Acyclic Tethers Mimicking Subunits of Polysaccharide Ligands: Selectin Antagonists

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Supporting Information

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I. Materials and Methods for Biological Evaluations

Immobilization of proteins on the sensor chip for surface plasmon resonance and **Determination of the IC50 by SPR**: see reference 22 of manuscript (ACS Med. Chem. Lett. **2012**)

Materials. Chinese hamster ovary (CHO) cells, human premyelocytic cell line HL-60 and human 293T kidney cells were obtained from the American Type Culture Collection (Rockville, MD). Dulbecco's Modified Eagle Medium (DMEM), Roswell Park Memorial Institute (RPMI) medium, penicillin-streptomycin and fetal bovine serum (FBS) used for cell culture were from Invitrogen Life Technologies (Burlington, Ontario, Canada). Fatty acid-free bovine serum albumin (BSA) (fraction V) and 4-(2-Hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) were from Sigma-Aldrich Co. (Oakville, ON, Canada) while goat anti-human IgG antibodies and sLe^x tetrasaccharide were obtained from Biosource International (Camarillo,CA, USA) and Calbiochem-Novabiochem Corporation (San Diego, CA, USA) respectively. CM5 sensor chip, N-Hydroxysuccinimide (NHS), N-Ethyl-N'-(3-dimethylaminopropyl)- carbodiimide hydrochloride (EDC) and surfactant P-20 were obtained from Biacore Inc (Piscataway, NJ, USA).

Animals: Male C57BL/6 mice between 10-14 weeks of age and weighing between 30.7 and 40.1 g were used. All procedures performed were approved by the IRCM Animal Ethic Committee. Mice were anesthetized with an intra muscular injection of 100 mg/kg ketamine hydrochloride and 10 mg/kg xylazine. Some mice received an intra-scrotal injection of 500 ng rmTNFα in 150 µL saline 2.5 to 3 hours before intravital microscopic observation. Before preparation of the cremaster muscle for intravital microscopy a cannulation of the left jugular vein to allow intravenous injection of compounds was performed. During the procedure, normothermia was maintained using a heating lamp and a small heating pad.

Intravital microscopy: The cremaster muscle was extracted through an incision in the scrotum. After removal of fat and connective tissue, an incision was made through the cremaster avoiding to severe major blood vessels. The cremaster muscle was then spread and pinned. During this

procedure and the intravital microscopic observation, the cremaster muscle was superfused with a thermo controlled bicarbonate-buffered solution (131.9 mmol/L NaCl, 18 mmol/L $NaHCO_3$, 4.7 mmol/L KCl, 2.0 mmol/L $CaCl_2$, and 2 mmol/L $MgSO_4$) through which a gas mixture of 5% CO_2 in N_2 was bubbled. Microscopic observations were made using a fluorescence reverse microscope. Venules with diameters between 30 and 60 μm were selected for observation and recorded via a CCD camera system. Venules were typically recorded in 30 seconds segments. Analyses were performed on data extracted off-line from the video recordings.

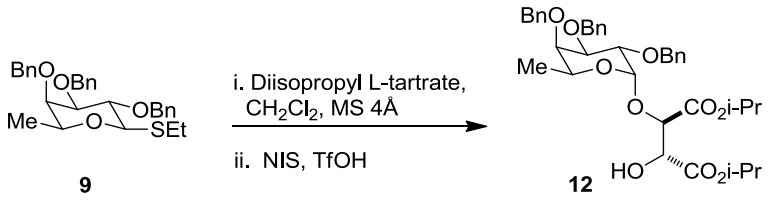
II. Materials and Methods for the Synthesis of sLe^x analogs

General Methods. All reactions requiring anhydrous conditions were conducted under a positive nitrogen atmosphere, in oven-dried glassware, using standard syringe techniques. The purity of the reported compounds herein was accessed by mass analysis or by NMR spectroscopic techniques. Tetrahydrofuran (THF) and ether were distilled from sodium/benzophenone immediately prior to use. Dichloromethane (CH_2Cl_2), dimethylsulfoxide (DMSO), and Et_3N were freshly distilled from CaH_2 under N_2 atmosphere. Methanol, benzene, *p*-toluenesulfonic acid (p-TsOH), triflic acid (TfOH), 4-dimehtylpyridine, N-iodosuccinimide (NIS), sodium hydride, 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), benzyl bromide, benzoyl chloride, acetic acid (99,9 %), palladium (10% on activated carbon), were used as received. Flash chromatography was performed on 0.040-0.063 mm silica gel using nitrogen pressure. Analytical thin-layer chromatography (TLC) was carried out on precoated (0.25 mm) silica gel plates. Melting points were determined on an electrothermal melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a 500 MHz NMR spectrometer using $CDCl_3$ (δ = 7.26 ppm) as an internal reference. ^{13}C NMR spectra were recorded at 125 MHz using $CDCl_3$ (δ = 77.1 ppm) as an internal reference. The data are reported as follows: chemical shift in ppm referenced to residual solvent ($CDCl_3$ δ 7.26 ppm), multiplicity (s = singlet, apps = apparent singlet, d = doublet, dd = doublet of doublets, ddd = douplet of douplets of douplets, appdd = apparent douplet of doubets, t = triplet, appt = apparent triplet, m = multiplet), coupling constants (Hz), and integration. Infrared spectra were recorded using a FTIR spectrophotometer. Electron impact (EI) mass spectra were recorded on an instrument operating at 70 eV. FAB mass spectra were recorded on a VG AutospecQ either with or without ionization.

Experimental Procedures and Characterization Data (12, 14, 16, 18, 19, 20, 21, 22, 23, 24, 25, 26, 28, 29, 30, 31, 32, 34, 35, 37, 38, 39, 40, 42, 43, 44, 46) :

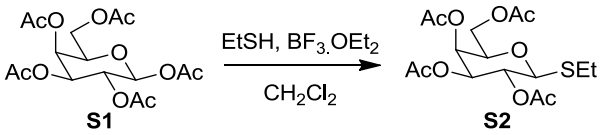
Precursors and intermediates not presented in the manuscript are numbered sequentially from **S1** to **S7** in the supporting information.

(2*R*, 3*R*) - 2 - Hydroxy- 3 - (3, 4, 5 - tri - O- benzyl - α- *L*- fucopyranos-l-yl)-succinic acid diisopropyl ester (12)



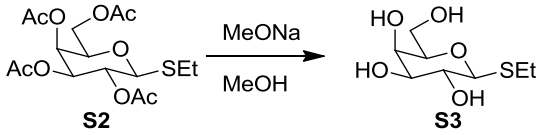
A solution of fucoside **9** (645 mg, 1.35 mmol) and diisopropyl-*L*-tartrate (0.84 mL, 5.13 mmol, 3.8 eq.) in CH_2Cl_2 (0.3M) was stirred 4 hours with 4Å molecular sieves (3.0 g/mmol) . The mixture was cooled at -30ºC and then NIS (911 mg, 4.05 mmol, 3.0 eq.) was added followed by triflic acid (0.06 mL, 0.41 mmol, 0.3 eq.). After 1 hour, the mixture was diluted with EtOAc to remove the molecular sieves and washed with a saturated solution of $NaHCO_3$ and 0.1M aqueous solution of $Na_2S_2O_3$. The organic layer was washed with water (2 x 25 mL) and brine, dried over $MgSO_4$ and filtered and concentrated *in vacuo*. Purification by flash chromatography (Toluene:EtOAc, 75:25) provided exclusively the α−glycoside **12** (659 mg, 75%) as a colorless oil. **Formula** : $C_{37}H_{46}O_{10}$; **MW** : 650.7551 g/mol; $\mathbf{[\alpha]_D^{25}}$ –83.0 (*c* 1.2, CH_2Cl_2); $\mathbf{R_f}$ = 0.48 (Toluene:EtOAc, 75:25); **^{1}H NMR** (500 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.27 (m, 15H), 5.07 (hept, *J* = 6.3 Hz, 1H), 4.99 (hept, *J* = 6.3 Hz, 1H), 5.02 – 4.91 (m, 2H), 4.78 (dd, *J* = 4.8, 11.5 Hz, 1H), 4.73 (dd, *J* =2.5, 11.5 Hz, 1H), 4.63 (d, *J* = 11.5 Hz, 1H), 4.52 (dd, *J* = 4.1, 7.0 Hz, 1H), 4.45 (d, J = 7.0 Hz, 1H), 4.27 (qd, *J* = 6.5, 0.8 Hz, 1H), 4.08 (m, 2H), 3.70 (s, 1H), 3.60 (d, *J* = 7.0 Hz, 1H), 1.31-1.22 (m, 12H), 1.08 (d, *J* = 6.5 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.2, 168.8, 138.8, 138.7, 138.3, 128.5, 128.42, 128.38, 128.3, 128.2, 127.7, 127.6, 127.5, 100.4, 79.7, 78.6, 77.7, 75.8, 75.0, 73.8, 73.0, 72.4, 69.9, 69.4, 67.8, 21.86, 21.86, 21.82, 21.80, 16.7, 14.3 ppm; **IR** (neat) ν_{max} 3458 (broad), 2981, 1749, 1455, 1374 cm^{-1}; **HRMS** calcd for $C_{37}H_{46}O_{10}Na$ $(M+Na)^+$: 673.2989, found : 673.2978 (+1.0 ppm); **Anal.** Calcd for $C_{37}H_{46}O_{10}$ (H_2O): C 66.45, H 7.23; found: C 66.78, H 7.23.

Ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside (S2)



To a solution of the β-D-galactose pentaacetate **S1** (5.3 g, 13.6 mmol) in CH_2Cl_2 (0.2M) was added EtSH (1.4 mL, 19.0 mmol, 1.4 eq.). The mixture was cooled at 0ºC, BF_3•OEt_2 (2.8 mL, 22.5 mmol, 1.66 eq.) was then added. The reaction was stirred 5 hours and a saturated solution of $NaHCO_3$ was added. The aqueous layer was extracted with CH_2Cl_2 (3 x 150 mL). The combined organic layers were washed with brine (100 ml), dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (Hexanes:EtOAc, 60:40) provided **S2** (5.16 g, 97%) as a colorless oil. ^{1}H NMR spectroscopic data correlate with the previously reported data for **24**[1]. **Formula** : $C_{16}H_{24}O_9S$; **MW** : 392.4214 g/mol; $\mathbf{R_f}$ = 0.53 (Hexanes:EtOAc, 50:50); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.44 (d, *J* = 3.7 Hz, 1H), 5.25 – 5.20 (m, 1H), 5.04 (dd, *J* = 10.1, 3.7 Hz, 2H), 4.49 (d, *J* = 10.1 Hz, 1H), 4.18 – 4.09 (m, 2H), 3.92 (td, *J* = 6.6, 0.9 Hz, 1H), 2.78 – 2.65 (m, 2H), 2.16 (s, 3H), 2.04(s, 3H), 2.02(s, 3H), 2.00 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 1H) ppm.

Ethyl 1-thio-β-D-galactopyranoside (S3)

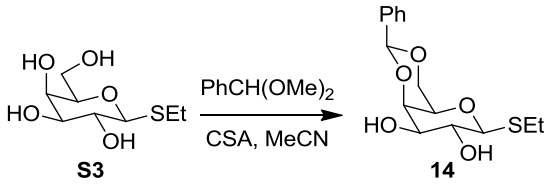


To a suspension of **S2** (2.22 g, 5.68 mmol) in MeOH (0.1M) at room temperature was added a solution MeONa (0.1M in MeOH, 2.84 mL, 2.84 mmol, 0.5 eq.). After the completion of reaction as indicated by TLC, Amberlite resin IR 120 (H^+) was added. The mixture was filtered and concentrated *in vacuo*. Purification by flash chromatography using silica gel pre-treated with 5% Et_3N in hexanes (CH_2Cl_2:EtOAc:MeOH, 50:40:10) provided **S3** (1.27 g, 100%) as a white solid. **Formula** : $C_8H_{16}O_5S$; **MW** : 224.2746 g/mol; $\mathbf{R_f}$ = 0.17 (CH_2Cl_2: MeOH, 90:10); $\mathbf{P_{fus}}$: 120.0 °C; $\mathbf{[\alpha]_D^{25}}$ –19.0 (*c* 0.01, MeOH); **^{1}H NMR** (500 MHz, CD_3OD) δ 4.34 (d, *J* = 9.6 Hz, 1H), 3.90 (d, *J* = 2.5 Hz, 1H), 3.76 (dd, *J* = 11.4, 6.8 Hz, 1H), 3.70 (dd, *J* = 11.4, 5.3 Hz, 1H), 3.59 –

[1] M. Weïwer, T. Sherwood, R. J. Linhardt, Journal of Carbohydrate Chemistry, 2008, 27:7, 420-427.

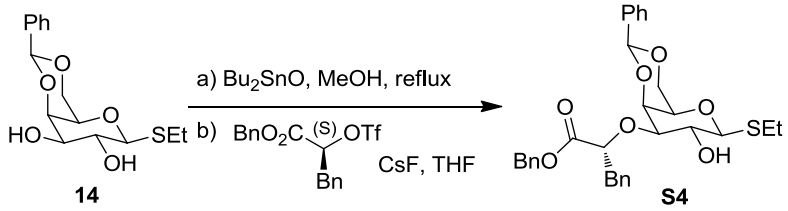
3.52 (m, 1H), 3.48 (dd, *J* = 9.2, 3.3 Hz, 1H), 2.84 – 2.69 (m, 2H), 1.31 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, CD_3OD) δ 87.5, 80.6, 76.3, 71.4, 70.5, 62.7, 24.9, 15.5 ppm; **IR** (neat) ν_{max} 3317 (broad), 2963, 2915, 2855 cm^{-1}; **MS (ES$^+$)** *m/z* 247 ($[M+Na]^+$,100); **HRMS** calcd for $C_8H_{16}NaO_5S$ $(M+Na)^+$: 247.0616, found : 247.0602 (-3.4 ppm).

Ethyl 4,6-O-benzylidene-1-thio-β-D-galactopyranoside (14)



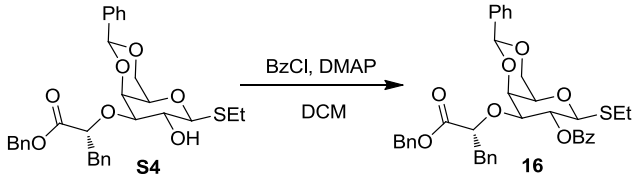
To a solution of the β-D-Thioethangalactoside **S3** (1.27 g, 5.66 mmol) in acetonitrile (56 mL, 0.1M) was added CSA (657 mg, 2.83 mmol, 0.5 eq.) and benzaldehyde dimethyl acetal (1.7 mL, 11.32 mmol, 2 eq.). The reaction was stirred 2.5 hours and neutralized with NEt_3. The mixture was evaporated and the purification by flash chromatography (DCM:EtOAc, 50:50) provided **14** (1.71 g, 97%) as a white solid. **Formula** : $C_{15}H_{20}O_5S$; **MW** : 312.3813 g/mol; $\mathbf{R_f}$ = 0.17 (DCM:EtOAc, 50:50); $\mathbf{P_{fus}}$: 153.8°C; $\mathbf{[\alpha]_D^{25}}$ –64.3 (*c* 0.03, CH_2Cl_2); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 – 7.35 (m, 5H), 5.55 (s, 1H), 4.37 – 4.36 (m, 1H), 4.34 (s app, 1H), 4.27 (d, *J* = 3.6 Hz, 1H), 4.04 (dd, *J* = 12.6, 1.8 Hz, 1H), 3.85 – 3.78 (m, 1H), 3.69 (dd, *J* = 9.4, 3.7 Hz, 1H), 3.54 (d, *J* = 1.2 Hz, 1H), 2.89 – 2.73 (m, 2H), 2.57 – 2.53 (m, 2H), 1.35 (t, *J* = 7.5 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 137.7, 129.5, 128.5, 126.6, 101.7, 85.5, 75.71, 75.70, 74.1, 70.3, 69.9, 69.5, 23.6 ppm; **MS (ES$^+$)** *m/z* 335 ($[M+Na]^+$,100); **IR** (neat) ν_{max} 3321, 3088, 2977, 2927, 2877, 1401 cm^{-1}; **HRMS** calcd for $C_{15}H_{20}NaO_5S$ $(M+Na)^+$: 335.0929, found : 335.0916 (-2.4 ppm); **Anal.** Calcd for $C_{15}H_{20}O_5S$: C 57.67, H 6.45; found: C 57.14, H 6.72.

(2R)-benzyl 2-((R)-6-(ethylthio)-7-hydroxy-2-phenylhexahydropyrano[3,2-d][1,3]dioxin-8-yloxy)-3-phenylpropanoate (S4)



A suspension of **14** (1.35 g, 4.32 mmol) in MeOH anhydrous (0.07 M) and Bu_2SnO (1.40 g, 5.62 mmol, 1.3 eq.) was heated under reflux for 2 hours. The solvent was removed with azeotrope with toluene and resulting colorless foam dried *in vacuo* for 2 h. The residue was dissolved in THF (0.07 M), activated CsF (1.97 g, 12.96 mmol, 3.0 eq) and (S)-benzyl 3-phenyl-2-(trifluoromethylsulfonyloxy)propanoate (5.03 g, 12.96 mmol, 3.0 eq) were added successively. The reaction was stirred 1h30 and water and EtOAc were added. The aqueous layer was extracted with EtOAc (3 x 150 mL). The combined organic layers were washed with brine (100 ml), dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (Hexanes:EtOAc, 60:40) provided **S4** (2.33 g, 98%) as a white foam. **Formula** : $C_{31}H_{34}O_7S$; **MW** : 550.6625 g/mol; $\mathbf{R_f}$ = 0.09 (Hexanes:EtOAc, 75:25); $\mathbf{[\alpha]_D^{25}}$ +12.4 (*c* 0.01., CH_2Cl_2); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 – 7.31 (m, 10H), 7.24 – 7.06 (m, 5H), 5.23 – 5.15 (m, 2H), 5.13 (s, 1H), 4.31 – 4.26 (m, 2H), 4.22 (dd, *J* = 12.3, 1.4 Hz, 1H), 4.08 – 4.01 (m, 1H), 4.03 (s, 1H), 3.81 (dd, *J* = 12.3, 1.5 Hz, 1H), 3.58 (d, *J* = 3.1 Hz, 1H), 3.25 – 3.21 (m, 2H), 3.13 (dd, *J* = 14.1, 3.2 Hz, 1H), 2.96 (dd, *J* = 14.1, 9.7 Hz, 1H), 2.86 – 2.69 (m, 2H), 1.31 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.1, 138.0, 137.4, 135.1, 129.6, 129.1, 128.9, 128.84, 128.81, 128.5, 128.3, 126.9, 126.5, 101.0, 85.0, 84.2, 80.5, 73.3, 70.0, 69.4, 67.7, 67.2, 39.6, 23.1, 15.2 ppm; **IR** (neat) ν_{max} 3442, 3086, 3070, 3033, 2957, 2931, 2866, 1731, 1497, 1455, 1170 cm^{-1}; **HRMS** calcd for $C_{31}H_{34}O_7SNa$ $(M+Na)^+$: 573.1923, found : 573.1895 (-3.94 ppm).

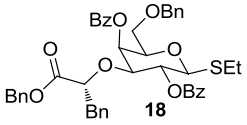
8-((*R*)-1-(benzyloxy)-1-oxo-3-phenylpropan-2-yloxy)-6-(ethylthio)-2-phenylhexahydropyrano[3,2-d][1,3]dioxin-7-yl benzoate (16)



To a solution of the alcohol **S4** (2.38 g, 4.32 mmol) in CH_2Cl_2 (0.1M) was added DMAP (2.20 g, 17.28 mmol, 4.0 eq.) and BzCl (1.5 mL, 12.96 mmol, 3.0 eq.,) at room temperature. The reaction was stirred over one hour and concentrated. Purification by flash chromatography (Hexanes:EtOAc, 75:25) provided **16** (2.62 g, 93%) as a white solid. **Formula** : $C_{38}H_{38}O_8S$; **MW** : 654.7685 g/mol; $\mathbf{R_f}$ = 0.16 (Hexanes:EtOAc, 75:25); $\mathbf{P_{fus}}$: 136.4°C; $\mathbf{[\alpha]_D^{25}}$ +49.5 (*c* 1.0., $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 – 8.05 (m, 2H), 7.59 – 7.53 (m, 1H), 7.48 – 7.27

(m, 10H), 7.12 – 6.96 (m, 7H), 5.73 (td, *J* = 9.7, 0.7 Hz, 1H), 5.31 (s, 1H), 4.78 – 4.65 (m, 2H), 4.51 (d, *J* = 9.7 Hz, 1H), 4.40 (dd, *J* = 7.3, 4.8 Hz, 1H), 4.30 (d, *J* = 12.4, 1.3 Hz, 1H), 3.99 (d, *J* = 3.2 Hz, 1H), 3.92 (dd, *J* = 12.4, 1.3 Hz, 1H), 3.86 (dd, *J* = 9.7, 3.2 Hz, 1H), 3.37 (dd, *J* = 1.3, 1.3 Hz, 1H), 2.97 – 2.71 (m, 4H), 1.26 (t, *J* = 7.5 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.2, 165.6, 137.7, 136.7, 135.4, 133.1, 130.4, 130.1, 129.7, 129.1, 128.6, 128.43, 128.44, 128.41, 128.3, 128.2, 126.6, 126.5, 101.0, 83.0, 79.1, 78.1, 73.3, 70.1, 69.5, 68.0, 66.5, 39.6, 22.9, 15.0 ppm; **IR** (neat) ν_{max} 2971, 1725, 1452, 1112, 1028 cm^{-1}; **HRMS** calcd for $C_{38}H_{38}O_8SNa$ $(M+Na)^+$: 677.2185, found : 677.2176 (-0.49 ppm); **Anal.** Calcd for $C_{38}H_{38}O_8S$: C 69.71, H 5.85; found: C 69.38, H 5.71.

2-(benzoyloxymethyl)-4-((*R*)-1-(benzyloxy)-1-oxo-3-phenylpropan-2-yloxy)-6-(ethylthio)tetrahydro-2H-pyran-3,5-diyl dibenzoate (18)

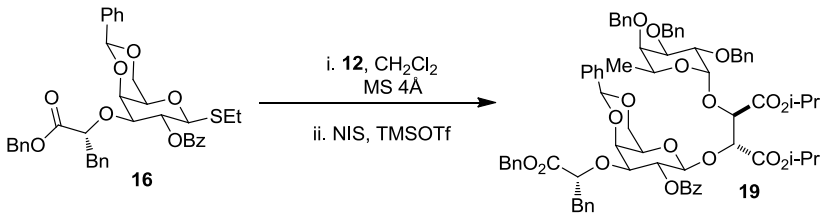


18

A suspension of **17** in MeOH (1 mmol in 15 ml) and Bu_2SnO (2.21 g, 8.87 mmol) was heated under reflux for 2h. Solvent was removed and resulting colorless foam was dried in vacuum for 16 h. Residue was dissolved in THF (1 mmol in 10 ml) and CsF (5 equiv.) and a solution of 10 in THF were added successively. Resulting solution was stirred until the diol was completely consumed by TLC (at least 60 min). When reaction was completed, a saturated aqueous solution of $NaHCO_3$ was poured onto the reaction mixture. After aqueous layer was extracted with EtOAc (3X), organic layers were combined, successively washed with brine, dried (MgSO4), filtered and concentrated. DMAP (3 equiv.) and Benzoyl chloride (2 equiv.) were added to solution of the crude at 0°C. After the reaction was completed as indicating by TLC, mixture was concentrated and purified on silica gel (20%EtOAc-Hexanes) provided **18** (532mg, 70%). **[α]D** = + 66.0 (c 1.0, CH_2Cl_2); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.14-8.06 (m, 4H), 7.66-7.60 (m, 1H), 7,59-7.54 (m, 1H), 7.53-7.42 (m, 2H), 7.47-7.41 (m, 2H), 7.36-7.19 (m, 8H), 7.11- 7.03 (m, 2H), 7.02-6.89 (m, 5H), 5.89 (d, J = 3.0 Hz, 1H), 5.56 (t, J = 9.9 Hz, 1H), 4.94 (d, J = 12.1 Hz, 1H), 4.79 (d, J = 12.1 Hz, 1H), 4.64 (d, J = 10.1 Hz, 1H), 4.60 (t, J = 6.2 Hz, 1H), 4.52 (d, J = 11.7 Hz, 1H), 4.45 (d, J = 11.7 Hz, 1H), 4.03 (dd, J = 3.0, 9.5 Hz, 1H), 3.91 (t, J = 6.8 Hz, 1H), 3.66 (dd, J = 5.9, 9.46.5, 1H), 3.56 (dd, J = 7.5, 9.4 Hz, 1H), 2.90-2.74 (m, 4H), 1.30 (t, J =7.5 Hz,

3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.9, 165.9, 165.8, 137.7, 135.9, 135.5, 133.6, 133.1, 130.5, 130.3, 130.3, 130.2, 129.8, 19.6, 128.7, 128.7, 128.7, 128.7, 128.6, 128.5, 128.2, 128.2, 128.1, 126.6, 84.3, 77.7, 77.1, 76.5, 69.4, 68.2, 66.7, 66.6, 39.2, 24.3, 15.7 ppm; **IR** (neat) ν_{max} 2869, 1724, 1452, 1266, 1110, 1070, 1028 cm^{-1}; **HRMS**: calcd for $C_{45}H_{44}O_9SNa$: m/z 783.2604, found: m/z 783.2587 (+0.9ppm).

