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

Supporting Information

Synthesis of fluoro- and seleno-containing D-lactose and D-galactose analogues

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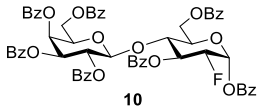
Experimental

General methods

Unless otherwise noted all reactions containing air- and moisture-sensitive reagents were carried out under an inert atmosphere of nitrogen in oven-dried glassware with magnetic stirring. All chemicals for the synthesis were purchased from commercial suppliers (and used without purification. Anhydrous CH_2Cl_2 and THF were obtained from a PureSolv-EN^{TM} solvent purification system (Innovative Technology Inc.). All other anhydrous solvents were used as purchased from Sigma-Aldrich in AcroSeal® bottles.
All reactions were monitored by thin-layer chromatography (TLC) on Merck DC-Alufolien plates precoated with silica gel 60 F254. Visualisation was performed with UV-light (254 nm) fluorescence quenching, and/or by staining with an 8% H_2SO_4 dip. Evaporation *in vacuo*/under vacuum refers to the removal at 40 °C, unless otherwise stated, of volatiles on a Buchi rotary evaporator with integrated vacuum pump. Silica gel flash column chromatography was carried out using *Davisil LC60A* (40-63 µm) silica gel or with automated flash column chromatography systems, Buchi Reveleris® X2 (UV 200-500 nm and ELSD detection, Reveleris® silica cartiges 40 µm, BÜCHI Labortechnik AG) and Biotage® SP4 HPFC (UV 200-500 nm, Biotage® SNAP KP-Sil 50 µm irregular silica, Biotage AB). ^{1}H NMR (400 or 500 MHz), ^{13}C NMR (101 MHZ or 126 MHz), ^{19}F NMR (376 or 470 MHz) spectra were recorded on Varian-inova spectrometers at 25 °C in chloroform-d1 ($CDCl_3$) or methanol-d4 (CD_3OD). ^{1}H NMR spectra were standardised against the residual solvent peak ($CDCl_3$, δ = 7.26 ppm; CD_3OD). ^{13}C NMR spectra were standardised against the residual solvent peak ($CDCl_3$, δ = 77.16 ppm; CD_3OD, δ = 49.00 ppm) All ^{19}F NMR are ^{13}C decoupled and ^{1}H coupled. All NMR data is represented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = doublet of doublets of doublets, dt = doublet of triplets, m = multiplet, br = broad signal, *a*d = apparent doublet, *a*t = apparent triplet), coupling constant in Hz, integration. Assignments were aided by homonuclear ^{1}H–^{1}H (COSY, TOCSY), and ^{1}H–^{13}C heteronuclear (HSQC, HMBC) two-dimensional correlation spectroscopies. ^{13}C chemical shifts were reported with one digit after the decimal point, unless an additional digit was reported to distinguish overlapping peaks. High-resolution mass spectrometry (HRMS) data were recorded on a Waters micromass LCT LC-Tof instrument using electrospray ionisation (ESI) in either positive or negative mode. Optical rotations were recorded on Perkin-Elmer polarimeter (Model 343) at the sodium D-line (589 nm) at 20 °C using a 1 dm cell. Samples were prepared at the concentration (g/mL) in the solvent indicated. Deprotected sugars were lyophilised using a freeze-dryer Alpha 1-2 LDplus (Christ Ltd). Pressure: 0.035 mbar; ice condenser temperature: –55 °C.

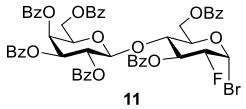
2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopranosyl-(1→4)-1,3,6-di-*O*-benzoyl-2-deoxy-2-fluoro-α-D-glucopyranoside (10)



10

SelectFluor (489.0 mg, 1.38 mmol) was added to a solution of **9** (1.00 g, 1.15 mmol) in $MeNO_2/H_2O$ (10 mL, 5:1) and the mixture was left stirring at room temperature. After 15 hours the mixture was heated under reflux for an additional hour, then evaporated *in vacuo*. The residue was dissolved in CH_2Cl_2 (20 mL) and washed with a saturated aqueous solution of $NaHCO_3$ (2 x 10 mL). The organic phase was dried over $MgSO_4$, filtered, and evaporated *in vacuo*, and dried for 2 hours. The residue was then dissolved in pyridine (10 mL), the solution cooled to 0 °C, benzoyl chloride (323.31 mg, 2.30 mmol) and catalytic DMAP were added. The mixture was allowed to reach room temperature and left stirring for 15 hours. The mixture was concentrated under vacuum and the residue co-evaporated with toluene (3 x 10 mL). The crude was purified by flash column chromatography (toluene/EtOAc, 9:1, v/v) and compound **10** (458 mg, 0.43 mmol, 56% yield) was isolated as a colourless amorphous solid, 10 % of the *manno*-compound was also isolated. R_f = 0.47, toluene/EtOAc, 10:1; $[\alpha]_D^{20}$= +63.9 (*c* 1; $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.68 (d, *J* = 3.9 Hz, 1H; H-1), 6.07 (ddd, *J* = 11.6, 9.5 Hz, 1H; H-3), 5.80 – 5.69 (m, 2H; H-4', H-2'), 5.37 (dd, *J* = 10.3, 3.4 Hz, 1H; H-3'), 5.00 – 4.81 (m, 2H; H-1', H-2), 4.56 – 4.44 (m, 2H; H-6a, H-6b), 4.30 – 4.14 (m, 2H; H-4, H-5), 3.98 – 3.85 (m, 2H; H-5', H-6'a), 3.75 – 3.61 (m, 1H; H-6'b); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 165.5, 165.4, 165.2, 165.2, 164.8, 164.5 (7 O*C*OPh), 133.9–125.3 (C_{Ar}), 101.2 (C-1'), 89.1 (d, *J* = 21.9 Hz; C-1), 86.7 (d, *J* = 196.1 Hz; C-2), 75.1 (d, *J* = 7.0 Hz; C-4), 72.0 (C-3'), 71.4 (C-5'), 71.0 (d, *J* = 19.0 Hz; C-3), 70.9 (C-5), 69.8, 67.4 (C-4', C-2'), 61.7 (C-6), 61.0 (C-6'); ^{19}F NMR (376 MHz, $CDCl_3$) δ –200.98 (dd, *J* = 48.5, 12.0 Hz; 1F, F-2); HRMS (ESI^+): *m/z* Calcd for $C_{61}H_{49}O_{17}NaF$: 1095.2851 $[M+Na]^+$; found, 1095.2855.

2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-fluoro-α-D-glucopyranosyl bromide (11)

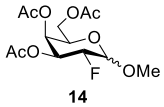


11

A solution of **10** (1.10 g, 1.02 mmol) in anhydrous CH_2Cl_2 (8.5 mL) was cooled to 0 °C and 33% HBr in AcOH (758 mg, 9.4 mmol) was added. The reaction was allowed to reach room temperature and was left stirring for 22 h. The mixture reaction was diluted with CH_2Cl_2 (20 mL), poured onto crushed ice/H_2O (50 mL), washed with saturated aqueous solution of $NaHCO_3$ (2 x 10 mL) and water (2 x 10 mL). The organic phase was dried over $MgSO_4$, filtered, and evaporated under vacuum to dryness. The crude was purified by flash column chromatography (toluene/EtOAc, 10:1, v/v) to give **11** as a white amorphous solid (947 mg, 0.92 mmol, 90% yield). R_f = 0.62, toluene/EtOAc, 10:1; $[\alpha]_D^{20}$= + 89.4 (*c* 1; $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (m, 2H; H_{Ar}), 7.96 (m, 4H; H_{Ar}), 7.88 (m, 2H; H_{Ar}), 7.71 (m, 2H; H_{Ar}), 7.66 – 7.52 (m, 2H; H_{Ar}), 7.51 – 7.34 (m, 8H; H_{Ar}), 7.33 – 7.10 (m, 10H; H_{Ar}), 6.53 (ad, J = 4.2 Hz, 1H; H-1), 5.99 (*a*dd, *J* = 20.1, 9.6 Hz, 1H; H-3), 5.81 – 5.67 (m, 2H; H-2', H-4'), 5.39 (dd, *J* = 10.3, 3.3 Hz, 1H; H-3'), 4.92 (d, *J* = 7.9 Hz, 1H; H-1'), 4.78 – 4.45 (m, 3H; H-2, H-6a, H-6b), 4.42 – 4.28 (m, 1H; H-5), 4.19 (*a*t, *J* = 9.6 Hz, 1H; H-4), 4.02 – 3.86 (m, 2H; H-5', H-6'a), 3.69 ppm (dd, *J* = 13.5, 9.2 Hz, 1H; H-6'b); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 165.5, 165.4, 165.2, 164.9, 164.6 (6 O*C*OCH$_3$), 137.8, 133.5, 133.5, 133.4, 133.4, 133.3, 129.9–128.2 (C_{Ar}), 100.9 (C-1), 86.7 (d, *J* = 199.1 Hz; C-2), 85.4 (d, *J* = 25.1 Hz; C-1), 74.3 (d, *J* = 6.9 Hz; C-4), 73.3 (C-5), 71.8 (C-3'), 71.4 (C-5'), 71.3 (d, *J* = 18.5 Hz; C-3), 69.8 (C-4'), 67.4 (C-2'), 61.3 (C-6), 61.0 (C-6'); ^{19}F NMR (376 MHz, $CHCl_3$) δ –187.57

(dd, *J* = 49.5, 10.7 Hz; 1F, F-2); HRMS (ESI$^+$): *m/z* Calcd for $C_{54}H_{44}O_{15}FNaBr$: 1053.1745 $[M+Na]^+$; found, 1053.1772.

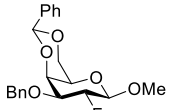
Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-fluoro-D-galactopyranoside (14)



14

To a suspension of compound **12** (2 g, 4.86 mmol) in water (60 mL) was added activated Zn powder (2 g, 31.6 mmol) followed by AcOH (60 mL). The mixture was stirred overnight, then the reaction was diluted with EtOAc (150 mL), and washed with water and sat. $NaHCO_3$. Organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude was purified by flash column chromatography (toluene/EtOAc, 8:2, v/v) to give the corresponding D-galactal (910 mg, 3.34 mmol, 69%) as a white foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.46 (dd, *J* = 6.3, 1.8 Hz, 1H, H-1), 6.50 – 6.41 (m, 1H, H-3), 5.48 – 5.38 (m, 1H, H-4), 4.73 (ddd, *J* = 6.3, 2.7, 1.4 Hz, 1H, H-2), 4.36 – 4.14 (m, 3H, H-5, H-6a, H-6b), 2.13 (s, 3H, $OCOCH_3$), 2.08 (s, 3H, $OCOCH_3$), 2.03 (s, 3H, $OCOCH_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 170.4, 170.3 (3 O*C*OCH$_3$), 145.6 (C-1), 99.0 (C-2), 73.0 (C-5), 64.0 (C-3), 63.9 (C-4), 62.1 (C-6), 21.0, 20.9, 20.8 (3 OCO*C*H$_3$). All analytical data were consistent with literature values.[1] Galactal (1 g, 3.7 mmol) was dissolved in $MeNO_2$/MeOH (9.2 mL, 5:1, v/v), then Selectfluor® (1.6 g, 4.4 mmol) was added and the mixture was stirred at room temperature for 4 hours, followed by heating at 90 °C for 45 minutes. The reaction was then cooled to room temperature and the solvents were evaporated *in vacuo*. Purification by flash column chromatography of the crude residue (toluene/EtOAc, 9:1, v/v) gave **14** (1 g, 3.1 mmol, 84%) as an α/β mixture (α/β, 1:2). R_f = 0.5, toluene/EtOAc 8:2; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.47 (dd, *J* = 3.4, 1.3 Hz, 1H, H-4α) 5.45 – 5.34 (m, 2H, H-4β, H-3α), 5.10 (ddd, *J* = 13.3, 9.6, 3.6 Hz, 1H, H-3β), 5.01 (d, *J* = 3.8 Hz, 1H, H-1α), 4.76 (ddd, *J* = 50.0, 10.2, 3.8 Hz, 1H, H-2α), 4.58 – 4.39 (m, 2H, H-1β, H-2β), 4.23 – 4.07 (m, 5H, H-6aβ, H-6bβ, H-6aα, H-6bα, H-5α), 3.92 (*d*td, *J* = 6.7, 1.2 Hz, 1H, H-5β), 3.60 (s, 3H, OCH_3β), 3.47 (s, 1H, OCH_3α), 2.16 – 2.01 (m, 18H, 6 $OCOCH_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.52 (O*C*OCH$_3$α), 170.48 (O*C*OCH$_3$β), 170.2 (O*C*OCH$_3$β), 170.13 (O*C*OCH$_3$α), 170.12 (O*C*OCH$_3$β), 170.05 (O*C*OCH$_3$α), 101.8 (d, *J* = 22.8 Hz, C-1β), 97.6 (d, *J* = 20.6 Hz, C-1α), 88.1 (d, *J* = 186.8 Hz, C-2β), 85.5 (d, *J* = 190.9 Hz, C-2α), 71.2 (d, *J* = 18.9 Hz, C-3β), 70.8 (C-5β), 68.8 (d, *J* = 7.7 Hz, C-4α), 68.3 (d, *J* = 19.0 Hz, C-3α), 67.8 (d, *J* = 8.3 Hz, C-4β), 66.5 (C-5α), 61.7 (C-6α), 61.2 (C-6β), 57.5 (OCH_3β), 55.8 (OCH_3α), 20.8 (OCO*C*H$_3$α), 20.8 (OCO*C*H$_3$β, OCO*C*H$_3$α), 20.71 (OCO*C*H$_3$β), 20.68 (OCO*C*H$_3$β, OCO*C*H$_3$α); ^{19}F NMR (376 MHz, $CDCl_3$) δ -207.06 (ddd, *J* = 52.7, 13.3, 2.5 Hz, F-2β), –208.89 (ddd, *J* = 50.0, 10.8, 3.3 Hz, F-2α); HRMS (ESI$^+$): m/z calcd for $C_{13}H_{19}FO_8$: 345.0962 $[M+Na]^+$; found: 345.0958. All analytical data were consistent with literature values.[2]

Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-fluoro-β-D-galactopyranoside (16)

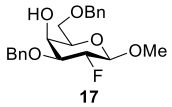


16

Compound **14** (1 g, 3.1 mmol) was dissolved in MeOH/CH_2Cl_2 (7 mL, 5:2, v/v) and reacted with solid NaOMe at pH = 11. Upon completion after 3 hours, the reaction was neutralized with Dowex 50WX8 H^+ resin, filtered, and evaporated under vacuum. The deacetylated compound was then dissolved in anhydrous DMF (20 mL) benzaldehyde dimethyl acetal (930 µL, 6.2 mmol) was added, followed by *p*-toluenesulfonic acid (160 mg, 0.93 mmol). The reaction was stirred at 50 °C under mild vacuum for 4 hours, then neutralized with Et_3N, and evaporated *in vacuo*. The crude residue was dissolved in anhydrous DMF (15 mL), then NaH (60%, 620 mg, 15.5 mmol) and benzyl bromide (2.2 mL, 18.6 mmol) were added

at 0 °C and the reaction was stirred at room temperature for 1 hour, diluted with MeOH, and evaporated under vacuum. Flash column chromatography purification (toluene/EtOAc, 9:1, v/v) gave **16** (658 mg, 1.75 mmol, 56%) as a white foam, as well as the α-anomer **16α** (220 mg, 0.58 mmol, 18%). R_f = 0.33, toluene/EtOAc 8:2; $[\alpha]_D^{20}$= +50.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 2H, H_{Ar}), 7.42 – 7.27 (m, 8H, H_{Ar}), 5.47 (s, 1H, CHPh), 4.84 – 4.65 (m, 3H, CH_2Ph, H-2), 4.42 (dd, *J* = 7.7, 3.5 Hz, 1H, H-1), 4.32 (dd, *J* = 12.4, 1.6 Hz, 1H, H-6a), 4.17 (ddd, *J* = 3.6, 2.2, 1.1 Hz, 1H, H-4), 4.03 (dd, *J* = 12.4, 1.8 Hz, 1H, H-6b), 3.66 (ddd, *J* = 13.0, 9.3, 3.6 Hz, 1H, H-3), 3.59 (s, 3H, OCH_3), 3.38 (m, 1H, H-5); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.9 (C_{Ar}), 137.7 (C_{Ar}), 129.2, 128.6, 128.3, 128.1, 128.0, 126.5 (10 C_{Ar}), 101.8 (d, *J* = 22.7 Hz, H-1), 101.4 (CHPh), 90.2 (d, *J* = 183.8 Hz, C-2), 77.4 (under $CDCl_3$ peak, C-3), 74.5 (d, *J* = 9.6 Hz, C-4), 72.0 (d, *J* = 1.6 Hz, CH_2Ph), 69.0 (C-6), 66.7 (C-5), 57.0 (OCH_3); ^{19}F NMR (376 MHz, $CDCl_3$) δ –205.61 (ddd, *J* = 52.1, 13.0, 2.2 Hz, F-2); HRMS (ESI$^+$): m/z calcd for $C_{21}H_{23}FO_5$: 397.1427 [M+Na]$^+$; found: 397.1431.

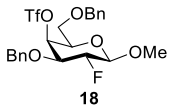
Methyl 3,6-di-*O*-benzyl-2-deoxy-2-fluoro-β-D-galactopyranoside (17)



17

Compound **16** (400 mg, 1.07 mmol) and $NaCNBH_3$ (873 mg, 13.9 mmol) were dissolved in anhydrous THF (43 mL) with 3Å molecular sieves (2 g) and stirred for 1 hour at room temperature. HCl (1M in Et_2O, 14 mL, 13.9 mmol) was then slowly dropped until pH = 2–3. The reaction was stirred for 1 hour, then it was neutralized with MeOH and Et_3N, filtered over Celite, and concentrated *in vacuo*. The crude was subsequently washed with water and extracted with CH_2Cl_2. Organic layers were dried over $MgSO_4$, filtered, and evaporated under vacuum. Purification by flash column chromatography (toluene/EtOAc, 8:2, v/v) gave **17** (364 mg, 0.97 mmol, 91%) as a clear oil. R_f = 0.62, toluene/EtOAc 7:3; $[\alpha]_D^{20}$= –1.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 10H, H_{Ar}), 4.79 (d, *J* = 11.9 Hz, 1H, CH*H*Ph), 4.72 (d, *J* = 11.9 Hz, 1H, C*H*HPh), 4.67 – 4.47 (m, 3H, CH_2Ph, H-2), 4.37 (dd, *J* = 7.7, 3.8 Hz, 1H, H-1), 4.06 (*a*dq, *J* = 3.1, 1.6 Hz, 1H, H-4), 3.83 – 3.70 (m, 2H, H-6a, H-6b), 3.64 – 3.53 (m, 5H, H-3, H-5, OCH_3), 2.57 (dd, *J* = 2.1, 1.3 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0 (C_{Ar}), 137.5 (C_{Ar}), 128.7, 128.6, 128.2, 128.04, 127.96, 127.9 (10 C_{Ar}), 101.7 (d, *J* = 23.3 Hz, C-1), 91.5 (d, *J* = 183.8 Hz, C-2), 78.7 (d, *J* = 16.8 Hz, C-3), 73.9 (CH_2Ph), 73.5 (C-5), 72.5 (d, *J* = 1.7 Hz, CH_2Ph), 69.0 (C-6), 67.8 (d, *J* = 9.0 Hz, C-4), 57.0 (OCH_3); ^{19}F NMR (376 MHz, $CDCl_3$) δ –205.65 (ddd, *J* = 51.2, 14.4, 3.8 Hz, F-2); HRMS (ESI$^+$): m/z calcd for $C_{21}H_{25}FO_5$: 399.1584 [M+Na]$^+$; found: 399.1570.

Methyl 3,6-di-*O*-benzyl-2-deoxy-2-fluoro-4-*O*-trifluoromethanesulfonyl-β-D-galactopyranoside (18)

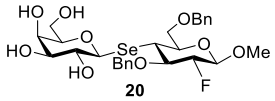


18

To a solution of **17** (150 mg, 0.39 mmol) in pyridine (2 mL) at 0 °C, was slowly added trifluoromethanesulfonic anhydride (80 µL, 0.48 mmol). The reaction was stirred at 0 °C for 20 min, then allowed to warm up to room temperature and stirred for another 2 hours. The solvent was removed and crude was purified by flash column chromatography (toluene/EtOAc, 95:5, v/v) to give **18** (175 mg, 0.34 mmol, 87%) as a transparent oil. R_f = 0.8, toluene/EtOAc 7:3; $[\alpha]_D^{20}$= +21.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.28 (m, 10H, H_{Ar}), 5.39 – 5.36 (m, 1H, H-4), 4.85 (d, *J* = 12.3 Hz, 1H, CH*H*Ph), 4.68 (d, *J* = 12.3 Hz, 1H, C*H*HPh), 4.64 (d, *J* = 11.4 Hz, 1H, CH*H*Ph), 4.60 – 4.34 (m, 3H, H-2, H-1, C*H*HPh), 3.80 – 3.57 (m, 4H, H-3, H-5, H-6a, H-6b), 3.55 (s, 3H, OCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3 (C_{Ar}), 136.6 (C_{Ar}), 128.6, 128.3, 128.2 (10 C_{Ar}), 118.6 (*a*d, *J* = 319.7 Hz, OSO_2CF_3), 101.9 (d, *J* = 23.6 Hz, C-1), 90.1 (d, *J* = 186.1 Hz, C-2), 81.6 (d, *J* = 9.6 Hz, C-4), 75.6 (d, *J* = 19.2 Hz, C-3), 739 (CH_2Ph), 72.7 (CH_2Ph), 71.4 (C-5), 66.8 (C-

6), 57.4 (OCH_3); ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.82 (s, OSO_2CF_3), -204.89 – -205.34 (m, F-2); HRMS (ESI^+): m/z calcd for $C_{22}H_{24}F_4O_7S$: 531.1077 $[M+Na]^+$; found: 531.1066.

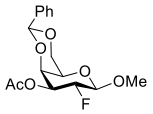
Methyl 4*Se*-β-D-galactopyranosyl-3,6-di-*O*-benzyl-2-deoxy-2-fluoro-4-seleno-β-D-glucopyranoside (20)



20

To a solution of **19** (30 mg, 39 µmol) in MeOH (1 mL) was added solid NaOMe until pH = 11. The reaction was stirred for 2 hours, then it was neutralized with Dowex 50WX8 H^+ resin, filtered, and concentrated under reduced pressure. Purification by flash column chromatography (CH_2Cl_2/MeOH, 9:1, v/v) gave **20** (21 mg, 35 µmol, 90%) as a white powder. R_f = 0.62, CH_2Cl_2/MeOH 9:1; $[\alpha]_D^{20}$= +2.1 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.27 (m, 10H, H_{Ar}), 4.98 (dd, *J* = 10.7, 1.5 Hz, 1H, CH*H*Ph), 4.75 – 4.62 (m, 3H, C*H*HPh, CH_2Ph), 4.60 (d, *J* = 9.7 Hz, 1H, H-1'), 4.39 – 4.35 (m, 1H, H-1), 4.36 (*a*dt, *J* = 52.6, 7.9 Hz, 1H, H-2), 4.07 (dd, *J* = 11.9, 2.0 Hz, 1H, H-6a), 4.00 (dd, *J* = 11.9, 4.5 Hz, 1H, H-6b), 3.95 (*a*d, *J* = 3.2 Hz, 1H, H-4'), 3.80 – 3.56 (m, 8H, H-2', H-6'a, H-6'b, H-3, H-5, OCH_3), 3.42 (*a*d, *J* = 8.8 Hz, 1H, H-3'), 3.36 (ddd, *J* = 5.4, 4.0, 1.2 Hz, 1H, H-5'), 3.25 – 3.13 (m, 2H, OH, H-4), 2.99 – 2.87 (m, 2H, 2 OH), 2.78 (s, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8 (C_{Ar}), 137.3 (C_{Ar}), 128.8, 128.7, 128.6, 128.5, 128.2, 128.0 (10 C_{Ar}), 101.1 (d, *J* = 22.9 Hz, C-1), 94.3 (d, *J* = 188.3 Hz, C-2), 81.2 (d, *J* = 17.1 Hz, C-3), 81.1 (C-1'), 79.4 (C-5'), 77.0 (C-5), 75.7 (CH_2Ph), 74.1 (CH_2Ph, C-3'), 70.5 (C-2'), 70.1 (C-4'), 69.5 (C-6), 63.2 (C-6'), 57.0 (OCH_3), 39.6 (d, *J* = 7.0 Hz, C-4); ^{19}F NMR (376 MHz, $CDCl_3$) δ –192.65 (*a*dd, *J* = 52.5, 13.8 Hz, F-2); HRMS (ESI^+): m/z calcd for $C_{27}H_{35}FO_9Se$: 625.1328 $[M+Na]^+$; found: 625.1346.

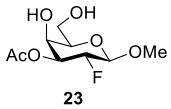
Methyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-2-fluoro-β-D-galactopyranoside (22)



22

To a solution of compound **15** (600 mg, 1.86 mmol) in MeOH (3 mL) was added solid NaOMe until pH = 11. The reaction was stirred at room temperature for 3 hours, then it was neutralized with Dowex 50WX8 H^+ resin, filtered, and concentrated to dryness. The crude residue was dissolved in anhydrous DMF (28 mL) and reacted with benzaldehyde dimethyl acetal (550 µL, 3.72 mmol) and *p*-toluenesulfonic acid (96 mg, 0.56 mmol) at 50 °C under reduced pressure for 4 hours. The reaction was then neutralized with Et_3N and solvents were removed *in vacuo*. The crude residue was dissolved in pyridine (5 mL) and Ac_2O (2.5 mL) and the reaction was stirred overnight. Solvents removal under vacuum and purification of the crude residue by flash column chromatography (toluene/EtOAc, 9:1, v/v) afforded compound **22** (360 mg, 1.10 mmol, 59%) as a white foam as well as the α-anomer **22α** (158 mg, 0.48 mmol, 26%). R_f = 0.4, toluene/EtOAc 7:3; $[\alpha]_D^{20}$= +83.4 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 2H, H_{Ar}), 7.41 – 7.32 (m, 3H, H_{Ar}), 5.49 (s, 1H, CHPh), 5.04 (ddd, *J* = 13.1, 9.5, 3.5 Hz, 1H, H-3), 4.71 (ddd, *J* = 52.0, 9.5, 7.8 Hz, 1H, H-2), 4.51 (ddd, *J* = 7.8, 3.4, 1H, H-1), 4.42 (ddd, *J* = 3.5, 2.1, 1.0 Hz, 1H, H-4), 4.35 (dd, *J* = 12.5, 1.2 Hz, 1H, H-6a), 4.06 (dd, *J* = 12.5, 1.8, 1H, H-6b), 3.62 – 3.58 (m, 3H, OCH_3), 3.55 – 3.52 (m, 1H, H-5), 2.22 – 2.07 (m, 3H, $OCOCH_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9 (O*C*OCH$_3$), 137.5 (C_{Ar}), 129.3 (C_{Ar}), 128.3 (2 C_{Ar}), 126.4 (2 C_{Ar}), 101.7 (d, *J* = 21.9 Hz, C-1), 101.2 (CHPh), 87.6 (d, *J* = 185.8 Hz, C-2), 74.1 (d, *J* = 8.4 Hz, C-4), 72.4 (d, *J* = 18.6 Hz, C-3), 68.9 (C-6), 66.5 (C-5), 57.16 (OCH_3), 21.1 (OCO*C*H$_3$); ^{19}F NMR (376 MHz, $CDCl_3$) δ –206.99 (ddd, *J* = 52.0, 13.1, 3.4 Hz, F-2); HRMS (ESI^+): m/z calcd for $C_{16}H_{19}FO_6$: 349.1063 $[M+Na]^+$; found: 349.1066.

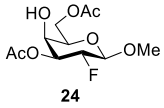
Methyl 3-*O*-acetyl-2-deoxy-2-fluoro-β-D-galactopyranoside (23)



23

Compound **22** (330 mg, 1.01 mmol) was dissolved in 80% aq. AcOH (13 mL) and stirred at 80 °C for 3 hours. The solvent was then removed by co-evaporation with toluene under vacuum and the crude residue was purified by flash column chromatography (toluene/acetone, 7:3, v/v) to give **23** (189 mg, 0.79 mmol, 78%) as a white amorphous solid. R_f = 0.23, toluene/acetone 7:3; $[\alpha]_D^{20}$= +52.2 (*c* 0.75, MeOH); ^{1}H NMR (400 MHz, CD_3OD) δ 5.04 – 4.93 (m, 1H, H-3), 4.56 – 4.37 (m, 2H, H-1, H-2), 4.12 (dd, *J* = 3.2, 1.0 Hz, 1H, H-4), 3.82 – 3.69 (m, 2H, H-6a, H-6b), 3.66 (ddd, *J* = 6.7, 5.4, 1.1 Hz, 1H, H-5), 3.58 (s, 3H, OCH_3), 2.15 (s, 3H, $OCOCH_3$); ^{13}C NMR (101 MHz, CD_3OD) δ 170.5 ($O\underline{C}OCH_3$), 101.6 (d, *J* = 22.8 Hz, C-1), 88.6 (d, *J* = 184.5 Hz, C-2), 74.9 (C-5), 74.2 (d, *J* = 16.9 Hz, C-3), 66.9 (d, *J* = 8.0 Hz, C-4), 60.5 (C-6), 55.76 (OCH_3), 19.4 ($OCO\underline{C}H_3$); HRMS (ESI$^+$): m/z calcd for $C_9H_{15}FO_6$: 261.0750 [M+Na]$^+$; found: 261.0742.

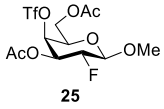
Methyl 3,6-di-*O*-acetyl-2-deoxy-2-fluoro-β-D-galactopyranoside (24)



24

To a solution of **23** (97 mg, 0.407 mmol) in CH_2Cl_2/CH_3CN (6 mL, 6:1, v/v) and pyridine (50 µL, 0.61 mmol) was added AcCl (30 µL, 0.45 mmol) at –30 °C. The mixture was stirred at the same temperature for 20 minutes, then it was allowed to warm up to room temperature. After 3 hours, the reaction was diluted with MeOH and water and extracted with CH_2Cl_2. Combined organic layers were dried over $MgSO_4$, filtered, and concentrated to dryness. Crude residue was purified by flash column chromatography (toluene/acetone, 8:2, v/v) giving **24** (93 mg, 0.33 mmol, 81%) as a white foam. R_f = 0.51, toluene/acetone 8:2; $[\alpha]_D^{20}$= +47.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.00 (ddd, *J* = 13.5, 9.3, 3.4, 1H, H-3), 4.66 – 4.42 (m, 2H, H-1, H-2), 4.36 – 4.22 (m, 2H, H-6a, H-6b), 4.05 (*a*d, *J* = 3.1 Hz, 1H, H-4), 3.75 (*a*t, *J* = 6.6, 1H, H-5), 3.58 (s, 3H, OCH_3), 2.17 (s, 3H, $OCO\underline{C}H_3$), 2.08 (s, 3H, $OCO\underline{C}H_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0 ($O\underline{C}OCH_3$), 170.2 ($O\underline{C}OCH_3$), 101.7 (d, *J* = 23.0 Hz, C-1), 88.3 (d, *J* = 186.3 Hz, C-2), 73.3 (d, *J* = 17.9 Hz, C-3), 71.9 (C-5), 67.5 (d, *J* = 8.0 Hz, C-4), 62.0 (C-6), 57.1 (OCH_3), 20.9 ($OCO\underline{C}H_3$), 20.8 ($OCO\underline{C}H_3$); ^{19}F NMR (376 MHz, $CDCl_3$) δ -208.02 (ddt, *J* = 50.7, 13.5, 3.6 Hz, F-2); HRMS (ESI$^+$): m/z calcd for $C_{11}H_{17}FO_7$: 303.0856 [M+Na]$^+$; found: 303.0871.

Methyl 3,6-di-*O*-acetyl-2-deoxy-2-fluoro-4-*O*-trifluoromethanesulfonyl-β-D-galactopyranoside (25)

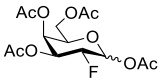


25

To a solution of **24** (80 mg, 0.28 mmol) in anhydrous pyridine (1.4 mL), trifluoromethanesulfonic anhydride (60 µL, 0.34 mmol) was slowly added at 0 °C. The reaction was kept at the same temperature for 15 minutes, then it was allowed to warm up to room temperature. Stirring was continued for 3 hours, then the solvent was removed under reduced pressure. Purification of the crude residue by flash column chromatography (toluene/acetone, 9:1, v/v) gave **25** (110 mg, 0.27 mmol, 95%) as a white foam. R_f = 0.77, toluene/acetone 8:2; $[\alpha]_D^{20}$= +12.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.24 (*a*t, *J* = 2.8 Hz, 1H, H-4), 5.18 (ddd, *J* = 12.7, 9.6, 3.2 Hz, 1H, H-3), 4.66 – 4.44 (m, 2H, H-1, H-2), 4.43 – 4.37 (m, 1H, H-6a), 4.06 – 3.97 (m, 2H, H-5, H-6b), 3.60 (s, 3H, OCH_3), 2.20 (s, 3H, $OCOCH_3$), 2.09 (s, 3H, $OCOCH_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.21 ($O\underline{C}OCH_3$), 170.19 ($O\underline{C}OCH_3$), 118.46 (*a*d, *J* = 319.3 Hz, OSO_2CF_3), 101.84 (d, *J* = 22.9 Hz, C-

1), 87.16 (d, *J* = 188.5 Hz, C-2), 81.30 (d, *J* = 8.7 Hz, C-4), 70.16 (d, *J* = 20.6 Hz, C-3), 70.11 (C-5), 60.54 (C-6), 57.57 (OCH_3), 20.73 ($OCO\underline{C}H_3$), 20.64 ($OCO\underline{C}H_3$); ^{19}F NMR (376 MHz, $CDCl_3$) δ –74.21 ($OSOCF_3$), –207.30 (ddd, *J* = 51.9, 12.7, 2.4 Hz, F-2); HRMS (ESI^+): m/z calcd for $C_{12}H_{16}F_4O_9S$: 435.0349 $[M+Na]^+$; found: 435.0330.

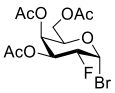
1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-fluoro-β-D-galactopyranoside (27)



27

Acetic anhydride (5 mL, 52 mmol) was added to a stirred solution of 3,4,6-Tri-*O*-acetyl-2-deoxy-2-fluoro-β-D-galactopyranose (5.5 g, 17.7 mmol) in pyridine (10 mL, 124 mmol). After 19 h, solvents were removed under reduced pressure to give **27** (6.1 g, 17 mmol, 98%) as a brown amorphous solid (α/β 73:27). R_f = 0.52, cyclohexane/EtOAc 1:1; ^1H NMR (400 MHz, $CDCl_3$) δ 6.45 (d, *J* = 3.9 Hz, 1H, H-1α), 5.78 (dd, *J* = 8.0, 4.1 Hz, 1H, H-1β), 5.50 (td, *J* = 3.5, 1.3 Hz, 1H, H-4α), 5.44 (t, *J* = 2.9 Hz, 1H, H-4β), 5.39 (td, *J* = 10.7, 3.5 Hz, 1H, H-3α), 5.17 (ddd, *J* = 13.1, 9.9, 3.6 Hz,1H, H-3β), 4.88 (ddd, *J* = 49.1, 10.2, 3.9 Hz, 1H, H-2α), 4.63 (ddd, *J* = 51.5, 9.8, 7.9 Hz, 1H, H-2β), 4.30 (td, *J* = 6.8, 1.4 Hz, 1H, H-5α), 4.18 – 4.09 (m, 2H, H-6aβ, H-6bβ), 4.09 – 4.03 (m, 3H, H-5β, H-6aα, H-6bα), 2.17 (s, 3H, $OCOCH_3$α), 2.17 (s, 3H, $OCOCH_3$β), 2.13 (s, 3H, $OCOCH_3$α), 2.13 (s, 3H, $OCOCH_3$β), 2.05 (s, 3H, $OCOCH_3$β), 2.04 (s, 3H, $OCOCH_3$α), 2.02 (s, 3H, $OCOCH_3$α), 2.02 (s, 3H, $OCOCH_3$β); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.41 ($O\underline{C}OCH_3$α), 170.41 ($O\underline{C}OCH_3$β), 170.1 ($O\underline{C}OCH_3$β), 170.03 ($O\underline{C}OCH_3$α), 169.99 ($O\underline{C}OCH_3$β), 169.88 ($O\underline{C}OCH_3$α), 168.92 ($O\underline{C}OCH_3$β), 168.90 ($O\underline{C}OCH_3$α), 91.7 (d, *J* = 24.5 Hz, C-1β), 89.1 (d, *J* = 22.8 Hz, C-1α), 86.8 (d, *J* = 188.4 Hz, C-2β), 84.2 (d, *J* = 190.9 Hz, C-2α), 71.8 (C-5β), 71.0 (d, *J* = 18.4 Hz, C-3β), 68.7 (C-5α), 68.3 (d, *J* = 18.5 Hz, C-3α), 68.0 (d, *J* = 7.7 Hz, C-4α), 67.6 (d, *J* = 8.4 Hz, C-4β), 61.1 (C-6α), 60.9 (C-6β), 21.0 ($OCO\underline{C}H_3$β), 20.9 ($OCO\underline{C}H_3$α), 20.73 ($OCO\underline{C}H_3$α), 20.73 ($O\underline{C}OCH_3$β), 20.65 ($OCO\underline{C}H_3$α), 20.65 ($O\underline{C}OCH_3$β), 20.62 ($OCO\underline{C}H_3$α), 20.62 ($O\underline{C}OCH_3$β); ^{19}F NMR (376 MHz, $CDCl_3$) δ –209.16 (ddd, *J* = 49.1, 11.0, 3.4 Hz, F-2α), –208.16 (dddd, *J* = 51.5, 13.0, 4.1, 2.6 Hz, F-2β).

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-fluoro-β-D-galactopyranosyl bromide (28)



28

Hydrogen bromide (33% in AcOH, 3.3 mL, 18.6 mmol), was added over 35 min to a stirred solution of **27** (650 mg, 1.9 mmol) in CH_2Cl_2 (5.6 mL) at 0 °C. The reaction mixture was left to reach room temperature. After 21 hours CH_2Cl_2 (25 mL) was added and the mixture was poured into Ice-water (40 mL). Phases were separated, and the organic phase was washed with $NaHCO_3$ (satd aq., 2x25 mL) and H_2O (10 mL). The organic phase was dried before removal of solvents under reduced pressure. Purification by flash column chromatography (cyclohexane:EtOAc, 8:2, v/v) gave **28** (533 mg, 1.4 mmol, 77%) as an amorphous solid. R_f = 0.78, cyclohexane/EtOAc 1:1; ^1H NMR (500 MHz, $CDCl_3$) δ 6.61 (dd, *J* = 4.2, 1.5 Hz, 1H, H-1), 5.53 (dt, *J* = 3.4, 2.0 Hz, 1H, H-4), 4.47 (td, *J* = 10.0, 3.5 Hz, 1H, H-3), 4.76 (ddd, *J* = 50.2, 10.0, 4.2 Hz, 1H, H-2), 4.51 (m, 1H, H-5), 4.17 (dd, *J* = 11.5, 6.4 Hz, 1H, H-6b), 4.12 (dd, *J* = 11.5, 6.8 Hz, 1H, H-6a), 2.14 (s, 3H, $OCOCH_3$), 2.06 (s, 3H, $OCOCH_3$), 2.05 (s, 3H, $OCOCH_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4, 169.9, 169.8 (3 $O\underline{C}OCH_3$), 86.9 (d, *J* = 25.4 Hz, C-1), 84.3 (d, *J* = 195.1 Hz, C-2), 71.4 (C-5), 69.1 (d, *J* = 18.0 Hz, C-3), 67.6 (d, *J* = 7.6 Hz, C-4), 60.8 (C-6) 20.8, 20.7, 20.6 (3 $OCO\underline{C}H_3$); ^{19}F NMR (376 MHz, $CDCl_3$) δ –195.05 (ddd, *J* 50.1, 10.1, 3.4 Hz, F-2). All analytical data were consistent with literature values.[3]

References

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2 M. Albert, D. Karl and J. Ortner, *Tetrahedron*, 1998, **54**, 4839–4848.

