Supplementary information for

Well-defined bridged dicopper(III) chloride, azide and amino complexes

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General

All solvents used for the reactions were HPLC grade. All commercially available chemicals were purchased from commercial suppliers (BLD Pharmatech, Sigma-Aldrich) and were used as received. Copper(III) trifluoromethyl hydroxide tetramer **1** was prepared according to known procedure reported by us.[1] Yields refer to isolated compounds (unless noted otherwise in the applications part). NMR spectra were recorded on a JEOL 400 MHz spectrometer in the solvent indicated using 5 mm diameter NMR tubes; chemical shifts (δ) are given in ppm relative to the residual solvent peak. The chemical shift values (*δ*) are reported in ppm relative to TMS (0 ppm for ^{1}H and ^{13}C NMR) and $CFCl_3$ (0 ppm for ^{19}F NMR). IR spectra were recorded on a Nicolet 6700 FTIR (Thermo Fisher Scientific) spectrometer. Elemental analysis for the determination of purity was performed by complexometric titration of copper with EDTA, due to unavailability of elemental analysis service for highly unstable and temperature-sensitive compounds. XPS analysis was carried out using an EnviroESCA spectrometer (SPECS Surface Nano Analysis GmbH, Berlin, Germany), equipped with a monochromatic Al Kα X-ray source (Excitation Energy = 1486.71 eV) and a PHOIBOS 150 analyzer operated in fixed analyzer transmission (FAT) mode. Measurements were performed under ultra-high vacuum ($p < 10^{-5}$mbar). Samples were prepared indium foil and measured in normal emission geometry at a source-to-sample angle of 55°. Instrument calibration followed the technical procedure provided by SPECS (calibration was performed according to ISO 15472). High-resolution spectra were recorded at a pass energy of 50 eV. Data fitting was conducted using the UNIFIT 2022 software, with a Shirley background and a Lorentzian-Gaussian (L-G) sum function.

X-ray crystallography (general procedure)

A crystal was mounted on a MiTeGen micromount with perfluoroether oil. Data were collected from a shock-cooled single crystal at 150.00 K on a Bruker D8 VENTURE dual wavelength Mo/Cu three-circle diffractometer with a microfocus sealed X-ray tube using a mirror optics as monochromator and a Bruker PHOTON II detector. The diffractometer was equipped with an Oxford Cryostream 700 low temperature device and used MoK_α radiation ($\lambda = 0.71073$ Å). All data were integrated with SAINT V8.41 and a multi-scan absorption correction using SADABS 2016/2 was applied.[2,3] The structure was solved by direct methods with SHELXT 2018/2 and refined by full-matrix least-squares methods against F^2 using XL.[4,5] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined isotropic on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre.[6] CCDC 2533527 (**3**), 2551392 (**4**), 2539161 (**4 · 0.5**$\mathbf{C_3H_6O}$), and 2533528 (**5**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures. The CIF files were generated using FinalCif.[7]

Synthesis of bis(μ₂-chlorido)dicopper(III) complex 3 $[Cu(CF_3)_2Cl \cdot H_2O]_2$

In a 10 ml round-bottomed Schlenk flask under argon atmosphere to the solid heterocubane **1** (21.8 mg, 0.025 mmol [0.1 mmol monomer]) dry dichloromethane (1 ml) was added and the mixture was cooled to −40°C. Trimethylsilyl chloride (25 µl, 0.2 mmol, 2 equiv.) was added with vigorous stirring. The mixture was stirred at −40°C for 1 hour; during this time the solution turned intensive yellow. It was concentrated to ca. 0.2 ml volume under vacuum, then layered with pentane (ca. 2 ml) containing 0.5% of acetone. Crystallization at −40°C for 2 days afforded yellow crystals of **bis(μ₂-chlorido)-diaqua-tetrakis(trifluoromethyl)dicopper(III) 3** with a composition $[Cu(CF_3)_2Cl \cdot H_2O]_2$ (11 mg, 43%), which were dried by a stream of argon at −40°C to −20°C (solvents including outer-sphere acetone are removed at this step) and collected. **^{19}F NMR** (376 MHz, CD_3CN, 293 K) δ −23.3 (br s, 6F); **^{19}F NMR** (CD_2Cl_2, 376 MHz, 213 K) δ −20.1 (br s, 6F); **^{13}C{^{19}F} NMR** (CD_2Cl_2, 101 MHz, 213 K) δ 121.2 (br) and 117.4 (br) [apparent d, $J_{C,\,Cu}$]; **IR** (ATR): $\tilde{\nu}$ = 3331, 1438, 1156, 1066, 1028, 727 cm^{-1}; Elem. Anal. calcd. for $C_4H_4F_{12}Cu_2Cl_2O_2$: 33.80% Cu, found: 33.37% Cu. **CCDC** 2533527.

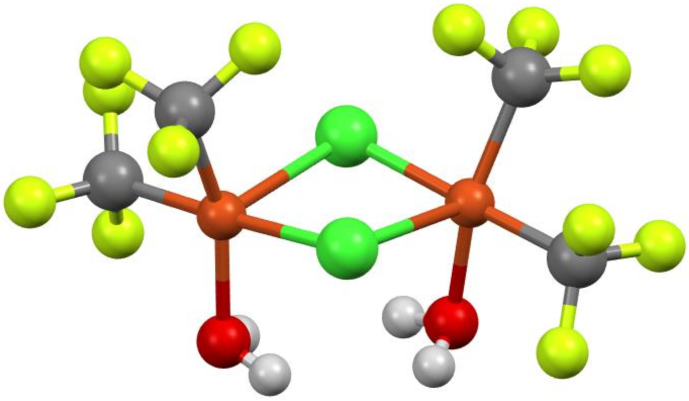


Figure S1. Crystal structure of bis(μ₂-chlorido)dicopper(III) complex ***3***

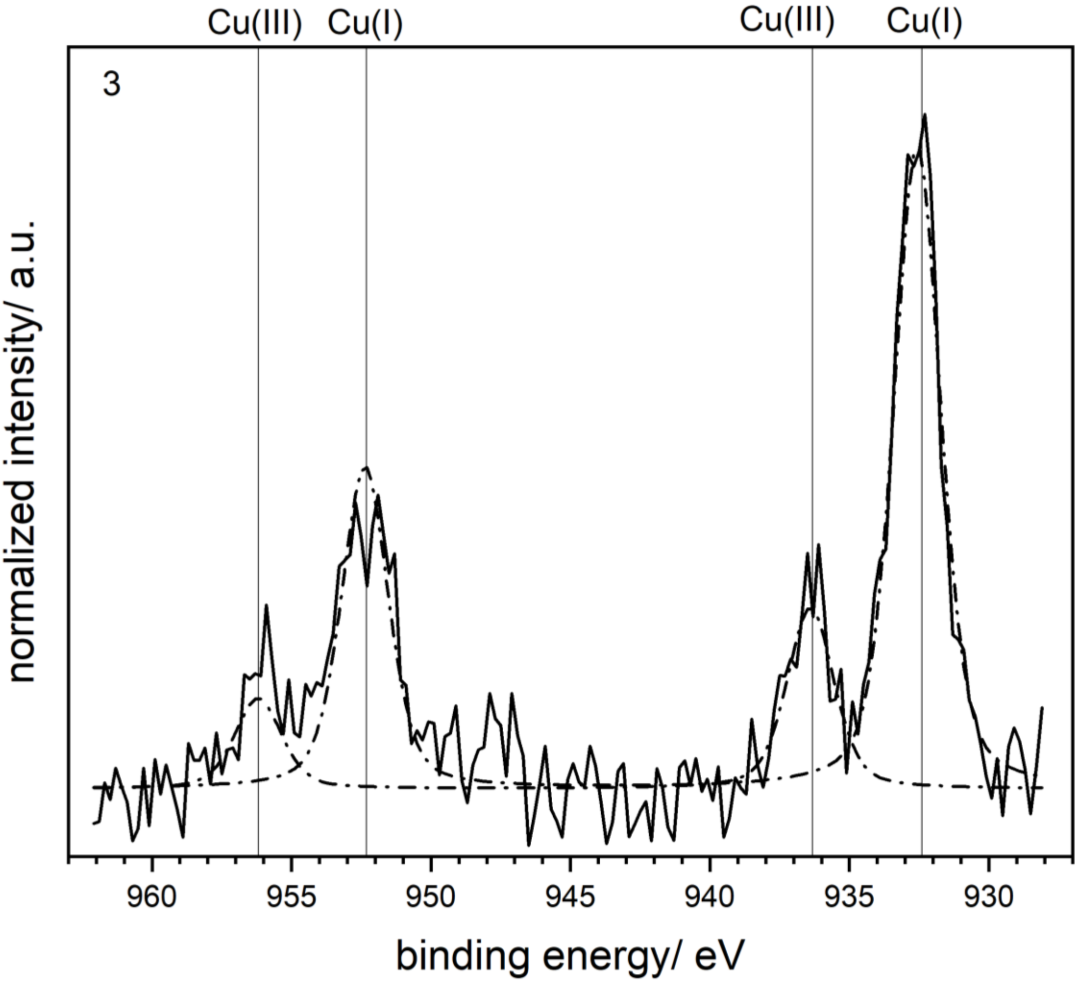


*Figure S2. Highly resolved Cu2p XPS spectrum of the chlorido complex **3** at room temperature (and its Cu(I) decomposition product)*

Table 1. Crystal data and structure refinement for **3**

CCDC number	2533527
Empirical formula	$C_2H_2ClCuF_6O(C_3H_6O)$
Formula weight	313.10
Temperature [K]	150.00
Crystal system	monoclinic
Space group (number)	$C2/c$ (15)
a [Å]	17.265(2)
b [Å]	8.0608(9)
c [Å]	15.617(2)
α [°]	90
β [°]	101.271(5)
γ [°]	90
Volume [Å^3]	2131.5(5)
Z	8
ρ_{calc} [gcm^{-3}]	1.951
μ [mm^{-1}]	2.362
F(000)	1232
Crystal size [mm^3]	0.08×0.151×0.396
Crystal colour	yellow
Crystal shape	needle
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	4.81 to 50.78 (0.83 Å)
Index ranges	$-20 \leq h \leq 20$ $-9 \leq k \leq 9$ $-18 \leq l \leq 18$
Reflections collected	27779
Independent reflections	1968 R_{int} = 0.0772 R_{sigma} = 0.0308
Completeness to θ = 25.242°	100.0 %
Data / Restraints / Parameters	1968 / 0 / 139
Absorption correction T_{min}/T_{max} (method)	0.5229 / 0.7452 (multi-scan)
Goodness-of-fit on F^2	1.186
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0298 wR_2 = 0.0652
Final R indexes [all data]	R_1 = 0.0447 wR_2 = 0.0781

Table 2. Bond lengths and angles for **3**

Atom–Atom	**Length [Å]**
Cu1–Cl1	2.2181(9)
Cu1–Cl1$^{\#1}$	2.7571(9)
Cu1–O1	1.946(2)
Cu1–C2	1.949(3)
Cu1–C1	1.960(4)
F5–C2	1.337(4)
F4–C2	1.328(4)
F6–C2	1.344(4)
F2–C1	1.327(4)
O1–H1A	0.8710
O1–H1B	0.8711
F3–C1	1.325(4)
F1–C1	1.323(4)
O2–C3	1.224(4)
C3–C5	1.480(5)
C3–C4	1.481(5)
C5–H5A	0.9800
C5–H5B	0.9800
C5–H5C	0.9800
C4–H4A	0.9800
C4–H4B	0.9800
C4–H4C	0.9800
Atom–Atom–Atom	**Angle [°]**
Cl1–Cu1–Cl1$^{\#1}$	87.32(3)
O1–Cu1–Cl1	92.01(7)
O1–Cu1–Cl1$^{\#1}$	94.63(7)
O1–Cu1–C2	90.07(13)
O1–Cu1–C1	159.52(13)
C2–Cu1–Cl1$^{\#1}$	91.08(10)
C2–Cu1–Cl1	177.47(11)
C2–Cu1–C1	87.60(15)
C1–Cu1–Cl1$^{\#1}$	105.75(12)
C1–Cu1–Cl1	90.94(11)
Cu1–Cl1–Cu1$^{\#1}$	91.37(3)
Cu1–O1–H1A	109.3
Cu1–O1–H1B	109.5
H1A–O1–H1B	104.4
O2–C3–C5	121.1(3)
O2–C3–C4	121.3(4)
C5–C3–C4	117.6(3)
F5–C2–Cu1	112.2(2)
F5–C2–F6	106.5(3)
F4–C2–Cu1	116.5(2)
F4–C2–F5	108.1(3)
F4–C2–F6	105.3(3)
F6–C2–Cu1	107.6(2)
F2–C1–Cu1	105.4(2)
F3–C1–Cu1	119.7(3)
F3–C1–F2	106.0(3)
F1–C1–Cu1	109.2(2)
F1–C1–F2	109.2(3)
F1–C1–F3	107.0(3)
C3–C5–H5A	109.5
C3–C5–H5B	109.5
C3–C5–H5C	109.5
H5A–C5–H5B	109.5
H5A–C5–H5C	109.5
H5B–C5–H5C	109.5
C3–C4–H4A	109.5
C3–C4–H4B	109.5
C3–C4–H4C	109.5
H4A–C4–H4B	109.5
H4A–C4–H4C	109.5
H4B–C4–H4C	109.5

Synthesis of bis(μ_2-(κ_1-azido))dicopper(III) complex 4 [$Cu(CF_3)_2(N_3)]_2$

In a 10 ml round-bottomed Schlenk flask under argon atmosphere, to the heterocubane **1** (21.8 mg, 0.025 mmol [0.1 mmol monomer]) dry dichloromethane (0.5 ml) was added and the mixture was cooled to −40°C. $TMSN_3$ (26.3 µl, 0.2 mmol, 2 equiv.) was added with vigorous stirring. The mixture was additionally stirred for 1 hour at −40°C, then connected to high vacuum and evaporated to dryness (several hours at room temperature) to completely remove silanol by-products to furnish the complex **4** as a bright yellow solid (yield 23.5 mg, 96%). Single crystal for X-ray crystallography was grown from 1:1 pentane/DCM [optionally with an addition of 0.5% of acetone for better quality crystals] at −20°C. **^{19}F NMR** ($CDCl_3$, 376 MHz, 293 K) δ −27.5 (s, 6F); **^{13}C{^{19}F} NMR** ($CDCl_3$, 101 MHz, 293 K) δ 121.4 (br) and 117.7 (br) [apparent d, $J_{C, Cu}$]; **IR** (ATR) (for non-solvated **4**): $\tilde{\nu}$ = 2117, 1298, 1143, 1086, 926, 717 cm^{-1}; **IR** (ATR) (for the crystals of acetone solvate **4** · $0.5C_3H_6O$): $\tilde{\nu}$ = 2114, 1659, 1295, 1148, 1080, 923, 738, 712, 576 cm^{-1}; Elem. Anal. calcd. for $C_4F_{12}Cu_2N_6$: 26.09% Cu, found: 25.88% Cu; **CCDC** 2551392 (non-solvated **4**), 2539161 (acetone solvate $[Cu(CF_3)_2(\mu_2\text{-}N_3)_2Cu(CF_3)_2\cdot 0.5C_3H_6O]$).

