Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

for

Synthesis and Characterization of Trifluoromethylcarboxonium Salts

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Experimental Details

General

Caution! Anhydrous HF, AsF_5, and SbF_5 can cause severe burns, contact with the skin must be avoided, and the compounds should only be handled in a well-ventilated fume hood. Appropriate safety precautions should be taken when working with these materials.

Materials and Apparatus

All reactions were carried out in Teflon-FEP ampules that were closed by stainless steel valves. Volatile materials were handled in grease-free Pyrex glass vacuum lines equipped with Kontes® HI-VAC® valves or in stainless steel/Teflon-FEP vacuum lines.[1] Reaction vessels and the stainless steel vacuum line were passivated with ClF_3 prior to use. Non-volatile materials were handled in the dry nitrogen atmosphere of a glove box. HF (Galaxy Chemicals) was dried by storage over BiF_5.[2] AsF_5 was prepared from AsF_3 and F_2.[3-5] SbF_5 (Ozark Mahoning) was freshly distilled before use. SO_2 (Matheson Tri-Gas) was dried by storage over CaH_2. Trifluoroacetic acid (Sigma-Aldrich) was distilled from P_2O_5, and trifluoroacetamide (PCR) was purified by sublimation.[6, 7] The NMR spectra were recorded at 298 K unless otherwise stated on a either a Bruker AMX-500 or Varian VNMRS-500 spectrometer. Spectra were externally referenced to 25% tetramethyl silane in dichloromethane-d_2 for ^1H and ^{13}C NMR spectra, and to 80% $CFCl_3$ in chloroform-*d* for ^{19}F NMR spectra. Raman spectra were recorded either directly in 9 mm Teflon-FEP ampules or J. Young NMR tubes in the range 4000–80 cm^{-1} on a Bruker Vertex 70/RAM II spectrophotometer, using a Nd-YAG laser at 1064 nm.

Crystal Structure Determination

Diffraction-quality crystals were grown from anhydrous HF solution inside Teflon-FEP ampules by slow evaporation of the HF solvent in a dynamic vacuum at –78 °C. The FEP reactors were cooled to –78 °C, opened under a stream of N_2 gas, and the crystalline content was dropped into the trough of a low-temperature crystal-mounting apparatus at –110 °C. A glass fiber that was attached to a magnetic CrystalCap™ and dipped into PFPE (perfluoropolyether) oil was used to mount the crystals on the goniometer with a magnetic base. The single-crystal X-ray diffraction data were collected on a Bruker SMART APEX DUO 3-circle platform diffractometer, equipped with an APEX II CCD, using Mo Kα radiation (TRIUMPH curved-crystal monochromator) from a fine-focus tube. The diffractometer was equipped with an Oxford Cryosystems Cryostream 700 apparatus for low-temperature data collection. The frames were integrated using the SAINT algorithm to give the *hkl* files corrected for Lp/decay.[8] The absorption correction was performed using the SADABS program.[9] The structures were solved by intrinsic phasing and refined on F^2 using the Bruker SHELXTL Software Package and SHELXle.[10-14] All non-hydrogen atoms were refined anisotropically. ORTEP drawings were prepared using the Mercury CSD program.[15]

Preparation of $[CF_3COH(X)][AsF_6]$ (X = OH, NH_2)

Anhydrous HF (3.0 mL) and AsF_5 (1 mmol) were added to a Teflon-FEP ampule containing a frozen sample of either trifluoroacetic acid or trifluoroacetamide (1.00 mmol) *in vacuo* at –196 °C. The mixture was warmed to –64 °C, kept at this temperature for 15 min, and sporadically agitated. The clear solution was cooled to –78 °C and the volatile compounds were removed *in vacuo* at –78 °C, leaving behind a colorless solid. Single crystals were grown from a concentration HF solution by slow evaporation of the solvent *in vacuo* at –78 °C.

$[CF_3C(OH)_2][AsF_6]$

^1H NMR (SO_2, unlocked, –60 °C) δ = -15.67 (s, Δ½ = 200 Hz, O***H***) ppm.
^{13}C NMR (SO_2, unlocked, –60 °C) δ = 174.3 (q, $^2J_{CF}$ = 48.8 Hz, ***C***$(OH)_2$), 113.8 (q, $^1J_{CF}$ = 284.8 Hz, ***C***F_3) ppm.
^{19}F NMR (SO_2, unlocked, –60 °C) δ = -58.2 (s, 6F, Δ½ = 830 Hz, As***F***$_6^-$), -72.8 (s, 3F, C***F***$_3$) ppm.

Raman (–90 °C, 350 mW): υ(rel. Intensity) = 1574.7 (0.9), 1270.2 (0.4), 1227.9 (0.3), 1193.3 (0.4), 823 (2.8), 690.5 (10), 597.8 (0.9), 578.0 (0.1), 538.3 (1.2), 449.3 (0.8), 426.2 (0.5), 402 (0.4), 370.7 (1.6), 358.4 (0.9), 260.2 (0.4), 251.8 (0.3), 239.7 (0.3), 151 (0.8), 142.8 (0.9) cm^{-1}.

$[CF_3C(OH)(NH_2)][AsF_6]$

^1H NMR (SO_2, unlocked, –60 °C) δ = -13.18 (s, 1H, O***H***), -10.94 (s, 1H, Δ½ = 93 Hz, N***H***H), -10.56 (s, 1H, Δ½ = 93 Hz, NH***H***) ppm.
^{13}C NMR (SO_2, unlocked, –60 °C) δ = 165.6 (q, $^2J_{CF}$ = 44.6 Hz, ***C***$(OH)(NH_2)$), 115.2 (q, $^1J_{CF}$ = 281.5 Hz, ***C***F_3) ppm.
^{19}F NMR (SO_2, unlocked, –60 °C) δ = -56.83 (s, 6F, Δ½ = 830 Hz, As***F***$_6^-$), -73.05 (s, 3F, C***F***$_3$) ppm.

Raman (–90 °C, 350 mW): υ(rel. Intensity) = 1765.2 (1.4), 1740.7 (0.4), 1589.9 (0.4), 1518.2 (1.2), 1275.5 (0.8), 1240.6 (0.7), 1221.2 (0.8), 1213.9 (0.7), 1101.7 (2.9), 806.0 (5.7), 718.3 (1.7), 690.3 (10.1), 671.7 (1.8), 644.8 (1.3), 599.3 (1.3), 589.0 (1.5), 546.6 (1.3), 508.2 (0.6), 432.7 (1.8), 410.7 (1.6), 378.0 (2.8), 371.6 (2.5), 364.0 (2.2) cm^{-1}.

Preparation of $[CF_3COH(X)][SbF_6]$ (X = OH, NH_2)

Anhydrous HF (3.0 mL) was condensed to a Teflon-FEP ampule containing a frozen sample of SbF_5 (1.00 mmol) at –196 °C. The mixture was warmed to –20 °C to form a clear colorless solution. The solution was cooled to –64 °C and, under a stream of dry nitrogen using an 18 gauge FEP tubing, transferred into a second Teflon-FEP ampule containing a sample of either trifluoroacetic acid or trifluoroacetamide (1.00 mmol) at –78 °C. The mixture was allowed to warm to –64 °C, kept at this temperature for 15 min and sporadically agitated. The clear solution was cooled to –78 °C and the volatile compounds were removed *in vacuo* at –78 °C, leaving behind a colorless solid. Single crystals were grown from a concentration HF solution by slow evaporation of the solvent *in vacuo* at –78 °C.

$[CF_3C(OH)_2][SbF_6]$

^{1}H NMR (SO_2, unlocked, –60 °C) δ = -16.01 (s, Δ½ = 290 Hz, O***H***), 13.57 (s, Δ½ = 230 Hz, O***H***) ppm.
^{13}C NMR (SO_2, unlocked, –60 °C) δ = 174.4 (q, $^2J_{CF}$ = 49.4 Hz, ***C***$(OH)_2$), 113.6 (q, $^1J_{CF}$ = 284.2 Hz, ***C***F_3) ppm.
^{19}F NMR (SO_2, unlocked, –60 °C) δ = -73.07 (s, 3F, C***F₃***), -115.70 (s, 6F, Δ½ = 750 Hz, Sb***F₆***$^-$) ppm.

Raman (–90 °C, 350 mW): υ(rel. Intensity) = 1575.8 (0.7), 1277.2 (0.1), 1266 (0.1), 1226.6 (0.1), 1197.5 (0.1), 825.4 (1.8), 698.9 (0.1), 689.9 (0.3), 657.1 (10), 606.3 (0.2), 593.5 (0.7), 579 (0.1), 533.2 (0.7), 444.1 (0.4), 409.9 (0.4), 382 (0.1), 276.5 (0.3), 253.5 (0.6), 152.6 (0.7), 141.2 (0.1) cm^{-1}.

$[CF_3C(OH)(NH_2)][SbF_6]$

^{1}H NMR (SO_2, unlocked, –60 °C) δ = -1212 (s, 1H, Δ½ = 30 Hz, O***H***), -10.55 (s, 1H, Δ½ = 54 Hz, N***H***H), -10.16 (s, 1H, Δ½ = 54 Hz, NH***H***) ppm.
^{13}C NMR (SO_2, unlocked, –60 °C) δ = 165.8 (q, $^2J_{CF}$ = 43.6 Hz, ***C***$(OH)(NH_2)$), 115.9 (q, $^1J_{CF}$ = 282.0 Hz, ***C***F_3) ppm.
^{19}F NMR (SO_2, unlocked, –60 °C) δ = -73.45 (s, 3F, C***F₃***), -113.08 (s, 6F, Δ½ = 4500 Hz, Sb***F₆***$^-$) ppm.

Raman (–90 °C, 350 mW): υ(rel. Intensity) = 1766.1 (0.5), 1749.0 (1.4), 1627.5 (0.5), 1527.7 (1.1), 1278.7 (1.0), 1248.8 (0.6), 1209.4 (0.8), 1189.4 (0.5), 1112.5 (2.3), 810.9 (3.4), 668.3 (10.0), 652.5 (3.0), 642.0 (8.9), 602.3 (1.0), 569.3 (1.5), 543.9 (1.2), 510.4 (0.6), 434.6 (1.7), 402.2 (2.4), 382.3 (1.0), 311.6 (1.0), 280.6 (4.8), 261.4 (1.3) cm^{-1}.

NMR Spectra

CF_3CO_2H

Figure S1: ^1H NMR spectrum of CF_3CO_2H.

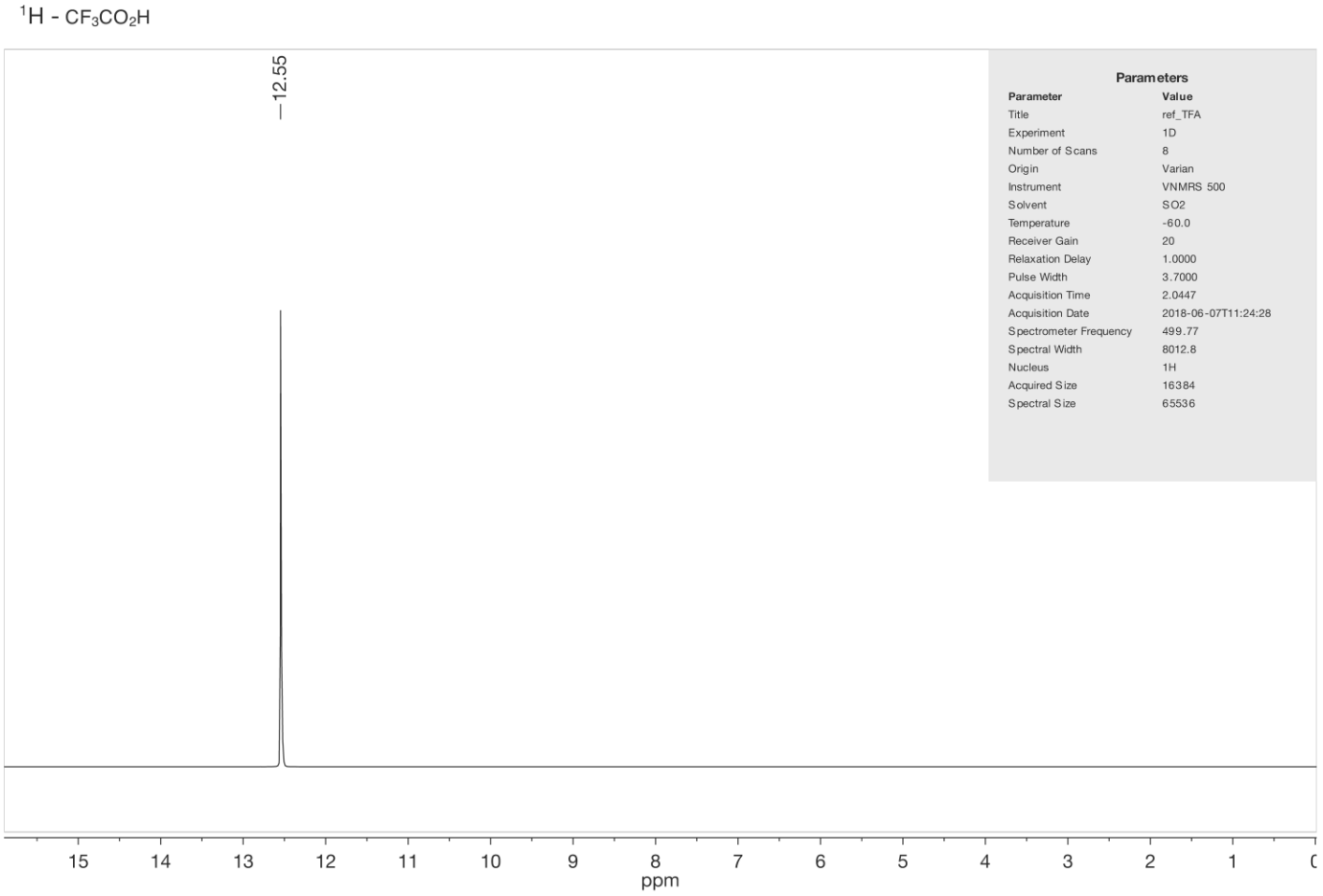


Figure S2: ^{13}C NMR spectrum of CF_3CO_2H.

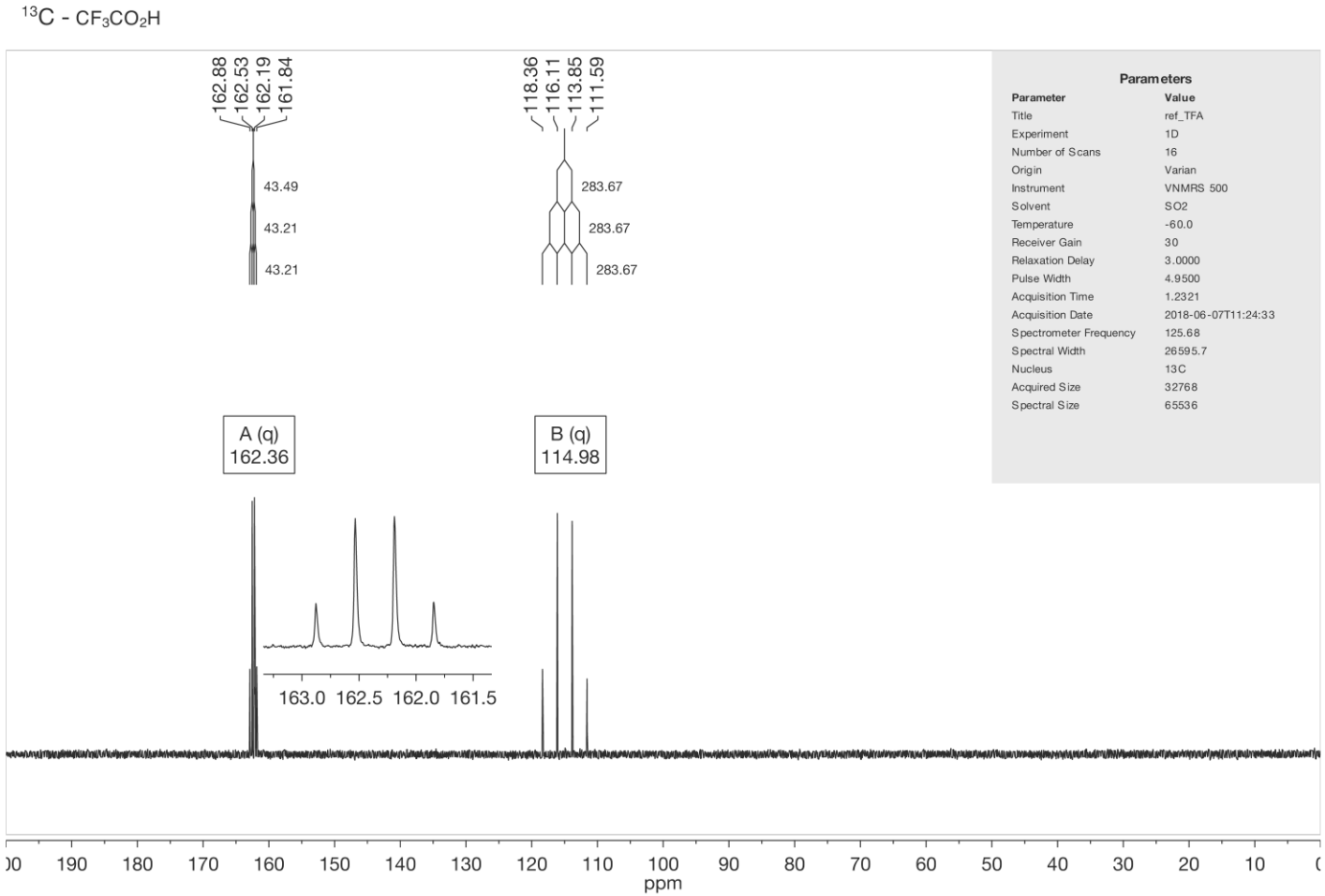
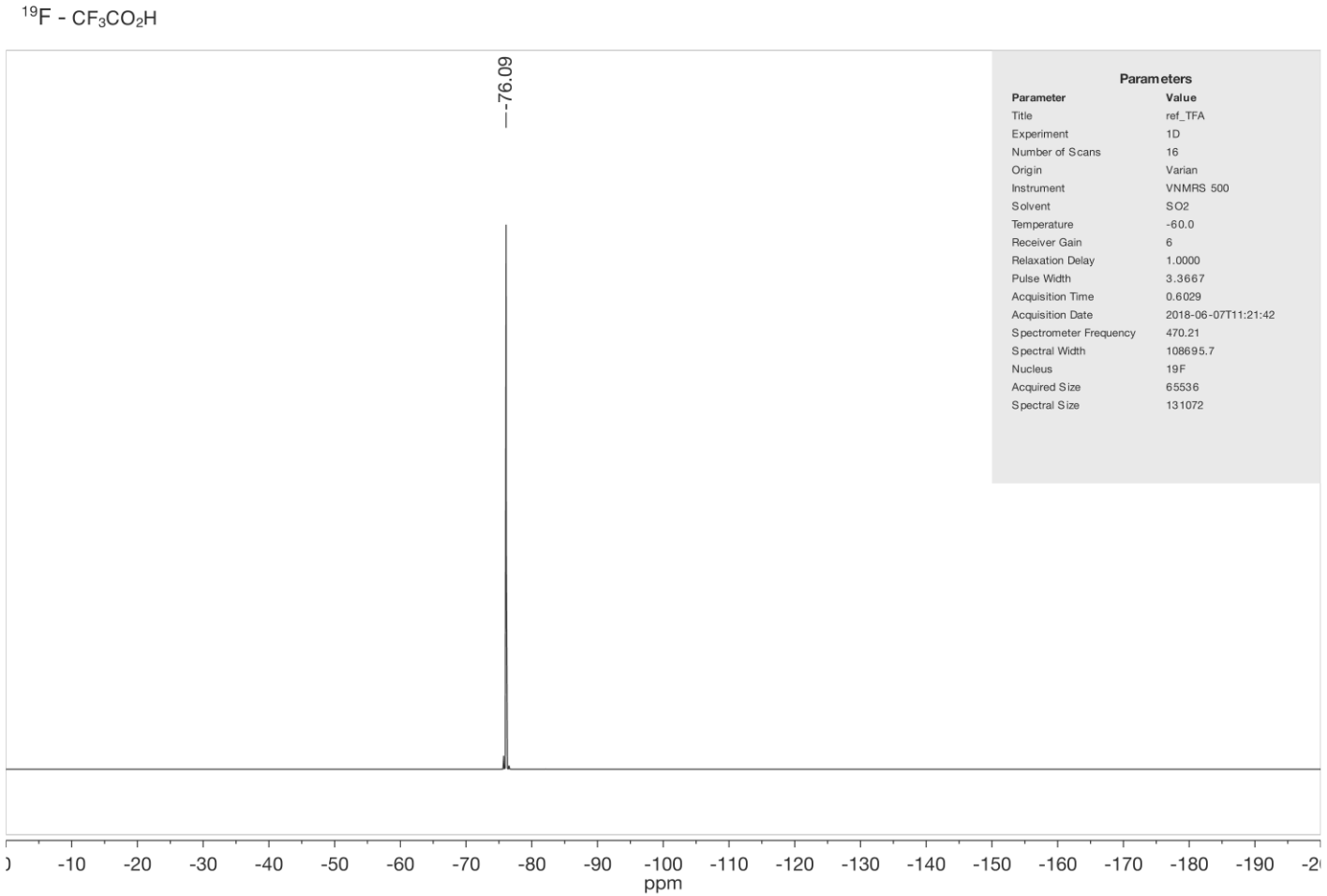


