Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information for

Fluorine-Directed 1,2-*trans* Glycosylation of Rare Sugars

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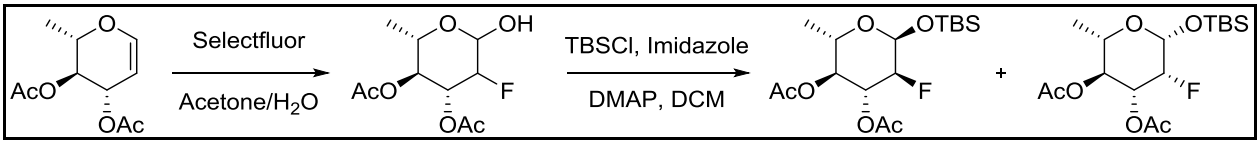
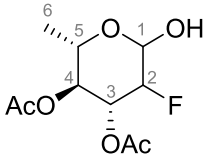
Methods and materials:

All chemicals were purchased as reagent grade and used without further purification. Solvents for extractions and flash column chromatography were technical grade and distilled prior to use. Solvents for reactions were dried by a *Grubbs* purification system including columns packed with molecular sieve and aluminium oxide. If necessary the reactions were performed under an argon atmosphere using schlenk-technique and dry glassware. For analytical thin layer chromatography (TLC,) pre-coated *Merck* SiO_2-60 F_{254} plates (0.25 mm) were used and visualised with a UV-lamp (254 nm) and CAM-stain (Cerium ammonium molybdate). Column chromatography was carried out on *Fluka* SiO_2-60 (230-400 mesh particle size) as stationary phase. NMR-spectra were recorded on Bruker's AVANCE 300 MHz, AVANCE 400 MHz, DRX 400 MHz and Agilent DD2 600 MHz spectrometers. The measurements were performed in deuterated chloroform or deuterated methylene chloride at 298 K at rt. Chemical shifts (δ values) in parts per million (ppm) are reported relative to the residual solvent peak ($CDCl_3$: δ_H 7.26, δ_C 77.16, CD_2Cl_2: δ_H 5.32, δ_C 54.0). For description of the splitting pattern, the following abbreviations are used: *s* = singlet, *d* = doublet, *t* = triplet, *sept* = septuplet, *m* = multiplet, *br* = broad. Obtained coupling constants (*J*) are given in Hertz (Hz). High-resolution mass spectra (HR ESI) were measured by the MS service of the Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster. Melting Points were measured on *a Büchi* B540 melting-point apparatus. Optical rotations were obtained using a *JASCO P-2000* polarimeter. IR spectra were recorded on a *Perkin-Elmer 100 FT-IR* spectrometer, selected adsorption bands are reported in wavenumbers (cm^{-1}) and intensities are reported as: w = weak, m = medium, s = strong and br = broad.

Experimental section:



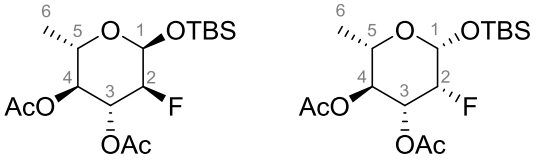
2,6-Dideoxy-2-fluoro-3,4-di-*O*-acetyl-L-manno/glucopyranose (**S1**)



SelectFluor™ (2.7 g, 7.8 mmol, 1.5 eq) was added at to a solution of 3,4-Di-*O*-acetyl-6-deoxy-L-glucal (1.0 mL, 5.2 mmol, 1.0 eq) in acetone (25 mL) and water (5 mL). The solution was stirred at room temperature for 20 h. The solvents were then evaporated and the residue dissolved in DCM and a sat. aq. solution of $NaHCO_3$. The aq. phase was extracted with DCM and the combined organic phases dried over $MgSO_4$, filtered and evaporated to dryness. The crude was filtered through silica using a mixture of cyclohexane and ethyl acetate as eluent (3:1), to afford an inseparable mixture of the gluco- and manno-configured products (1.14 g, 88%), that was used directly in the next step.

1-*O*-tert-butyldimethylsilyl-2, 6 -dideoxy-2-fluoro-3,4-di-*O*-acetyl-α-L-glucopyranose (**S2**) and

1-*O*-tert-butyldimethylsilyl-2, 6-dideoxy-2-fluoro-3,4-di-*O*-acetyl-β-L-mannopyranose (**S3**)

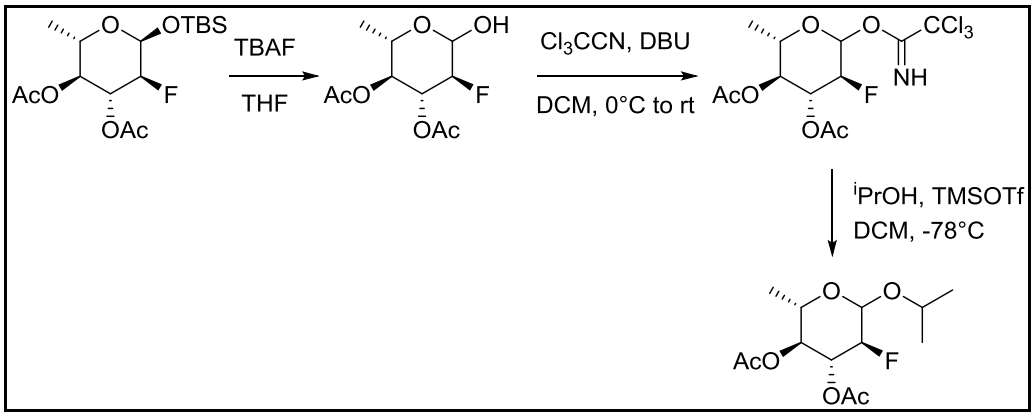


Under Ar, TBSCl (452 mg, 3.0 mmol, 1.5 eq) was added to a solution of 2,6-Dideoxy-2-fluoro-3,4-di-*O*-acetyl-L-manno/glucopyranose (500 mg, 2 mmol, 1.0 eq), imidazole (408 mg, 3 mmol, 1.5 eq), and DMAP (24 mg, 0.2 mmol, 0.1 eq) in 10 mL of anhydrous DCM. The mixture was allowed to stir at room temperature overnight. Water was added, and the organic phases were separated. The aq. phase was further extracted with DCM, and the combined organic layers dried with $MgSO_4$, filtered and evaporated. The crude was purified by silica gel chromatography using a 20:1 mixture of cyclohexane and ethyl acetate as eluent, affording **S2** as a white solid (300 mg, 41%) and **S3** as a white solid (370 mg, 51%).

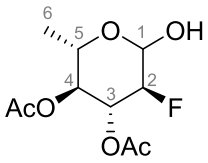
S2: White solid; **m.p.** 61-62°C; [***m/z* (ESI)** found: 387.1605 $(M+Na)^+$, $C_{16}H_{29}FO_6SiNa$ requires 387.1610]; $[\alpha]_D^{25}$ = -44 (*c* 0.92 in $CHCl_3$) ν_{max}(neat)/cm^{-1} 2933m, 2859m, 1745s, 1377m, 1362m, 1215s, 1027s, 837s.**^{1}H NMR** (400 MHz, $CDCl_3$) δ = 0.13 (s, 3H, CH_3), 0,14 (s, 3H, CH_3), 0,91 (s, 9H, ^{t}Bu), 1.22 (d, *J* = 6.2 Hz, 3H, H-C6), 2.03 (s, 3H, Ac), 2.07 (s, 3H, Ac), 3.57 (dq, *J* = 9.7, 6.2 Hz, 1H, H-C5), 4.19 (ddd, *J* = 50.8, 9.3, 7.4 Hz, 1H, H-C2), 4.77 (m, 2H, H-C1, H-C4), 5.24 (dt, *J* = 14.1, 9.4 Hz, 1H, H-C3) ppm.**^{13}C NMR** (150 MHz,

$CDCl_3$) δ = -5.0 (CH_3), -4.3 (CH_3), 17.5 (CH_3, C6), 18.2 (C), 20.8 (CH_3), 20.9 (CH_3), 25.7 (3xCH_3), 70.1 (CH, C5), 73.0 (d, $^2J_{CF}$ = 19.6 Hz, CH, C3), 73.4 (d, $^3J_{CF}$ = 7.2 Hz, CH, C4), 91.8 (d, $^1J_{CF}$ = 190.1 Hz, CH, C2), 95.2 (d, $^2J_{CF}$ = 22.6 Hz, CH, C1), 169.9 (C), 170.4 (C)ppm.**^{19}F NMR** (282 MHz, $CDCl_3$) δ = -198.67 (ddd, *J* = 50.8, 14.1, 2.9 Hz) ppm.

S3: White solid; **m.p.** 85-86°C; [***m/z* (ESI)** found: 387.1609 $(M+Na)^+$, $C_{16}H_{29}FO_6SiNa$ requires 387.1610]; $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = +20 (*c* 0.97 in $CHCl_3$) $\boldsymbol{\nu}_{\mathbf{max}}$ (neat)/cm^{-1} 2936m, 2859m, 1744s, 1371m, 1240s, 1218s, 1200s, 1077s, 1051s, 839s.**^{1}H NMR** (400 MHz, $CDCl_3$) δ = 0.13 (s, 3H, CH_3), 0,15 (s, 3H, CH_3), 0,90 (s, 9H, ^{t}Bu), 1.26 (d, *J* = 6.1 Hz, 3H, H-C6), 2.05 (s, 3H, Ac), 2.06 (s, 3H, Ac), 3.51 (dq, *J* = 9.6, 6.5 Hz, 1H, H-C5), 4.68 (dd, *J* = 51.4, 2.5 Hz, 1H, H-C2), 4.84 (d, *J* = 18.1 Hz, 1H, H-C1), 4.94 (ddd, *J* = 27.5, 10.1, 2.5 Hz, 1H, H-C3), 5.10 (m, 1H, H-C4) ppm.**^{13}C NMR** (150 MHz, $CDCl_3$) δ = -4.9 (CH_3), -4.0 (CH_3), 17.6 (CH_3, C6), 18.2 (C), 20.9 (2xCH_3), 25.8 (3xCH_3), 70.5 (CH, C5), 70.6 (CH, C4), 72.3 (d, $^2J_{CF}$ = 17.2 Hz, CH, C3), 88.7 (d, $^1J_{CF}$ = 190.2 Hz, CH, C2), 93.9 (d, $^2J_{CF}$ = 16.2 Hz, CH, C1), 169.9 (C), 170.4 (C) ppm.**^{19}F NMR** (282 MHz, $CDCl_3$) δ = -220.59 (ddd, *J* = 51.3, 27.5, 18.1 Hz) ppm.



2, 6 -Dideoxy-2-fluoro-3,4-di-*O*-acetyl- L-glucopyranose **(S4)**

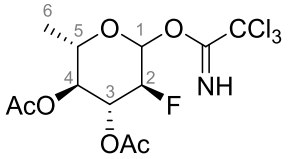


A 1M solution of TBAF in THF (0.56 mL, 0.56 mmol, 2 eq) was added dropwise to a solution of **S2** (70 mg, 0.28 mmol, 1 eq) in 0.8mL of THF at 0°C. The mixture was stirred for 1h at low temperature, and water was then added. The aq. phase was extracted with DCM, and the combined organic layers once washed with water to be then dried with $MgSO_4$, filtered and evaporated. The crude was filtered through silica/NEt_3 using a 3:1 mixture of cyclohexane and ethyl acetate as eluent. The final product was isolated as a colourless oil (52 mg, 75%, α:β = 2:1).

Colourless oil; [***m/z* (ESI)** found: 273.0744 $(M+Na)^+$, $C_{10}H_{15}FO_6Na$ requires 273.0745]; $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = -112 (*c* 2.30 in $CHCl_3$) $\boldsymbol{\nu}_{\mathbf{max}}$ (neat)/cm^{-1} 3460br, 2986w, 2944w, 1749s, 1370m, 1239s, 1216s, 1024s, 912m, 731m.**^{1}H NMR** (600 MHz, $CDCl_3$) δ = 1.17 (d, *J* = 6.3 Hz, 3H, H-C6α), 1.24 (d, *J* = 6.2 Hz, 1.5H, H-C6β), 2.04 (s, 1.5H, Acβ), 2.05 (s, 3H, Acα), 2.07 (s, 3H, Acα) 2.08 (s, 1.5H, Acβ), 3.64 (dq, *J* = 9.8, 6.2 Hz, 0.5H, H-C5β), 4.17 (dq, *J* = 9.9, 6.1 Hz, 1H, H-C5α), 4.25 (ddd, *J* = 51.0, 9.2, 7.7 Hz, 0.5H, H-C2β), 4.49 (ddd, *J* = 49.7, 9.5, 3.8 Hz, 1H, H-C2α), 4.75 (t, *J* = 9.6 Hz, 1H, H-C4α), 4.78 (t, *J* = 9.6 Hz, 0.5H, H-C4β), 4.87 (dd, *J* = 7.7, 2.8 Hz, 1H, H-C1β), 5.28 (dt, *J* = 14.1, 9.3 Hz, 0.5H, H-C3β), 5.41 (d, *J* = 3.7 Hz, 1H, H-C1α), 5.55 (dt, *J* = 12.2, 9.5

Hz, 1H, H-C3α) ppm.**^{13}C NMR** (150 MHz, $CDCl_3$) δ = 17.1 (CH_3, C6α), 17.3 (CH_3, β), 20.6 (CH_3, Acβ), 20.7 (CH_3, Acα), 20.7 (CH_3, Ac β, 20.7 (CH_3, Acα), 65.1 (CH, C5α), 70.2 (CH, C5β), 70.4 (d, $^2J_{CF}$ = 19.1 Hz, CH, C3α), 72.7 (d, $^2J_{CF}$ = 19.4 Hz, CH, C3β), 73.1 (d, $^3J_{CF}$ = 7.1 Hz, CH, C4β), 73.2 (d, $^3J_{CF}$ = 7.1 Hz, CH, C4α), 88.3 (d, $^1J_{CF}$ = 192.7 Hz, CH, C2α), 90.1 (d, $^2J_{CF}$ = 21.1 Hz, CH, C1α), 91.0 (d, $^1J_{CF}$ = 190.6 Hz, CH, C2β), 94.4 (d, $^2J_{CF}$ = 22.7 Hz, CH, C1β), 169.8 (C, Acβ), 170.0 (C, Acα), 170.1 (C, Acβ), 170.2 (C, Acα) ppm.**^{19}F NMR** (282 MHz, $CDCl_3$) δ = -199.28 (ddd, *J* = 51.0, 14.1, 2.8 Hz, β-anomer), -199.81 (dd, *J* = 49.8, 12.1 Hz, α-anomer) ppm.

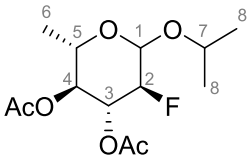
2, 6 -Dideoxy-2-fluoro-3,4-di-*O*-acetyl- L-glucopyranosyl trichloroacetimidate **(S5)**



DBU (2.0 µL, 12 µmol, 0.1 eq) was added to a solution of Cl_3CCN (0.12 mL, 1.2 mmol, 10 eq) and **S4** (30 mg, 0.12 mmol, 1.0 eq) in dry DCM (1.5 mL) at 0 °C under an atmosphere of Ar. Upon completion of the addition, the solution was allowed to warm to room temperature, stirred for 45 min and the solvents evaporated. Purification by silica gel chromatography (SiO_2/NEt_3) using a 7:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S5** as a colourless oil (36 mg, 77%, α:β = 6:1).

^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.16 (d, *J* = 6.3 Hz, 3H, H-C6), 2.00 (s, 3H, Ac), 2.02 (s, 3H, Ac), 3.42 (m, 0.5H), 4.05 (m, 1.5H), 4.64 (ddd, *J* = 48.3, 9.6, 3.9 Hz, 1H), 4.78 (t, *J* = 9.8 Hz, 1H), 5.52 (dt, *J* = 12.1, 9.6 Hz, 1H), 6.32 (dd, *J* = 6.3, 2.1 Hz, 1H, H-C1β), 6.48 (d, *J* = 3.9 Hz, 1H, H-C1α), 8.35 (s, 1H, NHβ), 8.68 (s, 1H, NHα) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -202.21 (ddd, *J* = 48.4, 12.1, 0.7 Hz, α-anomer), -204.49 (m, β-anomer) ppm.

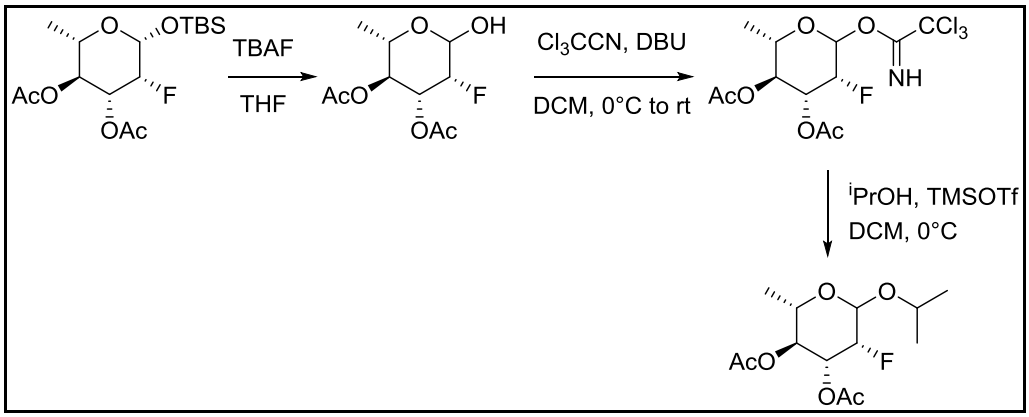
1-*O*-Isopropyl-2,6-dideoxy-2-fluoro-3,4-di-*O*-acetyl-L-glucopyranose **(S6)** – Table 2, entry 9



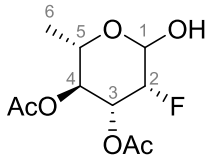
A 0.1M solution of TMSOTf (0.04 mL, 4 µmol, 0.1 eq) was added to a solution of **S5** (16 mg, 0.04 mmol, 1 eq) and isopropanol (0.03 mL, 0.40 mmol, 10 eq) in dry DCM (1 mL) under an Ar atmosphere at -78°C. The reaction was allowed to progress for 2h at -78°C, and then slowly warmed up to room temperature. NEt_3 was added to quench the reaction, and the solvent was removed under vacuum. Purification by silica gel chromatography using a 6:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S6** as a colourless oil (6 mg, 55%, α:β = 1:16).

Colourless oil; [***m/z* (ESI)** found: 315.1213 $(M+Na)^+$, $C_{13}H_{21}FO_6Na$ requires 315.1220]; $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = -18 (*c* 0.60 in $CHCl_3$) $\boldsymbol{\nu_{max}}$ (neat)/cm^{-1} 2922m, 2853m, 1751s, 1456w, 1372m, 1236s, 1215s, 1071s, 1043s, 1024s. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 1.21 (d, *J* = 6.2 Hz, 3H, H-C8), 1.23 (d, *J* = 6.2 Hz, 3H, H-C6), 1.27 (d, *J* = 6.2 Hz, 3H, H-C8), 2.04 (s, 3H, Ac), 2.07 (s, 3H, Ac), 3.57 (dq, *J* = 9.7, 6.2 Hz, 1H, H-C5), 4.01 (hept, *J* = 6.2 Hz, 1H, H-C7), 4.23 (ddd, *J* = 50.7, 9.2, 7.8 Hz, 1H, H-C2), 4.59 (dd, *J* = 7.8, 2.9 Hz, 1H, H-C1), 4.75 (t, *J* = 9.8 Hz, 1H, H-C4), 5.26 (dt, *J* = 14.5, 9.3 Hz, 1H, H-C3) ppm.**^{13}C NMR** (150 MHz, $CDCl_3$) δ = 17.3 (CH_3, C6), 20.6 (CH_3, Ac), 20.7 (CH_3, Ac), 21.8 (CH_3, C8), 23.3 (CH_3, C8), 69.9 (CH, C5), 72.5 (CH, C7), 73.0 (d, $^2J_{CF}$ = 19.6 Hz, CH, C3), 73.2 (d, $^3J_{CF}$ = 7.2 Hz, CH, C4), 89.76 (d, $^1J_{CF}$ = 190.3 Hz, CH, C2), 98.6 (d, $^2J_{CF}$ = 22.1 Hz, CH, C1), 169.7

(C, Ac), 170.1 (C, Ac) ppm.**^{19}F NMR** (282 MHz, $CDCl_3$) δ = -199.34 (ddd, *J* = 50.7, 14.5, 2.8 Hz, β-anomer), -200.73 (dd, *J* = 49.9, 11.8 Hz, α-anomer) ppm.



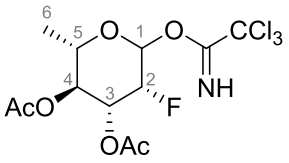
2, 6 -Dideoxy-2-fluoro-3,4-di-*O*-acetyl- L-mannopyranose (**S7**)



A 1M solution of TBAF in THF (0.56 mL, 0.56 mmol, 2 eq) was added dropwise to a solution of **S3** (102 mg, 0.28 mmol, 1 eq) in 0.8mL of THF at 0°C. The mixture was stirred for 1h at low temperature, and water was then added. The aq. phase was extracted with DCM, and the combined organic layers once washed with water to be then dried with $MgSO_4$, filtered and evaporated. The crude was filtered through silica/NEt_3 using a 3:1 mixture of cyclohexane and ethyl acetate as eluent. The final product was isolated as a colourless oil (63 mg, 90%, α:β = 5:1).

Colourless oil; [***m/z* (ESI)** found: 273.0743 $(M+Na)^+$, $C_{10}H_{15}FO_6Na$ requires 273.0745]; $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = -44 (*c* 0.95 in $CHCl_3$) $\boldsymbol{\nu_{max}}$ (neat)/cm^{-1} 3429br, 2984w, 2919w, 1734s, 1371m, 1220s, 1048s, 909s, 728s. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 1.12 (d, *J* = 6.3 Hz, 3H, H-C6α), 1.17 (d, *J* = 6.1 Hz, 0.6H, H-C6β), 1.96 (s, 3H, Acα), 1.97 (s, 3H, Acβ), 2.00 (s, 3H, Acα), 2.01 (s, 3H, Acβ), 3.47 (m, 0.2H, H-C5β), 4.02 (m, 1H, H-C5α), 4.69 (dt, *J* = 50.0, 2.3 Hz, 1H, H-C2α), 4.90 (ddd, *J* = 34.0, 6.0, 2.1 Hz, H-C2β), 5.02 (td, *J* = 9.9, 1.0 Hz, 1H, H-C4α), 5.15 (dd, *J* = 10.2, 2.6 Hz, 0.5H, H-C3α) 5.22-5.25 (m, 1.5H, H-C1α, H-C3α) ppm.**^{13}C NMR** (100 MHz, $CDCl_3$) δ = 14.2 (CH_3, C6β), 17.4 (CH_3, C6α), 20.6 (CH_3, Acβ), 20.7 (CH_3, Acβ), 20.7 (CH_3, Acα), 20.8 (CH_3, Acα), 66.4 (CH, C5α), 69.6 (d, $^2J_{CF}$ = 16.7 Hz, CH, C3α), 70.1 (CH, C4β), 70.4 (CH, C5β), 70.9 (CH, C4α), 71.4 (d, $^2J_{CF}$ = 17.0 Hz, CH, C3β), 86.7 (d, $^1J_{CF}$ = 178.1 Hz, CH, C2α), 88.6 (d, $^1J_{CF}$ = 184.4 Hz, CH, C2β), 91.6 (d, $^1J_{CF}$ = 29.6 Hz, CH, C1α), 92.6 (d, $^2J_{CF}$ = 17.4 Hz, CH, C1β), 169.7 (C, Acβ), 169.9 (C, Acα), 170.3 (C, Acα), 171.3 (C, Acβ) ppm.**^{19}F NMR** (282 MHz, $CDCl_3$) δ = -204.31 (dddt, *J* = 50.0, 28.8, 7.2, 1.0 Hz, α-anomer, -223.21 (m, β-anomer) ppm.

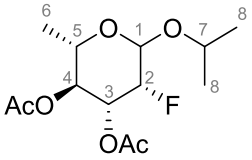
2, 6 -Dideoxy-2-fluoro-3,4-di-*O*-acetyl- L-mannopyranosyl trichloroacetimidate (**S8**)



DBU (40 µL, 25 µmol, 0.1 eq) was added to a solution of Cl_3CCN (0.25 mL, 2.5 mmol, 10 eq) and **S7** (63 mg, 0.25 mmol, 1.0 eq) in dry DCM (5 mL) at 0 °C under an atmosphere of Ar. Upon completion of the addition, the solution was allowed to warm to room temperature, stirred for 1h and the solvents evaporated. Purification by silica gel chromatography (SiO_2/NEt_3) using a 3:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S8** as a colourless oil (87 mg, 88%, α only).

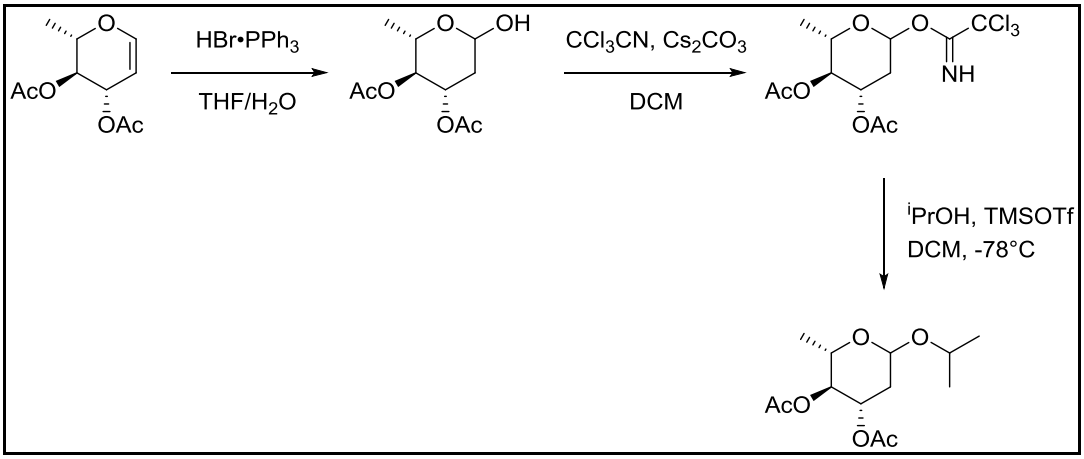
^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.21 (d, *J* = 6.2 Hz, 3H, H-C6), 2.01 (s, 3H, Ac), 2.05 (s, 3H, Ac), 4.04 (m, 1H), 4.88 (dt, *J* = 48.6, 2.2 Hz, 1H, H-C2), 5.11-5.28 (m, 2H), 6.32 (dd, *J* = 6.4, 2.1 Hz, 1H, H-C1), 8.70 (s, 1H, NH) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -204.49 (m) ppm.

1-*O*-Isopropyl-2,6-dideoxy-2-fluoro-3,4-di-*O*-acetyl-L-mannopyranose (**S9**) – Table 2, entry 10

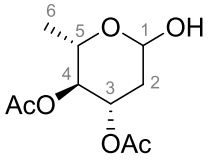


A 0.2M solution of TMSOTf (0.10 mL, 20 µmol, 0.1 eq) was added to a solution of **S8** (80 mg, 0.20 mmol, 1 eq) and isopropanol (0.15 mL, 2.00 mmol, 10 eq) in dry DCM (4 mL) under an Ar atmosphere at 0°C. The reaction was allowed to progress for 2h at 0°C, and then slowly warmed up to room temperature. NEt_3 was added to quench the reaction, and the solvent was removed under vacuum. Purification by silica gel chromatography using a 6:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S9** as a colourless oil (38 mg, 66%, α only).

Colourless oil; [***m/z* (ESI)** found: 315.1221 $(M+Na)^+$, $C_{13}H_{21}FO_6Na$ requires 315.1220]; $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = -69 (*c* 3.80 in $CHCl_3$) $\boldsymbol{\nu}_{\mathbf{max}}$ (neat)/cm^{-1} 2978w, 2938w, 1743s, 1371m, 1235s, 1217s, 1133m, 1072m, 1046s, 981m. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 1.15 (d, *J* = 6.1 Hz, 3H, H-C6), 1.20 (d, *J* = 6.3 Hz, 3H, H-C8), 1.22 (d, *J* = 6.3 Hz, 3H, H-C8), 2.04 (s, 3H, Ac), 2.08 (s, 3H, Ac), 3.88-3.96 (m, 2H, H-C5, H-C7), 4.66 (dt, *J* = 50.3, 2.3 Hz, 1H, H-C2), 4.99 (dd, *J* = 7.6, 2.0 Hz, 1H, H-C1), 5.08 (td, *J* = 9.9, 1.1 Hz, 1H, H-C4), 5.22 (ddd, *J* = 29.0, 10.1, 2.6 Hz, 1H, H-C3) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 17.3 (CH_3, C6), 20.7 (CH_3, Ac), 20.8 (CH_3, Ac), 21.3 (CH_3, C8), 23.2 (CH_3, C8), 70.0 (d, $^2J_{CF}$ = 16.6 Hz, CH, C3), 70.2 (CH, C4), 87.9 (d, $^1J_{CF}$ = 178.8 Hz, CH, C2), 95.1 (d, $^2J_{CF}$ = 29.0 Hz, CH, C1), 169.8 (C, Ac), 170.2 (C, Ac) ppm.**^{19}F NMR** (282 MHz, $CDCl_3$) δ -203.16 (dddt, *J* = 50.3, 29.0, 7.6, 1.1 Hz) ppm.



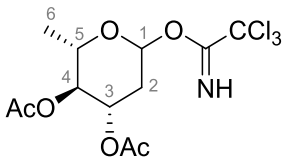
2, 6 -Dideoxy-3,4-di-*O*-acetyl- L-glucopyranose (**S10**)



3,4-Di-*O*-acetyl-6-deoxy-L-glucal (100 mg, 0.47 mmol, 1 eq) was dissolved in 1.5 mL of THF, and HBr•PPh_3 (16 mg, 0.05 mmol, 0.10 eq) was added as a solid. The mixture was stirred for 10 min at room temperature, and H_2O (0.01 mL, 0.71 mmol, 1.5 eq) was added. The reaction was allowed to progress overnight at r.t., and the following day it was quenched with $NaHCO_3$ and extracted with ethyl acetate. The organic layers were dried over $MgSO_4$, filtered and the solvent removed. Purification by silica gel chromatography using a 3:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S10** as a colourless oil (81 mg, 74%, α:β = 2:1).

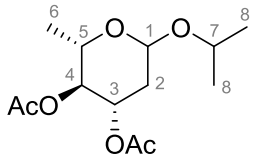
Colourless oil; [***m/z* (ESI)** found: 255.0839 $(M+Na)^+$, $C_{10}H_{16}O_6Na$ requires 255.0840]; $[\alpha]_D^{25}$ = -27 (*c* 4.10 in $CHCl_3$) ν_{max} (neat)/cm^{-1} 3434br, 3983w, 2941w, 1826w, 1738s, 1368m, 1224s, 1125m, 1046s, 1002m, 730s. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 1.16 (d, *J* = 6.3 Hz, 3H, H-C6α), 1.22 (d, *J* = 6.2 Hz, 1.5H, H-C6β), 1.66 (ddd, *J* = 12.4, 11.8, 9.7 Hz, 0.5H, H-C2β), 1.77 (ddd, *J* = 12.9, 11.7, 3.7 Hz, 1H, H-C2α), 2.00 (s, 3H, Acα), 2.02 (s, 1.5H, Acβ), 2.04 (s, 1.5H, Acβ), 2.05 (s, 3H, Acα), 2.26 (ddd, *J* = 12.8, 5.3, 1.4 Hz, 1H, H-C2α), 2.38 (ddd, *J* = 12.4, 5.2, 2.1 Hz, 0.5H, H-C2β), 3.53 (dq, *J* = 9.6, 6.2 Hz, 0.5H, H-C5β), 4.11 (dq, *J* = 9.8, 6.3 Hz, 1H, H-C5α), 4.74 (t, *J* = 9.8 Hz, 1.5H, H-C4α, H-C4β), 4.89 (d, *J* = 9.7 Hz, 0.5H, H-C1β), 4.98 (ddd, *J* = 11.8, 9.4, 5.3 Hz, 0.5H, H-C3β), 5.31 (m, 1H, H-C3α), 5.34 (m, 1H, H-C1α) ppm.**^{13}C NMR** (100 MHz, $CDCl_3$) δ = 17.6 (CH_3, C6α), 17.6 (CH_3, C6β), 20.8 (CH_3, Acβ), 20.8 (CH_3, Acα), 20.9 (CH_3, Acβ), 21.0 (CH_3, Acα), 35.4 (CH_2, C2α), 37.9 (CH_2, C2β), 65.7 (CH, C5α), 68.2 (CH, C3α), 70.1 (CH, C5β), 70.5 (CH, C3β), 70.4 (CH, C4β), 74.8 (CH, C4α), 94.5 (CH,C1α), 93.5 (CH, C1β), 170.0 (C, Acβ), 170.2 (C, Acα), 170.3 (C, Acα), 170.4 (C, Acβ) ppm.

2, 6 -Dideoxy-3,4-di-*O*-acetyl- L-glucopyranosyl trichloroacetimidate (**S11**)



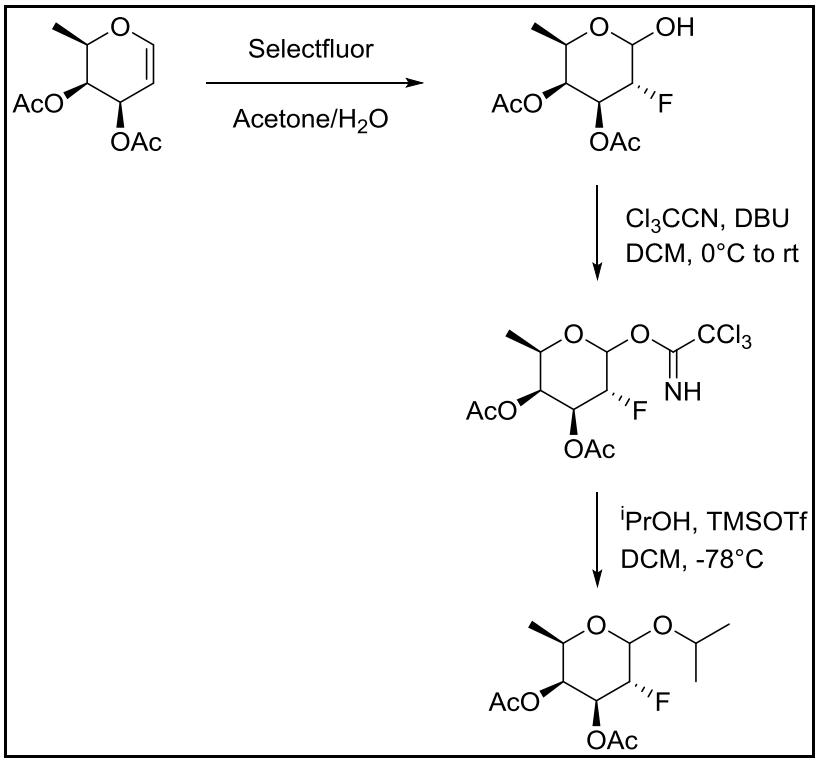
S10 (40 mg, 0.17 mmol, 1 eq) was dissolved in 1.5 mL of anh. DCM under an atmosphere of Ar. Cs_2CO_3 (10 mg, 0.03 mmol, 0.2 eq) was added in one portion, followed by Cl_3CCN (0.09 mL, 0.85 mmol, 5 eq). The mixture was stirred at room temperature for 2h, filtered through a celite pad and used in the following reaction with no further purification.

1-*O*-Isopropyl-2,6-dideoxy -3,4-di-*O*-acetyl-L-glucopyranose (**S12**) – Table 2, entry 12

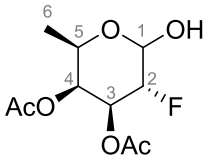


A 0.1M solution of TMSOTf (0.17 mL, 0.17 mmol, 0.1 eq) was added to a solution of **S11** (64 mg, 0.17 mmol, 1 eq) and isopropanol (0.13 mL, 1.70 mmol, 10 eq) in dry DCM (3.5 mL) under an Ar atmosphere at -78°C. The reaction was allowed to progress for 2h at -78°C, and then slowly warmed up to room temperature. NEt_3 was added to quench the reaction, and the solvent was removed under vacuum. Purification by silica gel chromatography using a 3:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S12** as a colourless oil (45 mg, 96%, α:β = 1:1).

Colourless oil; [***m/z*** **(ESI)** found: 297.1333 $(M+Na)^+$, $C_{13}H_{22}O_6Na$ requires 297.1309]; $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = -24 (*c* 4.50 in $CHCl_3$) $\boldsymbol{\nu_{max}}$ (neat)/cm^{-1} 29975w, 2938w, 1743s, 1368m, 1242s, 1222s, 1047s, 1007s, 921m, 731m. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 1.05-1.17 (m, 18H, H-C6α, H-C6β, H-C8α, H-C8β), 1.64 (td, *J* = 12.1, 9.7 Hz, 1H, H-C2β), 1.72 (ddd, *J* = 12.9, 11.7, 3.7 Hz, 1H, H-C2α), 1.93 (s, 3H, Ac), 1.95 (s, 3H, Ac), 1.97 (s, 3H, Ac), 1.98 (s, 3H, Ac), 2.08 (ddd, *J* = 12.7, 5.4, 1.4 Hz, 1H, H-C2α), 2.18 (ddd, *J* = 12.5, 5.3, 2.0 Hz, 1H, H-C2β), 3.39 (dq, *J* = 9.5, 6.2 Hz, 1H, H-C5β), 3.75-3.95 (m, 3H, H-C5α, H-C7α, H-C7β), 4.55 (dd, *J* = 9.7, 2.0 Hz, 1H, H-C1β), 4.66 (td, *J* = 9.6, 4.6 Hz, 2H, H-C4α, H-C4β), 4.87-4.93 (m, 2H, H-C1α, H-C3β), 5.22 (ddd, *J* = 11.7, 9.5, 5.3 Hz, 1H, H-C3α) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 17.5 (CH_3, C6), 17.7 (CH_3, C6), 20.8 (CH_3, Ac), 20.9 (CH_3, Ac), 21.0 (CH_3, Ac), 21.0 (CH_3, Ac), 21.3 (CH_3, C8), 21.8 (CH_3, C8), 23.3 (CH_3, C8), 21.4 (CH_3, C8), 35.8 (CH_2, C2α), 37.0 (CH_2, C2β), 65.5 (CH, C5α), 68.8 (CH, C7), 69.2 (CH, C3α), 69.9 (CH, C5β), 70.9 (CH, C3β), 71.0 (CH, C7), 74.2 (CH, C4), 75.1 (CH, C7), 94.5 (CH, C1α), 97.2 (CH, C1β), 170.0 (C, Ac), 170.2 (C, Ac), 170.3 (C, Ac), 170.4 (C, Ac) ppm.



2,6-Dideoxy-2-fluoro-3,4-di-*O*-acetyl-D-galactopyranose (**S13**)

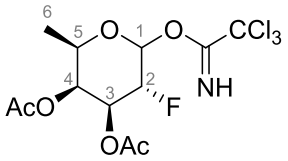


SelectFluor™ (250 mg, 0.71 mmol, 1.5 eq) was added at to a solution of 3,4-Di-*O*-acetyl-6-deoxy-D-fucal (100 mg, 0.47 mmol, 1.0 eq) in acetone (2 mL) and water (0.4 mL). The solution was stirred at room temperature for 20 h. The solvents were then evaporated and the residue dissolved in DCM and a sat. aq. solution of $NaHCO_3$. The aq. phase was extracted with DCM and the combined organic phases dried over $MgSO_4$, filtered and evaporated to dryness. The crude was filtered through silica using a mixture of cyclohexane and ethyl acetate as eluent (7:1), to afford **S13** as a white solid (92 mg, 79%, α:β = 2:1).

White solid; **m.p.** 128-130°C; [***m/z* (ESI)** found: 273.0745 $(M+Na)^+$, $C_{10}H_{15}FO_6Na$ requires 273.0745]; $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = +12 (*c* 0.45 in $CHCl_3$) $\boldsymbol{\nu}_{\mathbf{max}}$(neat)/$cm^{-1}$ 3399br, 1740s, 1716s, 1371m, 1249m, 1219m, 1044m. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 1.14 (d, *J* = 6.6 Hz, 3H, H-C6α), 1.22 (d, *J* = 6.4 Hz, 1.5H, H-C6β), 2.05 (s, 3H, Acα), 2.06 (s, 1.5H, Acβ), 2.16 (s, 3H, Acα), 2.17 (s, 1.5H, Acβ), 3.11 (brs, 1H, OHα), 3.57 (brs, 0.5H, OHβ), 3.89 (qd, *J* = 6.5, 1.2 Hz, 0.5H, H-C5β), 4.38-4.46 (m, 1.25H, H-C5α, H-C2β), 4.53 (dd, *J* = 9.9, 7.6 Hz, 0.25H, H-C2β), 4.71 (dd, *J* = 10.2, 3.8 Hz, 0.5H, H-C2α), 4.82-4.89 (m, 1H, H-C2α, H-C1β), 5.11 (ddd, *J* = 13.2, 9.8, 3.5 Hz, 0.5H, H-C3β), 5.27 (ddd, *J* = 3.8, 2.7, 1.1 Hz, 0.5H, H-C4β), 5.34 (td, *J* = 3.5, 1.3 Hz, 1H, H-C4α), 5.43-5.49 (m, 2H, H-C1α, H-C3α) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 15.8 (CH_3, C6α), 15.9 (CH_3, C6β), 20.5 (CH_3, Acβ), 20.6 (CH_3, Acα), 20.6 (CH_3, Acβ), 20.7 (CH_3, Acα), 64.7 (CH, C5α), 68.3 (d, $^2J_{CF}$ = 18.5 Hz, CH, C3α), 69.5 (CH, C5β), 70.9 (d, $^3J_{CF}$ = 8.2 Hz, CH, C4β), 71.3 (d, $^2J_{CF}$ = 18.5 Hz, CH, C3β), 71.7 (d, $^3J_{CF}$ = 7.7 Hz, CH, C4α), 85.9 (d, $^1J_{CF}$ = 188.5 Hz, CH, C2α), 89.3 (d, $^1J_{CF}$ = 186.3 Hz, CH, C2β), 90.7 (d, $^2J_{CF}$ = 21.3 Hz, CH, C1α), 94.8 (d, $^2J_{CF}$ = 23.1 Hz, CH, C1β), 170.1 (2xC, Ac), 170.5 (2xC, Ac) ppm. **^{19}F NMR** (282 MHz,

$CDCl_3$) δ = -207.51 (dddd, *J* = 51.8, 13.0, 3.9, 2.7 Hz, β-anomer), -207.80 (ddd, *J* = 50.3, 11.3, 3.4 Hz, α-anomer) ppm.

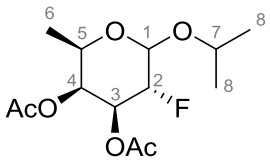
2,6-Dideoxy-2-fluoro-3,4-di-*O*-acetyl-D-galactopyranosyl trichloroacetimidate (**S14**)



DBU (60 µL, 40 µmol, 0.1 eq) was added to a solution of Cl_3CCN (0.36 mL, 3.6 mmol, 10 eq) and **X** (90 mg, 0.36 mmol, 1.0 eq) in dry DCM (3.0 mL) at 0 °C under an atmosphere of Ar. Upon completion of the addition, the solution was allowed to warm to room temperature, stirred for 45 min and the solvents evaporated. Purification by silica gel chromatography (SiO_2/NEt_3) using a 7:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S14** as a colourless oil (85 mg, 60%, α:β = 8:1). Only the α anomer was obtained pure after the filtration and used directly in the following reaction.

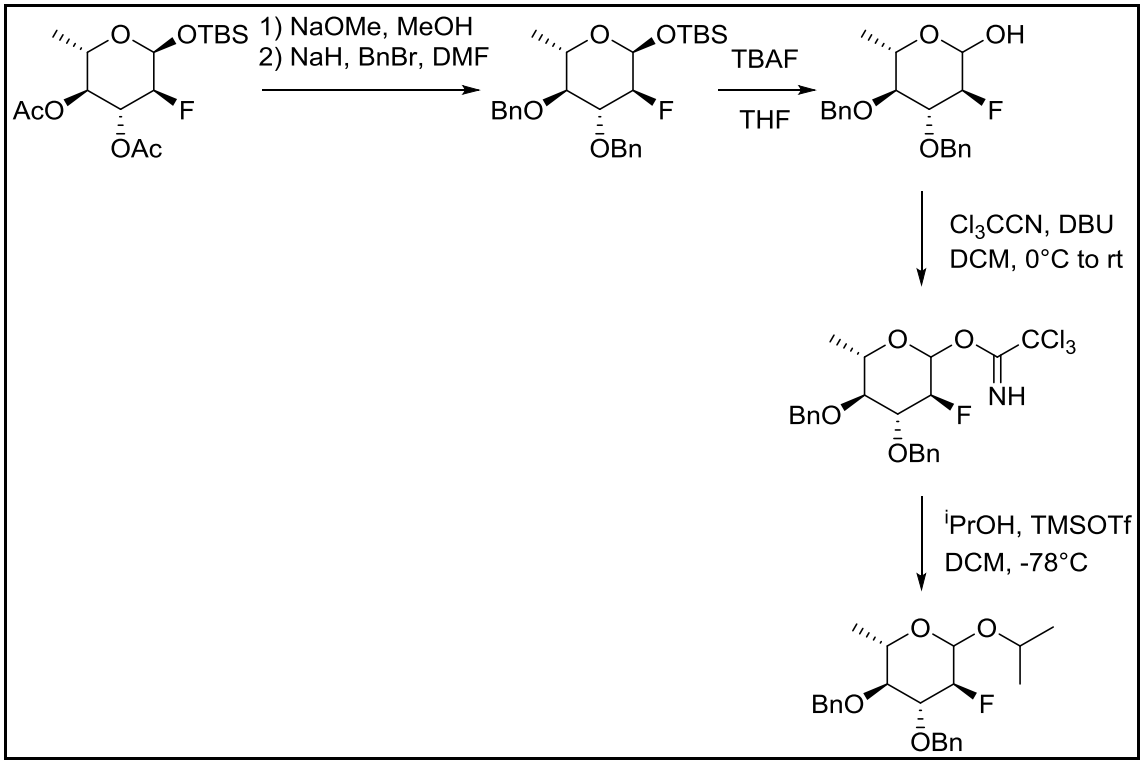
^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.19 (d, *J* = 6.5 Hz, 3H, H-C6), 2.08 (s, 3H, Ac), 2.19 (s, 3H, Ac), 4.39 (q, *J* = 6.4 Hz, 1H, H-C5), 4.98 (ddd, *J* = 49.0, 10.1, 3.9 Hz, 1H, H-C2), 5.42-5.47 (m, 1H), 5.51 (dd, *J* = 10.6, 3.5 Hz, 1H), 6.62 (d, *J* = 3.9 Hz, 1H, H-C1), 8.73 (s, 1H, NH) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -208.41 (dddd, *J* = 51.9, 13.1, 4.0, 2.7 Hz, β-anomer), -209.77 (ddd, *J* = 49.0, 10.9, 3.6 Hz, α-anomer) ppm.

1-*O*-Isopropyl-2,6-dideoxy-2-fluoro-3,4-di-*O*-acetyl-D-glucopyranose (**S15**) – Table 2, entry 11

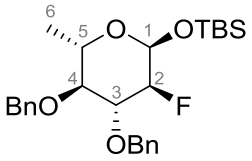


TMSOTf (4.0 µL, 20 µmol, 0.1 eq) was added to a solution of **S14** (73 mg, 0.19 mmol, 1 eq) and isopropanol (0.15 mL, 1.90 mmol, 10 eq) in dry DCM (4 mL) under an Ar atmosphere at -78°C. The reaction was allowed to progress for 2h at -78°C, and then slowly warmed up to room temperature. NEt_3 was added to quench the reaction, and the solvent was removed under vacuum. Purification by silica gel chromatography using a 7:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S15** as a white solid (49 mg, 86%, β only).

White solid; **m.p.** 97-99°C; [***m/z* (ESI)** found: 315.1214 $(M+Na)^+$, $C_{13}H_{21}FO_6Na$ requires 315.1214]; $[\alpha]_D^{25}$ = -33 (*c* 0.45 in $CHCl_3$) ν_{max} (neat)/cm^{-1} 1714s, 1604s, 1454m, 1251m, 1072m. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 1.20 (d, *J* = 6.0 Hz, 3H, H-C6), 1.21 (d, *J* = 6.0 Hz, 3H, H-C8), 1.28 (d, *J* = 6.0 Hz, 3H, H-C8), 2.04 (s, 3H, CH_3-Ac), 2.14 (s, 3H, CH_3-Ac), 3.80 (qd, *J* = 6.4, 1.2 Hz, 1H, H-C5), 4.01 (hept, *J* = 6.2 Hz, 1H, H-C7), 4.44 (ddd, *J* = 51.3, 9.8, 7.7 Hz, 1H, H-C2), 4.57 (dd, *J* = 7.7, 3.9 Hz, 1H, H-C1), 5.09 (ddd, *J* = 13.4, 9.7, 3.6 Hz, 1H, H-C3), 5.24 (ddd, *J* = 3.7, 2.6, 1.1 Hz, 1H, H-C4) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 16.0 (CH_3, C6), 20.6 (CH_3, Ac), 26.7 (CH_3, Ac), 21.7 (CH_3, C8), 23.3 (CH_3, C8), 69.0 (CH, C5), 70.9 (d, $^3J_{CF}$ = 8.3 Hz, CH, C4), 71.7 (d, $^2J_{CF}$ = 18.8 Hz, CH, C3), 88.0 (d, $^1J_{CF}$ = 186.2 Hz, CH, C2), 99.1 (d, $^2J_{CF}$ = 22.3 Hz, CH, C1), 170.1 (C, Ac), 170.5 (C, Ac) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -207.20 (dddd, *J* = 51.1, 13.3, 4.3, 2.6 Hz) ppm.



1-*O*-tert-butyldimethylsilyl-2, 6 -dideoxy-2-fluoro-3,4-di-*O*-benzyl-α-L-glucopyranose (**S16**)

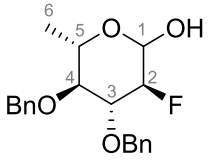


NaOMe (7 mg, 0.12 mmol, 0.4 eq) was added to a solution of **S2** (112 mg, 0.31 mmol, 1.0 eq) in MeOH (3 mL) at 0 °C. The solution was allowed to warm to room temperature and stirred for 1 h. The mixture was neutralized (~pH 7) with amberlite IR120 (prewashed with MeOH), filtered and evaporated to dryness. The residue was dissolved in DMF (1.5 mL), cooled to 0 °C and put under an Ar atmosphere. NaH (56 mg, 1.40 mmol, 4.5 eq., 60% in oil) was slowly added in portions, and the suspension stirred for 30 min while allowing it to reach room temperature. BnBr (0.17 mL, 1.40 mmol, 4.5 eq.) was added dropwise, and the reaction allowed to progress overnight. The reaction was quenched with H_2O and the crude extracted with DCM. The organic layers were dried over $MgSO_4$ and filtered, and the solvent removed. Purification by silica gel chromatography using a 7:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S16** as a colourless oil (141 mg, 99%).

Colourless oil; [***m/z* (ESI)** found: 483.2336 $(M+Na)^+$, $C_{26}H_{37}FO_6SiNa$ requires 483.2337]; $[\alpha]_D^{25}$ = 0 (*c* 1.40 in $CHCl_3$) ν_{max} (neat)/cm^{-1} 2927w, 2857w, 1454w, 1070s, 1027m, 838m, 733s. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 0.14 (s, 3H, CH_3), 0.14 (s, 3H, CH_3), 0.93 (s, 9H, 3xCH_3), 1.29 (d, *J* = 6.2 Hz, 3H, H-C6), 3.21 (t, *J* = 9.1 Hz, 1H, H-C4), 3.41 (dq, *J* = 9.6, 6.2 Hz, 1H, H-C5), 3.71 (dt, *J* = 14.8, 8.8 Hz, 1H, H-C3), 4.24 (ddd, *J* = 51.0, 8.8, 7.4 Hz, 1H, H-C2), 4.63 (d, *J* = 10.9 Hz, 1H, CH_2Ph), 4.68 (dd, *J* = 7.4, 3.1 Hz, 1H, H-C1), 4.73 (d, *J* = 11.1 Hz, 1H, CH_2Ph), 4.89 (dd, *J* = 11.1, 5.9 Hz, 2H, CH_2Ph), 7.28-7.37 (m, 10H, Ar) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = -5.2 (CH_3), -4.4 (CH_3), 17.9 (CH_3, C6), 18.1 (C), 25.6 (3xCH_3), 71.3 (CH, C5), 74.7 (CH_2, Bn), 75.3 (CH_2, Bn), 82.6 (d, $^3J_{CF}$ = 8.4 Hz, CH, C4), 83.2 (d, $^2J_{CF}$ = 16.2 Hz, CH, C3), 95.0 (d, $^2J_{CF}$ = 23.3 Hz, CH, C1), 95.5 (d, $^1J_{CF}$ = 186.8 Hz, CH, C2), 127.6 (CH, Ar), 127.8 (CH, Ar), 127.9 (CH, Ar), 128.0 (CH, Ar), 128.3 (CH, Ar), 128.4

(CH, Ar), 138.1 (C, Ar), 138.3 (C, Ar) ppm. **^{19}F NMR** (546 MHz, $CDCl_3$) δ = -194.56 (ddd, *J* = 51.2, 14.6, 2.7 Hz) ppm.