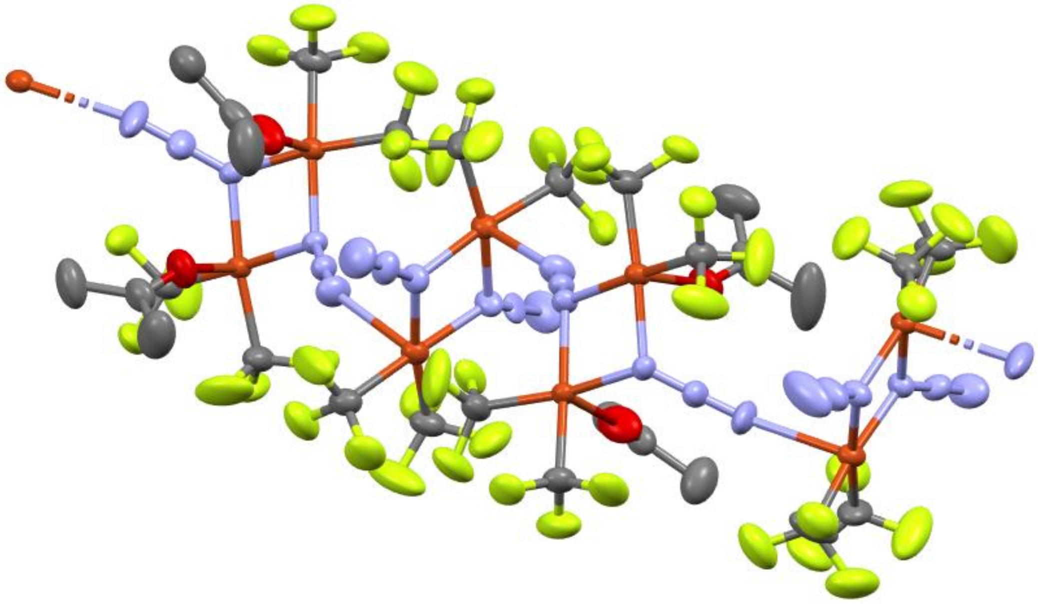


*Figure S3. Polymeric structure of azido complex **4** $[Cu(CF_3)_2(\mu_2\text{-}N_3)_2Cu(CF_3)_2\cdot 0.5C_3H_6O]_n$*

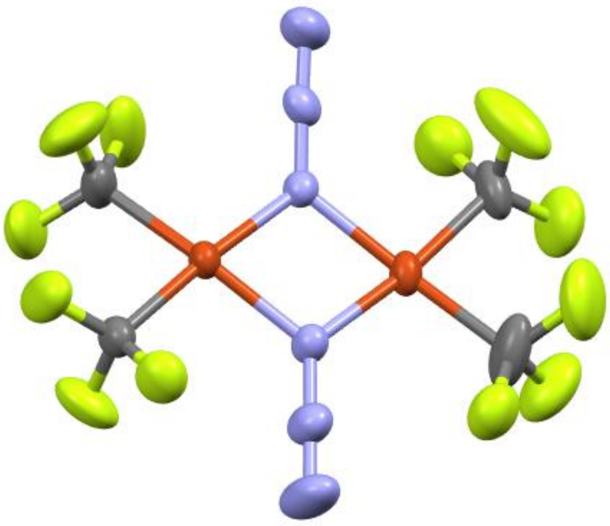


Figure S4. Dimer of the non-solvated azido complex ***4***

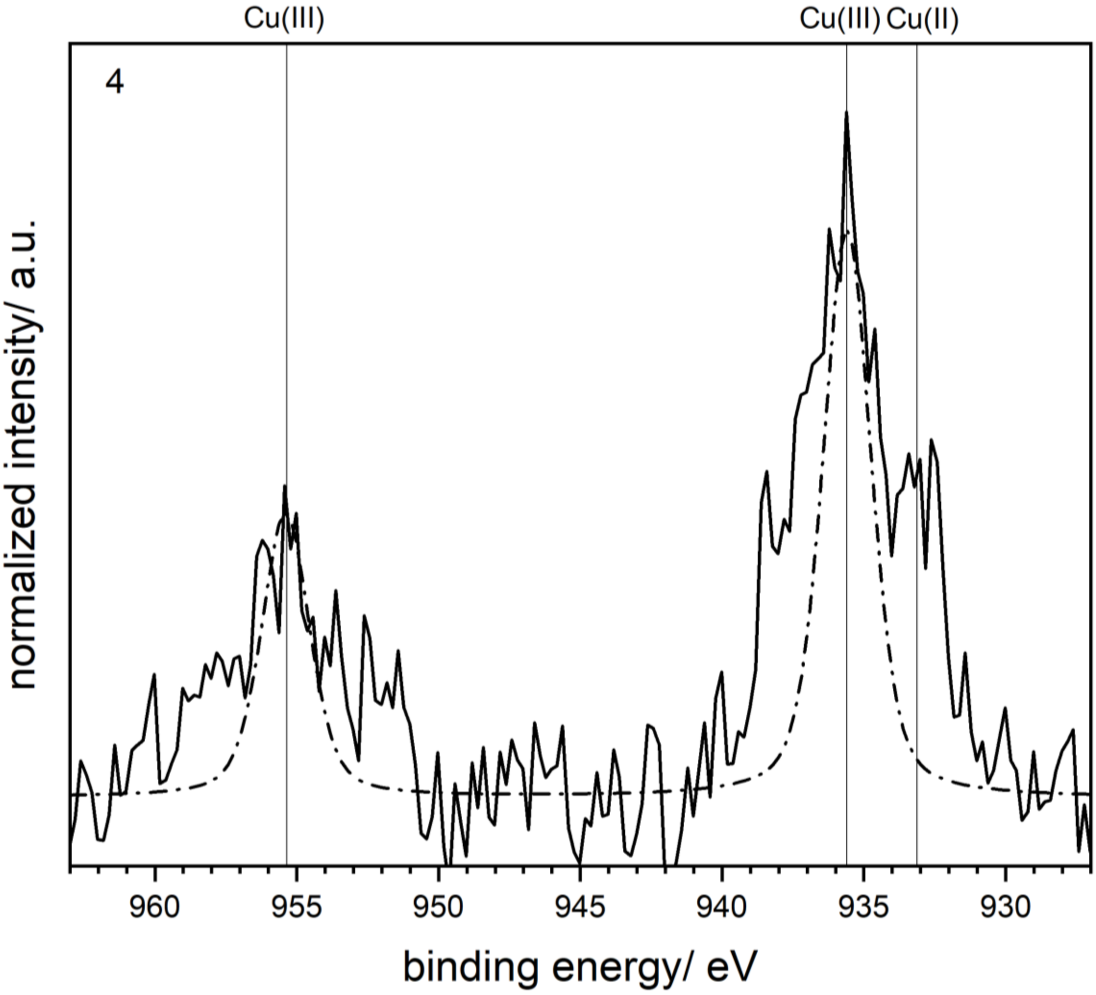


Figure S5. Highly resolved Cu2p XPS spectrum of the azido complex ***4***

Table 3. Crystal data and structure refinement for **4**

CCDC number	2551392
Empirical formula	$C_4Cu_2F_{12}N_6$
Formula weight	487.18
Temperature [K]	150.00
Crystal system	triclinic
Space group (number)	$P\overline{1}$ (2)
a [Å]	7.19(2)
b [Å]	9.098(19)
c [Å]	10.11(3)
α [°]	88.96(9)
β [°]	70.42(12)
γ [°]	87.96(11)
Volume [Å^3]	623(3)
Z	2
ρ_{calc} [gcm^{-3}]	2.597
μ [mm^{-1}]	3.577
F(000)	464
Crystal size [mm^3]	0.04×0.069×0.093
Crystal colour	yellow
Crystal shape	plate
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	4.28 to 51.19 (0.82 Å)
Index ranges	$-8 \leq h \leq 8$ $-10 \leq k \leq 10$ $0 \leq l \leq 12$
Reflections collected	2301
Independent reflections	2301 R_{int} = 0.1419 R_{sigma} = 0.0965
Completeness to θ = 25.242°	99.4 %
Data / Restraints / Parameters	2301 / 30 / 218
Absorption correction T_{min}/T_{max} (method)	0.4707 / 0.7452 (multi-scan)
Goodness-of-fit on F^2	1.063
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0952 wR_2 = 0.2119
Final R indexes [all data]	R_1 = 0.1514 wR_2 = 0.2571
Largest peak/hole [eÅ^{-3}]	2.58/−1.43

Table 4. Bond lengths and angles for **4**

Atom–Atom	**Length [Å]**
Cu1–Cu1$^{\#1}$	3.019(10)
Cu1–N1	1.953(15)
Cu1–N1$^{\#1}$	1.950(18)
Cu1–C1	1.92(2)
Cu1–C2	1.95(2)
Cu2–Cu2$^{\#2}$	3.031(11)
Cu2–N4	1.958(16)
Cu2–N4$^{\#2}$	1.922(15)
Cu2–C4	1.93(2)
Cu2–C3	1.95(2)
F6–C2	1.31(3)
F12–C4	1.39(2)
N1–N2	1.21(2)
F10–C4	1.31(3)
F3–C1	1.29(2)
N4–N5	1.23(2)
F9–C3	1.28(3)
F7–C3	1.26(3)
N2–N3	1.12(2)
F11–C4	1.29(2)
C1–F2	1.37(3)
C1–F1	1.27(3)
C2–F4	1.28(2)
C2–F5	1.34(3)
F8–C3	1.33(3)
N5–N6	1.10(2)
Atom–Atom–Atom	**Angle [°]**
N1–Cu1–Cu1$^{\#1}$	39.3(5)
N1$^{\#1}$–Cu1–Cu1$^{\#1}$	39.4(5)
N1$^{\#1}$–Cu1–N1	78.7(7)
N1$^{\#1}$–Cu1–C2	174.6(8)
N1–Cu1–C2	96.9(9)
C1–Cu1–Cu1$^{\#1}$	137.0(7)
C1–Cu1–N1$^{\#1}$	98.1(8)
C1–Cu1–N1	172.3(8)
C1–Cu1–C2	86.8(10)
C2–Cu1–Cu1$^{\#1}$	136.1(7)
N4–Cu2–Cu2$^{\#2}$	38.2(5)
N4$^{\#2}$–Cu2–Cu2$^{\#2}$	39.1(5)
N4$^{\#2}$–Cu2–N4	77.3(8)
N4$^{\#2}$–Cu2–C4	175.7(8)
N4$^{\#2}$–Cu2–C3	99.8(9)
C4–Cu2–Cu2$^{\#2}$	136.8(7)
C4–Cu2–N4	98.6(8)
C4–Cu2–C3	84.4(10)
C3–Cu2–Cu2$^{\#2}$	138.4(7)
C3–Cu2–N4	172.2(8)
Cu1$^{\#1}$–N1–Cu1	101.3(7)
N2–N1–Cu1	127.3(14)
N2–N1–Cu1$^{\#1}$	125.8(13)
Cu2$^{\#2}$–N4–Cu2	102.7(8)
N5–N4–Cu2	125.3(14)
N5–N4–Cu2$^{\#2}$	131.6(14)
N3–N2–N1	179(2)
F3–C1–Cu1	116.2(14)
F3–C1–F2	103.0(16)
F2–C1–Cu1	107.3(14)
F1–C1–Cu1	112.5(15)
F1–C1–F3	109.4(19)
F1–C1–F2	107.7(19)
F6–C2–Cu1	105.9(14)
F6–C2–F5	107(2)
F4–C2–Cu1	119.9(18)
F4–C2–F6	107.9(18)
F4–C2–F5	110(2)
F5–C2–Cu1	105.7(14)
N6–N5–N4	179(2)
F12–C4–Cu2	105.3(13)
F10–C4–Cu2	121.0(15)
F10–C4–F12	101.9(16)
F11–C4–Cu2	111.9(14)
F11–C4–F12	105.3(16)
F11–C4–F10	109.6(18)
F9–C3–Cu2	115.2(17)
F9–C3–F8	103.6(19)
F7–C3–Cu2	113.3(15)
F7–C3–F9	110(2)
F7–C3–F8	109(2)
F8–C3–Cu2	104.8(15)

Symmetry transformations used to generate equivalent atoms:
#1: 1-X, 1-Y, 1-Z; #2: -X, -Y, 1-Z;

Table 5. Crystal data and structure refinement for **4 · $0.5C_3H_6O$**

CCDC number	2539161
Empirical formula	$C_{28}H_{24}Cu_8F_{48}N_{24}O_4$
Formula weight	2181.03
Temperature [K]	150.00
Crystal system	triclinic
Space group (number)	$P\bar{1}$ (2)
a [Å]	11.5078(19)
b [Å]	14.270(3)
c [Å]	22.213(4)
α [°]	96.426(4)
β [°]	102.977(7)
γ [°]	103.826(5)

Volume [Å^3]	3398.4(10)
Z	2
ρ_{calc} [gcm^{-3}]	2.131
μ [mm^{-1}]	2.639
F(000)	2112
Crystal size [mm^3]	0.176×0.289×0.402
Crystal colour	yellow
Crystal shape	plate
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	3.82 to 50.71 (0.83 Å)
Index ranges	$-13 \le h \le 13$ $-17 \le k \le 17$ $-26 \le l \le 26$
Reflections collected	81671
Independent reflections	12416 R_{int} = 0.0706 R_{sigma} = 0.0412
Completeness to θ = 25.242°	99.9 %
Data / Restraints / Parameters	12416 / 417 / 1204
Absorption correction T_{min}/T_{max} (method)	0.4717 / 0.7452 (multi-scan)
Goodness-of-fit on F^2	1.092
Final R indexes [I≥2σ(I)]	R_1 = 0.0500 wR_2 = 0.1220
Final R indexes [all data]	R_1 = 0.0732 wR_2 = 0.1482
Largest peak/hole [eÅ^{-3}]	2.21/−0.72

Table 6. Bond lengths and angles for **4 · 0.5C_3H_6O**

Atom–Atom	**Length [Å]**
Cu3–Cu4	2.9844(10)
Cu3–N10	1.968(4)
Cu3–N7	1.977(4)
Cu3–O1	2.281(5)
Cu3–C5	1.949(6)
Cu3–C6	1.945(7)
Cu7–Cu8	3.0038(10)
Cu7–N22	1.972(4)
Cu7–O3	2.389(5)
Cu7–N19	1.970(4)
Cu7–C20	1.944(6)
Cu7–C19	1.934(7)
Cu4–N10	1.961(4)
Cu4–N7	1.965(4)
Cu4–O2	2.361(5)
Cu4–C7	1.939(6)
Cu4–C8	1.950(6)
Cu8–N22	1.959(4)
Cu8–N19	1.967(4)
Cu8–O4	2.278(5)
Cu8–C22	1.945(6)
Cu8–C21	1.946(6)
Cu6–Cu5	3.0251(10)
Cu6–N13	1.950(5)
Cu6–C18	1.937(6)
Cu6–C17	1.935(6)
Cu6–N16	1.951(5)
Cu2–Cu1	3.0333(10)
Cu2–N1	1.941(5)
Cu2–N4	1.956(5)
Cu2–C3	1.935(6)
Cu2–C4	1.951(7)
Cu5–N13	1.956(5)
Cu5–C15	1.943(6)
Cu5–C16	1.933(7)
Cu5–N16	1.955(5)
Cu1–N1	1.958(5)
Cu1–N4	1.952(5)
Cu1–C1	1.959(7)
Cu1–C2	1.923(8)
F20–C7	1.328(7)
F22–C8	1.310(7)
F36–C18	1.315(7)
F21–C7	1.329(8)
F19–C7	1.337(7)
F26–C15	1.322(8)
F33–C17	1.339(7)
F35–C18	1.353(7)
F7–C3	1.336(7)
F32–C17	1.314(8)
F29–C16	1.306(7)
N10–N11	1.209(6)
F34–C18	1.325(7)
F31–C17	1.324(8)
N8–N7	1.227(6)
N8–N9	1.134(7)
N22–N23	1.219(6)
F9–C3	1.319(7)
F8–C3	1.305(7)
F5–C2	1.307(9)
O3–C23	1.225(8)
N11–N12	1.133(7)
F6–C2	1.287(10)
N23–N24	1.142(7)
N2–N1	1.220(7)
N2–N3	1.127(7)
F30–C16	1.325(8)
N19–N20	1.221(7)
O2–C12	1.218(8)
F25–C15	1.341(9)
F11–C4	1.312(8)
F2–C1	1.263(8)
N4–N5	1.233(7)
F39A–C19	1.330(8)
O1–C9	1.204(7)
F41A–C20	1.321(8)
F1–C1	1.386(9)
F14A–C5	1.322(10)
N20–N21	1.134(8)
N13–N14	1.221(7)
F17A–C6	1.328(8)
F15A–C5	1.338(9)
F10–C4	1.318(9)
F38A–C19	1.353(8)
F12–C4	1.312(8)
N14–N15	1.127(7)
F23–C8	1.318(8)
F48A–C22	1.286(10)
F3–C1	1.274(9)
F24–C8	1.331(8)
F28–C16	1.313(8)
F16A–C6	1.305(9)
O4–C26	1.178(9)
F43A–C21	1.316(10)
N5–N6	1.118(8)
F40A–C20	1.338(8)
C15–F27	1.300(8)
F4–C2	1.423(11)
N17B–N18B	1.134(16)
N17B–N16	1.27(2)
C22–F47A	1.396(10)
C22–F46A	1.269(9)
C22–F46B	1.227(13)
C22–F47B	1.335(15)
C22–F48B	1.381(13)
F13A–C5	1.308(9)
F45A–C21	1.356(9)
C9–C11	1.482(9)
C9–C10	1.478(10)
F42A–C20	1.282(9)
C20–F42B	1.372(15)

C20–F41B	1.278(18)
C20–F40B	1.308(19)
C5–F15B	1.296(15)
C5–F14B	1.302(15)
C5–F13B	1.360(13)
C21–F44A	1.270(10)
C21–F44B	1.264(14)
C21–F45B	1.308(16)
C21–F43B	1.383(14)
C11–H11A	0.9800
C11–H11B	0.9800
C11–H11C	0.9800
F37A–C19	1.284(9)
C26–C28	1.526(12)
C26–C27	1.473(13)
C6–F18A	1.329(10)
C6–F18B	1.331(15)
C6–F16B	1.337(16)
C6–F17B	1.281(16)
C19–F37B	1.301(16)
C19–F38B	1.34(2)
C19–F39B	1.319(19)
C23–C25	1.483(10)
C23–C24	1.460(11)
C12–C14	1.486(11)
C12–C13	1.473(13)
C28–H28A	0.9800
C28–H28B	0.9800
C28–H28C	0.9800
C25–H25A	0.9800
C25–H25B	0.9800
C25–H25C	0.9800
C14–H14A	0.9800
C14–H14B	0.9800
C14–H14C	0.9800
C24–H24A	0.9800
C24–H24B	0.9800
C24–H24C	0.9800
C10–H10A	0.9800
C10–H10B	0.9800
C10–H10C	0.9800
C27–H27A	0.9800
C27–H27B	0.9800
C27–H27C	0.9800
C13–H13A	0.9800
C13–H13B	0.9800
C13–H13C	0.9800
N16–N17A	1.213(14)
N17A–N18A	1.129(13)
Atom–Atom–Atom	**Angle [°]**
N10–Cu3–Cu4	40.49(13)
N10–Cu3–N7	80.55(18)
N10–Cu3–O1	90.2(2)
N7–Cu3–Cu4	40.64(13)
N7–Cu3–O1	93.63(19)
O1–Cu3–Cu4	97.80(14)
C5–Cu3–Cu4	134.46(19)