Figure S3: ^{19}F NMR spectrum of CF_3CO_2H.



$[CF_3C(OH)_2][AsF_6]$

Figure S4: ^1H NMR spectrum of $[CF_3C(OH)_2][AsF_6]$.

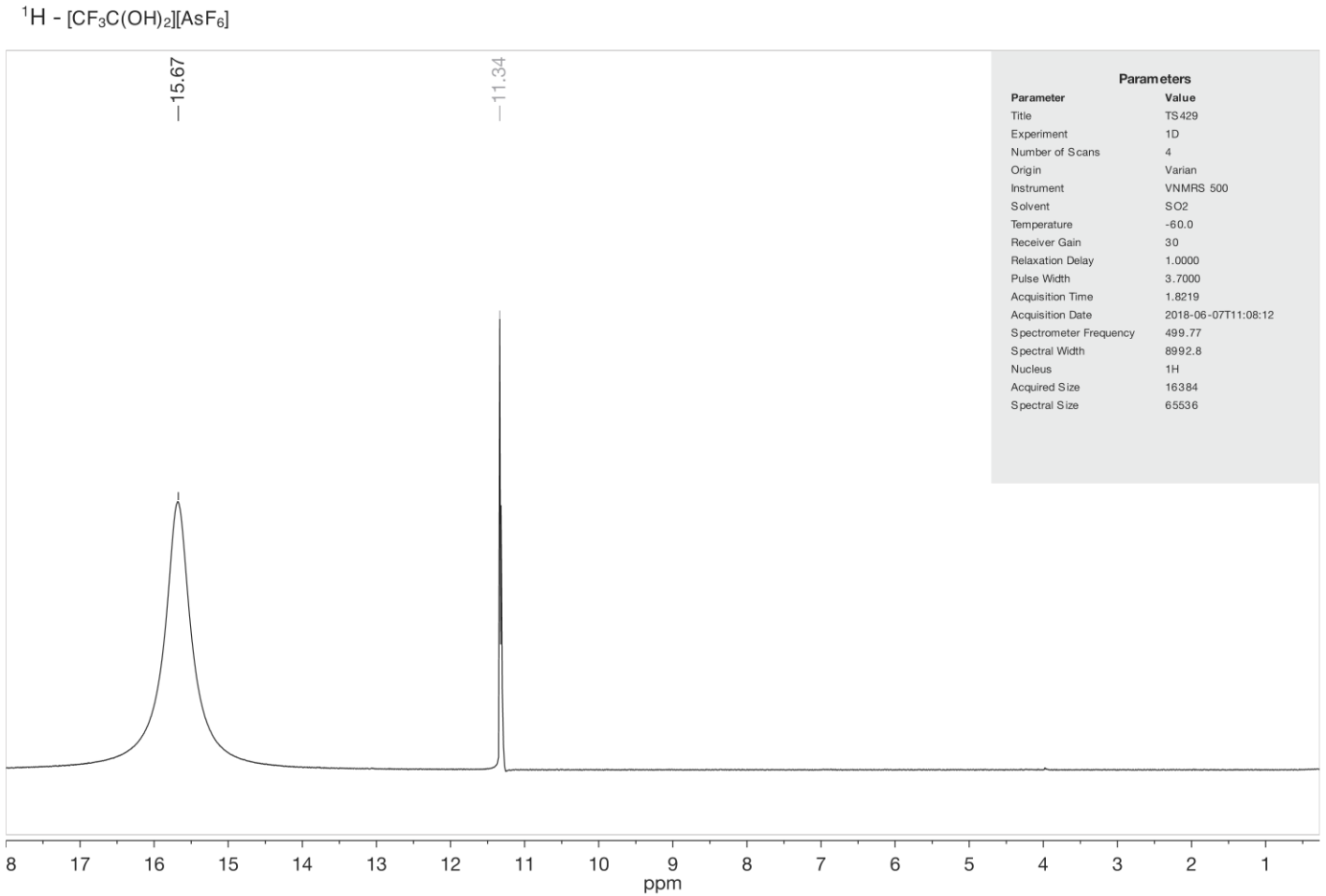


Figure S5: ^{13}C NMR spectrum of $[CF_3C(OH)_2][AsF_6]$.

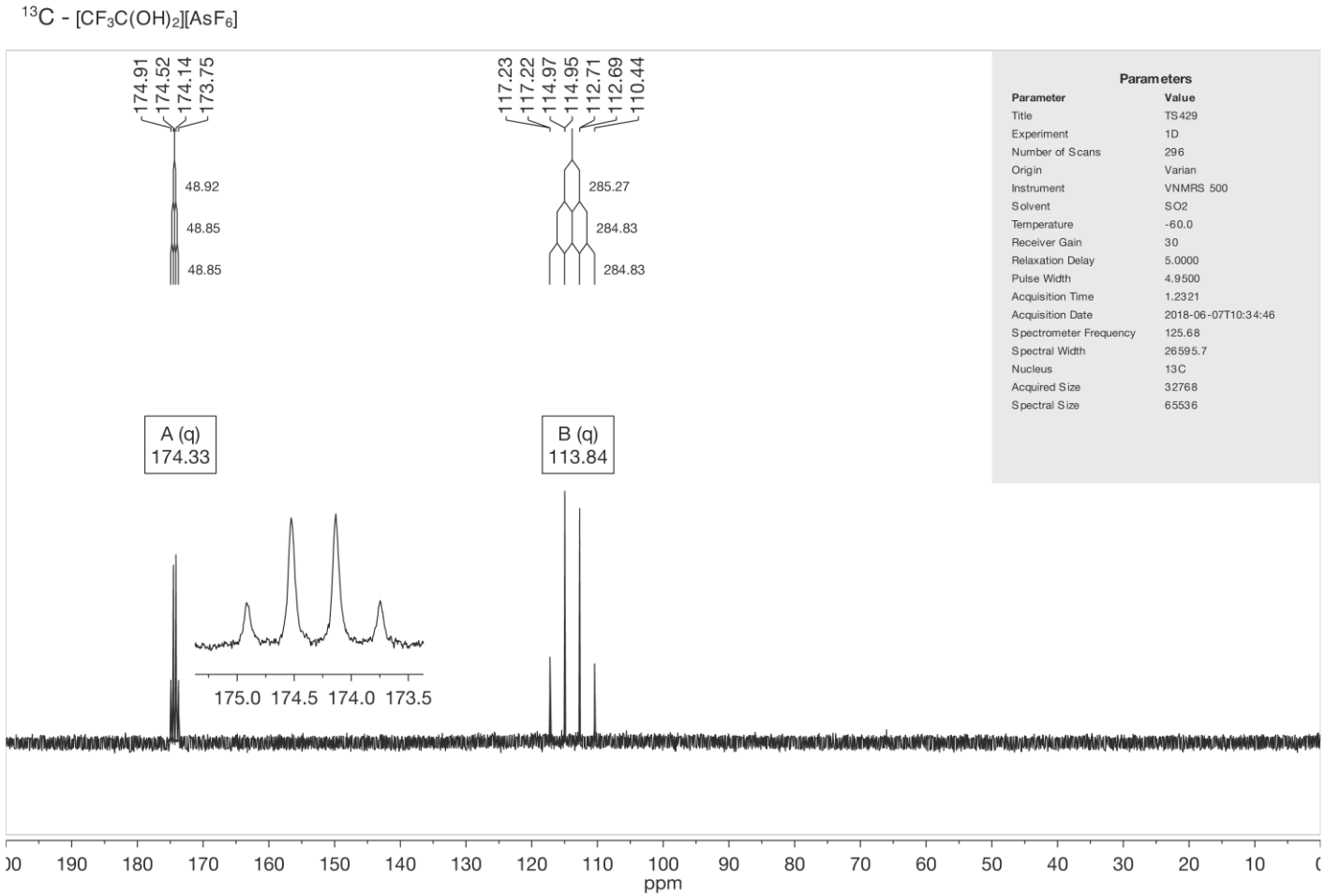
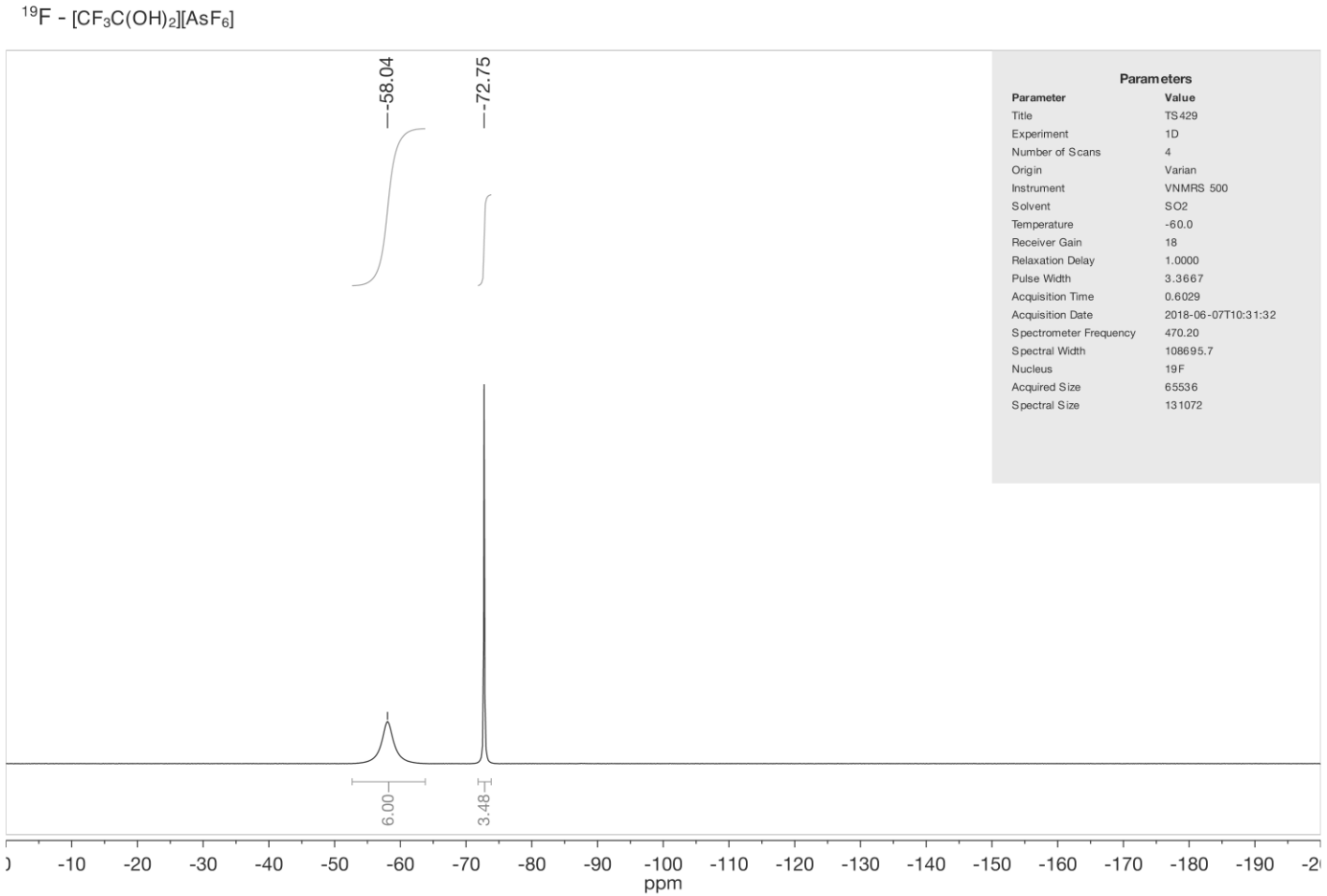


Figure S6: ^{19}F NMR spectrum of $[CF_3C(OH)_2][AsF_6]$.



$[CF_3C(OH)_2][SbF_6]$

Figure S7: ^{1}H-NMR spectrum of $[CF_3C(OH)_2][SbF_6]$.

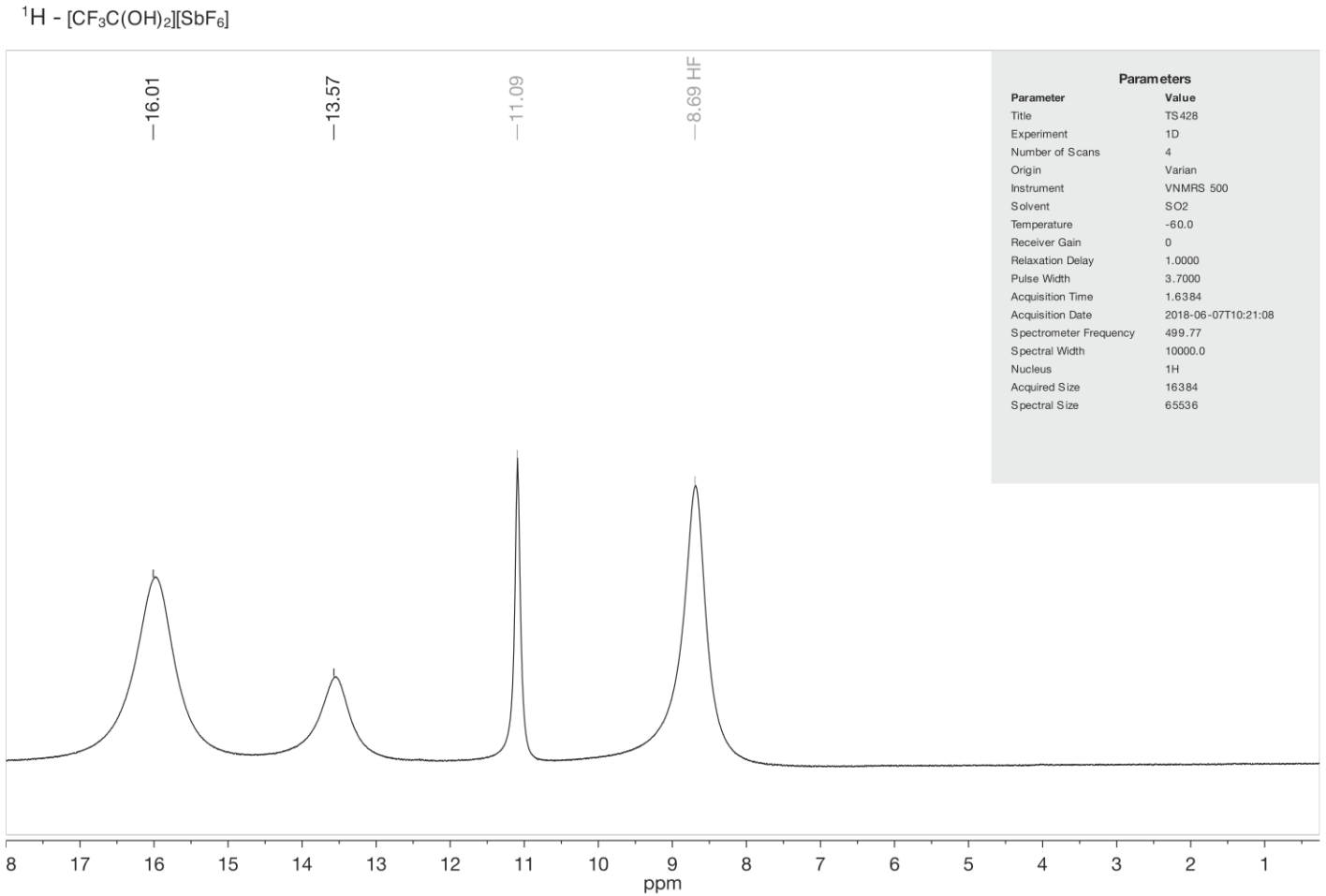


Figure S8: ^{13}C-NMR spectrum of $[CF_3C(OH)_2][SbF_6]$.