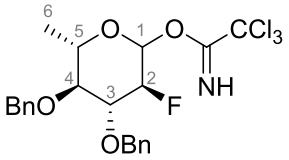
2, 6 -Dideoxy-2-fluoro-3,4-di-*O*-benzyl- L-glucopyranose (**S17**)



A 1M solution of TBAF in THF (0.56 mL, 0.56 mmol, 2 eq) was added dropwise to a solution of **S16** (120 mg, 0.26 mmol, 1 eq) in 0.8mL of THF at 0°C. The mixture was stirred for 45 min at low temperature, and water was then added. The aq. phase was extracted with DCM, and the combined organic layers once washed with water to be then dried with $MgSO_4$, filtered and evaporated. The crude was filtered through silica/NEt_3 using a 7:1 mixture of cyclohexane and ethyl acetate as eluent. The final product was isolated as a colourless oil (47 mg, 52%, α:β = 1.2:1).

Colourless oil; [***m/z* (ESI)** found: 369.1470 $(M+Na)^+$, $C_{20}H_{23}FO_4Na$ requires 369.1473]; $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = -10 (*c* 0.78 in $CHCl_3$) $\boldsymbol{\nu_{max}}$ (neat)/cm^{-1} 3400br, 2936w, 1454w, 1063s, 1024s, 737s. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 1.26 (d, *J* = 6.3 Hz, 3H, H-C6β), 1.31 (d, *J* = 6.2 Hz, 3H, H-C6α), 3.15 (t, *J* = 9.2 Hz, 1H, H-C5β), 3.22 (t, *J* = 9.2 Hz, 1H, H-C5α), 3.48 (dq, *J* = 9.4, 6.2 Hz, 1H, H-C4α), 3.75 (dt, *J* = 14.8, 8.8 Hz, 1H, H-C3α), 4.02-4.11 (m, 2H, H-C3β, H-C4β), 4.27 (ddd, *J* = 51.3, 8.8, 7.7 Hz, 1H, H-C2α), 4.50 (ddd, *J* = 49.7, 9.2, 3.8 Hz, 1H, H-C2β), 4.64 (dd, *J* = 10.8, 1.2 Hz, 2H, CH_2Bnα, CH_2Bnβ), 4.74-4.78 (m, 3H, CH_2Bnα, CH_2Bnβ, H-C1α), 4.88-4.92 (m, 2H, CH_2Bnα, CH_2Bnβ), 5.35 (d, *J* = 3.8 Hz, 1H, H-C1β) 7.28-7.38 (m, 10H, Arα, Arβ) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 17.7 (CH_3, C6α), 17.8 (CH_3, C6β), 66.8 (CH, C4β), 71.6 (CH, C4α), 74.9 (d, $^4J_{CF}$ = 2.8 Hz, CH_2, Bn), 75.1 (d, $^4J_{CF}$ = 2.0 Hz, CH_2, Bn), 75.3 (CH_2, Bn), 75.4 (CH_2, Bn), 80.0 (d, $^2J_{CF}$ = 15.9 Hz, CH, C3β), 82.4 (d, $^4J_{CF}$ = 7.4 Hz, CH, C5α), 82.7 (d, $^4J_{CF}$ = 8.1 Hz, CH, C5β), 82.9 (d, $^2J_{CF}$ = 16.0 Hz, CH, C3α), 90.5 (d, $^2J_{CF}$ = 21.6 Hz, CH, C1β), 92.0 (d, $^1J_{CF}$ = 190.0 Hz, CH, C2β), 94.3 (d, $^2J_{CF}$ = 12.6 Hz, CH, C1α), 95.0 (d, $^1J_{CF}$ = 197.7 Hz, CH, C2α), 127.7 (CH, Ar), 127.7 (CH, Ar), 127.8 (CH, Ar), 127.8 (CH, Ar), 127.8 (CH, Ar), 127.8 (CH, Ar), 127.9 (CH, Ar), 127.9 (CH, Ar), 128.3 (CH, Ar), 128.4 (CH, Ar), 128.4 (CH, Ar), 137.9 (C, Ar), 138.0 (C, Ar), 138.1 (C, Ar), 138.3 (C, Ar) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -195.63 (ddd, *J* = 51.0, 14.9, 2.8 Hz, β-anomer), -197.44 (dd, *J* = 49.7, 12.5 Hz, α-anomer) ppm.

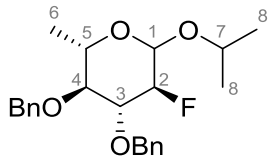
2, 6 -Dideoxy-2-fluoro-3,4-di-*O*-benzyl- L-glucopyranosyl trichloroacetimidate (**S18**)



DBU (2 µL, 0.8 µmol, 0.1 eq) was added to a solution of Cl_3CCN (0.08 mL, 0.80 mmol, 10 eq) and **S17** (26 mg, 0.08 mmol, 1.0 eq) in dry DCM (1 mL) at 0 °C under an atmosphere of Ar. Upon completion of the addition, the solution was allowed to warm to room temperature, stirred for 1h and the solvents evaporated. Purification by silica gel chromatography (SiO_2/NEt_3) using a 7:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S18** as a colourless oil (33 mg, 89%, α:β = 7:1).

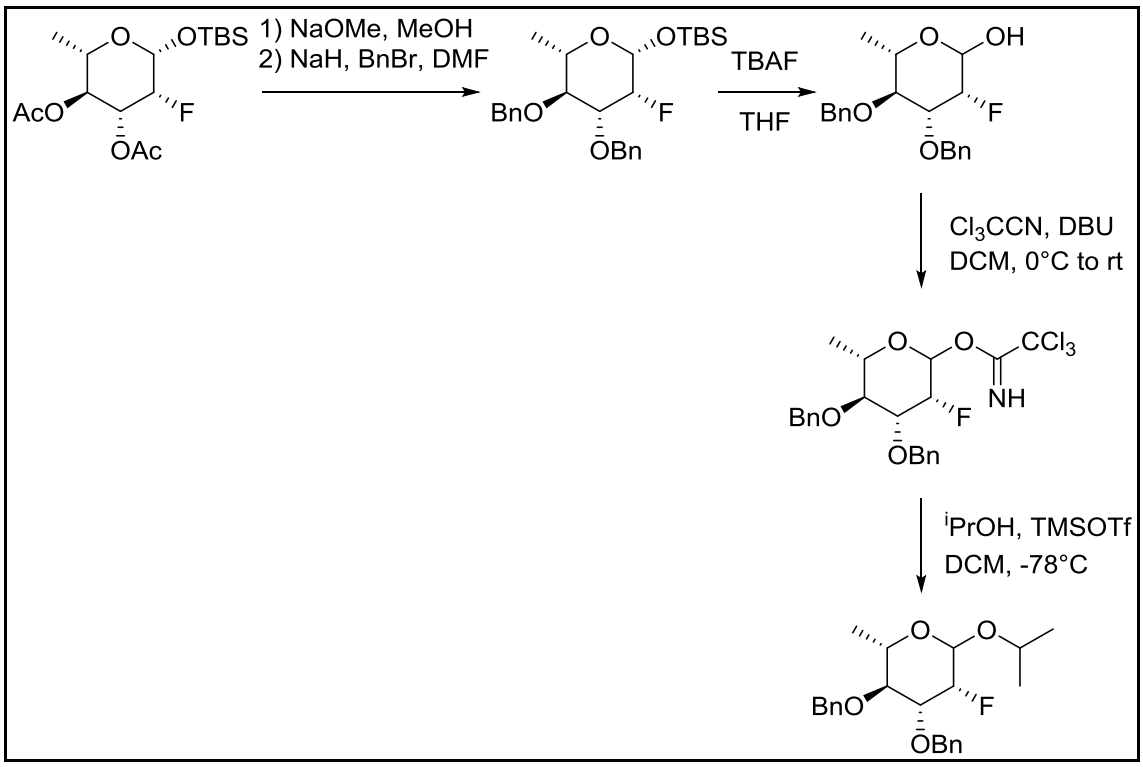
^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.29 (d, *J* = 6.2 Hz, 3H, H-C6α), 1.34 (d, *J* = 6.2 Hz, 0.6H, H-C6β), 3.24 (t, *J* = 9.4 Hz, 1H, H-C5α), 3.29 (t, *J* = 9.2 Hz, 0.2H, H-C5β), 3.97 (dq, *J* = 10.1, 6.2 Hz, 1H), 4.60 (dd, *J* = 9.3, 3.9 Hz, 0.5H, H-C2α), 4.65 (d, *J* = 10.8 Hz, 1H, CH_2Ph), 4.74-4.82 (m, 1.5H, H-C2α, CH_2Ph), 4.92 (dd, *J* = 10.8, 1.6 Hz, 2H, CH_2Ph), 5.86 (dd, *J* = 7.9, 3.4 Hz, 0.2H, H-C1β), 6.46 (d, *J* = 3.8 Hz, 1H, H-C1α), 7.29-7.41 (m, 10H, Ar), 8.66 (s, 1H, NHα), 8.69 (s, 1H, NHβ) ppm.**^{19}F NMR** (282 MHz, $CDCl_3$) δ = -196.42 (ddd, *J* = 51.7, 15.5, 3.8 Hz, β-anomer), -199.74 (dd, *J* = 48.5, 12.0 Hz, α-anomer) ppm.

1-*O*-Isopropyl-2,6-dideoxy-2-fluoro-3,4-di-*O*-benzyl-L-glucopyranose (**S19**) – Table 2, entry 1

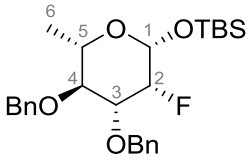


A 0.1M solution of TMSOTf (0.05 mL, 5 µmol, 0.1 eq) was added to a solution of **S18** (26 mg, 0.05 mmol, 1 eq) and isopropanol (0.04 mL, 0.50 mmol, 10 eq) in dry DCM (1 mL) under an Ar atmosphere at -78°C. The reaction was allowed to progress for 2h at -78°C, and then slowly warmed up to room temperature. NEt_3 was added to quench the reaction, and the solvent was removed under vacuum. Purification by silica gel chromatography using a 3:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S19** as a colourless oil (16 mg, 84%, α:β = 1:16).

Colourless oil; [***m/z* (ESI)** found: 411.1935 $(M+Na)^+$, $C_{23}H_{29}FO_4Na$ requires 411.1935]; $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = +14 (*c* 0.70 in $CHCl_3$) $\boldsymbol{\nu}_{\mathbf{max}}$ (neat)/cm^{-1} 2969w , 2896w, 1453m, 1355m, 1097s, 1058s, 1019s, 982s. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 1.22 (d, *J* = 6.1 Hz, 3H, H-C6), 1.27 (d, *J* = 6.3 Hz, 3H, H-C8), 1.30 (d, *J* = 6.1 Hz, 3H, H-C8), 3.20 (t, *J* = 9.1 Hz, 1H, H-C4), 3.40 (dq, *J* = 9.5, 6.2 Hz, 1H, H-C5), 3.73 (dt, *J* = 15.2, 8.7 Hz, 1H, H-C3), 3.99 (hept, *J* = 6.2 Hz, 1H, H-C7), 4.30 (dt, *J* = 50.8, 8.2 Hz, 1H, H-C2), 4.50 (dd, *J* = 7.8, 3.2 Hz, 1H, H-C1), 4.63 (d, *J* = 10.9 Hz, 1H, CH_2Ph), 4.74 (d, *J* = 11.2 Hz, 1H, CH_2Ph), 4.90 (dd, *J* = 11.0, 3.4 Hz, 2H, CH_2Ph), 7.29-7.38 (m, 10H, Ar) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 17.9 (CH_3, C6), 21.9 (CH_3, C8), 23.4 (CH_3, C8), 71.2 (CH, C5), 72.1 (CH, C7), 74.7 (d, $^{4}J_{CF}$ = 1.0 Hz, CH_2, Bn), 75.4 (CH_2, Bn), 82.56 (d, $^{3}J_{CF}$ = 8.5 Hz, CH, C4), 83.3 (d, $^{2}J_{CF}$ = 16.3 Hz, CH, C3), 93.7 (d, $^{1}J_{CF}$ = 187.0 Hz, CH, C2), 98.7 (d, $^{2}J_{CF}$ = 23.0 Hz, CH, C1), 127.8 (CH, Ph), 127.9 (CH, Ph), 128.0 (CH, Ph), 128.0 (CH, Ph), 128.3 (CH, Ph), 128.4 (CH, Ph), 138.0 (C, Ph), 138.2 (C, Ph) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -195.07 (ddd, *J* = 50.8, 15.2, 3.2 Hz, β-anomer), -198.37 (dd, *J* = 49.9, 12.1 Hz, α-anomer) ppm.



1-*O*-tert-butyldimethylsilyl-2, 6 -dideoxy-2-fluoro-3,4-di-*O*-benzyl-α-L-mannopyranose (**S20**)

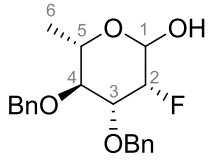


NaOMe (7 mg, 0.12 mmol, 0.4 eq) was added to a solution of **S3** (110 mg, 0.31 mmol, 1.0 eq) in MeOH (3 mL) at 0 °C. The solution was allowed to warm to room temperature and stirred for 1 h. The mixture was neutralized (~pH 7) with amberlite IR120 (prewashed with MeOH), filtered and evaporated to dryness. The residue was dissolved in DMF (5 mL), cooled to 0 °C and put under an Ar atmosphere. NaH (56 mg, 1.40 mmol, 4.5 eq., 60% in oil) was slowly added in portions, and the suspension stirred for 45 min while allowing it to reach room temperature. BnBr (0.17 mL, 1.40 mmol, 4.5 eq.) was added dropwise, and the reaction allowed to progress overnight. The reaction was quenched with H_2O and the crude extracted with DCM. The organic layers were dried over $MgSO_4$ and filtered, and the solvent removed. Purification by silica gel chromatography using a 7:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S20** as a colourless oil (141 mg, 99%).

Colourless oil; [***m/z*** **(ESI)** found: 483.2336 $(M+Na)^+$, $C_{26}H_{37}FO_6SiNa$ requires 483.2337]; $[\alpha]_D^{25}$ = +6 (*c* 1.80 in $CHCl_3$) ν_{max} (neat)/cm^{-1} 2929w, 2856w, 1454w, 1207w, 1077s, 873s, 781m, 733s. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 0.12 (s, 3H, CH_3), 0.15 (s, 3H, CH_3), 0.92 (s, 9H, 3xCH_3), 1.34 (d, *J* = 6.1 Hz, 3H, H-C6), 3.35 (dq, *J* = 8.6, 6.1 Hz, 1H, H-C5), 3.49-3.59 (m, 2H, H-C3, H-C4), 4.65 (d, *J* = 8.1 Hz, 2H, CH_2Ph, H-C2), 4.67 (dd, *J* = 51.3, 1.9 Hz, 1H, H-C1), 4.71 (d, *J* = 4.6 Hz, 1H, CH_2Ph), 4.79 (d, *J* = 11.8 Hz, 1H, CH_2Ph), 4.94 (d, *J* = 10.9 Hz, 1H, CH_2Ph), 7.30-7.38 (m, 10H, Ar) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = -5.0 (CH_3), -4.1 (CH_3), 17.9 (CH_3, C6), 25.8 (3xCH_3), 35.5 (C), 71.6 (CH_2, Bn), 71.7 (CH, C5), 75.5 (CH_2, Bn), 79.6 (CH, C4), 80.4 (d, $^2J_{CF}$ = 17.6 Hz, CH, C3), 88.2 (d, $^1J_{CF}$ = 188.3 Hz, CH, C1), 94.0 (d, $^2J_{CF}$ = 16.1 Hz, CH, C2), 127.6 (CH, Ph), 127.7

(CH, Ph), 127.8 (CH, Ph), 128.1 (CH, Ph), 128.4 (CH, Ph), 128.5 (CH, Ph), 137.8 (C, Ph), 138.3 (C, Ph) ppm. **^{19}F NMR** (546 MHz, $CDCl_3$) δ = -220.54 (ddd, *J* = 50.8, 30.8, 18.2 Hz) ppm.

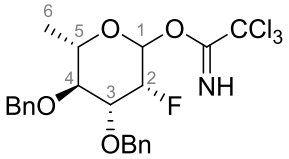
2, 6 -Dideoxy-2-fluoro-3,4-di-*O*-benzyl- L-mannopyranose (**S21**)



A 1M solution of TBAF in THF (0.51 mL, 0.51 mmol, 2 eq) was added dropwise to a solution of **S20** (120 mg, 0.26 mmol, 1 eq) in 1 mL of THF at 0°C. The mixture was stirred for 35 min at low temperature, and water was then added. The aq. phase was extracted with DCM, and the combined organic layers once washed with water to be then dried with $MgSO_4$, filtered and evaporated. The crude was filtered through silica/NEt_3 using a 7:1 mixture of cyclohexane and ethyl acetate as eluent. The final product was isolated as a colourless oil (58 mg, 64%, α:β = 3:1).

Colourless oil; [***m/z* (ESI)** found: 369.1480 $(M+Na)^+$, $C_{20}H_{23}FO_4Na$ requires 369.1473]; $[\alpha]_D^{25}$ = -18 (*c* 0.90 in $CHCl_3$) ν_{max} (neat)/cm^{-1} 3377br, 2934w, 1454m, 1057s, 977m, 735s, 696s. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 1.24 (d, *J* = 6.2 Hz, 3H, H-C6α), 1.28 (d, *J* = 5.9 Hz, 1H, H-C6β), 3.45 (td, *J* = 9.5, 1.1 Hz, 1H, H-C4α), 3.79 (dd, *J* = 9.4, 2.5 Hz, 0.5H, H-C3α), 3.93 – 3.84 (m, 1.5H, H-C5α, H-C3α), 4.58 (d, *J* = 10.9 Hz, 1H, Bn), 4.62 (t, *J* = 2.3 Hz, 0.5H, H-C2α), 4.75 (d, *J* = 4.2 Hz, 2H, Bn), 4.85 (t, *J* = 2.3 Hz, 0.5H, H-C2α), 4.94 (d, *J* = 10.9 Hz, 1H, Bn), 5.30 (dd, *J* = 7.3, 2.0 Hz, 1H, H-C1α), 7.29-7.41 (m, 13H, Ar) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 17.8 (CH_3, C6β), 17.9 (CH_3, C6α), 68.1 (CH, C5α), 71.7 (CH, C5β), 72.0 (CH_2, Bnβ), 72.2 (CH_2, Bnα), 75.5 (CH_2, Bnα), 77.9 (d, $^2J_{CF}$ = 17.1 Hz, CH, C3α), 79.3 (CH, C4β), 79.9 (CH, C4α), 87.3 (d, $^1J_{CF}$ = 175.3 Hz, C2α), 88.4 (d, $^1J_{CF}$ = 182.0 Hz, C2β), 92.1 (d, $^2J_{CF}$ = 30.0 Hz, C2α), 92.7 (d, $^2J_{CF}$ = 17.2 Hz, C2β), 127.7 (CH, Ph), 127.8 (CH, Ph), 127.8 (CH, Ph), 127.9 (CH, Ph), 127.9 (CH, Ph), 128.0 (CH, Ph), 128.1 (CH, Ph), 128.4 (CH, Ph), 128.5 (CH, Ph), 128.6 (CH, Ph), 137.5 (C, Phβ), 138.8 (C, Phα), 138.1 (C, Phβ), 138.3 (C, Phα) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -204.35 (ddd, *J* = 49.7, 30.0, 7.4 Hz, α-anomer), -223.31 (ddd, *J* = 48.7, 29.7, 18.1 Hz, β-anomer) ppm.

2, 6 -Dideoxy-2-fluoro-3,4-di-*O*-benzyl- L-mannopyranosyl trichloroacetimidate (**S22**)

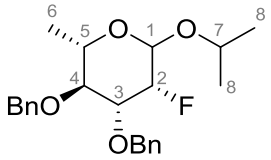


DBU (10 µL, 0.01 mmol, 0.1 eq) was added to a solution of Cl_3CCN (0.10 mL, 1.00 mmol, 10 eq) and **S21** (35 mg, 0.10 mmol, 1.0 eq) in dry DCM (1 mL) at 0 °C under an atmosphere of Ar. Upon completion of the addition, the solution was allowed to warm to room temperature, stirred for 40 min and the solvents evaporated. Purification by silica gel chromatography (SiO_2/NEt_3) using a 3:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S22** as a colourless oil (45 mg, 91%, α only).

^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.34 (d, *J* = 6.2 Hz, 3H, H-C6), 3.61 (td, *J* = 9.6, 0.9 Hz, 1H), 3.83-3.96 (m, 2H), 4.66-4.69 (m, 1.5H, CH_2Ph, H-C2), 4.77 (d, *J* = 2.3 Hz, 2H, CH_2Ph), 4.83 (t, *J* = 2.4 Hz, 0.5H, H-C1), 4.95

(d, *J* = 10.7 Hz, 1H, CH_2Ph), 6.31 (dd, *J* = 6.2, 2.1 Hz, 1H, H-C1), 7.29-7.41 (m, 10H, Ph), 8.64 (s, 1H, NH) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -204.63 (ddd, *J* = 48.9, 29.3, 6.2 Hz) ppm.

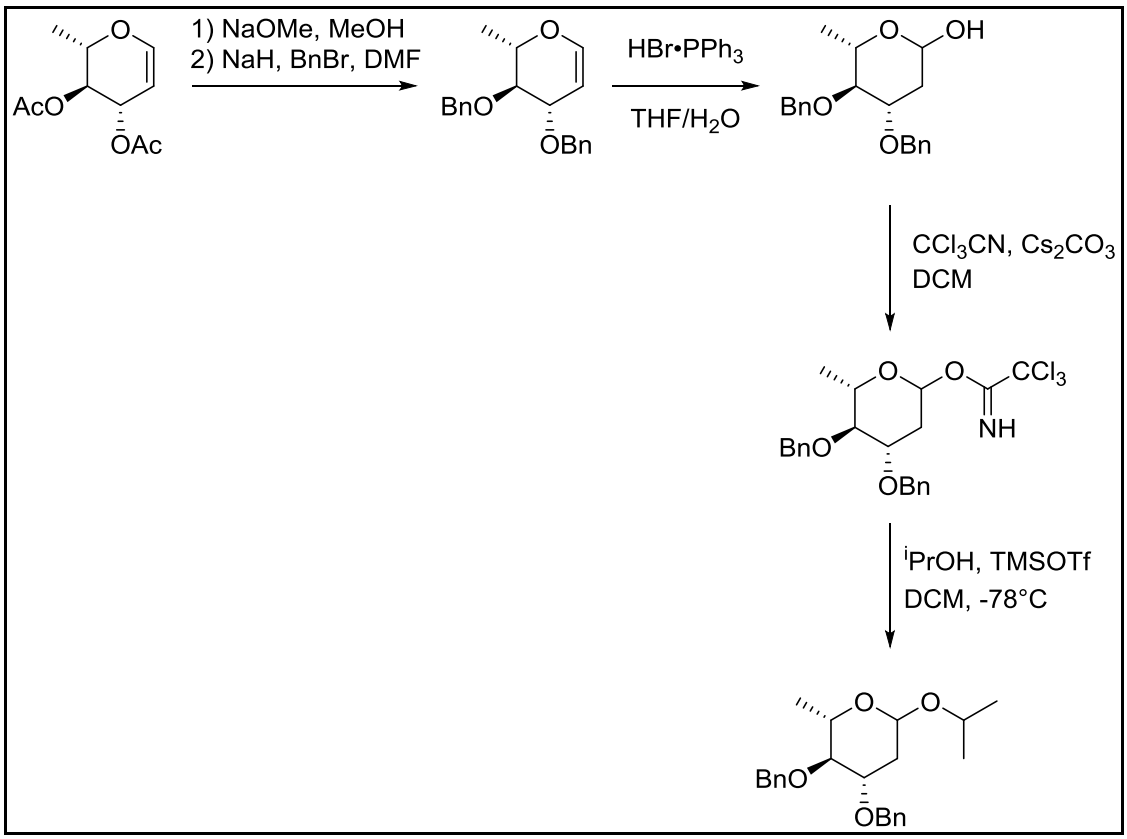
1-*O*-Isopropyl-2,6-dideoxy-2-fluoro-3,4-di-*O*-benzyl-L-mannopyranose (**S23**) – Table 2, entry 2



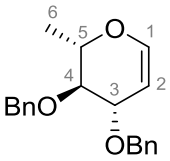
A 0.1M solution of TMSOTf (0.06 mL, 6 µmol, 0.1 eq) was added to a solution of **S22** (32 mg, 0.06 mmol, 1 eq) and isopropanol (0.05 mL, 0.60 mmol, 10 eq) in dry DCM (1 mL) under an Ar atmosphere at 0°C. The reaction was allowed to progress for 2h at 0°C, and then slowly warmed up to room temperature. NEt_3 was added to quench the reaction, and the solvent was removed under vacuum. Purification by silica gel chromatography using a 7:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S23** as a colourless oil (α-anomer: 12 mg, β-anomer: 11mg, 92% global yield).

α-anomer: **Colourless oil**; [***m/z* (ESI)** found: 411.1933 $(M+Na)^+$, $C_{23}H_{29}FO_4Na$ requires 411.1942]; $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = -33 (*c* 1.20 in $CHCl_3$) $\boldsymbol{\nu}_{\mathbf{max}}$ (neat)/cm^{-1} 2973w, 2915w, 1455w, 1115m, 1057s, 1028m, 981m. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 1.13 (d, *J* = 6.1 Hz, 3H, H-C8), 1.17 (d, *J* = 6.3 Hz, 3H, H-C8), 1.31 (d, *J* = 6.2 Hz, 3H, H-C6), 3.51 (td, *J* = 9.5, 1.0 Hz, 1H, H-C4), 3.76-3.85 (m, 1.5H, H-C3, H-C5), 3.86-3.94 (m, 1.5H, H-C3, H-C7), 4.61-4.65 (m, 1H, CH_2Ph), 4.69-4.78 (m, 2H, CH_2Ph), 4.92 (d, *J* = 10.8 Hz, 1H, CH_2Ph), 4.99 (dd, *J* = 7.8, 2.0 Hz, 1H, H-C1), 7.27-7.41 (m, 10H, Ph) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 17.9 (CH_3, C6), 21.4 (CH_3, C8), 23.3 (CH_3, C8), 67.8 (CH, C5), 69.7 (CH, C7), 72.1 (CH_2, Bn), 75.6 (CH_2, Bn), 78.8 (d, $^2J_{CF}$ = 17.2 Hz, CH, C3), 80.3 (CH, C4), 87.7 (d, $^1J_{CF}$ = 176.0 Hz, CH, C2), 95.4 (d, $^2J_{CF}$ = 29.0 Hz, CH, C1), 127.8 (CH, Ph), 127.9 (CH, Ph), 127.9 (CH, Ph), 128.3 (CH, Ph), 128.6 (CH, Ph), 138.3 (C, Ph), 138.5 (C, Ph) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -203.18 (ddd, *J* = 50.2, 30.2, 7.7 Hz) ppm.

β-anomer: **Colourless oil**; [***m/z* (ESI)** found: 411.1933 $(M+Na)^+$, $C_{23}H_{29}FO_4Na$ requires 411.1942]; $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = +15 (*c* 1.10 in $CHCl_3$) $\boldsymbol{\nu}_{\mathbf{max}}$ (neat)/cm^{-1} 2974w, 2871w, 1455w, 1369w, 1189w, 1103s, 1070s, 907w, 734s. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 1.10 (d, *J* = 6.1 Hz, 3H, H-C8), 1.20 (d, *J* = 6.2 Hz, 3H, H-C8), 1.28 (d, *J* = 6.1 Hz, 3H, H-C6), 3.27 (dq, *J* = 8.6, 6.2 Hz, 1H, H-C5), 3.41-3.52 (m, 2H, H-C3, H-C4), 3.94 (hept, *J* = 6.2 Hz, 1H, H-C7), 4.39 (d, *J* = 18.8 Hz, 1H, H-C1), 4.557-4.63 (m, 2.5H, CH_2Ph, H-C2), 4.71 (d, *J* = 11.9 Hz, 1H, CH_2Ph), 4.74 (d, *J* = 2.2 Hz, 0.5H, H-C2), 4.87 (d, *J* = 10.9 Hz, 1H, CH_2Ph), 7.21-7.32 (m, 10H, Ph) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 17.8 (CH_3, C6), 21.5 (CH_3, C8), 23.3 (CH_3, C8), 71.4 (CH, C7), 71.5 (CH_2, Bn), 71.6 (CH, C7), 75.6 (CH_2, Bn), 79.7 (CH, C4), 80.5 (d, $^2J_{CF}$ = 17.7 Hz, CH, C3), 87.7 (d, $^1J_{CF}$ = 187.1 Hz, CH, C2), 96.6 (d, $^2J_{CF}$ = 15.5 Hz, CH, C1), 127.8 (CH, Ph), 127.9 (CH, Ph), 128.1 (CH, Ph), 128.4 (CH, Ph), 128.5 (CH, Ph), 137.7 (C, Ph), 138.2 (C, Ph) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -219.31 (m) ppm.

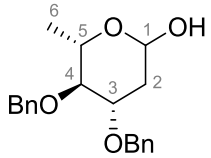


2, 6 -Dideoxy-3,4-di-*O*-benzyl- L-glucal (**S24**)



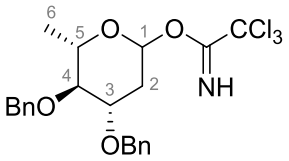
NaOMe (51 mg, 0.94 mmol, 0.4 eq) was added to a solution of 3,4-Di-*O*-acetyl-6-deoxy-L-glucal (500 mg, 2.34 mmol, 1.0 eq) in MeOH (20 mL) at 0 °C. The solution was allowed to warm to room temperature and stirred for 1 h. The mixture was neutralized (~pH 7) with amberlite IR120 (prewashed with MeOH), filtered and evaporated to dryness. The residue was dissolved in DMF (10 mL), cooled to 0 °C and put under an Ar atmosphere. NaH (421 mg, 10.53 mmol, 4.5 eq., 60% in oil) was slowly added in portions, and the suspension stirred for 30 min while allowing it to reach room temperature. BnBr (1.25 mL, 10.53 mmol, 4.5 eq.) was added dropwise, and the reaction allowed to progress overnight. The reaction was quenched with H_2O and the crude extracted with DCM. The organic layers were dried over $MgSO_4$ and filtered, and the solvent removed. Purification by silica gel chromatography using a 7:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S24** as a colourless oil (717 mg, 99%), the spectroscopical data of which coincided with previous literature reports (*Org. Lett*., **2013**, *15 (13),* 3428-31).

2, 6 -Dideoxy-3,4-di-*O*-benzyl- L-glucopyranose (**S25**)



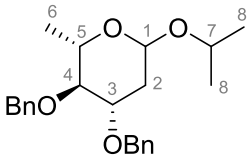
S24 (44 mg, 0.14 mmol, 1 eq) was dissolved in 0.5 mL of THF, and HBr•PPh_3 (2 mg, 7 µmol, 0.05 eq) was added as a solid. The mixture was stirred for 10 min at room temperature, and H_2O (4 µL, 0.21 mmol, 1.5 eq) was added. The reaction was allowed to progress overnight at r.t., and the following day it was quenched with $NaHCO_3$ and extracted with ethyl acetate. The organic layers were dried over $MgSO_4$, filtered and the solvent removed. Purification by silica gel chromatography using a 3:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S25** as a white solid (22 mg, 48%, α:β = 1.7:1), the spectroscopical data of which coincided with previous literature reports (*Angew. Chem. Int. Ed.,* **2007**, *46*, 2505-7).

2, 6 -Dideoxy-3,4-di-*O*-benzyl- L-glucopyranosyl trichloroacetimidate (**S26**)



S25 (19 mg, 0.06 mmol, 1 eq) was dissolved in 0.5 mL of anh. DCM under an atmosphere of Ar. Cs_2CO_3 (4 mg, 1.2 µmol, 0.2 eq) was added in one portion, followed by Cl_3CCN (0.03 mL, 0.30 mmol, 5 eq). The mixture was stirred at room temperature for 2h, filtered through a celite pad and used in the following reaction with no further purification.

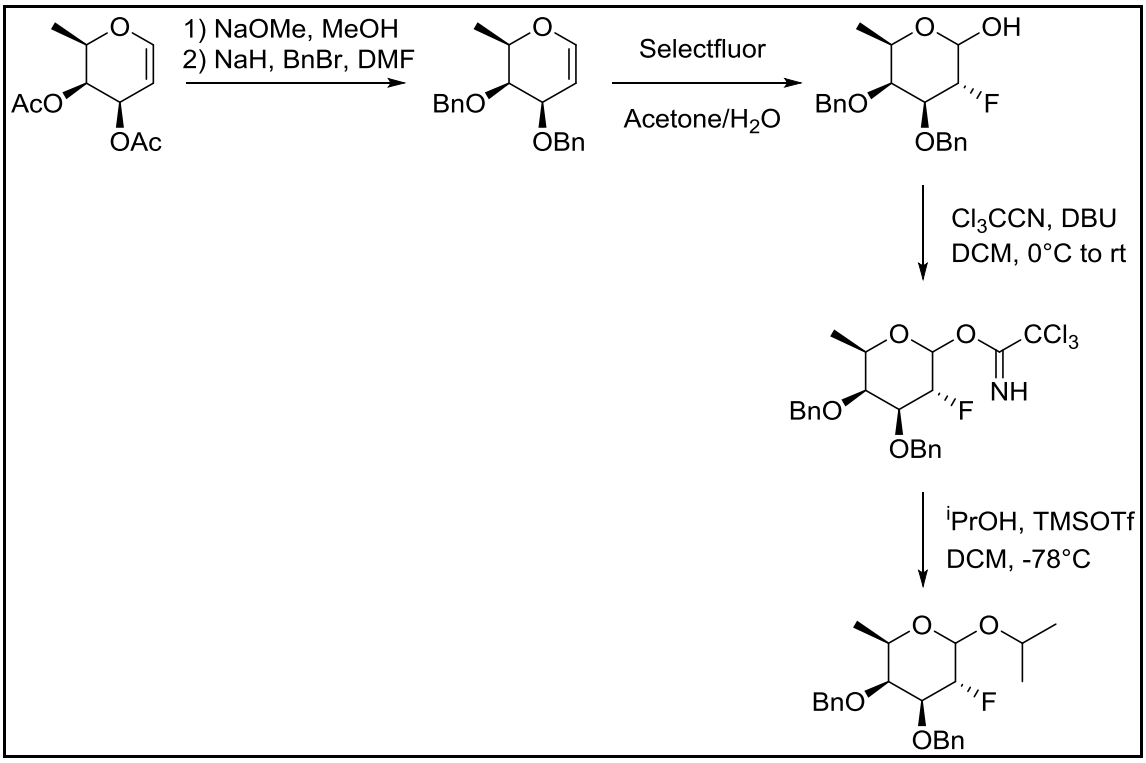
1-*O*-Isopropyl-2,6-dideoxy-3,4-di-*O*-benzyl-L-glucopyranose (**S27**) – Table 2, entry 4



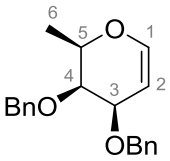
A 0.2M solution of TMSOTf (0.03 mL, 6 µmol, 0.1 eq) was added to a solution of **S26** (28 mg, 0.06 mmol, 1 eq) and isopropanol (0.05 mL, 0.60 mmol, 10 eq) in dry DCM (1 mL) under an Ar atmosphere at -78°C. The reaction was allowed to progress for 2h at -78°C, and then slowly warmed up to room temperature. NEt_3 was added to quench the reaction, and the solvent was removed under vacuum. Purification by silica gel chromatography using a 3:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S27** as a colourless oil (15 mg, 68%, α:β = 3.1:1).

Colourless oil; [***m/z* (ESI)** found: 393.2029 $(M+Na)^+$, $C_{23}H_{35}O_4Na$ requires 393.2036]; $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = -25 (*c* 1.50 in $CHCl_3$) $\boldsymbol{\nu_{max}}$ (neat)/cm^{-1} 2971w, 2932w, 1451w, 1380w, 1366w, 1092s, 1064s, 999s, 911w. $^{\mathbf{1}}$**H NMR** (600 MHz, $CDCl_3$) δ = 1.12 (d, *J* = 6.1 Hz, 3H, H-C8α), 1.15 (d, *J* = 6.1 Hz, 0.9H, H-C8β), 1.17 (d, *J* = 6.2 Hz, 3H, H-C6α), 1.24 (d, *J* = 6.2 Hz, 0.9H, H-C6β), 1.28 (d, *J* = 6.2 Hz, 3H, H-C8α), 1.32 (d, *J* = 6.2 Hz, 0.9H, H-C8β), 1.63 (m, 0.3H, H-C2β), 1.69 (ddd, *J* = 13.2, 11.5, 3.9 Hz, 1H, H-C2α), 2.25 (ddd, *J* = 12.8, 5.1, 1.3 Hz, 1H, H-C2α), 2.30 (ddd, *J* = 12.6, 5.2, 1.9 Hz, 0.3H, H-C2β), 3.13 (t, *J* = 8.9 Hz, 1.3H, H-C5α, H-C5β), 3.32 (dq, *J* =

9.2, 6.1 Hz, 0.3H, H-C3β), 3.63 (ddd, *J* = 12.2, 8.8, 5.4 Hz, 0.3H, H-C4β), 3.79 (dq, *J* = 9.7, 6.4 Hz, 1H, H-C3α), 3.86 (h, *J* = 6.2 Hz, 1.3H, H-C7α, H-C7β), 3.98 (ddd, *J* = 11.5, 8.8, 5.0 Hz, 1H, H-C4α), 4.50 (dd, *J* = 9.8, 2.0 Hz, 0.3H, H-C1β), 4.59-4.70 (m, 4H, CH_2Phα, CH_2Phβ), 4.95 (d, *J* = 10.7 Hz, 1.3H, CH_2Phα, CH_2Phβ), 4.97 (d, *J* = 3.6 Hz, 1H, H-C1α), 7.27-7.36 (m, 13H, Ar) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 18.1 (CH_3, C8α), 18.2 (CH_3, C8β), 21.2 (CH_3, C8α), 21.8 (CH_3, C8β), 23.3 (CH_3, C6α), 23.5 (CH_3, C6β), 36.2 (CH_2, C2α), 37.5 (CH_2, C2β), 67.1 (CH, C3α), 68.0 (CH, C7α, C7β), 71.3 (CH, C3β), 71.3 (CH_2, Bnβ), 71.7 (CH_2, Bnα), 75.2 (CH_2, Bnβ), 75.3 (CH_2, Bnα), 77.6 (CH, C4α), 79.4 (C4β), 83.7 (CH, C5β), 84.5 (CH, C5α), 94.7 (CH, C1α), 97.5 (CH, C1β), 127.5 (CH, Arα), 127.6 (CH, Arα), 127.6 (CH, Arβ), 128.0 (CH, Arα), 128.1 (CH, Arβ), 128.3 (CH, Arα), 128.4 (CH, Arα), 128.4 (CH, Arβ), 138.4 (C, Arβ), 138.5 (C, Arβ), 138.6 (C, Arα), 138.8 (C, Arα) ppm.



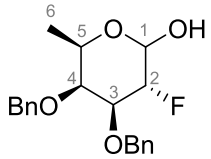
2, 6 -Dideoxy-3,4-di-*O*-benzyl- D-fucal (**S28**)



NaOMe (20 mg, 0.37 mmol, 0.4 eq) was added to a solution of 3,4-Di-*O*-acetyl-6-deoxy-D-fucal (200 mg, 0.93 mmol, 1.0 eq) in MeOH (1.8 mL) at 0 °C. The solution was allowed to warm to room temperature and stirred for 1 h. The mixture was neutralized (~pH 7) with amberlite IR120 (prewashed with MeOH), filtered and evaporated to dryness. The residue was dissolved in DMF (2.5 mL), cooled to 0 °C and put under an Ar atmosphere. NaH (171 mg, 4.19 mmol, 4.5 eq., 60% in oil) was slowly added in portions, and the suspension stirred for 30 min while allowing it to reach room temperature. BnBr (0.54 mL, 4.19 mmol, 4.5 eq.) was added dropwise, and the reaction allowed to progress overnight. The reaction was quenched with H_2O and the crude extracted with DCM. The organic layers were dried over $MgSO_4$ and

filtered, and the solvent removed. Filtration through silica gel using a 7:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S28** as a colourless oil that was directly used in the following step.

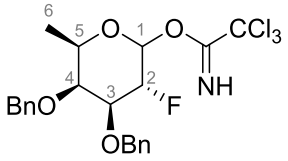
2,6-Dideoxy-2-fluoro-3,4-di-*O*-benzyl-D-galactopyranose (**S29**)



SelectFluor™ (149 mg, 0.42 mmol, 1.5 eq) was added at to a solution of 3,4-Di-*O*-benzyl-6-deoxy-D-fucal (87 mg, 0.28 mmol, 1.0 eq) in acetone (1 mL) and water (0.2 mL). The solution was stirred at room temperature for 20 h. The solvents were then evaporated and the residue dissolved in DCM and a sat. aq. solution of $NaHCO_3$. The aq. phase was extracted with DCM and the combined organic phases dried over $MgSO_4$, filtered and evaporated to dryness. The crude was filtered through silica using a mixture of cyclohexane and ethyl acetate as eluent (7:1), to afford **S29** as a colourless oil (51 mg, 53%, α:β = 2:1).

Colourless oil; [***m/z* (ESI)** found: 369.1471 $(M+Na)^+$, $C_{20}H_{23}FO_4Na$ requires 369.1473]; $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = +57 (*c* 1.00 in $CHCl_3$) $\boldsymbol{\nu_{max}}$ (neat)/cm^{-1} 3410br, 2882w, 1454w, 1132m, 1063s, 1025s, 732s, 696s. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 1.16 (d, *J* = 6.5 Hz, 3H, H-C6α), 1.21 (d, *J* = 6.4 Hz, 1.5H, H-C6β), 3.58 (m, 0.5H, H-C5β), 3.60-3.66 (m, 1H, H-C3β, H-C4β), 3.70 (ddd, *J* = 4.3, 3.0, 1.2 Hz, 1H, H-C4α), 4.04 (ddd, *J* = 10.7, 9.7, 3.0 Hz, 1H, H-C3α), 4.15 (q, *J* = 6.7 Hz, 1H, H-C5α), 4.59 (ddd, *J* = 10.3, 7.5, 1.4 Hz, 0.25H, H-C2β), 4.64-4.76 (m, 4H, CH_2Phα, CH_2Phβ, H-C1β, H-C2β), 4.82 (d, *J* = 7.2 Hz, 1H, CH_2Phα), 4.85 (d, *J* = 7.1 Hz, 0.5H, CH_2Phβ), 4.98 (d, *J* = 11.4 Hz, 1.5H, CH_2Phα, CH_2Phβ), 4.98 (ddd, *J* = 50.4, 9.8, 3.9 Hz, 1H, H-C2α), 5.44 (d, *J* = 3.9 Hz, 1H, H-C1α), 7.28-7.42 (m, 15H, Arα, Arβ) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 16.5 (CH_3, C6α), 16.7 (CH_3, C6β), 66.8 (CH, C5α), 71.3 (CH, C5β), 72.9 (d, $^4J_{CF}$ = 2.4 Hz, CH_2, Bnβ), 73.1 (d, $^4J_{CF}$ = 2.3 Hz, CH_2, Bnα), 74.9 (CH_2, Bnβ), 74.9 (CH_2, Bnα), 76.9 (d, $^2J_{CF}$ = 14.2 Hz, CH, C3α), 77.2 (CH, C4β), 78.2 (d, $^3J_{CF}$ = 8.5 Hz, CH, C4α), 80.4 (d, $^2J_{CF}$ = 15.7 Hz, CH, C3β), 89.8 (d, $^1J_{CF}$ = 185.5 Hz, CH, C2α), 91.1 (d, $^2J_{CF}$ = 21.5 Hz, CH, C1α), 93.6 (d, $^1J_{CF}$ = 182.9 Hz, CH, C2β), 95.2 (d, $^2J_{CF}$ = 24.1 Hz, CH, C1β), 127.5 (CH, Ph), 127.6 (CH, Ph), 127.7 (CH, Ph), 127.7 (CH, Ph), 127.8 (CH, Ph), 128.2 (CH, Ph), 128.3 (CH, Ph), 128.4 (CH, Ph), 128.4 (CH, Ph), 138.0 (2xC, Phβ), 138.2 (C, Phα), 138.3 (c, Phα) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -205.81 (m, β-anomer), -207.49 (ddd, *J* = 50.4, 10.8, 4.1 Hz, α-anomer) ppm.

2,6-Dideoxy-2-fluoro-3,4-di-*O*-benzyl-D-galactopyranosyl trichloroacetimidate (**S30**)

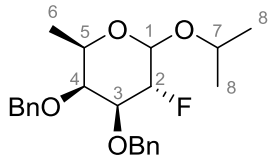


DBU (10 µL, 10 µmol, 0.1 eq) was added to a solution of Cl_3CCN (0.10 mL, 1.00 mmol, 10 eq) and **S29** (34 mg, 0.10 mmol, 1.0 eq) in dry DCM (2.0 mL) at 0 °C under an atmosphere of Ar. Upon completion of the addition, the solution was allowed to warm to room temperature, stirred for 30 min and the solvents evaporated. Purification by silica gel chromatography (SiO_2/NEt_3) using a 7:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S30** as a colourless oil (41 mg, 85%, α only).

^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.11 (d, *J* = 6.5 Hz, 3H, H-C6), 3.68 (m, 1H), 4.00-4.07 (m, 2H), 4.63 (dd, *J* = 14.4, 11.7 Hz, 2H, CH_2Ph), 4.79 (d, *J* = 12.0 Hz, 1H, CH_2Ph), 4.93 (d, *J* = 11.4 Hz, 1H, CH_2Ph), 5.10 (ddd, *J* =

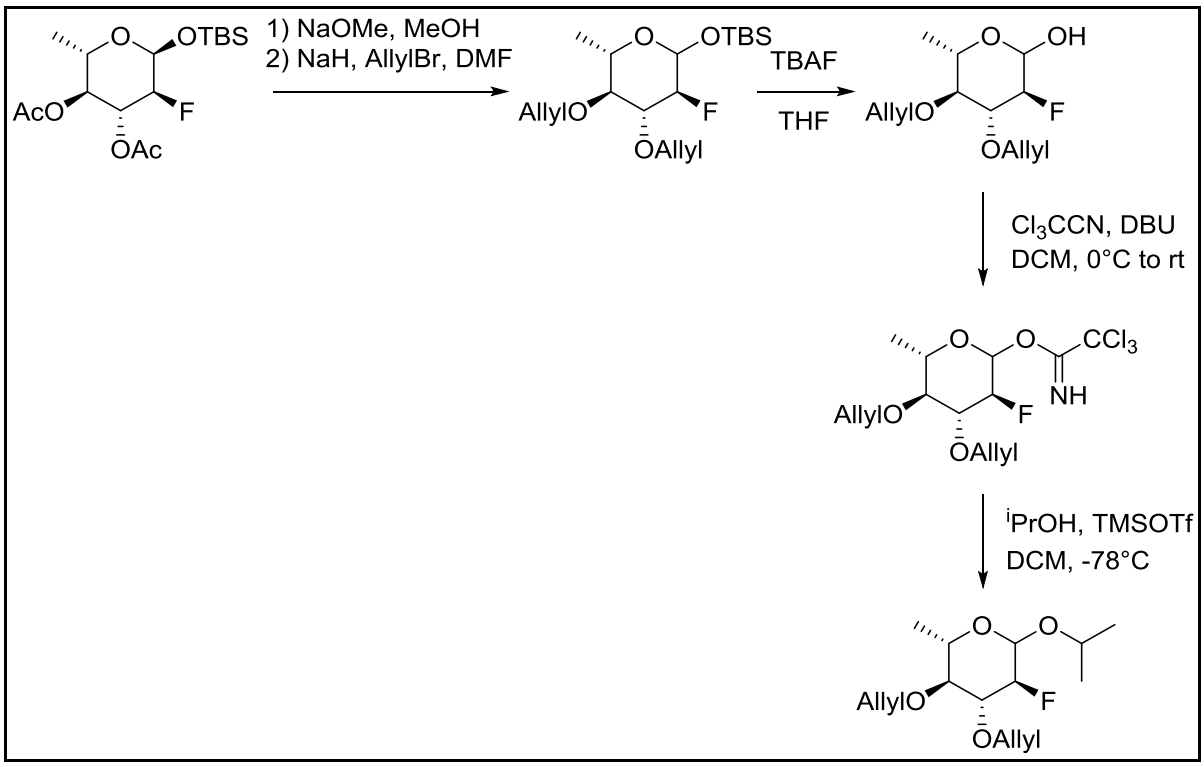
49.4, 9.9, 3.8 Hz, 1H, H-C2), 6.47 (d, *J* = 3.7 Hz, 1H, H-C1), 7.21-7.35 (m, 10H, Ar), 8.54 (s, 1H, NH) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -209.59 (ddd, *J* = 49.4, 10.1, 4.3 Hz) ppm.

1-*O*-Isopropyl-2,6-dideoxy-2-fluoro-3,4-di-*O*-benzyl-D-glucopyranose (**S31**) – Table 2, entry 3

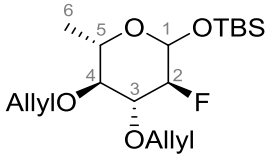


TMSOTf (4.0 µL, 20 µmol, 0.1 eq) was added to a solution of **S30** (100 mg, 0.20 mmol, 1 eq) and isopropanol (0.15 mL, 1.90 mmol, 10 eq) in dry DCM (4 mL) under an Ar atmosphere at -78°C. The reaction was allowed to progress for 2h at -78°C, and then slowly warmed up to room temperature. NEt_3 was added to quench the reaction, and the solvent was removed under vacuum. Purification by silica gel chromatography using a 7:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S31** as a colourless oil (72 mg, 91%, β only).

Colourless oil; [***m/z* (ESI)** found: 411.1945 $(M+Na)^+$, $C_{23}H_{29}FO_4Na$ requires 411.1942]; $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = -23 (*c* 0.50 in $CHCl_3$) $\boldsymbol{\nu_{max}}$ (neat)/cm^{-1} 2975m, 2874m, 1454m, 1364s, 1117s, 1065m, 1026s, 730s. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 1.20 (d, *J* = 6.4 Hz, 3H, H-C6), 1.21 (d, *J* = 6.1 Hz, 3H, H-C8), 1.28 (d, *J* = 6.2 Hz, 3H, H-C8), 3.49 (qd, *J* = 6.4, 1.0 Hz, 1H, H-C5), 3.60-3.64 (m, 2H, H-C3, H-C4), 4.01 (hept, *J* = 6.2 Hz, 1H, H-C7), 4.46 (dd, *J* = 7.6, 4.2 Hz, 1H, H-C1), 4.64 (ddt, *J* = 9.6, 7.6, 1.9 Hz, 0.5H, H-C2), 4.70-4.74 (m, 2.5H, CH_2Ph,H-C2), 4.83 (d, *J* = 12.2 Hz, 1H, CH_2Ph), 4.97 (d, *J* = 11.7 Hz, 1H, CH_2Ph), 7.26-7.41 (m, 10H, Ar) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 16.7 (CH_3, C6), 21.8 (CH_3, C8), 23.4 (CH_3, C8), 70.6 (CH, C5), 71.5 (CH, C7), 72.9 (d, $^4J_{CF}$ = 2.4 Hz, CH_2-Bn), 74.7 (CH_2-Bn), 76.9 (d, $^3J_{CF}$ = 8.9 Hz, CH, C4), 80.9 (d, $^2J_{CF}$ = 15.6 Hz, CH, C3), 91.9 (d, $^1J_{CF}$ = 182.7 Hz, CH, C2), 99.1 (d, $^2J_{CF}$ = 22.9 Hz, CH, C1), 127.5 (CH Ar), 127.6 (CH Ar), 127.7 (CH Ar), 128.2 (CH Ar), 128.4 (CH Ar), 128.6 (CH Ar), 138.2 (C Ar), 138.3 (C Ar) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -205.65 (ddt, *J* = 51.9, 11.3, 4.1 Hz) ppm.



