

ELECTRONIC SUPPORTING INFORMATION

Fluorocarbyne Complexes via Electrophilic Fluorination of Carbido Ligands

Richard A. Manzano and Anthony F. Hill*

General

Experimental work was performed using standard Schlenk techniques using dried and pre-purified nitrogen or in an inert atmosphere glovebox charged with an argon atmosphere unless specified otherwise. Reactions employed dried and degassed solvents distilled over sodium and benzophenone (ethers, arenes and paraffins) or calcium hydride (CH₂Cl₂, MeCN). The compounds [M(≡CBr)(CO)₂(Tp*)] (M = W **1c**, W **2c**),¹ and [AuCl(THT)]² have been described previously. All other reagents were used as received from commercial suppliers.

NMR spectra were obtained on a Bruker Avance 400 (¹H at 400.1 MHz, ¹³C{¹H} at 100.6 MHz, ³¹P{¹H} at 162.0 MHz, ¹⁹F{¹H} at 376.5 MHz), a Bruker Avance 600 (¹H at 600.0 MHz, ¹³C{¹H} at 150.9 MHz) or a Bruker Avance 700 (¹H at 700.0 MHz, ¹³C{¹H} at 176.1 MHz, ³¹P{¹H} at 283.4 MHz) spectrometers at the temperatures indicated. Chemical shifts (δ) are reported in ppm with coupling constants given in Hz and are referenced to the solvent resonance or external references (CFCl₃ for ¹⁹F{¹H}). The multiplicities of NMR resonances are denoted by the abbreviations s (singlet), d (doublet), t (triplet), m (multiplet), br (broad) and combinations thereof for more highly coupled systems. Where applicable, the stated multiplicity refers to that of the primary resonance exclusive of ¹⁸³W satellites. In select cases, distinct peaks were observed in the ¹H and ¹³C{¹H} NMR spectra, but to the level of accuracy that is reportable (i.e., two decimal places for ¹H NMR, one decimal place for ¹³C{¹H} NMR) they are reported as having the same chemical shift.

The abbreviation 'pz' is used to refer to the pyrazolyl rings on the hydridotris(3,5-dimethylpyrazol-1-yl)borate (Tp*) ligand. Spectra provided generally correspond to samples obtained directly from chromatography and may contain residual solvent as recrystallised samples often display reduced solubility. The BH protons give rise to very broad signals around 4–5 ppm in the ¹H NMR spectra due to coupling to the quadrupolar boron nuclei. These are generally not listed in the experimental NMR data as their chemical shifts and associated integrals are not determined accurately. The BH unit, being remote from the metal centre of interest is not particularly responsive to variations and accordingly ¹¹B{¹H} NMR spectra were not recorded.

Infrared spectra were obtained using a Shimadzu FTIR-8400 spectrometer (liquid) or Perkin Elmer FTIR Spectrum Two (solid state ATR, diamond anvil). Signals are denoted according to their absorption strength such as very sharp (vs), strong (s), medium (m), weak (w) or broad (br). Elemental microanalytical data were provided by Macquarie University, Australia, with the caveat that

compounds containing B–N bonds are considered prone to incomplete oxidation in the combustion analysis (formation of refractory boron nitride materials). Solvates evident from data were confirmed where possible by NMR spectroscopy. High and low resolution electrospray ionisation mass spectrometry (ESI-MS) was performed by the ANU Research School of Chemistry mass spectrometry service with acetonitrile or dichloromethane as the matrix.

Crystallographic Details

Data for X-ray crystallography were collected with Agilent Technologies Xcalibur or Supernova/EosS2-CCD diffractometers as indicated using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) or Cu-Kα radiation (λ = 1.54184 Å) employing the CrysAlis PRO-CCD and -RED software,³ with Gaussian absorption corrections being applied. The structures were solved using intrinsic phasing and refined by full-matrix least-squares on *F*² in an anisotropic (for non-hydrogen atoms) approximation using the SHELXS or SHELXT and SHELXL programs,^{4,5} implemented within the Olex2 suite of programs.⁶ Hydrogen atoms were located geometrically and refined using a riding model. Diagrams were produced using the CCDC visualisation program Mercury.^{7,8}

Electrochemical measurements were recorded using an E-corder 401 potentiostat system from eDAQ Pty Ltd. Electrochemical solutions contained 0.10 M [Bu₄N][PF₆] and ca 10⁻³ M analyte in CH₂Cl₂, and were purged and maintained under a nitrogen atmosphere. Analytes were internally referenced to the ferrocene/ferrocenium redox couple. Scan rates were typically 100 mV s⁻¹. The cell utilised platinum working- and auxiliary- electrodes and a silver wire reference electrode.

Computational Details

Computational studies were performed by using the SPARTAN20[®] suite of programs.⁹ Geometry optimisation (gas phase) for diatomics and metal complexes was performed at the DFT level of theory using the exchange functionals ωB97X-D of Head-Gordon.^{10,11} The Los Alamos effective core potential type basis set (LANL2DZ) of Hay and Wadt¹²⁻¹⁴ was used for I, Mo and W while Pople 6-31G* basis sets¹⁵ were used for all other atoms. Frequency calculations were performed for all compounds to confirm that each optimized structure was a local minimum and also to identify vibrational modes of interest. Cartesian atomic coordinates and thermodynamic properties are provided below.

Synthetic Procedures and Crystallographic Data

Synthesis of [W(≡CF)(CO)₂(Tp*)] (1a). A yellow solution of [W(≡CBr)(CO)₂(Tp*)] (**1c**: 200 mg, 0.32 mmol) in THF (5 mL) was cooled to -78°C (acetone/dry ice bath) and treated dropwise with ⁿBuLi (0.15 mL, 2.5 M soln. in ⁿhexane, 0.38 mmol) then

stirred for 30 minutes at this temperature providing a dark orange solution. The solution was then treated with *N*-fluorobenzenesulfonimide (120 mg, 0.38 mmol) and stirred overnight, allowing the solution to slowly warm to r.t. All volatiles were removed to leave a yellow solid residue that was re-dissolved in the minimum amount of 1:3 DCM:ⁿhexane, and purified by silica gel column chromatography using a mixture of DCM/ⁿhexane (1:3) as the eluent. The first yellow band was collected, and the solvent removed under reduced pressure to give **2a** as a yellow solid. Yield: 107 mg (0.29 mmol, 59%). IR (CH₂Cl₂, cm⁻¹): 1988 vs, 1888 vs (ν_{CO}); (ATR, cm⁻¹): 1990 vs, 1892 vs (ν_{CO}), 1367 vs (ν_{WCF}). ¹H NMR (700 MHz, CDCl₃, 298K): δ_H = 5.88 [s, 2 H, H⁴(pz)], 5.82 [s, 1 H, H⁴(pz)], 2.49 (s, 3 H, pzCH₃), 2.46 (s, 6 H, pzCH₃), 2.37 (s, 6 H, pzCH₃), 2.36 (s, 3 H, pzCH₃).

¹³C{¹H} NMR (151 MHz, CDCl₃, 298 K): δ_C = 220.1 (d + dd, ³J_{CF} = 5.3 Hz, ¹J_{CW} = 159.6 Hz, CO), 200.8 (d + dd, ¹J_{CF} = 527.9 Hz, ¹J_{CW} = 274.3 Hz ≡CF), 152.4 [C^{3,5}(pz)], 151.7 [C^{3,5}(pz)], 145.0 [C^{3,5}(pz)], 144.4 [C^{3,5}(pz)], 106.9 [C⁴(pz)], 106.5 [C⁴(pz)], 16.6 (pzCH₃), 15.5 (pzCH₃), 12.8 (pzCH₃), 12.7 (pzCH₃). ¹¹B{¹H} NMR (128 MHz, CDCl₃, 298 K): δ_B = -9.2 (s.br, N₃BH). ¹⁹F{¹H} NMR (659 MHz, CDCl₃, 298 K): δ_F = 45.5 (s + d, ²J_{WF} = 111.4 Hz, ≡CF). MS (ESI, +ve ion, *m/z*): Found: 591.1294 [M+Na]⁺. Calcd for C₁₈H₂₂¹¹BN₆O₂¹⁹F²³Na¹⁸⁴W: 591.1288 [M+Na]⁺. Elemental. Anal. Found: C, 38.10, 38.24; H, 4.16, 4.04; N, 14.69, 14.51%. Calcd. for C₁₈H₂₂BFN₆O₂W: C, 38.06; N, 14.79; H, 3.90%.

Crystals suitable for single crystal X-ray crystallographic study were grown from the slow evaporation of an acetonitrile solution. Due to twinning and positional disorder, an adequately precise structural model was not developed beyond confirmation of composition and connectivity (Figure S1). *Crystal data for* C₁₈H₂₂BFN₆O₂W: *M_w* = 568.06, monoclinic *P*2₁/*c*, *a* = 7.9234(6) Å, *b* = 13.8550(9) Å, *c* = 19.1371(14) Å, β = 96.429(7)°, *V* = 2087.6(3) Å³, *Z* = 4, *D_{calc}* = 1.727 Mg m⁻³, μ(Mo Kα) = 5.562 mm⁻¹, *T* = 150.0(1) K, yellow plate, 6705 independent reflections. *F²* refinement, *R*₁ = 0.097, *wR*₂ = 0.234 for 6204 reflections (*I* > 2σ(*I*), 2θ_{max} = 52.74°), 264 parameters. The structural model for this data set was plagued by positional disorder and twinning but clearly indicated that the crystal was isomorphous with that for **2a**. Thus whilst confirming connectivity and gross composition, the low precision makes detailed interrogation unrealistic. Accordingly, the CIF has not been deposited at the CCDC but was made available to referees.

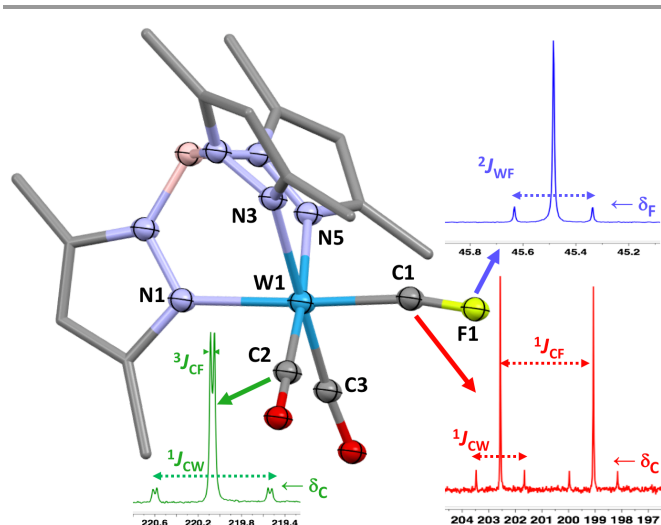


Figure S1: Molecular structure of [W(=CF)(CO)₂(Tp*)] (**1a**) in a crystal (Positional disorder of CF and CO ligands, one contributor shown; 50% displacement ellipsoids, pyrazolyl groups simplified). Insets = ¹⁹F{¹H} and ¹³C{¹H} NMR features of interest with associated ¹J_{WC}, ²J_{WF} and ¹J_{CF} couplings shown.

Synthesis of [Mo(≡CF)(CO)₂(Tp*)] (2a**).** A yellow solution of [Mo(≡CBr)(CO)₂(Tp*)] (**2c**: 200 mg, 0.37 mmol) in THF (5 mL) was cooled to -78°C (acetone/dry ice bath) and treated dropwise with ⁿBuLi (0.17 mL, 2.5 M soln. in ⁿhexane, 0.44 mmol) then stirred for 30 minutes at this temperature providing a dark orange solution. The solution was then treated with *N*-fluorobenzenesulfonimide (140 mg, 0.44 mmol) and stirred overnight, allowing the solution to slowly warm to r.t. All volatiles were removed to leave a yellow solid residue that was re-dissolved in the minimum amount of 1:3 DCM:ⁿhexane and purified by silica gel column chromatography using a mixture of DCM/ⁿhexane (1:3) as the eluent. The first yellow band was collected, and the solvent removed under reduced pressure to give **2a** as a yellow solid. Yield: 137 mg (0.29 mmol, 77%). IR (CH₂Cl₂, cm⁻¹): 2002 vs, 1910 vs (ν_{CO}). (ATR, cm⁻¹): 1991 vs, 1893 vs (ν_{CO}), 1367 vs (ν_{WCF}). ¹H NMR (700 MHz, CDCl₃, 298K): δ_H = 5.83 [s, 2 H, H⁴(pz)], 5.80 [s, 1 H, H⁴(pz)], 2.45 (s, 3 H, pzCH₃), 2.43 (s, 6 H, pzCH₃), 2.37 (s, 6 H, pzCH₃, overlapping), 2.37 (s, 3 H, pzCH₃, overlapping). ¹³C{¹H} NMR (151 MHz, CDCl₃, 298 K): δ_C = 222.8 (CO), 193.5 (d, ¹J_{CF} = 555.1 Hz, ≡CF), 151.5 [C^{3,5}(pz)], 151.0 [C^{3,5}(pz)], 145.0 [C^{3,5}(pz)], 144.5 [C^{3,5}(pz)], 106.6 [C⁴(pz)], 106.3 [C⁴(pz)], 15.78 (pzCH₃), 14.92 (pzCH₃), 12.86 (pzCH₃), 12.76 (pzCH₃). ¹¹B{¹H} NMR (128 MHz, CDCl₃, 298 K): δ_B = -9.4 (s.br, N₃BH). ¹⁹F{¹H} NMR (659 MHz, CDCl₃, 298 K): δ_F = 73.0 (s, ≡CF). MS (ESI, +ve ion, *m/z*): Found: 426.1040 [M-2CO]⁺. Calcd for C₁₆H₂₂¹¹BN₆¹⁹F⁹⁸Mo: 426.1037 [M-2CO]⁺. Elemental. Anal. Found: C, 45.01, 45.02; H, 4.17, 4.24; N, 17.44, 17.49%. Calcd. for C₁₈H₂₂BFN₆O₂Mo: C, 45.02; N, 17.50; H, 4.62%.

Crystals suitable for single crystal X-ray crystallographic analysis were grown from the slow evaporation of an acetonitrile, benzene, chloroform, dichloromethane, ethanol, tetrahydrofuran solution. *Crystal data for* C₁₈H₂₂BFMoN₆O₂: *M_w* = 480.16 gmol⁻¹, monoclinic *P*2₁/*c*, *a* = 7.9256(3) Å, *b* = 13.8329(7) Å, *c* = 19.1940(9) Å, β = 96.493(4)°, *V* = 2090.82(17) Å³, *Z* = 4, *D_{calc}* = 1.525 Mgm⁻³, μ(Mo Kα) = 0.66 mm⁻¹, *T* = 150.0(1)

K, yellow plate, 0.43 × 0.29 × 0.04 mm, 4958 independent reflections. R^2 refinement gave $R_1 = 0.063$ and $wR_2 = 0.149$ for 4423 reflections ($I > 2\sigma(I)$), $2\theta_{\max} = 52.8^\circ$) and 264 parameters with 1 restraint. CCDC 2226628

Synthesis of [W(Au(μ-CF)Cl(CO)₂(Tp*)) (3). A mixture of [W(≡CF)(CO)₂(Tp*)] (100 mg, 0.18 mmol) and [AuCl(SMe₂)] (52 mg, 0.18 mmol) were dissolved in DCM (5 mL) and stirred at r.t. for 30 minutes providing an orange solution. The solution was diluted with ⁿhexane (10 mL) with stirring, and then all the volatiles were removed under reduced pressure to provide an orange solid residue. The residue is washed with ⁿhexane (3 × 5 mL) and then dried under vacuo to give **3** as an orange solid. Yield: 114 mg (0.14 mmol, 80%). IR (CH₂Cl₂, cm⁻¹): 2017 vs, 1931 vs (ν_{CO}). ¹H NMR (700 MHz, CDCl₃, 298K): δ_H = 5.95 [s, 2 H, H⁴(pz)], 5.94 [s, 1 H, H⁴(pz)], 2.49 (s, 6 H, pzCH₃), 2.46 (s, 3 H, pzCH₃), 2.39 (s, 6 H, pzCH₃), 2.37 (s, 3 H, pzCH₃). ¹³C{¹H} NMR (151 MHz, CDCl₃, 298 K): δ_C = 236.6 (d + dd, ¹J_{CF} = 453.8 Hz, ¹J_{CW} = 143.8 Hz, μ-CF), 212.5 (s + d, ¹J_{CW} = 145.4 Hz, CO), 153.7 [C^{3,5}(pz)], 152.7 [C^{3,5}(pz)], 146.1 [C^{3,5}(pz)], 145.9 [C^{3,5}(pz)], 108.3 [C⁴(pz)], 108.0 [C⁴(pz)], 17.7 (pzCH₃), 16.0 (pzCH₃), 13.2 (pzCH₃), 12.8 (pzCH₃). ¹¹B{¹H} NMR (128 MHz, CDCl₃, 298 K): δ_B = -9.2 (s.br, N₃BH). ¹⁹F{¹H} NMR (376 MHz, CDCl₃, 298 K): δ_F = 34.7 (s + d, ²J_{FW} = 11.5 Hz, ≡CF). MS (ESI, +ve ion, *m/z*): Found: 823.0641 [M+Na]⁺. Calcd for C₁₈H₂₂¹¹BN₆O₂F₂₃Na³⁵Cl¹⁸⁴W¹⁹⁷Au: 823.0642 [M+Na]⁺. Elemental. Anal. Found: C, 27.08, 27.03; H, 2.55, 2.57; N, 10.97, 10.91%. Calcd. for C₁₈H₂₂AuBClFN₆O₂W: C, 27.01; H, 2.77%; N, 10.55%.

Crystals suitable for single crystal X-ray crystallographic study were grown from vapour diffusion of a hexane into a DCM solution. *Crystal data for C₁₈H₂₂AuBClFN₆O₂*: $M_w = 800.49$, monoclinic $P2_1/c$, $a = 11.6629(9)$ Å, $b = 10.2338(5)$ Å, $c = 20.6113(12)$ Å, $\beta = 150.774(7)^\circ$, $V = 2367.8(3)$ Å³, $Z = 4$, $D_{\text{calc}} = 2.246$ Mg m⁻³, $\mu(\text{Mo K}\alpha) = 11.19$ mm⁻¹, $T = 150.0(1)$ K, clear orange plate, 0.19 × 0.14 × 0.05 × 0.05 (radius) mm, 4839 independent reflections. R^2 refinement gave $R_1 = 0.040$ and $wR_2 = 0.073$ for 3942 reflections ($I > 2\sigma(I)$), $2\theta_{\max} = 52.8^\circ$), 290 parameters. CCDC 2226627

Synthesis of [W(≡CF)Cl₂(Tp*)] (4). A mixture of [W(≡CF)(CO)₂(Tp*)] (100 mg, 0.18 mmol) and iodobenzene dichloride (48 mg, 0.18 mmol) were dissolved in chloroform (5 mL) and stirred at r.t. for 30 minutes providing a dark purple/blue solution. The solution was diluted with ethanol (10 mL) and then concentrated under reduced pressure to ca 5 mL to provide a purple precipitate which was collected by filtration, washed with ethanol (3 × 10 mL) and then dried *in vacuo*. Yield: 56 mg (0.10 mmol, 55%). IR (ATR, cm⁻¹): 1449 vs (ν_{CF}). ¹H NMR (700 MHz, CDCl₃, 298K): δ_H = 5.96 [s, 2 H, H⁴(pz)], 5.88 [s, 1 H, H⁴(pz)], 2.53 (s, 3 H, pzCH₃), 2.49 (s, 6 H, pzCH₃), 2.40 (s, 3 H, pzCH₃), 2.39 (s, 6 H, pzCH₃). ¹³C{¹H} NMR (151 MHz, CDCl₃, 298 K): δ_C = 224.9 (d + dd, ¹J_{CF} = 512.8 Hz, ¹J_{CW} = 316 Hz, ≡CF), 154.4 [C^{3,5}(pz)], 153.9 [C^{3,5}(pz)], 146.6 [C^{3,5}(pz)], 143.4 [C^{3,5}(pz)], 108.3 [C⁴(pz)], 108.3 [C⁴(pz), overlapping], 18.3 (pzCH₃), 14.2 (pzCH₃), 12.9 (pzCH₃), 12.5 (pzCH₃). ¹¹B{¹H} NMR (128 MHz, CDCl₃, 298 K): δ_B = 9.0 (s.br, BH^{Me}Pz₃). ¹⁹F{¹H} NMR (376 MHz, CDCl₃, 298 K): δ_F = 74.7 (s + d, ²J_{FW} = 105.1 Hz, ≡CF). MS (ESI, +ve ion, *m/z*): Found: 583.0934 [M+H]⁺. Calcd for C₁₆H₂₃¹¹BN₆F³⁵Cl₂¹⁸⁴W: 583.0948

[M+H]⁺. Though spectroscopically pure, satisfactory elemental microanalytical data were not acquired. Found: C, 32.94, 32.69; H, 3.55, 3.44; N, 3.81, 3.86%. Calcd. for C₁₆H₂₂BCl₂FN₆W: C, 34.08; N, 14.90; H, 3.93%. This result should be considered anomalous, given that even exhaustive oxidation/hydrolysis of organometallic complexes in the 'W(Tp*)' series typically leave the pyrazolylborate cage intact and afford variants of the form [WCl(=O)₂(Tp*)] (N, 14.99), [W₄O₈(Tp*)₄] (N, 15.53) or [W(=O)Cl₂(Tp*)] (N, 14.49) or [WCl₃(Tp*)] (N, 14.02%), i.e., the low value of 3.81% nitrogen is implausible. NB: Compounds containing B–N bonds are considered prone to incomplete oxidation in the combustion analysis (formation of refractory boron nitride materials).

Optimised Geometries and Cartesian Coordinates

(a) [W(≡CF)(CO)₂(Tp)]

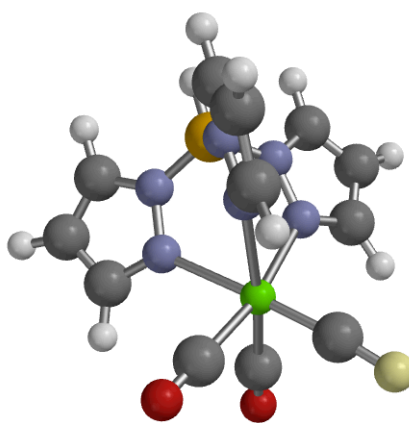


Figure S2: Optimised structure of [W(≡CF)(CO)₂(Tp)] (ω B97X-V/6-31G*/LANL2DZ/gas phase). Bond lengths (Å) and angles ($^\circ$) of interest: W=C 1.815, C–F 1.286, W–C–F 175.6.

Infrared absorptions of interest (cm⁻¹, scaled by 0.9420): 2435 ν_{BH}, 2009, 1939 ν_{CO}, 1435, 1431 ν_{WCF}.

Natural atomic charges of note: W (0.812), C (0.148), F(–0.298).

Natural Löwden bond orders of interest: W–CO (1.38), C=O (2.52), W=C (2.40), C–F (1.37).

Table S1. Cartesian Coordinates for [W(≡CF)(CO)₂(Tp)]

Atom	x	y	z
W	-0.246436	-1.704588	-0.285694
O	2.174798	-3.718033	-0.105146
O	-0.947764	-2.739265	-3.181786
N	1.148205	-0.143388	-1.196067
N	1.127451	1.141712	-0.781364
N	0.344393	-0.591634	1.567878
N	0.446198	0.755686	1.593989

N	-1.660474	0.028957	-0.425168
N	-1.281458	1.290730	-0.124883
C	-1.321086	-2.999214	0.393844
C	1.285491	-2.983639	-0.174799
C	-0.684723	-2.367576	-2.119877
C	2.081217	-0.233744	-2.145922
C	2.679460	1.010450	-2.355658
H	3.463450	1.259843	-3.053455
C	2.038977	1.853477	-1.463569
C	0.650269	-1.029971	2.789670
C	0.954801	0.045535	3.627805
H	1.238342	0.014757	4.668086
C	0.812839	1.160839	2.821747
C	-2.944339	0.082367	-0.782823
C	-3.412934	1.396799	-0.712557
H	-4.403499	1.760196	-0.937433
C	-2.317948	2.129925	-0.291471
B	0.158321	1.590277	0.332385
H	0.295313	2.763698	0.560710
H	-3.457037	-0.824302	-1.068723
H	-2.199097	3.185939	-0.099049
H	2.166121	2.907428	-1.264978
H	0.946800	2.211902	3.030349
H	2.270099	-1.184601	-2.623873
H	0.633990	-2.090272	2.995322
F	-2.039739	-3.980290	0.812508

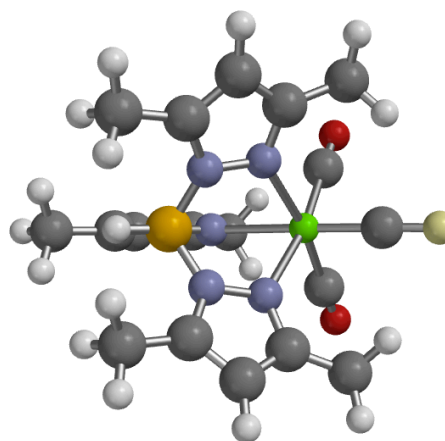


Figure S3: Optimised structure of $[W(=CF)(CO)_2(Tp^*)]$ (**1a**: ω B97X-D/6-31G*/LANL2DZ/gas phase). Bond lengths (Å) and angles (°) of interest: W=C 1.813, C-F 1.289, W-C-F 174.8.

Infrared absorptions of interest (cm^{-1} , scaled by 0.9420): 2472 ν_{BH} , 1992, 1918 ν_{CO} , 1424, 1420 ν_{WCF} .

Natural atomic charges of note: W (0.844), C (0.140), H (0.140), F(-0.302).

Natural Löwden bond orders of interest: W-CO (1.38), C=O (2.49), W=C (2.38), C-F (1.36).