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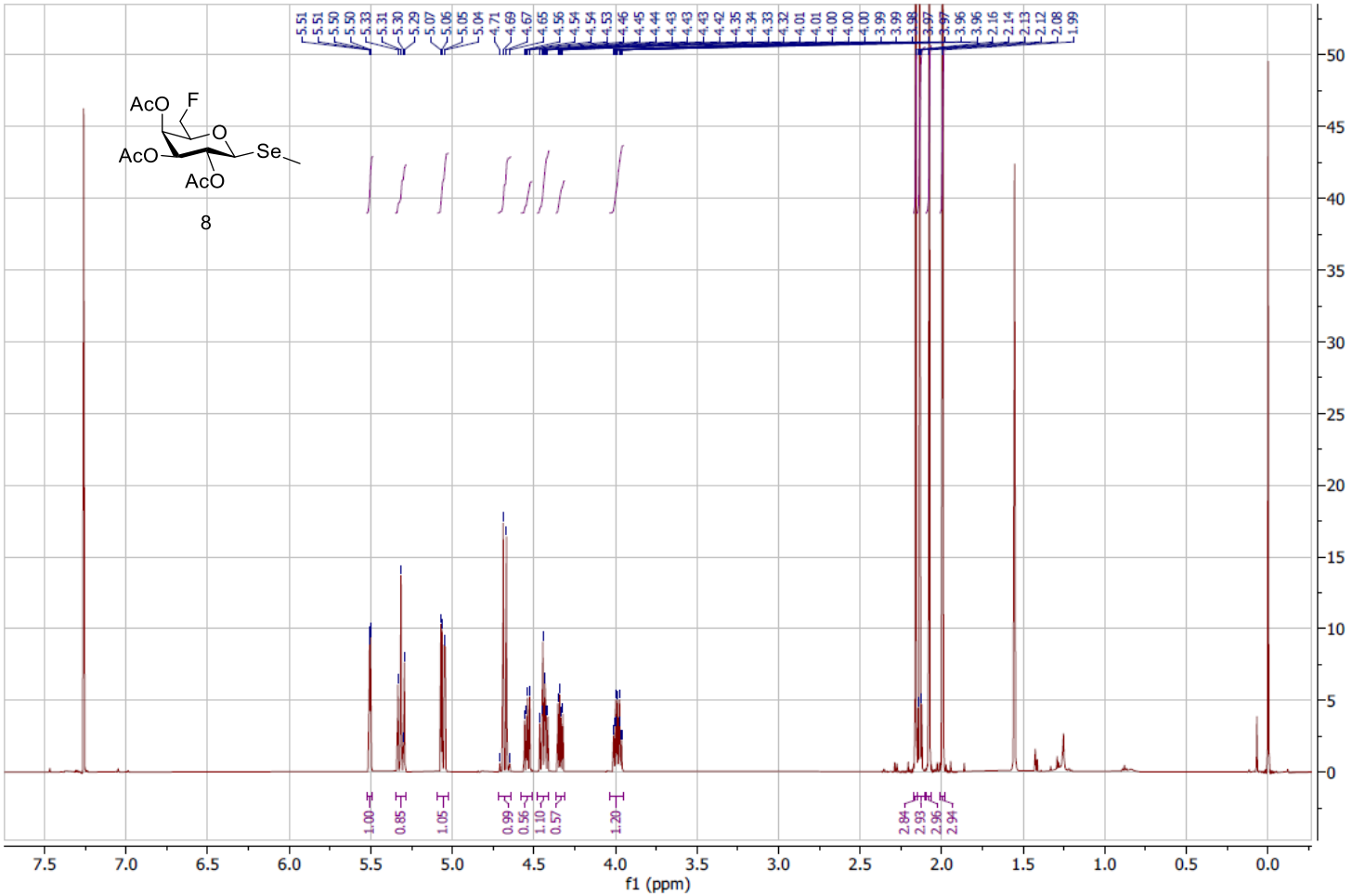
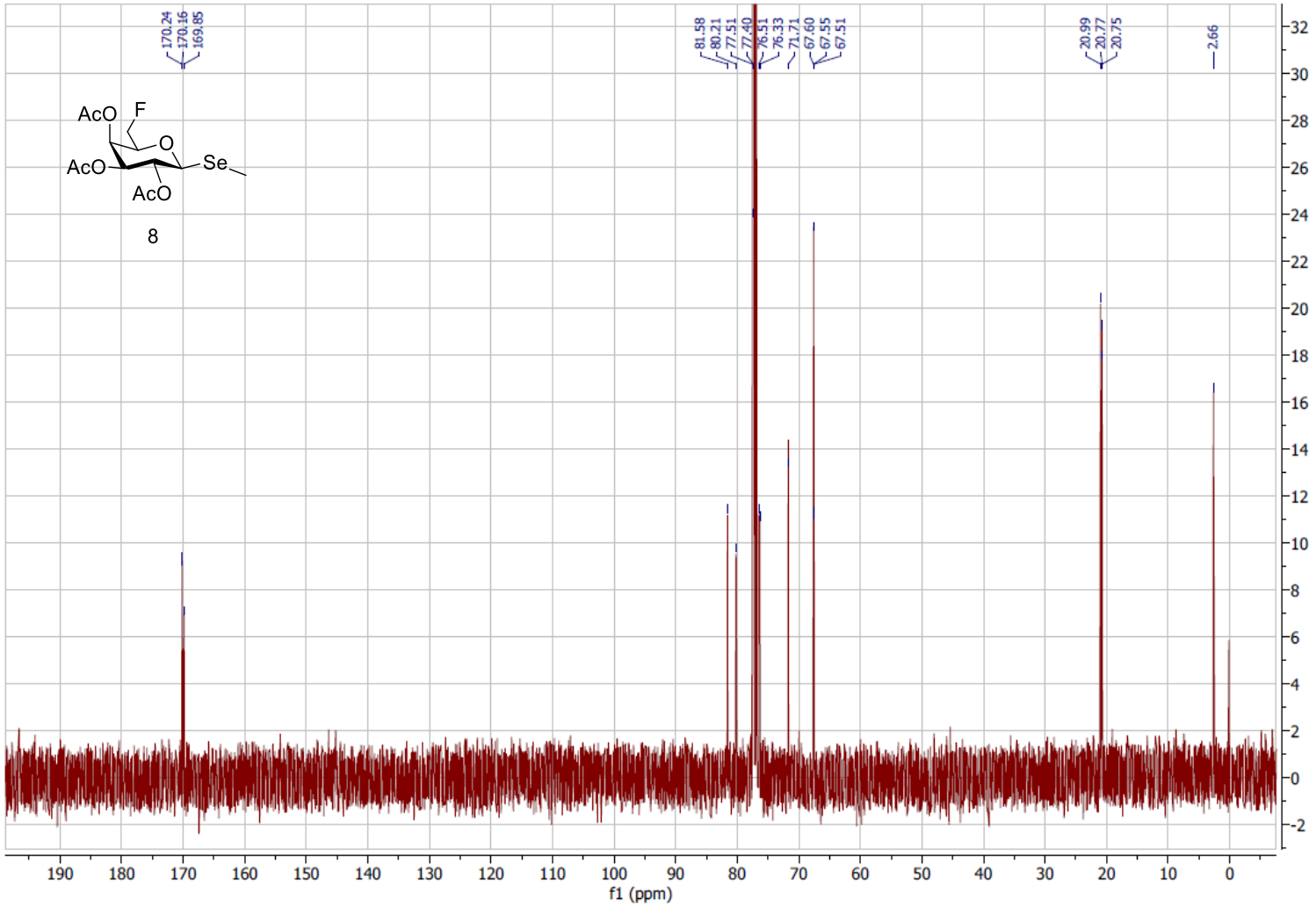
Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-fluoro-1-seleno-β-D-galactopyranoside (8)

^{1}H NMR, 500 MHz



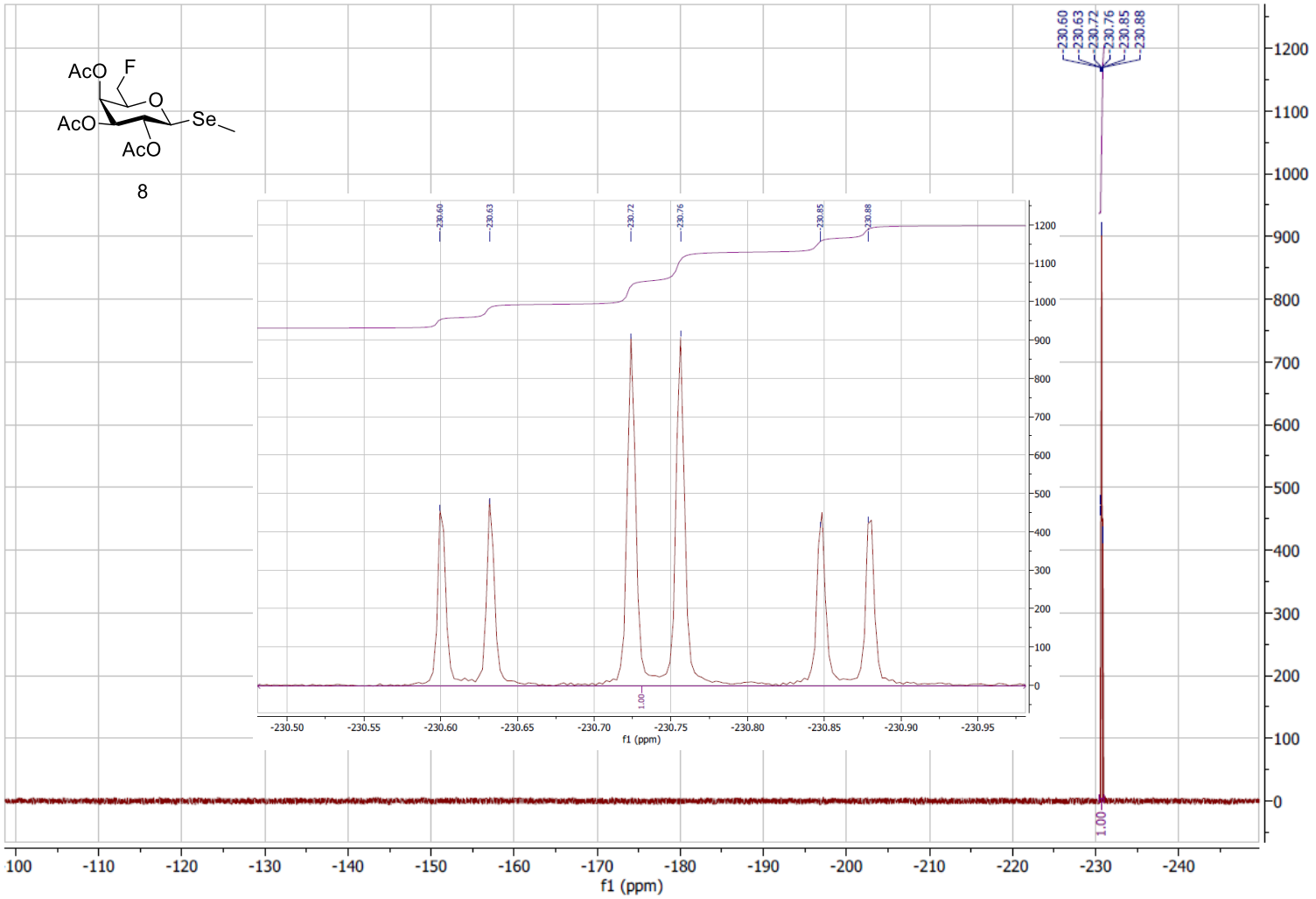
Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-fluoro-1-seleno-β-D-galactopyranoside (8)

^{13}C NMR, 126 MHz



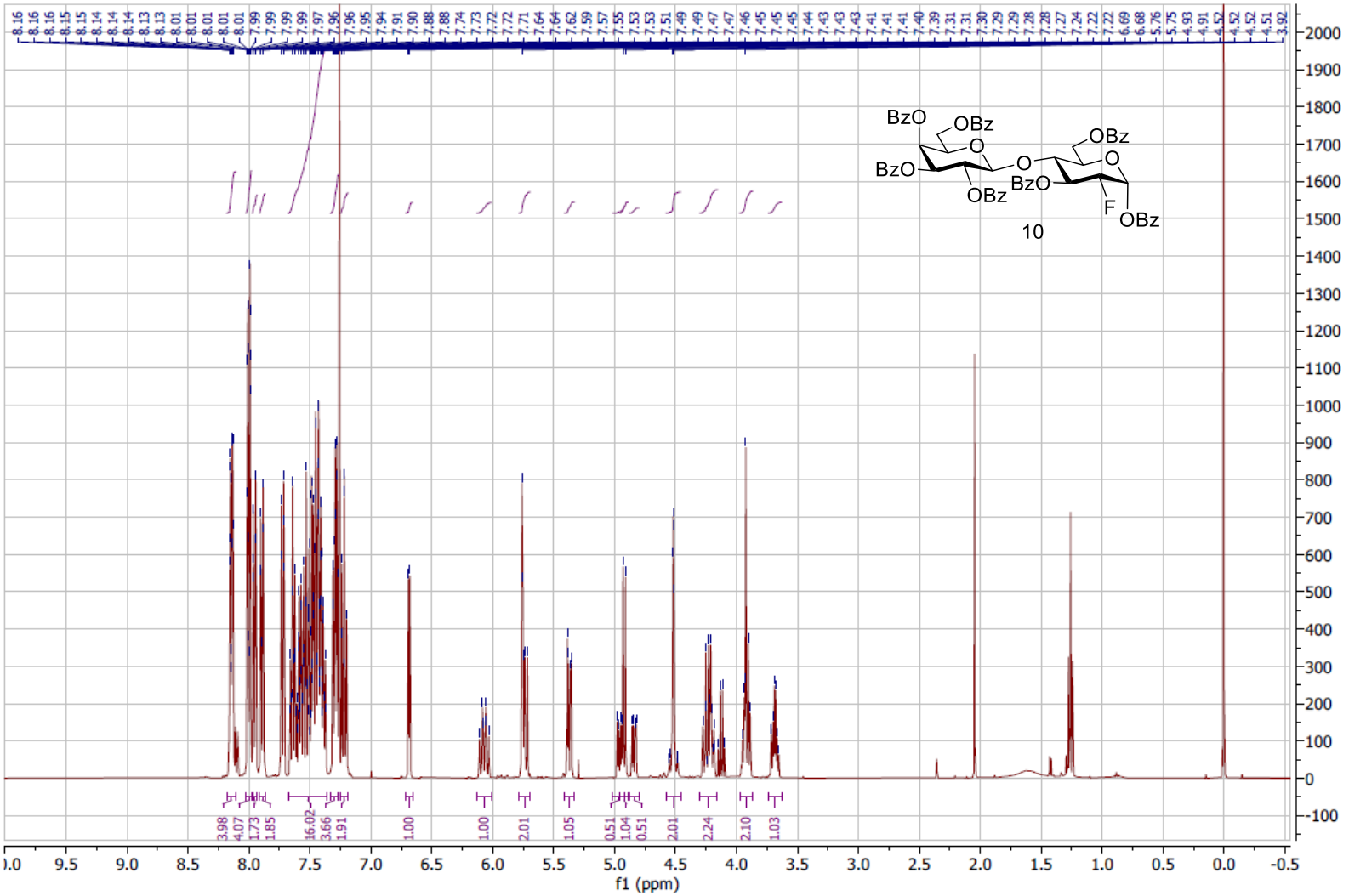
Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-fluoro-1-seleno-β-D-galactopyranoside (8)

^{19}F NMR, 376 MHz



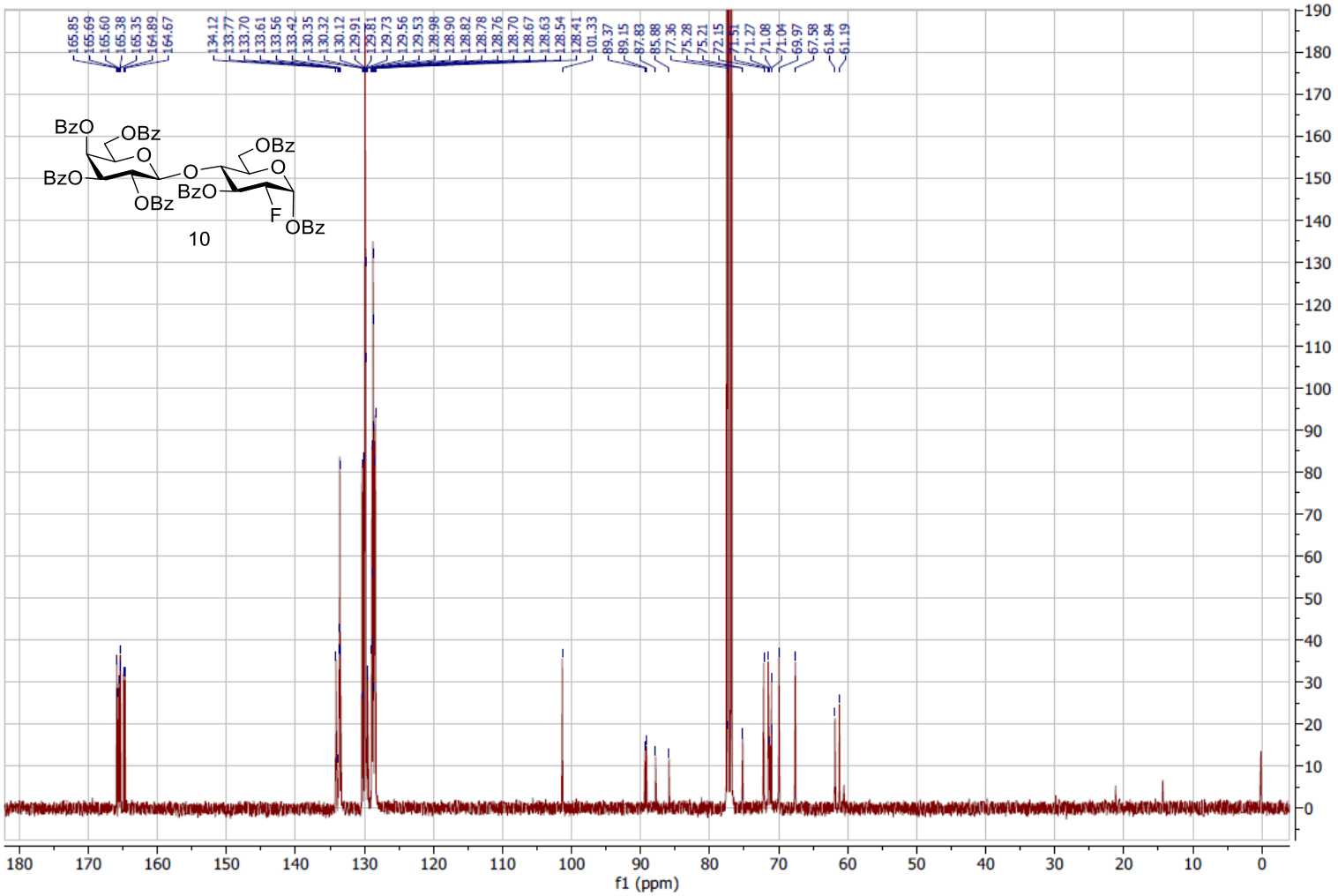
2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-fluoro-α-D-glucopyranosyl bromide (10)

^{1}H NMR, 400 MHz



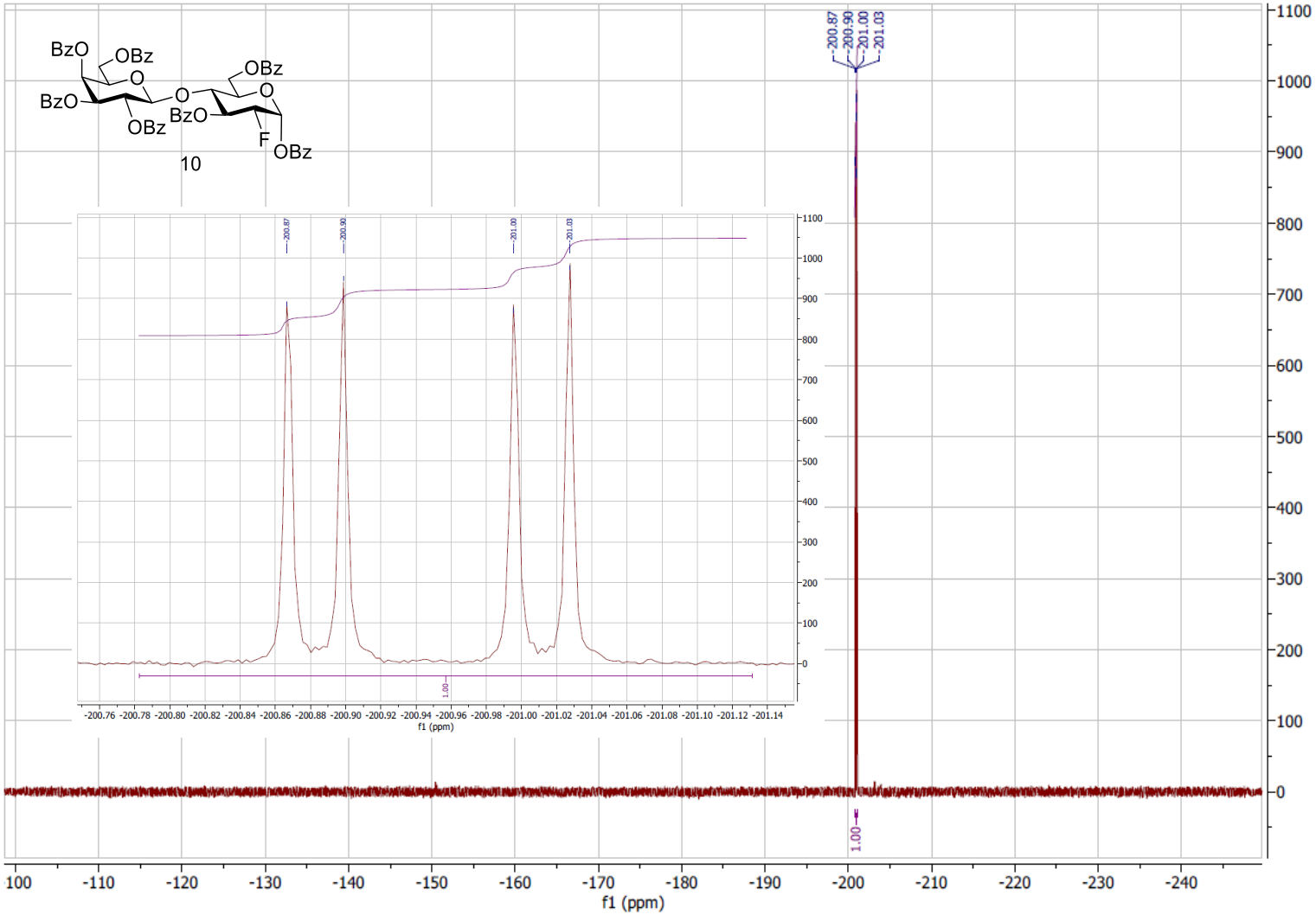
2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-fluoro-α-D-glucopyranosyl bromide (10)

^{13}C NMR, 101 MHz



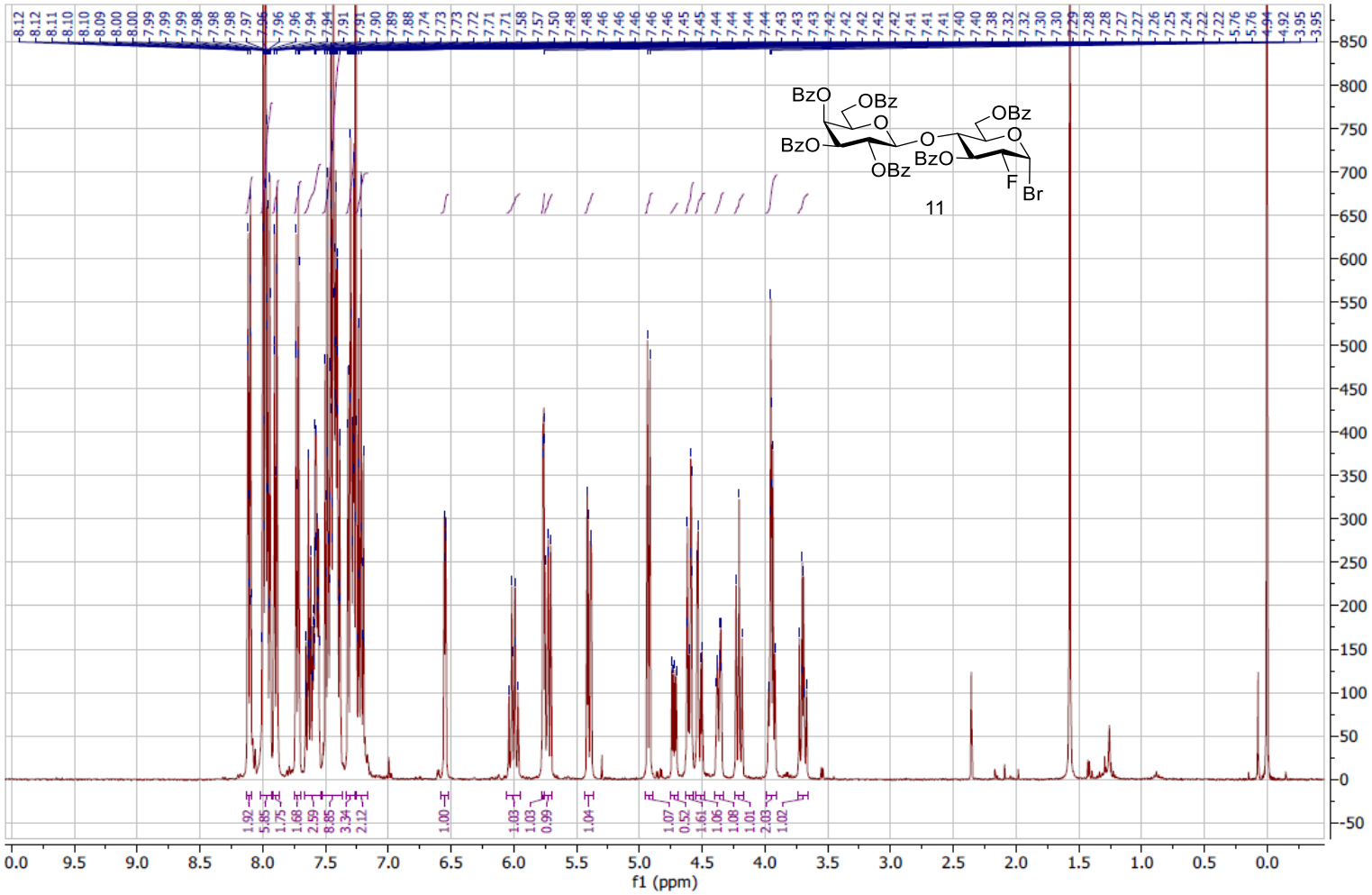
2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-fluoro-α-D-glucopyranosyl bromide (10)

^{19}F NMR, 376 MHz



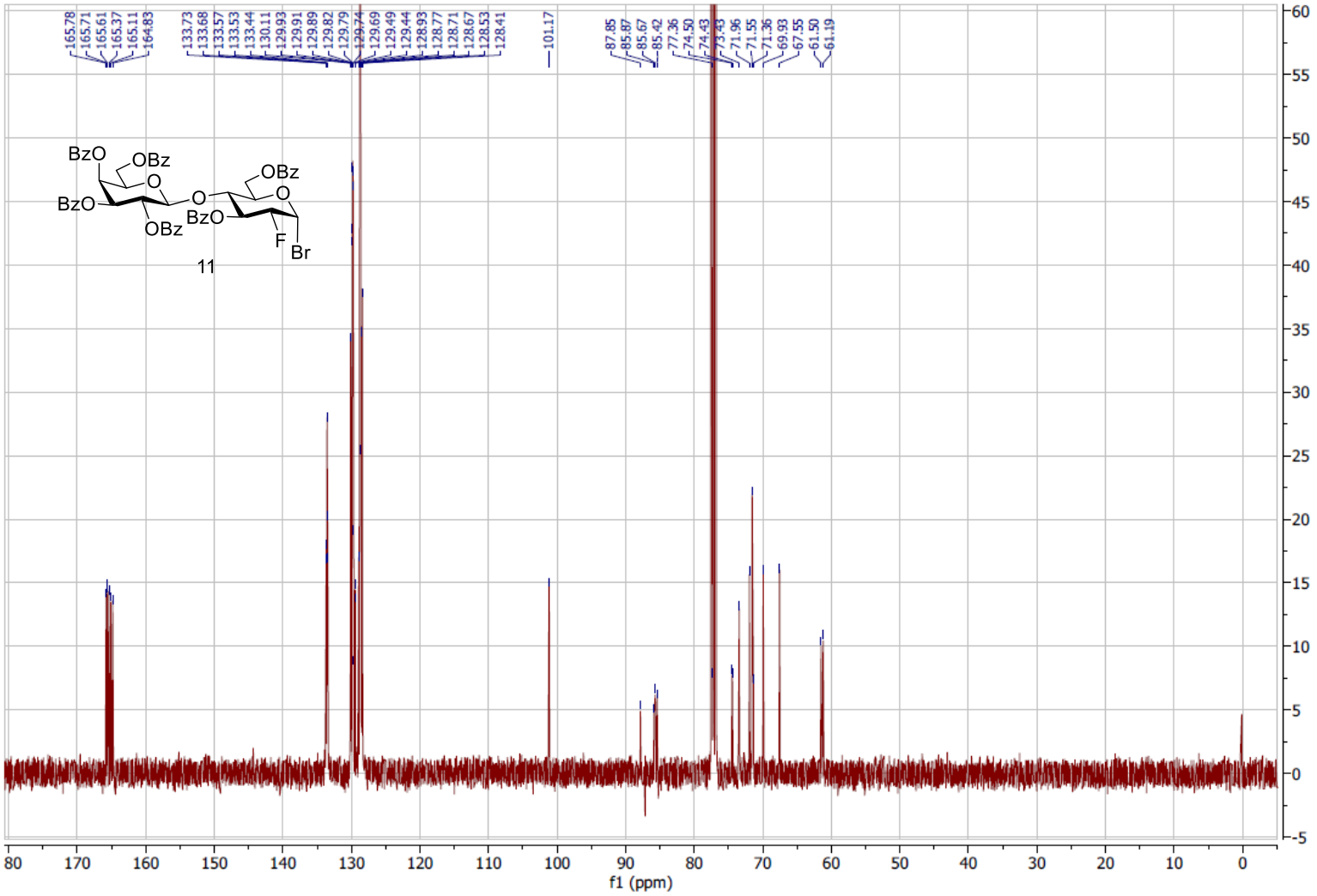
2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-fluoro-α-D-glucopyranosyl bromide (11)

^{1}H NMR, 400 MHz



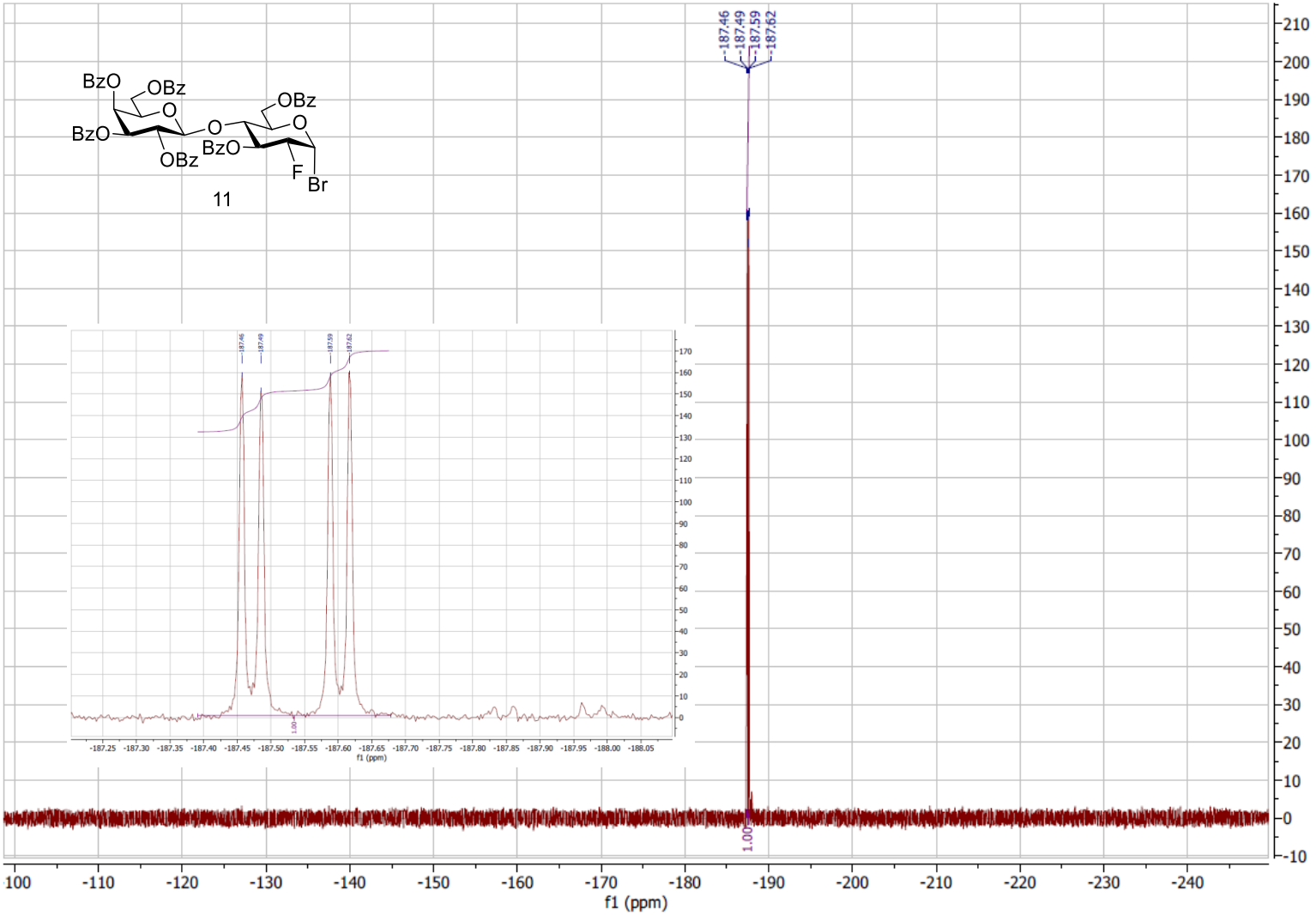
2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-fluoro-α-D-glucopyranosyl bromide (11)

^{13}C NMR, 101 MHz



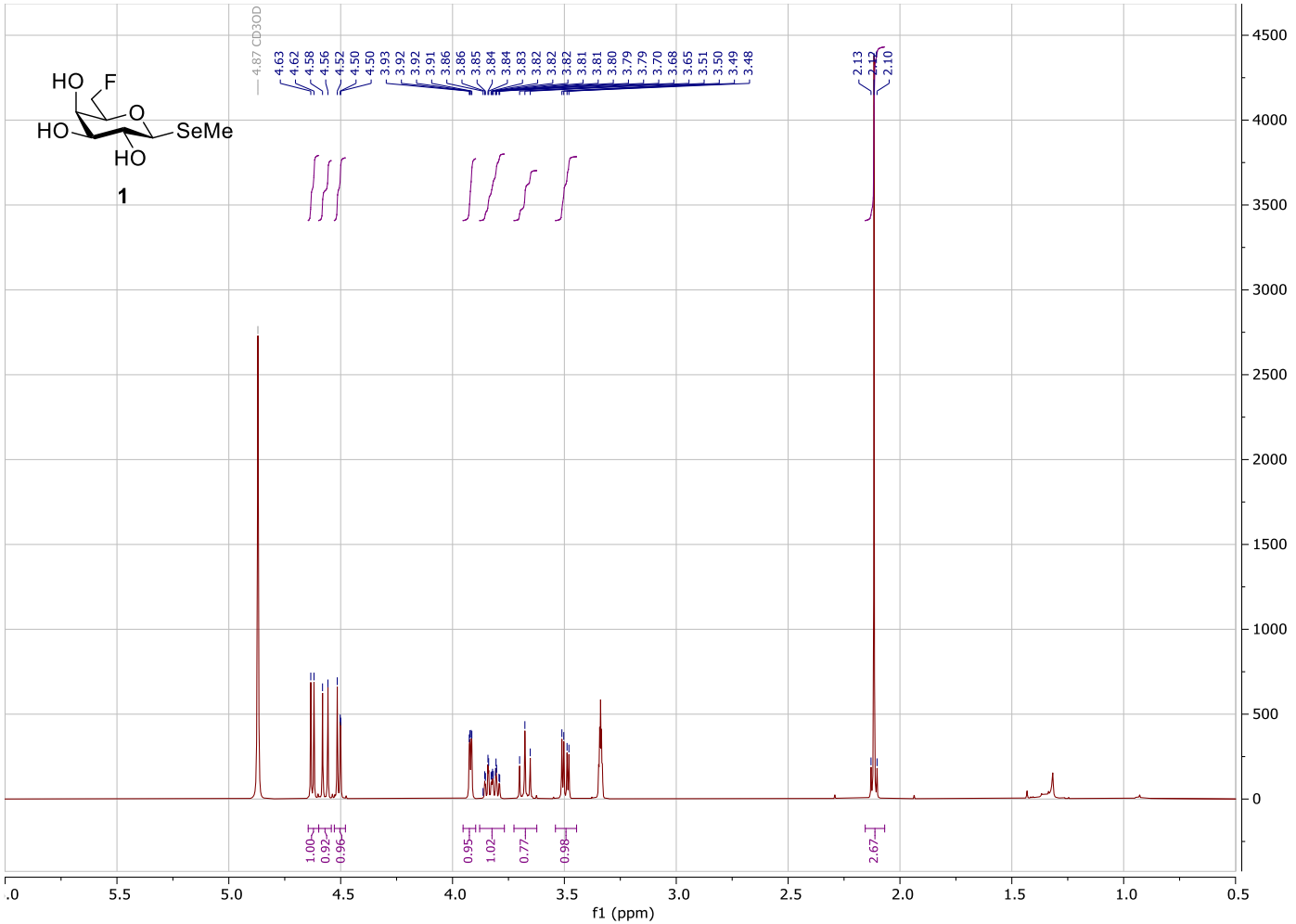
2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-fluoro-α-D-glucopyranosyl bromide (11)

^{19}F NMR, 376 MHz



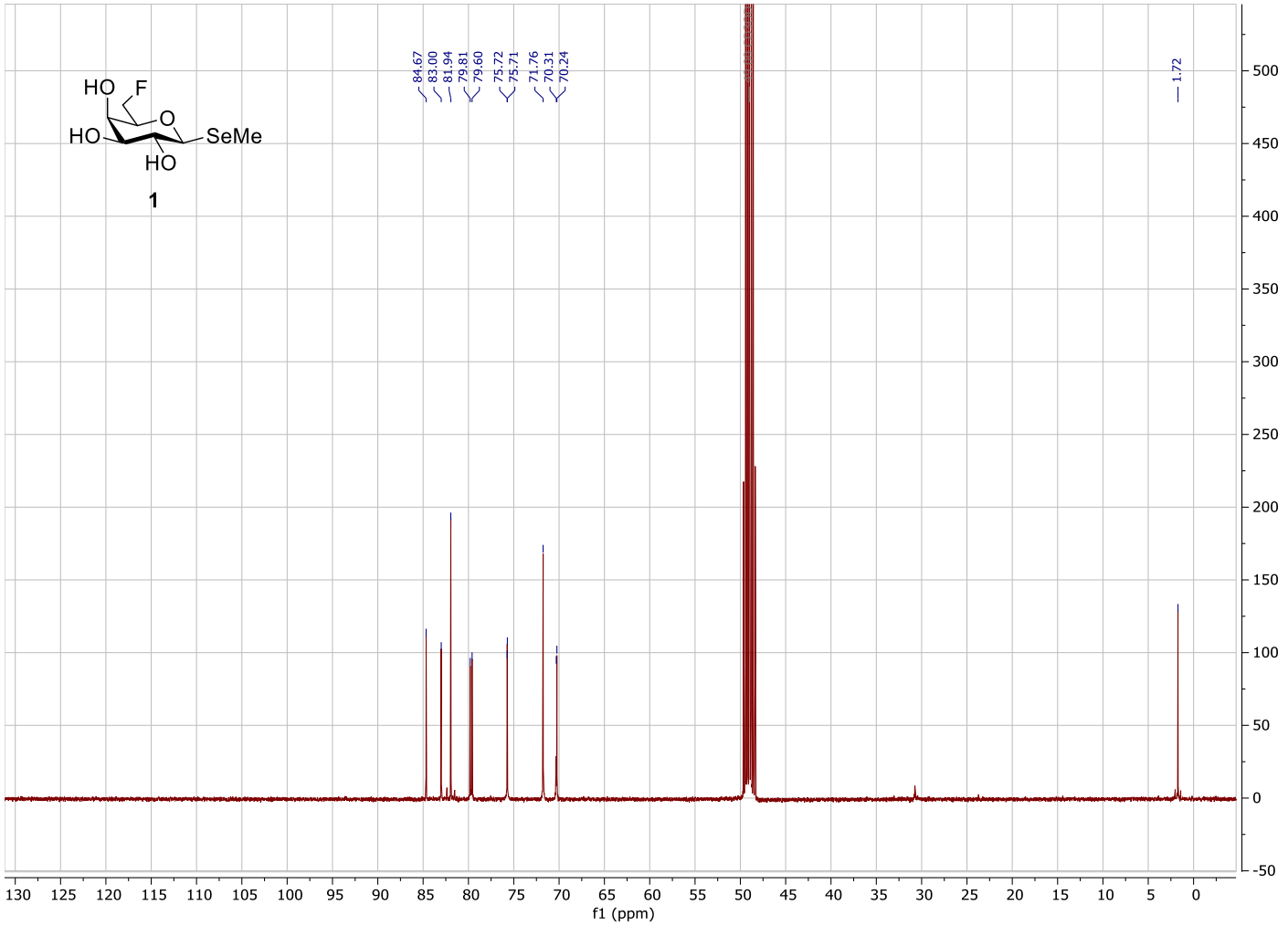
Methyl 6-deoxy-6-fluoro-1-seleno-β-D-galactopyranoside (1)

^{1}H NMR, 400 MHz



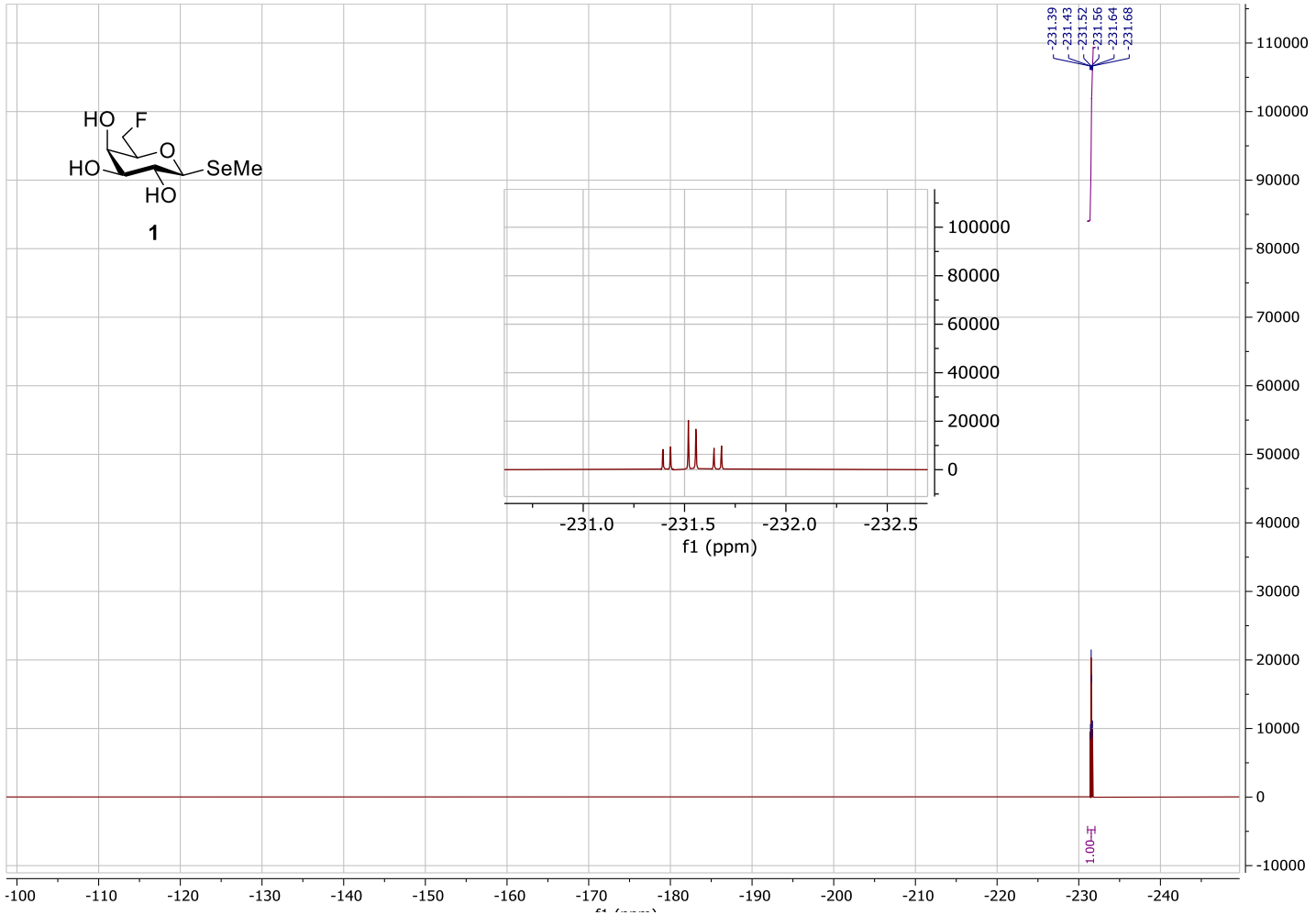
Methyl 6-deoxy-6-fluoro-1-seleno-β-D-galactopyranoside (1)