C5–Cu3–N10	96.2(2)
C5–Cu3–N7	170.8(2)
C5–Cu3–O1	95.0(3)
C6–Cu3–Cu4	132.28(19)
C6–Cu3–N10	169.0(3)
C6–Cu3–N7	94.1(2)
C6–Cu3–O1	99.8(3)
C6–Cu3–C5	87.6(3)
N22–Cu7–Cu8	40.02(12)
N22–Cu7–O3	86.23(18)
O3–Cu7–Cu8	91.45(12)
N19–Cu7–Cu8	40.23(13)
N19–Cu7–N22	79.98(18)
N19–Cu7–O3	90.37(19)
C20–Cu7–Cu8	134.68(19)
C20–Cu7–N22	96.1(2)
C20–Cu7–O3	97.0(3)
C20–Cu7–N19	171.5(3)
C19–Cu7–Cu8	136.02(19)
C19–Cu7–N22	175.0(3)
C19–Cu7–O3	97.3(3)
C19–Cu7–N19	96.5(2)
C19–Cu7–C20	87.0(3)
N10–Cu4–Cu3	40.65(13)
N10–Cu4–N7	81.01(18)
N10–Cu4–O2	88.91(18)
N7–Cu4–Cu3	40.94(12)
N7–Cu4–O2	89.20(18)
O2–Cu4–Cu3	94.10(12)
C7–Cu4–Cu3	137.09(18)
C7–Cu4–N10	176.4(2)
C7–Cu4–N7	97.2(2)
C7–Cu4–O2	94.2(2)
C7–Cu4–C8	87.6(3)
C8–Cu4–Cu3	131.96(18)
C8–Cu4–N10	93.7(2)
C8–Cu4–N7	169.4(2)
C8–Cu4–O2	99.9(2)
N22–Cu8–Cu7	40.34(13)
N22–Cu8–N19	80.36(18)
N22–Cu8–O4	91.7(2)
N19–Cu8–Cu7	40.31(13)
N19–Cu8–O4	94.2(2)
O4–Cu8–Cu7	97.55(14)
C22–Cu8–Cu7	133.88(18)
C22–Cu8–N22	168.4(2)
C22–Cu8–N19	95.8(2)
C22–Cu8–O4	99.5(3)
C22–Cu8–C21	87.9(3)
C21–Cu8–Cu7	133.14(19)
C21–Cu8–N22	94.3(2)
C21–Cu8–N19	170.3(2)
C21–Cu8–O4	94.0(3)
N13–Cu6–Cu5	39.31(14)
N13–Cu6–N16	78.40(19)
C18–Cu6–Cu5	137.94(18)
C18–Cu6–N13	173.4(2)
C18–Cu6–N16	98.7(2)

C17–Cu6–Cu5	134.14(19)
C17–Cu6–N13	97.9(2)
C17–Cu6–C18	86.4(3)
C17–Cu6–N16	164.6(2)
N16–Cu6–Cu5	39.29(14)
N1–Cu2–Cu1	39.14(14)
N1–Cu2–N4	78.18(19)
N1–Cu2–C4	98.8(2)
N4–Cu2–Cu1	39.05(13)
C3–Cu2–Cu1	136.39(18)
C3–Cu2–N1	175.2(2)
C3–Cu2–N4	97.3(2)
C3–Cu2–C4	85.9(3)
C4–Cu2–Cu1	136.6(2)
C4–Cu2–N4	168.1(3)
N13–Cu5–Cu6	39.17(14)
C15–Cu5–Cu6	133.6(2)
C15–Cu5–N13	171.6(3)
C15–Cu5–N16	94.4(2)
C16–Cu5–Cu6	139.2(2)
C16–Cu5–N13	100.0(2)
C16–Cu5–C15	87.1(3)
C16–Cu5–N16	175.6(3)
N16–Cu5–Cu6	39.20(13)
N16–Cu5–N13	78.17(19)
N1–Cu1–Cu2	38.73(13)
N1–Cu1–C1	95.9(3)
N4–Cu1–Cu2	39.14(14)
N4–Cu1–N1	77.85(19)
N4–Cu1–C1	173.3(3)
C1–Cu1–Cu2	134.6(2)
C2–Cu1–Cu2	139.2(3)
C2–Cu1–N1	172.2(3)
C2–Cu1–N4	100.4(3)
C2–Cu1–C1	85.5(4)
Cu4–N10–Cu3	98.87(19)
N11–N10–Cu3	125.2(4)
N11–N10–Cu4	118.9(4)
N9–N8–N7	179.0(6)
Cu8–N22–Cu7	99.64(19)
N23–N22–Cu7	119.4(4)
N23–N22–Cu8	122.7(4)
Cu4–N7–Cu3	98.42(19)
N8–N7–Cu3	120.1(4)
N8–N7–Cu4	120.9(4)
C23–O3–Cu7	146.2(5)
N12–N11–N10	178.9(6)
N24–N23–N22	178.9(6)
N3–N2–N1	178.4(6)
Cu8–N19–Cu7	99.46(19)
N20–N19–Cu7	122.5(4)
N20–N19–Cu8	121.9(4)
C12–O2–Cu4	150.5(5)
Cu2–N1–Cu1	102.1(2)
N2–N1–Cu2	126.4(4)
N2–N1–Cu1	128.1(4)
Cu1–N4–Cu2	101.8(2)
N5–N4–Cu2	127.5(4)
N5–N4–Cu1	130.2(4)
C9–O1–Cu3	170.3(6)
N21–N20–N19	179.2(7)
Cu6–N13–Cu5	101.5(2)
N14–N13–Cu6	126.3(4)
N14–N13–Cu5	132.0(4)
N15–N14–N13	179.5(8)
C26–O4–Cu8	169.4(7)
F36–C18–Cu6	116.9(4)
F36–C18–F35	104.8(5)
F36–C18–F34	108.6(5)
F35–C18–Cu6	106.2(4)
F34–C18–Cu6	112.7(4)
F34–C18–F35	106.8(5)
N6–N5–N4	179.3(9)
F26–C15–Cu5	106.9(4)
F26–C15–F25	103.4(6)
F25–C15–Cu5	107.8(4)
F27–C15–Cu5	123.1(5)
F27–C15–F26	108.6(6)
F27–C15–F25	105.4(6)
N18B–N17B–N16	173(3)
F48A–C22–Cu8	115.1(6)
F48A–C22–F47A	104.4(7)
F47A–C22–Cu8	110.7(5)
F46A–C22–Cu8	111.4(5)
F46A–C22–F48A	112.4(8)
F46A–C22–F47A	101.9(7)
F46B–C22–Cu8	113.1(8)
F46B–C22–F47B	115.0(14)
F46B–C22–F48B	102.7(12)
F47B–C22–Cu8	118.0(10)
F47B–C22–F48B	100.7(10)
F48B–C22–Cu8	104.4(6)
F7–C3–Cu2	107.4(4)
F9–C3–Cu2	118.3(4)
F9–C3–F7	103.2(5)
F8–C3–Cu2	111.1(4)
F8–C3–F7	106.7(5)
F8–C3–F9	109.3(5)
O1–C9–C11	121.8(7)
O1–C9–C10	120.8(7)
C10–C9–C11	117.4(6)
F29–C16–Cu5	113.2(5)
F29–C16–F30	107.6(5)
F29–C16–F28	108.4(6)
F30–C16–Cu5	114.4(5)
F28–C16–Cu5	108.6(4)
F28–C16–F30	104.1(6)
F41A–C20–Cu7	115.8(5)
F41A–C20–F40A	101.6(6)
F40A–C20–Cu7	107.3(4)
F42A–C20–Cu7	111.3(5)
F42A–C20–F41A	107.1(7)
F42A–C20–F40A	113.5(7)
F42B–C20–Cu7	108.4(8)
F41B–C20–Cu7	121.7(17)
F41B–C20–F42B	92.9(19)

F41B–C20–F40B	102(2)
F40B–C20–Cu7	117.2(15)
F40B–C20–F42B	112(2)
F33–C17–Cu6	106.4(4)
F32–C17–Cu6	110.3(4)
F32–C17–F33	107.6(6)
F32–C17–F31	108.9(6)
F31–C17–Cu6	118.1(5)
F31–C17–F33	105.0(5)
F20–C7–Cu4	114.4(4)
F20–C7–F21	108.2(5)
F20–C7–F19	106.0(5)
F21–C7–Cu4	112.0(4)
F21–C7–F19	107.1(5)
F19–C7–Cu4	108.6(4)
F14A–C5–Cu3	111.5(6)
F14A–C5–F15A	106.8(7)
F15A–C5–Cu3	113.2(5)
F13A–C5–Cu3	110.2(5)
F13A–C5–F14A	108.7(9)
F13A–C5–F15A	106.1(7)
F15B–C5–Cu3	111.9(10)
F15B–C5–F14B	114.6(16)
F15B–C5–F13B	104.5(13)
F14B–C5–Cu3	118.9(13)
F14B–C5–F13B	99.4(12)
F13B–C5–Cu3	105.0(7)
F43A–C21–Cu8	120.3(6)
F43A–C21–F45A	101.5(7)
F45A–C21–Cu8	107.3(5)
F44A–C21–Cu8	111.3(6)
F44A–C21–F43A	109.3(9)
F44A–C21–F45A	105.8(8)
F44B–C21–Cu8	111.6(8)
F44B–C21–F45B	119.5(15)
F44B–C21–F43B	101.2(13)
F45B–C21–Cu8	112.9(10)
F45B–C21–F43B	98.9(12)
F43B–C21–Cu8	111.0(8)
C9–C11–H11A	109.5
C9–C11–H11B	109.5
C9–C11–H11C	109.5
H11A–C11–H11B	109.5
H11A–C11–H11C	109.5
H11B–C11–H11C	109.5
F22–C8–Cu4	120.4(4)
F22–C8–F23	107.2(5)
F22–C8–F24	104.7(5)
F23–C8–Cu4	108.4(4)
F23–C8–F24	106.2(6)
F24–C8–Cu4	109.1(4)
O4–C26–C28	122.1(8)
O4–C26–C27	124.6(9)
C27–C26–C28	113.3(8)
F17A–C6–Cu3	108.3(5)
F17A–C6–F18A	106.0(7)
F16A–C6–Cu3	122.3(6)
F16A–C6–F17A	104.2(7)

F16A–C6–F18A	107.3(8)
F18A–C6–Cu3	107.6(5)
F18B–C6–Cu3	112.6(9)
F18B–C6–F16B	95.0(16)
F16B–C6–Cu3	108.5(11)
F17B–C6–Cu3	113.0(11)
F17B–C6–F18B	106.5(16)
F17B–C6–F16B	119.8(18)
F39A–C19–Cu7	116.0(5)
F39A–C19–F38A	100.5(6)
F38A–C19–Cu7	108.3(4)
F37A–C19–Cu7	113.4(5)
F37A–C19–F39A	107.8(7)
F37A–C19–F38A	109.9(7)
F37B–C19–Cu7	104.7(10)
F37B–C19–F38B	105(3)
F37B–C19–F39B	108(2)
F38B–C19–Cu7	113(3)
F39B–C19–Cu7	125.7(17)
F39B–C19–F38B	99(3)
F11–C4–Cu2	115.8(5)
F11–C4–F10	108.1(6)
F10–C4–Cu2	112.0(5)
F12–C4–Cu2	108.4(4)
F12–C4–F11	105.4(6)
F12–C4–F10	106.5(6)
O3–C23–C25	119.4(7)
O3–C23–C24	121.0(7)
C24–C23–C25	119.6(7)
F2–C1–Cu1	120.3(6)
F2–C1–F1	100.4(6)
F2–C1–F3	116.4(6)
F1–C1–Cu1	105.1(4)
F3–C1–Cu1	109.9(5)
F3–C1–F1	101.6(7)
O2–C12–C14	121.2(8)
O2–C12–C13	120.0(8)
C13–C12–C14	118.8(7)
C26–C28–H28A	109.5
C26–C28–H28B	109.5
C26–C28–H28C	109.5
H28A–C28–H28B	109.5
H28A–C28–H28C	109.5
H28B–C28–H28C	109.5
C23–C25–H25A	109.5
C23–C25–H25B	109.5
C23–C25–H25C	109.5
H25A–C25–H25B	109.5
H25A–C25–H25C	109.5
H25B–C25–H25C	109.5
F5–C2–Cu1	111.1(5)
F5–C2–F4	101.1(7)
F6–C2–Cu1	117.5(6)
F6–C2–F5	112.9(9)
F6–C2–F4	102.9(6)
F4–C2–Cu1	109.7(7)
C12–C14–H14A	109.5
C12–C14–H14B	109.5

C12–C14–H14C	109.5
H14A–C14–H14B	109.5
H14A–C14–H14C	109.5
H14B–C14–H14C	109.5
C23–C24–H24A	109.5
C23–C24–H24B	109.5
C23–C24–H24C	109.5
H24A–C24–H24B	109.5
H24A–C24–H24C	109.5
H24B–C24–H24C	109.5
C9–C10–H10A	109.5
C9–C10–H10B	109.5
C9–C10–H10C	109.5
H10A–C10–H10B	109.5
H10A–C10–H10C	109.5
H10B–C10–H10C	109.5
C26–C27–H27A	109.5
C26–C27–H27B	109.5
C26–C27–H27C	109.5
H27A–C27–H27B	109.5
H27A–C27–H27C	109.5
H27B–C27–H27C	109.5
C12–C13–H13A	109.5
C12–C13–H13B	109.5
C12–C13–H13C	109.5
H13A–C13–H13B	109.5
H13A–C13–H13C	109.5
H13B–C13–H13C	109.5
Cu6–N16–Cu5	101.5(2)
N17B–N16–Cu6	127.5(16)
N17B–N16–Cu5	125.6(16)
N17A–N16–Cu6	128.5(10)
N17A–N16–Cu5	129.9(10)
N18A–N17A–N16	177(3)

Table 7. Torsion angles for **4 · 0.5**$\mathbf{C_3H_6O}$

Atom–Atom–Atom–Atom	**Torsion Angle [°]**
Cu7–O3–C23–C25	−75.2(11)
Cu7–O3–C23–C24	108.1(10)
Cu4–O2–C12–C14	−61.0(13)
Cu4–O2–C12–C13	121.5(11)
Cu8–O4–C26–C28	17(4)
Cu8–O4–C26–C27	−163(3)

Synthesis of μ$_2$-(dimethylamino)-μ$_2$-hydroxy-dicopper(III) complex 5

$[(F_3C)_2Cu(\mu_2\text{-}OH)(\mu_2\text{-}NMe_2)Cu(CF_3)_2]$

In a 10 ml Schlenk tube under argon atmosphere to the solid heterocubane **1** (21.8 mg, 0.025 mmol [0.1 mmol monomer]) dry dichloromethane (1 ml) was added and the mixture was cooled to −78°C (acetone/dry ice). (N,N-Dimethylamino)trimethylsilane (8 µl, 0.05 mmol, 0.5 equiv.) was added with vigorous stirring via syringe. The resulting orange mixture was stirred at −78°C for 30 minutes, then layered with pentane (ca. 3 ml). Crystallization in the freezer at −80°C for 2 days afforded orange crystals of dimeric **μ$_2$-(dimethylamino)-μ$_2$-hydroxy-tetrakis(trifluoromethyl)dicopper(III) 5** (5.6 mg, 24%), which were immediately collected for X-ray and other measurements. The compound undergoes slow decomposition even at −78°C, and decomposes within minutes at ambient conditions to form dark green residue. **^{1}H NMR** (CD_2Cl_2, 400 MHz, 213 K): δ 2.50 (br s, OH), 1.18 (br s, 3H, Me), 0.88 (br s, 3H, Me); **^{19}F NMR** (376 MHz, CD_2Cl_2, 213 K): δ −30.2 (br s, 6F); **IR** (ATR): $\tilde{\nu}$ = 3652, 2969, 1477, 1261, 1097, 958, 723, 864, 547 cm^{-1}; **CCDC** 2533528.

