Rapid assembly of the complex, doubly-branched pentasaccharide domain of the immunoadjuvant jujuboside A via convergent $B(C_6F_5)_3$-catalyzed glycosylation of sterically-hindered precursors

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Supporting Information

A. MATERIALS AND METHODS

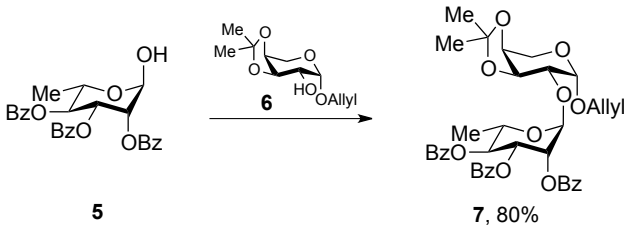
Reactions were performed in flame-dried sealed tubes or modified Schlenk (Kjeldahl shape) flasks fitted with a glass stopper under a positive pressure of argon, unless otherwise noted. Air- and moisture-sensitive liquids and solutions were transferred via syringe. The appropriate carbohydrate and sulfoxide reagents were dried via azeotropic removal of water with toluene. Molecular sieves were activated at 350 °C and were crushed immediately prior to use, then flame-dried under vacuum. Organic solutions were concentrated by rotary evaporation below 30 °C. Flash column chromatography was performed employing 230–400 mesh silica gel. Thin-layer chromatography was performed using glass plates pre-coated to a depth of 0.25 mm with 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm) and visualized under UV light (254 and 360 nm), or stained with Ceric Ammonium Molybdate in conc. H_2SO_4.

Dichloromethane, tetrahydrofuran, diethyl ether, and toluene were purified by passage through two packed columns of neutral alumina under an argon atmosphere.[1] Methanol was distilled from magnesium at 760 Torr. Trifluoromethanesulfonic anhydride was distilled from phosphorus pentoxide at 760 Torr. Boron trifluoride diethyl etherate was distilled from calcium hydride at 760 Torr. All other chemicals were obtained from commercial vendors and we[1]re used without further purification unless otherwise noted.

Automated flash chromatography was performed with an Isco Combiflash medium-pressure liquid chromatography with Redisep silica columns (47-60 μm). Infrared (IR) spectra were obtained using a Perkin Elmer Spectrum BX or a Bruker Tensor 27 spectrophotometer. Data are presented as the frequency of absorption (cm^{-1}). Proton and carbon-13 nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectra were recorded on a Bruker Avance III instrument; chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to residual proton in the NMR solvent (d-chloroform: δ 7.26 for ^{1}H NMR, δ 77.16 for ^{13}C NMR; d6-benzene: δ 7.16 for ^{1}H NMR, δ 128.06 for ^{13}C NMR; d4-methanol: δ 3.31 for ^{1}H NMR, δ 49.00 for ^{13}C NMR; d3-acetonitrile: δ 1.94 for ^{1}H NMR, δ 1.32 for ^{13}C NMR; deuterium oxide: δ 4.79 for ^{1}H NMR). Data are presented as follows: chemical shift, multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances), coupling constant in Hertz (Hz), integration, assignment.

[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J., *Organometallics* **1996**, *15*, 1518–1520.

B. SYNTHESIS OF DISACCHARIDE 3



5 **7**, 80%

(2*S*,3*R*,4*R*,5*S*,6*S*)-2-(((3a*S*,6*S*,7*R*,7a*S*)-6-(allyloxy)-2,2-dimethyltetrahydro-3a*H*-[1,3]dioxolo[4,5-*c*]pyran-7-yl)oxy)-6-methyltetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (7)
Tribenzoyl rhamnose **5**[2] (290 mg, 0.608 mmol, 2.8 equiv), phenyl sulfoxide (351 mg, 1.74 mmol, 8.0 equiv) and 2,4,6-tri-*tert*-butylpyridine (591 mg, 2.39 mmol, 11.0 equiv) were dissolved in CH_2Cl_2/PhMe (4 ml/10 mL) and cooled to –78 ºC. Tf_2O (102 μl, 0.608 mmol, 2.8 equiv) was added and after 15 min reaction mixture was warmed to –45 ºC and stirred for additional 1 hour. In a separate flask arabinose **6**[3] (50.0 mg, 0.217 mmol, 1 equiv) was dissolved in CH_2Cl_2 (5 mL) and cooled to –45 ºC. This solution of arabinose **6** was added to the reaction mixture via cannula. The reaction was stirred at this temperature for 30 min then at 0 ºC for another 30 min. The reaction mixture was diluted with 200 mL of CH_2Cl_2 and washed with saturated solution of $NaHCO_3$ (50 mL). Organic layer was dried over Na_2SO_4. Solids were removed by filtration and obtained solution was concentrated under reduced pressure. The residue was purified by automated SiO_2 column chromatography (10 g solid loading cartridge, 40 g column, 1-100% EtOAc gradient in hexanes) to yield disaccharide **7** (120 mg, 80%) as a white foamy solid.

TLC R_f 0.14 (hexanes:ethyl acetate 5:1); $[\alpha]_D^{19}$ +141.8 (*c* 1.00, C_6H_6); **FTIR** (NaCl film) 2985, 1730, 1601, 1452, 1264, 1106, 811, 803, 744, 729, 721, 676, 654, 643, 611; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.12 – 8.09 (m, 2H), 7.96 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.80 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.64 – 7.59 (m, 1H), 7.54 – 7.47 (m, 3H), 7.40 (dt, *J* = 17.5, 7.6 Hz, 3H), 7.26 – 7.22 (m, 2H), 6.02 (dddd, *J* = 16.9, 10.7, 6.0, 5.0 Hz, 1H), 5.88 (dd, *J* = 10.1, 3.4 Hz, 1H), 5.80 (dd, *J* = 3.4, 1.8 Hz, 1H), 5.64 (t, *J* = 9.9 Hz, 1H), 5.44 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.33 (d, *J* = 1.8 Hz, 1H), 5.30 (dd, *J* = 10.4, 1.5 Hz, 1H), 4.99 (d, *J* = 3.3 Hz, 1H), 4.44 (dd, *J* = 7.9, 5.6 Hz, 1H), 4.33 – 4.20 (m, 3H), 4.05 (dd, *J* = 13.2, 6.0 Hz, 1H), 4.01 (d, *J* = 2.1 Hz, 2H), 3.87 (dd, *J* = 7.9, 3.4 Hz, 1H), 1.56 (s, 3H), 1.37 (s, 3H), 1.34 (d, *J* = 6.2 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.85, 165.54, 165.53, 133.71, 133.56, 133.45, 133.17, 130.07, 129.83, 129.80, 129.58, 129.39, 129.35, 128.69, 128.54, 128.37, 117.88, 109.24, 98.45, 97.05, 77.37, 77.18, 77.16, 76.95, 74.91, 73.73, 72.05, 70.83, 69.91, 68.71, 67.09, 58.95, 28.45, 26.46, 17.91; **HRMS** (ESI) *m/z* Calcd for $C_{38}H_{40}O_{12}Na$ $[M+Na]^+$ 711.2417, found 711.2430.

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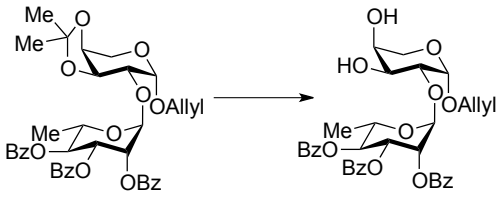
[2] P. Y. Jeong, M. Jung, Y. H. Yim, H. Kim, M. Park, E. M. Hong, W. Lee, Y. H. Kim, K. Kim and Y. K. Paik, *Nature*, 2005, **433**, 541-545.

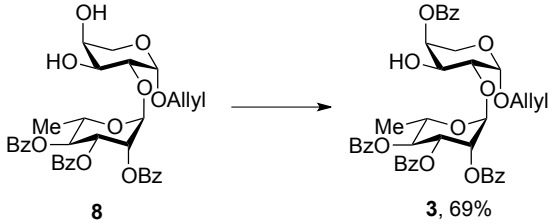
[3] (b) P. Finch, G. M. Iskander and A. H. Siriwardena, *Carbohydr. Res.*, 1991, **210**, 319-325.



7 **8**, 78%

(2S,3R,4R,5S,6S)-2-(((2S,3R,4S,5S)-2-(allyloxy)-4,5-dihydroxytetrahydro-2H-pyran-3-yl)oxy)-6-methyltetrahydro-2H-pyran-3,4,5-triyl tribenzoate (8) Disaccharide **7** (500 mg, 0.726 mmol, 1 equiv) was dissolved in CH_2Cl_2/MeOH (10 mL/ 20 mL) at ambient temperature. $TsOH{\cdot}H_2O$ (96.6 mg, 0.508 mmol, 0.7 equiv) was added and the reaction mixture was stirred for 4 hours. Et_3N (200 μl) was added to quench the reaction and concentrated. The residue was purified by automated SiO_2 column chromatography (10 g solid loading cartridge, 40 g column, 1-100% EtOAc in hexanes) to yield diol **8** (359 mg, 78%).

TLC R_f 0.12 (hexanes:ethyl acetate 3:2); $[\alpha]_D^{19}$ +90.7 (*c* 1.00, C_6H_6); **FTIR** (NaCl film) 3424, 2923, 1723, 1601, 1451, 1315, 1264, 1177, 1109, 1070, 1027, 709, 665; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.97 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.84 – 7.77 (m, 2H), 7.59 – 7.54 (m, 1H), 7.51 (td, *J* = 7.3, 1.4 Hz, 1H), 7.45 – 7.35 (m, 5H), 7.26 – 7.21 (m, 2H), 6.05 – 5.95 (m, 1H), 5.86 (dd, *J* = 10.0, 3.4 Hz, 1H), 5.83 (dd, *J* = 3.5, 1.7 Hz, 1H), 5.66 (t, *J* = 9.9 Hz, 1H), 5.40 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.26 (d, *J* = 1.8 Hz, 1H), 5.25 – 5.20 (m, 1H), 5.11 (d, *J* = 3.4 Hz, 1H), 4.40 (dq, *J* = 9.9, 6.2 Hz, 1H), 4.29 (ddt, *J* = 13.1, 5.2, 1.5 Hz, 1H), 4.22 (dt, *J* = 9.8, 3.8 Hz, 1H), 4.15 – 4.07 (m, 1H), 4.04 (dd, *J* = 9.7, 3.5 Hz, 1H), 3.97 (ddt, *J* = 13.0, 6.1, 1.5 Hz, 1H), 3.91 – 3.84 (m, 1H), 3.76 (dd, *J* = 12.5, 1.8 Hz, 1H), 3.56 (bs, 1H), 3.11 (bs, 1H), 1.33 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.90, 165.81, 165.74, 133.81, 133.68, 133.51, 133.35, 130.06, 129.86, 129.39, 129.34, 129.19, 128.71, 128.58, 128.46, 117.59, 99.90, 98.00, 79.21, 77.37, 77.16, 76.95, 71.77, 70.70, 70.20, 69.51, 68.75, 68.14, 67.27, 62.05, 17.97; **HRMS** (ESI) *m/z* Calcd for $C_{35}H_{36}O_{12}Na$ $[M+Na]^+$ 671.2104, found 671.2097.



8 **3**, 69%

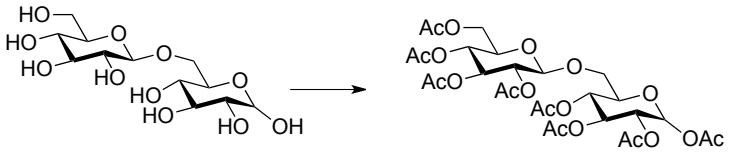
(2*S*,3*R*,4*R*,5*S*,6*S*)-2-(((2*S*,3*R*,4*S*,5*S*)-2-(allyloxy)-5-(benzoyloxy)-4-hydroxytetrahydro-2*H*-pyran-3-yl)oxy)-6-methyltetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (3)** *i*. Diol **8** (1.413 g, 2.178 mmol, 1 equiv.) and $Ph(OEt)_3$ (3.0 mL, 13 mmol, 6 equiv.) were dissolved in PhMe (30 mL) at ambient temperature. $TsOH{\cdot}H_2O$ (112.5mg, 0.6534 mmol, 0.3 equiv.) was added and the reaction mixture was stirred at this temperature for 90 min. The reaction was quenched by addition of Et_3N (0.5 mL), then diluted with CH_2Cl_2 (100 mL) and washed with H_2O (2 x 40 mL). Organic layer was dried over Na_2SO_4. Solids were removed by filtration and the obtained solution was concentrated. The residue obtained was used in the subsequent step.

ii. The residue from step *i* was dissolved in AcOH/H_2O (16 ml/ 4mL) and stirred for 90 min. At this point AcOH and H_2O were azeotropically removed with the aid of PhMe and the

residue was purified by automated SiO_2 column chromatography (10 g solid loading cartridge, 40 g column, 1-100% EtOAc in hexanes) to yield disaccharide **3** (1.125 g, 69%) as a white solid.

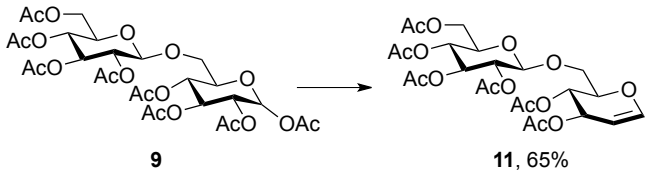
TLC R_f 0.40 (hexanes:ethyl acetate 2:1); $[\alpha]_D^{19}$ +188.3 (*c* 1.00, C_6H_6); **FTIR** (NaCl film) 3486, 2982, 1728, 1602, 1451, 1267, 1177, 1069, 1026, 928, 813, 804, 799, 791, 753, 739, 701, 664, 647, 633, 615; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.12 – 8.08 (m, 2H), 8.08 – 8.05 (m, 2H), 7.98 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.82 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.63 – 7.58 (m, 1H), 7.58 – 7.51 (m, 2H), 7.50 – 7.38 (m, 7H), 7.29 – 7.23 (m, 2H), 6.04 (dddd, *J* = 16.9, 10.8, 6.1, 5.0 Hz, 1H), 5.89 (dd, *J* = 10.1, 3.4 Hz, 1H), 5.78 (dd, *J* = 3.4, 1.8 Hz, 1H), 5.68 (t, *J* = 9.9 Hz, 1H), 5.54 – 5.48 (m, 1H), 5.44 (dq, *J* = 17.3, 1.6 Hz, 1H), 5.32 (d, *J* = 1.8 Hz, 1H), 5.29 (dd, *J* = 10.5, 1.4 Hz, 1H), 5.17 (d, *J* = 3.5 Hz, 1H), 4.44 (dt, *J* = 10.1, 4.0 Hz, 1H), 4.40 (dd, *J* = 9.8, 6.2 Hz, 1H), 4.32 (ddt, *J* = 13.0, 5.1, 1.5 Hz, 1H), 4.12 (dd, *J* = 10.0, 3.5 Hz, 1H), 4.05 – 4.02 (m, 1H), 4.02 – 3.99 (m, 1H), 3.88 (dd, *J* = 13.1, 1.9 Hz, 1H), 2.65 (d, *J* = 4.4 Hz, 1H), 1.36 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.49, 165.82, 165.70, 165.58, 133.66, 133.63, 133.51, 133.36, 133.27, 130.02, 129.99, 129.96, 129.85, 129.82, 129.41, 129.37, 129.25, 128.70, 128.58, 128.55, 128.41, 117.90, 99.80, 97.87, 79.04, 77.37, 77.16, 76.95, 72.31, 71.85, 70.69, 70.01, 68.88, 67.33, 67.02, 60.84, 17.98; **HRMS** (ESI) *m/z* Calcd for $C_{42}H_{40}O_{13}Na$ $[M+Na]^+$ 775.2367, found 775.2332.

C. SYNTHESIS OF TRISACCHARIDE 2



(2*S*,3*R*,4*S*,5*R*,6*R*)-6-((((2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)methyl)tetrahydro-2*H*-pyran-2,3,4,5-tetrayl tetraacetate (9) β-gentiobiose (350 mg, 0.892 mmol, 1 equiv.) was suspended in mixture of Py/Ac_2O (30 mL/ 45 mL) and heated to 60 ºC for 24 hrs. Reaction mixture was cooled to room temperature, diluted with EtOAc (500 mL), and washed sequentially with H_2O (2 x 100 mL), 1M HCl (2 x 150 mL), saturated solution of $NaHCO_3$ (150 mL) and brine (150 mL). Organic layer was dried on $MgSO_4$. Solids were removed by filtration and obtained solution was concentrated. The residue was purified by automated SiO_2 column chromatography (10 g solid loading cartridge, 40 g column, 1-100% EtOAc in hexanes) to yield β-gentiobiose octaacetate **9** (617.5 mg, 95%) as white solid.

TLC R_f 0.20 (hexanes:ethyl acetate 1:1); $[\alpha]_D^{19}$ +1.5 (*c* 1.00, C_6H_6); **FTIR** (NaCl film) 2945, 1753, 1433, 1369, 1220, 1038, 908, 734, 699; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.68 (d, *J* = 8.3 Hz, 1H), 5.22 (t, *J* = 9.4 Hz, 1H), 5.18 (t, *J* = 9.5 Hz, 1H), 5.10 – 5.03 (m, 2H), 5.01 – 4.95 (m, 2H), 4.53 (d, *J* = 8.0 Hz, 1H), 4.25 (dd, *J* = 12.3, 4.9 Hz, 1H), 4.11 (dd, *J* = 12.3, 2.3 Hz, 1H), 3.92 (dd, *J* = 11.4, 2.4 Hz, 1H), 3.78 (ddd, *J* = 10.2, 5.8, 2.4 Hz, 1H), 3.66 (ddd, *J* = 10.1, 4.8, 2.4 Hz, 1H), 3.56 (dd, *J* = 11.4, 5.7 Hz, 1H), 2.10 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.99 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.68, 170.27, 170.11, 169.54, 169.41, 169.40, 169.25, 168.83, 100.62, 91.58, 77.24, 77.03, 76.82, 73.88, 72.85, 72.73, 71.90, 70.86, 70.22, 68.39, 68.29, 67.49, 61.82, 20.82, 20.77, 20.64, 20.62, 20.60, 20.59, 20.58; **HRMS** (ESI) *m/z* Calcd for $C_{28}H_{38}O_{19}Na$ $[M+Na]^+$ 701.1905, found 701.1882.



