Supporting Information for

Photocatalyzed reductive fluoroalkylation of 2-acetoxyglycals towards the stereoselective synthesis of α-1-fluoroalkyl-*C*-glycosyl derivatives

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1. General Information

The solvents were distilled before use. Fluorinated reagents (perfluorobutyl iodide, perfluorohexyl iodide and trifluoroiodomethane), photocatalyst (Ir $[dF(CF_3)PPy]_2(dtbPy))PF_6$, Eosin Y, and Rose Bengal), bases (Me_2CO_3 (M = Li, Na, K, Cs), and *N,N,N'N'*-tetramethylethylenediamine), and hydrogen donors (2-mercaptoethanol, 1-adamantanethiol, and tris-(trimethylsilyl)trimethylsilane) were purchased from Sigma and used without further purification. 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) and 1,4-dinitrobenzene were ultra-pure grade reagents. Silica gel 60 Merck (0.063–0.200mm) was used for column chromatography. Preparative thin-layer chromatography separations were carried out on 0.50 mm E. Merck silica gel plates (60F-254). The spots were detected by UV light, or by charring with an ethanolic solution of phosphomolybdic acid and cerium sulfate, or an ethanolic solution of sulfuric acid and *p*-anisaldehyde or CAN (ceric ammonium nitrate) solution. The photocatalytic reactions were performed under irradiation with commercially available blue LEDs. ^1H, ^{19}F and ^{13}C NMR spectra were recorded at room temperature on a Bruker AC 200 (200 MHz), or on a Bruker Avance 600 (600 MHz) spectrometers. The residual signals of $CDCl_3$ (δ 7.26 ppm) for ^1H NMR assignment spectra and the carbon signals of $CDCl_3$ (δ 77.0 ppm) for ^{13}C NMR were used as references. The analyses of signals were assisted by the 2D experiments: ^1H-^1H COSY and ^1H-^{13}C HSQC. High-resolution mass spectra (HRMS) were obtained using micrOTOF-Q II mass spectrometer. Fluorescence spectra were determined in a Cary Eclipse Fluorescence Spectrophotometer and optical rotations in a Perkin-Elmer 343 polarimeter, the UV-VIS Spectrophotometer employed was a Jasco v-560.

2. Experimental Section

2.1 General Preparation of 2-Acetoxyglycals: 3,4,6-tri-*O*-acetyl-2-acetoxy-D-galactal (1a), 3,4,6-tri-*O*-acetyl-2-acetoxy-D-glucal (1b) and 3,4-di-*O*-acetyl-2-acetoxy-D-xylal (1c)

2-Acetoxyglycals were obtained as previously reported.[1] The peracetylated sugar (2.0 g, 5.13 or 6.29 mmol) was placed in a 100 mL flask and dissolved in anhydrous CH_2Cl_2 (10.0 mL), in the darkness. The solution was stirred and cooled to 0 °C in an ice

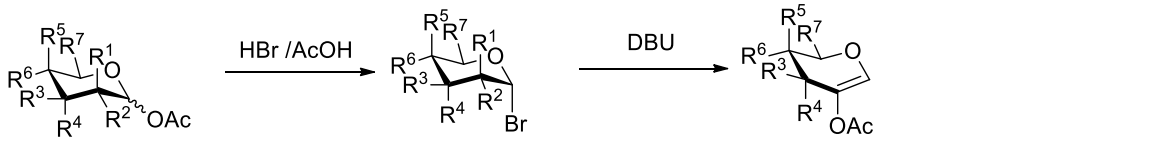
bath, then hydrogen bromide 33 wt% in acetic acid (2.04 mL, 0.0115 mol) was added over a period of 5 minutes.

The solution was stirred for 45 minutes at 0 °C and allowed to reach room temperature. Stirring was continued for additional 1 or 2 hours. Monitoring of the reaction was carried out by TLC (1:1 hexane / EtOAc). Complete conversion to the carbohydrate bromide was obtained in all cases. The carbohydrate bromide had a higher R_f than that obtained with the peracetylated sugar.

The mixture was diluted with CH_2Cl_2 (20 mL) and the solution was washed successively with saturated $NaHCO_3$ solution (2 x 10 ml) and distilled water (2 x 15 ml). The organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated.

The resulting compounds (yellowish syrups, in all cases) were dissolved in dry CH_2Cl_2 (15.0 mL) and placed in an ice-water bath, in the dark. To this mixture, was added dropwise and under magnetic stirring diazabicyclo[5.4.0]-undec-7-ene (DBU, 0.9 mL, 6 mmol). The solution was stirred for 30 minutes at 0 ° C, and then at room temperature for an additional 2 or 3 hours. Monitoring of the reaction was carried out by TLC (1:1 hexane / EtOAc). A conversion of 70-90%, to the corresponding glycals was obtained.

The mixture was diluted with CH_2Cl_2 (15 mL) and the solution was washed successively with 5% HCl solution (2 x 10 mL) and distilled water (2 x 15 mL). The organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The 2-acetoxylycas obtained were purified by column chromatography (8: 2 hexane: AcOEt). A final purification by preparative TLC (8 : 2 hexane : AcOEt) led to the final compounds.



***galacto* configuration:**
$R^1 = R^4 = R^6 = H$; $R^2 = R^3 = R^5 = OAc$, $R^7 = CH_2OAc$

***gluco* configuration:**
$R^1 = R^4 = R^5 = H$; $R^2 = R^3 = R^6 = OAc$, $R^7 = CH_2OAc$

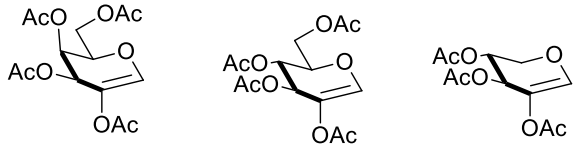
***xylo* configuration:**
$R^1 = R^4 = R^5 = R^7 = H$; $R^2 = R^3 = R^6 = OAc$

2-acetoxy-D-galactal
1, $R^1 = R^4 = R^6 = H$; $R^2 = R^3 = R^5 = OAc$, $R^7 = CH_2OAc$

2-acetoxy-D-glucal:
2, $R^1 = R^4 = R^5 = H$; $R^2 = R^3 = R^6 = OAc$, $R^7 = CH_2OAc$

2-acetoxy-D-xylal:
3, $R^1 = R^4 = R^5 = R^7 = H$; $R^2 = R^3 = R^6 = OAc$

Scheme S1. General preparation of the starting materials



1a 1b 1c

3,4,6-Tri-*O*-acetyl-2-acetoxy-D-galactal (1a) ^{1}H NMR (600 MHz, $CDCl_3$) δ: 6.63 (d, 1 H, $J_{1,3}$ = 1.2 Hz, H-1), 5.85 (ddd, 1 H, $J_{1,3}$ = 1.2, $J_{3,4}$ = 4.8, $J_{3,5}$ = 0.7 Hz, H-3), 5.49 (dd, 1 H, $J_{3,4}$ = 4.8, $J_{4,5}$ = 2.3 Hz, H-4), 4.39 (ddd, 1 H, $J_{3,5}$ = 0.7, $J_{5,6}$ = 7.6, $J_{5,6'}$ = 5.0 Hz, H-5), 4.32 (dd, 1 H, $J_{5,6}$ = 7.6, $J_{6,6'}$ = 11.7 Hz, H-6), 4.24 (dd, 1 H, $J_{5,6'}$ = 5.0, $J_{6,6'}$ = 11.7 Hz, H-6′), 2.14, 2.12, 2.09, 2.05 (C*H*$_3$CO). ^{13}C {^{1}H} NMR (150.9 MHz, $CDCl_3$) δ: 170.5, 170.0, 169.9, 169.3 (CH_3*C*O), 138.8 (C-1), 127.2 (C-2), 73.2 (C-5), 63.9 (× 2, C-3, C-4), 61.4 (C-6), 20.7, 20.6, 20.4 (*C*H_3CO).

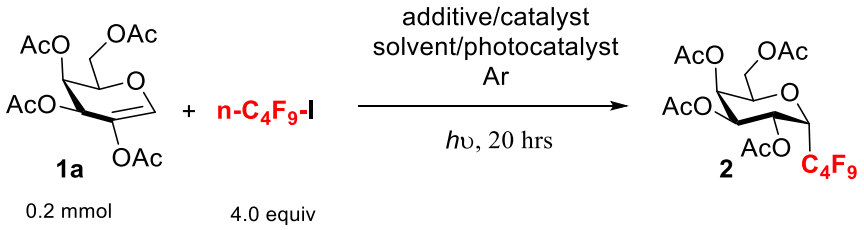
3,4,6-Tri-*O*-acetyl-2-acetoxy-D-glucal (1b) ^{1}H NMR (600 MHz, $CDCl_3$) δ: 6.70 (brs, 1 H, H-1), 5.50 (dd, 1 H, $J_{3,4}$ = 2.4, $J_{3,5}$ = 0.9 Hz, H-3), 5.25 (dd, 1 H, $J_{3,4}$ = 2.4, $J_{4,5}$ = 5.6 Hz, H-4), 4.46 (ddd, 1 H, $J_{3,4}$ = 5.6, $J_{5,6}$ = 3.7, $J_{5,6'}$ = 6.8 Hz, H-5), 4.44 (dd, 1 H, $J_{5,6}$ = 3.7, $J_{6,6'}$ = 12.0 Hz, H-6), 4.24 (dd, 1 H, $J_{5,6'}$ = 6.8, $J_{6,6'}$ = 12.0 Hz, H-6′), 2.12, 2.10, 2.09, 2.08 (C*H*$_3$CO). ^{13}C {^{1}H} NMR (150.9 MHz, $CDCl_3$) δ: 170.2, 170.0, 169.7, 169.1 (CH_3*C*O), 139.0 (C-1), 127.1 (C-2), 74.0 (C-5), 67.5 (C-4), 66.3 (C-3), 60.9 (C-6), 20.6, 20.5, 20.2 (*C*H_3CO).

3,4-Di-*O*-acetyl-2-acetoxy-D-xylal (1c) ^{1}H NMR (600 MHz, $CDCl_3$) δ: 6.73 (s, 1 H, H-1), 5.34 (dd, 1 H, $J_{3,4}$ = $J_{3,5}$ = 2.0 Hz, H-3), 4.96 (ddd, 1 H, $J_{3,4}$ = 2.0, $J_{4,5}$ = 2.4 Hz, $J_{4,5'}$ = 1.2 Hz, H-4), 4.23 (ddd, 1 H, $J_{3,5}$ = 2.0, $J_{4,5}$ = 2.4, $J_{5,5'}$ = 12.4 Hz H-5), 3.96 (dd, 1 H, $J_{4,5'}$ = 1.2, $J_{5,5'}$ = 12.4 Hz, H-5'), 2.12, 2.11, 2.07 (3 s, 3 H each, C*H*$_3$CO). ^{13}C {^{1}H} NMR (150.9 MHz, $CDCl_3$) δ: 169.98, 169.84, 169.83 (*C*O), 141.33 (C-1), 127.38 (C-2), 69.29 (C-), 64.24 (C-), 63.65 (C-5), 20.94, 20.86, 20.61 (*C*H_3CO).

2.2 Preparation of CF_3I Stock Solution in DMF

DMF (3 mL) was added to a glass Wheaton© vial under Argon (99.9998% purity) atmosphere. The screwed-capped vessel containing the solvent was weighed and tared. Next, CF_3I was bubbled through the DMF solution using a canula until the total volume of the solution reached approximately 4 mL. The tightly-closed vessel was again weighed. The concentration of the CF_3I stock solution was then calculated based on the weighed mass of CF_3I added and the total volume of the solution, and confirmed by ^{1}H and ^{19}F NMR spectroscopy measurements, using an internal standard of benzotrifluoride > 99%.

Table S1. Reaction Optimizations. Reactions of substrate **1** (0.2 mmol) with C_4F_9-I (4 equiv) in the presence of additives (1 equiv), photocatalyst (RB, Eosin Y, and 3CzCIIPN, 5 mol%, Ir-photocatalyst, 0.5 mol%) under irradiation or otherwise noted in indicated solvent (3 mL) for 20 hrs under Ar-atmosphere or otherwise specified



entry	Additive (equiv)/ Catalyst[a]	Irradiation sources	Solvent	Yield (%)[b]
	PC: RB, base & solvent			
1	Cs_2CO_3 (1)/RB	CFL	**MeCN**	24% (82%)
2	Cs_2CO_3 (1)/RB	CFL	MeCN	20%[c] (57%)
3	Cs_2CO_3 (1)/RB	CFL	**MeOH**	0%
4	TMEDA (1)/RB	CFL	MeCN	0%
	PC RB, H donor			
5	Cs_2CO_3 (1), TTMSS[d] (0.3)/RB	CFL	MeCN	33% (78%)
6	Cs_2CO_3 (1), TTMSS[d] (1)/RB	CFL	MeCN	37% (86%)
7	Cs_2CO_3 (1), *iso*propanol (1)/RB	CFL	MeCN	16%
8	Cs_2CO_3 (1), methanol (1)/RB	CFL	MeCN	8%
9	Cs_2CO_3 (1), acetone (1)/RB	CFL	MeCN	22% (56%)
10	Cs_2CO_3 (1), 1-adamantanethiol (1)/ RB	CFL	MeCN	0%
11	Cs_2CO_3 (1), 2-mercaptoethanol (1)/ RB	CFL	MeCN	7%
12	Cs_2CO_3 (1), H_2PO_3 (1)/RB	CFL	MeCN	4%
	Oxidant & PC			
13	Cs_2CO_3 (1), $K_3[Fe(CN)_6]$ (1)/RB	CFL	MeCN	5%
14	Cs_2CO_3 (1), $Cu(AcO)_2$ (1)/ RB	CFL	MeCN	0%
15	Cs_2CO_3 (1), $Cu(AcO)_2$ (1)/ Ir PC	Blue LED	MeCN	2%[e]
	PC / light source			
16	Cs_2CO_3 (1)/EY	CFL	MeCN	28%
17	Cs_2CO_3 (1)/ Ir PC	CFL	MeCN	53% (87%)
18	Cs_2CO_3 (1)/ Ir PC	Blue LED	MeCN	53% (87%)
19	Cs_2CO_3 (1)/ 3CzCIIPN PC	Blue LED	MeCN	11%
	PC Ir, base, H donor			
20	Li_2CO_3 (1)/ Ir PC	Blue LED	MeCN	0%
21	K_2CO_3 (1)/ Ir PC	Blue LED	MeCN	4%
22	Na_2CO_3 (1)/ Ir PC	Blue LED	MeCN	6%
23	Cs_2CO_3 (1)/ Ir PC	Blue LED	DMA	0%
24	Cs_2CO_3 (1)/ Ir PC	Blue LED	THF	0%
25	Cs_2CO_3 (1)/ Ir PC	Blue LED	DMF	3%
26	------/ Ir PC	Blue LED	MeCN	0%
27	Cs_2CO_3 (1), THF (1)/ Ir PC	Blue LED	MeCN	9%
28	Cs_2CO_3 (1), TMSS(1)/ Ir PC	Blue LED	MeCN	9%
29	Cs_2CO_3 (1), H_2PO_3 (1.5)/Ir PC	Blue LED	MeCN	3%
	No additive, or PC, or light, or presence of air			
30	----	Blue LED	MeCN	0%
31	Cs_2CO_3 (1)/-----	CFL	MeCN	10%
32	Cs_2CO_3 (1)/ Ir PC	---------	MeCN	0%
33	Cs_2CO_3 (1), air/RB[f]	CFL	MeCN	17%

[a]RB: Rose Bengal (3 mol%), EY: Eosin Y (3 mol%), Ir PC: (Ir [dF(CF$_3$)PPy]$_2$(dtbPy))PF$_6$ (0.5 mol%). [b]The yields of chromatographically isolated products are indicated, corrected values obtained after subtraction of remaining unreacted glycals are indicated in brackets. [c]48h-reaction. [d]TTMSS = tris(trimethylsilyl)silane.. [e]Yields obtained with Ir PC: 2%, with RB PC: 0%. [f]Not deoxygenated conditions

2.3 Mechanistic Probe Experiments

2.3.1. Light on/off Experiment

Substrate **1a** was employed under the conditions described under General Procedures. Over a 24 hour-period, measurements of product were made every 2 hours, in which the lamp was turned off and on at 2 hour-intervals. The product was quantified taking 10 µL-aliquots of the reaction mixture, evaporating the solvent, and dissolving the residues in deuterated solvent for ulterior NMR analysis (^{1}H-NMR and ^{19}F-NMR spectroscopy, adding benzotrifluoride as internal standard).

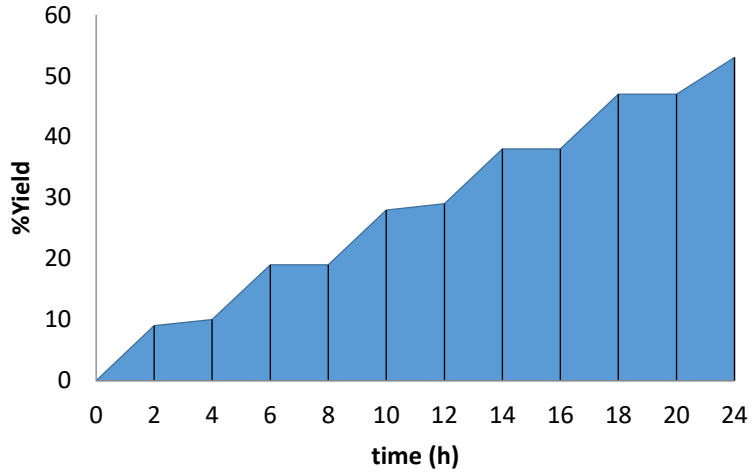


Figure S1. Plot of on/off light experiments

During the flat or demiflat portions of the plot (Figure S1), the lamp remained off, showing no accumulation of product, whereas a steady increase in product yields are observed while keeping the irradiation source on.

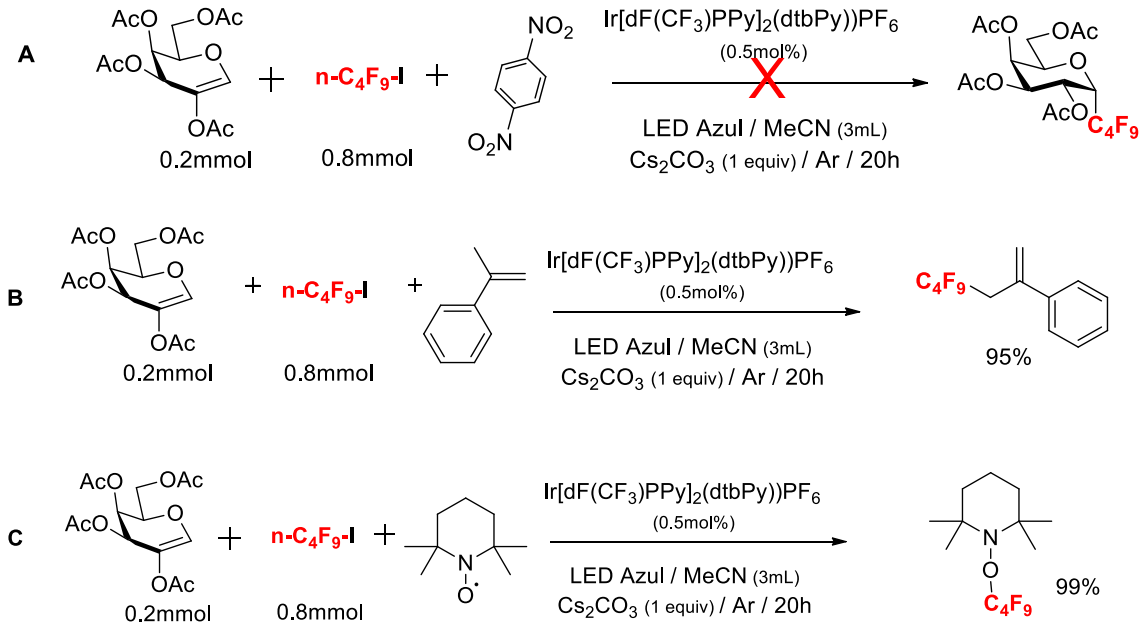
This light on/off experiments (Figure S1) was aimed at revealing the presence of chains in photoredox processes. However, ordinary lifetimes for radical chain events may commonly be on the second or sub-second time scale; and if product conversion is discontinued during dark intervals is only in agreement with chain processes that cease faster than the timescale of the analytical measurement employed.

2.3.2 Radical and Radical Ion Traps Experiments

Table S2. Mechanistic probe experiments

Entry	Additive (equiv)/ Catalyst[a]	Irradiation source	Solvent	Yield (%)
1	Cs_2CO_3 (1), TEMPO (1)/RB	CFL	MeCN	0
2	Cs_2CO_3 (1), *p*-dinitrobenzene (1)/RB	CFL	MeCN	0
3	Cs_2CO_3 (1), *p*-dinitrobenzene (1) /Ir	Blue LED	MeCN	0
4	Cs_2CO_3 (1), α-methylstyrene (1) /Ir	Blue LED	MeCN	0
5	Cs_2CO_3 (1) /Ir PC	Blue LED	MeCN-D_6	3

[a] RB: Rose Bengal (3 mol%), Ir PC: (Ir [dF(CF_3)PPy]$_2$(dtbPy))PF_6 (0.1 mol%).



Scheme S2. Mechanistic probe experiments for 1-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-1,1,2,2,3,3,4,4,4-nonafluorobutane **2**.

When 1,4-dinitrobenzene is used (A, Scheme S2), no product was found, indicating the presence of an ET process involving radical anions. This quenching is a result of being 1,4-dinitrobenzene a more suitable electron scavenger, accepting an electron from Ir(II)). The presence of anion radical in the catalytic cycle could be presumed at this point.

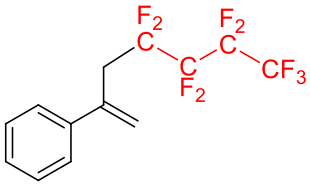
When α-methylstyrene is used (reaction B, Scheme 2), an almost quantitative yield of the product arising from the addition of C_4F_9 radicals to the double bond is found (α-methylstyrene being a better radical acceptor/trap than the glycal).

When TEMPO is employed (reaction C, Scheme S2), only the adduct TEMPO-C_4F_9 is found, and no glycal-derived C_4F_9 product is encountered. This indicated the presence of radicals in the process.

The reaction of **1a** according to the standard reaction conditions in CD_3CN as solvent afforded 3 % yield of product **2**, purporting that a large isotope effect is operating, and that the H-transfer step from the solvent can be rate-determining. Other sources of H-atom donor in the reaction medium cannot be discarded at this time, and this step of the reaction mechanism is being thoroughly investigated at present in our laboratory.

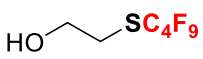
Characterization of products derived from mechanistic probe experiments

2-phenyl-4,4,5,5,6,6,7,7,7-nonafluoro-1-heptene



Obtained as indicated in Scheme S2B. Column chromatography (7:3 Hexane / EtOAc) gave compound **10** (67.2 mg, 95%) as a yellowish oil; R_f = 0.55 (1:1 Hexane / EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.30-7.38 (m, 5 H), 5.65 (s, 1 H), 5.38 (s, 1 H), 3.29 (t, 2 H, $J_{H\text{-}F}$ = 18.5). ^{13}C {^{1}H} NMR (150.9 MHz, $CDCl_3$) δ: 140.3, 136.1, 128.5, 128.0, 126.1, 120.6, 36.2 (t, $J_{C\text{-}CF}$ = 21.9) ppm. ^{19}F NMR (470.592 MHz, $CDCl_3$) δ: –81.1 (t, 3 F, C*F*$_3$), –112.6, –124.03, –125.9 (m, 6 F, 3× C*F*$_2$)

S-(perfluorobutyl)mercaptoethanol



Obtained as indicated in Table 1, entry 11. Column chromatography (8:2 Hexane / EtOAc) gave compound **12** (11 mg, 71%) as a yellowish oil; R_f = 0.77 (1:1 Hexane / EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 3.89 (t, 2 H, J = 6.1 Hz, C*H*$_2$OH), 3.14 (t, 2 H, J = 6.1 Hz, C*H*$_2$SRf), 1.97 (s, 1 H, O*H*). ^{13}C {^{1}H} NMR (150.9 MHz, $CDCl_3$) δ: 61.6

(*C*H_2O), 31.7 (*C*H_2S). ^{19}F NMR (470.592 MHz, $CDCl_3$) δ: –81.0 (t, 3 F, C*F*$_3$), –87.0, –120.7, –125.5 (m, 6 F, 3× C*F*$_2$)

2.3.3 Stern Volmer Plots

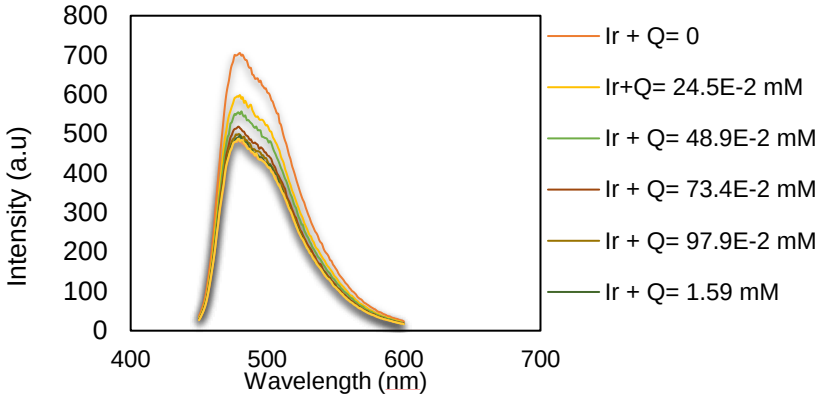


Figure S2. Suppression of the fluorescence of the photocatalyst, in the presence of Cs_2CO_3 (Q**)**

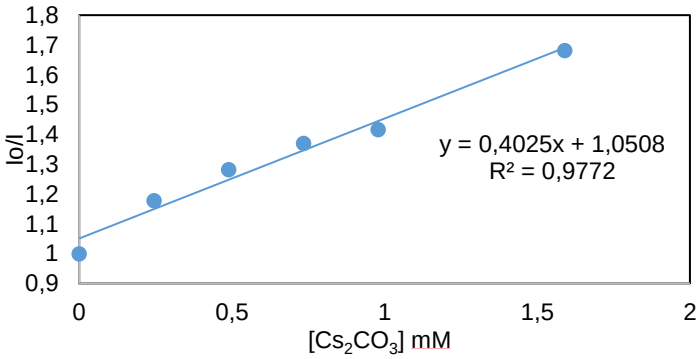


Figure S3. Fluorescence Quenching. Stern-Volmer Plots

To a stock solution of ((Ir[dF(CF$_3$)PPy]$_2$(dtbPy))PF$_6$ (1×10^{-3} mmol, 1×10^{-6} mM) in Ar-deoxygenated MeCN (3 mL) as solvent were added 2μL aliquots of a solution of Cs_2CO_3 (0.0368 mM) in Ar-deoxygenated MeCN. After stirring the solution, the fluorescence was determined **(**λ_{max} = 520 nm**)**. A decrease in the fluorescence of Ir[dF(CF$_3$)PPy]$_2$(dtbPy))PF$_6$ was steadily observed, due to the deactivation of the triplet state of the photocatalyst by the quencher.

Table S3. Quencher Concentration versus Intensity of Fluorescence

Quencher Concentration (M^{-1} x 1000)	**Fluorescence Intensity (λ = 520 nm)**
0	705.07
2.45×10^{-1}	598.3
4.89×10^{-1}	549.8
7.34×10^{-1}	514.5
9.79×10^{-1}	497.8
1.59	419.2
2.20	480.0
2.81	481.4

By plotting the ratios between the fluorescence intensity without quencher and those with the successive quencher concentrations added, the relationship I_o/I was obtained for each [Cs_2CO_3]. From the plot of I_o/I versus [Cs_2CO_3] mM, the Stern-Volmer constant was obtained = 402.5 M^{-1}.