^{13}C NMR, 101 MHz



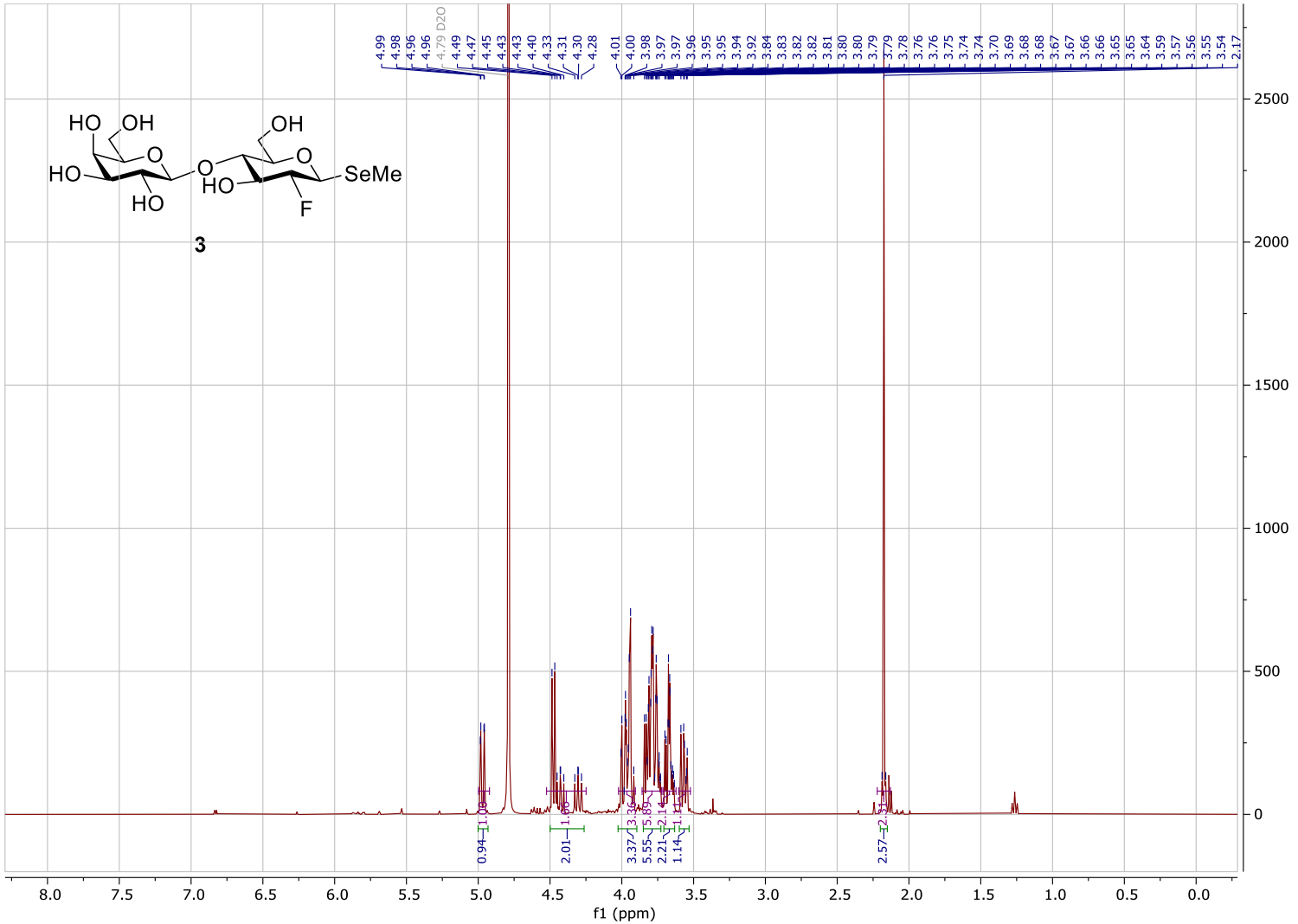
Methyl 6-deoxy-6-fluoro-1-seleno-β-D-galactopyranoside (1)

^{19}F NMR, 376 MHz



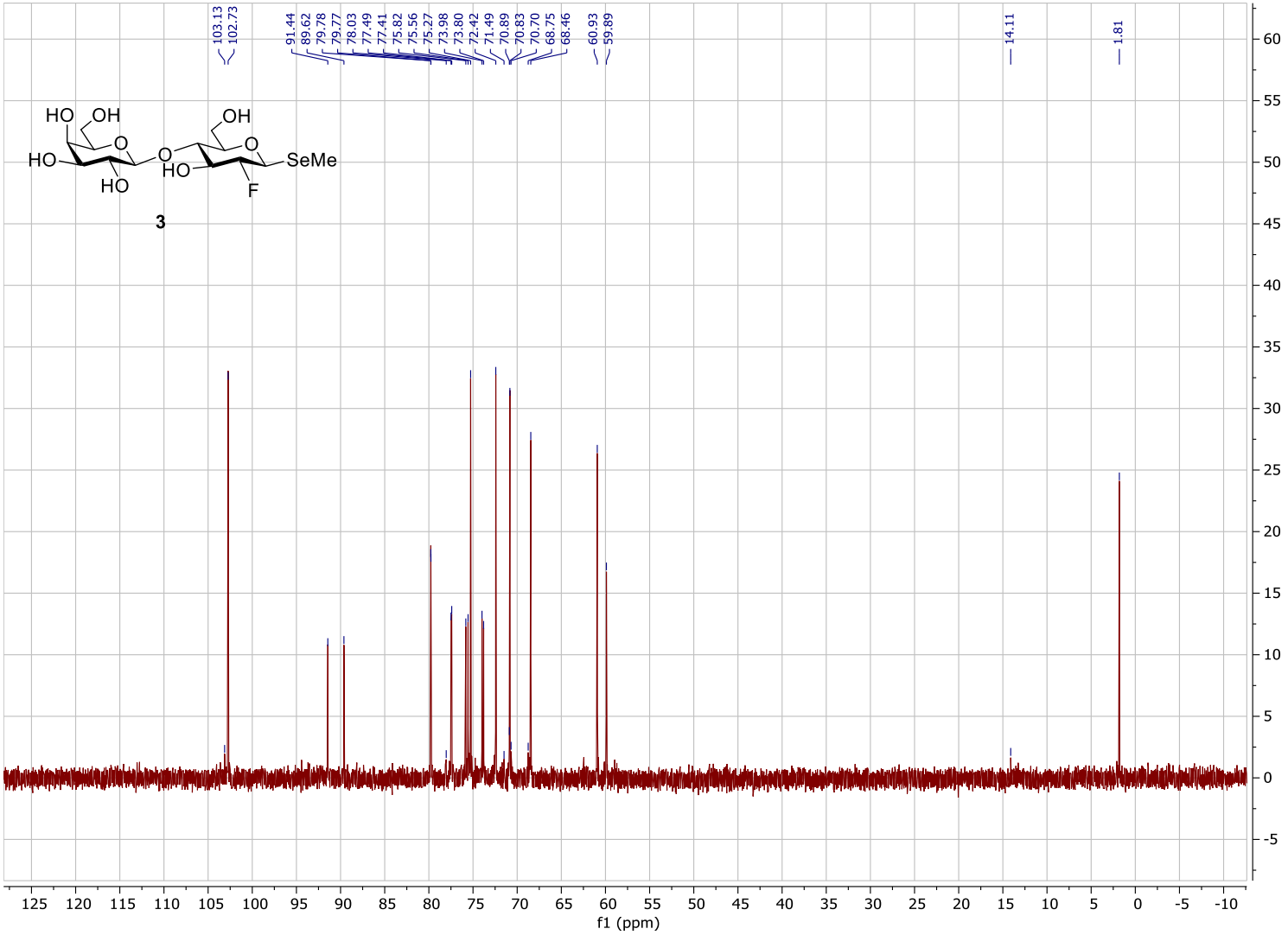
Methyl β-D-galactopyranosyl-(1→4)-2-deoxy-2-fluoro-1-seleno-α-D-glucopyranoside (3)

^{1}H NMR, 400 MHz



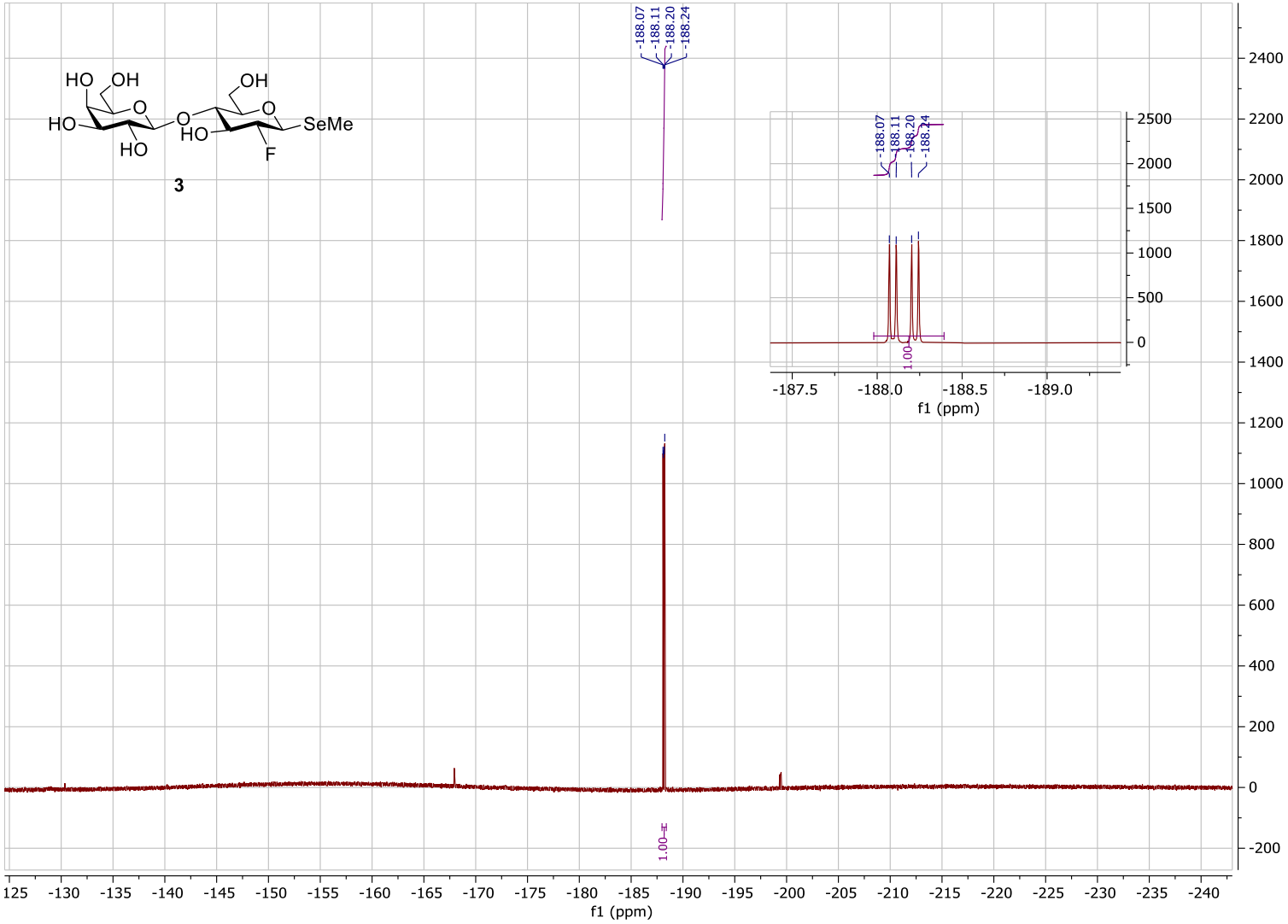
Methyl β-D-galactopyranosyl-(1→4)-2-deoxy-2-fluoro-1-seleno-α-D-glucopyranoside (3)

^{13}C NMR, 101 MHz



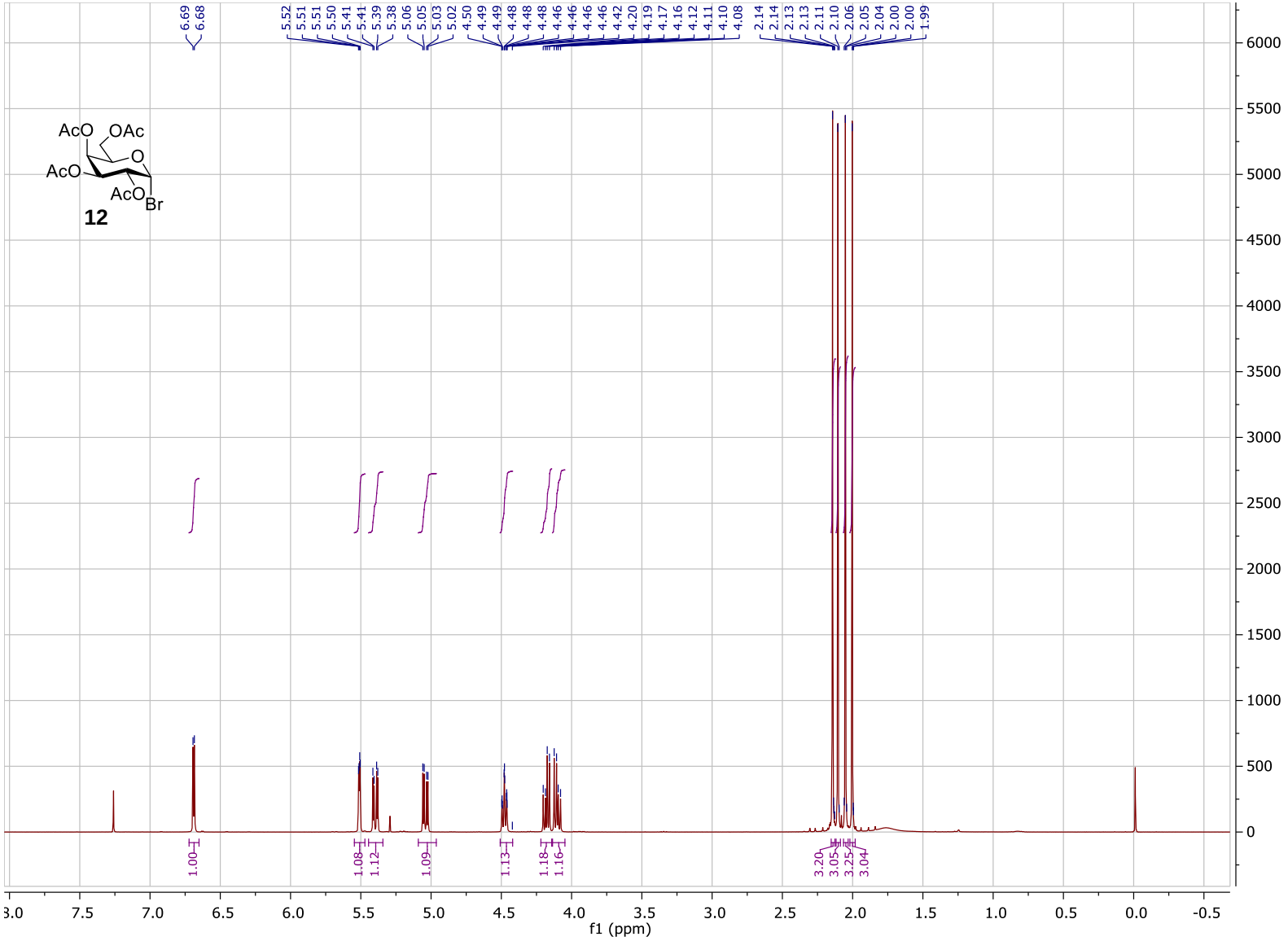
Methyl β-D-galactopyranosyl-(1→4)-2-deoxy-2-fluoro-1-seleno-α-D-glucopyranoside (3)

^{19}F NMR, 376 MHz



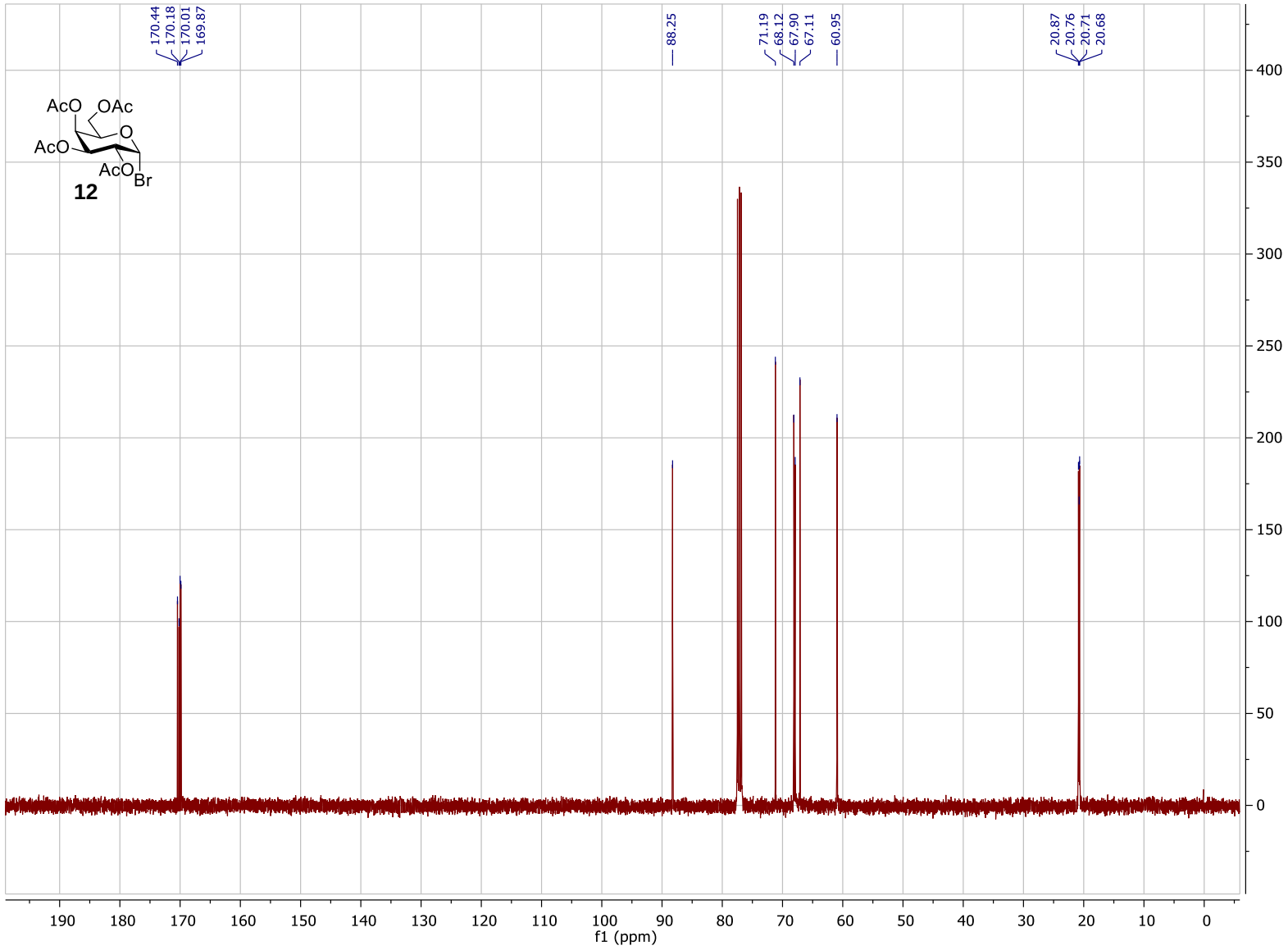
2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl bromide (12)

^{1}H NMR, 400 MHz



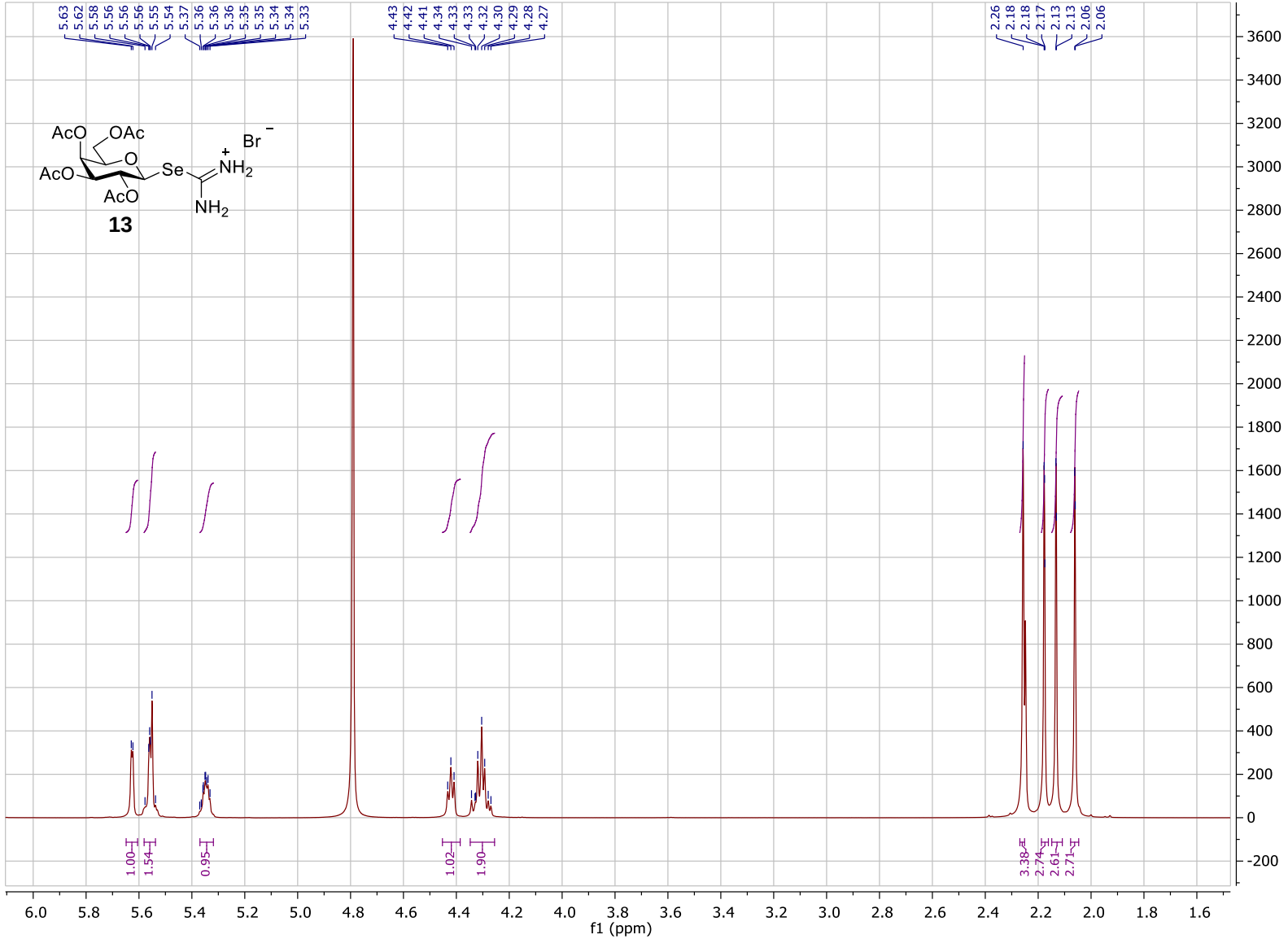
2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl bromide (12)

^{13}C NMR, 101 MHz



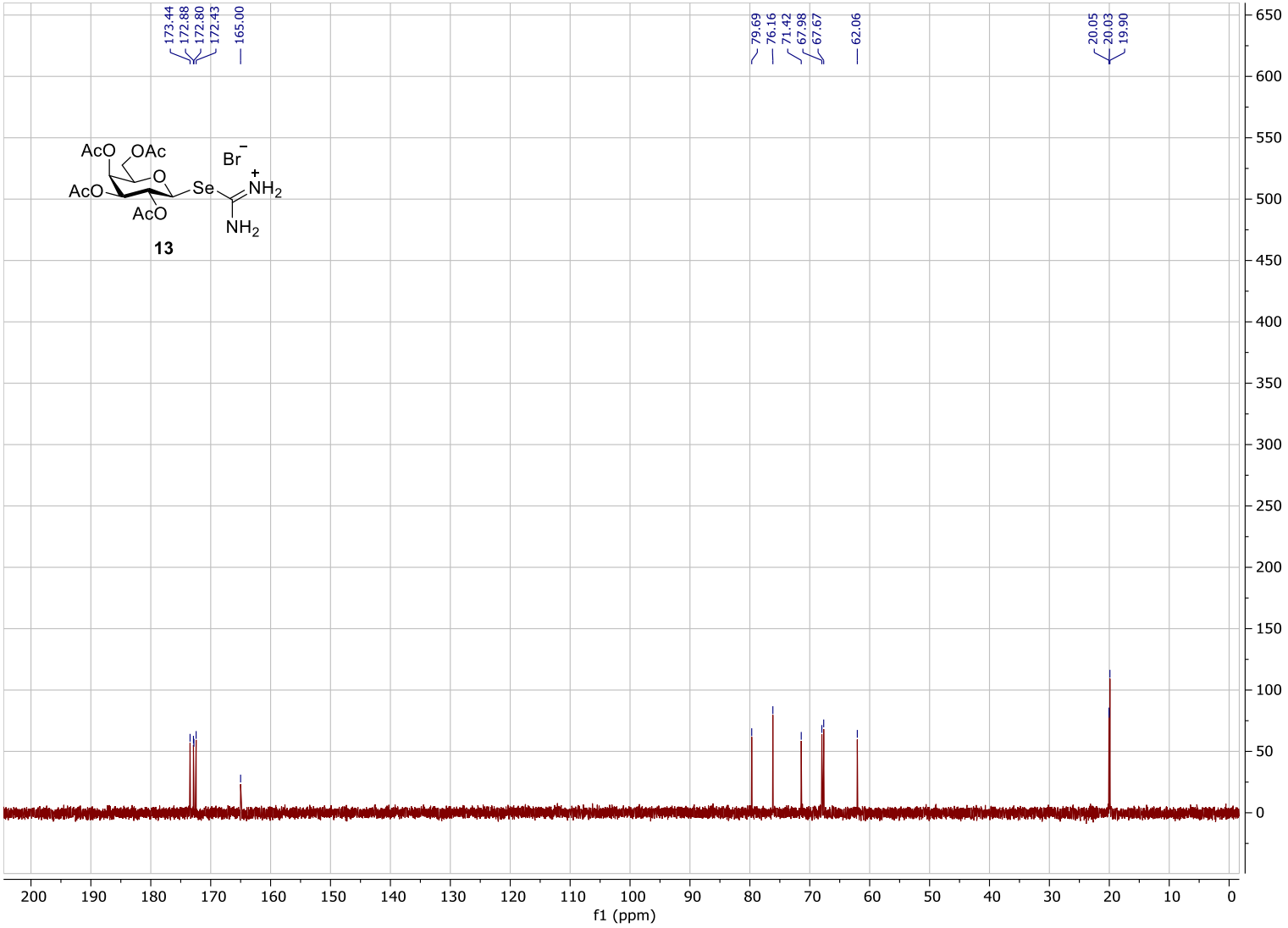
2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosylisoselenouronium bromide (13)

^{1}H NMR, 500 MHz



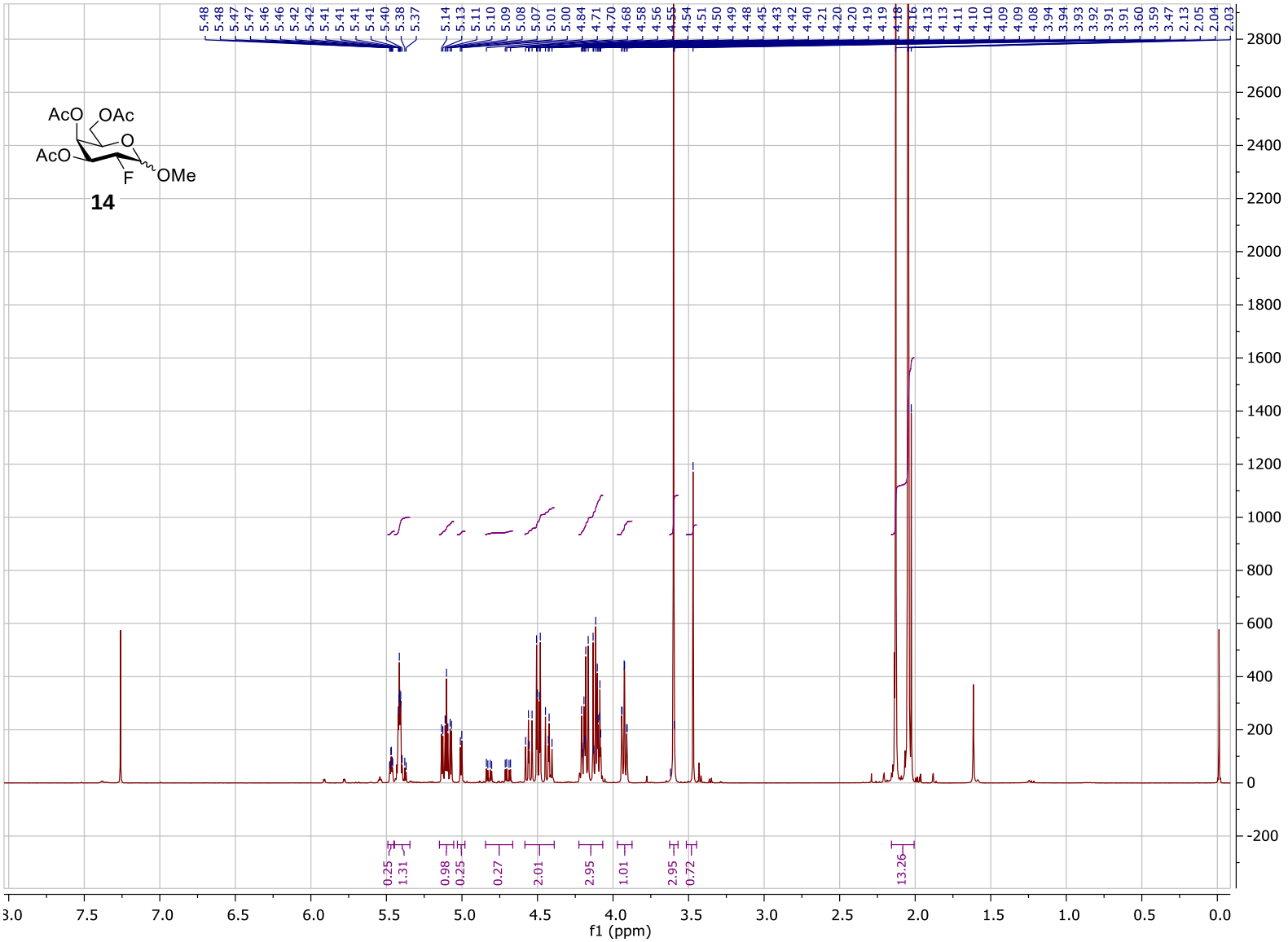
2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosylisoselenouronium bromide (13)

^{13}C NMR, 126 MHz



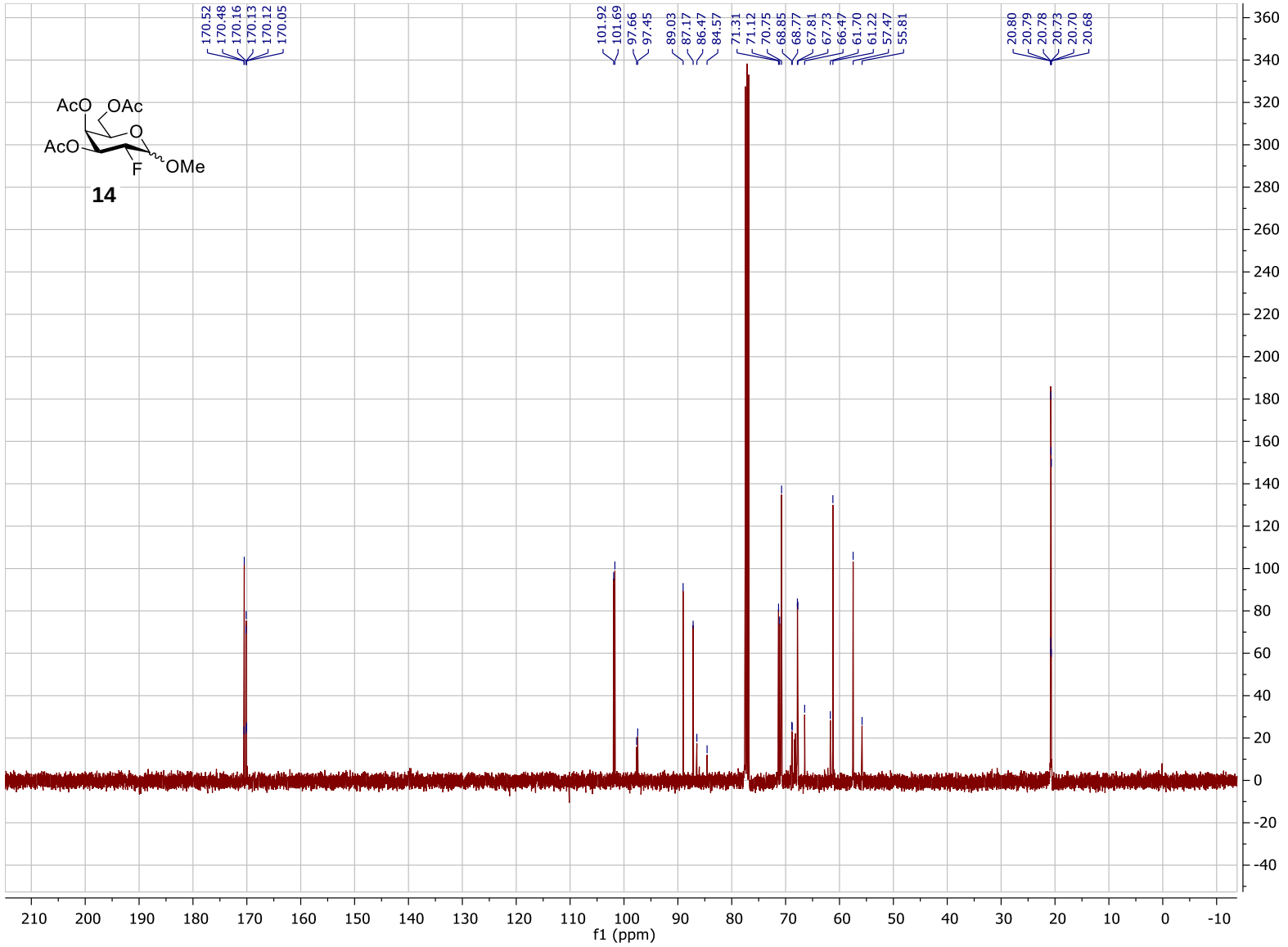
Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-fluoro-D-galactopyranoside (14)

^{1}H NMR, 400 MHz



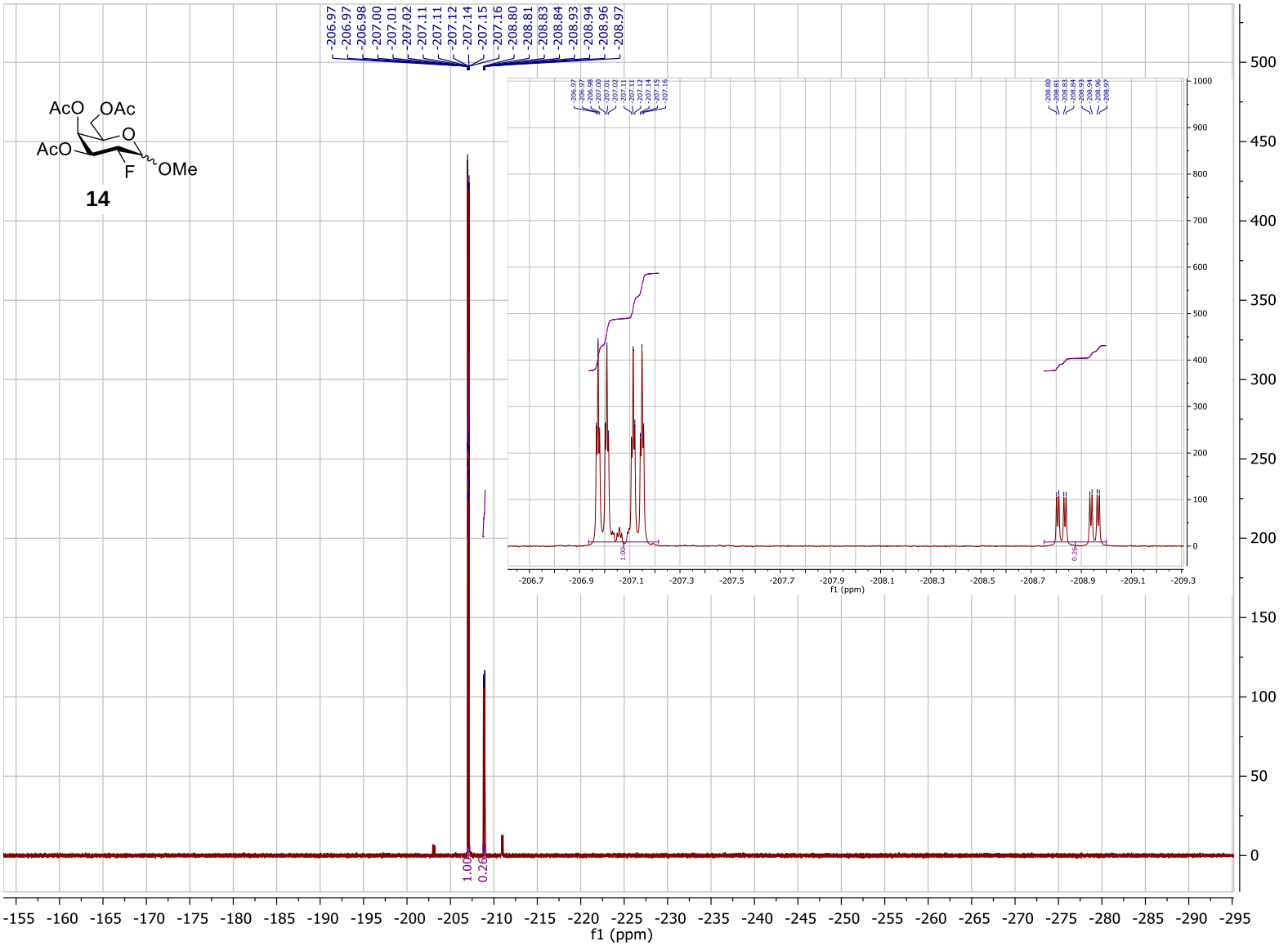
Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-fluoro-D-galactopyranoside (14)

^{13}C NMR, 101 MHz



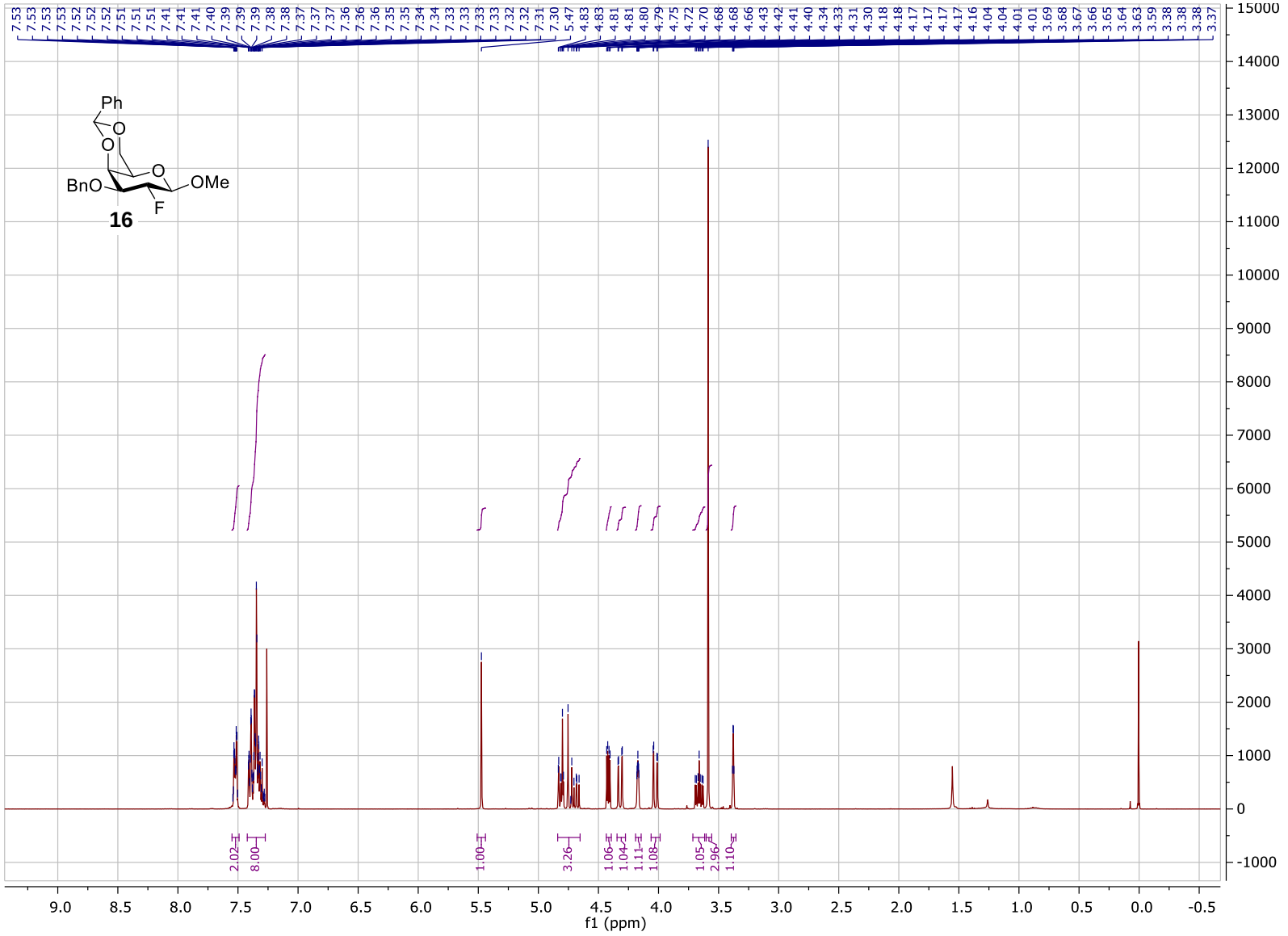
Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-fluoro-D-galactopyranoside (14)

^{19}F NMR, 376 MHz



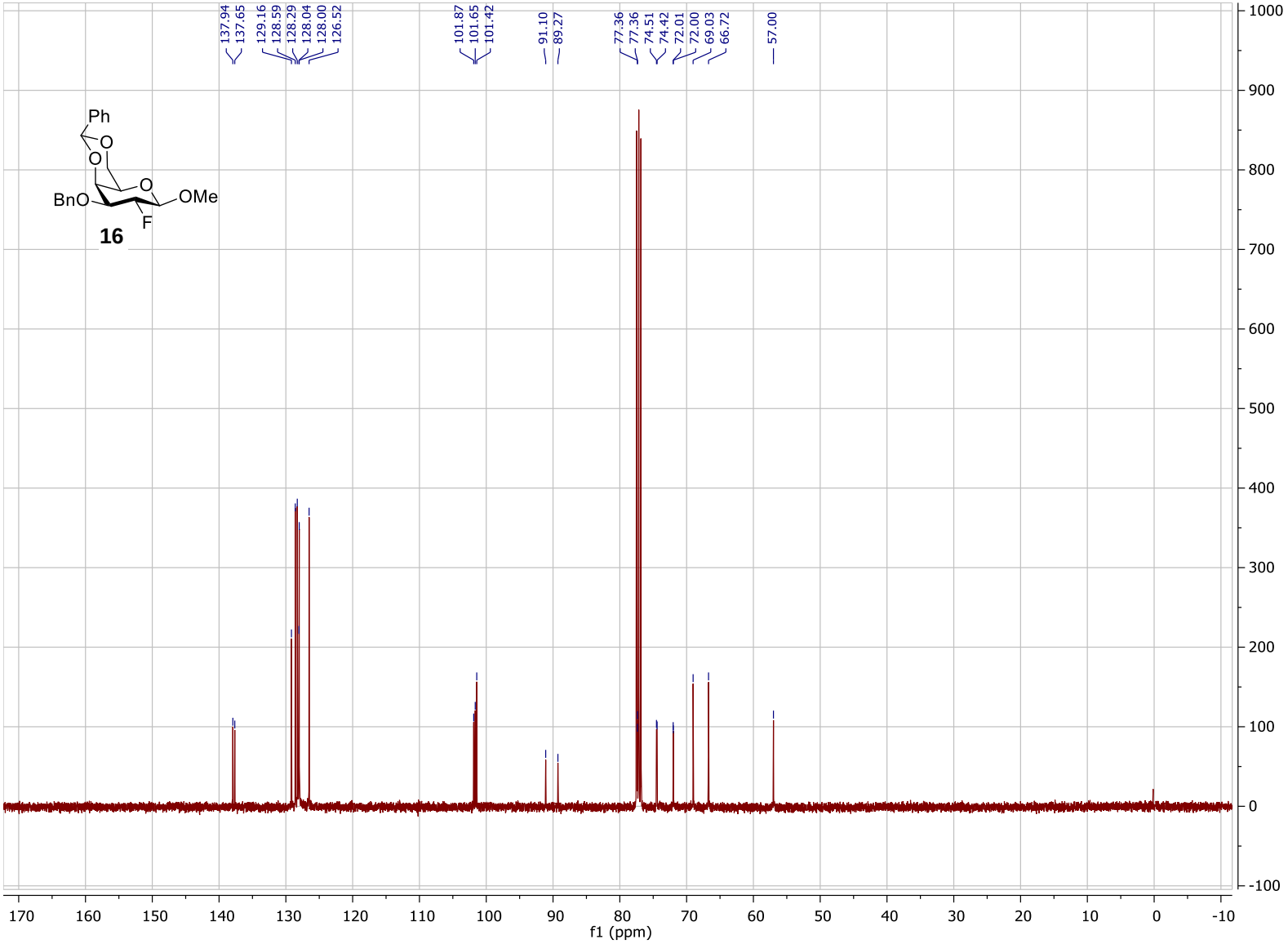
Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-fluoro-β-D-galactopyranoside (16)