(2*R*,3*R*,4*S*,5*R*,6*R*)-2-(acetoxymethyl)-6-(((2*R*,3*S*,4*R*)-3,4-diacetoxy-3,4-dihydro-2*H*-pyran-2-yl)methoxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (11) $TiBr_4$ (302 mg, 0.822, 0.6 equiv.) was suspended in CH_2Cl_2 (10 mL) at ambient temperature. AcOH (1 drop) was added and stirred for 5 min. Solution of β-gentiobiose octaacetate **9** (930.0 mg, 1.371 mmol, 1 equiv.) in CH_2Cl_2 (10 mL) was added dropwise. The addition funnel was rinsed with additional CH_2Cl_2 (10 mL) and added to the reaction mixture. Reaction mixture was stirred for 24 hrs and quenched by adding solid $NaHCO_3$ in 4 portions (500 mg each). Each portion was followed by addition of 30 drops of water. Additional water (50 mL) was added and extracted with CH_2Cl_2 (3 x 40 mL), dried over Na_2SO_4, filtered, concentrated to give crude glycosyl bromide as off white solid, which was carried to next step without further purification.

Glycosyl bromide (940 mg, 1.34 mmol, 1 equiv.), freshly activated zinc dust (439 mg, 6.72 mmol, 5 equiv.) and NH_4Cl (359 mg, 6.72 mmol, 5 equiv.) were combined in MeOH (1.6

mL) at ambient temperature. To this mixture V(O)Salen (**10**)[4] (13 mg, 0.040 mmol, 0.03 equiv.) was added. Reaction mixture was stirred for 30 min, filtered through a pad of Celite and concentrated. The residue was dissolved in EtOAc (100 mL), washed with saturated solution of $NaHCO_3$ (50 mL) and brine (50 mL), dried over $MgSO_4$. Solids were removed by filtration and obtained solution was concentrated. The residue was purified by automated SiO_2 column chromatography (10 g solid loading cartridge, 40 g column, 1-100% EtOAc in hexanes) to yield glucal **11** (553 mg, 73% over 2 steps) as a white solid.

TLC R_f 0.31 (hexanes:ethyl acetate 1:1); $[\alpha]_D^{19}$ -28.9 (*c* 1.00, C_6H_6); **FTIR** (NaCl film) 2959, 2891, 1753, 1650, 1433, 1371, 1224, 1174, 1136, 1039, 906, 820, 735, 701; **^{1}H NMR** (600 MHz, C_6D_6) δ 6.14 (dd, *J* = 6.2, 1.2 Hz, 1H), 5.43 (dt, *J* = 5.1, 1.2 Hz, 1H), 5.40 (t, *J* = 9.6 Hz, 1H), 5.35 (dd, *J* = 6.8, 5.1 Hz, 1H), 5.30 (dd, *J* = 9.6, 7.9 Hz, 1H), 5.25 (dd, *J* = 10.1, 9.3 Hz, 1H), 4.70 (dd, *J* = 6.0, 3.5 Hz, 1H), 4.29 (d, *J* = 7.9 Hz, 1H), 4.24 (dd, *J* = 12.3, 4.4 Hz, 1H), 4.17 (tdd, *J* = 6.6, 4.3, 1.0 Hz, 1H), 4.00 (dd, *J* = 12.4, 2.3 Hz, 1H), 3.97 (dd, *J* = 11.2, 4.4 Hz, 1H), 3.65 (dd, *J* = 11.2, 6.6 Hz, 1H), 3.18 (ddd, *J* = 10.1, 4.4, 2.3 Hz, 1H), 1.89 (s, 3H), 1.70 (s, 3H), 1.69 (s, 3H), 1.68 (s, 3H), 1.67 (s, 3H), 1.63 (s, 3H); **^{13}C NMR** (151 MHz, C_6D6) δ 170.07, 169.99, 169.88, 169.26, 169.09, 169.08, 145.83, 101.09, 98.91, 74.82, 73.26, 72.25, 71.63, 68.63, 67.92, 66.96, 66.92, 61.67, 20.57, 20.44, 20.37, 20.28, 20.25, 20.18; **HRMS** (ESI) *m/z* Calcd for $C_{24}H_{32}O_{15}Na$ $[M+Na]^+$ 583.1639, found 583.1630.

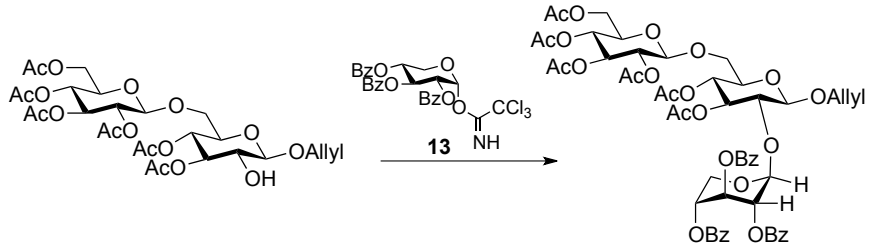
11 **12**

(2*R*,3*R*,4*S*,5*R*,6*R*)-2-(acetoxymethyl)-6-(((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4-diacetoxy-6-(allyloxy)-5-hydroxytetrahydro-2*H*-pyran-2-yl)methoxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (12) Glucal **11** (1.00 g, 1.78 mmol, 1 equiv.) was dissolved in CH_2Cl_2 (40 mL) and cooled to –78 ºC. Solution of dimethyldioxirane (0.065 M, 41.2 mL, 2.67 mmol, 1.5 equiv.) was added and the reaction mixture was stirred for 30 min at –78 ºC, then warmed to 0 ºC and stirred for another 20 min and concentrated under vacuum (at 0 ºC). The residue was dissolved in allyl alcohol (40 mL) and stirred for 5 hrs at ambient temperature. Excess allyl alcohol was removed by rotary evaporation and the residue was purified by automated SiO_2 column chromatography (10 g solid loading cartridge, 80 g column, 1-100% MTBE in PhMe) to yield disaccharide **12** (827 mg, 73%) as a white solid.

TLC R_f 0.13 (hexanes:ethyl acetate 1:1); $[\alpha]_D^{19}$ +9.0 (*c* 1.00, C_6H_6); **FTIR** (NaCl film) 3487, 2944, 1752, 1431, 1368, 1223, 1171, 1037, 907, 735, 699, 600; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.94 (dddd, *J* = 17.0, 10.4, 6.4, 5.1 Hz, 1H), 5.38 (dq, *J* = 17.3, 1.6 Hz, 1H), 5.28 (dq, *J* = 10.4, 1.3 Hz, 1H), 5.20 (t, *J* = 9.5 Hz, 1H), 5.13 (t, *J* = 9.6 Hz, 1H), 5.09 (t, *J* = 9.5 Hz, 1H), 5.02 (dd, *J* = 9.6, 8.0 Hz, 1H), 4.87 (dd, *J* = 10.1, 9.3 Hz, 1H), 4.61 (d, *J* = 8.0 Hz, 1H), 4.44 – 4.39 (m, 2H), 4.28 (dd, *J* = 12.3, 4.8 Hz, 1H), 4.20 – 4.12 (m, 2H), 3.89 (dd, *J* = 11.0, 2.1 Hz, 1H), 3.73 – 3.65 (m, 2H), 3.65 – 3.55 (m, 2H), 2.48 (d, *J* = 3.0 Hz, 1H), 2.11 (s, 3H), 2.09 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.81, 170.77,

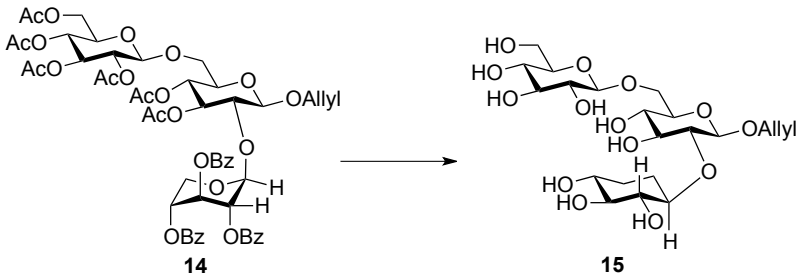
[4] Choudhary, N.; Hughes, D. L.; Kleinkes, U.; Larkworthy, L. F.; Leigh, G. J.; Maiwald, M.; Marmion, C. J.; Sanders, J. R.; Smith, G. W.; Sudbrake, C. *Polyhedron* **1997**, *16*, 1517–1528.

170.37, 169.95, 169.53, 169.39, 133.31, 118.58, 101.48, 100.84, 77.37, 77.16, 76.95, 74.50, 73.46, 72.87, 72.27, 72.03, 71.20, 70.45, 69.15, 68.35, 61.93, 20.95, 20.89, 20.82, 20.75, 20.74; **HRMS** (ESI) *m/z* Calcd for $C_{27}H_{38}O_{17}Na$ $[M+Na]^+$ 657.2007, found 657.2029.

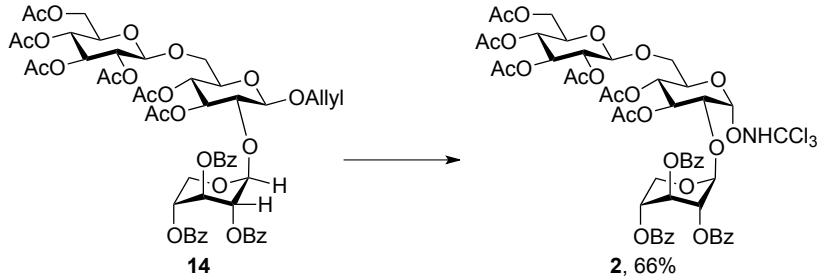


(2*S*,3*R*,4*S*,5*R*)-2-(((2*R*,3*R*,4*S*,5*R*,6*R*)-4,5-diacetoxy-2-(allyloxy)-6-((((2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)methyl)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (14) β-gentiobiose derivative **12** (160 mg, 0.252 mmol, 1 equiv.) and xylose trichloroimidate **13** (306 mg, 0.504 mmol, 2 equiv.) were azeotropically dried with PhMe (3 mL), then dissolved in CH_2Cl_2 (15 mL) and cooled to –20 ºC. Powdered 4A mol. sieves (100 mg) was added and the mixture was stirred for 10 min. TMSOTf (4.2 μl, 0.025 mmol, 0.12 equiv.) was added and the reaction mixture was stirred at – 20 ºC for 40 min, and then quenched by adding Et_3N (250 μl). The reaction mixture was allowed to warm to room temperature, filtered through a pad of celite and the obtained solution was concentrated. The residue was purified by automated SiO_2 column chromatography (10 g solid loading cartridge, 40 g column, 1-100% EtOAc in hexanes) to yield trisaccharide **14** (225 mg, 83%) as a white solid.

TLC R_f 0.29 (hexanes:ethyl acetate 1:1); $[\alpha]_D^{19}$ -46.9 (*c* 1.00, C_6H_6); **FTIR** (NaCl film) 3063, 2944, 2881, 1753, 1601, 1584, 1491, 1452, 1367, 1260, 1176, 1039, 906, 803, 736, 713, 599; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 2H), 7.91 – 7.85 (m, 2H), 7.83 – 7.76 (m, 2H), 7.50 – 7.38 (m, 3H), 7.33 – 7.28 (m, 4H), 7.22 – 7.16 (m, 2H), 5.84 (dddd, *J* = 16.9, 10.4, 6.3, 5.1 Hz, 1H), 5.55 (t, *J* = 5.9 Hz, 1H), 5.26 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.19 – 5.05 (m, 5H), 5.02 (d, *J* = 4.0 Hz, 1H), 4.98 (t, *J* = 9.7 Hz, 1H), 4.90 (dd, *J* = 9.6, 7.9 Hz, 1H), 4.67 (t, *J* = 9.7 Hz, 1H), 4.51 (dd, *J* = 12.9, 3.6 Hz, 1H), 4.48 (d, *J* = 8.0 Hz, 1H), 4.42 (d, *J* = 7.7 Hz, 1H), 4.38 – 4.32 (m, 1H), 4.16 (dd, *J* = 12.3, 4.8 Hz, 1H), 4.04 (dddd, *J* = 12.3, 9.2, 5.2, 1.8 Hz, 2H), 3.75 (dd, *J* = 11.1, 2.2 Hz, 1H), 3.70 (dd, *J* = 9.5, 7.7 Hz, 1H), 3.62 (dd, *J* = 12.8, 4.9 Hz, 1H), 3.57 (ddd, *J* = 10.0, 4.8, 2.5 Hz, 2H), 3.48 (dd, *J* = 11.0, 7.3 Hz, 1H), 1.98 (s, 3H), 1.94 (s, 3H), 1.92 (s, 3H), 1.90 (s, 3H), 1.87 (s, 3H), 1.77 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.74, 170.36, 170.10, 169.97, 169.53, 169.39, 165.76, 165.21, 165.17, 133.57, 133.52, 133.49, 133.33, 130.09, 129.96, 129.94, 129.51, 129.29, 129.23, 128.57, 128.52, 128.50, 128.47, 128.46, 128.44, 118.35, 100.84, 100.64, 99.16, 77.37, 77.16, 76.95, 76.76, 74.42, 73.11, 72.89, 72.05, 71.20, 70.53, 69.83, 69.57, 69.29, 68.70, 68.39, 68.34, 61.91, 60.64, 20.89, 20.83, 20.77, 20.75, 20.74, 20.70; **HRMS** (ESI) *m/z* Calcd for $C_{53}H_{58}O_{24}Na$ $[M+Na]^+$ 1101.3216, found 1101.3182.



Deprotection of the trisaccharide (14) To the solution of the trisaccharide **14** (6.0 mg, 0.0067 mmol, 1 equiv) in MeOH (1 mL) was added MeONa (3.6 mg, 0.067 mmol, 10 equiv). The reaction mixture was stirred at ambient temperature for 16 hrs and concentrated. Residue was dissolved in D_2O and analized by ^1H NMR.



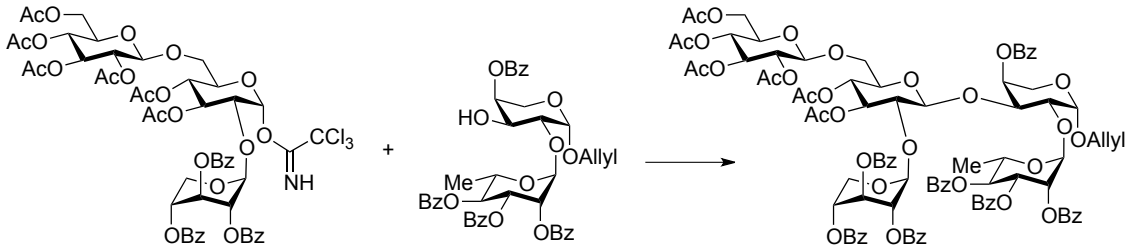
(2*S*,3*R*,4*S*,5*R*)-2-(((2*S*,3*R*,4*S*,5*R*,6*R*)-4,5-diacetoxy-6-((((2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)methyl)-2-(2,2,2-trichloro-1-iminoethoxy)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (2) Trisaccharide **14** (182 mg, 0.169 mmol, 1equiv) was dissolved in MeOH (10mL). $PdCl_2$ (15.0 mg 0.0844 mmol, 0.5 equiv) was added and the reaction mixture was stirred at ambient temperature for 4 hrs and concentrated. The residue was then dissolved in CH_2Cl_2 (10 mL) and filtered through a pad of Celite. The Celite layer was washed with additional CH_2Cl_2 (3x 10 mL). Combined CH_2Cl_2 layers were concentrated and carried to the next step without further purification.

The residue from the previous step was dissolved in CH_2Cl_2 (10 mL) at ambient temperature. K_2CO_3 (233 mg, 1.68 mmol, 10 equiv.), followed by Cl_3CCN (169 μL, 1.68 mmol, 10 equiv.) were added. Reaction mixture was stirred at ambient temperature for 24 hours. Solids were filtered off and the obtained solution was concentrated. The residue was purified by automated SiO_2 column chromatography (10 g solid loading cartridge, 40 g column, 1-100% EtOAc in hexanes) to yield trichloroimidate imidate **2** (132 mg, 66%) as a white solid.

TLC R_f 0.21 (hexanes:ethyl acetate 1:1); $[\alpha]_D^{19}$ +8.5 (*c* 1.00, C_6H_6); **FTIR** (NaCl film) 3320, 3064, 2961, 2886, 2360, 1755, 1677, 1432, 1368, 1177, 1096, 1069, 971, 712; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.03 – 7.97 (m, 2H), 7.92 (ddd, *J* = 10.9, 8.2, 1.4 Hz, 4H), 7.59 – 7.44 (m, 3H), 7.43 – 7.31 (m, 6H), 6.59 (d, *J* = 3.5 Hz, 1H), 5.70 (t, *J* = 7.2 Hz, 1H), 5.48 (t, *J* = 9.8 Hz, 1H), 5.32 – 5.24 (m, 2H), 5.17 (t, *J* = 9.5 Hz, 1H), 5.10 – 4.93 (m, 4H), 4.53 (d, *J* = 7.9 Hz, 1H), 4.39 (dd, *J* = 12.4, 4.2 Hz, 1H), 4.25 (dd, *J* = 12.3, 4.5 Hz, 1H), 4.16 – 4.07 (m, 3H), 3.96 (dd, *J* = 10.3, 3.1 Hz, 2H), 3.73 – 3.63 (m, 2H), 3.52 (dd, *J* = 11.1, 4.5 Hz, 1H), 2.08 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.71 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.81, 170.36, 169.70, 169.67, 169.62, 169.49, 165.62, 165.60, 164.87, 160.85,

133.57, 133.55, 133.44, 130.08, 130.07, 130.01, 129.90, 129.25, 129.23, 128.91, 128.56, 128.53, 128.51, 128.46, 101.90, 100.54, 94.68, 90.96, 77.37, 77.29, 77.16, 76.95, 72.89, 71.92, 71.04, 70.98, 70.79, 70.22, 70.14, 68.96, 68.35, 68.31, 67.25, 61.86, 61.36, 20.89, 20.82, 20.77, 20.74, 20.73, 20.38; **HRMS** (ESI) *m/z* Calcd for $C_{52}H_{54}NO_{24}Na$ $[M+Na]^+$ 1204.1999, found 1204.2045.