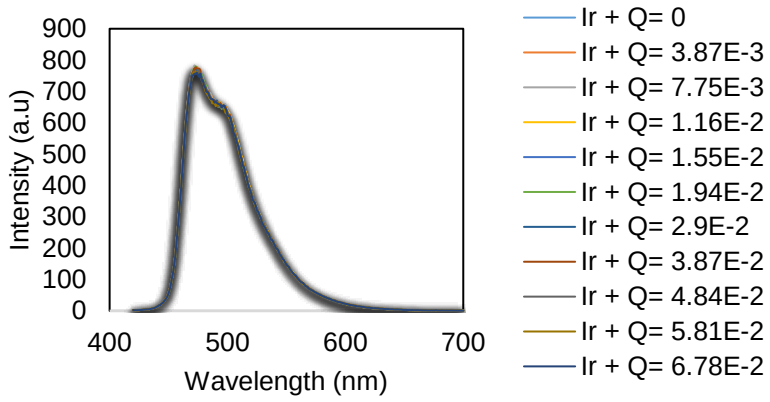


Figure S4. Suppression of the fluorescence of the photocatalyst, in the presence of perfluoroalkyl iodide (Q)

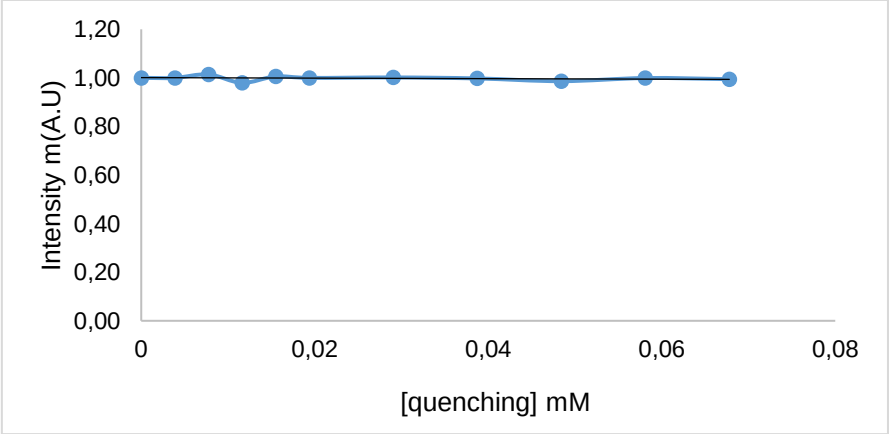


Figure S5. Fluorescence Quenching (Stern-Volmer)

To a stock solution of $(Ir[dF(CF_3)PPy]_2(dtbPy))PF_6$ (1 mg, 1×10^{-6} mM) photocatalyst, in MeCN (3 mL), 2 µL aliquots of neat reagent IC_4F_9 (which was previously filtered off through an alumina column to retain the excess of iodine) were added. The maximum intensity of fluorescence was determined for each solution of the photocatalyst to which IC_4F_9 was added. It was observed that the fluorescence of the photocatalyst remained constant in each experiment, therefore IC_4F_9 does not manage to deactivate the triplet state of the photocatalyst.

Furthermore, by plotting the relation I_o/I vs $[IC_4F_9]$ mM, a slope line approximately equal to zero (0) is obtained.

2.3.4 Determination of Quantum Yields and Propagation Chain Lengths

2.3.4.1 Determination of Quantum Yields. From Calibrated LEDs

The overall quantum yield for product formation from the perfluorobutylation of substrates **1a** can be calculated by dividing the moles of products **2,** formed by the einsteins of photons consumed (eq 1).

$$F = \frac{\text{moles of product formed}}{\text{flux of moles photons x second}} \qquad (1)$$

$$\text{flux of moles photons x second} = \frac{\lfloor E_T / hc/l \rfloor}{NA} \text{ x irradiation time (sec)} \qquad (2)$$

Absolute measurement of incident photon flux was achieved by means of calibrated photodiodes which are widely used for the detection of electromagnetic radiation in the ultraviolet and visible range.[2] Silicon photodiodes for light power measurement with resolution of 1 nW were employed. For LEDs with emission maxima at 390 nm a calibrated UV-enhanced silicon sensor for 250-400 nm range (Coherent OP-2 UV) was used. In all cases, measurements of the light that passed through the bottom of the vial were performed at the mouth of the vial (vial walls were covered with a bright white optical film to ensure total light reflection, Figure S1).The incident photon flux measured by photodiodes was corroborated by chemical actinometry (potassium ferrioxalate for $\lambda_{max} = 392$ nm.[3] Then, the expression of the flux of moles of photons can

be obtained from equation 2, where E_T is the radiant power, *h* de Planck's constant, c the light speed, λ the wavelength of the LED in meters, and NA the Avogradro's number.

For the 392 nm LED (E_T = 8 mWatt), the photon flux (number of photons per second) is calculated to be 1.5786×10^{16} photons/sec. These numbers should be divided by NA. Substrate **1a**, and additives are transparent at all PCs maxima absorption wavelengths or diode emissions so we could make the limiting assumption that the incident photon flux is absorbed solely by the photocatalyst. After 1 hour- irradiation, the number of moles of product **2** formed is quantified by ^{1}H and ^{19}F NMR spectroscopy using an internal standard (benzotrifluoride).

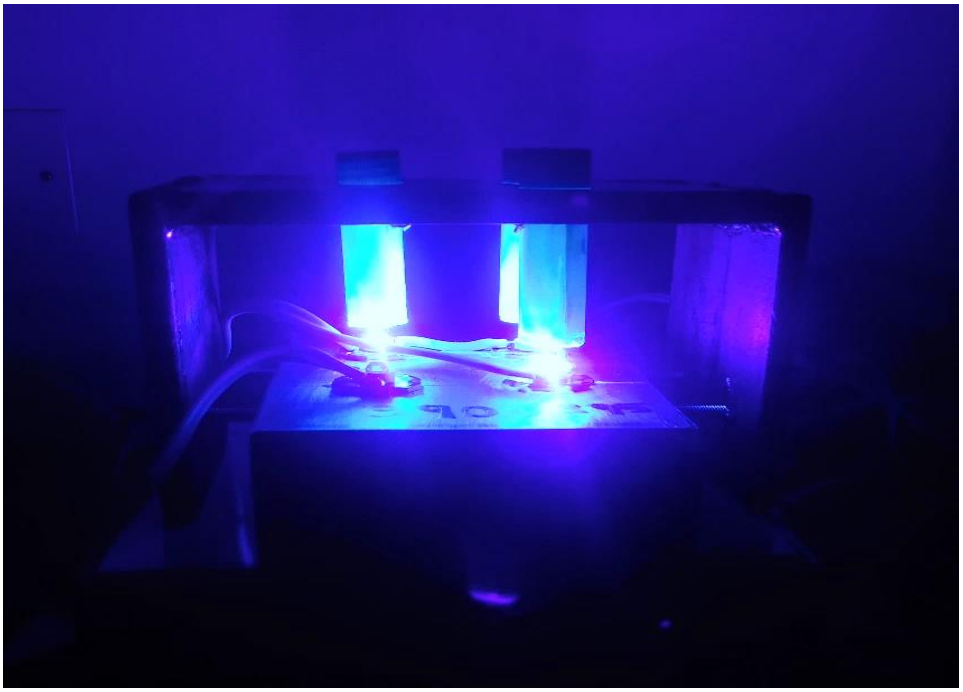


Figure S6. Calibrated violet (392 nm) LEDs arrangement for the measurement of quantum yields of reactions with Ir photocatalyst

The numerator of eq. 1 is calculated from the number of moles produced (1.98×10^{18}) × NA. The number of photons emitted are calculated from the photon flux (*vide infra*) times the irradiation time in sec.

According to the procedure of Yoon and colleagues,[4] the quenching fraction *Q* is calculated according to eq 3:

$$Q = \frac{k_{q\,(\mathbf{PC}\,)}[\mathbf{Q}]}{\tau^{-1} + k_{q(\mathbf{PC})}\,[\mathbf{Q}]} = \frac{K_{SV}\,[\mathbf{Q}]}{1 + K_{SV}\,[\mathbf{Q}]} \quad (3)$$

Where K_{SV} is the Stern-Volmer coefficient which is determined by Stern Volmer rate quenching experiments (Figure S2). Applying eq. 3, the *Q* value is 0.969. The chain length (***L***) is more accurately approximated by dividing the measured quantum yield ϕ by the quenching fraction *Q*.

2.3.4.2 Determination of Photon Flux by Chemical Actinometry

Determination of the light intensity at 392 nm: The photon flux of the high-power LED employed (392 nm, 8 mWatt) was also determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate in 30 mL of 0.05 M H_2SO_4. A buffered solution of phenanthroline was prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H_2SO_4. Both solutions were stored in the dark. To determine the photon flux of the diode, 2.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 90.0 seconds at λ = 392 nm. After irradiation, 0.35 mL of the phenanthroline solution was added to the cuvette. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm measured. Conversion was calculated using eq 4.

$$mol\ Fe^{2+} = \frac{V + \Delta A}{l + \varepsilon} \quad (4)$$

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.000 cm), and ε is the molar absorptivity at 510 nm (11,100 L mol^{-1} cm^{-1}). The photon flux can be calculated using eq 5.

$$photon\ flux = \frac{mol\ Fe^{2+}}{\phi \times t \times f} \quad (5)$$

Where Φ is the quantum yield for the ferrioxalate actinometer (1.15 for a 0.15 M solution at λ = 392 nm) t is the time (30.0 s), and f is the fraction of light absorbed at λ = 392 nm (0.99833, *vide infra*). The photon flux was calculated (average of three experiments) to be 1.783 x 10^{-8} Einstein s^{-1}. The ratio between the value obtained from diode calibration and that from chemical actinometry is 1.4.

$$\boldsymbol{L} = \frac{\phi}{Q}$$

Table S4. Values of quantum yield (ϕ), quenching fraction (Q), and Chain length (L) for the Ir-photocatalyzed perfluorobutylation of glycal derivative **1a**

ϕ (λ = 520 nm)	*Q*	*L*
0.196 +/-0.05	**0.969**	**0.20**

2.4 Calculation of Thermodynamic Parameters and Photocatalytic Cycle Proposed

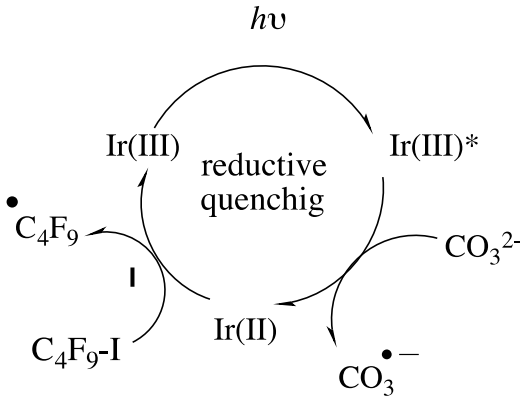
2.4.1 Gibbs Energy Differences

The proposed cycles for the production of C_4F_9 radicals with Ir photocatalyst is shown in Figures S2**A.** The Gibbs energy differences for the production of $^{\bullet}C_4F_9$ radicals with the three PCs are calculated according to the Rehm Weller equation 6.

$$\Delta G = E^{o}_{red}(D/D^{+}) - E^{o}_{red}(A/A^{-}) - E^{*}(0,0) - w \qquad (6)$$

Where $E^{o}_{red}(D/D^{+})$ is the reduction potential of the species that is being oxidized, $E^{o}_{red}(A/A^{-})$ the reduction potential of the species which is reduced, $E^{o,o}$ the excited state triplet energy, and *w* the coulombic term

In Figure S7, the use of PC-1 (i.e.: $Ir[(dF(CF_3)ppy]_2(dtbbpy)^{+}$) in a reductive quenching cycle affords C_4F_9 radicals from the reduction of *n*-C_4F_9-I by ground state Ir(II) (reductive ET). The ΔG is calculated to be exergonic by –0.1 V.



$$\Delta G_I = -1.37\,V + 1.27\,V = -0.1\,V$$

Figure S7. Proposed photoinitiated cycle ($Ir[(dF(CF_3)ppy]_2(dtbbpy)^+$) for the initiation (production of $^{\bullet}C_4F_9$ radicals) and calculation of the Gibbs energy involved in the process.

Metal-organo-photoredox catalysts[5] such as PC-1, can act in both oxidative and reductive quenching cycles. However, as fluorescence of PC-1* does not seem to be suppressed by *n*-C_4F_9-I (Figure S4), ET oxidation of Ir(III)* to Ir(IV) and concomitant reduction of n-C_4F_9-I to $^{\bullet}C_4F_9$ radicals is precluded, ruling out an oxidative quenching cycle with PC-1. Instead, the fluorescence of PC-1* is readily quenched by addition of Cs_2CO_3 DMF solution (Figure S2A), purporting that an ET reduction takes place between PC-1* and Cs_2CO_3, generating a carbonate radical anion ($ECO_3^{\bullet-}/CO_3^{2-}$ = +1.23 +/–0.15 V). The ΔG ET for this process is calculated to be slightly exergonic by –0.08V.

2.4.2 Table of Thermodynamic Parameters

Table S5. Redox Potentials and Rehm Weller Parameters

entry	**substrate**	E_{red} **(V)**	E_{ox} **(V)**	E^*_{ox} **(V)**	E^*_{red} **(V)**	E_T **(eV)**	λ_{max} **(nm)**	ΔG_{ET}[a] **(eV)**	ΔG_{ET}[a] **(Kcal/mol)**
1	**PC-1**	–1.37[b]	+1.69[b]	–0.89[b]	+1.21[b]	2.62[b]	392	–0.1[c]	–2.30
2	**Cs_2CO_3**		+1.23[d]						
3	***n*-C_4F_9I**	–1.27[e]							

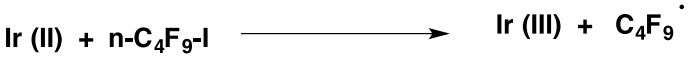
[a]From the Rehm Weller equation (see below). [b]Q.-Q. Zhou, Y.-Q. Zou, L.-Q. Lu, W.-J. Xiao, Visible-Light-Induced Organic Photochemical Reactions through Energy-Transfer Pathways, *Angew. Chemie Int. Ed.*, 2019, **58**, 1586-1604. [c]– $\Delta G_{ET} = E_{Ir(III)/Ir(II)} - E_{C4F9-I}$ = -1.37 V – (–1.27 V) = –0.1 eV. [d]D. A. Armstrong, W. L. Waltz, A. Rauk, Canadian Journal of Chemistry, 84, 1614-1619. [e]Measured in DMF: C.P. Andrieux, L.G. Clis, M. Medebielle, P. Pinson, J.M. Saveant, *J. Am. Chem. Soc.*, 1990, **112**, 3509-3520.

Rehm Weller equation:

$$\Delta G^{\circ} = E_{\left(\frac{D}{D^{+}}\right)} - E^{*} + \frac{Z_1 Z_2}{\varepsilon r_{12}} \quad (7)$$

Coulombic term taken as -0.05 eV

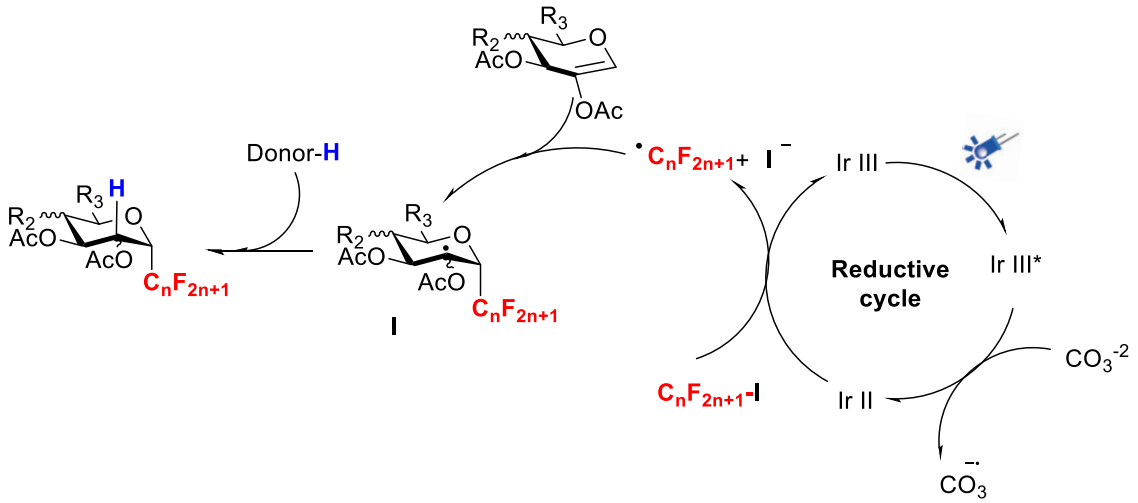
2.5 Determination of Gibbs Energies and ΔE from Measured Redox



ΔG_{ET} = E $_{Ir(III)/Ir(II)}$ - E $_{C4F9-I}$ = -1.37 V – (-1.27 V) = **-0.1 eV**

ΔG_{ET} = E $_{CO3^{2-}/CO3^{\bullet-}}$ E $_{Ir(III)/Ir(II)}$ – E_T –0.06 V = +1.23 V – (–1.37 V) – 2.62 V –0.06 V = **–0.08 V**

Proposed Mechanism:



Scheme S3. Proposed mechanism

The postulated mechanism begins with the excitation of the Ir (III) photocatalyst to the triplet state, which is capable of accepting an electron from Cs_2CO_3 to give Ir (II) and $CO_3^{\bullet}$ radicals (reductive cycle). This step is supported by suppression of Ir (III) * fluorescence by Cs_2CO_3. A reductive electronic transfer from Ir (II) to *n*-C_nF_{2n+1}-I produces the radicals $C_nF_{2n+1}^{\bullet}$ and regenerates Ir (III). Subsequently, these $C_nF_{2n+1}^{\bullet}$ radicals are added to position 1- of 2-acetoxygolic to give the radical adduct I. Adduct I will abstract an H atom from "the solvent", to give perfluoroalkylated *C*-glycosides at position 1.

3. References

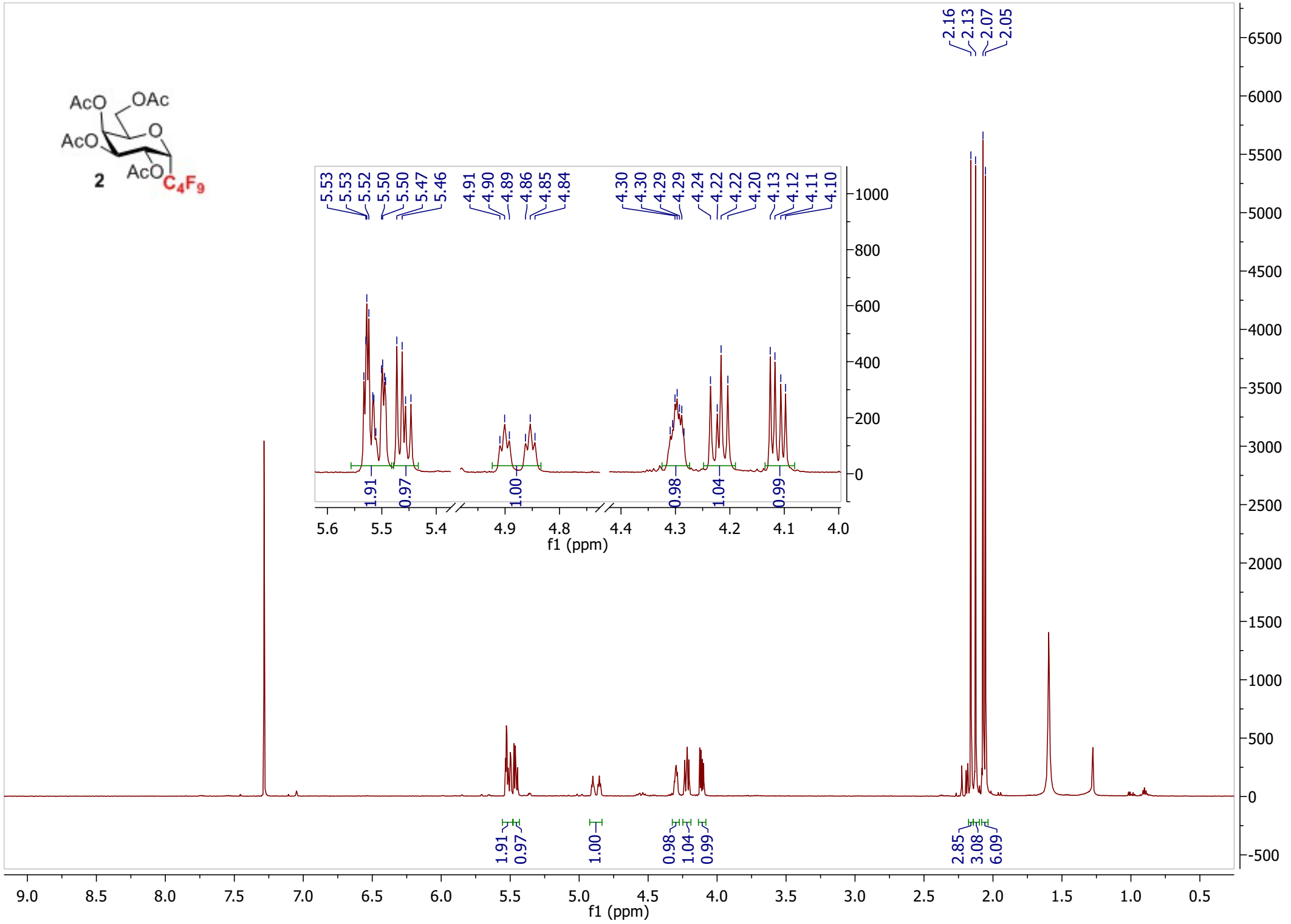
[1] V. E. Manzano, E. Repetto, M. L. Uhrig, M. Baráth, O. Varela, *Carbohydrate Proven Synthetic Methods*, Pavol Kováč Ed., CRC Press 2012, **1**, 295-301.

[2] H. J. Kuhn, S. E. Braslavsky, R. Schmidt, *Pure Appl. Chem*., 2004, **76**, 2105–2146.

[3] (a) G. H. Searle, G. S. Bull, D. A. House, *J. Chem. Ed*., 1989, **66**, 605-608; (b) A. W. Adamson, *J. Am. Chem. Soc*., 1958, **80**, 3183-3189.

[4] M. A. Cismesia, T. P. Yoon, *Chem. Sci*., 2015, **6**, 5426-5434.