Table S2: Thermodynamic Properties at 298.15 K

Zero Point Energy :	568.57	kJ/mol	(ZPE)
Temperature Correction :	47.41	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	615.97	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-1134.308109	au	(Electronic Energy + Enthalpy Correction)
Entropy :	546.07	J/mol•K	
Gibbs Energy :	-1134.370121	au	(Enthalpy - T*Entropy)
C_v :	327.72	J/mol•K	

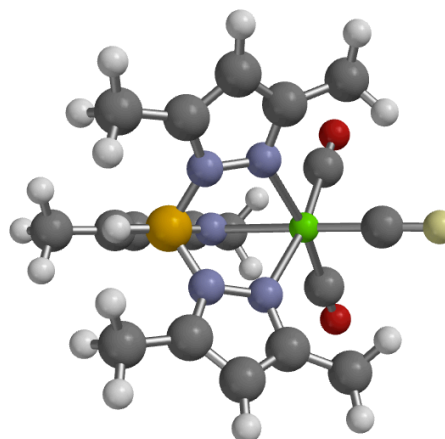
Table S3: Thermodynamic Properties at 298.15 K

Zero Point Energy :	987.70	kJ/mol	(ZPE)
Temperature Correction :	68.78	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	1056.49	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-1370.007365	au	(Electronic Energy + Enthalpy Correction)
Entropy :	684.34	J/mol•K	
Gibbs Energy :	-1370.085078	au	(Enthalpy - T*Entropy)
C_v :	480.61	J/mol•K	

(b) $[W(=CF)(CO)_2(Tp^*)]$ (**1a**)

Table S4. Cartesian Coordinates for $[W(=CF)(CO)_2(Tp^*)]$

Atom	x	y	z
W	-0.257937	-1.969196	-0.341623
O	2.086737	-4.050959	-0.007013
O	-0.893299	-3.080218	-3.221879
N	1.183518	-0.436078	-1.249445
N	1.149705	0.853131	-0.818985
N	0.275080	-0.870767	1.535277
N	0.392954	0.482639	1.546711
N	-1.670598	-0.245793	-0.538924
N	-1.284033	1.019301	-0.231965
C	-1.369857	-3.249983	0.299244
C	1.231805	-3.281570	-0.140100
C	-0.648453	-2.670095	-2.167262
C	2.131726	-0.514789	-2.192253
C	2.716189	0.743626	-2.364347
H	3.511463	1.004588	-3.047247
C	2.067373	1.586487	-1.477954
C	0.528405	-1.303899	2.775599
C	0.813529	-0.206909	3.596303
H	1.057794	-0.226101	4.648438
C	0.720176	0.909220	2.783011
C	-2.951254	-0.190218	-0.921777
C	-3.394149	1.135625	-0.856218
H	-4.378488	1.507169	-1.100876
C	-2.309439	1.874915	-0.416929
B	0.146131	1.294843	0.264644
H	0.282401	2.464613	0.488764
F	-2.112556	-4.234138	0.676629
C	2.282239	3.044403	-1.230111
H	3.091099	3.408158	-1.867885
H	2.551882	3.239916	-0.187763
H	1.381960	3.625511	-1.453116
C	2.460430	-1.773829	-2.927917
H	3.334866	-1.609441	-3.562225
H	1.631501	-2.089273	-3.568478
H	2.683384	-2.596897	-2.244691
C	-2.201070	3.345766	-0.170710
H	-1.430653	3.803112	-0.799404
H	-1.947654	3.561891	0.871804
H	-3.156349	3.824716	-0.397727
C	-3.725344	-1.399204	-1.334621
H	-3.267212	-1.887873	-2.199682
H	-4.746816	-1.114457	-1.599246
H	-3.766802	-2.134974	-0.525751
C	0.925281	2.349974	3.122187
H	1.740790	2.788373	2.538518
H	1.174114	2.444197	4.181783
H	0.025128	2.941255	2.927218
C	0.490588	-2.748073	3.152678
H	1.260588	-3.317981	2.623935
H	-0.476893	-3.194288	2.904356
H	0.660019	-2.856425	4.227024

(c) $[Mo(=CF)(CO)_2(Tp^*)]$ (2a)**Figure S4:** Optimised structure of $[Mo(=CF)(CO)_2(Tp^*)]$ (2a): ω B97X-D/6-31G*/LANL2DZ/gas phase). Bond lengths (Å) and angles ($^\circ$) of interest: Mo=C 1.801, C=F 1.286, W-C-F 173.6.

Infrared absorptions of interest (cm^{-1} , scaled by 0.9420): 2473 ν_{BH} , 2005, 1940 ν_{CO} , 1415, 1412 ν_{WCF} .

Natural atomic charges of note: Mo (0.513), C (0.264), F(-0.298).

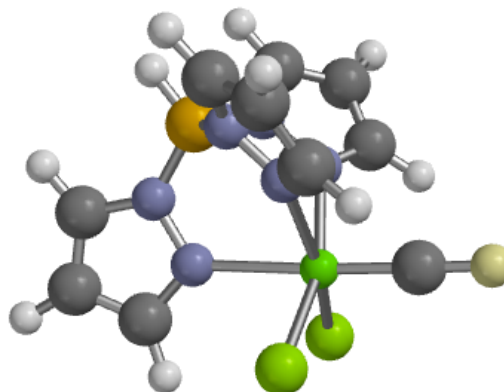
Natural Löwden bond orders of interest: Mo-CO (1.31), C=O (2.55), Mo=C (2.39), C-F (1.38).

Table S5: Thermodynamic Properties at 298.15 K

Zero Point Energy :	986.30	kJ/mol	(ZPE)
Temperature Correction :	69.08	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	1055.37	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-1369.699347	au	(Electronic Energy + Enthalpy Correction)
Entropy :	685.18	J/mol•K	
Gibbs Energy :	-1369.777155	au	(Enthalpy - T*Entropy)
C_v :	482.06	J/mol•K	

Table S6. Cartesian Coordinates for $[\text{Mo}(\equiv\text{CF})(\text{CO})_2(\text{Tp}^*)]$ (**2a**)

Atom	x	y	z
Mo	0.263660	0.353250	1.983007
O	-2.091623	0.019860	4.068580
O	0.941138	3.248398	3.063212
N	-1.202210	1.260892	0.445257
N	-1.154879	0.826390	-0.840086
N	-0.278828	-1.543042	0.885945
N	-0.391417	-1.541456	-0.466665
N	1.692717	0.548308	0.247909
N	1.289221	0.241121	-1.009148
C	1.363415	-0.284550	3.259105
C	-1.238546	0.153461	3.304159
C	0.679133	2.195885	2.671403
C	-2.159068	2.192154	0.514572
C	-2.734563	2.360703	-0.749462
H	-3.532041	3.037641	-1.019537
C	-2.070310	1.478493	-1.584609
C	-0.531132	-2.785697	1.305622
C	-0.807688	-3.599819	0.200251
H	-1.048900	-4.652808	0.208325
C	-0.711148	-2.775969	-0.907486
C	2.973522	0.920522	0.175666
C	3.402856	0.851038	-1.155428
H	4.384498	1.087308	-1.539891
C	2.306583	0.414480	-1.878478
B	-0.144709	-0.254449	-1.274237
H	-0.282632	-0.480147	-2.443512
F	2.082573	-0.649011	4.261273
C	-2.263936	1.234158	-3.046357
H	-3.078883	1.860698	-3.416294
H	-2.515398	0.188491	-3.249332
H	-1.361107	1.472949	-3.617150
C	-2.507732	2.909866	1.779210
H	-3.328872	3.606564	1.593267
H	-1.659059	3.482141	2.164795
H	-2.824727	2.214520	2.561814
C	2.182448	0.160257	-3.346198
H	1.417114	0.796801	-3.801357
H	1.912775	-0.880095	-3.553440
H	3.136734	0.370315	-3.835030
C	3.761950	1.325439	1.378382
H	3.337216	2.214981	1.853412
H	4.792753	1.549459	1.092306
H	3.776064	0.526558	2.126405
C	-0.910831	-3.103407	-2.351770
H	-1.723690	-2.514772	-2.788846
H	-1.161750	-4.161689	-2.455115
H	-0.008200	-2.905490	-2.938254
C	-0.499116	-3.167275	2.749259
H	-1.279541	-2.649487	3.315651
H	0.462888	-2.910415	3.203261
H	-0.656722	-4.243522	2.855634

(d) $[\text{W}(\equiv\text{CF})\text{Cl}_2(\text{Tp})]$ **Figure S5:** Optimised structure of $[\text{W}(\equiv\text{CF})\text{Cl}_2(\text{Tp})]$ ($\omega\text{B97X-D/6-31G}^*/\text{LANL2D}\zeta/\text{gas phase}$). Bond lengths (Å) and angles ($^\circ$) of interest: W=C 1.771, C-F 1.283, W-C-F 179.5.

Infrared absorptions of interest (cm^{-1} , scaled by 0.9420): 2440 ν_{BH} , 1508, 1507 ν_{WCF} , 315 $\nu_{\text{s}}(\text{WCl}_2)$, 309 $\nu_{\text{as}}(\text{WCl}_2)$.

Natural atomic charges of note: W (1.356), C (0.121), F(-0.297), Cl (-0.411).

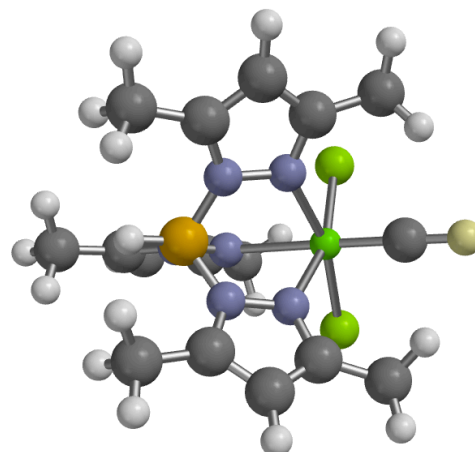
Natural Löwden bond orders of interest: W-Cl (1.41), W=C (2.63), C-F (1.37).

Table S7: Thermodynamic Properties at 298.15 K

Zero Point Energy :	535.11	kJ/mol	(ZPE)
Temperature Correction :	45.38	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	580.49	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-1828.141437	au	(Electronic Energy + Enthalpy Correction)
Entropy :	536.75	J/mol·K	
Gibbs Energy :	-1828.202389	au	(Enthalpy - T*Entropy)
C_v :	306.38	J/mol·K	

Table S8. Cartesian Coordinates for $[W(=CF)(CO)_2(Tp^*)]$

Atom	x	y	z
W	-0.188875	-1.889618	-0.399596
N	1.209425	-0.315642	-1.315443
N	1.195281	0.970694	-0.904562
N	0.292955	-0.810434	1.428592
N	0.502353	0.525621	1.457265
N	-1.592188	-0.225097	-0.448725
N	-1.213970	1.057362	-0.246967
C	-1.294286	-3.047733	0.358252
C	2.134855	-0.413652	-2.267518
C	2.736221	0.830368	-2.483916
H	3.517727	1.073304	-3.186802
C	2.105996	1.680326	-1.593439
C	0.532307	-1.280031	2.657978
C	0.909324	-0.235802	3.497574
H	1.170233	-0.290321	4.542628
C	0.871023	0.891692	2.691282
C	-2.892965	-0.213974	-0.760247
C	-3.367087	1.094756	-0.769300
H	-4.367163	1.433933	-0.988497
C	-2.266159	1.865645	-0.428095
B	0.228712	1.390943	0.202663
H	0.336386	2.560978	0.458876
H	-3.399263	-1.142875	-0.975168
H	-2.159192	2.932090	-0.296039
H	2.236973	2.735017	-1.400572
H	1.071021	1.929764	2.911935
H	2.314944	-1.367385	-2.741298
H	0.433794	-2.336725	2.855432
F	-2.098781	-3.878064	0.915205
Cl	-0.750138	-2.373802	-2.642593
Cl	1.790536	-3.151338	-0.128906

(e) $[W(=CF)Cl_2(Tp^*)]$ (4)**Figure S6:** Optimised structure of $[W(=CF)(CO)_2(Tp^*)]$ (4): ω B97X-D/6-31G*/LANL2DZ/gas phase). Bond lengths (Å) and angles (°) of interest: W=C 1.768, C-F 1.287, W–C–F 177.8.

Infrared absorptions of interest (cm^{-1} , scaled by 0.9420): 2472 ν_{BH} , 1504, 1496 ν_{WCF} , 305 $\nu_{\text{s}}(\text{WCl}_2)$, 300 $\nu_{\text{as}}(\text{WCl}_2)$.

Natural atomic charges of note: W (1.390), C (0.112), F(–0.302), Cl(–0.429).

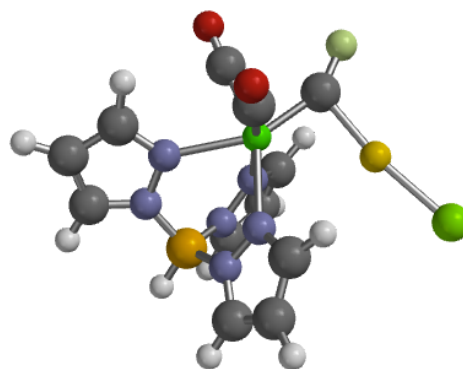
Natural Löwden bond orders of interest: W–Cl (1.36), W=C (2.64), C–F (1.35).

Table S9: Thermodynamic Properties at 298.15 K

Zero Point Energy :	955.09	kJ/mol	(ZPE)
Temperature Correction :	66.72	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	1021.81	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-2063.841079	au	(Electronic Energy + Enthalpy Correction)
Entropy :	674.35	J/mol•K	
Gibbs Energy :	-2063.917657	au	(Enthalpy - T*Entropy)
C_v :	458.82	J/mol•K	

Table S10. Cartesian Coordinates for $[W(=CF)(CO)_2(Tp^*)] (4)$

Atom	x	y	z
W	-0.174406	-2.081980	-0.433184
N	1.275146	-0.526761	-1.368947
N	1.232778	0.754411	-0.916624
N	0.212262	-1.034815	1.423728
N	0.456234	0.304804	1.429021
N	-1.603943	-0.460792	-0.522642
N	-1.206824	0.828280	-0.336108
C	-1.277993	-3.283179	0.248122
C	2.218315	-0.576973	-2.317315
C	2.790770	0.694049	-2.465140
H	3.582686	0.972720	-3.145035
C	2.140098	1.513488	-1.564033
C	0.351288	-1.479020	2.686353
C	0.701980	-0.404960	3.502556
H	0.895196	-0.434063	4.564715
C	0.751801	0.707623	2.675690
C	-2.917817	-0.444920	-0.813121
C	-3.358892	0.877013	-0.821543
H	-4.359632	1.225542	-1.029660
C	-2.252758	1.653128	-0.507217
B	0.223677	1.145588	0.155384
H	0.314846	2.311920	0.415867
F	-2.067684	-4.187407	0.712431
C	2.330811	2.970704	-1.292712
H	3.132597	3.357483	-1.925702
H	2.601400	3.153452	-0.247919
H	1.422492	3.544163	-1.504343
C	2.566478	-1.799356	-3.102701
H	3.586470	-1.706636	-3.485868
H	1.886014	-1.912900	-3.951413
H	2.500036	-2.703305	-2.496562
C	-2.152629	3.136389	-0.359364
H	-1.394841	3.552853	-1.029588
H	-1.883898	3.418821	0.663232
H	-3.114558	3.593632	-0.600935
C	-3.716249	-1.674537	-1.083805
H	-3.294291	-2.239298	-1.919795
H	-4.745474	-1.397519	-1.323734
H	-3.731375	-2.333474	-0.210474
C	1.059551	2.128484	3.019629
H	1.894449	2.509845	2.424516
H	1.328235	2.199098	4.075813
H	0.198106	2.779044	2.839080
C	0.156558	-2.901420	3.088076
H	0.835918	-3.560408	2.540270
H	-0.866155	-3.231688	2.884049
H	0.344751	-3.007541	4.159092
Cl	1.804469	-3.350894	-0.029276
Cl	-0.675990	-2.598686	-2.702867

(f) $[WAu(\mu-CF)Cl(CO)_2(Tp)]$ **Figure S7:** Optimised structure of $[WAu(\mu-CF)Cl(CO)_2(Tp)]$ (ω B97X-D/6-31G*/LANL2DZ/gas phase). Bond lengths (Å) and angles (°) of interest: W=C 1.893, W-Au 2.829, C-F 1.303, Au-Cl 2.333, Au-C 2.042, W-C-F 149.7, W-Au-Cl 146.8, Au-C-F 118.4.

Infrared absorptions of interest (scaled by 0.9420): 2451 ν_{BH} , 2029, 1967 ν_{CO} , 1329 ν_{C-F} , 316 ν_{AuCl} .

Natural atomic charges of note: W (0.772), C (-0.278), F (-0.301), Au (1.065) Cl (-0.826).

Natural Löwden Bond Orders: W-CO (1.30), C=O (2.55), W=C (1.80), C-F (1.29), W-Au (0.72), Au-Cl (1.29)

Table S17: Thermodynamic Properties at 298.15 K

Zero Point Energy :	574.96	kJ/mol	(ZPE)
Temperature Correction :	54.54	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	629.50	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-1730.020787	au	(Electronic Energy + Enthalpy Correction)
Entropy :	602.97	J/mol•K	
Gibbs Energy :	-1730.089260	au	(Enthalpy - T*Entropy)
C_p :	373.79	J/mol•K	

Table S18. Cartesian Coordinates for [W_{Au}(μ-CF)Cl(CO)₂(Tp)]

Atom	x	y	z
W	0.015742	0.520123	1.462011
O	-2.486020	0.207440	3.364721
O	0.076502	3.637304	1.924186
N	-1.303557	1.208329	-0.177012
N	-1.126263	0.751619	-1.437763
N	-0.443290	-1.436061	0.499013
N	-0.420344	-1.562595	-0.849488
N	1.574152	0.543046	-0.119464
N	1.305934	0.155149	-1.384058
C	-1.566994	0.323167	2.680890
C	0.048896	2.499701	1.757701
C	-2.319453	2.077929	-0.209739
C	-2.811609	2.190523	-1.507799
H	-3.625304	2.807485	-1.854998
C	-2.025689	1.324680	-2.250646
C	-0.808088	-2.622547	0.997121
C	-1.020230	-3.533758	-0.036046
H	-1.306762	-4.569903	0.048565
C	-0.763384	-2.814963	-1.189981
C	2.864665	0.882530	-0.079928
C	3.446825	0.714247	-1.337646
H	4.471175	0.897145	-1.621435
C	2.417064	0.247370	-2.134356
B	-0.092253	-0.358484	-1.749760
H	-0.148943	-0.663039	-2.910533
H	3.302620	1.219356	0.848204
H	2.393294	-0.027349	-3.178325
H	-2.047526	1.069113	-3.299622
H	-0.801831	-3.102861	-2.230110
H	-2.638897	2.570122	0.697519
H	-0.875635	-2.765545	2.065847
C	1.148968	0.752986	2.960763
Au	1.591159	-1.239549	3.018872
Cl	2.300179	-3.434157	3.369306
F	1.674898	1.531447	3.863989

Infrared absorptions of interest (scaled by 0.9420): 1551 ν_{C-F}, 680-685 ν_{W-F}.

Natural atomic charges of note: W (2.277), C (-0.201), (C)F (-0.291), (W)F (-0.592).

Natural Löwden Bond Orders: W=C (2.73), C-F (1.36), W-F (1.27).

Table S19: Thermodynamic Properties at 298.15 K

Zero Point Energy :	34.89	kJ/mol	(ZPE)
Temperature Correction :	18.97	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	53.86	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-505.201350	au	(Electronic Energy + Enthalpy Correction)
Entropy :	351.28	J/mol•K	
Gibbs Energy :	-505.241241	au	(Enthalpy - T*Entropy)
C _v :	91.76	J/mol•K	

Table S20. Cartesian Coordinates for [W(=CF)F₃]

Atom	x	y	z
W	0.002090	-0.000000	0.558201
C	-0.002135	-0.000000	-1.054594
F	-0.007004	0.000000	-2.508838
F	0.902770	1.561797	1.024878
F	0.902770	-1.561797	1.024878
F	-1.798292	0.000000	1.033913

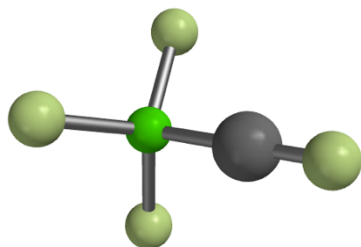
(g) [W(≡CF)F₃]

Figure S8: Optimised structure of [W(=CF)F₃] (ωB97X-D/6-31G*/LANL2DZ/gas phase). Bond lengths (Å) and angles (°) of interest: W=C 1.741, C-F 1.285, mean-W-F 1.859, W-C-F 180.0.

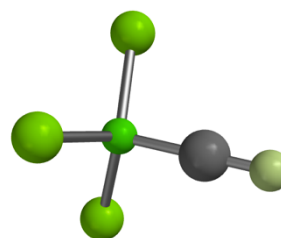
(h) [W(≡CF)Cl₃]

Figure S9: Optimised structure of [W(=CF)Cl₃] (ωB97X-D/6-31G*/LANL2DZ/gas phase). Bond lengths (Å) and angles (°) of interest: W=C 1.746, C-F 1.275, mean-W-Cl 2.270, W-C-F 180.0.

Infrared absorptions of interest (scaled by 0.9420): 1554 $\nu_{\text{C-F}}$, 356 ν_{WCl} .

Natural atomic charges of note: W (1.392), C (0.034), F (-0.276), Cl (-0.384).

Natural Löwden Bond Orders: W=C (2.68), C-F (1.40), W-Cl (1.64)

Table S21: Thermodynamic Properties at 298.15 K

Zero Point Energy :	27.69	kJ/mol	(ZPE)
Temperature Correction :	20.74	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	48.42	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-1586.305938	au	(Electronic Energy + Enthalpy Correction)
Entropy :	371.18	J/mol•K	
Gibbs Energy :	-1586.348089	au	(Enthalpy - T*Entropy)
C_v :	101.36	J/mol•K	

Table S22. Cartesian Coordinates for [W(=CF)Cl₃]

Atom	x	y	z
W	0.000927	-0.000000	0.512010
Cl	1.120150	1.939989	1.081857
Cl	1.120150	-1.939989	1.081857
Cl	-2.253109	-0.000000	1.087214
C	0.000617	0.000000	-1.235280
F	0.001100	0.000000	-2.509174

ELECTRONIC SUPPORTING INFORMATION

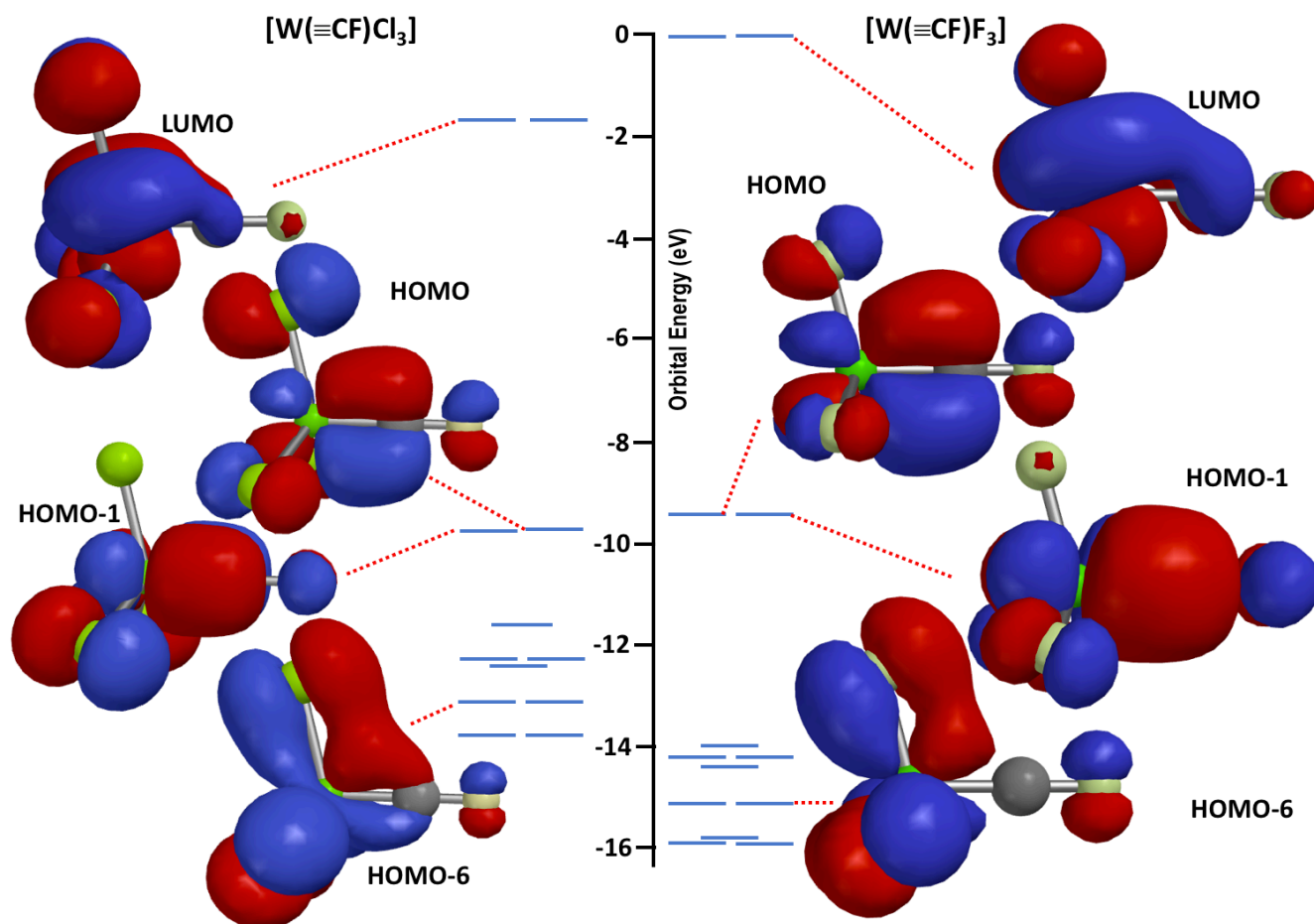


Figure S10. Frontier orbitals of interest for $[W(=CF)X_3]$ ($X = Cl$ left, F right; $\omega B97X-D/6-31G^*/LANL2DZ(W)/gas$ phase).

Electrochemistry

(a) $[W(=CF)(CO)_2(Tp^*)]$ (**1a**)

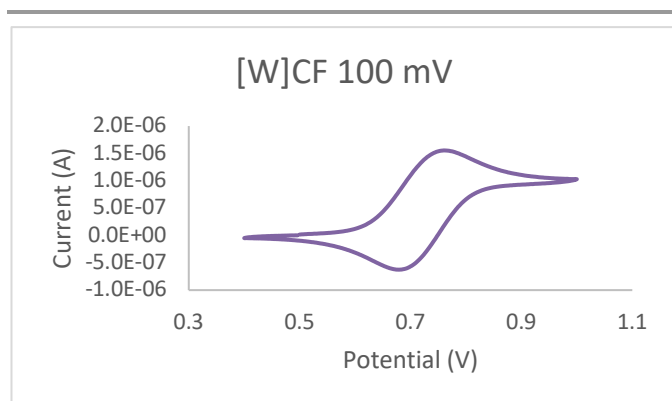


Figure S11. Cyclic voltammogram for $[W(=CF)(CO)_2(Tp^*)]$ (**1a**).

