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Supporting Information

Investigating the Influence of (Deoxy)fluorination on the Lipophilicity of Non-UV-Active Fluorinated Alkanols and Carbohydrates by a New log*P* Determination Method

Bruno Linclau, Zhong Wang, Guillaume Compain, Vincent Paumelle, Clement Q. Fontenelle, Neil Wells, and Alex Weymouth-Wilson*

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SUPPORTING INFORMATION

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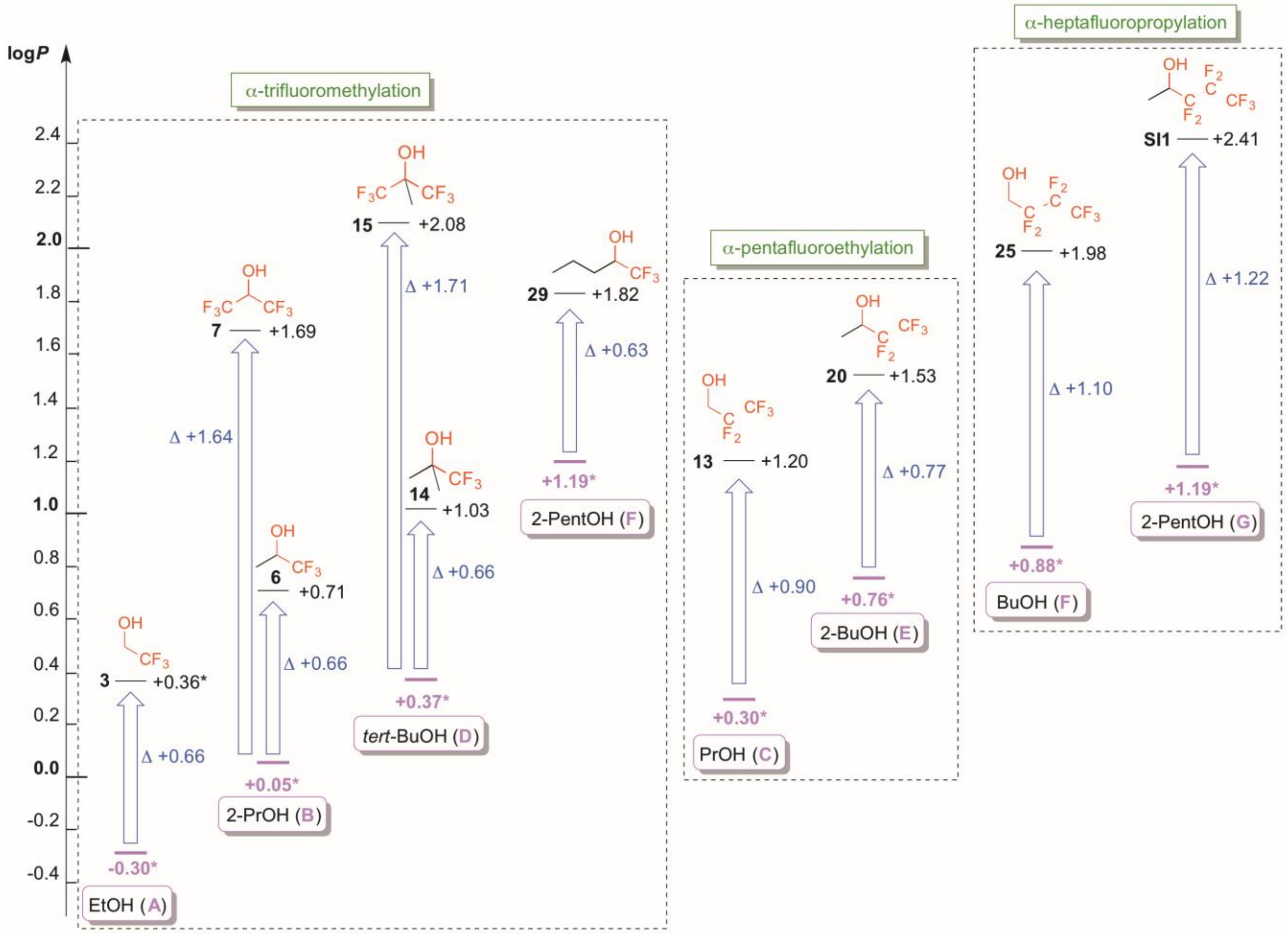
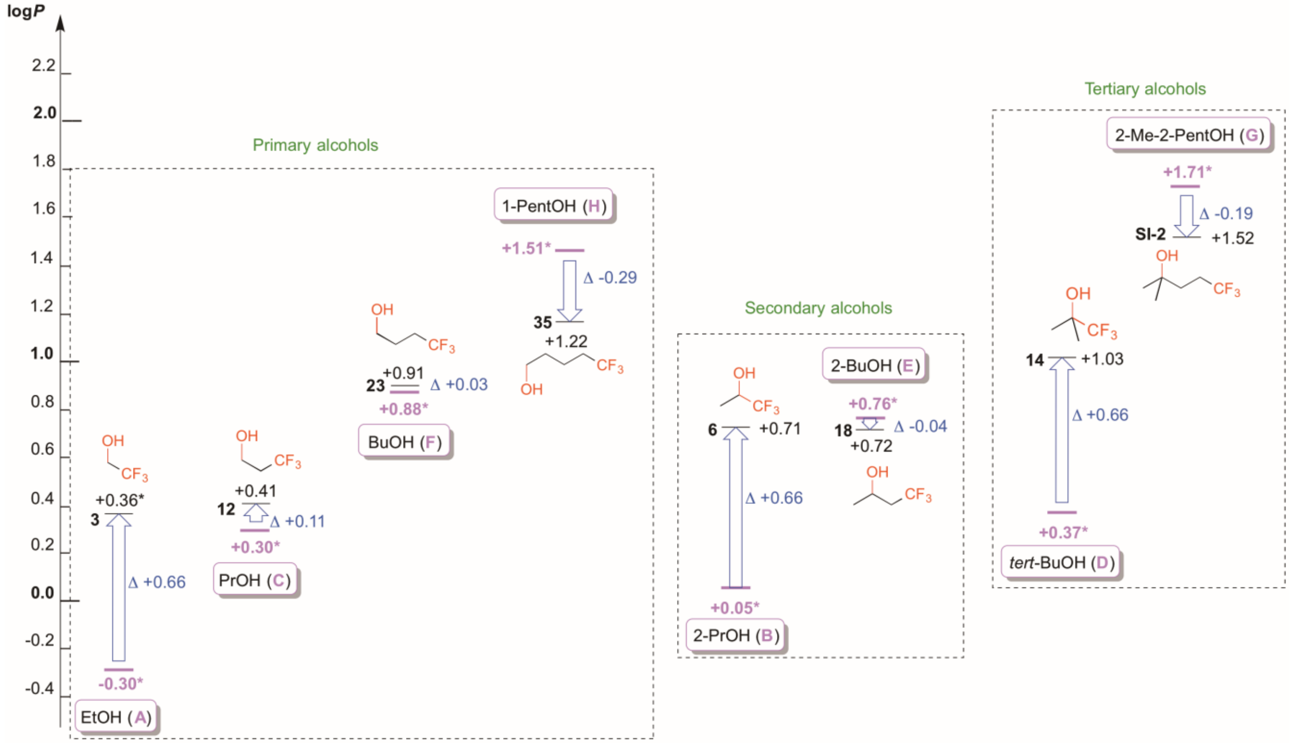


1.2. Omega-trifluoromethylation (Figure SI2)



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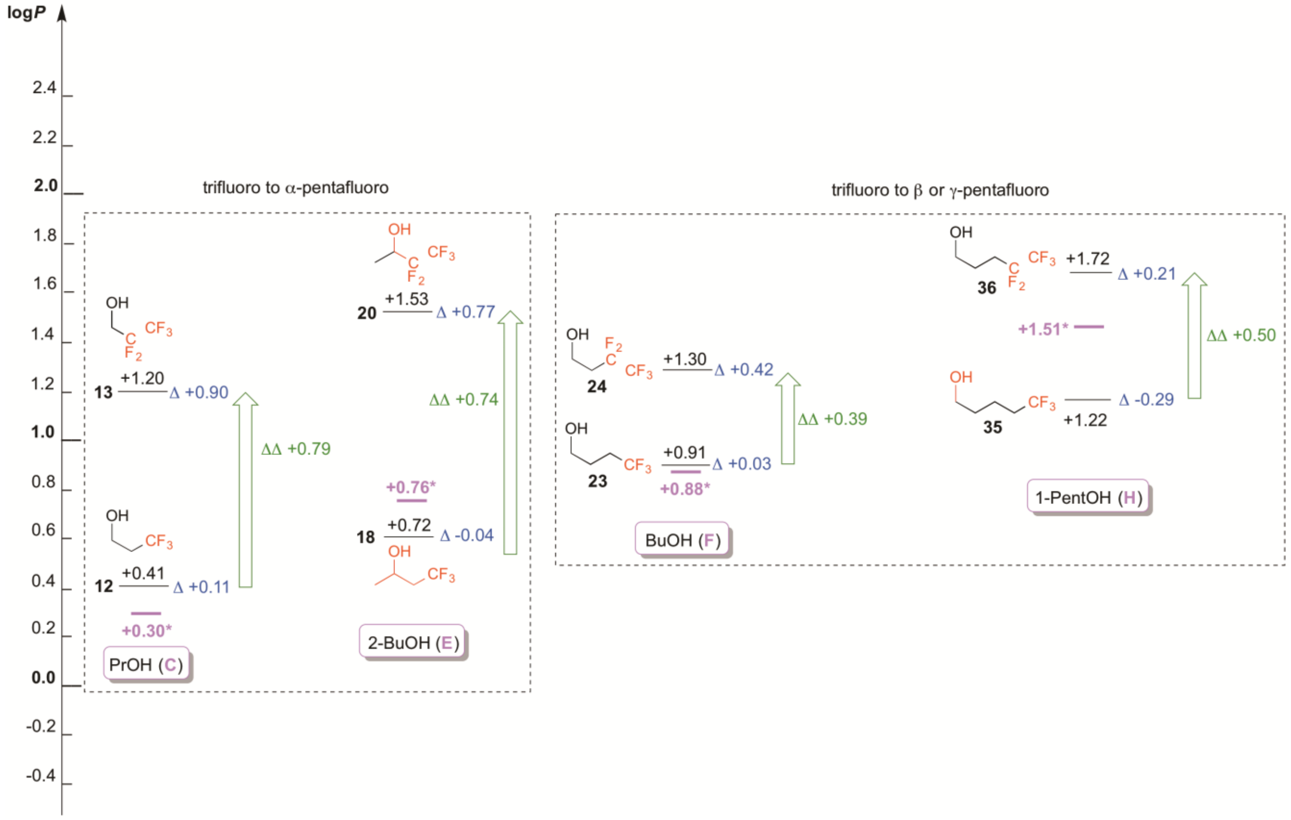

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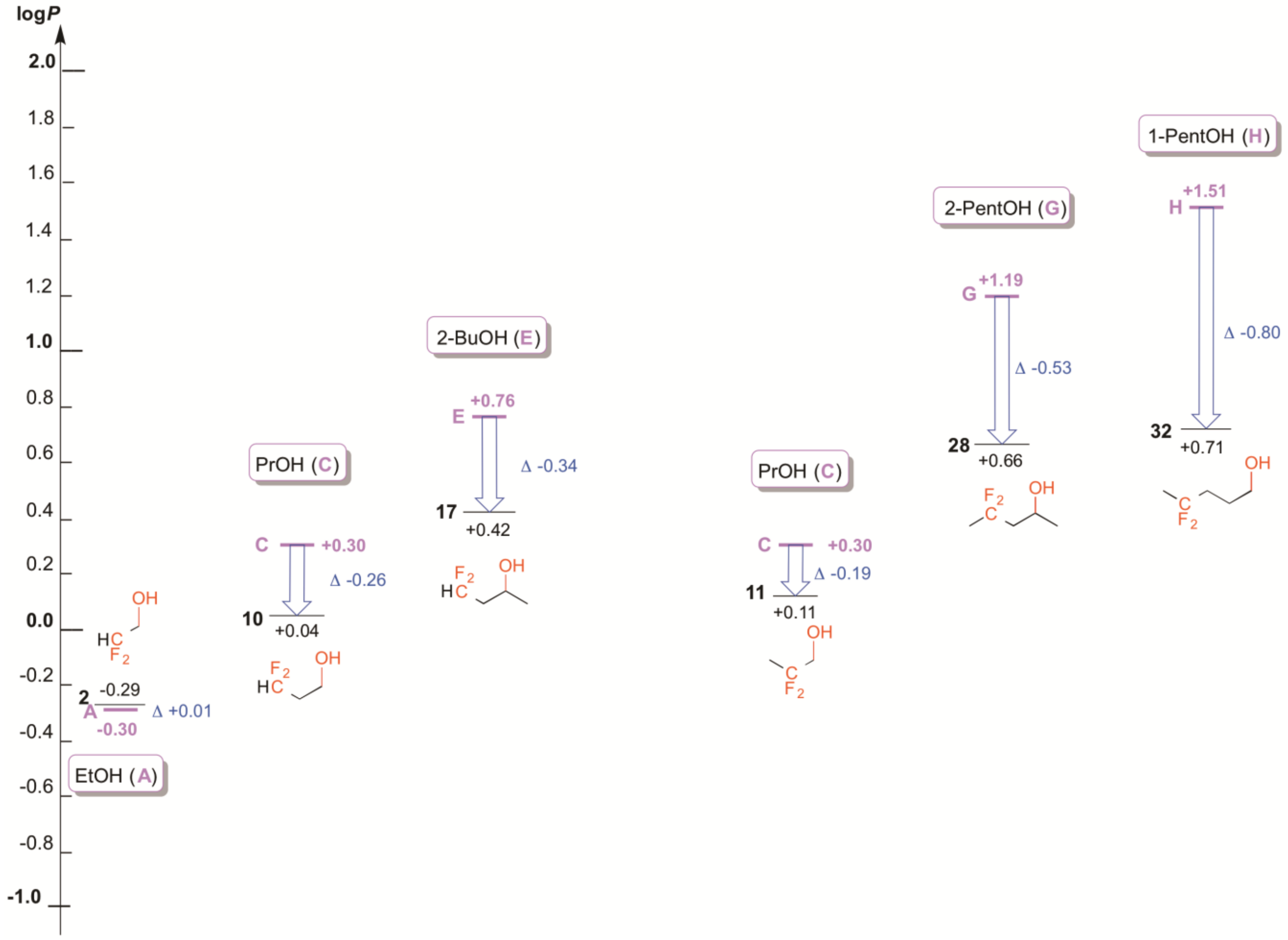

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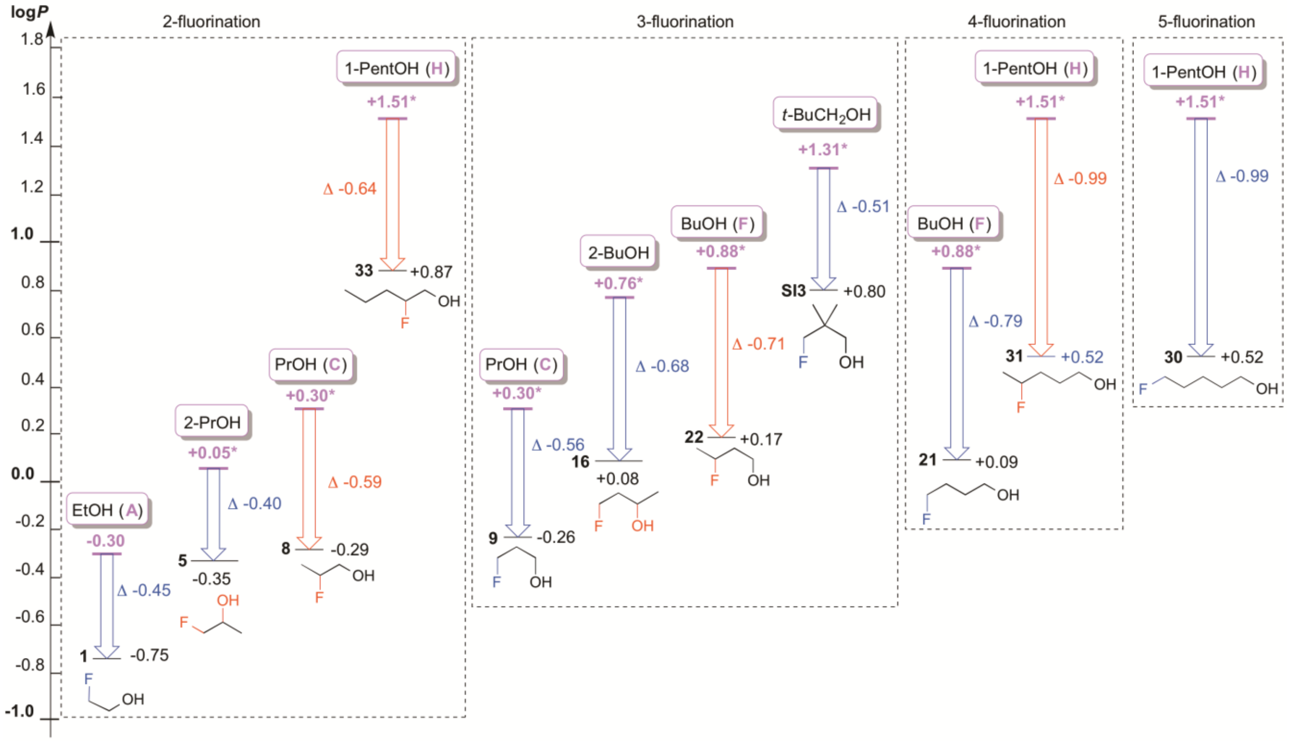

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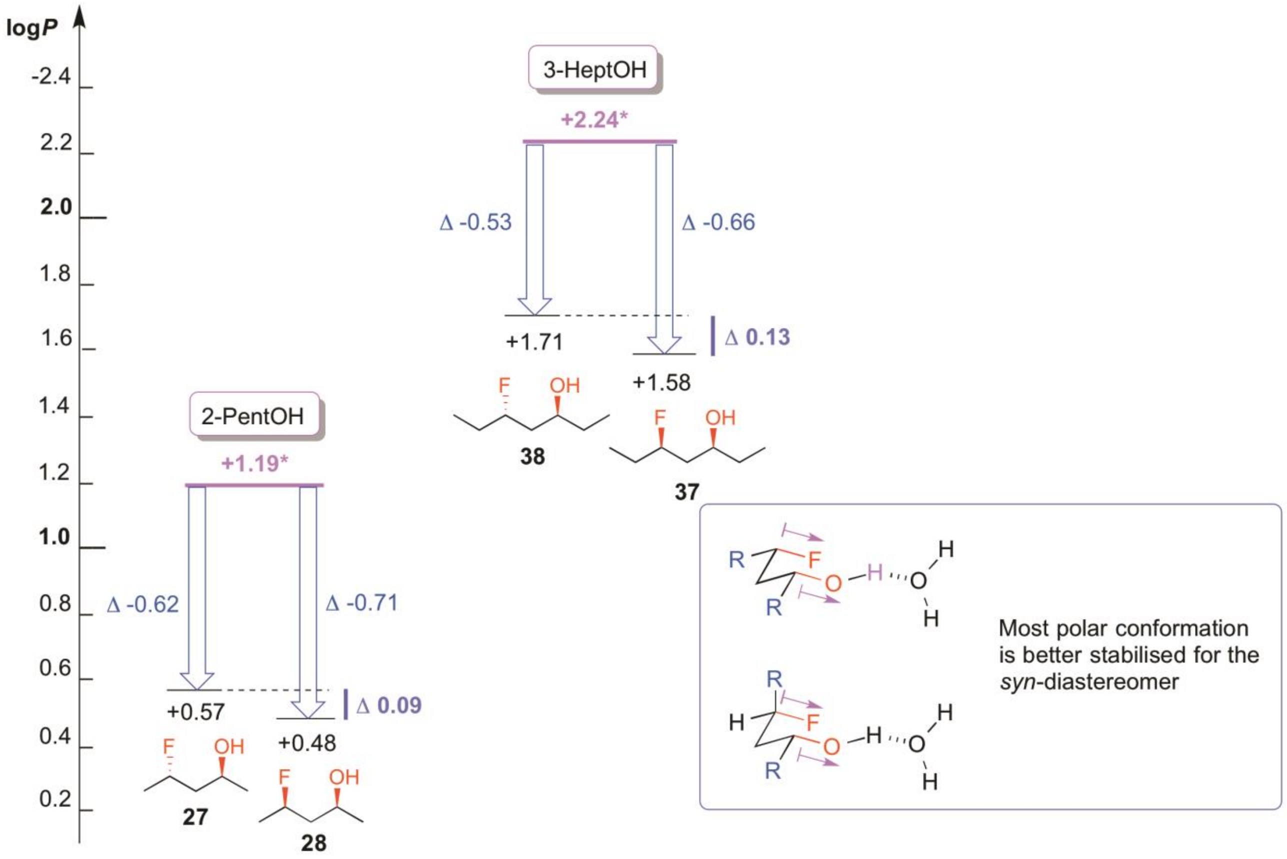
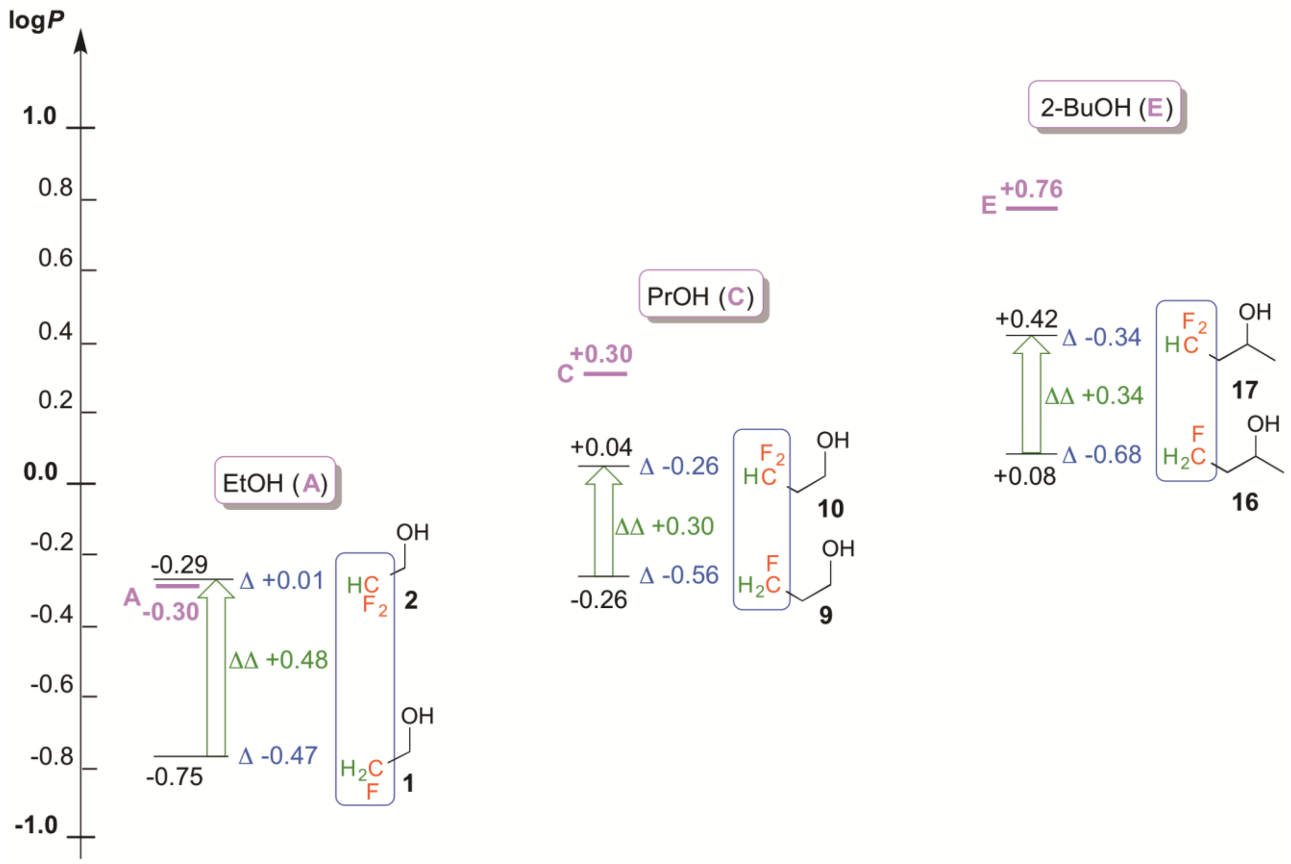


Most polar conformation is better stabilised for the *syn*-diastereomer

1.7. Adding fluorines: mono- to *gem*-difluorination 1 (Figure SI7)



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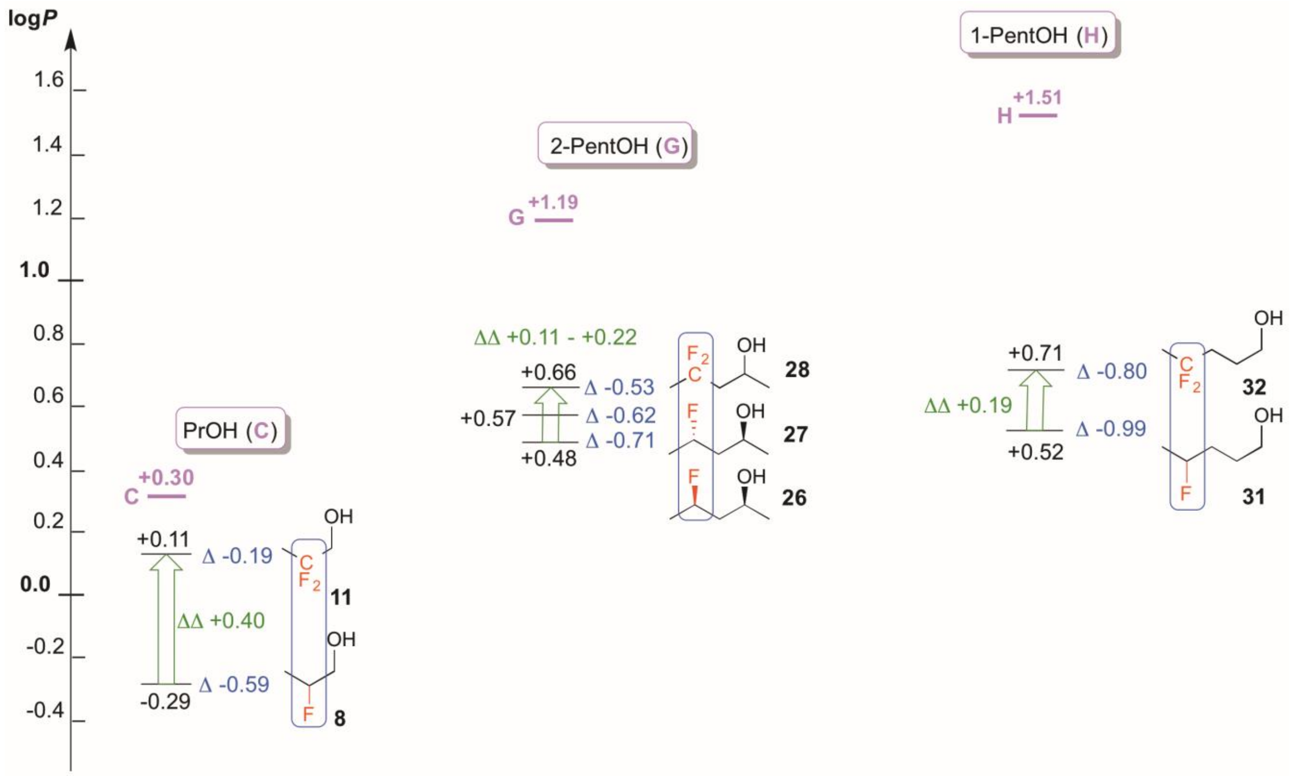

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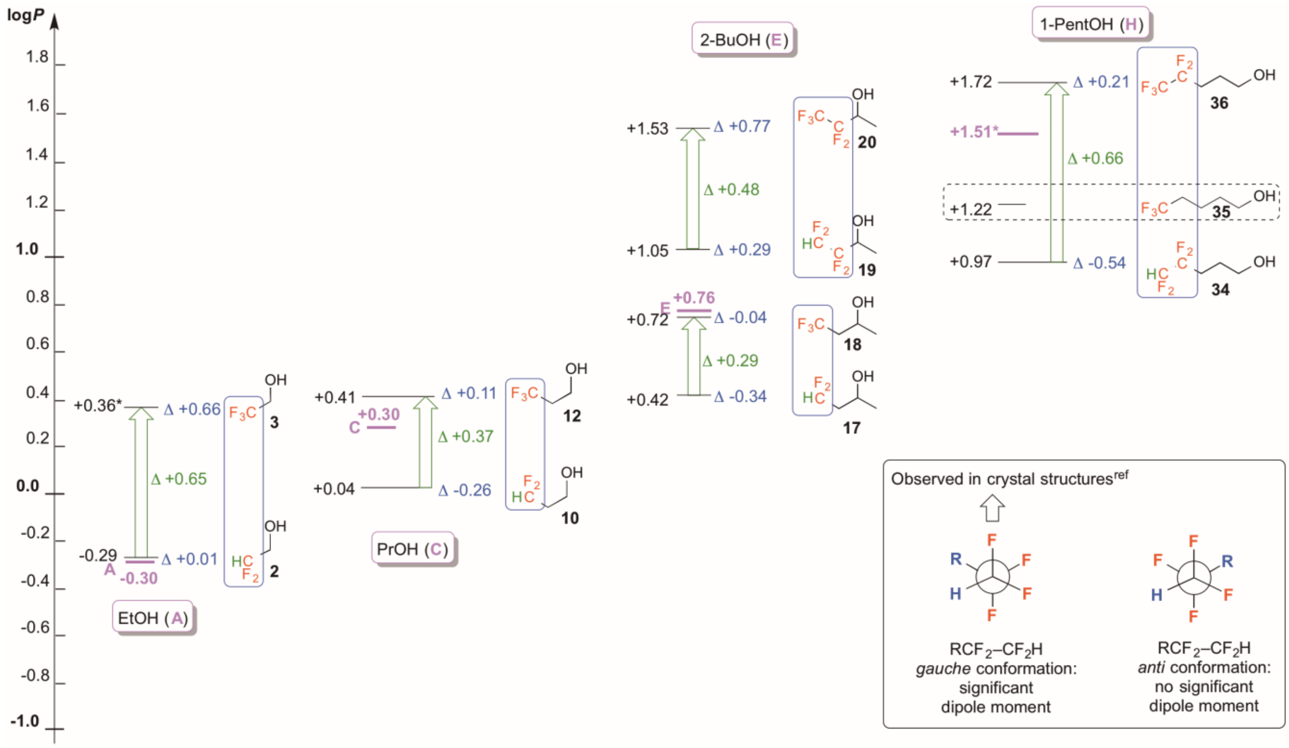

The –CF_2CF_2H *gauche*-conformation has been observed in crystal structures.[1]

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[1] (a) N. Lu, K.-Y. Lin, C.-C. Kung, J.-W. Jhuo, Y. Zhou, J. Liu, L. Sun, *RSC Adv.* **2014**, *4*, 27329-27336; (b) Q.-R. Sun, Z.-X. Chen, S. Li, Y.-M. Wu, W.-S. Tian, *Chin. J. Chem*. **2008**, *26*, 1887-1892; (c) Q.-Y. Chen, Y.-M. Wu, J. Deng, *Synlett* **2006**, 645-647; (d) Y. Xu, S. Z. Zhu, *Tetrahedron* **1999**, *55*, 13725-13734; (e) R. Touillaux, G. Germain, J. P. Declercq, M. Vanmeerssche, C. Wilante, G. Leroy, *J. Fluorine Chem*. **1982**, 20, 3-8.

2. Optimisation of the NMR method

Compound A: 2-fluoroethanol; Reference compound: 2,2,2-trifluoroethanol, log*P* +0.36;

NMR data: au0814zw2/au0814zw3 (NMR 400-3)

2.1. Importance of H-decoupling Influence of proton-decoupling (NOE)(Table SI1)

Entry 1	**SW (ppm)**	**O1P (ppm)**	**D1 (sec)**	**decoupled**	ρ_{oct}	ρ_{wat}	**log*P***	**Δlog*P***
1	300	-150	O 18.36/ W 34.97	yes	0.0832	1.0625	-0.75	0.00
2	300	-150	O 18.36/ W 34.97	no	0.0834	1.0749	-0.75	
3	250	-150	O 18.36/ W 34.97	yes	0.0821	1.0766	-0.76	-0.02
4	250	-150	O 18.36/ W 34.97	no	0.0860	1.0727	-0.74	
5	200	-150	O 18.36/ W 34.97	yes	0.0826	1.0704	-0.75	0.00
6	200	-150	O 18.36/ W 34.97	no	0.0832	1.0651	-0.75	
7	160	-150	O 18.36/ W 34.97	yes	0.0828	1.0675	-0.75	0.01
8	160	-150	O 18.36/ W 34.97	no	0.0806	1.0662	-0.76	
9	350	-70	O 18.36/ W 34.97	yes	0.0401	0.5438	-0.77	-0.01
10	350	-70	O 18.36/ W 34.97	no	0.0408	0.5379	-0.76	
11	350	-113	O 18.36/ W 34.97	yes	0.0660	0.8721	-0.76	0.00
12	350	-113	O 18.36/ W 34.97	no	0.0661	0.8672	-0.76	
13	350	-150	O 18.36/ W 34.97	yes	0.0847	1.0727	-0.74	0.01
14	350	-150	O 18.36/ W 34.97	no	0.0840	1.0723	-0.75	
15	350	-187	O 18.36/ W 34.97	yes	0.1069	1.3203	-0.73	0.00
16	350	-187	O 18.36/ W 34.97	no	0.1067	1.3217	-0.73	
17	350	-230	O 18.36/ W 34.97	yes	0.1643	2.0622	-0.74	-0.01
18	350	-230	O 18.36/ W 34.97	no	0.1686	2.0921	-0.73	
19	300	-150	O 1 / W 1	yes	0.0660	0.8082	-0.73	-0.04
20	300	-150	O 1 / W 1	no	0.0640	0.7209	-0.69	
21	300	-150	O 5 / W 5	yes	0.0746	0.8908	-0.72	-0.02
22	300	-150	O 5 / W 5	no	0.0748	0.8496	-0.70	
23	300	-150	O 18.36 / W 34.97	yes	0.0823	1.0732	-0.76	-0.01
24	300	-150	O 18.36/ W 34.97	no	0.0837	1.0704	-0.75	

As shown in the Table SI1, with the same SW, O1P, and D1 parameter settings, no large difference (up to 0.04 log*P* units) was observed for 12 pairs of experiments from using non-proton decoupled and proton-decoupled ^{19}F NMR. The integration ratios in NMR samples from both layers are also barely different. As described,[2] inverse-gated decoupling can remove the NOE and lead to a decoupled spectrum without NOE enhancement, and ''This is because any NOE that builds up during the acquisition time affects only longitudinal magnetization so does not influence the detected (transverse) signals.''

The benefit from using ^{19}F {^{1}H} NMR is that the decoupled spectrum has a higher signal-to-noise ratio (SNR), which provides higher accuracy for quantitative integration.

Conclusion: no significant influence from nOe *via* inverse gated decoupling.

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[2] T. Claridge, High-Resolution NMR Techniques in Organic Chemistry'', Pergamon, 1999, page 121, ISBN: 0080427987

2.2. Influence from SW (Table SI2)

Entry 1	SW (ppm)	O1P (ppm)	D1 (sec)	decoupled	ρ_{oct}	ρ_{wat}	logP
1	300	-150	O 18.36/ W 34.97	yes	0.0832	1.0625	-0.75
2	300	-150	O 18.36/ W 34.97	no	0.0834	1.0749	-0.75
3	250	-150	O 18.36/ W 34.97	yes	0.0821	1.0766	-0.76
4	250	-150	O 18.36/ W 34.97	no	0.0860	1.0727	-0.74
5	200	-150	O 18.36/ W 34.97	yes	0.0826	1.0704	-0.75
6	200	-150	O 18.36/ W 34.97	no	0.0832	1.0651	-0.75
7	160	-150	O 18.36/ W 34.97	yes	0.0828	1.0675	-0.75
8	160	-150	O 18.36/ W 34.97	no	0.0806	1.0662	-0.76

Note: the acquisition time is changed accordingly.

In Table SI2, with narrowing spectral width from 300 ppm to 160 ppm, the integration ratios in NMR samples from both layers as well as the final log*P* results remain nearly the same. Therefore, there is no influence from changing spectral width.

However, for compounds which are highly hydrophilic or liphophilic (hence resulting in a very low concentration in one of the phases), a narrower SW can result in higher digital resolution (dr) and high SNR, which is beneficial for quantitative integration.

2.3. Influence from O1P (Table SI3)

Entry 1	SW (ppm)	O1P (ppm)	D1 (sec)	decoupled	ρ_{oct}	ρ_{wat}	logP
9	350	-70	O 18.36/ W 34.97	yes	0.0401	0.5438	-0.77
10	350	-70	O 18.36/ W 34.97	no	0.0408	0.5379	-0.76
11	350	-113	O 18.36/ W 34.97	yes	0.0660	0.8721	-0.76
12	350	-113	O 18.36/ W 34.97	no	0.0661	0.8672	-0.76
13	350	-150	O 18.36/ W 34.97	yes	0.0847	1.0727	-0.74
14	350	-150	O 18.36/ W 34.97	no	0.0840	1.0723	-0.75
15	350	-187	O 18.36/ W 34.97	yes	0.1069	1.3203	-0.73
16	350	-187	O 18.36/ W 34.97	no	0.1067	1.3217	-0.73
17	350	-230	O 18.36/ W 34.97	yes	0.1643	2.0622	-0.74
18	350	-230	O 18.36/ W 34.97	no	0.1686	2.0921	-0.73

As indicated in Table SI3, the integration ratio in NMR sample from individual layer changed dramatically when changing the O1P setting, e.g., O1P at -70 ppm (ρ_{oct} 0.0401, Entry 9) to O1P at -350 ppm (ρ_{oct} 0.1686, Entry 17). The O1P setting is centered in Entry 13 and Entry 14, which is the optimum setting for quantitative integration.

However, the integration ratio changes seen in the two layers of a given partition experiment are increased/decreased proportionally and as a result, the obtained log*P* results remain nearly the same (with error up to 0.02 log*P* units). Because from the equation $\log P^{A} = \log P^{ref} + \log(\rho_{oct}/\rho_{wat})$, the final log*P* result depends on ρ_{oct}/ρ_{wat}, which is a ratio of a ratio. Therefore, all the systematic errors are canceled out. Due to this compensation effect, the log*P* results obtained have only very small error up to 0.02. For practical log*P* determination, the optimum O1P value (centered between the chemical shifts of the fluorine peaks) will be used. These chemical shifts, if unknown, can be obtained by initial acquisition of the respective ^{19}F NMR spectra in each solvent.

2.4. Influence from D1 (Table SI4)

	Tube Nr. 1	NMR: au0814zw2/au0814zw3 (NMR 400-3) logP -0.75					
Entry 1	SW (ppm)	O1P (ppm)	D1 (sec)	decoupled	ρ_{oct}	ρ_{wat}	logP
19	300	-150	O 1 / W 1	yes	0.0660	0.8082	-0.73
20	300	-150	O 1 / W 1	no	0.0640	0.7209	-0.69
21	300	-150	O 5 / W 5	yes	0.0746	0.8908	-0.72
22	300	-150	O 5 / W 5	no	0.0748	0.8496	-0.70
23	300	-150	O 18.36 / W 34.97	yes	0.0823	1.0732	-0.76
24	300	-150	O 18.36/ W 34.97	no	0.0837	1.0704	-0.75

In the Table SI4, NMR parameter experiments regarding pulse delay time were carried out. From the default D1 setting of 1 sec up to 5*T1 (which is the standard D1 setting for quantitative integration to allow the spins to fully relax before next pulse), the integration ratios from spectra acquired with short D1 have errors as insufficient pulse delay leads to the perturbation of the signal intensities.[3]

As the spin-lattice relaxation time (T1) for both diagnostic F nuclei are different in the octanol and water phase, systematic errors are not completely cancelled out (the compensation effect doesn't apply). Comparing Entry 20 and 24 (with non-proton decoupling), the error is up to 0.06 logP unit.

Therefore, it is recommended to have sufficient pulse delay (at least 5*T1) to obtain a more accurate integration ratio for the log*P* measurement.

2.5. Importance of S/N ratio.

For highly hydrophilic compounds, most of the compound will partition to the octanol layer. Thus, compound concentration in water layer will be relatively very low. Similarly, the concentration for highly hydrophilic compound in octanol will be very low.

Very low concentration leads to observed F signal with very low signal-to-noise ratio, which is not suitable for quantitative integration with high accuracy. The appropriate S/N ratio for quantitative analysis is recommended to be above 300:1.[4] A simple way to increase S/N ratio is to increase NS for NMR experiment.

As illustrated by the three examples below, the integration ratios obtained were increased significantly when increasing the number of scans from NS 64 to NS 4096. Interestingly, in these three cases, the integration ratios is nearly identical, leading to nearly same logP results.

Based on these examples, it is found that reliable integration ratios can be still obtained with S/N ratio lower than 100:1.

Example 1:

Reference: 2-fluorophenol, log*P* = +1.70;
NMR parameters: D1: 60 sec; SW: 100 ppm; O1P: centered.
The octanol phase [ZW7157-87-1 OCT, AVIIIHD400-3: ap0115zw3]: ρ_{oct} = 2.2293.

With NS 64 for the water phase:
[ZW7157-87-1 WAT, AVIIIHD400-3: ap0115zw4]
The reference: **S/N ratio** at δ_F -137.84 ppm**: 136.73/1**)
Compound A: **S/N ratio (**at δ_F -188.71 ppm): **89.06/1**;

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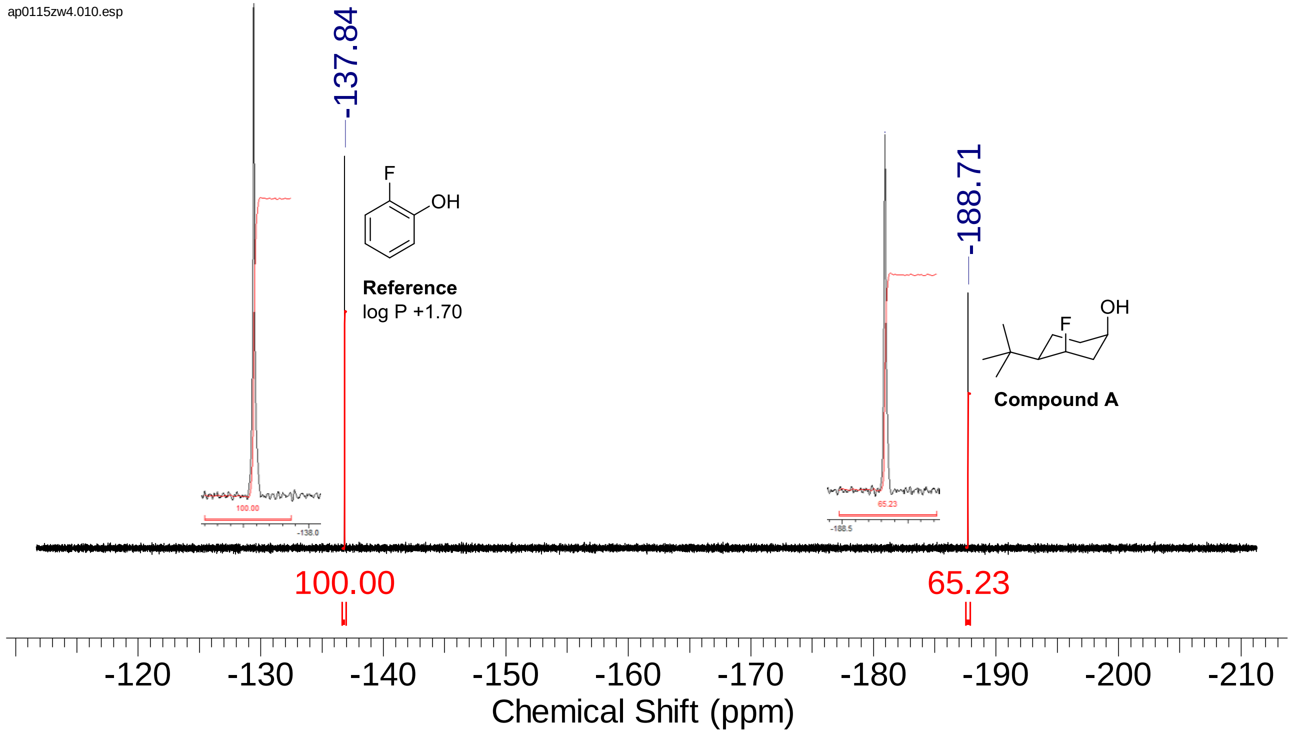
[3] T. Claridge, High-Resolution NMR Techniques in Organic Chemistry'', Pergamon, 1999, page 115, ISBN: 0080427987
[4] F.-F. Zhang, M.-H. Jiang, L.-L. Sun, F. Zheng, L. Dong, V. Shah, W.-B. Shen, Y. Ding, *Analyst* **2015**, *140*, 280-286;

The ρ_{wat} = 65.23/100.00 = **0.6523; hence log P = +2.234**



With NS 4096 for the water phase

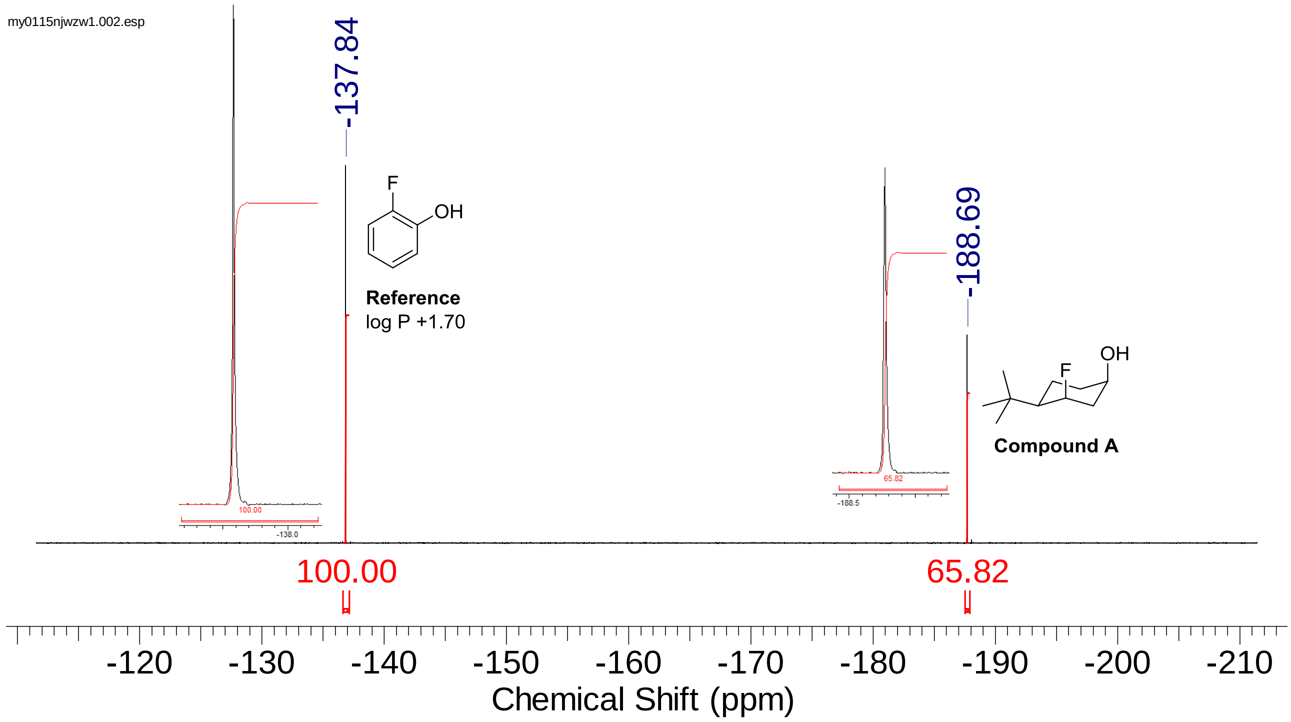
[ZW7157-87-1 WAT [AVII400-2: my0115njwzw1];

NMR parameters; D1: 60 sec; SW: 100 ppm; O1P: centered;

The reference: **S/N ratio** at δ_F -137.84 ppm: **1337.48/1;**

Compound A: **S/N ratio** at δ_F -188.71 ppm: **736.66/1**

This results in a ρ_{wat} = 65.82/100.00 = **0.6582; log P = +2.230 (ΔlogP 0.004)**



Example 2:

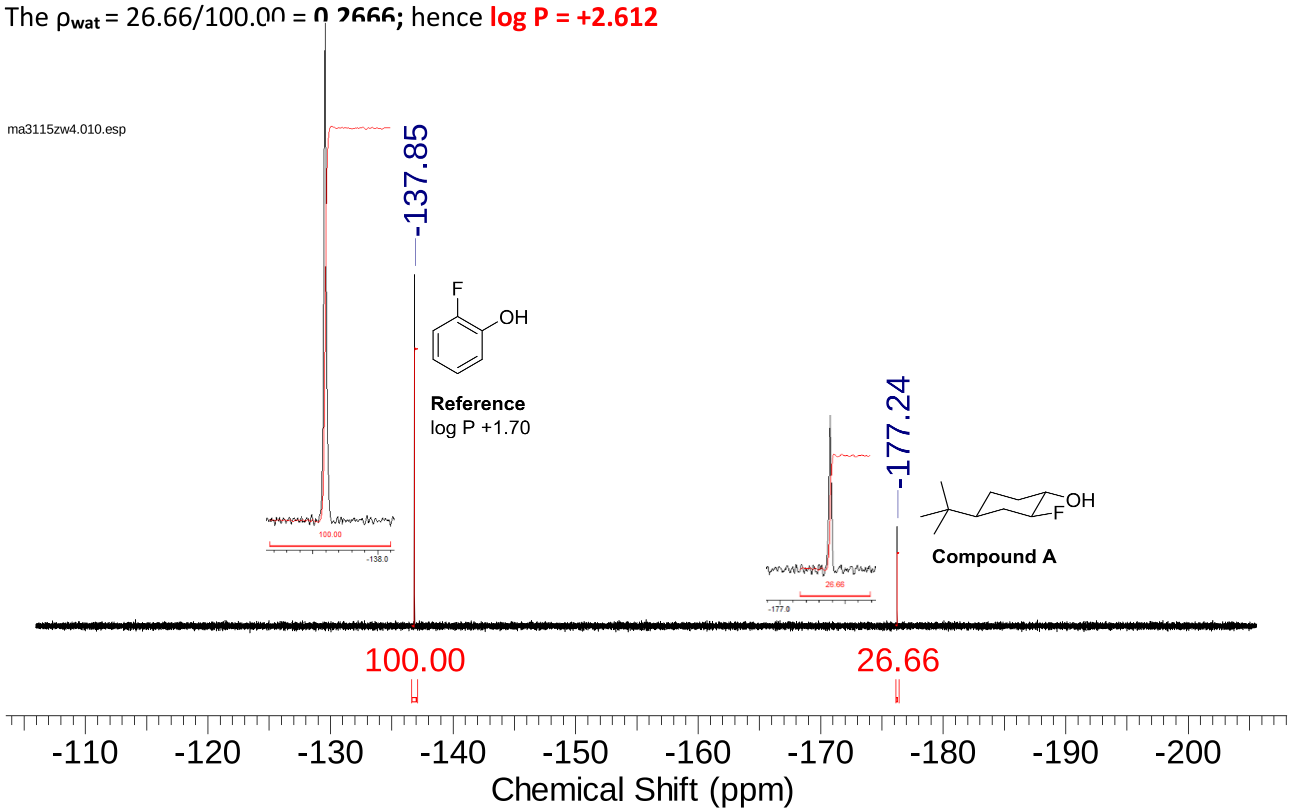
Reference: 2-fluorophenol log P +1.70;

NMR parameters: D1: 60 sec; SW: 100 ppm; O1P: centered

The octanol phase [ZW7157-82-1 OCT, AVII400-2: ma2715njwzw1]: ρ_{oct} = 2.1788

With NS 64 for the water phase:
ZW7157-82-1 WAT [AVIIIHD400-3: ma3115zw4]
The reference: **S/N ratio** at δ_F -137.85 ppm**: 129.86/1;**
Compound A: **S/N ratio** at δ_F -177.24 ppm: **36.67/1**;

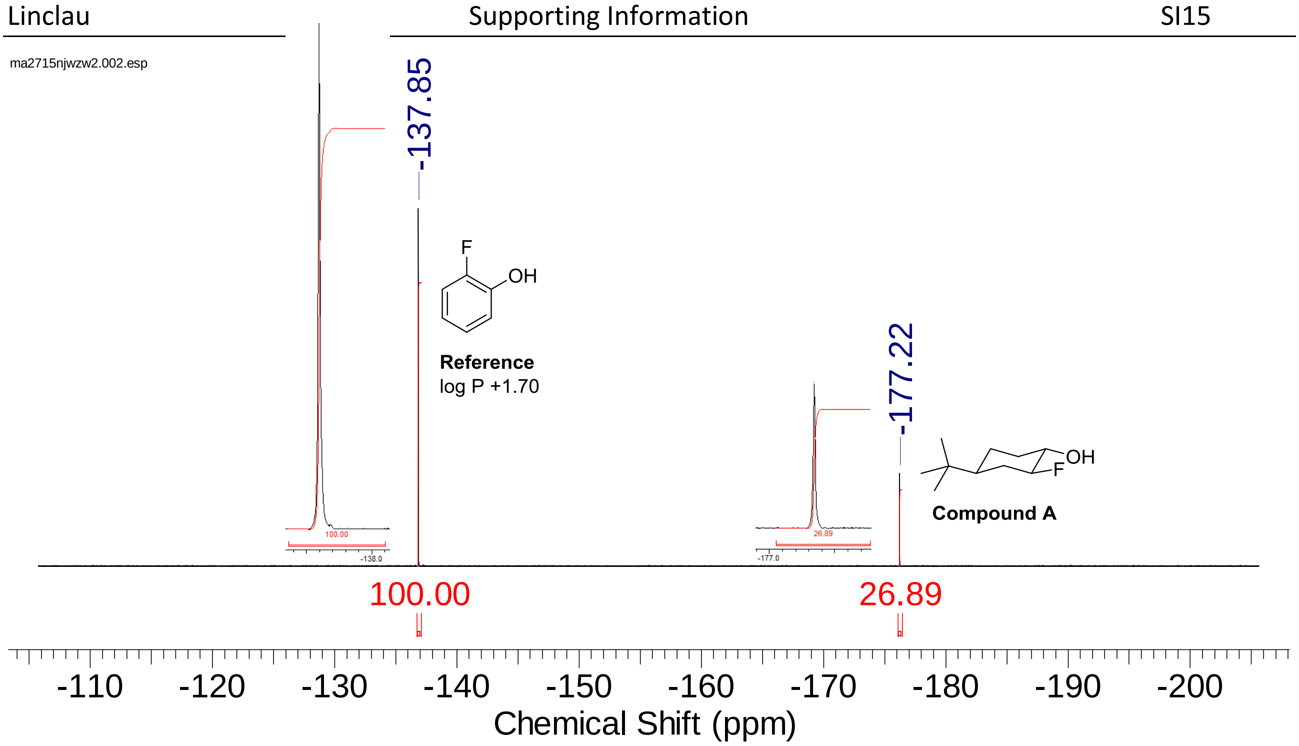
The ρ_{wat} = 26.66/100.00 = **0.2666;** hence **log P = +2.612**



With NS 4096 for the water phase:
[ZW7157-82-1 WAT [AVII400-2: ma2715njwzw2]
NMR parameters: D1: 60 sec; SW: 100 ppm; O1P: centered;

The reference: **S/N ratio** at δ_F -137.85 ppm**: 1433.39/1;**
Compound A: **S/N ratio** at δ_F -177.22 ppm: **371.30/1**;

This results in a ρ_{wat} = 26.89/100.00 = **0.2689;** hence **log P = +2.609.**



Example 3:

Reference: 2-fluorophenol log P +1.70

NMR parameters: D1: 60 sec; SW: 300 ppm; O1P: centered

The octanol phase [ZW7157-44 OCT, AVIIIHD400-3: nv1214zw3]: ρ_{oct} = 1.4736

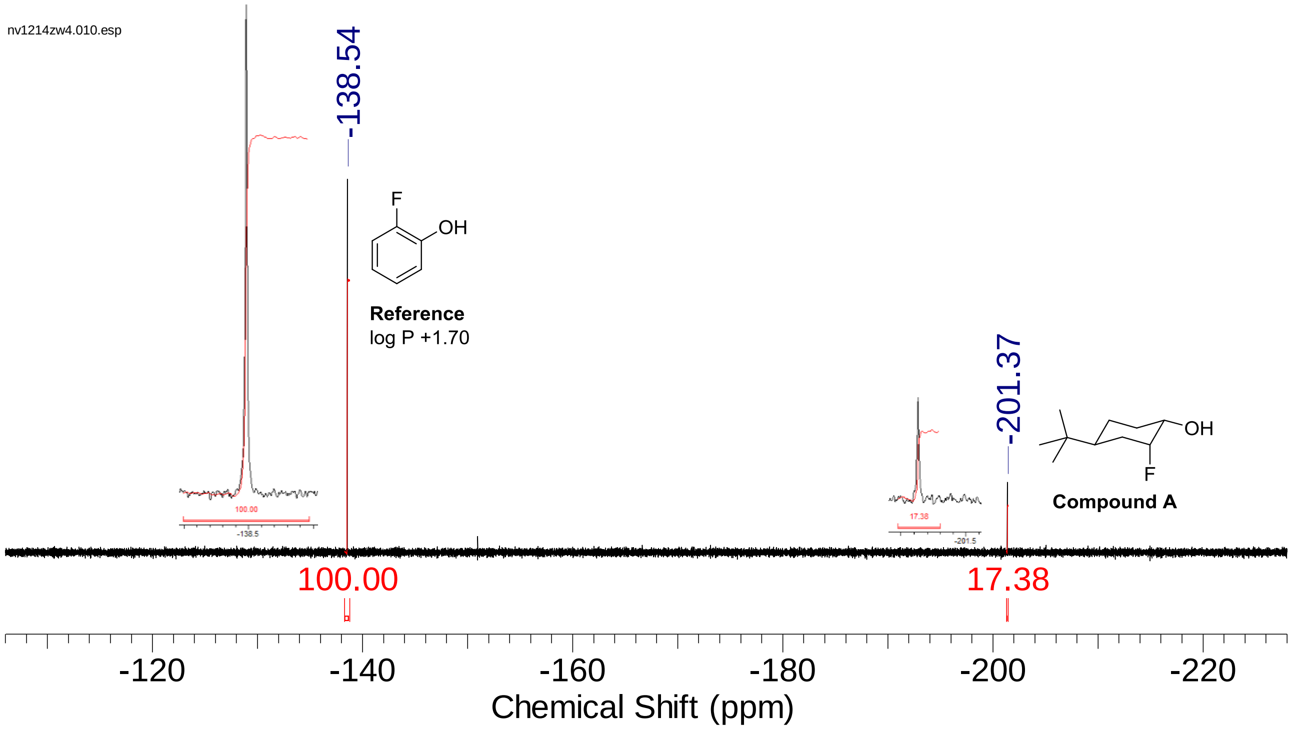
With NS 64 for the water phase:

ZW7157-44 WAT [AVIIIHD400-3: nv1214zw4];

The reference: **S/N ratio** at δ_F -138.54 ppm**: 114.34/1;**

Compound A: **S/N ratio** at δ_F -201.37 ppm: **21.51/1**;

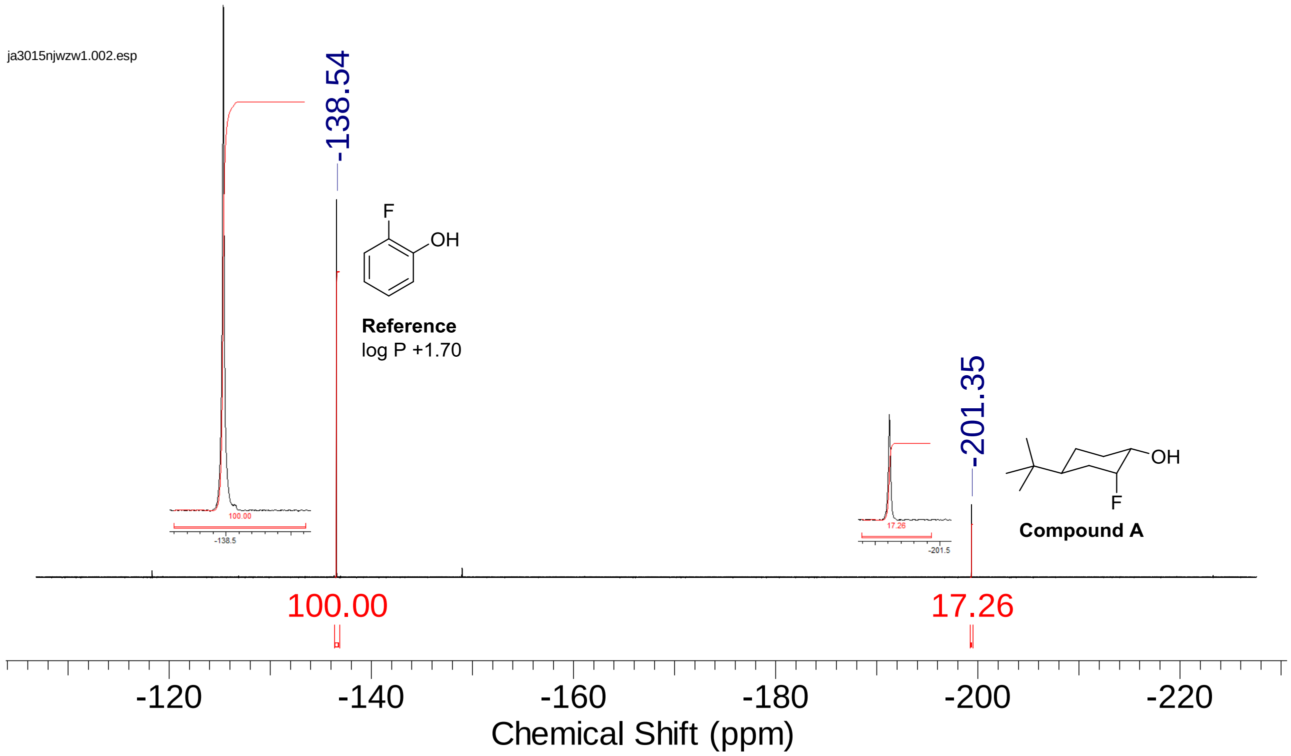
The ρ_{wat} = 17.38/100.00 = **0.1738;** hence **log P = +2.628**



With NS 4096 for the water phase:
ZW7157-44 WAT capillary for lock [AVII400-2: ja3015njwzw1];
NMR parameters: D1: 60 sec; SW: 120 ppm; O1P: centered;

The reference: **S/N ratio** at δ_F -138.54 ppm**: 1194.16/1;**
Compound A: **S/N ratio** at δ_F -201.35 ppm: **229.99/1**;

The $\rho_{\mathbf{wat}}$ = 17.26/100.00 = **0.1726;** hence **log P = +2.631**



3. T1 measurements

The spin-lattice relaxation time (T1) is a molecular property, depending on many external factors, such as impurities, oxygen content, temperature, solvent/solvent systems, compound concentration, etc. The NMR sample prepared from log*P* experiments is individually different (e.g., compound concentration, and compound mixture). In addition, an amount of acetone-d_6 is added as solvent lock, the volume of which is not precisely measured. Hence, there are no reported T1 values in the literature for such compounds in this solvent mixture. Therefore, T1 values for individual NMR tubes of the diagnostic F nucleus were measured, in order to allow appropriate D1 settings for accurate quantitative integration. The T1 value was measured for the appropriate F nucleus using inversion-recovery sequence.