1-*O*-tert-butyldimethylsilyl-2, 6 -dideoxy-2-fluoro-3,4-di-*O*-allyl-L-glucopyranose (**S32**)

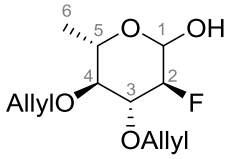


NaOMe (9 mg, 0.17 mmol, 0.4 eq) was added to a solution of **S2** (158 mg, 0.43 mmol, 1.0 eq) in MeOH (4 mL) at 0 °C. The solution was allowed to warm to room temperature and stirred for 1 h. The mixture was neutralized (~pH 7) with amberlite IR120 (prewashed with MeOH), filtered and evaporated to dryness. The residue was dissolved in DMF (1.5 mL), cooled to 0 °C and put under an Ar atmosphere. NaH (52 mg, 1.29 mmol, 3.0 eq., 60% in oil) was slowly added in portions, and the suspension stirred for 30 min while allowing it to reach room temperature. AllylBr (0.11 mL, 1.29 mmol, 3.0 eq.) was added dropwise, and the reaction allowed to progress overnight. The reaction was quenched with H_2O and the crude extracted with DCM. The organic layers were dried over $MgSO_4$ and filtered, and the solvent removed. Purification by silica gel chromatography using a 7:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S32** as a colourless oil (125 mg, 80%, α:β = 1:3).

Colourless oil; [***m/z* (ESI)** found: 383.2017 $(M+Na)^+$, $C_{18}H_{33}FO_4SiNa$ requires 383.2024]; $[\alpha]_D^{25}$ = -11 (*c* 0.84 in $CHCl_3$) ν_{max}(neat)/cm^{-1} 2929w, 2858w, 1254w, 1072s, 1028m, 923m, 838s, 782s. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 0.12 (s, 4H, CH_3), 0.13 (s, 4H, CH_3), 0.91 (s, 12H, 3xCH_3), 1.29 (d, *J* = 6.2 Hz, 3H, H-C6β), 1.31 (d, *J* = 6.2 Hz, 1H, H-C6α), 3.03 (t, *J* = 9.2 Hz, 1H, H-C4β), 3.02 (t, *J* = 9.2 Hz, 0.3H, H-C4α), 3.34 (dtd, *J* = 12.4, 6.2, 3.3 Hz, 1.3H, H-C5β, H-C5α), 3.51 (ddt, *J* = 21.7, 15.0, 8.8 Hz, 1.3H, H-C3β, H-C3α), 4.06 (dd, *J* = 8.8, 7.4 Hz, 0.5H, H-C2β), 4.11 – 4.22 (m, 2.3H, Allyl), 4.26 (dd, *J* = 8.8, 7.8 Hz, 0.15H, H-C2α), 4.30-4.37 (m, 2.3H, Allyl), 4.45 (dd, *J* = 7.8, 2.8 Hz, 0.3H, H-C1α), 4.63 (dd, *J* = 7.5, 3.1 Hz, 1H, H-C1β), 5.15-5.35 (m, 5.2H, Allyl), 5.87-5.97 (m, 2.6H, Allyl) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ = -5.2 (CH_3), -4.4 (CH_3), 17.8 (CH_3,

C6α, C6β), 25.6 (3xCH_3), 31.9 (C), 71.2 (CH, C5α, C5β), 73.6 (d, $^4J_{CF}$ =2.3 Hz, CH_2, Allylβ), 73.7 (d, $^4J_{CF}$ =2.3 Hz, CH_2, Allylα), 74.1 (CH_2, Allylβ), 74.2 (CH_2, Allylα), 82.3 (d, $^3J_{CF}$ = 8.5 Hz, CH, C4α), 82.4 (d, $^3J_{CF}$ = 8.3 Hz, CH, C4β), 82.6 (d, $^2J_{CF}$ = 16.2 Hz, CH, C3β), 82.7 (d, $^2J_{CF}$ = 16.2 Hz, CH, C3α), 93.1 (d, $^1J_{CF}$ = 187.7 Hz, CH, C2α), 95.0 (d, $^2J_{CF}$ = 23.2 Hz, CH, C1β), 95.1 (d, $^1J_{CF}$ = 186.8 Hz, CH, C2β), 99.1 (d, $^2J_{CF}$ = 22.8 Hz, CH, C1α), 116.9 (CH_2, Allylβ), 117.0 (CH_2, Allylα), 117.8 (CH_2, Allylβ), 117.2 (CH_2, Allylα), 134.6 (CH, Allylα), 134.7 (CH, Allylβ), 134.8 (CH, Allylα), 134.9 (CH, Allylβ) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -195.40 (ddd, *J* = 51.0, 15.0, 3.1 Hz, β-anomer), -196.37 (m, α-anomer) ppm.

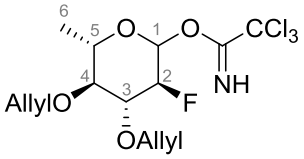
2, 6 -Dideoxy-2-fluoro-3,4-di-*O*-allyl- L-glucopyranose (**S33**)



A 1M solution of TBAF in THF (0.53 mL, 0.53 mmol, 2 eq) was added dropwise to a solution of **S32** (95 mg, 0.26 mmol, 1 eq) in 1mL of THF at 0°C. The mixture was stirred for 45 min at low temperature, and water was then added. The aq. phase was extracted with DCM, and the combined organic layers once washed with water to be then dried with $MgSO_4$, filtered and evaporated. The crude was filtered through silica/NEt_3 using a 7:1 mixture of cyclohexane and ethyl acetate as eluent. The final product was isolated as a colourless oil (31 mg, 48%, α:β = 1.3:1).

Colourless oil; [***m/z* (ESI)** found: 269.1160 $(M+Na)^+$, $C_{12}H_{19}FO_4Na$ requires 269.1172]; $[\alpha]_D^{25}$ = -37 (*c* 1.00 in $CHCl_3$) ν_{max} (neat)/cm^{-1} 3378br, 2935w, 1062s, 1024m, 923m. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 1.25 (d, *J* = 6.3 Hz, 3H, H-C6β), 1.31 (d, *J* = 6.2 Hz, 2.3H, H-C6α), 2.97 (t, *J* = 9.3 Hz, 1H, H-C4β), 3.04 (t, *J* = 9.2 Hz, 0.8H, H-C4α), 3.41 (dq, *J* = 9.5, 6.1 Hz, 0.8H, H-C5α), 3.54 (dt, *J* = 14.9, 8.8 Hz, 0.8H, H-C3α), 3.86 (dt, *J* = 12.7, 9.1 Hz, 1H, H-C3β), 3.96 (dq, *J* = 9.7, 6.3 Hz, 1H, H-C5β), 4.07 (dd, *J* = 8.8, 7.7 Hz, 0.4H, H-C2α), 4.11-4.25 (m, 4.4H, Allyl, H-C2α), 4.29-4.37 (m, 3.5H, Allyl, H-C2β), 4.43 (dd, *J* = 9.3, 3.9 Hz, 0.5H, H-C2β), 4.72 (dd, *J* = 7.7, 2.9 Hz, 0.8H, H-C1α), 5.16-5.32 (m, 8.2H, Allyl, H-C1β), 5.86-6.00 (m, 3.6H, Allyl) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 16.7 (2xCH_3, C6α, C6β), 65.6 (CH, C5β), 70.5 (CH, C5α), 72.7 (d, $^4J_{CF}$ = 2.3 Hz, CH_2, Allyl), 72.8 (d, $^4J_{CF}$ = 2.1 Hz, CH_2, Allyl), 73.2 (CH_2, Allyl), 78.5 (d, $^2J_{CF}$ = 16.1 Hz, CH, C3β), 81.3 (d, $^3J_{CF}$ = 8.3 Hz, CH, C4α), 81.5 (d, $^2J_{CF}$ = 16.4 Hz, CH, C3α), 81.6 (d, $^3J_{CF}$ = 8.2 Hz, CH, C4β), 89.4 (d, $^2J_{CF}$ = 21.4 Hz, CH, C1α), 90.5 (d, $^1J_{CF}$ = 190.2 Hz, CH, C2β), 93.3 (d, $^2J_{CF}$ = 23.4 Hz, CH, C1β), 93.4 (d, $^1J_{CF}$ = 187.3 Hz, CH, C2α), 115.9 (CH_2, Allyl), 116.1 (2xCH_2, Allyl), 116.3 (CH_2, Allyl), 133.6 (CH, Allyl), 133.7 (2xCH, Allyl), 138.9 (CH, Allyl) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -196.47 (ddd, *J* = 51.3, 15.0, 2.9 Hz, β-anomer), -197.99 (dd, *J* = 49.6, 12.8 Hz, α-anomer) ppm.

2, 6 -Dideoxy-2-fluoro-3,4-di-O-allyl- L-glucopyranosyl trichloroacetimidate (**S34**)

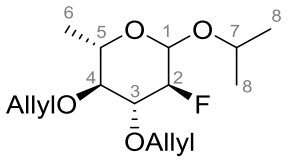


DBU (1 µL, 0.8 µmol, 0.1 eq) was added to a solution of Cl_3CCN (0.08 mL, 0.80 mmol, 10 eq) and **S33** (20 mg, 0.08 mmol, 1.0 eq) in dry DCM (1.5 mL) at 0 °C under an atmosphere of Ar. Upon completion of the addition, the solution was allowed to warm to room temperature, stirred for 30 min and the solvents

evaporated. Purification by silica gel chromatography (SiO_2/NEt_3) using a 7:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S34** as a colourless oil (27 mg, 88%, α:β = 10:1).

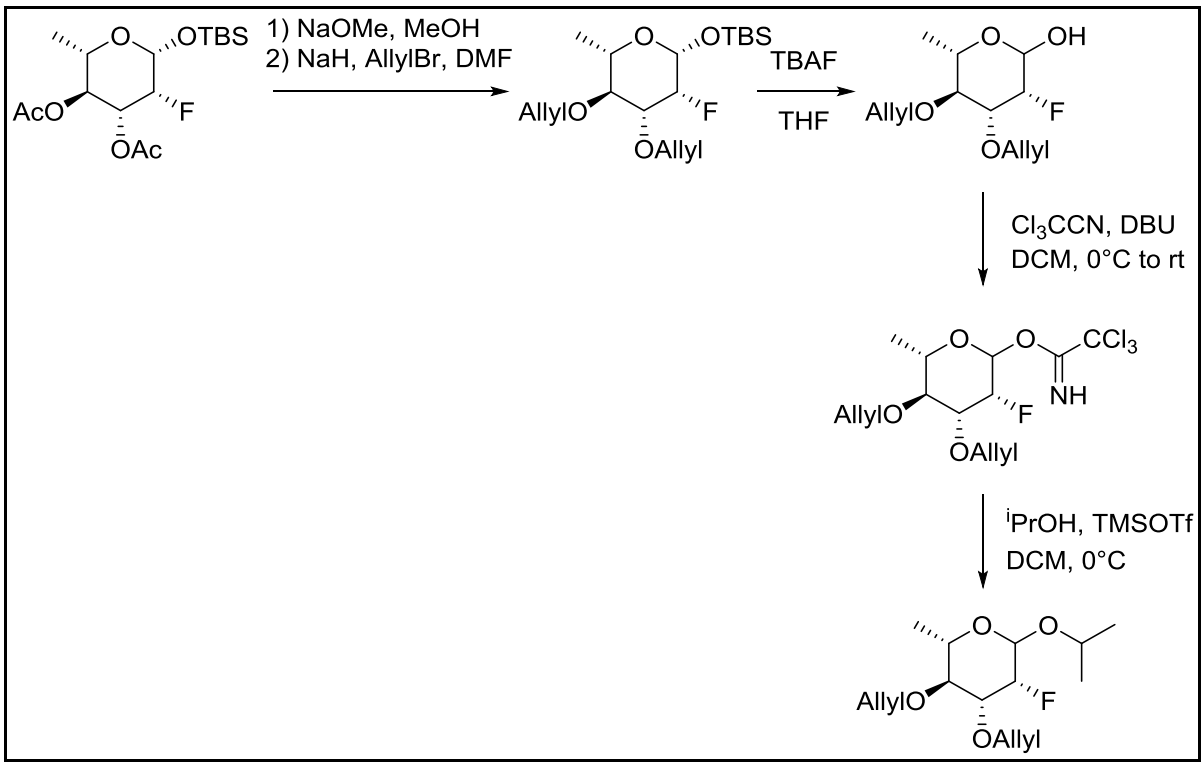
^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.30 (d, *J* = 6.2 Hz, 3H, H-C6), 3.07 (t, *J* = 9.4 Hz, 1H, H-C4), 3.87-3.98 (m, 2H), 4.13-4.28 (m, 2H, Allyl), 4.32-4.41 (m, 2H, Allyl), 4.56 (ddd, *J* = 48.5, 9.3, 3.8 Hz, 1H, H-C2), 5.20 (ddt, *J* = 10.3, 2.8, 1.3 Hz, 2H, Allyl), 5.30 (ddq, *J* = 17.2, 4.7, 1.6 Hz, 2H, Allyl), 5.86-6.02 (m, 2H, Allyl), 6.42 (d, *J* = 3.8 Hz, 1H, H-C1α), 8.65 (s, 1H, NH) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -197.25 (ddd, *J* = 51.5, 15.7, 3.4 Hz, β-anomer), -200.35 (dd, *J* = 48.5, 12.2 Hz, α-anomer) ppm.

1-*O*-Isopropyl-2,6-dideoxy-2-fluoro-3,4-di-*O*-allyl-L-glucopyranose (**S35**) – Table 2, entry 5

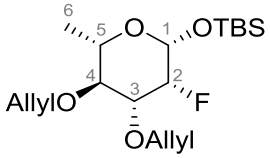


A 0.1M solution of TMSOTf (0.06 mL, 6 µmol, 0.1 eq) was added to a solution of **S34**(23 mg, 0.06 mmol, 1 eq) and isopropanol (0.05 mL, 0.60 mmol, 10 eq) in dry DCM (1 mL) under an Ar atmosphere at -78°C. The reaction was allowed to progress for 2h at -78°C, and then slowly warmed up to room temperature. NEt_3 was added to quench the reaction, and the solvent was removed under vacuum. Purification by silica gel chromatography using a 3:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S35** as a colourless oil (13 mg, 76%, α:β = 1:16).

Colourless oil; [***m/z* (ESI)** found: 311.1639 $(M+Na)^+$, $C_{15}H_{25}FO_4Na$ requires 311.1629]; $[\alpha]_D^{25}$ = -4 (*c* 1.80 in $CHCl_3$) ν_{max} (neat)/cm^{-1} 2977w, 2876w, 1383w, 1125m, 1102s, 1065s, 1026s, 921s, 832w. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 1.20 (d, *J* = 6.1 Hz, 3H, H-C8), 1.26 (d, *J* = 6.1 Hz, 3H, H-C8), 1.30 (d, *J* = 6.2 Hz, 3H, H-C6), 3.02 (t, *J* = 9.2 Hz, 1H, H-C3), 3.34 (dq, *J* = 9.4, 6.2 Hz, 1H, H-C5), 3.52 (dt, *J* = 15.4, 8.8 Hz, 1H, H-C4), 3.97 (hept, *J* = 6.2 Hz, 1H, H-C7), 4.07-4.24 (m, 3H, Allyl, H-C2), 4.33 (dddt, *J* = 11.1, 5.5, 2.6, 1.3 Hz, 2H, Allyl), 4.46 (dd, *J* = 7.8, 3.0 Hz, 1H, H-C1), 5.17 (dp, *J* = 10.3, 1.4 Hz, 2H, Allyl), 5.28 (ddq, *J* = 17.2, 10.6, 1.6 Hz, 2H, Allyl), 5.99 – 5.85 (m, 2H, Allyl) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 16.8 (CH_3, C6), 20.9 (CH_3, C8), 23.4 (CH_3, C8), 70.2 (CH, C5), 71.0 (CH, C7), 72.6 (d, $^4J_{CF}$ = 2.3 Hz, CH_2, Allyl), 73.2 (CH_2, Allyl), 81.3 (d, $^3J_{CF}$ = 8.4 Hz, CH, C4), 81.8 (d, $^2J_{CF}$ = 16.3 Hz, CH, C3), 92.2 (d, $^1J_{CF}$ = 187.1 Hz, CH, C2), 97.7 (d, $^2J_{CF}$ = 22.9 Hz, CH, C1), 116.0 (CH_2, Allyl), 116.2 (CH_2, Allyl), 133.7 (CH, Allyl), 133.9 (CH, Allyl) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -196.00 (ddd, *J* = 51.0, 15.4, 3.0 Hz, β-anomer) ppm.



1-*O*-tert-butyldimethylsilyl-2, 6 -dideoxy-2-fluoro-3,4-di-*O*-allyl-β-L-mannopyranose (**S36**)

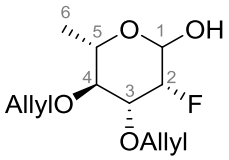


NaOMe (7mg, 0.13 mmol, 0.4 eq) was added to a solution of **S3** (119 mg, 0.33 mmol, 1.0 eq) in MeOH (3 mL) at 0 °C. The solution was allowed to warm to room temperature and stirred for 1 h. The mixture was neutralized (~pH 7) with amberlite IR120 (prewashed with MeOH), filtered and evaporated to dryness. The residue was dissolved in DMF (1 mL), cooled to 0 °C and put under an Ar atmosphere. NaH (60 mg, 1.49 mmol, 4.5 eq., 60% in oil) was slowly added in portions, and the suspension stirred for 45 min while allowing it to reach room temperature. AllylBr (0.13 mL, 1.49 mmol, 4.5 eq.) was added dropwise, and the reaction allowed to progress overnight. The reaction was quenched with H_2O and the crude extracted with DCM. The organic layers were dried over $MgSO_4$ and filtered, and the solvent removed. Purification by silica gel chromatography using a 7:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S36** as a colourless oil (96 mg, 81%).

Colourless oil; [***m/z* (ESI)** found: 383.2030 $(M+Na)^+$, $C_{18}H_{33}FO_4SiNa$ requires 383.2024]; $[\alpha]_D^{25}$ = +12 (*c* 1.20 in $CHCl_3$) ν_{max} (neat)/cm^{-1} 2928m, 2856m, 1129m, 1079s, 924m, 837s, 781s. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 0.12 (s, 3H, CH_3), 0.14 (s, 3H, CH_3), 0.91 (s, 9H, 3xCH_3), 1.34 (d, *J* = 5.7 Hz, 3H, H-C6), 3.285-3.35 (m, 2.5H, H-C5, H-C4, 0.5H-C3), 3.41 (dd, *J* = 9.2, 2.3 Hz, 0.5H, H-C3), 4.13 (ddq, *J* = 12.4, 6.0, 1.4 Hz, 2H, CH_2Allyl), 4.21 (ddt, *J* = 12.9, 5.8, 1.5 Hz, 1H, CH_2Allyl), 4.35 (ddt, *J* = 12.4, 5.6, 1.4 Hz, 1H, CH_2Allyl), 4.57 (d, *J* = 1.4 Hz, 0.5H, H-C2), 4.66-4.73 (m, 1.5H, H-C1, 0.5H-C2), 5.16 (dq, *J* = 10.3, 1.4 Hz, 1H, CH_2Allyl), 5.20 (dq, *J* = 10.4, 1.3 Hz, 1H, CH_2Allyl), 5.26 (dq, *J* = 17.2, 1.6 Hz, 1H, CH_2Allyl), 5.32 (dq, *J* = 17.3, 1.6 Hz, 1H, CH_2Allyl), 5.85-6.00 (m, 2H, CHAllyl) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = -4.9 (CH_3), -3.9 (CH_3), 0.91

(3xCH_3), 29.9 (C), 71.1 (CH_2, Allyl), 71.8 (CH, C5), 74.4 (CH_2, Allyl), 79.4 (CH, C4), 80.4 (d, $^2J_{CF}$ = 17.5 Hz, CH, C3), 88.7 (d, $^1J_{CF}$ = 187.9 Hz, CH, C2), 94.2 (d, $^2J_{CF}$ = 16.1 Hz, CH, C1), 117.2 (CH_2, Allyl), 117.6 (CH_2, Allyl), 134.7 (CH, Allyl), 135.0 (CH, Allyl) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -220.37 (m) ppm.

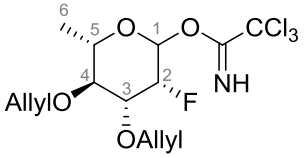
2, 6 -Dideoxy-2-fluoro-3,4-di-*O*-allyl- L-mannopyranose (**S37**)



A 1M solution of TBAF in THF (0.44 mL, 0.44 mmol, 2 eq) was added dropwise to a solution of **S36** (78 mg, 0.22 mmol, 1 eq) in 1mL of THF at 0°C. The mixture was stirred for 45 min at low temperature, and water was then added. The aq. phase was extracted with DCM, and the combined organic layers once washed with water to be then dried with $MgSO_4$, filtered and evaporated. The crude was filtered through silica/NEt_3 using a 7:1 mixture of cyclohexane and ethyl acetate as eluent. The final product was isolated as a colourless oil (36 mg, 68%, α:β = 3.5:1).

Colourless oil; [***m/z* (ESI)** found: 269.1158 $(M+Na)^+$, $C_{12}H_{19}FO_4Na$ requires 269.1160]; $[\alpha]_D^{25}$ = -19 (*c* 1.20 in $CHCl_3$) ν_{max} (neat)/cm^{-1} 3378br, 2935w, 1129m, 1060s, 989m, 925m. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 1.31 (d, *J* = 6.2 Hz, 3H, H-C6α), 1.35 (d, *J* = 6.0 Hz, 0.90H, H-C6β), 3.28 (m, 0.29H, H-C4β), 3.34 (m, 1H, H-C4α), 3.43 (ddd, *J* = 30.3, 9.2, 2.5 Hz, 0.29H, H-C3β), 3.73 (ddd, *J* = 30.3, 9.5, 2.5 Hz, 1H, H-C3α), 3.91 (dq, *J* = 9.5, 6.1 Hz, 1H, H-C5α), 4.11-4.24 (m, 4.5H, CH_2Allylα, CH_2Allylβ), 4.33-4.39 (m, 1.29H, CH_2Allylα, CH_2Allylβ), 4.74 (dt, *J* = 49.7, 2.4 Hz, 1H, H-C2α), 5.15-5.36 (m, 6.3H, H-C1α, H-C1β, CH_2Allylα, CH_2Allylβ), 5.87-6.01 (m, 2.6H, CHAllylα, CHAllylβ) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 17.8 (CH_3, C6α, C6β), 68.0 (CH, C5α), 71.3 (CH_2, Allylβ), 71.5 (CH_2, Allylα), 74.2 (CH_2, Allylβ), 74.3 (CH_2, Allylα), 77.34 (d, $^2J_{CF}$ = 28.4 Hz, CH, C3α), 79.0 (CH, C4β), 79.75 (d, $^3J_{CF}$ = 1.2 Hz, CH, C4α), 87.7 (d, $^1J_{CF}$ = 174.9 Hz, CH, C2α), 88.8 (d, $^1J_{CF}$ = 181.5 Hz, C2α), 92.1 (d, $^2J_{CF}$ = 30.1 Hz, C1α), 92.7 (d, $^2J_{CF}$ = 17.3 Hz, C1β), 117.0 (CH_2, Allylα), 117.2 (CH_2, Allylβ), 117.4 (CH_2, Allylβ), 117.8 (CH_2, Allylβ), 134.3 (CH, Allylβ), 134.6 (CH, Allylα), 134.7 (CH, Allylβ), 134.9 (CH, Allylα) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -204.24 (ddd, *J* = 49.7, 30.3, 7.4 Hz, α-anomer), -223.19 (ddd, *J* = 50.9, 30.0, 17.9 Hz, β-anomer) ppm.

2, 6 -Dideoxy-2-fluoro-3,4-di-O-allyl- L-mannopyranosyl trichloroacetimidate (**S38**)

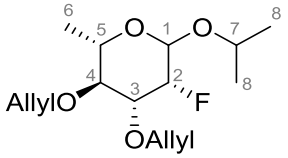


DBU (1 µL, 1 µmol, 0.1 eq) was added to a solution of Cl_3CCN (0.11 mL, 1.10 mmol, 10 eq) and **S37** (27 mg, 0.11 mmol, 1.0 eq) in dry DCM (2 mL) at 0 °C under an atmosphere of Ar. Upon completion of the addition, the solution was allowed to warm to room temperature, stirred for 45 min and the solvents evaporated. Purification by silica gel chromatography (SiO_2/NEt_3) using a 7:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S38** as a colourless oil (39 mg, 91%, α only).

^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.35 (d, *J* = 6.2 Hz, 3H, H-C6), 3.44 (td, *J* = 9.6, 1.2 Hz, 1H, H-C4), 3.77 (ddd, *J* = 29.6, 9.5, 2.5 Hz, 1H, H-C3), 3.90 (dq, *J* = 10.3, 6.2 Hz, 1H, H-C5), 4.13-4.24 (m, 3H, Allyl), 4.38 (ddt, *J* = 12.2, 5.7, 1.4 Hz, 1H, Allyl), 4.85 (dt, *J* = 48.9, 2.3 Hz, 1H, H-C2), 5.10-5.47 (m, 4H, Allyl), 5.81-6.05 (m, 2H,

Allyl), 6.34 (dd, *J* = 6.2, 2.1 Hz, 1H, H-C1), 8.68 (s, 1H, NH) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -204.44 (ddd, *J* = 48.8, 29.6, 6.3 Hz) ppm.

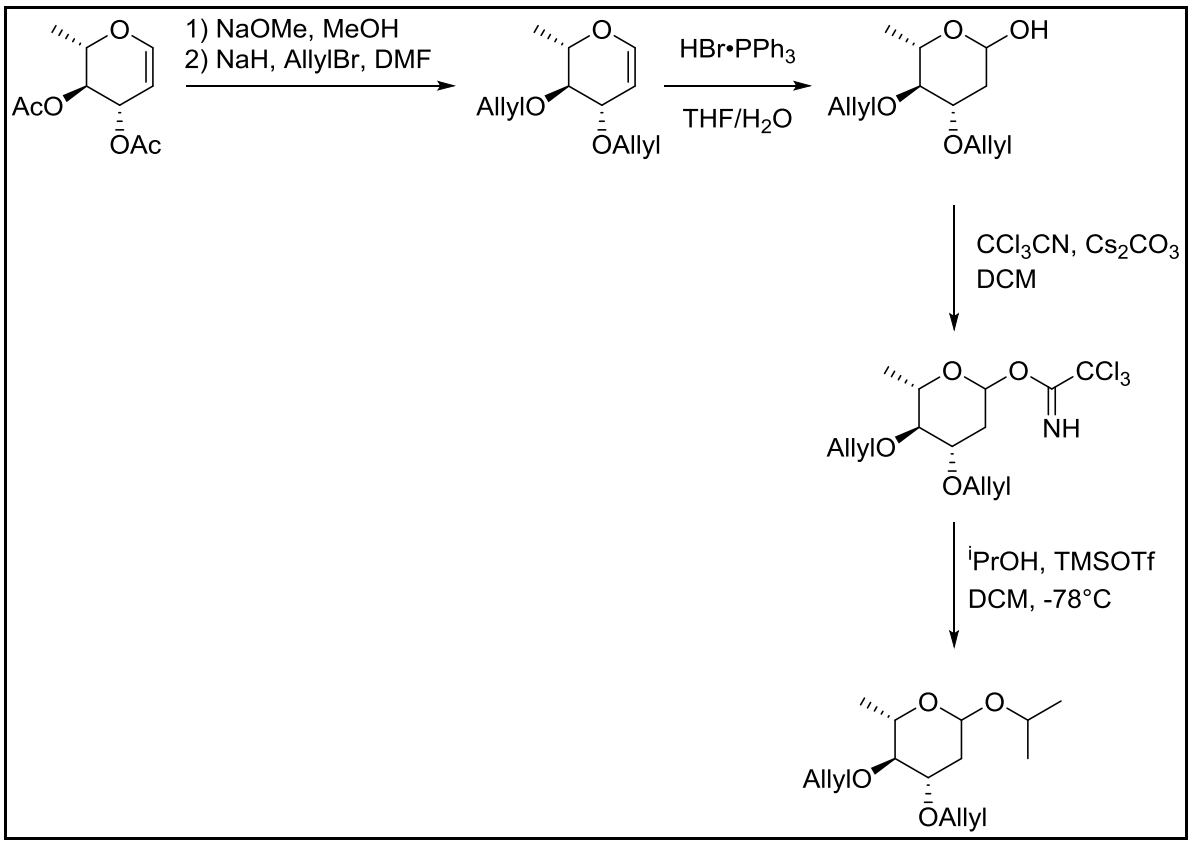
1-*O*-Isopropyl-2,6-dideoxy-2-fluoro-3,4-di-*O*-allyl-L-mannopyranose (**S39**) – Table 2, entry 6



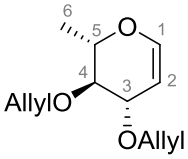
A 0.1M solution of TMSOTf (0.08 mL, 8 µmol, 0.1 eq) was added to a solution of **S38** (32 mg, 0.08 mmol, 1 eq) and isopropanol (0.06 mL, 0.80 mmol, 10 eq) in dry DCM (1.5 mL) under an Ar atmosphere at 0°C. The reaction was allowed to progress for 2h at 0°C, and then slowly warmed up to room temperature. NEt_3 was added to quench the reaction, and the solvent was removed under vacuum. Purification by silica gel chromatography using a 7:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S39** as a colourless oil (α-anomer: 8 mg, β-anomer: 9 mg, 74% global yield).

α-anomer: Colourless oil; [***m/z* (ESI)** found: 311.1641 $(M+Na)^+$, $C_{15}H_{25}FO_4Na$ requires 311.1629]; $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = -64 (*c* 0.80 in $CHCl_3$) $\boldsymbol{\nu}_{\mathbf{max}}$ (neat)/cm^{-1} 2975m, 2917w, 1457w, 1382w, 1056s, 979m, 924m. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 1.13 (d, *J* = 6.1 Hz, 3H, H-C8), 1.18 (d, *J* = 6.3 Hz, 3H, H-C8), 1.30 (d, *J* = 6.2 Hz, 3H, H-C6), 3.32 (td, *J* = 9.5, 1.1 Hz, 1H, H-C4), 3.63 (dd, *J* = 9.4, 2.6 Hz, 0.5H, H-C3), 3.70-3.76 (m, 1.5H, H-C3, H-C5), 3.91 (hept, *J* = 6.3 Hz, 1H, H-C7), 4.11-4.24 (m, 3H, Allyl), 4.36 (ddt, *J* = 12.2, 5.7, 1.4 Hz, 1H, Allyl), 4.63 (dt, *J* = 50.2, 2.3 Hz, 1H, H-C2), 5.18 (dddd, *J* = 10.0, 8.7, 2.4, 1.1 Hz, 2H, Allyl), 5.30 (ddq, *J* = 18.8, 17.2, 1.6 Hz, 2H, Allyl), 5.89-6.00 (m, 2H, Allyl) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 17.7 (CH_3, C6), 21.2 (CH_3, C8), 23.1 (CH_3, C8), 67.7 (CH, C5), 69.3 (CH, C7), 71.3 (CH_2, Allyl), 74.3 (CH_2, Allyl), 78.1 (d, $^2J_{CF}$ = 17.1 Hz, CH, C3), 88.0 (d, $^1J_{CF}$ = 175.5 Hz, CH, C2), 95.2 (d, $^2J_{CF}$ = 29.2 Hz, CH, C1), 117.1 (2xCH_2, Allyl), 134.7 (CH, Allyl), 134.9 (CH, Allyl) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -203.11 (ddd, *J* = 50.2, 30.5, 7.8 Hz) ppm.

β-anomer: Colourless oil; [***m/z* (ESI)** found: 311.1631 $(M+Na)^+$, $C_{15}H_{25}FO_4Na$ requires 311.1629]; $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = +32 (*c* 0.90 in $CHCl_3$) $\boldsymbol{\nu}_{\mathbf{max}}$ (neat)/cm^{-1} 2975w, 2868w, 1104s, 1070s, 987m, 922m, 785m. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 1.12 (d, *J* = 6.1 Hz, 3H-C8), 1.21 (d, *J* = 6.3 Hz, 3H, H-C8), 1.29 (d, *J* = 5.7 Hz, 3H, H-C6), 3.22-3.30 (m, 2.5H, H-C5, H-C4, H-C3), 3.36 (dd, *J* = 9.0, 2.4 Hz, 0.5H, H-C3), 3.95 (hept, *J* = 6.2 Hz, 1H, H-C7), 4.07 (ddt, *J* = 12.4, 6.0, 1.4 Hz, 2H, Allyl), 4.15 (ddt, *J* = 12.8, 5.8, 1.4 Hz, 1H, Allyl), 4.30 (ddt, *J* = 12.3, 5.7, 1.4 Hz, 1H, Allyl), 4.41 (d, *J* = 18.8 Hz, 1H, H-C1), 4.65 (dd, *J* = 51.5, 1.9 Hz, 1H, H-C2), 5.08-5.28 (m, 4H, Allyl), 5.81-5.92 (m, 2H, Allyl) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 17.8 (CH_3, C6), 21.6 (CH_3, C8), 23.3 (CH_3, C8), 70.9 (CH_2, Allyl), 71.4 (CH, C7), 71.6 (CH, C5), 74.3 (CH_2, Allyl), 79.4 (CH, C4), 80.3 (d, $^2J_{CF}$ = 17.6 Hz, CH, C3), 88.0 (d, $^1J_{CF}$ = 186.7 Hz, CH, C2), 96.6 (d, $^2J_{CF}$ = 15.5 Hz, CH, C1), 117.1 (CH_2, Allyl), 117.6 (CH_2, Allyl), 134.5 (CH, Allyl), 134.8 (CH, Allyl) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -219.26 (m) ppm.



2, 6 -Dideoxy-3,4-di-*O*-allyl- L-glucal (**S40**)

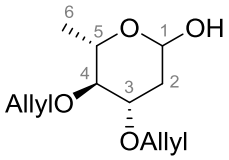


NaOMe (20 mg, 0.37 mmol, 0.4 eq) was added to a solution of 3,4-Di-*O*-acetyl-6-deoxy-L-glucal (200 mg, 0.93 mmol, 1.0 eq) in MeOH (10 mL) at 0 °C. The solution was allowed to warm to room temperature and stirred for 1 h. The mixture was neutralized (~pH 7) with amberlite IR120 (prewashed with MeOH), filtered and evaporated to dryness. The residue was dissolved in DMF (5 mL), cooled to 0 °C and put under an Ar atmosphere. NaH (167 mg, 4.19 mmol, 4.5 eq., 60% in oil) was slowly added in portions, and the suspension stirred for 30 min while allowing it to reach room temperature. AllylBr (0.36 mL, 4.19 mmol, 4.5 eq.) was added dropwise, and the reaction allowed to progress overnight. The reaction was quenched with H_2O and the crude extracted with DCM. The organic layers were dried over $MgSO_4$ and filtered, and the solvent removed. Purification by silica gel chromatography using a 3:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S40** as a colourless oil (195 mg, 99%).

Colourless oil; $[\alpha]_D^{25}$ = +25 (*c* 0.98 in $CHCl_3$) ν_{max}(neat)/cm^{-1} 2924m, 2855m, 1646m, 1243m, 1089s, 1056s, 920s, 739m. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ = 1.34 (d, *J* = 6.4 Hz, 3H, H-C6), 3.29 (dd, *J* = 8.8, 6.4 Hz, 1H, H-C4), 3.88 (dq, *J* = 8.8, 6.5 Hz, 1H, H-C5), 3.99-4.04 (m, 2H, Allyl, H-C3), 4.08-4.19 (m, 2H, Allyl), 4.30 (ddt, *J* = 12.7, 5.4, 1.5 Hz, 1H, Allyl), 4.79 (dd, *J* = 6.1, 2.5 Hz, 1H, H-C2), 5.15 (m, 1H, Allyl), 5.27 (ddq, *J* = 17.2, 5.3, 1.7 Hz, 2H, Allyl), 5.88-5.98 (m, 2H, Allyl), 6.31 (dd, *J* = 6.1, 1.4 Hz, 1H, H-C1) ppm.**^{13}C NMR** (100

MHz, CD_2Cl_2) δ = 17.7 (CH_3, C6), 69.9 (CH_2, Allyl), 73.3 (CH_2, Allyl), 74.5 (CH, C5), 76.6 (CH, C3), 80.0 (CH, C4), 100.9 (CH, C2), 116.6 (CH_2, Allyl), 116.8 (CH_2, Allyl), 135.8 (CH, Allyl), 135.9 (CH, Allyl), 145.0 (CH, C1) ppm.

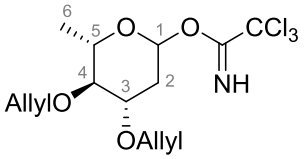
2, 6 -Dideoxy-3,4-di-*O*-allyl- L-glucopyranose (**S41**)



S40 (140 mg, 0.67 mmol, 1 eq) was dissolved in 2 mL of THF, and HBr•PPh_3 (23 mg, 60 µmol, 0.10 eq) was added as a solid. The mixture was stirred for 10 min at room temperature, and H_2O (20 µL, 1.0 mmol, 1.5 eq) was added. The reaction was allowed to progress for 2h at r.t., and it was quenched with $NaHCO_3$ and extracted with ethyl acetate. The organic layers were dried over $MgSO_4$, filtered and the solvent removed. Purification by silica gel chromatography using a 3:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S41** as a colourless oil (90 mg, 59%, α:β = 1.7:1).

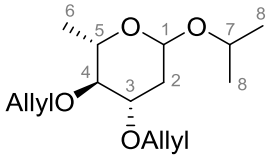
Colourless oil; [***m/z* (ESI)** found: 251.1251 $(M+Na)^+$, $C_{12}H_{20}O_4Na$ requires 251.1254]; $[\alpha]_D^{25}$ = -30 (*c* 3.00 in $CHCl_3$) ν_{max} (neat)/cm^{-1} 3409br, 2976w, 2934w, 1080s, 897s, 918s, 733m. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 1.26 (d, *J* = 6.3 Hz, 3H, H-C6α), 1.31 (d, *J* = 6.2 Hz, 1.8H, H-C6β), 1.47 (ddd, *J* = 12.5, 11.6, 9.7 Hz, 0.6H, H-C2β), 1.59 (ddd, *J* = 13.1, 11.5, 3.6 Hz, 1H, H-C2α), 2.21 (ddd, *J* = 13.1, 5.1, 1.5 Hz, 1H, H-C2α), 2.33 (ddd, *J* = 12.5, 5.0, 2.0 Hz, 0.6H, H-C2β), 2.94 (t, *J* = 9.1 Hz, 1H, H-C4α), 2.95 (t, *J* = 9.0 Hz, 0.6H, H-C4β), 3.34 (dq, *J* = 9.3, 6.2 Hz, 0.6H, H-C5β), 3.45 (ddd, *J* = 11.6, 8.6, 5.0 Hz, 0.6H, H-C3β), 3.80 (ddd, *J* = 11.5, 8.8, 5.0 Hz, 1H, H-C3α), 3.91 (dq, *J* = 9.5, 6.2 Hz, 1H, H-C5α), 4.03-4.16 (m, 4.8H, Allylα, Allylβ), 4.33-4.39 (m, 1.6H, Allylα, Allylβ), 4.76 (dd, *J* = 9.7, 2.1 Hz, 0.6H, H-C1β), 5.13-5.18 (m, 3.2H, Allylα, Allylβ), 5.23-5.31 (m, 4.2H, Allylα, Allylβ, H-C1α), 5.86-5.98 (m, 3.2H, Allylα, Allylβ) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 18.1 (2xCH_3, C6α, C6β), 35.9 (CH_2, C2α), 38.5 (CH_2, C2β), 67.4 (CH, C5α), 70.6 (CH_2, Allylβ), 70.9 (CH_2, Allylα), 71.5 (CH, C3β), 74.0 (2xCH_2, Allylα, Allylβ), 76.3 (CH, C3α), 78.7 (CH, C5β), 83.2 (CH, C4β), 84.2 (CH, C4α), 91.9 (CH, C1α), 93.9 (CH, C1β), 116.5 (CH_2, Allylα), 116.7 (CH_2, Allylα), 116.8 (CH_2, Allylβ), 116.9 (CH_2, Allylβ), 134.9 (CH, Allylβ), 135.0 (CH, Allylβ), 136.1 (2xCH, Allylα) ppm.

2, 6 -Dideoxy-3,4-di-*O*-allyl- L-glucopyranosyl trichloroacetimidate (**S42**)



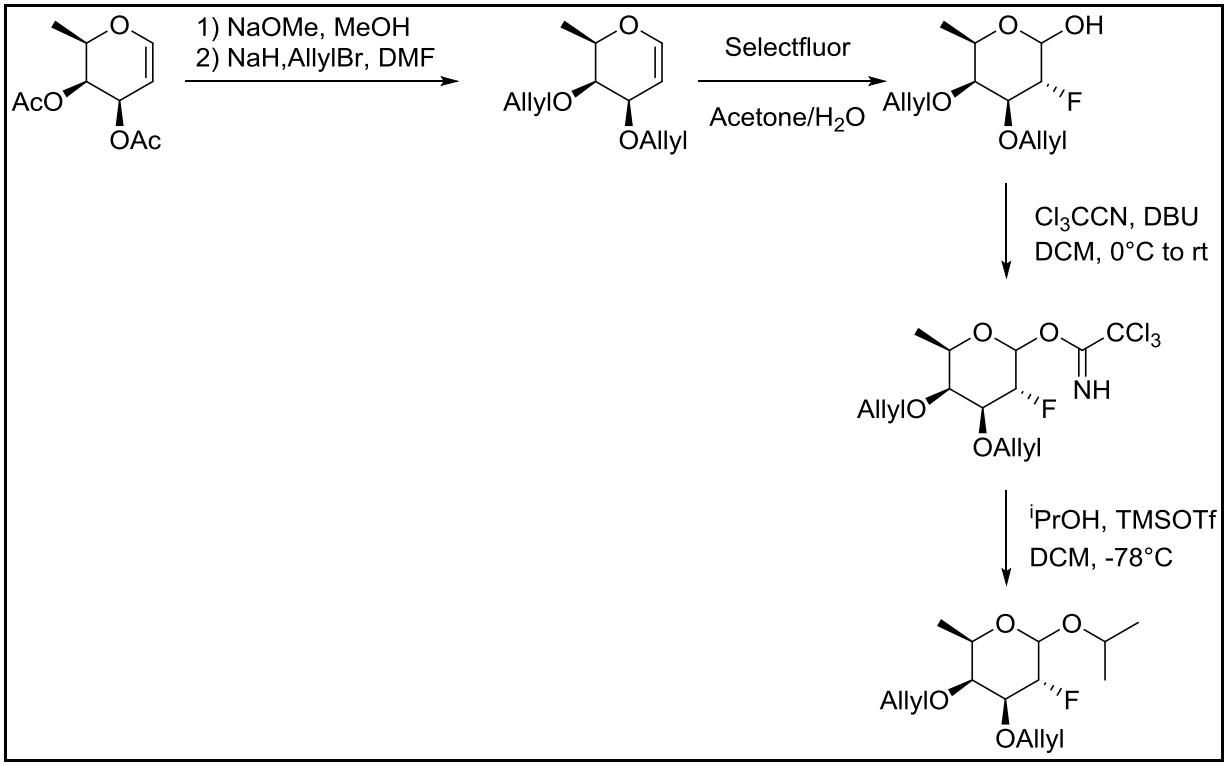
S41 (57 mg, 0.25 mmol, 1 eq) was dissolved in 2.5 mL of anh. DCM under an atmosphere of Ar. Cs_2CO_3 (16 mg, 0.05 mmol, 0.2 eq) was added in one portion, followed by Cl_3CCN (0.12 mL, 1.25 mmol, 5 eq). The mixture was stirred at room temperature for 2h, filtered through a celite pad and used in the following reaction with no further purification.

1-*O*-Isopropyl-2,6-dideoxy-3,4-di-*O*-allyl-L-glucopyranose (**S43**) – Table 2, entry 8

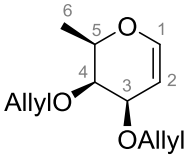


A 0.1M solution of TMSOTf (0.25 mL, 25 µmol, 0.1 eq) was added to a solution of **S42** (93 mg, 0.25 mmol, 1 eq) and isopropanol (0.19 mL, 2.50 mmol, 10 eq) in dry DCM (5 mL) under an Ar atmosphere at -78°C. The reaction was allowed to progress for 2h at -78°C, and then slowly warmed up to room temperature. NEt_3 was added to quench the reaction, and the solvent was removed under vacuum. Purification by silica gel chromatography using a 3:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S43** as a colourless oil (62 mg, 93%, α:β = 4:1).

Colourless oil; [***m/z* (ESI)** found: 293.1724 $(M+Na)^+$, $C_{15}H_{26}O_4Na$ requires 293.1723]; $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = -22 (*c* 6.20 in $CHCl_3$) $\boldsymbol{\nu_{max}}$ (neat)/cm^{-1} 2972w, 2933w, 1122s, 1092s, 1064s, 1000s, 919s. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 1.10 (d, *J* = 6.1 Hz, 3H, H-C8α), 1.16 (d, *J* = 6.2 Hz, 3H, H-C8α), 1.22 (d, *J* = 6.2 Hz, 0.75H, H-C8β), 1.25 (d, *J* = 6.3 Hz, 3H, H-C6α), 1.31 (d, *J* = 6.2 Hz, 0.75H, H-C6β), 1.53 (m, 0.25H, H-C2β), 1.59 (ddd, *J* = 13.0, 11.5, 3.8 Hz, 1H, H-C2α), 2.13 (ddd, *J* = 12.9, 5.1, 1.4 Hz, 1H, H-C2α), 2.20 (ddd, *J* = 12.5, 5.1, 2.0 Hz, 0.25H, H-C2β), 2.93 (m, 1.25H, H-C4α, H-C4β), 3.26 (dq, *J* = 9.3, 6.2 Hz, 0.25H, H-C5β), 3.44 (ddd, *J* = 11.7, 8.7, 5.1 Hz, 0.25H, H-C3β), 3.67-3.78 (m, 2H, H-C3α, H-C5α), 3.84 (h, *J* = 6.2 Hz, 1H, H-C7α), 3.97 (h, *J* = 6.2 Hz, 0.25H, H-C7β), 4.01-4.16 (m, 3.75H, Allylα, Allylβ), 4.33-4.39 (m, 1.25H, Allylα, Allylβ), 4.48 (dd, *J* = 9.8, 2.0 Hz, 0.25H, H-C1β), 4.93 (dd, *J* = 3.8, 1.3 Hz, 1H, H-C1α), 5.12-5.17 (m, 2.5H, Allylα, Allylβ), 5.22-5.30 (m, 2.5H, Allylα, Allylβ), 5.86-5.99 (m, 2.5H, Allylα, Allylβ) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 18.0 (CH_3, C6α), 18.2 (CH_3, C6β), 21.2 (CH_3, C8α), 21.8 (CH_3, C8β), 23.3 (CH_3, C8α), 23.5 (CH_3, C8β), 36.4 (CH_2, C2α), 37.6 (CH_2, C2β), 67.1 (CH, C5α), 67.9 (CH, C7α), 70.4 (CH, C7β), 70.5 (CH_2, Allylβ), 70.8 (CH_2, Allylα), 71.3 (CH, C5β), 74.0 (CH_2, Allylβ), 74.1 (CH_2, Allylα), 77.0 (CH, C3α), 79.2 (CH, C3β), 83.5 (CH, C4β), 84.5 (CH, C4α), 94.7 (CH, C1α), 97.5 (CH, C1β), 116.3 (CH_2, Allylα), 116.6 (CH_2, Allylβ), 116.7 (CH_2, Allylα), 116.8 (CH_2, Allylβ), 135.1 (CH, Allylβ), 135.2 (CH, Allylβ), 135.2 (CH, Allylα), 135.3 (CH, Allylα) ppm.

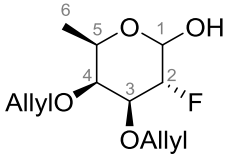


2, 6 -Dideoxy-3,4-di-*O*-allyl- D-fucal (**S44**)



NaOMe (11 mg, 0.20 mmol, 0.4 eq) was added to a solution of 3,4-di-*O*-acetyl-6-deoxy-D-fucal (108 mg, 0.50 mmol, 1.0 eq) in MeOH (3.0 mL) at 0 °C. The solution was allowed to warm to room temperature and stirred for 1 h. The mixture was neutralized (~pH 7) with amberlite IR120 (prewashed with MeOH), filtered and evaporated to dryness. The residue was dissolved in DMF (5.0 mL), cooled to 0 °C and put under an Ar atmosphere. NaH (90 mg, 2.25 mmol, 4.5 eq., 60% in oil) was slowly added in portions, and the suspension stirred for 30 min while allowing it to reach room temperature. AllylBr (0.19 mL, 2.25 mmol, 4.5 eq.) was added dropwise, and the reaction allowed to progress overnight. The reaction was quenched with H_2O and the crude extracted with DCM. The organic layers were dried over $MgSO_4$ and filtered, and the solvent removed. Filtration through silica gel using a 7:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S44** as a colourless oil that was directly used in the following step.

2,6-Dideoxy-2-fluoro-3,4-di-*O*-allyl-D-galactopyranose (**S45**)

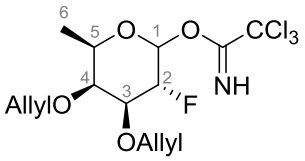


SelectFluor™ (260mg, 0.74 mmol, 1.5 eq) was added at to a solution of 3,4-Di-*O*-allyl-6-deoxy-D-fucal (102 mg, 0.49 mmol, 1.0 eq) in acetone (2 mL) and water (0.5 mL). The solution was stirred at room

temperature for 20 h. The solvents were then evaporated and the residue dissolved in DCM and a sat. aq. solution of $NaHCO_3$. The aq. phase was extracted with DCM and the combined organic phases dried over $MgSO_4$, filtered and evaporated to dryness. The crude was filtered through silica using a mixture of cyclohexane and ethyl acetate as eluent (3:1), to afford **S45** as a colourless oil (60 mg, 51%, α:β = 2:1).

Colourless oil; [***m/z* (ESI)** found: 269.1157 $(M+Na)^+$, $C_{12}H_{19}FO_4Na$ requires 269.1160]; $[\alpha]_D^{25}$ = +30 (*c* 2.00 in $CHCl_3$) ν_{max}(neat)/cm^{-1} 3378br, 1933w, 1169w, 1129m, 1108m, 1048s, 1028s, 999s, 924s, 813m. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 1.24 (d, *J* = 6.5 Hz, 3H, H-C6α), 1.30 (d, *J* = 6.4 Hz, 1.5H, H-C6β), 2.78 (brs, 1H, OHα), 3.22 (brs, 0.5H, OHβ), 3.49-3.58 (m, 1H, H-C3β, H-C4β), 3.60-3.65 (m, 1.5H, H-C5β, H-C4α), 3.90 (ddd, *J* = 10.9, 9.7, 3.0 Hz, 1H, H-C3α), 4.10-4.27 (m, 5.5H, H-C5α, 3xAllylβ, 3xAllylα), 4.38-4.46 (m, 1.75H, H-C2β, Allylα, Allylβ), 4.57 (dd, *J* = 9.1, 7.4 Hz, 0.25H, H-C2β), 4.57 (dd, *J* = 7.2, 5.0 Hz, 0.5H, H-C1β), 4.85 (ddd, *J* = 50.3, 9.8, 3.9 Hz, 1H, H-C2α), 5.16-5.36 (m, 6H, 4xAllylα, 4xAllylβ), 5.43 (d, *J* = 3.8 Hz, 1H, H-C1α), 5.88-5.99 (m, 3H, 2xAllylα, 2xAllylβ) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 16.4 (CH_3, C6α), 16.6 (CH_3, C6β), 66.6 (CH, C5α), 71.0 (CH, C5β), 71.6 (d, $^4J_{CF}$ = 1.8 Hz, CH_2, Allylα), 71.7 (d, $^4J_{CF}$ = 1.9 Hz, CH_2, Allylβ), 74.3 (2xCH_2, Allylα, Allylβ), 76.4 (d, $^2J_{CF}$ = 15.9 Hz, CH, C3α), 76.9 (d, $^3J_{CF}$ = 9.0 Hz, CH, C4α), 77.9 (d, $^3J_{CF}$ = 8.5 Hz, CH, C4β), 80.1 (d, $^2J_{CF}$ = 15.9 Hz, CH, C3β), 89.4 (d, $^1J_{CF}$ = 185.4 Hz, CH, C2α), 91.0 (d, $^2J_{CF}$ = 21.6 Hz, CH, C1α), 93.2 (d, $^1J_{CF}$ = 183.0 Hz, CH, C2β), 95.2 (d, $^2J_{CF}$ = 24.2 Hz, CH, C1β), 116.9 (CH_2, Allylα), 117.1 (CH_2, Allylβ), 117.4 (CH_2, Allylα), 117.6 (CH_2, Allylβ), 134.5 (CH, Allylβ), 134.6 (CH, Allylα), 135.0 (CH, Allylβ), 135.1 (CH, Allylα) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -206.31 (m, β-anomer), -207.85 (ddd, *J* = 50.3, 11.0, 4.1 Hz, α-anomer) ppm.

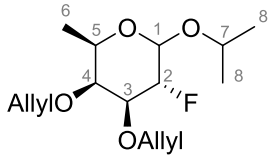
2,6-Dideoxy-2-fluoro-3,4-di-*O*-allyl-D-galactopyranosyl trichloroacetimidate (S46)



DBU (30 µL, 20 µmol, 0.1 eq) was added to a solution of Cl_3CCN (0.21 mL, 2.10 mmol, 10 eq) and **S45** (52 mg, 0.21 mmol, 1.0 eq) in dry DCM (4.0 mL) at 0 °C under an atmosphere of Ar. Upon completion of the addition, the solution was allowed to warm to room temperature, stirred for 30 min and the solvents evaporated. Purification by silica gel chromatography (SiO_2/NEt_3) using a 7:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S46** as a colourless oil (67 mg, 82%, α only).

