ELECTRONIC SUPPORTING INFORMATION

Thiocarbonylphosphorane and Arsorane Ligands

Liam K. Burt, Anthony F. Hill* and Stephanie L. Jones

Received 00th July 2022,
Accepted 00th August 2022

DOI: 10.1039/x0xx00000x

Research School of Chemistry, The Australian National University, Canberra, ACT 0200, Australia. Email: a.hill@anu.edu.au

CDCC 2180154–2180156 contain the supplementary crystallographic data for this paper, and are available free of charge from The Cambridge Crystallographic Data Centre

General Considerations

Experimental work was performed using standard Schlenk techniques using dried and pre-purified nitrogen or in an inert atmosphere glove-box 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 (CH_2Cl_2, MeCN). The compounds [M(≡CBr)(CO)$_2$(Tp*)] (M = Mo, W)[1] [W(≡CPR$_3$)(CO)$_2$(Tp*)]PF$_6$ {R$_3$ = PPh$_3$, PMePh$_2$, PMe$_2$Ph and PCy$_3$}[2] and [W(≡CAsMePh$_2$)(CO)$_2$(Tp*)]OTf[3] were prepared according to published procedures. All other reagents were used as received from commercial suppliers.

NMR spectra were obtained on a Bruker Avance 400 (^{1}H at 400.1, ^{13}C{^{1}H} at 100.6, ^{31}P{^{1}H} at 162.0 MHz) or a Bruker Avance 600 (^{1}H at 600.0, ^{13}C{^{1}H} at 150.9 MHz) or a Bruker Avance 700 (^{1}H at 700.1, ^{13}C{^{1}H} at 176.0 MHz) or a Bruker Avance 800 (^{1}H at 800.1, ^{13}C{^{1}H} at 201.2 MHz) spectrometer 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 {85% H_3PO_4 in H_2O for ^{31}P{^{1}H}}. 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 ^{183}W satellites. In select cases, distinct peaks were observed in the ^{1}H and ^{13}C{^{1}H} NMR spectra, but to the level of accuracy that is reportable (*i.e.*, 2 decimal places for ^{1}H NMR, 1 decimal place for ^{13}C{^{1}H} 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 B*H* protons give rise to very broad signals around 4–5 ppm in the ^{1}H NMR spectra due to coupling to the quadrupolar boron nuclei. These are 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 ^{11}B{^{1}H} NMR spectra were not recorded.

Infrared spectra were obtained using a Shimadzu FTIR-8400 spectrometer (liquid) or Perkin Elmer FTIR Spectrum 2 (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). Electronic spectra were collected at room temperature as a solution in 1 cm quartz cells using a PerkinElmer lambda 465 spectrophotometer. Solvates evident from data were confirmed where possible by NMR spectroscopy. High-resolution electrospray ionisation mass spectrometry (ESI-MS) was performed by the ANU Research School of Chemistry mass spectrometry service with acetonitrile, methanol or dichloromethane as the matrix. 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)

Data for X-ray crystallography were collected with Agilent Xcalibur or SuperNova CCD diffractometers using Mo-Kα radiation (λ = 0.71073 Å) or Cu-Kα radiation (λ = 1.54184 Å) employing the *CrysAlis PRO* software.[4] The structures were solved by direct or Patterson methods and refined by full-matrix least-squares on F^2 using the SHELXS or SHELXT and SHELXL programs.[5] Hydrogen atoms were located geometrically and refined using a riding model. Diagrams were produced using the CCDC visualisation program Mercury.[6]

Computational studies were performed by using the *SPARTAN20* suite of programs.[7] Geometry optimisation (gas Phase or with a polarisation continuum model with dielectric constant of 7.43) was performed at the DFT level of theory using the ωB97X-D or ωB97X-V exchange functional of Head-Gordon[8]. The Los Alamos effective core potential type basis set (LANL2Dζ) of Hay and Wadt[9] was used for W and Te and Pople 6-31G* basis sets[10] were used for all other atoms. Frequency calculations were performed to confirm that the optimized structure was a minimum and also to identify vibrational modes of interest (Table S2).[11] Cartesian atomic coordinates are provided in the electronic supporting information.

Compound Descriptors

a = PPh$_3$, **b** = PMePh$_2$ or AsMePh$_2$, **c** = PMe$_2$Ph, **d** = PCy$_3$.

Electronic data of published phosphoniocarbynes 1a-1d

For comparison with data for thiocarbonylphosphorane and arsorane complexes, the previously unreported electronic spectra of the precursor phosphoniocarbynes were recorded.

[W(≡CPPh$_3$)(CO)$_2$(Tp*)].PF$_6$ (**1a**)—UV-Vis [2.319(2)×10^{-4} molL^{-1}, nm(ε, Lmol^{-1}cm^{-1}), CH_2Cl_2]: λ_{max} = 262 sh (7103), 314 sh (3589), 521 (451).

[W(≡CPMePh$_2$)(CO)$_2$(Tp*)].PF$_6$ (**1b**)—UV-Vis [2.404(2)×10^{-4} molL^{-1}, nm(ε, Lmol^{-1}cm^{-1}), CH_2Cl_2]: λ_{max} =260 sh (6938), 304 (3922), 502 (297).

[W(≡CPMe$_2$Ph)(CO)$_2$(Tp*)].PF$_6$ (**1c**)—UV-Vis [2.475×10^{-4} molL^{-1}, nm(ε, Lmol^{-1}cm^{-1}), CH_2Cl_2]: λ_{max} = 268 sh (6467), 303 sh (3841), 503 (404).

[W(≡CPCy$_3$)(CO)$_2$(Tp*)].PF$_6$ (**1d**)—UV-Vis [2.830×10^{-4} molL^{-1}, nm(ε, Lmol^{-1}cm^{-1}), CH_2Cl_2]: λ_{max} = 264 sh (5776), 303 sh (3128), 496 (378).

Synthesis of [W(SCPPh$_3$)(CO)$_2$(Tp*)]PF$_6$·2(C$_4$H$_8$O) (2a). – A mixture of [W(≡CPPh$_3$)(CO)$_2$(Tp*)]PF$_6$ (**1a**: 202 mg, 0.211 mmol) and elemental sulfur (32 mg, 1.00 mg.atom, 5/8 equiv. S_8) were heated under reflux in THF (10 mL) for 2 hours. The volatiles were removed under reduced pressure and the crude residue was purified by flash chromatography through silica gel, eluting with 2% THF/CH_2Cl_2. The complex crystallised spontaneously upon solvent evaporation and

was collected *via* vacuum filtration, washing with toluene (4 x 10 mL) and *n*-hexane (4 x 10 mL) before drying *in vacuo* for 16 hours. This gave a THF bis-solvate (confirmed by NMR integration) of the title compound as a blue crystalline powder. Yield: 162 mg (0.144 mmol, 68%). Crystals of a toluene solvate suitable for single crystal X-ray diffractometry were grown by solvent diffusion of a CH_2Cl_2 solution of title compound layered with toluene, stored at 5 °C. IR (CH_2Cl_2, cm^{-1}): 2006 vs ν_{CO}, 1919 vs ν_{CO}. IR (ATR, cm^{-1}): 2574 w ν_{BH}, 1992 vs ν_{CO}, 1908 vs ν_{CO}, 839 vs ν_{PF}. UV-Vis [2.420(2)×10^{-5} $molL^{-1}$, nm(ε, $Lmol^{-1}cm^{-1}$), CH_2Cl_2]: λ_{max} = 269 (21820), 562 sh (15760), 627 (2222). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ_H = 7.89 (m, C_6H_5), 7.76 (m, C_6H_5), 5.99 (s, 3 H pzCH), 3.68 (m, 8 H, THF), 2.45 (s, 6 H, $pzCH_3$), 2.36 (s, 3 H, $pzCH_3$), 2.30 (s, 3 H, $pzCH_3$), 2.20 (s, 6 H, $pzCH_3$), 1.82 (m, 8 H, THF). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 25 °C): δ_C = 223.4 (d, $^3J_{CP}$ = 7 Hz, $^1J_{CW}$ = 145 Hz, CO), 220.7 (d, $^1J_{CP}$ = 54 Hz, $^1J_{CW}$ = 46 Hz, SCP], 153.9, 152.8, [C^5(pz)], 147.4, 146.5 [C^3(pz)], 136.3 [d, $^4J_{CP}$ = 3 Hz, $C^4(C_6H_5)$], 134.8 [d, $^2J_{CP}$ = 11 Hz, $C^{2,6}(C_6H_5)$], 131.0 [d, $^3J_{CP}$ = 13 Hz, $C^{3,5}(C_6H_5)$], 119.2 [d, $^1J_{CP}$ = 91 Hz, $C^1(C_6H_5)$], 109.3, 108.3 [C^4(pz)], 68.3 [THF], 26.2 [THF], 16.4, 14.7, 13.5, 12.9 ($pzCH_3$). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ_P = 26.84 (s, $^2J_{PW}$ = 91 Hz), –144.9 [hept, $^1J_{PF}$ = 706 Hz, PF_6]. MS (ESI, +ve ion, *m/z*): Found: 843.2034. Calcd for $C_{36}H_{37}{}^{11}BN_6O_2P^{32}S^{184}W$ $[M]^+$: 843.20332. Satisfactory analytical data were not obtained, possibly due to desolvation or air-sensitivity during shipping. Anal. Found: C, 41.66; H, 3.83; N, 7.43%.Calcd for $C_{36}H_{37}BF_6N_6O_2P_2SW$: C, 43.75; H, 3.77; N, 8.50. *Crystal data for* $C_{36}H_{37}BN_6O_2PSW{\cdot}PF_6{\cdot}C_7H_8$, M_w = 1080.46 $gmol^{-1}$, monoclinic, *I2/a*, *a* = 25.2847(5) Å, *b* = 13.3933(3) Å, *c* = 28.4487(5) Å, β = 92.090(2)°, *V* = 9627.6(3) $Å^3$, *Z* = 8, D_{calc} = 1.491 Mgm^{-3}, μ(Cu *K*α) = 6.03 mm^{-1}, *T* = 150.0(1) K, clear dark blue plate, 0.30 × 0.10 × 0.07 mm, 8711 independent measured reflections ($2\theta_{max}$ = 146.6°), R_1 = 0.064, wR_2 = 0.173 for 7942 reflections [$I > 2\sigma(I)$], 596 parameters, without restraints. CDCC 2180154.

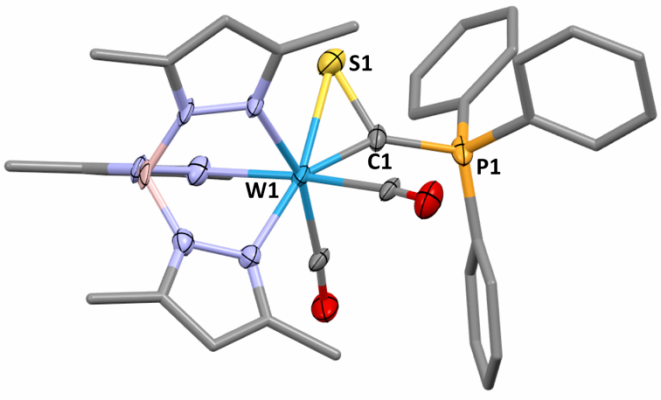


Figure S1: Molecular structure of the cation of **2b** in a crystal of **2b**.C_7H_8 (50% displacement ellipsoids, pyrazolyl and phenyl rings simplified. Solvent, hydrogens and PF_6 anion omitted).

Synthesis of [W(SCPMePh$_2$)(CO)$_2$(Tp*)]PF$_6$ (2b). A sample of [W(≡CPMePh$_2$)(CO)$_2$(Tp*)]PF_6 (**1b**: 0.101 g, 0.113 mmol) and elemental sulfur (18 mg, 0.56 mg.atom) were heated under reflux in THF (10 mL) for 6 hours. The initially pink solution darkened quickly to a deep blue colour, with this transformation clearly visible 2 hours into the reaction. The reaction mixture was cooled and solvent was removed under reduced pressure before being dissolved in CH_2Cl_2 (~2 mL) and diluted with Et_2O (20 mL) to afford a dark blue precipitate in addition to a pale pink supernatant. The deep blue solid was collected *via* vacuum filtration, washing with Et_2O (2 × 10 mL) and *n*-pentane (3 x 10 mL) before drying in vacuo for 16 hours. The title compound was obtained as a blue crystalline powder that resists dissolution in $CHCl_3$, Et_2O and hydrocarbons but is soluble in CH_2Cl_2, MeCN, THF or DMSO. Yield: 0.080 g (0.086 mmol, 76%). Crystals suitable for single crystal x-ray diffraction were grown from the liquid-liquid diffusion of Et_2O layered on a MeCN solution of the compound at –20 °C under an argon atmosphere over a week. IR (CH_2Cl_2, cm^{-1}): 1998 vs ν_{CO}, 1914 vs ν_{CO}. IR (ATR, cm^{-1}): 2563 w ν_{BH}, 1998 vs ν_{CO}, 1902 vs ν_{CO}, 836 vs ν_{PF}. UV-Vis [2.610(3)×10^{-5} $molL^{-1}$, nm (ε, $Lmol^{-1}cm^{-1}$), CH_2Cl_2]: λ_{max} = 266 sh (19520), 569 (1517), 622 (1520). ^{1}H NMR (700 MHz, CD_2Cl_2, 25 °C): δ_H = 7.89 (m, 6 H, C_6H_5), 7.73 (m, 4 H, C_6H_5), 6.02 (s, 1 H, pzCH), 5.95 (s, 2 H, pzCH), 2.85 (d, $^2J_{HP}$ = 13 Hz, 3 H, PCH_3), 2.44 (overlapping s, 3 H, $pzCH_3$], 2.43 (overlapping s, 6 H, $pzCH_3$), 2.37 (s, 3 H, $pzCH_3$), 1.96 (s, 6 H, $pzCH_3$). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 25°C): δ_C = 223.4 (d, $^3J_{CP}$ = 7 Hz, $^1J_{CW}$ = 145 Hz, CO), 219.0 (d, $^1J_{CP}$ = 56 Hz, $^1J_{CW}$ not resolved, SCP), 153.9, 152.7 [C^5(pz)], 147.3 146.3 [C^3(pz)], 135.9 [d, $^4J_{CP}$ = 4 Hz, $C^4(C_6H_5)$], 133.1 [d, $^2J_{CP}$ = 10 Hz, $C^{2,6}(C_6H_5)$], 130.8 [d, $^3J_{CP}$ = 13 Hz, $C^{3,5}(C_6H_5)$], 119.6 [d, $^1J_{CP}$ = 90 Hz, $C^1(C_6H_5)$], 109.1, 108.2 [C^4(pz)], 16.4, 14.0, 13.4, 12.7 ($pzCH_3$), 9.9 (d, $^1J_{CP}$ = 59 Hz, PCH_3). ^{31}P{^{1}H} NMR (283 MHz, CD_2Cl_2, 25°C): δ_P = 26.39 (s, $^2J_{PW}$ = 21 Hz, PCH_3), –144.5 (hept, $^1J_{PF}$ = 706 Hz, PF_6). MS (ESI, +ve ion, *m/z*): Found: 781.1900. Calcd for $C_{31}H_{35}{}^{11}BN_6O_2PS^{184}W$ $[M]^+$: 781.1882. Anal. Found: C, 40.20; H, 3.77; N, 9.07%. Calcd for $C_{31}H_{35}BF_6N_6O_2P_2SW$: C, 40.20; H, 3.81; N, 9.07%. *Crystal data for* $C_{31}H_{35}BN_6O_2PSW{\cdot}PF_6{\cdot}2(C_2H_3N)$, M_w = 1008.42 $gmol^{-1}$, monoclinic, $P2_1/c$, *a* = 14.1710(2) Å, *b* = 13.2958(1) Å, *c* = 22.8330(3) Å, β = 103.452(1)°, *V* = 4184.05(9) $Å^3$, *Z* = 4, D_{calc} = 1.601 Mgm^{-3}, μ(Cu *K*α) = 6.91 mm^{-1}, *T* = 150.0(1) K, clear dark blue plate, 0.14 × 0.09 × 0.03 mm, 7935 independent measured reflections ($2\theta_{max}$ = 147.2°), R_1 = 0.027, wR_2 = 0.065 for 7020 reflections [$I > 2\sigma(I)$], 514 parameters without restraints. CDCC 2180155.

Synthesis of [W(SCPMe$_2$Ph)(CO)$_2$(Tp*)]PF$_6$ (2c). A sample of [W(≡CPMe$_2$Ph)(CO)$_2$(Tp*)].PF_6 (**1c**: 0.099 g, 0.119 mmol) and elemental sulfur (0.038 g, 1.2 mg.atom) were heated under reflux in THF (10 mL) over 6 hours. The initially peach-coloured solution darkened quickly to a deep blue colour by 1 hour and transitioned to the final indigo colour by 2 hours. The reaction mixture was cooled and solvent removed under reduced pressure before dissolving in minimal CH_2Cl_2 (~2 mL). Et_2O (20 mL) was added to precipitate an indigo coloured solid and a pale orange supernatant phase. The precipitate was isolated by vacuum filtration and subsequently washed with Et_2O (3 × 10 mL) and *n*-pentane (3 × 5 mL) before drying *in vacuo* for 16 hours. The title compound was obtained as an indigo crystalline powder that resists dissolution in $CHCl_3$, Et_2O and hydrocarbons but is soluble in CH_2Cl_2, MeCN, THF or DMSO. Yield: 0.090 g (0.104 mmol, 87%). IR (CH_2Cl_2, cm^{-1}): 1999 vs ν_{CO}, 1912 vs ν_{CO}. IR (ATR, cm^{-1}): 2557 w ν_{BH}, 2001 vs ν_{CO}, 1884 vs ν_{CO}, 836 vs ν_{PF}. UV-Vis [2.498(3)×10^{-5} $molL^{-1}$, nm (ε, $Lmol^{-1}cm^{-1}$), CH_2Cl_2]: λ_{max} = 267 (18520), 552 (1531), 627 (1324). ^{1}H NMR (600 MHz, CD_2Cl_2, 25 °C): δ_H 7.95 (dd, J_{HH} = 13, 8 Hz, 2 H, C_6H_5), 7.85 (t, J_{HH} = 8 Hz, 1 H, C_6H_5), 7.74 (m, 2 H, C_6H_5), 6.01 (s, 1 H, pzCH), 5.93 (s, 2 H, pzCH), 2.55 (d, $^2J_{HP}$ =

13 Hz, 6 H, PCH_3), 2.45 (s, 3 H, $pzCH_3$), 2.42 (s, 6 H, $pzCH_3$), 2.37 (s, 3 H, $pzCH_3$), 1.94 (s, 6 H, $pzCH_3$). $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 25°C): δ_C = 223.5 (d, $^3J_{CP}$ = 6 Hz, $^1J_{CW}$ = 144 Hz, CO), 222.3 (d, $^1J_{CP}$ = 56 Hz, $^1J_{CP}$ = 55 Hz, SCP), 154.0, 153.0 [C^5(pz)], 147.4, 146.3 [C^3(pz)], 136.0 [d, $^4J_{CP}$ = 3 Hz, $C^4(C_6H_5)$], 131.9 [d, $^2J_{CP}$ = 10 Hz, $C^{2,6}(C_6H_5)$], 130.8 [d, $^3J_{CP}$ = 13 Hz, $C^{3,5}(C_6H_5)$], 119.5 [d, $^1J_{CP}$ = 88 Hz, $C^1(C_6H_5)$], 109.1, 108.3 [C^4(pz)], 16.6, 14.2, 13.6, 12.8 ($pzCH_3$), 9.3 (d, $^1J_{CP}$ = 59 Hz, PCH_3). $^{31}P\{^1H\}$ NMR (162 MHz, CD_3CN, 25°C): δ_P = 30.40 (s, $^2J_{PW}$ = 20 Hz, PCH_3), –144.6 [hept, $^1J_{PF}$ = 706 Hz, PF_6]. MS (ESI, +ve ion, *m/z*): Found: 719.1733. Calcd for $C_{26}H_{33}{}^{11}BN_6O_2PS^{184}W$ $[M]^+$: 719.1726. Anal. Found: C, 36.08; H, 3.83; N, 9.74; S, 3.99%. Calcd for $C_{26}H_{33}BF_6N_6O_2P_2SW$: C, 36.13; H, 3.85; N, 9.72; S, 3.71% Single crystals suitable for x-ray diffraction were not successfully acquired.

Synthesis of [W(SCPCy$_3$)(CO)$_2$(Tp*)]PF$_6$ (2d). A sample of [W(≡CPCy$_3$)(CO)$_2$(Tp*)]PF_6 (**1d**: 0.200 g, 0.205 mmol) and elemental sulfur (0.070 g, 2.2 mg.atom) were heated under reflux in THF (10 mL) over 16 hours. The initially orange suspension changed slowly due to poor solubility, although a deep blue colour developed overnight. TLC identified the prolonged heating resulted in several unidentified decomposition species, hence the reaction mixture was purified by short column chromatography (silica gel, N_2, CH_2Cl_2/THF gradient elution). Neat CH_2Cl_2 elution resulted in a black fraction wherein species could not be identified by spectroscopic analysis and this was discarded. Further elution with 2% THF/CH_2Cl_2 provided a deep blue band. This blue eluate was evaporated to dryness under reduced pressure and dissolved in a minimum of $CHCl_3$ (~2 mL) before precipitation of a dark blue solid with Et_2O (20 mL). The resulting solid was collected *via* vacuum filtration, washed with cold 50% $CHCl_3$/Et_2O until the washings were clear and somewhat pale blue (yield sacrificed for purity) and Et_2O (3 × 10 mL) before drying *in vacuo* for 16 hours. The title compound was obtained as a blue crystalline powder, although repeatably contained parent phosphoniocarbyne that resisted removal during purification without decomposition of the title species. Yield: 0.166 g (0.165 mmol, 80% yield at ~90% purity). Crystals suitable for single-crystal X-ray diffraction were grown from the slow evaporation of a CH_2Cl_2 solution of title compound layered with toluene, stored at 5 °C overnight. Crystals formed, however, no adequate structural model could be developed due to poor data from to weak diffraction. Synchrotron radiation did not improve the collected dataset.

IR (CH_2Cl_2, cm^{-1}): 1996 vs ν_{CO}, 1911 vs ν_{CO}. IR (ATR, cm^{-1}): 2571 w ν_{BH}, 1981 vs ν_{CO}, 1894 vs ν_{CO}, 840 vs ν_{PF}. UV-Vis [3.922(4)×10^{-5} $molL^{-1}$, nm (ε, $Lmol^{-1}cm^{-1}$), CH_2Cl_2]: λ_{max} = 255 (18440), 281 sh (13220), 627 (1175). ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δH = 6.09 (s, 1 H, pzCH), 6.02 (s, 2 H, pzCH), 2.51 (s, 3 H, $pzCH_3$), 2.49 (s, 6 H, $pzCH_3$), 2.43 (s, 3 H, $pzCH_3$), 2.25 (s, 6 H, $pzCH_3$), 2.04 (br.m, 10 H, PC_6H_{11}], 1.86 (m, 10 H, PCH_2), 1.44 (m, 10 H, PCH_2). Cyclohexyl ^1H resonances overlap with those of the impurity and therefore were not able to be assigned with certainty even from 2-D correlation spectra. $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 25 °C): δ_C = 226.8 (d, $^3J_{CP}$ = 4; $^1J_{CW}$ = 149 Hz, CO), 222.7 (d, $^1J_{CP}$ = 30; $^1J_{CW}$ = 45 Hz, SCP), 153.5, 152.4 [C^5(pz)], 147.2, 146.2 [C^3(pz)], 109.3, 108.2 [C^4(pz)], 35.3 [d, $^1J_{CP}$ = 39 Hz, $C^1(C_6H_{11})$], 28.3 [d, $^3J_{CP}$ = 4 Hz, $C^{3,5}(C_6H_{11})$], 27.2 [d, $^2J_{CP}$ = 12 Hz, $C^{2,6}(C_6H_{11})$], 25.8 [$C^4(C_6H_{11})$], 16.1, 14.8, 13.4, 12.8 ($pzCH_3$). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 25 °C): δ_P = 41.95 (s, $^1J_{PW}$ not resolved, PCy_3), –144. [hept, $^1J_{PF}$ = 706 Hz, PF]. MS (ESI, +ve ion, *m/z*): Found: 861.3465. Calcd for $C_{36}H_{55}{}^{11}BN_6O_2P^{32}S^{184}W$ $[M]^+$: 861.34417.

Synthesis of [W(CSAsMePh$_2$)(CO)$_2$(Tp*)]OTf (7b). A mixture of [W(≡CAsMePh$_2$)(CO)$_2$(Tp*)]OTf (**6b**: 0.090 g, 0.096 mmol) and elemental sulfur (0.040 g, 1.25 mg.atom,) were heated under reflux in THF (20 mL) for 16 hours during which time the initially orange solution darkened slowly, eventually to give a dark purple/black coloured solution. Thin layer chromatographic monitoring identified that much of the reaction mixture converts to a series of dark coloured decomposition species that were not identified by ^1H NMR spectroscopy, but that the extended reaction time was needed to ensure complete consumption of the arsoniocarbyne precursor. The mixture was concentrated under reduced pressure (~ 2 mL) before dilution with Et_2O to precipitate a dark solid from a black supernatant. The supernatant phase was removed *via* cannula filtration and the residue was thoroughly washed with Et_2O (3 × 15 mL). The remaining dark solid was dried in vacuo before being redissolved in minimal CH_2Cl_2 (~2 mL). Precipitation from CH_2Cl_2 with Et_2O (20 mL) resulted in a purple solid which was collected via vacuum filtration. This was washed with cold 50% $CHCl_3$/Et_2O until the washings were colourless followed by Et_2O (2 × 10 mL) and drying *in vacuo*. This afforded the title compound as a deep purple solid, although some impurities remained the main one being [W(≡CAsMePh$_2$)(CO)$_2$(Tp*)]OTf although this represents reversible loss of sulfur. Yield 12 mg (0.012 mmol, 13%). Further attempts at purification resulted in the decomposition of the already diminished, minimal yield. The sample employed for spectroscopic analysis contained **6b** (ca 10 %) that defied removal and is present as a minor impurity in spectra.

IR (CH_2Cl_2, cm^{-1}): 1995 vs ν_{CO}, 1909 vs ν_{CO}. IR (ATR, cm^{-1}): 2561 w ν_{BH}, 1987 vs ν_{CO}, 1897 vs ν_{CO}, 863 vs ν_{OTf}. ^1H NMR (800 MHz, CD_2Cl_2, 25 °C): δ_H = 7.84 (m, 6 H, C_6H_5), 7.74 (m, 4 H, C_6H_5), 6.00 (s, 1 H, pzCH), 5.95 (s, 2 H, pzCH), 2.84 (s, 3 H, $AsCH_3$), 2.42 (s, 6 H, $pzCH_3$), 2.36 (s, 6 H, $pzCH_3$), 2.04 (s, 6 H, $pzCH_3$). $^{13}C\{^1H\}$ NMR (200 MHz, CD_2Cl_2, 25 °C): δ_C = 226.0 ($^1J_{CW}$ = 41 Hz, SCAs), 223.4 ($^1J_{CW}$ = 145 Hz, CO), 153.8, 152.7 [C^5(pz)], 147.2, 146.2 [C^3(pz)], 135.1 [$C^4(C_6H_5)$], 132.4 [$C^{2,6}(C_6H_5)$], 131.4 [$C^{3,5}(C_6H_5)$], 128.9 [$C^1(C_6H_5)$], 108.9, 108.1 [C^4(pz)], 16.2, 14.1, 13.4, 12.7 ($pzCH_3$), 8.8 ($AsCH_3$). MS (ESI, *m/z*): Found: 825.1347. Calcd for $C_{31}H_{35}{}^{11}BN_6O_2{}^{75}As^{32}S^{184}W$ $[M]^+$: 825.1361. Insufficient material was obtained for the acquisition of elemental microanalytical data.

Synthesis of [Mo(≡CPPh$_3$)(CO)$_2$(Tp*)]PF$_6$ (3a). A mixture of [Mo(≡CBr)(CO)$_2$(Tp*)] (0.999 g, 1.85 mmol), PPh_3 (0.537 g, 2.05 mmol) and $NaPF_6$ (0.360 g, 2.14 mmol) were heated under reflux in in THF (40 mL) for 16 hours. The initially yellow solution darkened quickly to an orange colour, with this transformation clearly visible after 1 hour. The eventually red/pink mixture was cooled and solvent was removed under reduced pressure to give a crude orange residue. The residue was purified by flash column chromatography (silica gel, N_2, CH_2Cl_2/THF gradient elution) whereby a bright pink band was eluted with 2% THF/CH_2Cl_2. Concentration of this pink band under reduced pressure resulted in a pink foam which was ultrasonically triturated with *n*-pentane to provide a crystalline solid. This was collected *via* vacuum filtration and washed with *n*-pentane (3 x 10 mL) before drying in vacuo for 16 hours. The title compound was obtained as a pink crystalline powder. Yield 1.260 g (1.450 mmol,

78%). Crystals suitable for single-crystal x-ray diffraction were grown from the liquid-liquid diffusion of *n*-hexane into a THF solution of the compound at ambient temperature inside an argon glovebox for two weeks.

IR (CH_2Cl_2, cm^{-1}): 2039 vs ν_{CO}, 1965 vs ν_{CO}. IR (ATR, cm^{-1}): 2561 w ν_{BH}, 2026 vs ν_{CO}, 1944 vs ν_{CO}, 832 vs ν_{PF6}. UV-Vis [2.851(3)×10^{-4} $molL^{-1}$, nm(ε, $Lmol^{-1}cm^{-1}$), CH_2Cl_2]: λ_{max} = 267 (25820), 525 (379). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ_H = 7.86 (m, 3 H, C_6H_5), 7.71 (m, 12 H, C_6H_5), 5.92 (s, 2 H, pzCH), 5.78 (s, 1 H, pzCH), 2.42 (s, 6 H, $pzCH_3$), 2.32 (s, 3 H, $pzCH_3$), 2.28 (s, 3 H, $pzCH_3$), 2.00 (s, 6 H, $pzCH_3$). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$, 25 °C): δ_C = 251.0 (d, $^1J_{CP}$ = 21 Hz, Mo≡CP), 225.5 (d, $^2J_{CP}$ = 4 Hz, CO), 152.0, 150.7 [C^5(pz)], 146.8, 146.3 [C^3(pz)], 135.5 [d, $^4J_{CP}$ = 3 Hz, $C^4(C_6H_5)$], 133.7 [d, $^2J_{CP}$ = 11 Hz, $C^{2,6}(C_6H_5)$], 135.5 [d, $^3J_{CP}$ = 14 Hz, $C^{3,5}(C_6H_5)$], 119.9 [d, $^1J_{CP}$ = 90 Hz, $C^1(C_6H_5)$], 107.8, 107.4 [C^4(pz)], 16.1, 14.9, 13.0, 12.9 ($pzCH_3$). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ_P = –0.88 (s, PPh_3), –144.4 (hept, $^1J_{PF}$ = 706 Hz, PF_6). MS (ESI, +ve ion, *m/z*): Found: 725.1859. Calcd for $C_{36}H_{36}{}^{11}B^{98}MoN_6O_2P$ $[M]^+$: 725.18573. Anal. Found: C, 49.79; H, 4.37; N, 9.68%. Calcd for $C_{36}H_{37}BF_6MoN_6O_2P_2$: C, 49.79; H, 4.29; N, 9.68%.

Crystal data for $C_{36}H_{37}BMoN_6O_2P{\cdot}F_6P{\cdot}C_4H_8O$, M_w = 940.51 $gmol^{-1}$, monoclinic, $P2_1/n$, a = 9.2673 (1) Å, b = 18.2717 (2) Å, c = 25.4905 (2) Å, β = 91.331 (1)º, V = 4315.12 (7) $Å^3$, Z = 4, D_{calc} = 1.448 Mgm^{-3}, μ(Cu $K\alpha$) = 3.08 mm^{-1}, T = 150.0(1) K, clear light pink needle, 0.28 × 0.11 × 0.04 mm, 8599 independent measured reflections (2θ_{max} = 147.8), R_1 = 0.031, wR_2 = 0.081 for 7762 reflections [$I > 2\sigma(I)$], 542 parameters, 261 restraints. CDCC 2180156.

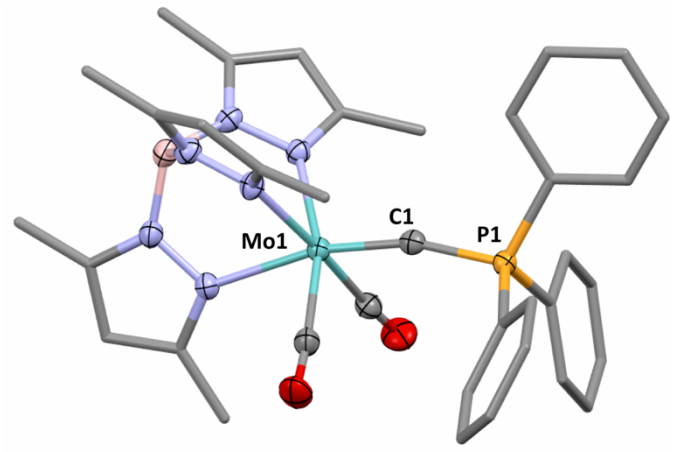


Figure S2: Molecular structure of the cation of **3a** in a crystal of **3a**.THF (50% displacement ellipsoids, pyrazolyl and phenyl rings simplified. Solvent, hydrogens and PF_6 anion omitted).

Synthesis of [Mo(η²-SCPPh₃)(CO)₂(Tp*)]PF₆ (4a). A sample of $[Mo(\equiv CPPh_3)(CO)_2(Tp^*)]PF_6$ (**3a**: 0.100 g, 0.115 mmol) and elemental sulfur (0.037 g, 1.2 mg.atom) were heated in THF (10 mL) at 60 °C for 4 hours. The initially pink solution darkened quickly to a deep blue colour. The reaction mixture was cooled and solvent was removed under reduced pressure to give a crude blue residue. The residue was dissolved in minimal $CHCl_3$ (~2 mL), followed by dilution with Et_2O to afford a dark solid which was ultrasonically triturated with Et_2O. The solid resulted was isolated by filtration followed by washing with minimal cold $CHCl_3$ (0.5 mL). Further washing with cold 40% $CHCl_3/Et_2O$ provided a bright blue solid which was further washed with Et_2O (2 × 10 mL) before drying *in vacuo* for 16 hours to give the title compound as a blue powder. Yield: 0.031 g (0.034 mmol, 30%).

IR (CH_2Cl_2, cm^{-1}): 2016 vs ν_{CO}, 1936 vs ν_{CO}. IR (ATR, cm^{-1}): 2569 w ν_{BH}, 2002 vs ν_{CO}, 1926 vs ν_{CO}, 845 vs ν_{PF6}. UV-Vis [2.731(3)×10^{-5} $molL^{-1}$, nm(ε, $Lmol^{-1}cm^{-1}$), CH_2Cl_2]: λ_{max} = 261 (17160), 630 (1550). ^{1}H NMR (600 MHz, CD_2Cl_2, 25 °C): δ_H = 7.95 (m, 3 H, C_6H_5), 7.87 (m, 6 H, C_6H_5), 7.77 (m, 6 H, C_6H_5), 5.95 (s, 1 H, pzCH), 5.92 (s, 2 H, pzCH), 2.42 (s, 6 H, $pzCH_3$), 2.38 (s, 3 H, $pzCH_3$), 2.25 (s, 3 H, $pzCH_3$), 2.12 (s, 6 H, $pzCH_3$). $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 25 °C): δ_C = 235.5 (d, $^1J_{CP}$ = 45 Hz, SCP), 227.0 (d, $^3J_{CP}$ = 7 Hz, CO), 153.1 151.9 [C^5(pz)], 147.3 146.4 [C^3(pz)], 136.4 [d, $^4J_{CP}$ = 3 Hz, $C^4(C_6H_5)$], 134.7 [d, $^2J_{CP}$ = 10 Hz, $C^{2,6}(C_6H_5)$], 131.0 [d, $^3J_{CP}$ = 14 Hz, $C^{3,5}(C_6H_5)$], 118.6 [d, $^1J_{CP}$ = 90 Hz, $C^1(C_6H_5)$], 108.6 107.8 [C^4(pz)], 15.8 14.3 13.4 12.8 [$pzCH_3$]. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 25 °C): δ_P = 20.95 (s, PPh_3), –144.5 (hept, $^1J_{PF}$ = 706 Hz, PF_6). MS (ESI, *m/z*): Found: 757.1589. Calcd for $C_{36}H_{37}{}^{11}B^{98}MoN_6O_2P^{32}S$ $[M]^+$: 757.15780. Single crystals suitable for x-ray diffraction were not successfully obtained.

Notes and references

1 T. Desmond, F. J. Lalor, G. Ferguson and M. Parvez, *J. Chem. Soc., Chem. Commun.*, 1984, 75–77.
2 G. M. Jamison, P. S. White and J. L. Templeton, *Organometallics*, 1991, **10**, 1954–1959.
3 B. J. Frogley and A. F. Hill, *Dalton Trans.*, 2022, **51**, 1907-1917.
4 *CrysAlisPRO, Oxford Diffraction,* Agilent Technologies UK Ltd, Yarnton, England.
5 (*a*) G. Sheldrick, *Acta Crystallogr., Sect A: Found Crystallogr.*, 2008, **64**, 112–122; (*b*) G. M. Sheldrick, *Acta Crystallogr., Sect C: Cryst. Struct. Commun.*, 2015, **71**, 3–8.
6 (*a*) 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; (*b*) 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.
7 *Spartan20®*, Wavefunction, Inc., 18401 Von Karman Ave., Suite 370, Irvine, CA 92612 U.S.A., 2020
8 (*a*) J.-D. Chai and M. Head-Gordon, *J. Chem. Phys.*, 2008, **128**, 0841061–18410615; (*b*) J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2014, **16**, 9904– 9924. (c) N. Mardirossian and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615– 6620
9 (*a*) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270–283; (*b*) W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284–298; (*c*) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299–310.
10 W. J. Hehre, R. Ditchfeld and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257–2261.

Computational Details

Results for $Me_3P{=}C{=}E$ (E = O, S, Se, Te) are provided for information only and do NOT constitute valid local minima due to, in each case, the retention of a single imaginary frequency. This corresponds to oscillation of the carbon atom perpendicular to the phosphorus-chalcogen vector.

1. $Me_3P{=}C{=}O$

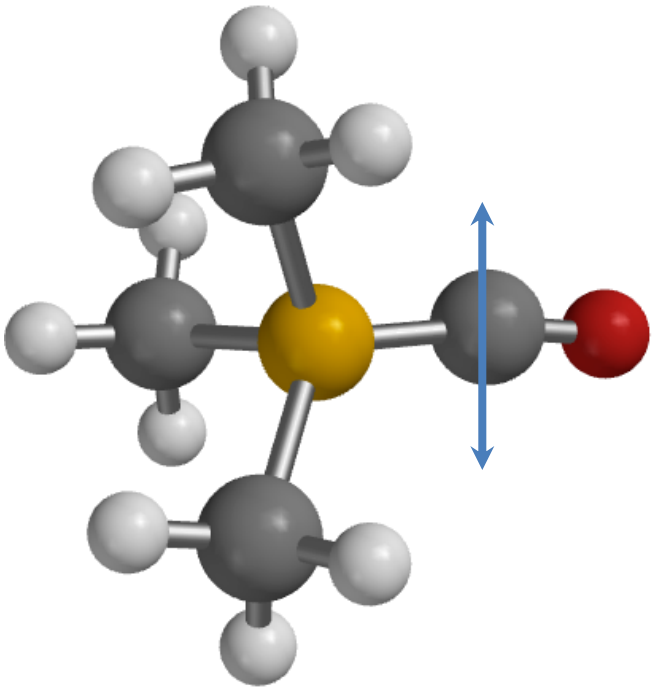


Figure S3: Optimised structure of $Me_3P{=}C{=}O$ (DFT: ωB97X–V, 6–31G*), NB: imaginary frequency (i727 cm^{-1}) with oscillation shown (blue arrow).

Cartesian Coordinates

Atom	x	y	z
P	0.013704	-0.000001	-0.425383
C	-1.689744	-0.000001	0.225094
H	-2.225304	0.893247	-0.099582
H	-1.622974	0.000001	1.316833
H	-2.225303	-0.893249	-0.099580
C	0.878429	1.414575	0.435469
H	0.329085	2.334437	0.219169
H	1.891406	1.514852	0.032222
H	0.948201	1.259448	1.519069
C	0.878429	-1.414576	0.435470
H	1.891406	-1.514853	0.032222
H	0.329084	-2.334438	0.219172
H	0.948202	-1.259448	1.519070
C	-0.115839	0.000003	-2.059616
O	-0.228782	0.000002	-3.269629

Thermodynamic Properties at 298.15 K

Zero Point Energy :	300.16	kJ/mol	(ZPE)
Temperature Correction :	24.43	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	324.59	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-574.063548	au	(Electronic Energy + Enthalpy Correction)
Entropy :	369.12	J/mol•K	
Gibbs Energy :	-574.105465	au	(Enthalpy - T*Entropy)
C_v :	120.08	J/mol•K	

2. $Me_3P{=}C{=}S$

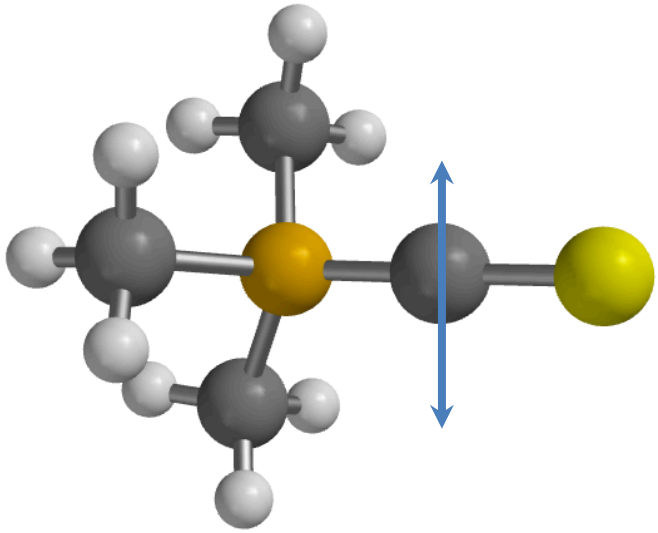


Figure S4: Optimised structure of $Me_3P{=}C{=}S$ (DFT: ωB97X–V, 6–31G*). NB: imaginary frequency (i440 cm^{-1}) with oscillation shown (blue arrow).