^{1}H NMR, 400 MHz



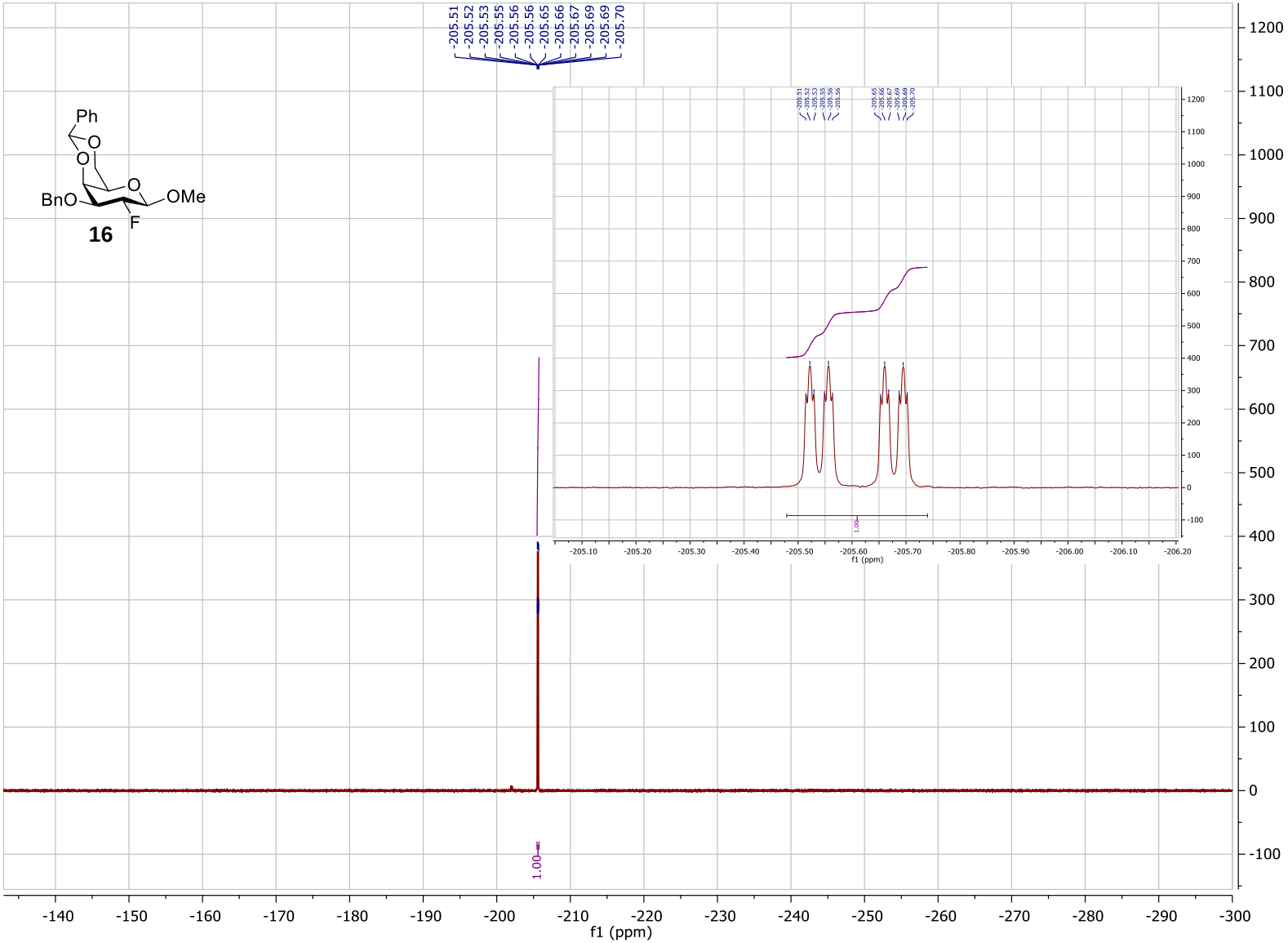
Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-fluoro-β-D-galactopyranoside (16)

^{13}C NMR, 101 MHz



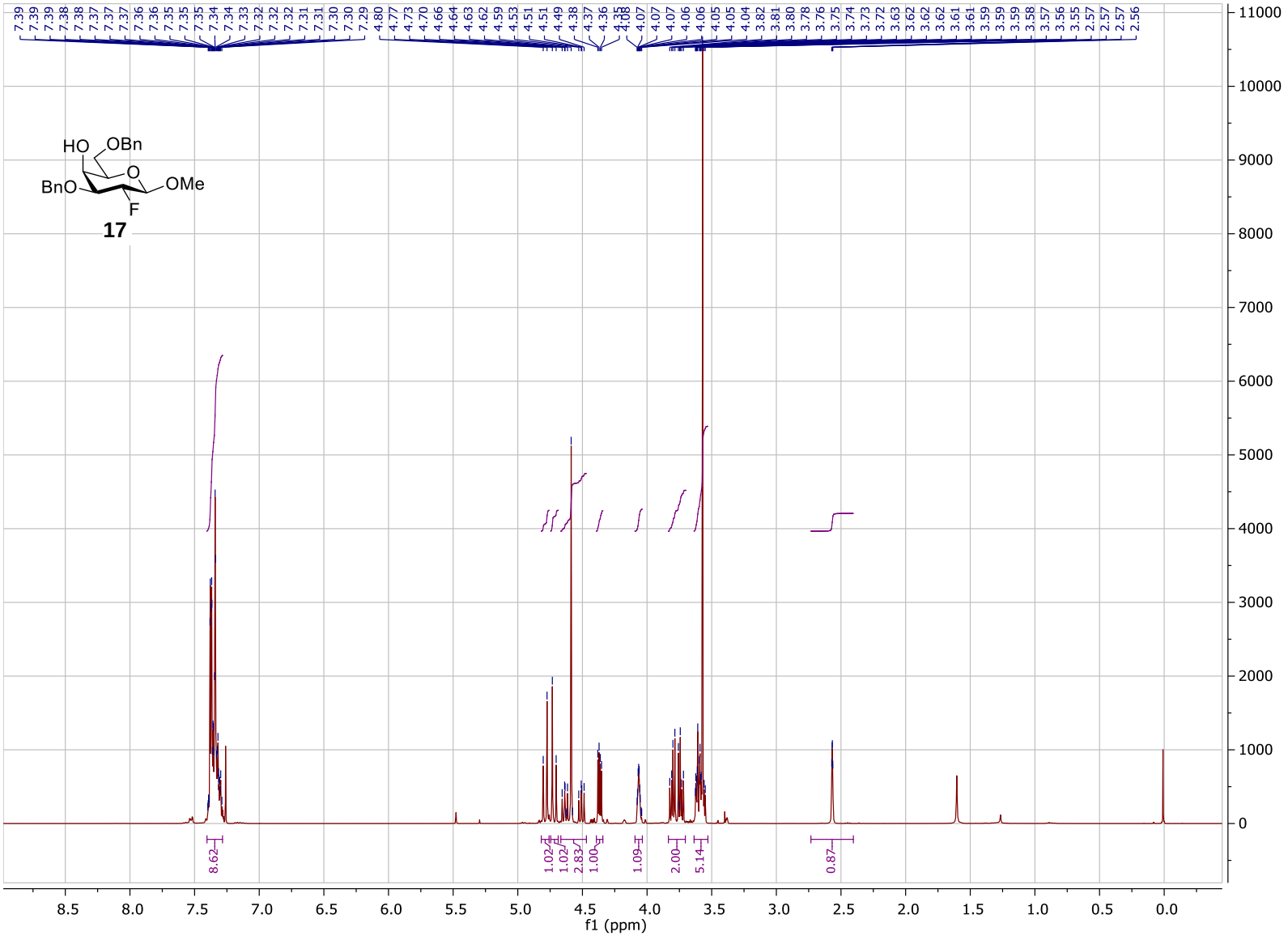
Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-fluoro-β-D-galactopyranoside (16)

^{19}F NMR, 376 MHz



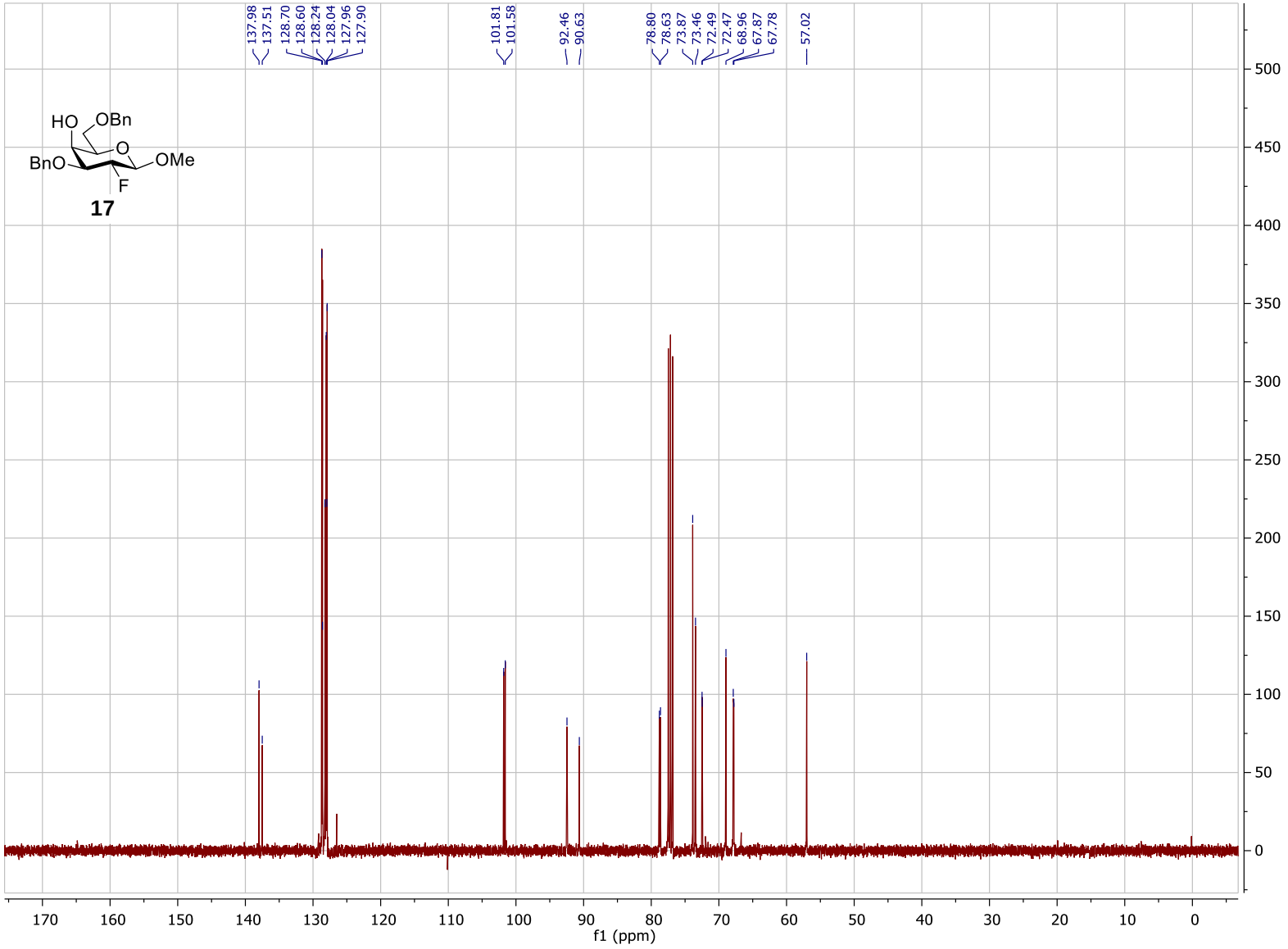
Methyl 3,6-di-*O*-benzyl-2-deoxy-2-fluoro-β-D-galactopyranoside (17)

^{1}H NMR, 400 MHz



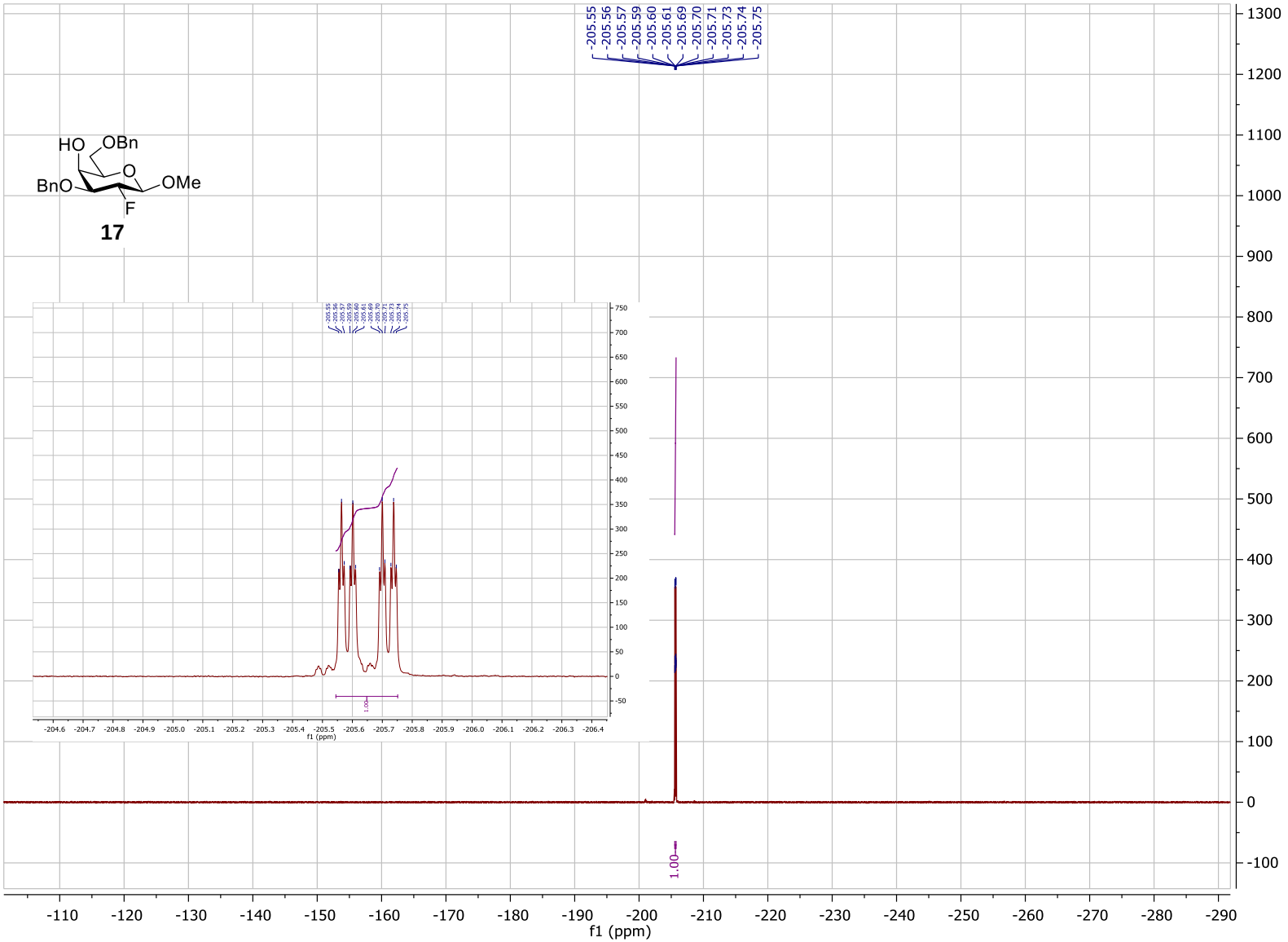
Methyl 3,6-di-*O*-benzyl-2-deoxy-2-fluoro-β-D-galactopyranoside (17)

^{13}C NMR, 101 MHz



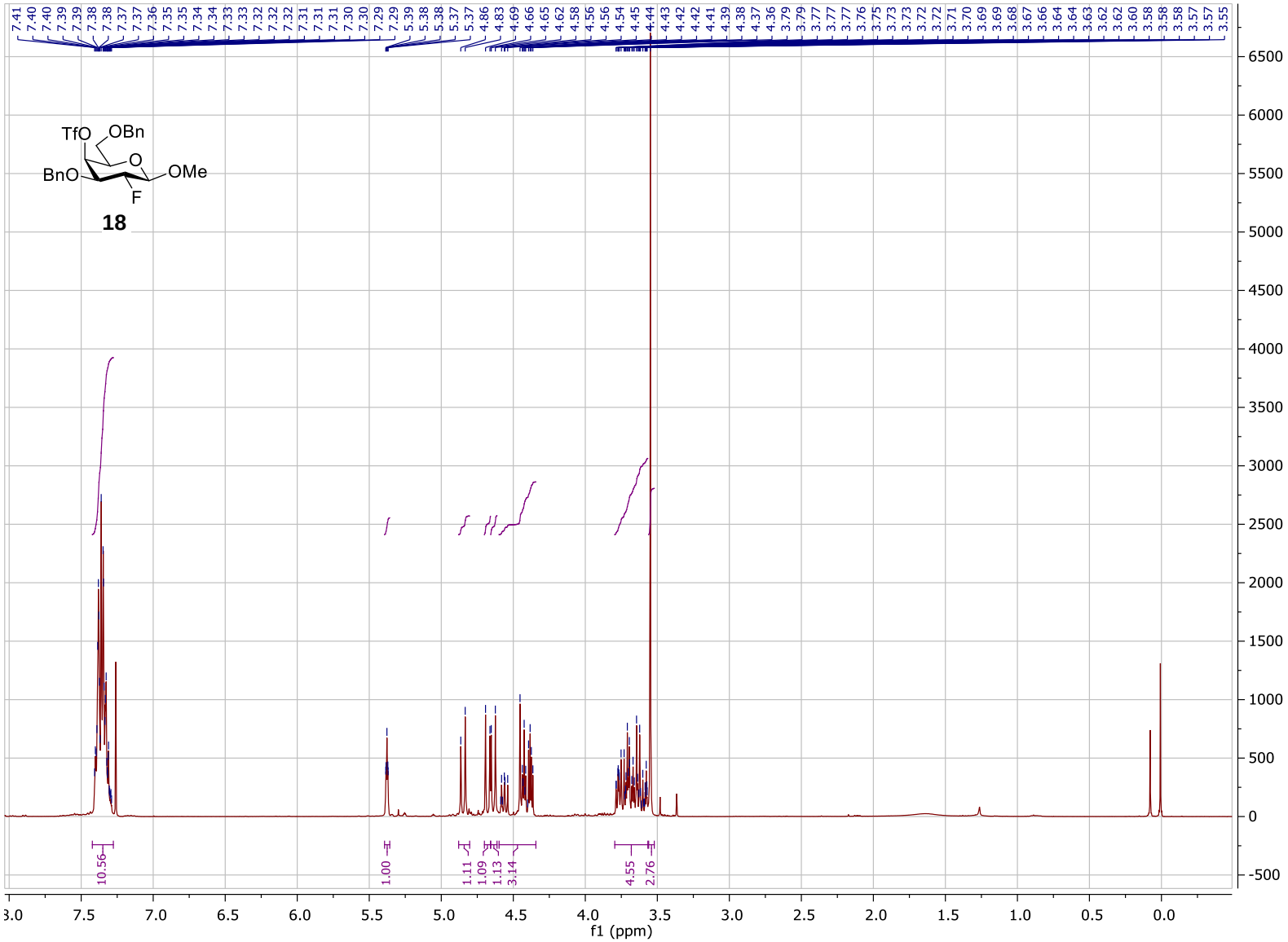
Methyl 3,6-di-*O*-benzyl-2-deoxy-2-fluoro-β-D-galactopyranoside (17)

^{19}f NMR, 376 MHz



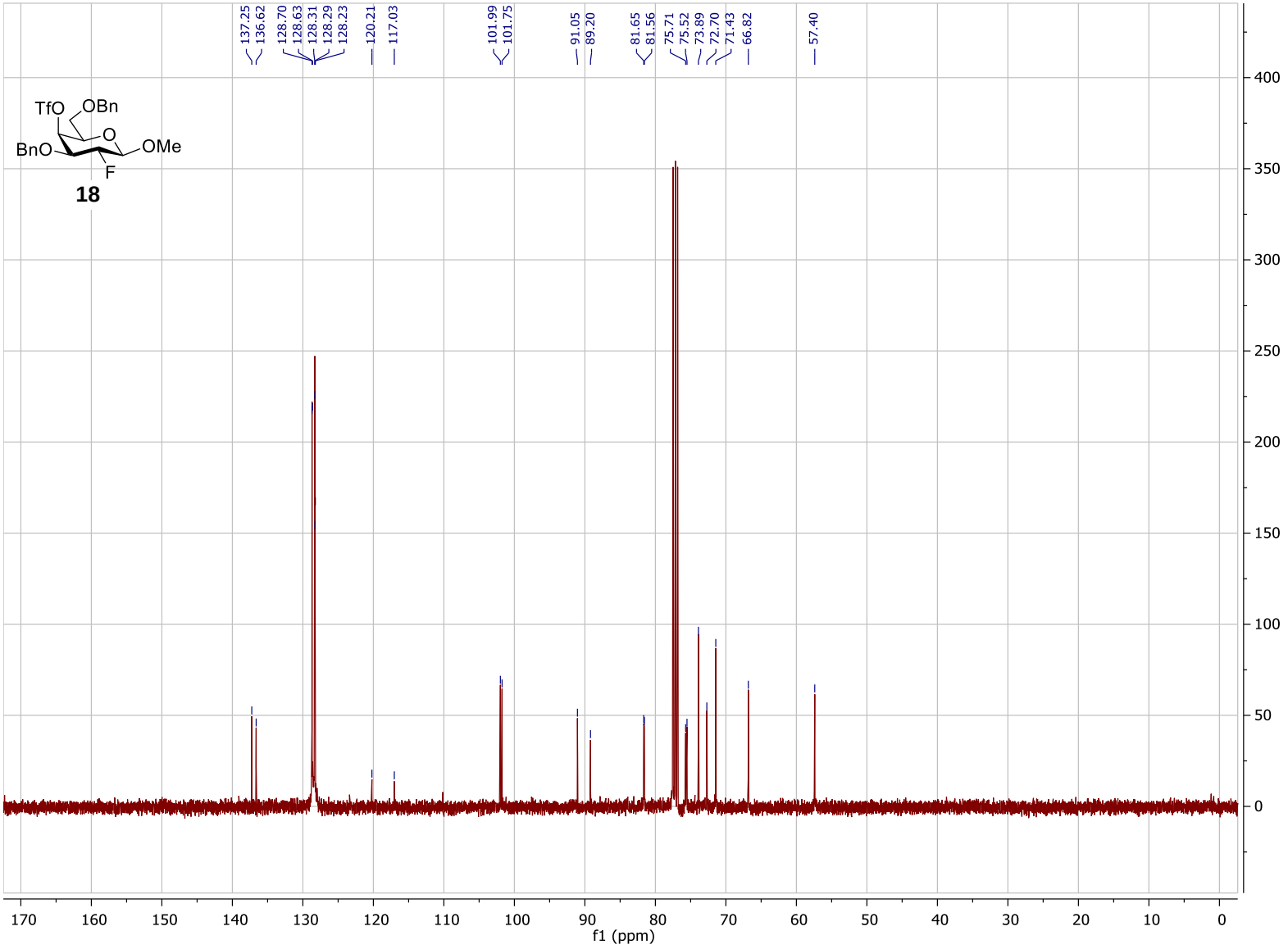
Methyl 3,6-di-*O*-benzyl-2-deoxy-2-fluoro-4-*O*-trifluoromethanesulfonyl-β-D-galactopyranoside (18)

^{1}H NMR, 400 MHz



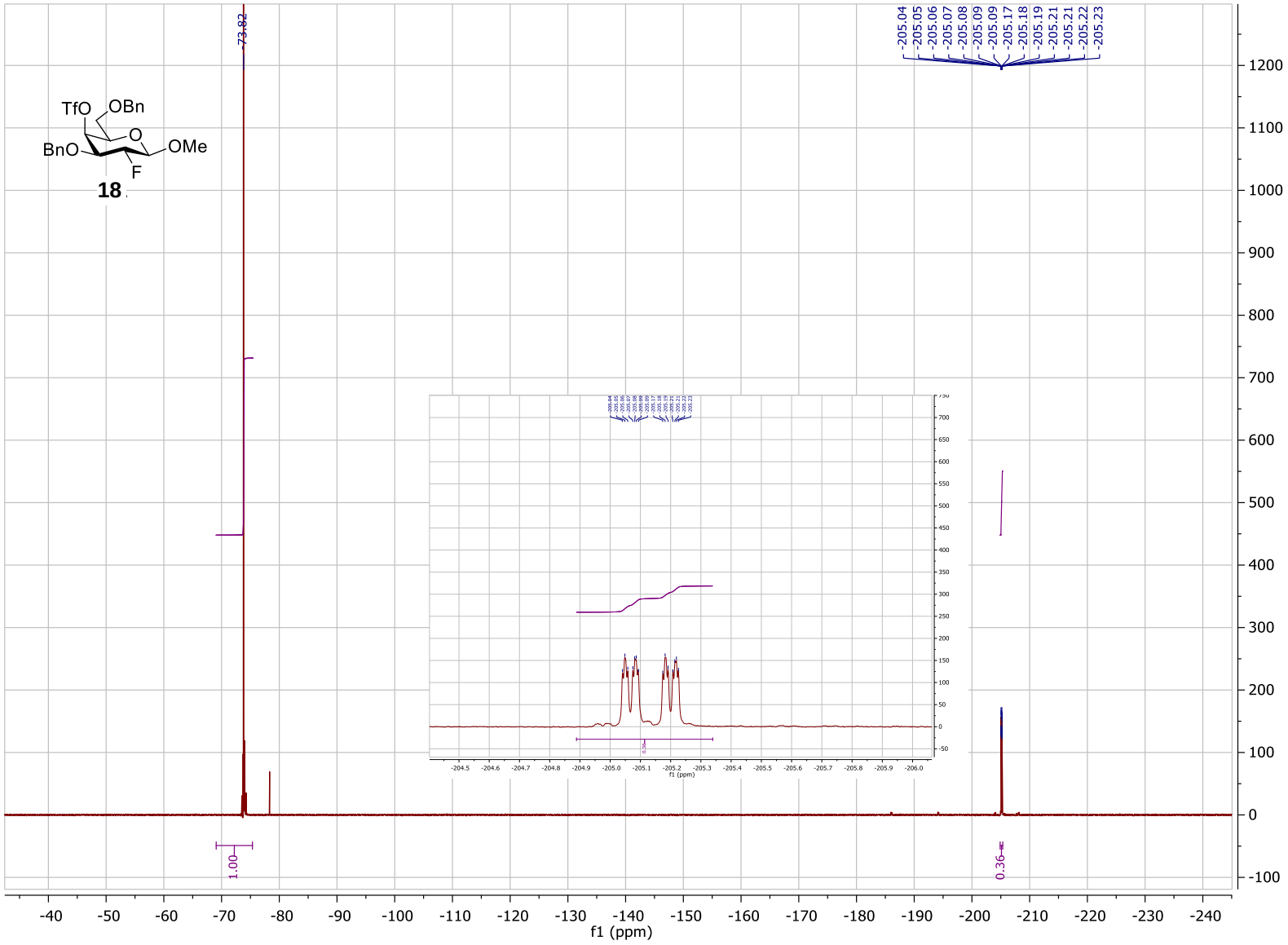
Methyl 3,6-di-*O*-benzyl-2-deoxy-2-fluoro-4-*O*-trifluoromethanesulfonyl-β-D-galactopyranoside (18)

^{13}C NMR, 101 MHz



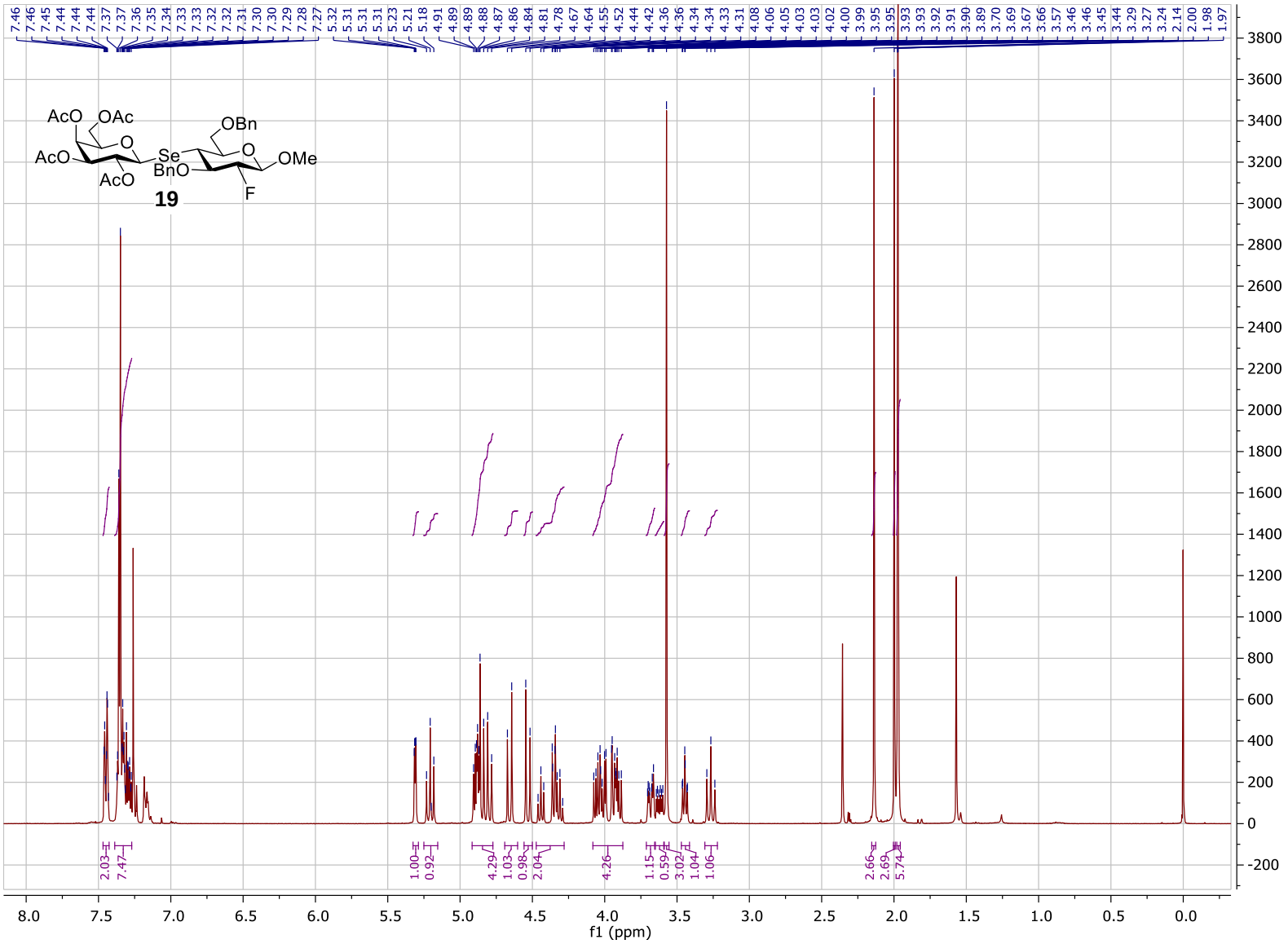
Methyl 3,6-di-*O*-benzyl-2-deoxy-2-fluoro-4-*O*-trifluoromethanesulfonyl-β-D-galactopyranoside (18)

^{19}F NMR, 376 MHz



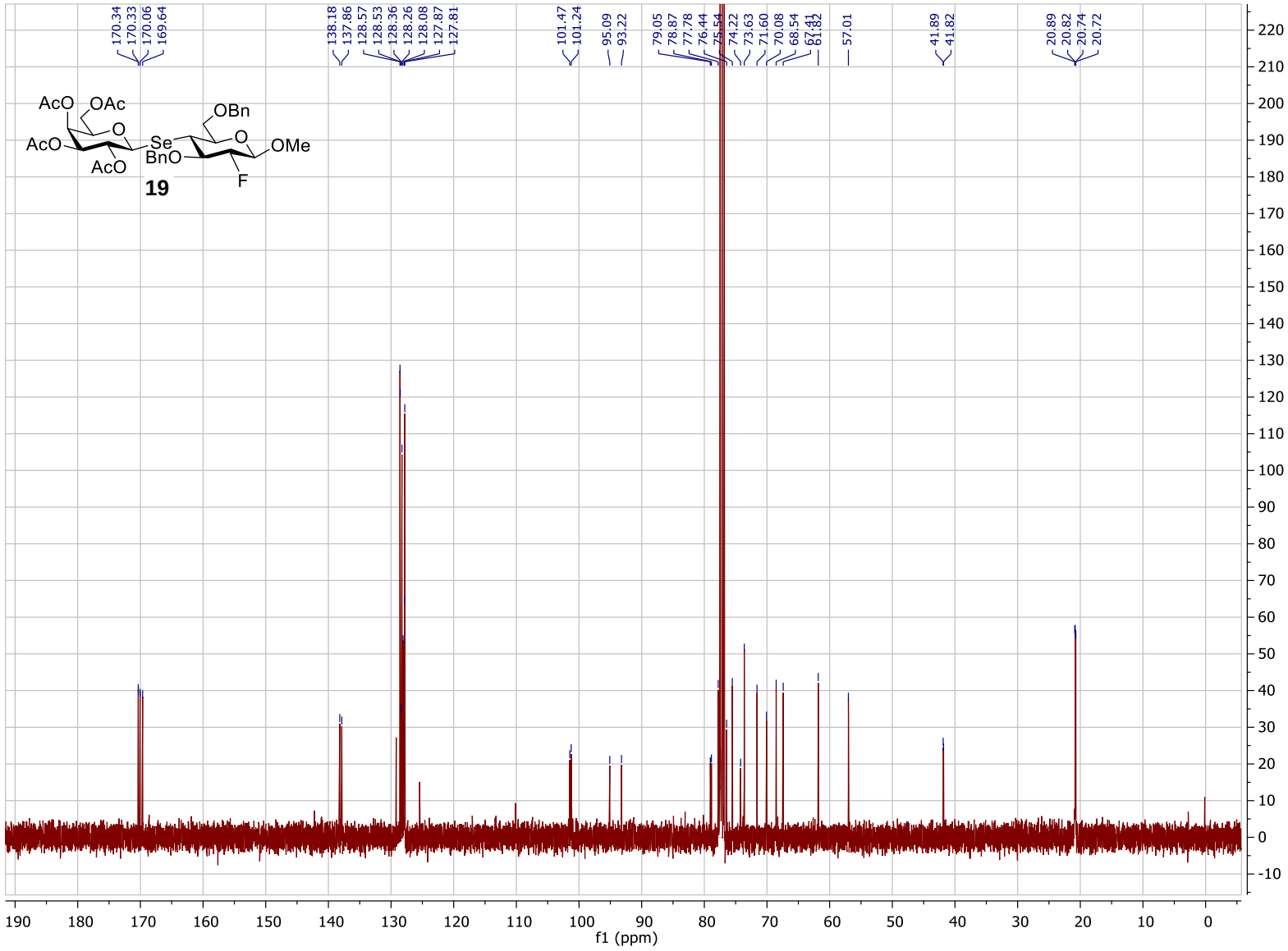
Methyl (2,3,4,6-tetra-*O*-acetyl-1-seleno-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-fluoro-β-D-glucopyranoside (19)

^{1}H NMR, 400 MHz



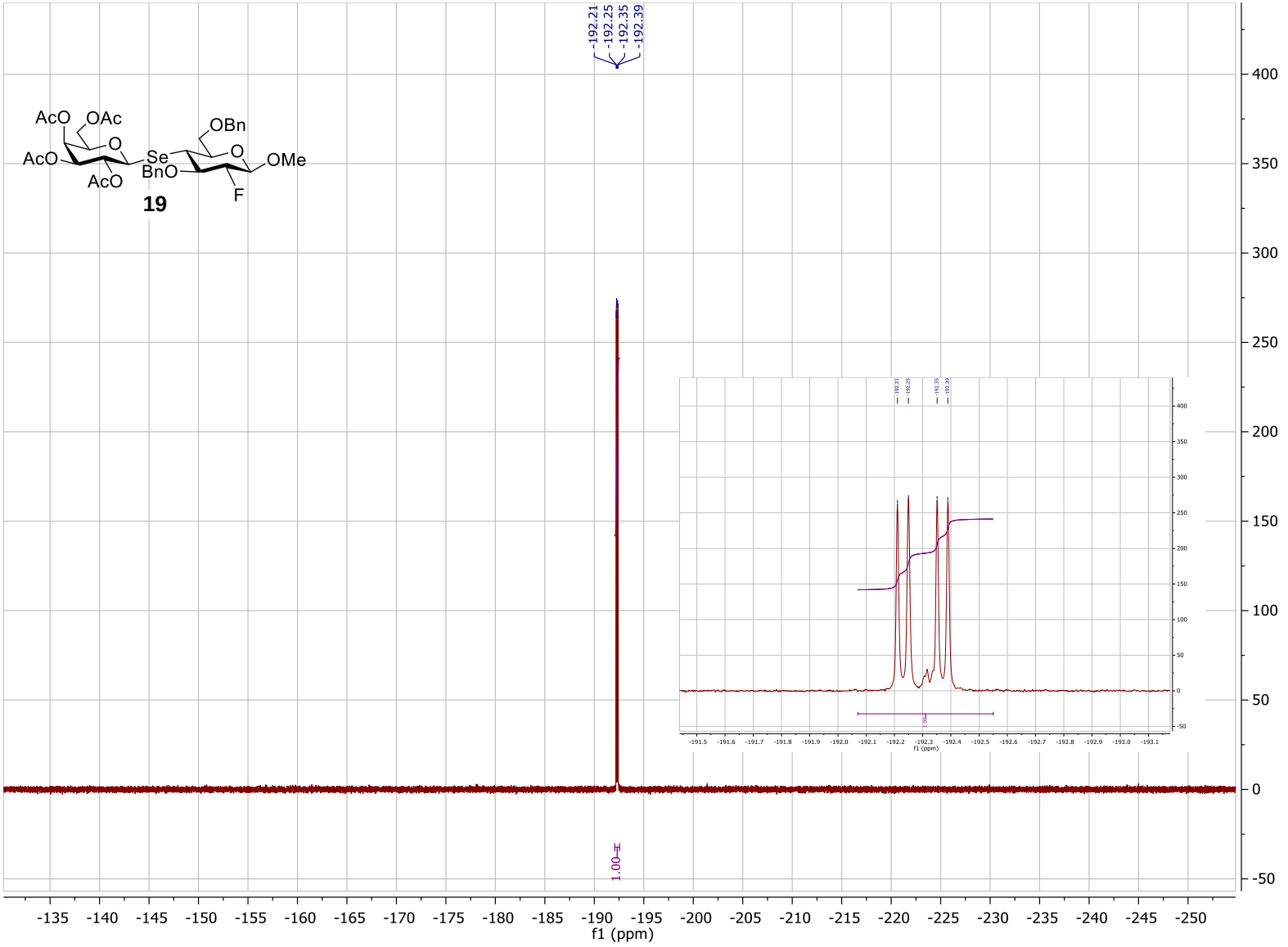
Methyl (2,3,4,6-tetra-*O*-acetyl-1-seleno-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-fluoro-β-D-glucopyranoside (19)

^{13}C NMR, 101 MHz



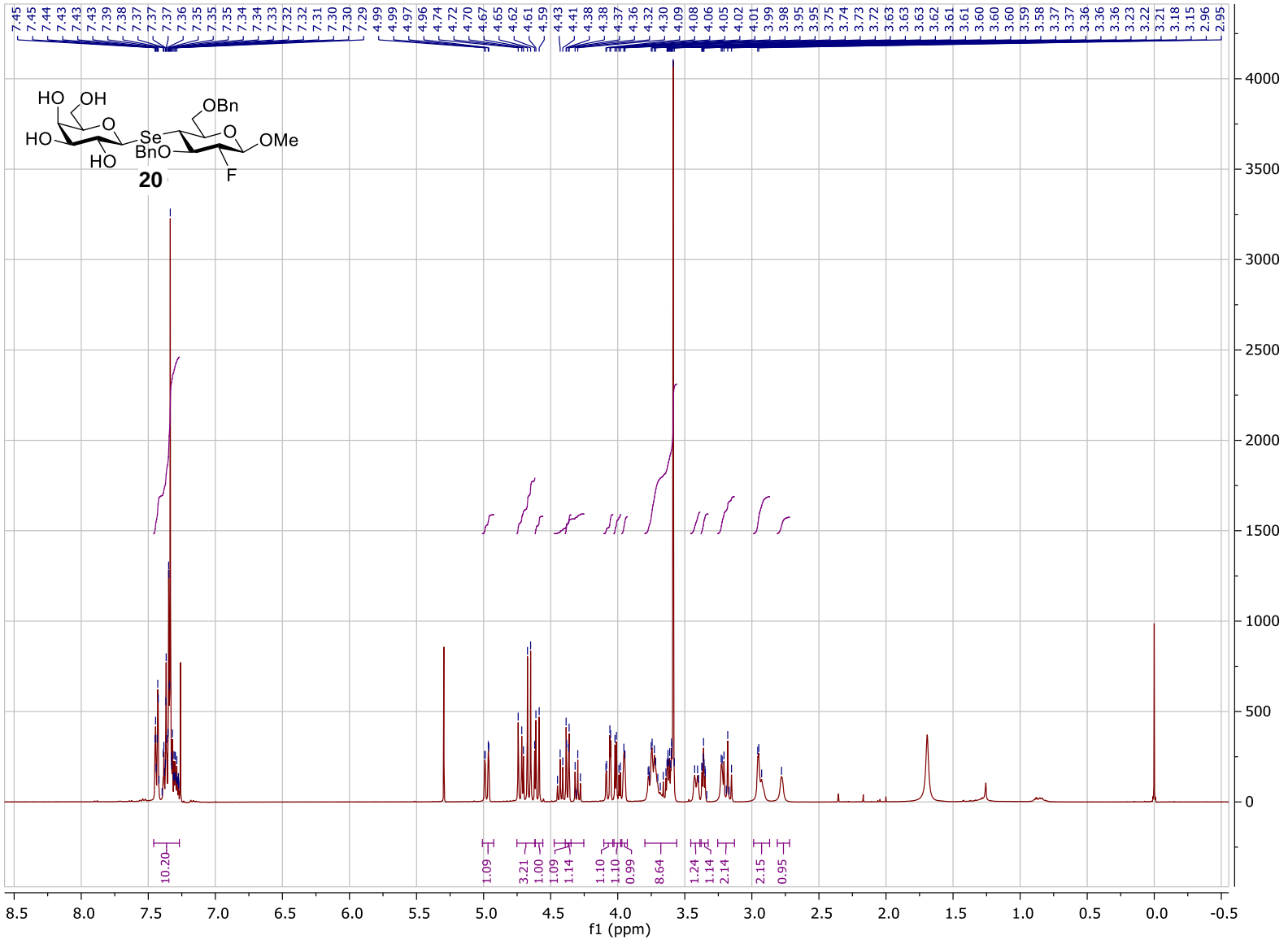
Methyl (2,3,4,6-tetra-*O*-acetyl-1-seleno-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-fluoro-β-D-glucopyranoside (19)