D. SYNTHESIS OF PENTASACCHARIDE 16

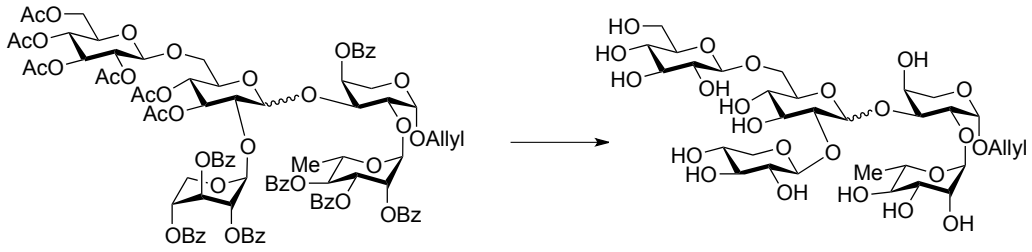


(2*S*,3*R*,4*R*,5*S*,6*S*)-2-(((2*S*,3*R*,4*S*,5*S*)-2-(allyloxy)-5-(benzoyloxy)-4-(((2*S*,3*R*,4*S*,5*R*,6*R*)-4,5-diacetoxy-6-((((2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)methyl)-3-(((2*S*,3*R*,4*S*,5*R*)-3,4,5-tris(benzoyloxy)tetrahydro-2*H*-pyran-2-yl)oxy)tetrahydro-2*H*-pyran-2-yl)oxy)tetrahydro-2*H*-pyran-3-yl)oxy)-6-methyltetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (β-16) Trichloroimidate **2** (12 mg, 0.010 mmol, 1 equiv) and disaccharide **3** (9 mg, 0.01 mmol, 1.2 equiv) were azeotropically dried with PhMe (0.5 mL) and dissolved in *t*-BuCN/CF_3Ph (150 μL /750 μL) solvent mixture. $B(C_6F_5)_3$ (0.5 mg, 0.001 mmol, 0.1 equiv.) was added and the reaction mixture was stirred at ambient temperature for 40 min, then quenched by adding 25 μl of Et_3N. The reaction mixture was concentrated and purified by automated SiO_2 column chromatography (5 g solid loading cartridge, 4 g column, 1-100% EtOAc in benzene) yielded pentasaccharides **β-16** (7.5 mg, 42%) and **α-16** (7 mg, 39%).

For β-16: TLC R_f 0.30 (benzene:ethyl acetate 2:1) $[\alpha]_D^{19}$ +27.2 (*c* 0.70, C_6H_6); **FTIR** (NaCl film) 2924, 1727, 1602, 1451, 1367, 1265, 1069, 710, 665; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 8.3, 1.4 Hz, 2H), 8.10 (dt, *J* = 8.2, 1.1 Hz, 4H), 8.04 (ddt, *J* = 17.7, 7.1, 1.4 Hz, 4H), 7.65 – 7.59 (m, 1H), 7.59 – 7.56 (m, 1H), 7.56 – 7.46 (m, 6H), 7.46 – 7.40 (m, 6H), 7.29 (tt, *J* = 7.5, 1.6 Hz, 4H), 7.25 – 7.22 (m, 1H), 7.16 (tt, *J* = 6.4, 2.4 Hz, 1H), 6.94 (dtd, *J* = 7.4, 6.1, 1.5 Hz, 3H), 6.88 – 6.83 (m, 4H), 6.03 – 5.95 (m, 2H), 5.92 (dd, *J* = 10.5, 9.4 Hz, 1H), 5.77 (q, *J* = 3.7, 3.0 Hz, 2H), 5.74 (d, *J* = 2.2 Hz, 1H), 5.73 – 5.69 (m, 2H), 5.63 (t, *J* = 9.2 Hz, 1H), 5.60 (d, *J* = 3.8 Hz, 1H), 5.35 (dd, *J* = 17.3, 1.5 Hz, 1H), 5.30 (d, *J* = 3.4 Hz, 1H), 5.26 (d, *J* = 7.7 Hz, 1H), 5.23 (dd, *J* = 10.4, 1.4 Hz, 1H), 5.19 (d, *J* = 9.5 Hz, 1H), 5.15 – 5.07 (m, 2H), 4.91 (d, *J* = 5.6 Hz, 1H), 4.81 – 4.71 (m, 2H), 4.57 (dd, *J* = 10.0, 3.8 Hz, 1H), 4.46 (dq, *J* = 9.4, 6.2 Hz, 1H), 4.41 – 4.34 (m, 2H), 4.34 – 4.27 (m, 2H), 4.24 (d, *J* = 13.2 Hz, 1H), 4.18 – 4.08 (m, 1H), 4.03 (ddd, *J* = 10.3, 8.0, 2.3 Hz, 1H), 3.98 (ddt, *J* = 12.2, 7.3, 1.2 Hz, 1H), 3.87 (td, *J* = 12.7, 12.1, 2.1 Hz, 2H), 3.82 – 3.72 (m, 2H), 3.66 (dd, *J* = 9.4, 7.7 Hz, 1H), 3.13 (dd, *J* = 13.2, 3.2 Hz, 1H), 2.33 (s, 3H), 2.11 (s, 3H), 2.04 (d, *J* = 2.3 Hz, 4H), 2.02 (s, 3H), 1.93 (s, 3H), 1.46 (s, 3H), 1.35 (d, *J* = 6.2 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.89, 170.30, 170.25, 169.79, 169.65, 168.84, 166.44, 166.13, 166.06, 166.02, 165.90, 165.86, 164.20, 133.94, 133.50, 133.43, 133.22, 133.07, 132.88, 132.78, 132.29, 130.54, 130.30, 130.19, 130.18, 130.03, 129.92, 129.77, 129.73, 129.66, 129.60, 129.59, 129.44, 129.20, 129.18, 128.71, 128.67, 128.59, 128.55, 128.35, 128.11, 127.60, 118.42, 102.13, 101.51, 101.30, 99.00, 98.09, 81.22, 77.37, 77.16, 76.95, 76.76, 74.97, 73.61, 73.53, 73.14, 72.72, 72.15, 72.01, 71.65, 71.23, 71.21, 70.83, 70.44, 69.74, 69.14, 68.85, 68.63, 68.06, 63.57, 62.03, 60.84, 21.47, 20.97, 20.89, 20.85, 20.81, 20.55, 18.43; **HRMS** (ESI) *m/z* Calcd for $C_{92}H_{92}O_{36}Na$ $[M+Na]^+$ 1795.5266, found 1795.5338.

For α-16: TLC R_f 0.41 (benzene:ethyl acetate 2:1); $[\alpha]_D^{18}$ +53.4 (*c* 0.44, C_6H_6); **FTIR** (NaCl film) 2935, 1730, 1601, 1451, 1368, 1262, 1177, 1069, 1028, 710; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.41 (dd, *J* = 6.7, 3.0 Hz, 2H), 8.04 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.93 (ddd, *J* = 10.0, 8.4, 1.5 Hz, 4H), 7.79 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.77 – 7.72 (m, 2H), 7.69 (td, *J* = 5.6, 4.7, 1.4 Hz, 5H), 7.60 (d, *J* = 7.4 Hz, 1H), 7.55 – 7.41 (m, 7H), 7.41 – 7.34 (m, 5H), 7.33 – 7.27 (m, 5H), 6.07 (ddt, *J* = 16.3, 10.7, 5.5 Hz, 1H), 5.81 (t, *J* = 2.0 Hz, 1H), 5.68 – 5.60 (m, 2H), 5.52 – 5.38 (m, 6H), 5.30 – 5.23 (m, 2H), 5.20 (d, *J* = 3.6 Hz, 1H), 5.14 – 5.09 (m, 2H), 5.07 (dd, *J* = 10.1, 9.0 Hz, 1H), 4.60 (td, *J* = 9.9, 5.7 Hz, 1H), 4.55 (t, *J* = 7.9 Hz, 2H), 4.52 – 4.48 (m, 1H), 4.48 – 4.44 (m, 1H), 4.41 (dq, *J* = 10.5, 6.1 Hz, 1H), 4.34 (dtd, *J* = 10.2, 5.1, 2.6 Hz, 3H), 4.32 – 4.27 (m, 2H), 4.23 – 4.18 (m, 2H), 4.10 (dd, *J* = 13.1, 2.0 Hz, 1H), 3.99 – 3.94 (m, 1H), 3.92 (d, *J* = 12.8 Hz, 1H), 3.86 (dd, *J* = 11.2, 1.7 Hz, 1H), 3.74 (ddd, *J* = 10.1, 4.5, 2.5 Hz, 1H), 3.67 (dd, *J* = 10.1, 3.5 Hz, 1H), 3.29 (t, *J* = 10.8 Hz, 1H), 2.10 (s, 3H), 2.02 (d, *J* = 1.5 Hz, 9H), 1.68 (s, 3H), 1.37 (d, *J* = 6.2 Hz, 3H), 0.96 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.93, 170.53, 170.45, 170.02, 169.59, 169.32, 166.72, 165.63, 165.59, 165.41, 165.24, 164.75, 164.16, 133.72, 133.53, 133.36, 133.33, 133.28, 133.24, 132.99, 130.66, 130.40, 130.06, 129.94, 129.91, 129.84, 129.80, 129.71, 129.69, 129.65, 129.41, 129.33, 129.26, 129.22, 129.12, 128.61, 128.57, 128.54, 128.51, 128.36, 128.30, 117.63, 103.77, 101.27, 100.87, 98.03, 93.58, 79.49, 77.90, 77.37, 77.16, 76.95, 73.01, 72.36, 71.87, 71.66, 71.28, 70.96, 70.70, 69.93, 69.23, 69.00, 68.68, 68.65, 68.12, 68.09, 67.73, 67.30, 67.05, 62.64, 62.12, 59.92, 20.88, 20.84, 20.82, 20.79, 20.43, 19.52, 18.00; **HRMS** (ESI) *m/z* Calcd for $C_{92}H_{92}O_{36}Na$ $[M+Na]^+$ 1795.5266 found 1795.5287.

E. DEPROTECTION OF TRISACCHARIDE 13 AND PENTASACCARIDES α-16 AND β-16



Deprotection of pentasaccharides α-16 and β-16. To the solution of the pentasaccharide **α-16** or **β-16** (8.5 mg, 0.0048 mmol, 1 equiv) in MeOH (1 mL) was added MeONa (4.4 mg, 0.082 mmol, 17 equiv). The reaction mixture was stirred at ambient temperature for 16 hrs and concentrated. Residue was dissolved in D_2O and analyzed by ^1H NMR.

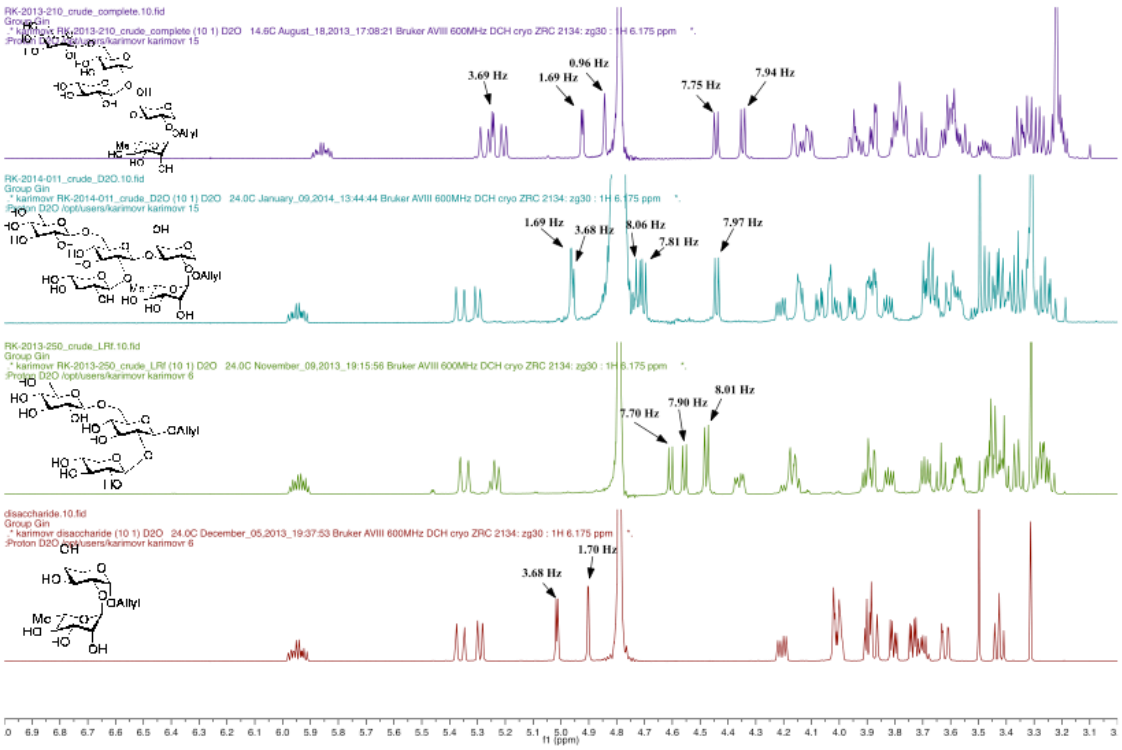
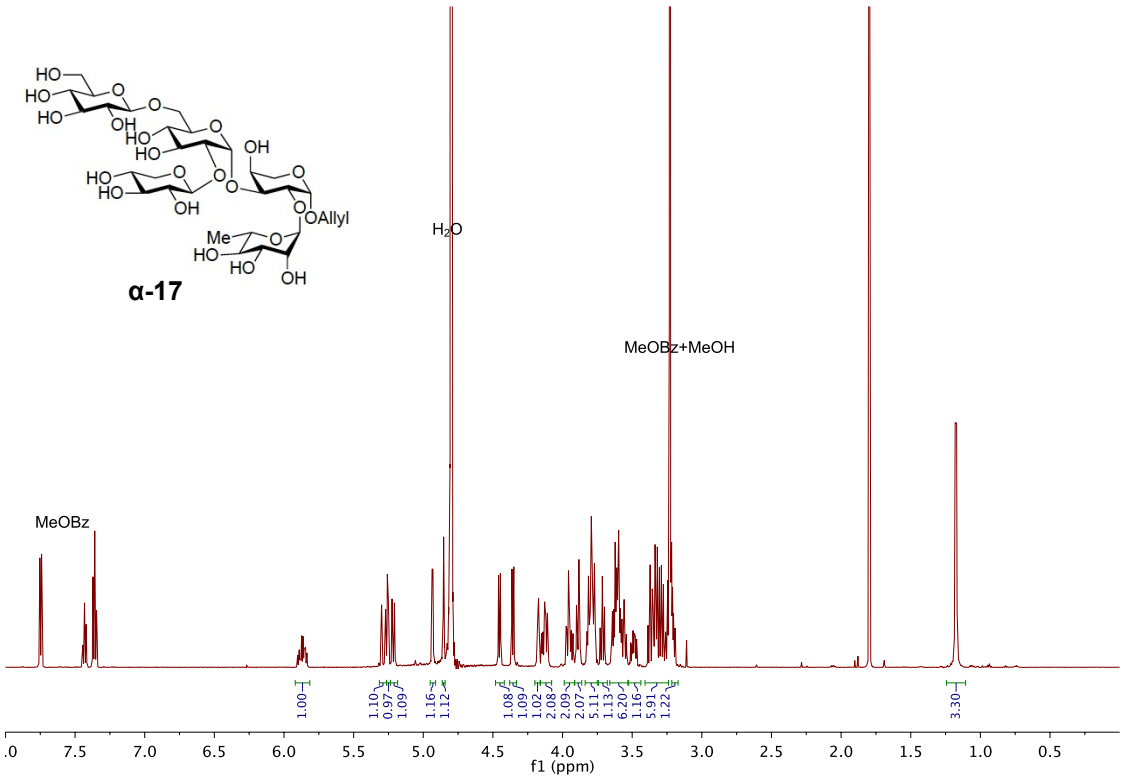
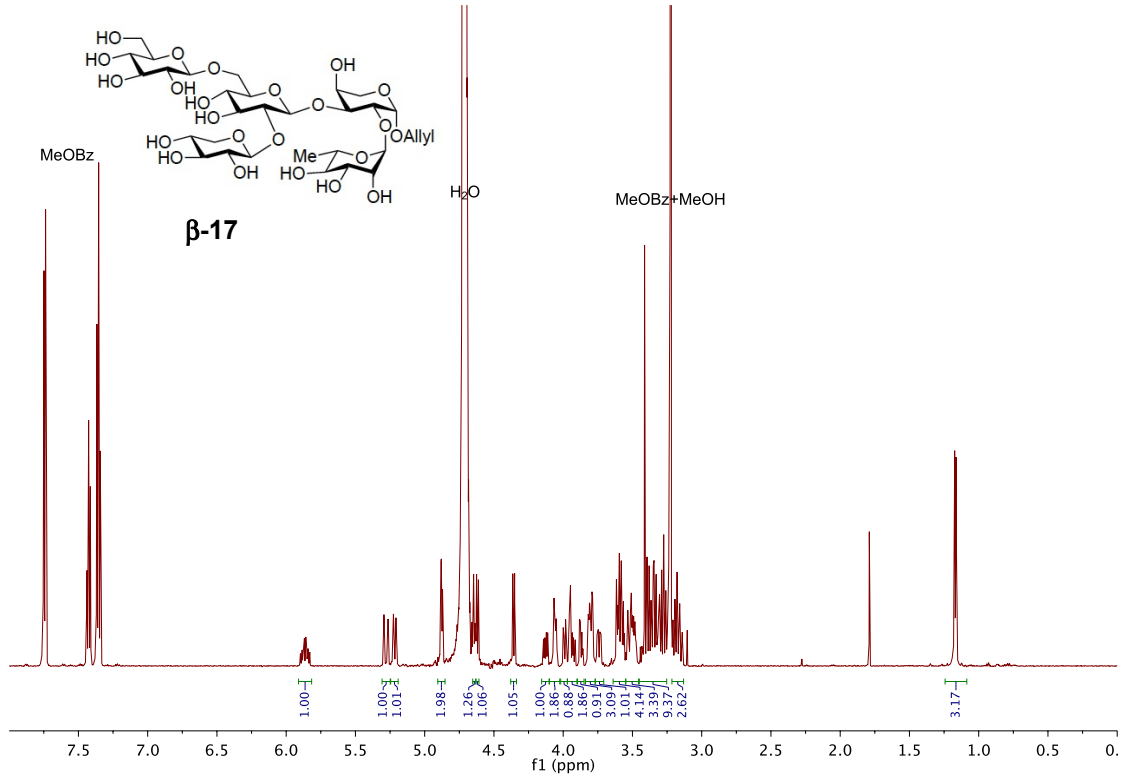
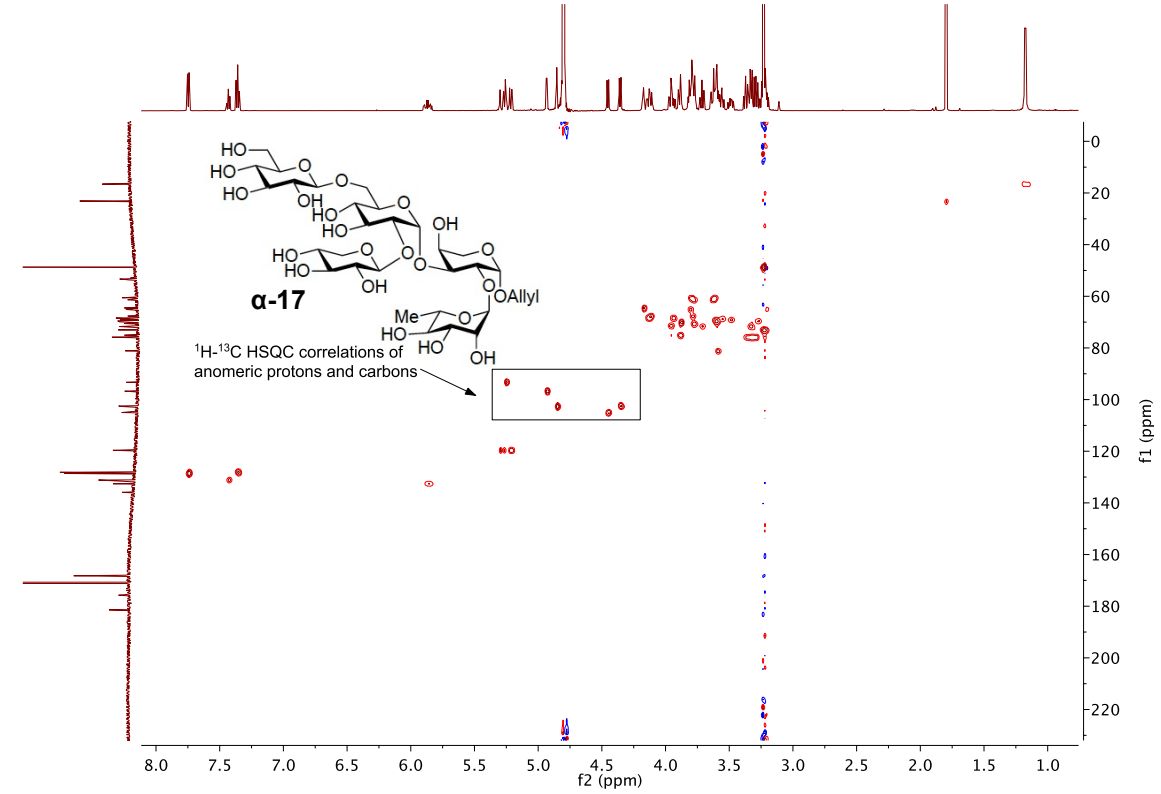