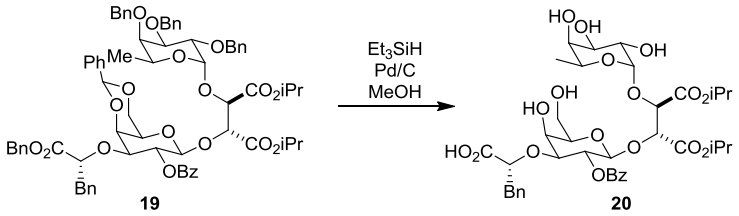
(2R,3R)-diisopropyl 2-(((2S,4aR,6S,7R,8S,8aS)-7-(benzoyloxy)-8-(((R)-1-(benzyloxy)-1-oxo-3-phenylpropan-2-yl)oxy)-2-phenylhexahydropyrano[3,2-d][1,3]dioxin-6-yl)oxy)-3-(((2S,5R,6S)-3,4,5-tris(benzyloxy)-6-methyltetrahydro-2H-pyran-2-yl)oxy)succinate (19)
sLex analog protected (19)



A solution of thiogalactoside **16** (642 mg, 0.98 mmol) and fucoside **12** (740 mg, 1.14 mmol, 1.16 eq) in CH_2Cl_2 (0.1M) was stirred 4 hours with 4Å molecular sieves (3.5 g/mmol). The mixture was cooled at -30ºC and then the NIS (661 mg, 2.94 mmol, 3.0 eq.) was added followed by TMSOTf (38 µL, 0.20 mmol, 0.2 eq.). After 1 hour, mixture was diluted with EtOAc to remove the molecular sieves and washed with a saturated solution of $NaHCO_3$ and 0.1M aqueous solution of $Na_2S_2O_3$. The organic layer was washed with water (2 x 100 mL) and brine, dried over $MgSO_4$ filtered and concentrated *in vacuo*. Purification by flash chromatography (Hexanes:EtOAc, 70:30) provided β−glycoside **19** (231 mg, 19%) as a colorless oil. **Formula** : $C_{73}H_{78}O_{18}$; **MW** : 1243.3896 g/mol; $\mathbf{R_f}$ = 0.29 (Hexanes:EtOAc, 70:30); $[\alpha]_D^{25}$ –14.0 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16 – 8.09 (m, 2H), 7.52 – 7.21 (m, 26H), 7.07 – 6.94 (m, 7H), 5.58 (dd, *J* = 10.1, 7.9 Hz, 1H), 5.17 (s, 1H), 5.00 – 4.85 (m, 5H), 4.71 – 4.68 (m, 4H), 4.67 – 4.51 (m, 5H), 4.28 (dd, *J* = 7.0, 4.9 Hz, 1H), 4.19 (qd, *J* = 6.5, 1.0 Hz, 1H), 4.13 (dt, *J* = 4.9, 2.4 Hz, 1H), 3.95 (dd, *J* = 10.2, 3.6 Hz, 1H), 3.87 (dd, *J* = 10.2, 2.7 Hz, 1H), 3.65 (d, *J* = 3.5 Hz, 1H), 3.62 (d, *J* = 1.6 Hz, 1H), 3.59 (dd, *J* = 12.0, 1.6 Hz, 1H), 3.46 (dd, *J* = 10.1, 3.5 Hz, 1H), 3.02 (s, 1H), 2.85 (qd, *J* = 14.0, 5.9 Hz, 2H), 1.19 (d, *J* = 6.2 Hz, 3H), 1.14 (d, *J* = 6.3 Hz,

6H), 1.12 (s, *J* = 6.2 Hz, 3H), 1.01 (d, *J* = 6.5 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$)δ 171.40, 168.58, 168.42, 165.80, 139.15, 139.08, 138.92, 138.11, 138.09, 136.87, 135.63, 132.84, 131.00, 130.24, 129.86, 129.28, 129.02, 128.64, 128.60, 128.56, 128.55, 128.48, 128.47, 128.43, 128.41, 128.37, 128.24, 128.20, 128.15, 127.82, 127.73, 127.53, 126.66, 125.54, 100.88, 99.67, 98.76, 79.39, 78.24, 77.65, 77.22, 76.79, 76.19, 75.03, 73.49, 73.18, 72.63, 70.52, 69.44, 68.65, 68.65, 67.51, 66.52, 66.41, 39.93, 21.86, 21.80, 21.70, 16.78.ppm; **IR** (neat) ν_{max} 3063, 3031, 2981, 2932, 1735, 1453, 1270, 1103 cm^{-1}; **HRMS** calcd for $C_{73}H_{79}O_{18}$ $(M+H)^+$: 1243.5266, found : 1243.5280 (+1.55 ppm).

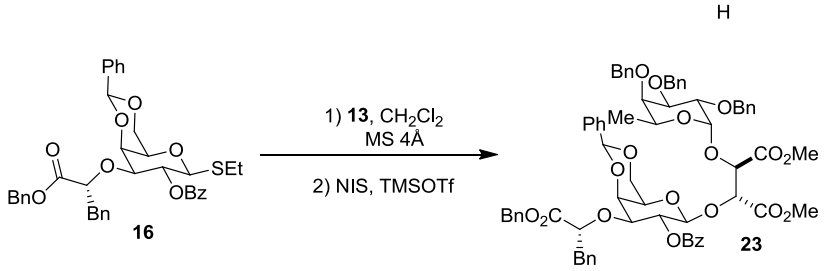
(R)-2-((2S,3R,4S,5S,6R)-3-(benzoyloxy)-2-((2R,3R)-1,4-diisopropoxy-1,4-dioxo-3-((2S,3S,4R,5S,6S)-3,4,5-trihydroxy-6-methyltetrahydro-2H-pyran-2-yloxy)butan-2-yloxy)-5-hydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-4-yloxy)-3-phenylpropanoic acid (20)



To a solution of compound **19** (45 mg, 0.22 mmol) in MeOH (0.1M) was added Pd/C (10 % wt., 234 mg). Et_3SiH (160 µL, 1 mmol, 30 eq) is added portion by portion. The mixture was stirred for 24h. The mixture was filtered on Celite®, washed with MeOH and concentrated *in vacuo.* Purification by flash chromatography (C18 reversed-phase silica, CH_3CN:H_2O, 35:65) provided **20** (15 mg, 53 %) as a white solid. Formula : $C_{38}H_{50}O_{18}$; **MW** : 794.7928 g/mol; $\mathbf{R_f}$ = 0.54 (EtOAc:*i*-PrOH:H_2O, 6:3:1); $\mathbf{[\alpha]_D^{25}}$ -23.6 (*c 1.0*, MeOH); **^{1}H NMR** (500 MHz, CD_3OD) δ 8.12 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.31 (s, *J* = 8.0 Hz, 2H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.18 – 7.13 (m, *J* = 7.3 Hz, 1H), 5.41 – 5.33 (m, 1H), 5.12 – 4.99 (m, 2H), 4.74 – 4.65 (m, 2H), 4.62 (d, *J* = 3.4 Hz, 1H), 4.57 (d, *J* = 8.0 Hz, 1H), 4.33 (d, *J* = 2.8 Hz, 1H), 4.29 (dd, *J* = 8.2, 4.3 Hz, 1H), 3.98 (dd, *J* = 13.0, 6.4 Hz, 1H), 3.86 (s, 1H), 3.78 – 3.59 (m, 5H), 3.49 (s, 1H), 3.41 (t, *J* = 5.9 Hz, 1H), 3.12 (dd, *J* = 13.9, 4.2 Hz, 1H), 2.89 (dd, *J* = 13.9, 8.4 Hz, 1H), 1.28 (dd, *J* = 8.4, 6.4 Hz, 5H), 1.19 (d, *J* = 6.3 Hz, 3H), 1.10 (d, *J* = 6.2 Hz, 3H), 0.96 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (126 MHz, CD_3OD) δ 177.53, 169.28, 167.66, 167.06, 139.04, 132.92, 130.37, 130.32, 129.41, 128.12, 128.08, 126.10, 102.04, 101.97, 81.61, 77.76, 77.55,

77.21, 77.19, 75.74, 72.27, 70.36, 70.13, 69.55, 68.52, 67.52, 66.95, 60.95, 39.64, 20.95, 20.77, 20.73, 20.67, 15.27; **IR** (neat) ν_{max} 3392 (broad), 3054, 2979, 2936, 2980, 1746, 1707, 1710, 1698, 1267, 1040 cm^{-1}; **HRMS** calcd for $C_{38}H_{49}O_{18}$ $(M-H)^-$:793.2919, found :793.2932 (+0.97 ppm)

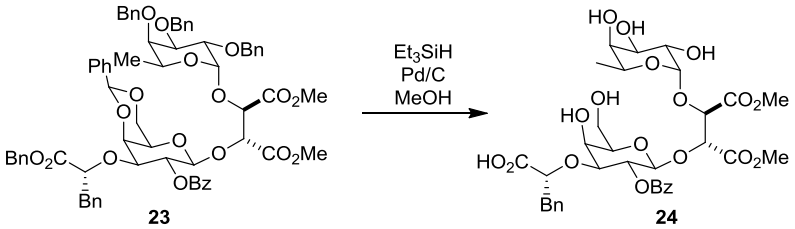
(2R,3R)-dimethyl-2-(((2S,4aR,6S,7R,8S,8aS)-7-(benzoyloxy)-8-(((R)-1-(benzyloxy)-1-oxo-3-phenylpropan-2-yl)oxy)-2-phenylhexahydropyrano[3,2-d][1,3]dioxin-6-yl)oxy)-3-(((2S,5R,6S)-3,4,5-tris(benzyloxy)-6-methyltetrahydro-2H-pyran-2-yl)oxy)succinate (23)



A solution of thiogalactoside **16** (510 mg, 0.779 mmol) and fucoside **1** (510 mg, 0.857 mmol, 1.1 eq) in CH_2Cl_2 (0.1M) was stirred 4 hours with 4Å molecular sieves (3.5 g/mmol). The mixture was cooled at -30ºC and then the NIS (525 mg, 2.33 mmol, 3 eq.) was added followed by TMSOTf (28 µL, 0.095 mmol, 0.2 eq.).. After 1 hour, the mixture was diluted with EtOAc to remove the molecular sieves and washed with a saturated solution of $NaHCO_3$ and 0.1M aqueous solution of $Na_2S_2O_3$. The organic layer was washed with water (2 x 100 mL) and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by flash chromatography (Hexanes:EtOAc, 70:30) provided β−glycoside **23** (463 mg, 50%) as a colorless oil. **Formula** : $C_{67}H_{70}O_{18}$; **MW** : 1187.28 g/mol; **[α]D** = + 4.81 (c 0.7, $CDCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.2 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.42 (dd, *J* = 13.4, 6.1 Hz, 6H), 7.35 – 7.29 (m, 11H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.03 (ddd, *J* = 26.2, 13.9, 6.3 Hz, 7H), 5.70 – 5.53 (m, 1H), 5.22 (s, 1H), 4.94 (dd, *J* = 9.2, 6.4 Hz, 3H), 4.81 (d, *J* = 4.3 Hz, 1H), 4.67 (ddd, *J* = 19.4, 16.1, 7.6 Hz, 9H), 4.38 – 4.29 (m, 1H), 4.17 (dd, *J* = 18.2, 9.3 Hz, 2H), 3.98 (dd, *J* = 10.1, 3.1 Hz, 1H), 3.88 (d, *J* = 9.9 Hz, 1H), 3.76 (d, *J* = 3.1 Hz, 1H), 3.65 (dd, *J* = 17.1, 10.7 Hz, 3H), 3.59 (d, *J* = 0.9 Hz, 3H), 3.41 (t, *J* = 10.7 Hz, 3H), 3.07 (s, 1H), 2.89 (qd, *J* = 13.9, 6.0 Hz, 2H), 2.38 (s, 1H), 1.57 (d, *J* = 21.3 Hz, 5H), 1.01 (dd, *J* = 18.3, 6.0 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.35, 169.61, 165.55, 139.10, 139.05, 138.89, 138.48, 137.95, 136.80, 136.74, 135.55, 132.93,

130.82, 130.76, 130.19, 130.01, 129.83, 129.80, 129.26, 129.11, 128.66, 128.57, 128.52, 128.49, 128.47, 128.41, 128.35, 128.22, 127.93, 127.78, 127.68, 127.66, 127.54, 127.29, 126.67, 126.57, 100.90, 99.72, 79.21, 78.05, 77.91, 76.62, 76.08, 74.98, 73.17, 73.12, 72.52, 69.96, 68.71, 67.67, 66.69, 66.51, 52.39, 39.82, 16.73; **IR** (neat) ν_{max} 3080, 3064, 3032, 2952, 2919, 2860, 1732, 1545, 1270, 1100 cm^{-1}; **HRMS** calcd for $C_{67}H_{71}O_{18}$ $(M+H)^+$:1187.4640, found :1187.4639 (+0.3694 ppm)

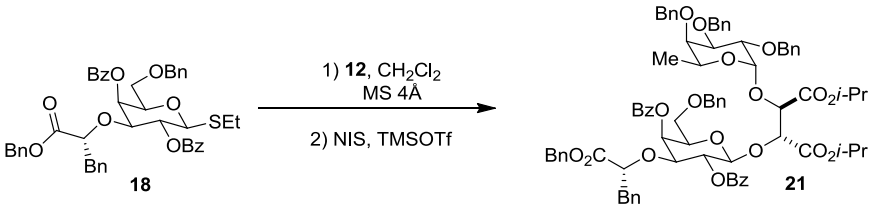
(R)-2-(((2S,3R,4S,5S,6R)-3-(benzoyloxy)-2-(((2R,3R)-1,4-dimethoxy-1,4-dioxo-3-(((2S,3S,4R,5S,6S)-3,4,5-trihydroxy-6-methyltetrahydro-2H-pyran-2-yl)oxy)butan-2-yl)oxy)-5-hydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-4-yl)oxy)-3-phenylpropanoic acid (24)



To a solution of compound **23** (40 mg, 0.033 mmol) in MeOH (0.1M) was added Pd/C (10 % wt., 234 mg). Et_3SiH (160 µL, 1 mmol, 30 eq) is added portion by portion. The mixture was stirred for 24h. The mixture was filtered on Celite®, washed with MeOH and concentrated *in vacuo.* Purification by flash chromatography (C18 reversed-phase silica, CH_3CN:H_2O, 35:65) provided **24** (15 mg, 53 %) as a white solid. [α]D = -6.86 (c 0.5, MeOH) ; **Formula**: $C_{34}H_{42}O_{18}$; **MW:** 738.6865; **^{1}H NMR** (500 MHz, CD_3OD) δ 8.10 (t, *J* = 15.4 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 7.1 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 5.45 – 5.26 (m, 1H), 4.85 – 4.72 (m, 3H), 4.59 (dd, *J* = 10.3, 5.9 Hz, 2H), 4.44 (d, *J* = 2.8 Hz, 1H), 4.28 (dd, *J* = 8.1, 4.5 Hz, 1H), 3.85 (dt, *J* = 29.6, 16.9 Hz, 3H), 3.83 – 3.69 (m, 6H), 3.73 – 3.54 (m, 3H), 3.50 – 3.42 (m, 4H), 3.32 (dt, *J* = 3.2, 1.6 Hz, 3H), 3.13 (dd, *J* = 13.9, 4.3 Hz, 1H), 2.90 (dd, *J* = 13.9, 8.1 Hz, 1H), 0.97 (dd, *J* = 23.7, 6.5 Hz, 3H) ; **^{13}C NMR** (126 MHz, CD_3OD) δ 177.56, 169.95, 169.31, 166.72, 139.01, 132.81, 130.60, 130.24, 129.45, 128.15, 128.03, 126.05, 102.51, 101.80, 81.35, 78.74, 77.34, 77.29, 75.80, 72.33, 71.96, 70.16, 68.64,

67.44, 66.79, 61.13, 51.94, 51.55, 39.55, 15.20; **IR** (Neat) υ_{max} 3343, 2919, 1725, 1602, 1274, 1115, 1040cm^{-1} **; HRMS** calcd for $C_{34}H_{41}O_{18}$ $(M-H)^-$:737.2293, found :737.2292 (-0.93 ppm)

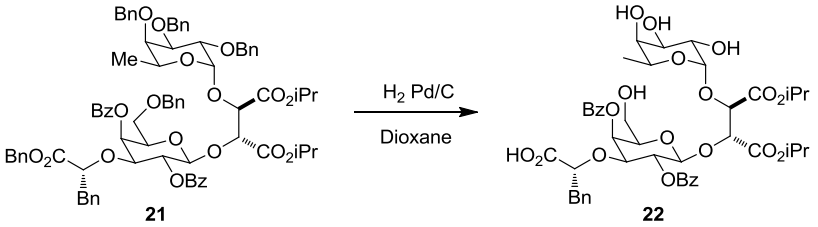
(2R,3R)-diisopropyl 2-(((2S,3R,4S,5S,6R)-3,5-bis(benzoyloxy)-4-(((R)-1-(benzyloxy)-1-oxo-3-phenylpropan-2-yl)oxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)-3-(((2S,5R,6S)-3,4,5-tris(benzyloxy)-6-methyltetrahydro-2H-pyran-2-yl)oxy)succinate (21)



A solution of thiogalactoside **18** (383 mg, 0.503 mmol) and fucoside **12** (360 mg, 0.553 mmol, 1.1 eq) in CH_2Cl_2 (0.1M) was stirred 4 hours with 4Å molecular sieves (3.5 g/mmol). The mixture was cooled at -30ºC and then the NIS (339 mg, 1.5 mmol, 3.0 eq.) was added followed by TMSOTf (18 µL, 0.1 mmol, 0.2 eq.). After 1 hour, mixture was diluted with EtOAc to remove the molecular sieves and washed with a saturated solution of $NaHCO_3$ and 0.1M aqueous solution of $Na_2S_2O_3$. The organic layer was washed with water (2 x 100 mL) and brine, dried over $MgSO_4$ filtered and concentrated *in vacuo*. Purification by flash chromatography (Hexanes:EtOAc, 70:30) provided β−glycoside **21** (340 mg, 50%) as a colorless oil. $\mathbf{[\alpha]_D^{25}}$ +10.8 (c =2, $CDCl_3$) ; **Formula** : $C_{80}H_{84}O_{19}$; **MW** : 1349.5116 g/mol ; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.14 – 8.06 (m, 4H), 7.64 – 7.51 (m, 2H), 7.48 – 7.42 (m, 5H), 7.36 – 7.29 (m, 13H), 7.05 – 6.89 (m, 8H), 5.78 – 5.69 (m, 1H), 5.63 – 5.48 (m, 1H), 5.07 – 5.03 (m, 1H), 5.01 – 4.84 (m, 6H), 4.84 – 4.39 (m, 14H), 4.18 – 4.07 (m, 1H), 4.03 – 3.88 (m, 2H), 3.83 (dd, *J* = 9.9, 3.3 Hz, 1H), 3.76 – 3.68 (m, 1H), 3.61 (dt, *J* = 12.3, 6.2 Hz, 1H), 3.57 – 3.40 (m, 2H), 2.81 (ddd, *J* = 20.6, 13.6, 6.2 Hz, 2H), 1.75 (d, *J* = 13.9 Hz, 1H), 1.27 – 1.11 (m, 14H), 1.00 (t, *J* = 7.0 Hz, 3H) ; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.76, 168.35, 168.21, 165.91, 165.69, 139.19, 139.18, 139.01, 137.83, 135.90, 135.51, 133.44, 132.78, 130.87, 130.26, 130.24, 129.77, 129.71, 128.65, 128.59, 128.52, 128.51, 128.37, 128.36, 128.29, 128.15, 128.12, 128.02, 127.94, 127.74, 127.67, 127.59, 127.59, 126.51, 100.29, 99.60, 79.66, 79.64, 79.63, 77.99, 77.89, 77.79, 77.51, 77.35, 77.01, 76.98, 75.91, 74.93, 74.00, 73.98, 73.06, 72.65, 71.48, 69.18, 69.17, 68.01, 68.00, 67.55, 66.59,

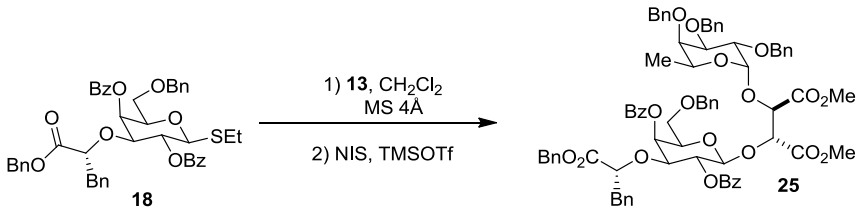
66.41, 39.38, 21.85, 21.83, 16.72; **IR** (Neat) υ_{max} 3091, 3059, 3032, 2876, 1731, 1496, 1453, 1267, 1175, 1104cm^{-1} **; HRMS** calcd for $C_{80}H_{84}O_{19}Na$ $(M+Na)^+$:1371.5505, found :1371.5552 (+3.85 ppm) ;

(2R)-2-((4-(((2R,3R)-1,4-diisopropoxy-1,4-dioxo-3-(((2S,3S,4R,5S,6S)-3,4,5-trihydroxy-6-methyltetrahydro-2H-pyran-2-yl)oxy)butan-2-yl)oxy)-4-(2-hydroxyethoxy)butan-2-yl)oxy)-3-phenylpropanoic acid (22)



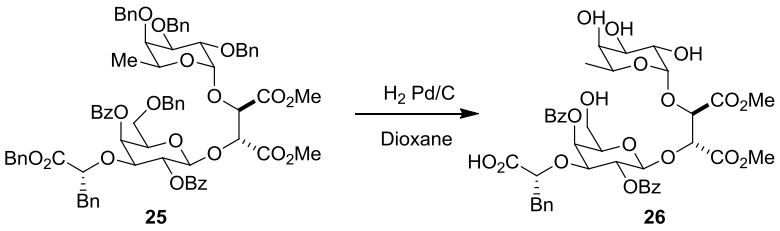
To a solution of compound **21** (35 mg, 0.026 mmol) in Dioxane (0.1M) under an inert atmosphere was added Pd/C (10 % wt.). The system was purged with H_2 three times and reaction mixture was stirred at room temperature overnight under one atm of H_2. The mixture was filtered on Celite®, washed with MeOH and concentrated *in vacuo*. Purification by flash chromatography (C18 reversed-phase silica, CH_3CN:H_2O, 40:60) provided **22** (15 mg, 65 %) as a white solid. **$[\alpha]_D^{25}$** +12.5 (c 1.0, MeOH); **Formula** : $C_{45}H_{54}O_{19}$; **MW** : 898.8989 g/mol; **^{1}H NMR** (500 MHz, CD_3OD) δ 8.22 (d, *J* = 7.5 Hz, 2H), 8.03 (d, *J* = 7.9 Hz, 2H), 7.62 (dt, *J* = 23.3, 7.5 Hz, 2H), 7.50 (td, *J* = 7.7, 2.8 Hz, 4H), 7.09 (d, *J* = 7.2 Hz, 2H), 6.85 (t, *J* = 7.5 Hz, 2H), 6.75 (t, *J* = 7.4 Hz, 1H), 5.81 (d, *J* = 2.8 Hz, 1H), 5.47 (dd, *J* = 9.9, 8.1 Hz, 1H), 5.06 (dt, *J* = 12.4, 6.2 Hz, 2H), 4.91 – 4.88 (m, 2H), 4.74 (d, *J* = 3.4 Hz, 1H), 4.72 – 4.63 (m, 2H), 4.41 (d, *J* = 3.4 Hz, 1H), 4.31 – 4.19 (m, 2H), 4.11 (q, *J* = 6.3 Hz, 1H), 3.85 (t, *J* = 6.2 Hz, 1H), 3.76 (dd, *J* = 10.2, 3.2 Hz, 1H), 3.66 (dd, *J* = 10.2, 4.0 Hz, 1H), 3.59 (dd, *J* = 8.4, 4.6 Hz, 3H), 2.81 (dd, *J* = 13.5, 5.9 Hz, 1H), 2.67 (dd, *J* = 13.4, 7.2 Hz, 1H), 1.29 (t, *J* = 8.0 Hz, 3H), 1.26 (d, *J* = 6.2 Hz, 4H), 1.19 (d, *J* = 6.3 Hz, 3H), 1.09 (d, *J* = 6.2 Hz, 3H), 1.03 (d, *J* = 6.5 Hz, 2H); **^{13}C NMR** (125 MHz, CD_3OD) δ 177.18, 169.15, 167.78, 167.21, 165.86, 138.23, 133.14, 132.72, 130.79, 130.47, 129.93, 129.81, 129.31, 128.26, 128.04, 127.42, 125.50, 102.20, 101.92, 80.01, 78.22, 77.79, 75.41, 74.91, 72.33, 71.76, 70.36, 70.19, 69.55, 68.66, 67.56, 66.74, 60.68, 39.50, 20.93, 20.82, 20.79, 20.69, 15.32; **IR** (Neat) υ_{max} 3393, 2981, 2935, 1724, 1601, 1495, 1452, 1375, 1270, 1098cm^{-1}; **HRMS** calcd for $C_{45}H_{53}O_{19}$ $(M-H)^-$:897.3181, found :897.3176 (-1.13 ppm);

(2R,3R)-dimethyl 2-(((2S,3R,4S,5S,6R)-3,5-bis(benzoyloxy)-4-(((R)-1-(benzyloxy)-1-oxo-3-phenylpropan-2-yl)oxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)-3-(((2S,5R,6S)-3,4,5-tris(benzyloxy)-6-methyltetrahydro-2H-pyran-2-yl)oxy)succinate (25)



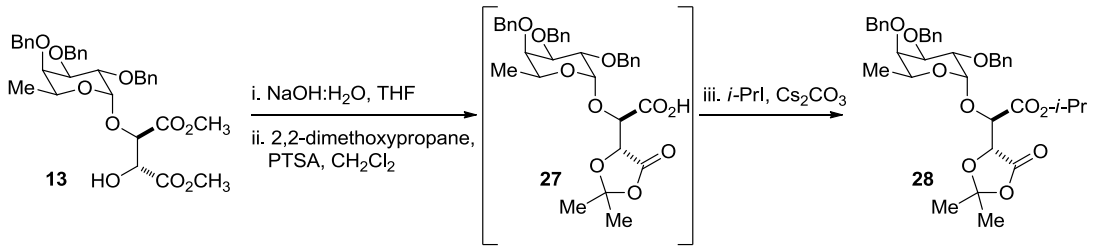
A solution of thiogalactoside **18** (383 mg, 0.503 mmol) and fucoside **12** (360 mg, 0.553 mmol, 1.1 eq) in CH_2Cl_2 (0.1M) was stirred 4 hours with 4Å molecular sieves (3.5 g/mmol). The mixture was cooled at -30ºC and then the NIS (339 mg, 1.5 mmol, 3.0 eq.) was added followed by TMSOTf (18 µL, 0.1 mmol, 0.2 eq.). After 1 hour, mixture was diluted with EtOAc to remove the molecular sieves and washed with a saturated solution of $NaHCO_3$ and 0.1M aqueous solution of $Na_2S_2O_3$. The organic layer was washed with water (2 x 100 mL) and brine, dried over $MgSO_4$ filtered and concentrated *in vacuo*. Purification by flash chromatography (Hexanes:EtOAc, 70:30) provided β−glycoside **25** (340 mg, 50%) as a colorless oil. $\mathbf{[\alpha]_D^{25}}$ (+9.15, c=2 , $CDCl_3$); **Formula** : $C_{76}H_{76}O_{19}$; **MW** : 1293.4052 g/mol; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.2 Hz, 4H), 7.60 (t, *J* = 7.4 Hz, 2H), 7.54 – 7.44 (m, 4H), 7.39 (dd, *J* = 14.9, 8.5 Hz, 7H), 7.30 – 7.18 (m, 13H), 7.03 – 6.85 (m, 8H), 5.75 (d, *J* = 2.9 Hz, 1H), 5.56 (dd, *J* = 9.8, 8.2 Hz, 1H), 4.92 (ddd, *J* = 17.1, 12.1, 6.2 Hz, 5H), 4.84 – 4.63 (m, 8H), 4.62 – 4.36 (m, 6H), 4.09 (q, *J* = 6.5 Hz, 1H), 3.96 (s, 2H), 3.90 (dd, *J* = 9.8, 3.2 Hz, 1H), 3.78 (t, *J* = 6.3 Hz, 1H), 3.62 (dd, *J* = 9.5, 5.7 Hz, 1H), 3.55 (s, 3H), 3.49 (s, 3H), 2.86 (dd, *J* = 13.6, 5.6 Hz, 1H), 2.76 (dd, *J* = 13.7, 7.0 Hz, 1H), 0.99 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.77, 169.58, 169.25, 166.01, 165.60, 139.19, 139.03, 138.94, 137.84, 135.87, 135.47, 134.46, 133.51, 132.87, 130.77, 130.32, 130.24, 129.75, 129.63, 128.72, 128.69, 128.63, 128.56, 128.54, 128.53, 128.52, 128.41, 128.39, 128.32, 128.14, 128.00, 127.99, 127.76, 127.70, 127.60, 127.57, 126.54, 100.44, 100.33, 79.59, 78.75, 77.60, 77.31, 76.93, 75.95, 74.92, 74.01, 73.28, 72.99, 72.90, 71.10, 68.16, 68.11, 67.73, 66.54, 66.49, 52.47, 52.30, 39.34, 16.69; **IR** (Neat) υ_{max} 3086, 3064, 3027, 2919, 1727, 1604, 1453, 1267, 1173, 1105 cm^{-1}; **HRMS** calcd for $C_{76}H_{76}O_{19}Na$ $(M+Na)^+$:1315.4878, found :1315.4915 (+3.2 ppm).