Cartesian Coordinates

Atom	x	y	z
P	0.020845	0.000000	-0.375249
C	-1.678880	-0.000000	0.282097
H	-2.210314	0.892083	-0.061597
H	-1.639872	0.000000	1.377432
H	-2.210314	-0.892083	-0.061597
C	0.869053	1.419980	0.444037
H	0.340143	2.343327	0.185500
H	1.895473	1.495782	0.065827
H	0.904500	1.301054	1.534940
C	0.869053	-1.419980	0.444037
H	1.895473	-1.495782	0.065826
H	0.340142	-2.343327	0.185501
H	0.904501	-1.301053	1.534940
C	-0.088424	0.000000	-2.013924
S	-0.211378	0.000000	-3.607771

Thermodynamic Properties at 298.15 K

Zero Point Energy :	317.35	kJ/mol	(ZPE)
Temperature Correction :	24.04	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	341.39	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-896.948792	au	(Electronic Energy + Enthalpy Correction)
Entropy :	372.04	J/mol•K	
Gibbs Energy :	-896.991041	au	(Enthalpy - T*Entropy)
C_v :	123.47	J/mol•K	

Thermodynamic Properties at 298.15 K

Zero Point Energy :	316.09	kJ/mol	(ZPE)
Temperature Correction :	24.32	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	340.41	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-2899.877429	au	(Electronic Energy + Enthalpy Correction)
Entropy :	382.06	J/mol•K	
Gibbs Energy :	-2899.920815	au	(Enthalpy - T*Entropy)
C_v :	124.62	J/mol•K	

3. $Me_3P{=}C{=}Se$

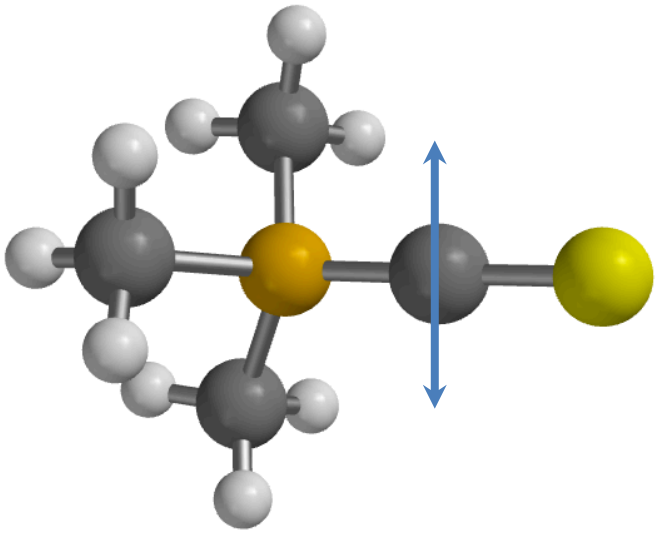


Figure S5: Optimised structure of $Me_3P{=}C{=}Se$ (DFT: ωB97X–V, 6–31G*). Imaginary frequency (i392 cm^{-1}) with oscillation (blue arrow).

Cartesian Coordinate

Atom	x	y	z
P	0.026736	0.007585	-0.364755
C	0.862201	1.428922	0.472168
H	1.894672	1.498798	0.107725
H	0.879431	1.320753	1.564951
H	0.342345	2.354137	0.198018
C	0.867881	-1.416146	0.437107
H	1.897887	-1.494170	0.069401
H	0.334966	-2.335050	0.171948
H	0.893085	-1.296267	1.528652
C	-1.675698	0.010990	0.287831
H	-2.202119	-0.883535	-0.056549
H	-2.208109	0.900149	-0.063147
H	-1.642361	0.019183	1.383409
C	-0.073733	-0.076613	-2.005487
Se	-0.197107	0.003936	-3.731178

4. $Me_3P{=}C{=}Te$

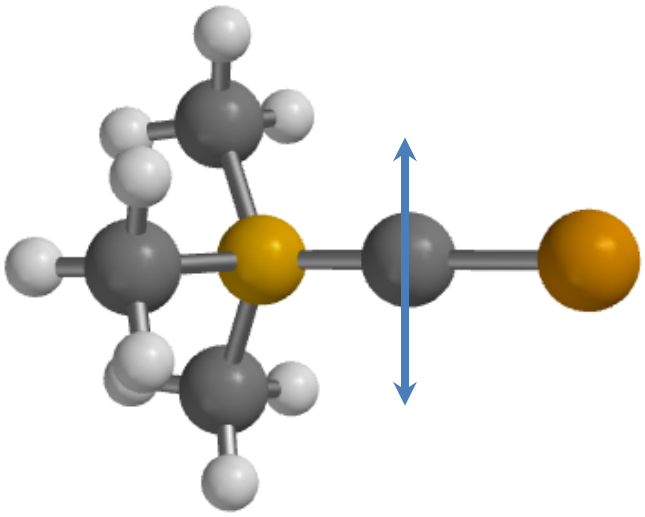


Figure S6: Optimised structure of $Me_3P{=}C{=}Te$ (DFT: ωB97X–V, 6–31G*, LANL2DZ(Te)). Imaginary frequency (i337 cm^{-1}) with oscillation (blue arrow).

Cartesian Coordinate

Atom	x	y	z
P	0.023171	-0.007771	-0.350371
C	-1.672687	-0.012587	0.319696
H	-2.202488	0.881879	-0.020167
H	-1.632880	-0.022572	1.415265
H	-2.208127	-0.900831	-0.029385
C	0.865129	1.416858	0.440303
H	0.336152	2.335325	0.166748
H	1.894367	1.488942	0.070222
H	0.892189	1.310702	1.532746
C	0.857787	-1.429597	0.476591
H	1.891840	-1.494616	0.116987
H	0.343600	-2.355511	0.195279
H	0.869540	-1.329844	1.569665
C	-0.072173	0.073220	-1.995429
Te	-0.185447	0.000686	-3.908232

Thermodynamic Properties at 298.15 K

Zero Point Energy :	315.07	kJ/mol	(ZPE)
Temperature Correction :	24.51	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	339.58	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-506.877546	au	(Electronic Energy + Enthalpy Correction)
Entropy :	388.83	J/mol•K	
Gibbs Energy :	-506.921701	au	(Enthalpy - T*Entropy)
C_v :	125.50	J/mol•K	

5. $(Me_3P)C=S$

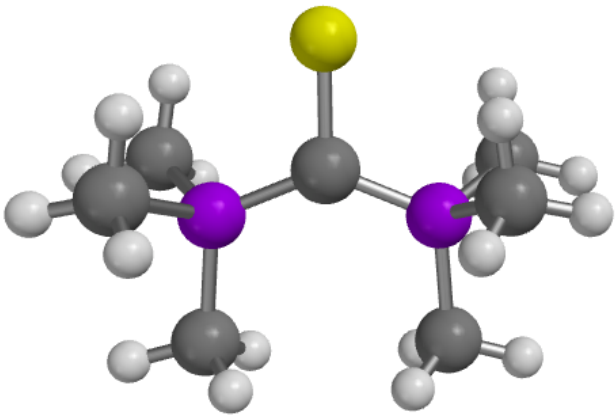


Figure S7: Optimised structure of $(Me_3P)_2C=S$ (DFT: ωB97X–V, 6–31G*).

Cartesian Coordinate

Atom	x	y	z
P	1.562380	0.000118	-0.132434
C	2.539218	-1.443126	-0.667705
H	2.387159	-1.544762	-1.748070
H	2.155592	-2.342954	-0.173271
H	3.605790	-1.322462	-0.444303
C	1.695254	0.000168	1.691533
H	1.225550	0.893476	2.116287
H	2.755424	-0.000058	1.970953
H	1.225237	-0.893380	2.115254
C	2.539262	1.443182	-0.667812
H	2.155696	2.343058	-0.173431
H	2.387214	1.544741	-1.748184
H	3.605825	1.322454	-0.444403
C	0.000013	-0.000000	-0.783249
P	-1.562341	-0.000118	-0.132375
C	-1.695273	-0.000168	1.691629
H	-1.225326	0.893346	2.115523
H	-1.225638	-0.893443	2.116556
H	-2.755467	0.000058	1.970938
C	-2.539194	1.443122	-0.667706
H	-2.155577	2.342960	-0.173285
H	-3.605768	1.322453	-0.444319
H	-2.387127	1.544745	-1.748074
C	-2.539238	-1.443178	-0.667812
H	-2.387182	-1.544724	-1.748187
H	-3.605804	-1.322445	-0.444419
H	-2.155681	-2.343064	-0.173446
S	0.000002	0.000000	-2.606187

Thermodynamic Properties at 298.15 K

Zero Point Energy :	593.29	kJ/mol	(ZPE)
Temperature Correction :	40.78	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	634.08	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-1357.912450	au	(Electronic Energy + Enthalpy Correction)
Entropy :	489.60	J/mol•K	
Gibbs Energy :	-1357.968049	au	(Enthalpy - T*Entropy)
C_v :	252.42	J/mol•K	

6. $Me_3P=C=C=S$

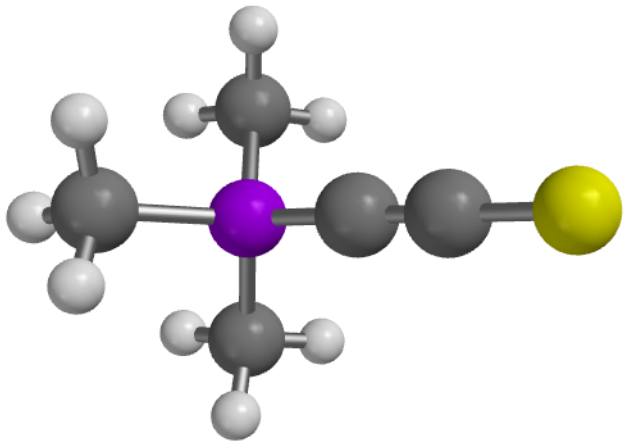


Figure S8: Optimised structure of $Me_3P=C=C=S$ (DFT: ωB97X–V, 6–31G*).

Cartesian Coordinate

Atom	x	y	z
S	-0.030247	-0.357752	4.545282
C	-0.019679	-0.219547	2.950146
C	-0.013063	-0.109392	1.701695
P	-0.000499	0.000127	0.054295
C	-0.841601	1.489452	-0.575341
H	-0.349916	2.379807	-0.169626
H	-1.882492	1.485087	-0.236203

Atom	x	y	z
H	-0.814429	1.522906	-1.671438
C	1.677408	0.060689	-0.655779
H	1.639062	0.132215	-1.749530
H	2.223636	-0.843625	-0.367686
H	2.208849	0.928695	-0.251186
C	-0.821973	-1.399837	-0.774583
H	-0.321734	-2.330324	-0.490057
H	-0.788266	-1.285912	-1.864754
H	-1.865057	-1.452591	-0.445235

Thermodynamic Properties at 298.15 K

Zero Point Energy :	335.18	kJ/mol	(ZPE)
Temperature Correction :	25.59	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	360.78	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-935.100010	au	(Electronic Energy + Enthalpy Correction)
Entropy :	384.79	J/mol•K	
Gibbs Energy :	-935.143707	au	(Enthalpy - T*Entropy)
C_v :	142.64	J/mol•K	

7. [W(SCPMe$_3$)(CO)$_2$(Tp*)]$^+$ (Gas Phase)

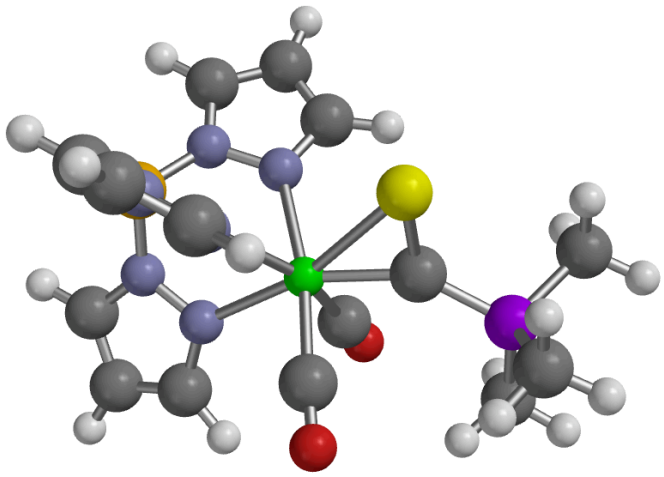


Figure S9: Optimised structure of the cation [W(SCPMe$_3$)(CO)$_2$(Tp*)]$^+$ [DFT: ωB97X–D/6–31G*/ LANL2DZ/gas phase].

Cartesian Coordinates

Atom	x	y	z
W	0.140660	-0.052217	-0.204197
P	-0.448678	3.158675	-1.669927
S	1.139509	2.143751	0.712769
C	1.109393	-0.072422	-1.931323
N	-0.348574	-2.167440	-0.554208
N	1.836696	-1.009616	0.785852
C	0.001392	1.851629	-0.558523
N	-0.763126	-0.331873	1.776251
N	-0.316623	-3.042176	0.481069
O	-2.820524	-0.007106	-1.459539
N	-0.626889	-1.495422	2.451356
N	1.661753	-2.057354	1.626645
O	1.688588	-0.041715	-2.990028
C	-1.656378	-0.007826	-1.012570
C	-0.734327	-2.852107	-1.642681
C	-0.958162	-4.187901	-1.313385
H	-1.273634	-4.989105	-1.967443
C	2.852587	-2.444326	2.114798
C	-1.266268	-1.408868	3.633552
C	-1.841569	-0.151657	3.733640
H	-2.422935	0.245775	4.554263
C	-0.671519	-4.261042	0.044415
C	-1.493335	0.488082	2.539101
C	3.839533	-1.625722	1.582269
H	4.903828	-1.666237	1.769506
C	3.149316	-0.742331	0.750180
B	0.244744	-2.628183	1.873425
H	0.274842	-3.575067	2.611598
C	-1.184039	4.513731	-0.723763
H	-2.115170	4.173582	-0.257202
H	-1.397466	5.365071	-1.379782
H	-0.484906	4.819563	0.062085
C	1.065928	3.734483	-2.476391
H	1.484839	2.923705	-3.083946
H	1.795737	4.014281	-1.709452
H	0.851024	4.595548	-3.119408
C	-1.607824	2.627659	-2.953704
H	-2.580882	2.375773	-2.520867
H	-1.205757	1.752888	-3.477357
H	-1.743538	3.440706	-3.676972
H	-1.711692	1.492869	2.197443
H	-1.267508	-2.249472	4.316242
H	3.517816	0.074719	0.141125
H	2.914452	-3.276784	2.804942
H	-0.693887	-5.099305	0.729806
H	-0.828105	-2.348983	-2.597826

Thermodynamic Properties at 298.15 K

Zero Point Energy :	913.66	kJ/mol	(ZPE)
Temperature Correction :	61.100	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	975.66	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-1893.315816	au	(Electronic Energy + Enthalpy Correction)
Entropy :	643.08	J/mol•K	
Gibbs Energy :	-1893.388843	au	(Enthalpy - T*Entropy)
C_v :	427.43	J/mol•K	

UV-Vis Allowed Transitions

nm ▼	strength	MO Component	
302.93	0.0206	HOMO -> LUMO+2	84%
336.80	0.0016	HOMO-3 -> LUMO	67%
360.69	0.0071	HOMO-1 -> LUMO+1	77%
451.70	0.0117	HOMO-1 -> LUMO	43%
		HOMO -> LUMO+1	41%
455.68	0.0233	HOMO -> LUMO+1	39%
		HOMO-1 -> LUMO	35%
607.20	0.0258	HOMO -> LUMO	82%

8. [W(SCPMe$_3$)(CO)$_2$(Tp*)]$^+$ -PCM κ = 7.43 (THF)

Geometry not visually different to that in Figure S8.

Cartesian Coordinates

Atom	x	y	z
W	0.220392	-0.013805	0.095220
S	-0.834715	1.184813	2.145245
P	0.735354	3.468403	0.786702
O	0.222869	1.692472	-2.563805
O	3.296398	0.231465	0.735238
N	0.833641	-1.498545	-1.418863
N	0.128874	-2.650555	-1.547686
N	-1.828140	-0.640229	-0.449804
N	-2.123238	-1.935121	-0.704079
N	0.109040	-1.839151	1.318800
N	-0.468669	-2.968322	0.848966
C	0.161685	1.775745	0.870242
C	0.264290	1.096020	-1.580965
C	2.168398	0.154666	0.501746
C	1.810835	-1.523480	-2.334280
C	1.741182	-2.703030	-3.070930
H	2.386651	-3.016648	-3.876557
C	0.664376	-3.389467	-2.531255
C	-2.947473	0.065858	-0.630140
C	-3.991091	-0.783371	-1.004816
H	-5.013962	-0.516695	-1.221540
C	-3.420475	-2.045028	-1.039176
C	0.542572	-2.101120	2.556793
C	0.234628	-3.417217	2.901086
H	0.447858	-3.924904	3.829003
C	-0.402074	-3.930589	1.782056
B	-1.031968	-3.011470	-0.586392
H	-1.468284	-4.096501	-0.848628
H	-2.942252	1.136656	-0.480428
H	1.041936	-1.331639	3.128371
H	-3.841797	-3.010372	-1.279443
H	-0.808221	-4.911870	1.583968
H	2.503586	-0.697185	-2.411700
H	0.244810	-4.354820	-2.774285
C	-0.645643	4.499014	0.256112
H	-0.324089	5.544270	0.245708
H	-1.475899	4.373518	0.955621
H	-0.956778	4.197605	-0.747347
C	1.284213	3.971149	2.429863
H	2.090471	3.309957	2.757963
H	0.446484	3.907579	3.128068
H	1.647451	5.001146	2.377267
C	2.113111	3.639578	-0.363390
H	2.928631	2.977302	-0.063335
H	2.456871	4.677328	-0.323307
H	1.798158	3.406591	-1.381887

Thermodynamic Properties at 298.15 K

Zero Point Energy :	862.53	kJ/mol	(ZPE)
Temperature Correction :	64.25	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	926.78	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-1893.502872	au	(Electronic Energy + Enthalpy Correction)
Entropy :	654.75	J/mol•K	
Gibbs Energy :	-1893.577225	au	(Enthalpy - T*Entropy)
C_v :	446.38	J/mol•K	

9. [W(CS)(PMe$_3$)(CO)$_2$(Tp*)]$^+$ -PCM κ = 7.43 (THF)

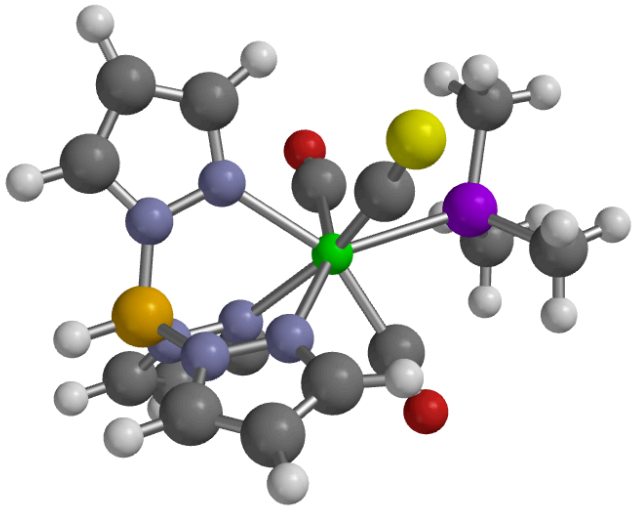


Figure S10: Optimised structure of the cation [W(CS)(PMe$_3$)(CO)$_2$(Tp*)]$^+$ [DFT: ωB97X–D/6–31G*/ LANL2Dζ/PCM κ = 7.43 (THF)].

Cartesian Coordinates

Atom	x	y	z
W	-0.228072	0.027033	0.303151
C	-1.376456	-1.638563	0.269695

Atom	x	y	z
O	-1.971262	-2.611546	0.142414
C	1.042161	0.036135	1.880710
O	1.857281	0.039913	2.687958
P	-1.636571	-0.003893	2.447072
B	1.668698	-0.014941	-2.464675
N	1.303307	-1.454503	-0.440507
N	1.957788	-1.260460	-1.606838
C	2.808213	-2.277009	-1.821933
C	2.709361	-3.166408	-0.764125
C	1.750039	-2.604929	0.078166
N	-0.779723	0.000026	-1.850348
N	0.167246	-0.014600	-2.816262
C	-0.423216	-0.010384	-4.023097
C	-1.796119	0.005911	-3.843940
C	-1.970167	0.013325	-2.460049
C	-1.341639	1.630560	0.303237
N	1.306084	1.454440	-0.446193
N	1.959724	1.234033	-1.609661
S	-2.115207	2.961601	0.081330
C	1.753794	2.613676	0.048752
C	2.811153	2.246492	-1.844160
C	2.714909	3.156013	-0.804402
H	1.361143	-2.963656	1.021165
H	-2.879209	0.030038	-1.875481
H	3.421853	-2.294754	-2.710927
H	0.176825	-0.018414	-4.921381
H	1.361972	2.992731	0.982147
H	3.422866	2.246702	-2.734591
C	-1.343265	-1.455640	3.515304
H	-0.299088	-1.484037	3.835889
H	-1.575134	-2.376403	2.974454
H	-1.988123	-1.384138	4.396552
C	-1.358695	1.413014	3.560138
H	-0.322105	1.422644	3.905184
H	-2.023241	1.312593	4.423549
H	-1.574005	2.350435	3.043627
C	-3.437531	-0.030025	2.164772
H	-3.719016	-0.933806	1.619089
H	-3.743596	0.845877	1.589329
H	-3.944027	-0.023697	3.134513
H	3.260516	4.078946	-0.682012
H	-2.560813	0.012388	-4.605255
H	3.253146	-4.087924	-0.623966
H	2.338203	-0.014794	-3.458396

Thermodynamic Properties at 298.15 K

Zero Point Energy :	861.44	kJ/mol	(ZPE)
Temperature Correction :	64.74	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	926.18	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-1893.491420	au	(Electronic Energy + Enthalpy Correction)
Entropy :	656.48	J/mol•K	
Gibbs Energy :	-1893.565970	au	(Enthalpy - T*Entropy)
C_v :	449.06	J/mol•K	

10. $[W(PMe_3)(CO)_3(Tp^*)]^+$ -PCM κ = 7.43 (THF)

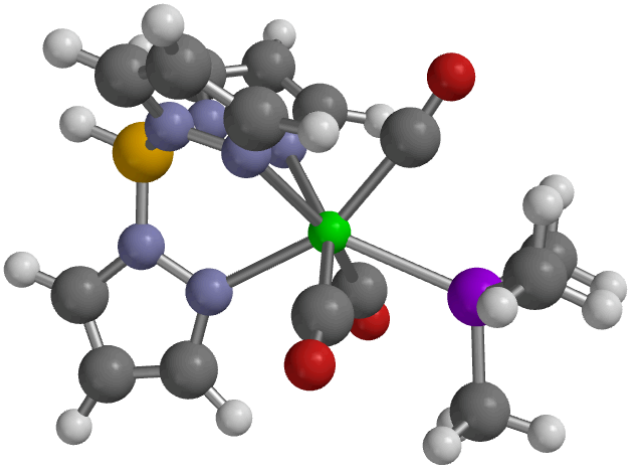


Figure S11: Optimised structure of the cation $[W(PMe_3)(CO)_3(Tp^*)]^+$ [DFT: ωB97X–D/6–31G*/ LANL2Dζ/PCM κ = 7.43 (THF)].

Cartesian Coordinates

Atom	x	y	z
W	-0.214572	-0.000118	0.306777
C	-1.349021	-1.656822	0.290584
O	-1.941134	-2.635358	0.172165
C	1.038187	0.004996	1.878279
O	1.851927	0.009293	2.690308
P	-1.633390	-0.000370	2.440757
B	1.656827	0.000651	-2.461077
N	1.301397	-1.458011	-0.436505
N	1.946794	-1.248506	-1.605983
C	2.800414	-2.260109	-1.835700
C	2.714013	-3.160304	-0.786978
C	1.757414	-2.611374	0.066926
N	-0.788924	-0.001273	-1.845873
N	0.155718	0.001614	-2.813673
C	-0.436312	0.004237	-4.019609
C	-1.809087	0.001613	-3.838357
C	-1.980663	-0.002992	-2.454236
C	-1.355639	1.652020	0.285842
N	1.299872	1.458965	-0.437113
N	1.948804	1.248665	-1.604911

Atom	x	y	z
O	-1.954150	2.626134	0.162486
C	1.753468	2.612285	0.067129
C	2.804632	2.259072	-1.832333
C	2.713288	3.159557	-0.784172
H	1.376323	-2.980551	1.008674
H	-2.889134	-0.005653	-1.868272
H	3.408236	-2.266346	-2.728870
H	0.162285	0.006769	-4.918949
H	1.369393	2.982251	1.007537
H	3.415140	2.264659	-2.723647
C	-1.360504	-1.438864	3.528838
H	-0.319033	-1.470943	3.857564
H	-1.595931	-2.364102	2.997477
H	-2.012516	-1.349224	4.403010
C	-1.361162	1.438322	3.528613
H	-0.320049	1.470471	3.858343
H	-2.013467	1.348871	4.402596
H	-1.595905	2.363388	2.996642
C	-3.433048	-0.000333	2.143377
H	-3.721227	-0.890153	1.578460
H	-3.721791	0.889205	1.578424
H	-3.952287	-0.000075	3.106477
H	3.261697	4.079719	-0.654007
H	-2.574476	0.002933	-4.598902
H	3.262641	-4.080620	-0.658920
H	2.326655	0.000571	-3.454445

Thermodynamic Properties at 298.15 K

Zero Point Energy :	867.42	kJ/mol	(ZPE)
Temperature Correction :	64.19	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	931.61	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-1570.556462	au	(Electronic Energy + Enthalpy Correction)
Entropy :	652.01	J/mol•K	
Gibbs Energy :	-1570.630505	au	(Enthalpy - T*Entropy)
C_v :	445.93	J/mol•K	

11. $[W(OCPMe_3)(CO)_2(Tp^*)]^+$ - PCM κ = 7.43 (THF)

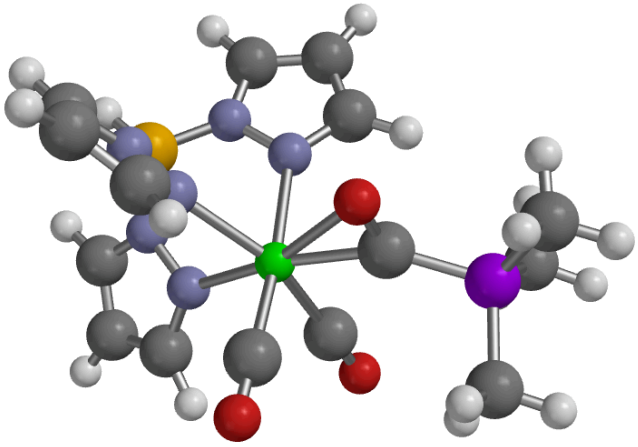


Figure S12: Optimised structure of the cation $[W(OCPMe_3)(CO)_2(Tp^*)]^+$ [DFT: ωB97X–D/6–31G*/ LANL2Dζ/PCM κ = 7.43 (THF)].

Cartesian Coordinates

Atom	x	y	z
W	0.672809	-0.146047	-0.024073
O	0.190868	1.042529	1.852714
P	0.480992	3.490980	0.766571
O	1.207667	1.636606	-2.602264
O	3.748586	-0.020401	0.496318
N	0.791705	-1.656776	-1.603380
N	-0.113985	-2.667100	-1.643306
N	-1.550862	-0.423166	-0.237219
N	-2.070645	-1.654245	-0.442250
N	0.459559	-1.949589	1.196300
N	-0.358891	-2.960432	0.819412
C	0.372646	1.659258	0.775527
C	1.000601	0.993265	-1.670244
C	2.600647	-0.060383	0.298755
C	1.651240	-1.858822	-2.610737
C	1.298344	-3.004306	-3.320595
H	1.792665	-3.426728	-4.181672
C	0.180444	-3.490294	-2.661838
C	-2.580615	0.428114	-0.209269
C	-3.784062	-0.255998	-0.395572
H	-4.781928	0.154257	-0.422944
C	-3.408839	-1.581041	-0.540262
C	1.036264	-2.314708	2.347936
C	0.581826	-3.575823	2.730324
H	0.855105	-4.139771	3.608794
C	-0.298029	-3.948246	1.724662
B	-1.145112	-2.876168	-0.508398
H	-1.772274	-3.881177	-0.695753
H	-2.411729	1.484339	-0.059046
H	1.738738	-1.652454	2.833712
H	-3.994750	-2.473150	-0.708008
H	-0.879977	-4.848511	1.589605
H	2.473383	-1.174960	-2.767229
H	-0.418829	-4.371659	-2.838874
C	-0.651579	4.137740	-0.474785

Atom	x	y	z
H	-0.530407	5.223949	-0.518106
H	-1.679212	3.895109	-0.193667
H	-0.419871	3.705338	-1.450876
C	0.054357	4.088359	2.408723
H	0.745957	3.659428	3.137833
H	-0.968674	3.786869	2.646818
H	0.132443	5.178891	2.419266
C	2.184380	3.898071	0.344498
H	2.856478	3.440747	1.074964
H	2.299152	4.985620	0.363324
H	2.413416	3.522488	-0.655687

Thermodynamic Properties at 298.15 K

Zero Point Energy :	867.74	kJ/mol	(ZPE)
Temperature Correction :	63.42	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	931.16	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-1570.515823	au	(Electronic Energy + Enthalpy Correction)
Entropy :	648.84	J/mol•K	
Gibbs Energy :	-1570.589504	au	(Enthalpy - T*Entropy)
C_v :	441.58	J/mol•K	

12. [W(CSe)(PMe$_3$)(CO)$_2$(Tp*)]$^+$ -PCM κ = 7.43 (THF)

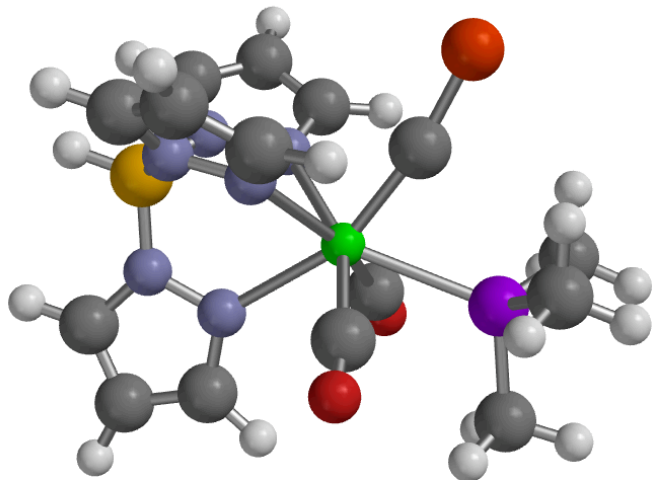


Figure S13: Optimised structure of the cation [W(CSe)(PMe$_3$)(CO)$_2$(Tp*)]$^+$ [DFT: ωB97X–D/6–31G*/ LANL2DZ/PCM κ = 7.43 (THF)].

Cartesian Coordinates

Atom	x	y	z
W	-0.235101	0.040087	0.299416
C	-1.388823	-1.626904	0.257780
O	-1.984479	-2.597899	0.125939
C	1.041850	0.056133	1.876859
O	1.858384	0.063283	2.681653
P	-1.635650	-0.011622	2.452588
B	1.671987	-0.021567	-2.464568
N	1.298093	-1.451072	-0.437700
N	1.957258	-1.264511	-1.602304
C	2.806993	-2.283158	-1.809130
C	2.702974	-3.166896	-0.746893
C	1.741418	-2.599487	0.088736
N	-0.778282	0.003483	-1.855227
N	0.171145	-0.019907	-2.818532
C	-0.416499	-0.015462	-4.026749
C	-1.789733	0.009446	-3.851376
C	-1.967159	0.022339	-2.468005
C	-1.346097	1.632462	0.306993
N	1.306115	1.457025	-0.452284
N	1.963392	1.229725	-1.612420
Se	-2.184169	3.083875	0.054662
C	1.753459	2.618310	0.038167
C	2.816541	2.240177	-1.849337
C	2.717846	3.155182	-0.814668
H	1.348410	-2.952894	1.032081
H	-2.877508	0.046950	-1.885841
H	3.423767	-2.306472	-2.695851
H	0.185776	-0.028573	-4.923490
H	1.358393	3.003003	0.967828
H	3.431003	2.235245	-2.737865
C	-1.328865	-1.469646	3.508461
H	-0.282673	-1.495267	3.822768
H	-1.559268	-2.387573	2.962079
H	-1.968710	-1.408337	4.394144
C	-1.356779	1.398910	3.572686
H	-0.321392	1.404223	3.921368
H	-2.024283	1.295404	4.433398
H	-1.568333	2.338622	3.058933
C	-3.436986	-0.045885	2.177228
H	-3.717481	-0.951873	1.634774
H	-3.747710	0.828070	1.601503
H	-3.938689	-0.039884	3.149415
H	3.264087	4.078121	-0.695225
H	-2.552326	0.018089	-4.614755
H	3.245004	-4.088389	-0.599931
H	2.343097	-0.024886	-3.457306

Thermodynamic Properties at 298.15 K

Zero Point Energy :	859.70	kJ/mol	(ZPE)
Temperature Correction :	65.17	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	924.86	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-3896.634478	au	(Electronic Energy + Enthalpy Correction)
Entropy :	661.98	J/mol•K	
Gibbs Energy :	-3896.709652	au	(Enthalpy - T*Entropy)
C_v :	450.79	J/mol•K	

13. [W(SeCPMe$_3$)(CO)$_2$(Tp*)]$^+$ -PCM κ = 7.43 (THF)

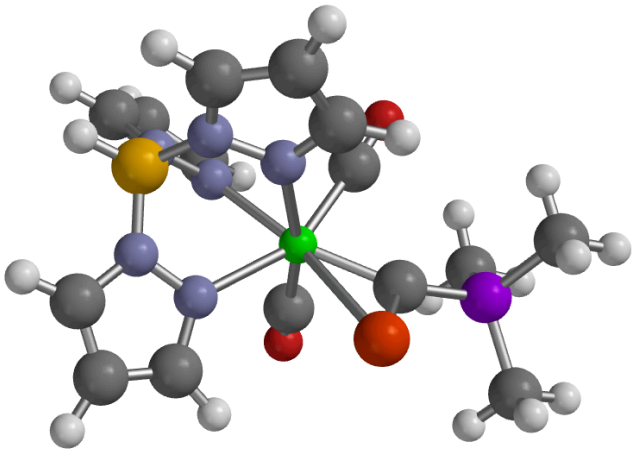


Figure S14: Optimised structure of the cation [W(SeCPMe$_3$)(CO)$_2$(Tp*)]$^+$ [DFT: ωB97X–D/6–31G*/ LANL2DζPCM κ = 7.43 (THF)].

Cartesian Coordinates

Atom	x	y	z
W	0.232594	-0.022942	0.143452
Se	-0.859769	1.154125	2.322021
P	0.724052	3.471938	0.766370
O	0.266136	1.658681	-2.531892
O	3.308752	0.212773	0.806881
N	0.837983	-1.504332	-1.385789
N	0.118034	-2.641829	-1.544808
N	-1.818608	-0.624602	-0.419135
N	-2.126072	-1.911091	-0.695969
N	0.117692	-1.880908	1.327036
N	-0.480417	-2.991880	0.838703
C	0.178567	1.776570	0.885129
C	0.301695	1.074096	-1.542756
C	2.184305	0.133428	0.563612
C	1.823701	-1.526014	-2.292260
C	1.745581	-2.689788	-3.051910
H	2.393360	-2.996467	-3.858426
C	0.651545	-3.369291	-2.538045
C	-2.929206	0.097390	-0.595002
C	-3.980187	-0.734216	-0.987479
H	-4.999837	-0.454122	-1.203177
C	-3.421980	-2.000487	-1.041170
C	0.570498	-2.179253	2.550309
C	0.254355	-3.500110	2.866190
H	0.479126	-4.033747	3.776763
C	-0.407079	-3.978285	1.745691
B	-1.049564	-3.002799	-0.593108
H	-1.499298	-4.077850	-0.873001
H	-2.912530	1.165219	-0.426540
H	1.087356	-1.430537	3.133486
H	-3.852993	-2.956955	-1.299009
H	-0.828076	-4.949563	1.529852
H	2.526341	-0.706393	-2.349256
H	0.216545	-4.320921	-2.806646
C	-0.671410	4.470292	0.206934
H	-0.362979	5.518875	0.171124
H	-1.501053	4.351447	0.908226
H	-0.976829	4.139676	-0.788981
C	1.269488	4.042843	2.387559
H	2.068775	3.391370	2.750216
H	0.429781	4.019904	3.085564
H	1.642262	5.066166	2.288559
C	2.101106	3.648538	-0.387291
H	2.923303	2.997131	-0.081103
H	2.434297	4.689998	-0.356814
H	1.790660	3.403921	-1.404107

Thermodynamic Properties at 298.15 K

Zero Point Energy :	861.28	kJ/mol	(ZPE)
Temperature Correction :	64.48	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	925.75	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-3896.658855	au	(Electronic Energy + Enthalpy Correction)
Entropy :	658.93	J/mol•K	
Gibbs Energy :	-3896.733682	au	(Enthalpy - T*Entropy)
C_v :	448.06	J/mol•K	

14. [W(CTe)(PMe$_3$)(CO)$_2$(Tp*)]$^+$ -PCM κ = 7.43 (THF)

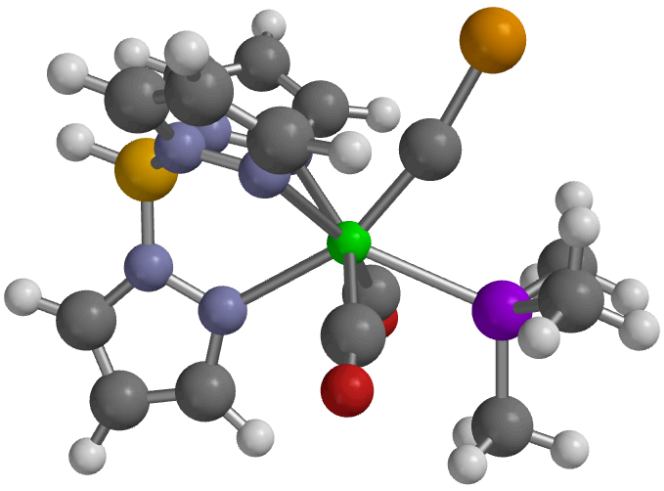


Figure S15: Optimised structure of the cation [W(CTe)(PMe$_3$)(CO)$_2$(Tp*)]$^+$ [DFT: ωB97X–D/6–31G*/ LANL2DζPCM κ = 7.43 (THF)].