^{19}F NMR, 376 MHz



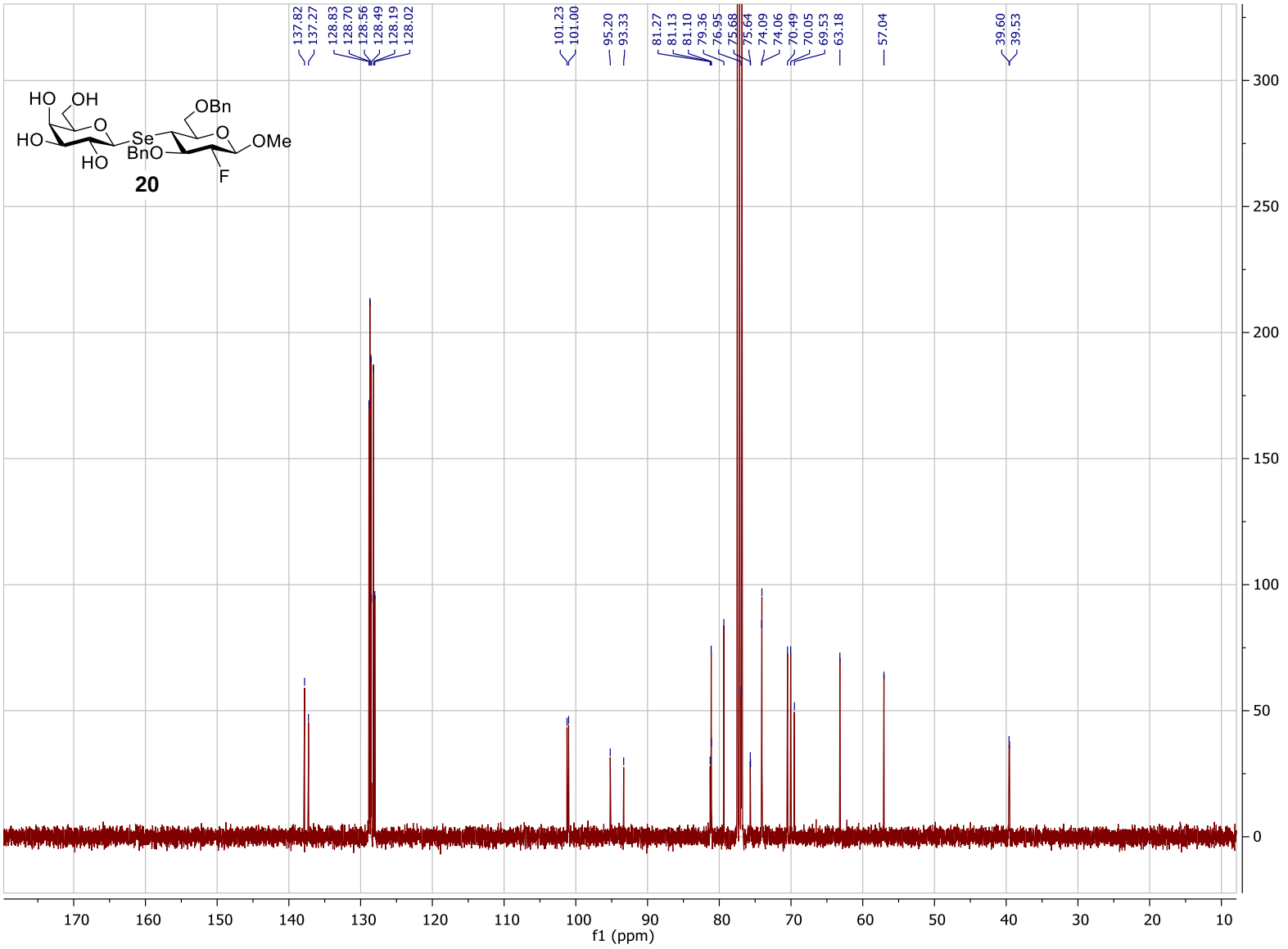
Methyl (1-seleno-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-fluoro-β-D-glucopyranoside (20)

^{1}H NMR, 400 MHz



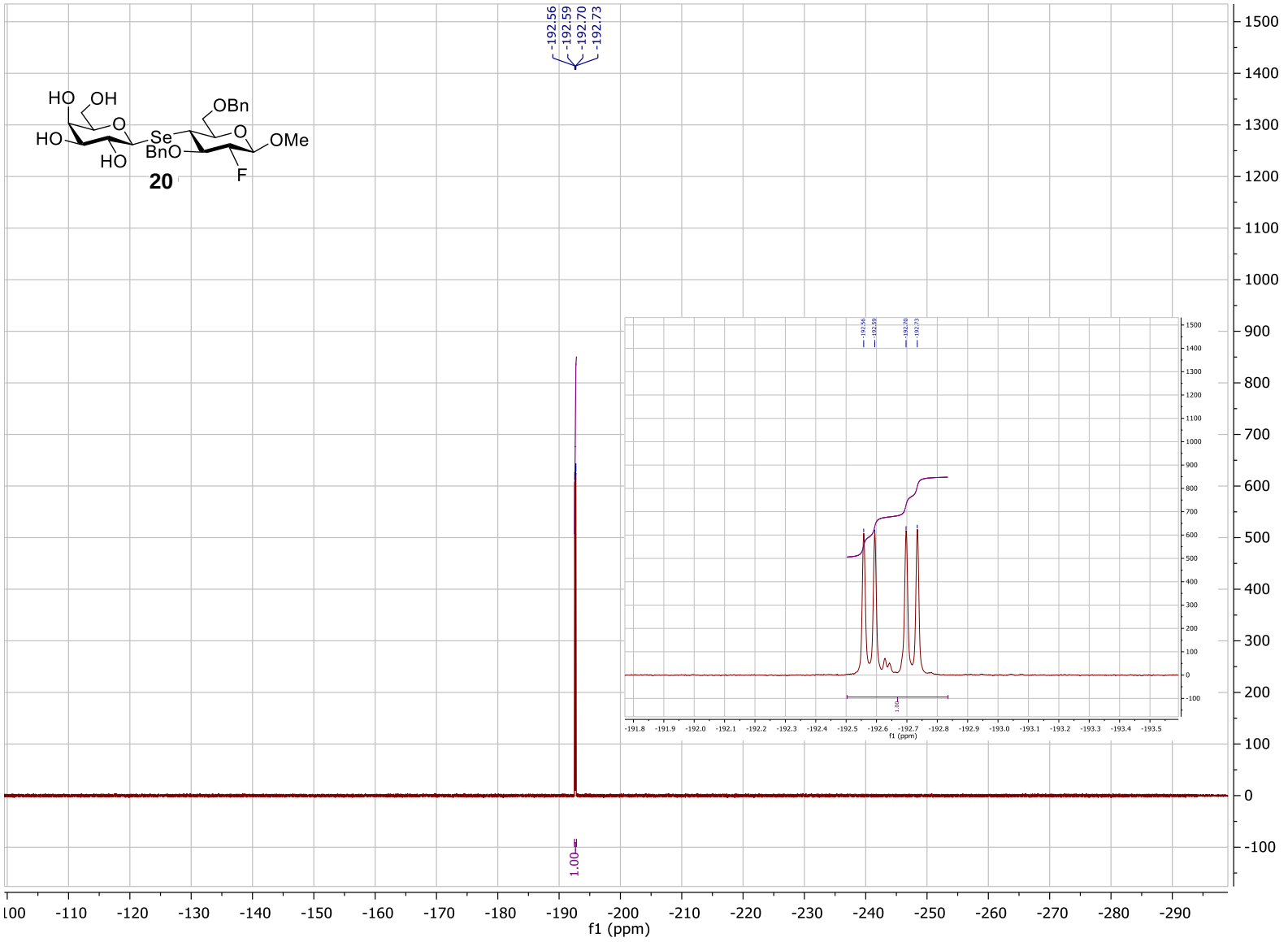
Methyl (1-seleno-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-fluoro-β-D-glucopyranoside (20)

^{13}C NMR, 101 MHz



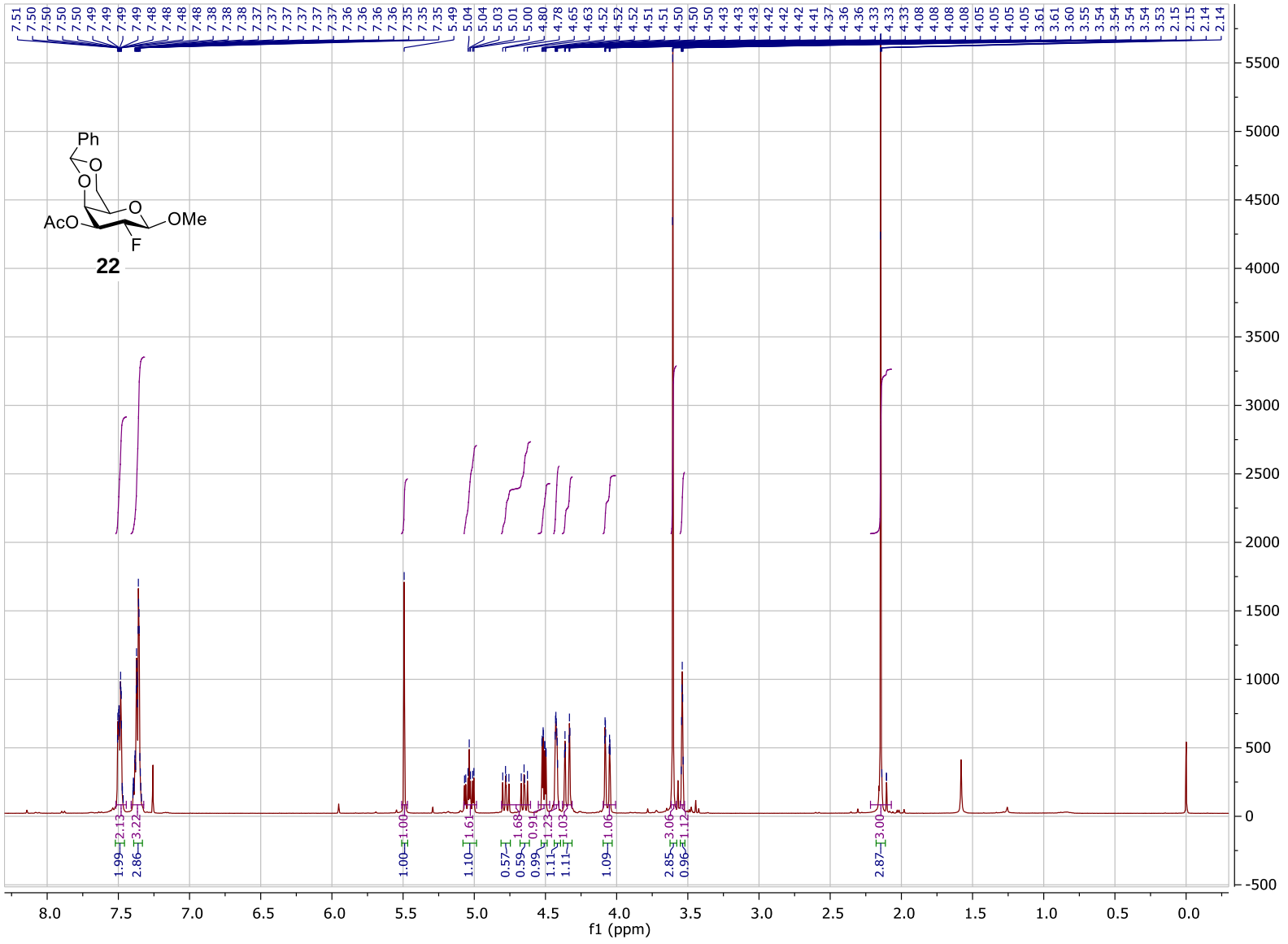
Methyl (1-seleno-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-fluoro-β-D-glucopyranoside (20)

^{19}F NMR, 376 MHz



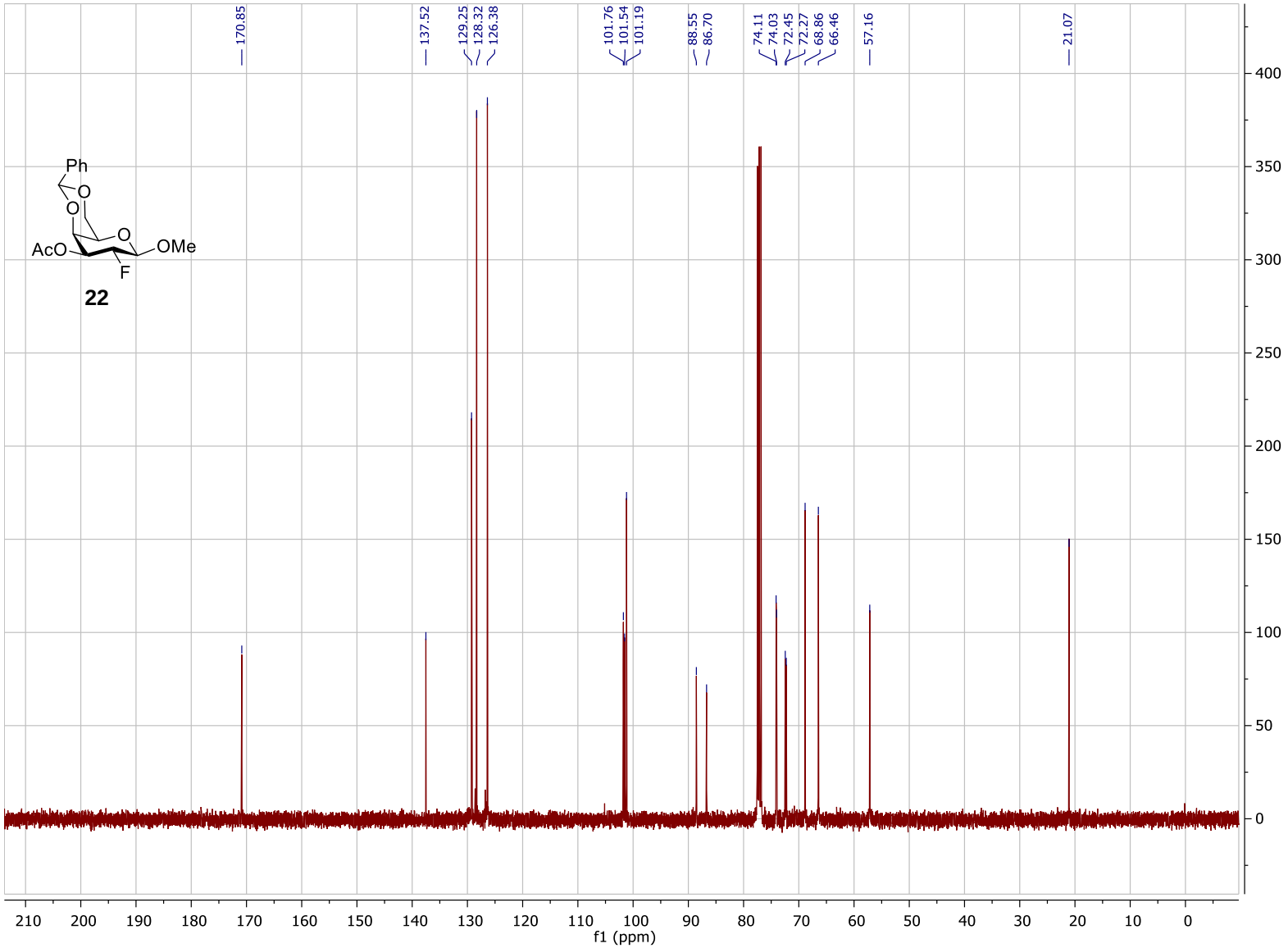
Methyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-2-fluoro-β-D-galactopyranoside (22)

^{1}H NMR, 400 MHz



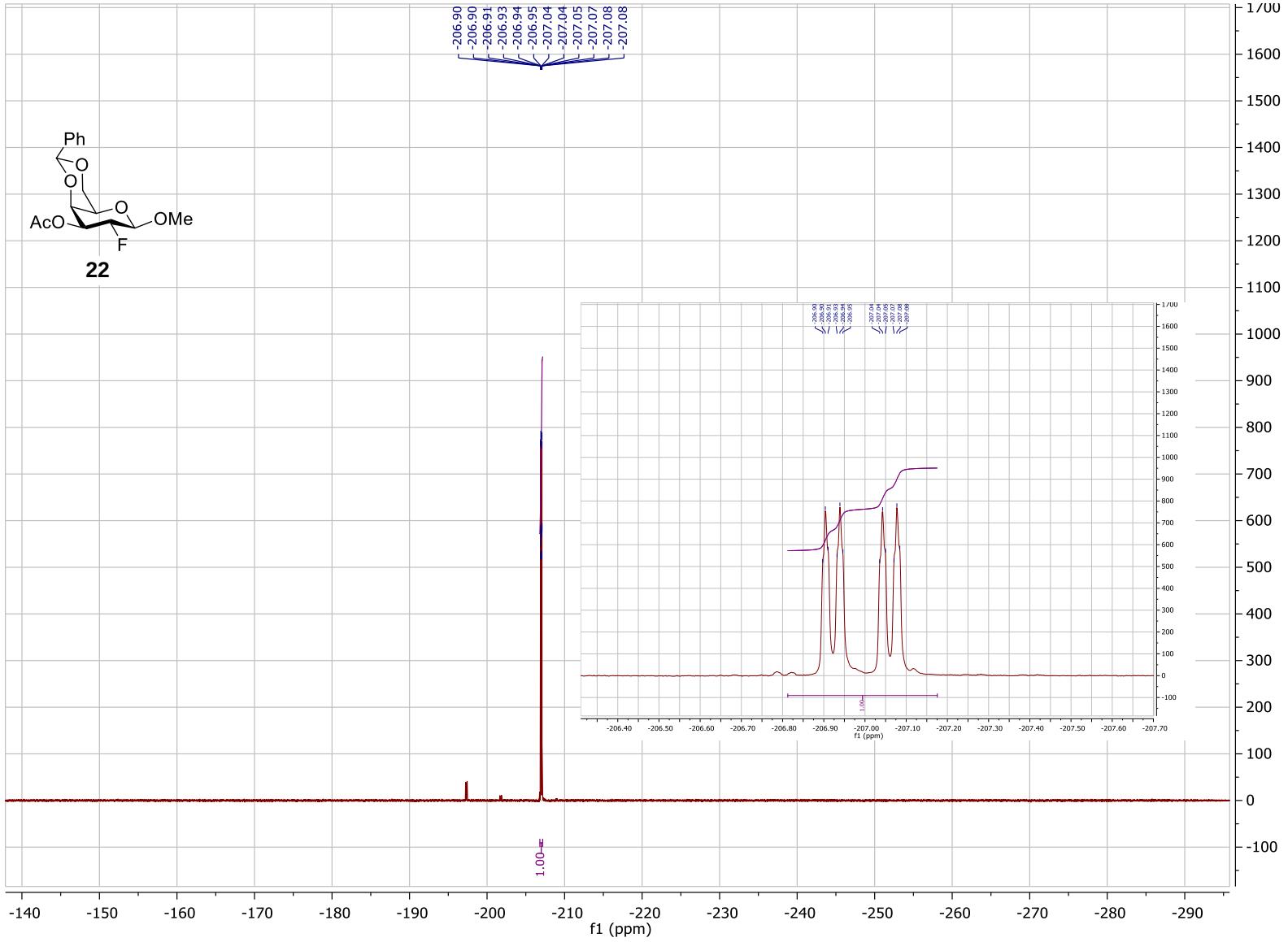
Methyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-2-fluoro-β-D-galactopyranoside (22)

^{13}C NMR, 101 MHz



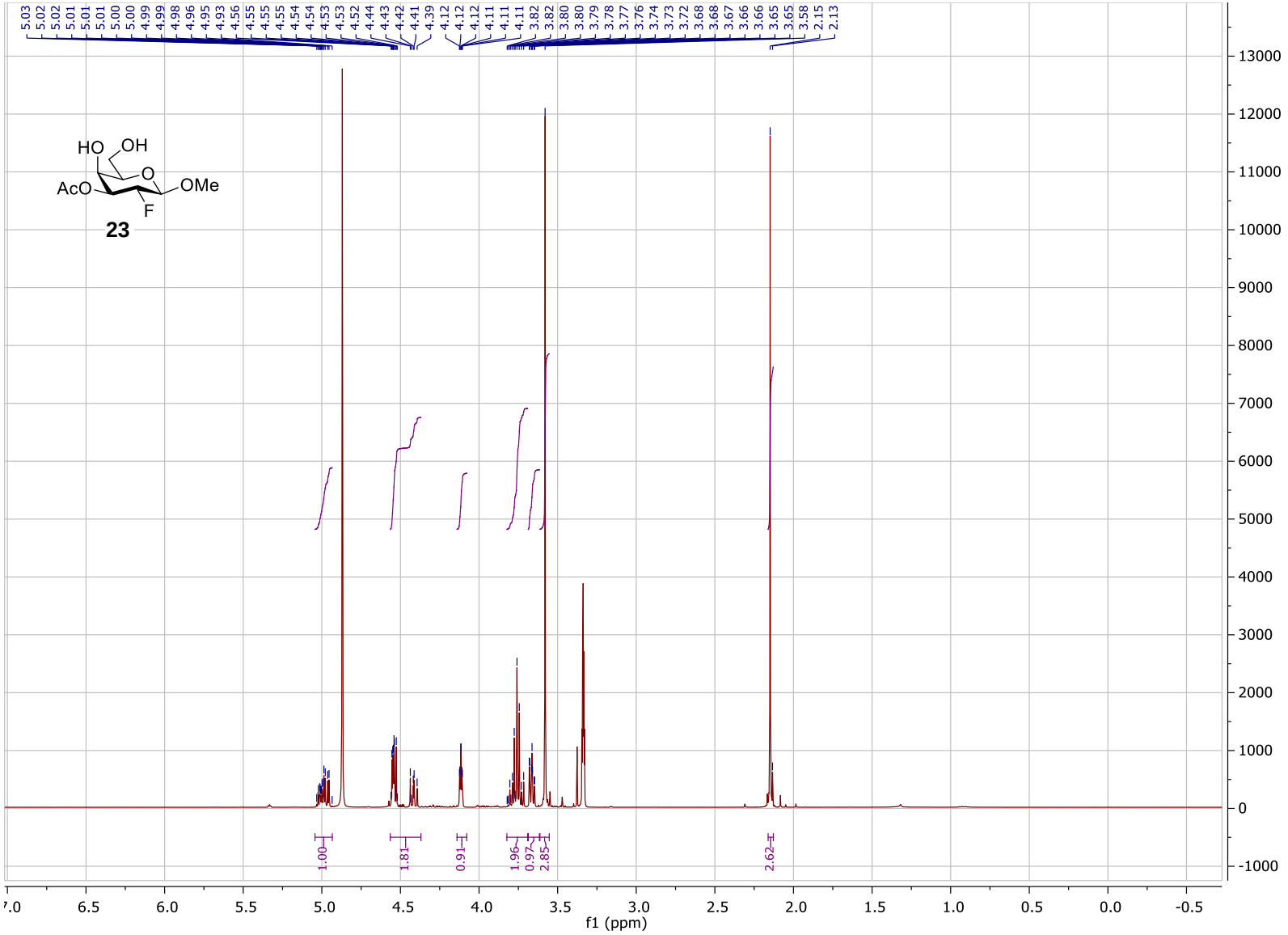
Methyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-2-fluoro-β-D-galactopyranoside (22)

^{19}F NMR, 376 MHz



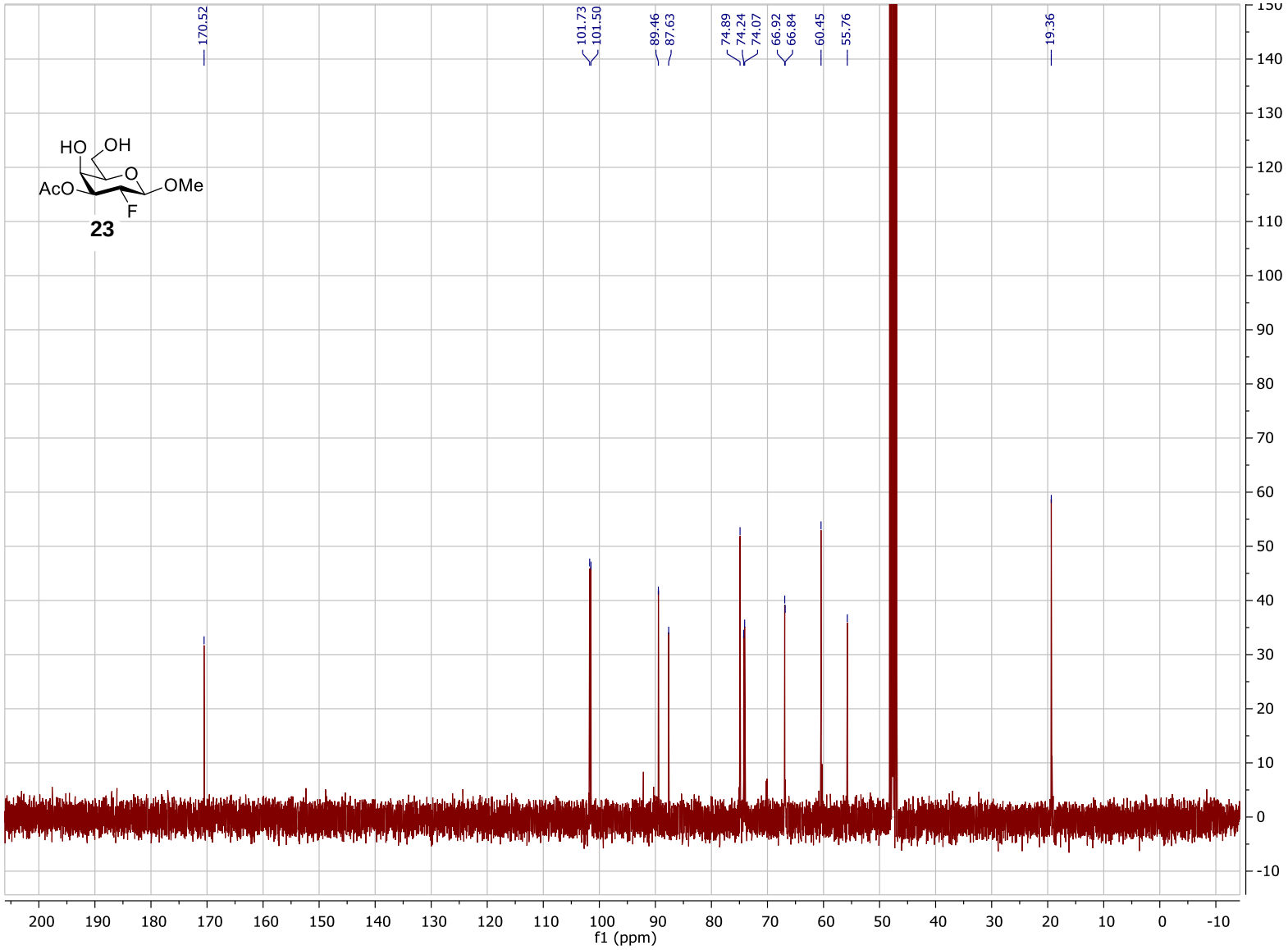
Methyl 3-*O*-acetyl-2-deoxy-2-fluoro-β-D-galactopyranoside (23)

^{1}H NMR, 400 MHz



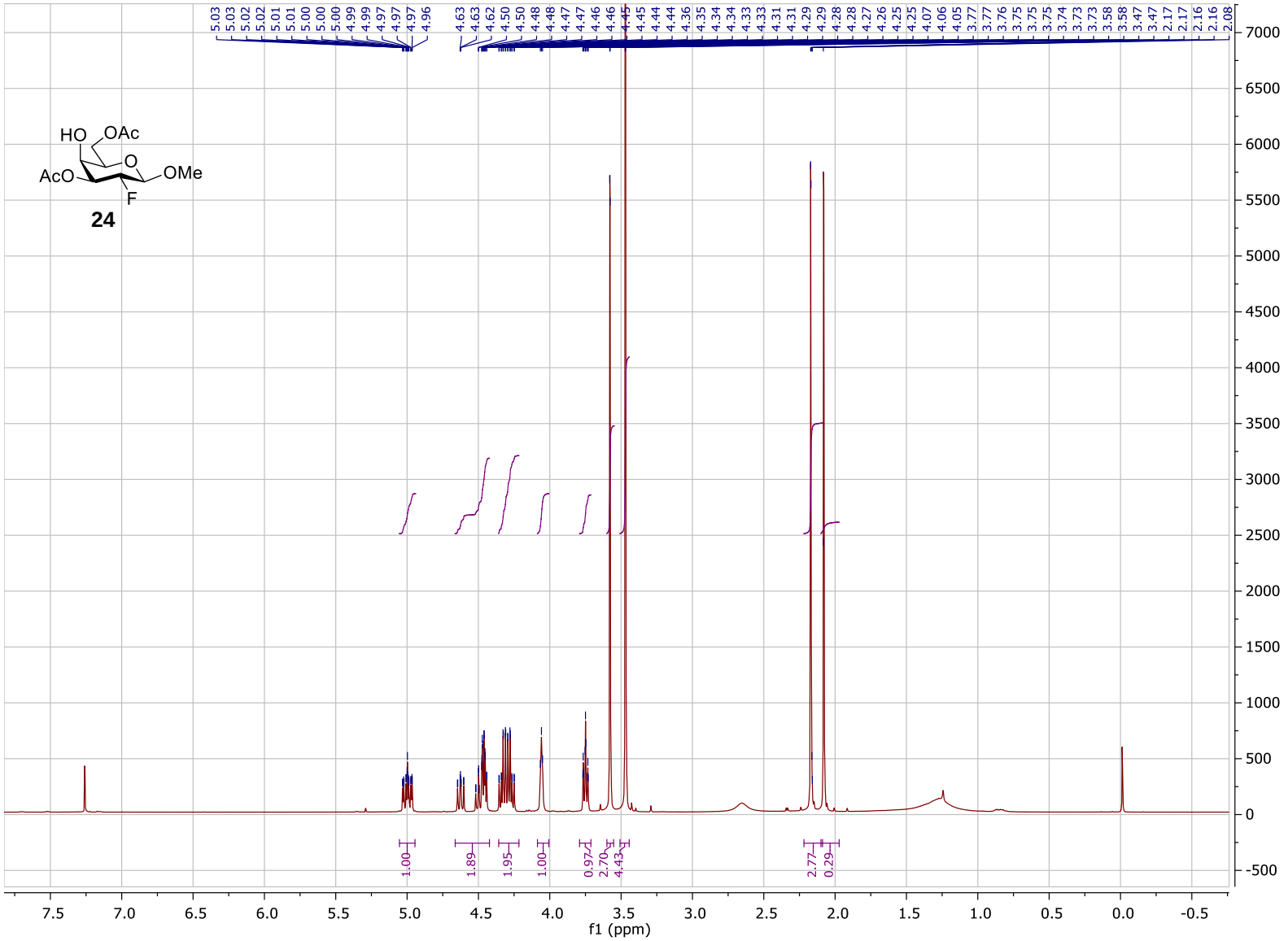
Methyl 3-*O*-acetyl-2-deoxy-2-fluoro-β-D-galactopyranoside (23)

^{13}C NMR, 101 MHz



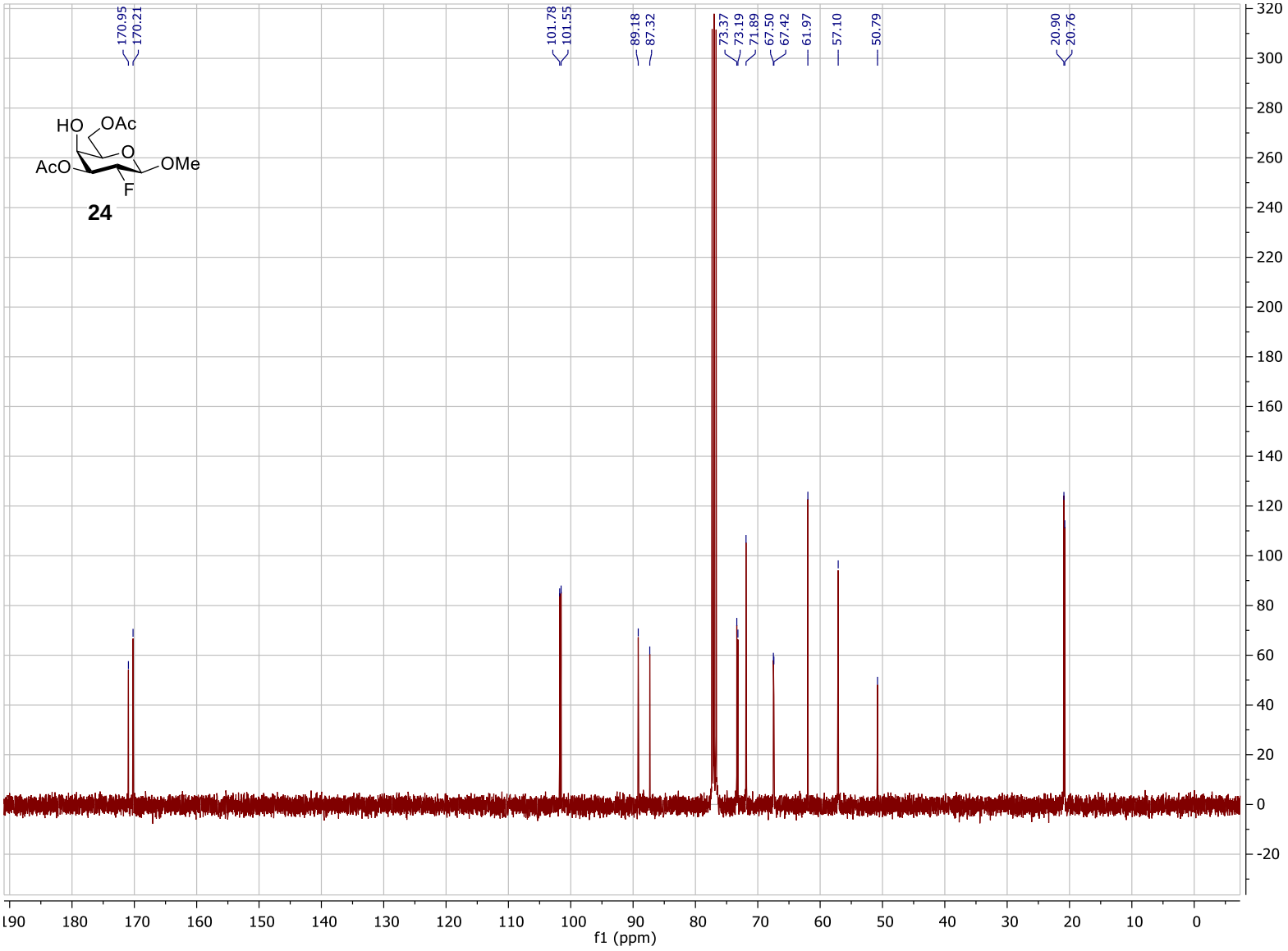
Methyl 3,6-di-*O*-acetyl-2-deoxy-2-fluoro-β-D-galactopyranoside (24)

^{1}H NMR, 400 MHz



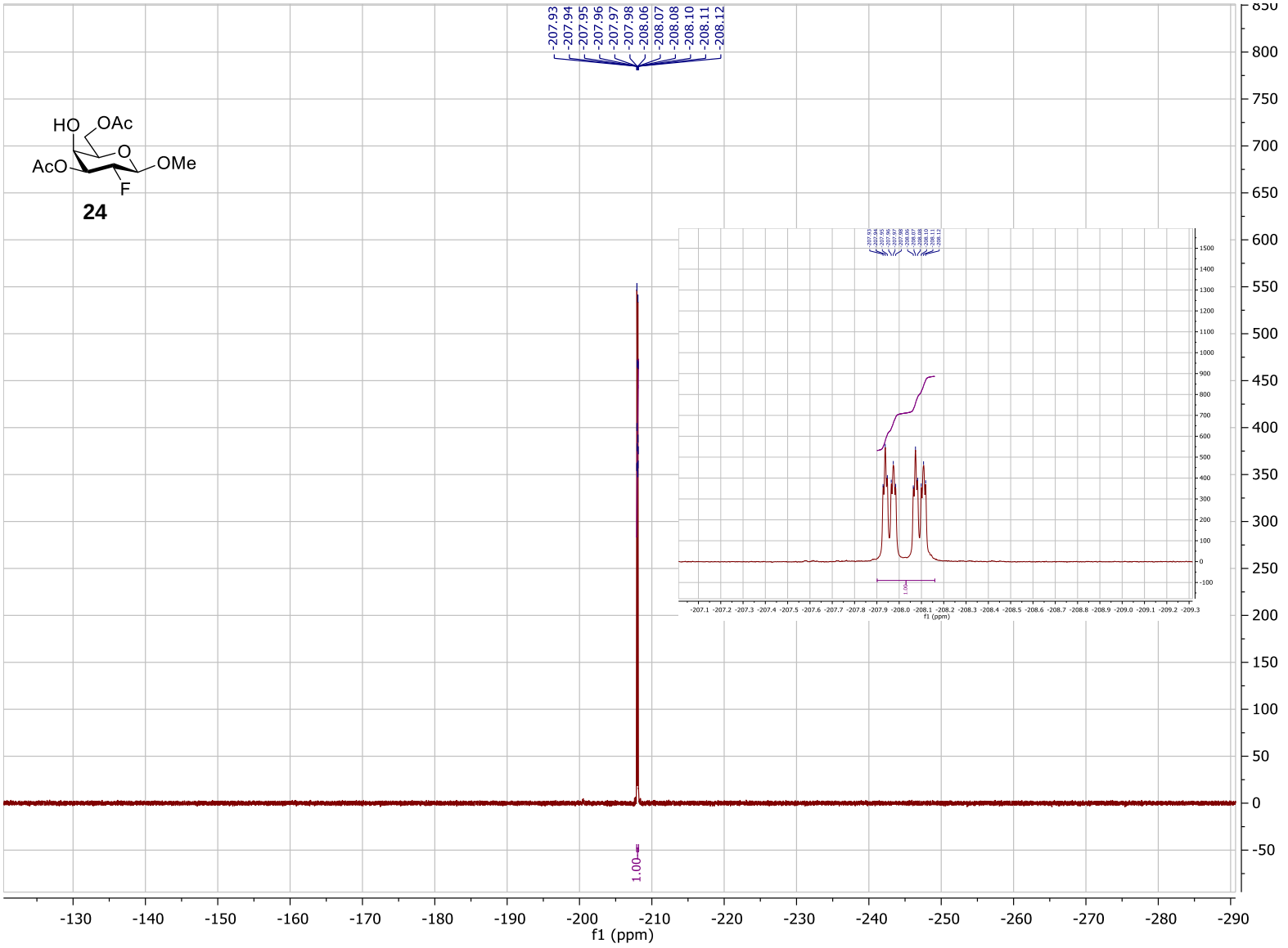
Methyl 3,6-di-*O*-acetyl-2-deoxy-2-fluoro-β-D-galactopyranoside (24)

^{13}C NMR, 101 MHz



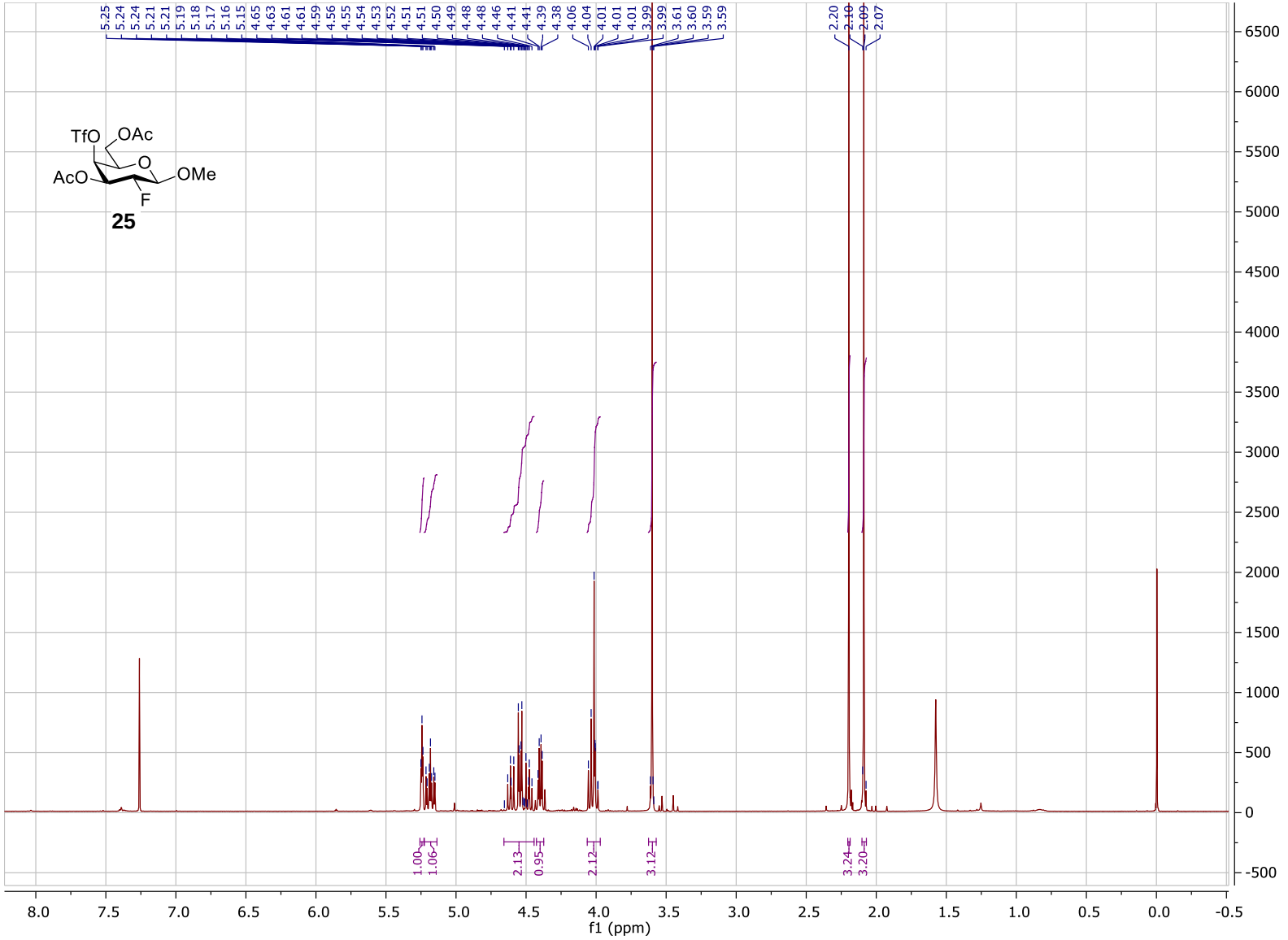
Methyl 3,6-di-*O*-acetyl-2-deoxy-2-fluoro-β-D-galactopyranoside (24)