[5] Q.-Q. Zhou, Y.-Q. Zou, L.-Q. Lu, W.-J. Xiao, *Angew. Chemie Int. Ed.*, 2019, **58**, 1586-1604.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4.90
4.89
4.86
4.85
4.84
4.30
4.30
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4.29
4.24
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4.22
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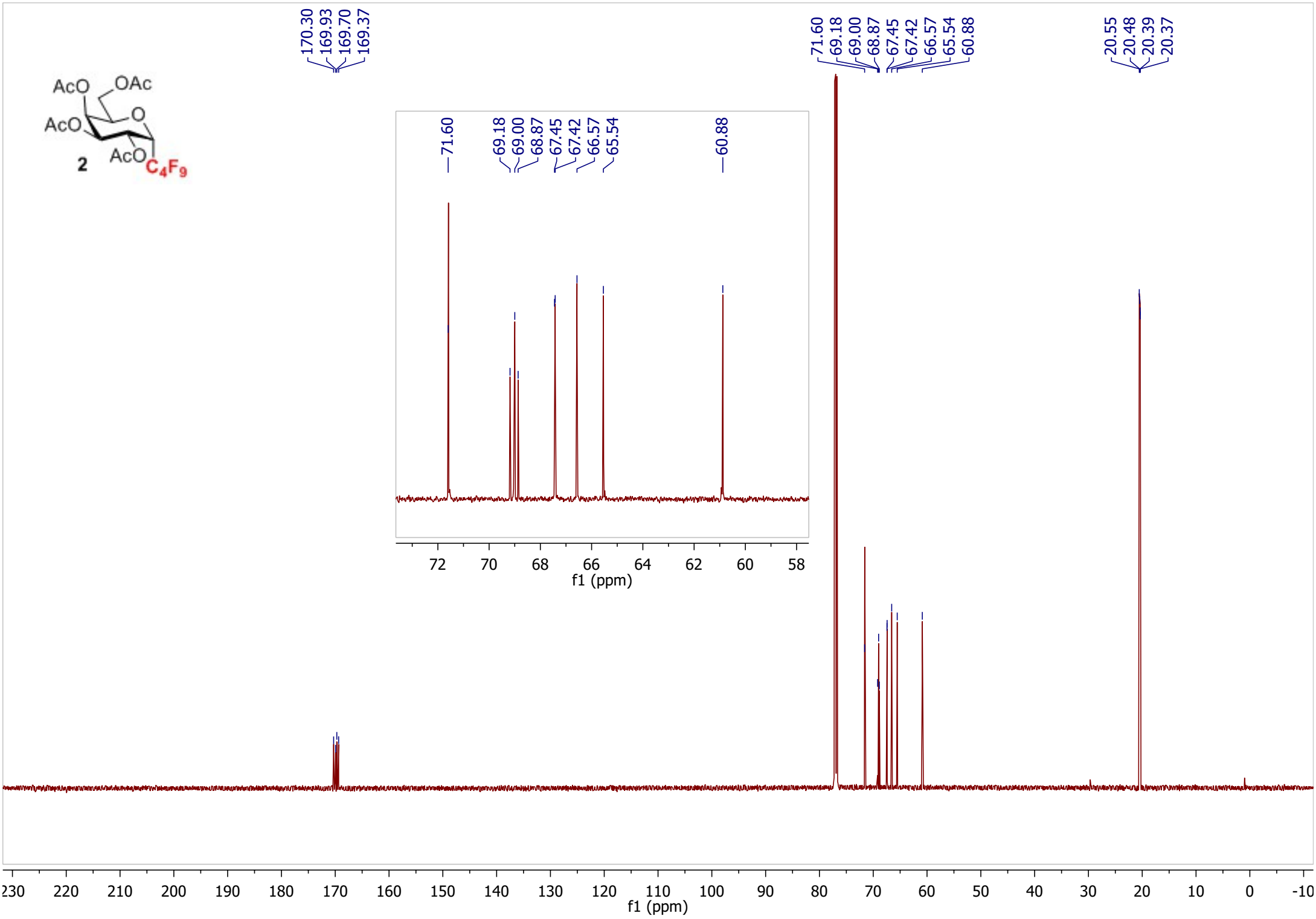
f1 (ppm)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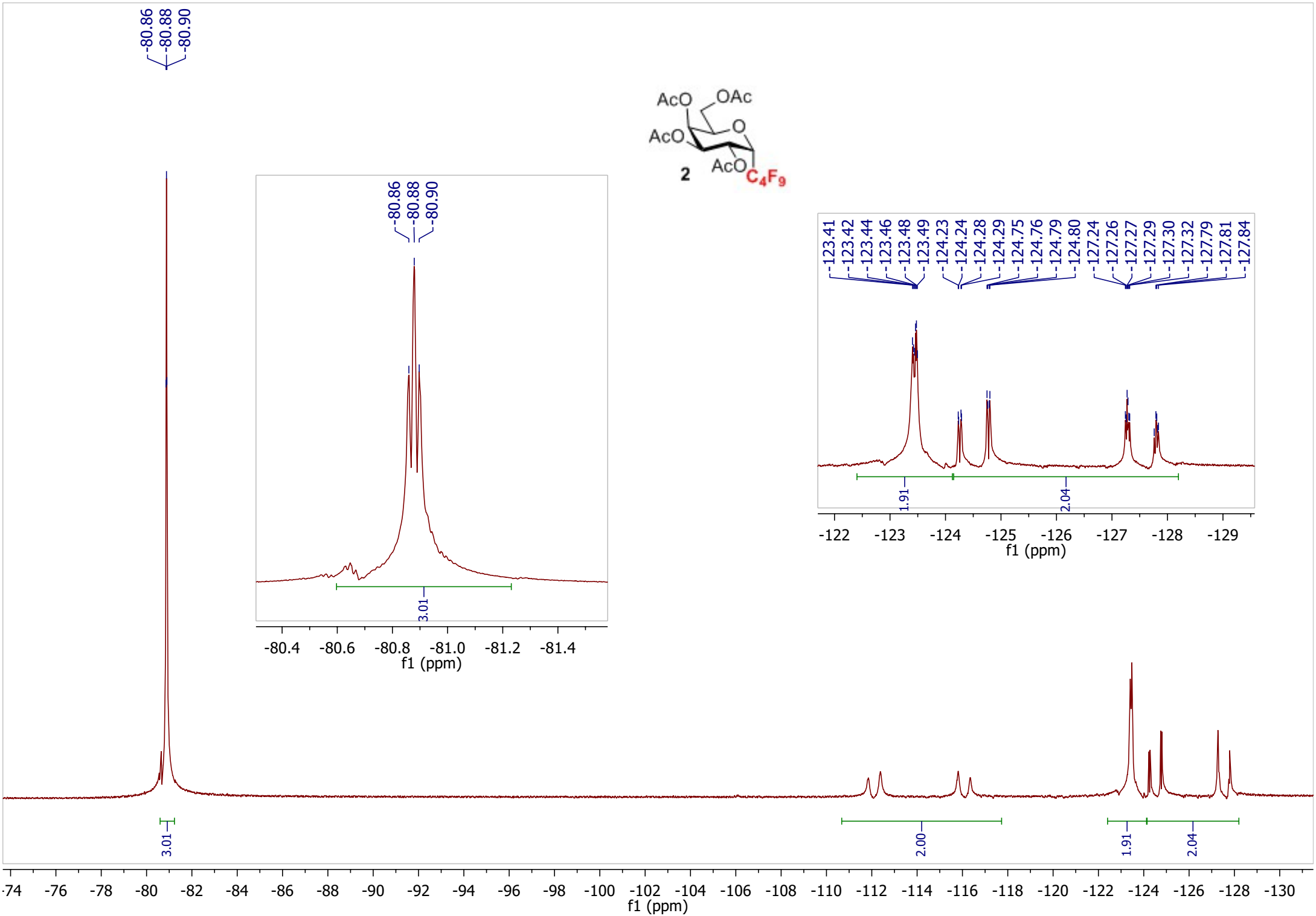
f1 (ppm)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127.79
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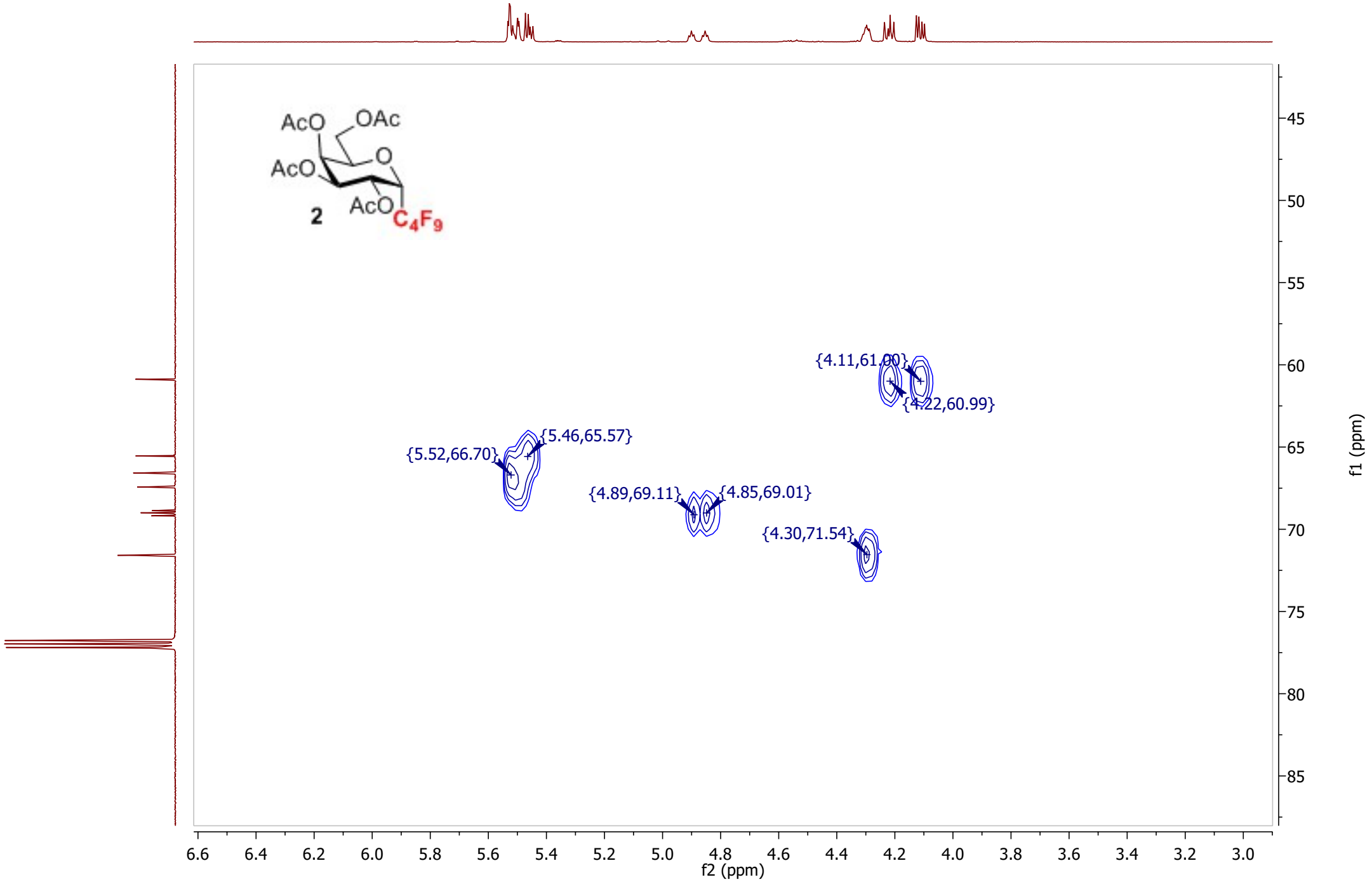
f1 (ppm)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Qualitative Compound Report

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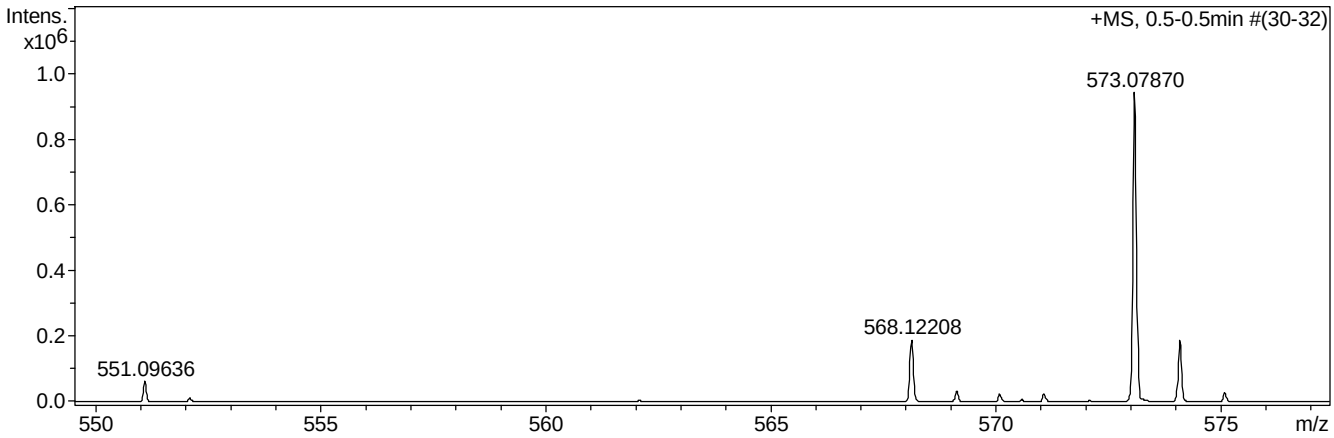

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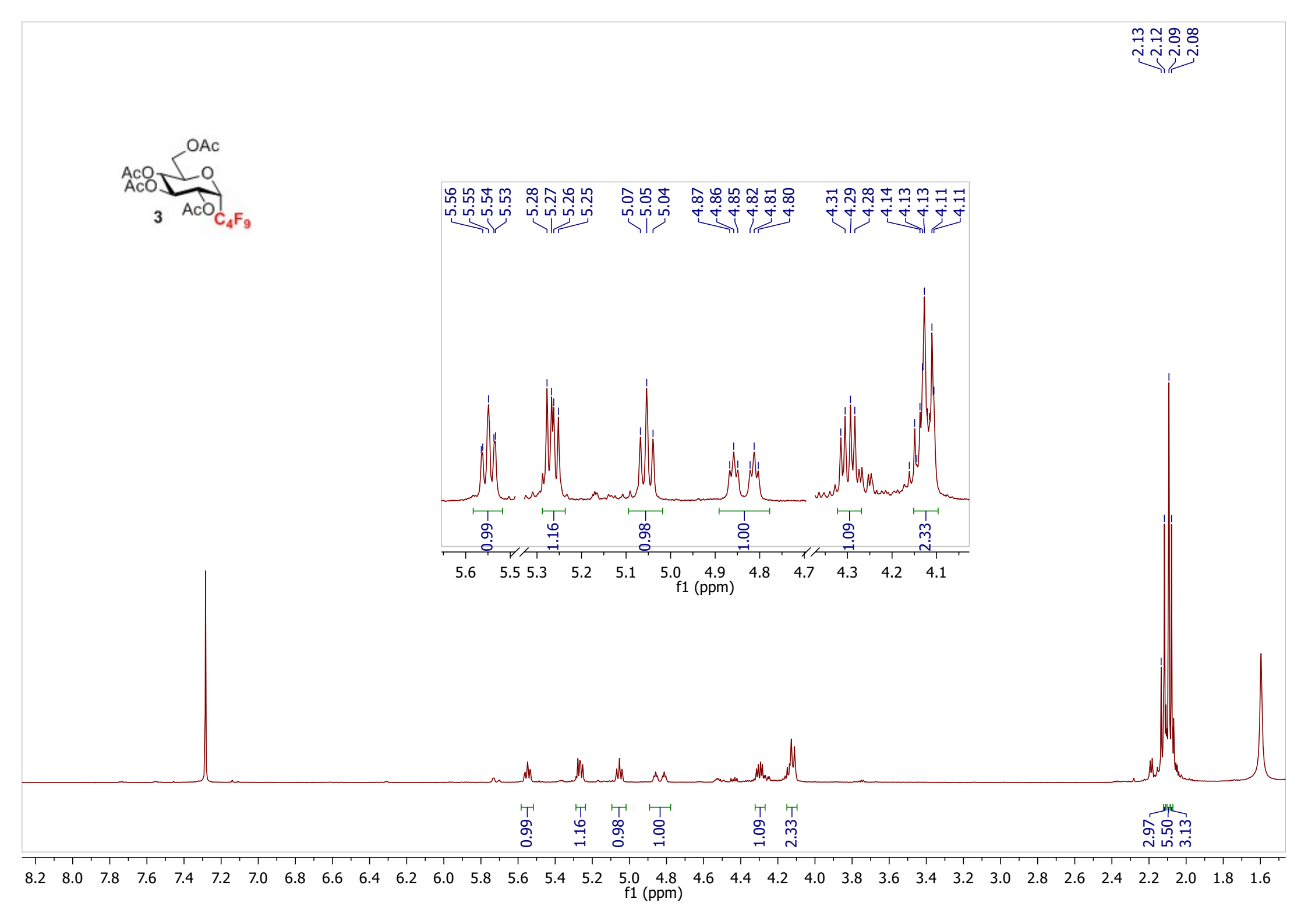
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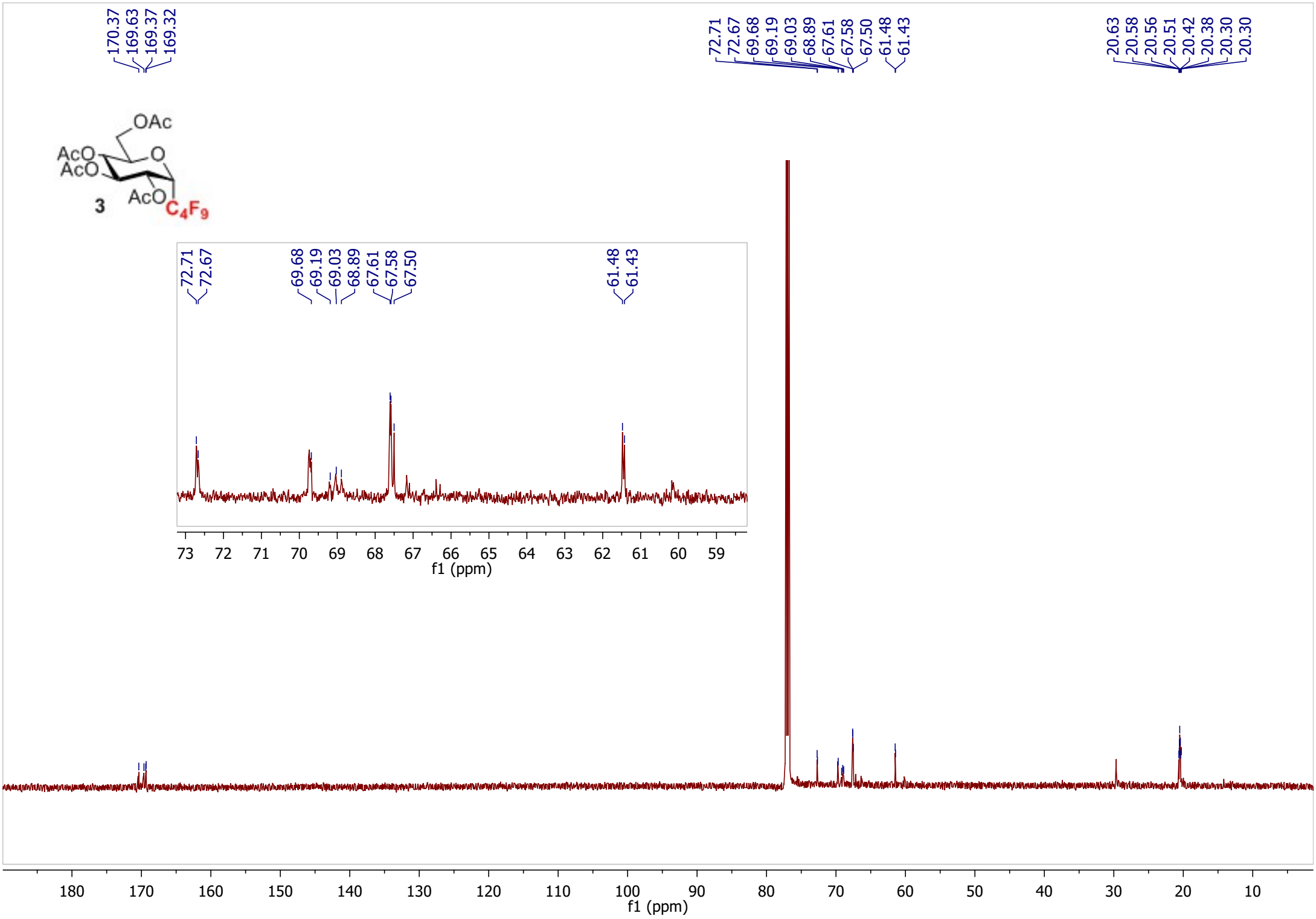
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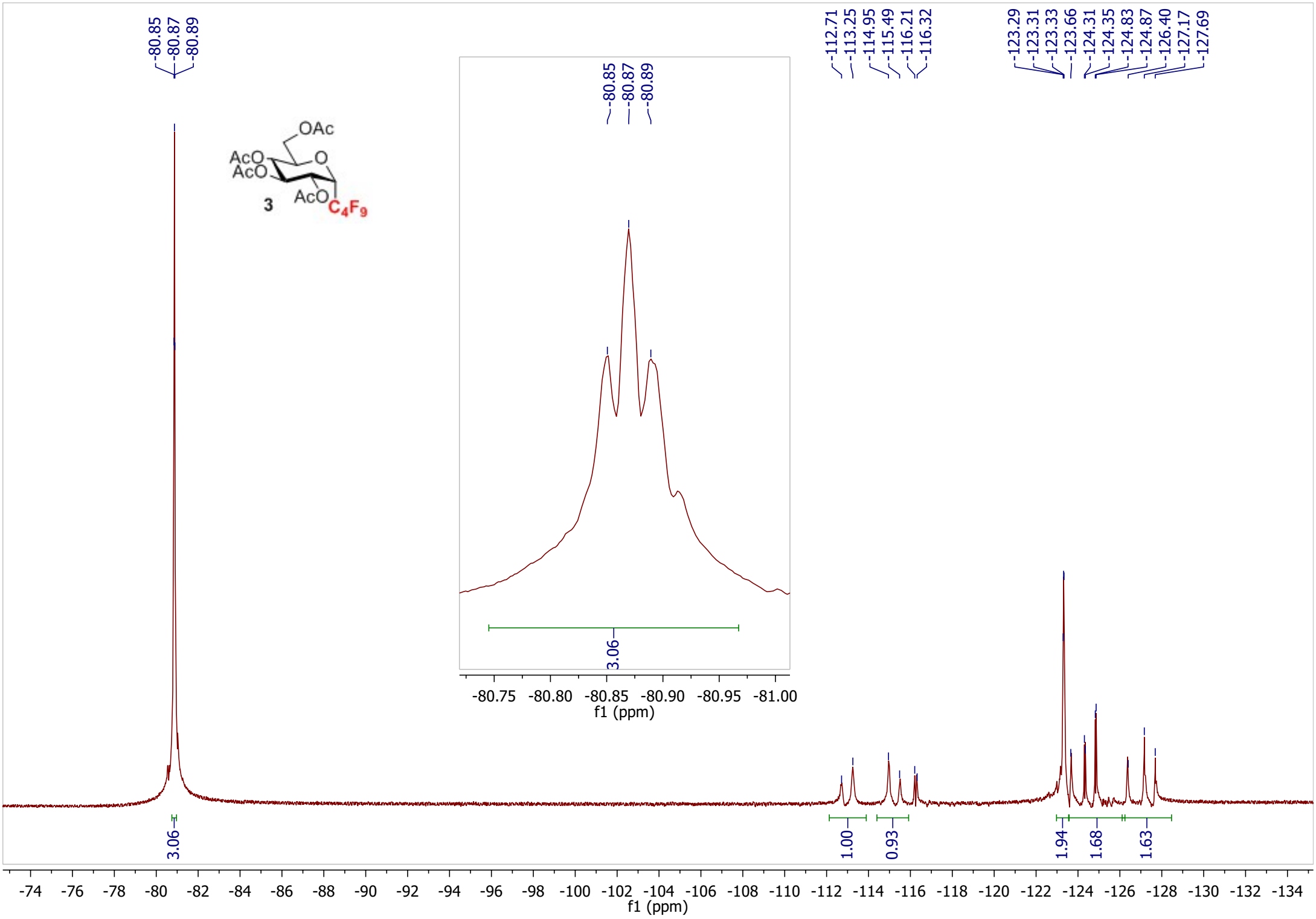
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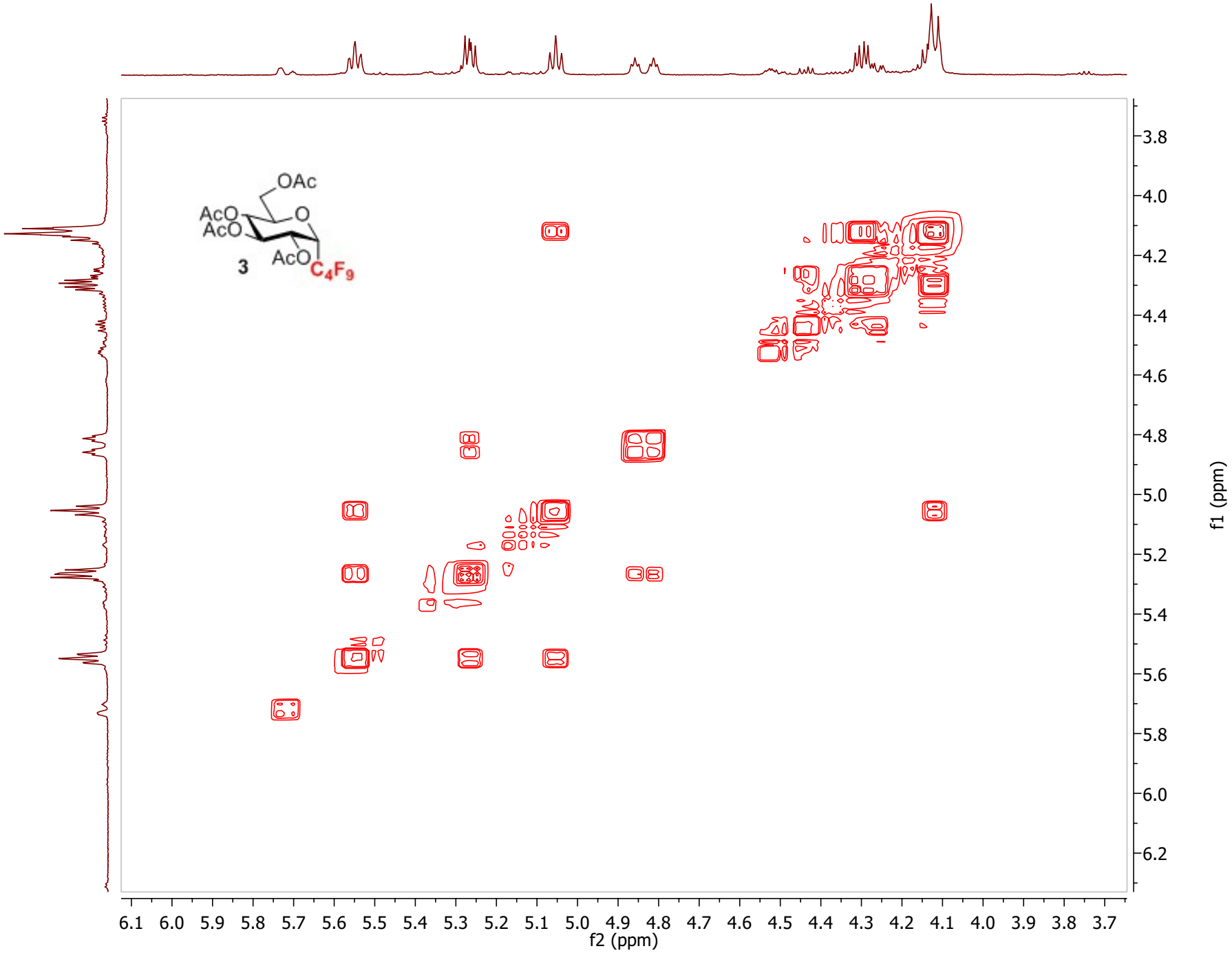
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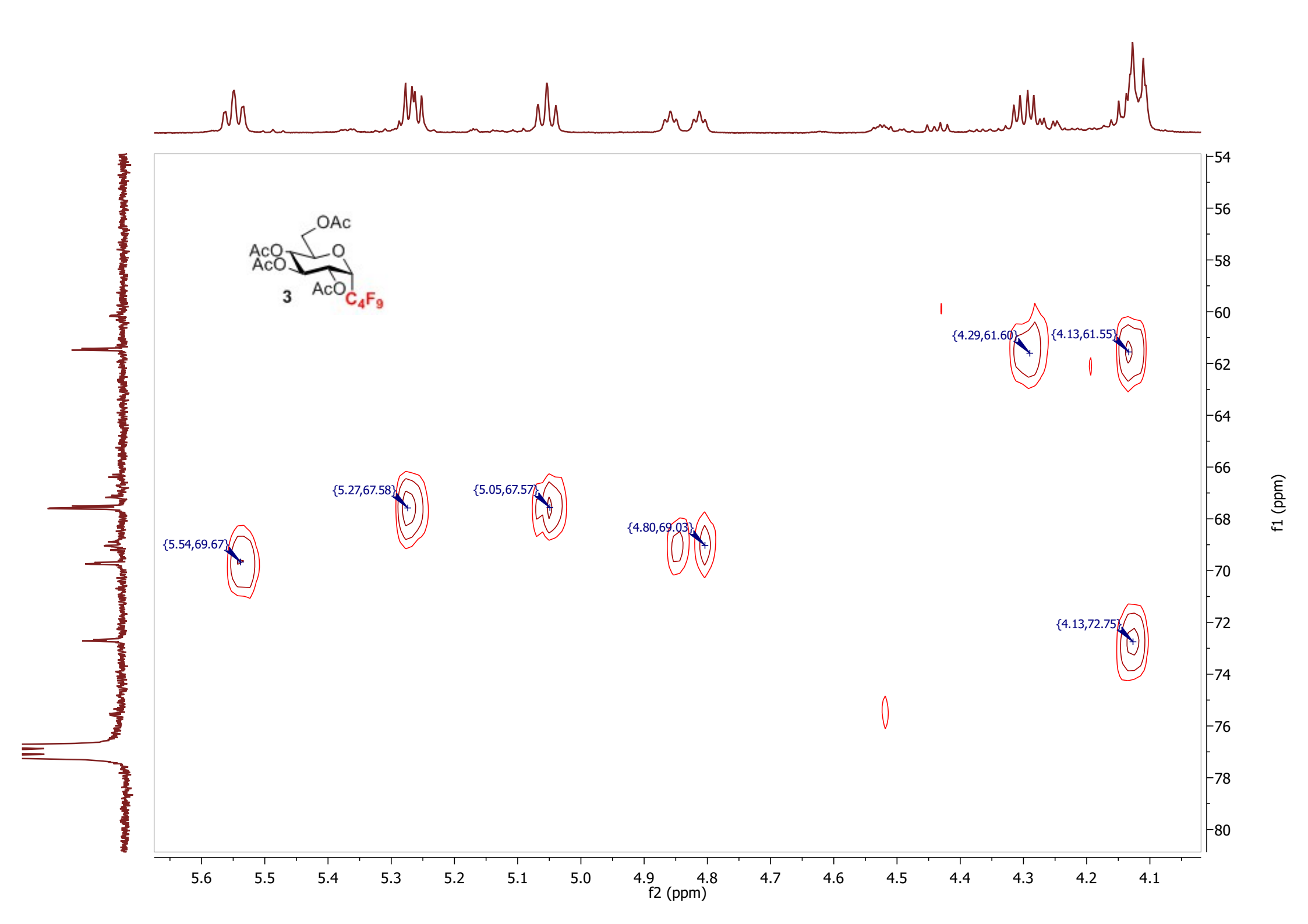
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Qualitative Compound Report

