH_2Bn), 80.9 (C-7'), 80.9 (C-2'), 81.2 (C-5), 81.9 (C-3'), 83.0 (C-4'), 86.8 (C-6'), 99.3 (C-1'), 111.9 (C-2), 128.4, 128.6, 129.1, 129.3 (C_{Ar}-Bn), 139.2, 139.4, 139.8 (C_q-Bn). IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3087, 3063, 2878, 1950, 1874, 1809, 1539, 1436. UV (MeOH): λ_{max} (lg ε) [nm] = 202.5 (4.54), 204.5 (4.54), 239.5 (4.13), 290.5 (3.31). MS (ESI): *m/z* (%) = 625.2 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 625.2408, found: 625.2402.

Enyne *pseudo*-Disaccharide **8**

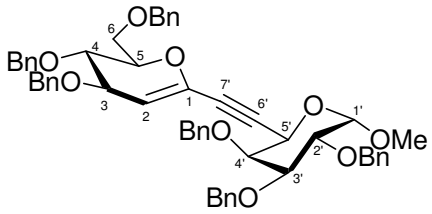


$C_{56}H_{56}O_9$ (873.04)

Carbohydrate **11** (64 mg, 0.106 mmol, 1.0 eq) was dissolved in DMF (2 mL) and the solution was cooled to 0 °C. NaH (60% in mineral oil, 21 mg, 0.530 mmol, 5.0 eq) was added and the reaction mixture was stirred for 30 min. Benzylbromide (60 µmol, 0.530 mmol, 5.0 eq) was added at 0 °C and the reaction mixture was allowed to warm to room temperature over night. The reaction was quenched by the addition of water. The aq layer was extracted with EtOAc (3×). The combined organic layers were washed with water (3×), brine (3×), dried over Na_2SO_4 and concentrated. The crude material was purified by silica flash column chromatography (Pentane/EtOAc = 10:1 to 6:1) to give 91.4 mg (99%) of *C*-glycoside **8**.

Analytical data of **8**: R_f: 0.24 (Hexane/EtOAc = 4:1). $[\alpha]_D^{20}$ = +22.5° (c = 0.40, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.38 (s, 3 H, OMe), 3.46–3.58 (m, 2 H, 5-H, 2'-H), 3.71–3.93 (m, 3 H, 4-H, 3'-H, 5'-H), 4.03–4.09 (m, 1 H, 4'-H), 4.21 (dd, *J* = 3.1, 6.4 Hz, 1 H, 3-H), 4.45–4.66 (m, 9 H, 6-H, 1-H, bn-H), 4.77–4.93 (m, 6 H, bn-H), 5.30 (d, *J* = 2.9 Hz, 1 H, 2-H), 7.20–7.37 (m, 30 H, bn-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 55.7 (OMe), 61.9 (C-6), 68.2 (CH_2Bn), 70.5 (CH_2Bn), 73.5 (CH_2Bn), 73.6 (CH_2Bn), 73.7 (C-4), 738. (CH_2Bn), 75.6 (CH_2Bn), 75.9 (C-5'), 76.2 (C-3), 77.8 (C-4'), 79.2 (C-5), 79.9 (C-7'), 80.9 (C-3'), 81.9 (C-2'), 86.1 (C-6'), 98.4 (C-1'), 107.4 (C-2), 127.5, 127.6, 127.8, 127.9, 128.1, 128.3, 128.4 (C_{Ar}-Bn), 137.5, 137.9, 138.0, 138.1 (C_q-Bn), 138.6 (C-1). IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 1946, 1866, 1806, 1739, 1605. UV (CH_3CN): λ_{max} (lg ε) [nm] = 204.5 (4.73), 241.0 (4.16). MS (ESI): *m/z* (%) = 895.4 (100). $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+NH_4]^+$: 890.4268, found: 890.4245.

Enyne *pseudo*-Disaccharide **9**

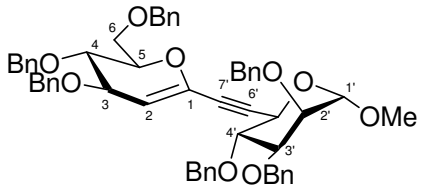


$C_{56}H_{56}O_9$ (873.04)

Carbohydrate **6a** (220 mg, 0.37 mmol, 1.0 eq) was dissolved in DMF (5 mL) and the solution was cooled to 0 °C. NaH (60% in mineral oil, 65.7 mg, 1.64 mmol, 4.5 eq) was added and the reaction mixture was stirred for 30 min. Benzylbromide (195 µmol, 1.64 mmol, 4.5 eq) was added at 0 °C and the reaction mixture was allowed to warm to room temperature over night. The reaction was quenched by the addition of water. The aq layer was extracted with EtOAc (3×). The combined organic layers were washed with water (3×), brine (3×), dried over Na_2SO_4 and concentrated. The crude material was purified by silica flash column chromatography (Pentane/EtOAc)= 6:1 to 2:1) to give 281 mg (87%) of *C*-glycoside **9**.

Analytical data of **x**: R_f: 0.08 (Pentane/EtOAc = 6:1). $[\alpha]_D^{20}$ = +28.8° (c = 0.48, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.38 (s, 3 H, OMe), 3.70–3.91 (m, 5 H, 5-H, 6-H, 3'-H*, 4'-H*), 3.99–4.06 (m, 2 H, 4-H*, 2'-H*), 4.21 (dd, *J* = 3.0, 6.3 Hz, 1 H, 3-H*), 4.44–4.98 (m, 14 H, CH_2Bn, 1'-H, 5'-H*), 5.27–5.29 (m, 1 H, 2-H), 7.16–7.45 (m, 30 H, Bn). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 55.9 (OMe), 62.2 (C-5'*), 68.2 (C-6), 70.4 (CH_2Bn), 73.1 (CH_2Bn), 73.5 (CH_2Bn), 73.7 (CH_2Bn), 73.8 (CH_2Bn), 73.8 (CH_2Bn), 75.0 (C-4*), 75.6 (C-3*), 76.1 (C-4'*), 77.0 (C-5*), 77.7 (C-3'*), 77.8 (C-2'*), 80.1 (C-7'*), 85.0 (C-6'*), 99.2 (C-1'), 107.5 (C-2), 127.4, 127.5, 127.6, 127.7, 128.0, 128.2, 128.3 (C_{Ar}-Bn), 137.4 (C-1), 137.9, 138.0, 138.2, 138.4 (C_q-Bn). UV (CH_3CN): λ_{max} (lg ε) = 241.5 nm (4.17). IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3087, 2991, 2862, 1951, 1869, 1453, 1349. MS (ESI): *m/z* (%) = 895.4 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 895.3817, found: 895.3831.

Enyne *pseudo*-Disaccharide **10**

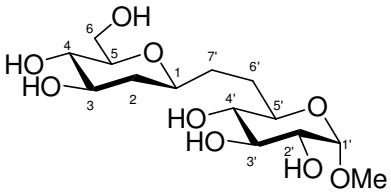


$C_{56}H_{56}O_9$ (873.04)

Carbohydrate **7a** (243 mg, 0.404 mmol, 1.0 eq) was dissolved in DMF (5 mL) and the solution was cooled to 0 °C. NaH (60% in mineral oil, 72.7 mg, 1.82 mmol, 4.5 eq) was added and the reaction mixture was stirred for 30 min. Benzylbromide (216 µmol, 1.82 mmol, 4.5 eq) was added at 0 °C and the reaction mixture was allowed to warm to room temperature over night. The reaction was quenched by the addition of water. The aq layer was extracted with EtOAc (3×). The combined organic layers were washed with water (3×), brine (3×), dried over Na_2SO_4 and concentrated. The crude material was purified by silica flash column chromatography (Pentane/EtOAc = 10:1 to 6:1) to give 289 mg (82%) of *C*-glycoside **10**.

Analytical data of **10**: R_f: 0.32 (Pentane/EtOAc = 3:1). $[\alpha]_D^{20}$ = +48.6° (c = 0.7, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 3.31 (s, 3 H, OMe), 3.71–3.72 (m, 1 H, 4-H*), 3.72–4.12 (m, 7 H, 4-H*, 5-H*, 6-H, 2'-H*, 3'-H*, 4'-H*), 4.23 (dd, *J* = 3.0, 6.5 Hz, 1 H, 3-H), 4.40–4.93 (m, 14 H, CH_2Bn, 1'-H, 5'-H*), 5.32 (d, *J* = 3.0 Hz, 1 H, 2-H), 7.11–7.39 (m, 30 H, Bn). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 55.3 (OMe), 63.2 (C-5'*), 68.3 (C-6), 70.5 (CH_2Bn), 72.6 (CH_2Bn), 73.0 (CH_2Bn), 73.5 (CH_2Bn), 73.8 (C-4*), 73.6 (CH_2Bn), 74.8 (CH_2Bn), 75.7 (C-3), 76.3 (C-4'*), 77.8 (C-5*), 78.6 (C-3'*), 79.0 (C-2'*), 79.6 (C-7'*), 86.4 (C-6'*), 99.4 (C-1'), 107.3 (C-2), 127.5, 127.6, 127.7, 127.8, 128.2, 128.3 (C_{Ar}-Bn), 137.7 (C-1), 138.0, 138.1, 138.2, 138.4 (C_q-Bn). IR (film): $\tilde{\nu}$ (cm^{-1}) = 2923, 1726, 1496, 1454. UV (CH_3CN): λ_{max} (lg ε) [nm] = 235.0 (4.02). MS (ESI): *m/z* (%) = 895.4 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 895.3817, found: 895.3829.

pseudo-Disaccharide **12**

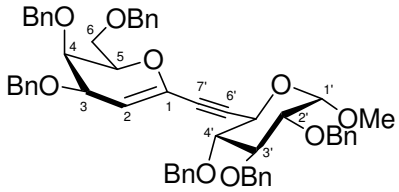


$C_{14}H_{26}O_9$ (338.35)

The carbohydrate **11** (50.0 mg, 8.0 µmol, 1.0 eq) was dissolved in MeOH (4 mL) in a 10 mL three neck flask connected to an argon bubbler. Pearlman's catalyst ($Pd(OH)_2$ (10 mg)) was added to the solution. The flask was flashed with argon (3×), evacuated (3×) and finally flashed with H_2 (1 bar). The solution was stirred over night. The reaction mixture was flashed through a pad of celite and purified by column chromatography ($MeOH/CH_2Cl_2$ = 3:1) on silica gel to give 25.3 mg (90%)of *C*-glycoside **12** as analytically pure sample.

Analytical data of **18**: R_f: 0.25 (CH_2Cl_2/MeOH = 3:1). $[\alpha]_D^{20}$ = +91.8° (c = 1.64, $CHCl_3$). ^{1}H-NMR (300 MHz, CD_3OD): δ = 1.23–1.45 (m, 2 H, 2-H, 6'-H), 1.49–1.61 (m, 1 H, 7'-H), 1.68–1.81 (m, 1 H, 7'-H), 1.90–2.13 (m, 2 H, 2-H, 6'-H), 3.01–3.21 (m, 2 H, 5-H, 4'-H), 3.29–3.69 (m, 10 H, OMe, 1-H, 3-H, 4-H, 6-H, 2'-H, 3'-H, 5'-H), 3.81–3.85 (m, 2 H, 6-H), 4.62 (d, *J* = 3.9 Hz, 1 H, 1'-H). ^{13}C-NMR (125 MHz, CD_3OD): δ = 28.9 (C-6'), 32.4 (C-7'), 40.6 (C-2), 55.4 (OMe), 63.3 (C-6), 72.3 (C-2'), 73.6 (C-1*, C-3*), 73.9 (C-4), 75.0 (C-4'), 75.6 (C-3'), 76.9 (C-5'), 81.6 (C-5), 101.0 (C-1'). IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3417, 2854, 2095, 1649, 894. UV (MeOH): λ_{max} (lg ε) [nm] = no absorbtion maximum from 190 to 350 nm. MS (ESI): *m/z* (%) = 361.1 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 361.1469, found 361.1471.

Enyne *pseudo*-Disaccharide **17**

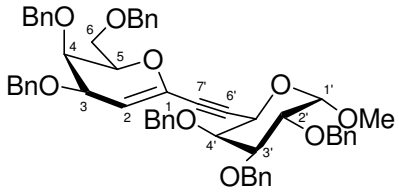


$C_{56}H_{56}O_9$ (873.04)

To a solution of lactone **15** (231 mg, 513 µmol, 1.0 eq) in THF (13 mL) at –78 °C were added HMPA (140 µL, 802 µmol, 1.5 eq), followed by potassium bis(trimethylsilyl)amide (0.5 M in toluene, 3.2 mL, 1.60 mmol, 3.0 eq). After 30 min at –78 °C *N*-phenyltrifuoromethanesulfonimide (572 mmol, 1.60 mmol, 3.0 eq) in THF (6 mL) was added to the solution and the resultant mixture was stirred at 0 °C for 1.5 h. Volatiles were removed in vacuo and to the residue a solution of alkyne **2** (193 mg, 421 µmol, 0.82 eq) in NEt_3 (15 mL) was added followed by the addition of $Pd(PPh_3)_2Cl_2$ (14.8 mg, 21 µmol, 0.05 eq) and CuI (8.0 mg, 42 µmol, 0.1 eq). The reaction mixture was stirred over night at room temperature. After evaporation of the solvents a silica flash column chromatography (Pentane/EtOAc = 4:1) furnished the desired *C*-glycoside **17** in 80% yield over two steps.

Analytical data of **17**: R_f: 0.39 (Pentane/EtOAc = 2:1). $[\alpha]_D^{20}$ = +7.9° (c = 1.64, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 3.41 (s, 3 H, OMe), 3.50–3.53 (m, 1 H, 2'-H), 3.54–3.59 (m, 1 H, 4'-H), 3.70–7.75 (m, 2 H, 6-H), 3.88–3.93 (m, 1 H, 3'-H), 3.98–4.00 (m, 1 H, 3-H), 4.19–4.25 (m, 2 H, 4-H, 5-H), 4.38–4.42 (m, 2 H, CH_2Bn), 4.45–4.51 (m, 4 H, 1'-H, 5'-H, CH_2Bn), 4.56–4.68 (m, 2 H, CH_2Bn), 4.79–4.96 (m, 6 H, CH_2Bn), 5.32–5.33 (m, 1 H, 2-H), 7.24–7.40 (m, 30 H, Bn). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 55.6 (OMe), 61.9 (C-5'), 67.9 (C-6), 70.0 (C-3), 70.8 (CH_2Bn), 73.4 (C-4), 73.5 (CH_2Bn), 73.6 (CH_2Bn), 75.6 (CH_2Bn), 75.9 (CH_2Bn), 76.4 (C-5), 79.2 (C-2'), 80.1 (C-7'), 80.8 (C-3'), 81.9 (C-4'), 85.6 (C-6'), 98.3 (C-1'), 107.5 (C-2), 127.2, 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4 (C_{Ar}-Bn), 136.6 (C-1), 137.7, 137.8, 137.9, 138.3, 138.5 (C_q-Bn). IR (Film): $\tilde{\nu}$ (cm^{-1}) = 3375, 3060, 3031, 2921, 1701, 1638, 1496. UV (CH_3CN): λ_{max} (lg ε) [nm] = 204.0 (4.69), 240.5 (4.10). MS (ESI): *m/z* (%) = 895.3 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 895.3817, found 895.3828.

Enyne *pseudo*-Disaccharide **18**

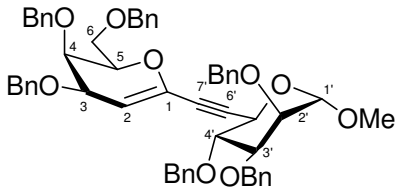


$C_{56}H_{56}O_9$ (873.04)

To a solution of lactone **15** (264 mg, 586 µmol, 1.0 eq) in THF (15 mL) at –78 °C were added HMPA (159 µL, 916 µmol, 1.5 eq), followed by potassium bis(trimethylsilyl)amide (0.5 M in toluene, 3.7 mL, 1.83 mmol, 3.0 eq). After 30 min at –78 °C *N*-phenyltrifuoromethanesulfonimide (653.7 mmol, 1.83 mmol, 3.0 eq) in THF (7 mL) was added to the solution and the resultant mixture was stirred at 0 °C for 1.5 h. Volatiles were removed in vacuo and to the residue a solution of alkyne **3** (280 mg, 611 µmol, 1.04 eq) in NEt_3 (22 mL) was added followed by the addition of $Pd(PPh_3)_2Cl_2$ (21.4 mg, 30 µmol, 0.05 eq) and CuI (11.6 mg, 60 µmol, 0.1 eq). The reaction mixture was stirred over night at room temperature. After evaporation of the solvents a silica flash column chromatography (Pentane/EtOAc = 6:1) furnished 383 mg (75% over two steps) of the desired *C*-glycoside **18**.

Analytical data of **18**: R_f: 0.61 (Pentane/EtOAc = 2:1). $[\alpha]_D^{20}$ = +12.1° (c = 0.14, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 3.37 (s, 3 H, OMe), 3.65–3.71 (m, 2 H, 6-H), 3.83 (dd, *J* = 4.5, 10.2 Hz, 1 H, 4'-H*), 3.86–3.89 (m, 1 H, 3'-H*), 3.93–3.96 (m, 1 H, 3-H*), 4.01 (dd, *J* = 4.5, 10.2 Hz, 1 H, 5-H*), 4.13–4.20 (m, 2 H, 2'-H*, 4-H*), 4.37–4.94 (m, 14 H, CH_2Bn, 1'-H, 5'-H), 5.25–5.28 (m, 1 H, 2-H), 7.15–7.44 (m, 30 H, Bn). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 55.9 (OMe), 62.2 (C-5'*), 67.8 (C-6), 70.1 (C-3*), 70.7 (CH_2Bn), 71.6 (C-4*), 73.1 (CH_2Bn), 73.4 (CH_2Bn), 73.6 (CH_2Bn), 73.7 (CH_2Bn) 75.0 (CH_2Bn), 75.6 (C-5*), 76.7 (C-2'*) 77.2 (C-3'*), 77.8 (C-4'*), 80.3 (C-7'), 84.6 (C-6'), 99.1 (C-1'), 107.6 (C-2), 127.3, 127.4, 127.5, 127.6, 127.7, 127.9 128.0, 128.1, 128.2, 128.3 (C_{Ar}-Bn), 136.6 (C-1), 137.8, 138.0, 138.2 138.3, 138.5 (C_q-Bn). IR (Film): $\tilde{\nu}$ (cm^{-1}) = 3373, 3062, 3030, 2921, 1638, 1496, 1454, 1351. UV (CH_3CN): λ_{max} (lg ε) = 239 nm (4.0688). MS (ESI): *m/z* (%) = 895.4 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 895.3817, found: 895.3817.

Enyne *pseudo*-Disaccharide **19**

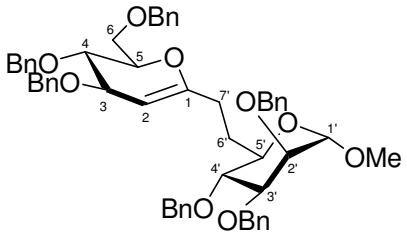


$C_{56}H_{56}O_9$ (873.04)

To a solution of lactone **15** (77.7 mg, 173 µmol, 1.0 eq) in THF (5 mL) at –78 °C were added HMPA (47 µL, 270 µmol, 1.5 eq), followed by potassium bis(trimethylsilyl)amide (0.5 M in toluene, 1.1 mL, 540 µmol, 3.0 eq). After 30 min at –78 °C *N*-phenyltrifuoromethanesulfonimide (193 mg, 540 µmol, 3.0 eq) in THF (2.5 mL) was added to the solution and the resultant mixture was stirred at 0 °C for 1.5 h. Volatiles were removed in vacuo and to the residue a solution of alkyne **4** (81 mg, 176 µmol, 1.0 eq) in NEt_3 (7 mL) was added followed by the addition of $Pd(PPh_3)_2Cl_2$ (8.4 mg, 11.7 µmol, 0.07 eq) and CuI (8.5 mg, 44.6 µmol, 0.2 eq). The reaction mixture was stirred over night at room temperature. After evaporation of the solvents a silica flash column chromatography (Pentane/EtOAc = 6:1 to 4:1) furnished 145 mg (96% over two steps) of the desired *C*-glycoside **19**.

Analytical data of **19**: R_f: 0.39 (Pentane/EtOAc = 2:1). $[\alpha]_D^{20}$ = +22.7° (c = 0.26, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 3.31 (s, 3 H, OMe), 3.67–3.76 (m, 4 H, 5-H*, 6-H, 2'-H*), 3.95–3.97 (m, 1 H, 3-H*), 4.00 (t, *J* = 9.5 Hz, 1 H, 4'-H*), 4.16–4.21 (m, 2 H, 4-H*, 3'-H*), 4.35–4.47 (m, 3 H, CH_2Bn, 5'-H*), 4.54–4.92 (m, 11 H, CH_2Bn, 1'-H), 5.28–5.33 (m, 1 H, 2-H), 7.14–7.39 (m, 30 H, Bn). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 55.2 (OMe), 63.1 (C-5'*), 67.9 (C-6), 70.2 (C-3*), 70.8 (CH_2Bn), 71.6 (C-4*), 72.7 (CH_2Bn), 72.9 (CH_2Bn), 73.4 (CH_2Bn), 73.5 (CH_2Bn), 74.8 (C-5*), 75.6 (CH_2Bn), 76.3 (C-3'*), 78.5 (C-4'*), 78.9 (C-2'*), 79.8 (C-7'), 85.9 (C-6'), 99.3 (C-1'), 107.3 (C-2), 127.3, 127.4, 127.5, 127.6, 127.7, 127.8, 127.9, 128.1, 128.2, 128.3 (C_{Ar}-Bn), 136.8 (C-1), 137.8, 138.1, 138.3, 138.4 (C_q-Bn). IR (Film): $\tilde{\nu}$ (cm^{-1}) = 3379, 3063, 3031, 2921, 1701, 1638, 1496. UV (CH_3CN): λ_{max} (lg ε) = 242.0 nm (4.09). MS (ESI): *m/z* (%) = 895.4 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 895.3817, found 895.3824.

Enolether *pseudo*-Disaccharide **23**[1]

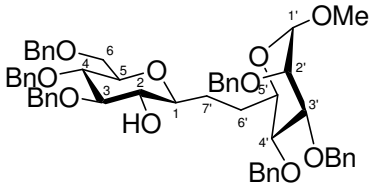


$C_{56}H_{60}O_9$ (877.07)

Raney-Nickel was washed with water until the pH value was nearly 7 (approximately 3×). Afterwards it was washed with MeOH (3×). A solution of carbohydrate **10** (202 mg, 0.231 mmol, 1.0 eq) in THF:MeOH (1:2, 15 mL) was added and a H_2 pressure of 1 bar was applied via a syringe technique until the TLC shows nearly full conversion (approximately 2.5 h). The Raney Nickel is removed via filtration through a pad of silica gel. The solution was evaporated and the residue was purified by silica flash column chromatography (Pentane/EtOAc = 6:1) to afford 162 mg (80%) of the desired *C*-glycoside **23**.

Analytical data of **23**: R_f: 0.35 (Pentane/EtOAc = 4:1). $[\alpha]_D^{20}$ = +23.1° (c = 0.13, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.62–1.79 (m, 1 H, 6'*-H), 2.00–2.19 (m, 2 H, 7'*-H), 2.25–2.48 (m, 1 H, 6'-H*), 3.25 (s, 3 H, OMe), 3.44–3.87 (m, 7 H, 3-H, 4-H, 6-H, 2'-H*, 4'-H, 5'-H), 4.01–4.09 (m, 1 H, 5-H*), 4.14–4.19 (m, 1 H, 3'-H), 4.45–4.95 (m, 14 H, CH_2Bn, 1'-H, 2-H), 7.19–7.39 (m, 30 H, Bn). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 29.0 (C-6'*), 29.7 (C-7'*), 54.6 (OMe), 68.6 (C-6), 70.1 (CH_2Bn), 70.8 (C-5'), 72.1 (CH_2Bn), 72.7 (CH_2Bn), 73.3 (CH_2Bn), 73.4 (CH_2Bn), 74.3 (C-4*), 74.6 (C-3*), 75.1 (CH_2Bn), 76.7 (C-3'), 77.0 (C-5*), 78.7 (C-2'*), 80.3 (C-4'), 94.8 (C-1), 98.9 (C-1'), 127.2, 127.4, 127.5, 127.6, 127.7, 127.8, 128.1, 128.2 (C_{Ar}-Bn), 138.1, 138.2, 138.4, 138.5 (C_q-Bn), 155.9 (C-2). IR (Film): $\tilde{\nu}$ (cm^{-1}) = 1674, 1496, 1454, 1364. UV (CH_3CN): λ_{max} (lg ε) [nm] = 251.5 (3.10), 257.5 (3.13), 263.0 (3.04). MS (ESI): *m/z* (%) = 899.4 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 899.1430, found: 899.4137.

pseudo-Disaccharide **24**

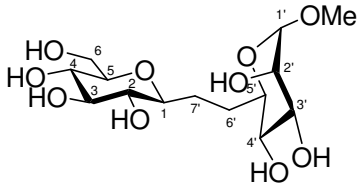


$C_{56}H_{62}O_{10}$ (895.09)

Carbohydrate **23** was coevaporated with toluene (3×). A solution of carbohydrate **23** (87 mg, 99 µmol, 1.0 eq) in dichloromethane (4 mL) was cooled to –78 °C. Freshly prepared DMDO (0.07 M in acetone, 3.5 mL, 2.5 eq) was added and the resulting mixture was stirred for 1 h. at -78 °C and then allowed to warm to 0 °C for 20 min. The volatiles were removed in vacuo at 0 °C and the resulting epoxide was used without further purification. It was resolved in dichloromethane (5 mL) and cooled back to -78 °C. DIBAL (1 M in THF, 992 µL, 10.0 eq) was added and the reaction mixture allowed to warm to room temperature until the TLC shows no starting material (approximately 1 h). The reaction was quenched with sat. NH_4Cl, extracted with dichloromethane (3×), dried over Na_2SO_4 and concentrated. Column chromatography on silica gel (Pentane/EtOAc = 3:1 to 2:1) furnished 59 mg (67% over two steps) *C*-glycoside **24**.

Analytical data of **24**: R_f: 0.21 (Pentane/EtOAc = 2:1). $[\alpha]_D^{20}$ = +22.1° (c = 0.34, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 1.48–1.61 (m, 2 H, 6'-H, 7'-H), 2.06–2.22 (m, 2 H, 6'-H, 7'-H), 3.12–3.17 (m, 1 H, 1-H), 3.25 (s, 3 H, OMe), 3.30 (t, *J* = 10.5 Hz, 1 H, 2-H), 3.37–3.40 (m, 1 H, 4-H), 3.45 (t, *J* = 9.9 Hz, 1 H, 4'-H*), 3.51 (dt, *J* = 3.6, 9.3 Hz, 1 H, 5-H*), 3.54–3.72 (m, 4 H, 6-H*, 2'-H*, 5'-H*), 3.74–3.76 (m, 1 H, 3-H*), 3.81 (dd, *J* = 4.6, 9.0 Hz, 1 H, 3'-H*), 4.48–4.62 (m, 6 H, CH_2Bn), 4.64 (d, *J* = 2.1 Hz, 1 H, 1'-H), 4.68–4.95 (m, 6 H, CH_2Bn), 7.14–7.39 (m, 30 H, Bn). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 27.5 (C-7'*), 28.1 (C-6'*), 54.6 (OMe), 69.1 (C-6), 71.7 (CH_2Bn), 72.1 (CH_2Bn), 72.7 (CH_2Bn), 73.6 (C-5'*), 73.6 (CH_2Bn), 74.1 (C-2*), 74.7 (CH_2Bn), 74.7 (CH_2Bn), 75.1 (C-3*), 78.5 (C-5*), 79.0 (C-1*), 79.1 (C-4*), 79.6 (C-2'*), 80.3 (C-3'*), 86.9 (C-4'*), 98.8 (C-1'), 127.4, 127.5, 127.7, 127.8, 127.9, 128.2, 128.5 (C_{Ar}-Bn), 138.1, 138.3, 138.5, 138.6 (C_q-Bn). IR (film): $\tilde{\nu}$ (cm^{-1}) = 3455, 3062, 3030, 1949, 1604. UV (CH_3CN): λ_{max} (lg ε) [nm] = 252.5 (3.14), 257.0 (3.16), 263.0 (2.97). MS (ESI): *m/z* (%) = 917.5 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 917.4235, found: 917.4247.

pseudo-Disaccharide **25**

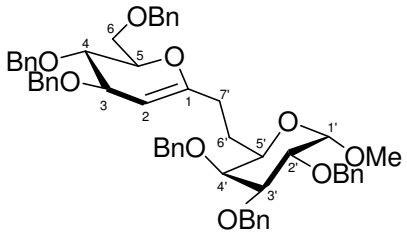


$C_{14}H_{26}O_{10}$ (354.35)

The carbohydrate **24** (15.6 mg, 17.4 µmol, 1.0 eq) was dissolved in MeOH:CH_2Cl_2:EtOAc (3:1:1, 5 mL) in a 10 mL three-neck flask connected to an argon bubbler. Pearlman's catalyst ($Pd(OH)_2$ (39 mg)) was added to the solution. The flask was flashed with argon (3×), evacuated (3×) and finally flashed with H_2 (2 bar). The solution was stirred over night. The product was isolated by flashing the solution through a pad of silica gel to give 6.1 mg (99%) of *C*-glycoside **25** as analytically pure sample.

Analytical data of **25**: R_f: 0.18 (CH_2Cl_2/MeOH 2:1). $[\alpha]_D^{20}$ = +33.1° (c = 0.61, MeOH). ^{1}H-NMR (300 MHz, CD_3OD): δ =1.23–1.53 (m, 2 H, 6'*-H), 2.15–2.24 (m, 2 H, 7'*-H), 3.01–3.52 (m, 10 H, OMe, 1-H*, 2-H*, 3-H*, 4-H*, 5-H*, 4'-H*, 5'-H*), 3.57–3.64 (m, 2 H, 6-H*, 3'-H*), 3.75–3.88 (m, 2 H, 6-H, 2'-H*), 4.57 (d, *J* = 1.8 Hz, 1 H, 1'-H). ^{13}C-NMR (125 MHz, CD_3OD): δ = 28.6 (C-7'*), 29.3 (C-6'*), 55.1 (OMe), 63.2 (C-6), 72.0, 72.1, 72.4, 72.5, 73.7, 75.5, 79.8, 81.1, 81.5 (C-1, C-2, C-3, C-4, C-5, C-2', C-3', C-4', C-5'*), 102.6 (C-1'). IR (film): $\tilde{\nu}$ (cm^{-1}) = 3392, 2922, 1714, 1646, 1418, 1362. UV (MeOH): λ_{max} (lg ε) [nm] = no absorbtion maximum from 190 to 350 nm. MS (ESI): *m/z* (%) = 377.2 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 377.1418, found: 377.1419.

Enolether *pseudo*-Disaccharide **26**[1], [2]

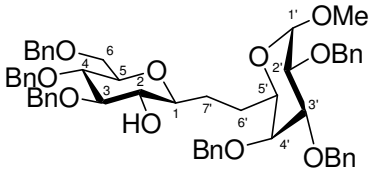


$C_{56}H_{60}O_9$ (877.07)

Raney-Nickel was washed with water until the pH-value was nearly 7 (approximately 5×). Afterwards it was washed with MeOH (4×). A solution of carbohydrate **9** (117 mg, 0.134 mmol, 1.0 eq) in THF:MeOH (1:2, 15 mL) was added and a H_2 pressure of 1 bar was applied via a syringe technique until the TLC shows nearly full conversion (approximately 3 h). The Raney-Nickel is removed via filtration through a pad of silica gel. The solution was evaporated and the residue was purified by silica flash column chromatography (Pentane/EtOAc = 4:1) to afford 71.5 mg (61%) of the desired *C*-glycoside **26**.

Analytical data of **26**: R_f: 0.27 (Pentane/EtOAc = 2:1). $[\alpha]_D^{20}$ = +9.2° (c = 0.97, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.20–1.53 (m, 2 H, 6'-H), 1.95 (m, 2 H, 7'-H), 3.15 (t, *J* = 9.6 Hz, 1 H, 4'-H), 3.31 (s, 3 H, OMe), 3.45 (dd, *J* = 3.6, 9.6 Hz, 1 H, 2'-H), 3.59 (t, *J* = 9.0 Hz, 1 H, 5'-H), 3.71 (d, *J* = 6.1 Hz, 2 H, 6-H), 3.89–3.96 (m, 2 H, 3-H, 3'-H), 4.11–4.20 (m, 2 H, 5-H, CH_2Bn), 4.11–4.96 (m, 14 H, 2-H, 4-H, 1'-H CH_2Bn), 7.24–7.33 (m, 30 H, Bn). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 29.0 (C-6'), 29.7 (C-7'), 55.1 (OMe), 68.3 (C-6), 69.5 (C-5'), 70.8 (CH_2Bn), 71.2 (CH_2Bn), 71.4 (CH_2Bn), 73.0 (CH_2Bn), 73.3 (C-4), 73.3 (CH_2Bn), 75.0 (C-3), 75.6 (CH_2Bn), 75.7 (C-5), 80.1 (C-2'), 81.9 (C-4'), 82.0 (C-3'), 94.9 (C-2), 97.7 (C-1'), 127.3, 127.4, 127.5, 127.8, 127.9, 128.2, 128.3 (C_{Ar}-Bn), 138.0, 138.1, 138.2, 138.5, 138.6, 138.7 (C_q-Bn), 154.8 (C-1). IR (Film): $\tilde{\nu}$ (cm^{-1}) = 2903, 1673, 1604, 1496, 1453, 1351. UV (CH_3CN): λ_{max} (lg ε) [nm] = 204.5 (4.76), 252.5 (2.99), 257.0 (3.05), 263.0 (3.08). MS (ESI): *m/z* (%) = 899.4 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 899.4130, found: 899.4135.

pseudo-Disaccharide **27**

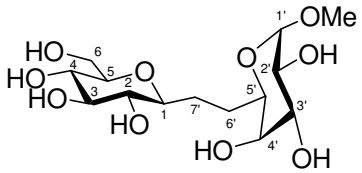


$C_{56}H_{62}O_{10}$ (895.06)

A solution of carbohydrate **26** (55 mg, 62.7 µmol, 1.0 eq) in toluene (5.4 mL) was cooled to 0 °C. BH_3·THF (1 M in THF, 627 µL, 627 µmol) was added to the cooled solution and the resultant mixture was allowed to warm to room temperature with ice-bad in place and stirred over night. The solution was cooled back to 0 °C and NaOH (1 M, 14 mL) and H_2O_2 (30%, 14 mL) were added in one portion. The resultant mixture was allowed to warm to room temperature over 2 h. The solution then was extracted with EtOAc and the combined organic layers were washed with sat. aq. $Na_2S_2O_3$ (1×), brine (1×), dried over Na_2SO_4, filtered and concentrated. Flash column chromatography on silica gel (Pentane/EtOAc = 2:1) furnished 29 mg (52%) of the desired *C*-glycoside **27**.