3.1. Protocol

The test sample in a sealed tube was inserted into the NMR spectrometer. Following automatic locking and gradient shimming, a simple ^{19}F spectrum was recorded on the non-spinning sample to assess the required SW and frequency offset (o1p). The 90° pulse was measured with the automated pulsecal routine (if the signal:noise was sufficient, else manually by adjusting the pulse width to find the signal null at the 360° pulse). The measured 90° pulse (and thus, calculated 180° pulse), SW and o1p were transferred into the inversion-recovery experiment and number of scans selected to afford suitable signal:noise for the calculation. The data were transferred into the “TopSpin T1/T2 Module” and fitted to provide the measured T1 value.

3.2. Results (Table SI5)

T1 measurement (sec)

		CF_3CH_2OH		FCH_2CH_2OH	
Entry	Experiment	Oct	Wat	Oct	Wat
1	VP7220-96-1	3.085	3.597	**3.671**	**6.994**
2	VP7220-96-2	2.298	2.884	**2.883**	**7.908**
3	VP7220-96-3	2.474	3.98	**3.78**	**7.219**
				$FCH_2CH(OH)CH_2F$	
4	VP7365-1-1	2.008	3.993	**2.737**	**5.946**
				CHF_2CH_2OH	
5	VP7365-2-1	2.377	4.089	**2.562**	**4.282**
				$CH_3CHF_2CH_2OH$	
6	VP7220-94-1	**2.343**	**4.177**	2.302	3.801

		CF_3CH_2OH		$CF_3CF_2CH_2OH$		$CF_3CF_2CH_2OH$	
		Oct	Wat	Oct	Wat	Oct	Wat
7	ZW7157-26-3	**2.394**	**4.223**	2.393	3.951	2.101	3.492
8	ZW7157-26-1	2.363	**4.062**	**2.406**	3.892	2.131	3.414
		$CF_3CF_2CH_2OH$		$CF_3CF_2CH_2OH$		FCH_2CH_2OH	
9	ZW7157-28-1	2.424	3.948	2.195	3.743	**4.589**	**7.663**
10	ZW7157-28-2	2.466	3.779	2.241	3.666	**3.953**	**7.615**
11	ZW7157-28-3	2.185	3.917	1.947	3.378	**3.347**	**7.229**

In all cases, the mixture of two compounds is partitioned between octanol and water, the phases separated, an aliquot of each phase transferred to an individual NMR tube, a quantity of acetone-d_6 added, and the tube sealed.

Entries 1–3 represent three experiments in which a mixture of trifluoroethanol and fluoroethanol is used (prepared independently, using different amounts of compound). It is easily seen that the determined T1 value varies between the different experiments. The same is observed in entries 7,8 and 9–11.

Overall, it can be seen that T1 for monofluorinated compounds are longer than that of di-and trifluorinated compounds. Also, the T1 in the octanol sample is shorter than that from the water sample.

The longest T1 value in octanol was observed for 2-fluoroethanol with T1 value of 4.589 sec (< 5 sec). Similarly, the longest T1 value in water NMR sample was observed for 2-fluoroethanol with T1 value of 7.908 sec (< 8 sec).

Because T1 determinations are very timeconsuming, and based on the dataset collected, **for practical purposes it is recommended to use a D1 of 30 sec for the octanol sample and of 60 sec for the water sample as pulse delay, given the D1 value should be greater than 5*T1 for quantitative integration.**

4. Influence of Intermolecular interactions (Table SI6)

(Concentration of samples – how much material can be used)

ca. 2 mL of octanol and ca. 2 mL of water were used for each partition;

Compound A: $CF_3CF_2CH_2OH$ (lit log*P* 1.23, see below Table SI12); Reference compound: CF_3CH_2OH;

Entry	**m_A* (mg)**	**m_{REF}* (mg)**	ρ_{oct}	ρ_{wat}	log*P*	average (error)
1	2.0	0.8	2.1983 (oc0214zw1)	0.3163 (oc0214zw2)	1.202	+1.200 (±0.001)
2	2.0	0.8	1.9761 (oc0214zw3)	0.2854 (oc0214zw4)	1.200	
3	2.0	0.8	2.3148 (oc0214zw5)	0.3352 (oc0214zw6)	1.199	
4	10.0	4.0	2.1598 (se1914zw1)	0.3117 (se1914zw2)	1.201	+1.199 (±0.003)
5	10.0	4.0	2.1723 (se1914zw3)	0.3140 (se1914zw4)	1.200	
6	10.0	4.0	2.1231 (se1914zw5)	0.3105 (se1914zw5)	1.195	
7	70.0	30.0	2.2576 (ju1215zw25)	0.3404 (ju1215zw26)	1.182	+1.181 (±0.001)
8	70.0	70.0	2.2214 (ju1215zw27)	0.3346 (ju1215zw28)	1.182	
9	70.0	70.0	2.2991 (ju1215zw29)	0.3488 (ju1215zw30)	1.179	
10	120.0	60.0	1.8726 (ju1215zw31)	0.2886 (ju1215zw32)	1.172	+1.175 (±0.002)
11	120.0	60.0	1.8875 (ju1215zw33)	0.2872 (ju1215zw34)	1.178	
12	120.0	60.0	1.9581 (ju1215zw35)	0.3002 (ju1215zw36)	1.174	

*The amount of compound A/REF used is the approximate mass.

As shown in the table, the difference of logP value due to **significantly** increased concentration (from 2 mg to 120 mg regarding substrate load of compound A) is only -0.025. Based on this dataset, it is proposed that intermolecular interactions have negligible influence for the substrate used.

The quantity that is generally used is between 5-10 mg.

5. Detailed logP determination protocol

1) Partitioning

To a 10 mL pear-shaped flask was added octanol (HPLC grade, ca. 2 mL), compound A (ca. 1–10 mg), reference compound R (ca. 1–10 mg, *primary reference 2,2,2-trifluoroethanol*) and water (HPLC grade, ca. 2 mL). The resulting biphasic mixture was stirred at 25 °C (temperature controlled by recirculating chiller) for 2 hours and then left to stand at 25 °C overnight to enable complete phase separation. In some cases the formation of a foam was observed, which resided at the octanol-water phase boundary. In this case, the vial was centrifuged for until disappearance of the foam.

2) Sample preparation

Using two 1 mL disposable syringes, ca. 0.7 – 0.85 mL was carefully taken from each layer. In particular for taking a water sample aliquot, ca. 0.05 mL of air was taken into syringe before putting the needle into the solution, and while moving through the upper octanol layer, the air was gently pushed out, in order to avoid the contamination of octanol phase, as very small amount of octanol phase may otherwise enter into the needle (which would cause a big error for lipophilic compounds). Upon reaching the water phase, all air bubbles are pushed out of the syringe, the aliquot takes, and the needle quickly removed from the solution. Then a small amount of water phase was discarded (to ensure all traces of octanol are out of the needle, leaving ca. 0.6 mL sample in the syringe. The needle was carefully wiped with dry tissue and then ca. 0.5 mL of sample was injected into the new NMR tube, followed by addition of ca. 0.1 mL acetone-d_6. The NMR tube was sealed (checking for leaks) using a blow torch, and inverted carefully for 20 times to obtain a homogenous solution for NMR measurement.

3) NMR measurement

^{19}F {^{1}H} NMR was firstly run with standard parameter conditions for chemical shift identification. The frequency offset point (O1P) is centered between the two diagnostic F signals. If T1 values had not been determined, a D1 of 30 sec for the octanol sample, and 60 sec for the water sample is chosen. The spectral width (SW) is left at 300 ppm (but can be reduced to obtain better SNR ratio is required (should be >250)). The number of transients (NS) is left at 64 (but can be increased if higher SNR is required).

4) Data processing

Data were processed using ACD/Labs NMR software.

The obtained FID file was reprocessed using following conditions: WFunction (LB 2 Exponential), Zero Filling (from 65536 to 262144) and then Fourier transform, followed by phasing with mouse and auto baseline correction. The integration ratio was obtained by manual integration (bias correction can be applied *via* adjusting tilt and slope if integral curve is not parallel to the baseline).

6. Reproducibility of the method

6.1. Multiple acquisitions (Table SI7)

In this control experiment, 2-fluoro-pentan-1-ol and 2,2,2-trifluoroethanol (reference compound) were partitioned between octanol and water, giving two NMR samples.

Sample: ZW7157-98-1 OCT (AVIIIHD400-3)
ZW7157-98-1 WAT (AVIIIHD400-3)

For each tube, seven acquisitions were taken, leading to seven sets of ρ values, giving seven log*P* values. As can be seen in the Table, the error is negligible.

Entry	**ρ_{oct} (ZW7157-98-1 OCT)**	**ρ_{wat} (ZW7157-98-1 WAT)**	**log*P***
1	0.5138 (my2315zw5)	0.3580 (my2315zw6)	0.5169
2	0.5138 (my2415zw1)	0.3550 (my2415zw2)	0.5206
3	0.5119 (my2615cqf2)	0.3574 (my2615cqf3)	0.5160
4	0.5116 (my2815cqf3)	0.3520 (my2815cqf4)	0.5224
5	0.5159 (ju0115cqf3)	0.3493 (ju0115cqf4)	0.5294
6	0.5085 (ju0315cqf6)	0.3510 (ju0315cqf7)	0.5210
7	0.5038 (ju1215zw23)	0.3475 (ju1215zw24)	0.5213
Average	0.5113	0.3529	0.5211
Standard deviation	**±0.0037 (0.73%)**	**±0.0037 (1.06%)**	**±0.0040 (0.77%)**

6.2. Multiple reprocessing (Table SI8)

In this control experiment, 2-fluoro-petan-1-ol and 2,2,2-trifluoroethanol (reference comopound) were partitioned between octanol and water, giving two NMR samples.

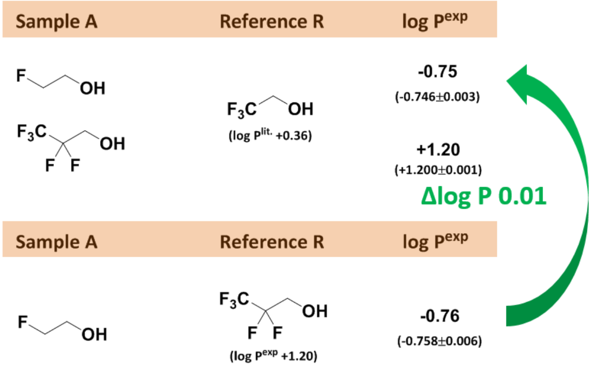
Sample: ZW7157-98-1 OCT (AVIIIHD400-3: my2315zw5)
ZW7157-98-1 WAT (AVIIIHD400-3: my2315zw6)

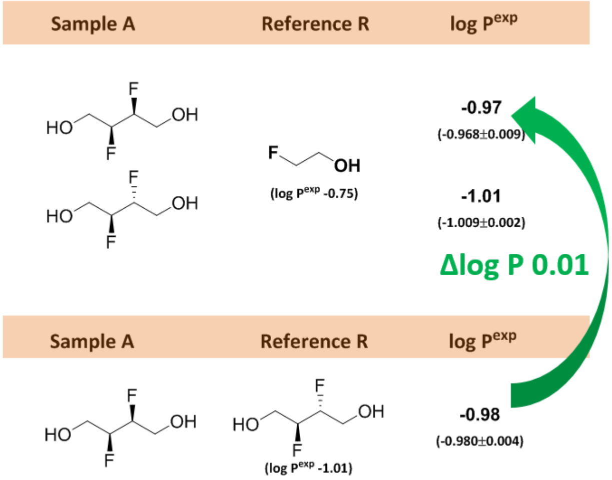
The obtained FID file of each was reprocessed using following conditions: WFunction (LB 2 Exponential), Zero Filling (from 65536 to 262144) and then Fourier transform, followed by phasing with mouse and auto baseline correction. The integration ratio was obtained by manual integration (bias correction can be applied *via* adjusting tilt and slope if integral curve is not parallel to the baseline). This was done 7 times independently. As can be seen in the Table, the error is negligible.

Entry	**ρ_{oct} (ZW7157-98-1 OCT)**	**ρ_{wat} (ZW7157-98-1 WAT)**	**log*P***
1	0.5138	0.3580	0.5169
2	0.5108	0.3594	0.5127
3	0.5143	0.3554	0.5205
4	0.5128	0.3575	0.5167
5	0.5146	0.3588	0.5166
6	0.5140	0.3544	0.5215
7	0.5146	0.3572	0.5186
Average	**0.5136**	**0.3572**	**0.5176**
Standard deviation	**±0.0013 (0.25%)**	**±0.0017 (0.46%)**	**±0.0027 (0.52%)**

7. Validation of the method.

7.1. Internal validation (Tables SI9,10)

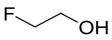
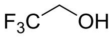
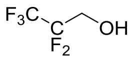
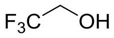
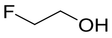
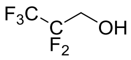
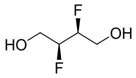
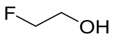


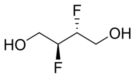
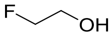


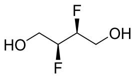
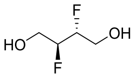
The log*P* of two compounds **1** and **13** is measured using trifluoroethanol as a reference. Then, the log*P* of **1** is measured using the just determined log*P* value of **13** as reference, and the two log*P* values of **1** are then compared.

Two examples are given, and in both cases both log*P* values only differ by 0.01 units. This indicates that the nature of the reference does not influence the log*P* determination.

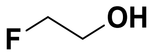
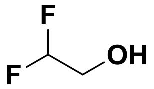
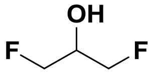
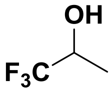
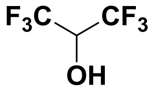
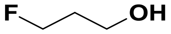
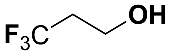
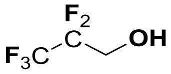
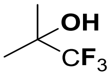
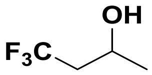
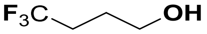
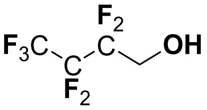
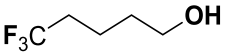
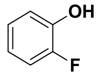
The raw data for these experiments are given in **Table SI11** (all measurements are carried out in triplicate):

Sample A	Reference	Experiment (octanol/water)	ρ_{oct}/ρ_{wat}	log*P*	Average log*P*	error
	 +0.36	au0814zw2/ au0814zw3	0.0832/ 1.0625	-0.746	-0.75	-0.746 (±0.003)
		au2614zw8/ au2614zw9	0.1102/ 1.4167	-0.749		
		au2614zw10/ au2614zw11	0.1040/ 1.3137	-0.741		
	 +0.36	oc0214zw1/ oc0214zw2	2.1983/ 0.3163	+1.202	+1.20	1.200 (±0.001)
		oc0214zw3/ oc0214zw4	1.9761/ 0.2854	+1.200		
		oc0214zw5/ oc0214zw6	2.3148/ 0.3352	+1.199		
	 +1.20^EXP	oc2414zw5/ oc0314zw2	0.1409/ 13.0222	-0.766	-0.76	-0.758 (±0.006)
		oc0314zw3/ oc0314zw4	0.1612/ 14.4914	-0.754		
		oc0314zw5/ oc0314zw6	0.1436/ 12.9114	-0.754		
	 -0.75	nv2914zw3/ nv2914zw4	1.5649/ 2.5229	-0.957	-0.97	-0.968 (±0.009)
		nv2914zw5/ nv2914zw6	1.3398/ 2.2144	-0.968		
		nv2914zw7/ nv2914zw8	1.0521/ 1.7864	-0.980		

	 -0.75	nv2714zw1/ nv2714zw2	1.5892/ 2.8679	-1.006	-1.01	-1.009 (±0.002)
		nv2714zw3/ nv2714zw4	1.4013/ 2.5419	-1.009		
		nv2714zw5/ nv2714zw6	0.7770/ 1.4206	-1.012		

	 -1.01^{EXP}	dc0414zw5/ dc0414zw6	0.7556/ 0.7076	-0.981	-0.98	-0.980 (±0.004)
		dc0414zw7/ dc0414zw8	0.9740/ 0.9168	-0.984		
		dc0414zw9/ dc0414zw10	1.1420/ 1.0534	-0.975		

7.2. Comparison between literature log*P*, and the log*P* measured (Table SI12)

Compound	Nr	log*P* (lit)	Reference[1]	exp. log*P*[2]	Δlog*P*
	**1**	-0.67[3] -0.92[5,6]	TFE[4] TFE	-0.75	-0.08 +0.17
	**2**	-0.33[3]	TFE	-0.29	+0.04
	**4**	-0.36[3]	TFE	-0.42	-0.06
	**6**	+0.70[4] +0.71[3,5,6]	TFE	+0.71	+0.01 +0.00
	**7**	+1.66[3]	TFE	+1.69	+0.03
	**9**	-0.28[3]	FE[7]	-0.26	+0.02
	**12**	+0.39[3,4]	TFE	+0.41	+0.02
	**13**	+1.23[3,6,9]	TFE	+1.20	-0.03
	**15**	+1.04[3,4]	TFE	+1.03	-0.01
	**18**	0.71[4]	TFE	+0.72	+0.01
	**23**	+0.90[3,4]	TFE	+0.91	+0.01
	**25**	+1.94[3] +1.81[9]	TFE	+1.98	+0.04 +0.18
	**35**	+1.15[4]	TFE	+1.22	+0.07
	**SI4**	+1.71[3,6,8] +1.64[6]	TFE	+1.70	-0.01 +0.06

[1] 2,2,2-Trifluoroethanol; log*P* +0.36[5] (method used for partition: shake-flask; method used for analysis: ^{1}H or ^{19}F NMR; temperature for log*P* measurement: not reported). **This value used as reference value**. Other values (+0.41 and +0.32) reported in a Table in ref [6] and in ref [7] (original source not published);

[2] Average log*P* value (at 25 °C, temperature controlled by recirculating chiller) from at least three experiments as listed in Table SI13;

[3] log*P* data retrieved from U.S. National Library of Medicine online database: http://chem.sis.nlm.nih.gov/chemidplus/; partition and analysis method as well as temperature for log*P* values are not provided;

[4] Value in ref 5; method used for partition: shake-flask; method used for analysis: ^{1}H or ^{19}F NMR; temperature for log*P* measurement: not reported;

[5] Value in ref [8]; method used for partition: shake-flask (method of Hansch and Muir[9]); method used for analysis: gas chromatography (method developed by Bluestein and Posmanter[10]; temperature for log*P* measurement: not reported;

[6] Value in ref 6. Partition and analysis method as well as temperature for log*P* values are not provided;

[7] FE = 2-fluoroethanol. Experimentally determined log*P* value (-0.75) for 2-fluoroethanol was used here as reference;

[8] Value in ref [11]. Method used for partition: shake-flask; analysis with Cary Model 14 spectrophotometer; temperature for log*P* measurement: 25 ± 5 °C.

[9] Value in ref 7, p534. Partition method: not described; analysis method: using vapor-phase chromatography; temperature for log*P* measurement: room temperature.

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[5] N. Muller, *J. Pharm. Sci.* **1986**, *75*, 987-991.

[6] C. Hansch, A. Leo, in *Substituent constants for correlation analysis in chemistry and biology*. Wiley,**1979**.; partition and analysis method as well as temperature for log*P* values are not provided.

[7] A. Leo, C. Hansch, D. Elkins, *Chem. Rev.* **1971**, *71*, 525-616.

[8] E. O. Dillingham, R. W. Mast, G. E. Bass, J. Autian, *J. Pharm. Sci.* **1973**, *62*, 22-30.

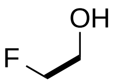
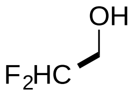
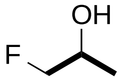
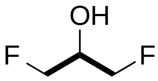
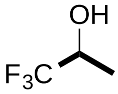
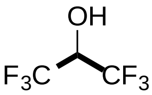
[9] C. Hansch, R. M. Muir, T. Fujita, P. P. Maloney, F. Geiger, M. Streich, *J. Am. Chem. Soc.* **1963**, *85*, 2817-2824.

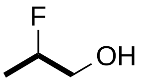
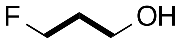
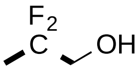
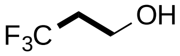
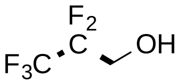
[10] C. Bluestein, H. N. Posmanter, *Anal. Chem.* **1966**, *38*, 1865-1869.

[11] T. Fujita, J. Iwasa, C. Hansch, *J. Am. Chem. Soc.* **1964**, *86*, 5175-5180.

8. Detailed experimental data for the log*P* determinations (ρ_{oct} and ρ_{wat} values for each experiment) (Table SI13)

Unless indicated, the general procedure as detailed above was followed (O1P centered; SW: 300 ppm; D1: oct 30 sec; wat: 60 sec; SR: 295.14 ppm; NMR machine: 400-3)
(TFE was used as primary reference; 4,4,4-trifluorobutan-1-ol (**TB**), 2-fluoroethanol (**FE**) and 2-fluorophenol were also used as reference for some cases)

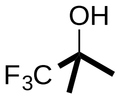
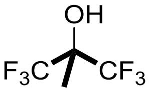
Compound	Nr	Experiment (octanol/water)	ρ_{oct}/ρ_{wat}	log*P*	Average log*P*	error
8.1. Ethanol series						
	**1**	au0814zw2/au0814zw3	0.0832/1.0625	-0.746	-0.75	-0.746 (±0.003)
		au2614zw8/au2614zw9	0.1102/1.4167	-0.749		
		au2614zw10/au2614zw11	0.1040/1.3137	-0.741		
	**2**	nv1014zw1/nv1014zw2	0.4596/2.0203	-0.283	-0.29	+0.285 (±0.001)
		nv1014zw3/nv1014zw4	0.4445/1.9680	-0.286		
		nv1014zw5/nv1014zw6	0.3238/1.4323	-0.286		
8.2. 2-Propanol series						
	4					
	**5**	nv2014zw3/nv2014zw4	0.8682/4.4354	-0.348	-0.35	+0.346 (±0.004)
		nv2014zw5/nv2014zw6	0.8193/4.1163	-0.341		
		nv2014zw7/nv2014zw8	0.9956/5.0887	-0.349		
	**4**	nv1114zw1/nv1114zw2	0.2925/1.7780	-0.424	-0.42	-0.421 (±0.003)
		nv1114zw3/nv1114zw4	0.2469/1.4886	-0.420		
		nv1114zw5/nv1114zw6	0.2773/1.6622	-0.418		
	**6**	jy0315zw5/jy0315zw6	1.2375/0.5507	+0.712	+0.71	+0.715 (±0.003)
		jy0315zw7/jy0315zw8	1.2811/0.5620	+0.718		
		jy0315zw9/jy0315zw10	1.2551/0.5551	+0.714		
	**7**	my3015zw5/my3015zw6	5.8692/0.2765	+1.687	+1.69	+1.694 (±0.005)
		my3015zw7/my3015zw8	4.5478/0.2081	+1.700		
		my3015zw9/my3015zw10	4.6120/0.2136	+1.694		

Compound	Nr	Experiment (octanol/water)	ρ_{oct}/ρ_{wat}	log*P*	Average log*P*	error
8.3. 1-Propanol series						
	**8**	nv2914zw13/ nv2914zw14	5.5538/ 1.9083	-0.286	-0.29[a]	-0.287 (±0.001)
		nv2914zw15/ nv2914zw16	3.3986/ 1.1753	-0.289		
		nv2914zw17/ nv2914zw18	3.3499/ 1.1540	-0.287		
	**9**	nv1414zw1/ nv1414zw2	3.3434/ 1.1035	-0.269	-0.26[a]	-0.260 (±0.007)
		nv1414zw3/ nv1414zw4	3.4050/ 1.0885	-0.255		
		nv1414zw5/ nv1414zw6	3.0305/ 0.9685	-0.255		
	**10**	ma1715zw3/ ma1715zw4	0.1111/ 0.2358	+0.033	+0.04	+0.038 (±0.004)
		ma1715zw5/ ma1715zw6	0.1112/ 0.2345	+0.036		
		ma1715zw7/ ma1715zw8	0.1128/ 0.2338	+0.043		
	**11**	nv1314zw1/ nv1314zw2	0.3455/ 0.6107	+0.113	+0.11	+0.110 (±0.003)
		nv1314zw3/ nv1314zw4	0.4166/ 0.7460	+0.107		
		nv1314zw5/ nv1314zw6	0.4318/ 0.7654	+0.111		
	**12**	ma1115zw3/ ma1115zw4	1.0328/ 0.9138	+0.413	+0.41	+0.414 (±0.001)
		ma1115zw5/ ma1115zw6	1.3310/ 1.1738	+0.415		
		ma1115zw7/ ma1115zw8	1.5206/ 1.3375	+0.416		
	**13**	oc0214zw1/ oc0214zw2	2.1983/ 0.3163	+1.202	+1.20	1.200 (±0.001)
		oc0214zw3/ oc0214zw4	1.9761/ 0.2854	+1.200		
		oc0214zw5/ oc0214zw6	2.3148/ 0.3352	+1.199		

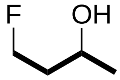
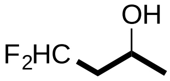
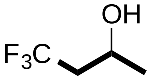
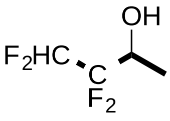
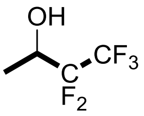
[a] Reference compound: FE

Compound	Nr	Experiment (octanol/water)	ρ_{oct}/ρ_{wat}	log*P*	Average log*P*	error

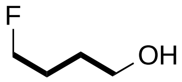
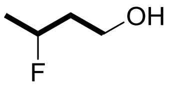
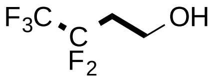
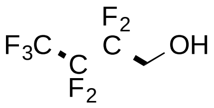
8.4. *tert*-Butanol series

Compound	Nr	Experiment (octanol/water)	ρ_{oct}/ρ_{wat}	log*P*	Average log*P*	error
	**14**	nv2314zw3/ nv2314zw4	5.9389/ 1.2568	+1.034	+1.03	+1.028 (±0.004)
		nv2314zw5/ nv2314zw6	9.1209/ 1.9688	+1.026		
		nv2314zw7/ nv2314zw8	5.4572/ 1.1808	+1.025		
	**15**	ju0515zw9/ ju0515zw10	5.7536/ 0.1164	+2.054	+2.08	+2.080 (±0.019)
		ju0515zw11/ ju0515zw12	5.8469/ 0.1069	+2.098		
		ju0515zw13/ ju0515zw14	6.0948/ 0.1137	+2.089		

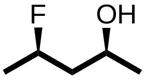
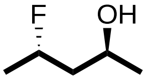
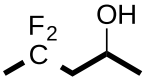
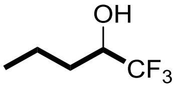
8.5. 2-Butanol series

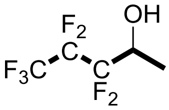
Compound	Nr	Experiment (octanol/water)	ρ_{oct}/ρ_{wat}	log*P*	Average log*P*	error
	**16**	ma1915zw1/ ma1915zw2	0.1211/ 0.2326	+0.077	+0.08	+0.084 (±0.007)
		ma1915zw3/ ma1915zw4	0.1237/ 0.2348	+0.082		
		ma1915zw5/ ma1915zw6	0.1282/ 0.2366	+0.094		
	**17**	ma2815zw3/ ma2815zw4	0.7442/ 0.6484	+0.420	+0.42	+0.417 (±0.002)
		ma2815zw5/ ma2815zw6	0.7388/ 0.6496	+0.416		
		ma2815zw7/ ma2815zw8	0.7412/ 0.6546	+0.414		
	**18**	jy0315zw11/ jy0315zw12	0.7712/ 0.3327	+0.725	+0.72	+0.721 (±0.003)
		jy0315zw13/ jy0315zw14	0.7502/ 0.3265	+0.721		
		jy0315zw15/ jy0315zw16	0.7634/ 0.3353	+0.717		
	**19**	ja0615zw3/ ja0615zw4	2.2187/ 1.5831	+1.057	+1.05[a]	+1.054 (±0.003)
		ja0615zw5/ ja0615zw6	1.4520/ 1.0433	+1.054		
		ja0615zw7/ ja0615zw8	1.7014/ 1.2318	+1.050		
	**20**	ap2515zw5/ ap2515zw6	4.5737/ 0.3075	+1.532	+1.53	+1.530 (±0.002)
		ap2515zw7/ ap2515zw8	4.5465/ 0.3072	+1.530		
		ap2515zw9/ ap2515zw10	4.4489/ 0.3018	+1.529		

[a] Reference compound: 4,4,4-trifluoro-1-butanol (**TB**, logP: +0.91^{EXP}).

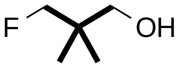
Compound	Nr	Experiment (octanol/water)	ρ_{oct}/ρ_{wat}	log*P*	Average log*P*	error
8.6. 1-Butanol series						
	**21**	nv1714zw3/nv1714zw4	1.5512/2.8742	+0.092	+0.09	+0.090 (±0.002)
		nv1714zw5/nv1714zw6	1.4427/2.6988	+0.088		
		nv1714zw7/nv1714zw8	1.5758/2.9372	+0.090		
	**22**	my3015zw11/my3015zw12	0.4122/0.6449	+0.166	+0.17	+0.173 (±0.006)
		my3015zw13/my3015zw14	0.4144/0.6279	+0.180		
		my3015zw15/my3015zw16	0.4146/0.6379	+0.173		
	**23**	nv2314zw9/nv2314zw10	0.8687/0.2406	+0.918	+0.91	+0.910 (±0.005)
		nv2314zw11/nv2314zw12	1.0628/0.3035	+0.904		
		nv2314zw13/nv2314zw14	0.9520/0.2691	+0.909		
		nv2314zw15/nv2314zw16	1.4533/0.4124	+0.907		
	**24**	nv2614zw1/nv2614zw2	7.2581/0.8504	+1.291	+1.30	+1.298 (0.005)
		nv2614zw3/nv2614zw4	9.8785/1.1251	+1.303		
		nv2614zw5/nv2614zw6	9.7072/1.1159	+1.299		
	**25**	nv2214zw9/nv2214zw10	15.3820/0.3601	+1.991	+1.98	+1.976 (±0.015)
		nv2214zw11/nv2214zw12	26.3642/0.6361	+1.977		
		nv2214zw13/nv2214zw14	30.1285/0.7556	+1.961		

8.7. 2-Pentanol series

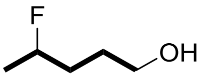
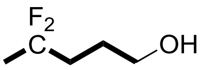
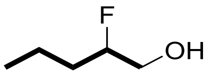
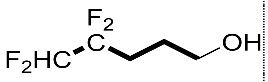
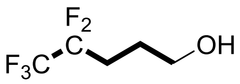
Compound	Nr	Experiment (octanol/water)	ρ_{oct}/ρ_{wat}	log*P*	Average log*P*	error
	**26**	dc1614zw3/ dc1614zw4	0.3660/ 0.2804	+0.476	+0.48	+0.477 (±0.001)
		dc1614zw5/ dc1614zw6	0.4450/ 0.3407	+0.476		
		dc1614zw7/ dc1614zw8	0.4663/ 0.3556	+0.478		
	**27**	dc1414zw1/ dc1414zw2	0.6245/ 0.3847	+0.570	+0.57	+0.569 (±0.003)
		dc1414zw3/ dc1414zw4	0.4612/ 0.2880	+0.564		
		dc1414zw5/ dc1414zw6	0.7161/ 0.4398	+0.572		
	**28**	ma2215zw1/ ma2215zw2	0.6733/ 0.3383	+0.659	+0.66	+0.662 (±0.003)
		ma2315zw1/ ma2315zw2	0.6715/ 0.3316	+0.666		
		ma2315zw3/ ma2315zw4	0.6782/ 0.3394	+0.661		
	**29**	my1615zw5/ my1615zw6	1.5849/ 0.0535	+1.832	+1.82	+1.817 (±0.011)
		my1615zw7/ my1615zw8	1.5285/ 0.0538	+1.813		
		my1615zw9/ my1615zw10	1.5499/ 0.0557	+1.804		

	**SI1**	ap2515zw23/ ap2515zw24	2.7176/ 0.02402	+2.414	+2.41	+2.409 (±0.012)
		ap2515zw25/ ap2515zw26	2.8090/ 0.02438	+2.422		
		ap2515zw27/ ap2515zw28	2.7523/ 0.02553	+2.393		

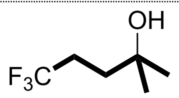
8.8. Neopentyl alcohol series

	**SI3**	ma2715zw7/ ma2715zw8	0.3694/ 0.1264	+0.826	+0.80	+0.796 (±0.021)
		ma2715zw9/ ma2715zw10	0.2208/ 0.0828	+0.786		
		ma2715zw11/ ma2715zw12	0.3175/ 0.1217	+0.776		

8.9. 1-Pentanol series

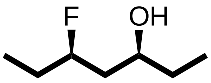
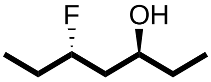
Compound	Nr	Experiment (octanol/water)	ρ_{oct}/ρ_{wat}	log*P*	Average log*P*	error
	**30**	my3115zw3/ my3115zw4	1.3428/ 0.9210	+0.524	+0.52	+0.524 (±0.002)
		my3115zw5/ my3115zw6	1.3407/ 0.9133	+0.527		
		my3115zw7/ my3115zw8	1.3500/ 0.9303	+0.522		
	**31**	my2315zw5/ my2315zw6	0.5138/ 0.3580	+0.517	+0.52	+0.522 (±0.004)
		my2315zw7/ my2315zw8	0.5189/ 0.3573	+0.522		
		my2315zw9/ my2315zw10	0.5237/ 0.3575	+0.526		
	**32**	my0915zw5/ my0915zw6	0.4653/ 0.2071	+0.712	+0.71	+0.708 (±0.005)
		my0915zw7/ my0915zw8	0.4598/ 0.2098	+0.701		
		my0915zw9/ my0915zw10	0.4674/ 0.2078	+0.712		
	**33**	ju1215zw9/ ju1215zw10	0.7883/ 0.2427	+0.872	+0.87	+0.868 (±0.003)
		ju1215zw11/ ju1215zw12	0.8108/ 0.2512	+0.869		
		ju1215zw13/ ju1215zw14	0.7916/ 0.2479	+0.864		
	**34**	ju0515zw21/ ju0515zw22	0.5401/ 0.1322	+0.971	+0.97	+0.974 (±0.002)
		ju0515zw23/ ju0515zw24	0.5476/ 0.1326	+0.976		
		ju0515zw25/ ju0515zw26	0.5373/ 0.1307	+0.974		
	**35**	nv2214zw3/ nv2214zw4	4.4606/ 0.6154	+1.220	+1.22	+1.222 (0.004)
		nv2214zw5/ nv2214zw6	4.2519/ 0.5881	+1.219		
		nv2214zw7/ nv2214zw8	3.0699/ 0.4159	+1.228		
	**36**	ap2515zw11/ ap2515zw12	3.3028/ 0.1425	+1.725	+1.72	+1.720 (±0.004)
		ap2515zw13/ ap2515zw14	3.1018/ 0.1356	+1.719		
		ap2515zw15/ ap2515zw16	3.3643/ 0.1480	+1.717		

8.10. 2-methyl-2-pentanol series

	**SI2**	ap2515zw17/ ap2515zw18	2.7049/ 0.1875	+1.519	+1.52	+1.519 (±0.002)
		ap2515zw19/ ap2515zw20	2.6849/ 0.1848	+1.522		
		ap2515zw21/ ap2515zw22	2.7060/ 0.1887	+1.517		

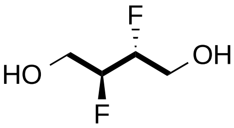
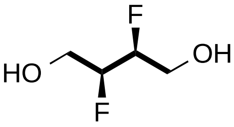
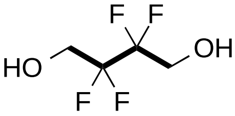
Compound	Nr	Experiment (octanol/water)	ρ_{oct}/ρ_{wat}	log*P*	Average log*P*	error

8.11. 3-Heptanol series

	**37**	dc0814zw3/ dc0814zw4	0.3801/ 0.0808	+1.582	+1.58[a]	+1.584 (±0.005)
		dc0814zw5/ dc0814zw6	0.5037/ 0.1049	+1.591		
		dc0814zw7/ dc0814zw8	0.4058/ 0.0867	+1.580		
	**38**	dc1114zw1/ dc1114zw2	1.0099/ 0.1686	+1.687	+1.71[a]	+1.710 (±0.017)
		dc1114zw3/ dc1114zw4	0.6804/ 0.1051	+1.721		
		dc1114zw5/ dc1114zw6	0.6872/ 0.1056	+1.723		

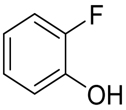
[a] Reference compound: 4,4,4-trifluoro-1-butanol (**TB**, logP: +0.91^{EXP})

8.12. 1,4-Butanediol series

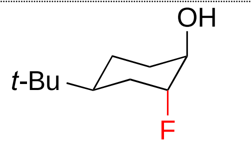
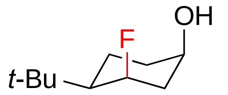
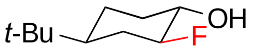
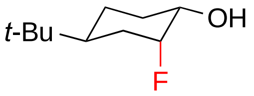
	**39**	nv2714zw1/ nv2714zw2	1.5892/ 2.8679	-1.006	-1.01[a]	-1.009 (±0.003)
		nv2714zw3/ nv2714zw4	1.4013/ 2.5419	-1.009		
		nv2714zw5/ nv2714zw6	0.7770/ 1.4206	-1.012		
	**40**	nv2914zw3/ nv2914zw4	1.5649/ 2.5229	-0.957	-0.97[a]	-0.968 (±0.009)
		nv2914zw5/ nv2914zw6	1.3398/ 2.2144	-0.968		
		nv2914zw7/ nv2914zw8	1.0521/ 1.7864	-0.980		
	**41**	dc0314zw1/ dc0314zw2	1.1289/ 3.4162	-0.121	-0.11	-0.109 (±0.009)
		dc0314zw3/ dc0314zw4	1.6429/ 4.8079	-0.106		
		dc0314zw5/ dc0314zw6	0.8021/ 2.3130	-0.100		

[a] Reference compound: **FE**.

8.13. Additional compound: *o*-fluorophenol

	**SI4**	ju1215zw15/ ju1215zw16	1.2149/ 0.0554	+1.701	+1.70	+1.696 (±0.004)
		ju1215zw17/ ju1215zw18	1.1761/ 0.0544	+1.695		
		ju1215zw19/ ju1215zw20	1.2282/ 0.0571	+1.693		

8.14. 4-*tert*-butylcyclohexanol series[a]

Compound	Nr	Experiment (octanol/water)	ρ_{oct}/ρ_{wat}	log*P*	Average log*P*	error
	**44**	ma2415zw3/[b] ap0215njwzw1[c]	0.8521/ 0.02657	+3.206	-	-
	**45**	ap0115zw3/[d] ap0115zw4	2.2293/ 0.6523	+2.234	+2.23	+2.229 (±0.005)
		ap0115zw5/ ap0115zw6	2.1797/ 0.6533	+2.223		
		ap0115zw3/ my0115njwzw1[e]	2.2293/ 0.6582	+2.230		
	**43**	ma2715njwzw1/[f] ma2715njwzw2	2.1788/ 0.2689	+2.609	+2.61	+2.608 (±0.009)
		ma3115zw3/ ma3115zw4	2.2142/ 0.2666	+2.619		
		ma2815zw9/ ma2815zw10	2.0216/ 0.2563	+2.597		
	**42**	nv1214zw3/ nv1214zw4	1.4736/ 0.1738	+2.628	+2.63	+2.630 (±0.002)
		nv1214zw3/ ja3015njwzw1[g]	1.4736/ 0.1726	+2.631		

[a] Reference: 2-fluorophenol (logP: $+1.70^{EXP}$);

[b] NS: 64; D1: 30 sec; SW: 100 ppm; centered O1P; NMR: 400-3;

[c] NS: 32768; D1: 15 sec; SW: 100 ppm; centered O1P; NMR: 400-2;

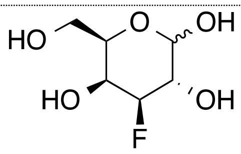
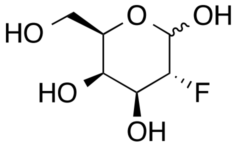
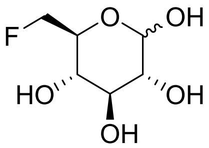
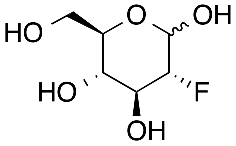
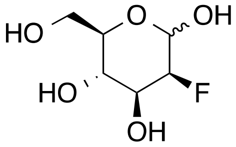
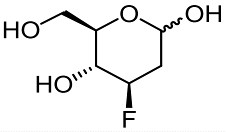
[d] SW for ap0115zw3-6 and my0115njwzw1: 100 ppm;

[e] NMR tube of ap0115zw4 was re-run on NMR machine 400-2 with extended NS of 4096;

[f] NMR tube of ma3115zw3/4 were re-run on NMR machine 400-2 with extended NS of 4096; SW for ma2715njwzw1/2 and ma3115zw3/4: 100 ppm;

[g] NMR tube of nv1214zw4 was re-run on NMR machine 400-2 with extended NS of 4096 and SW 100 ppm.

8.15. Fluorinated carbohydrates

Compound	Nr	Experiment (octanol/water)	ρ_{oct}/ρ_{wat}	log*P*	Average log*P*	error
	**46**	ju2614njwzw5/ ju2614njwzw6[12]	0.0371/ 1.9271[13]	-2.465	-	-
	**47**	ju2614njwzw3/ ju2614njwzw4[14]	0.0550/ 2.3122[15]	-2.374	-	-
	**48**	se1115njwzw2/ se1115njwzw1[16]	0.0992/ 3.9888	-2.354	-2.36	-2.355 (±0.001)
		oc0215njwzw1/ se3015njwzw1[17]	0.1182/ 4.7741	-2.356		
	**49**	ju2614njwzw1/[18] ju2614njwzw2[19]	0.0792/ 2.2992	-2.213	-	-
	**50**	ju2614njwzw7/ ju2614njwzw8[20]	0.1208/ 2.7976	-2.114	-	-
	**51**	ju22z4zw3/ ju2214zw4[21]	0.0755/ 4.8445	-1.447	-	-

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[12] For both oct and wat sample: D1: 15 sec; O1P: -150 ppm; NS: oct 3296; wat 2329; reference: **FE**;

[13] For data reprocessing of ju2614njwzw6: no zero-filling and LB value 0.15 for WF (exponential) as it was difficult to obtain good baseline with standard settings (doublezero-filling and LB value 2);

[14] For both oct and wat sample: D1: 15 sec; O1P: -150 ppm; NS: oct 3296; wat 2687; reference: **FE**;

[15] For data reprocessing of ju2614njwzw4: no zero-filling and LB value 0.15 for WF (exponential) as it was difficult to obtain good baseline with standard settings (doublezero-filling and LB value 2);

[16] For both oct and wat sample: D1: 15 sec; O1P: -230 ppm; NS: oct 4647; wat 512; Commercial compound was purified by flash chromatography and then used for log*P* partition. The sample after partition equilibrium was centrifuged for 4 times with each duration of 1 hr at 500 rpm to obtain clear water and octanol layer for NMR sample preparation; reference: **FE**;

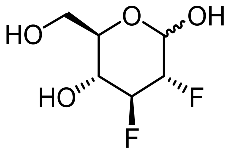
[17] For both oct and wat sample: D1: 15 sec; O1P: -230 ppm; NS: oct 9216; wat 512; reference: **FE**;

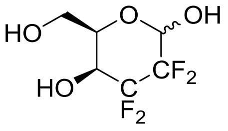
[18] For both oct and wat sample: D1: 15 sec; O1P: -150 ppm; NS: oct 3296; wat 1744; reference: **FE**;

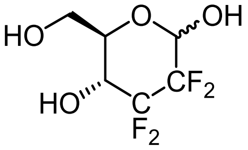
[19] For data reprocessing of ju2614njwzw2: no zero-filling and LB value 0.15 for WF (exponential) as it was difficult to obtain good baseline with standard settings (doublezero-filling and LB value 2);

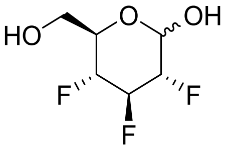
[20] For both oct and wat sample: D1: 15 sec; O1P: -150 ppm; NS: oct 3296; wat 427; reference: **FE**;

[21] For both oct and wat sample: D1: 50 sec; O1P -100 ppm; reference: **TFE**;

	**52**	jy0814zw4/ jy0814zw5[22]	0.8113/ 1.8759	-1.114	-	-

Compound	Nr	Experiment (octanol/water)	ρ_{oct}/ρ_{wat}	log*P*	Average log*P*	error
	**53**	my0915zw11/[23] my0915zw12	0.1232/ 1.0571	-0.574	-0.58	-0.576 (±0.005)
		my0915zw13/ my0915zw14	0.1186/ 1.0156	-0.573		
		my0915zw15/ my0915zw16	0.1270/ 1.1141	-0.583		

	**54**	ju2314zw1/[24] ju2314zw2	1.9975/ 9.4638	-0.316	-0.32	-

	**55**	nv2514zw1/ nv2514zw2	1.2117/ 0.3190	-0.170	-0.17[25]	-

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[22] For both oct and wat sample D1: 50 sec; O1P: -100 ppm; reference: **FE**.

[23] Reference: **TFE**;

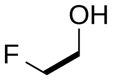
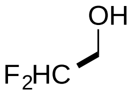
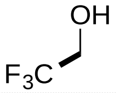
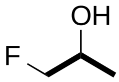
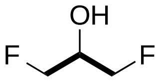
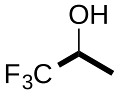
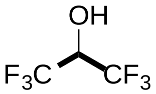
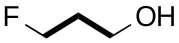
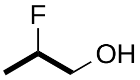
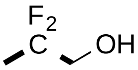
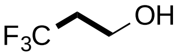
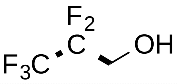
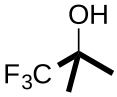
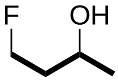
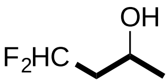
[24] O1P: -100 ppm; D1: 50 sec for both oct and wat sample; reference: **TFE**;

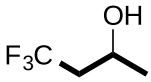
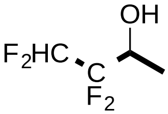
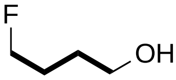
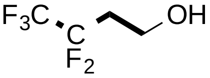
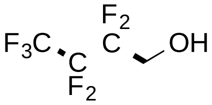
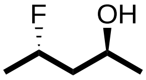
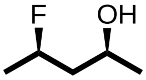
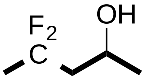
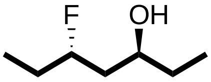
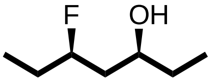
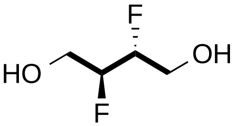
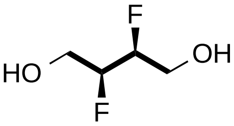
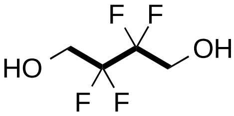
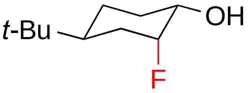
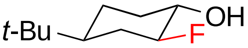
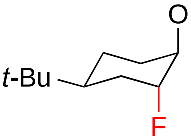
[25] Very low S/N ratios due to the fluorine coupling; reference: **FE**;

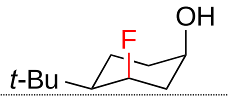
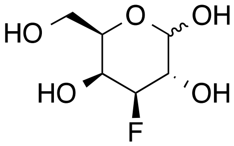
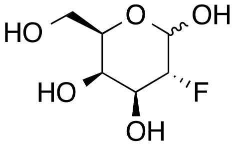
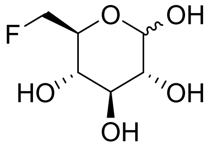
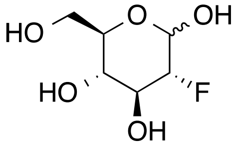
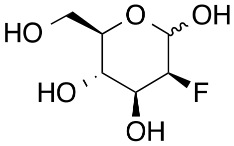
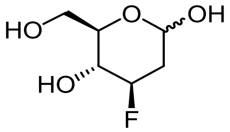
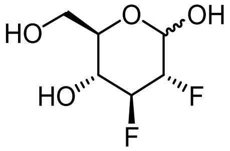
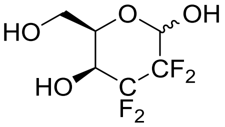
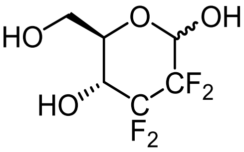
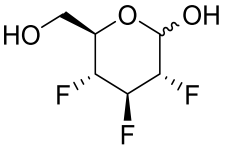
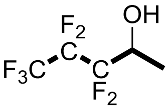
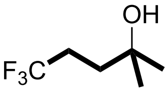
9. Comparison of clog*P* with experimental log*P* (Table SI14)

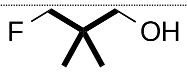
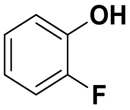
The log*P* values obtained by our method are compared with two calculated log*P* values.

Difference of <0.10 log*P*	🟩
Difference 0.10–0.49 log*P*	🟨
Difference 0.50–0.75 log*P*	🟧
Difference >0.75 log*P*	🟥

Compound	Nr	log*P* exp	clog*P*[a]	Δlog*P*	milog*P*[b]	Δlog*P*
	**1**	-0.75	-0.32	***+0.43***	-0.02	***+0.73***
	**2**	-0.29	-0.05	***+0.24***	+0.25	***+0.54***
	**3**	+0.36	+0.44	***+0.08***	+0.61	***+0.25***
	**5**	-0.35	+0.10	***+0.45***	+0.34	***+0.69***
	**4**	-0.42	-0.06	***+0.36***	+0.26	***+0.68***
	**6**	+0.70	+0.85	***+0.15***	+0.97	***+0.27***
	**7**	+1.69	+1.45	***+0.24***	+1.52	***+0.17***
	**9**	-0.26	-0.26	***0.00***	+0.25	***+0.51***
	**8**	-0.29	+0.10	***+0.39***	+0.34	***+0.63***
	**10**	+0.04	+0.22	***+0.18***	+0.52	***+0.48***
	**11**	+0.11	+0.20	***+0.09***	+0.70	***+0.59***
	**12**	+0.41	+0.49	***+0.08***	+0.88	***+0.47***
	**13**	+1.20	+1.14	***-0.06***	+1.25	***+0.05***
	**14**	+1.03	+1.13	***+0.10***	+1.42	***+0.39***
	**16**	+0.08	+0.16	***+0.08***	+0.61	***+0.53***
	**17**	+0.42	+0.63	***+0.21***	+0.88	***+0.46***

	**18**	+0.71	+0.90	***+0.19***	+1.24	***+0.53***
	**19**	+1.05	+1.06	***+0.01***	+1.61	***+0.56***
	**21**	+0.09	+0.26	***+0.17***	+0.52	***+0.43***
	**23**	+0.91	+1.00	***+0.09***	+1.15	***+0.24***
	**24**	+1.30	+1.41	***+0.11***	+1.52	***+0.22***
	**25**	+1.98	+1.84	***-0.14***	+1.89	***-0.09***
	**27**	+0.57	+0.58	***+0.01***	+0.97	***+0.40***
	**26**	+0.48	+0.58	***+0.10***	+0.97	***+0.49***
	**28**	+0.66	+0.88	***+0.22***	+1.33	***+0.67***
	**35**	+1.22	+1.44	***+0.22***	+1.65	***+0.43***
	**38**	+1.71	+1.62	***-0.09***	+1.98	***+0.27***
	**37**	+1.58	+1.62	***+0.04***	+1.98	***+0.40***
	**39**	-1.01	-0.69	***+0.32***	-0.38	***+0.63***
	**40**	-0.97	-0.69	***+0.28***	-0.38	***+0.59***
	**41**	-0.11	+0.19	***+0.30***	+0.33	***+0.44***
	**42**	+2.63	+2.42	***-0.21***	+2.70	***+0.07***
	**43**	+2.61	+2.42	***-0.19***	+2.70	***-0.09***
	**44**	+3.21	+2.42	***-0.79***	+2.70	***-0.51***

	**45**	+2.23	+2.11	***-0.12***	+2.70	***-0.47***
	**46**	-2.47	-2.04	***+0.43***	-2.15	***+0.32***
	**47**	-2.37	-2.04	***+0.33***	-1.93	***+0.44***
	**48**	-2.36	-2.04	***+0.32***	-1.71	***+0.65***
	**49**	-2.21	-2.04	***+0.17***	-1.93	***+0.28***
	**50**	-2.11	-2.04	***+0.07***	-1.93	***-0.18***
	**51**	-1.45	-1.14	***-0.31***	-1.23	***-0.22***
	**52**	-1.11	-1.15	***+0.04***	-1.22	***+0.14***
	**53**	-0.58	-0.27	***+0.31***	-0.51	***+0.07***
	**54**	-0.32	-0.27	***+0.05***	-0.51	***-0.19***
	**55**	-0.17	-0.26	***-0.09***	-0.29	***-0.12***
	**SI1**	+2.41	+2.25	***-0.19***	+2.25	***-0.19***
	**SI2**	+1.52	+1.69	***+0.17***	+1.96	***+0.44***

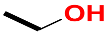
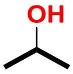
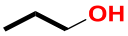
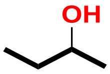
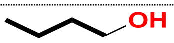
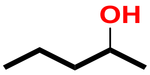
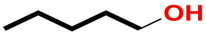
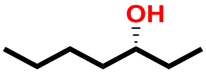
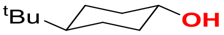
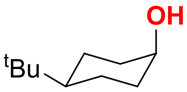
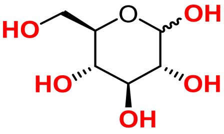
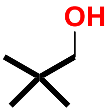
	**SI3**	+0.80	+0.71	***+0.09***	+1.14	***+0.34***
	**SI4**	+1.70	+1.81	***+0.11***	+1.83	***+0.13***

[a] Calculated log*P* using Marvin Sketch 14.8.4.0;

[b] milog*P* calculated log*P* using Molinspriation Cheminformatics on the Web: http://www.molinspiration.com/cgi-bin/properties

10. Literature log*P* values for non-fluorinated alcohols (Table SI15)

The first value was used to compare with the log*P* of the fluorohydrins. In general, this is the log*P* value catalogued by U.S. National Library of Medicine (NIH).

Compound	Nr	log*P* (lit) (*T*, method, analysis method [if reported])
	**A**	**-0.30**^{23}; -0.31^{1}; -0.15^{2}; -0.32^{2} (pH 6.00)
	**B**	**+0.05**^{1,2}
	**C**	**+0.30**^{2}; +0.25^{1};
	**D**	**+0.37**^{2}; +0.35^{1}
	**E**	**+0.76**^{2}; +0.61^{1}; 0.83^{2}; 0.65^{2};
	**F**	**+0.88**^{1,2}; 0.89^{2}; 0.32^{2};
	**G**	**+1.19**^{1} 1.16^{2};
	**H**	**+1.51**^{1} 1.40^{2};
	**I**	**+2.24**^{1};
	**J**	**-0.83**^{1};
	**K**	**+3.09**^{1};
	**L**	**+3.02**^{1};
	**Glucose**	**-3.24**^{1}; -2.84^{4} (5 °C, enzymatic) -2.82^{4} (20 °C, enzymatic) -3.10^{4} (25 °C, Radiochemical) -3.02^{4} (LC) -3.00^{4}/-3.24^{4};
		**+1.31**^{1}

^{1}log*P* data retrieved from U.S. National Library of Medicine online database: http://chem.sis.nlm.nih.gov/chemidplus/; partition and analysis method as well as temperature for log*P* values are not provided from the database;

^{2}Value in ref [26]. Partition and analysis method as well as temperature for logP values are not provided in this book;

^{3} Value in ref [27]. Method used for partition: shake-flask (method of Hansch and Muir[28]); method used for analysis: gas chromatography (method developed by Bluestein and Posmanter[29]; temperature for logP measurement: not reported;

^{4} Value in ref [30];

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[26] C. Hansch, A. Leo, in *Substituent constants for correlation analysis in chemistry and biology*. Wiley, **1979**.

[27] E. O. Dillingham, R. W. Mast, G. E. Bass, J. Autian, *J. Pharm. Sci.* **1973**, *62*, 22-30.

[28] C. Hansch, R. M. Muir, T. Fujita, P. P. Maloney, F. Geiger, M. Streich, *J. Am. Chem. Soc.* **1963**, *85*, 2817-2824.

[29] C. Bluestein, H. N. Posmanter, *Anal. Chem.* 1966, *38*, 1865-1869.

[30] M. F. Mazzobre, M. V. Roman, A. F. Mourelle, H. R. Corti, *Carbohydrate research*, **2005**, *340*, 1207-1211

11. List of commercially available and known compounds

11.1. Commercially available compounds

Fluorohydrins **1**, **2**, **4**, **5**, **6**, **7**, **8**, **9**, **11**, **12**, **13**, **14**, **15**, **18**, **19**, **20**, **21**, **23**, **24**, **25**, **35**, **36**, **41**, **SI1**, **SI2**, **SI4** were purchased from commercial suppliers and were checked by ^{1}H and ^{19}F NMR experiments. Carbohydrates **46, 47, 48, 49** and **50** were purchased from commercial supplier. Carbohydrate **46** was purified by flash chromatography before log*P* experiment.

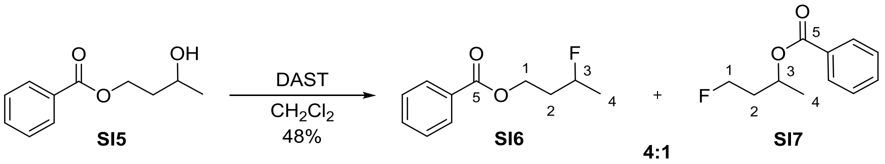
11.2. References to other compounds

The synthesis of **10**, **16**, **17**, **26**, **27**, **28**, **SI3** is reported.[31] The synthesis of **37** and **38** will be reported elsewhere. The synthesis of **39** is reported,[32] and the synthesis of **40** will be reported elsewhere. The synthesis of cyclic fluorohydrin **42**, **43**, **44**, **45** was reported in the literature.[33] The synthesis of **51** and **52** was reported in the literature.[34] The synthesis of **53** and **54** was reported in the literature.[35] Sugar derivative **55** was given by Prof David O'Hagan, and its synthesis is reported in the literature.[36]

12. Synthesis of novel compounds

12.1. Synthesis of 3-fluorobutan-1-ol (22)

12.1.1. Synthesis of 3-fluorobut-1-yl benzoate (SI6) and 4-fluorobut-2-yl benzoate (SI7)



To a solution of 3-hydroxybutyl benzoate **SI5**[37] (4.0 g, 20.6 mmol, 1 equiv) in CH_2Cl_2 (20 mL) at 0 °C was added DAST (5.40 mL, 41.2 mmol, 2 equiv) and the resulting mixture was stirred at rt for 21 h. The reaction mixture was diluted with CH_2Cl_2 (140 mL) then sat. aq. $NaHCO_3$ solution (70 mL) was added and the layers were separated. The aqueous phase was extracted with CH_2Cl_2 (2 × 140 mL) and the combined organic layers were dried ($MgSO_4$), filtered and concentrated to give 4.47 g of crude material. Column chromatography on silica gel eluting with petroleum ether 40–60 °C/Et_2O (96:4 to 90:10) gave 1.944 g (9.91 mmol, 48%) of a 4:1 mixture of **SI6** and **SI7**, which was used in the next step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 8.02 (m, 2H, H_{Ar}), 7.62 – 7.54 (m, 1H, H_{Ar}), 7.50 – 7.42 (m, 2H, H_{Ar}), 5.34 (m, 1H, H-3 **SI7**), 4.90 (ddqd, *J* = 48.9, 8.1, 6.1, 4.4 Hz, 1H, H-3, **SI6**), 4.59 (ddd, *J* = 47.2, 6.5, 5.5 Hz, 1H, H-1 **SI7**), 4.57 – 4.40 (m, 2H, H-1 **SI6**), 2.41 – 1.91 (m, 4H, H-2 **SI6** + **SI7**), 1.43 (d, *J* = 6.6 Hz, 3H, H-4 **SI7**), 1.43 (dd, *J* = 24.0, 6.1 Hz, 3H, H-4 **SI6**) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ –175.7 (ddqd, *J* = 48.9, 29.5, 17.1 Hz, 1F, $F_{\mathbf{SI6}}$), –220.5 (tdd, *J* = 47.2, 27.7, 22.5 Hz, 1F, $F_{\mathbf{SI7}}$) ppm.