^{19}F NMR, 376 MHz



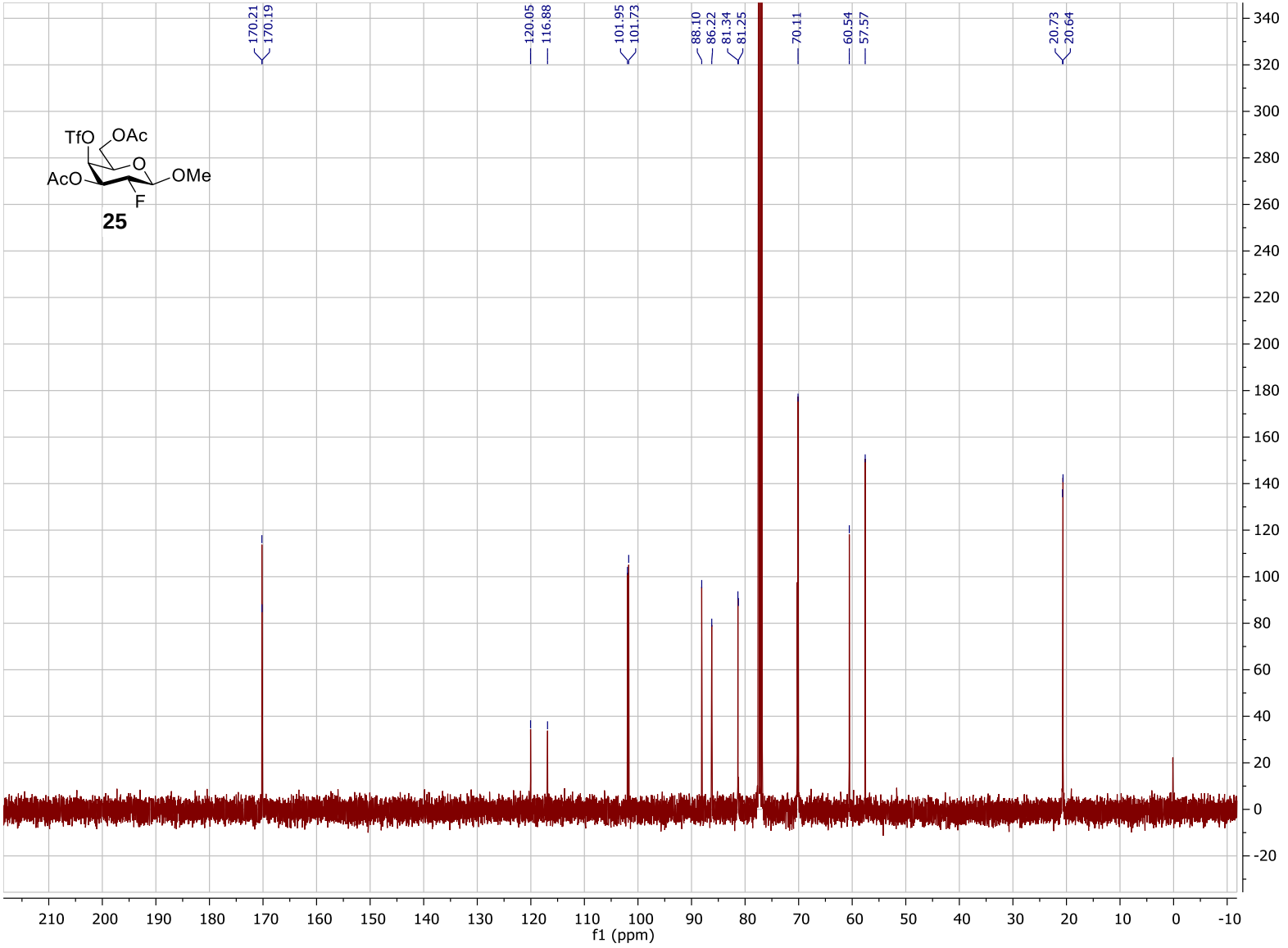
Methyl 3,6-di-*O*-acetyl-2-deoxy-2-fluoro-4-*O*-trifluoromethanesulfonyl-β-D-galactopyranoside (25)

^{1}H NMR, 400 MHz



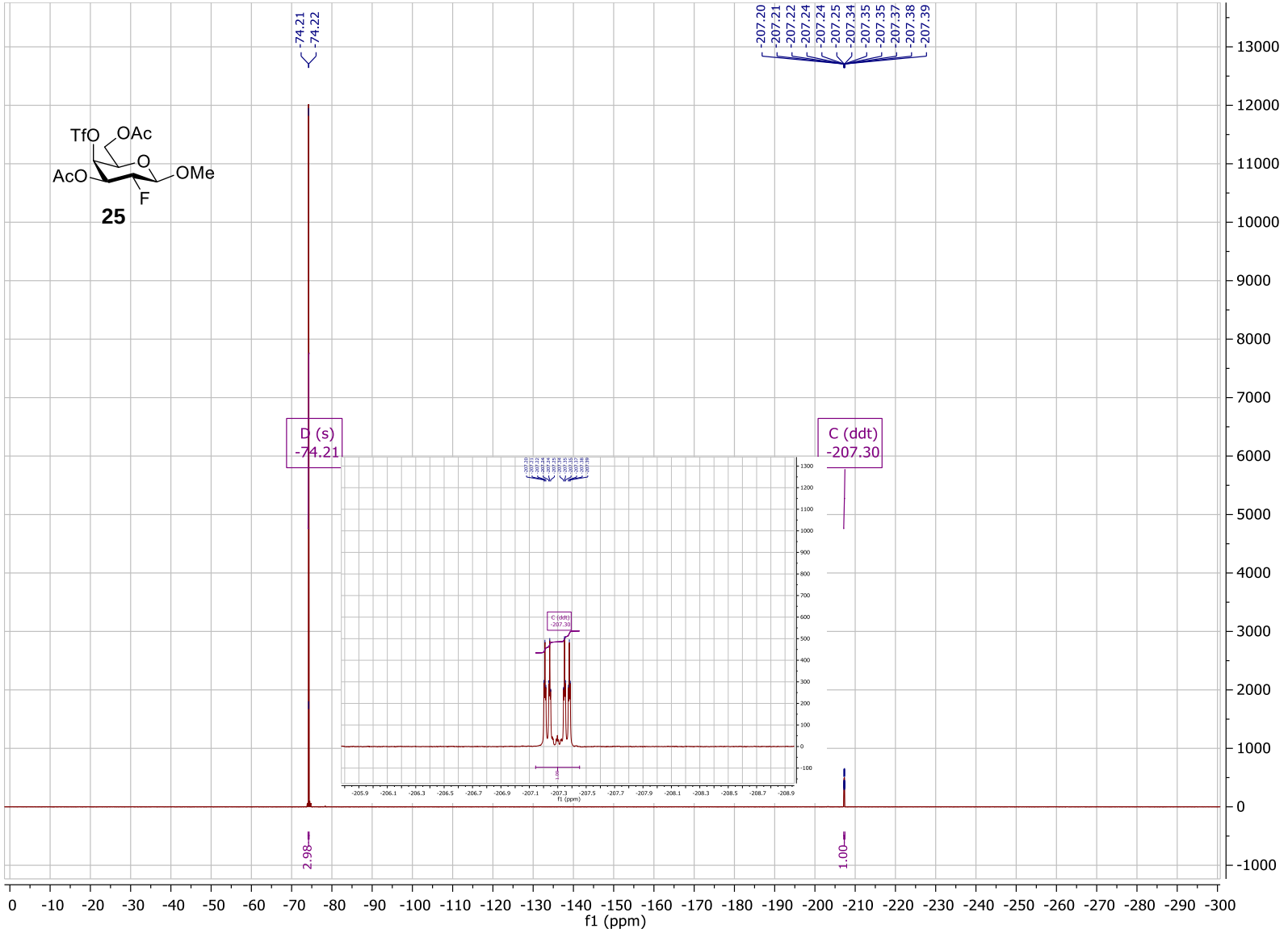
Methyl 3,6-di-*O*-acetyl-2-deoxy-2-fluoro-4-*O*-trifluoromethanesulfonyl-β-D-galactopyranoside (25)

^{13}C NMR, 101 MHz



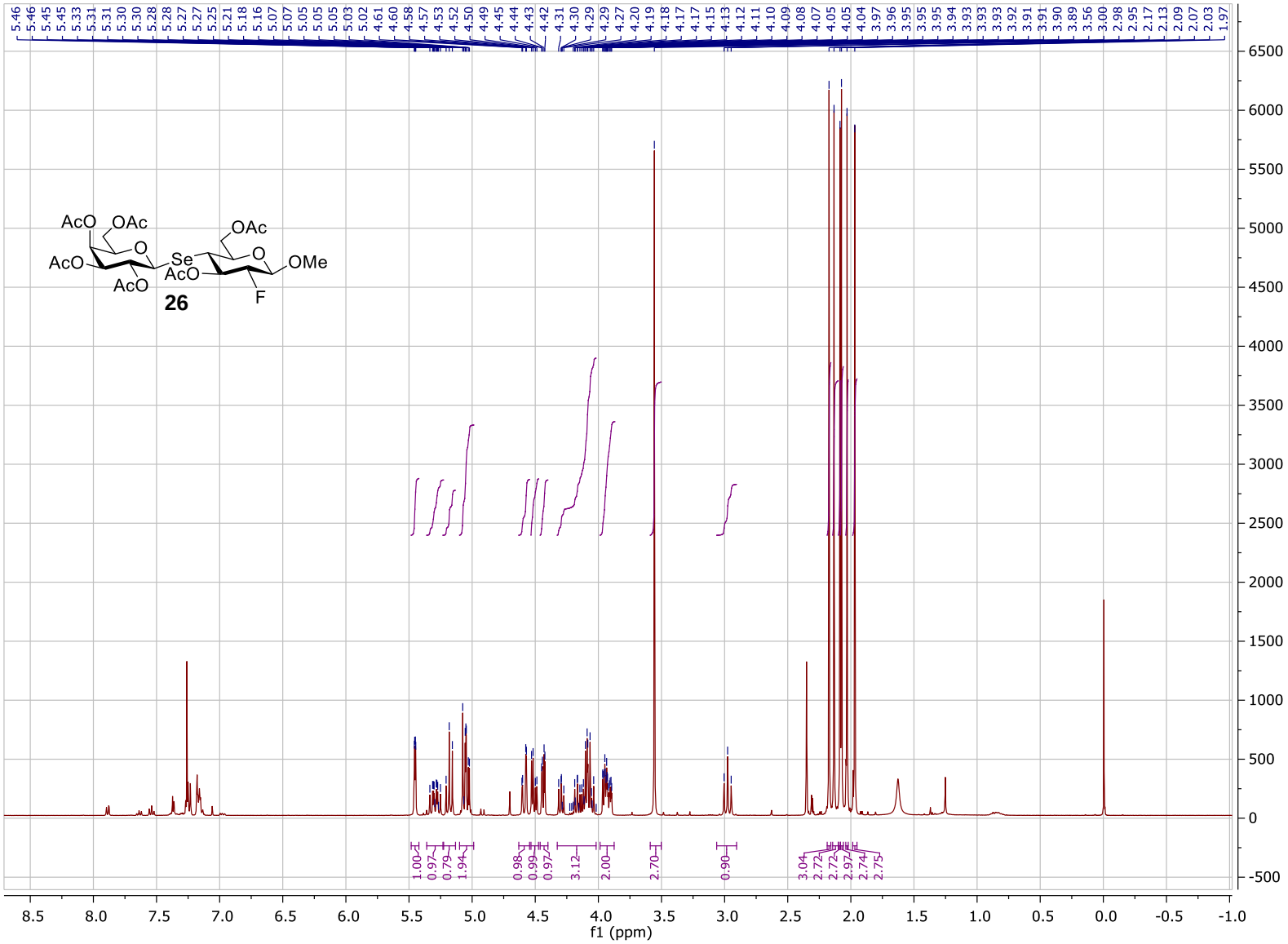
Methyl 3,6-di-*O*-acetyl-2-deoxy-2-fluoro-4-*O*-trifluoromethanesulfonyl-β-D-galactopyranoside (25)

^{19}F NMR, 376 MHz



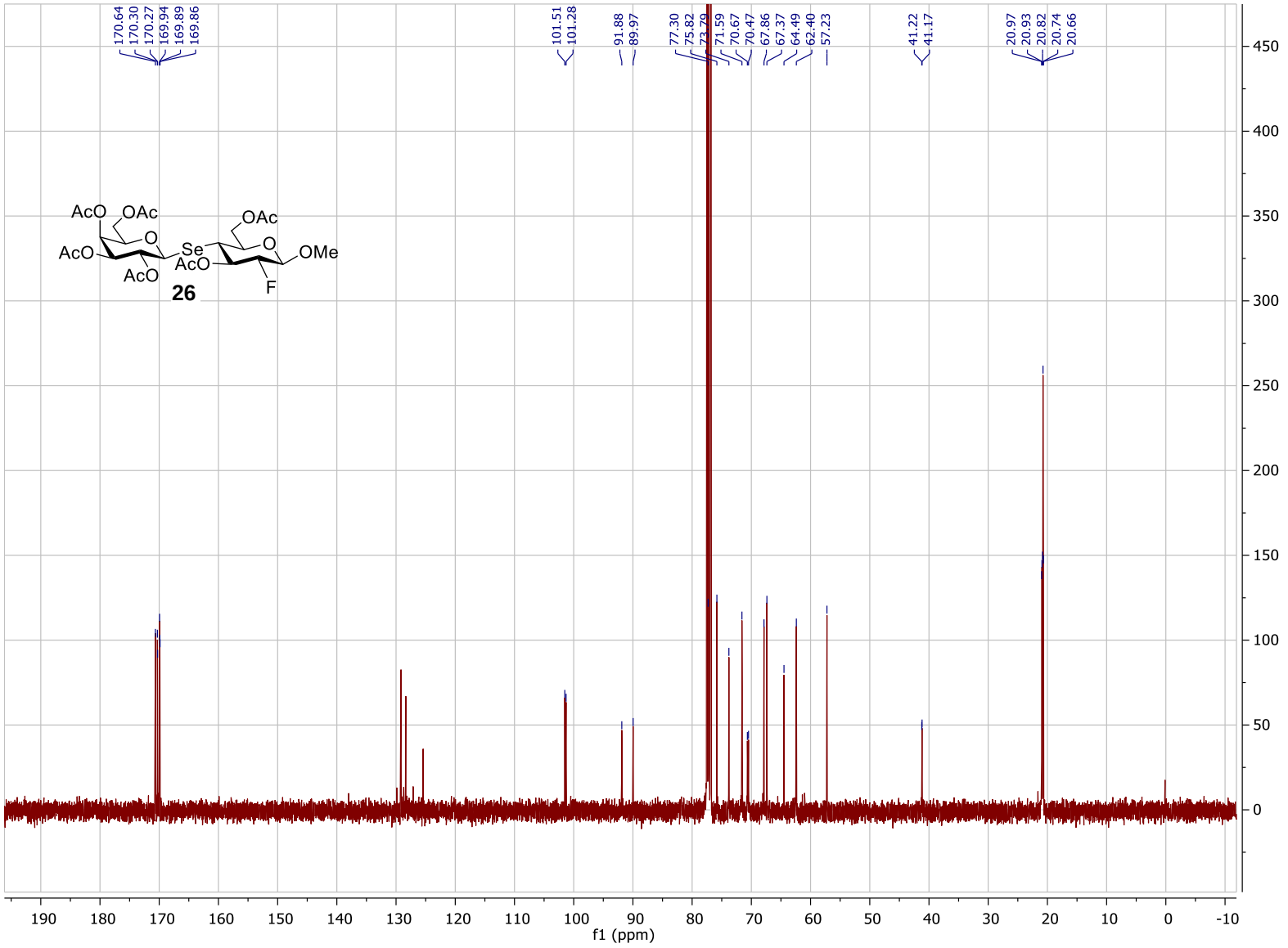
Methyl (2,3,4,6-tetra-*O*-acetyl-1-seleno-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-acetyl-2-deoxy-2-fluoro-β-D-glucopyranoside (26)

^{1}H NMR, 400 MHz



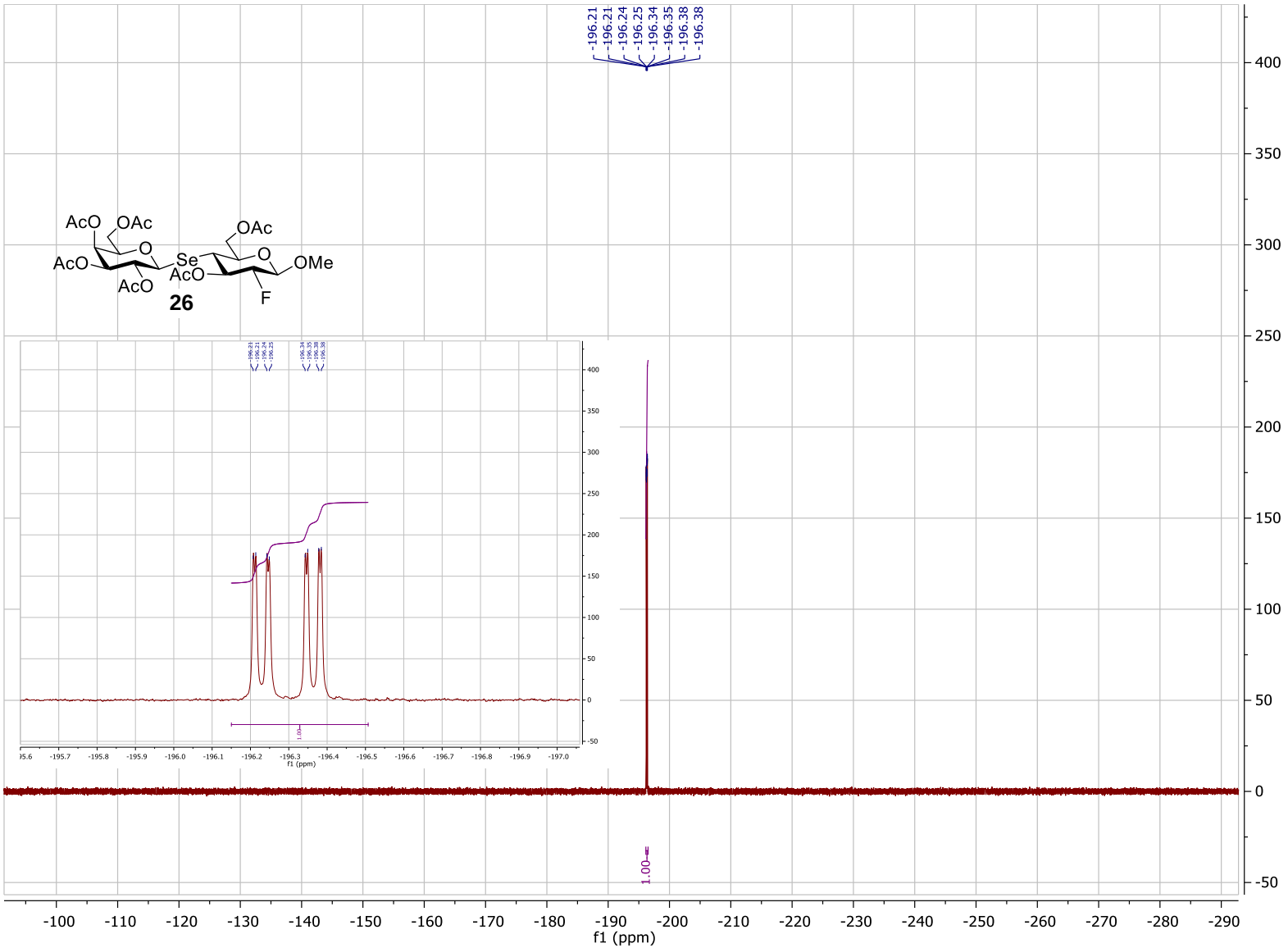
Methyl (2,3,4,6-tetra-*O*-acetyl-1-seleno-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-acetyl-2-deoxy-2-fluoro-β-D-glucopyranoside (26)

^{13}C NMR, 101 MHz



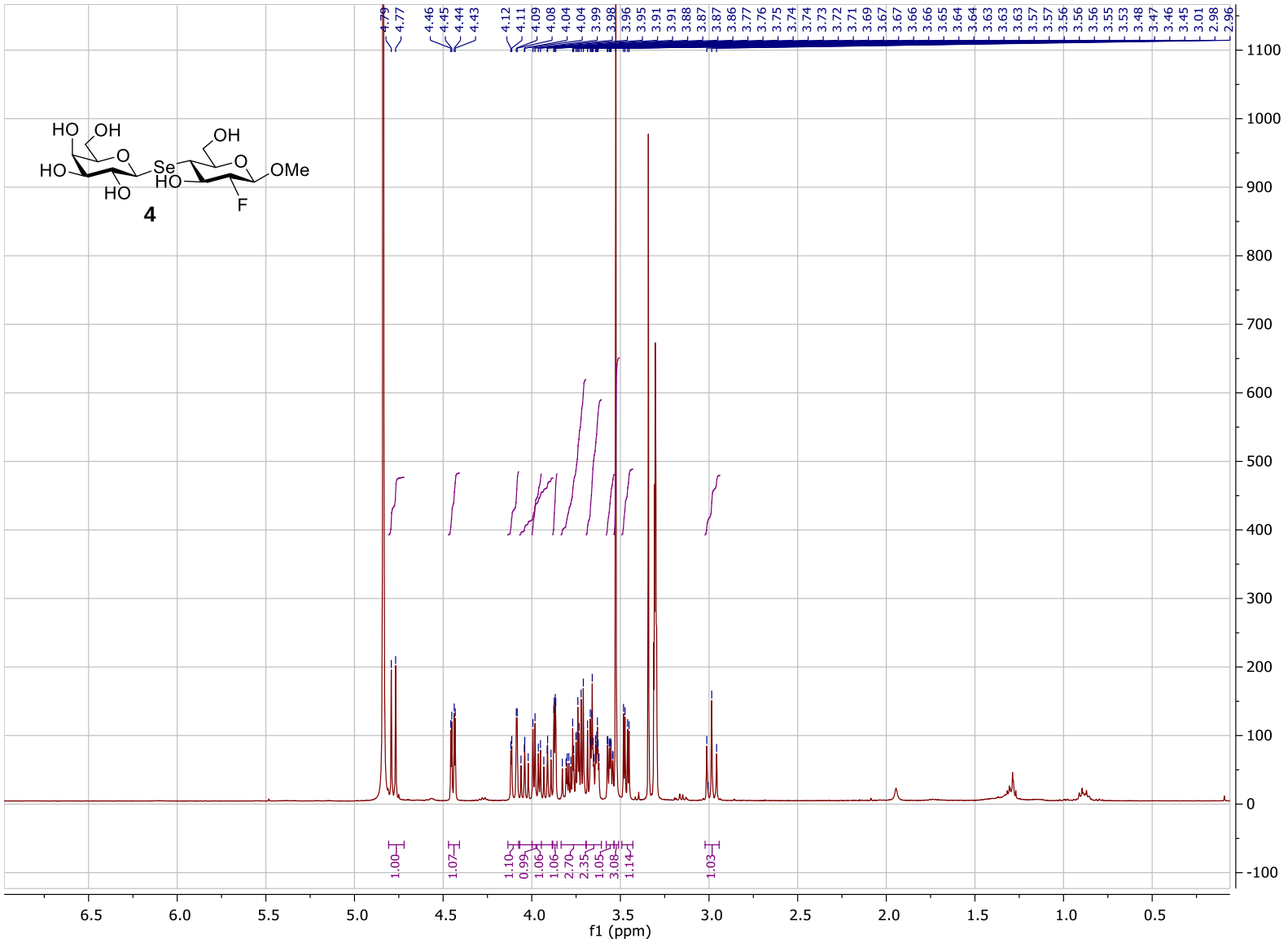
Methyl (2,3,4,6-tetra-*O*-acetyl-1-seleno-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-acetyl-2-deoxy-2-fluoro-β-D-glucopyranoside (26)

^{19}F NMR, 376 MHz



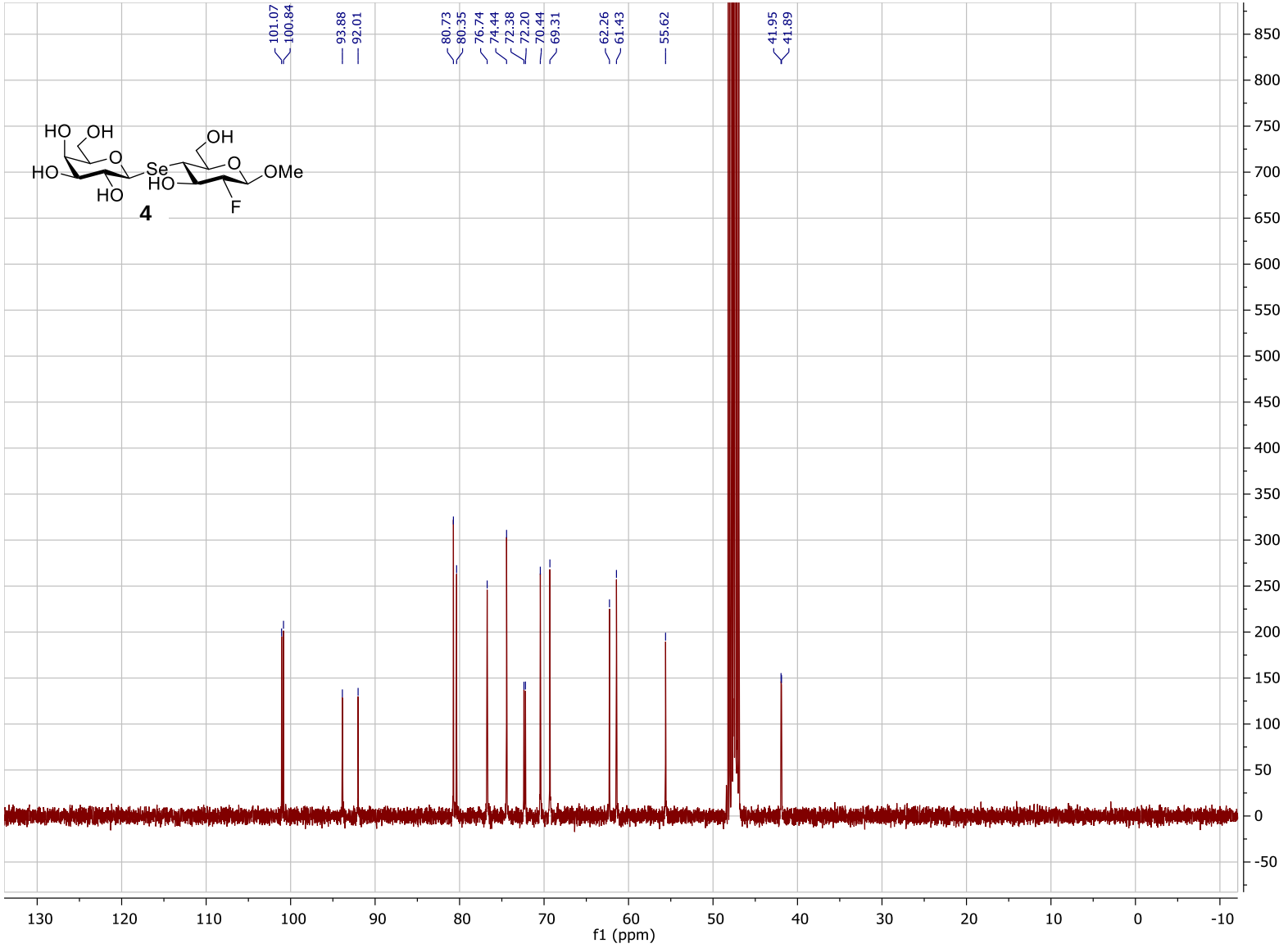
Methyl (1-seleno-β-D-galactopyranosyl)-(1→4)-2-deoxy-2-fluoro-β-D-glucopyranoside (4)

^{1}H NMR, 400 MHz



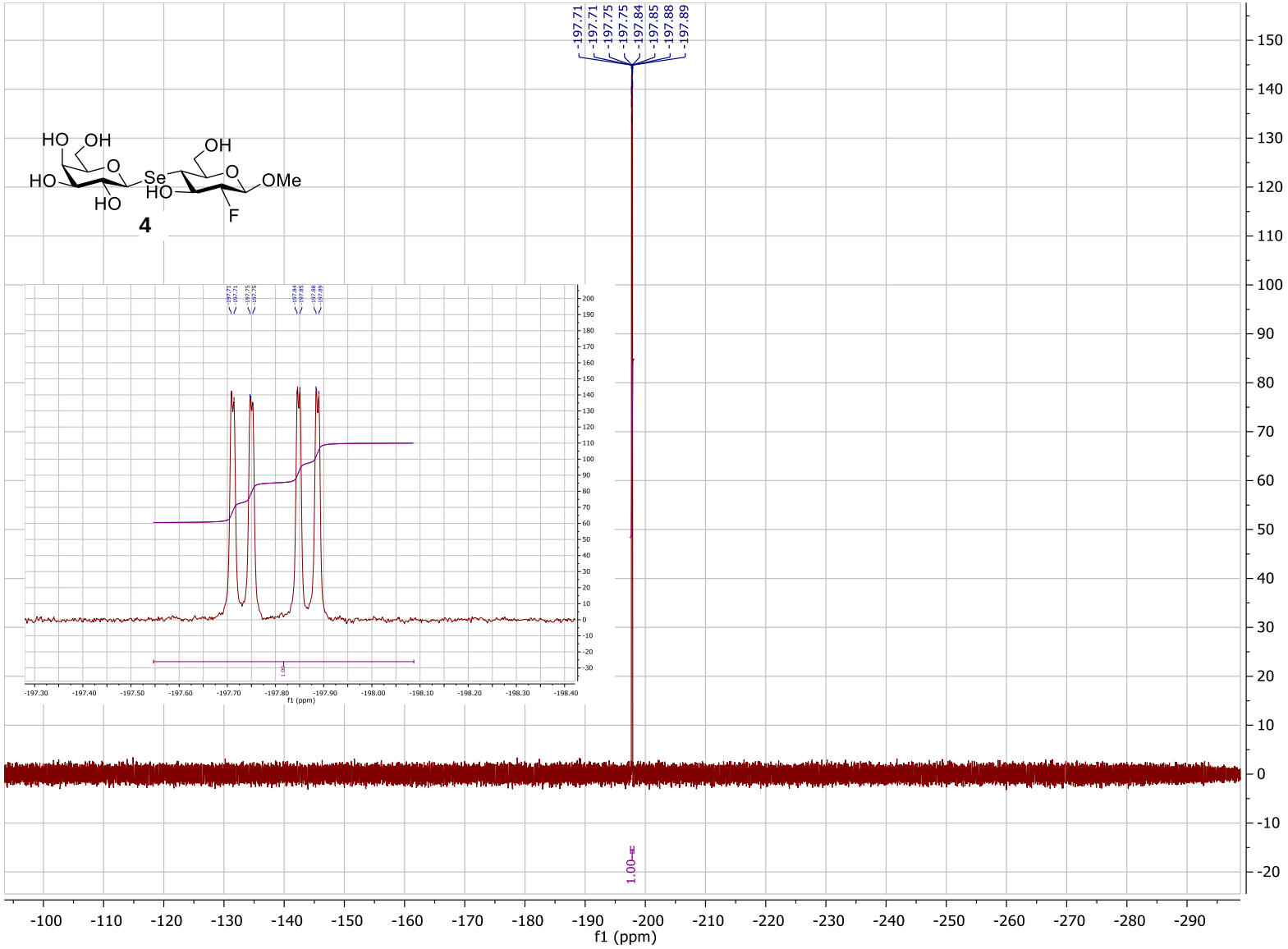
Methyl (1-seleno-β-D-galactopyranosyl)-(1→4)-2-deoxy-2-fluoro-β-D-glucopyranoside (4)

^{13}C NMR, 101 MHz



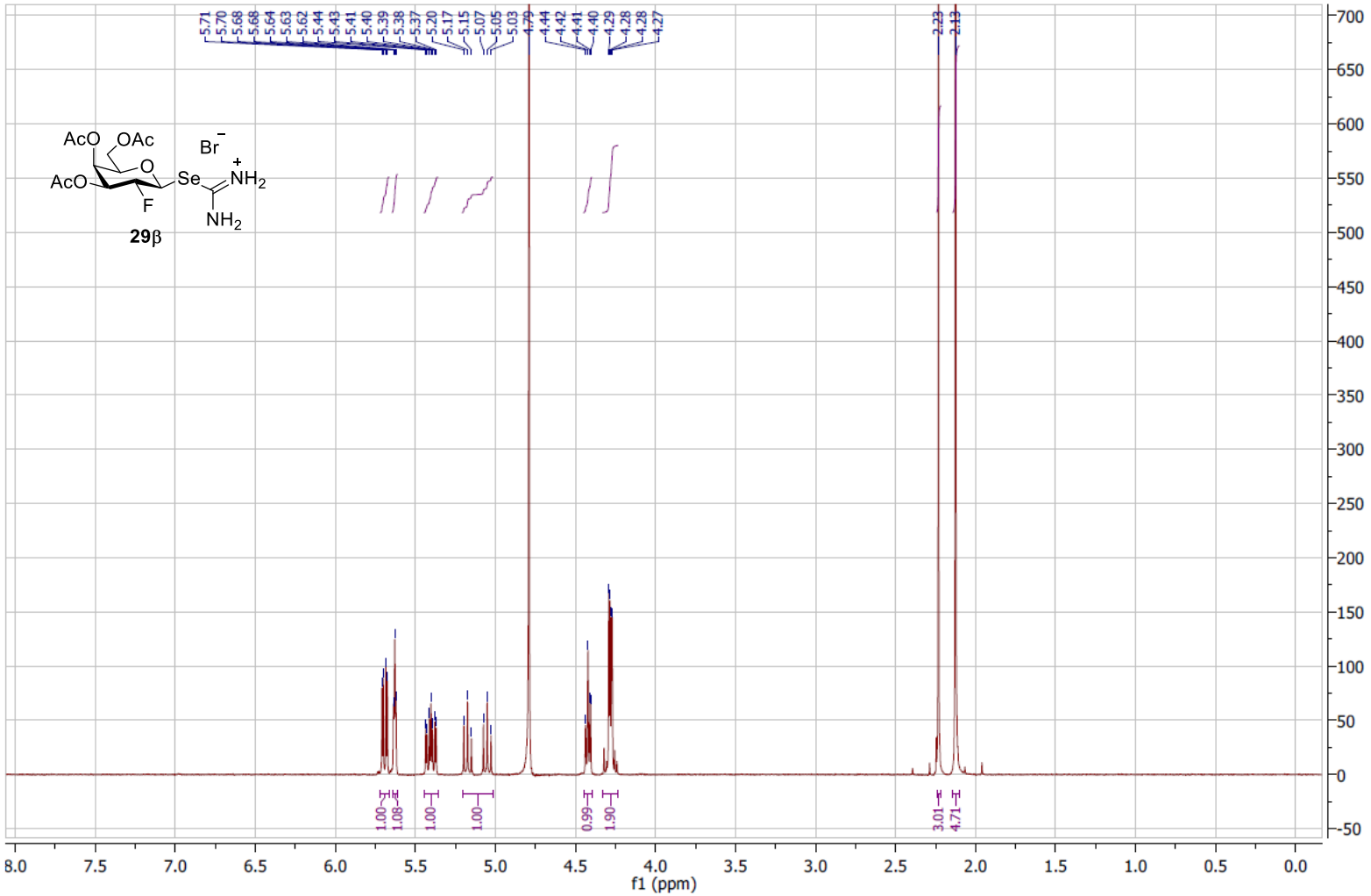
Methyl (1-seleno-β-D-galactopyranosyl)-(1→4)-2-deoxy-2-fluoro-β-D-glucopyranoside (4)

^{19}F NMR, 376 MHz



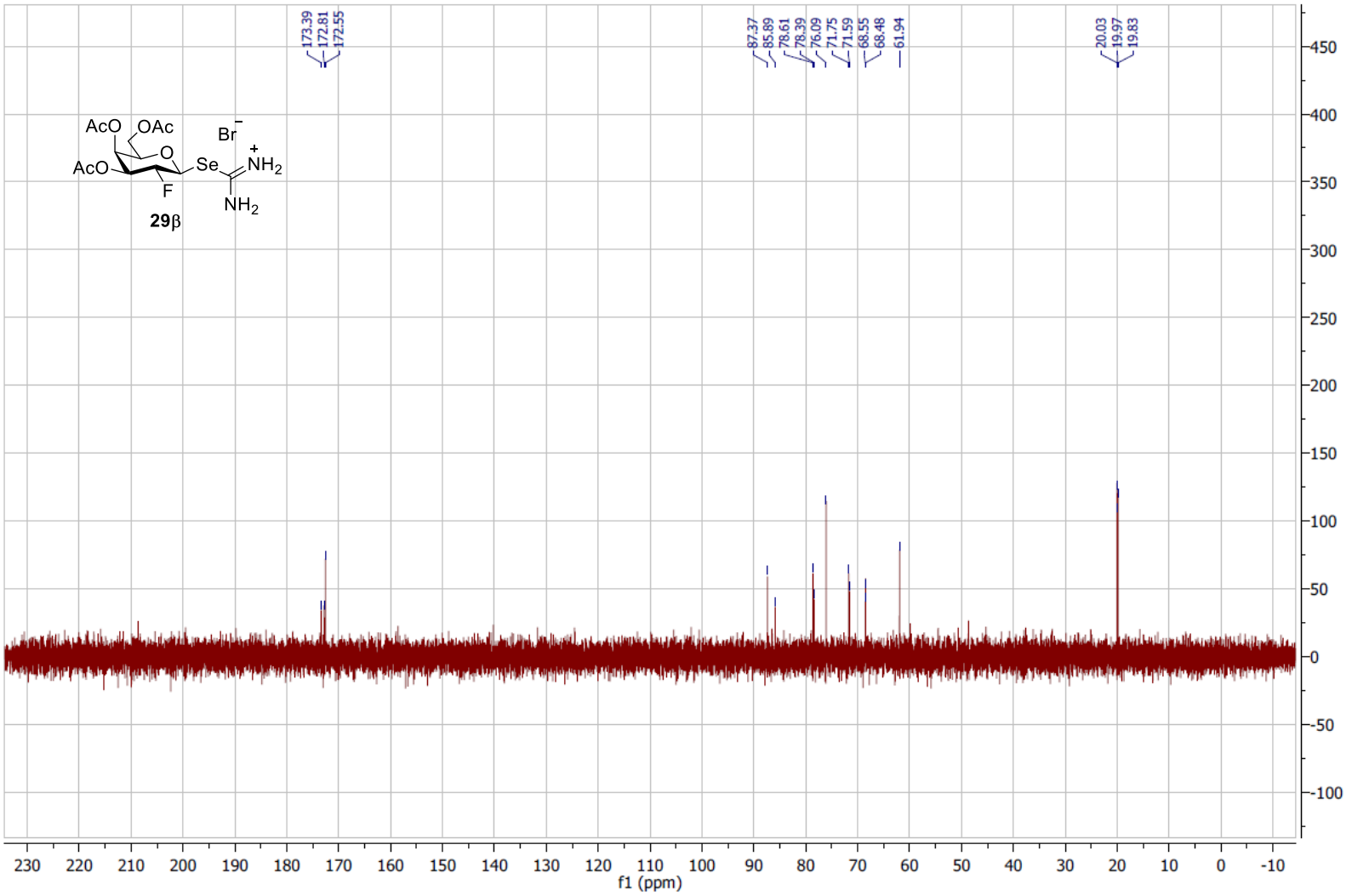
3,4,6-Tri-*O*-acetyl-2-deoxy-2-fluoro-β-D-galactopyranosylisoselenuronium bromide (29β)

^{1}H NMR, 400 MHz



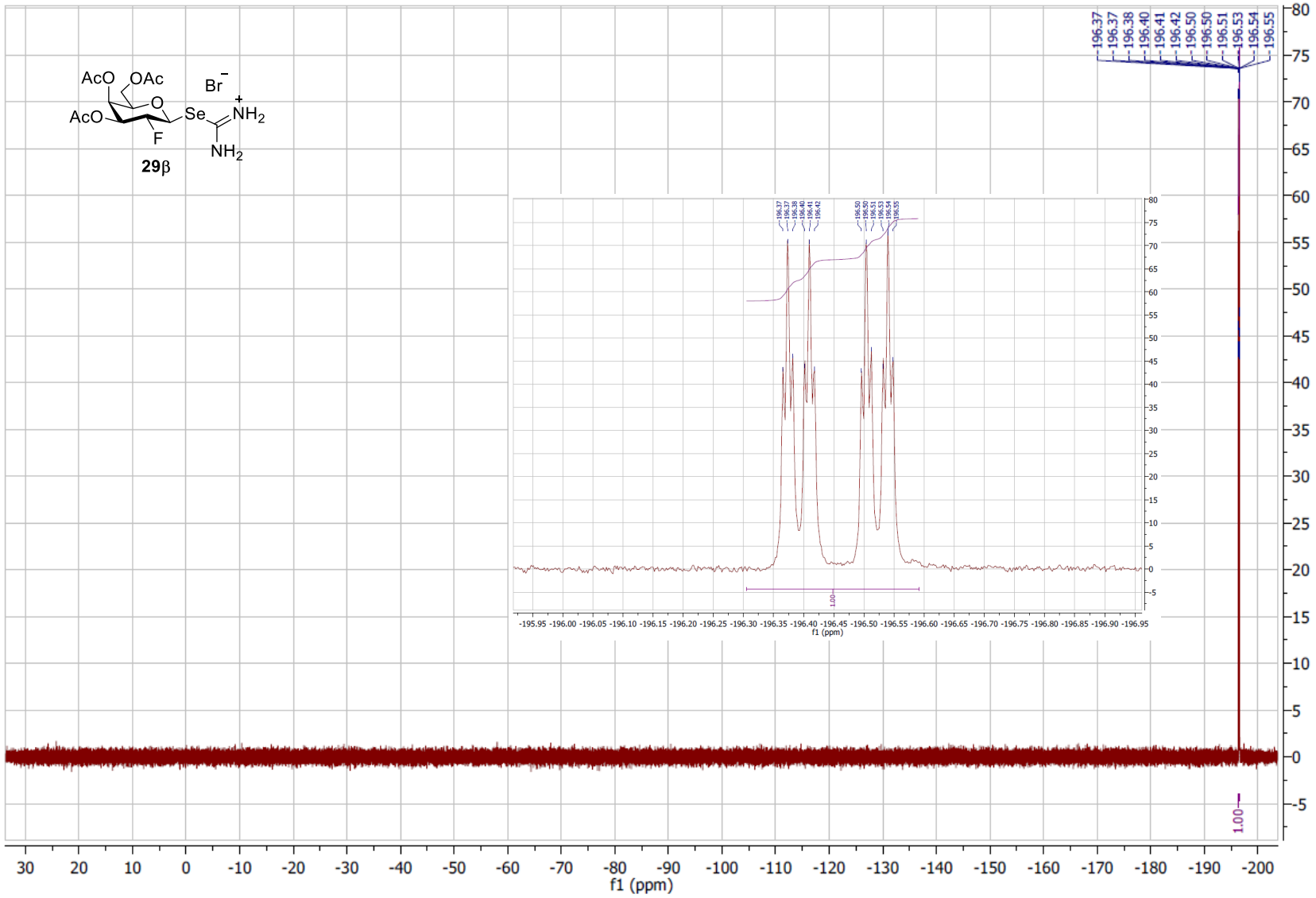
3,4,6-Tri-*O*-acetyl-2-deoxy-2-fluoro-β-D-galactopyranosylisoselenuronium bromide (29β)