(R)-2-(((2S,3R,4S,5S,6R)-3,5-bis(benzoyloxy)-2-(((2R,3R)-1,4-dimethoxy-1,4-dioxo-3-(((2S,3S,4R,5S,6S)-3,4,5-trihydroxy-6-methyltetrahydro-2H-pyran-2-yl)oxy)butan-2-yl)oxy)-6-(hydroxymethyl)tetrahydro-2H-pyran-4-yl)oxy)-3-phenylpropanoic acid (26)



To a solution of compound **25** (40 mg, 0.033 mmol) in Dioxane (0.1M) under an inert atmosphere was added Pd/C (10 % wt.). The system was purged with H_2 three times and reaction mixture was stirred at room temperature overnight under one atm of H_2. The mixture was filtered on Celite®, washed with MeOH and concentrated *in vacuo*. Purification by flash chromatography (C18 reversed-phase silica, CH_3CN:H_2O, 40:60) provided **26** (15 mg, 53 %) as a white solid. $[\alpha]_D^{25}$ +20.8 (c =2, MeOH; **Formula** : $C_{41}H_{46}O_{19}$; **MW** : 842.7925 g/mol; **^{1}H NMR** (500 MHz, CD_3OD) δ 8.10 (t, *J* = 15.4 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 7.1 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 5.45 – 5.26 (m, 1H), 4.85 – 4.72 (m, 2H), 4.59 (dd, *J* = 10.3, 5.9 Hz, 2H), 4.44 (d, *J* = 2.8 Hz, 1H), 4.28 (dd, *J* = 8.1, 4.5 Hz, 1H), 3.85 (dt, *J* = 29.6, 16.9 Hz, 3H), 3.83 – 3.69 (m, 4H), 3.73 – 3.54 (m, 5H), 3.50 – 3.42 (m, 3H), 3.32 (dt, *J* = 3.2, 1.6 Hz, 3H), 3.17 – 2.79 (m, 1H), 0.97 (dd, *J* = 23.7, 6.5 Hz, 3H); **^{13}C NMR** (126 MHz, CD_3OD) δ 177.17, 169.90, 169.21, 167.16, 165.94, 138.15, 133.17, 132.81, 130.74, 130.42, 129.92, 129.80, 129.30, 128.30, 128.14, 127.45, 125.54, 102.45, 101.98, 79.99, 78.65, 77.85, 75.40, 75.01, 72.34, 71.64, 70.26, 68.61, 67.57, 66.88, 60.76, 52.08, 51.66, 39.48, 15.26; **IR** (Neat) υ_{max} 3360, 3059, 2930, 1720, 1495, 1270, 1083 cm^{-1}; **HRMS** calcd for $C_{41}H_{45}O_{19}$ $(M-H)^-$:841.2555, found :841.2540 (-2.44 ppm)

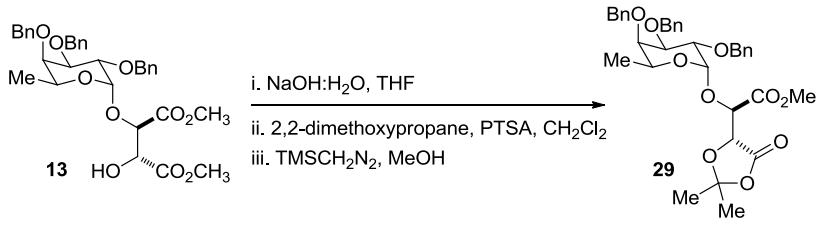
(*R*)-isopropyl 2-((*R*)-2,2-dimethyl-5-oxo-1,3-dioxolan-4-yl)-2-((2*S*,3*S*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methyltetrahydro-2*H*-pyran-2-yloxy)acetate (28)



To a solution of diester **13** (0.49 g, 0.83 mmol) in THF (0.1 M) at 25°C was added a 10% NaOH solution (5 mL). After 30 minutes, the reaction mixture was neutralized with a 1M HCl solution. The aqueous layer was extracted with AcOEt (4 x 10 mL). The combined organic layers were washed with brine (50 ml), dried over $MgSO_4$ and concentrated *in vacuo*. The residue obtained (a diacid) was then dissolved in DCM (0.1 M), treated with 2,3-dimethoxypropane (0.65 mL, 8.3 mmol, 10 equiv.) and PTSA (0.004 g, 0.02 mmol, 0.02 equiv.) under an inert atmosphere. After 32 hours, the reaction mixture is diluted with EtOAc (20 mL) and passed through a pad of silica gel. After *in vacuo* concentration of the resulting solution, the residue obtained (dioxolanone **27**) is dissolved in DMF (8.3 mL) at 25°C under an inert atmosphere and treated with Cs_2CO_3 (0.325 g, 1.00 mmol, 1.2 equiv.) and *i*-PrI (0.12 mL, 1.3 mmol, 1.5 equiv.). After maintaining the reaction mixture at 25°C for 16 hours, distilled water was added (8.3 mL). The aqueous layer was extracted with AcOEt (3 x 10 mL). The combined organic layers were washed with brine (50 ml), dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (Hexanes:EtOAc, 85:15) provided **28** (0.303 g, 56% over 3 steps) as a colorless oil.

Formula: $C_{37}H_{44}O_{10}$; **MW** : 648.29 g/mol; **R*f*** 0.76 (30 % EtOAc/Hexanes); $\mathbf{[\alpha]_D^{25}}$ – 83.3 (*c* 1.6, CH_2Cl_2); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46-7.42 (m, 2H), 7.40-7.26 (m, 13H), 5.09 (septet, *J* = 6.3 Hz, 1H), 5.02 (d, *J* = 3.7 Hz, 1H), 4.98 (d, *J* = 11.6 Hz, 1H), 4.88 (d, *J* = 2.1 Hz, 1H), 4.84 (d, *J* = 12.2 Hz, 1H), 4.78 (d, *J* = 11.7 Hz, 1H), 4.72 (d, *J* = 12.1 Hz, 1H), 4.66 (d, *J* = 11.6 Hz, 1H), 4.61 (d, *J* = 11.6 Hz, 1H), 4.47 (d, *J* = 2.1 Hz, 1H), 4.38 (q, *J* = 6.3 Hz, 1H), 4.05 (dd, *J* = 3.7, 10.3 Hz, 1H), 3.98 (dd, *J* = 2.7, 10.3Hz, 1H), 3.69 (d, *J* = 1.5 Hz, 1H), 1.58 (s, 3H), 1.54 (s, 3H), 1.28 (d, *J* = 3.8 Hz, 3H), 1.27 (d, *J* = 3.7 Hz, 3H), 1.06 (d, *J* = 6.5 Hz, 3H) ppm; **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 170.3, 168.3, 139.2, 138.9, 138.8, 128.6, 128.53, 128.47, 128.4, 128.2, 127.8, 127.6, 127.5, 113.2, 100.8, 78.9, 78.1, 77.1, 76.28, 76.26, 75.0, 73.2, 72.9, 69.7, 67.9, 27.6, 26.9, 22.0, 21.9, 16.8 ppm; **IR** (film) υ_{max} 2983 (broad), 1791, 1755, 1267, 1102, 738 cm^{-1}; **HRMS** (ESI) calculated for $C_{37}H_{48}O_{10}N$ $(M+NH4)^+$: 666.3273, found : 666.3269 (-0.5 ppm).

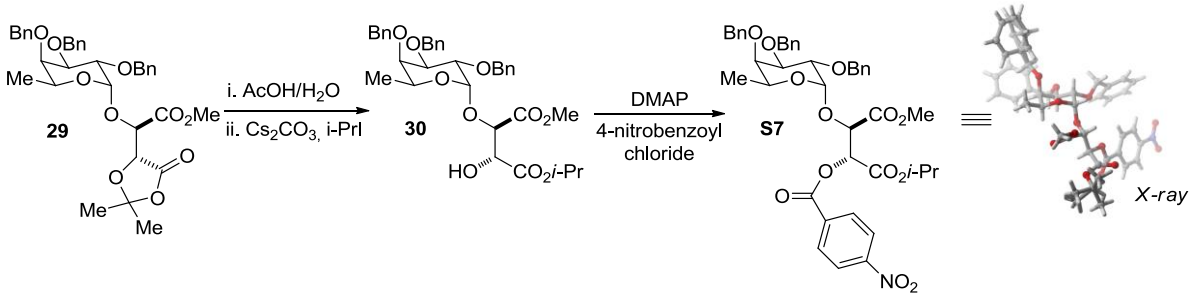
(*R*)-methyl 2-((*R*)-2,2-dimethyl-5-oxo-1,3-dioxolan-4-yl)-2-((2*S*,3*S*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methyltetrahydro-2*H*-pyran-2-yloxy)acetate (29)



To a solution of diester **13** (0.319 g, 0.531 mmol) in THF (0.1 M) at 25°C was added a 10% NaOH solution (6 mL). After 30 minutes, the reaction mixture was neutralized with a 1M HCl solution. The aqueous layer was extracted with AcOEt (4 x 10 mL). The combined organic layers were washed with brine (50 ml), dried over $MgSO_4$ and concentrated *in vacuo*. The residue obtained (a diacid) was then dissolved in DCM (0.1 M), treated with 2,3-dimethoxypropane (0.650 mL, 5.3 mmol, 10 equiv.) and PTSA (0.002 g, 0.01 mmol, 0.02 equiv.) under an inert atmosphere. After 32 hours, the reaction mixture is diluted with EtOAc (20 mL) and passed through a pad of silica gel. After *in vacuo* concentration of the resulting solution, the residue obtained (dioxolanone) is placed in benzene/MeOH (3/1) at 25°C under an inert atmosphere and treated with $TMSCH_2N_2$ until a persistent yellowish color is observed. The reaction mixture is then concentrated *in vacuo*. Purification by flash chromatography (Hexanes:EtOAc, 85:15) provided **27** (0.241 g, 72% over 3 steps) as a colorless oil.

Formula: $C_{35}H_{40}O_{10}$; **MW** : 620.26 g/mol; **R*f*** 0.72 (30 % EtOAc/Hexanes); $[\alpha]_D^{25}$ – 98.2 (*c* 1.2, CH2Cl2); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46-7.26 (m, 15H),5.03 (d, *J* = 3.9 Hz, 1H), 4.98 (d, *J* = 11.5 Hz, 1H), 4.89 (d, *J* = 1.9 Hz, 1H), 4.85 (d, *J* = 11.9 Hz, 1H), 4.77 (d, *J* = 11.5 Hz, 1H), 4.72 (d, *J* = 12.0 Hz, 1H), 4.66 (d, *J* = 11.7 Hz, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 1.9 Hz, 1H), 4.36 (q, *J* = 6.34 Hz, 1H), 4.05 (dd, *J* = 3.7, 10.3 Hz, 1H), 3.97 (dd, *J* = 2.7, 10.3 Hz, 1H), 3.79 (s, 3H), 3.69 (d, *J* = 1.71 Hz, 1H), 1.59 (s, 3H), 1.55 (s, 3H), 1.07 (d, *J* = 6.6 Hz, 3H) ppm; **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 170.1, 169.4, 139.2, 138.9, 138.8, 128.6, 128.55, 128.51, 128.4, 128.2, 127.8, 127.63, 127.59, 127.5, 113.2, 101.1, 78.9, 78.0, 76.4, 76.2, 75.0, 73.2, 73.0, 68.0, 52.7, 27.6, 26.9, 16.8 ppm; **IR** υ_{max} 2934 (broad), 1791, 1764, 1104, 1048, 738, 699 cm^{-1}; **HRMS** (ESI) calculated for $C_{35}H_{40}O_{10}Na$ $(M+Na)^+$: 643.2519, found : 643.2522 (+1.3 ppm).

(2*R*,3*R*)-1-isopropyl 4-methyl 2-hydroxy-3-((2*S*,3*S*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methyltetrahydro-2*H*-pyran-2-yloxy)succinate (30)



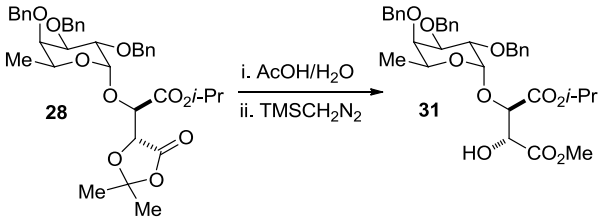
A solution of dioxolanone **29** (0.458 g, 0.736 mmol) in AcOH:H_2O (80:20, 10mL) was maintained at 50°C during 16 hours. The reaction mixture was then diluted with H_2O (10mL) and extracted with AcOEt (3 x 10 mL). The combined organic layers were washed with brine (50 ml), dried over $MgSO_4$ and concentrated *in vacuo*. After *in vacuo* concentration of the resulting solution, the residue obtained is dissolved in DMF (7.4 mL) at 25°C under an inert atmosphere and treated with Cs_2CO_3 (0.285 g, 0.883 mmol, 1.2 equiv) and i-PrI (0.107 mL, 1.10 mmol, 1.5 equiv). After maintaining the reaction mixture at 25°C for 16 hours, distilled water was added (8.3 mL). The aqueous layer was extracted with AcOEt (3 x 10 mL). The combined organic layers were washed with brine (50 ml), dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (Hexanes:EtOAc, 85:15) provided **30** (0.271 g, 59% over 2 steps) as a colorless oil.

Formula: $C_{35}H_{42}O_{10}$; **MW** : 622.28 g/mol; **R*f*** 0.45 (40 % EtOAc/Hexanes); **$[\alpha]_D^{25}$** -88.2 (*c* 1.7, CH_2Cl_2); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40-7.27 (m, 15H), 5.01 (septet, *J* = 6.3 Hz, 1H), 4.97 (d, *J* = 11.7 Hz, 1H), 4.93 (d, *J* = 2.9 Hz, 1H), 4.81 (d, *J* = 11.7 Hz, 1H), 4.80 (d, *J* = 11.5 Hz, 1H), 4.74 (d, *J* = 11.7 Hz, 1H), 4.74 (d, *J* = 11.5 Hz, 1H), 4.65 (d, *J* = 11.7 Hz, 1H), 4.52 (t, *J* = 4.4 Hz, 1H), 4.46 (d, *J* = 4.2 Hz, 1H), 4.23 (q, *J* = 6.3 Hz, 1H), 4.08 (dd, *J* = 3.2, 10.2 Hz, 1H), 4.05 (dd, *J* = 2.2, 10.2 Hz, 1H), 3.80-3.76 (m, 4H), 3.72 (s, 1H), 1.24 (d, *J* = 6.1 Hz, 3H), 1.22 (d, *J* = 6.3 Hz, 3H), 1.09 (d, *J* = 6.6 Hz, 3H) ppm; **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 170.2, 170.0, 138.8, 138.7, 138.3, 128.62, 128.58, 128.55, 128.45, 128.3, 127.91, 127.87, 127.8, 127.7, 100.6, 79.7, 78.8, 77.8, 77.6, 75.9, 75.1, 74.0, 73.1, 72.5, 70.1, 67.9, 52.6, 21.9, 16.8 ppm. **IR** (film) υ_{max} 2933 (broad), 1749, 1454, 1103, 1052, 739, 699 cm^{-1}. **HRMS** (ESI) calculated for $C_{35}H_{42}O_{10}Na$ $(M+Na)^+$: 645.2670, found : 645.2662 (-1.3 ppm).

(2*R*,3*R*)-1-isopropyl 4-methyl 2-(4-nitrobenzoyloxy)-3-((2*S*,3*S*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methyltetrahydro-2*H*-pyran-2-yloxy)succinate (S7)

Formula: $C_{42}H_{45}O_{13}$; **MM** : 771.29 g/mol; **RMN ^{1}H** (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.5 Hz, 2H), 8.11 (dd, *J* = 1.8, 6.8 Hz, 2H), 7.38-7.20 (m, 15H), 5.76 (d, *J* = 4.9 Hz, 1H), 5.45 (d, *J* = 3.4 Hz, 1H), 5.00 (st, *J* = 6.3 Hz, 1H), 4.99 (d, *J* = 11.5 Hz, 1H), 4. 80 (d, *J* = 12.0 Hz, 1H), 4.74 (d, *J* = 11.7 Hz, 1H), 4.72 (d, *J* = 5.4 Hz, 1H), 4.69 (d, *J* = 11.5 Hz, 1H), 4.66 (d, *J* = 12.0 Hz, 1H), 4.66 (d, *J* = 10.0 Hz, 1H), 4.19 (q, *J* = 6.3 Hz, 1H), 4.09 (dd, *J* = 3.4, 10.3 Hz, 1H), 4.03 (dd, *J* = 2.2, 10.3 Hz, 1H), 3.75 (s, 3H), 3.74 (s, 1H), 1.21 (d, *J* = 6.3 Hz, 3H), 1.20 (d, *J* = 6.3 Hz, 3H), 1.09 (d, *J* = 6.3 Hz, 3H). **RMN ^{13}C** (100.6 MHz, $CDCl_3$) δ 169.3, 165.9, 164.0, 150.9, 138.9, 138.8, 138.7, 134.72, 131.3, 128.6, 128.6, 128.5, 128.4, 127.9, 127.8, 127.7, 127.6, 127.6, 123.7, 100.4, 79.2, 77.8, 76.3, 75.1, 73.4, 73.3, 73.2, 70.8, 68.1, 52.8, 21.9, 21.8, 16.8.

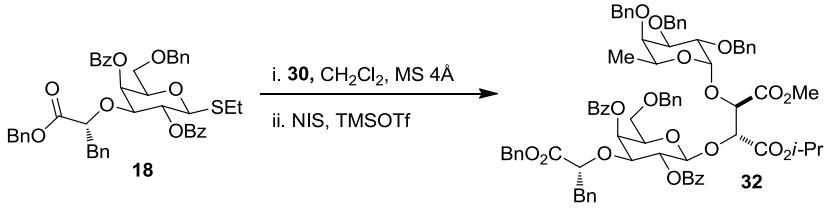
(2*R*,3*R*)-4-isopropyl 1-methyl 2-hydroxy-3-((2*S*,3*S*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methyltetrahydro-2*H*-pyran-2-yloxy)succinate (31)



A solution of dioxolanone **28** (0.303 g, 0.467 mmol) in AcOH:H_2O (80:20, 10mL) was maintained at 50^{o}C during 16 hours. The reaction mixture was then diluted with H_2O (10mL) and extracted with AcOEt (3 x 10 mL). The combined organic layers were washed with brine (30 ml), dried over $MgSO_4$ and concentrated *in vacuo*. After *in vacuo* concentration of the resulting solution, the residue obtained (dioxolanone) was dissolved in benzene/MeOH (3/1) at 25^{o}C under an inert atmosphere and was treated with $TMSCH_2N_2$ until a persistent yellowish color was observed. The reaction mixture was then concentrated *in vacuo*. Purification by flash chromatography (Hexanes:EtOAc, 80:20) provided **27** (0.191 g, 66% over 2 steps) as a colorless oil.

Formula: $C_{35}H_{42}O_{10}$; **MW** : 622.28 g/mol; **R*f*** 0.40 (40 % EtOAc/Hexanes); **$[\alpha]_D^{25}$** – 58.2 (*c* 1.3, CH_2Cl_2); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40-7.27 (m, 15H), 5.08 (septet, *J* = 6.1 Hz, 1H), 4.97 (d, *J* = 11.5 Hz, 1H), 4.91 (d, *J* = 2.7 Hz, 1H), 4.81 (d, *J* = 11.7 Hz, 1H), 4.80 (d, *J* = 11.5 Hz, 1H), 4.76 (d, *J* = 11.0 Hz, 1H), 4.74 (d, *J* = 11.5 Hz, 1H), 4.64 (d, *J* = 11.5 Hz, 1H), 4.56 (dd, *J* = 4.4, 7.1 Hz, 1H), 4.43 (d, *J* = 4.4 Hz, 1H), 4.28 (q, *J* = 6.6 Hz, 1H), 4.07 (dd, *J* = 3.0, 10.3 Hz, 1H), 4.04 (dd, *J* = 3.0, 10.3 Hz, 1H), 3.79 (d, *J* = 7.1 Hz, 1H), 3.72 (s, 1H), 3.68 (s, 3H), 1.28 (d, *J* = 3.4 Hz, 3H), 1.26 (d, *J* = 3.4 Hz, 3H), 1.10 (d, *J* = 6.3 Hz, 3H) ppm; **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 171.2, 168.8, 138.84, 138.77, 138.4, 128.64. 128.60, 128.53, 128.45, 128.3, 127.9, 127.85, 127.79, 127.7, 100.8, 79.8, 79.1, 77.7, 75.9, 75.1, 74.1, 73.0, 72.6, 69.6, 68.0, 52.8, 22.0, 21.9, 16.8 ppm; **IR** (film) υ_{max} 2933 (broad), 1753, 1263, 1101,1051, 739, 699 cm^{-1}; **HRMS** (ESI) calculated for $C_{35}H_{42}O_{10}Na$ $(M+Na)^+$: 645.2670, found : 645.2654 (- 2.5 ppm).

(2*R*,3*R*)-1-isopropyl 4-methyl 2-((2*S*,3*R*,4*S*,5*S*,6*R*)-3,5-bis(benzoyloxy)-4-((*R*)-1-(benzyloxy)-1-oxo-3-phenylpropan-2-yloxy)-6-(benzyloxymethyl)tetrahydro-2*H*pyran-2-yloxy)-3-((2*S*,3*S*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methyltetrahydro-2*H*-pyran-2-yloxy)succinate (32)

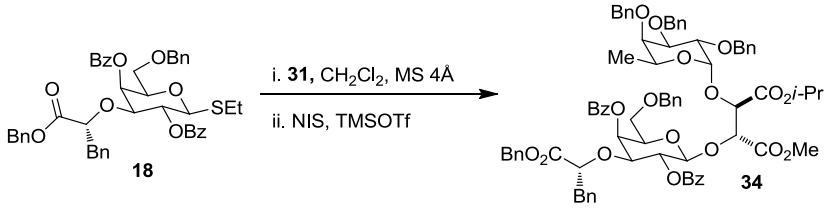


A solution of thiogalactoside **18** (451 mg, 0.593 mmol) and fucoside **30** (406 mg, 0.652 mmol) in CH_2Cl_2 (7 mL, 0.1M) was stirred 2 hours with 4Å molecular sieves (3.5 g/mmol). The mixture was cooled to -30ºC and then treated with NIS (398 mg, 1.77 mmol) and TMSOTf (11 µL, 0.065 mmol). After 1 hour, the mixture was diluted with EtOAc and washed with a saturated solution of $NaHCO_3$:$Na_2S_2O_3$ (10 mL, 1:1). The organic layer was washed with water (10 mL) and brine, dried over $MgSO_4$ filtered and concentrated *in vacuo*. Purification by flash chromatography (DCM:EtOAc, 75:25) provided β−galactoside **32** (695 mg, 81%) as a colorless oil.

