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Supporting Information

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Supporting Information

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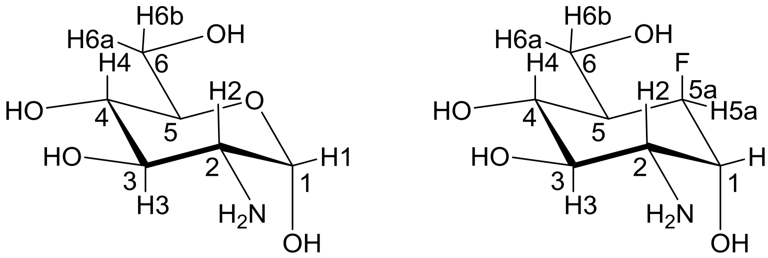


Figure S1. Numbering of sugars and carba-sugars used in the text and in experimental procedures. The numbering of α-D-glucosamine and (5a*R*)-fluoro-carba-α-D-glucosamine are shown. If not otherwise noted H6a refers to the downfield proton while H6b refers to the upfield proton at C6. Same applies for the two protons at C5a.

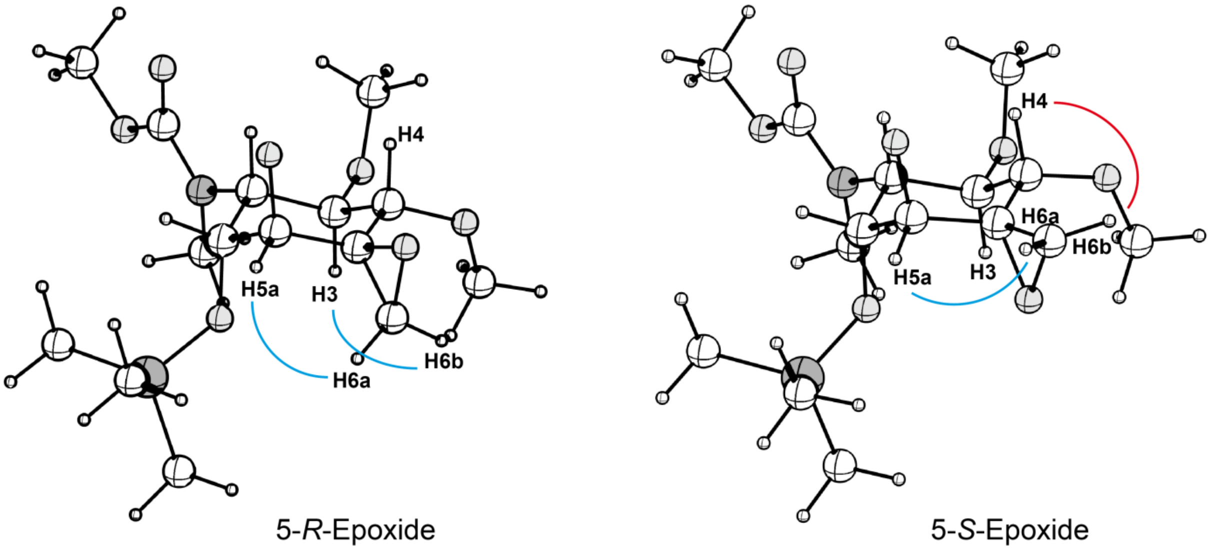


Figure S2. Optimized structures (BP/def2-TZVP) of the two possible isomers of **3** after epoxidation. The protection groups were simplified to reduce time of the DFT-calculations (all benzyl-groups are replaced by methyl). The expected NOE correlations are indicated in blue and red curves. Blue: correlations observed in 2D-ROESY at -40 °C. Red: NOE correlation that would be expected if **3** was present in D-configuration, but are absent in the experiment. The molecules were visualized using the ChemCraft program.

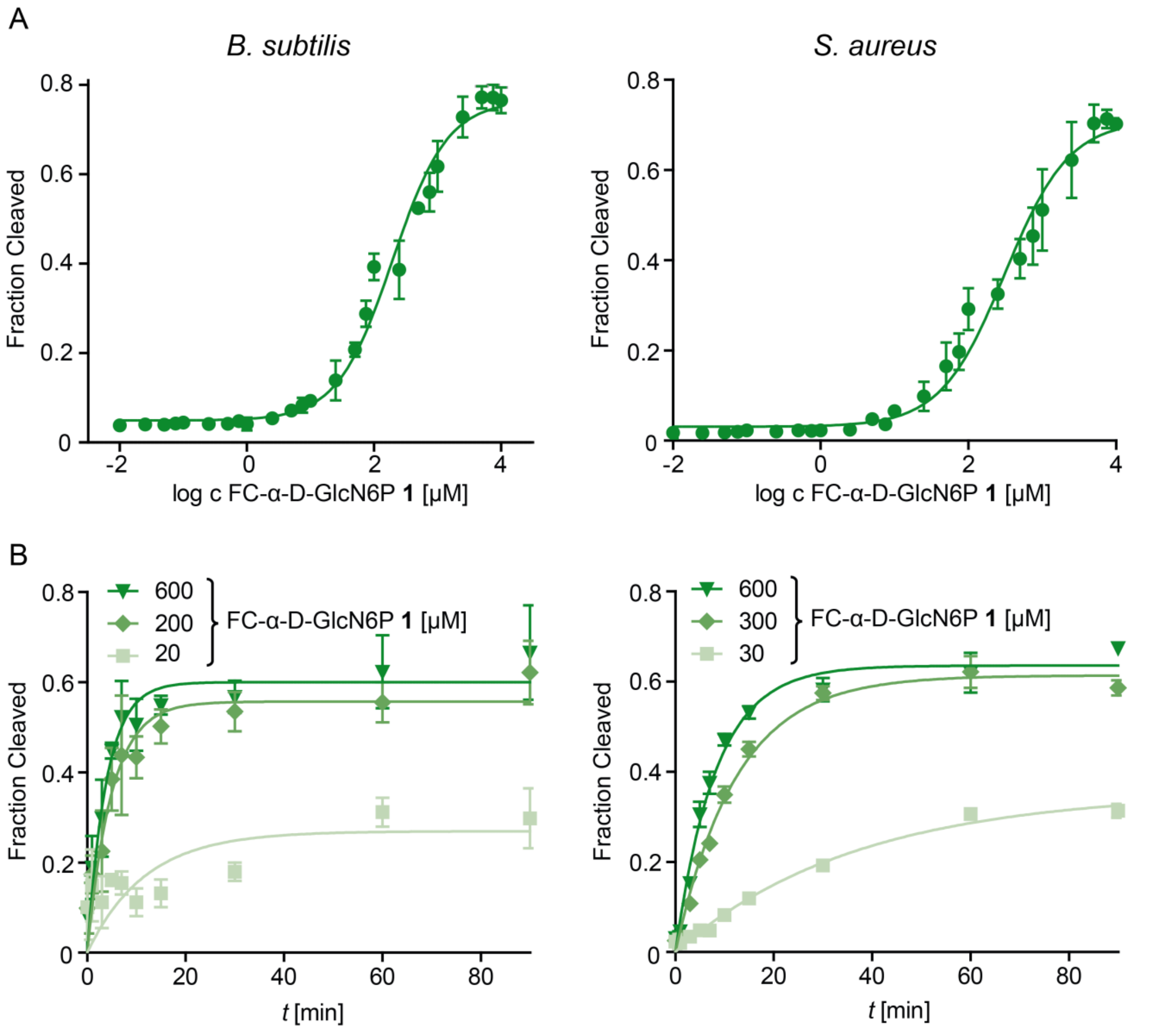


Figure S3. Characterization of carba-sugar derivatives in metabolite-dependent *glmS* ribozyme cleavage assay. (A) Cleavage of the *glmS* ribozymes in the presence of increasing concentrations of **1**. (B) Cleavage rates of the *glmS* ribozymes at different concentrations of **1**. Fractions cleaved as a function of time are shown. Error bars are s.d. of three independent analyses.

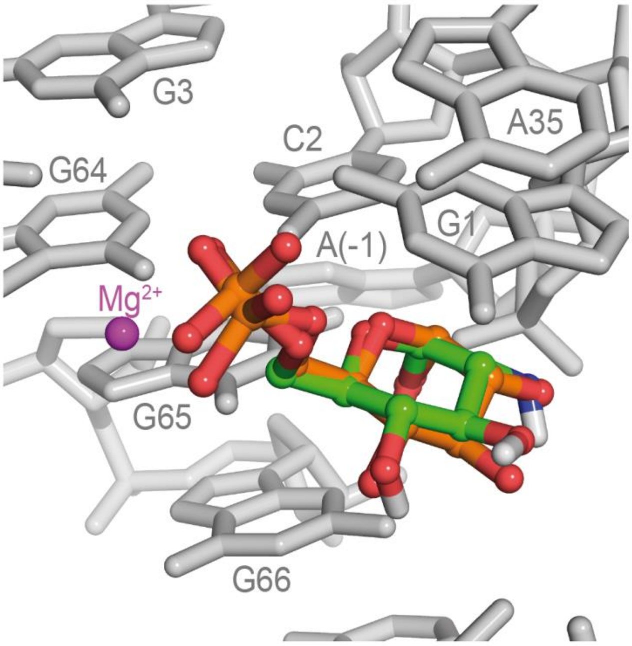


Figure S4. Overlay of the docked structure of α-D-glucosamine-6-phosphate (green) and α-D-glucose-6-phosphate bound to the *glmS* ribozyme of *Thermoanaerobacter tengcongensis*. The binding pose of GlcN6P with the lowest binding energy closely resembles the cleavage inhibitor Glc6P and thereby functions as a good verification of the fitness of the docking by the AutoDock Vina program.

I. Molecular Biological Methods

Preparation of RNA

The *glmS*-RNA from both *S. aureus* and *B. subtilis* were prepared as previously described.[1] Templates for transcription of *glmS* ribozymes of *S. aureus* and *B. subtilis* were prepared from genomic DNA by Pfu DNA-polymerase and 5'-primers containing the T7 promotor. The *glmS* ribozymes were prepared by in vitro transcription using T7 TNA polymerase (37 °C, 17 h). The transcription products were treated with DNase and separated by denaturing polyacrylamide gel electrophoresis (PAGE). The RNAs were dephosphorylated using calf intestine alkaline phosphatase (CIAP, Promega). Radioactive labeling was accomplished by phosphorylation of the 5'-end using the T4 polynucleotide kinase (PNK, NEB) and γ-^{32}P-ATP (10 mCi/mL BEBm Zaventem, Belgium). The ribozymes were desalted (G25 column, GE Healthcare) that had been equilibrated with DEPC-treated water.[1]

glmS Ribozyme Self-Cleavage Assay

The ribozyme self-cleavage assay was performed as previously described.[1] The ^{32}P-labeled *glmS*-RNA from either *B. subtilis* or *S. aureus* was incubated at 37 °C with GlcN, GlcN6P, carbasugar **1**, **2**, **14**, **18**, or without metabolite in the presence of 10 mM $MgCl_2$, 50 mM HEPES (pH 7.5) and 200 mM KCl. The reaction was stopped after 30 min by adding PAGE loading buffer (95% formamide, 10 mM EDTA, 0.1% (v/v) xylenecyanol and 0.1% (v/v) bromophenol blue), followed by separation by 17% denaturing PAGE. The radiolabeled cleavage products were detected via autoradiography on a phosphorimager FLA-3000 (Fujifilm) and AIDA software. k_{obs} values for ribozyme cleavage were determined using trace amounts of ^{32}P-labled

RNA incubated at 37 °C as described above with indicated concentration of fluoro-carba-α-D-GlcN6P. Aliquots were withdrawn at various time points and the reaction quenched by addition of PAGE loading buffer. The cleavage products were separated by denaturing PAGE and k_{obs} were determined by plotting the fraction cleaved as a function of time. Curves were then fitted according to pseudofirst order association kinetics.

II. Molecular Docking

For molecular docking the crystal structure of the glmS ribozyme from *T. tengcongensis* (PDB 2Z74) was used. Prior to docking the native ligand Glc6P was removed and polar hydrogens were added to the crystal structure using the WHAT IF program.[5] The structures of carba-sugars discussed in this work and GlcN6P were optimized with the ORCA[6] program pac kage at the BP86/def2-TZVPP/J level of theory including the COSMO model with the dielectric constant and refractive index of water. AutoDock Vina 1.1.2 program[7] was used to perform the docking studies. The grid map for docking was set to a dimension of 30x30x20 Å (XYZ-dimensions) centered at x = 42.845 y = 12.244 z = 13.958, which corresponds to the oxygen at C2 of Glc6P. The number of runs (exhaustiveness) was set to 100 and a maximal number of 50 modes were printed in the output. Docking poses of each ligand were analyzed with the Pymol program and poses selected that show a close resemblance to Glc6P in the crystal structure. From these, the pose with the lowest binding energy was used for discussion.

III. Synthesis of Fluoro-carbasugars

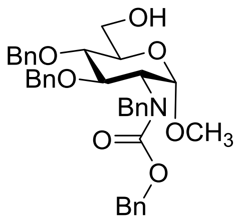
General Methods

All reactions involving moisture or air sensitive compounds were carried out under an argon atmosphere with dry solvents and heat-dried glassware. Anhydrous tetrahydrofuran (THF) and dimethylformamide (DMF) were purchased from Acros Organics and stored under argon. Toluene and Dichloromethane (Certified ACS) purchased from Fisher Scientific were dried by allowing them to stand over 3 Å molecular sieves for at least two days under argon.[8] Yields refer to chromatographically (LC-MS) homogeneous material, unless otherwise stated. All reagents were purchased from commercial suppliers and used without further purification. Reaction were monitored by LC-MS or analytical thin-layer chromatography (TLC) carried out on silica gel 60 F254 coated aluminum sheets (Merck) using UV light for visualization. A solution of ammoniummolybdate tetrahydrate (2.5 g), $Ce(SO_4)_2•4H_2O$ (1.0 g), H_2SO_4 (6 mL) in H_2O (94 mL) and heat was used as developing agent. Macherey-Nagel silica gel (60, particle size 0.040 – 0.063 mm) was used for manual flash column chromatography. Automated flash column chromatography was conducted on a puriFlash®430 system (Interchim) with puriFlash high performance silica columns. NMR spectra were recorded in $CDCl_3$ or D_2O on Bruker Avance III HD Cryo 700, Avance III 600, Avance III 400 instruments. Residual undeuterated solvents ($CDCl_3$: δH = 7.26 ppm and D_2O: δH = 4.79 ppm) were used as internal references. High-resolution mass spectra (HRMS) were recorded on an Orbitrap XL mass spectrometer (Bruker) using ESI (electrospray ionization). High performance liquid chromatography coupled mass spectra (LC-MS) were recorded on an Agilent Infinity 1100 HPLC system coupled to a Bruker HCT esquire ESI mass spectrometer. As eluent a gradient of A: H_2O + 0.1% formic acid and B: acetonitrile was used, unless otherwise noted.

General procedure 1 (GP1): Heterogenous hydrogenolysis of benzyl ethers and removal of Z-protection group

The benzylated pseudo-sugar was dissolved in 2 mL of Methanol (LC-MS grade) and 10% Pd/C (25% *w/w*) is added. After addition of trifluoroacetic acid (10 equiv) the reaction was placed in a laboratory autoclave and is stirred at room temperature under 10 bar hydrogen pressure for 1 hour. Then another 10% Pd/C (25% *w/w*) was added and the reaction stirred until HPLC-monitoring shows complete consumption of the starting material. The reaction was filtered through RC (regenerated cellulose) syringe filters (0.2 µm pore size), methanol was removed under reduced pressure and the resulting pseudo-sugar lyophilized.

Experimental Procedures and Physical Data of Compounds

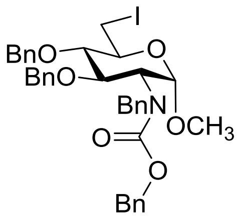


2-Amino-*N*-benzyl-*N*-benzyloxycarbonyl-3,4-*O*-benzyl-2-deoxy-1-*O*-methyl-α-D-Glycopyranoside (7) Trityl chloride (53.7 g, 0.193 mol) was presented in a 500 mL flask and methyl glycoside **6**[9] (30.0 g, 0.0917 mol) in pyridine (300 mL) was added and stirred at room temperature for 40 h. The solution was diluted with CH_2Cl_2 (500 mL), washed with brine (3x200 mL) and dried ($MgSO_4$). The solvents were removed under reduced pressure and the orange oil used in the next step without further purification.

NaH (22.1 g, 0.552 mol, 60% in mineral oil) was added to anhydrous DMF (200 mL) and cooled to 0 °C in an ice bath. Benzylbromide (65.6 mL, 0.552 mol) was added dropwise to the suspension. The crude product of tritylation was solved in anhydrous DMF (300 mL) and added dropwise to the suspension at 0 °C. The ice bath was removed, the suspension allowed to reach room temperature and stirred at room temperature for 17 h. Methanol (50 mL) and water (200 mL) were added successively to quench the reaction and then the pH was adjusted to pH 7 with acidic acid. The suspension was diluted with ethyl acetate (250 mL), the organic layer separated and the aqueous layer extracted with ethyl acetate (2x250 mL). The organic layer were combined and dried ($MgSO_4$). The solvents were removed under reduced pressure and the brown oil used in the next step without further purification.

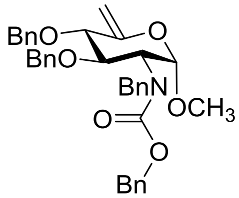
The benzylated crude product was solved in CH_2Cl_2 (500 mL) and cooled to 0 °C in an ice bath. Trifluoroacetic acid (60 mL) and triisopropylsilane (30 mL) were added successively at 0 °C. The ice bath was removed and the solution stirred at room temperature for 1.5 h. The solvents were reduced at reduced pressure and the brown crude product purified by manual flash chromatography (5:1 to 1:1 petroleum ether/ethyl acetate) yielding the alcohol **6** (27.8 g, 51% over three steps) as yellow oil.

R_f = 0.45 (silica, petroleum ether/ethylacetate 1:1), Seebach-reagent; **^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C)**: δ [ppm] = 7.35-7.01 (m, 20H, Ar-H), 5.21-5.05 (m, 2H, -N-C(O)-O-$\underline{C}H_2$-Ph), 4.89-4.27 (m, 8H, 2xO-C$\underline{H_2}$-Ph, N-C$\underline{H_2}$-Ph, H-1, H-2), 4.09 (br, 1H, H-3), 3.82-3.69 (m, 4H, H-4, H-5, H-6), 2.82 (s, 3H, CH3); **^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C)**: δ [ppm] = 138.1-125.7 (C^{Ar}), 99.9 (C-1), 79.7 (C-4), 77.4 (C-3), 75.0, 74.0 (2xO-$\underline{C}H_2$-Ph), 71.3 (C-5), 67.7 (-N-C(O)-O-$\underline{C}H_2$-Ph), 62.0 (C-6), 58.8 (br, C-2), 54.7 (CH_3); **RP-HPLC**: t_r = 15.1 min (ZORBAX SB-C18, 5 µm, 0.4 mL/min, 20-100% MeCN in 20 min); **MS (ESI)**: calcd for $C_{36}H_{39}NO_7Na$ $[M+Na]^+$, 620.2622, found, 620.2622.

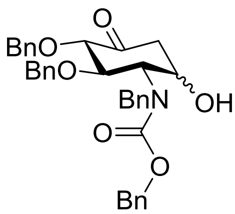


2-Amino-N-benzyl-N-benzyloxycarbonyl-3,4-di-*O*-benzyl-2-deoxy-6-iodo-1-*O*-methyl-α-D-glucopyranoside (S7). The methyl glycoside **7** (2.64 g, 4.42 mmol) was solved in anhydrous toluene (20 mL), triphenylphosphine (0.83 g, 7.52 mmol) and imidazole (0.72 g, 10.61 mmol) were added. The mixture was heated to 60 °C and iodine (1.35 g, 5.30 mmol) was added. After heating to 80 °C the reaction was stirred at 80 °C for 6 h. The solvent was removed under reduced pressure and the residue purified via flash chromatography (petroleum ether/ethylacetate 1:1) yielding the iodo-sugar **S7** (1.96 g, 63%) as colorless foam.

R_f = 0.59 (petroleum ether/ethylacetate 5:1), Seebach-reagent; **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ [ppm] = 7.28-6.93 (m, 20H, Ar-H), 5.15-4.97 (m, 2H, -N-C(O)-O-$\underline{C}H_2$-Ph), 4.87-4.64 (m, 7H, O-C$\underline{H_2}$-Ph, H-1, H-2, N-C$\underline{H_2}$-Ph), 4.25-4.14 (m, 1H, N-C$\underline{H_2}$-Ph), 4.00 (br, 1H, H-3), 3.52-3.20 (m, 4H, H-4, H-5, H-6ab), 2.77 (s, 3H, CH_3); **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ [ppm] = 157.8 (C=O), 140.1-125.6 (C^{Ar}), 99.7 (C-1), 83.6 (C-4), 81.9 (C-4), 76.8 (C-3), 75.3 (O-$\underline{C}H_2$-Ph), 74.1 (O-$\underline{C}H_2$-Ph), 70.0 (C-5), 67.7 (-N-C(O)-O-$\underline{C}H_2$-Ph), 58.6 (br, C-2), 55.0 (CH_3), 47.3 (br, N-$\underline{C}H_2$-Ph) 7.4 (C-6); **RP-HPLC**: t_r = 11.3 min (EC 125/4 Nucleodur C-18 Gravity, 3 µm, 0.4 mL/min, 80-100% MeCN in 10 min); **HRMS**: calcd for $C_{36}H_{38}INO_6Na$ $[M+Na]^+$, 730.1636, found, 730.1631.



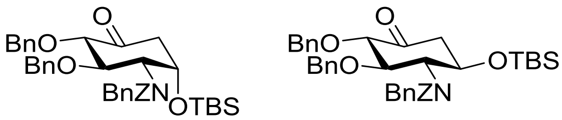
2-Amino-N-benzyl-N-benzyloxycarbonyl-3,4-di-*O*-benzyl-2-deoxy-1-*O*-methyl-α-D-gluco-hex-5-enopyranoside (8). The iodo sugar **S7** (1.00 g, 1.41 mmol) was solved in anhydrous DMF (10 mL) and added dropwise to a suspension of NaH (60% in mineral oil, 0.23 g, 5.64 mmol) in anhydrous DMF (10 mL) at 0 °C. The suspension was stirred at room temperature for 2 h. The reaction was cooled to 0 °C and methanol was added dropwise to quench residual NaH. The solution was concentrated under reduced pressure and the residue diluted with ethylacetate (50 mL). Aqueous 1M HCl was carefully added until the aqueous reached a slightly acidic pH. The organic layer was separated and the pH of the aqueous phase adjusted to pH > 8. The aqueous phase was extracted with ethylacetate (3x100 mL). The combined organic layers were washed with aqueous sat. $NaHCO_3$ (100 mL), aqueous sat. NaCl (100 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue purified by automated flash chromatography (100% petroleum ether to 80:20 petroleum ether/ethylacetate in 30 min) yielding the alkene **8** (0.51 g, 62%) as colorless oil.
R_f = 0.50 (petroleum ether/ethylacetate 5:1), Seebach-reagent; **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ [ppm] = 7.41-6.99 (m, 20H, Ar-H), 5.22-5.07 (m, 2H, -N-C(O)-O-<u>C</u>H$_2$-Ph), 4.89-4.45 (m, 8H, O-C<u>H$_2$</u>-Ph, H-1, H-2, H-6ab), 4.26-4.01 (m, 4H, N-C<u>H$_2$</u>-Ph, H-3, H-4), 2.90 (s, CH_3); **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ [ppm] = 157.9 (C=O), 153.9 (<u>C</u>=CH$_2$), 140.0-125.7 (C^{Ar}), 100.5 (C-1), 97.1 (C-6), 81.9 (C-4), 76.0 (C-3), 74.4 (O-<u>C</u>H$_2$-Ph), 74.1 (O-<u>C</u>H$_2$-Ph), 67.7 (-N-C(O)-O-<u>C</u>H$_2$-Ph), 58.5 (br, C-2), 55.0 (CH_3), 47.0 (N-<u>C</u>H$_2$-Ph); **RP-HPLC**: t_r = 19.1 min (ZORBAX SB-C18, 5 µm, 0.4 mL/min, 80-100% MeCN in 20 min); **HRMS**: calcd for $C_{36}H_{37}NO_6Na$ $[M+Na]^+$, 602.2513; found, 602.2515.



Benzyl benzyl((1R,2R,3S)-2,3-bis(benzyloxy)-6-hydroxy-4-oxocyclohexyl)-carbamate. (5) The alkene **8** (14.7 g, 19.5 mmol) was solved in 2:1 dioxane/aqueous 5 mM H_2SO_4 (225 mL), $HgSO_4$ (0.174 g, 0.585 mmol) was added and the resulting mixture was stirred at 80 °C for 3 h. Aqueous sat. NaCl (100 mL) and CH_2Cl_2, (400 mL) were added. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (3x200 mL). The organic phases were combined, dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was purified via flash chromatography (2x40 g silica, 100% petroleum ether to 100%

ethylacetate in 60 min) yielding the cyclohexanone **5** as a mixture of isomers (9.55 g, 86%, 77:23 axial/equatorial ratio) as colorless foam. The isomers were not separated prior to the next step.

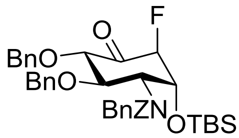
R_f(axial) = 0.60, **R_f(equatorial)** = 0.50 (petroleum ether/ethylacetate 1:1), Seebach-reagent; Assignment for most abundant isomer with 1-OH in axial configuration: **^{1}H-NMR (500 MHz, $CDCl_3$)**: δ [ppm] = 7.45-7.21 (m, 20H, Ar-H), 5.18-5.14 (m, 2H, -N-C(O)-O-C*H*2-Ph), 5.01-4.48 (m, 5H, O-CH2-Ph, H-2), 5.37-4.01 (m, 2H, N-CH2-Ph), 4.11 (br, 1H, H-1), 4.73 (m, 1H, H-3),), 4.07 (s, 1H, H-4), 2.53 (dd, *J* = 14.3, 3.9 Hz, 1H, H-5aa), 2.29, (d, *J* = 11.7 Hz, 1H, H-5ab); **^{13}C-NMR (125.7 MHz, $CDCl_3$)**: δ [ppm] = 203.7 (C=O), 158.4 (N-C=O), 138.3-127.5 (C^{Ar}), 88.2 (C-4), 77.2 (C-3), 75.6 (O-CH_2-Ph), 73.7 (O-CH2-Ph), 69.5 (C-1), 68.3 (-N-C(O)-O-CH_2-Ph), 55.2 (br, C-2), 53.6, 53.2 (N-CH_2-Ph), 46.4 (C-5a); **RP-HPLC**: t_r(axial) = 16.7 min, t_r(equatorial) = 16.0 min (ZORBAX SB-C18, 5 µm, 0.4 mL/min, 80-100% MeCN in 20 min); **HRMS**: calcd for $C_{35}H_{35}NO_6Na$ $[M+Na]^+$, 588.2357; found, 588.2348.



Benzyl benzyl((1R,2R,3S,6R)-2,3-bis(benzyloxy)-6-((tert-butyldimethylsilyl)-oxy)-4-oxocyclohexyl)carbamate (9a/9b) The isomeric mixture of cyclohexanone **5** (2.00 g, 3.54 mmol) was presented in a heat-dried schlenk tube and solved in anhydrous CH_2Cl_2 (20 mL). The solution was cooled to 0 °C and 2,6-lutidine (0.9 mL, 8.13 mmol) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (1.9 mL, 8.13 mmol) were added successively at 0 °C. The cooling was removed and the reaction was stirred at room temperature for 1.5 h. The reaction mixture was diluted with CH_2Cl_2 (20 mL) and washed with 1N aqueous HCl (20 mL) and sat. aqueous NaCl (20 mL). The organic layer was dried ($MgSO_4$) and the solvent removed under reduced pressure. The residue was purified via automated flash chromatography (100% petroleum ether to 73:27 petroleum ether/ethylacetate in 54 min) yielding the protected α-cyclohexanone **9a** (1.64 g, 68%) and the β-cyclohexanone **9b** (0.49 g, 21%) as colorless oils.

R_f9a = 0.45, **R_f9b** = 0.40 (petroleum ether/ethylacetate 3:1), Seebach-reagent; assignment of **9a**: **^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C)**: δ [ppm] = 7.40-6.98 (m, 20H, Ar-H), 5.11 and 5.05 (d, *J* = 12.5 Hz, 2H, -N-C(O)-O-CH_2-Ph), 4.93-3.68 (m, 12H, 3xO-CH_2-Ph, N-CH_2-Ph, H-2, H-1, H-3, H-4), 2.70 (d, *J* = 13.5 Hz, 1H, H-5a, eq), 2.59 (dd, *J* = 14.0, 4.0 Hz, 1H, H-5a,ax), 0.88 (s, 9H, Si-*t*-Bu), 0.11 (s, 3H, Si-CH_3), (-0.11) (s, 3H, Si-CH_3); **^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C)**: δ [ppm] = 203.5 (C-5), 157.4 (C=O), 138.9-126.1 (C^{Ar}), 88.1 (C-4), 77.0 (C-3), 73.6 (O-CH_2-Ph), 73.2 (O-CH_2-Ph), 70.4 (H-1), 67.4 (O-CH_2-Ph), 61.6 (C-2), 48.5 (N-CH_2-Ph), 46.4 (C-5a), 25.8 (Si-*t*-Bu), -4.0, -5.1 (Si-CH_3); assignment of **9b**: **^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C)**: δ [ppm] = 7.40-7.04 (m, 20H, Ar-H), 5.20 and 5.07 (d, *J* = 12.3 Hz, 2H, -N-C(O)-O-CH_2-Ph), 4.94-4.36 (m, 11H, 3xO-CH_2-Ph, N-CH_2-Ph, H-2, H-1, H-3), 4.10 (d, *J* = 9.5 Hz, 1H, H-4), 2.75 (dd, *J* = 13.7, 5.0 Hz, 1H, H-5a,eq), 2.51 (dd, *J* = 13.8, 10.8 Hz, 1H, H-

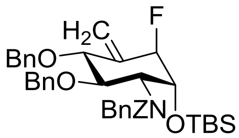
5a,ax), 0.89 (s, 9H, Si-*t*-Bu), 0.9 (s, 3H, Si-CH_3), (-0.03) (s, 3H, Si-CH_3); **^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C)**: δ [ppm] = 203.5 (C-5), 155.5 (C=O), 138.4-127.2 (C^{Ar}), 87.0 (C-4), 76.4 (C-3), 75.1 (O-C<u>H</u>$_2$-Ph), 73.4 (O-C<u>H</u>$_2$-Ph), 70.0 (H-2), 67.1 (O-C<u>H</u>$_2$-Ph), 66.2 (C-1), 56.0 (N-C<u>H</u>$_2$-Ph), 48.2 (C-5a), 25.8 (Si-*t*-Bu), -4.8, -4.9 (Si-CH_3); **RP-HPLC**: t_r**9a** = 4.8 min, t_r**9b** = 5.9 min (ZORBAX SB-C18, 5 µm, 0.4 mL/min, 80-100% MeCN in 20 min); **HRMS**: calcd for $C_{41}H_{49}FNO_6SiNa$ $[M+Na]^+$, 702.3221; found, 702.3225.



Benzyl benzyl((1R,2R,3S,5S,6R)-2,3-bis(benzyloxy)-6-((tert-butyldimethylsilyl)oxy)-5-fluoro-4-oxocyclohexyl)carbamate (10) LDA-solution in anhydrous THF (0.2 M) was freshly prepared by addition of *n*-BuLi (1.01 mL, 1.62 mmol, 1.6 M in hexane) to an ice-cold solution of (*i*-Pr)$_2$NH (0.25 mL, 1.78 mmol) in anhydrous THF (6.8 mL), stirred for 30 min at 0 °C. The cyclohexanone **9a** (1.00 g, 1.477 mmol) was solved in anhydrous THF (7 mL) under argon atmosphere, cooled to -74 °C and the LDA-solution added dropwise over 15 min. After stirring at -74 °C for 3.5 h, NFSI (0.51 g, 1.62 mmol) solved in THF (6.5 mL) was added slowly. After 1.5 h water (3 mL) and CH_2Cl_2 were added to the cold solution and the aqueous acidified with sat. aqueous NH_4Cl. The organic layer was separated and the aqueous layer extracted with CH_2Cl_2 (4x20 mL) and the combined organic phases dried ($MgSO_4$) and the solvent removed under reduced pressure. The residue was purified via flash chromatography (98:2 to 85:15 petroleum ether/ethylacetate in 60 min) yielding the fluorocyclohexanone **10** (476.52 mg, 46%) as colorless oil.

R_f = 0.50 (petroleum ether/ethylacetate 5:1), Seebach-reagent; ^{19}F-NMR at -40°°C shows three distinct signals, indicating three conformers A, B, C in a ratio 1.00:3.49:1.52. Assignment for conformer A: **^{19}F-NMR (470 MHz, $CDCl_3$, -40 °C)**: δ [ppm] = -187.1. Most probably the least abundant conformer A is not observed/distinguishable in HMQC, thus no assignment could be made for ^{1}H- or ^{13}C-NMR. Assignment for conformer B: **^{1}H-NMR (500 MHz, $CDCl_3$, -40 °C)**: δ [ppm] = 7.43-6.95 (m, 20H, Ar-H), 5.40-5.04 (m, 2H, -N-C(O)-O-<u>C</u>H$_2$-Ph), 4.99 (d, *J* = 11.7 Hz, 1H, H-2), 4.87-4.31 (m, 4H, N-C<u>H</u>$_2$-Ph), 4.73-4.70 (m, 1H, H-4), 4.53 (dd, *J* = 50.9, 6.0 Hz, 1H, H-5a), 4.31-4.26 (m, 1H, H-1b), 4.05-3.98 (m, 1H, H-3), 0.84 (s, 9H, Si-*t*-Bu), 0.09, -0.21 (s, 6H, Si-CH_3), **^{13}C-NMR (126 MHz, $CDCl_3$, -40 °C)**: δ [ppm] = 200.6 or 200.3 (d, *J* = 19.7 or 19.3 Hz, C=O), 157.5 (C=O (CBz)), 128.8-125.9 (C^{Ar}), 90.8 (d, *J* = 186 Hz, C-5a), 85.6 or 85.4 (C-4), 76.9 (C-3), 73.7 (O-<u>C</u>H$_2$-Ph), 73.1 (O-<u>C</u>H2-Ph), 71.7 (d, *J* = 23.9 Hz, C-1), 67.7 or 67.6 (-N-C(O)-O-<u>C</u>H$_2$-Ph), 56.8 or 56.6 (C-2), 48.9 (N-<u>C</u>H$_2$-Ph), 25.7 (-Si-<u>C</u>-CH_3), 18.0 (-Si-C-<u>C</u>H$_3$), (-4.0)-(-5.6) (-Si-CH_3-); **^{19}F-NMR (470 MHz, $CDCl_3$, -40 °C)**: δ [ppm] = -187.9; Assignment for conformer C: **^{1}H-NMR (500 MHz, $CDCl_3$, -40 °C)**: δ [ppm] = 7.43-6.95 (m, 20H, Ar-H), 5.40-5.04 (m, 2H, -N-C(O)-O-<u>C</u>H$_2$-Ph), 5.14-5.10 (m, 1H, H-2), 4.87-4.31 (m, 4H, N-

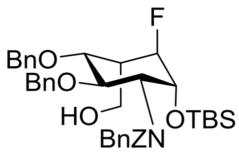
C$\underline{H_2}$-Ph), 4.78-4.76 (m, 1H, H-4), 4.57 (dd, J = 49.4, 7.4 Hz, 1H, H-5a), 4.53-4.48 (m, 1H, H-1), 4.05-3.98 (m, 1H, H-3), 0.87, (s, 9H, Si-*t*-Bu), 0.03, 0.17 (s, 3H, CH_3); **^{13}C-NMR (126 MHz, $CDCl_3$, -40 °C)**: δ [ppm] = 200.6 or 200.3 (d, *J* = 19.7 or 19.4 Hz, C=O), 156.6 (C=O (CBz)), 128.8-125.9 (C^{Ar}), 91.0 (d, *J* = 185 Hz, C-5a), 85.4 (C-4), 76.4 (C-3), 73.7 (O-$\underline{C}H_2$-Ph), 73.1 (O-$\underline{C}$H2-Ph), 70.8 (d, *J* = 38.4 Hz, C-1), 67.8 (-N-C(O)-O-$\underline{C}H_2$-Ph), 56.8 or 56.6 (C-2), 48.0 (N-$\underline{C}H_2$-Ph), 25.7 (-Si-$\underline{C}$-CH_3), 17.9 (-Si-C-$\underline{C}H_3$), (-4.0)-(-5.6) (-Si-CH_3-); **^{19}F-NMR (470 MHz, $CDCl_3$, -40°C)**: δ [ppm] = -188.4; **RP-HPLC**: t_r = 5.9 min (ZORBAX SB-C18, 5 µm, 0.4 mL/min, 80-100% MeCN in 20 min); **HRMS**: calcd for $C_{41}H_{48}FNO_6SiNa$ $[M+Na]^+$, 720.3127; found, 720.3121.



Benzyl benzyl((1R,2R,3R,5S)-2,3-bis(benzyloxy)-6-((tert-butyldimethylsilyl)oxy)-5-fluoro-4-methylenecyclohexyl)carbamate (4)
Cyclohexanone **10** (290.60 mg, 0.416 mmol) was presented in a heat-dried schlenk-tube, coevaporated two times with toluene and dried under vacuum for 19 h. The starting material was solved in anhydrous toluene (2 mL) and freshly prepared Cp_2TiMe_2[10] (0.25 M, 6.7 mL, 1.66 mmol) was added under argon atmosphere. The reaction was heated in an oil-bath to 70 °C and stirred for 3 h, after which the solution was allowed to reach room temperature. Water (5 mL), petroleum ether/ethylacetate (5:1, 10 mL) were added and the mixture stirred at room temperature for 24 h, resulting in an orange suspension. After filtration through Celite® 545, the filter cake was washed with ethylacetate and the filtrate was washed with sat. aqueous NaCl and dried ($MgSO_4$). The solvents were removed under reduced pressure and the residue purified by automated flash chromatography (100% cyclohexane to 9:1 cyclohexane/ethylacetate in 45 min) yielding olefin **4** (175.72 mg, 61%) as slightly yellow oil.

R_f = 0.75 (petroleum ether/ethylacetate 5:1), Seebach-reagent; The ^{19}F-NMR at -40 °C shows four distinct signals, indicating four conformers A, B, C, D in a ratio of 1.00:3.48:15.91:8.36. Only two sets of signals are observed in HMQC, most probably belonging to most abundant conformers C and D. Assignment for conformer A: **^{19}F-NMR (471 MHz, $CDCl_3$, -40 °C)**: δ [ppm] = -176.1; Assignment for conformer B: **^{19}F-NMR (471 MHz, $CDCl_3$, -40 °C)**: δ [ppm] = -176.6; Assignment for conformer C: **^{1}H-NMR (500 MHz, $CDCl_3$, -40 °C)**: δ [ppm] = 7.45-6.92 (m, 20H, Ar-H), 5.56 (s, 1H, H-6a), 5.40-5.04 (m, 2H, N-C(O)-O-C$\underline{H_2}$-Ph), 5.28 (s, 1H, H-6b), 4.91-3.39 (m, 2H, (C-3)-O-C$\underline{H_2}$-Ph), 4.87-4.85 (m, 1H, H-2), 4.83 (dd, *J* = 48.6, 5.4 Hz, 1H, H-5a), 4.82-4.37 (m, 2H, N-C$\underline{H_2}$-Ph), 4.64-4.55 (m, 2H, (C-4)-O-C$\underline{H_2}$-Ph), 4.45-4.38 (m, 1H, H-4), 3.80 (q, J = 8.8 Hz, 1H, H-3), 0.86 or 0.84 (s, 9H, *t*-Bu), 0.09-(-0.22) (s, 3H, CH_3); **^{13}C-NMR (160 MHz, $CDCl_3$, -40 °C)**: δ [ppm] = 157.3 or 156.6 (C=O), 139.3-125.9 (C^{Ar}), 116.9 (C-6), 92.5 (d, *J* = 171 Hz, C-5a), 82.3 (C-4), 77.2 (C-3), 73.6 or 73.5 (O-$\underline{C}H_2$-Ph), 72.7 (O-$\underline{C}H_2$-Ph), 71.1 (d, *J* = 29 Hz, C-1), 67.3 or 67.2 (N-C(O)-O-$\underline{C}H_2$-Ph), 57.5 (C-2), 49.1 or 48.3 (N-$\underline{C}H_2$-Ph), 25.7 (-Si-$\underline{C}$-CH_3), 17.8-17.4 (-Si-C-$\underline{C}H_3$), (-3.8)-(-

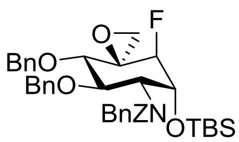
5.6) (-Si-CH_3-); **^{19}F-NMR (471 MHz, $CDCl_3$, -40 °C)**: δ [ppm] = -177.9; Assignment for conformer D: **^{1}H-NMR (500 MHz, $CDCl_3$, -40 °C)**: δ [ppm] = 7.45-6.92 (m, 20H, Ar-H), 5.56 (s, 1H, H-6a), 5.40-5.04 (m, 2H, N-C(O)-O-C$\underline{H_2}$-Ph), 5.28 (s, 1H, H-6b), 4.91-3.39 (m, 2H, (C-3)-O-C$\underline{H_2}$-Ph), 4.82-4.37 (m, 2H, N-C$\underline{H_2}$-Ph), 4.80 (dd, *J* = 46.9, 6.2 Hz, 1H, H-5a), 4.78-4.74 (s, 1H, H-2b), 4.64-4.55 (m, 2H, (C-4)-O-C$\underline{H_2}$-Ph), 4.45-4.38 (m, 1H, H-4), 4.15 (q, *J* = 3.1 Hz, 1H, H-1), 3.80 (q, J = 8.8 Hz, 1H, H-3), 0.86 or 0.84 (s, 9H, *t*-Bu), 0.09-(-0.22) (s, 3H, CH_3); **^{13}C-NMR (160 MHz, $CDCl_3$, -40 °C)**: δ [ppm] = 157.3 or 156.6 (C=O), 139.3-125.9 (C^{Ar}), 116.9 (C-6), 93.8 (d, *J* = 168 Hz, C-5a), 82.6 (C-4), 77.2 (C-3), 73.6 or 73.5 (O-$\underline{C}H_2$-Ph), 72.7 (O-$\underline{C}H_2$-Ph), 72.0 (d, *J* = 29 Hz, C-1), 67.3 or 67.2 (N-C(O)-O-$\underline{C}H_2$-Ph), 57.6 (C-2), 49.1 or 48.3 (N-$\underline{C}H_2$-Ph), 25.7 (-Si-$\underline{C}$-CH_3), 17.8-17.4 (-Si-C-$\underline{C}H_3$), (-3.8)-(-5.6) (-Si-CH_3-); **^{19}F-NMR (471 MHz, $CDCl_3$, -40 °C)**: δ [ppm] = -178.7; **RP-HPLC**: t_r = 8.9 min (ZORBAX SB-C18, 5 µm, 0.4 mL/min, 80-100% MeCN in 20 min); **HRMS**: calcd for $C_{42}H_{50}FNO_5SiNa$ $[M+Na]^+$, 718.3334; found, 718.3328.