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[31] B. Linclau, F. Peron, E. Bogdan, N. Wells, Z. Wang, G. Compain, C. Fontenelle, N. Galland, J.-Y. Le Questel, J. Graton, *Chem. Eur. J. accepted for publication DOI* 10.1002/chem.201503253.

[32] B. Linclau, L. Leung, J. Nonnenmacher, G. Tizzard, *Beilstein J. Org. Chem.* **2010**, *6*, No 62.

[33] J. Graton, Z. Wang, A.-M. Brossard, D. Gonçalves Monteiro, J.-Y. Le Questel, B. Linclau, *Angew Chem Int. Ed.* **2012**, *51*, 6176-6180.

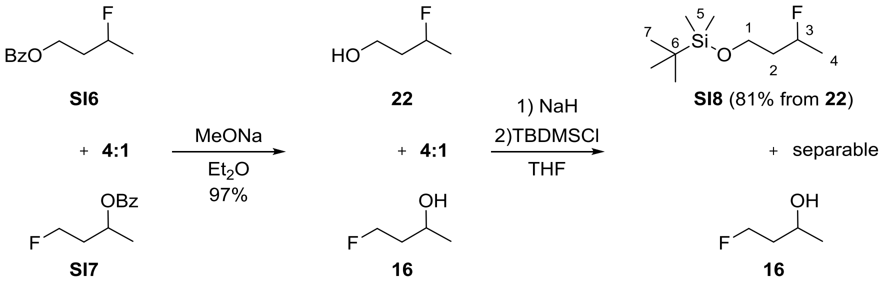
[34] L. Mtashobya, L. Quiquempoix, B. Linclau, *J. Fluorine Chem.* **2015**, *171*, 92-96.

[35] R. S. Timofte, B. Linclau, *Org. Lett.* **2008**, *10*, 3673-3676

[36] a) S. Bresciani, T. Lebl, A. M. Z. Slawin, D. O'Hagan, *Chem. Commun.* **2010**, *46*, 5434-5436; b) M. J. Corr, D. O'Hagan, *J. Fluorine Chem.* **2013**, *155*, 72-77.

[37] Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4743-4763.

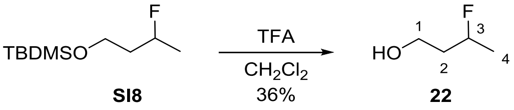
12.1.2. Synthesis of 1-tert-butyldimethylsilyloxy-3-fluorobutane (SI8)



To a solution of the mixture obtained above (1.90 g, 9.68 mmol, 1 equiv) in dry Et_2O (20 mL) was added MeONa solution (25 %wt in MeOH, 4.4 mL, 19 mmol, 2 equiv) and the resulting mixture was stirred at rt for 21.5 h. The reaction mixture was neutralized with aq. HCl (1 M, 20 mL) and extracted with Et_2O (3 × 60 mL) and the combined organic layers were dried ($MgSO_4$), filtered and evaporated at 750 mbar/30 °C. Column chromatography on silica gel eluting with pentane/Et_2O (90:10 to 40:60) gave approximately 0.87 g (9.4 mmol, 97%) of an inseparable 4:1 mixture of fluorohydrins **22** and **16** in solution in pentane/Et_2O (1:2, 15 mL). To 9 mL of this solution (corresponding approximately to 0.41 g, 4.5 mmol, 1.1 equiv of **22**) was added dry THF (6 mL) then NaH (60% in mineral oil, 162 mg, 4.05 mmol, 1 equiv) at 0 °C. The reaction mixture was stirred at rt for 0.5 h then TBDMSCl (610 mg, 4.05 mmol, 1 equiv) in solution in dry THF (4 mL) was added dropwise (20 min) at 0 °C. The reaction mixture was stirred at rt for 18 h after which water (15 mL) was added and layers separated. The aqueous phase was extracted with Et_2O (3 × 20 mL) and the combined organic layers were dried ($MgSO_4$), filtered and concentrated carefully at 750 mbar/30 °C. Column chromatography on silica gel eluting with pentane afforded a 2:1 mixture of **SI8** and pentane (calc mass: 680 mg, 3.29 mmol, 81%).

R$_f$ 0.21 (pentane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.84 (ddqd, $^2J_{H3\text{-}F}$ = 49.1, $^3J_{H3\text{-}H2}$ = 8.4, $^3J_{H3\text{-}H4}$ = 6.2, $^3J_{H3\text{-}H2}$ = 4.0 Hz, 1H, H-3), 3.77 (ddd, $^2J_{H1\text{-}H1'}$ = 10.3, $^3J_{H1\text{-}H2}$ = 8.3, $^3J_{H1\text{-}H2'}$ = 5.2 Hz, 1H, H-1), 3.74 – 3.68 (m, 1H, H-1'), 1.93 – 1.65 (m, 2H, H-2 + H-2'), 1.36 (dd, $^3J_{H4\text{-}F}$ = 24.1, $^3J_{H4\text{-}H3}$ = 6.2 Hz, 3H, H-4), 0.90 (s, 9H, CH_3 tBu), 0.07 (s, 3H, CH_3), 0.07 (s, 3H, CH_3) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 88.0 (d, $^1J_{C3\text{-}F}$ = 163.6 Hz, C-3), 59.0 (d, $^3J_{C1\text{-}F}$ = 5.9 Hz, C-1), 40.0 (d, $^2J_{C2\text{-}F}$ = 20.5 Hz, C-2), 25.9 (C-7), 21.2 (d, $^2J_{C4\text{-}F}$ = 22.7 Hz, C-4), 18.3 (C-6), -5.4 (C-5), -5.4 (C-5') ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ –175.9 (ddqd, J = 49.2, 32.0, 24.1, 14.7 Hz, 1F, F-3) ppm.

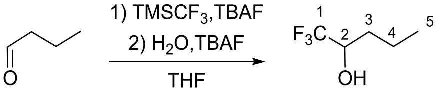
12.1.3. Synthesis of 3-fluorobutan-1-ol (22)



The solution obtained above (approx. mass of **SI8**: 680 mg, 3.29 mmol) was stirred in a 3% TFA solution of CH_2Cl_2 (15 mL) at rt for 7.5 h after which sat. aq. $NaHCO_3$ solution (5 mL) was added and layers separated. The aqueous phase was extracted with CH_2Cl_2 (2 × 10 mL) and the combined organic layers were dried ($MgSO_4$), filtered and concentrated carefully at 700 mbar/30 °C. Column chromatography on silica gel eluting with pentane/Et_2O (70:30 to 50:50) afforded 110 mg of **22** (1.19 mmol, 36%).

R$_f$ 0.33 (pentane/Et_2O 60:40). **IR** (neat) 3334 (br., w), 2961 (w), 2940 (w), 1386, (m), 1051 (s), 888 (m). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.89 (ddqd, $^2J_{H3\text{-}F}$ = 49.3, $^3J_{H3\text{-}H2}$ = 8.6, $^3J_{H3\text{-}H4}$ = 6.1, $^3J_{H3\text{-}H2'}$ = 3.8 Hz, 1H, H-3), 3.88 – 3.74 (m, 2H, H-1), 1.98 – 1.72 (m, 2H, H-2), 1.64 (br s, 1H, OH), 1.38 (dd, $^3J_{H4\text{-}F}$ = 24.2, $^3J_{H4\text{-}H3}$ = 6.1 Hz, 3H, H-4) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 89.2 (d, $^1J_{C3\text{-}F}$ = 162.9 Hz, C-3), 59.4 (d, $^3J_{C1\text{-}F}$ = 4.4 Hz, C-1), 39.5 (d, $^2J_{C2\text{-}F}$ = 19.8 Hz, C-2), 21.2 (d, $^2J_{C4\text{-}F}$ = 22.0 Hz, C-4) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ –175.3 (ddqdd, $^2J_{F\text{-}H3}$ = 49.3, $^3J_{F\text{-}H2}$ = 32.9, $^3J_{F\text{-}H4}$ = 24.3, $^3J_{F\text{-}H2'}$ = 15.6, $J_{F\text{-}H}$ = 3.5 Hz, 1F, F-3) ppm. **HRMS** (MS+) for C_4H_9FO, calcd 92.0632, found 92.0650.

12.2. Synthesis of 1,1,1-trifluoropentan-2-ol (29)



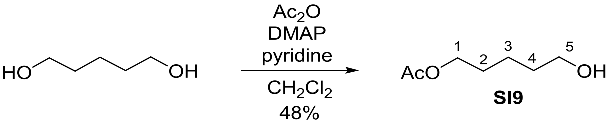
29

The following is an adaptation of a procedure from Kelly *et al.*[38] To a mixture of *n*-butanal (0.90 mL, 10.0 mmol, 1 equiv) and trifluoromethyltrimethylsilane (0.5 M in THF, 24 mL, 12.0 mmol, 1.2 equiv) at 0 °C was added TBAF solution (1.0 M in THF, 0.1 mL, 0.1 mmol, 0.01 equiv). After 10 min stirring, the ice-water bath was removed and the reaction mixture was stirred at rt for 5.5 h. After cooling at 0 °C, water (1 mL, 5.5 equiv) then TBAF (1.0 M in THF, 1 mL, 1 mmol, 0.1 equiv) were added and the resultant mixture was stirred at rt for 1.5 h. Brine (50 mL) then Et_2O (75 mL) were added and layers were partitioned. The aqueous phase was extracted with Et_2O (3 × 25 mL) then the combined organic layers were dried ($MgSO_4$), filtered and carefully concentrated. Column chromatography on silica gel eluting with pentane/Et_2O (93:7 to 75:25) gave the desired fluorohydrin **29** in solution in pentane/Et_2O. The product was then distilled using a Kugelrohr heating up to 90 °C at atmospheric pressure gave 91 mg (0.64 mmol, 6.4%) of the pure fluorohydrin **29** as a colourless oil (procedure not optimized). The spectral data matched with the literature.[39]

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.00 – 3.88 (m, 1H, H-2), 1.96 (d, $^3J_{H2\text{-}OH}$ = 6.2 Hz, 1H, OH), 1.75 – 1.39 (m, 4H, H-3 + H-4), 0.99 (t, $^3J_{H5\text{-}H4}$ = 7.1 Hz, 3H, H-5) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 125.2 (q, $^1J_{C1\text{-}F}$ = 281.7 Hz, C-1), 70.3 (q, $^2J_{C2\text{-}F}$ = 31.1 Hz, C-2), 31.6 (q, $^3J_{C3\text{-}F}$ = 1.6 Hz, C-3), 18.2 (C-4), 13.6 (C-5) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ –80.4 (d, $^3J_{F\text{-}H2}$ = 6.9 Hz, 3F, F-1) ppm.

12.3. Synthesis of 5-fluoro-1-pentanol (30)

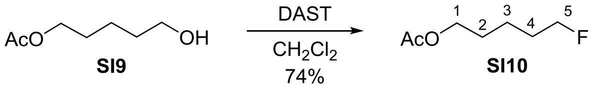
12.3.1. Synthesis of 5-hydroxypentyl acetate (SI9)



To a round-bottom flask were added 1,5-pentanediol (10 mL, 95.4 mmol, 1 equiv), DCM (200 mL, 2 mL/mmol), pyridine (9.78 mL, 120.9 mmol, 1.27 equiv), 4-DMAP (1.40 g, 11.5 mmol, 0.12 equiv) and acetic anhydride (9.02 mL, 95.4 mmol, 1 equiv). The resulting reaction solution was stirred at 0°C for 45 min and then quenched with water (150 mL), followed by extraction with DCM (150 mL× 3). The combined organic layer was washed with aq. HCl solution (1M, 150 mL), dried over $MgSO_4$, filtered and concentrated. The crude was purified by flash chromatography eluting with acetone/petroleum ether (10:90 to 40:60) to give 6.65 g (45.5 mmol, 48%) of the desired monoacetate **SI9** as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.00 (t, J = 6.7 Hz, 2H, H-1), 3.55 (t, J = 6.5 Hz, 2H, H-5), 3.09 (br. s., 1H, -OH), 1.97 (s, 3H, CH_3), 1.43 - 1.69 (m, 4H, H-2 + H-4), 1.29 - 1.42 (m, 2H, H-3) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.2, 64.3, 62.2, 32.0, 28.2, 22.0, 20.8 ppm; NMR data were consistent with the data reported in the literature.[40]

12.3.2. Synthesis of 5-fluoropentyl acetate (SI10)



To a round-bottom flask were added 5-hydroxypentyl acetate **SI9** (6.65 g, 45.5 mmol, 1 equiv), DCM (anhydrous, 100 mL) and DAST (9.02 mL, 68.2 mmol, 1.5 equiv). The resulting reaction

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[38] C. B. Kelly, M. A. Mercadante, T. A.; Hamlin, M. H. Fletcher, N. E. Leadbeater, *J. Org. Chem.* **2012,** *77*, 8131-8141.

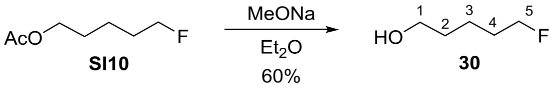
[39] K.-R. Gassen, W. Kirmse, *Chem. Ber.* **1986**, *119*, 2233-2248.

[40] K**.** Yoshida, T**.** Furuta**,** T**.** Kawabata *Angew. Chem. Int. Ed.* **2011**, *50*, 4888-4898.

mixture was stirred at room temperature overnight and then quenched by sat. aq. $NaHCO_3$ solution (150 mL), followed by extraction with DCM (150 mL× 3). The combined organic layer was dried over $MgSO_4$, filtered and concentrated. The crude was purified by flash chromatography eluting with DCM/pentane (20:80) and then acetone (100%) to give 5.0* g (33.7* mmol, 74%*, *calculated based on ^{1}H NMR) of the desired 5-fluoropentyl acetate (**SI10**). Due to the presumed volatility of this fluorinated pentyl acetate, this compound (containing eluting solvents) was used directly for next step without further removal of the solvent residue.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.46 (dt, *J* = 47.9, 6.3 Hz, 2H, H-5), 4.09 (t, *J* = 6.2 Hz, 2H, H-1), 2.06 (s, 3H, CH_3), 1.62 - 1.85 (m, 4H, H-4 + H-2), 1.41 - 1.60 (m, 2H, H-3) ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -218.7 (tt, *J* = 46.7, 26.4 Hz, 1F) ppm; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -218.7 (s, 1 F) ppm;

12.3.3. Synthesis of 5-fluoro-1-pentanol (30)

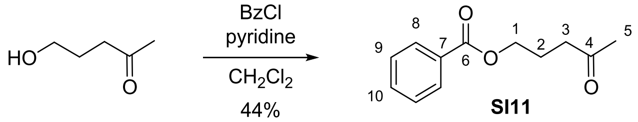


To a round-bottom flask were added 5-fluoropentyl acetate **SI10** (5.0 g, 33.7 mmol, 1 equiv), diethyl ether (50 mL) and NaOMe solution (25% w/w in MeOH, 15.4 mL, 67.4 mmol, 2 equiv). The resulting reaction mixture was stirred at room temperature overnight and then neutralized with aq. HCl solution (1M) up to ca. pH 7, followed by extraction with DCM (100 mL× 3). The combined organic layer was dried over $MgSO_4$, filtered and concentrated. The crude was purified by flash chromatography eluting with diethyl ether/DCM (4:94-20:80) to give 2.16 g (20.35 mmol, 60%) of the desired product (**30**) as colorless oil.

R$_f$ 0.25 (Et_2O/DCM 8:92). **IR** (neat) 3334 (br., w), 2939 (m), 1391, (w), 1055 (s), 1029 (s), 1006 (m), 990 (m). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.45 (dt, *J* = 47.4, 6.1 Hz, 2H, H-5), 3.65 (t, *J* = 6.2 Hz, 2H, H-1), 1.55 - 1.81 (m, 5H, H-4 + -OH + H-2), 1.42 - 1.54 (m, 2H, H-3) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 84.0 (d, *J* = 164.7 Hz, C-5), 62.6 (C-1), 32.2 (C-2), 30.1 (d, *J* = 19.6 Hz, C-4), 21.5 (d, *J* = 5.5 Hz, C-3) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -218.4 (tt, *J* = 48.1, 25.1 Hz, 1F) ppm. **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -218.4 (s, 1F) ppm. **MS** (EI) *m/z* (%) 86 (2) $[M\text{-}HF]^{+\bullet}$, 85 (3) $[M\text{-}HF\text{-}H^{\bullet}]^+$, 68 (49) $[M\text{-}H_2O\text{-}HF]^{+\bullet}$, 67 (26) $[M\text{-}H_2O\text{-}HF\text{-}H^{\bullet}]^+$, 56 (100) $[C_4H_8]^{+\bullet}$, 55 (47) $[C_4H_7]^+$, 41 (52) $[C_3H_5]^+$. **HMRS** (MS+) for $C_5H_{11}FO$, calcd 106.0788, found 106.0774. .

12.4. Synthesis of 4-fluoropentan-1-ol (31)

12.4.1. Synthesis of 4-oxopentyl benzoate (SI11)



To a mixture of 5-hydroxypentan-2-one (10 mL, 98 mmol, 1 equiv) and pyridine (16 mL, 196 mmol, 2 equiv) in CH_2Cl_2 at 0°C was added slowly benzoyl chloride (13.6 mL, 118 mmol, 1.2 equiv). After stirring the reaction mixture at rt for 42.5 h, water (150 mL) was added and the mixture was extracted with CH_2Cl_2 (2 × 300 mL). The combined organic extracts were successively washed with aq. HCl (1.0 M, 100 mL) and sat. aq. $NaHCO_3$ (200 mL) then dried ($MgSO_4$), filtered and concentrated *in vacuo*. Column chromatography on silica gel eluting with petroleum ether 40–60 °C/EtOAc (90:10 to 75:25) gave 8.90 g (43 mmol, 44%) of **SI11** as a pale yellow oil.

R$_f$ 0.21 (petroleum ether 40–60 °C/EtOAc 85:15). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.8 Hz, 2H, H_{Ar}), 7.60 – 7.53 (m, 1H, H_{Ar}), 7.48 – 7.41 (m, 2H, H_{Ar}), 4.34 (t, $^3J_{H\text{-}H}$ = 6.4 Hz, 2H, H-1), 2.61 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 2H, H-3), 2.18 (s, 3H, H-5), 2.07 (app. quin, $^3J_{H\text{-}H}$ = 6.8 Hz, 2H, H-2) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.6 (C-4), 166.5 (C-6), 132.9 (C-10), 130.2 (C-7), 129.5 (C-8), 128.3 (C-9), 64.1 (C-1), 39.9 (C-3), 30.0 (C-5), 22.9 (C-2) ppm. The spectral data matched with the literature.[41]

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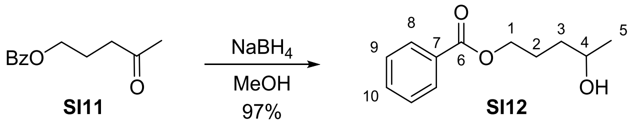
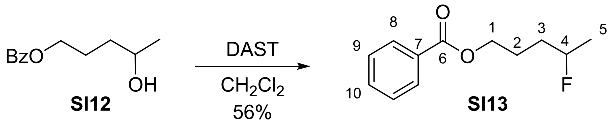
[41] T. Nishimura, N. Kakiuchi, T. Onoue, K. Ohe, S. Uemura, *J. Chem. Soc., Perkin Trans. 1* **2000**, 1915-1918.

12.4.2. Synthesis of 4-hydroxypentyl benzoate (SI12)



To the ketone **SI11** (4.0 g, 19.4 mmol, 1 equiv) in dry MeOH (40 mL) at 0 °C was added portion wise sodium borohydride (734 mg, 19.4 mmol, 1 equiv). After stirring for 0.5 h at rt, EtOAc (100 mL) was added and the reaction mixture was washed successively with water (50 mL) and brine (30 mL), dried (MgSO4), filtered and concentrated to give 3.90 g (18.7 mmol, 97%) of the alcohol **SI12** as a pale yellow oil which was directly used without purification.
R$_f$ 0.23 (petroleum ether 40-60 °C/EtOAc 70:30). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, J = 7.8 Hz, 2H, H_{Ar}), 7.60 – 7.53 (m, 1H, H_{Ar}), 7.48 – 7.41 (m, 2H, H_{Ar}), 4.36 (t, J = 6.6 Hz, 2H, H-5), 3.89 (app. sxt, J = 6.2 Hz, 1H, H-2), 2.01 – 1.76 (m, 2H, H-4), 1.65 – 1.57 (m, 2H, H-3), 1.53 (br s, 1H, OH), 1.25 (d, J = 6.1 Hz, 3H, H-1) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.6 (C-6), 132.9 (C-10), 130.3 (C-7), 129.5 (C-8), 128.3 (C-9), 67.6 (C-1), 64.9 (C-4), 35.5 (C-3), 25.1 (C-2), 23.6 (C-5) ppm. The spectral data matched with the literature.[42]

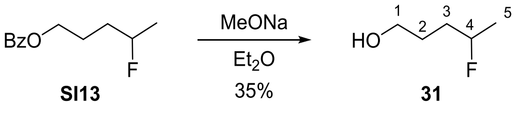
12.4.3. Synthesis of 4-fluoropentyl benzoate (SI13)



To the crude alcohol (**SI12**) obtained above (3.70 g, 17.8 mmol, 1 equiv) in dry CH_2Cl_2 (20 mL) at 0 °C was added DAST (3.49 mL, 26.7 mmol, 1.5 equiv). After stirring at rt for 14.5 h, 0.5 equiv of DAST was added and stirring was continued for 6 h. The reaction mixture was diluted with CH_2Cl_2 (140 mL), quenched with sat. aq. $NaHCO_3$ (70 mL) and layers were separated. The aqueous phase was extracted with CH_2Cl_2 (2 × 140 mL) and the combined organic layers were dried ($MgSO_4$), filtered and concentrated. Column chromatography on silica gel eluting with petroleum ether 40–60 °C/Et_2O (97:3 to 90:10) gave 2.11 g (10.0 mmol, 56%) of **SI13** as a pale yellow oil.

R$_f$ 0.31 (petroleum ether 40-60 °C/Et_2O 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 – 8.03 (m, 2H, H_{Ar}), 7.61 – 7.54 (m, 1H, H_{Ar}), 7.49 – 7.42 (m, 2H, H_{Ar}), 4.85 – 4.63 (m, $^2J_{H4\text{-}F}$ = 48.9 Hz, 1H, H-4), 4.44 – 4.31 (m, 2H, H-1), 2.05 – 1.62 (m, 4H, H-2 + H-3), 1.37 (dd, $^3J_{H5\text{-}F}$ = 24.0, $^3J_{H5\text{-}H4}$ = 6.1 Hz, 3H, H-5) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.6 (C-6), 132.9 (C-10), 130.3 (C-7), 129.5 (C-8), 128.3 (C-9), 90.4 (d, $^1J_{C4\text{-}F}$ = 165.1 Hz, C-4), 64.6 (C-1), 33.5 (d, $^2J_{C3\text{-}F}$ = 21.3 Hz, C-3), 24.6 (d, $^3J_{C2\text{-}F}$ = 5.1 Hz, C-2), 21.0 (d, $^2J_{C5\text{-}F}$ = 22.7 Hz, C-5) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -173.7 (ddqd, $^2J_{F\text{-}H4}$ = 48.5, $^3J_{F\text{-}H3}$ = 29.5, $^3J_{F\text{-}H5}$ = 24.3, $^3J_{F\text{-}H3'}$ = 17.3 Hz, 1F, F-4) ppm. **MS** (ESI) *m*/*z* 211 $(M + H)^+$.

12.4.4. Synthesis of 4-fluoropentan-1-ol (31)



To a solution of benzoate **SI13** (2.00 g, 9.51 mmol, 1 equiv) in dry Et_2O (20 mL) was added MeONa solution (25 %wt in MeOH, 4.35 mL, 19.0 mmol, 2 equiv) and the resulting mixture was stirred at rt for 22 h. The reaction mixture was neutralized with aq. HCl (1 M, 20 mL) and extracted with Et_2O (3 × 60 mL) then the combined organic layers were dried ($MgSO_4$), filtered and evaporated at 750 mbar/30 °C. Column chromatography on silica gel eluting with CH_2Cl_2/Et_2O (100:0 to 80:20) gave the desired fluorohydrin **31** in solution in CH_2Cl_2/Et_2O. The product was then distilled using a Kugelrohr heating at 170 °C at atmospheric pressure but subsequent NMR analysis revealed that approximately 20 % of the product had cyclised to give 2-

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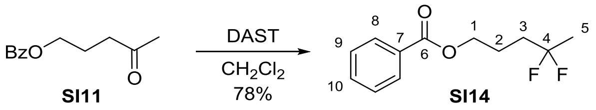
[42] S. Caddick, A. J. McCarroll, D. A. Sandham, *Tetrahedron* **2001**, *57*, 6305-6310.

methyltetrahydrofuran. Column chromatography of the mixture obtained on silica gel eluting with pentane/Et_2O (80:20 to 40:60) followed by HPLC (pentane/Et_2O, 70:30) gave 353 mg (3.33 mmol, 35%) of the pure fluorohydrin **31** as a colourless oil.

R$_f$ 0.29 (pentane/Et_2O 60:40). **IR** (neat) 3335 (br., w), 2939 (m), 1386, (m), 1058 (s), 1037 (s), 1007 (s), 988 (s). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.83 – 4.60 (m, $^2J_{H4\text{-}F}$ = 48.9 Hz, 1H, H-4), 3.78 – 3.63 (m, 2H, H-1), 1.82 – 1.56 (m, 4H, H-2 + H-3), 1.41 – 1.30 (m, 1H, OH), 1.35 (dd, $^3J_{H5\text{-}F}$ = 23.8, $^3J_{H5\text{-}H4}$ = 6.1 Hz, 3H, H-5) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 90.9 (d, $^1J_{C4\text{-}F}$ = 164.3 Hz, C-4), 62.6 (C-1), 33.2 (d, $^2J_{C3\text{-}F}$ = 21.3 Hz, C-3), 28.3 (d, $^3J_{C2\text{-}F}$ = 4.4 Hz, C-2), 21.0 (d, $^2J_{C5\text{-}F}$ = 22.7 Hz, C-5) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ –173.2 – –172.6 (m, 1F, F-4) ppm. **MS** (EI) *m/z* (%) 88 (2) $[M\text{-}H_2O]^{+\bullet}$, 86 (2) $[M\text{-}HF]^{+\bullet}$, 73 (18) $[M\text{-}H_2O\text{-}Me^\bullet]^+$, 71 (9) $[M\text{-}HF\text{-}Me^\bullet]^+$ 56 (100) $[C_4H_8]^{+\bullet}$, 55 (20) $[C_4H_7]^+$, 41 (52) $[C_3H_5]^+$. **HMRS** (MS+) for $C_5H_{11}FO$, calcd 106.0788, found 106.0800.

12.5. Synthesis of 4,4-difluoropentan-1-ol (32)

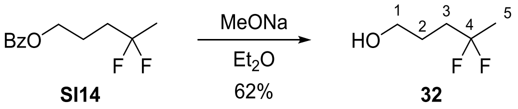
12.5.1. Synthesis of 4,4-difluoropentyl benzoate (SI14)



To the ketone **SI11** obtained above (4.00 g, 19.4 mmol, 1 equiv) in dry CH_2Cl_2 (10 mL) at rt was added DAST (5.1 mL, 39 mmol, 2.0 equiv). After stirring at 50 °C for 16 h, 10 drops of HF-pyridine were added and stirring at 50 °C was continued for 24 h. The reaction mixture was diluted with CH_2Cl_2 (150 mL), quenched with sat. aq. $NaHCO_3$ (75 mL) and layers were separated. The aqueous phase was extracted with CH_2Cl_2 (2 × 150 mL) and the combined organic layers were dried ($MgSO_4$), filtered and concentrated. Column chromatography on silica gel eluting with petroleum ether 40–60 °C/Et_2O (98:2 to 90:10) gave 3.47 g (15.2 mmol, 78%) of **SI14** as a pale yellow oil.

R$_f$ 0.26 (petroleum ether 40-60 °C/Et_2O 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, $^3J_{H\text{-}H}$ = 8.1 Hz, 2H, H_{Ar}), 7.62 – 7.54 (m, 1H, H_{Ar}), 7.51 – 7.42 (m, 2H, H_{Ar}), 4.38 (t, $^3J_{H1\text{-}H2}$ = 5.9 Hz, 2H, H-1), 2.11 – 1.94 (m, 4H, H-2 + H-3), 1.65 (t, $^3J_{H5\text{-}F}$ = 18.3 Hz, 3H, H-5) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.5 (C-6), 133.0 (C-10), 130.2 (C-7), 129.5 (C-8), 128.4 (C-9), 123.8 (t, $^1J_{C4\text{-}F}$ = 238.4 Hz, C-4), 64.1 (C-1), 34.7 (t, $^2J_{C3\text{-}F}$ = 26.0 Hz, C-3), 23.4 (t, $^2J_{C5\text{-}F}$ = 27.9 Hz, C-5), 22.2 (t, $^3J_{C2\text{-}F}$ = 4.8 Hz, C-2) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ –91.4 - –91.7 (m, 2F, F-4) ppm. **MS** (ESI) *m/z* 229 $(M + H)^+$.

12.5.2. Synthesis of 4,4-difluoropentan-1-ol (32)



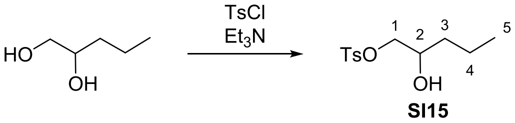
To a solution of benzoate **SI14** (3.30 g, 14.5 mmol, 1 equiv) in dry Et_2O (30 mL) was added MeONa solution (25 %wt in MeOH, 6.6 mL, 29 mmol, 2 equiv) and the resulting mixture was stirred at rt for 22 h. The reaction mixture was neutralized with aq. HCl (1 M, 30 mL) and extracted with Et_2O (3 × 90 mL) then the combined organic layers were dried ($MgSO_4$), filtered and evaporated at 750 mbar/30 °C. Column chromatography on silica gel eluting with CH_2Cl_2/Et_2O (100:0 to 80:20) gave the desired fluorohydrin **32** in solution in CH_2Cl_2/Et_2O. The product was then distilled using a Kugelrohr heating at 170 °C at atmospheric pressure gave 1.12 g (9.02 mmol, 62%) of the pure fluorohydrin **32** as a colourless oil.

R$_f$ 0.17 (CH_2Cl_2). Bp 150-160 °C. **IR** (neat) 3335 (br., w), 2948 (w), 1393, (s), 1025 (s), 913 (s). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.71 (app. q, $^3J_{H1\text{-}H2}$ = $^3J_{H1\text{-}OH}$ = 5.9 Hz, 2H, H-1), 2.03 – 1.89 (m, 2H, H-3), 1.81 – 1.72 (m, 2H, H-2), 1.62 (t, $^3J_{H5\text{-}F}$ = 18.3 Hz, 3H, H-5), 1.36 (br s, 1H, OH) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 124.2 (t, $^1J_{C4\text{-}F}$ = 237.3 Hz, C-4), 62.0 (C-1), 34.3 (t, $^2J_{C3\text{-}F}$ = 26.0 Hz, C-3), 25.8 (t, $^3J_{C2\text{-}F}$ = 4.4 Hz, C-2), 23.3 (t, $^3J_{C5\text{-}F}$ = 27.9 Hz, C-5) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -91.1 (app. sxt, $J_{F\text{-}H}$ = 17.7 Hz, 2F, F-4) ppm. **MS** (EI) *m/z* (%) 91 (10) $[M\text{-}H_2O\text{-}Me^\bullet]^+$, 89 (10) [M-HF-

$Me^{\bullet}]^+$, 87 (7) $[M-H_2O-F^{\bullet}]^+$, 86 (4) $[M-H_2O-HF]^{+\bullet}$, 84 (6) $[M-2HF]^{+\bullet}$, 74 (100) $[C_4H_7F]^{+\bullet}$, 73 (23) $[C_4H_6F]^+$, 59 (65) $[C_3H_4F]^+$. **HRMS** (MS+) for $C_5H_{10}F_2O$, calcd 124.0636, found 124.0694.

12.6. Synthesis of 2-fluoropentan-1-ol (33)

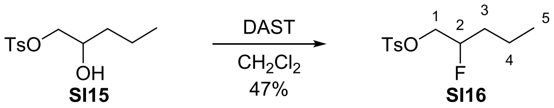
12.6.1. Synthesis of 2-hydroxypentyl tosylate (SI15)



To a round-bottom flask were added 1,2-pentanediol (6.41 mL, 59.8 mmol, 2 equiv), triethylamine (4.4 mL, 31.4 mmol, 1.05 equiv) and tosyl chloride (5.7 g, 29.9 mmol, 1 equiv). The resulting reaction mixture was stirred at room temperature overnight and then quenched by water (50 mL), followed by extraction with ethyl acetate (70 mL × 3). The combined organic layer was dried over $MgSO_4$, filtered and concentrated. The crude was used directly for next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H, H_{Ar}), 7.38 (d, *J* = 8.3 Hz, 2H, H_{Ar}), 4.00 - 4.11 (m, 1H, H-2), 3.81 - 3.97 (m, 2H, H-1), 2.48 (s, 3H, $ArCH_3$), 1.20 - 1.68 (m, 4H, H-3 + H-4), 0.92 (t, *J* = 6.9 Hz, 3H, H-5) ppm;

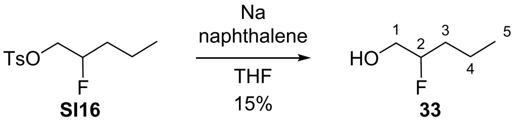
12.6.2. Synthesis of 2-fluoropentyl tosylate (SI16)



To a round-bottom flask were added 2-hydroxypentyl tosylate (**SI15**) (780 mg, 3.02 mmol, 1 equiv), DCM (anhydrous, 20 mL) and DAST (1.20 mL, 9.06 mmol, 3 equiv). The resulting reaction solution was stirred at room temperature overnight uncer argon and the quenched by sat. aq. $NaHCO_3$ solution (50 mL), followed by extraction with ethyl acetate (50 mL × 3). The combined organic layer was dried over $MgSO_4$, filtered and concentrated. The crude was purified by flash chromatography eluting with acetone/petroleum ether (10:90 to 30:70) to give 372 mg (1.43 mmol, 47%) of the desired tosylate product **SI16** as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H, H_{Ar}), 7.36 (d, *J* = 8.1 Hz, 2H, H_{Ar}), 4.48 - 4.80 (m, 1H, H-2, a doublet with 48.5 Hz can be observed), 3.98 - 4.23 (m, 2H, H-1), 2.46 (s, 3H, $ArCH_3$), 1.29 - 1.75 (m, 4H, H-3 + H-4), 0.93 (t, *J* = 7.2 Hz, 3H, H-5) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.0 (C_{Ar}), 132.7 (C_{Ar}), 129.9 (C_{Ar}), 127.9 (C_{Ar}), 90.2 (d, *J* 174.6 Hz, C-2), 70.7 (d, *J* 23.7 Hz, C-1), 32.9 (d, *J* 20.4 Hz, C-3), 21.6 ($ArCH_3$), 17.9 (d, *J* 4.6 Hz, C-4), 13.7 (C-5) ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -187.8 - -187.2 (m, 1F) ppm; **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -187.5 (s, 1F) ppm;

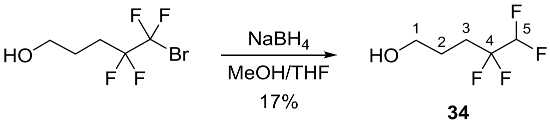
12.6.3. Synthesis of 2-fluoropentan-1-ol (33)



A mixture of sodium (154 mg, 6.70 mmol, 5.6 equiv) and naphthalene (944 mg, 7.37 mmol, 6.2 equiv) in dry THF (15 mL) was sonicated for 30 min. The characteristic dark green solution obtained was cooled to -70 °C and tosylate **SI16** (310 mg, 1.19 mmol, 1 equiv) in THF (15 mL) was added dropwise over 15 min. After stirring for 30 min, the reaction mixture was quenched with NH_4Cl (sat aq, 15 mL) and extracted with Et_2O (15 mL then 2 × 30 mL). The combined organic phases were dried ($MgSO_4$), filtered and evaporated at 750 mbar/30 °C leading to the crude

product in THF (≈ 20 mL). The crude mixture was diluted with pentane (40 mL), loaded onto silica gel and purified by column chromatography eluting with pentane/Et_2O (100:0 to 50:50). A second column chromatography eluting with pentane/Et_2O (80:20) followed by HPLC (pentane/Et_2O, 77:23) afforded 19 mg (0.179 mmol, 15%) of fluorohydrin **33** as a colourless oil.
R_f 0.4 (pentane/Et_2O 70:30). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.70 – 4.50 (m, $^2J_{H2\text{-}F}$ = 49.8 Hz, 1H, H-2), 3.80 – 3.61 (m, 2H), 1.78 (t, $^3J_{OH\text{-}H1}$ = 6.5 Hz, 1H), 1.76 – 1.35 (m, 4H, H-3 + H-4), 0.97 (t, $^3J_{H5\text{-}H4}$ = 7.2 Hz, 3H, H-5) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 94.5 (d, $^1J_{C2\text{-}F}$ = 167.3 Hz, C-2), 65.1 (d, $^2J_{C1\text{-}F}$ = 22.0 Hz, C-1), 33.0 (d, $^2J_{C3\text{-}F}$ = 19.8 Hz, C-3), 18.2 (d, $^3J_{C4\text{-}F}$ = 5.1 Hz, C-4), 13.9 (C-5) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ –190.1 – –190.5 (m, 1F, F-2) ppm. The spectral data matched with the literature.[43]

12.7. Synthesis of 4,4,5,5-tetrafluoropentan-1-ol (34)



34

To a mixture of 5-bromo-4,4,5,5-tetrafluoropentan-1-ol (1.0 g, 4.18 mmol, 1 equiv) in dry THF/MeOH (10:1, 11 mL) under argon was added $NaBH_4$ (177 mg, 4.68 mmol, 1.1 equiv) and the resulting mixture was stirred at rt. After 20 h, 177 mg (1.1 equiv) of $NaBH_4$ was added and stirring was continued for 5 h after which 322 mg (2 equiv) of $NaBH_4$ were added again. After 3 h of stirring, aq. H_2SO_4 (2 M, 25 mL) was added and layers were separated. The aqueous layer was extracted with Et_2O (3 × 50 mL) and the combined organic layers were dried ($MgSO_4$), filtered and concentrated at 725 mbar/30 °C. Column chromatography on silica gel eluting with pentane/Et_2O (80:20 to 60:40) gave 116 mg (0.725 mmol, 17%) of the desired fluorohydrin **34** as a colorless oil.
R_f 0.28 (pentan/Et_2O 70:30). **IR** (neat) 3359 (br., w), 2954 (w), 1207, (w), 1097 (s), 1056 (m), 1006 (s). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.74 (tt, J = 54.0, 2.8 Hz, 1H, H-5), 3.74 (t, J = 6.2 Hz, 2H, H-1), 2.19 – 2.02 (m, 2H, H-3), 1.90 – 1.80 (m, 2H, H-2), 1.43 – 1.32 (m, 1H, OH) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 118.1 (tt, J = 245.8, 28.5 Hz, C-4), 110.3 (tt, J = 249.1, 41.4 Hz, C-5), 61.8 (C-1), 26.3 (t, J = 22.4 Hz, C-3), 23.6 (t, J = 3.7 Hz, C-2) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ –116.3 (t, J = 18.6 Hz, 2F, H-4), –135.5 (d, J = 53.8 Hz, 2F, F-5) ppm. **MS** (EI) *m/z* (%) 160 (2) $[M]^{+\bullet}$, 159 (3) $[M\text{-}H^\bullet]^+$, 140 (5) $[M\text{-}HF]^{+\bullet}$, 139 (12) $[M\text{-}HF\text{-}H^\bullet]^+$, 123 (4) $[M\text{-}H_2O\text{-}F^\bullet]^+$, 120 (3) $[M\text{-}2HF]^{+\bullet}$, 119 (3) $[M\text{-}2HF\text{-}H^\bullet]^+$, 110 (16) $[C_4H_5F_3]^{+\bullet}$, 91 (42) $[C_4H_5F_2]^+$, 90 (26) $[C_4H_4F_2]^{+\bullet}$, 89 (29) $[C_4H_3F_2]^+$, 77 (39) $[C_3H_3F_2]^+$, 59 (100) $[C_3H_4F]^+$. **HRMS** (MS+) for $C_5H_8F_4O$, calcd 160.0506, found, 160.0482.

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[43] M. Marigo, D. Fielenbach, A. Braunton, A. Kjærsgaard, K. A. Jørgensen, *Angew. Chem., Int. Ed.* **2005**, *44*, 3703-3706

13. Selected NMR spectra for logP determination, with detailed NMR parameter information and integration details after reprocessing

ZW7157-26-1 OCT

SW: 300 ppm

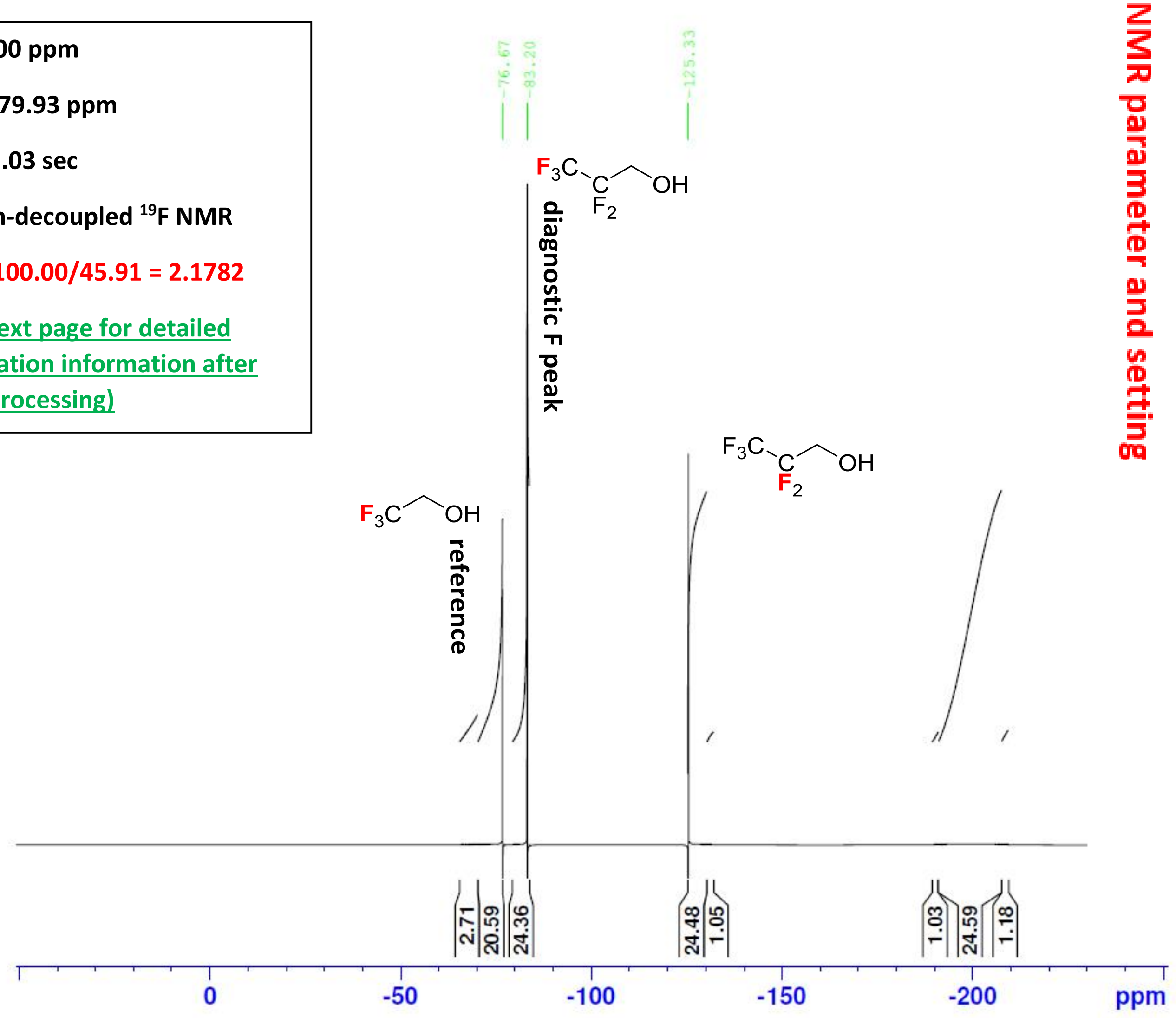
O1P: -79.93 ppm

D1: 12.03 sec

Proton-decoupled ^{19}F NMR

ρ_{oct} = 100.00/45.91 = 2.1782

(see next page for detailed integration information after data processing)



NMR parameter and setting

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PROCNO                    1

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SOLVENT             Acetone
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DS                        4
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FIDRES           0.866977 Hz
AQ              0.5767168 sec
RG                   212.69
DW                  4.400 usec
DE                   6.50 usec
TE                  298.0 K
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D11            0.03000000 sec
D12            0.00002000 sec
TD0                       1

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NUC1                    19F
P1                  11.70 usec
PLW1          32.00000000 W

======== CHANNEL f2 ========
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NUC2                     1H
CPDPRG[2            waltz16
PCPD2               70.00 usec
PLW2          32.00000000 W
PLW12          0.31999999 W

F2 - Processing parameters
SI                    65536
SF           376.4980709 MHz
WDW                      EM
SSB         0
LB                     0.30 Hz
GB          0
PC                     1.00
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ZW7157-26-1 OCT

Acquisition Time (sec)	0.5767	***Comment***	ZW7157-26-1 OCT			***Date***	24 Sep 2014 14:56:16
Date Stamp	24 Sep 2014 14:56:16			***File Name***	\\soton.ac.uk\ude\personalfiles\users\zw3g10\mydesktop\se2414zw1\10\fid		
Frequency (MHz)	376.47	***Nucleus***	19F	***Number of Transients***	64	***Origin***	spect
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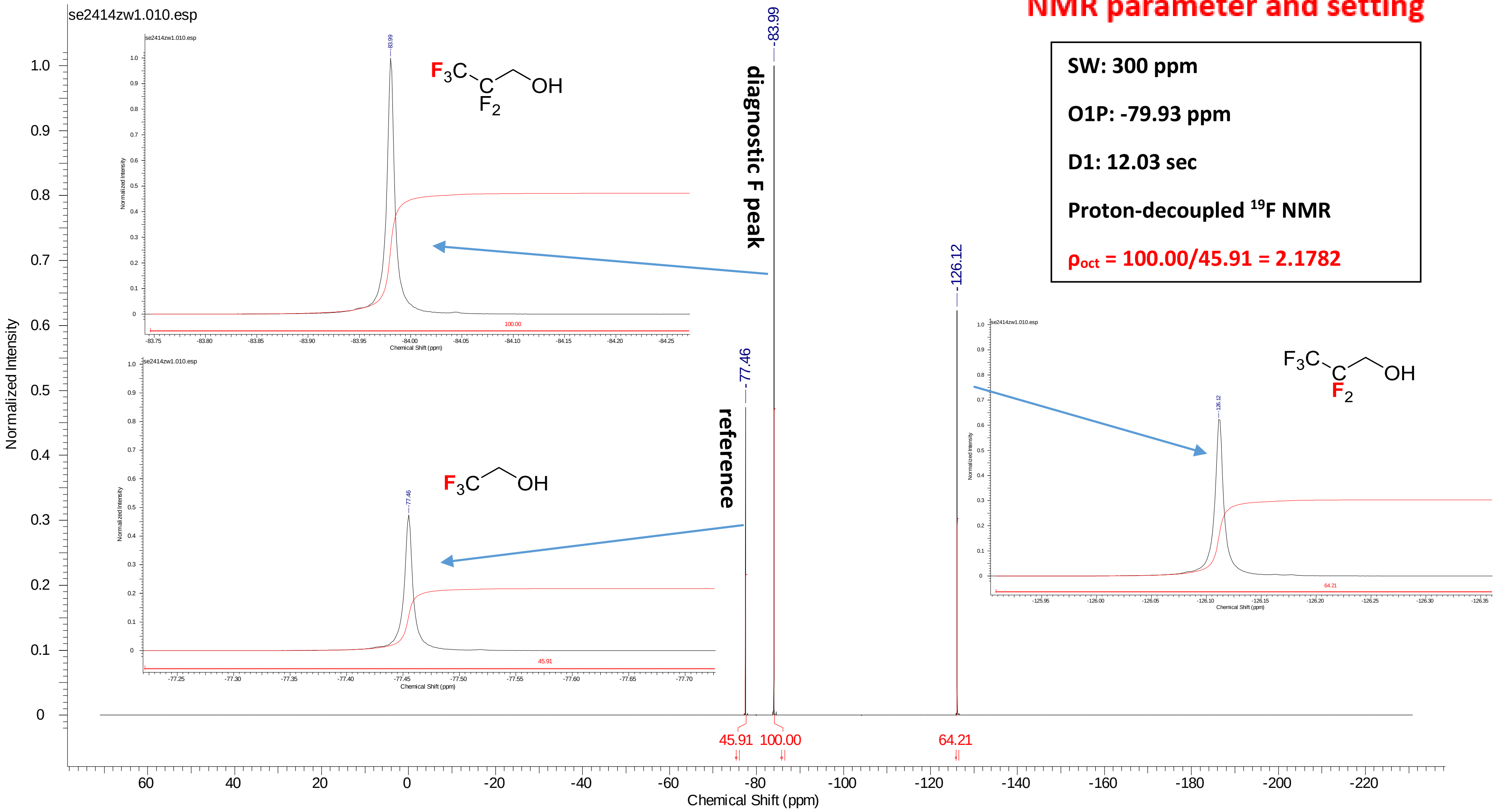
Receiver Gain	212.69	***SW(cyclical) (Hz)***	113636.36	***Solvent***	Acetone	***Spectrum Offset (Hz)***	-30093.4484
Spectrum Type	STANDARD	***Sweep Width (Hz)***	113635.93	***Temperature (degree C)***	25.000		



NMR parameter and setting

SW: 300 ppm

O1P: -79.93 ppm

D1: 12.03 sec

Proton-decoupled ^{19}F NMR

ρ_{oct} = 100.00/45.91 = 2.1782

ZW7157-26-1 WAT

SW: 300 ppm

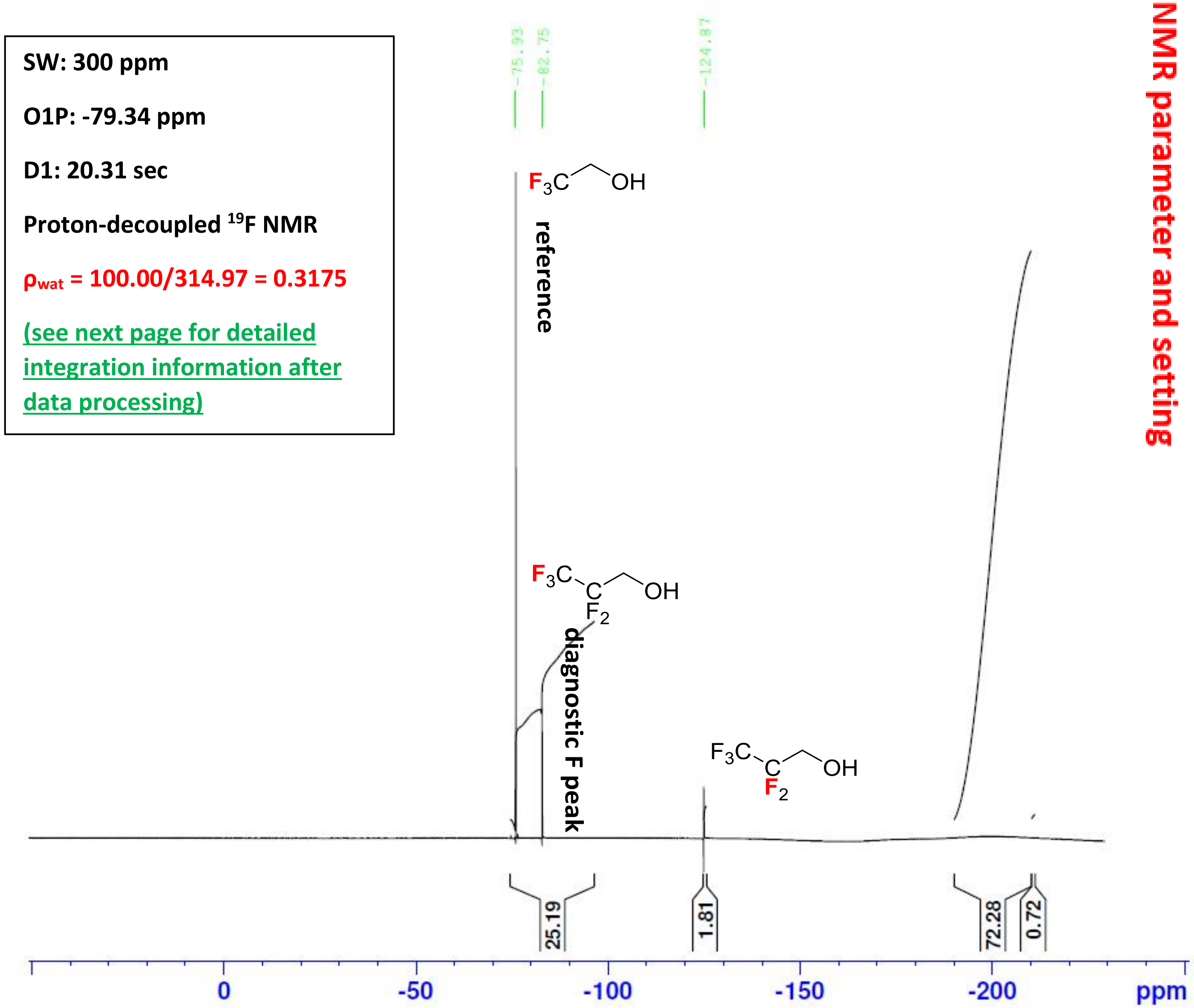
O1P: -79.34 ppm

D1: 20.31 sec

Proton-decoupled ^{19}F NMR

$\rho_{wat} = 100.00/314.97 = 0.3175$

(see next page for detailed integration information after data processing)



NMR parameter and setting

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PROCNO                   1

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DS                       4
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FIDRES            0.866977 Hz
AQ               0.5767168 sec
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DE                    6.50 usec
TE                   298.0 K
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D11             0.03000000 sec
D12             0.00002000 sec
TD0                      1

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P1                   11.70 usec
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======== CHANNEL f2 ========
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NUC2                    1H
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PCPD2                70.00 usec
PLW2           32.00000000 W
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F2 - Processing parameters
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ZW7157-26-1 WAT

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Original Points Count	65536	***Owner***	nmr	***Points Count***	262144	***Pulse Sequence***	zgfhigqn.2
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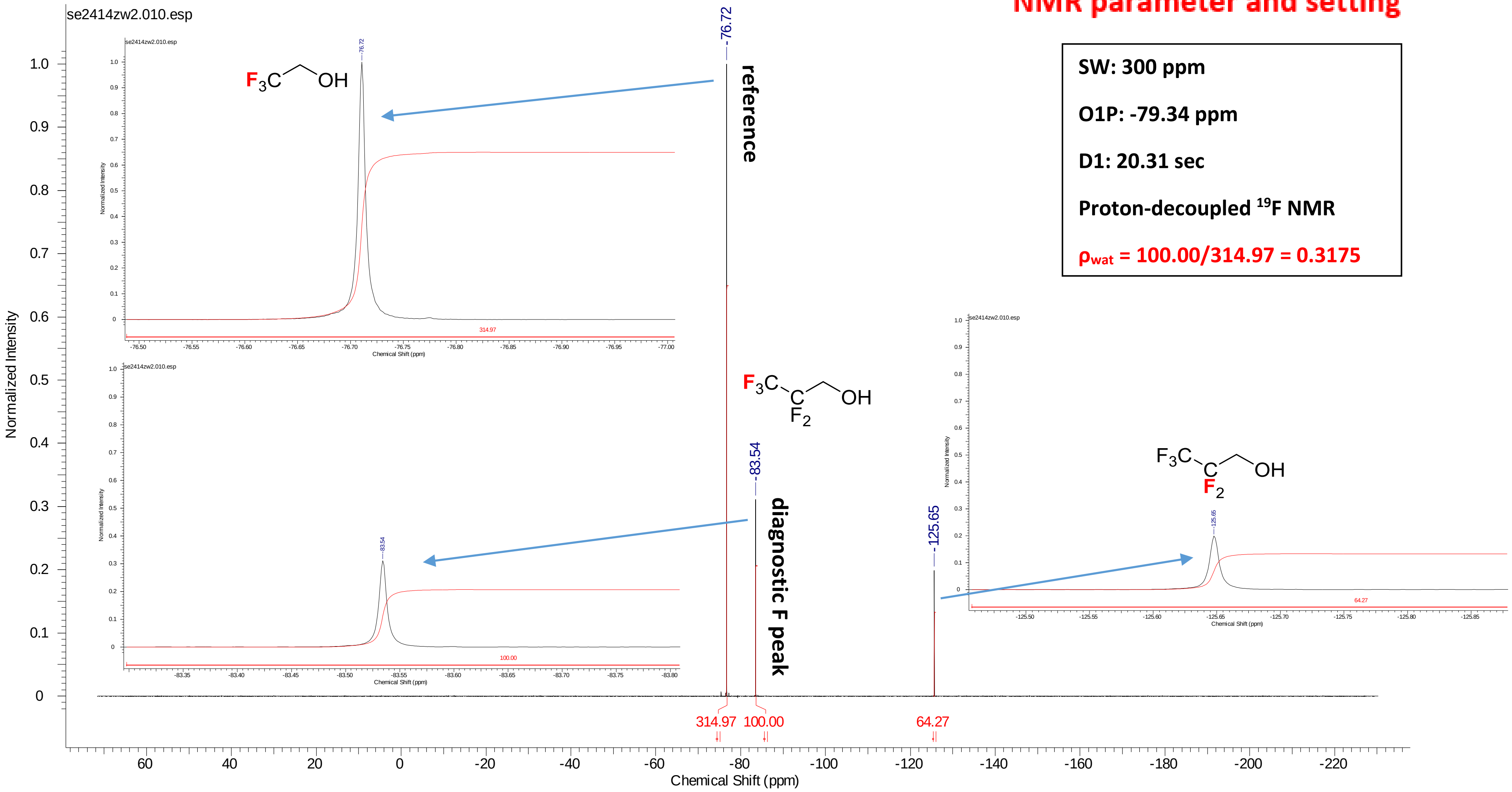


NMR parameter and setting

SW: 300 ppm

O1P: -79.34 ppm

D1: 20.31 sec

Proton-decoupled ^{19}F NMR

ρ_{wat} = 100.00/314.97 = 0.3175

ZW7157-26-1 OCT

SW: 300 ppm

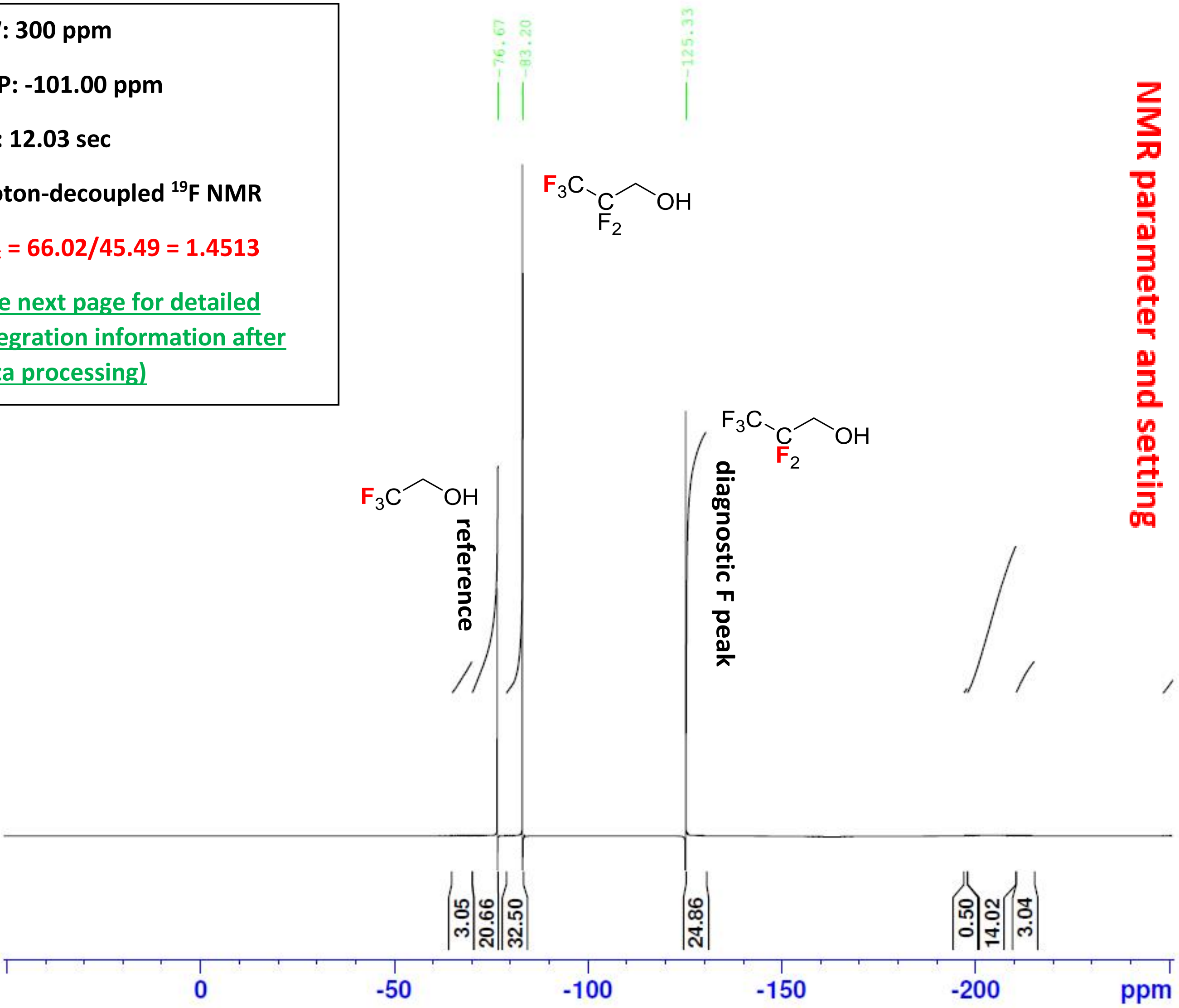
O1P: -101.00 ppm

D1: 12.03 sec

Proton-decoupled ^{19}F NMR

ρ_{oct} = 66.02/45.49 = 1.4513

(see next page for detailed integration information after data processing)