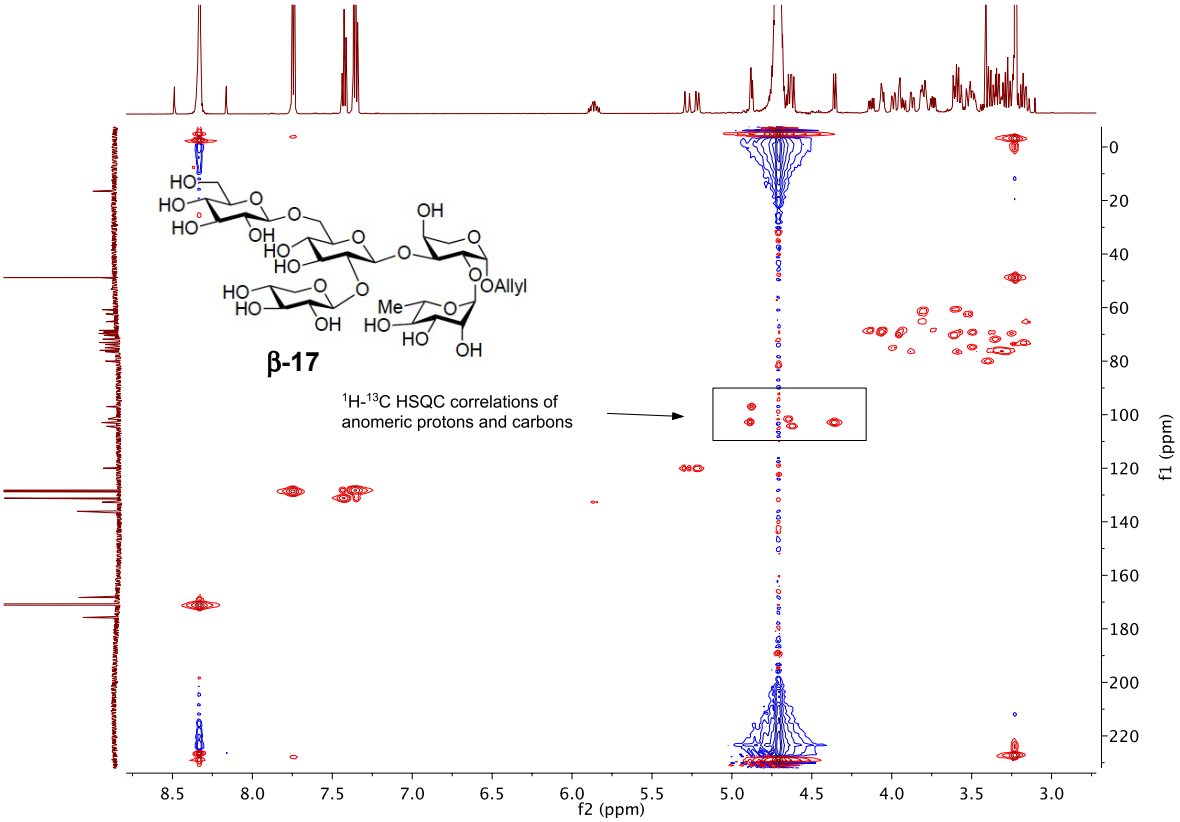
Figure S1. ^1H NMR analysis of deprotected di-, tri- and pentasaccharides.

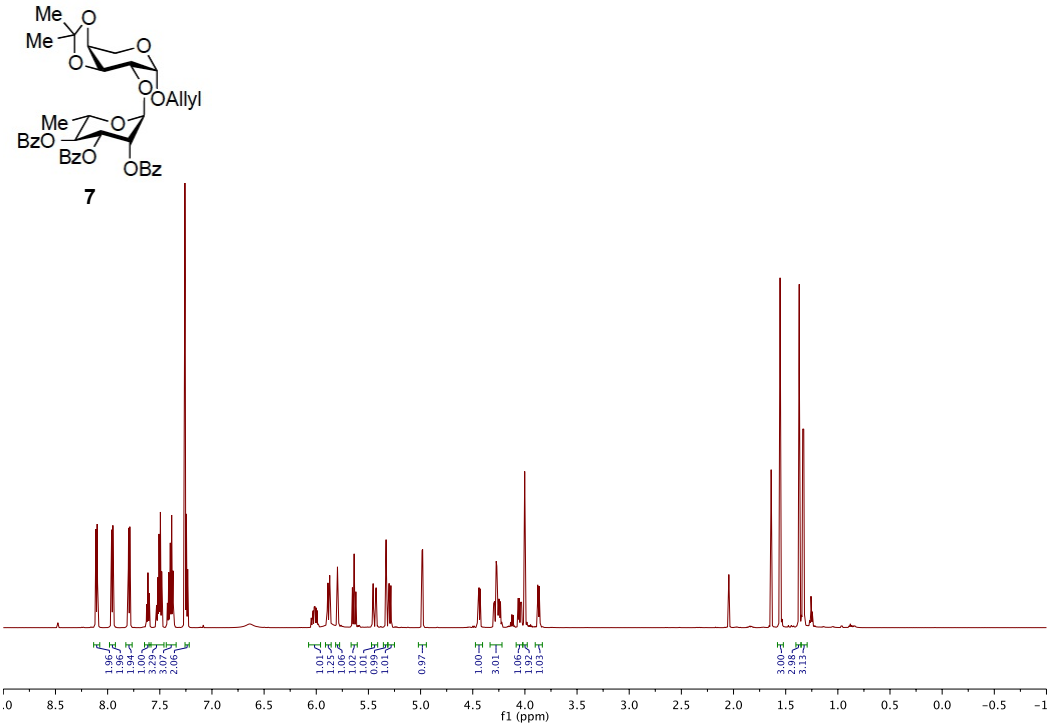
F. ^{1}H AND ^{13}C NMR SPECTRA

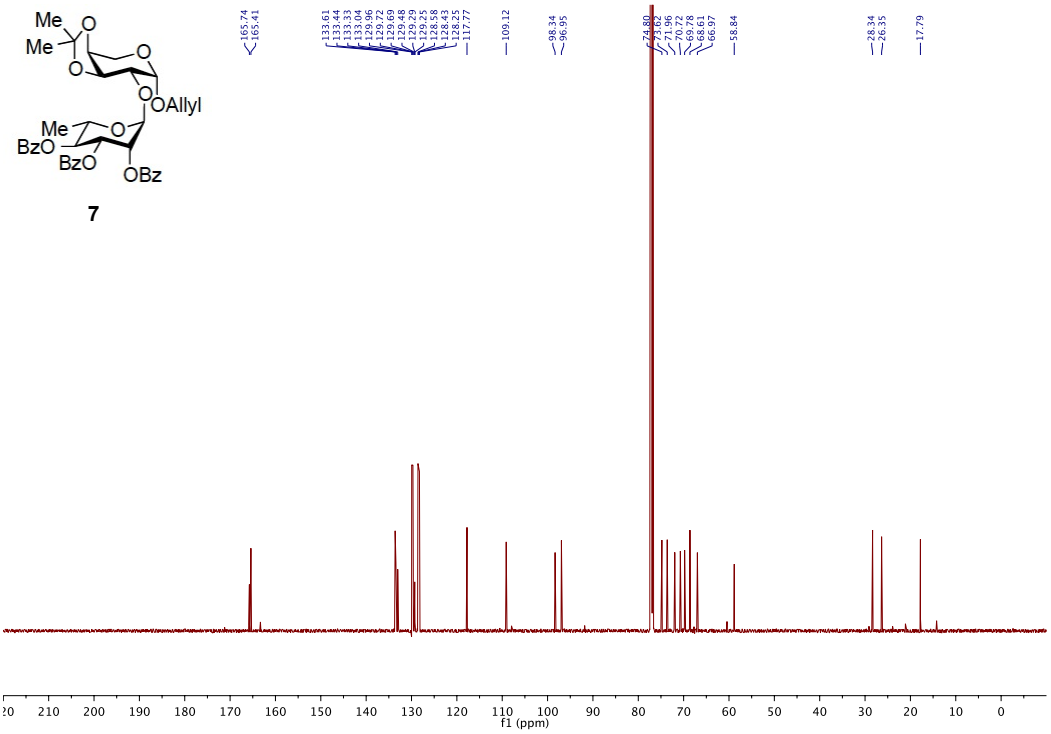





α-17
^{1}H-^{13}C HSQC correlations of anomeric protons and carbons
f2 (ppm)
f1 (ppm)


β-17
^{1}H-^{13}C HSQC correlations of anomeric protons and carbons
f2 (ppm)
f1 (ppm)


Me
Me
O
O
O
O
OAllyl
Me
BzO
BzO
O
OBz
7
f1 (ppm)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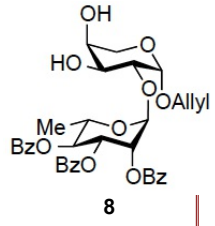
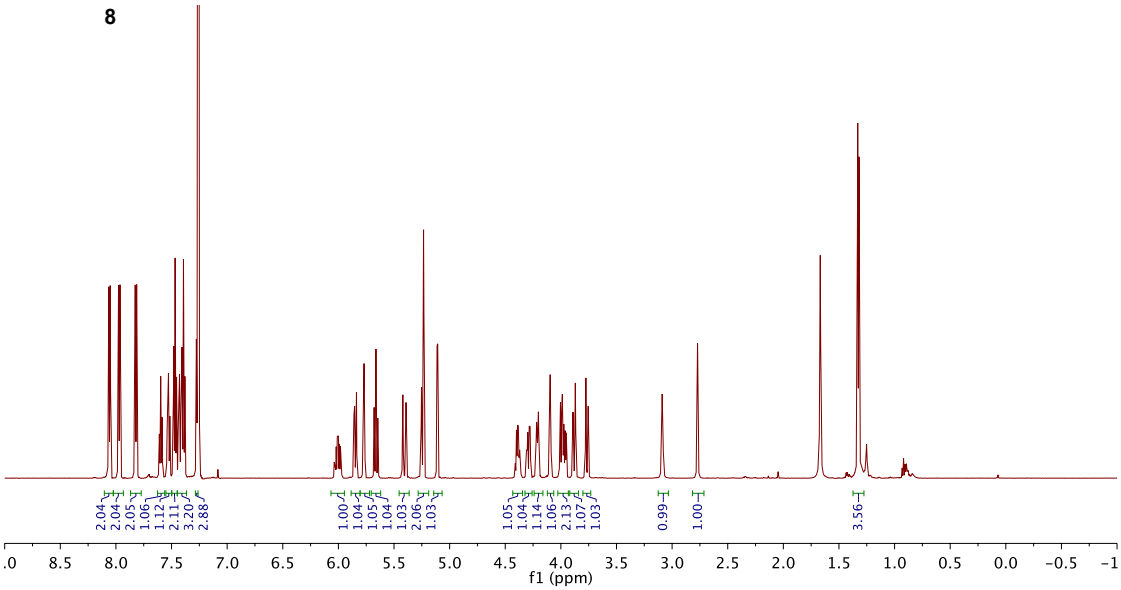
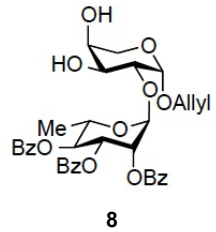
Me
O
O
O
O
OAllyl
Me
BzO
BzO
O
OBz
7
165.74
165.41
133.61
133.44
133.33
133.04
129.96
129.72
129.69
129.48
129.29
128.55
128.43
128.25
117.77
109.12
98.34
96.95
74.80
74.62
71.96
70.72
69.78
68.61
66.61
66.97
58.84
28.34
25.35
17.79
f1 (ppm)


OH
HO
O
O
OAllyl
Me
O
BzO
BzO
OBz

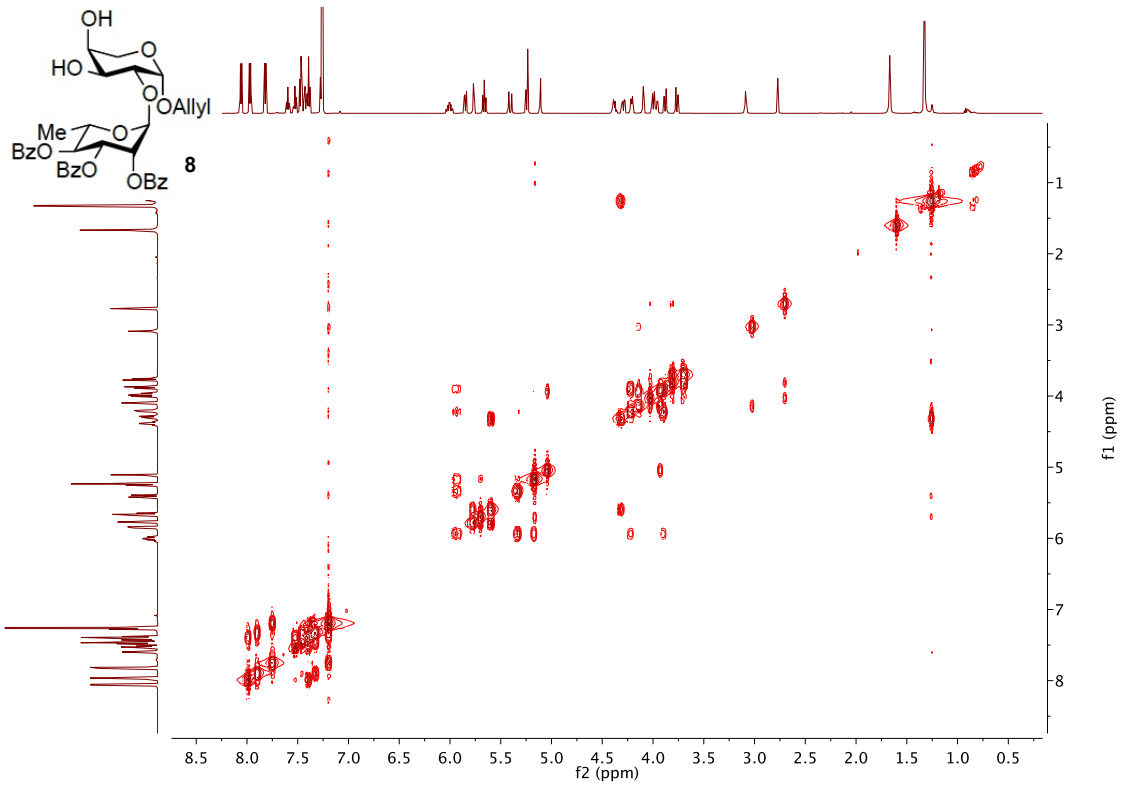
8

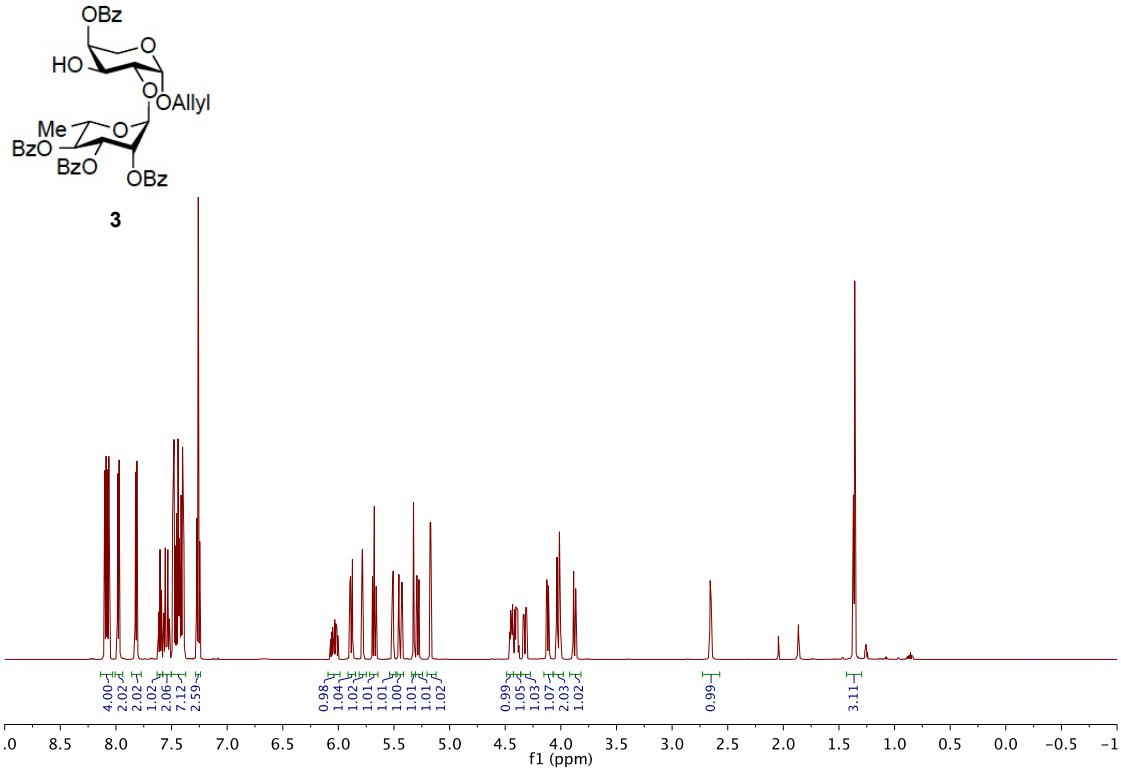

2.04
2.04
2.05
1.06
1.12
2.11
3.20
2.88
1.00
1.04
1.05
1.04
1.03
2.06
1.03
1.05
1.04
1.14
1.06
2.13
1.07
1.03
0.99
1.00
3.56
f1 (ppm)