Cartesian Coordinates

Atom	x	y	z
W	-0.245535	0.058621	0.294868
C	-1.405510	-1.613965	0.241509
O	-1.998168	-2.584766	0.106755
C	1.042666	0.085997	1.873668
O	1.860926	0.098927	2.674687

Atom	x	y	z
P	-1.633517	-0.018648	2.459437
B	1.676726	-0.031847	-2.462058
N	1.291024	-1.449471	-0.432274
N	1.953607	-1.274014	-1.595603
C	2.800792	-2.295479	-1.793633
C	2.692822	-3.171739	-0.725609
C	1.730627	-2.595846	0.103733
N	-0.776908	0.009555	-1.860897
N	0.176421	-0.026515	-2.820467
C	-0.406586	-0.022701	-4.030735
C	-1.780302	0.014050	-3.860628
C	-1.963152	0.035229	-2.478327
C	-1.349609	1.633049	0.316106
N	1.307228	1.460065	-0.458478
N	1.973726	1.219745	-1.611065
Te	-2.277092	3.268657	0.018040
C	1.750291	2.626947	0.022605
C	2.825459	2.229794	-1.854343
C	2.718661	3.155964	-0.830298
H	1.332713	-2.941973	1.047837
H	-2.875372	0.071077	-1.899619
H	3.422106	-2.325003	-2.677008
H	0.198863	-0.043760	-4.925094
H	1.348020	3.021523	0.944985
H	3.442486	2.218210	-2.740985
C	-1.311392	-1.487708	3.495896
H	-0.262745	-1.511404	3.802400
H	-1.540005	-2.400728	2.940473
H	-1.945061	-1.441627	4.386932
C	-1.350928	1.379034	3.592664
H	-0.317303	1.376435	3.946488
H	-2.022137	1.268509	4.449557
H	-1.556611	2.324516	3.087207
C	-3.434651	-0.064086	2.189829
H	-3.712901	-0.973291	1.651554
H	-3.752880	0.806831	1.613715
H	-3.930455	-0.059064	3.164980
H	3.262428	4.081143	-0.717713
H	-2.540085	0.024861	-4.626680
H	3.231535	-4.093936	-0.571036
H	2.349777	-0.041168	-3.453373

Thermodynamic Properties at 298.15 K

Zero Point Energy :	858.03	kJ/mol	(ZPE)
Temperature Correction :	65.36	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	923.39	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-1503.353367	au	(Electronic Energy + Enthalpy Correction)
Entropy :	666.47	J/mol•K	
Gibbs Energy :	-1503.429051	au	(Enthalpy - T*Entropy)
C_v :	452.41	J/mol•K	

15. [W(TeCPMe$_3$)(CO)$_2$(Tp*)]$^+$ -PCM κ = 7.43 (THF)

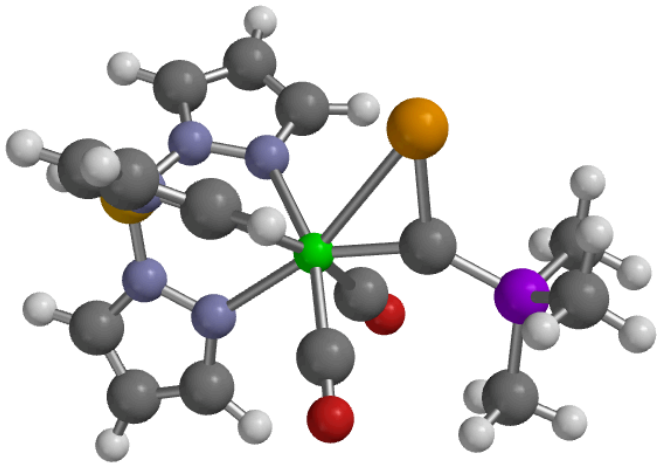


Figure S16: Optimised structure of the cation [W(TeCPMe$_3$)(CO)$_2$(Tp*)]$^+$ [DFT: ωB97X–D/6–31G*/ LANL2Dζ/PCM κ = 7.43 (THF)].

Cartesian Coordinates

Atom	x	y	z
W	0.058614	0.035266	0.111607
Te	-1.322415	1.306055	2.364660
P	0.808422	3.439167	0.816094
O	0.001685	1.794080	-2.508102
O	3.155282	0.255790	0.675910
N	0.749316	-1.426436	-1.400979
N	0.135247	-2.631478	-1.509442
N	-1.926575	-0.717268	-0.499004
N	-2.153995	-2.033321	-0.706627
N	0.046735	-1.794667	1.345902
N	-0.467870	-2.957377	0.883847
C	0.089533	1.810019	0.910601
C	0.052434	1.175485	-1.539647
C	2.025294	0.198131	0.463339
C	1.709063	-1.381949	-2.335725
C	1.722001	-2.570535	-3.059119
H	2.375766	-2.840226	-3.874086
C	0.708455	-3.332994	-2.497828
C	-3.065411	-0.070843	-0.769519
C	-4.050895	-0.981583	-1.152716
H	-5.072881	-0.771755	-1.428282
C	-3.424426	-2.215999	-1.101875
C	0.517938	-2.030974	2.575352
C	0.300741	-3.364529	2.920584
H	0.563890	-3.859615	3.842650
C	-0.323537	-3.915598	1.812890
B	-1.010254	-3.049115	-0.553285
H	-1.381826	-4.160178	-0.805495
H	-3.116466	1.004199	-0.667794
H	0.979303	-1.234505	3.141853
H	-3.788727	-3.208468	-1.324058
H	-0.668716	-4.920512	1.617648
H	2.332014	-0.504073	-2.435114
H	0.356086	-4.326881	-2.733079
C	-0.471675	4.600275	0.292503

Atom	x	y	z
H	-0.037511	5.603023	0.247797
H	-1.294651	4.583462	1.010734
H	-0.837057	4.311508	-0.696288
C	1.444175	3.921356	2.434612
H	2.174879	3.180368	2.769282
H	0.623364	3.980941	3.152452
H	1.925761	4.898714	2.339542
C	2.179112	3.525779	-0.358690
H	2.982132	2.853215	-0.049985
H	2.553386	4.553856	-0.357641
H	1.844262	3.270189	-1.365475

Thermodynamic Properties at 298.15 K

Zero Point Energy :	859.87	kJ/mol	(ZPE)
Temperature Correction :	64.63	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	924.50	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-1503.391182	au	(Electronic Energy + Enthalpy Correction)
Entropy :	662.68	J/mol•K	
Gibbs Energy :	-1503.466436	au	(Enthalpy - T*Entropy)
C_v :	449.33	J/mol•K	

16. [W(CNMe)(PMe$_3$)(CO)$_2$(Tp*)]$^+$ -PCM κ = 7.43 (THF)

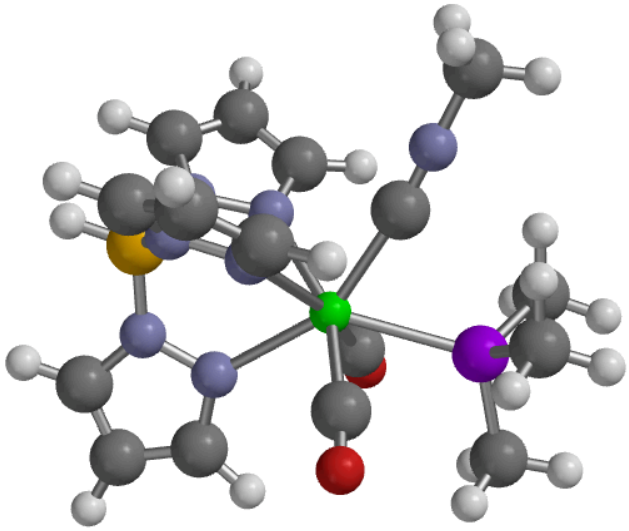


Figure S17: Optimised structure of the cation [W(CNMe)(PMe$_3$)(CO)$_2$(Tp*)]$^+$ [DFT: ωB97X–D/6–31G*/ LANL2Dζ/PCM κ = 7.43 (THF)].

Cartesian Coordinates

Atom	x	y	z
W	-0.399008	-0.031070	0.353294
C	-2.051605	1.062363	0.378210
O	-3.041648	1.653680	0.281431
C	-0.458849	-1.245853	1.919088
O	-0.484578	-2.050241	2.750269
P	-0.304218	1.415984	2.429943
B	-0.308934	-1.866930	-2.453546
N	-1.817825	-1.559629	-0.451881
N	-1.569524	-2.184895	-1.625090
C	-2.561069	-3.053600	-1.890819
C	-3.485275	-2.996767	-0.862544
C	-2.972483	-2.042251	0.018068
N	-0.360476	0.565709	-1.809018
N	-0.322297	-0.362679	-2.790348
C	-0.315366	0.245772	-3.988780
C	-0.348014	1.615350	-3.787344
C	-0.375950	1.764688	-2.399454
C	1.338139	1.122265	0.271567
N	1.098503	-1.527010	-0.395739
N	0.927657	-2.155157	-1.580020
C	2.240362	-1.979965	0.130851
C	1.951804	-2.998060	-1.797128
C	2.822436	-2.918699	-0.723227
H	-3.369495	-1.680698	0.956051
H	-0.405325	2.662970	-1.798758
H	-2.535479	-3.648223	-2.792338
H	-0.289473	-0.339573	-4.896417
H	2.579100	-1.608554	1.087899
H	1.985667	-3.593267	-2.698068
C	-1.709761	1.205455	3.577541
H	-1.752065	0.174161	3.935688
H	-2.647823	1.444664	3.071040
H	-1.579396	1.877825	4.430746
C	1.153537	1.143341	3.497590
H	1.166039	0.106625	3.843569
H	1.102778	1.813107	4.361469
H	2.071797	1.342123	2.939951
C	-0.286194	3.216183	2.115684
H	-1.194314	3.503636	1.579648
H	0.582668	3.484370	1.510023
H	-0.242865	3.752520	3.068479
H	3.743497	-3.462335	-0.578909
H	-0.352944	2.392279	-4.536361
H	-4.398437	-3.563206	-0.763144
H	-0.284480	-2.526122	-3.454483
N	2.333372	1.701692	0.107482
C	3.552672	2.400743	-0.097600
H	4.356475	1.677239	-0.246703
H	3.762701	3.013021	0.781428
H	3.455964	3.037019	-0.979292

Thermodynamic Properties at 298.15 K

Zero Point Energy :	967.61	kJ/mol	(ZPE)
Temperature Correction :	68.46	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	1036.07	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-1589.931991	au	(Electronic Energy + Enthalpy Correction)
Entropy :	681.06	J/mol•K	
Gibbs Energy :	-1590.009332	au	(Enthalpy - T*Entropy)
C_v :	476.30	J/mol•K	

17. [W(MeNCPMe$_3$)(CO)$_2$(Tp*)]$^+$ -PCM κ = 7.43 (THF)

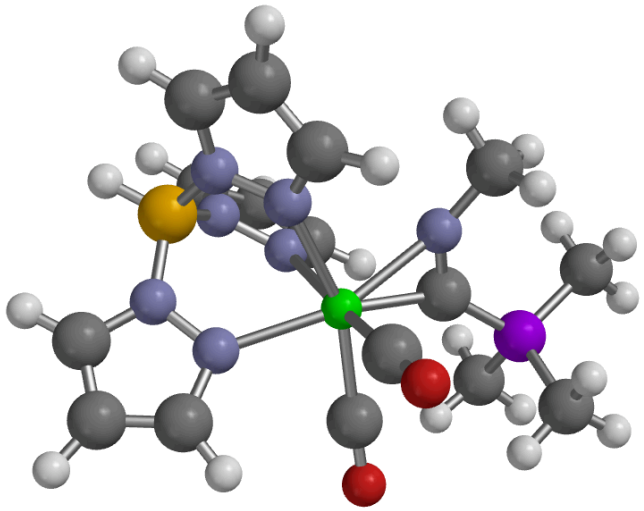


Figure S18: Optimised structure of the cation [W(MeNCPMe$_3$)(CO)$_2$(Tp*)]$^+$ [DFT: ωB97X–D/6–31G*/ LANL2DζPCM κ = 7.43 (THF)].

Cartesian Coordinates

Atom	x	y	z
W	0.754490	-0.255601	-0.256462
P	0.356727	3.413770	0.430489
O	1.814911	1.499209	-2.665631
O	3.781608	-0.155941	0.437018
N	0.805004	-1.827027	-1.798656
N	-0.119725	-2.817981	-1.833742
N	-1.504554	-0.479274	-0.594177
N	-2.060267	-1.704641	-0.721860
N	0.468008	-2.074154	0.968882
N	-0.416689	-3.037696	0.624820
C	0.235618	1.615005	0.529959
C	1.384436	0.856341	-1.801977
C	2.637501	-0.189733	0.171982
C	1.660091	-2.060059	-2.802864
C	1.283944	-3.204268	-3.504683
H	1.770127	-3.645332	-4.361525
C	0.153620	-3.658063	-2.844476
C	-2.505750	0.401029	-0.666275
C	-3.727150	-0.255929	-0.842129
H	-4.708806	0.182463	-0.937094
C	-3.391803	-1.598654	-0.873664
C	1.006416	-2.433078	2.139322
C	0.462129	-3.644820	2.566561
H	0.692309	-4.194384	3.466472
C	-0.434090	-3.993105	1.567428
B	-1.176241	-2.959355	-0.718284
H	-1.838306	-3.946662	-0.885324
H	-2.307782	1.460228	-0.591418
H	1.753090	-1.804836	2.604532
H	-4.000580	-2.482759	-0.997805
H	-1.076658	-4.855084	1.459635
H	2.500444	-1.400267	-2.963325
H	-0.469294	-4.523868	-3.016875
C	-0.520566	3.946442	-1.048749
H	-0.327825	5.012254	-1.199347
H	-1.594466	3.786211	-0.917959
H	-0.163329	3.382056	-1.914162
C	-0.324140	4.248964	1.876487
H	0.288755	4.031615	2.754473
H	-1.351669	3.914537	2.041765
H	-0.315319	5.326170	1.685259
C	2.118816	3.765155	0.273827
H	2.651268	3.335972	1.127755
H	2.255812	4.850410	0.255890
H	2.497485	3.329267	-0.653904
N	0.149314	0.835771	1.517309
C	0.199249	0.981322	2.955400
H	1.226080	1.215604	3.258006
H	-0.098754	0.036774	3.411412
H	-0.473489	1.776002	3.287688

Thermodynamic Properties at 298.15 K

Zero Point Energy :	969.39	kJ/mol	(ZPE)
Temperature Correction :	66.91	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	1036.31	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-1589.908638	au	(Electronic Energy + Enthalpy Correction)
Entropy :	670.18	J/mol•K	
Gibbs Energy :	-1589.984743	au	(Enthalpy - T*Entropy)
C_v :	468.42	J/mol•K	

Table S1. Gibbs Energy (au)[a] for Isomeric $[W(ECPMe_3)(CO)_2(Tp)]^+$ **2^E** *vs* $[W(CE)(PMe_3)(CO)_2(Tp)]^+$ **8^E**.

	8^E	**2^E**	**8^E** → **2^E**	
	ΔG°	ΔG°	ΔΔG°	ΔΔG°
E	a.u.	a.u.	a.u.	kcalmol^{-1}
O	-1570.911292	-1570.870482	+0.04081	+25.61
S	-1893.844183	-1893.855864	-0.011681	-7.33
Se	-3896.986728	-3897.011456	-0.024728	-15.52
Te	-1503.705068	-1503.743305	-0.038237	-24.00
NMe	-1590.326609	-1590.303348	+0.023261	+14.60

[a]DFT: ωB97X-D/6-31G*/LANL2Dζ/polarization continuum model (ε = 7.43).

Table S2. Calculated Infrared data for $[W(ECPMe_3)(CO)_2(Tp)]^+$ **2^E** *vs* $[W(CE)(PMe_3)(CO)_2(Tp)]^+$ **8^E**.

E	$[W(CE)(PMe_3)(CO)_2(Tp)]^+$ **8^E**			$[W(ECPMe_3)(CO)_2(Tp)]^+$ **2^E**		
	ν_{CO} [cm^{-1}]	ν_{CO}[cm^{-1}]	k_{CO} [Ncm^{-1}]	ν_{CO} [cm^{-1}]	ν_{CO} [cm^{-1}]	k_{CO} [Ncm^{-1}]
	Raw	Scaled[a]		Raw	Scaled[a]	
O	2160	2034		2106	1984	
	2050	1931	*b*	1976	1861	14.92
S	2135	2011[d]		2118	1995	
	2068	1948	15.80	2025	1908	15.36
Se	2137	2013		2123	2000	
	2034	1916[e]	15.57	2034	1916	15.47
Te	2143	2019[f]		2125	2002	
	2088	1967	16.02	2041	1923	15.54
NMe	2078[g]	1957[i]		2052	1933	
	1990	1975	15.59	1924	1812	14.15

[a]λ = 0.942: [b]Molecule has C_{3v} symmetry, *i.e.*, modes not directly comparable. [c]Experimentally determined for $[W(CO)_3(PMe_3)(Tp^*)]^+$ ν_{CO} = 2040, 1943 cm^{-1} in CH_2Cl_2. [d]ν_{CS} = 1210 cm^{-1}. [e]ν_{CSe} = 1057 cm^{-1}. [f]ν_{CTe} = 980 cm^{-1}. [g]ν_{CN} = 2205 cm^{-1}.

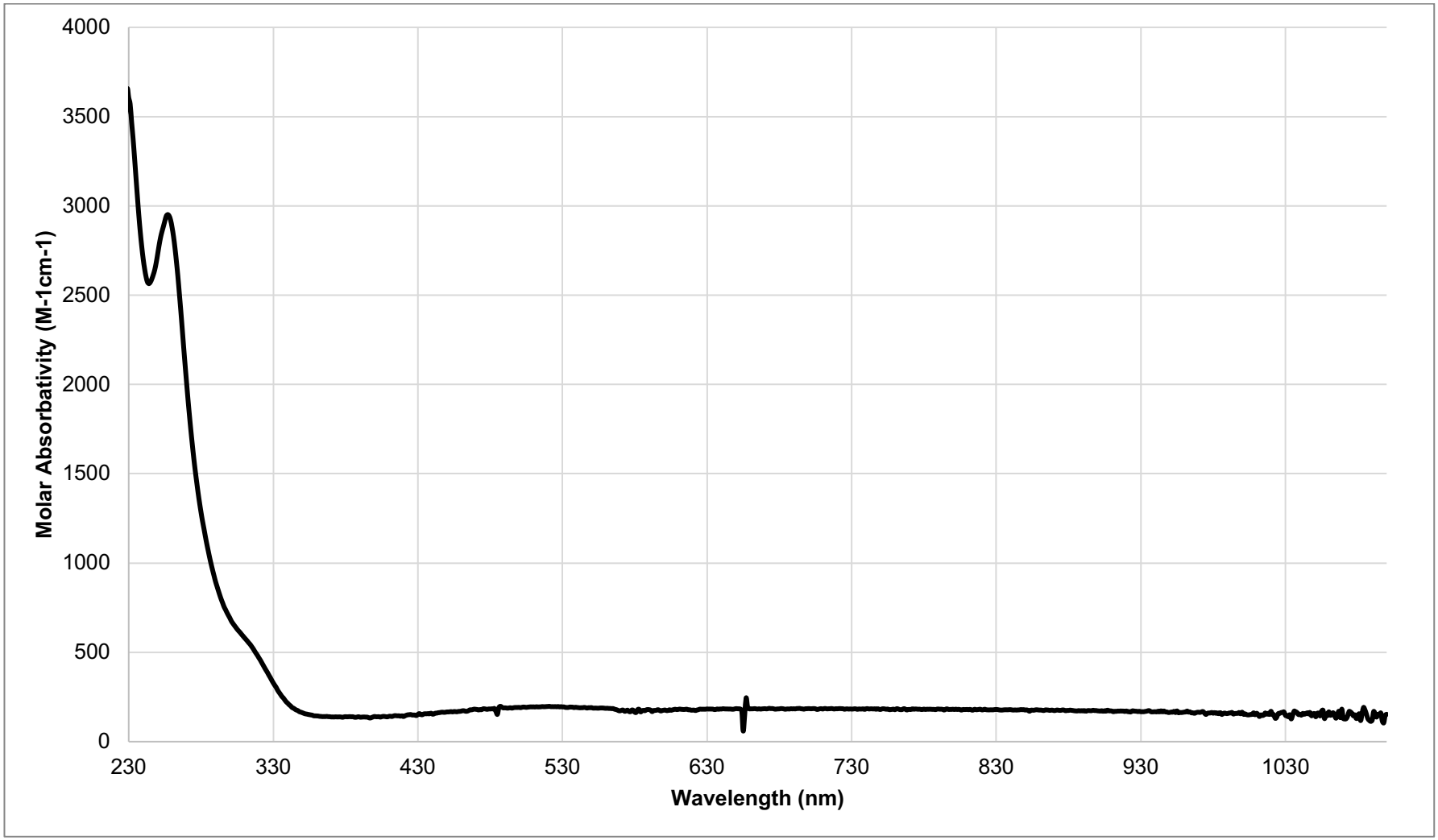


Figure S19 Electronic spectrum of $[W(CPPh_3)(CO)_2(Tp^*)].PF_6$· in CH_2Cl_2 [1a; M = 2.319(2)×10^{-5} molL^{-1}].

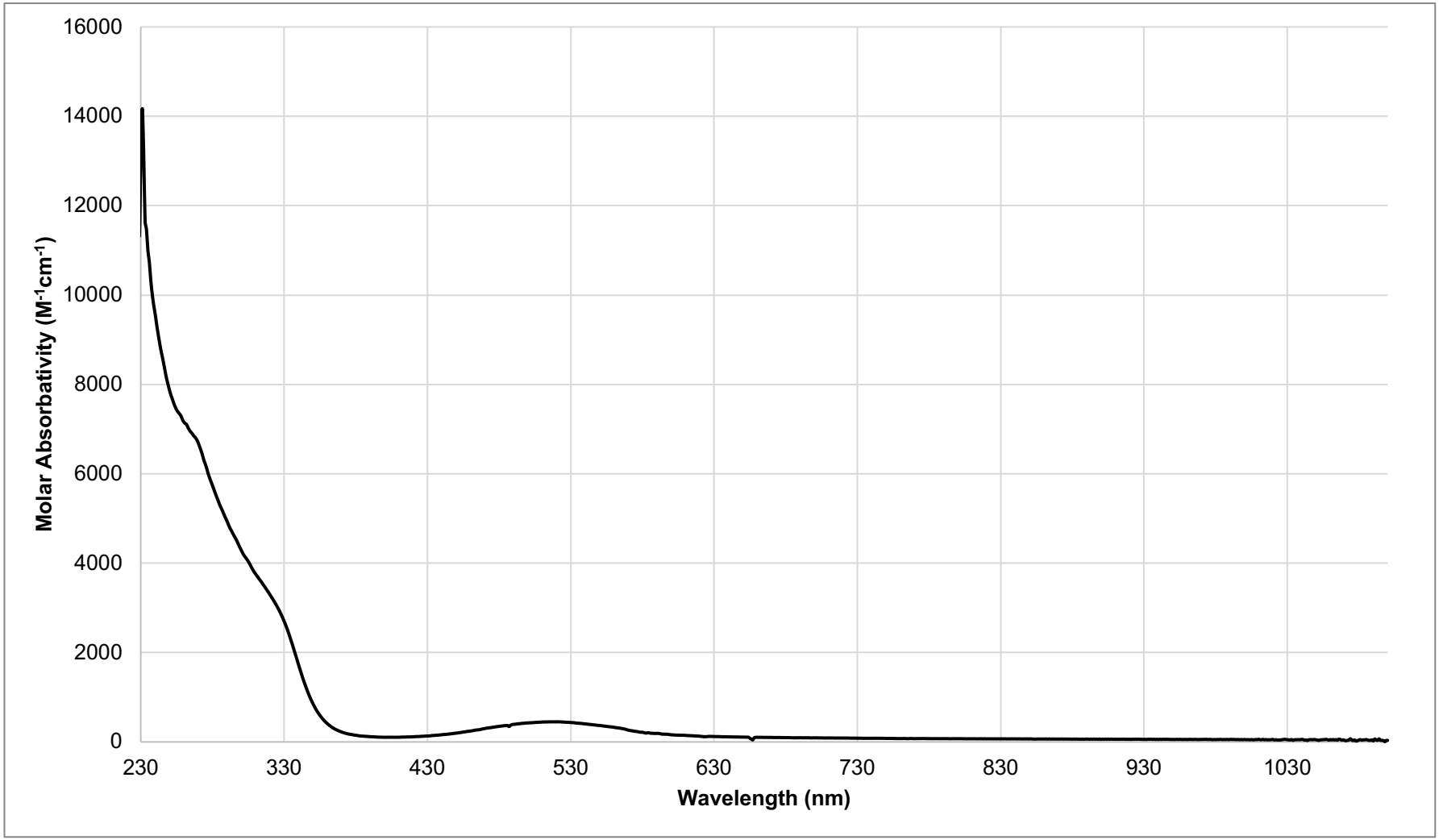


Figure S20: Electronic spectrum of $[W(CPPh_3)(CO)_2(Tp^*)].PF_6$· in CH_2Cl_2 [1a; M = 2.319(2)×10^{-4} molL^{-1}].

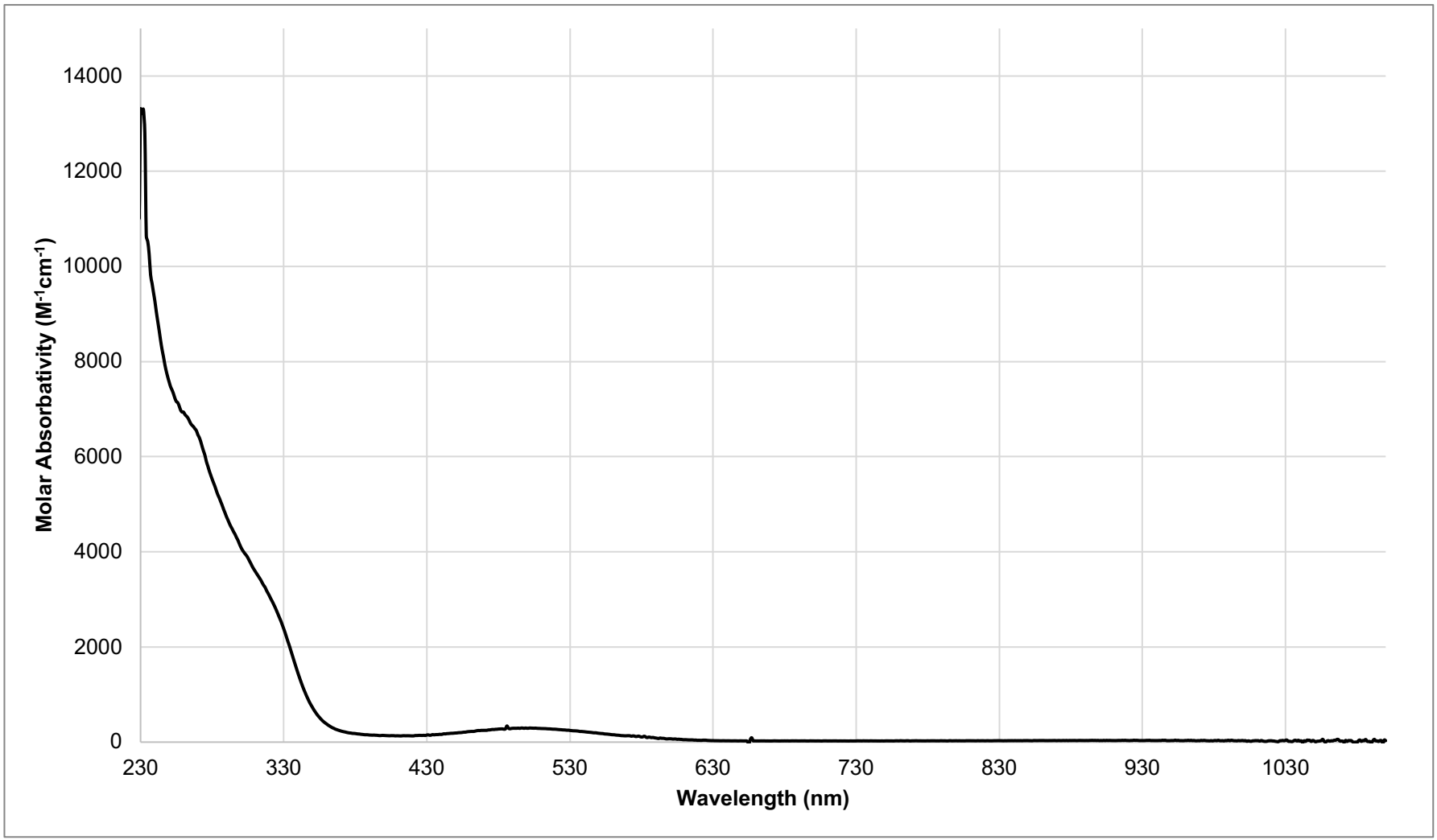


Figure S21: Electronic spectrum of $[W(CPMePh_2)(CO)_2(Tp^*)].PF_6$· in CH_2Cl_2 [1b; M = 2.404(2)×10^{-4} molL^{-1}].

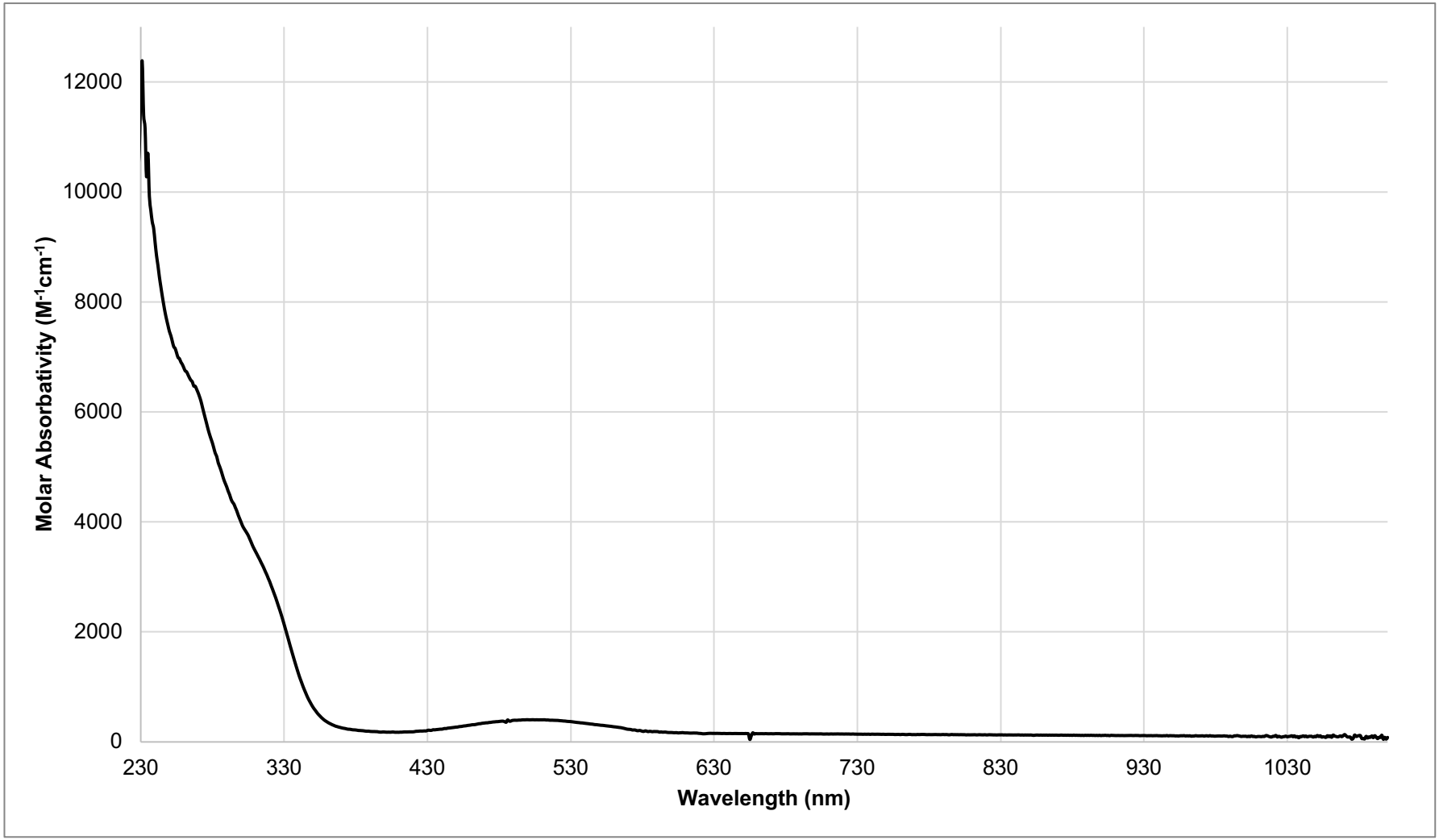


Figure S22: Electronic spectrum of [W(CPMe$_2$Ph)(CO)$_2$(Tp*)].PF$_6$· in CH$_2$Cl$_2$ [1b; M = 2.475(2)×10^{-4} molL^{-1}].

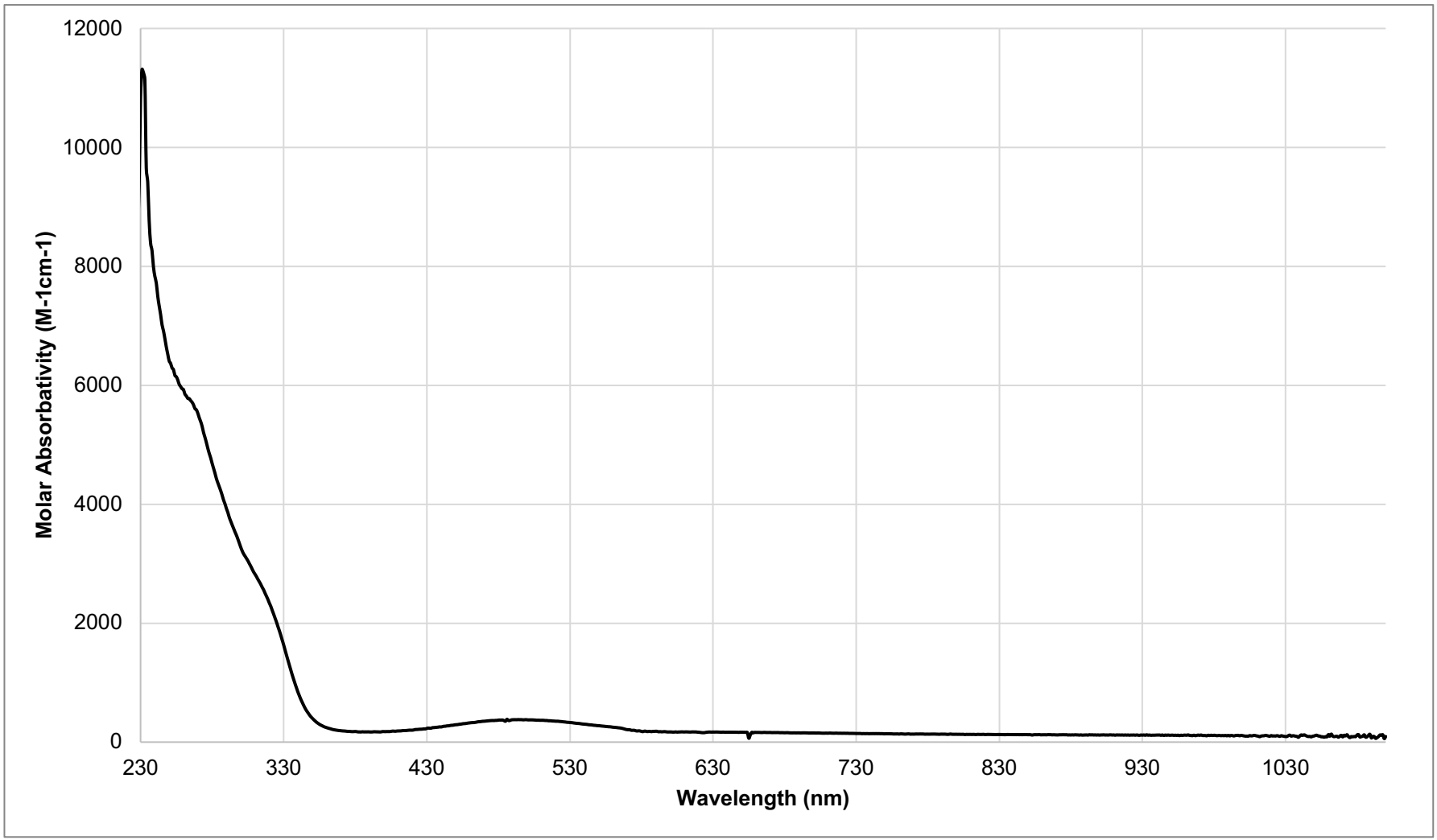


Figure S23: Electronic spectrum of $[W(CPCy_3)(CO)_2(Tp^*)].PF_6$· in CH_2Cl_2 [1d; M = 2.830(3)×10^{-4} molL^{-1}].

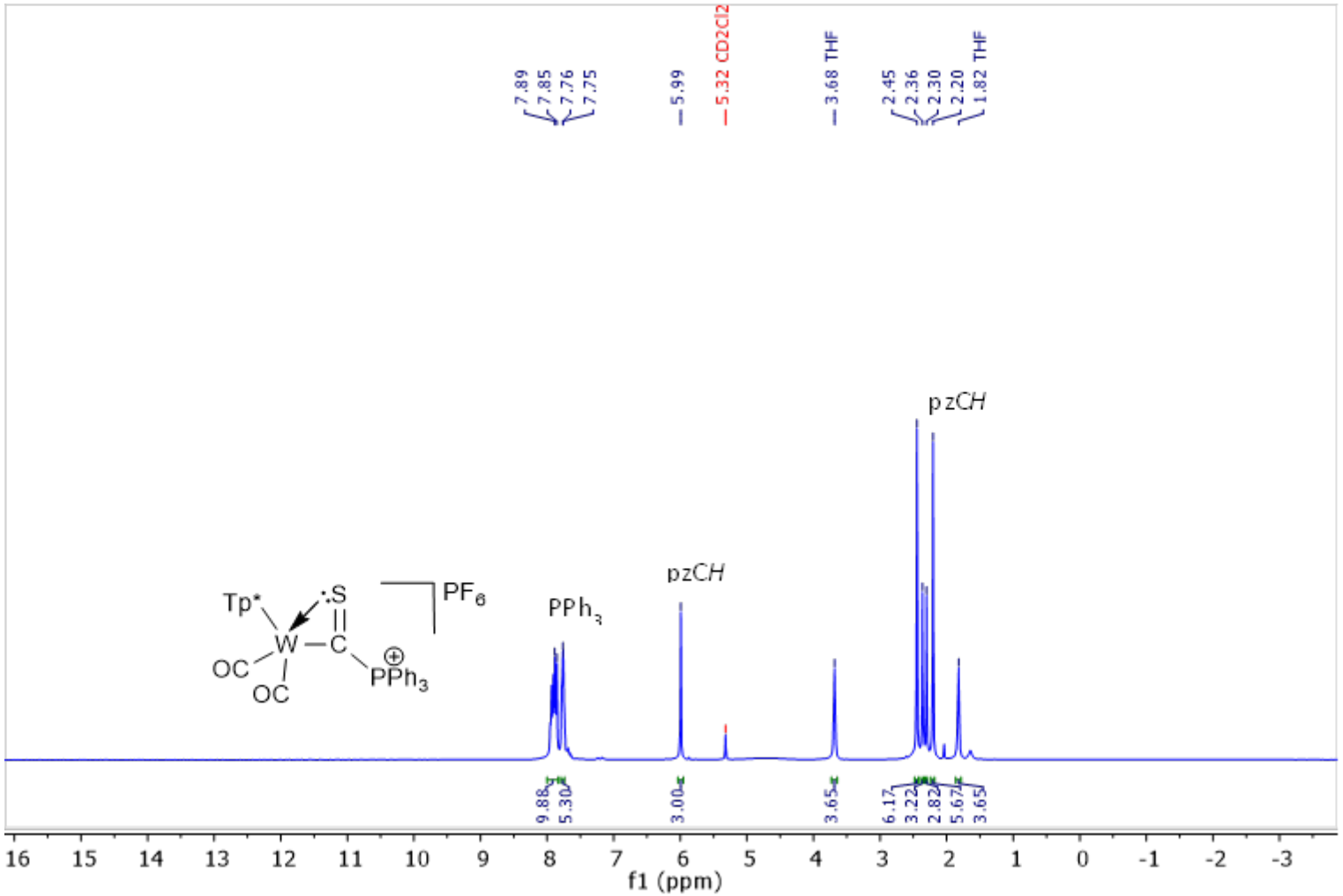


Figure S24: ^{1}H NMR Spectrum of $[W(CSPPh_3)(CO)_2(Tp^*)]PF_6 \cdot 2(C_4H_4O)$ (2a; 400 MHz, CD_2Cl_2, 25 °C, δ)

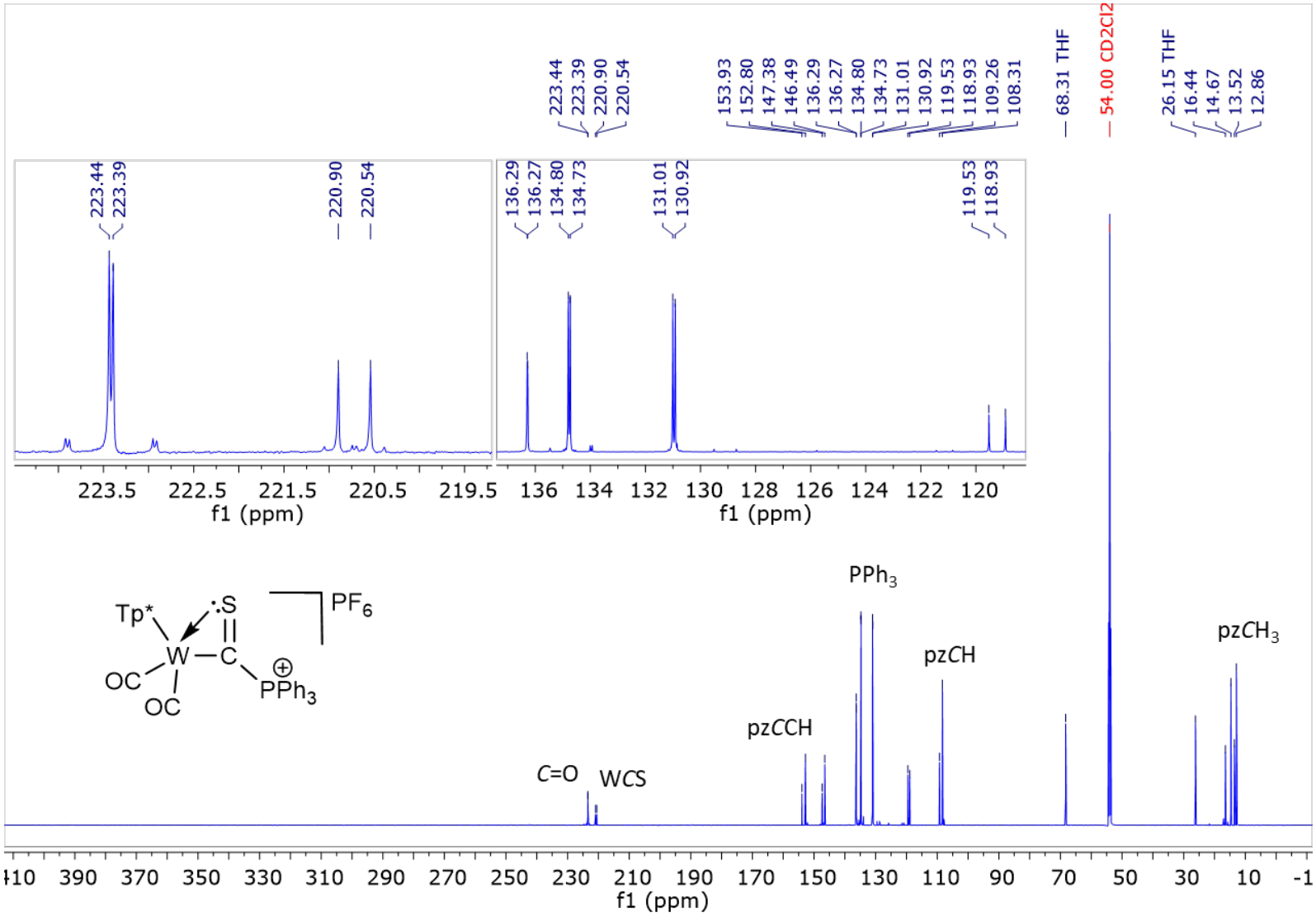


Figure S25: $^{13}C\{^1H\}$ NMR Spectrum of $[W(CSPPh_3)(CO)_2(Tp^*)]PF_6 \cdot 2(C_4H_4O)$ (2a; 151 MHz, CD_2Cl_2, 25 °C, δ)