NMR parameter and setting

UNIVERSITY OF Southampton

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EXPNO                      13
PROCNO                      1

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DS                          4
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D12                0.00002000 sec
TD0                         1

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NUC1                      19F
P1                      11.70 usec
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======== CHANNEL f2 ========
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NUC2                       1H
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PCPD2                   70.00 usec
PLW2              32.00000000 W
PLW12              0.31999999 W

F2 - Processing parameters
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WDW                        EM
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PC                       1.00
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ZW7157-26-1 OCT

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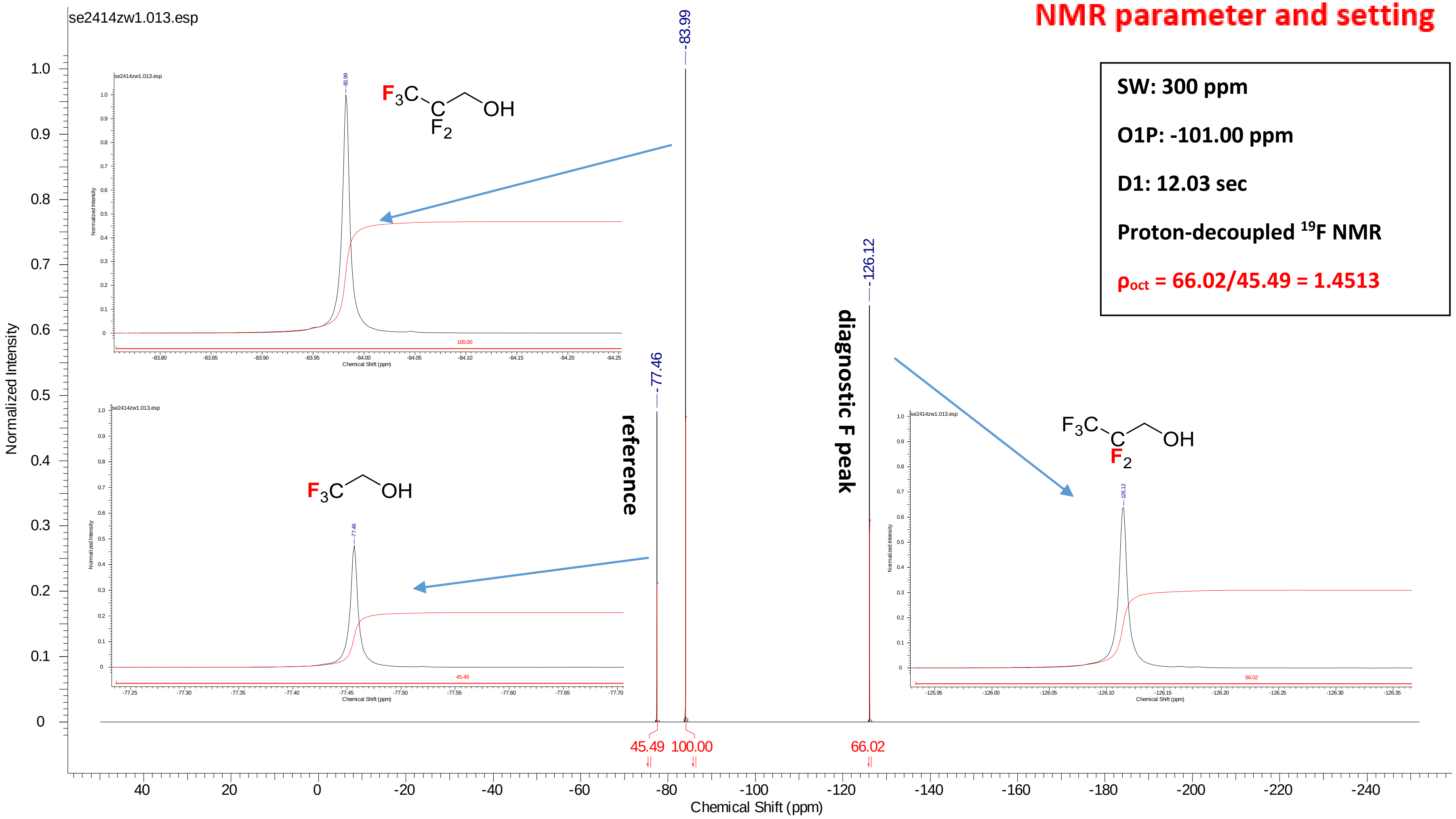

NMR parameter and setting

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O1P: -101.00 ppm

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Proton-decoupled ^{19}F NMR

ρ_{oct} = 66.02/45.49 = 1.4513

ZW7157-26-1 WAT

SW: 300 ppm

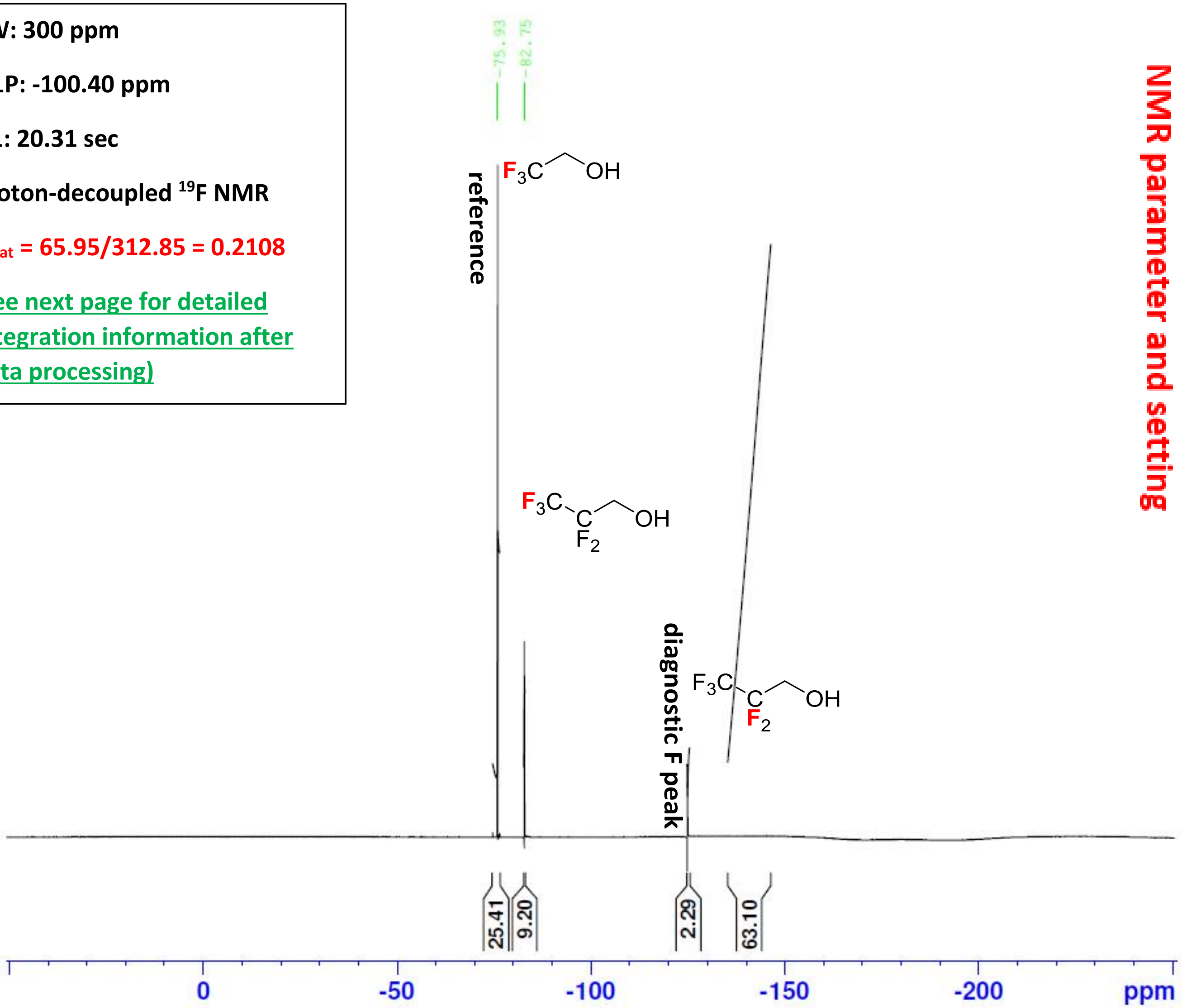
O1P: -100.40 ppm

D1: 20.31 sec

Proton-decoupled ^{19}F NMR

$\rho_{wat} = 65.95/312.85 = 0.2108$

(see next page for detailed integration information after data processing)



NMR parameter and setting

UNIVERSITY OF Southampton

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AVIIIHD400 [3]

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EXPNO                    13
PROCNO                    1

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SOLVENT             Acetone
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FIDRES             0.866977 Hz
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D12              0.00002000 sec
TD0                       1

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======== CHANNEL f2 ========
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NUC2                     1H
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PCPD2                 70.00 usec
PLW2            32.00000000 W
PLW12            0.31999999 W

F2 - Processing parameters
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PC                     1.00
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ZW7157-26-1 WAT

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Receiver Gain	212.69	***SW(cyclical) (Hz)***	113636.36	***Solvent***	Acetone	***Spectrum Offset (Hz)***	-37800.3984
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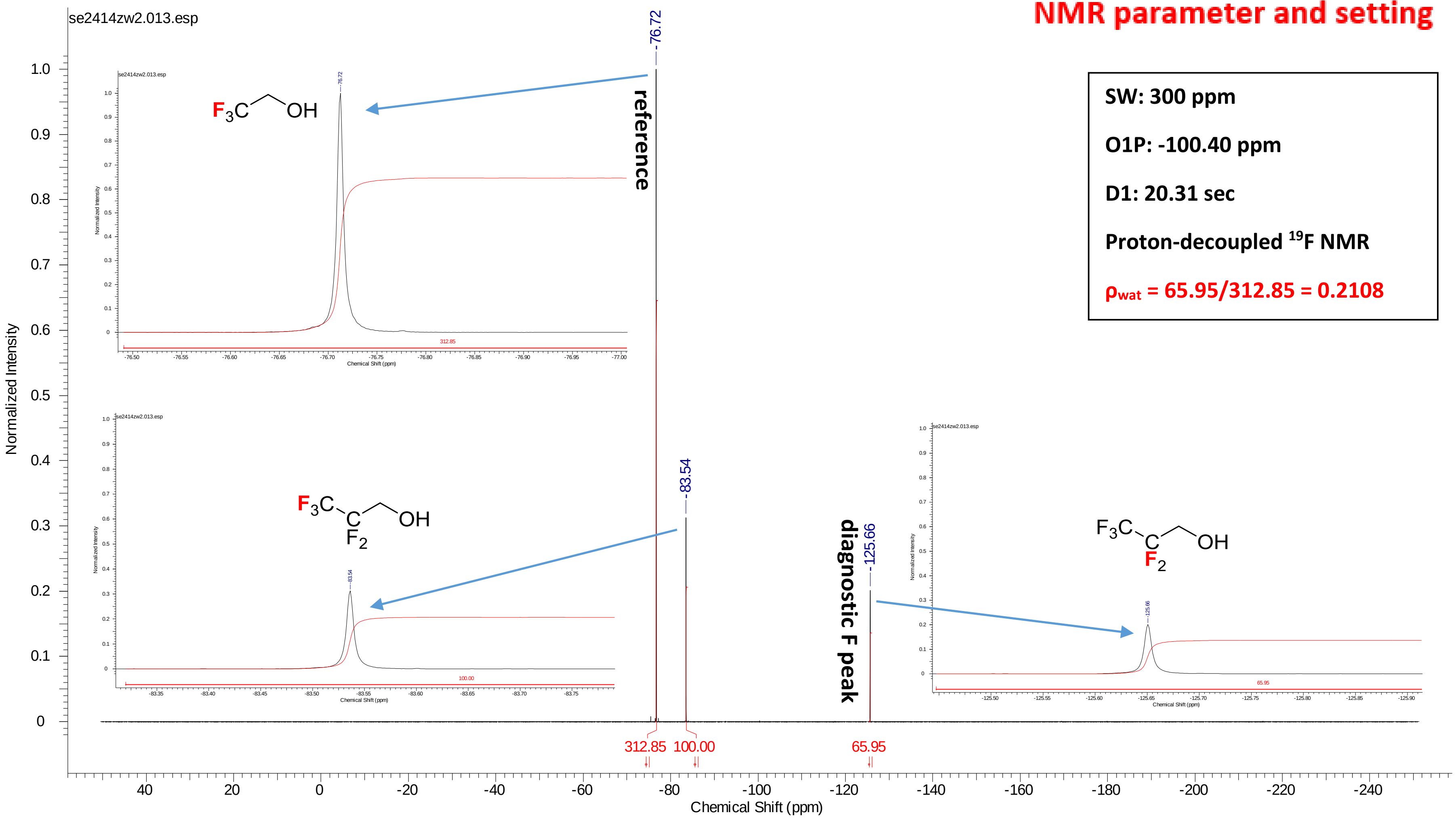
NMR parameter and setting



SW: 300 ppm

O1P: -100.40 ppm

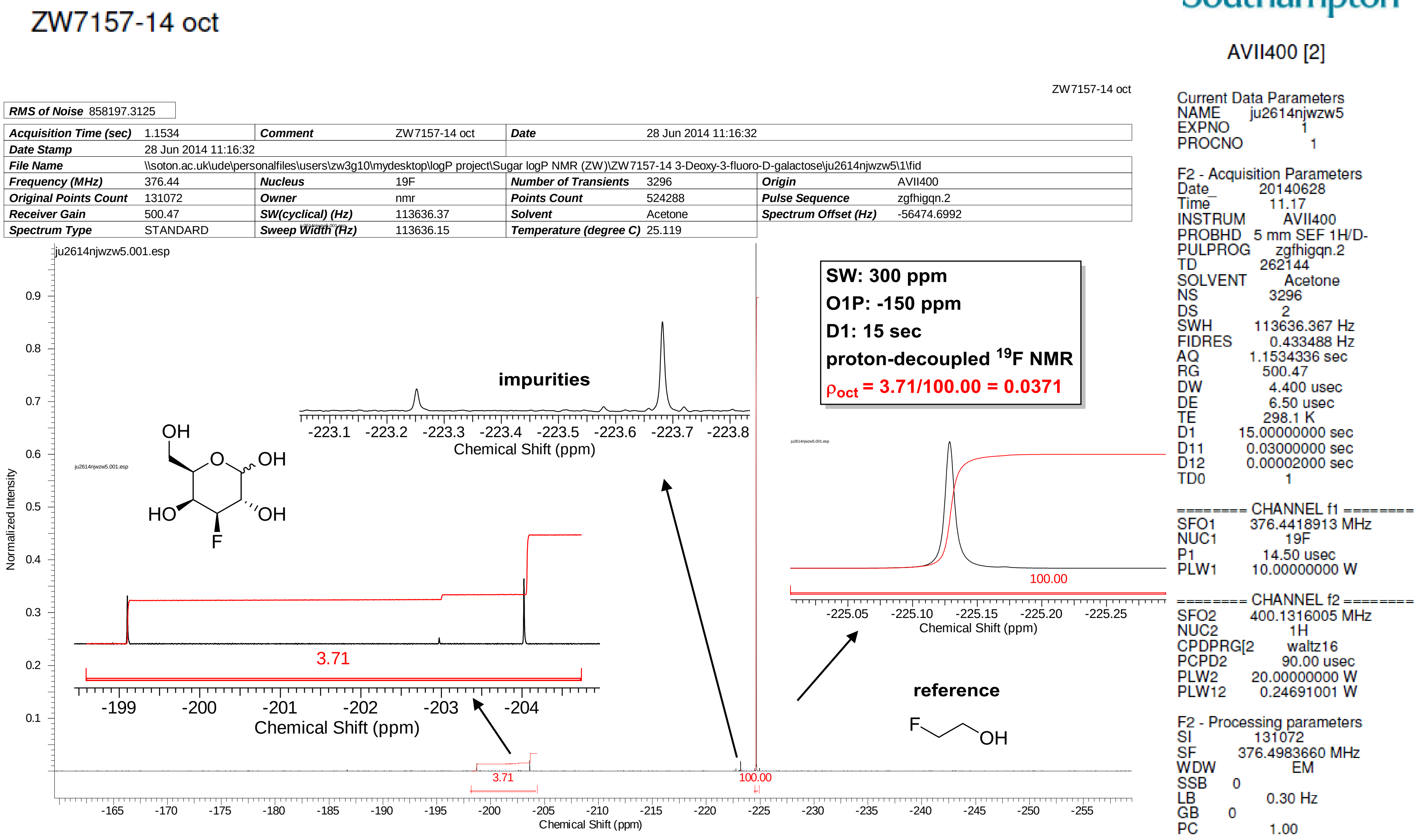
D1: 20.31 sec

Proton-decoupled ^{19}F NMR

ρ_{wat} = 65.95/312.85 = 0.2108

14. NMR spectra for fluorinated carbohydrates

14.1. 3-Fluoro-3-deoxy-D-galactose (46), Entry 1, octanol sample



ZW7157-14 oct

AVII400 [2]

ZW7157-14 oct

RMS of Noise	858197.3125

Acquisition Time (sec)	1.1534	**Comment**	ZW7157-14 oct	**Date**	28 Jun 2014 11:16:32		
Date Stamp	28 Jun 2014 11:16:32						
File Name	\\soton.ac.uk\ude\personalfiles\users\zw3g10\mydesktop\logP project\Sugar logP NMR (ZW)\ZW7157-14 3-Deoxy-3-fluoro-D-galactose\ju2614njwzw5\1\fid						
Frequency (MHz)	376.44	**Nucleus**	19F	**Number of Transients**	3296	**Origin**	AVII400
Original Points Count	131072	**Owner**	nmr	**Points Count**	524288	**Pulse Sequence**	zgfhigqn.2
Receiver Gain	500.47	**SW(cyclical) (Hz)**	113636.37	**Solvent**	Acetone	**Spectrum Offset (Hz)**	-56474.6992
Spectrum Type	STANDARD	**Sweep Width (Hz)**	113636.15	**Temperature (degree C)**	25.119		

SW: 300 ppm

O1P: -150 ppm

D1: 15 sec

proton-decoupled ^{19}F NMR

ρ_{oct} = 3.71/100.00 = 0.0371

Current Data Parameters
NAME ju2614njwzw5
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140628
Time 11.17
INSTRUM AVII400
PROBHD 5 mm SEF 1H/D-
PULPROG zgfhigqn.2
TD 262144
SOLVENT Acetone
NS 3296
DS 2
SWH 113636.367 Hz
FIDRES 0.433488 Hz
AQ 1.1534336 sec
RG 500.47
DW 4.400 usec
DE 6.50 usec
TE 298.1 K
D1 15.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 376.4418913 MHz
NUC1 19F
P1 14.50 usec
PLW1 10.00000000 W

======== CHANNEL f2 ========
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 20.00000000 W
PLW12 0.24691001 W

F2 - Processing parameters
SI 131072
SF 376.4983660 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

14.2. 3-Fluoro-3-deoxy-D-galactose[44] (46), Entry 1, water sample

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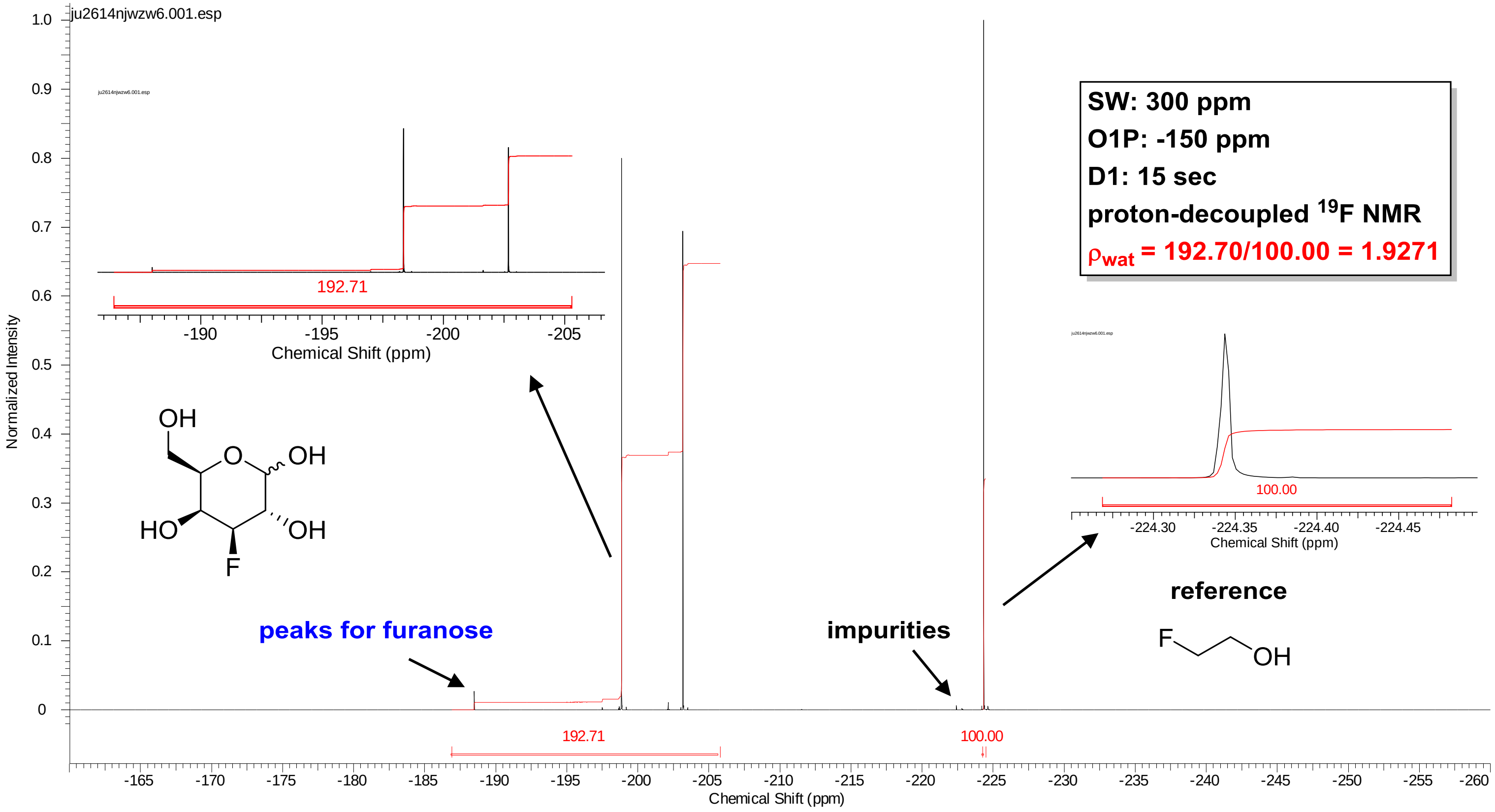
AVII400 [2]

ZW7157-14 wat

ZW7157-14 wat

Acquisition Time (sec)	1.1534	***Comment***	ZW7157-14 wat	***Date***	29 Jun 2014 12:37:36		
Date Stamp	29 Jun 2014 12:37:36						
File Name	\\soton.ac.uk\ude\personalfiles\users\zw3g10\mydesktop\Sugar logP NMR (ZW)\ZW7157-14 3-Deoxy-3-fluoro-D-galactose\ju2614njwzw6\1\fid						
Frequency (MHz)	376.44	***Nucleus***	19F	***Number of Transients***	2329	***Origin***	AVII400
Original Points Count	131072	***Owner***	nmr	***Points Count***	131072	***Pulse Sequence***	zgfhigqn.2
Receiver Gain	405.33	***SW(cyclical) (Hz)***	113636.37	***Solvent***	Acetone	***Spectrum Offset (Hz)***	-56474.6992
Spectrum Type	STANDARD	***Sweep Width (Hz)***	113635.50	***Temperature (degree C)***	25.119		



SW: 300 ppm

O1P: -150 ppm

D1: 15 sec

proton-decoupled ^{19}F NMR

ρ_{wat} = 192.70/100.00 = 1.9271

```
Current Data Parameters
NAME       ju2614njwzw6
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_          20140629
Time              12.38
INSTRUM         AVII400
PROBHD   5 mm SEF 1H/D-
PULPROG      zgfhigqn.2
TD               262144
SOLVENT         Acetone
NS                 2329
DS                    2
SWH          113636.367 Hz
FIDRES         0.433488 Hz
AQ            1.1534336 sec
RG               405.33
DW                4.400 usec
DE                 6.50 usec
TE                298.1 K
D1          15.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        376.4418913 MHz
NUC1                19F
P1                14.50 usec
PLW1        10.00000000 W

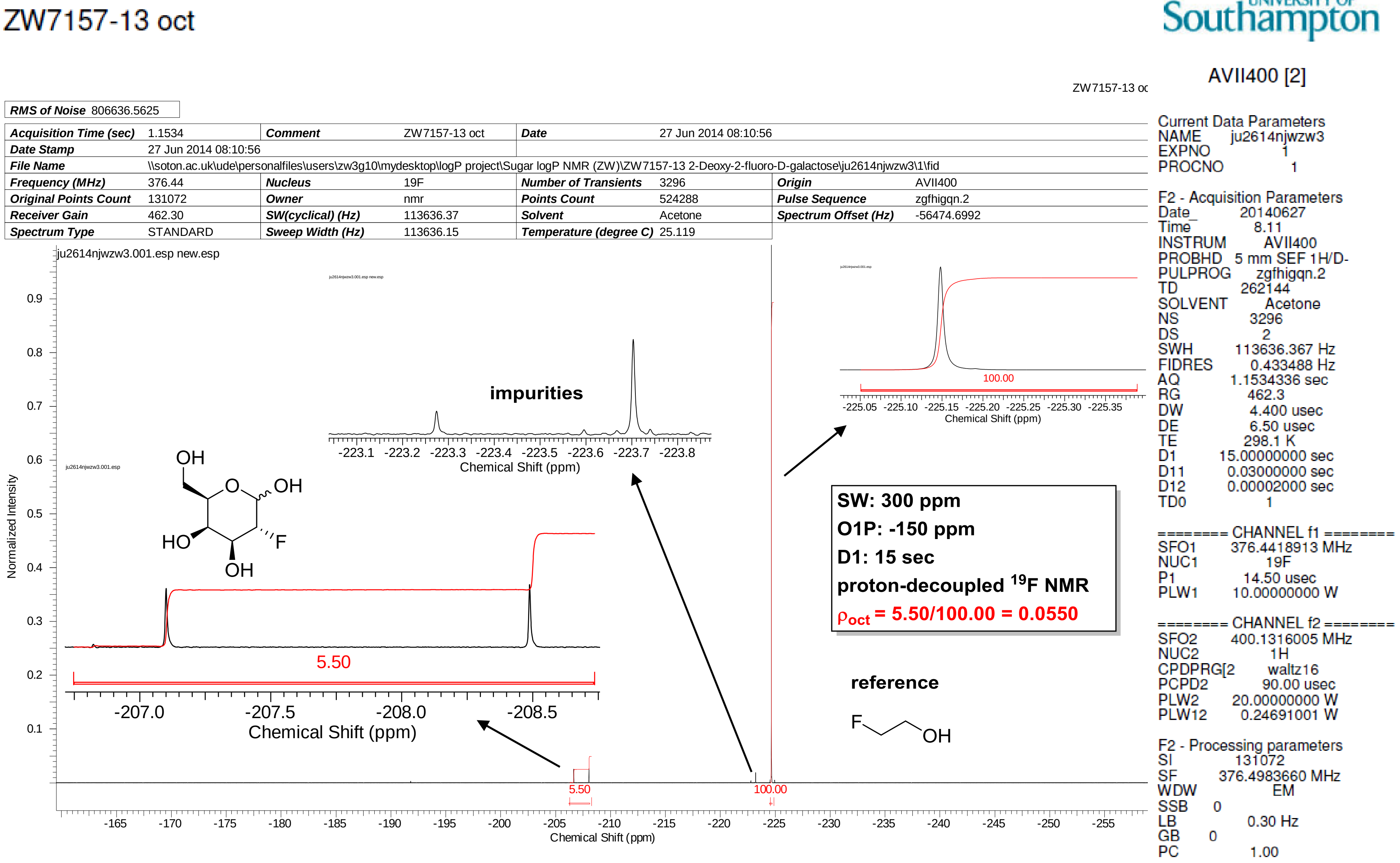
======== CHANNEL f2 ========
SFO2        400.1316005 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2        20.00000000 W
PLW12        0.24691001 W

F2 - Processing parameters
SI               131072
SF          376.4983660 MHz
WDW                  EM
SSB     0
LB                 0.30 Hz
GB      0
PC                 1.00
```

---

[44] Chemical shift for furanose was consistent with the data reported in the following paper: L. A. Mulard, P. Kováč, C. P. J. Glaudemans, *Carbohydr. Res.* **1994**, *259*, 21-34.

14.3. 2-Fluoro-2-deoxy-D-galactose (47), Entry 1, octanol sample



ZW7157-13 oct

ZW7157-13 oc

AVII400 [2]

RMS of Noise 806636.5625

Acquisition Time (sec)	1.1534	***Comment***	ZW7157-13 oct	***Date***	27 Jun 2014 08:10:56		
Date Stamp	27 Jun 2014 08:10:56						
File Name	\\soton.ac.uk\ude\personalfiles\users\zw3g10\mydesktop\logP project\Sugar logP NMR (ZW)\ZW7157-13 2-Deoxy-2-fluoro-D-galactose\ju2614njwzw3\1\fid						
Frequency (MHz)	376.44	***Nucleus***	19F	***Number of Transients***	3296	***Origin***	AVII400
Original Points Count	131072	***Owner***	nmr	***Points Count***	524288	***Pulse Sequence***	zgfhigqn.2
Receiver Gain	462.30	***SW(cyclical) (Hz)***	113636.37	***Solvent***	Acetone	***Spectrum Offset (Hz)***	-56474.6992
Spectrum Type	STANDARD	***Sweep Width (Hz)***	113636.15	***Temperature (degree C)***	25.119		

```
Current Data Parameters
NAME      ju2614njwzw3
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_        20140627
Time             8.11
INSTRUM       AVII400
PROBHD   5 mm SEF 1H/D-
PULPROG     zgfhigqn.2
TD            262144
SOLVENT       Acetone
NS              3296
DS                 2
SWH       113636.367 Hz
FIDRES      0.433488 Hz
AQ         1.1534336 sec
RG             462.3
DW             4.400 usec
DE              6.50 usec
TE             298.1 K
D1       15.00000000 sec
D11       0.03000000 sec
D12       0.00002000 sec
TD0                1

======== CHANNEL f1 ========
SFO1     376.4418913 MHz
NUC1             19F
P1             14.50 usec
PLW1     10.00000000 W

======== CHANNEL f2 ========
SFO2     400.1316005 MHz
NUC2              1H
CPDPRG[2       waltz16
PCPD2          90.00 usec
PLW2     20.00000000 W
PLW12     0.24691001 W

F2 - Processing parameters
SI            131072
SF       376.4983660 MHz
WDW               EM
SSB    0
LB              0.30 Hz
GB     0
PC              1.00
```

SW: 300 ppm

O1P: -150 ppm

D1: 15 sec

proton-decoupled ^{19}F NMR

ρ_{oct} = 5.50/100.00 = 0.0550

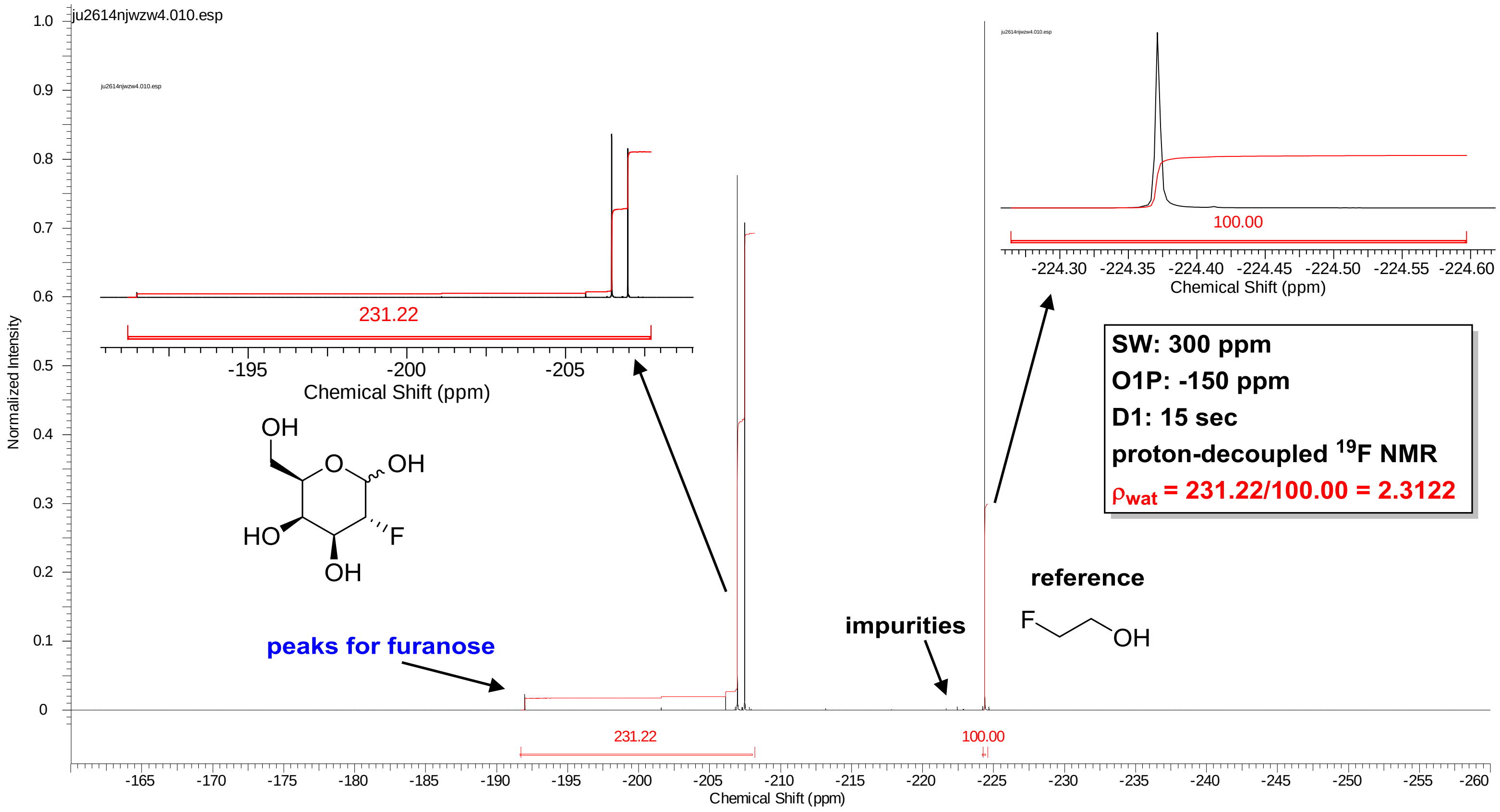
14.4. 2-Fluoro-2-deoxy-D-galactose (47), Entry 1, water sample

ZW7157-13 wat

ZW7157-13 wat

AVII400 [2]

Acquisition Time (sec)	1.1534	***Comment***	ZW7157-13 wat	***Date***	28 Jun 2014 11:05:52		
Date Stamp	28 Jun 2014 11:05:52						
File Name	\\soton.ac.uk\ude\personalfiles\users\zw3g10\mydesktop\Sugar logP NMR (ZW)\ZW7157-13 2-Deoxy-2-fluoro-D-galactose\ju2614njwzw4\10\fid						
Frequency (MHz)	376.44	***Nucleus***	19F	***Number of Transients***	2687	***Origin***	AVII400
Original Points Count	131072	***Owner***	nmr	***Points Count***	131072	***Pulse Sequence***	zgfhigqn.2
Receiver Gain	405.33	***SW(cyclical) (Hz)***	113636.37	***Solvent***	Acetone	***Spectrum Offset (Hz)***	-56474.6992
Spectrum Type	STANDARD	***Sweep Width (Hz)***	113635.50	***Temperature (degree C)***	25.119		



SW: 300 ppm
O1P: -150 ppm
D1: 15 sec
proton-decoupled ^{19}F NMR
ρ_{wat} = 231.22/100.00 = 2.3122

Current Data Parameters
NAME ju2614njwzw4
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140628
Time 11.06
INSTRUM AVII400
PROBHD 5 mm SEF 1H/D-
PULPROG zgfhigqn.2
TD 262144
SOLVENT Acetone
NS 2687
DS 2
SWH 113636.367 Hz
FIDRES 0.433488 Hz
AQ 1.1534336 sec
RG 405.33
DW 4.400 usec
DE 6.50 usec
TE 298.1 K
D1 15.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 376.4418913 MHz
NUC1 19F
P1 14.50 usec
PLW1 10.00000000 W

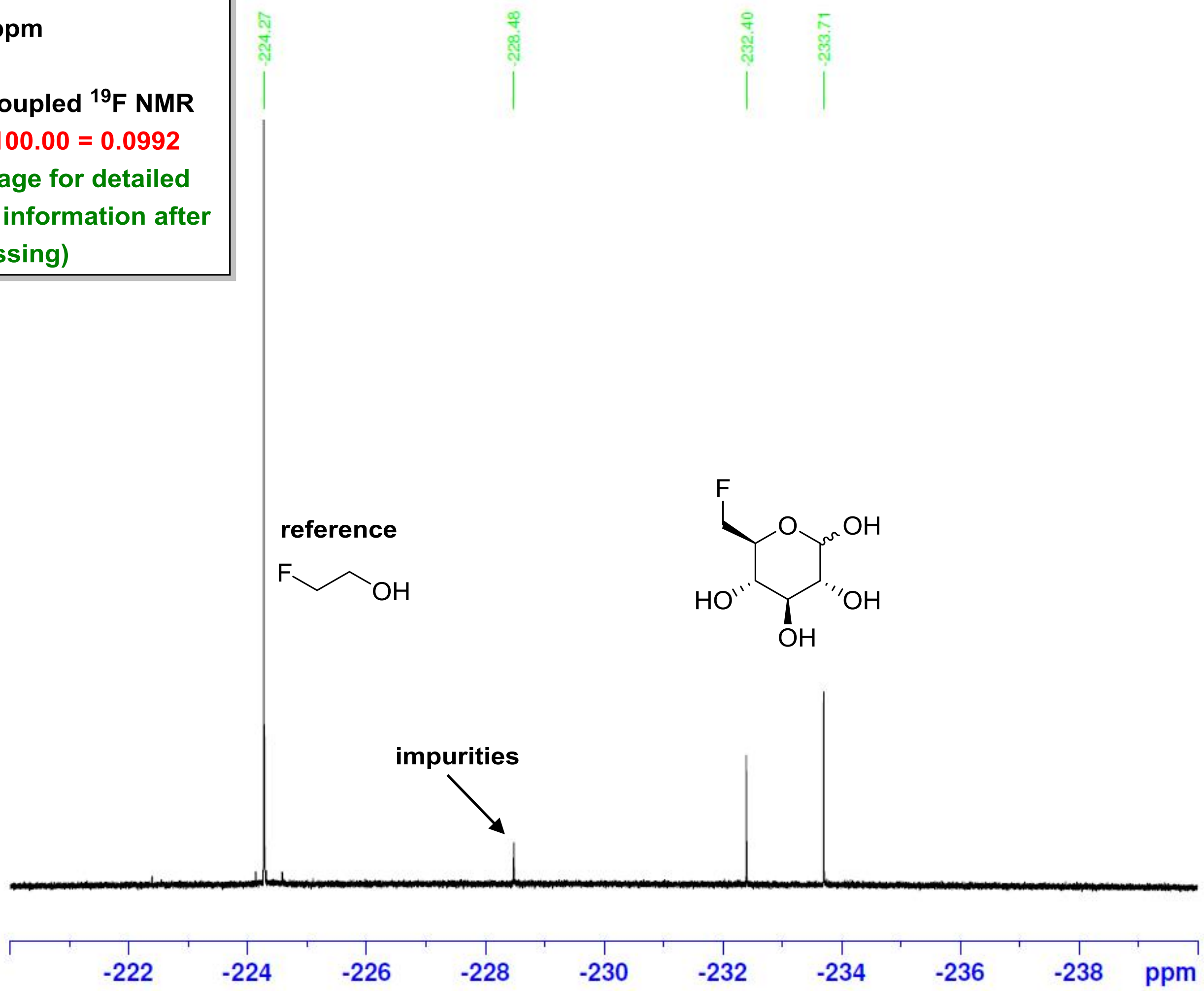
======== CHANNEL f2 ========
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 20.00000000 W
PLW12 0.24691001 W

F2 - Processing parameters
SI 131072
SF 376.4983660 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

14.5. 6-Fluoro-6-deoxy-D-glucose (48), Entry 1, octanol sample

ZW 7601-17 oct

SW: 100 ppm
O1P: -230 ppm
D1: 15 sec
proton-decoupled ^{19}F NMR
ρ_{oct} = 9.92/100.00 = 0.0992
(see next page for detailed integration information after data processing)



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AVII400 [2]

```
Current Data Parameters
NAME      se1115njwzw2
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_         20150915
Time              7.52
INSTRUM        AVII400
PROBHD   5 mm SEF 1H/D-
PULPROG    zgfhigqn.njw
TD              262144
SOLVENT        Acetone
NS                4647
DS                   2
SWH       37593.984 Hz
FIDRES     0.143410 Hz
AQ        3.4865153 sec
RG              588.36
DW          13.300 usec
DE            7.98 usec
TE             298.1 K
D1      15.00000000 sec
D11      0.03000000 sec
D12      0.00002000 sec
TD0                  1

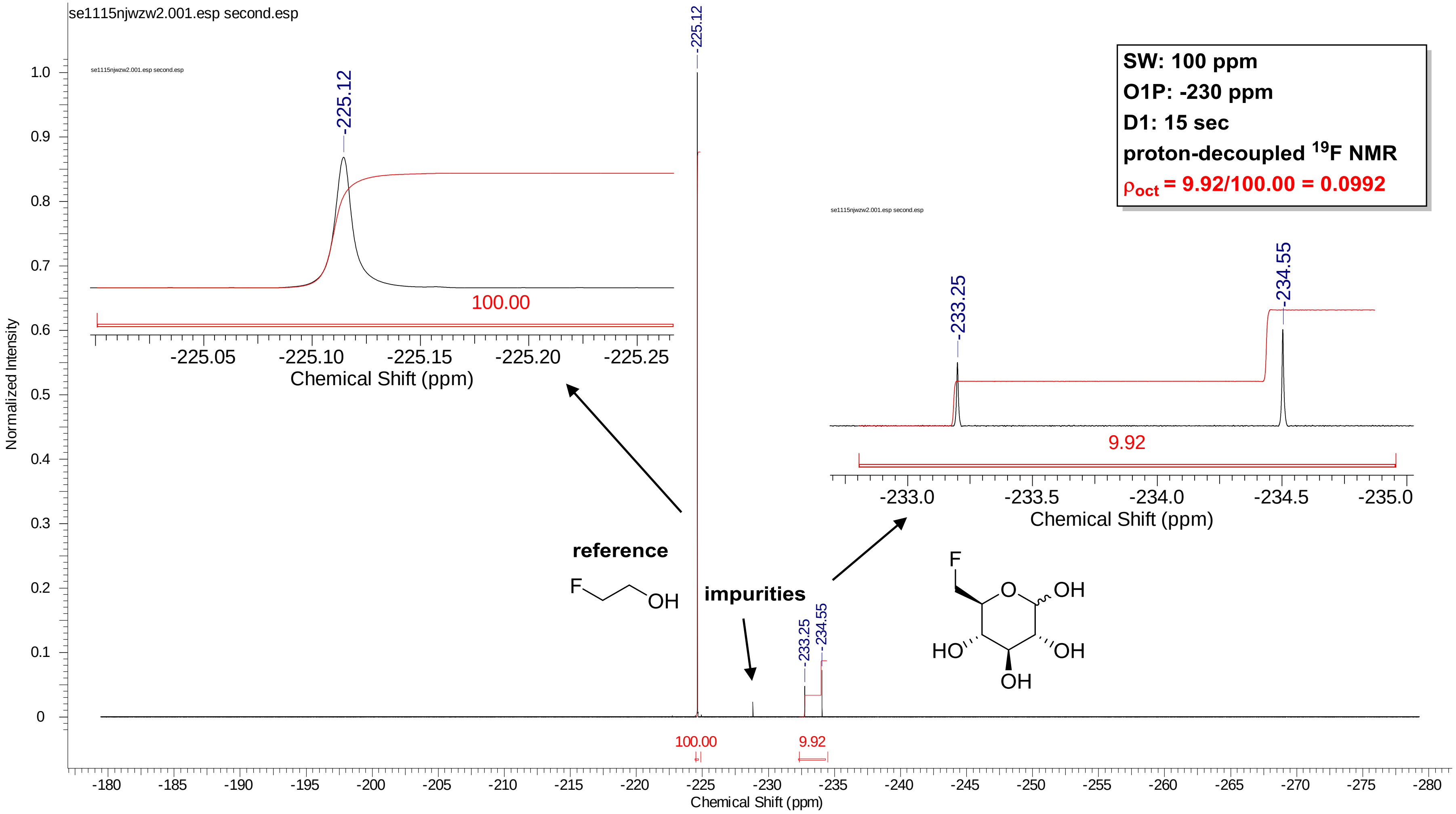
======== CHANNEL f1 ========
SFO1     376.4118486 MHz
NUC1               19F
P1           14.50 usec
PLW1      10.00000000 W

======== CHANNEL f2 ========
SFO2     400.1316005 MHz
NUC2                1H
CPDPRG[2        waltz16
PCPD2        90.00 usec
PLW2      20.00000000 W
PLW12      0.24691001 W

F2 - Processing parameters
SI              262144
SF       376.4980668 MHz
WDW                 EM
SSB     0
LB             0.15 Hz
GB      0
PC                1.00
```

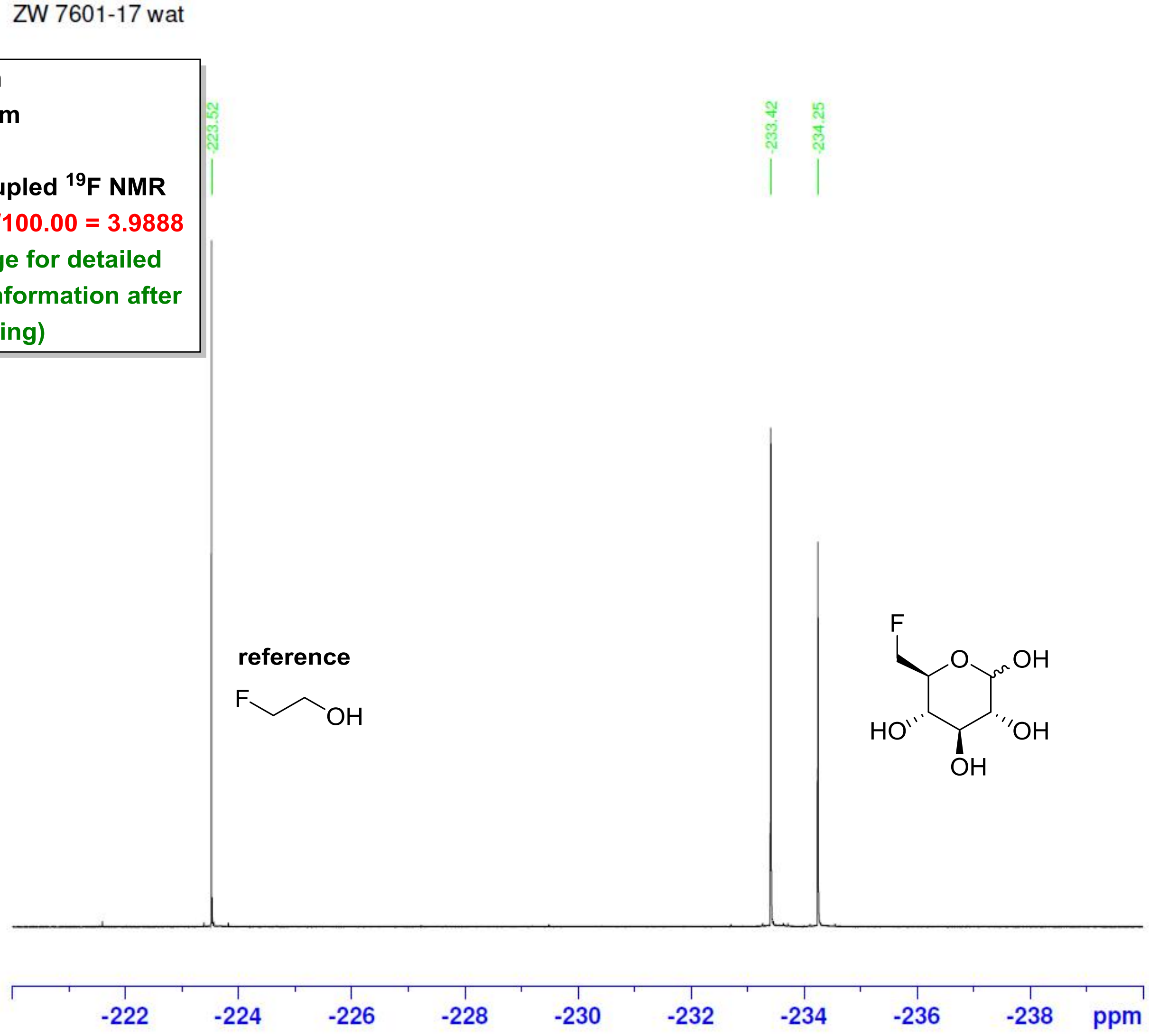
ZW 7601-17 oct

Acquisition Time (sec)	3.4865	***Comment***	ZW 7601-17 oct	***Date***	15 Sep 2015 07:51:44		
Date Stamp	15 Sep 2015 07:51:44			***File Name***	\\soton.ac.uk\ude\personalfiles\users\zw3g10\mydesktop\zw7601-17 6Fglu\se1115njwzw2\1\fid		
Frequency (MHz)	376.41	***Nucleus***	19F	***Number of Transients***	4647	***Origin***	AVII400
Original Points Count	131072	***Owner***	nmr	***Points Count***	524288	***Pulse Sequence***	zgfhigqn.njw
Receiver Gain	588.36	***SW(cyclical) (Hz)***	37593.98	***Solvent***	Acetone	***Spectrum Offset (Hz)***	-86517.4453
Spectrum Type	STANDARD	***Sweep Width (Hz)***	37593.91	***Temperature (degree C)***	25.119		



14.6. 6-Flouro-6-deoxy-D-glucose (48), Entry 1, water sample

SW: 100 ppm
O1P: -230 ppm
D1: 15 sec
proton-decoupled ^{19}F NMR
ρ_{wat} = 398.88/100.00 = 3.9888
(see next page for detailed integration information after data processing)



AVII400 [2]

Current Data Parameters
NAME se1115njwzw1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150911
Time 11.56
INSTRUM AVII400
PROBHD 5 mm SEF 1H/D-
PULPROG zgfhigqn.njw
TD 262144
SOLVENT Acetone
NS 512
DS 2
SWH 37593.984 Hz
FIDRES 0.143410 Hz
AQ 3.4865153 sec
RG 373.48
DW 13.300 usec
DE 7.98 usec
TE 298.1 K
D1 15.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
TD0 1

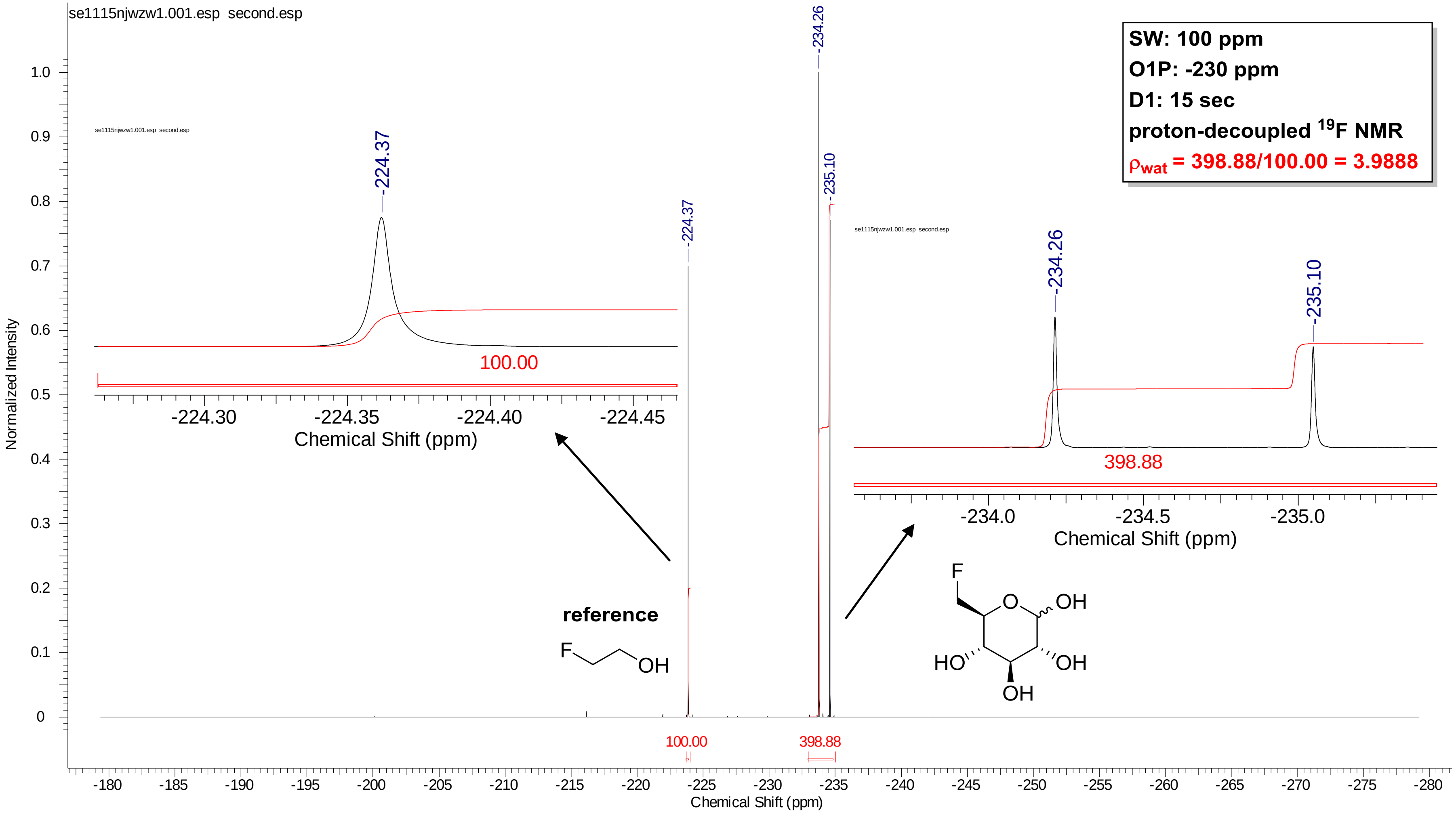
======== CHANNEL f1 ========
SFO1 376.4118711 MHz
NUC1 19F
P1 14.50 usec
PLW1 10.00000000 W

======== CHANNEL f2 ========
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 20.00000000 W
PLW12 0.24691001 W

F2 - Processing parameters
SI 262144
SF 376.4980668 MHz
WDW EM
SSB 0
LB 0.15 Hz
GB 0
PC 1.00

ZW 7601-17 wat

Acquisition Time (sec)	3.4865	***Comment***	ZW 7601-17 wat	***Date***	11 Sep 2015 11:57:04		
Date Stamp	11 Sep 2015 11:57:04			***File Name***	\\soton.ac.uk\ude\personalfiles\users\zw3g10\mydesktop\zw7601-17 6Fglu\se1115njwzw1\1\fid		
Frequency (MHz)	376.41	***Nucleus***	19F	***Number of Transients***	512	***Origin***	AVII400
Original Points Count	131072	***Owner***	nmr	***Points Count***	524288	***Pulse Sequence***	zgfhigqn.njw
Receiver Gain	373.48	***SW(cyclical) (Hz)***	37593.98	***Solvent***	Acetone	***Spectrum Offset (Hz)***	-86494.8516
Spectrum Type	STANDARD	***Sweep Width (Hz)***	37593.91	***Temperature (degree C)***	25.119		



SW: 100 ppm

O1P: -230 ppm

D1: 15 sec

proton-decoupled ^{19}F NMR

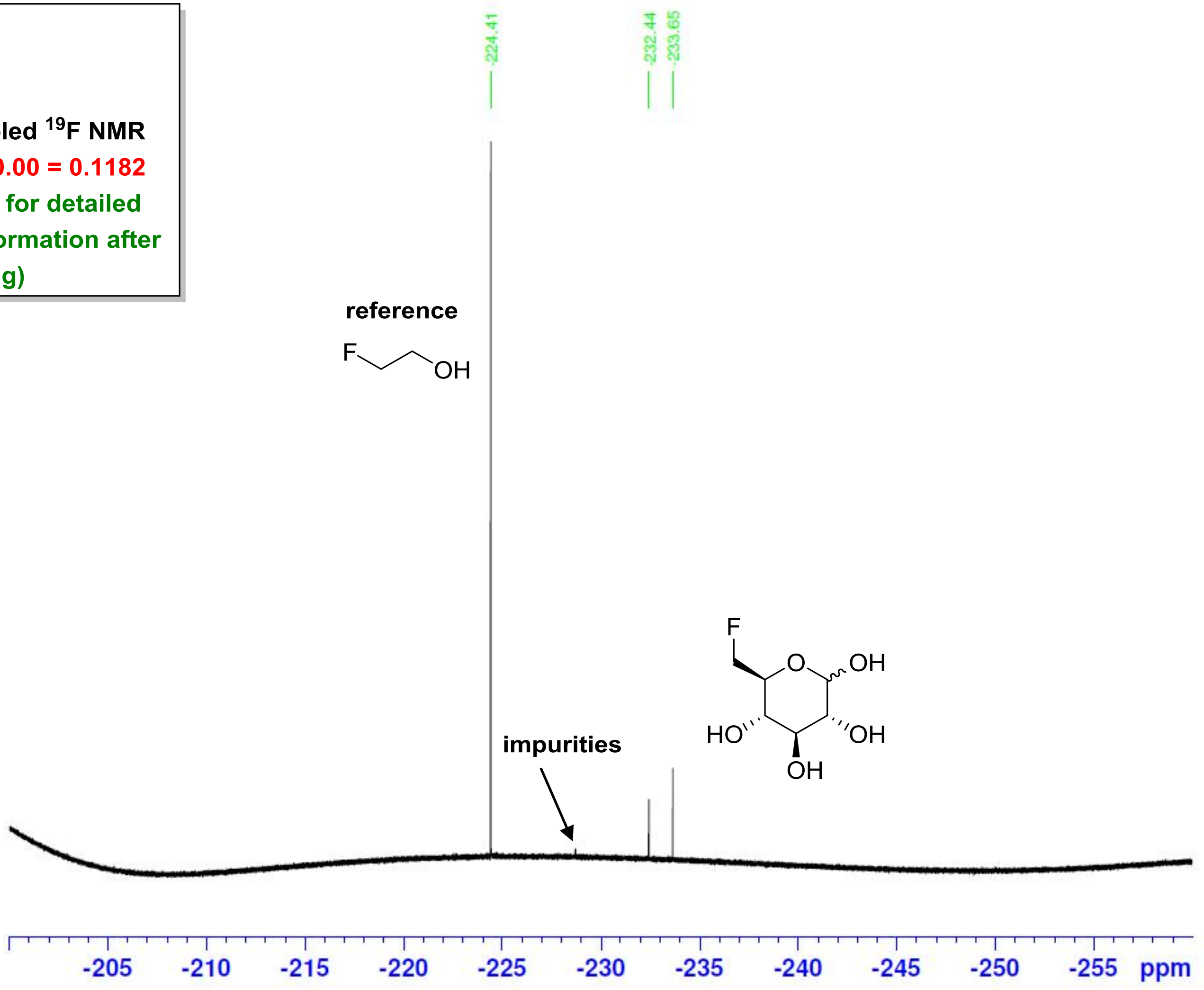
ρ_{wat} = 398.88/100.00 = 3.9888

reference

14.7. 6-Fluoro-6-deoxy-D-glucose (48), Entry 2, octanol sample

ZW 7601-19 oct

SW: 100 ppm
O1P: -230 ppm
D1: 15 sec
proton-decoupled ^{19}F NMR
ρ_{oct} = 11.82/100.00 = 0.1182
(see next page for detailed integration information after data processing)