Analytical data of **27**: R_f: 0.18 (Pentane/EtOAc = 2:1). $[\alpha]_D^{20}$ = +28.5° (c = 1.41, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.19–1.97 (m, 4 H, 6'-H, 7'-H), 3.02–3.11 (m, 1 H, 1-H), 3.16–3.24 (m, 1 H, 3-H), 3.29–3.45 (m, 5 H, OMe, 5-H, 2'-H), 3.56–3.69 (m, 4 H, 4-H, 6-H, 5'-H), 3.87 (dd, *J* = 3.0, 10.1 Hz, 1 H, 4'-H), 4.01 (dd, *J* = 3.7, 10.1 Hz, 1 H, 3'-H), 4.45–4.96 (m, 14 H, CH_2Bn, 1'-H, 3'-H), 7.11–7.45 (m, 30 H, Bn). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 26.8 (C-6'*), 28.4 (C-7'*), 55.2 (OMe), 69.0 (C-6), 70.5 (C-5'*), 73.3 (CH_2Bn), 73.4 (CH_2Bn), 73.5 (C-2*), 73.9 (CH_2Bn), 74.6 (CH_2Bn), 74.7 (CH_2Bn), 75.1 (C-3*), 76.5 (C-5*), 78.4 (C-1*), 78.9 (C-4*), 79.3 (C-3'*), 79.5 (C-4'*), 86.8 (C-2'*), 98.6 (C-1'), 127.3, 127.5, 127.7, 127.8, 128.0, 128.2, 128.3, 128.6 (C_{Ar}-Bn), 138.0, 138.5, 138.6, 138.8 (C_q-Bn). IR (film): $\tilde{\nu}$ (cm^{-1}) = 3465, 3062, 3030, 2904, 1725, 1604, 1496, 1453, 1354. UV (CH_3CN): λ_{max} (lg ε) [nm] = 252.0 (3.01), 257.5 (3.08), 263.5 (3.11). MS (ESI): *m/z* (%) = 914.42 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 917.4235, found: 917.4234.

pseudo-Disaccharide **28**

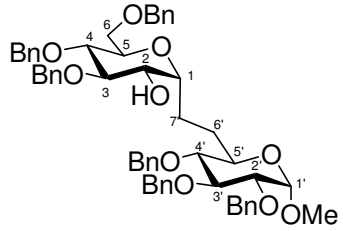


$C_{14}H_{26}O_{10}$ (354.35)

The carbohydrate **27** (12.5 mg, 13.4 µmol, 1.0 eq) was dissolved in MeOH:CH_2Cl_2:EtOAc (3:1:1, 5 mL) in a 10 mL three-neck flask connected to an argon bubbler. Pearlman's catalyst ($Pd(OH)_2$ (52 mg)) was added to the solution. The flask was flashed with argon (3×), evacuated (3×) and finally flashed with H_2 (2 bar). The solution was stirred over night. The product was isolated by flashing the solution through a pad of silica gel to give 4.7 mg (99%) of *C*-glycoside **28** as analytically pure sample.

Analytical data of **28**: R_f: 0.15 (CH_2Cl_2/MeOH = 2:1). $[\alpha]_D^{20}$ = +86.8° (c = 0.4, MeOH). ^{1}H-NMR (300 MHz, CD_3OD): δ =1.36–1.50 (m, 2 H, 6'-H*), 1.65–1.84 (m, 2 H, 7'-H*), 3.03–3.35 (m, 5 H, 2-H*, 3-H*, 4-H*, 5-H*, 4'-H*), 3.38 (s, 3 H, OMe), 3.58–3.87 (m, 6 H, 1-H*, 6-H, 2'-H*, 3'-H*, 5'-H*), 4.66 (d, *J* = 3.2 Hz, 1 H, 1'-H). ^{13}C-NMR (125 MHz, CD_3OD): δ = 27.6 (C-7'*), 29.5 (C-6'*), 55.5 (OMe), 63.1 (C-6), 70.1, 71.6, 71.7, 72.0, 72.5, 75.4, 79.7, 80.9, 81.5 (C-1, C-2, C-3, C-4, C-5, C-2', C-3', C-4', C-5'), 101.3 (C-1'). IR (Film): $\tilde{\nu}$ (cm^{-1}) = 3392, 2922, 1645. UV (MeOH): λ_{max} (lg ε) [nm] = no absorbtion maximum from 190 to 350 nm. MS (ESI): *m/z* (%) = 377.2 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 377.1418, found: 377.1417.

pseudo-Disaccharide **29**

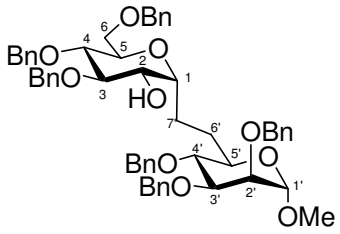


$C_{56}H_{62}O_{10}$ (895.08)

To a solution of enol ether **22** (23.4 mg, 27 µmol, 1.0 eq) in dichloromethane (1 mL) at –78 °C was added DMDO (0.06 M in acetone, 1.11 mL, 2.5 eq). The reaction mixture was warmed to –50 °C over 30 min. The stirring is continued for 15 min at 0 °C. The volatiles were removed in vacuo at 0 °C. The resulting epoxide was used without further purification. To a solution of the resulting epoxide in THF (2 mL) was added $LiBHEt_3$ (1 M in THF, 1.06 mL, 1.06 mmol, 40.0 eq). After being stirred for 3 h, the mixture was diluted with EtOAc. The organic layer was washed with sat. aqueous NH_4Cl (1×) and brine (1×), dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel (Pentane/EtOAc = 2:1) to afford 16 mg (67%) of *C*-glycoside **29**.

Analytical data of **29**: R_f: 0.08 (Hexane/EtOAc = 2:1). $[\alpha]_D^{20}$ = +25.5° (c = 0.88, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.40–1.65 (m, 2 H, 6'-H, 7'-H), 1.70–1.95 (m, 2 H, 6'-H, 7'-H), 2.74 (d, *J* = 7.4 Hz, 1 H, OH), 3.16 (t, *J* = 8.8 Hz, 1 H, 4'-H), 3.31 (s, 3 H, OMe), 3.48 (dd, *J* = 3.8, 10.6 Hz, 1 H, 2'-H), 3.56–3.75 (m, 6 H, 2-H, 4-H, 6-H, 5-H, 5'-H), 3.80–3.97 (m, 3 H, 1-H, 3-H, 3'-H), 4.44–4.98 (m, 13 H, 1'-H, bn-H), 7.18–7.36 (m, 30 H, Bn-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 23.8 (C-6'), 27.5 (C-7'), 55.0 (OMe), 68.3 (C-6), 69.7 (C-5), 69.7 (C-5'), 69.8 (C-1), 71.8 (C-3), 73.0 (CH_2Bn), 73.2 (CH_2Bn), 73.2 (CH_2Bn), 73.2 (CH_2Bn), 73.2 (CH_2Bn), 73.5 (C-2), 75.3 (C-1), 75.6 (CH_2Bn), 78.5 (C-4), 80.1 (C-2'), 82.0 (C-4'), 82.1 (C-3'), 97.6 (C-1'), 127.3, 127.4, 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.2, 128.3, 128.4 (C_{Ar}-Bn), 137.4, 137.9, 138.0, 138.1, 138.2, 138.7 (C_q-Bn). IR (Film): $\tilde{\nu}$ (cm^{-1}) = 3535, 2081, 1952, 1875, 1810, 1737, 1547. UV (MeOH): λ_{max} (lg ε) [nm] = 192.5 (5.18), 252.0 (3.00), 257.5 (3.08), 263.0 (2.98). MS (ESI): *m/z* (%) = 917.42 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 917.42352, found: 917.42344.

pseudo-Disaccharide **31**

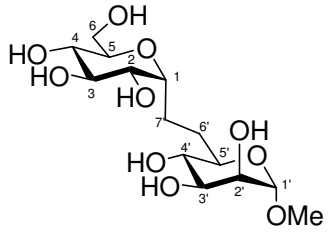


$C_{56}H_{62}O_{10}$ (895.08)

To a solution of enol ether **23** (35 mg, 39.9 µmol, 1.0 eq) in dichloromethane (1 mL) at –78 °C was added DMDO (0.07 M in acetone, 1.14 mL, 2.0 eq). The reaction mixture was warmed to -50 °C over 30 min. The stirring is continued for 15 min at 0 °C. The volatiles were removed in vacuo at 0 °C. The resulting epoxide was used without further purification. To a solution of the resulting epoxide in THF (2 mL) was added $LiBHEt_3$ (1 M in THF, 1.6 mL, 1.60 mmol, 40.0 eq). After being stirred for 3 h, the mixture was diluted with EtOAc. The organic layer was washed with sat. aqueous NH_4Cl (1×) and brine (1×), dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel (Pentane/EtOAc = 2:1) to afford 19 mg (56% over two steps) of *C*-glycoside **31**.

Analytical data of **31**: R_f: 0.23 (2:1 Pentane/EtOAc). $[\alpha]_D^{20}$ = +34.7° (c = 1.5, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.62–1.75 (m, 2 H, 6'-H, 7'-H), 1.87–2.02 (m, 2 H, 6'-H, 7'-H), 3.25 (s, 3 H, OMe), 3.49–3.59 (m, 1 H, 5'-H*), 3.61–3.98 (m, 10 H, 1-H, 2-H, 3-H, 4-H, 5-H*, 6-H, 2'-H, 3'-H, 4'-H), 4.43–4.97 (m, 13 H, CH_2Bn, 1'-H), 7.16–7.38 (m, 30 H, Bn). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 23.8 (C-7'*), 27.6 (C-6'*), 54.6 (OMe), 68.3 (C-6), 69.7 (C-5*), 71.2 (C-5'*), 72.0 (CH_2Bn), 72.6 (C-1*), 72.8 (C-3*), 73.1 (CH_2Bn), 73.3 (CH_2Bn), 73.5 (CH_2Bn), 74.7 (CH_2Bn), 75.1 (C-2*), 75.5 (CH_2Bn), 78.6 (C-4*), 78.9 (C-2'*), 78.9 (C-4'*), 80.2 (C-3'*), 98.7 (C-1'), 127.3, 127.4, 127.5, 127.6, 127.7, 127.8 128.0, 128.1, 128.2, 128.3, 128.4 (C_{Ar}-Bn), 137.5, 138.0, 138.2, 138.4, 138.5 (C_q-Bn). IR (film): $\tilde{\nu}$ (cm^{-1}) = 3030, 2918, 1605, 1454. UV (CH_3CN): λ_{max} (lg ε) [nm] = 257.5 (3.04), 225.0 (2.96), 263.0 (2.96). MS (ESI): *m/z* (%) = 917.43 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 917.42352, found: 917.42340.

pseudo-Disaccharide **32**

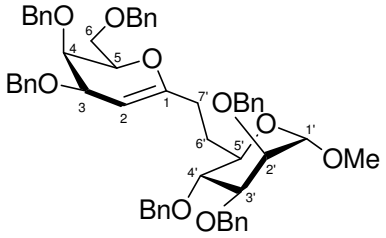


$C_{14}H_{26}O_{10}$ (354.59)

The carbohydrate **31** (12.5 mg, 14.0 µmol, 1.0 eq) was dissolved in MeOH:CH_2Cl_2 (3:1, 4 mL) in a 10 mL three-neck flask connected to an argon bubbler. Pearlman's catalyst ($Pd(OH)_2$ (9 mg)) was added to the solution. The flask was flashed with argon (3×), evacuated (3×) and finally flashed with H_2 (2 bar). The solution was stirred over night. The product was isolated by flashing the solution through a pad of silica gel to give 4.0 mg (81%) of *C*-glycoside **32** as analytically pure sample.

Analytical data of **32**: R_f: 0.14 (CH_2Cl_2MeOH = 2:1). $[\alpha]_D^{20}$ = +100.5° (c = 0.4, MeOH). ^{1}H-NMR (300 MHz, CD_3OD): δ =1.66–2.14 (m, 4 H, 6'-H, 7'-H), 3.22–3.37 (m, 4 H, OMe, 4'-H*), 3.39–3.44–3.80 (m, 9 H, 1-H, 2-H, 3-H, 4-H, 5-H, 6-H, 2'-H, 5'-H), 3.88–3.94 (m, 1 H, 3'-H*), 4.58 (d, *J* = 1.7 Hz, 1 H, 1'-H). ^{13}C-NMR (125 MHz, CD_3OD): δ = 21.6 (C-6'*), 28.4 (C-7'*), 55.2 (OMe), 63.1 (C-6), 72.0, 72.4, 72.6, 72.8, 73.1, 74.1, 75.3, 76.9 (C-1, C-2, C-3, C-4, C-5, C-2', C-3', C-4', C-5'), 102.6 (C-1'). IR (Film): $\tilde{\nu}$ (cm^{-1}) = 3392, 2922, 1645. UV (MeOH): λ_{max} (lg ε) [nm] = no absorbtion maximum from 190 to 350 nm. MS (ESI): *m/z* (%) = 377.1 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 377.1418, found: 377.1416.

Enolether *pseudo*-Disaccharide **33**

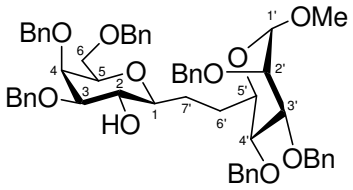


$C_{56}H_{60}O_9$ (877.07)

Raney-Nickel was washed with water until the pH value was nearly 7 (approximately 3×). Afterwards it was washed with MeOH (3×). A solution of carbohydrate **19** (80 mg, 91 µmol, 1.0 eq) in THF:MeOH (1:2, 7.5 mL) was added and a H_2 pressure of 1 bar was applied via a syringe technique until the TLC shows nearly full conversion (approximately 2.5 h). The Raney Nickel is removed via filtration through a pad of silica gel. The solution was evaporated and the residue was purified by silica flash column chromatography on silica gel (Pentane/EtOAc = 4:1) to afford 59 mg (75%) of the desired *C*-glycoside **33**.

Analytical data of **33**: R_f: 0.44 (Pentane/EtOAc = 2:1). $[\alpha]_D^{20}$ = +2.5° (c = 0.32, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.58–2.39 (m, 4 H, 6'-H, 7'-H), 3.24 (s, 3 H, OMe), 3.39–3.94 (m, 7 H, 3-H*, 4-H*, 5-H*, 6-H, 3'-H*, 5'-H*), 4.05–4.21 (m, 2 H, 4-H*, 2'-H*), 4.52–4.94 (m, 14 H, CH_2Bn, 1'-H, 2-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 29.0 (C-6'*), 29.7 (C-7'*), 54.6 (OMe), 68.3 (C-6), 70.7 (CH_2Bn), 70.7 (C-5'*), 71.2 (C-4*), 71.5 (C-3*), 72.1 (CH_2Bn), 72.7 (CH_2Bn), 72.9 (CH_2Bn), 73.3 (CH_2Bn), 74.6 (C-5*), 74.9 (CH_2Bn), 75.6 (C-2'*), 78.8 (C-4'*), 80.2 (C-3'*), 94.8 (C-2), 98.8 (C-1'), 127.3, 127.5, 127.7, 128.0, 128.1, 128.2 (C_{Ar}-Bn), 138.2, 138.5, 138.6 (C_q-Bn), 155.0 (C-1). IR (Film) $\tilde{\nu}$ (cm^{-1}) = 1671, 1604, 1496, 1453, 1363. UV (CH_3CN): λ_{max} (lg ε) [nm] = 204.5 (4.70), 252.5 (3.07), 258.0 (3.15), 263.0 (2.98). MS (ESI): *m/z* (%) = 917.4 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 899.4130, found: 899.4139.

pseudo-Disaccharide **34**

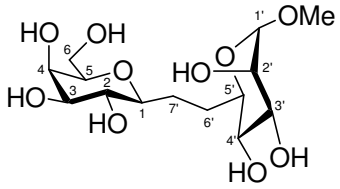


$C_{56}H_{62}O_{10}$ (895.09)

A solution of carbohydrate **33** (19 mg, 21.6 µmol, 1.0 eq) in toluene/THF (1:1, 4 mL) was cooled to 0 °C. BH_3·THF (1 M in THF, 325 µL, 325 µmol) was added to the cooled solution and the resultant mixture was allowed to warm to room temperature with ice-bad in place and stirred over night. The solution was cooled back to 0 °C and NaOH (1 M, 4.8 mL) and H_2O_2 (30%, 4.8 mL) were added in one portion. The resultant mixture was allowed to warm to room temperature over 2 h. The solution then was extracted with EtOAc and the combined organic layers were washed with sat. aq. $Na_2S_2O_3$ (1×), brine (1×), dried over Na_2SO_4, filtered and concentrated. Flash column chromatography on silica gel (Pentane/EtOAc = 2:1) furnished 13 mg (69%) of the desired *C*-glycoside **34**.

Analytical data of **34**: R_f: 0.50 (Pentane/EtOAc = 1:1). $[\alpha]_D^{20}$ = +4.7° (c = 0.17, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 1.50–1.61 (m, 2 H, 7'-H*), 2.16–2.25 (m, 2 H, 6'-H*), 3.16 (dt, *J* = 2.5, 9.1 Hz, 1 H, 1-H*), 3.24 (s, 3 H, OMe), 3.36 (dd, *J* = 2.8, 9.6 Hz, 1 H, 3-H*), 3.49 (dt, *J* = 1.3, 9.7 Hz, 1 H, 5-H*), 3.54–3.65 (m, 4 H, 6-H, 2'-H, 4'-H), 3.73–3.82 (m, 3 H, 2-H, 3'-H, 5'-H), 4.02 (d, *J* = 2.9 Hz, 1 H, 4-H), 4.39–4.95 (m, 13 H, CH_2Bn, 1'-H), 7.19–7.37 (m, 30 H, Bn). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 27.8 (C-7'*), 28.4 (C-6'*), 54.5 (OMe), 68.7 (C-6), 70.8 (C-2), 71.6 (CH_2Bn), 71.7 (CH_2Bn), 72.1 (CH_2Bn), 72.6 (C-5), 72.7 (CH_2Bn), 73.5 (C-4), 74.3 (CH_2Bn), 74.7 (C-5'), 75.1 (CH_2Bn), 76.9 (C-2'), 79.1 (C-4'), 80.2 (C-1), 80.3 (C-3'), 84.3 (C-3), 98.7 (C-1'), 127.3, 127.4, 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4 (C_{Ar}-Bn), 137.8, 138.2, 138.2, 138.5, 138.6 (C_q-Bn). MS (ESI): *m/z* (%) = 917.5 (90) $[M+Na]^+$. IR (Film) $\tilde{\nu}$ (cm^{-1}) = 3033, 2989, 2045, 1951, 1730, 1454, 1375, 1103. UV (CH_3CN): λ_{max} (lg ε) [nm] = 252.0(3.00), 257.5 (3.04), 263.0 (3.02). HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 917.4235, found 917.4205.

pseudo-Disaccharide **35**

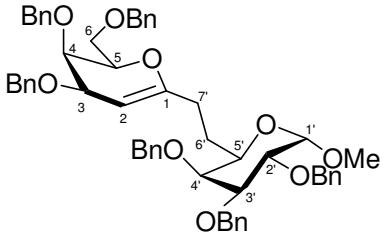


$C_{14}H_{26}O_{10}$ (354.35)

The carbohydrate **34** (7.4 mg, 8.3 µmol, 1.0 eq) was dissolved in MeOH:CH_2Cl_2:EtOAc (3:1:1, 5 mL) in a 10 mL three neck flask connected to an argon bubbler. Pearlman's catalyst ($Pd(OH)_2$ (29 mg)) was added to the solution. The flask was flashed with argon (3×), evacuated (3×) and finally flashed with H_2 (2 bar). The solution was stirred over night. The product was isolated by flashing the solution through a pad of silica gel to give 2.9 mg (99%) of *C*-glycoside **35** as analytically pure sample.

Analytical data of **35**: R_f: 0.16 (CH_2Cl_2/MeOH = 2:1). $[\alpha]_D^{20}$ = +21.3° (c = 0.45, MeOH). ^{1}H-NMR (300 MHz, CD_3OD): δ =1.38–1.50 (m, 2 H, 6'-H, 7'-H), 2.12–2.27 (m, 2 H, 6'-H, 7'-H), 3.06–3.89 (m, 14 H, 1-H, 2-H, 3-H, 4-H, 5-H, 6-H, 2'-H, 3'-H, 4'-H, 5'-H), 4.58 (d, *J* = 1.7 Hz, 1 H, 1'-H). ^{13}C-NMR (125 MHz, CD_3OD): δ =28.9 (C-6'*), 29.3 (C-7'*), 55.1 (OMe), 62.8 (C-6), 70.9, 72.0, 72.4, 72.5, 72.7, 73.7, 76.4, 80.0, 81.8 (C-1, C-2, C-3, C-4, C-5, C-2', C-3', C-4', C-5'), 102.5 (C-1'). IR (Film): $\tilde{\nu}$ (cm^{-1}) = 3392, 2922, 1646. UV (MeOH): λ_{max} (lg ε) [nm] = no absorption maximum from 190 to 350 nm. MS (ESI): *m/z* (%) = 377.1 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 377.1418, 377.1422.

Enolether *pseudo*-Disaccharide **36**

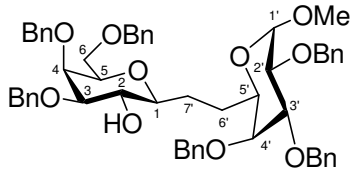


$C_{56}H_{60}O_9$ (877.07)

Raney-Nickel was washed with water until the pH value was nearly 7 (approximately 7×). Afterwards it was washed with MeOH (5×). A solution of carbohydrate **18** (126 mg, 0.144 mmol, 1.0 eq) in THF:MeOH (1:2, 11.25 mL) was added and a H_2 pressure of 1 bar was applied via a syringe technique until the TLC shows nearly full conversion (approximately 3.5 h). The Raney-Nickel was removed via filtration through a pad of silica gel. The solution was evaporated and the residue was purified by silica flash column chromatography on silica gel (Pentane/EtOAc = 6:1 to 4:1) to afford 48 mg (38%, 76% b.o.r. SM) of the desired *C*-glycoside **36**.

Analytical data of **36**: R_f: 0.44 (Pentane/EtOAc = 2:1). $[\alpha]_D^{20}$ = –4.1° (c = 0.27, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.48–2.15 (m, 4 H, 6'-H, 7'-H), 3.30 (s, 3 H, OMe), 3.57–3.77 (m, 4 H, 6-H, 4'-H, 5'-H), 3.82–3.90 (m, 2 H, 3'-H, 3-H), 4.00 (dd, *J* = 4.1, 10.4 Hz, 1 H, 2'-H), 4.05–4.18 (m, 2 H, 4-H, 5-H), 4.54–4.70 (m, 11 H, CH_2Bn, 1'-H, 2-H), 4.76–4.95 (m, 3 H, CH_2Bn), 7.18–7.37 (m, 30 H, Bn). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 28.0 (C-6'*), 29.9 (C-7'*), 55.3 (OMe), 68.2 (C-6), 69.4 (C-5'*), 70.8 (CH_2Bn), 71.5 (C-4*), 71.6 (C-3*), 72.9 (CH_2Bn), 73.2 (CH_2Bn) 73.3 (CH_2Bn), 73.4 (CH_2Bn), 74.7 (CH_2Bn), 75.5 (C-5*), 76.4 (C-2'*), 77.0 (C-4'*), 79.5 (C-3'*), 95.3 (C-2), 98.6 (C-1'), 127.3, 127.4, 127.5, 127.6, 127.7, 128.0, 128.2 (C_{Ar}-Bn), 138.0, 138.4, 138.5 138.8 (C_q-Bn), 154.4 (C-1). IR (Film): $\tilde{\nu}$ (cm^{-1}) = 2922, 1669, 1604, 1453, 1351. UV (CH_3CN): λ_{max} (lg ε) [nm] = 205.5 (4.79), 252.0 (3.12), 257.5 (3.15), 264.0 (3.00). MS (ESI): *m/z* (%) = 899.5 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 899.4130, found 899.4146.

pseudo-Disaccharide **37**



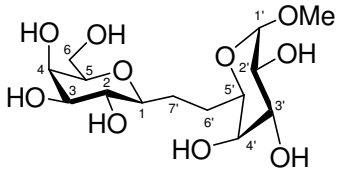
$C_{56}H_{62}O_{10}$ (895.09)

A solution of carbohydrate **36** (47 mg, 53.6 µmol, 1.0 eq) in THF (5 mL) was cooled to 0 °C. BH_3·THF (1 M in THF, 805 µL, 805 µmol) was added to the cooled solution and the resultant mixture was allowed to warm to room temperature with ice-bad in place and stirred over night. The solution was cooled back to 0 °C and NaOH (1 M, 12 mL) and H_2O_2 (30%, 12 mL) were added in one portion. The resultant mixture was allowed to warm to room temperature over 2 h. The solution then was extracted with EtOAc and the combined organic layers were washed with sat. aq. $Na_2S_2O_3$ (1×), brine (1×), dried over Na_2SO_4, filtered and concentrated. Flash column chromatography on silica gel (Pentane/EtOAc = 2:1) furnished 30 mg (63%) of the desired *C*-glycoside **37**.

Analytical data of **37**: R_f: 0.44 (Pentane/EtOAc = 1:1). $[\alpha]_D^{20}$ = +23.8° (c = 1.43, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 1.22–1.36 (m, 1 H, 6'*-H), 1.51–1.58 (m, 1 H, 7'*-H), 1.63–1.71 (m, 7'* H), 1.89–1.95 (m, 6'* H), 3.07 (dt, *J* = 2.7, 8.9 Hz, 1 H, 5'*-H), 3.28 (s, 3 H, OMe), 3.33 (dd, *J* = 2.9, 8.8 Hz, 1 H, 3'*-H), 3.50–3.54 (m, 2 H, 6-H, 1*-H), 3.56–3.61 (m, 2 H, 6-H, 5*-H), 3.64–3.69 (m, 2 H, 4'*-H, 4*-H), 3.86 (dd, *J* = 2.5, 10.7 Hz, 1 H, 3*-H), 3.98–4.02 (m, 2 H, 2'*-H, 2*-H), 4.41–4.94 (m, 13 H, CH_2Bn, 1'-H), 7.11–7.38 (m, 30 H, Bn). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 26.9 (C-7'*), 28.4 (C-6'*), 55.1 (OMe), 68.6 (C-6), 70.4 (C-5*), 70.6 (C-4'*), 71.5 (CH_2Bn), 72.6 (C-2'*), 73.3 (CH_2Bn), 73.4 (CH_2Bn), 73.5 (CH_2Bn), 74.4 (CH_2Bn), 74.5 (CH_2Bn), 76.5 (C-2*), 76.8 (C-4*), 79.6 (C-3*), 79.9 (C-5'*), 84.2 (C-3'*), 98.5 (C-1'), 127.3, 127.4, 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.5 (C_{Ar}-Bn), 136.8, 137.7, 137.8, 138.5, 138.8 (C_q-Bn). IR (Film): $\tilde{\nu}$ (cm^{-1}) = 3460, 3062, 3030, 2908, 1722, 1604, 1496, 1453, 1351. UV (CH_3CN): λ_{max} (lg ε) [nm] = 252.5 (2.99), 257.5 (3.05), 263.0 (3.11).

MS (ESI): *m/z* (%) = 917.5 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 917.4235, found: 917.4239.

pseudo-Disaccharide **38**

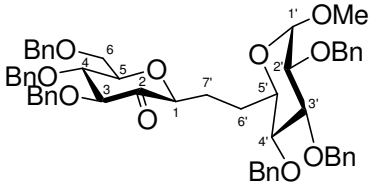


$C_{14}H_{26}O_{10}$ (354.35)

The carbohydrate **37** (12.9 mg, 14.4 µmol, 1.0 eq) was dissolved in MeOH:CH_2Cl_2:EtOAc (3:1:1, 5 mL) in a 10 mL three neck flask connected to an argon bubbler. Pearlman's catalyst ($Pd(OH)_2$ (42 mg)) was added to the solution. The flask was flashed with argon (3×), evacuated (3×) and finally flashed with H_2 (2 bar). The solution was stirred over night. The product was isolated by flashing the solution through a pad of silica gel to give 5.1 mg (99%) of *C*-glycoside **38** as analytically pure sample.

Analytical data of **38**: R_f: 0.23 (CH_2Cl_2/MeOH = 2:1). $[\alpha]_D^{20}$ = +113.3° (c = 0.4, MeOH). ^{1}H-NMR (300 MHz, CD_3OD): δ =1.36–1.53 (m, 1 H, 6'*-H), 1.67–1.85 (m, 2 H, 7'*-H), 2.01–2.16 (m, 1 H, 6'*-H), 3.06–3.15 (m, 1 H, 5'*-H), 3.28–3.46 (m, 4 H, 4'*-H, 3*-H, 4*-H, 5*-H), 3.63–3.78 (m, 5 H, 6-H, 2'-H, 1*-H, 2*-H), 3.88 (d, *J* = 2.4 Hz, 1 H, 3'*-H), 4.66 (d, *J* = 3.7 Hz, 1 H, 1'-H). ^{13}C-NMR (125 MHz, CD_3OD): δ =27.9 (C-7'*), 29.5 (C-6'*), 55.5 (OMe), 62.8 (C-6), 70.1 (C-3*), 70.8 (C-3'*), 71.6 (C-1*), 72.5 (C-2*), 76.3 (C-4*), 79.9 (C-5*), 81.5 (C-5'*), 101.2 (C-1'). IR (Film): $\tilde{\nu}$ (cm^{-1}) = 3391, 2922, 1417. UV (MeOH): λ_{max} (lg ε) [nm] = no absorbtion maximum from 190 to 350 nm. MS (ESI): *m/z* (%) = 377.1 (45) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 377.1418, found: 377.1419.

pseudo-Disaccharide **39**

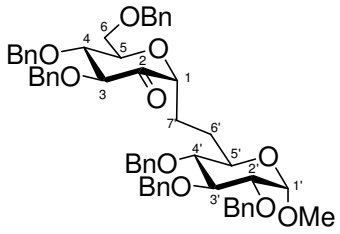


$C_{56}H_{60}O_{10}$ (892.42)

To a solution of carbohydrate **21** (32.0 mg, 35.8 µmol, 1.0 eq) in dichloromethane (1 mL) was added DMP (75.4 mg, 178 µmol, 5.0 eq). The reaction mixture was allowed to stir at room temperature over night and diluted with EtOAc. The mixture was stirred for 15 min. after the addition of sat. aq. $NaHCO_3$ and sat. aq. $Na_2S_2O_3$. The aq. layer was extracted with EtOAc (3×). The combined organic layers were washed with sat. aq. $NaHCO_3$ (2×), brine (2×), dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel (Pentane/EtOAc = 2:1) to afford 23 mg (72%) *C*-glycoside **39**.

Analytical data of **39:** R_f: 0.50 (Pentane/EtOAc = 3:1). $[\alpha]_D^{20} = -3.6°$ (c = 0.9, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.34–1.51 (m, 1 H, 6'-H), 1.53–1.67 (m, 2 H, 7'-H), 1.93–2.11 (m, 1 H, 6'-H), 3.19 (t, *J* = 9.2 Hz, 1 H, 4'-H), 3.34 (s, 3 H, OMe), 3.52 (dd, *J* = 3.7, 9.7 Hz, 1 H, 2'-H*), 3.56–3.78 (m, 6 H, 5'-H, 1-H, 4-H, 5-H, 6-H), 3.81–3.90 (m, 1 H, 5'-H*), 3.95 (t, *J* = 8.9 Hz, 1 H, 3'-H*), 4.14 (d, *J* = 8.8 Hz, 1 H, 3-H*), 4.45–5.05 (m, 13 H, 1'-H, CH_2Bn), 7.12–7.55 (m, 30 H, Bn). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 24.7 (C-7'*), 27.4 (C-6'*), 55.1 (OMe), 69.0 (C-4*), 70.0 (C-5'*), 73.3 (CH_2Bn), 73.5 (CH_2Bn), 73.7 (CH_2Bn), 74.9 (CH_2Bn), 75.1 (CH_2Bn), 75.7 (CH_2Bn), 79.2 (C-6*), 80.1 (C-2'*), 80.2 (C-5*), 80.9 (C-1*), 81.8 (C-4'*), 82.0 (C-3'*), 86.6 (C-3*), 97.7 (C-1'), 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3 (C_{Ar}-Bn), 137.5, 137.7, 137.9, 138.1, 138.3, 138.7 (C_q-Bn), 201.9 (C-2). IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3028, 2923, 1730, 1452, 1359, 1050. UV (CH_3CN): λ_{max} (lg ε) [nm] = 251.5 (4.19), 257.0 (3.29), 263.0 (2.25). MS (ESI): *m/z* (%) = 915.41 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 915.4078, found: 915.4079.

pseudo-Disaccharide **39α**

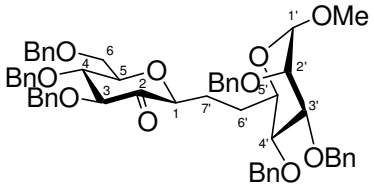


$C_{56}H_{60}O_{10}$ (892.41)

To a solution of carbohydrate **29** (32.0 mg, 35.8 µmol, 1.0 eq) in dichloromethane (1 mL) was added DMP (75.4 mg, 178 µmol, 5.0 eq). The reaction mixture was allowed to stir at room temperature over night and diluted with EtOAc. The mixture was stirred for 15 min. after the addition of sat. aq. $NaHCO_3$ and sat. aq. $Na_2S_2O_3$. The aq. layer was extracted with EtOAc (3×). The combined organic layers were washed with sat. aq. $NaHCO_3$ (2×), brine (2×), dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel (Pentane/EtOAc = 2:1) to afford 23 mg (72%) of *C*-glycoside **39α**.