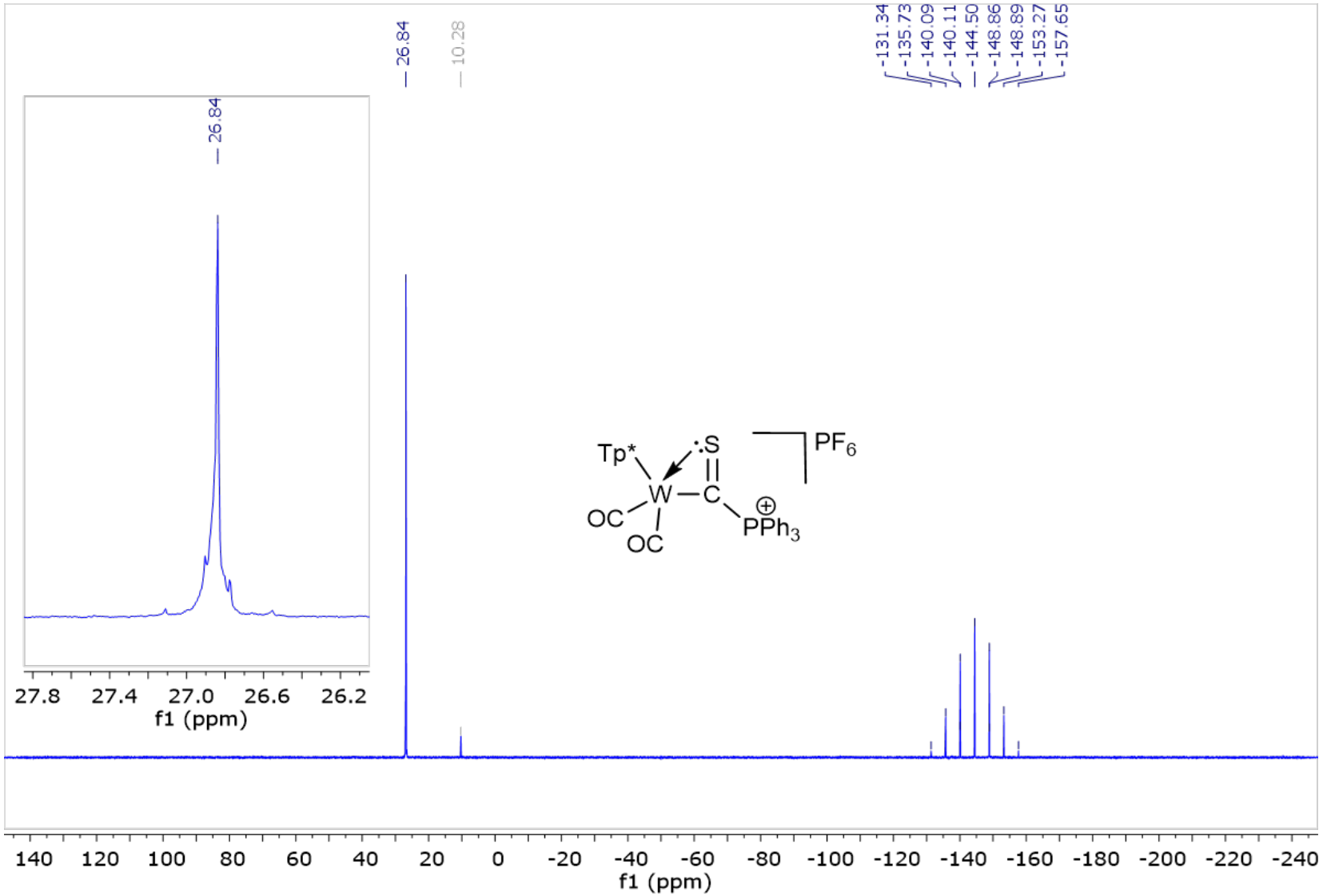


Figure S26: $^{31}P\{^{1}H\}$ NMR Spectrum of $[W(CSPPh_3)(CO)_2(Tp^*)]PF_6 \cdot 2(C_4H_4O)$ (2a; 162 MHz, $CDCl_3$, 25 °C, δ)

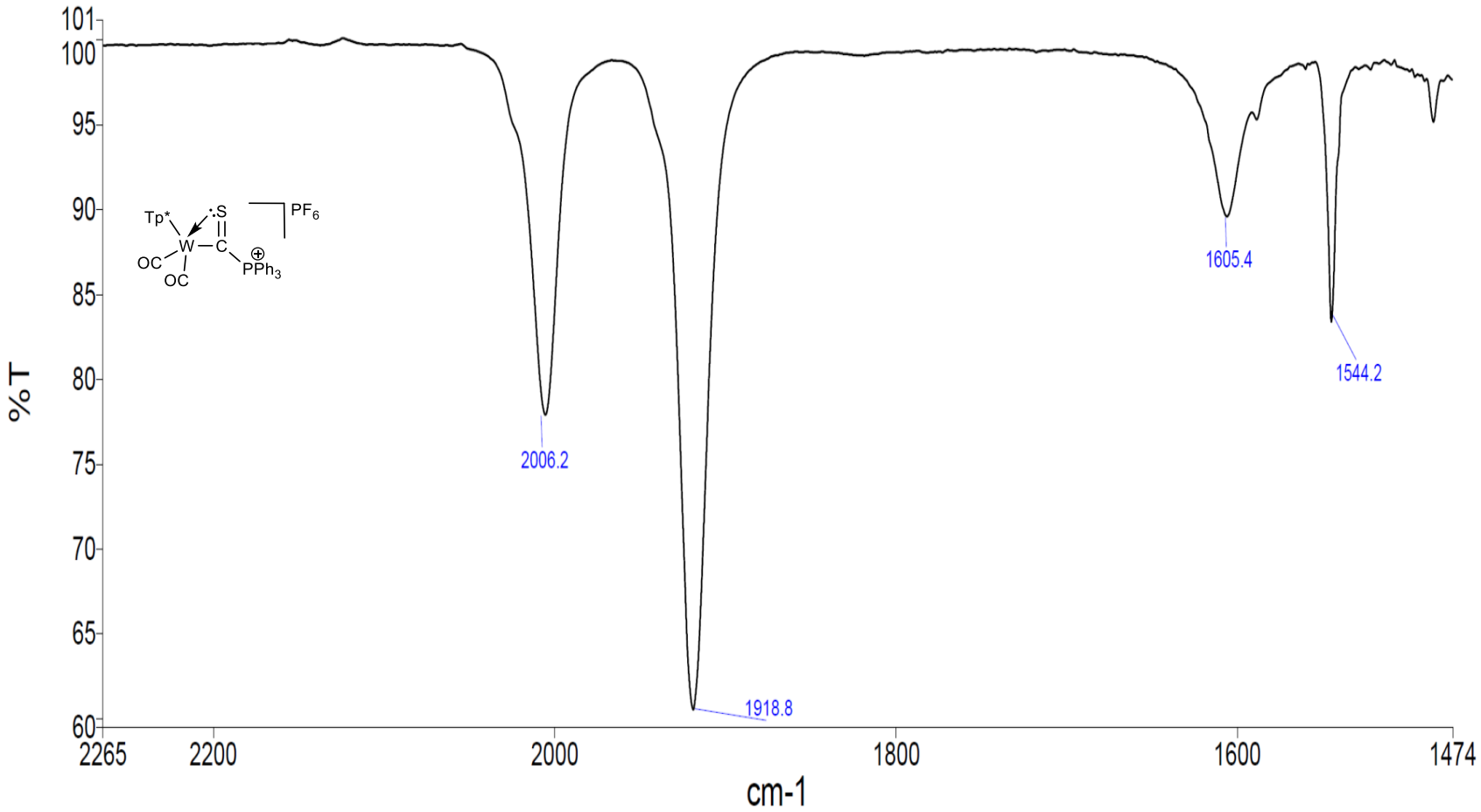


Figure S27: Infrared Spectrum of $[W(CSPPh_3)(CO)_2(Tp^*)]PF_6 \cdot 2(C_4H_4O)$ (2a; CH_2Cl_2, 25 °C, ν)

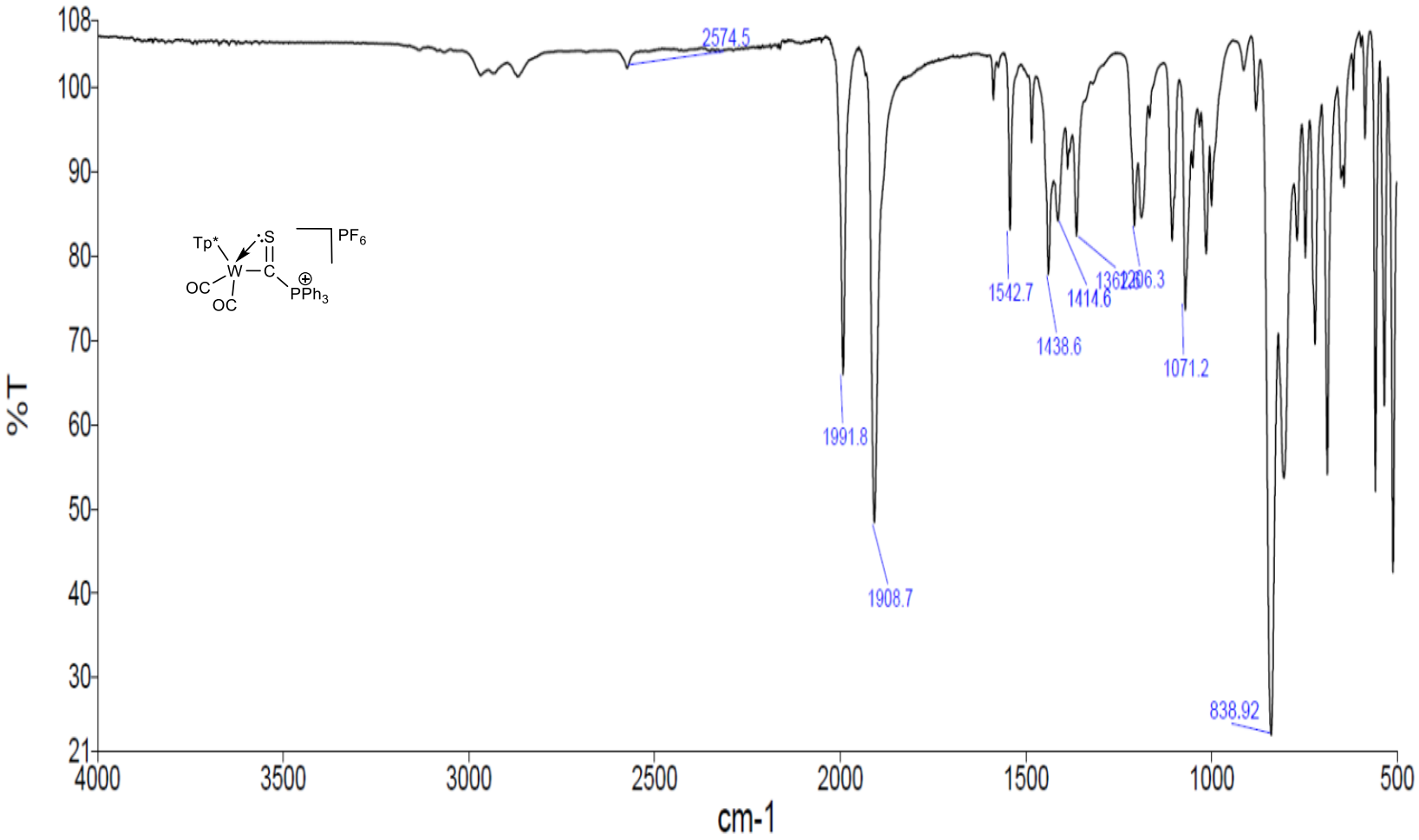


Figure S28: Infrared Spectrum of $[W(CSPPh_3)(CO)_2(Tp^*)]PF_6 \cdot 2(C_4H_4O)$ (2a; ATR, 25 °C, ν)

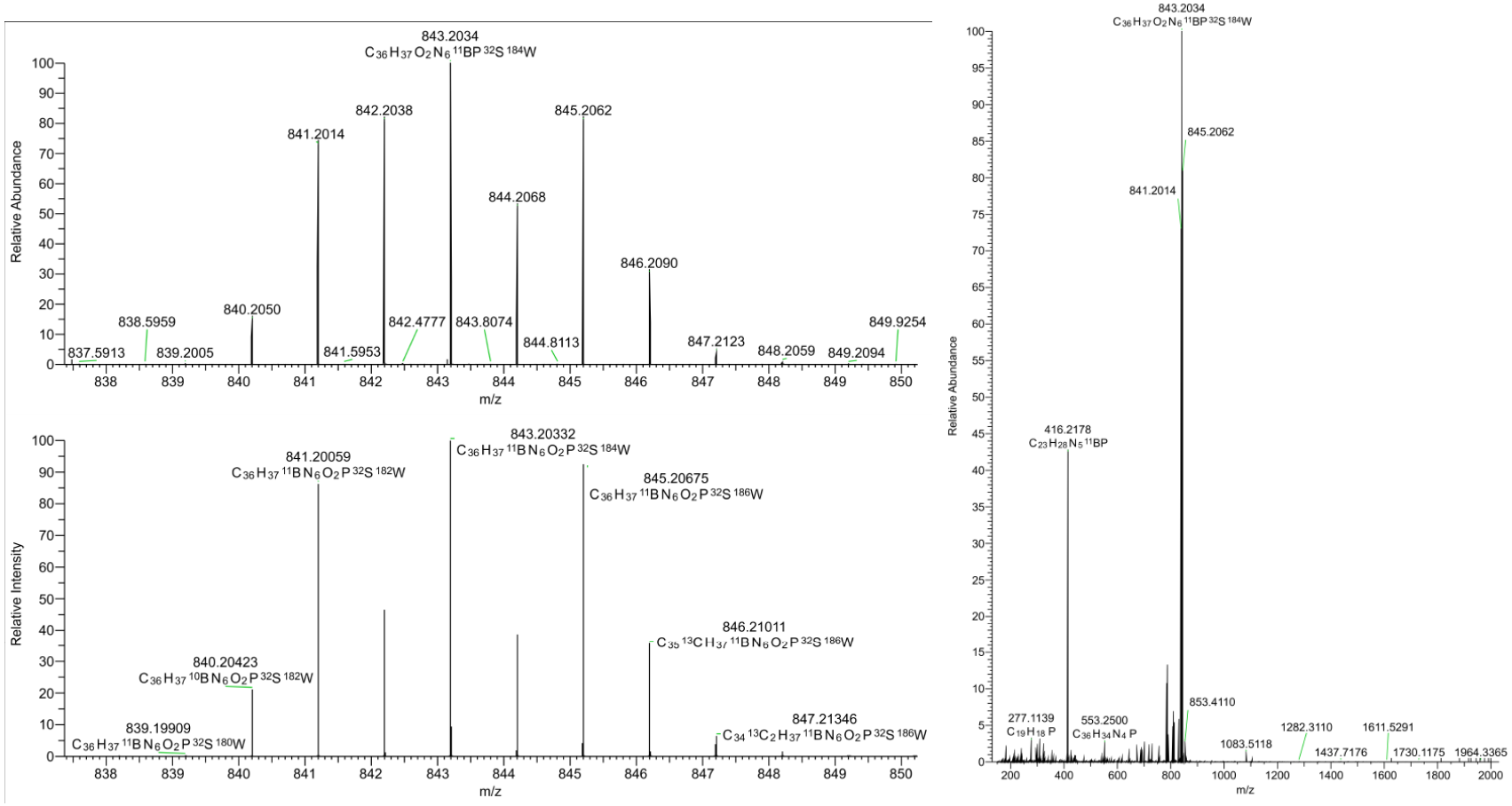


Figure S29: Mass Spectrum (ESI, +ve ion) of $[W(SCPPh_3)(CO)_2(Tp^*)]PF_6 \cdot 2(C_4H_4O)$ (2a)

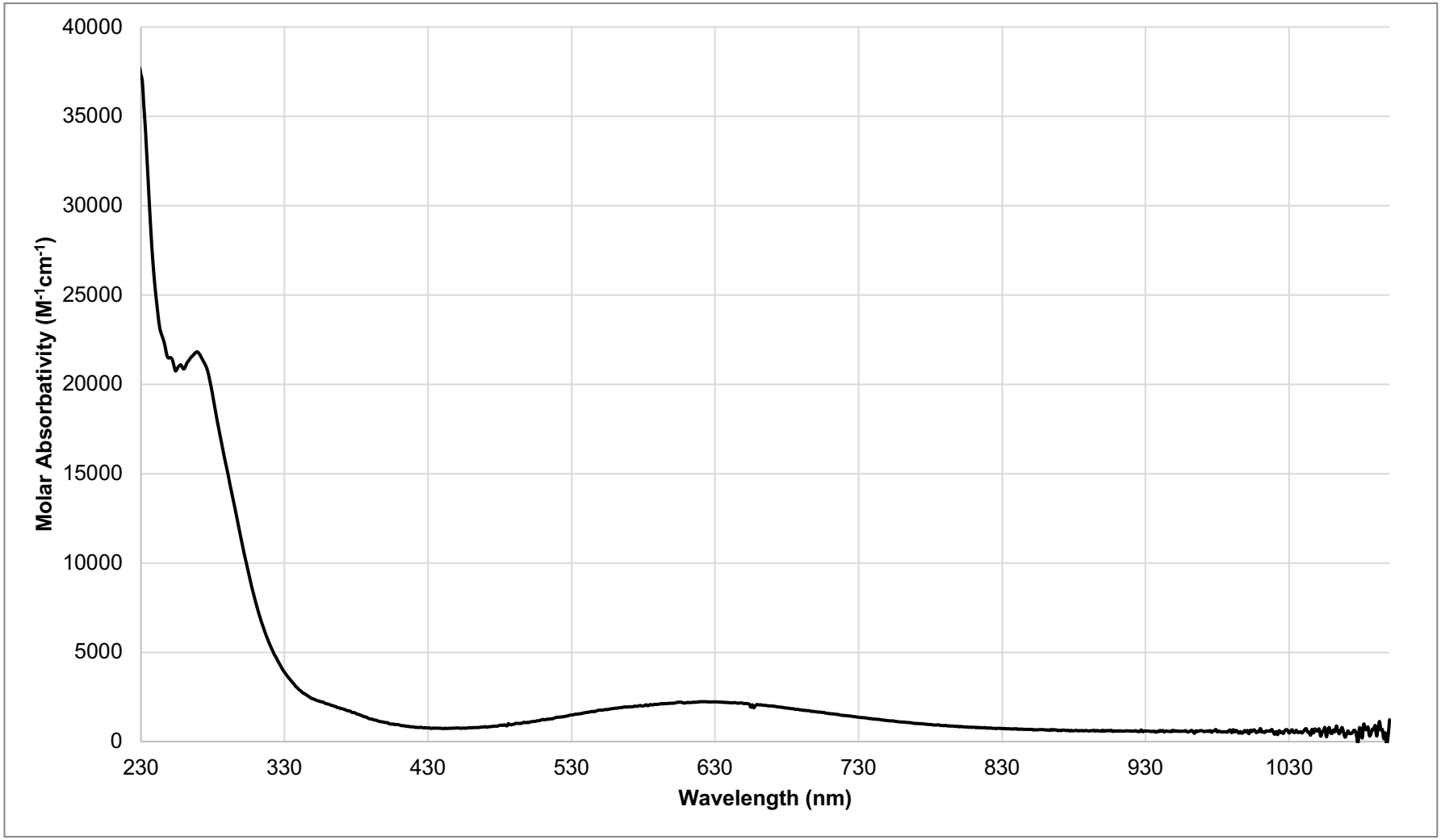


Figure S30: Electronic spectrum of $[W(SCPPh_3)(CO)_2(Tp^*)].PF_6 \cdot 2(C_4H_4O)$ in CH_2Cl_2 [2a; M = 2.420(2)×10^{-5} molL^{-1}].

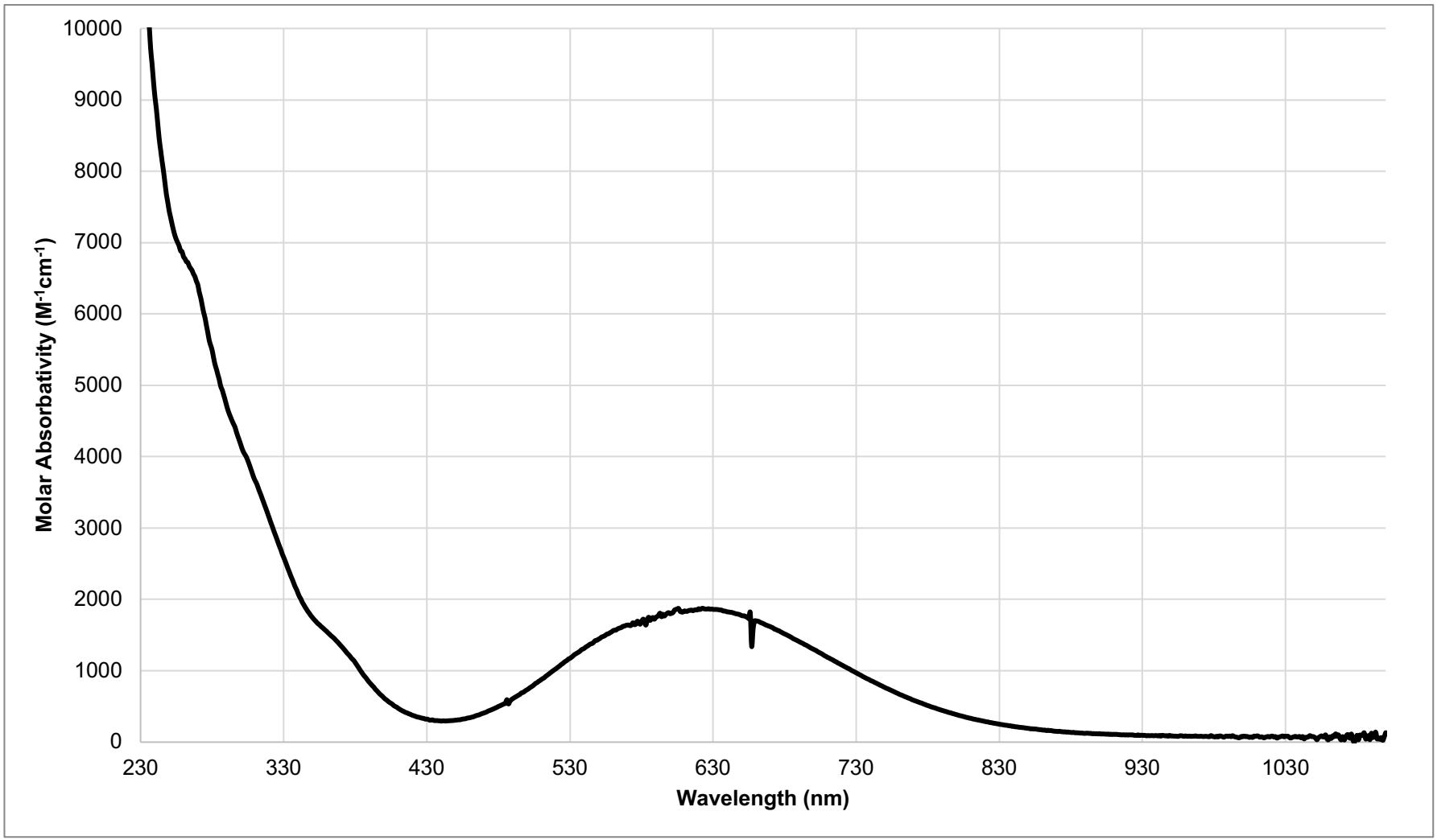


Figure S31: Electronic spectrum of $[W(SCPPh_3)(CO)_2(Tp^*)].PF_6 \cdot 2(C_4H_4O)$ in CH_2Cl_2 [2a; M = 2.420(2)×10^{-4} molL^{-1}].

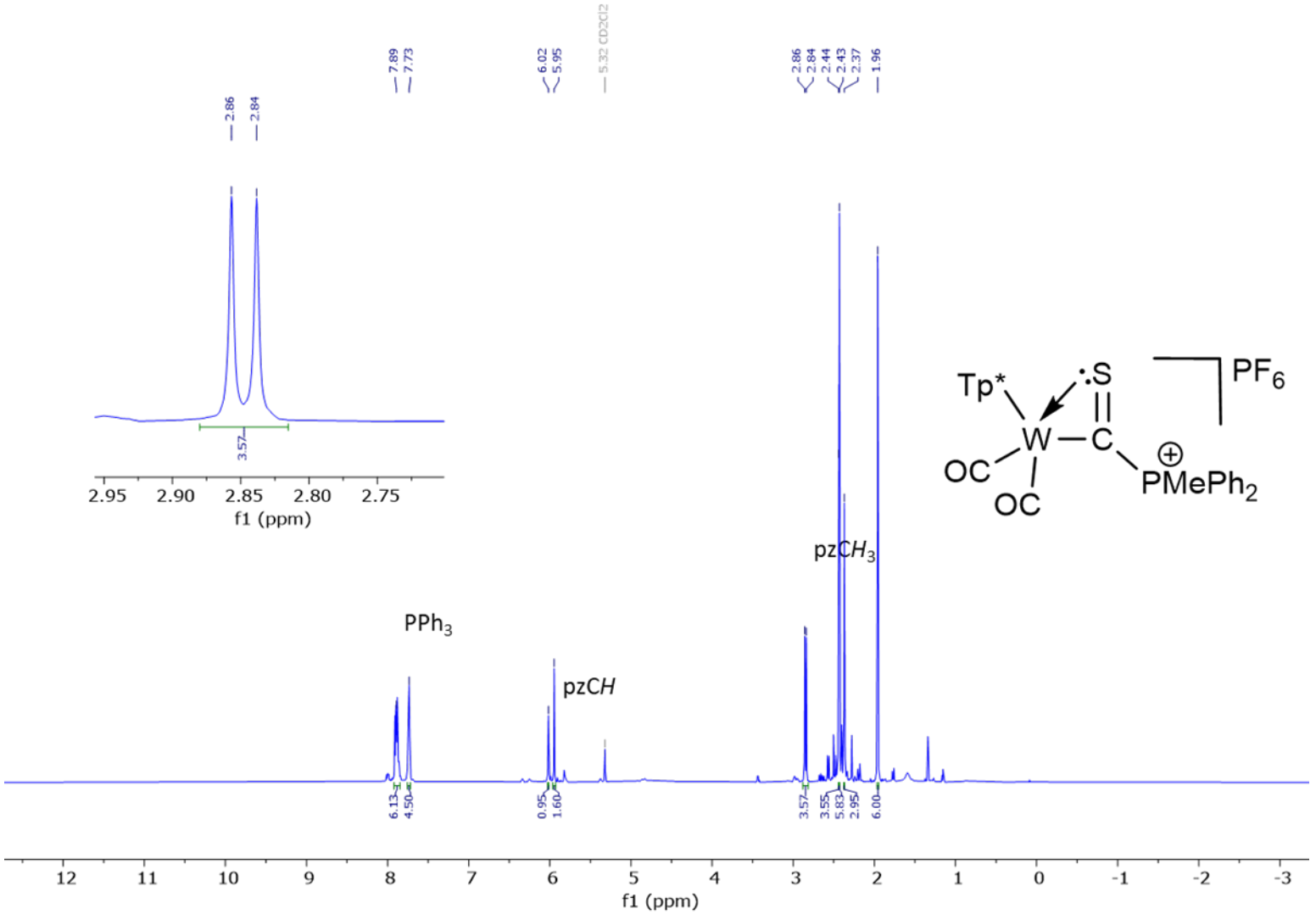


Figure S32: ^{1}H NMR Spectrum of [W(SCPMePh$_2$)(CO)$_2$(Tp*)]PF$_6$ (2b; 700 MHz, CD$_2$Cl$_2$, 25 °C, δ):

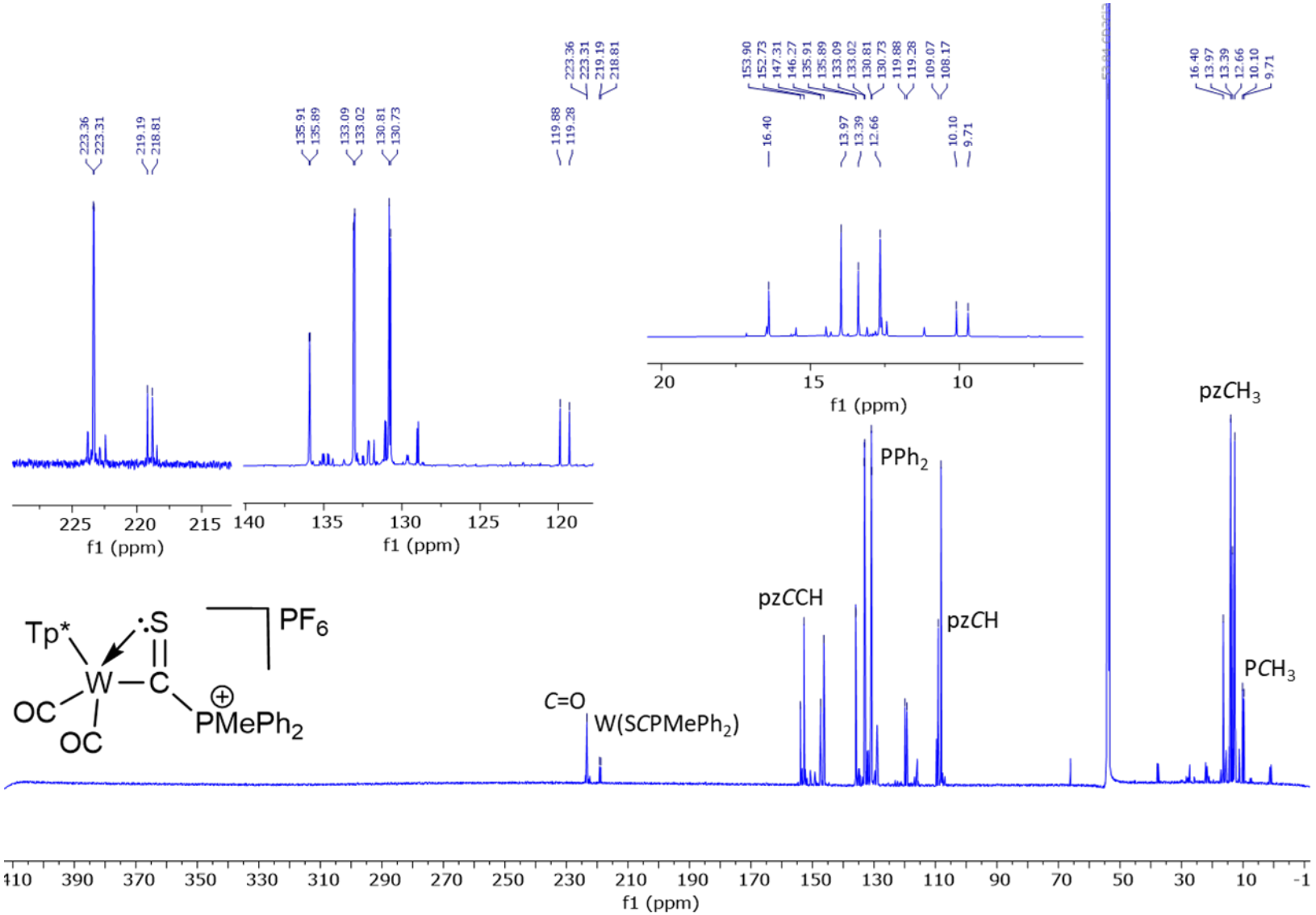


Figure S33: $^{13}C\{^1H\}$ NMR Spectrum of $[W(SCPMePh_2)(CO)_2(Tp^*)]PF_6$ (2b; 151 MHz, CD_2Cl_2, 25 °C, δ)

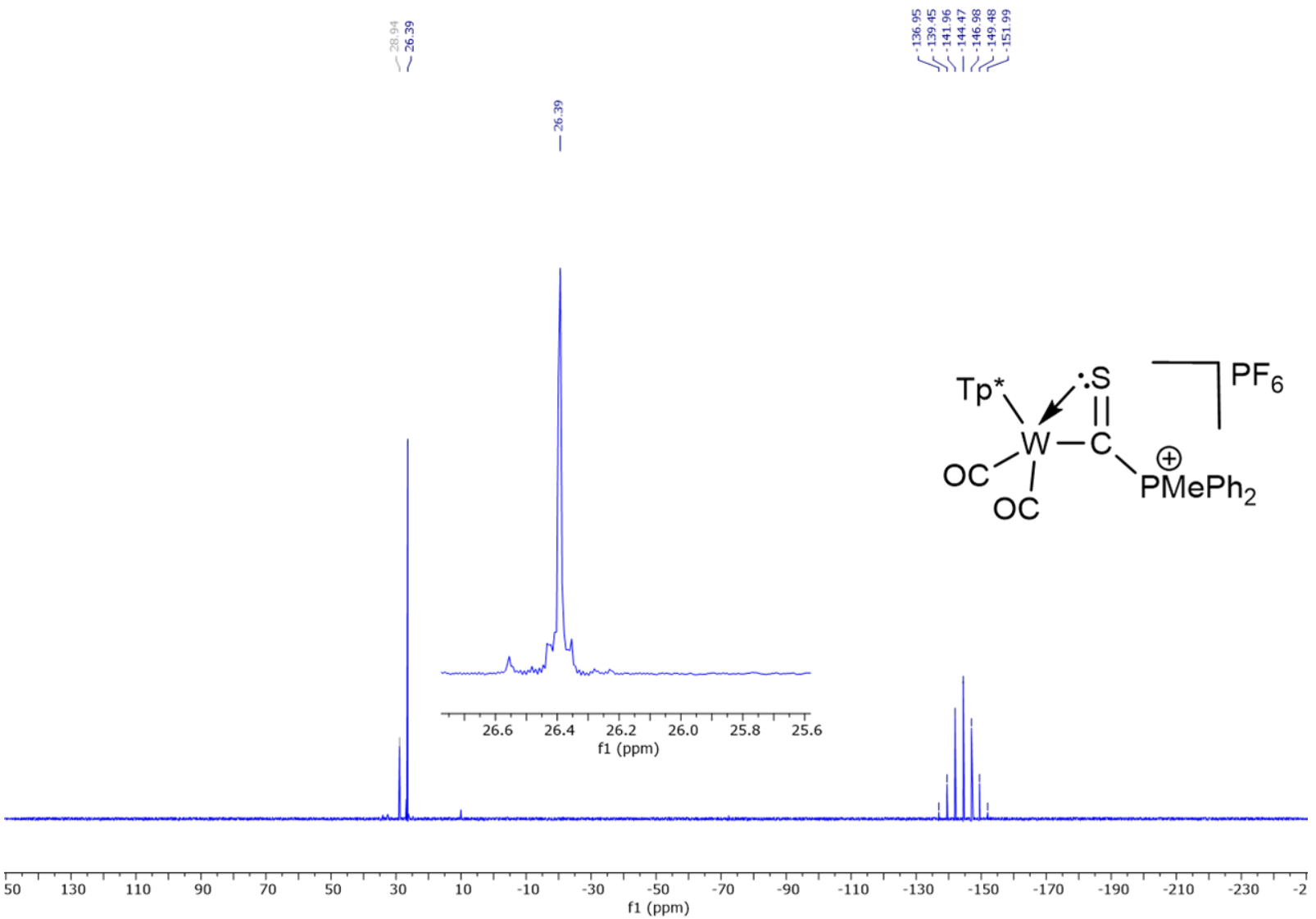


Figure S34: $^{31}P\{^{1}H\}$ NMR Spectrum of $[W(SCPMePh_2)(CO)_2(Tp^*)]PF_6$ (2b, 283 MHz, CD_2Cl_2, 25 °C, δ)

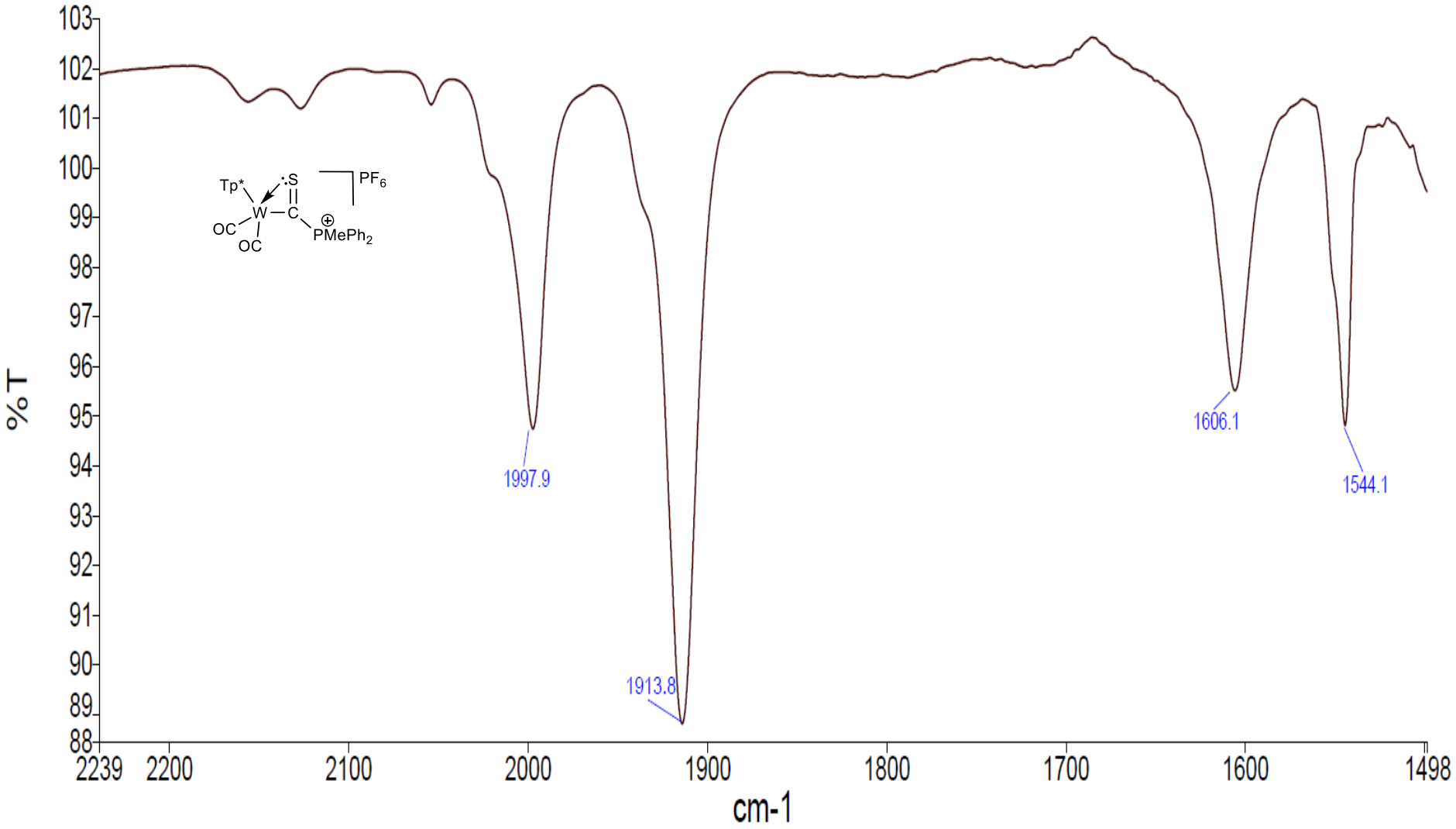


Figure S35: Infrared Spectrum of [W(SCPMePh$_2$)(CO)$_2$(Tp*)]PF$_6$ (2b; CH$_2$Cl$_2$, 25 °C, ν)