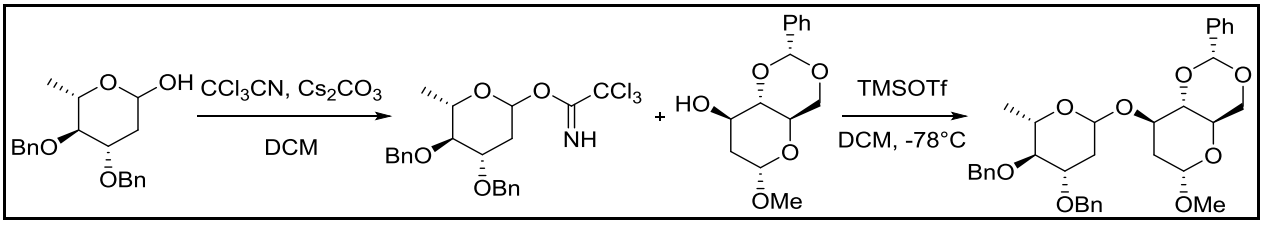
^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.27 (d, *J* = 6.5 Hz, 3H, H-C6), 3.70 (ddd, *J* = 4.3, 3.0, 1.2 Hz, 1H), 3.99 (td, *J* = 10.1, 3.0 Hz, 1H), 4.10-4.20 (m, 3H, Allyl), 4.27 (ddt, *J* = 13.0, 5.3, 1.6 Hz, 1H, Allyl), 4.43 (ddt, *J* = 12.6, 5.3, 1.4 Hz, 1H, Allyl), 5.04 (ddd, *J* = 49.3, 9.9, 3.8 Hz, 1H, H-C2), 5.17-5.26 (m, 2H, Allyl), 5.33 (dq, *J* = 17.2, 1.7 Hz, 1H, Allyl), 5.87-6.00 (m, 2H, Allyl), 6.53 (d, *J* = 3.8 Hz, 1H, C1), 8.62 (s, 1H, NH) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -209.99 (ddd, *J* = 49.3, 10.3, 4.3 Hz) ppm.

1-*O*-Isopropyl-2,6-dideoxy-2-fluoro-3,4-di-*O*-allyl-D-glucopyranose (**S47**) – Table 2, entry 7

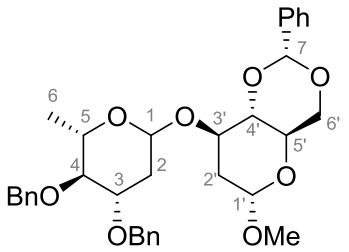


TMSOTf (3.0 µL, 6 µmol, 0.1 eq) was added to a solution of **S46** (22 mg, 0.06 mmol, 1 eq) and isopropanol (0.05 mL, 0.60 mmol, 10 eq) in dry DCM (1 mL) under an Ar atmosphere at -78°C. The reaction was allowed to progress for 2h at -78°C, and then slowly warmed up to room temperature. NEt_3 was added to quench the reaction, and the solvent was removed under vacuum. Purification by silica gel chromatography using a 3:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S47** as a colourless oil (14 mg, 88%, β only).

Colourless oil; [***m/z* (ESI)** found: 311.1628 $(M+Na)^+$, $C_{15}H_{25}FO_4Na$ requires 311.1629]; $[\alpha]_D^{25}$ = -4 (*c* 1.40 in $CHCl_3$) ν_{max} (neat)/cm^{-1} 2976w, 2875w, 1182m, 1065s, 1029s, 921m, 827w. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 1.18 (d, *J* = 6.1 Hz, 3H, H-C8), 1.25 (d, *J* = 6.3 Hz, 3H, H-C8), 1.28 (d, *J* = 6.4 Hz, 3H, H-C6), 3.44-3.56 (m, 3H, H-C3, H-C4, H-C5), 3.99 (hept, *J* = 6.1 Hz, H-C7), 4.10-4.17 (m, 2H, CH_2-Allyl), 4.22 (ddt, *J* = 13.1, 5.3, 1.8 Hz, 1H, CH_2-Allyl), 4.38 (ddt, *J* = 12.7, 5.3, 1.4 Hz, 1H, CH_2-Allyl), 4.41-4.47 (m, 1.5H, H-C1, H-C2), 4.57 (dd, *J* = 9.2, 7.6, Hz, 0.5H, H-C2), 5.16 (ddt, *J* = 10.3, 2.1, 1.2 Hz, 1H, CH_2-Allyl), 5.20 (dq, *J* = 10.5, 1.6 Hz, 1H, CH_2-Allyl), 5.23 (dq, J = 18.9, 1.6 Hz, 1H, CH_2-Allyl), 5.31 (dq, *J* = 17.2, 1.7 Hz, 1H, CH_2-Allyl), 5.87-5.97 (m, 2H, CH-Allyl) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 16.7 (CH_3, C6), 21.7 (CH_3, C8), 23.4 (CH_3, C8), 70.4 (CH, C5), 71.4 (CH, C7), 71.6 (d, $^4J_{CF}$ = 1.9 Hz, CH_2-Allyl), 74.1 (CH_2-Allyl), 76.8 (d, $^3J_{CF}$ = 9.0 Hz, CH, C4), 80.5 (d, $^2J_{CF}$ = 15.8 Hz, CH, C3), 91.5 (d, $^1J_{CF}$ = 182.6 Hz, CH, C2), 99.0 (d, $^2J_{CF}$ = 22.9 Hz, CH, C1), 117.0 (CH_2-Allyl), 117.3 (CH_2-Allyl), 134.7 (CH-Allyl), 135.4 (CH-Allyl) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -206.27 (m) ppm.



Methyl (2,6-dideoxy-3,4-di-*O*-benzyl-L-glucopyranosyl)-(1→3)- 2-deoxy-4,6-*O*-benzylidene-β-D-glucopyranoside (**S48**) – Table 3, entry 2

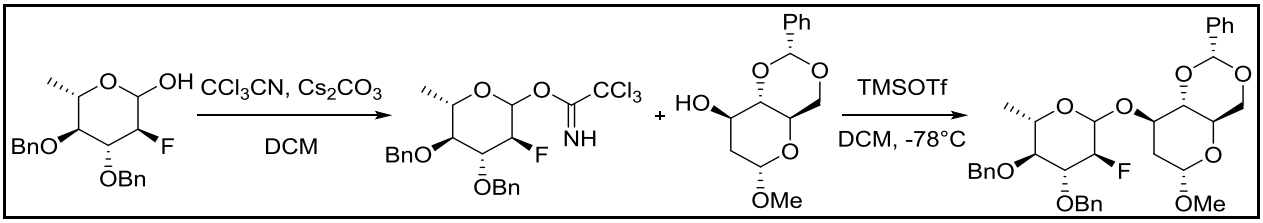


S25 (30 mg, 0.09 mmol, 1 eq) was dissolved in 1 mL of anh. DCM under an atmosphere of Ar. Cs_2CO_3 (6 mg, 0.02 mmol, 0.2 eq) was added in one portion, followed by Cl_3CCN (0.05 mL, 0.45 mmol, 5 eq). The

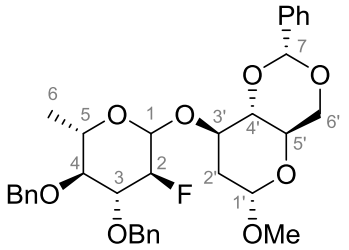
mixture was stirred at room temperature for 2h, filtered through a celite pad and used in the following step with no further purification.

A 0.1M solution of TMSOTf (0.09 mL, 9 µmol, 0.1 eq) was added to a solution of the previously prepared trichloroacetimidate donor and 1-Methoxy-2-deoxy-4,6-*O*-benzylidene-β-D-glucopyranoside (29 mg, 0.11 mmol, 1.2 eq) in dry DCM (2 mL) under an Ar atmosphere at -78°C. The reaction was allowed to progress for 2h at -78°C, and then NEt_3 was added to quench the reaction. The solvent was removed under vacuum. Purification by silica gel chromatography using a 7:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S48** as a colorless oil (39 mg, 75%, α:β = 3:1). Further separation of the anomers by preparative TLC using a 7:1 mixture of cyclohexane and ethyl acetate as eluent afforded a pure fraction of the α anomer, which was fully characterized.

Colourless oil; [***m/z* (ESI)** found: 599.2602 $(M+Na)^+$, $C_{34}H_{40}O_8Na$ requires 599.2621]; $[\alpha]_D^{25}$ = -50 (*c* 0.20 in $CHCl_3$). ν_{max} (neat)/cm^{-1} 2929m, 1855w, 1365m, 1208m, 1124s, 1094s, 1028s, 982s, 910s, 733s, 696s. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 1.04 (d, *J* = 6.2 Hz, 3H, H-C6), 1.66-1.72 (m, 2H, H-C2, H-C2'), 2.22 (dtd, *J* = 13.2, 5.0, 1.1 Hz, 2H, H-C2, H-C2'), 3.08 (t, *J* = 9.2 Hz, H-C4), 3.33 (s, 3H, OMe), 3.55 (t, *J* = 9.3 Hz, 1H, H-C4'), 3.76 (t, *J* = 10.2 Hz, 1H, H-C6'), 3.81 (dd, *J* = 9.5, 4.6 Hz, 1H, H-C5'), 3.95 (ddd, *J* = 11.4, 8.7, 5.1 Hz, 1H, H-C3), 4.10 (dq, *J* = 9.6, 6.2 Hz, 1H, H-C5), 4.18 (ddd, *J* = 11.1, 9.4, 5.2 Hz, 1H, H-C3'), 4.26 (dd, *J* = 9.9, 4.5 Hz, 1H, H-C6'), 4.60 (dd, *J* = 11.3, 2.1 Hz, 1H, CH_2Ph), 4.63 (d, *J* = 3.3 Hz, 2H, CH_2Ph), 4.80 (d, *J* = 3.5 Hz, 1H, H-C1'), 4.88 (d, *J* = 11.2 Hz, 1H, CH_2Ph), 4.95 (d, *J* = 3.5 Hz, 1H, H-C1), 5.58 (s, 1H, H-C7), 7.22-7.35 (m, 13H, Ph), 7.47-7.49 (m, 2H, Ph) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 17.8 (CH_3, C6), 35.6 (CH_2, C2'), 36.0 (CH_2, C2), 54.7 (CH_3, OMe), 63.2 (CH, C5'), 66.9 (CH, C5), 68.9 (CH, C3'), 69.1 (CH_2, C6'), 71.8 (CH_2, Bn), 74.6 (CH_2, Bn), 77.3 (CH, C3), 81.3 (CH, C4'), 84.5 (CH, C4), 94.2 (CH, C1), 99.0 (CH, C1'), 101.4 (CH, C7), 127.3 (CH, Ph), 127.4 (CH, Ph), 127.5 (CH, Ph), 127.6 (CH, Ph), 128.0 (CH, Ph), 128.2 (CH, Ph), 128.3 (CH, Ph), 128.3 (CH, Ph), 137.5 (C, Ph), 138.9 (C, Ph), 139.0 (C, Ph) ppm.



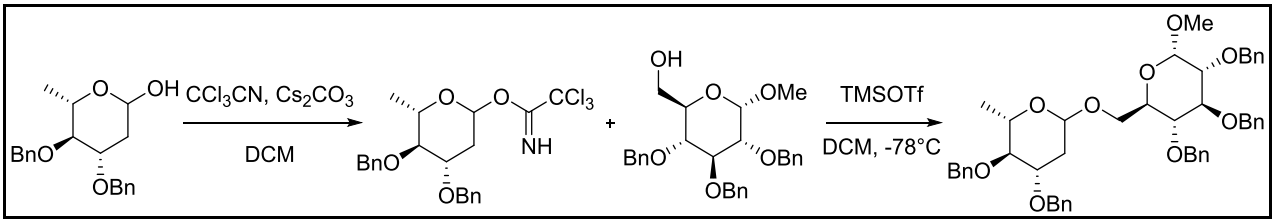
Methyl (2,6-dideoxy-2-fluoro-3,4-di-*O*-benzyl-L-glucopyranosyl)-(1→3)- 2-deoxy-4,6-*O*-benzylidene-β-D-glucopyranoside (**S49**) – Table 3, entry 1



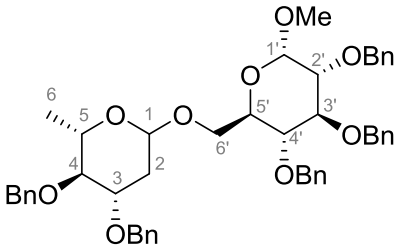
S17 (19 mg, 0.05 mmol, 1 eq) was dissolved in 1 mL of anh. DCM under an atmosphere of Ar. Cl_3CCN (0.05 mL, 0.50 mmol, 10 eq) was added, followed by DBU (0.7 µL, 5 µmol, 0.1 eq). The mixture was stirred at room temperature for 45 min, filtered through silica/NEt_3 using a 7:1 mixture of cyclohexane and ethyl acetate as eluent and used directly in the following step.

A 0.1M solution of TMSOTf (0.04 mL, 4 µmol, 0.1 eq) was added to a solution of the previously prepared trichloroacetimidate donor and 1-Methoxy-2-deoxy-4,6-*O*-benzylidene-β-D-glucopyranoside (13 mg, 0.05 mmol, 1.2 eq) in dry DCM (1 mL) under an Ar atmosphere at -78°C. The reaction was allowed to progress for 2h at -78°C, and then NEt_3 was added to quench the reaction. The solvent was removed under vacuum. Purification by silica gel chromatography using a 7:1 mixture of cyclohexane and ethyl acetate as eluent, afforded **S49** as a colourless oil (17 mg, 68%, α:β = 1:3.3). NOTE: the reaction was repeated for characterization purposes, and the purification was carried out with a 4:1 mixture of cyclohexane and ethyl acetate as eluent in silica/NEt_3. This quicker purification method afforded the final product as a mixture of α and β anomers, enriched in α product with regard to the crude.

Colourless oil; [***m/z* (ESI)** found: 617.2511 $(M+Na)^+$, $C_{34}H_{39}O_8FNa$ requires 617.2521]; $[\alpha]_D^{25}$ = +10 (*c* 0.20 in $CHCl_3$). ν_{max} (neat)/cm^{-1} 3372w, 3244w, 1694s, 1610w, 1454m, 1384m, 1358m, 1092s, 1072s, 1026s, 833s, 733s, 694s . **^{1}H NMR** (600 MHz, CD_2Cl_2) δ = 1.00 (d, *J* = 6.2 Hz, 3H, H-C6α), 1.28 (d, *J* = 6.1 Hz, 3H, H-C6β), 1.78 (ddd, *J* = 13.3, 11.2, 3.8 Hz, 1H, H-C2'α), 1.84 (ddd, *J* = 13.5, 11.3, 3.8 Hz, 1H, H-C2'β), 2.25 (dddd, *J* = 18.9, 13.3, 5.3, 1.2 Hz, 2H, H-C2'α, β), 3.09 (dd, *J* = 9.7, 8.8 Hz, 1H, H-C4α), 3.16 (t, *J* = 9.1 Hz, 1H, H-C4β), 3.34 (s, 3H, OMeα, β), 3.35-3.38 (m, 1H, H-C5β), 3.62-3.70 (m, 2H, H-C3β, H-C3'α, β), 3.74-3.83 (m, 3H, H-C6', H-C5', H-C4'α, β), 4.00 (dt, *J* = 12.4, 9.1 Hz, 1H, H-C3α), 4.11-4.16 (m, 1H, H-C5α), 4.18-4.28 (m, 2H, H-C2β, H-C6'α, β), 4.44 (ddd, *J* = 49.9, 9.3, 3.9 Hz, 1H, H-C2α), 4.57 (d, *J* = 11.1 Hz, 1H, Bn), 4.61 (d, *J* = 10.9 Hz, 1H, Bn), 4.73 (dd, *J* = 11.2, 2.4 Hz, 2H, Bn), 4.79-4.87 (m, 2H, H-C1β, H-C1'α, β), 4.98 (d, *J* = 3.9 Hz, 1H, H-C1α), 5.60 (s, 1H, H-C7α), 5.61 (s, 1H, H-C7β), 7.24-7.49 (m, 15H, Arα, β) ppm.**^{13}C NMR** (150 MHz, CD_2Cl_2) δ = 17.6 (CH_3, C6α), 17.6 (CH_3, C6β), 35.4 (CH_2, C2'α), 37.1 (CH_2, C2'β), 54.5 (CH_3, OMeα, β), 62.7 (CH, C4'β), 63.2 (CH, C4'α), 66.3 (CH, C5α), 69.0 (CH_2, C6'α, β), 70.4 (CH, C5'α, β), 71.1 (CH, C5β), 74.6 (d, $^4J_{CF}$ = 2.6 Hz, CH_2, Bnβ), 74.7 (d, $^4J_{CF}$ = 2.2 Hz, CH_2, Bnα), 74.8 (CH_2, Bnα), 75.1 (CH_2, Bnβ), 80.3 (d, $^2J_{CF}$ = 16.1 Hz, CH, C3α), 81.2 (CH, C3'α, β), 82.6 (d, $^3J_{CF}$ = 8.1 Hz, CH, C4β), 83.1 (m, 2xCH, C3β, C4α), 91.4 (d, $^1J_{CF}$ = 191.3 Hz, CH, C2α), 93.7 (d, $^1J_{CF}$ = 187.7 Hz, CH, C2β), 93.7 (d, $^2J_{CF}$ = 20.6 Hz, CH, C1α), 98.9 (CH, C1'α, β), 100.3 (d, $^2J_{CF}$ = 22.6 Hz, CH, C1β), 101.1 (CH, C7β), 101.4 (CH, C7α), 125.9 (CH, Ph), 126.0 (CH, Ph), 127.4 (CH, Ph), 127.5 (CH, Ph), 127.6(CH, Ph), 127.7 (CH, Ph), 127.7 (CH, Ph), 127.8 (CH, Ph), 127.9 (CH, Ph), 128.0 (CH, Ph), 128.1 (CH, Ph), 128.2 (CH, Ph), 128.2 (CH, Ph), 128.2 (CH, Ph), 137.8 (C, Phα), 137.8 (C, Phβ), 138.3 (C, Phβ), 138.4(C, Phβ), 138.6 (C, Phα), 138.8 (C, Phα) ppm. . **^{19}F NMR** (564 MHz, $CDCl_3$) δ = -195.64 (ddd, *J* = 51.0, 15.0, 1.9 Hz) β-anomer), -198.90 (dd, *J* = 49.8, 12.4 Hz, α-anomer) ppm.



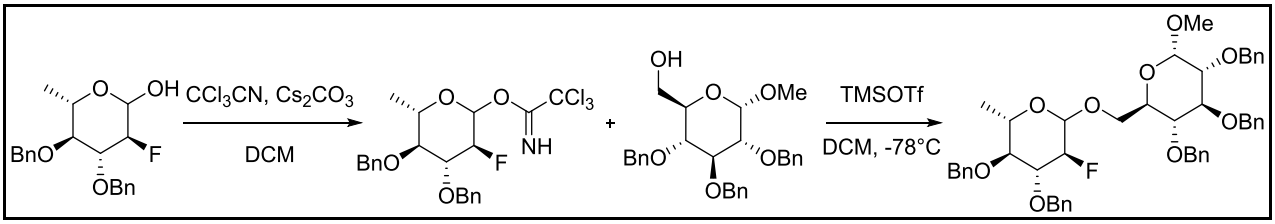
Methyl (2,6-dideoxy-3,4-di-*O*-benzyl-L-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-β-D-glucopyranoside (**S50**) – Table 3, entry 4



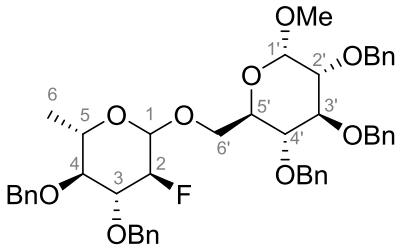
S25 (50 mg, 0.15 mmol, 1 eq) was dissolved in 3 mL of anh. DCM under an atmosphere of Ar. Cs_2CO_3 (10 mg, 0.03 mmol, 0.2 eq) was added in one portion, followed by Cl_3CCN (0.08 mL, 0.75 mmol, 5 eq). The mixture was stirred at room temperature for 2.5h, filtered through a celite pad and used in the following step with no further purification.

A 0.1M solution of TMSOTf (0.15 mL, 15 µmol, 0.1 eq) was added to a solution of the previously prepared trichloroacetimidate donor and 1-Methoxy-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (105 mg, 0.23 mmol, 1.5 eq) in dry DCM (3 mL) under an Ar atmosphere at -78°C. The reaction was allowed to progress for 2.5h at -78°C, and then allowed to reach room temperature and quenched with NEt_3. The solvent was removed under vacuum. Purification by silica gel chromatography using a mixture of cyclohexane and ethyl acetate as eluent (9:1→3:1), afforded **S50** as a colorless oil (71 mg, 61%, α:β = 3.4:1). Further separation of the anomers by silica gel chromatography using a 7:1 mixture of cyclohexane and ethyl acetate as eluent afforded a pure fraction of the α anomer, which was fully characterized.

Colorless oil; [***m/z* (ESI)** found: 797.3639 $(M+Na)^+$, $C_{48}H_{54}O_9Na$ requires 797.3660]; $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = -5 (*c* 0.50 in $CHCl_3$) $\boldsymbol{\nu_{max}}$ (neat)/cm^{-1} 3035w, 2908w, 2854w, 1454w, 1396w, 1134w, 1064s, 1020, 740s. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 1.24 (d, *J* = 6.2 Hz, 3H, H-C6), 1.61 (m, 1H, H-C2), 2.19 (ddd, *J* = 12.9, 5.1, 1.4 Hz, 1H, H-C2), 2.39 (ddd, *J* = 12.5, 5.1, 1.9 Hz, 0.3H, H-C2β), 3.11 (td, *J* = 9.0, 2.7 Hz, 1H, H-C4), 3.34 (s, 3H, OMe), 3.36 (s, 1H, OMeβ), 3.43 (t, *J* = 5.4 Hz, 1H, H-C6'), 3.45 (m, 1H, H-C4'), 3.51 (dd, *J* = 9.6, 3.5 Hz, 1H, H-C2'), 3.58-3.65 (m, 0.6H, H-C4β, H-C5β), 3.70-3.74 (m, 2H, H-C5, H-C5'), 3.79 (dd, *J* = 10.8, 1.8 Hz, 1H, H-C6'), 3.90 (ddd, *J* = 11.4, 8.8, 5.0 Hz, 1H, H-C3), 3.97 (td, *J* = 9.3, 7.0 Hz, 1H, H-C3'), 4.20 (dd, *J* = 11.1, 3.5 Hz, 0.3H, H-C3β), 4.47 (dd, *J* = 9.8, 1.9 Hz, 0.3H, H-C1β), 4.53 (d, *J* = 11.1 Hz, 1H, Bn), 4.59 (d, *J* = 3.6 Hz, 1H, H-C1'), 4.62 (s, 2H, Bn), 4.65 (d, *J* = 10.8 Hz, 1H, Bn), 4.68 (d, *J* = 12.1 Hz, 1H, Bn), 4.73 (dd, *J* = 3.7, 1.2 Hz, 1H, H-C1), 4.80 (t, *J* = 10.5 Hz, 2H, Bn), 4.87 (d, *J* = 10.9 Hz, 1H, Bn), 4.93 (d, *J* = 10.9 Hz, 1H, Bn), 4.98 (d, *J* = 10.8 Hz, 1H, Bn), 7.24-7.38 (m, 25H, Ar) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 18.1 (CH_3, C6), 35.8 (CH_2, C2), 55.0 (CH_3, OMe), 65.8 (CH_2, C6'), 67.2 (CH, C5'), 69.9 (CH, C5), 71.8 (CH_2, Bn), 73.3 (CH_2, Bn), 74.9 (CH_2, Bn), 75.2 (CH_2, Bn), 75.8 (CH_2, Bn), 77.8 (CH, C4'), 80.0 (CH, C2'), 82.1 (CH, C3'), 84.3 (CH, C4), 97.3 (CH, C1), 97.8 (CH, C1), 127.5 (CH, Ph), 127.6 (CH, Ph), 127.7 (CH, Ph), 127.7 (CH, Ph), 127.9 (CH, Ph), 128.0 (CH, Ph), 128.1 (CH, Ph), 128.3 (CH, Ph), 128.4 (CH, Ph), 128.5 (CH, Ph), 138.1 (C, Ph), 138.2 (C, Ph), 138.5 (C, Ph), 138.6 (C, Ph), 138.7 (C, Ph) ppm.



Methyl (2,6-dideoxy-2-fluoro-3,4-di-*O*-benzyl-L-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-β-D-glucopyranoside (**S51**) – Table 3, entry 4



S17 (90 mg, 0.26 mmol, 1 eq) was dissolved in 5 mL of anh. DCM under an atmosphere of Ar. Cl_3CCN (0.26 mL, 2.60 mmol, 10 eq) was added, followed by DBU (4 µL, 26 µmol, 0.1 eq). The mixture was stirred at room temperature for 45 min, filtered through silica/NEt_3 using a 7:1 mixture of cyclohexane and ethyl acetate as eluent and used directly in the following step.

A 0.1M solution of TMSOTf (0.12 mL, 12 µmol, 0.1 eq) was added to a solution of the previously prepared trichloroacetimidate donor and 1-Methoxy-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (84 mg, 0.18 mmol, 1.5 eq) in dry DCM (2.5 mL) under an Ar atmosphere at -78°C. The reaction was allowed to progress for 1h at -78°C, and then NEt_3 was added to quench the reaction. The solvent was removed under vacuum. Purification by silica gel chromatography using a mixture of cyclohexane and ethyl acetate as eluent (7:1→3:1), afforded **X** as a colourless oil (65 mg, 68%, α:β = 1:3.2). Further separation of the anomers by silica gel chromatography using a 7:1 mixture of cyclohexane and ethyl acetate as eluent afforded a pure fraction of the β anomer, which was fully characterized.

Colorless oil; [***m/z* (ESI)** found: 815.3599 $(M+Na)^+$, $C_{48}H_{53}O_9FNa$ requires 815.3566]; $[\alpha]_D^{25}$ = +13 (*c* 0.40 in $CHCl_3$). ν_{max} (neat)/cm^{-1} 3032w, 2909w, 1497w, 1358w, 1065s, 1011s, 910w, 737s, 694s. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 1.26 (d, *J* = 6.1 Hz, 3H, H-C6), 3.18 (t, *J* = 9.1 Hz, 1H, H-C4), 3.38 (s, 3H, OMe), 3.38-3.41 (m, 2H, H-C5), 3.55 (dd, *J* = 9.7, 3.5 Hz, 1H, H-C2'), 3.62 (dd, *J* = 9.9, 9.0 Hz, 1H, H-C4'), 3.70-3.76 (m, 2H, H-C3, H-C5'), 3.78 (m, 1H, H-C6'), 3.99 (t, *J* = 9.3 Hz, 1H, H-C3'), 4.10 (dd, *J* = 11.3, 4.1 Hz, 1H, H-C6'), 4.33 (ddd, *J* = 51.0, 8.6, 7.8 Hz, 1H, H-C2), 4.54 (dd, *J* = 7.8, 2.9 Hz, 1H, H-C1), 4.62 (d, *J* = 17.3 Hz, 1H, Bn), 4.63 (d, *J* = 2.8 Hz, 1H, H-C1), 4.67 (d, *J* = 12.1 Hz, 1H, Bn), 4.69 (d, *J* = 10.7 Hz, 1H, Bn), 4.73 (d, *J* = 11.2 Hz, 1H, Bn), 4.80 (d, *J* = 12.1 Hz, 1H, Bn), 4.84 (d, *J* = 11.0 Hz, 1H, Bn), 4.86-4.90 (m, 3H, Bn), 4.98 (d, *J* = 10.9 Hz, 1H, Bn), 7.27-7.37 (m, 20H, Ar) ppm.**^{13}C NMR** (150 MHz, $CDCl_3$) δ = 17.7 (CH_3, C6), 55.1 (CH_3, OMe), 67.3 (CH_2, C6'), 70.0 (CH, C5'), 71.3 (CH, C5), 73.4 (CH_2, Bn), 74.8 (d, $^4J_{CF}$ = 2.8 Hz, CH_2, Bn), 75.0 (CH_2, Bn), 75.4 (CH_2, Bn), 75.7 (CH_2, Bn), 77.5 (CH, C4'), 79.9 (CH, C2'), 82.0 (CH, C3'), 82.5 (d, $^3J_{CF}$ = 8.3 Hz, CH, C4), 83.2 (d, $^2J_{CF}$ = 16.1 Hz, CH, C3), 93.5 (d, $^1J_{CF}$ = 187.6 Hz, CH, C2), 98.1 (CH, C1'), 99.9 (d, $^2J_{CF}$ = 23.2 Hz, CH, C1), 127.5 (CH, Ph), 127.6 (CH, Ph), 127.7 (CH, Ph), 127.8 (CH, Ph), 127.9 (CH, Ph), 128.0 (CH, Ph), 128.0 (CH, Ph), 128.0 (CH, Ph), 128.1 (CH, Ph), 128.3 (CH, Ph), 128.4 (CH, Ph), 128.4 (CH, Ph), 128.4 (CH, Ph), 128.4 (CH, Ph), 137.9 (C, Ph), 138.1 (CH, Ph), 138.2 (CH, Ph), 138.4 (CH, Ph), 138.8 (CH, Ph) ppm. **^{19}F NMR** (564 MHz, $CDCl_3$) δ = -194.76 (ddd, *J* = 51.4, 15.7, 2.6 Hz, β-anomer), -198.33 (dd, *J* = 49.7, 12.0 Hz, α-anomer) ppm.

Computational section:

Methods and References:

To visualize the ESP maps and compute the Mulliken atomic charges, first the energetic minima conformers of the molecules had to be identified. Conformational searches were performed using the OPLS-2005 force field in MacroModel 10.0.[S1] All structures within 5 kcal/mol of the energetic minimum were subsequently optimized using Gaussian09[S2] at the M062X[S3]/6-31+G(d,p) level of theory. Solvation by dichloromethane was taken into account using the integral equation formalism polarizable continuum model (IEF-PCM)[S4] using Truhlar's SMD solvation model.[S5] All optimized geometries were verified by frequency calculations as minima (zero imaginary frequency). Entropic corrections to the free energies were calculated using Truhlar's quasi-harmonic approximation (vibrational frequencies lower than 100 cm^{-1} are set equal to 100 cm^{-1} to correct for the breakdown of the harmonic oscillator approximation for low frequencies).[S6] GaussView 5.0[S7] was used to generate input and visualize output structures and to render the ESP maps. CYLview[S8] was used to render the computed structures.

(S1) *MacroModel*, version 10.6, Schrödinger, LLC, New York, NY, **2014**.

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(S6) (a) R. F. Ribeiro, A. V. Marenich, C. J. Cramer, and D. G. Truhlar, *J. Phys. Chem. B* **2011**, *115*, 14556. (b) Y. Zhao, and D. G. Truhlar, *Phys. Chem. Chem. Phys.* **2008**, *10*, 2813.

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(S8) C. Y. Legault, *CYLview*, version 1.0b, Université de Sherbrooke, Sherbrooke, Québec, Canada, **2009**.

Coordinates and energies of conformers in Figure 2:

Upper Left:

C	-1.79370	-0.66349	0.54286
C	-0.63196	-1.64759	0.63606
C	-0.78768	0.20763	-1.56222
C	-1.37537	0.59668	-0.22140
H	0.15218	-1.17451	1.24223
H	-2.13197	-0.39555	1.54700
H	-1.54619	-0.22979	-2.21789
H	-0.63665	1.15294	0.36482
C	0.33865	-0.80447	-1.37266
O	-0.10207	-1.92171	-0.67631
C	-1.02139	-2.97942	1.23819
H	-1.42389	-2.82861	2.24371
H	-0.14267	-3.62509	1.30702
O	-2.85784	-1.29636	-0.17757
O	-2.50994	1.41815	-0.48531
F	-0.27526	1.33255	-2.19223
H	0.72711	-1.14721	-2.33667
H	-1.77842	-3.47142	0.62260
C	-4.12764	-1.02473	0.19383
O	-4.40597	-0.29563	1.11904
C	-5.10836	-1.73580	-0.68738
H	-6.11651	-1.59601	-0.30016
H	-5.03874	-1.32622	-1.69950
H	-4.86317	-2.79945	-0.73718
C	-2.93692	2.20631	0.53138
O	-2.34874	2.28364	1.58448
C	-4.19465	2.92816	0.16312
H	-4.06153	3.45545	-0.78452
H	-4.99438	2.19272	0.03507
H	-4.45937	3.62792	0.95439
O	1.36747	-0.11117	-0.66365
C	2.53962	-0.74557	-0.46765
C	3.50708	0.23191	0.22035
Cl	2.77046	0.75421	1.76336
Cl	3.73830	1.65065	-0.83828
Cl	5.07161	-0.51924	0.54430
N	2.88652	-1.92135	-0.74578
H	2.13022	-2.46724	-1.16226

SCF energy: -2452.409083 hartree
zero-point correction: +0.279918 hartree
enthalpy correction: +0.304899 hartree
free energy correction: +0.223193 hartree
quasiharmonic free energy correction: +0.229334 hartree

Upper right:

C	-1.81631	-0.54519	0.50264
C	-0.63683	-1.49108	0.70826
C	-0.79998	0.13560	-1.68040
C	-1.39471	0.63308	-0.37323
H	0.13013	-0.93737	1.26795
H	-2.17895	-0.19368	1.47162
H	-1.56759	-0.37844	-2.26634
H	-0.67232	1.23918	0.18253
C	0.30988	-0.85957	-1.39432
O	-0.08578	-1.89836	-0.55605
C	-1.00789	-2.75420	1.45369
H	-1.43260	-2.49808	2.42860
H	-0.11809	-3.36846	1.61205
O	-2.85657	-1.27111	-0.16690
O	-2.53261	1.43595	-0.70523
H	0.68874	-1.32362	-2.31027
H	-1.74322	-3.33114	0.88701
C	-4.13488	-0.98460	0.14806
O	-4.44809	-0.17072	0.98885
C	-5.08894	-1.79126	-0.68015
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C	2.53018	-0.72951	-0.51598
C	3.50537	0.28919	0.10079
Cl	5.08093	-0.43256	0.44143
Cl	2.78170	0.87966	1.62671
Cl	3.71762	1.66072	-1.02146
N	2.86259	-1.93380	-0.66584
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SCF energy: -2353.202843 hartree
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enthalpy correction: +0.311898 hartree
free energy correction: +0.231347 hartree
quasiharmonic free energy correction: +0.238096 hartree

Lower left:

C	1.82388	0.90857	-0.57107
C	0.56917	1.77140	-0.74586
C	0.61409	-0.92523	-1.75382
C	1.47462	-0.58210	-0.55046
H	-0.06631	1.64903	0.14186
H	2.54051	1.10936	-1.37559
H	1.19707	-0.85436	-2.67732
H	0.94968	-0.83276	0.37793
C	-0.58082	0.01089	-1.86553
O	-0.15390	1.33288	-1.90812
C	0.89510	3.23278	-0.95820
H	1.44422	3.62203	-0.09748
H	-0.02791	3.80697	-1.07028
O	2.37846	1.29911	0.68601
O	2.64795	-1.38632	-0.68074
F	0.16047	-2.23020	-1.63549
H	-1.15342	-0.18002	-2.77863
H	1.50544	3.35907	-1.85776
C	3.71762	1.25218	0.85367
O	4.48145	0.90807	-0.01945
C	4.09613	1.66844	2.24096
H	3.66406	2.64628	2.46795
H	3.68520	0.94423	2.95037
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C	3.27454	-1.80752	0.43941
O	2.88419	-1.54297	1.55368
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H	4.22007	-3.43677	-0.56437
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H	4.93925	-2.99791	1.01598
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C	-2.58430	0.38095	-0.63885
C	-3.33880	-0.17399	0.58133
Cl	-4.88441	0.64767	0.81620
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N	-3.08408	1.27761	-1.36406
H	-2.45921	1.57086	-2.11671

SCF energy: -2452.406541 hartree
zero-point correction: +0.279741 hartree
enthalpy correction: +0.304827 hartree
free energy correction: +0.221966 hartree
quasiharmonic free energy correction: +0.229095 hartree

Lower right:

C	-1.83638	-0.92311	-0.43733
C	-0.58294	-1.80343	-0.36747
C	-0.60743	0.56826	-2.01964
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H	0.03287	-1.46290	0.47745
H	-2.53507	-1.31095	-1.18738
H	-1.20001	0.24951	-2.88348
H	-0.96120	0.97309	0.09166
C	0.56805	-0.37982	-1.89788
O	0.17237	-1.67790	-1.57954
C	-0.91446	-3.27131	-0.20885
H	-1.48613	-3.43066	0.70852
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O	-2.42032	-1.00848	0.86714
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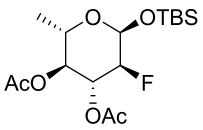
C	-4.16330	-0.99959	2.43555
H	-5.24869	-0.96036	2.51533
H	-3.78462	-1.92336	2.88103
H	-3.71544	-0.15813	2.97144
C	-3.28523	1.93282	-0.07794
O	-2.89728	1.94101	1.06963
C	-4.51710	2.61699	-0.58713
H	-4.95915	3.21606	0.20779
H	-4.27040	3.24511	-1.44636
H	-5.22897	1.85530	-0.91870
O	1.41847	0.16473	-0.87227
C	2.58140	-0.45680	-0.61122
C	3.34891	0.36795	0.43697
Cl	2.31427	0.56622	1.88015
Cl	3.70797	1.97412	-0.25794
Cl	4.86092	-0.41608	0.90797
N	3.06393	-1.52085	-1.07795
H	2.43206	-1.97539	-1.73878
H	-0.25088	1.58562	-2.19934

SCF energy: -2353.200593 hartree
zero-point correction: +0.287629 hartree
enthalpy correction: +0.311827 hartree
free energy correction: +0.232372 hartree
quasiharmonic free energy correction: +0.237580 hartree

Spectra: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F
OAc

S2

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5.98
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
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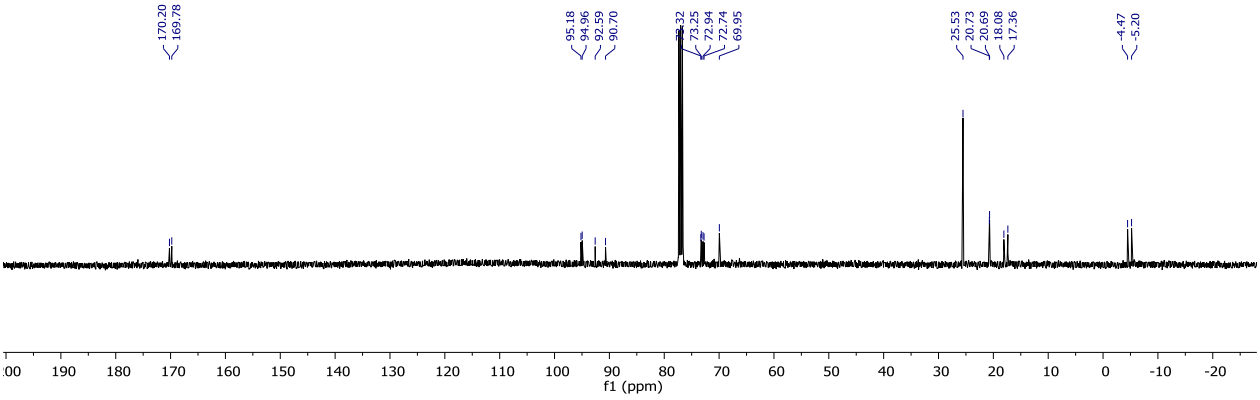
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20.73
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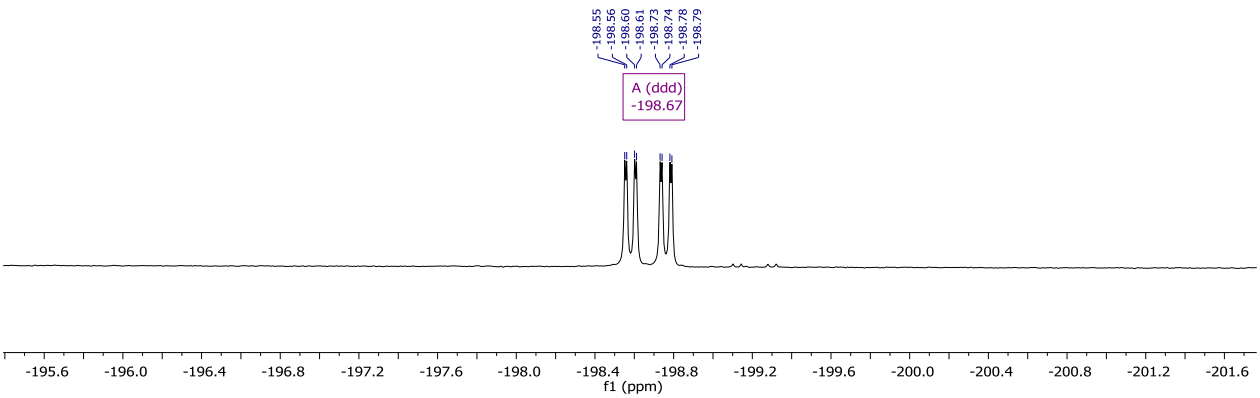
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A (ddd)
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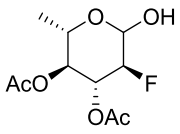
f1 (ppm)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F
OAc

S4

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2.59
1.49
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2.81
8.0
7.5
7.0
6.5
6.0
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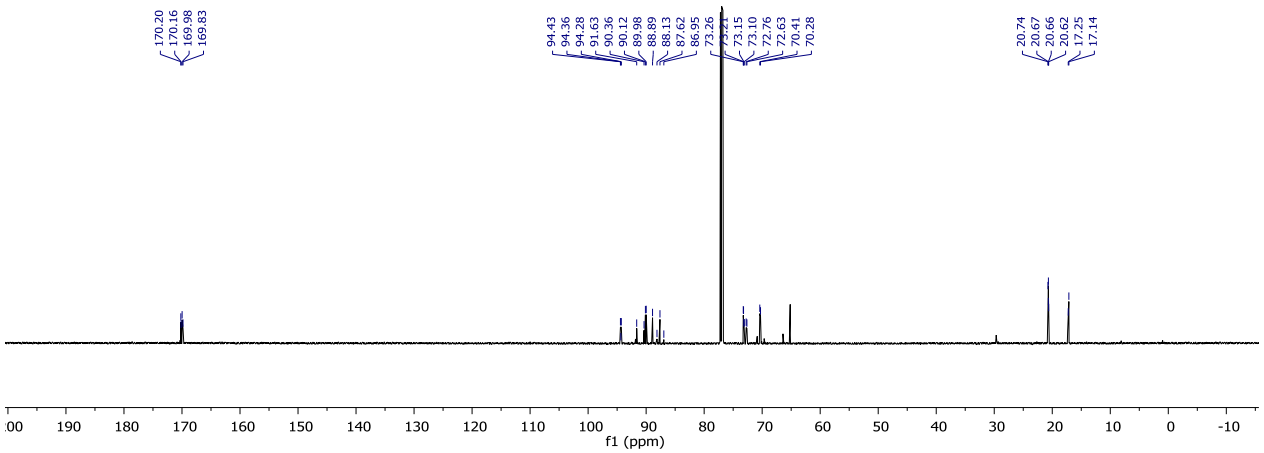
f1 (ppm)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17.14
190
180
170
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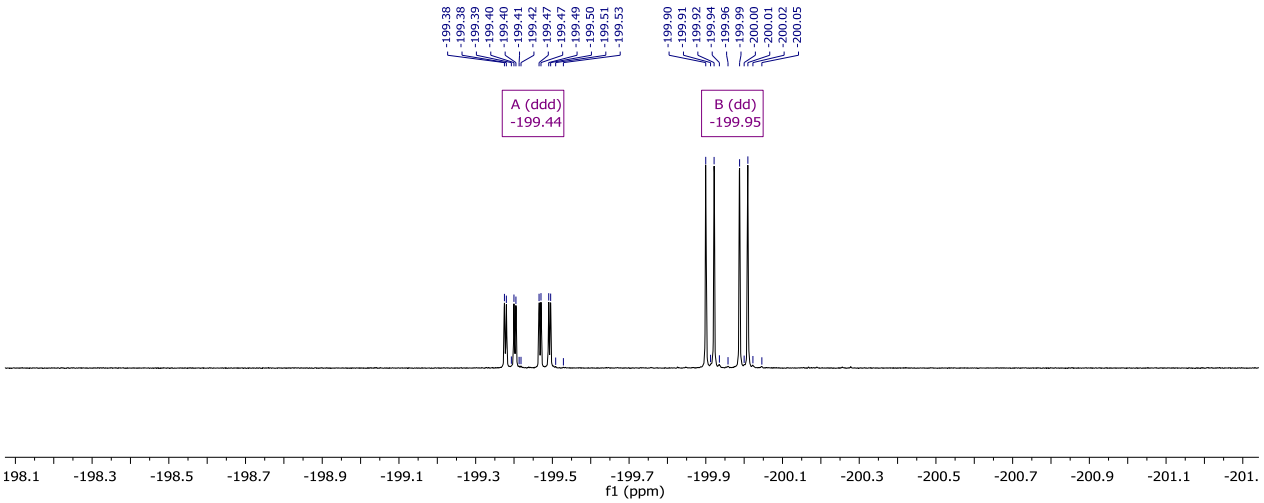
f1 (ppm)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A (ddd)
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B (dd)
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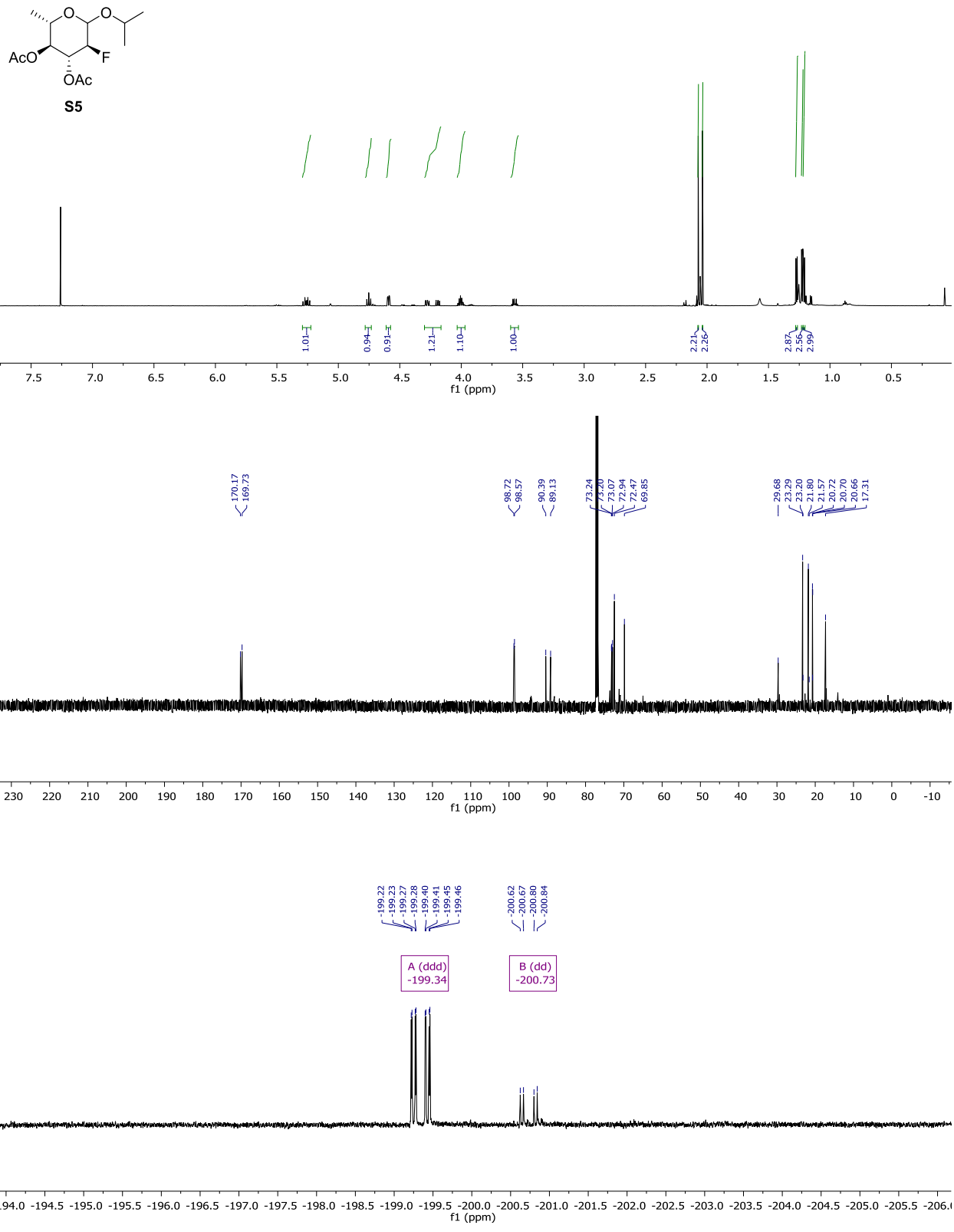
f1 (ppm)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2.99
f1 (ppm)
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98.72
98.57
90.39
89.13
73.24
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73.07
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72.47
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29.68
23.29
23.20
21.80
21.57
20.72
20.70
20.66
17.31
f1 (ppm)
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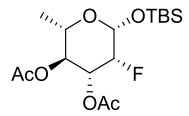
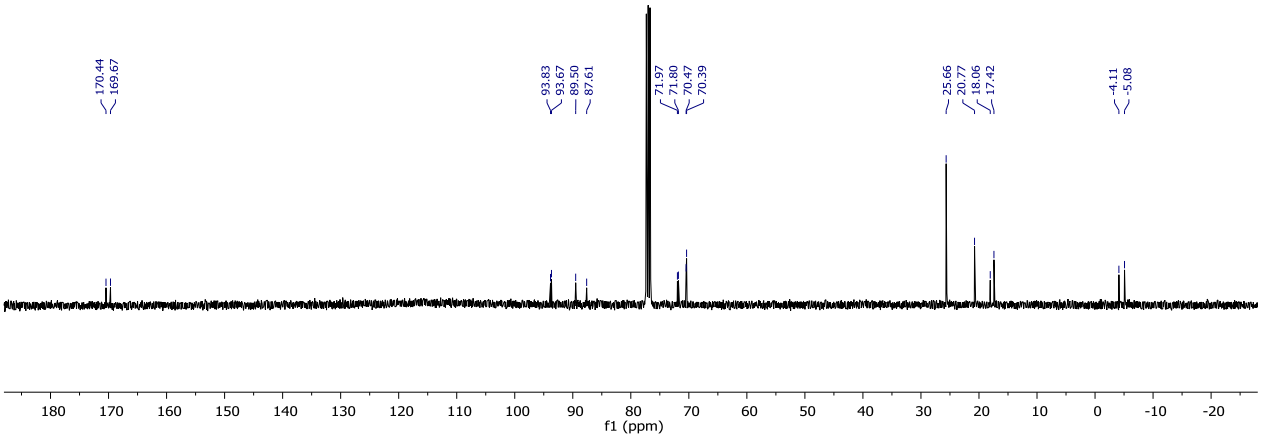
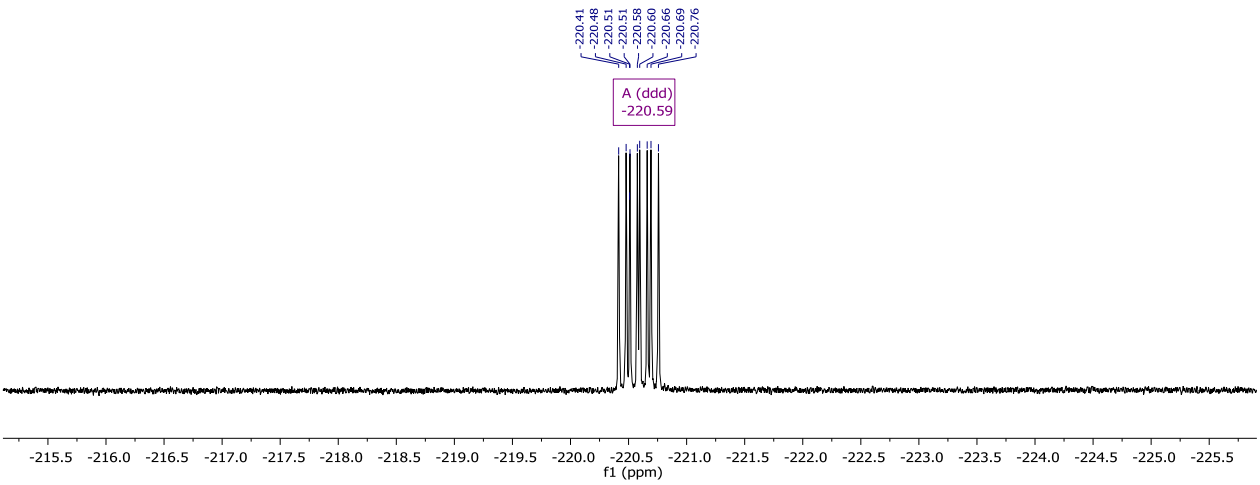
-199.46
-200.62
-200.67
-200.80
-200.84
A (ddd)
-199.34
B (dd)
-200.73
f1 (ppm)