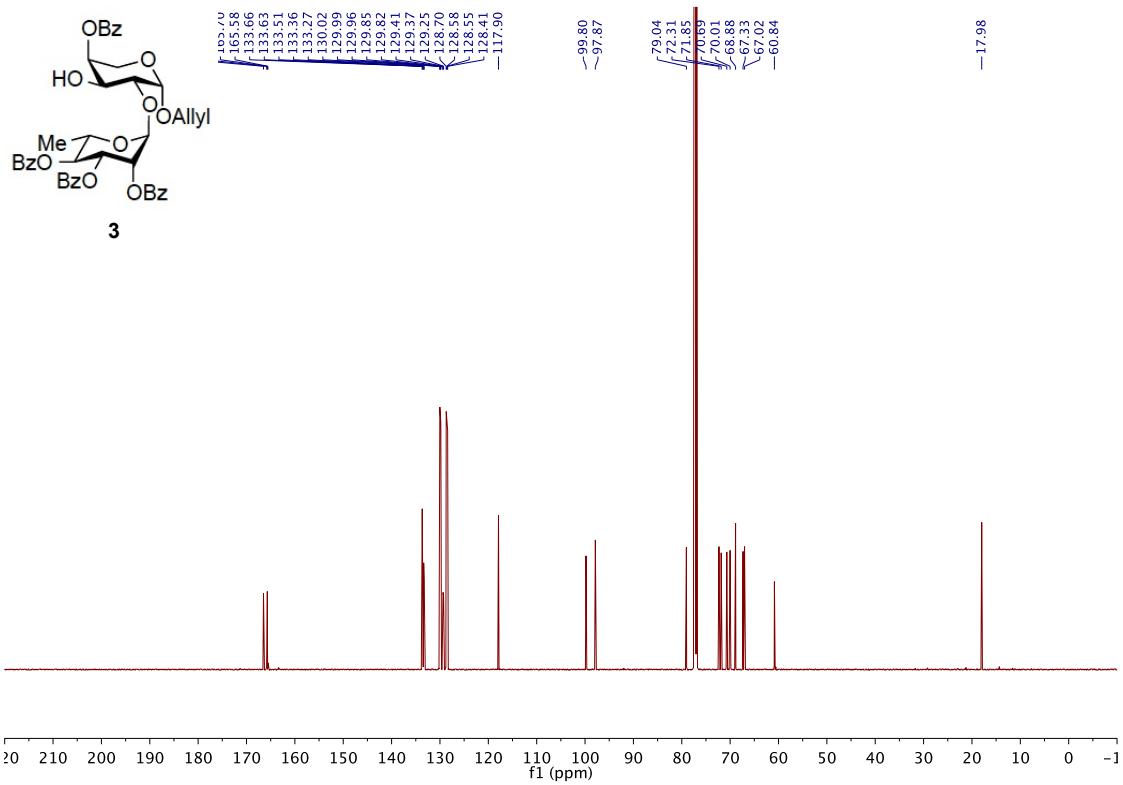

OH
HO
O
O
OAllyl
Me
O
BzO
BzO
OBz

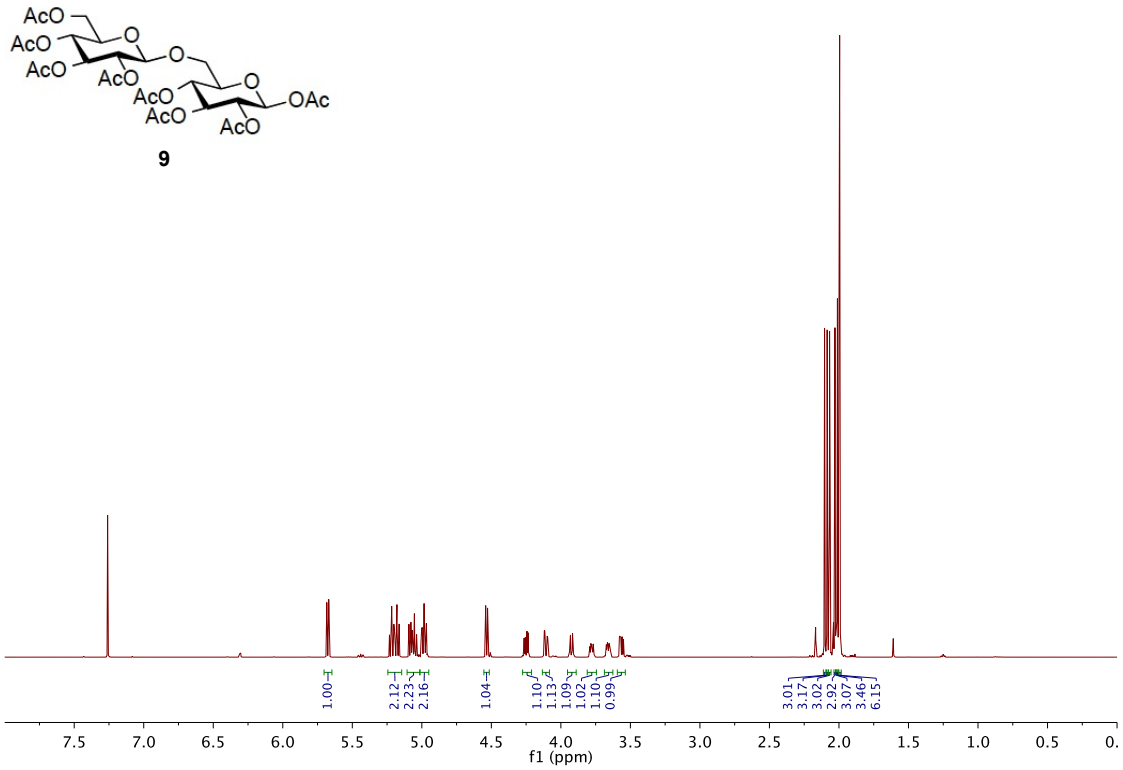
8

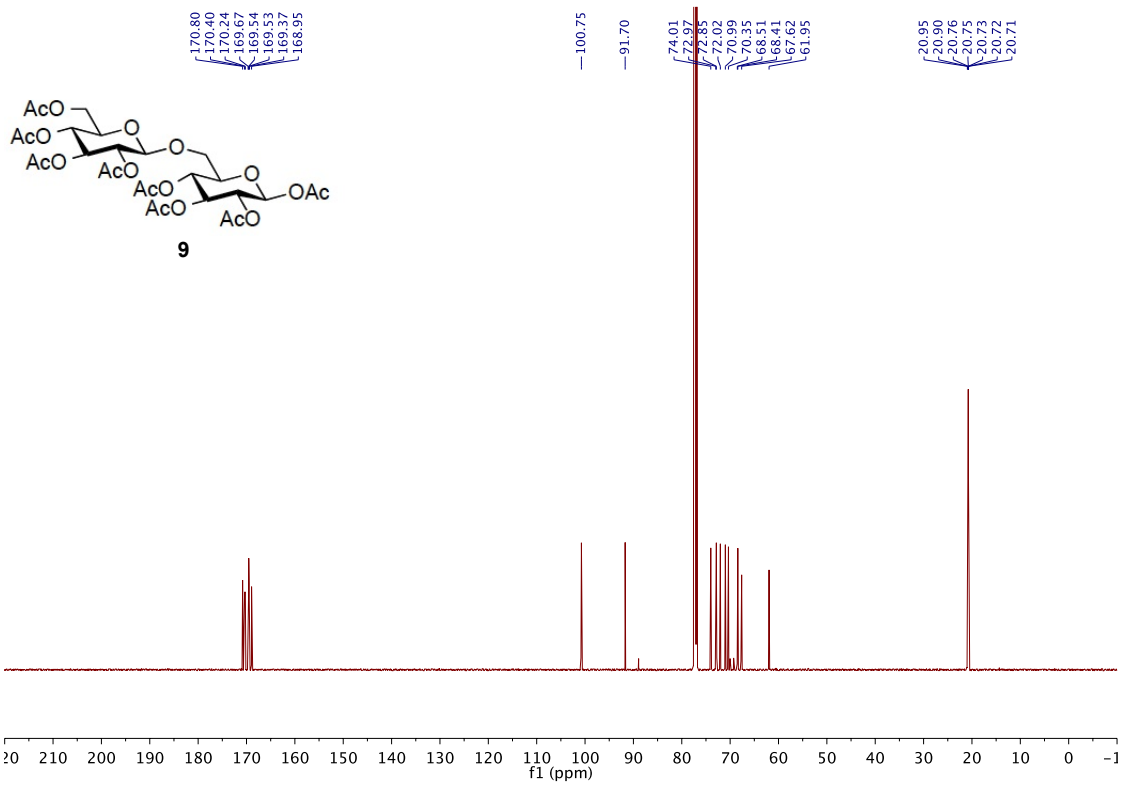
165.90
165.81
165.74
133.81
133.68
133.51
133.35
130.06
129.85
129.39
129.34
129.19
128.71
128.58
128.45
117.59
99.90
98.00
79.21
77.37
77.16
76.95
71.77
70.70
70.20
69.51
68.75
68.14
67.27
62.05
17.97
f1 (ppm)

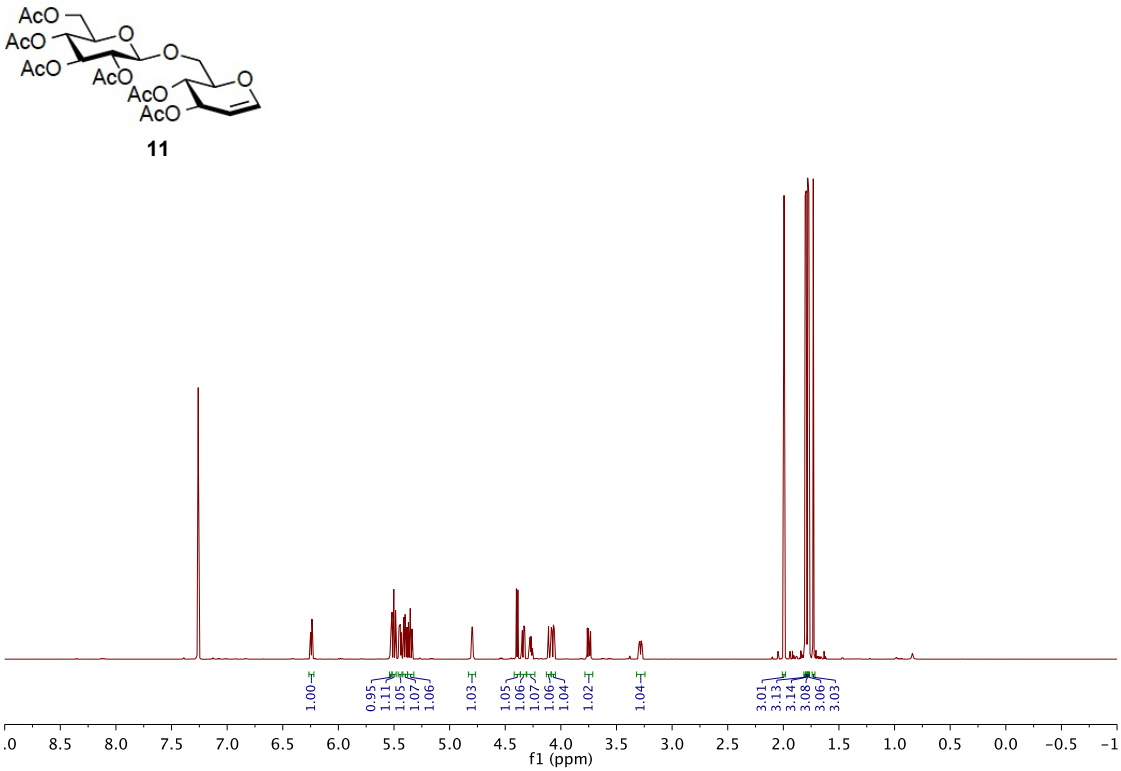

OH
HO
O
O
OAllyl
Me
BzO
O
BzO
OBz
8
f2 (ppm)
f1 (ppm)

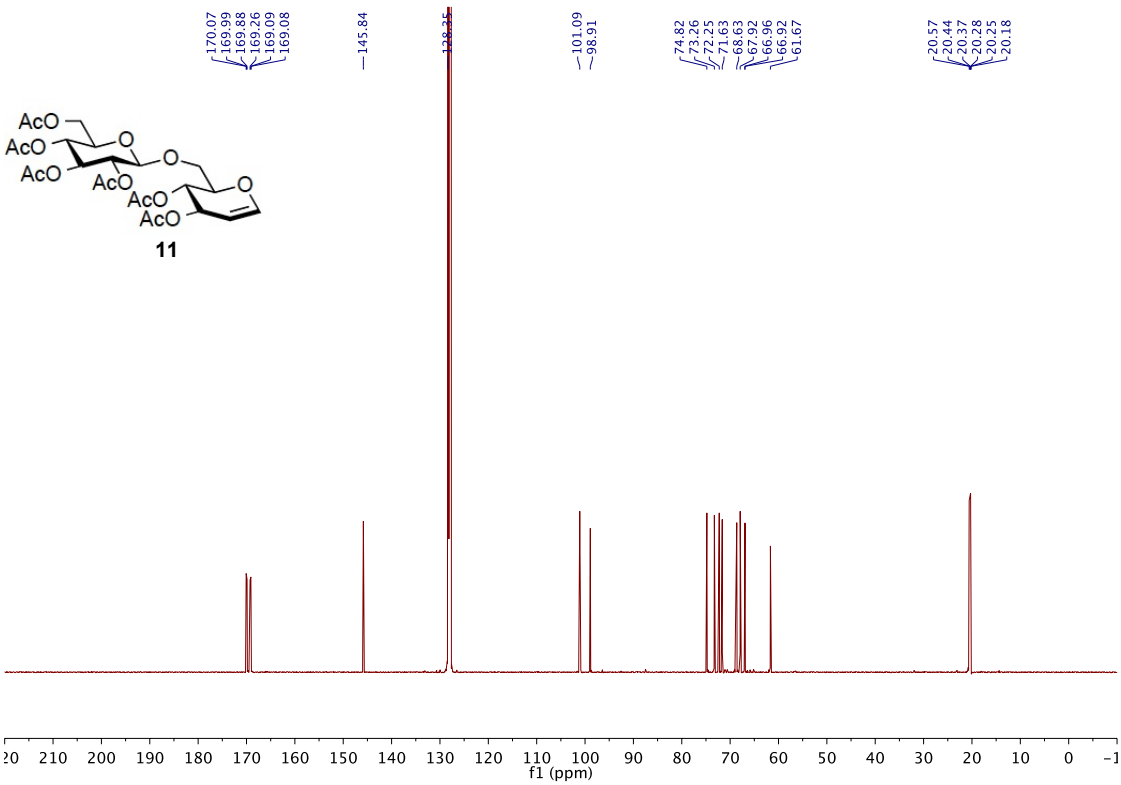

OBz
HO
O
O
OAllyl
Me
BzO
O
BzO
OBz
3
f1 (ppm)