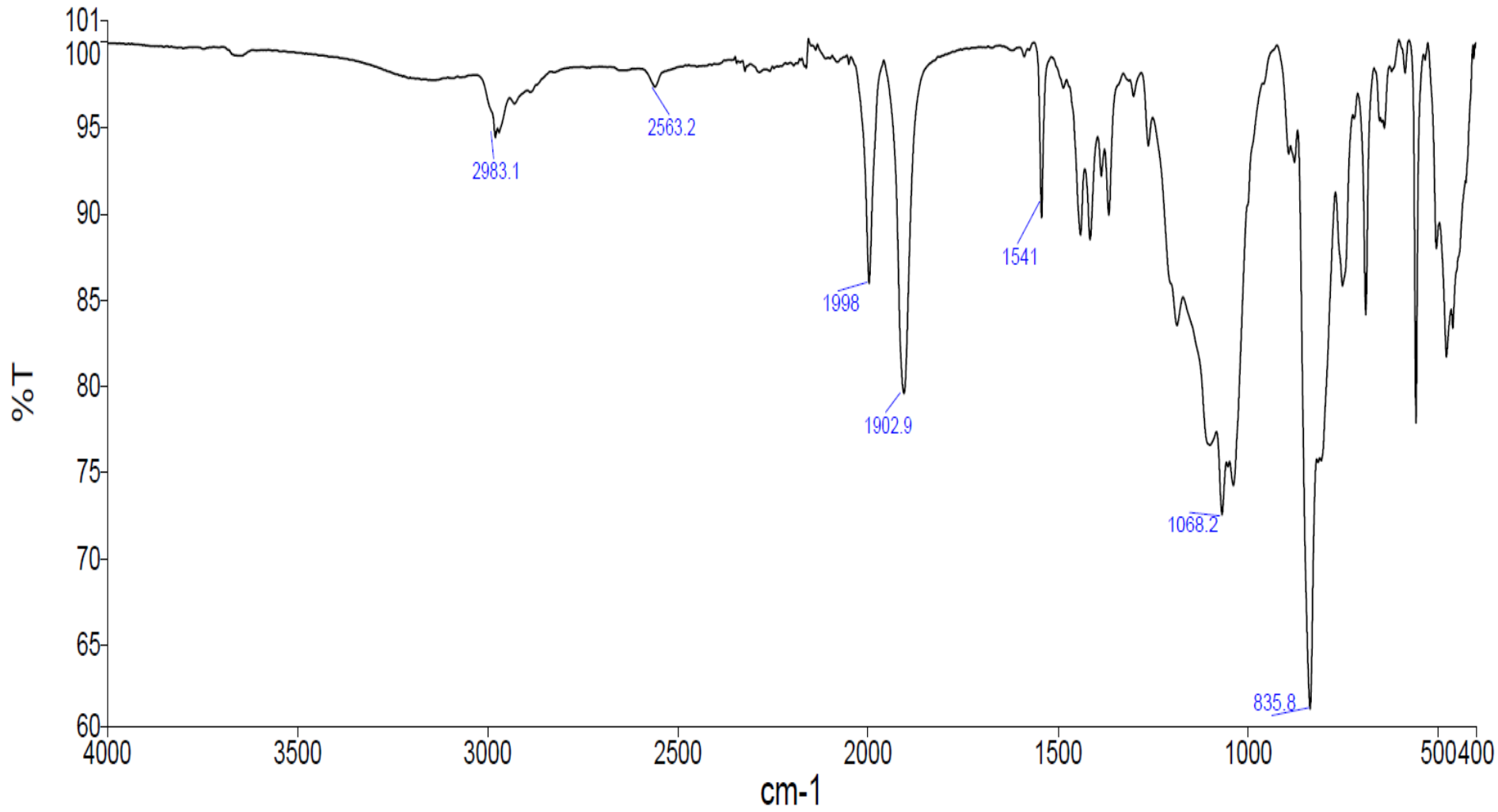


Figure S36: Infrared Spectrum of $[W(SCPMePh_2)(CO)_2(Tp^*)]PF_6$ (2b; ATR, 25 °C, ν)

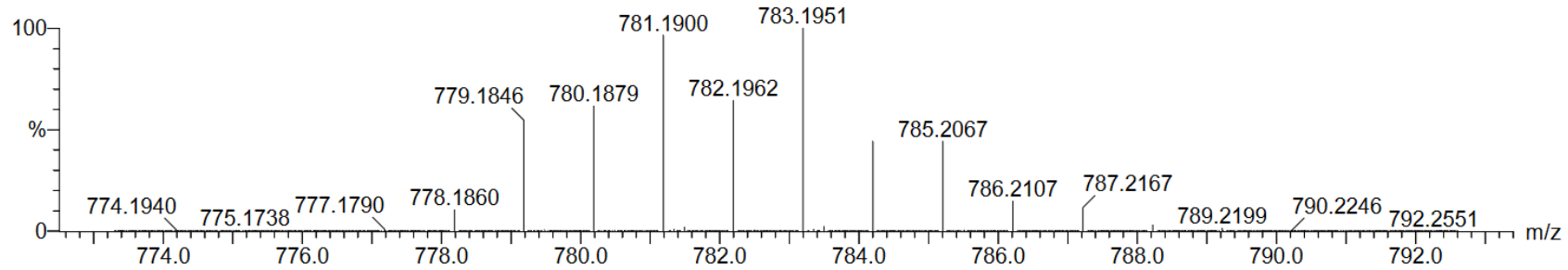
Elemental Composition Report

Multiple Mass Analysis: 2 mass(es) processed

Tolerance = 3.0 PPM / DBE: min = -1.5, max = 20.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Odd and Even Electron Ions
1670 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-50 H: 0-50 11B: 0-1 N: 0-6 O: 0-2 P: 0-1 S: 0-1 184W: 0-1

SJ-1-9/AJ SYNAPTG2-Si#NotSet 09-Feb-2022
66949 10:35:20
2035 95 (0.209) Cm (95:120)
1: TOF MS ES+ 1.70e+007



Minimum:	90.00				-1.5		
Maximum:	100.00		25.0	3.0	20.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
781.1900	96.53	781.1882	1.8	2.3	20.0	1595.4	C31 H35 11B N6 O2 P S 184W
783.1951	100.00	---					

Figure S37: Mass Spectrum (ESI, +ve ion) of $[W(SCPMePh_2)(CO)_2(Tp^*)]PF_6$ (2b)

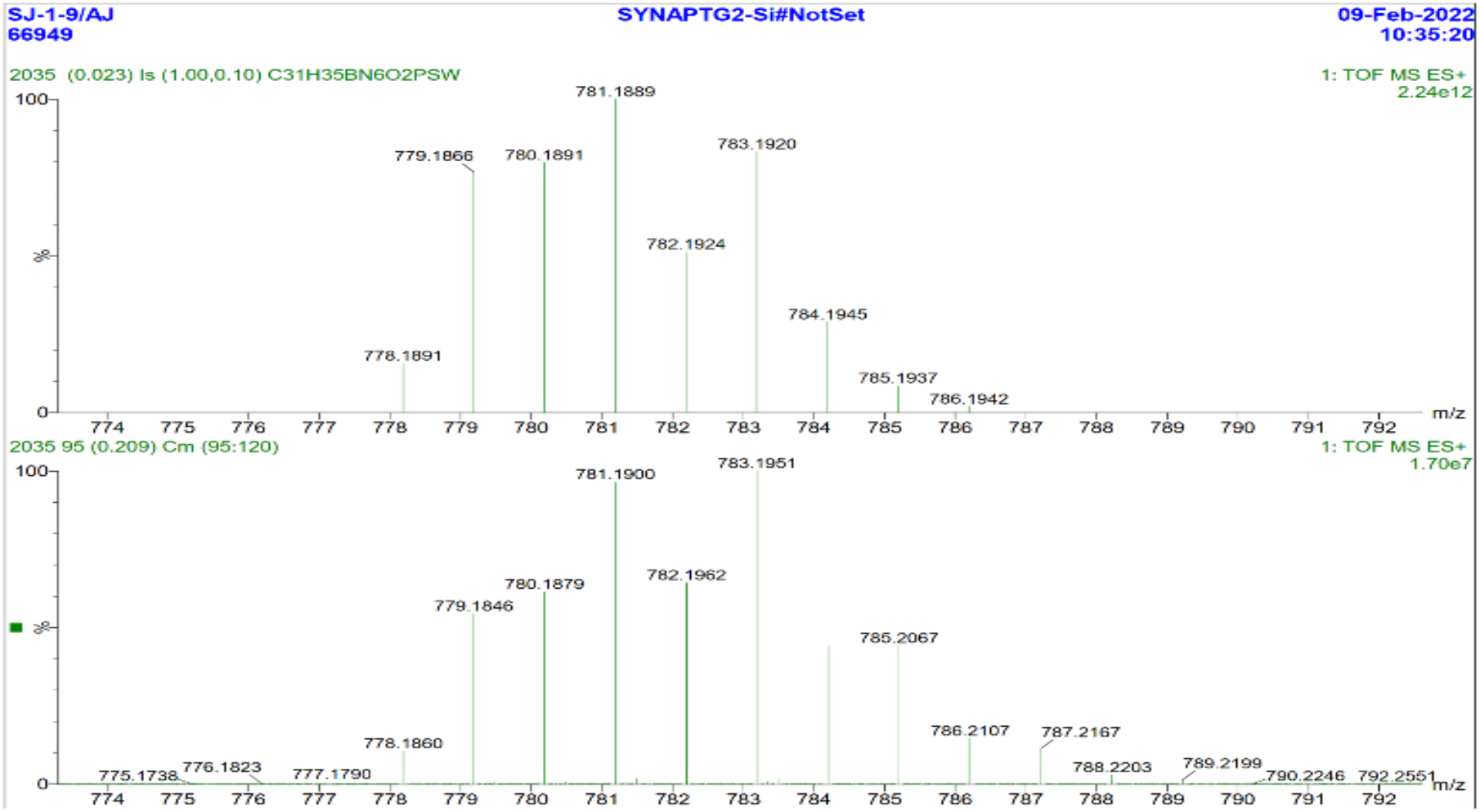


Figure S38: Mass Spectrum (ESI, +ve ion) of $[W(SCPMePh_2)(CO)_2(Tp^*)]PF_6$ (2b)

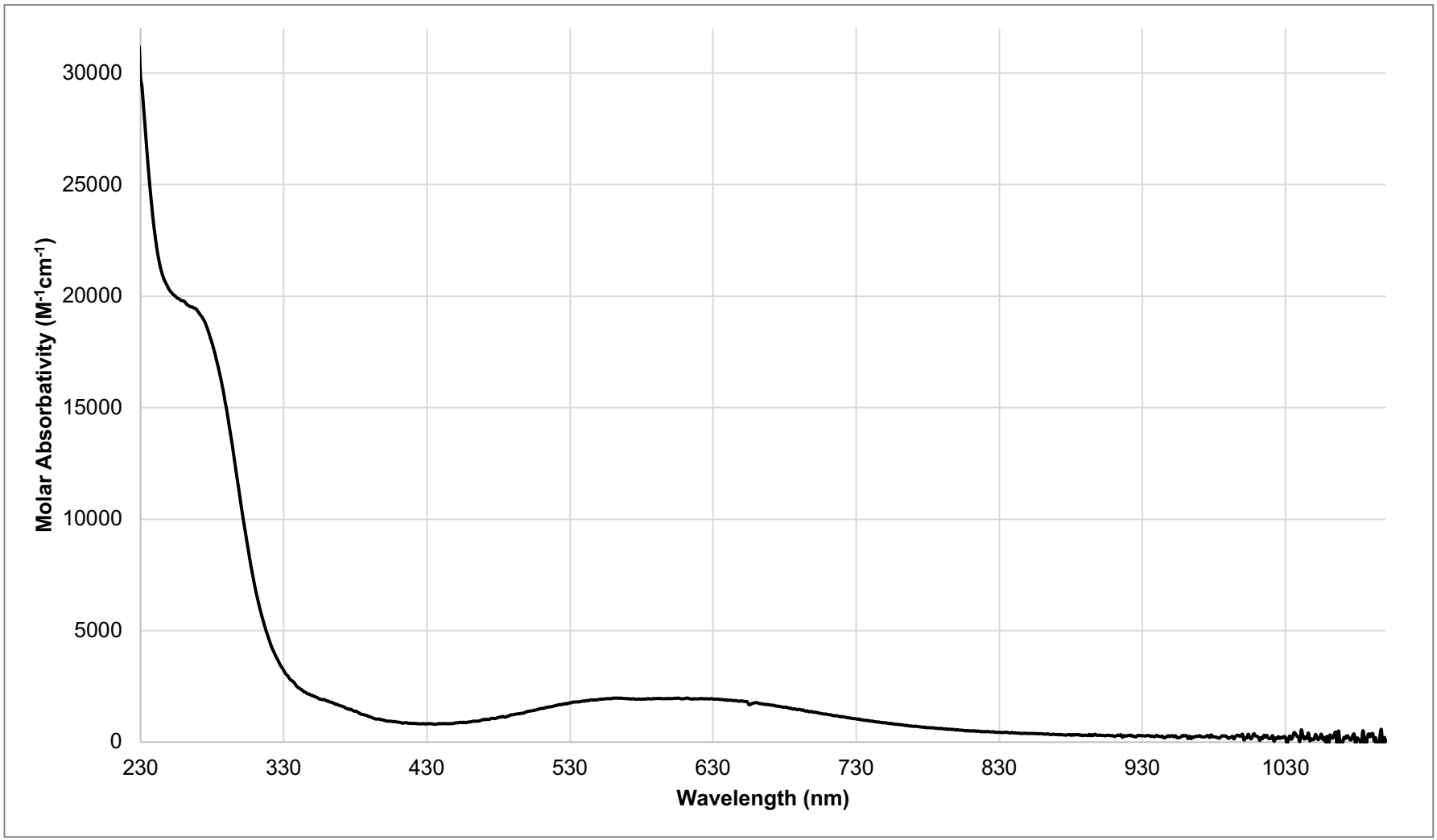


Figure S39: Electronic spectrum of $[W(SCPMePh_2)(CO)_2(Tp^*)].PF_6$· in CH_2Cl_2 [2b; M = 2.610(3)×10^{-5} molL^{-1}].

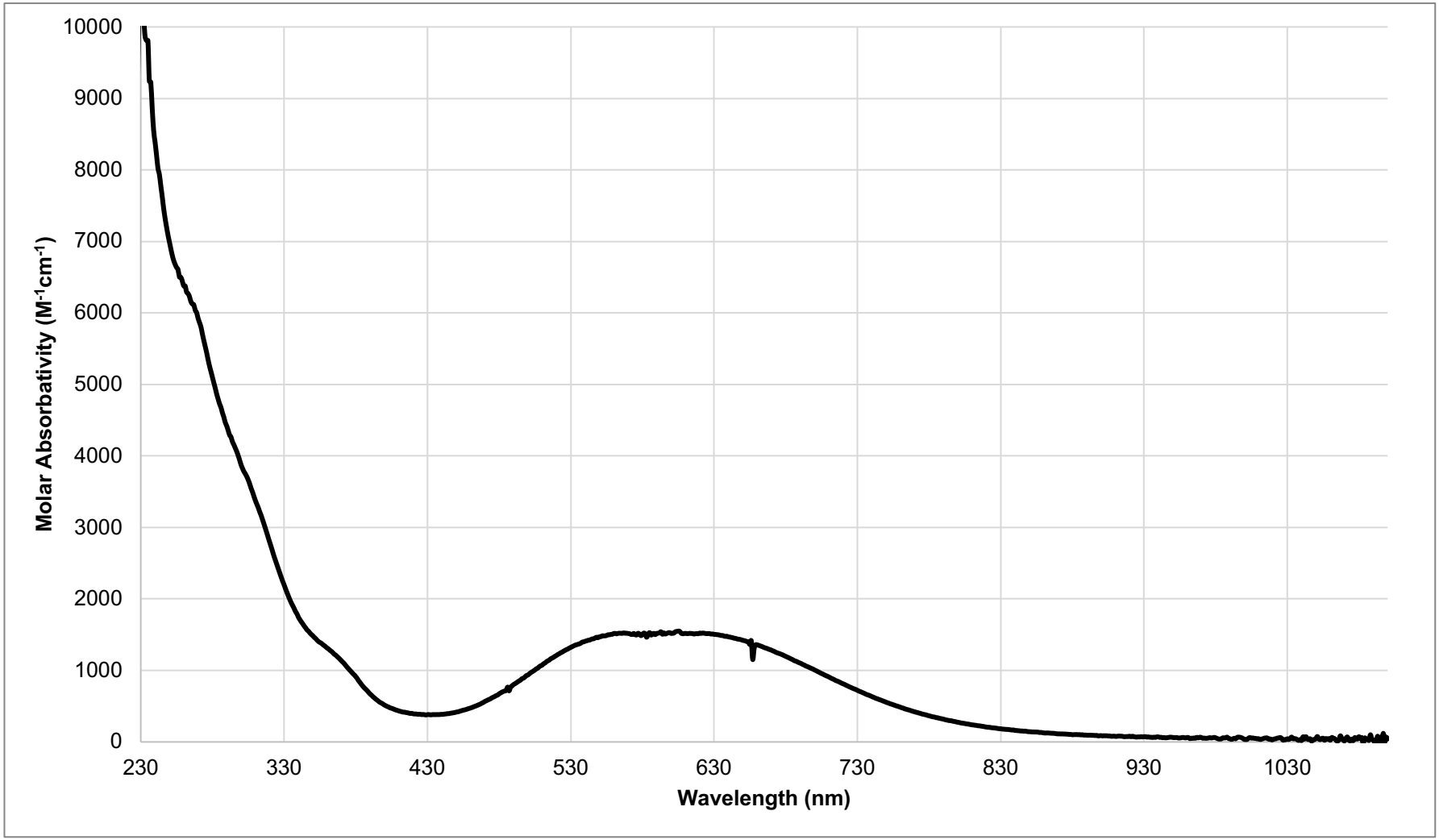


Figure S40: Electronic spectrum of $[W(SCPMePh_2)(CO)_2(Tp^*)].PF_6$· in CH_2Cl_2 [2b; M = 2.610(3)×10^{-4} molL^{-1}].

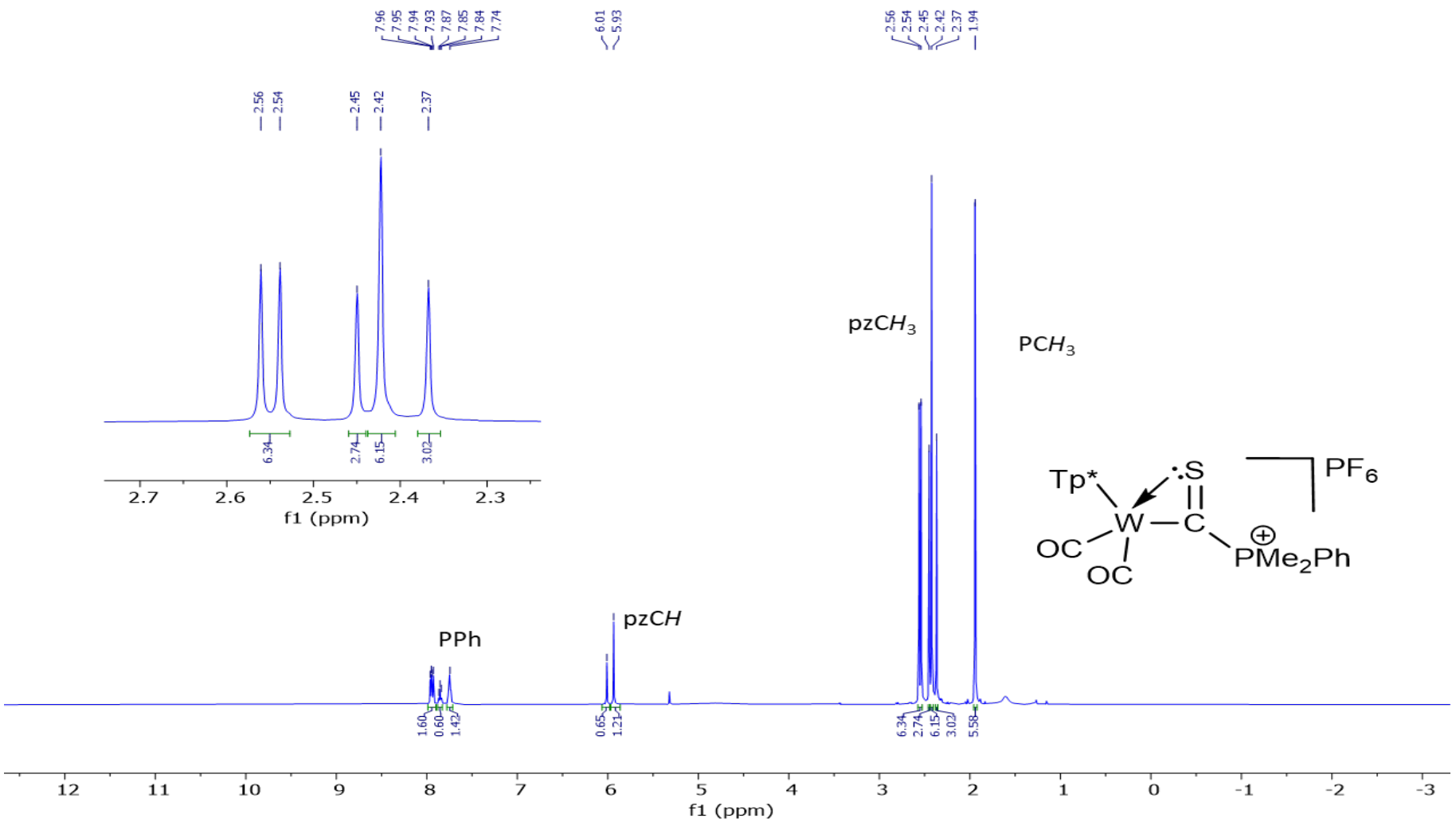


Figure S41: ^{1}H NMR Spectrum of [W(SCPMe$_2$Ph)(CO)$_2$(Tp*)]PF$_6$ (2c; 600 MHz, CD$_2$Cl$_2$, 25 °C, δ)

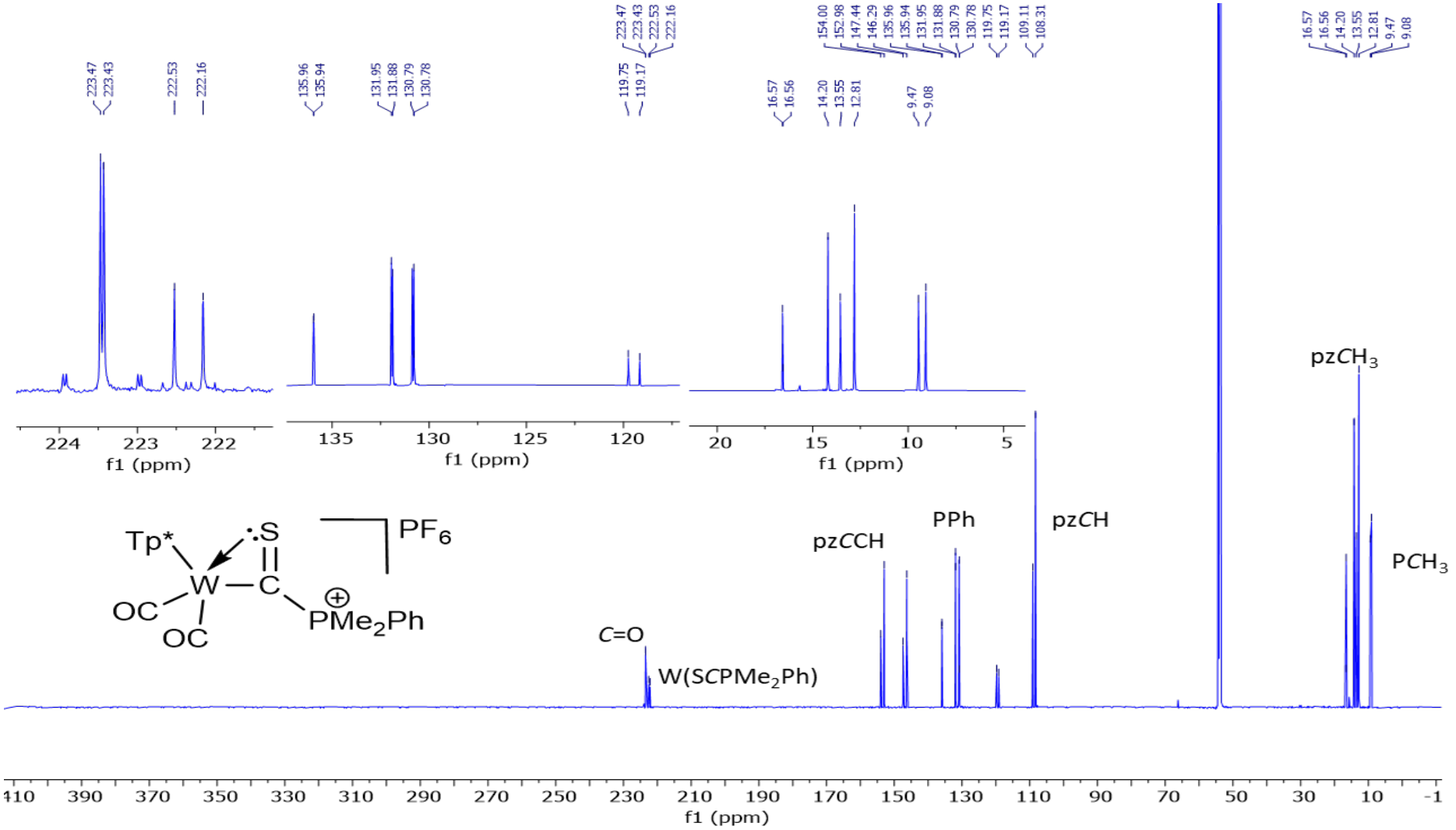


Figure S42: $^{13}C\{^1H\}$ NMR Spectrum of $[W(SCPMe_2Ph)(CO)_2(Tp^*)]PF_6$ (151 MHz, CD_2Cl_2, 25 °C, δ)

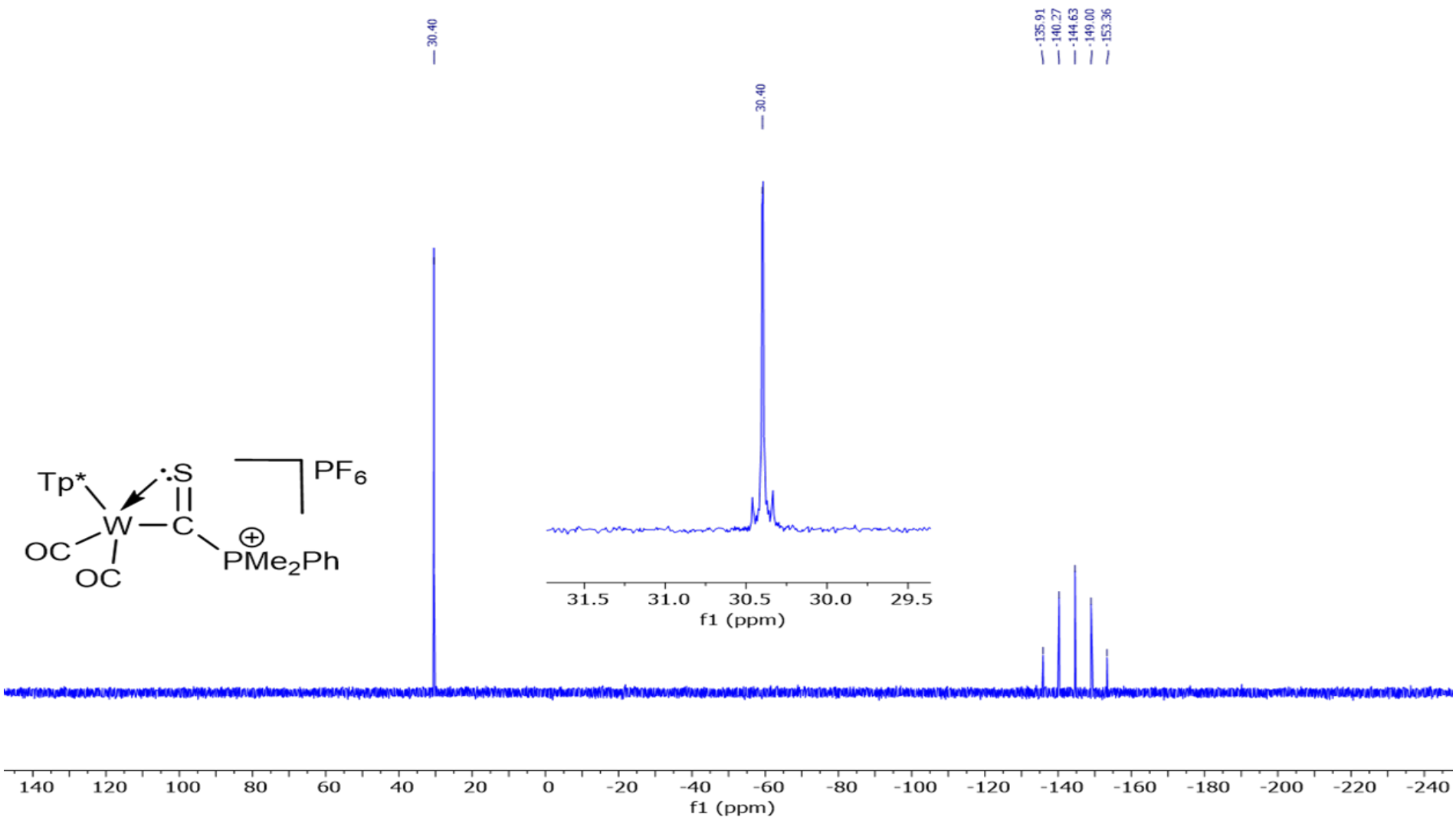


Figure S43: $^{31}P\{^{1}H\}$ NMR Spectrum of $[W(SCPMe_2Ph)(CO)_2(Tp^*)]PF_6$ (2c; 162 MHz, CD_3CN, 25 °C, δ)

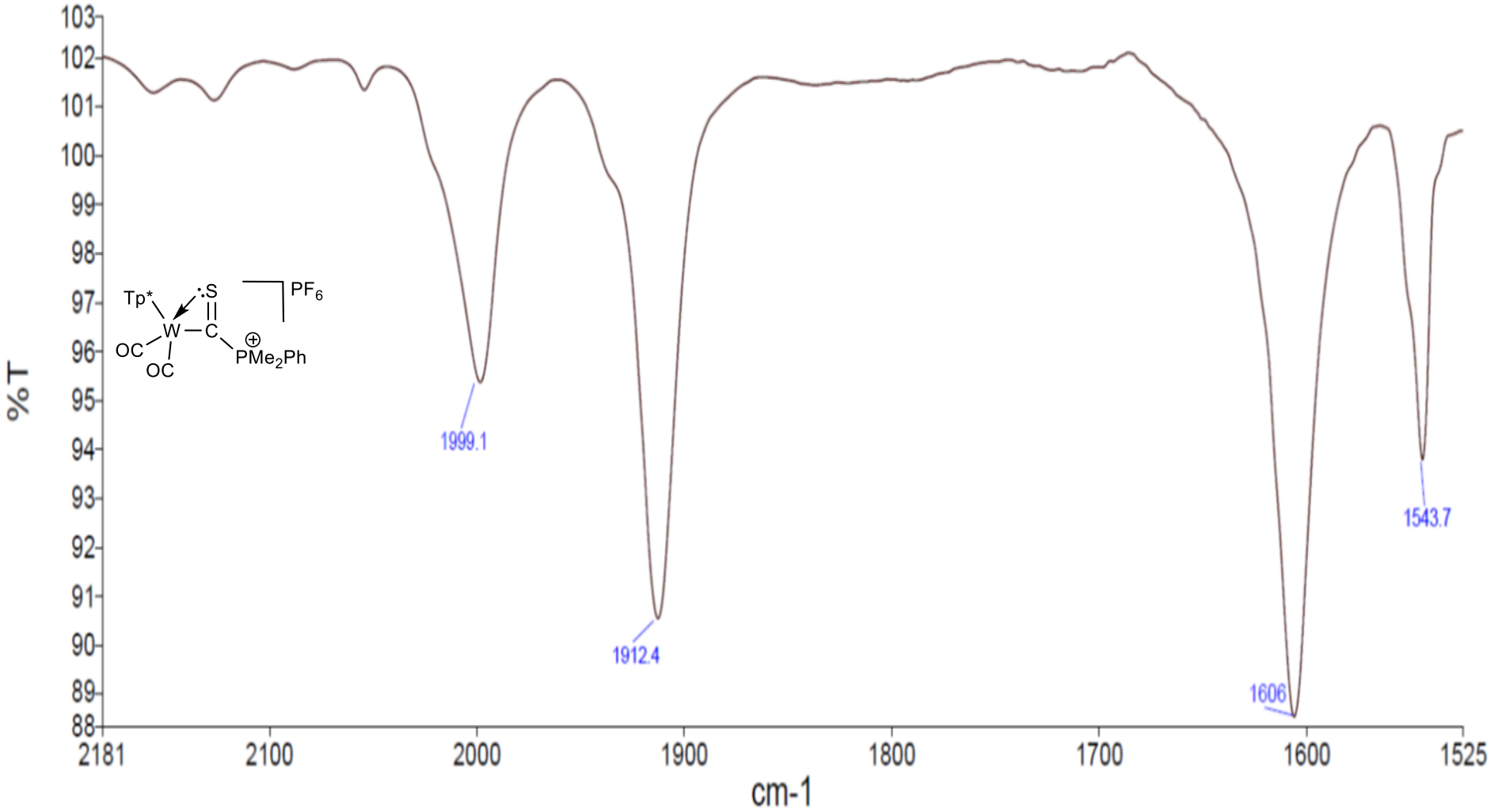


Figure S44: Infrared Spectrum of [W(SCPMe$_2$Ph)(CO)$_2$(Tp*)]PF$_6$ (2c; CH$_2$Cl$_2$, 25 °C, ν)

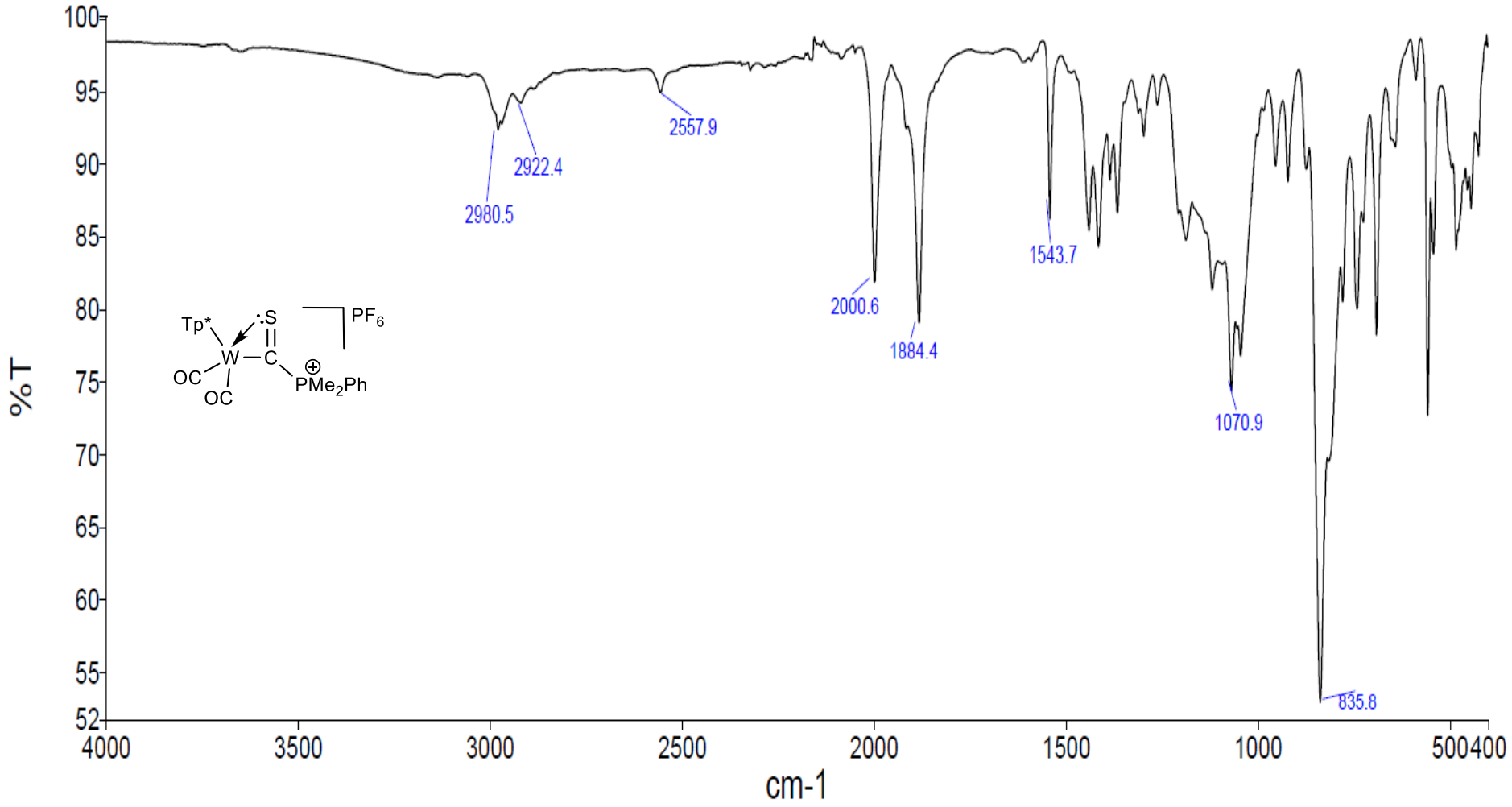


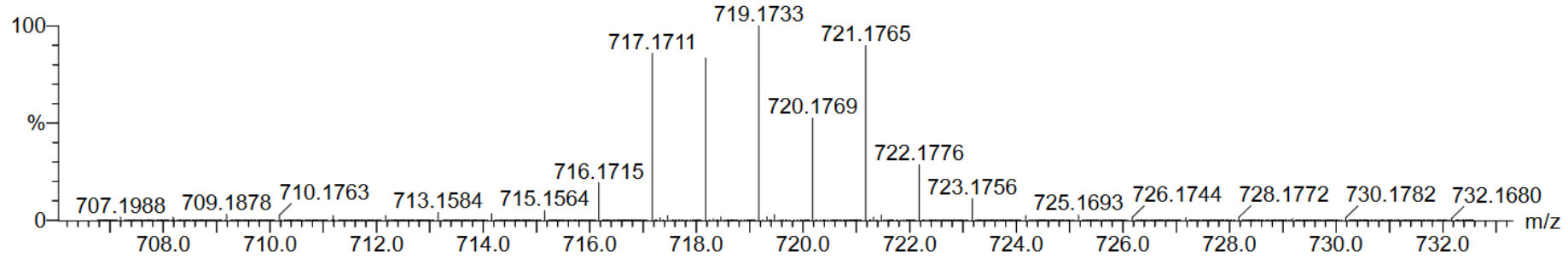
Figure S45: Infrared Spectrum of [W(SCPMe$_2$Ph)(CO)$_2$(Tp*)]PF$_6$ (2c; ATR, 25 °C, ν)

Elemental Composition Report

Tolerance = 3.0 PPM / DBE: min = -1.5, max = 18.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Odd and Even Electron Ions
1138 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-50 H: 0-50 11B: 0-1 N: 0-6 O: 0-2 P: 0-1 S: 0-1 184W: 0-1

SJ-1-8/AJ SYNAPTG2-Si#NotSet 09-Feb-2022
66947 10:12:15
2034 136 (0.287) Cm (133:147)
1: TOF MS ES+ 1.59e+007



Minimum:	90.00				-1.5				
Maximum:	100.00		25.0	3.0	18.0				
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
719.1733	100.00	719.1726	0.7	1.0	16.0	871.6	n/a	n/a	C26 H33 11B N6 O2 P S 184W

Figure S46: Mass Spectrum (ESI, +ve ion) of $[W(SCPMe_2Ph)(CO)_2(Tp^*)]PF_6$ (2c)

