

Heterobimetallic μ_2 -Halocarbyne complexes

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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 (CH_2Cl_2 , MeCN). The compounds $[\text{M}(\equiv\text{CCl})(\text{CO})_2(\text{Tp}^*)]$ ($\text{M} = \text{Mo}$ **1a**, W **1b**),¹ $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{PPh}_3)_2]$,² $[\text{Pt}(\text{nbe})_3]$,³ $[\text{AuCl-SMe}_2]$ ⁴ 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, $^{13}\text{C}\{^1\text{H}\}$ at 100.6 MHz, $^{31}\text{P}\{^1\text{H}\}$ at 162.0 MHz, $^{195}\text{Pt}\{^1\text{H}\}$ at 85.7 MHz), a Bruker Avance 600 (^1H at 600.0 MHz, $^{13}\text{C}\{^1\text{H}\}$ at 150.9 MHz) or a Bruker Avance 700 (^1H at 700.0 MHz, $^{13}\text{C}\{^1\text{H}\}$ at 176.1 MHz, $^{31}\text{P}\{^1\text{H}\}$ 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 {85% H_3PO_4 in H_2O for $^{31}\text{P}\{^1\text{H}\}$, 1.2M Na_2PtCl_6 for $^{195}\text{Pt}\{^1\text{H}\}$. 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 or ^{195}Pt satellites. In select cases, distinct peaks were observed in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, but to the level of accuracy that is reportable (i.e., two decimal places for ^1H NMR, one decimal place for $^{13}\text{C}\{^1\text{H}\}$ 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 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 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 $^{11}\text{B}\{^1\text{H}\}$ 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). This may account for unsatisfactory data (%N) for **2a** and **3b**. 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 or dichloromethane as the matrix.

Crystallographic Details

Data for X-ray crystallography were collected with Agilent Technologies Xcalibur or Supernova/EosS2-CCD diffractometers using graphite monochromated Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) or Cu- $\text{K}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$) employing the CrysAlis PRO-CCD and -RED software,⁵ 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,^{6,7} Implemented within the Olex2 suite of programs.⁸ Hydrogen atoms were located geometrically and refined using a riding model. Diagrams were produced using the CCDC visualisation program Mercury.^{9,10}

Computational Details

Computational studies were performed by using the SPARTAN20[®] suite of programs.¹¹ Geometry optimisation (gas phase) for diatomics and metal complexes was performed at the DFT level of theory using the exchange functionals $\omega\text{B97X-D}$ of Head-Gordon,^{12,13} The Los Alamos effective core potential type basis set (LANL2DZ) of Hay and Wadt¹⁴⁻¹⁶ was used for I, Mo and W while Pople 6-31G* basis sets¹⁷ were used for all other atoms. For the free ligands $\text{CX}^+/\text{CO}/\text{CN}^-$, geometries were optimised using the $\omega\text{BP97X-V}/6-31\text{G}^*$ functional. 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 are provided below.

Synthetic Procedures and Crystallographic Data

Crystallisation of $[\text{Mo}(\text{CBr})(\text{CO})_2(\text{Tp}^*)]$ (1b**).** Crystals suitable for X-ray diffraction studies were grown from liquid-liquid diffusion of petroleum ether 40–60 into an acetone solution of **1c** and vapour diffusion of hexane into a CHCl_3 solution of **1c** at 5 °C. *Crystal data for $\text{C}_{18}\text{H}_{22}\text{BBrMoN}_6\text{O}_2$, $M_w = 541.07 \text{ gmol}^{-1}$, orthorhombic, $Pnma$ (No. 62), $a = 20.4940(4) \text{ \AA}$, $b = 13.7716(3) \text{ \AA}$, $c = 7.9961(1) \text{ \AA}$, $V = 2256.78(7) \text{ \AA}^3$, $Z = 4$, $D_{\text{calc}} = 1.591 \text{ Mgm}^{-3}$, $\mu(\text{Mo K}\alpha) = 2.38 \text{ mm}^{-1}$, $T = 150.0(1) \text{ K}$, clear light orange block, $0.38 \times 0.35 \times 0.16 \text{ mm}$, 2684 independent measured reflections ($2\theta_{\text{max}} = 55.0^\circ$), $R_1 = 0.056$, $wR_2 = 0.143$ for 2020 reflections [I*

$>2\sigma(I)$ and 174 parameters with 14 restraints. CDCC 2173049. A hexane hemisolvate was also prepared by the vapour diffusion of *n*-hexane into a CHCl_3 solution of **1c**. *Crystal data for* $\text{C}_{18}\text{H}_{22}\text{BBrMoN}_6\text{O}_2 \cdot 0.5(\text{C}_6\text{H}_{14})$ $M_w = 584.16 \text{ gmol}^{-1}$, orthorhombic, *Fdd2* (No. 43), $a = 38.1509(8) \text{ \AA}$, $b = 33.3659(8) \text{ \AA}$, $c = 7.9763(1) \text{ \AA}$, $V = 10153.3(3) \text{ \AA}^3$, $Z = 16$, $D_{\text{calc}} = 1.529 \text{ Mgm}^{-3}$, $\mu(\text{Cu K}\alpha) = 6.30 \text{ mm}^{-1}$, $T = 150.0(1) \text{ K}$, clear light yellow plate, $0.45 \times 0.10 \times 0.05 \text{ mm}$, 4659 independent measured reflections ($2\theta_{\text{max}} = 146.2^\circ$), $R_1 = 0.045$, $wR_2 = 0.111$ for 4561 reflections [$I > 2\sigma(I)$] and 308 parameters with 49 restraints. CDCC 2173045.

Crystallisation of $[\text{W}(\text{CBr})(\text{CO})_2(\text{Tp}^*)]$ (1d**).** Crystals suitable for X-ray diffraction studies were grown from the vapour diffusion of *n*-hexane into a CHCl_3 solution of the title compound at ambient temperature over a week. *Crystal data for* $\text{C}_{18}\text{H}_{22}\text{BBrN}_6\text{O}_2\text{W}$, $M_w = 628.98 \text{ gmol}^{-1}$, orthorhombic, *Pnma* (No. 62), $a = 20.2626(3) \text{ \AA}$, $b = 13.7288(3) \text{ \AA}$, $c = 7.9566(2) \text{ \AA}$, $V = 2213.38(8) \text{ \AA}^3$, $Z = 4$, $D_{\text{calc}} = 1.888 \text{ Mgm}^{-3}$, $\mu(\text{Cu K}\alpha) = 12.00 \text{ mm}^{-1}$, $T = 150.0(1) \text{ K}$, clear light yellow plate, $0.18 \times 0.12 \times 0.06 \text{ mm}$, 2185 independent measured reflections ($2\theta_{\text{max}} = 140.2^\circ$), $R_1 = 0.057$, $wR_2 = 0.128$ for 2051 reflections [$I > 2\sigma(I)$] and 165 parameters with 9 restraints. CDCC 2173044.

Synthesis of $[\text{MoAu}(\mu\text{-Cl})\text{Cl}(\text{CO})_2(\text{Tp}^*)]$ (2a**).** The halocarbonyne $[\text{Mo}(\equiv\text{C})\text{Cl}(\text{CO})_2(\text{Tp}^*)]$ (**1a**: 200 mg, 0.403 mmol) and $[\text{AuCl}(\text{SMe}_2)]$ (0.120 g, 0.407 mmol) were dissolved in CH_2Cl_2 (10 mL) to initially provide a yellow solution that changed to orange within one minute. The subsequent reaction was monitored by infra-red spectroscopy, which indicated reaction completion after 90 minutes. During the reaction the flask was covered with aluminium foil to largely exclude light, thereby minimising formation of colloidal gold. Upon completion, the solution was eluted through diatomaceous earth which was further washed with CH_2Cl_2 prior to dilution with *n*-hexane and concentration under reduced pressure to provide a bright orange powder which was isolated *via* vacuum filtration. The product was washed with *n*-hexane (2 x 10 mL) and *n*-pentane (1 x 10 mL) and dried *in vacuo* to provide **2a** as a fine orange powder (0.220 g, 0.302 mmol, 75% isolated yield). Crystals suitable for X-ray diffraction studies were grown by vapour diffusion of cyclohexane into a CHCl_3 solution of the title compound at 5°C .

IR (CH_2Cl_2 , cm^{-1}): 2031 vs ν_{CO} , 1957 vs ν_{CO} . IR (ATR, cm^{-1}): 2556 w ν_{BH} , 2020 vs ν_{CO} , 1962 vs ν_{CO} . $^1\text{H NMR}$ (700 MHz, CDCl_3 , 25°C) δ_{H} 5.90 (s, 3 H, pzCH), 2.44 (s, 6 H, pzCH₃), 2.24 (s, 3 H, pzCH₃), 2.38 (s, 6 H, pzCH₃), 2.35 (s, 3 H, pzCH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, CDCl_3 , 25°C): δ_{C} 230.4 ($\mu\text{-Cl}$), 218.1 (CO), 152.5, 151.9 [$\text{C}^5(\text{pz})$], 146.3, 145.9 [$\text{C}^3(\text{pz})$], 108.1 107.7 [$\text{C}^4(\text{pz})$], 16.9, 15.4, 13.2, 12.9 (pzCH₃). MS (ESI, +ve ion, m/z): Found: 731.0084. Calcd for $\text{C}_{18}\text{H}_{23}^{11}\text{BN}_6\text{O}_2^{35}\text{Cl}_2^{98}\text{Mo}^{197}\text{Au}$ [$\text{M}+\text{H}$] $^+$: 731.0072. Anal. Found: C, 29.68; H, 3.17; N, 10.92%. Calcd for $\text{C}_{18}\text{H}_{22}\text{AuBCl}_2\text{MoN}_6\text{O}_2$: C, 29.66; H, 3.04; N, 11.53%.

Crystal data for $2(\text{C}_{18}\text{H}_{22}\text{AuBCl}_2\text{MoN}_6\text{O}_2)$, $M_w = 1458.06 \text{ gmol}^{-1}$, monoclinic, *P2₁/c* (No. 13), $a = 25.4253(3) \text{ \AA}$, $b = 10.9689(1) \text{ \AA}$, $c = 19.7589(2) \text{ \AA}$, $\beta = 108.022(1)^\circ$, $V = 5240.15(10) \text{ \AA}^3$, $Z = 4$, $D_{\text{calc}} = 1.848 \text{ Mgm}^{-3}$, $\mu(\text{Cu K}\alpha) = 16.38 \text{ mm}^{-1}$, $T =$

$150.0(1) \text{ K}$, clear light orange plate, $0.16 \times 0.12 \times 0.05 \text{ mm}$, 10256 independent measured reflections ($2\theta_{\text{max}} = 147.8^\circ$), $R_1 = 0.042$, $wR_2 = 0.102$ for 9646 reflections [$I > 2\sigma(I)$] and 565 parameters without restraints. CDCC 2173041.

Synthesis of $[\text{WAu}(\mu\text{-Cl})\text{Cl}(\text{CO})_2(\text{Tp}^*)]$ (2b**)** A mixture of $[\text{W}(\equiv\text{C})\text{Cl}(\text{CO})_2(\text{Tp}^*)]$ (**1b**: 200 mg, 0.342 mmol) and $[\text{AuCl}(\text{SMe}_2)]$ (0.100 g, 0.340 mmol) was dissolved in CH_2Cl_2 (10 mL) and stirred for 90 minutes by which time the reaction was deemed to be complete (IR). During the reaction the flask was covered with aluminium foil. The solution was eluted through diatomaceous earth which was washed with further CH_2Cl_2 prior to dilution with *n*-hexane and concentrating under reduced pressure. This provided a bright orange powder which was collected *via* vacuum filtration and washed with *n*-hexane (2 x 10 mL) and *n*-pentane (1 x 10 mL) before drying *in vacuo*. This afforded **2b** as a fine orange powder (0.184 g, 0.225 mmol, 66% isolated yield). Crystals suitable for X-ray diffraction studies were grown by vapour diffusion of cyclohexane into a CHCl_3 solution of the title compound at 5°C .

IR (CH_2Cl_2 , cm^{-1}): 2018 vs ν_{CO} , 1934 vs ν_{CO} . IR (ATR, cm^{-1}): 2559 w ν_{BH} , 2008 vs ν_{CO} , 1943 s ν_{CO} , 1933 vs ν_{CO} . $^1\text{H NMR}$ (700 MHz, CDCl_3 , 25°C): δ_{C} 5.95 (s, 2 H, pzCH), 5.93 (s, 1 H, pzCH), 2.48 (s, 9 H, pzCH₃), 2.38 (s, 6 H, pzCH₃), 2.34 (s, 3 H, pzCH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, CDCl_3 , 25°C): δ_{C} 222.2 ($^1J_{\text{CW}} = 125 \text{ Hz}$, $\mu\text{-Cl}$), 213.8 ($^1J_{\text{CW}} = 152 \text{ Hz}$, CO), 153.7, 151.8 [$\text{C}^5(\text{pz})$], 146.2, 145.9 [$\text{C}^3(\text{pz})$], 108.4, 108.0 [$\text{C}^4(\text{pz})$], 17.6, 16.0, 13.2, 12.8 (pzCH₃). MS (ESI, +ve ion, m/z): Found: 839.0344. Calcd for $\text{C}_{18}\text{H}_{22}^{11}\text{BN}_6\text{O}_2^{23}\text{Na}^{35}\text{Cl}_2^{184}\text{W}^{197}\text{Au}$ [M] $^+$: 839.0347. Anal. Found: C, 28.01; H, 3.03; N, 10.12%. Calcd for $\text{C}_{18}\text{H}_{22}\text{AuBCl}_2\text{N}_6\text{O}_2\text{W}$: C, 26.46; H, 2.71; N, 10.29%. We attribute, without evidence, the unsatisfactory elemental microanalytical data to partial desolvation of cyclohexane during extended drying under vacuum, noting that Calcd for $\text{C}_{18}\text{H}_{22}\text{AuBCl}_2\text{N}_6\text{O}_2\text{W} \cdot 0.25\text{C}_6\text{H}_{12}$: C, 27.95; H, 3.01; N, 10.03%.

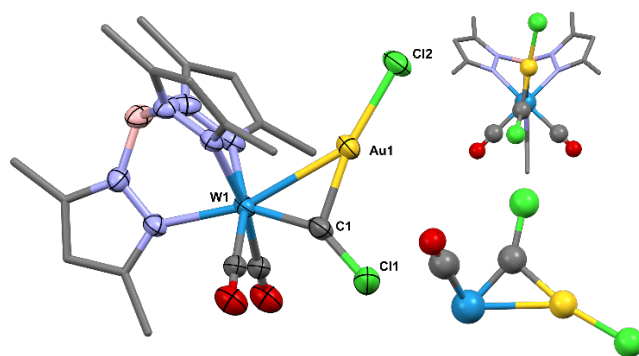


Figure S1: Molecular structure of **2b** in a crystal of $2\text{b} \cdot 0.5\text{C}_6\text{H}_{12}$ (50% displacement ellipsoids, pyrazolyl ligands simplified and hydrogen atoms and solvent omitted). Selected bond lengths (\AA) and angles ($^\circ$): W1–C1 1.891(6), C1–Cl1 1.697(6), Au1–Cl2 2.277(2), W1–Au1 2.7926(5), C1–Au1 2.026(6), Au1–C1–Cl1 120.2(3), W1–C1–Cl1 148.9(4). Insets: view along the W–C axis and a model showing the tilting of the chlorocarbonyne ligand.

Crystal data for $C_{18}H_{22}AuBrClMoN_6O_2W \cdot C_3H_6$, $M_w = 859.02$ $gmol^{-1}$, monoclinic, $P2_1/n$ (No. 14) $a = 13.3472(2)$ Å, $b = 10.4746(1)$ Å, $c = 19.2527(3)$ Å, $\beta = 102.807(1)^\circ$, $V = 2624.69(6)$ Å³, $Z = 4$, $D_{calc} = 2.174$ Mgm^{-3} , $\mu(Cu K\alpha) = 20.46$ mm^{-1} , $T = 150.0(1)$ K, clear light orange plate, $0.15 \times 0.06 \times 0.04$ mm, 5126 independent measured reflections ($2\theta_{max} = 147.0^\circ$), $R_1 = 0.032$, $wR_2 = 0.087$ for 4570 reflections [$I > 2\sigma(I)$] and 301 parameters without restraints. CDCC 2173040

Synthesis of [MoAu(μ -CBr)Cl(CO)₂(Tp*)] (2c). A mixture of [Mo(\equiv CBr)(CO)₂(Tp*)] (**1c**: 94 mg, 0.173 mmol) and [AuCl(SMe₂)] (50 mg, 0.170 mmol) was dissolved in CH₂Cl₂ (10 mL) in a flask wrapped in aluminum foil to exclude light. The initially bright yellow solution darkened over 10 minutes to bright orange. The ensuing reaction was monitored by infra-spectroscopy which indicated that the reaction was complete after ~90 minutes. At this point, the reaction mixture was eluted through a flash column (diatomaceous earth, neat CH₂Cl₂) to remove traces of colloidal gold and provide a bright orange solution. This was diluted with *n*-hexane and concentrated under reduced pressure to provide an orange solid. Following ultrasonic trituration for 5 minutes, the orange solid was collected via vacuum filtration, washed with *n*-hexane (2 x 10 mL) and *n*-pentane (1 x 10 mL) before drying *in vacuo* for 4 hours, to give **2c** (110 mg, 0.142 mmol, 84% yield). Crystals suitable for single-crystal X-ray diffraction studies were grown by vapour diffusion of *n*-hexane into a CH₂Cl₂ solution of compound at 5 °C overnight.

IR (CH₂Cl₂, cm^{-1}): 2032 vs ν_{CO} , 1960 vs ν_{CO} . IR (ATR, cm^{-1}): 2562 w ν_{BH} , 2024 vs ν_{CO} , 1957 vs ν_{CO} , 1946 vs ν_{CO} . ¹H NMR (600 MHz, CDCl₃, 25 °C) δ_H 5.92 (s, 3 H, pzCH), 2.48 (s, 6 H, pzCH₃), 2.45 (s, 3 H, pzCH₃), 2.40 (s, 6 H, pzCH₃), 2.37 (s, 3 H, pzCH₃). ¹³C{¹H} NMR (151 MHz, CDCl₃, 25 °C): δ_C 224.4 (μ -C-Cl), 218.5 (CO), 152.5, 151.9 [C⁵(pz)], 146.4, 145.9 [C³(pz)], 108.1, 107.7 [C⁴(pz)], 16.9, 15.4, 13.3, 12.9 [pzCH₃]. MS (ESI, +ve ion, m/z): Found: 740.9482. Calcd for C₁₆H₂₂¹¹B¹¹N₆²³Na³⁵Cl⁷⁹Br⁹⁸Mo¹⁹⁷Au [M-2CO+Na]⁺: 740.9488. Anal. Found: C, 27.92; H, 2.88; N, 10.62%. Calcd for C₁₈H₂₂AuBBrClMoN₆O₂: C, 27.95; H, 2.87; N, 10.87%.

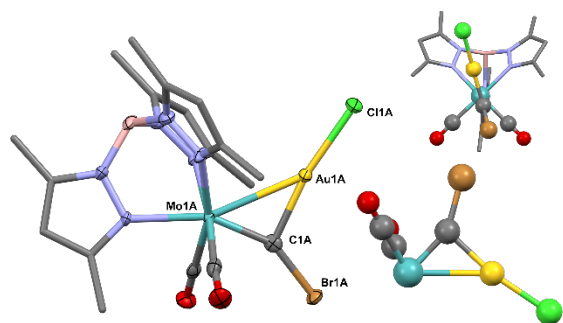


Figure S2: Molecular structure of **2c** in a crystal of **2c**·0.5CH₂Cl₂ (50% displacement ellipsoids, pyrazolyl ligands simplified and hydrogen atoms and solvent omitted). Selected bond lengths (Å) and angles (°): Mo1A–C1A 1.887(9), C1A–Br1A 1.846(9), Au1A–C1A 2.289(2), Mo1A–Au1A 2.7830(7), C1A–Au1A 2.039(9), Au1A–C1A–Br1A 118.2(4), Mo1A–C1A–Br1A 151.5(5). Insets: view along the Mo–C axis and a model showing the tilting of the bromocarbene ligand.

Crystal data for $2(C_{18}H_{22}AuBBrClMoN_6O_2) \cdot CH_2Cl_2$, $M_w = 1631.91$ $gmol^{-1}$, orthorhombic, $Pca2_1$ (No. 21), $a = 19.9121(1)$ Å, $b = 10.8854(1)$ Å, $c = 23.8615(1)$ Å, $V = 5172.01(6)$ Å³, $Z = 4$, $D_{calc} = 2.096$ Mgm^{-3} , $\mu(Cu K\alpha) = 18.43$ mm^{-1} , $T = 150.0(1)$ K, clear light orange block $0.37 \times 0.25 \times 0.09$ mm, 10173 independent measured reflections ($2\theta_{max} = 147.4^\circ$), $R_1 = 0.032$, $wR_2 = 0.080$ for 10151 reflections [$I > 2\sigma(I)$] and 587 parameters with 16 restraints. CDCC 2173050.

Synthesis of [WAu(μ -CBr)Cl(CO)₂(Tp*)] (2d). To a flask containing [W(\equiv CBr)(CO)₂(Tp*)] (**1d**: 0.100 g, 0.159 mmol) and [AuCl(SMe₂)] (0.047 g, 0.160 mmol) was added CH₂Cl₂ (5 mL) and the resulting mixture was stirred for 30 min, during which time the yellow solution turned orange. The mixture was filtered through diatomaceous earth and ethanol was added to the filtrate. This was concentrated under reduced pressure to precipitate an orange solid, which was filtered and washed with pentane to yield **2d** (0.091 g, 0.106 mmol, 66%). Single crystals suitable for X-ray diffractometry were grown by slow evaporation of a CH₂Cl₂/*n*-hexane mixture.

IR (CH₂Cl₂, cm^{-1}): 2019 vs, 1935 vs ν_{CO} . ¹H NMR (400 MHz, CDCl₃, 25 °C) δ_H 5.96 (s, 2 H, pzCH), 5.94 (s, 1 H, pzCH), 2.48 (s, 9 H, pzCH₃), 2.38 (s, 6 H, pzCH₃), 2.34 (s, 3 H, pzCH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃, 298 K): δ_C 214.4 (CO, ¹J_{WC} = 153 Hz), 212.1 (μ -CBr, ¹J_{WC} = 122.2 Hz), 153.8, 152.9 [C⁵(pz)], 146.5, 146.1 [C³(pz)], 108.7, 108.1 [C⁴(pz)], 17.8, 16.2, 13.4, 13.0 (pzCH₃). MS (ESI, +ve ion, m/z): Found: 866.0492. Calc. for C₂₀H₂₅Au¹¹B⁷⁹BrN₇O₂¹⁸⁴W [M-Cl+CH₃CN]⁺: 866.0522. Anal. Found: C, 24.89; H, 2.44; N, 9.89%. Calc. for C₁₈H₂₂AuBBrClN₆O₂W: C, 25.10; H, 2.57; N, 9.76%.

Crystal data for $C_{18}H_{22}AuBBrClN_6O_2W$, $M_w = 861.40$ $gmol^{-1}$, monoclinic, space group $P2_1/c$ (no. 14), $a = 25.3829(4)$ Å, $b = 10.9902(1)$ Å, $c = 19.8684(3)$ Å, $\beta = 107.856(2)^\circ$, $V = 5275.57(14)$ Å³, $Z = 8$, $T = 150.0(1)$ K, $\mu(Cu K\alpha) = 21.163$ mm^{-1} , $D_{calc} = 2.169$ Mgm^{-3} , 31402 reflections measured ($8.84^\circ \leq 2\theta \leq 146.06^\circ$), 10375 unique ($R_{int} = 0.0499$, $R_{sigma} = 0.0499$) which were used in all calculations. The final R_1 was 0.0513 ($I > 2\sigma(I)$) and wR_2 was 0.1366 (all data) for 557 refined parameters without restraint. CCDC 2033040.

Synthesis of [MoPt(μ -C-Cl)(PPh₃)₂(CO)₂(Tp*)] (3a). A mixture of [Mo(\equiv CCl)(CO)₂(Tp*)] (**1a**: 0.098 g, 0.197 mmol) and [Pt(η^2 -C₂H₄)(PPh₃)₂] (0.161 g, 0.215 mmol) were dissolved in toluene (10 mL) to give a yellow solution. A small amount of gas was steadily liberated. The solution darkened over 90 minutes to an orange colour, after which the reaction was confirmed to be completed by infrared spectroscopy. The solvent was then removed under reduced pressure before the residue was then crystallised from a mixture of THF and EtOH affording a yellow powder identified as **3a** (0.190 g, 0.156 mmol, 79% isolated yield). Crystals suitable for X-ray diffractometry were acquired by vapour diffusion of *n*-hexane into a THF solution of compound **3a** at 5 °C overnight.

IR (CH₂Cl₂, cm^{-1}): 1906 vs ν_{CO} , 1823 vs ν_{CO} . Note: The complex is only briefly stable in CH₂Cl₂ as other bands at 1960/1870 arise from the onset of isomerisation to a μ -carbido complex **6**. IR

(ATR, cm^{-1}): 2518 w ν_{BH} , 1898 vs ν_{CO} , 1830 vs ν_{CO} , 1816 vs ν_{CO} . ^1H NMR (700 MHz, C_6D_6 , 25 °C): δ_{H} 7.96 (m, 6 H, C_6H_5), 7.50 (m, 6 H, C_6H_5), 6.99 (m, 9 H, C_6H_5), 6.87 (m, 9 H, C_6H_5), 5.66 (s, 2 H, pzCH), 5.52 (s, 1 H, pzCH), 2.53 (s, 6 H, pzCH₃), 2.25 (s, 3 H, pzCH₃), 2.19 (s, 6 H, pzCH₃), 2.16 (s, 3 H, pzCH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, C_6D_6 , 25 °C): δ_{C} 314.8 (dd, $^2J_{\text{CP}} = 75$, 6 Hz, $\mu\text{-CCl}$), 228.5 (m, $^2J_{\text{CP}} = 70$ Hz, CO), 153.1, 150.5 [$\text{C}^5(\text{pz})$], 144.1, 143.2 [$\text{C}^3(\text{pz})$], 136.6 [d, $^1J_{\text{CP}} = 38$ Hz, $\text{C}^1(\text{C}_6\text{H}_5)$], 135.6 [d, $^2J_{\text{CP}} = 13$ Hz, $\text{C}^{2,6}(\text{C}_6\text{H}_5)$], 135.1 [d, $^2J_{\text{CP}} = 12$ Hz, $\text{C}^{2,6}(\text{C}_6\text{H}_5)$], 134.3 [d, $^1J_{\text{CP}} = 46$ Hz, $\text{C}^1(\text{C}_6\text{H}_5)$], 129.5 [d, $^3J_{\text{CP}} = 10$ Hz, $\text{C}^{3,5}(\text{C}_6\text{H}_5)$], 128.4 [$\text{C}^4(\text{C}_6\text{H}_5)$], 127.6 [d, $^3J_{\text{CP}} = 10$ Hz, $\text{C}^{3,5}(\text{C}_6\text{H}_5)$], 106.7, 106.5 [$\text{C}^4(\text{pz})$], 16.1, 15.8, 13.0, 12.7 (pzCH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , 25 °C): δ_{P} 38.24 (d, $^2J_{\text{PP}} = 24$ Hz, $^1J_{\text{PPt}} = 4391$ Hz), 25.82 (d, $^2J_{\text{PP}} = 24$ Hz, $^1J_{\text{PPt}} = 2758$ Hz). $^{195}\text{Pt}\{^1\text{H}\}$ NMR (150 MHz, C_6D_6 , 25 °C): δ_{Pt} -3940 (dd, $^1J_{\text{PtP}} = 4398$, 2761 Hz). MS (ESI, +ve ion, m/z): Found: 1217.2092. Calcd for $\text{C}_{54}\text{H}_{52}^{11}\text{BN}_6\text{O}_2\text{P}_2^{35}\text{Cl}^{98}\text{Mo}^{195}\text{Pt}$ [M]⁺: 1217.2110. Anal. Found: C, 53.34; H, 4.29; N, 6.67%. Calcd for $\text{C}_{54}\text{H}_{52}\text{BClMoN}_6\text{O}_2\text{P}_2\text{Pt}$: C, 53.33; H, 4.31; N, 6.91%.

Crystal data for $2(\text{C}_{54}\text{H}_{52}\text{BClMoN}_6\text{O}_2\text{P}_2\text{Pt}) \cdot 2.5(\text{C}_2\text{H}_3\text{N})$, $M_w = 2535.12$, triclinic, $P\bar{1}$ (No. 2), $a = 11.5634(2)$ Å, $b = 21.0076(4)$ Å, $c = 24.0458(5)$ Å, $\alpha = 71.105(2)^\circ$, $\beta = 80.456(2)^\circ$, $\gamma = 78.496(2)^\circ$, $V = 5383.22(19)$ Å³, $Z = 2$, $D_{\text{calc}} = 1.564$ Mg m⁻³, $\mu(\text{Cu K}\alpha) = 8.10$ mm⁻¹, $T = 150.0(1)$ K, clear light orange block, $0.20 \times 0.09 \times 0.05$ mm, 20974 independent measured reflections ($2\theta_{\text{max}} = 147.4^\circ$), $R_1 = 0.037$, $wR_2 = 0.087$ for 19434 reflections [$I > 2\sigma(I)$] and 1303 parameters with 15 restraints. CDCC 2173043.