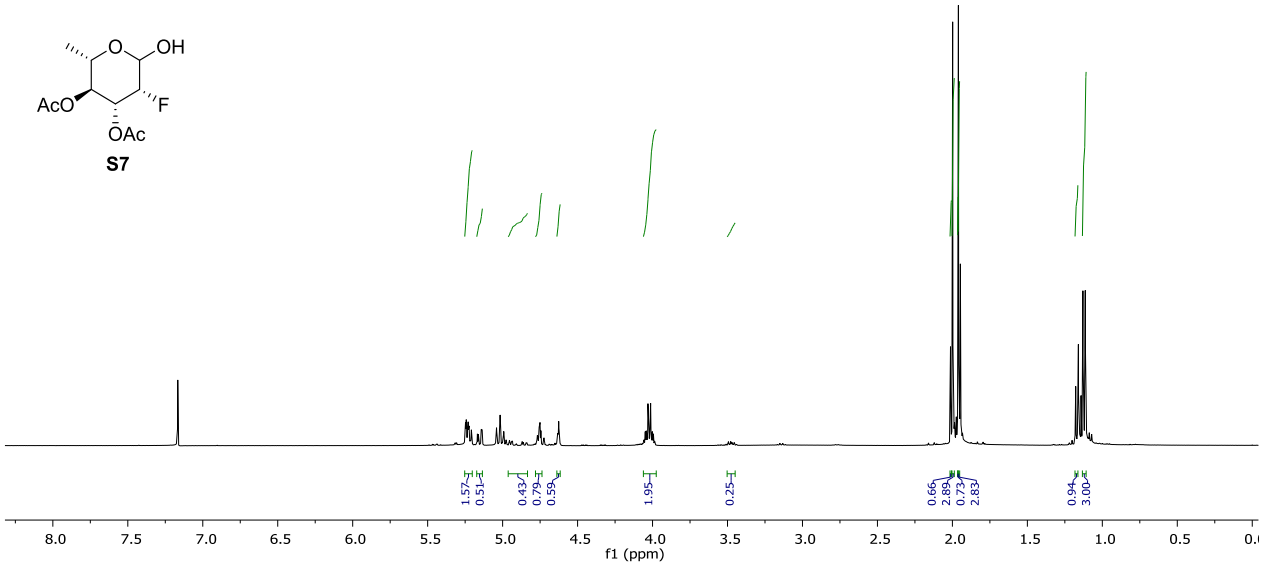

O
OTBS
AcO
F
OAc

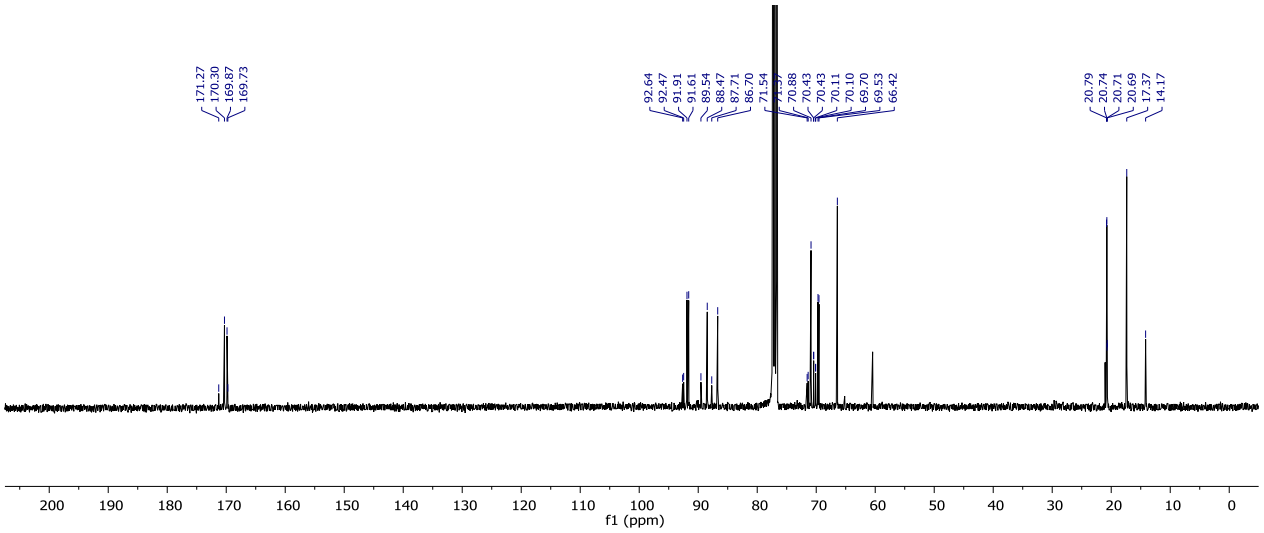
S3

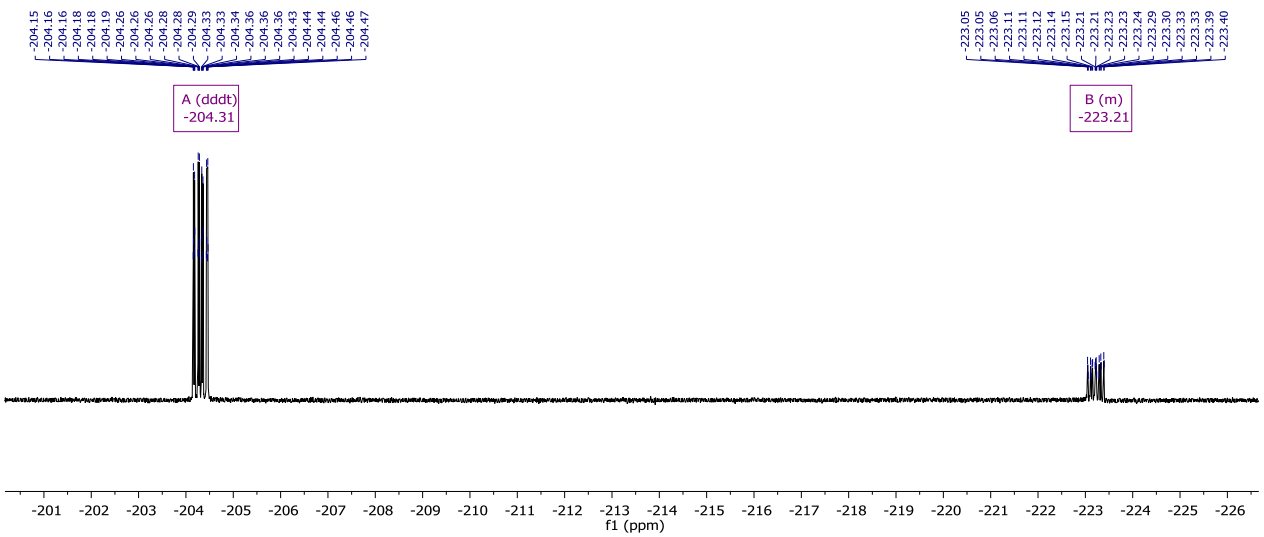
0.88
0.93
0.92
0.95
0.91
2.62
2.92
3.00
8.81
2.88
2.78
f1 (ppm)

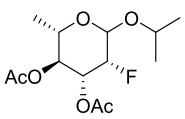

170.44
169.67
93.83
93.67
89.50
87.61
71.97
71.80
70.47
70.39
25.66
20.77
18.06
17.42
-4.11
-5.08
f1 (ppm)


-220.41
-220.48
-220.51
-220.51
-220.58
-220.60
-220.66
-220.69
-220.76
A (ddd)
-220.59
f1 (ppm)


OH
O
AcO
F
OAc
S7
1.57
0.51
0.43
0.79
0.59
1.95
0.25
0.66
2.89
0.73
2.83
0.94
3.00
f1 (ppm)

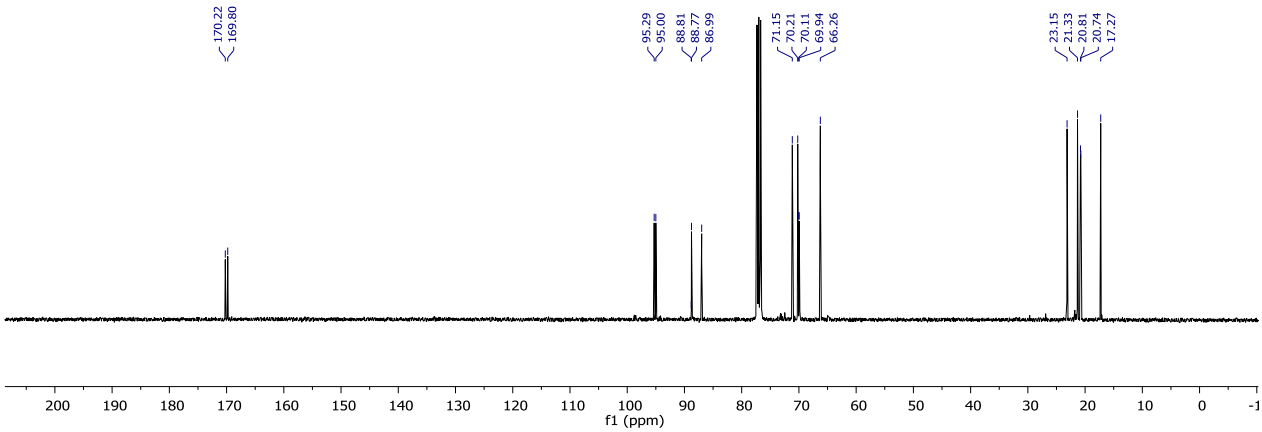

171.27
170.30
169.87
169.73
92.64
92.47
91.91
91.61
89.54
88.47
87.71
86.70
71.54
70.88
70.43
70.43
70.11
70.10
69.70
69.53
66.42
20.79
20.74
20.71
20.69
17.37
14.17
f1 (ppm)

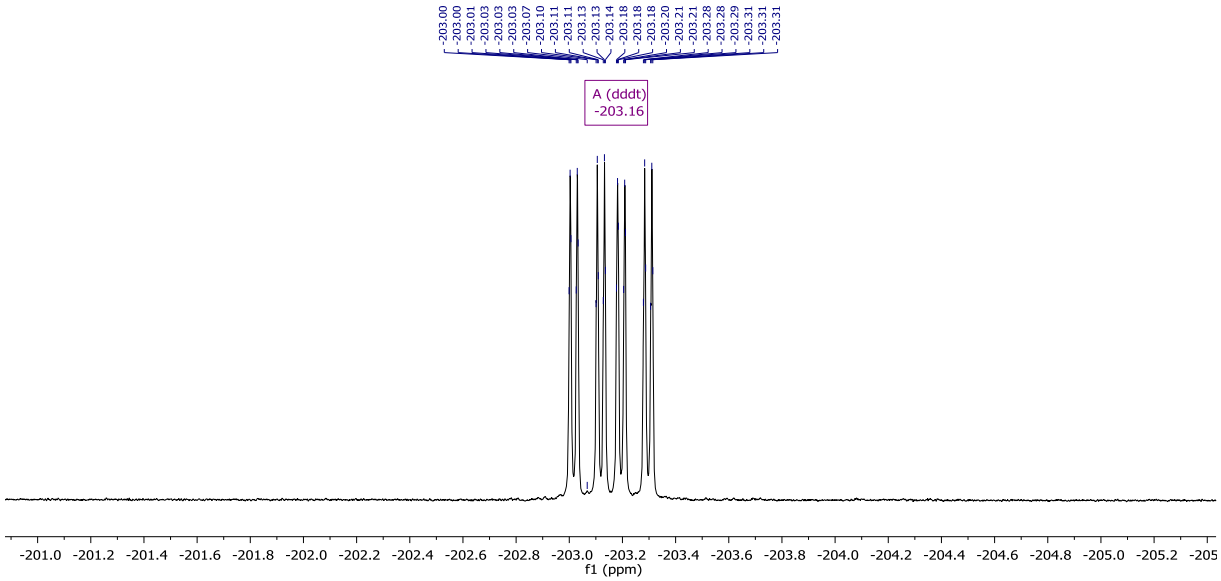

A (dddt)
-204.31
B (m)
-223.21
f1 (ppm)

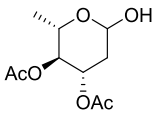

AcO
O
O
F
OAc

S9

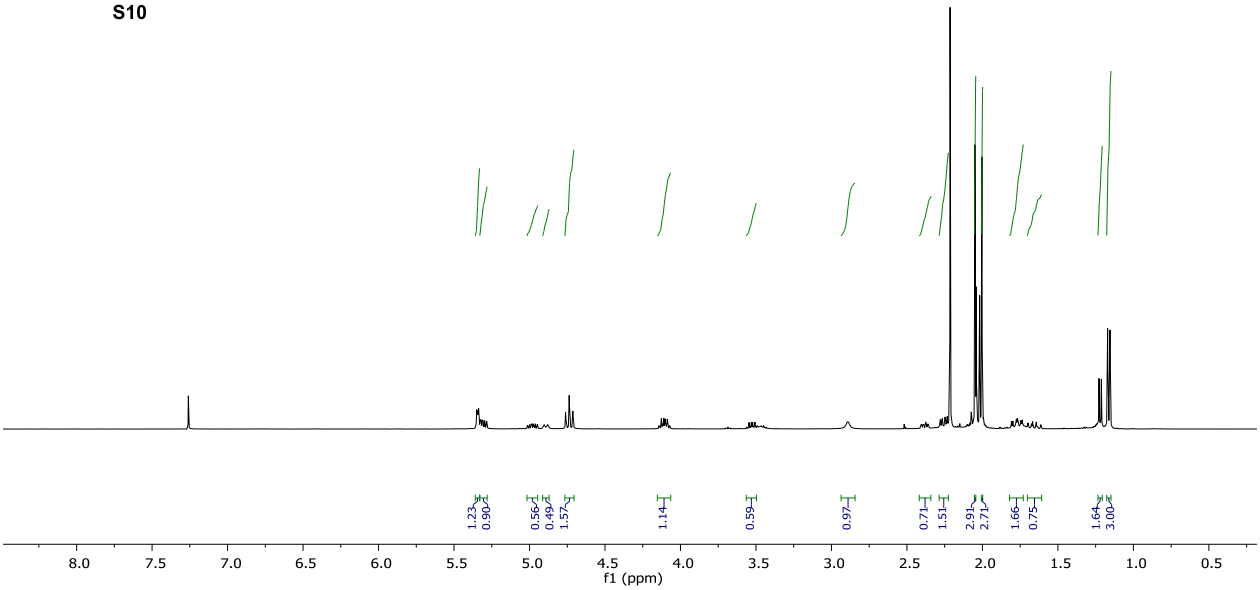
1.05
1.00
0.95
1.05
1.94
2.81
2.93
6.15
3.00
f1 (ppm)

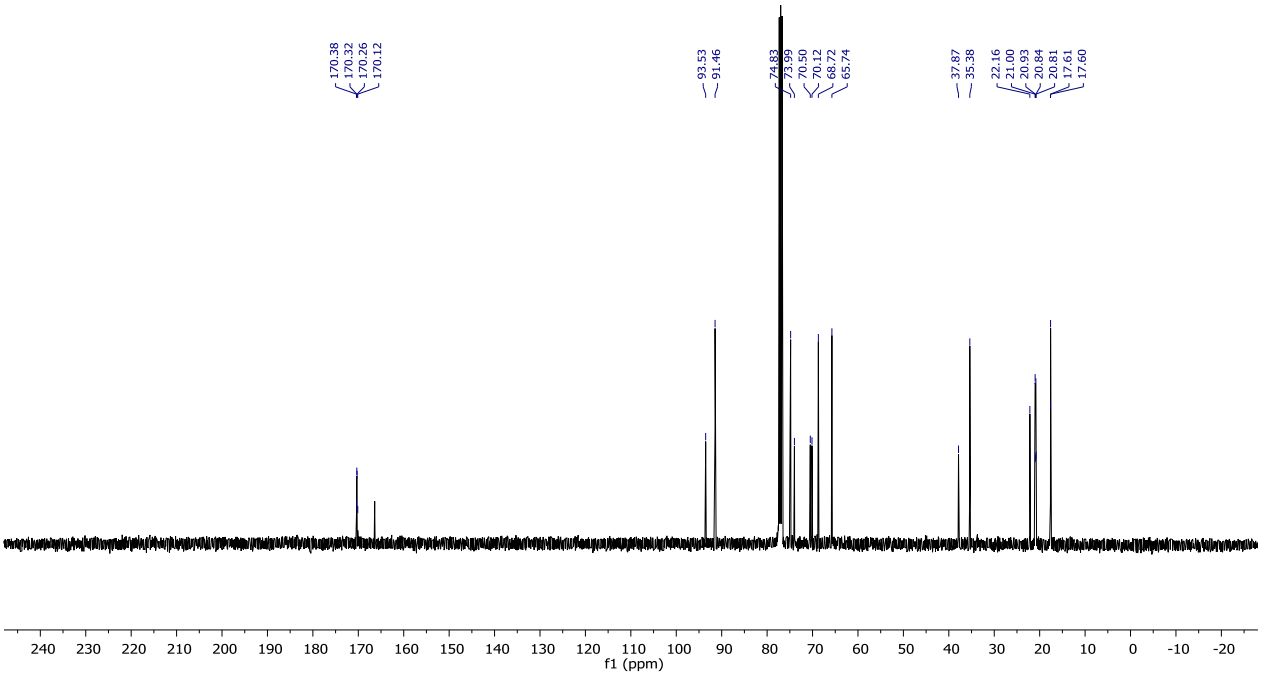

170.22
169.80
95.29
95.00
88.81
88.77
86.99
71.15
70.21
70.11
69.94
66.26
23.15
21.33
20.81
20.74
17.27
f1 (ppm)

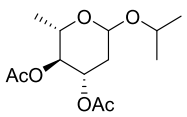

A (dddt)
-203.16
f1 (ppm)


O
OH
AcO
OAc

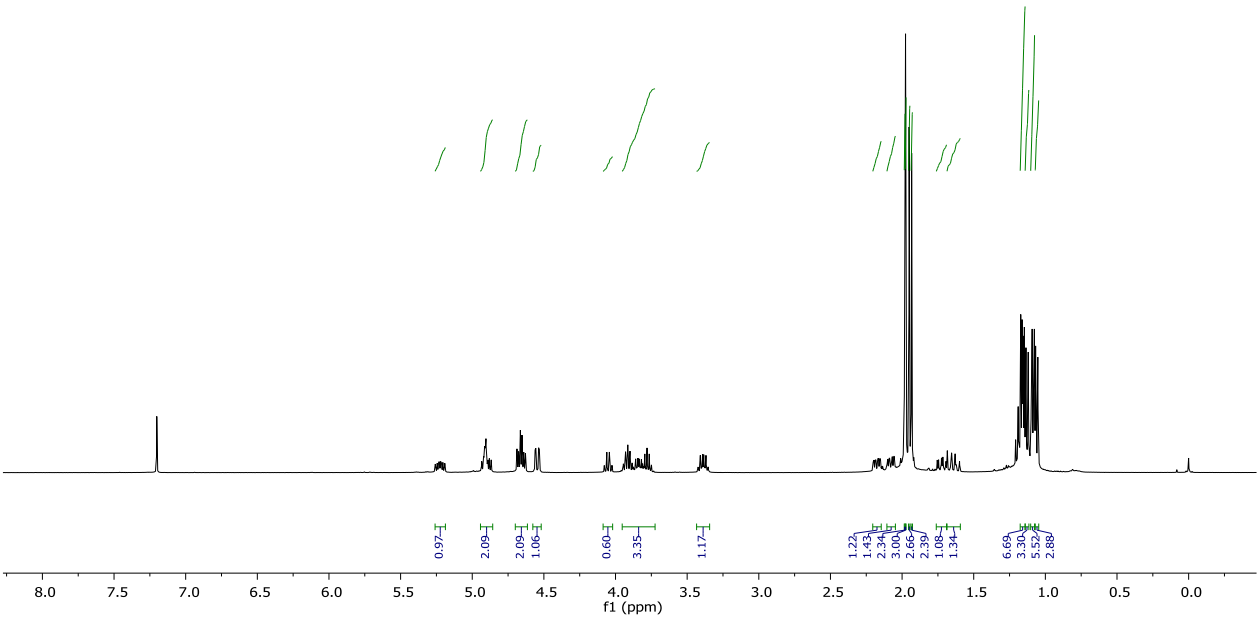
S10

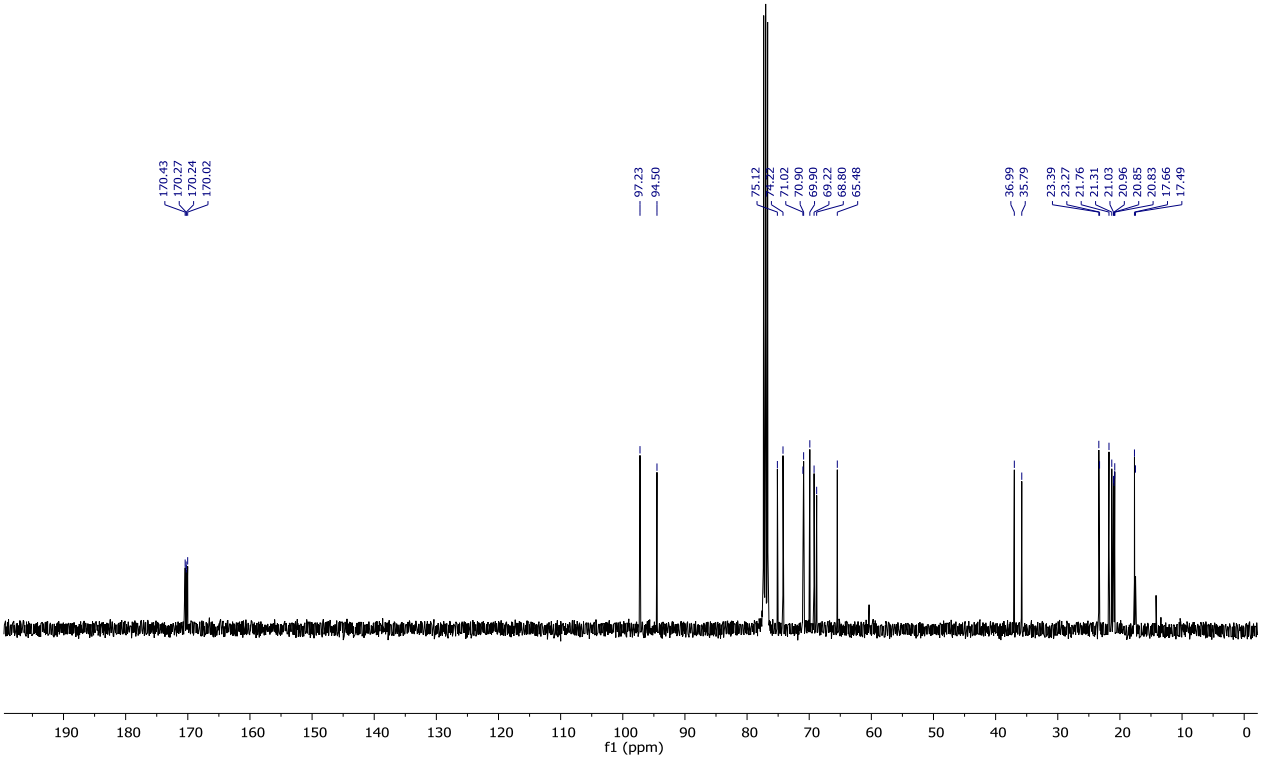

1.23
0.90
0.56
0.49
1.57
1.14
0.59
0.97
0.71
1.51
2.91
2.71
1.66
0.75
1.64
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

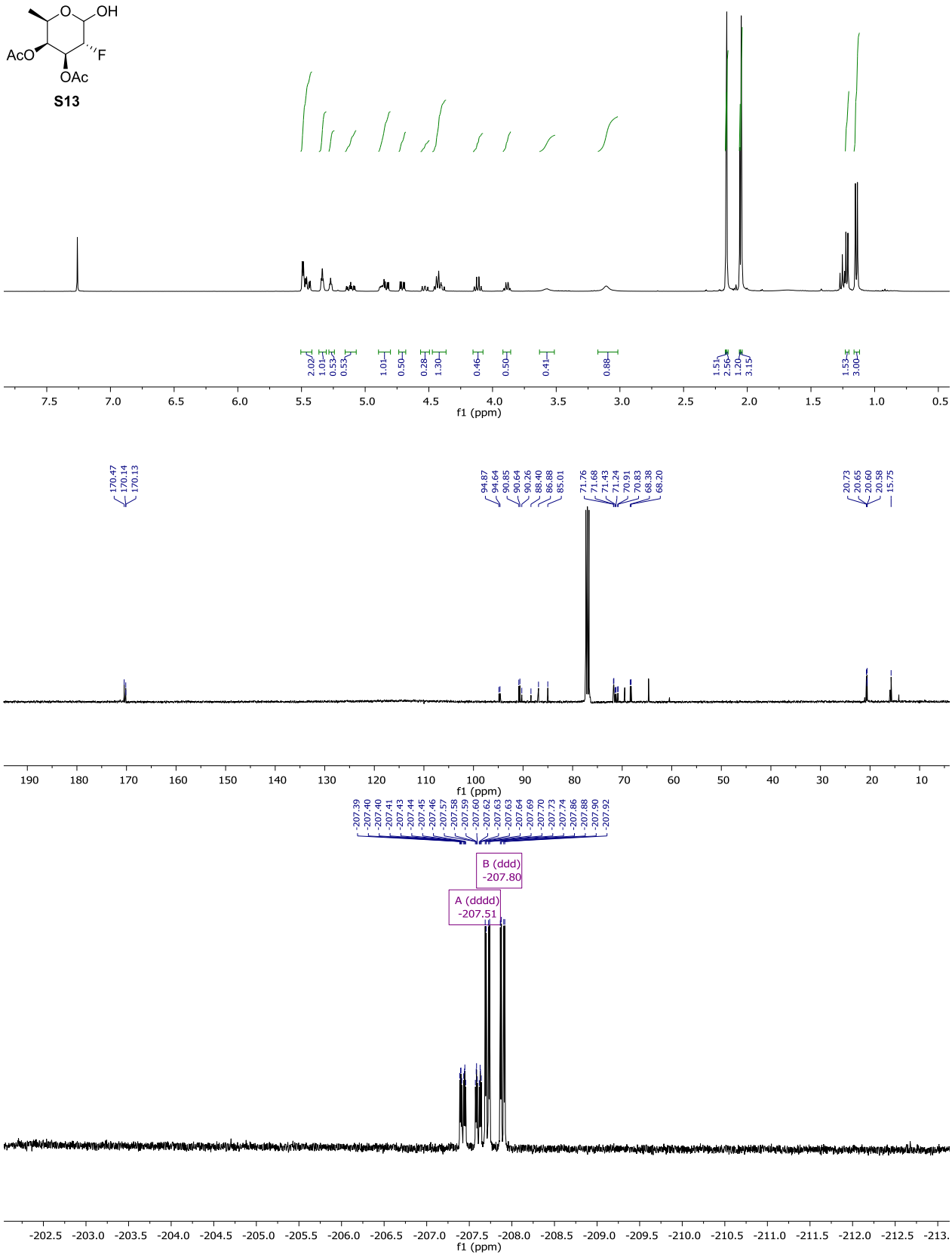

170.38
170.32
170.26
170.12
93.53
91.46
74.83
73.99
70.50
70.12
68.72
65.74
37.87
35.38
22.16
21.00
20.93
20.84
20.81
17.61
17.60
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

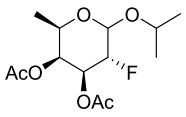

AcO
OAc

S12


0.97
2.09
2.09
1.06
0.60
3.35
1.17
1.22
1.43
2.34
3.00
2.66
2.39
1.08
1.34
6.69
3.30
5.52
2.88
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

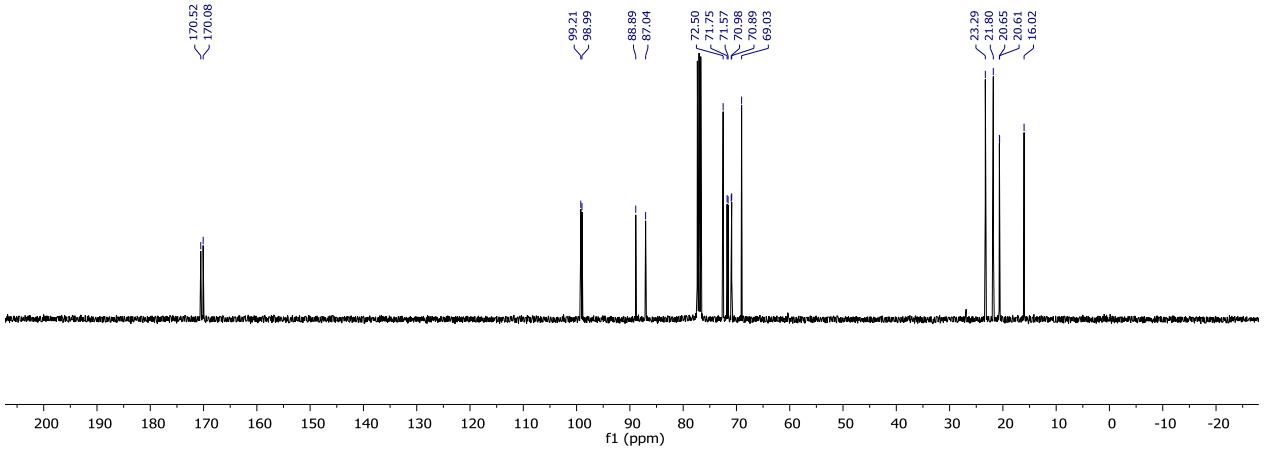

170.43
170.27
170.24
170.02
97.23
94.50
75.12
74.22
71.02
70.90
69.90
69.22
68.80
65.48
36.99
35.79
23.39
23.27
21.76
21.31
21.03
20.96
20.85
20.83
17.66
17.49
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

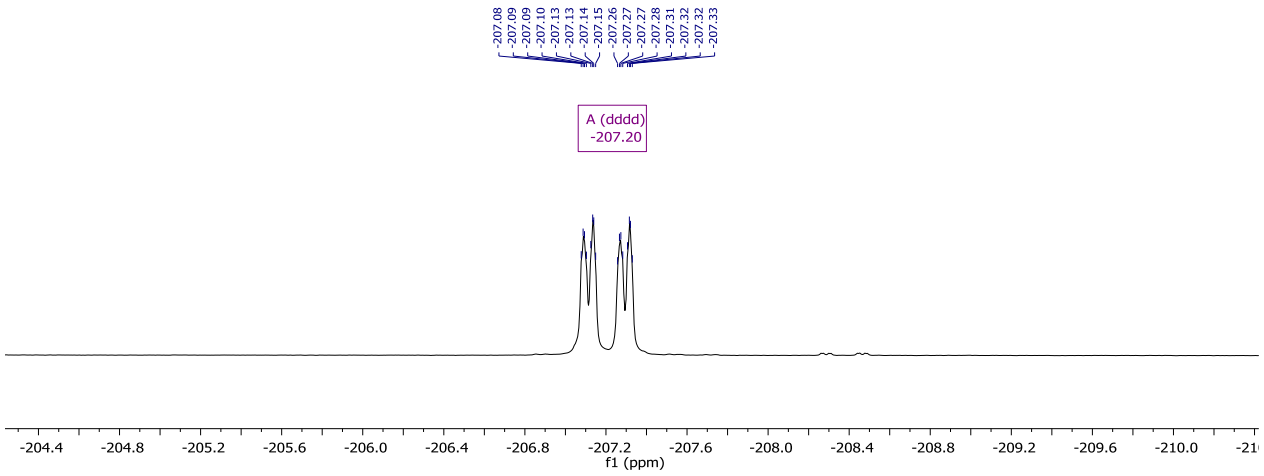

AcO
OAc
F
OH
S13
2.02
1.01
0.53
0.53
1.01
0.50
0.28
1.30
0.46
0.50
0.41
0.88
1.51
2.56
1.20
3.15
1.53
3.00
f1 (ppm)
170.47
170.14
170.13
94.87
94.64
90.85
90.64
90.26
88.40
86.88
85.01
71.76
71.68
71.43
71.24
70.91
70.83
68.38
68.20
20.73
20.65
20.60
20.58
15.75
f1 (ppm)
B (ddd)
-207.80
A (dddd)
-207.51
f1 (ppm)

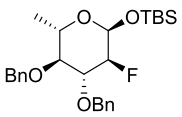

O
O
AcO
F
OAc

S15

1.04
1.09
1.04
1.15
1.09
1.07
2.97
3.00
3.03
6.26
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

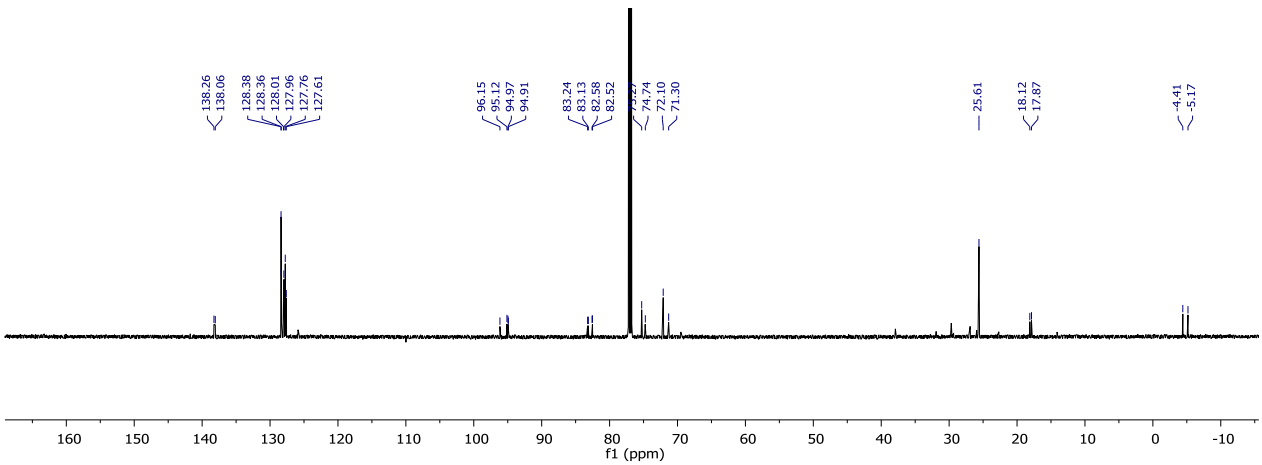

170.52
170.08
99.21
98.99
88.89
87.04
72.50
71.75
71.57
70.98
70.89
69.03
23.29
21.80
20.65
20.61
16.02
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

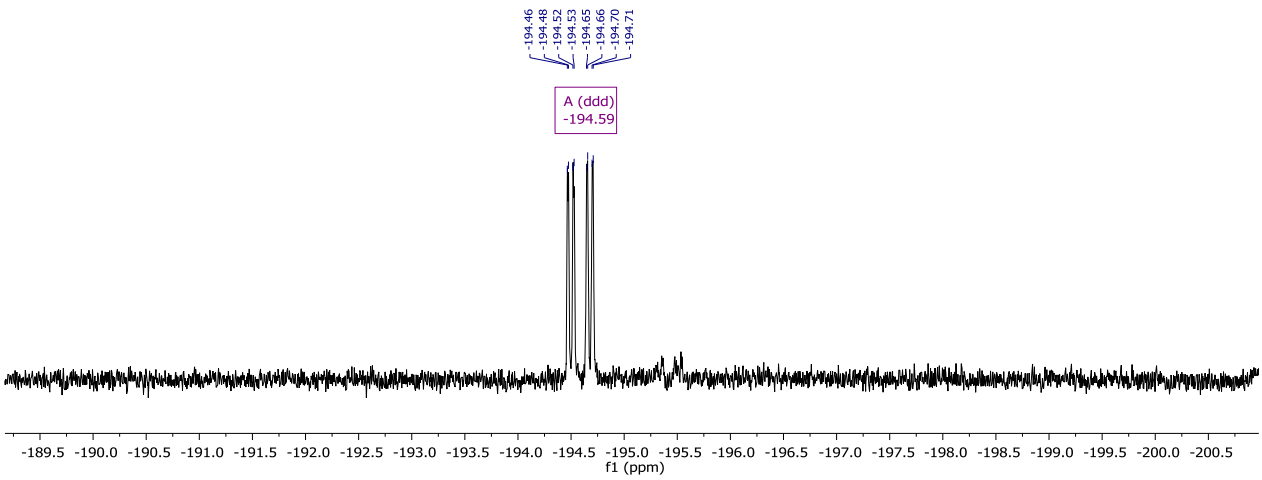

-207.08
-207.09
-207.09
-207.10
-207.13
-207.13
-207.14
-207.15
-207.26
-207.27
-207.27
-207.28
-207.31
-207.32
-207.32
-207.33
A (dddd)
-207.20
-204.4
-204.8
-205.2
-205.6
-206.0
-206.4
-206.8
-207.2
-207.6
-208.0
-208.4
-208.8
-209.2
-209.6
-210.0
f1 (ppm)

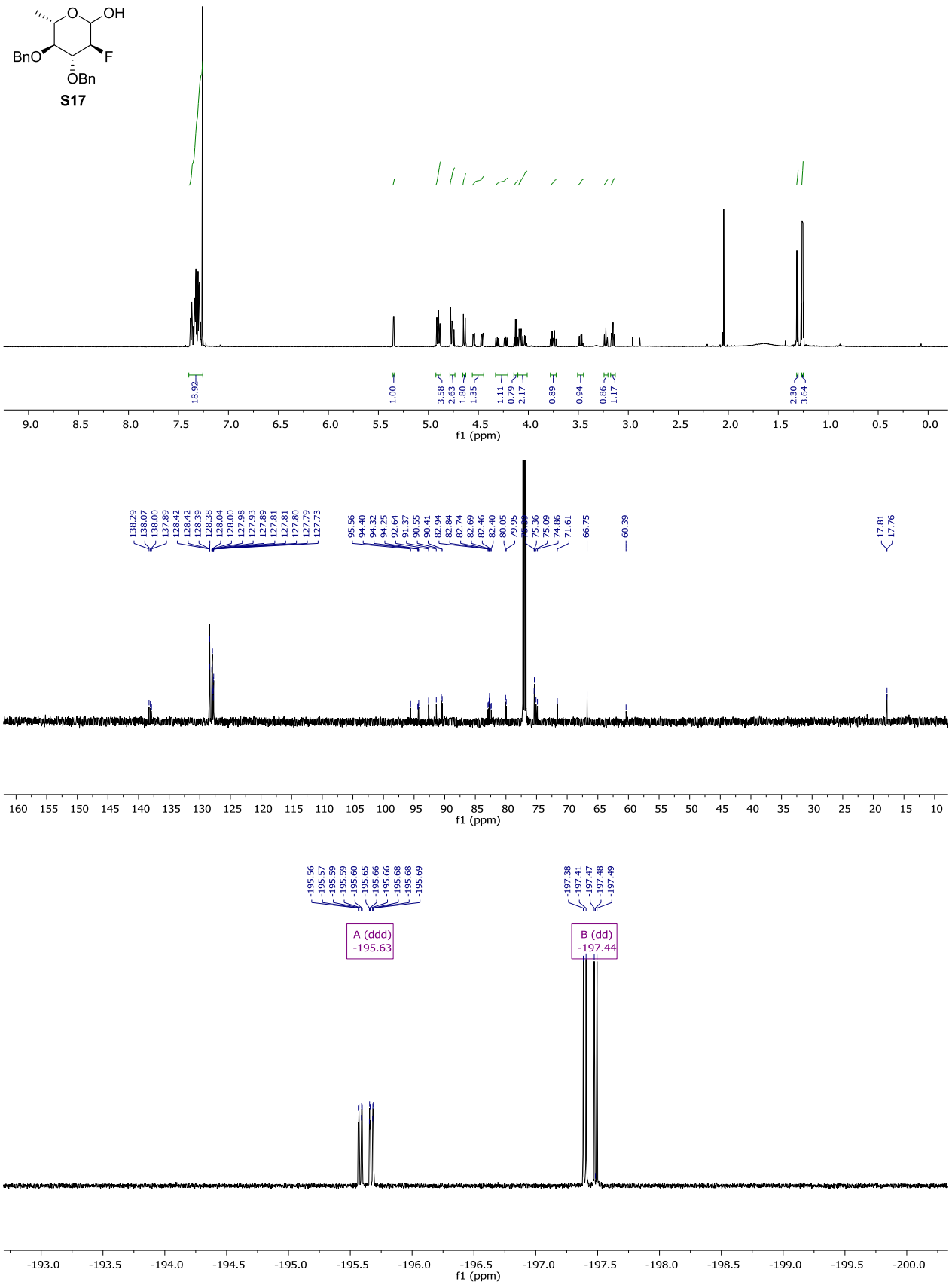

OTBS
BnO
F
OBn

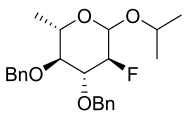
S16

17.43
1.74
1.05
1.13
0.91
1.38
1.10
1.10
1.07
2.94
6.99
4.74
f1 (ppm)

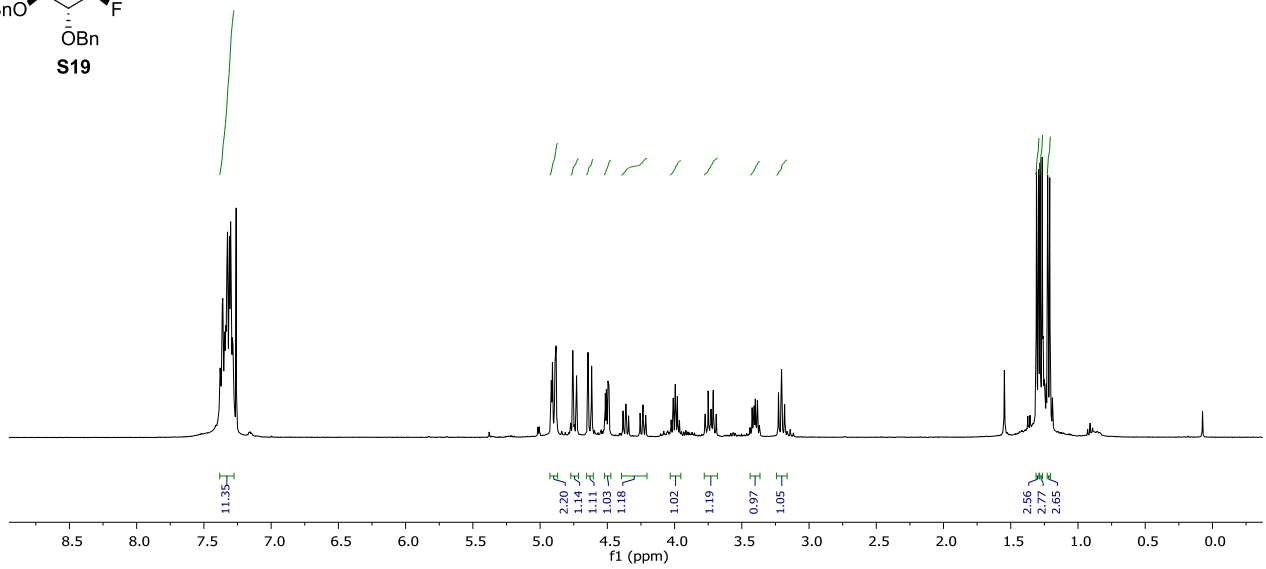

138.26
138.06
128.38
128.36
128.01
127.96
127.76
127.61
96.15
95.12
94.97
94.91
83.24
83.13
82.58
82.52
74.74
72.10
71.30
25.61
18.12
17.87
-4.41
-5.17
f1 (ppm)

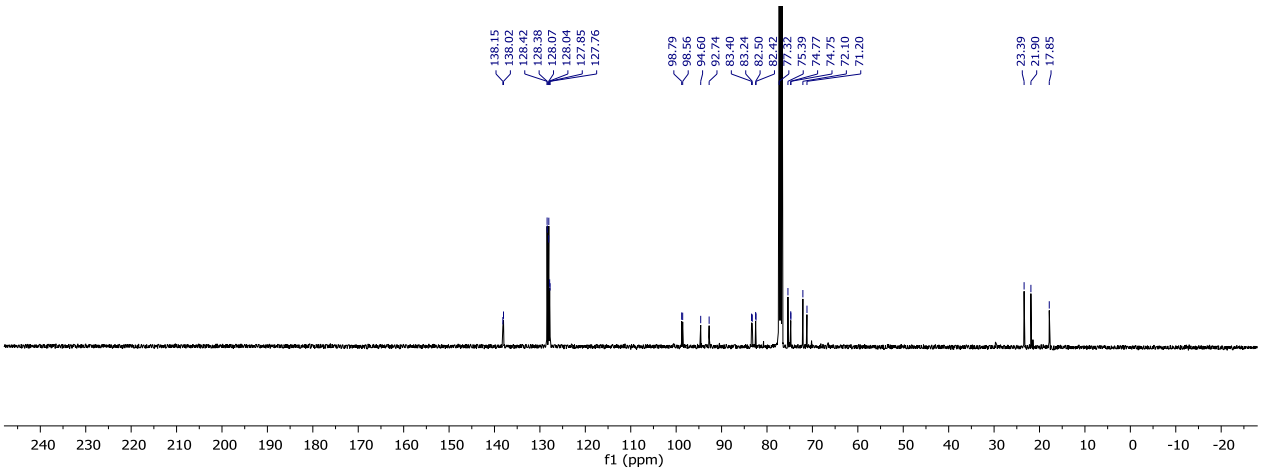

-194.46
-194.48
-194.52
-194.53
-194.65
-194.66
-194.70
-194.71
A (ddd)
-194.59
f1 (ppm)

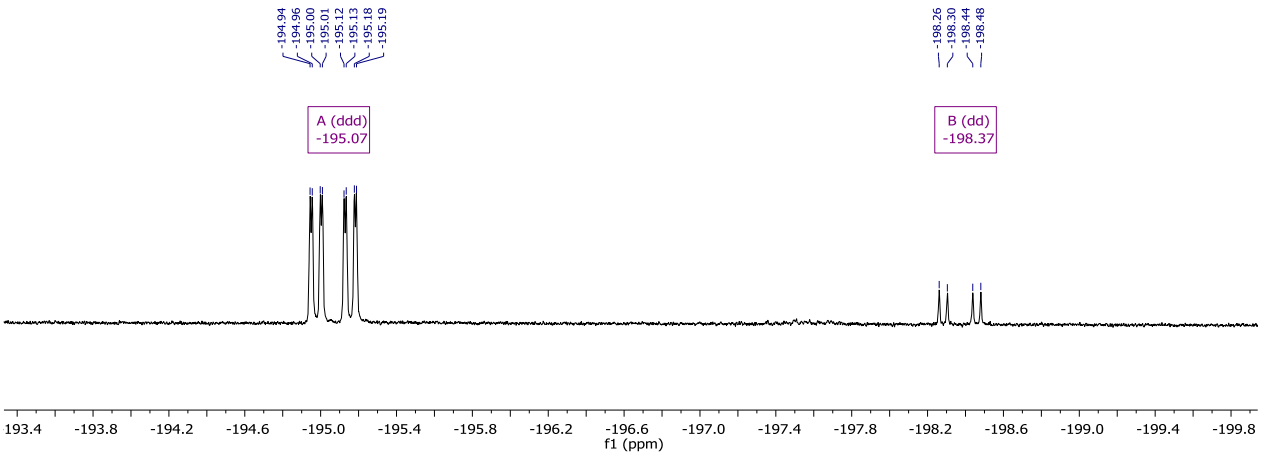

BnO
OH
F
OBn
S17
18.92
1.00
3.58
2.63
1.80
1.35
1.11
0.79
2.17
0.89
0.94
0.86
1.17
2.30
3.64
f1 (ppm)
138.29
138.07
138.00
137.89
128.42
128.42
128.39
128.38
128.04
128.00
127.98
127.93
127.89
127.81
127.81
127.80
127.79
127.73
95.56
94.40
94.32
94.25
92.64
91.37
90.55
90.41
82.94
82.84
82.74
82.69
82.46
82.40
80.05
79.95
75.36
75.09
74.86
71.61
66.75
60.39
17.81
17.76
f1 (ppm)
-195.56
-195.57
-195.59
-195.59
-195.60
-195.65
-195.66
-195.66
-195.68
-195.68
-195.69
A (ddd)
-195.63
-197.38
-197.41
-197.47
-197.48
-197.49
B (dd)
-197.44
f1 (ppm)

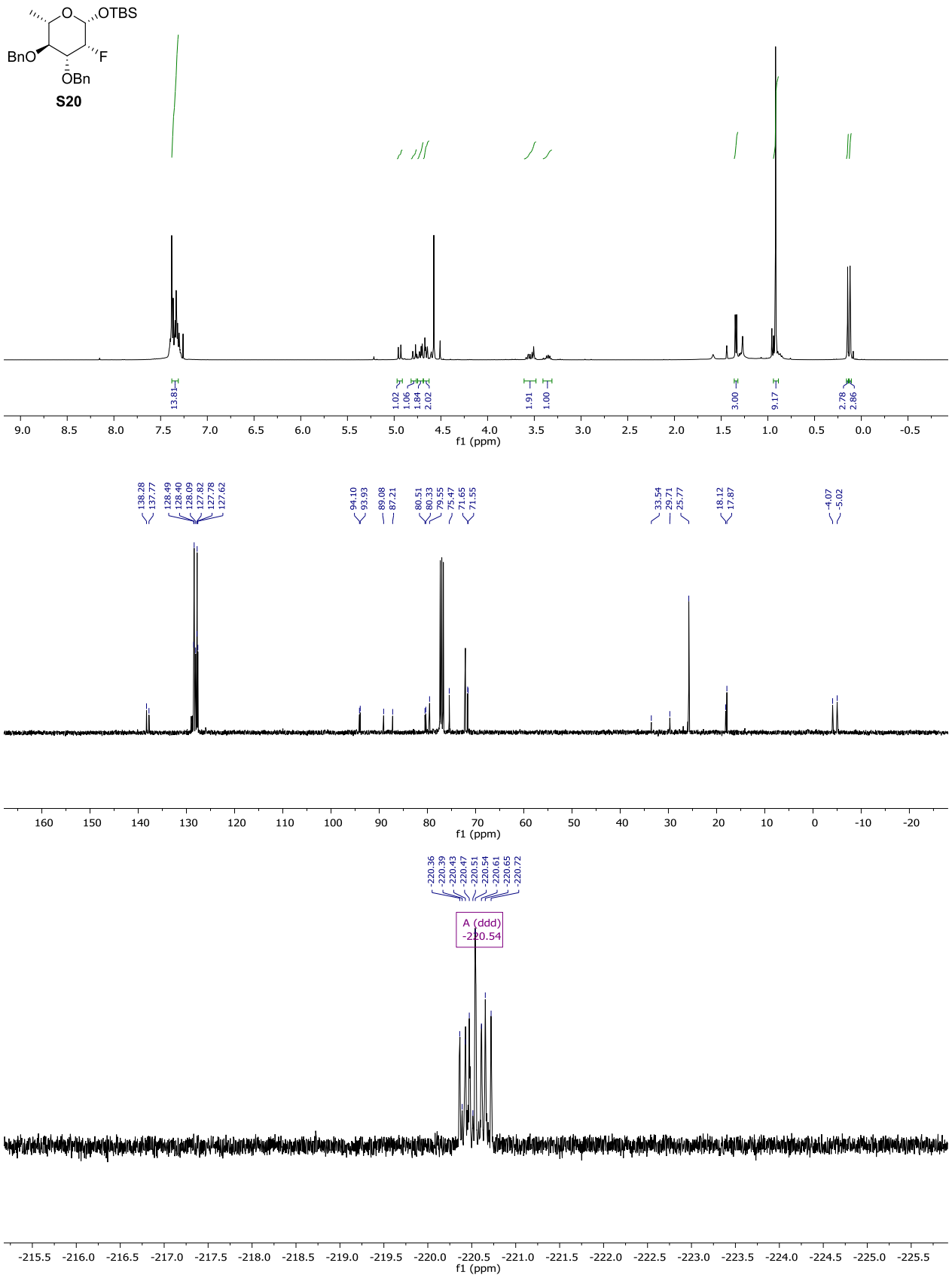

BnO
F
OBn

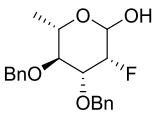
S19


11.35
2.20
1.14
1.11
1.03
1.18
1.02
1.19
0.97
1.05
2.56
2.77
2.65
f1 (ppm)