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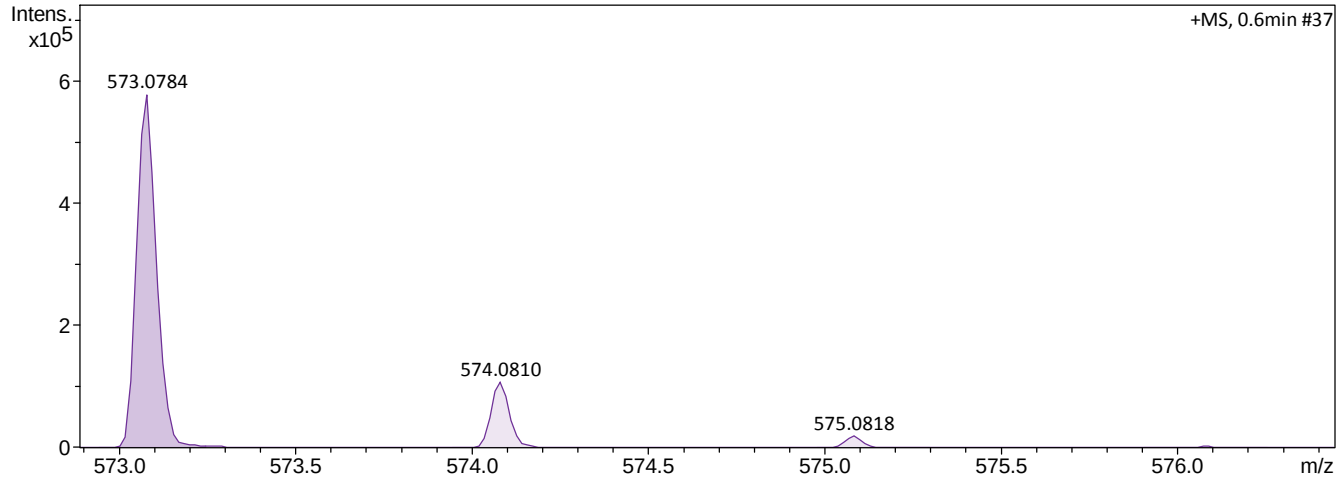

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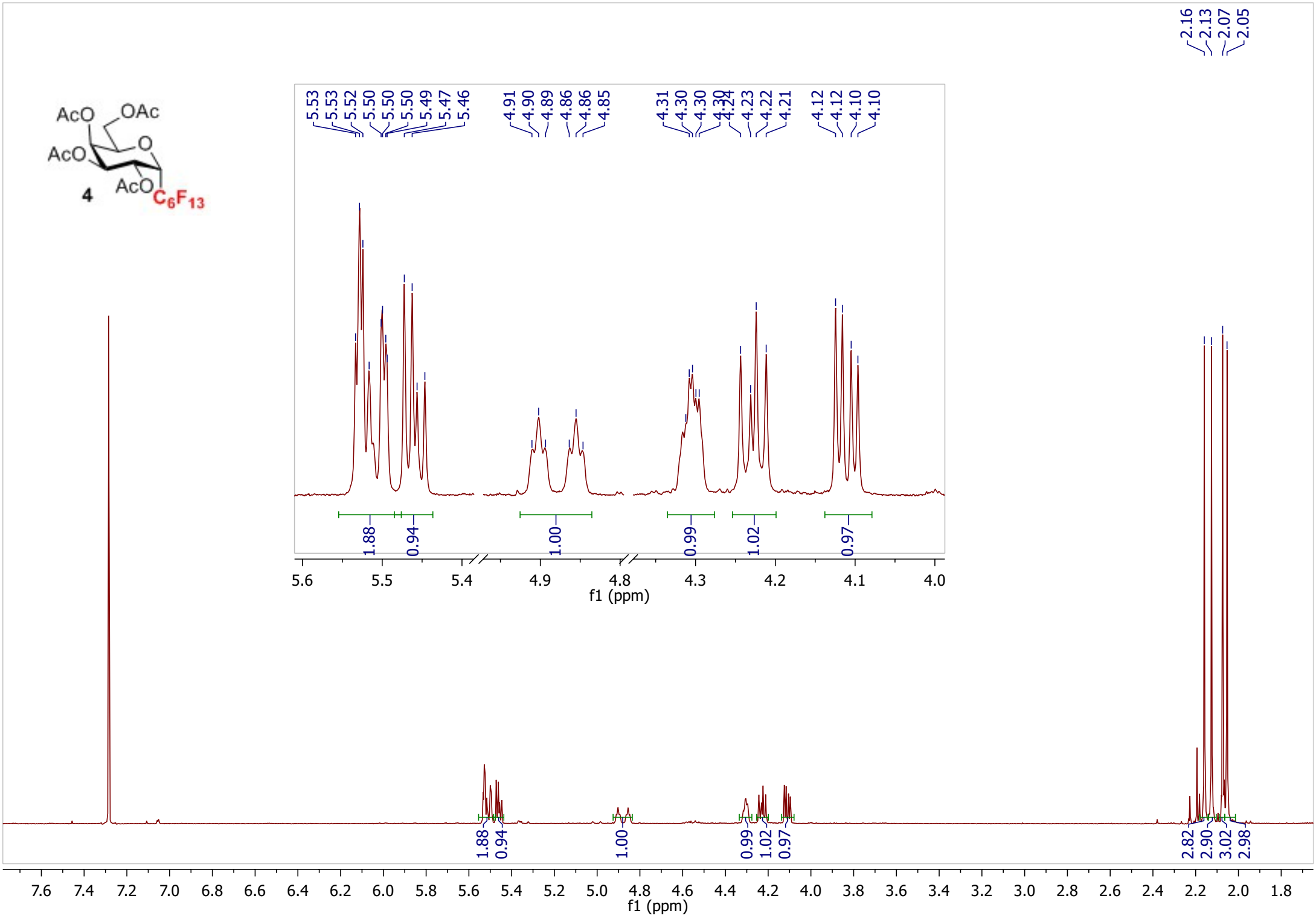
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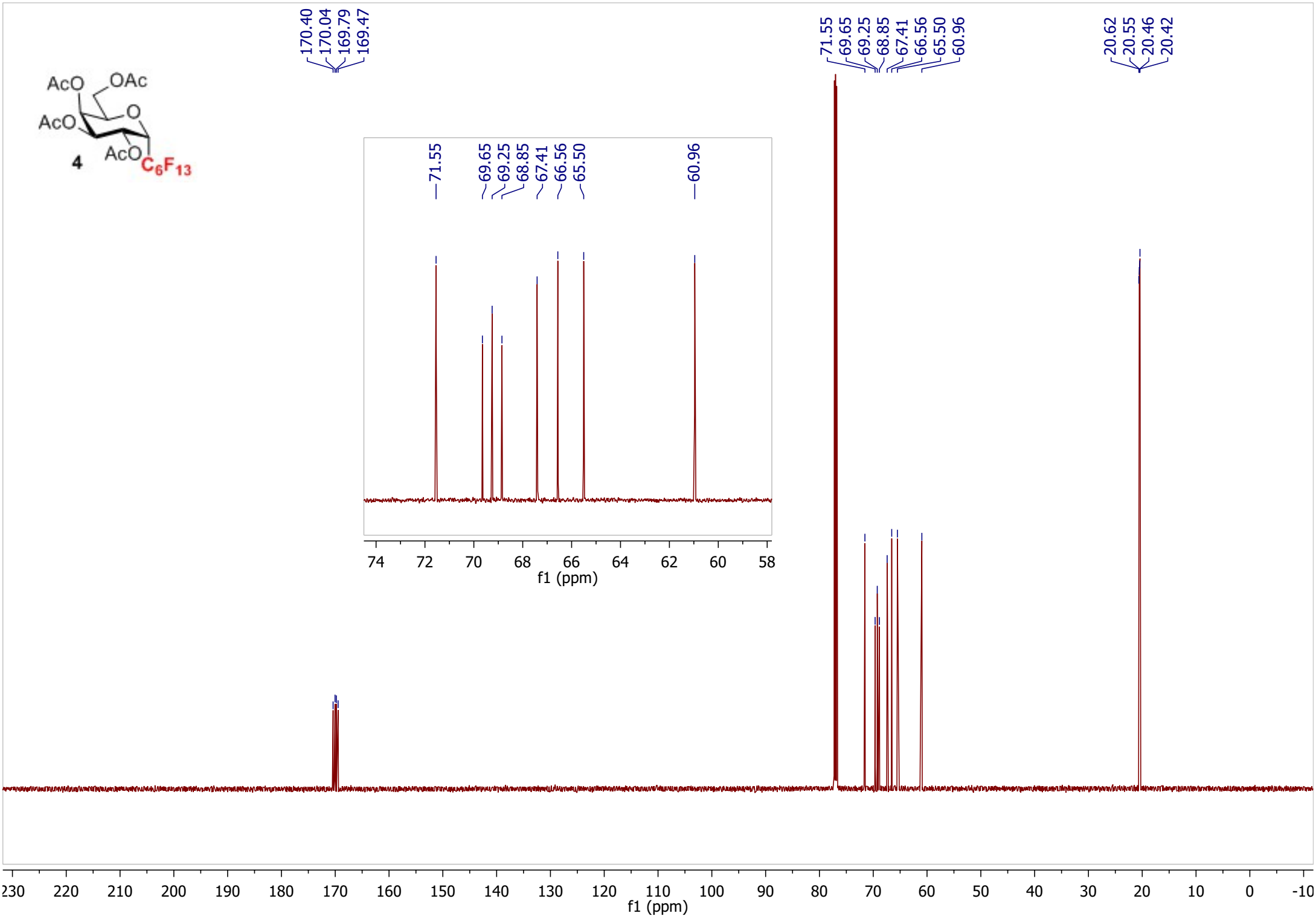
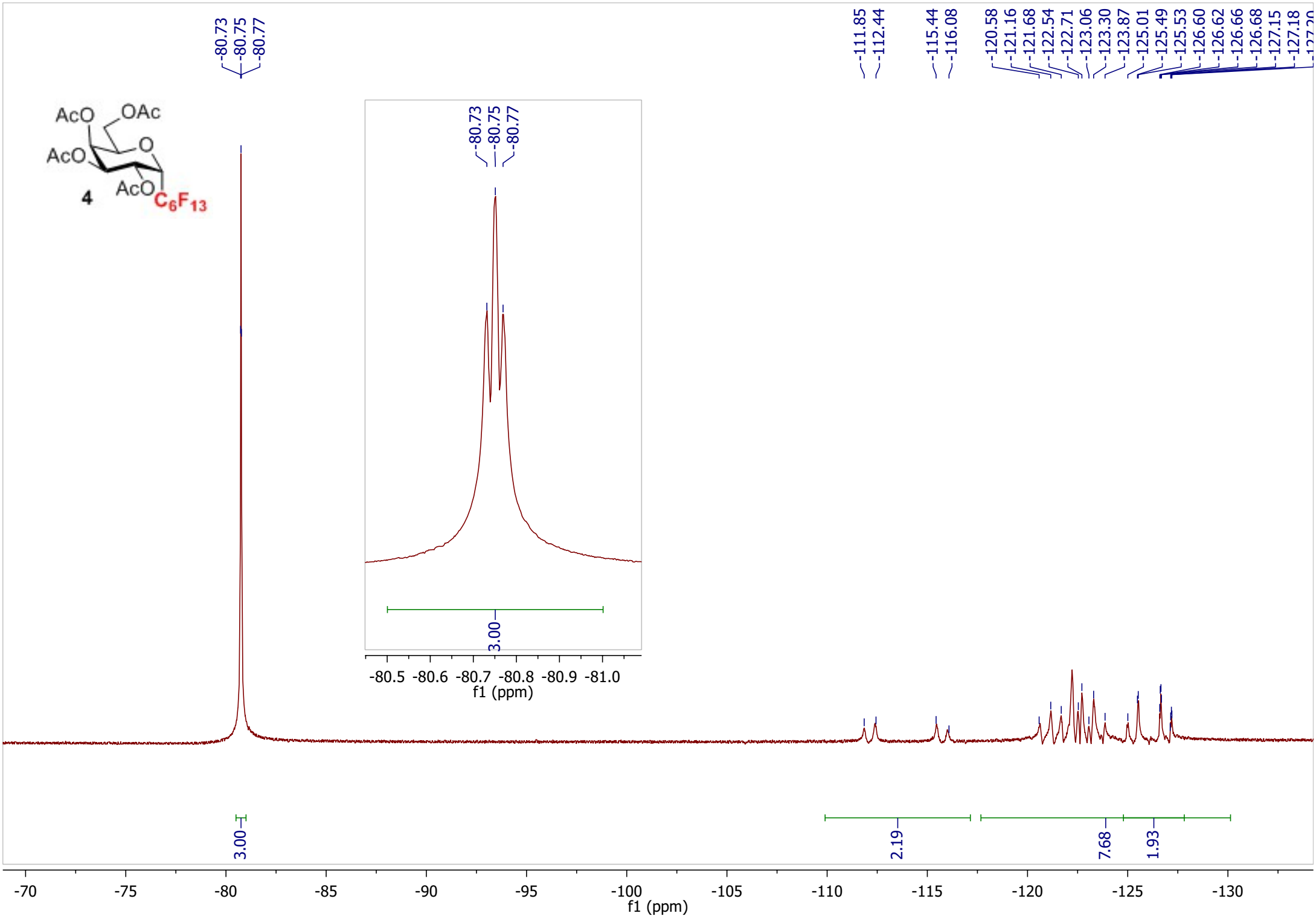
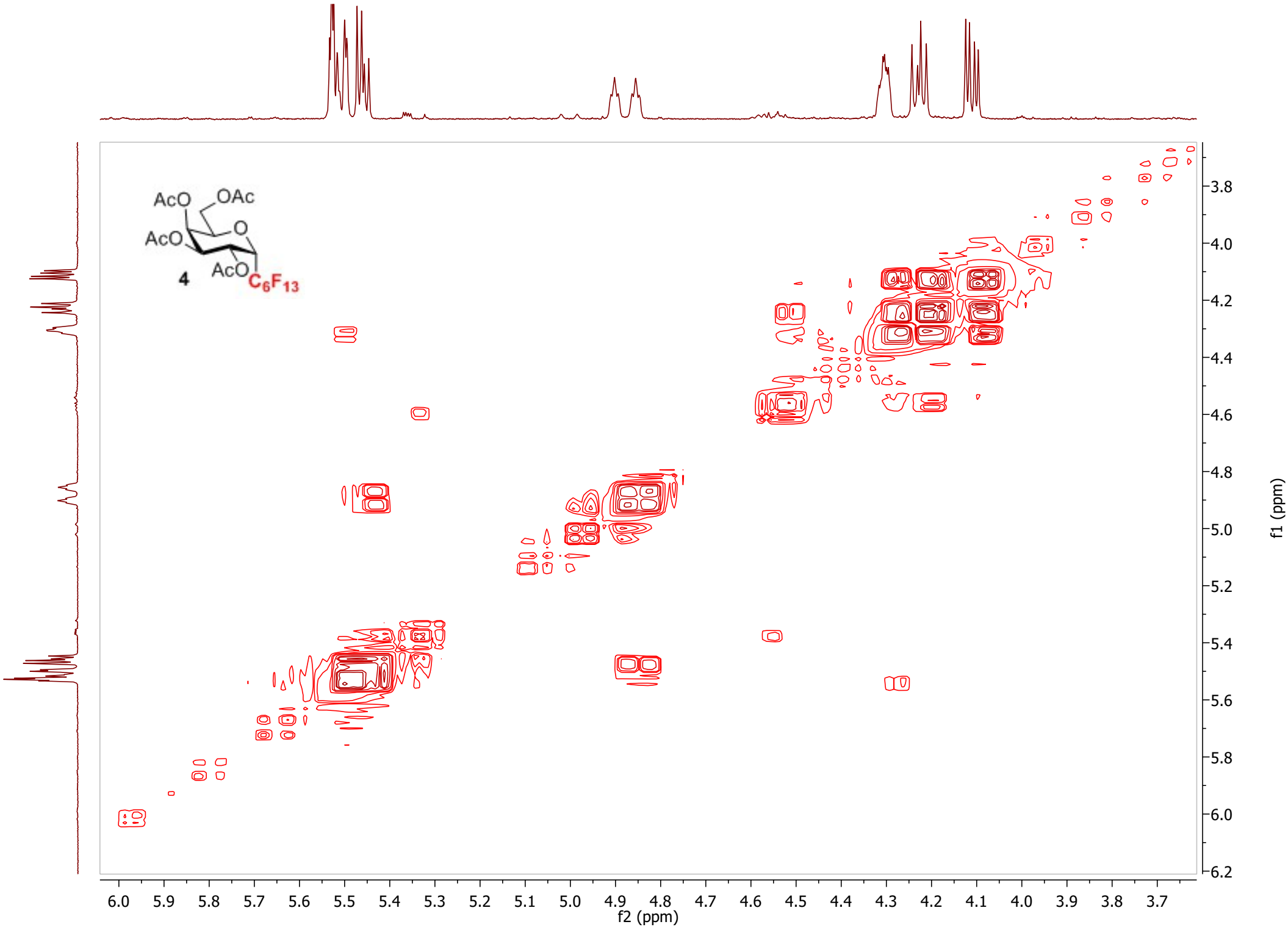
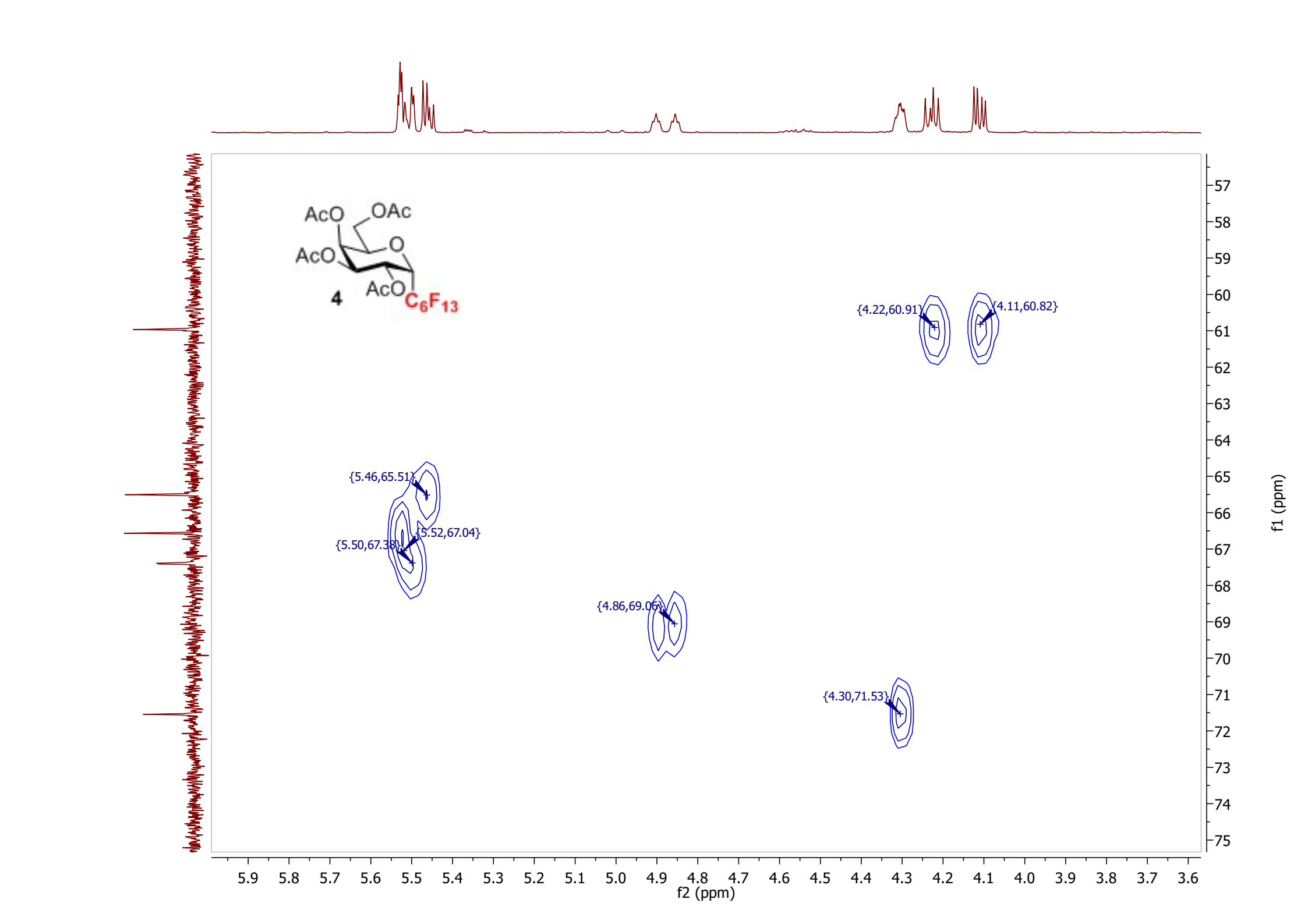
OAc
AcO
O
AcO
C6F13
4
5.53 5.53 5.52 5.50 5.50 5.50 5.49 5.47 5.46
4.91 4.90 4.89 4.86 4.86 4.85
4.31 4.30 4.30 4.24 4.23 4.22 4.21
4.12 4.12 4.10 4.10
1.88 0.94 1.00 0.99 1.02 0.97
5.6 5.5 5.4 4.9 4.8 4.3 4.2 4.1 4.0
f1 (ppm)
2.16 2.13 2.07 2.05
1.88 0.94 1.00 0.99 1.02 0.97 2.82 2.90 3.02 2.98
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8
f1 (ppm)


AcO
OAc
AcO
O
AcO
C_6F_{13}
4
170.40
170.04
169.79
169.47
71.55
69.65
69.25
68.85
67.41
66.56
65.50
60.96
20.62
20.55
20.46
20.42
f1 (ppm)
f1 (ppm)


-80.73
-80.75
-80.77
-111.85
-112.44
-115.44
-116.08
-120.58
-121.16
-121.68
-122.54
-122.71
-123.06
-123.30
-123.87
-125.01
-125.49
-125.53
-126.60
-126.62
-126.66
-126.68
-127.15
-127.18
AcO
OAc
AcO
O
AcO
C6F13
4
3.00
-80.5 -80.6 -80.7 -80.8 -80.9 -81.0
f1 (ppm)
3.00
2.19
7.68
1.93
-70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130
f1 (ppm)


AcO
OAc
AcO
O
AcO
C6F13
4
f2 (ppm)
f1 (ppm)


AcO
OAc
AcO
O
AcO
C_6F_{13}
4
{4.22,60.91}
{4.11,60.82}
{5.46,65.51}
{5.50,67.38}
{5.52,67.04}
{4.86,69.06}
{4.30,71.53}
f2 (ppm)
f1 (ppm)

Qualitative Compound Report

Analysis Info

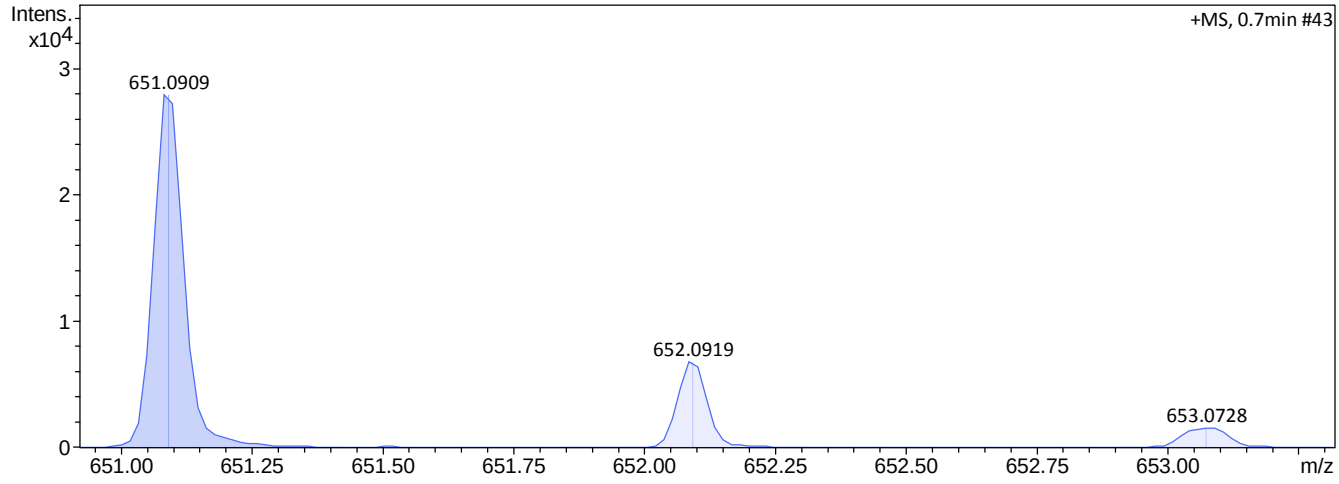
Acquisition Date 3/21/2019 2:38:01 PM

Analysis Name	D:\Data\ggc\19-031901_P1-F-1_01_915.d		
Method	lc_ms_181025.m	Operator	Gabriel Cases
Sample Name	19-031901	Instrument	micrOTOF-Q II
Comment	EWF-24 Sv: DCM + MeOH Erwin Mora / Albeto Postigo		