Synthesis of [WPt($\mu\text{-CCl}$)(PPh₃)₂(CO)₂(Tp*)] (3b). A mixture of [W($\equiv\text{CCl}$)(CO)₂(Tp*)] (**1b**: 0.115 g, 0.197 mmol) and [Pt($\eta^2\text{-C}_2\text{H}_4$)(PPh₃)₂] (0.165 g, 0.221 mmol) was dissolved in THF (10 mL) and heated under reflux with stirring for 30 minutes and cooled for 30 minutes. During this time, the initially yellow solution developed an orange colour after which the reaction was deemed to be complete by infra-red spectroscopy. The solvent was removed under reduced pressure to give an orange solid, which could be recrystallised from THF and *n*-hexane and collected *via* vacuum filtration and washed with ethanol (2 x 10 mL) and *n*-hexane (10 mL). The collected sample was dried *in vacuo* for 4 hours to give a yellow powder identified as **3b** (0.108 g, 0.083 mmol, 42% isolated yield). The same scale reaction performed in toluene (10 mL) at room temperature with stirring for 60 minutes returned comparable yields. Crystals suitable for single-crystal X-ray diffraction studies were grown from the vapour diffusion of MeCN into a THF solution of the compound at ambient temperature over 4 days.

IR (CH_2Cl_2 , cm^{-1}): 1895 vs ν_{CO} , 1810 vs ν_{CO} . IR (ATR, cm^{-1}): 2529 w ν_{BH} , 1897 sh ν_{CO} , 1888 vs ν_{CO} , 1818 vs ν_{CO} , 1806 vs ν_{CO} . ^1H NMR (700 MHz, C_6D_6 , 25 °C): δ_{H} 8.00 (m, 6 H, C_6H_5), 7.53 (m, 6 H, C_6H_5), 7.00 (m, 10 H, C_6H_5), 6.89 (m, 8 H, C_6H_5), 5.64 (s, 2 H, pzCH), 5.46 (s, 1 H, pzCH), 2.65 (s, 6 H, pzCH₃), 2.27 (s, 3 H, pzCH₃), 2.13 (s, 6 H, pzCH₃), 2.09 (s, 3 H, pzCH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6 , 25 °C): δ_{C} 297.2 (dd, $^2J_{\text{CP}} = 76$, 5 Hz, $\mu\text{-CCl}$), 223.2 (d, $^3J_{\text{CP}} = 5$ Hz, $^1J_{\text{CW}} = 67$ Hz, CO), 153.6, 151.0 [$\text{C}^5(\text{pz})$], 143.8, 142.7 [$\text{C}^3(\text{pz})$], 136.5 [d, $^1J_{\text{CP}} = 37$ Hz, $\text{C}^1(\text{C}_6\text{H}_5)$], 135.3 [d, $^2J_{\text{CP}} = 13$ Hz, $\text{C}^{2,6}(\text{C}_6\text{H}_5)$], 134.7 [d, $^2J_{\text{CP}} = 12$ Hz, $\text{C}^{2,6}(\text{C}_6\text{H}_5)$], 134.3 [d, $^1J_{\text{CP}} = 45$ Hz, $\text{C}^1(\text{C}_6\text{H}_5)$], 128.9 [d, $^3J_{\text{CP}} = 12$ Hz, $\text{C}^{3,5}(\text{C}_6\text{H}_5)$], 128.0

[$\text{C}^4(\text{C}_6\text{H}_5)$], 127.1 [d, $^3J_{\text{CP}} = 12$ Hz, $\text{C}^{3,5}(\text{C}_6\text{H}_5)$], 106.6, 106.4 [$\text{C}^4(\text{pz})$], 16.4, 15.9, 12.4, 12.2 (pzCH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , 25 °C): δ_{P} 41.89 (d, $^2J_{\text{PP}} = 23$ Hz, $^1J_{\text{PPt}} = 4312$ Hz), 24.39 (d, $^2J_{\text{PP}} = 23$ Hz, $^1J_{\text{PPt}} = 2762$ Hz). $^{195}\text{Pt}\{^1\text{H}\}$ NMR (85.7 MHz, CDCl_3 , 25 °C): δ_{Pt} -3992 (dd, $^1J_{\text{PtP}} = 4316$, 2760 Hz, $^1J_{\text{PtW}} = 345$ Hz). MS (ESI, +ve ion, m/z): Found: 1347.20589. Calcd for $\text{C}_{54}\text{H}_{52}^{11}\text{B}^{79}\text{BrN}_6\text{O}_2\text{P}_2^{195}\text{Pt}^{184}\text{W}$ [M]⁺: 1347.20534. Anal. Found: C, 49.73; H, 4.16; N, 7.08%. Calcd for $\text{C}_{54}\text{H}_{52}\text{BClN}_6\text{O}_2\text{P}_2\text{PtW}$: C, 49.73; H, 4.02; N, 6.44%.

Crystal data for $2(\text{C}_{54}\text{H}_{52}\text{BClN}_6\text{O}_2\text{P}_2\text{PtW}) \cdot 2(\text{C}_2\text{H}_3\text{N})$, $M_w = 2690.41$, triclinic, $P\bar{1}$ (No. 2), $a = 11.5580(2)$ Å, $b = 21.0234(3)$ Å, $c = 24.0391(5)$ Å, $\alpha = 71.013(2)^\circ$, $\beta = 80.492(2)^\circ$, $\gamma = 78.102(1)^\circ$, $V = 5374.3(2)$ Å³, $Z = 2$, $D_{\text{calc}} = 1.663$ Mg m⁻³, $\mu(\text{Cu K}\alpha) = 10.10$ mm⁻¹, $T = 150.0(1)$ K, clear light red block $0.09 \times 0.05 \times 0.05$ mm, 21031 independent measured reflections ($2\theta_{\text{max}} = 147.4^\circ$), $R_1 = 0.044$, $wR_2 = 0.100$ for 18930 reflections [$I > 2\sigma(I)$] with 1357 parameters and 22 restraints. CDCC 2173046.

Synthesis of [MoPt($\mu\text{-CCl}$)($\mu\text{-CO}$)(dppe)(CO)(Tp*)] (4). A yellow solution containing [Mo($\equiv\text{CCl}$)(CO)₂(Tp*)] (0.100 g, 0.201 mmol) and [Pt($\eta^2\text{-C}_2\text{H}_4$)(PPh₃)₂] (0.165 g, 0.221 mmol) was heated under reflux in THF (10 mL) for 30 minutes. The resulting orange solution was cooled before a solution of dppe (0.094 g, 0.235 mmol) in THF (5 mL) was added. The mixture was stirred at ambient temperature for 16 hours during which time the colour darkened to red. Volatiles were removed under reduced pressure to give an orange/red residue that was then crystallised from a mixture of CH_2Cl_2 and EtOH to give a red solid, which was collected *via* vacuum filtration, washed with EtOH (1 x 10 mL) and *n*-hexane (2 x 10 mL) and dried *in vacuo* for 4 hours to provide **4** (0.136 g, 0.125 mmol, 62% isolated yield). Crystals suitable for single-crystal X-ray diffraction were grown from the vapour diffusion of *n*-hexane into a THF solution of the compound at ambient temperature. IR (CH_2Cl_2 , cm^{-1}): 1911 vs ν_{CO} , 1808 sh ν_{CO} , 1772 s $\nu_{\mu\text{-CO}}$. IR (ATR, cm^{-1}): 2544 w ν_{BH} , 2526 w ν_{BH} , 1885 vs ν_{CO} , 1786 s $\nu_{\mu\text{-CO}}$, 1767 vs $\nu_{\mu\text{-CO}}$. ^1H NMR (700 MHz, C_6D_6 , 25 °C): δ_{H} 7.73 (m, 4 H, C_6H_5), 7.51 (m, 4 H, C_6H_5), 6.96 (m, 3 H, C_6H_5), 6.92 (m, 3 H, C_6H_5), 6.83 (m, 3 H, C_6H_5), 6.79 (m, 3 H, C_6H_5), 5.40 (s, 2 H, pzCH), 5.26 (s, 1 H, pzCH), 2.53 (s, 3 H, pzCH₃), 2.16 (s, 6 H, pzCH₃), 1.96 (s, 6 H, pzCH₃), 1.90 (s, 3 H, pzCH₃), 1.84 (m, 4 H, PCH₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6 , 25 °C): δ_{C} 324.2 (d, $^2J_{\text{CP}} = 73$ Hz, CCl), 232.9 (CO), 152.7, 150.3 [$\text{C}^5(\text{pz})$], 144.0, 143.1 [$\text{C}^3(\text{pz})$], 134.5 [d, $^2J_{\text{CP}} = 12$ Hz, $\text{C}^{2,6}(\text{C}_6\text{H}_5)$], 133.5 [d, $^2J_{\text{CP}} = 12$ Hz, $\text{C}^{2,6}(\text{C}_6\text{H}_5)$], 132.7 [dd, $^1J_{\text{CP}} = 36$; $^2J_{\text{CP}} = 5$ Hz, $\text{C}^1(\text{C}_6\text{H}_5)$], 130.5 [$\text{C}^4(\text{C}_6\text{H}_5)$], 130.3 [$\text{C}^4(\text{C}_6\text{H}_5)$], 128.6 [$\text{C}^{3,5}(\text{C}_6\text{H}_5)$], 107.1, 106.6 [$\text{C}^4(\text{pz})$], 31.1 [dd, $^1J_{\text{CP}} = 34$; $^2J_{\text{CP}} = 14$ Hz, PCH₂], 16.1, 15.0, 12.9, 12.7 (pzCH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , 25 °C): δ_{P} 48.17 (d, $^2J_{\text{PP}} = 40$ Hz, $^1J_{\text{PPt}} = 2675$ Hz), 47.84 (d, $^2J_{\text{PP}} = 40$ Hz, $^1J_{\text{PPt}} = 4031$ Hz). $^{195}\text{Pt}\{^1\text{H}\}$ NMR (85.7 MHz, C_6D_6 , 25 °C): δ_{Pt} -4203 (dd, $^1J_{\text{PtP}} = 4031$, 2673 Hz). MS (ESI, +ve ion, m/z): Found: 1035.1771. Calcd for $\text{C}_{42}\text{H}_{46}^{11}\text{BN}_6\text{P}_2^{35}\text{Cl}^{98}\text{Mo}^{195}\text{Pt}$ [M-2CO]⁺: 1035.1743. Anal. Found: C, 48.46; H, 4.57; N, 7.54%. Calcd for $\text{C}_{44}\text{H}_{46}\text{BClMoN}_6\text{O}_2\text{P}_2\text{Pt}$: C, 48.48; H, 4.25; N, 7.71%.

Crystal data for $\text{C}_{44}\text{H}_{46}\text{BClMoN}_6\text{O}_2\text{P}_2\text{Pt}$, $M_w = 1090.10$ gmol⁻¹, triclinic, $P\bar{1}$ (No. 2), $a = 10.6762(2)$ Å, $b = 13.5205(4)$ Å, $c = 15.4074(4)$ Å, $\alpha = 83.317(2)^\circ$, $\beta = 89.918(2)^\circ$, $\gamma = 87.946(2)^\circ$, $V =$

2207.48(10) Å³, $Z = 2$, $D_{\text{calc}} = 1.640 \text{ Mg m}^{-3}$, $\mu(\text{Cu } K\alpha) = 9.76 \text{ mm}^{-1}$, $T = 150.0(1) \text{ K}$, clear light red block $0.21 \times 0.19 \times 0.14 \text{ mm}$, 8625 independent measured reflections ($2\theta_{\text{max}} = 145.2^\circ$), $R_1 = 0.029$, $wR_2 = 0.067$ for 8509 reflections [$I > 2\sigma(I)$], 548 parameters with 7 restraints. CDCC 2173047.

Synthesis of [W₂Pt(μ-Cl)₂(μ-CO)₂(CO)₂(Tp*)₂] (5). A yellow solution containing [W(≡CCl)(CO)₂(Tp*)] (**1b**: 0.050 g, 0.085 mmol) and [Pt(nbe)₃] (0.025 g, .052 mmol) was stirred in THF (20 mL) for 5 days at ambient temperature. The reaction was observed to darken to orange over several hours, and after 24 hours was a deep-red colour. At this point solvent was removed under reduced pressure to give a red residue which was purified via flash column chromatography (silica gel, neat petroleum ether then 1:1 CH₂Cl₂/petroleum ether 60–80) to provide a red eluate which upon concentration gave a maroon powder. The resulting solid was collected via vacuum filtration, washed with *n*-hexane (3 x 10 mL) and dried *in vacuo* to afford a red microcrystalline powder (0.031 g, 0.023 mmol, 46% isolated yield). Crystals suitable for X-ray diffraction were grown from the slow evaporation of Et₂O at 0 °C. IR (CH₂Cl₂, cm⁻¹): 2555 w ν_{BH}, 1967 vs ν_{CO}, 1865 vs ν_{CO}, 1606 s ν_{μ-CO}. IR (ATR, cm⁻¹): 2542 w ν_{BH}, 1963 vs ν_{CO}, 1852 vs ν_{CO}, 1606 s ν_{μ-CO}. ¹H NMR (700 MHz, CDCl₃, 25 °C): δ_H 5.92 (br, 2 H, pzCH), 5.85 (s, 2 H, pzCH), 5.81 (s, 2 H, pzCH), 2.66 (s, 6 H, pzCH₃), 2.43 (br, 12 H, pzCH₃), 2.36 (m, 12 H, pzCH₃), 2.30 (br, 6 H, pzCH₃). ¹H NMR (700 MHz, CDCl₃, -40 °C): δ_H 5.94, 5.87, 5.81 [s x 3, 2 H x 3, pzCH], 2.65, 2.43, 2.40, 2.34, 2.33, 2.24 (s x 6, 6 H x 6, pzCH₃). ¹³C{¹H} NMR (151 MHz, CDCl₃, -40 °C): δ_C 267.9 (CCl), 227.2, 219.2 (CO), 153.4, 153.1, 152.5 [C⁵(pz)], 145.6, 144.1, 143.9 [C³(pz)], 107.5, 107.2, 106.8 [C⁴(pz)], 17.3, 15.6, 15.5 [pzCH₃], 13.07 13.05 13.02 (overlapping singlets, pzCH₃). ¹⁹⁵Pt{¹H} NMR (150 MHz, CDCl₃, -40 °C): δ_{Pt} -2062 (s.br.). MS (ESI, +ve ion, *m/z*): Found: 1363.1827. Calcd for C₃₆H₄₄¹¹B₂³⁵Cl³⁷CIN₁₂O₄¹⁹⁵Pt¹⁸³W₂ [M]⁺: 1363.1827. Anal. Found: C, 31.78; H, 3.28; N, 12.14%. Calcd for C₃₆H₄₄B₂Cl₂N₁₂O₄PtW₂: C, 31.70; H, 3.25; N, 12.32%. All single crystals selected for analysis suffered from rotational disorder of CO and Cl ligands in addition to multiple sites for the central platinum atom. For this reason this structural model is reported as a confirmation of connectivity but does not return metrical parameters of sufficient precision for detailed analysis.

Crystal data for C_{25.96}H₄₄B₂Cl₂N₁₂O₄Pt_{0.8}W₂·0.19(Pt), $M_w = 1361.59$, triclinic, $P\bar{1}$ (No. 2), $a = 10.4275(7) \text{ \AA}$, $b = 10.6735(7) \text{ \AA}$, $c = 11.3340(9) \text{ \AA}$, $\alpha = 73.274(6)^\circ$, $\beta = 64.083(7)^\circ$, $\gamma = 83.109(5)^\circ$, $V = 1086.56(15) \text{ \AA}^3$, $Z = 1$, $D_{\text{calc}} = 2.081 \text{ Mg m}^{-3}$, $\mu(\text{Cu } K\alpha) = 16.98 \text{ mm}^{-1}$, $T = 150.0(1) \text{ K}$, clear dark red plate, $0.10 \times 0.06 \times 0.04 \text{ mm}$, 4291 independent measured reflections ($2\theta_{\text{max}} = 146.8^\circ$), $R_1 = 0.037$, $wR_2 = 0.088$ for 3579 reflections [$I > 2\sigma(I)$], 324 parameters without restraints CDCC 2173039.

Synthesis of [WPt(μ-C)Cl(PPh₃)₂(CO)₂(Tp*)] (6). A yellow solution containing [(Tp*)W(≡CCl)(CO)₂] (**1b**: 0.204 g, 0.349 mmol) and [Pt(PPh₃)₄] (0.431 g, 0.346 mmol) was heated in THF (20 mL) under reflux for 2 days. The solvent was removed from the resulting orange solution under reduced pressure to give an orange residue. The ³¹P{¹H} NMR spectrum of this material

revealed a sample of the bridging halocarbonyne **3b** was generated. Attempts to isolate the halocarbonyne compound included purification by flash column chromatography (silica gel, neat petroleum ether then neat CH₂Cl₂) eluting a major orange compound before removing solvent under reduced pressure. This was identified as pure title compound, **6**, where isomerisation of **3b** occurs on silica gel with CH₂Cl₂. Recrystallization from a mixture of CH₂Cl₂ and EtOH gave a yellow solid which was collected *via* vacuum filtration. The solid was washed with EtOH (2 x 10 mL) and *n*-hexane (10 mL) before drying *in vacuo* for 3 hours to afford compound **6** as a fine orange powder (0.124 g, 0.0951 mmol, 27% isolated yield). Crystals suitable for X-ray diffraction were grown from the vapour diffusion of *n*-hexane into a CHCl₃ solution of the title compound at 5 °C overnight.

IR (CH₂Cl₂, cm⁻¹): 1945 vs ν_{CO}, 1852 vs ν_{CO}. IR (ATR, cm⁻¹): 2548 w ν_{BH}, 2539 w ν_{BH}, 1933 vs ν_{CO}, 1836 vs ν_{CO}. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ_H 7.96–7.90 (m, 6 H, C₆H₅), 7.43–7.40 (m, 9 H, C₆H₅), 7.39–7.34 (m, 6 H, C₆H₅), 7.14 (m, 3 H, C₆H₅), 6.96 (m, 6 H, C₆H₅), 5.55 (s, 2 H, pzCH), 5.51 (s, 1 H, pzCH), 2.57 (s, 6 H, pzCH₃), 2.32 (s, 6 H, pzCH₃), 2.19 (s, 3 H, pzCH₃), 2.00 (s, 3 H, pzCH₃). ¹³C{¹H} NMR (151 MHz, CDCl₃, 25 °C): δ_C 318.8 (t, ²J_{CP} = 7 Hz, W≡C–Pt), 230.7 (¹J_{CW} = 179 Hz, CO), 151.7, 151.1 [C⁵(pz)], 143.6, 143.2 [C³(pz)], 135.2, 135.2 [overlapping doublets, ²J_{CP} = 11 Hz, C^{2,6}(C₆H₅)], 132.4 [dd, ¹J_{CP} = 53 Hz, ³J_{CP} = 5 Hz, C¹(C₆H₅)], 131.7, 130.7 [dd, ¹J_{CP} = 53 Hz, ³J_{CP} = 5 Hz, C¹(C₆H₅)], 130.0, 129.8 [C⁴(C₆H₅)], 128.0 [d, ²J_{CP} = 11 Hz, C^{3,5}(C₆H₅)], 127.2 [d, ²J_{CP} = 10 Hz, C^{3,5}(C₆H₅)], 106.7, 106.0 [C⁴(pz)], 17.2, 14.8, 12.9, 12.4 (pzCH₃). ³¹P{¹H} NMR (162 MHz, CDCl₃, 25 °C): δ_P 28.32 (d, ²J_{PP} = 443 Hz, ¹J_{PPt} = 3200 Hz), 24.01 (d, ²J_{PP} = 443 Hz, ¹J_{PPt} = 3223 Hz). ¹⁹⁵Pt{¹H} NMR (85.7 MHz, CDCl₃, 25 °C): δ_{Pt} -3718 (t, ¹J_{PtP} = 3223 Hz). MS (ESI, +ve ion, *m/z*): Found: 1268.2902. Calcd for C₅₄H₅₂¹¹BN₆O₂P₂¹⁹⁵Pt¹⁸⁴W [M–Cl]⁺: 1268.2877. Anal. Found: C, 49.82; H, 4.08; N, 6.47%. Calcd for C₅₄H₅₂BCIN₆O₂P₂PtW: C, 49.73; H, 4.02; N, 6.44%.

Crystal data for C₅₄H₅₂BCIN₆O₂P₂PtW, $M_w = 1304.15 \text{ g mol}^{-1}$, monoclinic, $P2_1/n$, $a = 9.5614(1) \text{ \AA}$, $b = 22.6311(2) \text{ \AA}$, $c = 23.3107(3) \text{ \AA}$, $\beta = 98.430(1)^\circ$, $V = 4989.59(9) \text{ \AA}^3$, $Z = 4$, $D_{\text{calc}} = 1.736 \text{ Mg m}^{-3}$, $\mu(\text{Cu } K\alpha) = 10.21 \text{ mm}^{-1}$, $T = 150.0(1) \text{ K}$, clear light yellow plate, $0.1 \times 0.06 \times 0.05 \text{ mm}$, 9939 independent measured reflections ($2\theta_{\text{max}} = 147.2^\circ$), $R_1 = 0.032$, $wR_2 = 0.086$ for 8797 reflections [$I > 2\sigma(I)$] with 623 parameters and no restraints. CDCC 2173042.

Observations concerning the isomerism of 3b to 6. As noted above, attempts to purify **3b** by column chromatography on silica gel eluting with dichloromethane resulted in immediate conversion to the μ-carbido complex **6**. Initially it was suspected that polar solvents favoured this isomerism, perhaps *via* ionisation to form an intermediate cationic μ-carbido complex. The following observations however argue against this interpretation in that whilst C–Cl ionisation still seems plausible, we suspect it is adventitious proton sources that initiate isomerism, most likely by assisting chloride dissociation.

- (i) A solution of **3b** in dry (ex CaH₂) CD₂Cl₂ shows no conversion to spectroscopically discernible

($^{31}\text{P}\{^1\text{H}\}$ NMR) amounts of **6** over 24 hours at room temperature.

- (ii) A sample of **3b** in was heated to 60 °C in CD_3CN (distilled from CaH_2 , stored over 3 Å molecular sieves) for 2 days. The bulk of the solid remained undissolved while the small amount that dissolved was primarily isomerised μ -carbido complex **6**. This was decanted from the solid which was then dissolved in purified CDCl_3 and found to be pure **3b**. Thus, while the very small proportion of the solid that dissolves does isomerise to the μ -carbido, the bulk remains as a solid α -that does not interconvert.
- (iii) A sample of **3b** in d_8 -toluene was heated to 60 °C for 48 hours and found to comprise exclusively the μ -chlorocarbonyne **3b** with no sign of measurable conversion to **6**.
- (iv) A sample of **3b** in CDCl_3 (distilled and stored over silver wire) was heated to 60 °C for 4 hours, assayed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy and then heated for a further 2 days and re-assayed. A second sample of **3b** was treated similarly except that 'bench-top' CDCl_3 as received from the supplier was used. Integration of signals due to **6** against those for **3b** provided the following

Time (min)	at °C	% Conversion to (6) Purified CDCl_3	% Conversion to (6) 'Benchtop' CDCl_3
30	25 °C	0	0
60	60 °C	$\approx 0^a$	$\approx 0^a$
240	60 °C	9	19
960	60 °C	50	75
2880	60 °C	83	100 ^b

^a Discernible, but below accurate integration levels. ^b Accompanied by onset of decomposition.

- (v) A sample of **3b** (21 mg) was dissolved in dichloromethane and chromatographed on silica gel eluting with the same solvent to afford an orange eluate that was freed of volatiles and found to be pure **6**, with no traces of **3b**.

Together these observations suggest that either adventitious water/HCl or the hydroxylic surface of silica gel accelerate the isomerism of the chlorocarbonyne **3b** to the μ -carbido complex **6**.

Synthesis of $[\text{WPt}(\mu_2\text{-CCl})(\text{CO})_3(\text{PPh}_3)(\text{Tp}^*)]$ (7**).** A yellow solution of $[\text{W}(\equiv\text{CCl})(\text{CO})_2(\text{Tp}^*)]$ (**1b**: 0.203 g, 0.347 mmol) and $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{PPh}_3)_2]$ (0.257 g, 0.344 mmol) in THF (36 mL) was stirred for 2 hours at 60 °C. The solution darkened gradually to orange-red. Upon cooling to ambient temperature, carbon monoxide (CO) was bubbled through the mixture, which immediately changed colour from orange to dark red. After one hour, excess CO was purged from the flask with N_2 and the mixture was then freed of volatiles under reduced pressure to

give a yellow/red solid that could be purified by flash column chromatography (silica gel, petroleum ether/ CH_2Cl_2 gradient elution). After eluting a yellow band of unreacted $[\text{W}(\equiv\text{CCl})(\text{CO})_2(\text{Tp}^*)]$, further elution with 20% CH_2Cl_2 /petroleum ether provided a deep red coloured band that could be recrystallised by concentration. The resulting olive coloured solid was collected *via* vacuum filtration, washing with *n*-hexane (3 × 10 mL) before drying *in vacuo* for 16 hours. The olive coloured solid was confirmed as the title compound (0.126 g, 0.118 mmol, 34% isolated yield), noting the deep red colour returns when redissolved. Furthermore, the yield of this reaction is reduced as heat also provides the μ_2 -carbido complex $[\text{WPt}(\mu_2\text{-C})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2(\text{Tp}^*)]$ and incomplete consumption retains μ_2 -halocarbonyne $[\text{WPt}(\mu_2\text{-CCl})(\text{PPh}_3)_2(\text{CO})_2(\text{Tp}^*)]$. Crystals suitable for X-ray diffraction were grown from the vapour diffusion of *n*-hexane into a THF solution of compound at 0 °C.

IR (CH_2Cl_2 , cm^{-1}): 2027 vs ν_{CO} , 1917 vs ν_{CO} , 1833 vs ν_{CO} . IR (ATR, cm^{-1}): 2545 w ν_{BH} , 2040 vs ν_{CO} , 1917 vs ν_{CO} , 1843 vs ν_{CO} . ^1H NMR (600 MHz, CDCl_3 , 25 °C): δ_{H} 7.56 (m, 6 H, C_6H_5), 7.39 (m, 9 H, C_6H_5), 5.83 (s, 1 H, pzCH), 5.77 (s, 2 H, pzCH), 2.74 (s, 3 H, pzCH₃), 2.41 (s, 6 H, pzCH₃), 2.34 (s, 3 H, pzCH₃), 2.06 (s, 6 H, pzCH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 25 °C): δ_{C} 295.6 (d, $^1J_{\text{CP}} = 6$; $^1J_{\text{CW}} = 151$; $^1J_{\text{CPT}} = 885$ Hz, CCl), 225.2 (d, $^1J_{\text{CW}} = 152$ Hz, W-CO), 196.8 ($^1J_{\text{CPT}} = 1381$ Hz, PtCO), 154.0, 151.0 [$\text{C}^5(\text{pz})$], 145.1, 143.5 [$\text{C}^3(\text{pz})$], 134.1 [d, $^2J_{\text{CP}} = 12$ Hz, $\text{C}^{2,6}(\text{C}_6\text{H}_5)$], 132.8 [d, $^1J_{\text{CP}} = 50$ Hz, $\text{C}^1(\text{C}_6\text{H}_5)$], 130.5 [d, $^4J_{\text{CP}} = 3$ Hz, $\text{C}^4(\text{C}_6\text{H}_5)$], 128.4 [d, $^3J_{\text{CP}} = 11$ Hz, $\text{C}^{3,5}(\text{C}_6\text{H}_5)$], 107.5, 106.6 [$\text{C}^4(\text{pz})$], 16.7, 15.6, 12.9 [pzCH₃]. $^{31}\text{P}\{^1\text{H}\}$ NMR (283 MHz, CDCl_3 , 25 °C): δ_{P} 35.69 ($^1J_{\text{PPt}} = 3857$ Hz). $^{195}\text{Pt}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3 , 25 °C): δ_{Pt} -4197 (d, $^1J_{\text{PtP}} = 3840$; $^1J_{\text{PtW}} = 295$ Hz). MS (ESI, +ve ion, m/z): Found: 1041.1670. Calcd for $\text{C}_{36}\text{H}_{37}^{11}\text{BN}_6\text{O}_2\text{P}^{35}\text{Cl}^{184}\text{W}^{195}\text{Pt}$ [M-CO]⁺: 1041.1654. Anal. Found: C, 41.50; H, 3.60; N, 7.64%. Calc. for $\text{C}_{37}\text{H}_{37}\text{BClN}_6\text{O}_3\text{PPtW}$: C, 41.54; H, 3.49; N, 7.86%.

Crystal data for $\text{C}_{37}\text{H}_{37}\text{BClN}_6\text{O}_3\text{PPtW}$, $M_w = 1069.89$ g mol^{-1} , monoclinic, $P2_1/n$, $a = 15.0798(1)$ Å, $b = 16.5138(1)$ Å, $c = 15.4322(3)$ Å, $\beta = 93.404(1)^\circ$, $V = 3836.22(4)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.852$ Mg m^{-3} , $\mu(\text{Cu K}\alpha) = 13.57$ mm^{-1} , $T = 150(0)$ K, clear light pink prism $0.18 \times 0.10 \times 0.08$ mm, 7008 independent measured reflections ($2\theta_{\text{max}} = 147.4^\circ$), $R_1 = 0.024$, $wR_2 = 0.058$ for 6747 reflections [$I > 2\sigma(I)$], 466 parameters without restraints. CDCC 2173048.