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AVII400 [2]

```
Current Data Parameters
NAME      oc0215njwzw1
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_        20151004
Time            15.49
INSTRUM       AVII400
PROBHD   5 mm SEF 1H/D-
PULPROG   zgfhigqn.njw
TD             262144
SOLVENT       Acetone
NS               9216
DS                  2
SWH       37593.984 Hz
FIDRES     0.143410 Hz
AQ        3.4865153 sec
RG             128.42
DW         13.300 usec
DE           7.98 usec
TE            298.1 K
D1     15.00000000 sec
D11     0.03000000 sec
D12     0.00002000 sec
TD0                 1

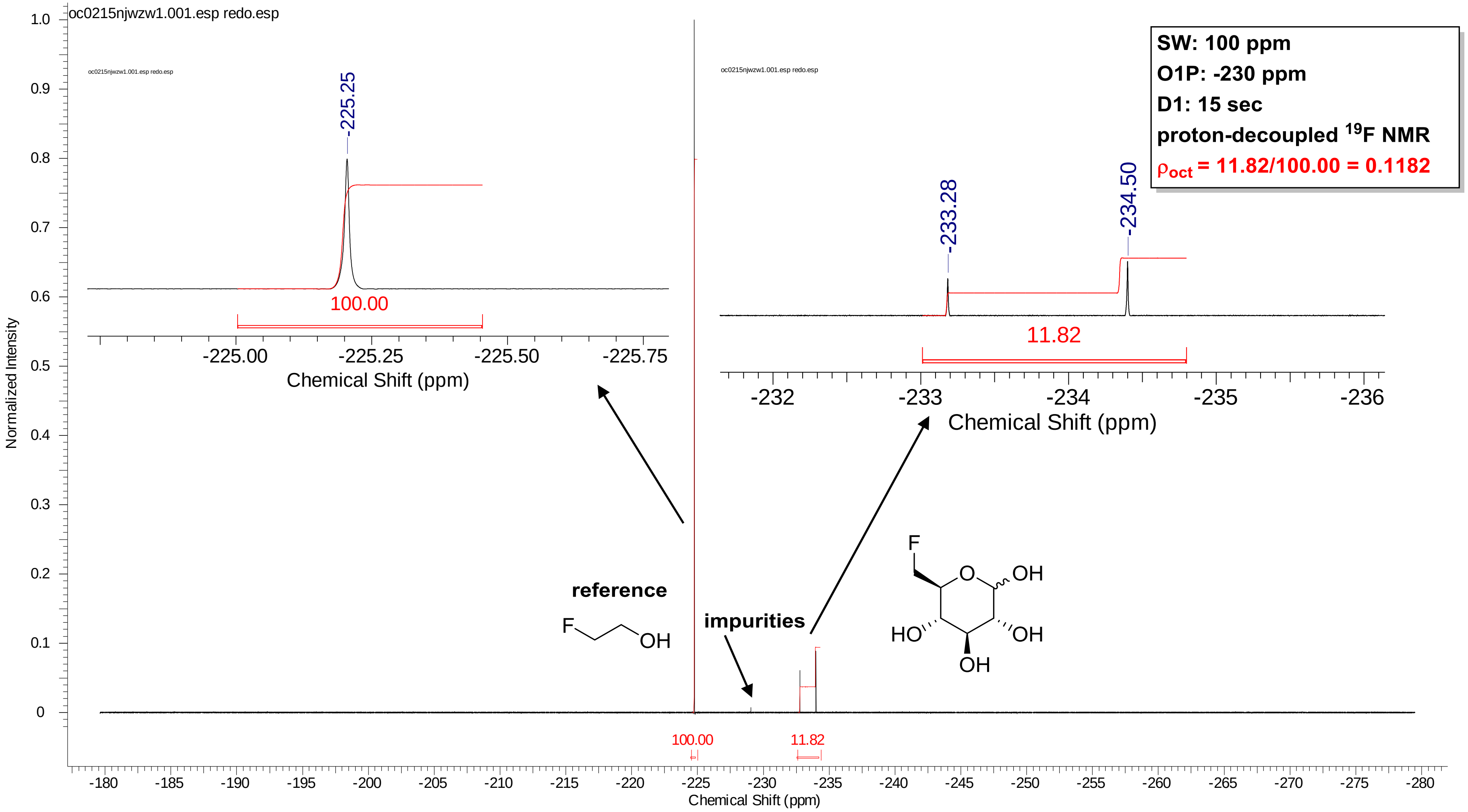
======== CHANNEL f1 ========
SFO1     376.4117714 MHz
NUC1              19F
P1          14.50 usec
PLW1      10.00000000 W

======== CHANNEL f2 ========
SFO2     400.1316005 MHz
NUC2               1H
CPDPRG[2       waltz16
PCPD2       90.00 usec
PLW2      20.00000000 W
PLW12      0.24691001 W

F2 - Processing parameters
SI             262144
SF     376.4980668 MHz
WDW                EM
SSB      0
LB            0.15 Hz
GB       0
PC              1.00
```

ZW 7601-19 oct

Acquisition Time (sec)	3.4865	***Comment***	ZW 7601-19 oct			***Date***	04 Oct 2015 15:49:36
Date Stamp	04 Oct 2015 15:49:36			***File Name***	\\soton.ac.uk\ude\personalfiles\users\zw3g10\mydesktop\oc0215njwzw1\1\fid		
Frequency (MHz)	376.41	***Nucleus***	19F	***Number of Transients***	9216	***Origin***	AVII400
Original Points Count	131072	***Owner***	nmr	***Points Count***	524288	***Pulse Sequence***	zgfhigqn.njw
Receiver Gain	128.42	***SW(cyclical) (Hz)***	37593.98	***Solvent***	Acetone	***Spectrum Offset (Hz)***	-86594.6250
Spectrum Type	STANDARD	***Sweep Width (Hz)***	37593.91	***Temperature (degree C)***	25.119		



SW: 100 ppm

O1P: -230 ppm

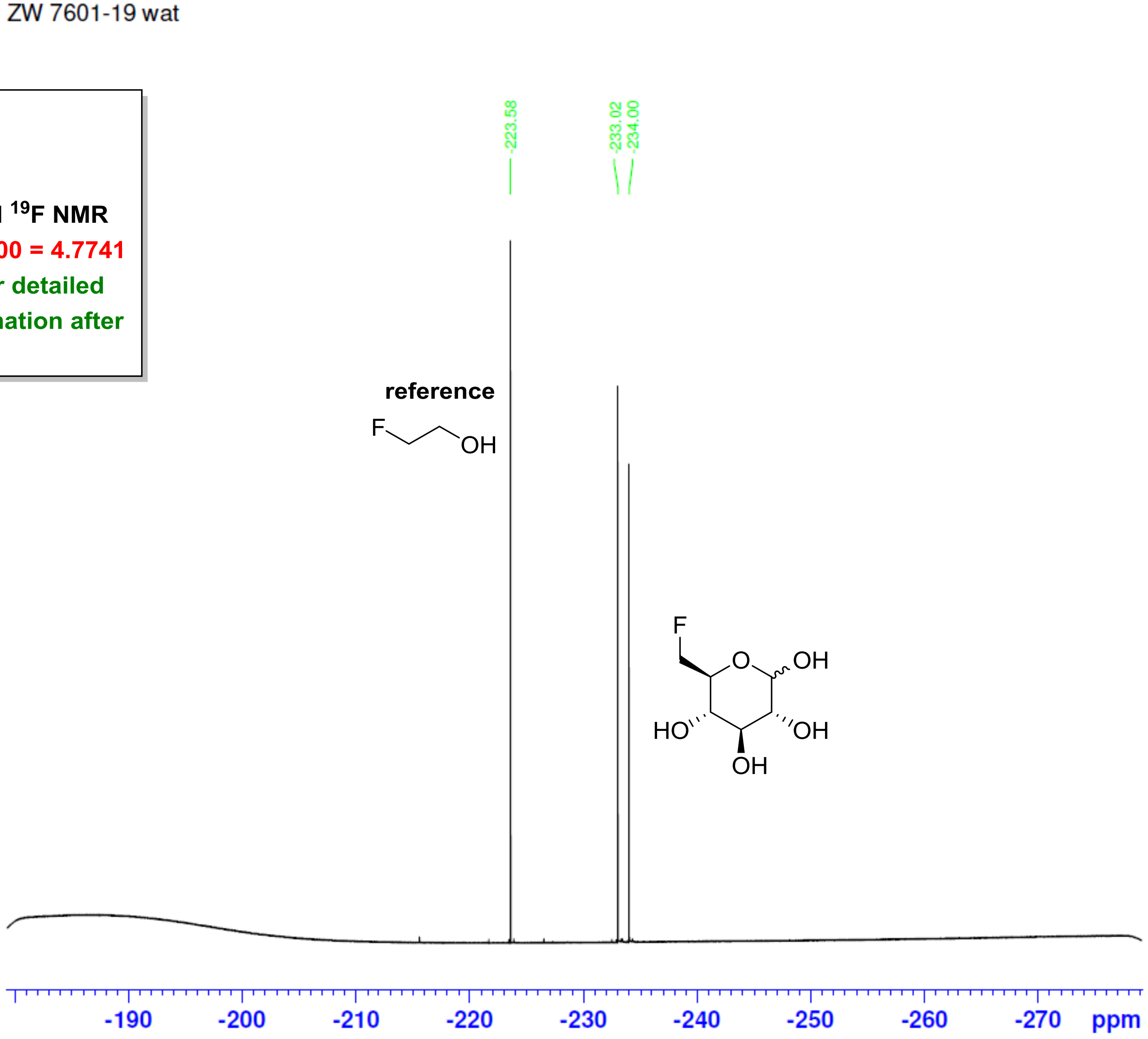
D1: 15 sec

proton-decoupled ^{19}F NMR

ρ_{oct} = 11.82/100.00 = 0.1182

14.8. 6-Fluoro-6-deoxy-D-glucose (48), Entry 2, water sample

SW: 100 ppm
O1P: -230 ppm
D1: 15 sec
proton-decoupled ^{19}F NMR
ρ_{wat} = 477.41/100.00 = 4.7741
(see next page for detailed integration information after data processing)



AVII400 [2]

```
Current Data Parameters
NAME      se3015njwzw1
EXPNO               1
PROCNO              1

F2 - Acquisition Parameters
Date_       20151001
Time           12.57
INSTRUM      AVII400
PROBHD  5 mm SEF 1H/D-
PULPROG   zgfhigqn.njw
TD            262144
SOLVENT       Acetone
NS               512
DS                 2
SWH        37593.984 Hz
FIDRES      0.143410 Hz
AQ         3.4865153 sec
RG              63.4
DW            13.300 usec
DE              7.98 usec
TE             298.1 K
D1       15.00000000 sec
D11       0.03000000 sec
D12       0.00002000 sec
TD0                1

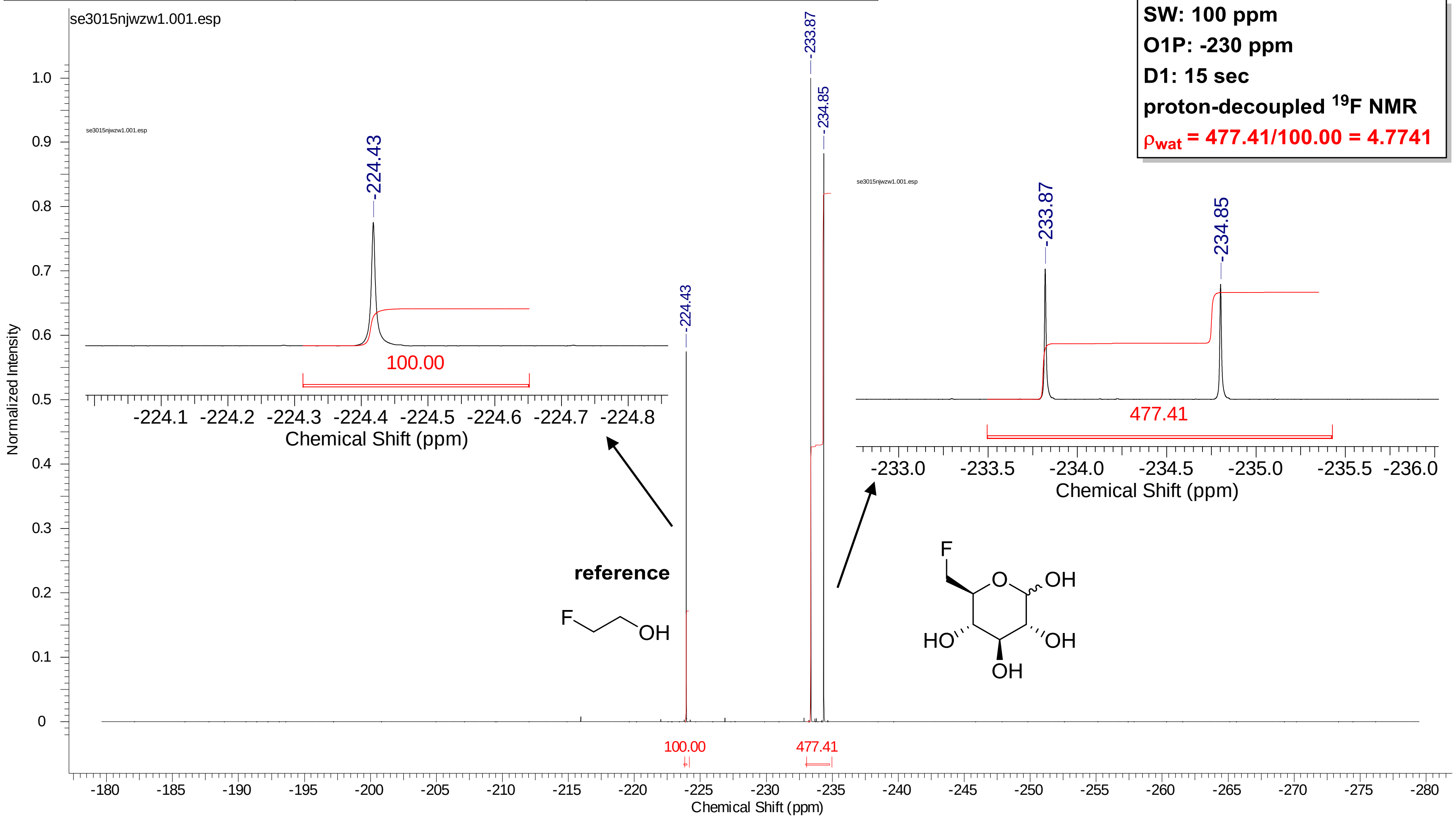
======== CHANNEL f1 ========
SFO1     376.4117714 MHz
NUC1             19F
P1             14.50 usec
PLW1     10.00000000 W

======== CHANNEL f2 ========
SFO2     400.1316005 MHz
NUC2              1H
CPDPRG[2       waltz16
PCPD2          90.00 usec
PLW2     20.00000000 W
PLW12     0.24691001 W

F2 - Processing parameters
SI            262144
SF       376.4980668 MHz
WDW               EM
SSB     0
LB              0.15 Hz
GB      0
PC              1.00
```

ZW 7601-19 wat

Acquisition Time (sec)	3.4865	***Comment***	ZW 7601-19 wat			***Date***	01 Oct 2015 12:56:48
Date Stamp	01 Oct 2015 12:56:48			***File Name***	\\soton.ac.uk\ude\personalfiles\users\zw3g10\mydesktop\se3015njwzw1\1\fid		
Frequency (MHz)	376.41	***Nucleus***	19F	***Number of Transients***	512	***Origin***	AVII400
Original Points Count	131072	***Owner***	nmr	***Points Count***	524288	***Pulse Sequence***	zgfhigqn.njw
Receiver Gain	63.40	***SW(cyclical) (Hz)***	37593.98	***Solvent***	Acetone	***Spectrum Offset (Hz)***	-86594.6250
Spectrum Type	STANDARD	***Sweep Width (Hz)***	37593.91	***Temperature (degree C)***	25.119		



SW: 100 ppm
O1P: -230 ppm
D1: 15 sec
proton-decoupled ^{19}F NMR
ρ_{wat} = 477.41/100.00 = 4.7741

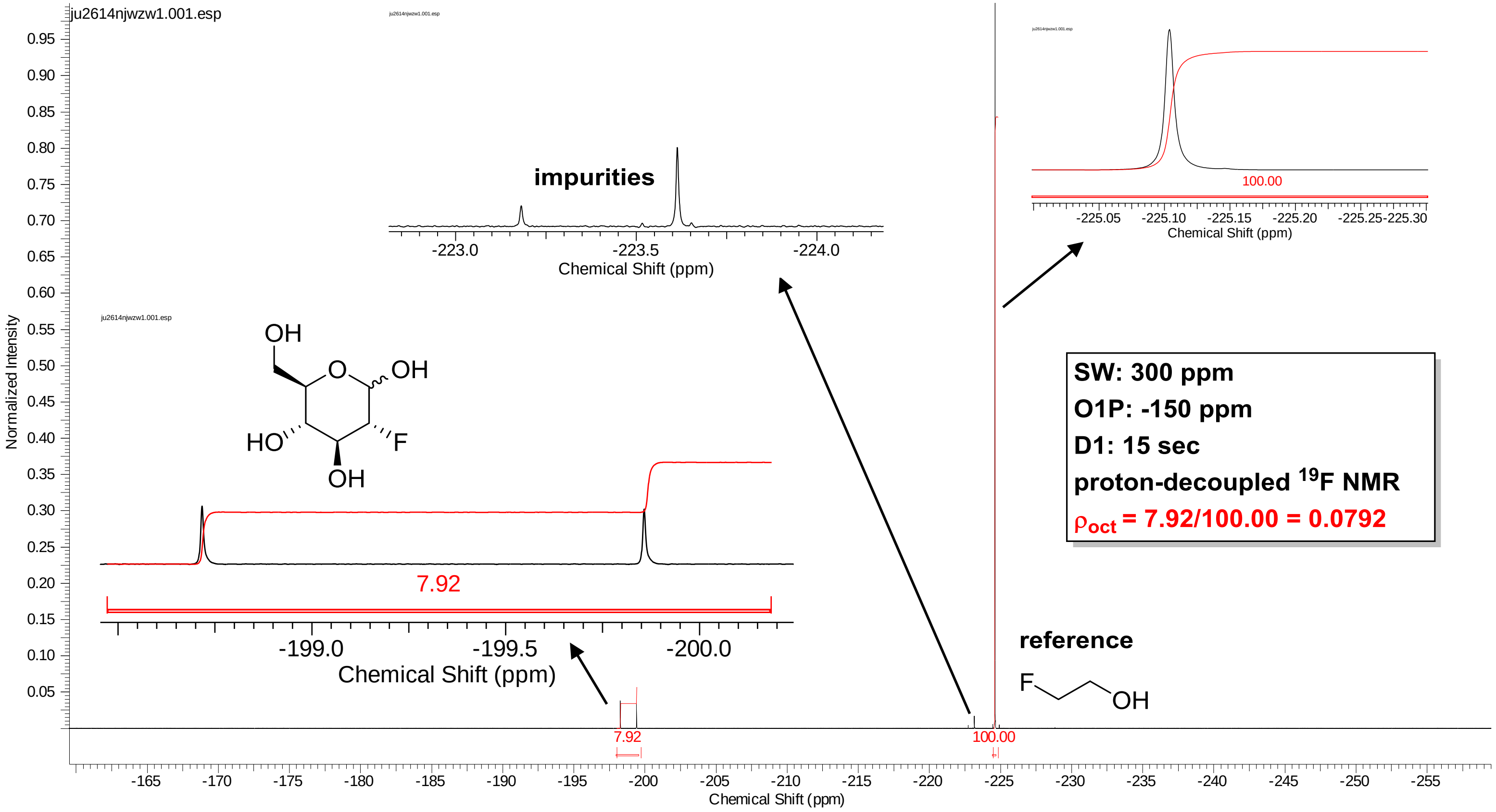
14.9. 2-Fluoro-2-deoxy-D-glucose (49), Entry 1, octanol sample

ZW7157-12 oct

AVII400 [2]

ZW7157-12 oct

Acquisition Time (sec)	1.1534	**Comment**	ZW7157-12 oct	**Date**	26 Jun 2014 09:17:04		
Date Stamp	26 Jun 2014 09:17:04						
File Name	\\soton.ac.uk\ude\personalfiles\users\zw3g10\mydesktop\logP project\Sugar logP NMR (ZW)\ZW7157-12 2-Deoxy-2-fluoro-D-glucose\ju2614njwzw1\1\fid						
Frequency (MHz)	376.44	**Nucleus**	19F	**Number of Transients**	3296	**Origin**	AVII400
Original Points Count	131072	**Owner**	nmr	**Points Count**	524288	**Pulse Sequence**	zgfhigqn.2
Receiver Gain	500.47	**SW(cyclical) (Hz)**	113636.37	**Solvent**	Acetone	**Spectrum Offset (Hz)**	-56474.6992
Spectrum Type	STANDARD	**Sweep Width (Hz)**	113636.15	**Temperature (degree C)**	25.245		



SW: 300 ppm

O1P: -150 ppm

D1: 15 sec

proton-decoupled ^{19}F NMR

ρ_{oct} = 7.92/100.00 = 0.0792

Current Data Parameters
NAME ju2614njwzw1
EXPNO 1
PROCNO 1

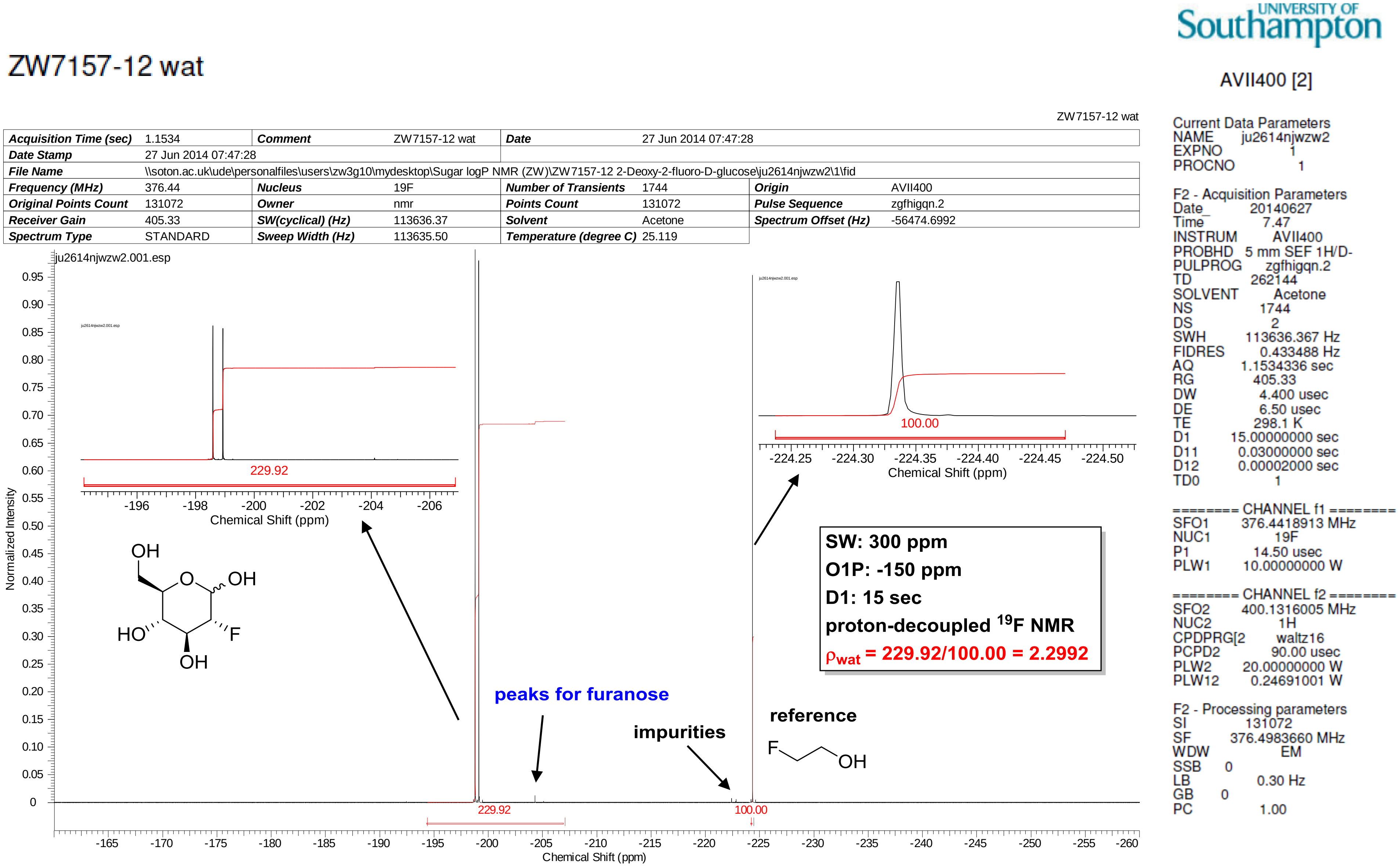
F2 - Acquisition Parameters
Date_ 20140626
Time 9.16
INSTRUM AVII400
PROBHD 5 mm SEF 1H/D-
PULPROG zgfhigqn.2
TD 262144
SOLVENT Acetone
NS 3296
DS 2
SWH 113636.367 Hz
FIDRES 0.433488 Hz
AQ 1.1534336 sec
RG 500.47
DW 4.400 usec
DE 6.50 usec
TE 298.2 K
D1 15.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 376.4418913 MHz
NUC1 19F
P1 14.50 usec
PLW1 10.00000000 W

======== CHANNEL f2 ========
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 20.00000000 W
PLW12 0.24691001 W

F2 - Processing parameters
SI 131072
SF 376.4983660 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

14.10. **2-Fluoro-2-deoxy-D-glucose (49), Entry 1, water sample**



ZW7157-12 wat

AVII400 [2]

ZW7157-12 wat

Acquisition Time (sec)	1.1534	***Comment***	ZW7157-12 wat	***Date***	27 Jun 2014 07:47:28		
Date Stamp	27 Jun 2014 07:47:28						
File Name	\\soton.ac.uk\ude\personalfiles\users\zw3g10\mydesktop\Sugar logP NMR (ZW)\ZW7157-12 2-Deoxy-2-fluoro-D-glucose\ju2614njwzw2\1\fid						
Frequency (MHz)	376.44	***Nucleus***	19F	***Number of Transients***	1744	***Origin***	AVII400
Original Points Count	131072	***Owner***	nmr	***Points Count***	131072	***Pulse Sequence***	zgfhigqn.2
Receiver Gain	405.33	***SW(cyclical) (Hz)***	113636.37	***Solvent***	Acetone	***Spectrum Offset (Hz)***	-56474.6992
Spectrum Type	STANDARD	***Sweep Width (Hz)***	113635.50	***Temperature (degree C)***	25.119		

```
Current Data Parameters
NAME      ju2614njwzw2
EXPNO              1
PROCNO              1

F2 - Acquisition Parameters
Date_        20140627
Time             7.47
INSTRUM        AVII400
PROBHD   5 mm SEF 1H/D-
PULPROG      zgfhigqn.2
TD           262144
SOLVENT        Acetone
NS              1744
DS                 2
SWH        113636.367 Hz
FIDRES       0.433488 Hz
AQ          1.1534336 sec
RG             405.33
DW              4.400 usec
DE              6.50 usec
TE             298.1 K
D1        15.00000000 sec
D11        0.03000000 sec
D12        0.00002000 sec
TD0                1

======== CHANNEL f1 ========
SFO1       376.4418913 MHz
NUC1              19F
P1              14.50 usec
PLW1       10.00000000 W

======== CHANNEL f2 ========
SFO2       400.1316005 MHz
NUC2               1H
CPDPRG[2        waltz16
PCPD2             90.00 usec
PLW2       20.00000000 W
PLW12        0.24691001 W

F2 - Processing parameters
SI              131072
SF         376.4983660 MHz
WDW                EM
SSB     0
LB               0.30 Hz
GB     0
PC               1.00
```

SW: 300 ppm

O1P: -150 ppm

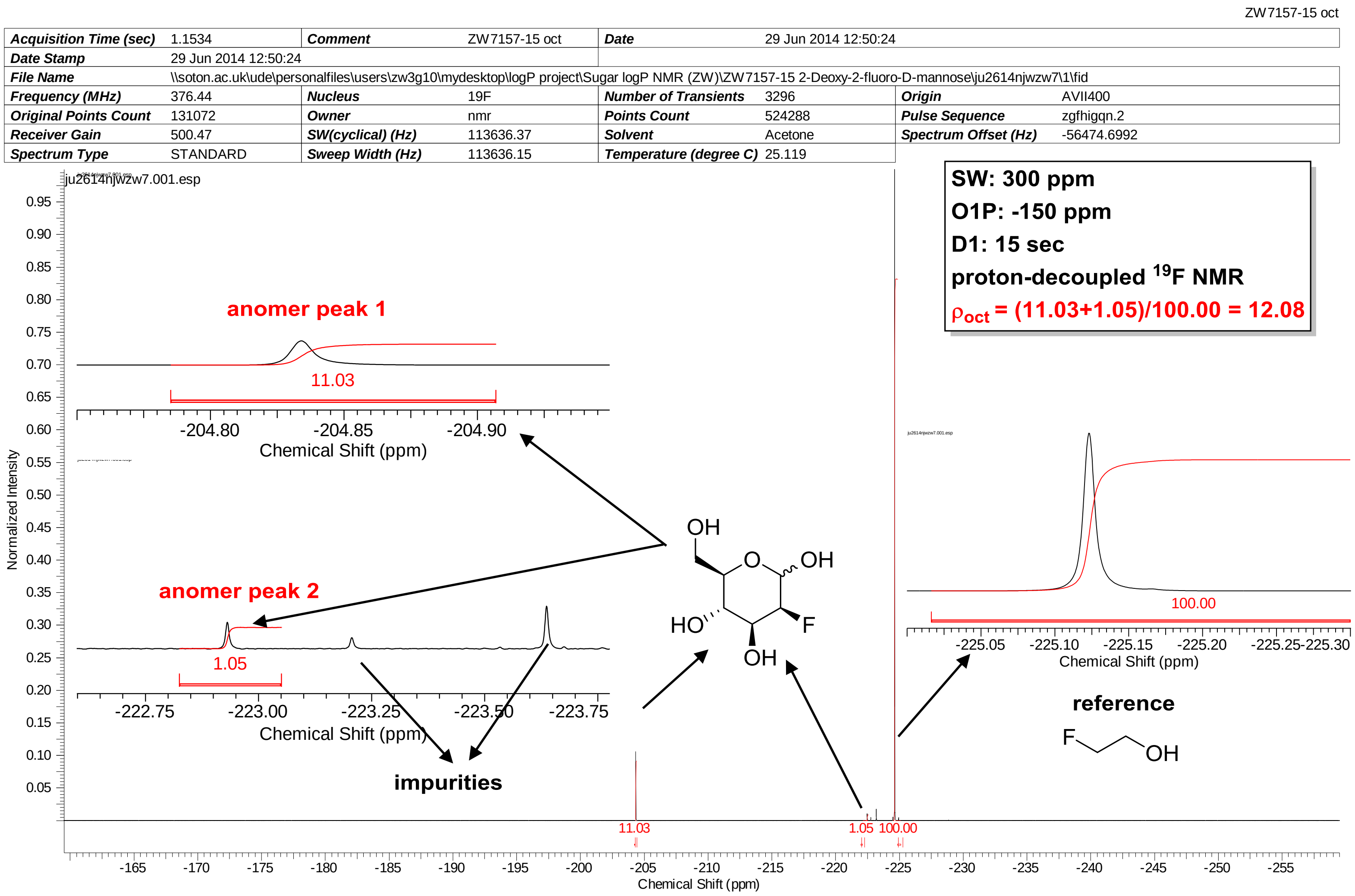
D1: 15 sec

proton-decoupled ^{19}F NMR

ρ_{wat} = 229.92/100.00 = 2.2992

14.11. 2-Fluoro-2-deoxy-D-mannose (50), Entry 1, octanol sample

ZW7157-15 oct



ZW7157-15 oct

Acquisition Time (sec)	1.1534	***Comment***	ZW7157-15 oct	***Date***	29 Jun 2014 12:50:24		
Date Stamp	29 Jun 2014 12:50:24						
File Name	\\soton.ac.uk\ude\personalfiles\users\zw3g10\mydesktop\logP project\Sugar logP NMR (ZW)\ZW7157-15 2-Deoxy-2-fluoro-D-mannose\ju2614njwzw7\1\fid						
Frequency (MHz)	376.44	***Nucleus***	19F	***Number of Transients***	3296	***Origin***	AVII400
Original Points Count	131072	***Owner***	nmr	***Points Count***	524288	***Pulse Sequence***	zgfhigqn.2
Receiver Gain	500.47	***SW(cyclical) (Hz)***	113636.37	***Solvent***	Acetone	***Spectrum Offset (Hz)***	-56474.6992
Spectrum Type	STANDARD	***Sweep Width (Hz)***	113636.15	***Temperature (degree C)***	25.119		

SW: 300 ppm
O1P: -150 ppm
D1: 15 sec
proton-decoupled ^{19}F NMR
ρ_{oct} = (11.03+1.05)/100.00 = 12.08

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AVII400 [2]

Current Data Parameters

NAME	ju2614njwzw7
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20140629
Time	12.51
INSTRUM	AVII400
PROBHD	5 mm SEF 1H/D-
PULPROG	zgfhigqn.2
TD	262144
SOLVENT	Acetone
NS	3296
DS	2
SWH	113636.367 Hz
FIDRES	0.433488 Hz
AQ	1.1534336 sec
RG	500.47
DW	4.400 usec
DE	6.50 usec
TE	298.1 K
D1	15.00000000 sec
D11	0.03000000 sec
D12	0.00002000 sec
TD0	1

======== CHANNEL f1 ========

SFO1	376.4418913 MHz
NUC1	19F
P1	14.50 usec
PLW1	10.00000000 W

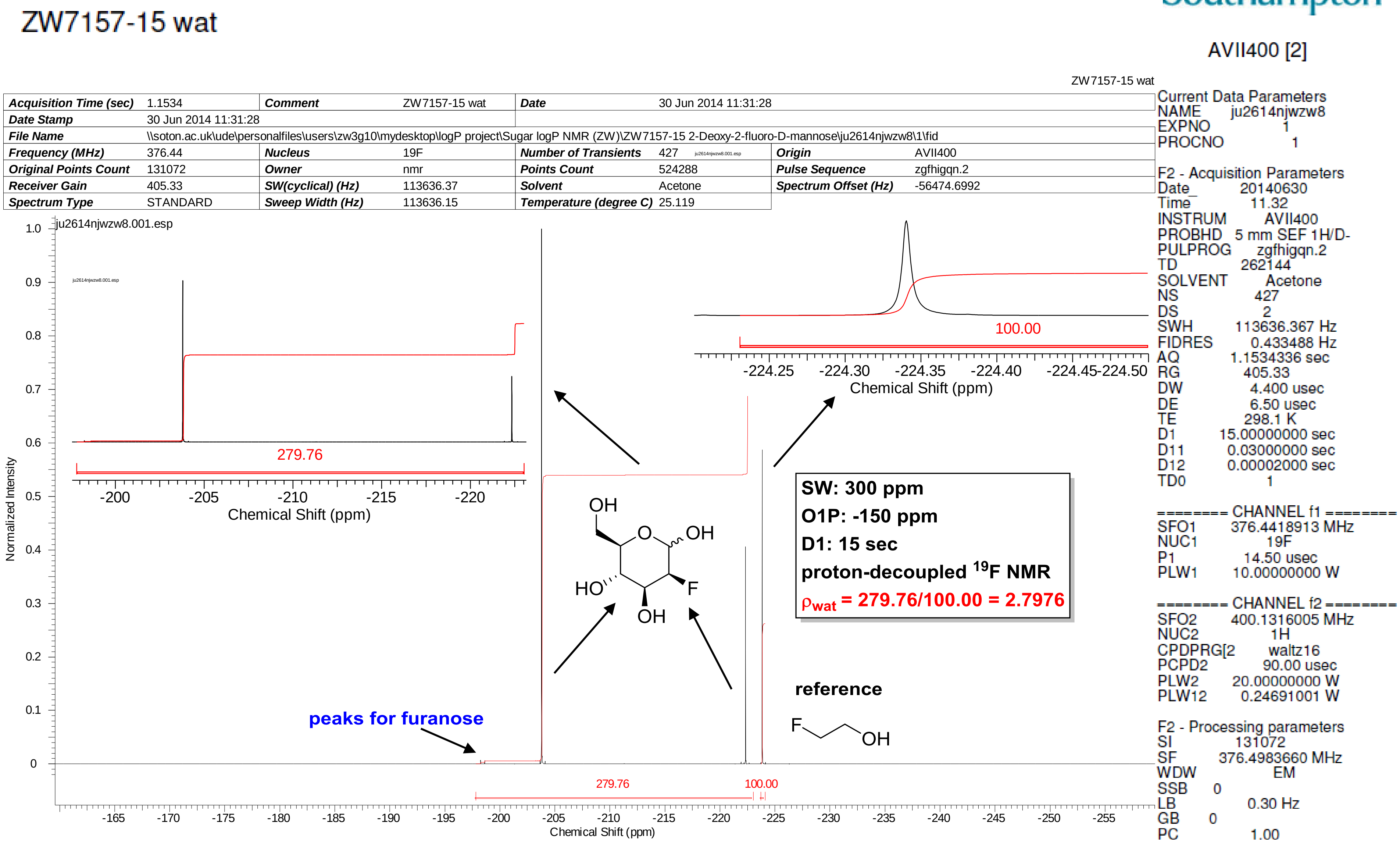
======== CHANNEL f2 ========

SFO2	400.1316005 MHz
NUC2	1H
CPDPRG[2	waltz16
PCPD2	90.00 usec
PLW2	20.00000000 W
PLW12	0.24691001 W

F2 - Processing parameters

SI	131072
SF	376.4983660 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

14.12. 2-Fluoro-2-deoxy-D-mannose (50), Entry 1, water sample



ZW7157-15 wat

AVII400 [2]

ZW7157-15 wat

Acquisition Time (sec)	1.1534	***Comment***	ZW7157-15 wat	***Date***	30 Jun 2014 11:31:28		
Date Stamp	30 Jun 2014 11:31:28						
File Name	\\soton.ac.uk\ude\personalfiles\users\zw3g10\mydesktop\logP project\Sugar logP NMR (ZW)\ZW7157-15 2-Deoxy-2-fluoro-D-mannose\ju2614njwzw8\1\fid						
Frequency (MHz)	376.44	***Nucleus***	19F	***Number of Transients***	427	***Origin***	AVII400
Original Points Count	131072	***Owner***	nmr	***Points Count***	524288	***Pulse Sequence***	zgfhigqn.2
Receiver Gain	405.33	***SW(cyclical) (Hz)***	113636.37	***Solvent***	Acetone	***Spectrum Offset (Hz)***	-56474.6992
Spectrum Type	STANDARD	***Sweep Width (Hz)***	113636.15	***Temperature (degree C)***	25.119		

SW: 300 ppm

O1P: -150 ppm

D1: 15 sec

proton-decoupled ^{19}F NMR

ρ_{wat} = 279.76/100.00 = 2.7976

Current Data Parameters

NAME	ju2614njwzw8
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20140630
Time	11.32
INSTRUM	AVII400
PROBHD	5 mm SEF 1H/D-
PULPROG	zgfhigqn.2
TD	262144
SOLVENT	Acetone
NS	427
DS	2
SWH	113636.367 Hz
FIDRES	0.433488 Hz
AQ	1.1534336 sec
RG	405.33
DW	4.400 usec
DE	6.50 usec
TE	298.1 K
D1	15.00000000 sec
D11	0.03000000 sec
D12	0.00002000 sec
TD0	1

======== CHANNEL f1 ========

SFO1	376.4418913 MHz
NUC1	19F
P1	14.50 usec
PLW1	10.00000000 W

======== CHANNEL f2 ========

SFO2	400.1316005 MHz
NUC2	1H
CPDPRG[2	waltz16
PCPD2	90.00 usec
PLW2	20.00000000 W
PLW12	0.24691001 W

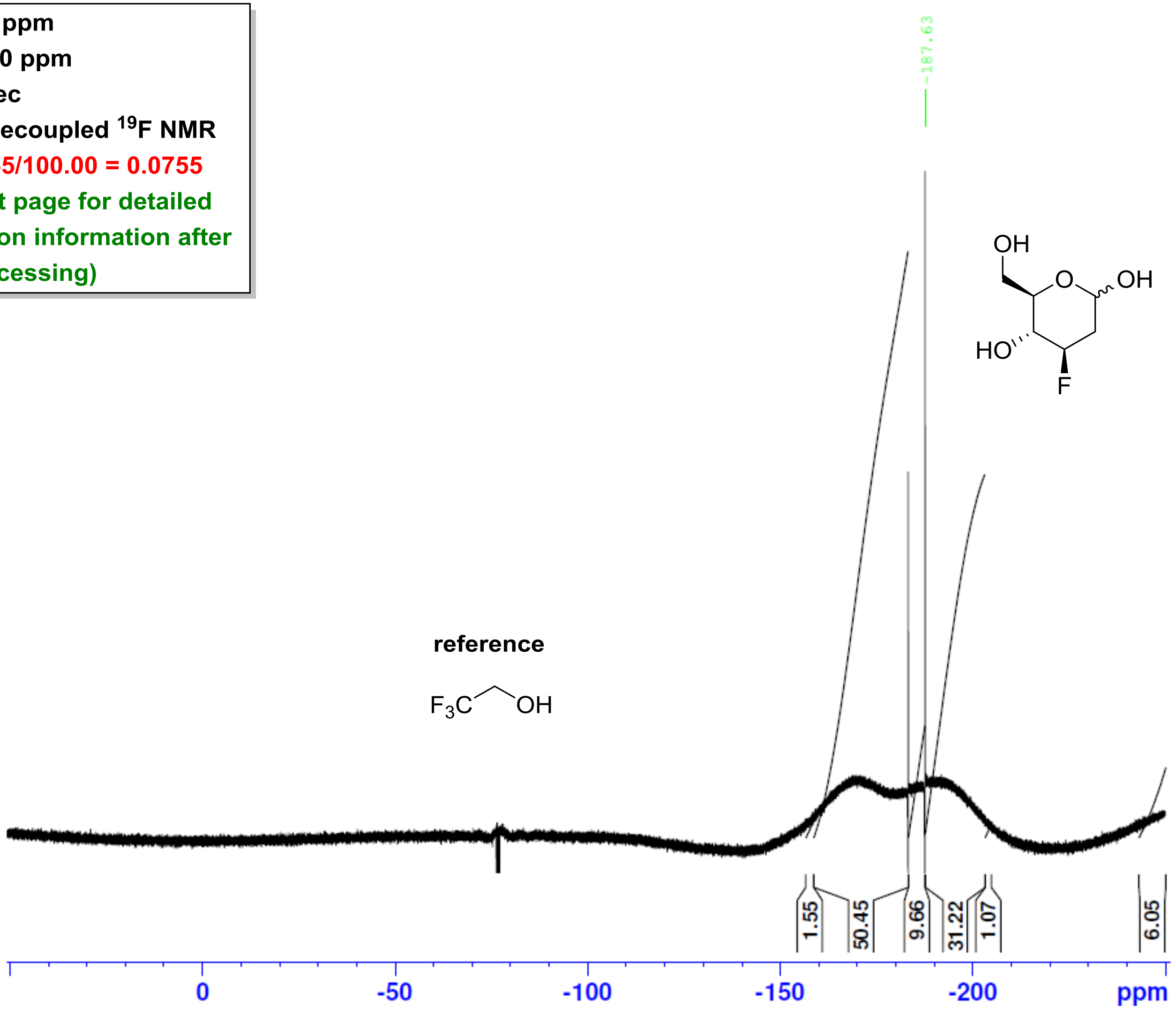
F2 - Processing parameters

SI	131072
SF	376.4983660 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

14.13. 2,3-Dideoxy-3-fluoro-D-glucopyranose (51), Entry 1, octanol sample

ZW7157-9 OCT

SW: 100 ppm
O1P: -100 ppm
D1: 50 sec
proton-decoupled ^{19}F NMR
ρ_{oct} = 7.55/100.00 = 0.0755
(see next page for detailed integration information after data processing)



AVIIIHD400 [3]

```
Current Data Parameters
NAME             ju2214zw3
EXPNO                   11
PROCNO                   1

F2 - Acquisition Parameters
Date_             20140622
Time                 13.03
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG        zgfhigqn.2
TD                  131072
SOLVENT            Acetone
NS                      64
DS                       4
SWH            113636.367 Hz
FIDRES           0.866977 Hz
AQ              0.5767168 sec
RG                  212.69
DW                   4.400 usec
DE                    6.50 usec
TE                   298.0 K
D1             50.00000000 sec
D11             0.03000000 sec
D12             0.00002000 sec
TD0                      1

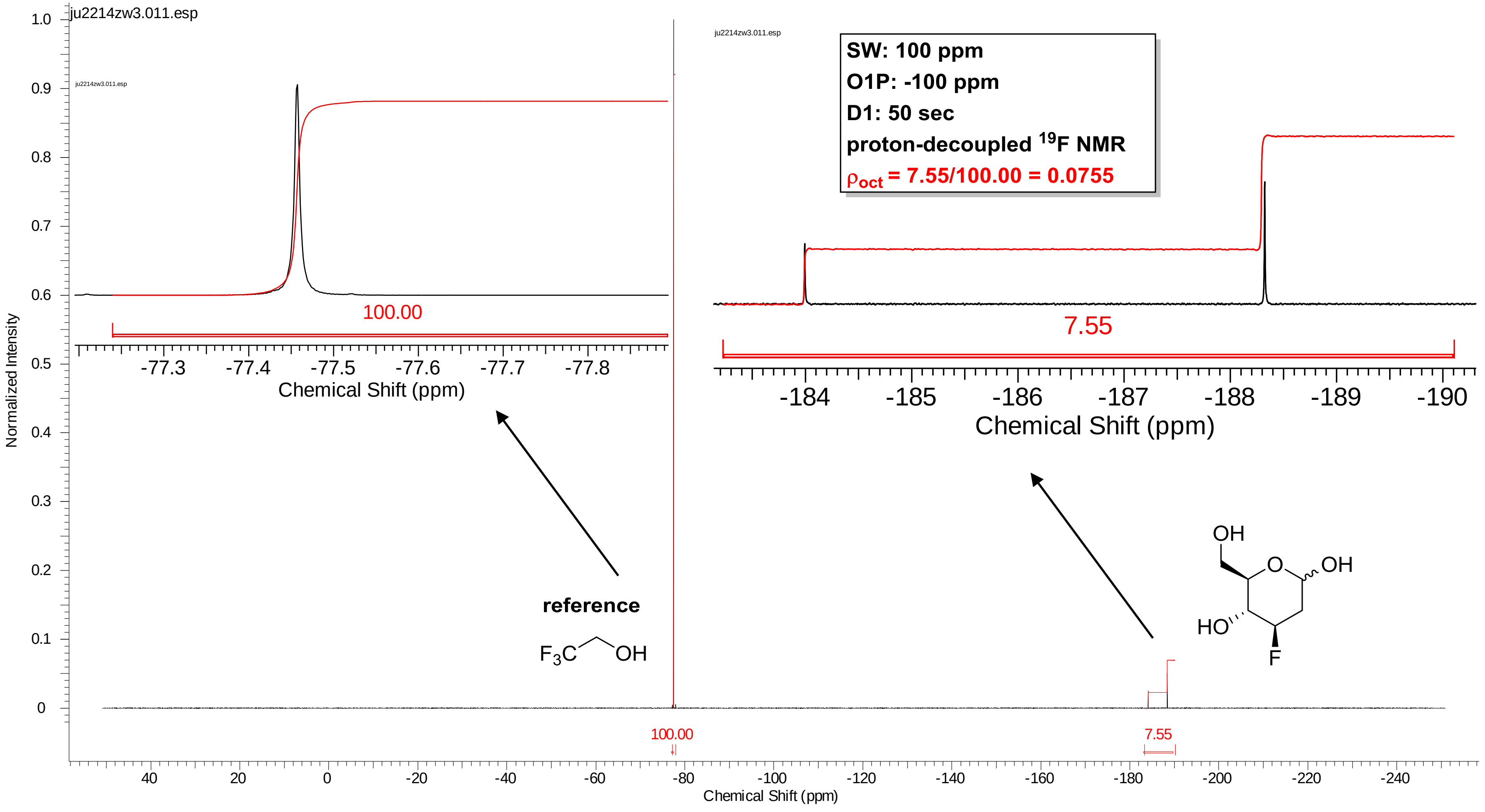
======== CHANNEL f1 ========
SFO1         376.4607164 MHz
NUC1                   19F
P1                   11.70 usec
PLW1           32.00000000 W

======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                70.00 usec
PLW2           32.00000000 W
PLW12           0.31999999 W

F2 - Processing parameters
SI                   65536
SF           376.4980709 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```

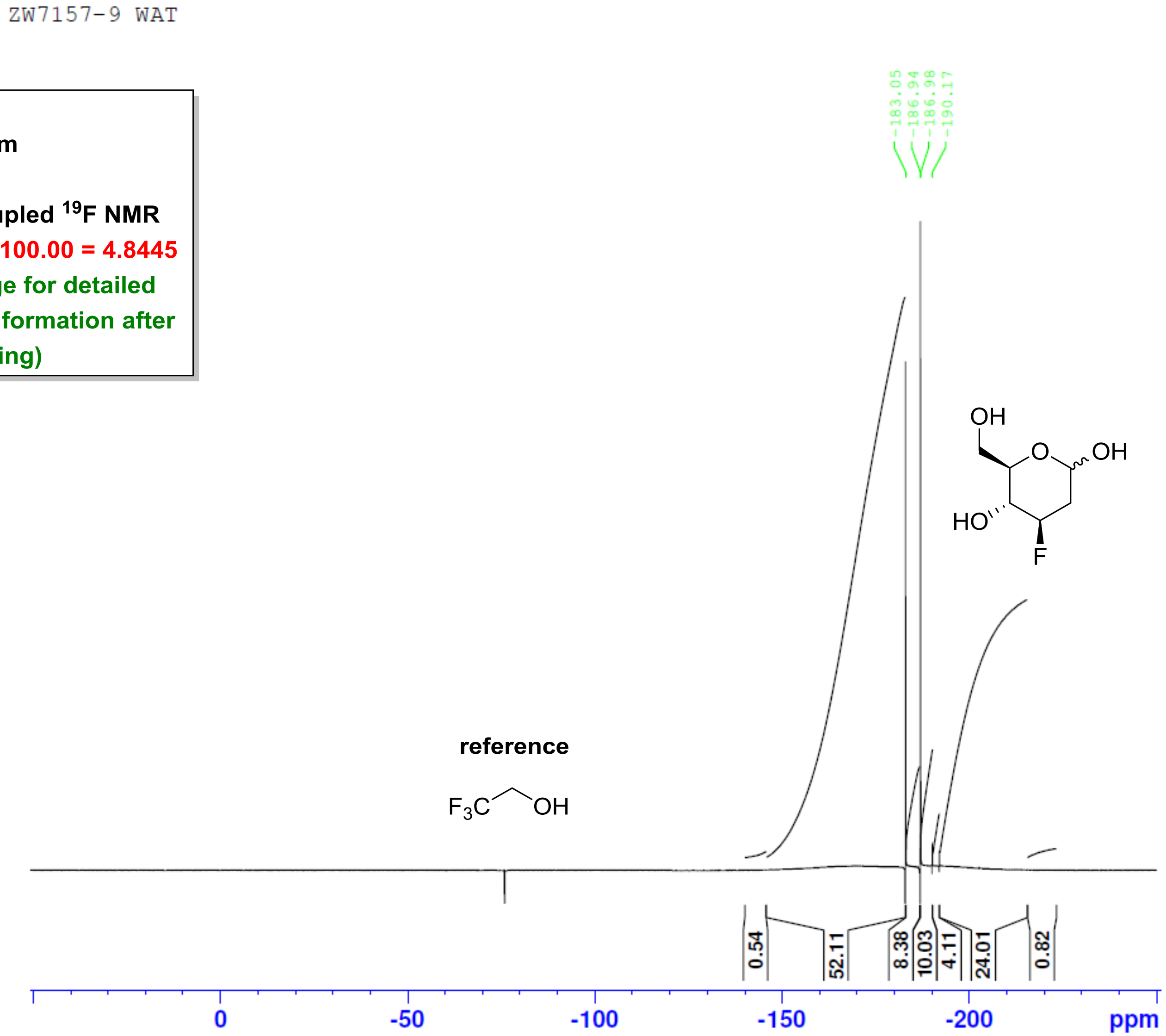
ZW7157-9 OCT

Acquisition Time (sec)	0.5767	***Comment***	ZW7157-9 OCT	***Date***	22 Jun 2014 13:03:12		
Date Stamp	22 Jun 2014 13:03:12						
File Name	\\soton.ac.uk\ude\personalfiles\users\zw3g10\mydesktop\logP project\Sugar logP NMR (ZW)\Lucas 3-fluoroglucose\ju2214zw3\11\fid						
Frequency (MHz)	376.46	***Nucleus***	19F	***Number of Transients***	64	***Origin***	spect
Original Points Count	65536	***Owner***	nmr	***Points Count***	262144	***Pulse Sequence***	zgfhigqn.2
Receiver Gain	212.69	***SW(cyclical) (Hz)***	113636.36	***Solvent***	Acetone	***Spectrum Offset (Hz)***	-37649.6211
Spectrum Type	STANDARD	***Sweep Width (Hz)***	113635.93	***Temperature (degree C)***	24.990		



14.14. 2,3-Dideoxy-3-fluoro-D-glucopyranose (51), Entry 1, water sample

SW: 100 ppm
O1P: -100 ppm
D1: 50 sec
proton-decoupled ^{19}F NMR
ρ_{wat} = 484.45/100.00 = 4.8445
(see next page for detailed integration information after data processing)



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AVIIIHD400 [3]

```
Current Data Parameters
NAME              ju2214zw4
EXPNO                    11
PROCNO                    1

F2 - Acquisition Parameters
Date_              20140622
Time                  14.08
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG         zgfhigqn.2
TD                   131072
SOLVENT             Acetone
NS                       64
DS                        4
SWH             113636.367 Hz
FIDRES             0.866977 Hz
AQ                0.5767168 sec
RG                   212.69
DW                    4.400 usec
DE                     6.50 usec
TE                    298.0 K
D1              50.00000000 sec
D11              0.03000000 sec
D12              0.00002000 sec
TD0                       1

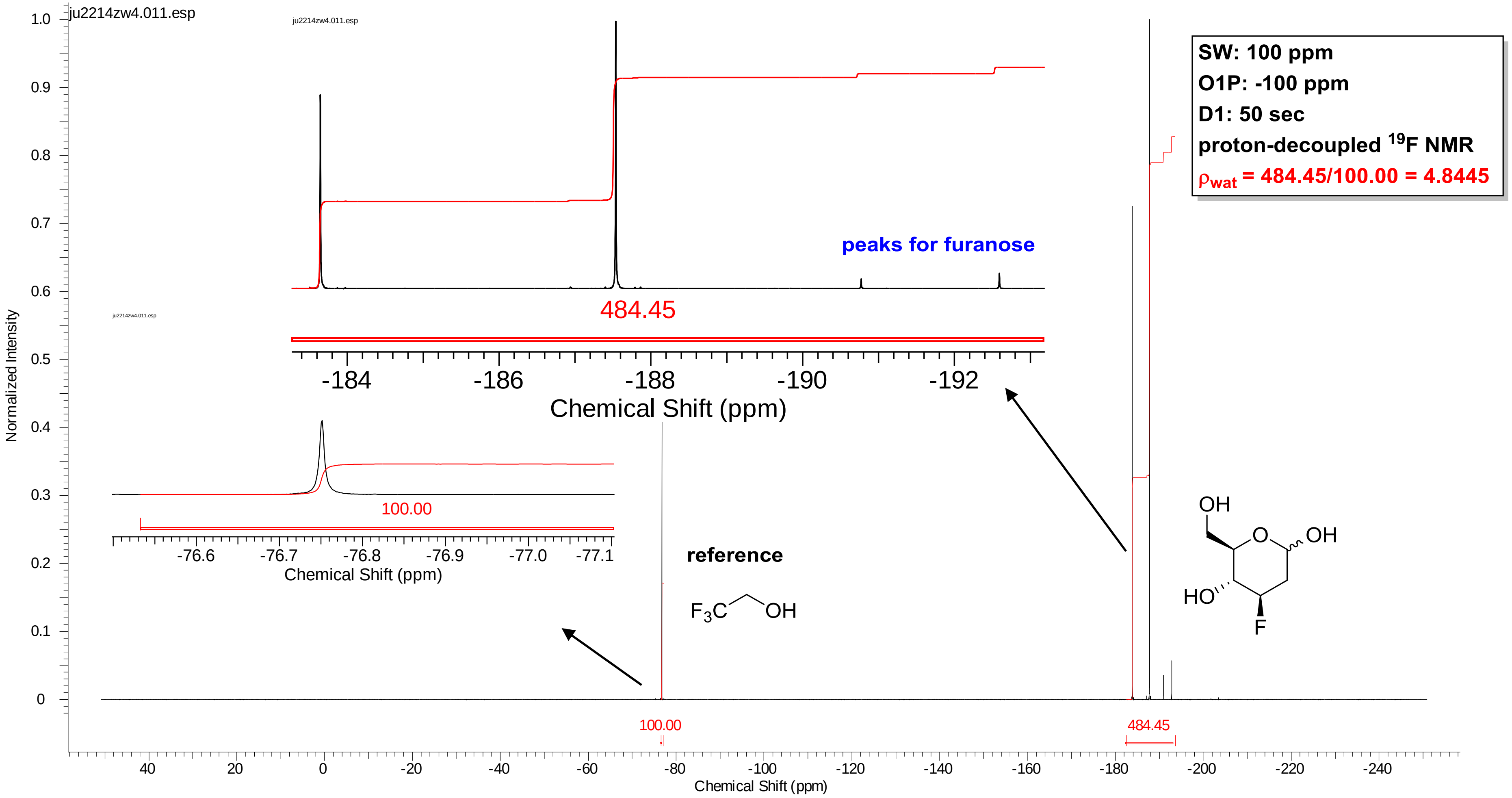
======== CHANNEL f1 ========
SFO1         376.4607164 MHz
NUC1                     19F
P1                     11.70 usec
PLW1             32.00000000 W

======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2                      1H
CPDPRG[2             waltz16
PCPD2                  70.00 usec
PLW2             32.00000000 W
PLW12             0.31999999 W