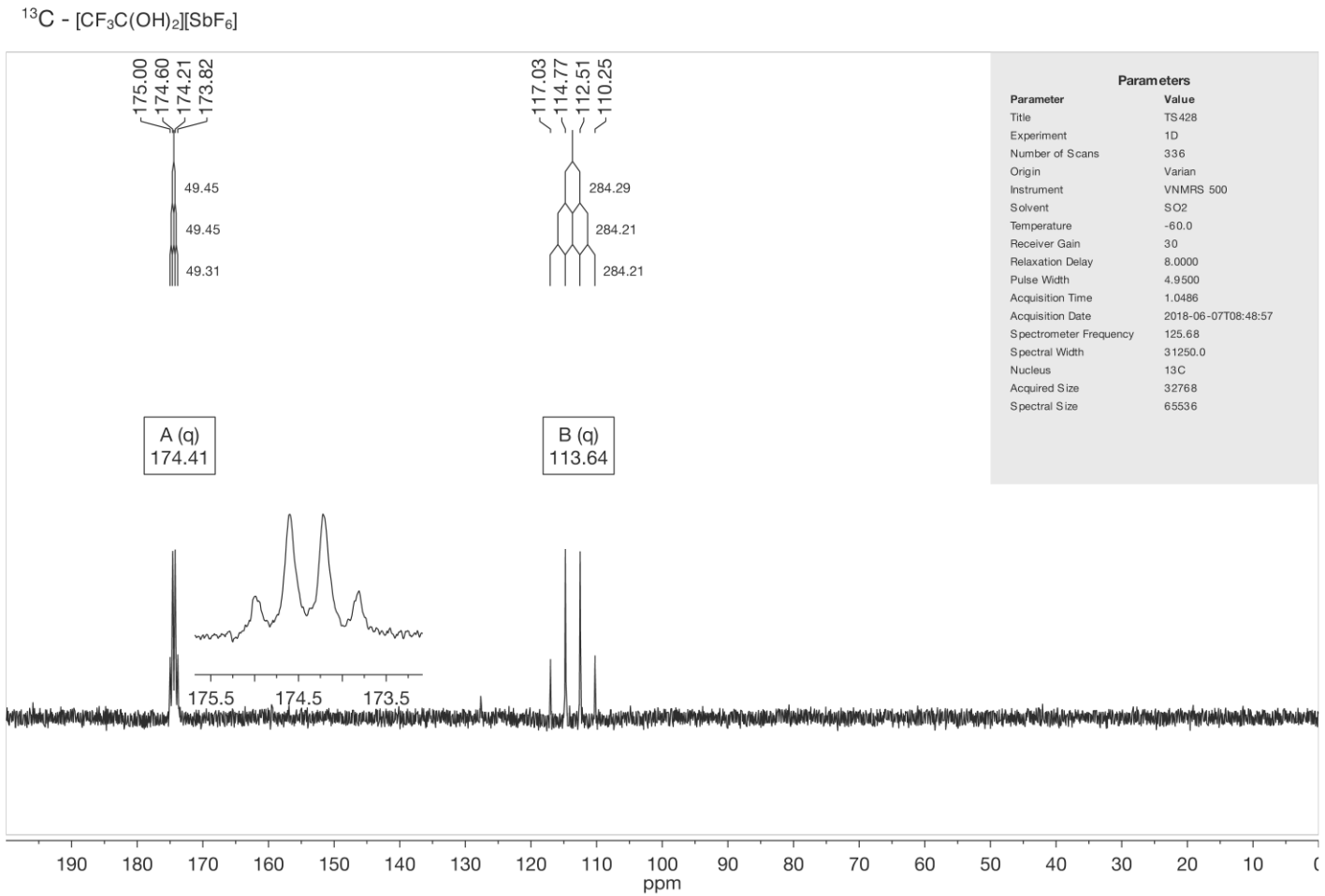
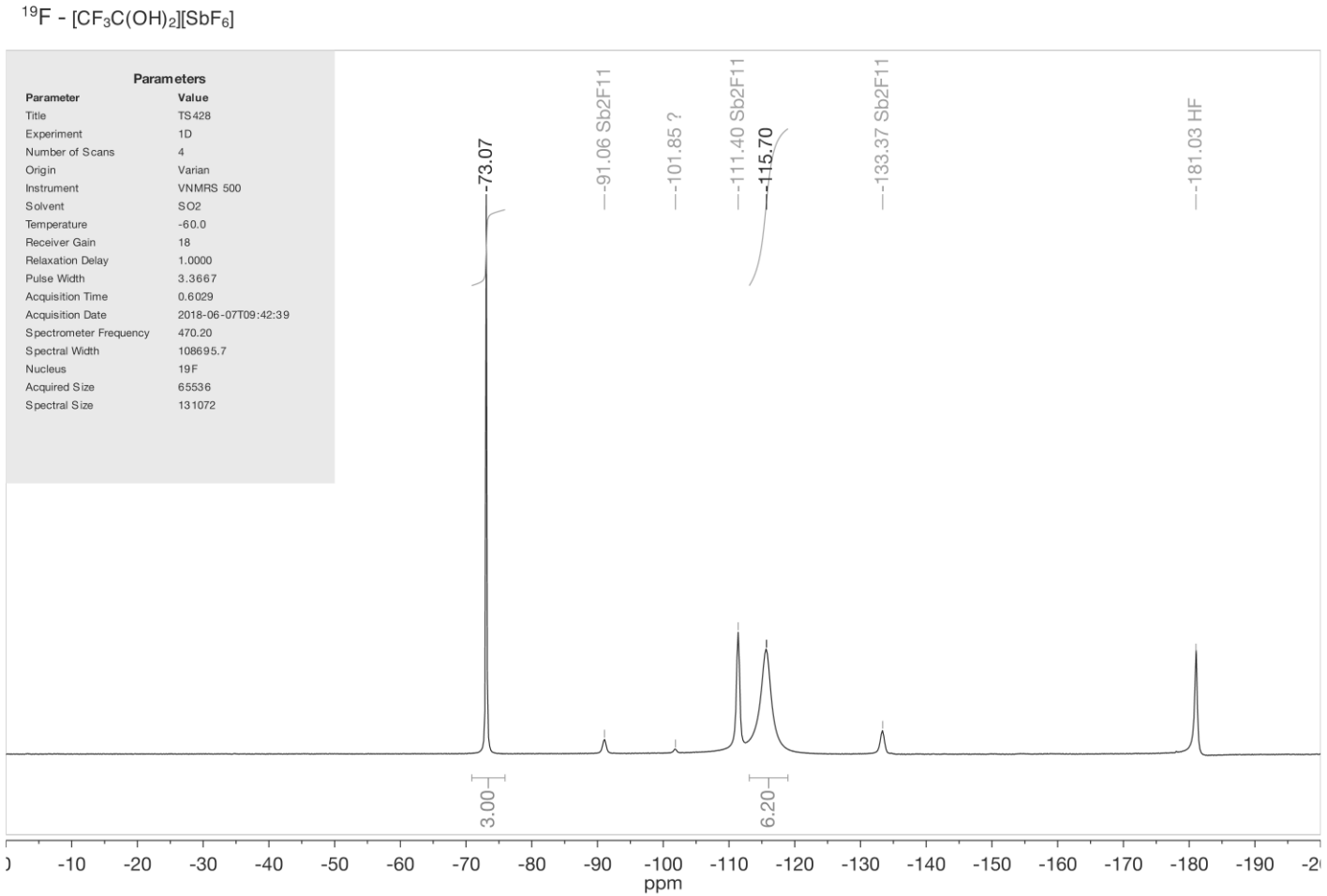


Figure S9: ^{19}F-NMR spectrum of $[CF_3C(OH)_2][SbF_6]$.



$CF_3CO(NH_2)$

Figure S10: ^{1}H-NMR spectrum of $CF_3CO(NH_2)$.

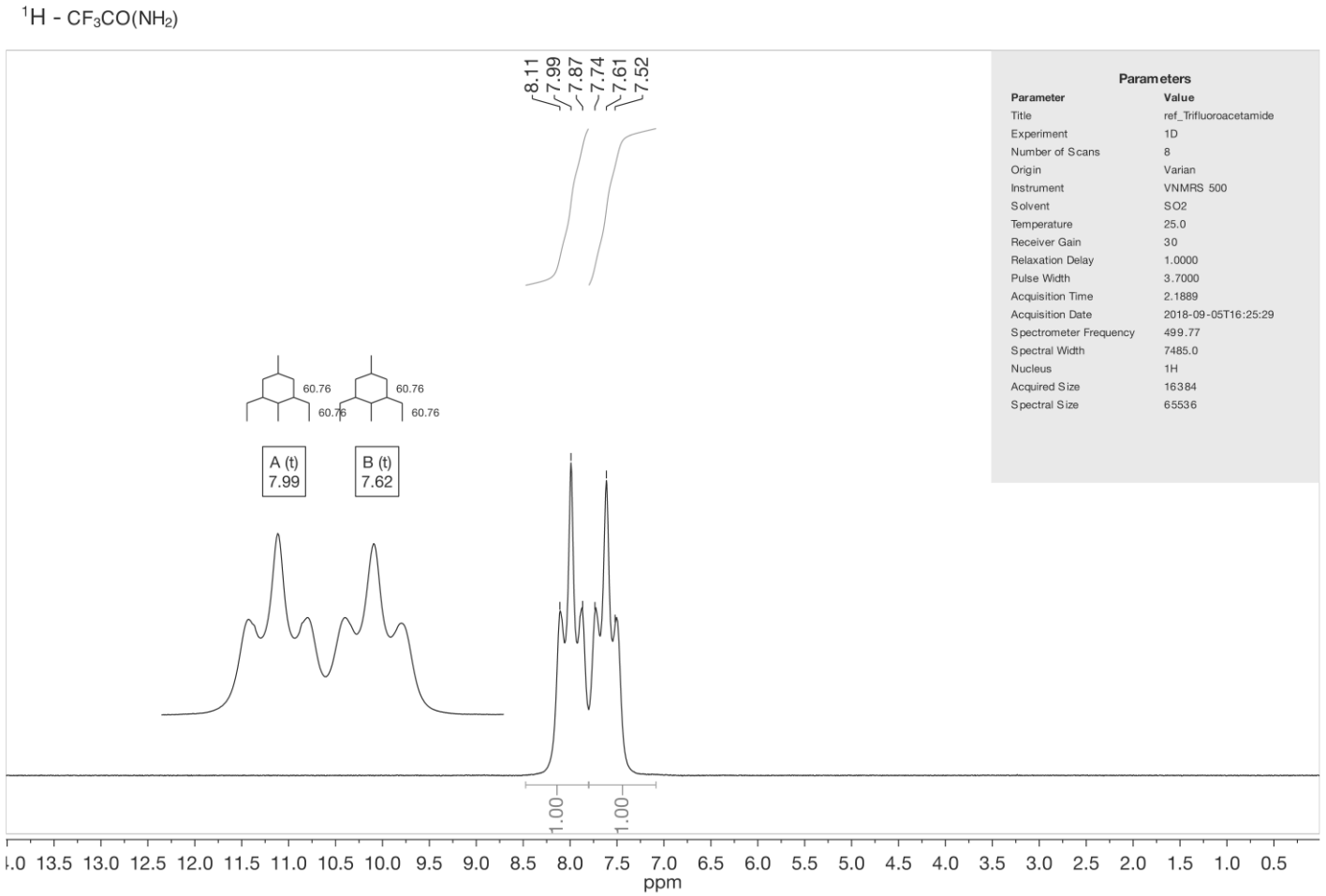


Figure S11: ^{13}C-NMR spectrum of $CF_3CO(NH_2)$.

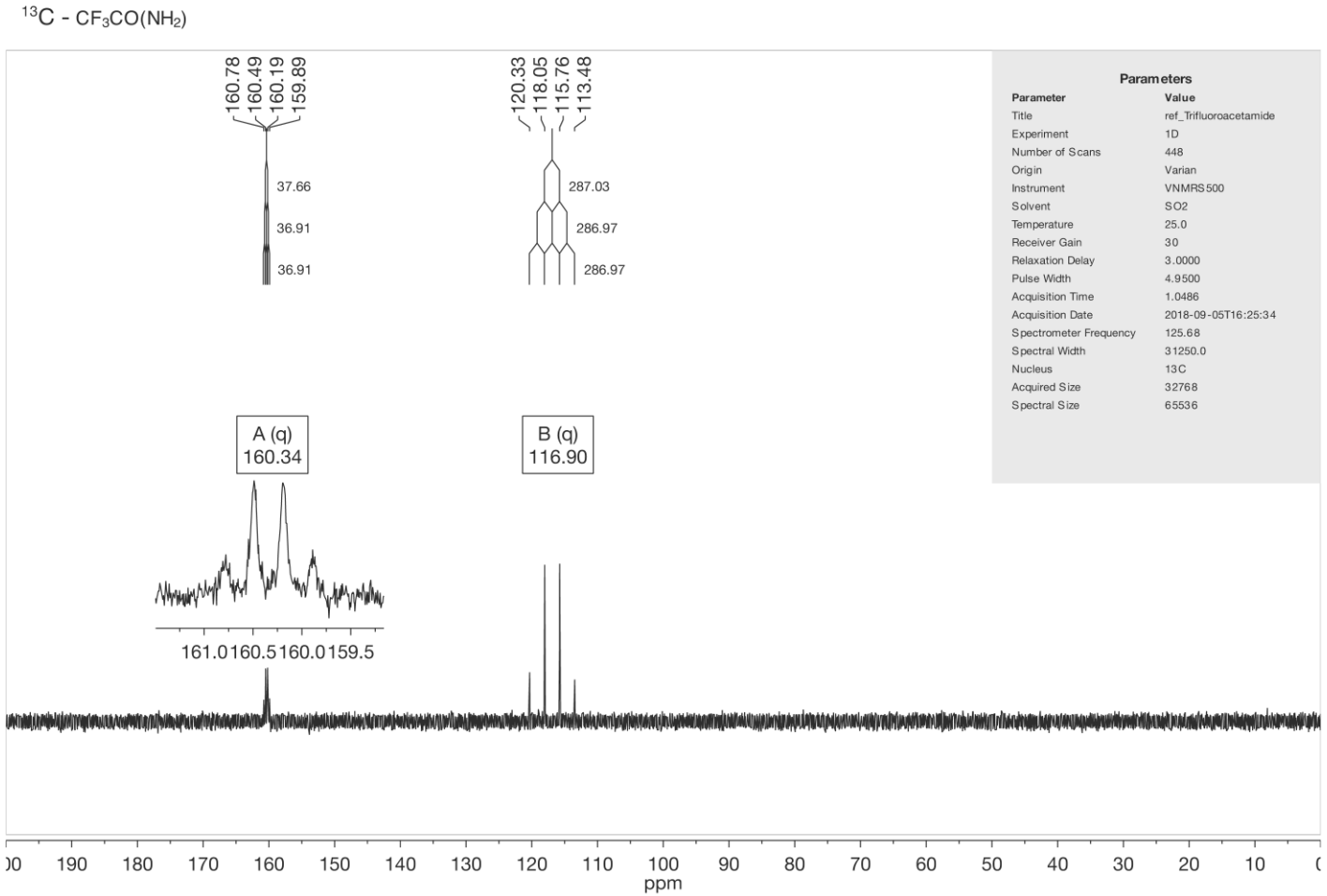
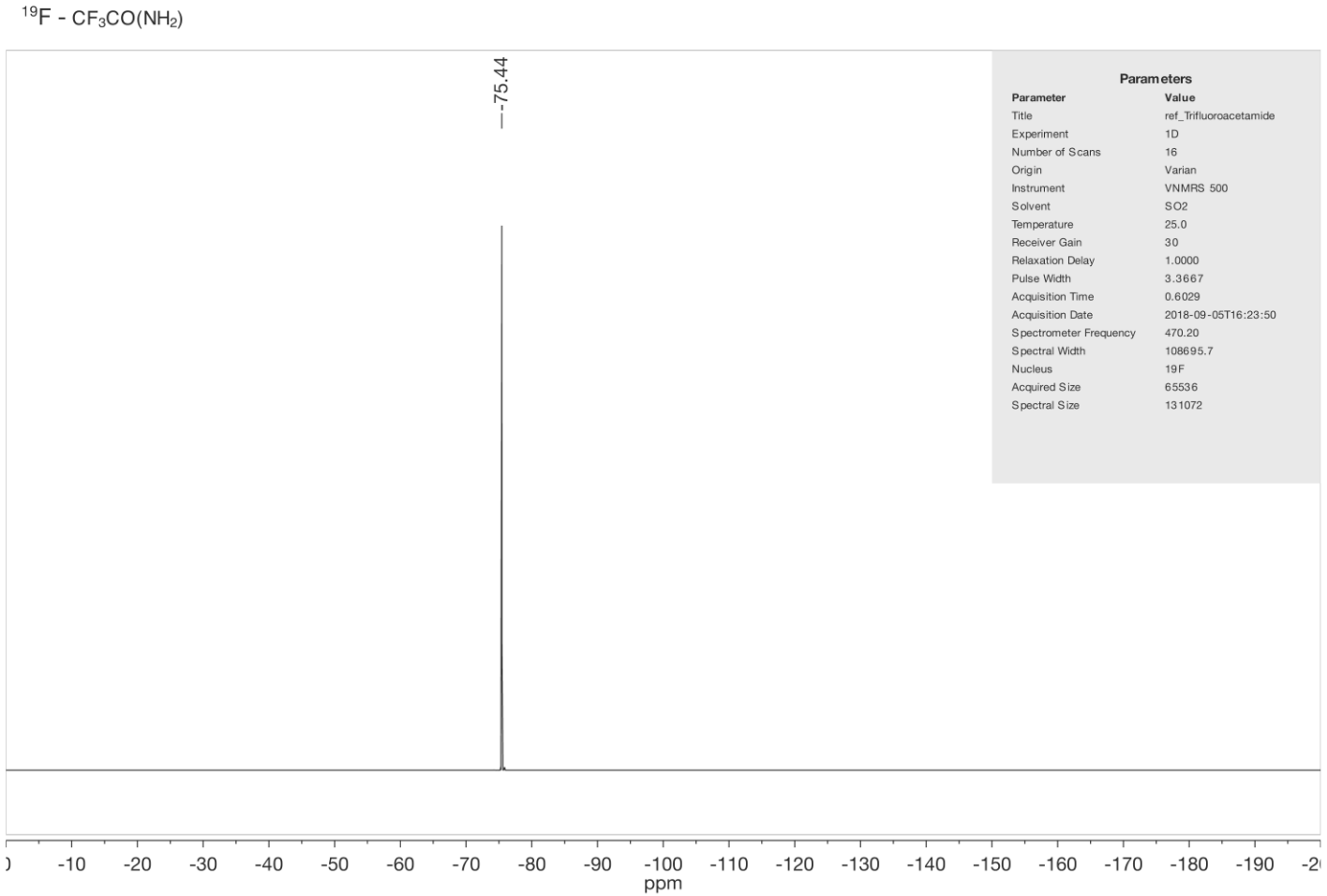


Figure S12: ^{19}F-NMR spectrum of $CF_3CO(NH_2)$.