(5a*R*)-2-Amino-*N*-benzyl-N-benzyloxycarbonyl-3,4-di-*O*-benzyl-2-deoxy-5a-fluoro-carba-idose (11) To the olefin **4** (481.36 mg, 0.692 mmol) solved in anhydrous THF (5 mL) was added a solution of 9-BBN in THF (8.3 mL, 4.150 mmol, 0.5 M) at room temperature. After stirring at room temperature for 2 h the temperature was increased to 66 °C. No starting material could be detected via TLC after additional 3.5 h and the solution was cooled to 0 °C. 3N NaOH aqueous solution (2.8 mL, 8.400 mmol) and 35%wt H_2O_2 solution (2.8 mL) were successively added at 0 °C. The solution was stirred for 2 h at room temperature before stopping the reaction with 0.5 N $Na_2S_2O_3$ aqueous solution (10 mL) and diluting with CH_2Cl_2 (60 mL). The organic phase was separated and the aqueous phase extracted with CH_2Cl_2 (3x20 mL). The combined organic layers were washed with sat. aqueous NaCl, followed by drying with $MgSO_4$. The solvent was removed under reduced pressure and the residue purified by automated flash chromatography (40 g silica, 95:5 to 75:25 petroleum ether/ethylacetate in 90 min) yielding the protected fluoro-carba-β-L-idosamine **11** (249.05 mg, 50%) as a colorless foam.

The ^{19}F-NMR at -40 °C shows three distinct signals, indicating three conformers A, B, C in a ratio of 1.00:10.90:21.98. Assignment for conformer A: **^{1}H-NMR (500 MHz, $CDCl_3$, -40 °C)**: δ [ppm] = 7.48-6.95 (m, 20H, Ar-H), 5.43-3.41 (m, N-C(O)-O-C$\underline{H_2}$-Ph), 5.07-4.49 (m, 4H, O-C$\underline{H_2}$-Ph), 4.89-4.07 (m, 2H, N-C$\underline{H_2}$-Ph), 4.68-4.84 (m, 1H, H-2), 4.65-4.56 (m, 1H, H-5a), 4.30- 3.67 (m, 2H, H6a and b), 4.18 (br, 1H, H-1); 4.17-4.15 (m, 2H, H-3 and H-4), 2.79 (br, 1H, H-5), 0.98-0.95 (m, 9H, *t*-Bu-Si), 0.13-(-0.20) (m, 6H, Me_2-Si); **^{13}C-NMR (126 MHz, $CDCl_3$, -40 °C)**: δ [ppm] 157.0 or 156.4 or 155.2 (C=O), 139.1-125.9 (C^{Ar}), 91.6 or 91.5 or 91.3 (d, *J* = 174 or 175 Hz, C-5a), 82.4 or 82.0 (C-4), 74.1 or 73.7 or 73.2 or 73.1 or 72.4 or 72.1 (O-$\underline{C}H_2$-Ph), 73.6 (C-3), 72.4 (d, *J* = 29 Hz, C-1), 67.4 or 67.2 or 66.5 (N-C(O)-O-$\underline{C}H_2$-Ph), 61.1 or 60.8 or

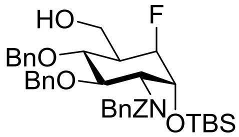
60.7 (d, J = 11 Hz, C-6a and b), 57.8 (C-2), 52.9 or 49.6 or 49.0 (N-<u>C</u>H_2-Ph), 44.6 or 43.8 or 43.6 (d, J = 18 Hz, C-5), 26.0, 25.8 (*t*-Bu-Si), -4.4, -4.7, -5.0, -5.4, -5.9, -6.0 (Me_2-Si); **^{19}F-NMR (470 MHz, $CDCl_3$, -40 °C)**: δ [ppm] = -179.98 (s, 1F); Assignment for conformer B: **^{1}H-NMR (500 MHz, $CDCl_3$, -40 °C)**: δ [ppm] = 7.48-6.95 (m, 20H, Ar-H), 5.49 (t, J = 10.3 Hz, 1H, H-3), 5.43-3.41 (m, N-C(O)-O-C<u>H_2</u>-Ph), 5.07-4.49 (m, 4H, O-C<u>H_2</u>-Ph), 4.89-4.07 (m, 2H, N-C<u>H_2</u>-Ph), 4.65-4.56 (m, 1H, H-5a), 4.30- 3.67 (m, 2H, H6a and b), 4.13 (m, 1H, H-1), 3.92 (dd, 1H, J = 9.6, 5.4 Hz, H-4), 3.22 (br, 1H, H-2), 2.79 (br, 1H, H-5), 0.98-0.95 (m, 9H, *t*-Bu-Si), 0.13-(-0.20) (m, 6H, Me_2-Si); **^{13}C-NMR (126 MHz, $CDCl_3$, -40 °C)**: δ [ppm] = 157.0 or 156.4 or 155.2 (C=O), 139.1-125.9 (C^{Ar}), 91.6 or 91.5 or 91.3 (d, J = 174 or 175 Hz, C-5a), 83.1 (C-4), 74.9 (C-3), 74.1 or 73.7 or 73.2 or 73.1 or 72.4 or 72.1 (O-<u>C</u>H_2-Ph), 70.4 (d, J = 28 Hz, C-1), 67.4 or 67.2 or 66.5 (N-C(O)-O-<u>C</u>H_2-Ph), 63.6 (C-2), 61.1 or 60.8 or 60.7 (d, J = 11 Hz, C-6), 52.9 or 49.6 or 49.0 (N-<u>C</u>H_2-Ph), 44.6 or 43.8 or 43.6 (d, J = 18 Hz, C-5), 26.0, 25.8 (*t*-Bu-Si), -4.4, -4.7, -5.0, -5.4, -5.9, -6.0 (Me_2-Si); **^{19}F-NMR (470 MHz, $CDCl_3$, -40 °C)**: δ [ppm] = -180.93 (s, 1F); Assignment for conformer C: **^{1}H-NMR (500 MHz, $CDCl_3$, -40 °C)**: δ [ppm] = 7.48-6.95 (m, 20H, Ar-H), 5.43-3.41 (m, N-C(O)-O-C<u>H_2</u>-Ph), 5.07-4.49 (m, 4H, O-C<u>H_2</u>-Ph), 4.89-4.07 (m, 2H, N-C<u>H_2</u>-Ph), 4.80-4.76 (m, 1H, H-2), 4.70-4.62 (m, 1H, H-5a), 4.40 (br, 1H, H-1), 4.30-3.67 (m, 2H, H6a and b), 4.17-4.15 (m, 2H, H-3 and H-4), 2.79 (br, 1H, H-5), 0.98 or 0.97 or 0.95 (m, 9H, *t*-Bu-Si), 0.13-(-0.20) (m, 6H, Me_2-Si); **^{13}C-NMR (126 MHz, $CDCl_3$, -40 °C)**: δ [ppm] = 157.0 or 156.4 or 155.2 (C=O), 139.1-125.9 (C^{Ar}), 91.6 or 91.5 or 91.3 (d, J = 174 or 175 Hz, C-5a), 82.4 or 82.0 (C-4), 74.1 or 73.7 or 73.2 or 73.1 or 72.4 or 72.1 (O-<u>C</u>H_2-Ph), 73.6 (C-3), 71.0 (d, J = 28 Hz, C-1), 67.4 or 67.2 or 66.5 (N-C(O)-O-<u>C</u>H_2-Ph), 61.1 or 60.8 or 60.7 (d, J = 11 Hz, C-6a and b), 58.1 (C-2), 52.9 or 49.6 or 49.0 (N-<u>C</u>H_2-Ph), 44.6 or 43.8 or 43.6 (d, J = 18 Hz, C-5), 26.0, 25.8 (*t*-Bu-Si), -4.4, -4.7, -5.0, -5.4, -5.9, -6.0 (Me_2-Si); **^{19}F-NMR (470 MHz, $CDCl_3$, -40 °C)**: δ [ppm] = -182.03 (s, 1F); **RP-HPLC**: t_r = 14.2 min (ZORBAX SB-C18, 5 µm, 0.4 mL/min, 60-80 % MeCN in 20 min); **HRMS**: calcd for $C_{42}H_{53}FNO_6Si$ $[M+H]^+$, 714.3621 found, 714.3617.



Benzyl benzyl((3S,4S,5R,6R,7R,8S)-4,5-bis(benzyloxy)-7-((tert-butyldimethylsilyl)oxy)-8-fluoro-1-oxaspiro[2.5]octan-6-yl)carbamate (3) The olefin **4** (281.68 mg, 0.4047 mmol) was solved in CH_2Cl_2 (10 mL). The solution was cooled to 0 °C and *m*CPBA (1.2 g, 5.26 mmol, 77%) solved in CH_2Cl_2 (6 mL) was added. The cloudy suspension was stirred at room temperature for 6 days. HPLC shows ~50% conversion, another portion of *m*CPBA (90 mg, 0.40 mmol, 77%) was added. After 10 days again *m*CPBA (90 mg, 0.40 mmol) is added and the reaction stirred at room temperature for additional 4 days after which HPLC-monitoring shows almost complete conversion. Sat. aqueous Na_2SO_3 (10 mL) was added and the suspension through a RC-syringe filter (0.2 µm) and the filtrate diluted with CH_2Cl_2 (60 mL). The organic layer is washed with sat. aqueous Na_2SO_3 (3x30 mL), sat. aqueous $NHCO_3$ and sat. aqueous NaCl, followed by drying with $MgSO_4$. The solvent was removed under reduced pressure and the residue purified by automated flash chromatography (40 g silica, 100% petroleum ether to 90:10 petroleum ether/ethylacetate in 30 min). Fractions containing product were combined and freeze-dried, yielding the epoxide **3** (170.93 mg, 59%) as colorless solid.

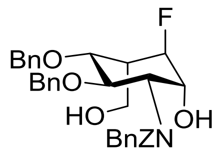
The ^{19}F-NMR at -40 °C shows three distinct signals, indicating three conformers A, B, C in a ratio of 1.00:2.37:1.26. Conformers A and C could not be distinguished in HSQC due to similar intensity. Assignment for conformer A or C: **^{1}H-NMR (500 MHz, $CDCl_3$, -40 °C)**: δ [ppm] = 7.44-6.89 (m, 20H, Ar-H), 5.39-4.94 (m, 2H, N-C(O)-O-C$\underline{H}_2$-Ph), 4.97-4.42 (m, 2H, O-C$\underline{H}_2$-Ph), 4.82-3.39 (m, 2H, O-C$\underline{H}_2$-Ph), 4.79-4.38 (m, 2H, N-C$\underline{H}_2$-Ph), 4.75 (s, 1H, H-2), 4.24 (d, *J* = 8.5 Hz, 1H, H-4), 4.16 (br, 1H, H-1), 4.16 (d, *J* = 46.9 Hz, 1H, H-5a), 3.90 (q, *J* = 10.9 Hz, 1H, H-3), 3.38 (br, 1H, H-6a), 2.69 (br, 1H, H-6b), 0.87 (s, 9H, *t*-Bu), 0.06-(-0.28) (s, 3H, CH_3); **^{13}C-NMR (176 MHz, $CDCl_3$, -20 °C)**: δ [ppm] = 157.2 or 156.5 (C=O), 138.6-125.9 (C^{Ar}), 94.2 (d, *J* = 178 Hz, C-5a), 78.3 (C-4), 75.8 (O-$\underline{C}H_2$-Ph), 75.3 (C-3), 72.7 or 72.5 (O-$\underline{C}H_2$-Ph), 71.5 (d, *J* = 26.4 Hz, H-1), 67.3 (N-C(O)-O-$\underline{C}H_2$-Ph), 57.1 (C-2), 49.1 (N-$\underline{C}H_2$-Ph), 48.4 or 48.2 (C-6), 25.9 (-Si-*t*-Bu), 17.7 (Si-C-), 1.3-(-6.3) (-Si-CH_3-); **^{19}F-NMR (470 MHz, $CDCl_3$, -40 °C, ^{1}H-coupled)**: δ [ppm] = -190.47 (d, *J* = 49.9 Hz) or -191.92 (d, J = 48.6 Hz); Assignment for conformer B: **^{1}H-NMR (500 MHz, $CDCl_3$, -40 °C)**: δ [ppm] = 7.44-6.89 (m, 20H, Ar-H), 5.39-4.94 (m, 2H, N-C(O)-O-C$\underline{H}_2$-Ph), 4.97-4.42 (m, 2H, O-C$\underline{H}_2$-Ph), 4.82-3.39 (m, 2H, O-C$\underline{H}_2$-Ph), 4.70-4.38 (m, 2H, N-C$\underline{H}_2$-Ph), 4.85 (br, 1H, H-2), 4.40 (br, 1H, H-1), 4.28 (d, *J* = 8.8 Hz, 1H, H-4), 4.16 (d, *J* = 46.9 Hz, 1H, H-5a), 3.90 (q, *J* = 10.9 Hz, 1H, H-3), 3.38 (br, 1H, H-6a), 2.69 (br, 1H, H-6b), 0.87 (s, 9H, *t*-Bu), 0.06-(-0.28) (s, 3H, CH_3); **^{13}C-NMR (176 MHz, $CDCl_3$, -20 °C)**: δ [ppm] = 157.2 or 156.5 (C=O), 138.6-125.9 (C^{Ar}), 94.2 (d, *J* = 178 Hz, C-5a), 78.1 (C-4), 75.3 (C-3), 72.7 or 72.5 (O-$\underline{C}H_2$-Ph), 70.4 (d, *J* = 26.1 Hz, H-1), 67.4 (N-C(O)-O-$\underline{C}H_2$-Ph), 57.1 (C-2), 48.4 or 48.2 (C-6), 48.4 or 48.2 (N-$\underline{C}H_2$-Ph), 25.9 (-Si-*t*-Bu), 17.7 (Si-C-), 1.3-(-6.3) (-Si-CH_3-); **^{19}F-NMR (470 MHz, $CDCl_3$, -40 °C, ^{1}H-coupled)**: δ [ppm] = -191.47 (d, J = 48.2 Hz); Assignment for conformer A or C: **^{1}H-NMR (500 MHz, $CDCl_3$, -40 °C)**: δ [ppm] = 7.44-6.89 (m, 20H, Ar-H), 5.39-4.94 (m, 2H, N-C(O)-O-C$\underline{H}_2$-Ph), 5.26 (br, 1H, H-3), 4.97-4.42 (m, 2H, O-C$\underline{H}_2$-Ph), 4.82-3.39 (m, 2H, O-C$\underline{H}_2$-Ph), 4.85-4.08 (m, 2H, N-C$\underline{H}_2$-Ph), 4.16 (d, *J* = 46.9 Hz, 1H, H-5a), 4.12 (br, 1H, H-1), 4.03 (*J* = 9.5 Hz, 1H, H-4), 3.34 (br, 1H, H-2), 3.38 (br, 1H, H-6a), 2.69 (br, 1H, H-6b), 0.87 (s, 9H, *t*-Bu), 0.06-(-0.28) (s, 3H, CH_3); **^{13}C-NMR (176 MHz, $CDCl_3$, -20 °C)**: δ [ppm] = 157.2 or 156.5 (C=O), 138.6-125.9 (C^{Ar}), 94.2 (d, *J* = 178 Hz, C-5a), 78.6 (C-4), 75.8 (O-$\underline{C}H_2$-Ph), 72.7 or 72.5 (O-$\underline{C}H_2$-Ph), 69.4 (d, *J* = 25.2 Hz), 66.5 (N-C(O)-O-$\underline{C}H_2$-Ph), 63.0 (C-2), 52.9 (N-$\underline{C}H_2$-Ph), 48.4 or 48.2 (C-6), 25.9 (-Si-*t*-Bu), 17.7 (Si-C-), 1.3-(-6.3) (-Si-CH_3-); **^{19}F-NMR (470 MHz, $CDCl_3$, -40 °C, ^{1}H-coupled)**: δ [ppm] = -190.47 (d, *J* = 49.9 Hz) or -191.92 (d, J = 48.6 Hz); **RP-HPLC**: t_r = 8.2 min (ZORBAX SB-C18, 5 µm, 0.4 mL/min, 80-100% MeCN in 20 min); **HRMS**: calcd for $C_{42}H_{50}FNO_6SiH$ $[M+H]^+$, 712.3464; found, 712.3450.

*assignment through HSQC



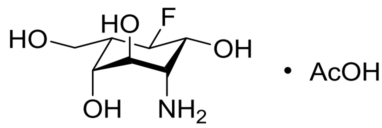
(5a*R*)-2-Amino-*N*-benzyl-*N*-benzyloxycarbonyl-3,4-di-*O*-benzyl-2-deoxy-5a-fluoro-1-O-*tert*-butyldimethylsilyl-carba-glucose (12) The epoxide **3** (47.17 mg, 0.0663 mmol) was transferred to a heat-dried schlenk-tube with toluene. The toluene was removed under reduced pressure and the starting material dried under vacuum (~10^{-2} mbar) for 17 h. Manganese powder (5.46 mg, 0.0994 mmol) together with 2,4,6-collidine hydrochloride (15.67 mg, 0.0994 mmol) were presented in a heat-dried schlenk-tube and heated under oil-pump vacuum until slight sublimation of collidine was observed. The reagents were cooled to room temperature and Cp_2TiCl_2 (4.95 mg, 0.0199 mmol) was added under argon atmosphere. Anhydrous and degassed THF (0.4 mL) was added and the suspension stirred 30 min until color change to green was completed after which 1,4-cyclohexadiene (28 µL) was added. The epoxide was solved in degassed, anhydrous THF (0.3 mL) and slowly added to the green suspension, upon that a slight color change to light green-yellow could be observed. The reaction was heated to 50 °C in an oil bath and stirred under argon atmosphere for 1 h. The reaction temperature was increased to 55 °C and the reaction stirred for another 30 min. The reaction temperature was increased to 60 °C and the reaction stirred for 1.5 h, when HPLC-monitoring showed 90% consumption of the epoxide. The reaction was cooled to room temperature and 1M HCl (1 mL) was added slowly. The reaction was diluted with 5 mL ethylacetate, the organic layer was separated and the aqueous phase extracted with ethylacetate (3x10 mL) and CH_2Cl_2 (2x10 mL). The aqueous phase was basified with sat. aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (2x10 mL). The combined organic phases were washed with sat. aqueous $NaHCO_3$ and, sat. aqueous NaCl and subsequently dried with $MgSO_4$. The solvent was removed under reduced pressure and the residue purified via RP-HPLC (Gemini® C18, 110 Å, 5 µm, 50x30 mm, 80-100% MeCN in 10 min). Fractions containing product were combined and freeze-dried yielding the alcohole **12** (15.41 mg, 33%) as a white solid.

The ^{19}F-NMR shows two broad signals, indicating conformers that interchange quickly at room temperature, thus the conformers were not distinguishable for ^{1}H and ^{13}C-NMR assignment. **^{1}H-NMR (700 MHz, $CDCl_3$)**: δ [ppm] = 7.42–7.00 (m, 20H, Ar-H), 5.36-4.99 (m, 2H, N-C(O)-O-C<u>H$_2$</u>-Ph), 4.91-4.51 (m, 8H, 2xO-C<u>H$_2$</u>-Ph, N-C<u>H$_2$</u>-Ph, H2, H5a), 4.21 (br, 1H, H-1,conformer A), 3.99-3.83 (m, 5H, H-1, conformer B, H-6, H-3, H-4), 2.31-2.23 (m, 1H, H-5), 0.88 (s, 9H, *t*-Bu), 0.04 (s, 3H, CH_3); **^{13}C-NMR (176 MHz, $CDCl_3$)**: δ [ppm] = 156.9 (C=O), 138.7-126.7 (C^{Ar}), 91.8 (d, *J* = 171 Hz, C-5a), 81.1 (C-4), 77.5 (C-3), 75.5 (O-<u>C</u>H$_2$-Ph), 72.7 and 72.2 (br, C-1), 67.2 (N-C(O)-O-<u>C</u>H$_2$-Ph), 61.6 (C-6), 57.0 (C-2), 49.2 (N-<u>C</u>H$_2$-Ph), 43.3 (d, *J* = 18 Hz, C-5), 26.0 (-Si-*t*-Bu), -5.0 (-Si-CH3-); **^{19}F-NMR (470 MHz, $CDCl_3$)**: δ [ppm] = -196.3 (br), -197.0; **RP-HPLC**: t_r =4.1 min (ZORBAX SB-C18, 5 µm, 0.4 mL/min, 80-100% MeCN in 20 min); **HRMS**: calcd for $C_{42}H_{52}FNO_6SiNa$ $[M+Na]^+$, 736.3440; found, 736.3421.



Dibenzyl (5a*R*)-2-Amino-N-benzyl-N-benzyloxycarbonyl-3,4-di-O-benzyl-2-deoxy-5a-fluoro-carba-idose-6-phosphate (13) To the silylated fluoro-carba-sugar precursor **11** (18.01 mg, 0.0252 mmol) solved in DMF (150 µL) was added a solution of TAS-F (30 µL, 0.0303 mmol, 1N in DMF). The reaction was stirred for 1.5 h at 23 °C. The reaction was diluted with 1 mL acetonitrile/water (50:50) and the solution loaded directly onto a C18-HPLC column (Gemini® C18, 110 Å, 5 µm, 50x30 mm), utilizing a gradient of 40-80% MeCN (A: 0.1% formic acid in H_2O) in 10 min. Fractions containing the product were combined and freeze-dried yielding the benzylated pseudo-sugar precursor **13** (15.07 mg, 99%) as colorless foam.

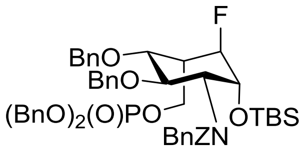
^{1}H-NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.33-7.18 (m, 20H, Ar-H), 5.17 (q, *J* = 12.1 Hz, 2H, N-C(O)-O-C<u>H</u>$_2$-Ph), 5.06 and 4.09 (d, *J* = 15.3 Hz, 2H, , N-C<u>H</u>$_2$-Ph), 4.86 and 4.44 (d, *J* = 10.8 Hz, 2H, O-C<u>H</u>$_2$-Ph), 4.77-4.66 (m, 3H, H-3, O-C<u>H</u>$_2$-Ph), 4.57 (dd, *J* = 2.5, 2.8 Hz, 1H, H-5a), 3.99 (dd, *J* = 12.1, 6.7 Hz, 1H, H-6a), 3.92 (br, 1H, H-1), 3.89 (dd, *J* = 9.4, 6.3 Hz, 1H, H-4), 3.84 (dd, *J* = 12.2, 5.4 Hz, 1H, H-6b), 3.37 (d, *J* = 10.9 Hz, 1H, H-2), 2.71 (ddd, *J* = 12.1, 5.9 Hz, 1H, H-5); **^{13}C-NMR (126 MHz, $CDCl_3$)**: δ [ppm] = 159.4 (C=O), 138.6-127.8 (C^{Ar}), 91.3 (d, *J* = 171.7 Hz, C-5a), 82.5 (C-4), 75.6 (O-<u>C</u>H$_2$-Ph), 75.3 (C-3), 73.8 (O-<u>C</u>H$_2$-Ph), 72.8 (d, *J* = 28.4 Hz, C-1), 68.5 (N-C(O)-O-<u>C</u>H$_2$-Ph), 63.7 (C-2), 60.8 (d, *J* = 12.1 Hz, C-6), 56.2 (N-<u>C</u>H$_2$-Ph), 44.7 (d, *J* = 17.8 Hz, C-5); **^{19}F-NMR (471 MHz, $CDCl_3$)**: δ [ppm] = -185.40; **RP-HPLC**: t_r = 14.3 min (ZORBAX SB-C18, 5 µm, 0.4 mL/min, 20-100% MeCN in 20 min); **HRMS**: calcd for $C_{36}H_{38}FNO_6Na$ $[M+Na]^+$, 622.2575; found, 622.2579.



(5a*R*)-2-Amino-2-deoxy-5a-fluoro-carba-idose acetate (14) Perbenzylated fluoro-carba compound **13** (22.65 mg, 0.0378 mmol) was deprotected according to **GP1**, with the difference that only one portion of 10% Pd/C (100% *w/w*) was added. The reaction was finished after 7 h. The lyophilized pseudo-sugar was purified via HILIC (NUCLEODUR® HILIC 5 µm, 150x4.6 mm, 98-90% MeCN in 20 min, A: 20 mM NH_4OAc in water pH 5.4). Due to missing UV-absorption of the product the fractions collected in time slices were analyzed via LC-MS (0-10 0% MeCN in 2 min). Fractions containing the target-mass were combined and freeze-dried yielding the pseudo-sugar **14** (3.26 mg, 34%) as the acetate salt.

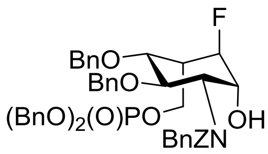
^{1}H-NMR (700 MHz, $CDCl_3$): δ [ppm] = 4.90 (dt, *J* = 47.4, 7.2 Hz, 1H, H-5a), 4.33 (ddd, *J* = 11.1, 6.9, 4.5 Hz, 1H, H-1), 4.13 (dt, *J* = 6.2, 2.8 Hz, 1H, H-4), 4.09 (t, *J* = 5.9 Hz, 1H, H-3), 3.95 (ddd, *J* = 11.4, 6.0 Hz, 2H, H-6), 3.58 (brt, *J* = 6.0 Hz, 1H, H-2), 2.48 (dp, *J* = 11.8, 6.4 Hz, 1H, H-5); **^{13}C-NMR (176 MHz, $CDCl_3$)**: δ [ppm] = 91.0

(d, J = 171.9 Hz, C-5a), 70.7 (d, J = 5.8 Hz, C-4), 68.1 (C-3), 67.4 (d, J = 23.9 Hz, C-1), 58.28 (d, J = 6.6 Hz, C-6), 54.86 (d, J = 5.3 Hz, C-2), 43.41 (d, J = 17.2 Hz, C-5); **^{19}F-NMR (282 MHz, CDCl$_3$)**: δ [ppm] = -125.18; **HRMS**: calcd for $C_7H_{15}FNO_4Na$ $[M+H]^+$, 196.0980; found,196.0977.



Dibenzyl (5a*R*)-2-Amino-*N*-benzyl-*N*-benzyloxycarbonyl-3,4-di-*O*-benzyl-2-deoxy-5a-fluoro-1-O-*tert*-butyldimethylsilyl-carba-idose-6-phosphate (15) The unphosphorylated fluoro-carba-sugar precursor **11** (24.63 mg, 0.0345 mmol) was transferred to a heat-dried schlenk-tube with anhydrous CH_2Cl_2. The CH_2Cl_2 was removed under reduced pressure and 1H-Tetrazole (12.08 mg, 0.173 mmol), anhydrous CH_2Cl_2 (4 mL) and dibenzyl *N,N*-diisopropylphosphoramidite (29 µL, 0.0862 mmol) were added successively. The mixture was stirred for 3 h at room temperature and HPLC-monitoring showed complete consumption of starting material. The reaction was cooled to 0 °C and *m*-CPBA (70%, 25.5 mg, 0.104 mmol) was added. After another hour HPLC shows completion of the reaction, the mixture was diluted with CH_2Cl_2 (30 mL) and 10 mL of aqueous 10% Na_2SO_3 was added. The mixture was stirred for 15 min, then the organic layer was separated and washed with aqueous 10% Na_2SO_3 (1x10 mL), 1M HCl (2x10 mL), saturated $NaHCO_3$ (2x10 mL) and brine (1x10 mL). The organic layer was dried ($MgSO_4$) and the solvent removed under reduced pressure. The reaction was purified via RP-HPLC (Gemini® C18, 110 Å, 5 µm, 50x30 mm, 80-100% MeCN in 10 min, A: 0.1% formic acid in H_2O). Fractions containing product were combined and freeze-dried yielding the phosphorylated pseudo-sugar precursor **15** (43.42 mg, 99%) as colorless foam.

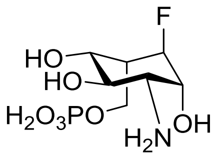
^{1}H-NMR (700 MHz, CDCl$_3$): δ [ppm] = 7.41-6.89 (m, 30H, Ar-H), 5.32 and 5.15 (d, J = 12.4 Hz, 2H, N-C(O)-O-C$\underline{H_2}$-Ph), 5.03-4.98 (m, 4H, P-O-C$\underline{H_2}$-Ph), 4.85-4.32 (m, 10H, 2xO-C$\underline{H_2}$-Ph, N-C$\underline{H_2}$-Ph, H-5a, H-2, H-6), 4.21 (d, J = 12.0 Hz, 1H, H-1), 3.93 (br, 1H, H-4), 3.77 (br, 1H, H-3), 2.82-2.75 (m, 1H, H-5), 0.89 (s, 9H, *t*-Bu), 0.07 and 0.01 (s, 6H, 2xCH_3); **^{13}C-NMR (176 MHz, CDCl$_3$)**: δ [ppm] = 156.6 (C=O), 138.8-125.7 (C^{Ar}), 90.67 (d, J = 173.1 Hz, C-5a) and 90.00 (d, J = 170.5 Hz), 78.7 (C-4), 73.8 (C-3), 73.57 (d, J = 27.4 Hz, C-1), 72.3, 72.2. 71.6 (O-$\underline{C}H_2$-Ph), 69.4 (P(O)-(O-C$\underline{H_2}$-Ph)$_2$), 67.5 (N-C(O)-O-$\underline{C}H_2$-Ph), 64.28 (dd, J = 10.0, 5.6 Hz, C-6), 58.3 (C-2), 50.0 (N-$\underline{C}H_2$-Ph), 42.12 (d, J = 19.0 Hz, H-5), 34.4 (Si-$\underline{C}$-(CH_3)$_3$), 26.1 (Si-C-($\underline{C}H_3$))$_3$, -4.5, -5.3, -5.5 (Si-CH_3); **^{31}P-NMR (121 MHz, CDCl$_3$)**: δ [ppm] = -0.02; **^{19}F-NMR (282 MHz, CDCl$_3$)**: δ [ppm] = -185.12, -185.92 (br); **RP-HPLC**: t_r =9.6 min (ZORBAX SB-C18, 5 µm, 0.4 mL/min, 80-100% MeCN in 20 min); **HRMS**: calcd for $C_{56}H_{66}FNO_9PSi$ $[M+H]^+$, 974.4223; found, 996.4230.



Dibenzyl (5a*R*)-2-Amino-*N*-benzyl-*N*-benzyloxycarbonyl-3,4-di-*O*-benzyl-2-deoxy-5a-fluoro-carba-idose-6-phosphate (16) To the silylated fluoro-carba precursor **15** (15.0 mg, 0.0154 mmol) solved in anhydrous THF (192.5 µL), were added K_2HPO_4-Buffer (1.8 µL, pH 7) and a solution of TBAF (7.7 µL, 0.0077 mmol, 1M in anhydrous THF stored over 2 Å molecular sieve). The reaction was stirred at 23 °C and after 4 h HPLC showed completion of the reaction. After dilution with 500 µL of Acetonitril/H_2O (1:1) the reaction was directly loaded onto a C18-HPLC column (Gemini® C18, 110 Å, 5 µm, 50x30 mm), utilizing a gradient of 40-100% MeCN (A: 0.1% formic acid in H_2O) in 15 min. Fractions containing the target-mass were combined and freeze-dried yielding the benzylated pseudo-sugar precursor **16** (5.44 mg, 41%) as colorless foam.

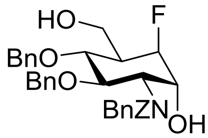
^{1}H-NMR (700 MHz, $CDCl_3$): δ [ppm] = 7.45-6.99 (m, 30H, Ar-H), 5.18 and 5.12 (d, *J* = 12.3 Hz, 2H, N-C(O)-O-C<u>H</u>$_2$-Ph), 5.03-5.02 (m, 4H, P-O-C<u>H</u>$_2$-Ph), 4.98 and 4.10 (d, *J* = 15.5 Hz, 2H, N-C<u>H</u>$_2$-Ph); 4.74-4.34 (m, 8H, 2xO-C<u>H</u>$_2$-Ph, H-5a, H-3, H-6), 4.01 (br, 1H, H-1), 3.83 (t, J = 7.6 Hz, 1H, H-4), 3.28 (br, 1H, H-2), 2.82 (br, 1H, H-5); **^{13}C-NMR (176 MHz, $CDCl_3$)**: δ [ppm] = 159.3 (C=O), 138.7-127.8 (C^{Ar}), 89.08 (d, *J* = 173.3 Hz, C-5a), 80.8 (C-4), 75.6 (O-<u>C</u>H$_2$-Ph), 74.6 (C-3), 73.5 (br, C-1), 72.9 (O-<u>C</u>H$_2$-Ph), 69.6 (P(O)-(O-<u>C</u>H$_2$-Ph)$_2$), 68.5 (N-C(O)-O-<u>C</u>H$_2$-Ph), 64.9 (C-6), 61.3 (C-2)*, 55.5 (N-<u>C</u>H$_2$-Ph)*, 43.2 (br, C-5); **^{31}P-NMR (121 MHz, $CDCl_3$)**: δ [ppm] = -1.16; **^{19}F-NMR (282 MHz, $CDCl_3$)**: δ [ppm] = -187.92; **RP-HPLC**: t_r = 17.9 min (ZORBAX SB-C18, 5 µm, 0.4 mL/min, 20-100% MeCN in 20 min); **HRMS**: calcd for $C_{50}H_{51}FNO_9PNa$ $[M+Na]^+$, 882.3178; found, 882.3179.

*assignment through HSQC



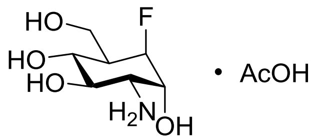
(5a*R*)-2-Amino-2-deoxy-5a-fluoro-carba-idose-6-phosphate (2) Perbenzylated fluoro-carba compound **16** (5.44 mg, 0.00633 mmol) was deprotected according to **GP1**. The reaction was finished after 24 h. The lyophilized pseudo-sugar was purified via HILIC (NUCLEODUR® HILIC 5 µm, 150x4.6 mm, 98-90% MeCN in 20 min, A: 20 mM NH_4OAc in water pH 5.4), due to missing UV-absorption of the product, the fractions collected in time slices were analyzed via LC-MS (0-100% MeCN in 2 min). Fractions containing the target-mass were combined and freeze-dried, yielding the pseudo-sugar **2** (1.18 mg, 68%) as colorless foam.

^{1}H-NMR (500 MHz, D_2O): δ [ppm] = 4.98 (dt, *J* = 46.9, 7.0 Hz, 1H, H-5a), 4.35 (ddd, *J* = 11.2, 6.8, 4.7 Hz, 1H, H-1), 4.22 (t, *J* = 6.1 Hz, 1H, H-3), 4.19 – 4.16 (m, 2H, H-4, H-6a), 4.08 (dt, *J* = 11.2, 6.3 Hz, 1H, H-6b), 3.63 (t, *J* = 6.1 Hz, 1H, H-2), 2.66 – 2.47 (m, 1H, H-5); **^{13}C-NMR (126 MHz, D_2O)**: δ [ppm] = 90.1 (d, *J* = 171.7 Hz, C-5a), 70.4 (d, *J* = 5.3 Hz, C-4), 67.6 (C-3), 67.0 (d, *J* = 24.4 Hz, C-1), 60.6 (C-2), 54.9 (C-5); **^{31}P-NMR (202 MHz, D_2O)**: δ [ppm] = 2.84; **^{19}F-NMR (282 MHz, D_2O)**: δ [ppm] = no signal; **HRMS**: calcd for $C_7H_{14}FNO_7P$ $[M+H]^+$, 274.0486; found, 274.0483.



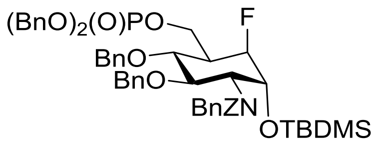
(5a*R*)-2-Amino-*N*-benzyl-*N*-benzyloxycarbonyl-3,4-di-*O*-benzyl-2-deoxy-5a-fluoro-carba-glucose (17) To the silylated fluoro-carba precursor **12** (15.123 mg, 0.0212 mmol) solved in 500 µL anhydrous THF, were added 3.9 µL K_2HPO_4-Buffer (pH 7) and 84.7 µL 1 M TBAF (0.0847 mmol) in anhydrous THF, stored over 2 Å molecular sieve. After 4 h HPLC shows completion of the reaction. After dilution with 500 µL of Acetonitril/H_2O (1:1) the reaction was directly loaded onto C18-HPLC column (Gemini® C18, 110 Å, 5 µm, 50x30 mm), utilizing a gradient of 40-100% MeCN (A: 0.1% formic acid in H_2O) in 15 min. Fractions containing the target-mass were combined and freeze-dried yielding the benzylated pseudo-sugar precursor **17** (11.46 mg, 90%) as colorless foam.

^{1}H-NMR (700 MHz, $CDCl_3$): δ [ppm] = 7.35-7.18 (m, 20H, Ar-H), 5.22 and 5.17 (d, J = 12.2 Hz, N-C(O)-O-C<u>H</u>$_2$-Ph), 5.09 and 4.11 (br, 2H, N-C<u>H</u>$_2$-Ph), 4.93 and 4.68 (d, *J* = 10.9 Hz, 2H, O-C<u>H</u>$_2$-Ph), 4.81 and 4.47 (d, *J* = 10.9 Hz, 2H, O-C<u>H</u>$_2$-Ph), 4.69 (ddd, *J* = 47.3, 4.0, 2.1 Hz, 1H, H-5a), 4.63 (br, 1H, H-3), 3.93 (br, 1H, H6a), 3.92 (br, 1H, H-1), 3.84 (br, 1H, H6b), 3.73 (t, *J* = 10.0 Hz, 1H, H-4), 3.32 (br, 1H, H-2), 2.37 (ddt, *J* = 39.5, 10.1, 4.7 Hz, 1H, H-5);**^{13}C-NMR (176 MHz, $CDCl_3$)**: δ [ppm] = 159.3 (C=O), 138.4, 138.2, 135.8, 128.9-127.8 (C^{Ar}), 92.5 (d, *J* = 172 Hz, C-5a) 81.2 (C-4), 78.7 (C-3), 75.5, 75.4 (O-<u>C</u>H$_2$-Ph), 72.1 (d, *J* = 26 Hz, C-1), 68.5 (N-C(O)-O-<u>C</u>H$_2$-Ph), 63.5 (br, C-2), 62.1 (d, *J* = 2 Hz, C-6), 56.4 (N-<u>C</u>H$_2$-Ph), 43.0 (d, *J* = 17 Hz, C-5); **^{19}F-NMR (470 MHz, $CDCl_3$)**: δ [ppm] = -199.03 (s, 1F); **RP-HPLC**: t_r = 14.2 min (ZORBAX SB-C18, 5 µm, 0.4 mL/min, 20-100% MeCN in 20 min); **HRMS**: calcd for $C_{36}H_{39}FNO_6$ $[M+H]^+$, 600.2756; found, 600.2754.



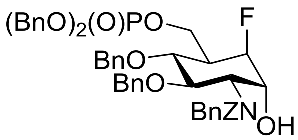
(5a*R*)-2-Amino-2-deoxy-5a-fluoro-carba-glucose (18) The perbenzylated fluoro-carba-idosamine **17** (14.93 mg, 0.0174 mmol) was deprotected according to **GP1**. After a reaction time of 7 h LC-MS monitoring showed completion of the reaction. The lyophilized raw product was purified via HILIC (NUCLEODUR® HILIC 5 µm, 150x4.6 mm, 98-90% MeCN in 20 min, A: 20 mM NH_4OAc in water pH 5.4). Due to missing UV-absorption of the product the fractions collected in time slices were analyzed via LC-MS (0-100% MeCN in 2 min). Fractions containing the target-mass were combined and freeze-dried yielding the pseudo-sugar **18** (2.42 mg, 53%) as the acetate salt.

^{1}H-NMR (500 MHz, $CDCl_3$): δ [ppm] = 4.97 (ddd, *J* = 45.5, 4.0, 2.0 Hz, 1H, H-5a), 4.35 (dd, *J* = 7.2, 3.7 Hz, 1H, H-1), 3.99 (dd, *J* = 11.3, 4.3 Hz, 1H, H-6a), 3.80 (dd, *J* = 11.3, 9.3 Hz, 1H, H-6b), 3.74 (dd, *J* = 10.8, 9.1 Hz, 1H, H-3), 3.54 (dd, *J* = 11.2, 9.2 Hz, 1H, H-4), 3.37 (dt, *J* = 10.8, 3.0 Hz, 1H, H-2), 2.12 (dtdd, *J* = 36.2, 9.3, 4.4, 2.2 Hz, 1H, H-5), **^{13}C-NMR (126 MHz, $CDCl_3$)**: δ [ppm] = 89.8 (d, *J* = 173.7 Hz, C-5a), 71.1 (C-3), 69.7 (d, *J* = 2.0 Hz, C-4); 66.0 (d, *J* = 27.3 Hz, C-1), 58.3 (d, *J* = 3.7 Hz, C-6), 52.9 (C-2), 42.5 (d, *J* = 18.2 Hz, H-5); **^{19}F-NMR (470 MHz, $CDCl_3$)**: δ [ppm] = -201.74 (s, 1F); **RP-HPLC**: t_r = 14.2 min (ZORBAX SB-C18, 5 µm, 0.4 mL/min, 20-100% MeCN in 20 min); **HRMS**: calcd for $C_{36}H_{39}FNO_6$ $[M+H]^+$, 600.2756; found, 600.2754.