Analytical data of **39α**: R_f: 0.34 (Hexane:EtOAc = 2:1).$[\alpha]_D^{20}$ = +27.5° (c = 0.2, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 1.45–1.50 (m, 1 H, 6'-H*), 1.60–1.66 (m, 2 H, 7'-H*), 1.82–1.92 (m, 1 H, 6'-H*), 3.12 (t, *J* = 9.2 Hz, 1 H, 4'-H*), 3.29 (s, 3 H, OMe), 3.45 (dd, *J* = 3.7, 9.7 Hz, 1 H, 2'-H*), 3.55 (dt, *J* = 2.0, 9.7 Hz, 1 H, 5'-H*), 3.57–3.59 (m, 2 H, 6-H), 3.89–3.96 (m, 4 H, 2-H, 4-H 3'-H, 5'-H), 4.12–4.15 (m, 1 H, 1-H*), 4.31–4.96 (m, 14 H, 3-H, 1'-H, CH_2Bn), 7.12–7.55 (m, 30 H, Bn). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 25.9 (C-6'*), 26.9 (C-7'*), 55.1 (OMe), 69.2 (C-5'*), 69.4 (C-6), 73.2 (CH_2Bn), 73.3 (CH_2Bn), 73.9 (CH_2Bn), 74.4 (C-2'*), 74.4 (CH_2Bn), 75.2 (CH_2Bn), 75.6 (CH_2Bn), 78.3 (C-4), 80.0 (C-5*), 80.2 (C-1*), 81.8 (C-3'*), 81.9 (C-4'*), 84.2 (C-3*), 97.7 (C-1'), 127.4, 127.5, 127.6, 127.7, 127.8, 127.9, 128.2, 128.3 (C_{Ar}-Bn), 137.4, 137.6, 137.7, 138.0, 138.6 (C_q-Bn), 207.8 (C-2). IR (Film): $\tilde{\nu}$ (cm^{-1}) = 2925, 1724, 1453, 1272, 1097. UV (CH_3CN): λ_{max} (lg ε) = 227.5 nm (4.15), 257.0 (3.34). MS (ESI): *m/z* (%) = 915.41 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 915.4078, found: 915.4079.

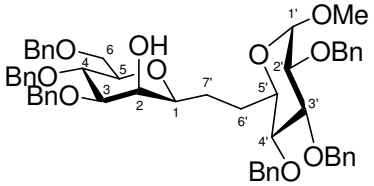
pseudo-Disaccharide **40**



$C_{56}H_{60}O_{10}$ (892.41)

To a solution of carbohydrate **24** (10.3 mg, 11.5 µmol, 1.0 eq) in dichloromethane (1 mL) was added DMP (24.4 mg, 57.6 µmol, 5.0 eq). The reaction mixture was allowed to stir at room temperature over night and diluted with EtOAc. The mixture was stirred for 15 min. after the addition of sat. aq. $NaHCO_3$ and sat. aq. $Na_2S_2O_3$. The aq. layer was extracted with EtOAc (3×). The combined organic layers were washed with sat. aq. $NaHCO_3$ (2×), brine (2×), dried over Na_2SO_4, filtered and concentrated. The residue was purified by silica flash column chromatography on silica gel (Pentane/EtOAc = 2:1) to afford 6.9 mg (68%) of *C*-glycoside **40**.
Analytical data of **40**: R_f: 0.43 (Pentane/EtOAc = 2:1). $[\alpha]_D^{20}$ = –7.7° (c = 0.13, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.55–1.70 (m, 2 H, 6'-H, 7'-H), 2.05–2.15 (m, 2 H, 6'-H, 7'-H), 3.26 (s, 3 H, OMe), 3.53–3.87 (m, 8 H, 2-H, 4-H, 5-H, 6-H, 2'-H, 4'-H, 5'-H), 4.13–4.16 (m, 1 H, 3-H), 4.46–4.72 (m, 12 H, CH_2Bn), 4.82–4.99 (m, 1 H, 1'-H), 7.15–7.40 (m, 30 H, Bn). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 24.8 (C-7'*), 27.5 (C-6'*), 54.6 (OMe), 69.0 (C-6), 71.4 (C-5'*), 72.1 (CH_2Bn), 72.7 (CH_2Bn), 73.5 (CH_2Bn), 73.5 (C-2'*), 73.6 (CH_2Bn), 74.6 (CH_2Bn), 74.9 (CH_2Bn), 75.1 (C-4*), 78.6 (C-5*), 79.2 (C-1*), 80.2 (C-3'*), 81.0 (C-4'*), 86.6 (C-3*), 98.9 (C-1'), 127.4, 127.5, 127.6, 127.8, 127.9, 128.0, 128.2, 128.3 (C_{Ar}-Bn), 137.5, 137.8, 137.9, 138.2, 138.4, 138.5 (C_q-Bn), 201.9 (C-2). IR (Film): $\tilde{\nu}$ (cm^{-1}) = 1724, 1602, 1453, 1271, 1114. UV (CH_3CN): λ_{max} (lg ε) [nm] = 228.5 (4.3073), 272.0 (3.3283), 279.5 (3.2516). MS (ESI): *m/z* (%) = 915.4 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 915.4079, found: 915.4086.

pseudo-Disaccharide **41**

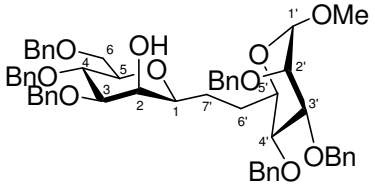


$C_{56}H_{62}O_{10}$ (894.43)

Carbohydrate **39** (6.0 mg, 6.7 µmol, 1.0 eq) was dissolved in CH_2Cl_2/MeOH (1:1, 3 mL). The solution was cooled to 0 °C and $NaBH_4$ (3.3 mg, 87 µmol, 13.0 eq) was added. After stirring for 3 h at 0 °C the mixture was allowed to warm to room temperature. Water was added to stop the reaction. The aq layer was extracted with dichloromethane. The combined organic layers were washed with water (2×), 1% citric acid (2×), again water (2×), dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel (Pentane/EtOAc = 3:1) to give 4.9 mg (83%) of the desired *C*-glycoside **41**.

Analytical data of **41**: R_f: 0.12 (Pentane/EtOAc = 3:1). $[\alpha]_D^{20}$ = +12.7° (c = 0.45, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.23–1.30 (m, 1 H, 6'-H), 1.67–1.75 (m, 2 H, 7'-H), 1.89–1.99 (m, 1 H, 6'-H), 3.16 (t, *J* = 8.9 Hz, 1 H, 4'-H*), 3.20 (t, *J* = 8.5 Hz, 1 H, 1-H*), 3.33 (s, 3 H, OMe), 3.34–3.36 (m, 1 H, 5-H*), 3.48 (dd, *J* = 3.6, 9.7 Hz, 1 H, 2'-H*), 3.54 (dd, *J* = 3.3, 9.1 Hz, 1 H, 4-H*), 3.55–3.60 (m, 1 H, 5'-H*), 3.64–3.71 (m, 2 H, 6-H), 3.74 (t, *J* = 9.1 Hz, 1 H, 3-H*), 3.81–3.83 (m, 1 H, 2-H*), 3.94 (t, *J* = 8.9 Hz, 1 H, 3'-H*), 4.46–4.99 (m, 13 H, 1'-H, CH_2Bn), 7.17–7.48 (m, 30 H, Bn). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 29.6 (C-7'), 28.0 (C-6'), 55.1 (OMe), 67.8 (C-2), 69.4 (C-6), 70.0 (C-5'), 71.6, 73.3, 73.5 (CH_2Bn), 74.7 (C-3), 75.1, 75.2, 75.8 (CH_2Bn), 78.0 (C-1), 79.2 (C-5), 80.1 (C-2'), 81.9 (C-4'), 82.1 (C-3'), 83.5 (C-4), 97.8 (C-1'), 127.4, 127.5, 127.6, 127.8, 127.9, 128.0, 128.2, 128.3, 128.4, 128.5 (C_{Ar}-Bn), 138.1, 138.2, 138.3, 138.7 (C_q-Bn). IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3449, 3030, 2924, 1454, 1371, 1106. UV (CH_3CN): λ_{max} (lg ε) [nm] = 191.0 (4.15), 205.0 (3.52), 251.5 (2.99), 257.1 (3.15), 263.0 (3.12). MS (ESI): *m/z* (%) = 917.42 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 917.4235, found: 917.4230.

pseudo-Disaccharide **42**



$C_{56}H_{62}O_{10}$ (895.08)

Carbohydrate **40** (4.3 mg, 4.8 µmol, 1.0 eq) was dissolved in CH_2Cl_2/MeOH (1:1, 2 mL). The solution was cooled to 0 °C and $NaBH_4$ (2.4 mg, 63 µmol, 13.0 eq) was added. After stirring for 3 h at 0 °C the mixture was allowed to warm to room temperature. Water was added to stop the reaction. The aq layer was extracted with dichloromethane (3×). The combined organic layers were washed with water (2×), 1% citric acid (2×), again water (2×), dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel (Pentane/EtOAc = 2:1) to give 3.9 mg (91%) of the desired *C*-glycoside **42**.

Analytical data of **42**: R_f: 0.22 (Pentane/EtOAc = 2:1). $[\alpha]_D^{20}$ = +5.5° (c = 0.11, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 1.48–1.50 (m, 1 H, 6'-H), 1.82–1.90 (m, 2 H, 7'-H), 2.03–2.06 (m, 1 H, 6'-H), 2.30–2.31 (m, 1 H, OH), 3.21–3.25 (m, 4 H, OMe, 1-H*), 3.34–3.36 (m, 1 H, 4-H*) 3.49–3.56 (m, 2 H, 2-H, 4'-H*), 3.62–3.70 (m, 3 H, 6-H*, 2'-H*), 3.75–3.87 (m, 4 H, 3-H*, 5-H*, 3'-H*, 5'-H*), 4.49–4.92 (m, 13 H, CH_2Bn, 1'-H), 7.16–7.35 (m, 30 H, Bn). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 27.1 (C-6'), 28.3 (C-7'), 54.6 (OMe), 68.1 (C-5'), 69.5 (C-6), 71.4 (C-2), 71.5 (CH_2Bn), 72.1 (CH_2Bn), 72.8 (CH_2Bn), 73.5 (CH_2Bn), 74.6 (CH_2Bn), 74.7 (C-3), 75.1 (CH_2Bn), 75.1 (C-5), 78.3 (C-1), 78.8 (C-2'), 79.3 (C-4), 80.3 (C-3'), 83.5 (C-4'), 98.9 (C-1'), 127.4, 127.5, 127.8, 128.2, 128.4 (C_{Ar}-Bn), 137.7, 138.2, 138.4, 138.6 (C_q-Bn). IR (film): $\tilde{\nu}$ (cm^{-1}) = 3467, 3085, 2902, 1739, 1612, 1104. UV (CH_3CN): λ_{max} (lg ε) [nm] = 252.0 (2.96), 257.0 (3.07), 263.0 (3.01). MS (ESI): *m/z* (%) = 917.4 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calcd for $[M+Na]^+$: 917.4235, found: 917.4222.

Additional References:

Compound **20** has been prepared by metathesis and is analytically characterized in the literature:

[1] Postema, M. H. D.; Calimente, D.; Liu, L.; Behrmann, T. L. *J. Org. Chem.* **2000**, *65*, 6061-6068.

[2] Postema, M. H. D.; Calimente, D. *Tetrahedron Lett.* **1999**, *40*, 4755-4759.

Compound **21** has been prepared before and is analytically characterized in the literature:

[3] Postema, H. M. D.; Piper, J. L.; Liu, L.; Shen, J.; Faust, M.; Andreana, P. *J. Org. Chem.* **2003**, *68*, 4748-4754.

Compound **22** has been prepared before and is analytically characterized in the literature:

[4] Rouzaud, D.; Sinaÿ, P. G. *J. Chem. Soc., Chem. Commun.* **1983**, *22*, 1353-1354.

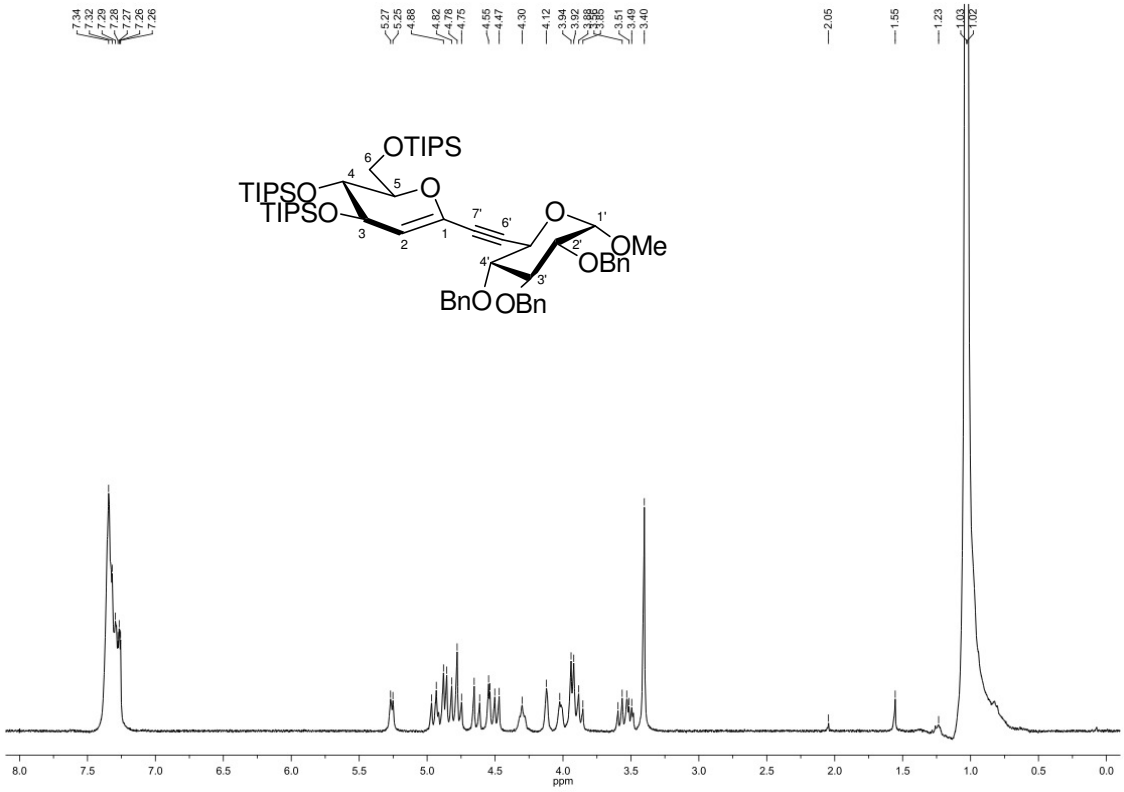
[5] Dondoni, A.; Zuurmond, H. M.; Boscarato, A. *J. Org. Chem.* **1997**, *62*, 8114-8124.

[6] Dondoni, A.; Marra, A.; Mizuno, M.; Giovanni; P. P. *J. Org. Chem.* **2002**, *67*, 4186-4199.

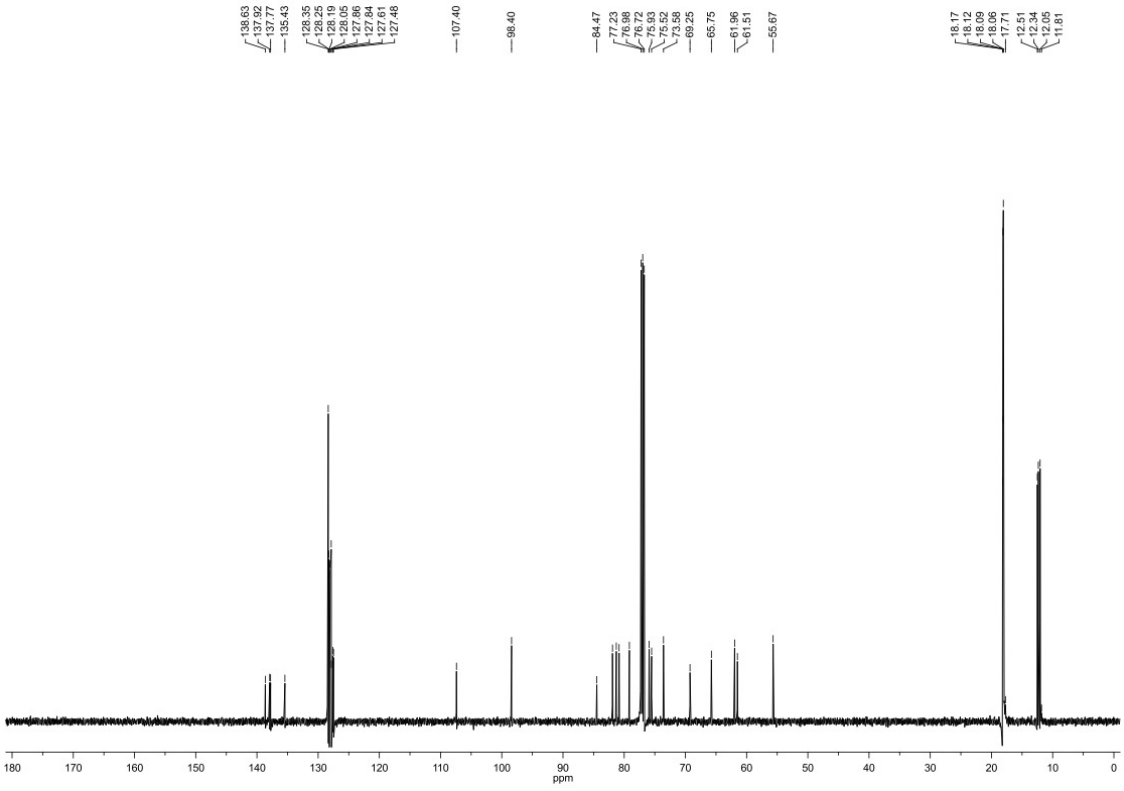
Compound **30** has been prepared before and is analytically characterized in the literature:

[7] Leeuwenburgh, M. A.; Timmers, C. M.; van der Marel, G. A.; Boom, J. H.; Mallet; J.-M.; Sinaÿ, P. G. *Tetrahedron Lett.* **1997**, *38*, 6251-6254.

Enyne *pseudo*-Disaccharide **5**

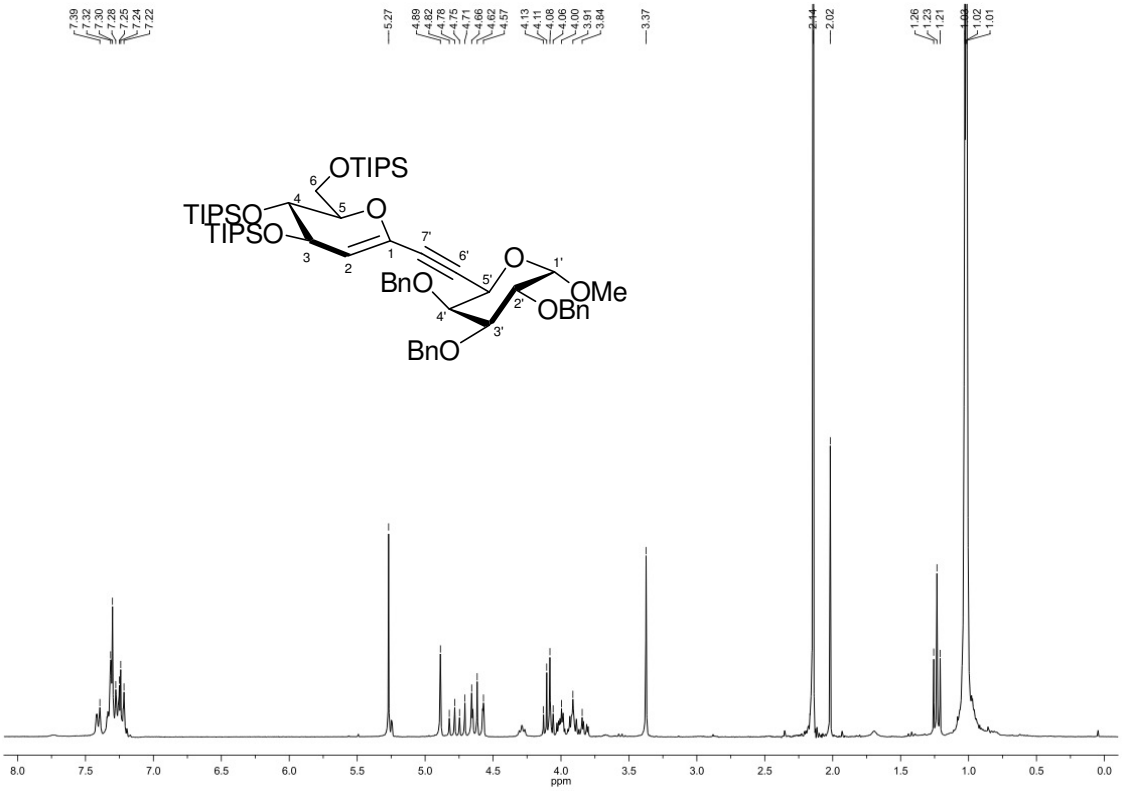


^{1}H NMR (300 MHz, $CDCl_3$)

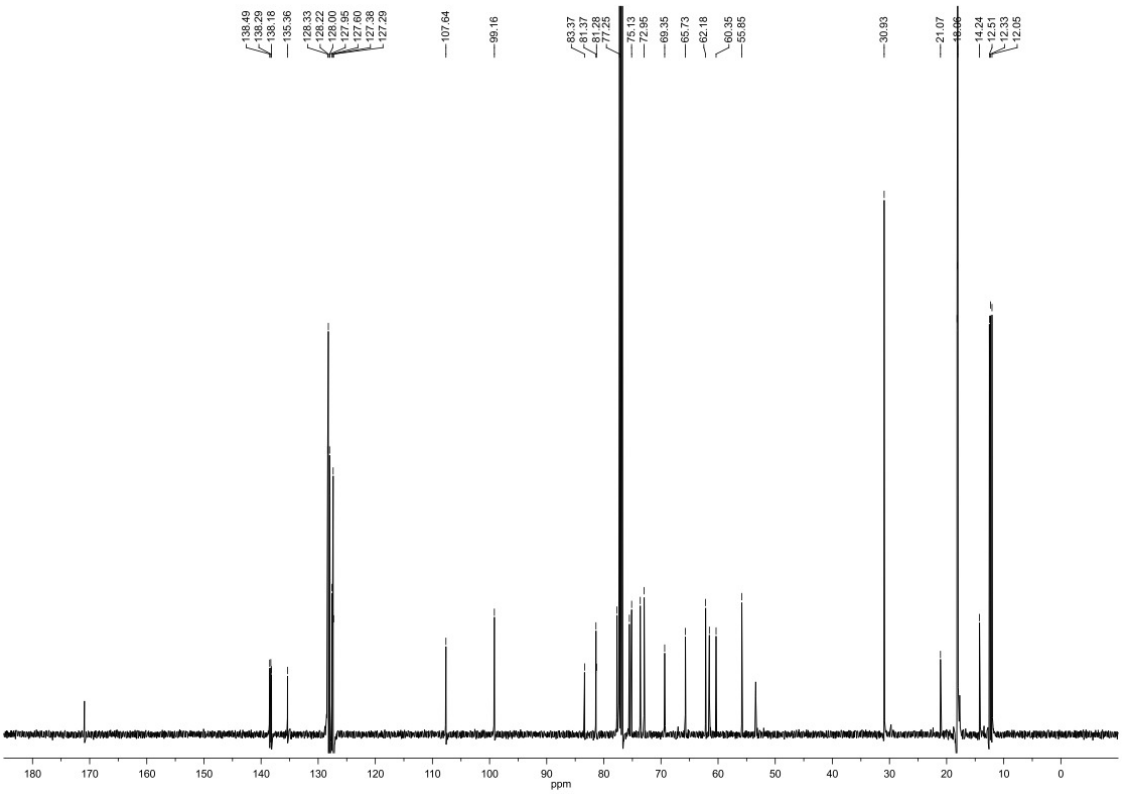


^{13}C NMR (125 MHz, $CDCl_3$)

Enyne *pseudo*-Disaccharide **6**

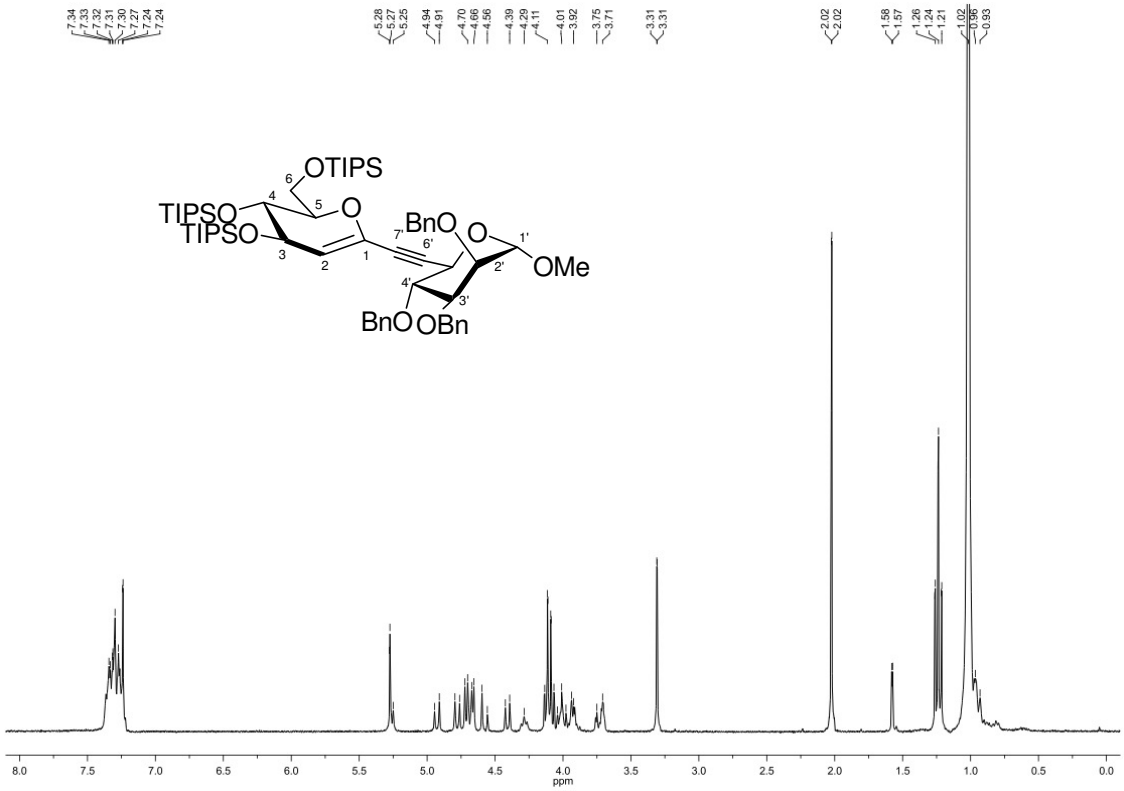


^{1}H NMR (300 MHz, $CDCl_3$)

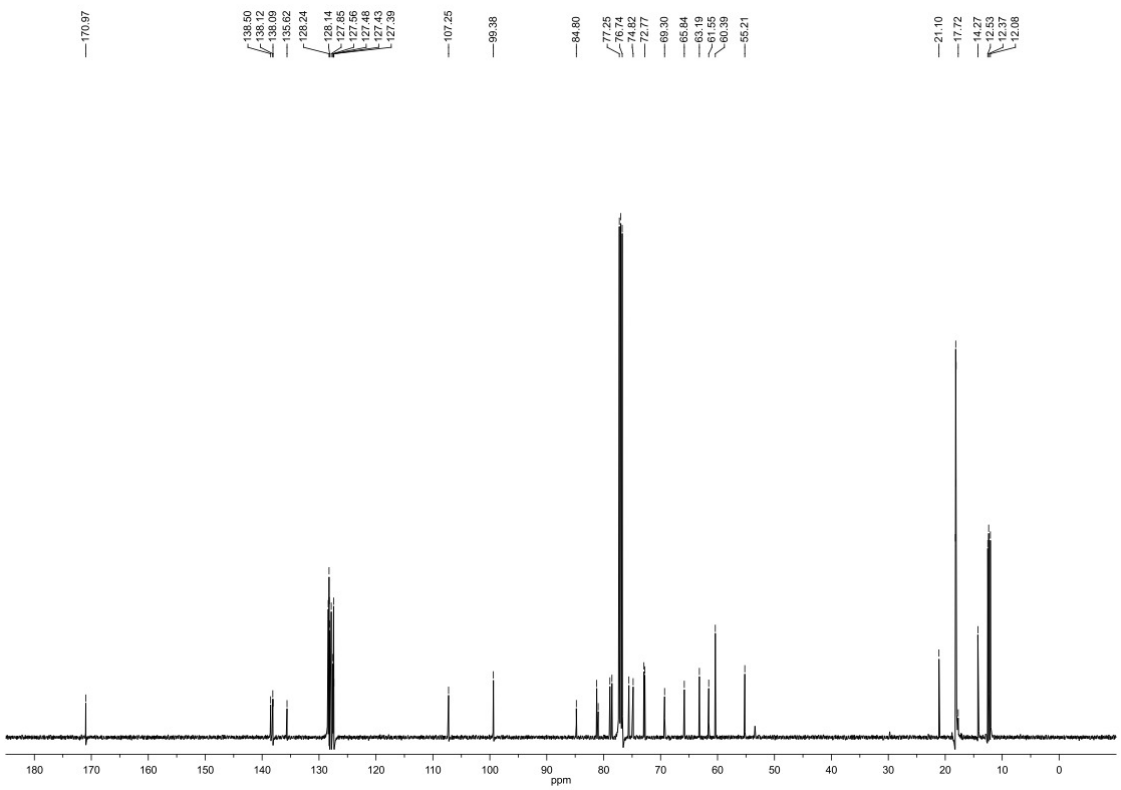


^{13}C NMR (125 MHz, $CDCl_3$)

Enyne *pseudo*-Disaccharide **7**

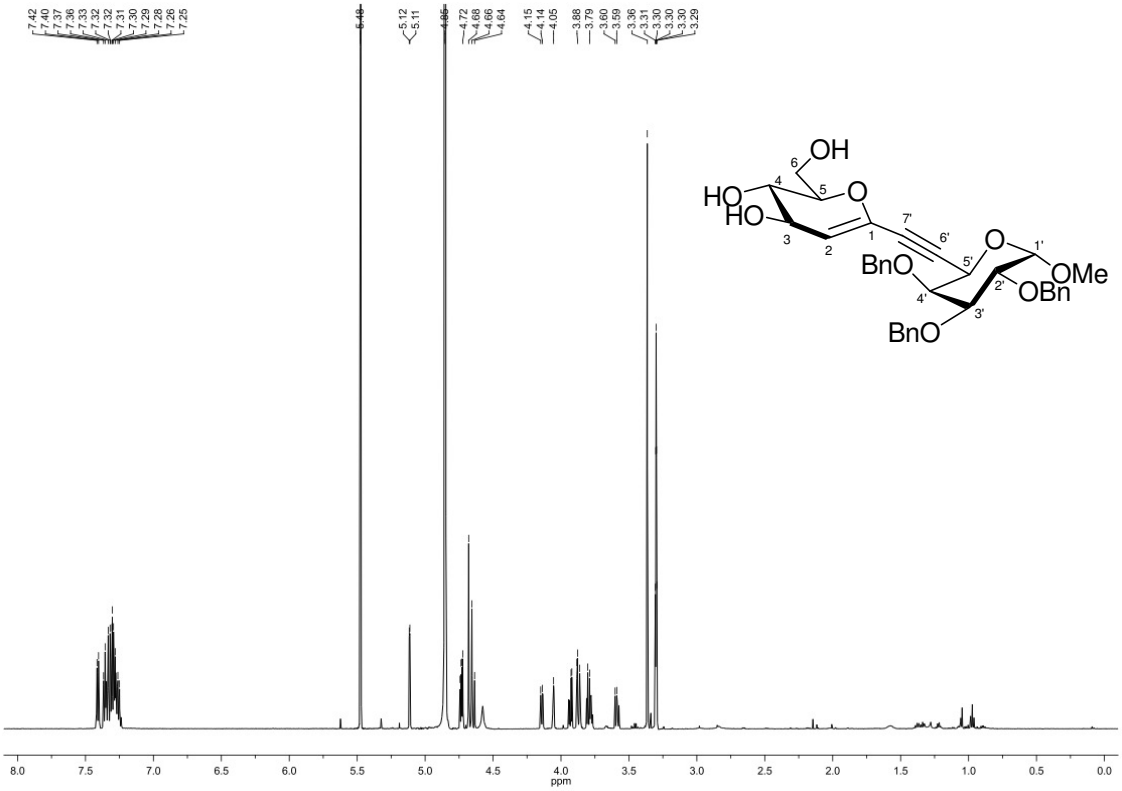


^{1}H NMR (600 MHz, $CDCl_3$)

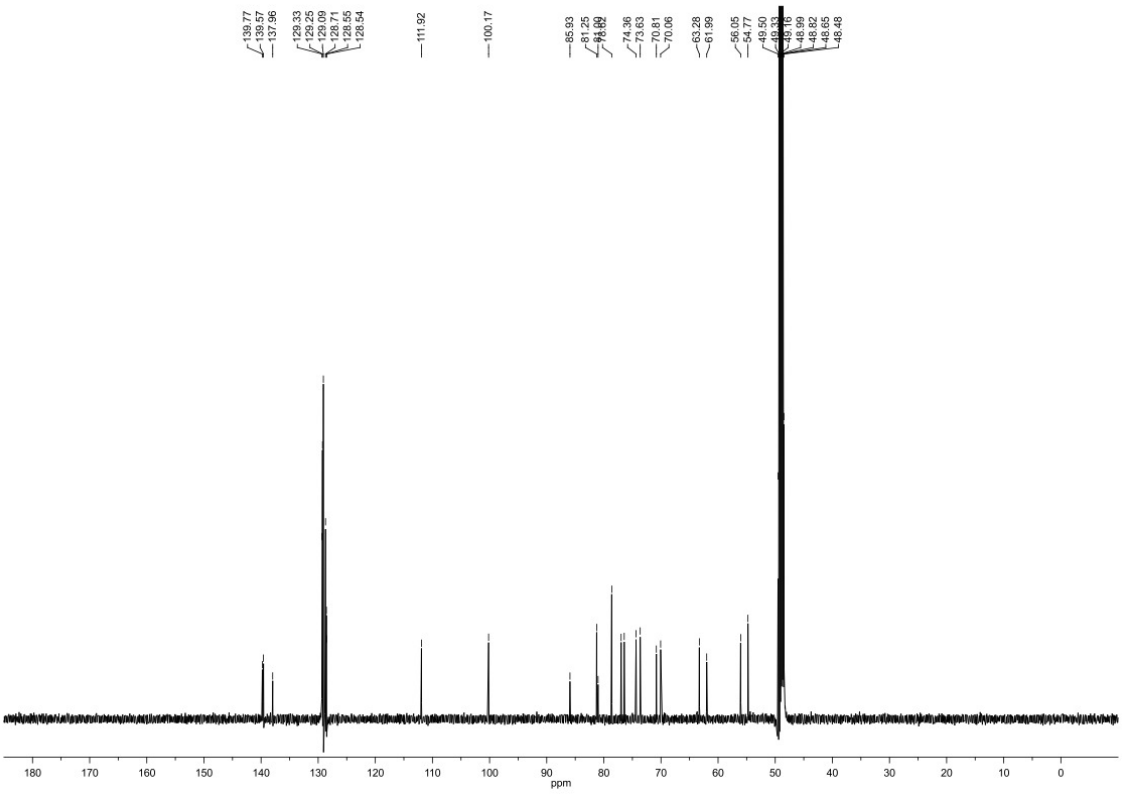


^{13}C NMR (125 MHz, $CDCl_3$)