$[CF_3C(OH)(NH_2)][AsF_6]$

Figure S13: ^{1}H-NMR spectrum of $[CF_3C(OH)(NH_2)][AsF_6]$.

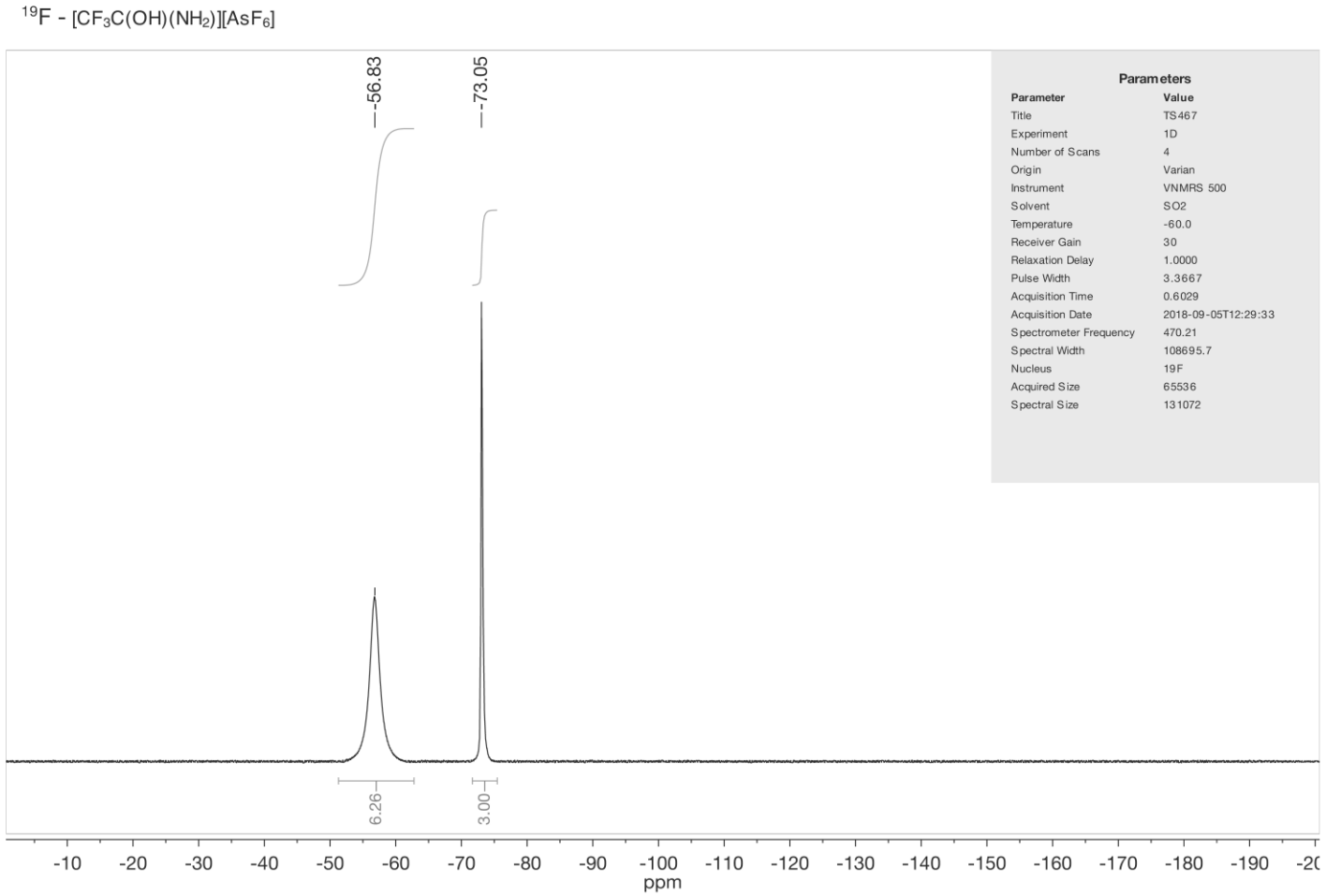


Figure S14: ^{13}C-NMR spectrum of $[CF_3C(OH)(NH_2)][AsF_6]$.

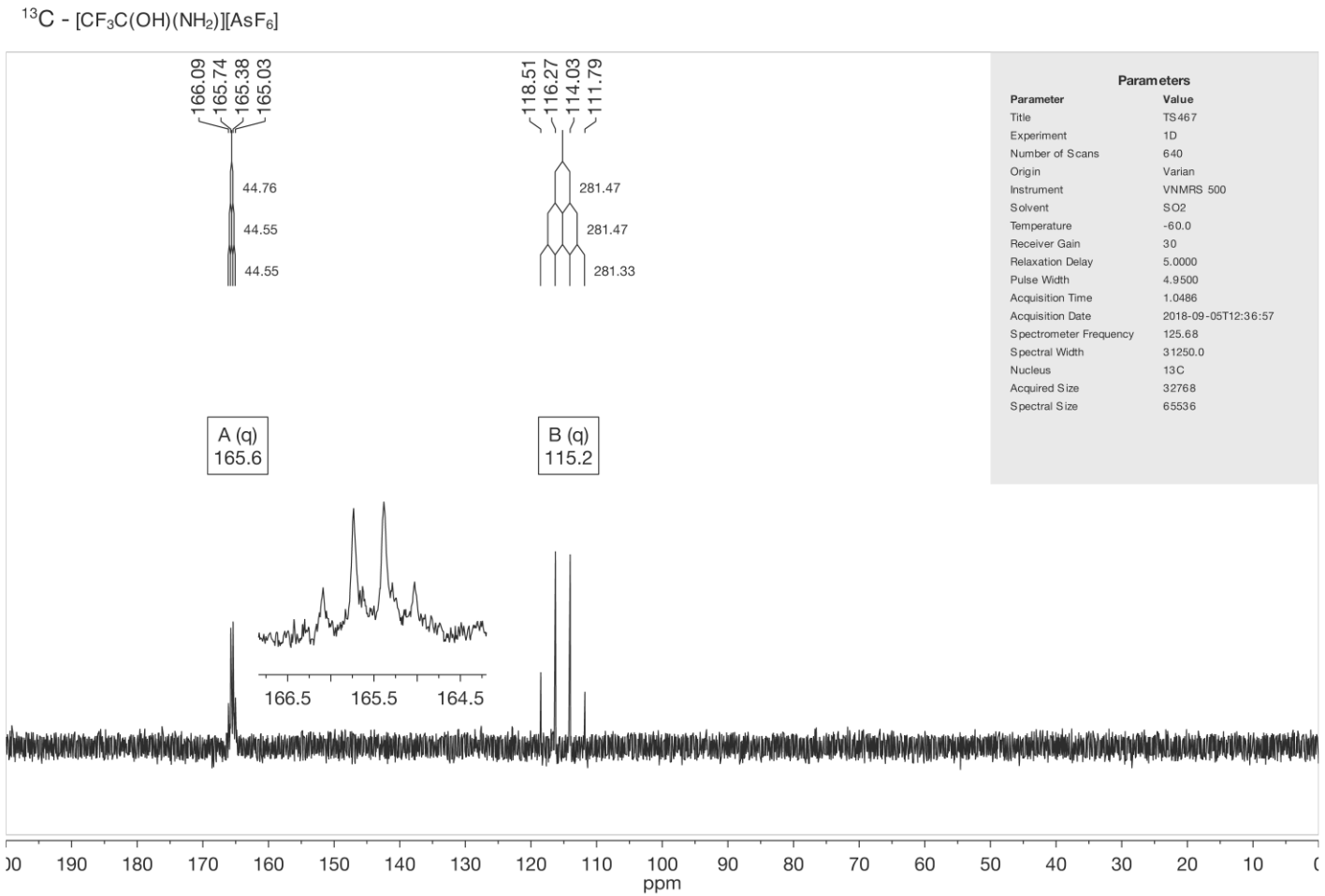
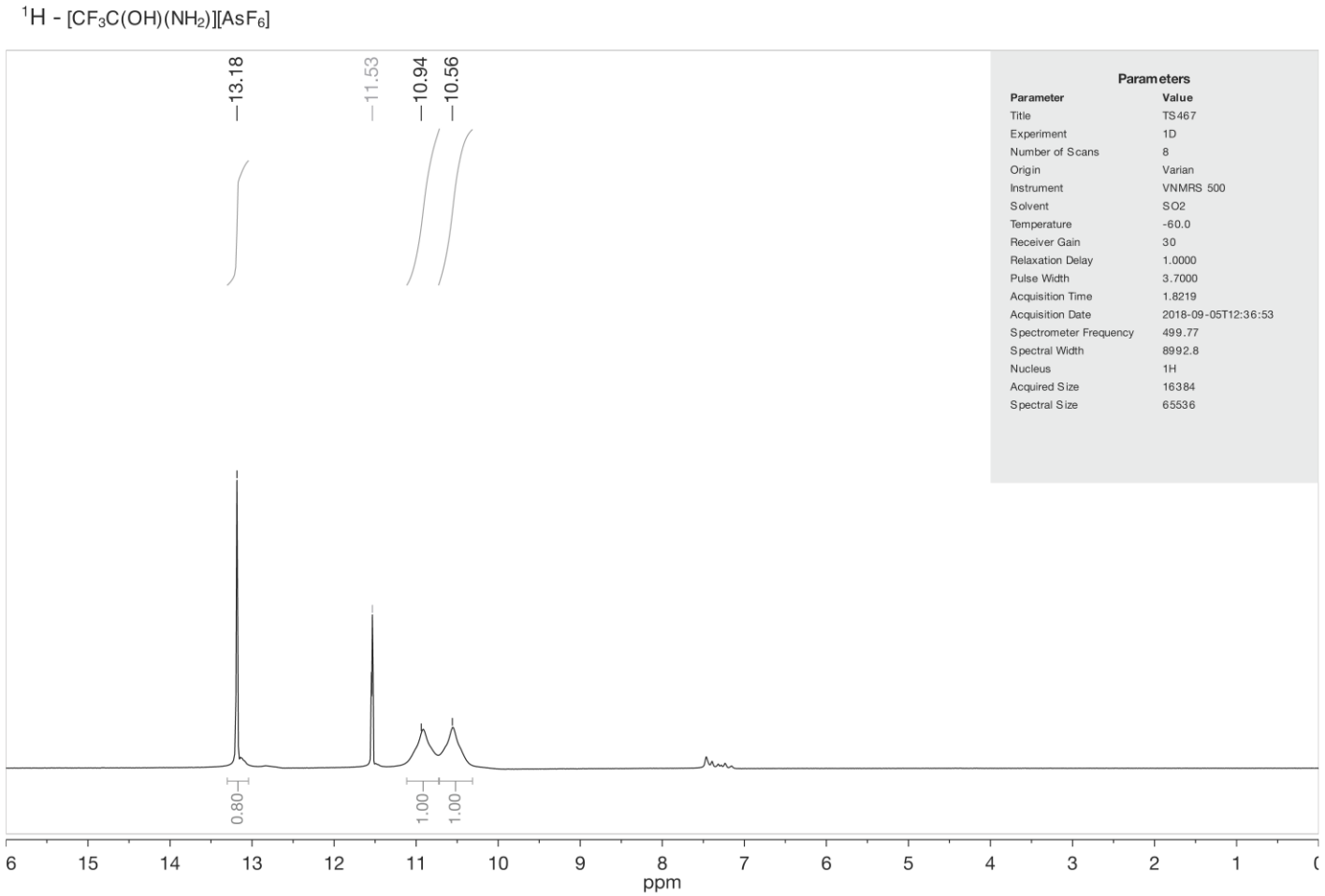


Figure S15: ^{19}F-NMR spectrum of $[CF_3C(OH)(NH_2)][AsF_6]$.



$[CF_3C(OH)(NH_2)][SbF_6]$

Figure S18, ^{1}H-NMR spectrum of $CF_3C(OH)(NH_2)][SbF_6]$.

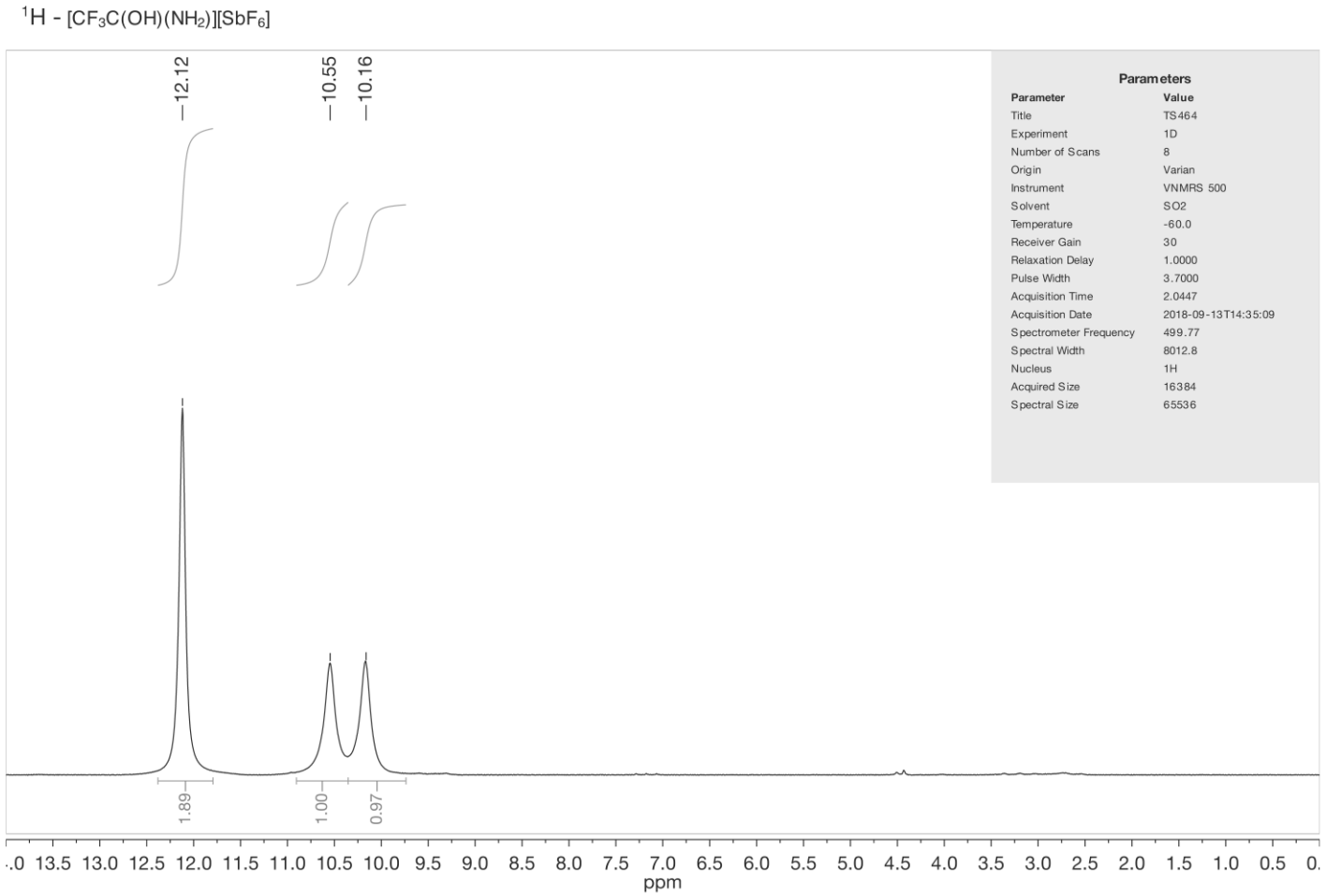


Figure S19, ^{13}C-NMR spectrum of $CF_3C(OH)(NH_2)][SbF_6]$.