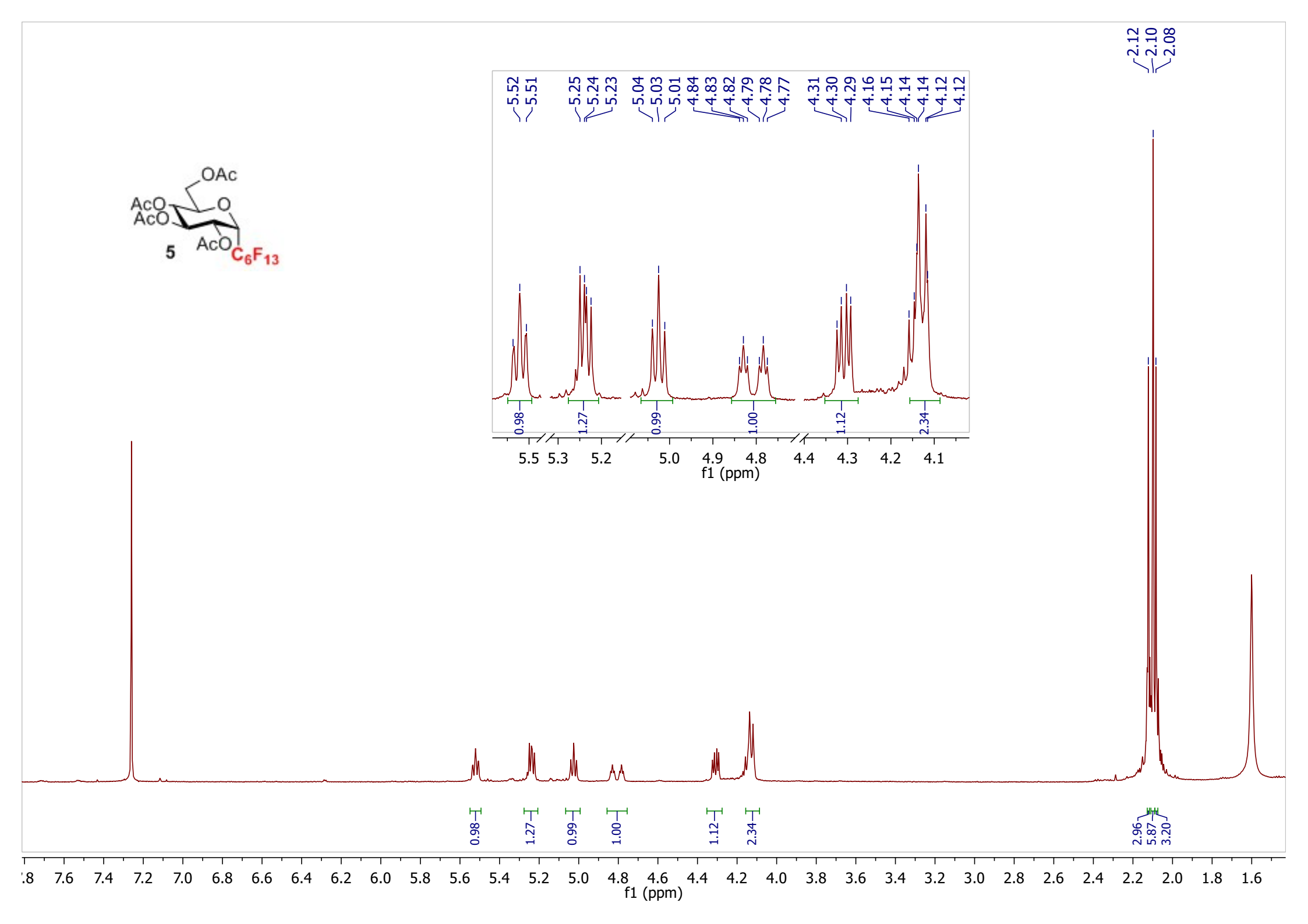
UMYMFOR CONICET FCEN - UBA

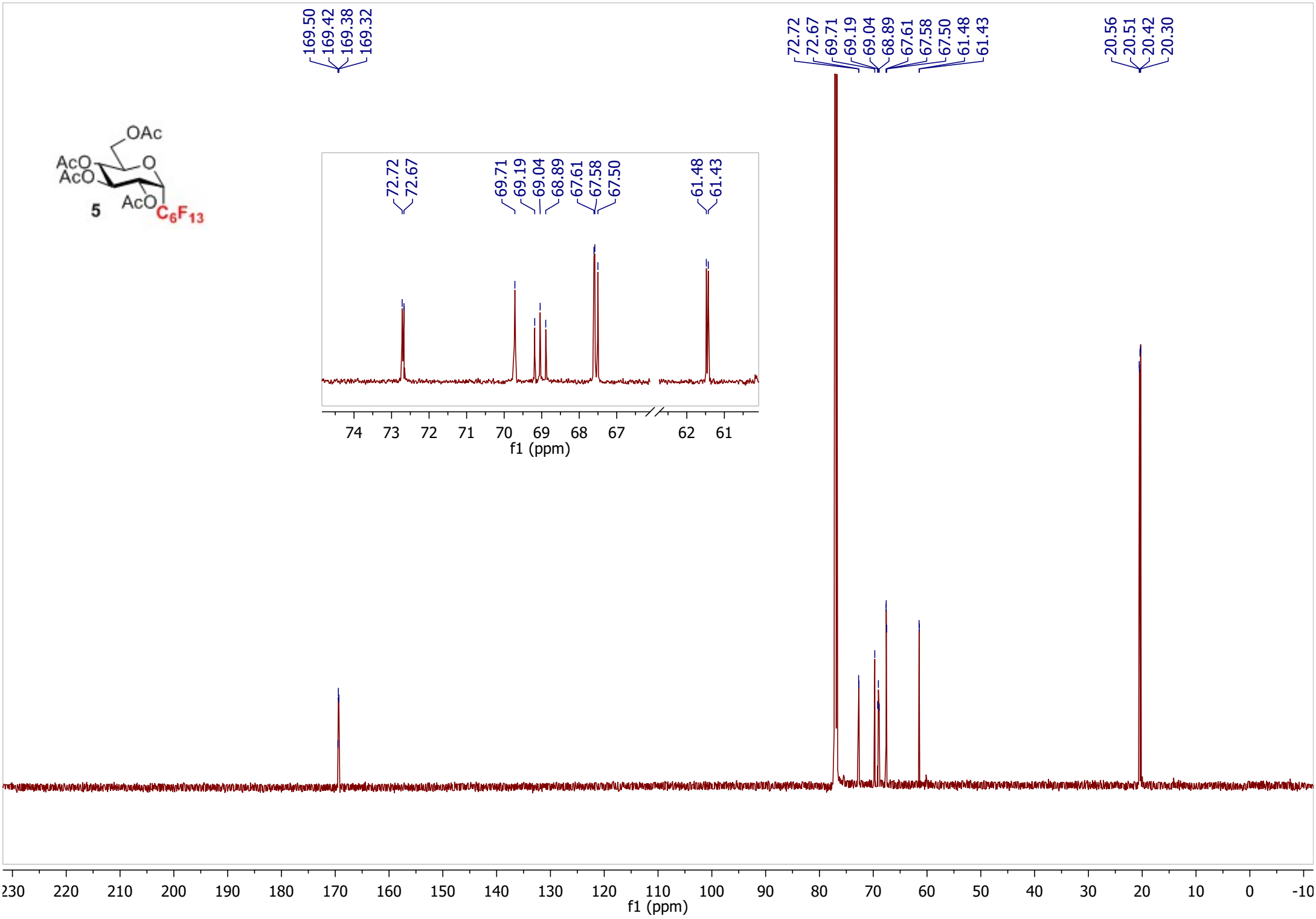
Acquisition Parameter

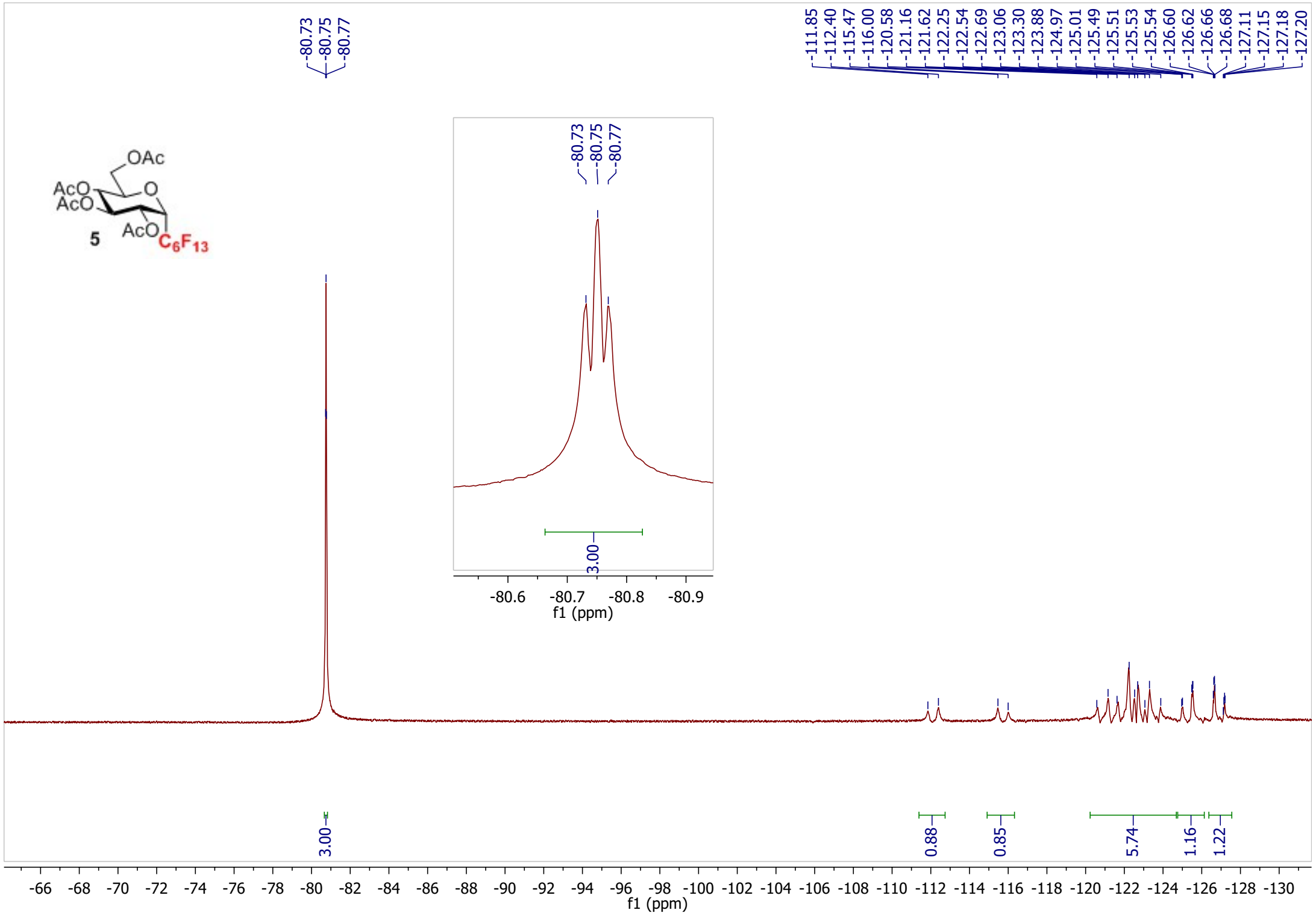
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1300 m/z	Set Collision Cell RF	250.0 Vpp	Set Divert Valve	Source

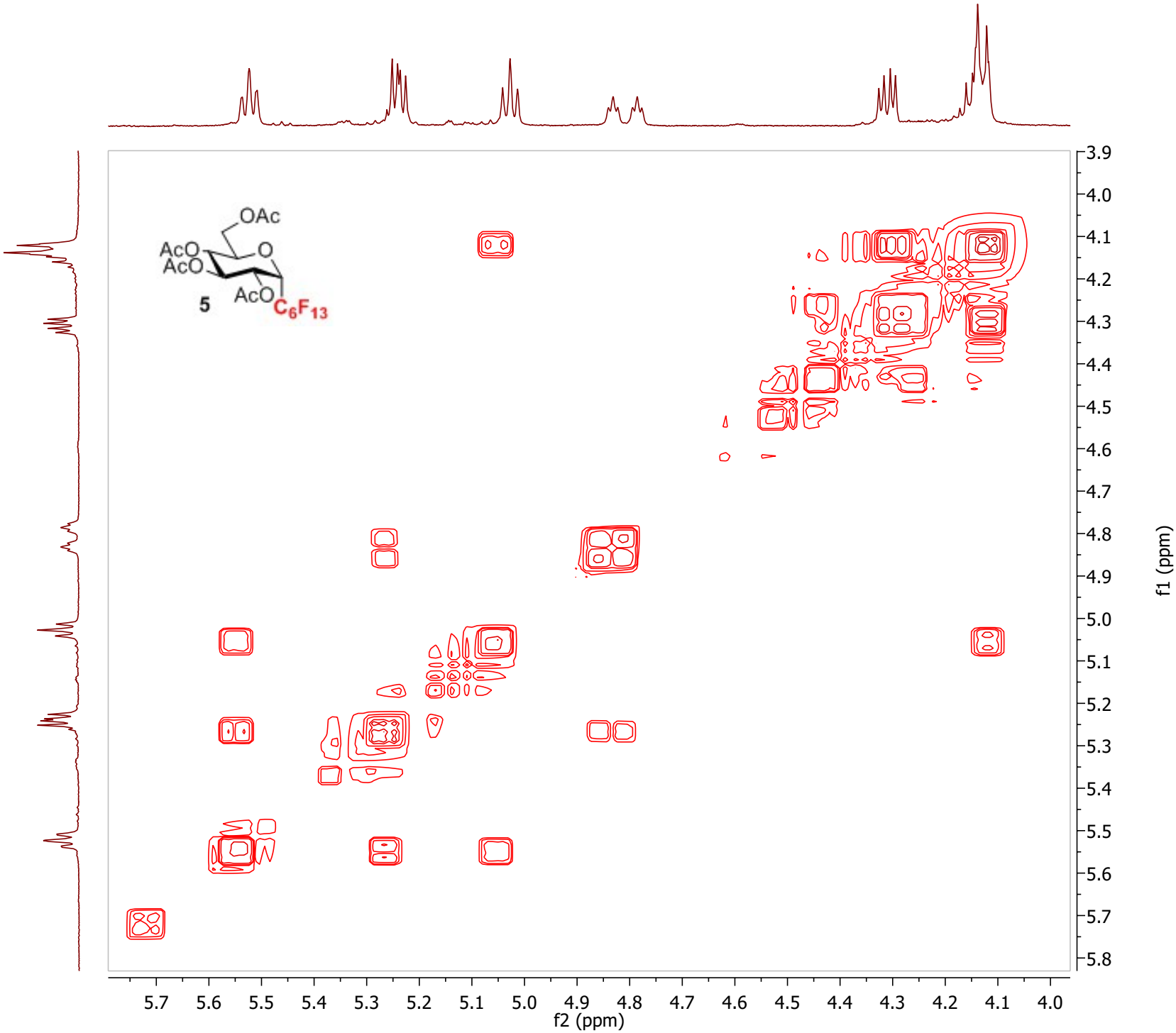


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
651.0909	1	C20H20F13O9	651.0894	-2.3	26.8	3	43.62	4.5	even	ok


OAc
AcO
AcO
O
AcO
C_6F_{13}
5
5.52
5.51
5.25
5.24
5.23
5.04
5.03
5.01
4.84
4.83
4.82
4.79
4.78
4.77
4.31
4.30
4.29
4.16
4.15
4.14
4.14
4.12
4.12
0.98
1.27
0.99
1.00
1.12
2.34
5.5 5.3 5.2 5.0 4.9 4.8 4.4 4.3 4.2 4.1
f1 (ppm)
2.12
2.10
2.08
0.98
1.27
0.99
1.00
1.12
2.34
2.96
5.87
3.20
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6
f1 (ppm)


169.50
169.42
169.38
169.32
72.72
72.67
69.71
69.19
69.04
68.89
67.61
67.58
67.50
61.48
61.43
20.56
20.51
20.42
20.30
OAc
AcO
AcO
O
AcO
C6F13
5
f1 (ppm)
f1 (ppm)


-80.73
-80.75
-80.77
-111.85
-112.40
-115.47
-116.00
-120.58
-121.16
-121.62
-122.25
-122.54
-122.69
-123.06
-123.30
-123.88
-124.97
-125.01
-125.49
-125.51
-125.53
-125.54
-126.60
-126.62
-126.66
-126.68
-127.11
-127.15
-127.18
-127.20
OAc
AcO
AcO
O
AcO
C_6F_{13}
5
3.00
-80.6
-80.7
-80.8
-80.9
f1 (ppm)
3.00
0.88
0.85
5.74
1.16
1.22
-66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90 -92 -94 -96 -98 -100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130
f1 (ppm)


OAc
AcO
AcO
O
AcO
5
C_6F_{13}
f2 (ppm)
f1 (ppm)

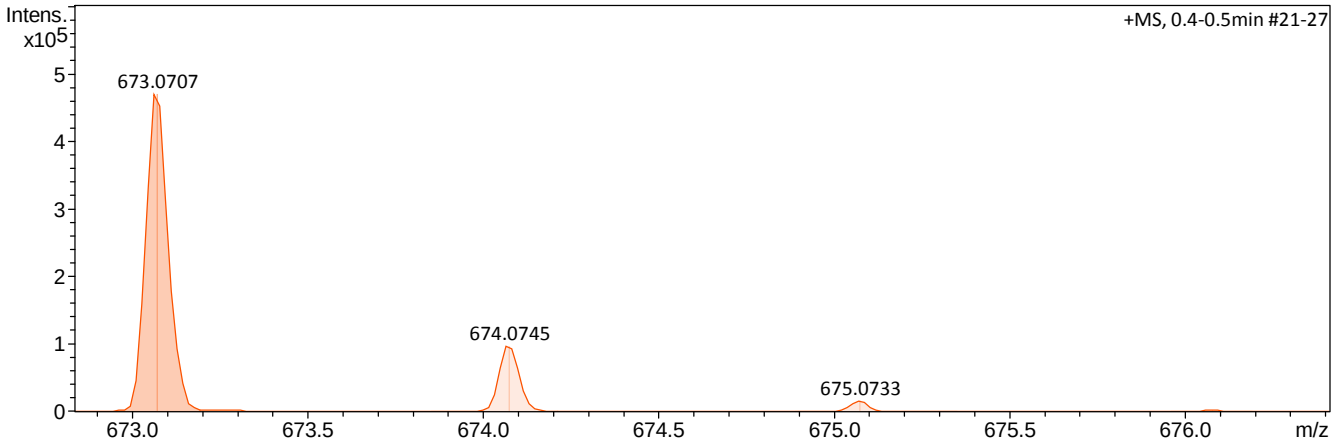
Qualitative Compound Report

Analysis Info

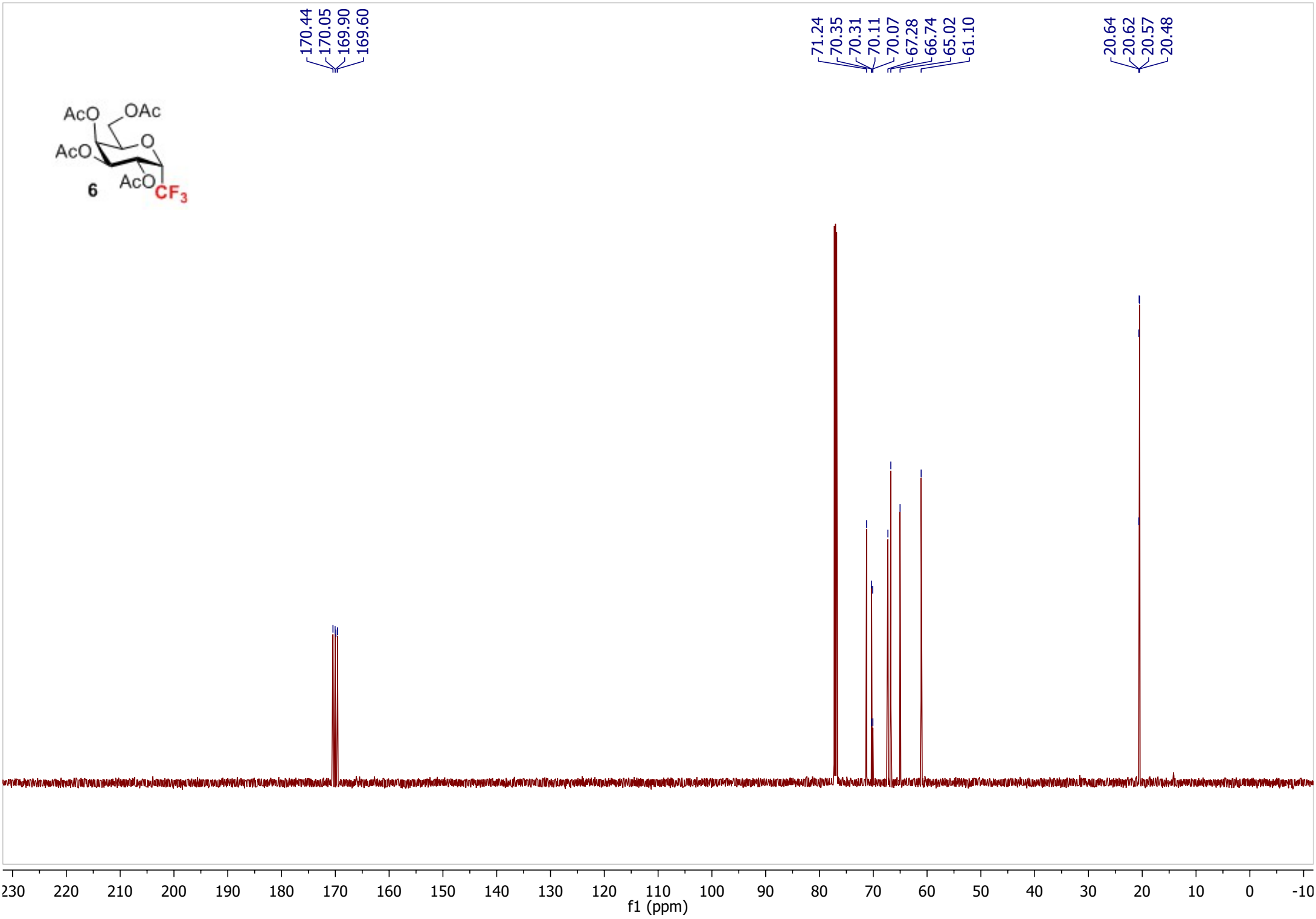
Analysis Name	D:\Data\ggc\19-100202_P1-C-2_01_2068.d	Acquisition Date	10/28/2019 11:12:02 AM
Method	tune_pos_formate lcms.m	Operator	GC
Sample Name	19-100202	Instrument	micrOTOF-Q II
Comment	Glu-C6F13 Sv: DCM + MeOH Erwin Mora / Alberto Postigo		

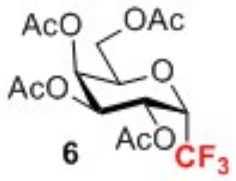
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	3.5 Bar
Focus	Not active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
673.0707	1	C20H19F13NaO9	673.0714	1.0	10.7	1	100.00	4.5	even	ok


170.44
170.05
169.90
169.60
71.24
70.35
70.31
70.11
70.07
67.28
66.74
65.02
61.10
20.64
20.62
20.57
20.48
AcO
OAc
AcO
O
AcO
CF3
6
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
f1 (ppm)

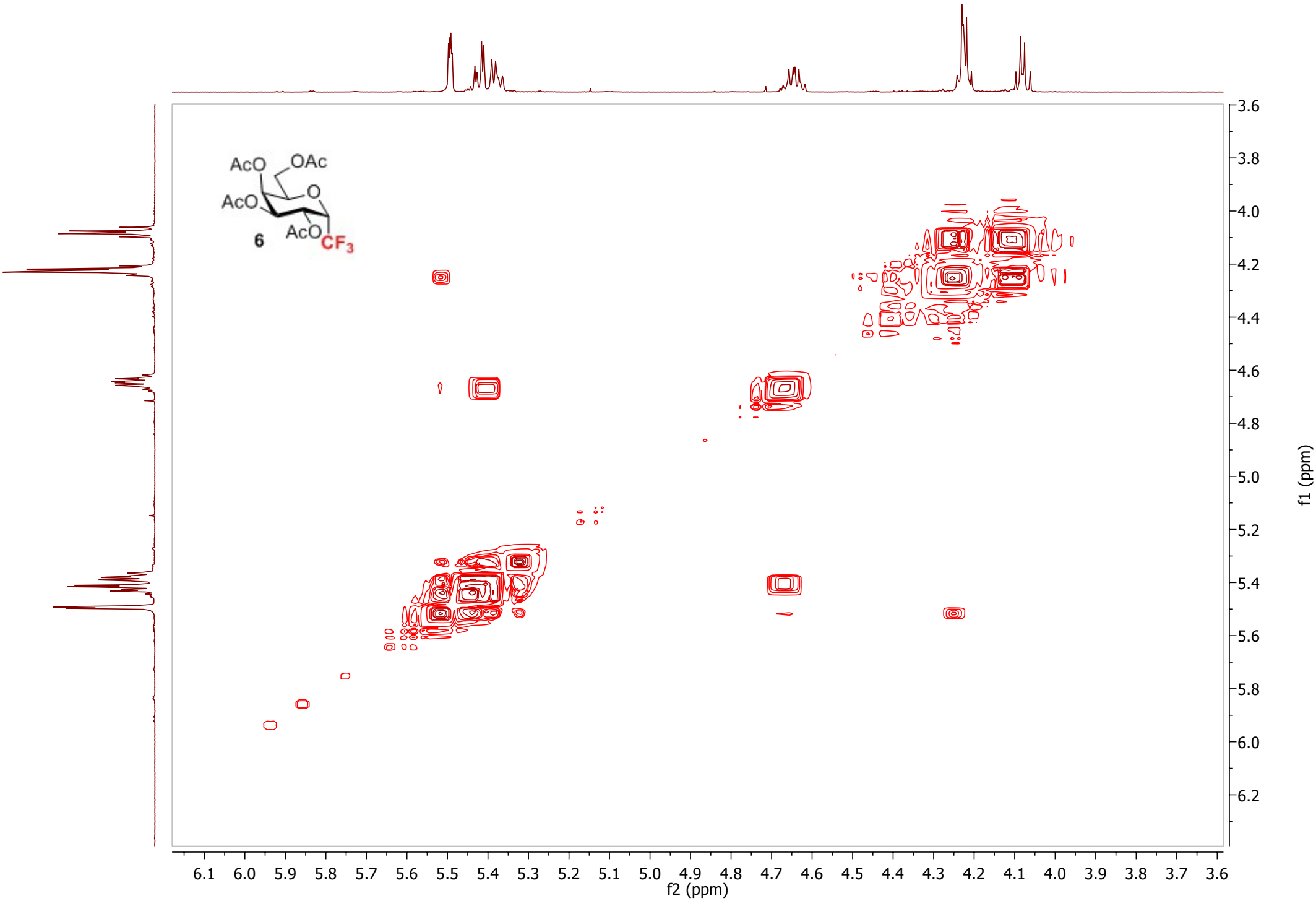


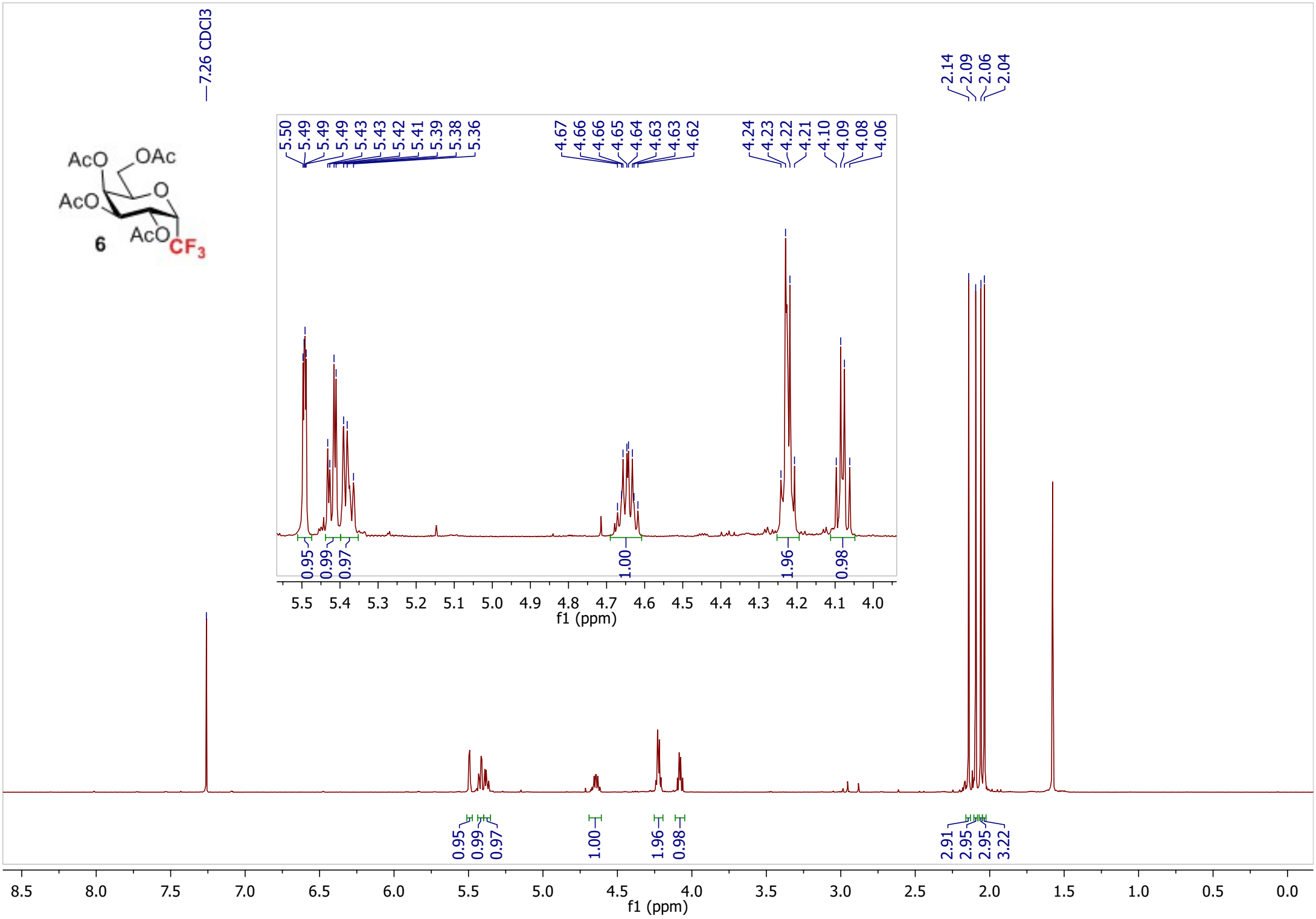
6

-67.62

-66.0 -66.2 -66.4 -66.6 -66.8 -67.0 -67.2 -67.4 -67.6 -67.8 -68.0 -68.2 -68.4 -68.6 -68.8 -69.0 -69.2

f1 (ppm)