^{13}C NMR, 101 MHz



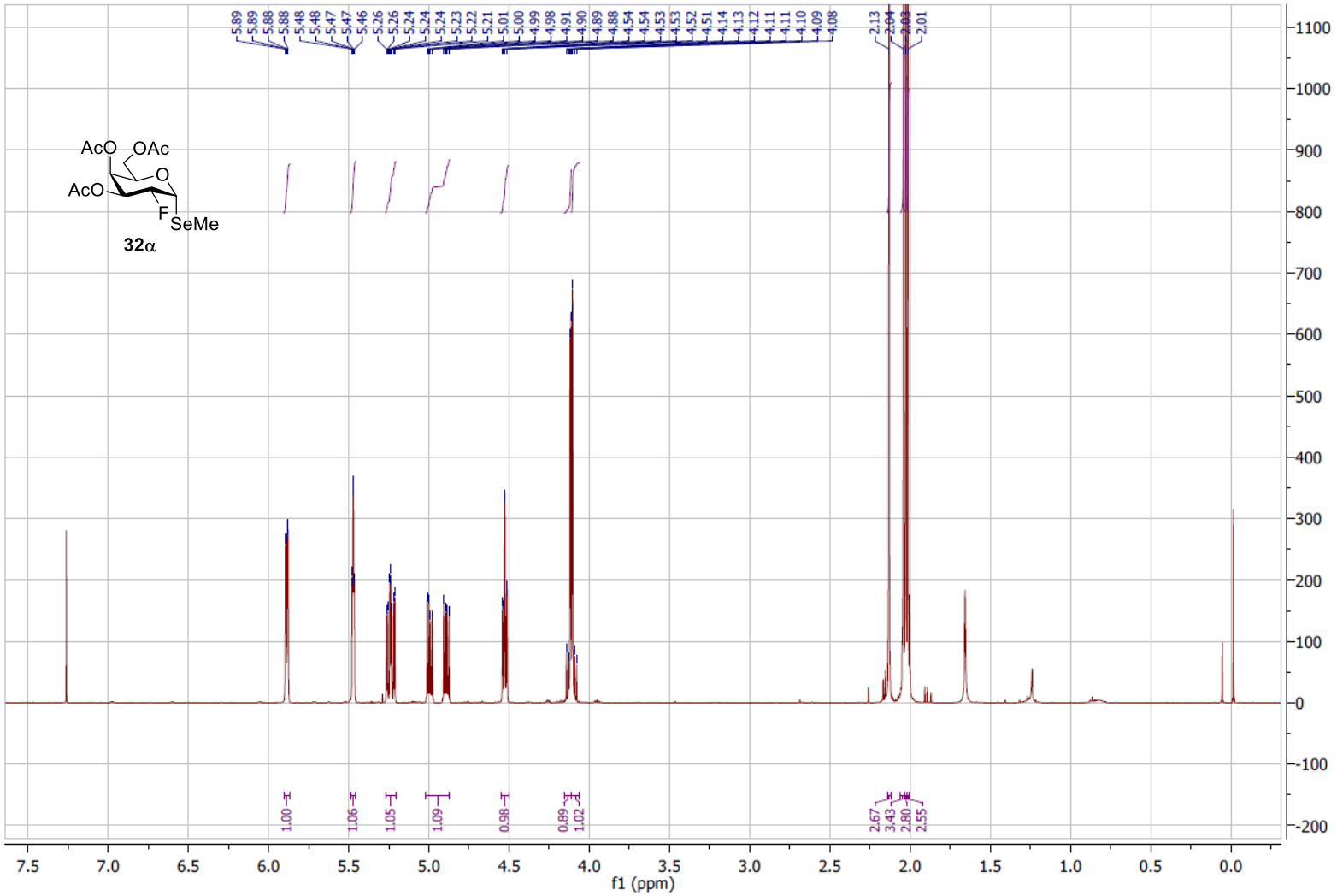
3,4,6-Tri-*O*-acetyl-2-deoxy-2-fluoro-β-D-galactopyranosylisoselenuronium bromide (29β)

^{19}F NMR, 376 MHz



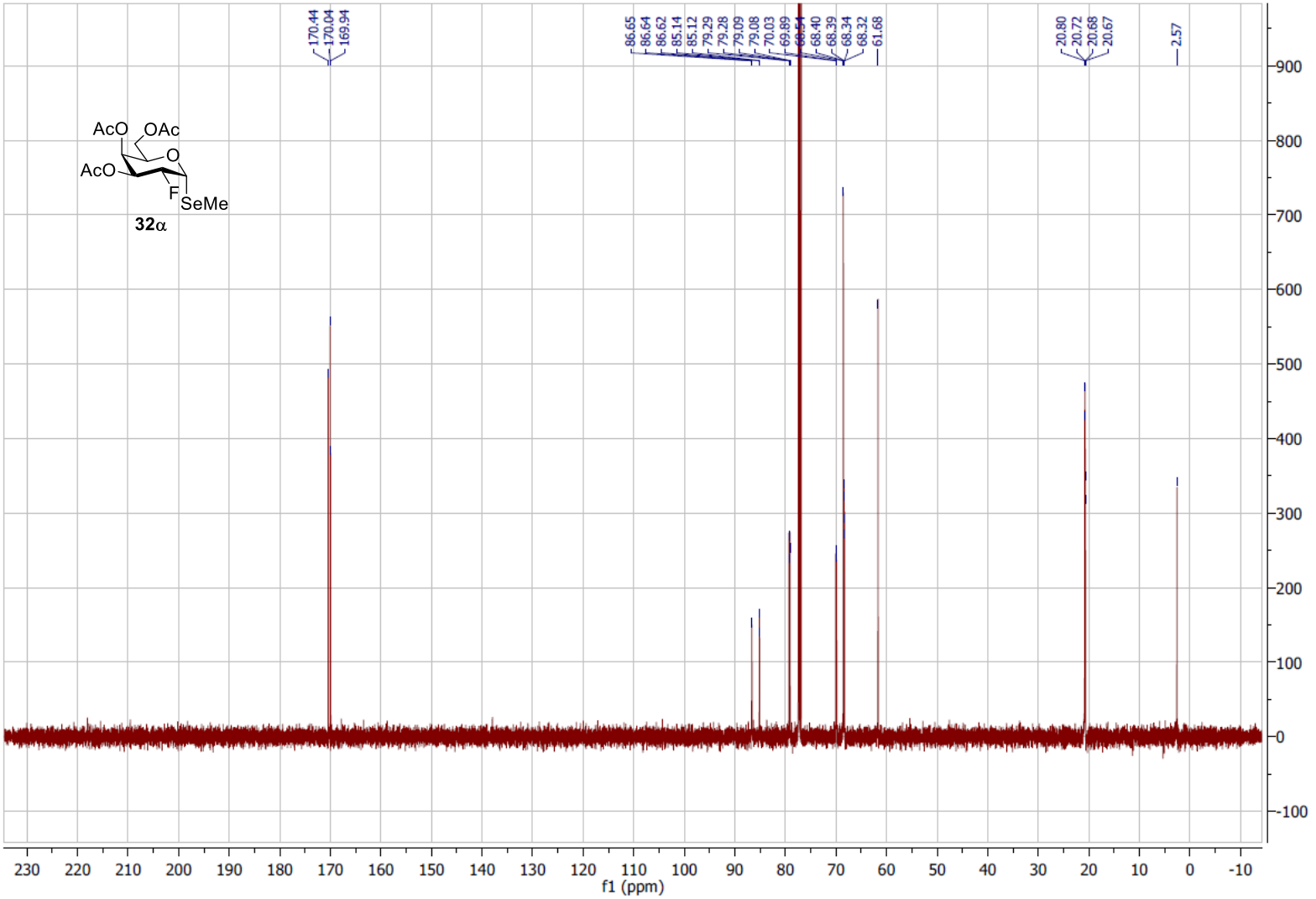
Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-fluoro-1-seleno-α-D-galactopyranoside (32α)

^{1}H NMR, 400 MHz



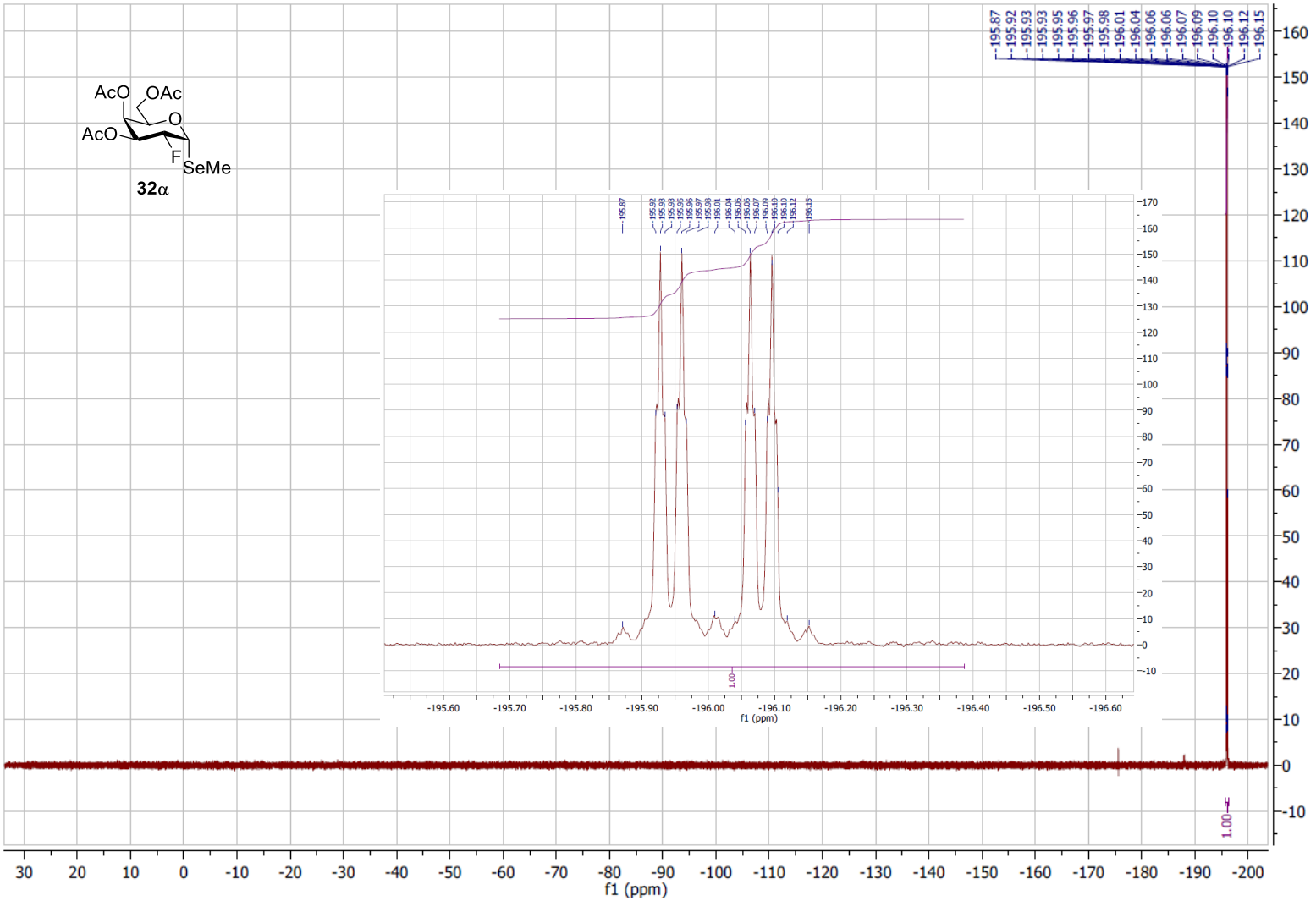
Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-fluoro-1-seleno-α-D-galactopyranoside (32α)

^{13}C NMR, 101 MHz



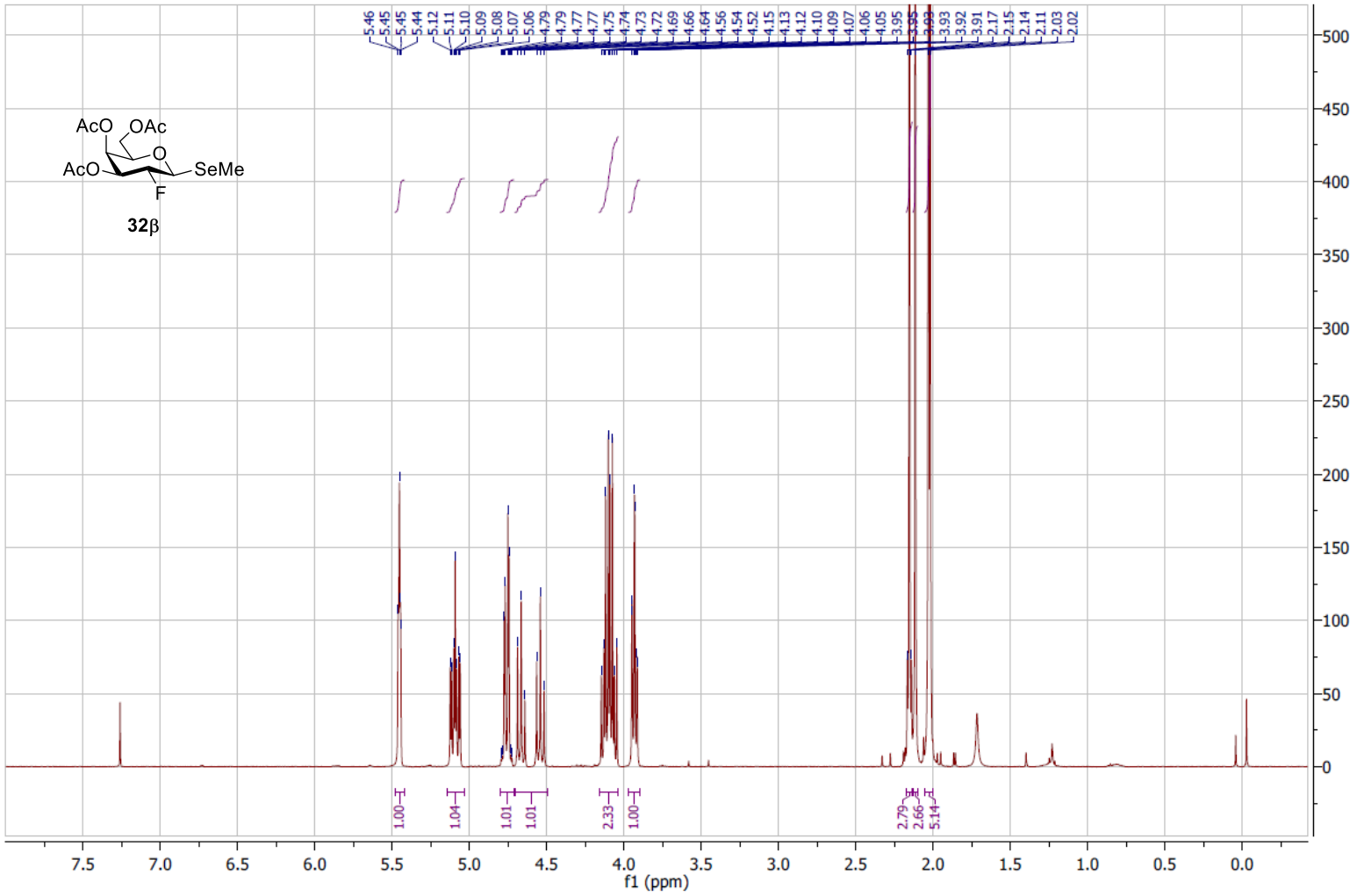
Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-fluoro-1-seleno-α-D-galactopyranoside (32α)

^{19}F NMR, 376 MHz



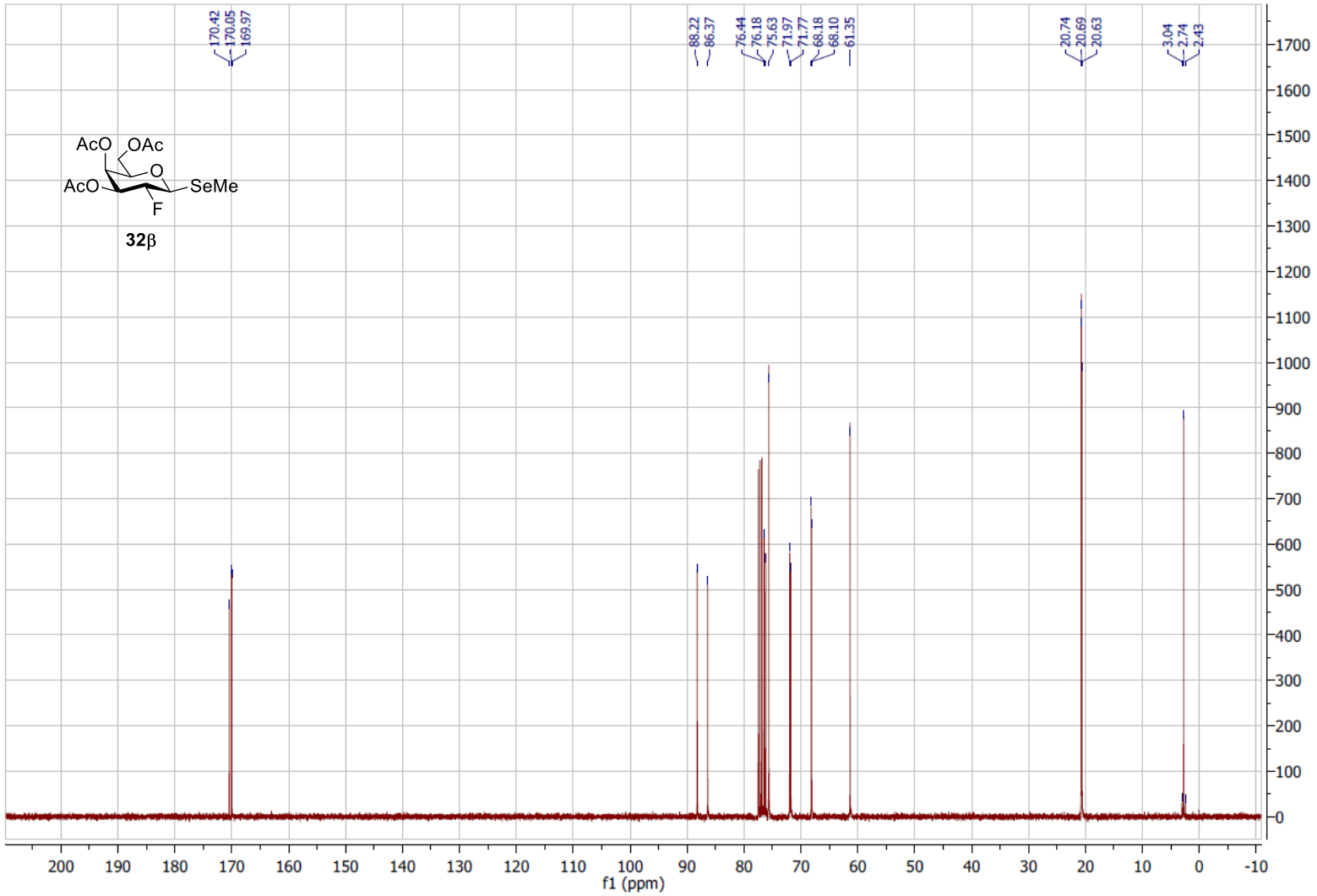
Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-fluoro-1-seleno-β-D-galactopyranoside (32β)

^{1}H NMR, 400 MHz



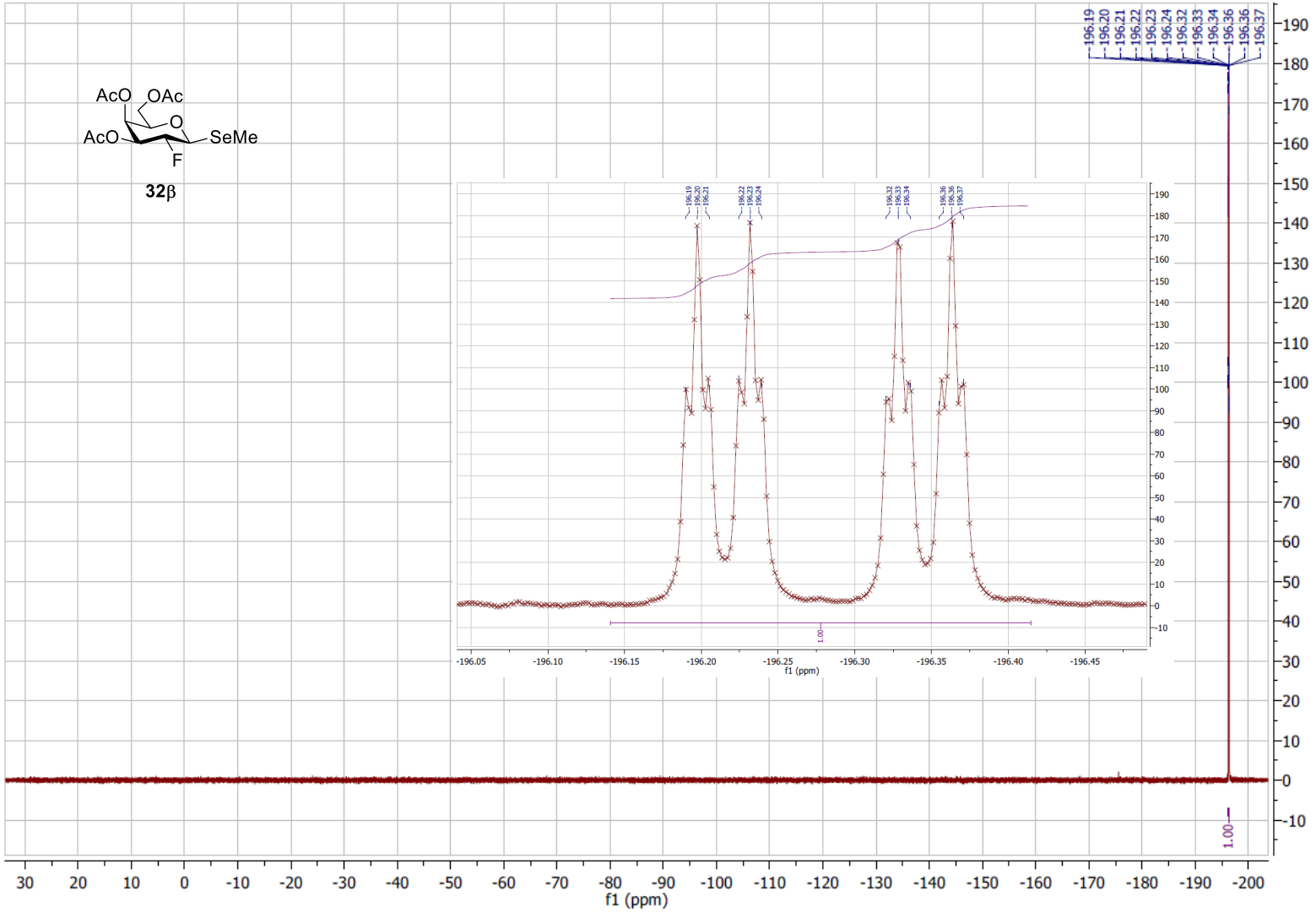
Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-fluoro-1-seleno-β-D-galactopyranoside (32β)

^{13}C NMR, 101 MHz



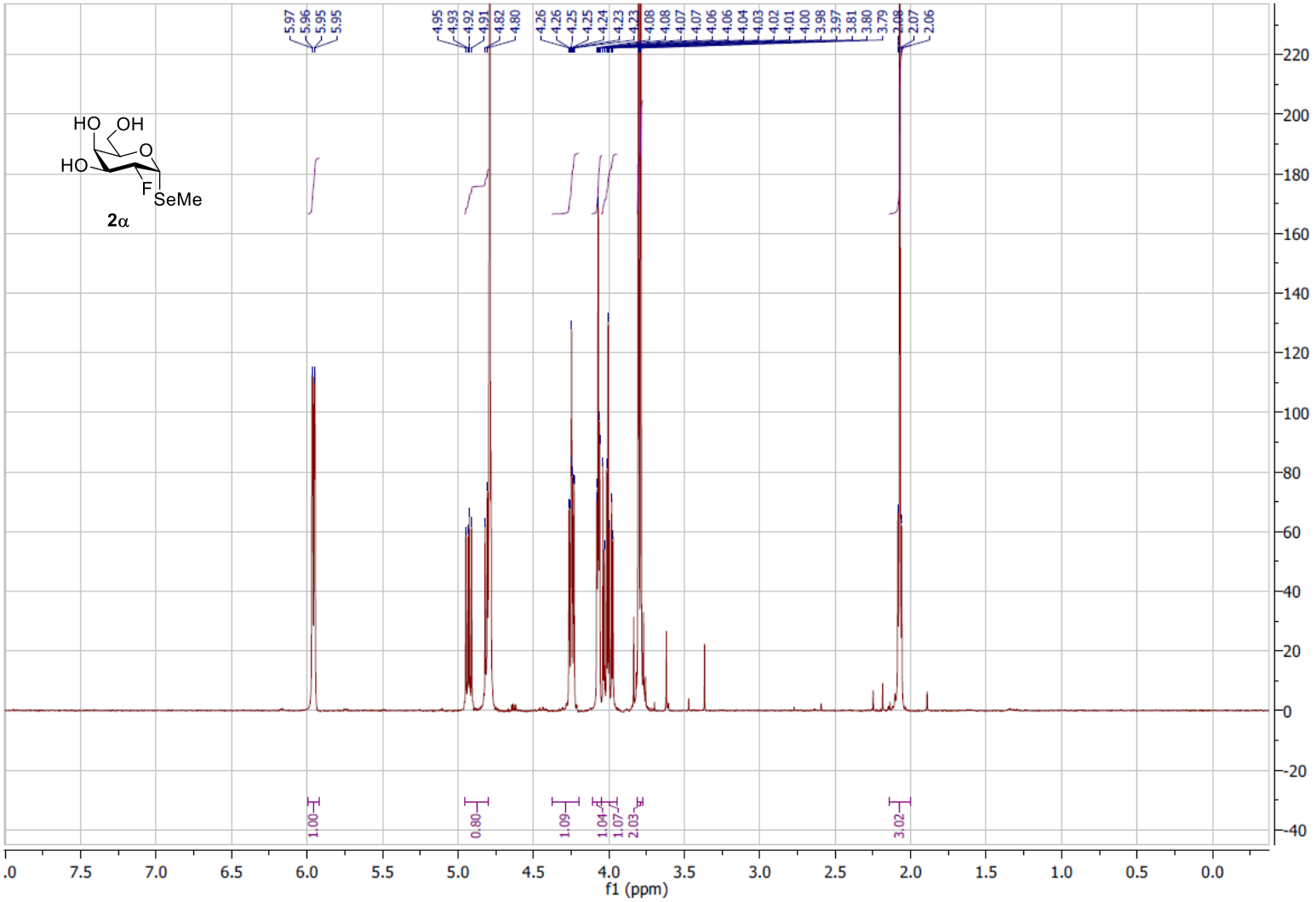
Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-fluoro-1-seleno-β-D-galactopyranoside (32β)

^{19}F NMR, 376 MHz



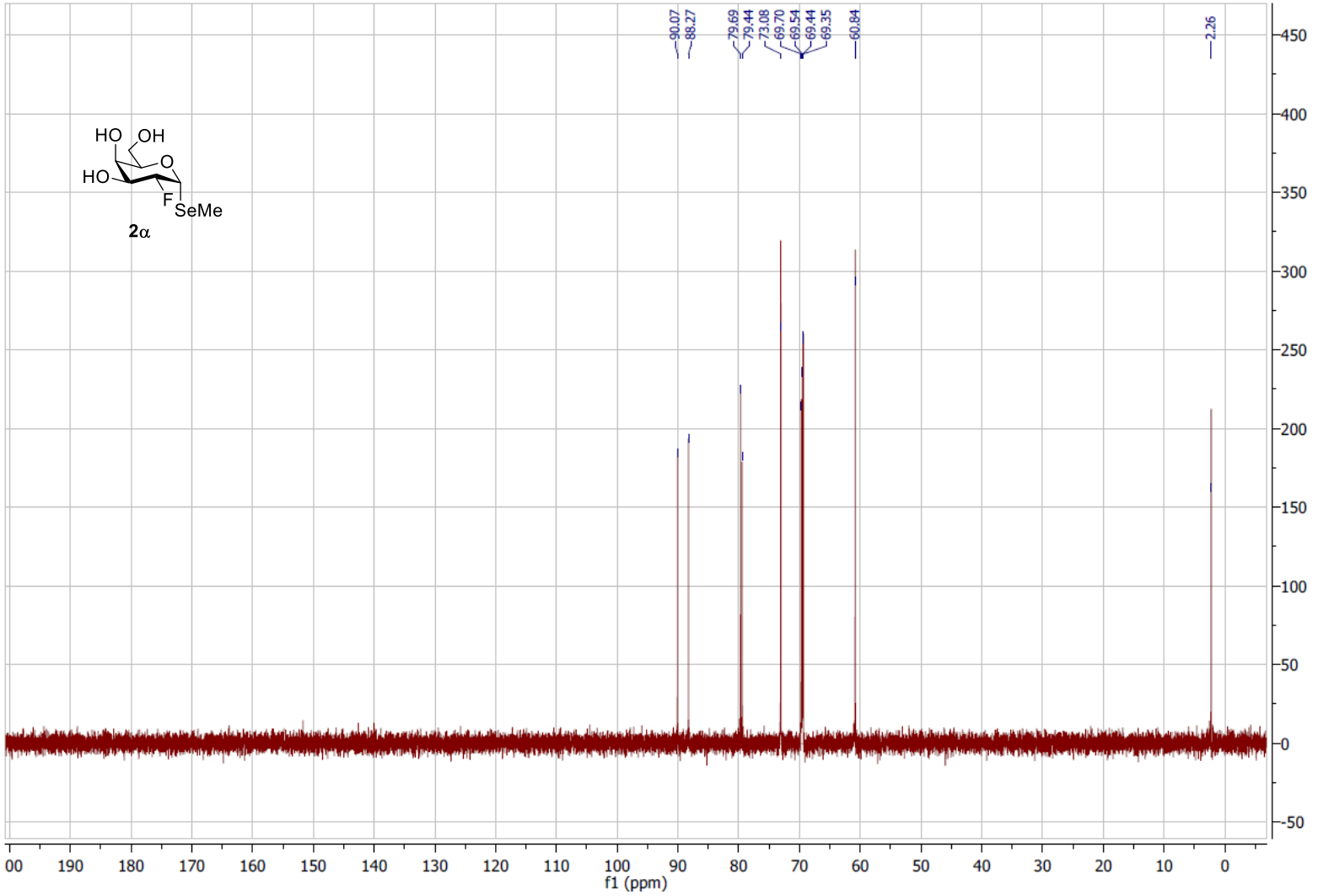
Methyl 2-deoxy-2-fluoro-1-seleno-α-D-galactopyranoside (2α)

^{1}H NMR, 400 MHz



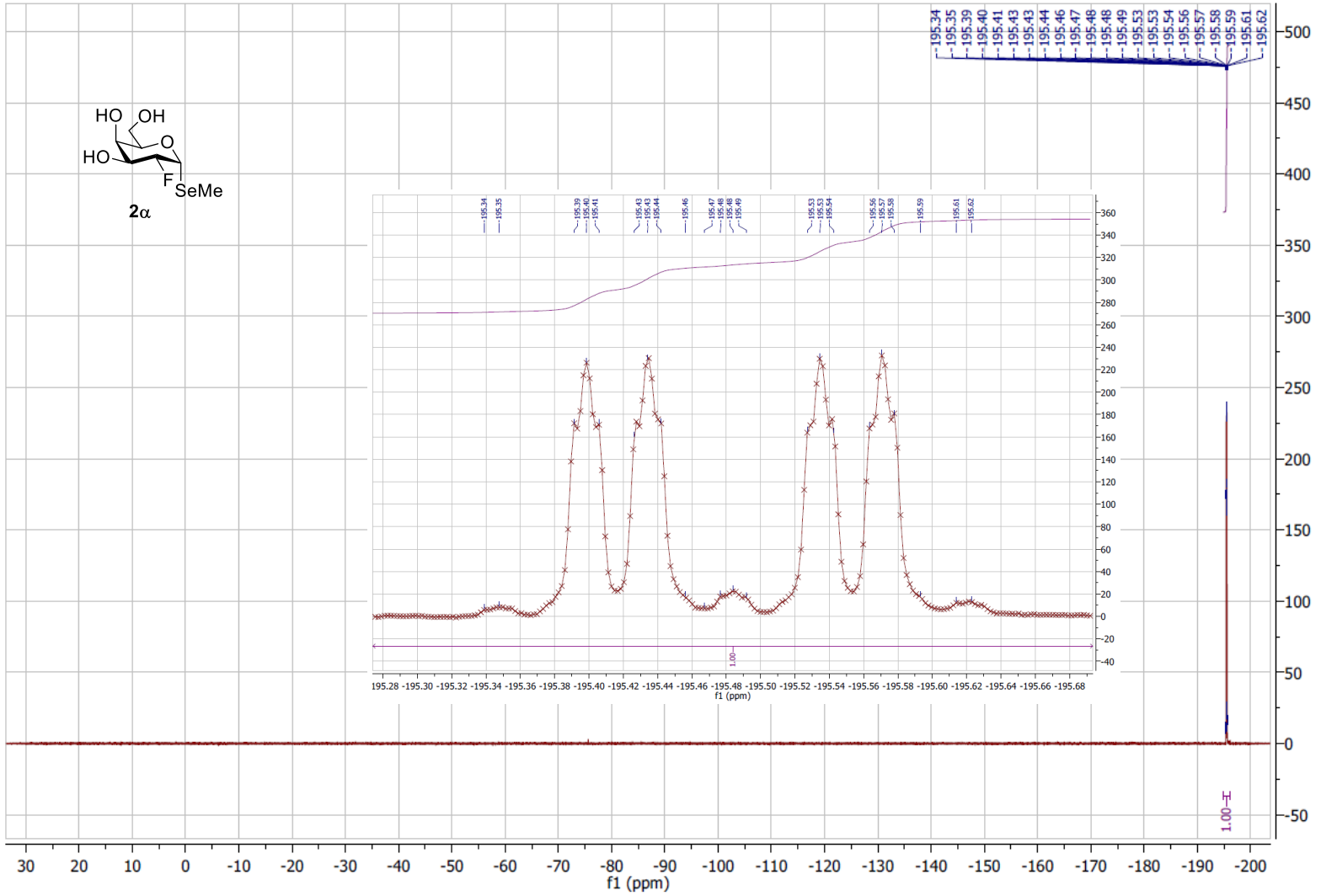
Methyl 2-deoxy-2-fluoro-1-seleno-α-D-galactopyranoside (2α)

^{13}C NMR, 101 MHz



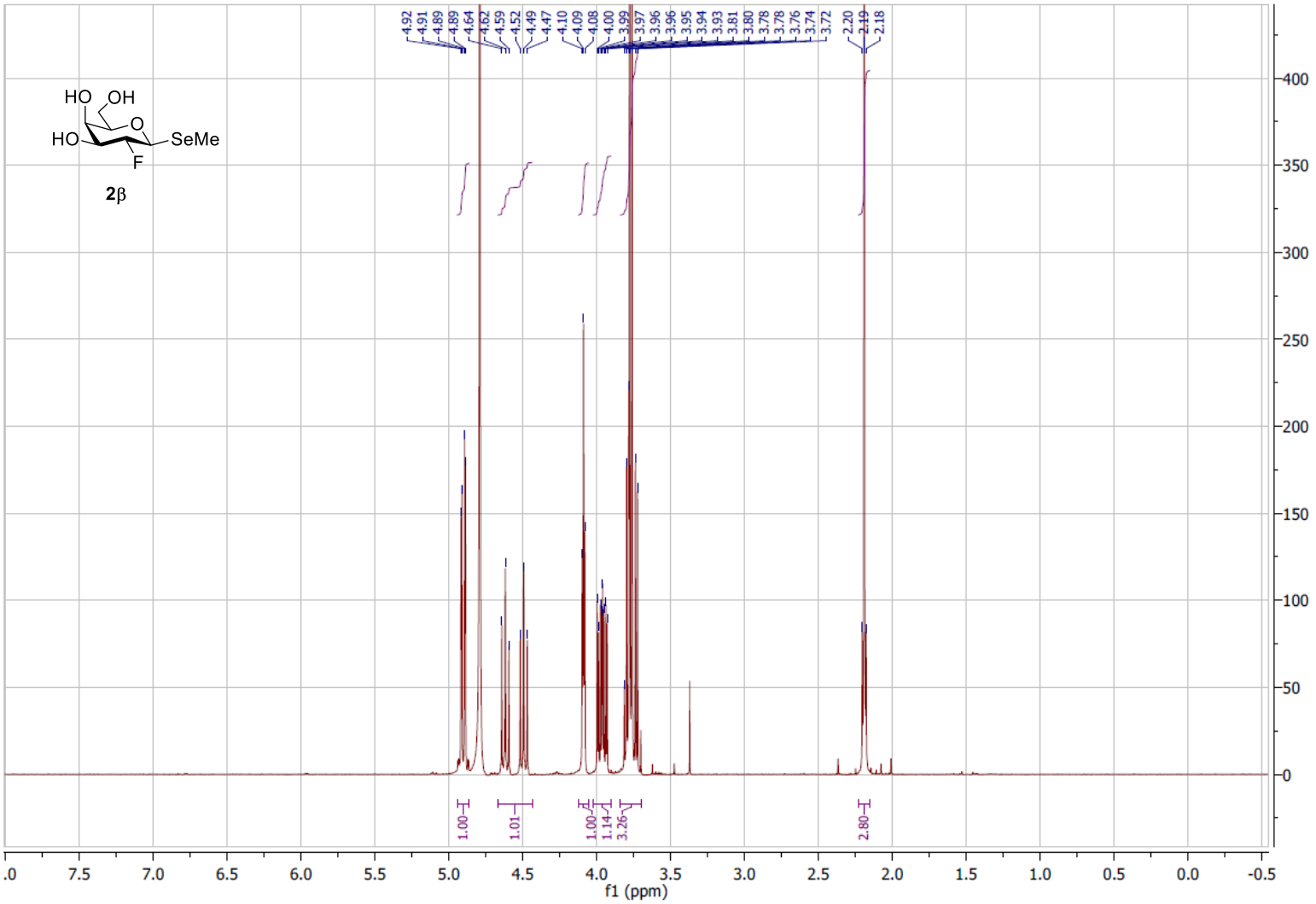
Methyl 2-deoxy-2-fluoro-1-seleno-α-D-galactopyranoside (2α)

^{19}F NMR, 376 MHz



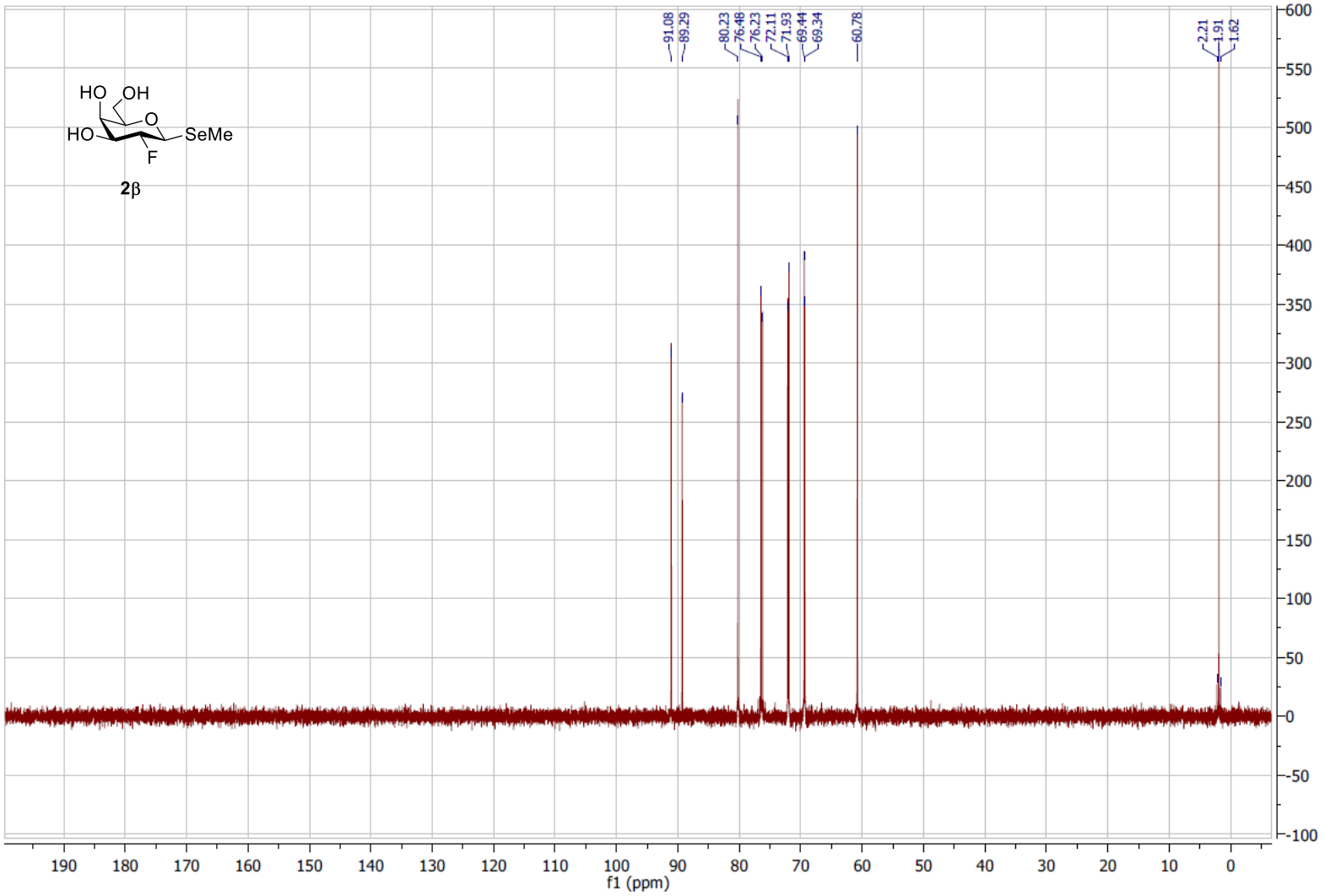
Methyl 2-deoxy-2-fluoro-1-seleno-β-D-galactopyranoside (2β)

^{1}H NMR, 400 MHz



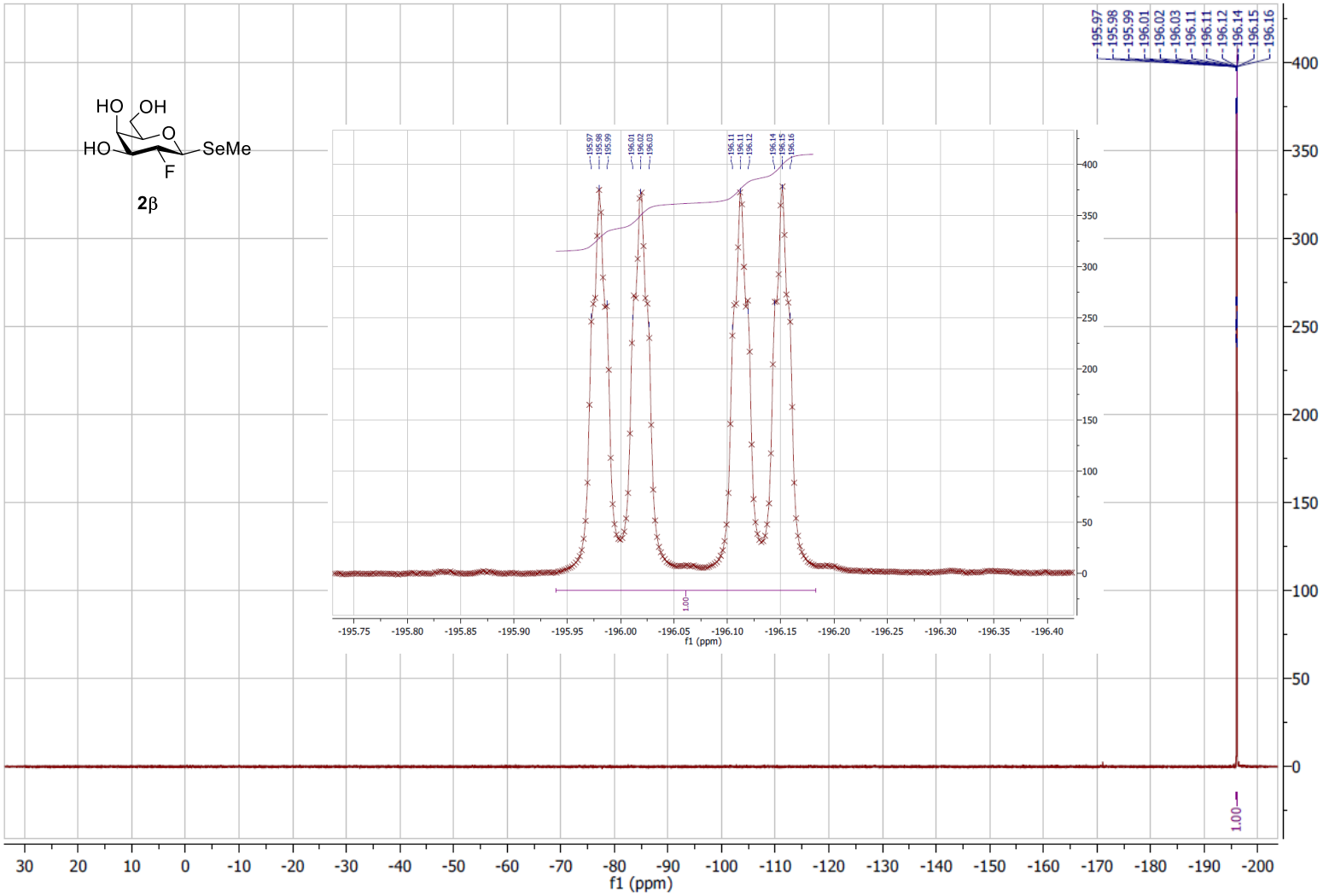
Methyl 2-deoxy-2-fluoro-1-seleno-β-D-galactopyranoside (2β)