Enyne *pseudo*-Disaccharide **6a**

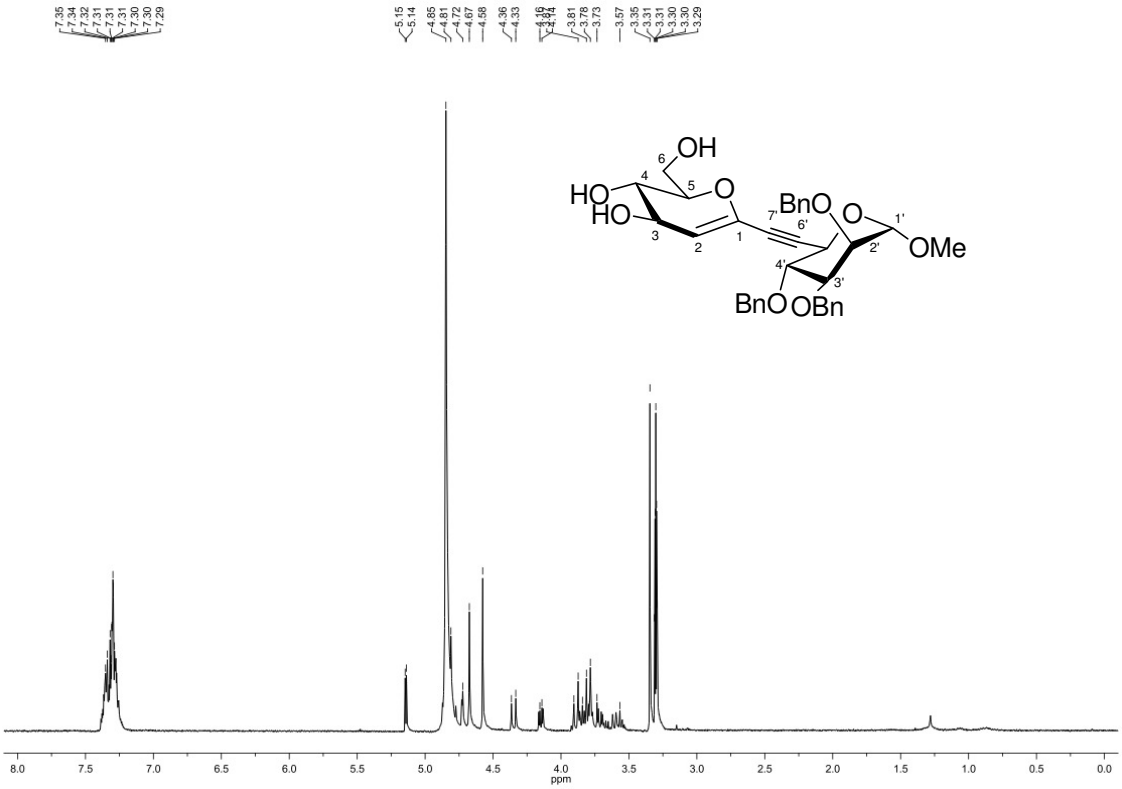


^{1}H NMR (600 MHz, $CDCl_3$)

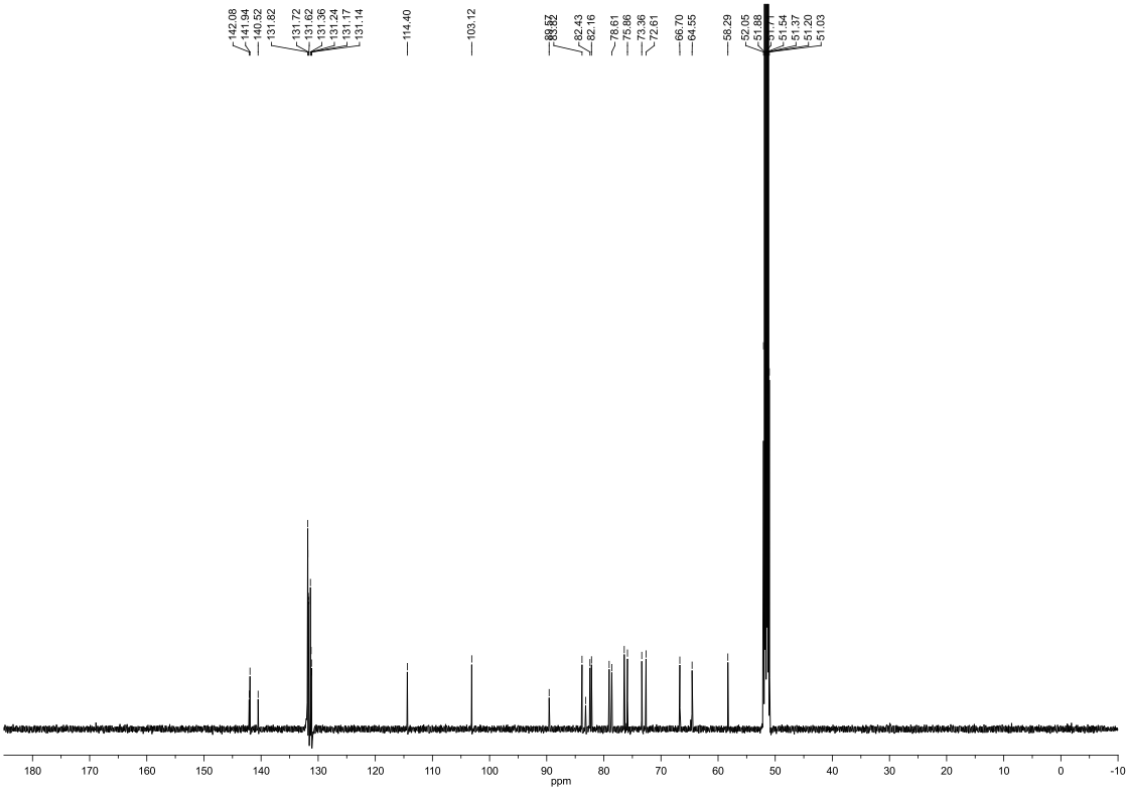


^{13}C NMR (125 MHz, $CDCl_3$)

Enyne *pseudo*-Disaccharide **7a**

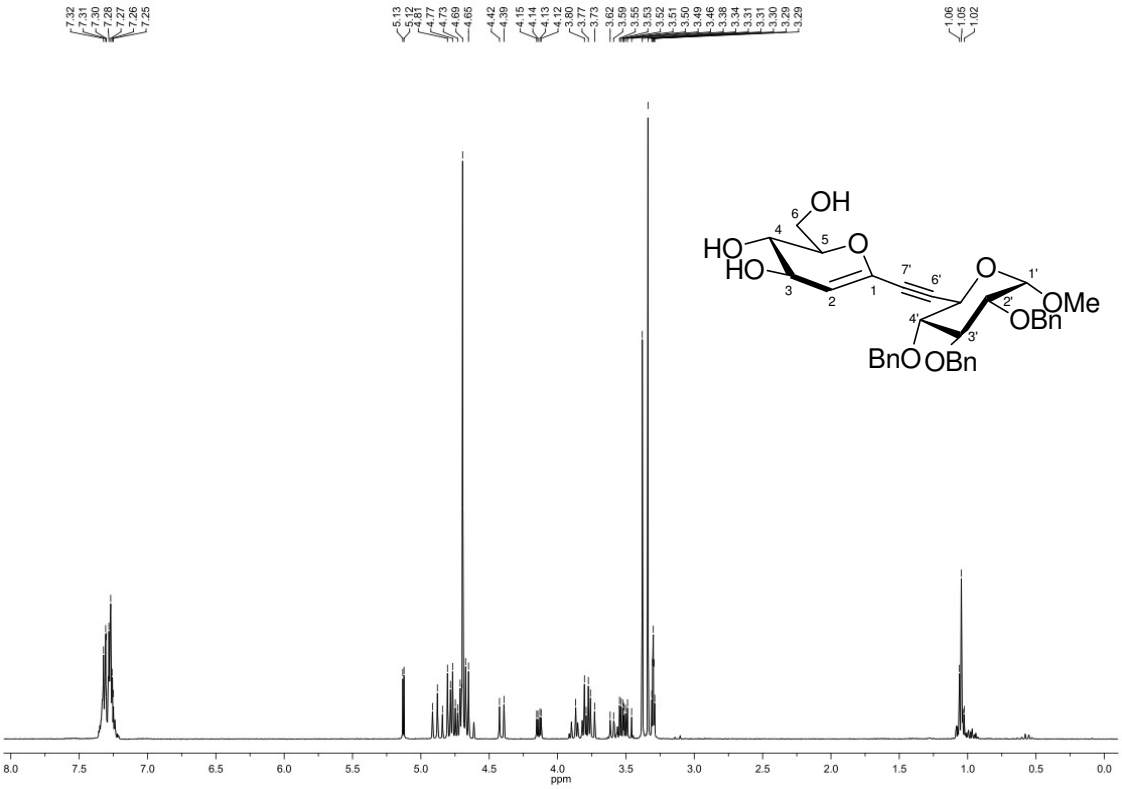


^{1}H NMR (300 MHz, CD_3OD)

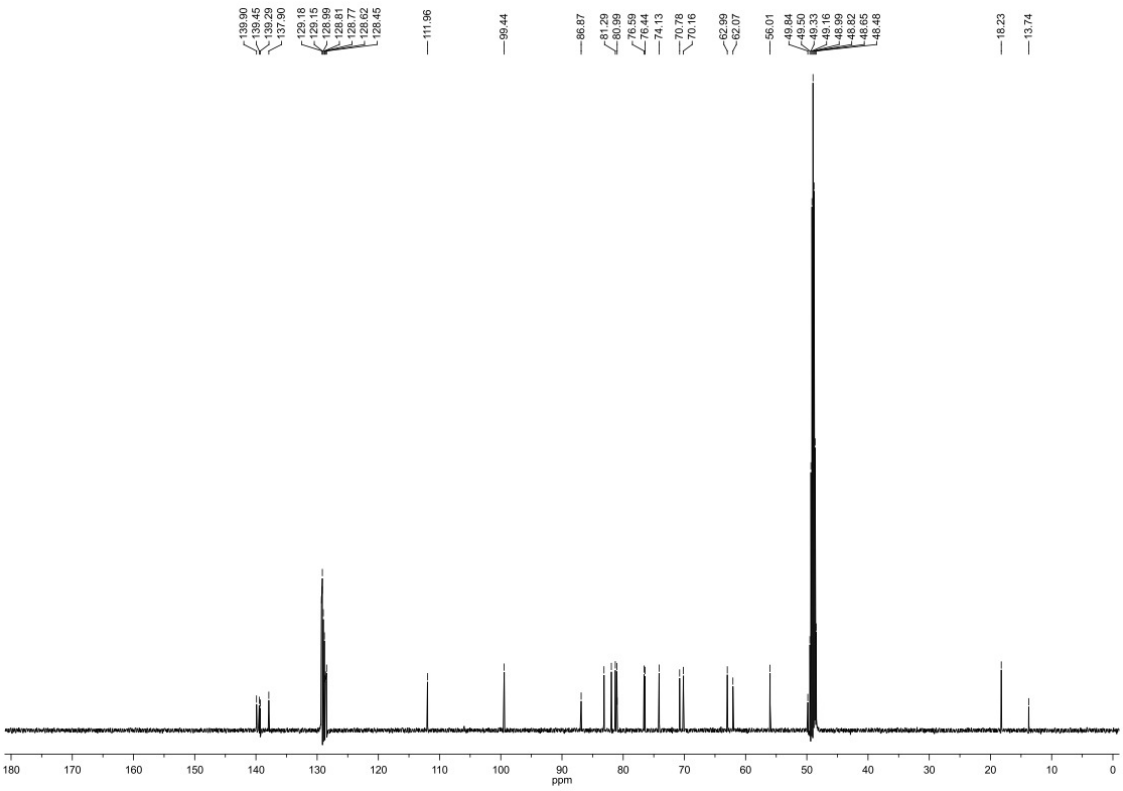


^{13}C NMR (125 MHz, CD_3OD)

Enyne *pseudo*-Disaccharide **11**

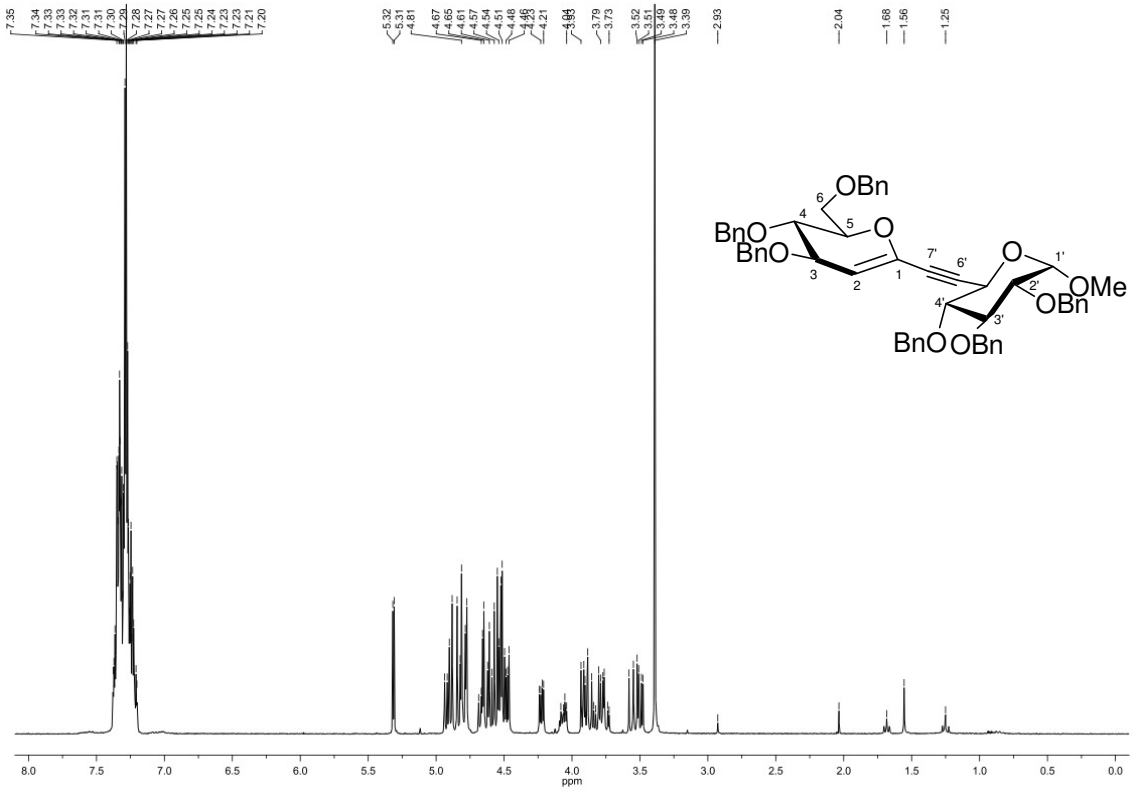


^{1}H NMR (300 MHz, CD_3OD)

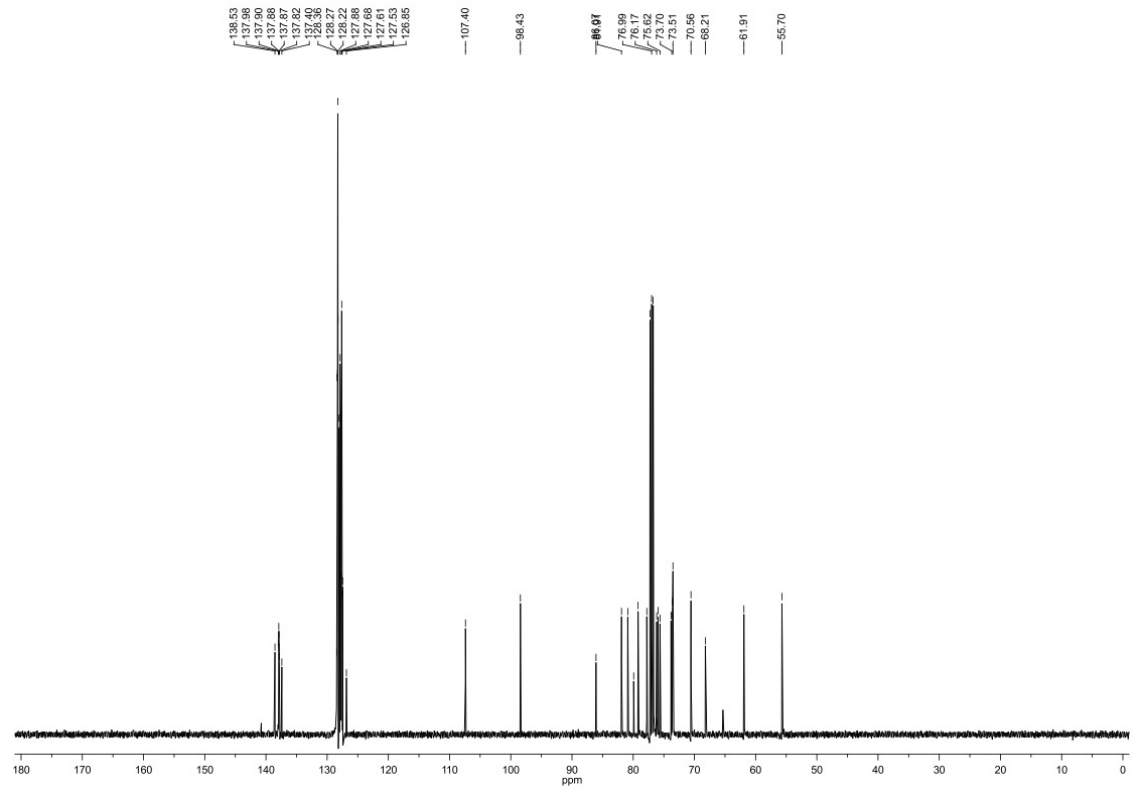


^{13}C NMR (125 MHz, CD_3OD)

Enyne *pseudo*-Disaccharide **19**

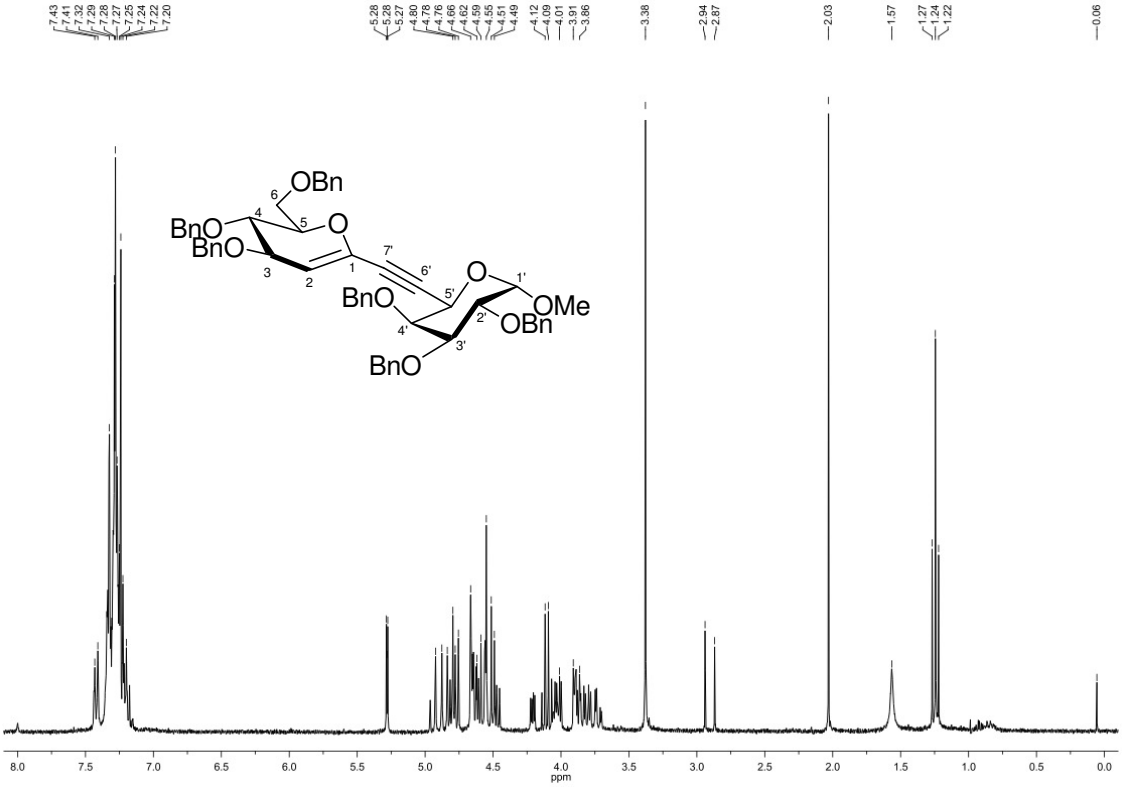


^{1}H NMR (300 MHz, $CDCl_3$)

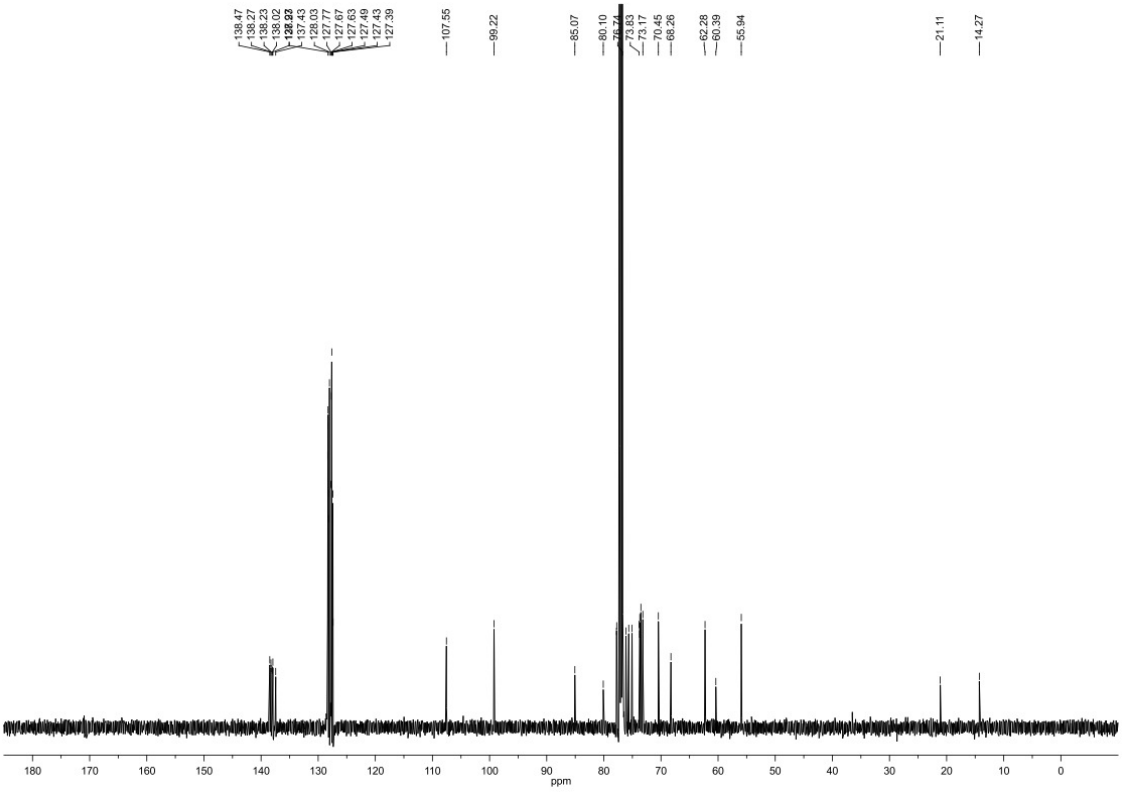


^{13}C NMR (125 MHz, $CDCl_3$)

Enyne *pseudo*-Disaccharide **20**

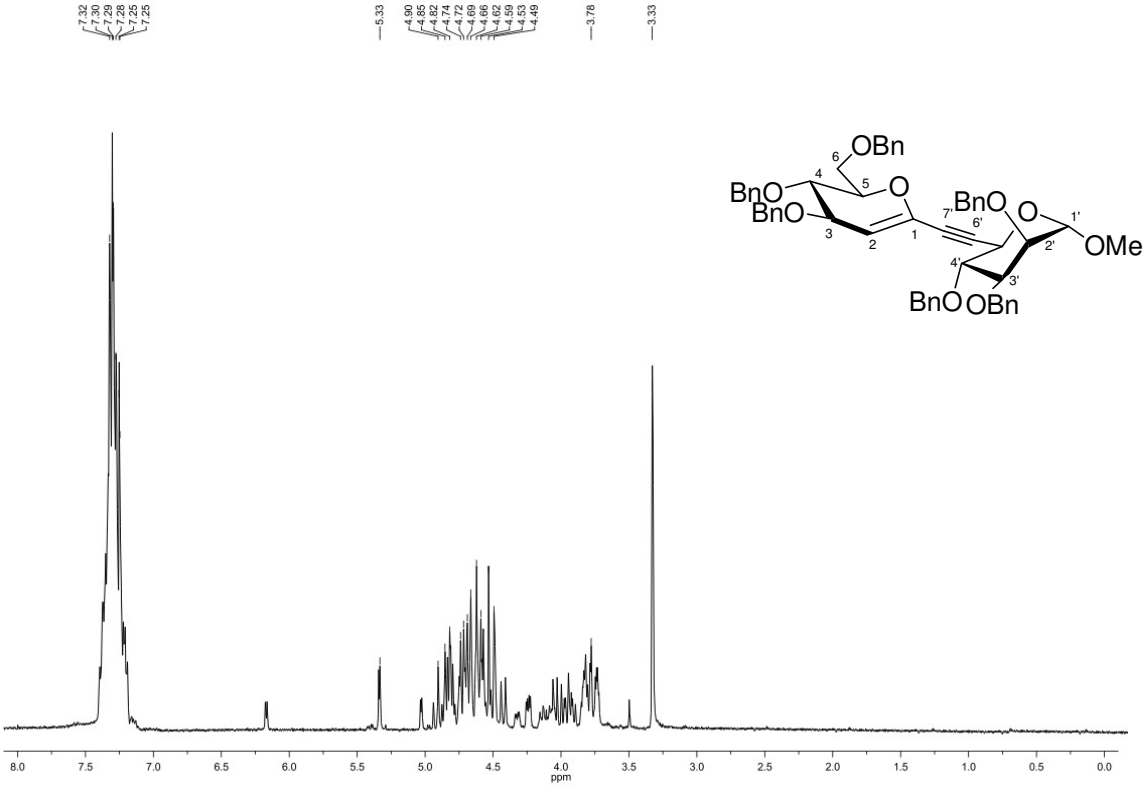


^{1}H NMR (300 MHz, $CDCl_3$)

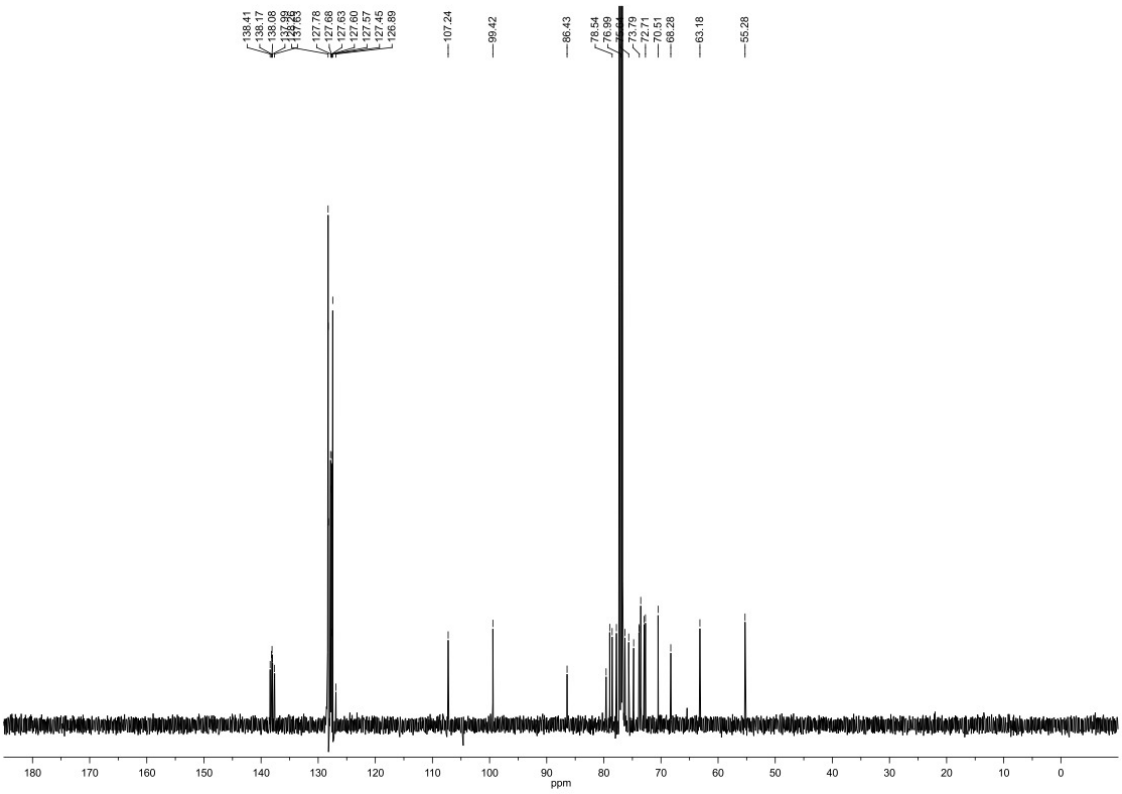


^{13}C NMR (125 MHz, $CDCl_3$)

Enyne *pseudo*-Disaccharide **21**

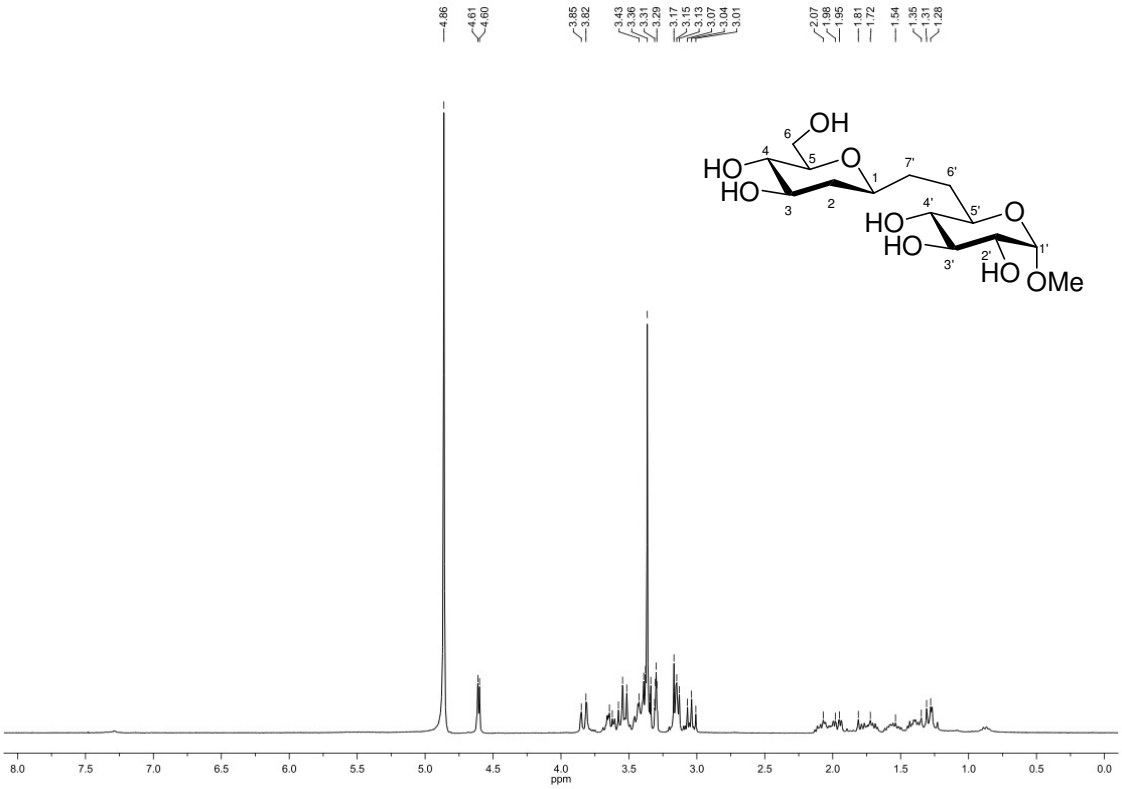


^{1}H NMR (600 MHz, $CDCl_3$)