Formula: $C_{78}H_{80}O_{19}$; **MW** : 1320.53 g/mol; **R*f*** 0.69 (40 % EtOAc/Hexanes); **$[\alpha]_D^{25}$** = +42.3 (*c* 1.6, CH_2Cl_2); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.10-8.06 (m, 3H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.50-7.18 (m, 30H), 7.01-6.86 (m, 6H), 5.73 (d, *J* = 2.7 Hz, 1H), 5.55 (appt, *J* = 8.3 Hz, 1H), 4.98 (d,

J = 8.1 Hz, 1H), 4.92 (septet, *J* = 6.10 Hz, 1H), 4.91 (d, *J* = 11.7 Hz, 1H), 4.88-4.83 (m, 2H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.74-4.62 (m, 5H), 4.58 (d, *J* = 11.7 Hz, 1H), 4.54-4.44 (m, 3H), 4.41 (d, *J* = 12.0 Hz, 1H), 4.00 (q, *J* = 6.6 Hz, 1H), 3.96 (dd, *J* = 2.2, 10.3 Hz, 1H), 3.92 (dd, *J* = 3.2, 10.3 Hz, 1H), 3.85 (dd, *J* = 3.2, 10.0 Hz, 1H), 3.74 (t, *J* = 6.3 Hz, 1H), 3.58 (dd, J = 5.7, 9.3 Hz, 1H), 3.52 (s, 3H), 3.52-3.46 (m, 2H), 2.84 (dd, *J* = 5.9, 13.7 Hz, 1H), 2.74 (dd, *J* = 6.8, 13.7 Hz, 1H), 1.18 (d, *J* = 6.3 Hz, 3H), 1.16 (d, *J* = 6.3 Hz, 3H), 0.96 (d, *J* = 6.3 Hz, 3H) ppm; **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 170.8, 169.6, 168.1, 166,0, 165.6, 139.2, 139.1, 139.0, 137.8, 135.9, 135.5, 133.5, 132.8, 130.9, 130.3, 130.2, 129.8, 129.7, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.63, 127.58, 126.5, 100.5, 100.1, 79.6, 78.8, 77.8, 77.7, 77.5, 76.9, 75.9, 74.9, 74.0, 73.14, 73.08, 72.8, 71.4, 69.3, 68.1, 67.6, 66.6, 66.5, 52.2, 39.3, 21.9, 21.8, 16.7 ppm; **IR** (film) υ_{max} 2930 (broad), 1726, 1268, 1105, 738, 700 cm^{-1}; **HRMS** (ESI) calculated for $C_{78}H_{80}O_{19}Na$ $(M+Na)^+$: 1343.5186, found : 1343.5208 (+1.6 ppm); **Analyse** calculated for $C_{78}H_{80}O_{19}$: C 70.89, H 6.10, found : C 70.90, H 6.13.

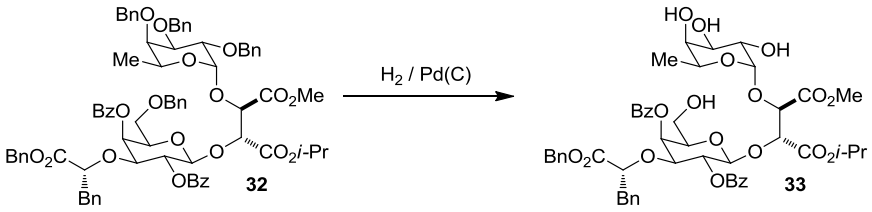
(2*R*,3*R*)-4-isopropyl 1-methyl 2-((2*S*,3*R*,4*S*,5*S*,6*R*)-3,5-bis(benzoyloxy)-4-((*R*)-1-(benzyloxy)-1-oxo-3-phenylpropan-2-yloxy)-6-(benzyloxymethyl)tetrahydro-2*H*pyran-2-yloxy)-3-((2*S*,3*S*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methyltetrahydro-2*H*-pyran-2-yloxy)succinate (34)



A solution of thiogalactoside **18** (428 mg, 0.562 mmol) and fucoside **30** (385 mg, 0.619 mmol) in CH_2Cl_2 (7 mL, 0.1M) was stirred 2 hours with 4Å molecular sieves (3.5 g/mmol). The mixture was cooled to -30ºC and then treated with NIS (378 mg, 1.68 mmol) and TMSOTf (11 µL, 0.0669 mmol). After 2 hours, the mixture was diluted with EtOAc and washed with a saturated solution of $NaHCO_3$:$Na_2S_2O_3$ (1:1). The organic layer was washed with water (100 mL) and brine, dried over $MgSO_4$ filtered and concentrated *in vacuo*. Purification by flash chromatography (DCM:EtOAc, 75:25) provided β−galactoside **34** (554 mg, 75%) as a colorless oil.

Formula: $C_{78}H_{80}O_{19}$; **MW** : 1320.53 g/mol; **R*f*** 0.67 (40 % EtOAc/Hexanes); **$[\alpha]_D^{25}$** +35.3 (*c* 1.6, CH_2Cl_2); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11-8.05 (m, 4H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.50-7.42 (m, 3H), 7.42-7.18 (m, 25H), 6.99-6.88 (m, 7H), 5.71 (d, *J* = 3.4 Hz, 1H), 5.53 (dd, *J* = 8.1, 9.8 Hz, 1H), 5.05 (d, *J* = 8.1 Hz, 1H), 4.95-4.88 (m, 3H), 4.84 (d, *J* = 12.2 Hz, 1H), 4.79 (d, *J* = 5.1 Hz, 1H), 4.74 (d, *J* = 12.2 Hz, 1H), 4.73 (d, *J* = 11.7 Hz, 1H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.64 (d, *J* = 11.7 Hz, 1H), 4.62 (d, *J* = 12.2 Hz, 1H), 4.58 (d, *J* = 11.7 Hz, 1H), 4.54 (d, *J* = 4.9 Hz, 1H), 4.50 (dd, *J* = 5.9, 6.8 Hz, 1H), 4.47 (d, *J* = 11.7 Hz, 1H), 4.41 (d, *J* = 11.7 Hz, 1H), 4.16 (q, *J* = 6.2 Hz, 1H), 3.94 (dd, *J* = 3.2, 10.3 Hz, 1H), 3.91 (dd, *J* = 2.2, 10.3 Hz, 1H), 3.84 (dd, *J* = 3.3, 9.8 Hz, 1H), 3.73 (appt, *J* = 6.2, 9.5 Hz, 1H), 3.63 (dd, *J* = 5.5, 9.5 Hz, 1H), 4.52-3.44 (m, 5H), 2.84 (dd, *J* = 5.7, 13.9 Hz,1H), 2.74 (dd, *J* = 7.1, 13.7 Hz, 1H), 1.21 (d, *J* = 6.1 Hz, 3H), 1.17 (d, *J* = 6.3 Hz, 3H), 1.00 (d, *J* = 6.6 Hz, 3H) ppm; **^{13}C NMR** (100.6 MHz, CDCl3) δ 170.8, 169.4, 168.4, 166.0, 165.7, 139.2, 139.1, 139.0, 137.9, 135.9, 135.5, 133.5 132.9, 130.8, 130.3, 129.8, 129.7, 128.7, 128.63, 128.60, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.59, 127.58, 126.6,100.1, 99.9, 79.7, 78.2, 77.6, 77.4, 77.3, 75.9, 74.9, 74.0, 73.2, 73.0, 72.8, 71.3, 69.3, 68.0, 67.6, 66.6, 66.5, 52.3, 39.4, 21.9, 21.8, 16.8 ppm; **IR** (film) υ_{max} 2930 (broad), 1728, 1268, 1104, 739, 700 cm^{-1}; **HRMS** (ESI) calculated for $C_{78}H_{80}O_{19}Na$ (M+Na)+ : 1343.5186, found : 1343.5189 (+0.2 ppm); **Analyse** calculated for $C_{78}H_{80}O_{19}$: C 70.89, H 6.10, found : C 70.87 H 6.13.

(*R*)-2-((2*R*,3*S*,4*S*,5*R*,6*S*)-3,5-bis(benzoyloxy)-2-(hydroxymethyl)-6-((2*R*,3*R*)-1-isopropoxy-4-methoxy-1,4-dioxo-3-((2*S*,3*S*,4*R*,5*S*,6*S*)-3,4,5-trihydroxy-6-methyltetrahydro-2*H*-pyran-2-yloxy)butan-2-yloxy)tetrahydro-2*H*-pyran-4-yloxy)-3-phenylpropanoic acid (33)

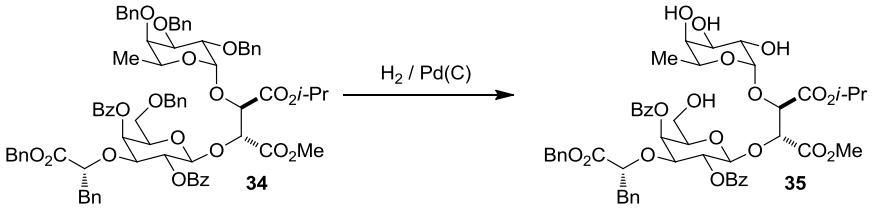


To a solution of compound **32** (234 mg, 0.177 mmol) in THF:MeOH (4:1, 0.1M) under an inert atmosphere was added Pd/C (234 mg, 10 % wt.). The system was purged with H_2 three times and reaction mixture was stirred at room temperature overnight under one atm of H_2. The mixture was filtered on Celite®, washed with MeOH and concentrated in vacuo. Purification by flash

chromatography (C18 reversed-phase silica, CH_3CN:H_2O, 20:80) provided **33** (36 mg, 23 %) as a white solid.

Formula: $C_{43}H_{50}O_{19}$; **MW** : 870.29 g/mol; **R*f*** 0.34 (10 % MeOH/chloroforme); **m.p. :** 122.7 °C; **$[\alpha]_D^{25}$** 4.5 (*c* 0.2, MeOH); **^{1}H NMR** (500 MHz, CD_3OD) δ 8.11 (d, *J* = 7.7 Hz, 4H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.05 (d, *J* = 7.5 Hz, 2H), 6.89 (t, *J* = 7.5 Hz, 2H), 6.82 (t, *J* = 7.3 Hz, 1H), 5.80 (d, *J* = 2.7 Hz, 1H), 5.52 (appt, *J* = 8.9 Hz, 1H), 5.07 (septet, *J* = 6.1 Hz, 1H), 4.92 (d, *J* = 8.3 Hz, 1H), 4.75 (d, *J* = 3.6 Hz, 1H), 4.72 (d, *J* = 4.2 Hz, 1H), 4.48 (m, 2H), 4.19 (dd, *J* = 2.9, 9.9 Hz, 1H), 4.06 (q, *J*= 6.5 Hz, 1H), 3.89 (t, *J* = 6.4 Hz, 1H), 3.75 (dd, *J* = 3.2, 10.3 Hz, 1H), 3.67-3.56 (m, 4H), 3.46 (s, 3H), 2.81 (dd, *J* = 5.9, 14.9 Hz, 1H), 2.78 (dd, *J* = 6.0, 14.2 Hz, 1H), 1.31 (d, *J* = 6.1 Hz, 3H), 1.27 (d, *J* = 6.1 Hz, 3H), 1.02 (d, *J* = 6.6 Hz, 3H) ppm; **^{13}C NMR** (100.6 MHz, CD_3OD) δ 169.3, 168.7, 166.4, 166.0, 136.5, 133.4, 132.8, 130.6, 130.1, 129.9, 129.7, 129.4, 128.4, 128.0, 127.6, 126.0, 102.3, 101.8, 78.4, 76.4, 74.3, 72.4, 71.3, 70.4, 70.0, 68.9, 67.5, 66.6, 60.3, 51.5, 39.0, 20.9, 20.8, 15.3 ppm. **HRMS** (ESI) calculated for $C_{43}H_{50}O_{19}Na$ $(M+Na)^+$: 893.2839, found : 893.2850 (+1.3 ppm). **Analyse** calculated for $C_{43}H_{50}O_{19}\cdot 2H_2O$: C 56.95, H 6.00, found C 57.29, H 5.94.

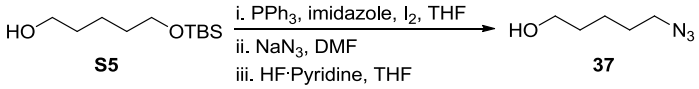
(*R*)-2-((2*R*,3*S*,4*S*,5*R*,6*S*)-3,5-bis(benzoyloxy)-2-(hydroxymethyl)-6-((2*R*,3*R*)-4-isopropoxy-1-methoxy-1,4-dioxo-3-((2*S*,3*S*,4*R*,5*S*,6*S*)-3,4,5-trihydroxy-6-methyltetrahydro-2*H*-pyran-2-yloxy)butan-2-yloxy)tetrahydro-2*H*-pyran-4-yloxy)-3-phenylpropanoic acid (35)



To a solution of compound **34** (198 mg, 0.150 mmol) in THF:MeOH (4:1, 0.1M) under an inert atmosphere was added Pd/C (198 mg, 10 % wt.). The system was purged with H_2 three times and reaction mixture was stirred at room temperature overnight under one atm of H_2. The mixture was filtered on Celite®, washed with MeOH and concentrated *in vacuo*. Purification by flash chromatography (C18 reversed-phase silica, CH_3CN:H_2O, 20:80) provided **35** (26 mg, 20 %) as a white solid.

Formula: $C_{43}H_{50}O_{19}$; **MW** : 870.29 g/mol; **R*f*** 0.35 (10:90; MeOH/chloroformes); **m.p. :** 120.2 °C; **$[\alpha]_D^{25}$** +5.0 (*c* 0.3, MeOH); **^{1}H NMR** (500MHz, CD_3OD) δ 8.16 (d, *J* = 7.6 Hz, 2H), 8.04 (d, *J* = 7.6 Hz, 2H), 7.66 (t, *J* = 7.3Hz, 1H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.56-7.44 (m, 4H), 7.06 (d, *J* = 7.3 Hz, 2H), 6.84 (t, *J* = 7.3 Hz, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 5.78 (d, *J* = 2.4 Hz, 1H), 5.52 (dd, *J* = 8.1, 10.0 Hz, 1H), 4.99 (d, *J* = 8.1 Hz, 1H), 4.80 (d, *J* = 4.2 Hz, 1H), 4.73 (septet, *J* = 6.1 Hz, 1H), 4.66 (d, *J* = 3.9 Hz, 1H), 4.41 (d, *J* = 4.2 Hz, 1H), 4.33 (t, *J* = 6.1 Hz, 1H), 4.26 (dd, *J* = 2.7, 10.0 Hz, 1H), 4.12 (q, *J* = 6.8 Hz, 1H), 3.85 (t, *J* = 6.1 Hz, 1H), 3.76 (dd, *J* = 3.2, 10.2 Hz, 1H), 3.73 (s, 3H), 3.64 (dd, *J* = 3.9, 10.2 Hz, 1H), 3.62-3.56 (m, 3H), 2.80 (dd, *J* = 5.6, 13.7 Hz, 1H), 2.73 (dd, *J* = 6.7, 13.7 Hz, 1H). 1.21 (d, *J* = 6.1 Hz, 3H), 1.12 (d, *J* = 6.3 Hz, 3H), 1.04 (d, *J* = 6.3 Hz, 3H) ppm; **^{13}C NMR** (100.6 MHz, CD_3OD) δ 169.8, 168.1, 166.9, 166.1, 137.5, 133.4, 132.9, 130.7, 130.3, 129.9, 129.6, 129.3, 128.4, 128.1, 127.5, 125.7, 102.2, 101.8, 78.7, 78.1, 75.7, 74.7, 72.3, 71.5, 70.2, 69.7, 68.7, 67.5, 66.8, 60.7, 52.0, 39.3, 21.0, 20.7, 15.4 ppm. **HRMS** (ESI) calculated for $C_{43}H_{50}O_{19}Na$ $(M+Na)^+$: 893.2839, found : 893.2857 (+ 2.1 ppm). **Analyse** calculated for $C_{43}H_{50}O_{19}\cdot 5H_2O$: C 53.75, H 6.29, found C 53.64, H 5.91.

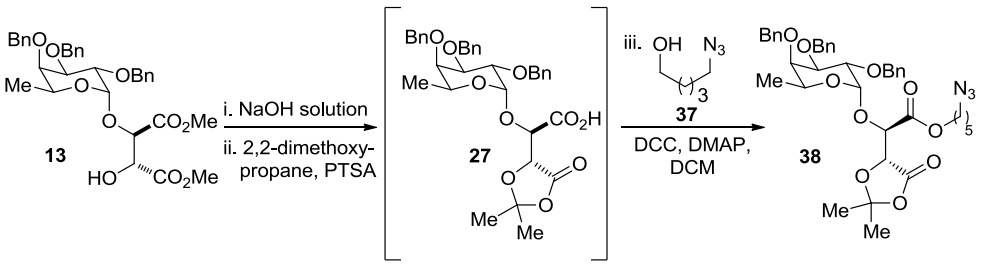
5-azidopentan-1-ol (37)



A solution of alcohol **S5** (2.0 g, 9.2 mmol) in THF (92 mL) at 25°C under an inert atmosphere was treated with PPh_3 (7.3 g, 28 mmol) and CBr_4 (9.3 g, 28 mmol). After 16 hours, the reaction mixture was concentrated *in vacuo* and passed over a pad of silica gel (5 % EtOAc/Hex). After *in vacuo* concentration, the residue was diluted with DMF (90 mL) under an inert atmosphere at 25°C. NaN_3 (2.4g, 37 mmol) was added to the resulting solution, which was then maintained at 25°C for 16 hours before being diluted with H_2O (100mL) and extracted with AcOEt (3 x 10 mL). The combined organic layers were washed with brine (30 ml), dried over $MgSO_4$ and concentrated *in vacuo*. The residue obtained was passed over a pad of silica gel (5 % EtOAc/Hex). After *in vacuo* concentration, the residue was dissolved in THF (100 mL) under an inert atmosphere at 25°C and treated with HF·Pyridine (9.2 mL). After 4 hours, a saturated of solution of $NaHCO_3$ was poured into the reaction mixture. The aqueous layer was extracted with EtOAc (3 x 100mL). The combined organic phase were washed with brine (100 mL), dried over

$MgSO_4$ filtered and concentrated *in vacuo*. Purification by flash chromatography (Hexanes:EtOAc, 85:15) provided alcohol **37** (475 mg, 40% over 3 steps) as a yellowish oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.66 (t, *J* = 6.5 Hz, 2H), 3.28 (t, *J* = 6.8 Hz, 2H), 1.56-1.68 (m, 5H), 1.42-1.50 (m, 2H) ppm; **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 62.9, 51.6, 32.4, 28.9, 23.2 ppm. **IR** (film) υ_{max} 3335 (broad), 2939 (broad), 2097, 1262, 1054 cm^{-1}.

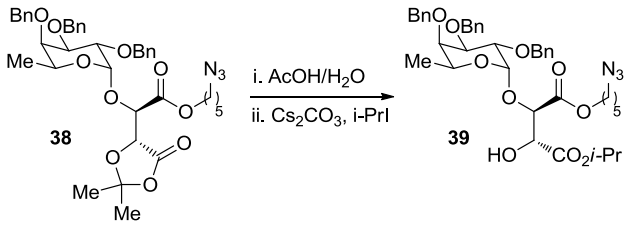
(*R*)-5-azidopentyl 2-((*R*)-2,2-dimethyl-5-oxo-1,3-dioxolan-4-yl)-2-((2*S*,3*S*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methyltetrahydro-2*H*-pyran-2-yloxy)acetate (38)



To a solution of diester **13** (1.01 g, 1.76 mmol) in THF (0.1 M) at 25°C was added a 10% NaOH solution (10 mL). After 30 minutes, the reaction mixture was neutralized with a 1M HCl solution. The aqueous layer was extracted with AcOEt (4 x 20 mL). The combined organic layers were washed with brine (100 ml), dried over $MgSO_4$ and concentrated *in vacuo*. The residue obtained (diacid) was then dissolved in DCM (0.1 M), treated with 2,3-dimethoxypropane (2.2 mL, 18 mmol, 10 equiv.) and PTSA (0.0061 g, 0.035 mmol) under an inert atmosphere. After 32 hours, the reaction mixture is diluted with EtOAc (20 mL) and passed through a pad of silica gel. After *in vacuo* evaporation, the residue was dissolved in DCM (18 mL) at 25°C was added alcohol **37** (0.452 g, 3.5 mmol), DMAP (0.04 g, 0.3 mmol) and DCC (0.43 g, 2.1 mmol). After maintaining the reaction mixture at 25°C for 16 hours, distilled water was added (8.3 mL). The aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine (50 ml), dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (Hexanes:EtOAc, 85:15) provided **38** (0.648 g, 52% over 3 steps) as a colorless oil. **Formula:** $C_{39}H_{47}N_3O10$; **MW** : 717.33 g/mol; **R*f*** 0.58 (35 % EtOAc/hexanes); **$[\alpha]_D^{25}$** -103.5 (*c* 1.6, CH2Cl2); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46-7.42 (m, 2H), 7.39-7.26 (m, 13H), 5.03 (d, *J* = 3.7 Hz, 1H), 4.98 (d, *J* = 11.7 Hz, 1H), 4.88 (d, *J* = 2.0 Hz, 1H), 4.84 (d, *J* = 12.2 Hz, 1H), 4.77 (d, *J* = 11.5 Hz, 1H), 4.72 (d, *J* = 12.2 Hz, 1H), 4.66 (d, *J* =

11.7 Hz, 1H), 4.61 (d, *J* = 11.7 Hz, 1H), 4.51 (d, *J* = 2.0 Hz, 1H), 4.37 (q, *J* = 6.6 Hz, 1H), 4.20 (t, *J* = 6.6 Hz, 2H), 4.05 (dd, *J* = 3.7, 10.2 Hz, 1H), 3.97 (dd, *J* = 2.7, 10.2 Hz, 1H), 3.69 (d, *J* = 1.5 Hz, 1H), 3.29 (t, *J* = 6.8 Hz, 2H), 1.71 (qt, *J* = 7.1 Hz, 2H), 1.64 (qt, *J* = 7.1 Hz 2H), 1.58 (s, 3H), 1.55 (s, 3H), 1.50-1.41 (m, 2H), 1.06 (d, *J* = 6.6 Hz, 3H) ppm; **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 170.1, 168.8, 139.1, 138.84, 138.75, 128.6, 128.53, 128.47, 128.4, 128.2, 127.8, 127.61, 127.56, 127.5, 113.3, 100.9, 78.8, 78.0, 76.9, 76.3, 76.2, 75.0, 73.1, 73.0, 67.9, 65.4, 51.4, 28.7, 28.3, 27.6, 26.9, 23.3, 16.8 ppm; **IR** (film) υ_{max} 2935 (broad), 2096, 1791, 1761, 1267, 1105, 1048, 738, 698 cm^{-1}. **HRMS** (ESI) calculated for C39H47O10N3Na $(M+Na)^+$: 740.3154, found :740.3177 (+3.2 ppm).

(2*R*,3*R*)-1-(5-azidopentyl) 4-isopropyl 3-hydroxy-2-((2*S*,3*S*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methyltetrahydro-2*H*-pyran-2-yloxy)succinate (39)

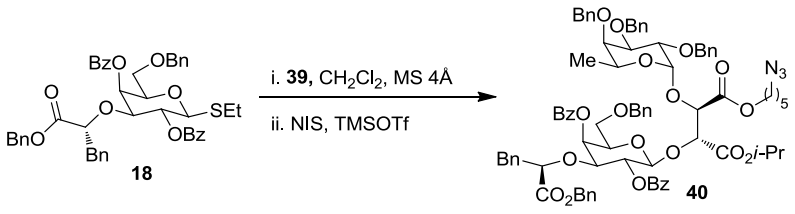


A solution of dioxolanone **38** (0.332 g, 0.462 mmol) in AcOH:H_2O (80:20, 10mL) was maintained at 50°C during 16 hours. The reaction mixture was then diluted with H_2O (10mL) and extracted with AcOEt (3 x 10 mL). The combined organic layers were washed with brine (50 ml), dried over $MgSO_4$ and concentrated *in vacuo*. After *in vacuo* concentration of the resulting solution, the residue obtained is dissolved in DMF (4.6 mL) at 25°C under an inert atmosphere and treated with Cs_2CO_3 (0.180 g, 0.554 mmol) and i-PrI (0.067 mL, 0.69 mmol). After maintaining the reaction mixture at 25°C for 16 hours, deionized water was added (7 mL). The aqueous layer was extracted with AcOEt (3 x 10 mL). The combined organic layers were washed with brine (30 ml), dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (Hexanes:EtOAc, 85:15) provided **39** (0.218 g, 66%) as a colorless oil.