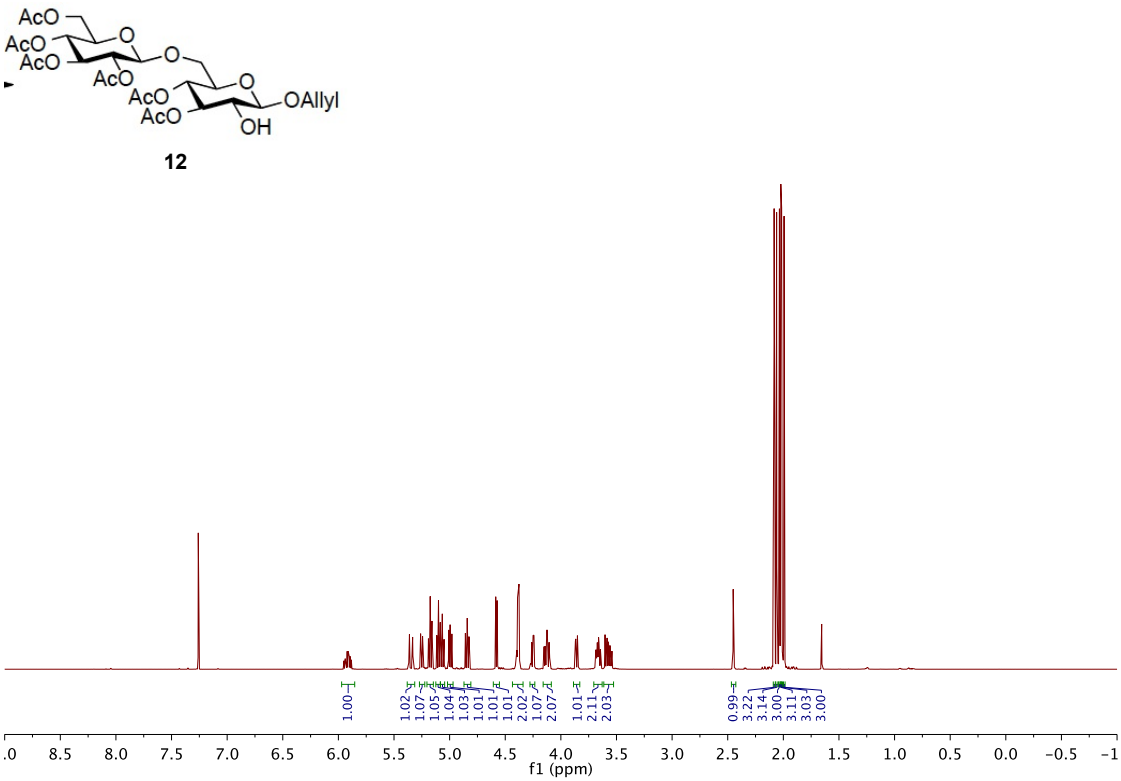

OBz
HO
O
O
OAllyl
Me
O
BzO
BzO
OBz
3
165.58
133.66
133.63
133.51
133.36
133.27
130.02
129.99
129.96
129.85
129.82
129.41
129.37
129.25
128.70
128.58
128.55
128.41
117.90
99.80
97.87
79.04
72.31
71.85
70.69
70.01
68.88
67.33
67.02
60.84
17.98
f1 (ppm)

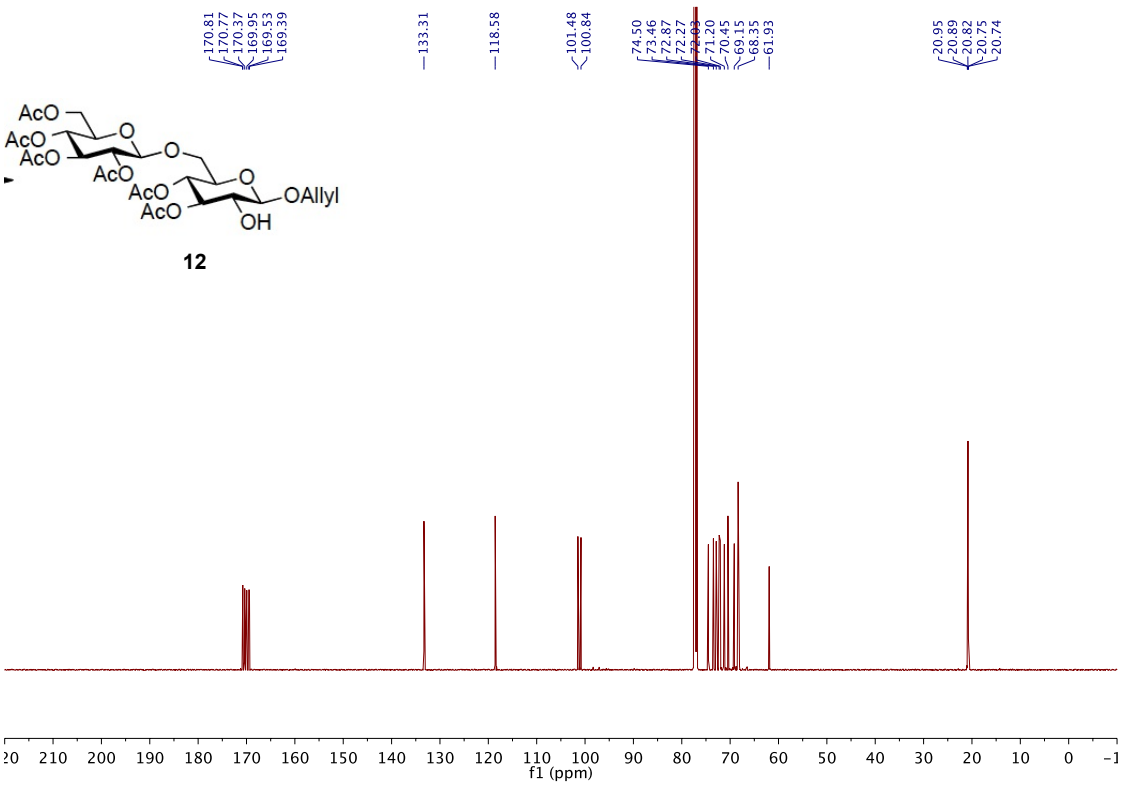

AcO
AcO
AcO
O
O
AcO
AcO
AcO
AcO
O
OAc
AcO
9
1.00
2.12
2.23
2.16
1.04
1.10
1.13
1.09
1.02
1.10
0.99
3.01
3.17
3.02
2.92
3.07
3.46
6.15
f1 (ppm)


170.80
170.40
170.24
169.67
169.54
169.53
169.37
168.95
100.75
91.70
74.01
72.97
72.85
72.02
70.99
70.35
68.51
68.41
67.62
61.95
20.95
20.90
20.76
20.75
20.73
20.72
20.71
AcO
AcO
AcO
AcO
AcO
AcO
AcO
OAc
9
f1 (ppm)

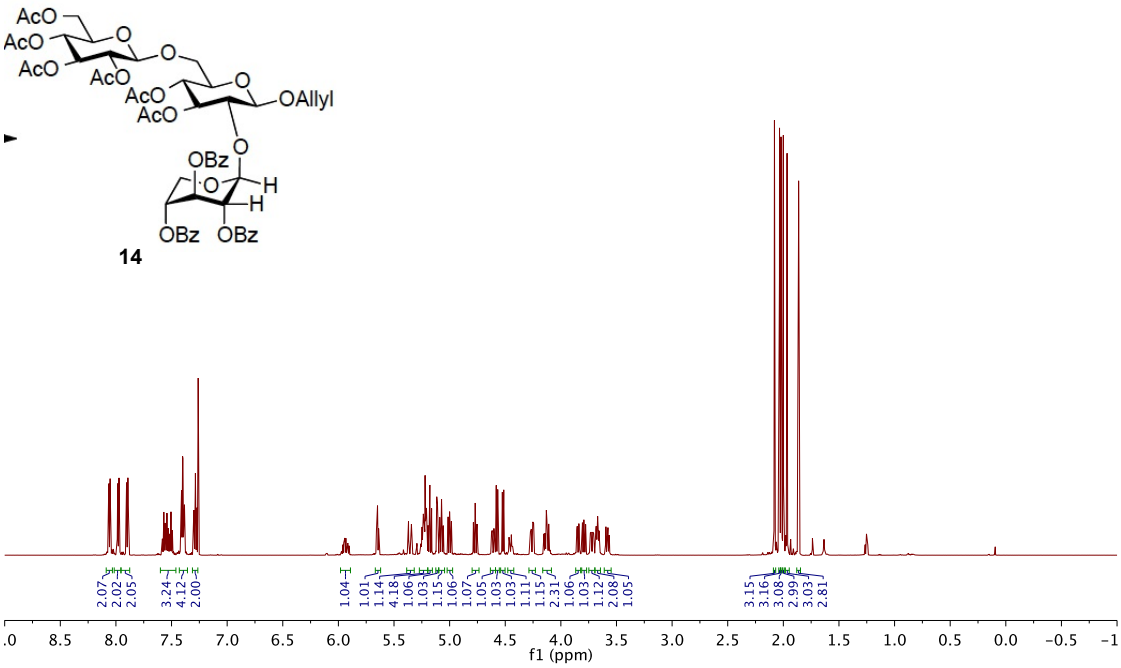

AcO
AcO
AcO
AcO
AcO
AcO
11
1.00
0.95
1.11
1.05
1.07
1.06
1.03
1.05
1.06
1.07
1.06
1.04
1.02
1.04
3.01
3.13
3.14
3.08
3.06
3.03
f1 (ppm)


170.07
169.99
169.88
169.26
169.09
169.08
145.84
128.25
101.09
98.91
74.82
73.26
72.25
71.63
68.63
67.32
66.96
66.92
61.67
20.57
20.44
20.37
20.28
20.25
20.18
AcO
AcO
AcO
AcO
AcO
AcO
O
O
O
11
f1 (ppm)

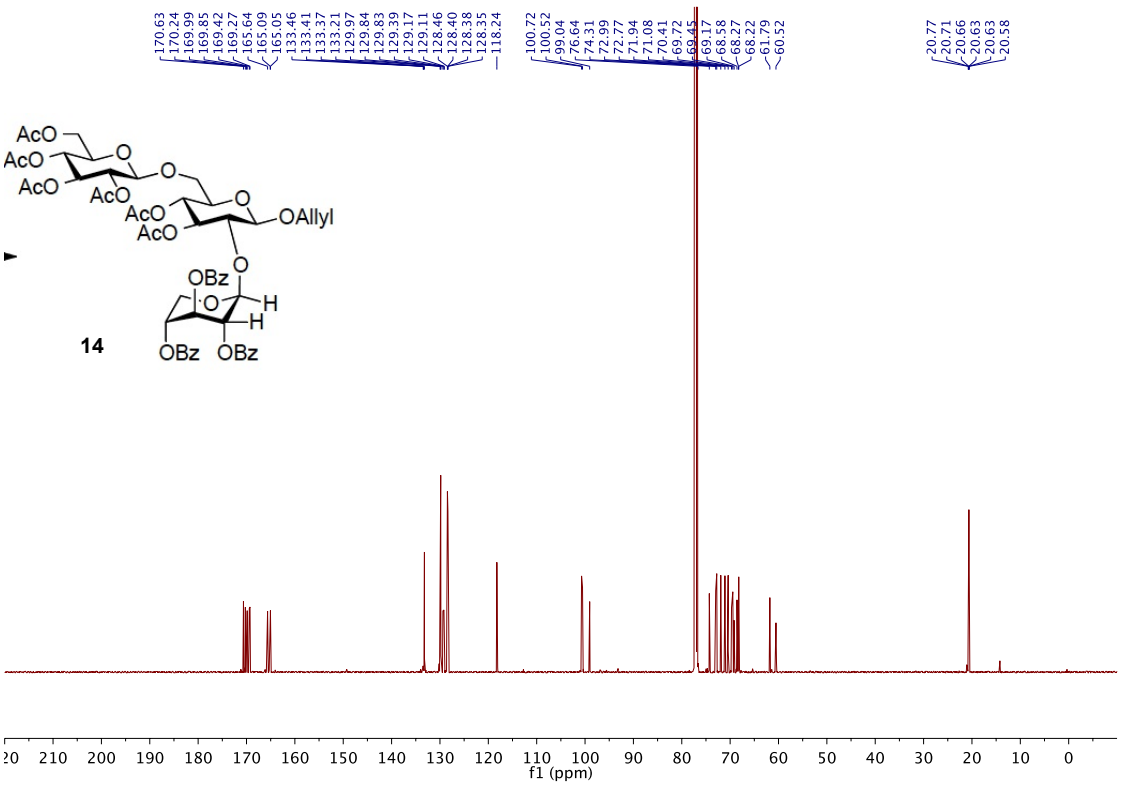

AcO
AcO
AcO
AcO
AcO
AcO
O
O
O
OAllyl
OH
12
1.00
1.02
1.07
1.05
1.04
1.03
1.01
1.01
1.01
2.02
2.07
2.07
1.01
2.11
2.03
0.99
3.22
3.14
3.00
3.11
3.03
3.00
f1 (ppm)

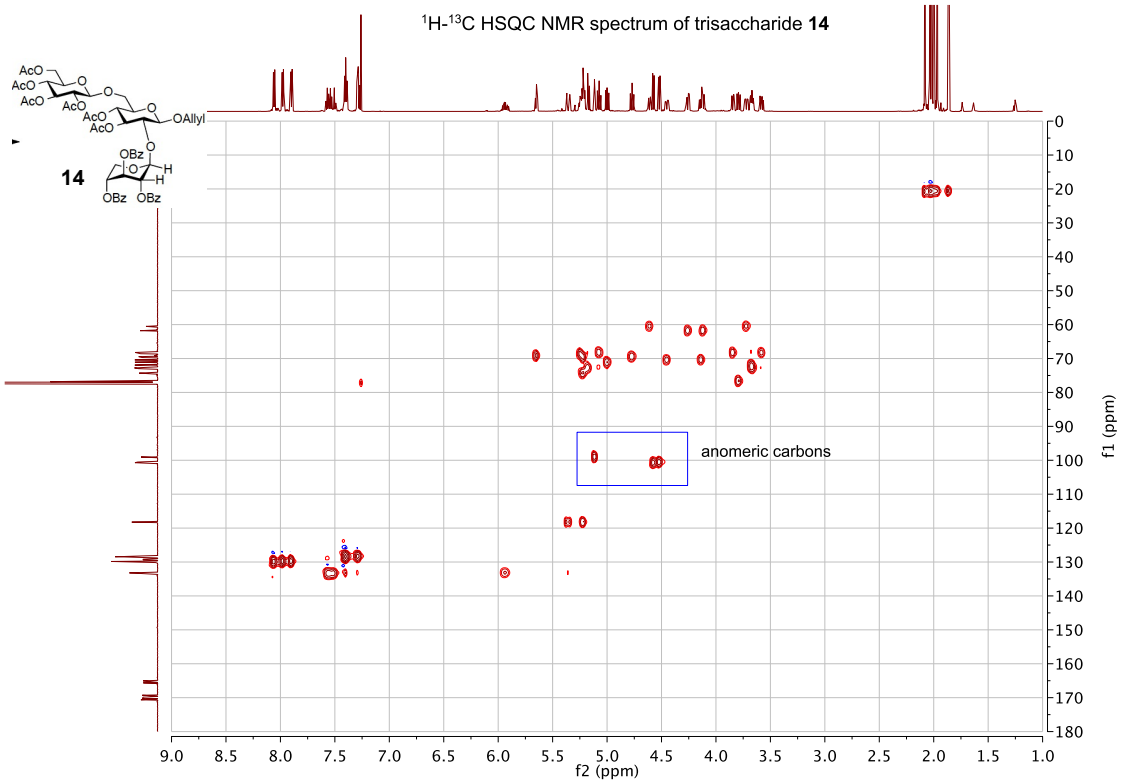

170.81
170.77
170.37
169.95
169.53
169.39
133.31
118.58
101.48
100.84
74.50
73.46
72.87
72.27
71.20
70.45
69.15
68.35
61.93
20.95
20.89
20.82
20.75
20.74
AcO
AcO
AcO
AcO
AcO
AcO
O
O
O
OAllyl
OH
f1 (ppm)

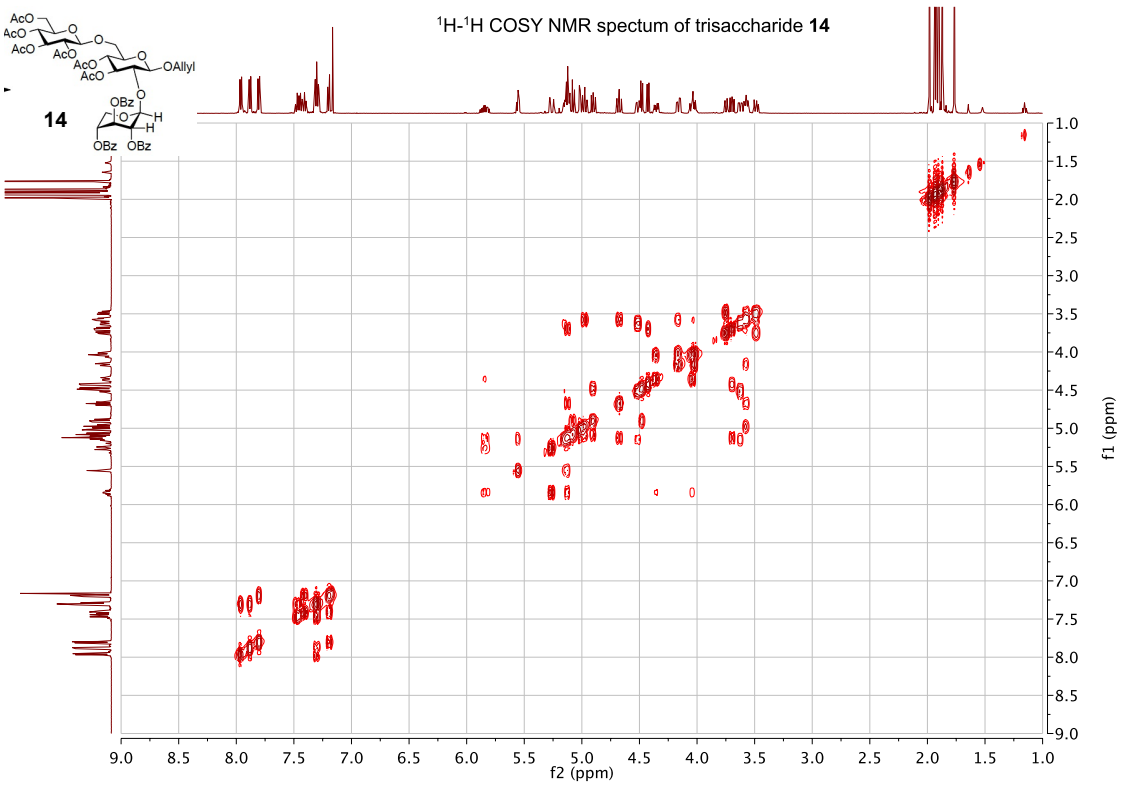
12

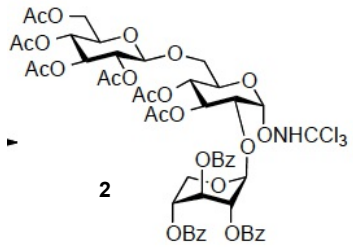

AcO
AcO
AcO
AcO
AcO
AcO
O
O
O
OAllyl
OBz
OBz
OBz
H
H
2.07
2.02
2.05
3.24
4.12
2.00
1.04
1.01
1.14
4.18
1.06
1.03
1.15
1.06
1.07
1.05
1.03
1.03
1.11
1.15
2.31
1.06
1.03
1.12
2.08
1.05
3.15
3.16
3.08
2.99
3.03
2.81
f1 (ppm)