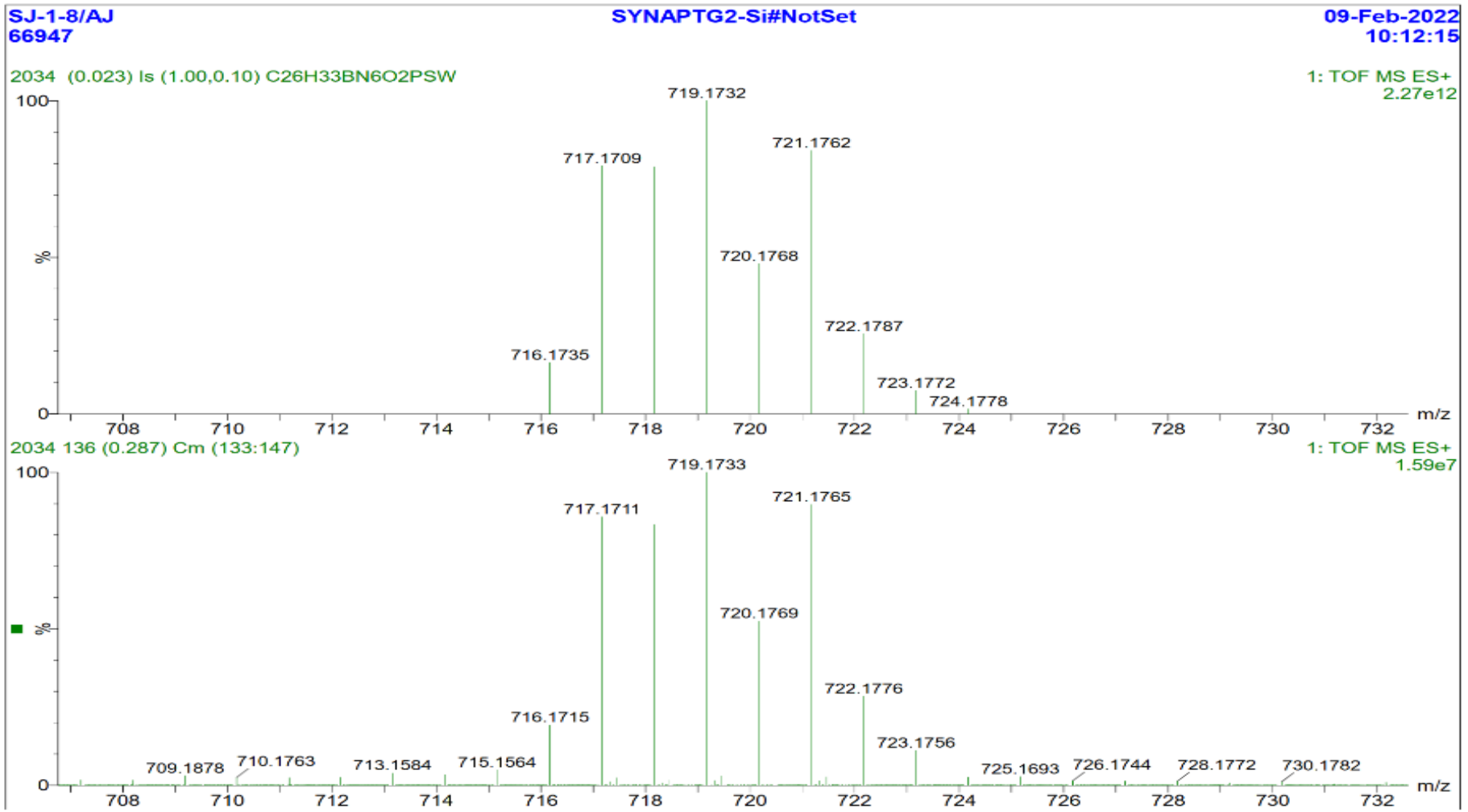


Figure S47: Mass Spectrum (ESI, +ve ion) of $[W(SCPMe_2Ph)(CO)_2(Tp^*)]PF_6$ (2c)

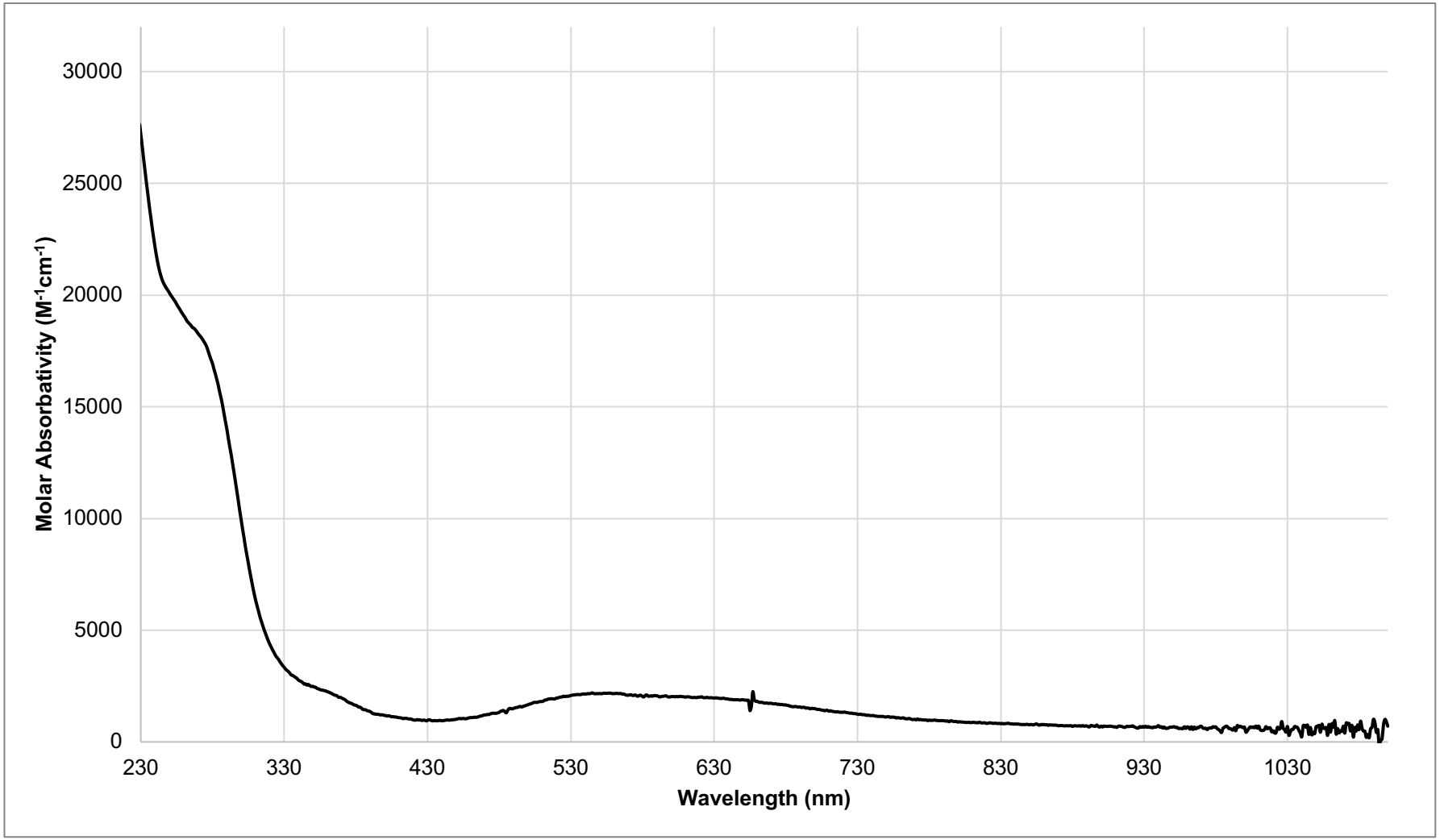


Figure S48: Electronic spectrum of [W(SCPMe$_2$Ph)(CO)$_2$(Tp*)].PF$_6$· in CH$_2$Cl$_2$ [2c; M = 2.498(3)×10^{-5} molL^{-1}].

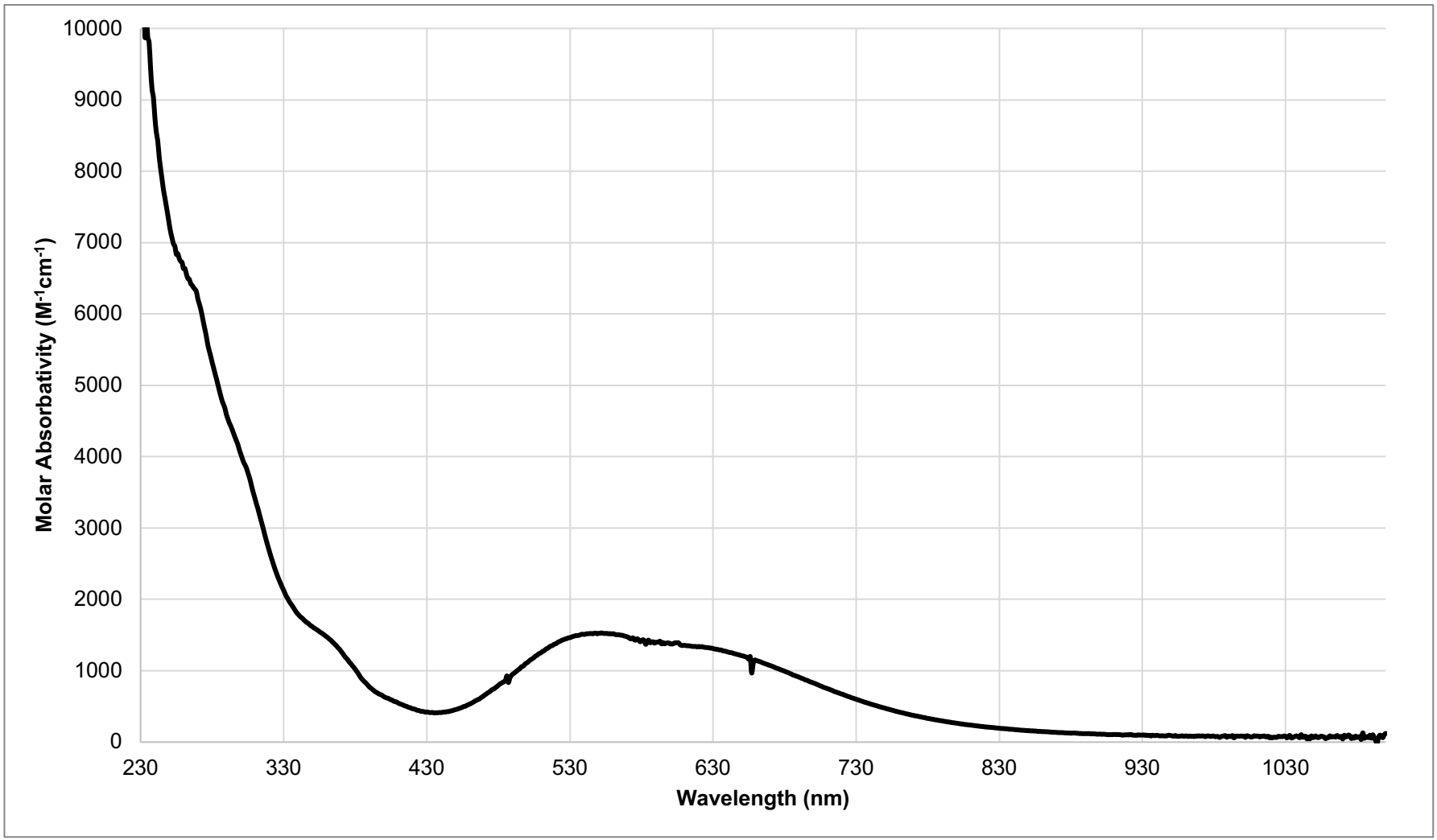


Figure S49: Electronic spectrum of $[W(SCPMe_2Ph)(CO)_2(Tp^*)].PF_6$· in CH_2Cl_2 [2c; M = 2.498(3)×10^{-4} molL^{-1}].

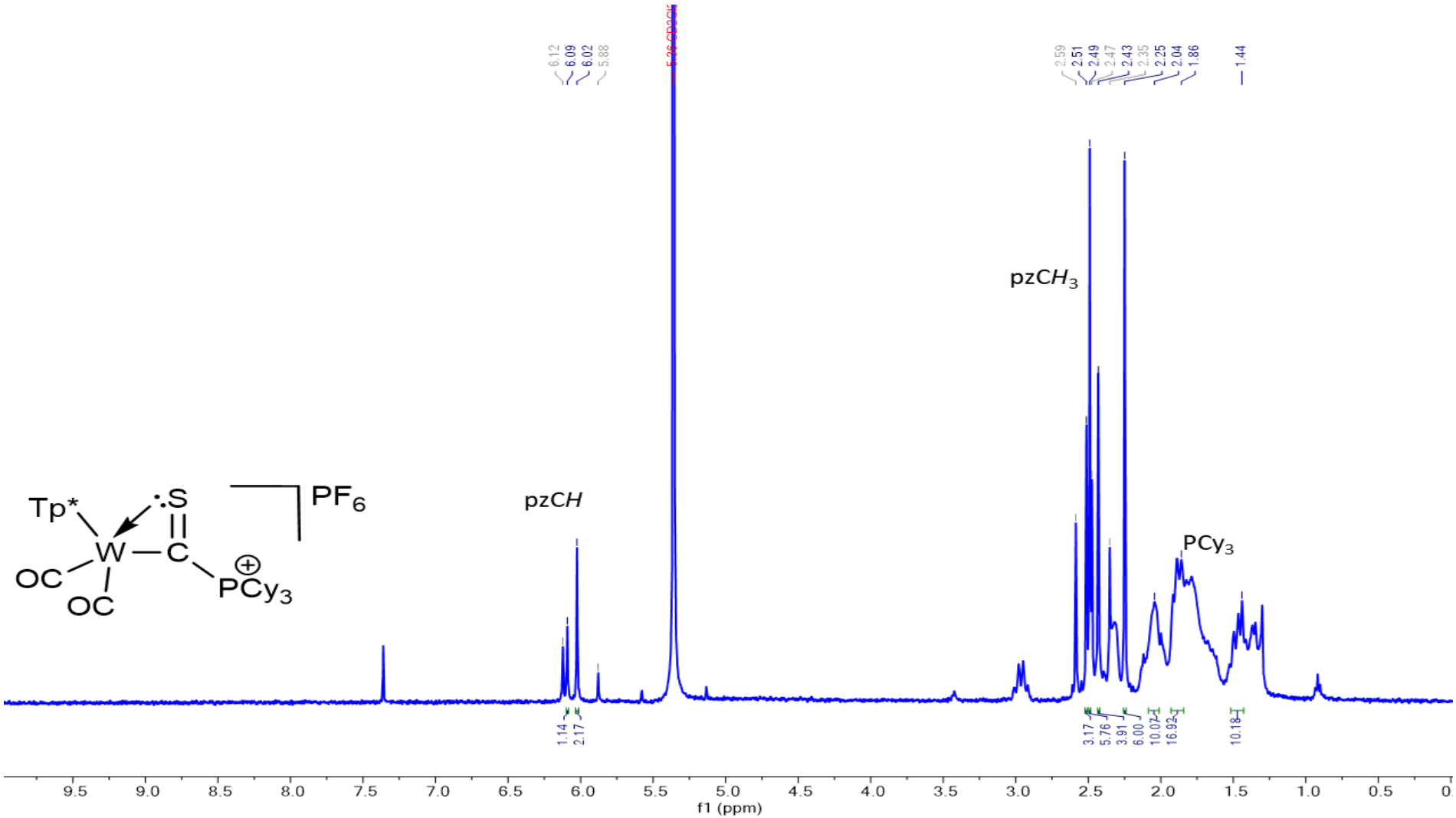


Figure S50: ^{1}H NMR Spectrum of [(Tp*)(CO)$_2$W(SCPCy$_3$)]PF$_6$ (2d; 400 MHz, CD_2Cl_2, 25 °C, δ)

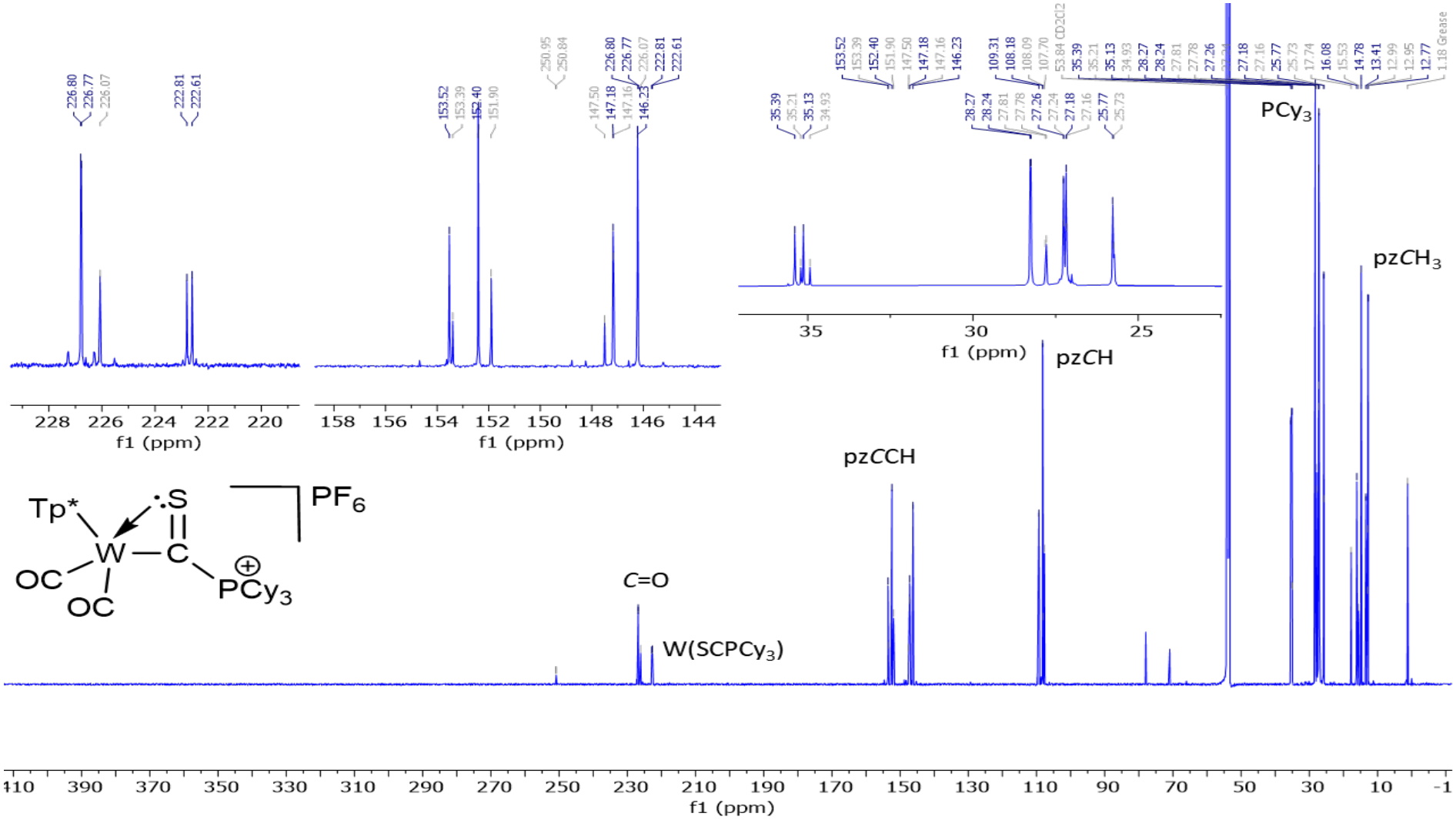


Figure S51 $^{13}C\{^{1}H\}$ NMR Spectrum of $[(Tp^*)(CO)_2W(SCPCy_3)]PF_6$ (2d; 151 MHz, CD_2Cl_2, 25 °C, δ)

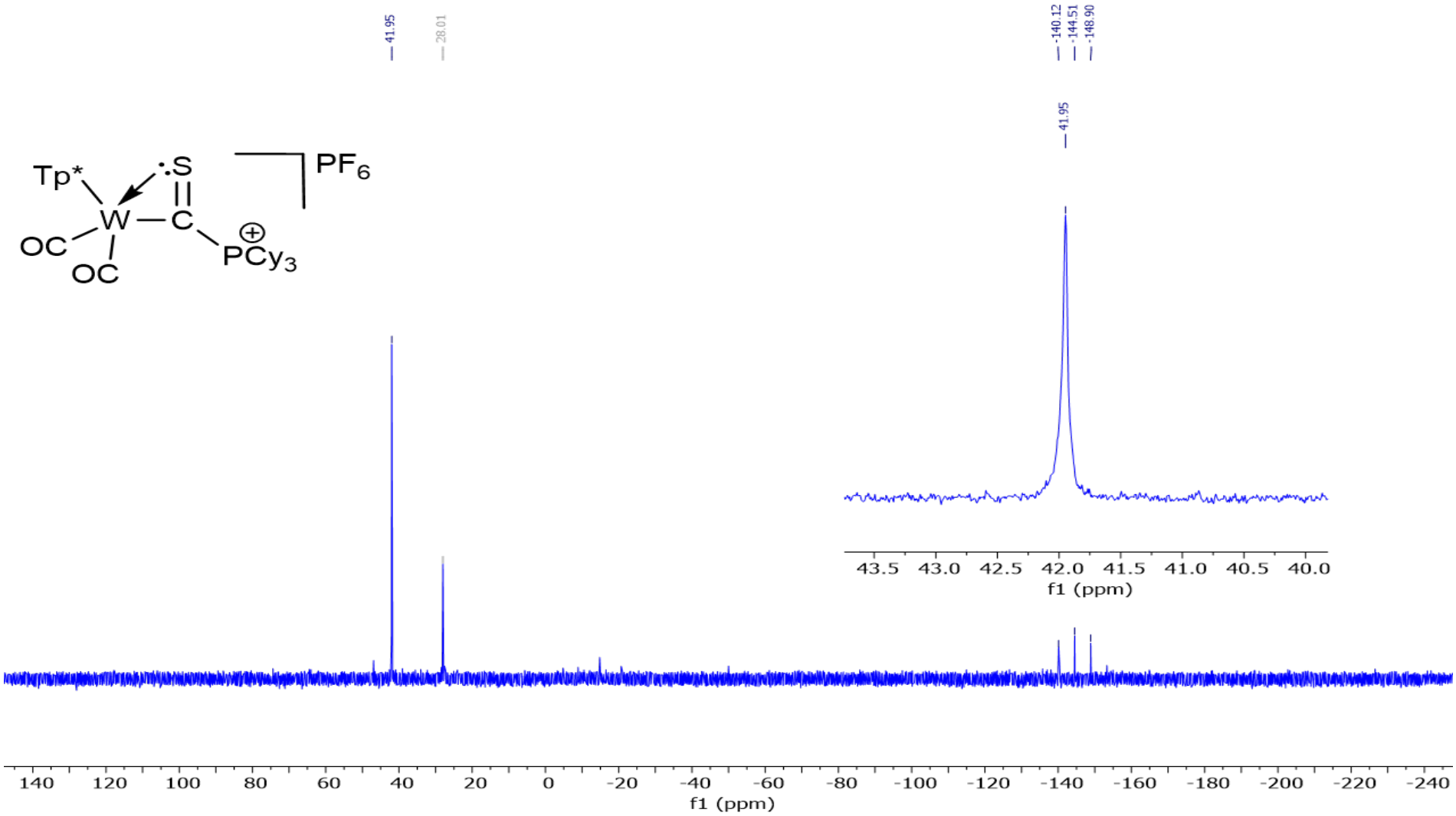


Figure S52: $^{31}P\{^{1}H\}$ NMR Spectrum of $[W(SCPCy_3)(CO)_2(Tp^*)]PF_6$ (2d; 162 MHz, CD_2Cl_2, 25 °C, δ)

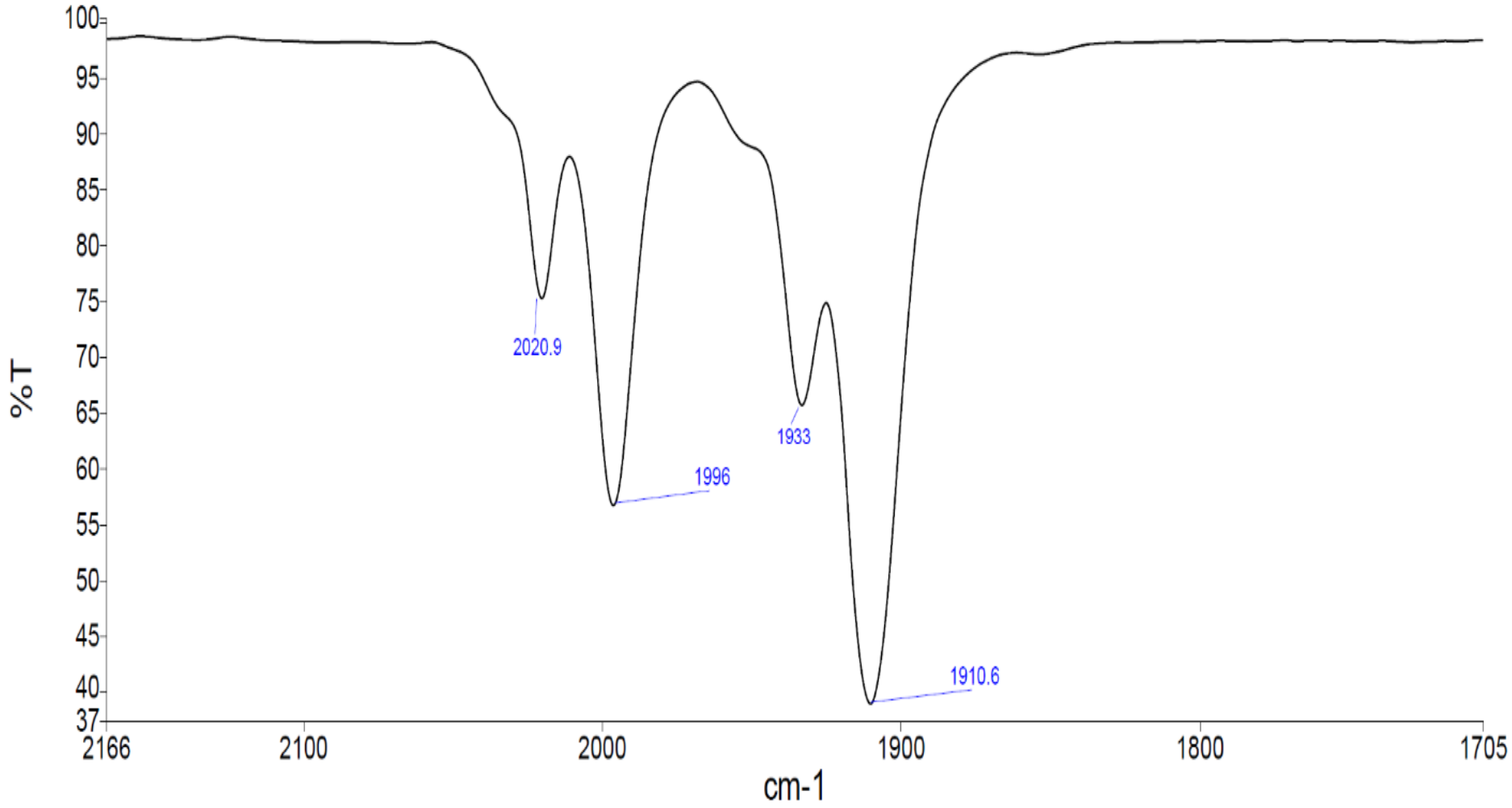


Figure S53: Infrared Spectrum of $[W(SCPCy_3)(CO)_2(Tp^*)]PF_6$ (2d; CH_2Cl_2, 25 °C, ν)

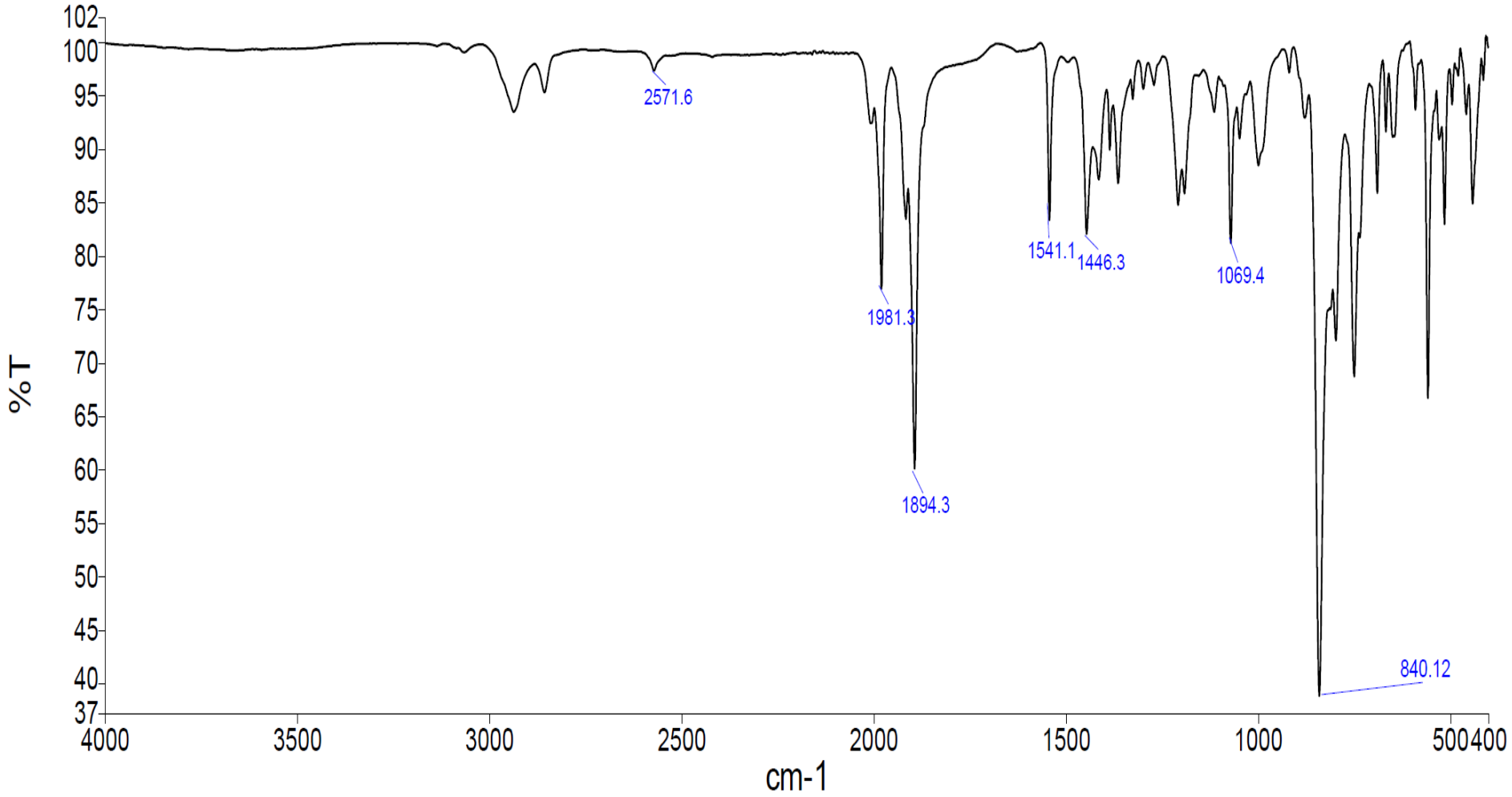


Figure S54: Infrared Spectrum of $[W(SCPCy_3)(CO)_2(Tp^*)]PF_6$ (2d; ATR, 25 °C, ν)

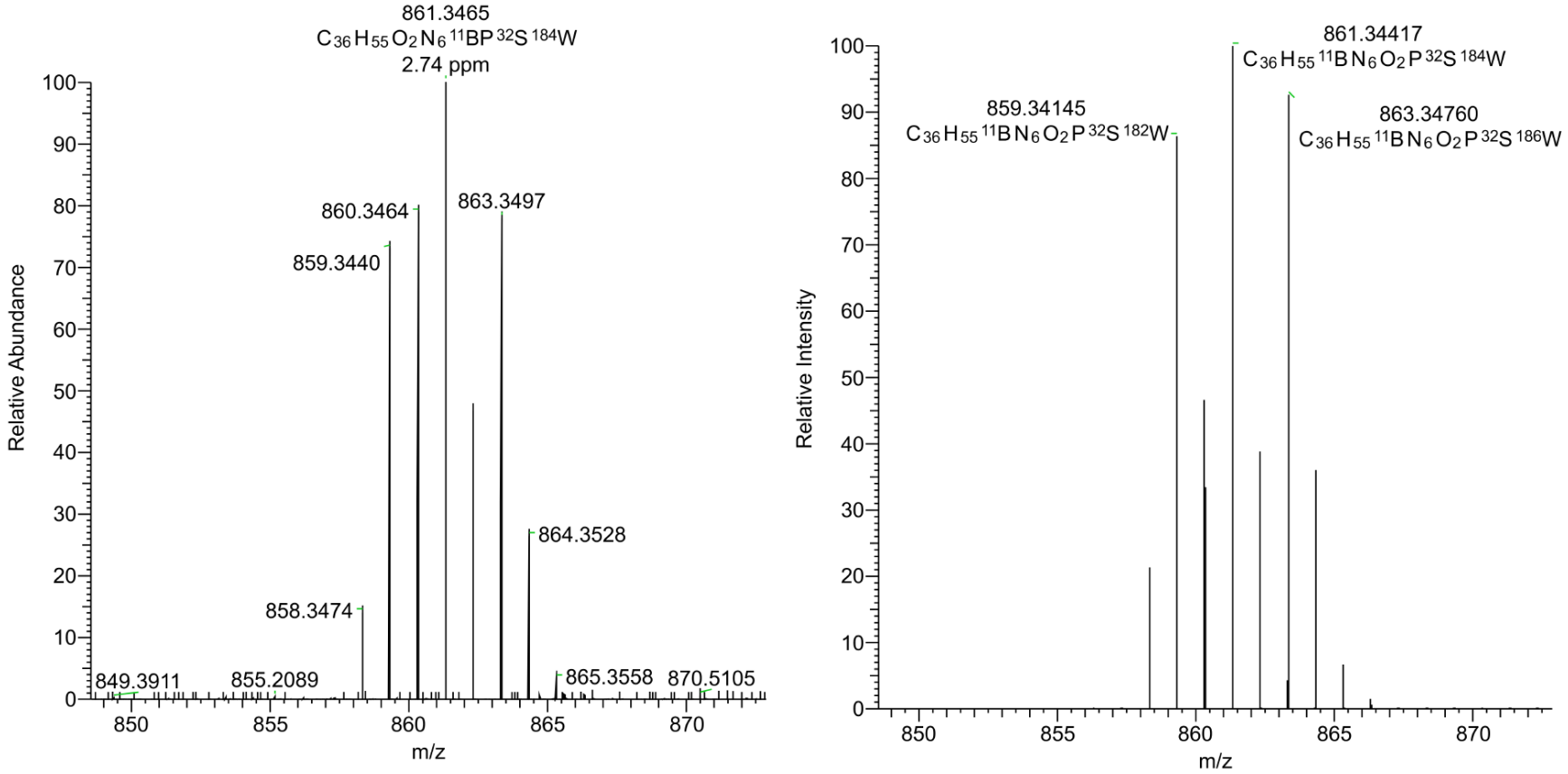


Figure S55: Mass Spectrum (ESI, +ve ion) of [W(SCPCy$_3$)(CO)$_2$(Tp*)]PF$_6$(2d)

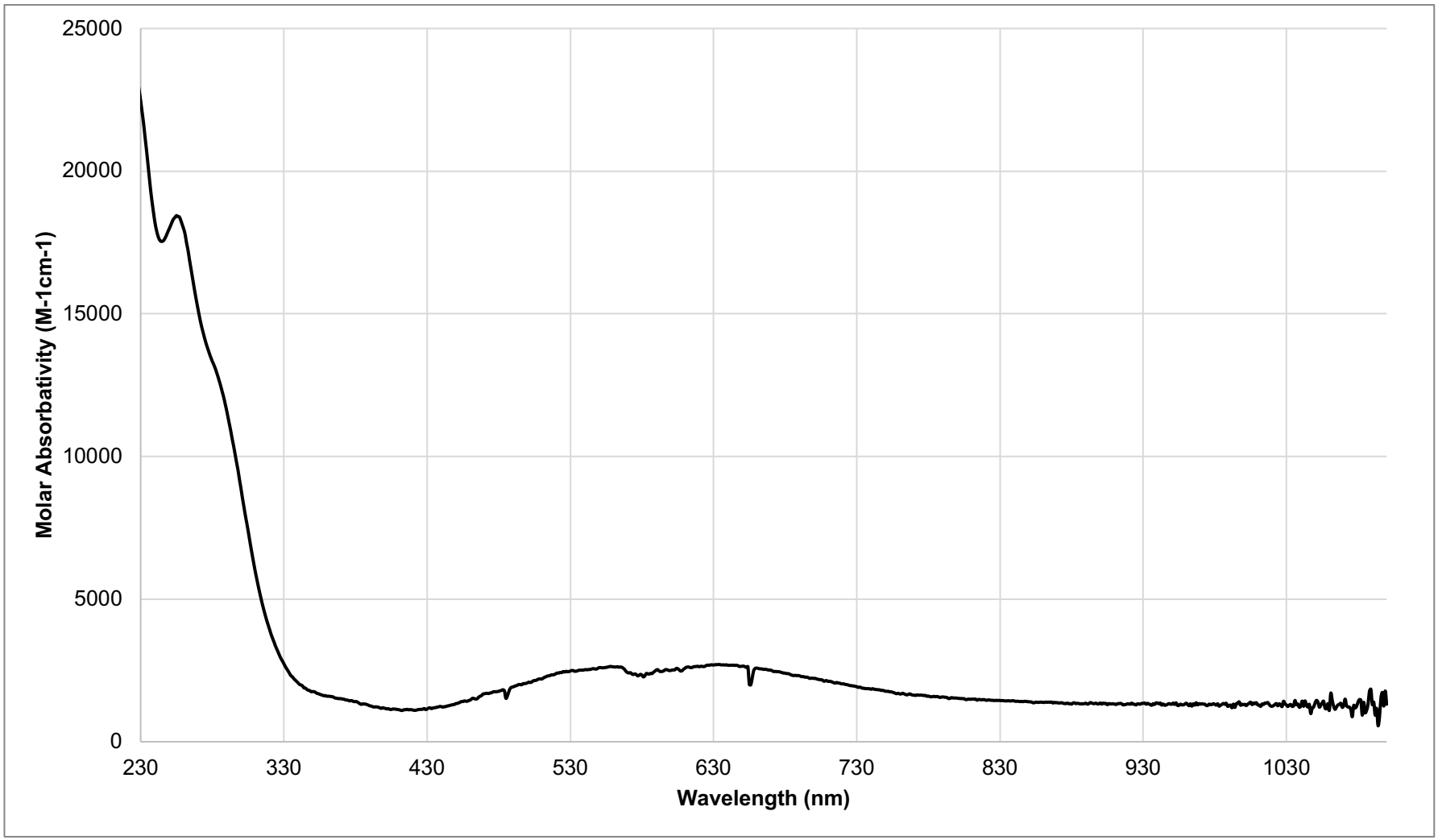


Figure S56: Electronic spectrum of $[W(SCPCy_3)(CO)_2(Tp^*)].PF_6\cdot$ in CH_2Cl_2 [2d; M = $3.922(4)\times10^{-5}$ $molL^{-1}$].

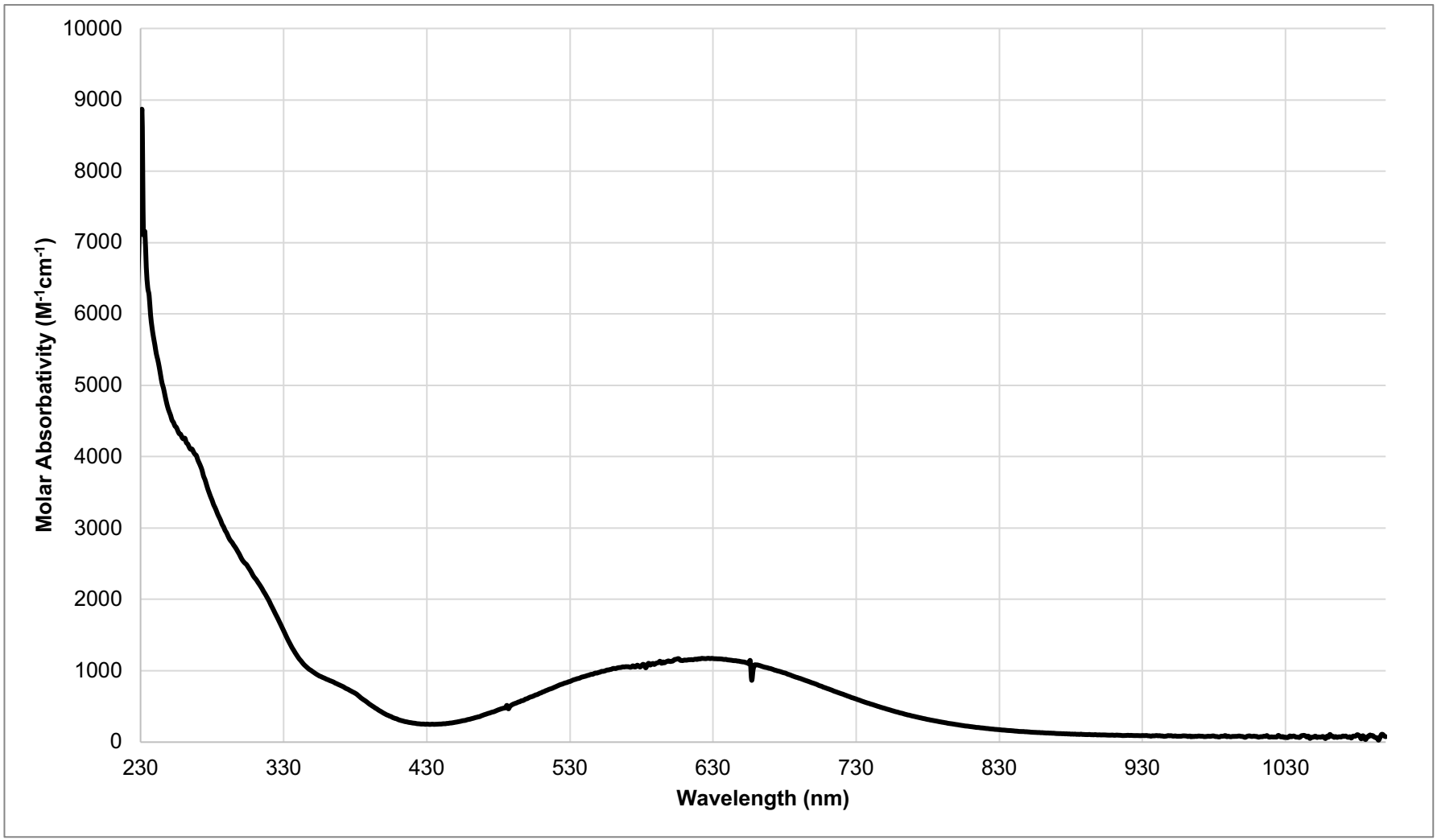


Figure S57: Electronic spectrum of $[W(SCPCy_3)(CO)_2(Tp^*)].PF_6\cdot$ in CH_2Cl_2 [2d; M = $3.922(4)\times10^{-4}$ $molL^{-1}$].