F2 - Processing parameters
SI                     65536
SF              376.4980709 MHz
WDW                       EM
SSB      0
LB                      0.30 Hz
GB       0
PC                      1.00
```

ZW7157-9 WAT

Acquisition Time (sec)	0.5767	***Comment***	ZW7157-9 WAT	***Date***	22 Jun 2014 14:09:20		
Date Stamp	22 Jun 2014 14:09:20						
File Name	\\soton.ac.uk\ude\personalfiles\users\zw3g10\mydesktop\logP project\Sugar logP NMR (ZW)\Lucas 3-fluoroglucose\ju2214zw4\11\fid						
Frequency (MHz)	376.46	***Nucleus***	19F	***Number of Transients***	64	***Origin***	spect
Original Points Count	65536	***Owner***	nmr	***Points Count***	262144	***Pulse Sequence***	zgfhigqn.2
Receiver Gain	212.69	***SW(cyclical) (Hz)***	113636.36	***Solvent***	Acetone	***Spectrum Offset (Hz)***	-37649.6211
Spectrum Type	STANDARD	***Sweep Width (Hz)***	113635.93	***Temperature (degree C)***	25.003		



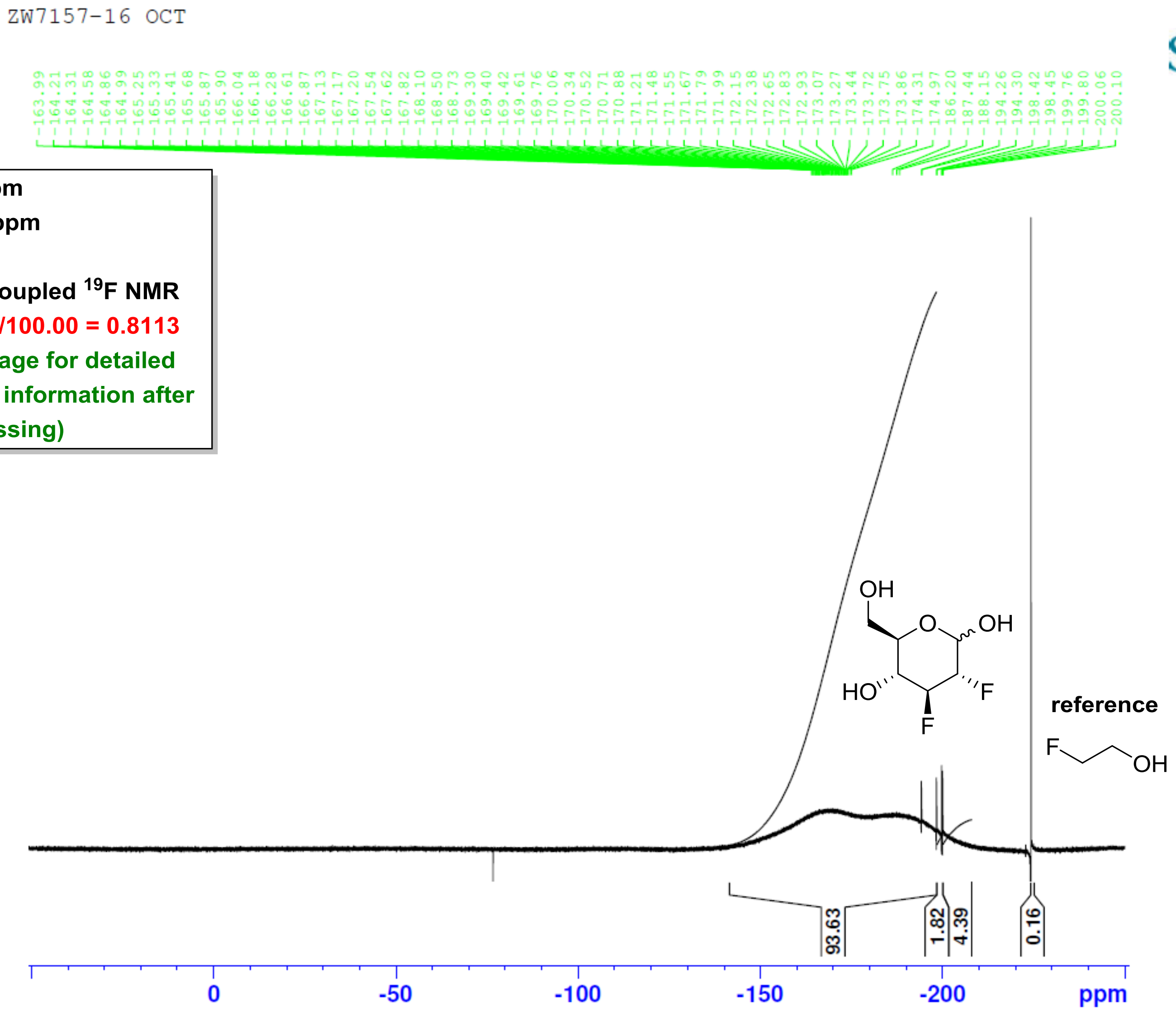
SW: 100 ppm
O1P: -100 ppm
D1: 50 sec
proton-decoupled ^{19}F NMR
ρ_{wat} = 484.45/100.00 = 4.8445

peaks for furanose

reference

14.15. 2,3-Dideoxy-2,3-difluoro-D-glucopyranose (52), Entry 1, octanol sample

SW: 300 ppm
O1P: -100 ppm
D1: 50 sec
proton-decoupled ^{19}F NMR
ρ_{oct} = 81.13/100.00 = 0.8113
(see next page for detailed integration information after data processing)



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```
AVIIIHD400 [3]

Current Data Parameters
NAME            jy0814zw4
EXPNO                  12
PROCNO                  1

F2 - Acquisition Parameters
Date_            20140708
Time                23.38
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG       zgfhigqn.2
TD                 131072
SOLVENT           Acetone
NS                     64
DS                      4
SWH            113636.367 Hz
FIDRES           0.866977 Hz
AQ              0.5767168 sec
RG                 212.69
DW                  4.400 usec
DE                   6.50 usec
TE                  298.0 K
D1            50.00000000 sec
D11            0.03000000 sec
D12            0.00002000 sec
TD0                     1

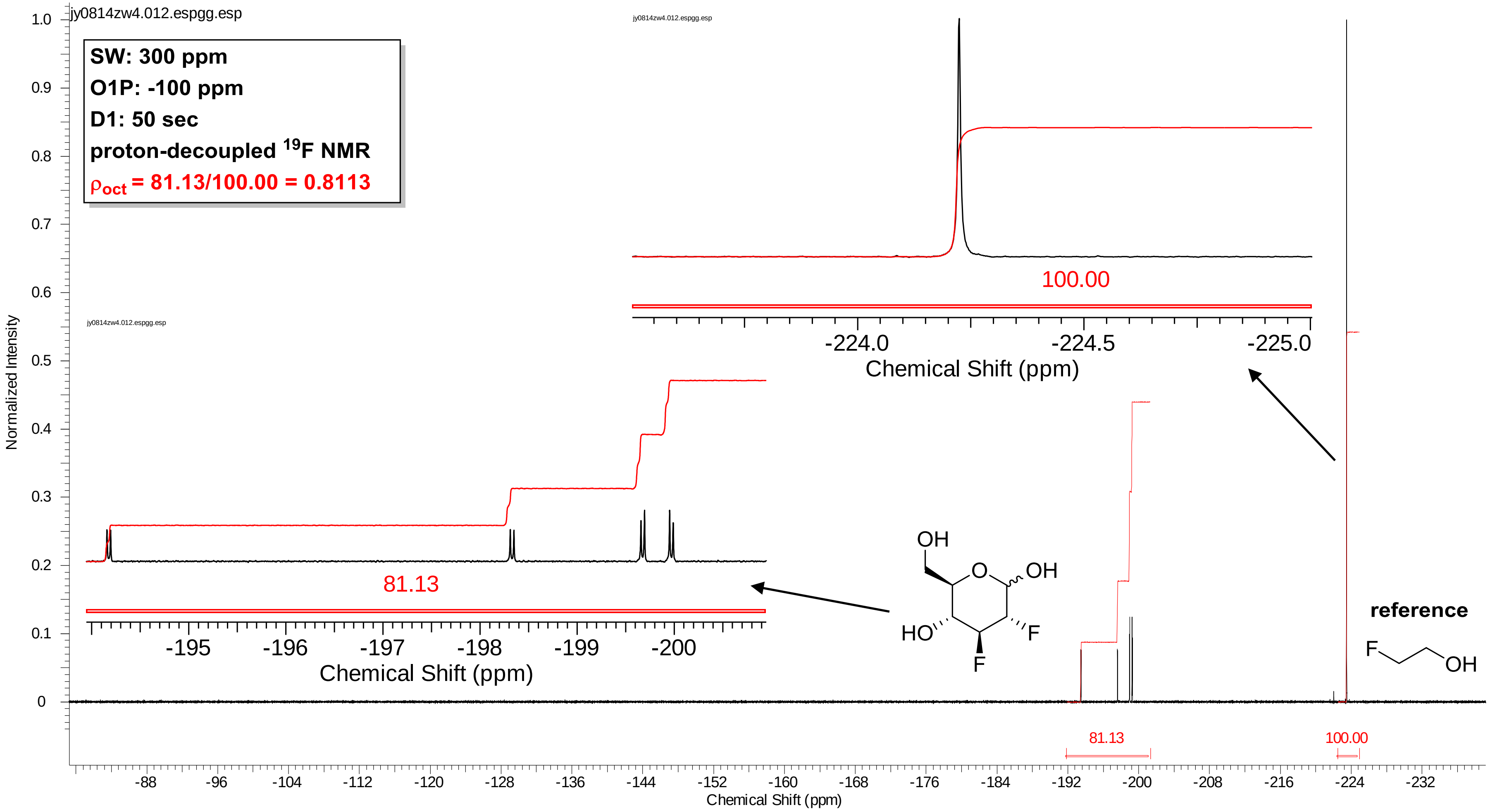
======== CHANNEL f1 ========
SFO1          376.4607164 MHz
NUC1                  19F
P1                  11.70 usec
PLW1          32.00000000 W

======== CHANNEL f2 ========
SFO2          400.1316005 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               70.00 usec
PLW2          32.00000000 W
PLW12          0.31999999 W

F2 - Processing parameters
SI                  65536
SF            376.4980709 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

ZW7157-16 OCT

Acquisition Time (sec)	0.5767	***Comment***	ZW7157-16 OCT	***Date***	08 Jul 2014 23:38:56		
Date Stamp	08 Jul 2014 23:38:56						
File Name	C:\Documents and Settings\Samuel Golten\Desktop\Sugar logP NMR\ZW7157-16 Compound Code LQ7219-68\jy0814zw4\12\fid						
Frequency (MHz)	376.50	***Nucleus***	19F	***Number of Transients***	64	***Origin***	spect
Original Points Count	65536	***Owner***	nmr	***Points Count***	262144	***Pulse Sequence***	zgfhigqn.2
Receiver Gain	212.69	***SW(cyclical) (Hz)***	113636.37	***Solvent***	Acetone	***Spectrum Offset (Hz)***	-37354.4844
Spectrum Type	STANDARD	***Sweep Width (Hz)***	113635.94	***Temperature (degree C)***	24.996		



SW: 300 ppm

O1P: -100 ppm

D1: 50 sec

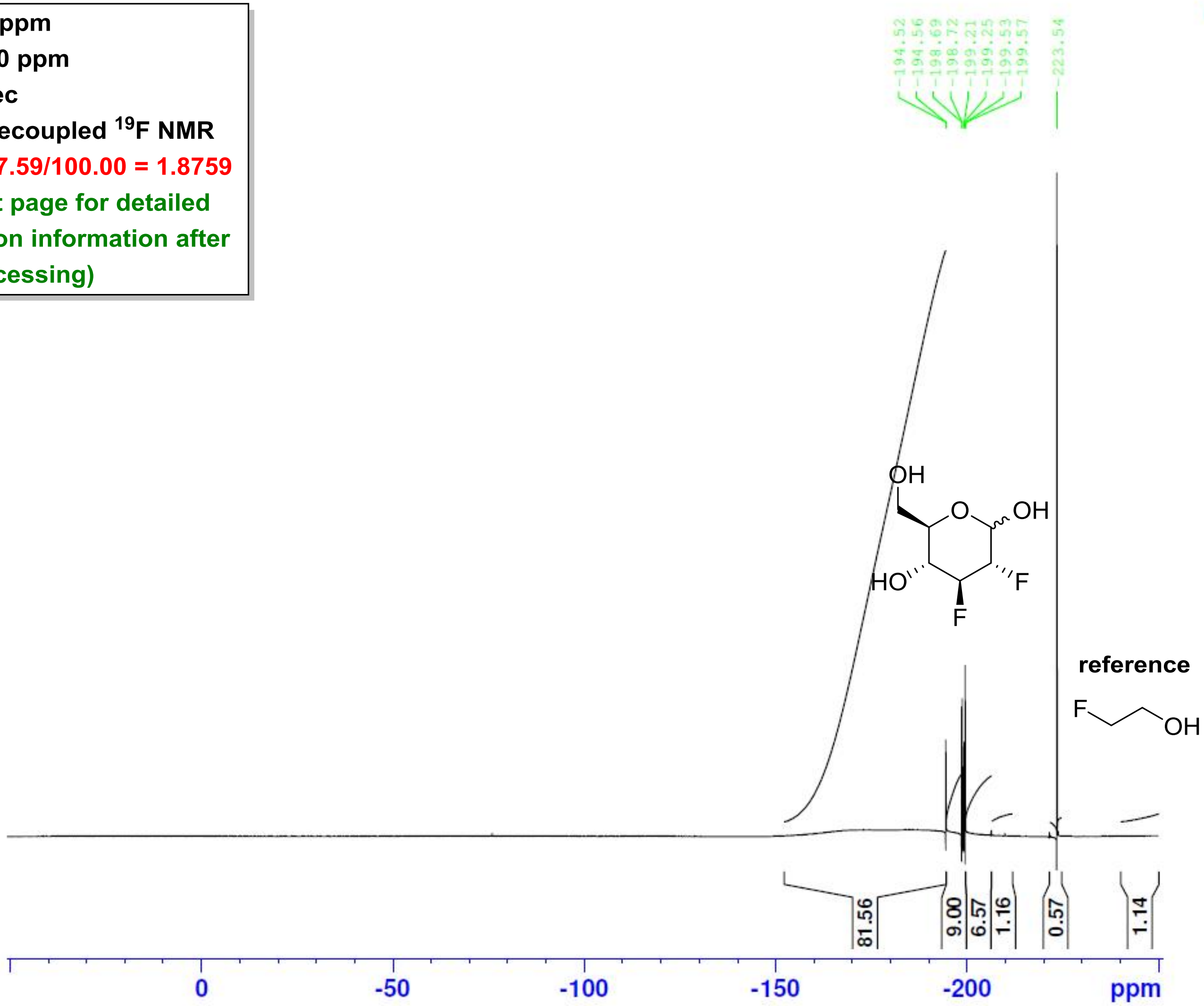
proton-decoupled ^{19}F NMR

ρ_{oct} = 81.13/100.00 = 0.8113

14.16. 2,3-Dideoxy-2,3-difluoro-D-glucopyranose (52), Entry 1, water sample

ZW7157-16 WAT

SW: 300 ppm
O1P: -100 ppm
D1: 50 sec
proton-decoupled ^{19}F NMR
ρ_{wat} = 187.59/100.00 = 1.8759
(see next page for detailed integration information after data processing)



AVIIIHD400 [3]

```
Current Data Parameters
NAME              jy0814zw5
EXPNO                    12
PROCNO                    1

F2 - Acquisition Parameters
Date_              20140709
Time                   1.01
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG         zgfhigqn.2
TD                   131072
SOLVENT             Acetone
NS                       64
DS                        4
SWH             113636.367 Hz
FIDRES            0.866977 Hz
AQ               0.5767168 sec
RG                   212.69
DW                    4.400 usec
DE                     6.50 usec
TE                    298.0 K
D1              50.00000000 sec
D11              0.03000000 sec
D12              0.00002000 sec
TD0                       1

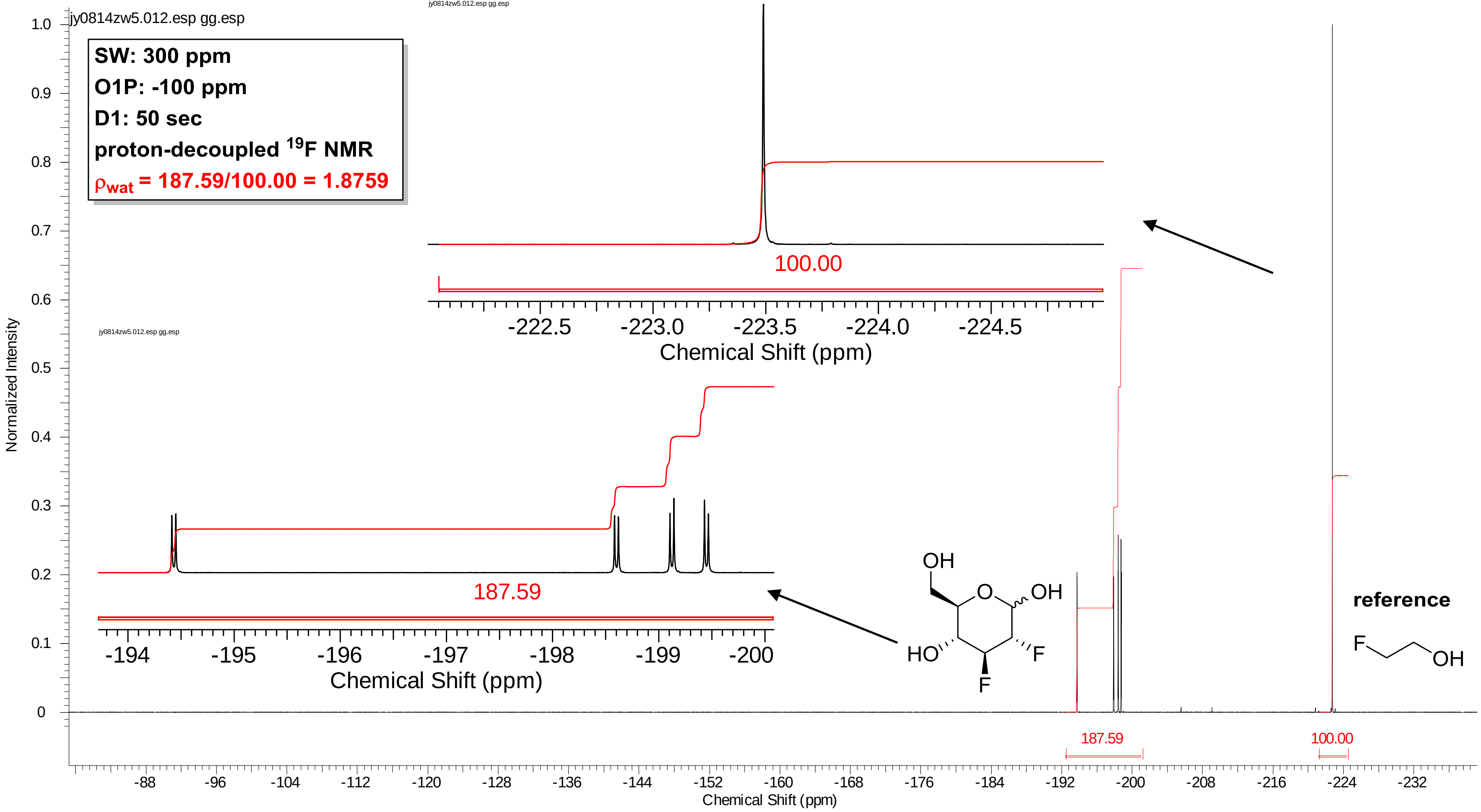
======== CHANNEL f1 ========
SFO1         376.4607164 MHz
NUC1                     19F
P1                     11.70 usec
PLW1             32.00000000 W

======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2                      1H
CPDPRG[2             waltz16
PCPD2                  70.00 usec
PLW2             32.00000000 W
PLW12             0.31999999 W

F2 - Processing parameters
SI                     65536
SF               376.4980709 MHz
WDW                       EM
SSB      0
LB                      0.30 Hz
GB       0
PC                      1.00
```

ZW7157-16 WAT

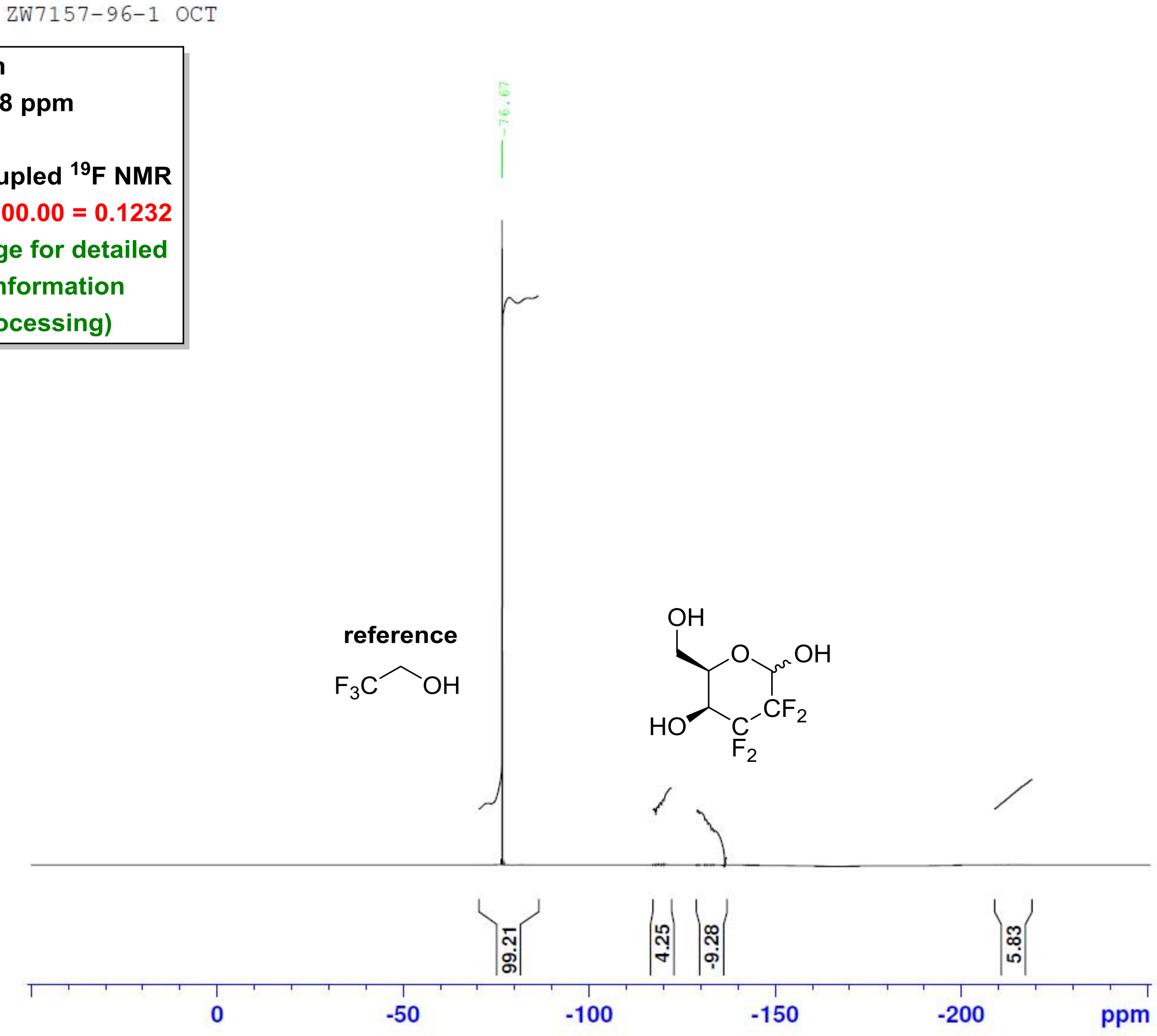
Acquisition Time (sec)	0.5767	***Comment***	ZW7157-16 WAT	***Date***	09 Jul 2014 01:02:08		
Date Stamp	09 Jul 2014 01:02:08						
File Name	C:\Documents and Settings\Samuel Golten\Desktop\Sugar logP NMR\ZW7157-16 Compound Code LQ7219-68\jy0814zw5\12\fid						
Frequency (MHz)	376.50	***Nucleus***	19F	***Number of Transients***	64	***Origin***	spect
Original Points Count	65536	***Owner***	nmr	***Points Count***	262144	***Pulse Sequence***	zgfhigqn.2
Receiver Gain	212.69	***SW(cyclical) (Hz)***	113636.37	***Solvent***	Acetone	***Spectrum Offset (Hz)***	-37354.4844
Spectrum Type	STANDARD	***Sweep Width (Hz)***	113635.94	***Temperature (degree C)***	25.003		



SW: 300 ppm
O1P: -100 ppm
D1: 50 sec
proton-decoupled ^{19}F NMR
ρ_{wat} = 187.59/100.00 = 1.8759

14.17. 2,3-Dideoxy-2,2,3,3-tetrafluoro-D-*threo*-hexopyranose (53), Entry 1, octanol sample

SW: 300 ppm
O1P: -101.768 ppm
D1: 30 sec
proton-decoupled ^{19}F NMR
ρ_{oct} = 12.32/100.00 = 0.1232
(see next page for detailed integration information after data processing)



```
AVIIIHD400 [3]

Current Data Parameters
NAME              my0915zw11
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_               20150509
Time                   20.55
INSTRUM                spect
PROBHD     5 mm PABBO BB/
PULPROG          zgfhigqn.2
TD                    131072
SOLVENT              Acetone
NS                        64
DS                         4
SWH             113636.367 Hz
FIDRES            0.866977 Hz
AQ               0.5767168 sec
RG                    212.69
DW                     4.400 usec
DE                      6.50 usec
TE                     299.2 K
D1               30.00000000 sec
D11               0.03000000 sec
D12               0.00002000 sec
TD0                        1

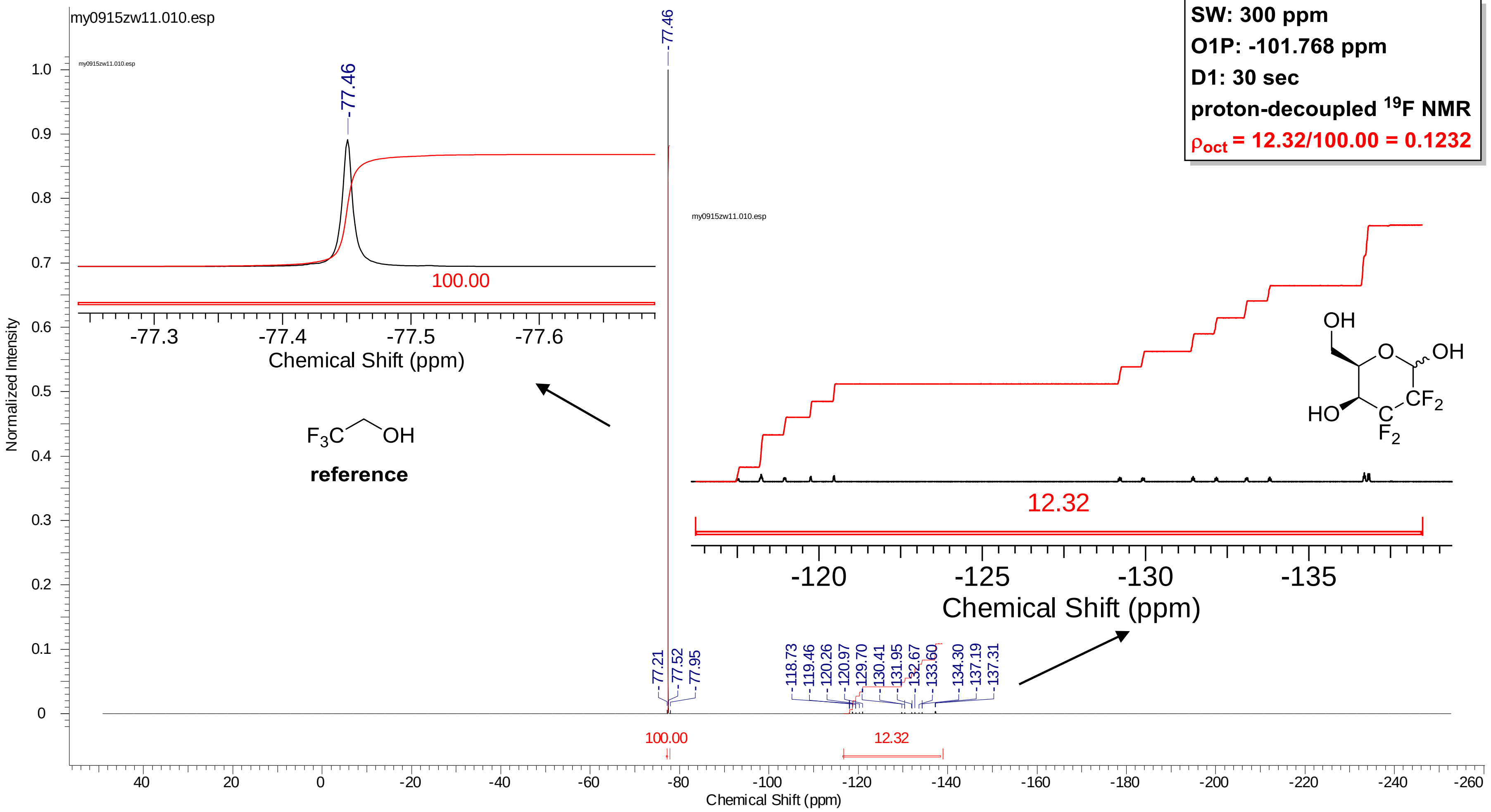
======== CHANNEL f1 ========
SFO1           376.4600506 MHz
NUC1                     19F
P1                     11.70 usec
PLW1             32.00000000 W

======== CHANNEL f2 ========
SFO2           400.1316005 MHz
NUC2                      1H
CPDPRG[2             waltz16
PCPD2                  70.00 usec
PLW2             32.00000000 W
PLW12             0.31999999 W

F2 - Processing parameters
SI                     65536
SF             376.4980709 MHz
WDW                       EM
SSB      0
LB                      0.30 Hz
GB       0
PC                      1.00
```

ZW7157-96-1 OCT

Acquisition Time (sec)	0.5767	***Comment***	ZW7157-96-1 OCT			***Date***	09 May 2015 20:54:40
Date Stamp	09 May 2015 20:54:40						
File Name	\\soton.ac.uk\ude\personalfiles\users\zw3g10\mydesktop\Meine Arbeit 2015\zw7157-96\my0915zw11\10\fid					***Frequency (MHz)***	376.46
Nucleus	19F	***Number of Transients***	64	***Origin***	spect	***Original Points Count***	65536
Owner	nmr	***Points Count***	262144	***Pulse Sequence***	zgfhigqn.2	***Receiver Gain***	212.69
SW(cyclical) (Hz)	113636.37	***Solvent***	Acetone	***Spectrum Offset (Hz)***	-38315.4492	***Spectrum Type***	STANDARD
Sweep Width (Hz)	113635.94	***Temperature (degree C)***	26.234				



SW: 300 ppm

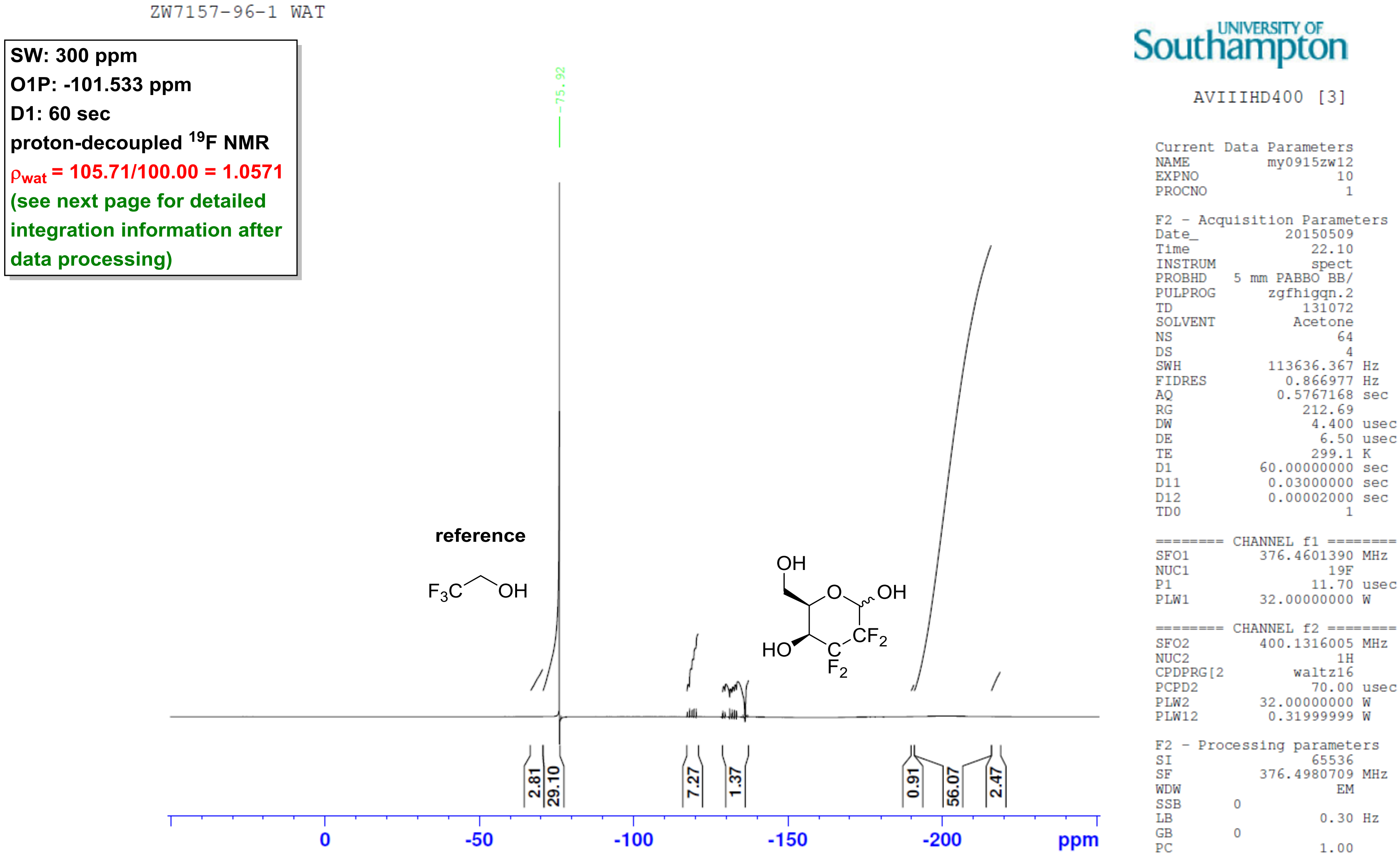
O1P: -101.768 ppm

D1: 30 sec

proton-decoupled ^{19}F NMR

ρ_{oct} = 12.32/100.00 = 0.1232

14.18. 2,3-Dideoxy-2,2,3,3-tetrafluoro-D-*threo*-hexopyranose (53), Entry 1, water sample



SW: 300 ppm
O1P: -101.533 ppm
D1: 60 sec
proton-decoupled ^{19}F NMR
ρ_{wat} = 105.71/100.00 = 1.0571
(see next page for detailed integration information after data processing)

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AVIIIHD400 [3]

Current Data Parameters
NAME            my0915zw12
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150509
Time                 22.10
INSTRUM              spect
PROBHD     5 mm PABBO BB/
PULPROG        zgfhigqn.2
TD                  131072
SOLVENT            Acetone
NS                      64
DS                       4
SWH             113636.367 Hz
FIDRES            0.866977 Hz
AQ               0.5767168 sec
RG                  212.69
DW                   4.400 usec
DE                    6.50 usec
TE                   299.1 K
D1             60.00000000 sec
D11             0.03000000 sec
D12             0.00002000 sec
TD0                      1

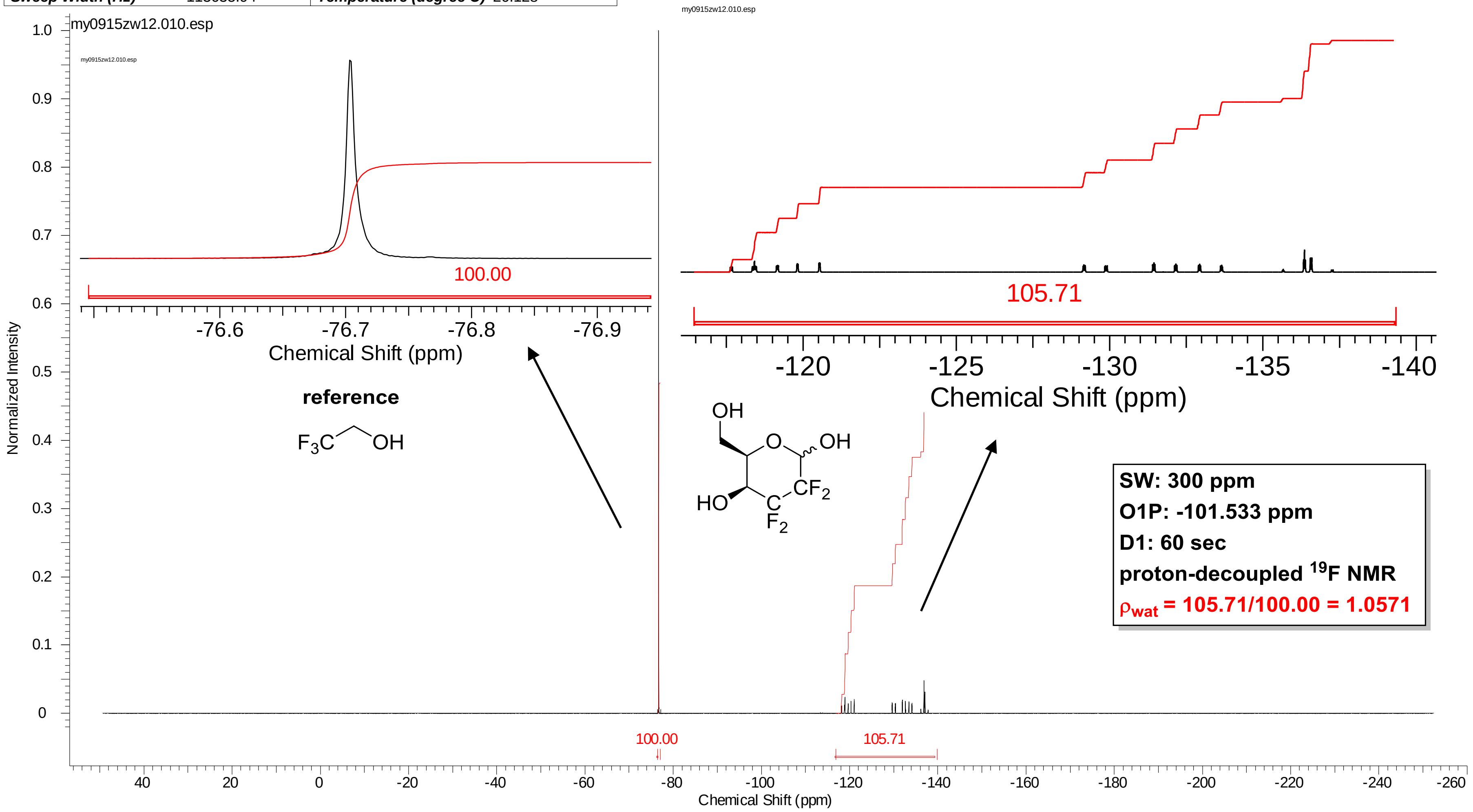
======== CHANNEL f1 ========
SFO1           376.4601390 MHz
NUC1                   19F
P1                   11.70 usec
PLW1           32.00000000 W

======== CHANNEL f2 ========
SFO2           400.1316005 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                70.00 usec
PLW2           32.00000000 W
PLW12           0.31999999 W

F2 - Processing parameters
SI                   65536
SF             376.4980709 MHz
WDW                     EM
SSB        0
LB                    0.30 Hz
GB         0
PC                    1.00
```

ZW7157-96-1 WAT

Acquisition Time (sec)	0.5767	***Comment***	ZW7157-96-1 WAT			***Date***	09 May 2015 22:11:28
Date Stamp	09 May 2015 22:11:28						
File Name	\\soton.ac.uk\ude\personalfiles\users\zw3g10\mydesktop\Meine Arbeit 2015\zw7157-96\my0915zw12\10\fid					***Frequency (MHz)***	376.46
Nucleus	19F	***Number of Transients***	64	***Origin***	spect	***Original Points Count***	65536
Owner	nmr	***Points Count***	262144	***Pulse Sequence***	zgfhigqn.2	***Receiver Gain***	212.69
SW(cyclical) (Hz)	113636.37	***Solvent***	Acetone	***Spectrum Offset (Hz)***	-38226.9727	***Spectrum Type***	STANDARD
Sweep Width (Hz)	113635.94	***Temperature (degree C)***	26.128				



SW: 300 ppm

O1P: -101.533 ppm

D1: 60 sec

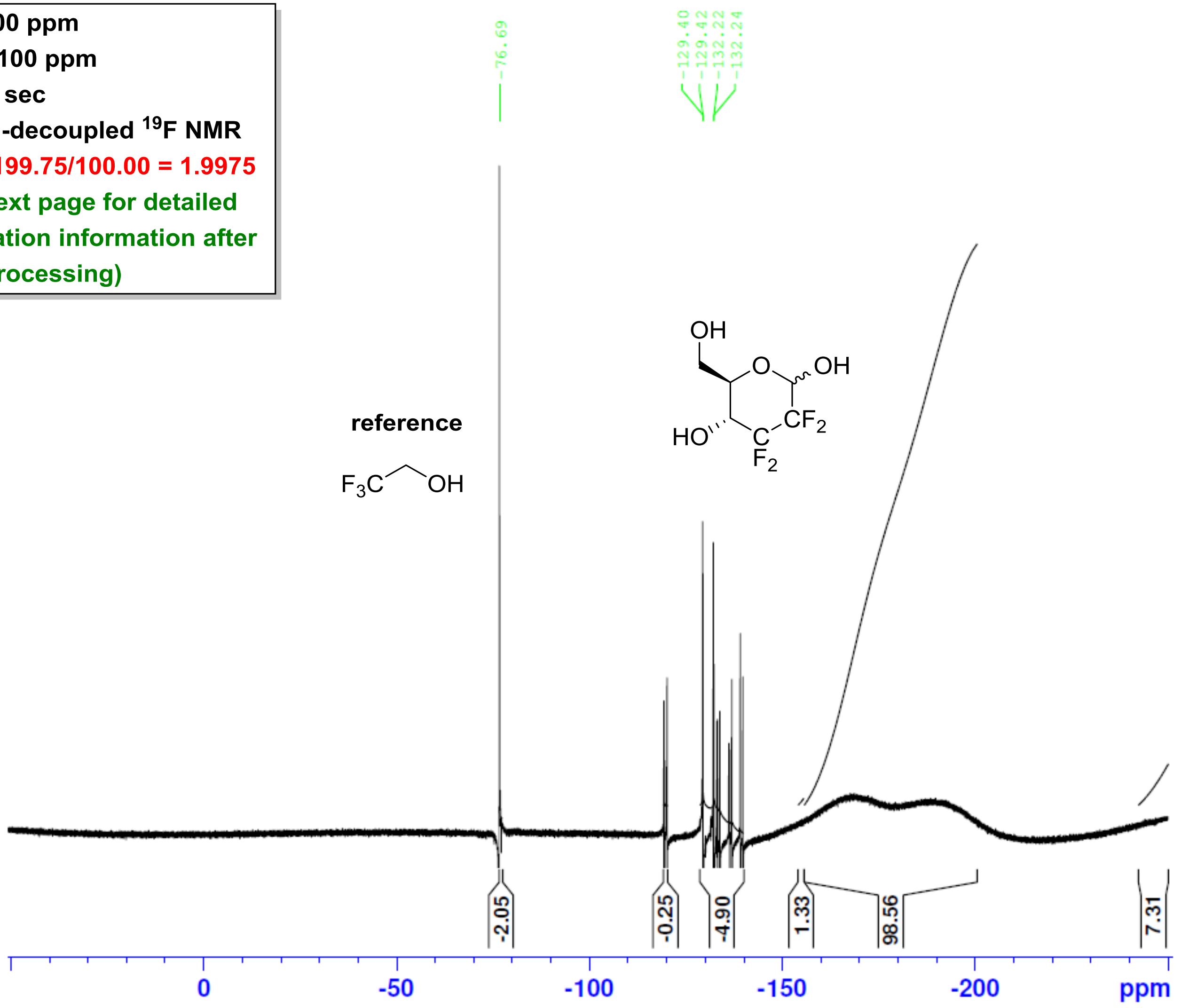
proton-decoupled ^{19}F NMR

ρ_{wat} = 105.71/100.00 = 1.0571

14.19. 2,3-Dideoxy-2,2,3,3-tetrafluoro-D-*erythro*-hexopyranose (54), Entry 1, octanol sample

ZW7157-11 OCT

SW: 300 ppm
O1P: -100 ppm
D1: 50 sec
proton-decoupled ^{19}F NMR
ρ_{oct} = 199.75/100.00 = 1.9975
(see next page for detailed integration information after data processing)



AVIIIHD400 [3]

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Current Data Parameters
NAME              ju2314zw1
EXPNO                    11
PROCNO                    1

F2 - Acquisition Parameters
Date_              20140623
Time                  10.34
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG         zgfhigqn.2
TD                   131072
SOLVENT             Acetone
NS                       64
DS                        4
SWH            113636.367 Hz
FIDRES           0.866977 Hz
AQ              0.5767168 sec
RG                   212.69
DW                    4.400 usec
DE                     6.50 usec
TE                    298.0 K
D1              50.00000000 sec
D11              0.03000000 sec
D12              0.00002000 sec
TD0                       1

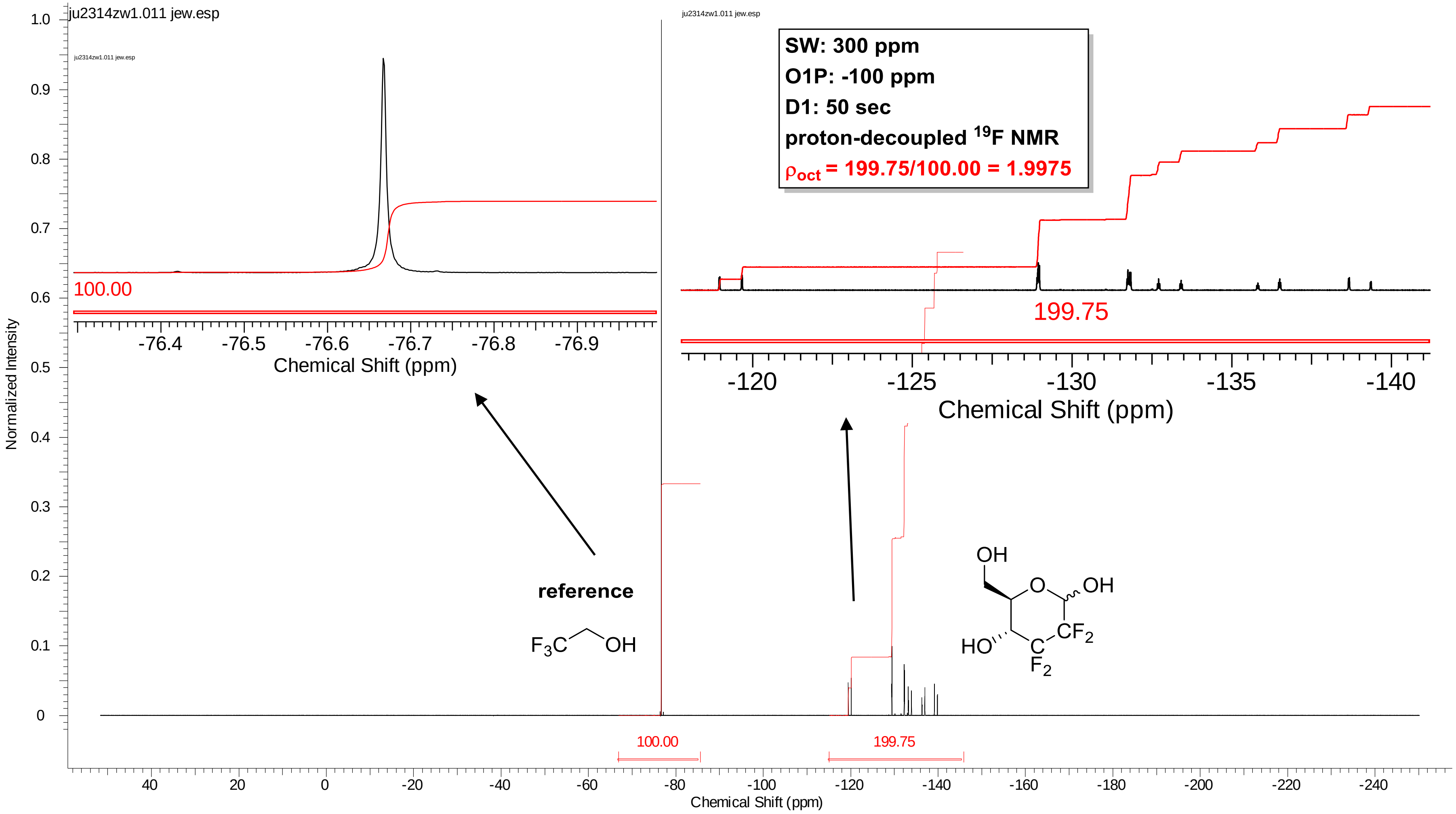
======== CHANNEL f1 ========
SFO1           376.4607164 MHz
NUC1                    19F
P1                    11.70 usec
PLW1            32.00000000 W

======== CHANNEL f2 ========
SFO2           400.1316005 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2                 70.00 usec
PLW2            32.00000000 W
PLW12            0.31999999 W

F2 - Processing parameters
SI                    65536
SF             376.4980709 MHz
WDW                      EM
SSB      0
LB                     0.30 Hz
GB       0
PC                     1.00
```

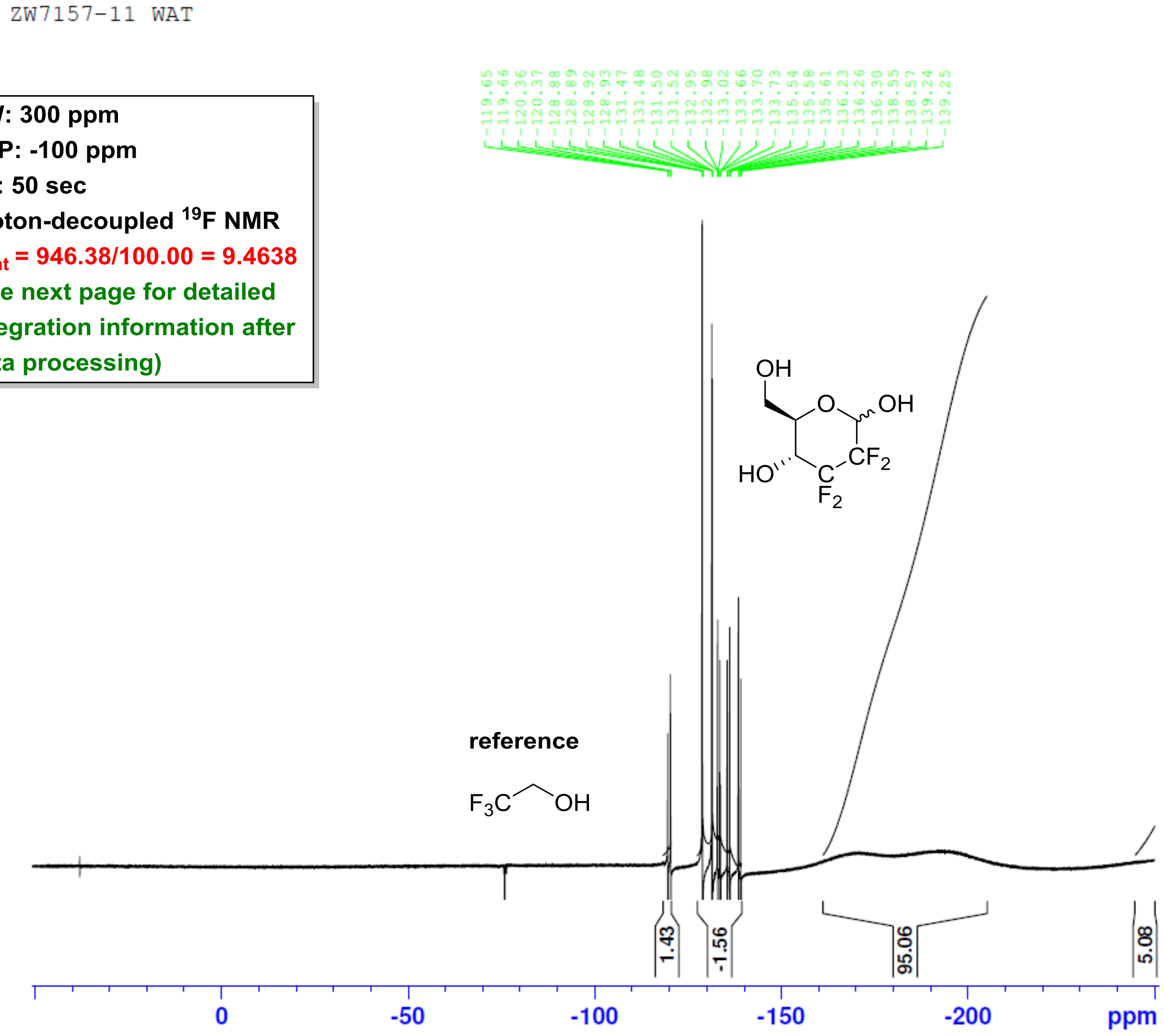
ZW7157-11 OCT

Acquisition Time (sec)	0.5767	***Comment***	ZW7157-11 OCT			***Date***	23 Jun 2014 10:33:52
Date Stamp	23 Jun 2014 10:33:52			***File Name***	C:\Documents and Settings\Samuel Golten\Desktop\log NMR\SG sugar\ju2314zw1\11\fid		
Frequency (MHz)	376.50	***Nucleus***	19F	***Number of Transients***	64	***Origin***	spect
Original Points Count	65536	***Owner***	nmr	***Points Count***	262144	***Pulse Sequence***	zgfhigqn.2
Receiver Gain	212.69	***SW(cyclical) (Hz)***	113636.37	***Solvent***	Acetone	***Spectrum Offset (Hz)***	-37354.4844
Spectrum Type	STANDARD	***Sweep Width (Hz)***	113635.94	***Temperature (degree C)***	24.995		



14.20. 2,3-Dideoxy-2,2,3,3-tetrafluoro-D-*erythro*-hexopyranose (54), Entry 1, water sample

SW: 300 ppm
O1P: -100 ppm
D1: 50 sec
proton-decoupled ^{19}F NMR
ρ_{wat} = 946.38/100.00 = 9.4638
(see next page for detailed integration information after data processing)



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AVIIIHD400 [3]

Current Data Parameters
NAME              ju2314zw2
EXPNO                    11
PROCNO                    1

F2 - Acquisition Parameters
Date_              20140623
Time                  11.39
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG          zgfhigqn.2
TD                   131072
SOLVENT             Acetone
NS                       64
DS                        4
SWH              113636.367 Hz
FIDRES             0.866977 Hz
AQ                0.5767168 sec
RG                   212.69
DW                    4.400 usec
DE                     6.50 usec
TE                    298.0 K
D1              50.00000000 sec
D11              0.03000000 sec
D12              0.00002000 sec
TD0                       1

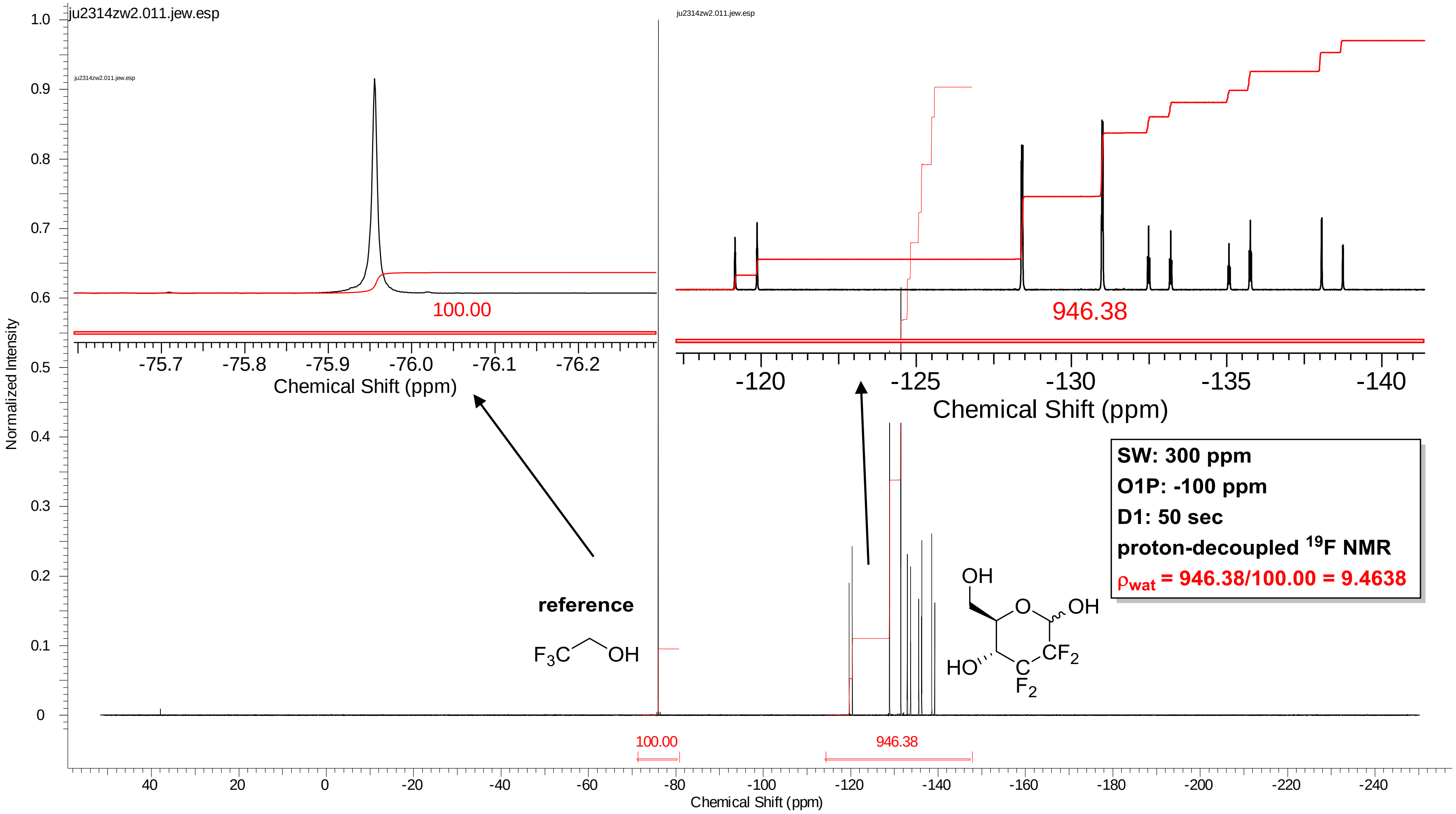
======== CHANNEL f1 ========
SFO1            376.4607164 MHz
NUC1                    19F
P1                    11.70 usec
PLW1            32.00000000 W

======== CHANNEL f2 ========
SFO2            400.1316005 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2                 70.00 usec
PLW2            32.00000000 W
PLW12            0.31999999 W

F2 - Processing parameters
SI                    65536
SF              376.4980709 MHz
WDW                      EM
SSB      0
LB                     0.30 Hz
GB       0
PC                     1.00
```

ZW7157-11 WAT

Acquisition Time (sec)	0.5767	***Comment***	ZW7157-11 WAT			***Date***	23 Jun 2014 11:40:00
Date Stamp	23 Jun 2014 11:40:00			***File Name***	C:\Documents and Settings\Samuel Golten\Desktop\log NMR\SG sugar\ju2314zw2\11\fid		
Frequency (MHz)	376.50	***Nucleus***	19F	***Number of Transients***	64	***Origin***	spect
Original Points Count	65536	***Owner***	nmr	***Points Count***	262144	***Pulse Sequence***	zgfhigqn.2
Receiver Gain	212.69	***SW(cyclical) (Hz)***	113636.37	***Solvent***	Acetone	***Spectrum Offset (Hz)***	-37354.4844
Spectrum Type	STANDARD	***Sweep Width (Hz)***	113635.94	***Temperature (degree C)***	24.990		



SW: 300 ppm

O1P: -100 ppm

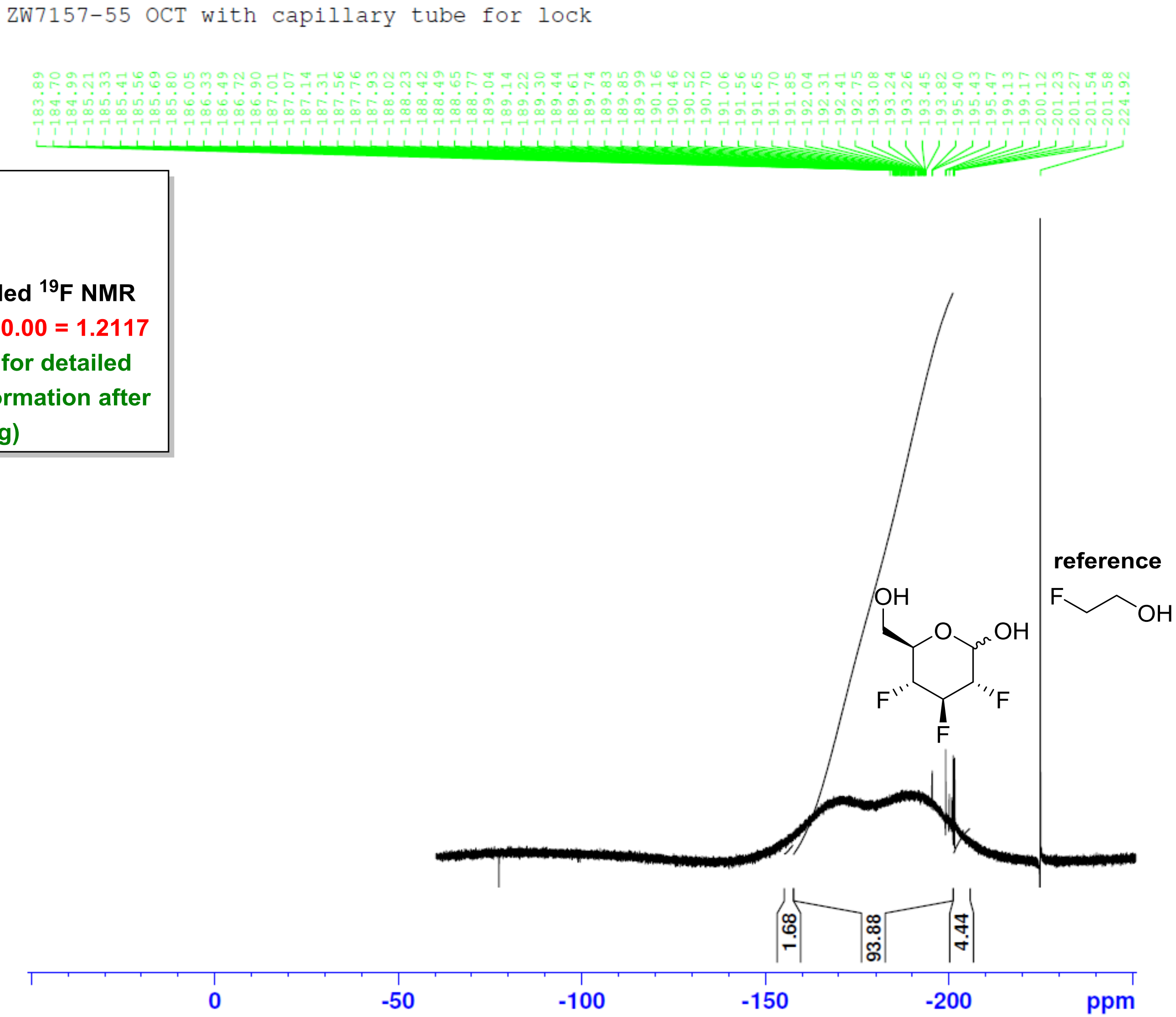
D1: 50 sec

proton-decoupled ^{19}F NMR

ρ_{wat} = 946.38/100.00 = 9.4638

14.21. 2,3,4-Trideoxy-2,3,4-trifluoro-D-glucose (55), Entry 1, octanol sample

SW: 300 ppm
O1P: -210 ppm
D1: 60 sec
proton-decoupled ^{19}F NMR
ρ_{oct} = 121.17/100.00 = 1.2117
(see next page for detailed integration information after data processing)



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AVIIIHD400 [3]