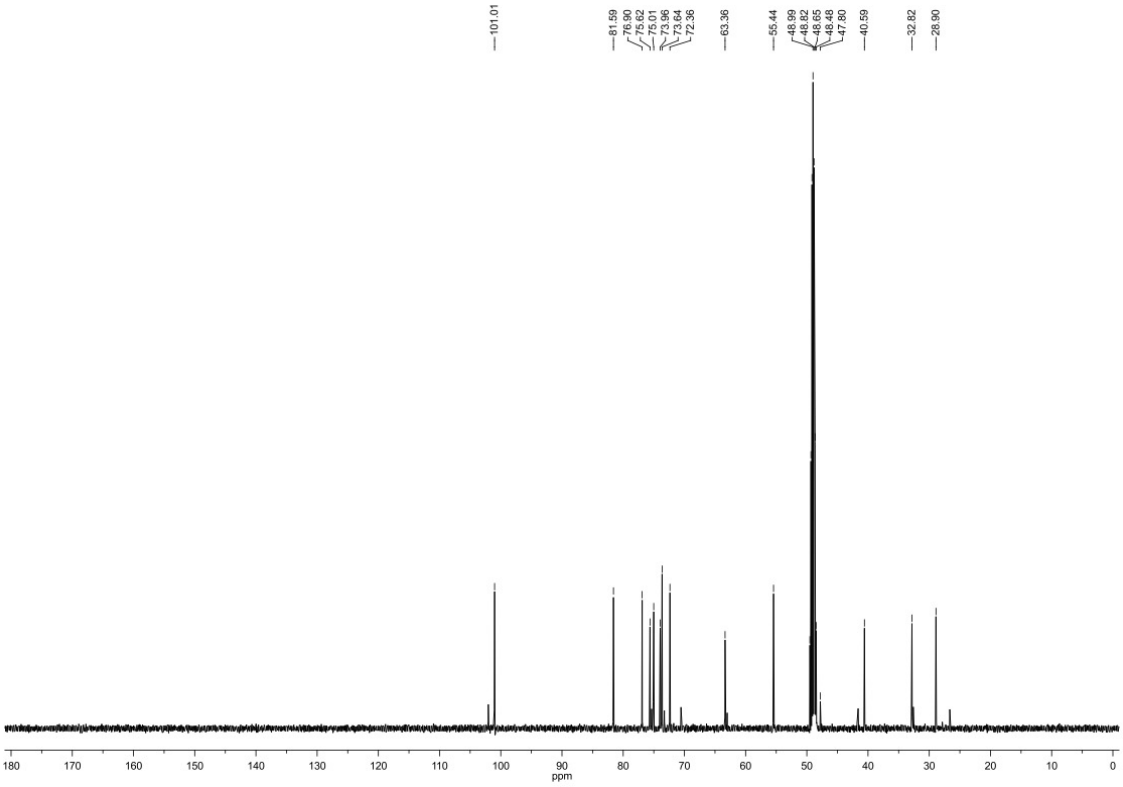


^{13}C NMR (125 MHz, $CDCl_3$)

pseudo-Disaccharide **12**

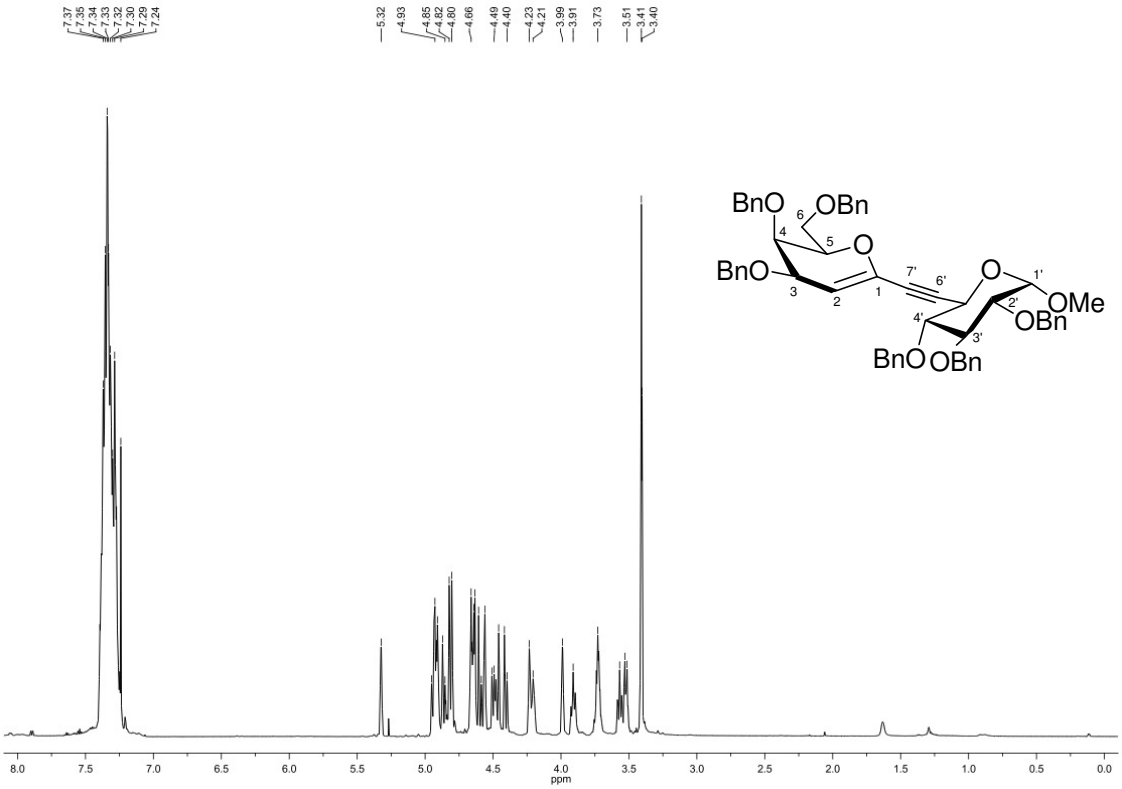


^{1}H NMR (300 MHz, CD_3OD)

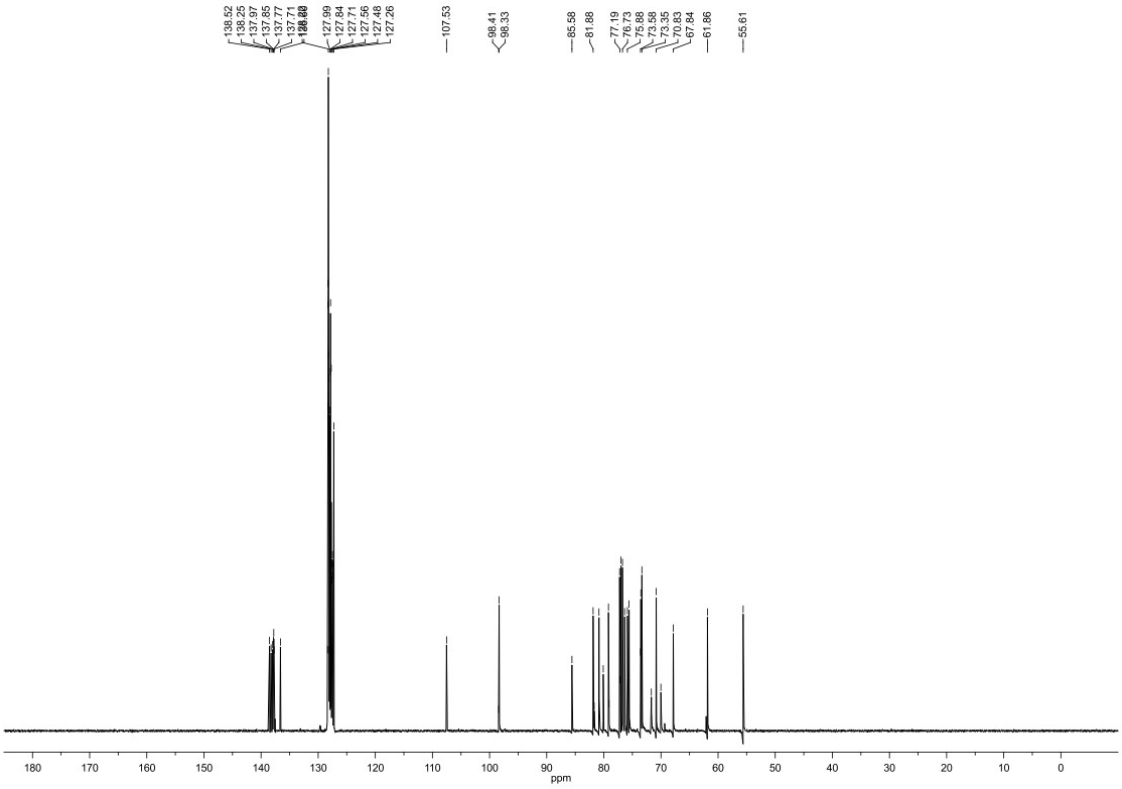


^{13}C NMR (125 MHz, CD_3OD)

Enyne *pseudo*-Disaccharide **17**

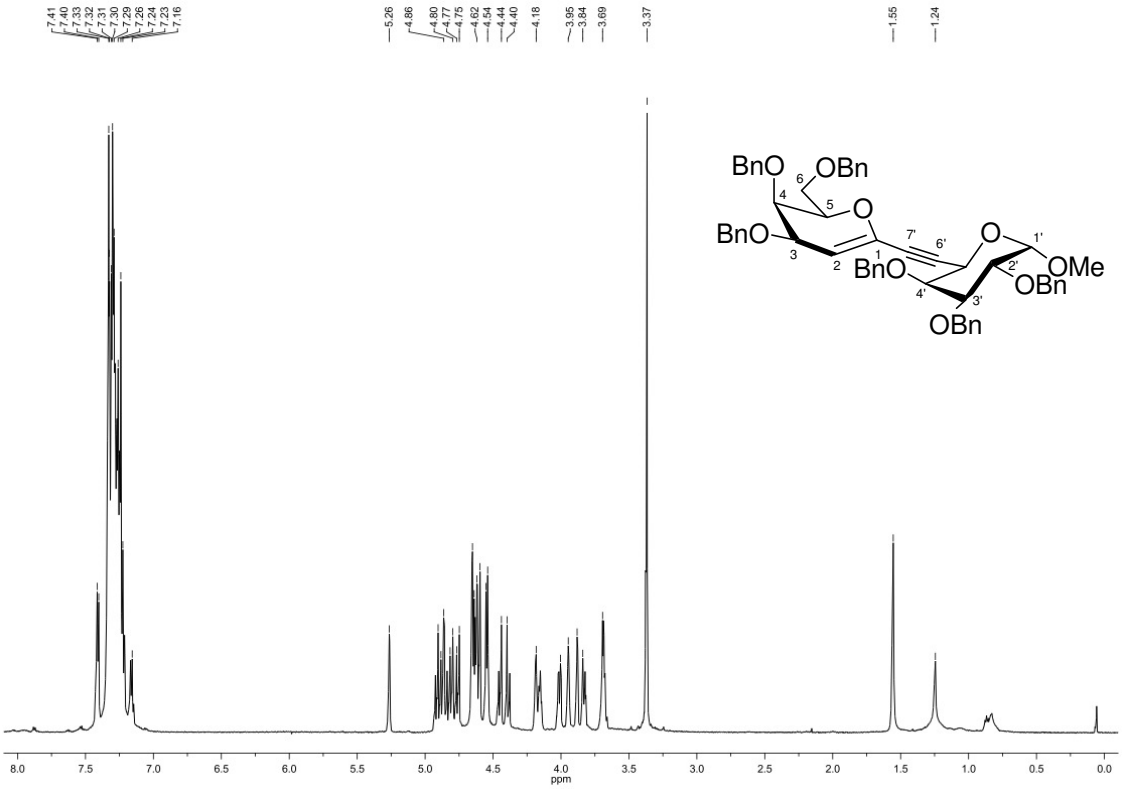


^{1}H NMR (600 MHz, $CDCl_3$)

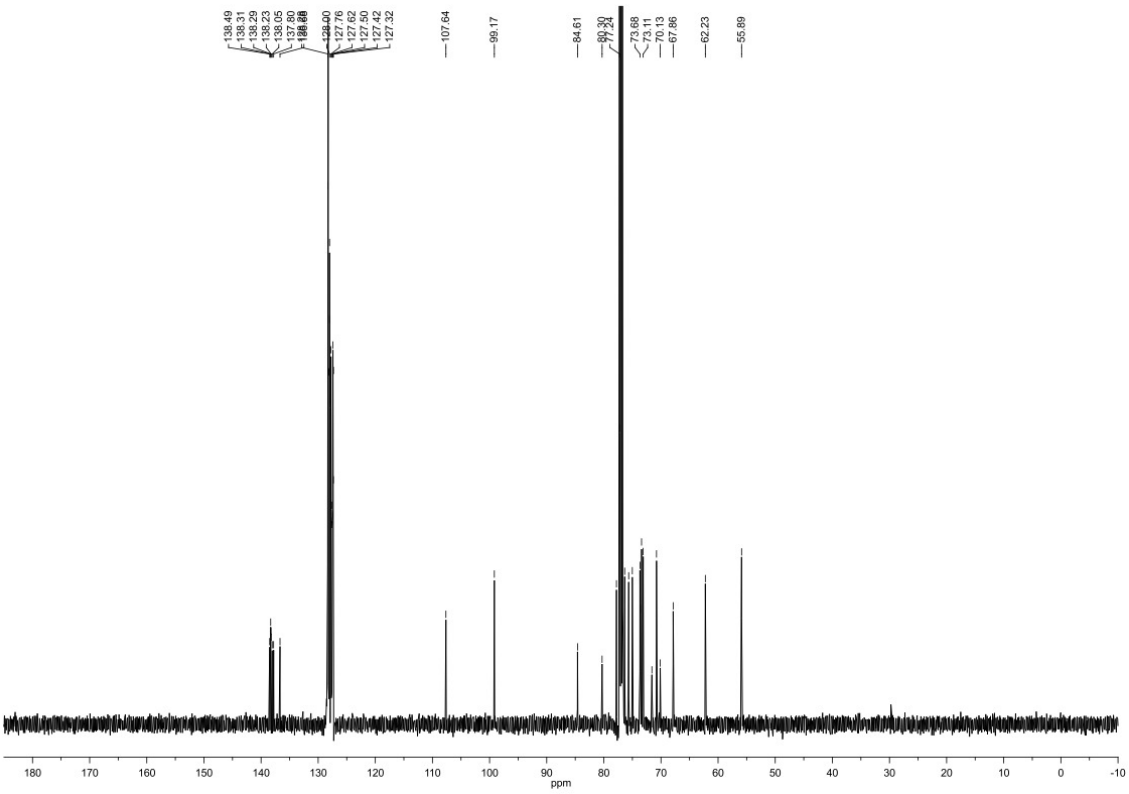


^{13}C NMR (125 MHz, $CDCl_3$)

Enyne *pseudo*-Disaccharide **18**

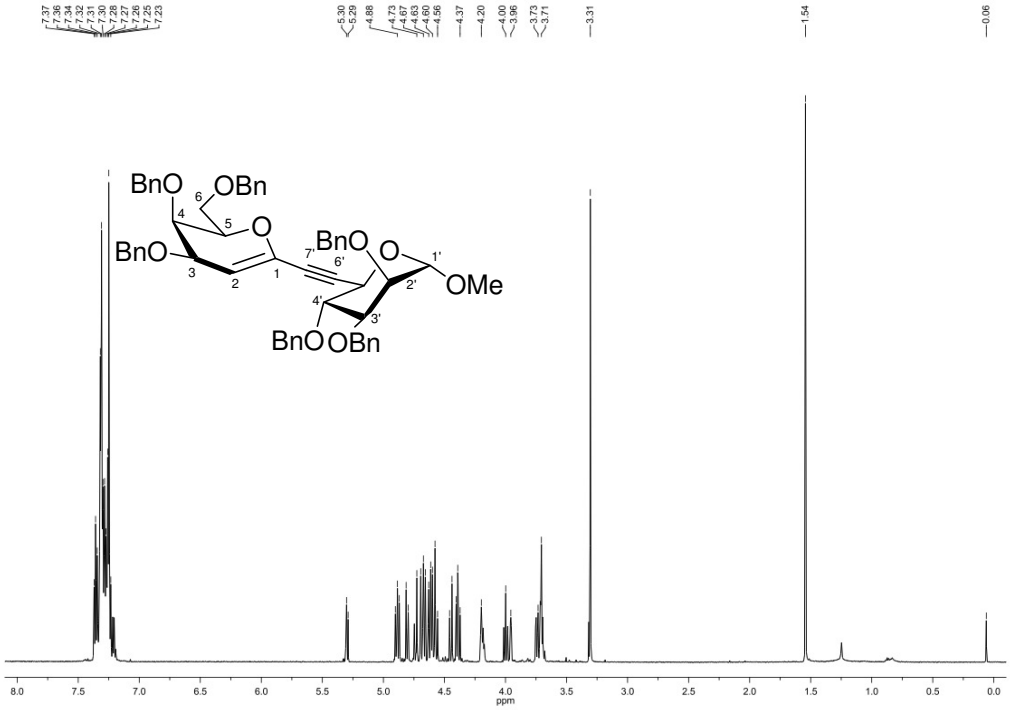


^{1}H NMR (600 MHz, $CDCl_3$)

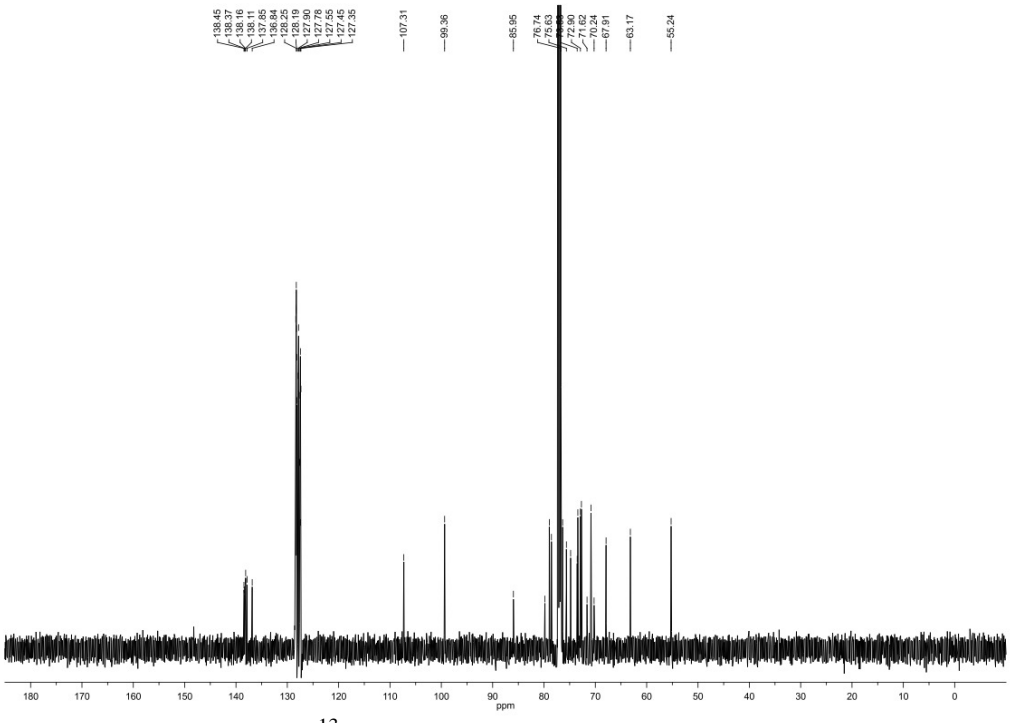


^{13}C NMR (125 MHz, $CDCl_3$)

Enyne *pseudo*-Disaccharide **19**

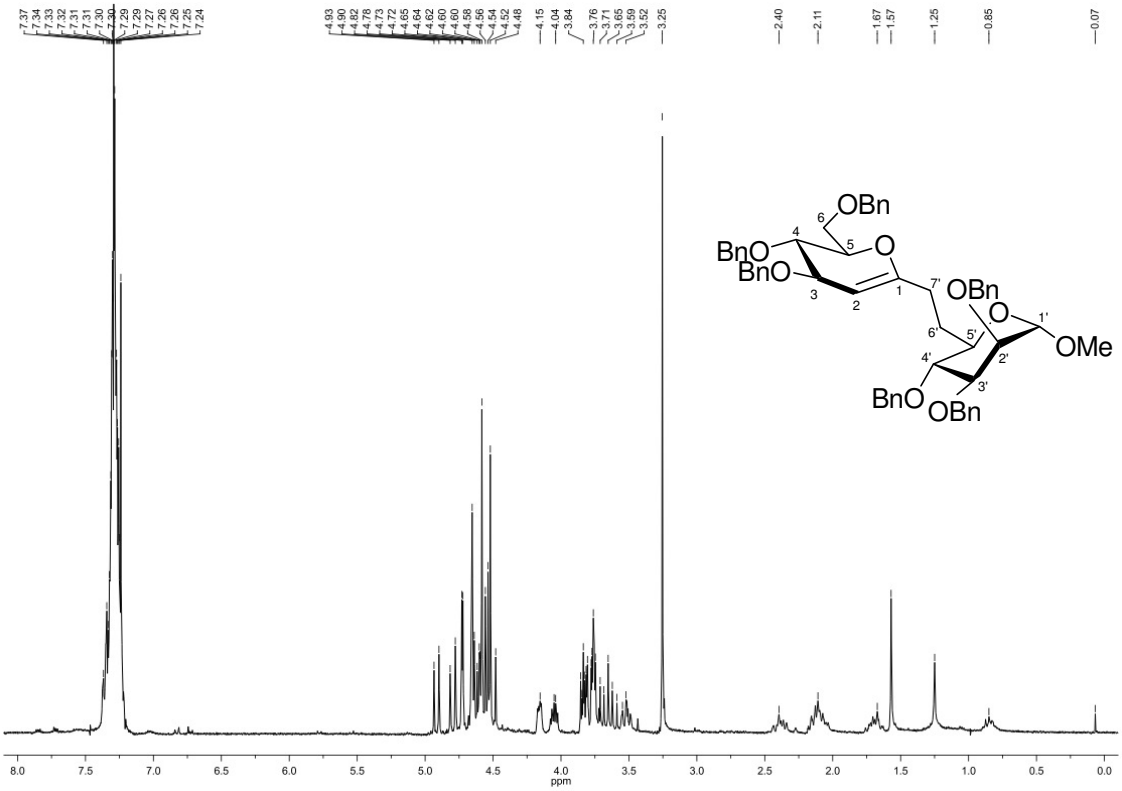


^{1}H NMR (600 MHz, $CDCl_3$)

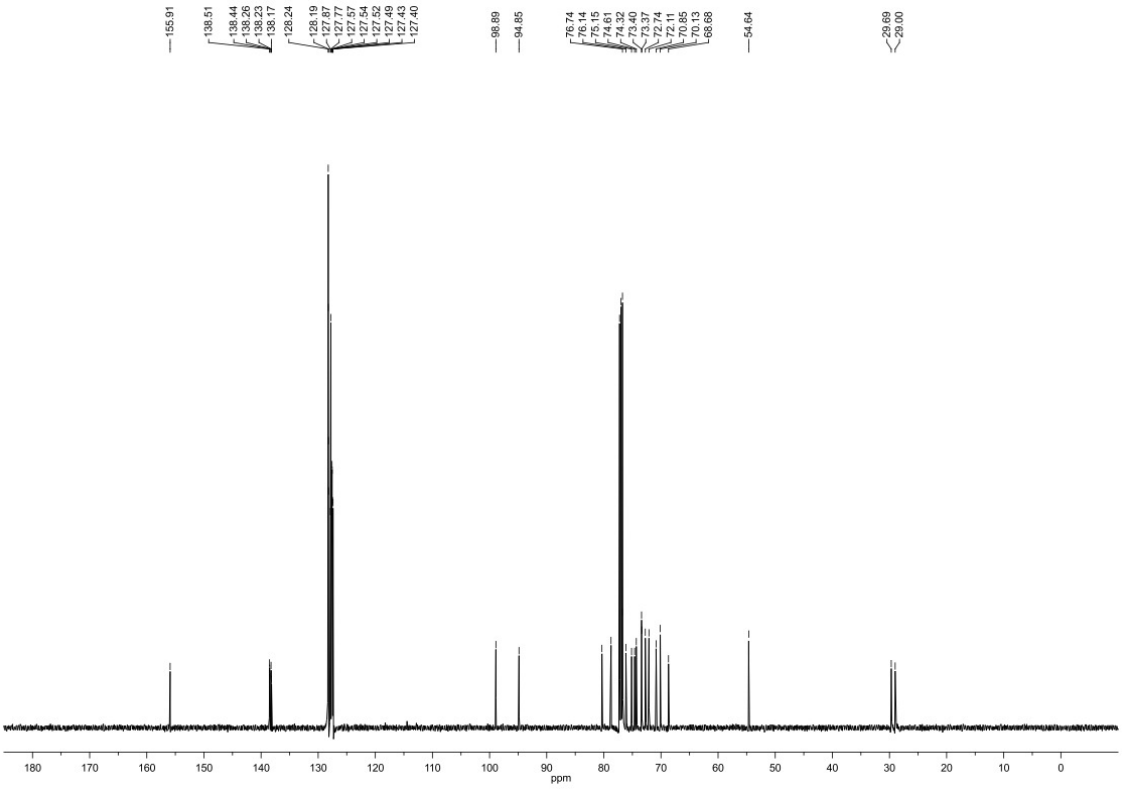


^{13}C NMR (125 MHz, $CDCl_3$)

Enolether *pseudo*-Disaccharide **23**

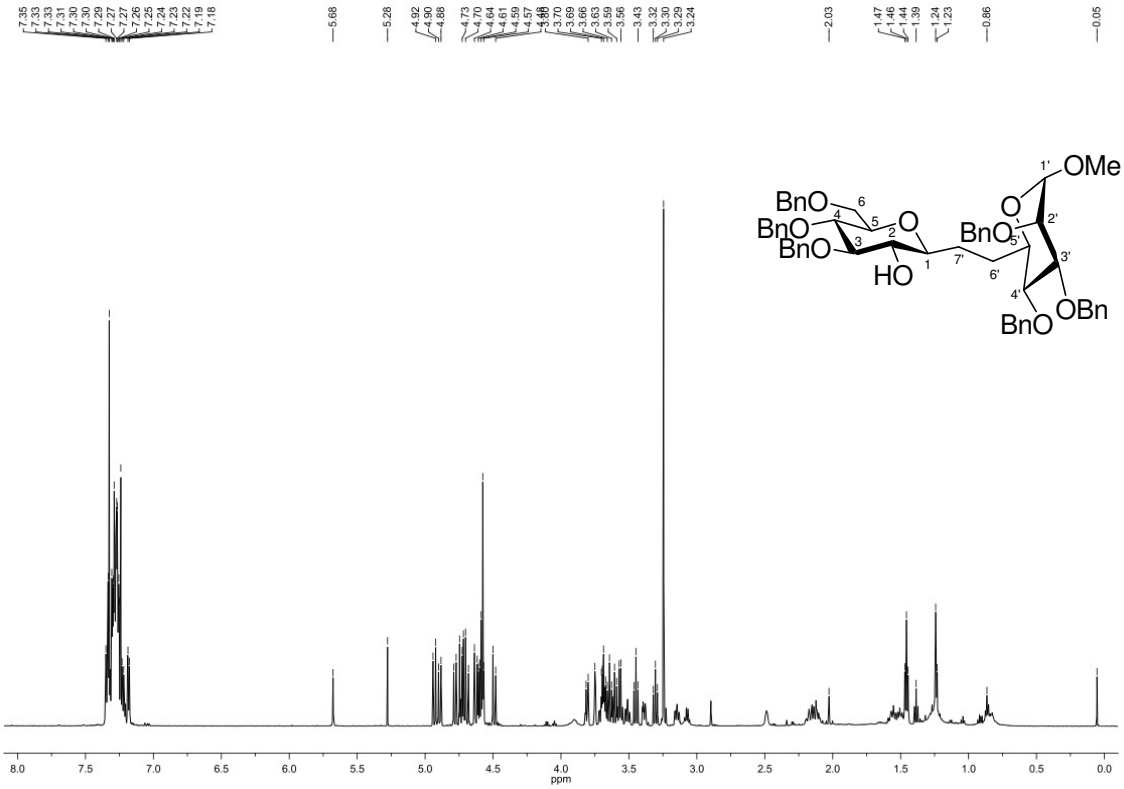


^{1}H NMR (300 MHz, $CDCl_3$)

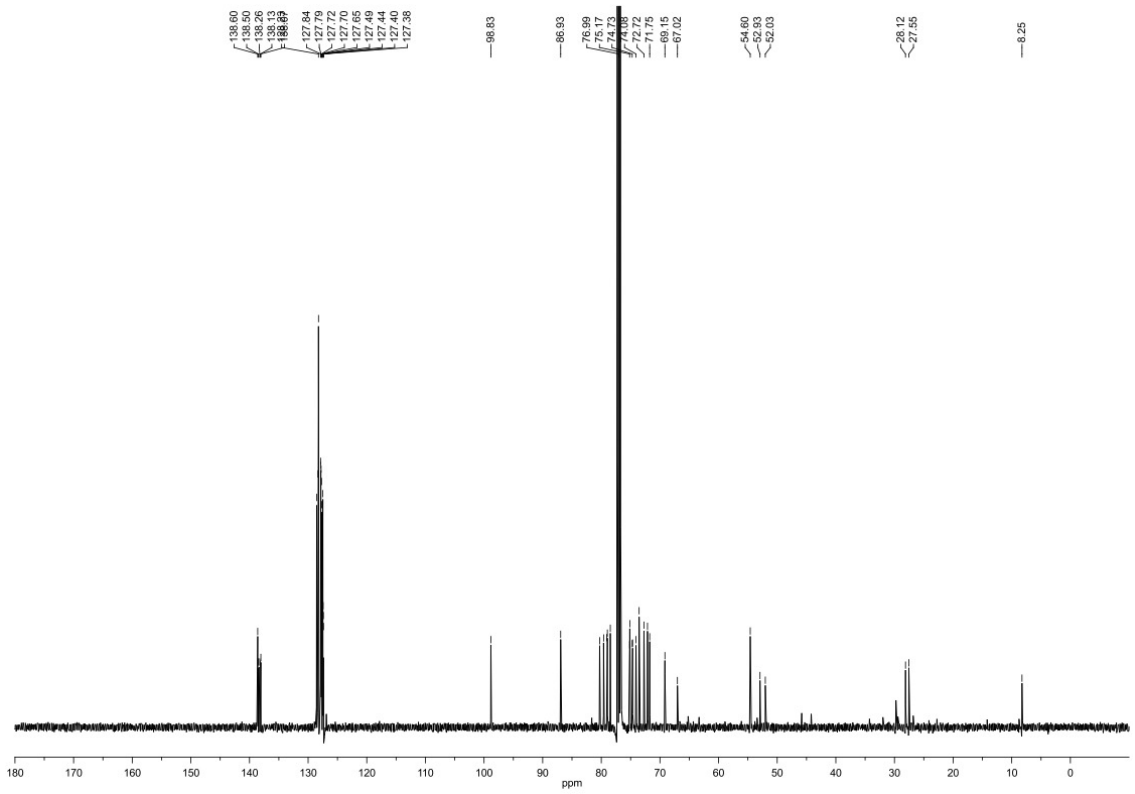


^{13}C NMR (125 MHz, $CDCl_3$)

pseudo-Disaccharide **24**

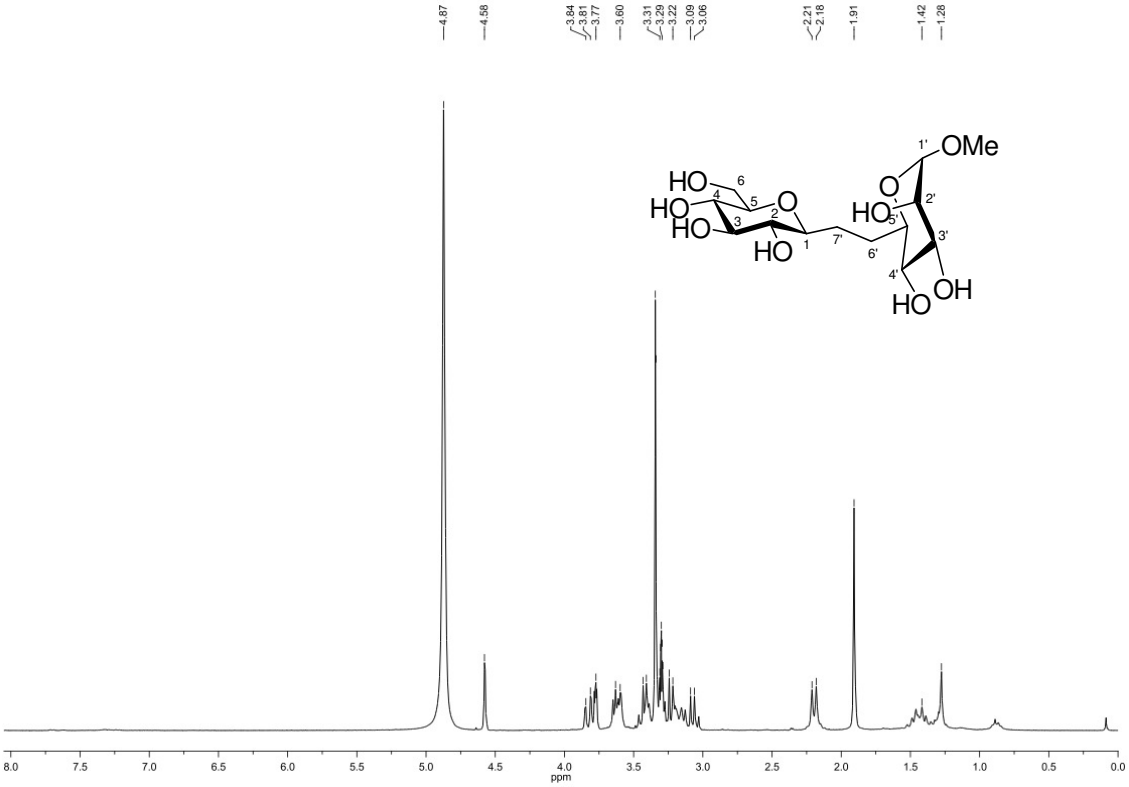


^{1}H NMR (600 MHz, $CDCl_3$)