Formula: $C_{39}H_{49}N_3O_{10}$; **MW** : 719.34 g/mol; **R*f*** 0.50 (35/65, EtOAc/hexanes); **$[\alpha]_D^{25}$** –45.3 (*c* 1.2, CH2Cl2); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41- 7.27 (m, 15H), 5.0 (st, *J* = 6.3 Hz, 1H), 4.98 (d, *J* = 11.7 Hz, 1H), 4.94 (d, *J* = 2.7 Hz, 1H), 4.81 (d, *J* = 11.7 Hz, 1H), 4.80 (d, *J* = 11.7 Hz, 1H), 4.75 (d, *J* = 11.7 Hz, 1H), 4.74 (d, *J* = 11.7 Hz, 1H), 4.65 (d, *J* = 11.5 Hz, 1H), 4.52 (dd, *J* =

4.0 Hz, 1H), 4.47 (d, *J* = 3.9 Hz, 1H), 4.26 (q, *J* = 6.3 Hz, 1H), 4.18 (t, *J* = 6.8 Hz, 2H), 4.08 (dd, *J* = 3.0, 10.3 Hz, 1H), 4.05 (dd, *J* = 3.0, 10.3 Hz, 1H) 3.73 (s, 1H), 3.64 (d, *J* = 6.8 Hz, 1H), 3.29 (t, *J* = 6.8 Hz, 2H), 1.72 (qt, *J* = 7.3 Hz, 2H), 1.63 (qt, *J* = 8.0 Hz, 2H), 1.50-1.42 (m, 2H), 1.24 (d, *J* = 6.1 Hz, 3H), 1.22 (d, *J* = 6.3 Hz, 3H), 1.09 (d, *J* = 6.6Hz, 3H) ppm; **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 170.2, 169.5, 138.8, 138.7, 138.4, 128.62, 128.58, 128.53, 128.46, 128.3, 127.9, 127.8, 127.6, 100.6, 79.7, 78.7, 77.7, 75.9, 75.1, 74.0, 73.1, 72.5, 70.1, 67.9, 65.4, 51.4, 28.7, 28.3, 23.3, 22.0, 21.9, 16.8 ppm; **IR** (film) υ_{max} 3466 (broad), 2936 (broad), 2097, 1753, 1263, 1104, 1053, 739, 699 cm^{-1}. **HRMS** (ESI) calculated for $C_{39}H_{49}O_{10}N_3Na$ $(M+Na)^+$: 742.3310, found : 742.3311 (+0.1 ppm).

Azide (40)

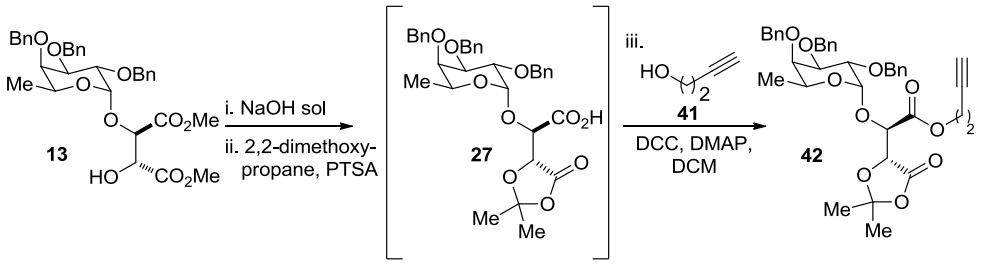


A solution of thiogalactoside **18** (121 mg, 0.159 mmol) and fucoside **30** (163 mg, 0.227 mmol) in CH_2Cl_2 (1.9 mL, 0.1M) was stirred 2 hours with 4Å molecular sieves (3.5 g/mmol). The mixture was cooled to -30ºC and then treated with NIS (155 mg, 0.681 mmol) and TMSOTf (0.005, 0.03 mmol). After 2 hours, the mixture was diluted with EtOAc (5 mL) and washed with a saturated solution of $NaHCO_3$:$Na_2S_2O_3$ (1:1, 5 mL). The organic layer was dried over $MgSO_4$ filtered and concentrated *in vacuo*. Purification by flash chromatography (DCM:EtOAc, 75:25) provided β−galactoside **40** (156 mg, 69%) as a colorless oil.

Formula: $C_{82}H_{87}N_3O_{19}$; **MW** : 1417.59 g/mol; **R*f*** 0.68 (30 % EtOAc/Hexanes); **$[\alpha]_D^{25}$** – 25.3 (*c* 1.3, CH_2Cl_2); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.09-8.04 (m, 4H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.48-7.37 (m, 5H), 7.37-7.16 (m, 23H), 6.98-6.85 (m, 7H), 5.70 (d, *J* = 3.2 Hz, 1H), 5.52 (dd, *J* = 8.2, 10.0 Hz, 1H), 5.0 (d, *J* = 7.8 Hz, 1H), 4.91 (st, *J* = 6.3 Hz, 1H), 4.90 (d, *J* = 11.5 Hz, 1H), 4.86 (d, *J* = 3.2 Hz, 1H), 4.83 (d, *J* = 12.0 Hz, 1H), 4.74 (d, *J* = 11.7 Hz, 1H), 4.72-4.58 (m, 5H), 4.56 (d, *J* = 11.7 Hz, 1H), 4.51-4.42 (m, 3H), 4.39 (d, *J* = 11.7 Hz, 1H), 4.02 (q, *J* = 6.4 Hz, 1H), 3.99-3.88 (m, 4H), 3.82 (dd, *J* = 3.3, 9.8 Hz, 1H), 3.72 (t, *J* = 6.4 Hz, 1H), 3.57 (dd, *J* = 5.6, 9.5 Hz, 1H), 3.51 (s, 1H), 3.47 (dd, *J* = 7.3, 9.3 Hz, 1H), 3.23 (t, *J* = 6.8 Hz, 2H), 2.82 (dd, *J* = 5.6,

13.7 Hz, 1H), 2.72 (dd, *J* = 7.1, 13.7 Hz, 1H), 1.62-1.50 (m, 4H), 1.47-1.29 (m, 2H), 1.17 (d, *J* = 6.4 Hz, 3H), 1.15 (d, *J* = 6.6 Hz, 3H), 0.96 (d, *J* = 6.3 Hz, 3H) ppm; **^{13}C NMR**(100.6 MHz, $CDCl_3$) δ 170.8, 169.0, 168.1, 166.0, 165.6, 139.2, 139.1, 138.9, 137.8, 135.9, 135.5, 133.5, 132.8, 130.9, 130.2, 129.8, 129.7, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.6, 127.5, 126.5, 100.4, 99.8, 79.6, 78.3, 77.8, 77.7, 76.9, 75.9, 75.0, 74.0, 73.1, 73.0, 72.8, 71.4, 69.3, 68.1, 67.6, 66.6, 66.4, 65.0, 51.4, 39.4, 28.7, 28.1, 23.3, 21.8, 16.7 ppm, **IR** (film) υ_{max} 2934 (broad), 2097, 1729, 1453, 1269, 1105, 738, 700 cm^{-1}. **HRMS** (ESI) calculated for $C_{82}H_{87}O_{19}N_3Na$ $(M+Na)^+$: 1440.5826, found : 1440.5832 (+ 0.4 ppm).

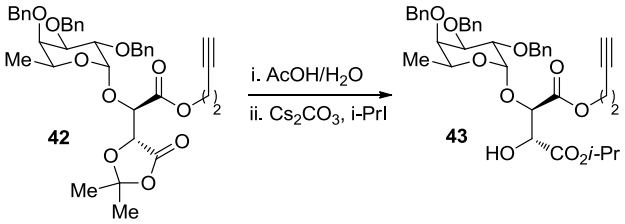
(2*R*,3*R*)-1-but-3-ynyl 4-isopropyl 3-hydroxy-2-((2*S*,3*S*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methyltetrahydro-2*H*-pyran-2-yloxy)succinate (42)



To a solution of diester **13** (0.519 g, 0.874 mmol) in THF (0.1 M) at 25°C was added a 10% NaOH solution (6 mL). After 30 minutes, the reaction mixture was neutralized with a 1M HCl solution. The aqueous layer was extracted with AcOEt (4 x 10 mL). The combined organic layers were washed with brine (50 ml), dried over $MgSO_4$ and concentrated *in vacuo*. The residue obtained (diacid) was then dissolved in DCM (9 mL, 0.1 M), treated with 2,3-dimethoxypropane (1.1 mL, 8.7 mmol) and PTSA (0.004 g, 0.02 mmol) under an inert atmosphere. After 32 hours, the reaction mixture is diluted with EtOAc (10 mL) and passed through a pad of silica gel. After *in vacuo* evaporation, the residue was dissolved in DCM (10 mL) at 25°C was added alcohol **41** (0.132 mL, 1.74 mmol), DMAP (0.016 mg, 0.13 mmol) and DCC (0.230 mg, 1.1 mmol). After maintaining the reaction mixture at 25°C for 16 hours, distilled water was added (10 mL). The aqueous layer was extracted with AcOEt (3 x 10 mL). The combined organic layers were washed with brine (30 ml), dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (Hexanes:EtOAc, 85:15) provided **42** (0.305 g, 53% over 3 steps) as a colorless oil.

Formula: $C_{38}H_{42}O_{10}$; **MW** : 658.28 g/mol; **R*f*** 0.63 (30 % EtOAc/Hexanes); **$[\alpha]_D^{25}$** –59.0 (*c* 0.9, CH_2Cl_2); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48-7.27 (m, 15H), 5.06 (d, *J* = 3.7 Hz, 1H), 5.00 (d, *J* = 11.5 Hz, 1H), 4.93 (d, *J* = 2.0 Hz, 1H), 4.86 (d, *J* = 12.0 Hz, 1H), 4.79 (d, *J* = 11.5 Hz, 1H), 4.74 (d, *J* = 12.2 Hz, 1H), 4.68 (d, *J* = 11.5 Hz, 1H), 4.63 (d, *J* = 11.7 Hz, 1H), 4.58 (d, *J* = 2.2 Hz, 1H), 4.38 (q, *J* = 6.3 Hz, 1H), 4.35-4.26 (m, 2H), 4.08 (dd, *J* = 3.7, 10.3 Hz, 1H), 3.99 (dd, *J* = 2.7, 10.3 Hz, 1H), 3.70 (d, *J* = 1.5 Hz, 1H), 2.57 (td, *J* = 2.7, 6.6 Hz, 2H), 2.00 (t, *J* = 2.7 Hz, 1H), 1.60 (s, 3H), 1.56 (s, 3H), 1.08 (d, *J* = 6.3 Hz, 3H) ppm; **^{13}C NMR**(100.6 MHz, $CDCl_3$) δ 170.0, 168.6, 139.2, 138.9, 138.8, 128.63, 128.57, 128.5, 128.4, 128.3, 127.8, 127.7, 127.63, 127.56, 113.3, 101.0, 79.7, 78.8, 78.1, 76.2, 76.1, 75.1, 73.2, 73.0, 70.5, 68.0, 63.3, 27.6, 26.9, 19.2, 16.8 ppm; **IR** (film) υ_{max} 3289, 2934, 1791, 1765, 1455, 1272, 912, 738, 699 cm^{-1}. **HRMS** (ESI) calculated for $C_{38}H_{42}O_{10}Na$ $(M+Na)^+$: 681.2670, found : 681.2688 (+2.7 ppm).

(2*R*,3*R*)-1-but-3-ynyl 4-isopropyl 3-hydroxy-2-((2*S*,3*S*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methyltetrahydro-2*H*-pyran-2-yloxy)succinate (43)



A solution of dioxolanone **42** (0.305 g, 0.463 mmol) in AcOH:H_2O (80:20, 10mL) was maintained at 50°C during 16 hours. The reaction mixture was then diluted with H_2O (10mL) and extracted with AcOEt (3 x 10 mL). The combined organic layers were washed with brine (50 ml), dried over $MgSO_4$ and concentrated *in vacuo*. After *in vacuo* concentration of the resulting solution, the residue obtained is dissolved in DMF (4.6 mL) at 25°C under an inert atmosphere and treated with Cs_2CO_3 (0.18 g, 0.55 mmol) and i-PrI (0.068 mL, 0.69 mmol). After maintaining the reaction mixture at 25°C for 16 hours, deionized water was added (7 mL). The aqueous layer was extracted with AcOEt (3 x 10 mL). The combined organic layers were washed with brine (30 ml), dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (Hexanes:EtOAc, 85:15) provided **43** (0.177 g, 58%) as a colorless oil.

Formula: $C_{38}H_{44}O_{10}$; **MW** : 660.29 g/mol; **R*f*** 0.55 (30/100; EtOAc/Hexanes); **$[\alpha]_D^{25}$** -59.2 (*c* 1.3, CH_2Cl_2); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41-7.27 (m, 15H), 5.01 (t, *J* = 6.3 Hz, 1H), 4.98

(d, *J* = 11.5 Hz, 1H), 4.94 (d, *J* = 2.9 Hz, 1H), 4.81 (d, *J* = 11.7 Hz, 1H), 4.80 (d, *J* = 11.7 Hz, 1H), 4.75 (d, *J* = 11.7 Hz, 1H), 4.74 (d, *J* = 11.7 Hz, 1H), 4.65 (d, *J* = 11.7 Hz, 1H), 4.53 (m, 1H), 4.52 (d, *J* = 3.9 Hz, 1H), 4.28 (t, *J* = 6.8 Hz, 2H), 4.27 (q, *J* = 6.3 Hz, 1H), 4.09 (dd, *J* = 2.7, 10.3 Hz, 1H), 4.06 (dd, *J* = 2.0, 10.3 Hz, 1H), 3.72 (s, 1H), 3.67 (d, *J* = 7.1 Hz, 1H), 2.58 (dd, *J* = 2.7, 6.8 Hz, 1H), 2.56 (dd, *J* = 2.7, 6.7 Hz, 1H), 1.98 (t, *J* = 2.7 Hz, 1H), 1.25 (d, *J* = 6.1 Hz, 3H), 1.22 (d, *J* = 6.3 Hz, 3H), 1.10 (d, *J* = 6.6 Hz, 3H) ppm; **^{13}C NMR**(100.6 MHz, $CDCl_3$) δ 170.3, 169.3, 138.9, 138.7, 138.4, 128.64, 128.60, 128.55, 128.5, 128.3, 127.9, 127.8, 127.7, 100.4, 79.8, 79.7, 78.4, 77.7, 75.9, 75.1, 74.0, 73.1, 72.4, 70.4, 70.2, 68.0, 63.3, 22.00, 21.97, 19.1, 16.8 ppm; **IR** (film) υ_{max} 3481 (broad), 3289 (broad), 2933 (broad), 1746, 1260, 1102, 1052, 738, 699 cm^{-1}. **HRMS** (ESI) calculated for $C_{38}H_{44}O_{10}Na$ $(M+Na)^+$: 683.2827, found : 683.2836 (+1.3 ppm).

7

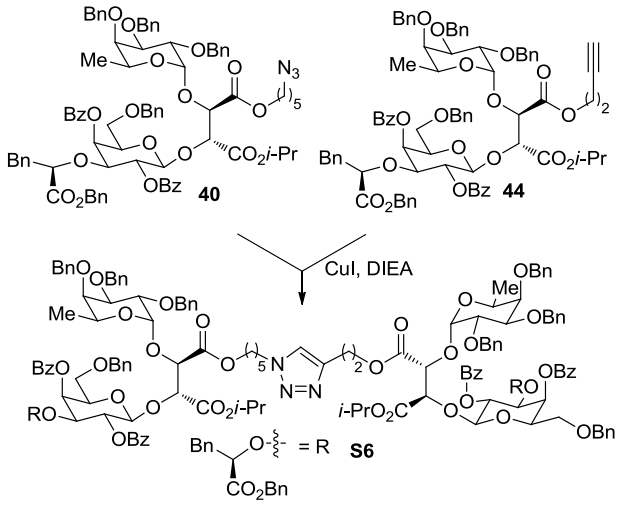
Alkyne 44

A solution of thiogalactoside **18** (573 mg, 0.754 mmol) and fucoside **48** (548 mg, 0.829 mmol) in CH_2Cl_2 (8 mL, 0.1M) was stirred 2 hours with 4Å molecular sieves (3.5 g/mmol). The mixture was cooled to -30ºC and then treated with NIS (0.56 g, 0.25 mmol) and TMSOTf (0.015 mL, 0.08 mmol). After 2 hours, the mixture was diluted with EtOAc (5 mL) and washed with a saturated solution of $NaHCO_3$:$Na_2S_2O_3$ (1:1, 10 mL). The organic layer was dried over $MgSO_4$ filtered and concentrated *in vacuo*. Purification by flash chromatography (DCM:EtOAc, 98:2) provided β−galactoside **44** (648 mg, 64%) as a colorless oil.

Formula: $C_{81}H_{82}O_{19}$; **MW** : 1358.55 g/mol; **$[\alpha]_D^{25}$** – 12.2 (*c* 5.2, CH_2Cl_2); **R*f*** 0.65 (30 % EtOAc/Hexanes); **^{1}H NMR** (500 MHz, C_6D_6) 8.38 (dd, *J* = 1.2, 8.3 Hz, 2H), 8.20 (dd, *J* = 1.2, 8.3 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.40-7.32 (m, 4H), 7.31-7.03 (m, 20H), 7.03-6.94 (m, 6H), 6.90-6.82 (m, 4H), 6.80 -6.75 (m, 1H), 6.10 (appt, *J*= 8.5 Hz, 1H), 5.84 (d, *J* = 3.2 Hz, 1H), 5.32 (d, *J* = 8.1 Hz, 1H), 5.12 (d, *J* = 3.4 Hz, 1H), 5.00 (d, *J* = 5.4 Hz, 1H), 4.94 (d, *J* = 11.2 Hz, 1H), 4.88 (septet, *J* = 6.1 Hz, 1H), 4.82-4.74 (m, 4H), 4.73 (appt, *J* = 6.3 Hz, 1H), 4.68 (d, *J* = 12.0

Hz, 1H), 4.59 (d, *J* = 12.4 Hz, 1H), 4.56 (d, *J* = 12.4 Hz, 1H), 4.47 (d, *J* = 11.2 Hz, 1H), 4.34 (q, *J* = 6.3 Hz, 1H), 4.26 (d, *J* = 11.7 Hz, 1H), 4.19 (dd, *J* = 3.6, 10.3 Hz, 1H), 4.16 (d, *J* = 11.7 Hz, 1H), 4.12 (dd, *J* = 2.7, 10.3 Hz, 1H), 4.08-3.99 (m, 2H), 3.96-3.89 (m, 1H), 3.65 (t, *J* = 6.1 Hz, 1H), 3.60 (t, *J* = 5.6 Hz, 1H), 3.50 (dd, *J* = 6.6, 9.3 Hz, 1H), 3.35 (s, 1H), 2.94 (dd, *J* = 5.4, 13.7 Hz, 1H), 2.84 (dd, *J* = 7.1, 13.7 Hz, 1H), 2.18 (tt, *J* = 1.5, 6.6 Hz, 2H), 1.72 (t, *J*= 2.4 Hz, 1H), 1.16 (d, *J* = 6.6 Hz, 3H), 0.97 (d, *J* = 6.1 Hz, 3H), 0.95 (d, *J* = 6.1 Hz, 3H) ppm; **^{13}C NMR**(100.6 MHz, C6D6) δ 170.6, 168.7, 167.8, 166.0, 165.5, 139.7, 139.5, 138.3, 136.2, 135.9, 133.1, 132.4, 131.5, 130.5, 130.2, 129.94, 129.90, 128.7, 128.6, 128.5, 128.33, 128.25, 128.2, 128.0, 127.8, 127.6, 127.5, 127.4, 126.4, 100.6, 100.1, 80.1, 79.6, 78.4, 78.3, 77.9, 77.5, 77.2, 76.5, 75.2, 73.7, 73.3, 72.9, 72.8, 71.7, 70.5, 69.0, 68.6, 67.9, 67.0, 66.2, 62.8, 39.4, 21.5, 18.7, 16.8 ppm; **IR** (film) υ_{max} 2925, 1726, 1453, 1268, 1105, 738.4, 700 cm^{-1}; **HRMS** (ESI) calculated for $C_{81}H_{82}O_{19}Na$ $(M+Na)^+$: 1381.5343, found : 1381.5356 (+ 0.9 ppm).

Triazol dimer (S6)

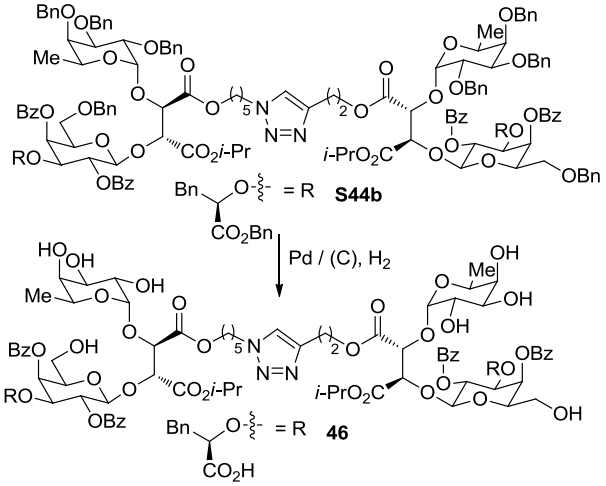


A solution of azide **40** (173 mg, 0.122 mmol) and alkyne **44** (182 mg, 0.133 mmol) in THF (8 mL, 0.1M) was treated with CuI (0.050 g, 0.26 mmol) and DIEA (0.068 mL, 0.39 mmol). After 16 hours, the mixture was concentrated *in vacuo*. Purification by flash chromatography (DCM:EtOAc, 55:45) provided **S6** (203 mg, 60%) as a colorless oil.

Formula: $C_{163}H_{169}N_3O_{38}$; **MW** : 2776.14 g/mol; **R*f*** 0.30 (45 % EtOAc/Hexanes); **$[\alpha]_D^{25}$+** 35.2 (*c* 1.1, CH_2Cl_2); *Due to the complexity of the molecule, all protons and carbons could not be reported.* **^{1}H NMR** (500 MHz, C_6D_6) δ 8.45 (da, *J* = 7.1 Hz, 1H), 8.40 (dd, *J* = 1.5, 8.3 Hz, 1H), 8.18 (da,

J = 7.3 Hz, 1H), 8.10 (da, *J* = 7.1 Hz, 1H), 7.56-7.50 (appt, *J* = 6.8 Hz, 2H), 7.42-6.94 (m, 67H), 6.92-6.80 (m, 8H), 6.09 (appt, *J* = 8.5 Hz, 1H), 6.02 (appt, *J* = 8.3 Hz, 1H), 5.93 (d, *J* = 3.2 Hz, 1H), 5.90 (d, J = 3.2 Hz, 1H), 5.54 (d, *J* = 8.1 Hz, 1H), 5.38 (d, *J* = 8.1 Hz, 1H), 5.16-5.11 (m, 1H), 5.05-4.99 (m, 1H), 4.99-4.53 (m, 22H), 4.99 (appt, *J* = 9.5 Hz, 1H), 4.44-4.36 (m, 1H), 4.34-4.08 (m, 9H), 4.06-3.99 (m, 2H), 3.97-3.86 (m, 2H), 3.86-3.76 (m, 3H), 3.71- 3.65 (m, 1H), 3.58-3.51 (m, 2H), 3.46 (s, 1H), 3.41 (s, 1H), 3.20-3.10 (m, 1H), 3.08- 2.92 (m, 3H), 2.90-2.81 (m, 2H), 1.79-1.66 (m, 2H), 1.38-1.11 (m, 15H), 1.01-0.91 (m, 6H), 0.88 (d, *J* = 6.1 Hz, 3H), 0.82 (d, *J* = 6.3 Hz, 3H) ppm; **^{13}C NMR** (100.6 MHz, C_6D_6) δ 170.8, 168.8, 168.1, 166.0, 165.7, 144.2, 139.1, 138.9, 137.8, 135.9, 135.5, 133.5, 132.9, 130.8, 130.3, 129.8, 128.6, 128.4, 128.1, 127.8, 127.5, 126.5, 122.7, 100.3, 100.0, 99.2, 79.6, 78.3, 77.9, 75.8, 75.0, 74.1, 73.4, 73.2, 72.9, 72.7, 72.5, 71.5, 69.6, 69.3, 68.1, 67.7, 66.9, 66.7, 66.4, 65.0, 64.7, 50.2, 39.5, 30.3, 30.0, 28.0, 25.7, 23.0, 21.9, 16.8 ppm. **IR** (film) υ_{max} 2929, 1726, 1453, 1269, 1106, 700 cm^{-1}; **HRMS** (ESI) calculated for $C_{163}H_{169}O_{38}N_3Na_2$ $(M+2Na)^{2+/2}$: 1411.0587, found: 1411.0570 (+0.3 ppm).