Current Data Parameters
NAME              nv2514zw1
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20141125
Time                  15.14
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG          zgfhigqn.2
TD                   131072
SOLVENT             Acetone
NS                       64
DS                        4
SWH              113636.367 Hz
FIDRES             0.866977 Hz
AQ                0.5767168 sec
RG                   212.69
DW                    4.400 usec
DE                     6.50 usec
TE                    298.0 K
D1              60.00000000 sec
D11              0.03000000 sec
D12              0.00002000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            376.4185522 MHz
NUC1                    19F
P1                    11.70 usec
PLW1            32.00000000 W

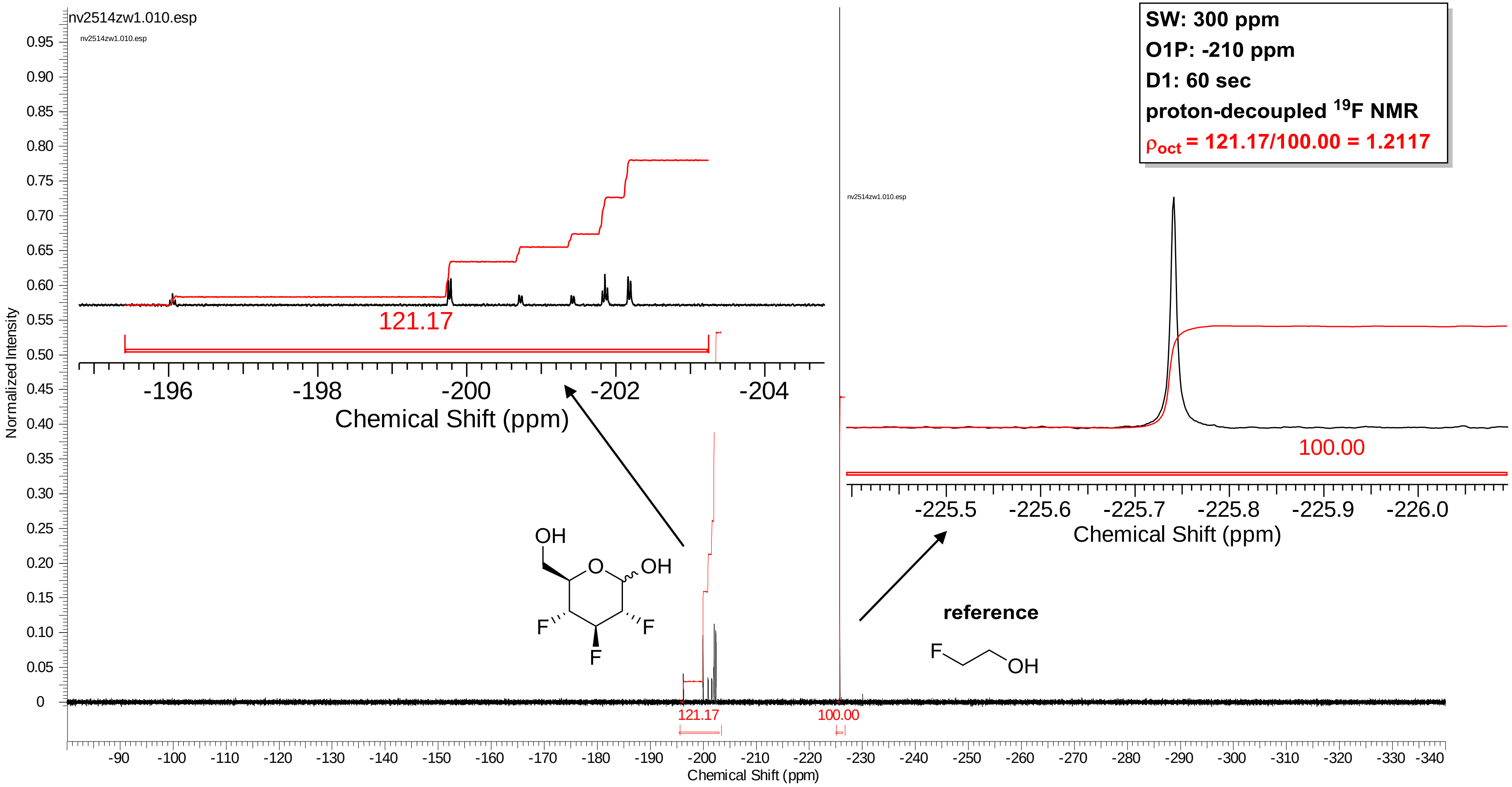
======== CHANNEL f2 ========
SFO2            400.1316005 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2                 70.00 usec
PLW2            32.00000000 W
PLW12            0.31999999 W

F2 - Processing parameters
SI                    65536
SF              376.4980709 MHz
WDW                      EM
SSB      0
LB                     0.30 Hz
GB       0
PC                     1.00
```

ZW7157-55 OCT with capillary tube for lock

RMS of Noise 86845.1172

Acquisition Time (sec)	0.5767	***Comment***	ZW7157-55 OCT with capillary tube for lock			***Date***	25 Nov 2014 15:13:04
Date Stamp	25 Nov 2014 15:13:04			***File Name***	\\soton.ac.uk\ude\personalfiles\users\zw3g10\mydesktop\nv2514zw1\10\fid		
Frequency (MHz)	376.42	***Nucleus***	19F	***Number of Transients***	64	***Origin***	spect
Original Points Count	65536	***Owner***	nmr	***Points Count***	262144	***Pulse Sequence***	zgfhigqn.2
Receiver Gain	212.69	***SW(cyclical) (Hz)***	113636.36	***Solvent***	Acetone	***Spectrum Offset (Hz)***	-79813.8125
Spectrum Type	STANDARD	***Sweep Width (Hz)***	113635.93	***Temperature (degree C)***	25.004		



SW: 300 ppm

O1P: -210 ppm

D1: 60 sec

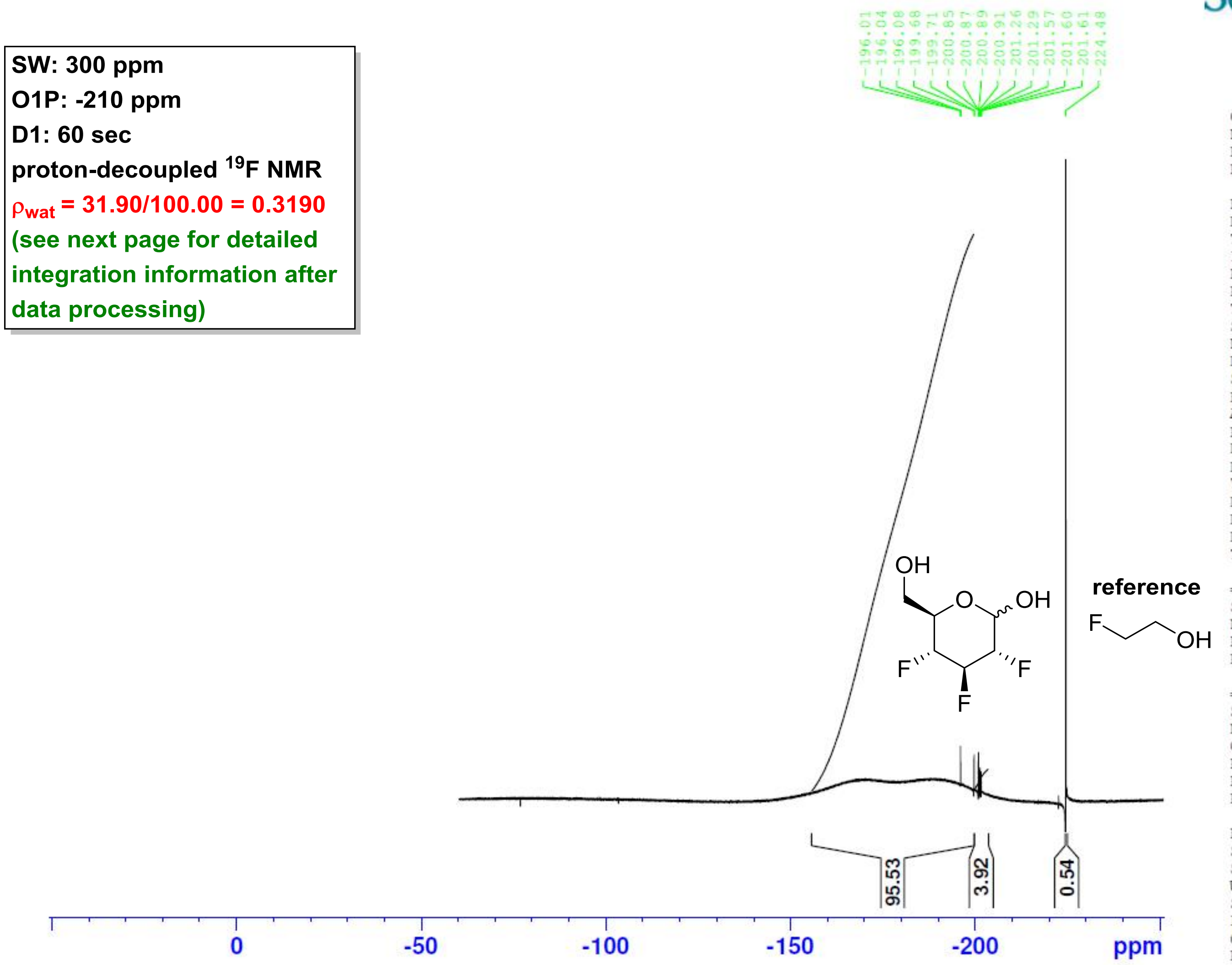
proton-decoupled ^{19}F NMR

ρ_{oct} = 121.17/100.00 = 1.2117

14.22. 2,3,4-Trideoxy-2,3,4-trifluoro-D-glucose (55), Entry 1, water sample

ZW7157-55 WAT with capillary tube for lock

SW: 300 ppm
O1P: -210 ppm
D1: 60 sec
proton-decoupled ^{19}F NMR
ρ_{wat} = 31.90/100.00 = 0.3190
(see next page for detailed integration information after data processing)



UNIVERSITY OF Southampton

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AVIIIHD400 [3]

Current Data Parameters
NAME              nv2514zw2
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20141125
Time                  16.28
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG          zgfhigqn.2
TD                   131072
SOLVENT             Acetone
NS                       64
DS                        4
SWH              113636.367 Hz
FIDRES             0.866977 Hz
AQ                0.5767168 sec
RG                   212.69
DW                    4.400 usec
DE                     6.50 usec
TE                    298.0 K
D1              60.00000000 sec
D11              0.03000000 sec
D12              0.00002000 sec
TD0                       1

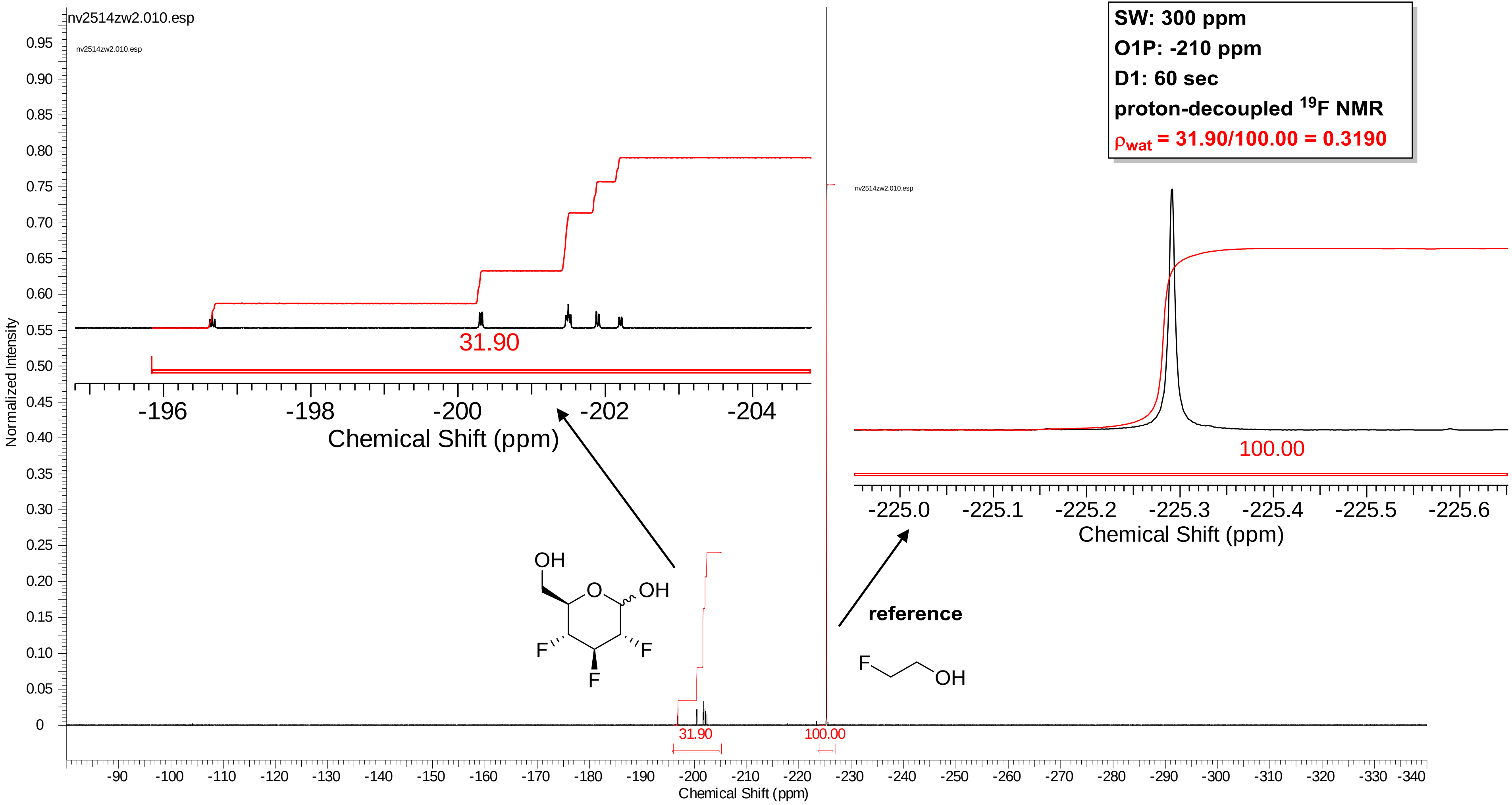
======== CHANNEL f1 ========
SFO1            376.4185522 MHz
NUC1                    19F
P1                    11.70 usec
PLW1            32.00000000 W

======== CHANNEL f2 ========
SFO2            400.1316005 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2                 70.00 usec
PLW2            32.00000000 W
PLW12            0.31999999 W

F2 - Processing parameters
SI                    65536
SF              376.4980709 MHz
WDW                      EM
SSB      0
LB                     0.30 Hz
GB       0
PC                     1.00
```

ZW7157-55 WAT with capillary tube for lock

Acquisition Time (sec)	0.5767	***Comment***	ZW7157-55 WAT with capillary tube for lock			***Date***	25 Nov 2014 16:27:44
Date Stamp	25 Nov 2014 16:27:44			***File Name***	\\soton.ac.uk\ude\personalfiles\users\zw3g10\mydesktop\nv2514zw2\10\fid		
Frequency (MHz)	376.42	***Nucleus***	19F	***Number of Transients***	64	***Origin***	spect
Original Points Count	65536	***Owner***	nmr	***Points Count***	262144	***Pulse Sequence***	zgfhigqn.2
Receiver Gain	212.69	***SW(cyclical) (Hz)***	113636.36	***Solvent***	Acetone	***Spectrum Offset (Hz)***	-79813.8125
Spectrum Type	STANDARD	***Sweep Width (Hz)***	113635.93	***Temperature (degree C)***	25.006		



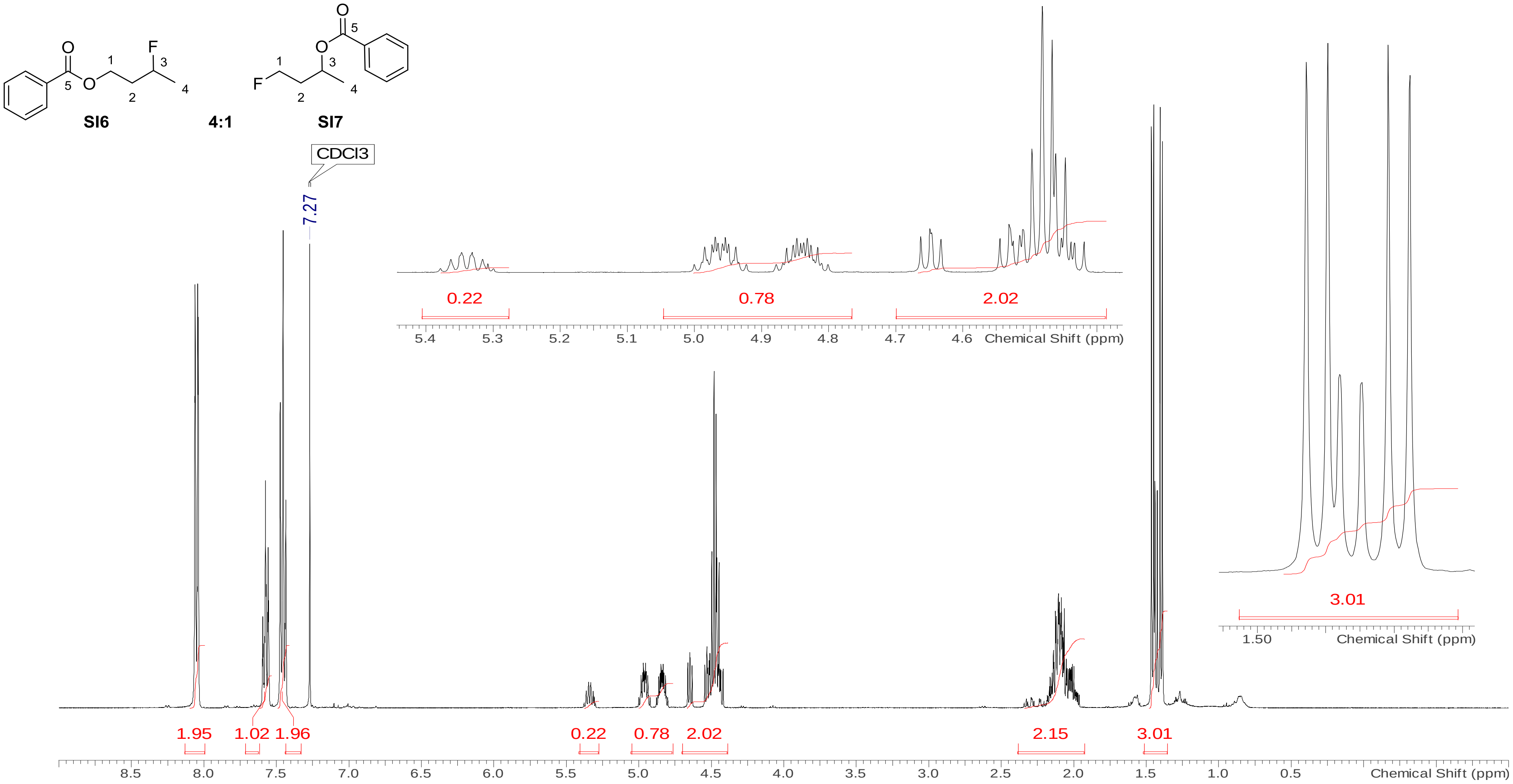
SW: 300 ppm
O1P: -210 ppm
D1: 60 sec
proton-decoupled ^{19}F NMR
ρ_{wat} = 31.90/100.00 = 0.3190

15. NMR spectra for novel compounds

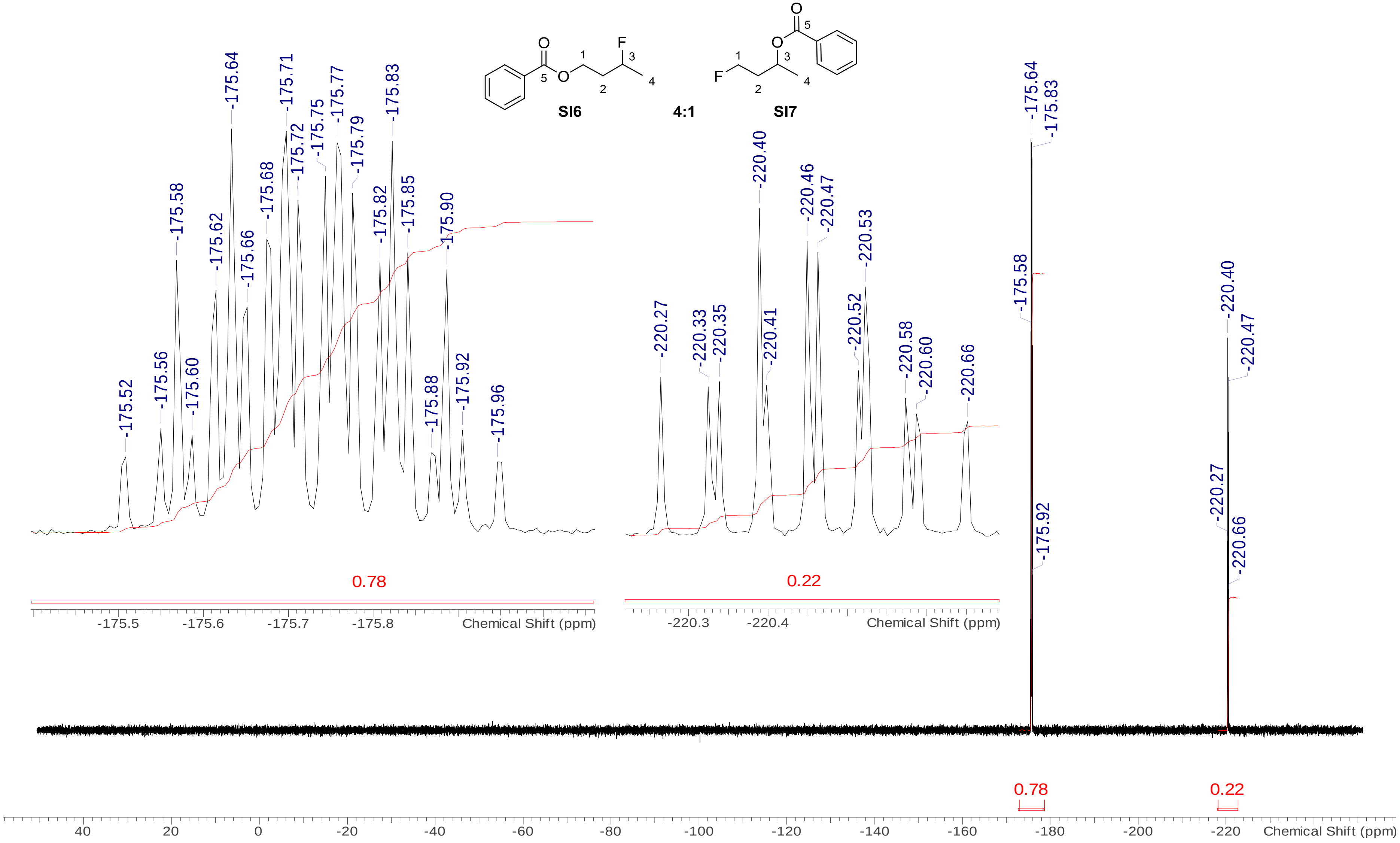
15.1. Synthesis of 3-fluorobutan-1-ol (22)

15.1.1. Synthesis of 3-fluorobut-1-yl benzoate (SI6) and 4-fluorobut-2-yl benzoate (SI7)

^{1}H NMR, CDCl$_3$, 400 MHz

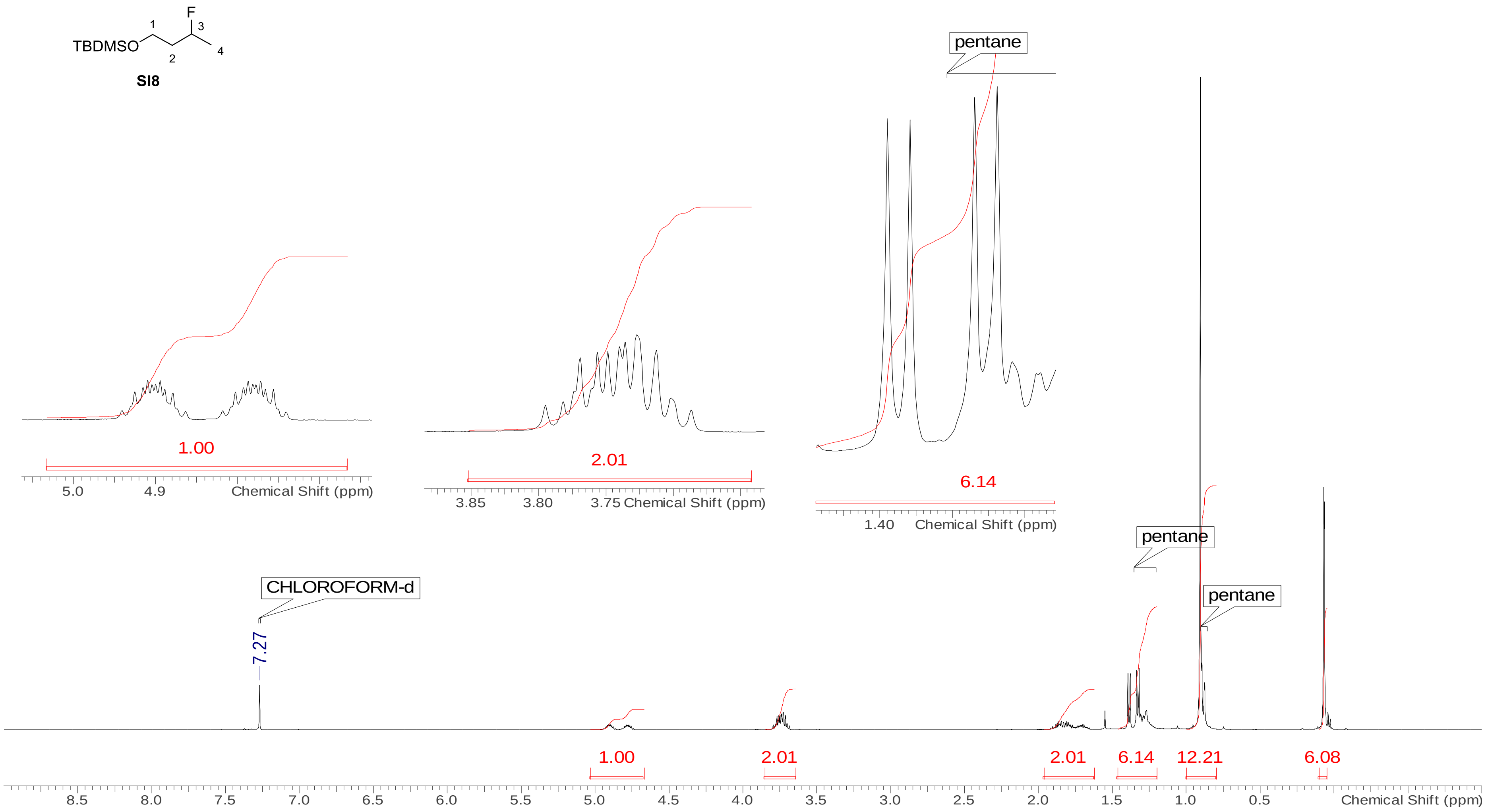


^{19}F NMR, CDCl$_3$, 376 MHz



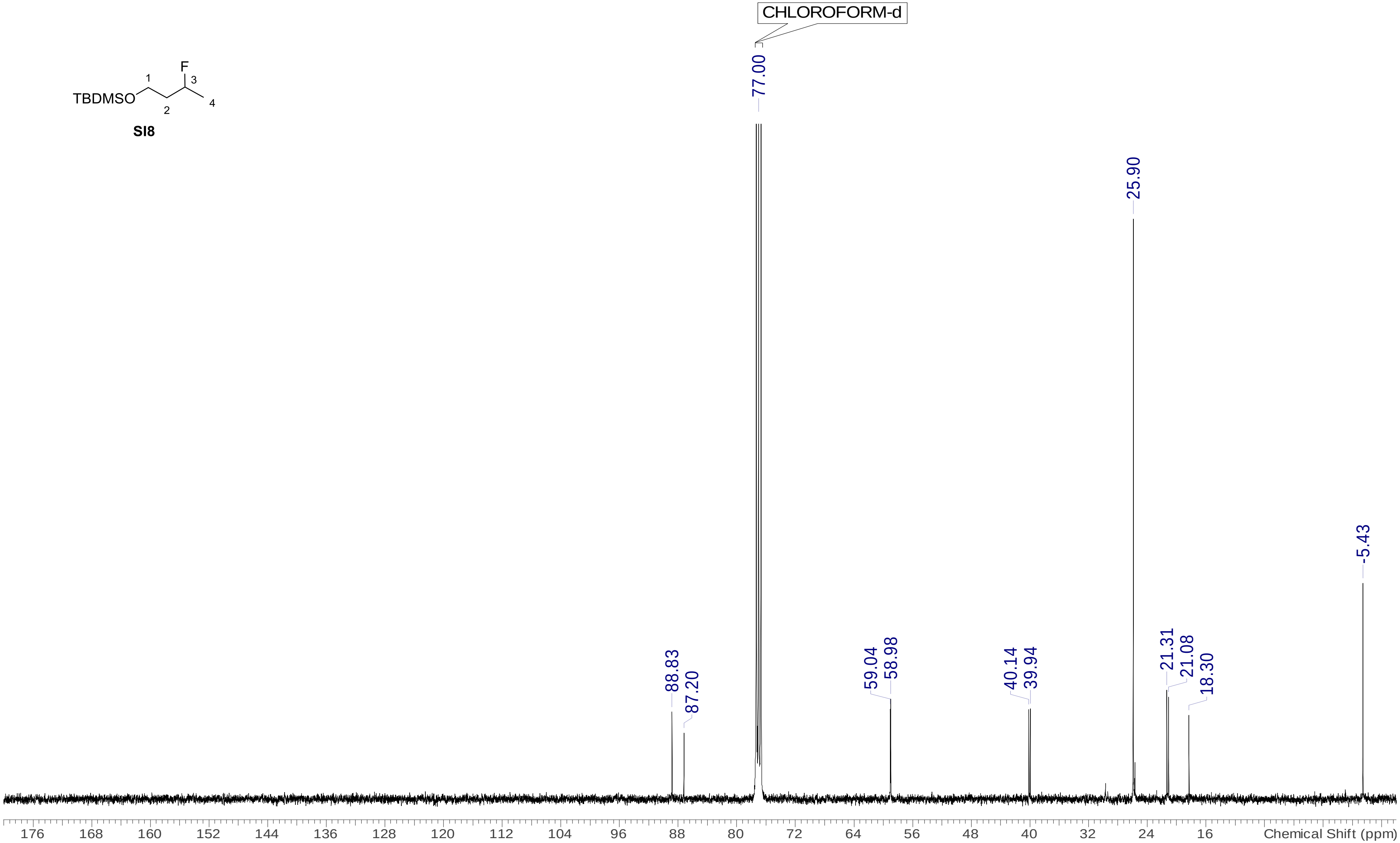
15.1.2. Synthesis of 1-tert-butyldimethylsilyloxy-3-fluorobutane (SI8)

^{1}H NMR, CDCl$_3$, 400 MHz

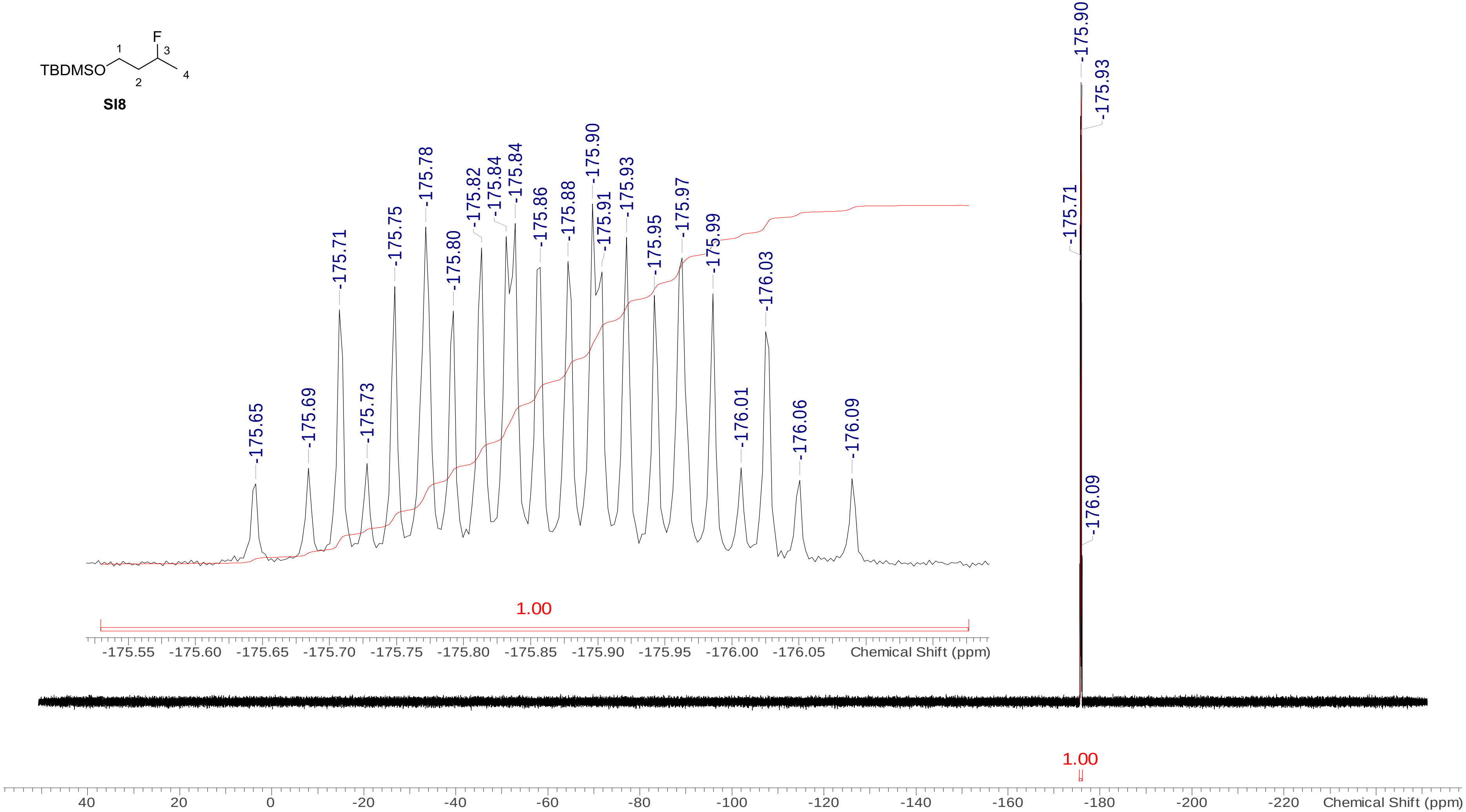


^{13}C NMR, CDCl$_3$, 101 MHz

SI8



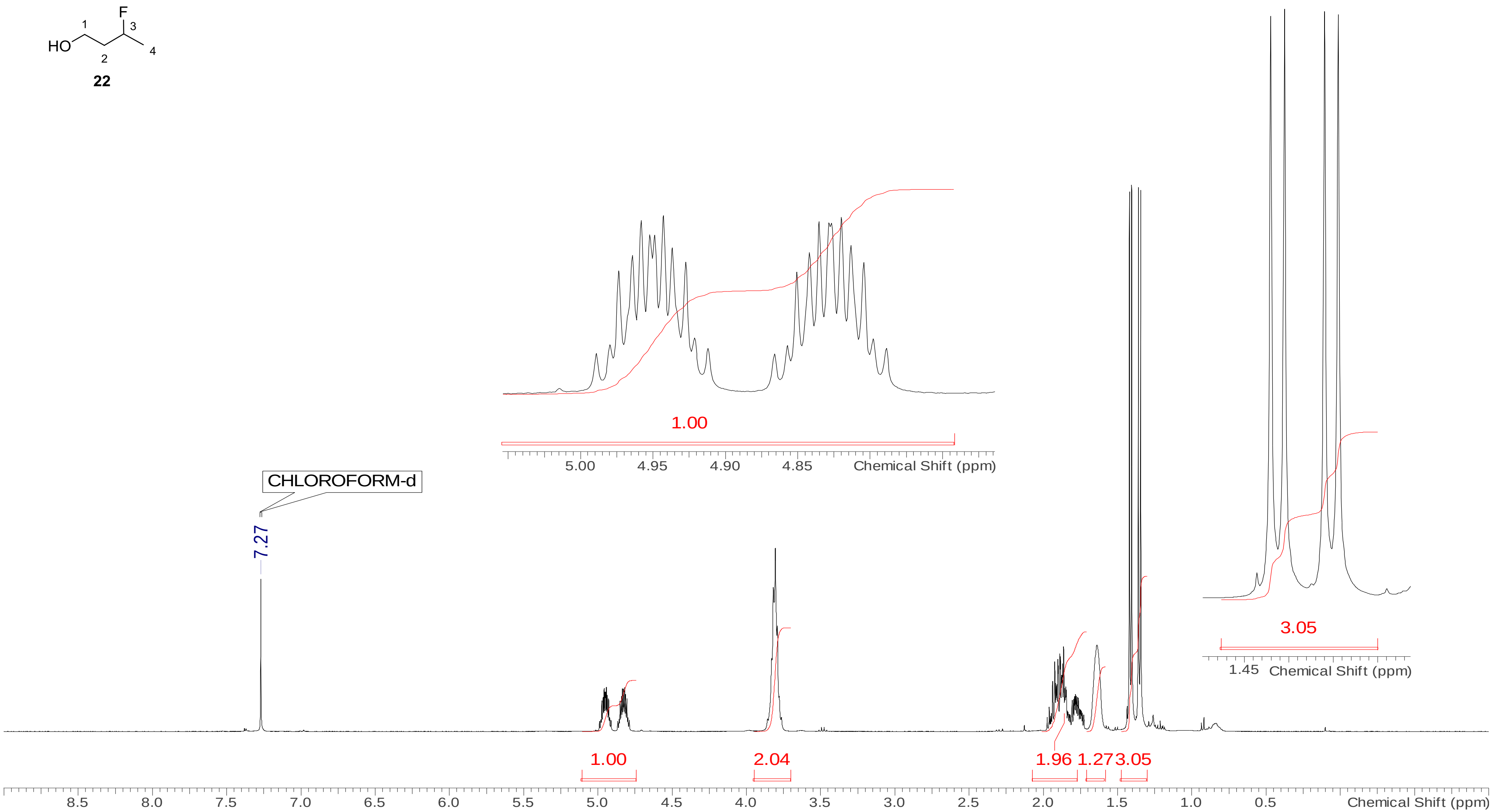
^{19}F NMR, CDCl$_3$, 376 MHz



SI8

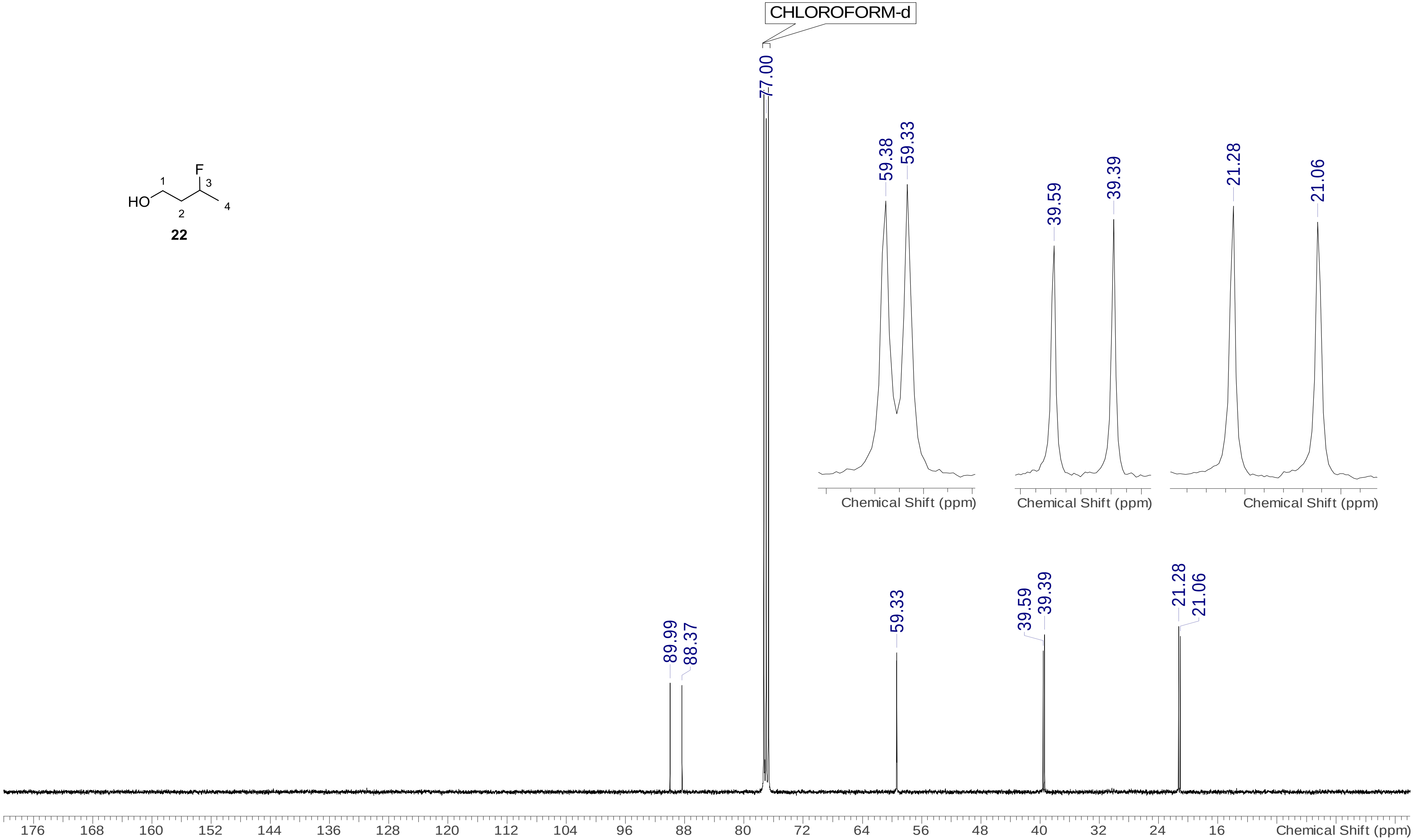
15.1.3. Synthesis of 3-fluorobutan-1-ol (22)

^{1}H NMR, $CDCl_3$, 400 MHz

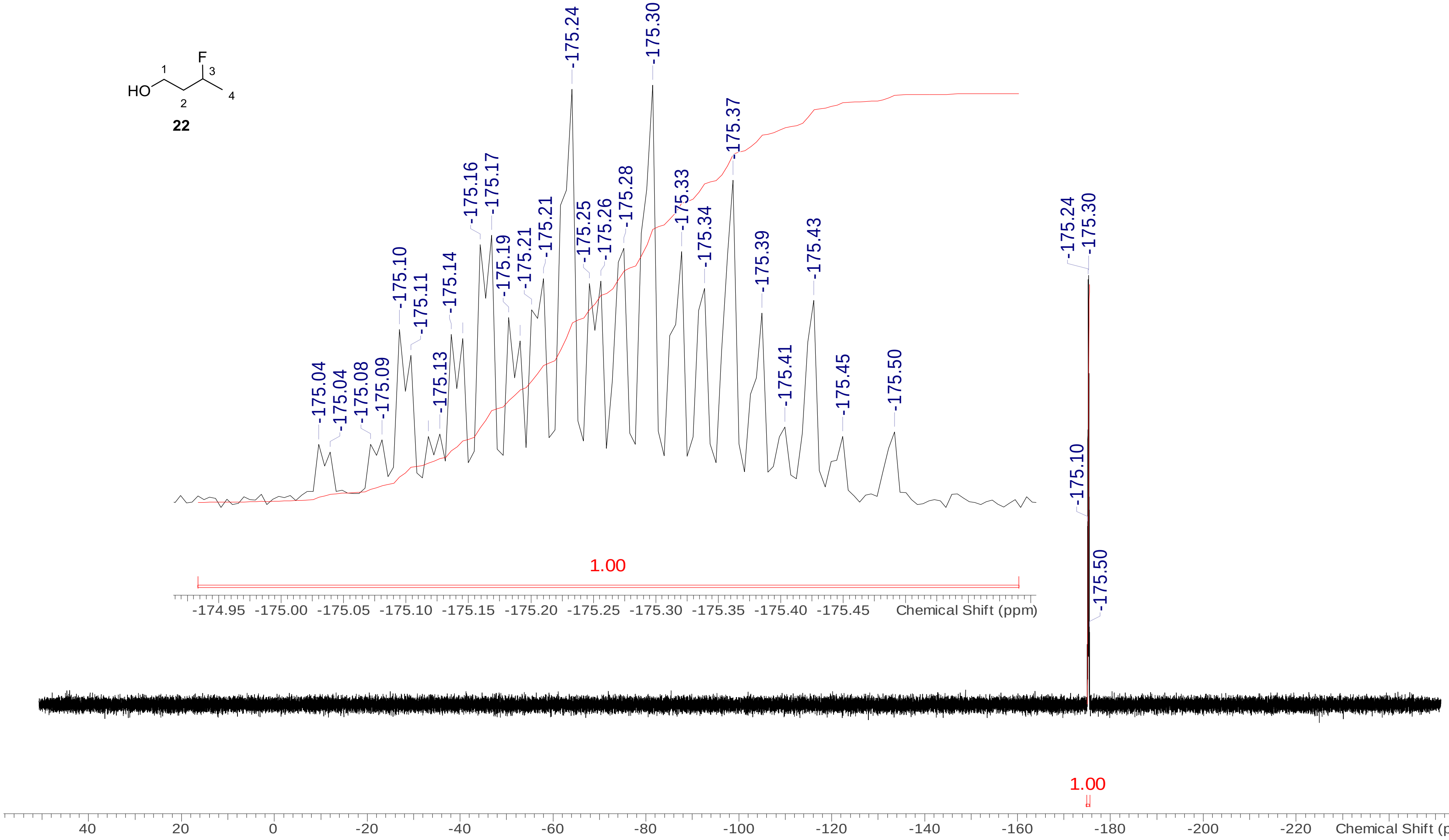


^{13}C NMR, CDCl$_3$, 101 MHz

22



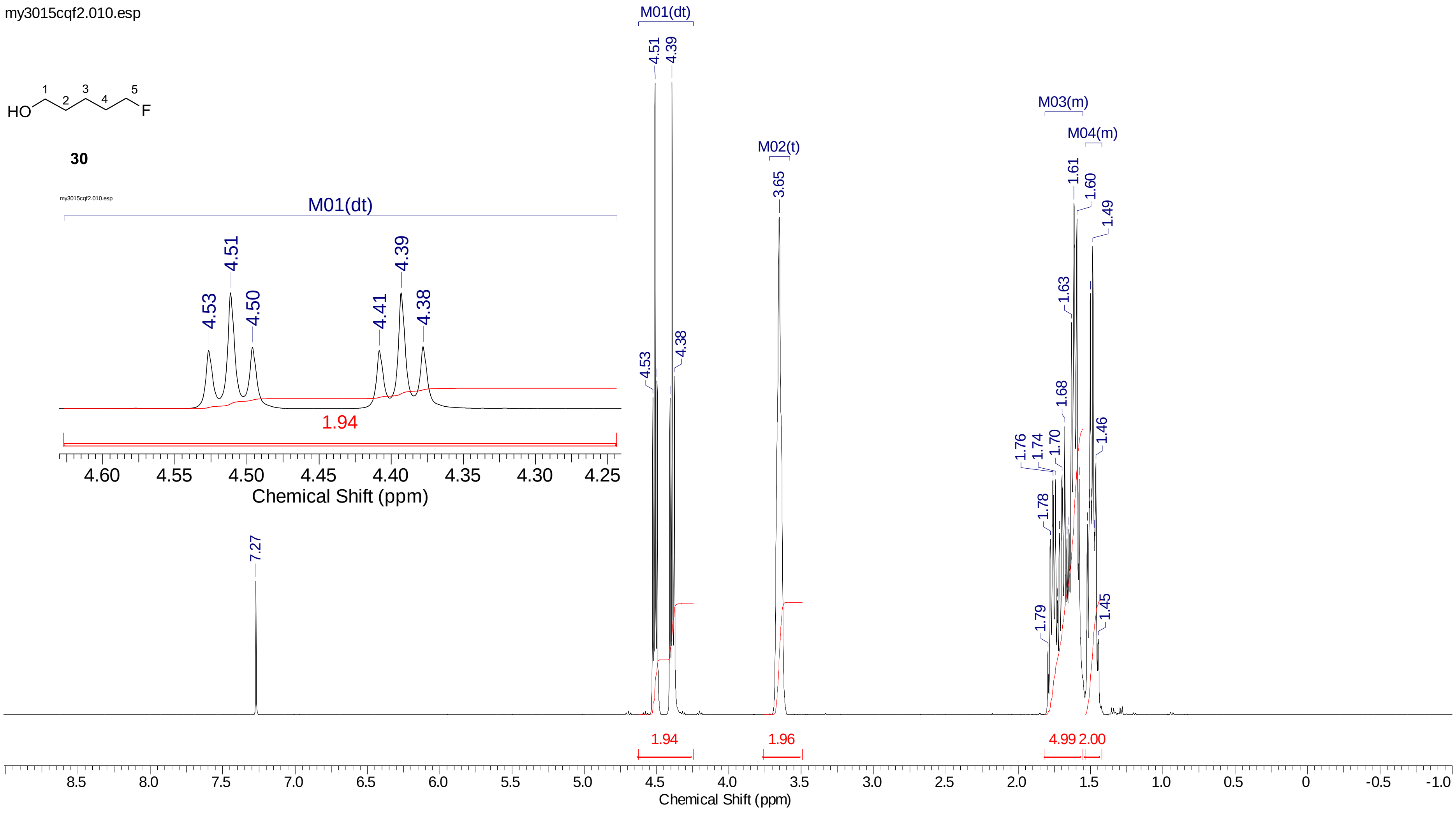
^{19}F NMR, $CDCl_3$, 376 MHz



22

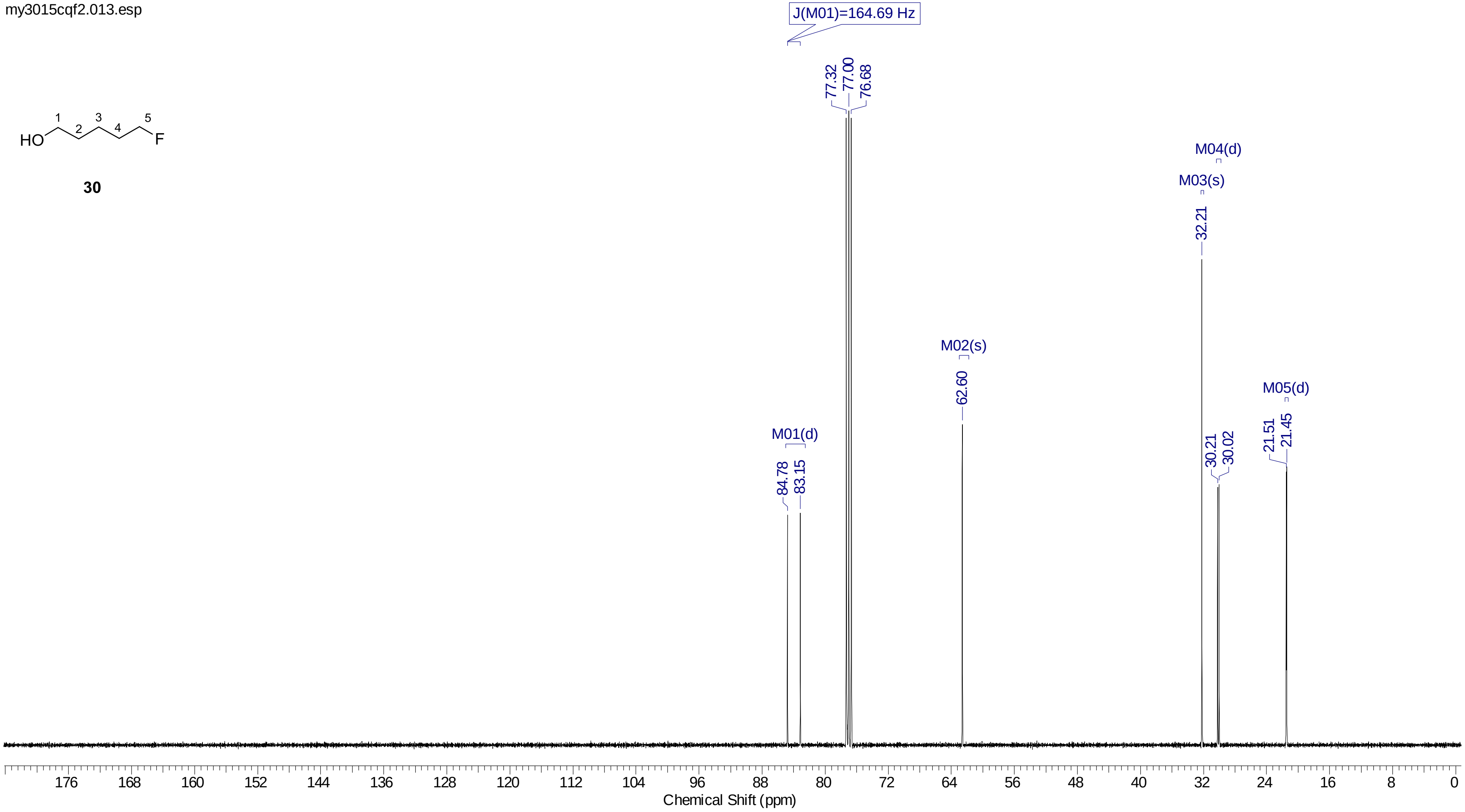
15.2. Synthesis of 5-fluoro-1-pentanol (30)

^{1}H NMR, $CDCl_3$, 400 MHz



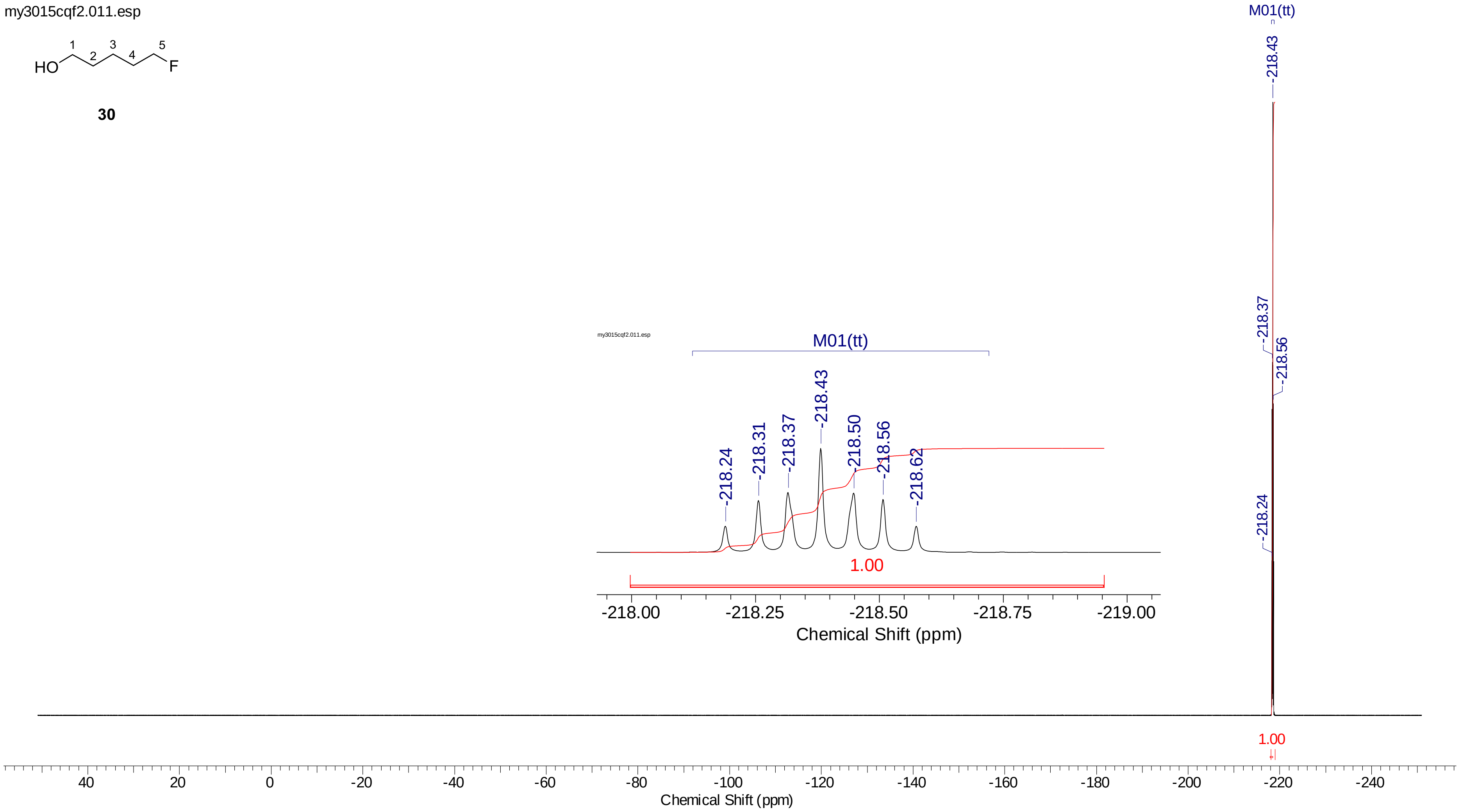
^{13}**C NMR**, $CDCl_3$, 101 MHz

my3015cqf2.013.esp



30

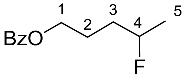
^{19}F NMR, $CDCl_3$, 376 MHz



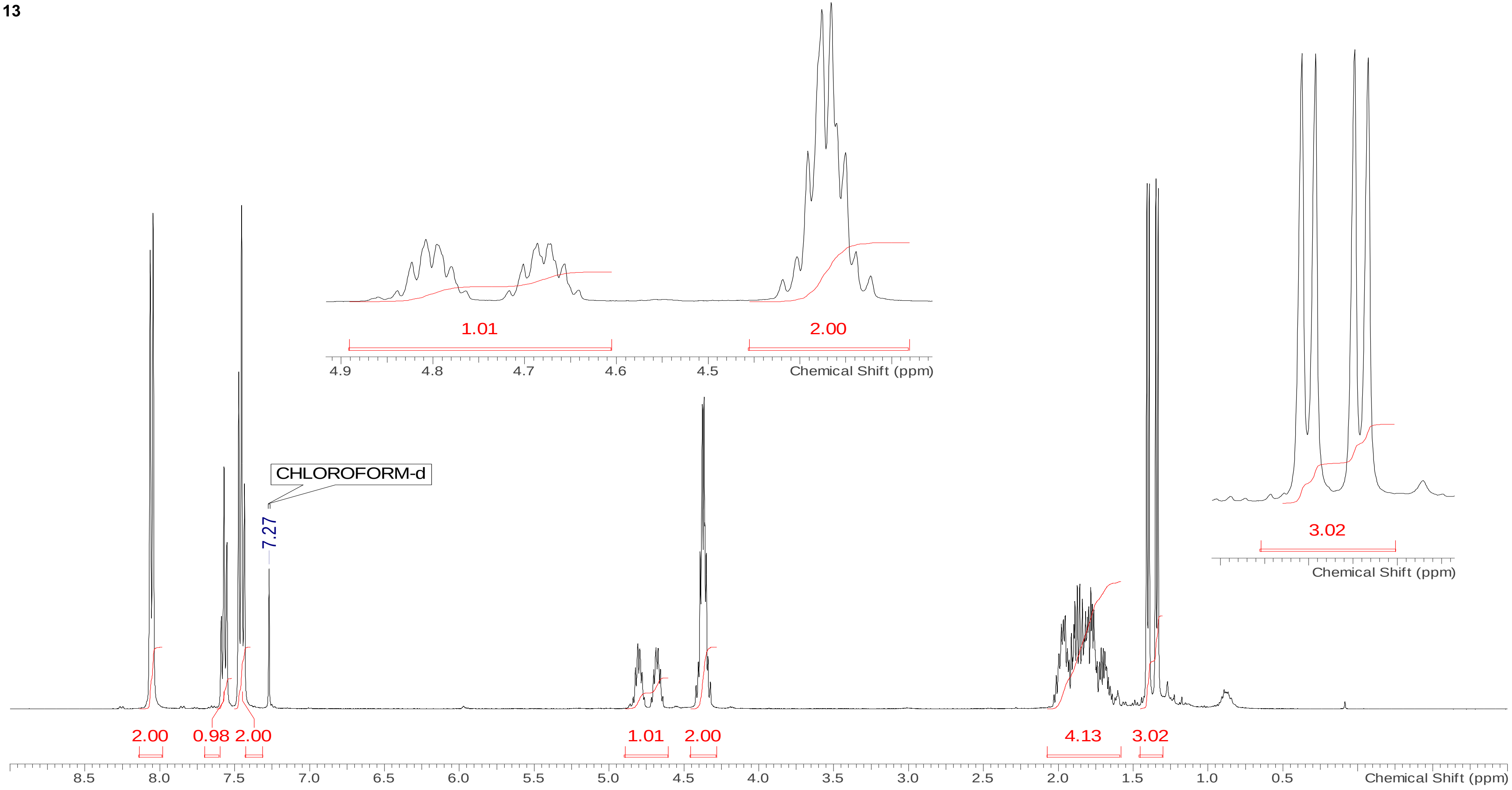
15.3. Synthesis of 4-fluoropentan-1-ol (31)