AcO
OAc
O
AcO
AcO
CF3
6
6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6
f2 (ppm)
3.6 3.8 4.0 4.2 4.4 4.6 4.8 5.0 5.2 5.4 5.6 5.8 6.0 6.2
f1 (ppm)


7.26 CDCl3
2.14
2.09
2.06
2.04
AcO
OAc
AcO
O
AcO
CF3
6
5.50
5.49
5.49
5.49
5.43
5.43
5.42
5.41
5.39
5.38
5.36
4.67
4.66
4.66
4.65
4.64
4.63
4.63
4.62
4.24
4.23
4.22
4.21
4.10
4.09
4.08
4.06
0.95
0.99
0.97
1.00
1.96
0.98
5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0
f1 (ppm)
0.95
0.99
0.97
1.00
1.96
0.98
2.91
2.95
2.95
3.22
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)

Qualitative Compound Report

Analysis Info

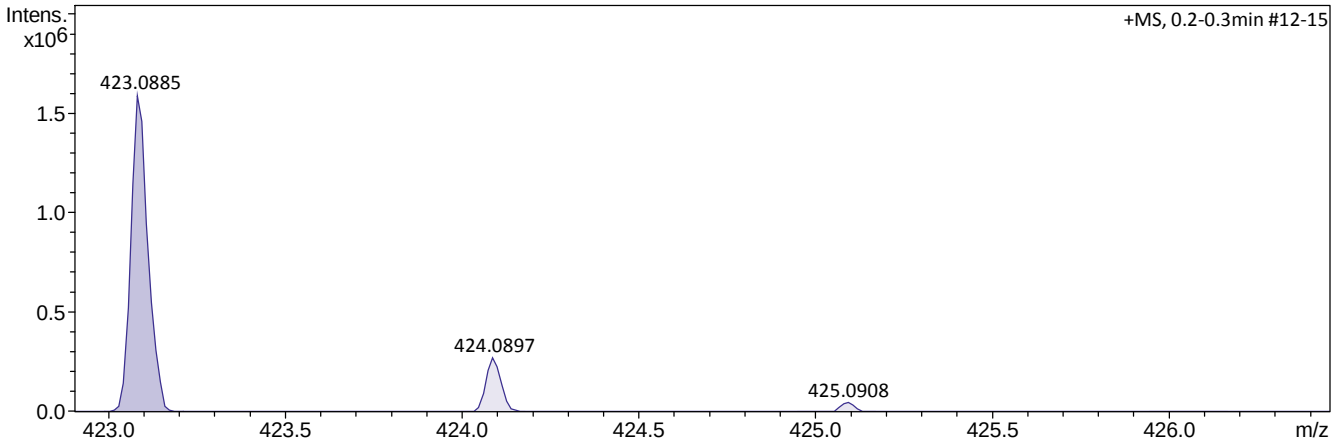
Acquisition Date 10/28/2019 11:22:23 AM

Analysis Name	D:\Data\ggc\19-100204_P1-C-4_01_2070.d		
Method	tune_pos_formate lcms.m	Operator	GC
Sample Name	19-100204	Instrument	micrOTOF-Q II
Comment	Gal-CF3 Sv: DCM + MeOH Erwin Mora / Alberto Postigo		

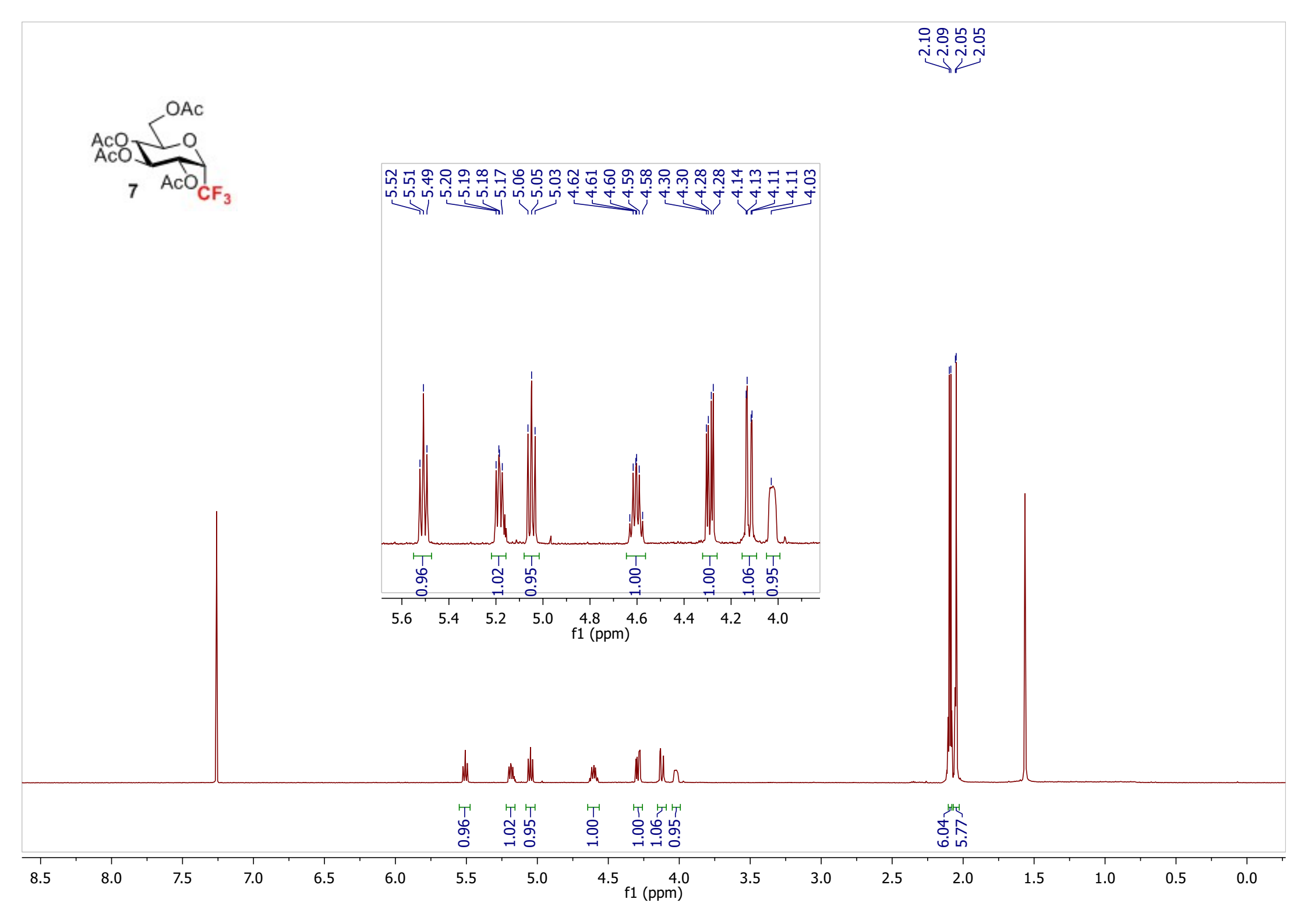
UMYMFOR CONICET FCEN - UBA

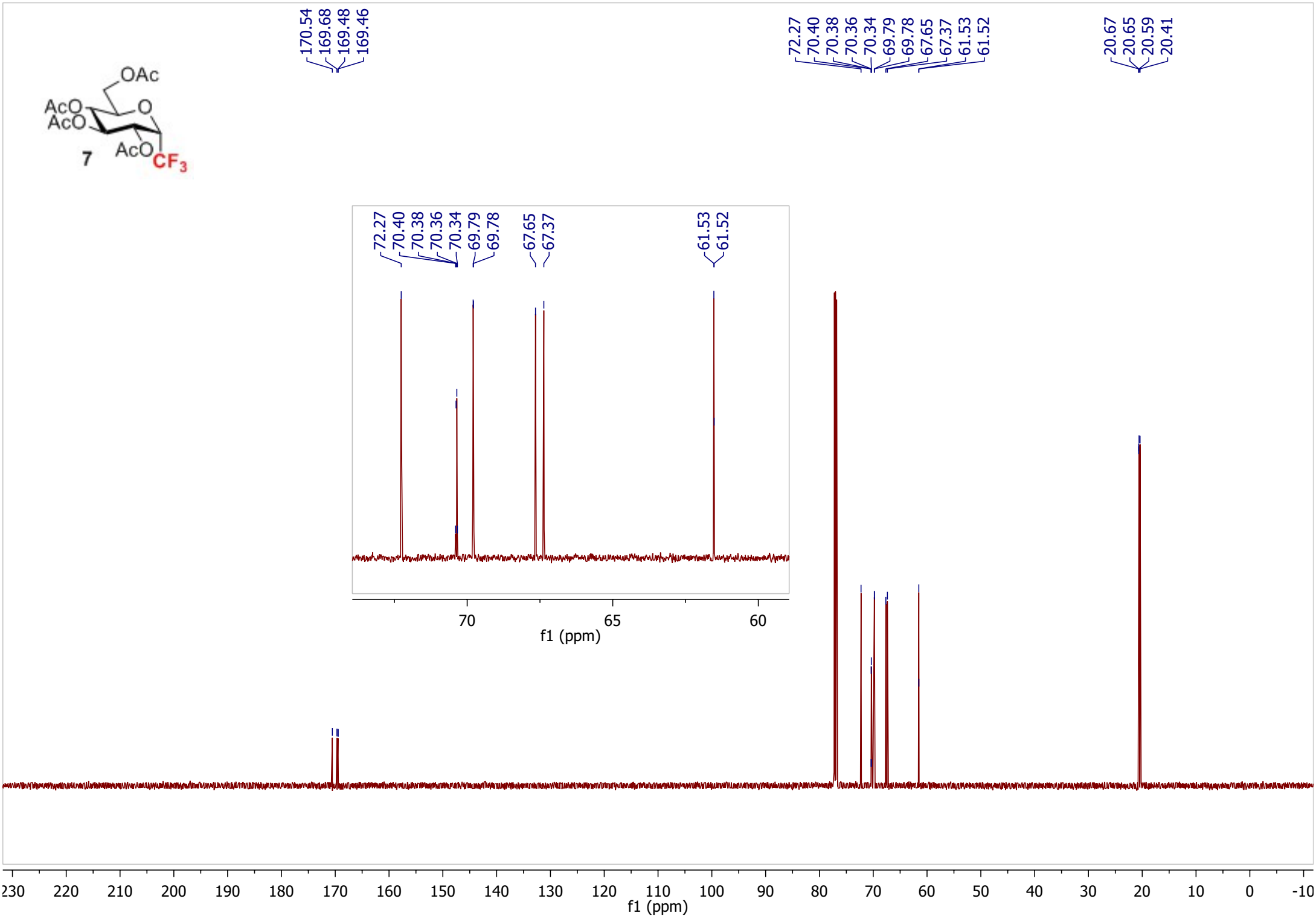
Acquisition Parameter

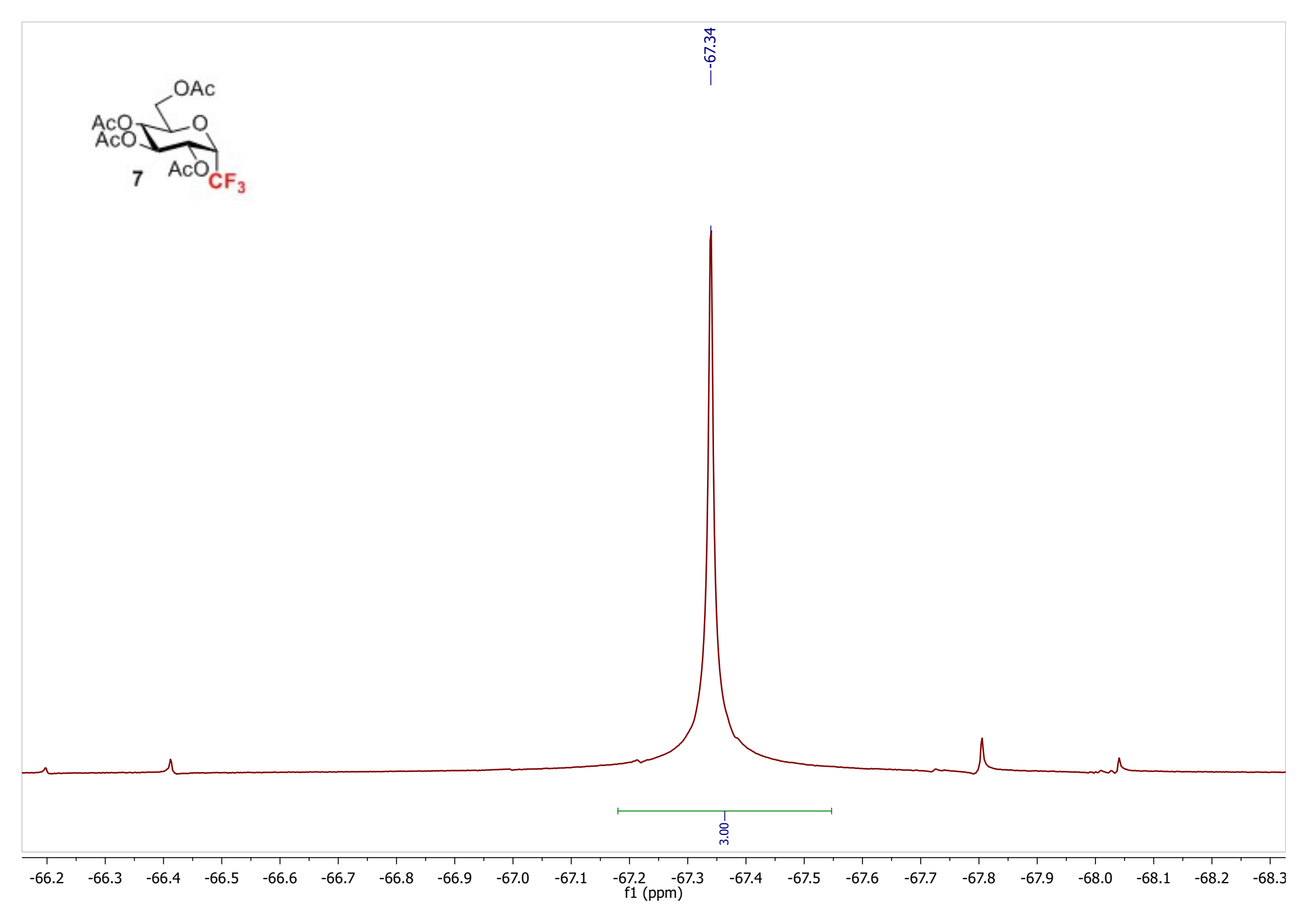
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	3.5 Bar
Focus	Not active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Source

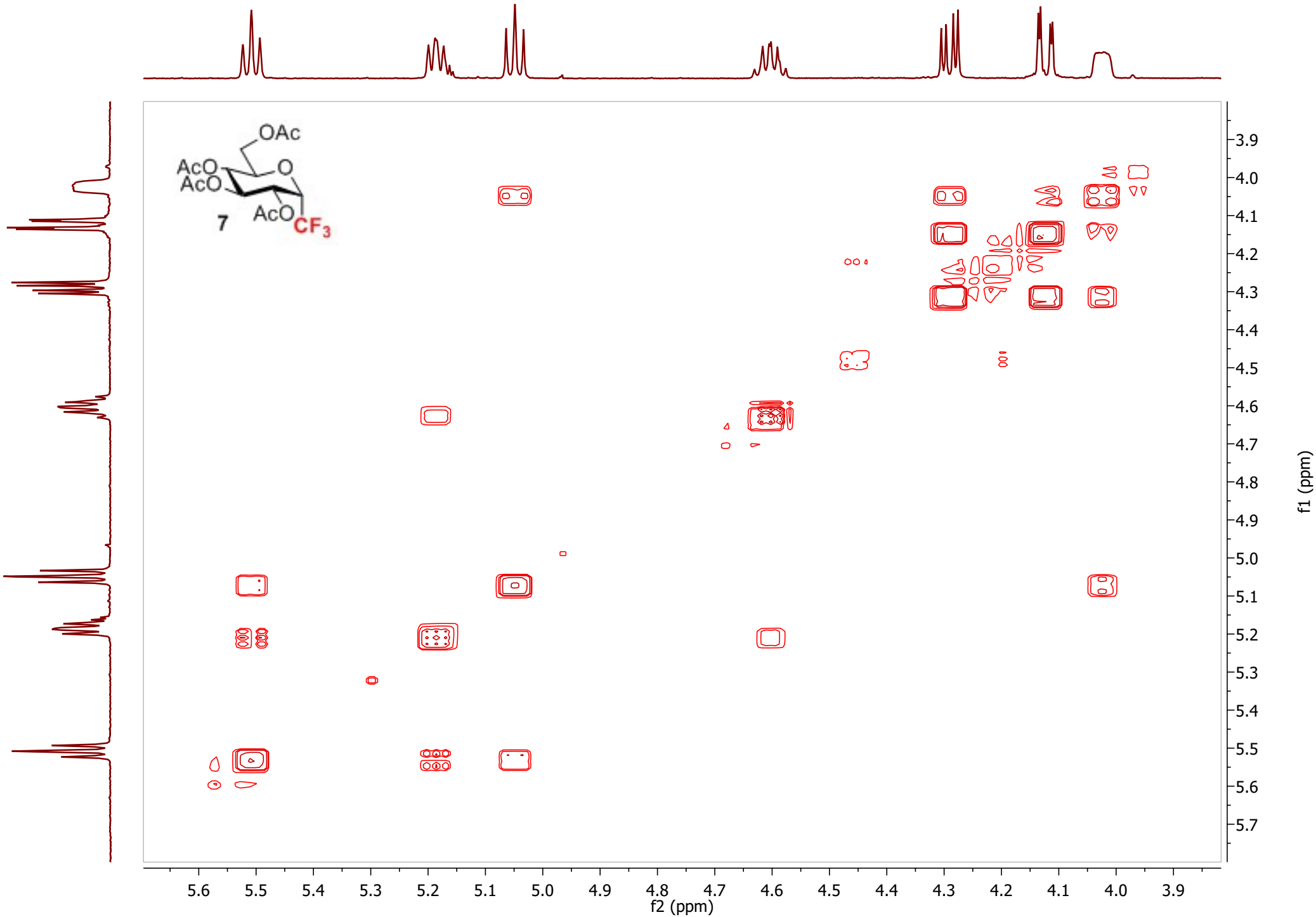


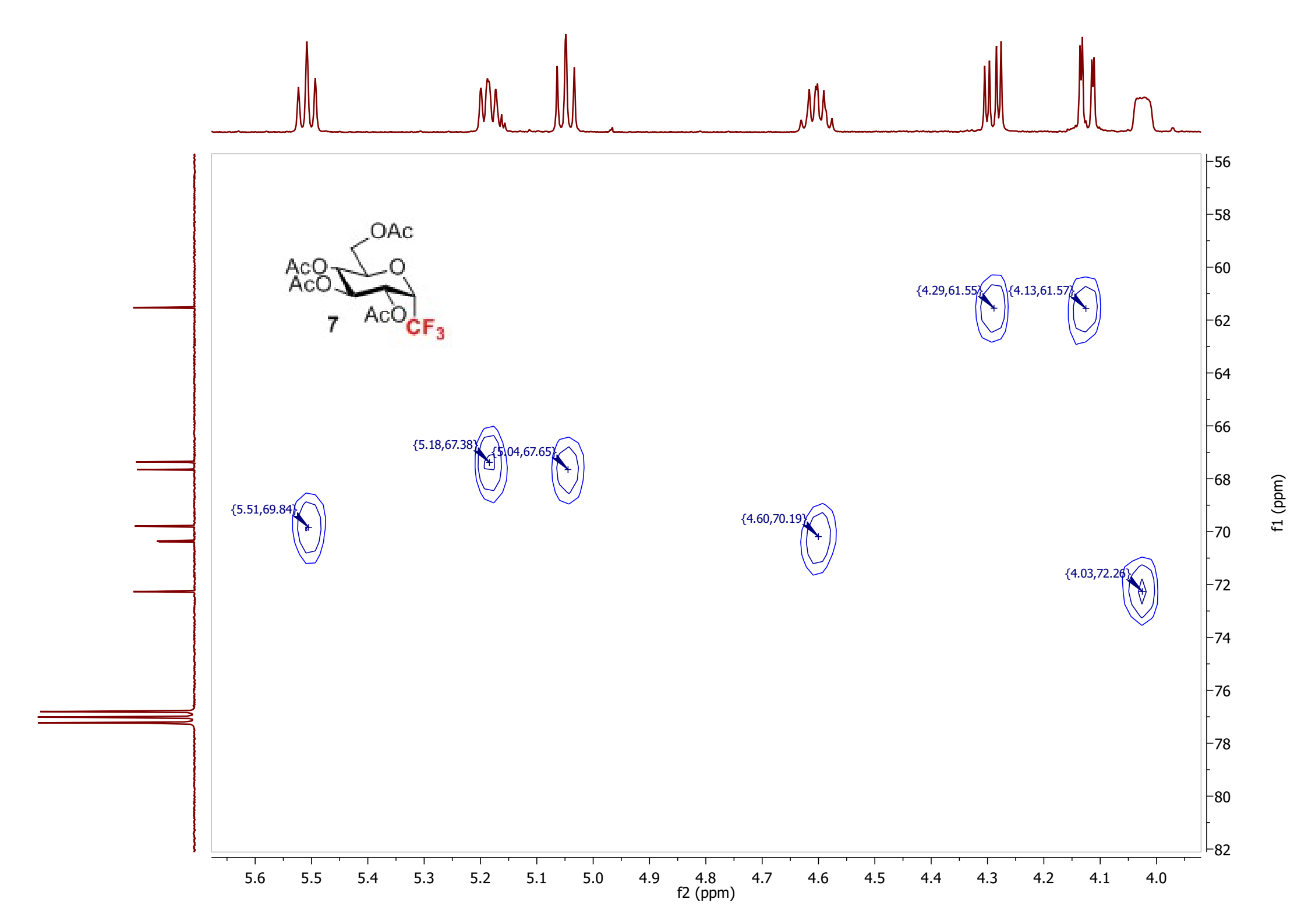
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e¯ Conf	N-Rule
423.0885	1	C15H19F3NaO9	423.0873	-2.8	2.0	1	68.81	4.5	even	ok


OAc
AcO
AcO
O
AcO
CF3
7
2.10
2.09
2.05
2.05
5.52
5.51
5.49
5.20
5.19
5.18
5.17
5.06
5.05
5.03
4.62
4.61
4.60
4.59
4.58
4.30
4.30
4.28
4.28
4.14
4.13
4.11
4.11
4.03
0.96
1.02
0.95
1.00
1.00
1.06
0.95
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
f1 (ppm)
0.96
1.02
0.95
1.00
1.00
1.06
0.95
6.04
5.77
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)


170.54
169.68
169.48
169.46
72.27
70.40
70.38
70.36
70.34
69.79
69.78
67.65
67.37
61.53
61.52
20.67
20.65
20.59
20.41
OAc
AcO
AcO
O
AcO
CF3
7
f1 (ppm)
f1 (ppm)


OAc
AcO
AcO
O
AcO
CF3
7
-67.34
3.00
-66.2
-66.3
-66.4
-66.5
-66.6
-66.7
-66.8
-66.9
-67.0
-67.1
-67.2
-67.3
-67.4
-67.5
-67.6
-67.7
-67.8
-67.9
-68.0
-68.1
-68.2
-68.3
f1 (ppm)


OAc
AcO
AcO
O
AcO
CF3
7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
f2 (ppm)
3.9
4.0
4.1
4.2
4.3
4.4
4.5
4.6
4.7
4.8
4.9
5.0
5.1
5.2
5.3
5.4
5.5
5.6
5.7
f1 (ppm)


OAc
AcO
AcO
O
AcO
CF3
7
{4.29,61.55}
{4.13,61.57}
{5.18,67.38}
{5.04,67.65}
{5.51,69.84}
{4.60,70.19}
{4.03,72.26}
f2 (ppm)
f1 (ppm)

Qualitative Compound Report

Analysis Info

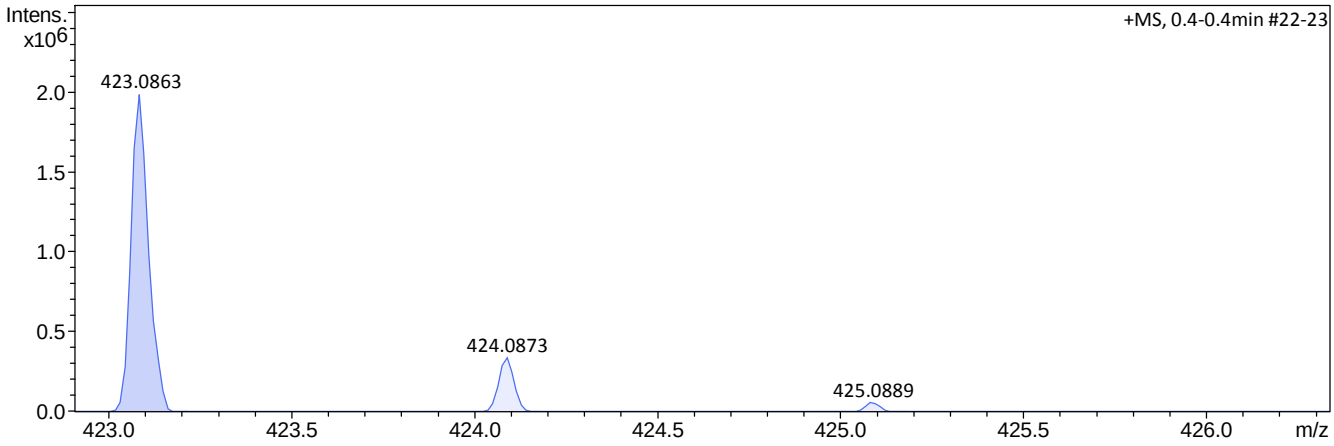
Acquisition Date 10/28/2019 11:17:10 AM

Analysis Name	D:\Data\ggc\19-100203_P1-C-3_01_2069.d		
Method	tune_pos_formate lcms.m	Operator	GC
Sample Name	19-100203	Instrument	micrOTOF-Q II
Comment	Glu-CF3 Sv: DCM + MeOH Erwin Mora / Alberto Postigo		