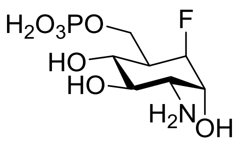
Dibenzyl (5a*R*)-2-amino-*N*-benzyl-*N*-benzyloxycarbonyl-3,4-di-O-benzyl-2-deoxy-5a-fluoro-1-O-*tert*-butyldimethylsilyl-carba-glucose-6-phosphate (19) The unphosphorylated fluoro-carba precursor 18 (17.75 mg, 0.0249 mmol) solved in toluene was transferred to a heat-dried schlenk-tube. The toluene was removed under reduced pressure and the starting material dried under vacuum (~10^{-2} mbar) for 2 h. 1H-Tetrazole (8.71 mg, 0.124 mmol), anhydrous CH_2Cl_2 (2.1 mL) and dibenzyl *N,N*-diisopropylphosphoramidite (21 µL, 0.0622 mmol) were added under argon atmosphere. The mixture was stirred for 2 h at room temperature after which HPLC-monitoring showed completion of the reaction. The reaction was cooled to 0 °C and *m*-CPBA (70%, 18.39 mg, 0.0746 mmol) was added. After another 1 h HPLC shows completion of the reaction, the mixture was diluted with CH_2Cl_2 (20 mL) and 5 mL of aqueous 10% Na_2SO_3 was added and the mixture stirred for 30 min. The organic layer was separated and washed with aqueous 10% Na_2SO_3 (1x10 mL), 1M HCl (2x10 mL), saturated $NaHCO_3$ (2x10 mL) and brine (1x10 mL). The organic layer was dried with $MgSO_4$ and concentrated. The reaction was purified via RP-HPLC (Gemini® C18, 110 Å, 5 µm, 50x30 mm, 80-100% MeCN in 10 min). Fractions containing product were combined and freeze-dried yielding the phosphorylated pseudo-sugar precursor **19** (22.76 mg, 94%) as colorless foam.

^{1}H-NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.50-6.94 (m, 30H, Ar-H), 5.18-5.00 (m, 6H, N-C(O)-O-C$\underline{H}_2$-Ph and P(O)-(O-C$\underline{H}_2$-Ph)$_2$), 4.90-4.42 (m, 6H, O-C$\underline{H}_2$-Ph and N-C$\underline{H}_2$-Ph), 4.73 (d, *J* = 46.4 Hz, 1H, H-5a), 4.67 (br, 1H, H-2), 4.33 (dt, *J* = 9.6, 4.7 Hz, 1H, H-6a), 4.23 (br, 0.5H, H-1), 4.12 (td, *J* = 9.9, 5.5 Hz, 1H, H-6b), 3.97 (br, 1H, H-3), 3.89 (br, 0.5H, H-1), 3.66 (s, 1H, H-4), 2.45 (dt, *J* = 34.5, 9.4 Hz, 1H, H-5), 0.83 (s, 9H, *t*-Bu), 0.03 (s, 3H, CH_3); **^{13}C-NMR (176 MHz, $CDCl_3$)**: δ [ppm] = 156.8 (C=O), 138.6-126.3 (C^{Ar}), 88.8 (d, *J* = 171 Hz, C-5a), 79.5 (C-4), 77.3 (C-3), 75.2 (O-$\underline{C}H_2$-Ph), 72.4 (br, C-1), 69.4 (P(O)-(O-C$\underline{H}_2$-Ph)$_2$), 67.2 (N-C(O)-O-$\underline{C}H_2$-Ph), 64.3 (C-6), 56.8 (C-2), 50.0 (dd, 17.9, 8.0 Hz, C-5), 49.1 (N-C̲H$_2$-Ph), 25.8 (*t*-Bu), 18.0 (Si-C-), -5.2 (CH_3); **^{31}P-NMR (202 MHz, $CDCl_3$)**: δ [ppm] = -0.78, -0.95, -1.02; **^{19}F-NMR (470 MHz, $CDCl_3$)**: δ [ppm] = -198.46 (br), -198.9; **RP-HPLC**: t_r =9.7 min (ZORBAX SB-C18, 5 µm, 0.4 mL/min, 80-100% MeCN in 20 min); **HRMS**: calcd for $C_{56}H_{65}FNO_9PSiNa$ [M+Na]$^+$, 996.4042; found, 996.4054.



Dibenzyl (5a*R*)-2-amino-*N*-benzyl-*N*-benzyloxycarbonyl-3,4-di-*O*-benzyl-2-deoxy-5a-fluoro-carba-glucose-6-phosphate (20) To the silylated fluoro-carba precursor **19** (14.93 mg, 0.0174 mmol) solved in 500 µL anhydrous THF, were added 3.7 µL K_2HPO_4-Buffer (pH 7) and 56.5 µL 1 M TBAF (4 eq) in anhydrous THF, stored over 2 Å molecular sieve. The reaction was stirred at 23 °C and after 1 h HPLC showed completion of the reaction. After dilution with 500 µL of Acetonitril/H_2O (1:1) the reaction was directly loaded onto a C18-HPLC column (Gemini® C18, 110 Å, 5 µm, 50x30 mm), utilizing a gradient of 40-100% MeCN (A: 0.1% formic acid in H_2O) in 15 min. Fractions containing the target-mass were combined and freeze-dried yielding the benzylated pseudo-sugar precursor **20** (10.62 mg, 87%) as colorless foam.

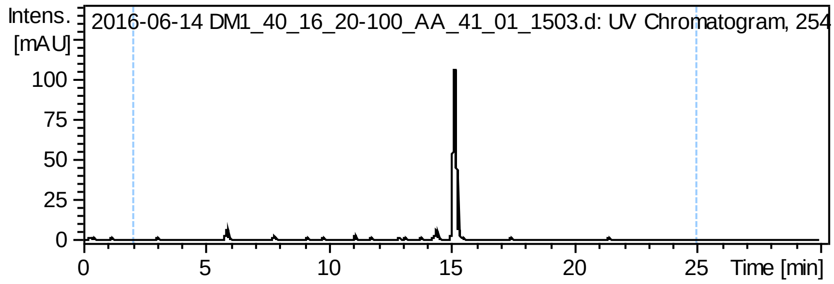
^{1}H-NMR (700 MHz, $CDCl_3$): δ [ppm] = 7.32-7.16 (m, 30H, Ar-H), 5.24 and 5.18 (d, J = 12.0 Hz, N-C(O)-O-CH̲$_2$-Ph), 5.11 and 4.10 (br, 2H, N-CH̲$_2$-Ph), 5.03 (br, 4H, P(O)-(O-CH̲$_2$-Ph)$_2$), 4.84 and 4.51 (d, *J* = 11.0 Hz, 2H, O-CH̲$_2$-Ph), 4.78 and 4.45 (d, *J* = 11.0 Hz, 2H, O-CH̲$_2$-Ph), 4.65 (d, *J* = 47.8 Hz, 1H, H-5a), 4.62 (br, 1H, H-3), 4.29 (br, 1H, H6a), 4.08 (br, 1H, H6b), 3.92 (br, 1H, H-1), 3.46 (t, *J* = 47.8 Hz, 1H, H-4), 3.30 (br, 1H, H-2), 2.55 (d, *J* = 36.9 Hz, 1H, H-5);**^{13}C-NMR (176 MHz, $CDCl_3$)**: δ [ppm] = 159.0 (C=O), 138.2, 137.9, 128.5-127.7 (C^{Ar}), 89.0 (d, C-5a) 79.7 (C-4), 78.5 (C-3), 75.2 (O-C̲H$_2$-Ph), 75.0 (O-C̲H$_2$-Ph), 71.8 (d, C-1), 69.4 (P(O)-(O-C̲H$_2$-Ph)$_2$), 68.4 (N-C(O)-O-C̲H$_2$-Ph), 64.6 (C-6), 63.3 (br, C-2), 56.2 (N-C̲H$_2$-Ph), 41.5 (C-5); **^{31}P-NMR (202 MHz, $CDCl_3$)**: δ [ppm] = -1.28 (s, 1P); **^{19}F-NMR (470 MHz, $CDCl_3$)**: δ [ppm] = -201.56 (s, 1F); **RP-HPLC**: t_r = 17.8 min (ZORBAX SB-C18, 5 µm, 0.4 mL/min, 20-100% MeCN in 20 min); **HRMS**: calcd for $C_{50}H_{52}FNO_9P$ [M+H]$^+$, 860.3358; found, 860.3357.

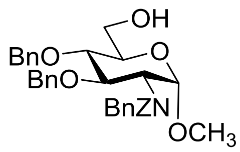


(5a*R*)-2-Amino-2-deoxy-5a-fluoro-carba-glucose-6-phosphate (1) Perbenzylated fluoro-carba compound **20** (10.62 mg, 0.0124 mmol) was deprotected according to **GP1**. The reaction was finished after 3 h. The lyophilized pseudo-sugar was purified via C18-HPLC (NUCLEODUR® C18, 110 Å, 5 µm, 150x4.6 mm, 100% H_2O for 5 min, then 0-100% acetonitrile in 5 min). Due to missing UV-absorption of the product the fractions collected in time slices were analyzed via LC-MS (0-100% MeCN in 2 min). Fractions containing the target-mass were combined and freeze-dried yielding the pseudo-sugar **1** (2.39 mg, 70%) as colorless foam.

^{1}H-NMR (500 MHz, D_2O): δ [ppm] = 5.03 (d, *J* = 45.3 Hz, 1H, H-5a), 4.38 (d, *J* = 3.6, 1H, H-1), 4.19 (dt, *J* = 10.4, 5.1 Hz, 1H, H-6a), 3.98 (td, *J* = 10.6, 10.1, 7.5 Hz, 1H, H-6b), 3.80 (t, *J* = 9.9 Hz, 1H, H-3), 3.59 (t, *J* = 10.1 Hz, 1H, H-4), 3.44 (dt, *J* = 11.3, 3.2 Hz, 1H, H-2), 2.27 (dt, *J* = 38.3, 11.0 Hz, 1H, H-5); **^{13}C-NMR (126 MHz, D_2O)**: δ [ppm] = 89.5 (d, *J* = 174.1 Hz, C-5a), 70.6 (C-4), 69.5 (C-3); 65.7 (d, *J* = 26.7 Hz, C-1), 61.2 (C-6), 53.1 (C-2); 41.7 (dd, *J* = 18.0, 6.6 Hz, C-5) **^{31}P-NMR (202 MHz, D_2O)**: δ [ppm] = 2.49 (s, 1P); **^{19}F-NMR (471 MHz, D_2O)**: δ [ppm] = -201.77 (br, 1F); **HRMS**: calcd for $C_7H_{14}NO_7PF$ $[M+H]^+$, 274.0486; found, 274.0484.

NMR Spectra





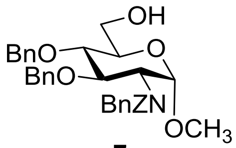
7

HPLC

ZORBAX SB-C18, 5 µm,

0.4 mL/min,

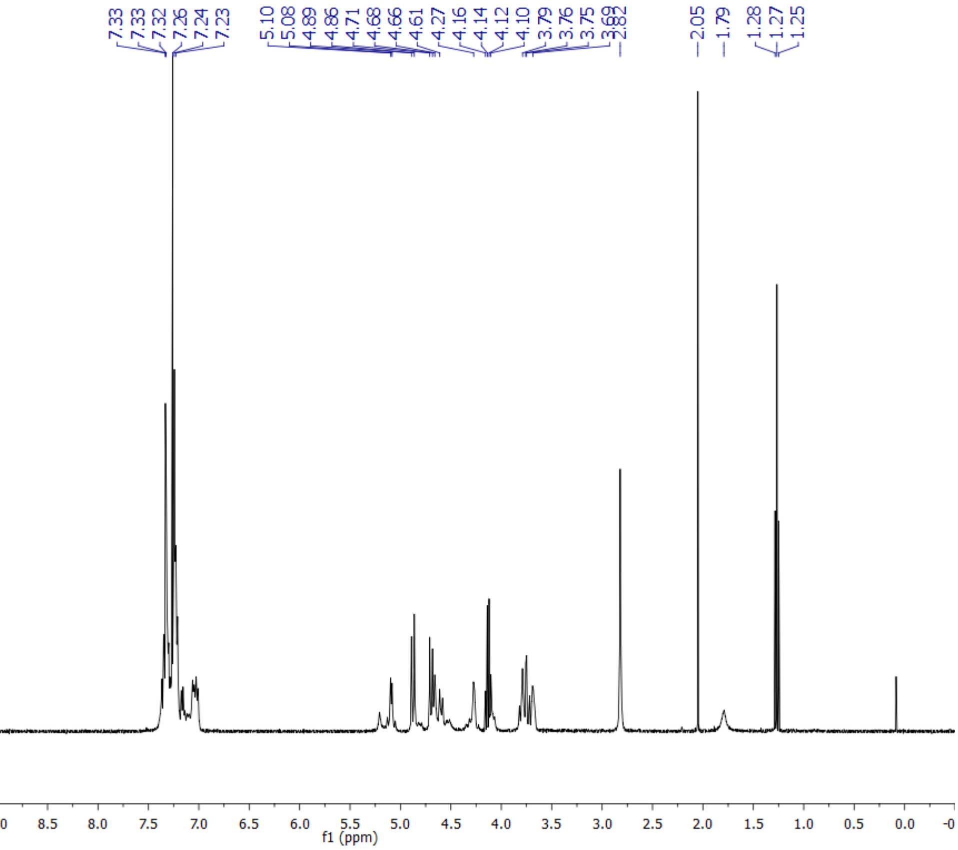
20-100% MeCN in 20 min

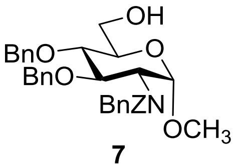


7

^{1}H NMR

($CDCl_3$, 400 MHz)

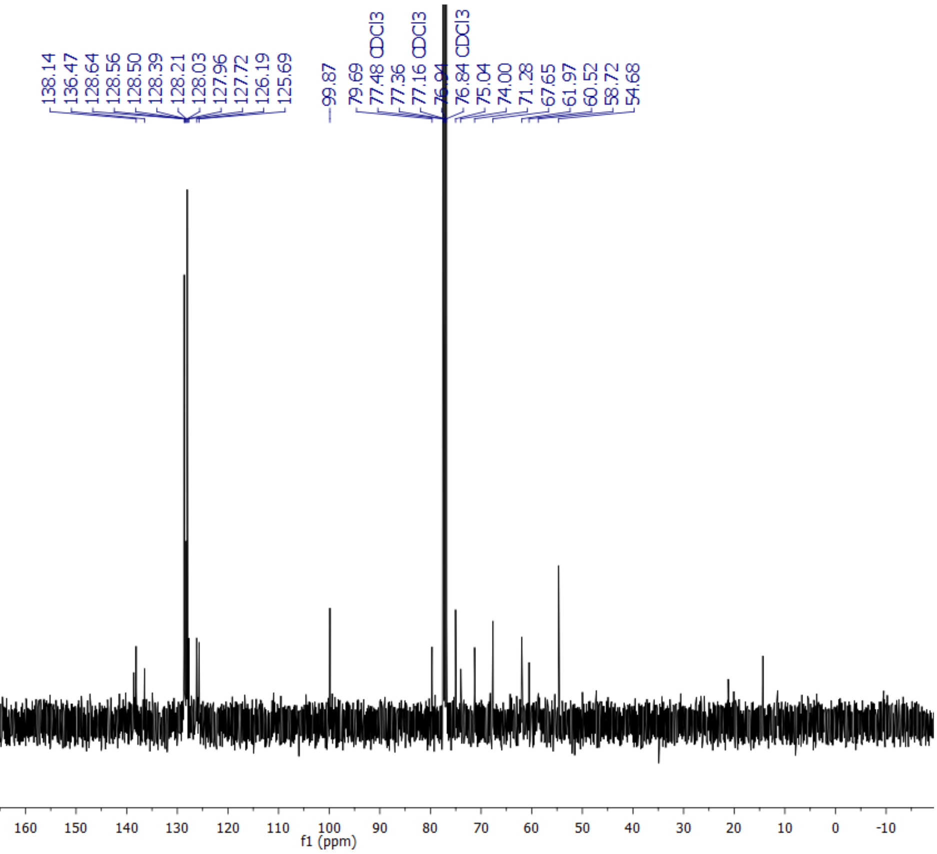


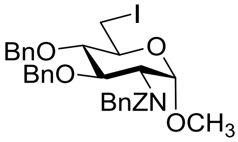


7

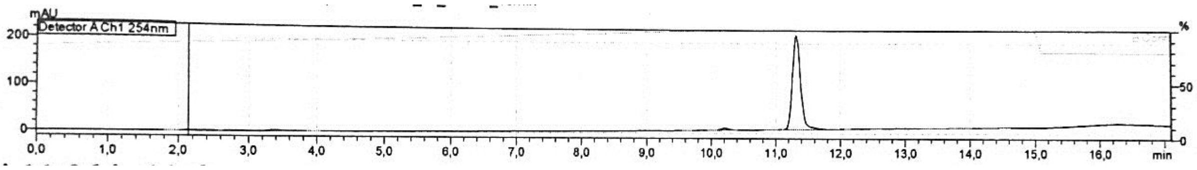
^{13}C NMR

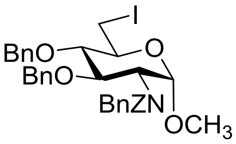
($CDCl_3$, 400 MHz)



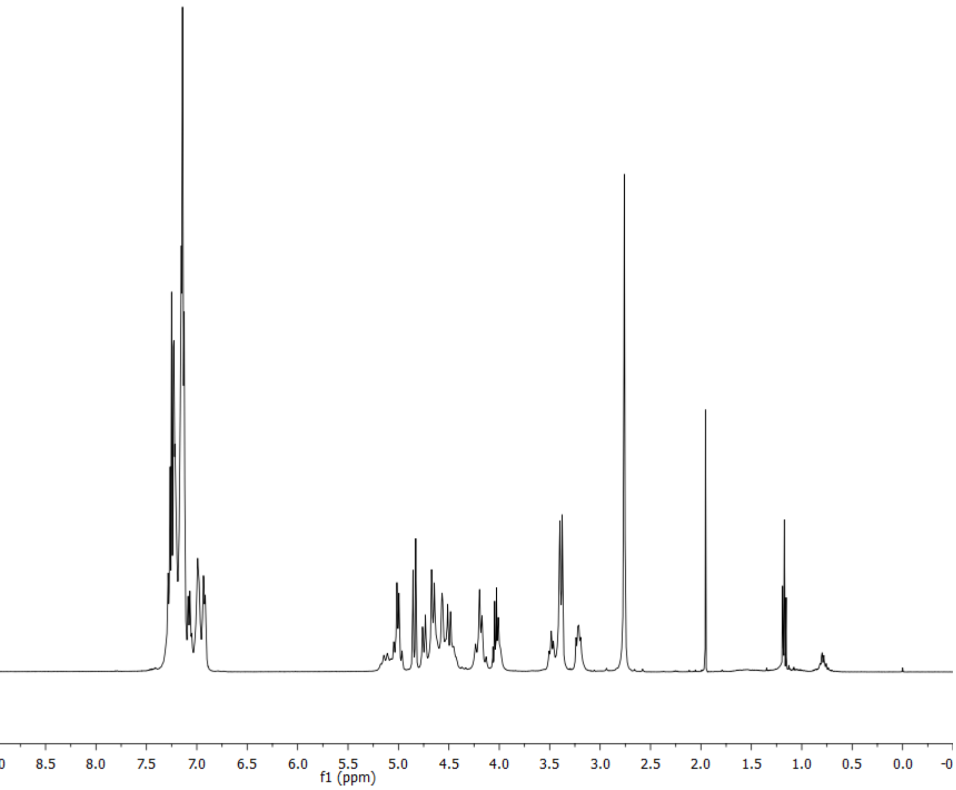


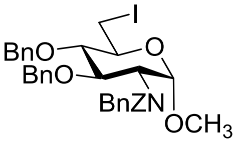
S7
HPLC
EC 125/4 Nucleodur C-18 Gravity, 3 µm,
0.4 mL/min,
80-100% MeCN in 10 min





S7
^1H NMR
($CDCl_3$, 400 MHz)

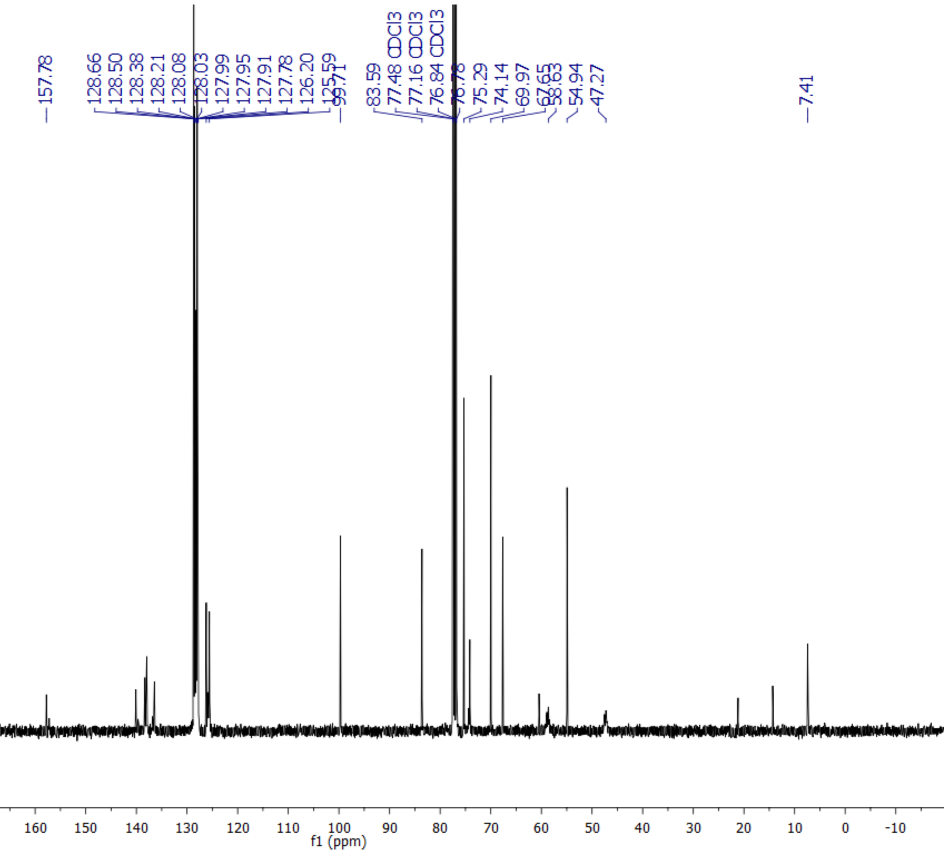


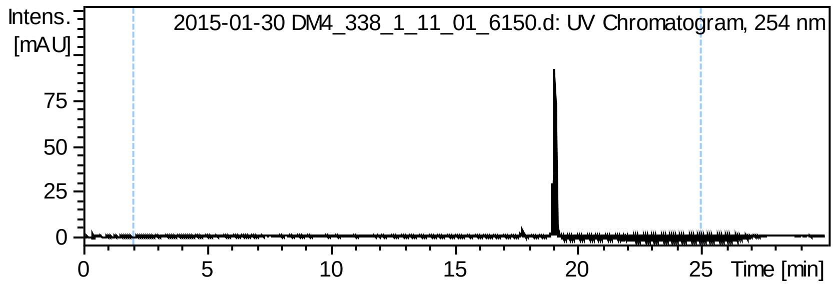


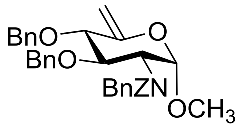
S7

^{13}C NMR

($CDCl_3$, 100 MHz)







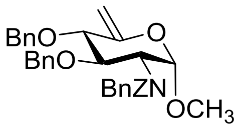
8

HPLC

ZORBAX SB-C18, 5 µm,

0.4 mL/min,

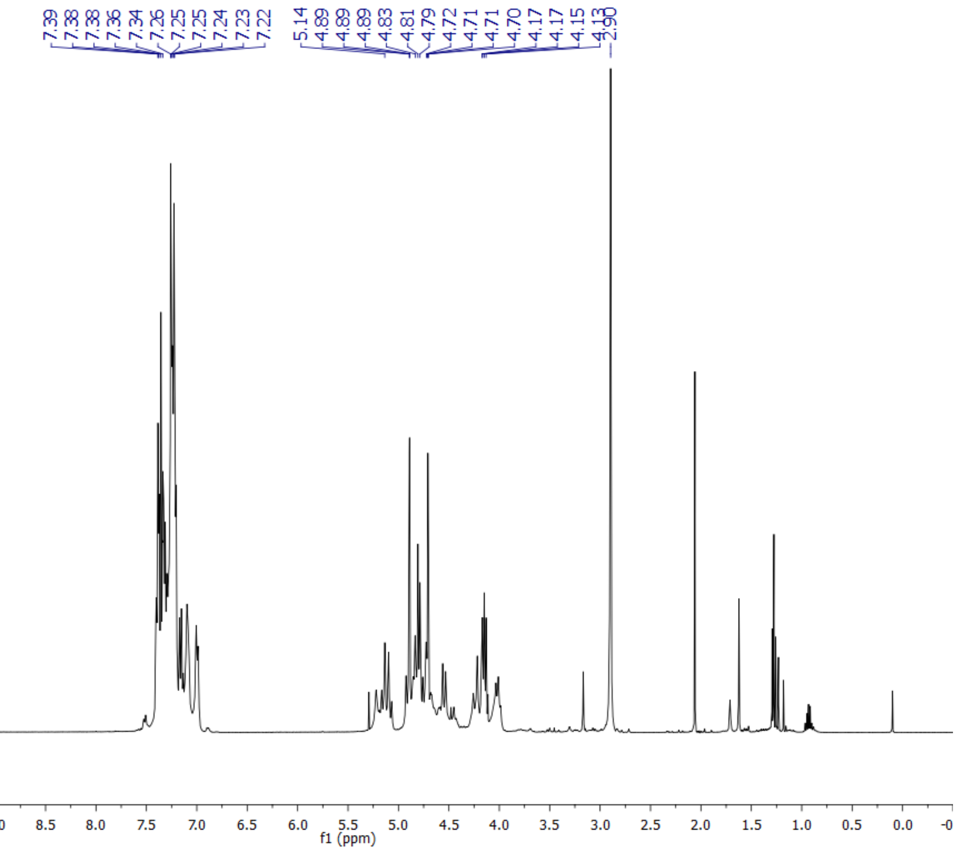
80-100% MeCN in 20 min

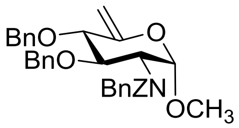


8

^{1}H NMR

($CDCl_3$, 400 MHz)

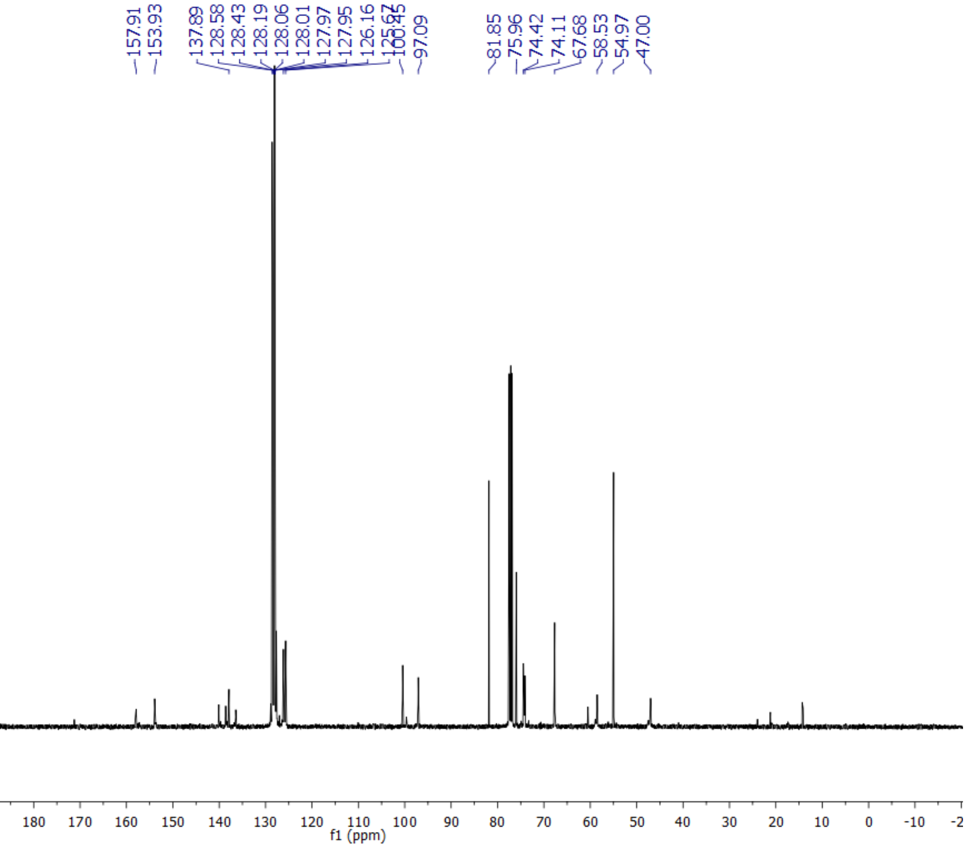


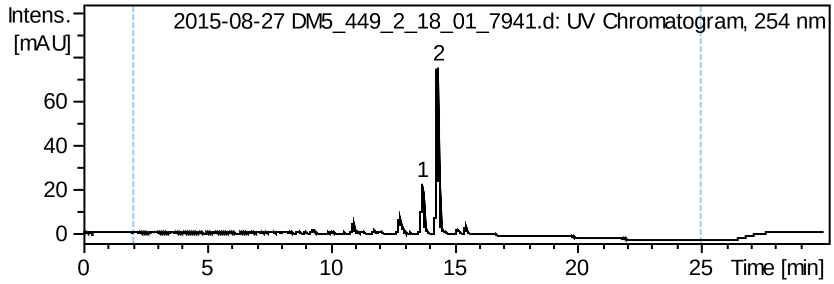


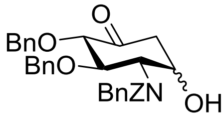
8

^{13}C NMR

($CDCl_3$, 100 MHz)







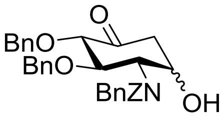
5

HPLC

ZORBAX SB-C18, 5 μm,

0.4 mL/min,

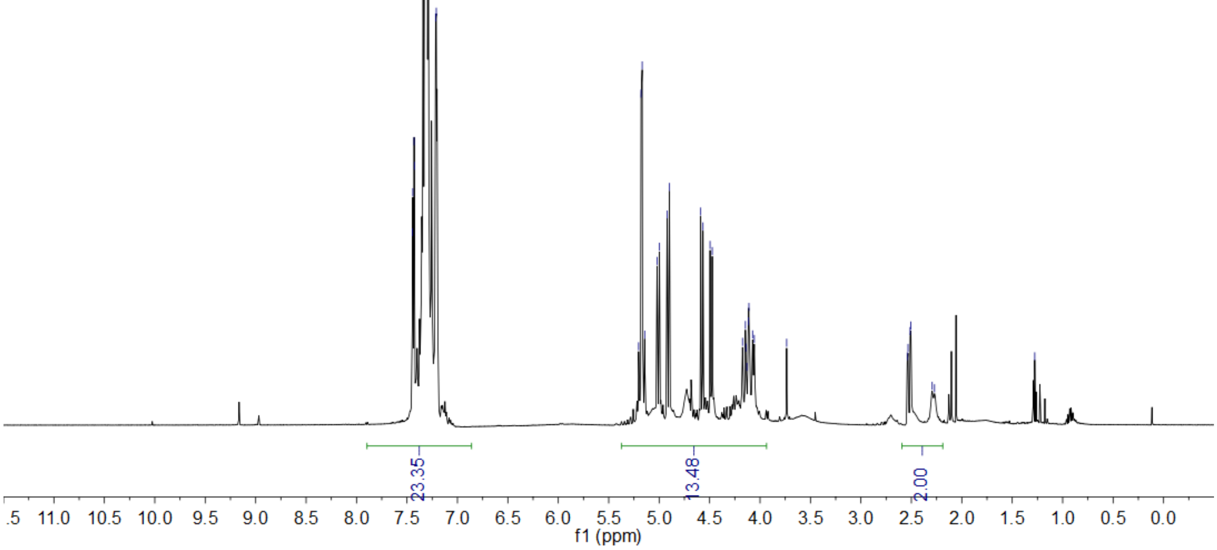
80-100% MeCN in 20 min

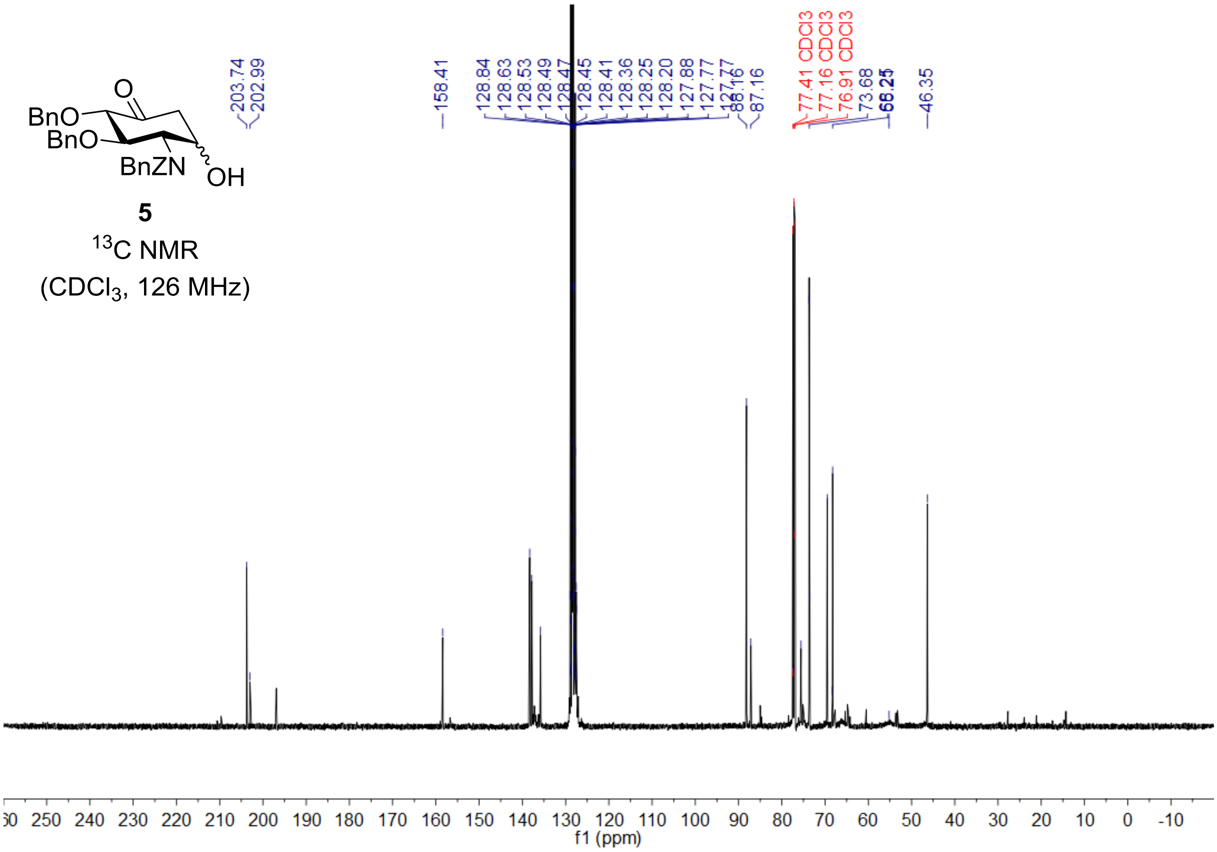


5

^{1}H NMR

($CDCl_3$, 500 MHz)

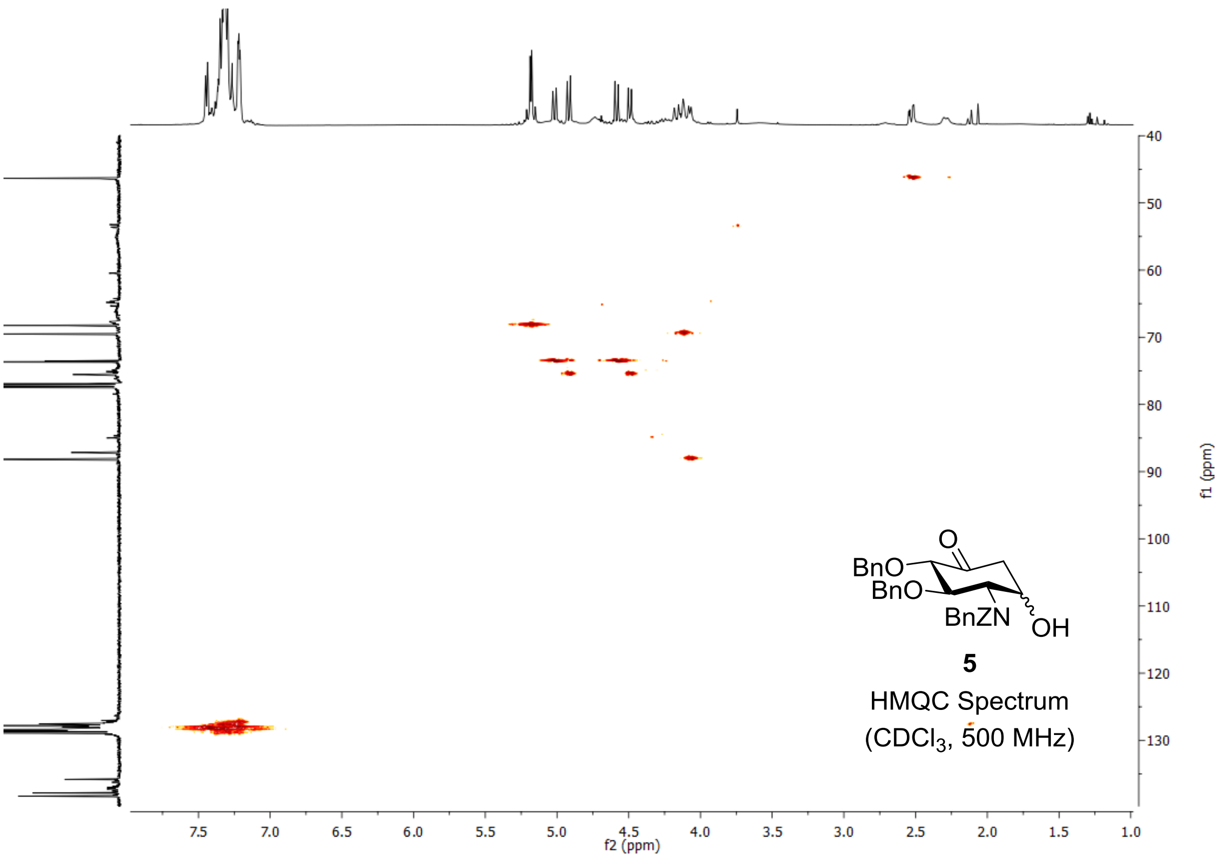




5

^{13}C NMR

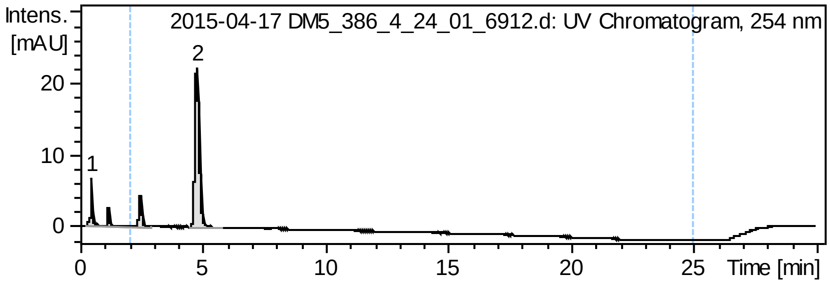
($CDCl_3$, 126 MHz)

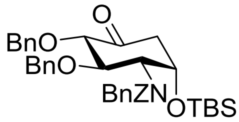


5

HMQC Spectrum

($CDCl_3$, 500 MHz)