Synthesis of $[\text{WCl}_3(\text{Tp}^*)]$ (8**) and $[\text{W}(\equiv\text{CCl})\text{Cl}_2(\text{Tp}^*)]$ (**9**).** To a flask containing $[\text{W}(\equiv\text{CBr})(\text{CO})_2(\text{Tp}^*)]$ (**1d**: 0.150 g, 0.238 mmol) and PhICl_2 (0.130 g, 0.473 mmol) was added CH_2Cl_2 (5 mL) and the resulting mixture was stirred for 1 hour, during which time the yellow solution turned dark red-green. The volatiles were removed under vacuum and the residue was subjected to column chromatography (10 × 1 cm silica gel column), eluting with petroleum ether initially and gradually increasing the polarity to 2:1 v/v petrol/ CH_2Cl_2 . The first intense blue band was collected, and the volatiles were removed under reduced pressure to give a bright blue solid of pure **9** (0.035 g, 0.035 mmol, 15%). Single crystals suitable for X-ray diffractometry were grown by slow evaporation of a CH_2Cl_2 /*n*-hexane mixture.

^1H NMR (600 MHz, CDCl_3 , 25 °C): δ_{H} 2.37 (s, 9 H, pzCH₃), 2.48 (s, 3 H, pzCH₃), 2.57 (s, 6 H, pzCH₃), 5.84 (s, 1 H, pzCH), 5.97 (s, 2 H, pzCH). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 25 °C): δ_{C} 12.7, 13.2, 14.3, 18.1 (pzCH₃), 108.5, 108.7 (pzCH), 143.6, 147.0, 154.2, 155.4 [$\text{C}^{3,5}(\text{pz})$], 240.9 (W \equiv C). MS (ESI, +ve ion, m/z): Found: 563.0876. Calc. for $\text{C}_{16}\text{H}_{22}^{11}\text{B}^{35}\text{Cl}_2\text{N}_6^{184}\text{W}$ [$\text{M}-\text{Cl}$]⁺: 563.0882. Anal. Found: C, 31.87; H, 3.62; N, 13.89%. Calc. for $\text{C}_{16}\text{H}_{22}\text{BCl}_3\text{N}_6\text{W}$: C, 32.06; H, 3.70; N, 14.02%.

Crystal data for $\text{C}_{16}\text{H}_{22}\text{BCl}_3\text{N}_6\text{W}$: $M_{\text{w}} = 599.40 \text{ gmol}^{-1}$, orthorhombic, $Pnma$ (no. 62), $a = 16.2810(4) \text{ \AA}$, $b = 12.8355(3) \text{ \AA}$, $c = 13.3658(3) \text{ \AA}$, $V = 2793.09(11) \text{ \AA}^3$, $Z = 4$, $T = 150.0(1) \text{ K}$, $\mu(\text{Cu K}\alpha) = 10.390 \text{ mm}^{-1}$, $D_{\text{calc}} = 1.425 \text{ Mgm}^{-3}$, 17210 reflections measured ($2\theta_{\text{max}} = 170.30^\circ$), 2930 unique ($R_{\text{int}} = 0.0462$, $R_{\text{sigma}} = 0.0280$) which were used in all calculations. The final R_1 was 0.0401 ($I > 2\sigma(I)$) and wR_2 was 0.1116 (all data) for 143 refined parameters without restraint. A solvent mask was calculated for hexane solvent molecules that could not be modelled satisfactorily, and 212 electrons were found in a volume of 928 \AA^3 in 1 void per unit cell. This is consistent with the presence of one C_6H_{14} solvate per asymmetric unit which accounts for 200 electrons per unit cell. CCDC 2033076.

The reaction to form **9** also yielded compound **8** as the major product, isolated as the second yellow-green band by column chromatography. Volatiles were removed to afford **8** as a yellow-green solid (0.093 g, 0.16 mmol, 66%). Single crystals suitable for X-ray diffraction were grown by slow evaporation of a $\text{CH}_2\text{Cl}_2/n$ -hexane mixture. ^1H NMR (600 MHz, CDCl_3 , 25 °C): δ_{H} 1.28 (s, 9 H, pzCH₃), 1.52 (s, 3 H, pzCH₃), 2.40 (s, 6 H, pzCH₃), 9.41 (s, 1 H, pzCH), 10.6 (s, 2 H, pzCH). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 25 °C): δ_{C} 11.2, 12.4, 13.9, 14.1 (pzCH₃), 100.0 (pzCH), 139.5, 163.1 (pzC^{3,5}CH₃). MS (ESI, +ve ion, m/z): Found: 609.0446. Calc for $\text{C}_{15}\text{H}_{22}^{11}\text{B}^{35}\text{Cl}_3\text{N}_6^{184}\text{WNa}$ [$\text{M}+\text{Na}$]⁺: 609.0452. Satisfactory elemental analytical data were not obtained. *Crystal data for $\text{C}_{15}\text{H}_{22}\text{BCl}_3\text{N}_6\text{W}$* : $M_{\text{w}} = 587.39 \text{ gmol}^{-1}$; monoclinic, $P2_1/m$ (No. 11), $a = 8.0658(3) \text{ \AA}$, $b = 14.0050(6) \text{ \AA}$, $c = 9.0433(3) \text{ \AA}$, $\beta = 99.903(3)^\circ$, $V = 1006.32(7) \text{ \AA}^3$, $Z = 2$, $T = 150.0(1) \text{ K}$, $\mu(\text{Mo K}\alpha) = 6.150 \text{ mm}^{-1}$, $D_{\text{calc}} = 1.939 \text{ Mgm}^{-3}$, 4499 reflections measured ($2\theta_{\text{max}} = 116.56^\circ$), 2381 unique ($R_{\text{int}} = 0.0357$, $R_{\text{sigma}} = 0.0576$) which were used in all calculations. The final R_1 was 0.0329 ($I > 2\sigma(I)$) and wR_2 was 0.0684 (all data) for 124 refined parameters with one restraint. CCDC 2033078.

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Optimised Geometries and Cartesian Coordinates

Free [CF]⁺

Figure S3: Optimised structure of [CF]⁺ in the gas phase

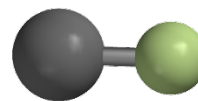


Table S1: Cartesian coordinates of optimised [CF]⁺

Atom	X	Y	Z
C	0.000000	0.000000	0.582764
F	0.000000	0.000000	-0.582764

Free [CCl]⁺

Figure S4: Optimised structure of [CCl]⁺ in the gas phase

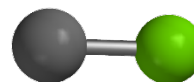
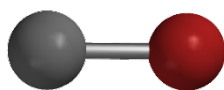
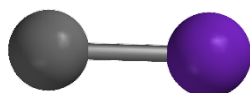


Table S2: Cartesian coordinates of optimised [CCl]⁺

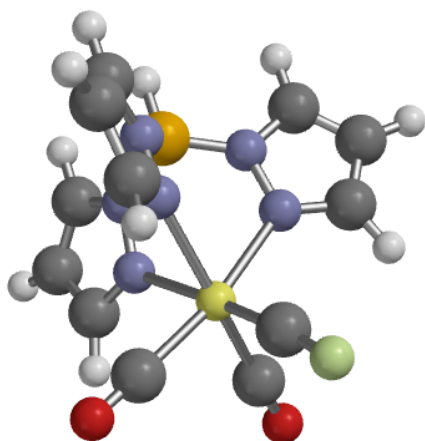
Atom	X	Y	Z
Cl	0.000000	0.000000	-0.770898
C	0.000000	0.000000	0.770898

Free [CBr]⁺Figure S5: Optimised structure of [CBr]⁺ in the gas phaseTable S3: Cartesian coordinates of optimised [CBr]⁺

Atom	X	Y	Z
C	0.000000	0.000000	0.847017
Br	0.000000	0.000000	-0.847017

Free [CI]⁺Figure S6: Optimised structure of [CI]⁺ in the gas phaseTable S4: Cartesian coordinates of optimised [CI]⁺

Atom	X	Y	Z
C	0.000000	0.000000	0.948345
I	0.000000	0.000000	-0.948345

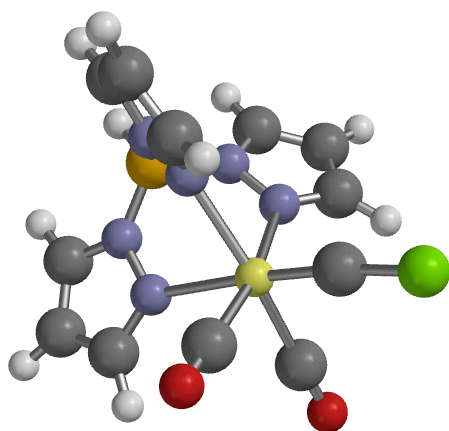
[Mo(≡CF)(CO)₂(Tp)]Figure S7: Optimised structure of [Mo(CF)(CO)₂(Tp)] in the gas phaseTable S5: Cartesian Coordinates for [Mo(CF)(CO)₂(Tp)]

Atom	x	y	z
Mo	-0.253260	-1.720173	-0.287322
O	2.180068	-3.733371	-0.069343

Atom	x	y	z
O	-0.977286	-2.753815	-3.190713
N	1.161480	-0.151808	-1.213326
N	1.128985	1.126991	-0.784227
N	0.349696	-0.608101	1.586879
N	0.444245	0.738240	1.596516
N	-1.684584	0.022630	-0.432587
N	-1.288633	1.276472	-0.129088
C	-1.320535	-3.005386	0.389567
C	1.291512	-3.006895	-0.157340
C	-0.705677	-2.387314	-2.133902
C	2.096086	-0.221181	-2.161671
C	2.685038	1.030969	-2.357752
H	3.467417	1.296157	-3.051646
C	2.035212	1.856441	-1.456881
C	0.662832	-1.028362	2.811961
C	0.966353	0.058590	3.637670
H	1.254289	0.042746	4.677236
C	0.814082	1.162029	2.818085
C	-2.966049	0.095364	-0.790161
C	-3.417847	1.416736	-0.718565
H	-4.403014	1.794706	-0.943393
C	-2.312992	2.132191	-0.294168
B	0.154235	1.565678	0.329211
H	0.291386	2.740436	0.557880
H	-3.492977	-0.802960	-1.077768
H	-2.178964	3.185716	-0.098160
H	2.151715	2.909221	-1.245761
H	0.942385	2.216589	3.012462
H	2.295508	-1.163829	-2.651780
H	0.652991	-2.085821	3.033434
F	-2.023697	-3.998889	0.794652

Table S6: Thermodynamic Properties at 298.15 K

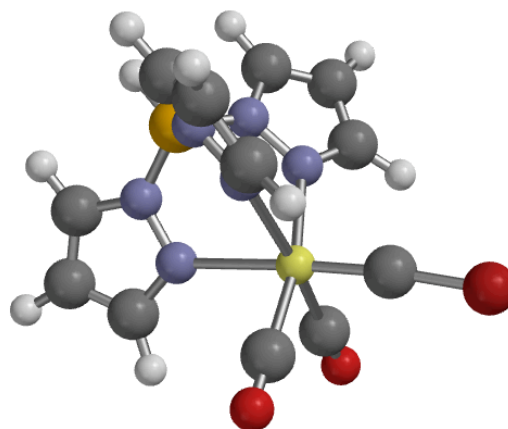
Zero Point Energy :	567.71	kJ/mol	(ZPE)
Temperature Correction :	47.65	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	615.36	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-1134.001045	au	(Electronic Energy + Enthalpy Correction)
Entropy :	545.14	J/mol•K	
Gibbs Energy :	-1134.062951	au	(Enthalpy - T*Entropy)
C _v :	328.61	J/mol•K	

[Mo(≡CCl)(CO)₂(Tp)]Figure S8: Optimised structure of [Mo(CCl)(CO)₂(Tp)] in the gas phaseTable S7. Cartesian Coordinates for [Mo(CCl)(CO)₂(Tp)]

Atom	x	y	z
Mo	-0.255342	-1.710905	-0.284200
O	2.165554	-3.745197	-0.056387
O	-1.017252	-2.770420	-3.174037
N	1.170627	-0.131035	-1.229599
N	1.140719	1.145793	-0.790753
N	0.355942	-0.597202	1.579140
N	0.452757	0.749407	1.589332
N	-1.678549	0.030613	-0.428609
N	-1.279888	1.286600	-0.135722
C	-1.303278	-3.004401	0.383196
C	1.289366	-3.006745	-0.153954
C	-0.727196	-2.387856	-2.129103
C	2.109023	-0.195585	-2.174518
C	2.702157	1.056589	-2.358417
H	3.488704	1.324767	-3.046609
C	2.051445	1.877921	-1.454384
C	0.665990	-1.019954	2.804394
C	0.970674	0.065922	3.630838
H	1.255793	0.048864	4.671245
C	0.823102	1.170557	2.811595
C	-2.960200	0.100861	-0.787387
C	-3.409795	1.423327	-0.726620
H	-4.394773	1.801810	-0.951818
C	-2.303716	2.140968	-0.308417
B	0.162104	1.578835	0.323016
H	0.297201	2.752486	0.555343
H	-3.488329	-0.800093	-1.064377
H	-2.169310	3.195957	-0.120885
H	2.170988	2.928514	-1.233948
H	0.953991	2.224553	3.007167
H	2.309305	-1.134763	-2.670959
H	0.650421	-2.077476	3.024966
Cl	-2.198238	-4.322712	0.900473

Table S8: Thermodynamic Properties at 298.15 K

Zero Point Energy :	563.64	kJ/mol	(ZPE)
Temperature Correction :	48.38	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	612.02	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-1494.373267	au	(Electronic Energy + Enthalpy Correction)
Entropy :	550.92	J/mol•K	
Gibbs Energy :	-1494.435829	au	(Enthalpy - T*Entropy)
C _v :	332.51	J/mol•K	

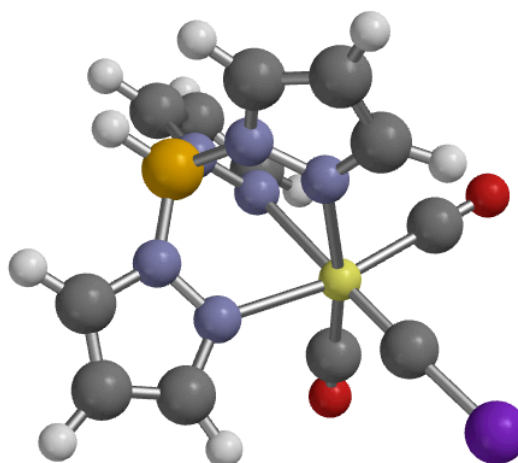
[Mo(≡CBr)(CO)₂(Tp)]Figure S9: Optimised structure of [Mo(CBr)(CO)₂(Tp)] in the gas phaseTable S9. Cartesian Coordinates for [Mo(CBr)(CO)₂(Tp)]

Atom	x	y	z
Mo	-0.253195	-1.707774	-0.289345
O	2.165978	-3.746114	-0.054444
O	-1.014308	-2.771914	-3.180060
N	1.184023	-0.127277	-1.230936
N	1.148468	1.150294	-0.795371
N	0.356282	-0.596141	1.572257
N	0.458022	0.750058	1.583852
N	-1.668924	0.035537	-0.440352
N	-1.271560	1.290658	-0.141452
C	-1.299981	-2.991819	0.389348
C	1.292034	-3.005748	-0.154332
C	-0.723655	-2.387882	-2.136154
C	2.119483	-0.189140	-2.178908

Atom	x	y	z
C	2.706229	1.065458	-2.367236
H	3.489141	1.335845	-3.058567
C	2.053706	1.885477	-1.463331
C	0.656453	-1.020792	2.799227
C	0.959333	0.063616	3.628184
H	1.237947	0.044862	4.670232
C	0.820506	1.169373	2.809052
C	-2.952829	0.105182	-0.790637
C	-3.404926	1.426165	-0.718886
H	-4.391914	1.802580	-0.938108
C	-2.298359	2.143936	-0.302353
B	0.170657	1.581816	0.317813
H	0.303768	2.755306	0.551229
H	-3.480279	-0.795442	-1.069995
H	-2.165019	3.198029	-0.109002
H	2.167764	2.937470	-1.246810
H	0.953243	2.222820	3.006402
H	2.322606	-1.128551	-2.673982
H	0.634990	-2.078430	3.018997
Br	-2.275683	-4.417459	0.993667

Table S10: Thermodynamic Properties at 298.15 K

Zero Point Energy :	562.15	kJ/mol	(ZPE)
Temperature Correction :	48.82	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	610.97	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-3608.108907	au	(Electronic Energy + Enthalpy Correction)
Entropy :	557.13	J/mol•K	
Gibbs Energy :	-3608.172175	au	(Enthalpy - T*Entropy)
C _v :	334.24	J/mol•K	

[Mo(≡Cl)(CO)₂(Tp)]Figure S10: Optimised structure of [Mo(Cl)(CO)₂(Tp)] in the gas phaseTable S11. Cartesian Coordinates for [Mo(Cl)(CO)₂(Tp)]

Atom	x	y	z
Mo	-0.249275	-1.705333	-0.290963
O	2.166647	-3.748165	-0.026470
O	-0.993872	-2.786882	-3.181969
N	1.192263	-0.117302	-1.240061
N	1.156943	1.158624	-0.799539
N	0.362886	-0.592192	1.566430
N	0.464618	0.753873	1.578865
N	-1.662031	0.036307	-0.442799
N	-1.265551	1.292469	-0.147013
C	-1.309050	-2.976107	0.381716
C	1.295530	-3.007053	-0.140172
C	-0.710184	-2.393829	-2.139901
C	2.125665	-0.174809	-2.189954
C	2.710869	1.081215	-2.374940
H	3.492242	1.354839	-3.066707
C	2.060454	1.897390	-1.466103
C	0.662689	-1.019073	2.792781
C	0.964645	0.064205	3.623294
H	1.242275	0.044853	4.665676
C	0.825938	1.171166	2.805270
C	-2.948085	0.102353	-0.786292
C	-3.402825	1.422228	-0.713530
H	-4.391893	1.795529	-0.928071
C	-2.295633	2.142664	-0.302943
B	0.175859	1.586380	0.313723
H	0.306413	2.759797	0.550113
H	-3.474135	-0.800695	-1.060842
H	-2.164537	3.196959	-0.109635
H	2.172966	2.948927	-1.246560
H	0.957624	2.224459	3.004189
H	2.327679	-1.111860	-2.690059

Atom	x	y	z
H	0.640311	-2.076886	3.011668
I	-2.437446	-4.524052	1.050798

Table S12: Thermodynamic Properties at 298.15 K

Zero Point Energy :	561.07	kJ/mol	(ZPE)
Temperature Correction :	49.10	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	610.17	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-1045.586777	au	(Electronic Energy + Enthalpy Correction)
Entropy :	562.28	J/mol•K	
Gibbs Energy :	-1045.650629	au	(Enthalpy - T*Entropy)
C _v :	335.44	J/mol•K	

I-C≡N

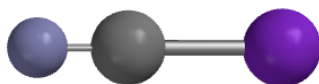


Figure S11: Optimised structure of I-CN in the gas phase

Table S13. Cartesian Coordinates for I-C≡N

Atom	x	y	z
N	0.000000	0.000000	1.436388
C	0.000000	0.000000	0.276632
I	0.000000	0.000000	-1.713020

I-C≡C-H

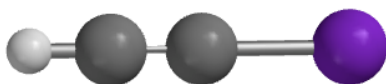
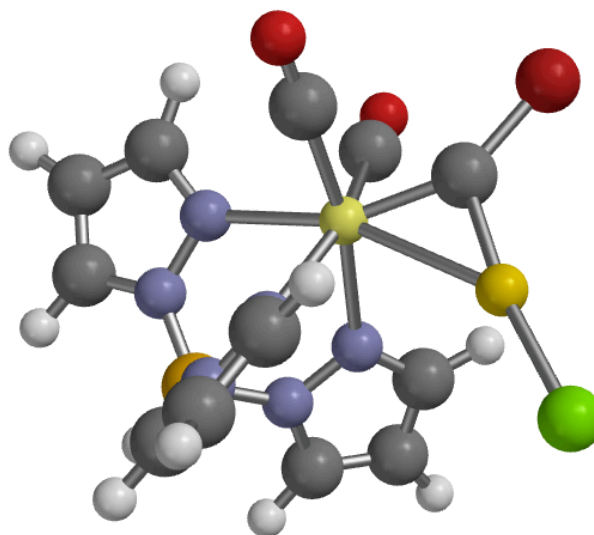


Figure S12: Optimised structure of I-CC-H in the gas phase

Table S14. Cartesian Coordinates for I-CC-H

Atom	x	y	z
C	0.000000	0.000000	-0.373061
H	0.000000	0.000000	1.899368
C	0.000000	0.000000	0.832528
I	0.000000	0.000000	-2.358835

[MoAu(μ-CBr)Cl(CO)₂(Tp)]Figure S13: Optimised structure of [MoAu(μ-CBr)Cl(CO)₂(Tp)] in the gas phaseTable S15. Cartesian Coordinates for [MoAu(μ-CBr)Cl(CO)₂(Tp)]

Atom	x	y	z
Au	3.567785	-0.387285	-0.075193
Mo	1.130936	1.058446	-0.084642
Br	4.140950	2.798720	-1.002091
Cl	4.629765	-2.409821	0.371369
N	-1.054954	1.484567	0.149809
N	-1.923598	0.447319	0.139377
O	1.598065	3.091150	2.297799
N	0.433628	-0.490769	-1.531110
N	-0.672783	-1.216544	-1.273349
O	0.743772	3.263586	-2.318863
C	0.895742	2.480756	-1.496512
C	2.918449	1.493950	-0.509853
N	-0.483456	-1.291974	1.218200
N	0.634767	-0.551200	1.382810
C	1.429727	2.360451	1.430016
C	0.108716	-1.923831	-3.220887
H	0.239244	-2.465391	-4.144601
C	1.242879	-0.997480	2.484482
C	-0.886997	-2.087929	-2.275541
C	-0.576974	-2.195341	2.209054
C	0.514097	-2.046791	3.046207
H	0.754333	-2.620275	3.927512
C	-3.174075	0.911983	0.286375
C	-3.129222	2.292209	0.389520
H	-3.956850	2.973045	0.513362
C	-1.772473	2.601207	0.301580
C	0.914208	-0.905862	-2.703427

Atom	x	y	z
B	-1.443371	-1.025658	0.043794
H	-2.388878	-1.766109	0.092343
H	1.815713	-0.463098	-3.102077
H	-1.730057	-2.761629	-2.239294
H	-1.412752	-2.878141	2.244359
H	2.177975	-0.558849	2.801630
H	-4.007327	0.225522	0.310402
H	-1.276983	3.561066	0.337439

[MoPt(μ -Cl)(CO)₂(PMe₃)₂(Tp)]

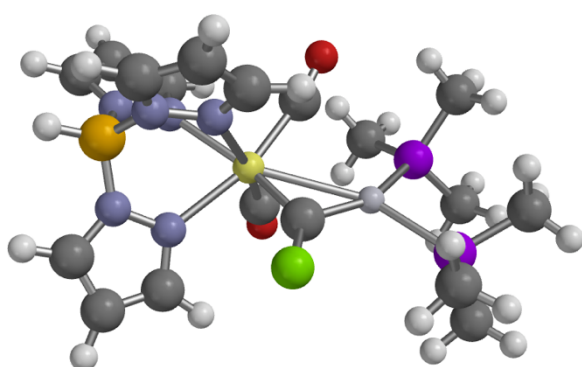


Figure S14: Optimised structure of [MoPt(μ -Cl)(CO)₂(PMe₃)₂(Tp)] in the gas phase

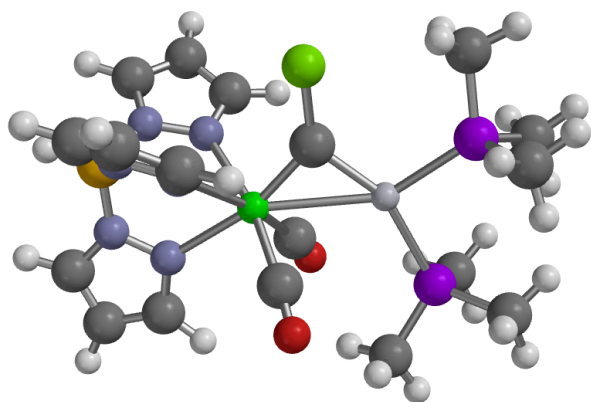
Table S16. Cartesian Coordinates for [MoPt(μ -Cl)(CO)₂(PMe₃)₂(Tp)]

Atom	x	y	z
Pt	-1.090707	0.846749	-0.906141
Mo	0.587426	-0.694264	0.744041
P	-1.916864	2.800475	0.199275
P	-2.137871	1.148917	-2.921619
Cl	0.050670	-2.029051	-2.304755
O	-2.064440	-0.500176	2.449337
N	0.595079	-2.961129	0.906133
N	2.659688	-1.096027	-0.089729
N	3.454960	-2.066271	0.404622
O	1.295796	2.328085	1.200179
N	1.783417	-1.013170	2.687602
N	2.721688	-1.974859	2.795850
N	1.703269	-3.649666	1.248476
C	3.308910	-0.542839	-1.111879
C	-1.115035	-0.540424	1.784715
C	0.946148	1.243048	0.943827
C	2.698181	-0.902789	4.732470
H	2.916631	-0.594027	5.742985
C	1.441425	-4.968882	1.247667
C	-0.138288	-0.847820	-1.042662
C	3.286710	-1.929134	4.014129
C	1.760187	-0.359705	3.849075
C	0.118568	-5.152584	0.889284

Atom	x	y	z
H	-0.415332	-6.084776	0.788410
C	-0.365986	-3.855875	0.686467
C	4.552129	-1.159285	-1.290510
H	5.303952	-0.937060	-2.031832
C	4.599378	-2.123345	-0.300196
B	3.008506	-2.917195	1.608400
H	3.867907	-3.709762	1.901232
H	2.215677	-5.677356	1.502535
H	5.361185	-2.844483	-0.043386
H	4.065181	-2.629021	4.279751
H	1.074067	0.464063	3.985737
H	2.842346	0.260827	-1.662987
H	-1.347705	-3.519185	0.386279
C	-1.892492	2.795846	2.035567
H	-0.868562	2.652187	2.386200
H	-2.503017	1.970119	2.408243
H	-2.278125	3.742647	2.428580
C	-1.016045	4.350930	-0.192198
H	0.031191	4.216477	0.090971
H	-1.432382	5.206264	0.350327
H	-1.060140	4.547596	-1.266836
C	-3.937265	0.776096	-2.951220
H	-4.460660	1.394535	-2.217467
H	-4.080893	-0.271795	-2.672650
H	-4.367581	0.948685	-3.943895
C	-2.063755	2.851539	-3.615781
H	-1.013915	3.133765	-3.739986
H	-2.528538	3.567333	-2.932881
H	-2.568877	2.909380	-4.586009
C	-1.543614	0.173821	-4.355864
H	-0.470509	0.333616	-4.491403
H	-2.077415	0.464632	-5.267149
H	-1.699224	-0.890478	-4.166139
C	-3.674500	3.264145	-0.097807
H	-4.316253	2.428745	0.198311
H	-3.849966	3.472398	-1.156715
H	-3.954313	4.149513	0.483025

Table S17: Thermodynamic Properties at 298.15 K

Zero Point Energy :	1146.36	kJ/mol	(ZPE)
Temperature Correction :	85.05	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	1231.41	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-2535.526172	au	(Electronic Energy + Enthalpy Correction)
Entropy :	794.48	J/mol•K	
Gibbs Energy :	-2535.616393	au	(Enthalpy - T*Entropy)
C _v :	597.04	J/mol•K	

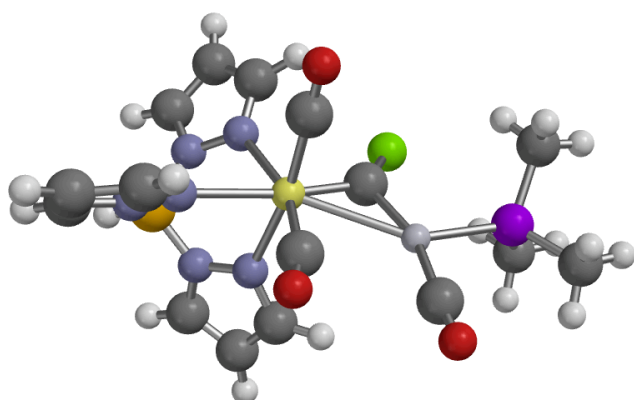
[WPt(μ -Cl)(CO)₂(PMe₃)₂Tp)]Figure S15: Optimised structure of [WPt(μ -Cl)(CO)₂(PMe₃)₂(Tp)] in the gas phaseTable S18. Cartesian Coordinates for [WPt(μ -Cl)(CO)₂(PMe₃)₂(Tp)]

Atom	x	y	z
Pt	-1.085342	0.835616	-0.905861
W	0.616316	-0.695395	0.732445
P	-1.907674	2.784999	0.200622
P	-2.155528	1.137094	-2.909997
Cl	0.090455	-2.012060	-2.348288
O	-2.026784	-0.485416	2.435397
N	0.630042	-2.938097	0.885828
N	2.671555	-1.109427	-0.068124
N	3.477943	-2.071728	0.427812
O	1.297563	2.330038	1.211335
N	1.781134	-1.017680	2.663451
N	2.718130	-1.977783	2.802289
N	1.720946	-3.646397	1.246589
C	3.316167	-0.546986	-1.090032
C	-1.075265	-0.529422	1.766307
C	0.966433	1.235824	0.952653
C	2.642750	-0.888131	4.728151
H	2.835737	-0.570114	5.740851
C	1.438805	-4.960253	1.227383
C	-0.104752	-0.848595	-1.061936
C	3.251253	-1.919780	4.033307
C	1.728504	-0.351748	3.818277
C	0.120907	-5.120290	0.839257
H	-0.424769	-6.043131	0.718776
C	-0.340885	-3.816440	0.637166
C	4.565869	-1.148545	-1.264307
H	5.315883	-0.916927	-2.004431
C	4.623416	-2.112922	-0.274282
B	3.026532	-2.925851	1.625525
H	3.880843	-3.717677	1.930469
H	2.196802	-5.682554	1.492098
H	5.393486	-2.825014	-0.016830
H	4.024173	-2.615504	4.324625
H	1.039394	0.473063	3.929104