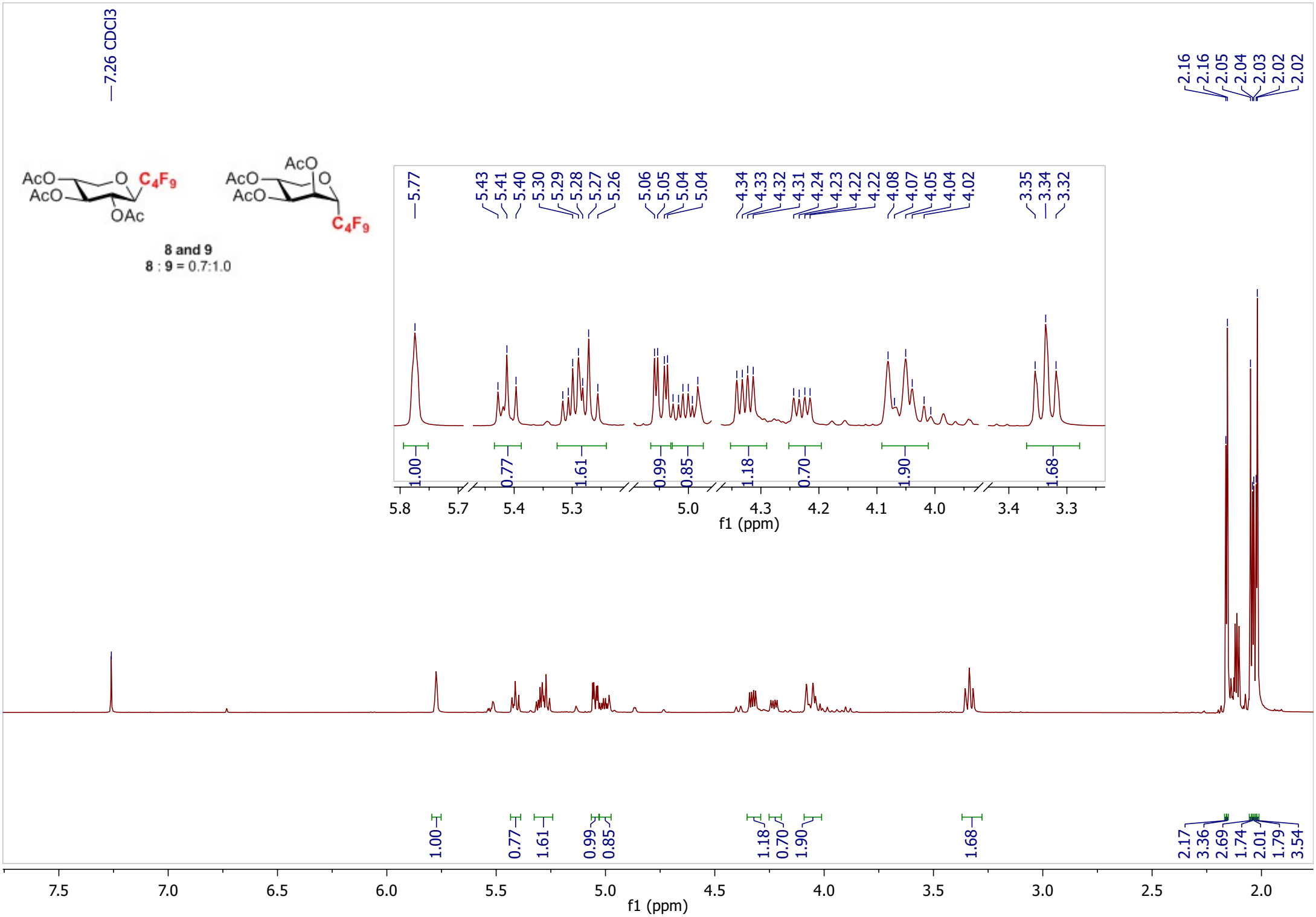
UMYMFOR CONICET FCEN - UBA

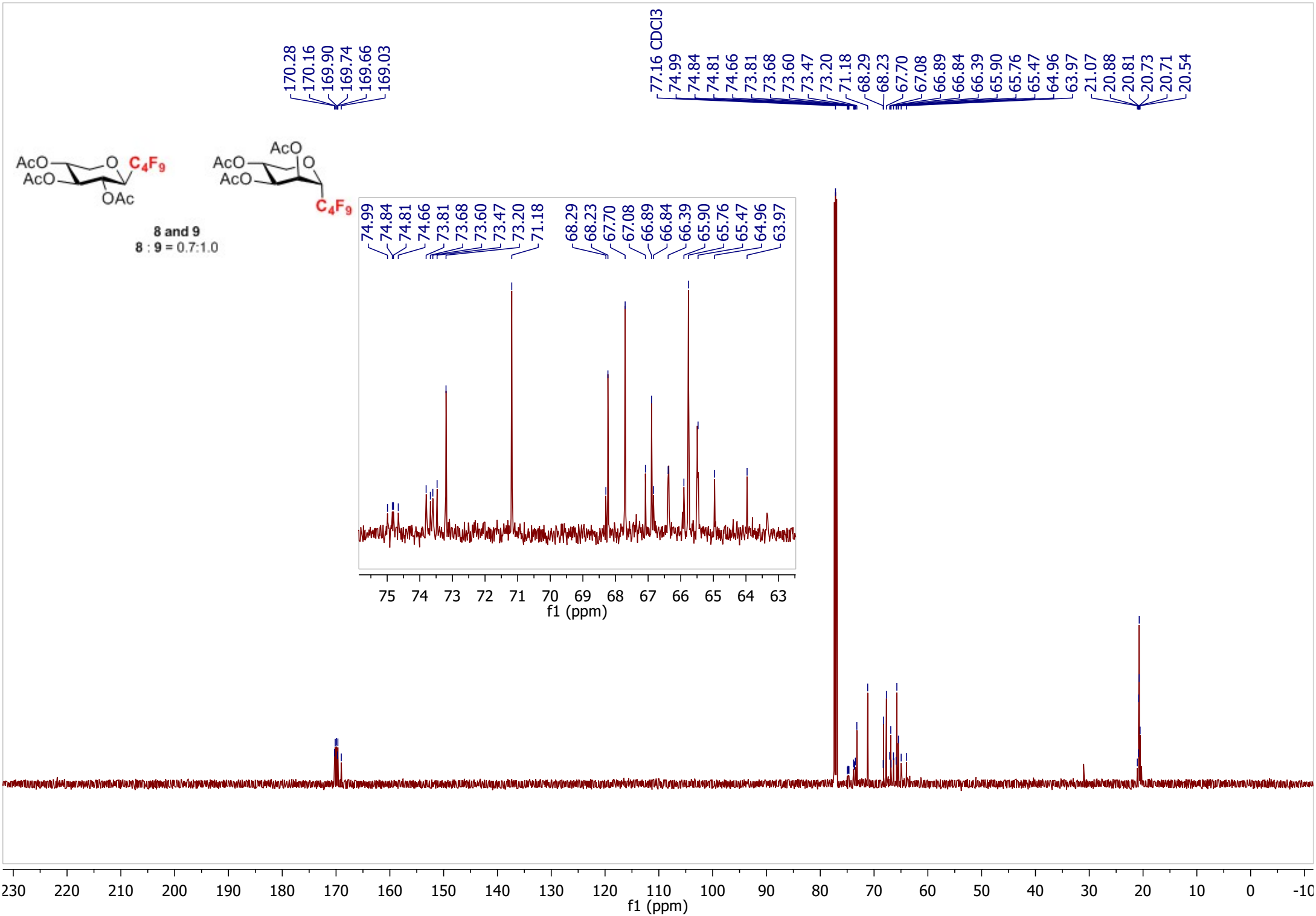
Acquisition Parameter

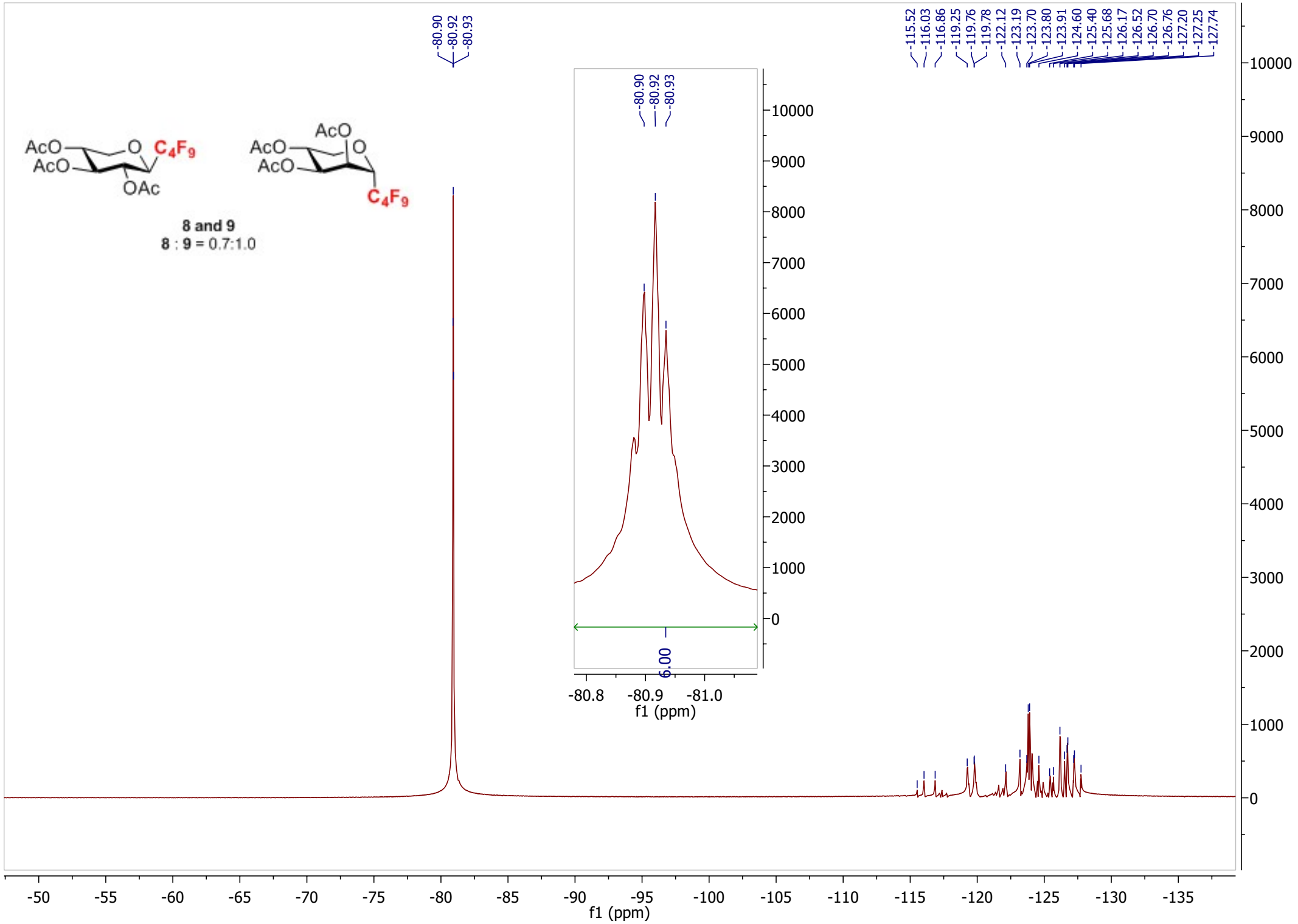
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	3.5 Bar
Focus	Not active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Source

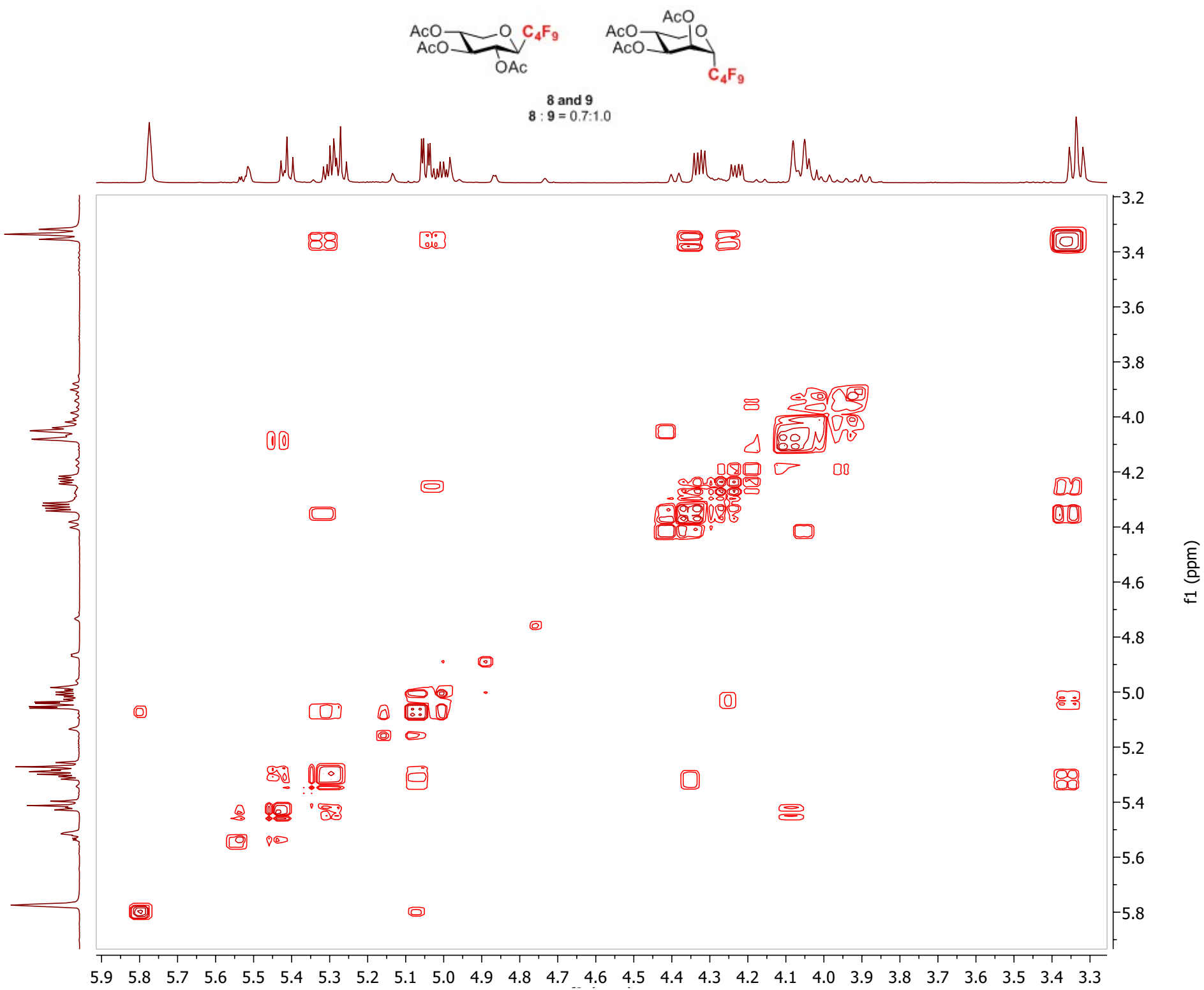


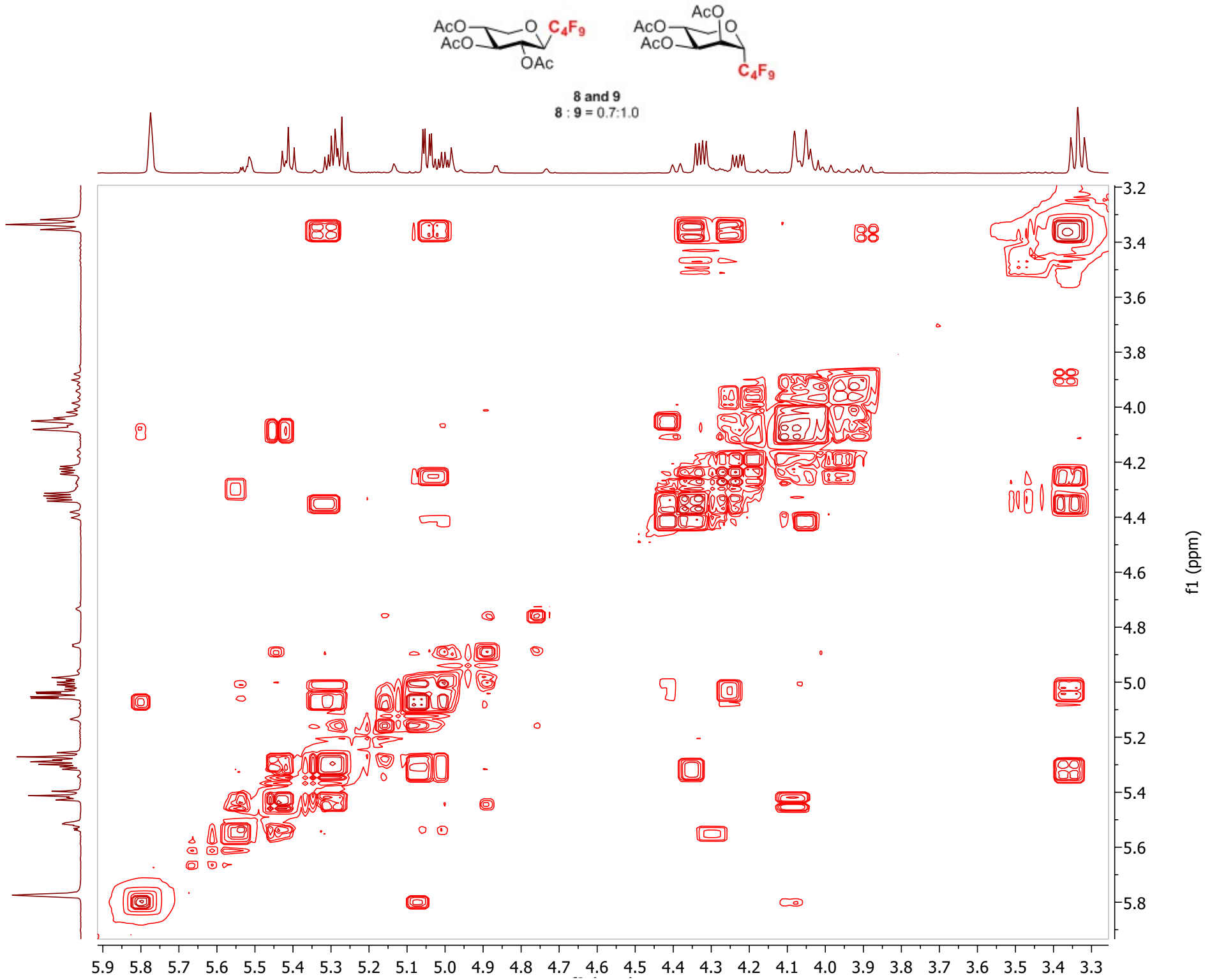
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e¯ Conf	N-Rule
423.0863	1	C15H19F3NaO9	423.0873	2.3	2.3	1	75.37	4.5	even	ok

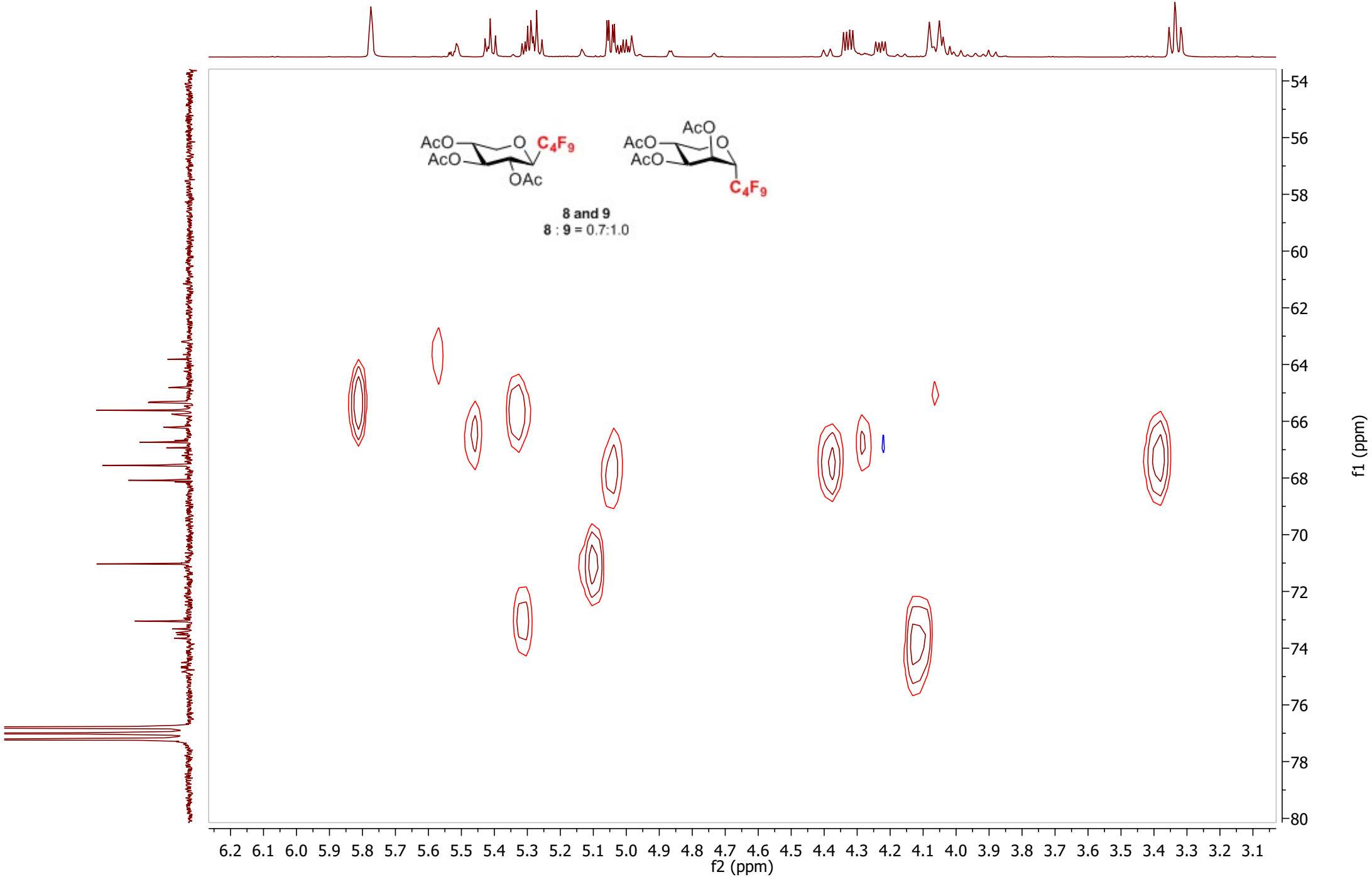

7.26 CDCl3
2.16
2.16
2.05
2.04
2.03
2.02
2.02
AcO
AcO
OAc
C4F9
AcO
AcO
C4F9
8 and 9
8 : 9 = 0.7:1.0
5.77
5.43
5.41
5.40
5.30
5.29
5.28
5.27
5.26
5.06
5.05
5.04
5.04
4.34
4.33
4.32
4.31
4.24
4.23
4.22
4.22
4.08
4.07
4.05
4.04
4.02
3.35
3.34
3.32
1.00
0.77
1.61
0.99
0.85
1.18
0.70
1.90
1.68
5.8
5.7
5.4
5.3
5.0
4.3
4.2
4.1
4.0
3.4
3.3
f1 (ppm)
1.00
0.77
1.61
0.99
0.85
1.18
0.70
1.90
1.68
2.17
3.36
2.69
1.74
2.01
1.79
3.54
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)


170.28
170.16
169.90
169.74
169.66
169.03
77.16 CDCl3
74.99
74.84
74.81
74.66
73.81
73.68
73.60
73.47
73.20
71.18
68.29
68.23
67.70
67.08
66.89
66.84
66.39
65.90
65.76
65.47
64.96
63.97
21.07
20.88
20.81
20.73
20.71
20.54
AcO
AcO
O
C4F9
OAc
AcO
AcO
O
C4F9
8 and 9
8 : 9 = 0.7:1.0
f1 (ppm)
f1 (ppm)


AcO
AcO
OAc
O
C4F9
AcO
AcO
O
C4F9
8 and 9
8 : 9 = 0.7:1.0
-80.90
-80.92
-80.93
-115.52
-116.03
-116.86
-119.25
-119.76
-119.78
-122.12
-123.19
-123.70
-123.80
-123.91
-124.60
-125.40
-125.68
-126.17
-126.52
-126.70
-126.76
-127.20
-127.25
-127.74
6.00
-80.8
-80.9
-81.0
f1 (ppm)
f1 (ppm)


AcO
AcO
O
C4F9
OAc
AcO
AcO
O
C4F9
8 and 9
8 : 9 = 0.7:1.0
f1 (ppm)
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3


AcO
AcO
O
C4F9
OAc
AcO
AcO
O
C4F9
8 and 9
8 : 9 = 0.7:1.0
f1 (ppm)
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3


AcO
AcO
O
C_4F_9
OAc
AcO
AcO
O
C_4F_9
8 and 9
8 : 9 = 0.7:1.0
f2 (ppm)
f1 (ppm)