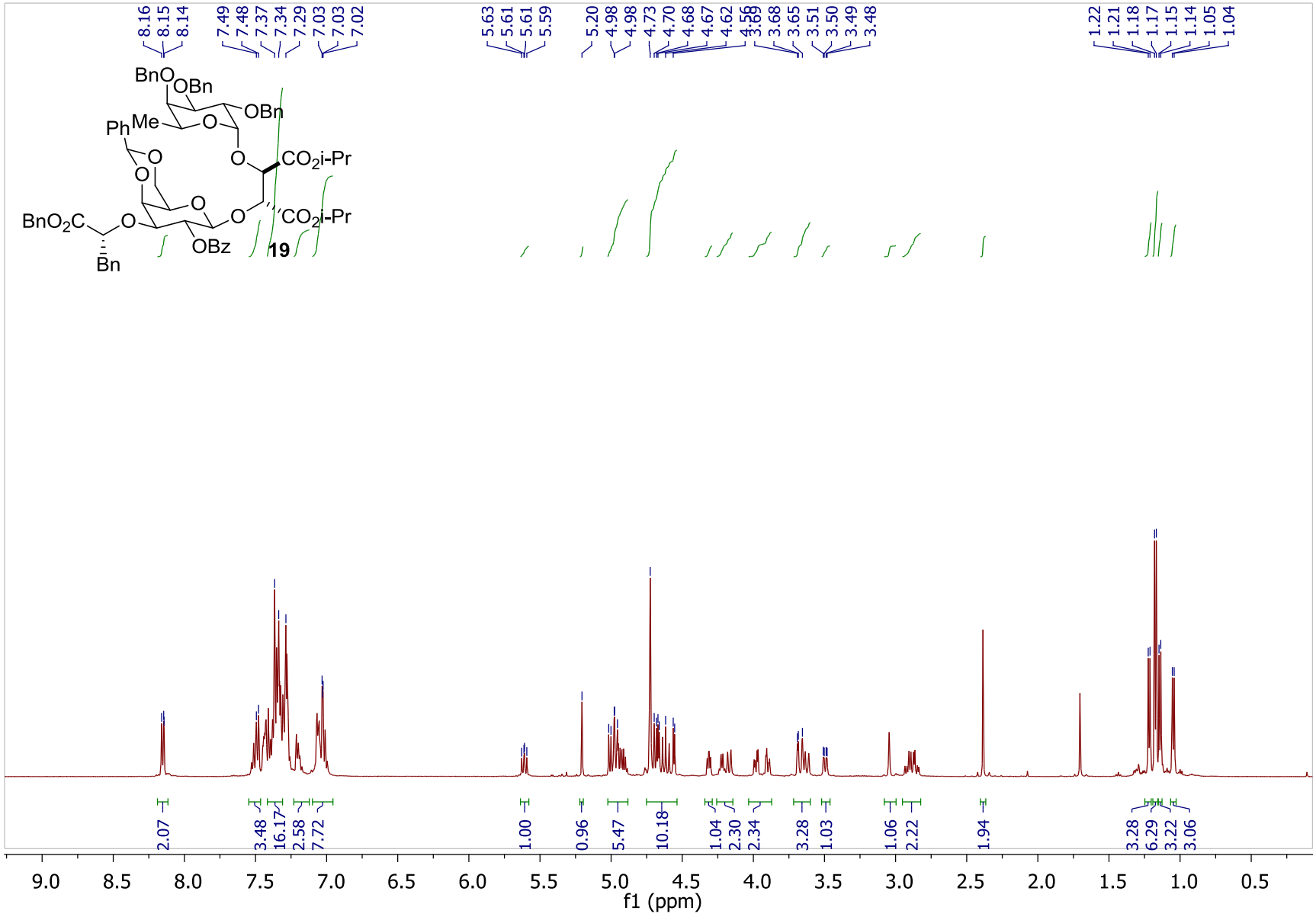
sLe^x dimer 46



To a solution of compound **S6** (78 mg, 0.03 mmol) in THF:MeOH (4:1, 0.1M) under an inert atmosphere was added Pd/C (160 mg, 10 % wt.). The system was purged with H_2 three times and reaction mixture was stirred at room temperature overnight under one atm of H_2. The mixture was filtered on Celite®, washed with MeOH and concentrated *in vacuo*. Purification by flash chromatography (C18 reversed-phase silica, CH_3CN:H_2O, 40:60) provided **46** (11 mg, 19 %) as a white powder.

Formula: $C_{93}H_{109}N_3O_{38}$**; MW** : 1875.67 g/mol; $\mathbf{[\alpha]_D^{25}}$ 14.0 (*c* 0.4, MeOH); **R*f*** 0.65 (6/3/1 EtOAc/*i*-PrOH/H_2O); *Due to the complexity of the molecule, all protons and carbons could not be reported.* **^{1}H NMR**(500 MHz, CD_3OD) δ 8.24-8.16 (m, 4H), 8.04-7.96 (m, 4H), 7.94-7.88 (m, 1H), 7.67-7.61 (m, 2H), 7.60-7.54 (m, 2H), 7.52-7.44 (m, 8H), 7.11-7.05 (m, 4H), 6.87-6.80 (m, 4H), 6.76-6.70 (m, 2H), 5.83- 5.72 (m, 2H), 5.53-5.46 (m, 2H), 5.10-4.50 (m), 4.48-4.40 (m, 4H), 4.32-4.22 (m, 4H), 4.18-4.02 (m, 5H), 3.90-3.84 (m, 2H), 3.84-3.72 (m, 5H), 3.67-3.54 (m, 9H), 3.40-3.25 (m), 2.99-2.90 (m, 2H), 2.84-2.76 (m, 2H), 2.71-2.64 (m, 3H), 2.91-1.85 (m, 2H), 1.33-1.20 (m, 16H), 1.02 (d, *J* = 6.6 Hz, 3H), 0.99 (d, *J* = 6.3 Hz, 3H) ppm; **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 168.9, 168.8, 168.5, 167.0, 165.8, 138.1, 133.2, 132.7, 130.9, 130.4, 129.9, 129.8, 129.3, 128.3, 128.1, 127.4, 125.5, 102.1, 102.0, 101.9, 78.4, 78.2, 77.9, 75.4, 74.7, 72.3, 71.6, 70.3, 70.1, 68.7, 67.6, 66.7, 65.0, 64.1, 60.7, 50.1, 39.4, 29.8, 27.7, 22.7, 20.8, 15.43, 15.35 ppm; **HRMS** (ESI) calculated for $C_{93}H_{110}O_{38}N_3$ (M+H)+ : 1876.6767 found: 1876.6770 (+0.4 ppm).