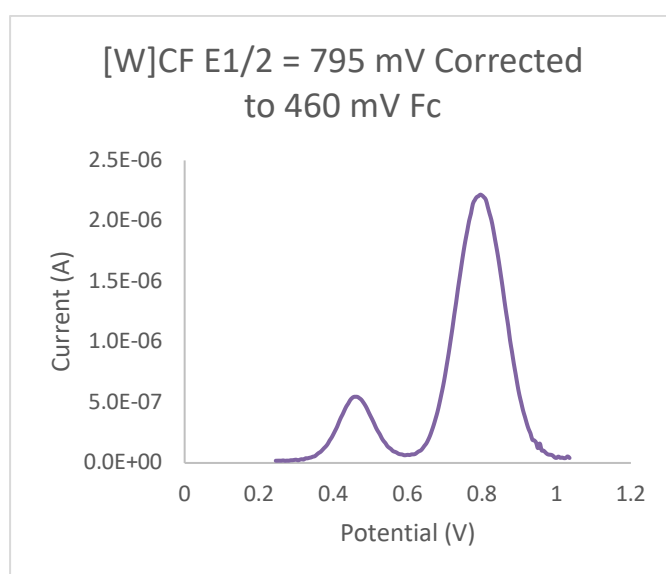
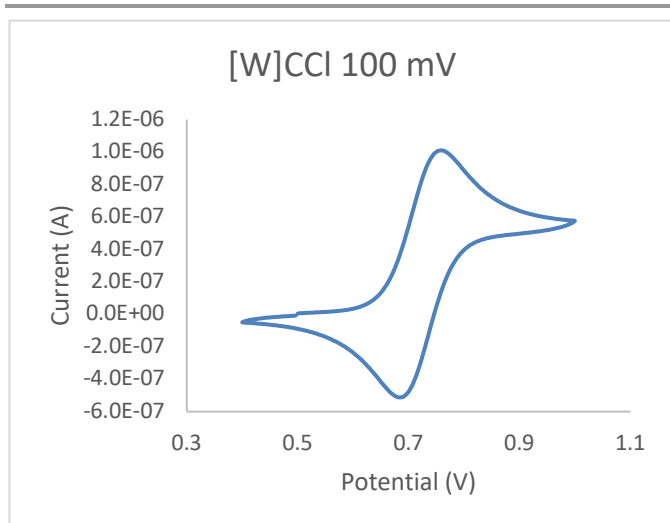
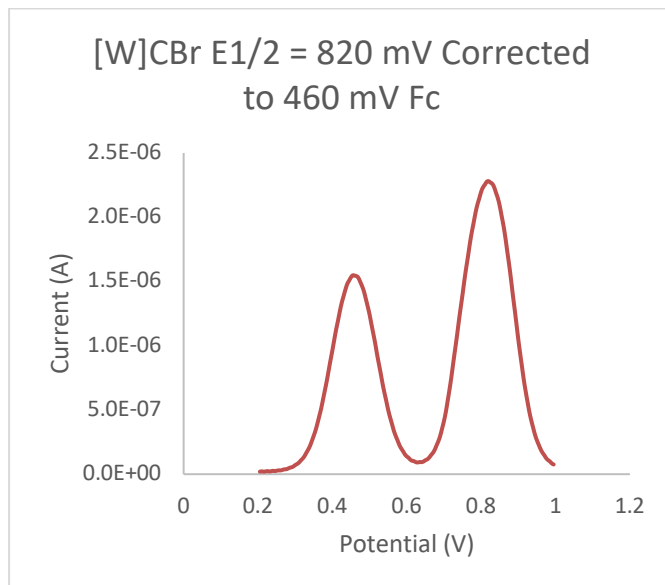
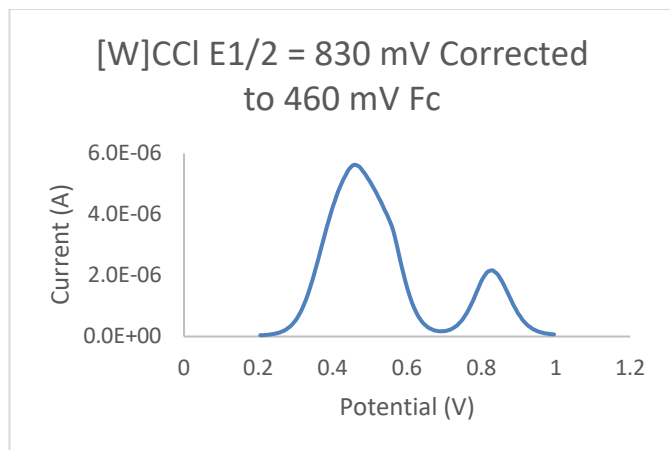
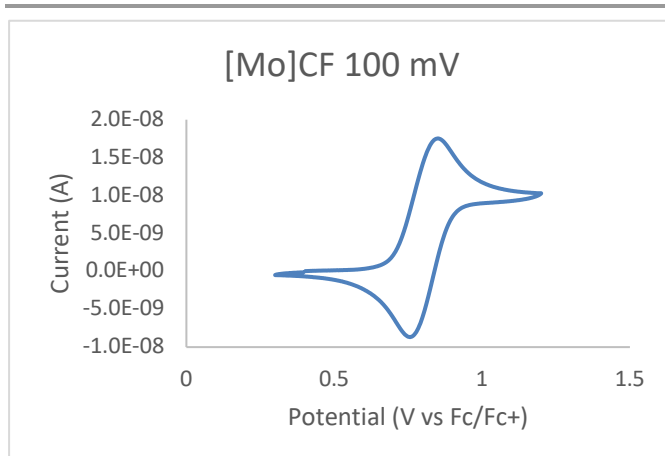
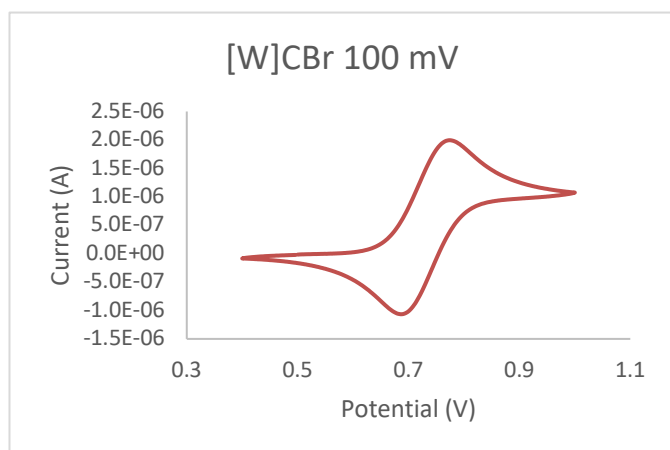
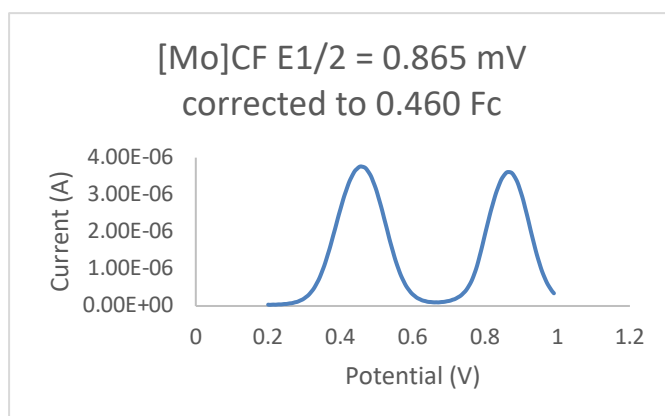
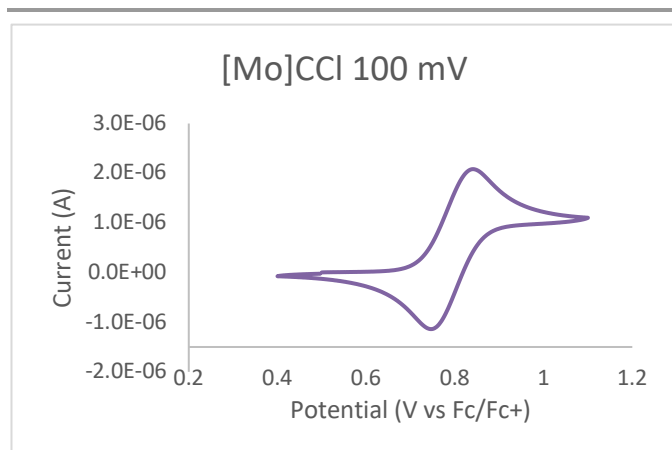
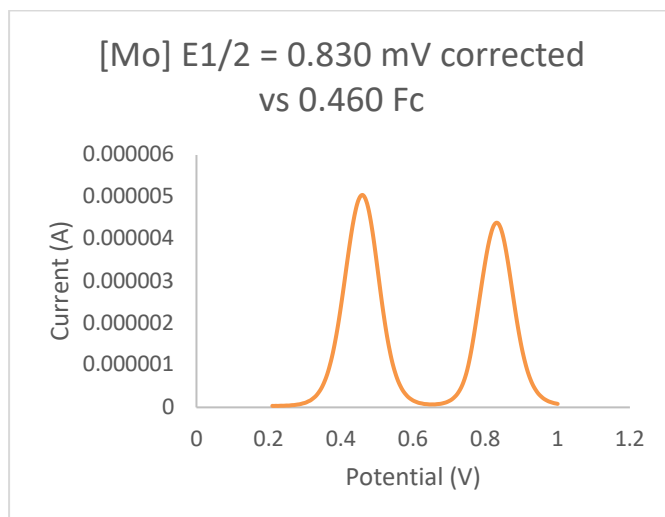
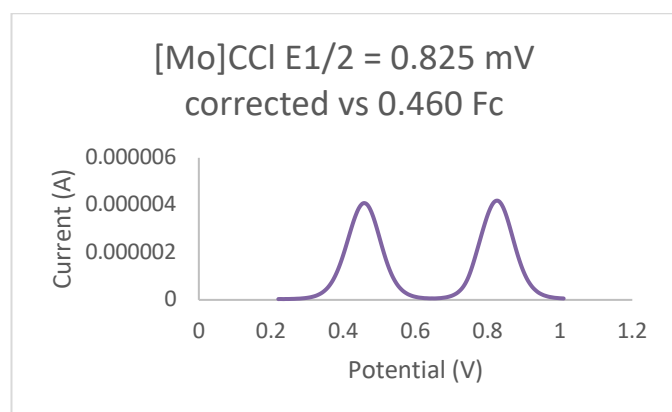
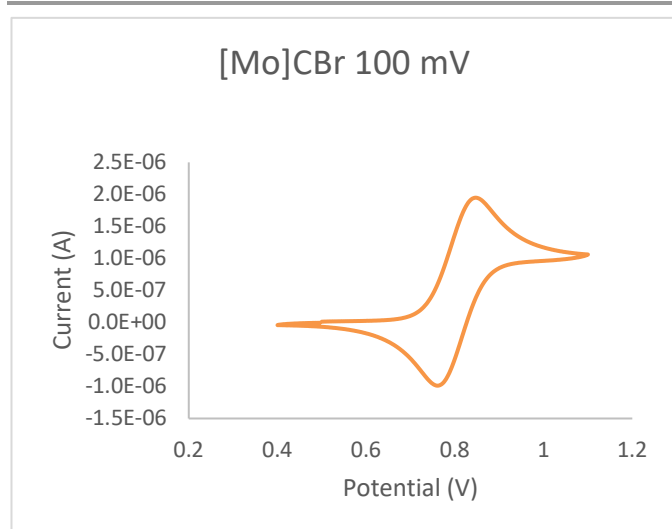
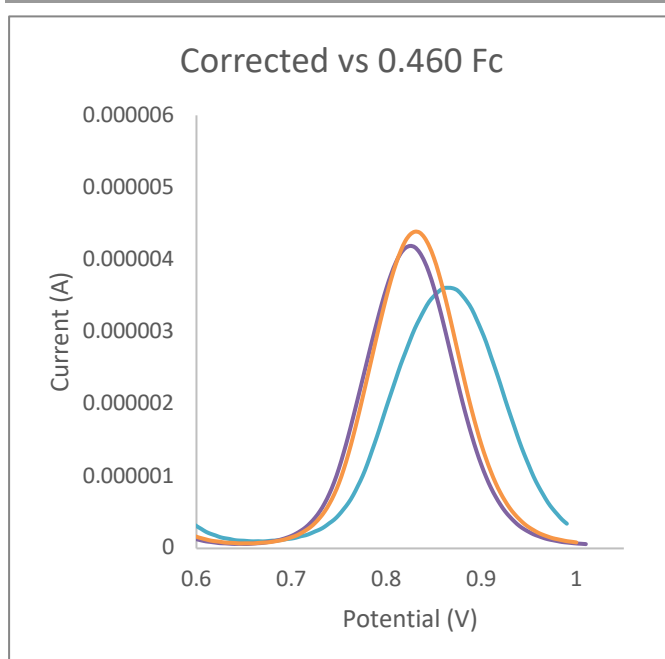


Figure S12. Square-wave voltammogram for $[W(=CF)(CO)_2(Tp^*)]$ (**1a**).

(b) [W(=CCl)(CO)₂(Tp*)] (1b)Figure S13. Cyclic voltammogram for [W(=CCl)(CO)₂(Tp*)] (1b).Figure S16. Square-wave voltammogram for [W(=CBr)(CO)₂(Tp*)] (1c).Figure S14. Square-wave voltammogram for [W(=CCl)(CO)₂(Tp*)] (1b).**(d) [Mo(=CF)(CO)₂(Tp*)] (2a)**Figure S17. Cyclic voltammogram for [Mo(=CF)(CO)₂(Tp*)] (2a).**(c) [W(=CBr)(CO)₂(Tp*)] (1c)**Figure S15. Cyclic voltammogram for [W(=CBr)(CO)₂(Tp*)] (1c).Figure S18. Square-wave voltammogram for [Mo(=CF)(CO)₂(Tp*)] (2a).

(e) [Mo(=CCl)(CO)₂(Tp*)] (2b)Figure S19. Cyclic voltammogram for [Mo(=CCl)(CO)₂(Tp*)] (2b).Figure S22. Square-wave voltammogram for [Mo(=CBr)(CO)₂(Tp*)] (2c).Figure S20. Square-wave voltammogram for [Mo(=CCl)(CO)₂(Tp*)] (2b).**(f) [Mo(=CBr)(CO)₂(Tp*)] (2c)**Figure S21. Cyclic voltammogram for [Mo(=CBr)(CO)₂(Tp*)] (2c).**(g) [Mo(=CX)(CO)₂(Tp*)] (X = F 2a, Cl 2b, Br 2c)**Figure S23. Superposition of square-wave voltammograms for [Mo(=CX)(CO)₂(Tp*)] (X = F 2a, Cl 2b, Br 2c).

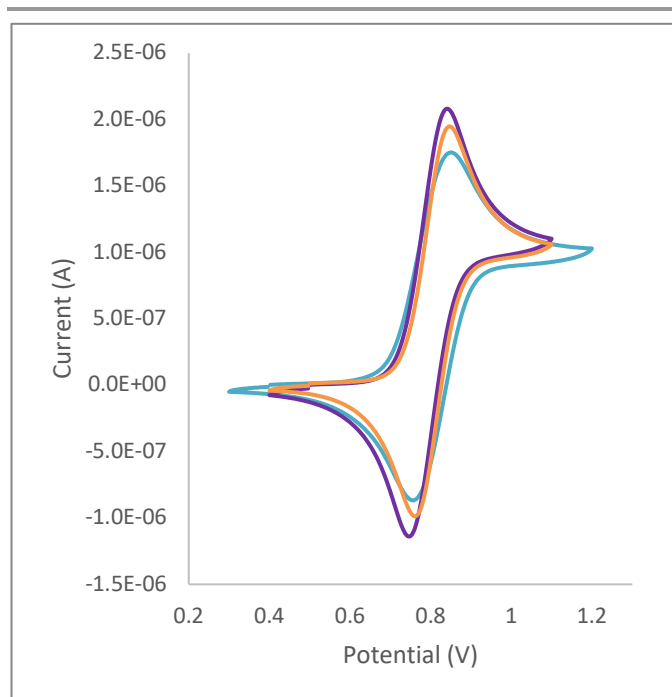


Figure S24. Superposition of cyclic voltammograms for $[\text{Mo}(=\text{CX})(\text{CO})_2(\text{Tp}^*)]$ ($\text{X} = \text{F}$ 2a, Cl 2b, Br 2c).

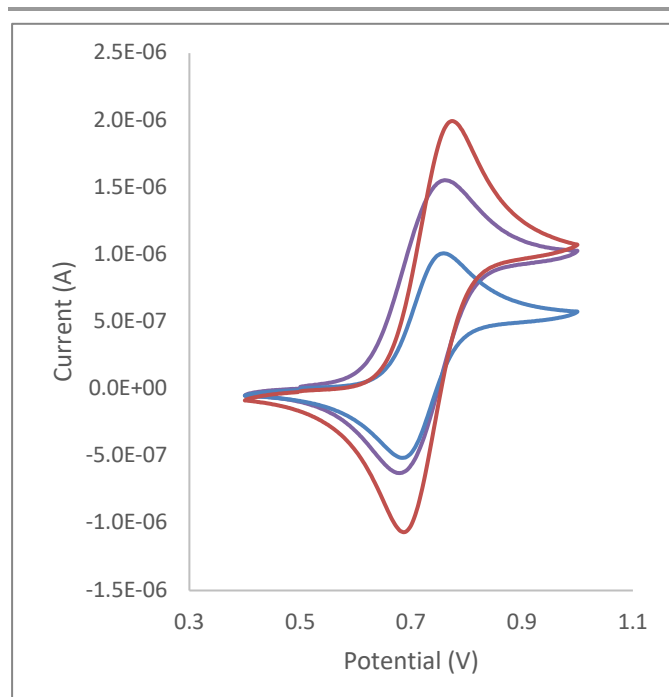


Figure S26. Superposition of cyclic voltammograms for $[\text{W}(=\text{CX})(\text{CO})_2(\text{Tp}^*)]$ ($\text{X} = \text{F}$ 2a, Cl 2b, Br 2c).

(h) $[\text{W}(=\text{CX})(\text{CO})_2(\text{Tp}^*)]$ ($\text{X} = \text{F}$ 1a, Cl 1b, Br 1c)

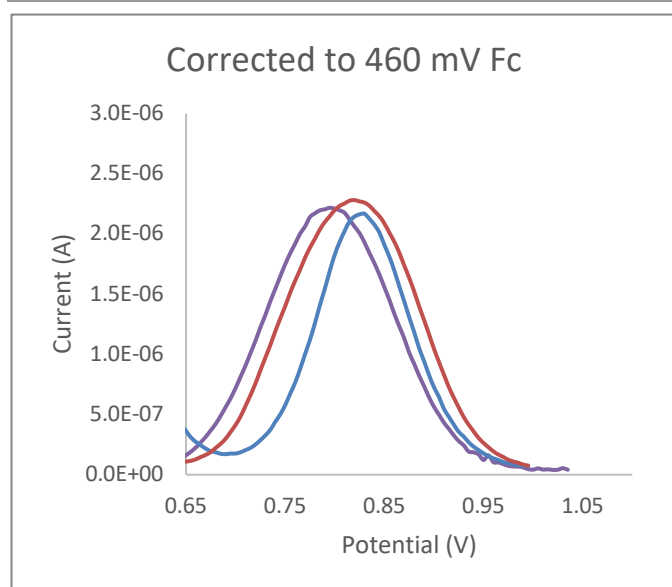


Figure S25. Superposition of square-wave voltammograms for $[\text{W}(=\text{CX})(\text{CO})_2(\text{Tp}^*)]$ ($\text{X} = \text{F}$ 1a, Cl 1b, Br 1c).

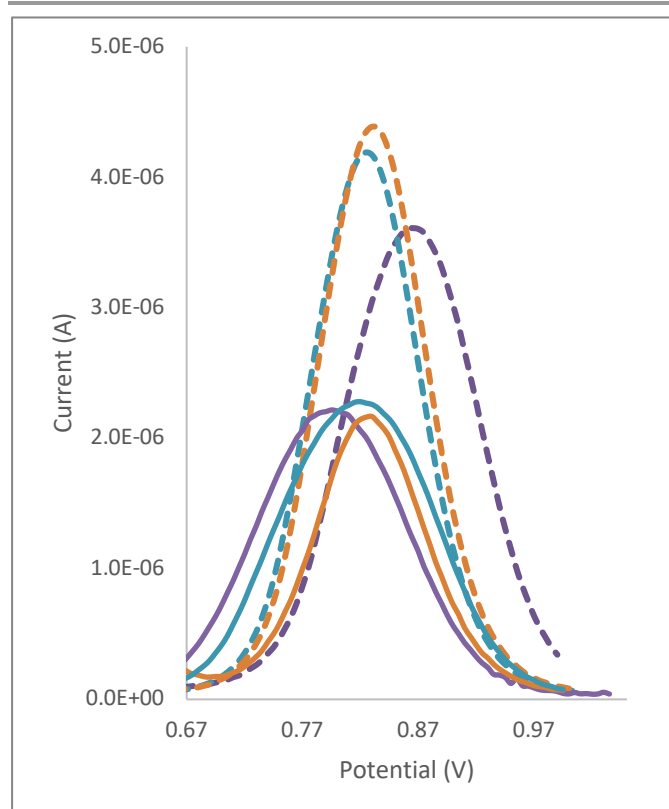


Figure S27. Superposition of cyclic voltammograms for $[\text{M}(=\text{CX})(\text{CO})_2(\text{Tp}^*)]$ ($\text{X} = \text{F}$, Cl, Br; $\text{M} = \text{W}$ solid line, Mo dashed line).

References

- 1 T. Desmond, F. J. Lalor, G. Ferguson and M. Parvez, *J. Chem. Soc., Chem. Commun.*, 1983, 457-459.
- 2 AuCl.THT
- 3 Agilent, *Journal*, 2014.
- 4 G. Sheldrick, *Acta Crystallogr. Sect. A: Found. Crystallogr.*, 2008, **64**, 112-122.
- 5 G. M. Sheldrick, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.*, 2015, **71**, 3-8.
- 6 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallog.*, **2009**, *42*, 339-341.
- 7 C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Crystallogr.*, 2006, **39**, 453-457.
- 8 C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Crystallogr.*, 2008, **41**, 466-470.
- 9 *Spartan 20*[®] (2020) Wavefunction, Inc., 18401 Von Karman Ave., Suite 370 Irvine, CA 92612 U.S.A.
- 10 J. D. Chai and M. Head-Gordon, *J Chem Phys.*, 2008, **128**, 084106.
- 11 J. D. Chai and M. Head-Gordon, *Phys Chem Chem Phys*, 2008, **10**, 6615-6620.
- 12 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270-283.
- 13 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299-310.
- 14 W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284-298.
- 15 W. J. Hehre, R. Ditchfeld and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257-2261.

ELECTRONIC SUPPORTING INFORMATION

PerkinElmer Spectrum Version 10.4.3
Thursday, 29 September 2022 4:11 PM

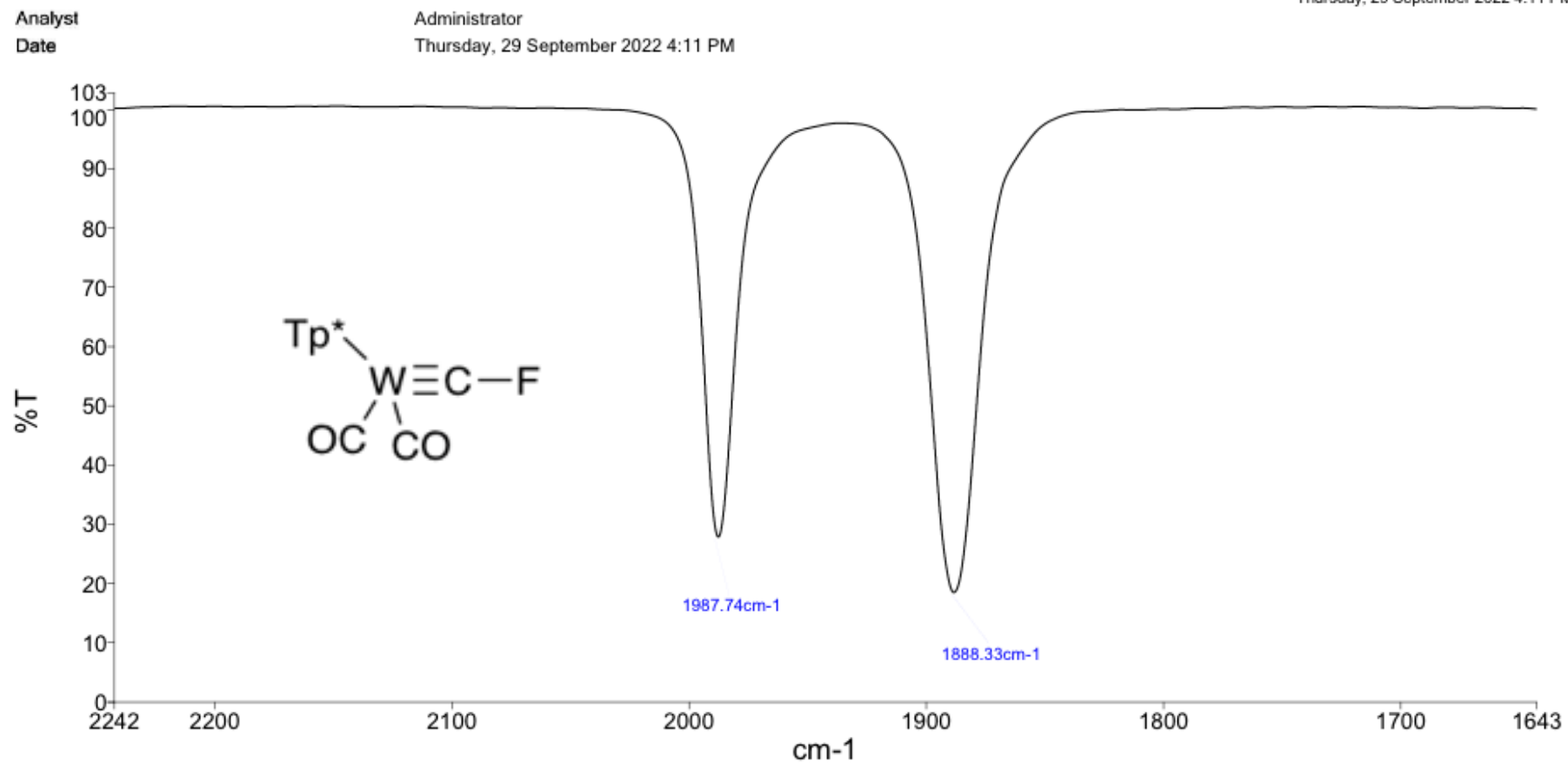


Figure S28. Solution IR of $[\text{W}(\equiv\text{CF})(\text{CO})_2(\text{Tp}^*)]$ (**1a**) in CH_2Cl_2