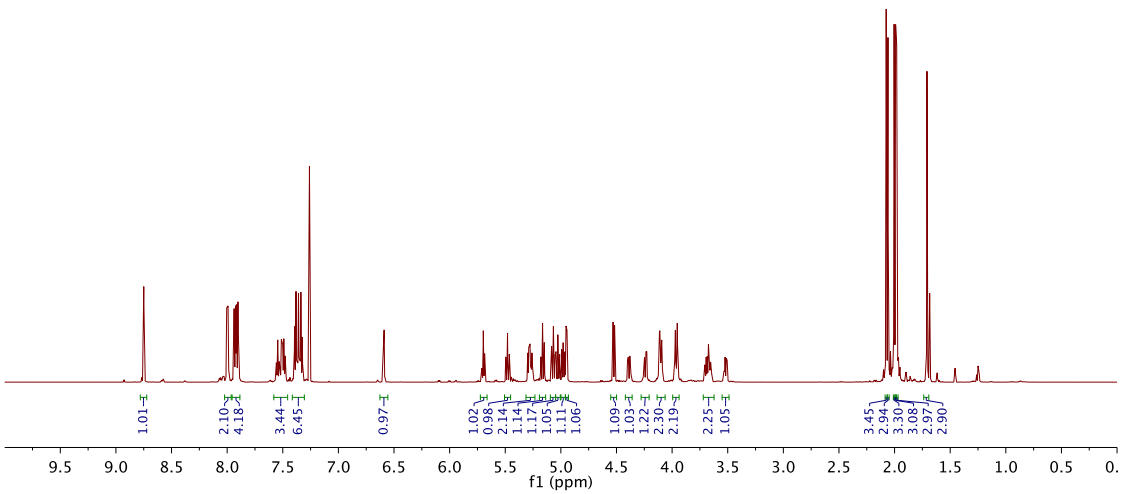
14

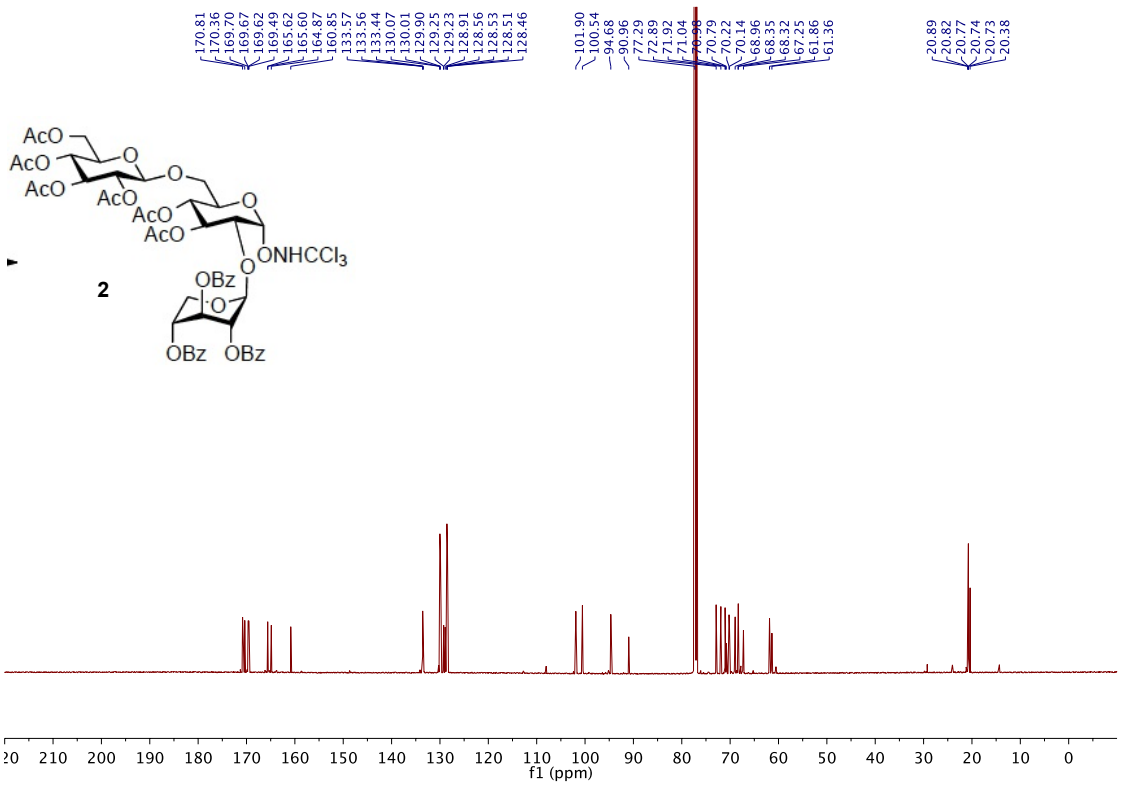

170.63
170.24
169.99
169.85
169.42
169.27
165.64
165.09
165.05
133.46
133.41
133.37
133.21
129.97
129.84
129.83
129.39
129.17
129.11
128.46
128.40
128.38
128.35
118.24
100.72
100.52
99.04
76.64
74.31
72.99
72.77
71.94
71.08
70.41
69.72
69.45
69.17
68.58
68.27
68.22
61.79
60.52
20.77
20.71
20.66
20.63
20.63
20.58
AcO
AcO
AcO
AcO
AcO
AcO
OAllyl
OBz
OBz
OBz
H
H
14
f1 (ppm)

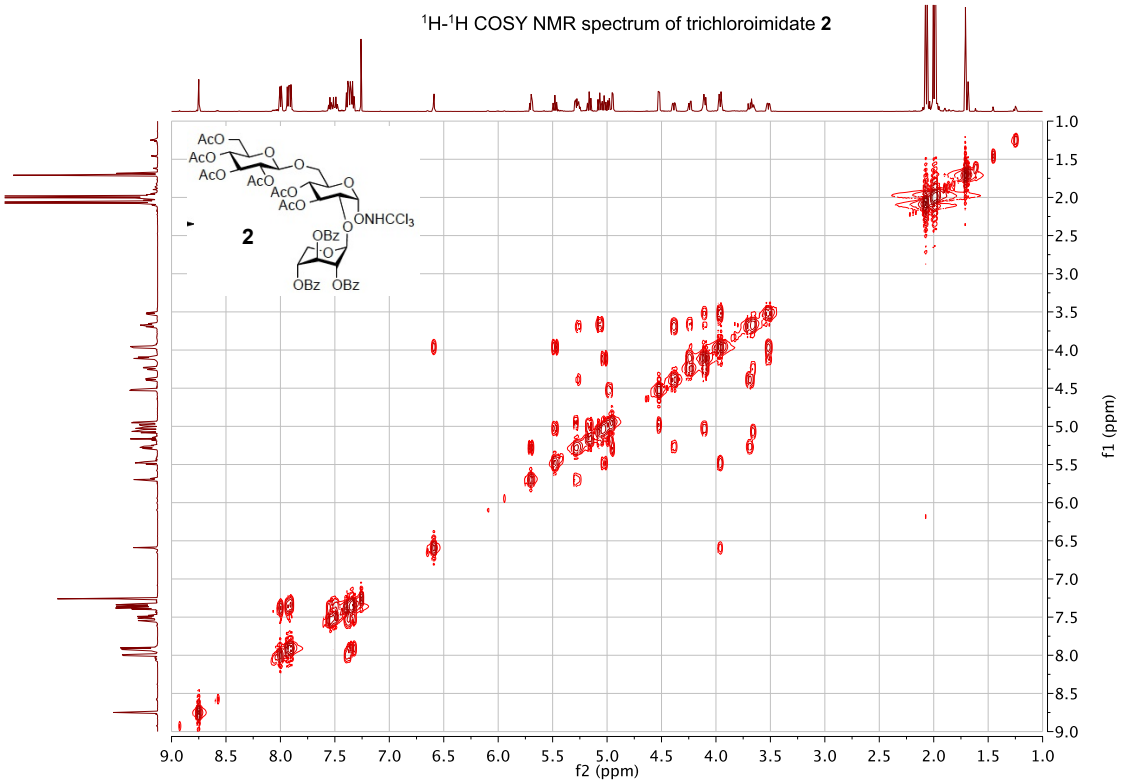

^{1}H-^{13}C HSQC NMR spectrum of trisaccharide **14**
AcO
AcO
AcO
AcO
AcO
AcO
OAllyl
OBz
OBz
OBz
H
14
anomeric carbons
f2 (ppm)
f1 (ppm)


^{1}H-^{1}H COSY NMR spectum of trisaccharide **14**
14
f2 (ppm)
f1 (ppm)

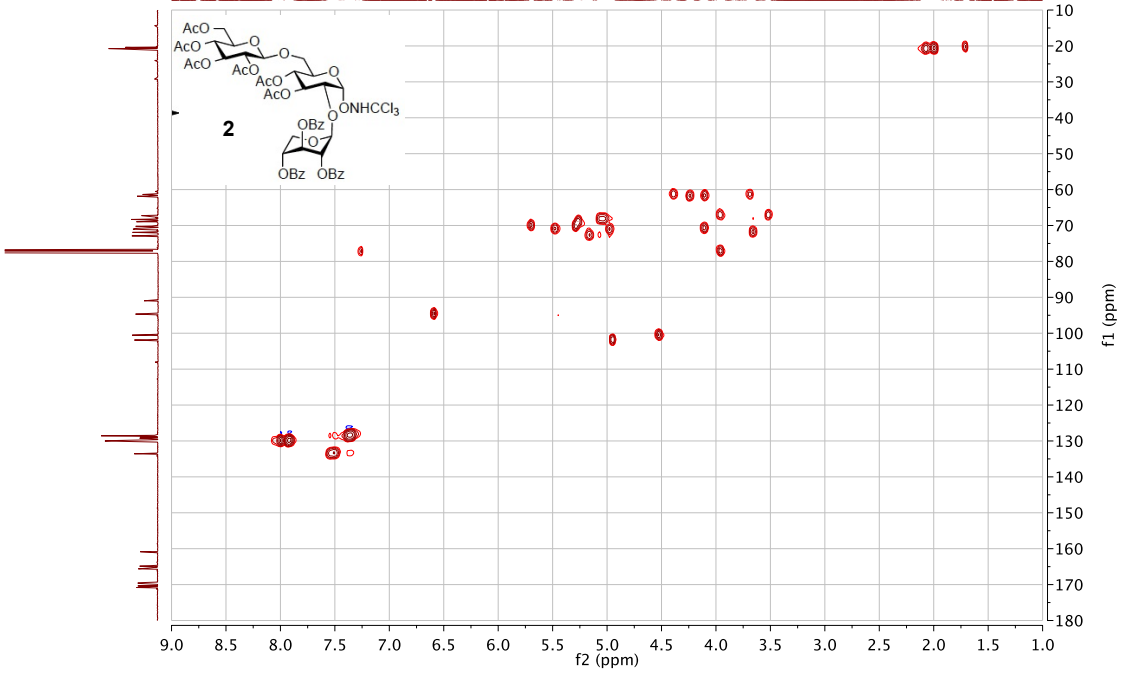

2

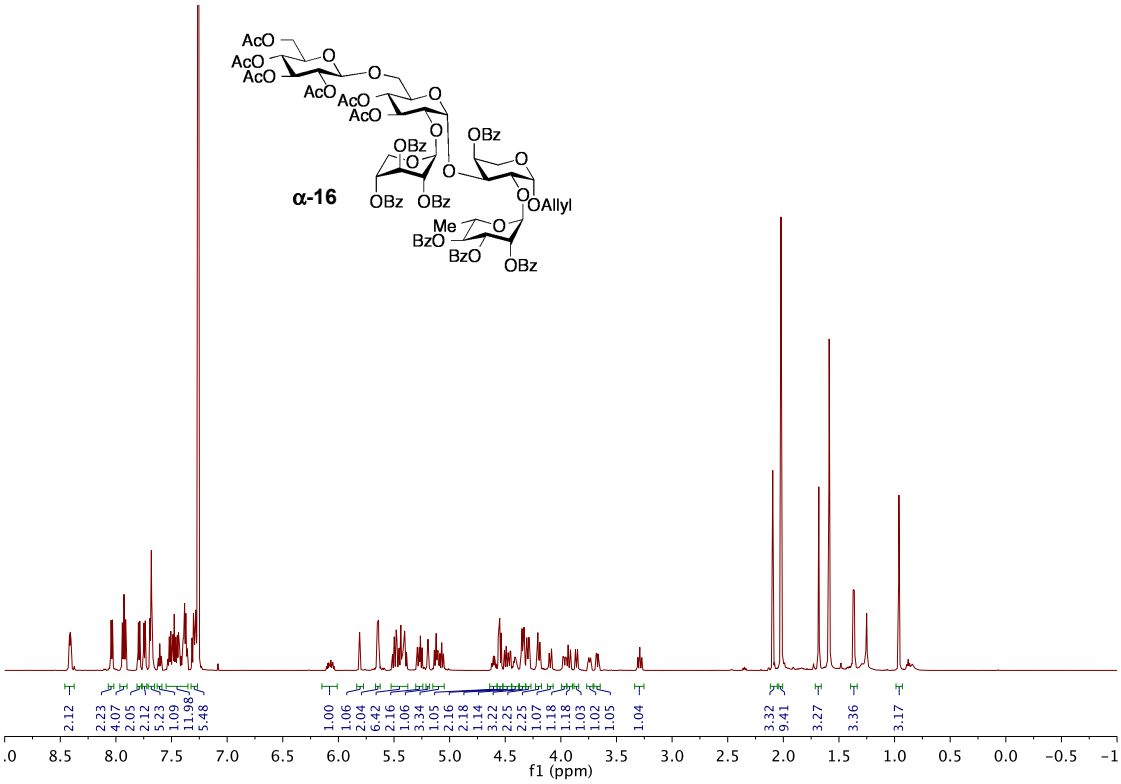

f1 (ppm)

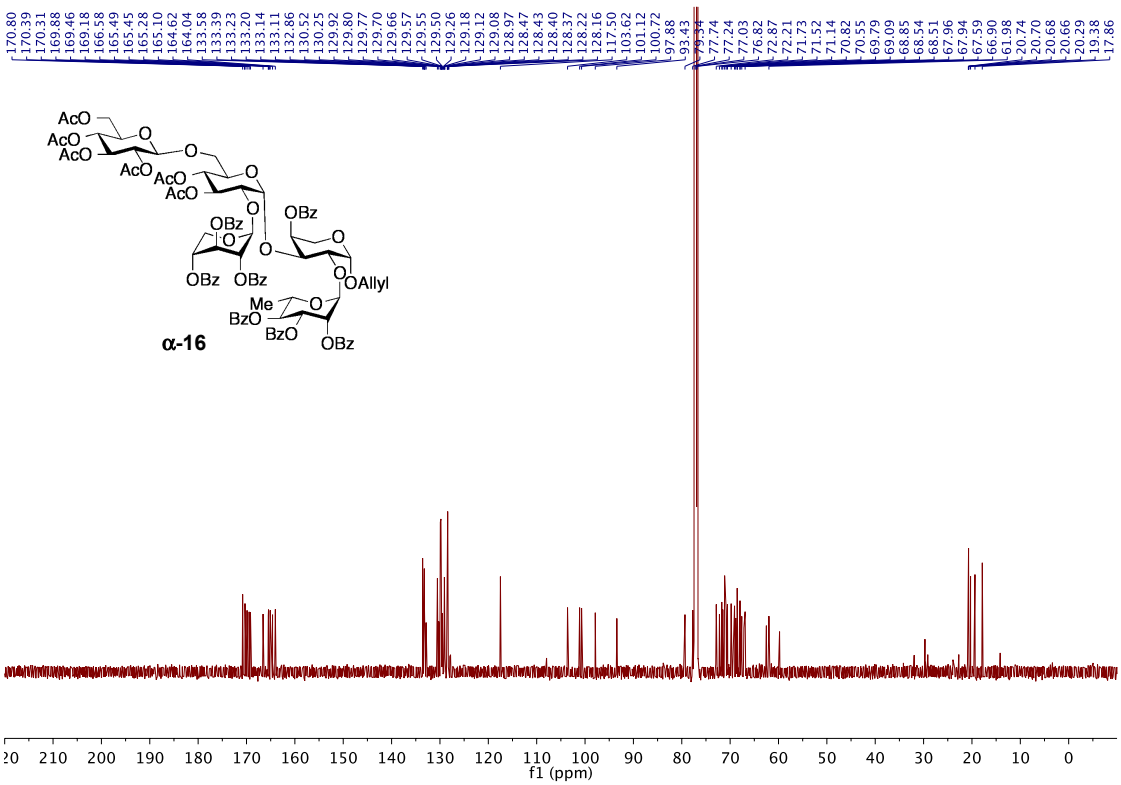

170.81
170.36
169.70
169.67
169.62
169.49
165.62
165.60
164.87
161.85
133.57
133.56
133.44
130.07
130.01
129.90
129.25
129.23
128.91
128.56
128.53
128.51
128.46
101.90
100.54
94.68
90.96
77.29
72.89
71.92
71.04
70.98
70.79
70.22
70.14
68.96
68.35
68.32
67.25
61.86
61.36
20.89
20.82
20.77
20.74
20.73
20.38
AcO
AcO
AcO
AcO
AcO
AcO
O
O
O
O
ONHCCl3
OBz
OBz
OBz
2
f1 (ppm)