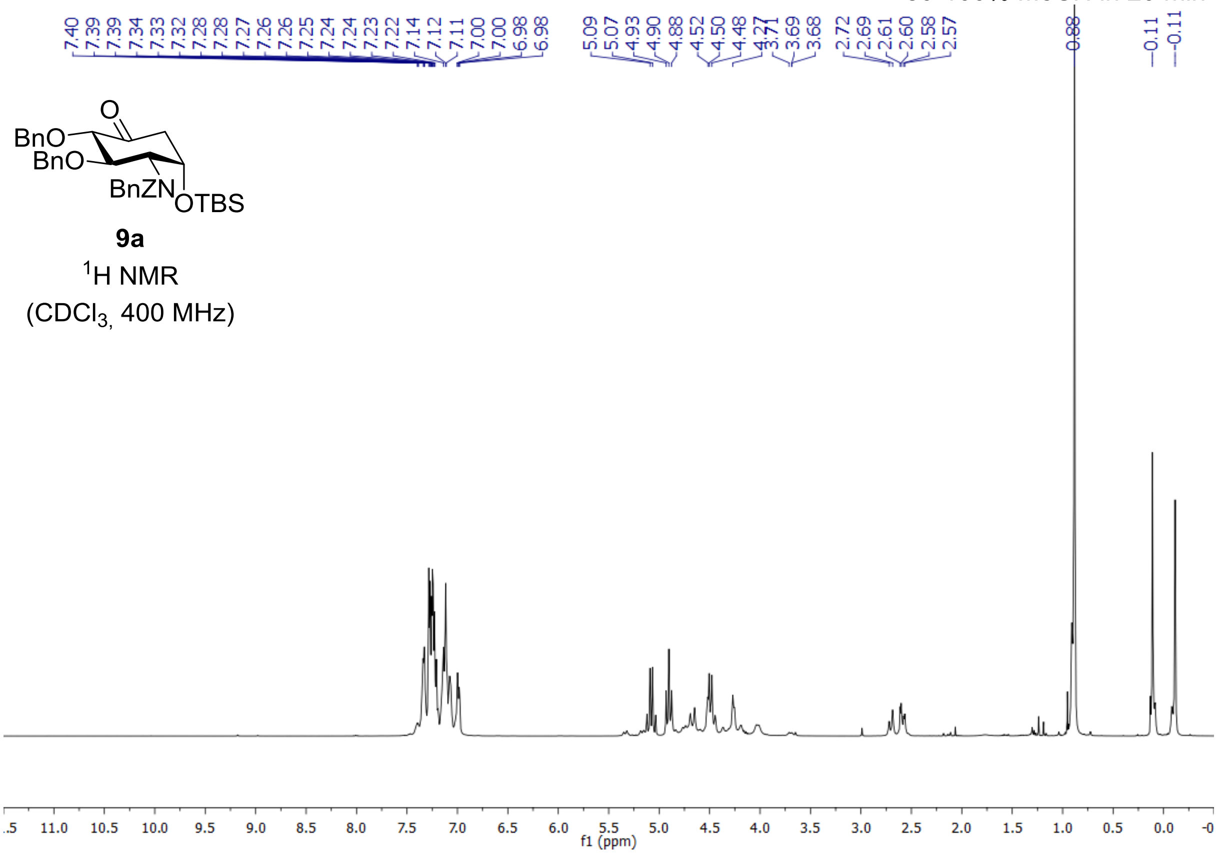
9a

HPLC

ZORBAX SB-C18, 5 µm,

0.4 mL/min,

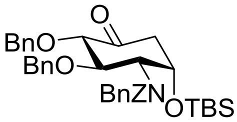
80-100% MeCN in 20 min



9a

^1H NMR

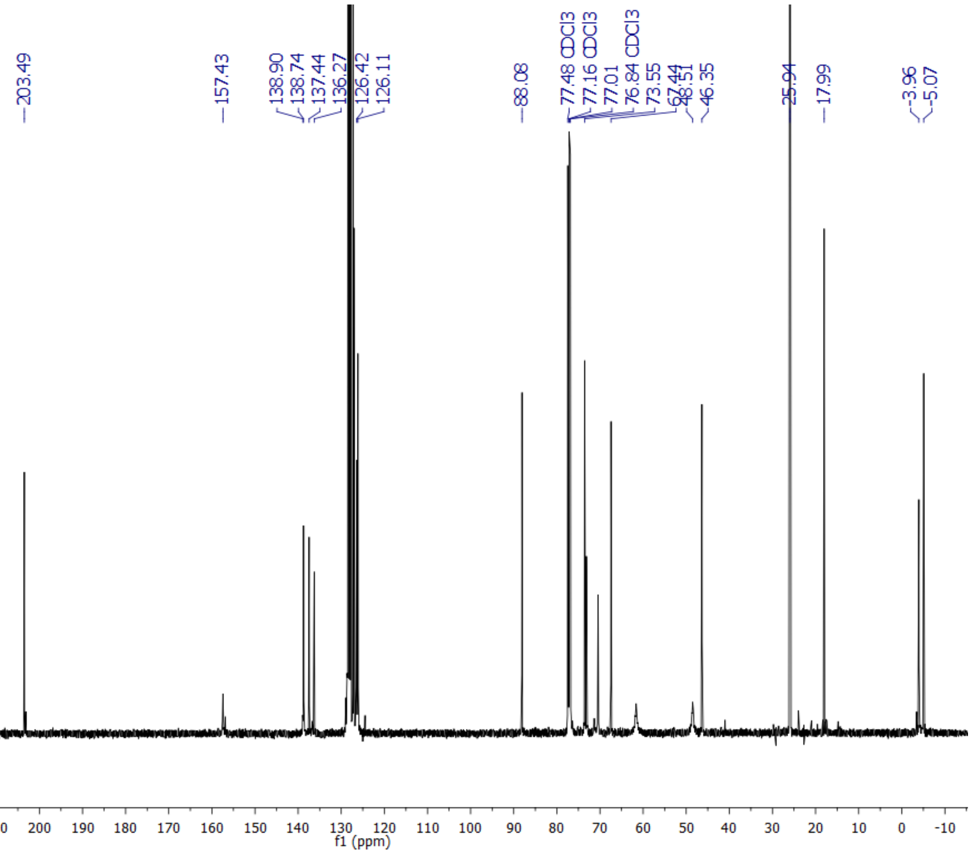
($CDCl_3$, 400 MHz)

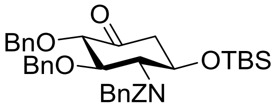


9a

^{13}C NMR

($CDCl_3$, 100 MHz)

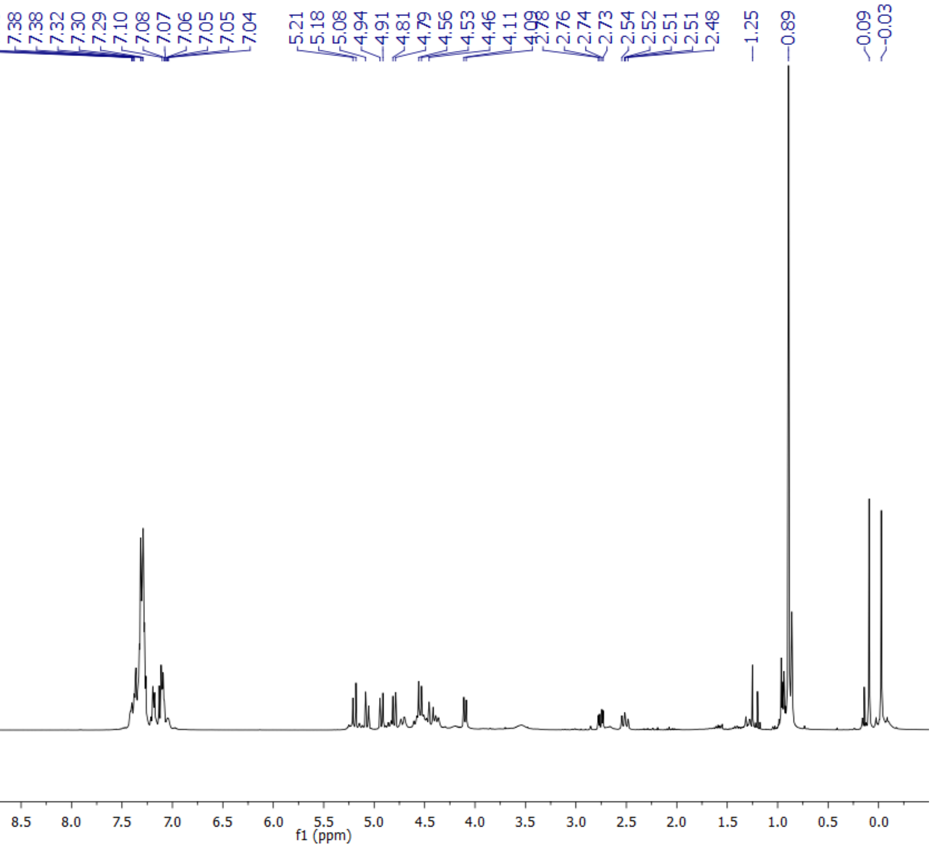


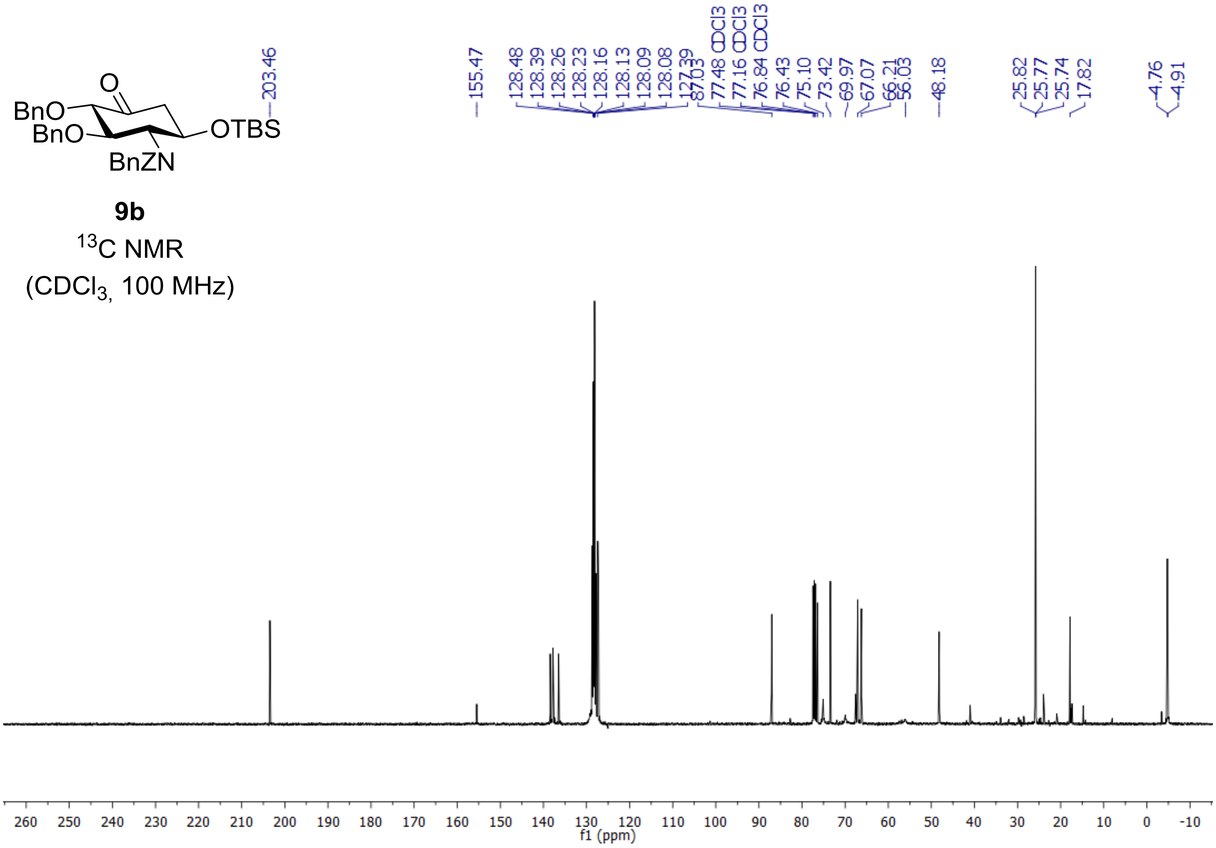


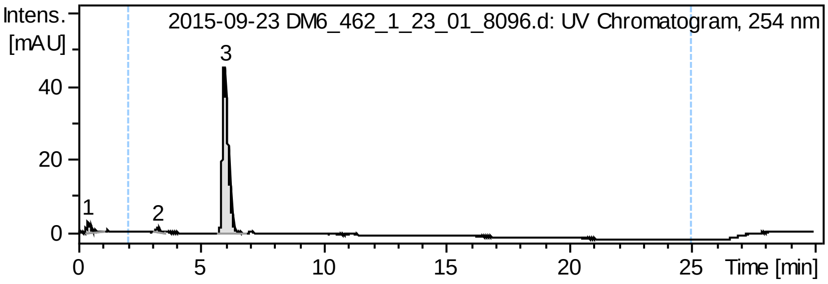
9b

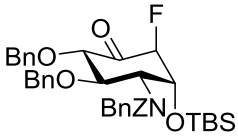
^{1}H NMR

($CDCl_3$, 400 MHz)




BnO
BnO
O
OTBS
BnZN
9b
^{13}C NMR
(CDCl$_3$, 100 MHz)
203.46
155.47
128.48
128.39
128.26
128.23
128.16
128.13
128.09
128.08
127.39
87.03
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
76.43
75.10
73.42
69.97
67.07
66.21
56.03
48.18
25.82
25.77
25.74
17.82
-4.76
-4.91
f1 (ppm)





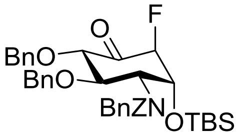
10

HPLC

ZORBAX SB-C18, 5 μm,

0.4 mL/min,

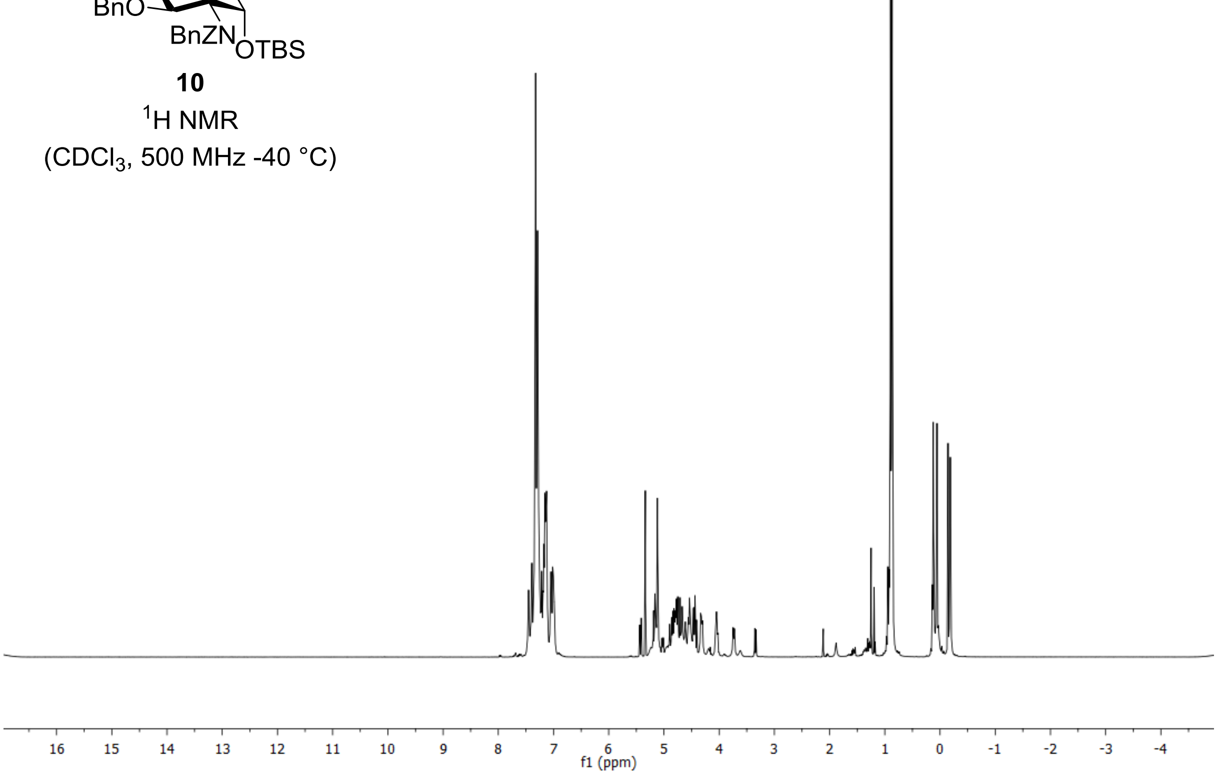
80-100% MeCN in 20 min

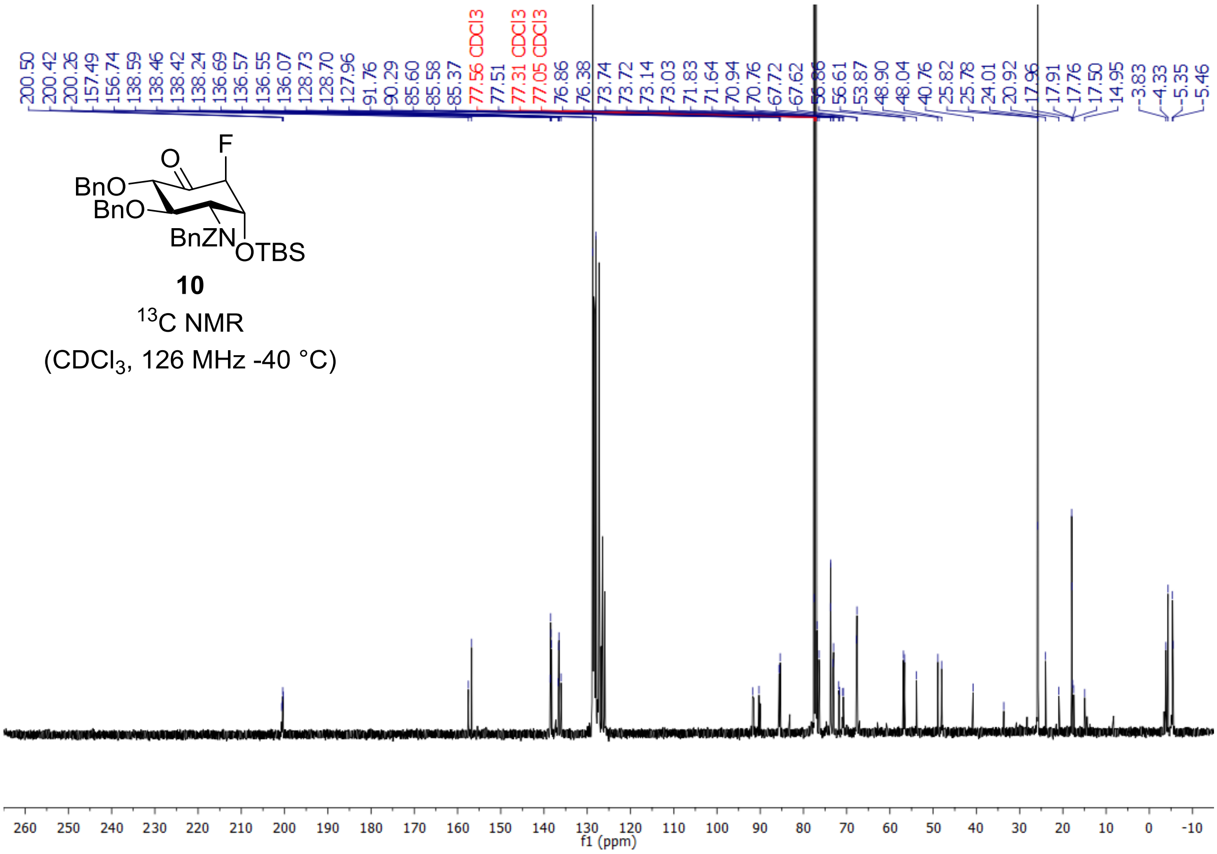


10

^{1}H NMR

($CDCl_3$, 500 MHz -40 °C)

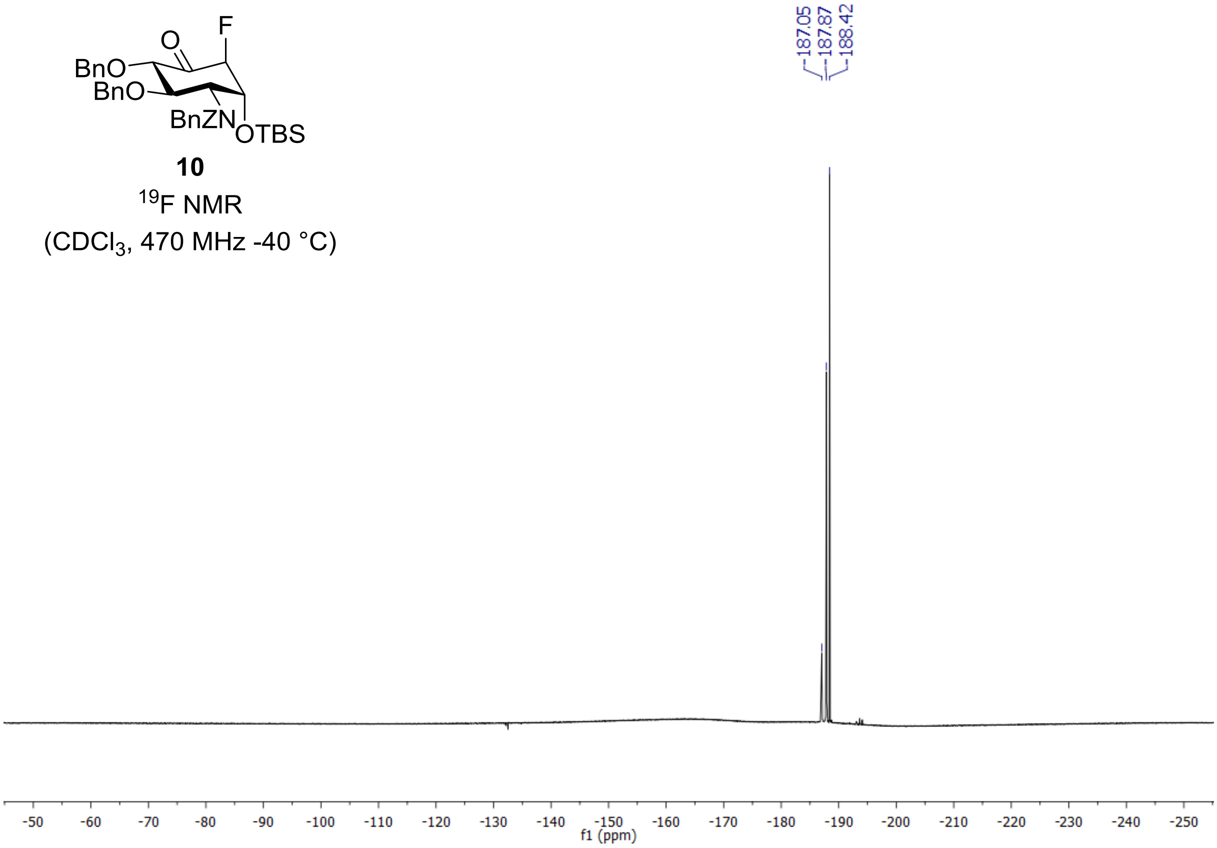




10

^{13}C NMR

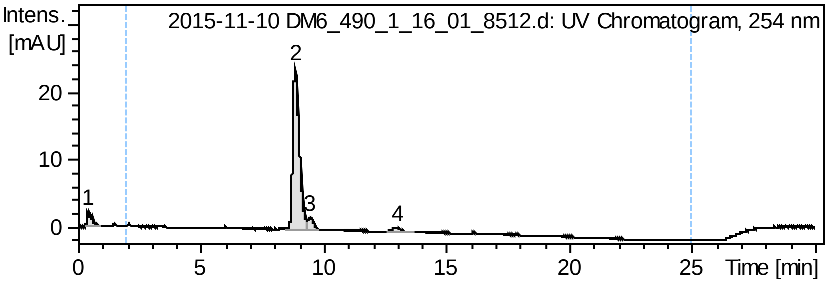
($CDCl_3$, 126 MHz -40 °C)

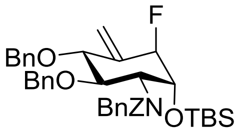


10

^{19}F NMR

($CDCl_3$, 470 MHz -40 °C)





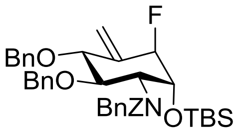
4

HPLC

ZORBAX SB-C18, 5 μm,

0.4 mL/min,

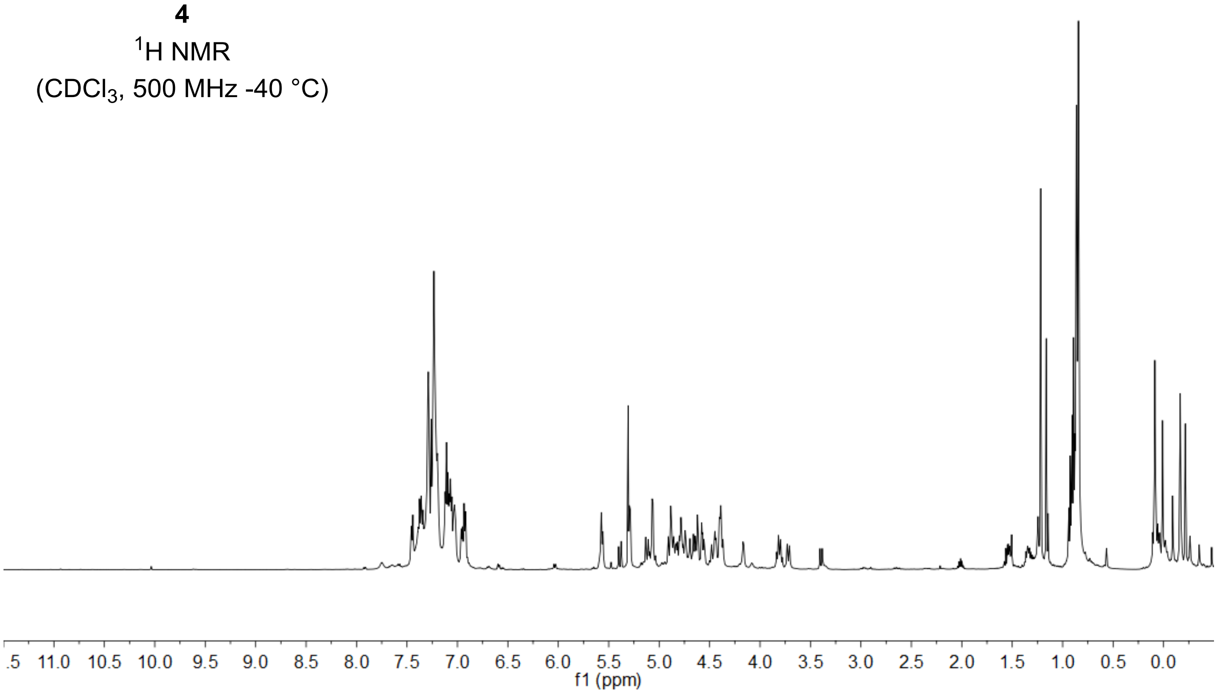
80-100% MeCN in 20 min

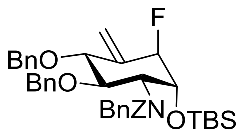


4

^{1}H NMR

($CDCl_3$, 500 MHz -40 °C)

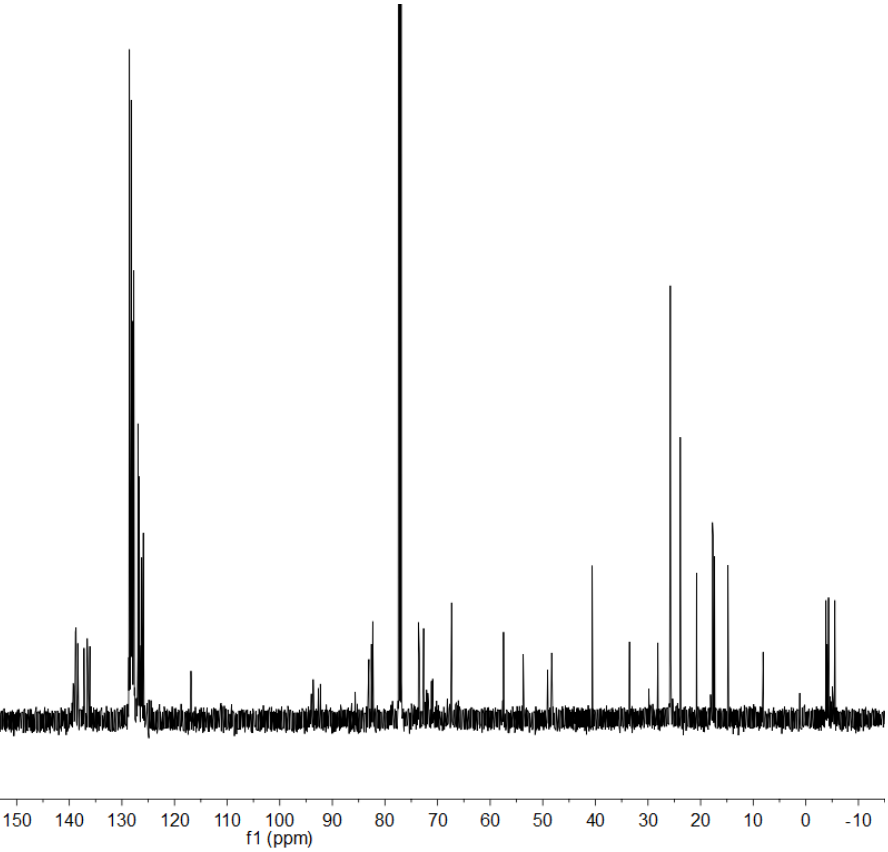


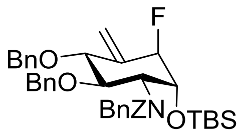


4

^{13}C NMR

($CDCl_3$, 126 MHz -40 °C)

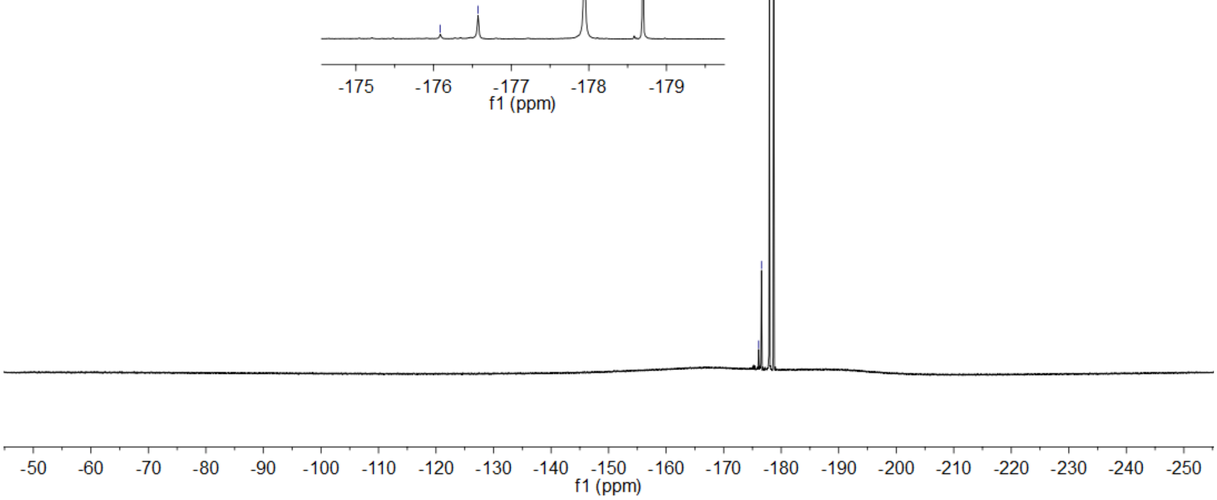


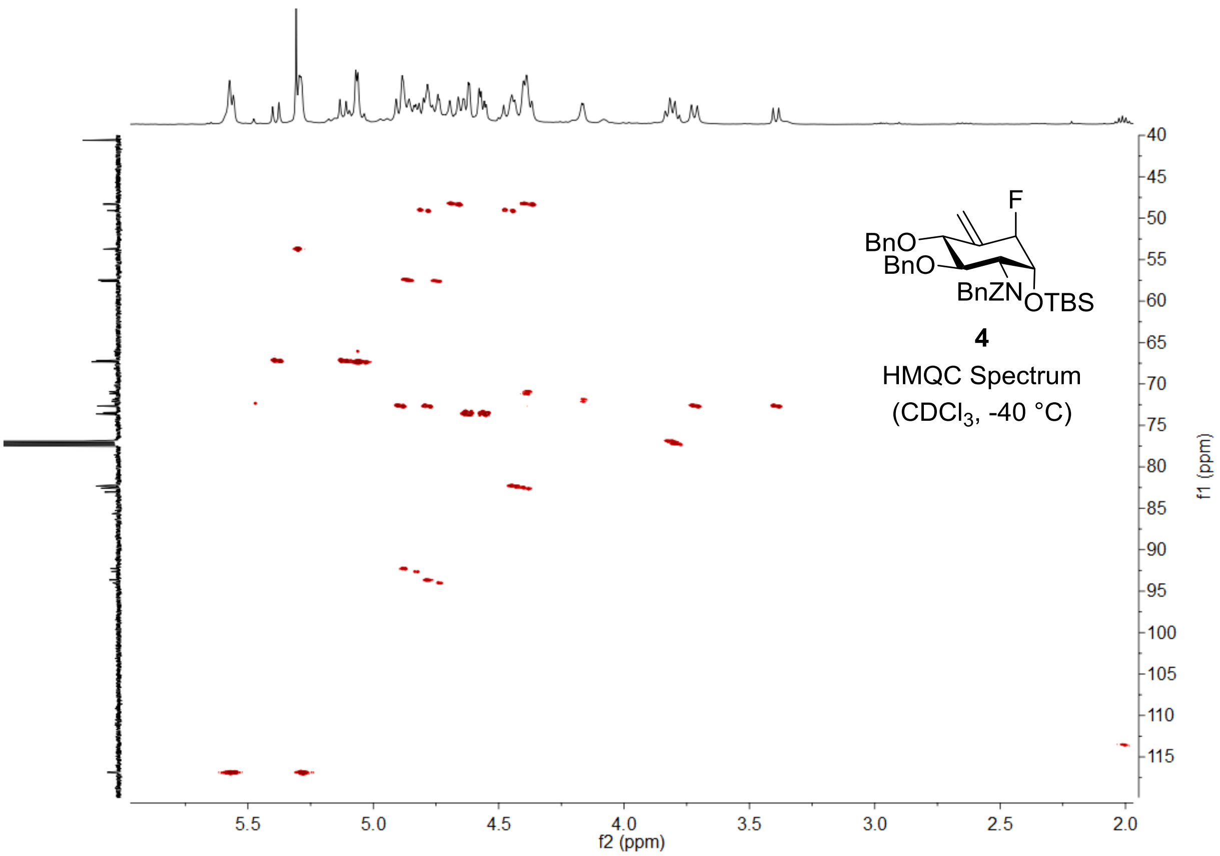


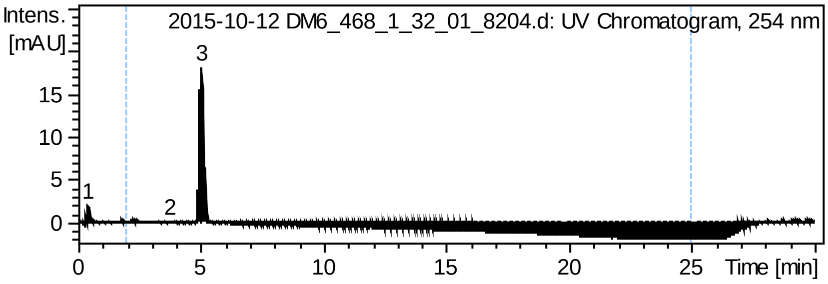
4

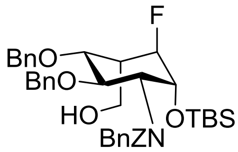
^{19}F NMR (^1H-decoupled)

($CDCl_3$, 471 MHz -40 °C)




F
BnO
BnO
BnZN
OTBS
4
HMQC Spectrum
(CDCl3, -40 °C)
f1 (ppm)
f2 (ppm)





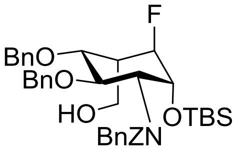
11

HPLC

ZORBAX SB-C18, 5 µm,

0.4 mL/min,

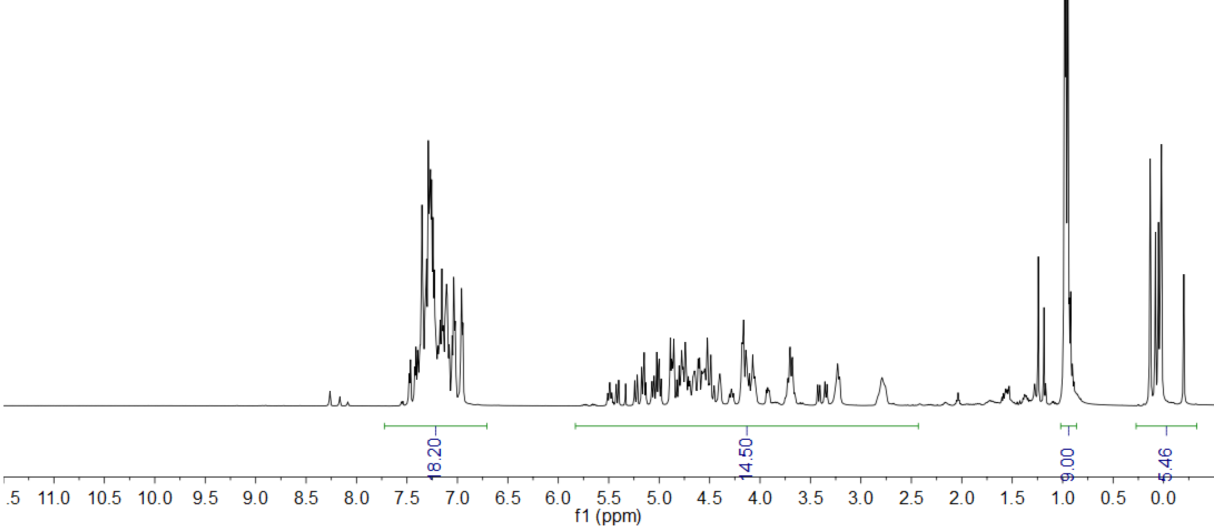
60-80 % MeCN in 20 min

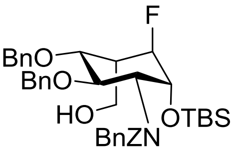


11

^{1}H NMR

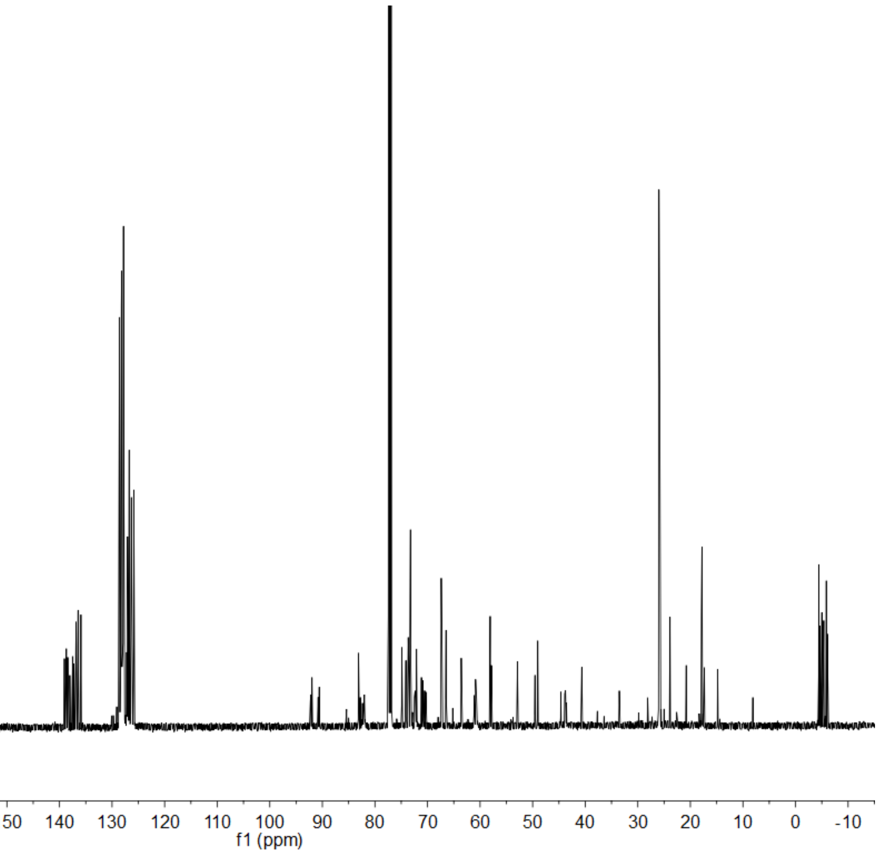
($CDCl_3$, 500 MHz, -40°C)

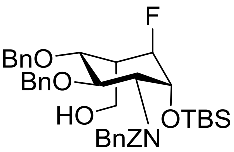




11

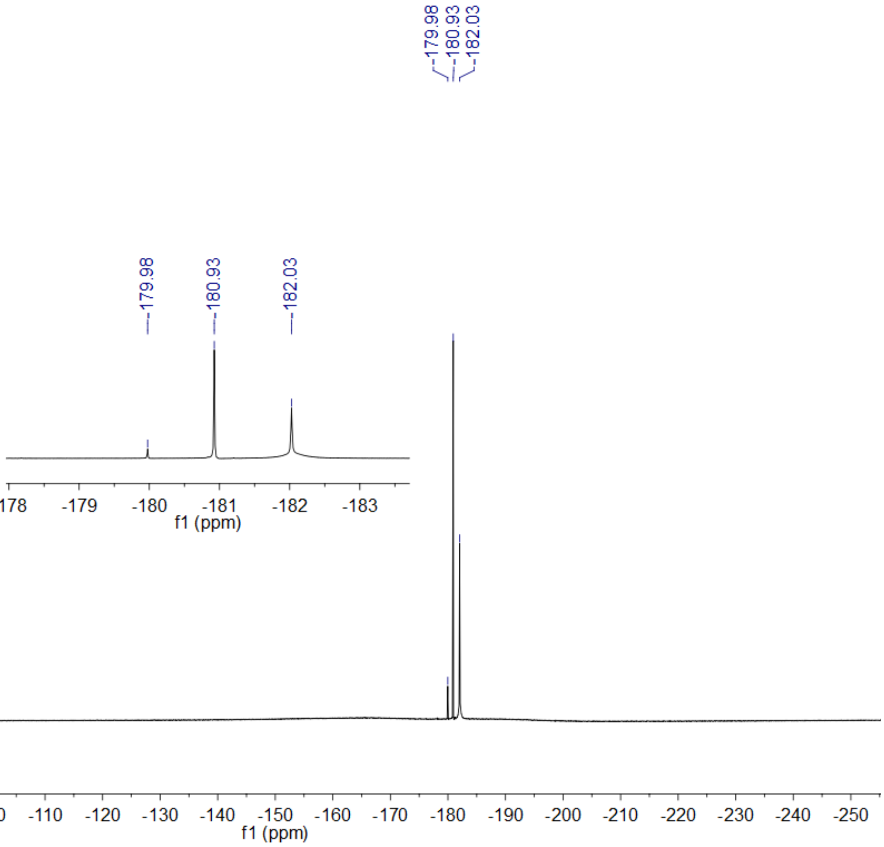
^{13}C NMR
($CDCl_3$, 126 MHz, -40 °C)