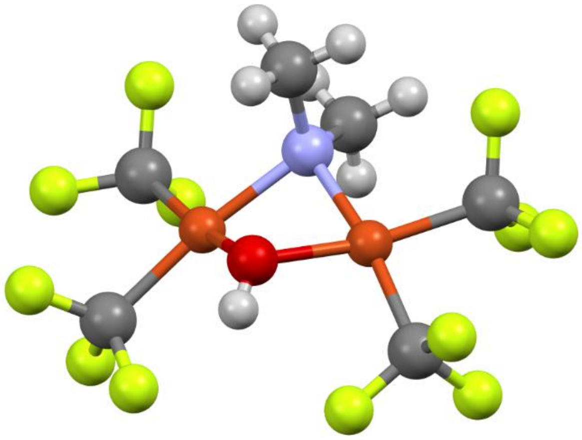


Figure S6. Crystal structure of tetrakis(trifluoromethyl)-μ$_2$-(hydroxy)-μ$_2$-(dimethylamino)dicopper(III) **5**

Table 8. Crystal data and structure refinement for **5**

CCDC number	2533533
Empirical formula	$C_9H_{13}Cu_2F_{12}NO_2$
Formula weight	522.28
Temperature [K]	150.00
Crystal system	orthorhombic
Space group (number)	$P2_12_12_1$ (19)
a [Å]	6.9282(4)
b [Å]	10.9375(8)
c [Å]	22.2948(17)
α [°]	90
β [°]	90
γ [°]	90
Volume [Å^3]	1689.4(2)
Z	4
ρ_{calc} [gcm^{-3}]	2.053
μ [mm^{-1}]	2.646
F(000)	1024
Crystal size [mm^3]	0.37×0.431×0.463
Crystal colour	orange
Crystal shape	block
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	4.15 to 50.73 (0.83 Å)
Index ranges	$-8 \le h \le 8$ $-13 \le k \le 13$ $-26 \le l \le 26$
Reflections collected	30495
Independent reflections	3113 R_{int} = 0.0701 R_{sigma} = 0.0308
Completeness to θ = 25.242°	99.9 %
Data / Restraints / Parameters	3113 / 2 / 206
Absorption correction T_{min}/T_{max} (method)	0.4914 / 0.7452 (multi-scan)
Goodness-of-fit on F^2	1.047
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0298 wR_2 = 0.0756

Final *R* indexes [all data]	R_1 = 0.0338 wR_2 = 0.0786
Largest peak/hole [eÅ^{-3}]	0.57/−0.48
Flack X parameter	0.45(2)

Table 9. Bond lengths and angles for **5**

Atom–Atom	**Length [Å]**
Cu2–Cu1	2.7034(9)
Cu2–O1	1.850(4)
Cu2–N1	1.948(5)
Cu2–C3	1.947(6)
Cu2–C4	1.931(7)
Cu1–O1	1.878(4)
Cu1–N1	1.959(5)
Cu1–C2	1.940(7)
Cu1–C1	1.925(6)
F7–C3	1.345(7)
F3–C1	1.337(7)
F2–C1	1.323(7)
F4–C2	1.335(7)
F9–C3	1.335(7)
F6–C2	1.365(7)
F1–C1	1.352(7)
F5–C2	1.339(7)
O1–H1	0.80(3)
F11–C4	1.341(8)
F10–C4	1.327(9)
F12–C4	1.353(8)
F8–C3	1.337(7)
N1–C6	1.477(8)
N1–C5	1.486(7)
C6–H6A	0.9800
C6–H6B	0.9800
C6–H6C	0.9800
C5–H5A	0.9800
C5–H5B	0.9800
C5–H5C	0.9800
Atom–Atom–Atom	**Angle [°]**
O1–Cu2–Cu1	43.92(12)
O1–Cu2–N1	80.23(19)
O1–Cu2–C3	94.6(2)
O1–Cu2–C4	166.4(3)
N1–Cu2–Cu1	46.40(14)
C3–Cu2–Cu1	124.39(18)
C3–Cu2–N1	169.8(2)
C4–Cu2–Cu1	140.2(2)
C4–Cu2–N1	97.4(3)
C4–Cu2–C3	89.7(3)
O1–Cu1–Cu2	43.10(12)
O1–Cu1–N1	79.26(19)
O1–Cu1–C2	95.0(2)
O1–Cu1–C1	167.9(2)
N1–Cu1–Cu2	46.06(14)
C2–Cu1–Cu2	126.47(19)
C2–Cu1–N1	172.5(2)
C1–Cu1–Cu2	139.09(19)
C1–Cu1–N1	97.0(2)
C1–Cu1–C2	89.6(3)
Cu2–O1–Cu1	92.98(18)
Cu2–O1–H1	118(3)
Cu1–O1–H1	114(3)
Cu2–N1–Cu1	87.5(2)
C6–N1–Cu2	117.0(4)
C6–N1–Cu1	118.3(4)
C6–N1–C5	110.3(5)
C5–N1–Cu2	111.7(4)
C5–N1–Cu1	110.3(4)
N1–C6–H6A	109.5
N1–C6–H6B	109.5
N1–C6–H6C	109.5
H6A–C6–H6B	109.5
H6A–C6–H6C	109.5
H6B–C6–H6C	109.5
F4–C2–Cu1	114.2(4)
F4–C2–F6	105.9(5)
F4–C2–F5	107.0(5)
F6–C2–Cu1	109.6(4)
F5–C2–Cu1	115.0(4)
F5–C2–F6	104.4(5)
F3–C1–Cu1	111.1(4)
F3–C1–F1	103.6(5)
F2–C1–Cu1	110.8(4)
F2–C1–F3	107.6(5)
F2–C1–F1	106.4(5)
F1–C1–Cu1	116.7(4)
N1–C5–H5A	109.5
N1–C5–H5B	109.5
N1–C5–H5C	109.5
H5A–C5–H5B	109.5
H5A–C5–H5C	109.5
H5B–C5–H5C	109.5
F7–C3–Cu2	109.4(4)
F9–C3–Cu2	114.8(4)
F9–C3–F7	105.5(5)
F9–C3–F8	107.3(5)
F8–C3–Cu2	114.0(4)
F8–C3–F7	105.1(5)
F11–C4–Cu2	110.4(5)
F11–C4–F12	105.0(6)
F10–C4–Cu2	110.8(5)
F10–C4–F11	108.5(6)
F10–C4–F12	106.5(6)
F12–C4–Cu2	115.3(5)

Table 10. Torsion angles for **5**

Atom–Atom–Atom–Atom	**Torsion Angle [°]**
N1–Cu2–O1–Cu1	33.90(18)
N1–Cu1–O1–Cu2	−33.80(18)

C2–Cu1–O1–Cu2	141.3(2)
C1–Cu1–O1–Cu2	−107.0(11)
C3–Cu2–O1–Cu1	−137.2(2)
C4–Cu2–O1–Cu1	114.8(10)

Calculations and oxidation state analysis of complexes

The optimization of geometries for compounds in solution was done at the B3LYP level[8] with Zero-Order Regular Approximation relativistic Hamiltonian[9] using the ZORA-def2-TZVP[10] basis set with D3(BJ)[11] dispersion correction as implemented in the ORCA 6.1.0 software[12] (defgrid 3) for singlet state of all complexes **3-5**. The solvent environment was represented as CPCM(DCM)[13] solvation model. The single point energy calculations were done at the ωB97X-D3(BJ)[11]/def2-TZVPPD level of theory (method 1) or at the DLPNO-CCSD(T)[14]/ZORA-def2-TZVP[10] level with an improved tightPNO implementation[15] (method 2) using the B3LYP-D3(BJ)[11]/ZORA-def2-TZVP optimal geometries. Vibrational frequencies and thermochemistry were calculated on the same level as geometries; final results of optimization contain no imaginary frequencies. The computed geometry can be found in the separately provided .xyz files. Natural bonding orbital (NBO)[16] analysis including NPA charge calculations was performed on ωB97X-D3(BJ)/def2-QZVPPD level of theory using the B3LYP-D3(BJ)/ZORA-def2-TZVP optimal geometries. Visualization of the orbitals was accomplished using ChemCraft[17] and IboView[18] software. OSLO[19] oxidation state analysis was performed using APOST-3D[20] program with a Topological Fuzzy-Voronoi cells (TFVC)[21] approximation, where copper atoms, bridging ligands, and CF_3 groups were identified as separate fragments for orbital localization.

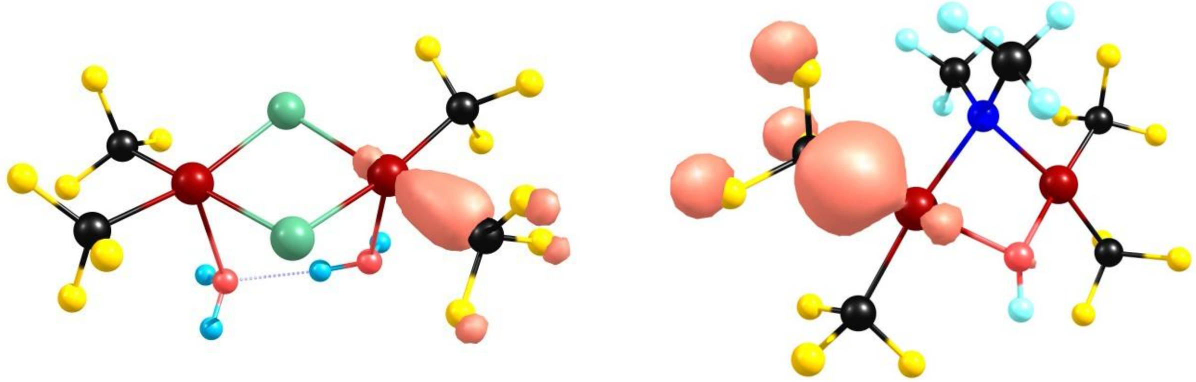
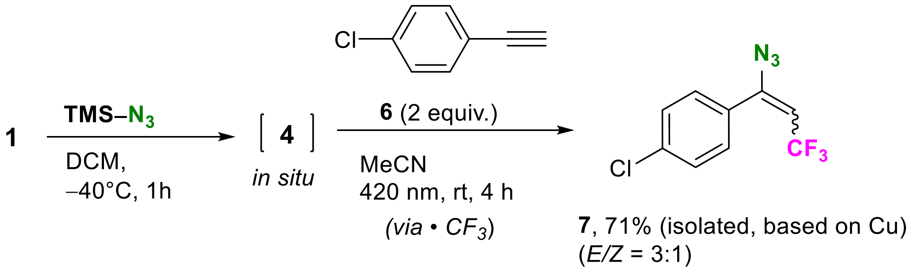


*Figure S7. Illustration of the last localized orbitals in OSLO for chloride complex **3** (left) and amino complex **5** (right).*

Transformations and applications of complexes

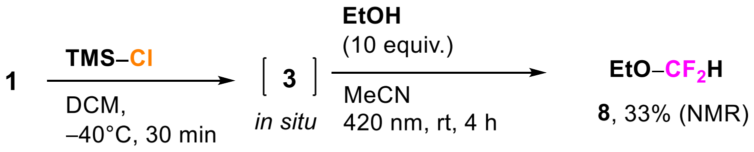
Synthesis of vinyl azides 7 from copper(III) azide 4



In a 10 ml round-bottomed Schlenk flask under argon atmosphere, a solution of heterocubane **1** (21.8 mg, 0.025 mmol [0.1 mmol monomer]) in acetonitrile (1.5 ml) was cooled to −40°C. $TMSN_3$ (26.3 µl, 0.2 mmol, 2 equiv.) was added with vigorous stirring under positive pressure of argon. The mixture was additionally stirred for 1 hour at −40°C, then ammonium persulfate (45 mg, 0.2 mmol, 2 equiv.) and 1-chloro-4-ethynylbenzene **6** (27 mg, 0.2 mmol, 2 equiv.) were sequentially added. The mixture was taken out of the cooling bath and irradiated by 420 nm LED (2*30 W) for 4 hours, while warming up to room temperature. Afterwards it was directly subjected to column chromatography in pentane to give vinyl azides (*E*)-**7a** (13.1 mg) and (*Z*)-**7b** (4.4 mg) as colorless oils. Total yield 17.5 mg, 71% based on Cu(III).

Major isomer ((*E*)-1-(1-azido-3,3,3-trifluoroprop-1-en-1-yl)-4-chlorobenzene): **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.46-7.42 (m, 2H), 7.34-7.30 (m, 2H), 5.55 (q, *J* = 7.7 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 149.0 (br s), 136.8, 131.7, 129.7, 129.2, 122.9 (q, *J* = 268.5 Hz), 105.3 (q, *J* = 36.0 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ −54.5 (d, *J* = 7.7 Hz, 3F). Characterization matches previously reported data.[22] **Minor isomer** ((*Z*)-1-(1-azido-3,3,3-trifluoroprop-1-en-1-yl)-4-chlorobenzene): **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.48-7.46 (m, 2H), 7.40-7.38 (m, 2H), 5.25 (q, *J* = 7.8 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 137.2, 131.7, 130.2, 129.7, 128.8, 122.3 (q, *J* = 270.4 Hz), 105.7 (q, *J* = 36.1 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ −57.3 (d, *J* = 7.8 Hz, 3F).

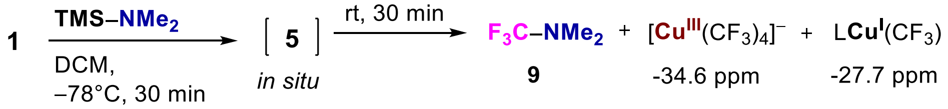
Difluoromethylation of alcohol



In a 10 ml round-bottomed Schlenk flask under argon atmosphere to the solid heterocubane **1** (11.0 mg, 0.0125 mmol [0.05 mmol monomer]) acetonitrile (1 ml) was added and the mixture was cooled to −40°C. Trimethylsilyl chloride (25 µl, 0.2 mmol, 2 equiv.) was added with vigorous stirring. The mixture was stirred at −40°C for 1 hour; during this time the solution turned intensive yellow. Then ethanol (28 µl, 0.5

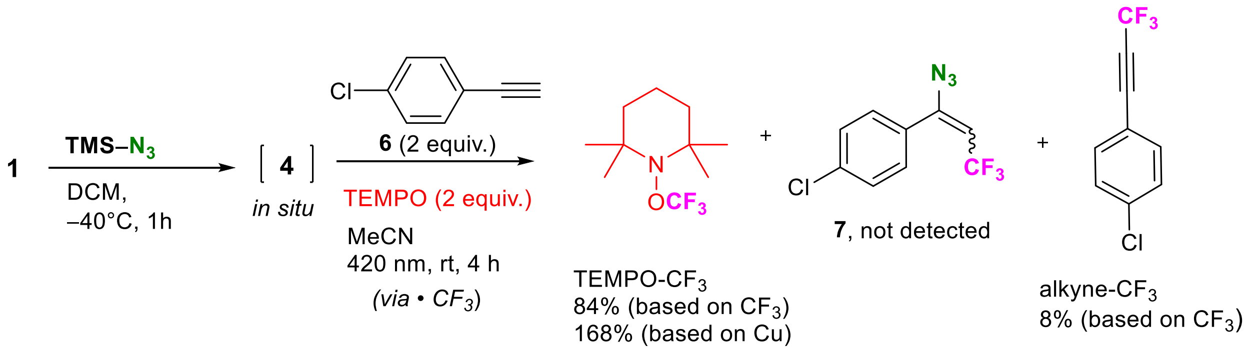
mmol, 10 equiv.) was added in one portion under argon, and the mixture was taken out of the cooling bath and irradiated by 420 nm LED (2*30 W) for 4 hours, while warming up to room temperature. Then C_6F_6 (0.1 mmol) was added and the mixture was analyzed by ^{19}F NMR, which indicated formation of EtO−CF_2H **8** (δ = −84.0 ppm) in 33% yield. NMR matched previously reported data.[23]

Formation of *N*-trifluoromethylamine 9 via reductive elimination in 5



In a 10 ml round-bottomed Schlenk flask under argon atmosphere to the solid heterocubane **1** (21.8 mg, 0.025 mmol [0.1 mmol monomer]) dry CD_2Cl_2 (0.7 ml) was added and the mixture was cooled to −78°C (dry ice/acetone). (N,N-Dimethylamino)trimethylsilane (8 µl, 0.05 mmol, 0.5 equiv.) was added with vigorous stirring. The mixture was stirred 1 hour; ^{19}F NMR (at −60°C) indicated formation of **5**. Then C_6F_6 (0.1 mmol) was added and the mixture was warmed up to room temperature upon vigorous stirring. The mixture turned dark green within 1-2 minutes, then the intensive color ceased. ^{19}F NMR recorded after 30 minutes indicated formation of *N*-trifluoromethylamine **9** $Me_2N−CF_3$ (δ = −69.8 ppm),[23,24] $[Cu(CF_3)_4]^-$ (δ = −34.6 ppm)[25] and $CuCF_3$ species[26] (likely additionally coordinated to the amine or hydroxyl group) as by-products, as both $[Cu^{III}(CF_3)_4]^-$ and $[Cu^{I}(CF_3)_2]^-$ were detected by negative ESI-MS.

Control experiment with TEMPO



In a 10 ml round-bottomed Schlenk flask under argon atmosphere, a solution of heterocubane **1** (21.8 mg, 0.025 mmol [0.1 mmol monomer]) in acetonitrile (1.5 ml) was cooled to −40°C. $TMSN_3$ (26.3 µl, 0.2 mmol, 2 equiv.) was added with vigorous stirring under positive pressure of argon. The mixture was additionally stirred for 1 hour at −40°C, then ammonium persulfate (45 mg, 0.2 mmol, 2 equiv.), 4-chloro-1-ethynylbenzene **6** (27 mg, 0.2 mmol, 2 equiv.) and TEMPO (31 mg, 0.2 mmol, 2 equiv.) were sequentially added. The mixture was taken out of the cooling bath and irradiated by 420 nm LED (2*30 W) for 4 hours, while warming up to room temperature. Then C_6F_6 (0.1 mmol) was added and the mixture was analyzed by

^{19}F NMR, which indicated formation of TEMPO-CF$_3$ adduct (δ = −55.6 ppm) in 84% yield based on CF$_3$ group (168% based on copper) and traces of CF$_3$-alkyne (δ = −50.0 ppm).