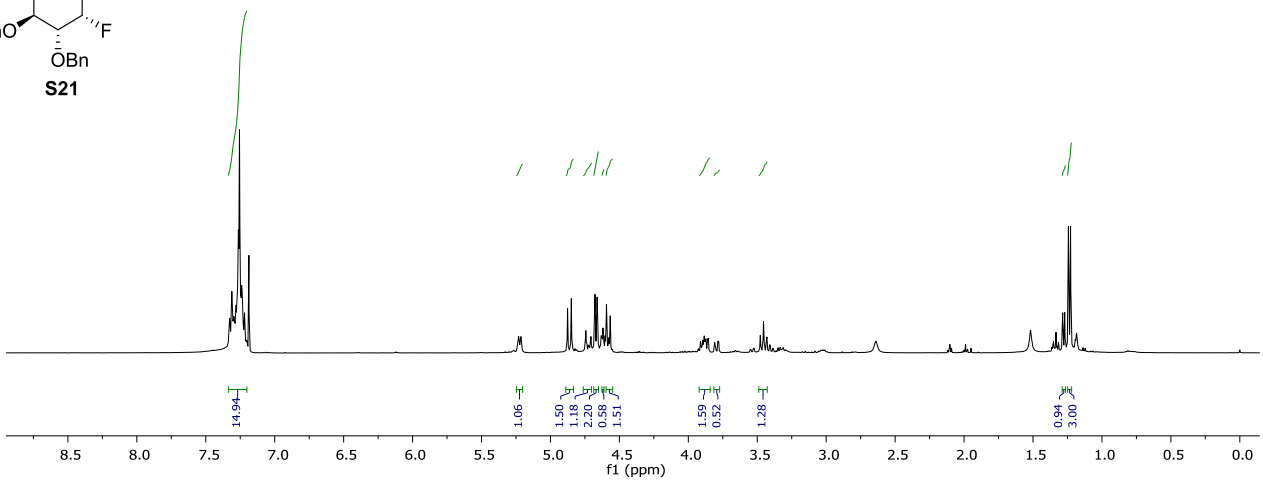

138.15
138.02
128.42
128.38
128.07
128.04
127.85
127.76
98.79
98.56
94.60
92.74
83.40
83.24
82.50
82.42
77.32
75.39
74.77
74.75
72.10
71.20
23.39
21.90
17.85
f1 (ppm)

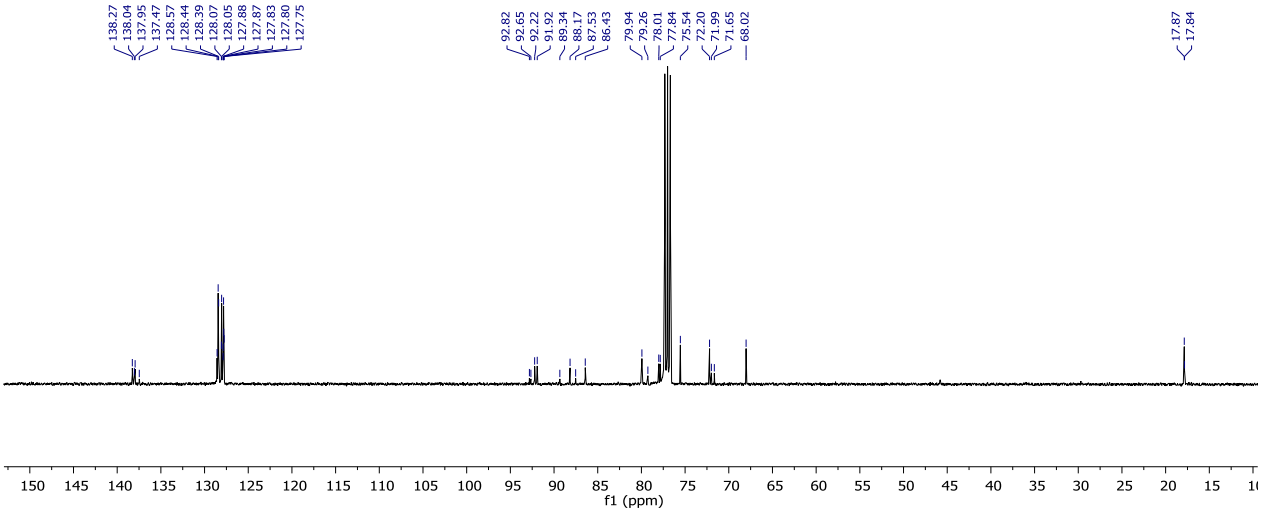

-194.94
-194.96
-195.00
-195.01
-195.12
-195.13
-195.18
-195.19
A (ddd)
-195.07
-198.26
-198.30
-198.44
-198.48
B (dd)
-198.37
f1 (ppm)

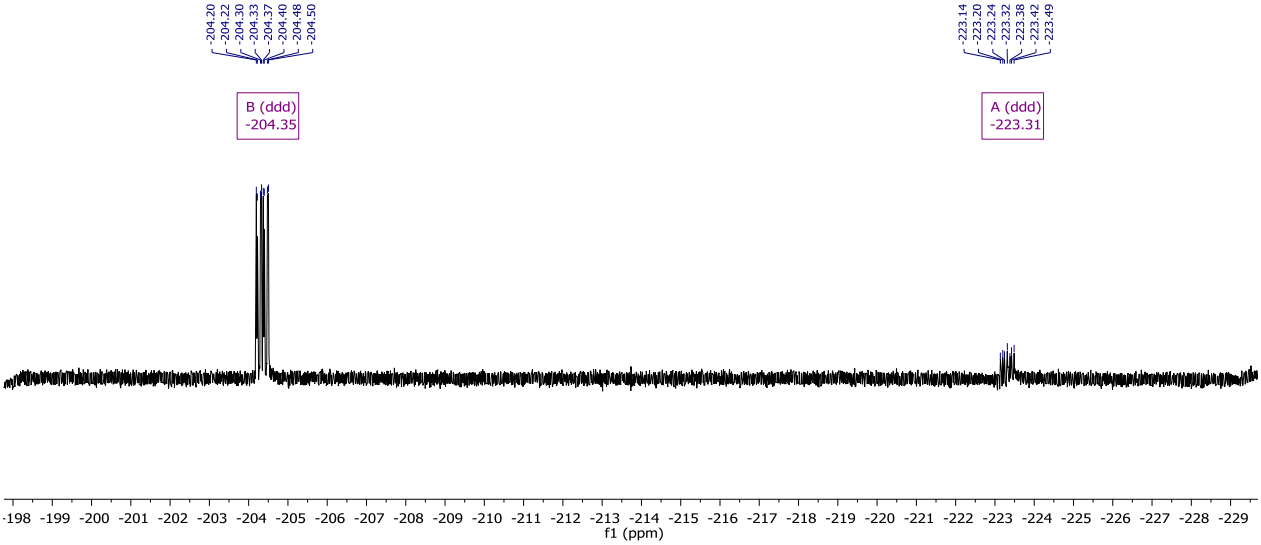

OTBS
BnO
F
OBn
S20
13.81
1.02
1.06
1.84
2.02
1.91
1.00
3.00
9.17
2.78
2.86
f1 (ppm)
138.28
137.77
128.49
128.40
128.09
127.82
127.78
127.62
94.10
93.93
89.08
87.21
80.51
80.33
79.55
75.47
71.65
71.55
33.54
29.71
25.77
18.12
17.87
-4.07
-5.02
f1 (ppm)
-220.36
-220.39
-220.43
-220.47
-220.51
-220.54
-220.61
-220.65
-220.72
A (ddd)
-220.54
f1 (ppm)

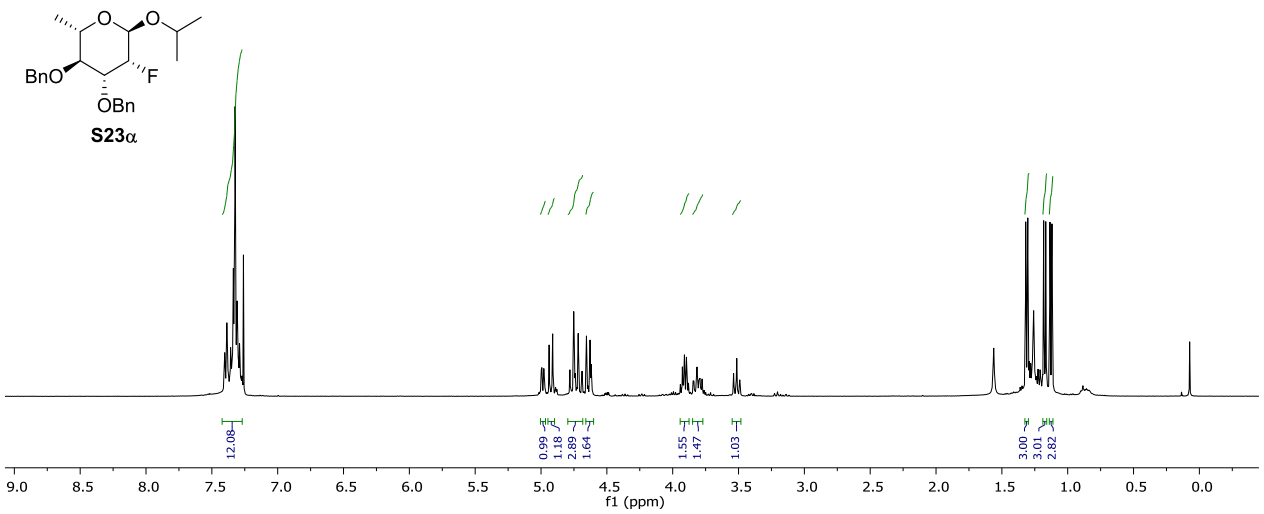

O
OH
BnO
F
OBn

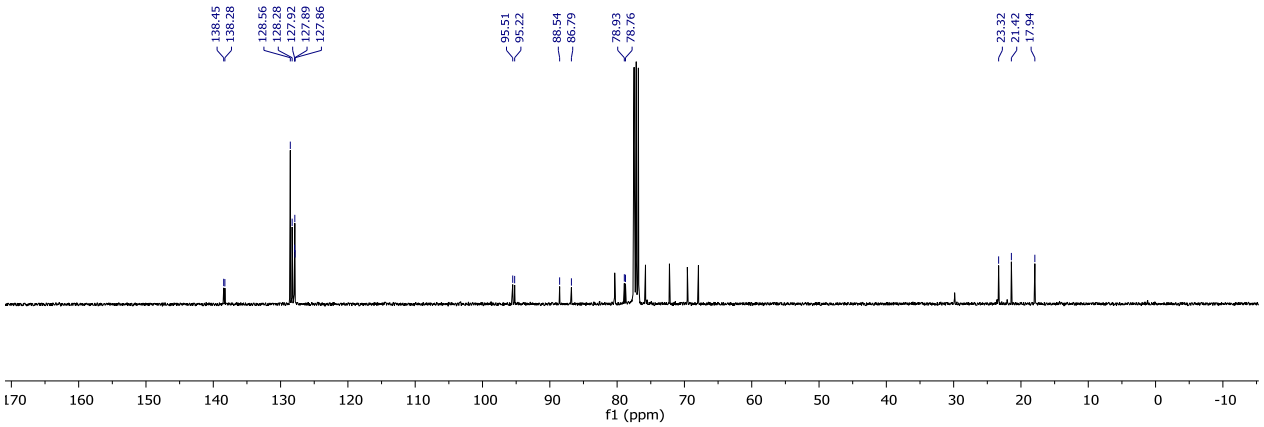
S21

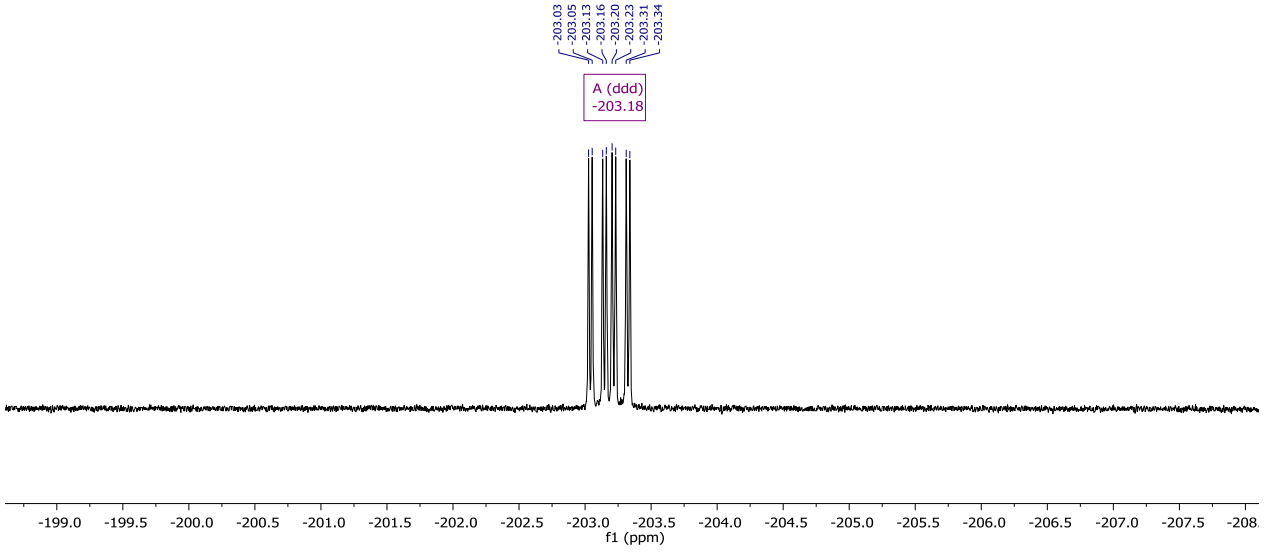

14.94
1.06
1.50
1.18
2.20
0.58
1.51
1.59
0.52
1.28
0.94
3.00
f1 (ppm)

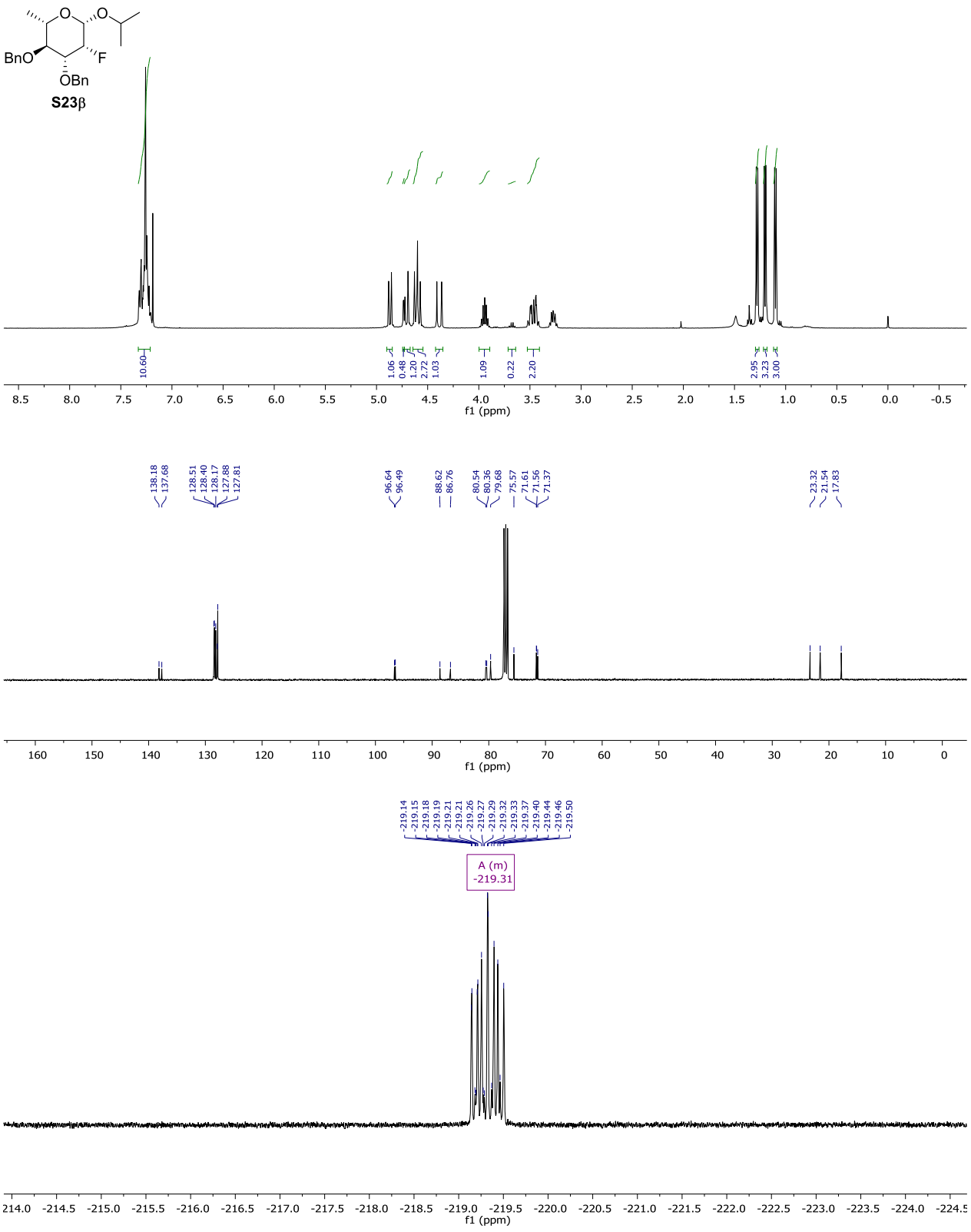

138.27
138.04
137.95
137.47
128.57
128.44
128.39
128.07
128.05
127.88
127.87
127.83
127.80
127.75
92.82
92.65
92.22
91.92
89.34
88.17
87.53
86.43
79.94
79.26
78.01
77.84
75.54
72.20
71.99
71.65
68.02
17.87
17.84
f1 (ppm)

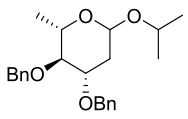

-204.20
-204.22
-204.30
-204.33
-204.37
-204.40
-204.48
-204.50
B (ddd)
-204.35
-223.14
-223.20
-223.24
-223.32
-223.38
-223.42
-223.49
A (ddd)
-223.31
f1 (ppm)


BnO
O
O
F
OBn
S23α
12.08
0.99
1.18
2.89
1.64
1.55
1.47
1.03
3.00
3.01
2.82
f1 (ppm)

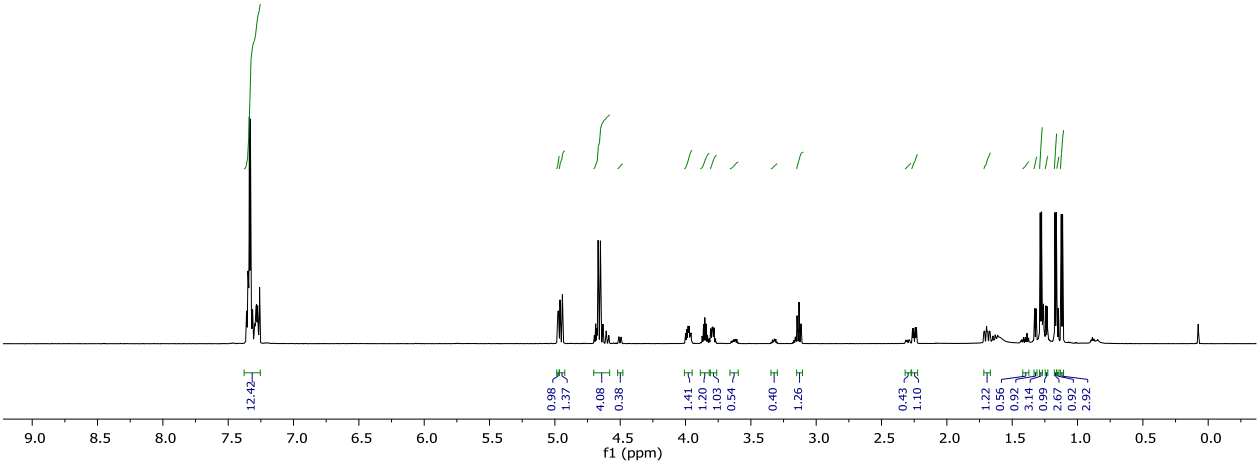

138.45
138.28
128.56
128.28
127.92
127.89
127.86
95.51
95.22
88.54
86.79
78.93
78.76
23.32
21.42
17.94
f1 (ppm)

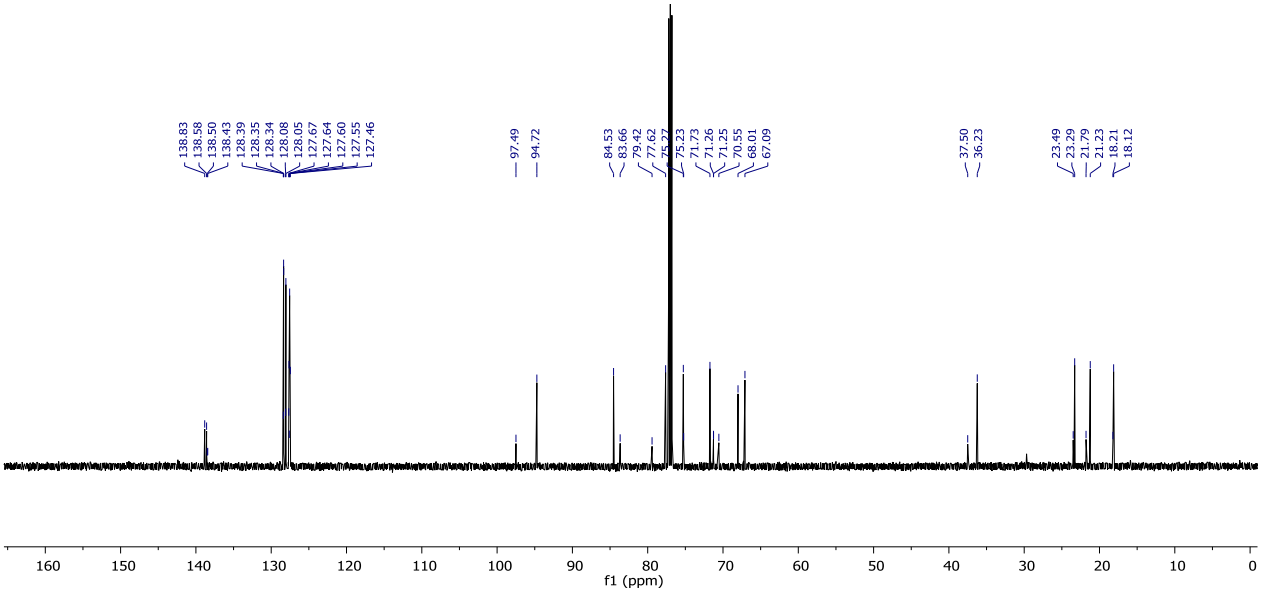

-203.03
-203.05
-203.13
-203.16
-203.20
-203.23
-203.31
-203.34
A (ddd)
-203.18
f1 (ppm)

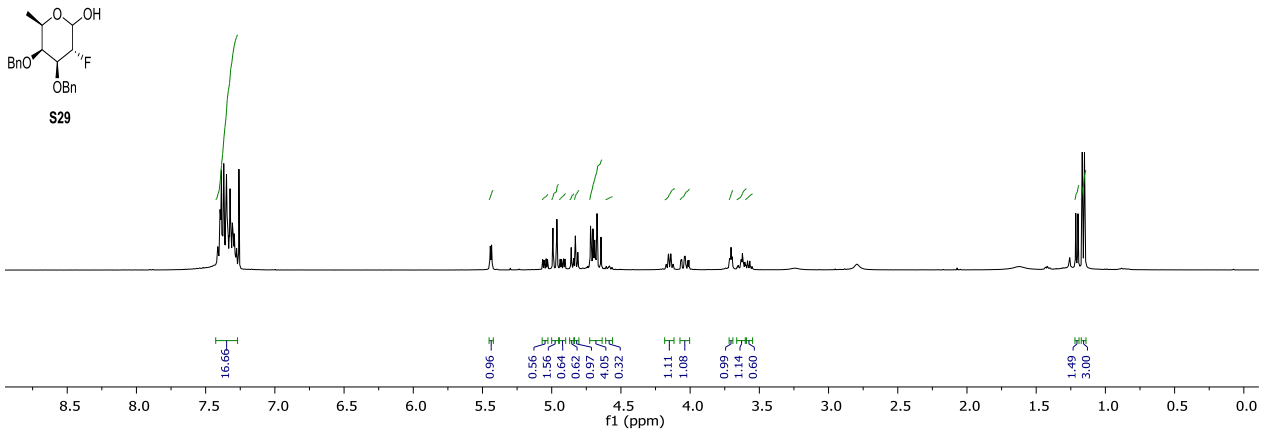

BnO
O
O
F
OBn
S23β
10.60
1.06
0.48
1.20
2.72
1.03
1.09
0.22
2.20
2.95
3.23
3.00
f1 (ppm)
138.18
137.68
128.51
128.40
128.17
127.88
127.81
96.64
96.49
88.62
86.76
80.54
80.36
79.68
75.57
71.61
71.56
71.37
23.32
21.54
17.83
f1 (ppm)
-219.14
-219.15
-219.18
-219.19
-219.21
-219.21
-219.26
-219.27
-219.29
-219.32
-219.33
-219.37
-219.40
-219.44
-219.46
-219.50
A (m)
-219.31
f1 (ppm)

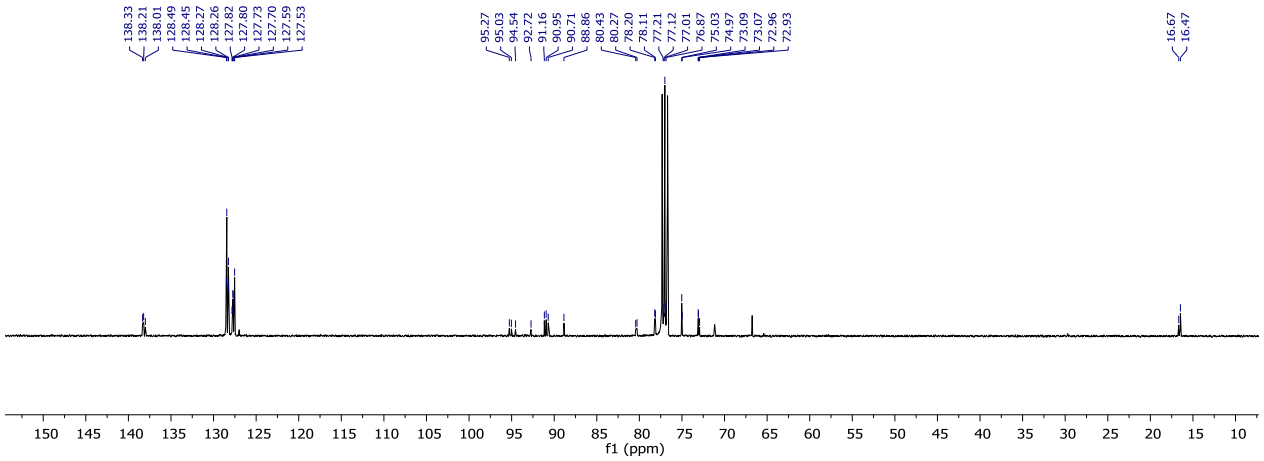

O
O
BnO
OBn

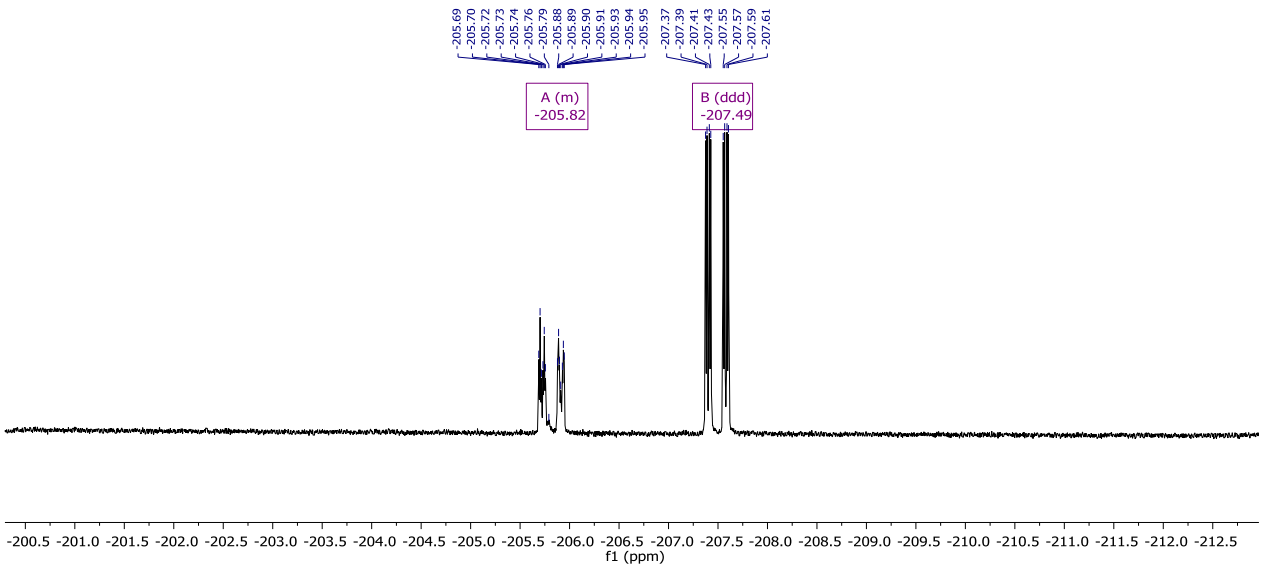
S27

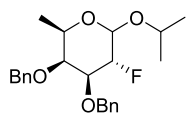

12.42
0.98
1.37
4.08
0.38
1.41
1.20
1.03
0.54
0.40
1.26
0.43
1.10
1.22
0.56
0.92
3.14
0.99
2.67
0.92
2.92
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


138.83
138.58
138.50
138.43
128.39
128.35
128.34
128.08
128.05
127.67
127.64
127.60
127.55
127.46
97.49
94.72
84.53
83.66
79.42
77.62
75.37
75.23
71.73
71.26
71.25
70.55
68.01
67.09
37.50
36.23
23.49
23.29
21.79
21.23
18.21
18.12
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

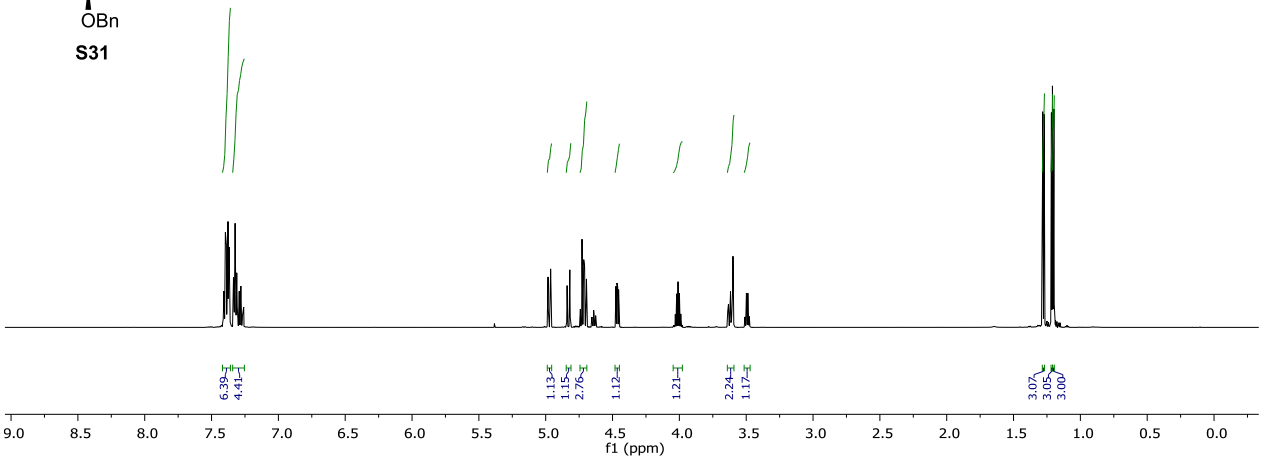

BnO
OH
F
OBn
S29
16.66
0.96
0.56
1.56
0.64
0.62
0.97
4.05
0.32
1.11
1.08
0.99
1.14
0.60
1.49
3.00
f1 (ppm)

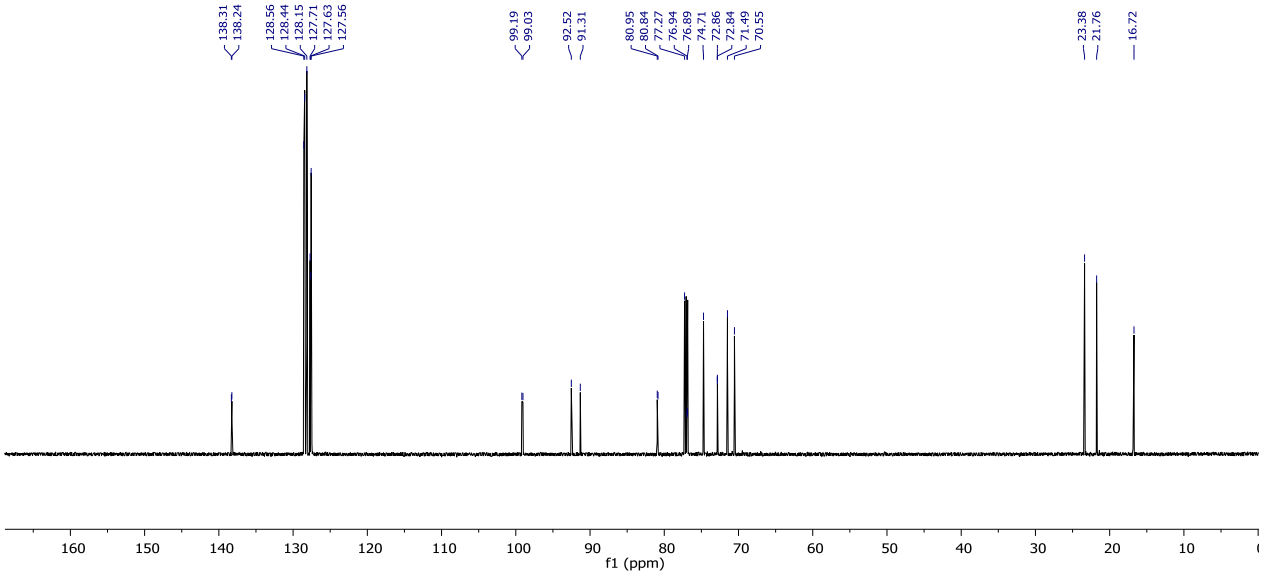

138.33
138.21
138.01
128.49
128.45
128.27
128.26
127.82
127.80
127.73
127.70
127.59
127.53
95.27
95.03
94.54
92.72
91.16
90.95
90.71
88.86
80.43
80.27
78.20
78.11
77.21
77.12
77.01
76.87
75.03
74.97
73.09
73.07
72.96
72.93
16.67
16.47
f1 (ppm)

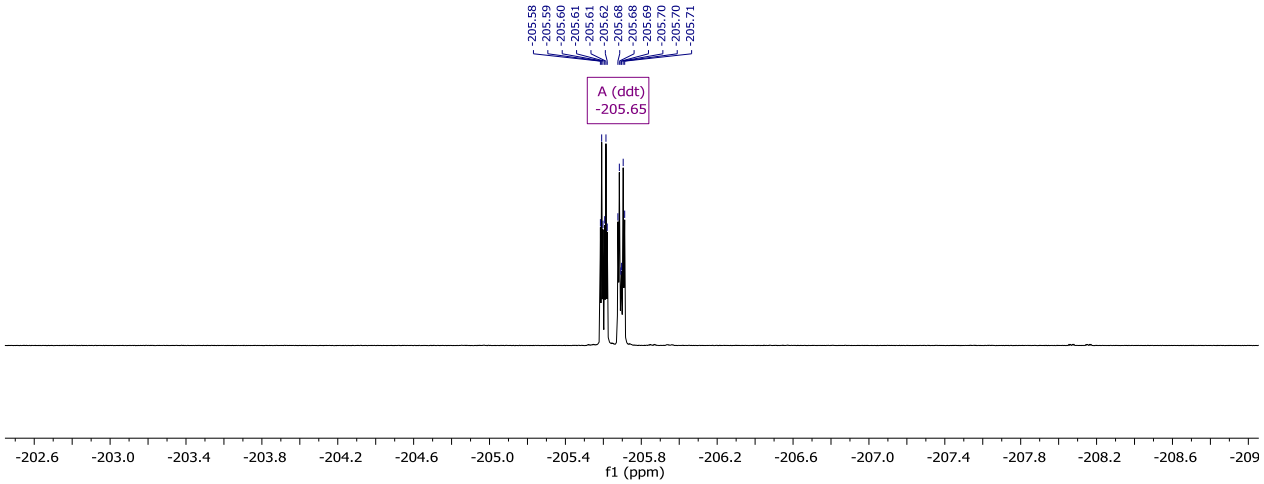

-205.69
-205.70
-205.72
-205.73
-205.74
-205.76
-205.79
-205.88
-205.89
-205.90
-205.91
-205.93
-205.94
-205.95
-207.37
-207.39
-207.41
-207.43
-207.55
-207.57
-207.59
-207.61
A (m)
-205.82
B (ddd)
-207.49
f1 (ppm)

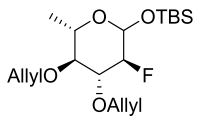

BnO
O
O
F
OBn

S31


6.39
4.41
1.13
1.15
2.76
1.12
1.21
2.24
1.17
3.07
3.05
3.00
f1 (ppm)

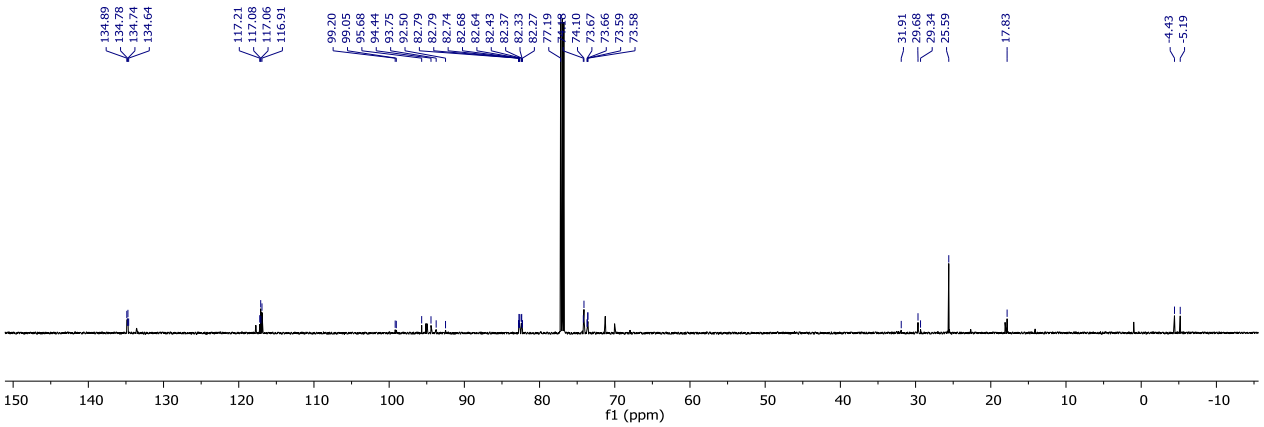

138.31
138.24
128.56
128.44
128.15
127.71
127.63
127.56
99.19
99.03
92.52
91.31
80.95
80.84
77.27
76.94
76.89
74.71
72.86
72.84
71.49
70.55
23.38
21.76
16.72
f1 (ppm)

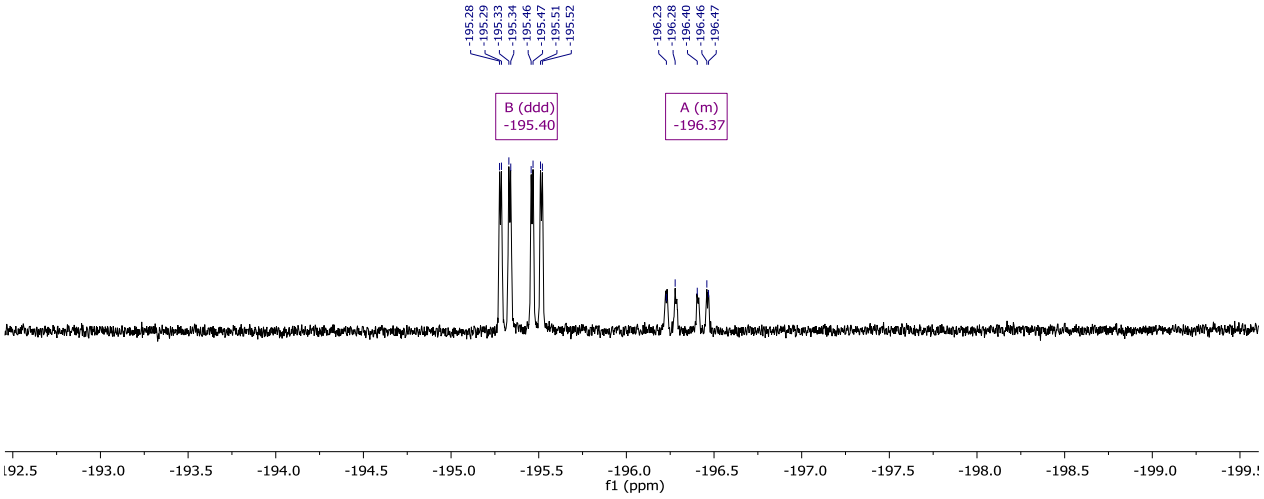

-205.58
-205.59
-205.60
-205.61
-205.61
-205.62
-205.68
-205.68
-205.69
-205.70
-205.70
-205.71
A (ddt)
-205.65
f1 (ppm)

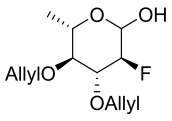

O
OTBS
AllylO
F
OAllyl

S32

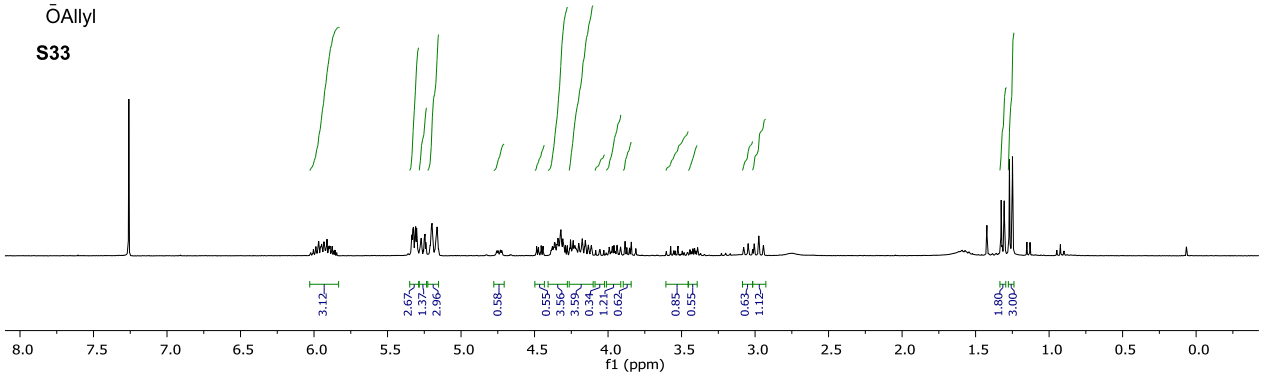
4.53
5.53
3.92
1.25
0.63
4.37
0.51
2.62
3.17
1.10
1.84
1.85
4.11
10.00
2.85
2.80
f1 (ppm)

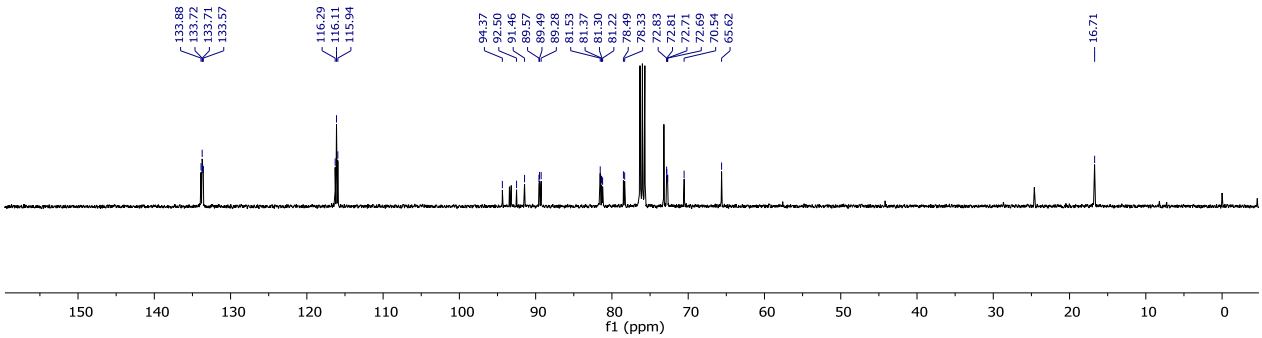

134.89
134.78
134.74
134.64
117.21
117.08
117.06
116.91
99.20
99.05
95.68
94.44
93.75
92.50
82.79
82.79
82.74
82.68
82.64
82.43
82.37
82.33
82.27
77.19
74.10
73.67
73.66
73.59
73.58
31.91
29.68
29.34
25.59
17.83
-4.43
-5.19
f1 (ppm)

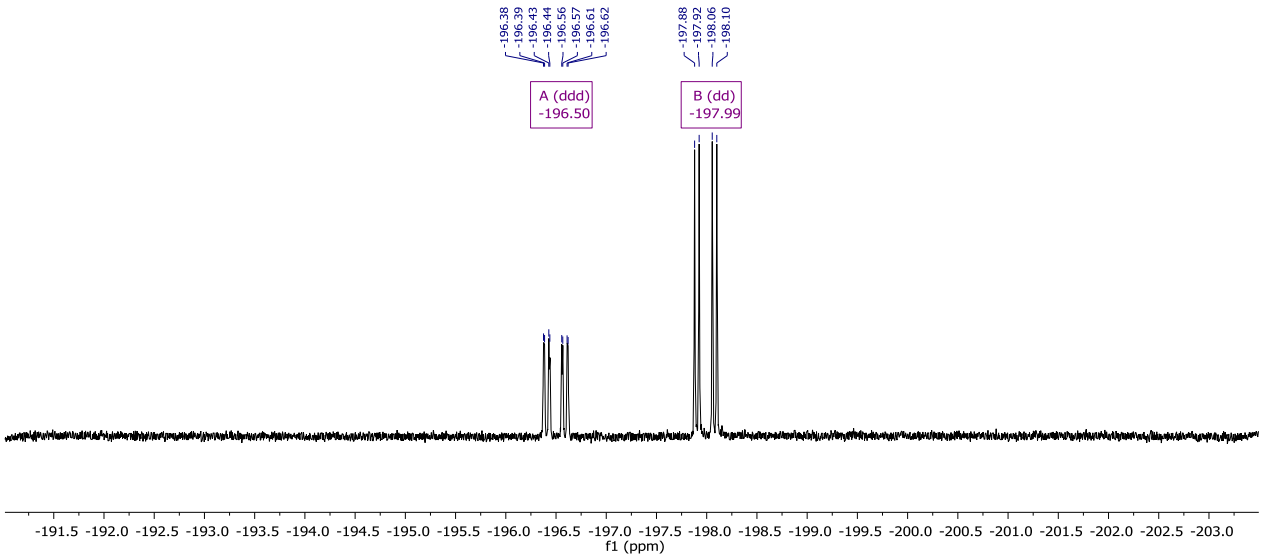

-195.28
-195.29
-195.33
-195.34
-195.46
-195.47
-195.51
-195.52
-196.23
-196.28
-196.40
-196.46
-196.47
B (ddd)
-195.40
A (m)
-196.37
f1 (ppm)

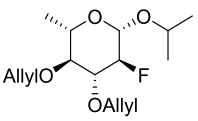

O
OH
AllylO
F
OAllyl

S33

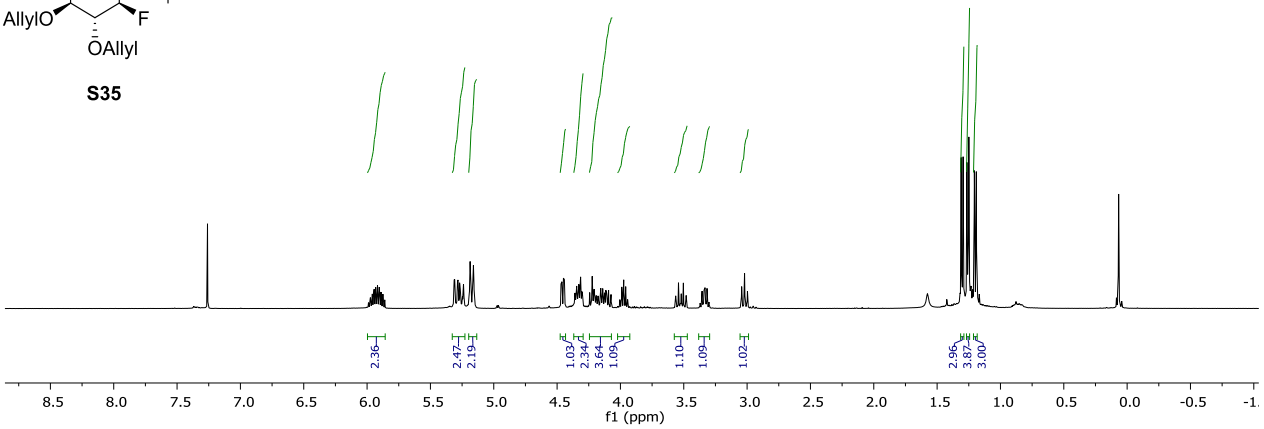

3.12
2.67
1.37
2.96
0.58
0.55
3.56
3.59
0.34
1.21
0.62
0.85
0.55
0.63
1.12
1.80
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

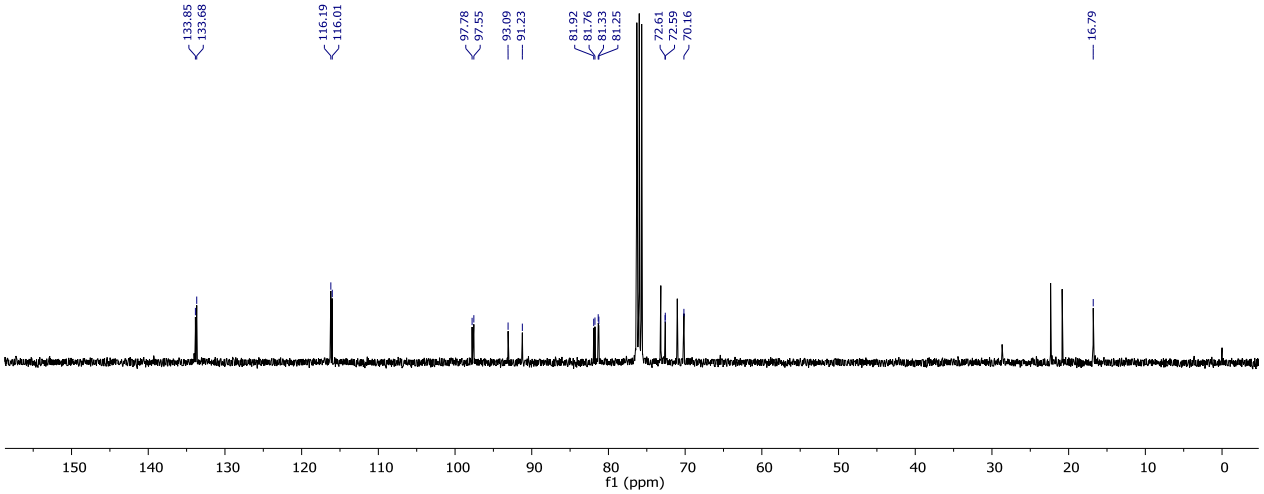

133.88
133.72
133.71
133.57
116.29
116.11
115.94
94.37
92.50
91.46
89.57
89.49
89.28
81.53
81.37
81.30
81.22
78.49
78.33
72.83
72.81
72.71
72.69
70.54
65.62
16.71
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

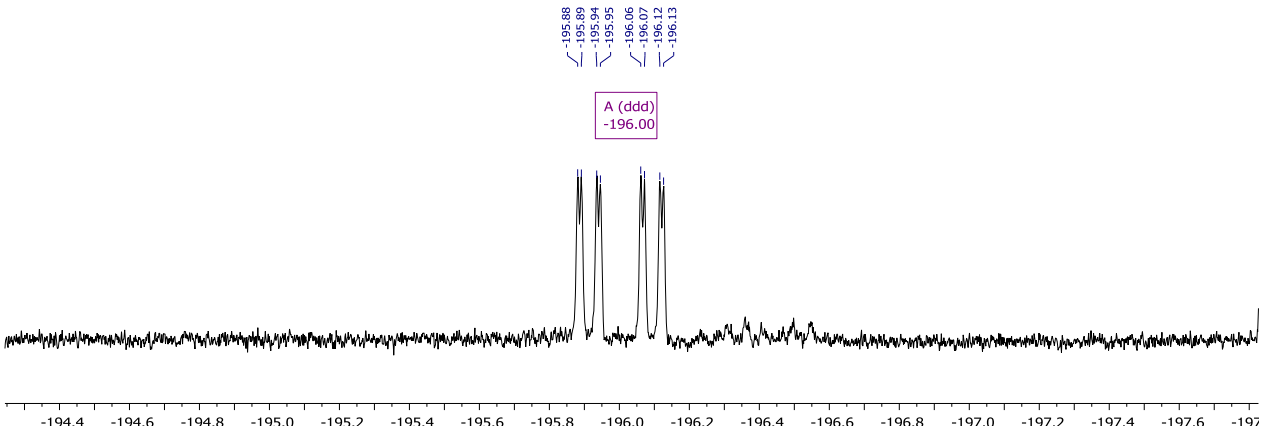

-196.38
-196.39
-196.43
-196.44
-196.56
-196.57
-196.61
-196.62
-197.88
-197.92
-198.06
-198.10
A (ddd)
-196.50
B (dd)
-197.99
-191.5 -192.0 -192.5 -193.0 -193.5 -194.0 -194.5 -195.0 -195.5 -196.0 -196.5 -197.0 -197.5 -198.0 -198.5 -199.0 -199.5 -200.0 -200.5 -201.0 -201.5 -202.0 -202.5 -203.0
f1 (ppm)