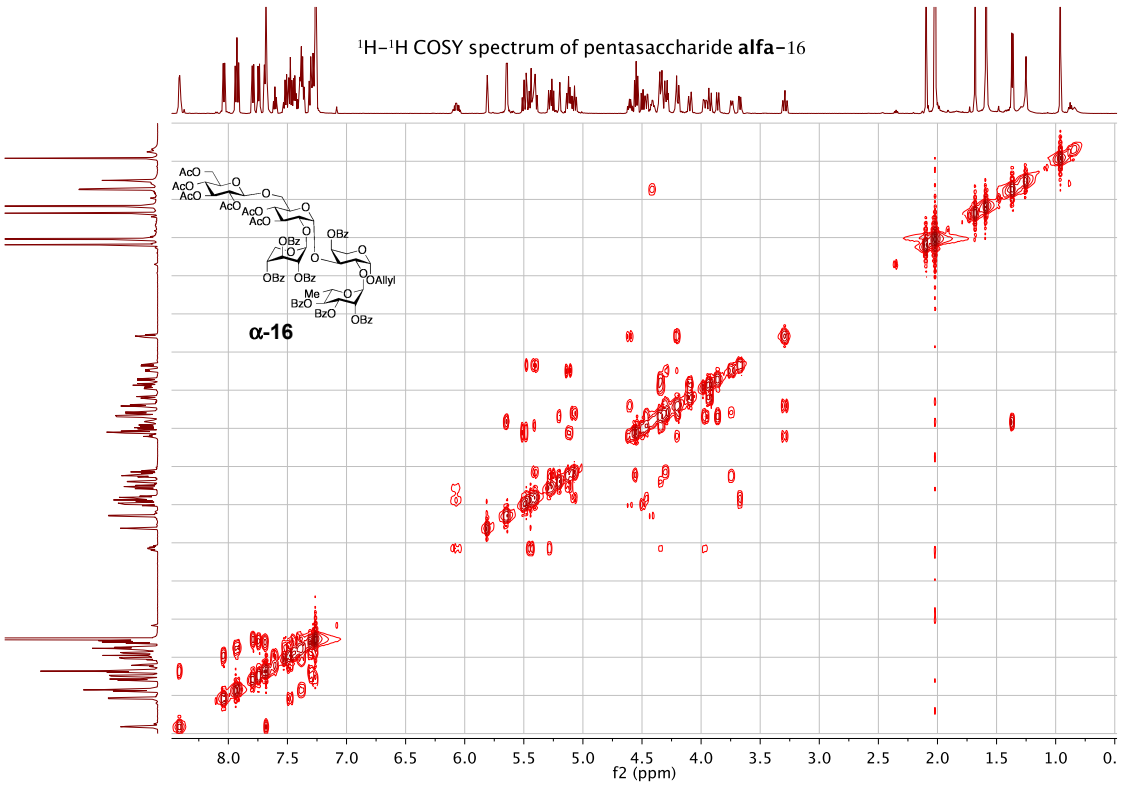

1H-1H COSY NMR spectrum of trichloroimidate 2
AcO
AcO
AcO
AcO
AcO
AcO
O
O
O
O
ONHCCl3
OBz
OBz
OBz
2
f2 (ppm)
f1 (ppm)

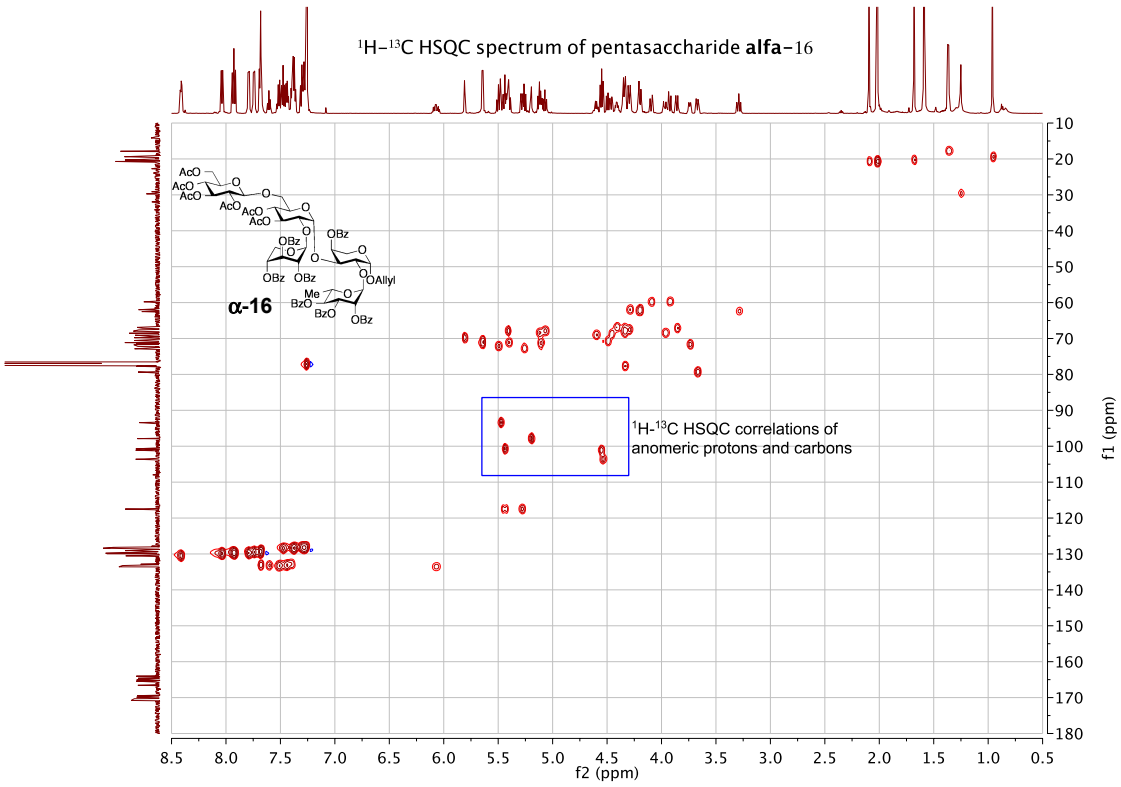
^{1}H-^{13}C HSQC NMR spectrum of trichloroimidate **2**

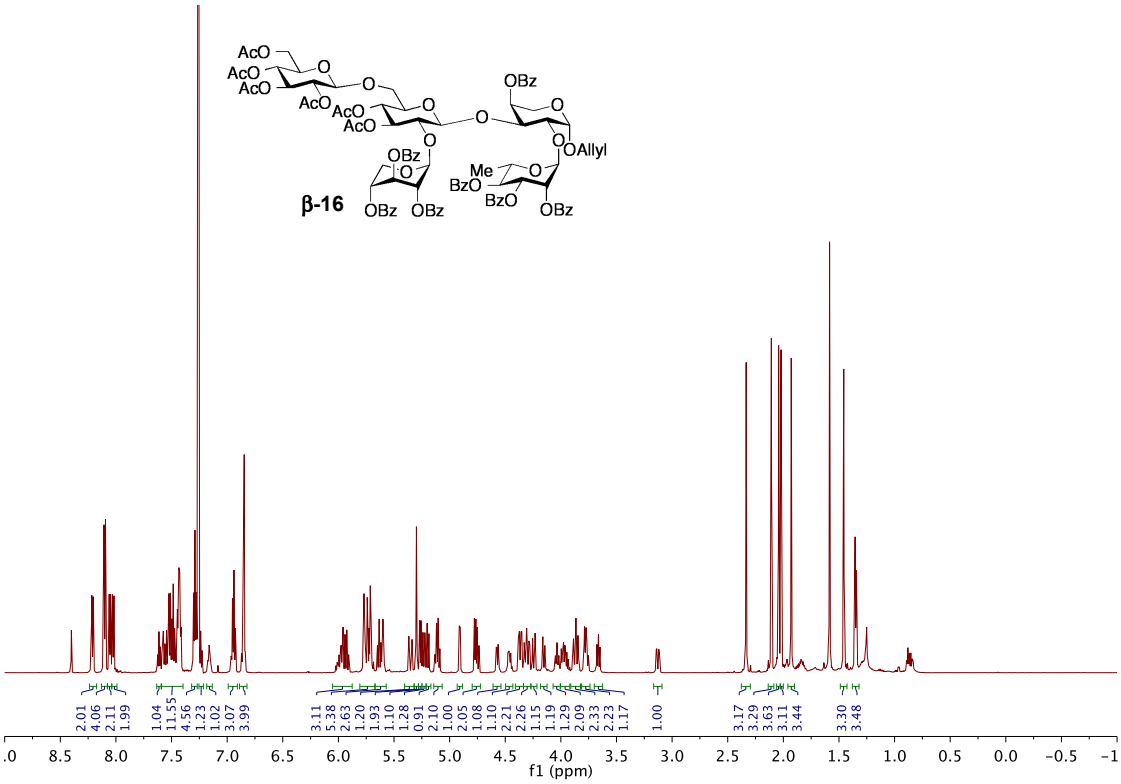


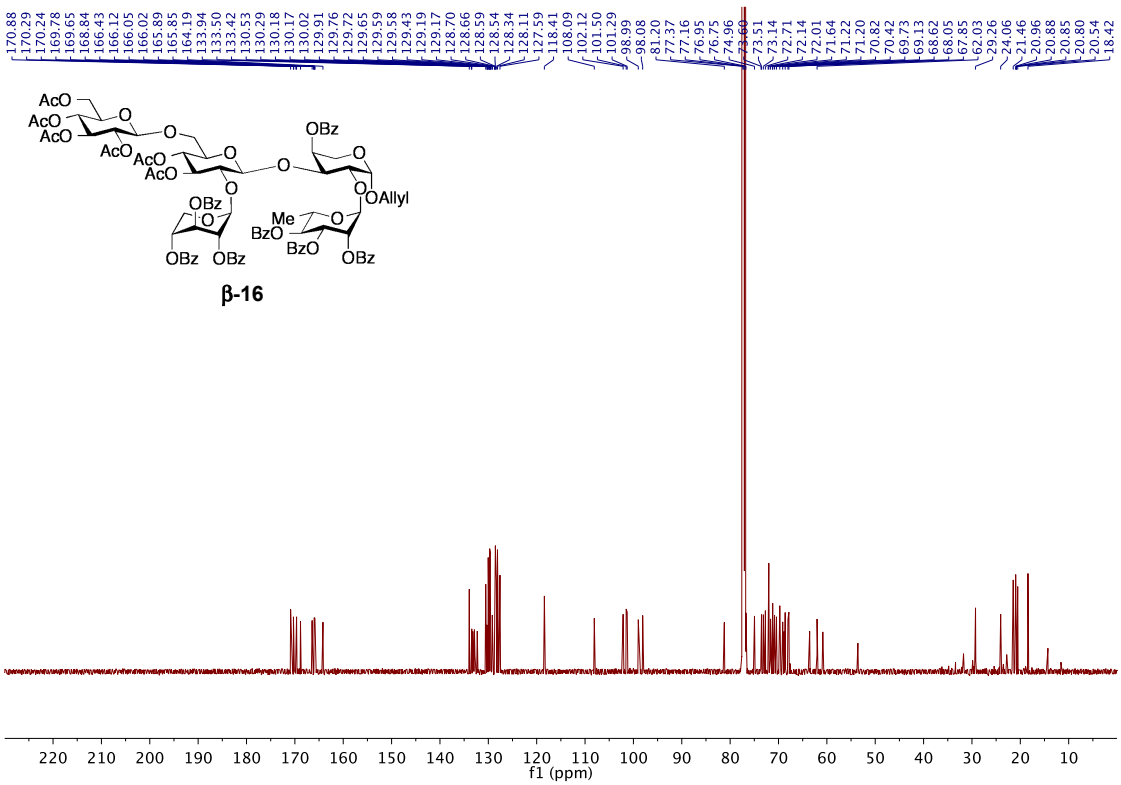


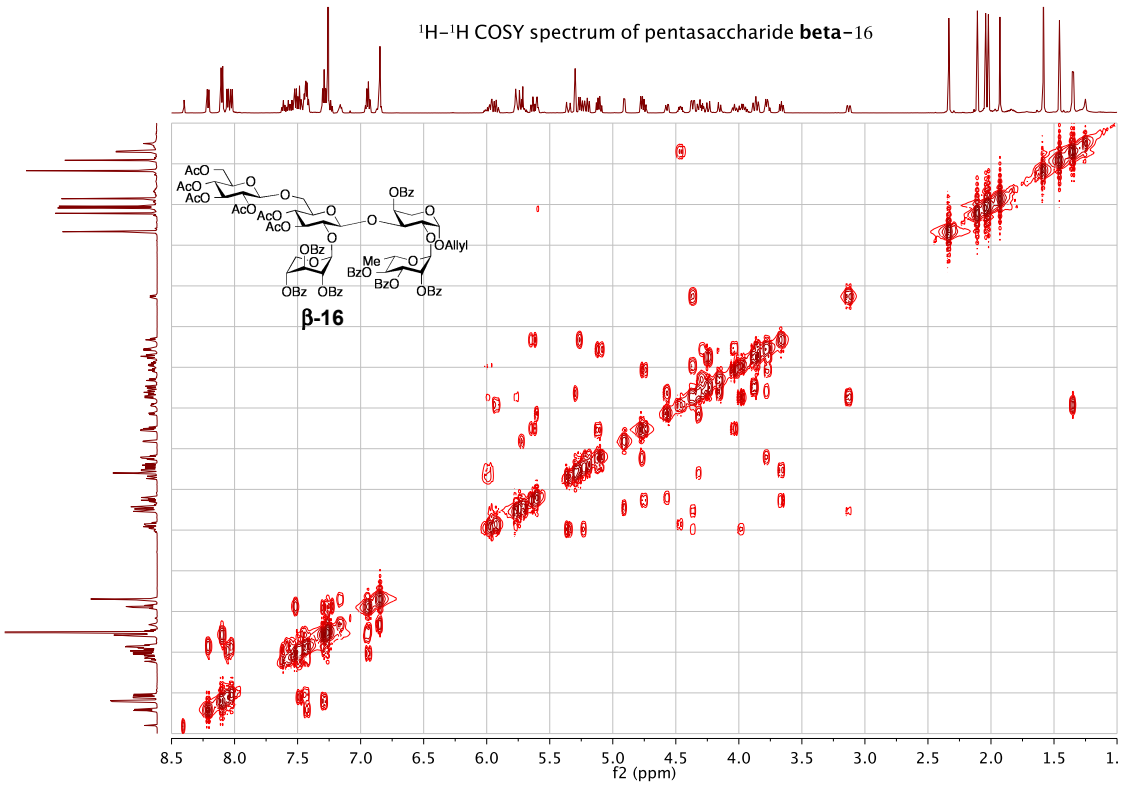

170.80
170.39
170.31
169.88
169.46
169.18
166.58
165.49
165.45
165.28
165.10
164.62
164.04
133.58
133.39
133.23
133.20
133.14
133.11
132.86
130.52
130.25
129.92
129.80
129.77
129.70
129.66
129.57
129.55
129.50
129.26
129.18
129.12
129.08
128.97
128.47
128.43
128.40
128.37
128.22
128.16
117.50
101.62
101.12
100.72
97.88
93.43
79.34
77.74
77.24
77.03
76.82
72.87
72.21
71.73
71.52
71.14
70.82
70.55
69.79
69.09
68.85
68.54
68.51
67.96
67.94
67.59
66.90
61.98
20.74
20.70
20.68
20.66
20.29
19.38
17.86
AcO
AcO
AcO
AcO
AcO
AcO
AcO
OBz
OBz
OBz
OBz
OBz
OAllyl
Me
BzO
BzO
OBz
α-16
f1 (ppm)

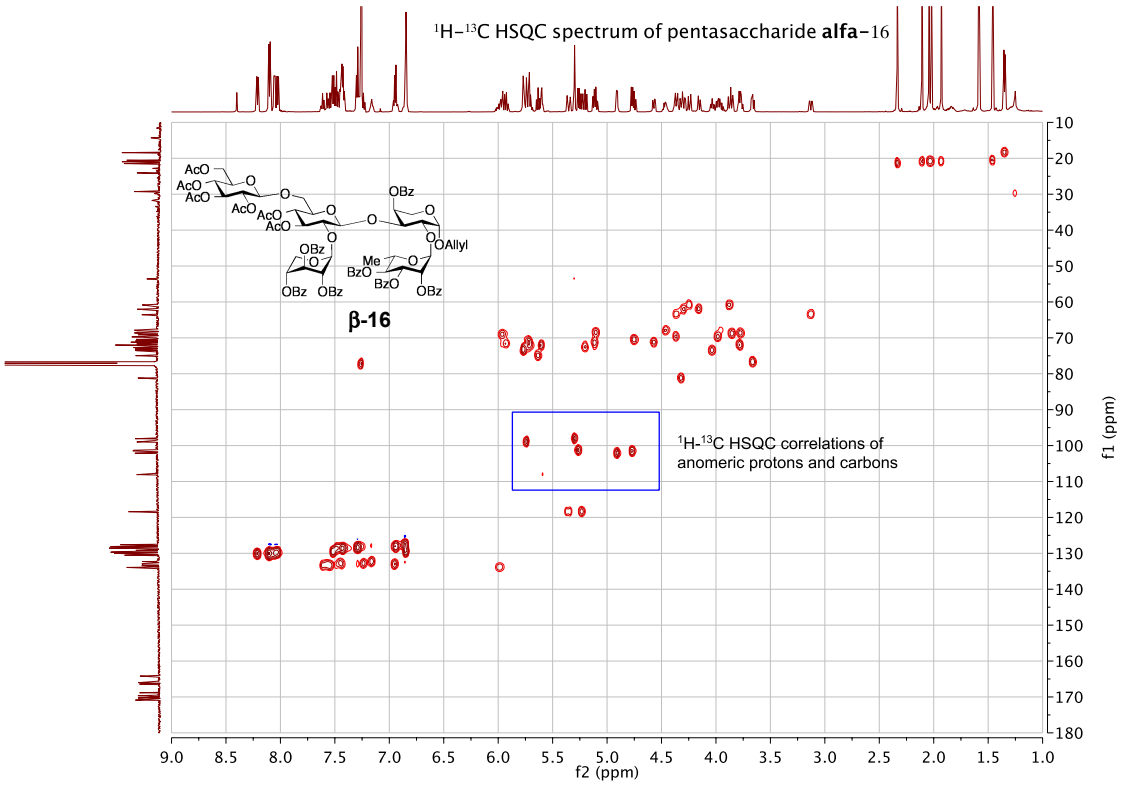

^{1}H–^{1}H COSY spectrum of pentasaccharide **alfa**–16
α-16
f2 (ppm)


^{1}H–^{13}C HSQC spectrum of pentasaccharide **alfa**–16
α-16
^{1}H-^{13}C HSQC correlations of anomeric protons and carbons
f2 (ppm)
f1 (ppm)


β-16
f1 (ppm)


β-16
f1 (ppm)


^{1}H–^{1}H COSY spectrum of pentasaccharide **beta**–16
β-16
f2 (ppm)


^{1}H–^{13}C HSQC spectrum of pentasaccharide **alfa**–16
β-16
^{1}H-^{13}C HSQC correlations of anomeric protons and carbons
f2 (ppm)
f1 (ppm)