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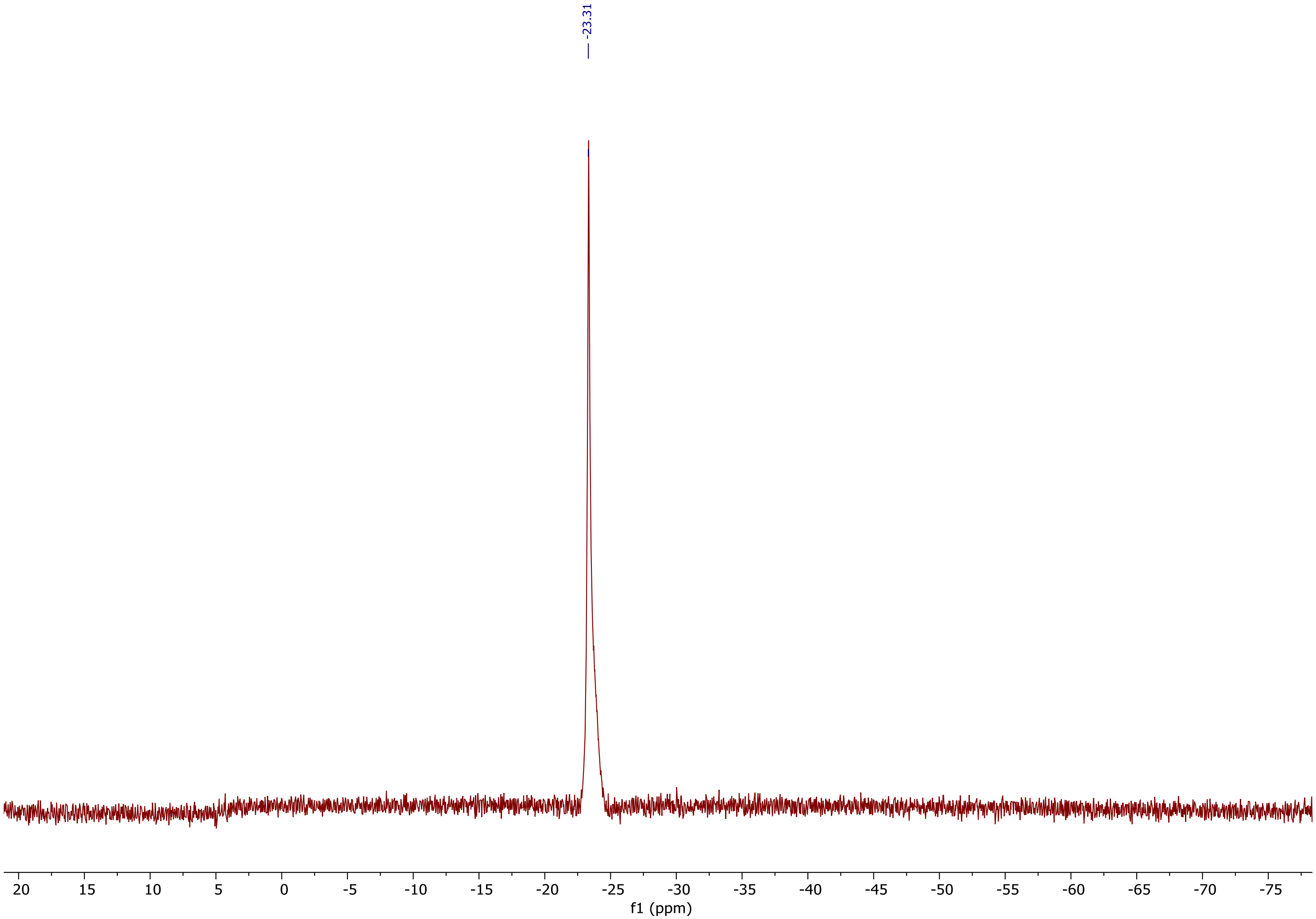
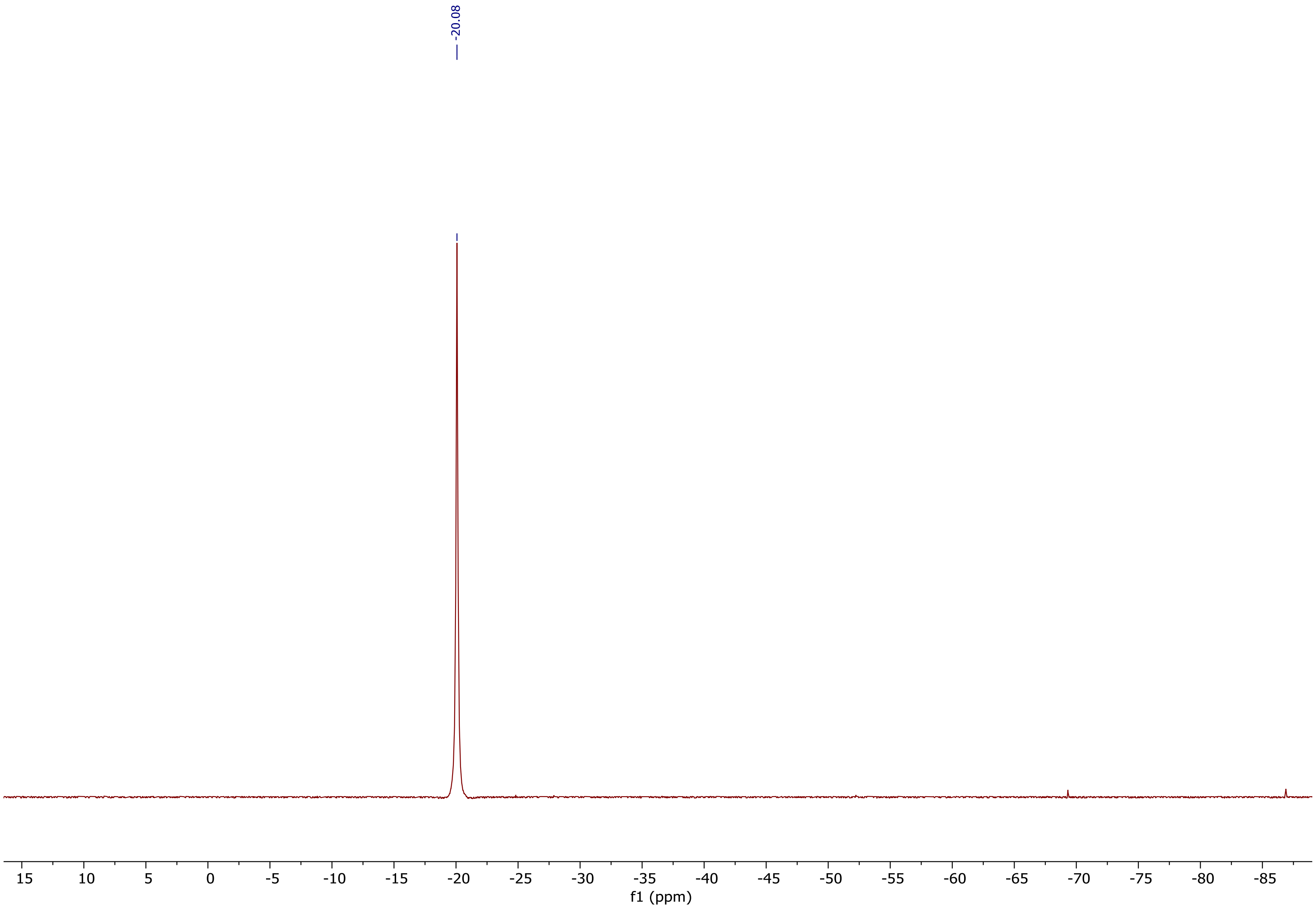
Copies of NMR spectra

Bis(μ_2-chlorido)-diaqua-tetrakis(trifluoromethyl)dicopper(III) 3

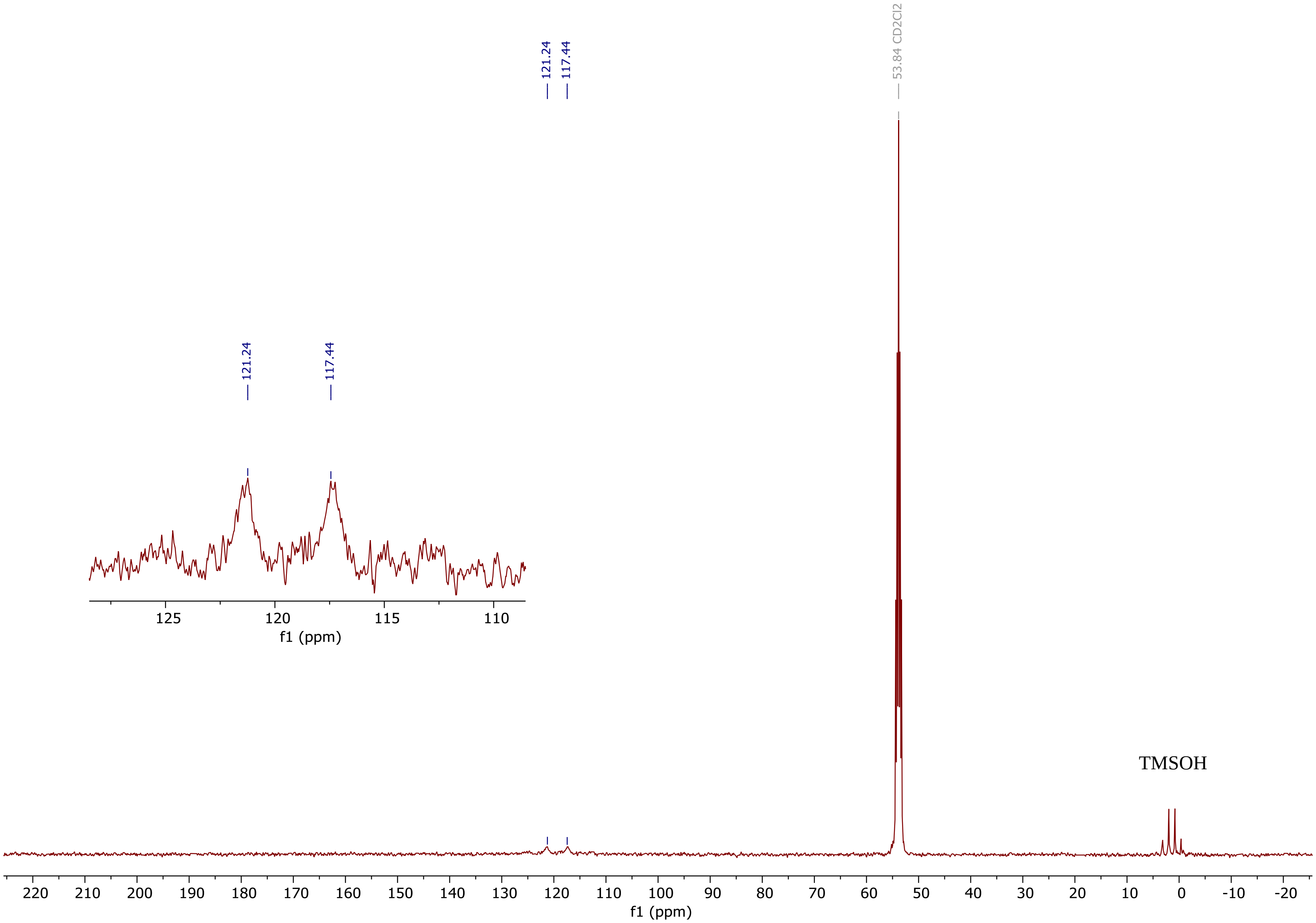
^{19}F NMR (CD_3CN, 376 MHz, 293 K)



^{19}F NMR (CD_2Cl_2, 376 MHz, 213 K)

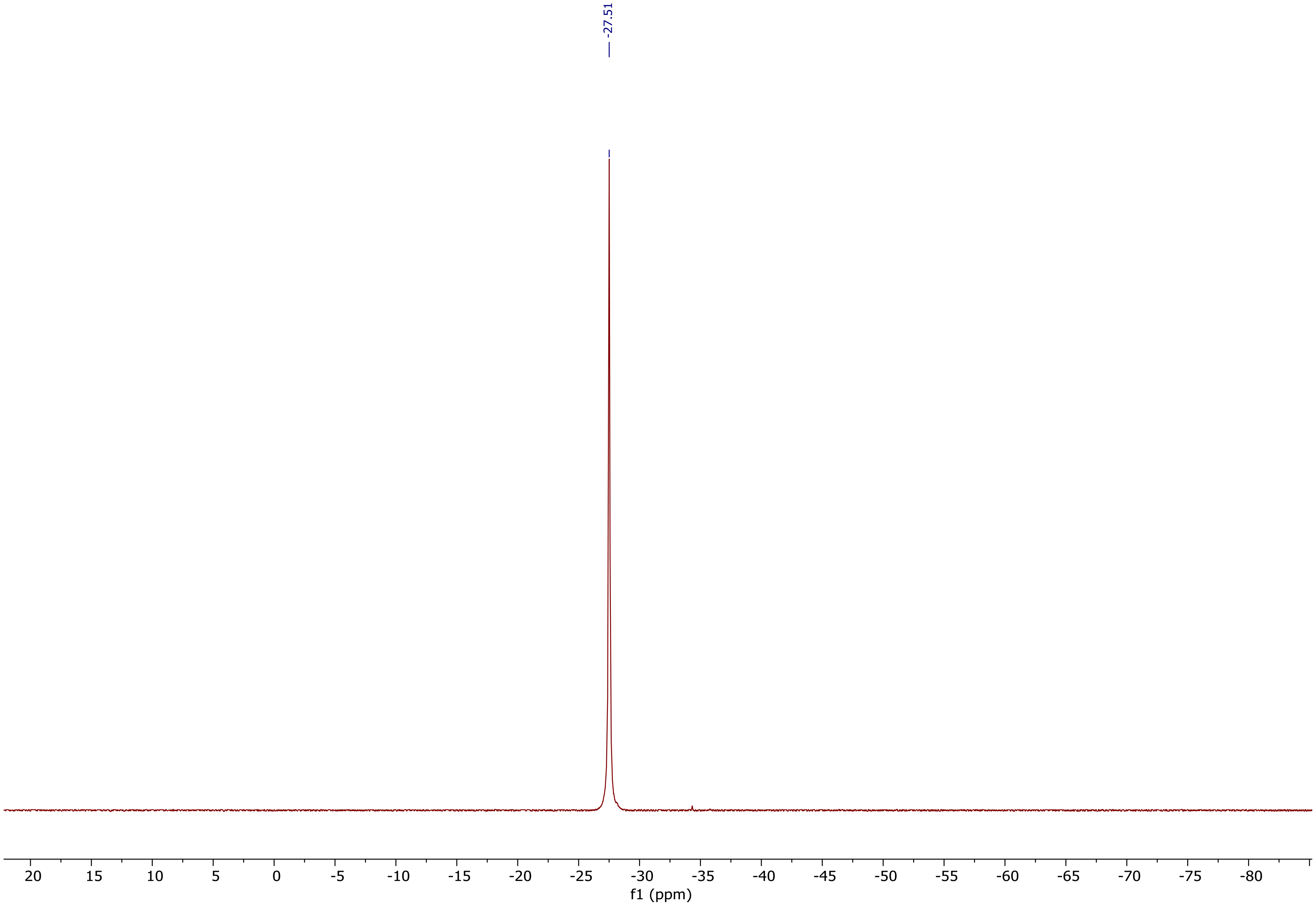


$^{13}C\{^{19}F\}$ NMR (CD_2Cl_2, 101 MHz, 213 K) (from the concentrated reaction mixture)