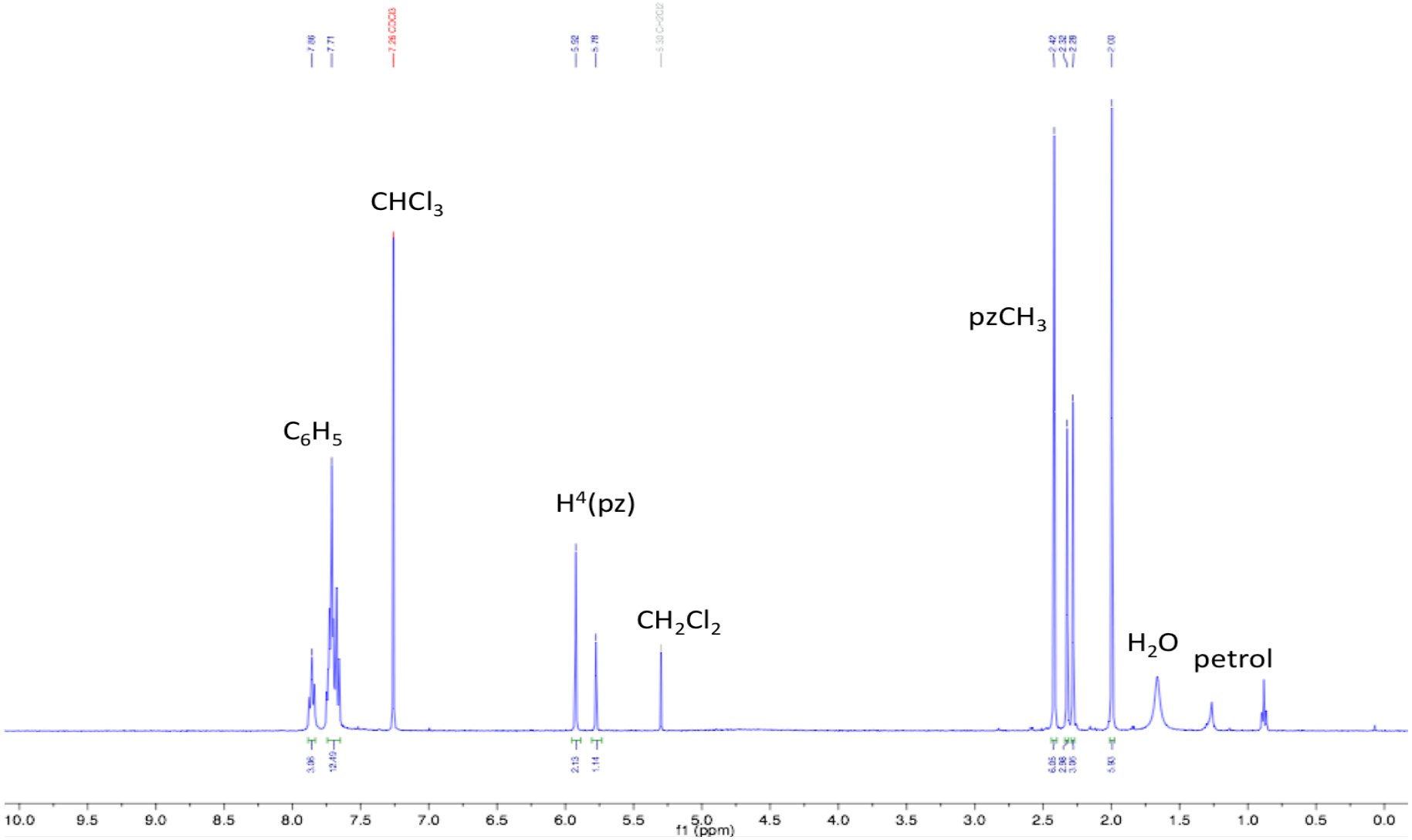


Figure S58: ^{1}H NMR Spectrum of [Mo(≡CPPh$_3$)(CO)$_2$(Tp*)]PF$_6$ (3a; 400 MHz, CDCl$_3$, 25 °C, δ)

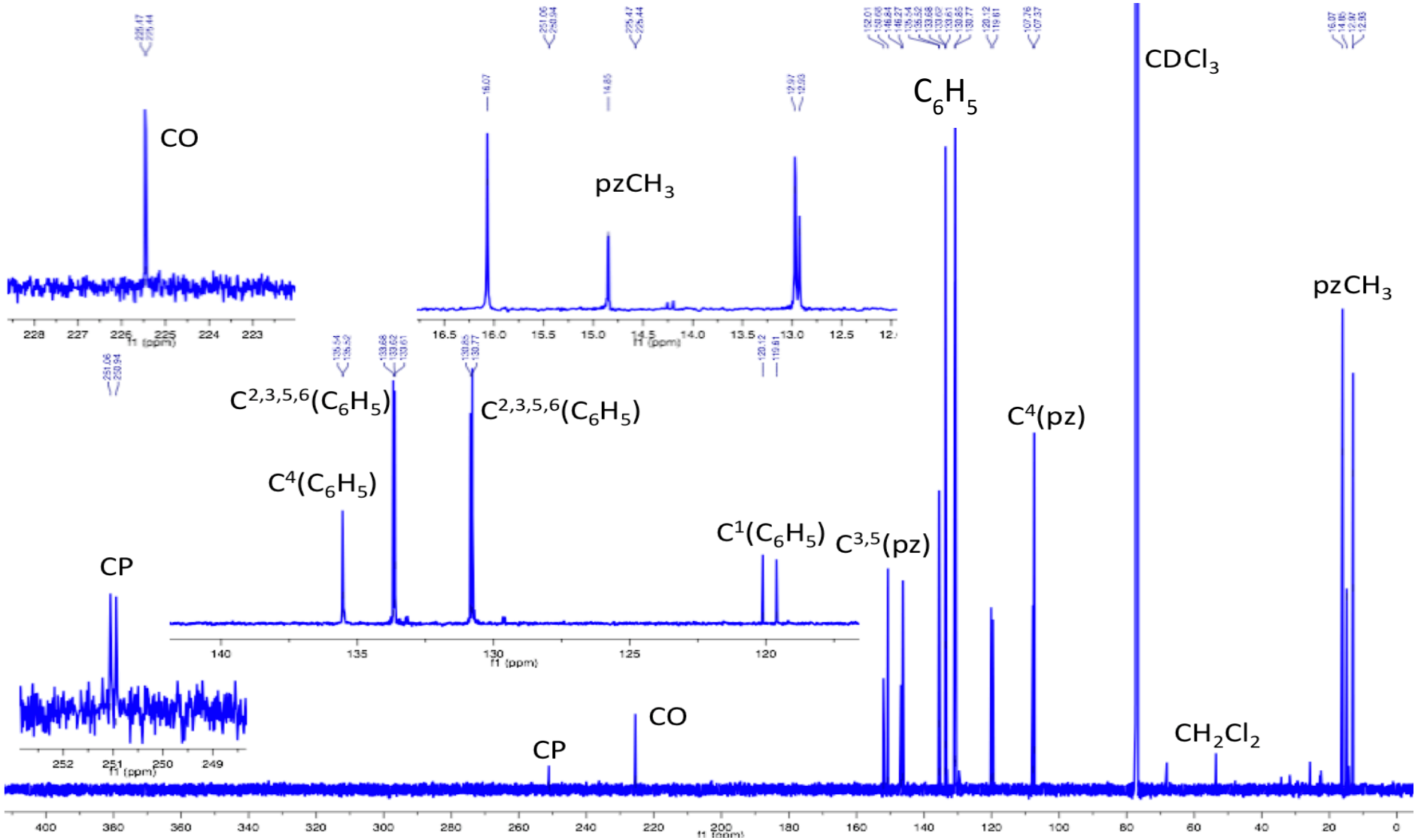


Figure S59: $^{13}C\{^1H\}$ NMR Spectrum of $[Mo(\equiv CPPh_3)(CO)_2(Tp^*)]PF_6$ (3a; 176 MHz, $CDCl_3$, 25 °C, δ)

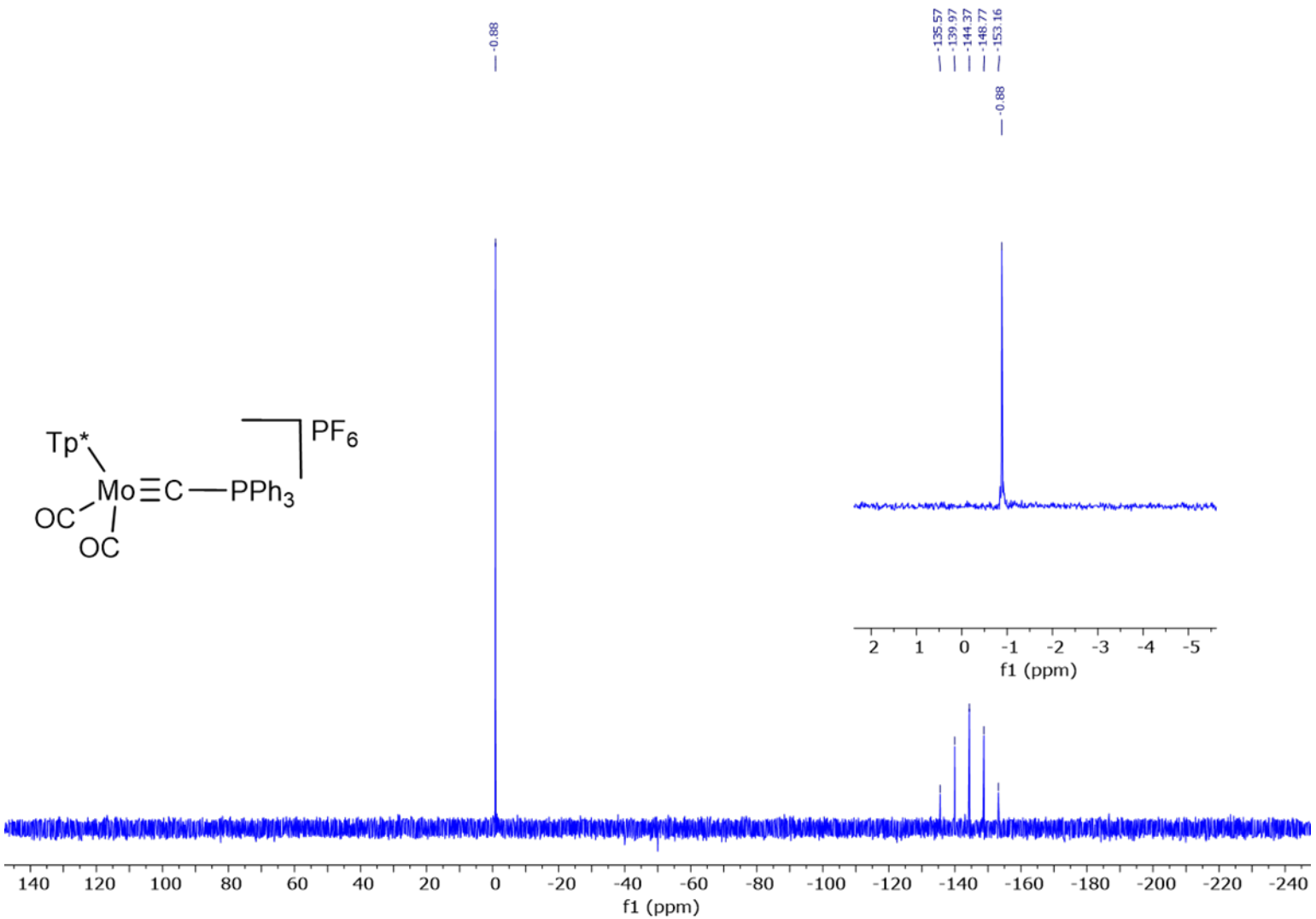


Figure S60: $^{31}P\{^{1}H\}$ NMR Spectrum of $[Mo(\equiv CPPh_3)(CO)_2(Tp^*)]PF_6$ (3a; 162 MHz, $CDCl_3$, 25 °C, δ)

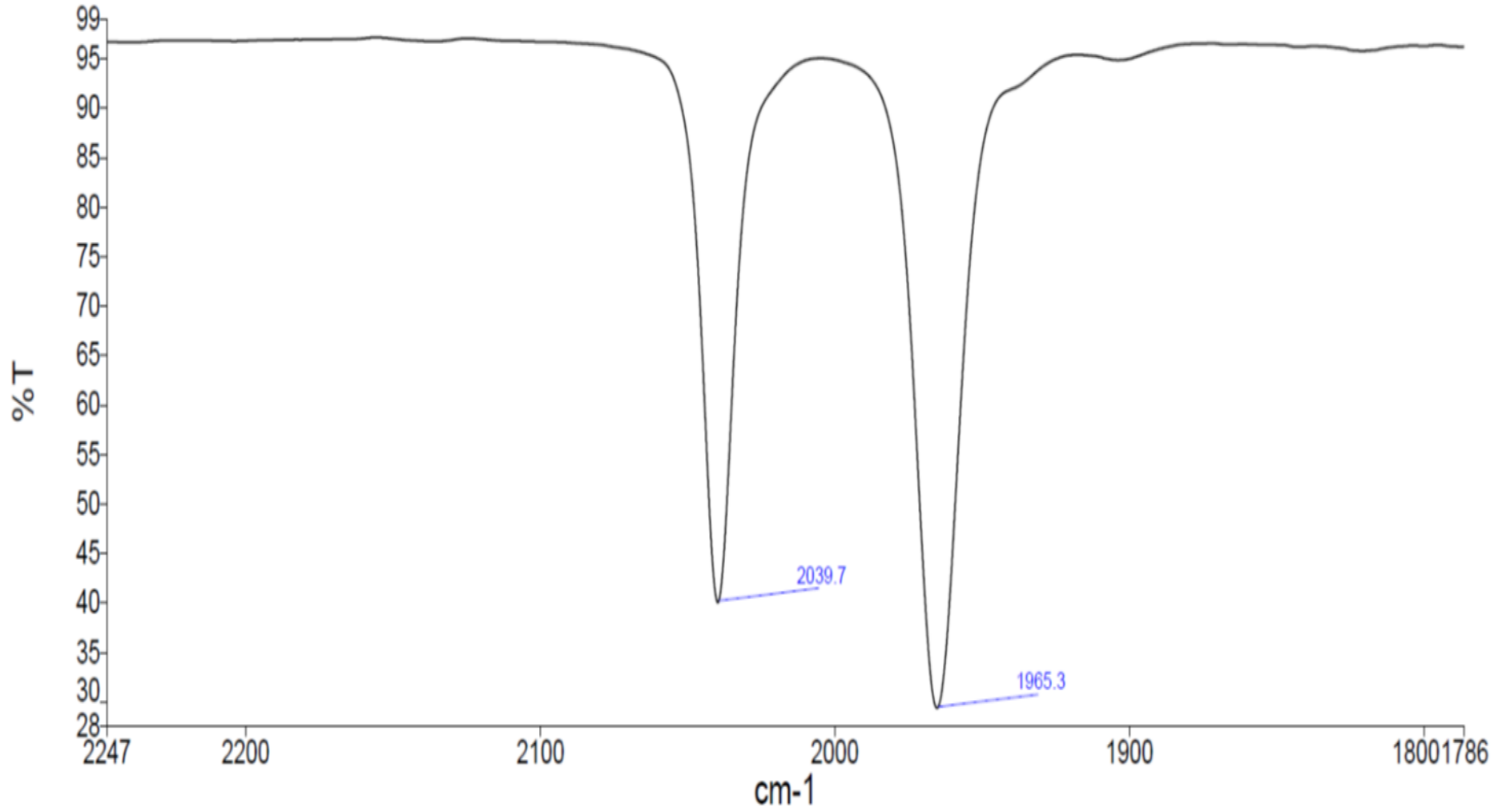


Figure S61: Infrared Spectrum of $[Mo(\equiv CPPh_3)(CO)_2(Tp^*)]PF_6$ (3a; CH_2Cl_2, 25 °C, ν)

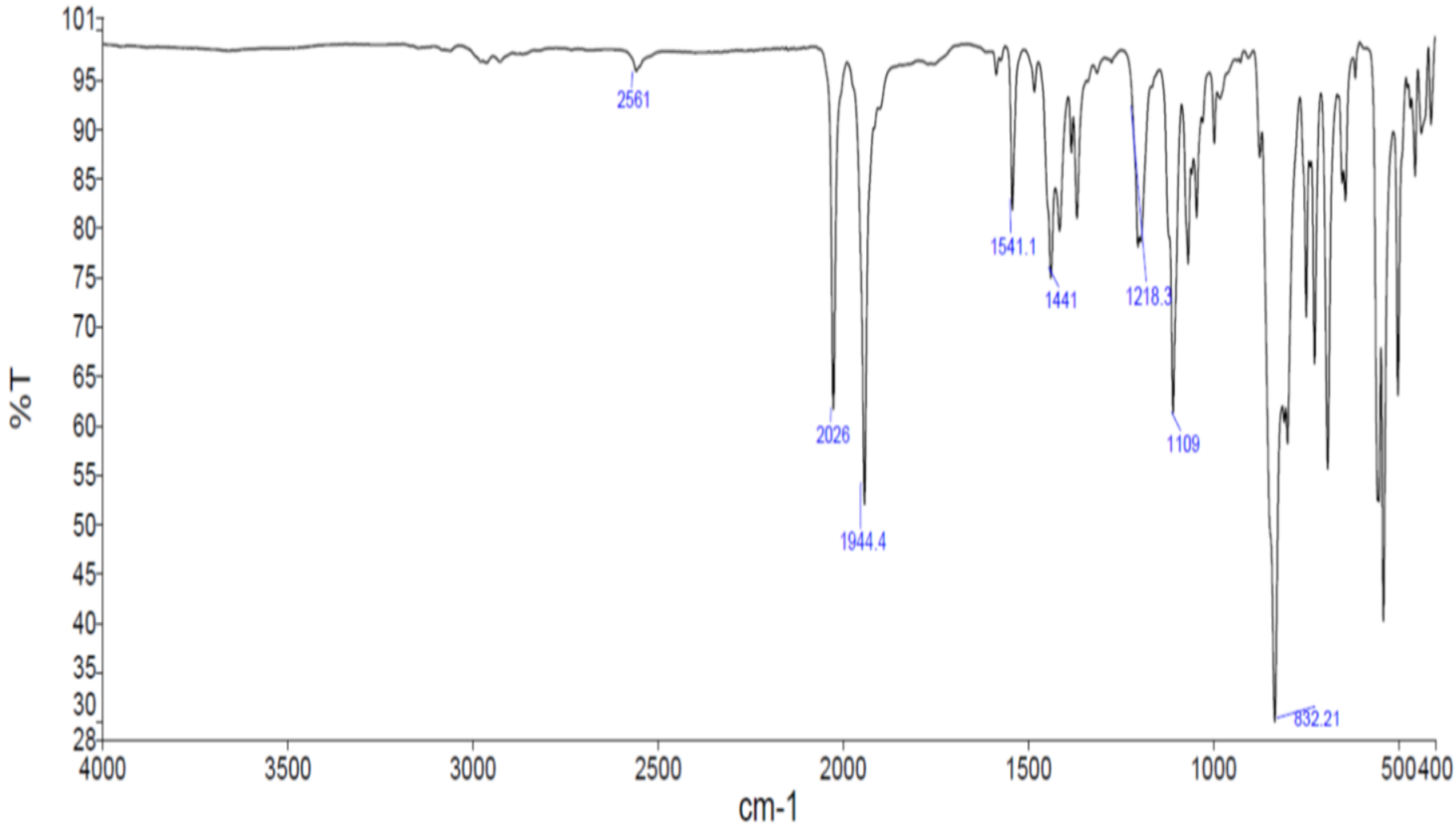


Figure S62: Infrared Spectrum of $[Mo(CPPh_3)(CO)_2(Tp^*)]PF_6$ (3a; ATR, 25 °C, ν)

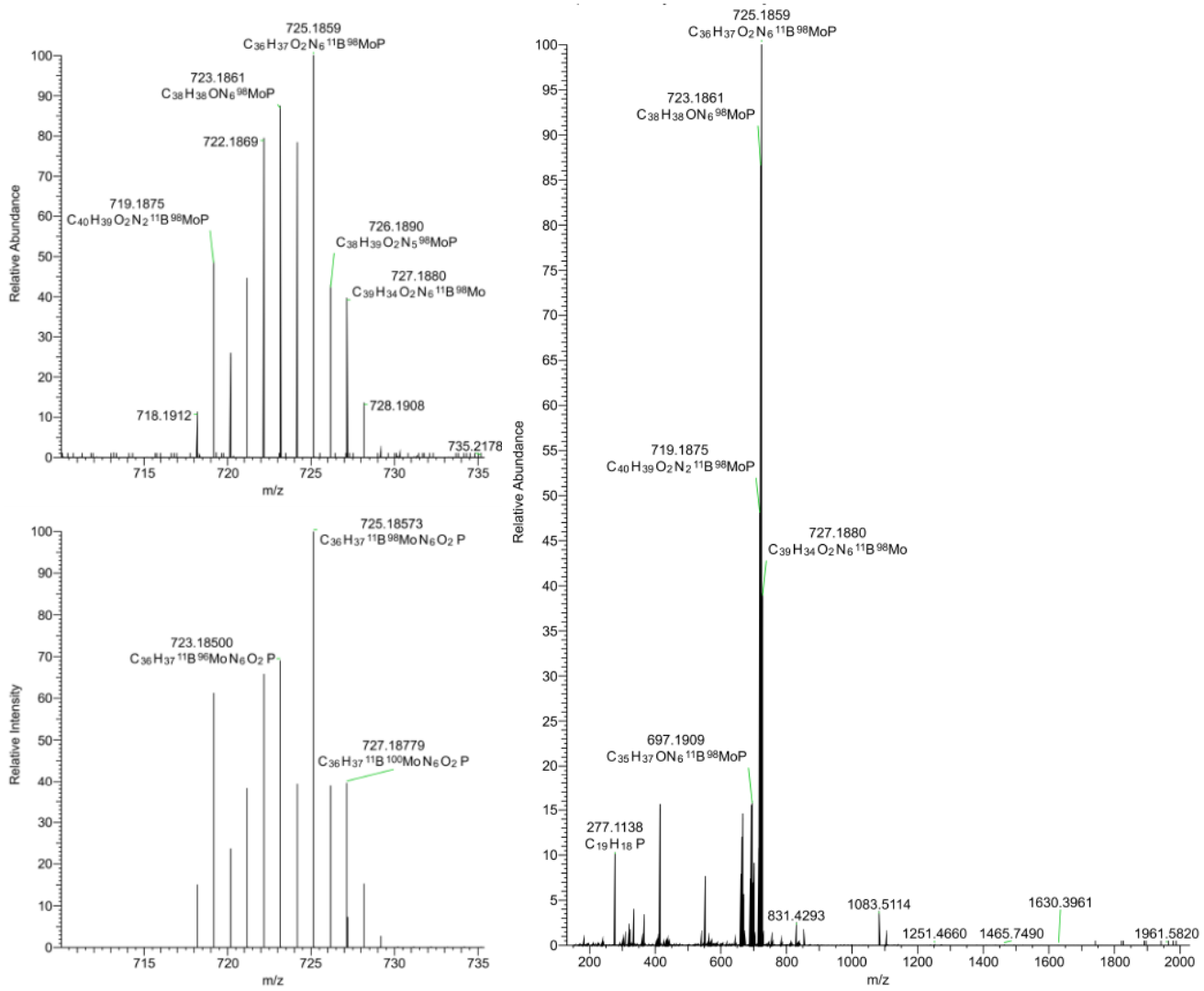


Figure S63: Mass Spectrum of (ESI, +ve ion) [Mo(≡CPPh$_3$)(CO)$_2$(Tp*)]PF$_6$ (3a)

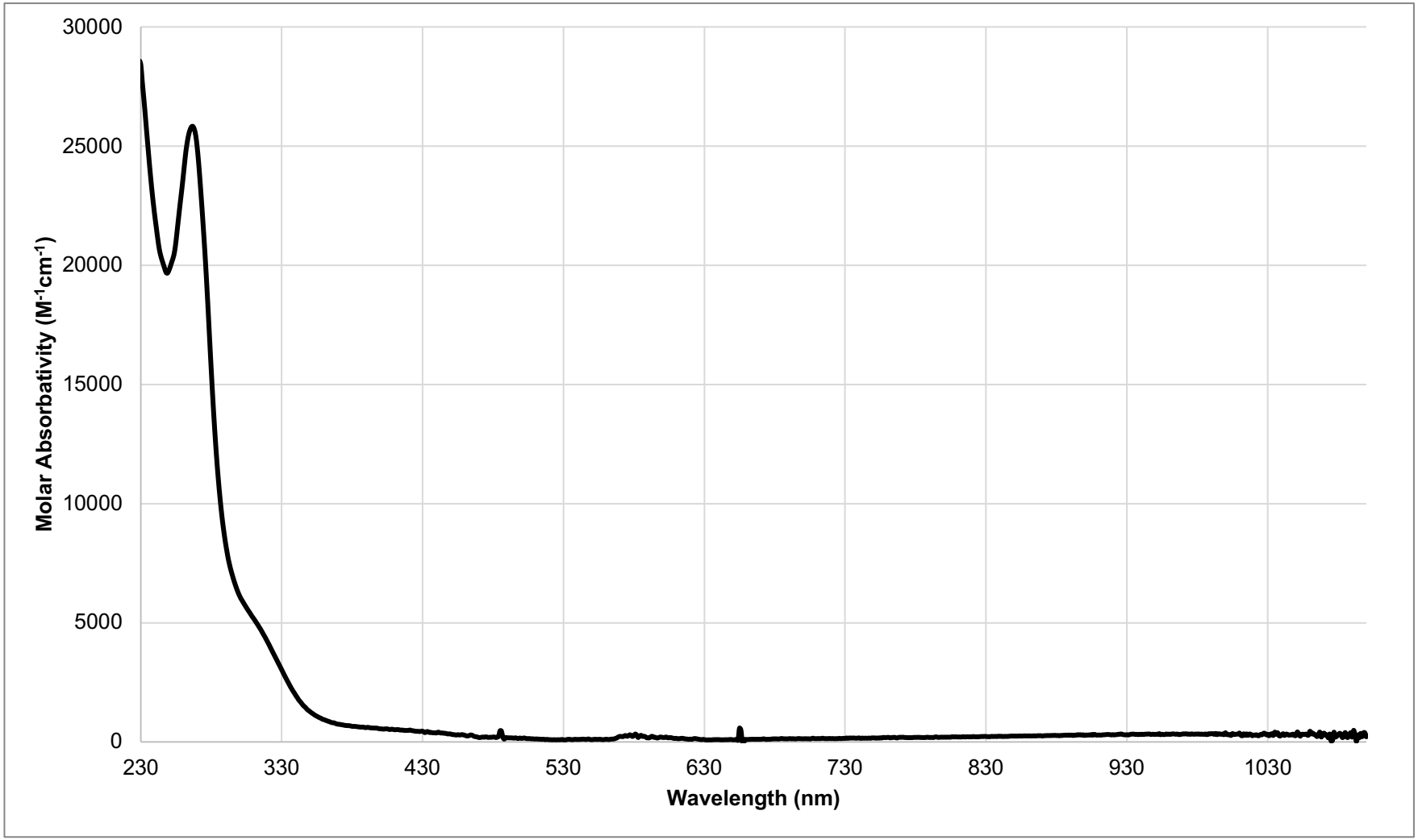


Figure S64: Electronic spectrum of $[Mo(CPPh_3)(CO)_2(Tp^*)].PF_6$· in CH_2Cl_2 [3a; M = 2.851(3)×10^{-5} molL^{-1}].

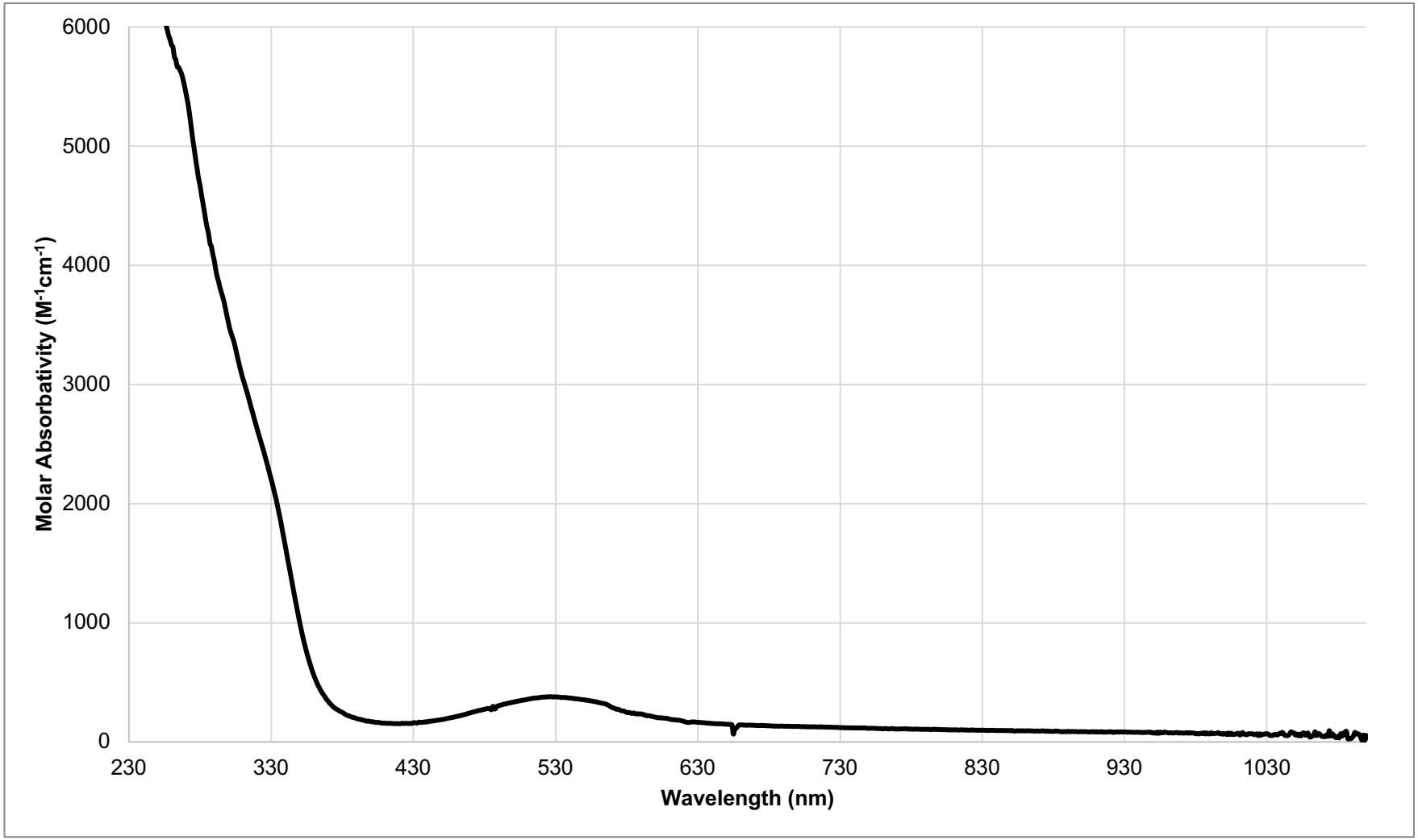


Figure S65: Electronic spectrum of $[Mo(CPPh_3)(CO)_2(Tp^*)].PF_6$· in CH_2Cl_2 [3a; M = 2.851(3)×10^{-4} molL^{-1}].

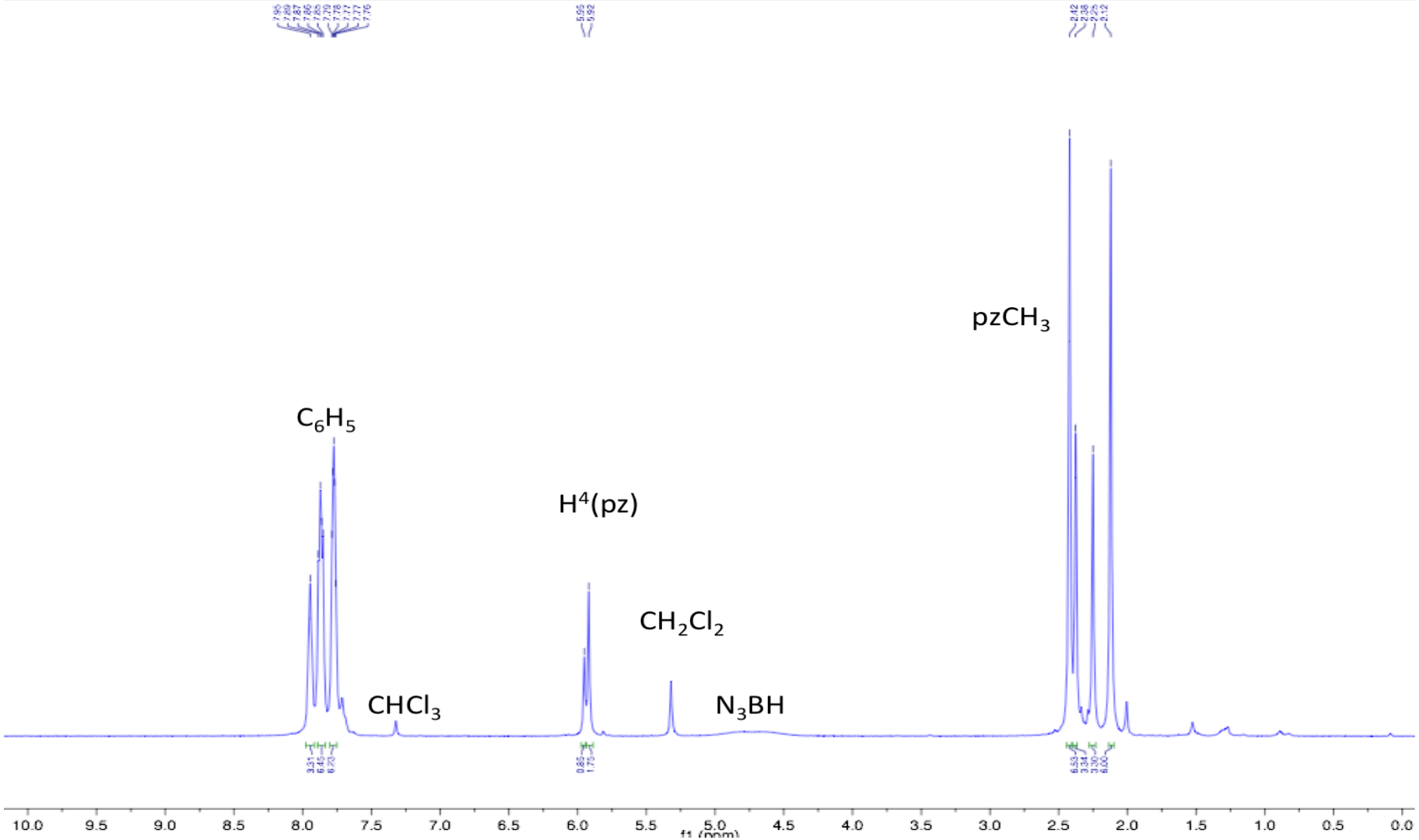


Figure S66: ^{1}H NMR Spectrum of [Mo(SCPPh$_3$)(CO)$_2$(Tp*)]PF$_6$ (4a; 400 MHz, CD$_2$Cl$_2$, 25 °C, δ)

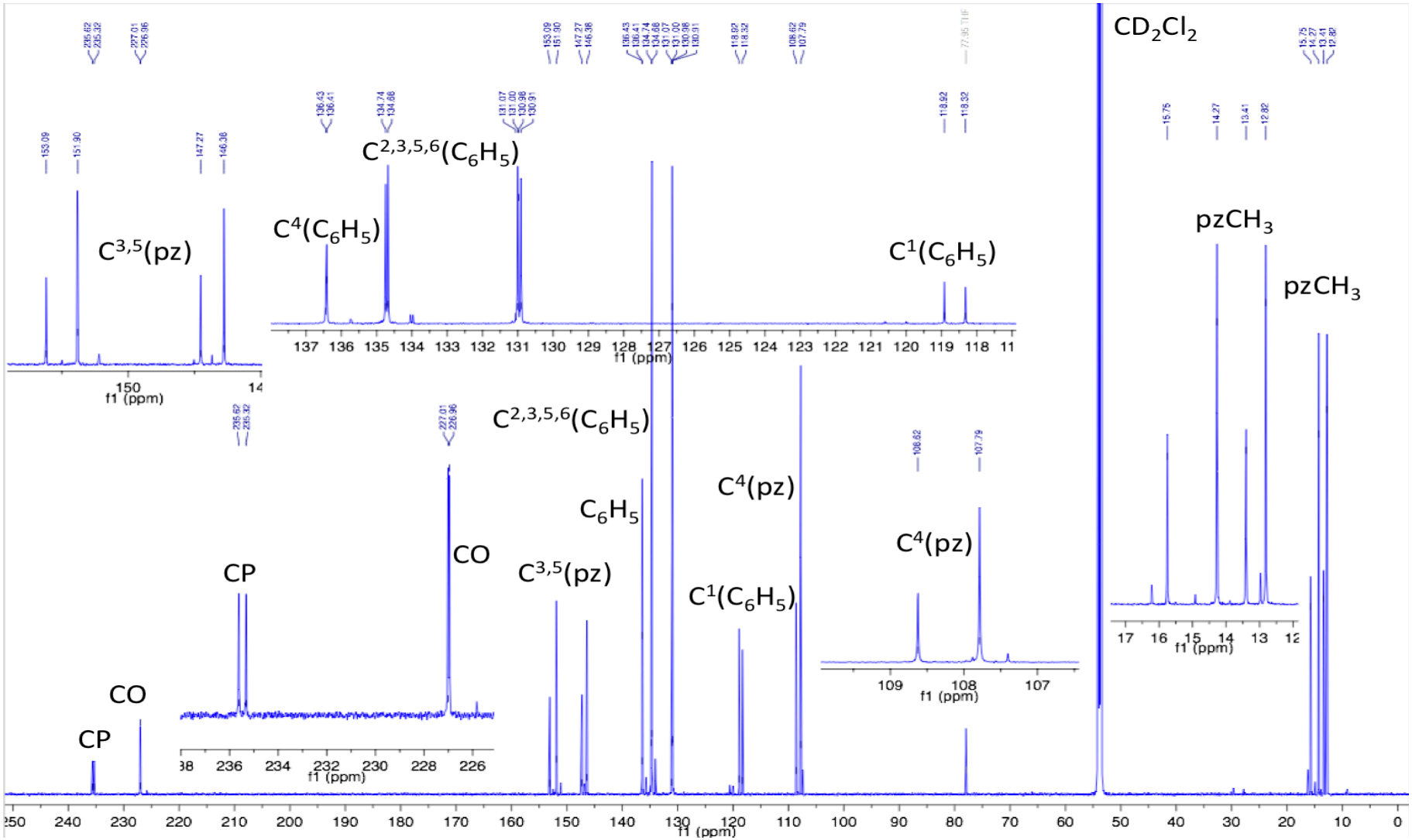


Figure S67: $^{13}C\{^{1}H\}$ NMR Spectrum of $[Mo(SCPPh_3)(CO)_2(Tp^*)]PF_6$ (4a; 151 MHz, CD_2Cl_2, 25 °C, δ)