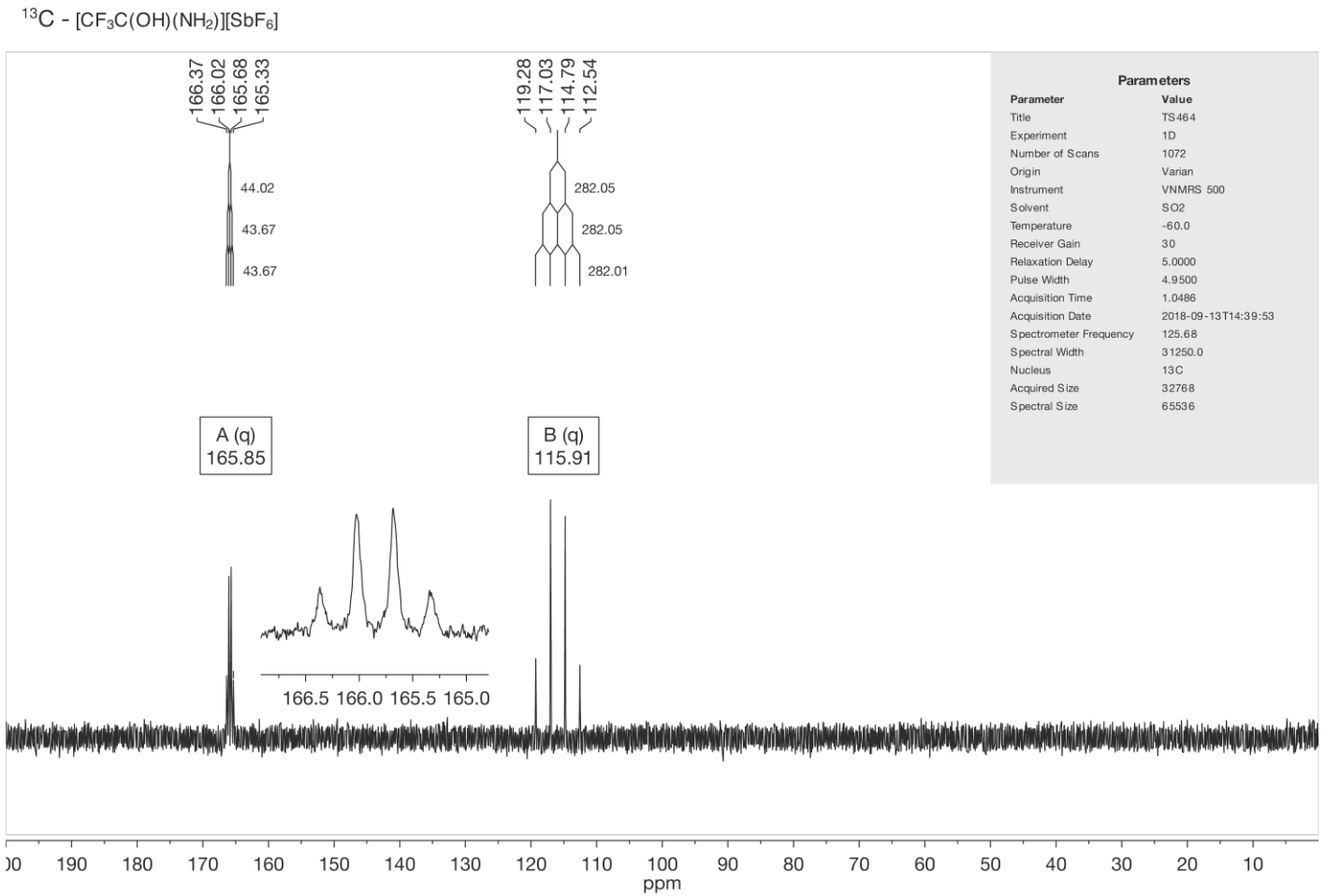
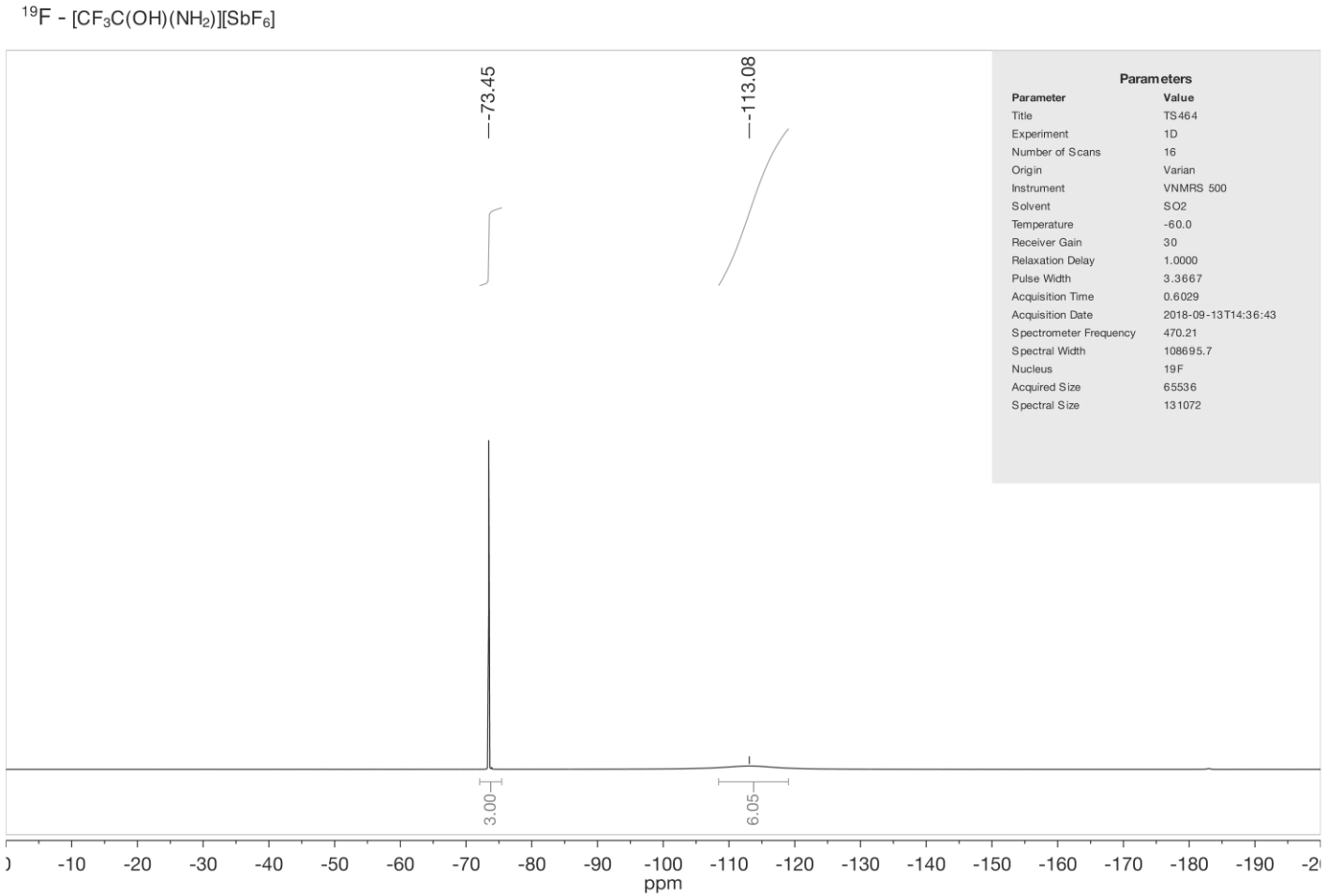


Figure S20, ^{19}F-NMR spectrum of $CF_3C(OH)(NH_2)][SbF_6]$.



Raman Spectra

Figure S21: Raman spectrum of CF_3CO_2H.

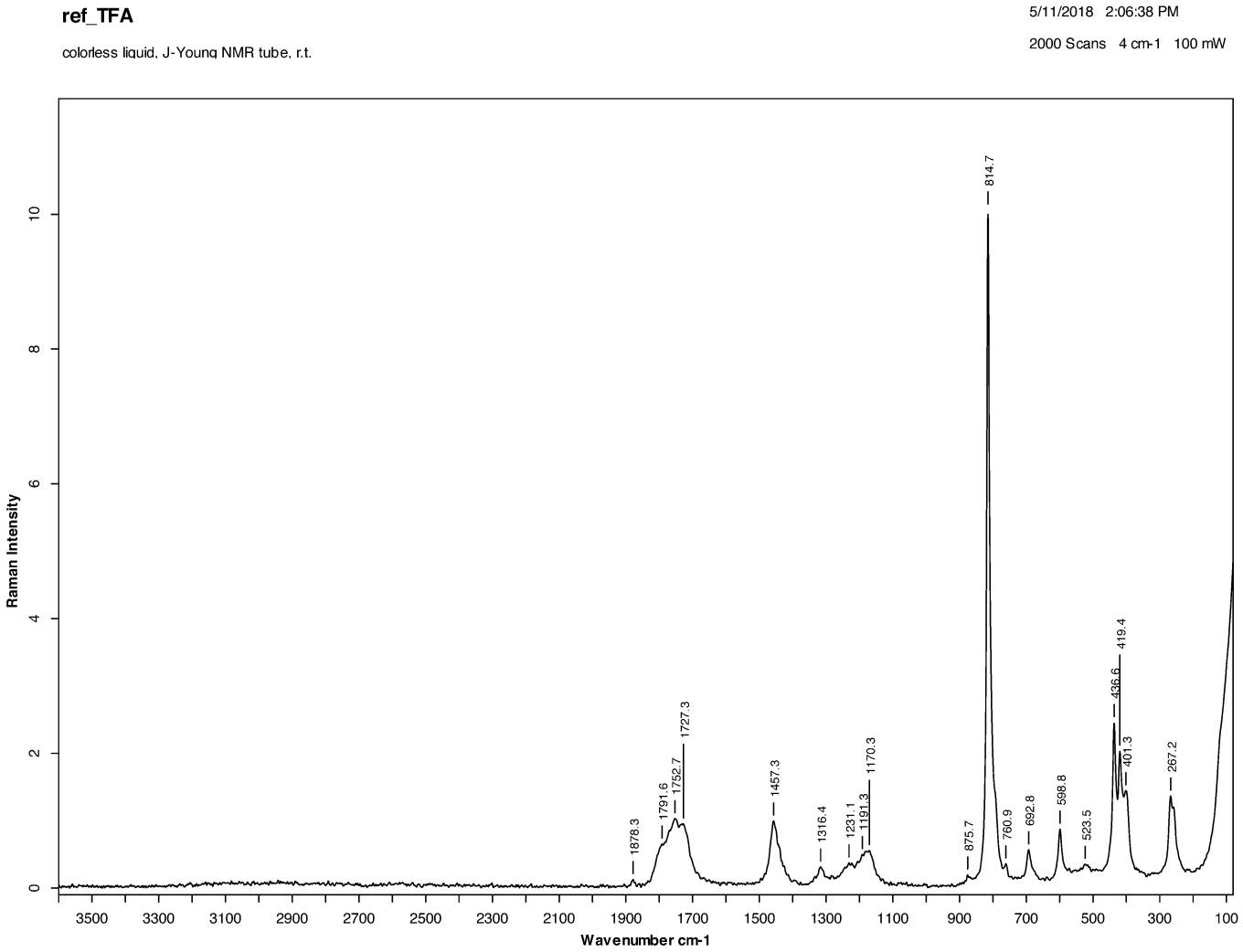


Figure S22: Raman spectrum of $[CF_3C(OH)_2][AsF_6]$.

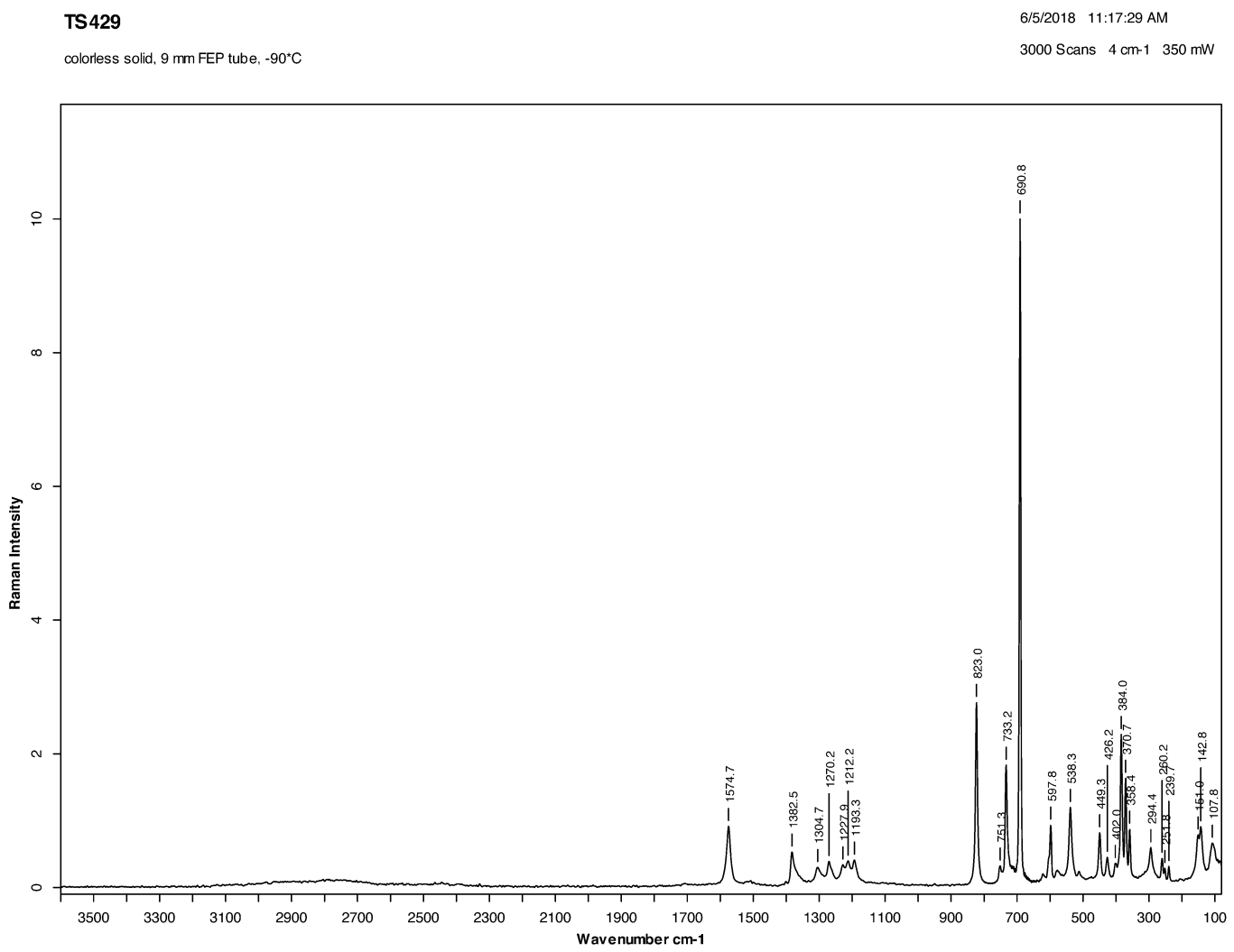


Figure S23: Raman spectrum of $[CF_3C(OH)_2][SbF_6]$.

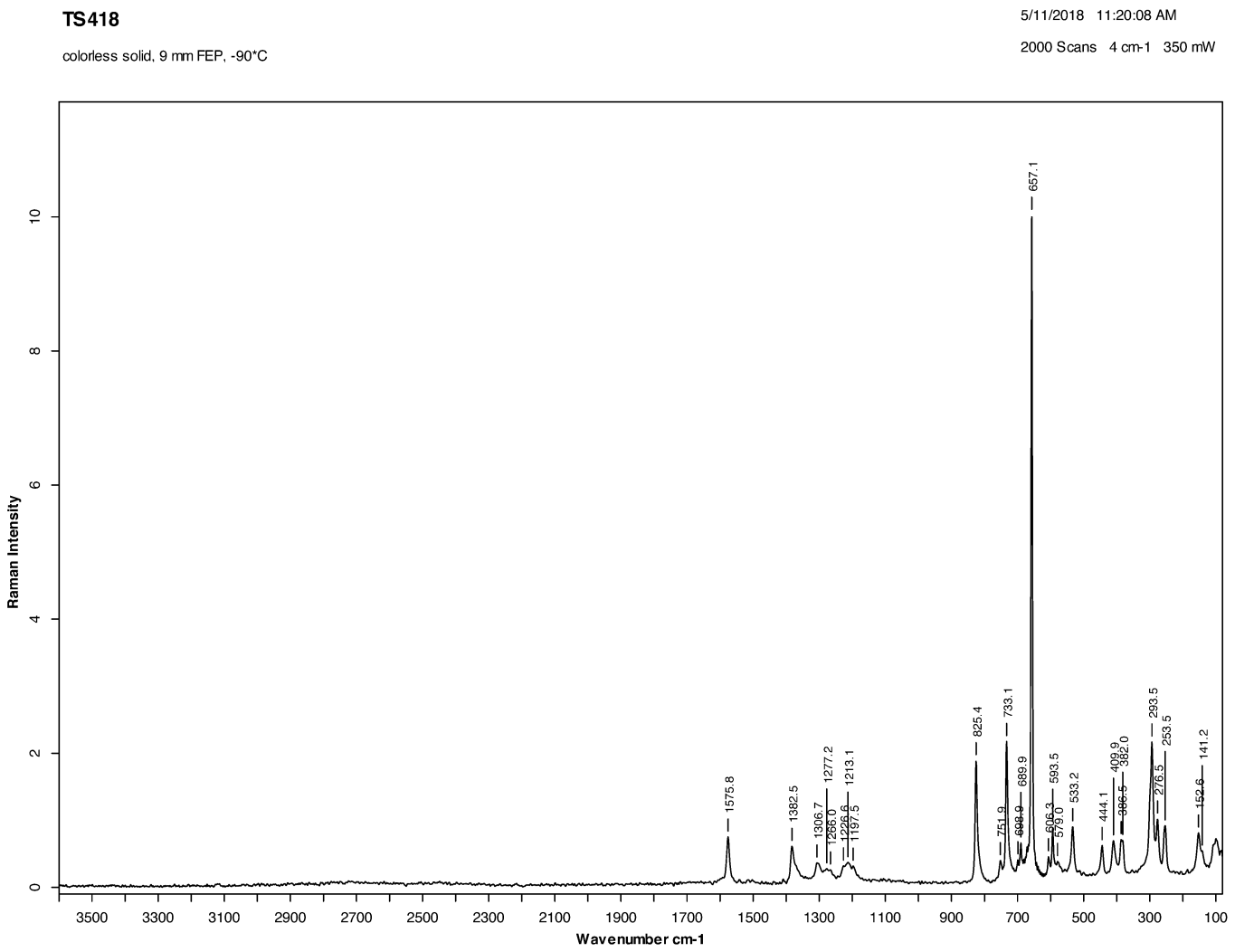


Table S1. Observed and unscaled calculated vibrational frequencies and intensities of $[CF_3C(OH)_2]^+$.