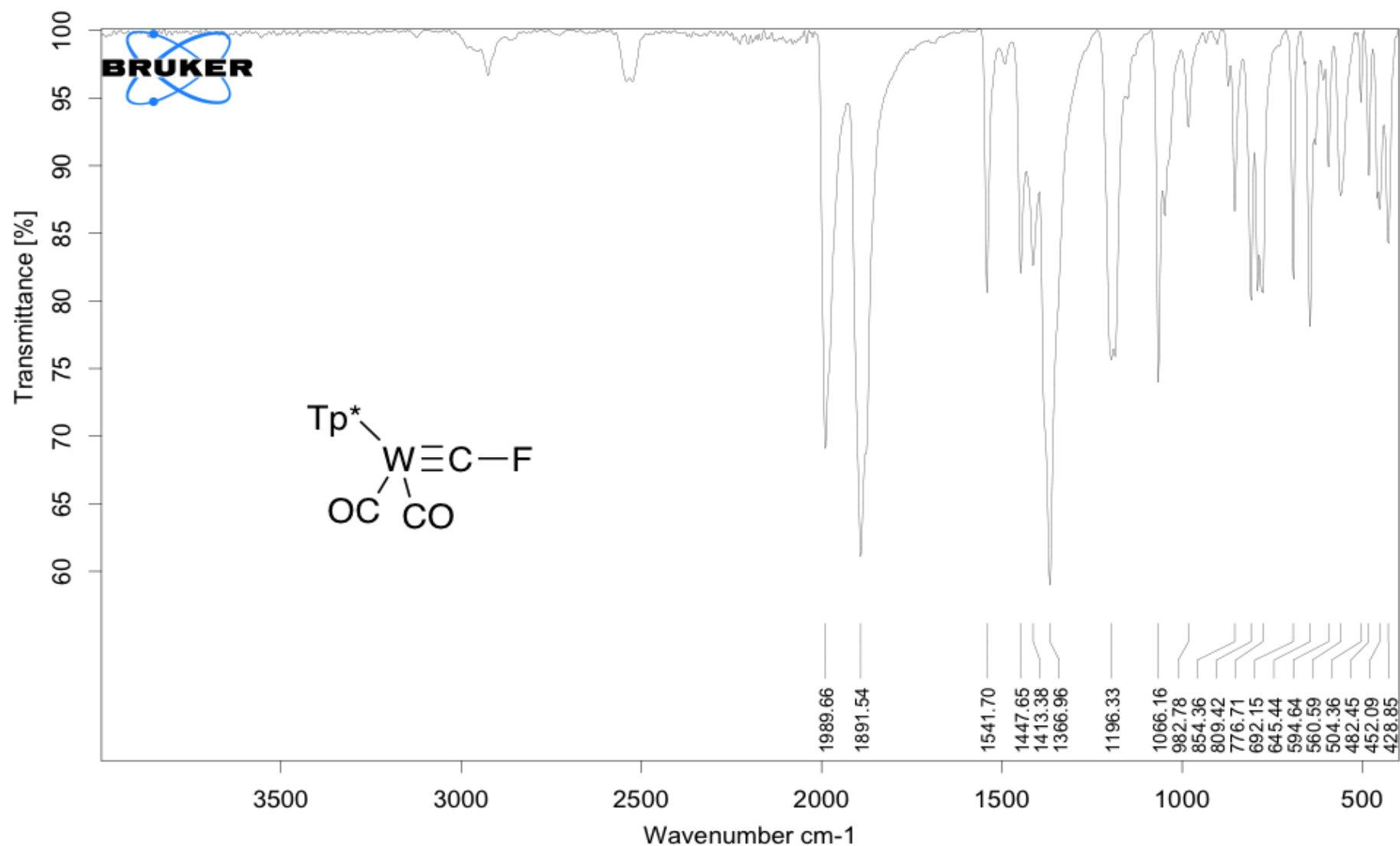


Figure S29. Solid State (ATR) IR of $[\text{W}(\equiv\text{CF})(\text{CO})_2(\text{Tp}^*)]$ (**1a**) in CH_2Cl_2

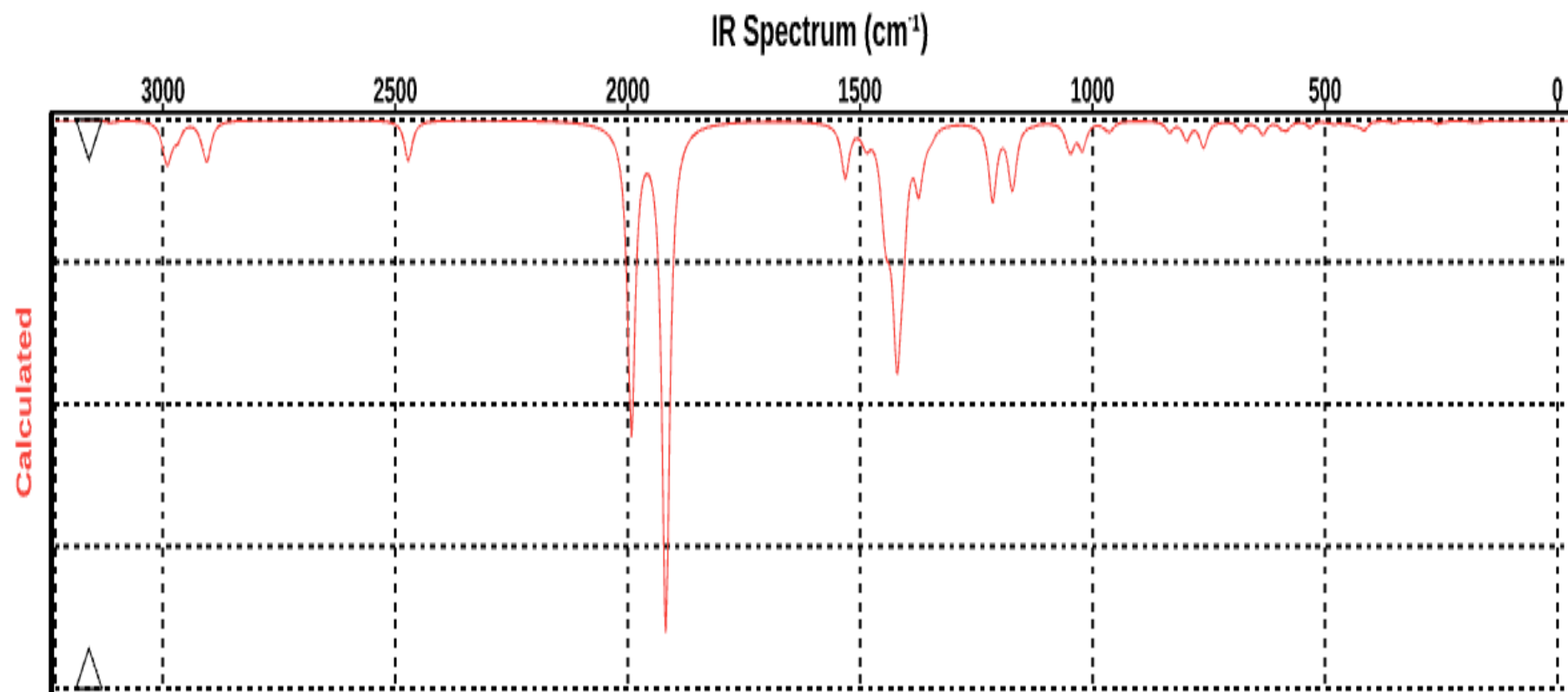


Figure S30. Calculated IR of $[\text{W}(\equiv\text{CF})(\text{CO})_2(\text{Tp}^*)]$ (**1a**) in the gas phase (wb97X-D/6-31G*/LANL2D ζ)

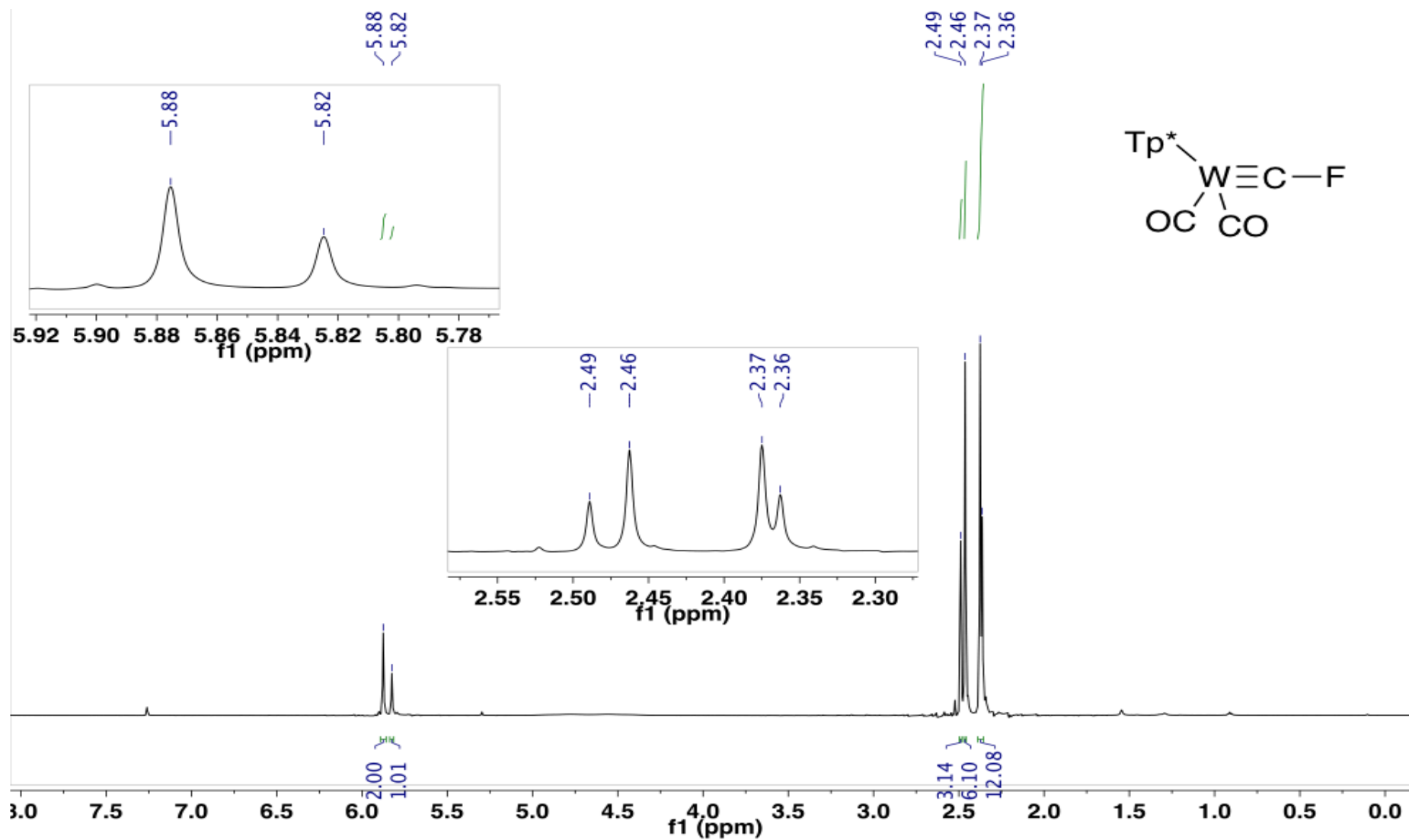


Figure S31. ^1H NMR Spectrum of $[\text{W}(\equiv\text{CF})(\text{CO})_2(\text{Tp}^*)]$ (1a) (600 MHz, CDCl_3 , 25°C , δ):

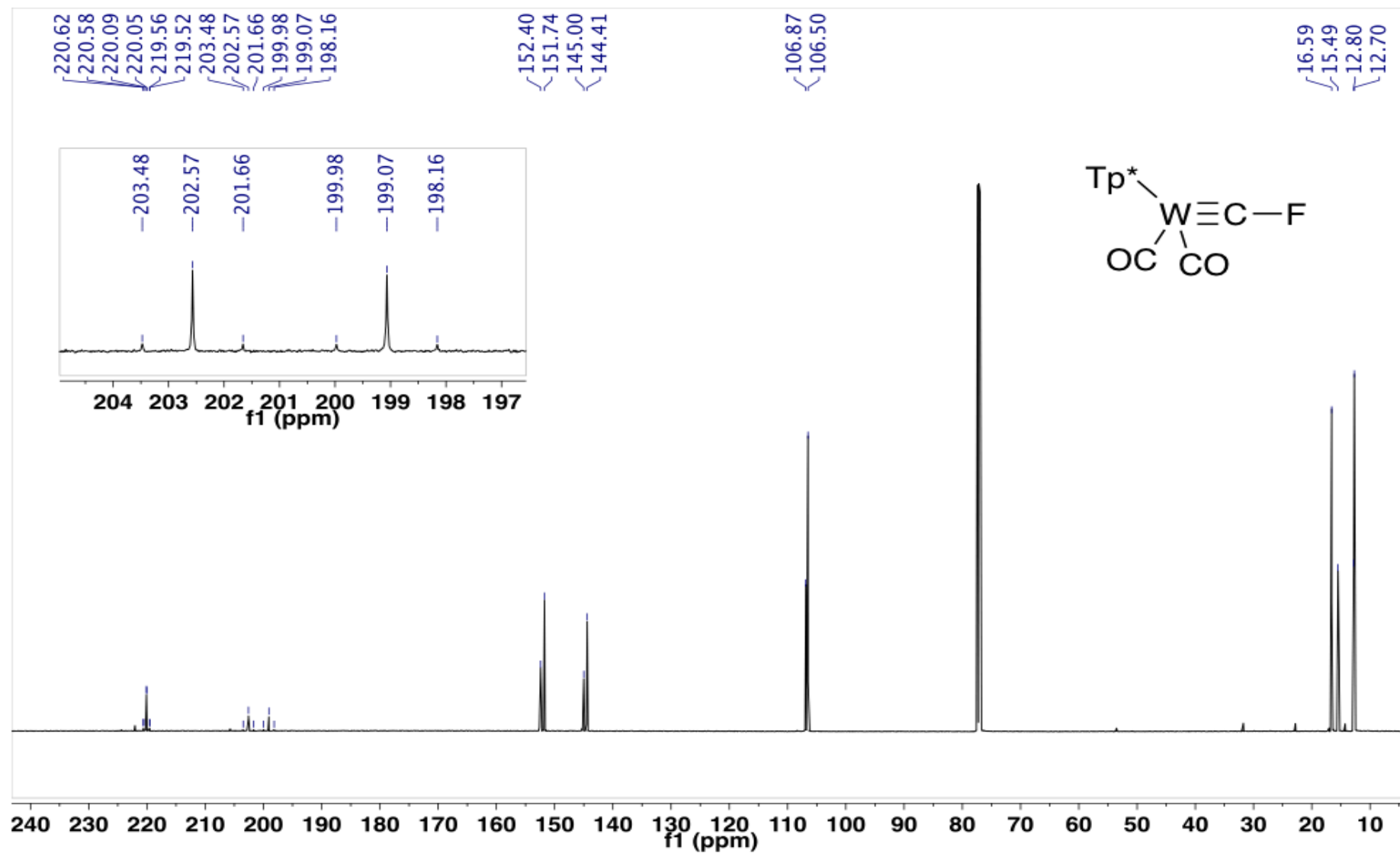


Figure S32. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of $[\text{W}(\equiv\text{CF})(\text{CO})_2(\text{Tp}^*)]$ (**1a**) (150.9 MHz, CDCl_3 , 25°C , δ):

20

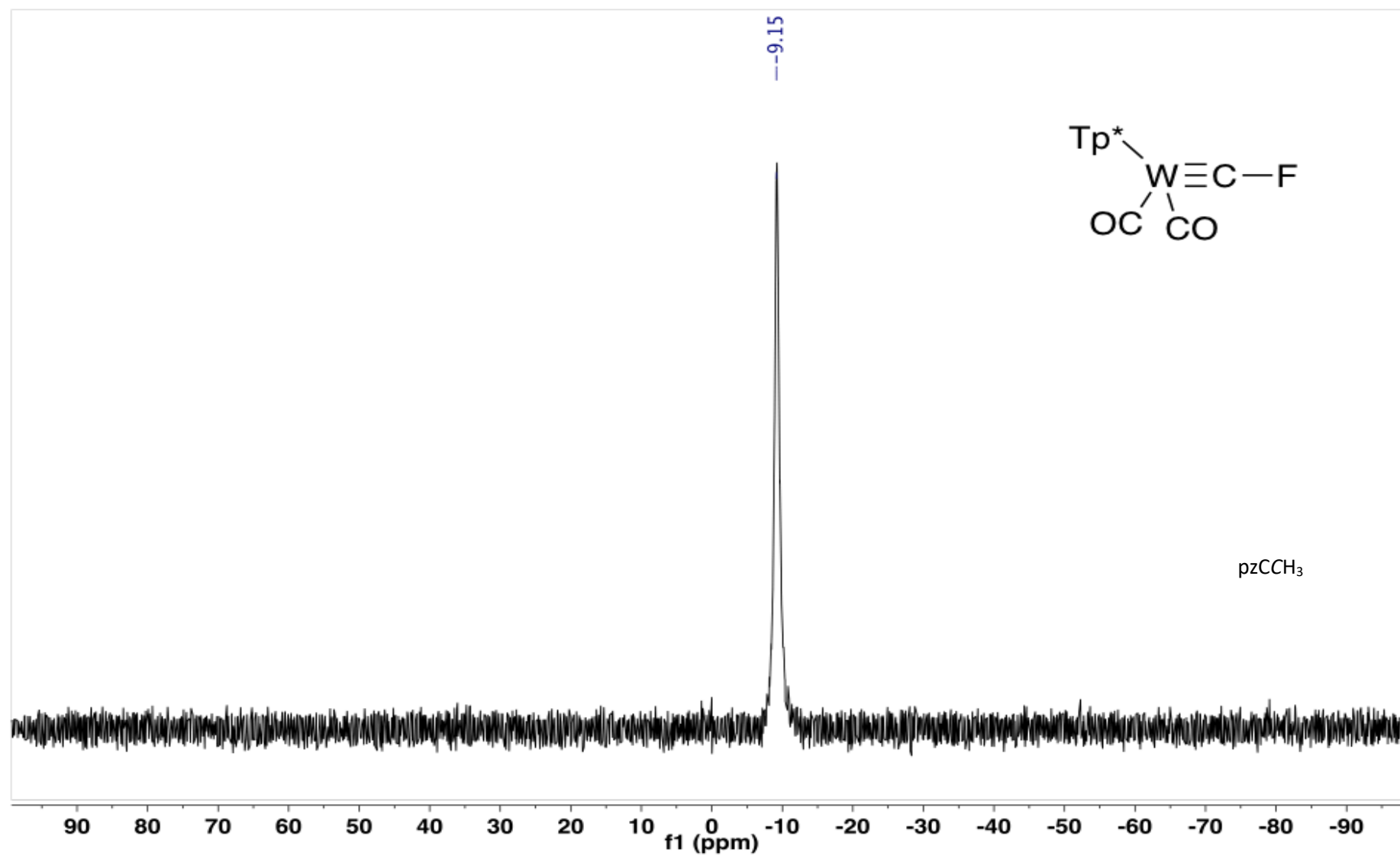


Figure S33. $^{11}\text{B}\{^1\text{H}\}$ NMR Spectrum of $[\text{W}(\equiv\text{CF})(\text{CO})_2(\text{Tp}^*)]$ (1a) (128.4 MHz, CDCl_3 , 25 °C, δ):

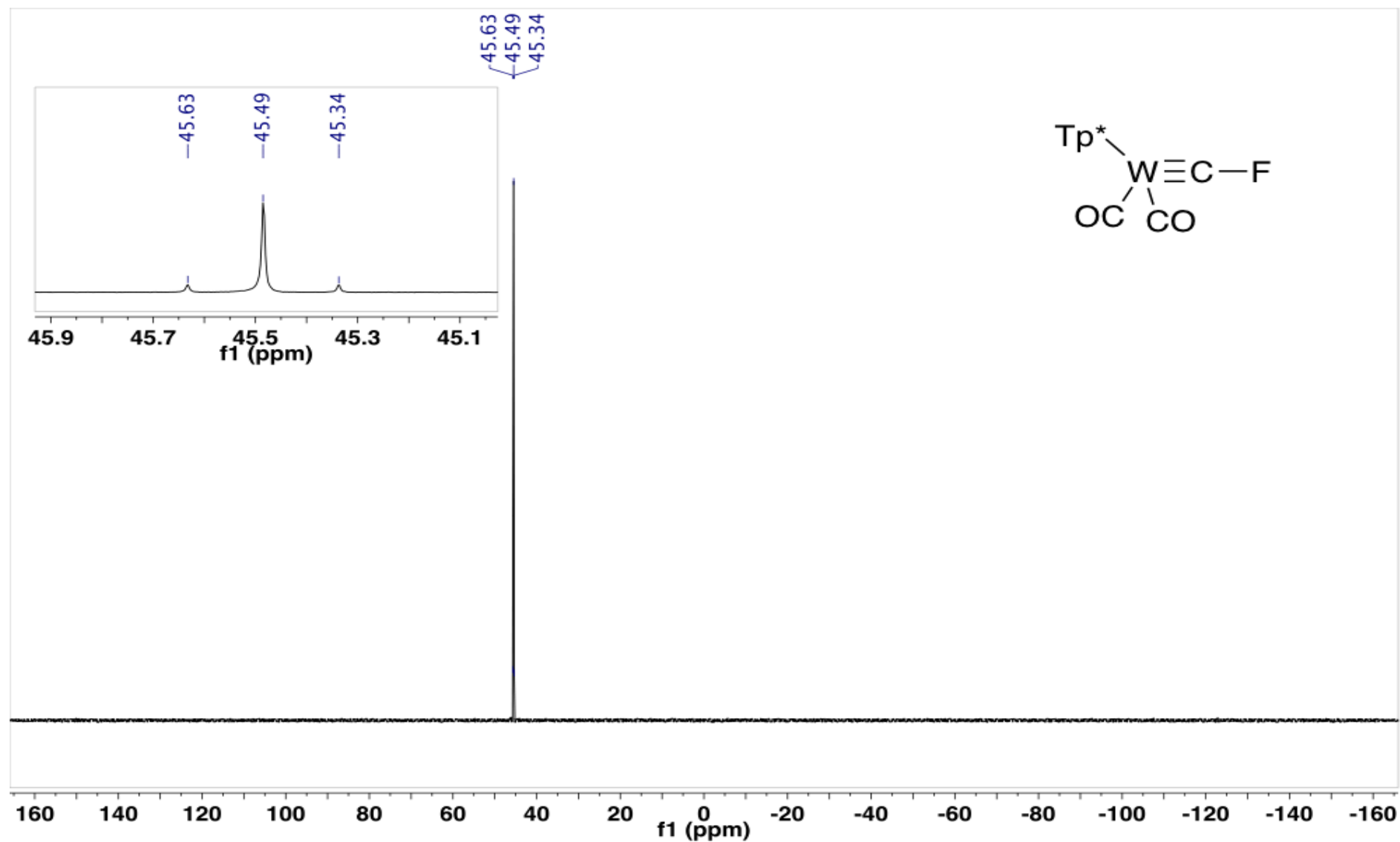


Figure S34. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum of $[\text{W}(\equiv\text{CF})(\text{CO})_2(\text{Tp}^*)]$ (**1a**) (377 MHz, CDCl_3 , 25 °C, δ):

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 3.0 PPM / DBE: min = -1.5, max = 15.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions

1456 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 0-50 H: 0-50 11B: 0-1 N: 0-6 O: 0-2 19F: 0-1 23Na: 0-1 184W: 0-1

rm-068b-DCM+MeOH/AJ

SYNAPTG2-Si#NotSet

28-Oct-2022

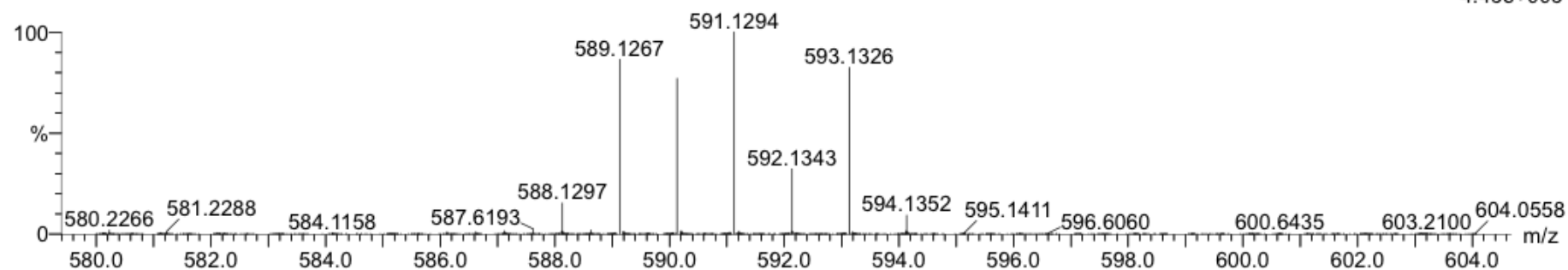
67326

10:17:17

3943B 49 (0.115) Cm (49:94-22:48)

1: TOF MS ES+

4.43e+005



Minimum: -1.5
 Maximum: 5.0 3.0 15.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
591.1294	591.1288	0.6	1.0	12.0	1718.8	C18 H22 11B N6 O2 19F 23Na 184W