Atom	x	y	z
H	2.839770	0.250600	-1.640953
H	-1.309662	-3.460264	0.319214
C	-1.883543	2.777133	2.036270
H	-0.859926	2.624364	2.383764
H	-2.498807	1.954539	2.407928
H	-2.260697	3.726667	2.431066
C	-0.995360	4.329664	-0.189207
H	0.050945	4.184566	0.092507
H	-1.403416	5.187952	0.355229
H	-1.039141	4.527977	-1.263720
C	-3.960920	0.792121	-2.917230
H	-4.467472	1.422465	-2.182526
H	-4.115713	-0.251560	-2.629321
H	-4.399957	0.962927	-3.906458
C	-2.064210	2.832076	-3.621069
H	-1.012445	3.094103	-3.768670
H	-2.500682	3.561531	-2.933889
H	-2.588506	2.892135	-4.581045
C	-1.601294	0.141470	-4.347025
H	-0.528868	0.284496	-4.502840
H	-2.147377	0.432546	-5.250949
H	-1.767586	-0.918505	-4.144390
C	-3.660644	3.269106	-0.097287
H	-4.312053	2.438835	0.192182
H	-3.831073	3.486085	-1.155488
H	-3.931398	4.154202	0.488281

Table S19: Thermodynamic Properties at 298.15 K

Zero Point Energy :	1148.09	kJ/mol	(ZPE)
Temperature Correction :	84.71	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	1232.80	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-2535.833458	au	(Electronic Energy + Enthalpy Correction)
Entropy :	793.09	J/mol•K	
Gibbs Energy :	-2535.923521	au	(Enthalpy - T*Entropy)
C _v :	595.44	J/mol•K	

[MoPt(μ -Cl)(CO)₃(PMe₃)Tp]Figure S16: Optimised structure of [WPt(μ -Cl)(CO)₃(PMe₃)(Tp)] in the gas phaseTable S20. Cartesian Coordinates for [MoPt(μ -Cl)(CO)₃(PMe₃)Tp]

Atom	x	y	z
Pt	-1.147014	1.888804	-0.917156
Mo	-0.063442	0.074356	0.946641
P	-2.497201	1.969276	-2.815006
Cl	-1.553544	-1.359870	-1.763042
O	-2.780224	0.145970	2.578791
N	0.011540	-2.188760	1.083241
N	1.991924	-0.192270	0.056830
N	2.832263	-1.156849	0.483722
O	0.597940	2.997128	1.867062
N	1.160275	-0.291772	2.869056
N	2.159238	-1.197378	2.899290
N	1.167571	-2.844111	1.323568
C	2.594395	0.431960	-0.954182
C	-1.792060	0.139802	1.985370
C	0.269349	1.993200	1.380490
C	2.120683	-0.238272	4.894474
H	2.347263	0.028137	5.915061
C	0.940011	-4.167884	1.382818
C	-1.033127	-0.086797	-0.699432
C	2.750964	-1.184747	4.105427
C	1.130078	0.295899	4.065592
C	-0.407112	-4.391809	1.166522
H	-0.925499	-5.337768	1.144703
C	-0.943705	-3.112985	0.989371
C	3.852323	-0.131341	-1.191936
H	4.577566	0.154521	-1.937905
C	3.959425	-1.138333	-0.249657
B	2.455716	-2.072131	1.662515
H	3.354990	-2.838647	1.896623
H	1.753020	-4.851012	1.579833
H	4.752819	-1.842338	-0.046453
H	3.576855	-1.849000	4.313433
H	0.407259	1.074419	4.263933
H	2.085707	1.245996	-1.450789

Atom	x	y	z
H	-1.962605	-2.812830	0.793918
C	-4.109036	1.119995	-2.642148
H	-4.670806	1.583241	-1.826375
H	-3.937048	0.070879	-2.390232
H	-4.690737	1.183639	-3.567749
C	-2.979934	3.652413	-3.358353
H	-2.082185	4.232945	-3.589905
H	-3.515184	4.157034	-2.548970
H	-3.620975	3.614807	-4.245273
C	-1.767311	1.246368	-4.329979
H	-0.858826	1.797948	-4.587758
H	-2.470329	1.293154	-5.168408
H	-1.496575	0.205550	-4.137692
C	-0.854133	3.779398	-0.665442
O	-0.690562	4.910064	-0.564443

Table S21: Thermodynamic Properties at 298.15 K

Zero Point Energy :	877.18	kJ/mol	(ZPE)
Temperature Correction :	73.14	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	950.32	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-2187.857604	au	(Electronic Energy + Enthalpy Correction)
Entropy :	718.84	J/mol•K	
Gibbs Energy :	-2187.939235	au	(Enthalpy - T*Entropy)
C _v :	509.61	J/mol•K	

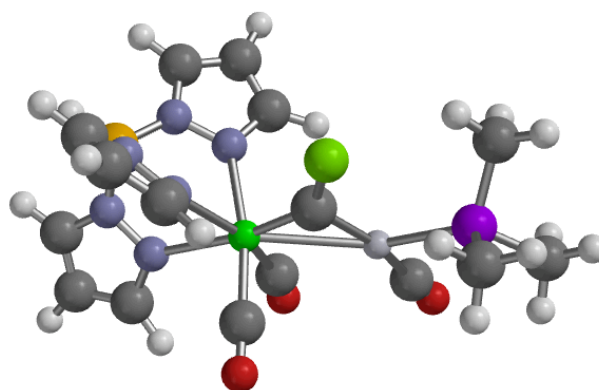
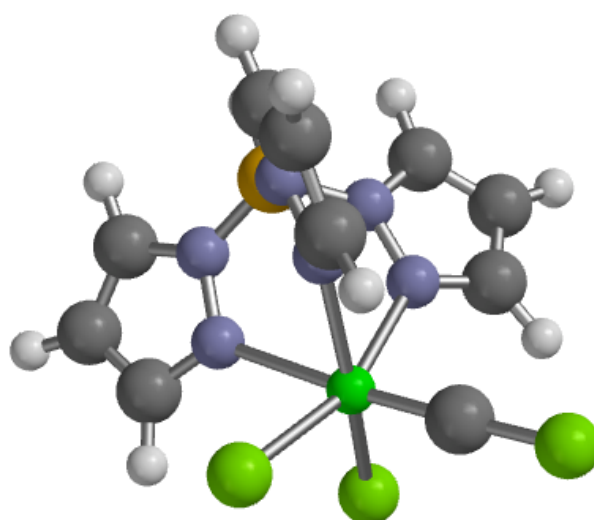
[WPt(μ -Cl)(CO)₃(PMe₃)Tp]Figure S17: Optimised structure of [WPt(μ -Cl)(CO)₃(PMe₃)(Tp)] in the gas phase

Table S22. Cartesian Coordinates for [WPt(μ -Cl)(CO)₃(PMe₃)Tp]

Atom	x	y	z
Pt	-1.135888	1.875694	-0.923839
W	-0.024641	0.071976	0.929765
P	-2.510154	1.964384	-2.809286
Cl	-1.506737	-1.363854	-1.810220
O	-2.712545	0.193632	2.578810
N	0.036533	-2.164052	1.066974
N	2.015367	-0.225028	0.068922
N	2.862193	-1.182439	0.502984
O	0.652569	3.004408	1.826326
N	1.170255	-0.299023	2.836671
N	2.158922	-1.215488	2.900931
N	1.175927	-2.847953	1.316411
C	2.622331	0.410437	-0.934093
C	-1.730025	0.168367	1.968053
C	0.324845	1.986988	1.360120
C	2.083798	-0.228046	4.881143
H	2.290003	0.049369	5.902991
C	0.912939	-4.164008	1.378162
C	-0.995427	-0.099562	-0.724361
C	2.721846	-1.192153	4.119223
C	1.118132	0.305895	4.025425
C	-0.438736	-4.353483	1.155253
H	-0.980516	-5.286013	1.130517
C	-0.943387	-3.063841	0.971675
C	3.886473	-0.140649	-1.159869
H	4.615416	0.154087	-1.898490
C	3.995309	-1.149195	-0.218908
B	2.470996	-2.098779	1.674030
H	3.358331	-2.873330	1.921263
H	1.706645	-4.867375	1.582273
H	4.794116	-1.845170	-0.009595
H	3.536142	-1.861489	4.354894
H	0.399058	1.094081	4.195984
H	2.109691	1.220434	-1.432475
H	-1.952965	-2.737687	0.772477
C	-4.107234	1.086372	-2.631830
H	-4.668679	1.531438	-1.805783
H	-3.914415	0.037965	-2.392036
H	-4.698919	1.149321	-3.551270
C	-3.030280	3.645207	-3.326772
H	-2.146240	4.245882	-3.559138
H	-3.566170	4.128836	-2.505031
H	-3.680141	3.607352	-4.207371
C	-1.792784	1.271807	-4.344816
H	-0.894003	1.837373	-4.606054
H	-2.506910	1.321461	-5.173805
H	-1.507711	0.231740	-4.169511
C	-0.865080	3.766099	-0.666018
O	-0.708249	4.898011	-0.560705

Table S23: Thermodynamic Properties at 298.15 K

Zero Point Energy :	878.69	kJ/mol	(ZPE)
Temperature Correction :	72.84	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	951.53	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-2188.165747	au	(Electronic Energy + Enthalpy Correction)
Entropy :	718.94	J/mol•K	
Gibbs Energy :	-2188.247390	au	(Enthalpy - T*Entropy)
C _v :	508.16	J/mol•K	

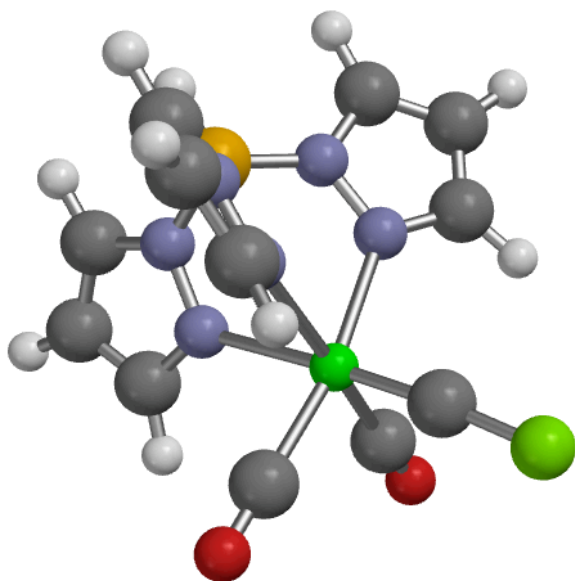
[W(\equiv CCl)Cl₂(Tp)]**Figure S18:** Optimised structure of [W(CCl)Cl₂(Tp)] in the gas phase**Table S24.** Cartesian Coordinates for [Mo(CCl)(CO)₂(Tp)]

Atom	x	y	z
W	-1.830143	0.000509	0.671090
Cl	-2.374033	-1.831782	2.044201
Cl	-4.655793	0.002792	-1.280440
N	1.367991	-0.000054	1.201375
N	-0.713558	1.353293	-0.616755
N	0.615570	1.235939	-0.838939
N	0.178733	0.000425	1.838980
C	1.815182	-0.001783	3.366406
H	2.333924	-0.003601	4.312401
C	-1.133657	2.449197	-1.258120
C	2.369043	-0.003143	2.099075
C	0.433999	0.001303	3.145218
C	1.025150	2.248728	-1.613765
C	-3.295682	0.000721	-0.316048

Atom	x	y	z
C	-0.061741	3.060639	-1.901646
H	-0.073459	3.960622	-2.495970
B	1.393778	0.001033	-0.325699
H	2.517815	-0.000482	-0.750909
N	-0.712823	-1.352056	-0.616318
N	0.615328	-1.233951	-0.840063
C	-1.131511	-2.449500	-1.255809
C	1.026323	-2.246289	-1.614345
C	-0.059538	-3.060331	-1.899854
H	-0.069065	-3.961731	-2.492064
Cl	-2.374332	1.830989	2.046206
H	2.061816	-2.312976	-1.913514
H	-0.384162	0.004617	3.850659
H	3.398126	-0.007735	1.770787
H	2.060563	2.316364	-1.912644
H	-2.173282	2.735127	-1.204087
H	-2.170715	-2.736669	-1.199890

Table S25: Thermodynamic Properties at 298.15 K

Zero Point Energy :	535.99	kJ/mol	(ZPE)
Temperature Correction :	45.88	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	581.87	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-2188.515258	au	(Electronic Energy + Enthalpy Correction)
Entropy :	541.17	J/mol•K	
Gibbs Energy :	-2188.576712	au	(Enthalpy - T*Entropy)
C _v :	308.52	J/mol•K	

[W(≡CCl)(CO)₂(Tp)]Figure S19: Optimised structure of [W(CCl)(CO)₂(Tp)] in the gas phaseTable S26. Cartesian Coordinates for [Mo(CCl)(CO)₂(Tp)]

Atom	x	y	z
W	-0.443779	-0.861948	1.438553
O	-1.800865	0.641636	3.860367
O	1.765186	-2.054841	3.352732
N	0.881935	0.977851	1.046584
N	1.060856	1.449791	-0.206083
N	-1.687836	0.186809	-0.094789
N	-1.144455	0.780528	-1.180401
N	0.602487	-1.538938	-0.415672
N	0.837622	-0.708625	-1.455574
C	-1.468823	-2.294104	1.850731
C	-1.296069	0.094041	2.978261
C	0.958602	-1.609375	2.657365
C	1.580642	1.766460	1.865409
C	2.225650	2.769085	1.138156
H	2.861955	3.555412	1.513050
C	1.864239	2.525242	-0.175893
C	-3.008149	0.358589	-0.174467
C	-3.333709	1.073732	-1.329508
H	-4.313165	1.368209	-1.672330
C	-2.115106	1.321339	-1.936178
C	1.096004	-2.732681	-0.748566
C	1.660396	-2.683822	-2.025504
H	2.135674	-3.484189	-2.570735
C	1.473245	-1.375278	-2.434149
B	0.379141	0.761369	-1.407405
H	0.662387	1.326794	-2.430970
H	1.014357	-3.555955	-0.054090
H	1.746039	-0.869240	-3.348332

Atom	x	y	z
H	2.120564	3.039165	-1.090601
H	-1.866827	1.842838	-2.848670
H	1.581128	1.570859	2.928469
H	-3.645704	-0.043029	0.599480
Cl	-2.383624	-3.597723	2.370757

Table S27: Thermodynamic Properties at 298.15 K

Zero Point Energy :	570.59	kJ/mol	(ZPE)
Temperature Correction :	47.86	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	618.45	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-1494.680366	au	(Electronic Energy + Enthalpy Correction)
Entropy :	550.28	J/mol·K	
Gibbs Energy :	-1494.742855	au	(Enthalpy - T*Entropy)
C _v :	329.18	J/mol·K	

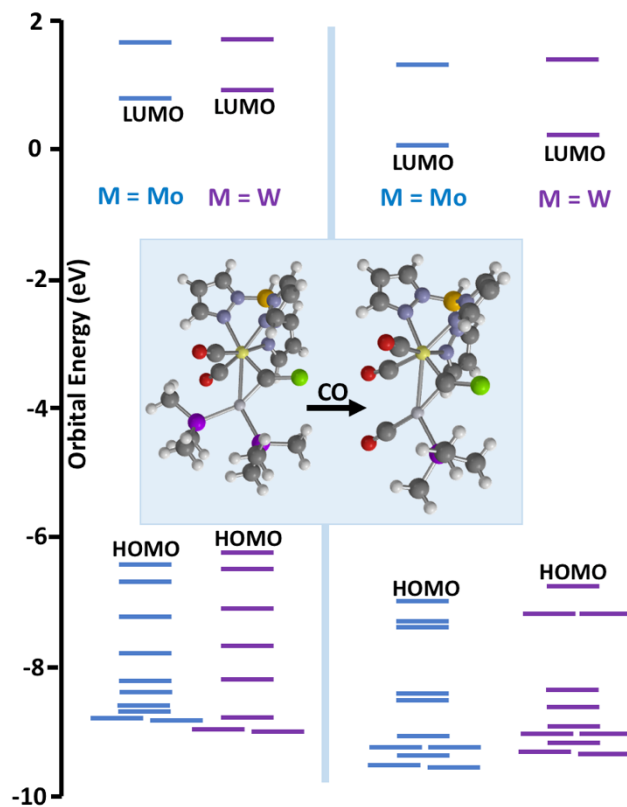
Figure S20. Orbital energies for the complexes [Mpt(μ-CCl)(CO)₂(L)(PMe₃)(Tp*)] (L = PMe₃, CO; M = Mo, W, DFT:ωBP96-X/6-31G*/LANL2DZ/gas phase).

Figure S21. ^1H NMR Spectrum of $[\text{MoAuCl}(\mu\text{-CCl})(\text{CO})_2(\text{Tp}^*)]$ (**2a**) (700 MHz, CDCl_3 , 25°C , δ)

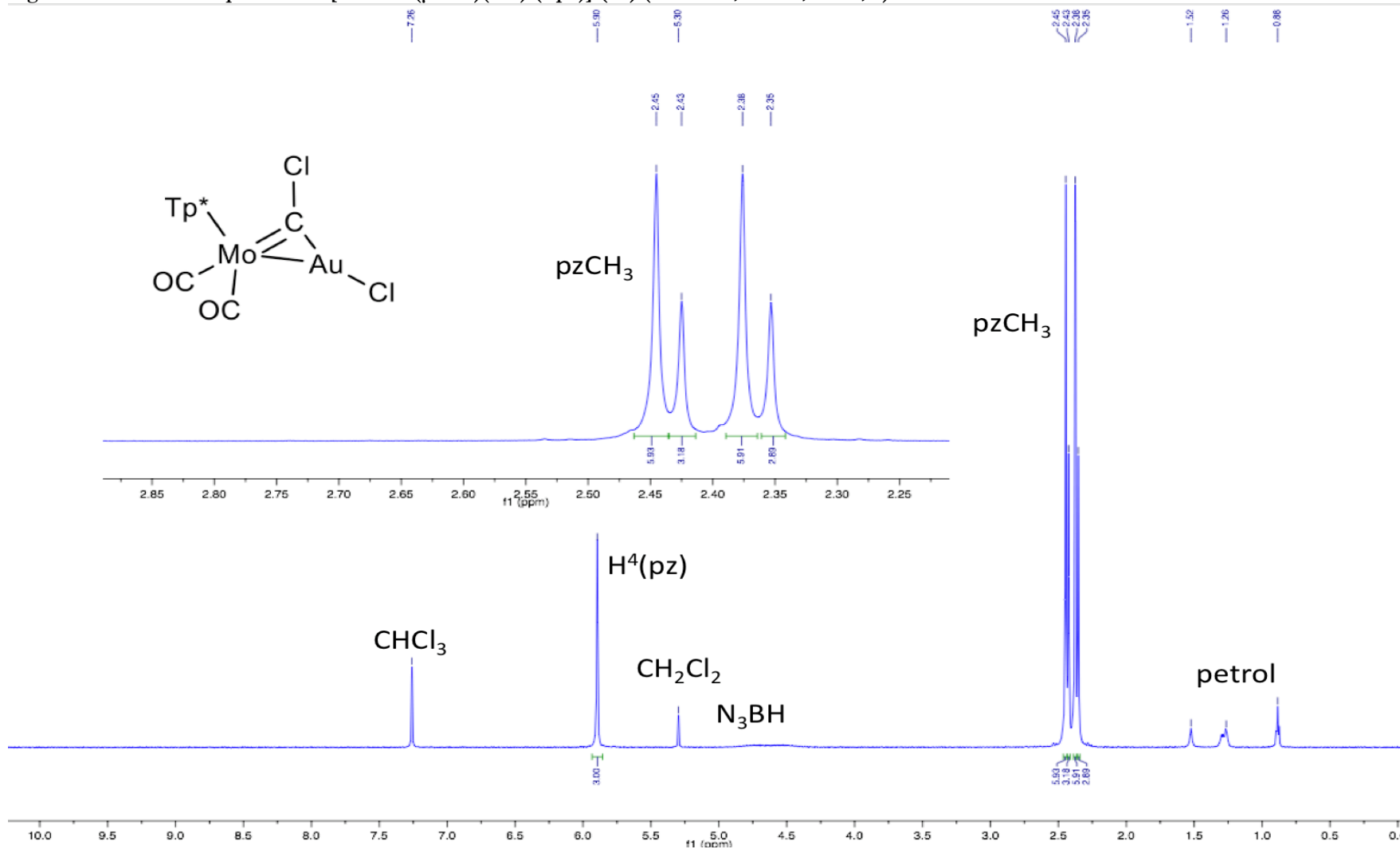


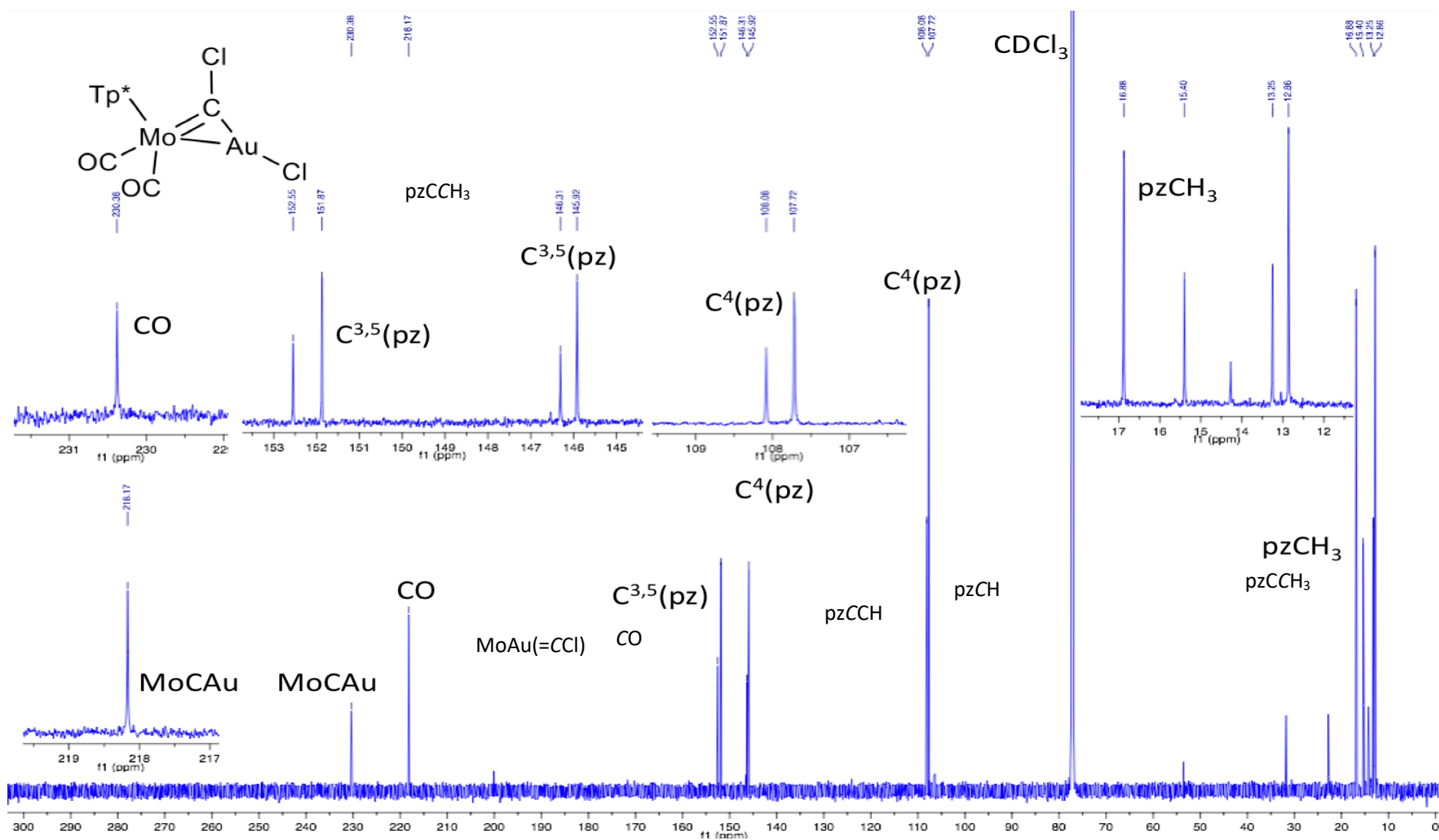
Figure S22. $^{13}\text{C}\{\text{H}\}$ NMR Spectrum of $[\text{MoAuCl}(\mu\text{-Cl})(\text{CO})_2(\text{Tp}^*)]$ (2a) (176 MHz, CDCl_3 , 25 °C, δ):

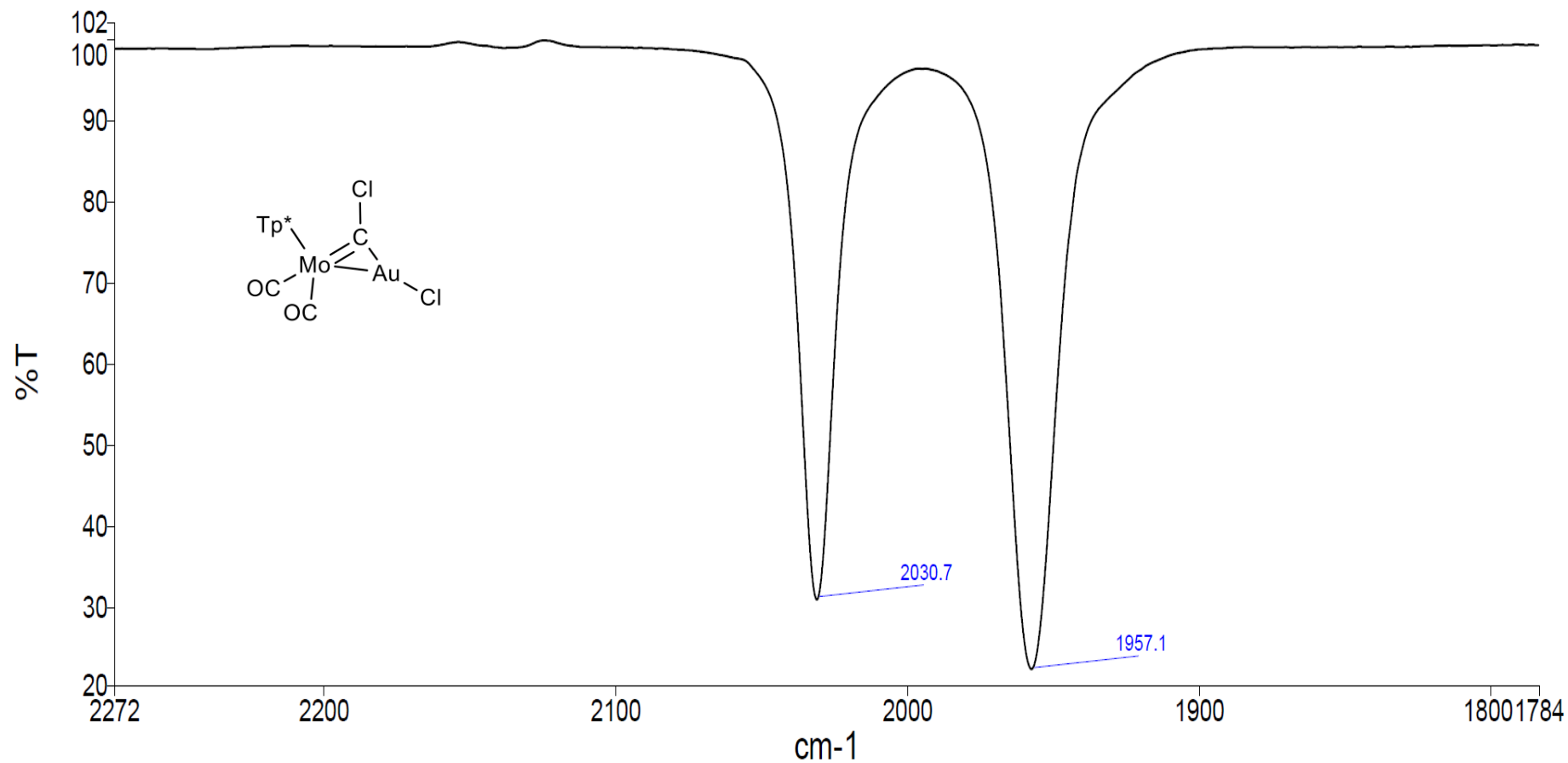
Figure S23. Infrared Spectrum of $[\text{MoAuCl}(\mu\text{-Cl})(\text{CO})_2(\text{Tp}^*)]$ (2a) (CH_2Cl_2 , 25 °C, ν):