$[CF_3C(OH)_2]^+$			
Observed Raman[a]		Calculated	Approximate mode
AsF_6^-	SbF_6^-	(IR)[Raman][b]	description
		3598.2 (116.7)[91.4]	ν_s(OH)
		3583.7 (500.7)[23.4]	ν_{as}(OH)
		1691.1 (258.9)[1.1]	ν_{as}(CO)
1574.7 (0.9)	1575.8 (0.7)	1552.6 (143.5)[5.8]	ν_s(CO)
1382.5 (0.5)	*1382.5 (0.6)*		*FEP*
1304.7 (0.3)	*1306.7 (0.2)*		*FEP*
1270.2 (0.4)	1277.2 (0.1)	1260.2 (278.3)[1.9]	ν(CF)
	1266 (0.1)	1248.7 (120.7)[1.8]	ν(CF) + δ(COH)
1227.9 (0.3)	1226.6 (0.1)	1186.0 (372.5)[5.6]	δ(COH) + ν(CF)
1212.2 (0.4)	*1213.1 (0.3)*		*FEP*
1193.3 (0.4)	1197.5 (0.1)	1181.7 (372.5)[1.6]	δ(COH)
		1144.7 (193.0)[1.1]	δ(COH) + ν(CC)
823 (2.8)	825.4 (1.8)	804.1 (20.6)[8.8]	ν(CC)
		795.4 (33.9)[0.2]	$\omega(CO_2)$
751.3 (0.3)	*751.9 (0.2)*		*FEP*
733.2 (1.8)	*733.1 (1.9)*		*FEP*
	698.9 (0.1)	707.5 (36.9)[0.8]	δ(COH)
690.5 (10)			AsF_6^-
[d]	689.9 (0.3)	676.0 (207.8)[0.4]	δ(COH)
	657.1 (10)		SbF_6^-
		648.1 (60.8)[1.2]	$\delta(CO_2)$
	606.3 (0.2)		SbF_6^-
597.8 (0.9)	593.5 (0.7)	591.5 (1.3)[0.9]	$\delta(CF_3)$
[d]	579 (0.1)		SbF_6^-
578.0 (0.1)			AsF_6^-
538.3 (1.2)	533.2 (0.7)	501.0 (0.5)[0.4]	$\delta(CF_3)$
449.3 (0.8)	444.1 (0.4)	420.2 (2.4)[1.3]	$\delta(CF_3)$
426.2 (0.5)			AsF_6^-
402 (0.4)	409.9 (0.4)		?
384 (2.3)	*386.5 (0.5)*		*FEP*
	382 (0.1)	365.3 (15.4)[2.0]	δ(COO)
370.7 (1.6)			AsF_6^-
358.4 (0.9)			AsF_6^-
294.4 (0.6)	*293.5 (2.1)*		*FEP*
	276.5 (0.3)		SbF_6^-
260.2 (0.4)			AsF_6^-
251.8 (0.3)	253.5 (0.6)	230.2 (4.3)[0.1]	δ(CCF)
239.7 (0.3)			AsF_6^-
151 (0.8)	152.6 (0.7)	226.7 (0.0)[0.6]	$\tau(CF_3)$
142.8 (0.9)	141.2 (0.1)		?
		37.6 (0.8)[0.8]	τ(CCO)

[a] Observed Raman frequencies are given in cm^{-1} with intensities in parenthesis in arbitrary units normalized to the most intense band of the spectrum set at 10.0. [b] Calculated at the B3LYP//aug-CC-pVTZ level of theory. [c] ν: stretching vibration (s symmetric, as asymmetric), δ: bending, ω: wagging, τ: twisting. [d] Hidden by bands from the anion/FEP.

Figure S24: Raman spectrum of $CF_3CO(NH_2)$.

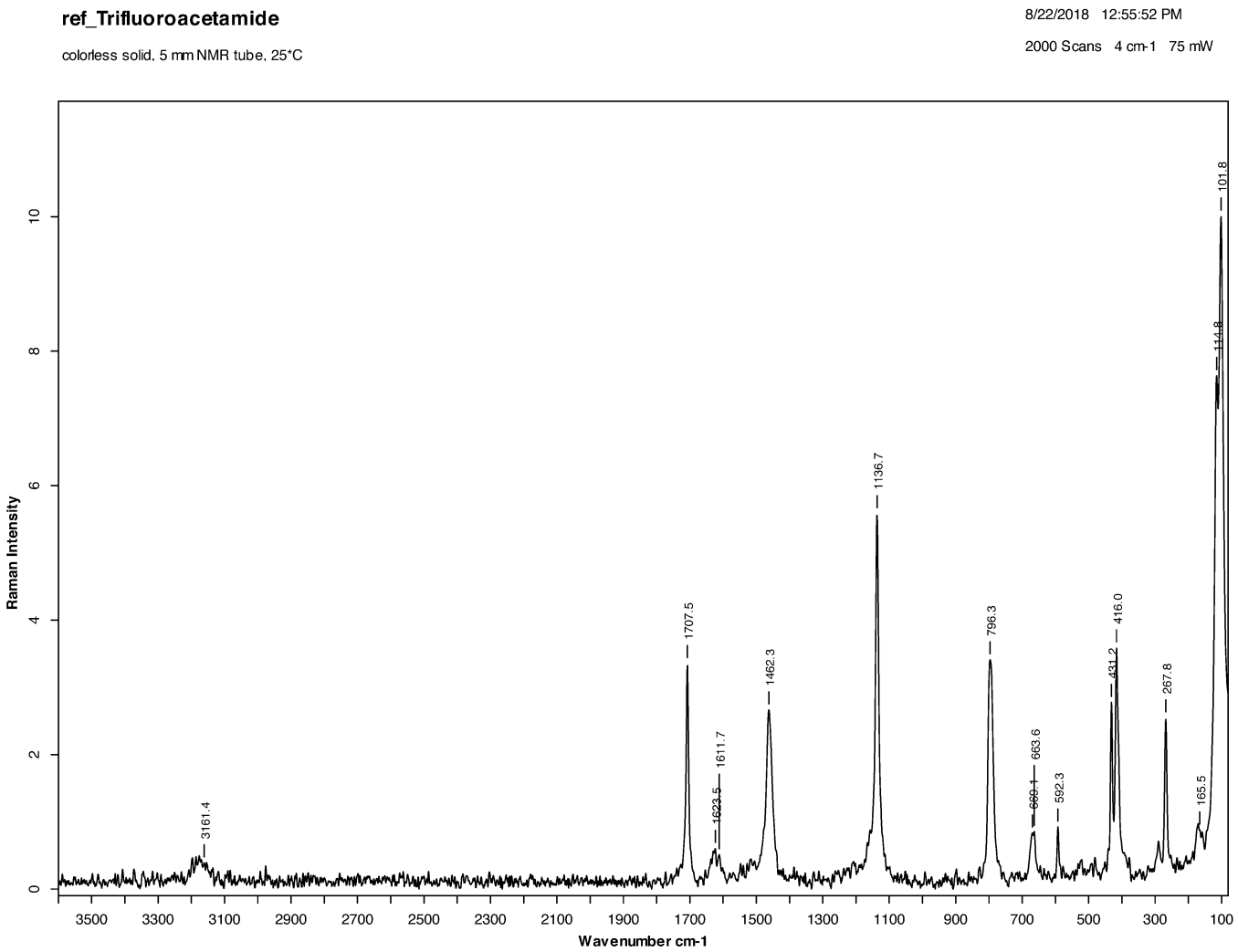


Figure S25: Raman spectrum of $[CF_3C(OH)(NH_2)][AsF_6]$.

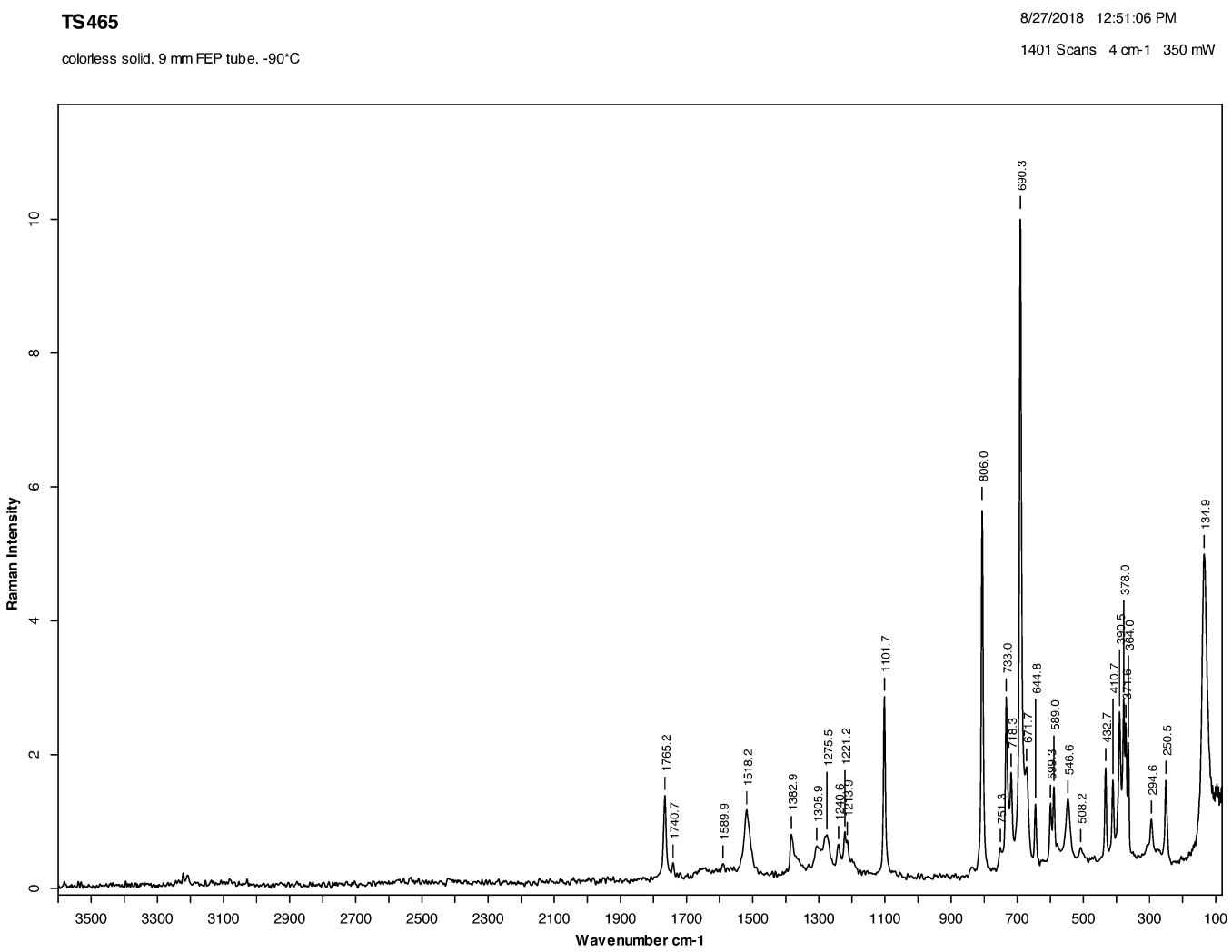


Figure S26: Raman spectrum of $[CF_3C(OH)(NH_2)][SbF_6]$.

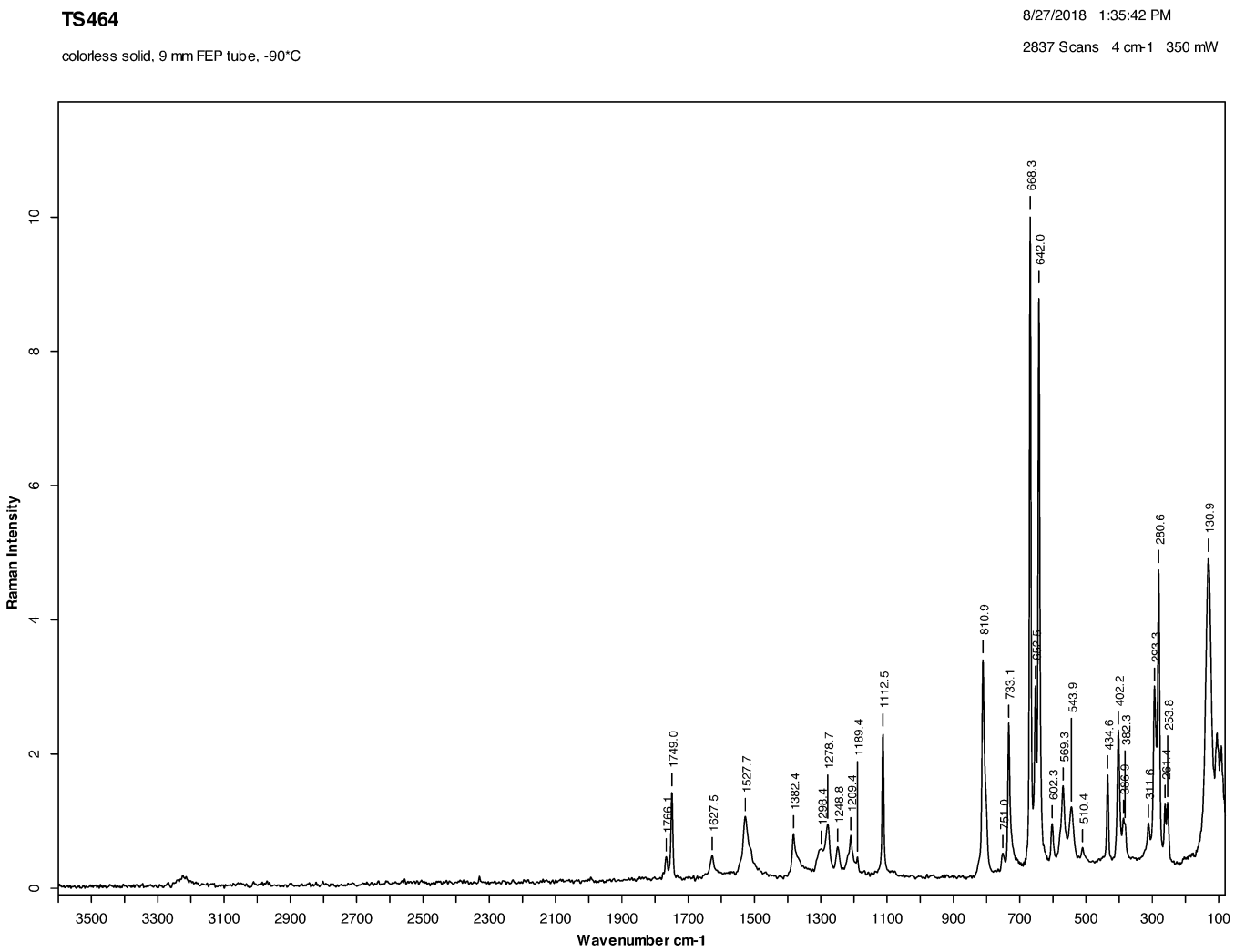
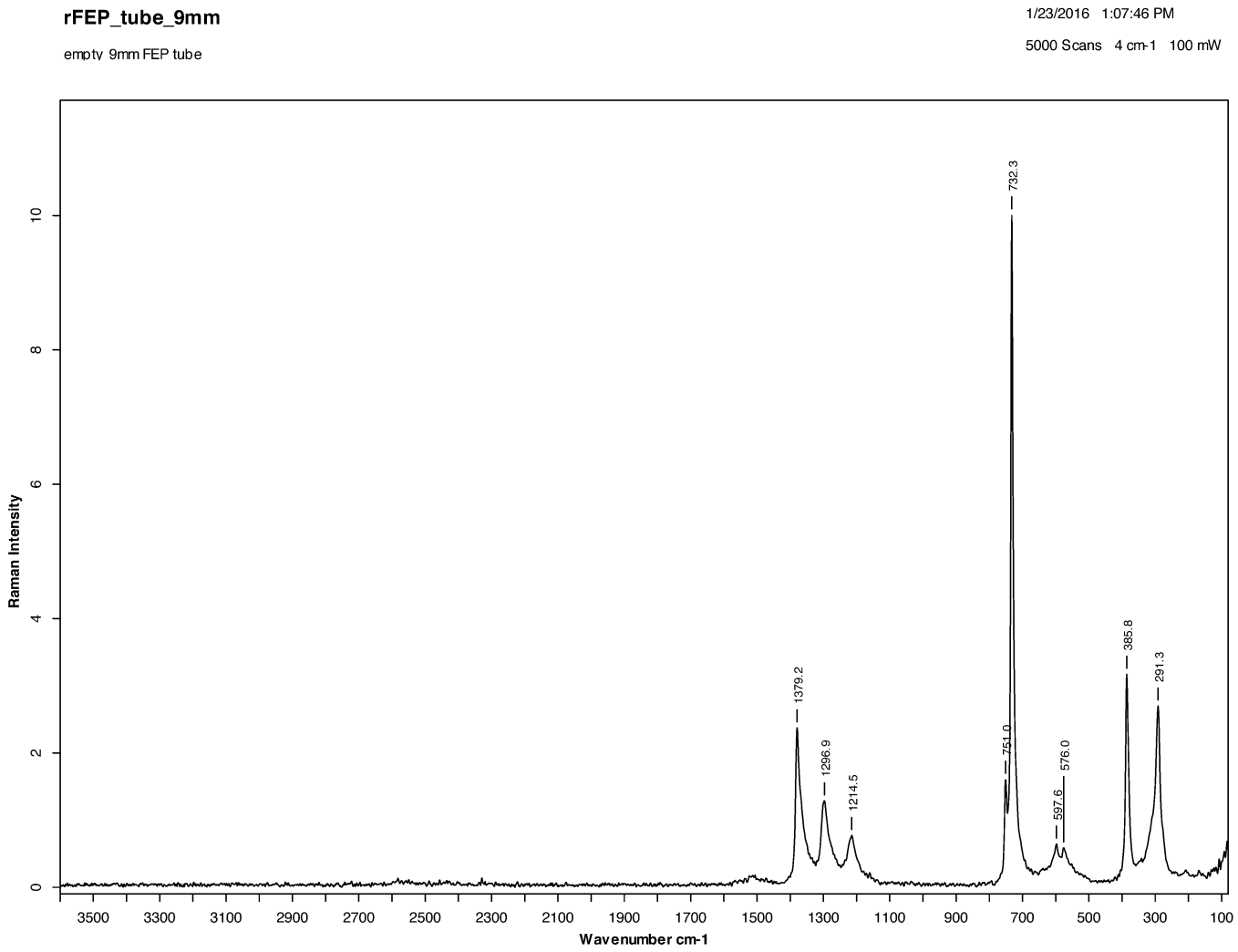


Table S2. Observed and unscaled calculated vibrational frequencies and intensities of $[CF_3C(OH)(NH_2)]^+$.