^{13}C NMR, 101 MHz



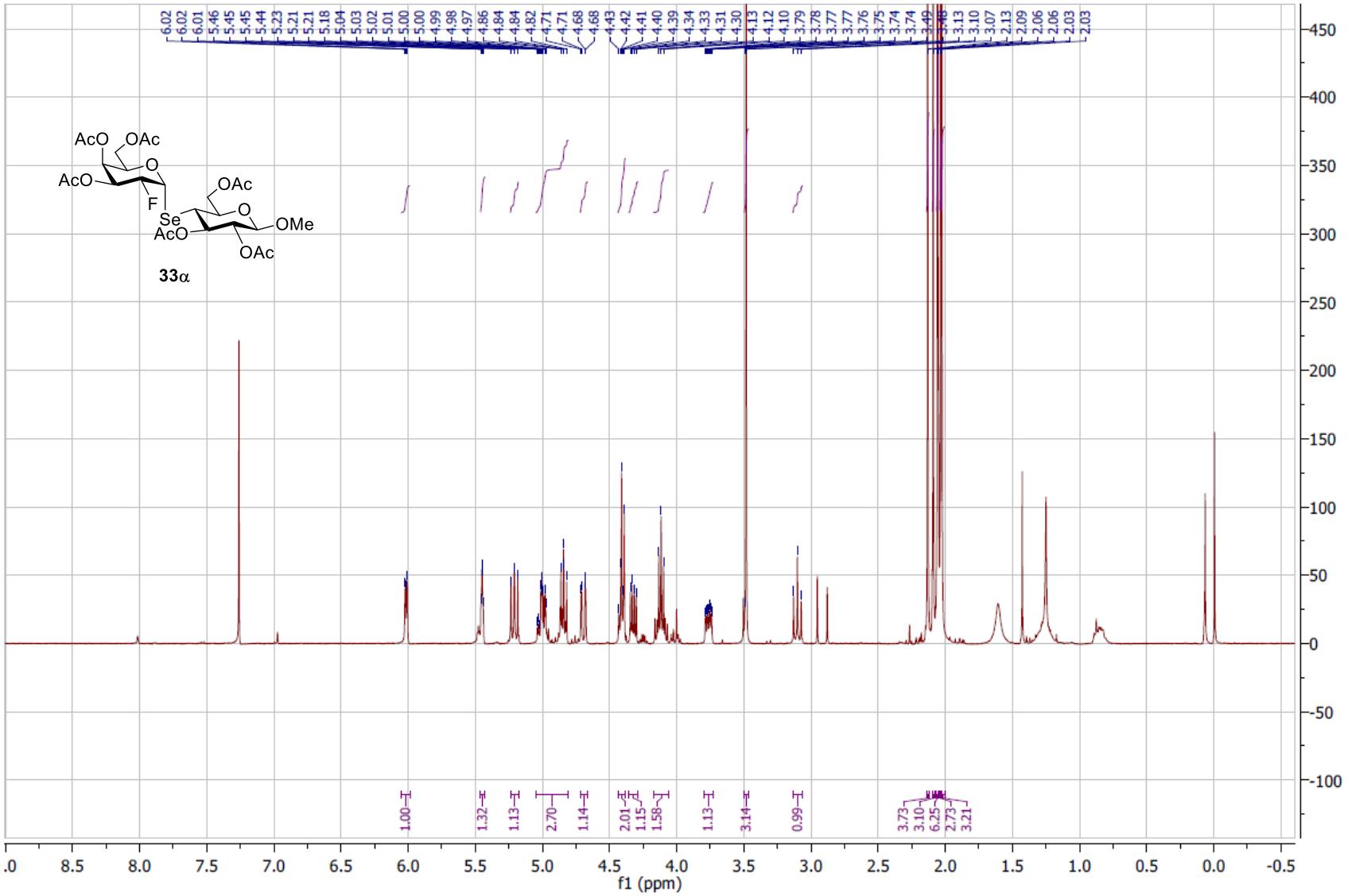
Methyl 2-deoxy-2-fluoro-1-seleno-β-D-galactopyranoside (2β)

^{19}F NMR, 376 MHz



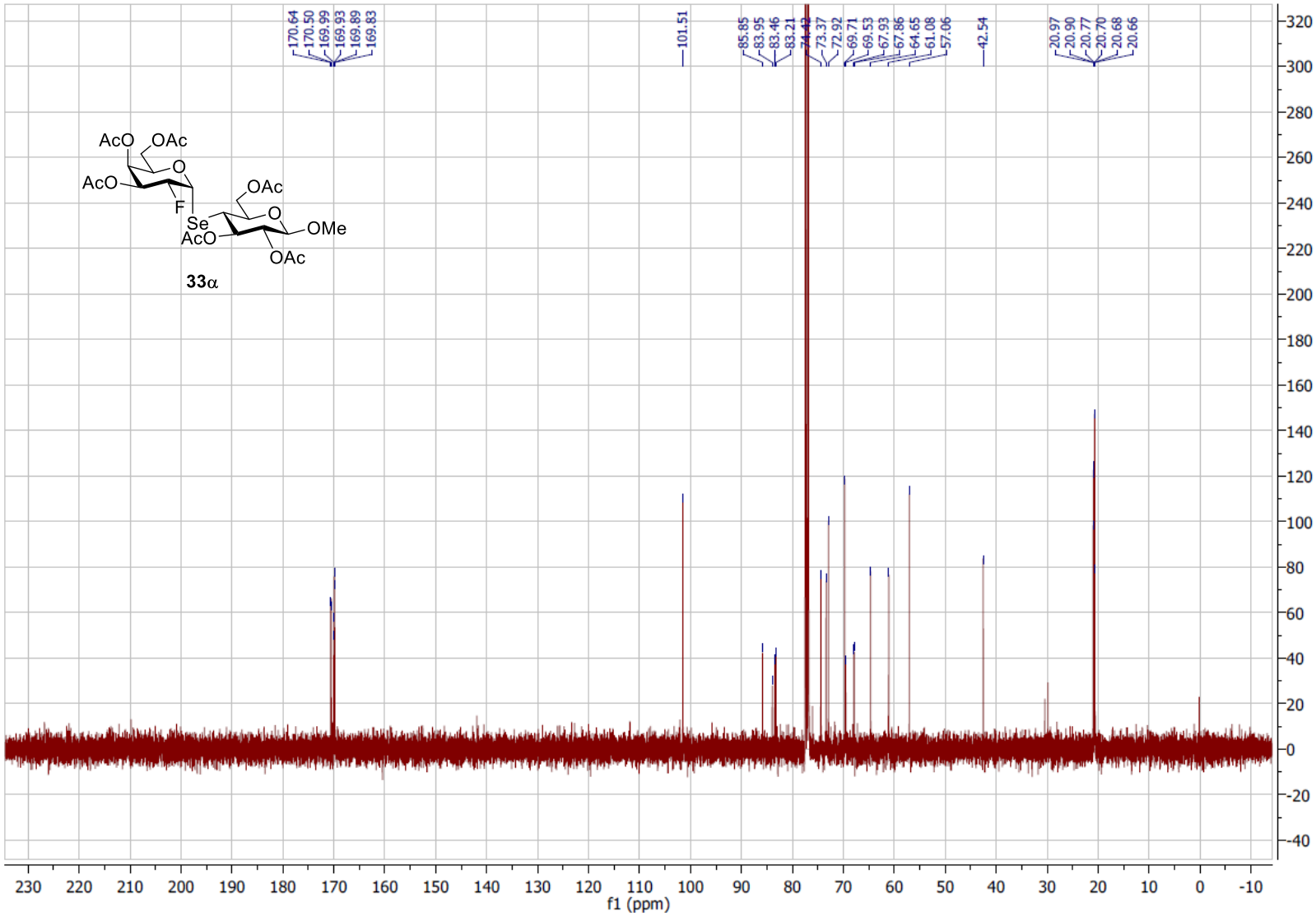
Methyl 4-*Se*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-fluoro-α-D-galactopyranosyl)-2,3,6-tri-*O*-acetyl-4-seleno-β-D-glucopyranoside (33α)

^{1}H NMR, 400 MHz



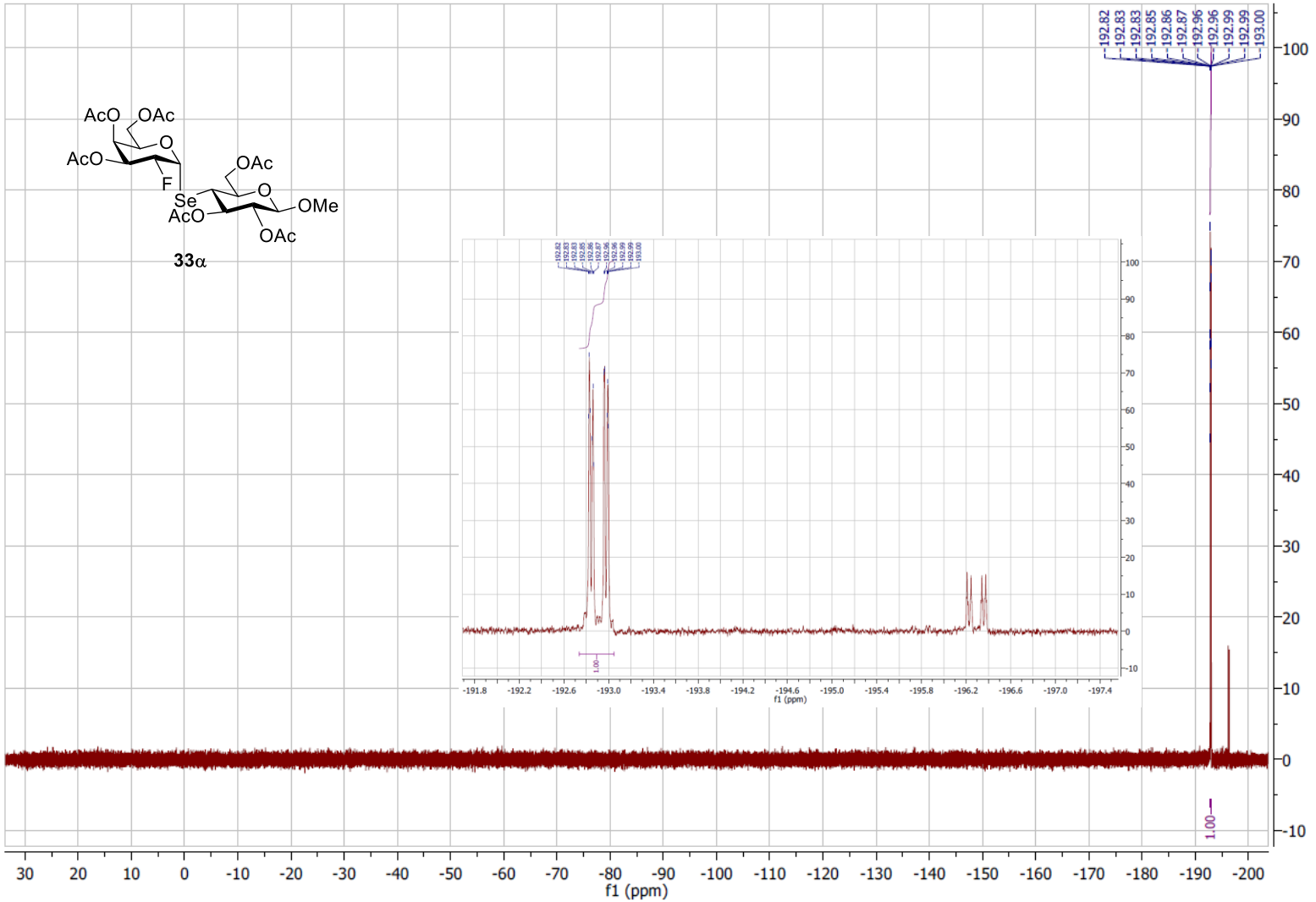
Methyl 4-*Se*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-fluoro-α-D-galactopyranosyl)-2,3,6-tri-*O*-acetyl-4-seleno-β-D-glucopyranoside (33α)

^{13}C NMR, 101 MHz



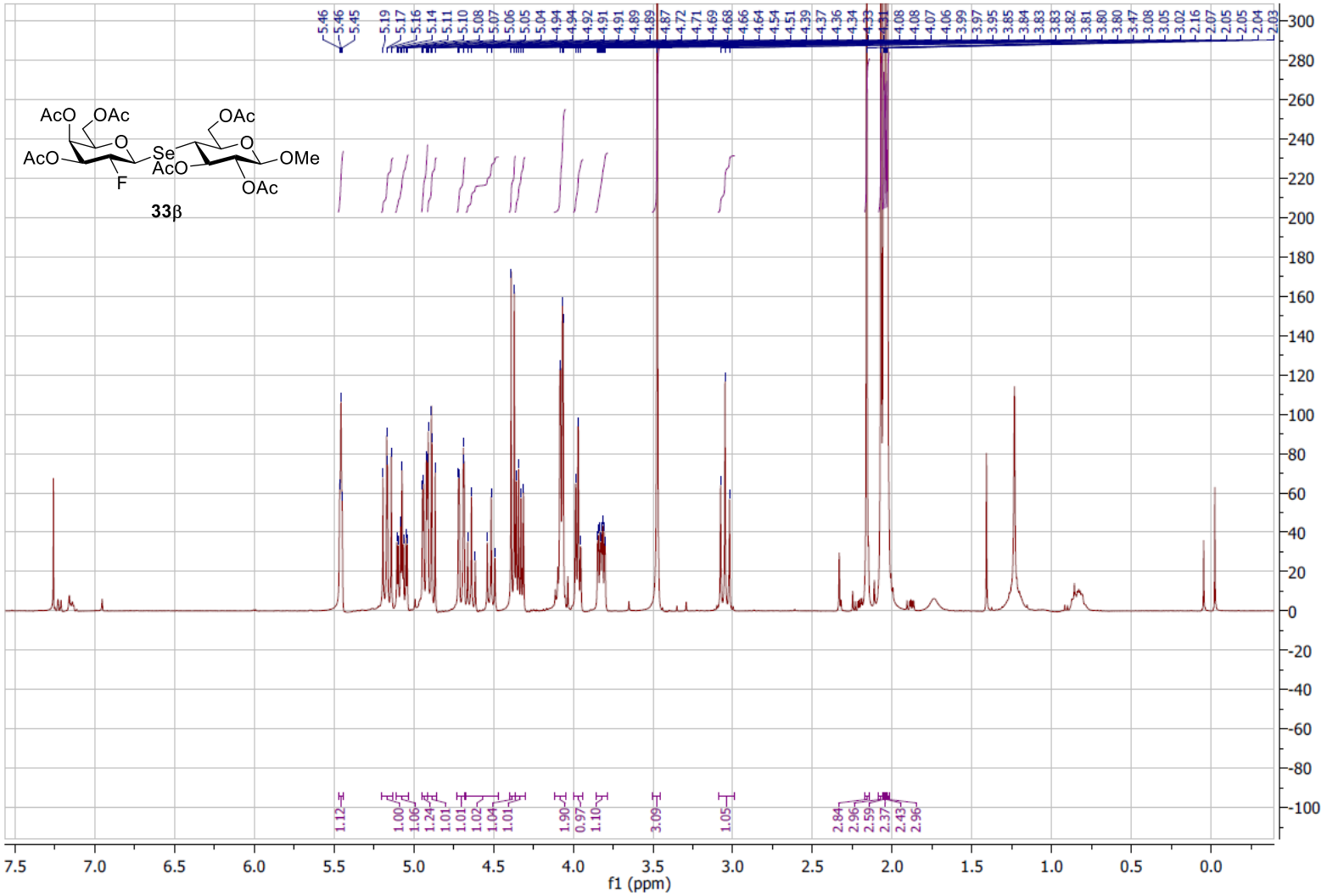
Methyl 4-*Se*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-fluoro-α-D-galactopyranosyl)-2,3,6-tri-*O*-acetyl-4-seleno-β-D-glucopyranoside (33α)

^{19}F NMR, 376 MHz



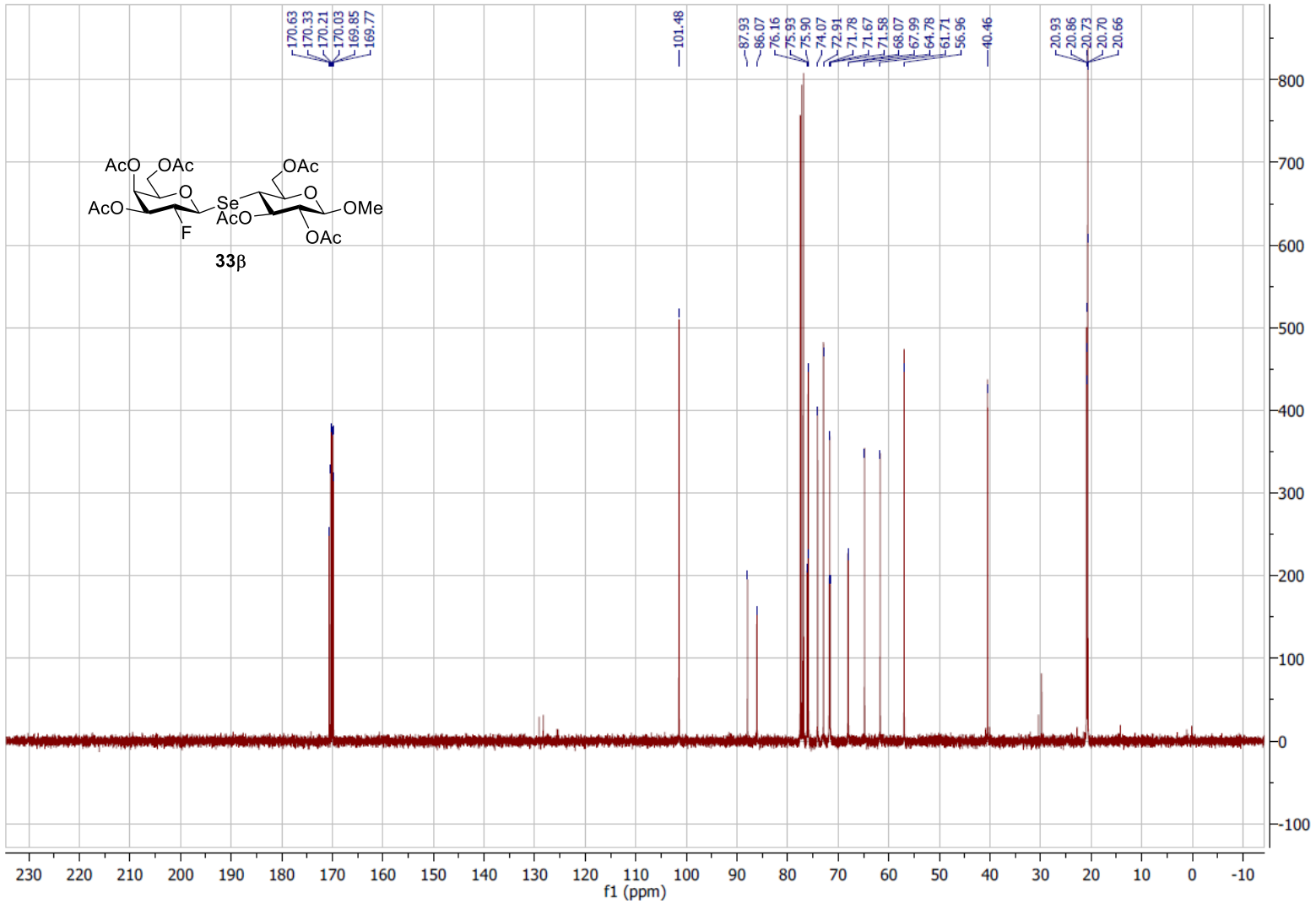
Methyl 4-*Se*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-fluoro-β-D-galactopyranosyl)-2,3,6-tri-*O*-acetyl-4-seleno-β-D-glucopyranoside (33β)

^{1}H NMR, 400 MHz



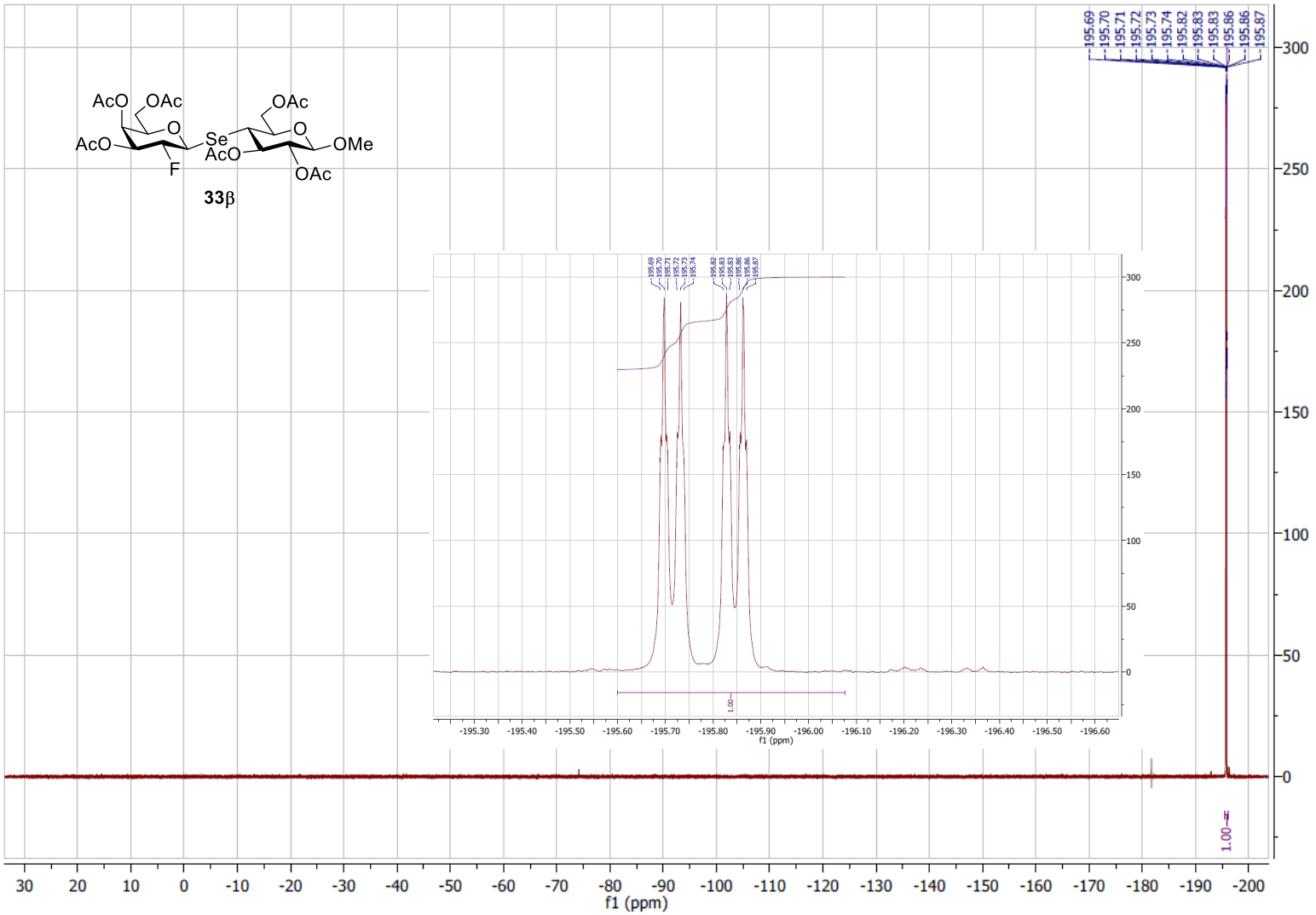
Methyl 4-*Se*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-fluoro-β-D-galactopyranosyl)-2,3,6-tri-*O*-acetyl-4-seleno-β-D-glucopyranoside (33β)

^{13}C NMR, 101 MHz



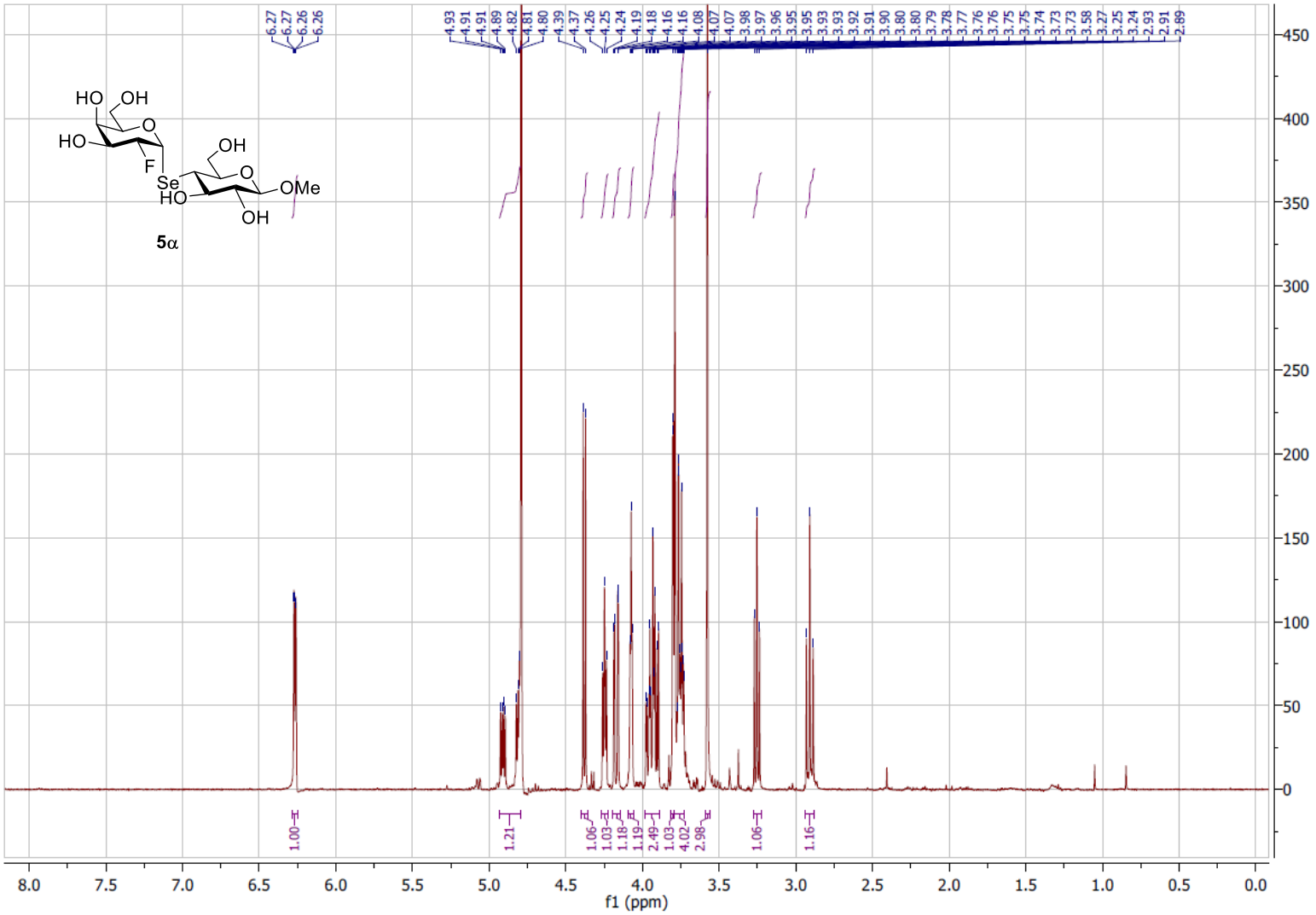
Methyl 4-*Se*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-fluoro-β-D-galactopyranosyl)-2,3,6-tri-*O*-acetyl-4-seleno-β-D-glucopyranoside (33β)

^{19}F NMR, 376 MHz



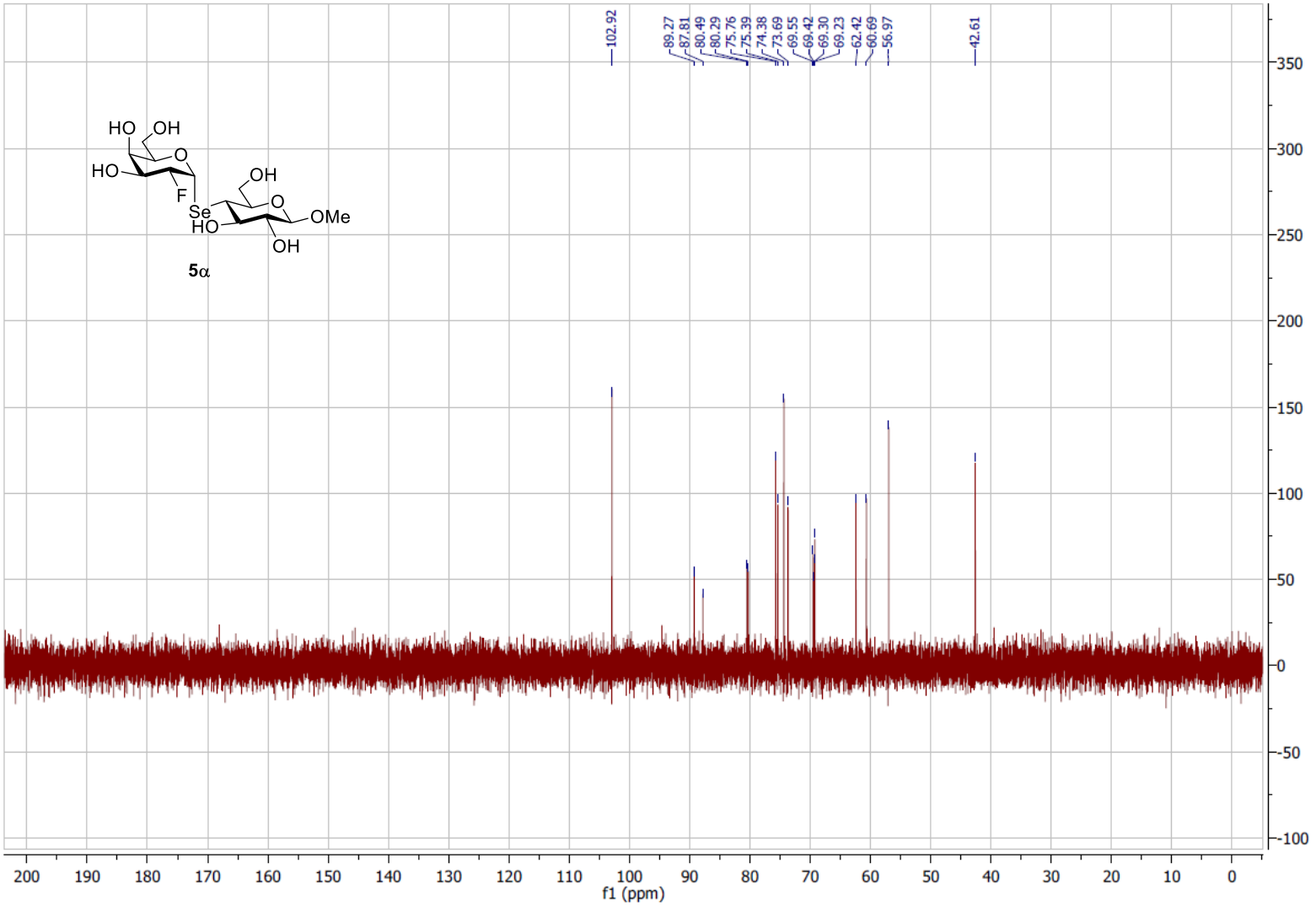
Methyl 4-*Se*-(2-deoxy-2-fluoro-α-D-galactopyranosyl)-4-seleno-β-D-glucopyranoside (5α)

^{1}H NMR, 400 MHz



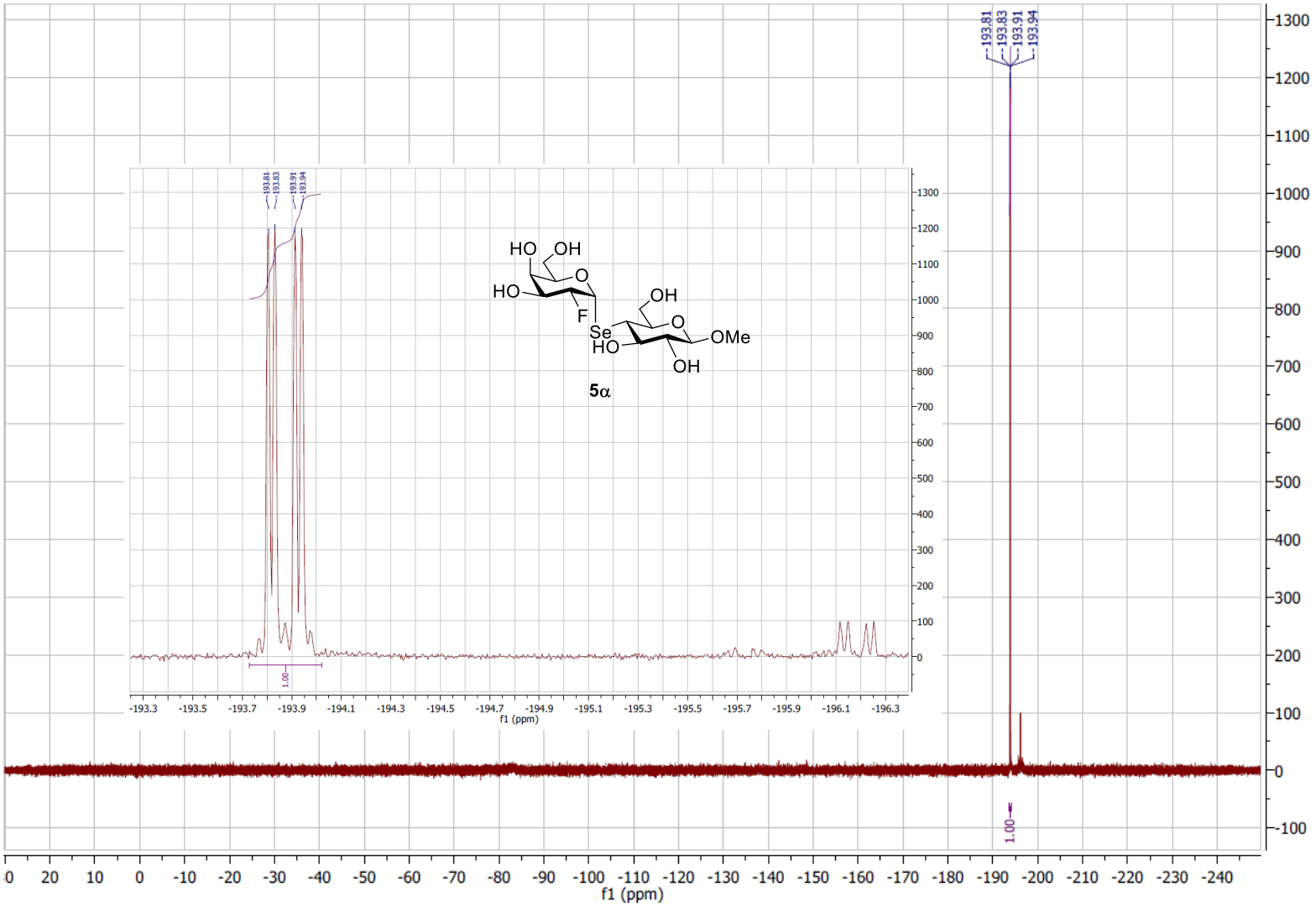
Methyl 4-*Se*-(2-deoxy-2-fluoro-α-D-galactopyranosyl)-4-seleno-β-D-glucopyranoside (5α)

^{13}C NMR, 101 MHz



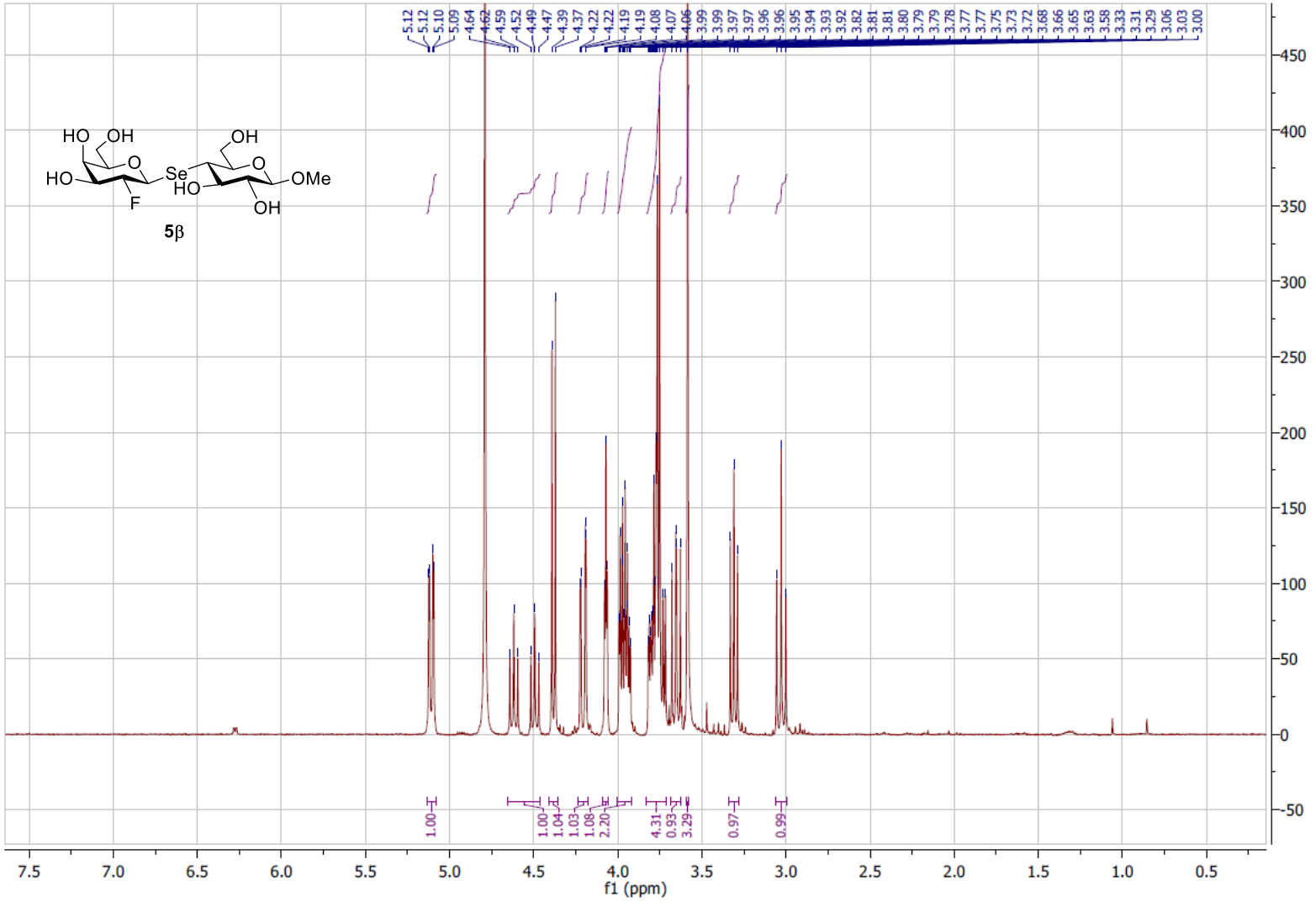
Methyl 4-*Se*-(2-deoxy-2-fluoro-α-D-galactopyranosyl)-4-seleno-β-D-glucopyranoside (5α)

^{19}F NMR, 376 MHz



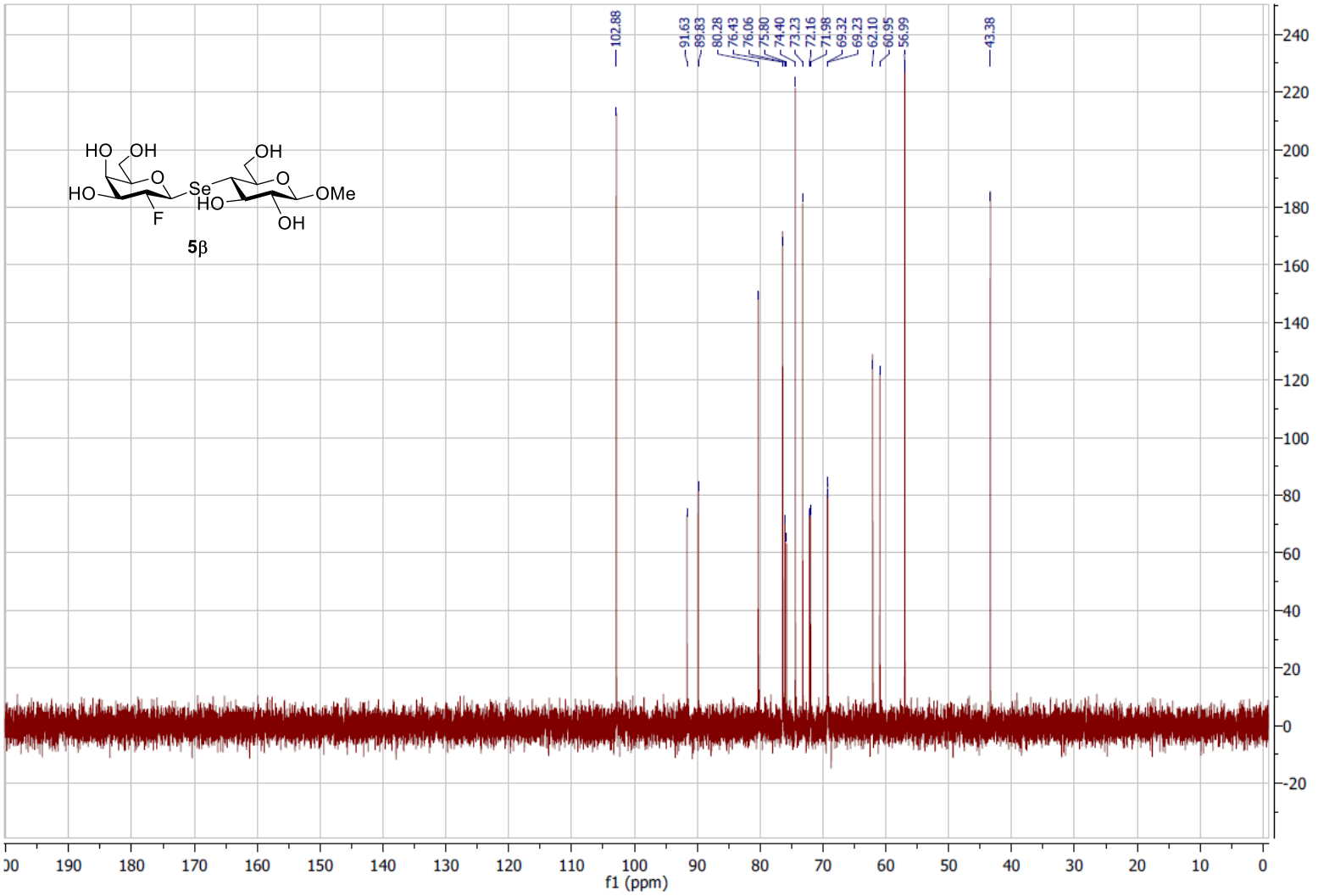
Methyl 4-*Se*-(2-deoxy-2-fluoro-β-D-galactopyranosyl)-4-seleno-β-D-glucopyranoside (5β)

^{1}H NMR, 400 MHz



Methyl 4-*Se*-(2-deoxy-2-fluoro-β-D-galactopyranosyl)-4-seleno-β-D-glucopyranoside (5β)

^{13}C NMR, 101 MHz



Methyl 4-*Se*-(2-deoxy-2-fluoro-β-D-galactopyranosyl)-4-seleno-β-D-glucopyranoside (5β)

^{19}F NMR, 376 MHz