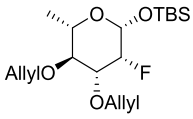

AllylO
O
O
F
OAllyl

S35


2.36
2.47
2.19
1.03
2.34
3.64
1.09
1.10
1.09
1.02
2.96
3.87
3.00
f1 (ppm)

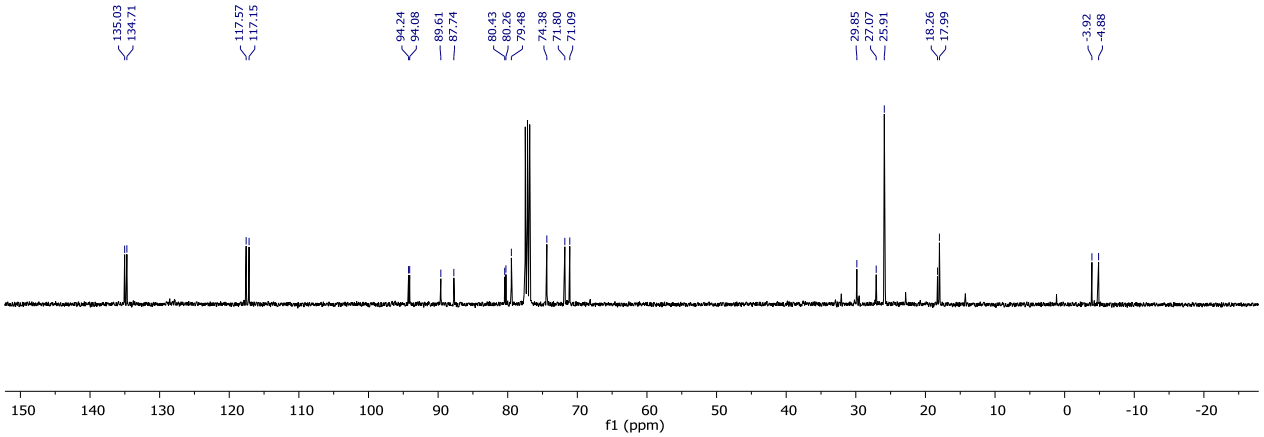

133.85
133.68
116.19
116.01
97.78
97.55
93.09
91.23
81.92
81.76
81.33
81.25
72.61
72.59
70.16
16.79
f1 (ppm)

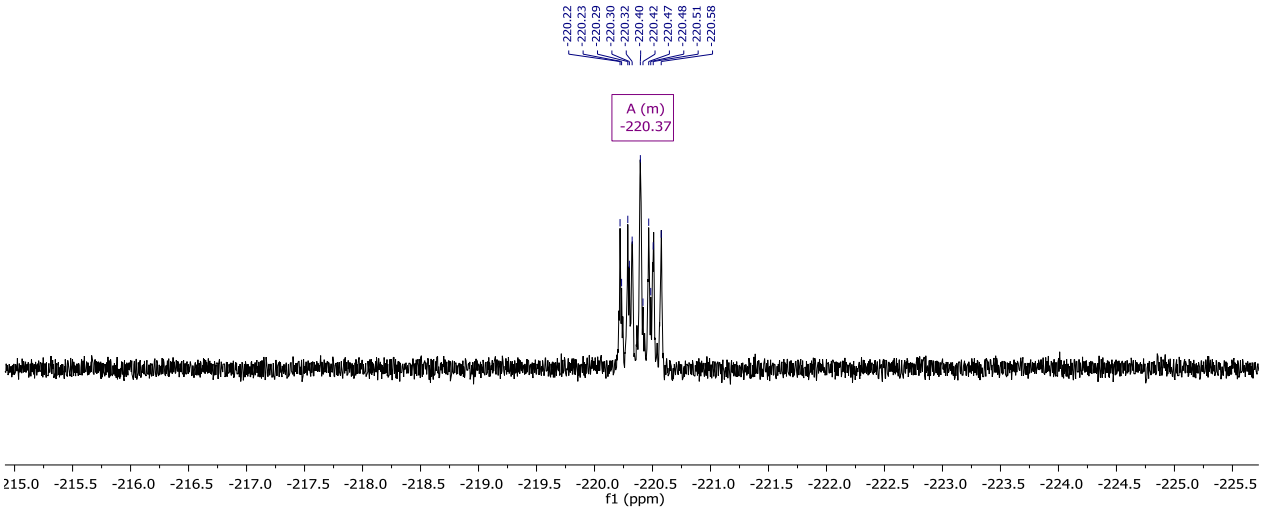

-195.88
-195.89
-195.94
-195.95
-196.06
-196.07
-196.12
-196.13
A (ddd)
-196.00

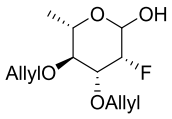

O
OTBS
AllylO
F
OAllyl

S36

2.39
1.30
1.33
1.10
1.09
1.53
0.47
1.26
1.26
2.18
0.46
2.48
3.12
8.99
2.69
2.79
f1 (ppm)

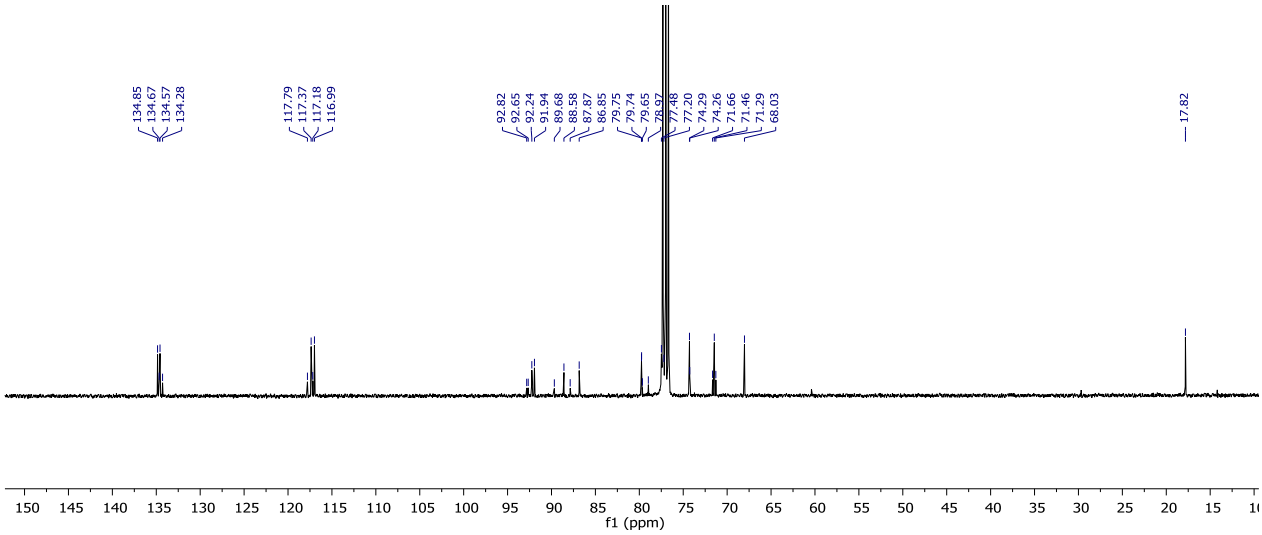

135.03
134.71
117.57
117.15
94.24
94.08
89.61
87.74
80.43
80.26
79.48
74.38
71.80
71.09
29.85
27.07
25.91
18.26
17.99
-3.92
-4.88
f1 (ppm)

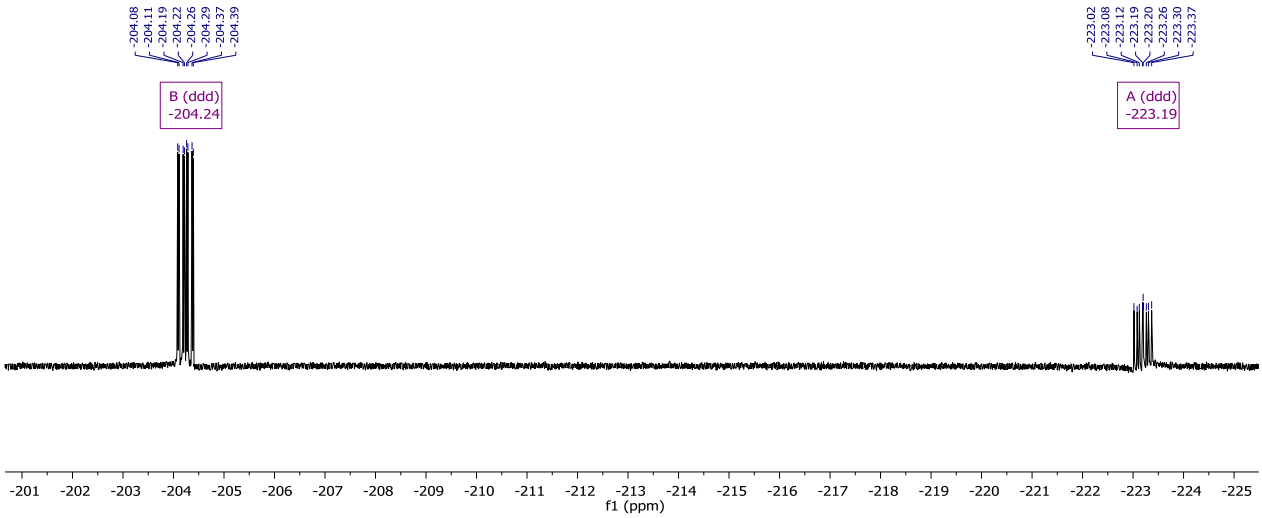

-220.22
-220.23
-220.29
-220.30
-220.32
-220.40
-220.42
-220.47
-220.48
-220.51
-220.58
A (m)
-220.37
f1 (ppm)

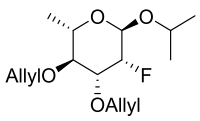

O
OH
AllylO
F
OAllyl

S37

2.76
6.85
1.61
1.46
4.56
1.06
1.04
0.57
1.39
0.41
0.89
3.00
f1 (ppm)

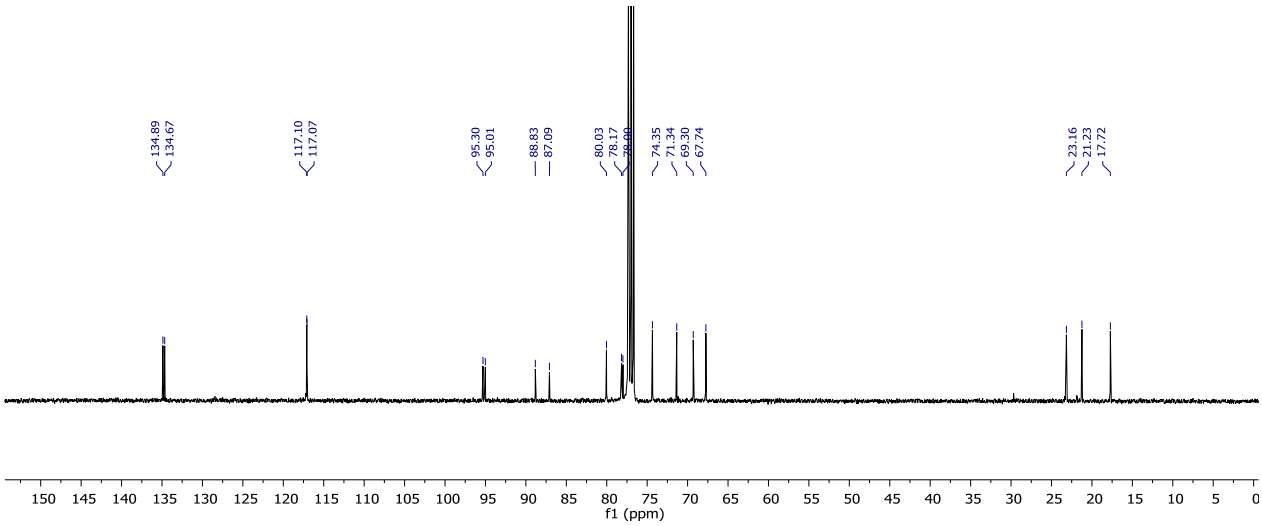

134.85
134.67
134.57
134.28
117.79
117.37
117.18
116.99
92.82
92.65
92.24
91.94
89.68
88.58
87.87
86.85
79.75
79.74
79.65
78.97
77.48
77.20
74.29
74.26
71.66
71.46
71.29
68.03
17.82
f1 (ppm)

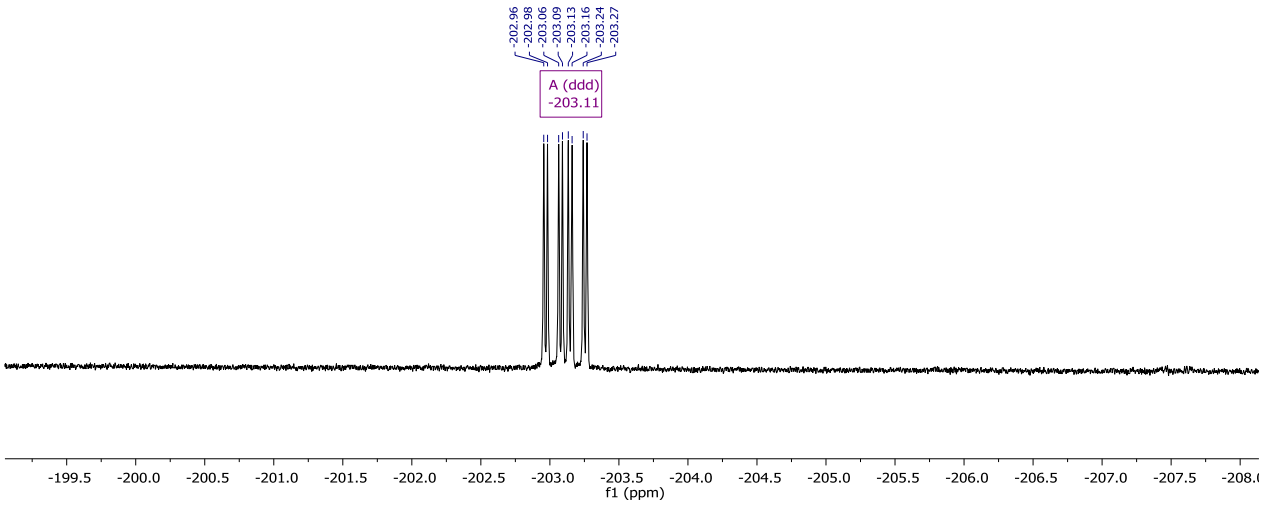

-204.08
-204.11
-204.19
-204.22
-204.26
-204.29
-204.37
-204.39
B (ddd)
-204.24
-223.02
-223.08
-223.12
-223.19
-223.20
-223.26
-223.30
-223.37
A (ddd)
-223.19
f1 (ppm)

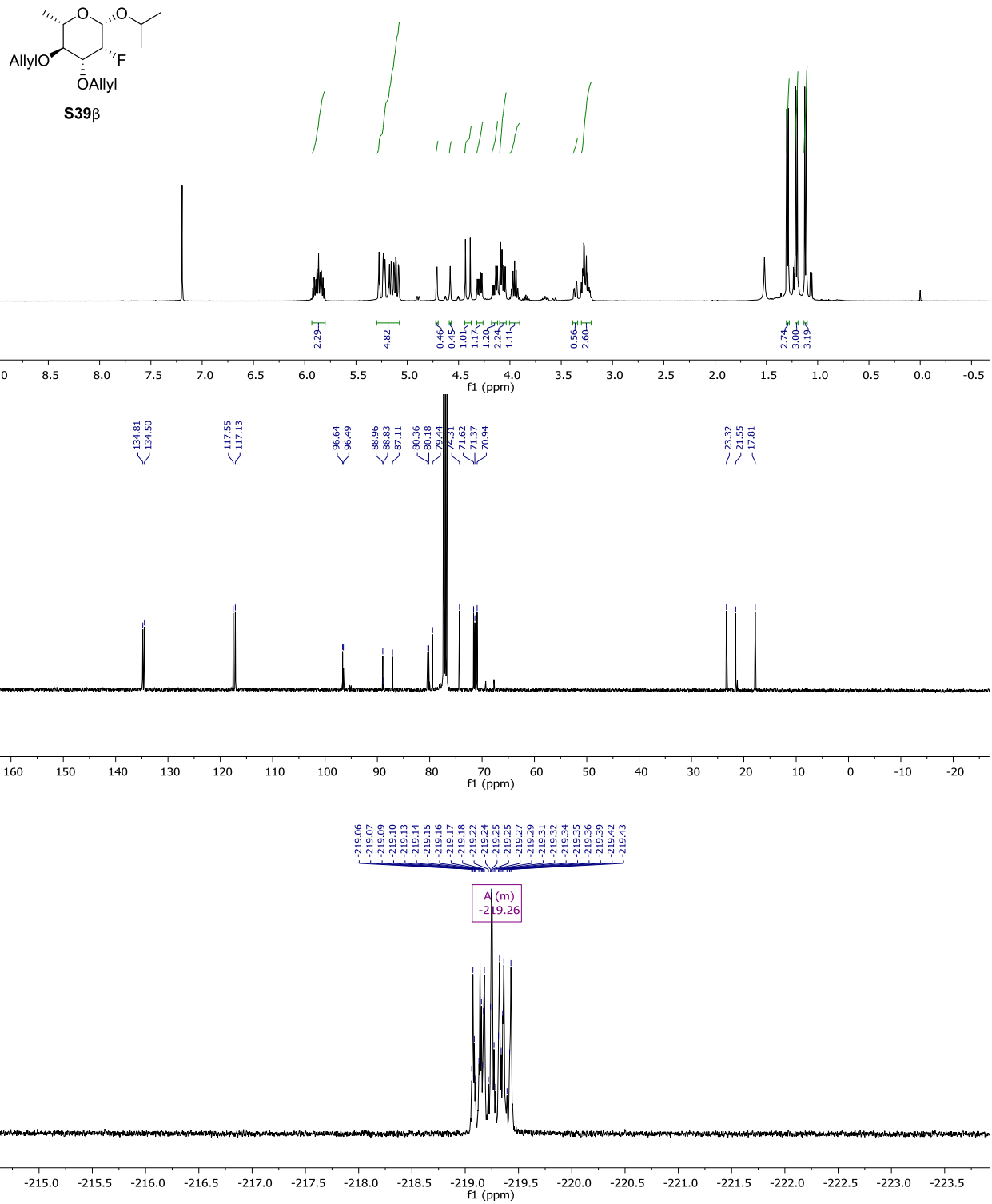

AllylO
O
O
F
OAllyl

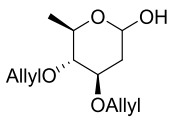
S39α

2.20
2.33
2.16
0.96
0.99
1.15
3.39
1.03
1.46
0.45
1.06
3.00
3.10
2.84
f1 (ppm)

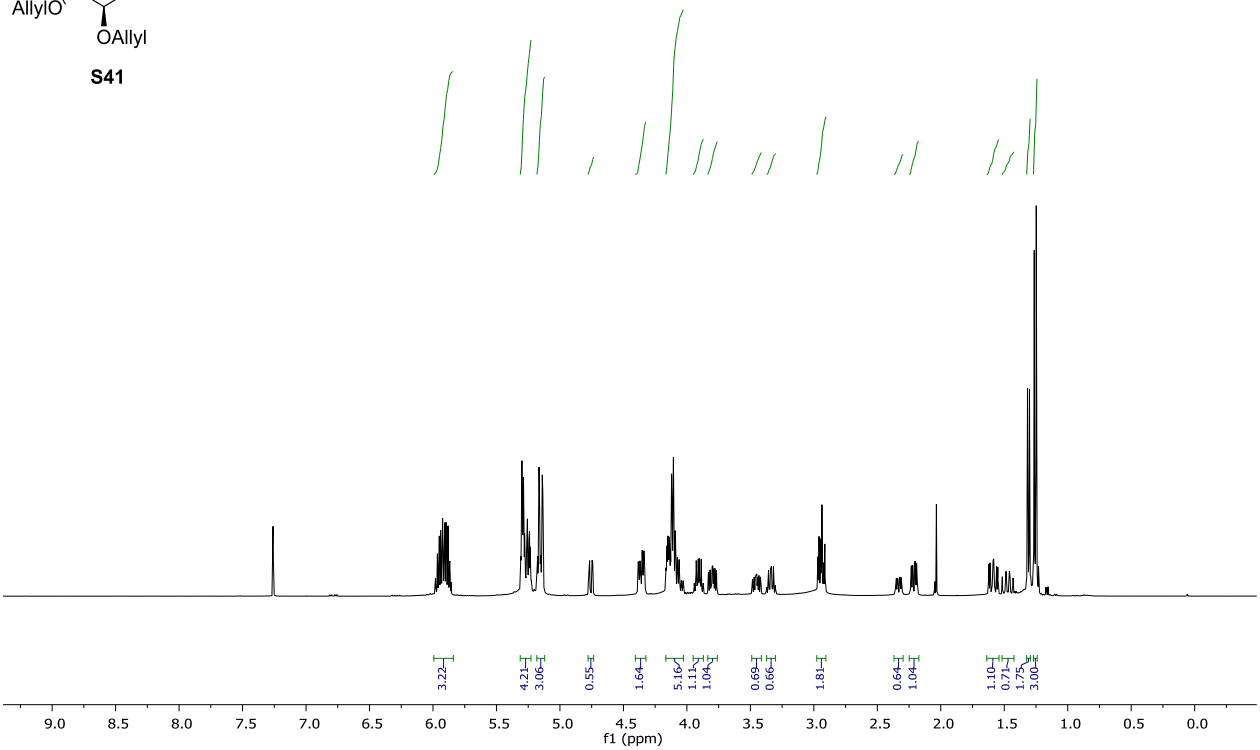

134.89
134.67
117.10
117.07
95.30
95.01
88.83
87.09
80.03
78.17
78.00
74.35
71.34
69.30
67.74
23.16
21.23
17.72
f1 (ppm)

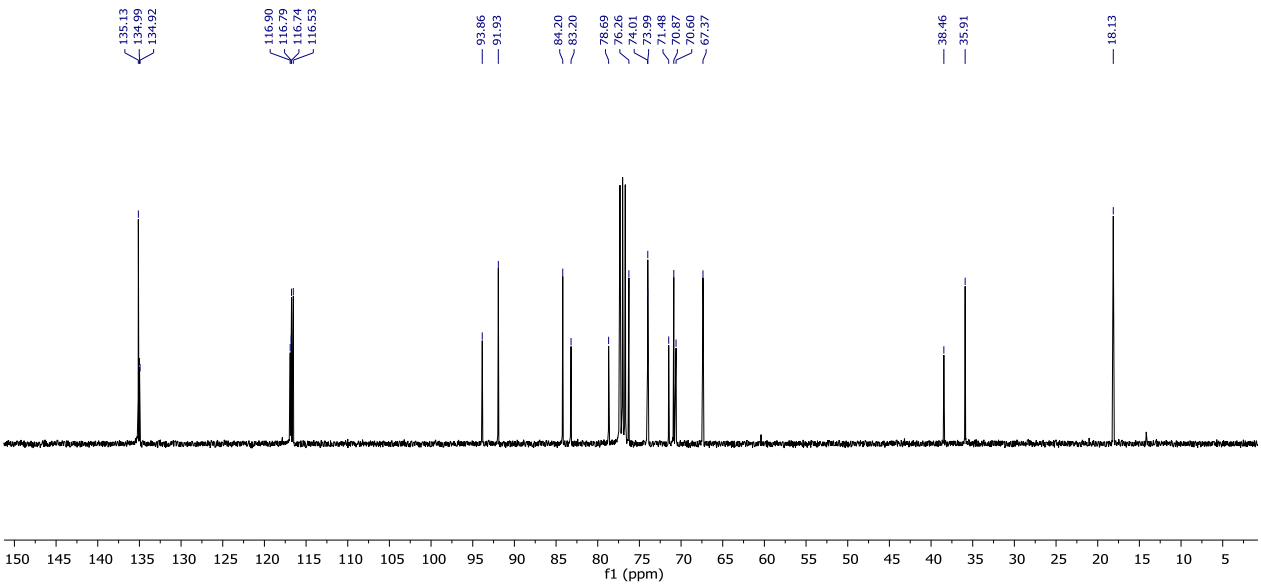

-202.96
-202.98
-203.06
-203.09
-203.13
-203.16
-203.24
-203.27
A (ddd)
-203.11
f1 (ppm)

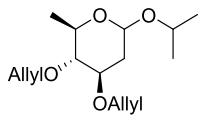

AllylO
O
O
F
OAllyl
S39β
2.29
4.82
0.46
0.45
1.01
1.17
1.20
2.24
1.11
0.56
2.60
2.74
3.00
3.19
f1 (ppm)
134.81
134.50
117.55
117.13
96.64
96.49
88.96
88.83
87.11
80.36
80.18
79.44
74.31
71.62
71.37
70.94
23.32
21.55
17.81
f1 (ppm)
-219.06
-219.07
-219.09
-219.10
-219.13
-219.14
-219.15
-219.16
-219.17
-219.18
-219.22
-219.24
-219.25
-219.25
-219.27
-219.29
-219.31
-219.32
-219.34
-219.35
-219.36
-219.39
-219.42
-219.43
A (m)
-219.26
f1 (ppm)


O
OH
AllylO
OAllyl

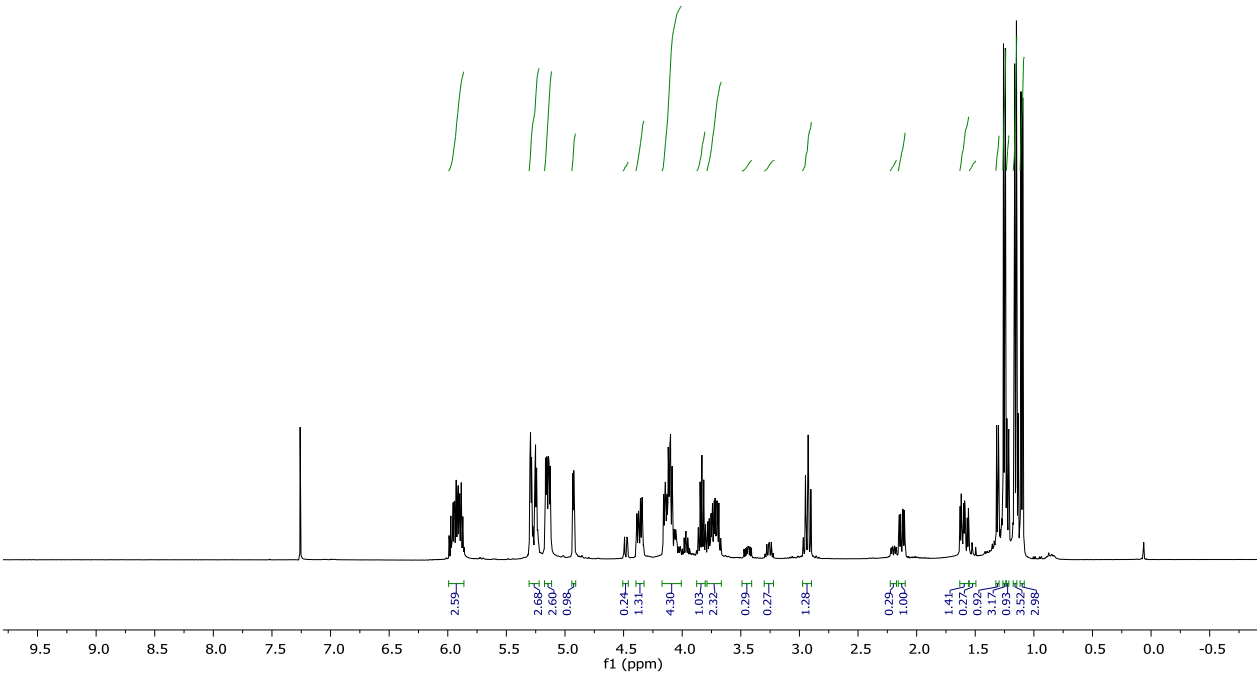
S41

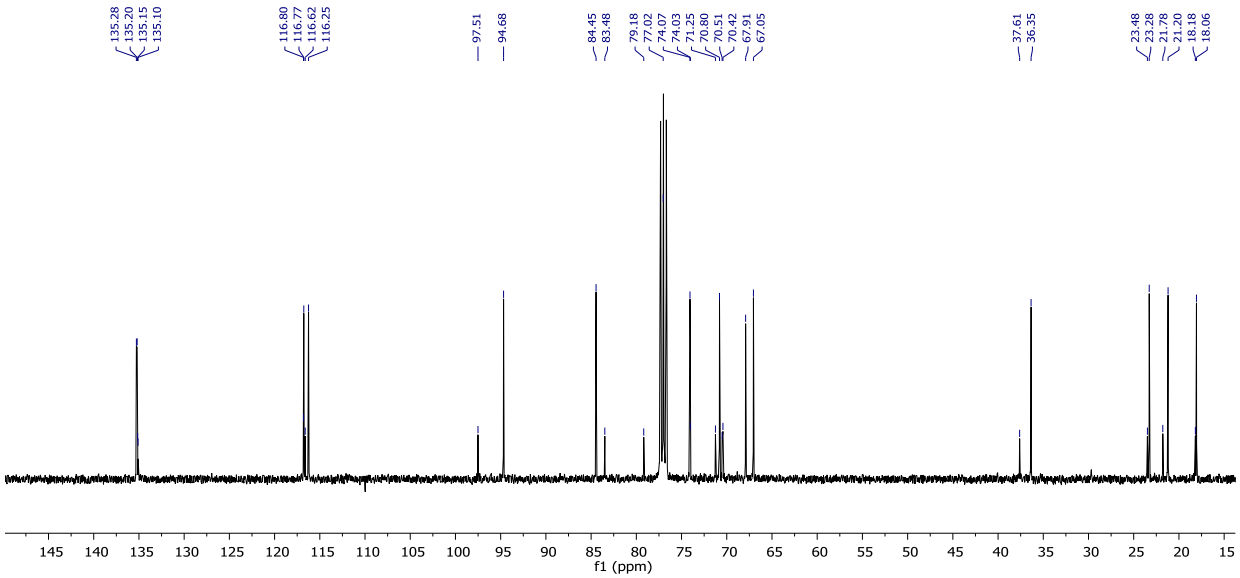

3.22
4.21
3.06
0.55
1.64
5.16
1.11
1.04
0.69
0.66
1.81
0.64
1.04
1.10
0.71
1.75
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

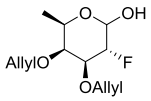

135.13
134.99
134.92
116.90
116.79
116.74
116.53
93.86
91.93
84.20
83.20
78.69
76.26
74.01
73.99
71.48
70.87
70.60
67.37
38.46
35.91
18.13
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)


O
O
AllylO
OAllyl

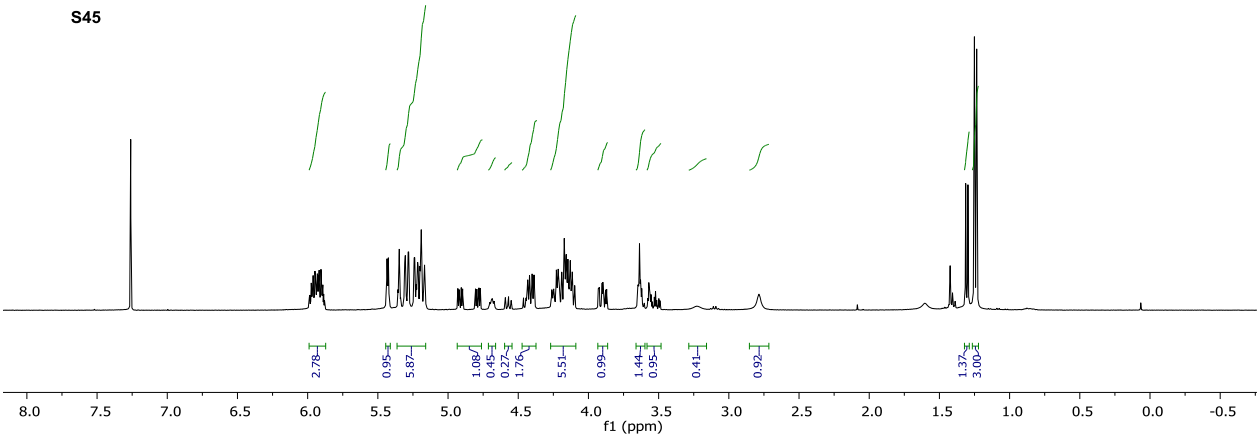
S43

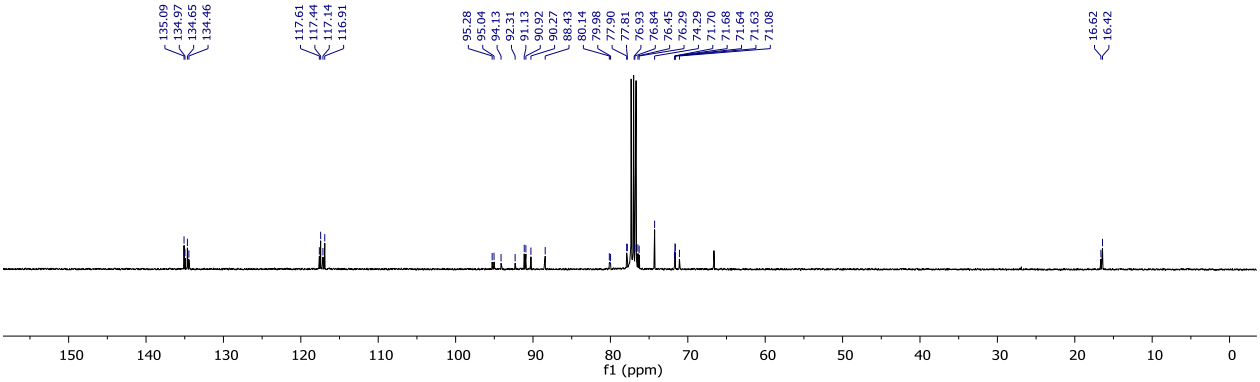

2.59
2.68
2.60
0.98
0.24
1.31
4.30
1.03
2.32
0.29
0.27
1.28
0.29
1.00
1.41
0.27
0.92
3.17
0.93
3.52
2.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

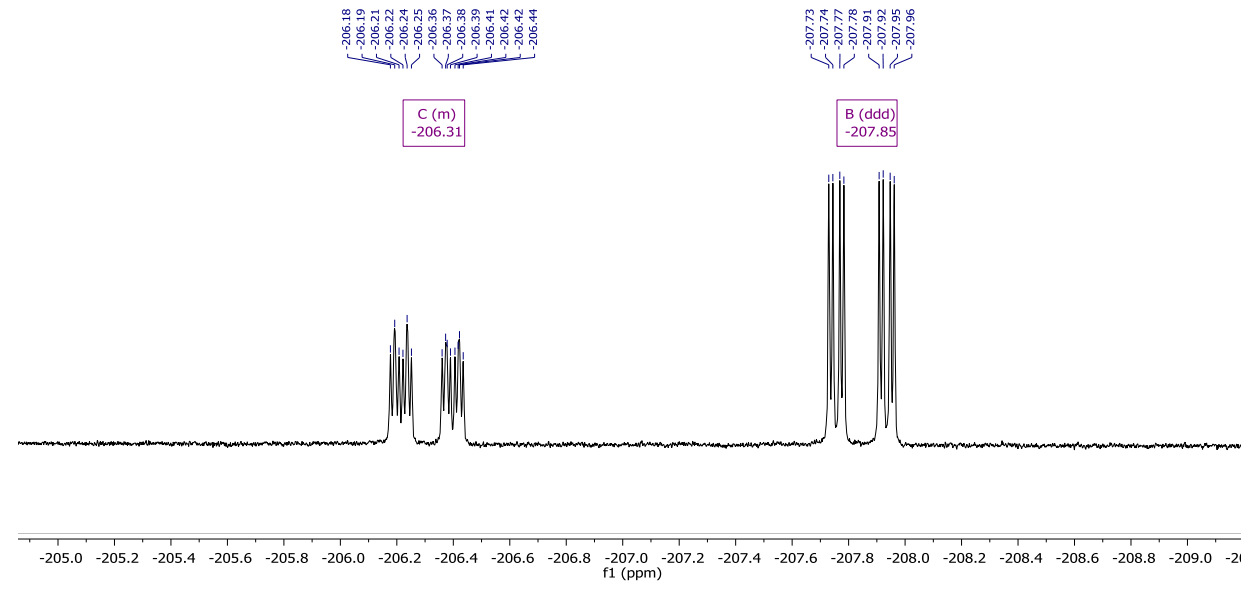

135.28
135.20
135.15
135.10
116.80
116.77
116.62
116.25
97.51
94.68
84.45
83.48
79.18
77.02
74.07
74.03
71.25
70.80
70.51
70.42
67.91
67.05
37.61
36.35
23.48
23.28
21.78
21.20
18.18
18.06
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)

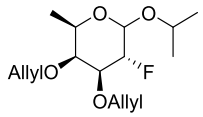

O
OH
AllylO
F
OAllyl

S45


2.78
0.95
5.87
1.08
0.45
0.27
1.76
5.51
0.99
1.44
0.95
0.41
0.92
1.37
3.00
f1 (ppm)

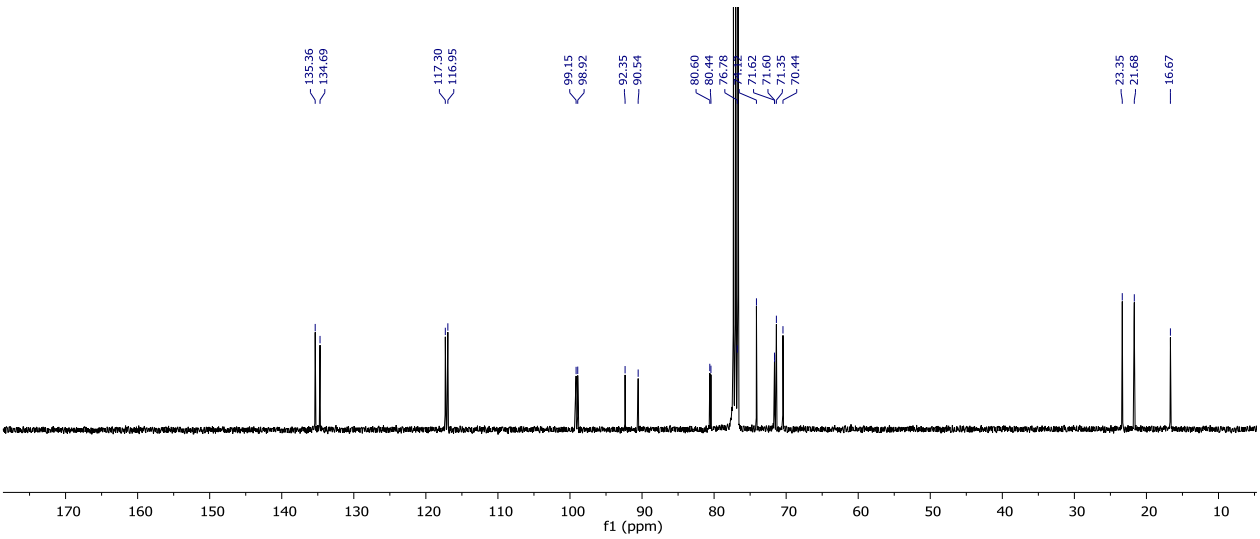

135.09
134.97
134.65
134.46
117.61
117.44
117.14
116.91
95.28
95.04
94.13
92.31
91.13
90.92
90.27
88.43
80.14
79.98
77.90
77.81
76.93
76.84
76.45
76.29
74.29
71.70
71.68
71.64
71.63
71.08
16.62
16.42
f1 (ppm)

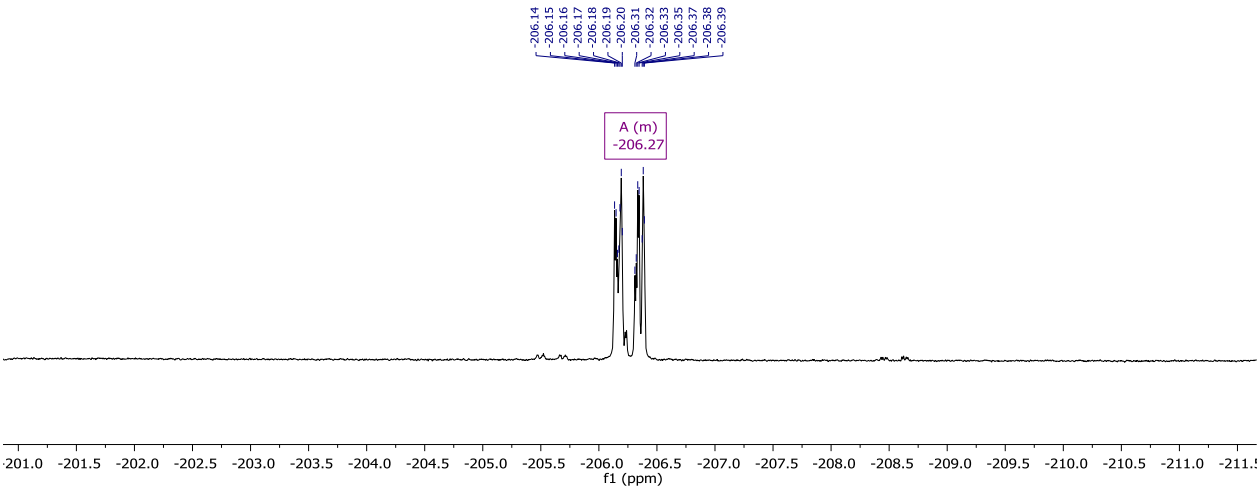

-206.18
-206.19
-206.21
-206.22
-206.24
-206.25
-206.36
-206.37
-206.38
-206.39
-206.41
-206.42
-206.42
-206.44
-207.73
-207.74
-207.77
-207.78
-207.91
-207.92
-207.95
-207.96
C (m)
-206.31
B (ddd)
-207.85
f1 (ppm)

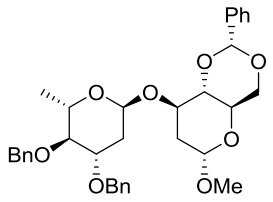

O
O
AllylO
F
OAllyl

S47

2.00
1.07
2.06
1.06
0.49
1.49
1.09
1.11
2.13
1.20
2.88
3.09
2.55
3.03
2.88
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

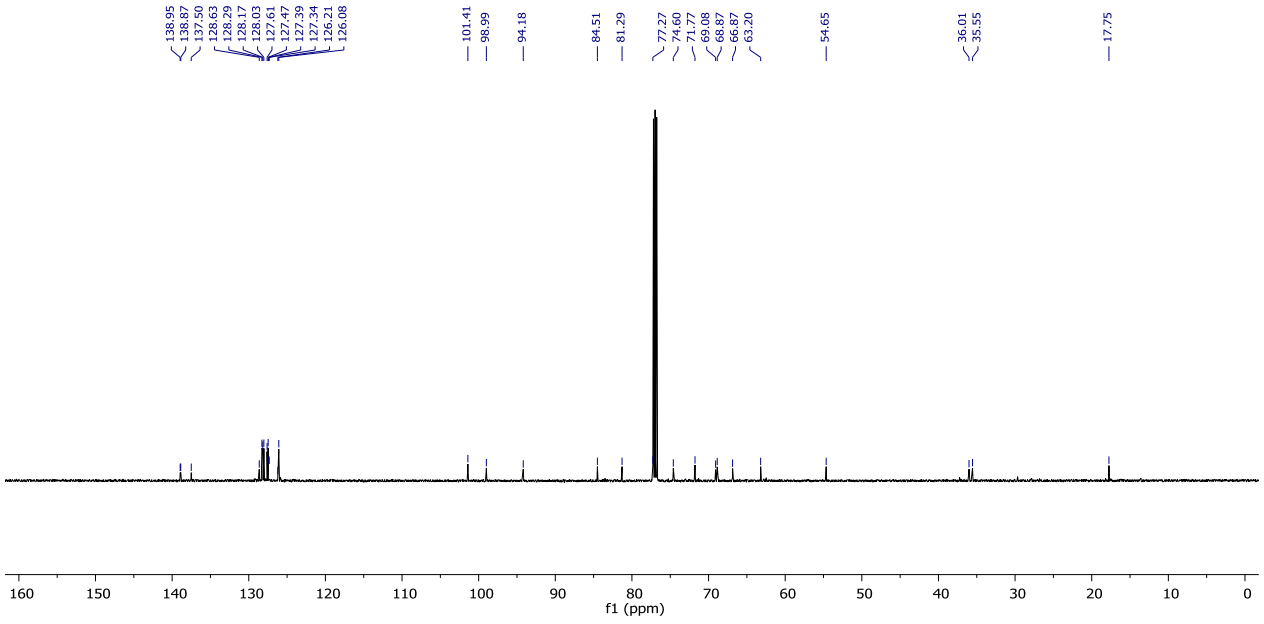

135.36
134.69
117.30
116.95
99.15
98.92
92.35
90.54
80.60
80.44
76.78
71.62
71.60
71.35
70.44
23.35
21.68
16.67
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

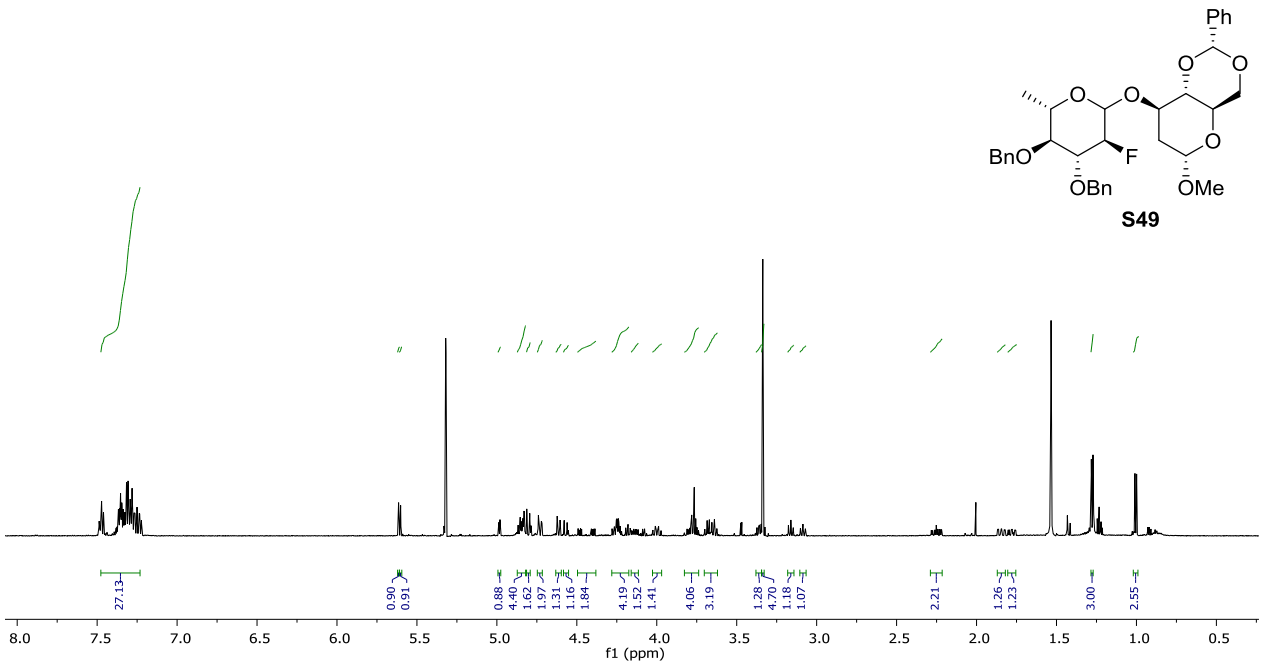

-206.14
-206.15
-206.16
-206.17
-206.18
-206.19
-206.20
-206.31
-206.32
-206.33
-206.35
-206.37
-206.38
-206.39
A (m)
-206.27
-201.0 -201.5 -202.0 -202.5 -203.0 -203.5 -204.0 -204.5 -205.0 -205.5 -206.0 -206.5 -207.0 -207.5 -208.0 -208.5 -209.0 -209.5 -210.0 -210.5 -211.0
f1 (ppm)


Ph
O
O
O
O
O
BnO
OBn
OMe

S48

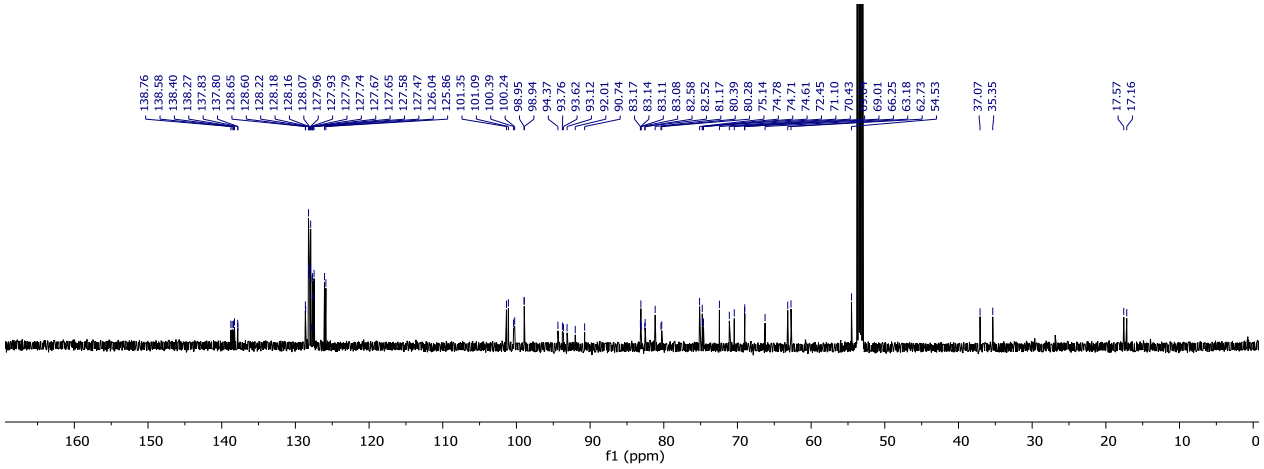
1.92
15.13
1.00
0.89
0.91
0.90
1.28
1.11
1.25
1.26
1.16
1.13
1.01
1.22
1.11
2.49
1.04
2.10
2.22
2.70
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

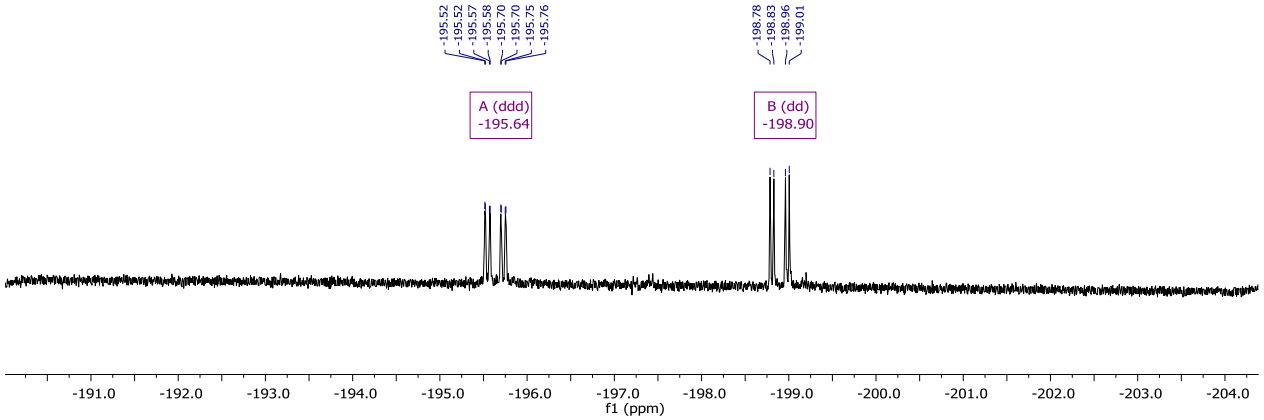

138.95
138.87
137.50
128.63
128.29
128.17
128.03
127.61
127.47
127.39
127.34
126.21
126.08
101.41
98.99
94.18
84.51
81.29
77.27
74.60
71.77
69.08
68.87
66.87
63.20
54.65
36.01
35.55
17.75
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