$[CF_3C(OH)(NH_2)]^+$			
Observed Raman[a]		Calculated	Approximate mode
$[AsF_6]^-$	$[SbF_6]^-$	(IR)[Raman][b]	description
		3678.8 (273.0)[48.8]	ν(OH)
		3602.7 (194.8)[25.2]	ν_s(NH)
		3489.8 (233.4)[75.1]	ν_{as}(NH)
	1766.1 (0.5)		
1765.2 (1.4)	1749.0 (1.4)	1762.0 (265.0)[2.4]	ν(CN)
1740.7 (0.4)			
1589.9 (0.4)	1627.5 (0.5)	1599.0 (17.3)[4.5]	ν(CO) + $\delta(NH_2)$
1518.2 (1.2)	1527.7 (1.1)	1519.5 (98.7)[7.6]	ν(CO) + ν(CC)
1382.9 (0.8)	*1382.4 (0.8)*		*FEP*
1305.9 (0.6)	*1298.4 (0.6)*		*FEP*
1275.5 (0.8)	1278.7 (1.0)	1256.1 (166.1)[1.6]	ν(CF)
1240.6 (0.7)	1248.8 (0.6)	1223.5 (315.3)[5.4]	δ(COH) + ν(CF)
1221.2 (0.8)			
1213.9 (0.7)	1209.4 (0.8)	1207.9 (309.2)[4.1]	δ(COH)
	1189.4 (0.5)	1173.4 (142.7)[0.7]	ν_s(CF) + ν(CC)
1101.7 (2.9)	1112.5 (2.3)	1099.6 (28.4)[2.7]	ν(CO) + δ(CNH)
806.0 (5.7)	810.9 (3.4)	799.8 (8.7)[8.1]	ν(CC)
	sh	790.7 (52.0)[0.5]	ω(NCO)
751.3 (0.6)	*751.0 (0.5)*		*FEP*
733.0 (2.9)	*733.1 (2.5)*		*FEP*
		726.9 (173.9)[0.0]	$\omega(NH_2)$
718.3 (1.7)			AsF_6^-
690.3 (10.1)			AsF_6^-
671.7 (1.8)	[d]	701.7 (1.2)[0.2]	$\tau(NH_2)$
	668.3 (10.0)		SbF_6^-
644.8 (1.3)	652.5 (3.0)	625.9 (18.8)[1.2]	δ(NCO)
	642.0 (8.9)		SbF_6^-
599.3 (1.3)	602.3 (1.0)	589.4 (1.4)[1.1]	δ(CCN)
589.0 (1.5)			AsF_6^-
	569.3 (1.5)		SbF_6^-
546.6 (1.3)	543.9 (1.2)	538.4 (73.9)[0.3]	ω(COH)
508.2 (0.6)	510.4 (0.6)	499.6 (8.9)[0.7]	$\delta(CF_3)$
432.7 (1.8)	434.6 (1.7)	415.8 (8.7)[1.4]	$\delta(CF_3)$
410.7 (1.6)			AsF_6^-
	402.2 (2.4)		SbF_6^-
390.5 (2.6)	*386.9 (1.0)*		*FEP*
378.0 (2.8)	382.3 (1.0)	369.8 (18.2)[1.9]	δ(NCO)
371.6 (2.5)			AsF_6^-
364.0 (2.2)			AsF_6^-
	311.6 (1.0)		SbF_6^-
294.6 (1.0)	*293.3 (3.0)*		*FEP*
	280.6 (4.8)		SbF_6^-
	261.4 (1.3)		SbF_6^-
250.5 (1.6)	253.8 (1.3)	233.4 (0.7)[0.6]	$\delta(CF_3)$
134.9 (5.0)	130.9 (4.9)	231.8 (5.4)[0.2]	δ(CCO)
		22.6 (0.5)[1.5]	τ(CCO)

[a] Observed Raman frequencies are given in cm^{-1} with intensities in parenthesis in arbitrary units normalized to the most intense band of the spectrum set at 10.0.[b] Calculated at the B3LYP//aug-CC-pVTZ level of theory. [c] ν: stretching vibration (s: symmetric, as: asymmetric), δ: bending, ω: wagging, τ: twisting. [d] Hidden by bands from the anion/FEP.

Figure S27: Raman spectrum of empty FEP tube.



Crystallographic Details

$[CF_3C(OH)_2][SbF_6]$

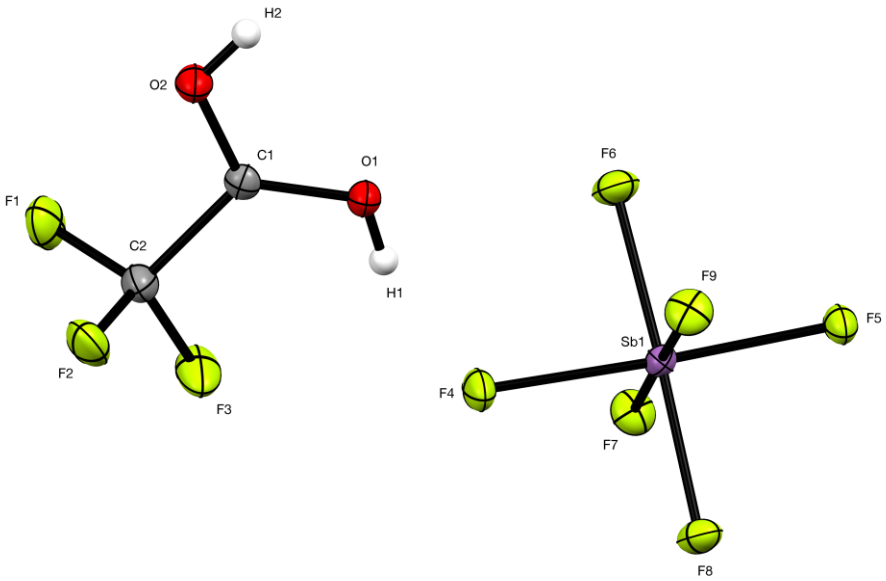


Figure S28: Asymmetric unit in the crystal structure of $[CF_3C(OH)_2][SbF_6]$.

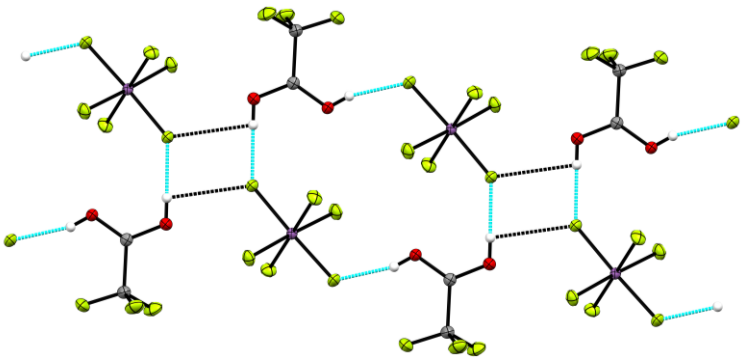


Figure S29: Hydrogen bonding in the crystal structure of $[CF_3C(OH)_2][SbF_6]$. Hydrogen bonds in cyan.

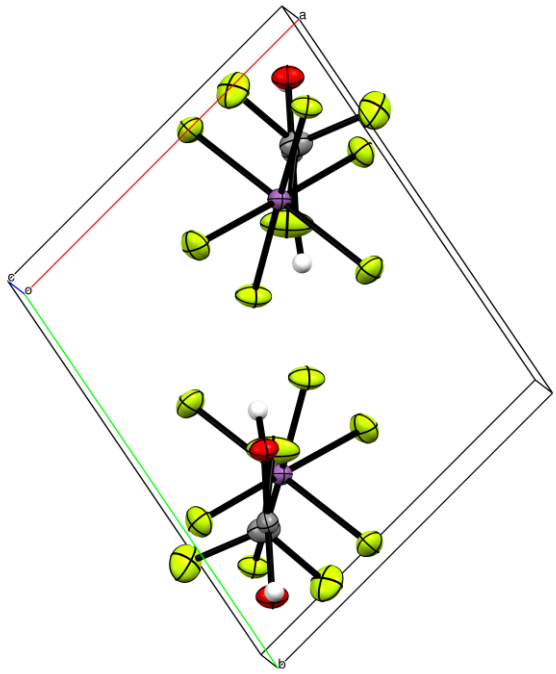


Figure S30: Packing diagram of $[CF_3C(OH)_2][SbF_6]$. View along the 001 direction.

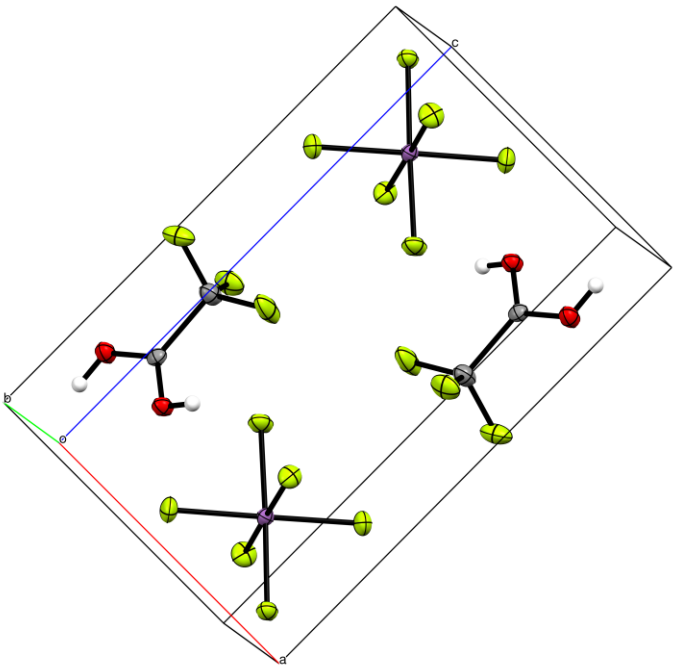


Figure S31: Packing diagram of $[CF_3C(OH)_2][SbF_6]$. View along the 010 direction.

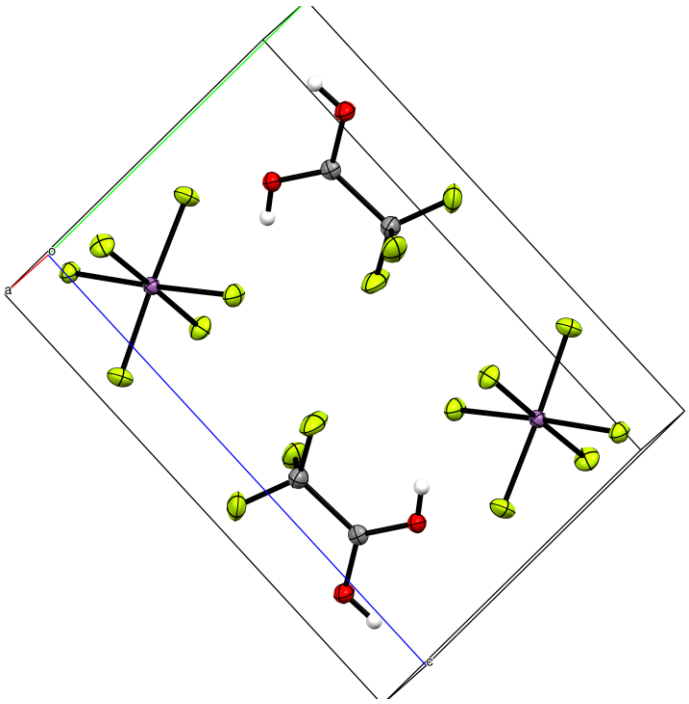


Figure S32: Packing diagram of $[CF_3C(OH)_2][SbF_6]$. View along the 100 direction.

Table S3: Sample and crystal data for $[CF_3C(OH)_2][SbF_6]$.

Identification code	TS417	
Chemical formula	$C_2H_2F_9O_2Sb$	
Formula weight	350.79 g/mol	
Temperature	108(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 5.8318(4) Å	α = 91.6940(10)°
	b = 6.7790(5) Å	β = 90.2280(10)°
	c = 10.4261(7) Å	γ = 100.8210(10)°
Volume	404.66(5) $Å^3$	
Z	2	
Density (calculated)	2.879 g/cm^3	
Absorption coefficient	3.545 mm^{-1}	
F(000)	324	

Table S4: Data collection and structure refinement for $[CF_3C(OH)_2][SbF_6]$.

Diffractometer	Bruker APEX DUO	
Radiation source	fine-focus tube, MoKα	
Theta range for data collection	1.95 to 30.55°	
Index ranges	-8<=h<=8, -9<=k<=9, -14<=l<=14	
Reflections collected	10127	
Independent reflections	2453 [R(int) = 0.0293]	
Coverage of independent reflections	98.9%	
Absorption correction	multi-scan	
Structure solution technique	direct methods	
Structure solution program	SHELXTL XT 2014/4 (Bruker AXS, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXTL XL 2014/7 (Bruker AXS, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2453 / 0 / 135	
Goodness-of-fit on F^2	1.031	
Δ/σ_{max}	0.001	
Final R indices	2233 data; I>2σ(I)	R1 = 0.0195, wR2 = 0.0407
	all data	R1 = 0.0246, wR2 = 0.0423
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0193P)^2+0.2321P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.658 and -0.676 $eÅ^{-3}$	
R.M.S. deviation from mean	0.126 $eÅ^{-3}$	

Table S5: Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for $[CF_3C(OH)_2][SbF_6]$.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.8042(4)	0.2360(3)	0.7523(2)	0.0131(4)
C2	0.8208(4)	0.2236(3)	0.6044(2)	0.0186(4)
O1	0.7058(3)	0.3613(2)	0.81020(15)	0.0152(3)
O2	0.9040(3)	0.1143(2)	0.80952(17)	0.0174(3)
F1	0.7622(3)	0.0357(2)	0.56232(14)	0.0257(3)
F2	0.0400(3)	0.2937(2)	0.57223(14)	0.0268(3)
F3	0.6829(3)	0.3338(3)	0.55322(14)	0.0337(4)
F4	0.5009(2)	0.6182(2)	0.71201(13)	0.0199(3)
F5	0.1128(2)	0.8457(2)	0.94587(12)	0.0166(3)
F6	0.2143(2)	0.4828(2)	0.89651(13)	0.0206(3)
F7	0.0561(2)	0.6753(2)	0.71043(13)	0.0190(3)
F8	0.3944(2)	0.98458(19)	0.74985(13)	0.0186(3)
F9	0.5561(2)	0.8015(2)	0.94146(13)	0.0202(3)
Sb1	0.30546(2)	0.73613(2)	0.82676(2)	0.01143(5)

Table S6: Bond lengths (Å) for $[CF_3C(OH)_2][SbF_6]$.

C1-O1	1.253(3)	C1-O2	1.258(3)
C1-C2	1.547(3)	C2-F1	1.317(3)
C2-F3	1.317(3)	C2-F2	1.325(3)
O1-H1	0.72(3)	O2-H2	0.77(3)
F4-Sb1	1.9146(13)	F5-Sb1	1.9043(12)
F6-Sb1	1.8693(13)	F7-Sb1	1.8673(13)
F8-Sb1	1.8718(13)	F9-Sb1	1.8640(13)

Table S7: Bond angles (°) for $[CF_3C(OH)_2][SbF_6]$.

O1-C1-O2	123.0(2)	O1-C1-C2	122.66(19)
O2-C1-C2	114.35(18)	F1-C2-F3	110.2(2)
F1-C2-F2	108.83(18)	F3-C2-F2	109.6(2)
F1-C2-C1	110.32(19)	F3-C2-C1	109.61(18)
F2-C2-C1	108.24(18)	C1-O1-H1	116.(3)
C1-O2-H2	113.(2)	F9-Sb1-F7	178.93(6)
F9-Sb1-F6	91.69(6)	F7-Sb1-F6	89.37(6)
F9-Sb1-F8	90.12(6)	F7-Sb1-F8	88.82(6)
F6-Sb1-F8	177.53(6)	F9-Sb1-F5	89.72(6)
F7-Sb1-F5	90.32(6)	F6-Sb1-F5	90.17(6)
F8-Sb1-F5	91.52(6)	F9-Sb1-F4	89.18(6)
F7-Sb1-F4	90.83(6)	F6-Sb1-F4	87.84(6)

F8-Sb1-F4	90.51(6)	F5-Sb1-F4	177.69(6)

Table S8: Torsion angles (°) for $[CF_3C(OH)_2][SbF_6]$.