I. ^{1}H NMR and ^{13}C NMR spectra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3.50
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O
CO2i-Pr
BnO2C
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OBz
Bn
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3.22
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6.5
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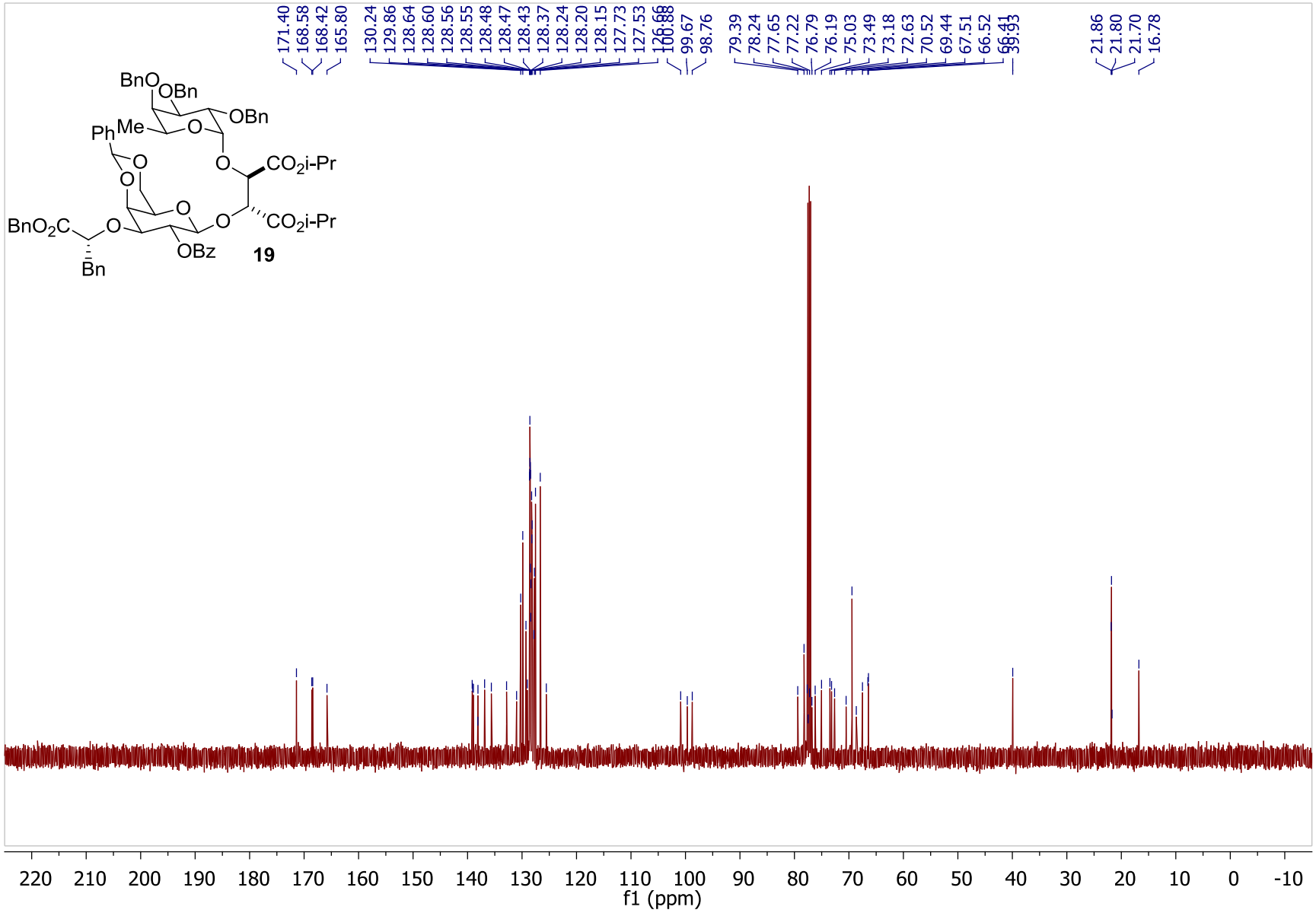
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CO2i-Pr
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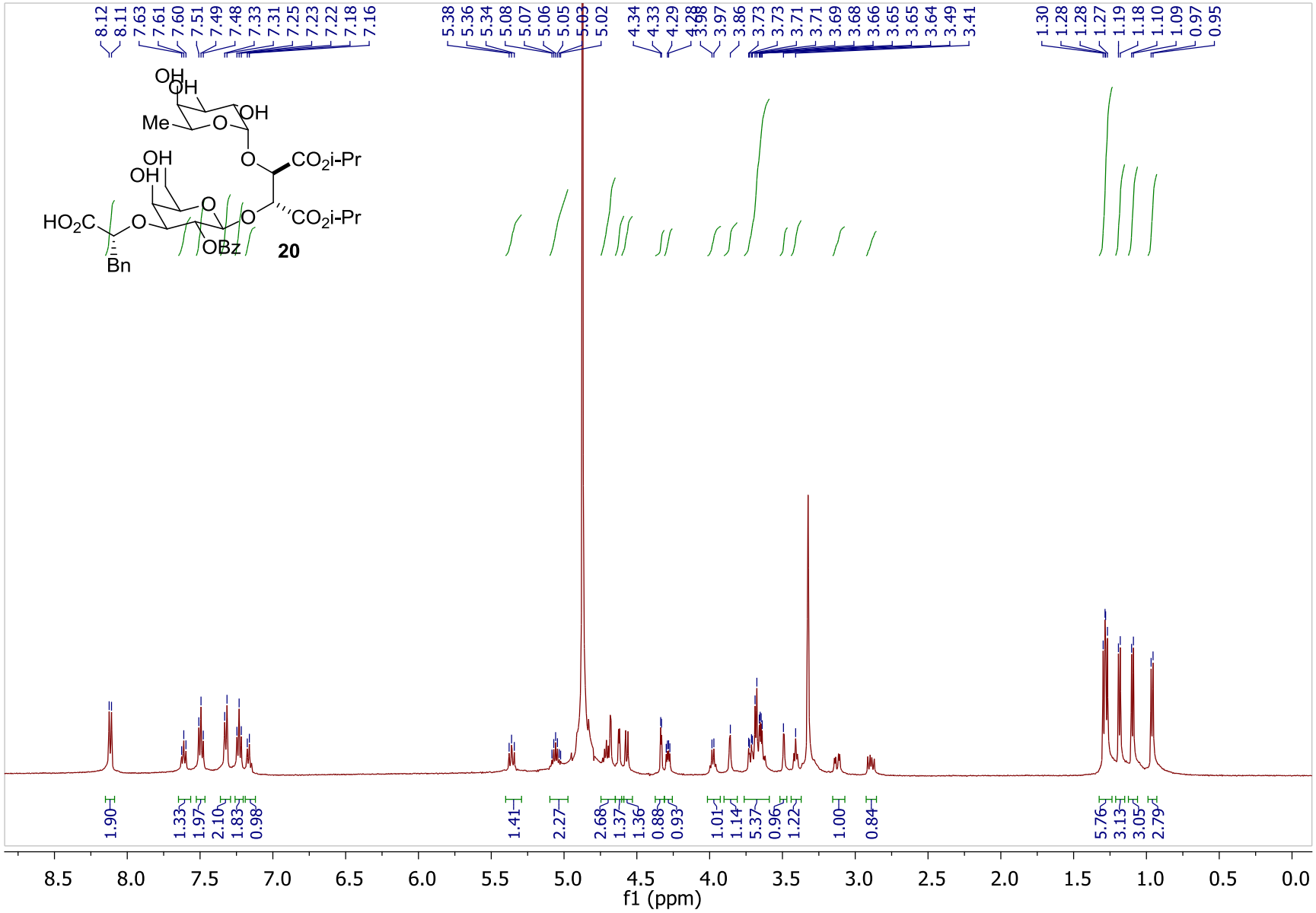
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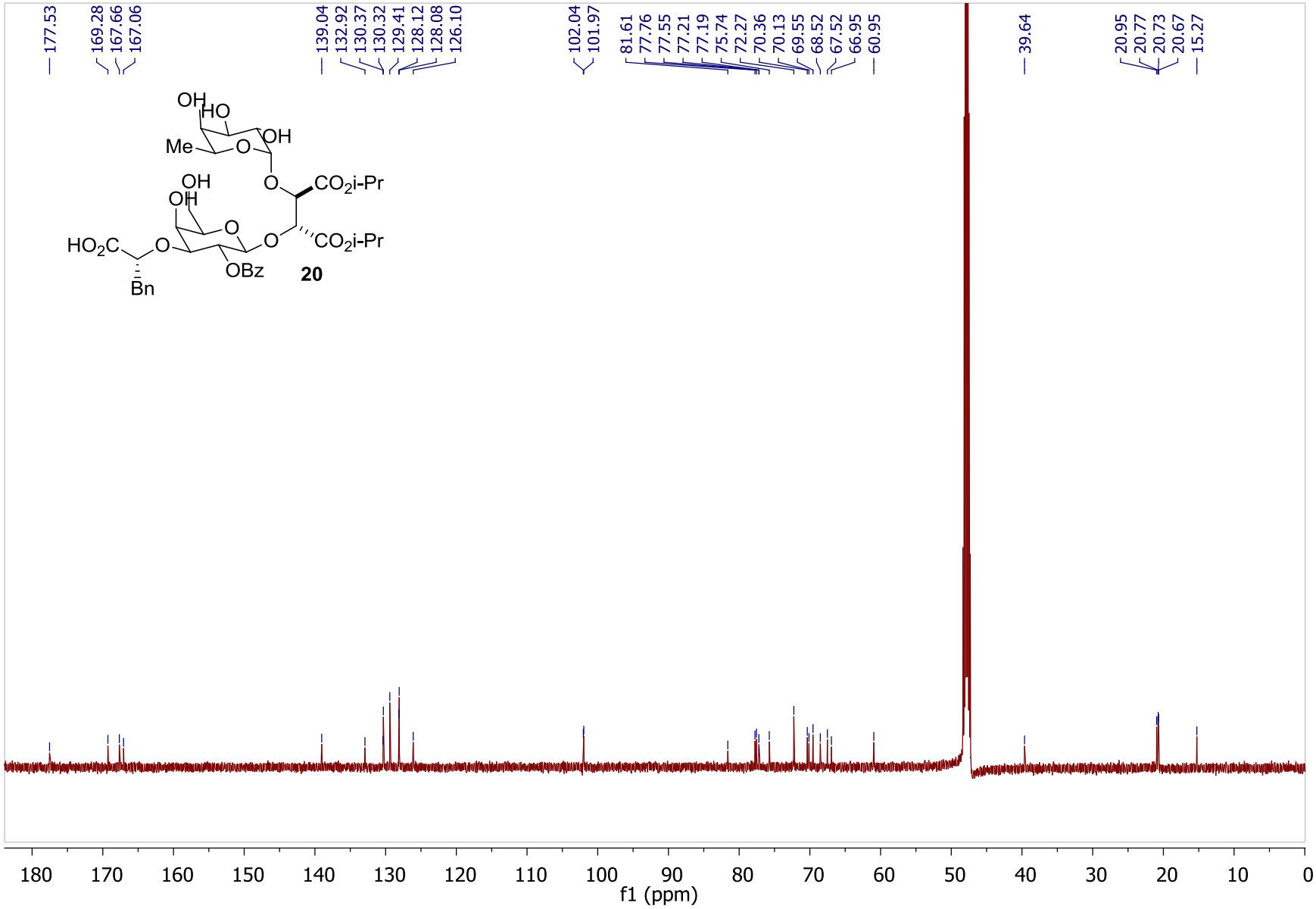
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CO2i-Pr
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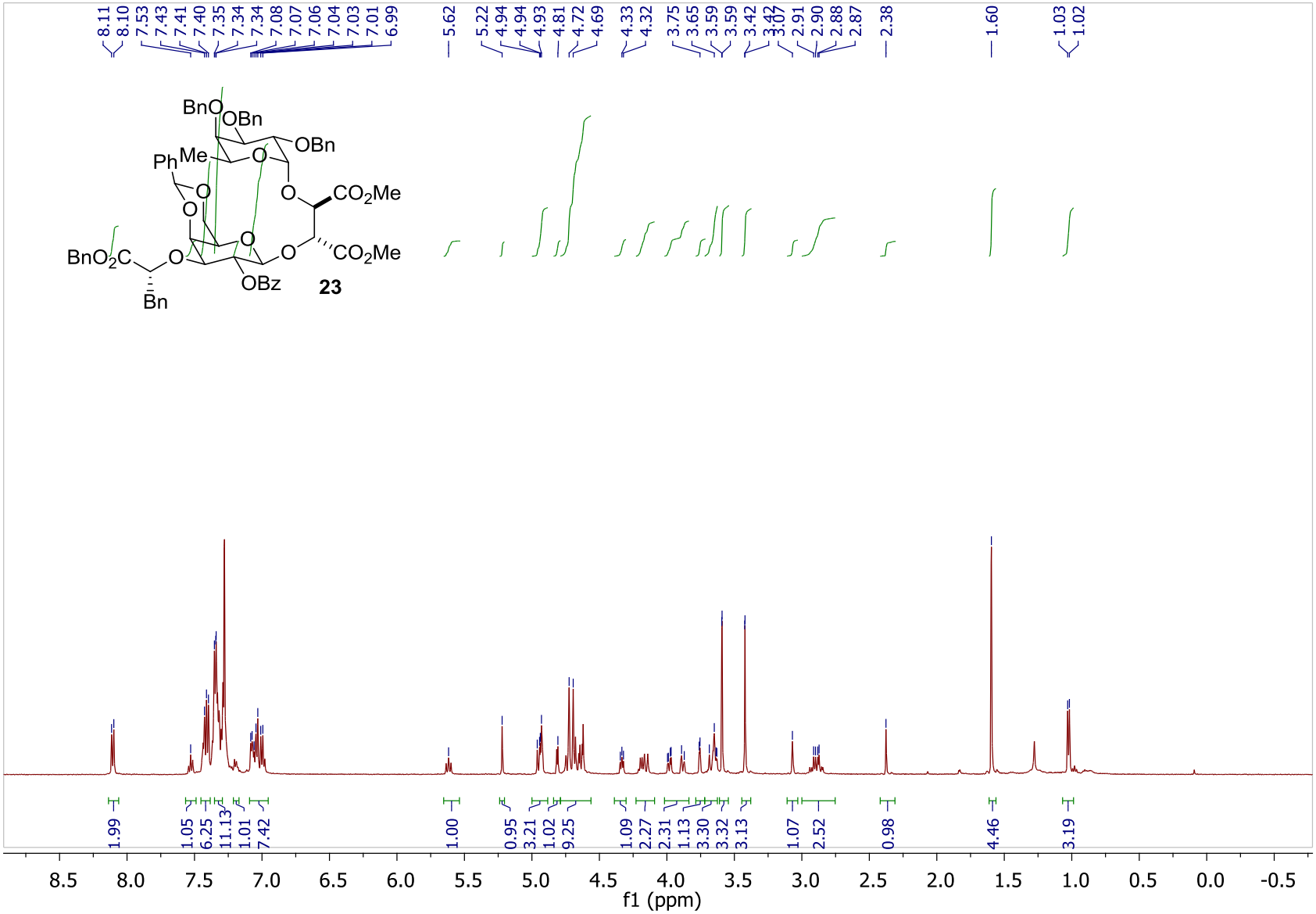
f1 (ppm)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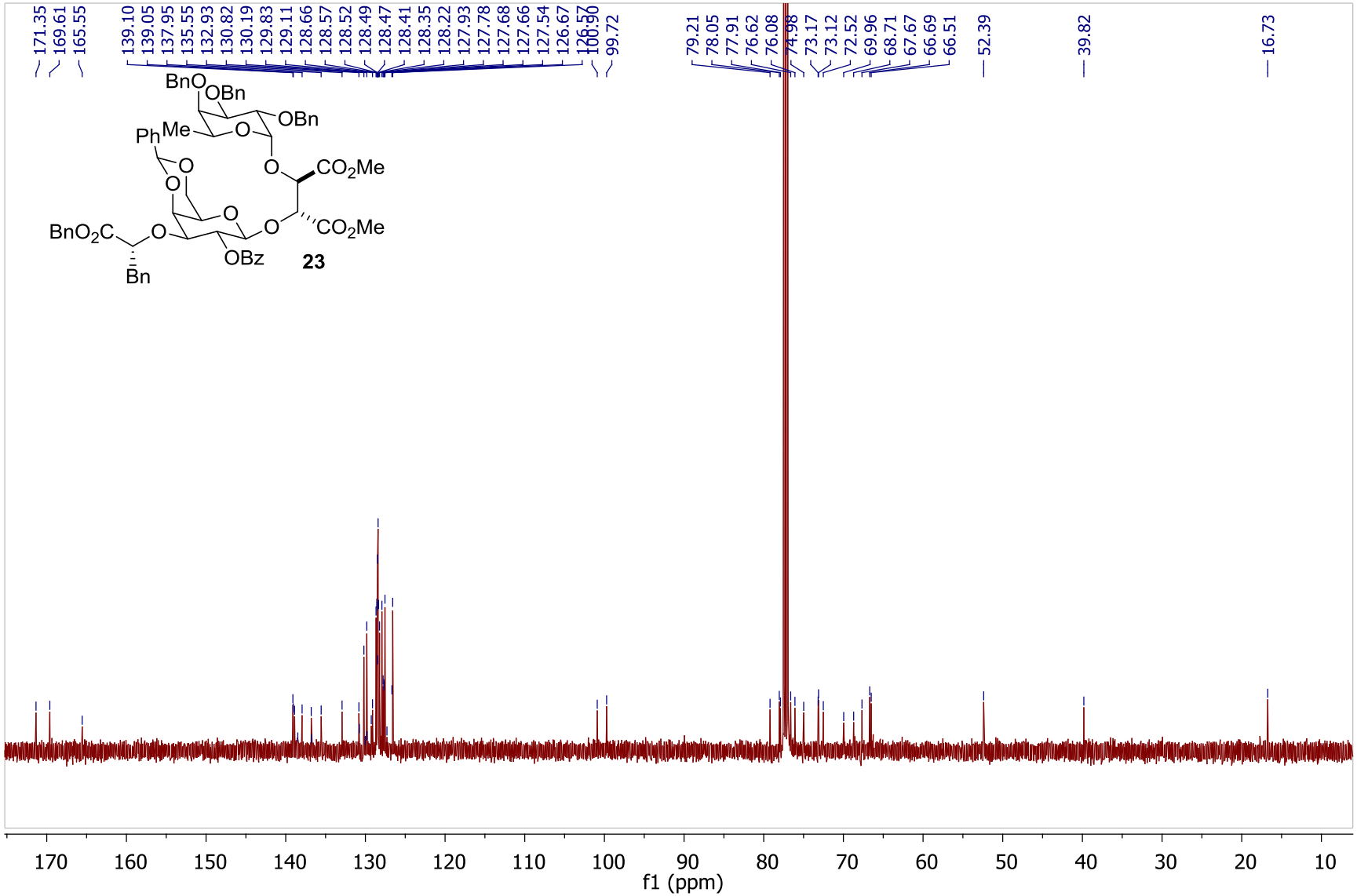
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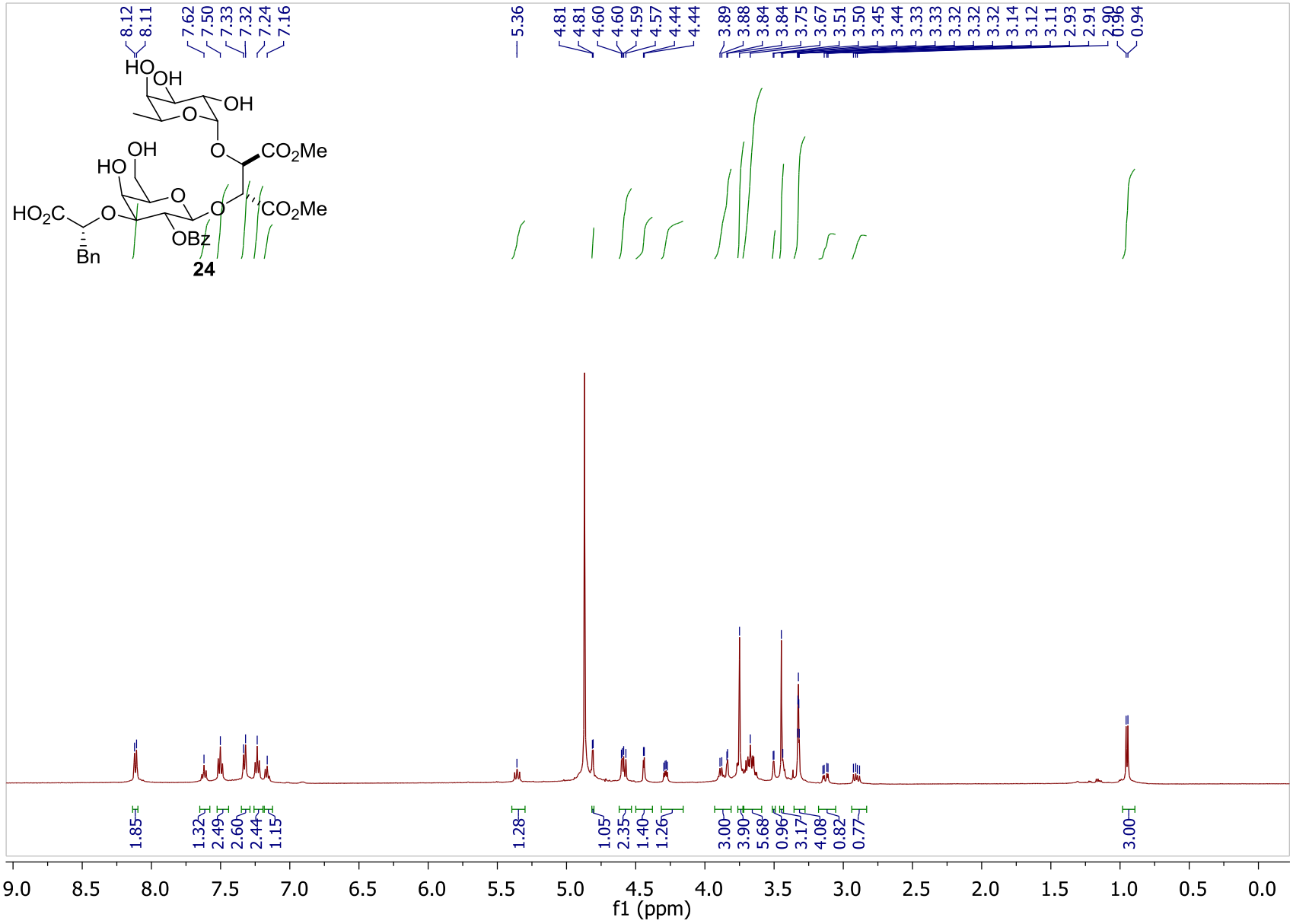
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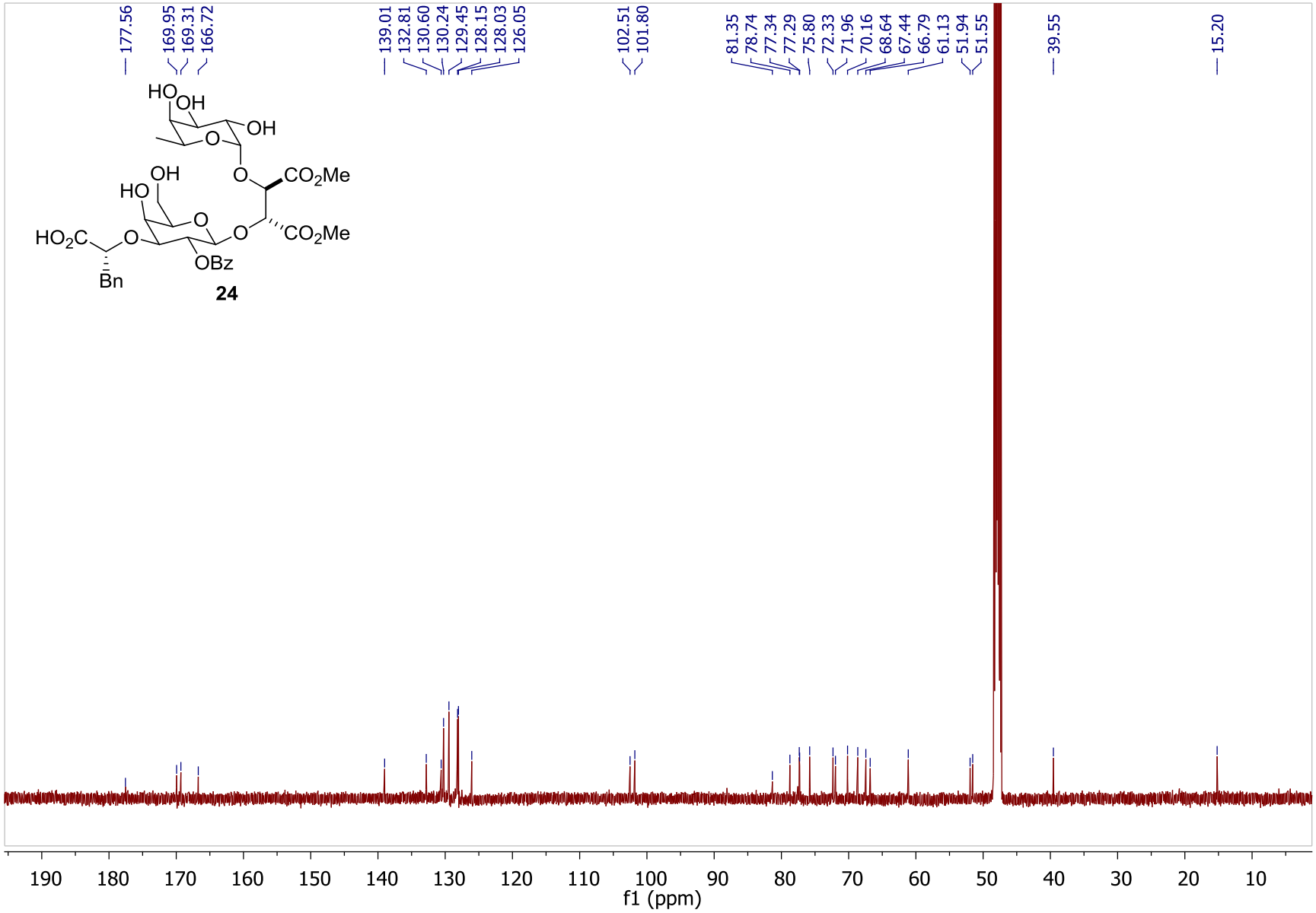
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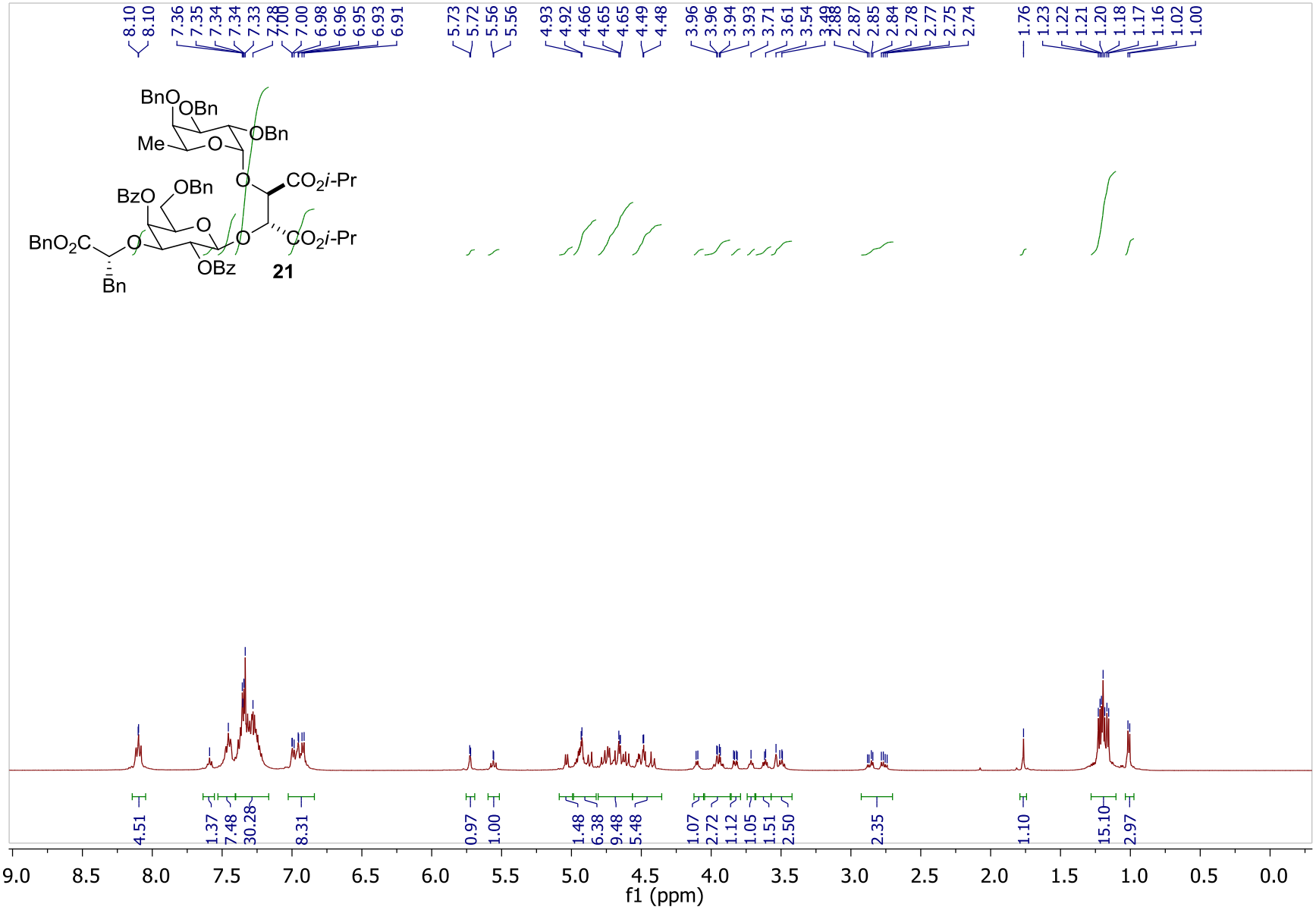
f1 (ppm)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OBn
Me
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OBn
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CO2i-Pr
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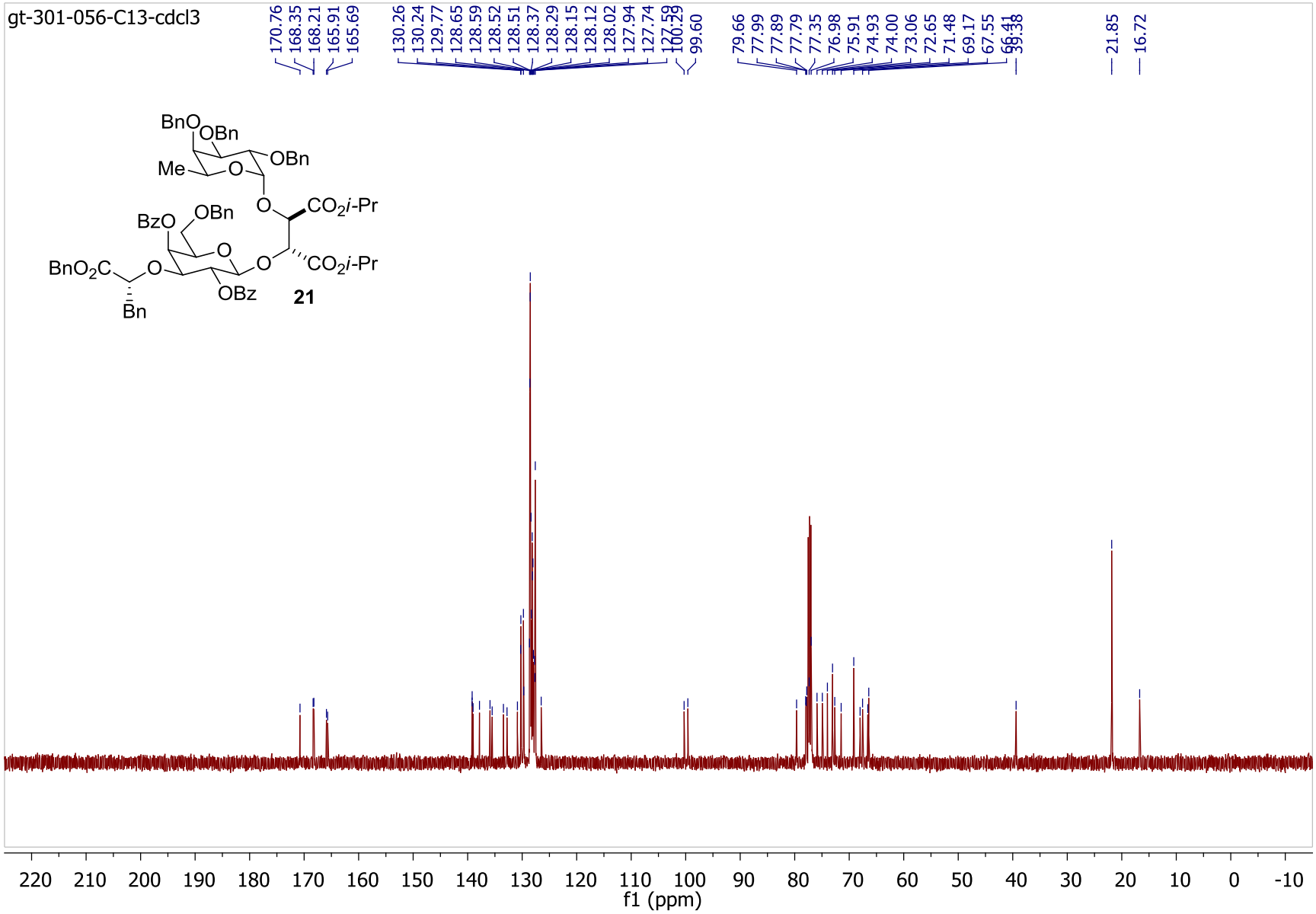
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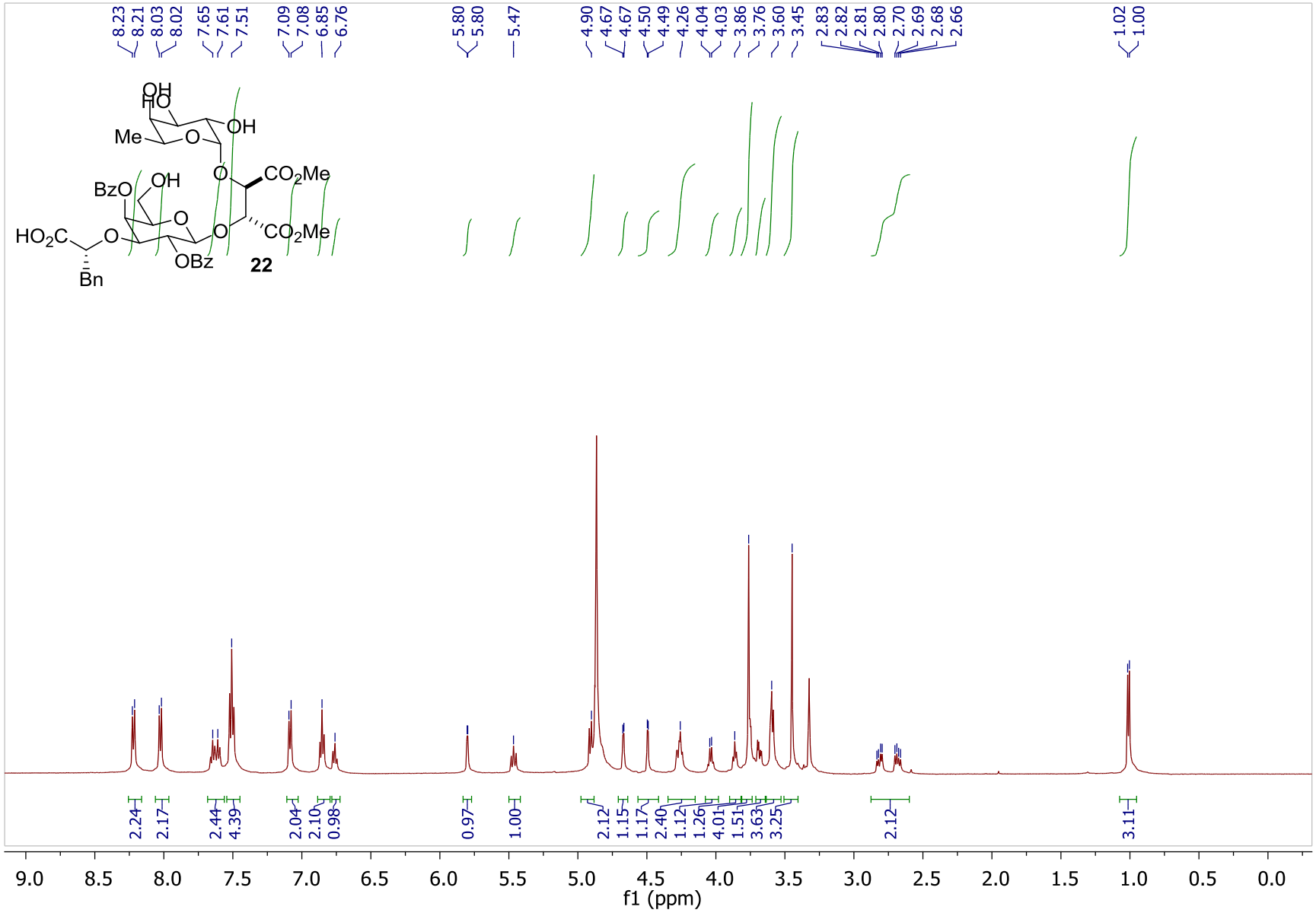
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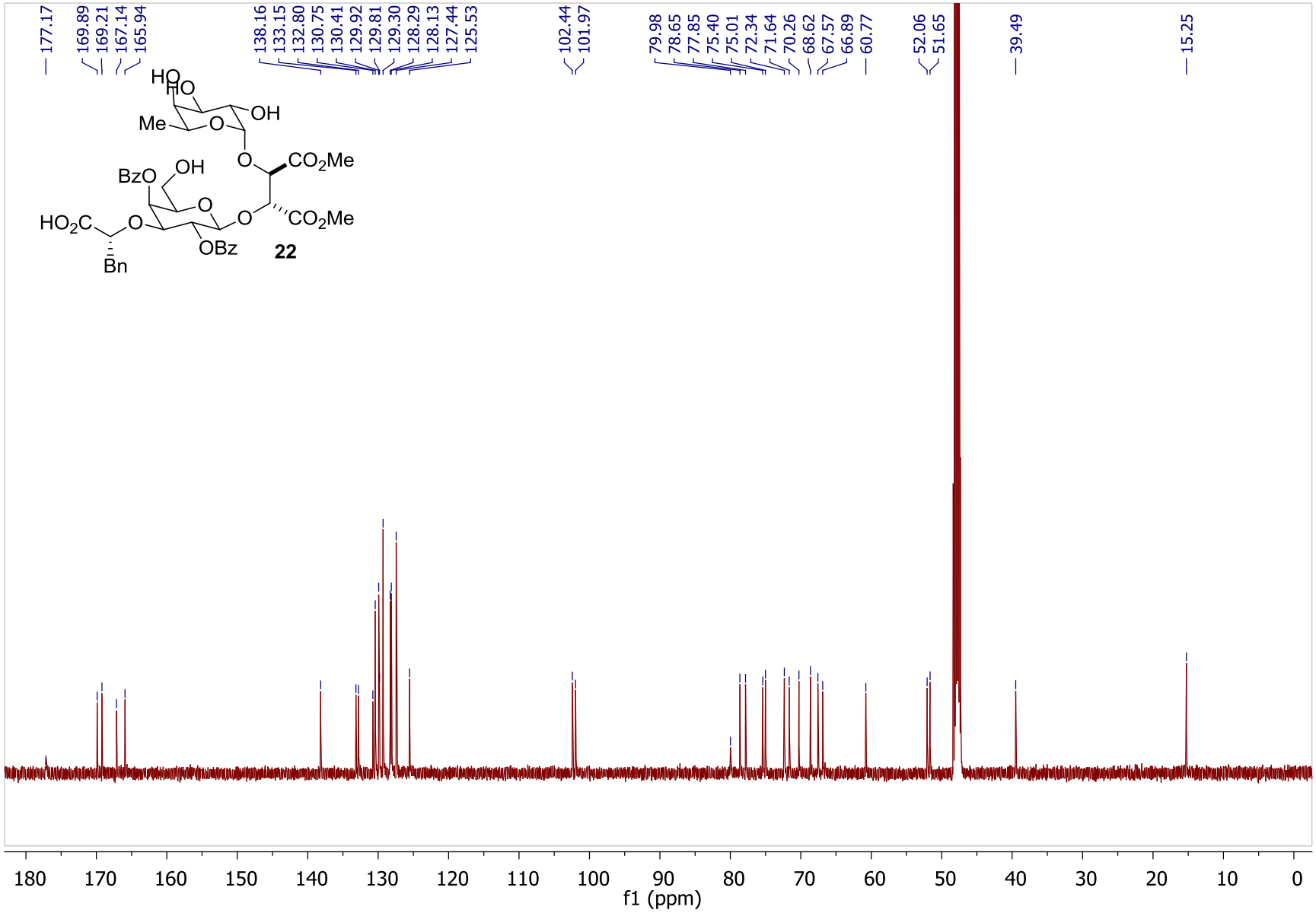
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Bn
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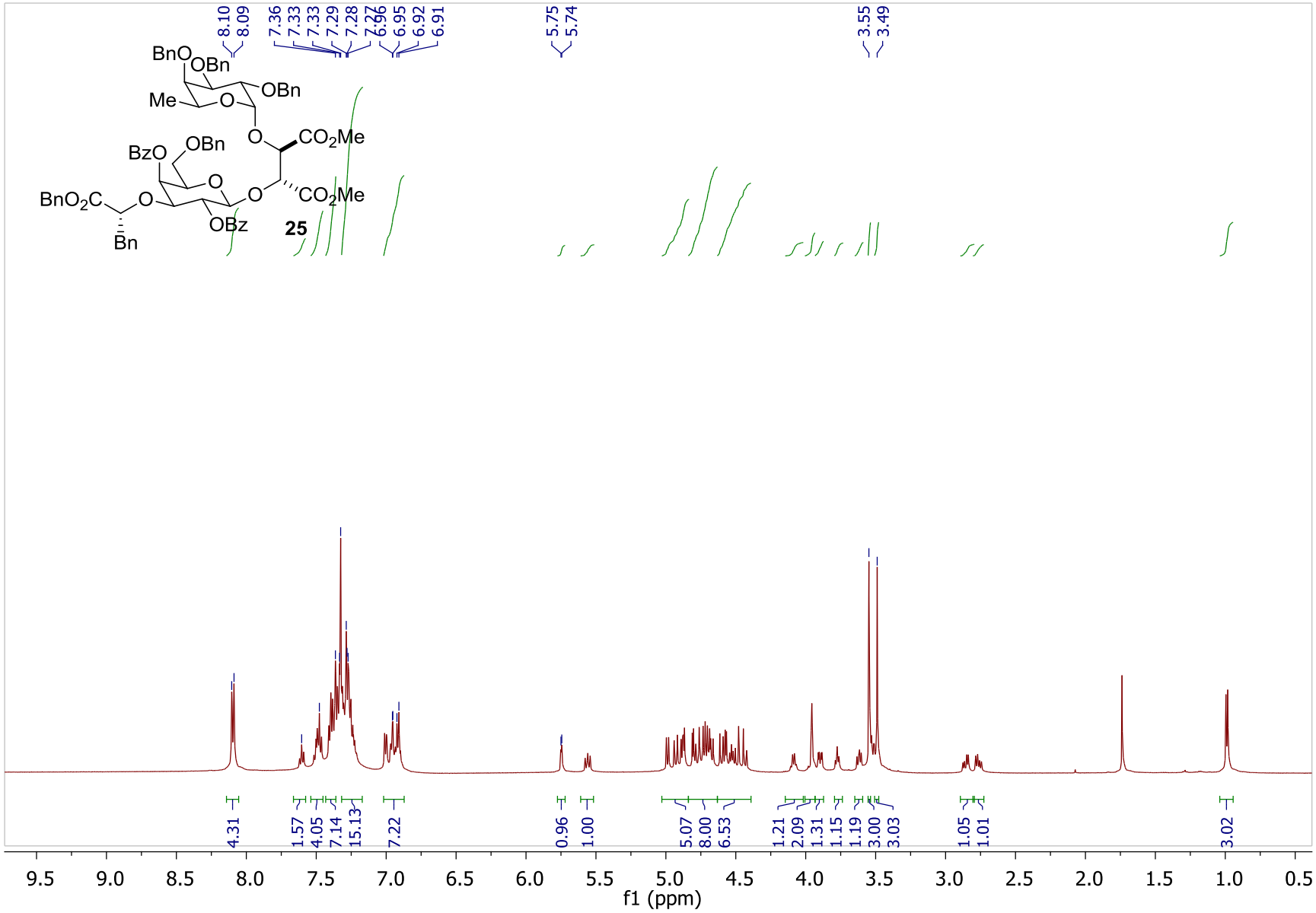
f1 (ppm)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OBn
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CO2Me
BnO2C
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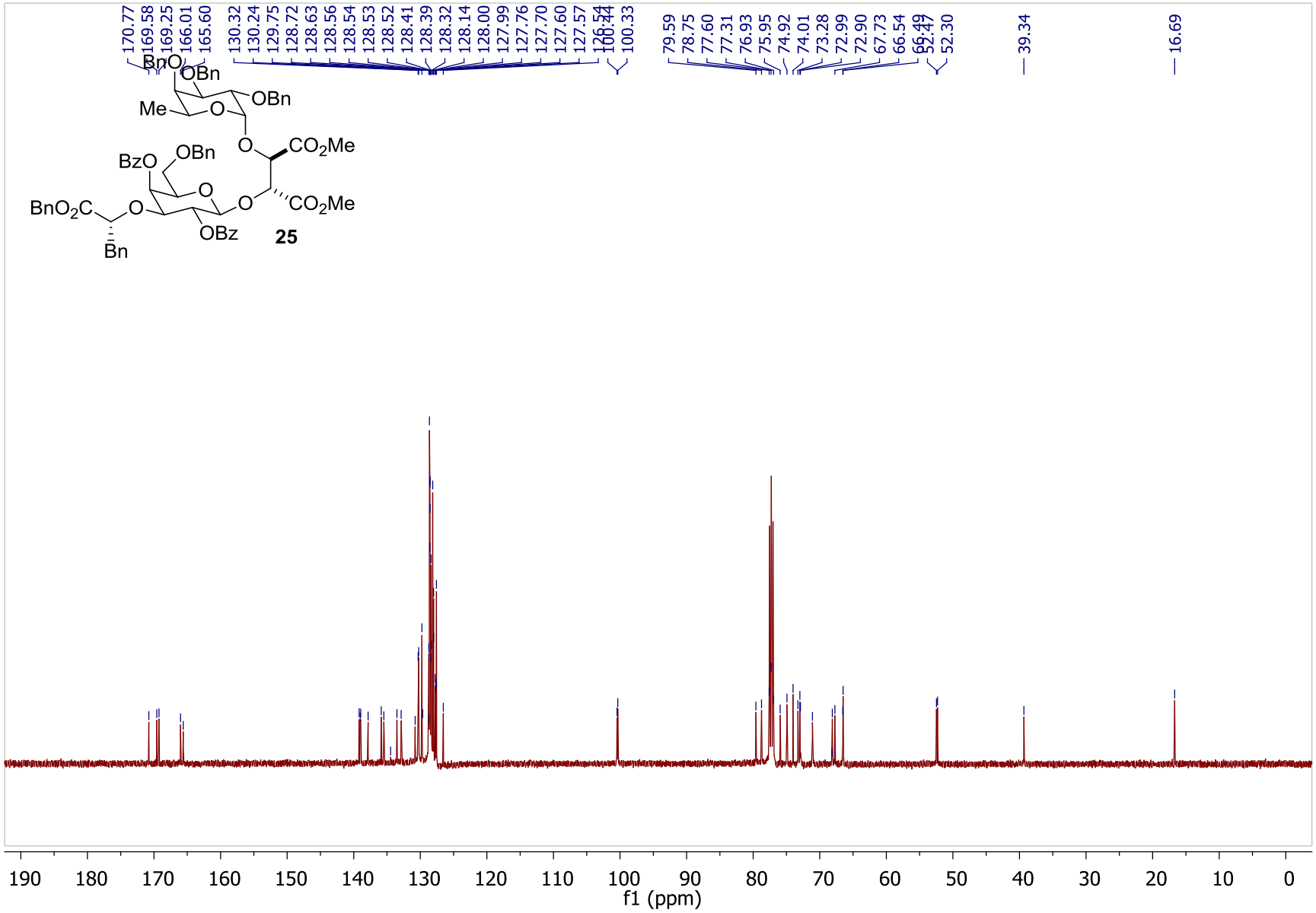
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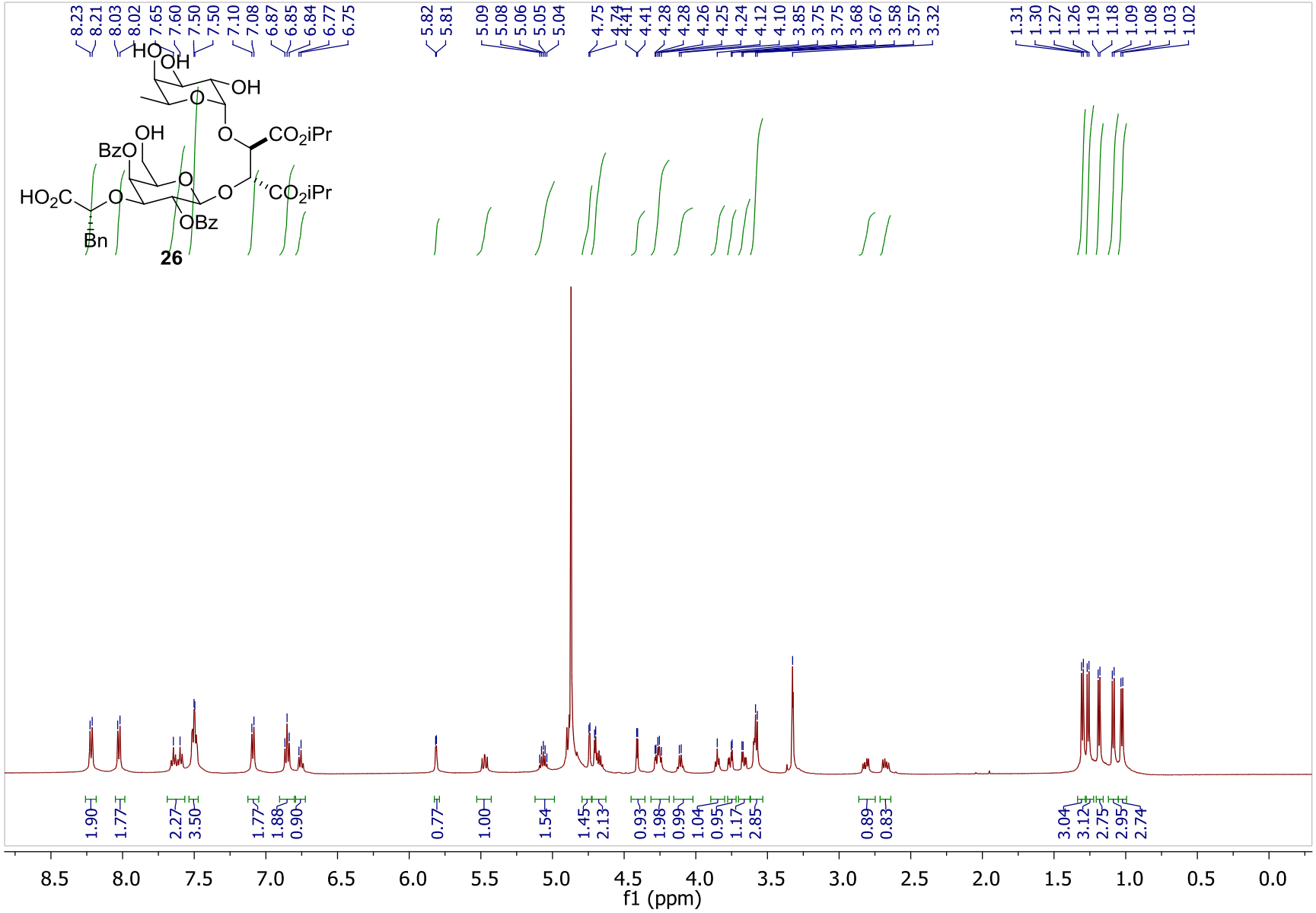
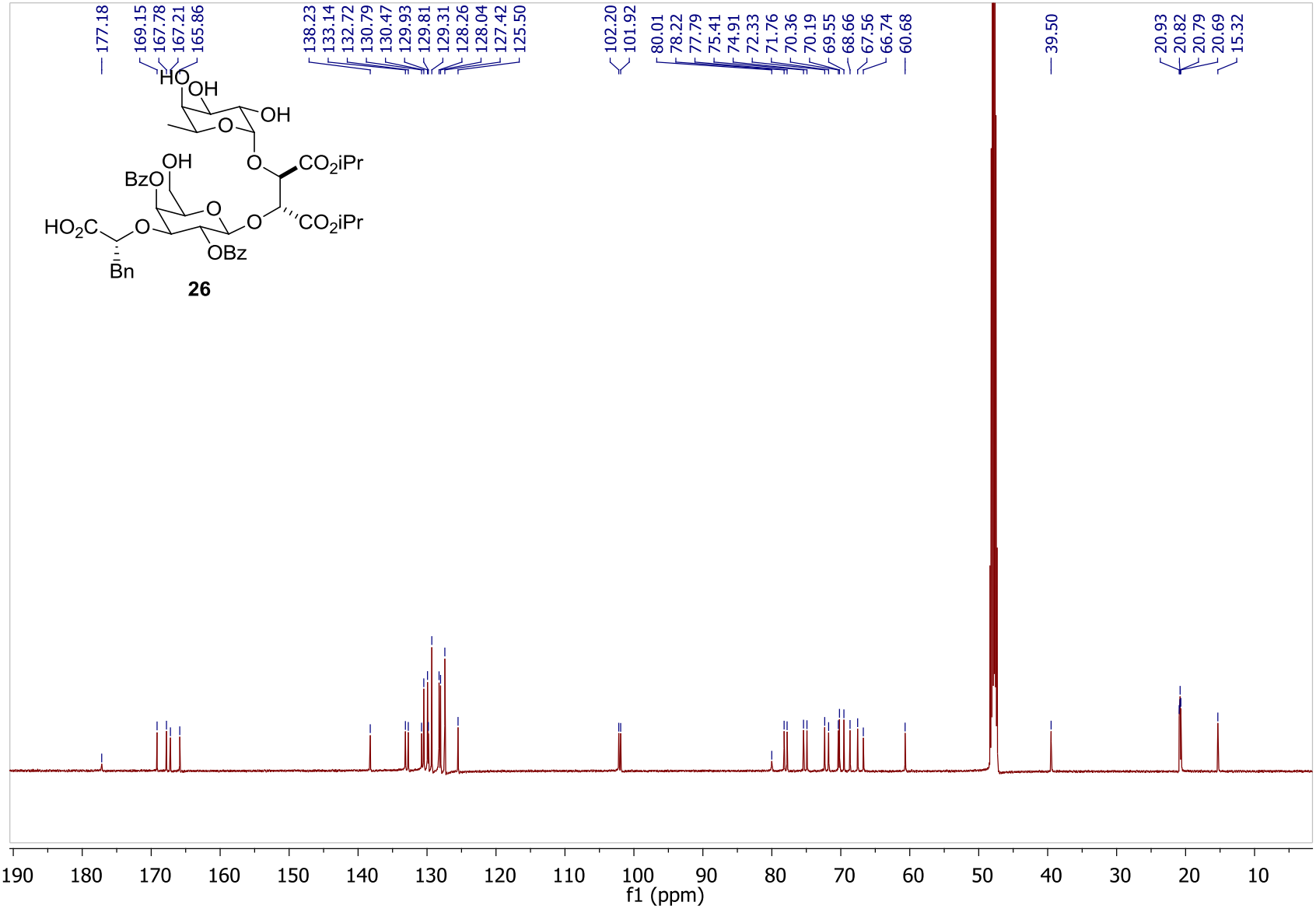
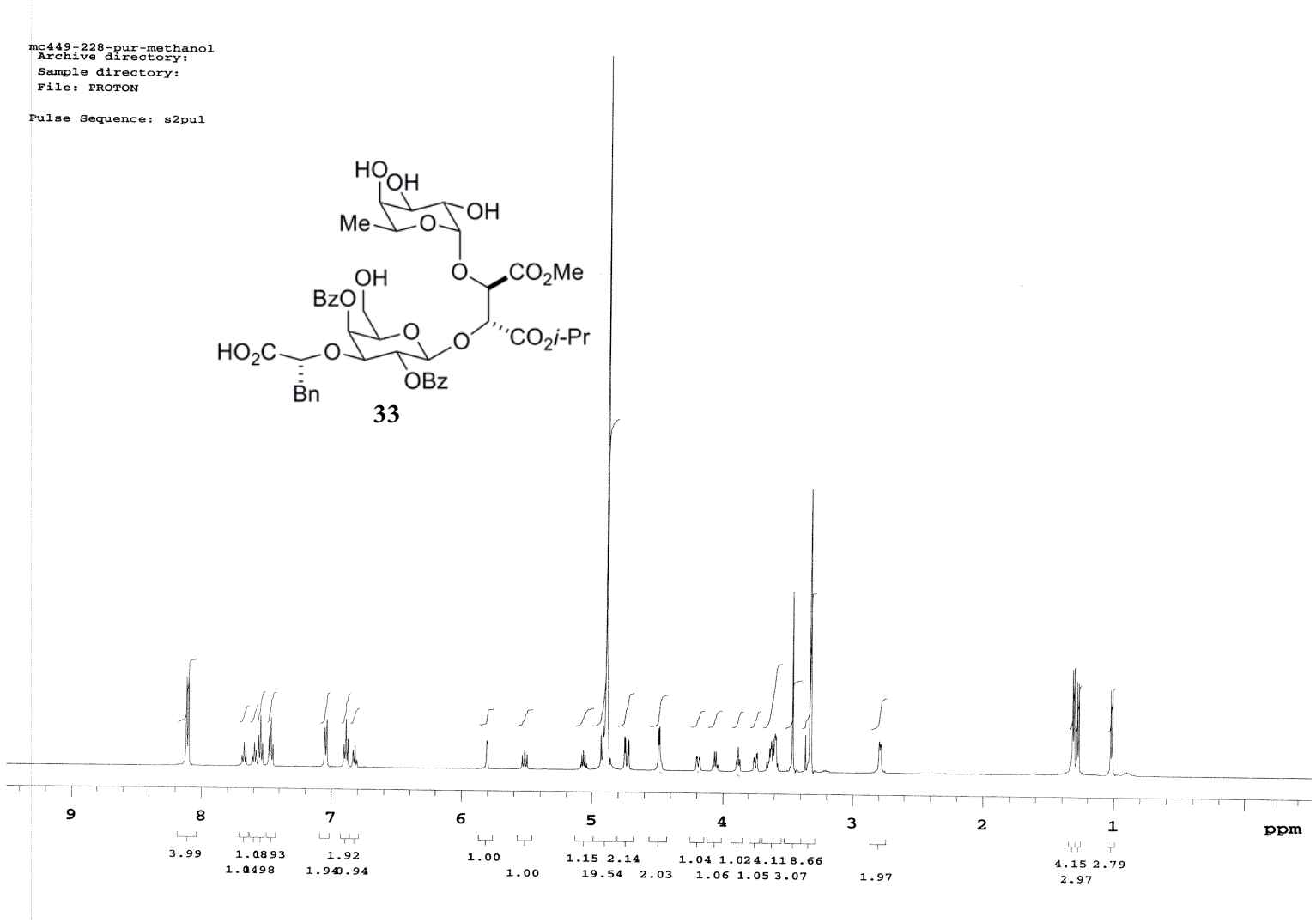
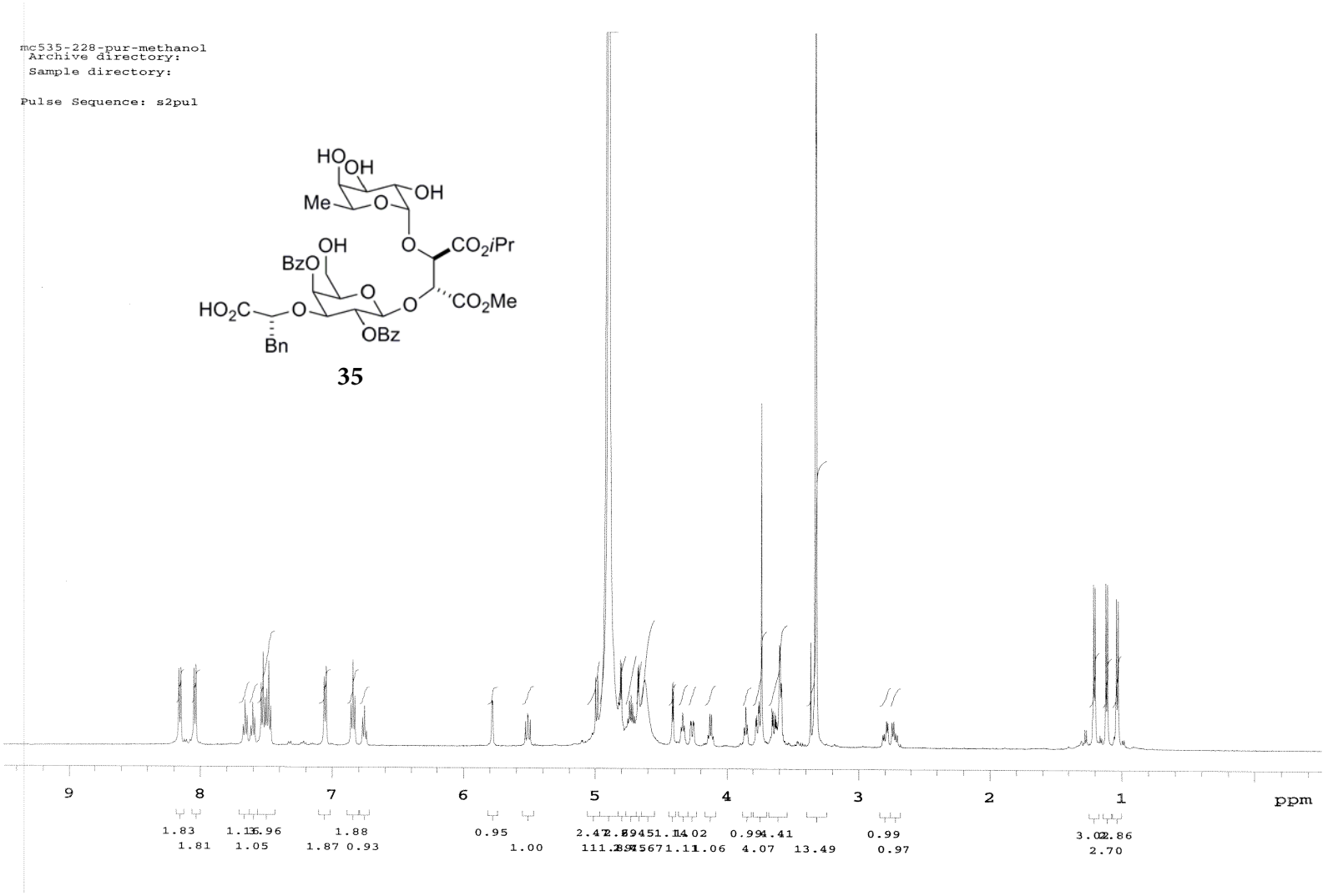
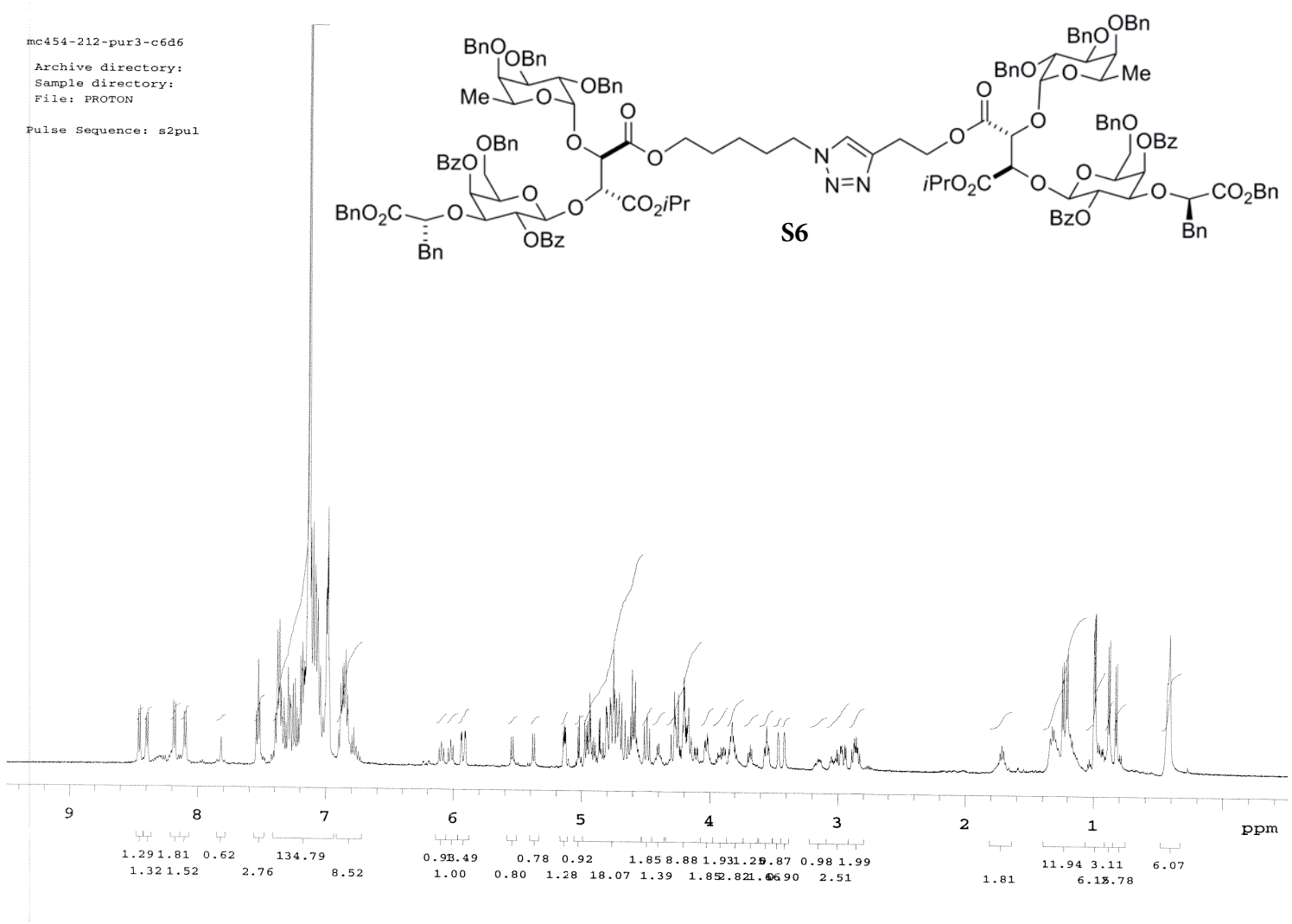
127.57
100.33
79.59
78.75
77.60
77.31
76.93
75.95
74.92
74.01
73.28
72.99
72.90
67.73
66.54
52.30
39.34
16.69
BnO
OBn
Me
O
OBn
O
CO2Me
BzO
OBn
O
O
CO2Me
BnO2C
O
OBz
Bn
25
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.23
8.21
8.03
8.02
7.65
7.60
7.50
7.50
7.10
7.08
6.87
6.85
6.84
6.77
6.75
5.82
5.81
5.09
5.08
5.06
5.05
5.04
4.75
4.74
4.41
4.41
4.28
4.28
4.26
4.25
4.24
4.12
4.10
3.85
3.75
3.75
3.68
3.67
3.58
3.57
3.32
1.31
1.30
1.27
1.26
1.19
1.18
1.09
1.08
1.03
1.02
HO
OH
OH
O
OH
BzO
O
CO2iPr
HO2C
O
O
CO2iPr
OBz
Bn
26
1.90
1.77
2.27
3.50
1.77
1.88
0.90
0.77
1.00
1.54
1.45
2.13
0.93
1.98
0.99
1.04
0.95
1.17
2.85
0.89
0.83
3.04
3.12
2.75
2.95
2.74
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