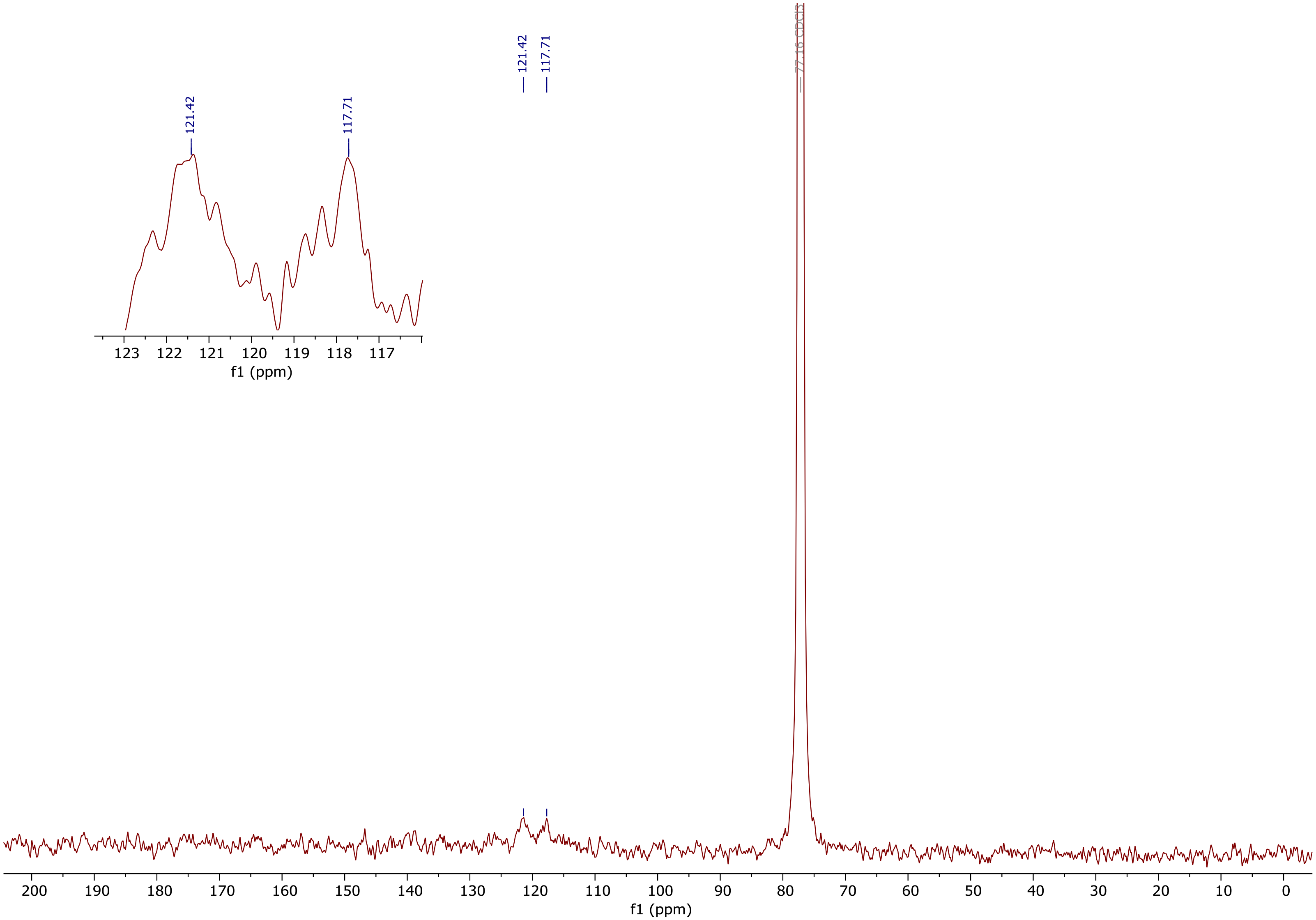


Bis(μ_2-(κ_1-azido))tetrakis(trifluoromethyl)dicopper(III) 4

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

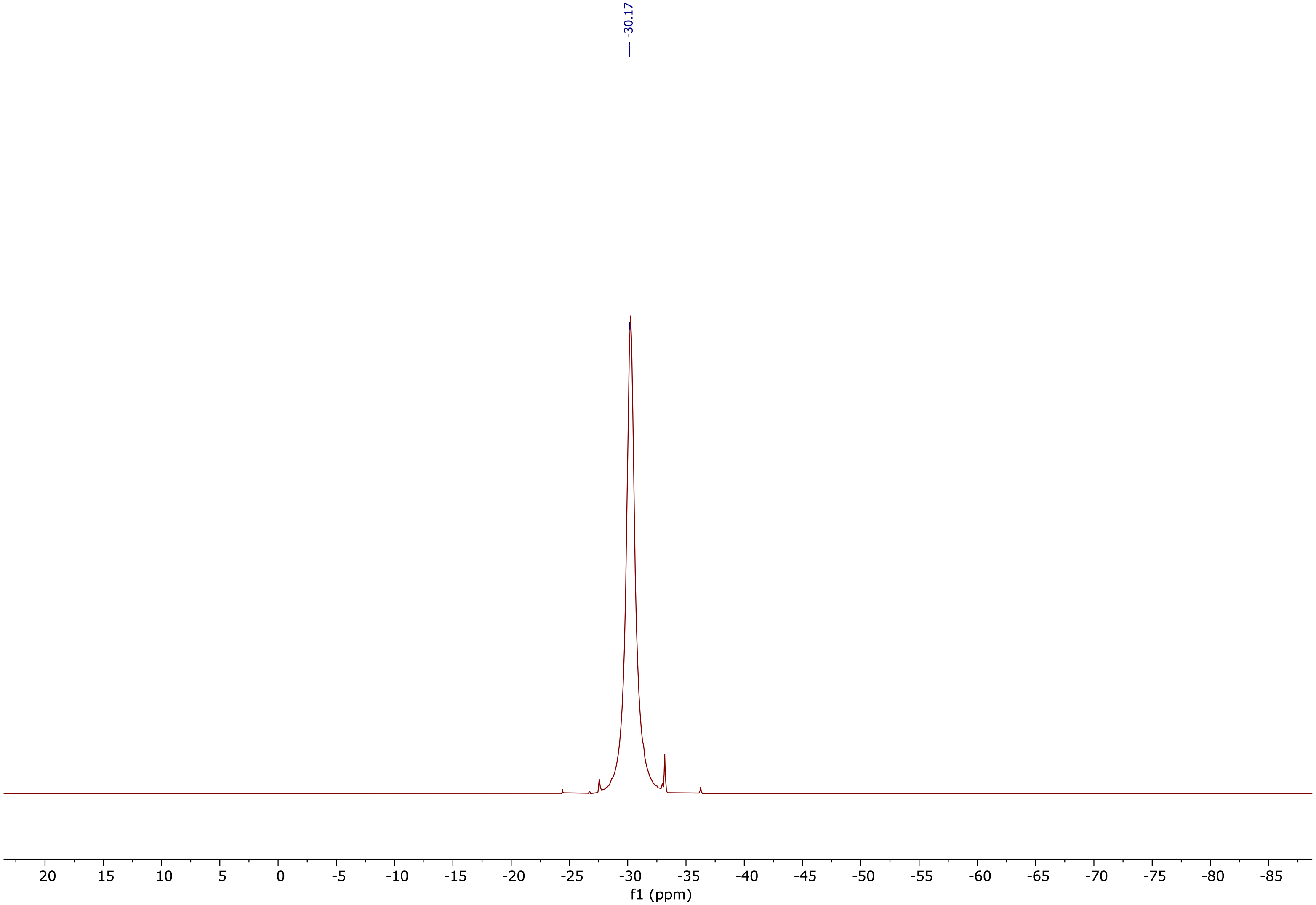


$^{13}C\{^{19}F\}$ NMR ($CDCl_3$, 101 MHz)

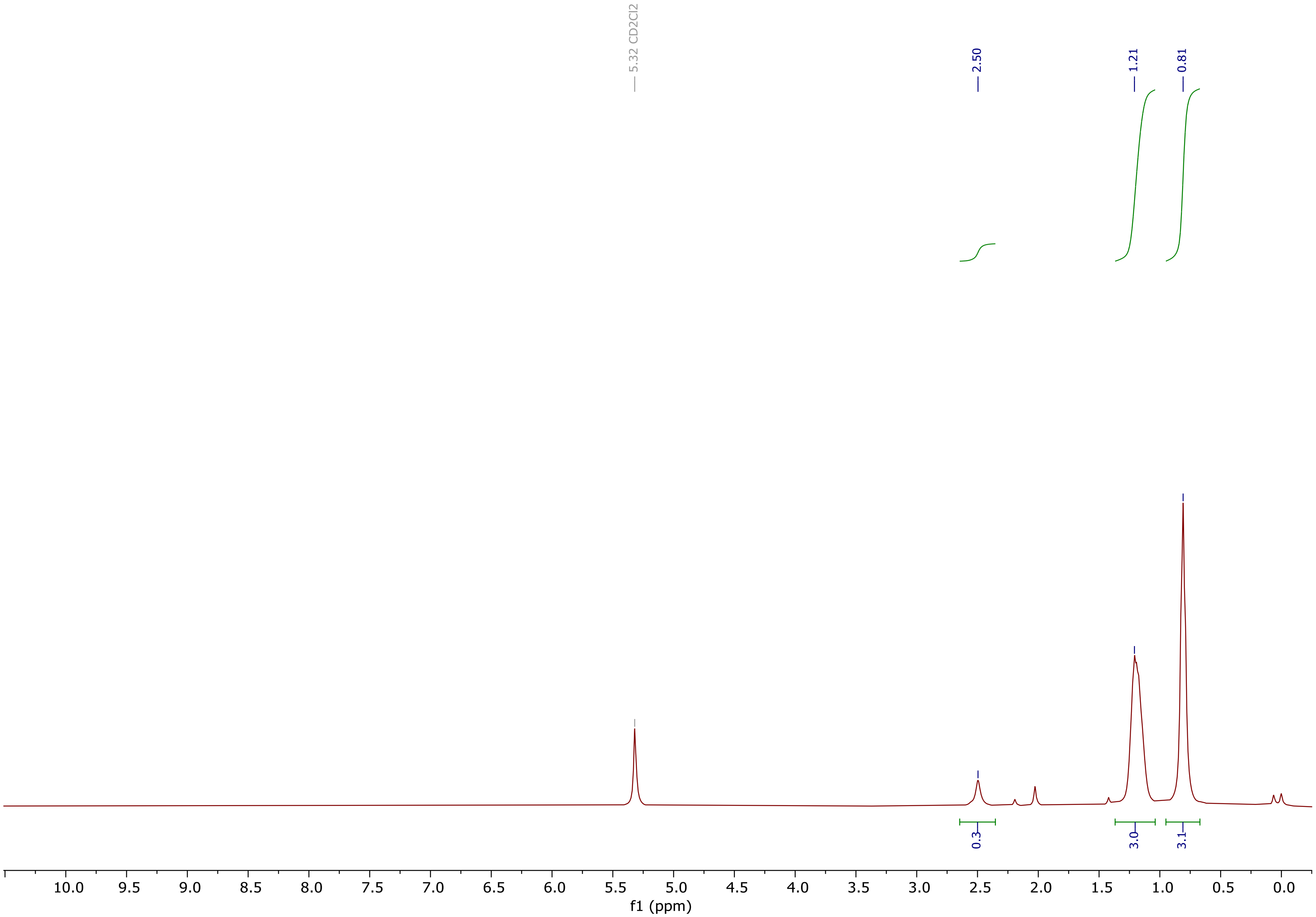


μ2-(Dimethylamino)-μ2-hydroxy-tetrakis(trifluoromethyl)dicopper(III) 5

^{19}F NMR (CD_2Cl_2, 376 MHz, 213 K)

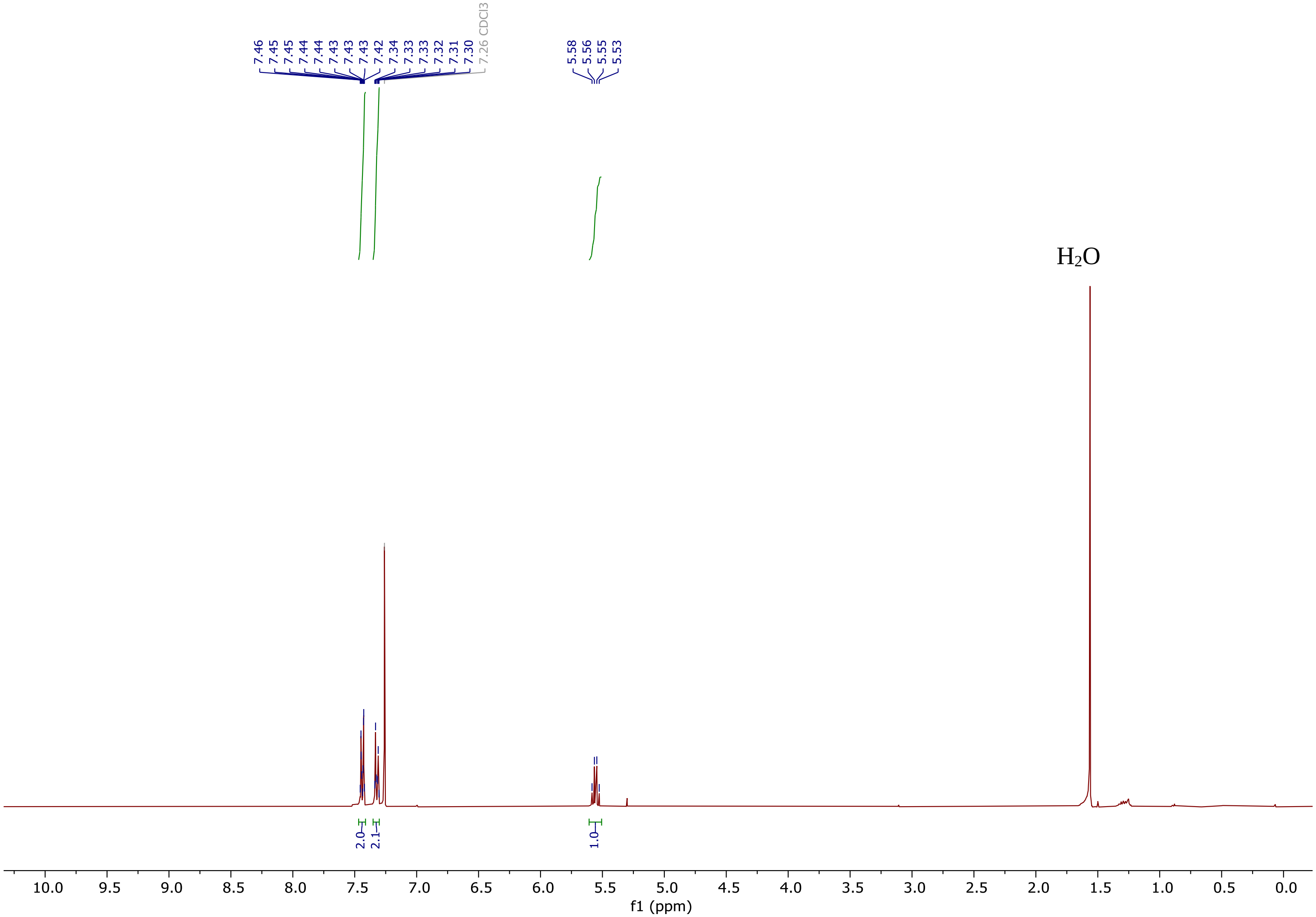


^{1}H NMR (CD_2Cl_2, 400 MHz, 213 K)

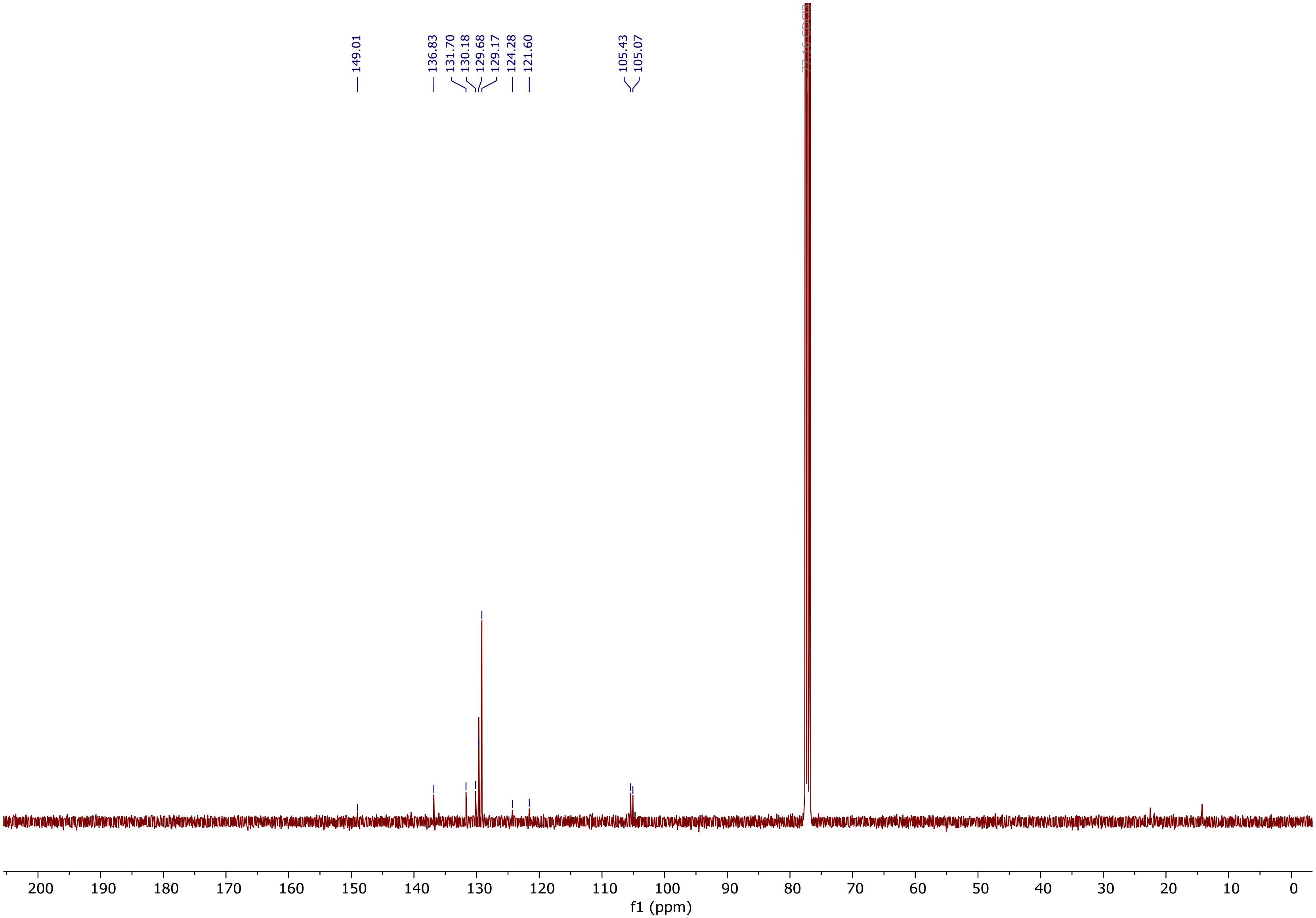


(*E*)-1-(1-azido-3,3-trifluoroprop-1-en-1-yl)-4-chlorobenzene 7a (major isomer)