O1-C1-C2-F1	-133.1(2)	O2-C1-C2-F1	49.0(3)
O1-C1-C2-F3	-11.6(3)	O2-C1-C2-F3	170.6(2)
O1-C1-C2-F2	107.9(2)	O2-C1-C2-F2	-69.9(2)

Table S9: Anisotropic atomic displacement parameters (Å^2) for $[CF_3C(OH)_2][SbF_6]$.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0107(9)	0.0132(10)	0.0150(10)	0.0003(8)	0.0007(7)	0.0009(7)
C2	0.0242(12)	0.0188(11)	0.0142(10)	0.0004(8)	0.0015(9)	0.0080(9)
O1	0.0182(8)	0.0151(8)	0.0137(7)	0.0006(6)	0.0020(6)	0.0066(6)
O2	0.0215(8)	0.0188(8)	0.0136(8)	0.0008(6)	-0.0003(6)	0.0085(6)
F1	0.0329(8)	0.0224(7)	0.0201(7)	-0.0083(6)	0.0018(6)	0.0020(6)
F2	0.0307(8)	0.0274(8)	0.0207(7)	0.0004(6)	0.0115(6)	0.0015(6)
F3	0.0498(10)	0.0455(10)	0.0149(7)	0.0034(7)	-0.0021(7)	0.0323(8)
F4	0.0237(7)	0.0232(7)	0.0162(6)	0.0009(5)	0.0050(5)	0.0130(5)
F5	0.0183(6)	0.0200(7)	0.0136(6)	0.0004(5)	0.0020(5)	0.0089(5)
F6	0.0242(7)	0.0144(6)	0.0236(7)	0.0064(5)	0.0016(6)	0.0034(5)
F7	0.0166(6)	0.0230(7)	0.0167(6)	-0.0017(5)	-0.0047(5)	0.0023(5)
F8	0.0190(7)	0.0151(6)	0.0222(7)	0.0065(5)	0.0017(5)	0.0034(5)
F9	0.0164(6)	0.0243(7)	0.0199(7)	-0.0002(6)	-0.0070(5)	0.0043(5)
Sb1	0.01159(7)	0.01115(7)	0.01203(7)	0.00057(5)	0.00013(5)	0.00333(5)

Table S10: Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for $[CF_3C(OH)_2][SbF_6]$.

	x/a	y/b	z/c	U(eq)
H1	0.661(6)	0.431(5)	0.770(3)	0.036(10)
H2	0.894(5)	0.122(5)	0.883(3)	0.030(9)

$[CF_3C(OH)(NH_2)][SbF_6]$

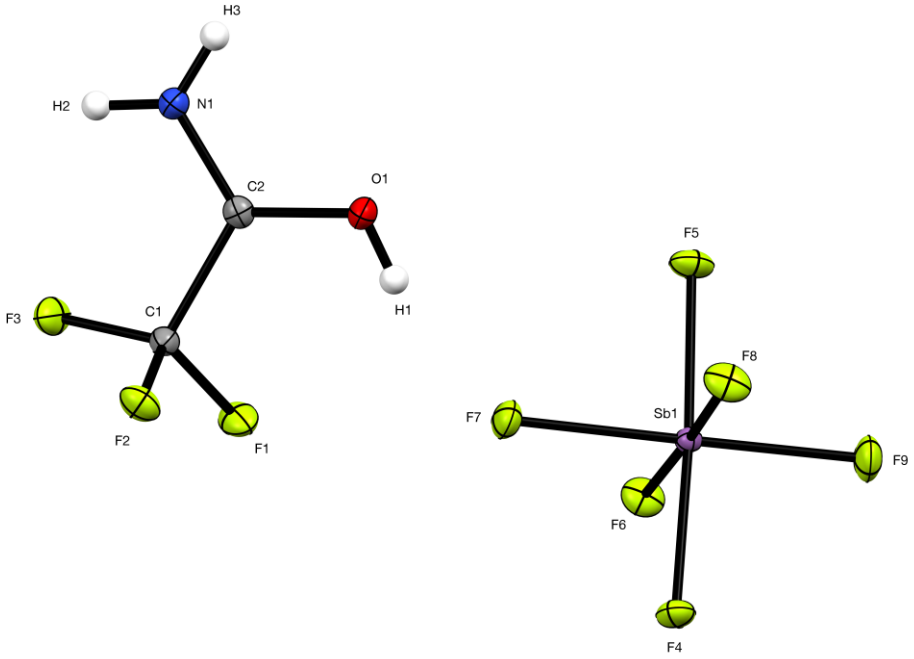


Figure S32: Asymmetric unit in the crystal structure of $[CF_3C(OH)(NH_2)][SbF_6]$.

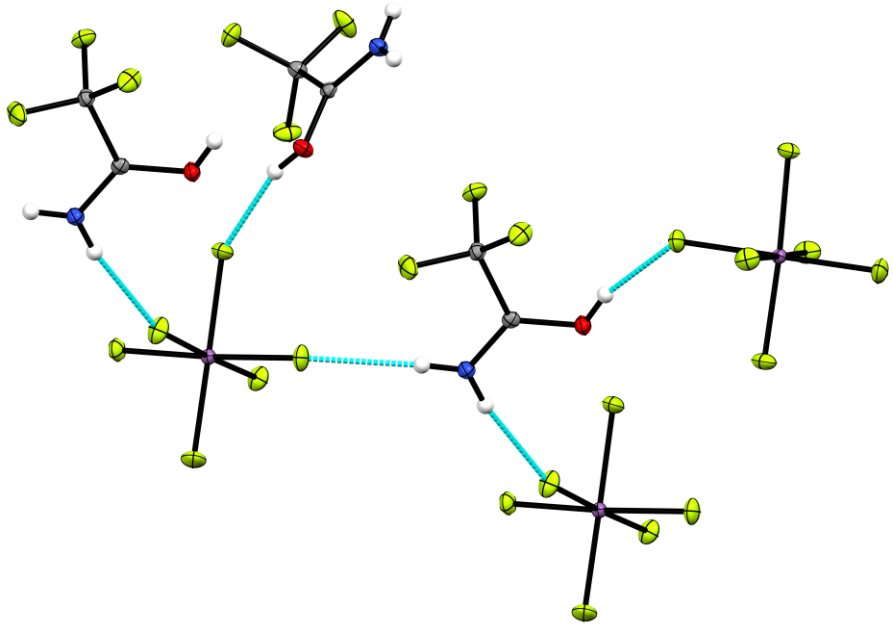


Figure S33: Hydrogen bonding in the crystal structure of $[CF_3C(OH)(NH_2)][SbF_6]$. Hydrogen bonds in cyan.

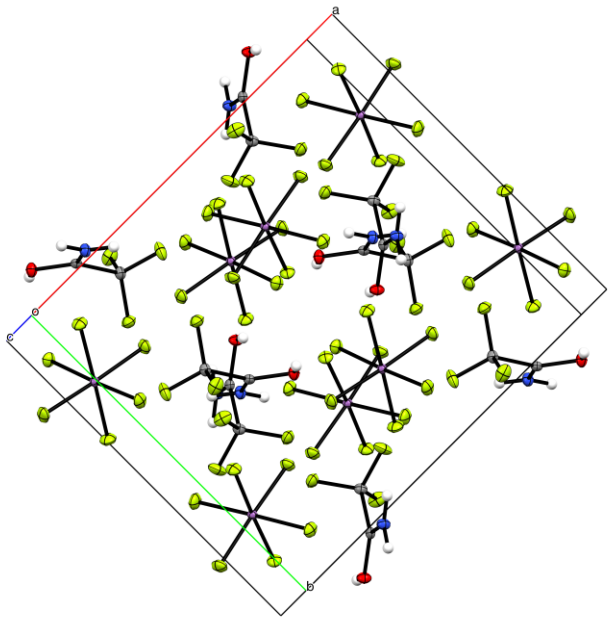


Figure S34: Packing diagram of $[CF_3C(OH)(NH_2)][SbF_6]$. View along the 001 direction.

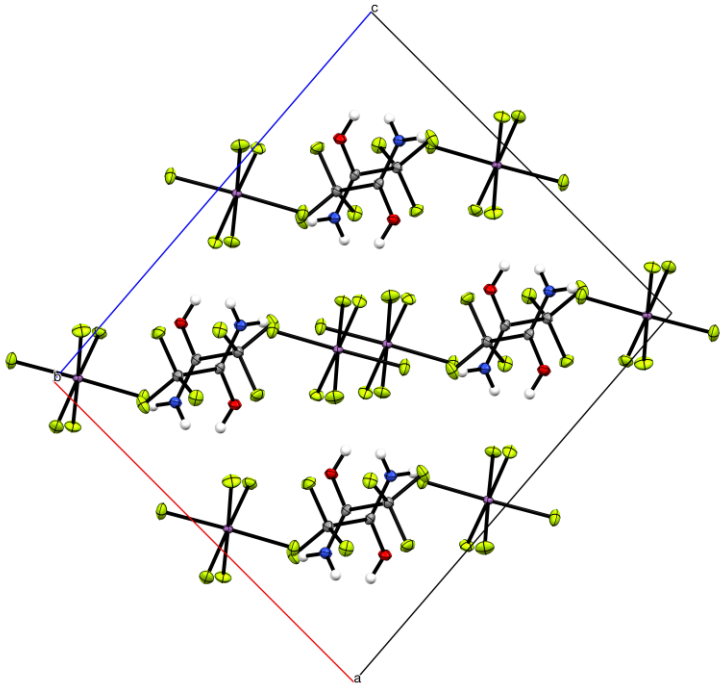


Figure S35: Packing diagram of $[CF_3C(OH)(NH_2)][SbF_6]$. View along the 010 direction.

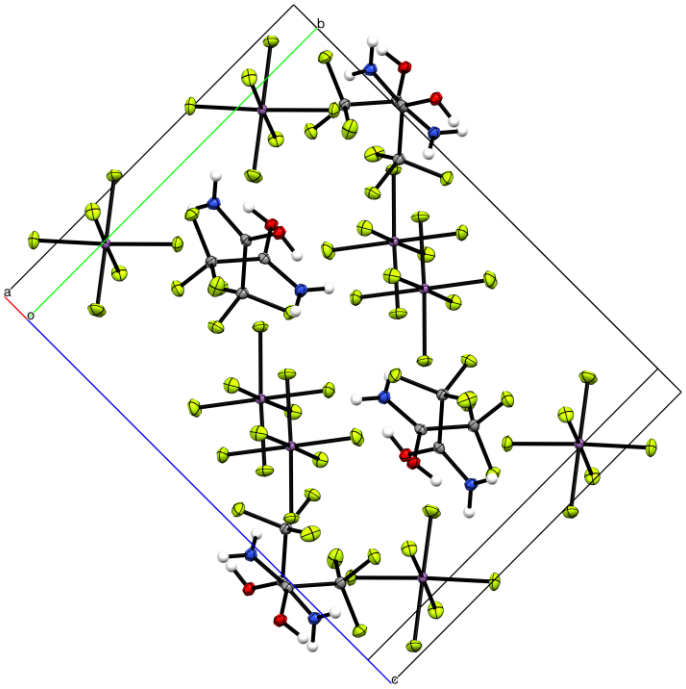


Figure S36: Packing diagram of $[CF_3C(OH)(NH_2)][SbF_6]$. View along the 100 direction.

Table S11: Sample and crystal data for $[CF_3C(OH)(NH_2)][SbF_6]$.

Identification code	TS464	
Chemical formula	$C_2H_3F_9NOSb$	
Formula weight	349.80 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.316 x 0.318 x 0.396 mm	
Crystal habit	clear colourless prism	
Crystal system	monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 11.4747(12) Å	α = 90°
	b = 10.4829(11) Å	β = 94.205(2)°
	c = 13.1367(13) Å	γ = 90°
Volume	1575.9(3) $Å^3$	
Z	8	
Density (calculated)	2.949 g/cm^3	
Absorption coefficient	3.635 mm^{-1}	
F(000)	1296	

Table S12: Data collection and structure refinement for $[CF_3C(OH)(NH_2)][SbF_6]$.

Diffractometer	Bruker APEX DUO	
Radiation source	fine-focus tube, MoKα	
Theta range for data collection	2.63 to 30.56°	
Index ranges	-16<=h<=16, -14<=k<=14, -18<=l<=18	
Reflections collected	18920	
Independent reflections	2403 [R(int) = 0.0193]	
Coverage of independent reflections	99.8%	
Absorption correction	multi-scan	
Structure solution technique	direct methods	
Structure solution program	SHELXTL XT 2014/4 (Bruker AXS, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXTL XL 2014/7 (Bruker AXS, 2014)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2403 / 0 / 139	
Goodness-of-fit on F^2	1.289	
Δ/σ_{max}	0.004	
Final R indices	2356 data; I>2σ(I)	R1 = 0.0127, wR2 = 0.0321
	all data	R1 = 0.0133, wR2 = 0.0324

Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0130P)^2+1.6814P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.387 and -0.783 eÅ^{-3}
R.M.S. deviation from mean	0.108 eÅ^{-3}

Table S13: Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for $[CF_3C(OH)(NH_2)][SbF_6]$.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Sb1	0.53971(2)	0.73531(2)	0.53965(2)	0.00743(3)
N1	0.75128(11)	0.52036(12)	0.14654(9)	0.0114(2)
O1	0.63992(9)	0.58244(10)	0.26967(8)	0.01200(18)
C1	0.78555(11)	0.41494(13)	0.31108(10)	0.0104(2)
F1	0.80320(8)	0.46420(9)	0.40409(6)	0.01733(18)
C2	0.72232(11)	0.51255(12)	0.23894(10)	0.0093(2)
F2	0.71922(8)	0.31153(8)	0.31680(7)	0.01550(17)
F3	0.88644(8)	0.38185(10)	0.27667(7)	0.01838(18)
F5	0.57568(8)	0.85227(9)	0.43796(7)	0.01536(17)
F4	0.50814(8)	0.61198(8)	0.63692(6)	0.01383(16)
F6	0.68690(8)	0.76237(8)	0.60781(7)	0.01509(17)
F9	0.47277(8)	0.86451(9)	0.61389(7)	0.01809(18)
F8	0.39390(8)	0.70219(9)	0.46829(7)	0.01624(17)
F7	0.60482(8)	0.60287(9)	0.46226(7)	0.01504(17)

Table S14: Bond lengths (Å) for $[CF_3C(OH)(NH_2)][SbF_6]$.

Sb1-F9	1.8670(9)	Sb1-F4	1.8717(8)
Sb1-F6	1.8743(9)	Sb1-F5	1.8812(9)
Sb1-F8	1.8892(9)	Sb1-F7	1.9054(9)
N1-C2	1.2844(17)	N1-H2	0.80(2)
N1-H3	0.81(2)	O1-C2	1.2844(16)
O1-H1	0.75(2)	C1-F3	1.3197(15)
C1-F1	1.3283(15)	C1-F2	1.3298(16)
C1-C2	1.5397(18)		

Table S15: Bond angles (°) for $[CF_3C(OH)(NH_2)][SbF_6]$.

F9-Sb1-F4	92.11(4)	F9-Sb1-F6	91.80(4)
F4-Sb1-F6	89.49(4)	F9-Sb1-F5	91.04(4)

F4-Sb1-F5	176.85(4)	F6-Sb1-F5	90.21(4)
F9-Sb1-F8	90.53(4)	F4-Sb1-F8	90.18(4)
F6-Sb1-F8	177.66(4)	F5-Sb1-F8	89.99(4)
F9-Sb1-F7	178.75(4)	F4-Sb1-F7	87.94(4)
F6-Sb1-F7	89.45(4)	F5-Sb1-F7	88.91(4)
F8-Sb1-F7	88.22(4)	C2-N1-H2	118.5(16)
C2-N1-H3	117.5(15)	H2-N1-H3	124.(2)
C2-O1-H1	114.6(18)	F3-C1-F1	109.80(11)
F3-C1-F2	108.98(11)	F1-C1-F2	108.31(11)
F3-C1-C2	110.46(11)	F1-C1-C2	109.94(11)
F2-C1-C2	109.31(11)	O1-C2-N1	120.54(13)
O1-C2-C1	120.68(12)	N1-C2-C1	118.76(12)

Table S16: Torsion angles (°) for $[CF_3C(OH)(NH_2)][SbF_6]$.

F3-C1-C2-O1	-161.41(12)	F1-C1-C2-O1	-40.07(17)
F2-C1-C2-O1	78.69(15)	F3-C1-C2-N1	20.50(17)
F1-C1-C2-N1	141.83(13)	F2-C1-C2-N1	-99.40(14)

Table S17: Anisotropic atomic displacement parameters ($Å^2$) for $[CF_3C(OH)(NH_2)][SbF_6]$.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sb1	0.00760(5)	0.00734(5)	0.00741(5)	0.00017(3)	0.00096(3)	-0.00020(3)
N1	0.0119(5)	0.0121(5)	0.0104(5)	0.0009(4)	0.0022(4)	0.0018(4)
O1	0.0129(4)	0.0134(5)	0.0100(4)	-0.0003(4)	0.0028(4)	0.0030(4)
C1	0.0106(6)	0.0113(6)	0.0093(5)	0.0001(4)	0.0009(4)	0.0014(4)
F1	0.0254(5)	0.0161(4)	0.0097(4)	-0.0022(3)	-0.0038(3)	0.0029(3)
C2	0.0081(5)	0.0085(5)	0.0112(5)	-0.0005(4)	0.0001(4)	-0.0015(4)
F2	0.0167(4)	0.0107(4)	0.0188(4)	0.0027(3)	-0.0003(3)	-0.0018(3)
F3	0.0111(4)	0.0263(5)	0.0182(4)	0.0059(4)	0.0039(3)	0.0078(3)
F5	0.0159(4)	0.0158(4)	0.0144(4)	0.0066(3)	0.0017(3)	-0.0026(3)
F4	0.0161(4)	0.0138(4)	0.0120(4)	0.0044(3)	0.0034(3)	-0.0011(3)
F6	0.0113(4)	0.0164(4)	0.0169(4)	0.0006(3)	-0.0037(3)	-0.0028(3)
F9	0.0200(4)	0.0132(4)	0.0219(4)	-0.0043(3)	0.0073(4)	0.0040(3)
F8	0.0117(4)	0.0177(4)	0.0184(4)	0.0026(3)	-0.0051(3)	-0.0037(3)
F7	0.0187(4)	0.0134(4)	0.0137(4)	-0.0032(3)	0.0055(3)	0.0015(3)

Table S18: Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for $[CF_3C(OH)(NH_2)][SbF_6]$.

	x/a	y/b	z/c	U(eq)
H1	0.6293(19)	0.574(2)	0.3247(18)	0.024(6)

H2	0.8028(19)	0.475(2)	0.1292(17)	0.025(6)
H3	0.7161(18)	0.572(2)	0.1091(16)	0.020(5)

References

1. K. O. Christe, R. D. Wilson, C. J. Schack and D. D. Desmarteau, *Inorganic Syntheses*, John Wiley & Sons, Inc., 1986, 3-6.
2. K. O. Christe, W. W. Wilson and C. J. Schack, *J. Fluorine Chem,* 1978**, 11**, 71-85.
3. H. P. A. Mercier, J. C. P. Sanders, G. J. Schrobilgen and S. S. Tsai, *Inorg. Chem.,* 1993, ***32***, 386-393.
4. H. Moissan, G. Steinheil, Paris, 1900, **396**, 1.
5. O. Ruff and H. Graf, *Ber. deutsch. chem. Ges.* 1906, **39**, 67-71.
6. W. L. F. Armarego and C. L. L. Chai, Chapter 4 in *Purification of Laboratory Chemicals (Sixth Edition)*, Butterworth-Heinemann, Oxford, 2009, 189.
7. D. R. Schaad and C. R. Landis, *Organomet.* 1992, **11**, 2024-2029.
8. *SAINT+ Vol. 8.27B*. Bruker AXS: Madison, WI, 2011.
9. *SADABS Vol. 2012-1*. Bruker AXS: Madison, WI, 2012.
10. G. M. Sheldrick, SHELX. *Acta Cryst A,* 2008**, 64**, 112-122.
11. G. M. Sheldrick, SHELXL. *Acta Cryst. C,* 2015, **71**, 3-8.
12. C. B. Hubschle, G. M. Sheldrick and B. Dittrich, B., ShelXle, *J. Appl. Crystall.* 2011, **44,** 1281-1284.
13. *SHELXT*. G. M. Sheldrick: 2012.
14. *SHELXTL 2014/7*. Bruker AXS: Madison, WI, 2014.
15. *Mercury CSD*. CCDC: 2017.