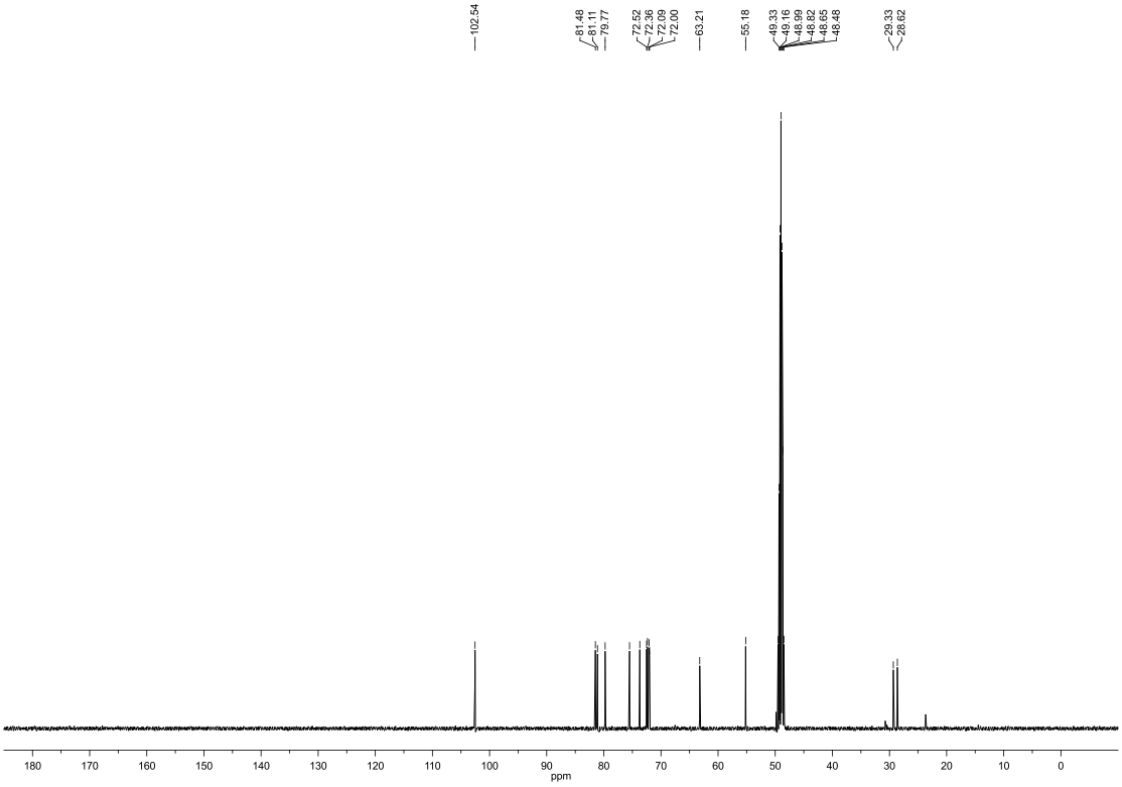


^{13}C NMR (125 MHz, $CDCl_3$)

pseudo-Disaccharide **25**

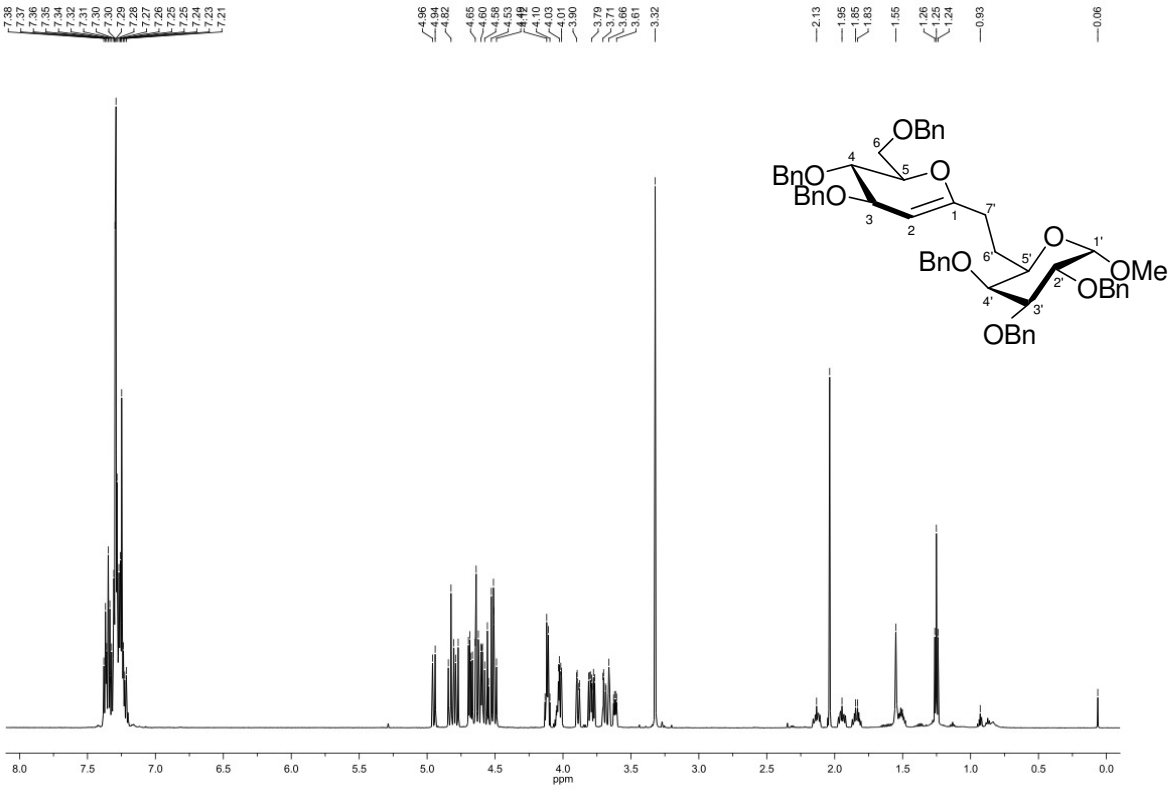


^{1}H NMR (300 MHz, CD_3OD)

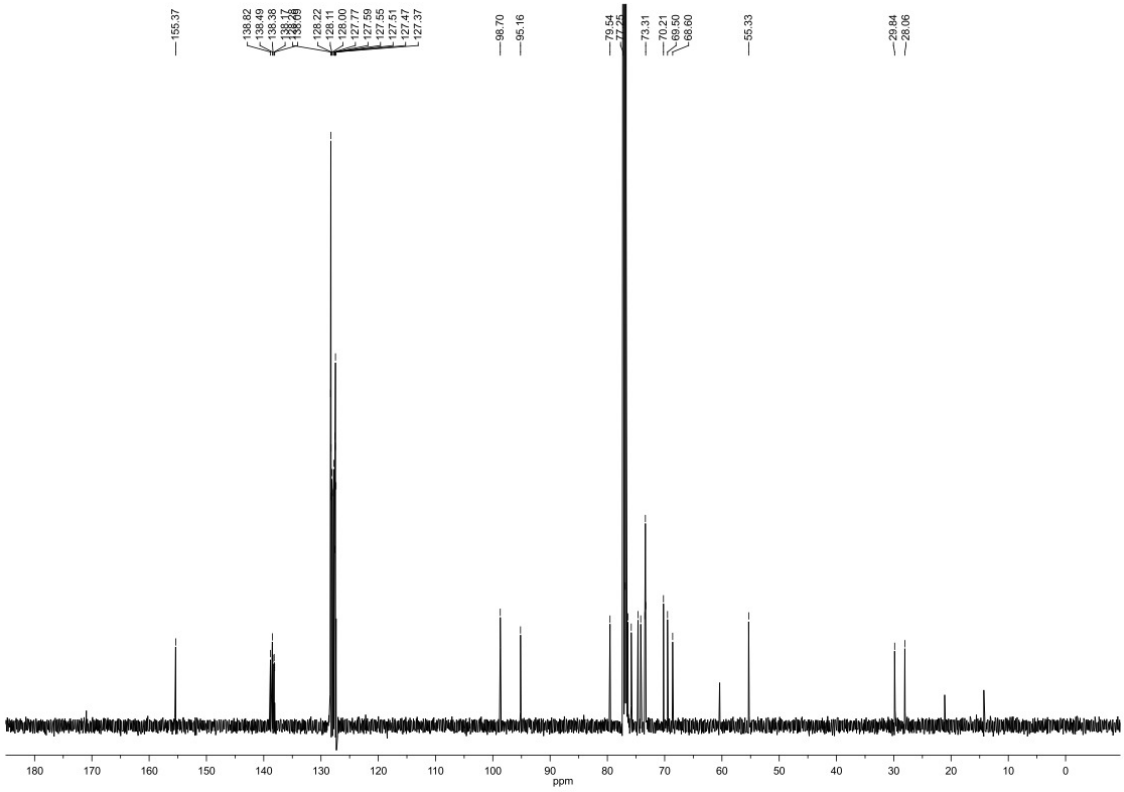


^{13}C NMR (125 MHz, CD_3OD)

Enolether *pseudo*-Disaccharide **26**

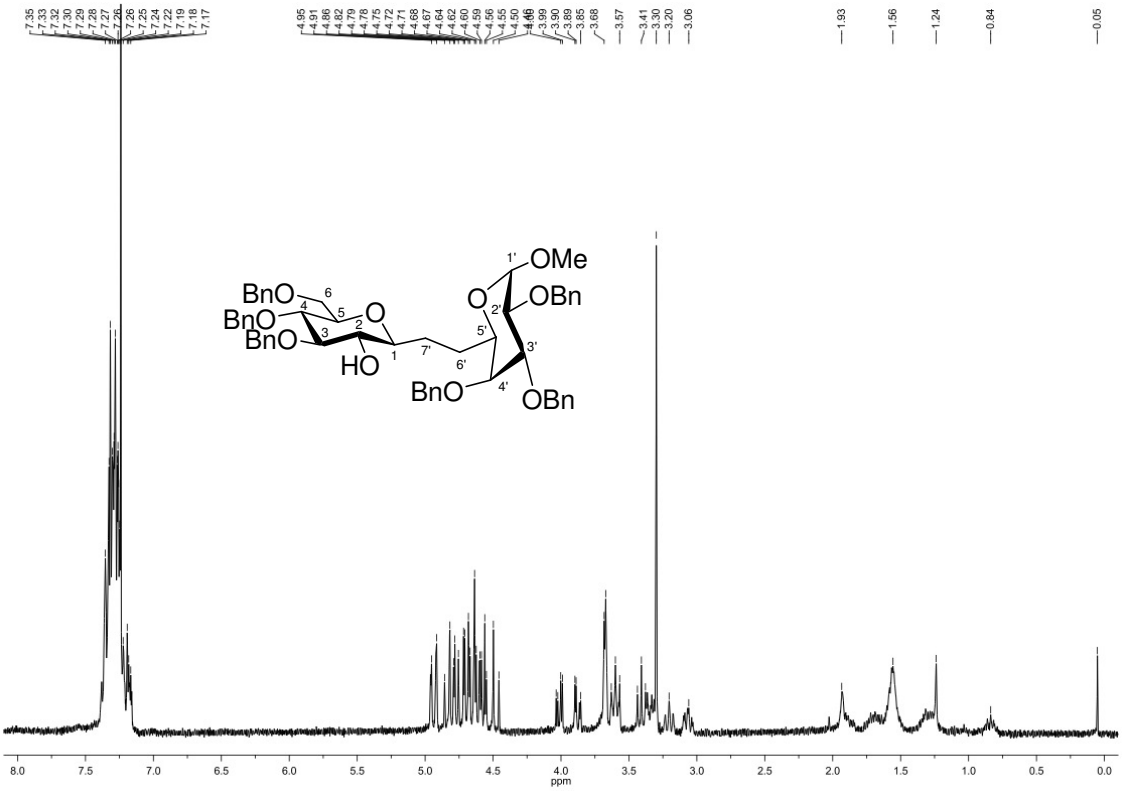


^{1}H NMR (600 MHz, $CDCl_3$)

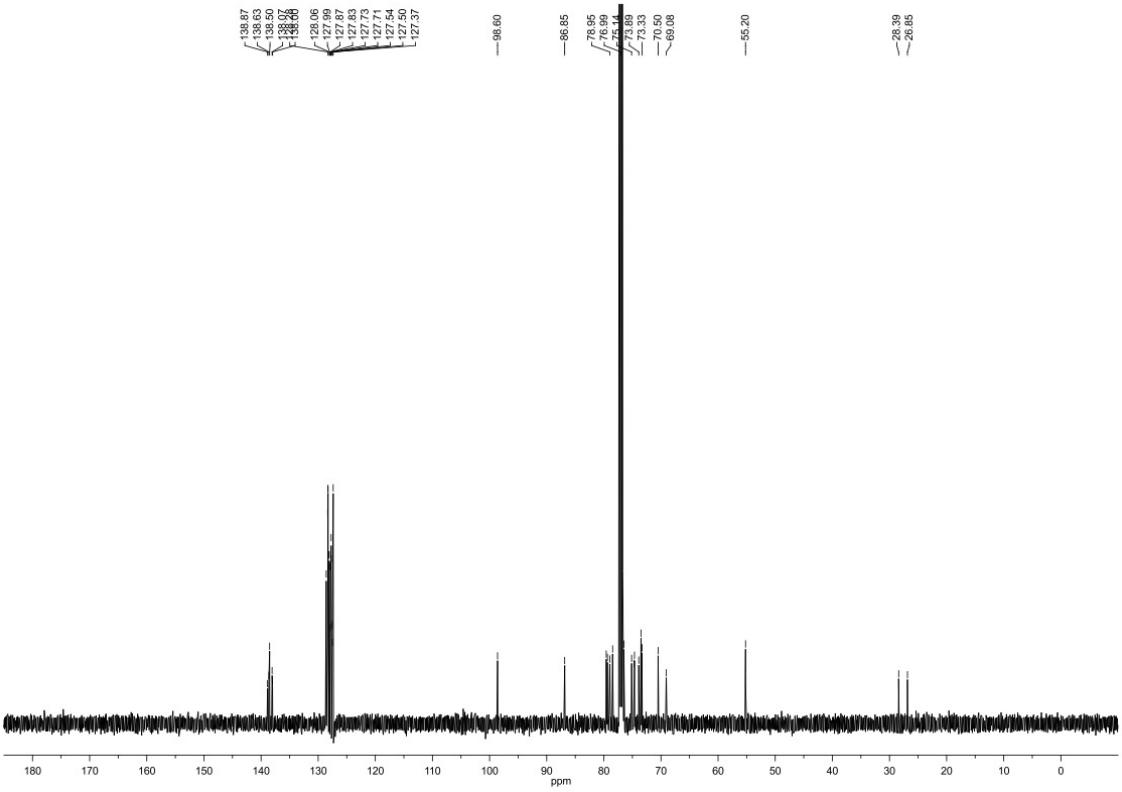


^{13}C NMR (125 MHz, $CDCl_3$)

pseudo-Disaccharide **27**

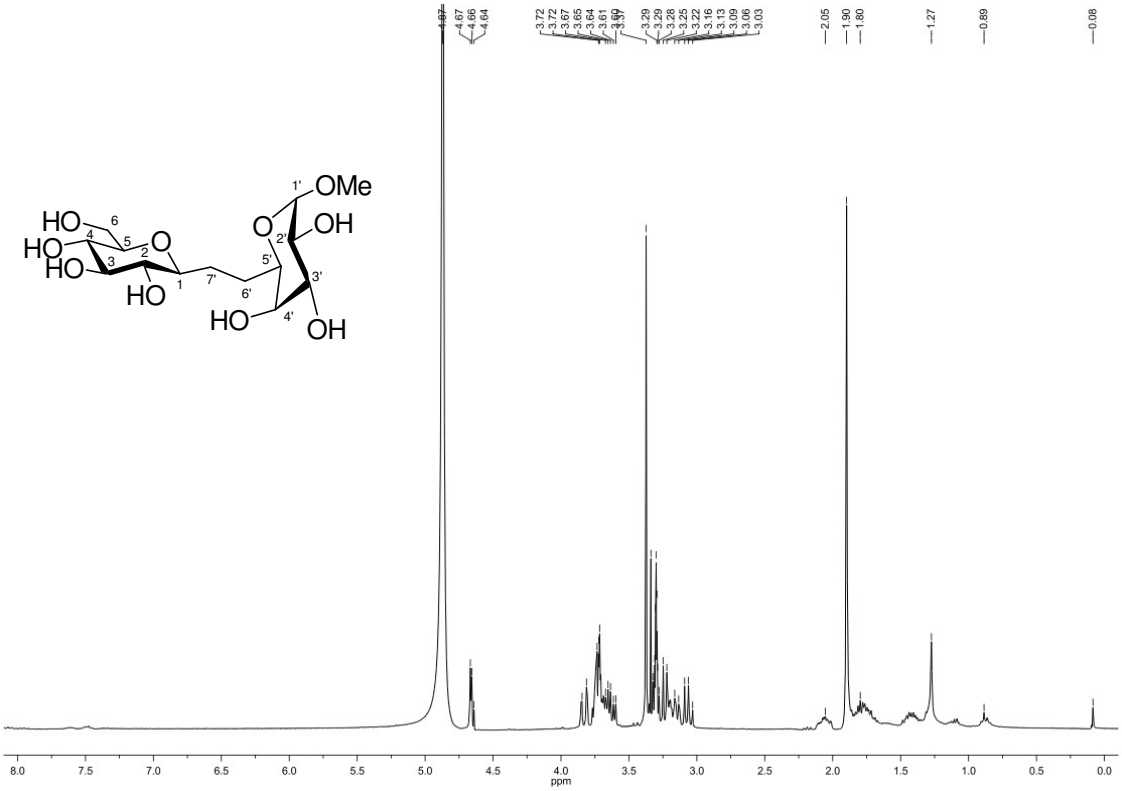


^{1}H NMR (300 MHz, $CDCl_3$)

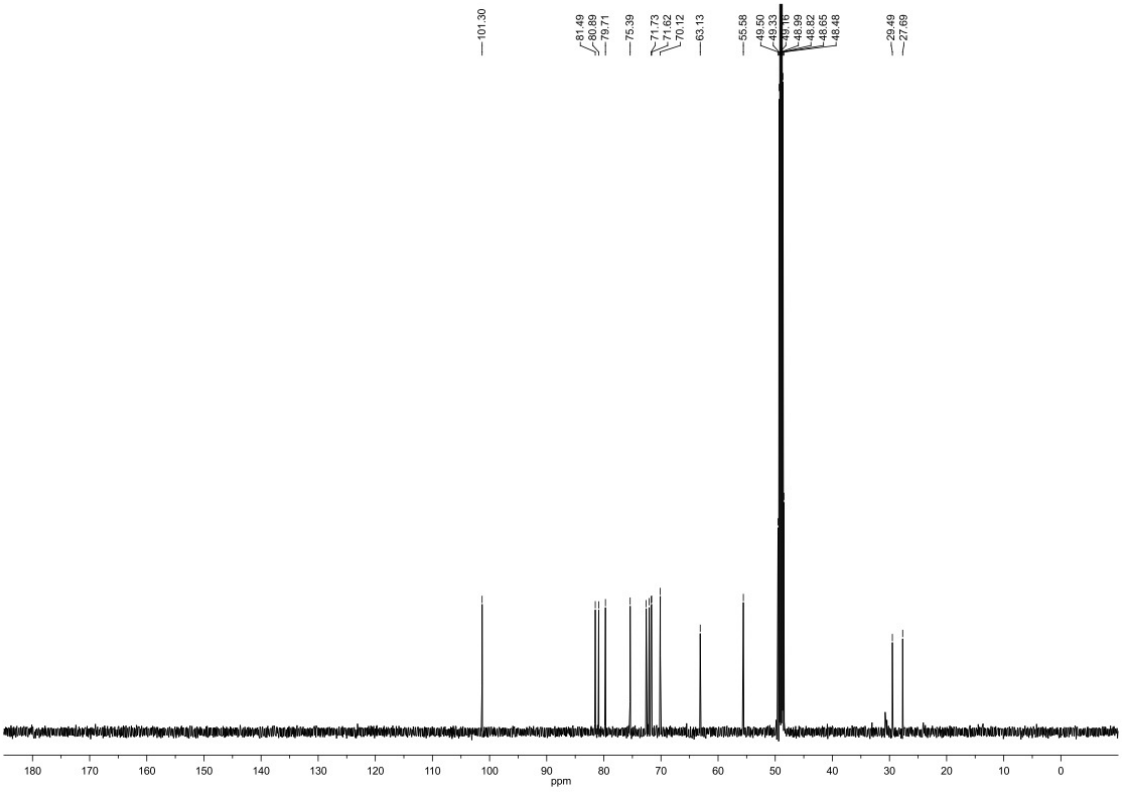


^{13}C NMR (125 MHz, $CDCl_3$)

pseudo-Disaccharide **28**

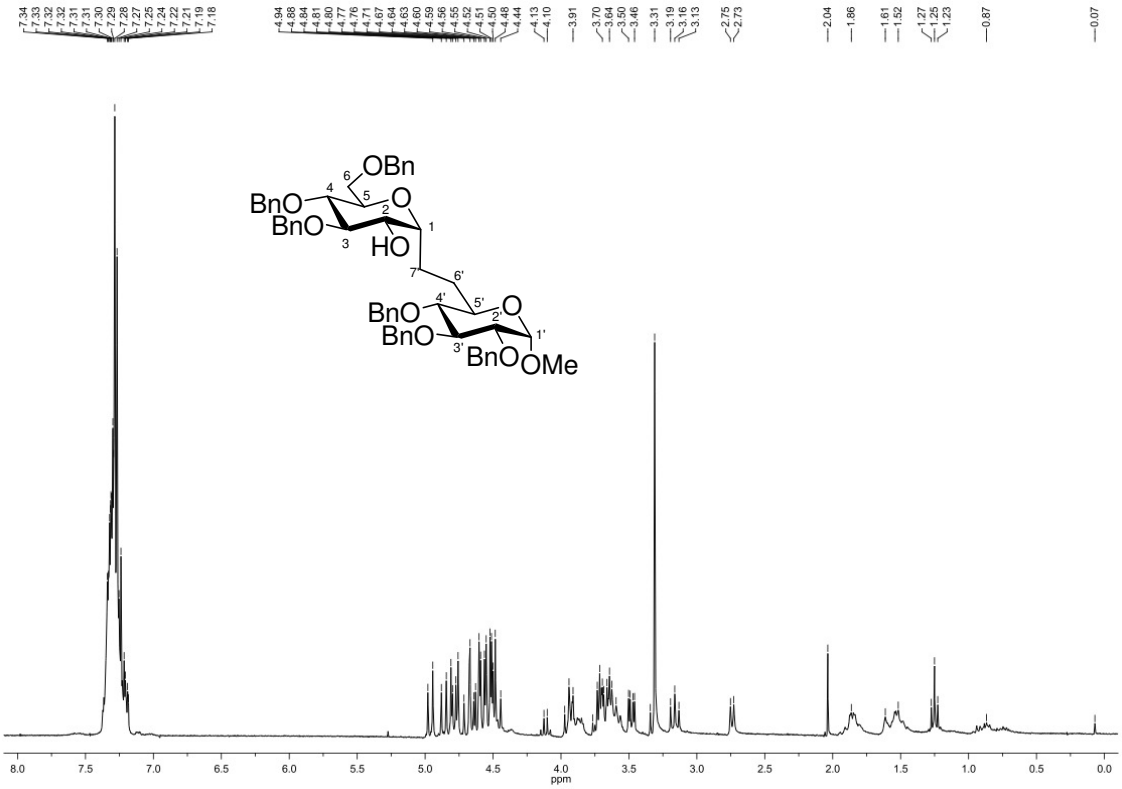


^{1}H NMR (300 MHz, CD_3OD)

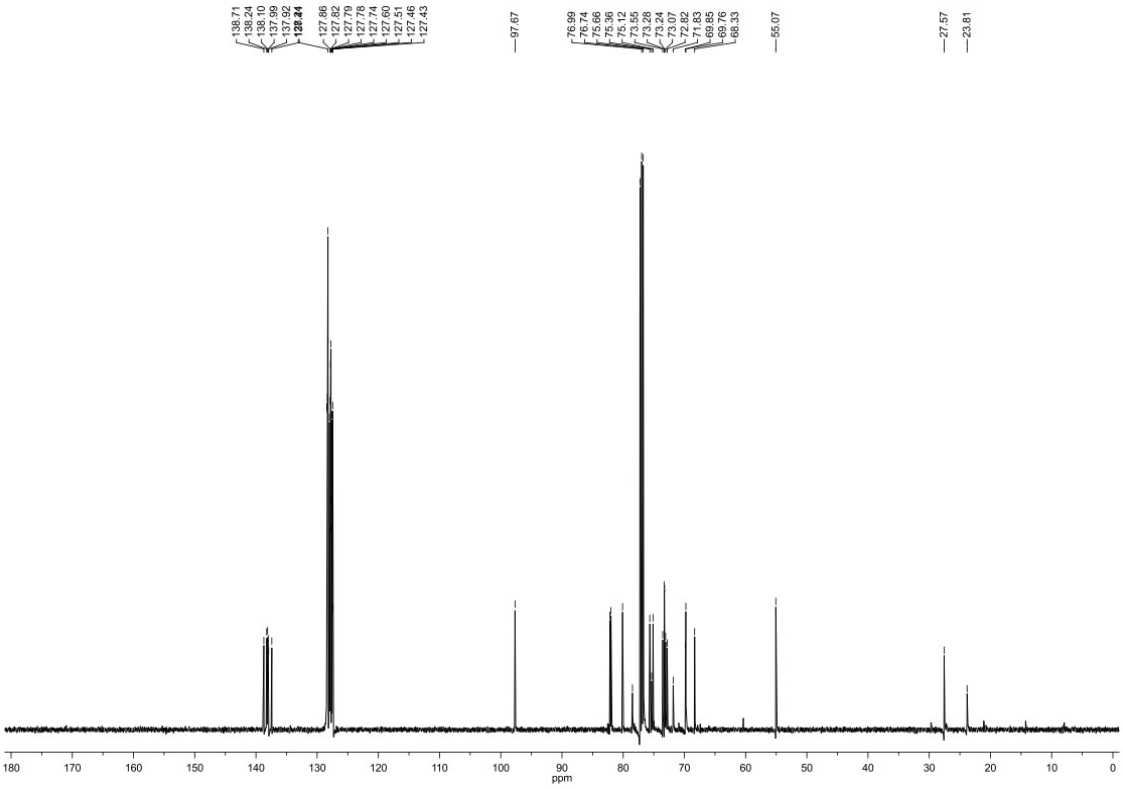


^{13}C NMR (125 MHz, CD_3OD)

pseudo-Disaccharide **29**

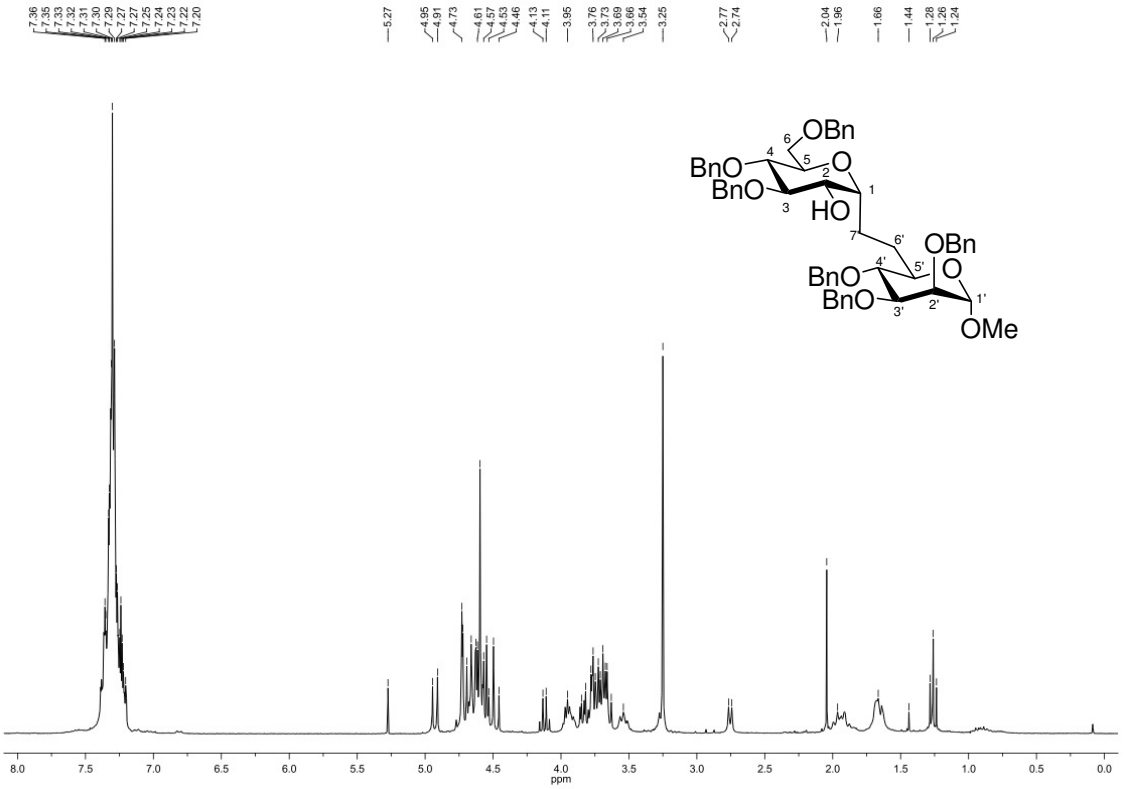


^{1}H NMR (300 MHz, $CDCl_3$)

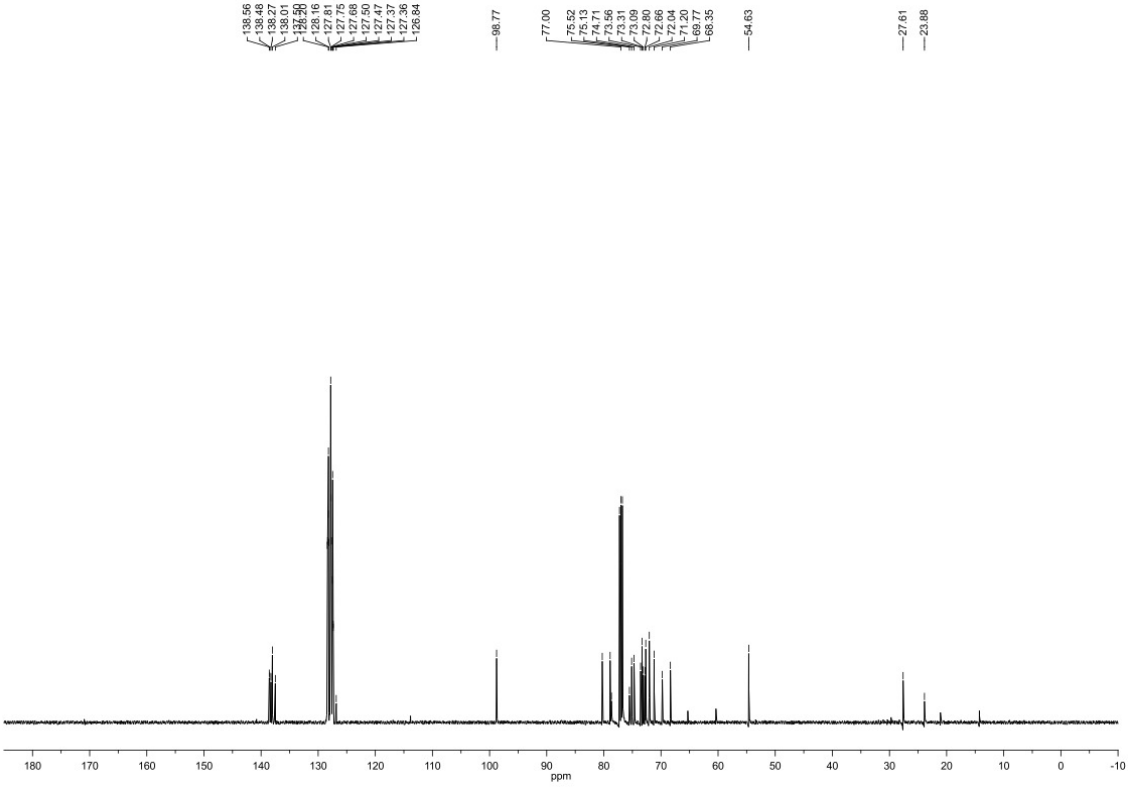


^{13}C NMR (125 MHz, $CDCl_3$)

pseudo-Disaccharide **31**

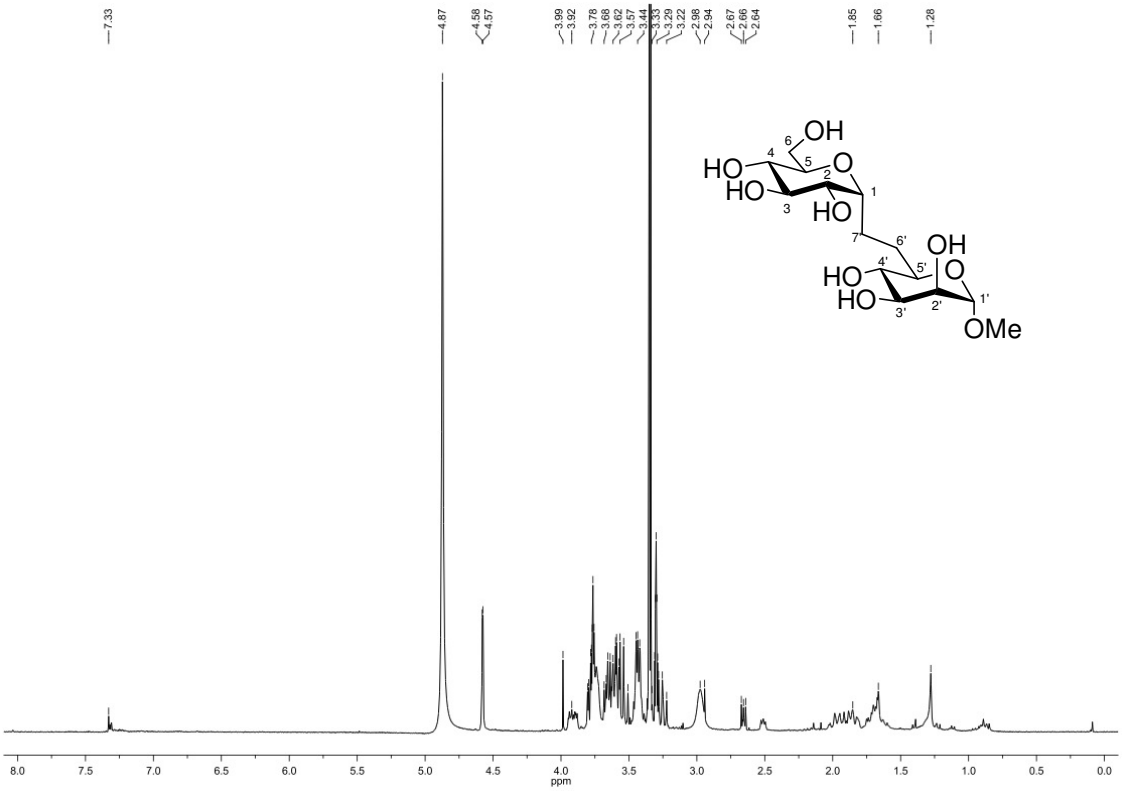


^{1}H NMR (300 MHz, $CDCl_3$)