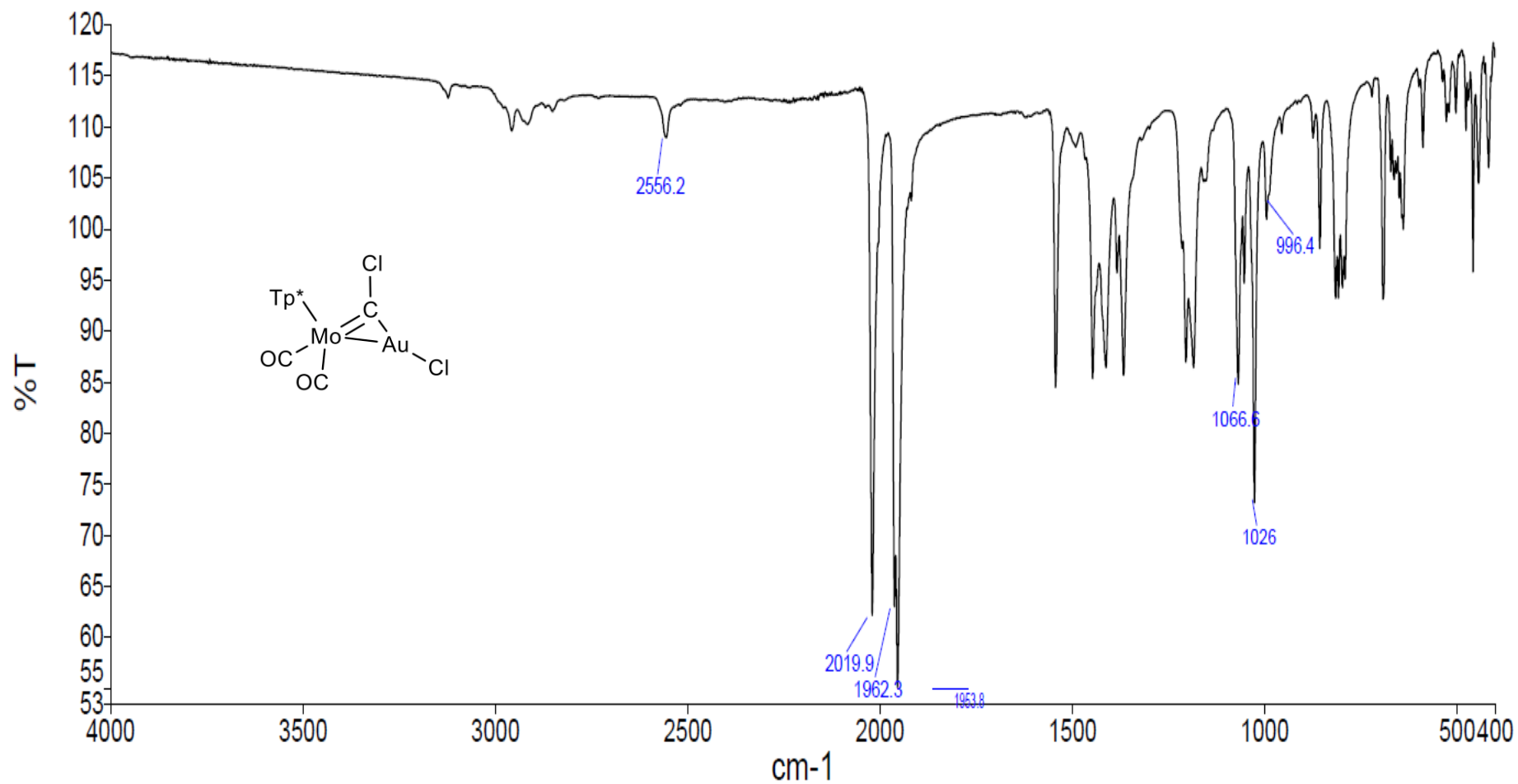
Figure S24. Infrared Spectrum of $[\text{MoAuCl}(\mu\text{-Cl})(\text{CO})_2(\text{Tp}^*)]$ (2a) (ATR, 25 °C, ν):

Figure S25. Mass Spectrum of $[\text{MoAuCl}(\mu\text{-CCl})(\text{CO})_2(\text{Tp}^*)] (2a)$:**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, Even Electron Ions

491 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 35Cl: 0-2 98Mo: 0-1 197Au: 0-1

LB-5-82/AJ

SYNAPTG2-Si#NotSet

11-Feb-2021

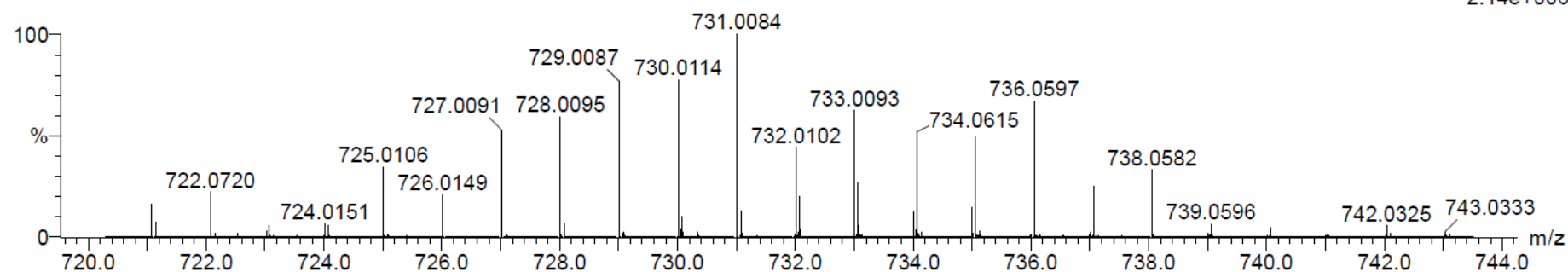
66384

16:04:37

0138 61 (0.138) Cm (33:151)

1: TOF MS ES+

2.14e+006



Minimum: -1.5
 Maximum: 5.0 3.0 12.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
731.0084	731.0072	1.2	1.6	10.5	4137.6	n/a	n/a	C18 H23 11B N6 O2 35Cl2 98Mo 197Au

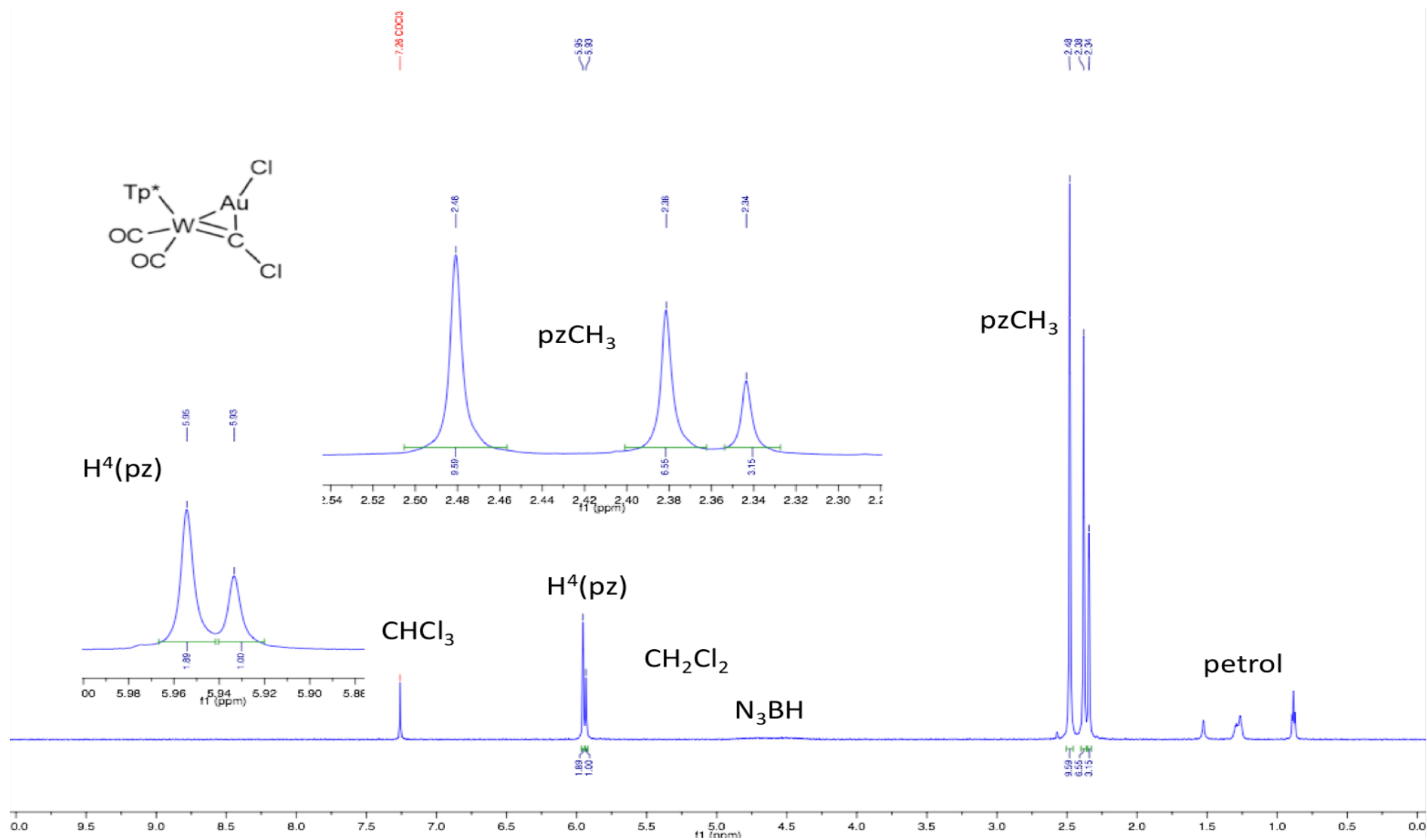
Figure S26. ^1H NMR Spectrum of $[\text{WAuCl}(\mu\text{-Cl})(\text{CO})_2(\text{Tp}^*)]$ (2b) (700 MHz, CDCl_3 , 25 $^\circ\text{C}$, δ):

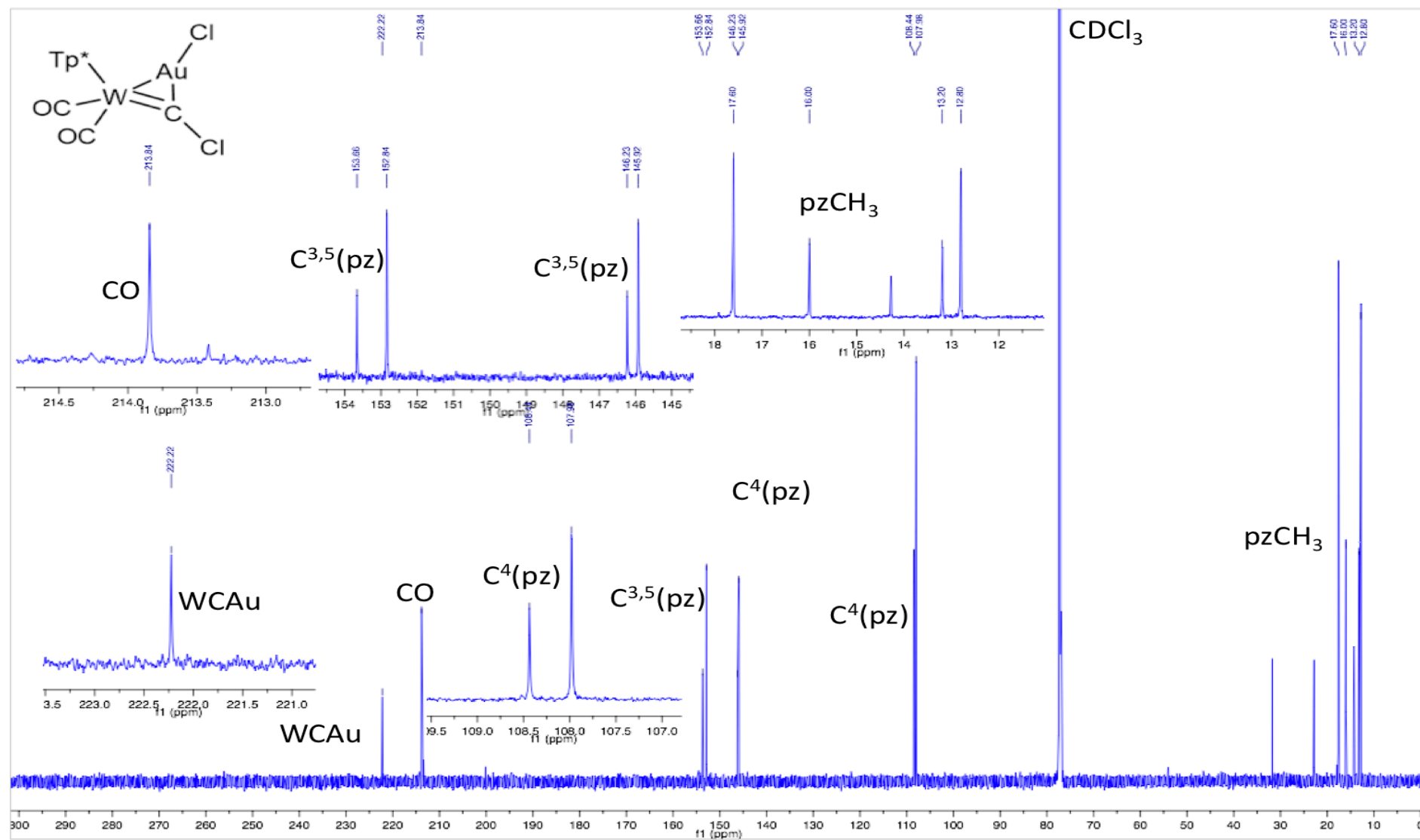
Figure S27. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of $[\text{W}(\text{AuCl}(\mu\text{-Cl})(\text{CO})_2(\text{Tp}^*))_2]$ (2b) (176 MHz, CDCl_3 , 25 °C, δ):

Figure S28. Infrared Spectrum of $[\text{WAuCl}(\mu\text{-CCl})(\text{CO})_2(\text{Tp}^*)]$ (2b) (CH_2Cl_2 , 25 °C, ν):

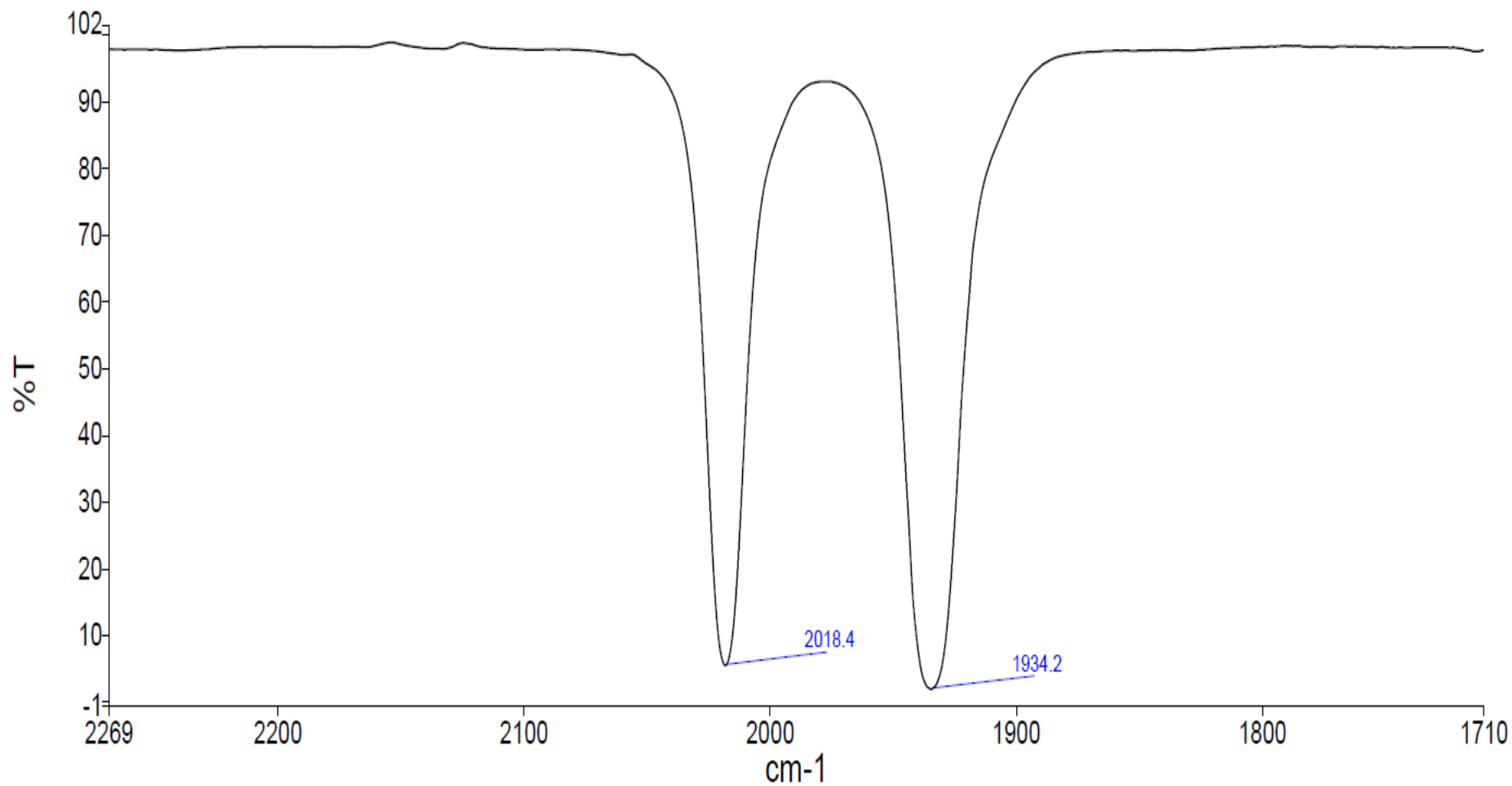


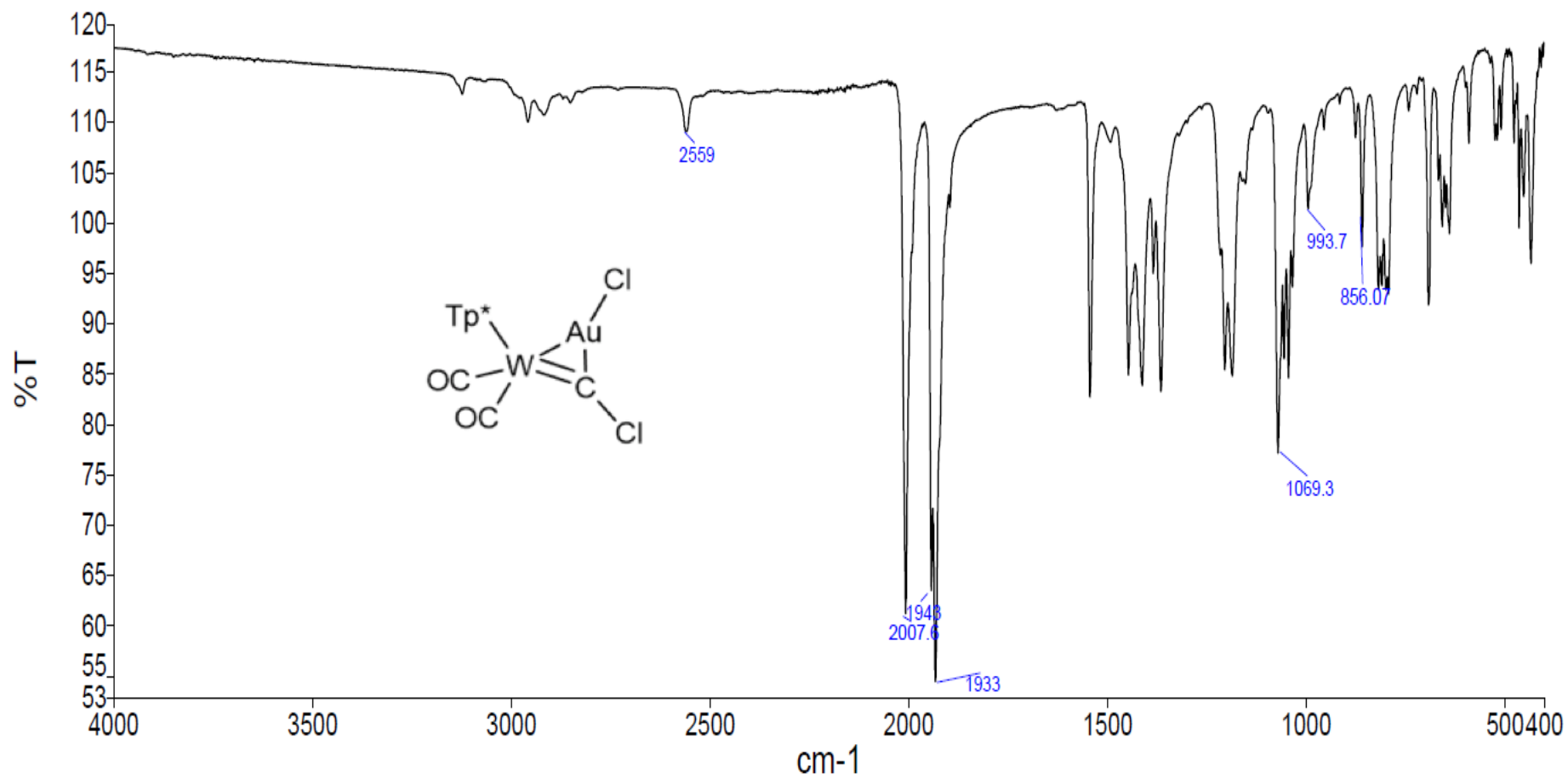
Figure S29. Infrared Spectrum of $[\text{WAuCl}(\mu\text{-Cl})(\text{CO})_2(\text{Tp}^*)]$ (2b) (ATR, 25 °C, ν):

Figure S30. Mass Spectrum of [WAuCl(μ -Cl)(CO)₂(Tp*)] (2b):**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

1519 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 23Na: 1-1 35Cl: 0-2 37Cl: 0-2 184W: 0-1 197Au: 0-1

LB-5-81/AJ

SYNAPTG2-Si#NotSet

11-Feb-2021

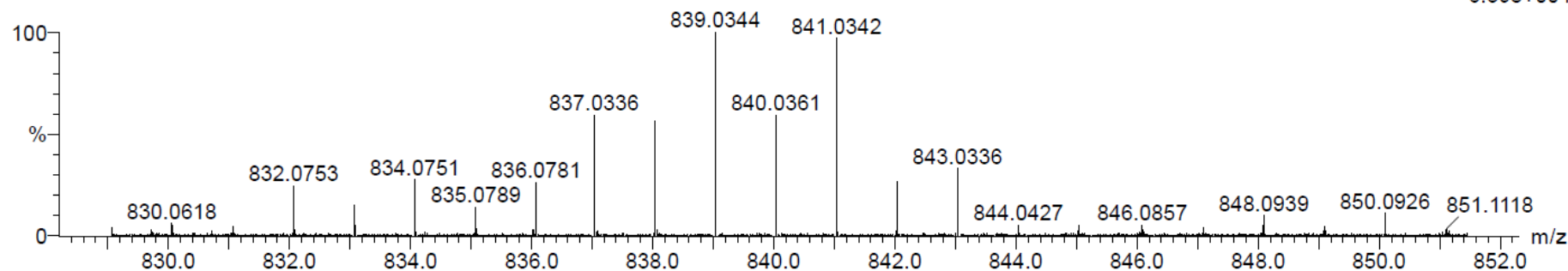
66385

16:08:15

0139 390 (0.783) Cm (387:403)

1: TOF MS ES+

6.39e+004



Minimum: -1.5
 Maximum: 5.0 3.0 12.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
839.0344	839.0347	-0.3	-0.4	12.0	2140.7	n/a	n/a	C18 H22 11B N6 O2 23Na 35Cl2 184W 197Au

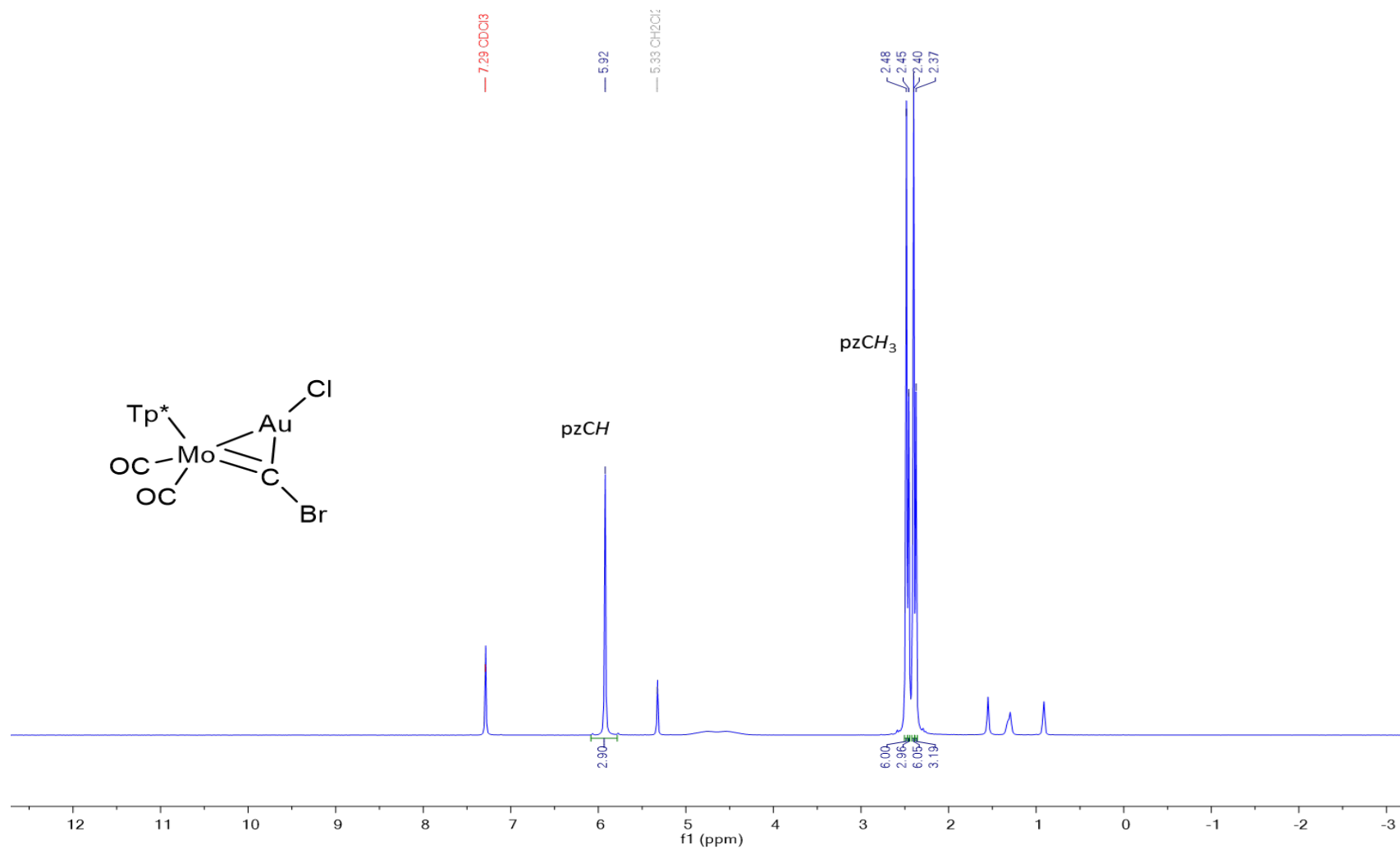
Figure S31. ^1H NMR Spectrum of $[\text{MoAu}(\mu_2\text{-CBr})\text{Cl}(\text{CO})_2(\text{Tp}^*)]$ (2c) (600 MHz, CDCl_3 , 25 °C, δ):

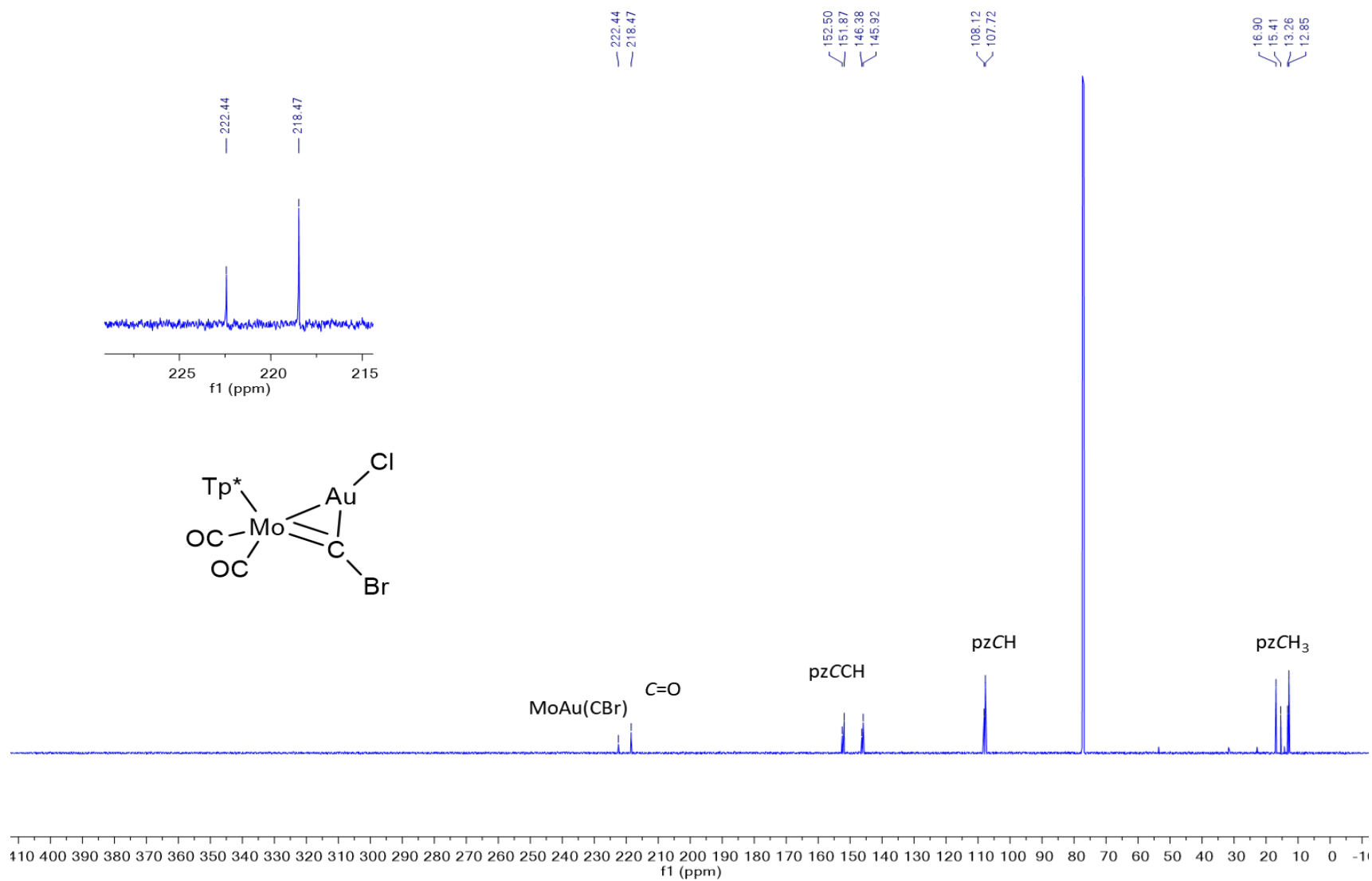
Figure S32. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of $[\text{MoAu}(\mu_2\text{-CBr})\text{Cl}(\text{CO})_2(\text{Tp}^*)]$ (2c) (151 MHz, CDCl_3 , 25 °C, δ):