15.3.1. Synthesis of 4-fluoropentyl benzoate (SI13)

^{1}H NMR, CDCl$_3$, 400 MHz

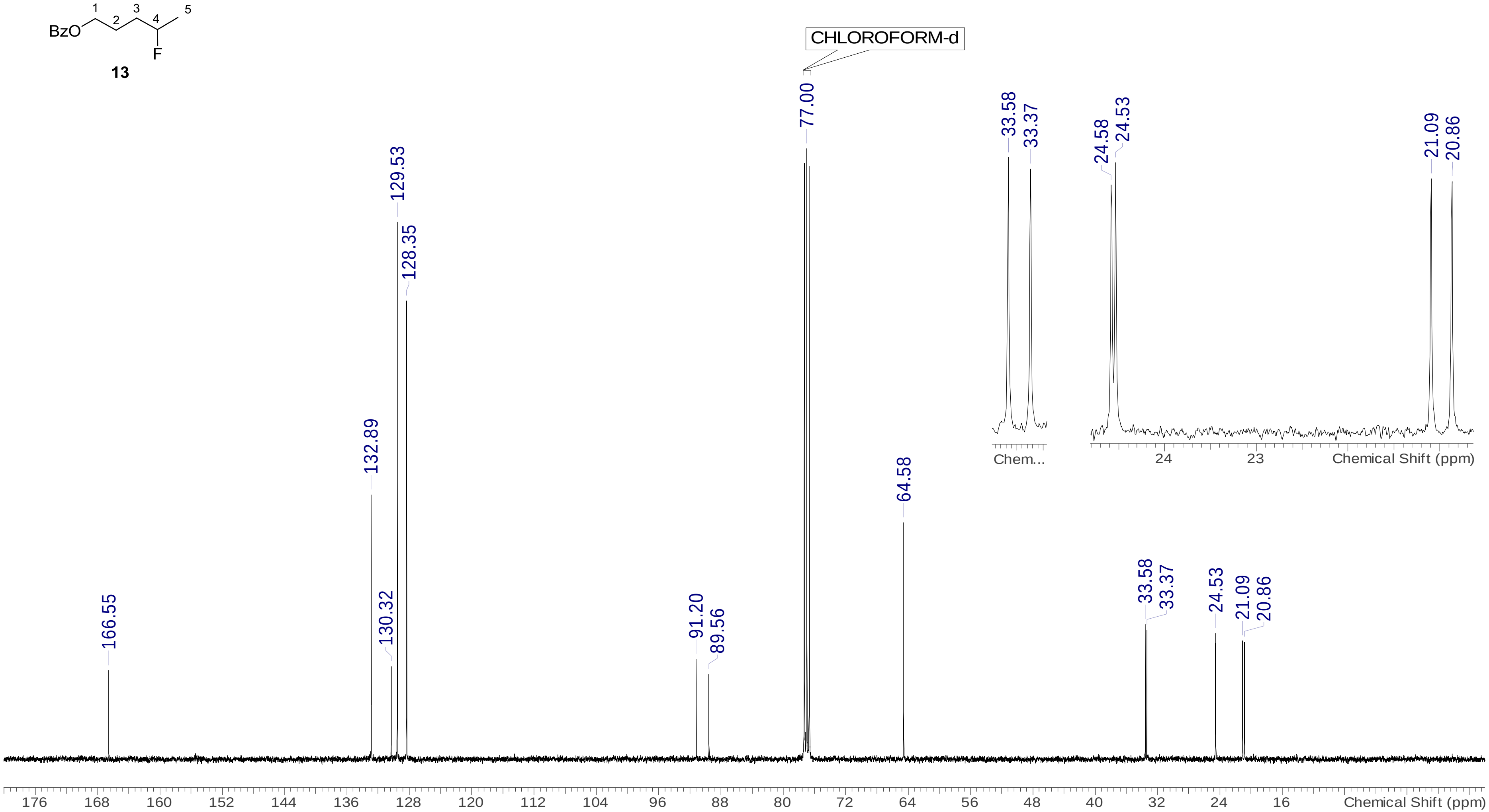


13



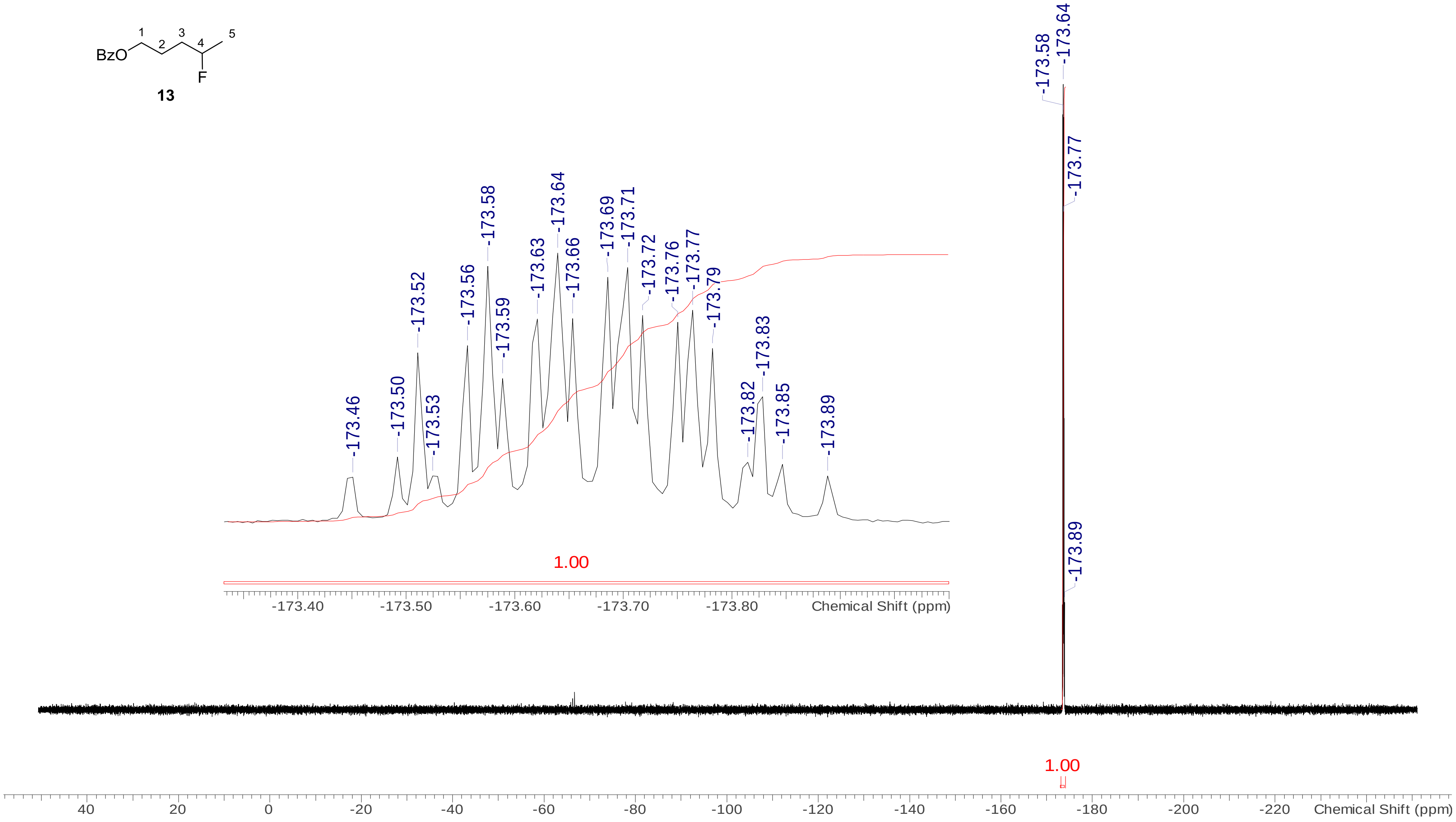
^{13}C NMR, CDCl$_3$, 101 MHz

13



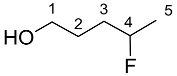
^{19}F NMR, $CDCl_3$, 376 MHz

13

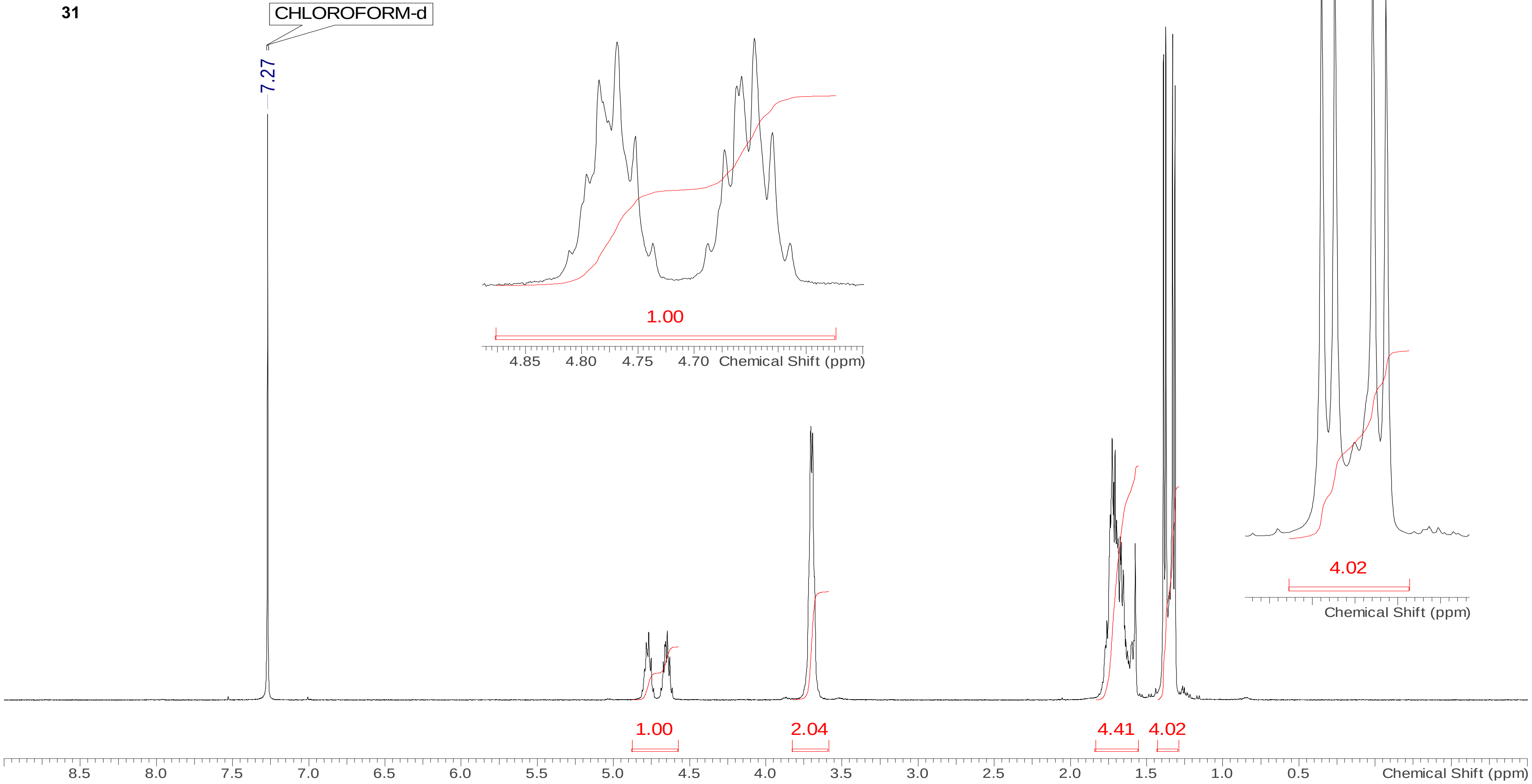


15.3.2. Synthesis of 4-fluoropentan-1-ol (31)

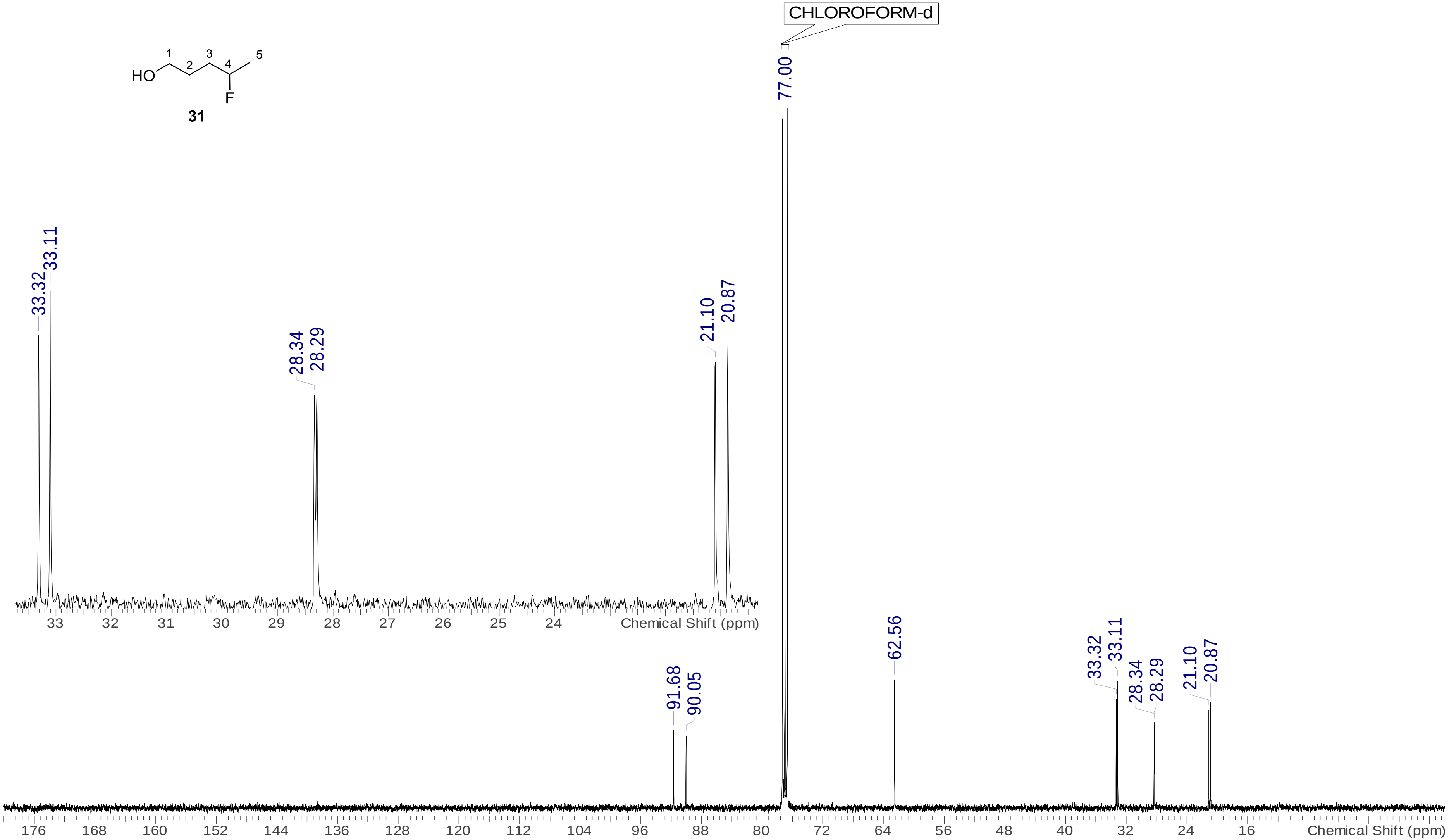
^{1}H NMR, $CDCl_3$, 400 MHz



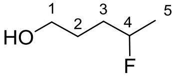
31



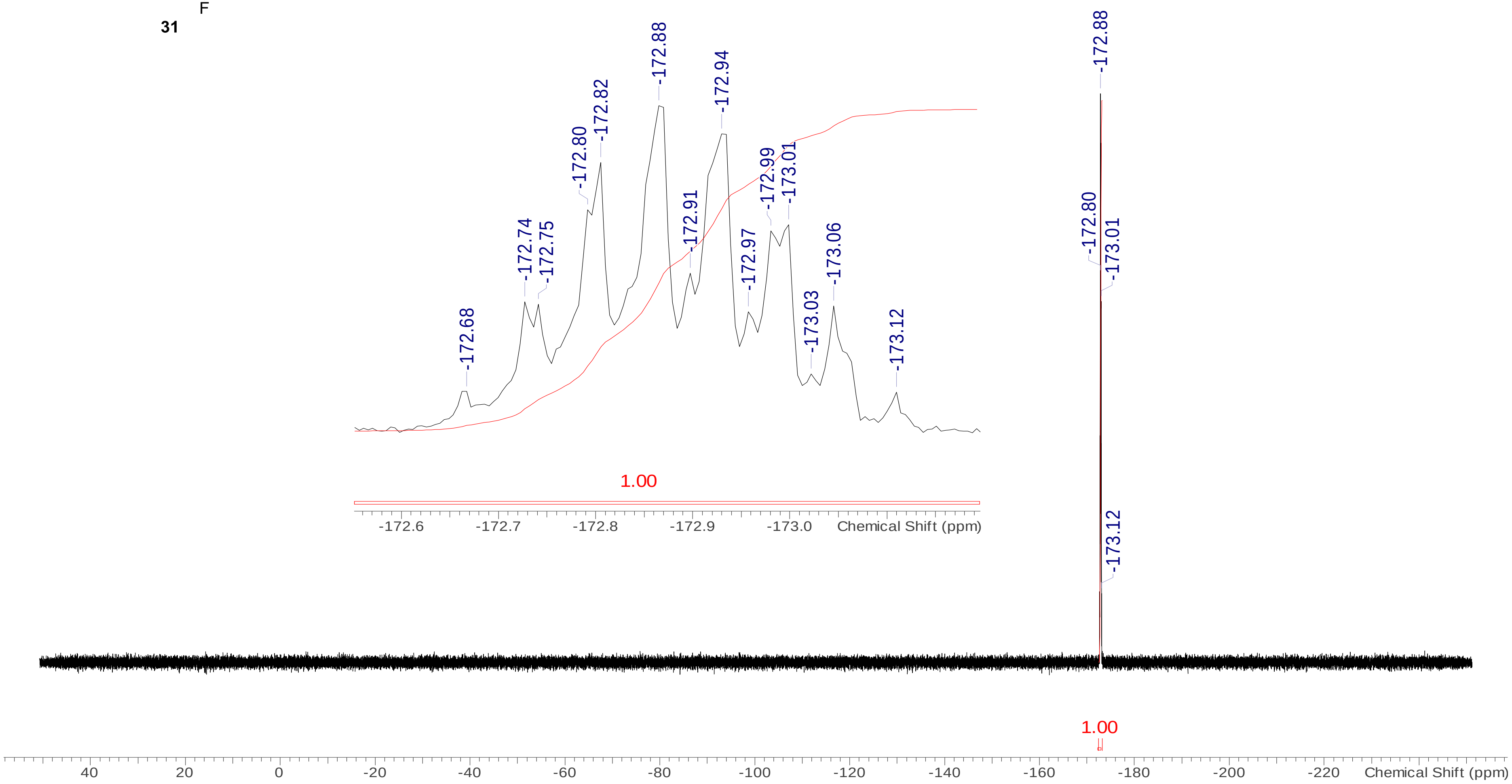
^{13}C NMR, CDCl$_3$, 101 MHz



^{19}F NMR, CDCl$_3$, 376 MHz



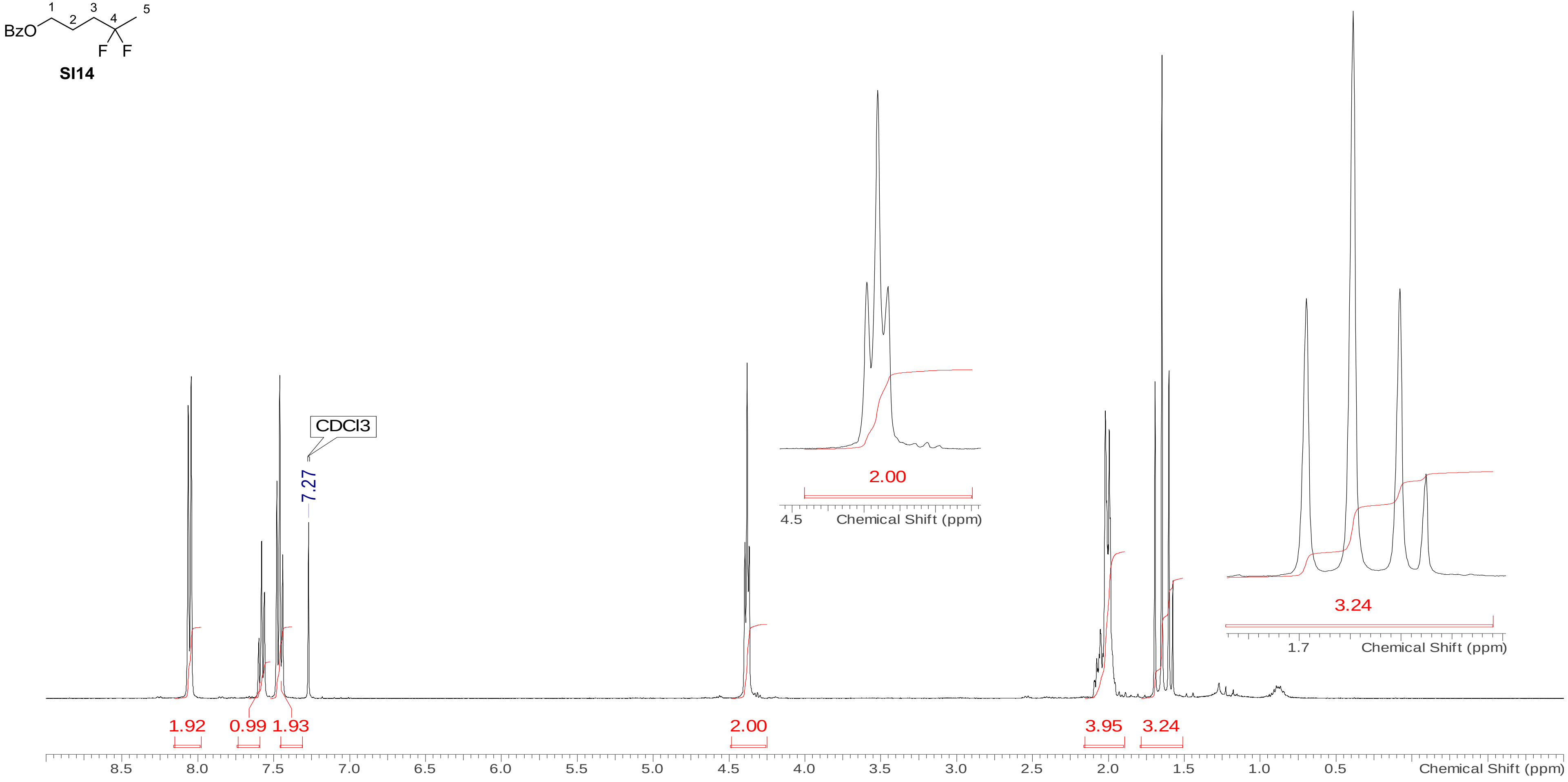
31



15.4. Synthesis of 4,4-difluoropentan-1-ol (32)

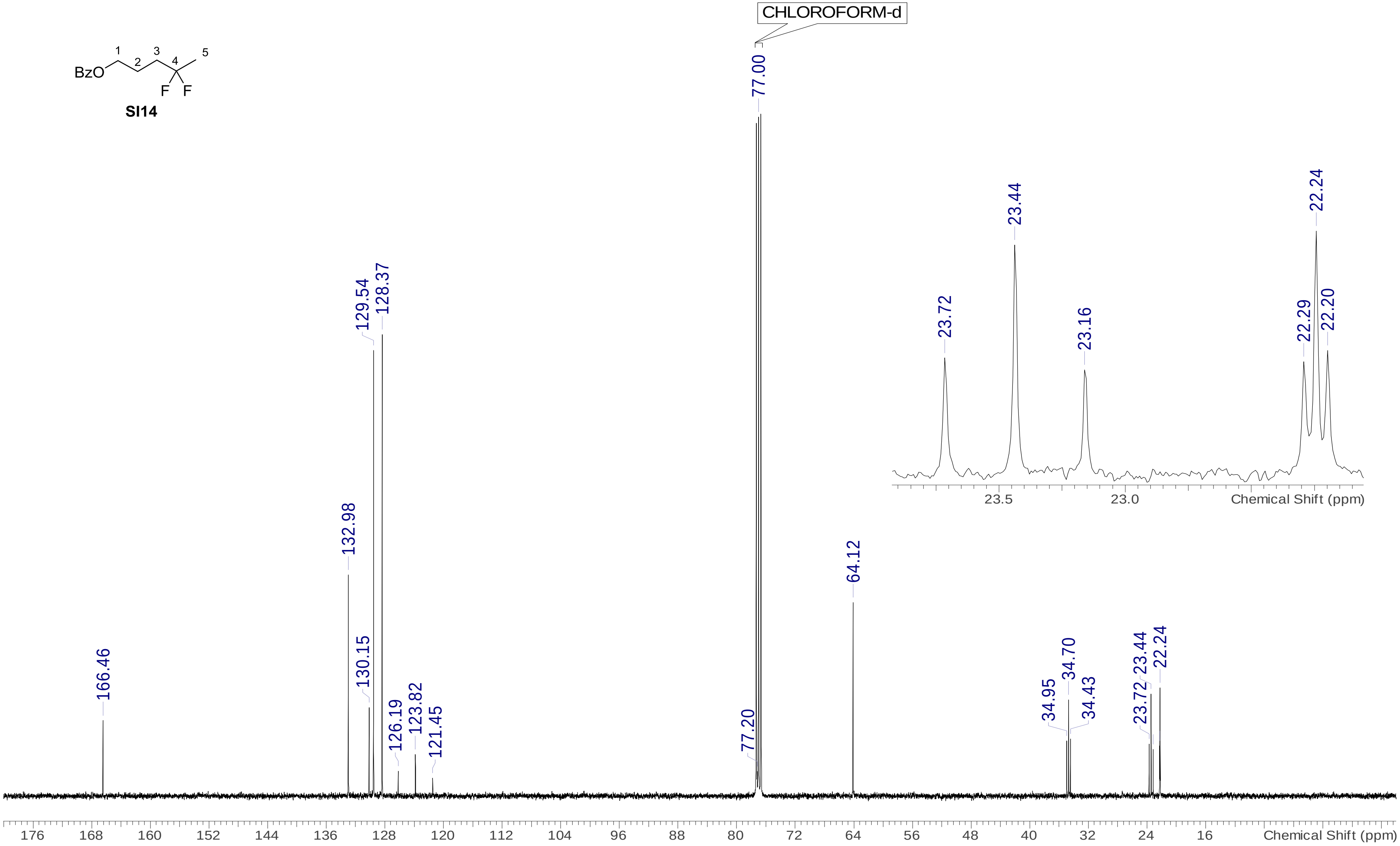
15.4.1. Synthesis of 4,4-difluoropentyl benzoate (SI14)

^{1}H NMR, CDCl$_3$, 400 MHz

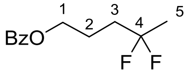


^{13}C NMR, CDCl$_3$, 101 MHz

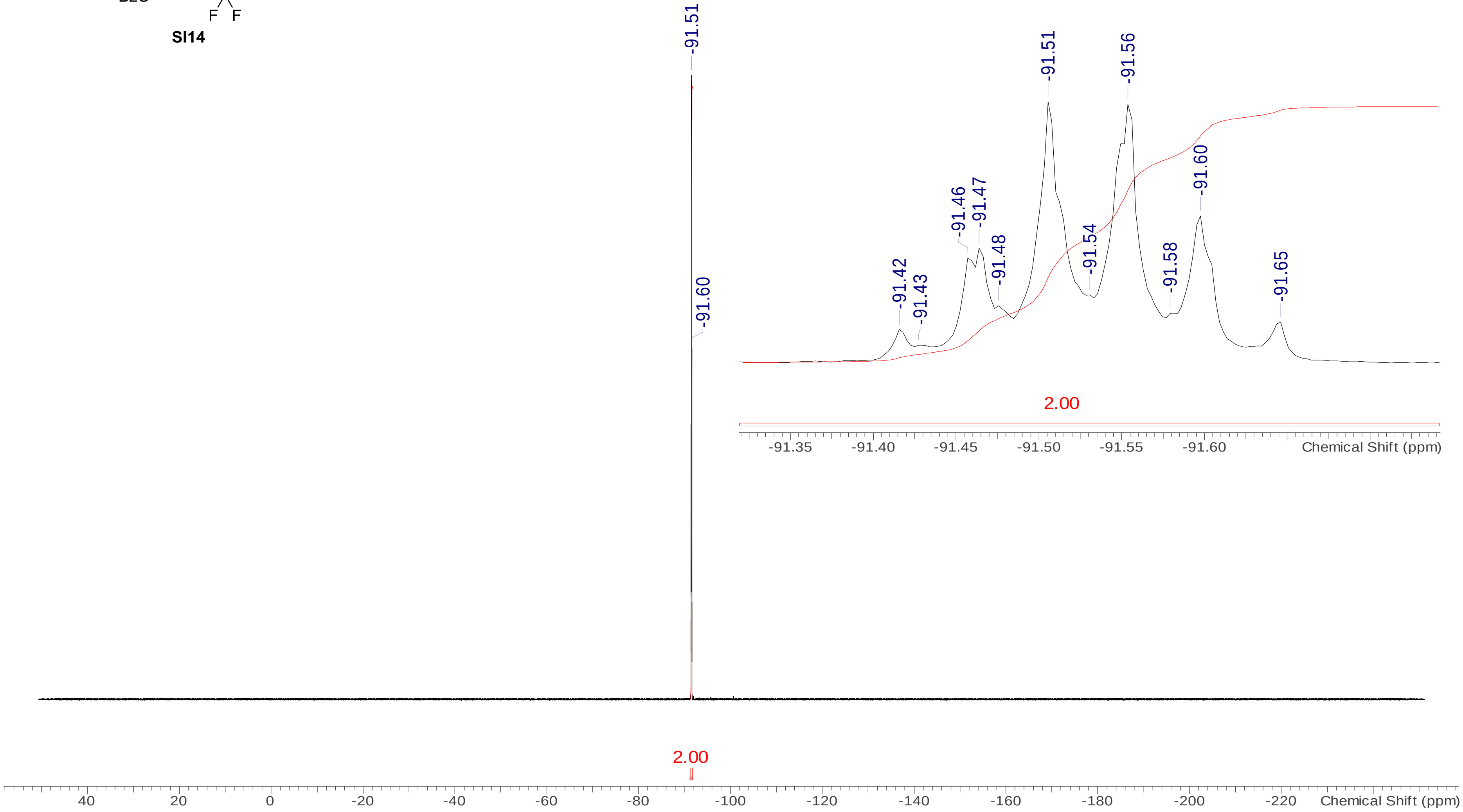
SI14



^{19}F NMR, CDCl$_3$, 376 MHz

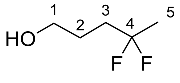


SI14

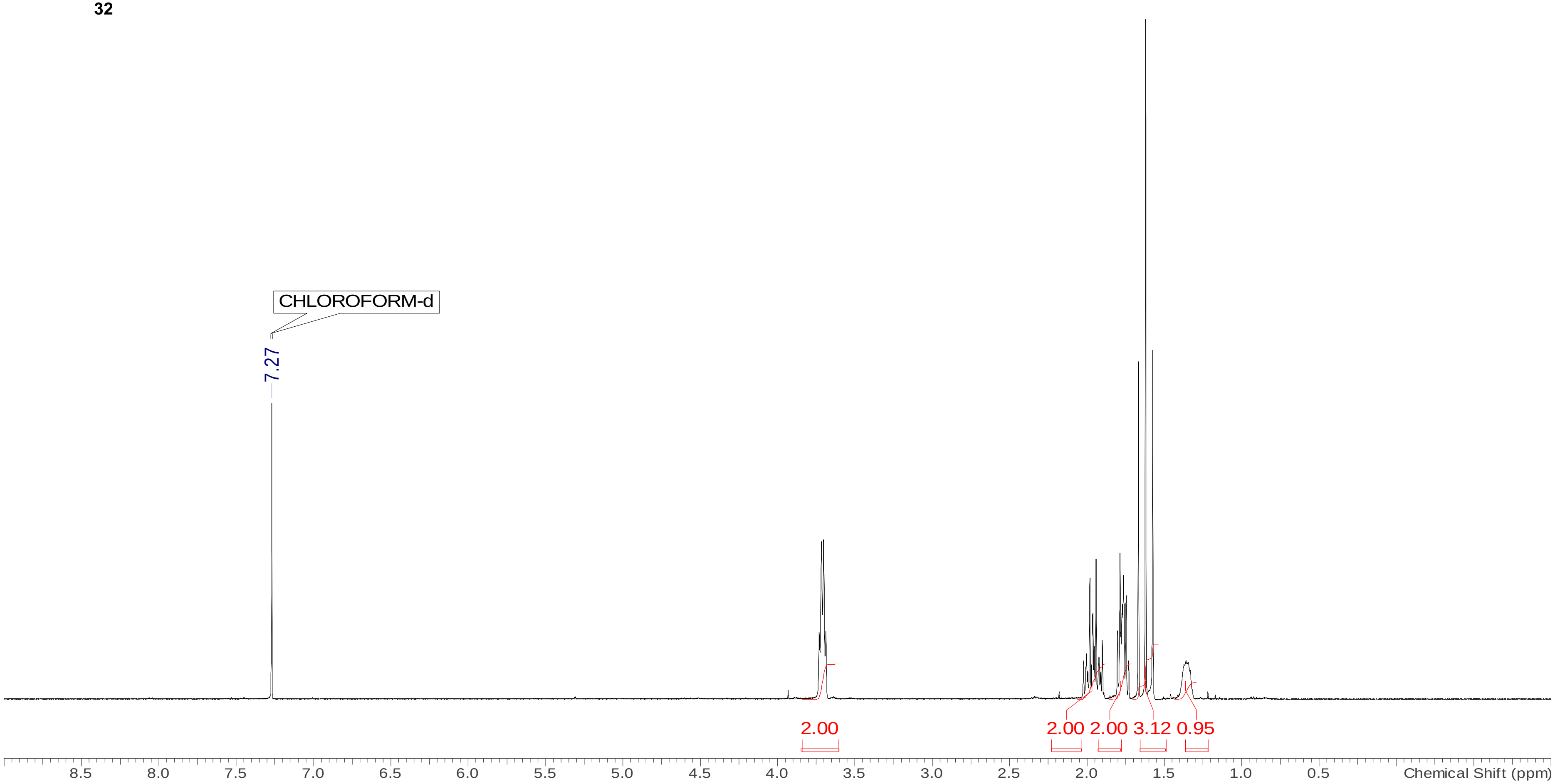


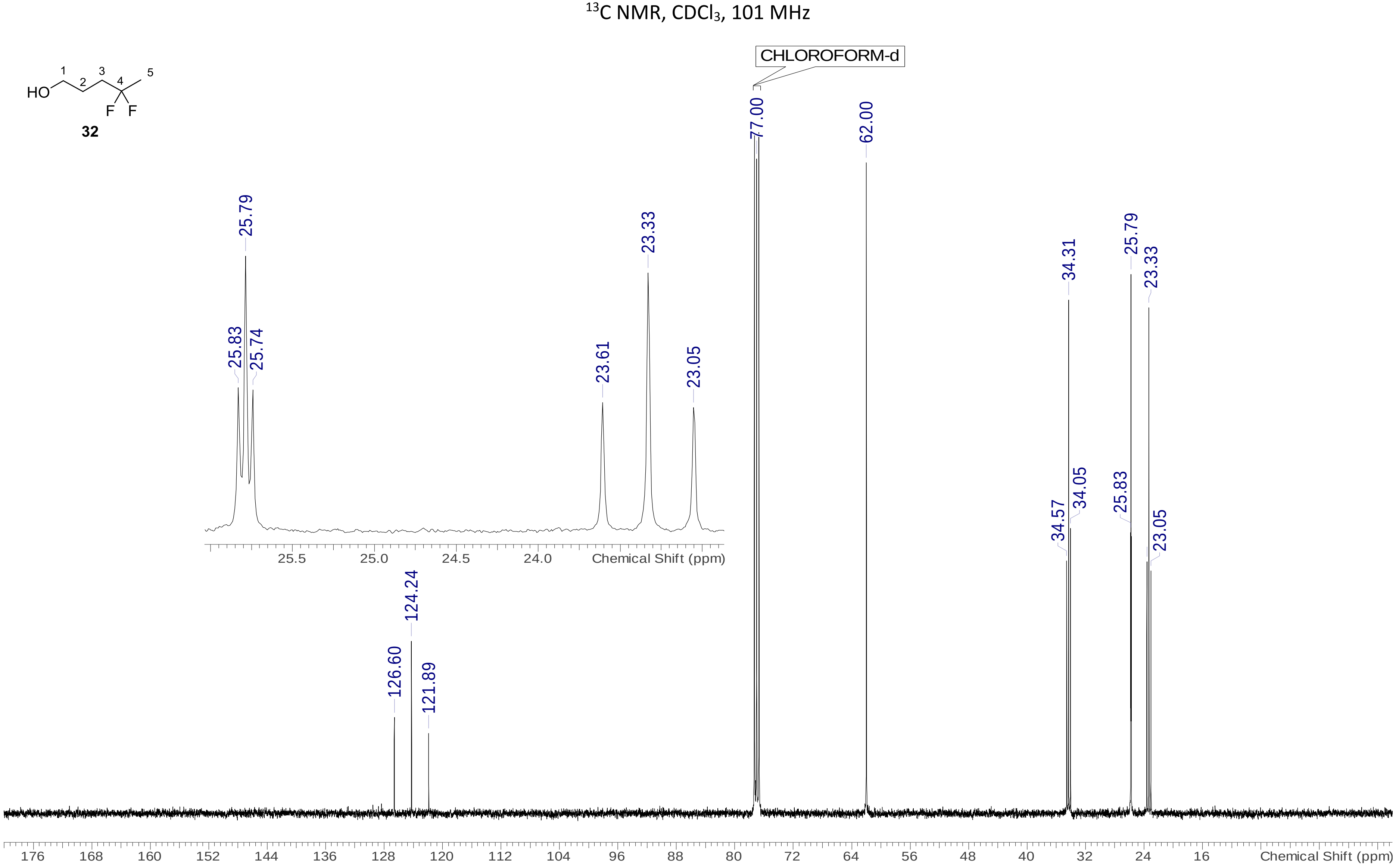
15.4.2. Synthesis of 4,4-difluoropentan-1-ol (32)

^{1}H NMR, CDCl$_3$, 400 MHz



32

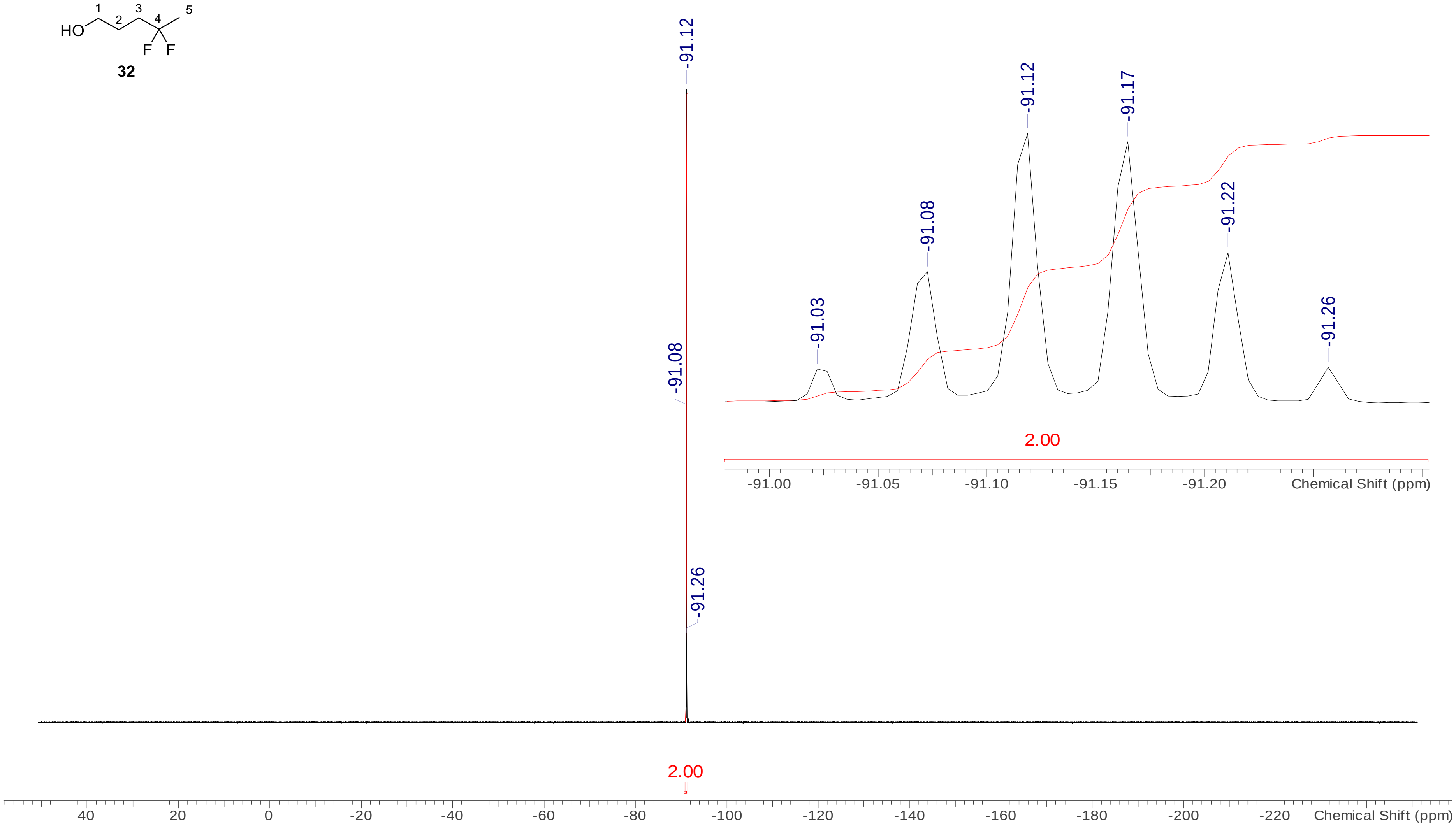




32

^{13}C NMR, CDCl$_3$, 101 MHz
CHLOROFORM-d
77.00
62.00
34.57
34.31
34.05
25.83
25.79
25.74
23.61
23.33
23.05
126.60
124.24
121.89
Chemical Shift (ppm)

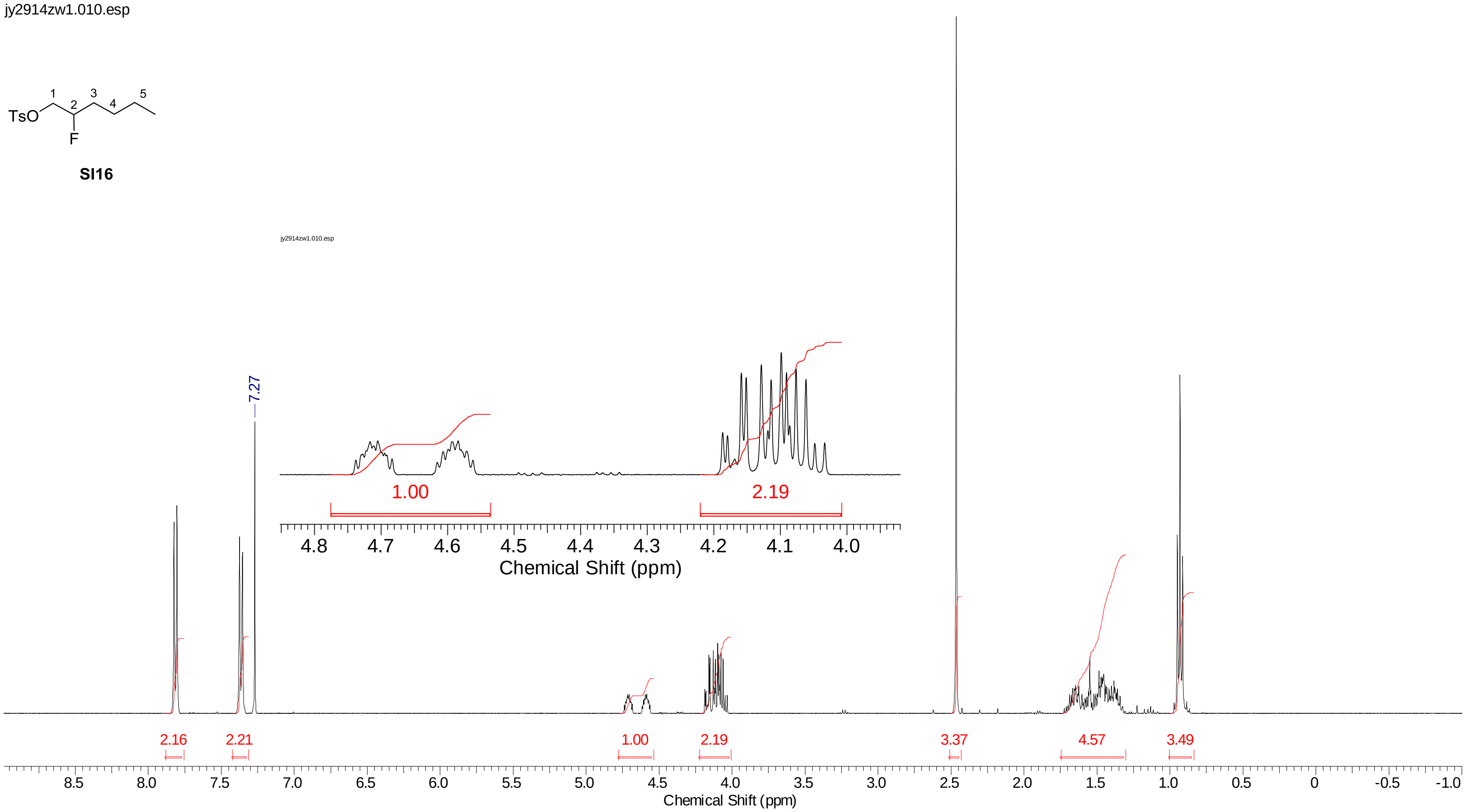
^{19}F NMR, $CDCl_3$, 376 MHz



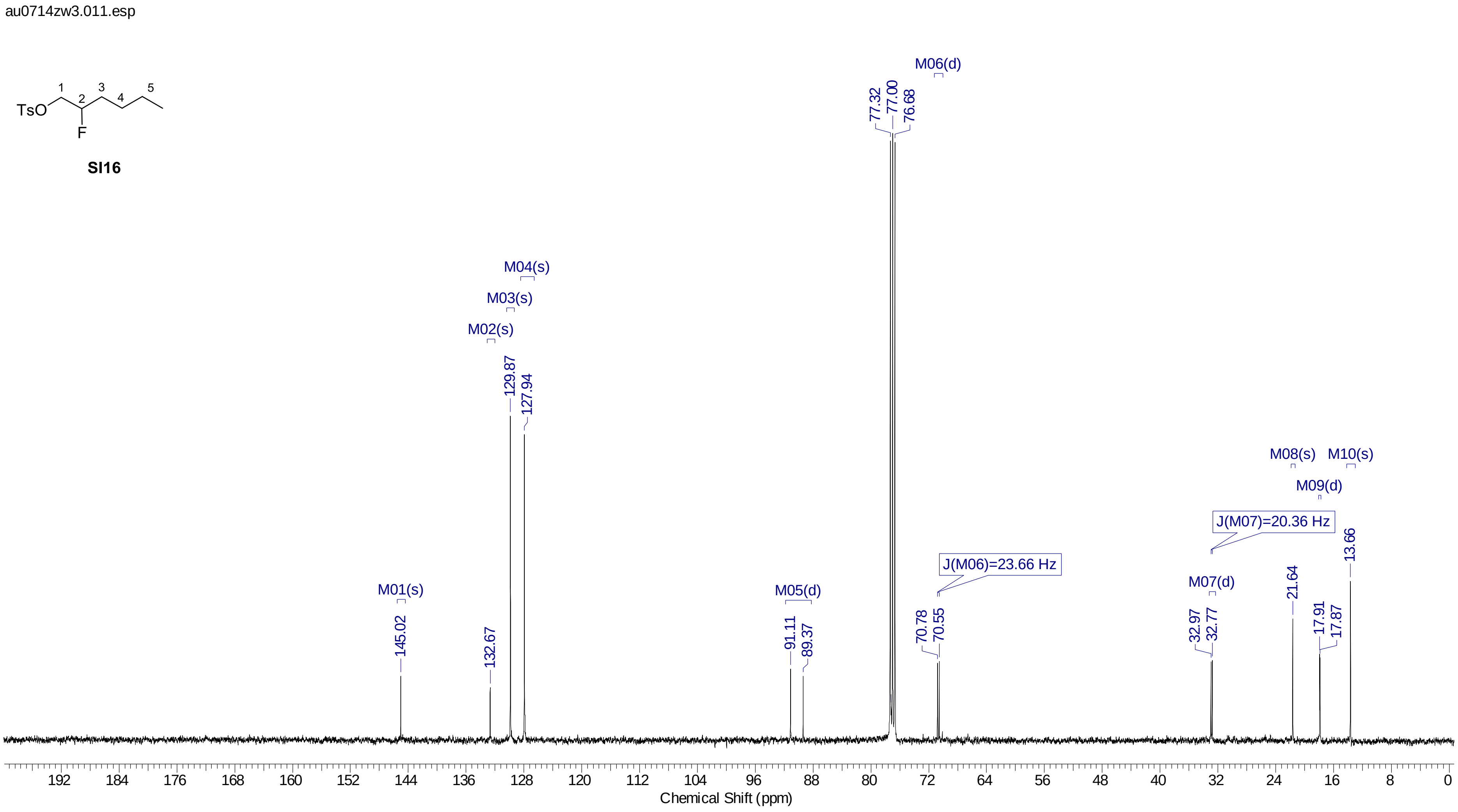
32

15.5. Synthesis of 2-fluoropentyl tosylate (SI16)

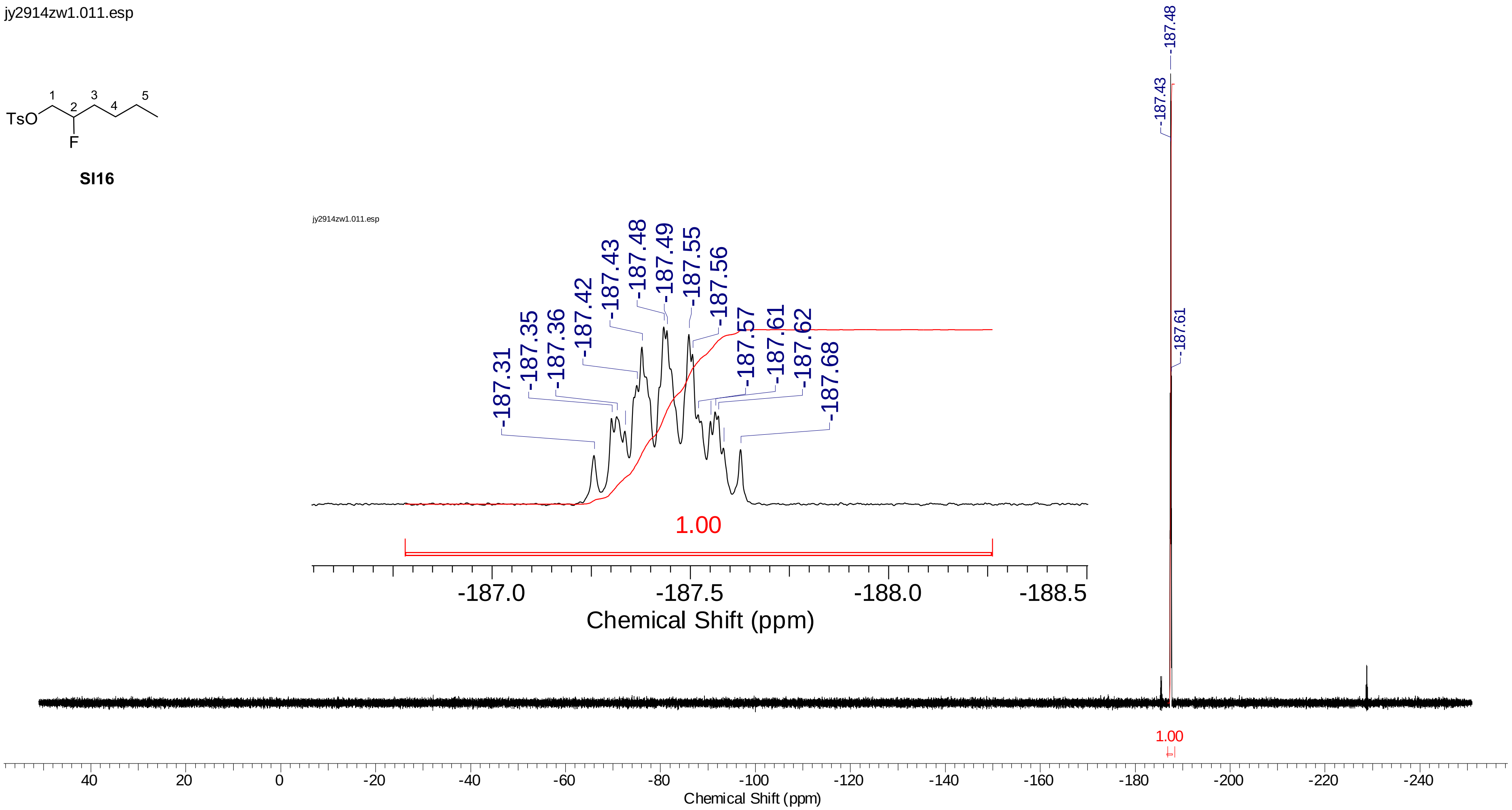
^{1}H NMR, $CDCl_3$, 400 MHz



^{13}**C NMR**, $CDCl_3$, 101 MHz

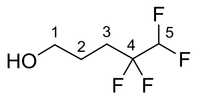


^{19}F NMR, $CDCl_3$, 376 MHz



15.6. Synthesis of 4,4,5,5-tetrafluoropentan-1-ol (34)

^{1}H NMR, $CDCl_3$, 400 MHz



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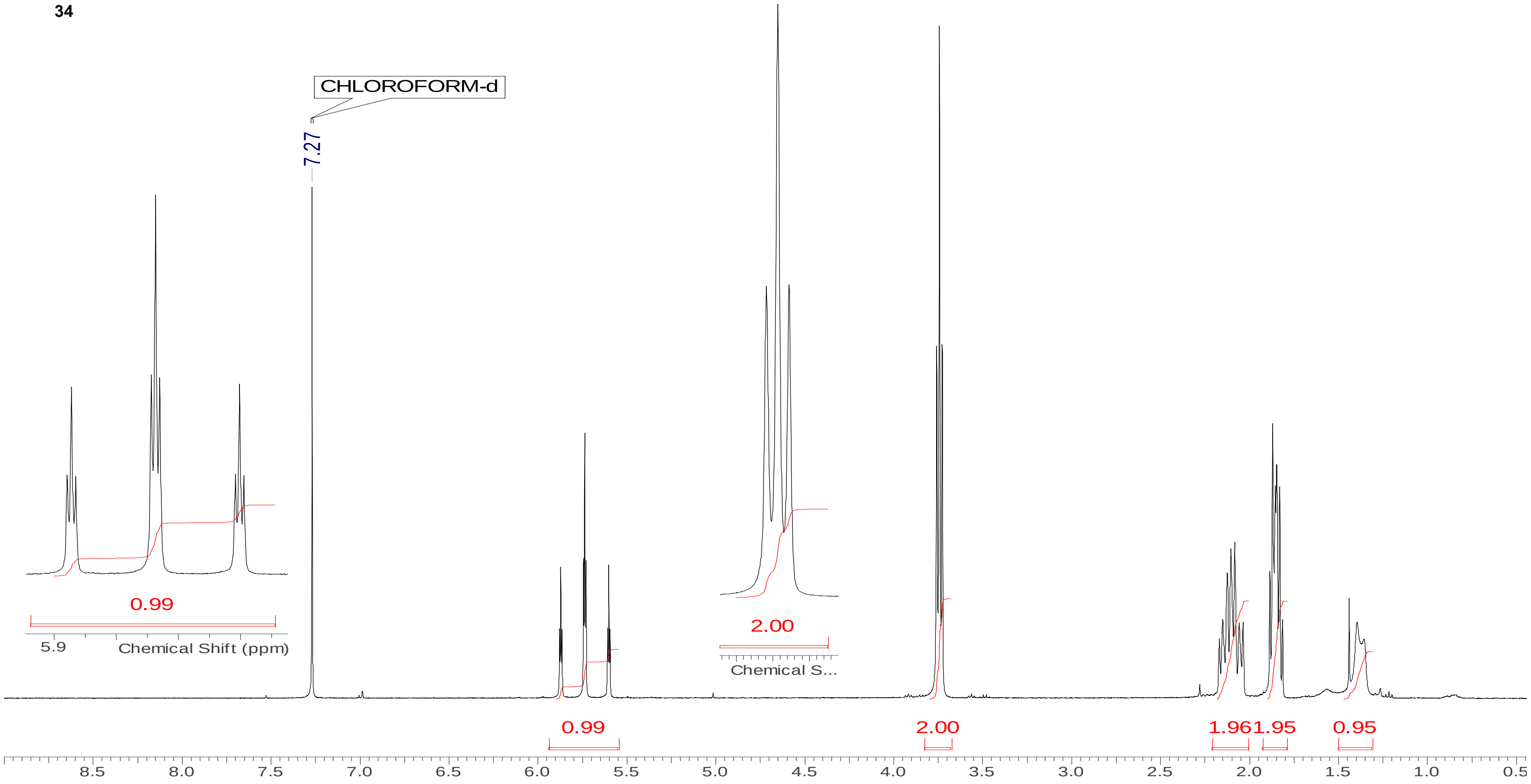
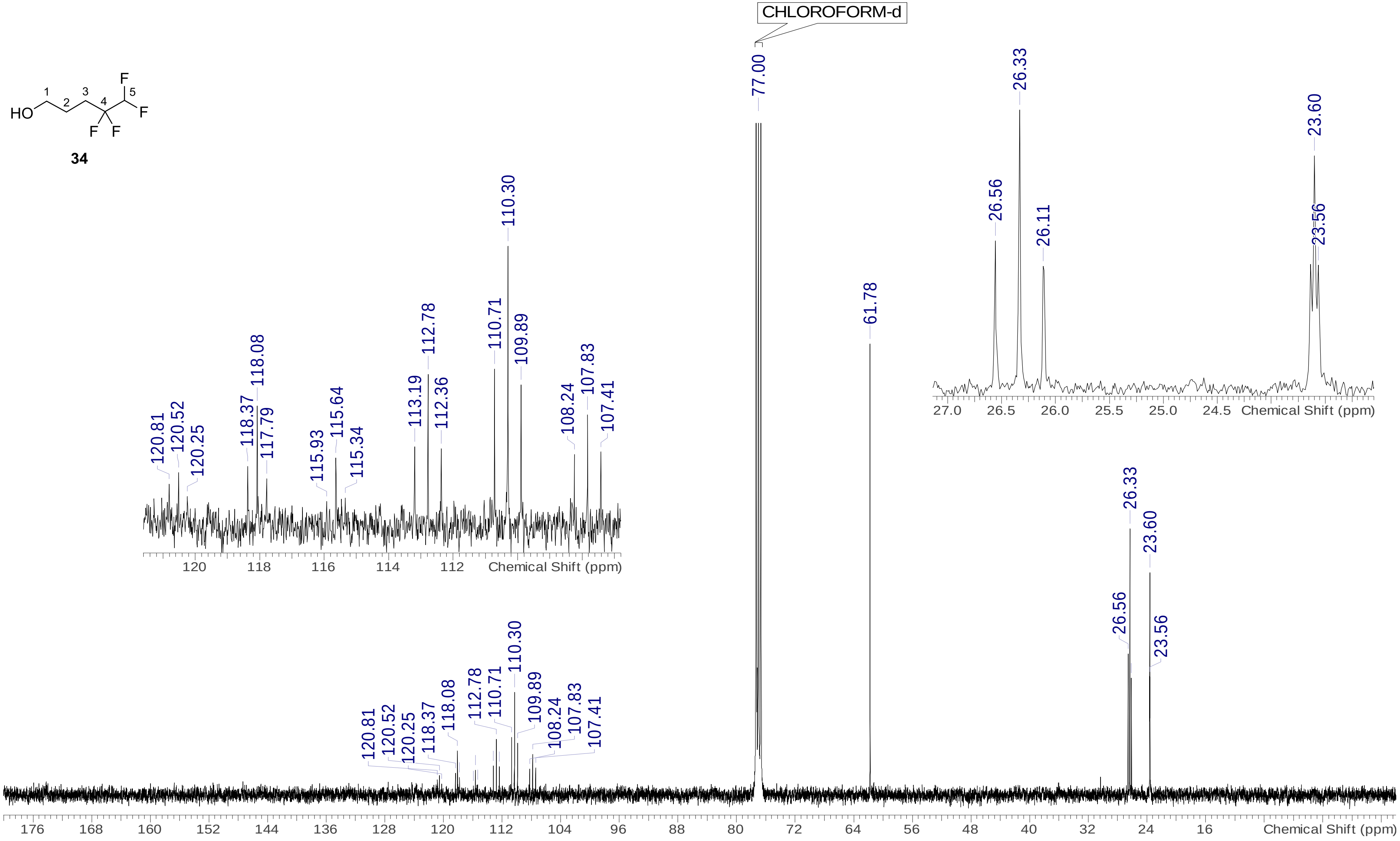
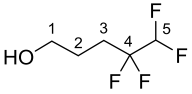


34

^{13}C NMR, CDCl$_3$, 101 MHz



^{19}F NMR, CDCl$_3$, 376 MHz



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