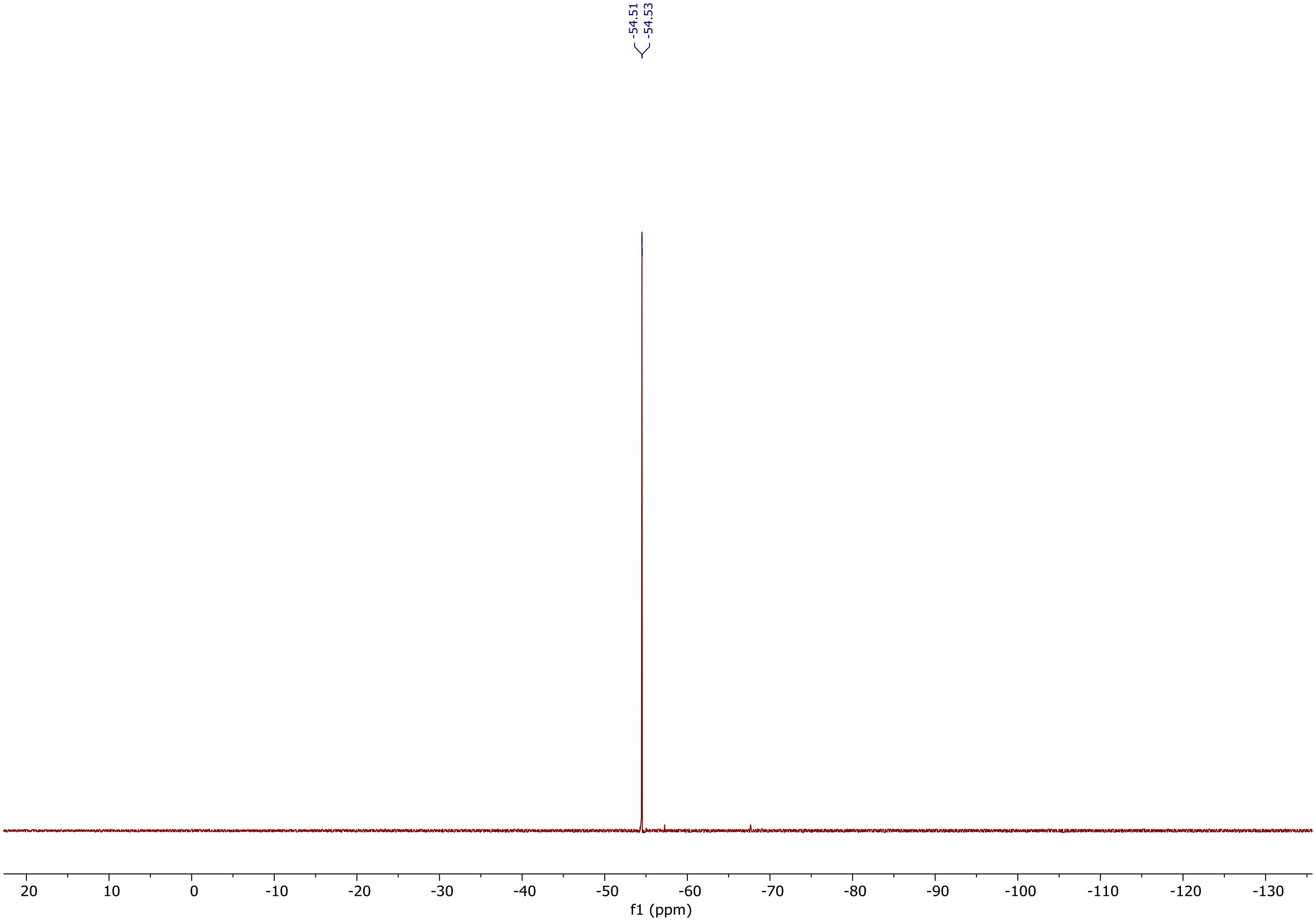
^{1}H NMR ($CDCl_3$, 400 MHz, 293 K)



^{13}C NMR (CDCl$_3$, 101 MHz, 293 K)

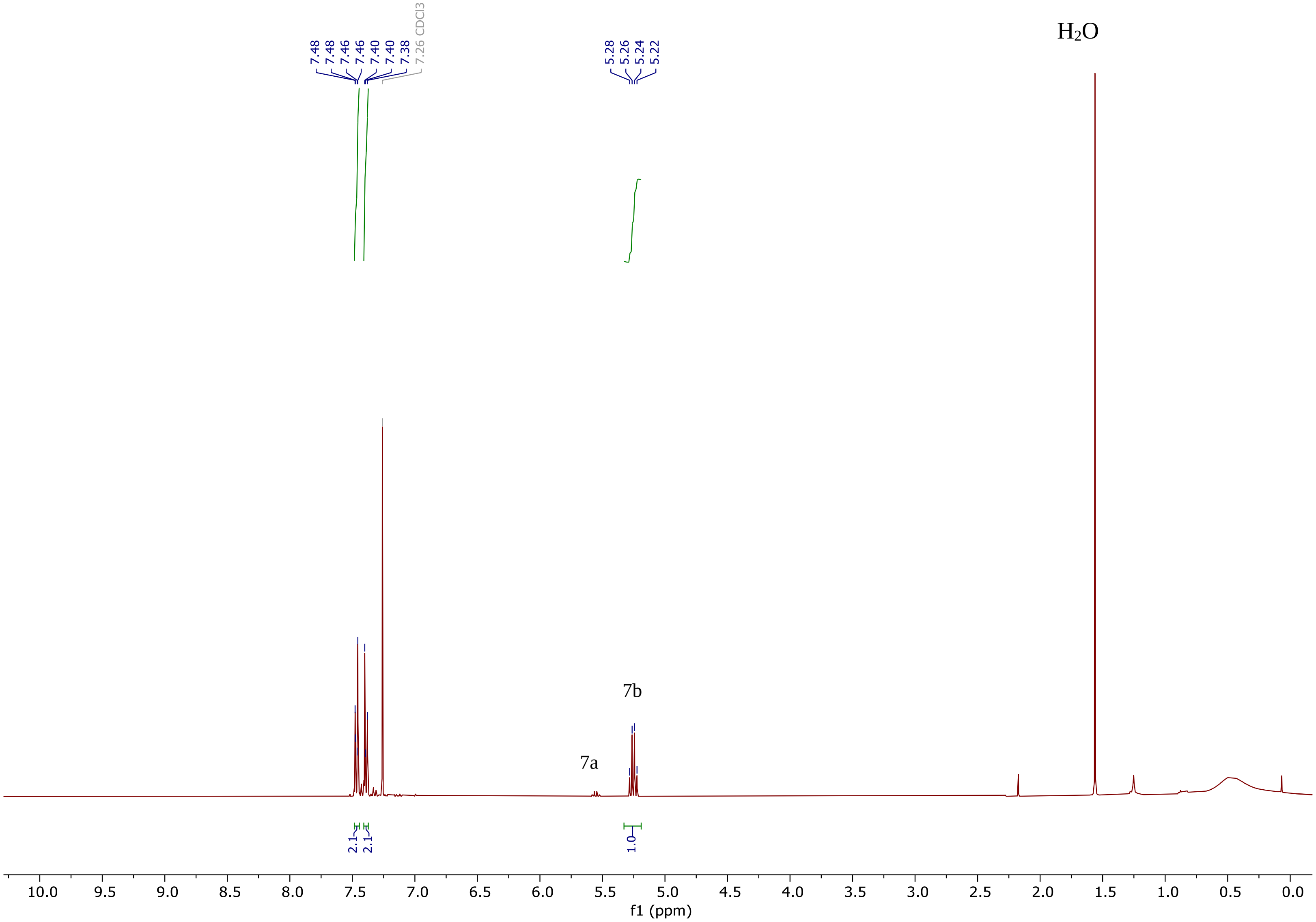


^{19}F NMR (CDCl$_3$, 376 MHz, 293 K)

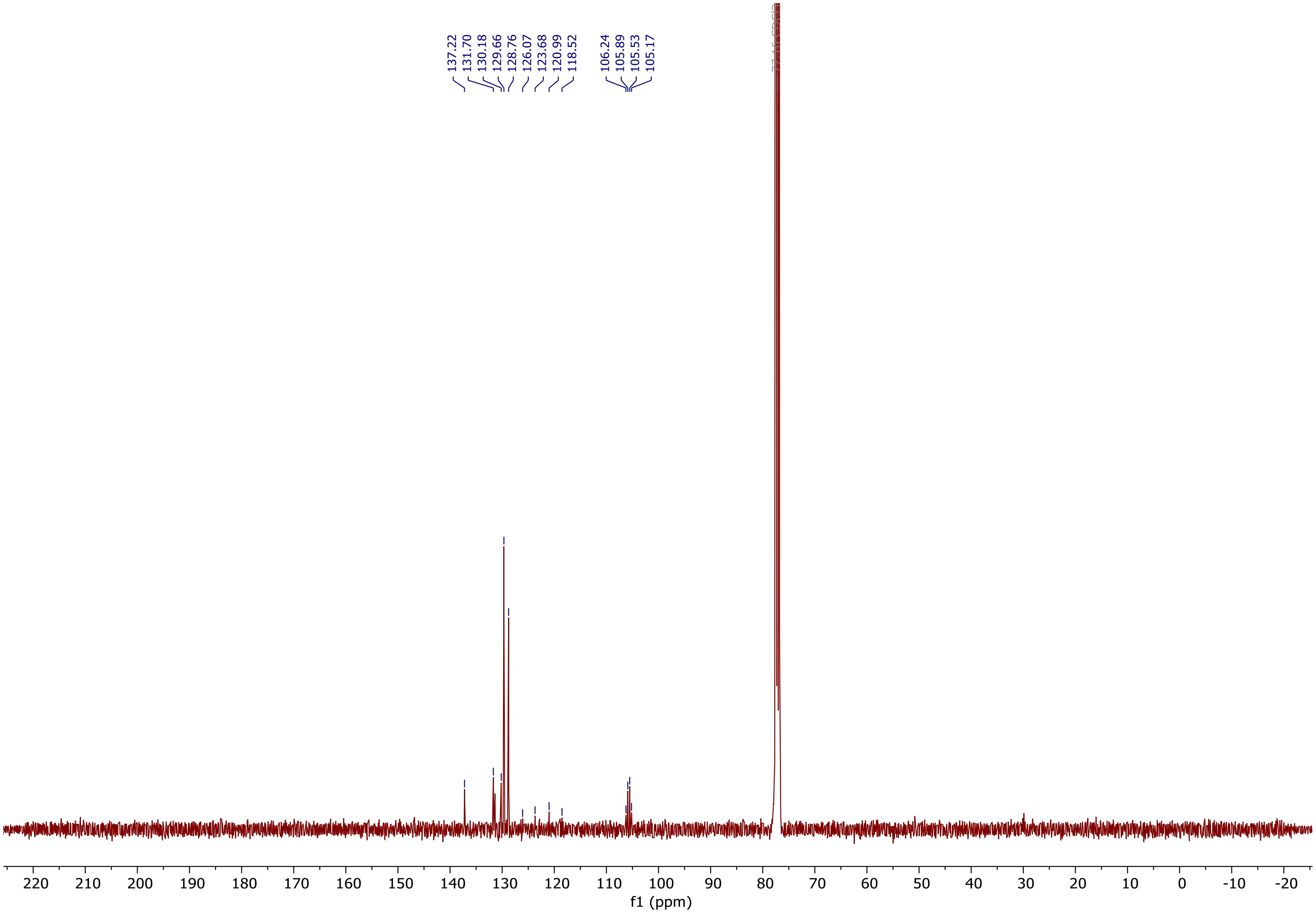


(*Z*)-1-(1-azido-3,3,3-trifluoroprop-1-en-1-yl)-4-chlorobenzene 7b (minor isomer with traces of major (*E*)-isomer)

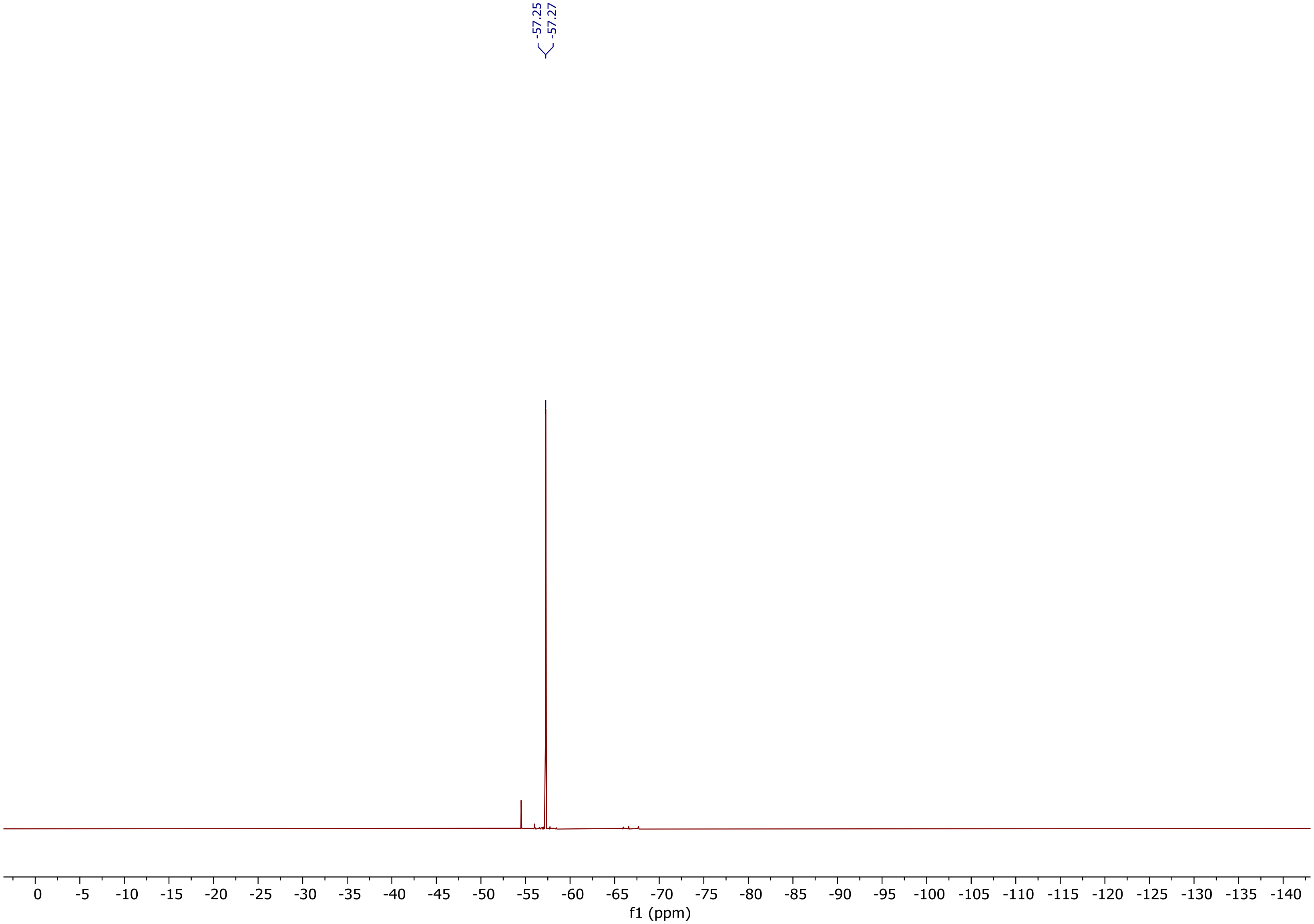
^{1}H NMR (CDCl$_3$, 400 MHz, 293 K)



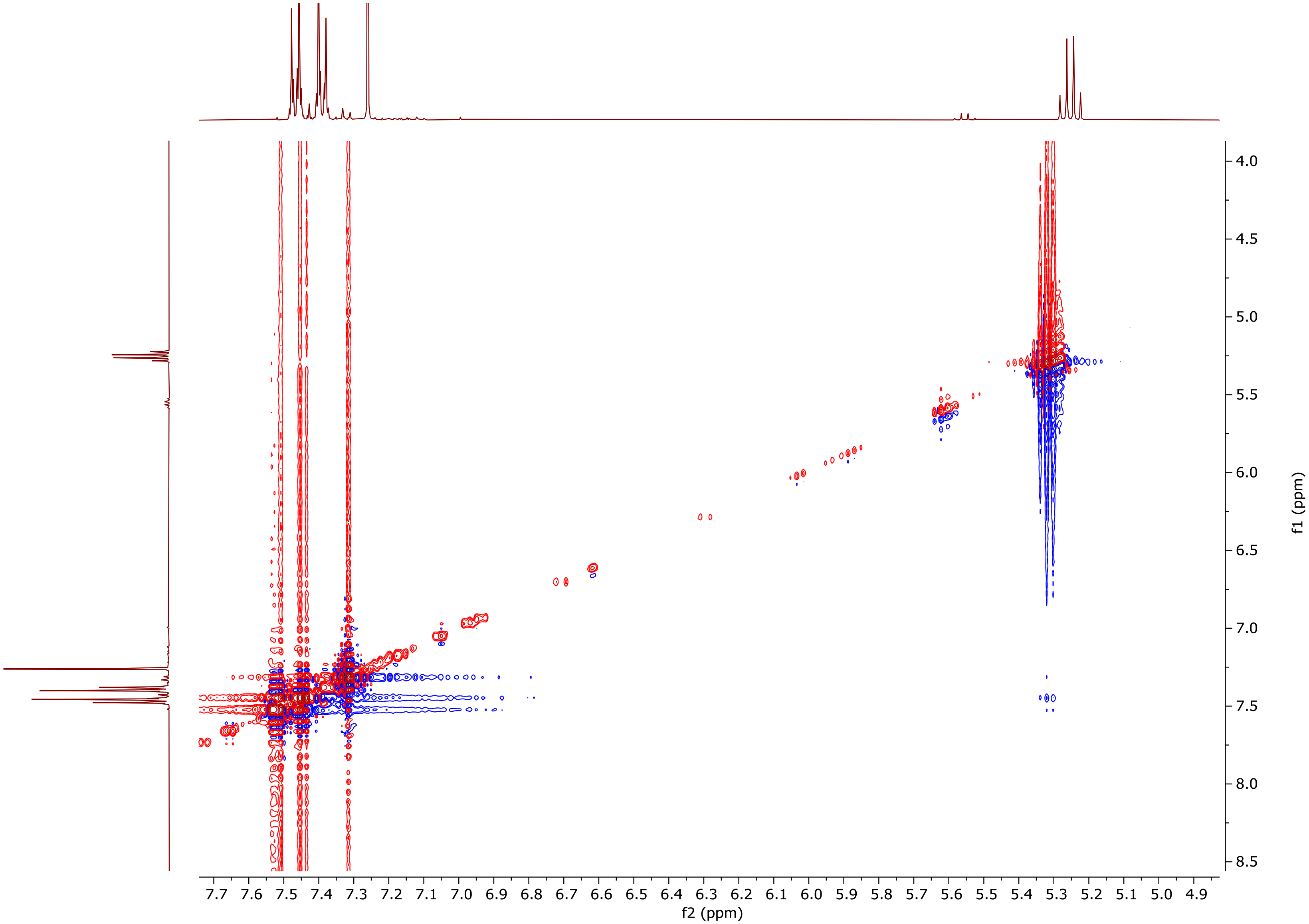
^{13}C NMR (CDCl$_3$, 101 MHz, 293 K)