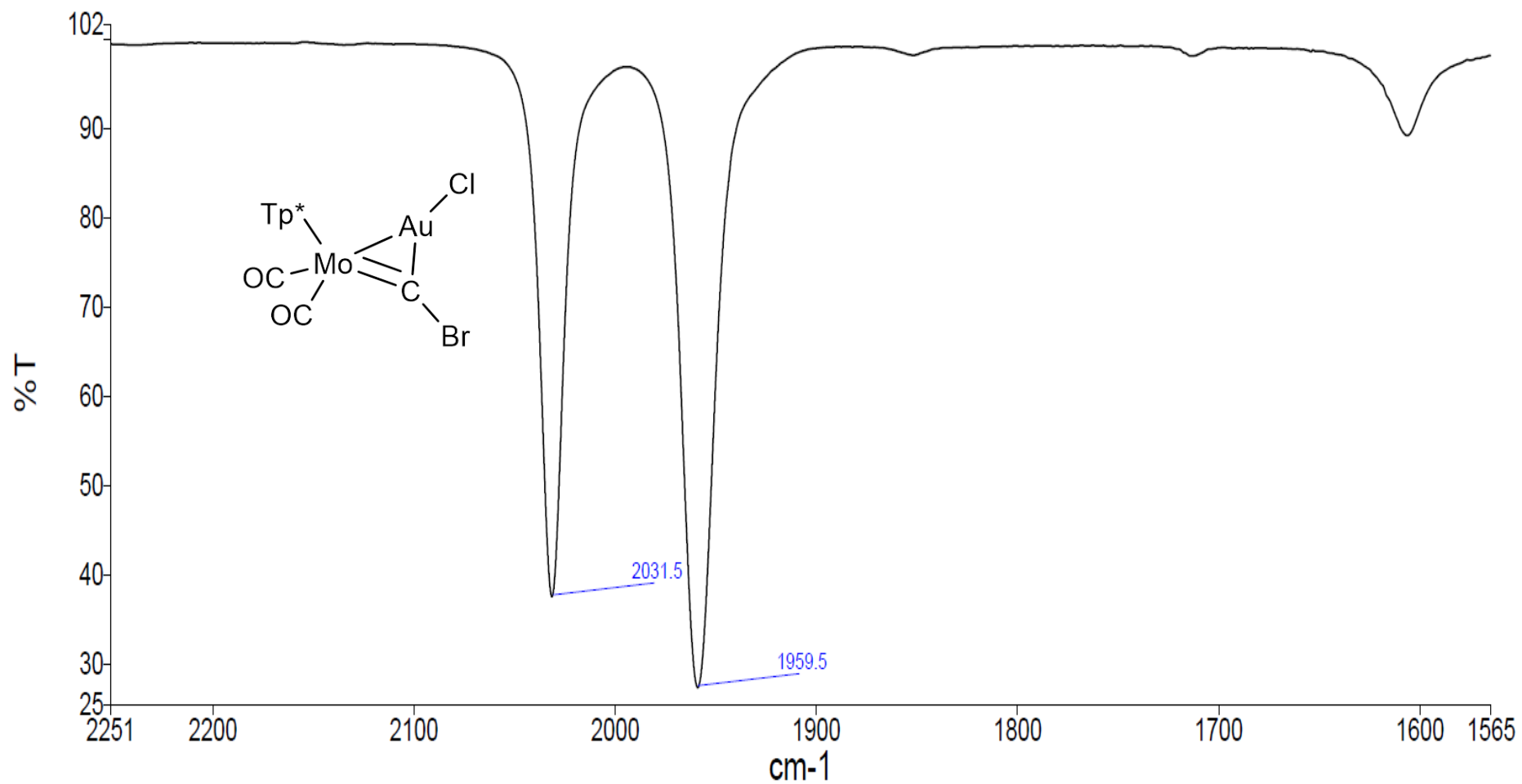
Figure S33. Infrared Spectrum of $[\text{MoAu}(\mu_2\text{-CBr})\text{Cl}(\text{CO})_2(\text{Tp}^*)]$ (2c) (CH_2Cl_2 , 25 °C, ν):

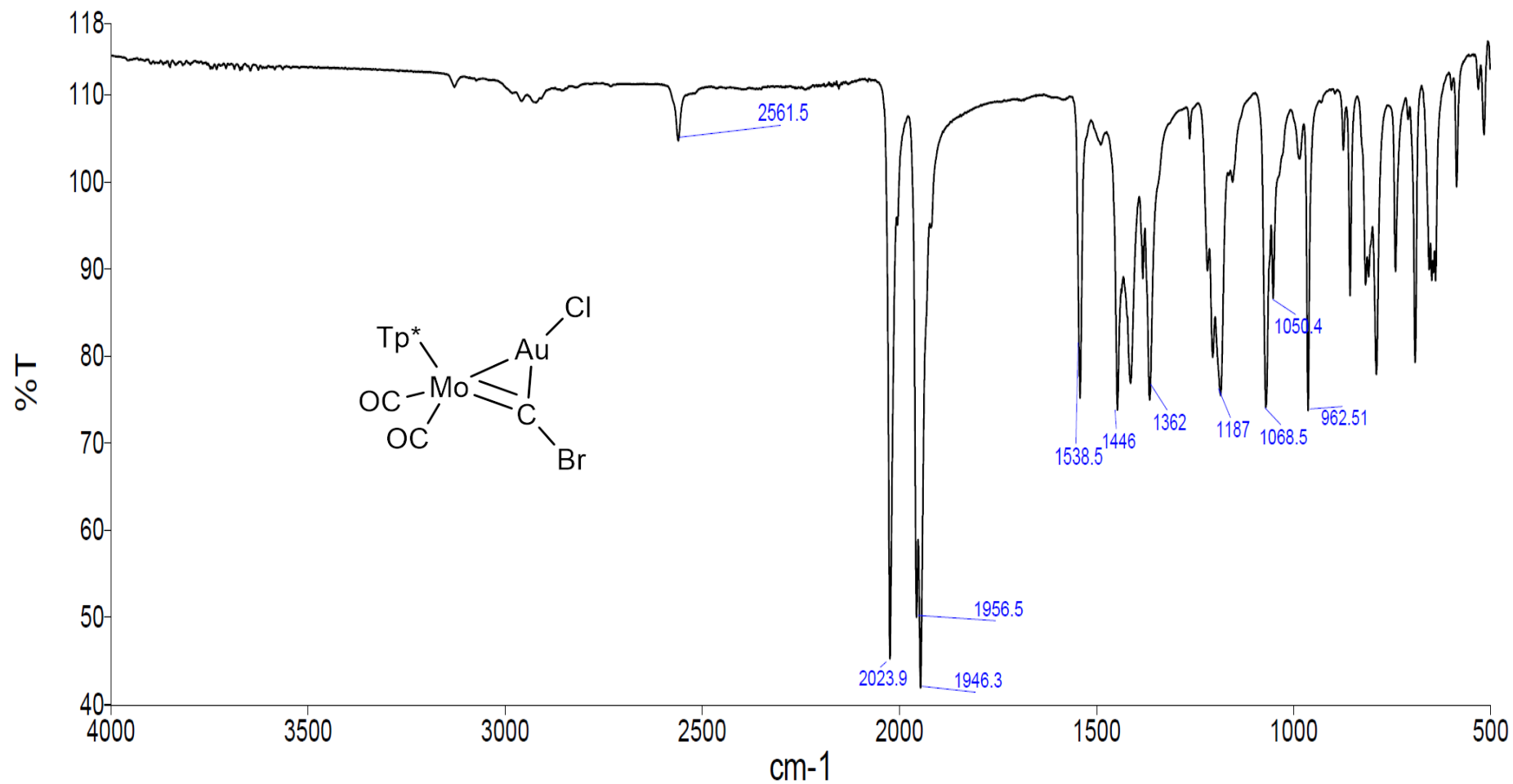
Figure S34. Infrared Spectrum of $[\text{MoAu}(\mu_2\text{-CBr})\text{Cl}(\text{CO})_2(\text{Tp}^*)]$ (**2c**) (ATR, 25 °C, ν):

Figure S35a. Mass Spectrum of $[\text{MoAu}(\mu_2\text{-CBr})\text{Cl}(\text{CO})_2(\text{Tp}^*)] (2c)$:**Single Mass Analysis**

Tolerance = 3.0 PPM / DBE: min = -1.5, max = 10.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

1941 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 23Na: 0-1 35Cl: 0-1 37Cl: 0-1 79Br: 0-1 81Br: 0-1 98Mo: 0-1

197Au: 0-1

LB-6-33/AJ

66728

0641 62 (0.144) Cm (55:62)

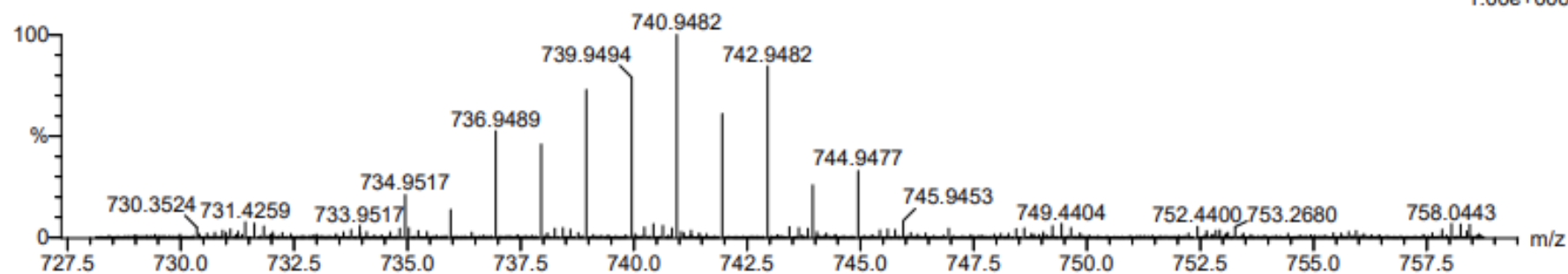
1: TOF MS ES+

SYNAPTG2-Si#NotSet

17-Jun-2021

14:26:04

1.00e+006



Minimum:

Maximum: 5.0 3.0 -1.5 10.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
740.9482	740.9488	-0.6	-0.8	8.5	2332.9	n/a	n/a	C16 H22 11B N6 23Na 35Cl 79Br 98Mo 197Au

Figure S35b. Mass Spectrum of $[\text{MoAu}(\mu_2\text{-CBr})\text{Cl}(\text{CO})_2(\text{Tp}^*)] (2c)$:

32

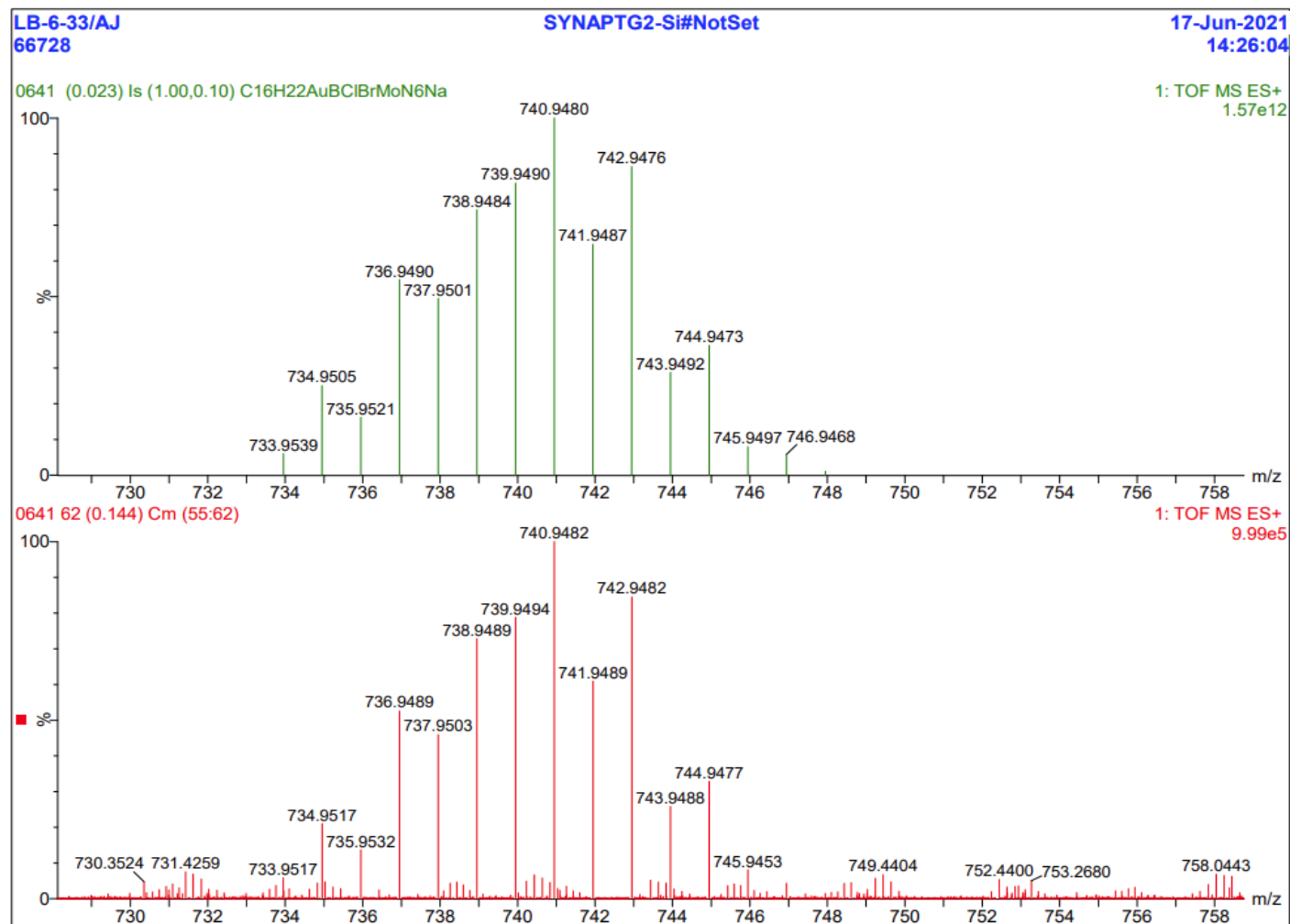


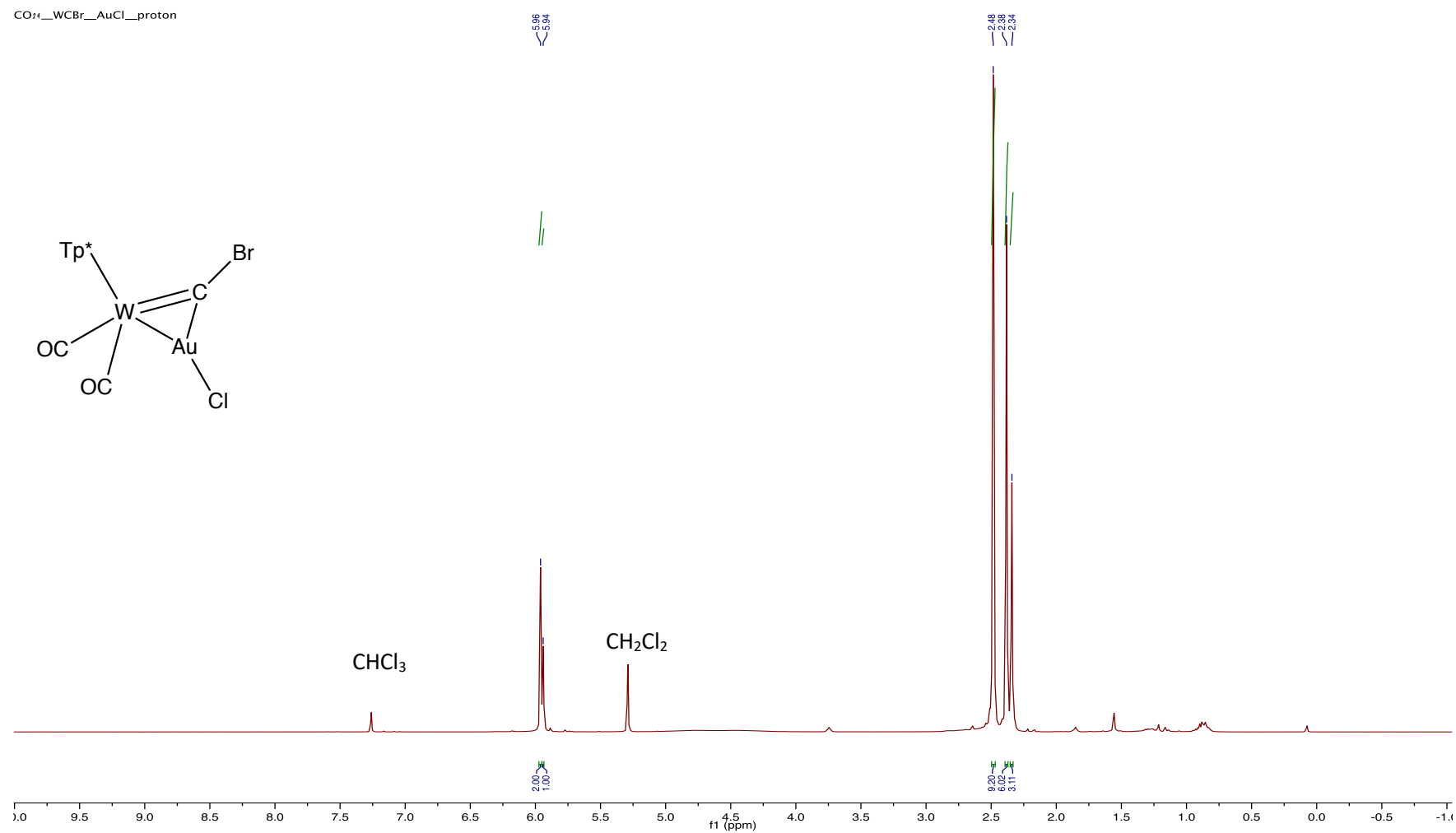
Figure S36. ^1H NMR Spectrum of $[\text{WAu}(\mu_2\text{-CBr})\text{Cl}(\text{CO})_2(\text{Tp}^*)]$ (2d) (400 MHz, CDCl_3 , 25 °C, δ):

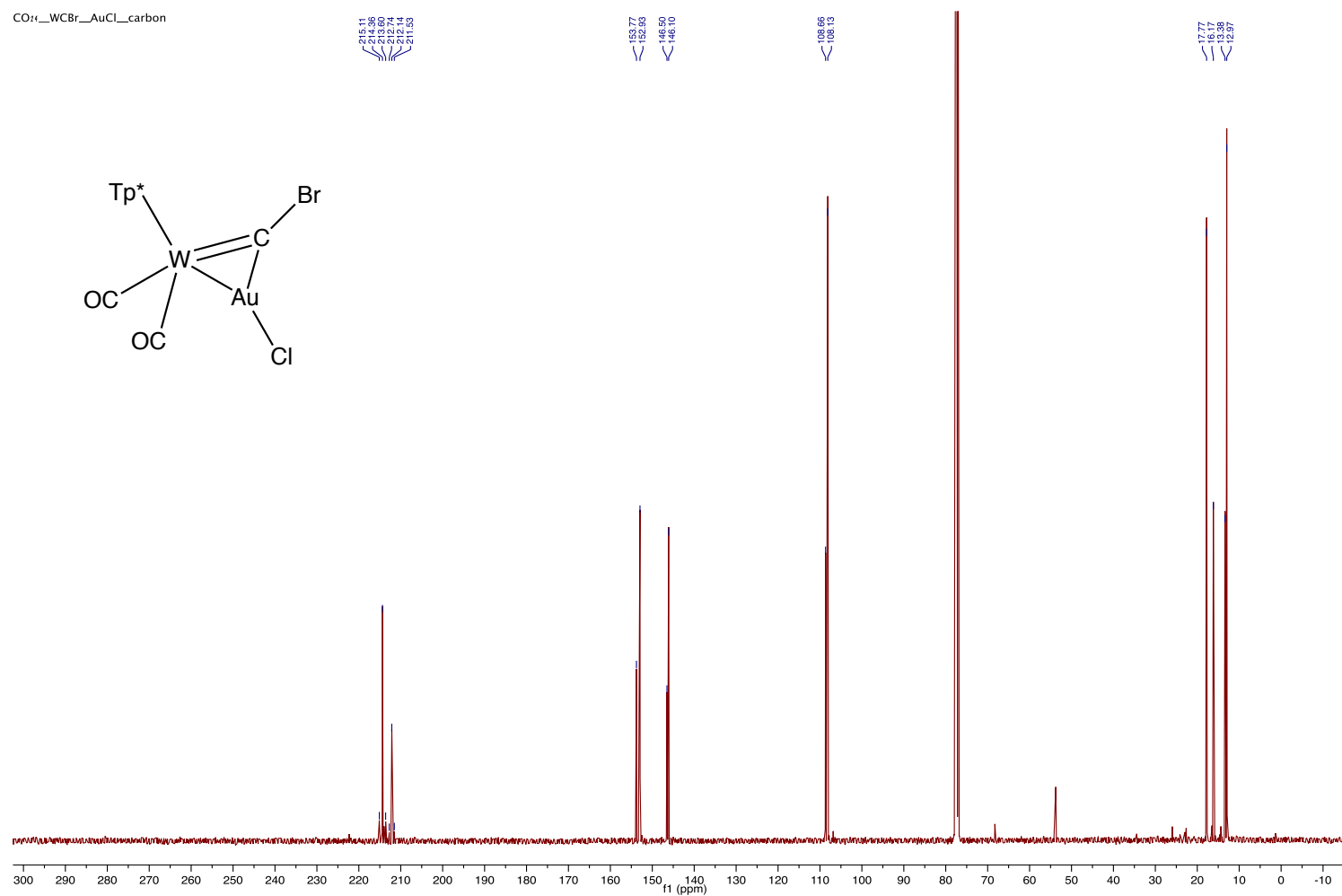
Figure S37. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of $[\text{WAu}(\mu_2\text{-CBr})\text{Cl}(\text{CO})_2(\text{Tp}^*)]$ (2d) (101 MHz, CDCl_3 , 25 °C, δ):

Figure S38. Infrared Spectrum of $[\text{WAu}(\mu_2\text{-CBr})\text{Cl}(\text{CO})_2(\text{Tp}^*)]$ (2d) (CH_2Cl_2 , 25 °C, ν):

Date

Wednesday, 25 November 2020 1:28 PM

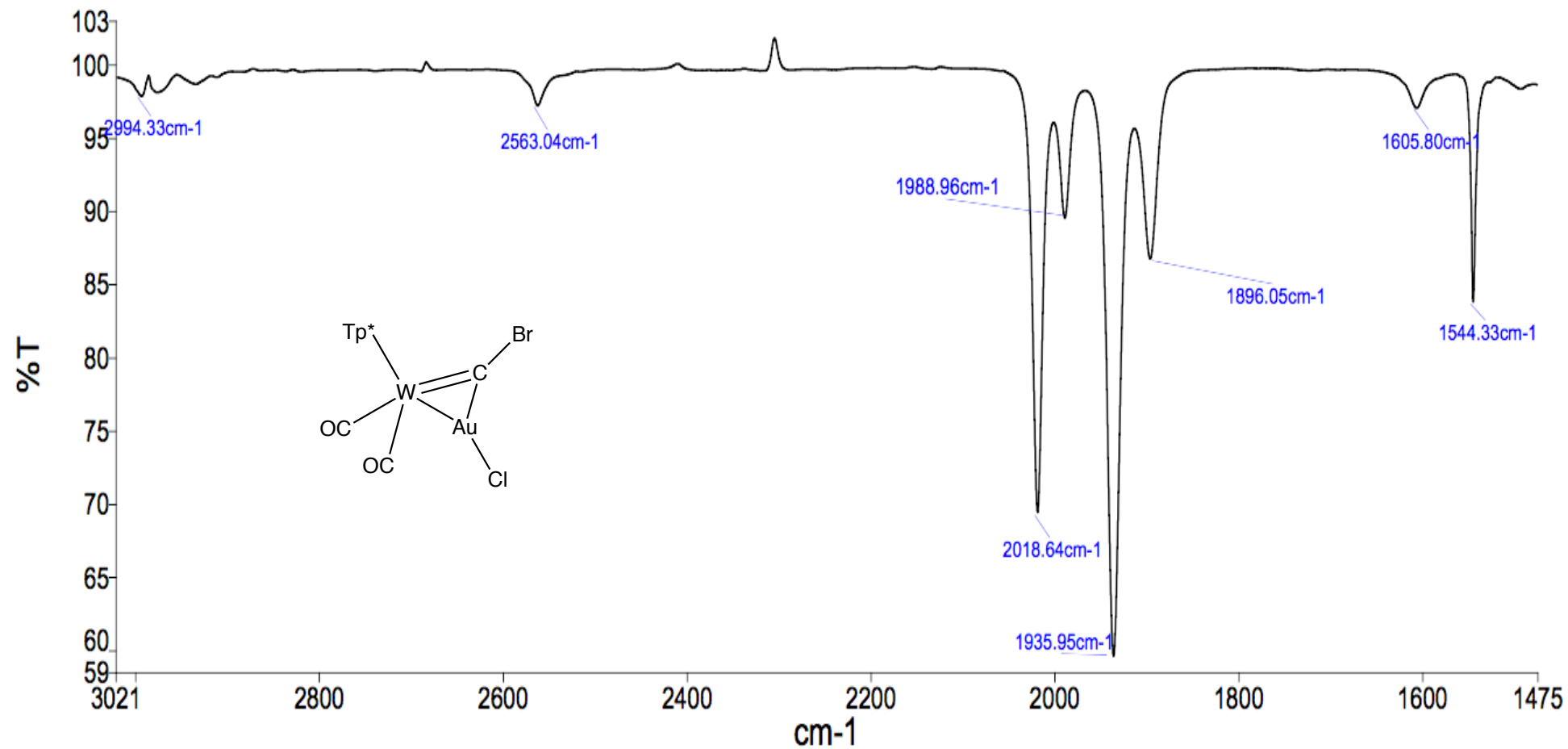


Figure S39. Mass Spectrum of $[\text{WAu}(\mu_2\text{-CBr})\text{Cl}(\text{CO})_2(\text{Tp}^*)]$ (2d):**Single Mass Analysis**

Tolerance = 3.0 PPM / DBE: min = -1.5, max = 10.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

1941 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 23Na: 0-1 35Cl: 0-1 37Cl: 0-1 79Br: 0-1 81Br: 0-1 98Mo: 0-1

197Au: 0-1

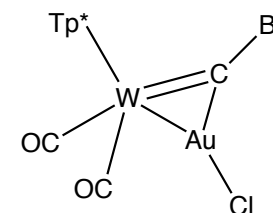
LB-6-33/AJ

66728

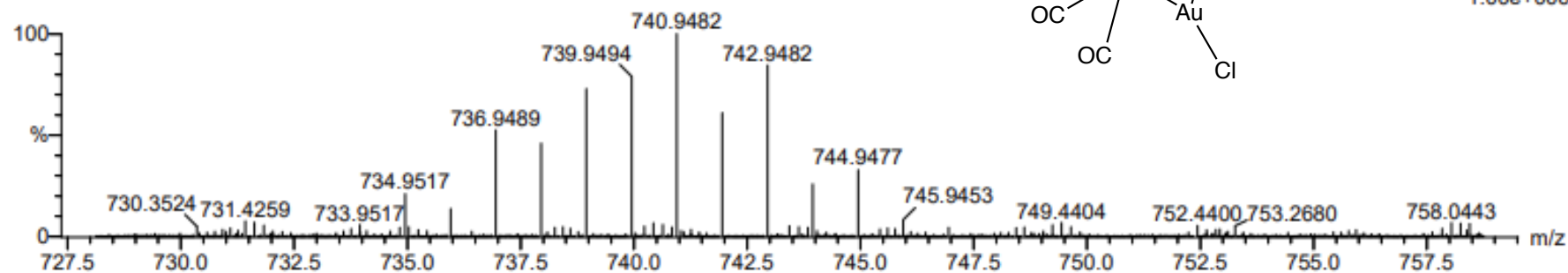
0641 62 (0.144) Cm (55:62)