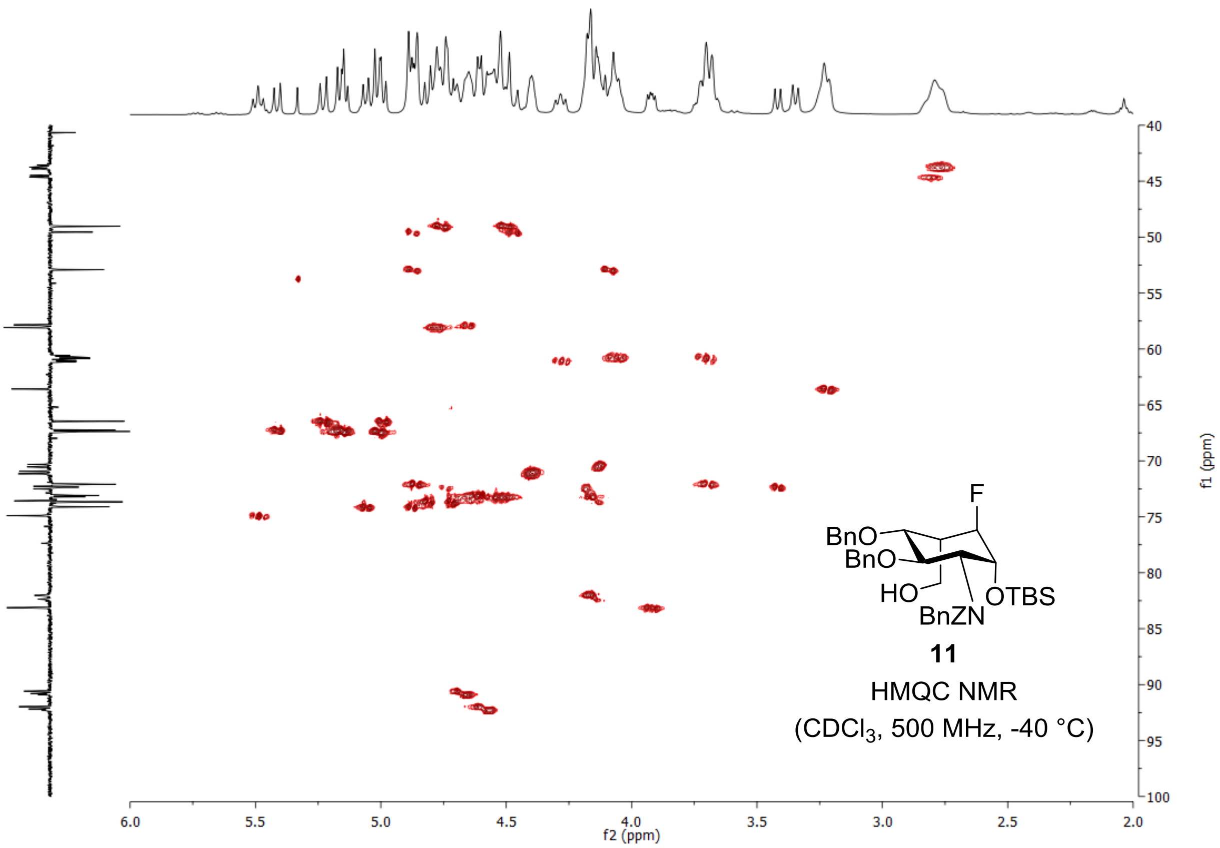




11

^{19}F NMR (^{1}H-decoupled)
($CDCl_3$, 470 MHz, -40 °C)

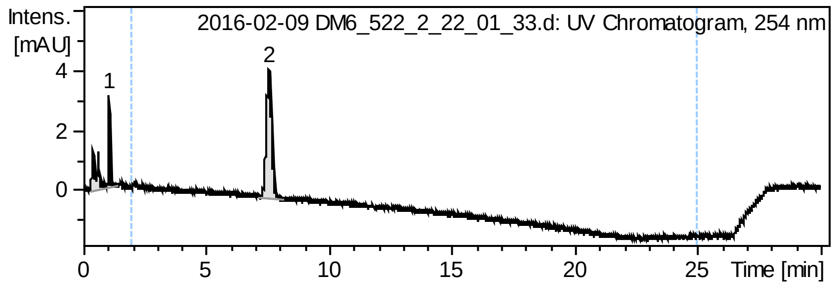


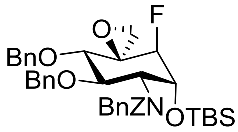


11

HMQC NMR

($CDCl_3$, 500 MHz, -40 °C)





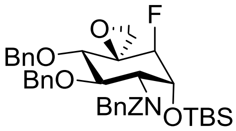
3

HPLC

ZORBAX SB-C18, 5 µm,

0.4 mL/min,

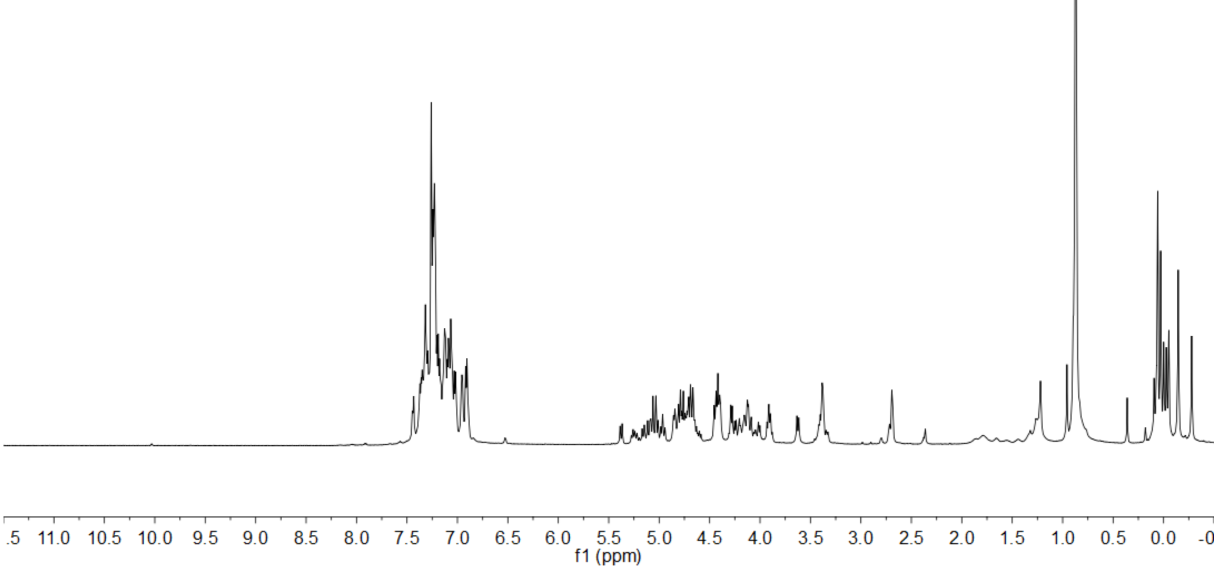
80-100% MeCN in 20 min

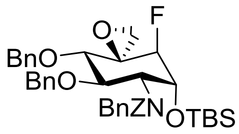


3

^1H NMR

($CDCl_3$, 600 MHz, -40 °C)

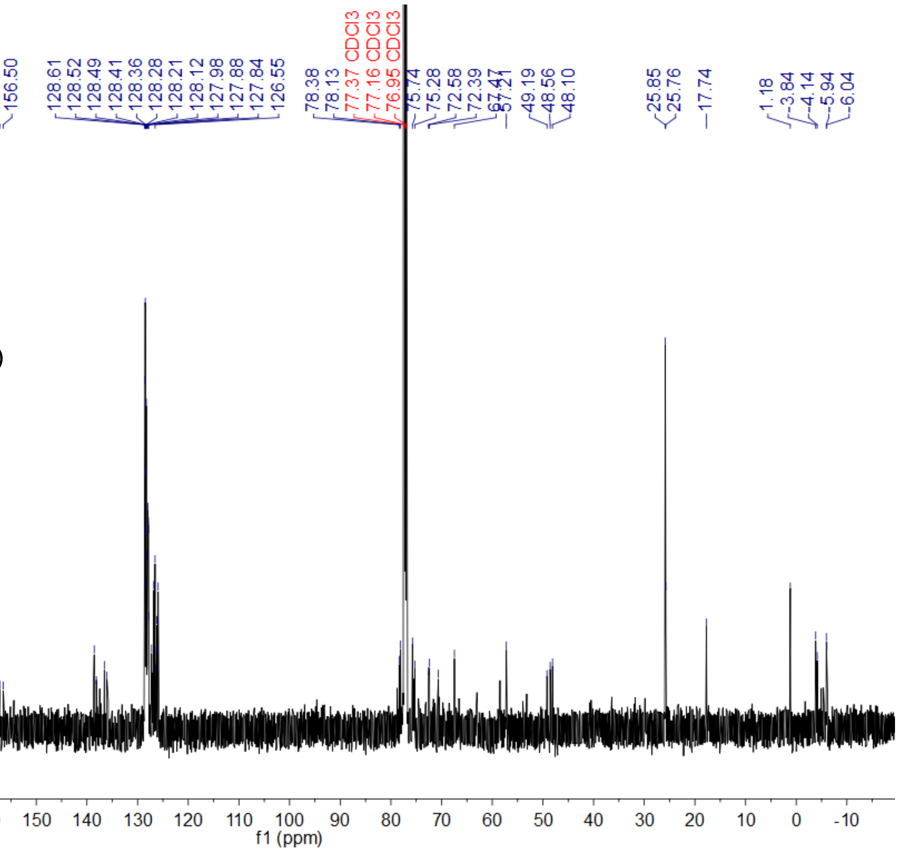


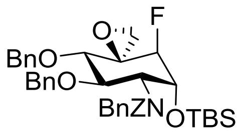


3

^{13}C NMR

(D_2O, 151 MHz, -20 °C)

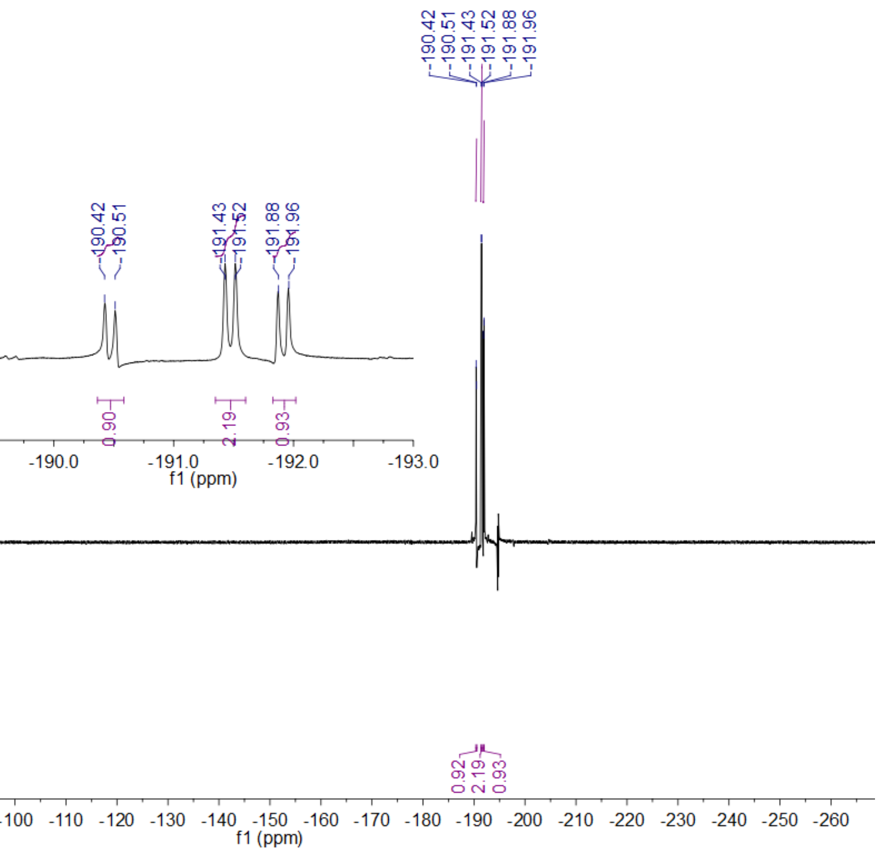


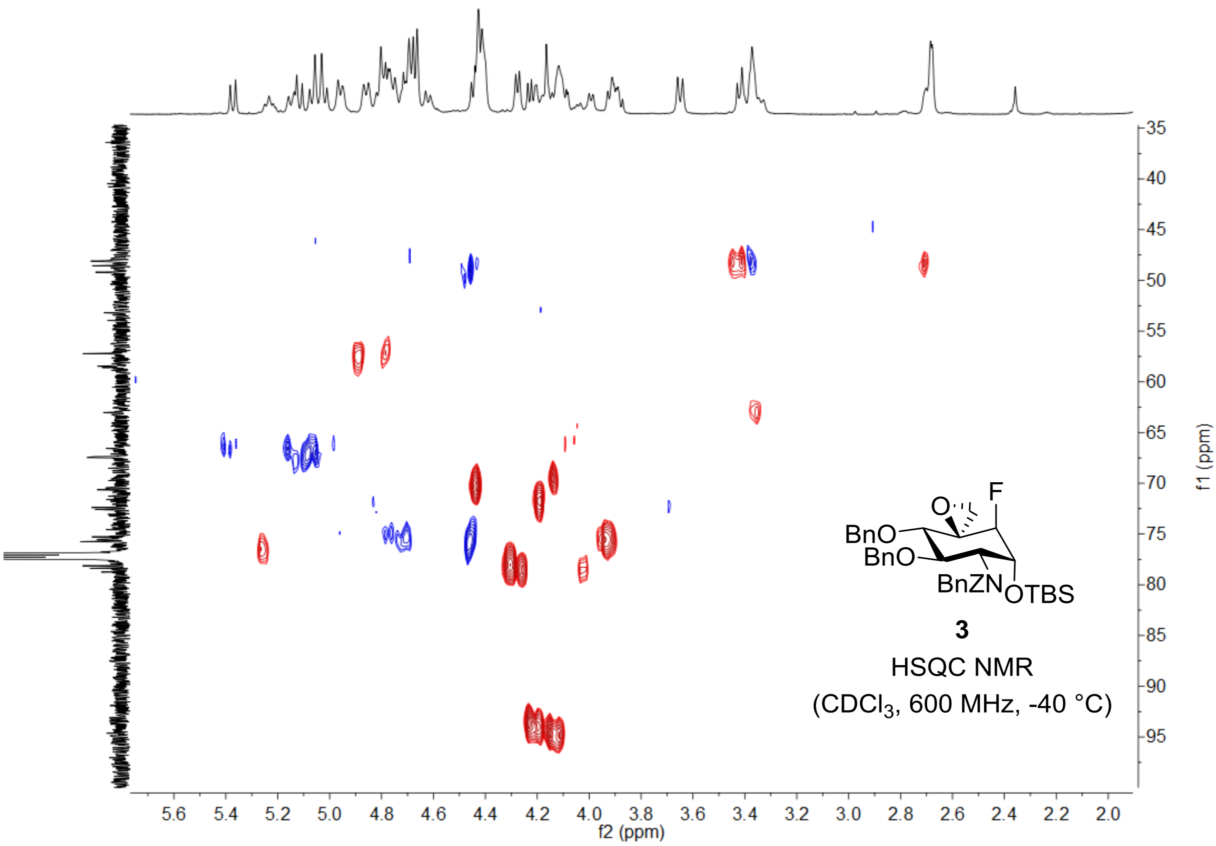


3

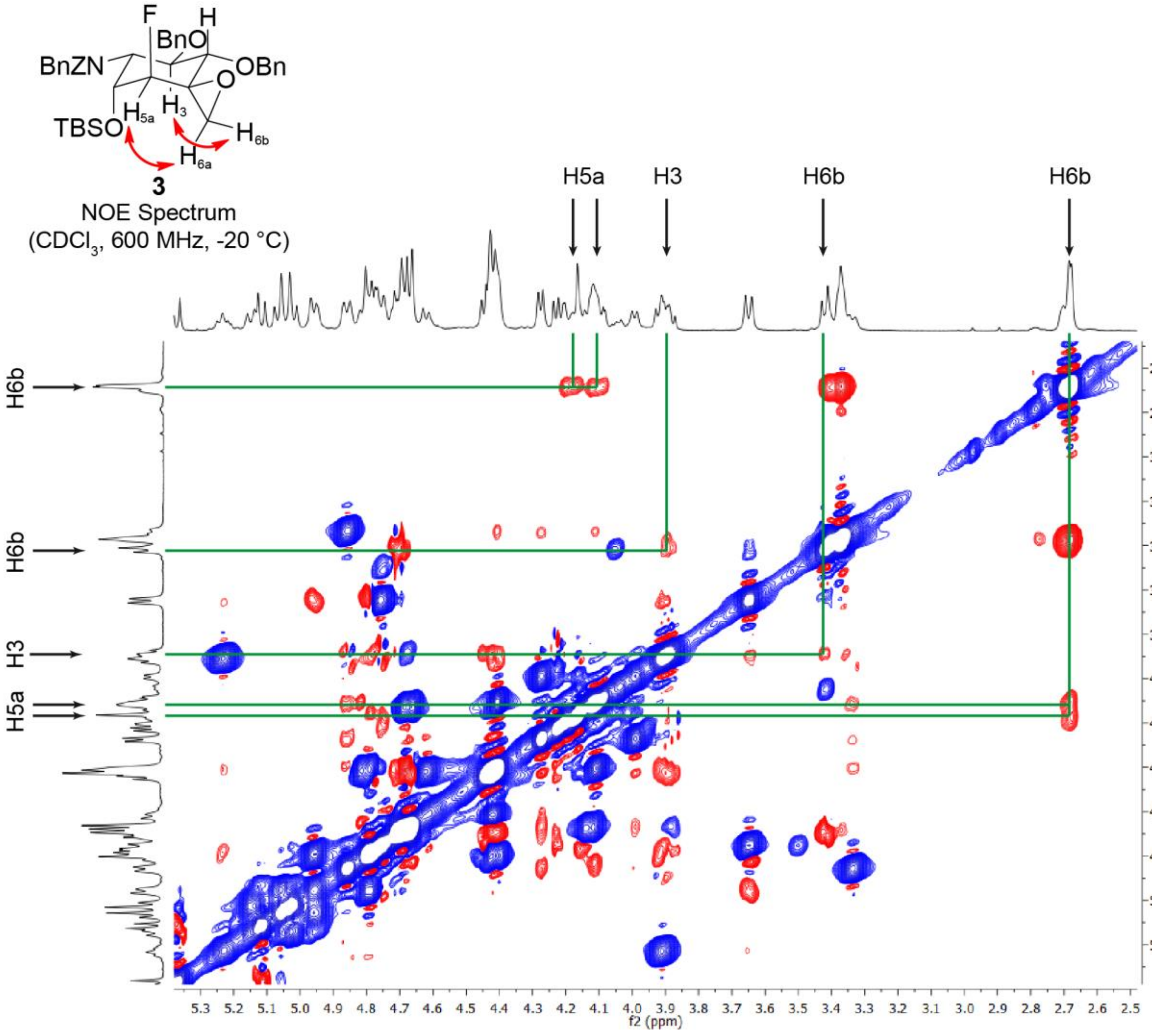
^{19}F NMR (^{1}H-coupled)

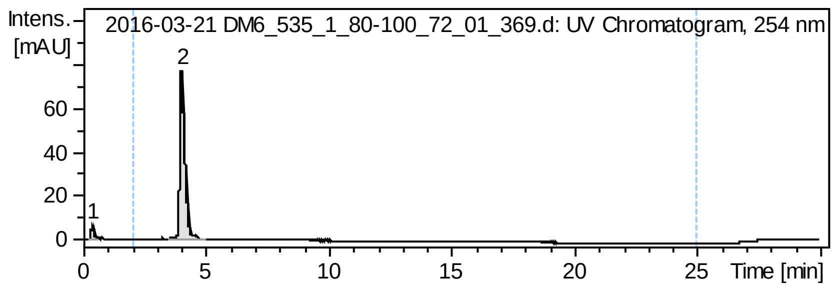
($CDCl_3$, 565 MHz, -40 °C)

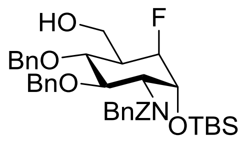




BnO
BnO
O
F
BnZN
OTBS
3
HSQC NMR
($CDCl_3$, 600 MHz, -40 °C)
f1 (ppm)
f2 (ppm)


F
H
BnO
BnZN
OBn
O
TBSO
H_{5a}
H_3
H_{6b}
H_{6a}
3
NOE Spectrum
(CDCl$_3$, 600 MHz, -20 °C)
H5a
H3
H6b
H6b
H6b
H6b
H3
H5a
f1 (ppm)
f2 (ppm)





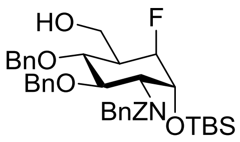
12

HPLC

ZORBAX SB-C18, 5 µm,

0.4 mL/min,

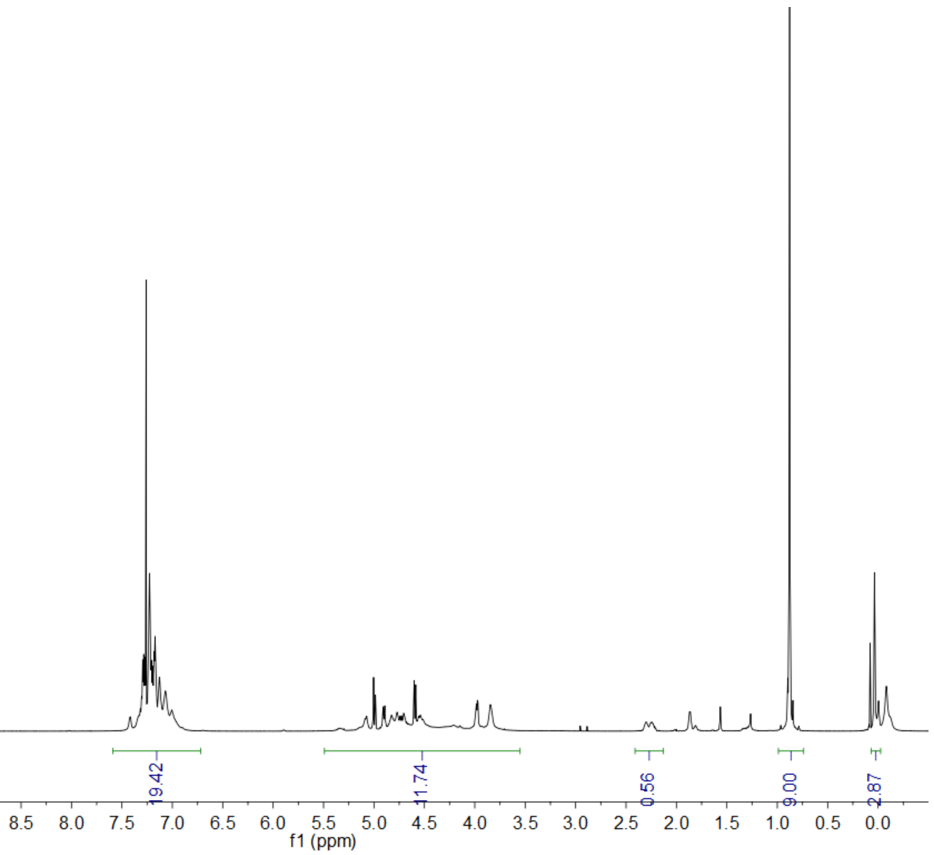
80-100 % MeCN in 20 min

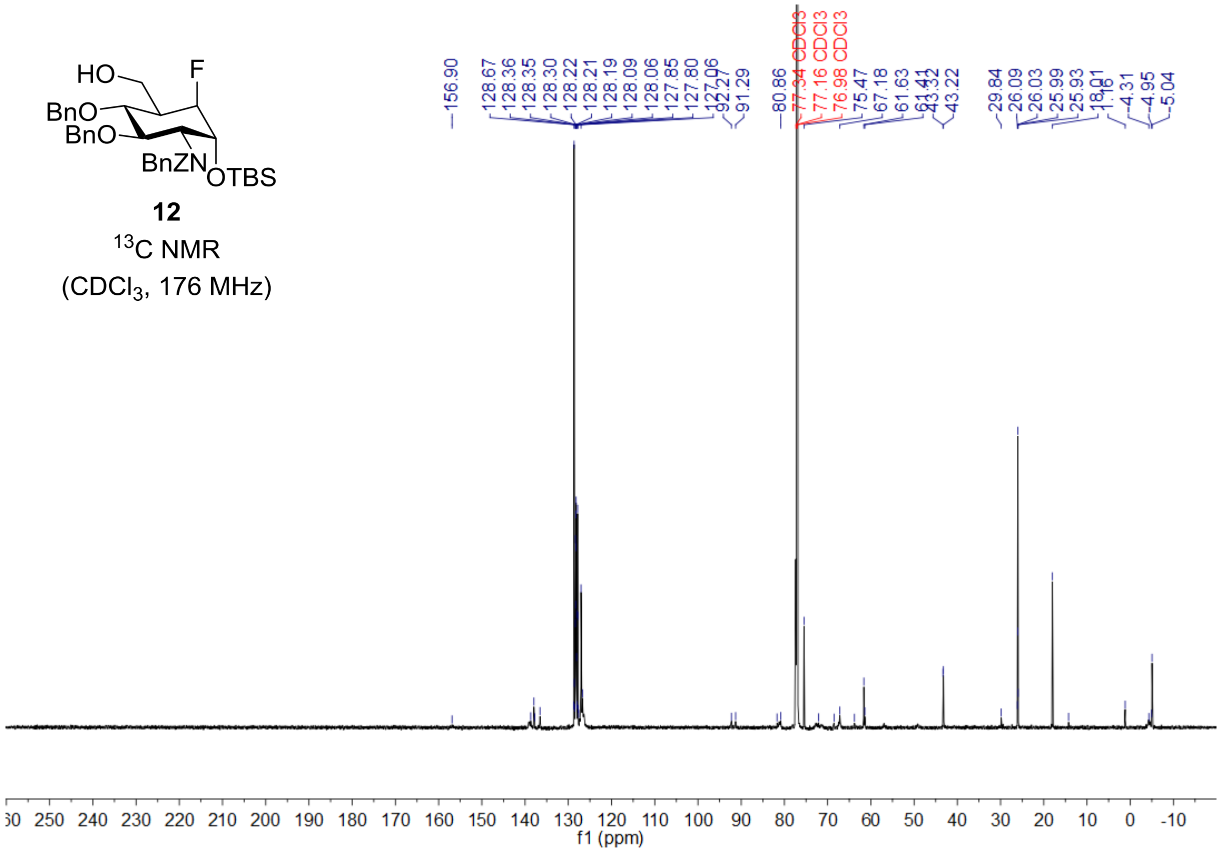


12

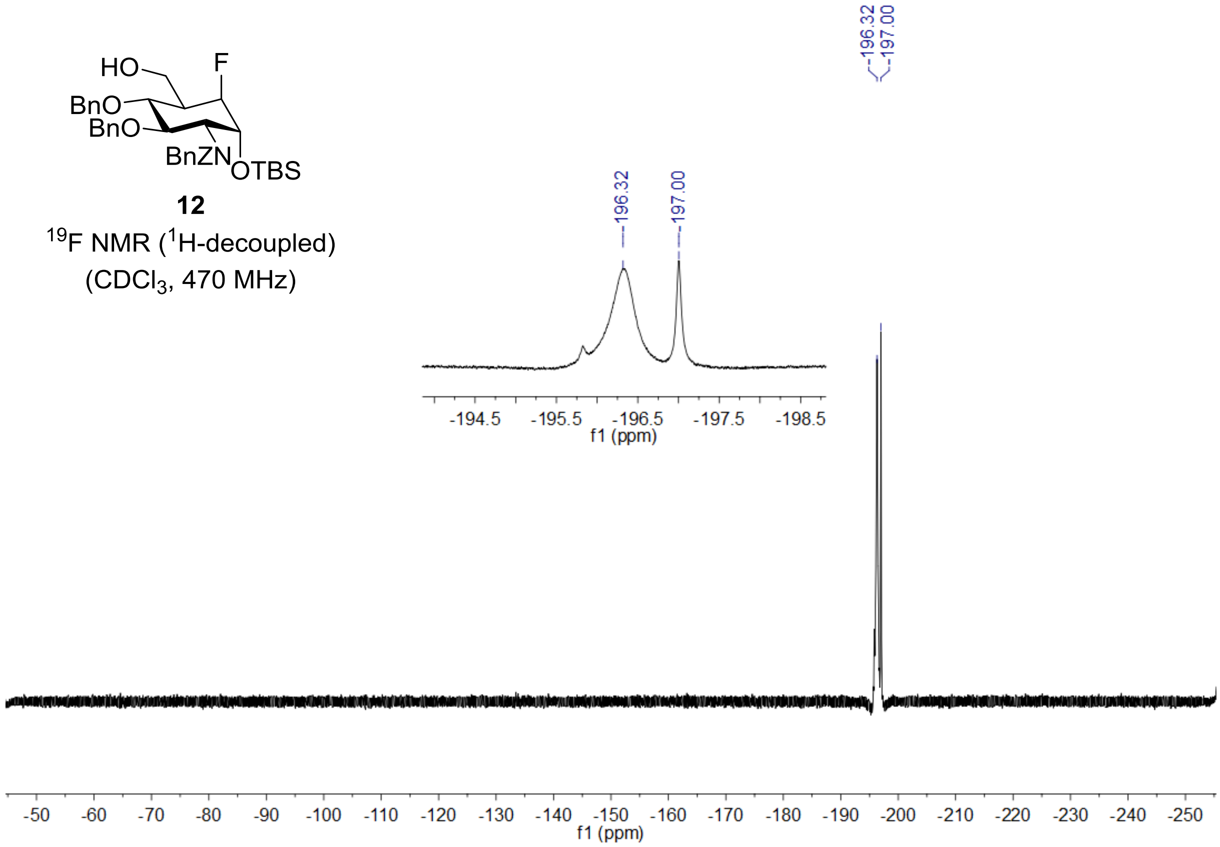
^{1}H NMR

($CDCl_3$, 700 MHz)

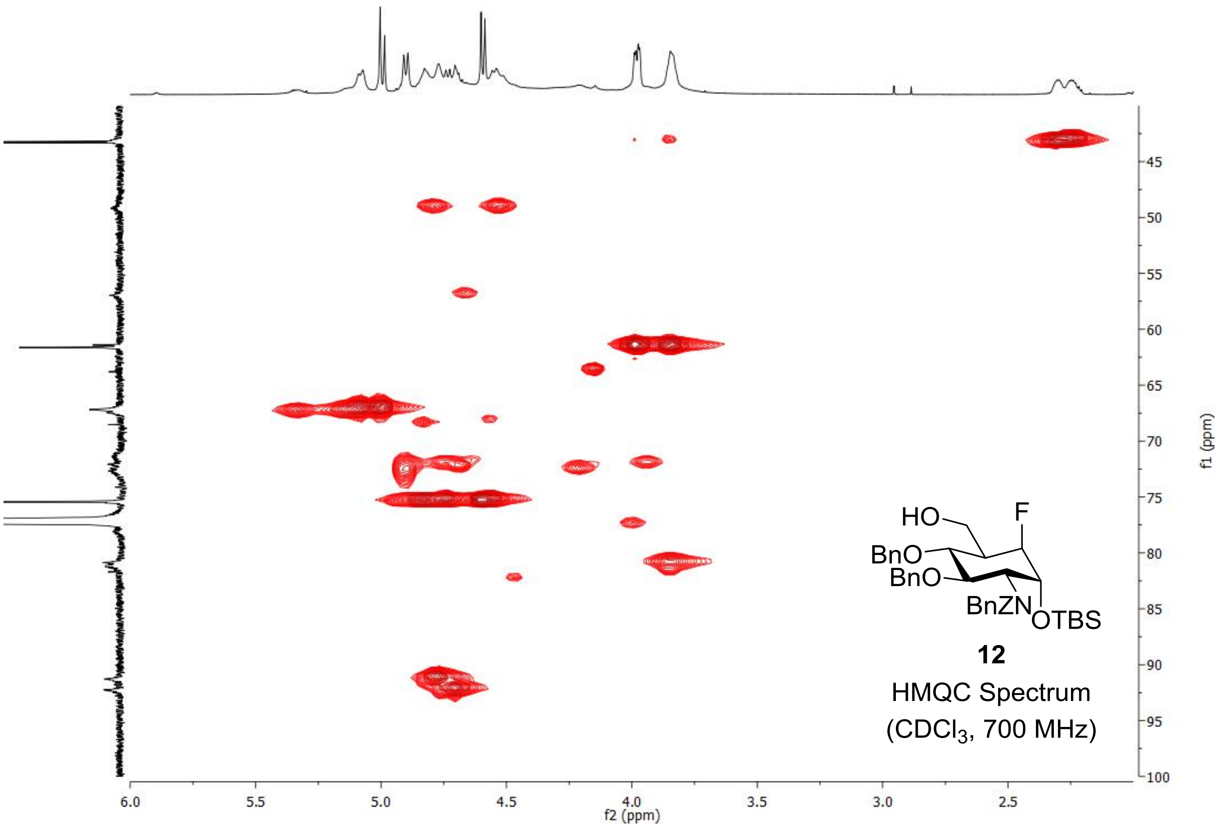




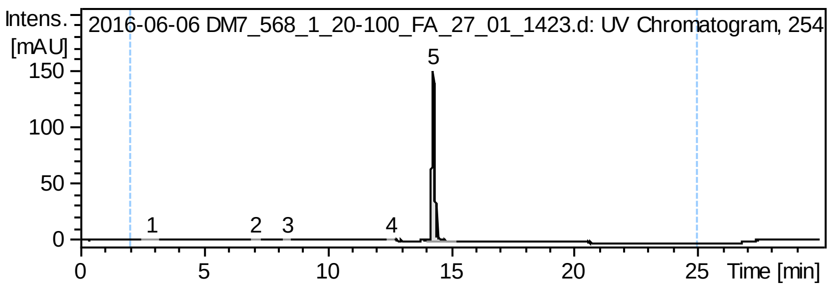
12
^{13}C NMR
($CDCl_3$, 176 MHz)

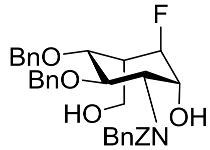


12
^{19}F NMR (^{1}H-decoupled)
($CDCl_3$, 470 MHz)



12
HMQC Spectrum
($CDCl_3$, 700 MHz)





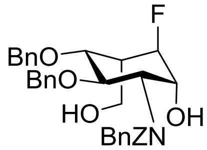
13

HPLC

ZORBAX SB-C18, 5 µm,

0.4 mL/min,

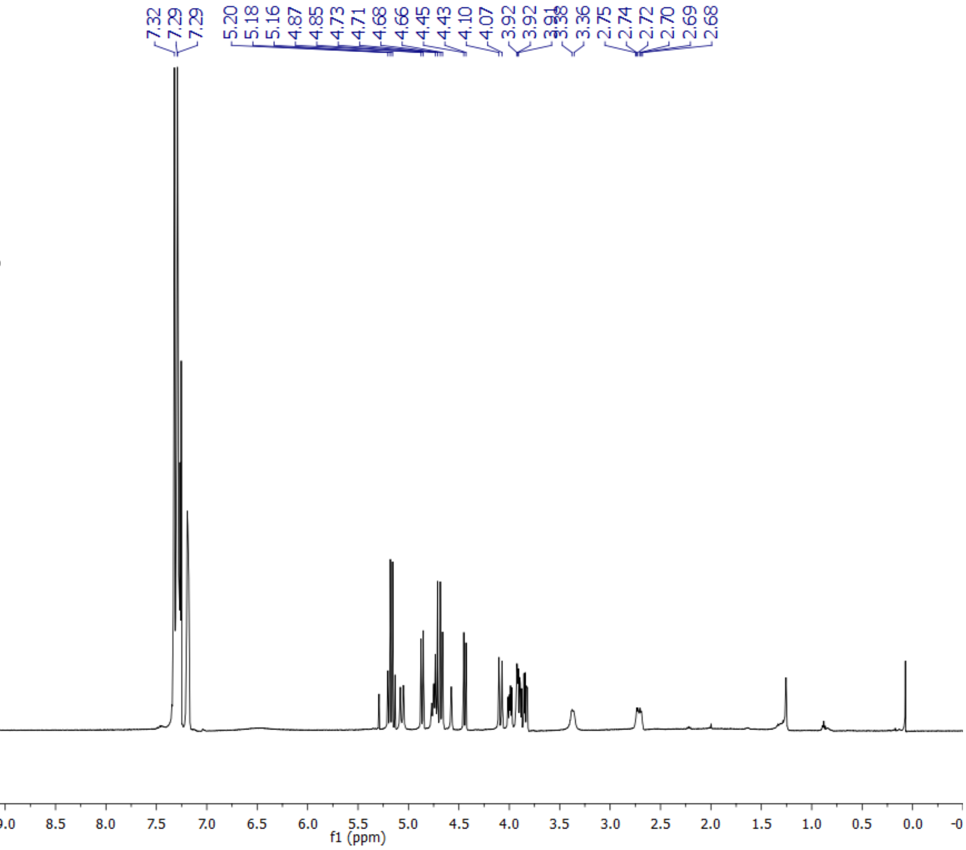
20-100% MeCN in 20 min

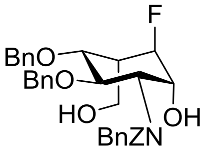


13

^{1}H NMR

($CDCl_3$, 500 MHz)

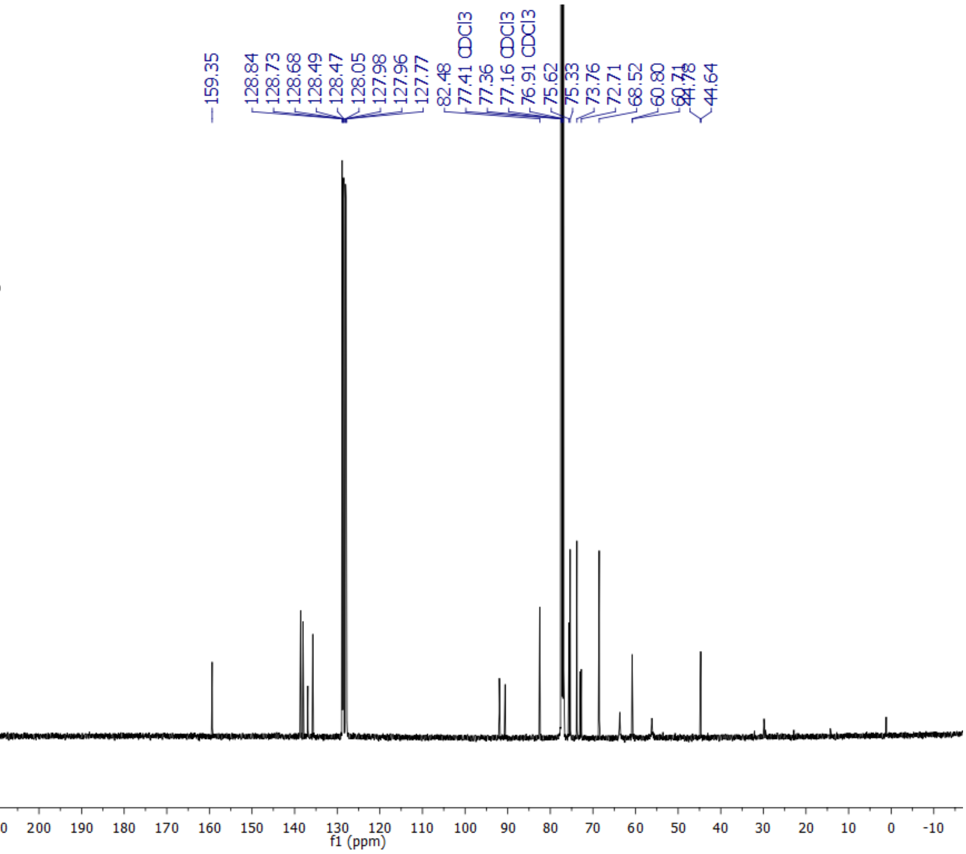


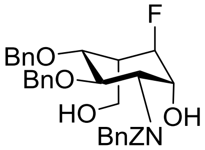


13

^{13}C NMR

($CDCl_3$, 126 MHz)