Figure S35. ESI-MS of $[W(\equiv CF)(CO)_2(Tp^*)]$ (**1a**): $[M+Na]^+$

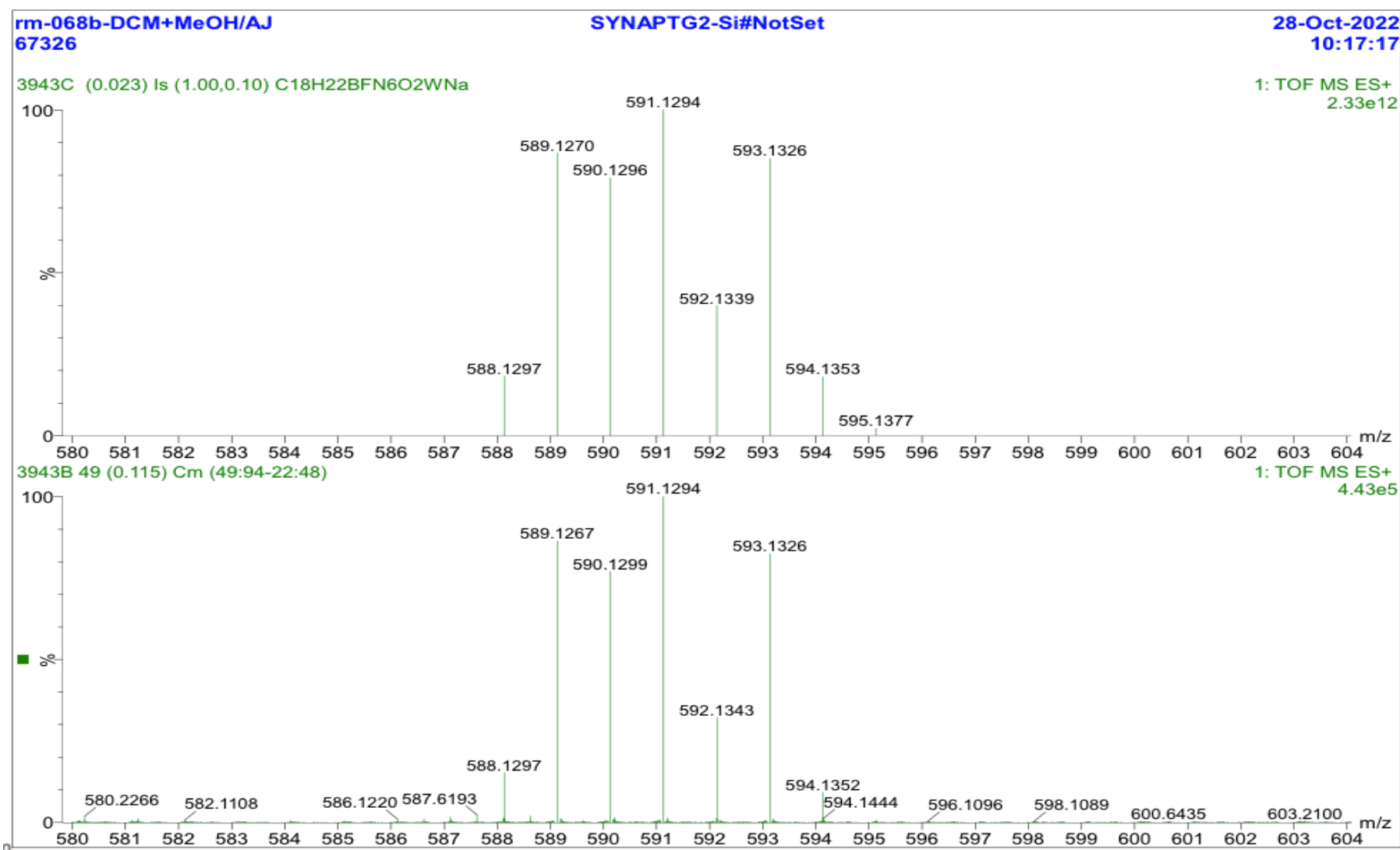
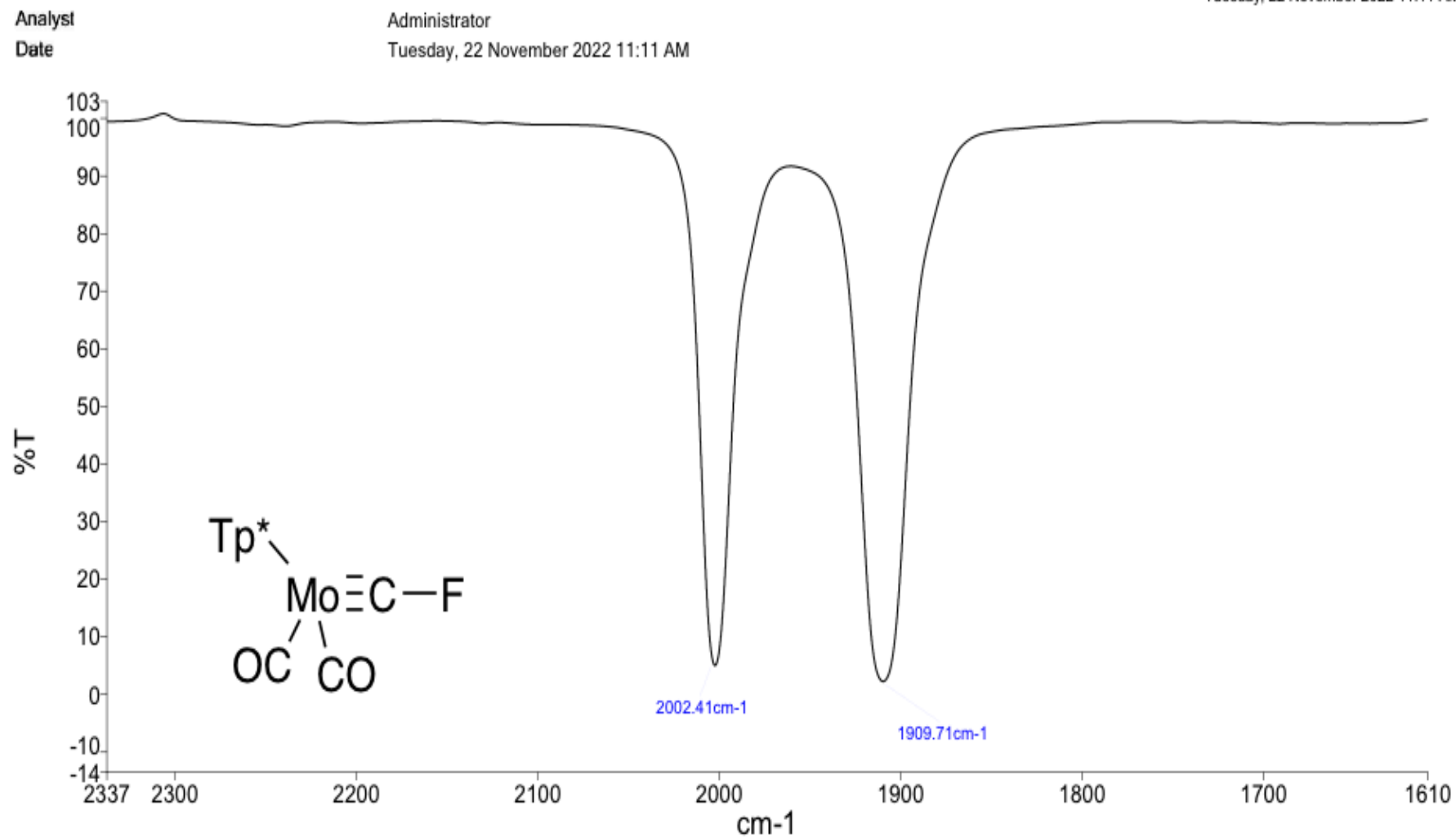


Figure S36. ESI-MS of $[W(\equiv CF)(CO)_2(Tp^*)]$ (**1a**): $[M+Na]^+$ with simulation

PerkinElmer Spectrum Version 10.4.3
Tuesday, 22 November 2022 11:11 AM**Figure S37.** Solution IR of $[\text{Mo}(\equiv\text{CF})(\text{CO})_2(\text{Tp}^*)]$ (**2a**) in CH_2Cl_2

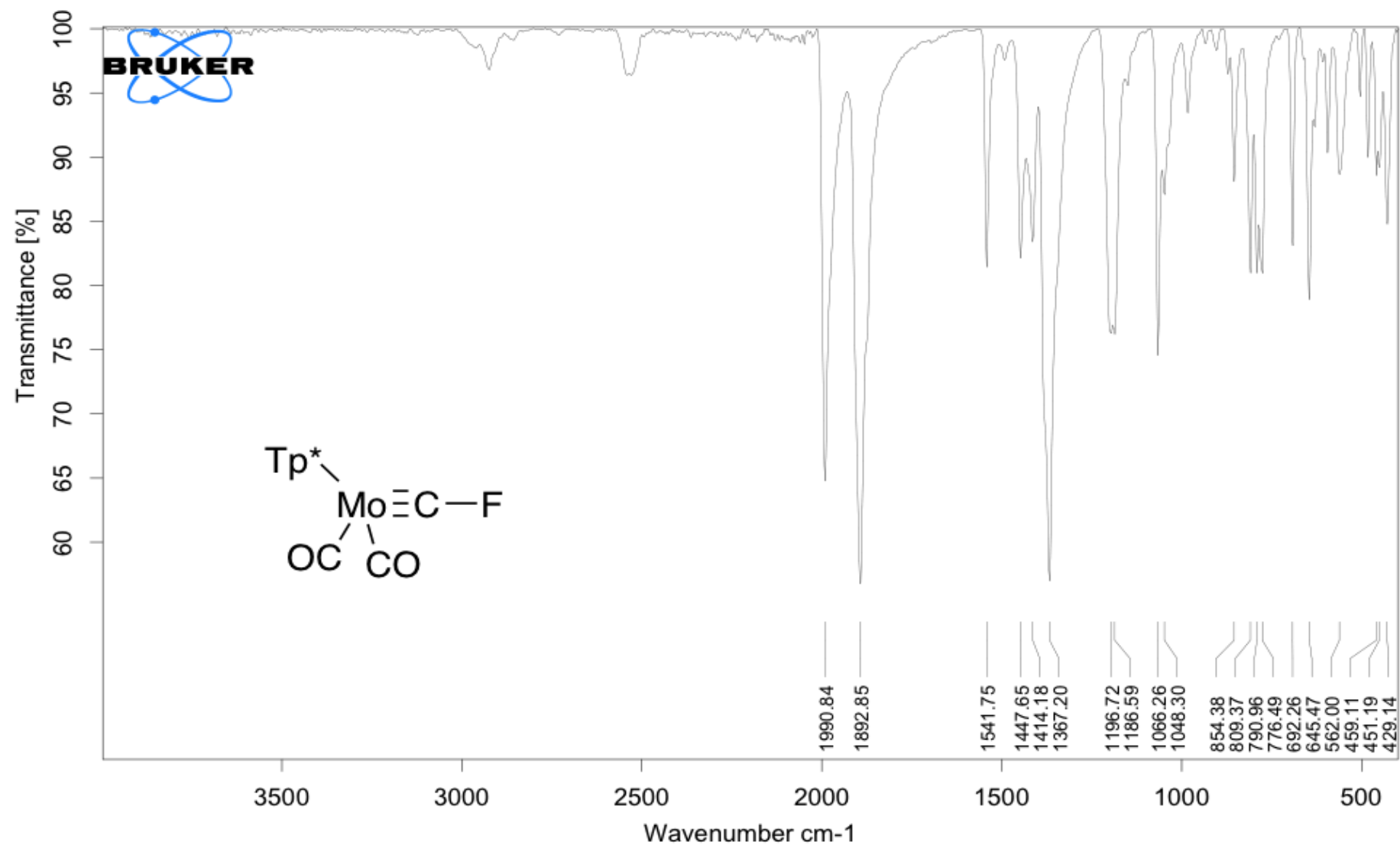


Figure S38. Solid State (ATR) IR of $[Mo(\equiv CF)(CO)_2(Tp^*)]$ (2a) in CH_2Cl_2

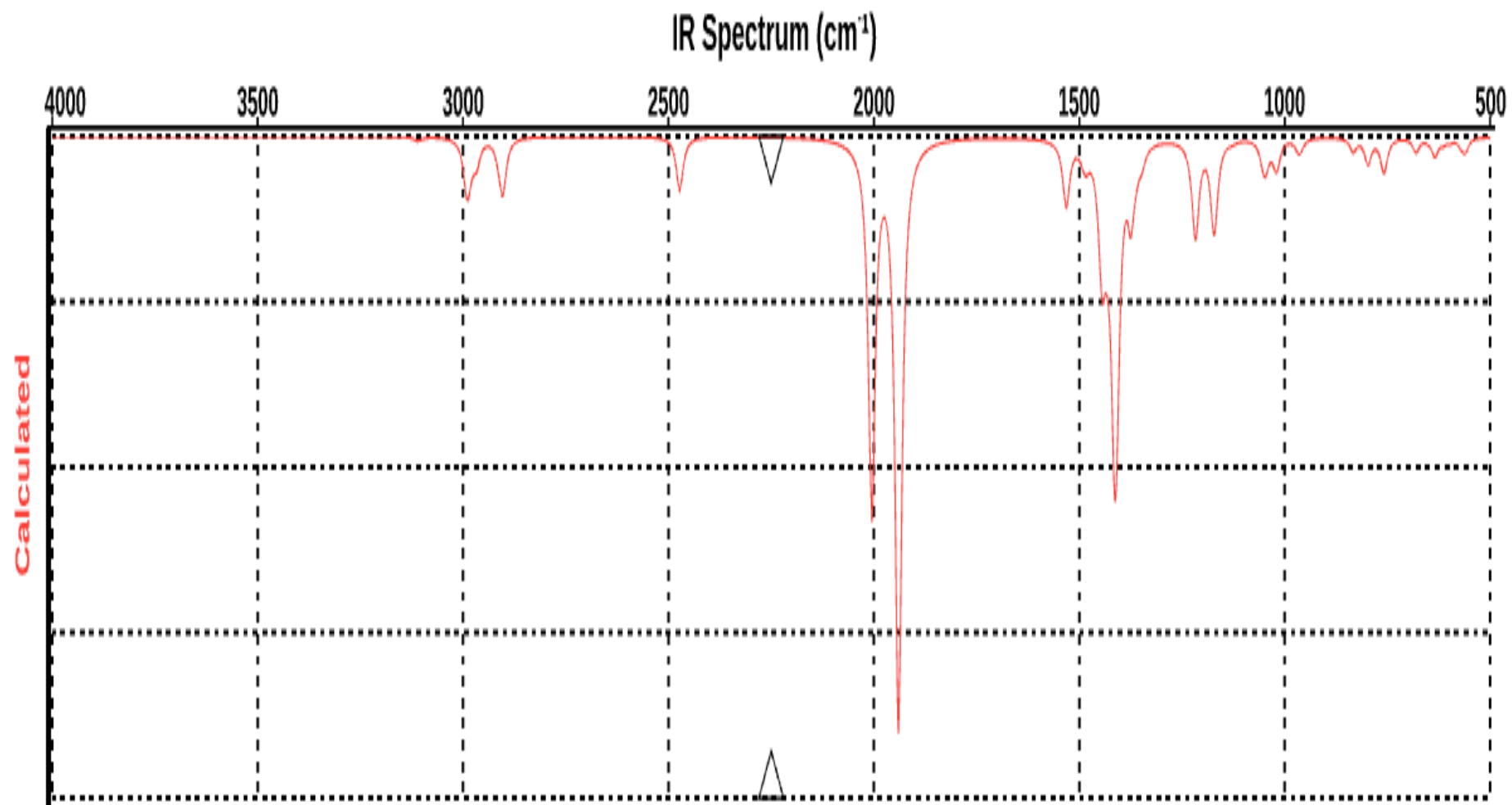


Figure S39. Calculated IR of $[\text{Mo}(\equiv\text{CF})(\text{CO})_2(\text{Tp}^*)]$ (**2a**) in the gas phase (wB97X-D/6-31G*/LANL2D \square)

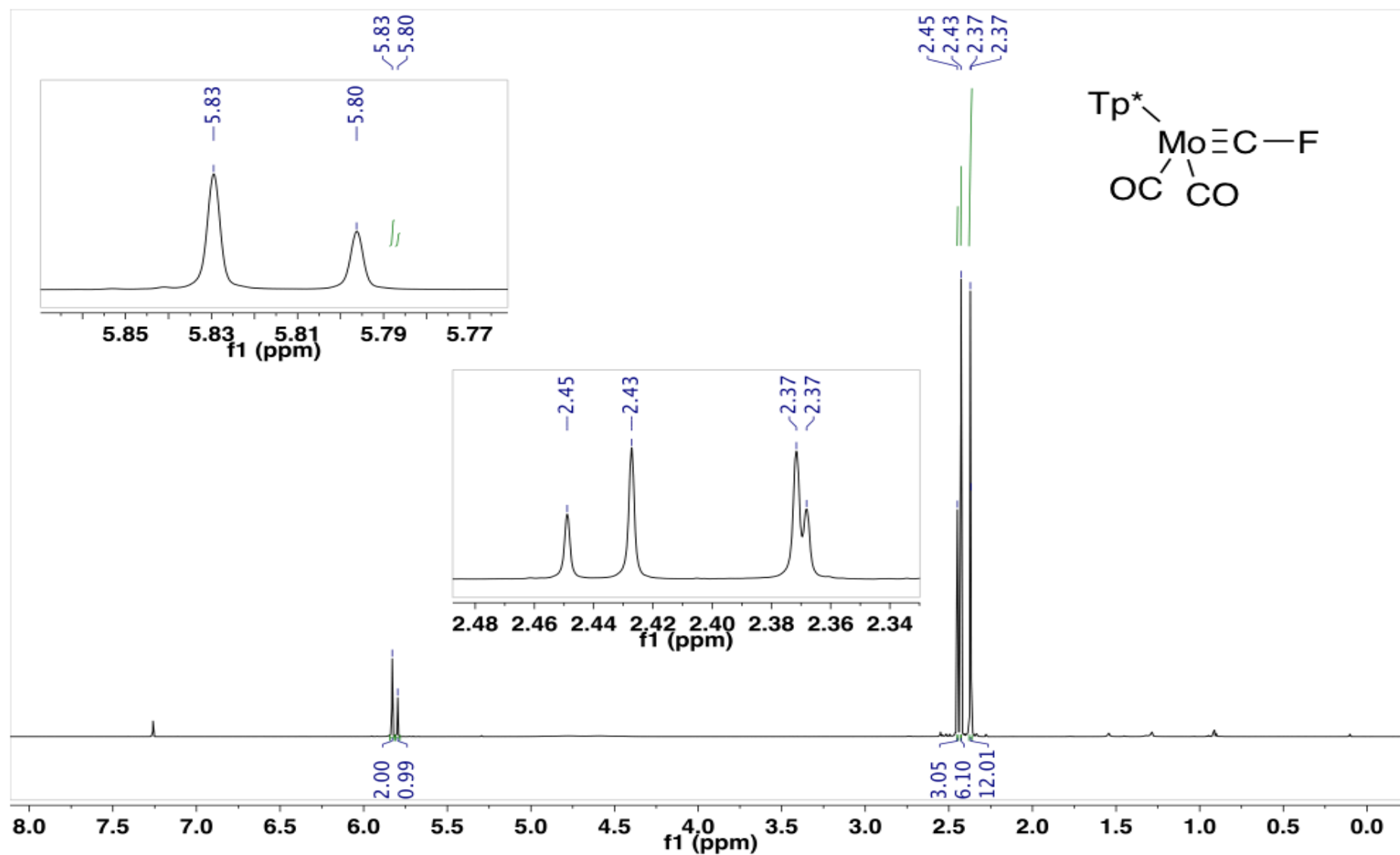


Figure S40. ^1H NMR Spectrum of $[\text{Mo}(\equiv\text{CF})(\text{CO})_2(\text{Tp}^*)]$ (2a) (600 MHz, CDCl_3 , 25°C , δ):

28

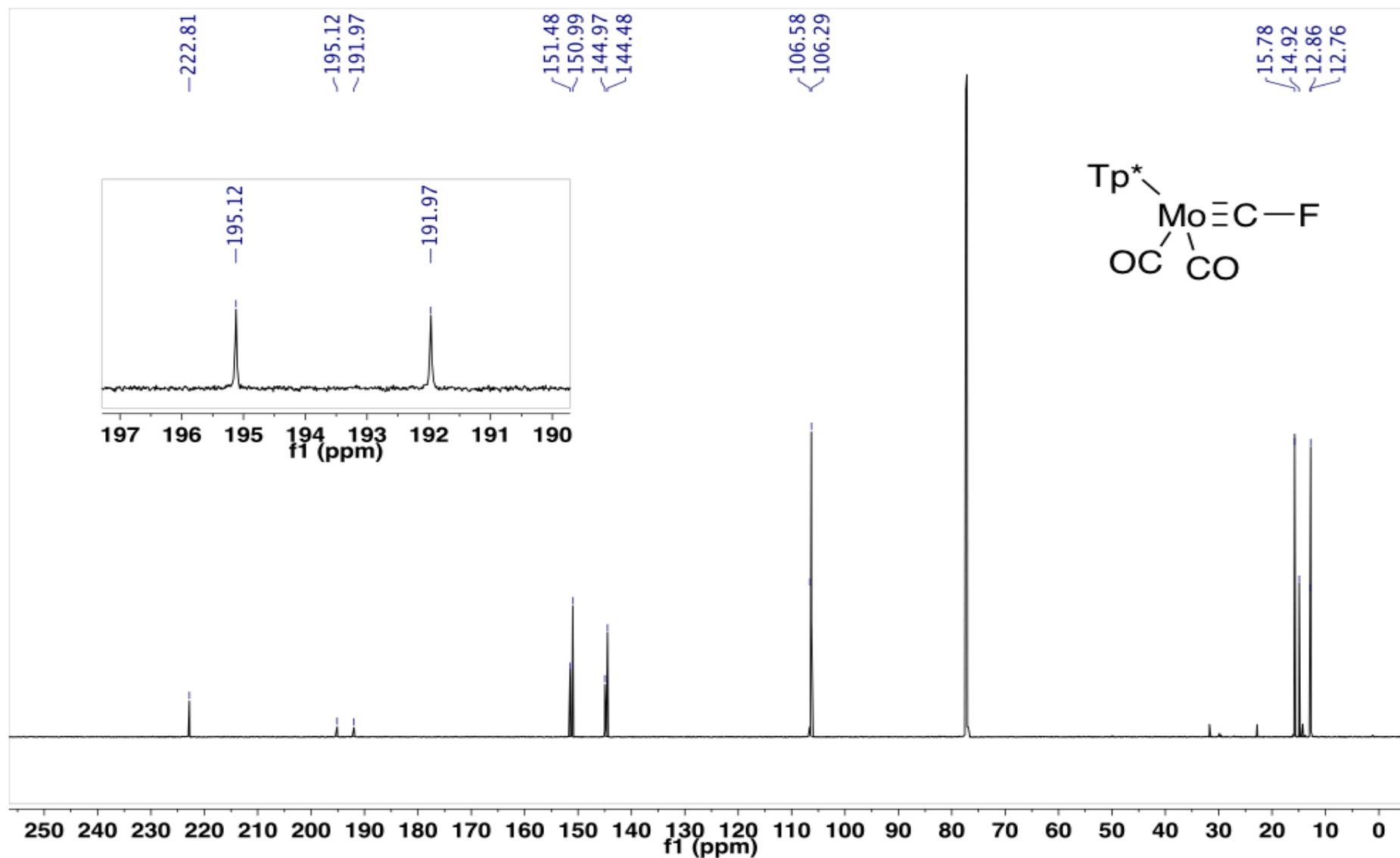


Figure S41. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of $[\text{Mo}(\equiv\text{CF})(\text{CO})_2(\text{Tp}^*)]$ (2a) (150.9 MHz, CDCl_3 , 25°C , δ):

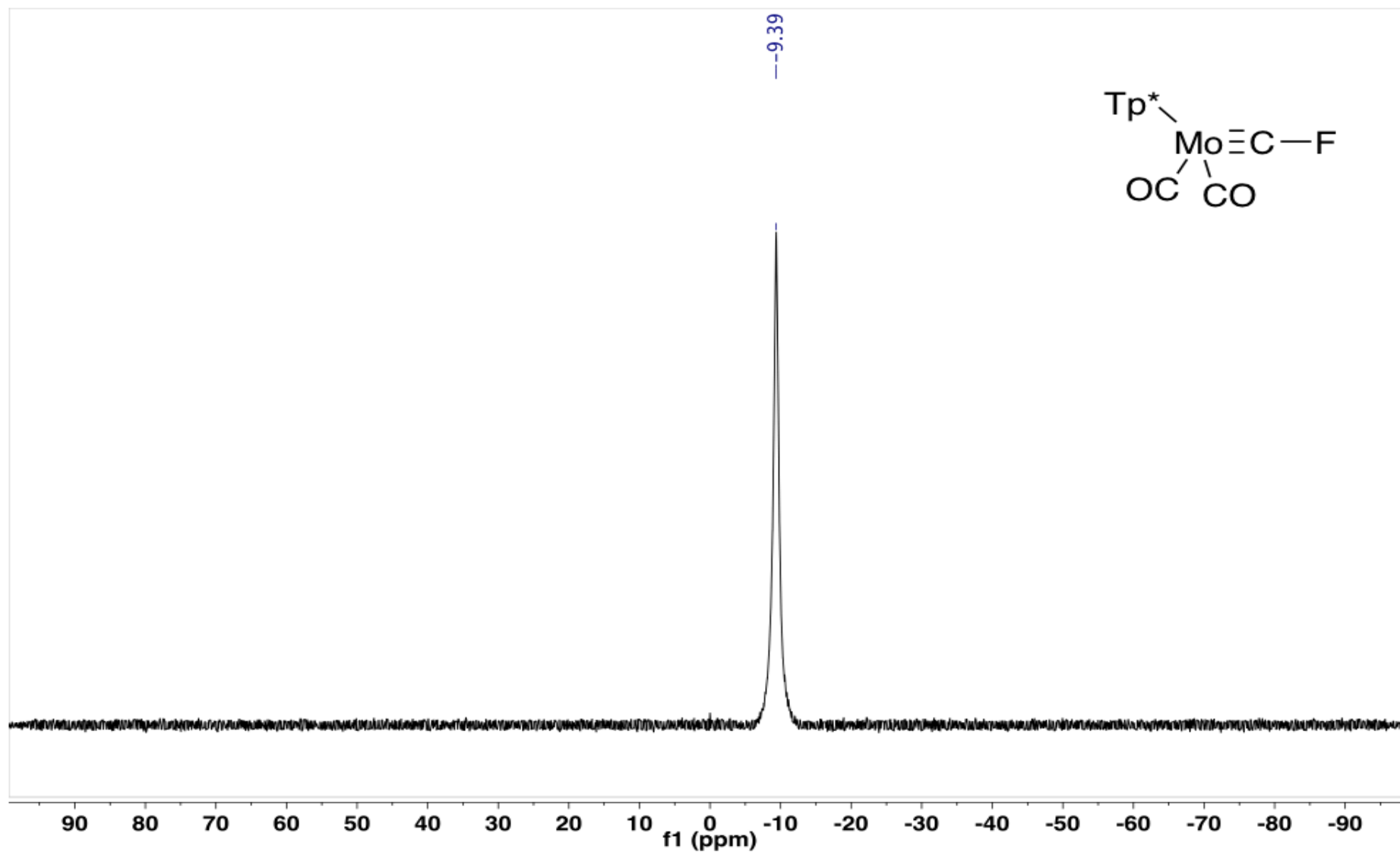


Figure S42. $^{11}\text{B}\{^1\text{H}\}$ NMR Spectrum of $[\text{Mo}(\equiv\text{CF})(\text{CO})_2(\text{Tp}^*)]$ (2a) (128.4 MHz, CDCl_3 , 25 °C, δ):