Qualitative Compound Report

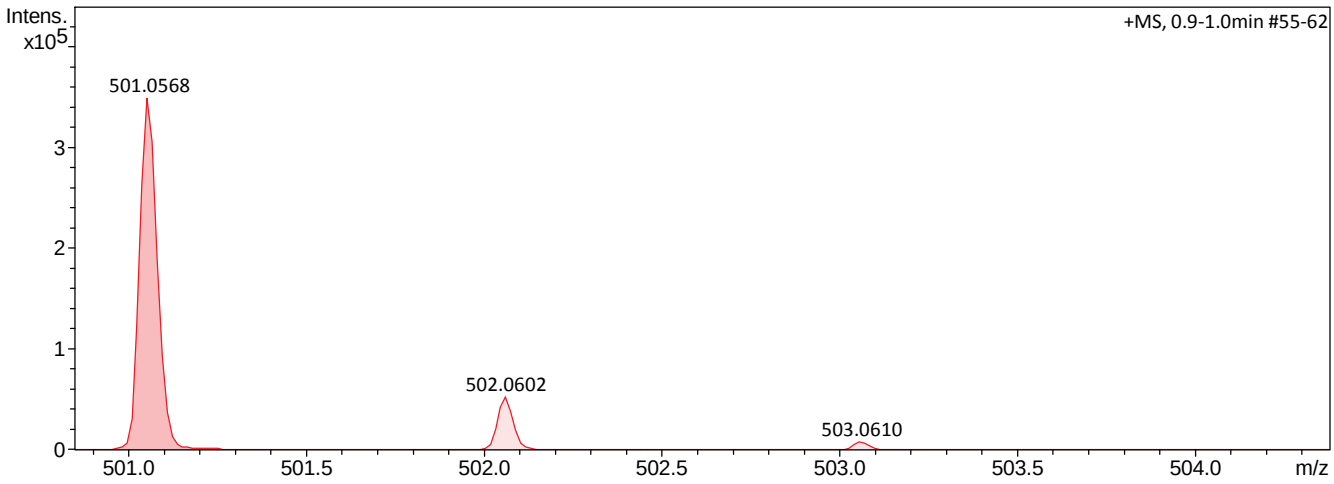
Analysis Info

Acquisition Date 7/20/2020 10:48:40 AM

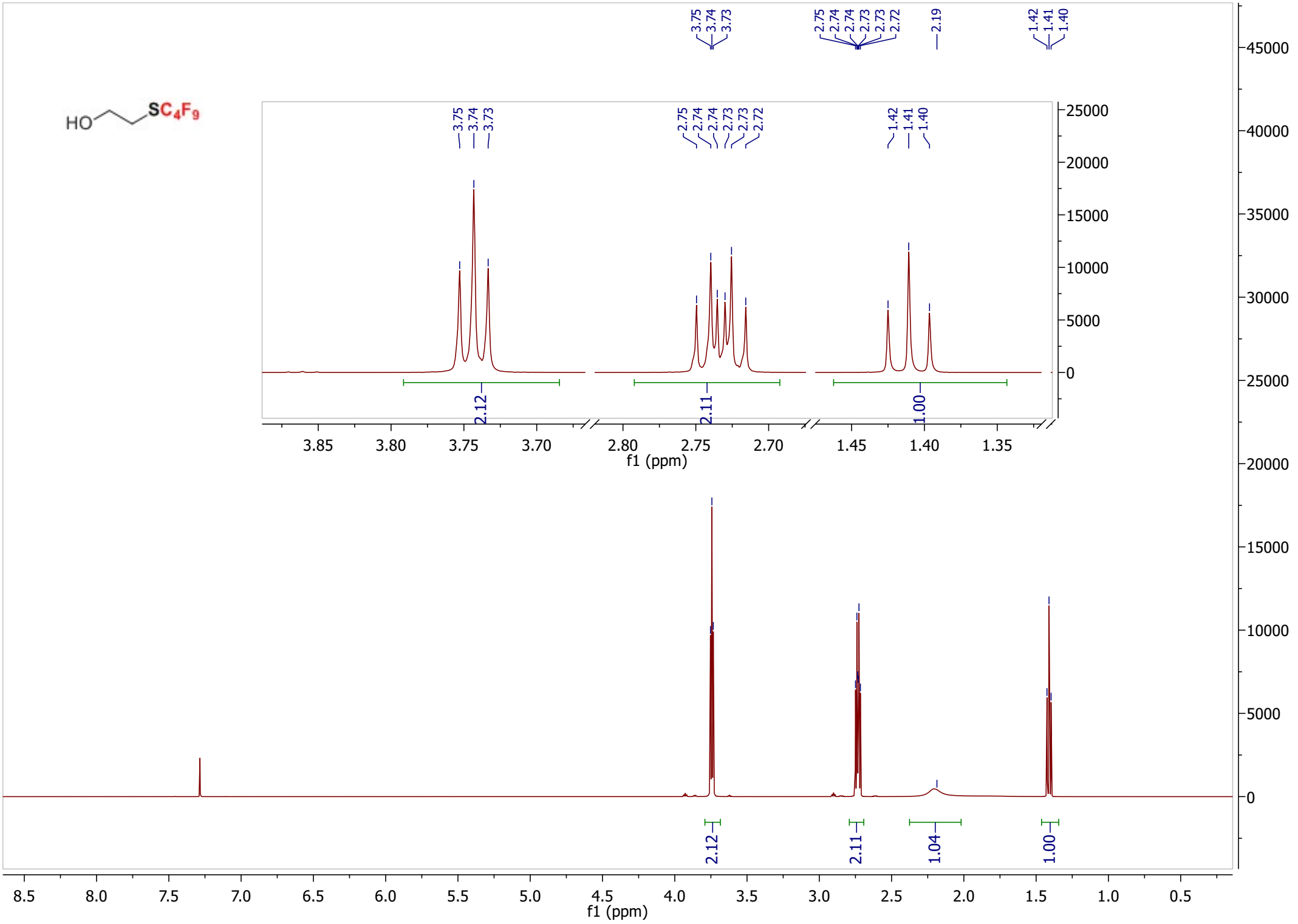
Analysis Name	D:\Data\ggc\Xilo-C4F9.d		
Method	Tune_low_formate 210120.m	Operator	GC
Sample Name	Xilo-C4F9	Instrument	micrOTOF-Q II
Comment	Sv: ACN Erwin Mora / A. Postigo		

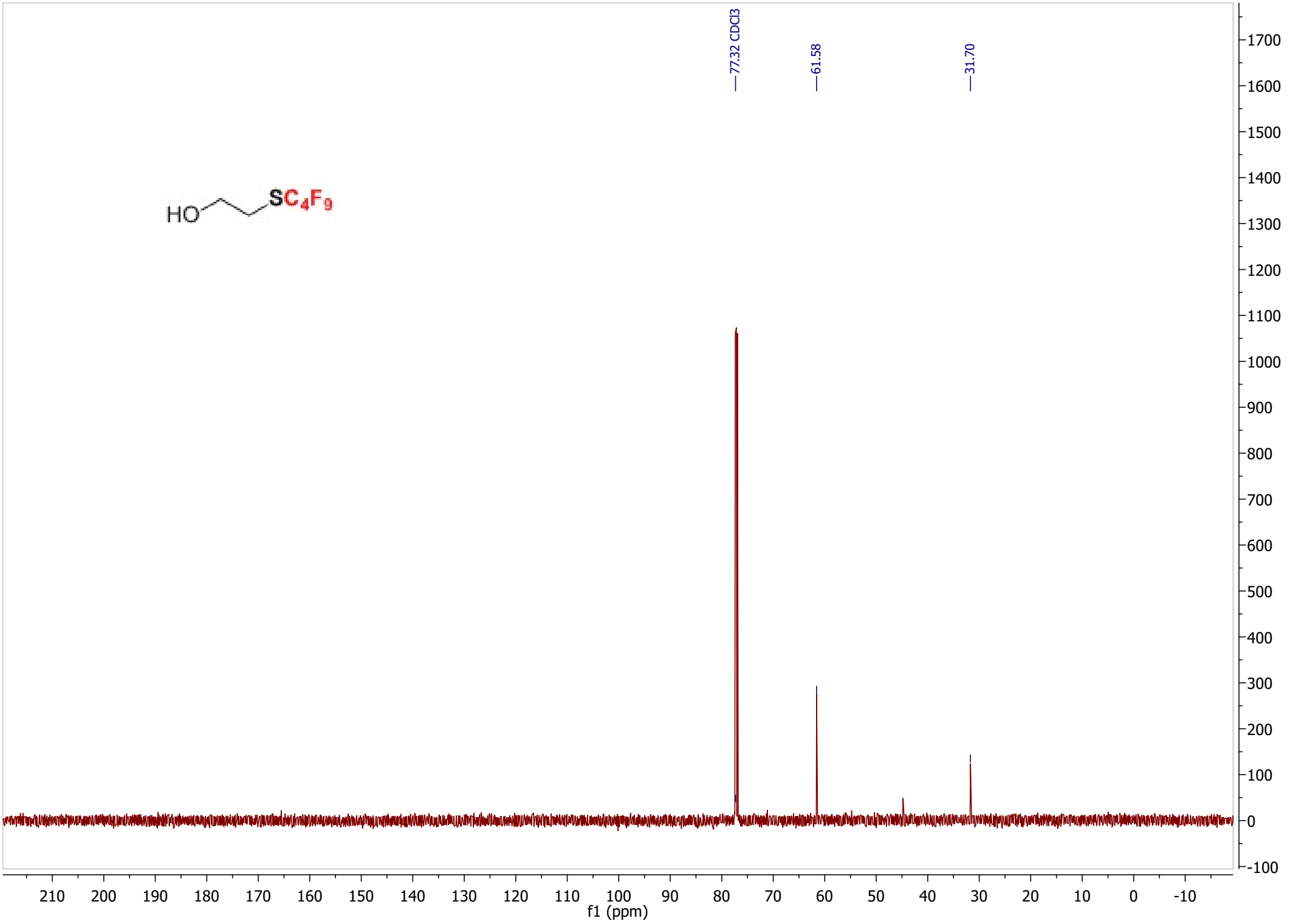
Acquisition Parameter

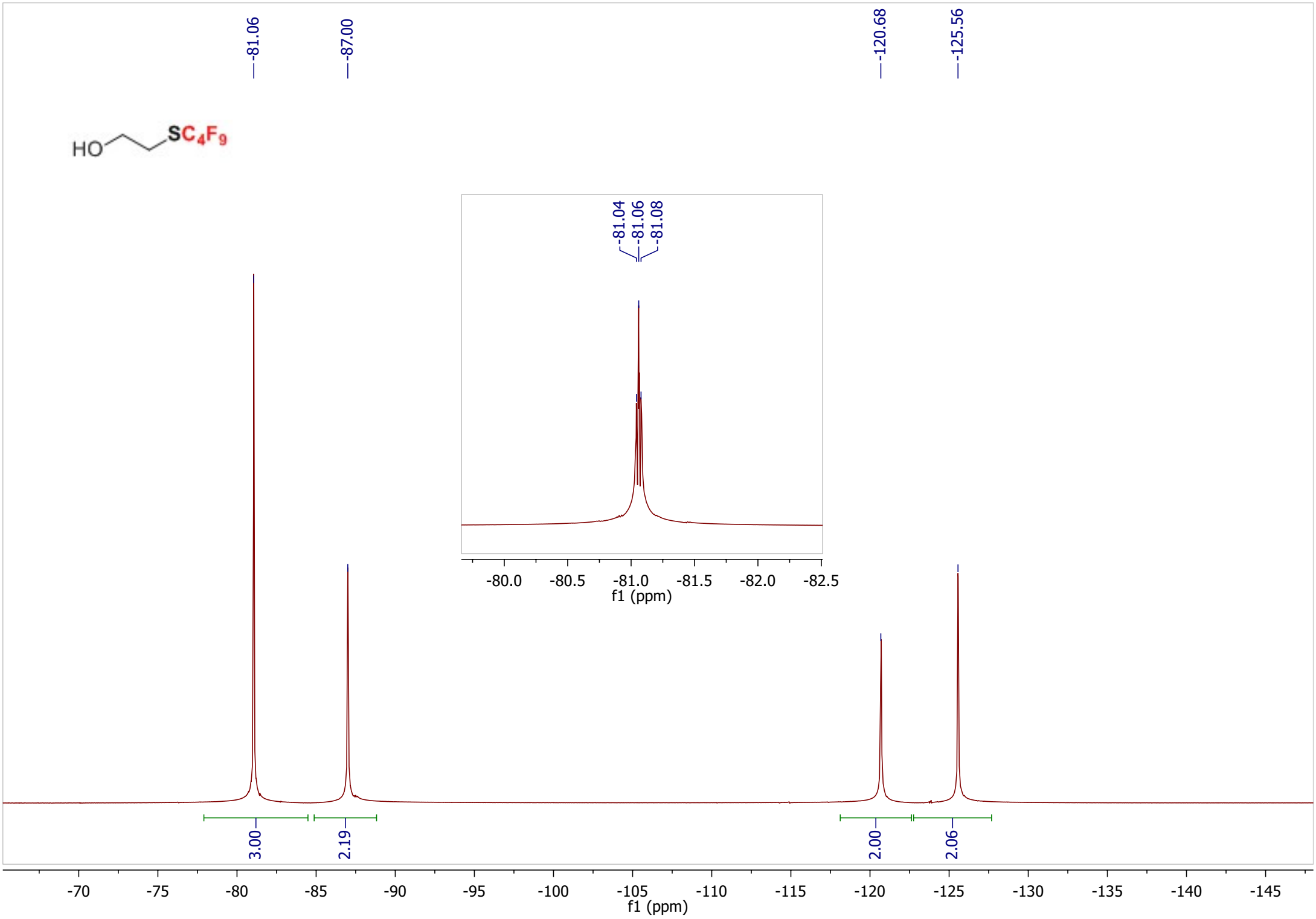
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	950 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Source

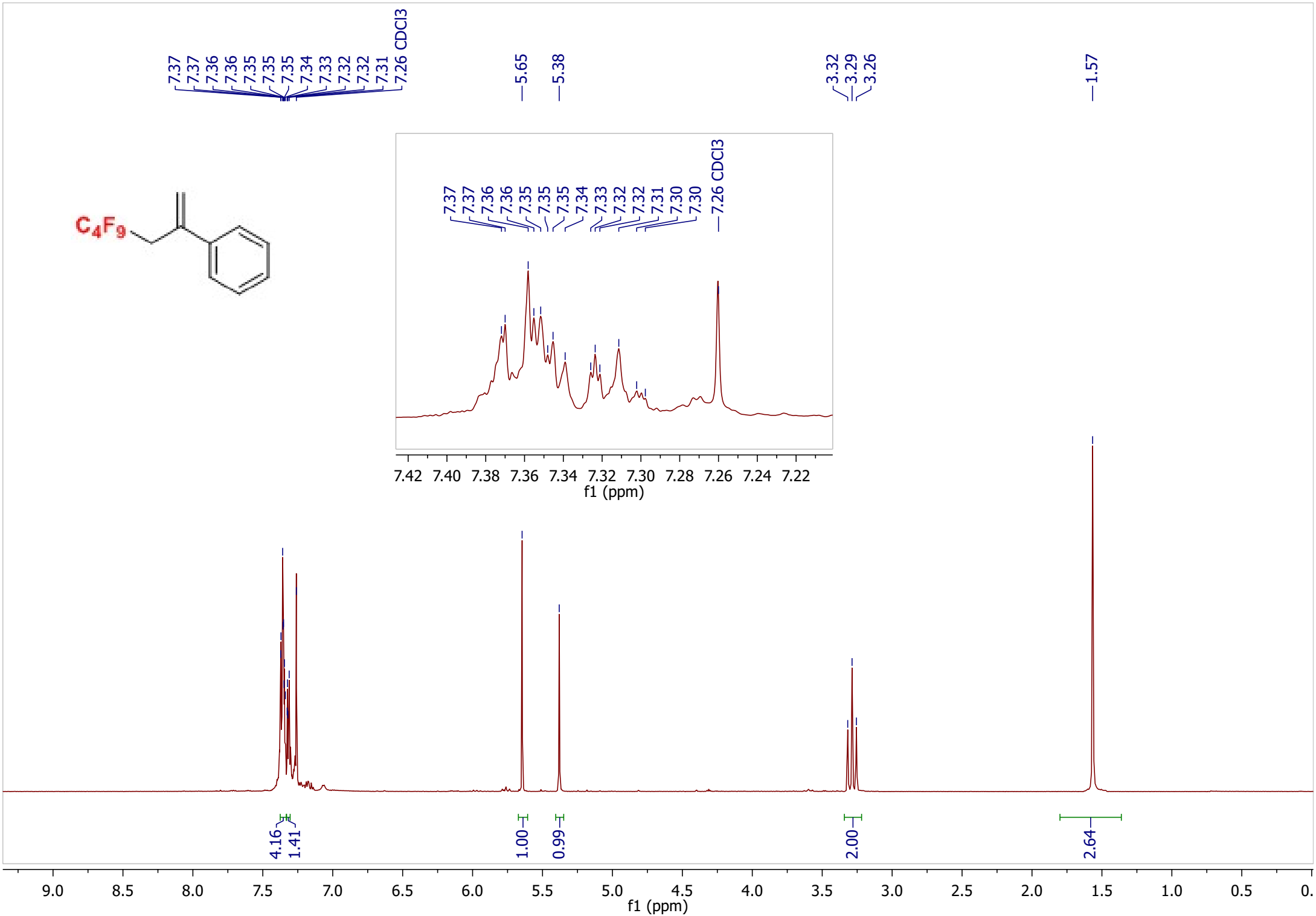


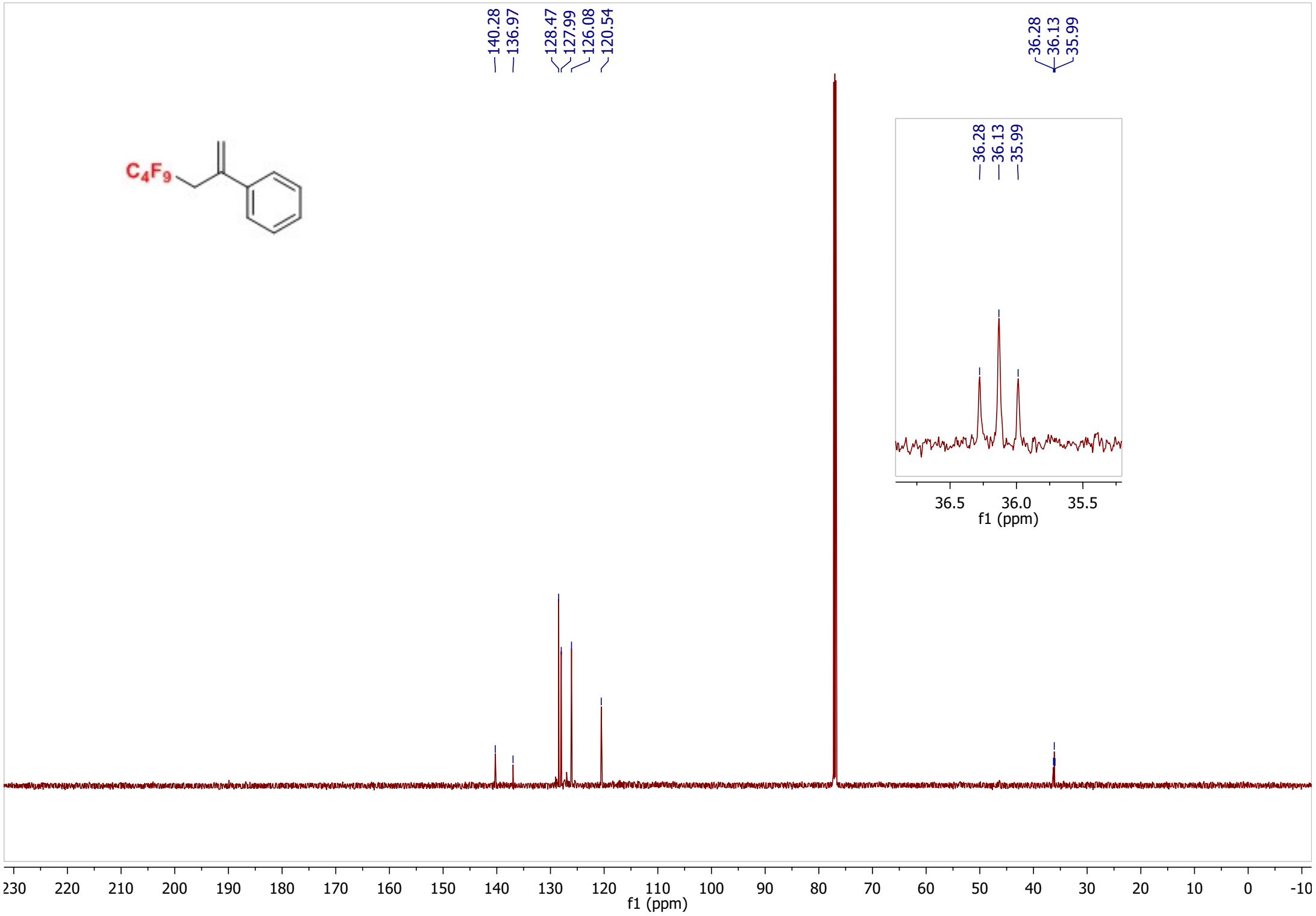
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
501.0568	1	C15H15F9NaO7	501.0566	-0.3	10.7	1	100.00	3.5	even	ok

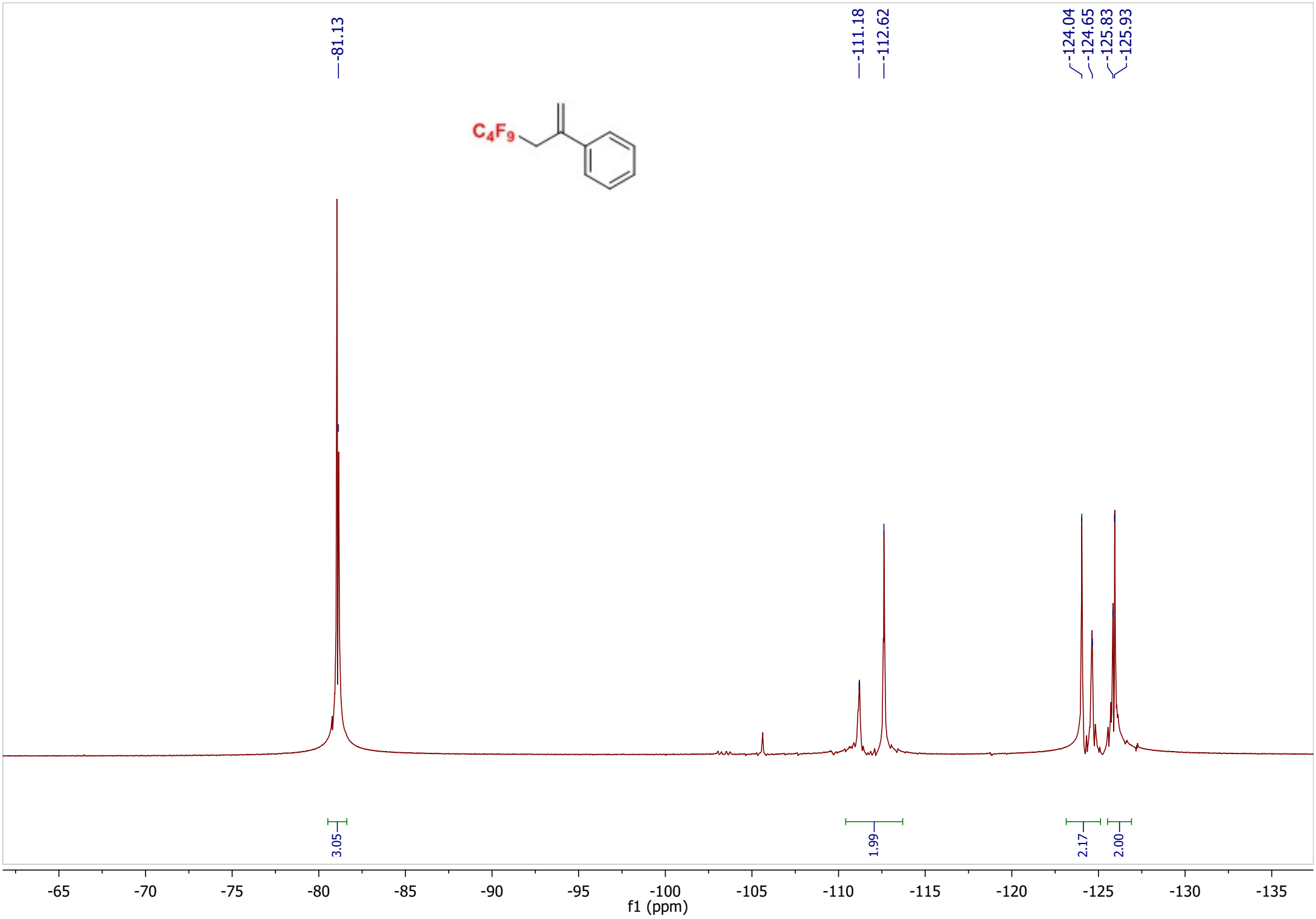

HO
SC4F9
3.75
3.74
3.73
2.75
2.74
2.74
2.73
2.73
2.72
2.19
1.42
1.41
1.40
2.12
2.11
1.00
f1 (ppm)
2.12
2.11
1.04
1.00
f1 (ppm)

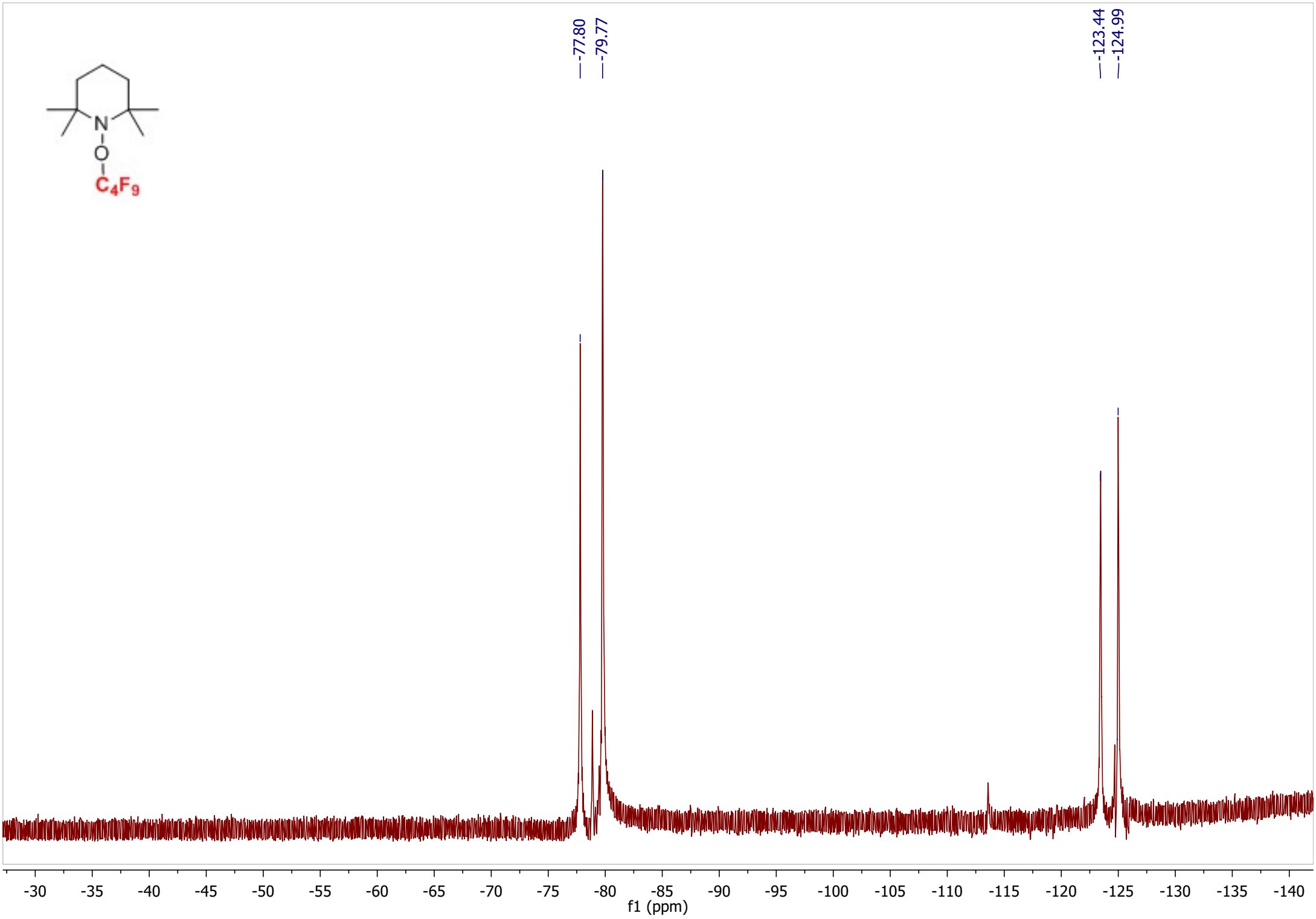

77.32 CDCl3
61.58
31.70
HO
SC4F9
f1 (ppm)


-81.06
-87.00
-120.68
-125.56
HO
SC4F9
-81.04
-81.06
-81.08
-80.0
-80.5
-81.0
-81.5
-82.0
-82.5
f1 (ppm)
3.00
2.19
2.00
2.06
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
f1 (ppm)


7.37
7.37
7.36
7.36
7.35
7.35
7.35
7.34
7.33
7.32
7.32
7.31
7.26 CDCl3
5.65
5.38
3.32
3.29
3.26
1.57
C4F9
7.37
7.37
7.36
7.36
7.35
7.35
7.35
7.34
7.33
7.32
7.32
7.31
7.30
7.30
7.26 CDCl3
7.42 7.40 7.38 7.36 7.34 7.32 7.30 7.28 7.26 7.24 7.22
f1 (ppm)
4.16
1.41
1.00
0.99
2.00
2.64
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.
f1 (ppm)


140.28
136.97
128.47
127.99
126.08
120.54
36.28
36.13
35.99
C4F9
36.28
36.13
35.99
36.5
36.0
35.5
f1 (ppm)
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
f1 (ppm)


-81.13
-111.18
-112.62
-124.04
-124.65
-125.83
-125.93
C4F9
3.05
1.99
2.17
2.00
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
f1 (ppm)


-77.80
-79.77
-123.44
-124.99
N
O
C4F9
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
f1 (ppm)