177.18
169.15
167.78
167.21
165.86
138.23
133.14
132.72
130.79
130.47
129.93
129.81
129.31
128.26
128.04
127.42
125.50
102.20
101.92
80.01
78.22
77.79
75.41
74.91
72.33
71.76
70.36
70.19
69.55
68.66
67.56
66.74
60.68
39.50
20.93
20.82
20.79
20.69
15.32
HO
OH
OH
O
O
CO2iPr
OH
BzO
O
O
CO2iPr
HO2C
O
OBz
Bn
26
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


mc449-228-pur-methanol
Archive directory:
Sample directory:
File: PROTON
Pulse Sequence: s2pul
HO
OH
OH
Me
O
O
CO2Me
OH
BzO
O
O
CO2i-Pr
HO2C
O
OBz
Bn
33
9
8
7
6
5
4
3
2
1
ppm
3.99
1.08
93
1.04
98
1.92
1.94
0.94
1.00
1.00
1.15
2.14
19.54
2.03
1.04
1.02
4.11
8.66
1.06
1.05
3.07
1.97
4.15
2.79
2.97

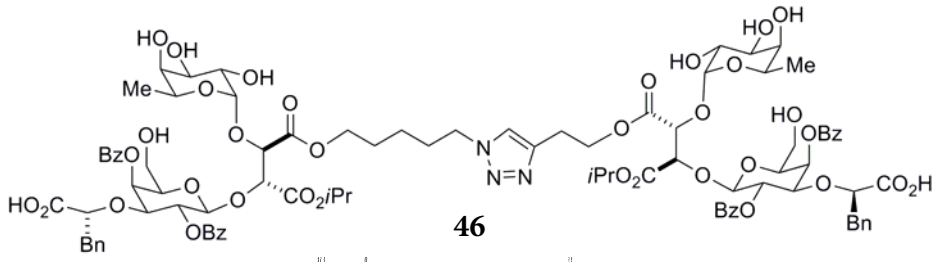

mc535-228-pur-methanol
Archive directory:
Sample directory:
Pulse Sequence: s2pul
HO
OH
Me
O
OH
O
CO2iPr
OH
BzO
O
HO2C
O
O
CO2Me
OBz
Bn
35
9
8
7
6
5
4
3
2
1
ppm
1.83
1.81
1.15
1.05
6.96
1.88
1.87
0.93
0.95
1.00
0.99
4.07
4.41
13.49
0.99
0.97
3.02
2.86
2.70


mc454-212-pur3-c6d6
Archive directory:
Sample directory:
File: PROTON
Pulse Sequence: s2pul
S6
ppm

mc541-228-pur-methanol

Archive directory:
Sample directory:
File: PROTON

Pulse Sequence: s2pul



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