1: TOF MS ES+

SYNAPTG2-Si#NotSet

17-Jun-2021
14:26:04

1.00e+006



Minimum: -1.5

Maximum: 5.0 3.0 10.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
740.9482	740.9488	-0.6	-0.8	8.5	2332.9	n/a	n/a	C16 H22 11B N6 23Na 35Cl 79Br 98Mo 197Au

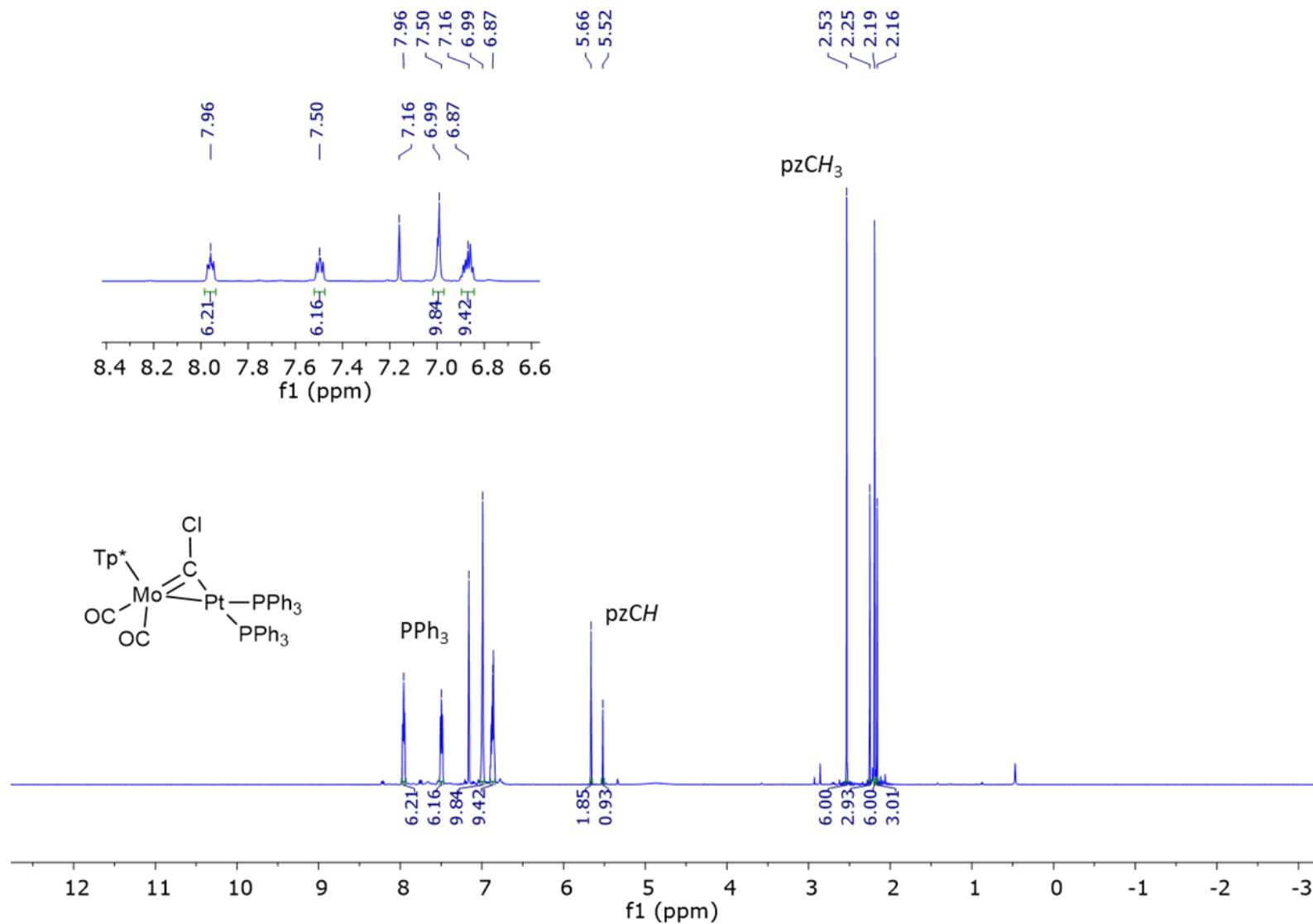
Figure S40. ^1H NMR Spectrum of $[\text{MoPt}(\mu_2\text{-Cl})(\text{PPh}_3)_2(\text{CO})_2(\text{Tp}^*)]$ (3a) (700 MHz, C_6D_6 , 25 $^\circ\text{C}$, δ):

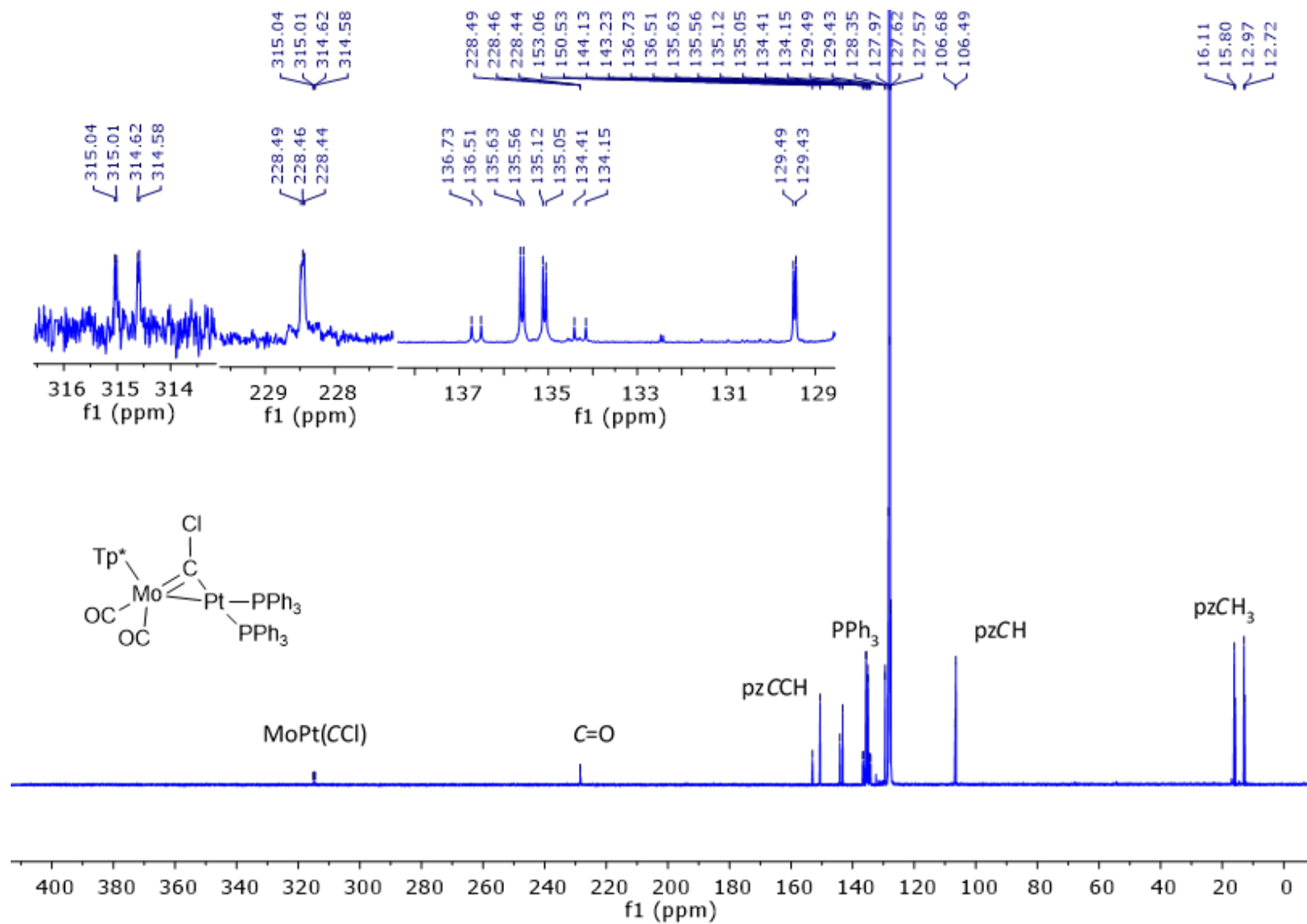
Figure S41. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of $[\text{MoPt}(\mu_2\text{-CCl})(\text{PPh}_3)_2(\text{CO})_2(\text{Tp}^*)]$ (3a) (176 MHz, C_6D_6 , 25 °C, δ):

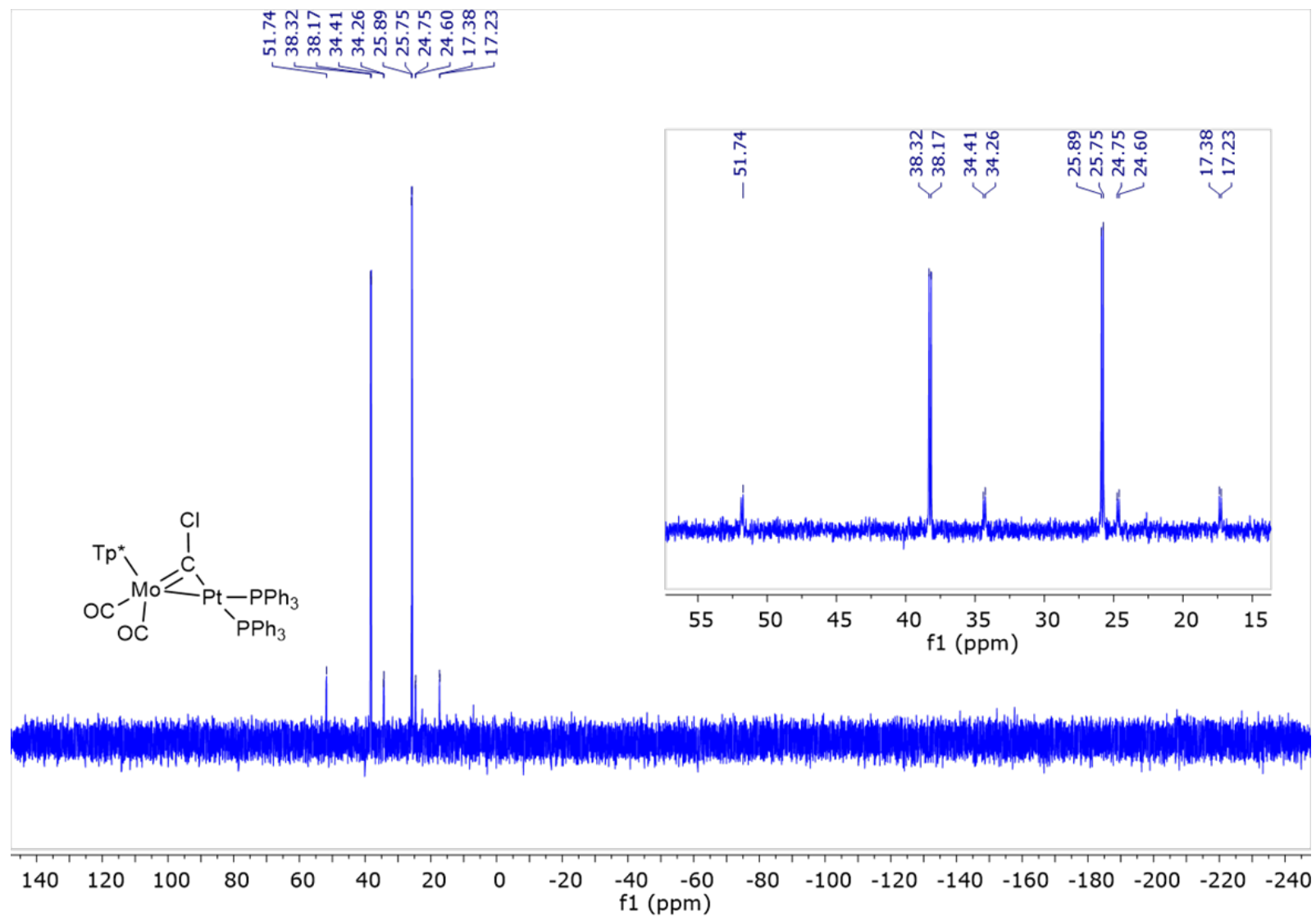
Figure S42. $^3\text{1P}\{^1\text{H}\}$ NMR Spectrum of $[\text{MoPt}(\mu_2\text{-CCl})(\text{PPh}_3)_2(\text{CO})_2(\text{Tp}^*)]$ (3a) (162 MHz, C_6D_6 , 25 °C, δ):

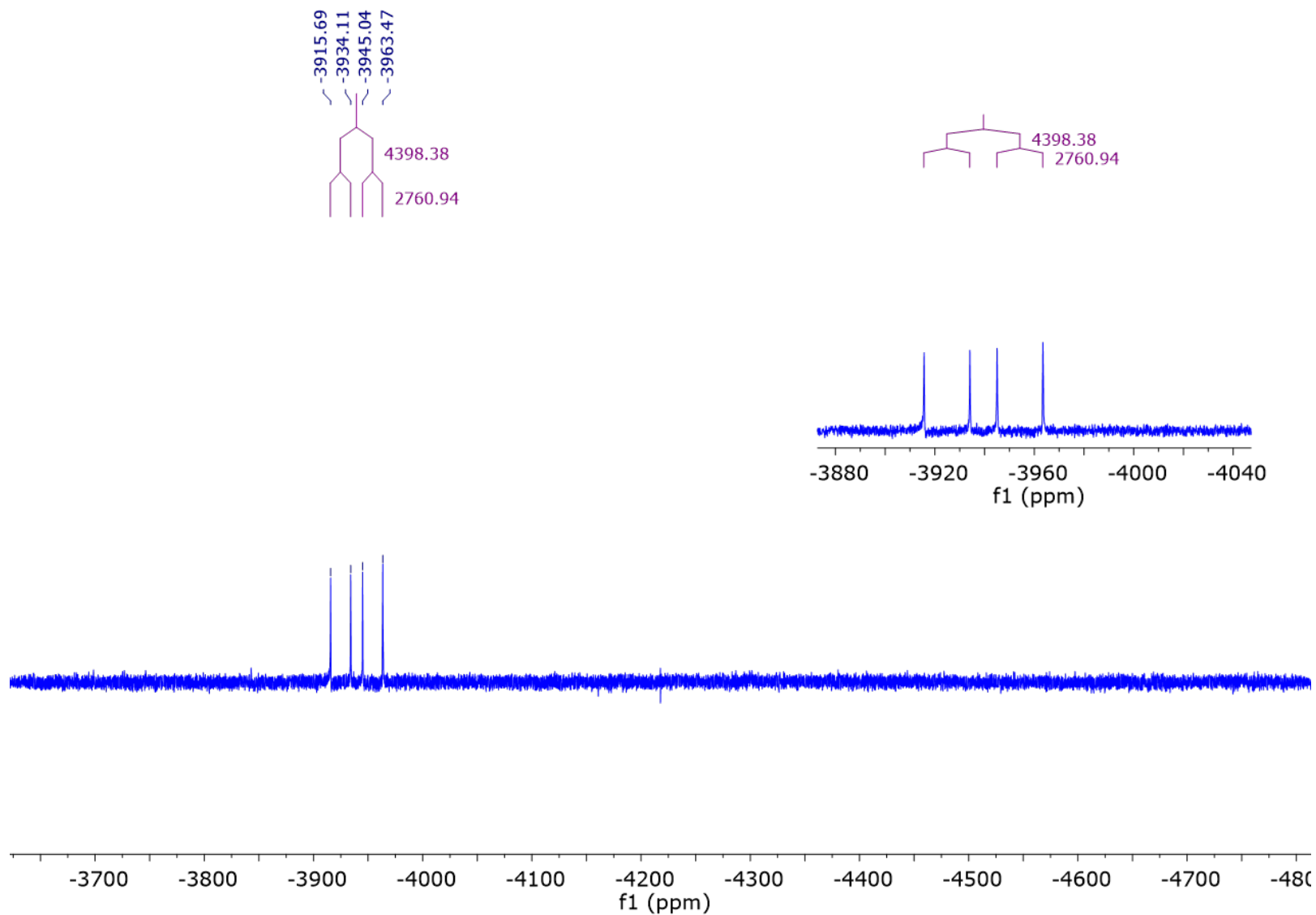
Figure S43. $^{195}\text{Pt}\{^1\text{H}\}$ NMR Spectrum of $[\text{MoPt}(\mu_2\text{-CCl})(\text{PPh}_3)_2(\text{CO})_2(\text{Tp}^*)]$ (3a) (150 MHz, C_6D_6 , 25 °C, δ):

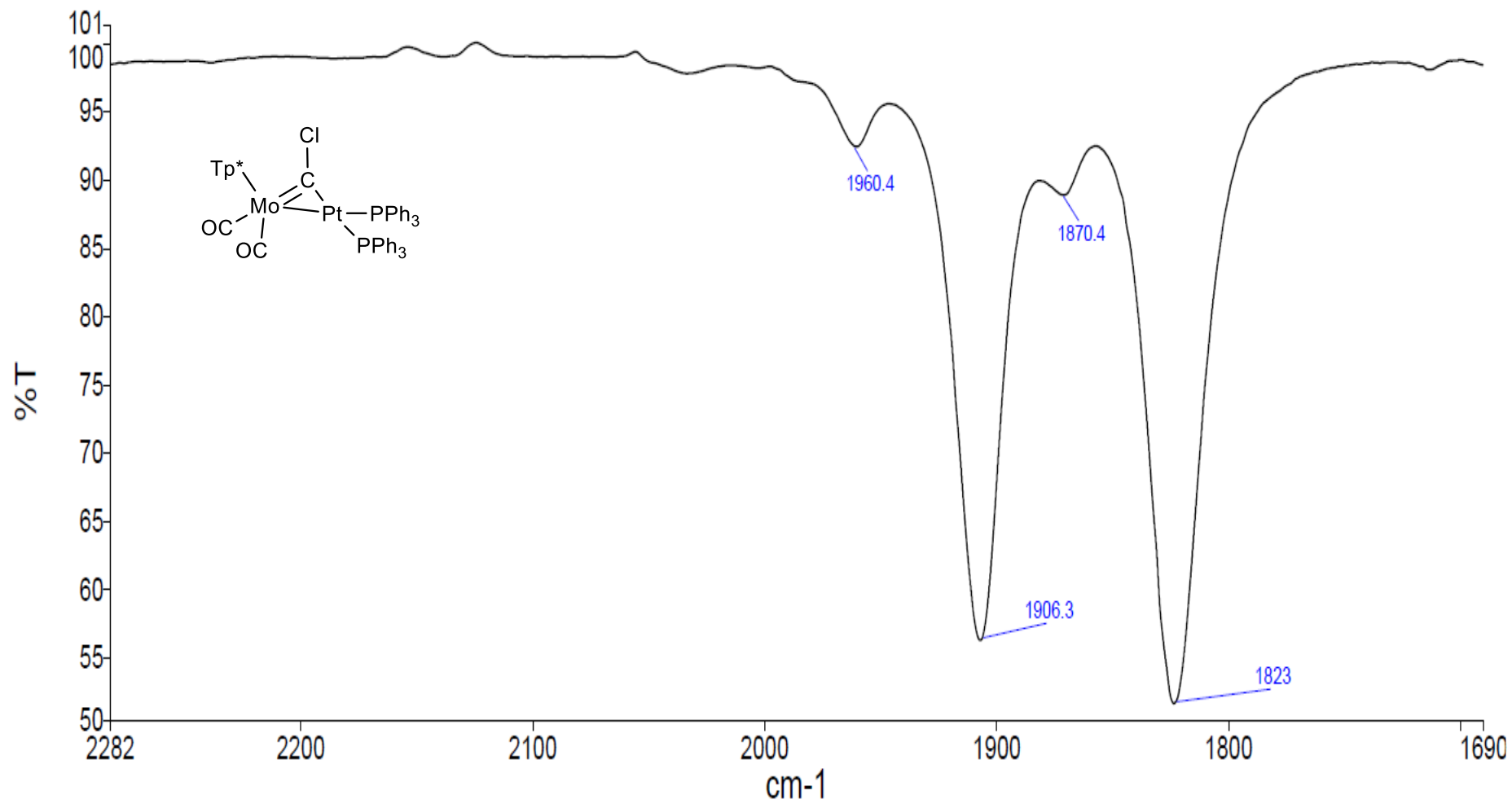
Figure S44. Infrared Spectrum of $[\text{MoPt}(\mu_2\text{-Cl})(\text{PPh}_3)_2(\text{CO})_2(\text{Tp}^*)]$ (3a) (CH_2Cl_2 , 25 °C, ν):

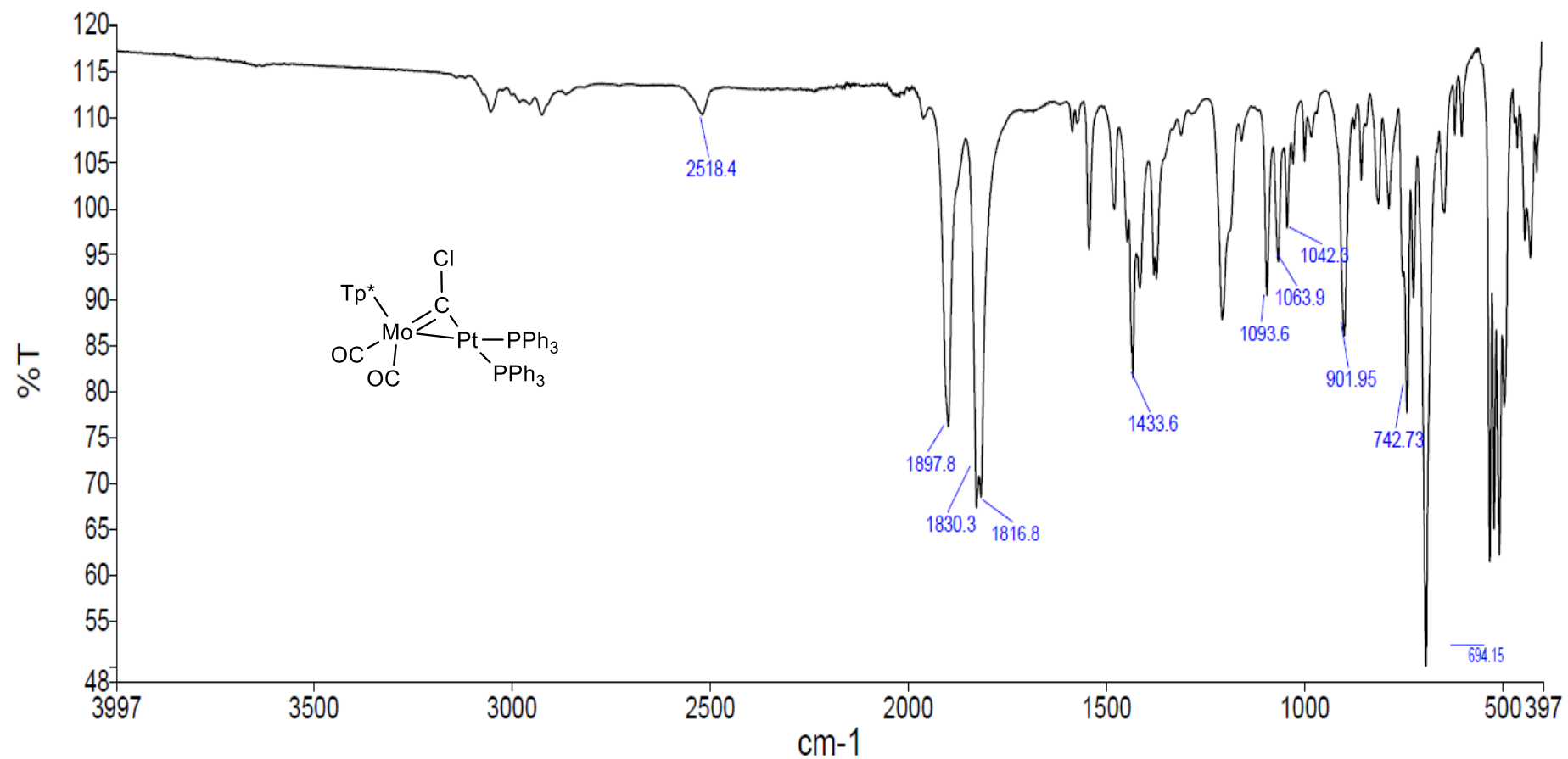
Figure S45. Infrared Spectrum of $[\text{MoPt}(\mu_2\text{-Cl})(\text{PPh}_3)_2(\text{CO})_2(\text{Tp}^*)]$ (3a) (ATR, 25 °C, ν):

Figure S46. Mass Spectrum of $[\text{MoPt}(\mu_2\text{-CCl})(\text{PPh}_3)_2(\text{CO})_2(\text{Tp}^*)]$ (3a) (ESI):

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 3.0 PPM / DBE: min = -1.5, max = 35.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions

1825 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 0-55 H: 0-55 11B: 0-1 N: 0-6 O: 0-2 P: 0-2 35Cl: 0-1 37Cl: 0-1 98Mo: 0-1 195Pt: 0-1

LB-5-75/AJ

66382

0136 66 (0.147) Cm (66:73)

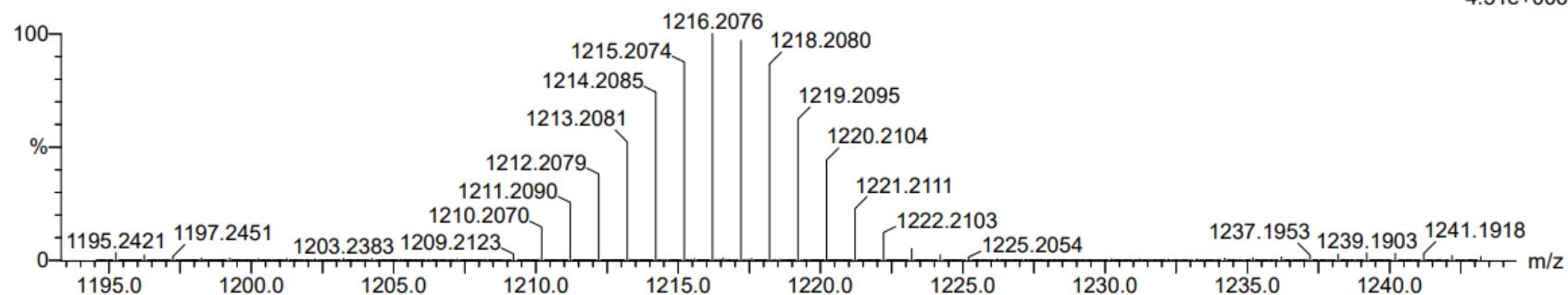
SYNAPTG2-Si#NotSet

11-Feb-2021

15:57:21

1: TOF MS ES+

4.31e+006



Minimum:

Maximum: 5.0 3.0 -1.5

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
1217.2092	1217.2110	-1.8	-1.5	34.0	1240.5	n/a	n/a	C ₅₄ H ₅₂ 11B N ₆ O ₂ P ₂ 35Cl 98Mo 195Pt

Figure S47. Mass Spectrum of $[\text{MoPt}(\mu_2\text{-CCl})(\text{PPh}_3)_2(\text{CO})_2(\text{Tp}^*)]$ (3a) (ESI):