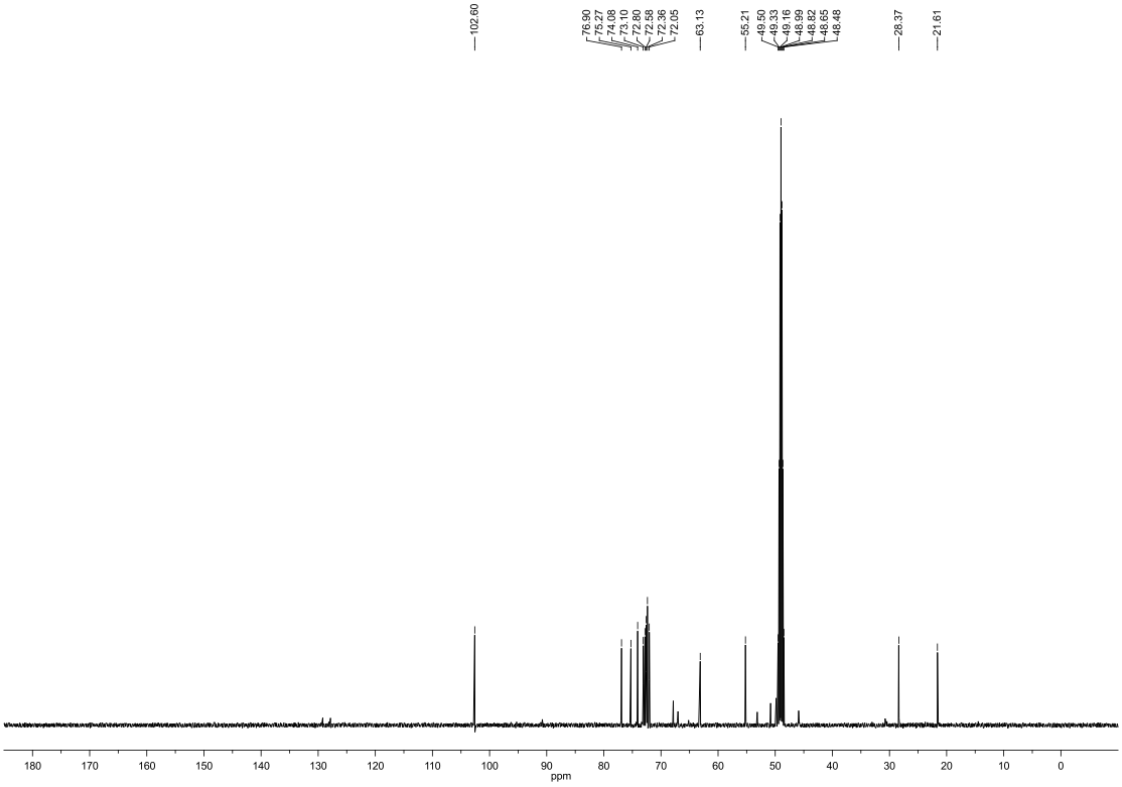


^{13}C NMR (125 MHz, $CDCl_3$)

pseudo-Disaccharide **32**

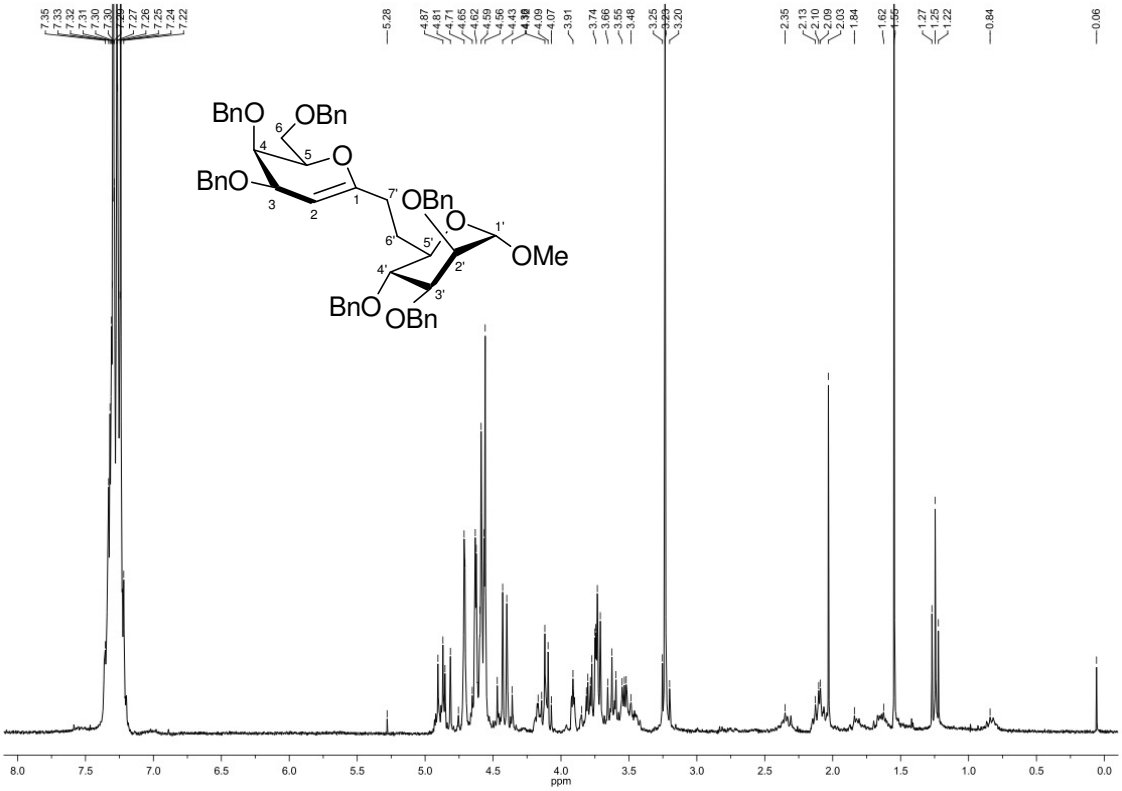


^{1}H NMR (300 MHz, CD_3OD)

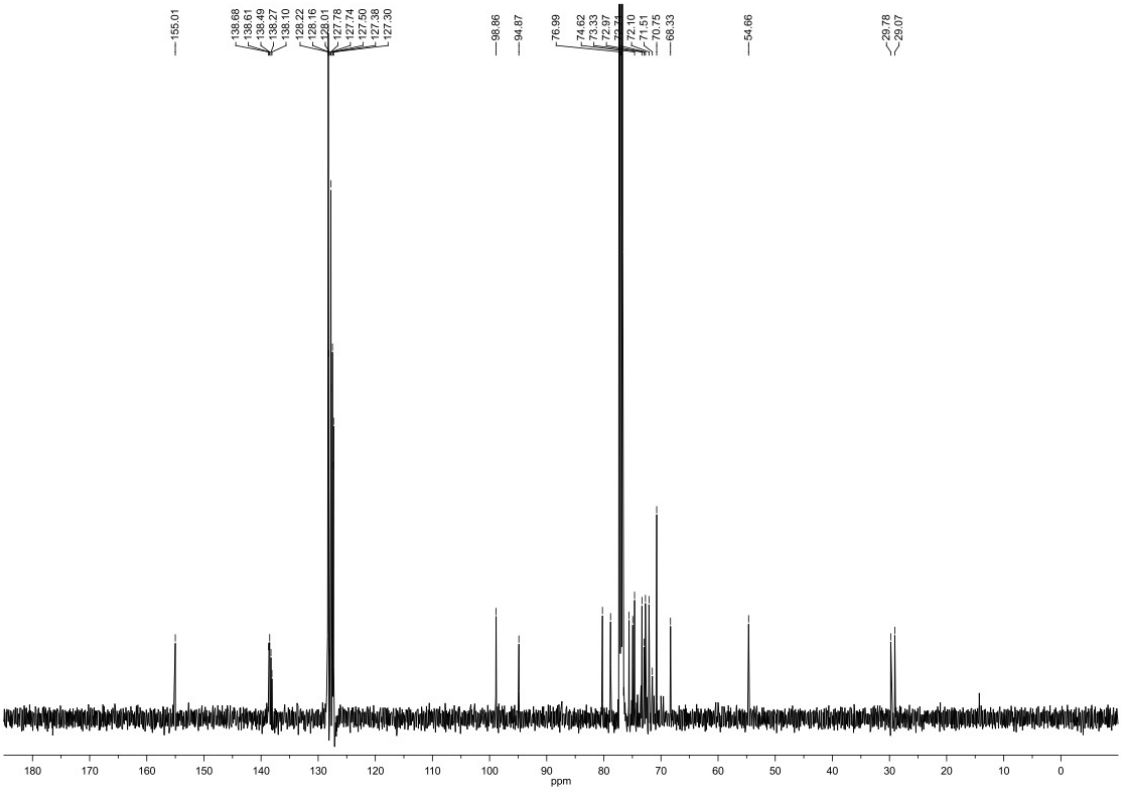


^{13}C NMR (125 MHz, CD_3OD)

Enolether *pseudo*-Disaccharide **33**

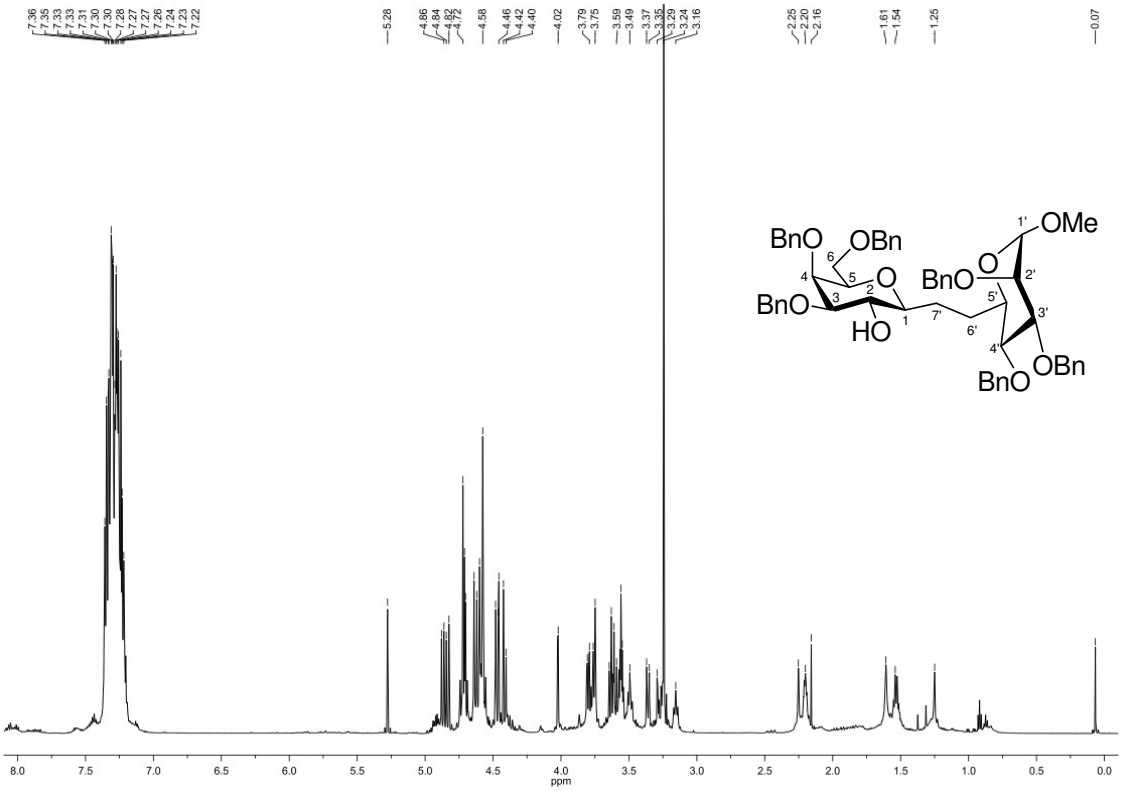


^{1}H NMR (300 MHz, $CDCl_3$)

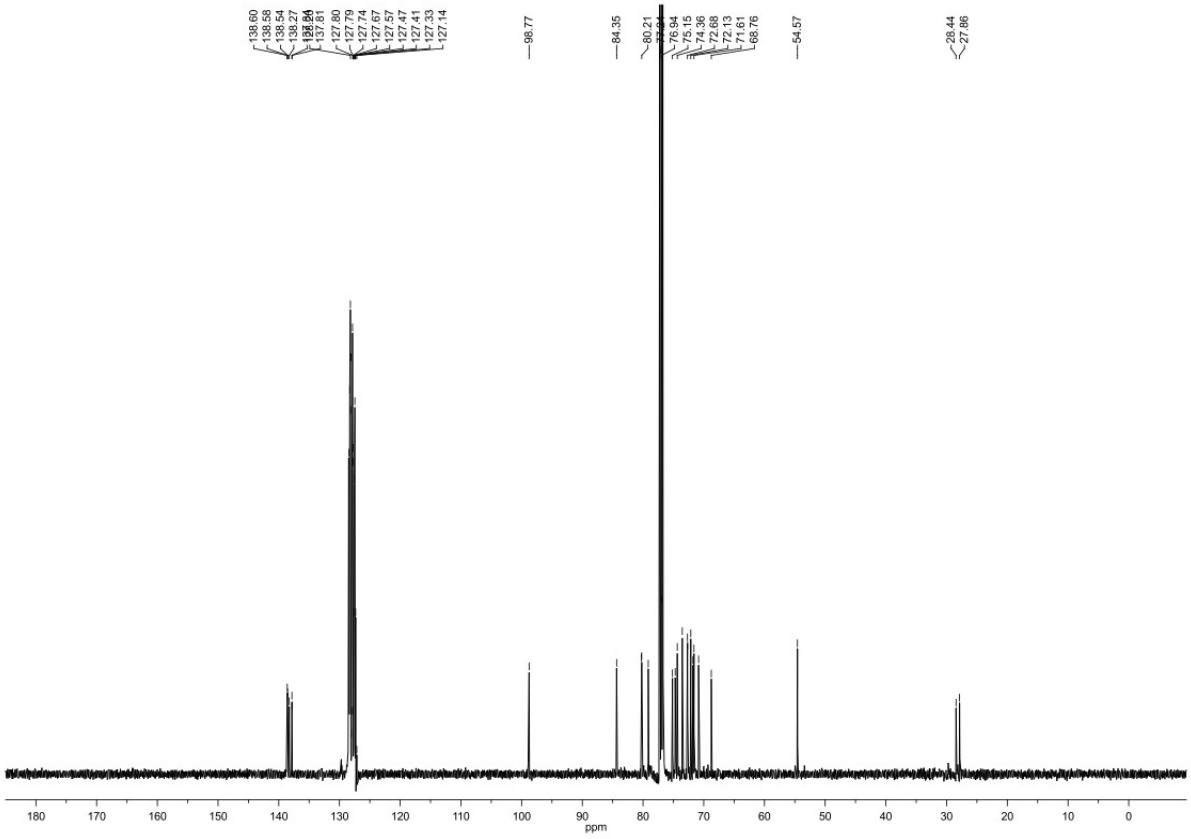


^{13}C NMR (125 MHz, $CDCl_3$)

pseudo-Disaccharide **34**

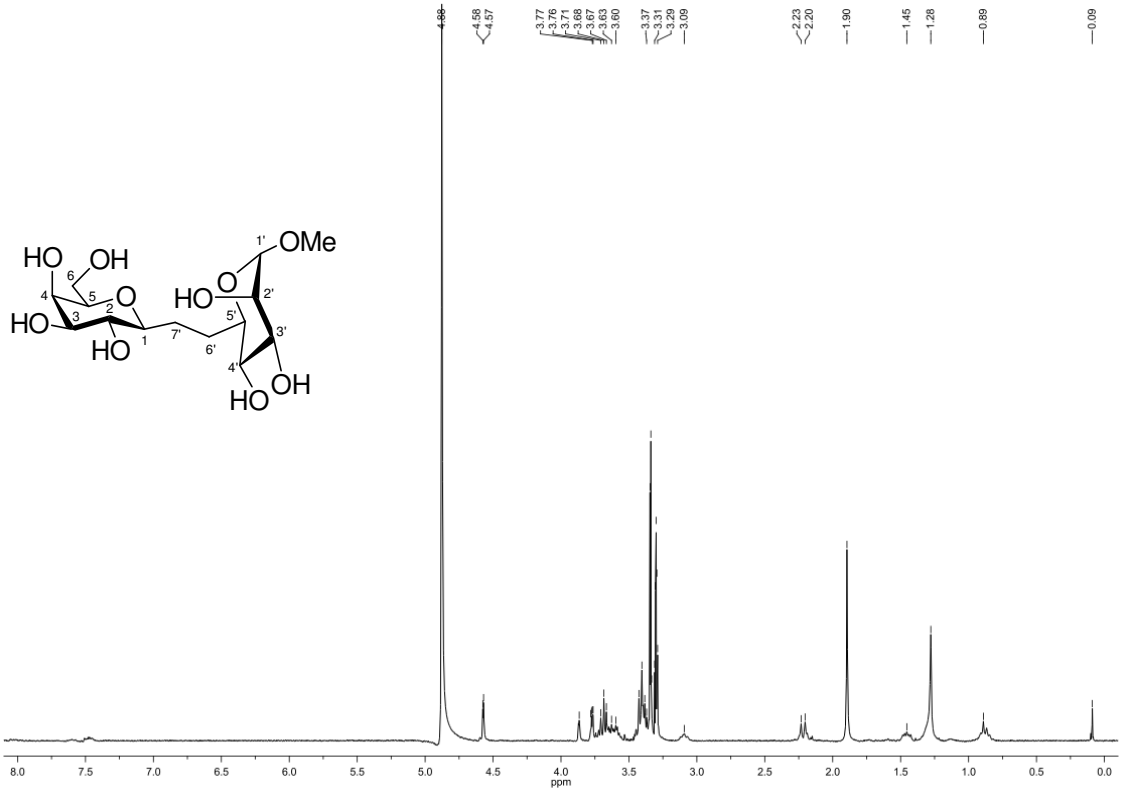


^{1}H NMR (600 MHz, $CDCl_3$)

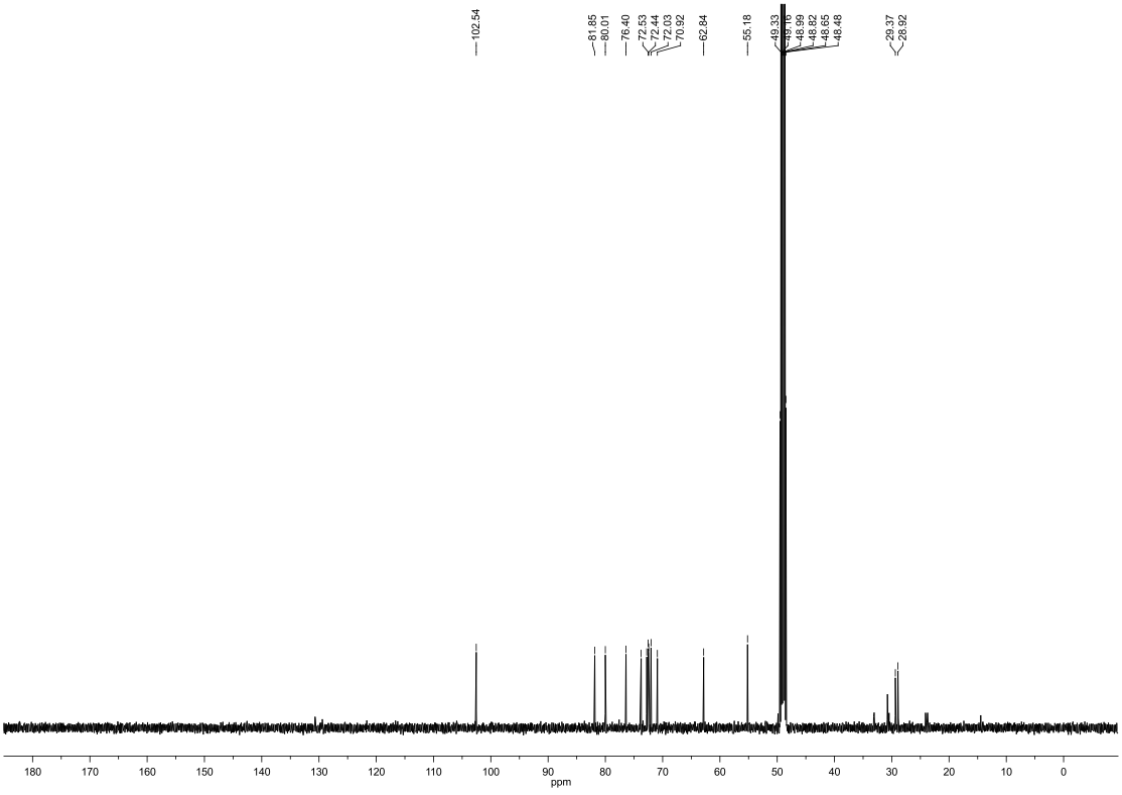


^{13}C NMR (125 MHz, $CDCl_3$)

pseudo-Disaccharide **35**

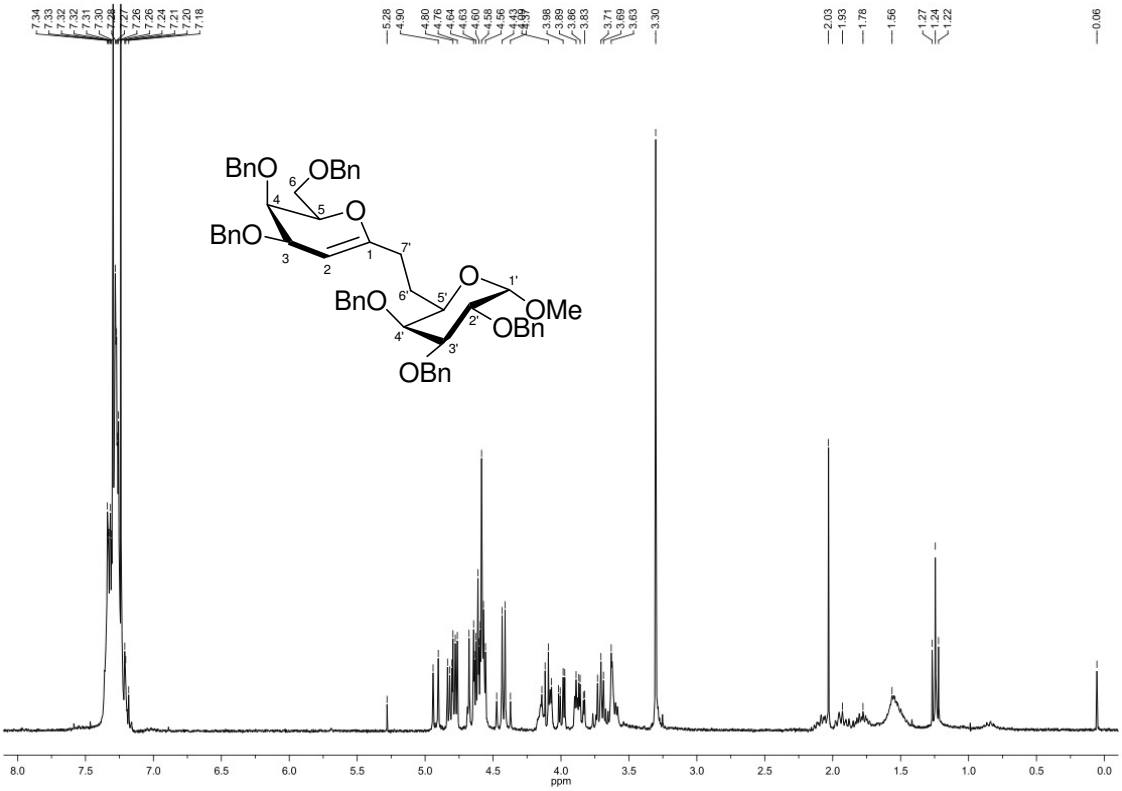


^{1}H NMR (300 MHz, CD_3OD)

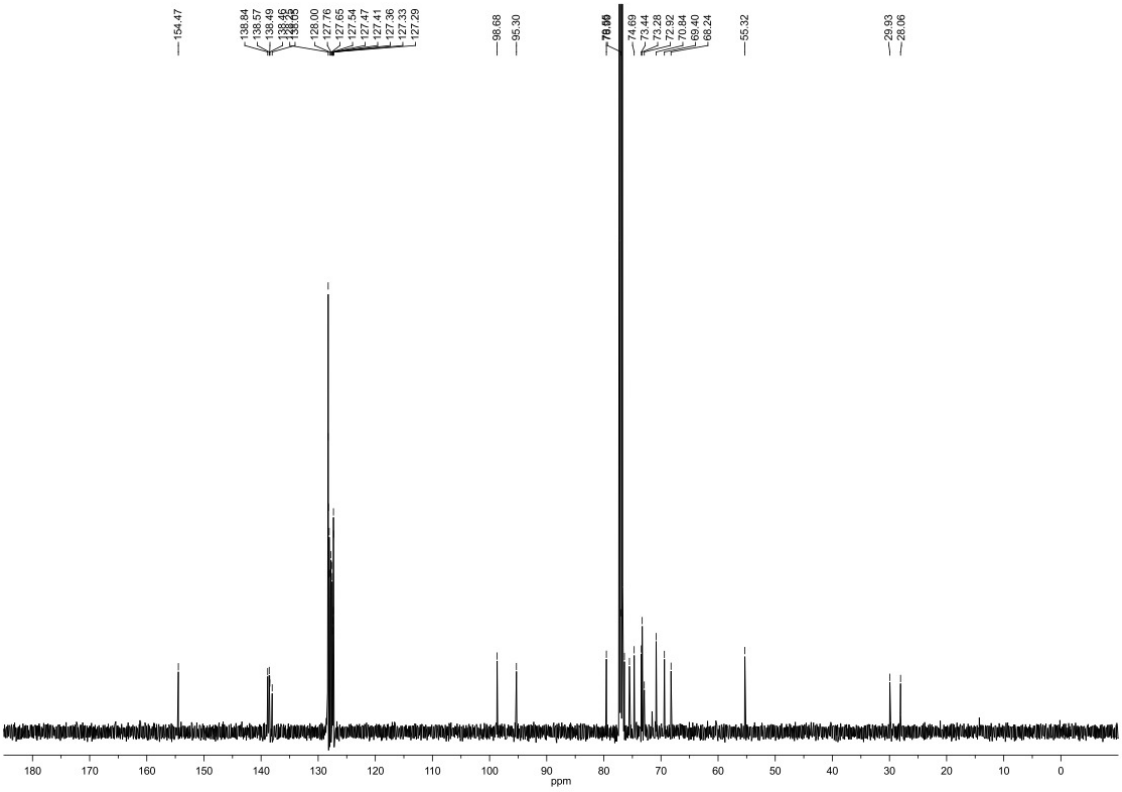


^{13}C NMR (125 MHz, CD_3OD)

Enolether *pseudo*-Disaccharide **36**

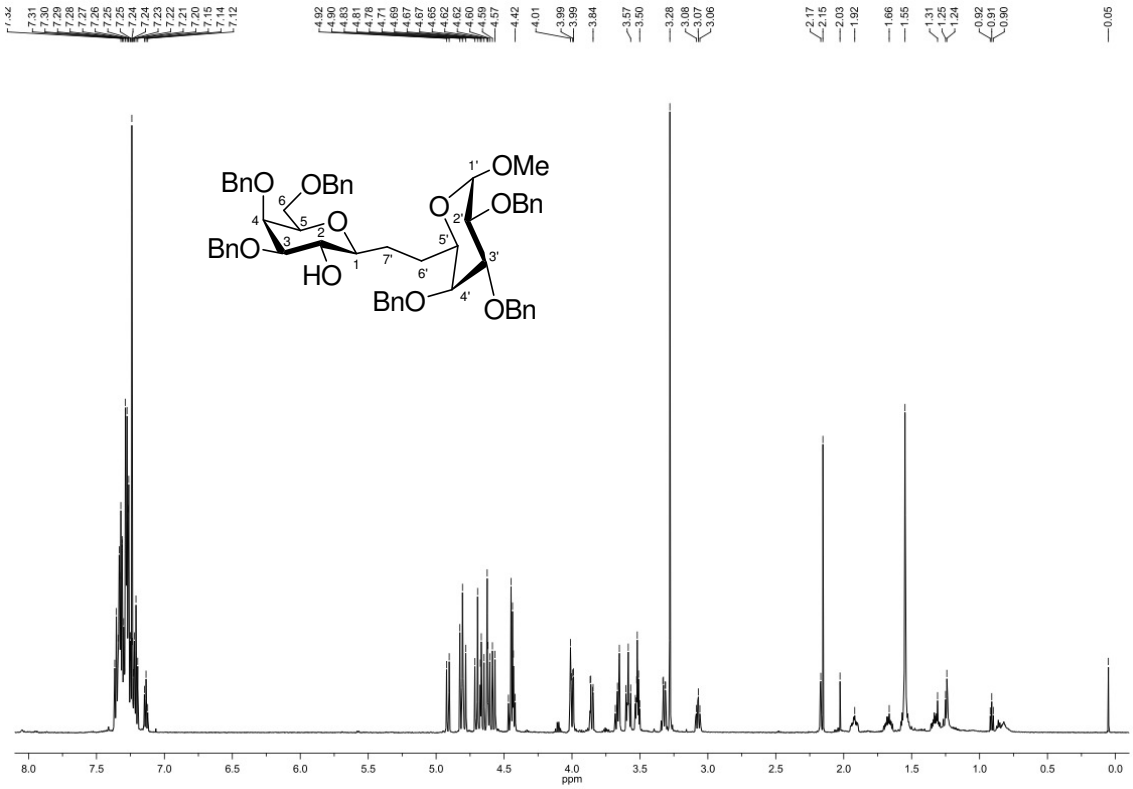


^{1}H NMR (300 MHz, $CDCl_3$)

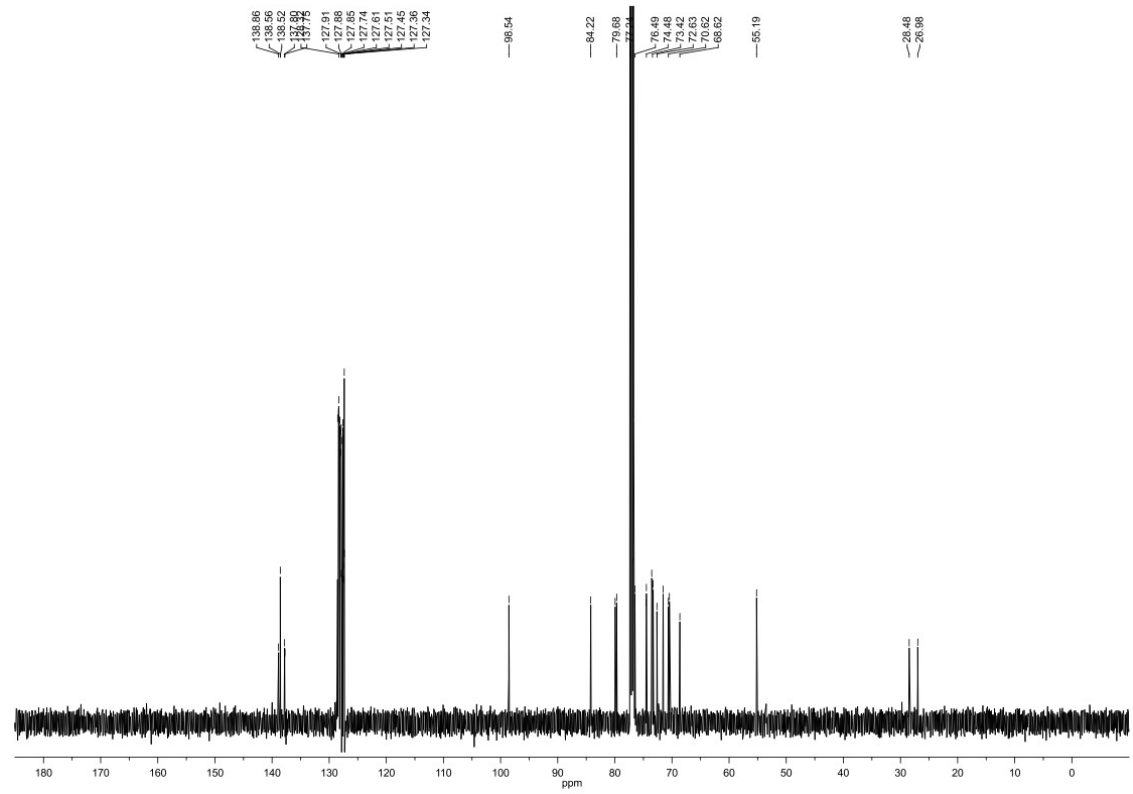


^{13}C NMR (125 MHz, $CDCl_3$)

pseudo-Disaccharide **37**

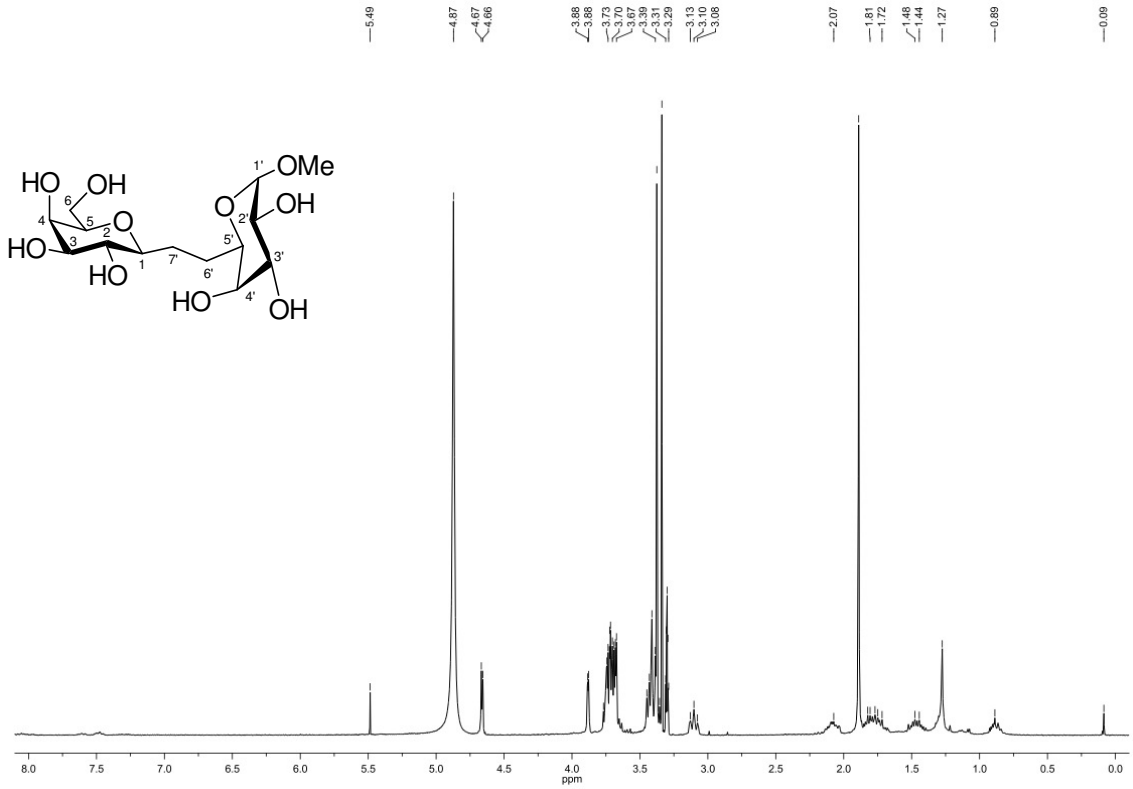


^{1}H NMR (600 MHz, $CDCl_3$)