30

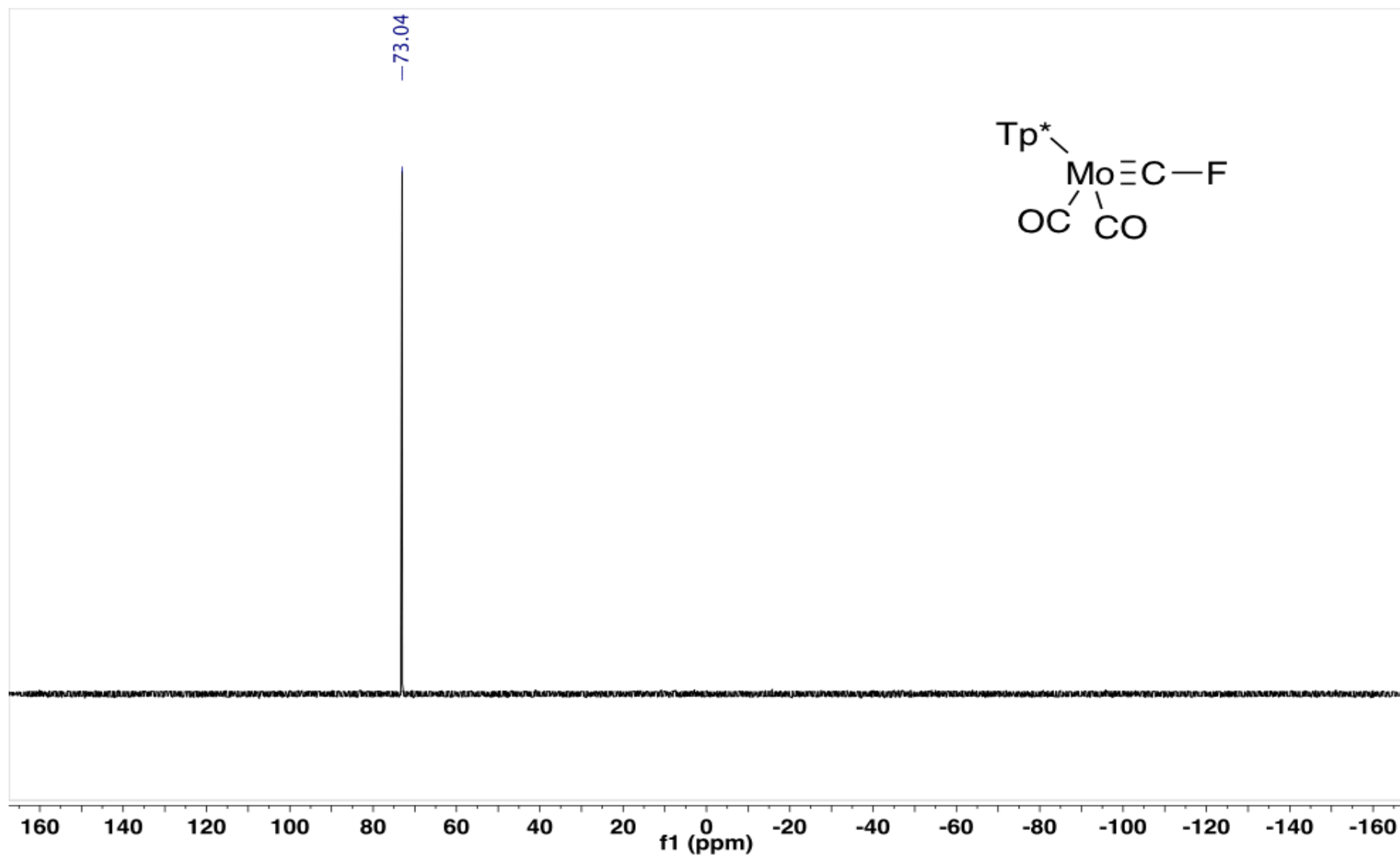


Figure S43. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum of $[\text{Mo}(\equiv\text{CF})(\text{CO})_2(\text{Tp}^*)]$ (**2a**) (376.5 MHz, CDCl_3 , 25 °C, δ):

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 3.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions

121 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 0-20 H: 0-30 11B: 0-1 N: 4-6 O: 0-2 19F: 0-1 98Mo: 0-1

RM-075-2022-DCM/AJ

SYNAPTG2-Si#NotSet

23-Nov-2022

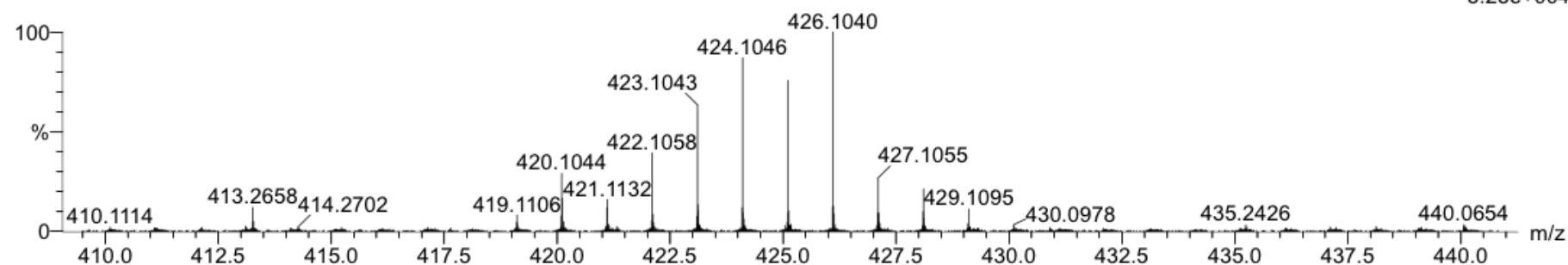
67375

11:04:38

4086B 87 (0.192) Cm (54:88)

1: TOF MS ES+

3.23e+004



Minimum: -1.5
 Maximum: 5.0 3.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
426.1040	426.1037	0.3	0.7	9.0	1596.3	C16 H22 11B N6 19F 98Mo

Figure S44. ESI-MS of $[\text{Mo}(\equiv\text{CF})(\text{CO})_2(\text{Tp}^*)]$ (**1a**): $[\text{M}]^+$

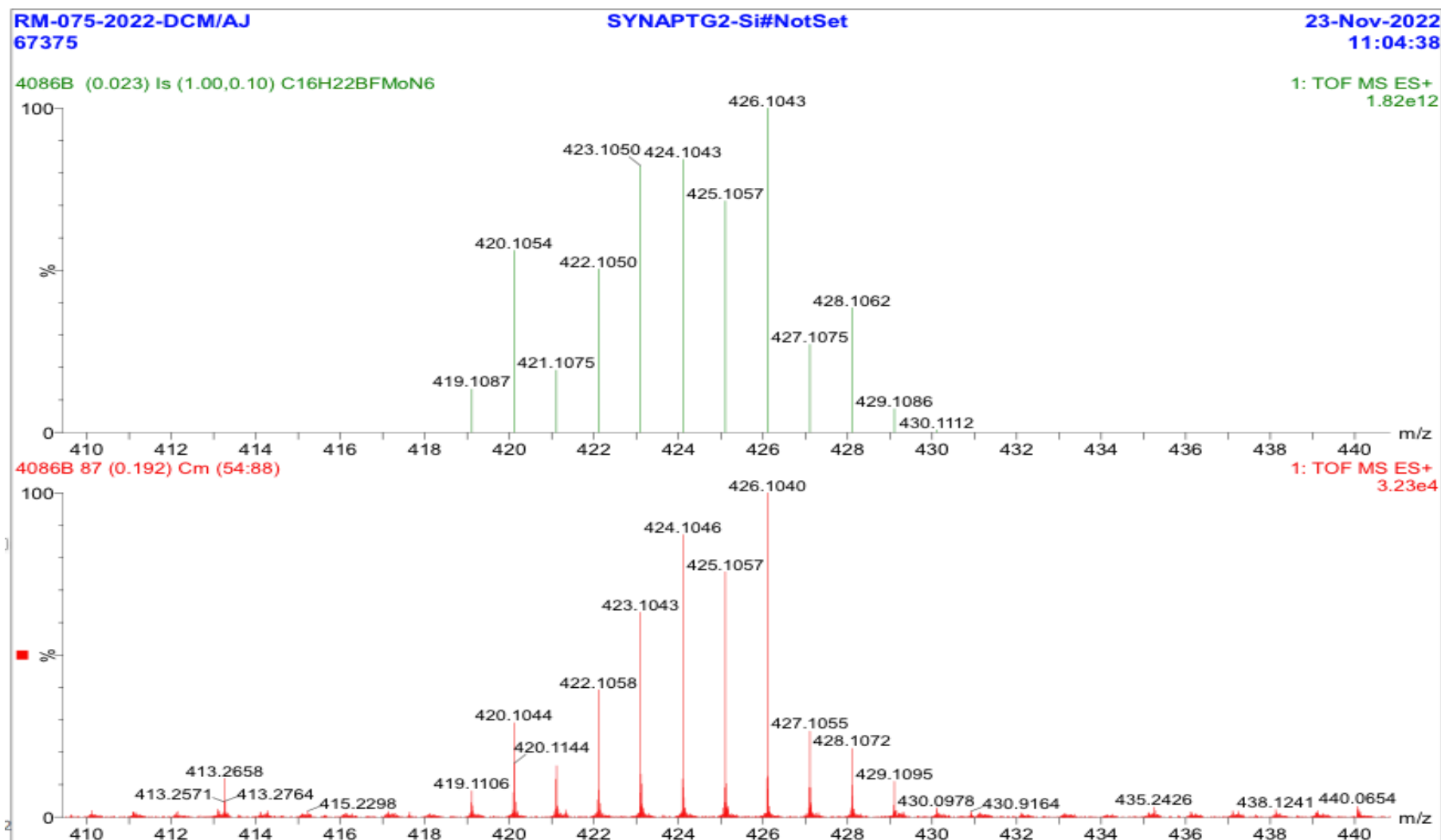


Figure S45. ESI-MS of $[\text{Mo}(\equiv\text{CF})(\text{CO})_2(\text{Tp}^*)]$ (**1a**): $[\text{M}]^+$ with simulation.

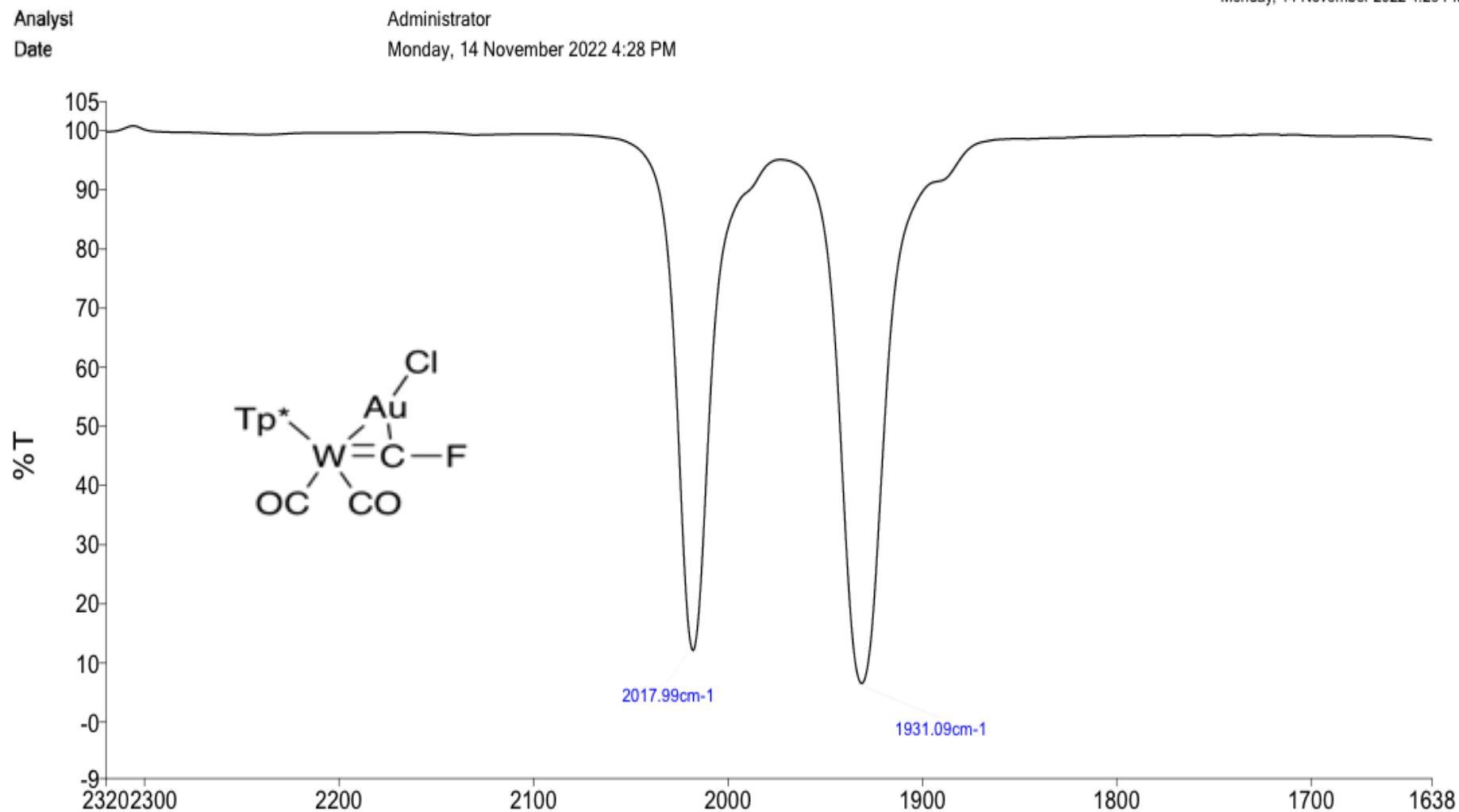


Figure S46. Solution IR spectrum of [WAu(μ-CF)Cl(CO)₂(Tp*)] (**3**) in CH₂Cl₂

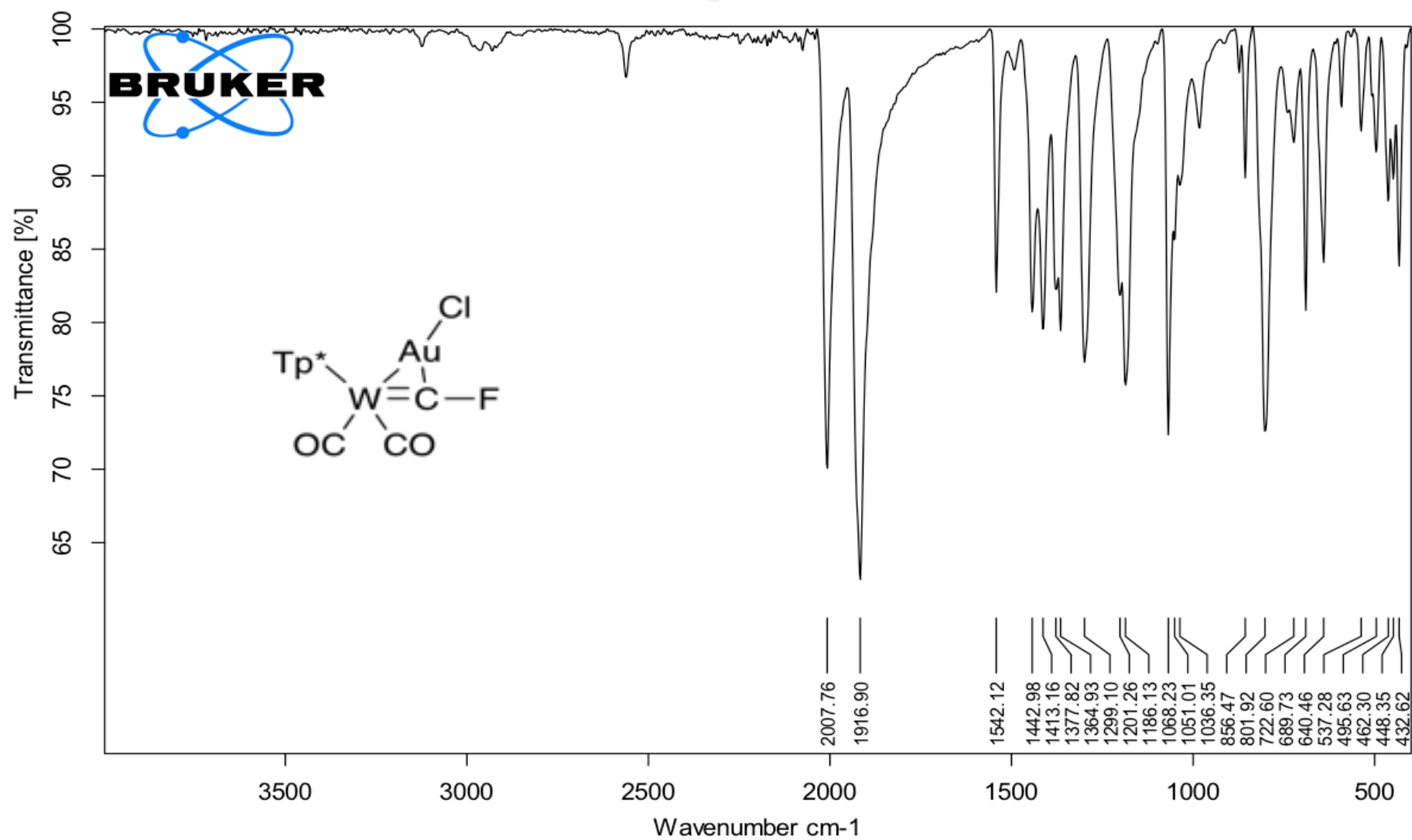


Figure S47. Solid State (ATR) IR spectrum of $[WAu(\mu-CF)Cl(CO)_2(Tp^*)]$ (**3**).

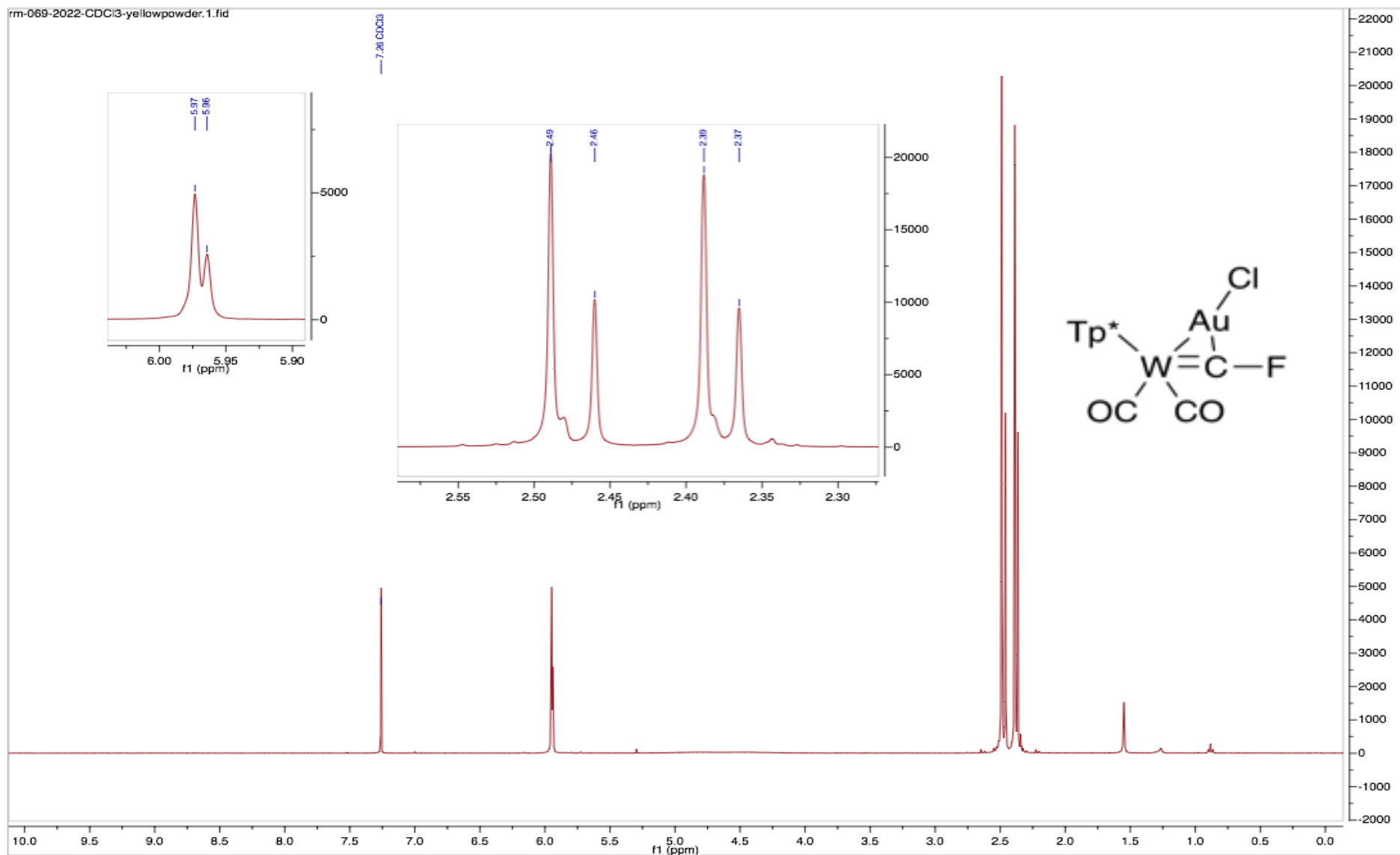


Figure S48. 1H NMR Spectrum of $[WAu(\mu-CF)Cl(CO)_2(Tp^*)]$ (**3**). (400 MHz, $CDCl_3$, 25 °C, δ).

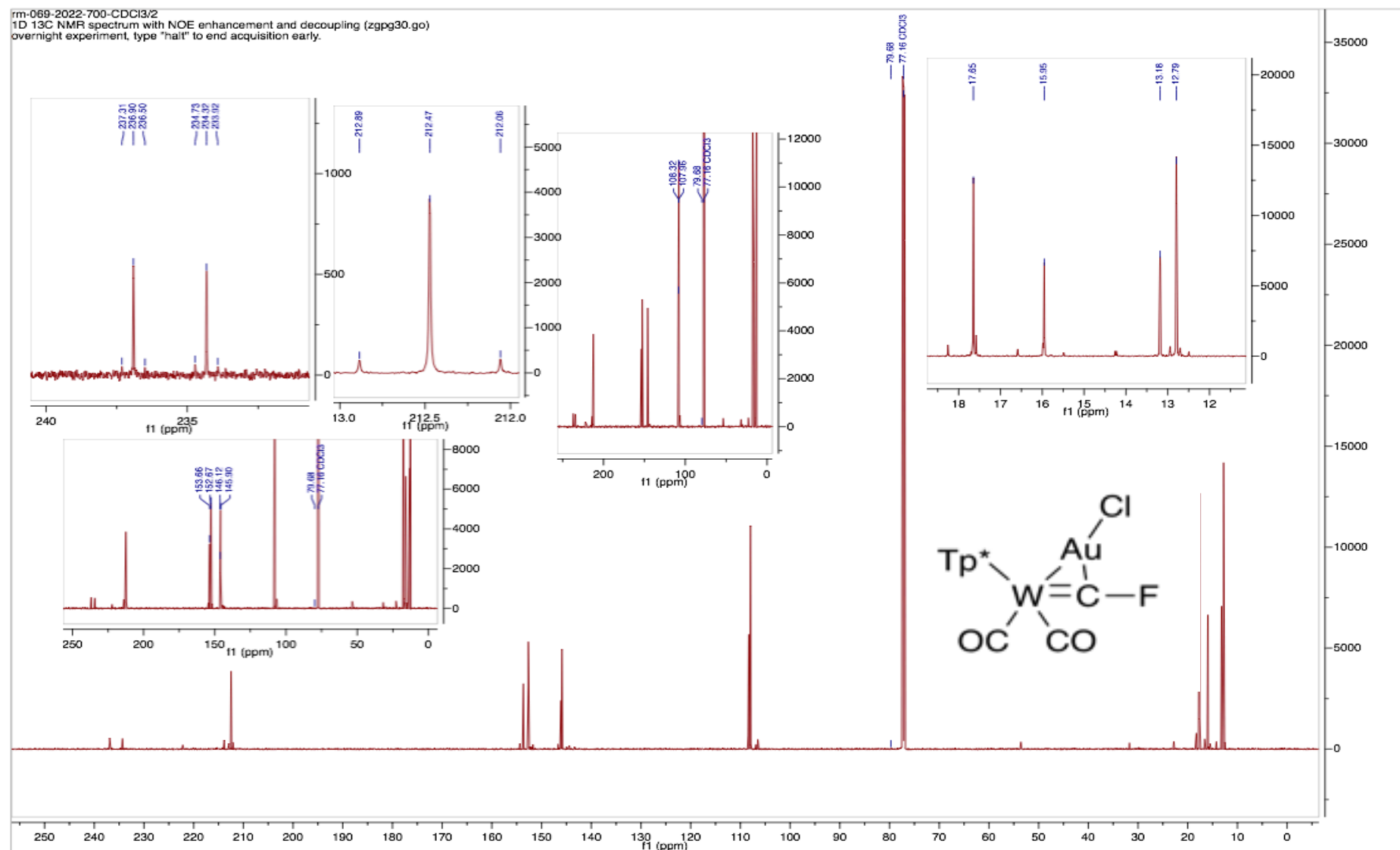


Figure S49. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of $[\text{WAu}(\mu\text{-CF})\text{Cl}(\text{CO})_2(\text{Tp}^*)]$ (**3**). (176 MHz, CDCl_3 , 25 °C, δ).