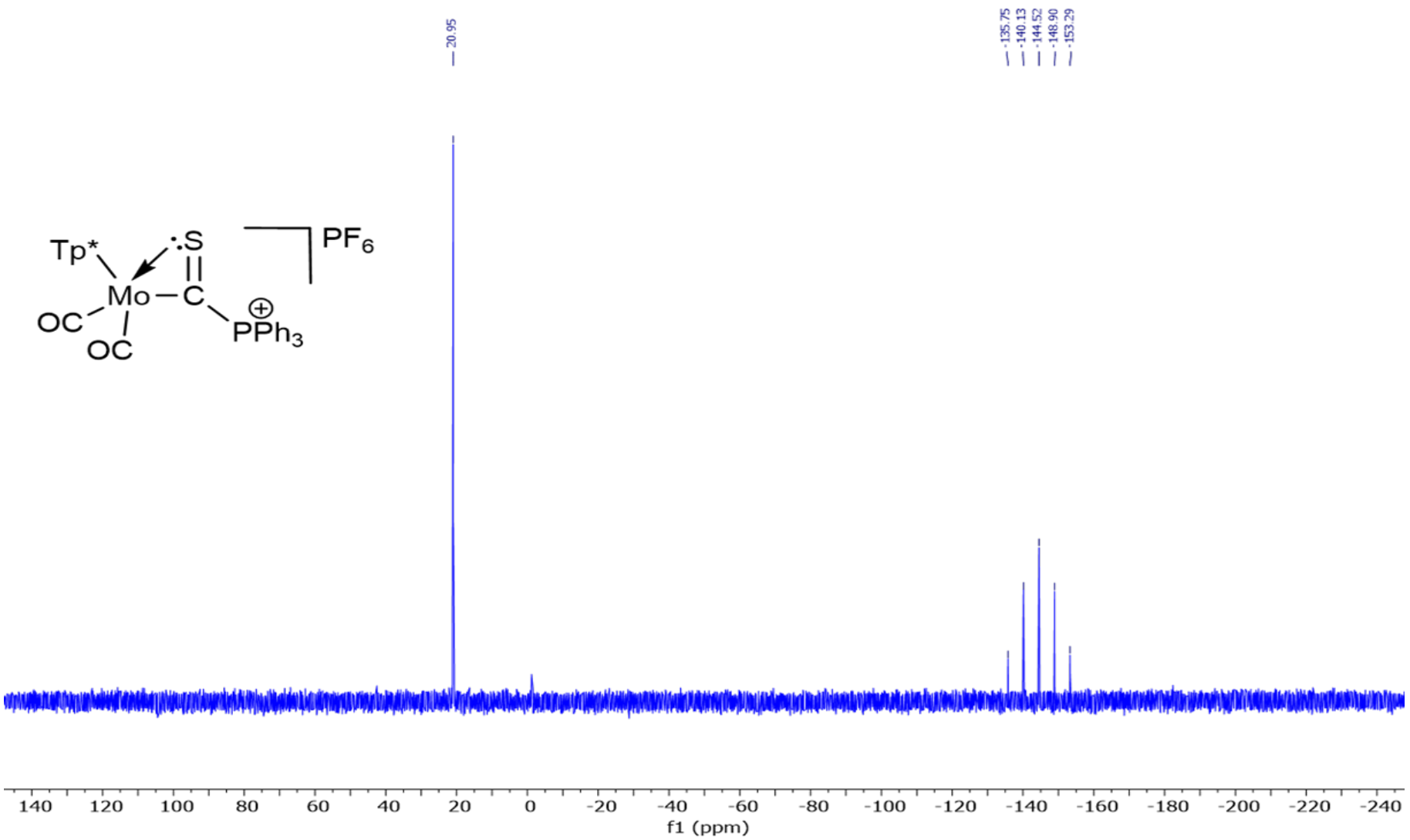


Figure S68: $^{31}P\{^{1}H\}$ NMR Spectrum of $[Mo(SCPPh_3)(CO)_2(Tp^*)]PF_6$ (4a; 162 MHz, CD_2Cl_2, 25 °C, δ)

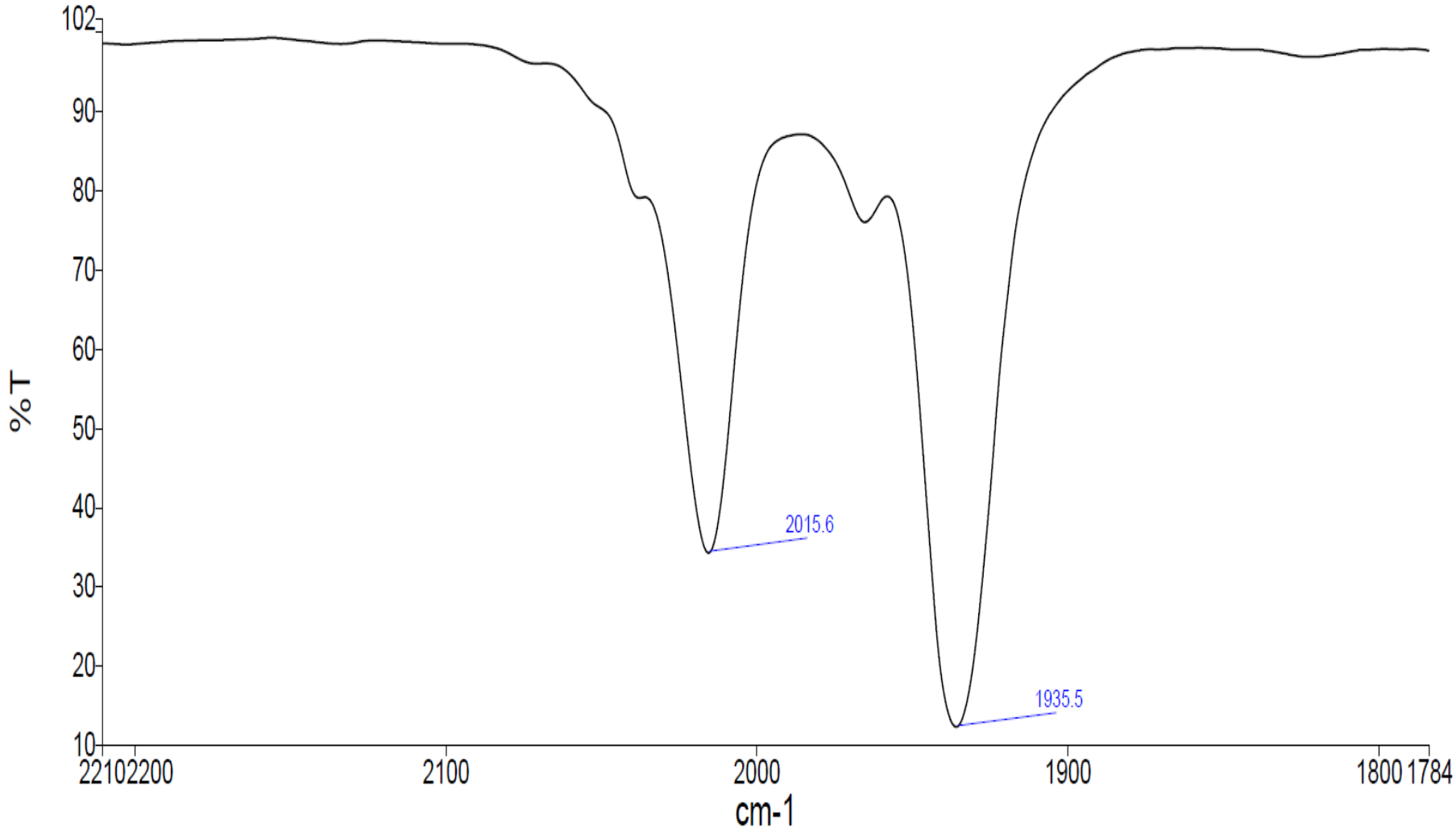


Figure S69: Infrared Spectrum of $[Mo(SCPPh_3)(CO)_2(Tp^*)]PF_6$ (4a; CH_2Cl_2, 25 °C, ν)

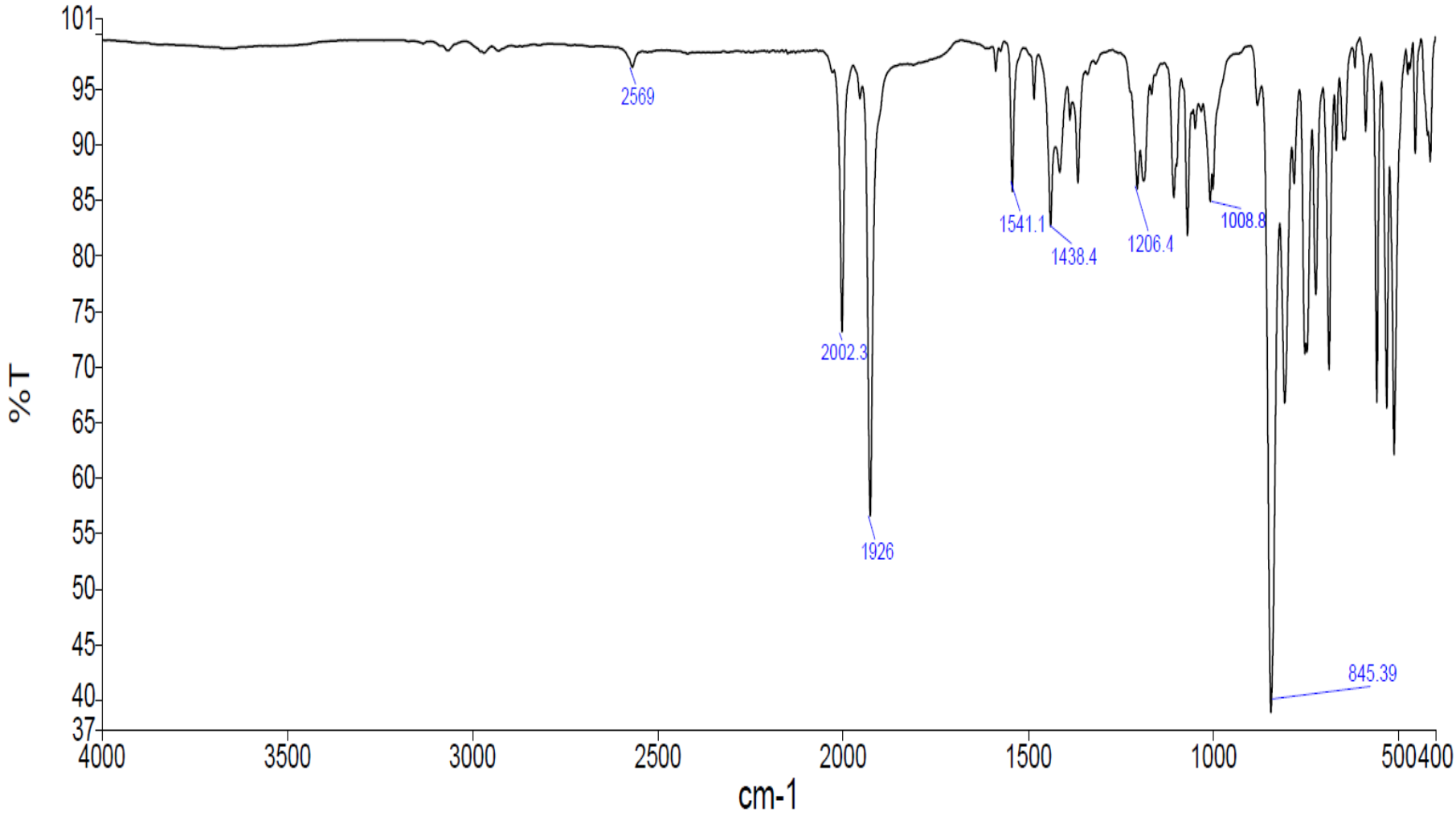


Figure S70: Infrared Spectrum of $[Mo(SCPPh_3)(CO)_2(Tp^*)]PF_6$ (4a; ATR, 25 °C, ν)

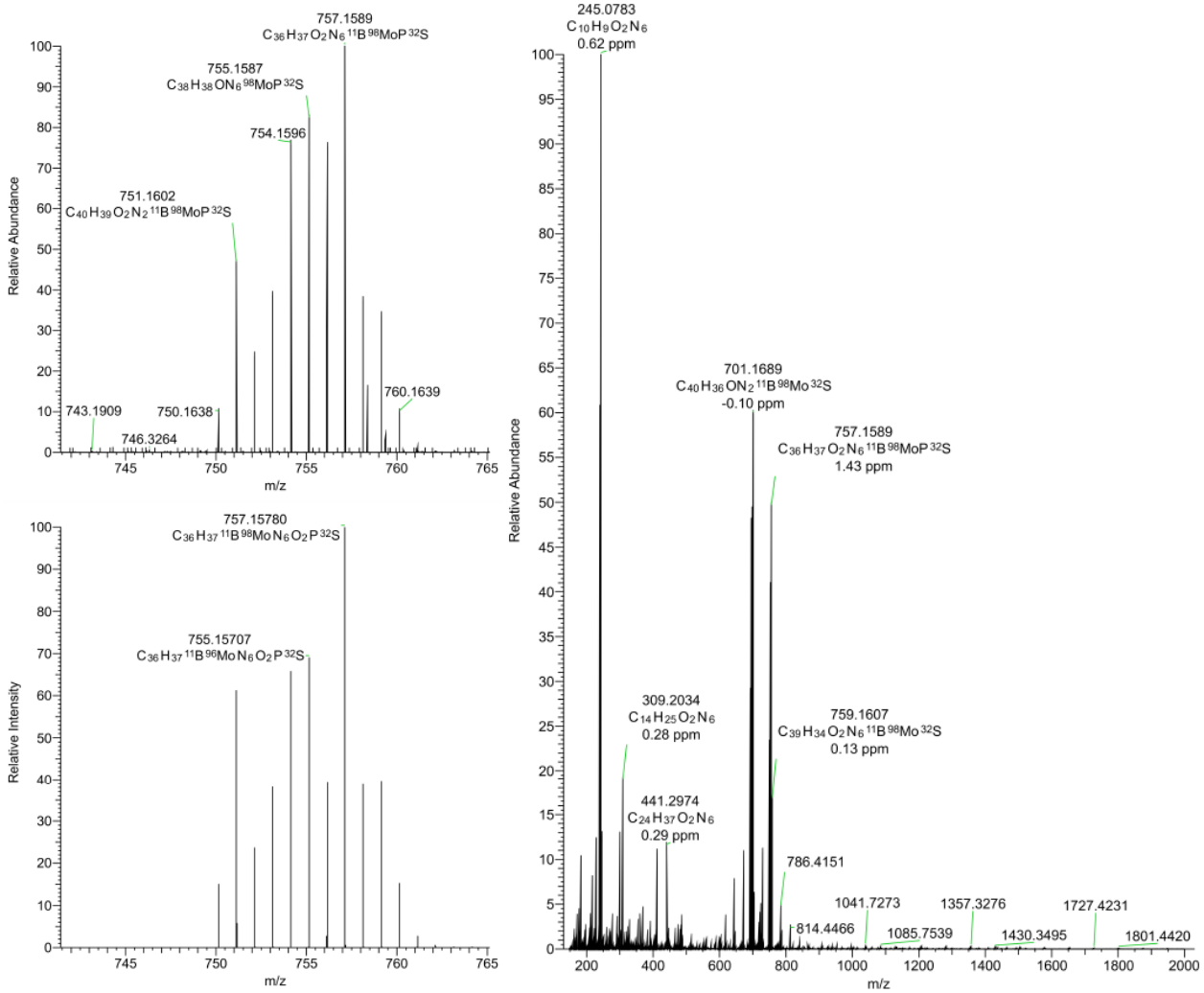


Figure S71: Mass Spectrum (ESI, +ve ion) of $[Mo(SCPPh_3)(CO)_2(Tp^*)]PF_6$ (4a)

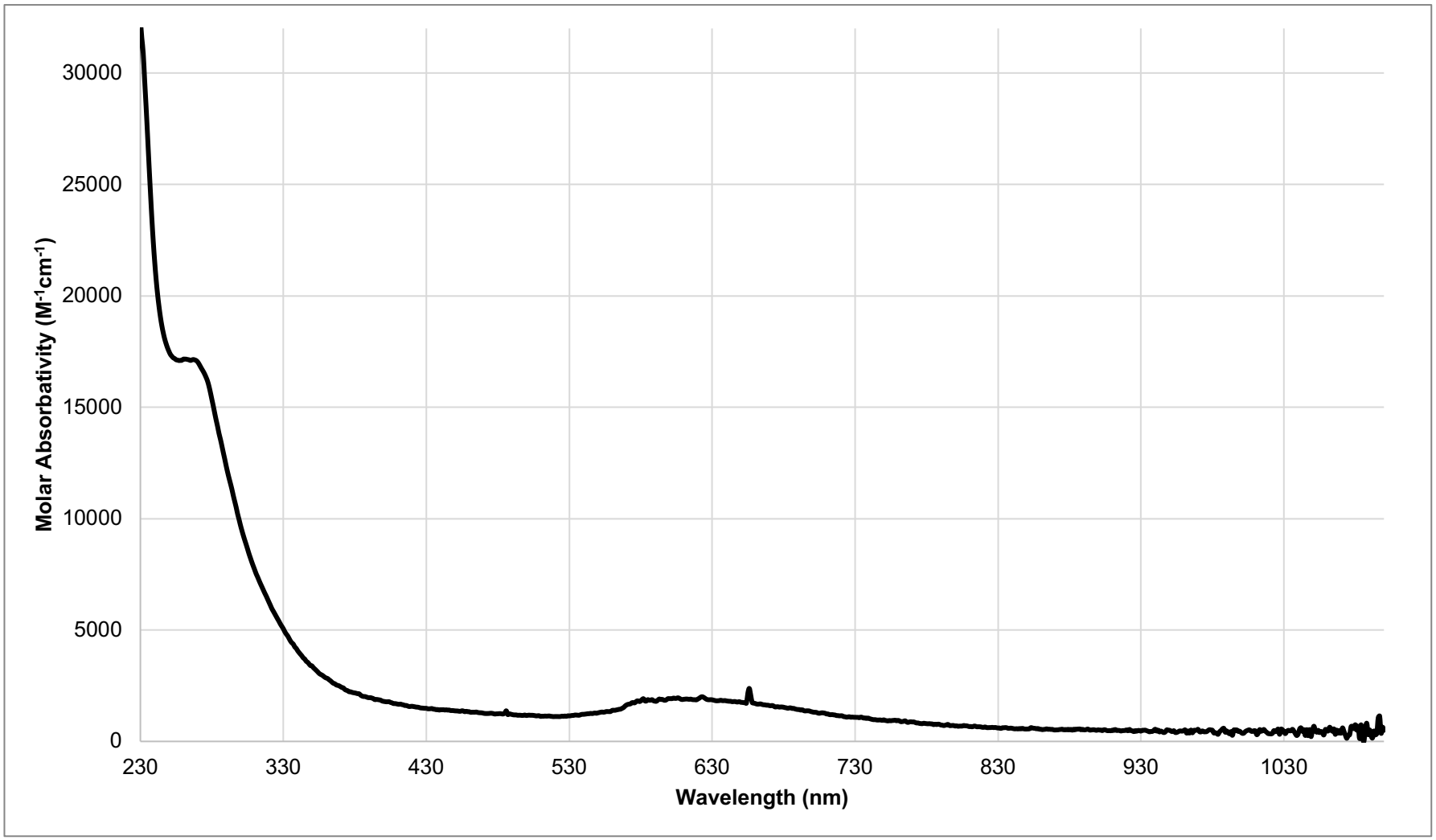


Figure S72: Electronic spectrum of $[Mo(SCPPh_3)(CO)_2(Tp^*)].PF_6$ in CH_2Cl_2 [4a; M = 2.731(3)×10^{-5} molL^{-1}].

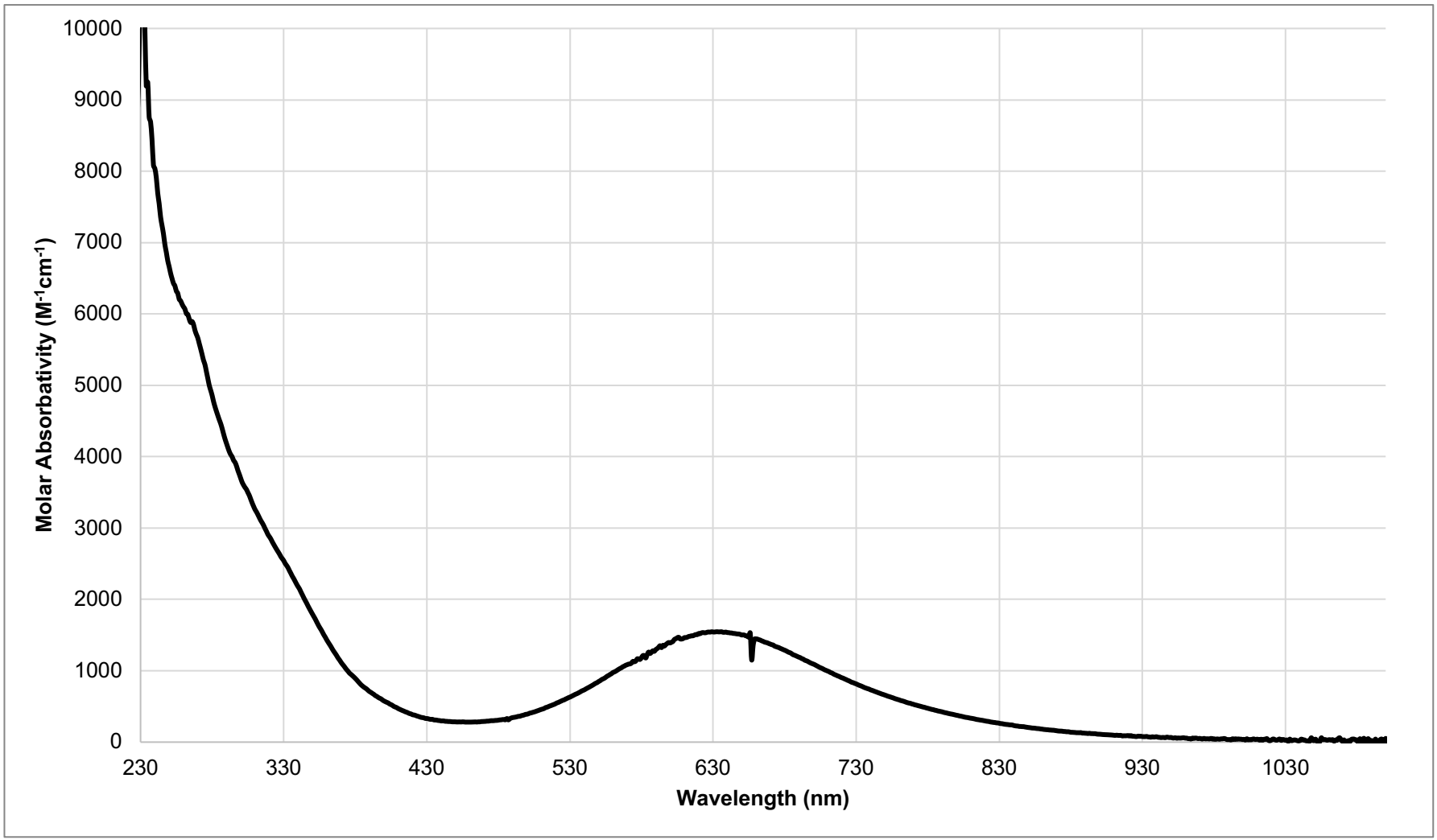


Figure S73: Electronic spectrum of $[Mo(SCPPh_3)(CO)_2(Tp^*)].PF_6$ in CH_2Cl_2 [4a; M = 2.731(3)×10^{-4} molL^{-1}].

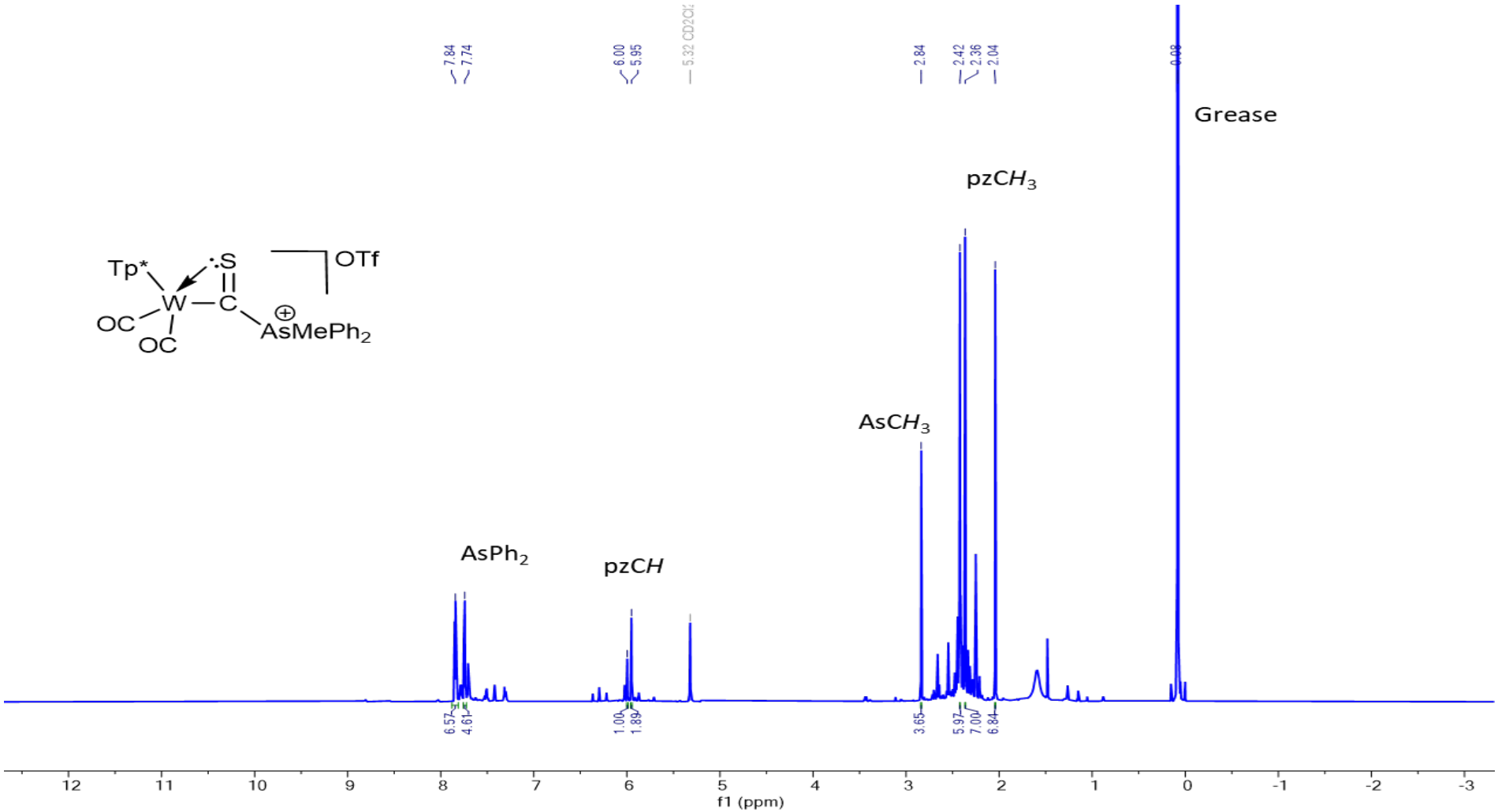


Figure S74: ^{1}H NMR Spectrum of [W(SCAsMePh$_2$)(CO)$_2$(Tp*)]PF$_6$ (7b; 800 MHz, CD$_2$Cl$_2$, 25 °C, δ)

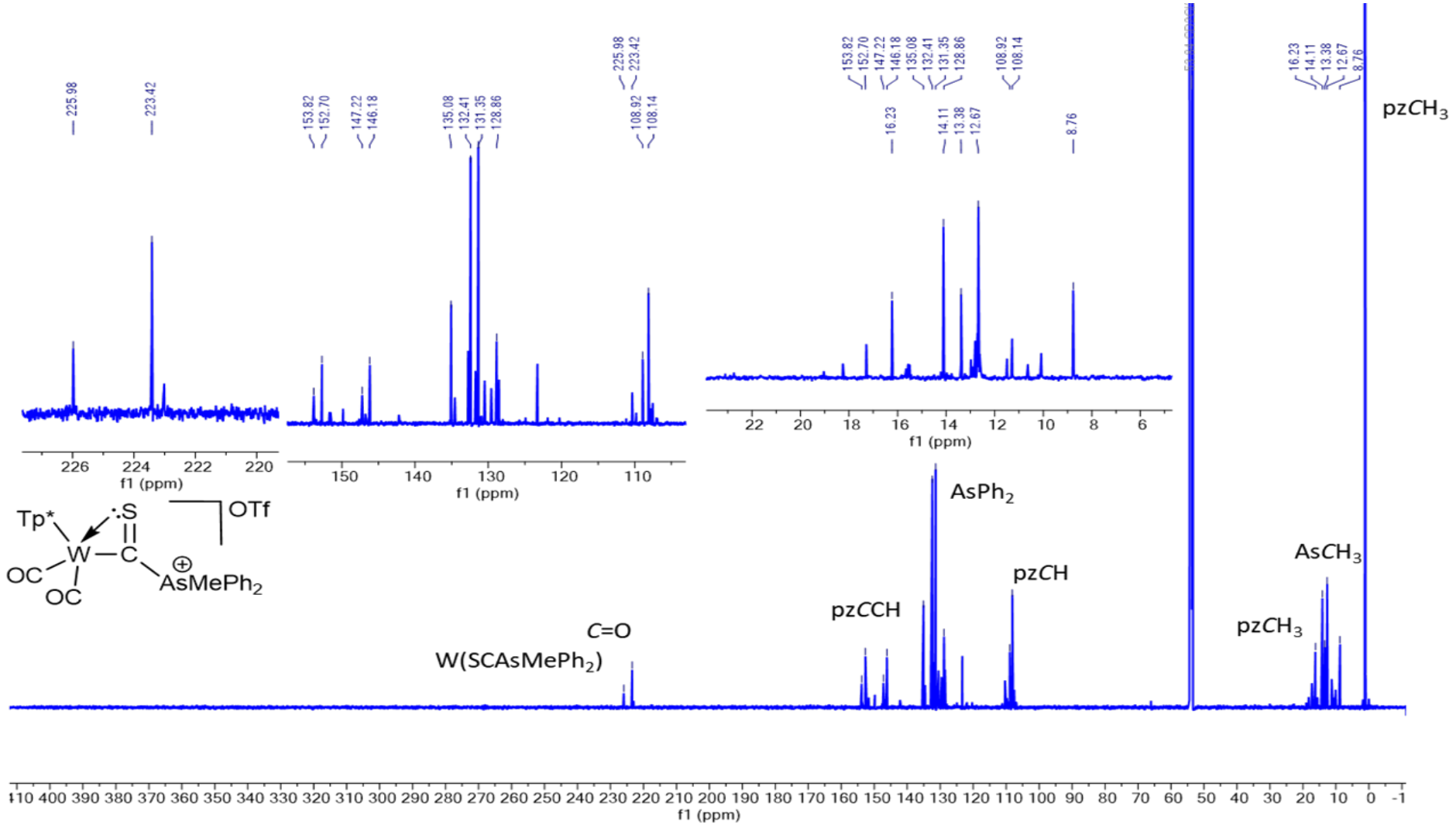


Figure S75: $^{13}C\{^1H\}$ NMR Spectrum of $[W(SCAsMePh_2)(CO)_2(Tp^*)]PF_6$ (7b; 200 MHz, CD_2Cl_2, 25 °C, δ)

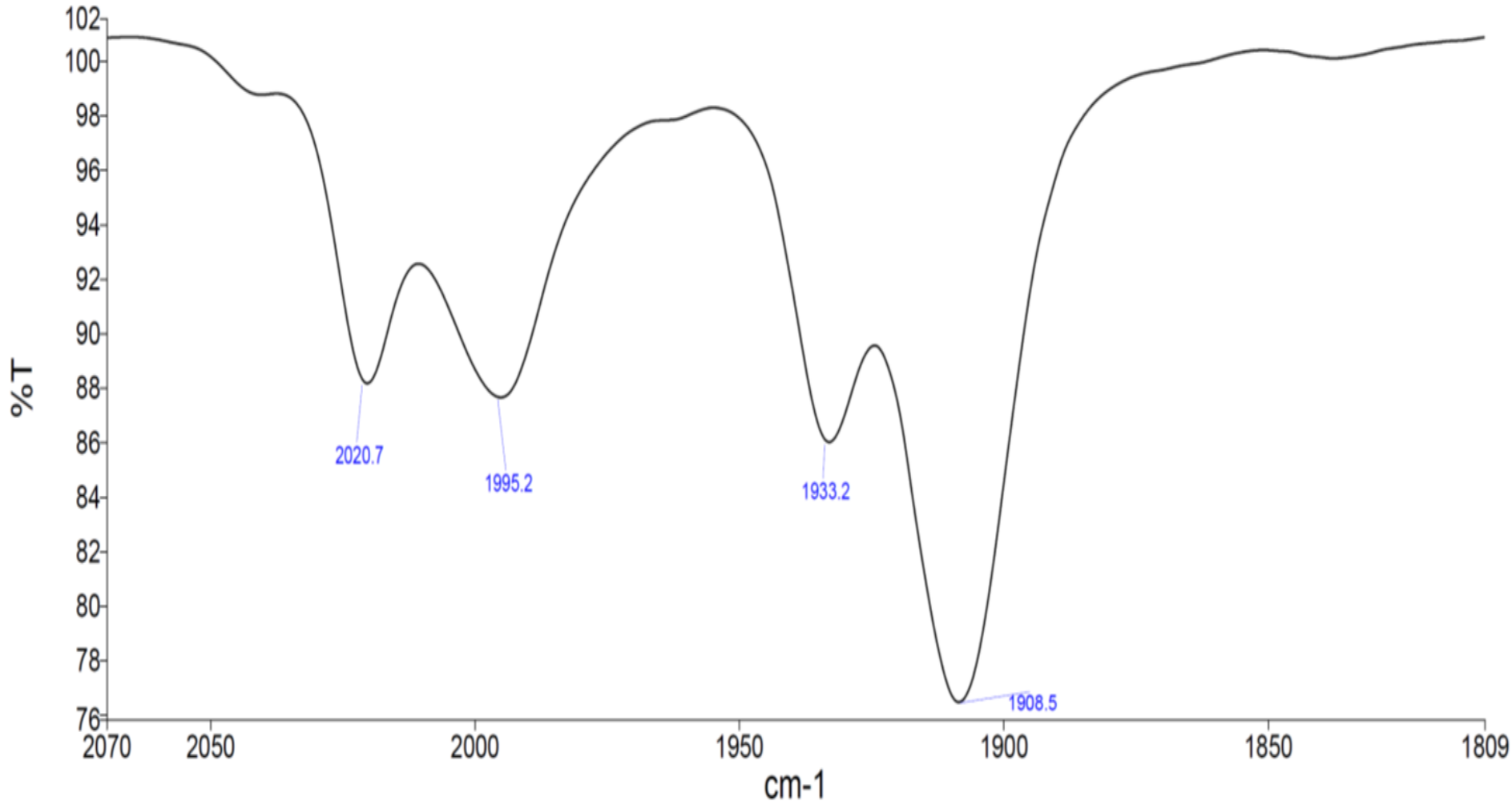


Figure S76: Infrared Spectrum of $[W(SCAsMePh_2)(CO)_2(Tp^*)]PF_6$ (7b; CH_2Cl_2, 25 °C, ν)

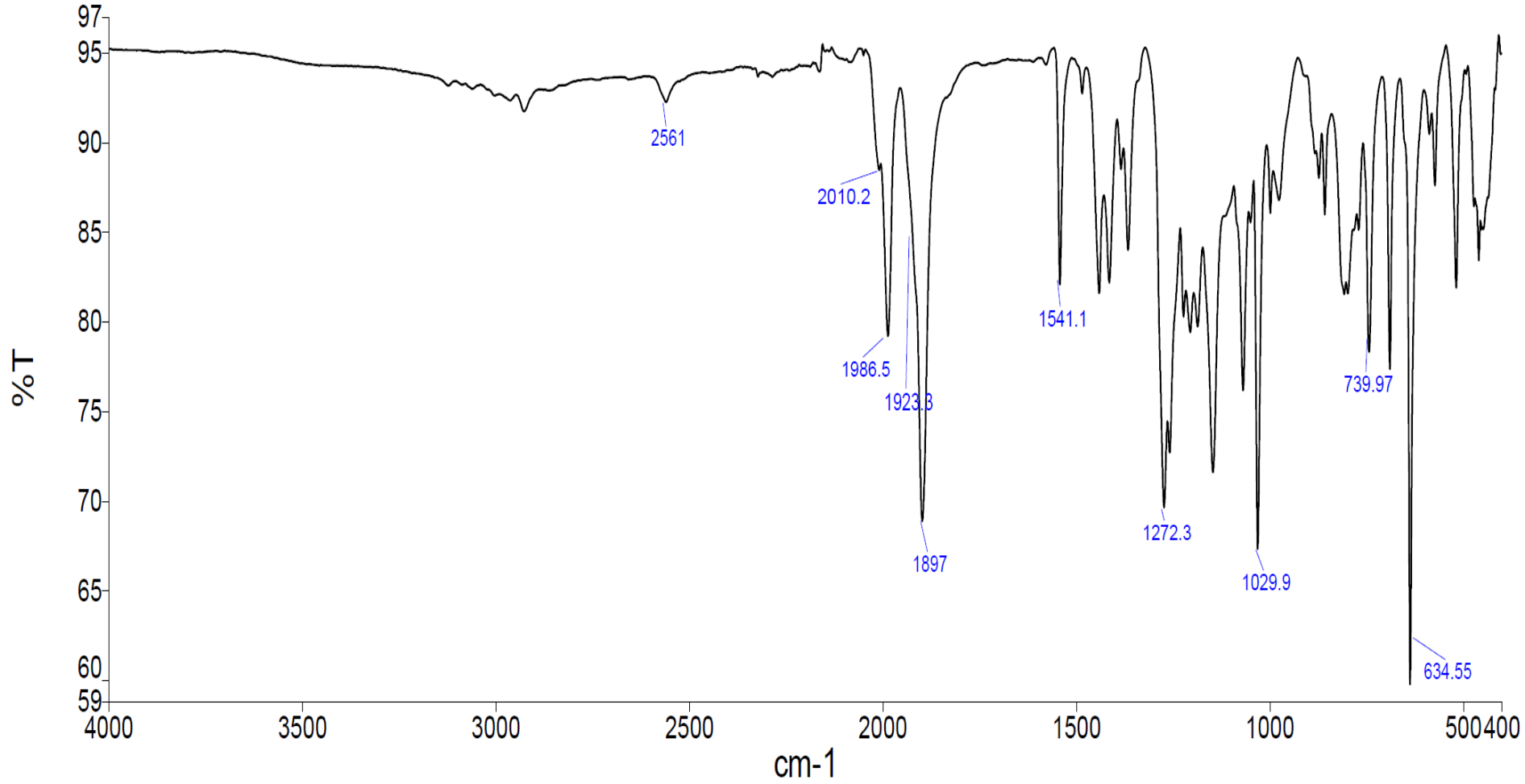


Figure S77: Infrared Spectrum of $[W(SCAsMePh_2)(CO)_2(Tp^*)]PF_6$ (7b; ATR, 25 °C, ν)

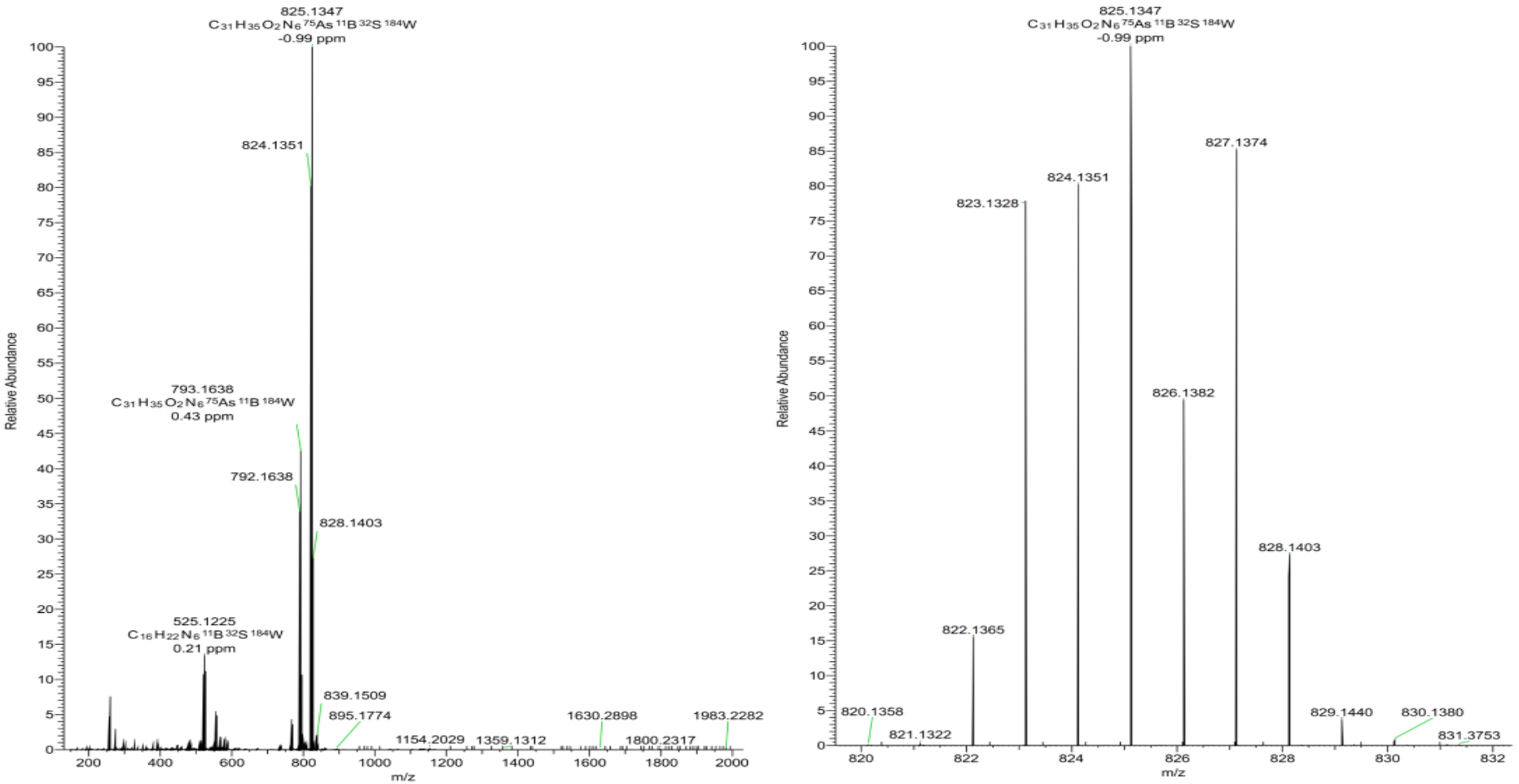


Figure S78: Mass Spectrum (ESI, +ve ion) of $[W(SCAsMePh_2)(CO)_2(Tp^*)]PF_6$ (7b)