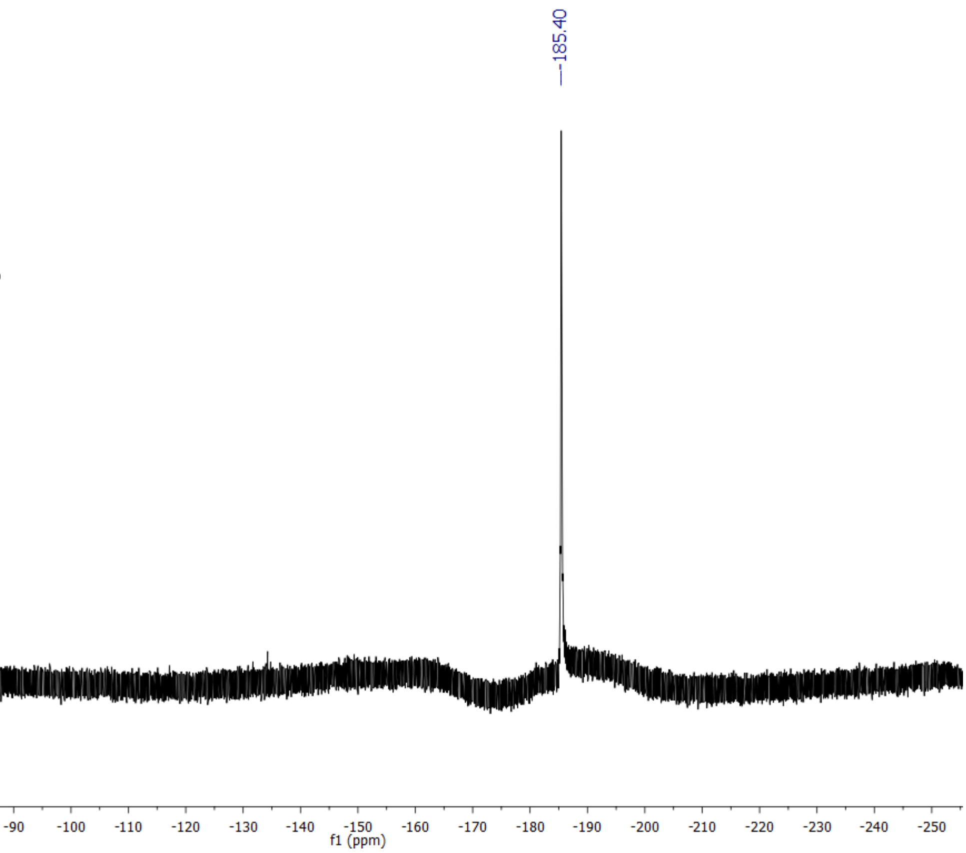


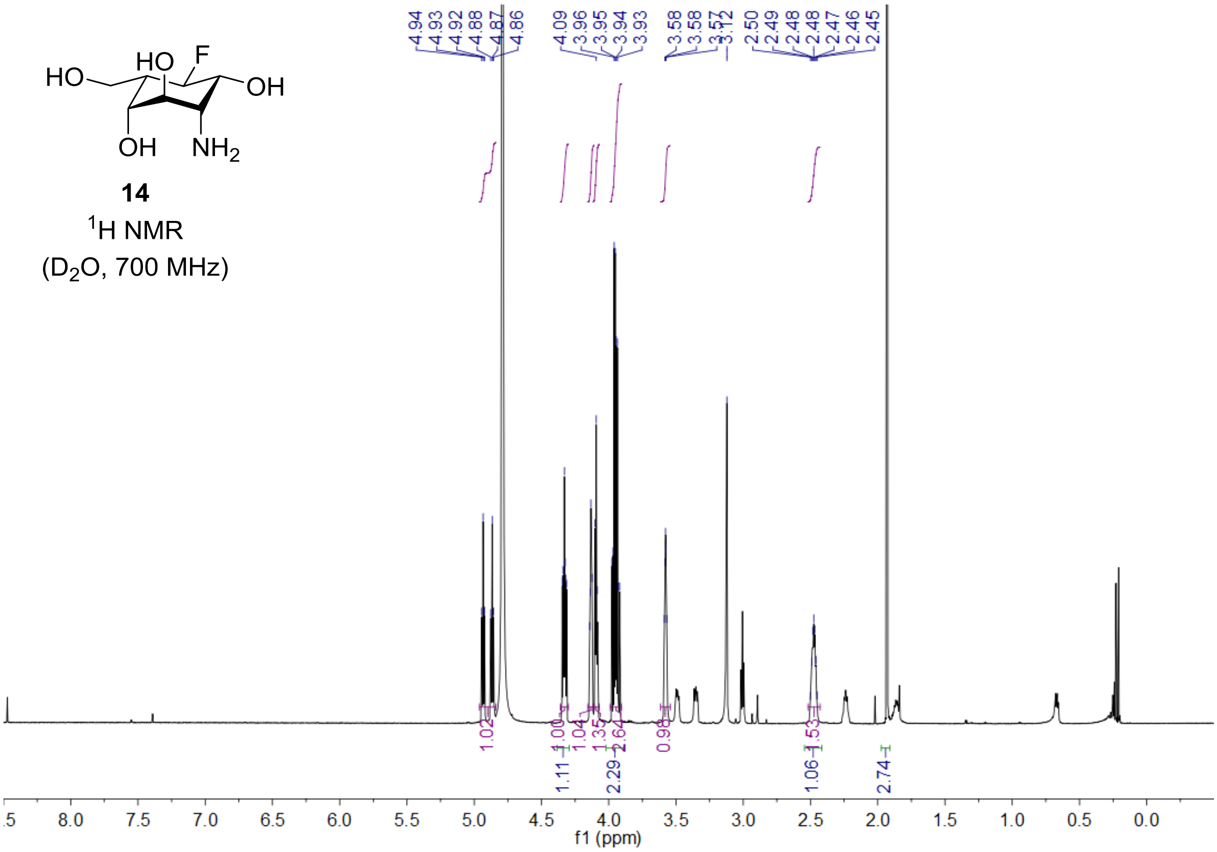


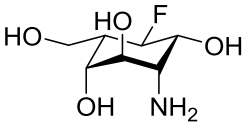
13

^{19}F NMR

($CDCl_3$, 471 MHz)



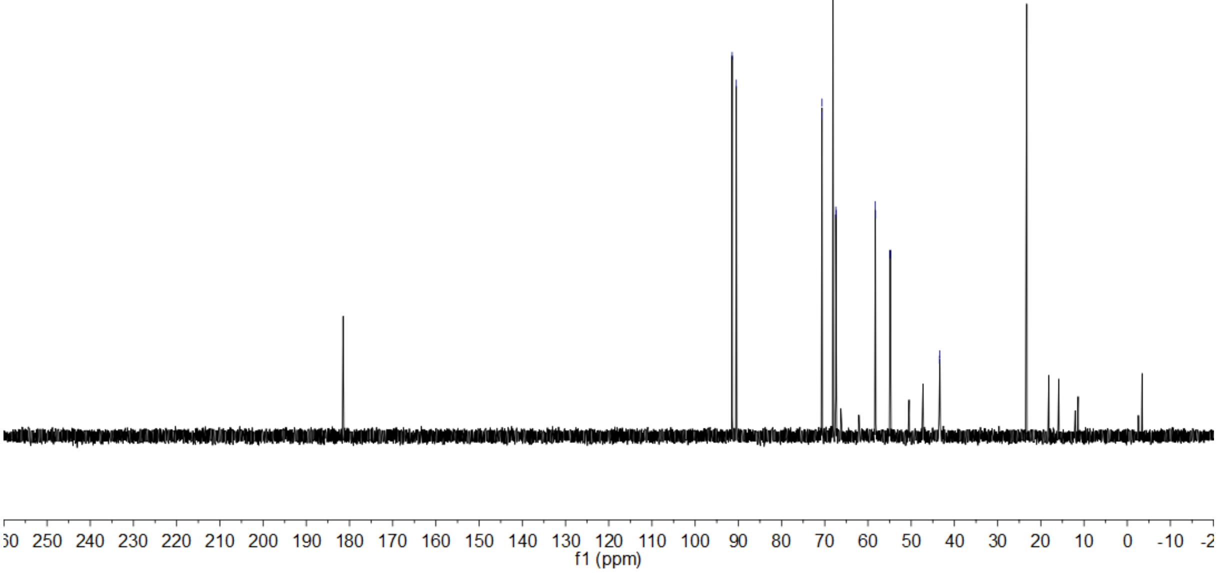

HO
HO
F
OH
OH
NH2
14
1H NMR
(D2O, 700 MHz)
f1 (ppm)

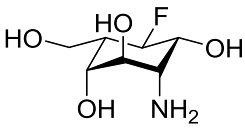


14

^{13}C NMR

(D_2O, 176 MHz)

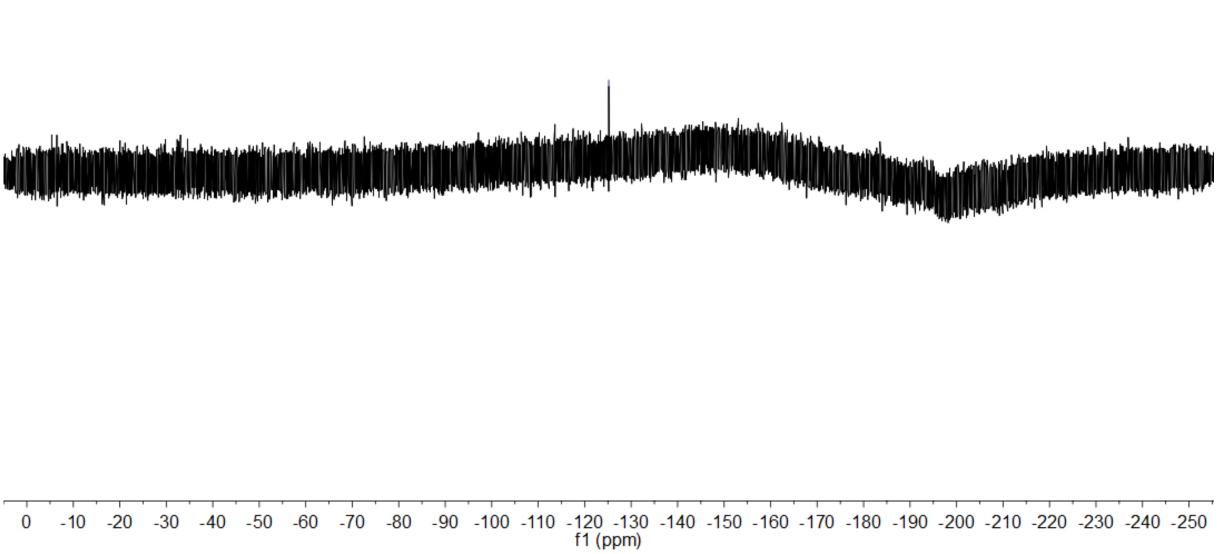


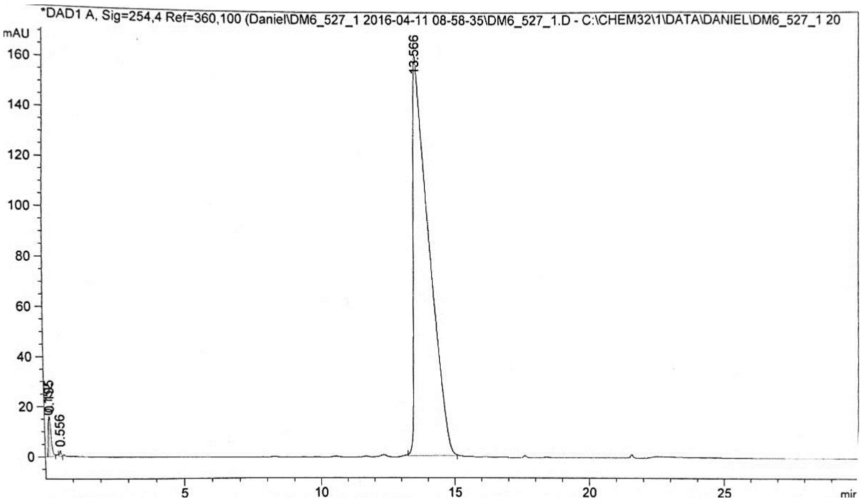


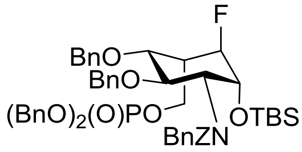
14

^{19}F NMR (^{1}H-decoupled)

(D_2O, 659 MHz)







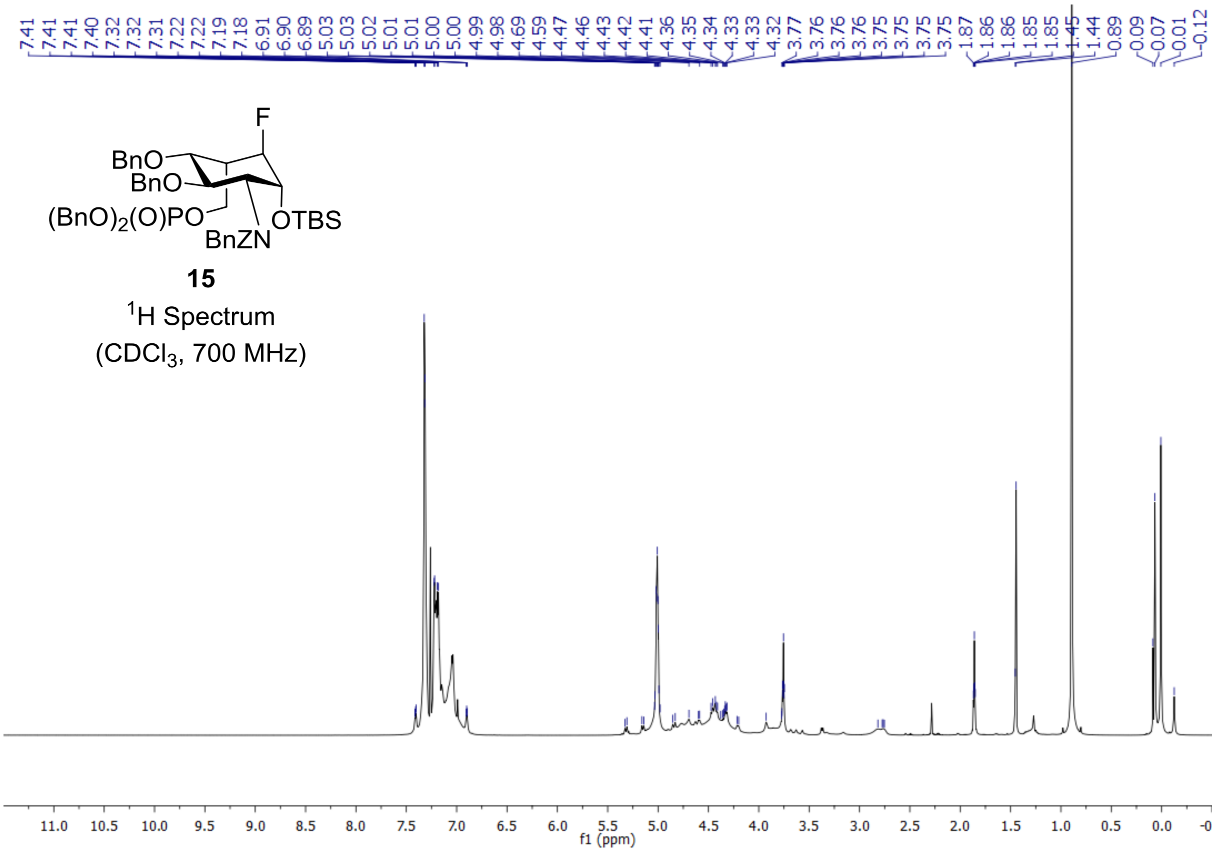
15

HPLC

Kinetex EVO C18, 2.6 µm,

0.8 mL/min,

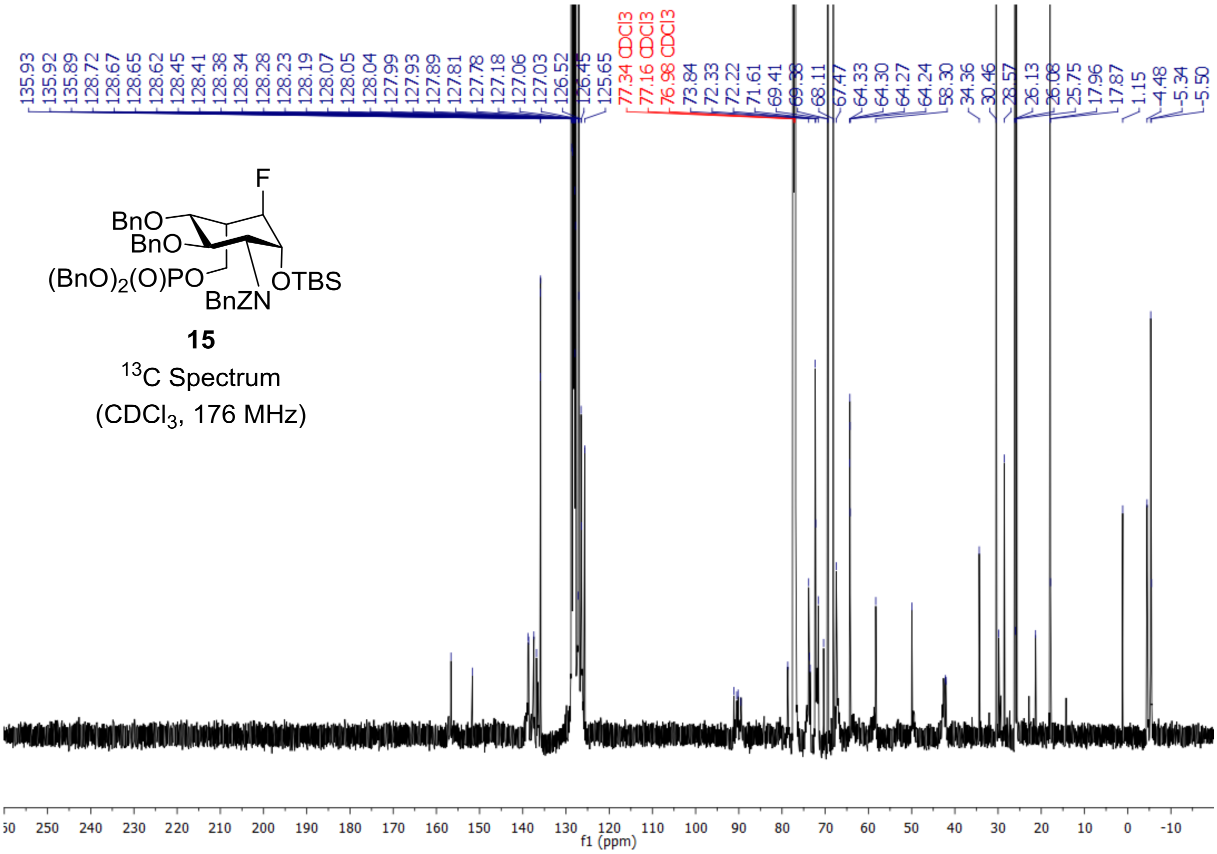
60-80 % MeCN in 15 min

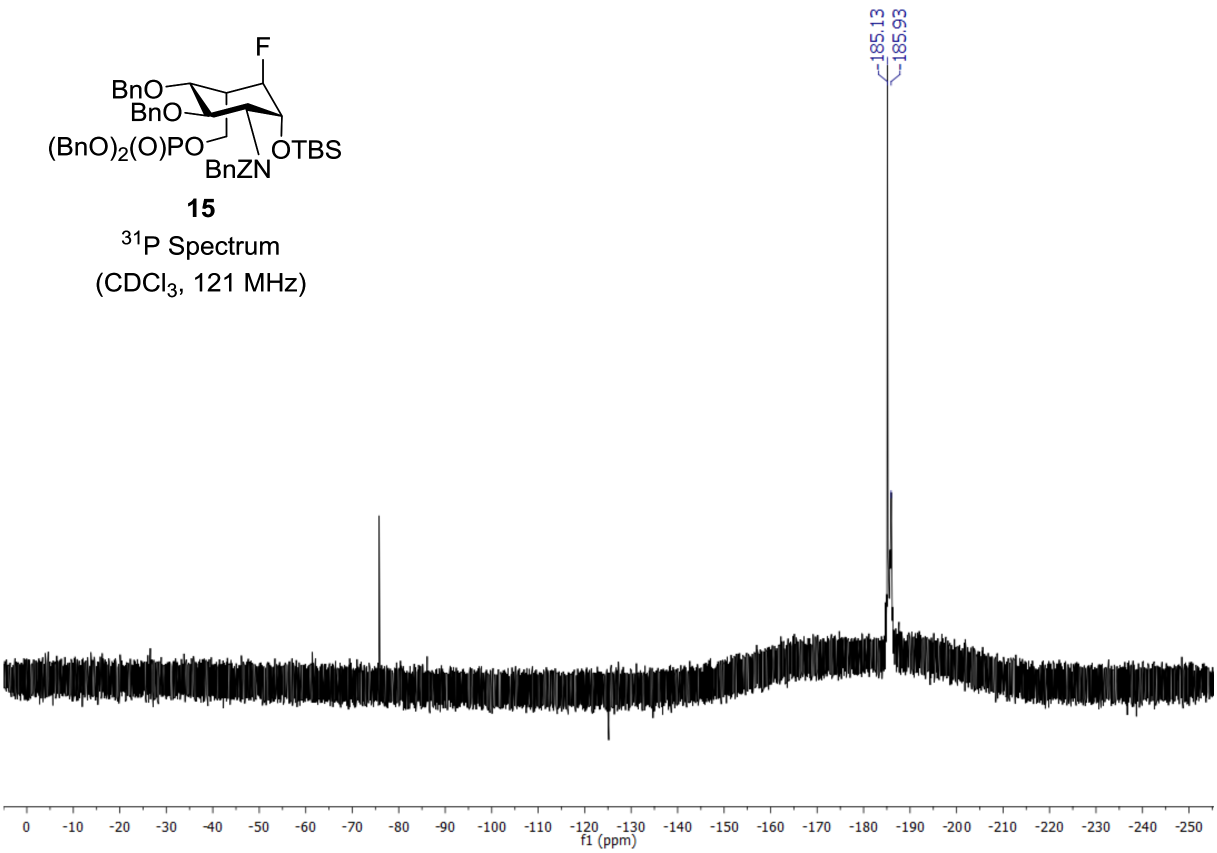


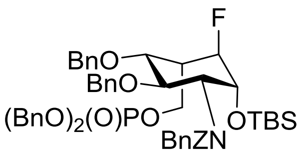
15

^{1}H Spectrum

($CDCl_3$, 700 MHz)


15
^{13}C Spectrum
($CDCl_3$, 176 MHz)
f1 (ppm)

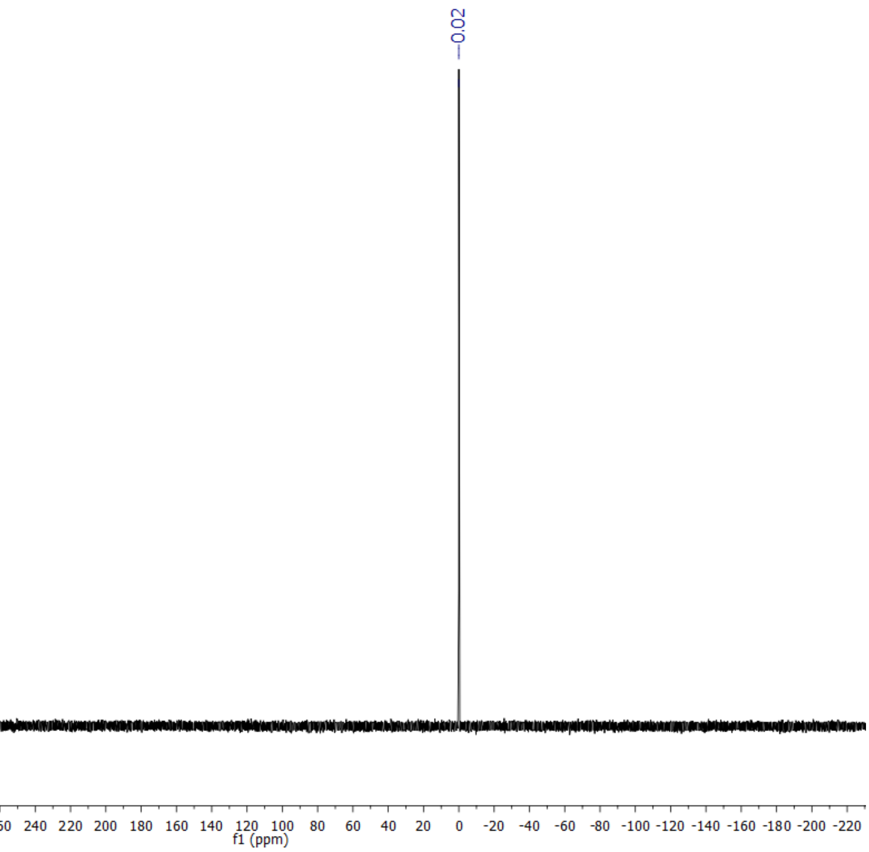

15
^{31}P Spectrum
($CDCl_3$, 121 MHz)
-185.13
-185.93
f1 (ppm)

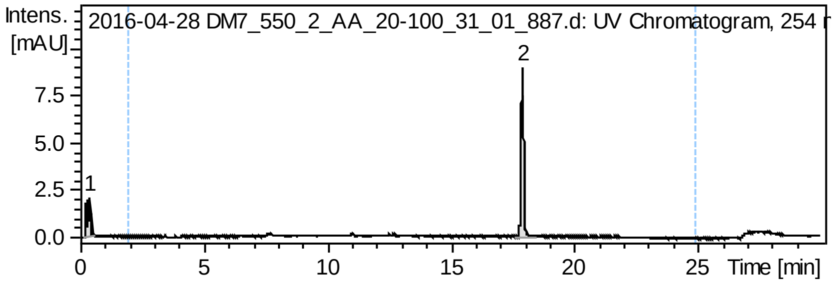


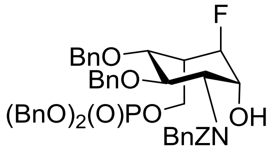
15

^{19}F Spectrum

($CDCl_3$, 282 MHz)







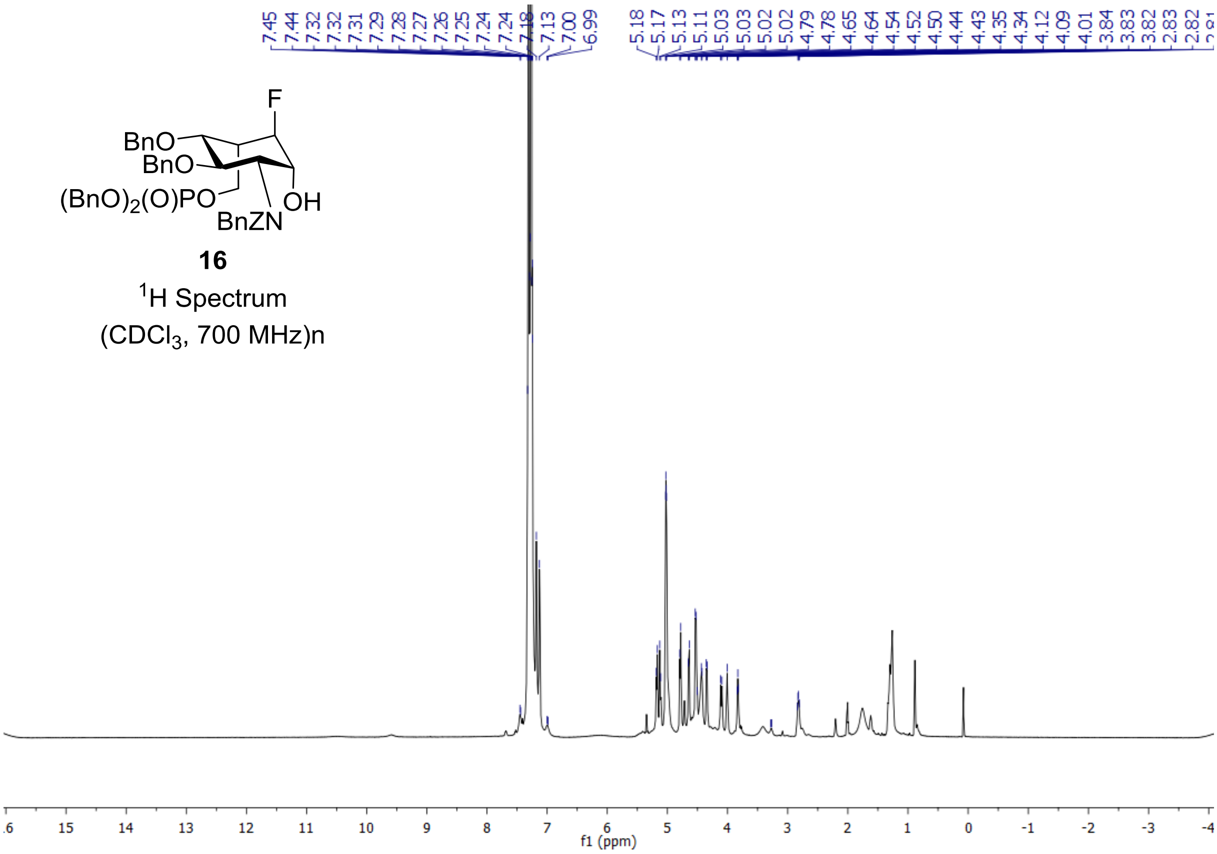
16

HPLC

ZORBAX SB-C18, 5 µm,

0.4 mL/min,

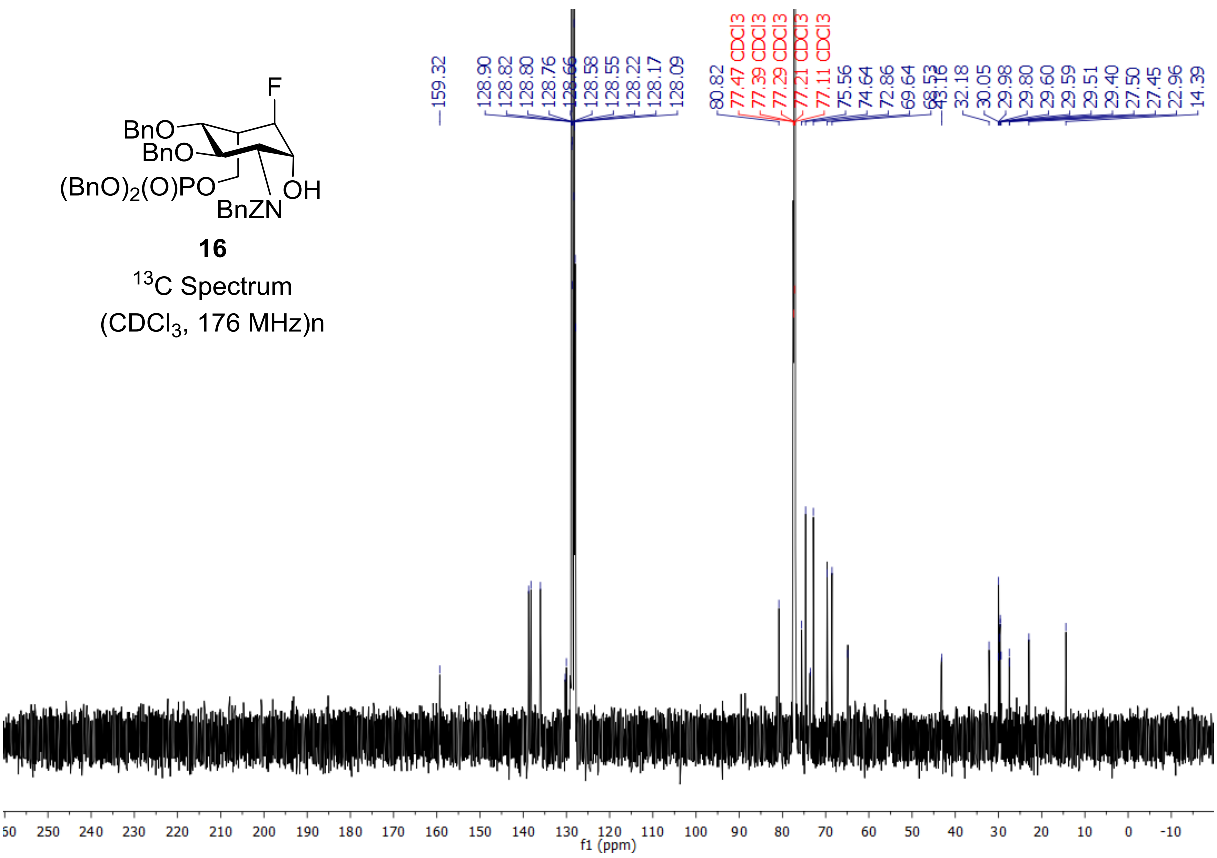
20-100% MeCN in 20 min



16

[1]H Spectrum

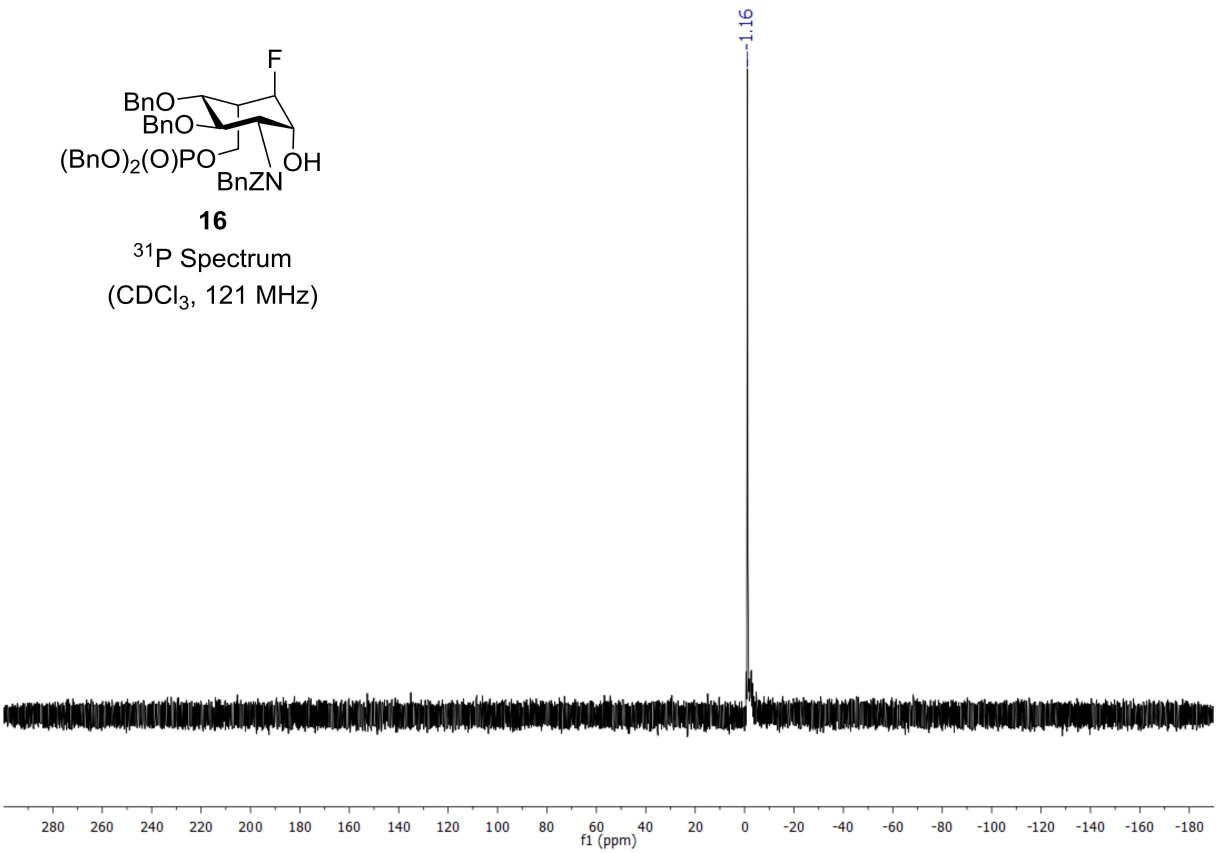
($CDCl_3$, 700 MHz)n



16

^{13}C Spectrum

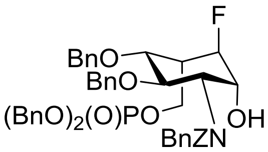
($CDCl_3$, 176 MHz)n



16

^{31}P Spectrum

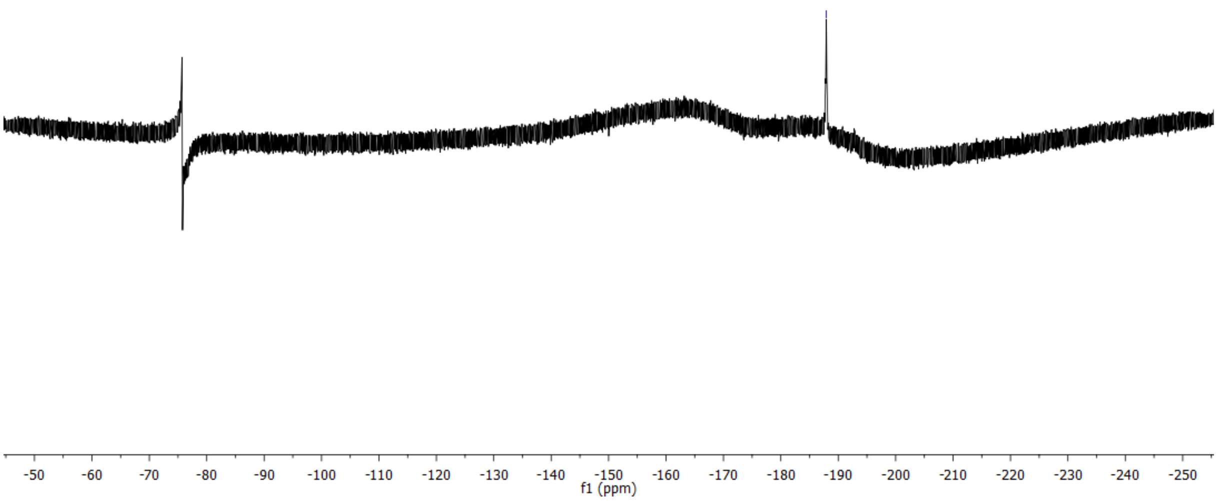
($CDCl_3$, 121 MHz)

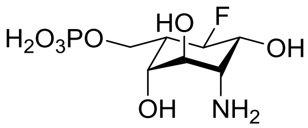


16

^{19}F Spectrum

($CDCl_3$, 282 MHz)

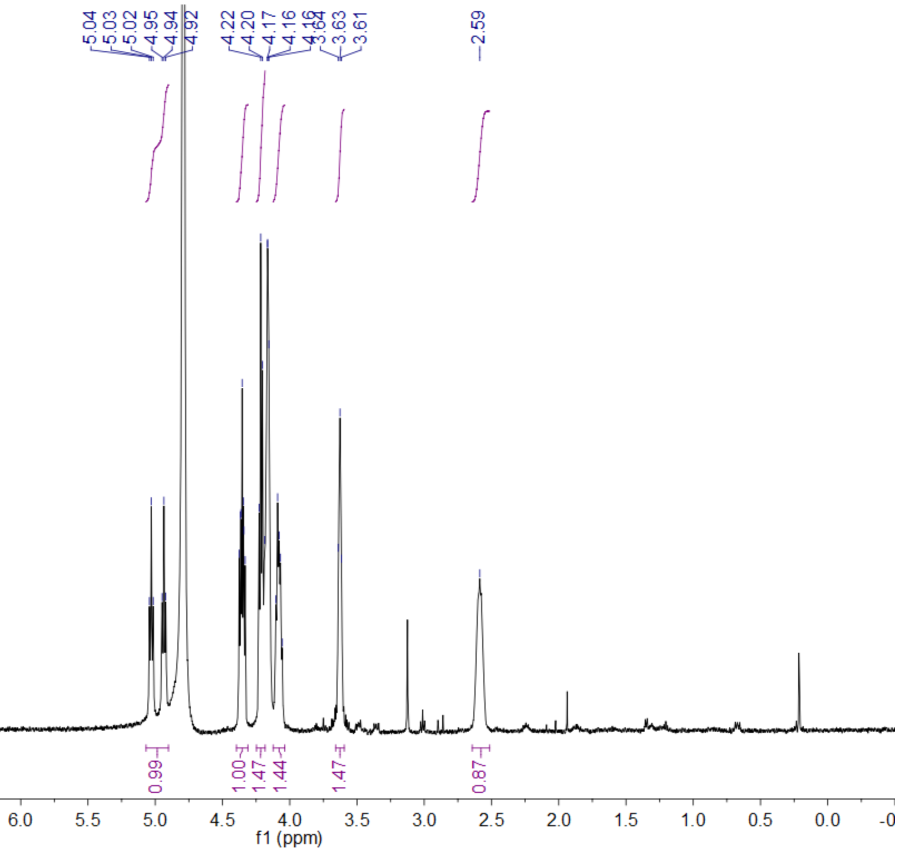


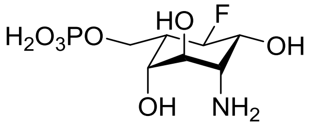


2

^{1}H NMR

(D_2O, 500 MHz)

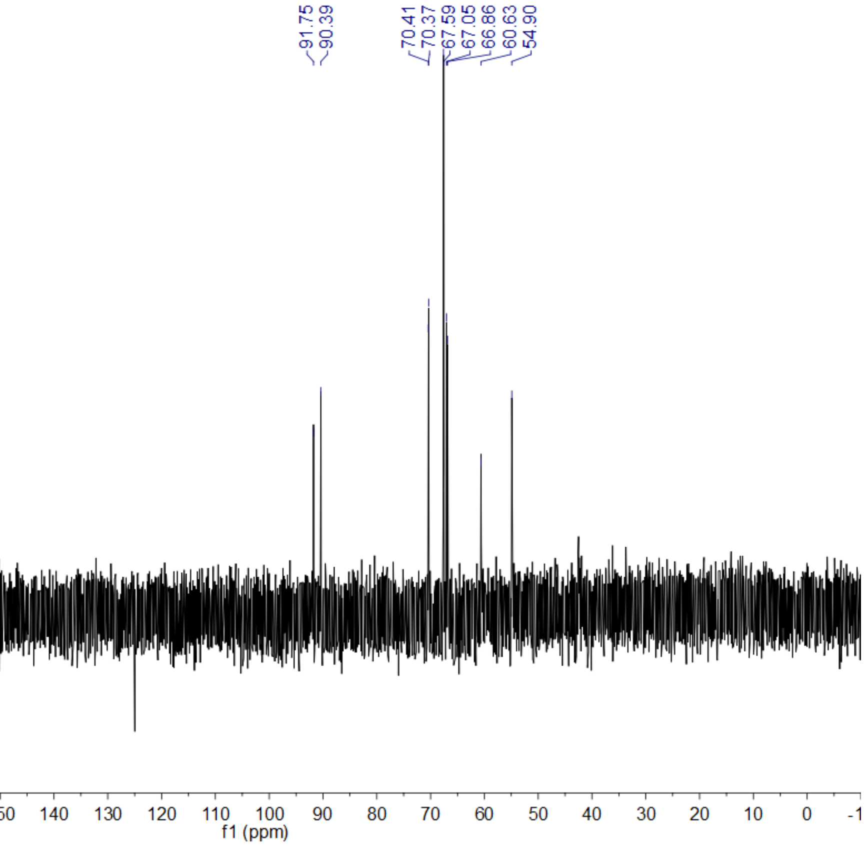


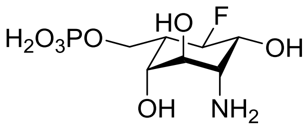


2

^{13}C NMR

(D_2O, 126 MHz)