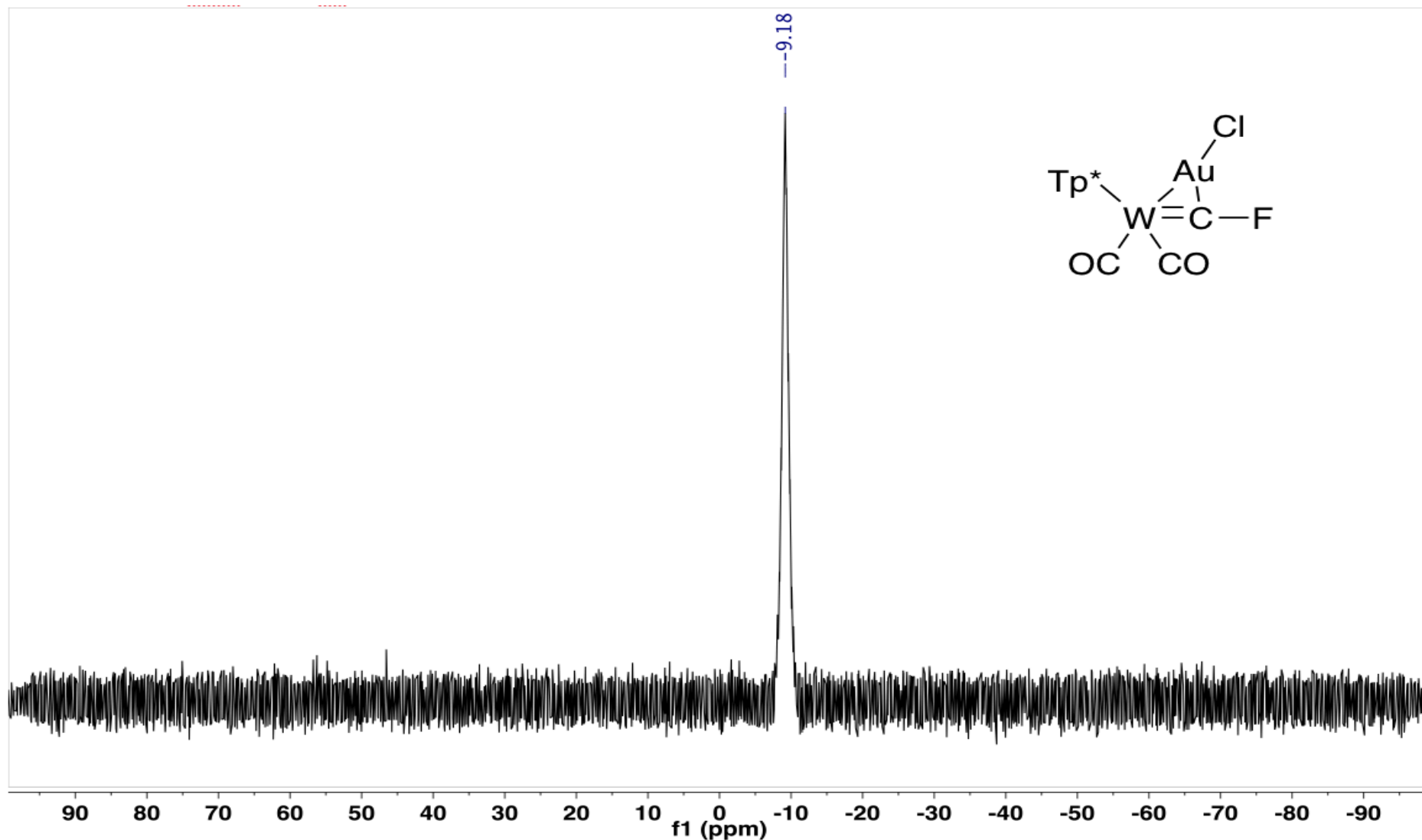


Figure S50. $^{11}\text{B}\{^1\text{H}\}$ NMR of $[\text{W}(\mu\text{-CF})(\text{AuCl})(\text{CO})_2(\text{Tp}^*)]$ (**3**) (128MHz, CDCl_3 , 25 °C, δ):

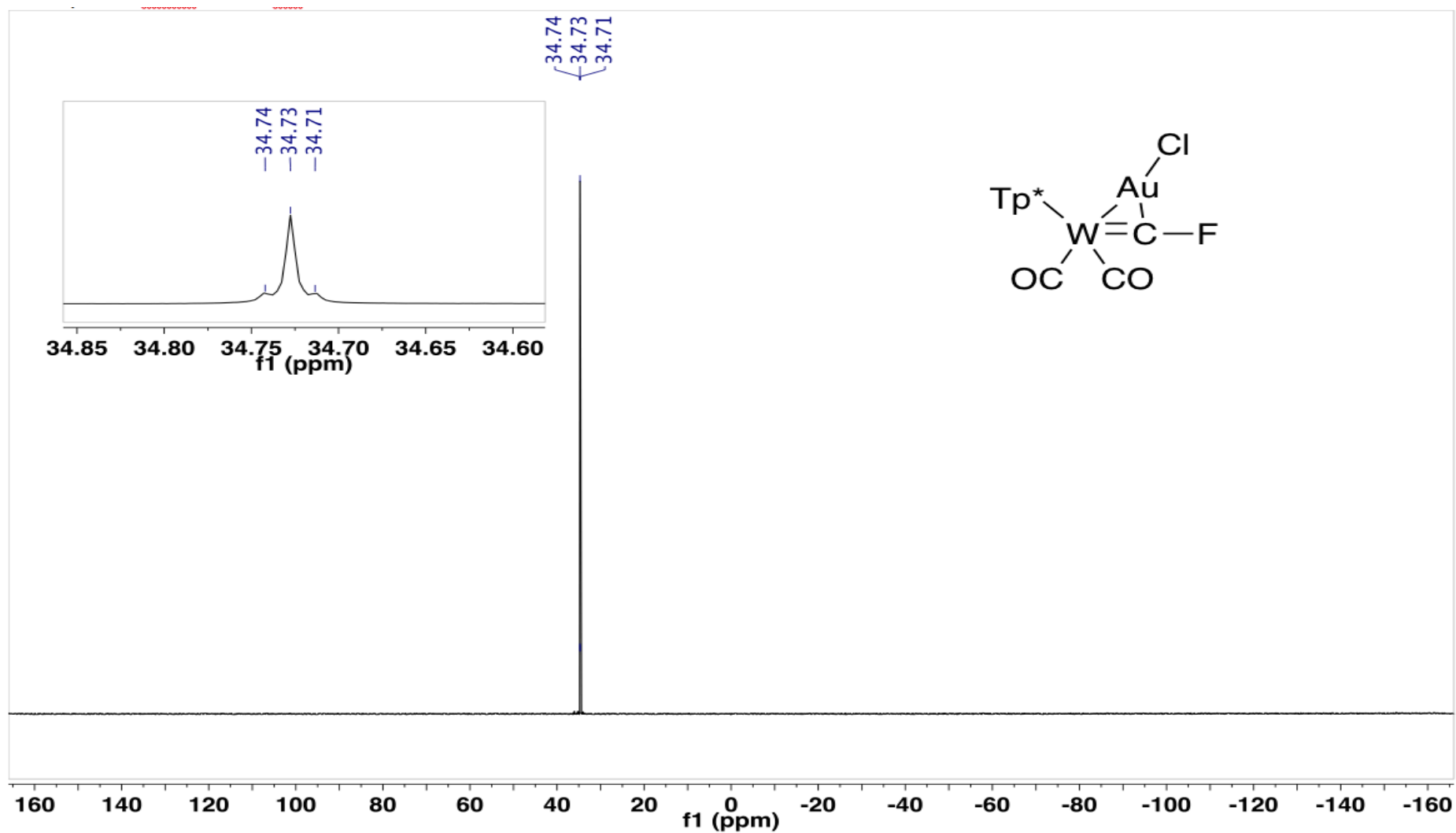


Figure S51. $^{19}\text{F}\{^1\text{H}\}$ NMR of $[\text{W}(\mu\text{-CF})(\text{AuCl})(\text{CO})_2(\text{Tp}^*)]$ (3) (377 MHz, CDCl_3 , 25 °C, δ).

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 3.0 PPM / DBE: min = -1.5, max = 12.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions

2594 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

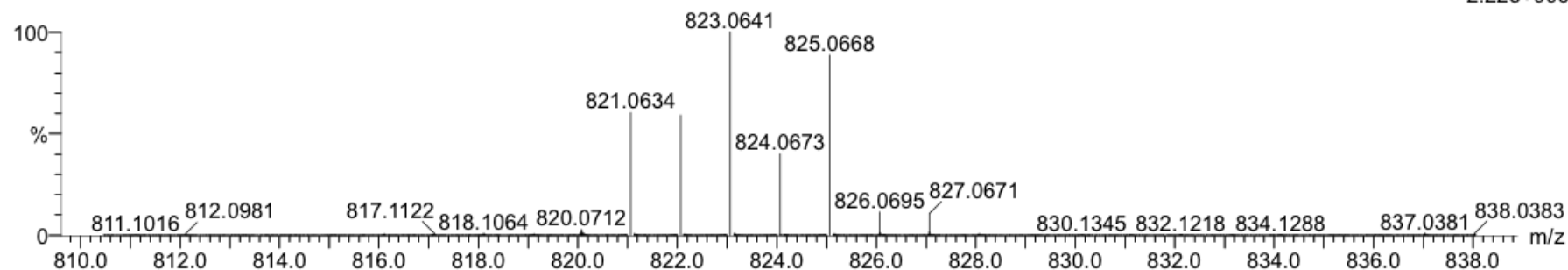
C: 0-20 H: 0-25 11B: 0-1 N: 0-6 O: 0-2 F: 0-1 23Na: 0-1 35Cl: 0-1 37Cl: 0-1 184W: 0-1 197Au: 0-1

rm-069-Ch3CN/AJ
67364
4043 173 (0.361)
1: TOF MS ES+

SYNAPTG2-Si#NotSet

14-Nov-2022
15:31:55

2.22e+006



Minimum: -1.5
Maximum: 5.0 3.0 12.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
823.0641	823.0642	-0.1	-0.1	12.0	3142.4	C18 H22 11B N6 O2 F 23Na 35Cl 184W 197Au

Figure S52. ESI-MS of $[\text{WAu}(\mu\text{-CF})\text{Cl}(\text{CO})_2(\text{Tp}^*)] [\text{M}+\text{Na}]^+$ (**3**)

40

| Chem. Sci., 2023, ESI

This journal is © The Royal Society of Chemistry 2023

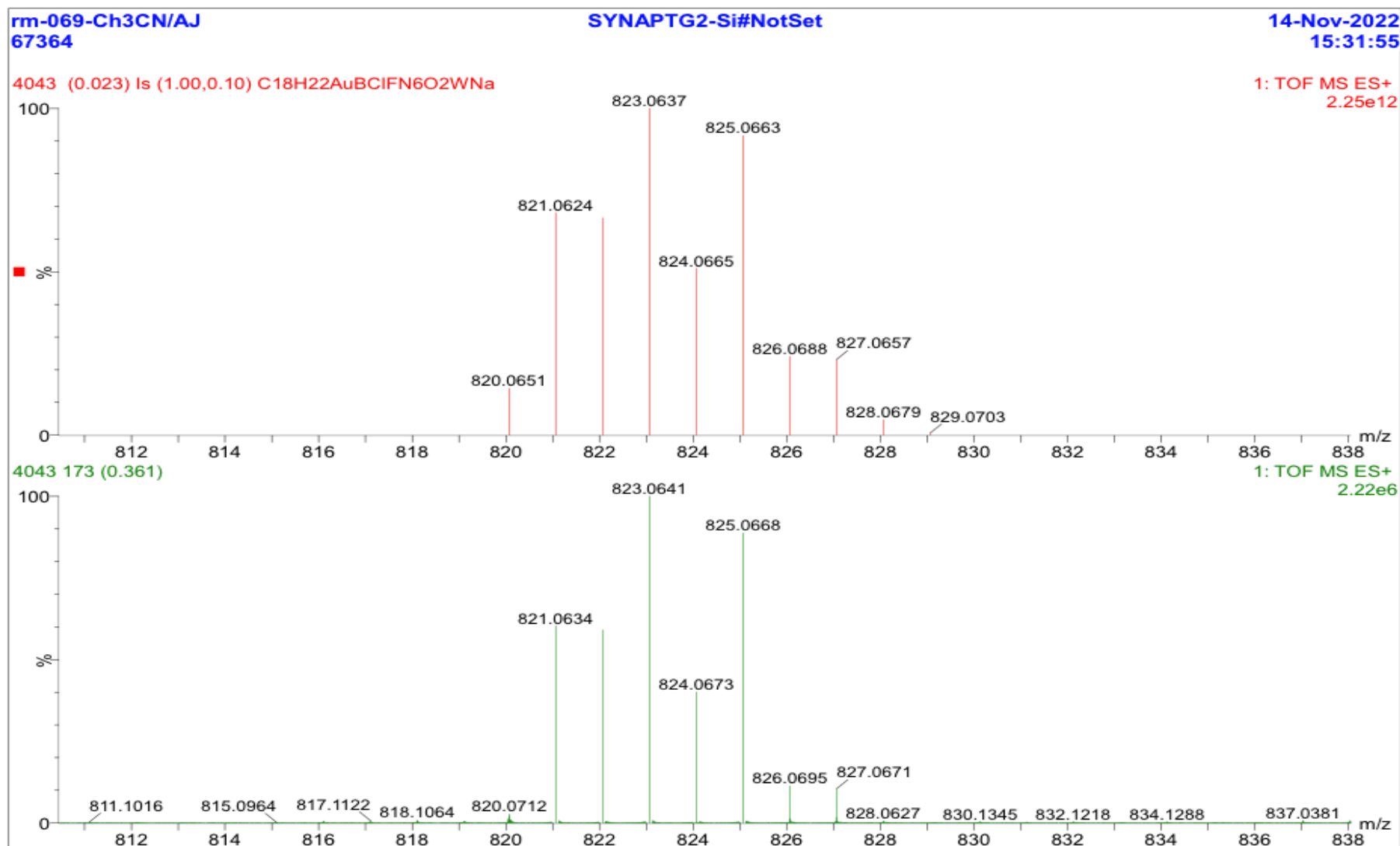


Figure S53. ESI-MS of [WAu(μ -CF)Cl(CO)₂(Tp*)] [M+Na]⁺ (**3**) with simulation

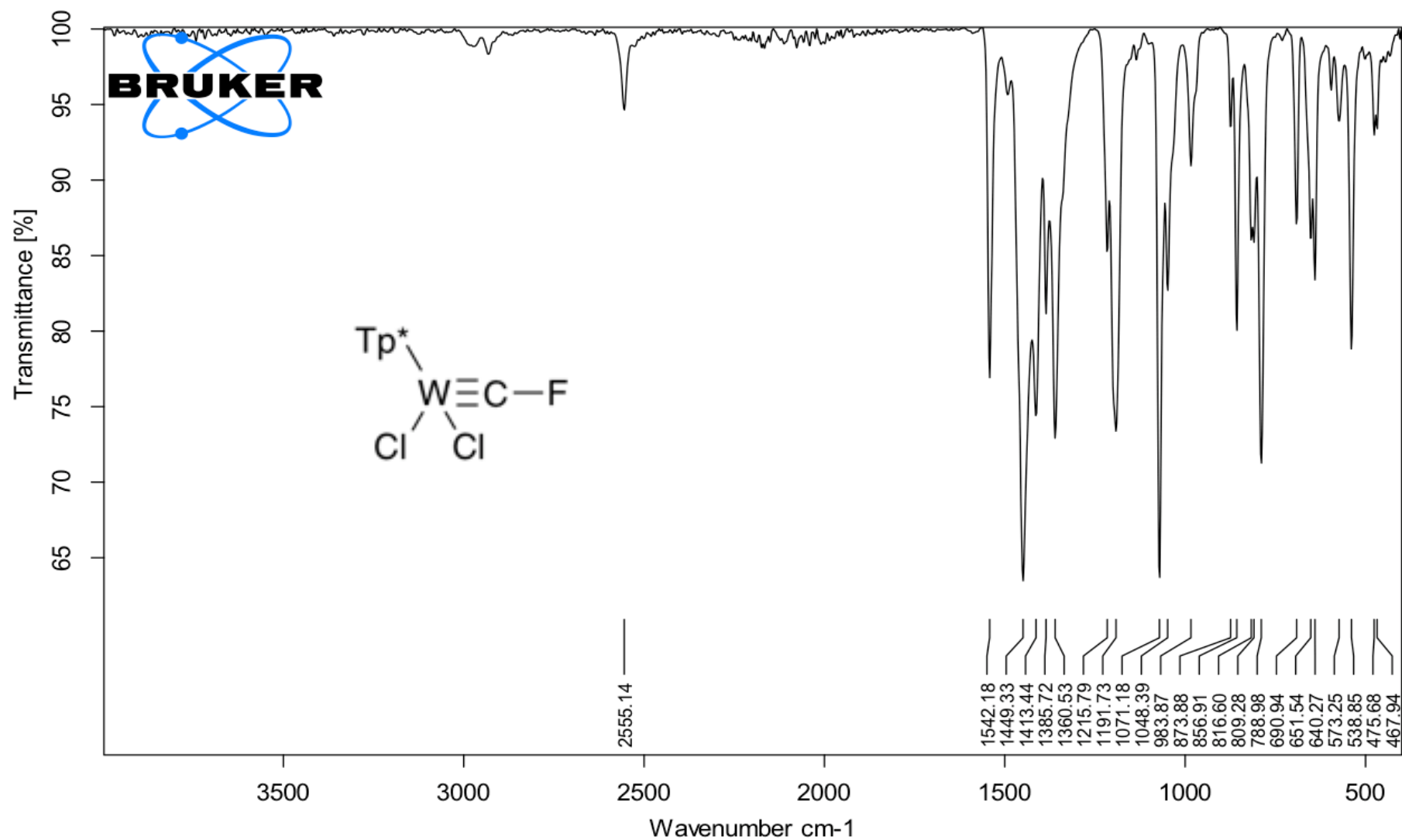


Figure S54. Solid State (ATR) IR spectrum of $\text{W}(\equiv\text{CF})\text{Cl}_2(\text{Tp}^*)$ (4)

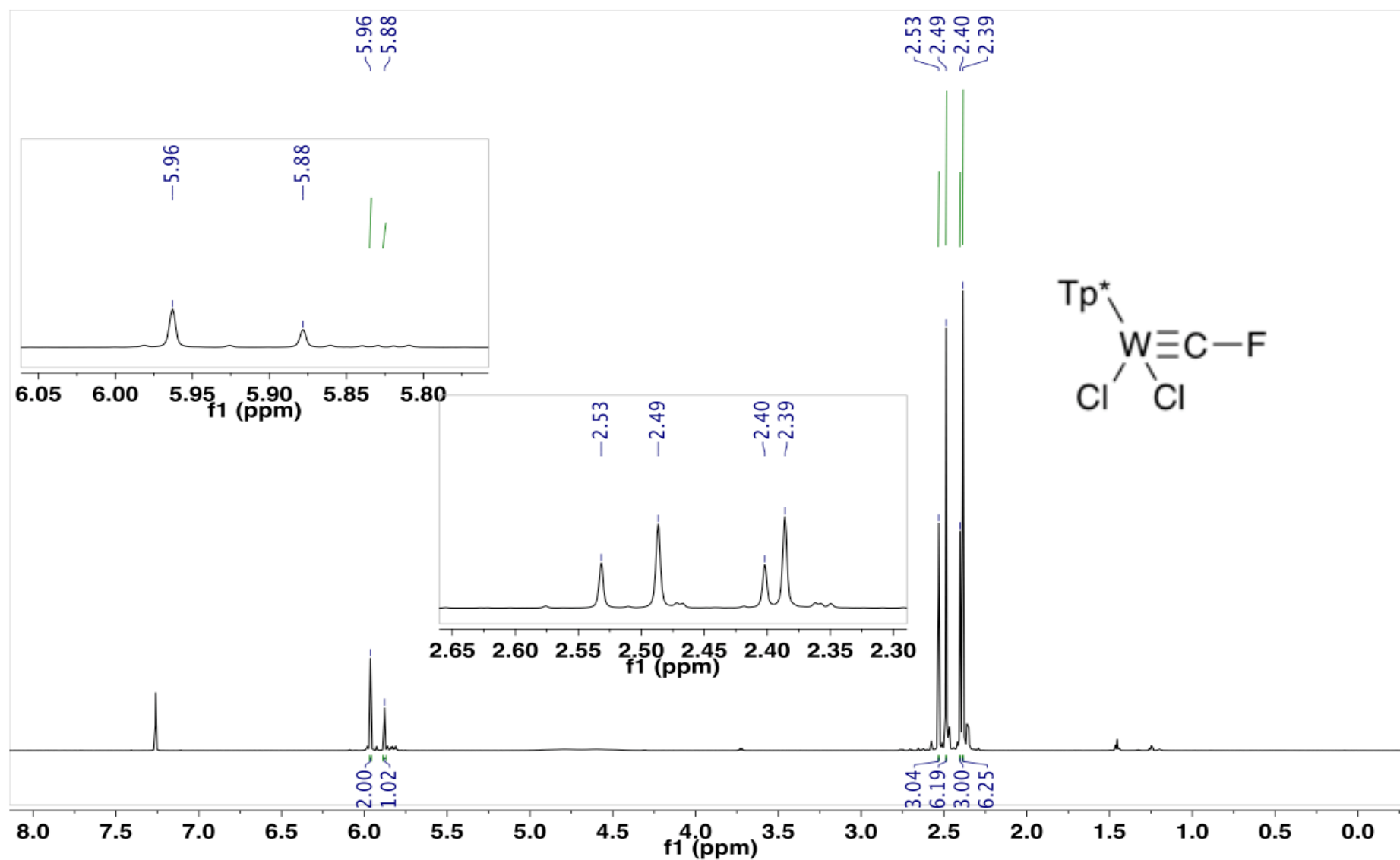


Figure S55. ^1H NMR Spectrum of $\text{W}(\equiv\text{CF})\text{Cl}_2(\text{Tp}^*)$ (4). (700 MHz, CDCl_3 , 25°C , δ):

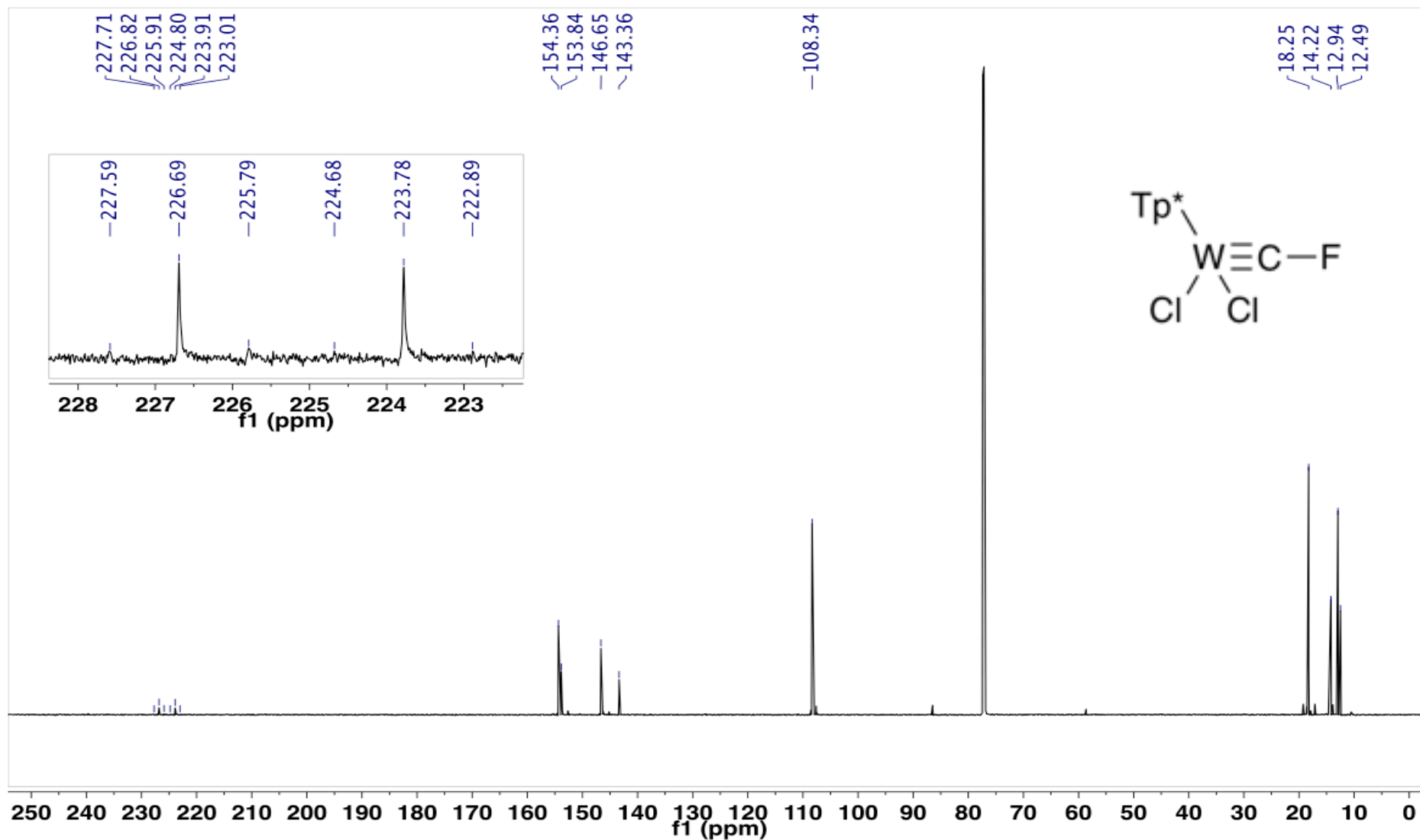


Figure S56. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of $\text{W}(\equiv\text{CF})\text{Cl}_2(\text{Tp}^*)$ (**4**). (176 MHz, CDCl_3 , 25 °C, δ):

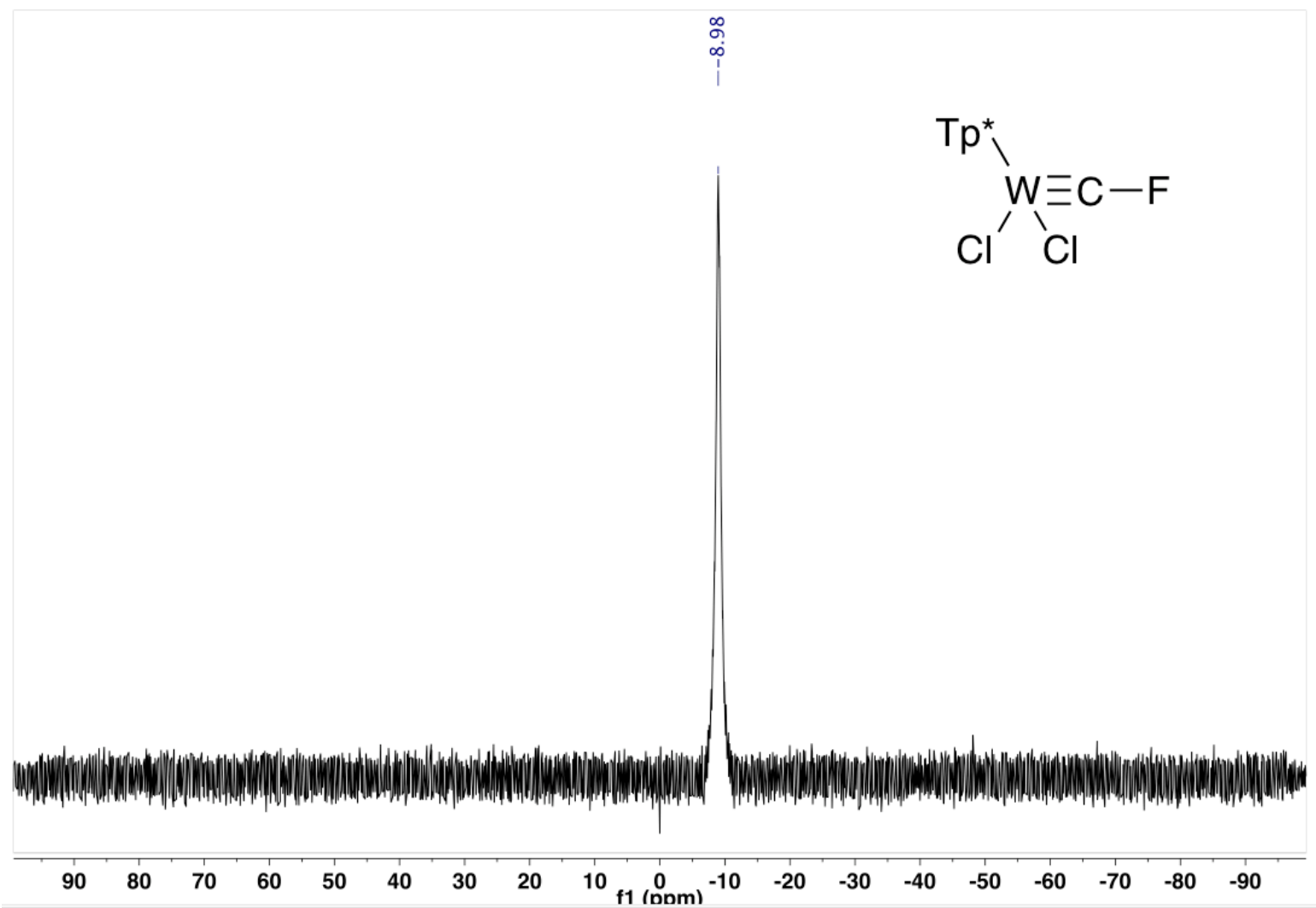


Figure S57. $^{11}\text{B}\{^1\text{H}\}$ NMR Spectrum of $\text{W}(\equiv\text{CF})\text{Cl}_2(\text{Tp}^*)$ (**4**) (128 MHz, CDCl_3 , 25 °C, δ).