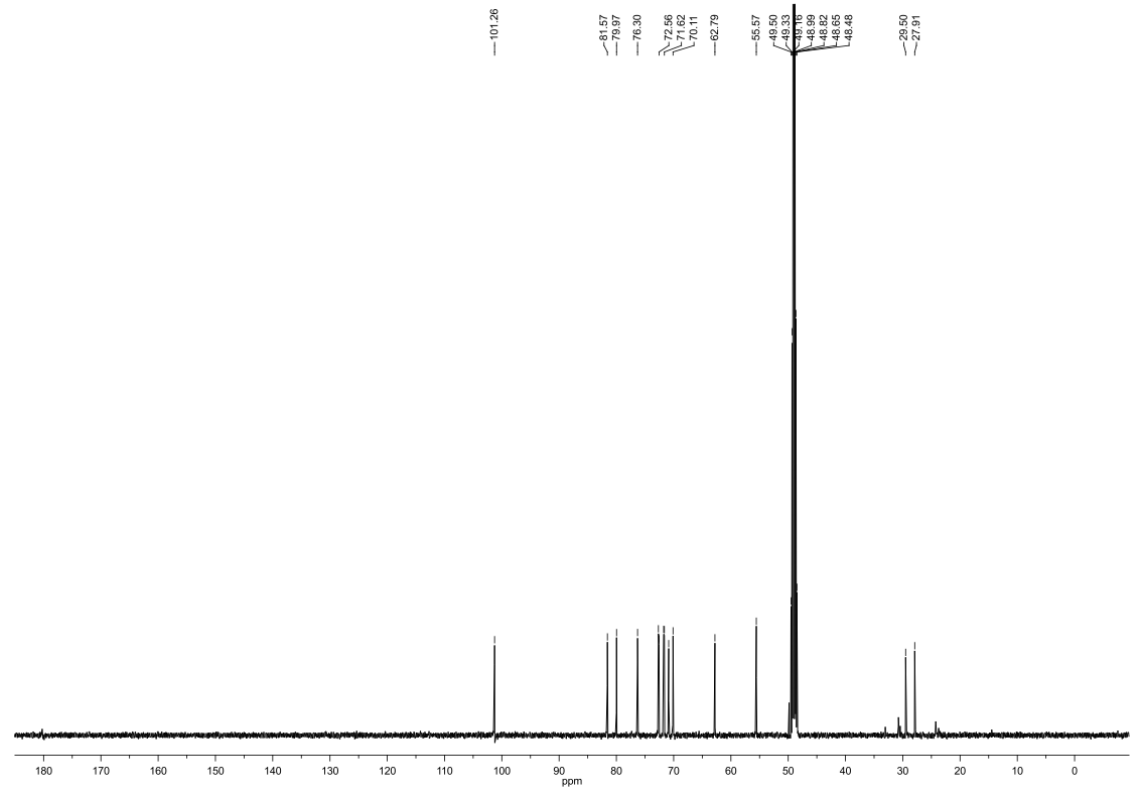


^{13}C NMR (125 MHz, $CDCl_3$)

pseudo-Disaccharide **38**

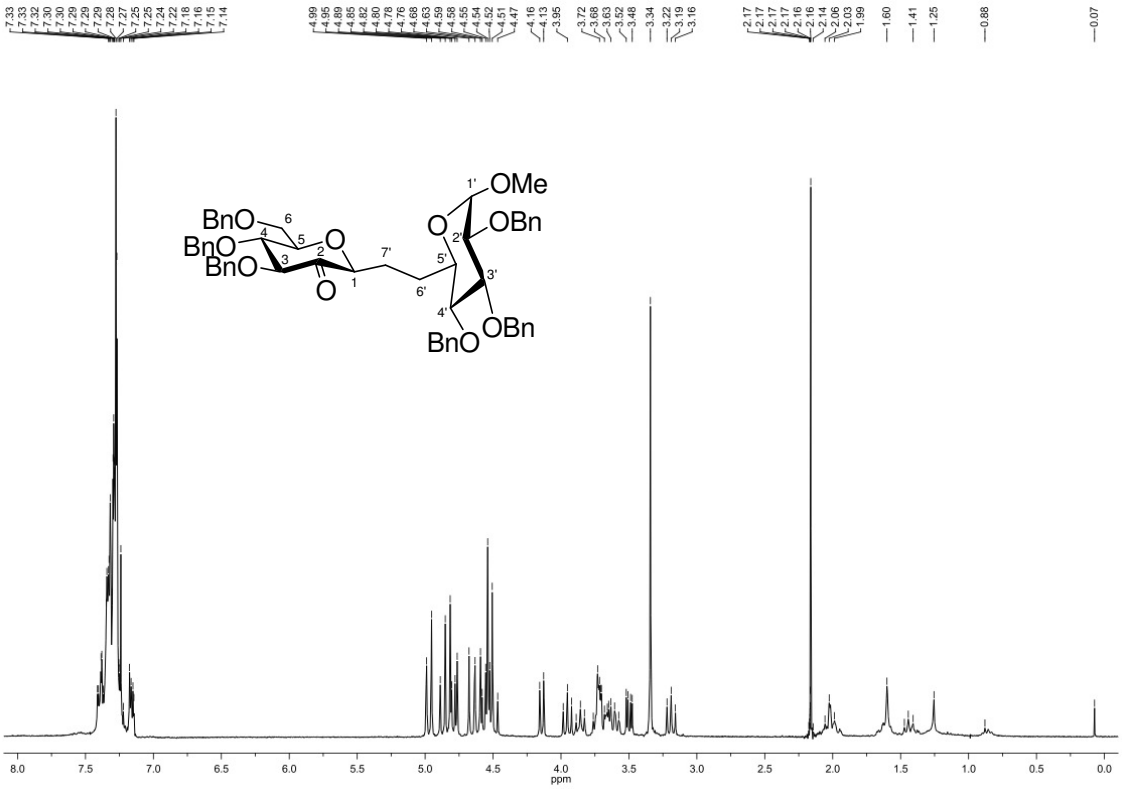


^{1}H NMR (300 MHz, CD_3OD)

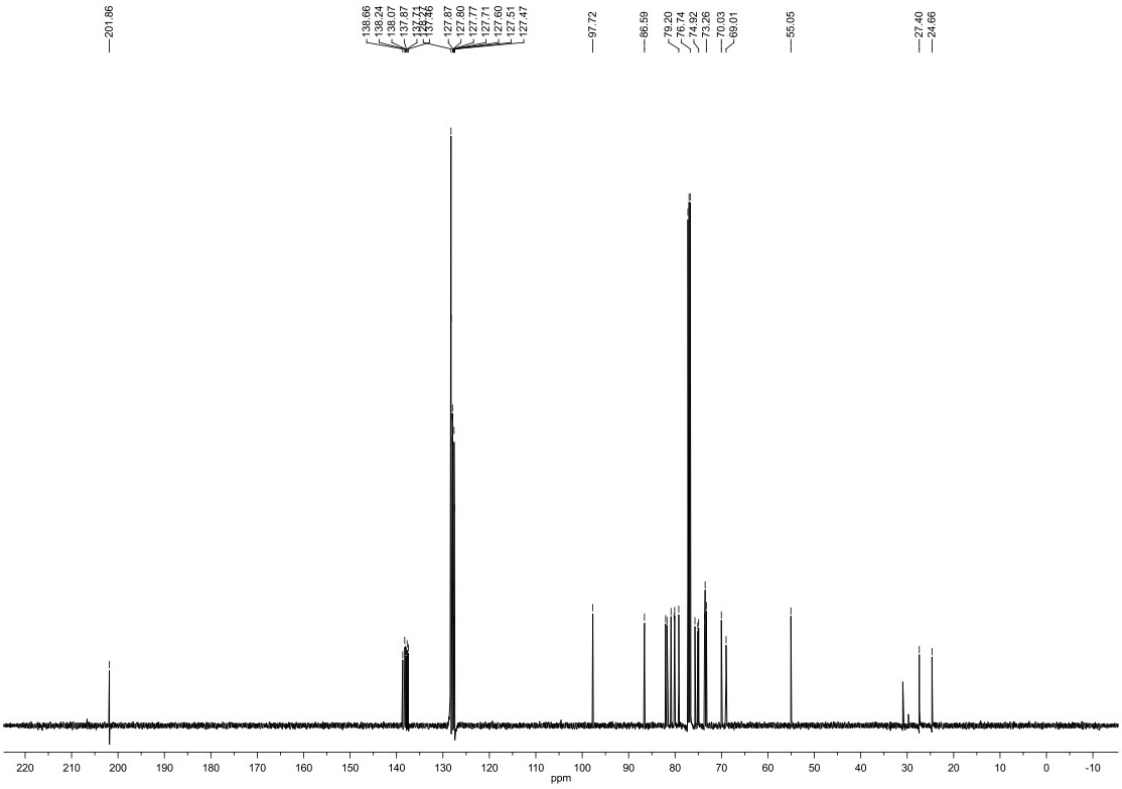


^{13}C NMR (125 MHz, CD_3OD)

pseudo-Disaccharide **39**

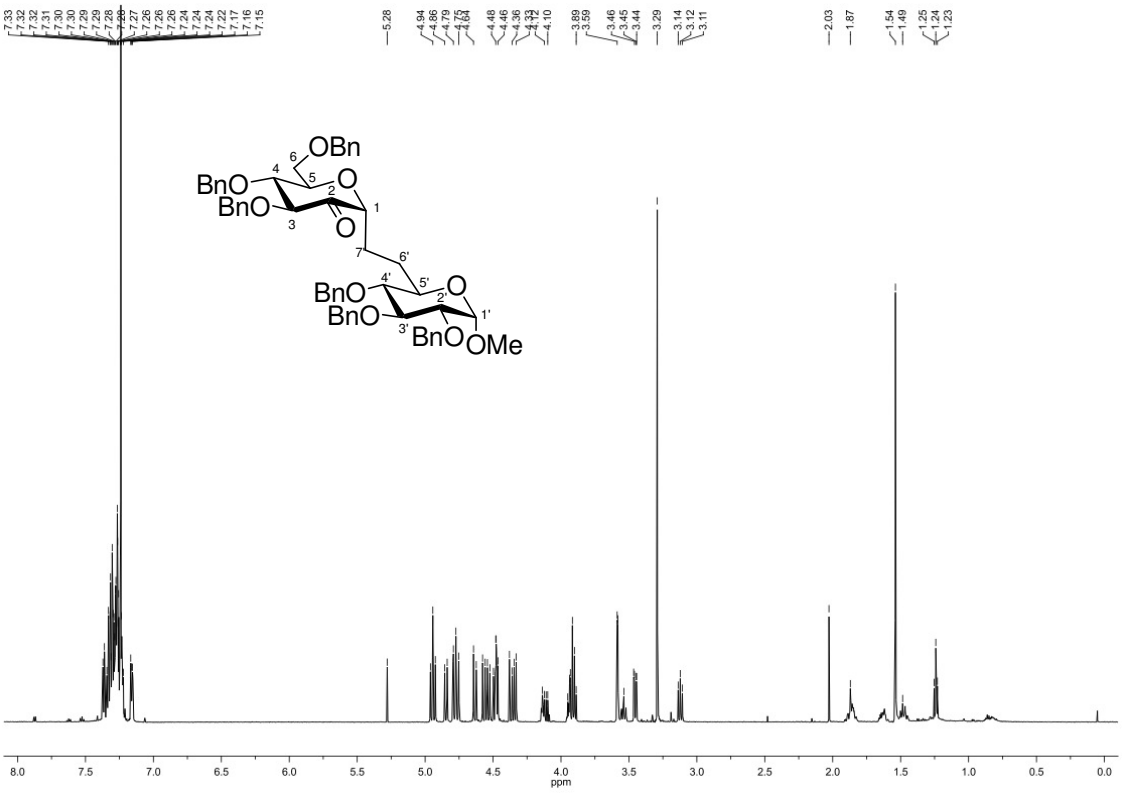


^{1}H NMR (300 MHz, $CDCl_3$)

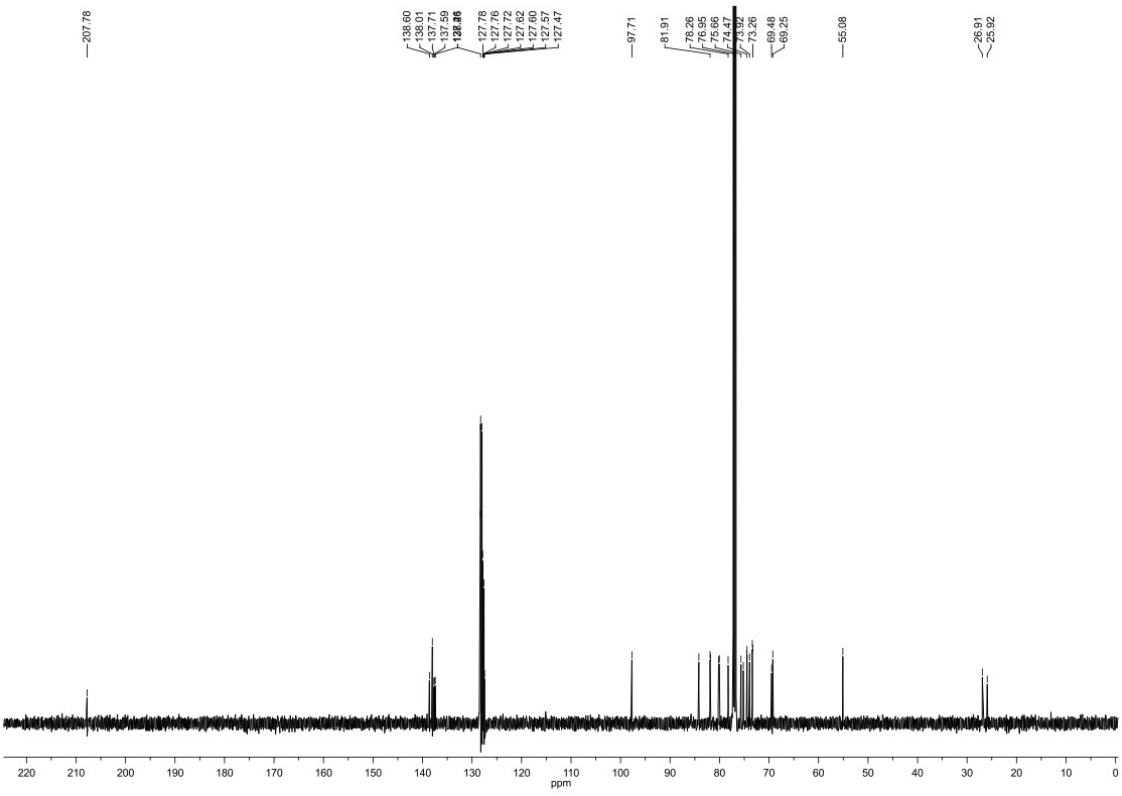


^{13}C NMR (125 MHz, $CDCl_3$)

pseudo-Disaccharide **39α**

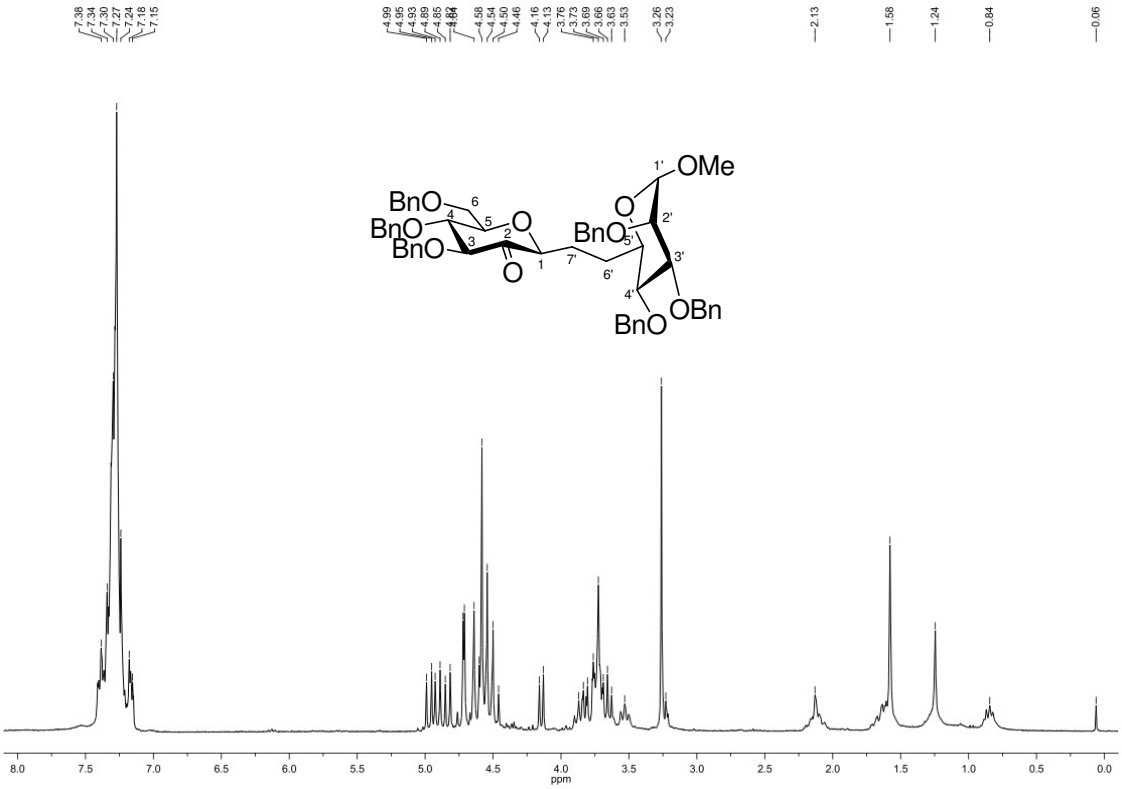


^{1}H NMR (600 MHz, $CDCl_3$)

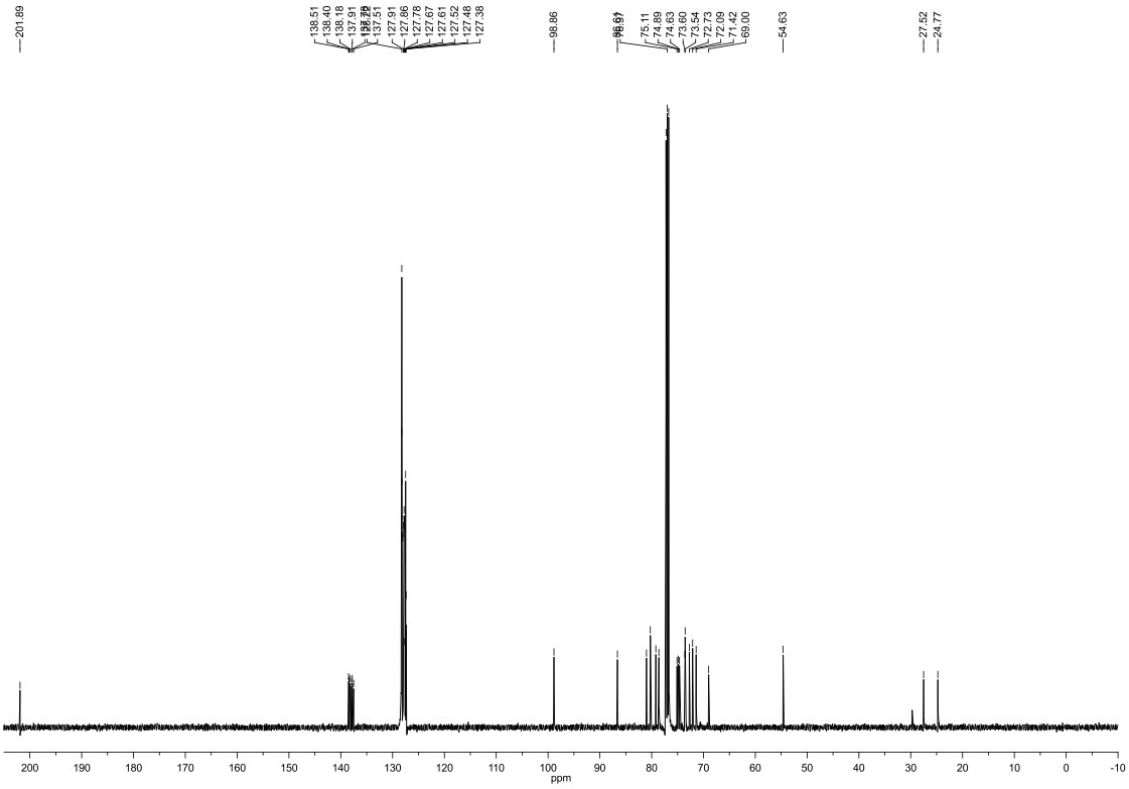


^{13}C NMR (125 MHz, $CDCl_3$)

pseudo-Disaccharide **40**

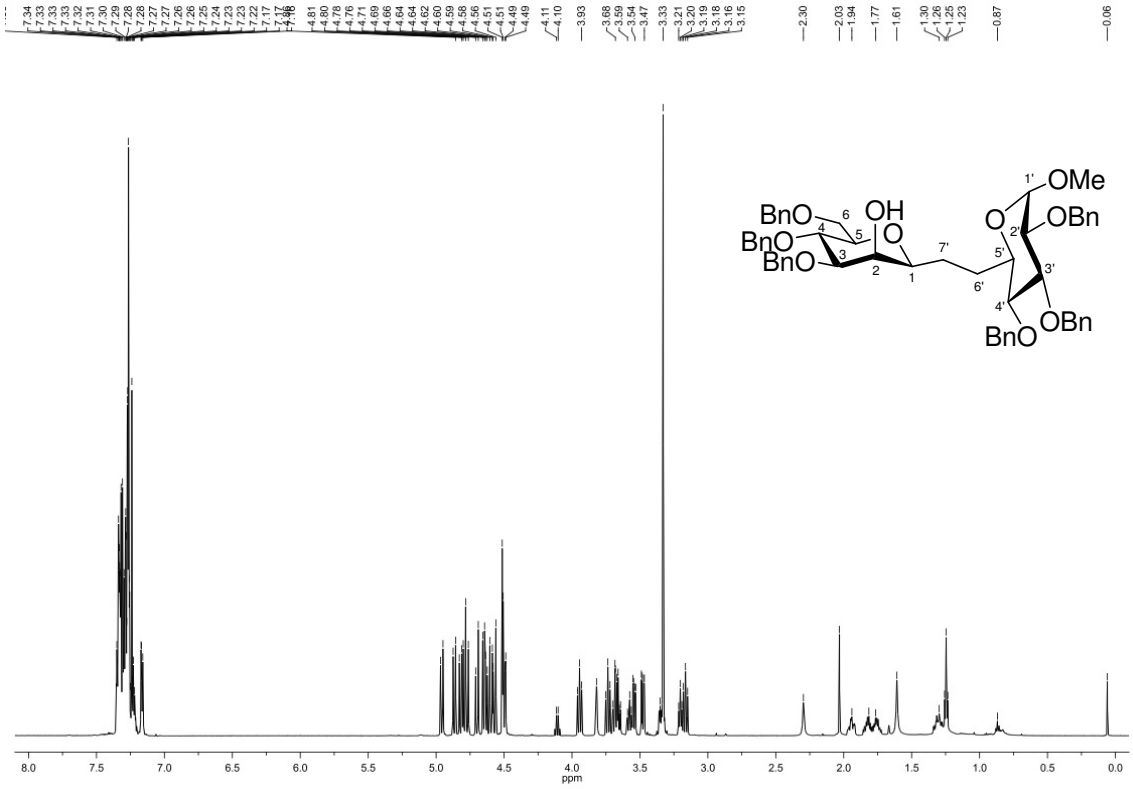


^{1}H NMR (300 MHz, $CDCl_3$)

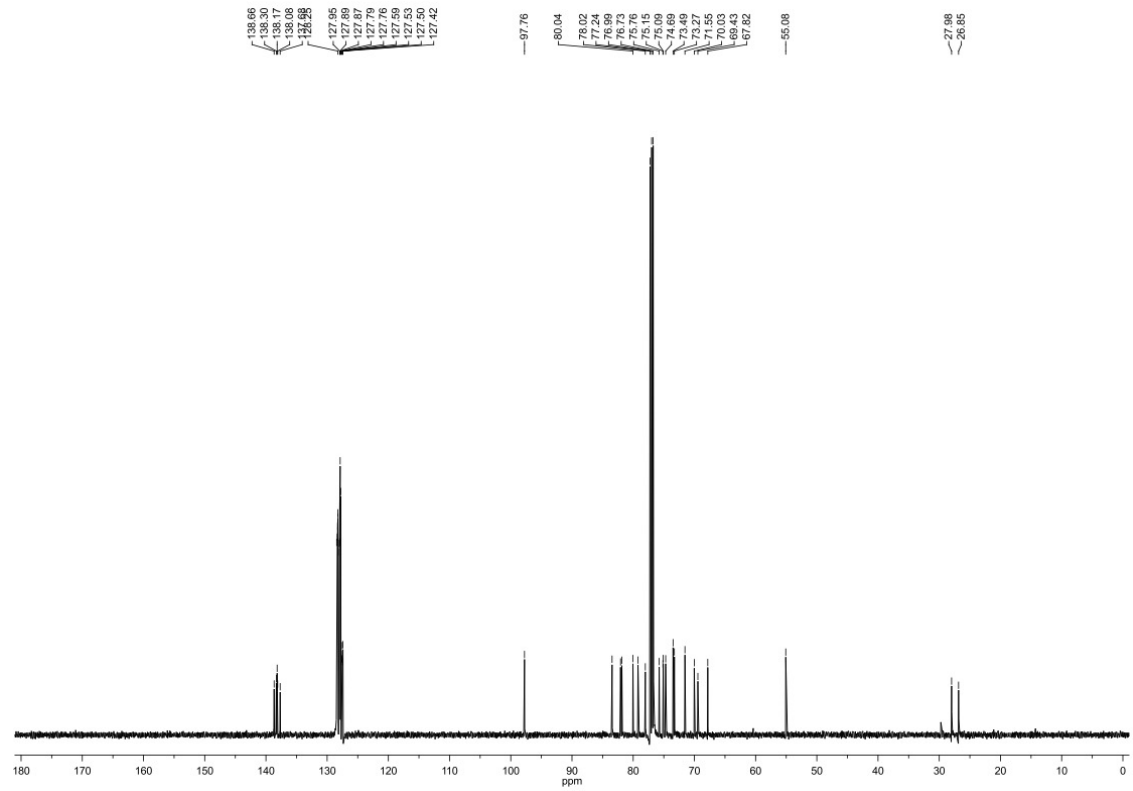


^{13}C NMR (125 MHz, $CDCl_3$)

pseudo-Disaccharide **41**

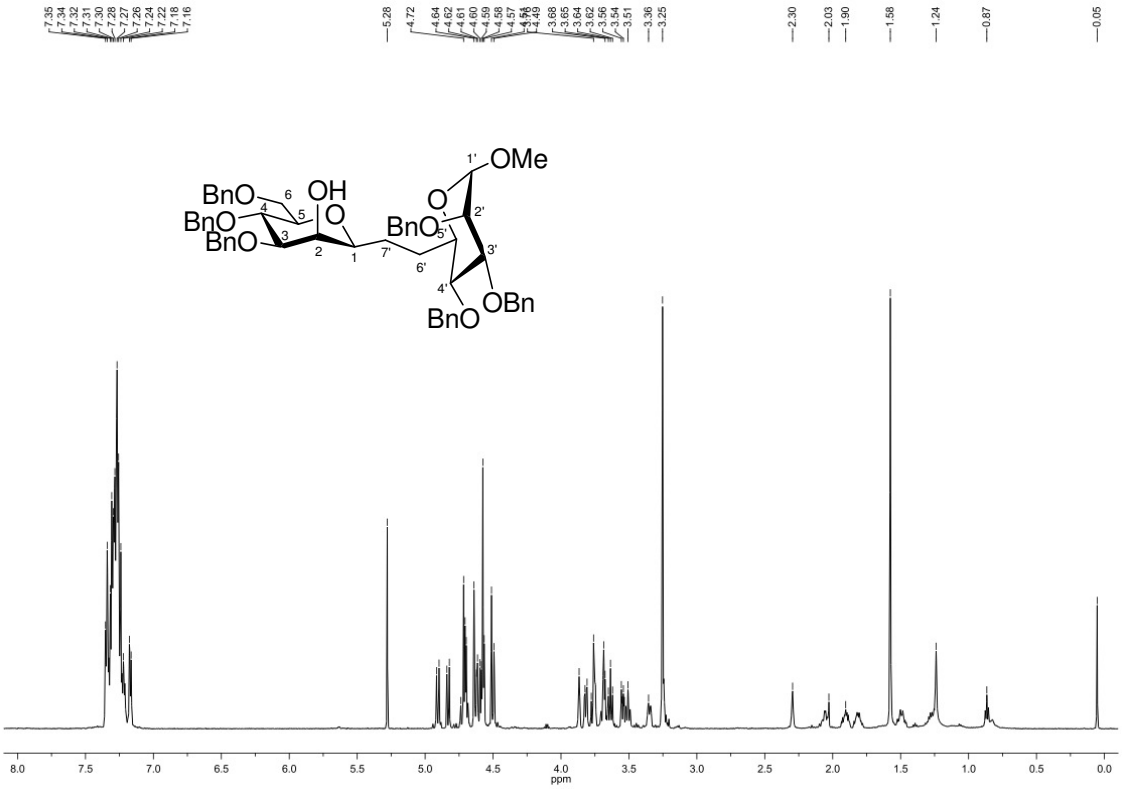


^{1}H NMR (600 MHz, $CDCl_3$)

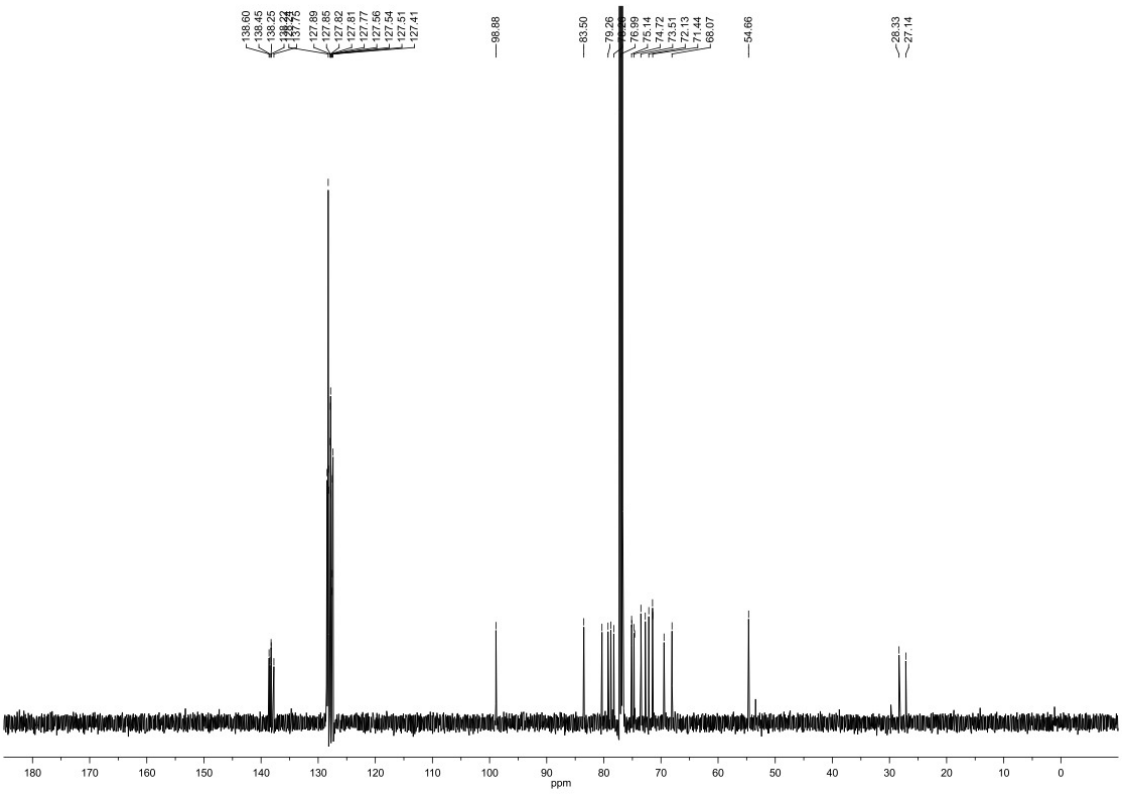


^{13}C NMR (125 MHz, $CDCl_3$)

pseudo-Disaccharide **42**



^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)