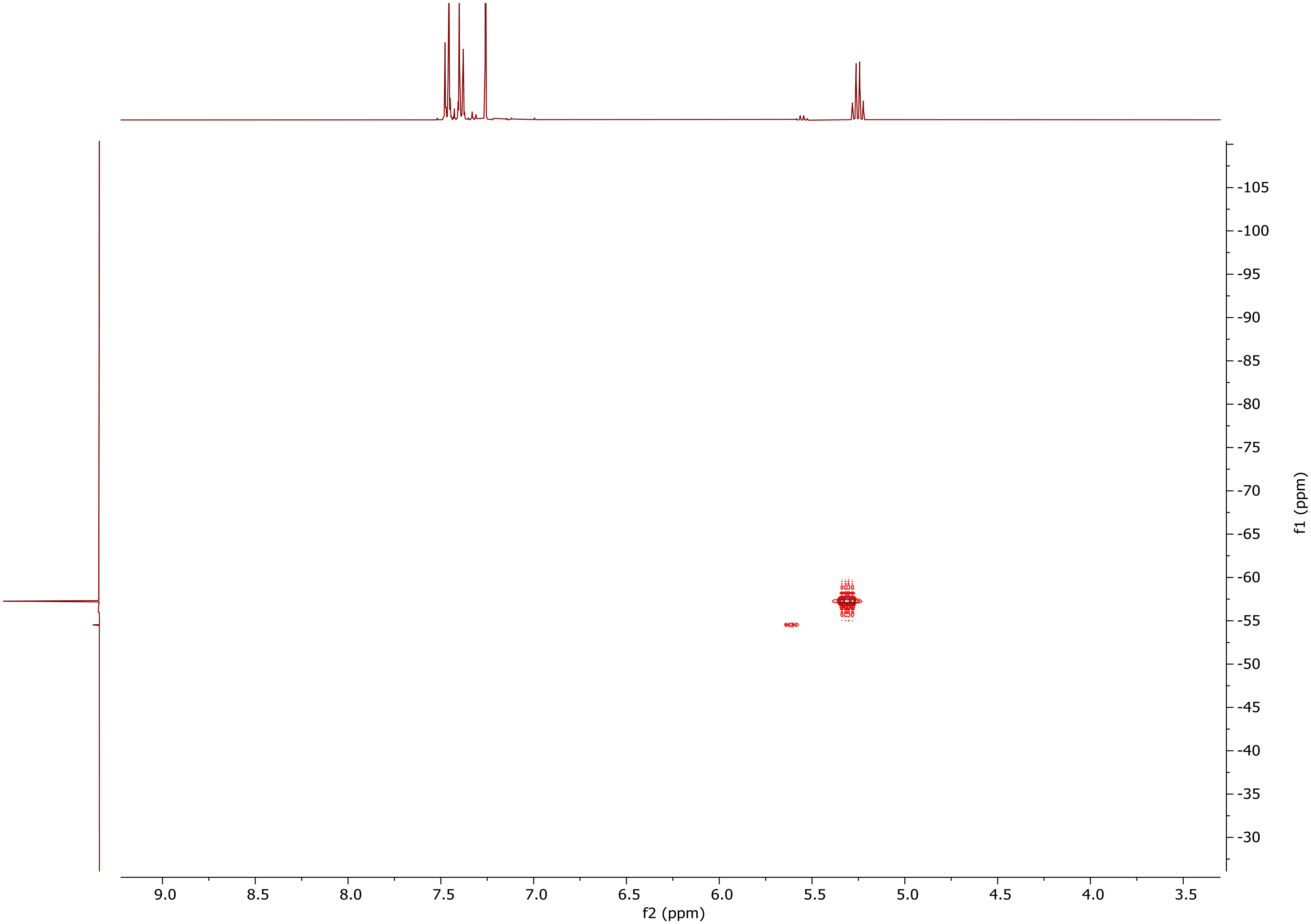
^{19}F NMR (CDCl$_3$, 400 MHz, 293 K)



^{1}H-^{1}H NOESY NMR (CDCl$_3$, 400 MHz, 293 K)

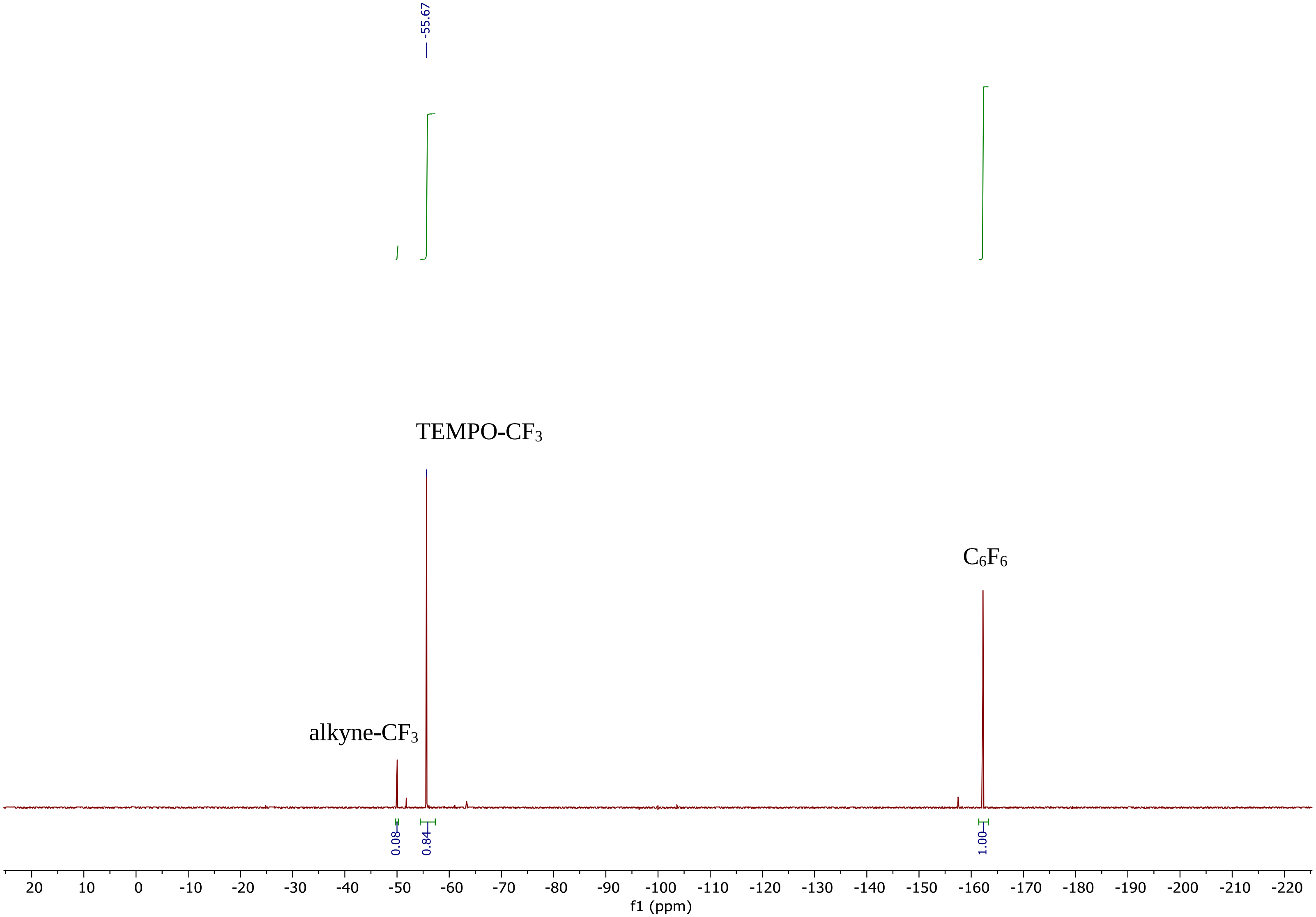


$^1H,^{19}F$-HETCOR NMR ($CDCl_3$, 293 K)



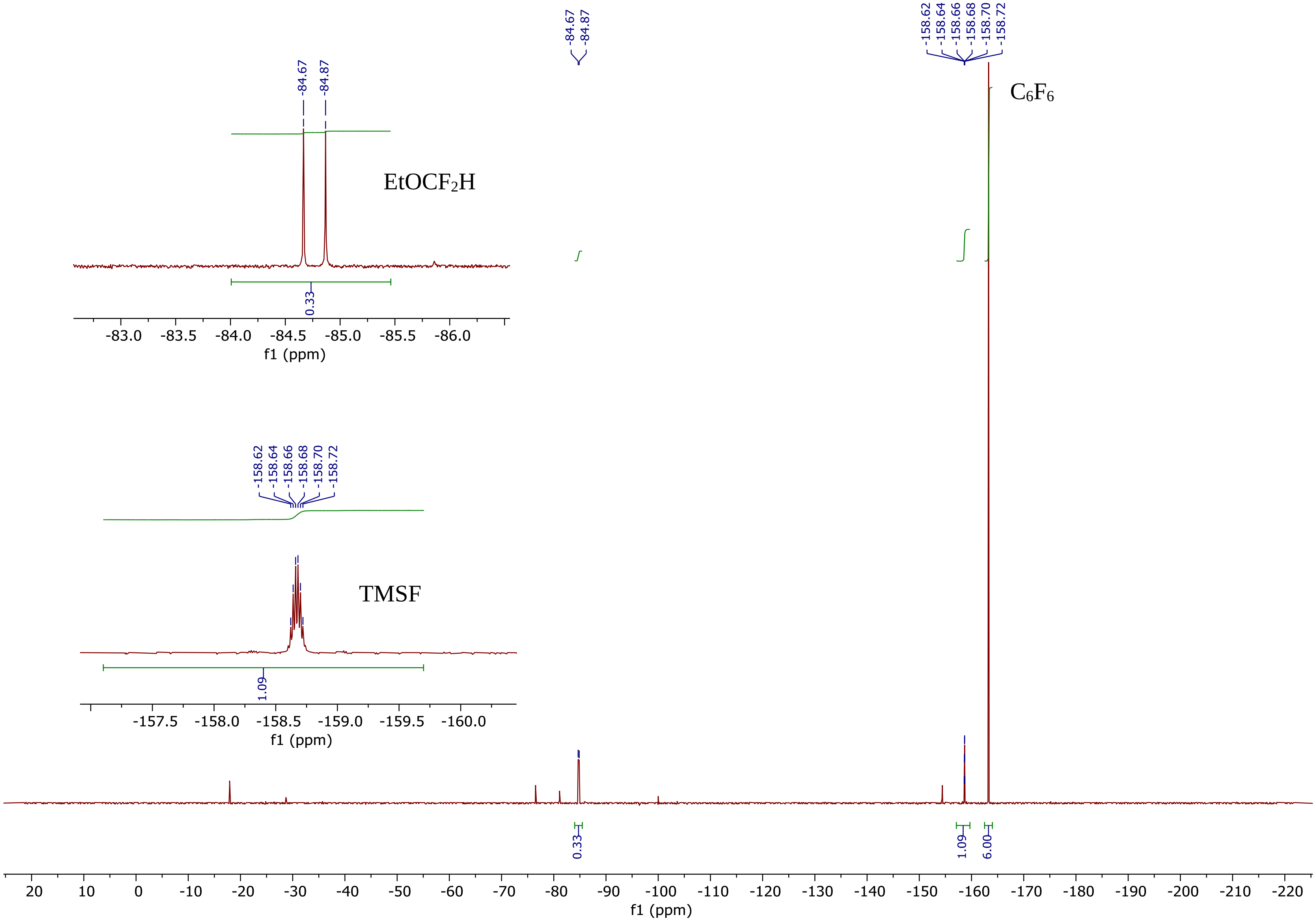
Detection of TEMPO-CF_3 adduct

^{19}F NMR ($CDCl_3$, 376 MHz) [+ 1 equiv. C_6F_6]



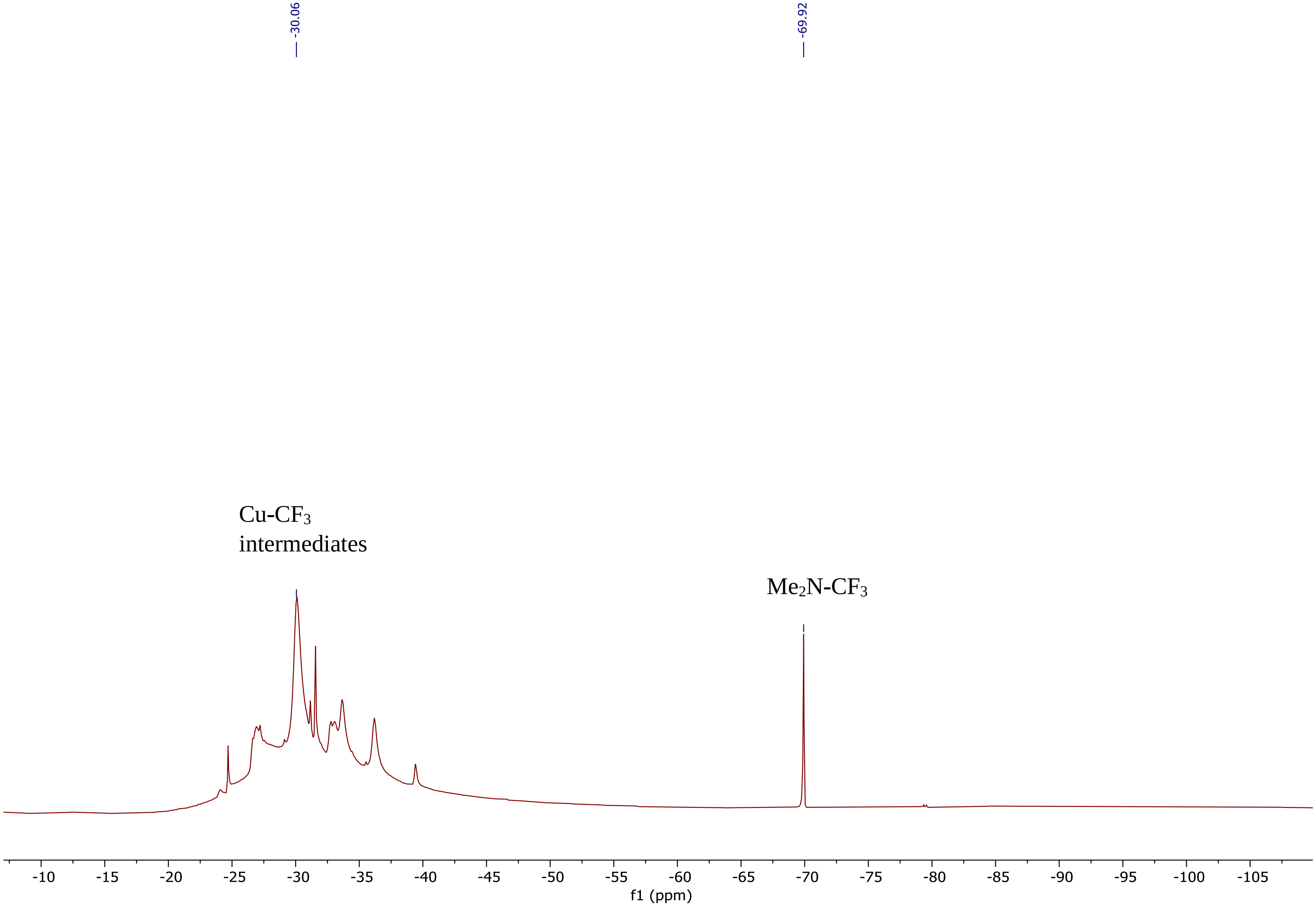
Detection of O-(difluoromethyl)ethanol 8

^{19}F NMR ($CDCl_3$, 376 MHz) [+ 2 equiv. C_6F_6]



Detection of Me_2N-CF_3 (9) via reductive elimination of 5

^{19}F NMR (CD_2Cl_2, 376 MHz, 293 K), 5 minutes after warming up to room temperature



^{19}F NMR (CD_2Cl_2, 376 MHz, 293 K), 30 minutes after warming up to room temperature