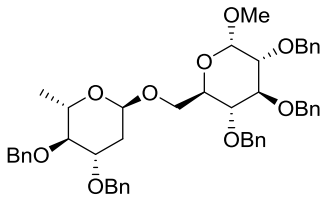

Ph
O
O
O
O
O
BnO
F
OBn
OMe

S49

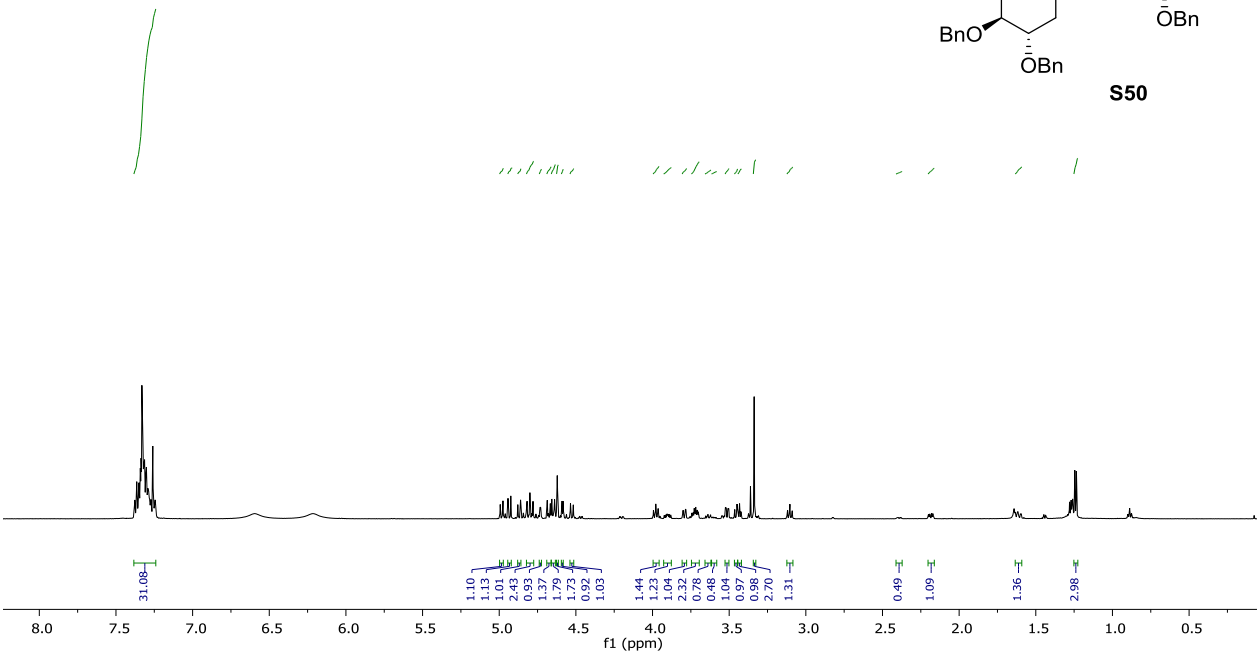
27.13
0.90
0.91
0.88
4.40
1.62
1.97
1.31
1.16
1.84
4.19
1.52
1.41
4.06
3.19
1.28
4.70
1.18
1.07
2.21
1.26
1.23
3.00
2.55
f1 (ppm)

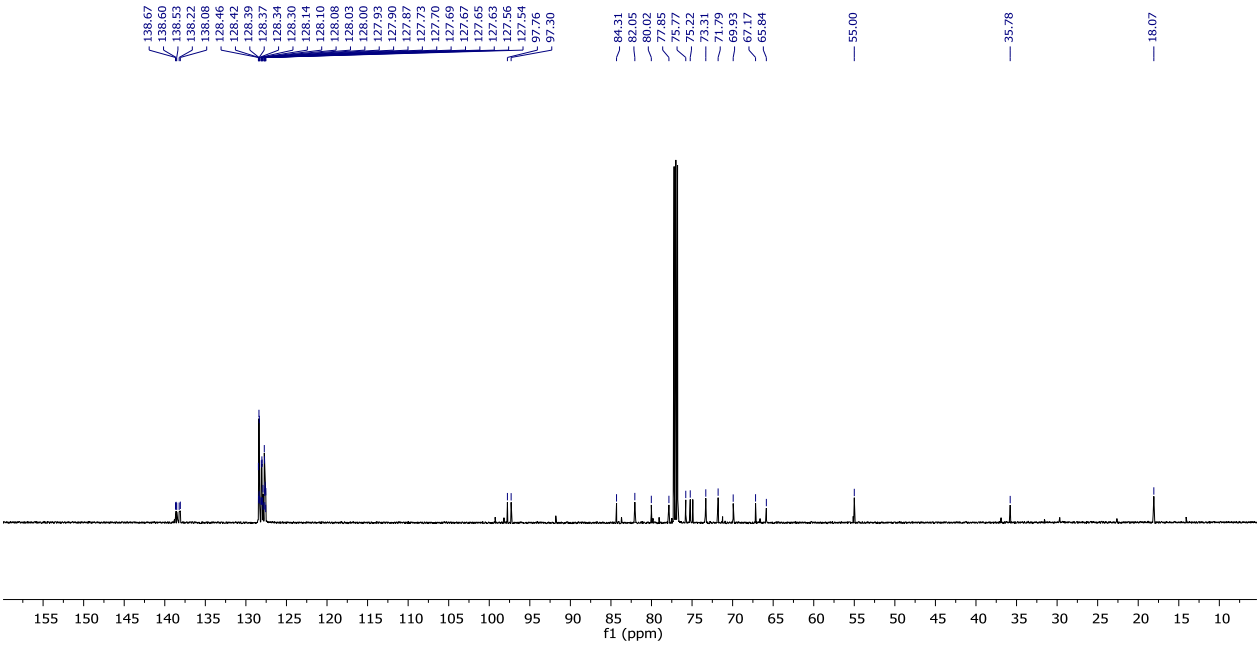

138.76
138.58
138.40
138.27
137.83
137.80
128.65
128.60
128.22
128.18
128.16
128.07
127.96
127.93
127.79
127.74
127.67
127.65
127.58
127.47
126.04
125.86
101.35
101.09
100.39
100.24
98.95
98.94
94.37
93.76
93.62
93.12
92.01
90.74
83.17
83.14
83.11
83.08
82.58
82.52
81.17
80.39
80.28
75.14
74.78
74.71
74.61
72.45
71.10
70.43
69.01
66.25
63.18
62.73
54.53
37.07
35.35
17.57
17.16
f1 (ppm)

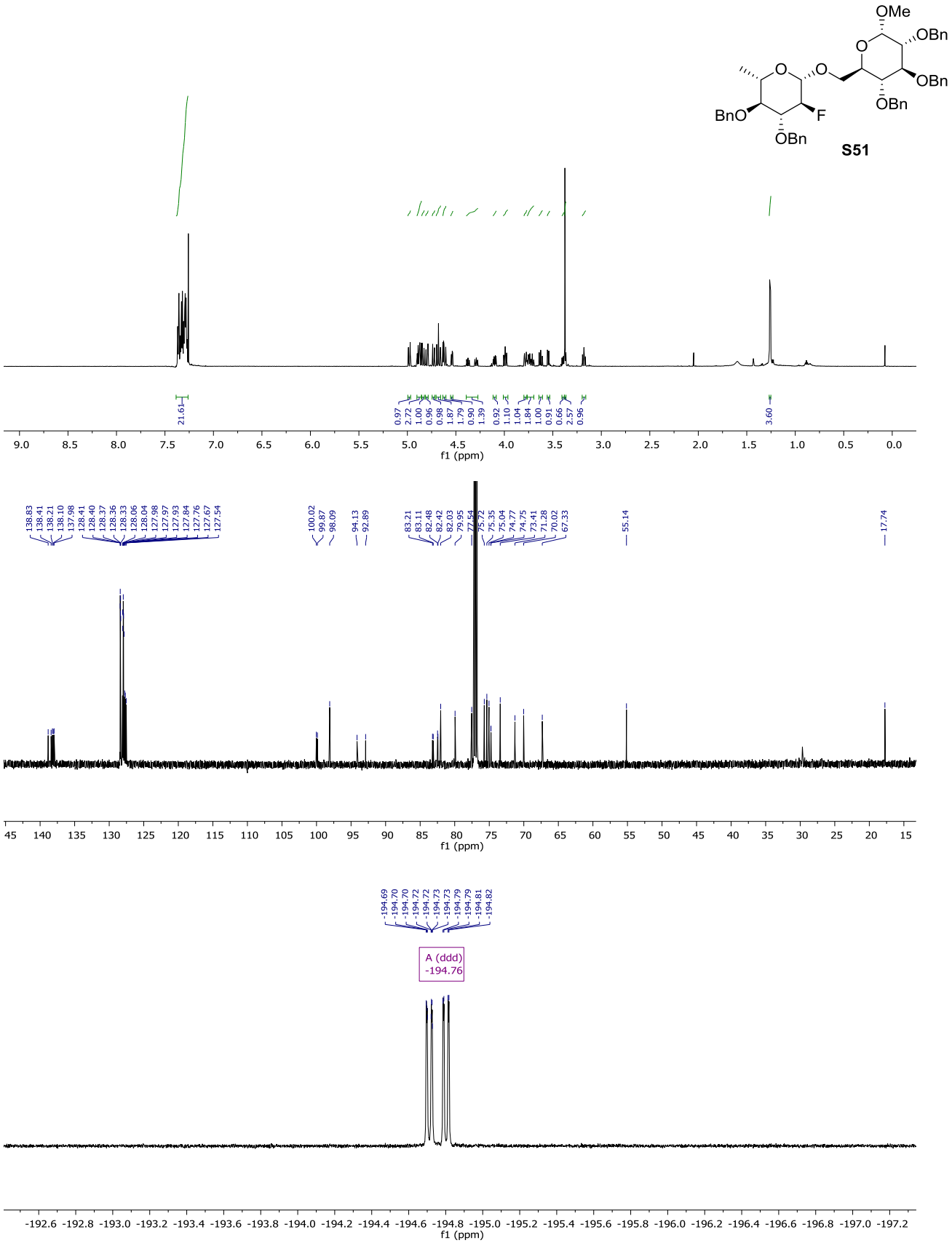

-195.52
-195.52
-195.57
-195.58
-195.70
-195.70
-195.75
-195.76
-198.78
-198.83
-198.96
-199.01
A (ddd)
-195.64
B (dd)
-198.90
f1 (ppm)


OMe
OBn
OBn
OBn
BnO
OBn

S50


31.08
1.10
1.13
1.01
2.43
0.93
1.37
1.79
1.73
0.92
1.03
1.44
1.23
1.04
2.32
0.78
0.48
1.04
0.97
0.98
2.70
1.31
0.49
1.09
1.36
2.98
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


138.67
138.60
138.53
138.22
138.08
128.46
128.42
128.39
128.37
128.34
128.30
128.14
128.10
128.08
128.03
128.00
127.93
127.90
127.87
127.73
127.70
127.69
127.67
127.65
127.63
127.56
127.54
97.76
97.30
84.31
82.05
80.02
77.85
75.77
75.22
73.31
71.79
69.93
67.17
65.84
55.00
35.78
18.07
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)


OMe
OBn
OBn
OBn
BnO
F
OBn
S51
f1 (ppm)
f1 (ppm)
A (ddd)
-194.76
f1 (ppm)

Selected ^{1}H and ^{19}F-NMR of glycosylation crudes

Table 2, entry 9

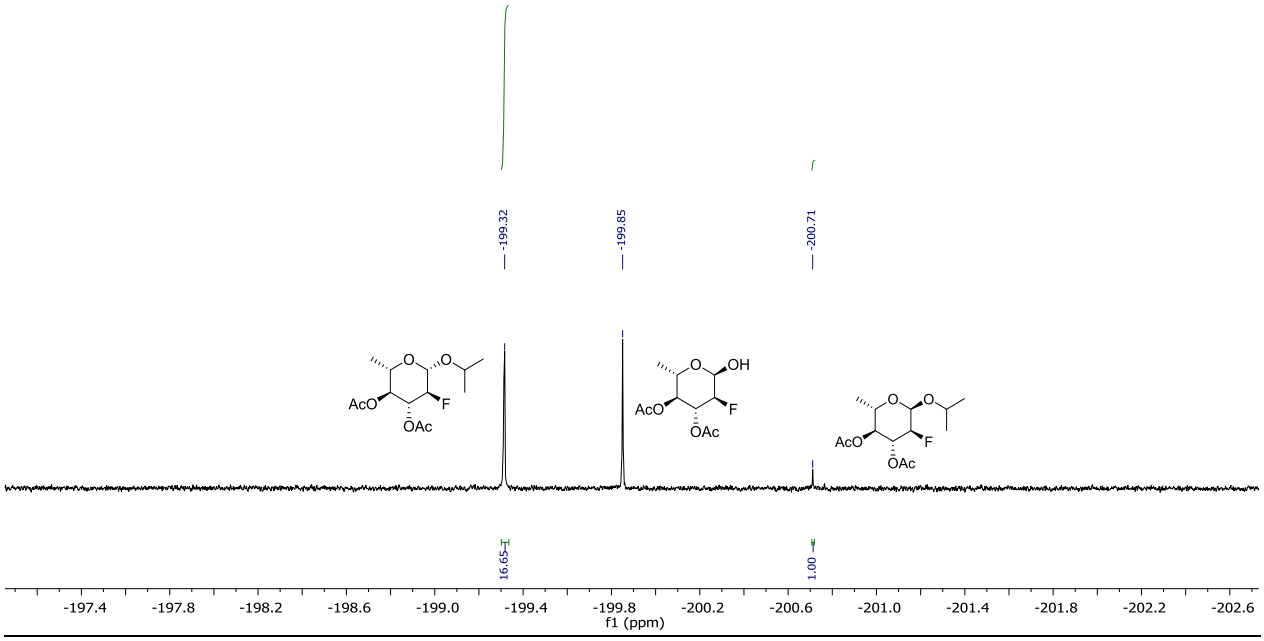


Table 2, entry 10

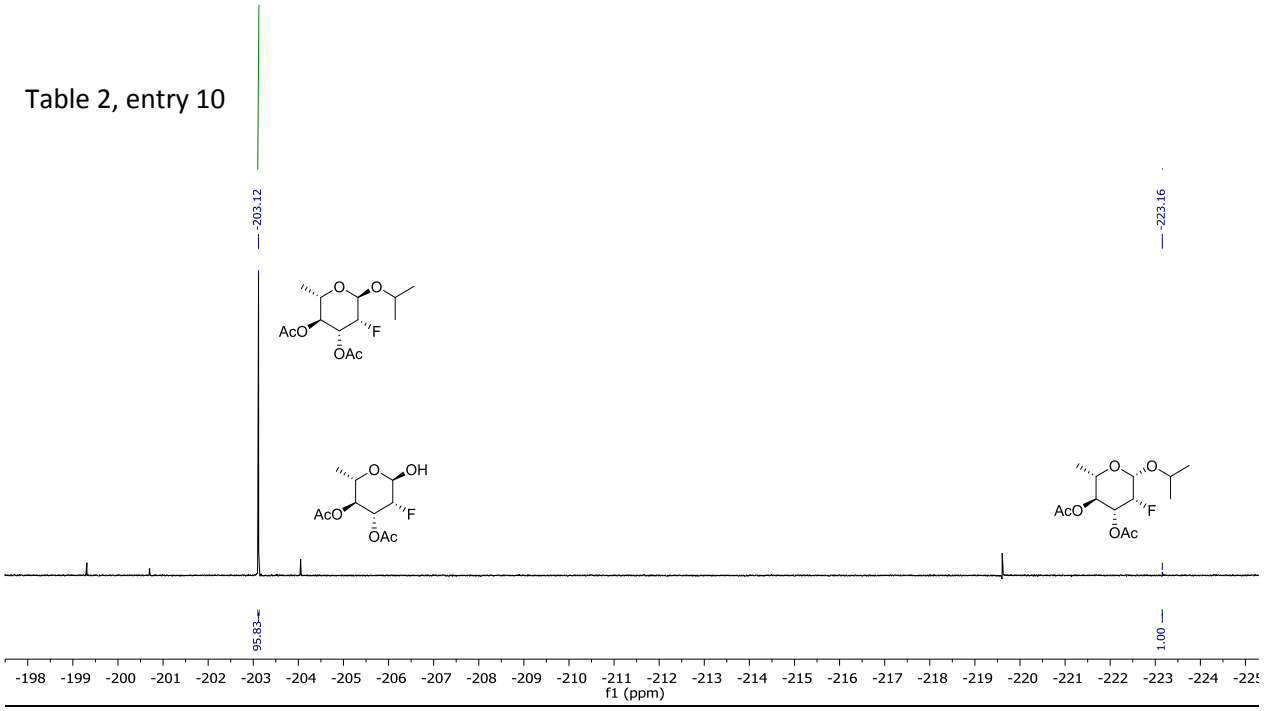


Table 2, entry 12

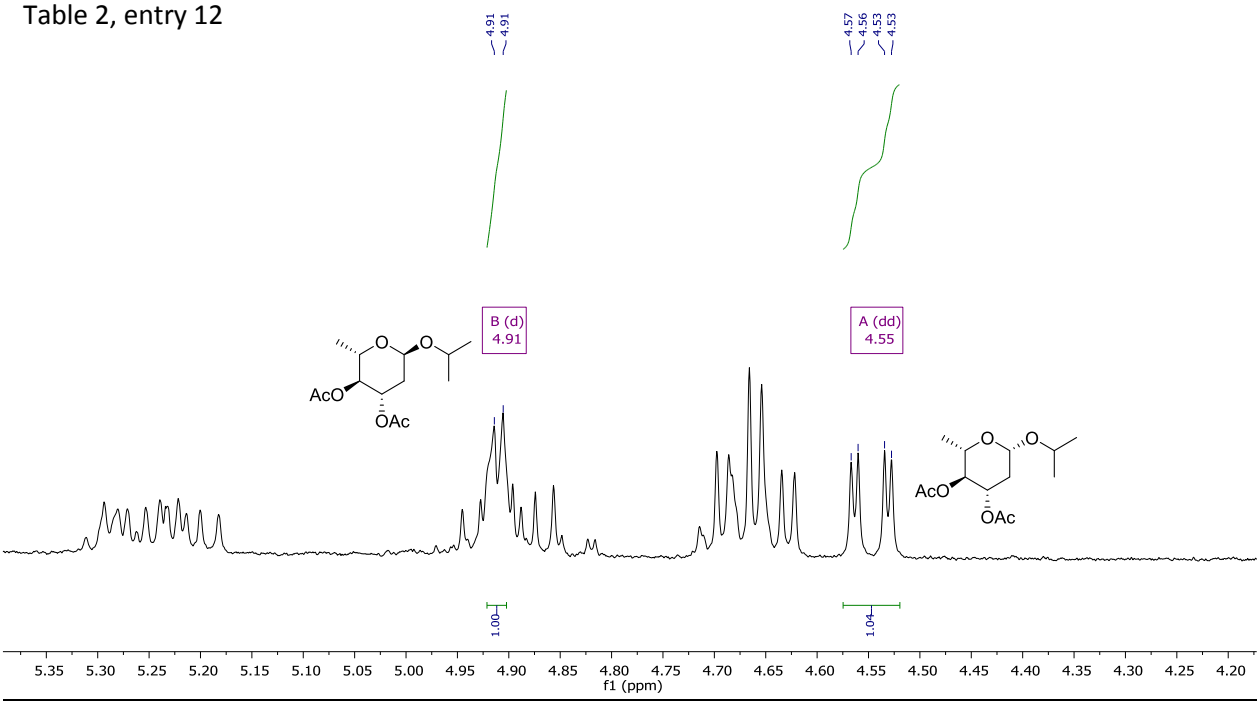


Table 2, entry 11

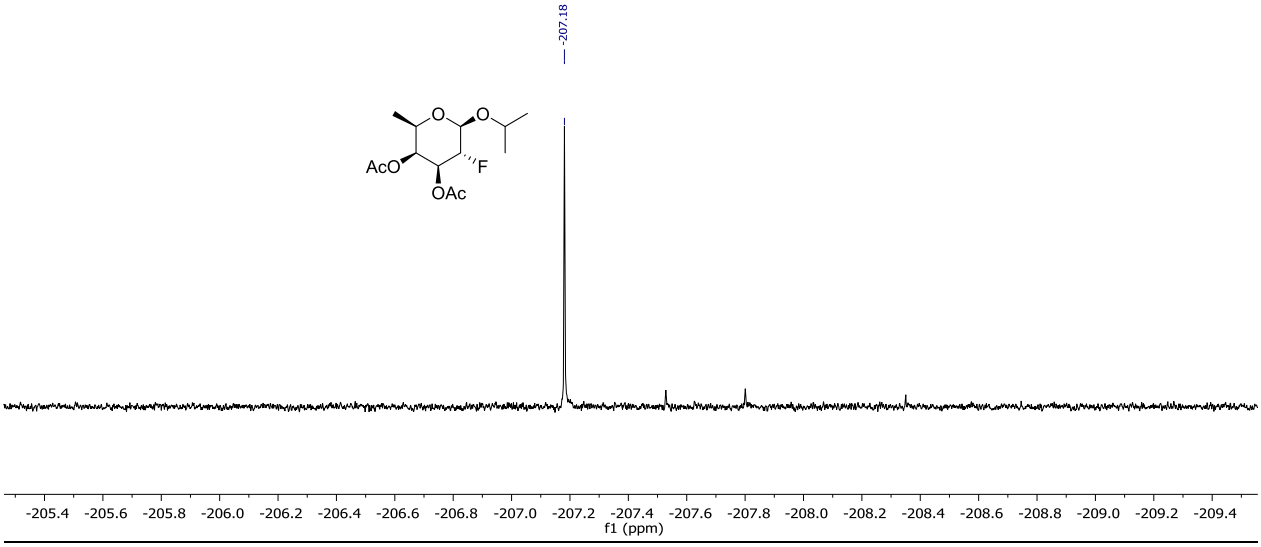


Table 2, entry 1

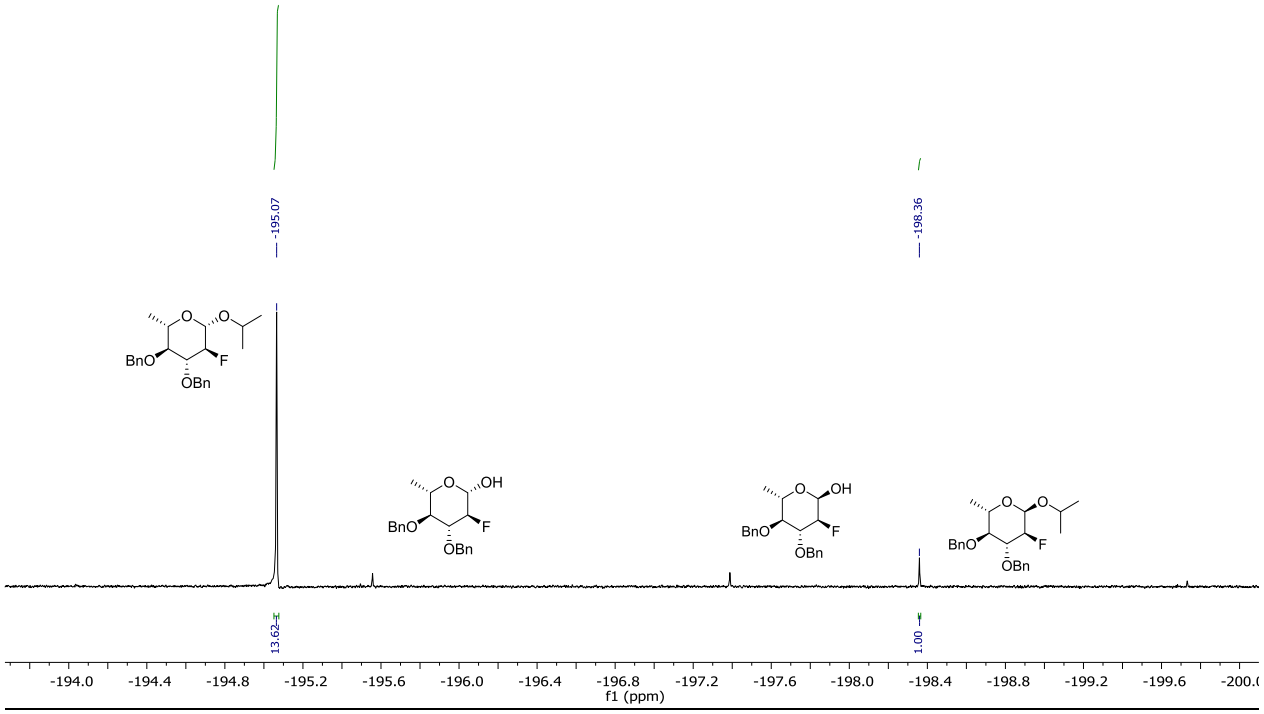


Table 2, entry 2

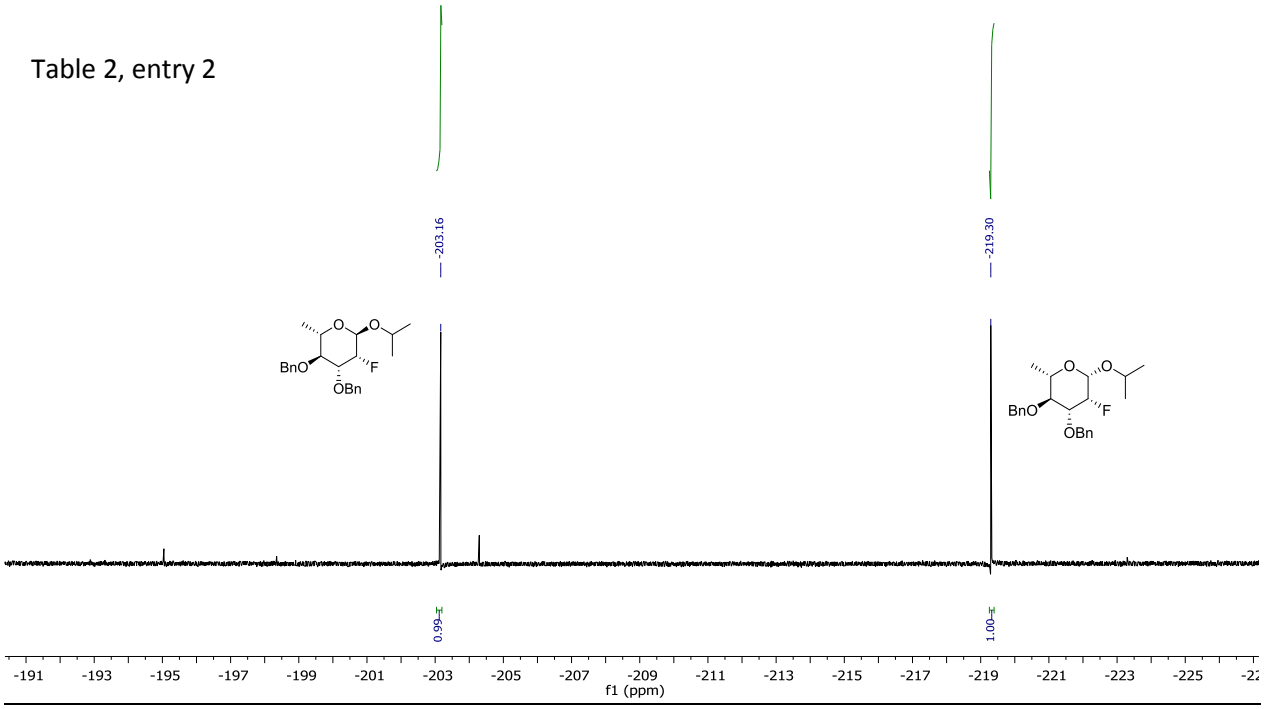


Table 2, entry 4

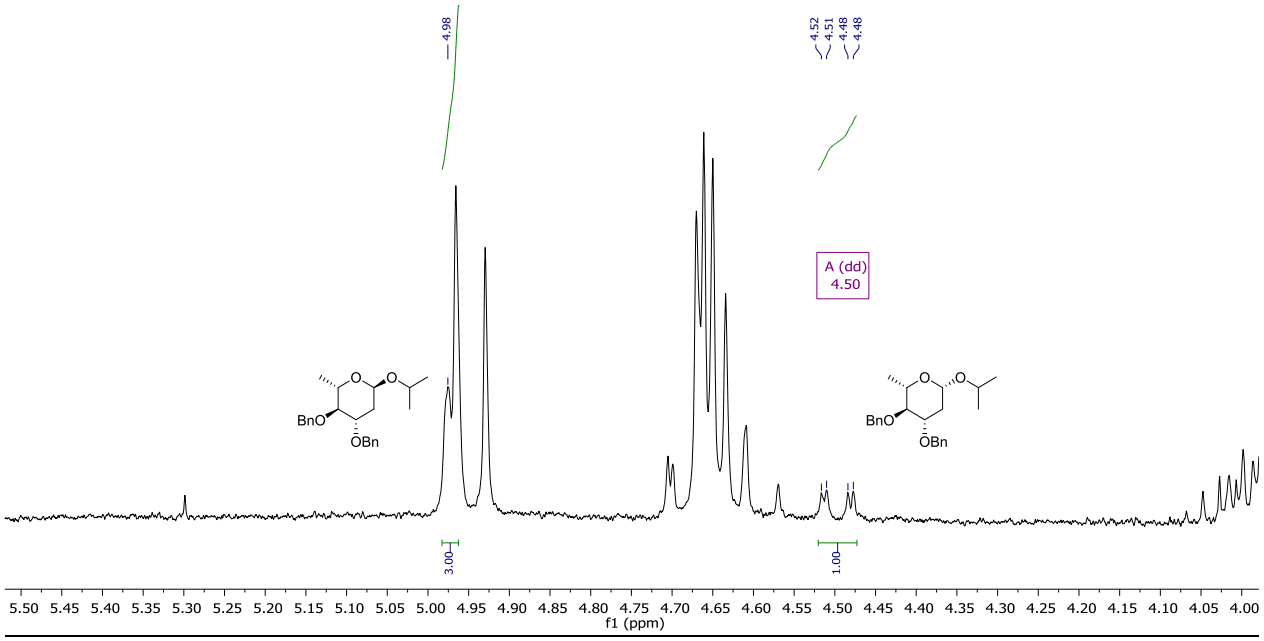
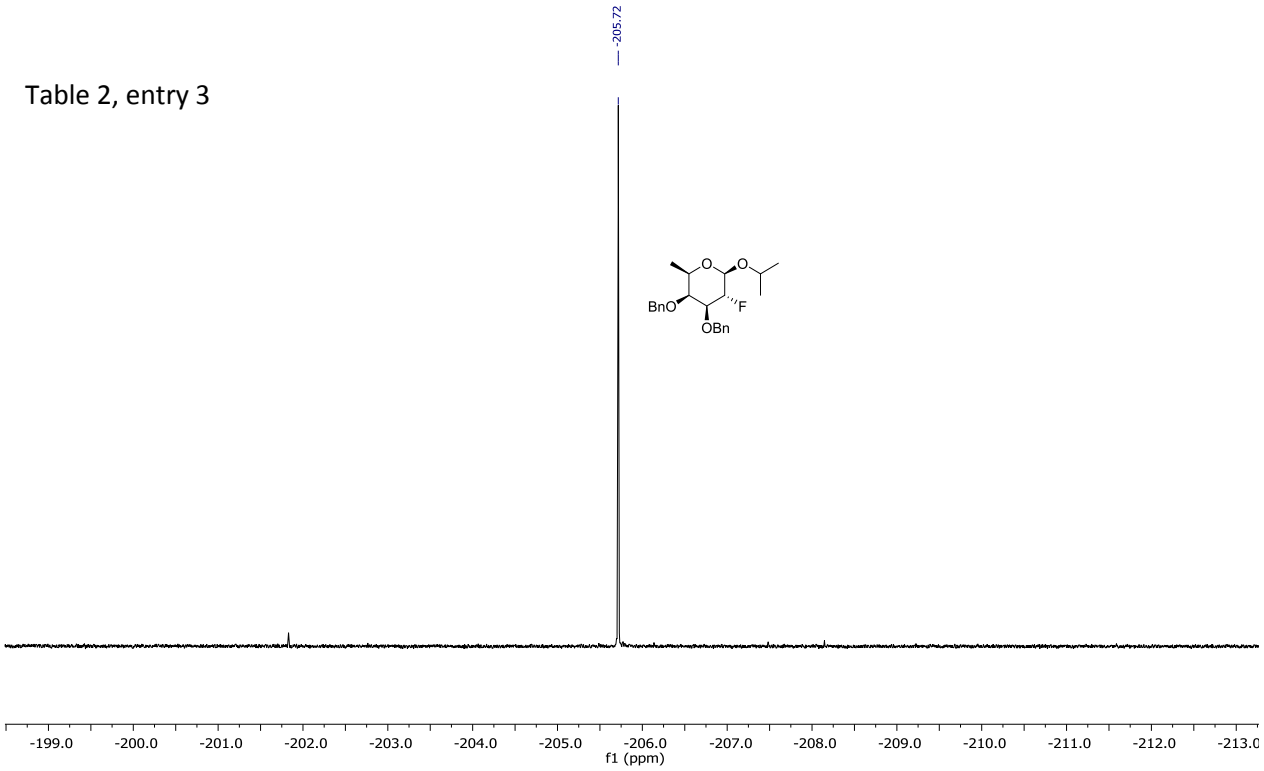


Table 2, entry 3



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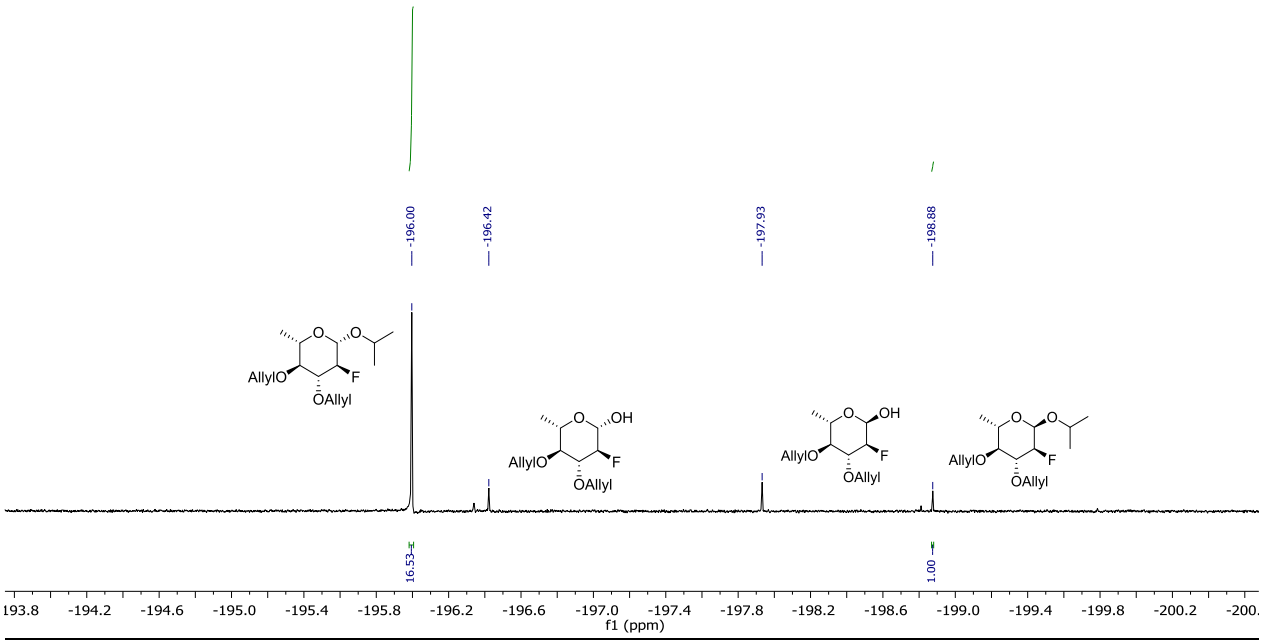

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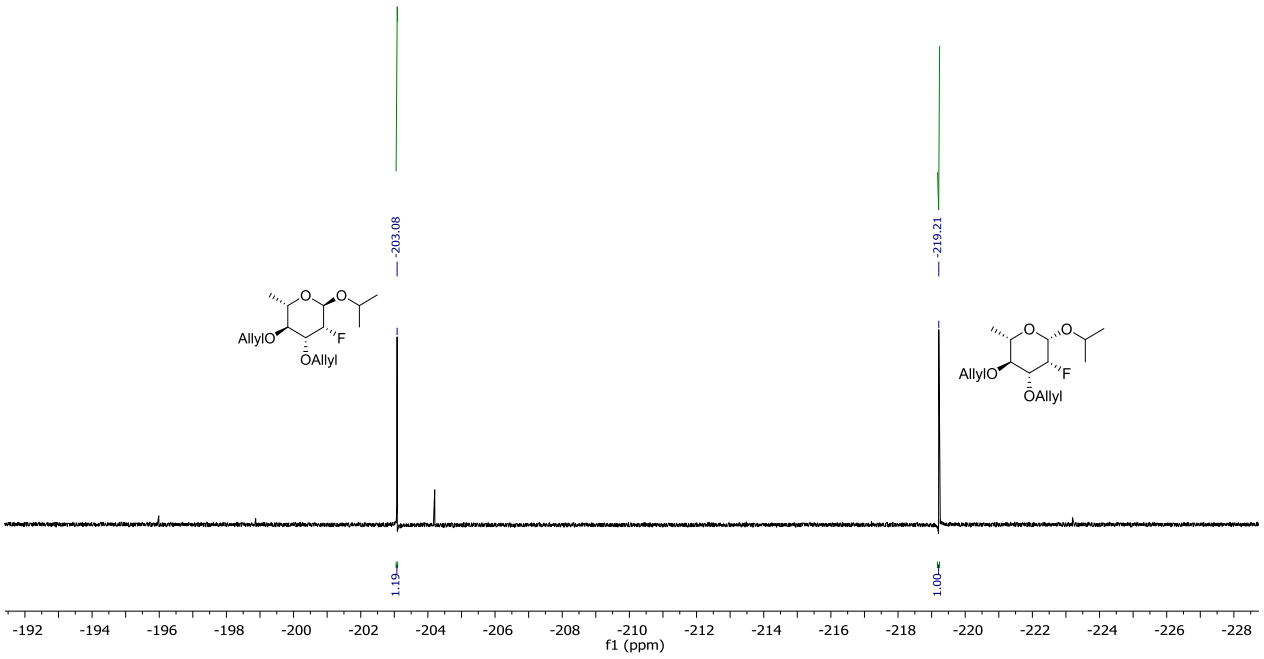

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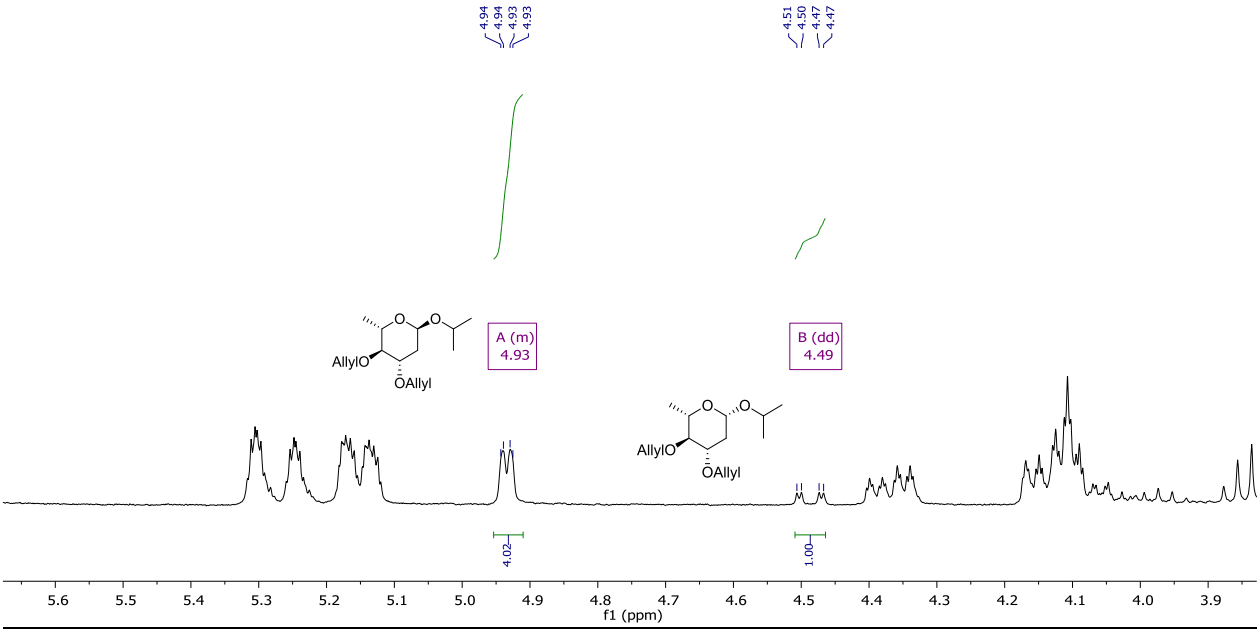

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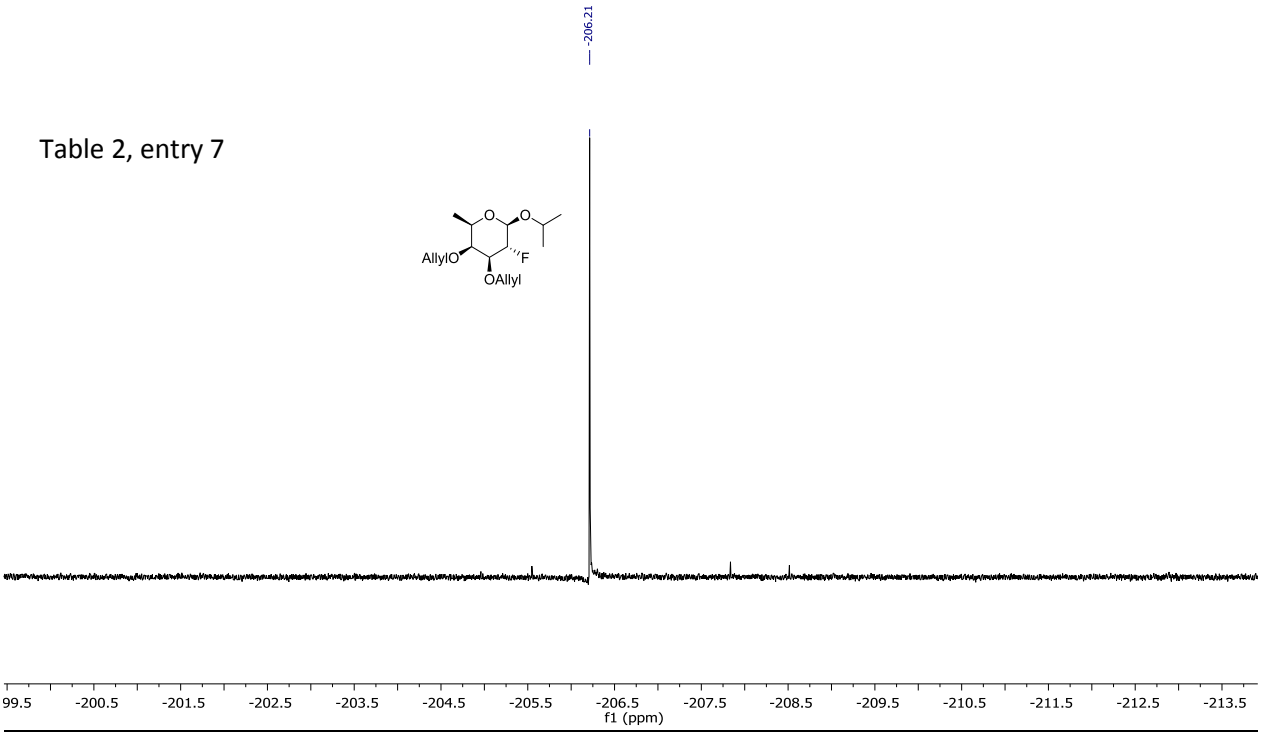
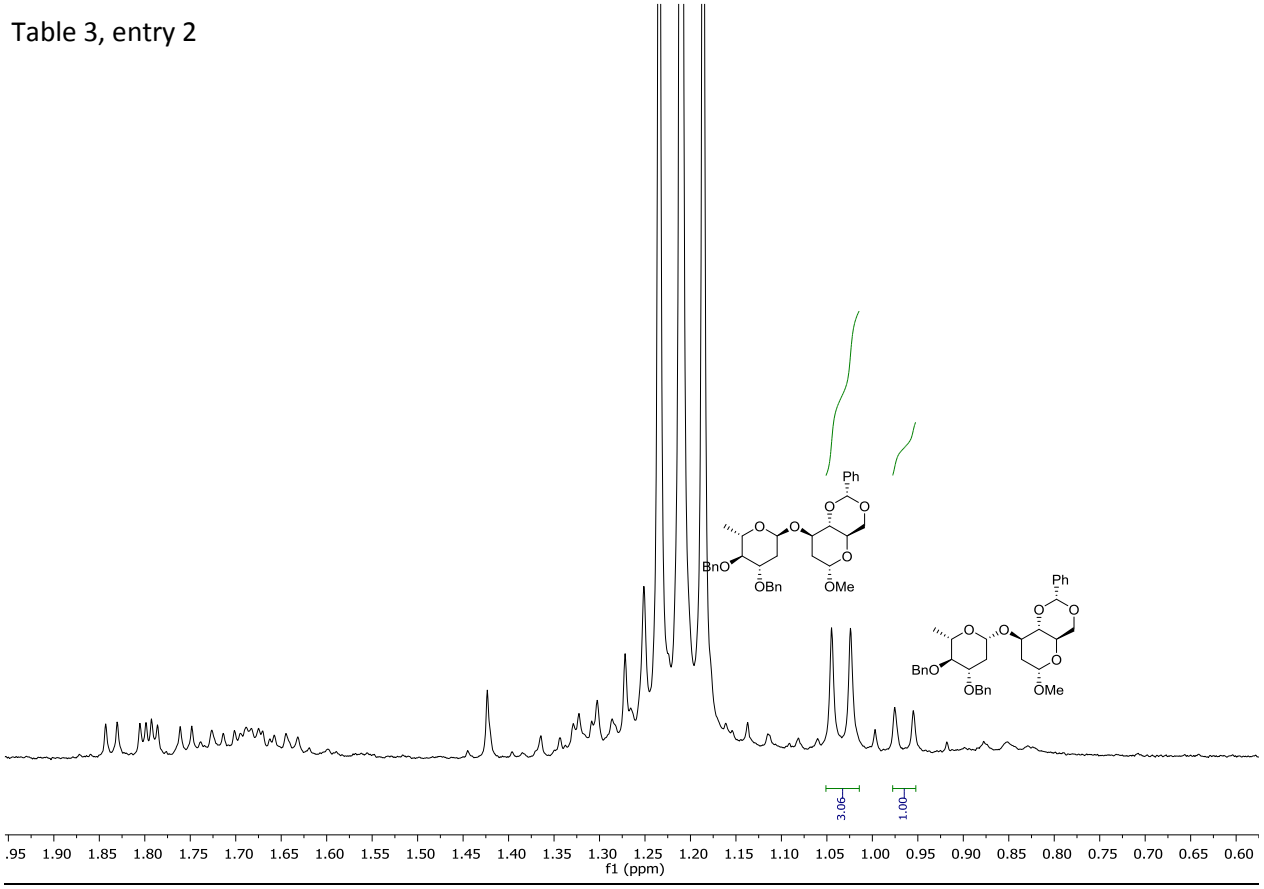


Table 3, entry 2



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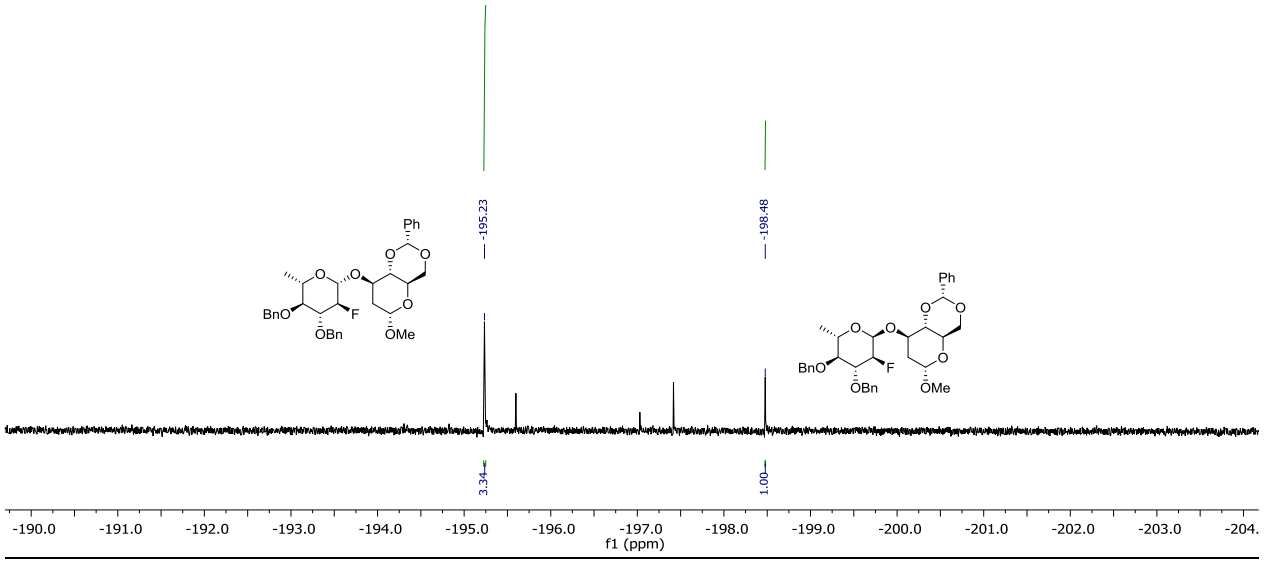

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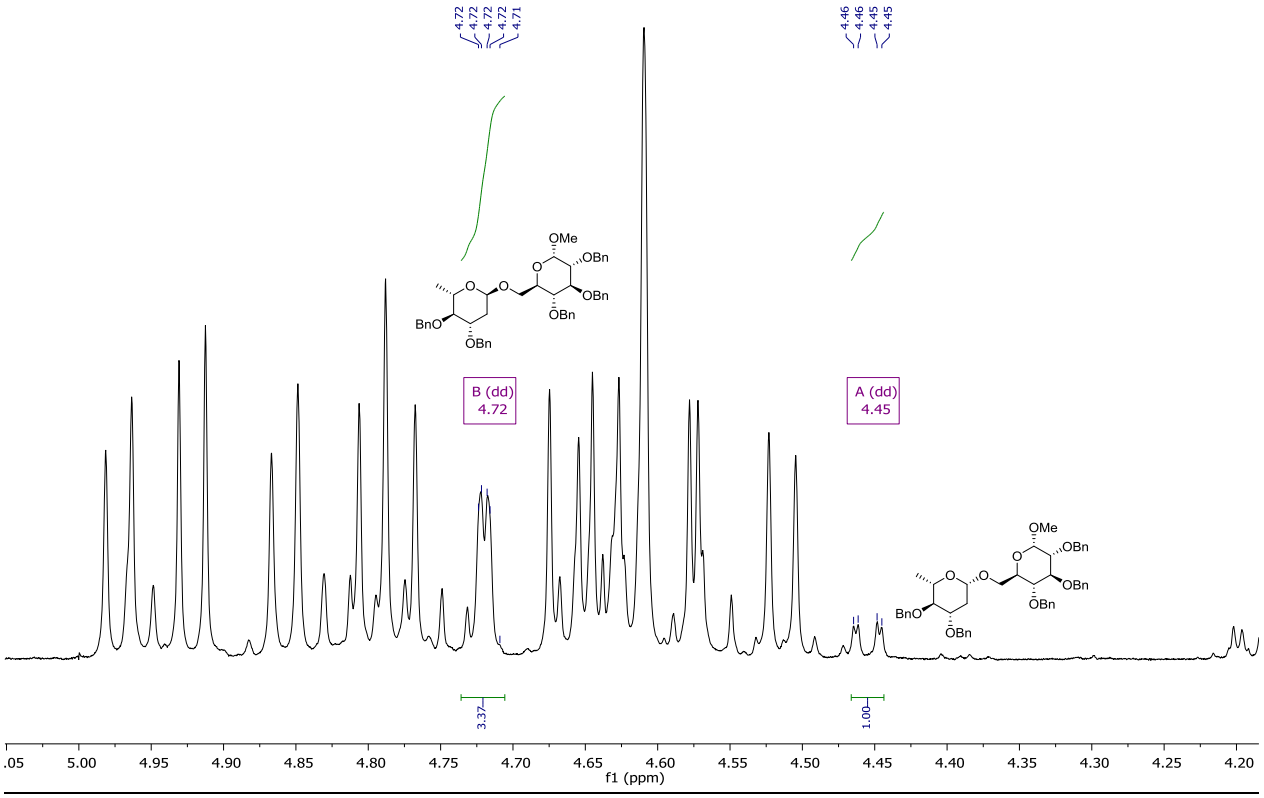

Table 3, entry 3