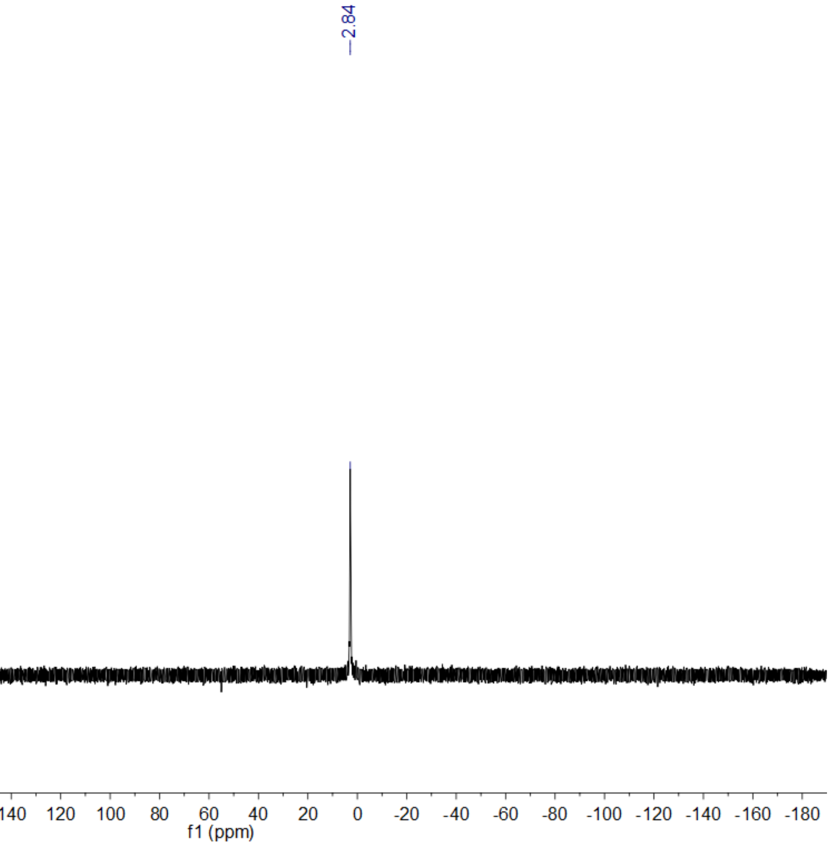


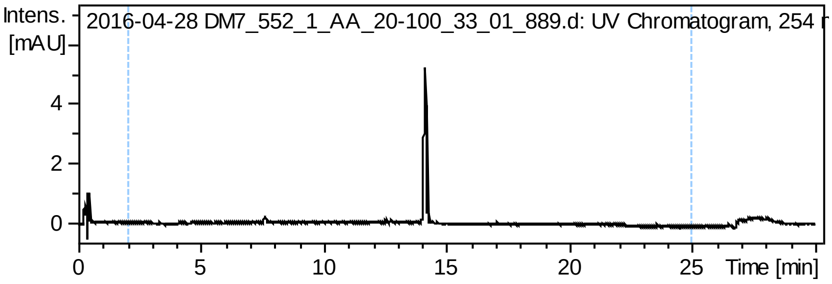


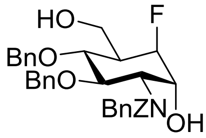
2

^{31}P NMR

(D_2O, 202 MHz)







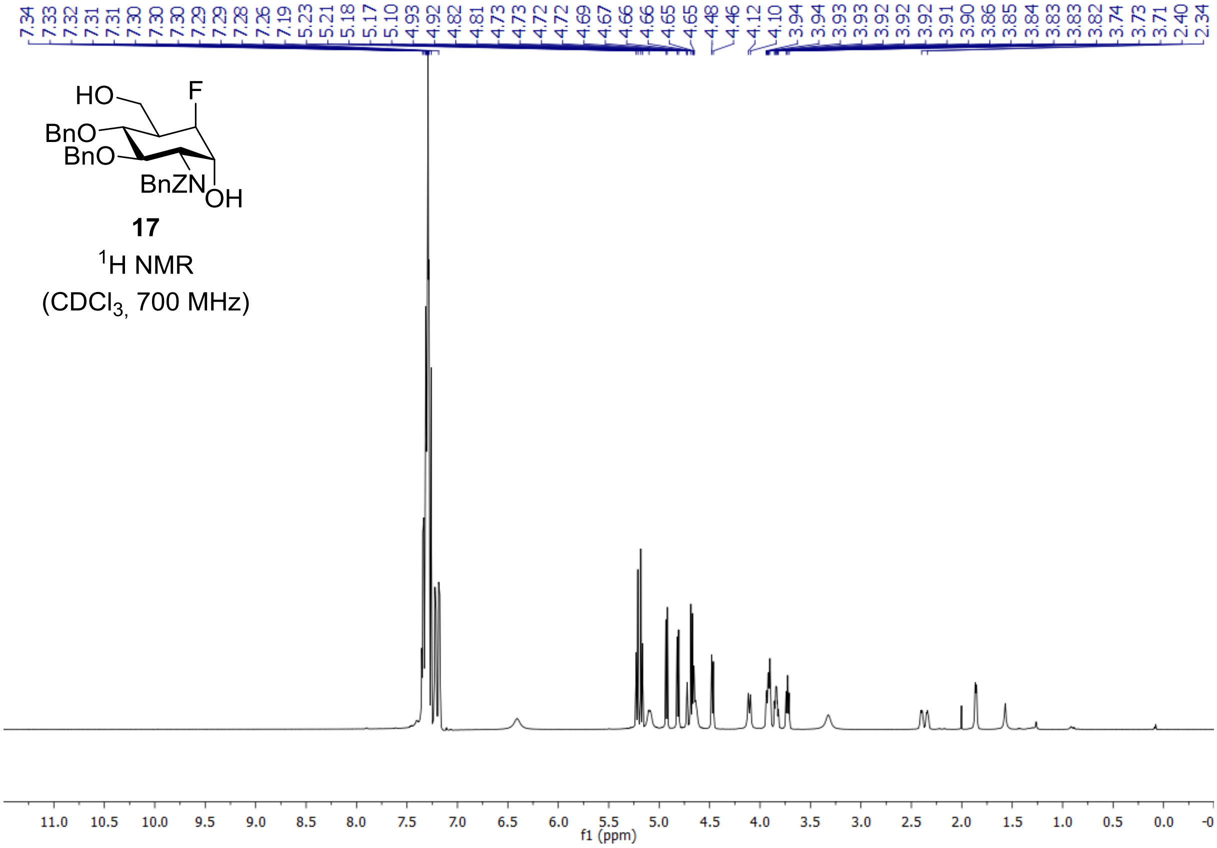
17

HPLC

ZORBAX SB-C18, 5 µm,

0.4 mL/min,

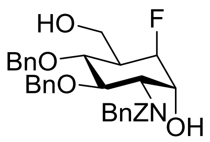
20-100 % MeCN in 20 min



17

^{1}H NMR

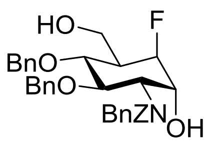
($CDCl_3$, 700 MHz)



17

^{13}C NMR

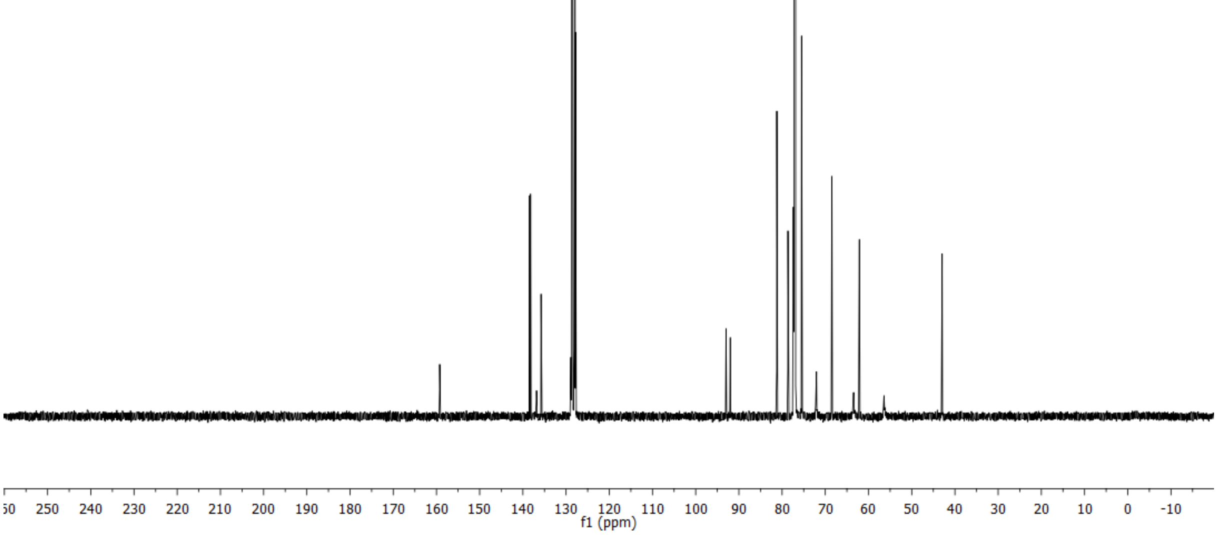
($CDCl_3$, 176 MHz)

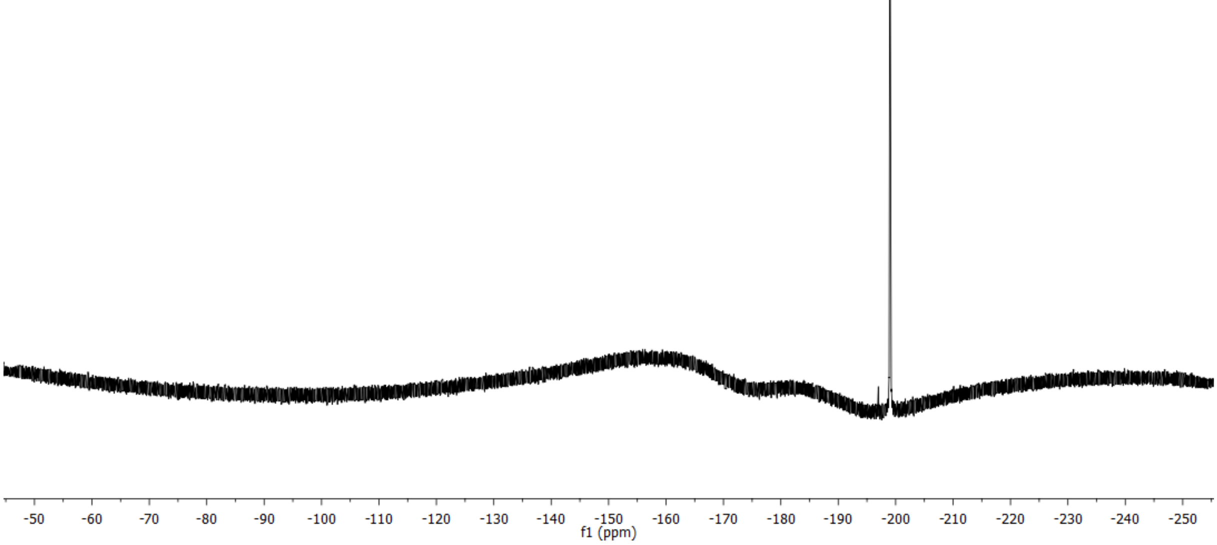


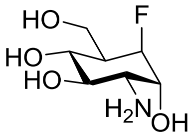
17

^{19}F NMR

($CDCl_3$, 471 MHz)



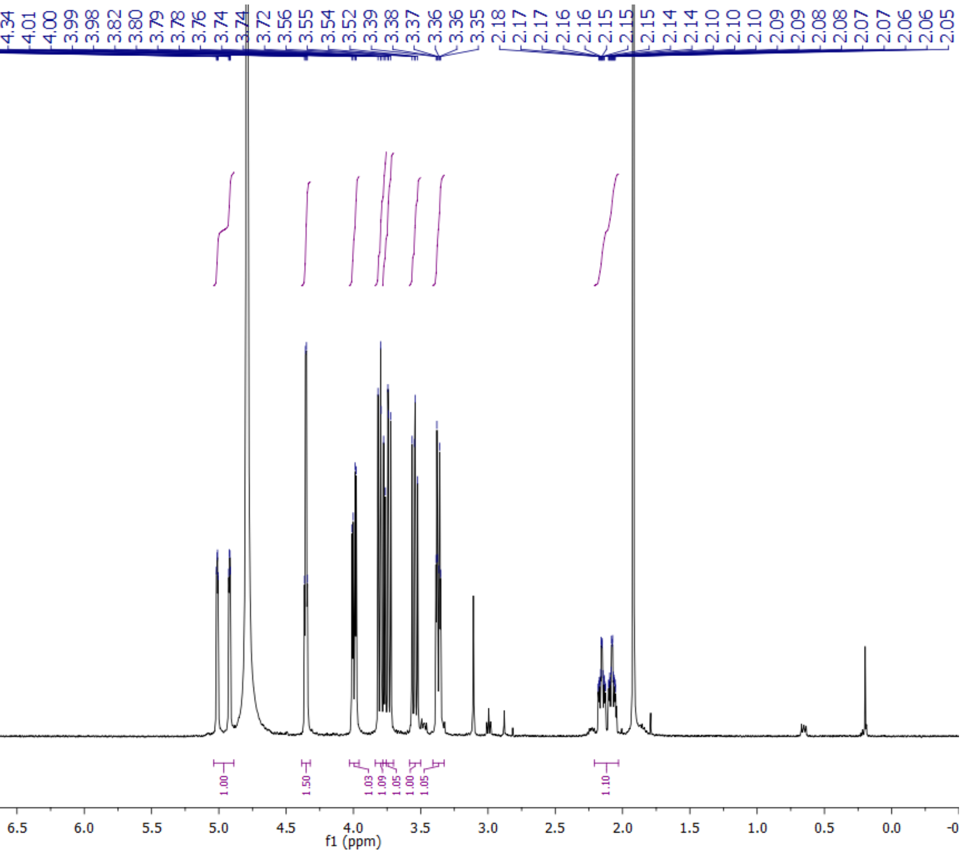


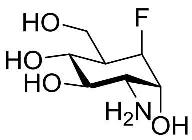


18

^{1}H NMR

(D_2O, 500 MHz)

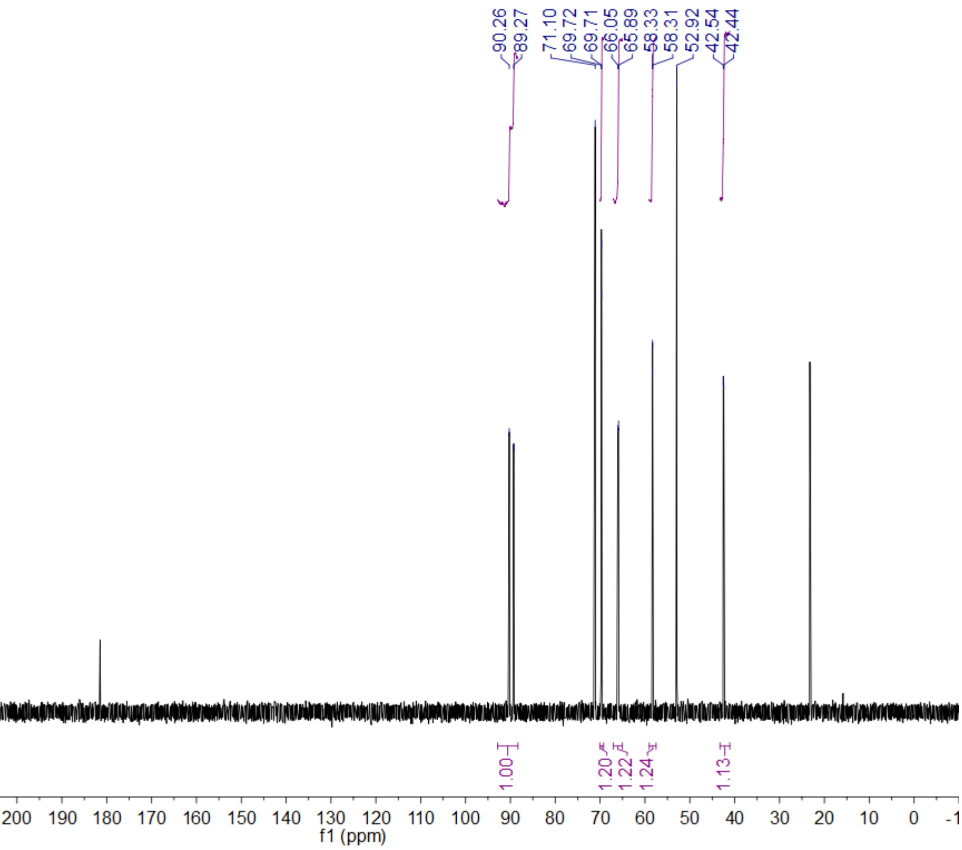


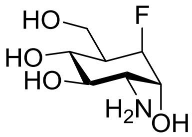


18

^{13}C NMR

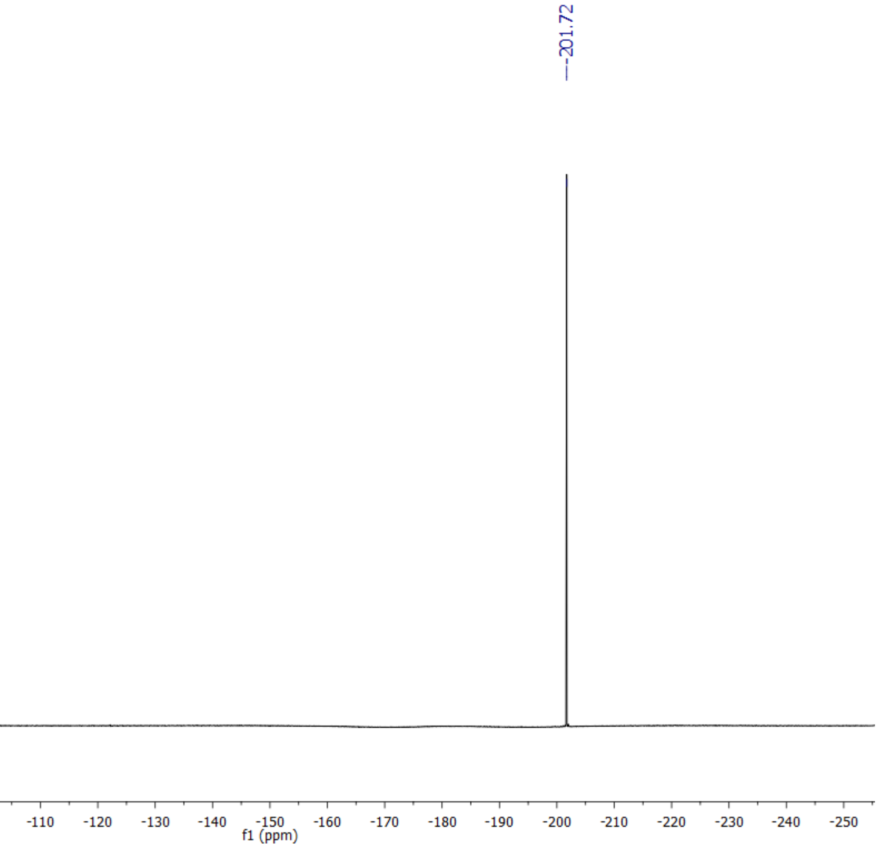
(D_2O, 126 MHz)

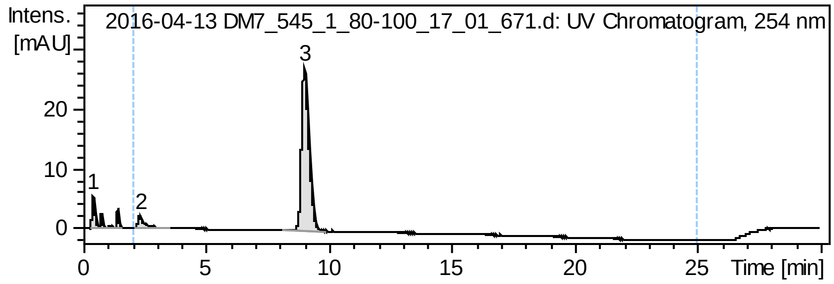


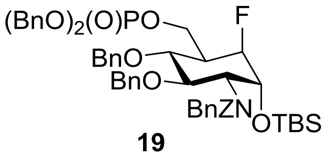


18

^{19}F NMR (^{1}H-decoupled)
(D_2O, 470 MHz)







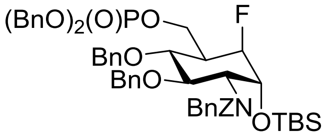
19

HPLC

ZORBAX SB-C18, 5 μm,

0.4 mL/min,

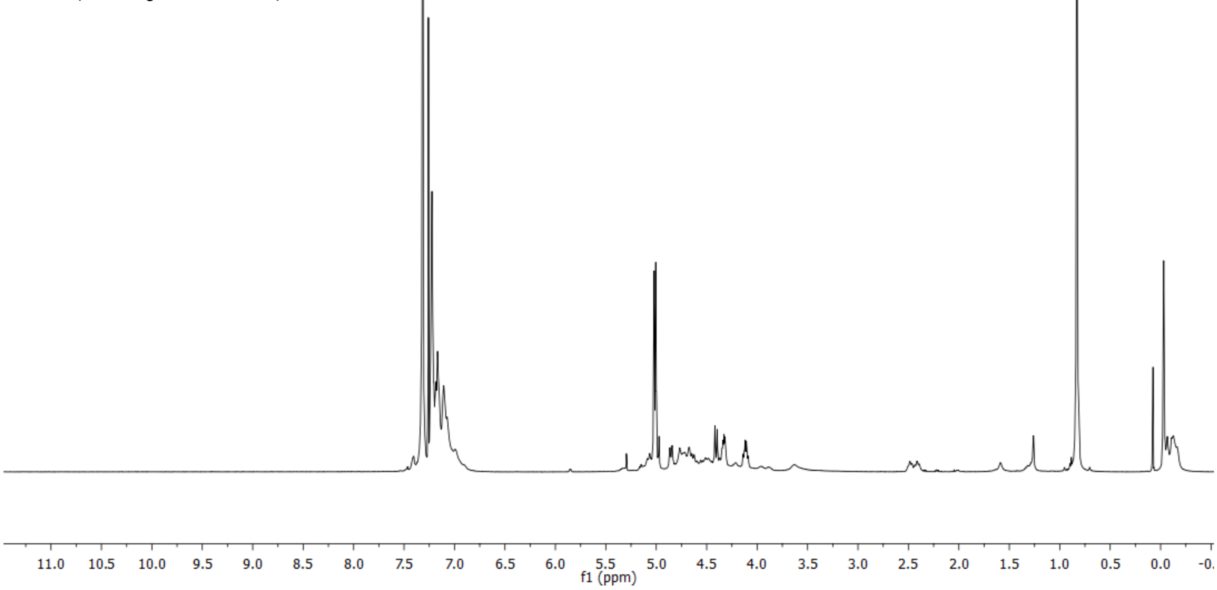
80-100 % MeCN in 20 min

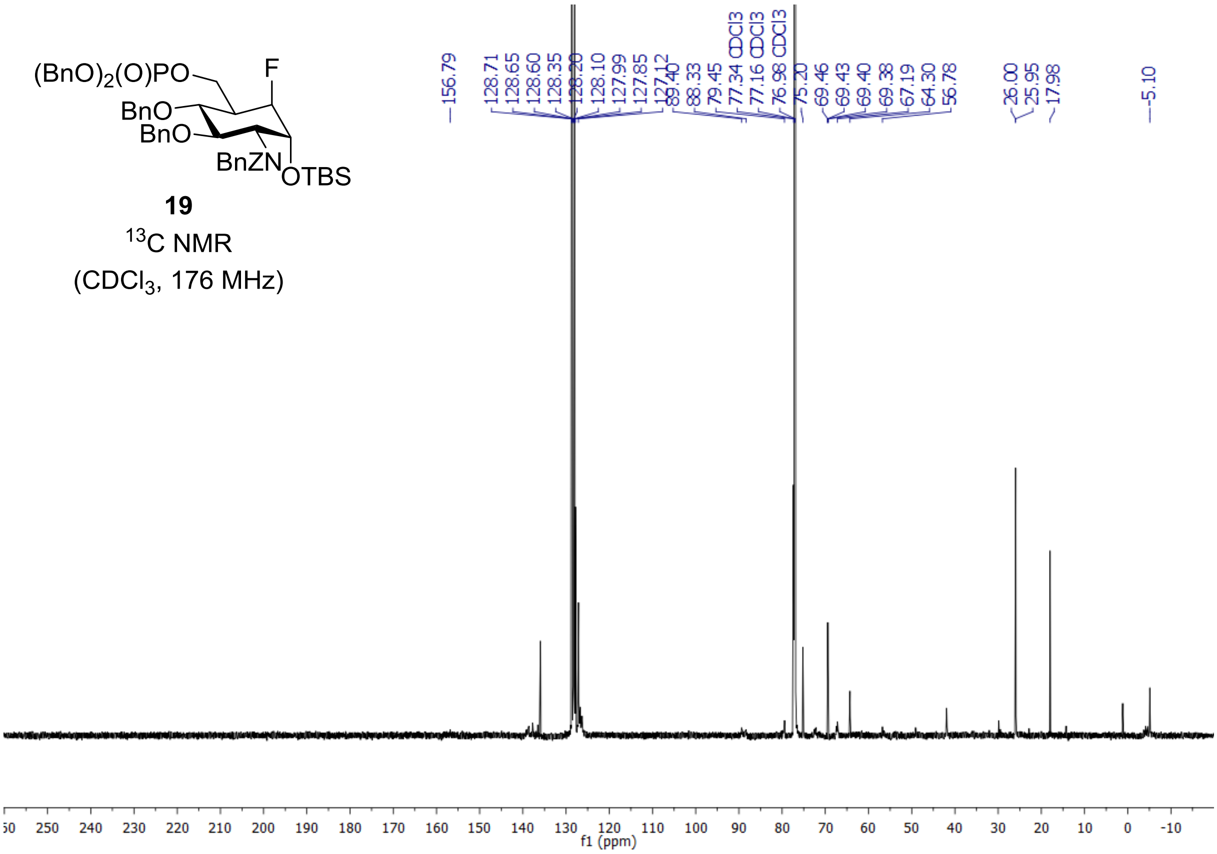


19

^{1}H NMR

($CDCl_3$, 500 MHz)

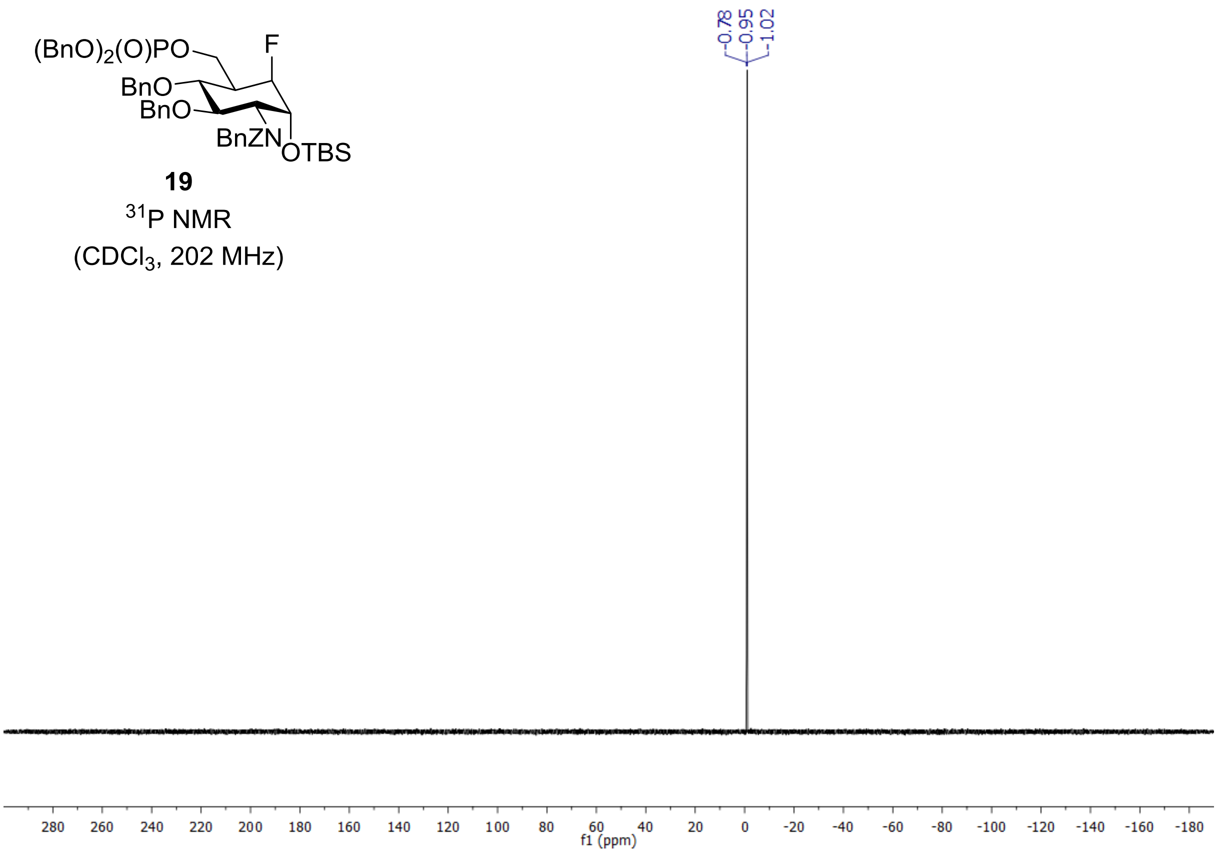




19

^{13}C NMR

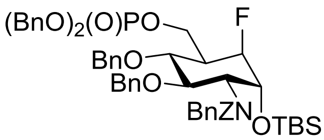
($CDCl_3$, 176 MHz)



19

^{31}P NMR

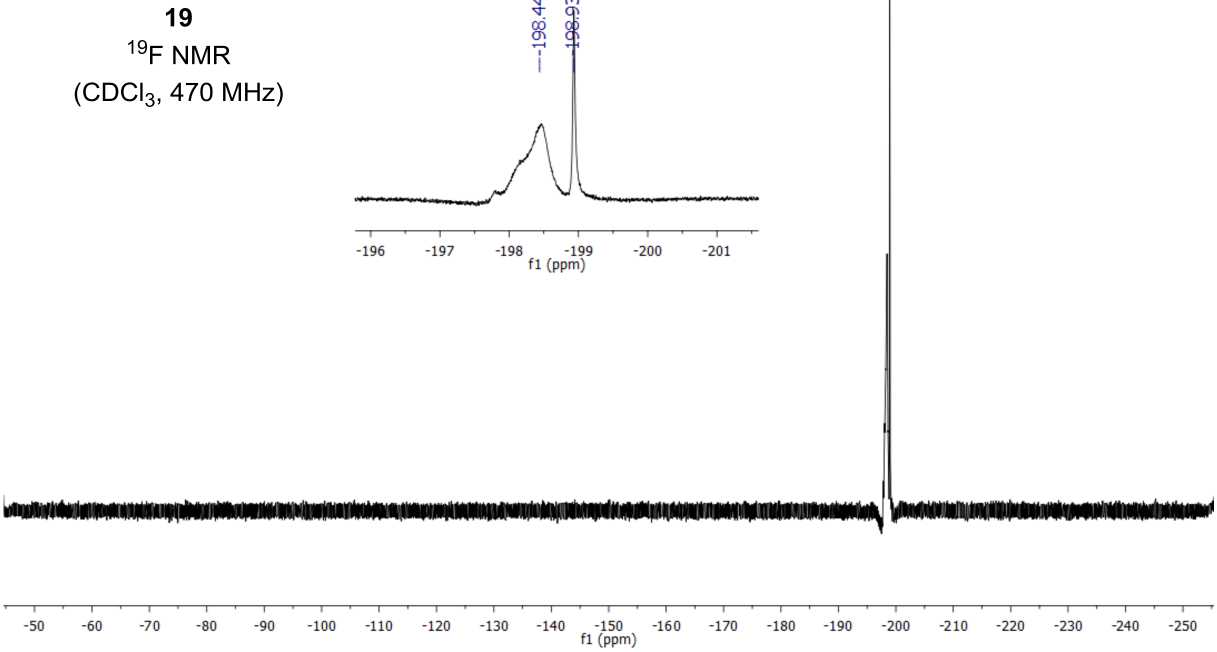
($CDCl_3$, 202 MHz)

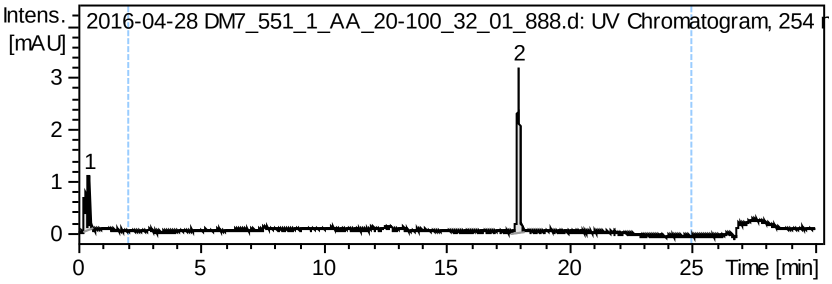


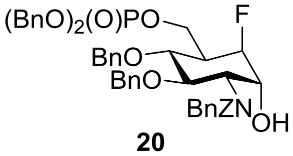
19

^{19}F NMR

($CDCl_3$, 470 MHz)







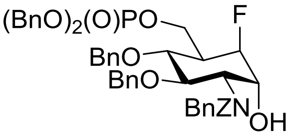
20

HPLC

ZORBAX SB-C18, 5 µm,

0.4 mL/min,

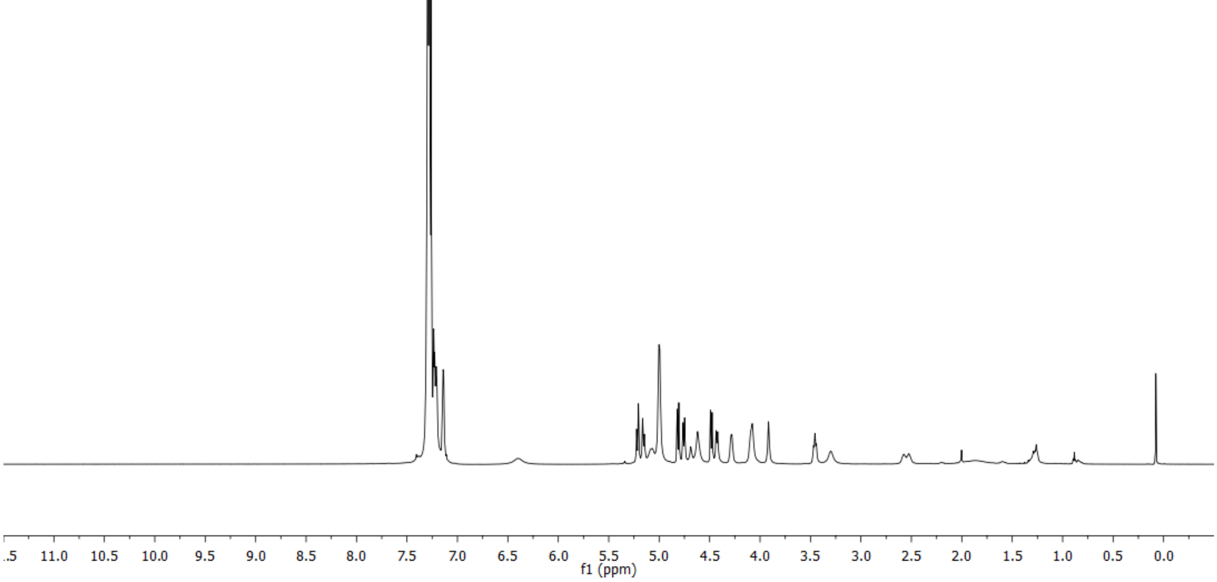
20-100 % MeCN in 20 min

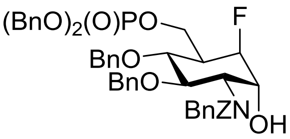


20

^1H NMR

($CDCl_3$, 700 MHz)

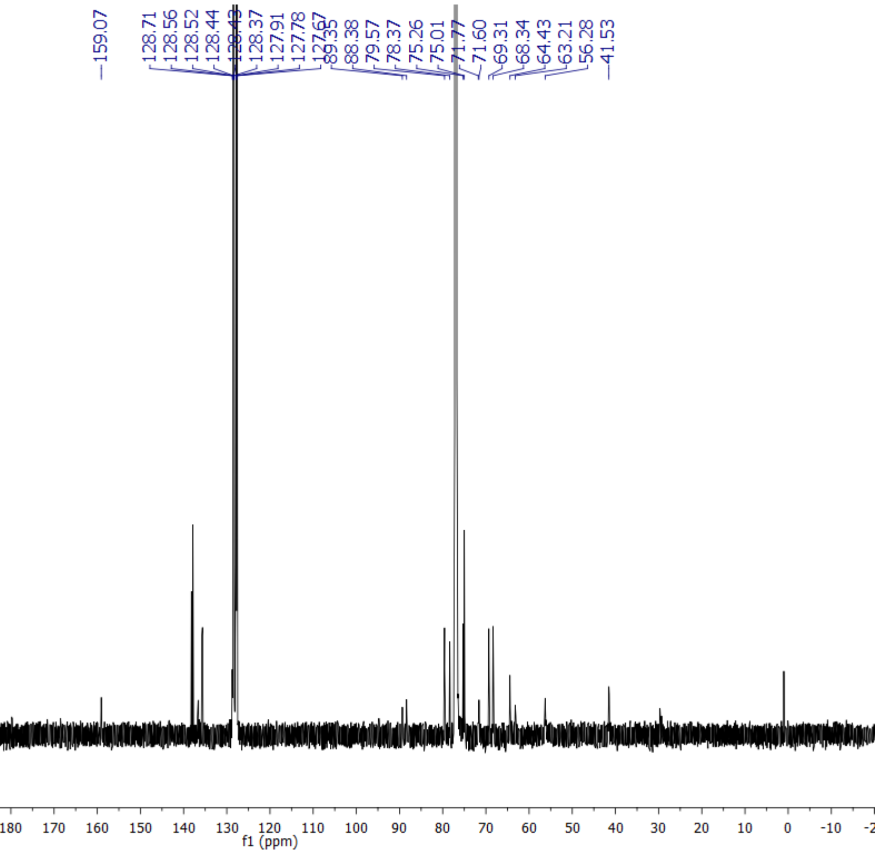


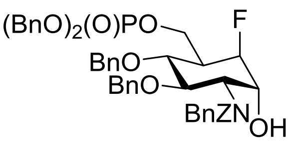


20

^{13}C NMR

($CDCl_3$, 176 MHz)

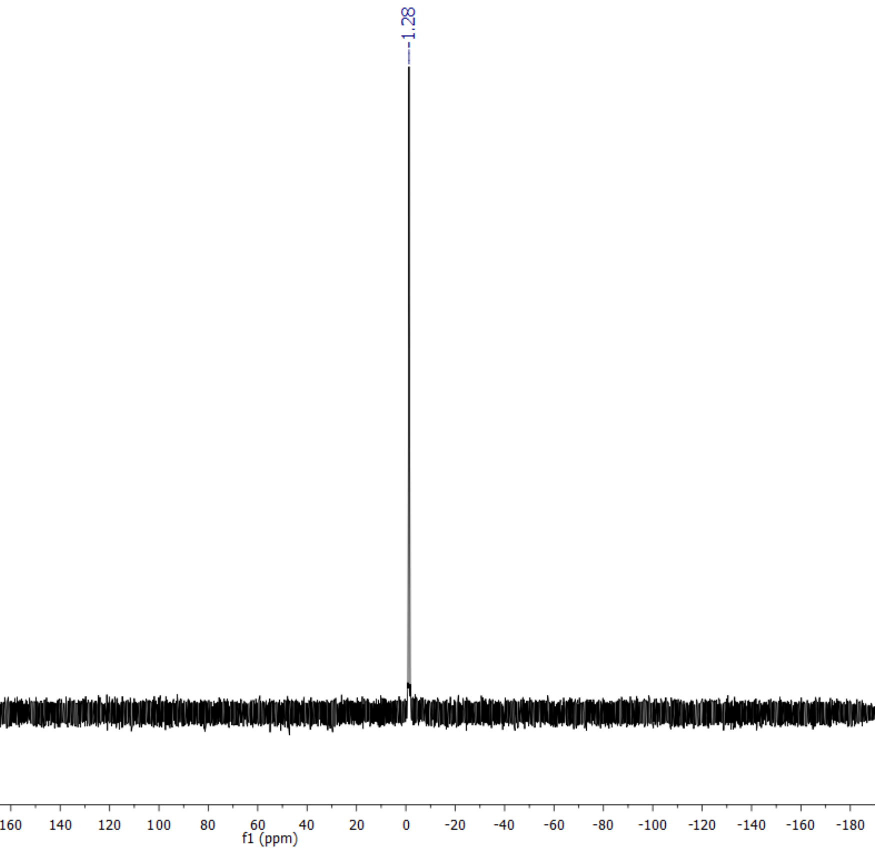


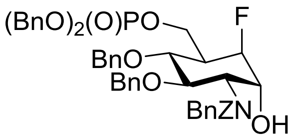


20

^{31}P NMR

($CDCl_3$, 202 MHz)