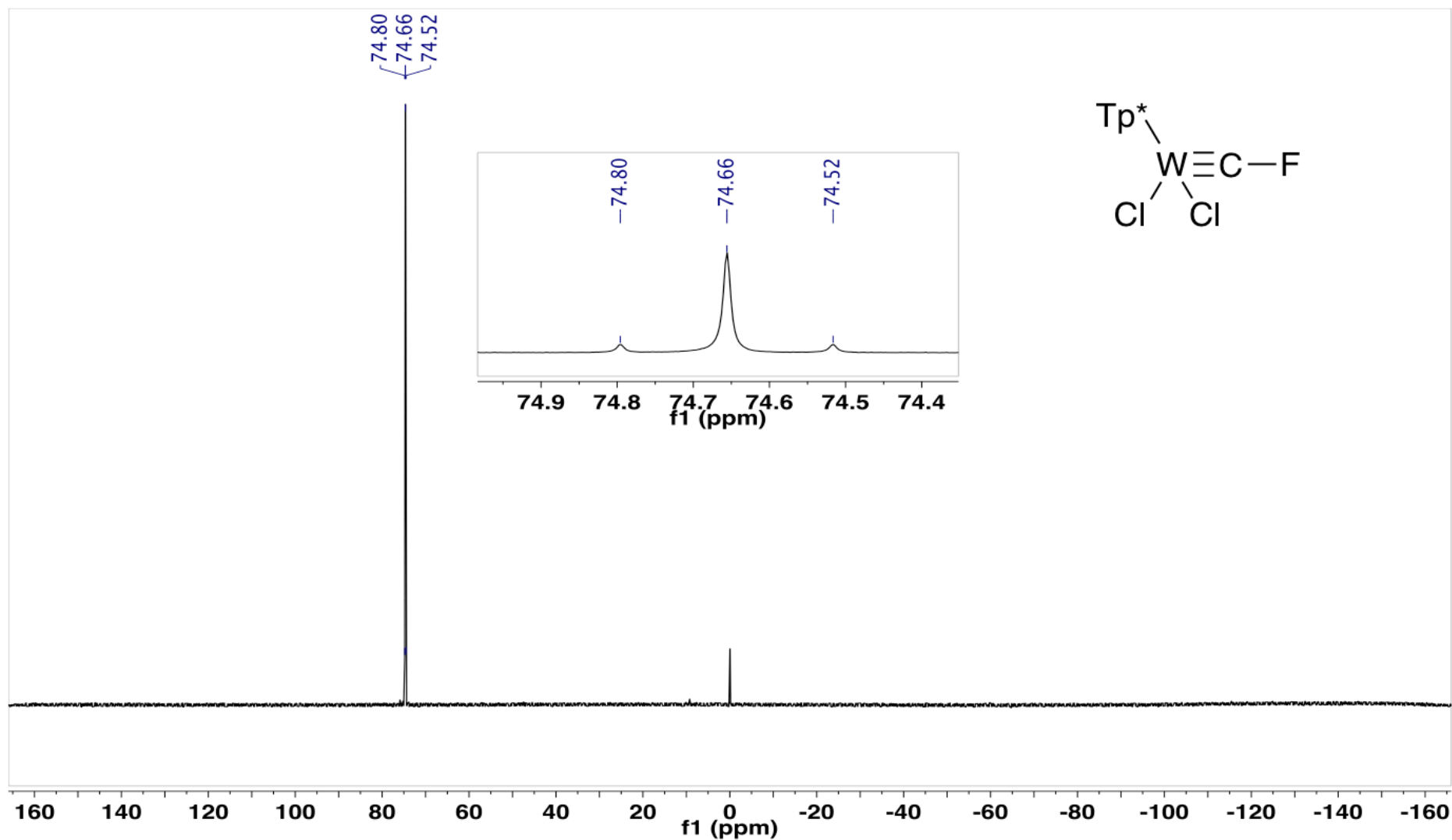


Figure S58. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum of $\text{W}(\equiv\text{CF})\text{Cl}_2(\text{Tp}^*)$ (**4**) (376 MHz, CDCl_3 , 25 °C, δ).

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions

167 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 0-20 H: 0-30 11B: 0-1 N: 0-6 F: 0-1 35Cl: 0-2 184W: 0-1

rm-076-2022

SYNAPTG2-Si#NotSet

29-Nov-2022

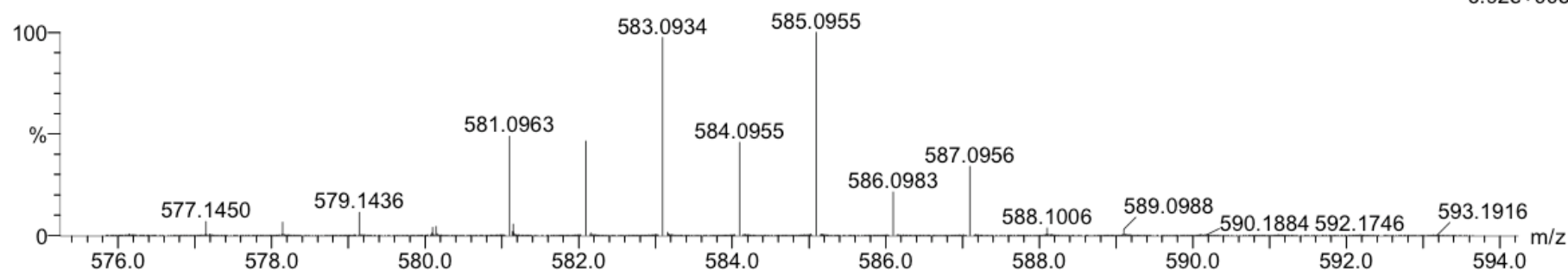
67388

09:52:48

4154 56 (0.128) Cm (45:68)

1: TOF MS ES+

6.92e+005



Minimum: -1.5
 Maximum: 5.0 5.0 100.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
583.0934	583.0948	-1.4	-2.4	9.0	2003.5	C16 H23 11B N6 F 35Cl2 184W

Figure S59. ESI-MS of $W(=CF)Cl_2(Tp^*)$ (**4**)

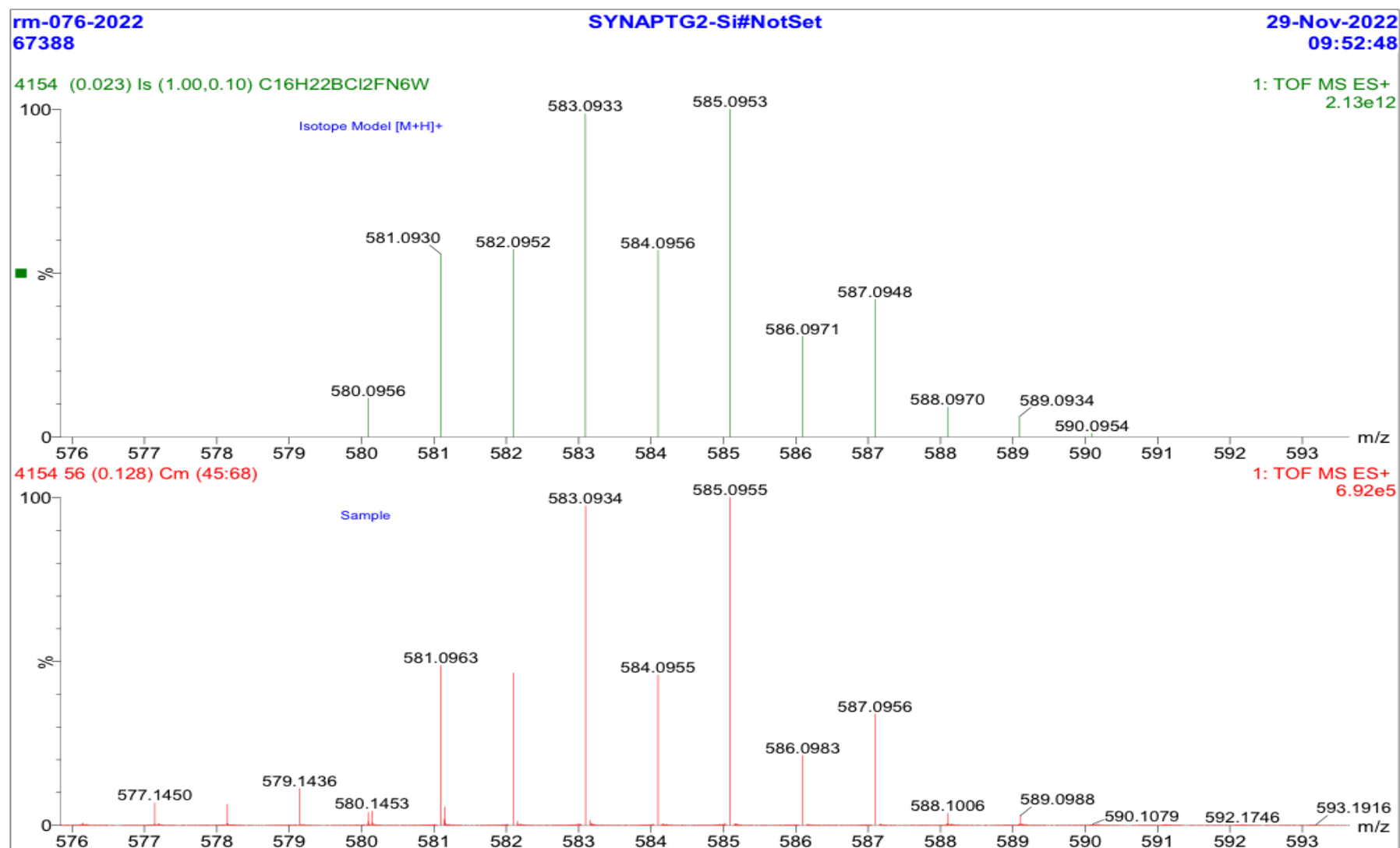


Figure S60. ESI-MS of $W(\equiv CF)Cl_2(Tp^*)$ (**4**) with simulation

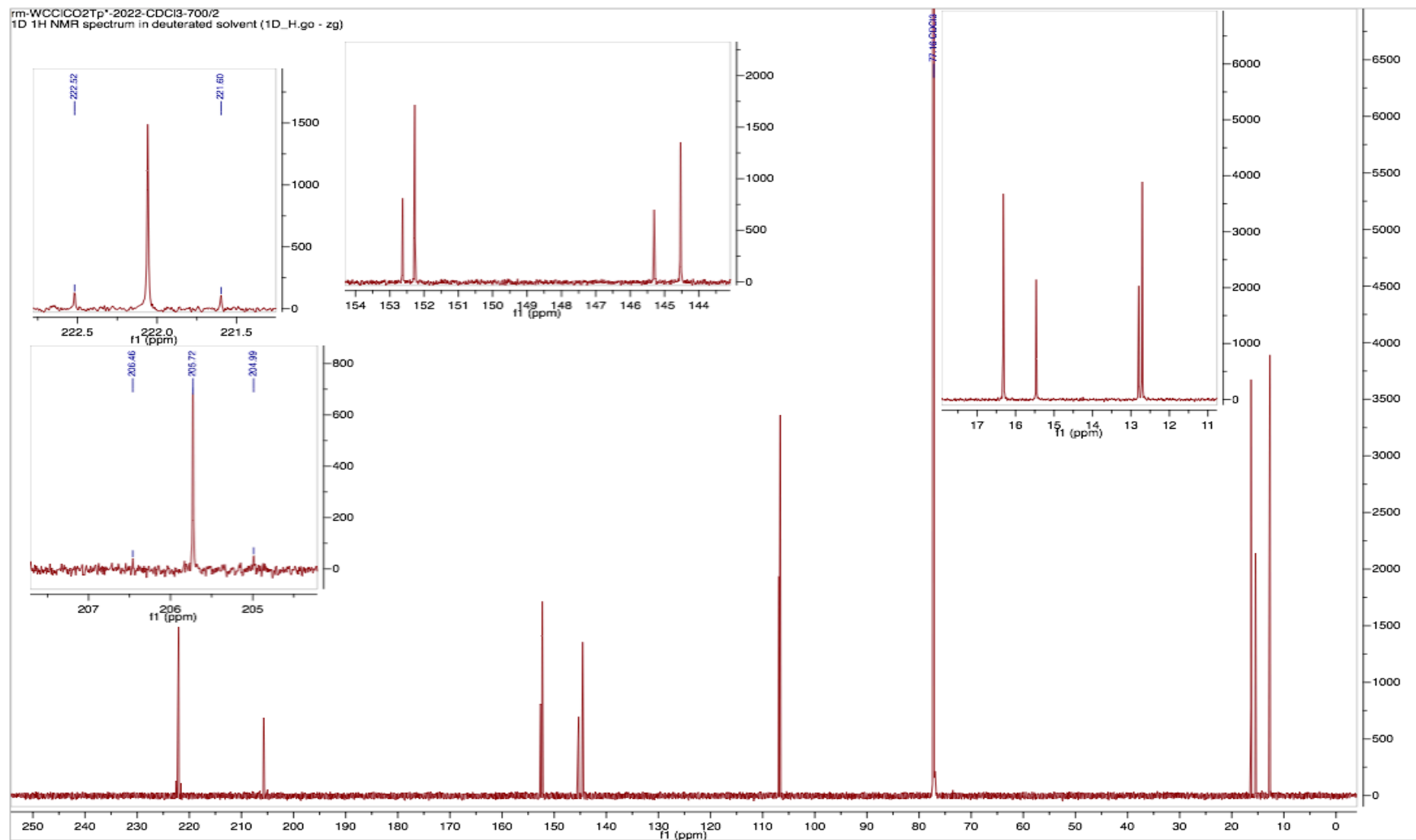


Figure S61. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of $[\text{W}(\equiv\text{CCl})(\text{CO})_2(\text{Tp}^*)]$ (**1b**) (176 MHz, CDCl_3 , 25°C , δ).

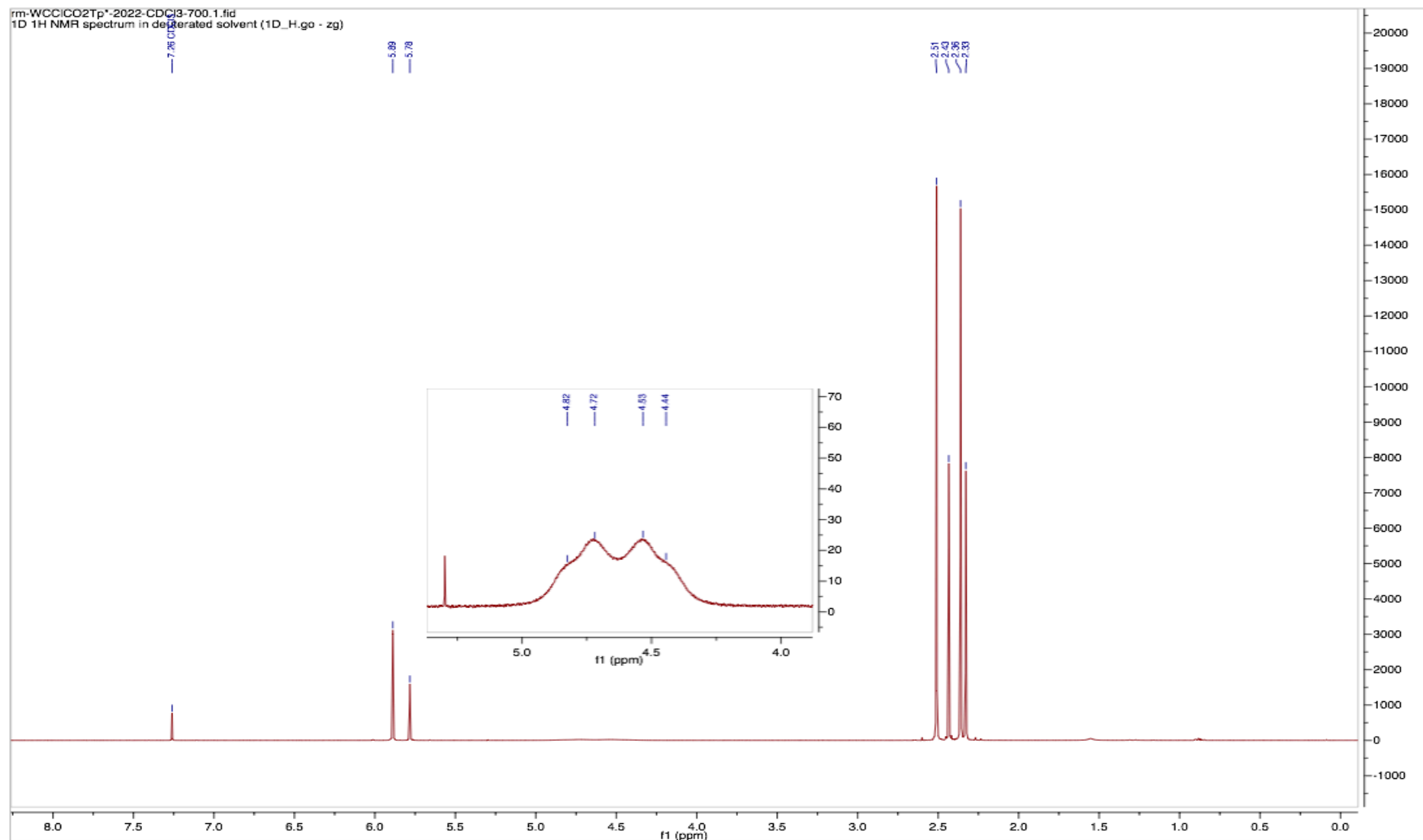


Figure S62. ^1H NMR Spectrum of $[\text{W}(\equiv\text{CCl})(\text{CO})_2(\text{Tp}^*)]$ (**1b**) (700 MHz, CDCl_3 , 25 $^\circ\text{C}$, δ).

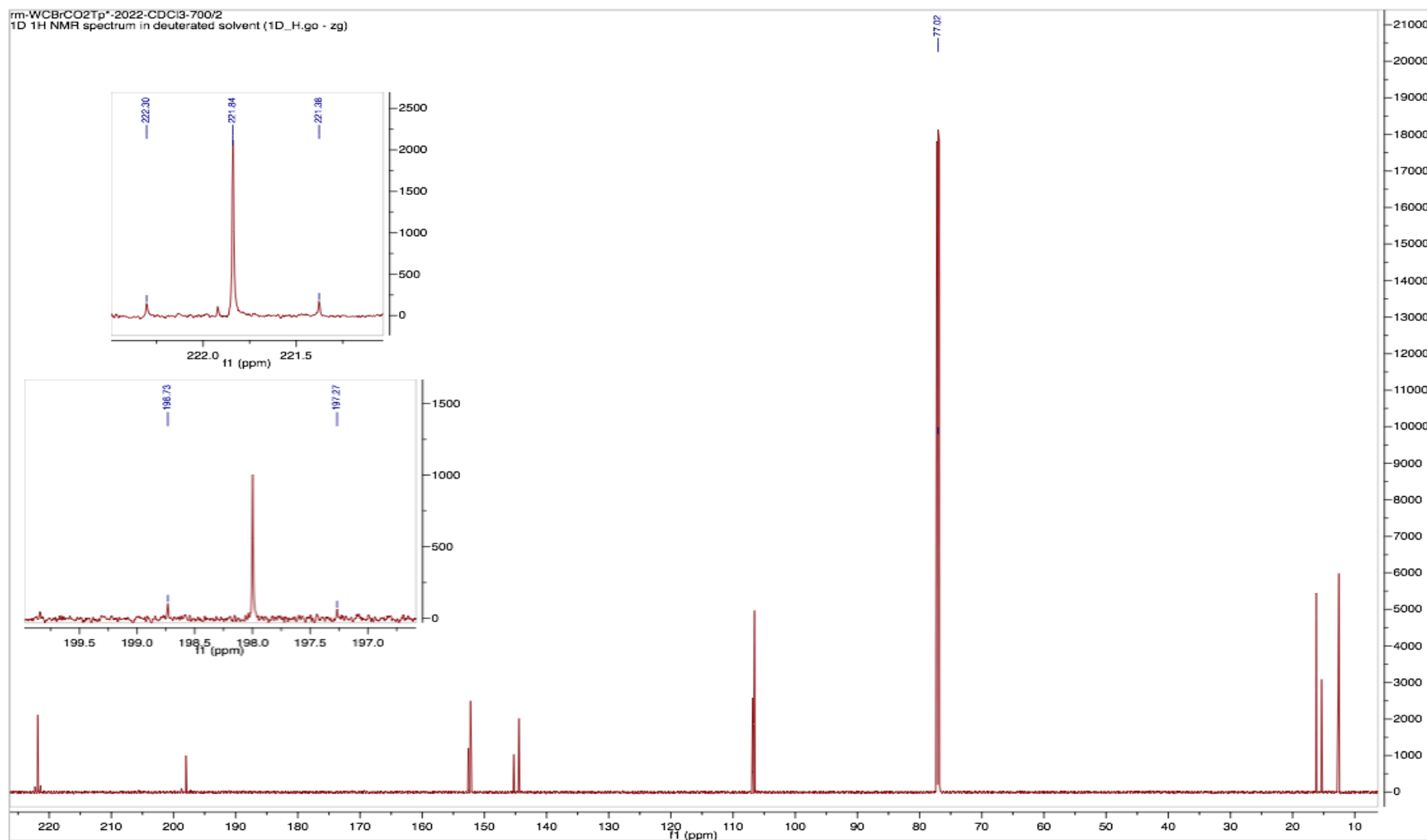


Figure S63. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of $[\text{W}(\equiv\text{CBr})(\text{CO})_2(\text{Tp}^*)]$ (**1c**) (176 MHz, CDCl_3 , 25 °C, δ).

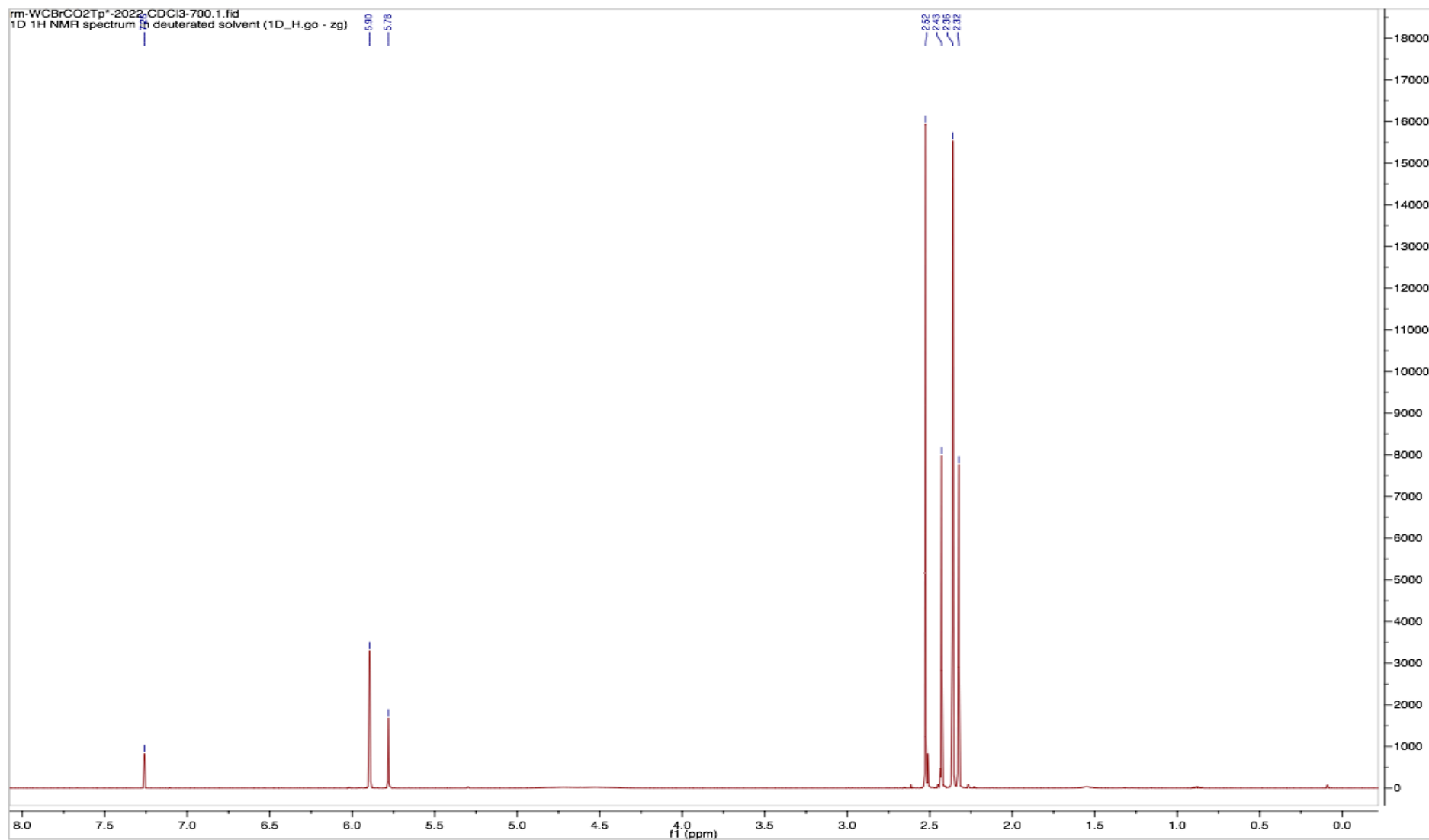


Figure S64. ^1H NMR Spectrum of $[\text{W}(\equiv\text{CBr})(\text{CO})_2(\text{Tp}^*)]$ (**1c**) (700 MHz, CDCl_3 , 25 °C, δ).