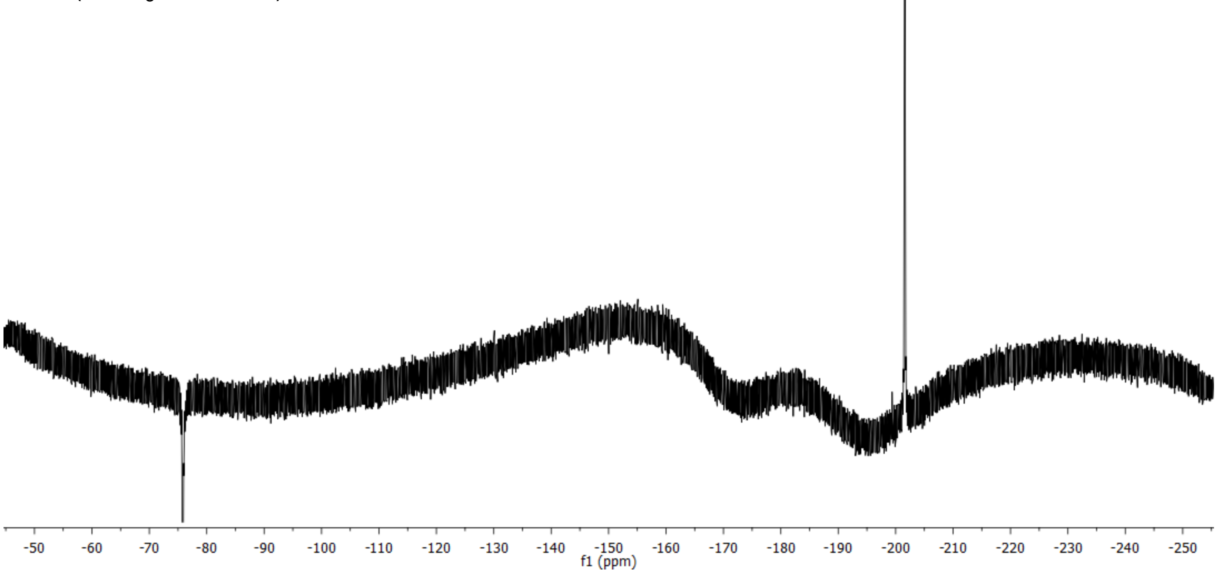


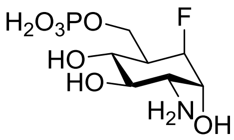


20

^{19}F NMR

($CDCl_3$, 471 MHz)

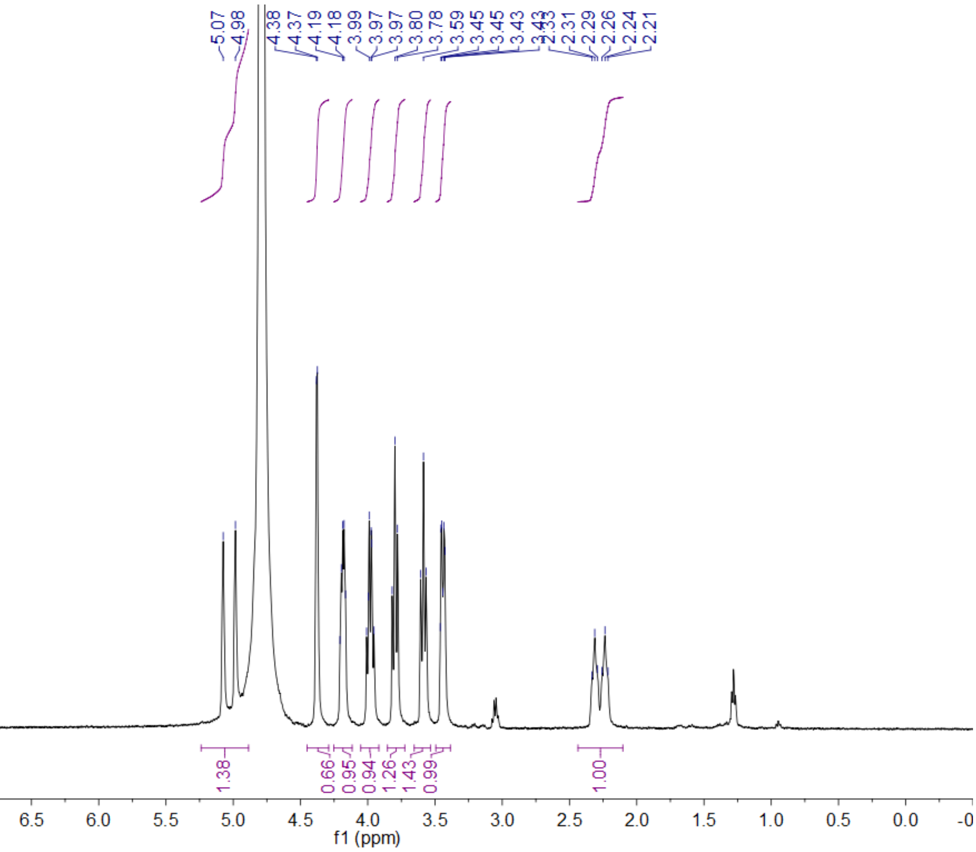


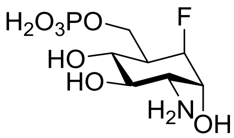


1

^{1}H NMR

(D_2O, 500 MHz)

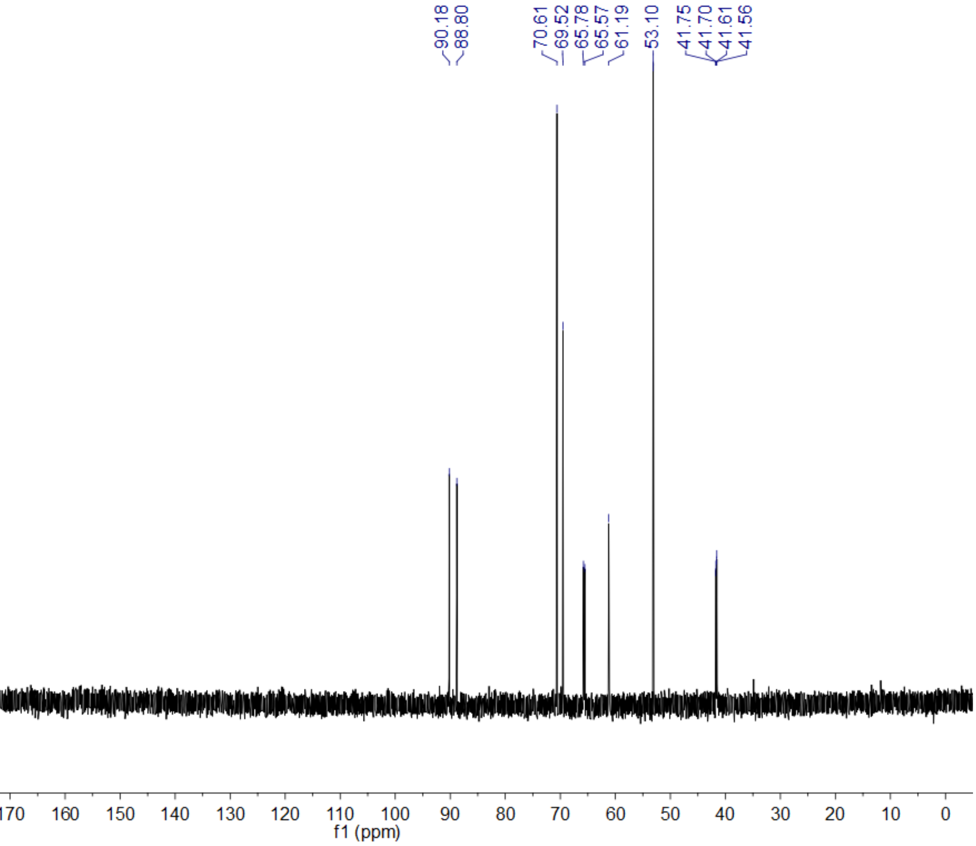


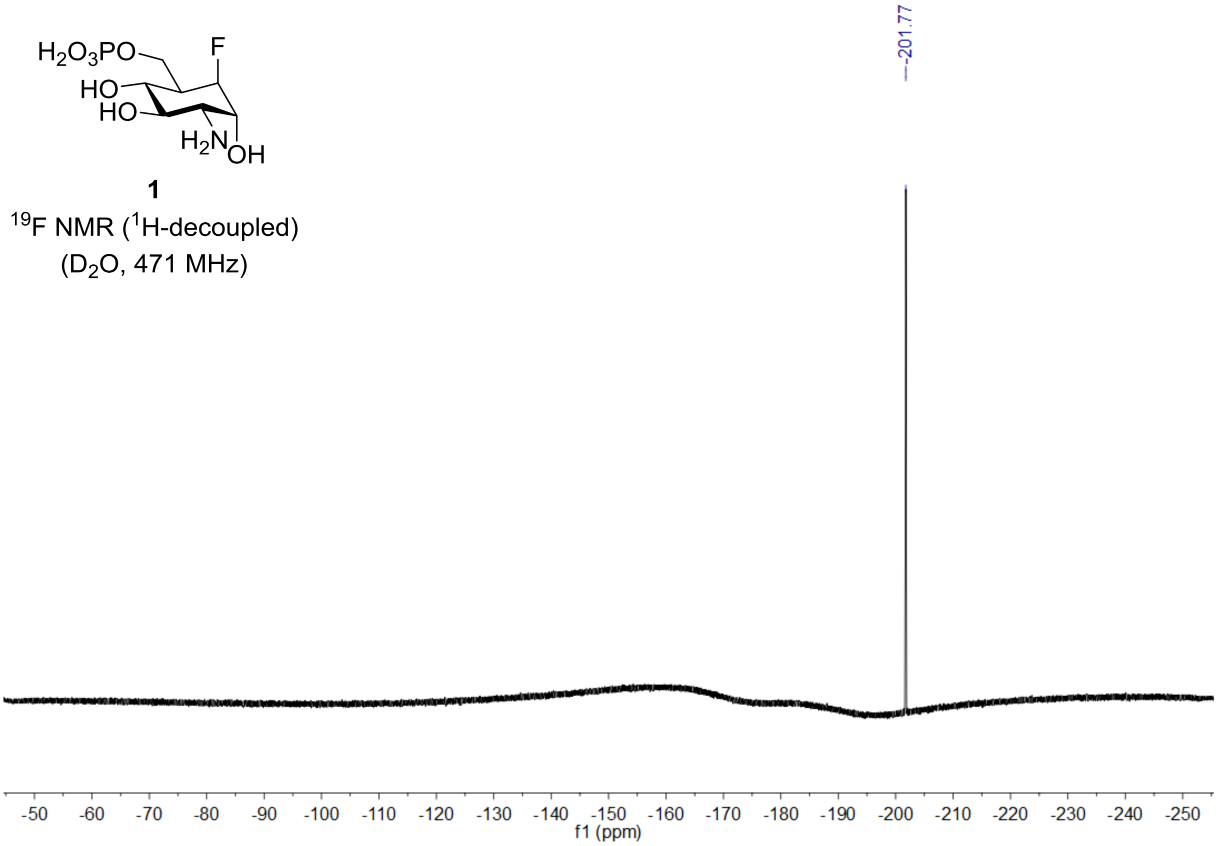


1

^{13}C NMR

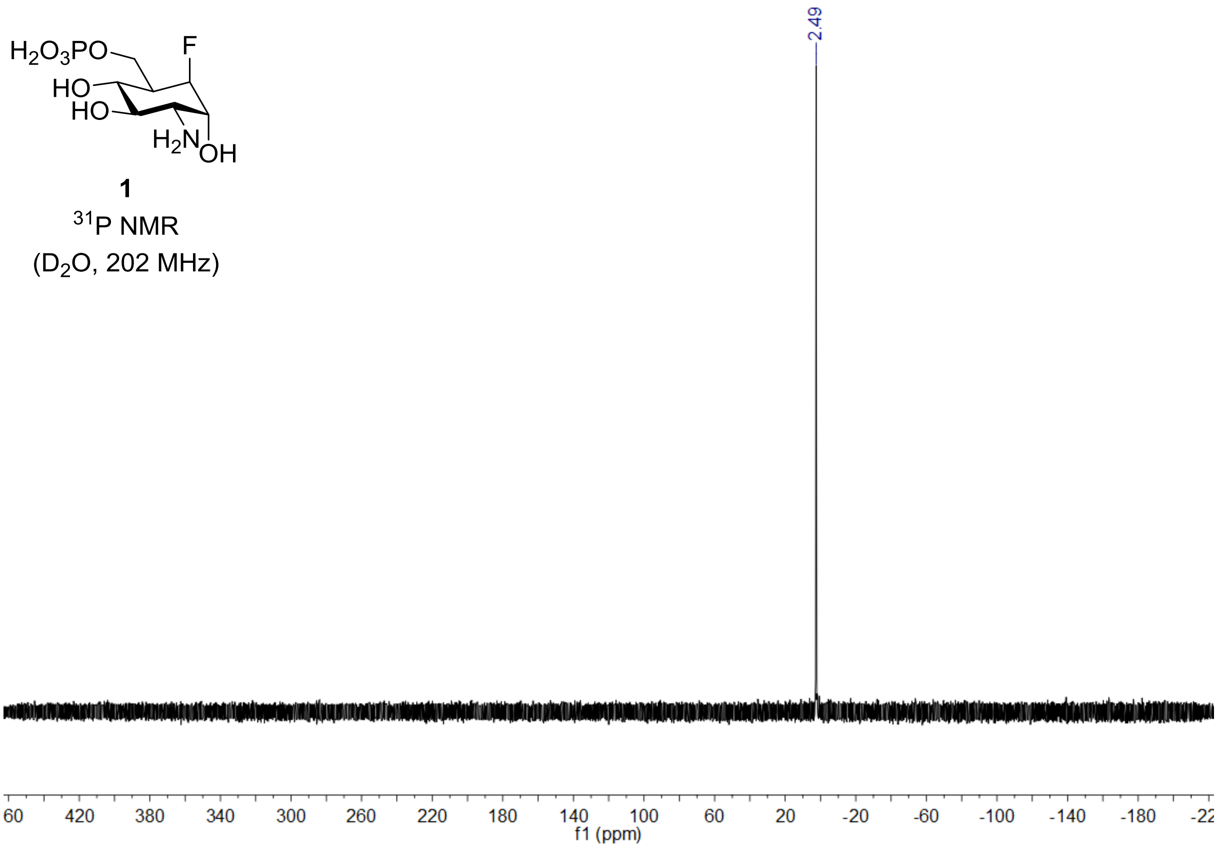
(D_2O, 126 MHz)





1

^{19}F NMR (^{1}H-decoupled)
(D_2O, 471 MHz)



1

^{31}P NMR
(D_2O, 202 MHz)

IV. Theoretical Section

Cartesian Coordinates of optimized structures:

L-configurated epoxide 3 (BP/def2-TZVP)

C	0.502129	1.183639	-0.333672
C	1.461300	0.033221	0.055388
C	0.738923	-1.336339	-0.000793
C	-0.497418	-1.360713	0.922084
C	-1.462426	-0.237810	0.509682
C	-0.799149	1.123337	0.478787
O	-1.735788	2.196783	0.245387
H	-2.342886	-0.214848	1.169316
O	1.106337	2.475986	-0.308691
C	2.087835	2.735815	0.697279
O	2.670356	0.043789	-0.704790
C	2.539947	-0.024627	-2.127949
N	1.654134	-2.454528	0.239629
C	1.731182	-3.417711	-0.737046
O	2.718855	-4.325803	-0.459469
O	1.014097	-3.485111	-1.729703
C	2.834142	-5.383788	-1.430546
C	2.642471	-2.387579	1.318654
O	-0.142982	-1.176949	2.294719
Si	-0.797480	-2.068547	3.569615
C	-0.349462	-3.887544	3.396873
C	-0.011729	-1.315914	5.096643
C	-2.672557	-1.895303	3.615942
H	0.200970	1.045327	-1.386012
H	1.802331	0.202297	1.088034
H	0.347476	-1.500743	-1.015834
H	-1.009553	-2.327744	0.765365
F	-1.931533	-0.537234	-0.791069

H	-0.366813	-1.822919	6.006293
H	-0.260049	-0.248613	5.188684
H	1.084140	-1.407070	5.068141
H	-3.084483	-2.459212	4.467547
H	-3.149435	-2.294159	2.707782
H	-2.987098	-0.847731	3.732645
C	-1.118440	2.101791	1.536562
H	3.063514	-4.977172	-2.424092
H	1.903254	-5.963600	-1.489558
H	3.657193	-6.013091	-1.074310
H	2.823424	-3.389758	1.720962
H	2.243406	-1.756023	2.118120
H	3.597634	-1.968421	0.966807
H	0.738178	-4.042280	3.437313
H	-0.714375	-4.315459	2.451405
H	-0.802470	-4.470208	4.213766
H	2.309643	3.807721	0.618792
H	3.010547	2.160308	0.522498
H	1.722911	2.529175	1.719262
H	3.563435	-0.111438	-2.512608
H	2.086105	0.890007	-2.543221
H	1.964905	-0.906040	-2.457779
H	-0.401484	2.894928	1.760402
H	-1.781647	1.809063	2.357658

D-configurated epoxide 3 (BP/def2-TZVP)

C	0.435911	1.120390	-0.414906
C	1.439330	0.042059	0.056678
C	0.763158	-1.353617	-0.023038
C	-0.493596	-1.424448	0.871738
C	-1.490692	-0.318109	0.479955
C	-0.856474	1.059444	0.407912

C	-1.716608	2.244893	0.541962
H	-2.329604	-0.298087	1.191901
O	0.975866	2.431458	-0.519379
C	1.822111	2.881651	0.551070
O	2.681051	0.090639	-0.643009
C	2.615738	-0.001667	-2.069089
N	1.703260	-2.446167	0.234857
C	1.832196	-3.401588	-0.742685
O	2.835019	-4.284896	-0.439123
O	1.148311	-3.482414	-1.758216
C	3.011119	-5.331642	-1.412786
C	2.655409	-2.367968	1.346343
O	-0.147469	-1.266906	2.244437
Si	-0.871764	-2.054633	3.546454
C	-0.723255	-3.919646	3.334200
C	0.101754	-1.452685	5.030382
C	-2.689517	-1.586560	3.704654
H	0.132419	0.870703	-1.447305
H	1.715483	0.246041	1.102083
H	0.406380	-1.523606	-1.050528
H	-0.980436	-2.400328	0.687239
F	-2.016690	-0.633727	-0.796480
H	-0.292512	-1.889785	5.959796
H	0.043777	-0.357923	5.119502
H	1.162851	-1.730697	4.953397
H	-3.112547	-2.020284	4.624412
H	-3.293664	-1.963997	2.865777
H	-2.818252	-0.495579	3.759466
O	-0.900989	1.798106	1.649871
H	-1.387010	3.177254	0.077731
H	-2.795628	2.117242	0.678920

H	3.258748	-4.911522	-2.396273
H	2.100179	-5.938406	-1.504167
H	3.841241	-5.939039	-1.035378
H	2.798388	-3.360324	1.788464
H	2.243507	-1.701825	2.109726
H	3.631398	-1.982515	1.014849
H	0.325982	-4.230231	3.224016
H	-1.275788	-4.285120	2.455608
H	-1.134900	-4.440453	4.212795
H	2.052155	3.928435	0.315959
H	2.761780	2.308370	0.580691
H	1.313820	2.832042	1.524933
H	3.656443	-0.065619	-2.409267
H	2.154394	0.895115	-2.514311
H	2.078975	-0.903429	-2.408687

TS-A

C	0.909878	1.780789	0.966563
C	1.449807	0.410650	0.503122
C	0.355743	-0.635872	0.780648
C	0.001473	-0.722819	2.274742
C	-0.310160	0.660167	2.854110
C	0.639926	1.747764	2.462958
H	-0.456307	0.609966	3.935612
O	1.692012	2.892941	0.532980
C	3.084887	2.820850	0.851655
O	1.882454	0.405689	-0.856350
C	0.892156	0.777670	-1.821206
N	0.687292	-1.948354	0.221873
C	-0.294844	-2.586274	-0.476095
O	0.157908	-3.759472	-1.016788
O	-1.447540	-2.188035	-0.605683

C	-0.864571	-4.509889	-1.707283
C	2.060355	-2.458284	0.280011
O	1.062239	-1.333881	3.003814
Si	0.965688	-2.524874	4.183772
C	2.411289	-3.668271	3.815170
C	1.229117	-1.739520	5.868773
C	-0.673629	-3.499263	4.166245
H	-0.055516	1.952591	0.465072
H	2.353737	0.171404	1.071280
H	-0.565497	-0.325948	0.278432
H	-0.911059	-1.319211	2.360339
F	-1.620574	0.990484	2.306656
H	1.092078	-2.476809	6.669041
H	0.534105	-0.913202	6.054865
H	2.251661	-1.353773	5.958198
C	0.377438	3.109745	3.077347
H	-1.277742	-3.921944	-2.530049
H	-1.667494	-4.780403	-1.017066
H	-0.356185	-5.399328	-2.080338
H	2.039609	-3.544847	0.355884
H	2.536128	-2.051290	1.170784
H	2.628381	-2.161860	-0.607879
H	3.331633	-3.088377	3.677673
H	2.250936	-4.259676	2.907506
H	2.585256	-4.362641	4.645143
H	3.516170	3.760526	0.499479
H	3.566041	1.982549	0.335731
H	3.244902	2.734002	1.932575
H	1.370270	0.649010	-2.794128
H	0.596604	1.826964	-1.700418
H	0.006346	0.131593	-1.768882

H	1.259945	3.749593	2.937192
H	-0.458053	3.594027	2.541570
H	-2.450158	2.880610	3.092010
H	-3.757962	1.860543	5.167616
C	-2.679591	3.409671	4.004871
C	-3.371688	2.865550	5.102734
Cl	-1.435865	0.977860	6.333163
O	0.096246	3.020598	4.451318
C	-2.276135	4.728413	4.349860
H	-1.702220	5.403569	3.728690
Ti	-1.092271	3.281772	5.831874
C	-3.399946	3.835605	6.138163
H	1.400414	2.198470	7.260123
H	1.697291	4.568270	6.015965
C	-2.750184	5.000421	5.655160
H	-3.846363	3.708168	7.114662
C	0.770699	3.068845	7.376026
C	0.927642	4.308990	6.728080
C	-0.411241	3.138274	8.171621
H	-2.624365	5.926661	6.195905
H	-0.815111	2.333328	8.767044
C	-0.175390	5.127572	7.065427
H	-0.339727	6.138305	6.719081
C	-0.986713	4.407174	7.994132
H	-1.898925	4.762841	8.451718
C	-0.993147	-4.088648	2.776968
H	-0.157836	-4.678839	2.382856
H	-1.864066	-4.755339	2.850819
H	-1.235946	-3.317387	2.040880
C	-1.861819	-2.646026	4.658620
H	-2.087905	-1.811736	3.987326

H	-2.764056	-3.270969	4.720730
H	-1.676526	-2.226339	5.652597
C	-0.493860	-4.679114	5.152697
H	-1.426857	-5.257412	5.202101
H	0.302613	-5.360527	4.834037
H	-0.264996	-4.335860	6.167876
C	5.586862	2.032691	3.352778
H	6.567030	1.948348	3.850859
H	5.753442	0.010748	2.449411
H	5.802697	2.609046	2.434865
C	5.075491	0.667124	2.991351
C	3.847936	0.233670	3.321343
H	3.531116	-0.767198	3.044529
H	2.252031	0.533682	4.752603
C	2.868720	1.073733	4.031945
H	1.919546	1.348956	3.219439
C	3.407714	2.344540	4.540520
H	2.761040	2.931103	5.184103
C	4.633305	2.797821	4.225345
H	4.976651	3.751942	4.620664

TS-B

C	-1.659075	1.659277	-0.138968
C	-0.433160	0.718673	-0.255814
C	-0.977022	-0.719837	-0.334146
C	-1.811655	-1.128230	0.892325
C	-2.849536	-0.052186	1.272844
C	-2.398693	1.373838	1.158866
H	-3.242084	-0.268999	2.271360
O	-1.379659	3.035559	-0.370860
C	-0.189190	3.576960	0.223524
O	0.413363	1.022144	-1.366976

C	-0.222492	1.032260	-2.649869
N	0.078082	-1.696979	-0.613568
C	-0.223767	-2.688992	-1.497186
O	0.855502	-3.496470	-1.736735
O	-1.321946	-2.864037	-2.014757
C	0.563607	-4.606281	-2.613887
C	1.409090	-1.538657	-0.023446
O	-0.975030	-1.426524	2.019181
Si	-1.177771	-2.941490	2.722238
C	-0.842805	-4.303875	1.473617
C	0.051239	-3.010240	4.164600
C	-2.948815	-3.099060	3.340054
H	-2.341322	1.396186	-0.959208
H	0.205570	0.850923	0.621471
H	-1.665493	-0.777825	-1.182992
H	-2.383636	-2.020150	0.600694
F	-3.941086	-0.263407	0.358082
H	-3.126334	-4.086247	3.782693
H	-3.665632	-2.980676	2.518614
H	-3.185198	-2.344791	4.099278
C	-2.069059	2.109603	2.427859
H	0.214802	-4.243147	-3.583147
H	-0.201789	-5.248416	-2.170929
H	1.508626	-5.140552	-2.714312
H	1.871016	-2.517963	0.093373
H	1.292082	-1.083966	0.959661
H	2.044512	-0.902274	-0.647518
H	0.179387	-4.259264	1.084219
H	-1.525735	-4.244590	0.618506
H	-0.985457	-5.287630	1.937585
H	-0.244484	4.652703	0.048294

H	0.702831	3.166833	-0.264717
H	-0.148671	3.397716	1.300770
H	0.574515	1.235697	-3.367445
H	-0.975696	1.826718	-2.711012
H	-0.679246	0.063076	-2.889058
H	-2.116806	3.192210	2.242489
H	-2.846116	1.868688	3.165019
H	1.884740	2.678345	2.056427
H	2.508027	4.347455	4.060059
C	1.994911	2.405515	3.095218
C	2.316514	3.289389	4.156025
Cl	-0.287231	4.776135	3.700259
O	-0.775885	1.820751	2.965666
C	1.763028	1.125674	3.647233
H	1.427811	0.254675	3.104010
Ti	0.022261	2.563988	4.482162
C	2.273155	2.560077	5.364635
H	-1.155989	4.667684	6.423302
H	-2.915727	3.364604	4.876815
C	1.924364	1.216197	5.050110
H	2.471743	2.955379	6.350272
C	-1.217356	3.596179	6.306381
C	-2.149865	2.905681	5.484432
C	-0.351122	2.647832	6.880656
H	1.823862	0.402922	5.752948
H	0.465045	2.857668	7.556597
C	-1.861562	1.526395	5.565108
H	-2.362700	0.735219	5.025259
C	-0.735415	1.360209	6.406453
H	-0.281336	0.419074	6.674960
C	-0.225240	-1.833915	5.117736

H	-1.218087	-1.911703	5.575607
H	0.514334	-1.828412	5.932420
H	-0.169633	-0.876016	4.592390
C	1.501391	-2.918561	3.651215
H	2.202759	-2.946084	4.497066
H	1.748532	-3.754353	2.987641
H	1.678646	-1.989837	3.101272
C	-0.122824	-4.337207	4.932517
H	-1.135346	-4.443416	5.337864
H	0.082060	-5.205457	4.296048
H	0.578183	-4.374577	5.778055
C	-5.315932	3.750379	3.106944
C	-5.384537	2.762113	2.196986
C	-4.735911	2.858241	0.880572
C	-4.264921	4.201838	0.515654
C	-4.191693	5.203941	1.408033
C	-4.616596	5.053138	2.839922
H	-5.793264	3.628076	4.077432
H	-5.910250	1.839867	2.436383
H	-5.231626	2.301908	0.081248
H	-3.671524	2.117739	0.960479
H	-3.921208	4.357705	-0.502651
H	-3.802314	6.173196	1.105414
H	-5.263593	5.894561	3.136756
H	-3.729993	5.152404	3.493599

Radical intermediate of the epoxide opening $C_{28}H_{44}ClFNO_6SiTi$

C	0.936583	1.409220	0.707777
C	1.132332	-0.024111	0.166214
C	-0.119134	-0.860405	0.505574
C	-0.262882	-0.955605	2.030877
C	-0.467352	0.440045	2.619875

C	0.545035	1.413601	2.159648
H	-0.555010	0.417360	3.707550
O	2.050457	2.273010	0.441664
C	3.313080	1.744129	0.856691
O	1.480514	-0.053834	-1.213351
C	0.542297	0.558220	-2.106056
N	-0.106475	-2.168811	-0.148132
C	-1.136039	-2.446184	-1.002798
O	-0.936652	-3.646255	-1.629022
O	-2.120109	-1.741912	-1.197105
C	-2.003601	-4.015327	-2.529217
C	1.091096	-3.018447	-0.111010
O	0.926819	-1.522356	2.575150
Si	1.246962	-2.227039	4.058625
C	2.879044	-3.099317	3.741413
C	1.479255	-0.912548	5.376010
C	-0.110921	-3.465228	4.551881
H	0.116383	1.872346	0.133968
H	1.991267	-0.474785	0.668570
H	-1.021115	-0.364511	0.136902
H	-1.135541	-1.574407	2.265320
F	-1.777574	0.878595	2.149125
H	1.841254	-1.359633	6.310565
H	0.549687	-0.376970	5.596311
H	2.220272	-0.174333	5.047051
C	0.806359	2.665561	2.944442
H	-2.111829	-3.266180	-3.317182
H	-2.946496	-4.105345	-1.984466
H	-1.700414	-4.976615	-2.944758
H	0.803883	-4.056406	0.065624
H	1.714993	-2.680700	0.713548

H	1.648240	-2.951253	-1.050777
H	3.607364	-2.392062	3.326904
H	2.770411	-3.922522	3.026518
H	3.303258	-3.508555	4.665183
H	4.011987	2.583177	0.840301
H	3.660228	0.966270	0.165970
H	3.261324	1.330844	1.874868
H	0.886391	0.304437	-3.110631
H	0.543292	1.650291	-1.994090
H	-0.473297	0.168639	-1.963585
H	1.876034	2.921681	2.900276
H	0.279480	3.506772	2.452572
H	-2.008701	3.128151	2.826501
H	-3.653268	2.568884	4.837257
C	-2.107228	3.710008	3.731653
C	-2.978111	3.409046	4.796239
Cl	-1.745394	1.014570	6.041270
O	0.419377	2.555628	4.285233
C	-1.341054	4.849424	4.101910
H	-0.566243	5.320094	3.511057
Ti	-0.717774	3.116575	5.624839
C	-2.751805	4.346154	5.837251
H	1.108728	1.256780	7.261983
H	2.332537	3.271608	5.994849
C	-1.758141	5.256194	5.390119
H	-3.254723	4.364464	6.794284
C	0.834974	2.300035	7.311820
C	1.481548	3.360989	6.654240
C	-0.291540	2.834663	8.008149
H	-1.373854	6.101284	5.942201
H	-1.003145	2.262397	8.584887

C	0.734887	4.542829	6.880151
H	0.969967	5.525784	6.495260
C	-0.341773	4.215578	7.761813
H	-1.084302	4.903033	8.141211
C	-0.429054	-4.399726	3.366654
H	0.459774	-4.947670	3.032802
H	-1.183700	-5.141154	3.664445
H	-0.824536	-3.849043	2.506491
C	-1.400360	-2.748924	5.004360
H	-1.843348	-2.141015	4.208828
H	-2.151490	-3.493139	5.305026
H	-1.222243	-2.089334	5.859186
C	0.410361	-4.315769	5.731819
H	-0.364588	-5.027978	6.048107
H	1.300216	-4.893162	5.457169
H	0.660686	-3.695361	6.600493

Fluoro-carba-β-L-IdoN6P $^{1}C_{4}$-configuration (TPSS-D3/def2-TZVP)

C	0.340321	0.726911	-0.920991
C	0.923208	-0.650998	-0.550475
C	-0.175388	-1.649553	-0.162906
C	-1.118424	-1.109489	0.921040
C	-1.655556	0.298438	0.577025
C	-0.519174	1.248098	0.225986
F	-1.099528	2.493725	-0.171021
O	-2.409372	0.778774	1.697870
N	-0.521433	-1.038361	2.270393
O	1.842570	-0.561930	0.557023
C	1.439011	1.712112	-1.324470
H	1.452517	-1.046041	-1.433544
O	-1.001759	-1.943048	-1.307937
H	-1.982157	-1.778979	0.979349

H	-2.336005	0.239052	-0.278180
H	0.087272	1.477732	1.106910
H	-1.919033	0.384417	2.459912
H	0.463367	-0.777299	2.184667
H	-0.550151	-1.954962	2.712447
H	2.267891	0.334035	0.449222
H	-0.424399	-2.289768	-2.009348
H	0.300376	-2.568969	0.206519
H	2.004351	1.309709	-2.175558
O	2.326980	1.895097	-0.207438
H	1.009874	2.678630	-1.611735
P	3.803637	2.696992	-0.522084
O	4.450104	2.646471	0.860838
O	3.390981	4.091649	-0.995794
H	-0.310049	0.575092	-1.792412
O	4.496898	1.852092	-1.592447

fluoro-carba-β-L-IdoN6P $^{4}C_{1}$-configuration (TPSS-D3/def2-TZVP)

C	1.285120	1.154398	0.079973
C	1.509918	-0.265308	0.581247
C	0.688395	-1.243098	-0.262569
C	-0.810005	-0.921601	-0.135609
C	-1.111882	0.563112	-0.392202
C	-0.179491	1.587181	0.269359
O	2.210194	2.001482	0.802739
O	2.901400	-0.619498	0.458050
N	0.898152	-2.659956	0.073259
O	-1.308585	-1.342703	1.139611
H	1.540447	1.185101	-0.986797
H	1.208430	-0.341156	1.638123
H	0.980942	-1.098443	-1.311068
H	-1.347961	-1.497238	-0.898862

H	2.368315	2.798427	0.271004
H	3.390049	0.173546	0.748728
H	0.513343	-2.811523	1.008256
H	1.901531	-2.832197	0.145984
H	-1.432393	-0.518390	1.695233
H	-2.152745	0.796400	-0.145578
F	-0.970019	0.745150	-1.814761
C	-0.525482	1.879799	1.757283
H	-0.329190	2.516872	-0.291738
H	0.381757	1.791661	2.361726
O	-1.502417	0.986313	2.322872
H	-0.899464	2.902271	1.857887
P	-3.104527	1.586942	2.503288
O	-3.586970	1.889945	1.082689
O	-2.945710	2.827743	3.382057
O	-3.767460	0.387449	3.172524

Fluoro-carba-α-D-glucosamine-6-phosphate (BP/def2-TZVPP)

C	0.834963	1.197334	-0.234840
C	1.424064	-0.060262	0.400332
C	0.708531	-1.323249	-0.076881
C	-0.818056	-1.229396	0.159877
C	-1.427046	0.089242	-0.324089
C	-0.657001	1.327912	0.119890
C	-1.284456	2.616732	-0.424778
O	1.600822	2.318974	0.237512
O	2.819179	-0.201093	0.073407
N	1.193045	-2.481088	0.699988
O	-1.094828	-1.367062	1.556997
H	-2.476523	0.149739	0.001056
O	-0.636297	3.736506	0.195525
P	-0.995386	5.300868	-0.438148

O	-0.100569	6.171548	0.447758
O	-0.587761	5.241263	-1.914215
O	-2.502023	5.470474	-0.207222
H	0.941652	1.121634	-1.335028
H	1.315988	0.028933	1.498038
H	0.889318	-1.429678	-1.160904
H	-1.308379	-2.044701	-0.405216
F	-1.459407	0.027438	-1.751977
H	-0.742435	1.353439	1.221093
H	-1.159144	2.676474	-1.519688
H	-2.366319	2.638161	-0.202307
H	0.957999	3.079716	0.254699
H	3.247982	0.629345	0.348253
H	2.205625	-2.411842	0.819221
H	1.020449	-3.349857	0.189562
H	-0.354639	-1.948115	1.861714

Fluoro-carba-β-L-idosamine-6-phosphate $^{1}C_{4}$-configuration (BP/def2-TZVPP)

C	0.680988	0.957754	-0.400531
C	1.258523	-0.313453	0.252528
C	0.287268	-1.502274	0.164480
C	-1.118950	-1.172703	0.705655
C	-1.689777	0.109081	0.051732
C	-0.705878	1.271475	0.155022
F	-1.257692	2.374780	-0.573399
O	-2.939883	0.427946	0.674580
N	-1.213705	-1.017631	2.170946
O	1.576105	-0.120981	1.651698
C	1.622843	2.165791	-0.220383
H	2.173276	-0.583265	-0.296367
O	0.172453	-1.878292	-1.225479
H	-1.785480	-2.000575	0.423321

H	-1.887241	-0.080970	-1.013738
H	-0.644603	1.619505	1.199240
H	-2.799027	0.122832	1.603703
H	-0.376822	-0.551254	2.530438
H	-1.258340	-1.932154	2.620754
H	2.331635	0.490790	1.689994
H	0.472022	-2.796651	-1.309921
H	0.705457	-2.335916	0.749558
H	1.274879	3.005302	-0.842522
O	2.984857	1.860445	-0.511921
H	1.580700	2.499131	0.832501
P	3.531628	2.131950	-2.105901
O	5.007195	1.732022	-1.974809
O	3.298562	3.630684	-2.361662
H	0.601195	0.740526	-1.477601
O	2.694761	1.215706	-3.009025

Fluoro-carba-β-L-idosamine-6-phosphate $^4C_1$-configuration (BP/def2-TZVPP)

C	0.979516	1.172371	0.152493
C	1.615795	-0.180500	0.469462
C	0.929366	-1.300749	-0.329231
C	-0.574776	-1.340746	-0.038990
C	-1.239667	0.037603	-0.192412
C	-0.526530	1.211491	0.477855
O	1.744230	2.162292	0.876631
O	3.007619	-0.170454	0.098848
N	1.507818	-2.636715	-0.136419
O	-0.753686	-1.834964	1.300298
H	1.111709	1.349589	-0.929407
H	1.530807	-0.388940	1.552171
H	1.038981	-1.044644	-1.396553
H	-1.046888	-2.030981	-0.758584

H	1.583554	3.028006	0.465682
H	3.356879	0.680800	0.423114
H	1.354365	-2.923358	0.833926
H	2.521249	-2.576591	-0.257614
H	-1.697386	-2.030595	1.425798
H	-2.278890	-0.011973	0.161419
F	-1.312184	0.296938	-1.604138
C	-0.836653	1.292012	1.989590
H	-0.965957	2.126472	0.047192
H	-0.474061	0.394587	2.511312
O	-2.239781	1.388321	2.237191
H	-0.315015	2.166101	2.408135
P	-2.927865	2.943401	2.313235
O	-2.711009	3.582123	0.931849
O	-2.188718	3.667708	3.450369
O	-4.389131	2.594078	2.629478

Carba-α-D-glucosamine-6-phosphate (BP/def2-TZVPP)

C	0.822410	1.207243	-0.188953
C	1.415534	-0.064880	0.411134
C	0.701941	-1.318086	-0.093463
C	-0.823559	-1.224591	0.143126
C	-1.415754	0.089876	-0.358810
C	-0.669161	1.328975	0.160580
C	-1.282139	2.611054	-0.408279
O	1.598290	2.314921	0.304204
O	2.813018	-0.191562	0.078541
N	1.199414	-2.493684	0.648614
O	-1.089837	-1.377552	1.549069
H	-2.476831	0.136621	-0.070592
O	-0.628542	3.750410	0.172939
P	-0.992783	5.296824	-0.490874

O	-0.095275	6.188775	0.371899
O	-0.592580	5.210161	-1.968124
O	-2.498852	5.473402	-0.257261
H	0.923901	1.154561	-1.293941
H	1.310203	-0.004084	1.510900
H	0.878850	-1.395317	-1.182159
H	-1.300317	-2.059860	-0.405662
H	-1.388769	0.078291	-1.461742
H	-0.756677	1.367111	1.260168
H	-1.159518	2.635089	-1.507682
H	-2.363776	2.649762	-0.187070
H	0.968470	3.085453	0.289194
H	3.231917	0.644181	0.352837
H	2.214946	-2.432257	0.746197
H	1.011221	-3.349976	0.122656
H	-0.366427	-1.981481	1.842174

α-D-Glucosamine-6-phosphate (BP/def2-TZVPP)

C	0.902343	1.222809	-0.173631
C	1.481217	-0.066088	0.394984
C	0.705494	-1.286143	-0.098944
C	-0.821797	-1.089277	0.096549
O	-1.281725	0.166440	-0.366258
C	-0.589164	1.307624	0.184222
C	-1.267807	2.545609	-0.400211
O	1.641385	2.322970	0.373648
O	2.858238	-0.249562	0.017333
N	1.109423	-2.466138	0.686089
O	-1.151517	-1.271267	1.468097
O	-0.629749	3.699490	0.152297
P	-1.080939	5.236735	-0.492184
O	-0.174126	6.154647	0.331015

O	-0.747096	5.159570	-1.985549
O	-2.578650	5.355011	-0.185878
H	0.997876	1.207387	-1.278203
H	1.410490	-0.010719	1.497883
H	0.893818	-1.397562	-1.181037
H	-1.376576	-1.813977	-0.523467
H	-0.694814	1.317149	1.283400
H	-1.168737	2.540720	-1.501018
H	-2.342319	2.537579	-0.148251
H	1.016449	3.094110	0.318155
H	3.346448	0.521799	0.355693
H	2.123861	-2.462589	0.810209
H	0.881969	-3.327444	0.184794
H	-0.409085	-1.834442	1.802234

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