44

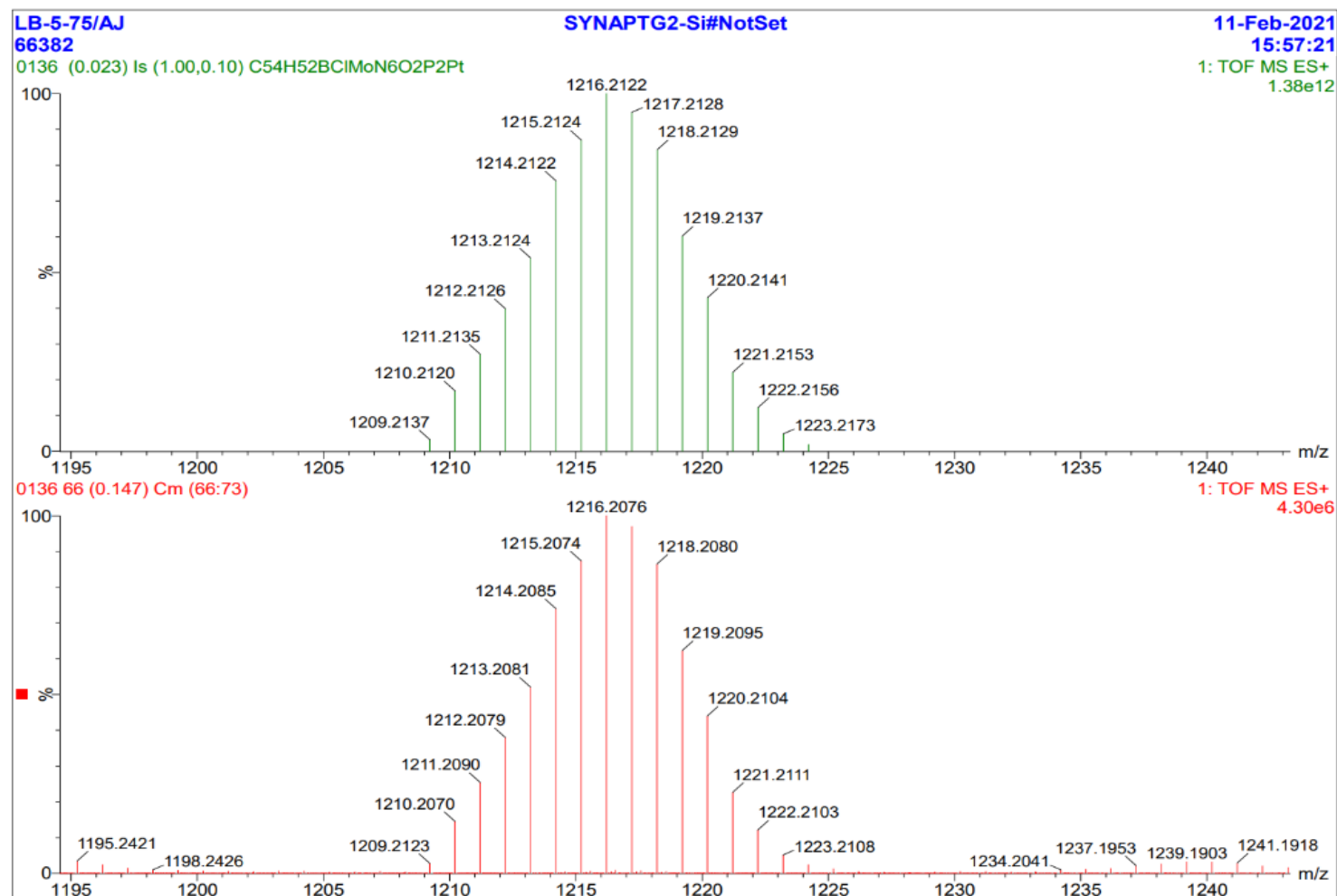
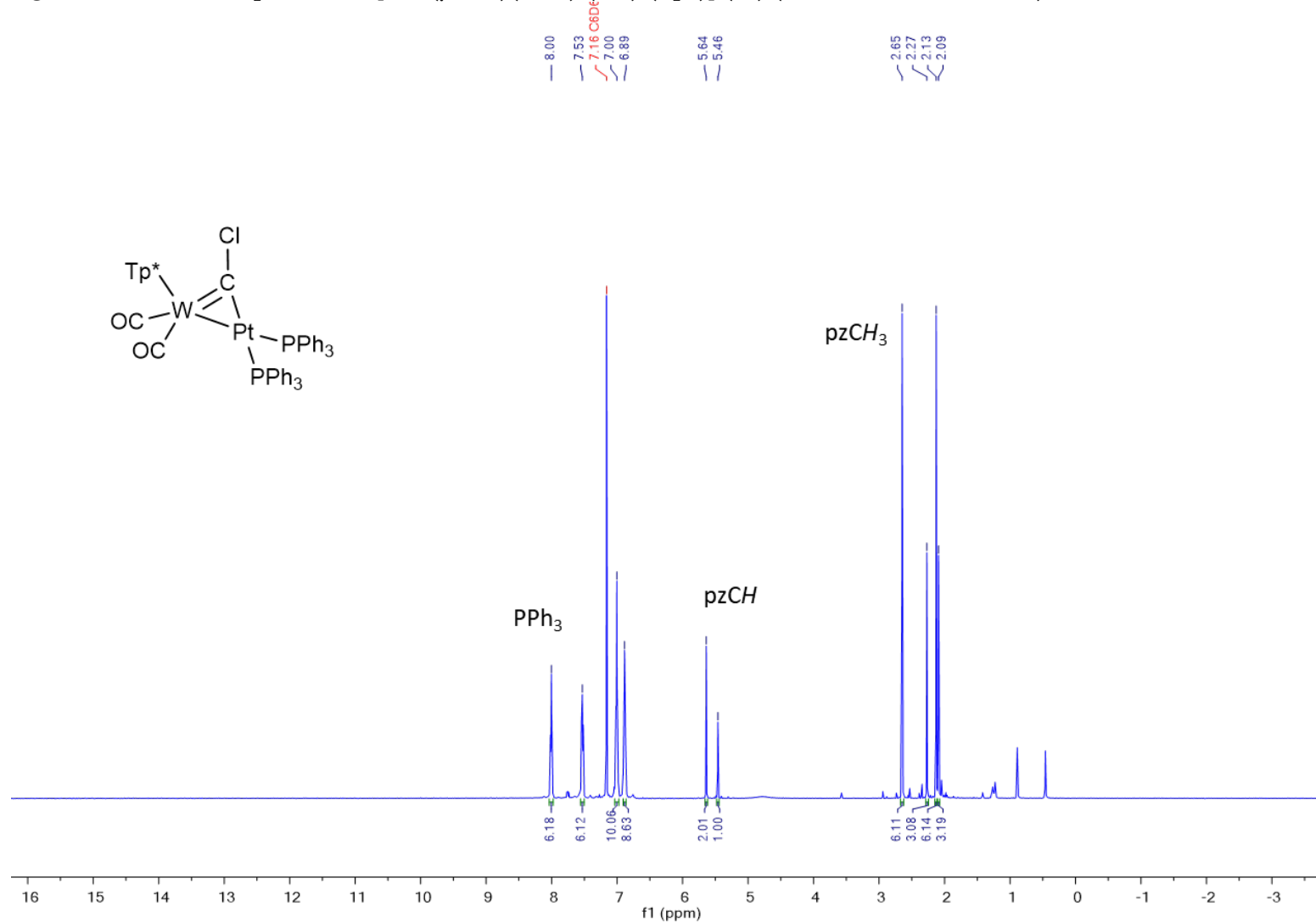


Figure S48. ^1H NMR Spectrum of $[\text{WPt}(\mu\text{-CCl})(\text{PPh}_3)_2(\text{CO})_2(\text{Tp}^*)]$ (3b) (700 MHz, C_6D_6 , 25 $^\circ\text{C}$, δ):Figure S49. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of $[\text{WPt}(\mu\text{-CCl})(\text{PPh}_3)_2(\text{CO})_2(\text{Tp}^*)]$ (3b) (151 MHz, C_6D_6 , 25 $^\circ\text{C}$, δ):

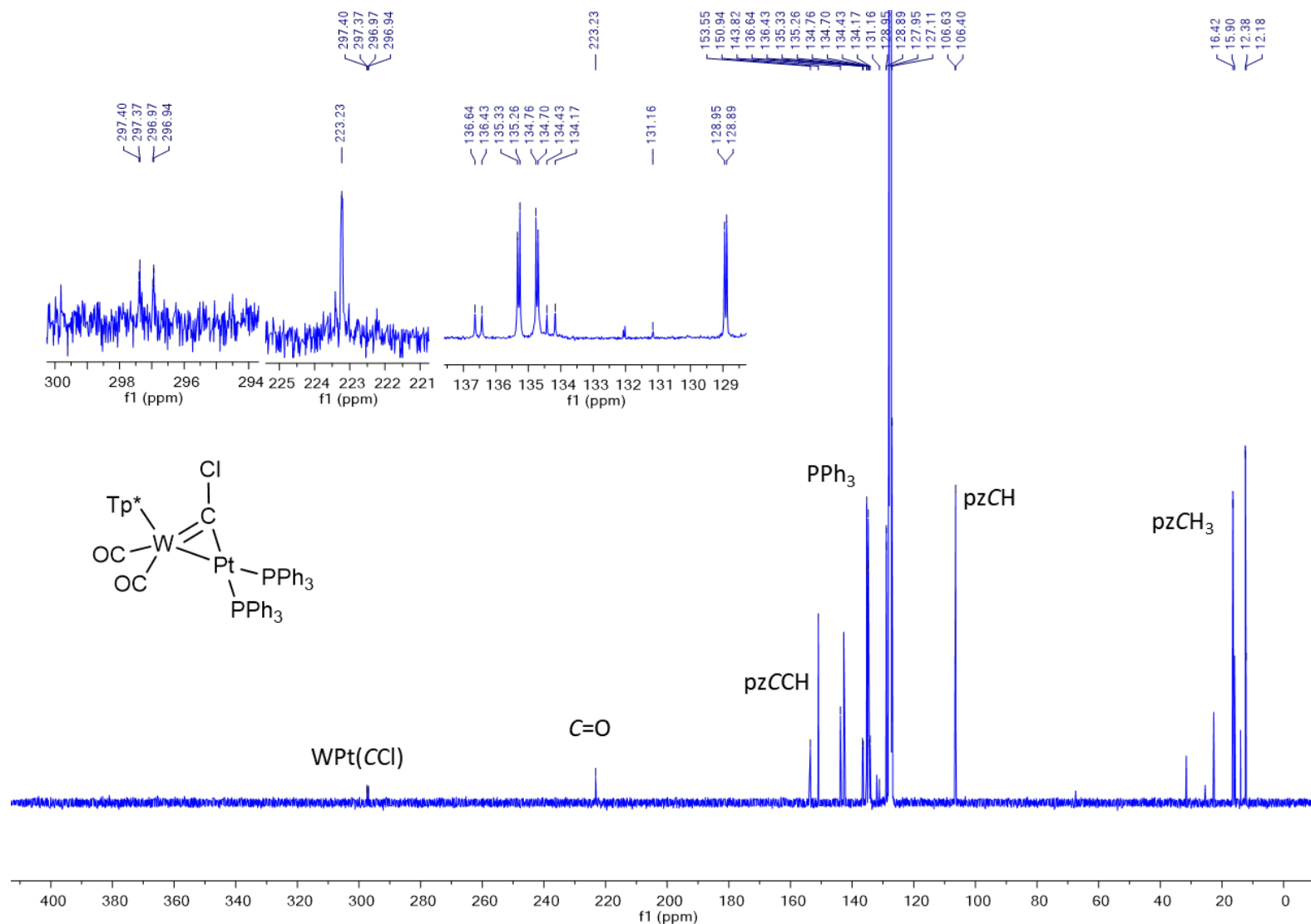


Figure S50. $^{31}P\{^1H\}$ NMR Spectrum of $[WPt(\mu\text{-CCl})(PPh_3)_2(CO)_2(Tp^*)]$ (3b) (162 MHz, C₆D₆, 25 °C, δ):

ELECTRONIC SUPPORTING INFORMATION

Dalton Transactions

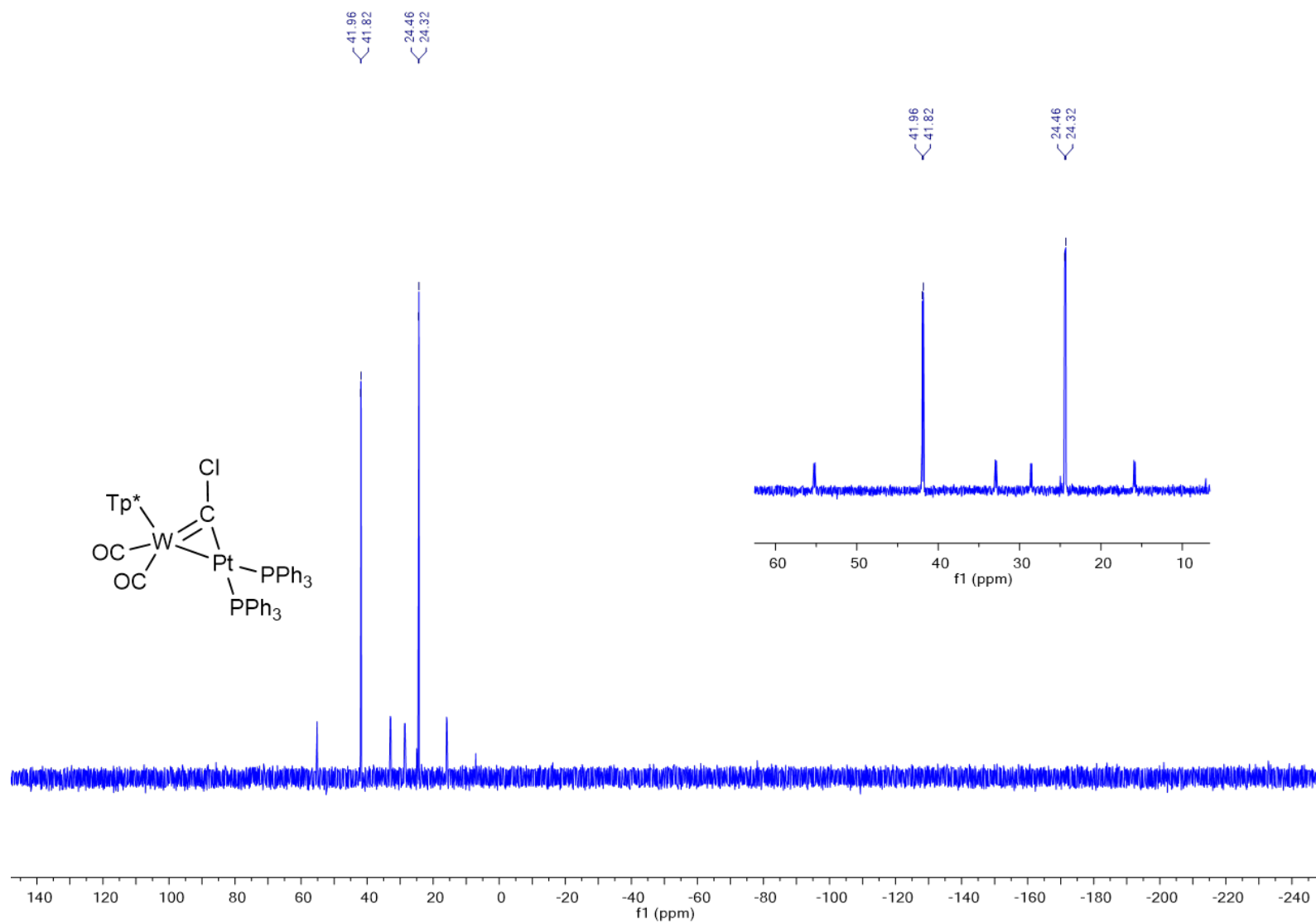


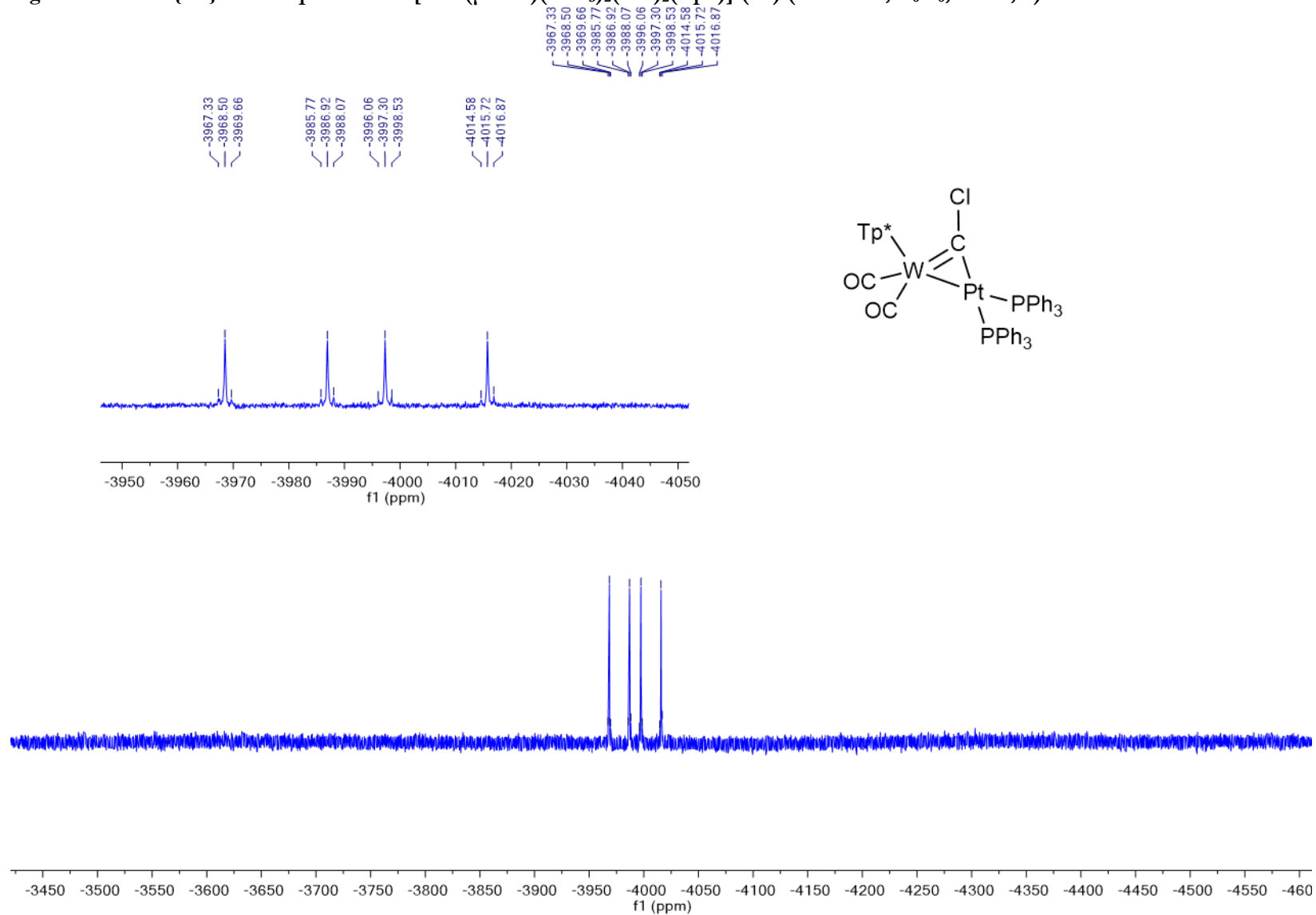
Figure S51. $^{195}\text{Pt}\{^1\text{H}\}$ NMR Spectrum of $[\text{WPt}(\mu\text{-CCl})(\text{PPh}_3)_2(\text{CO})_2(\text{Tp}^*)]$ (3b) (150 MHz, C_6D_6 , 25 °C, δ):

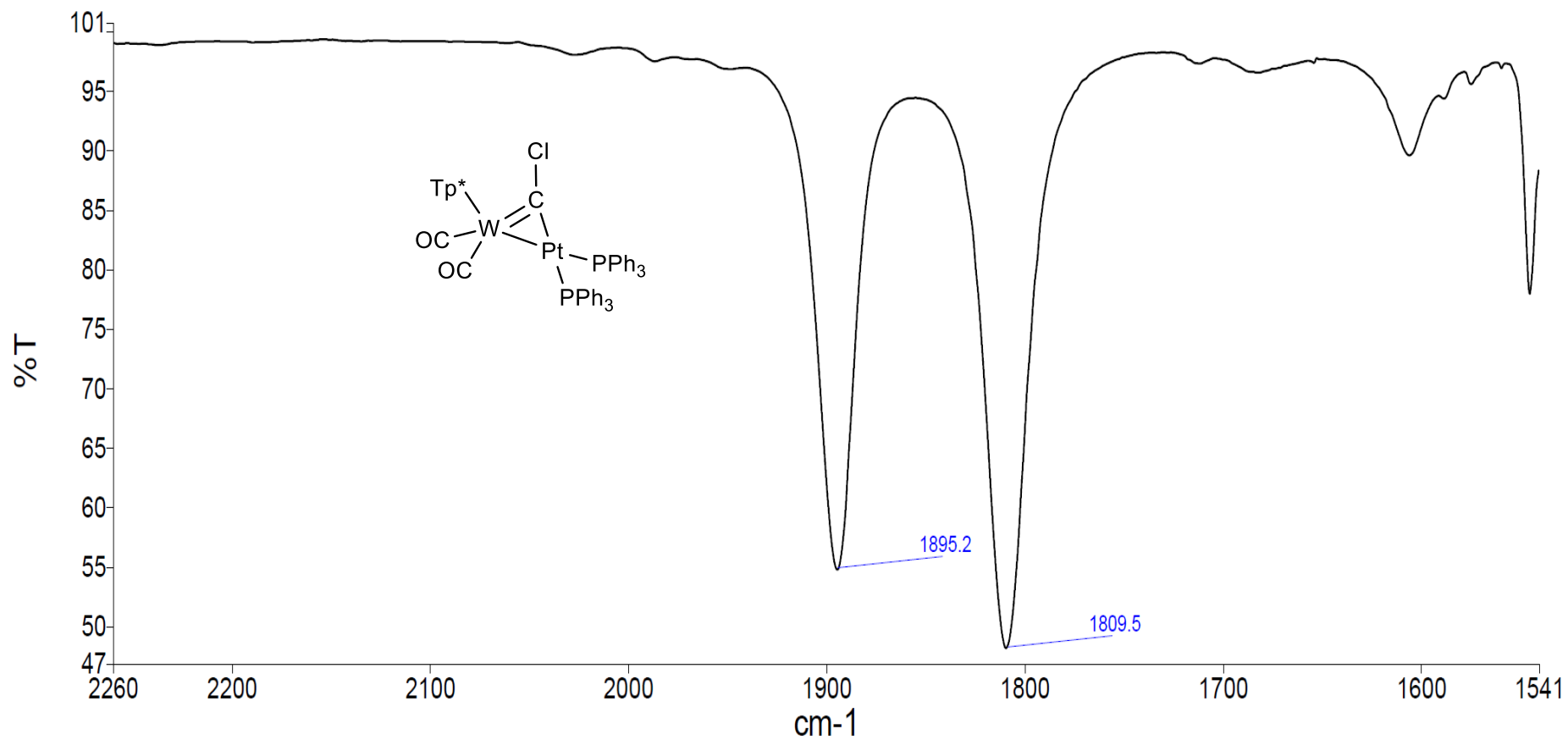
Figure S52. Infrared Spectrum of $[\text{WPt}(\mu\text{-Cl})(\text{PPh}_3)_2(\text{CO})_2(\text{Tp}^*)]$ (3b) (CH_2Cl_2 , 25 °C, ν):

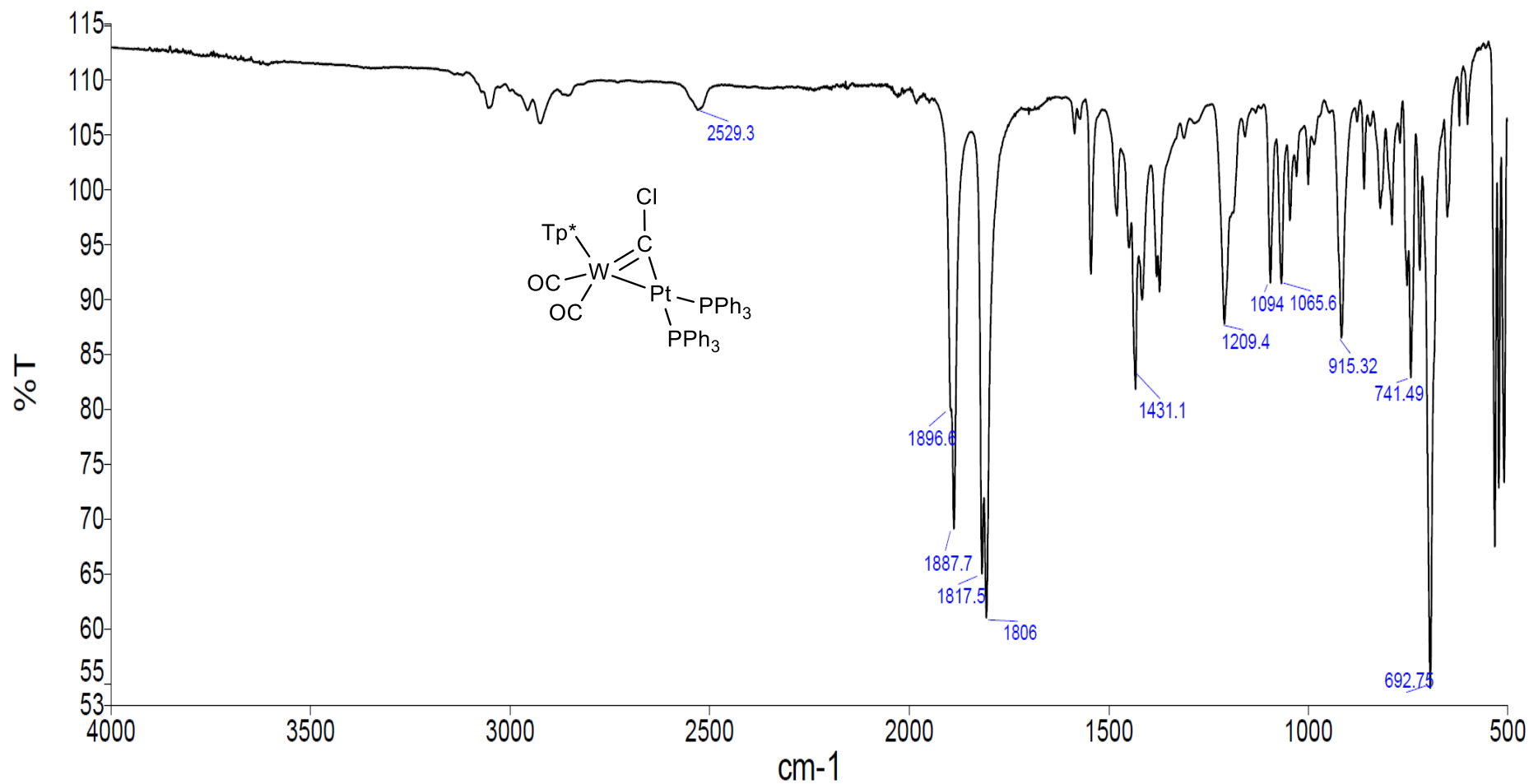
Figure S53. Infrared Spectrum of $[\text{WPt}(\mu\text{-Cl})(\text{PPh}_3)_2(\text{CO})_2(\text{Tp}^*)]$ (3b) (ATR, 25 °C, ν):

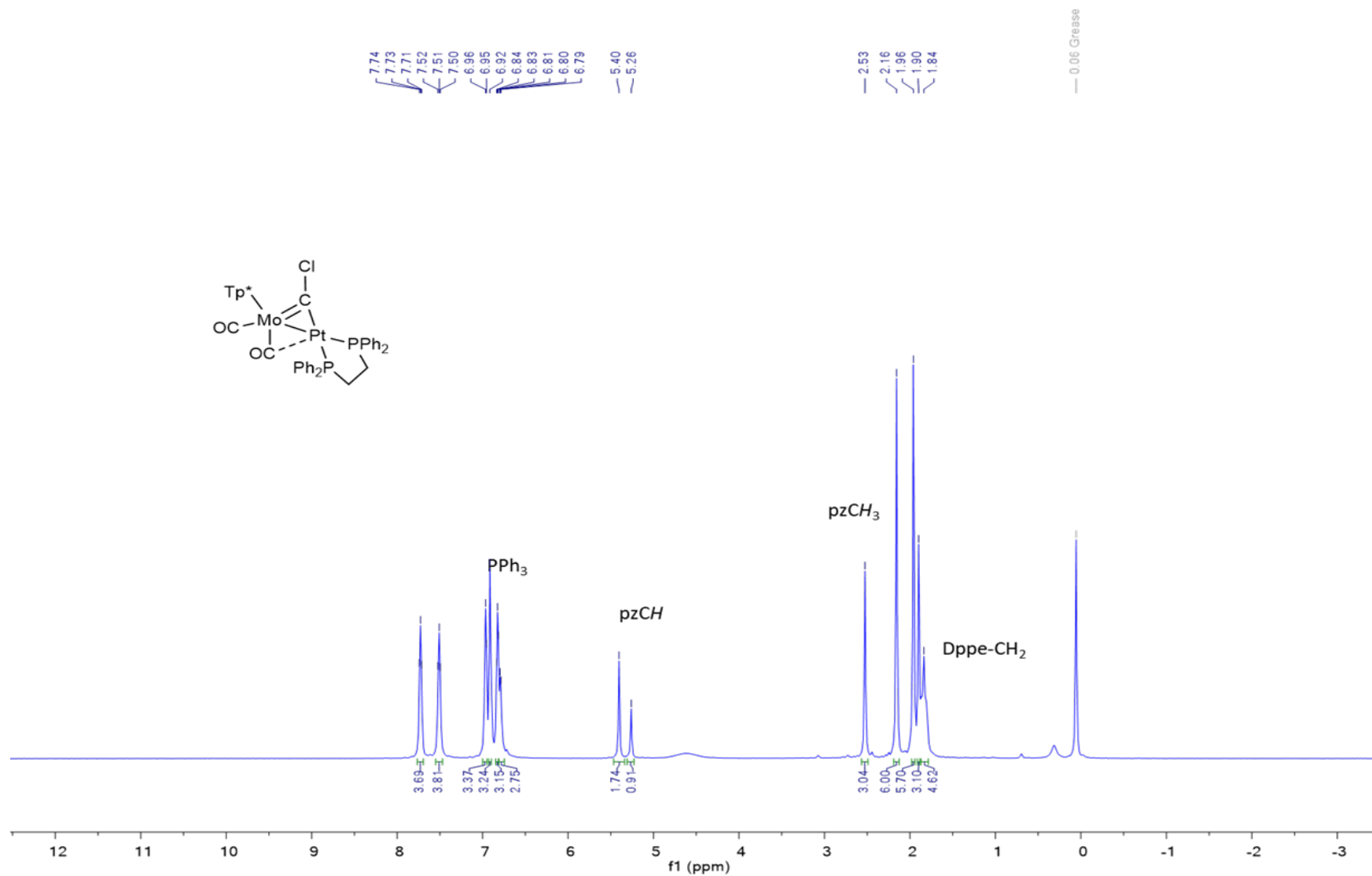
Figure S54. ^1H NMR Spectrum of $[\text{MoPt}(\mu_2\text{-CCl})(\mu\text{-CO})(\text{dppe})(\text{CO})(\text{Tp}^*)]$ (4) (400 MHz, CDCl_3 , 25 $^\circ\text{C}$, δ):

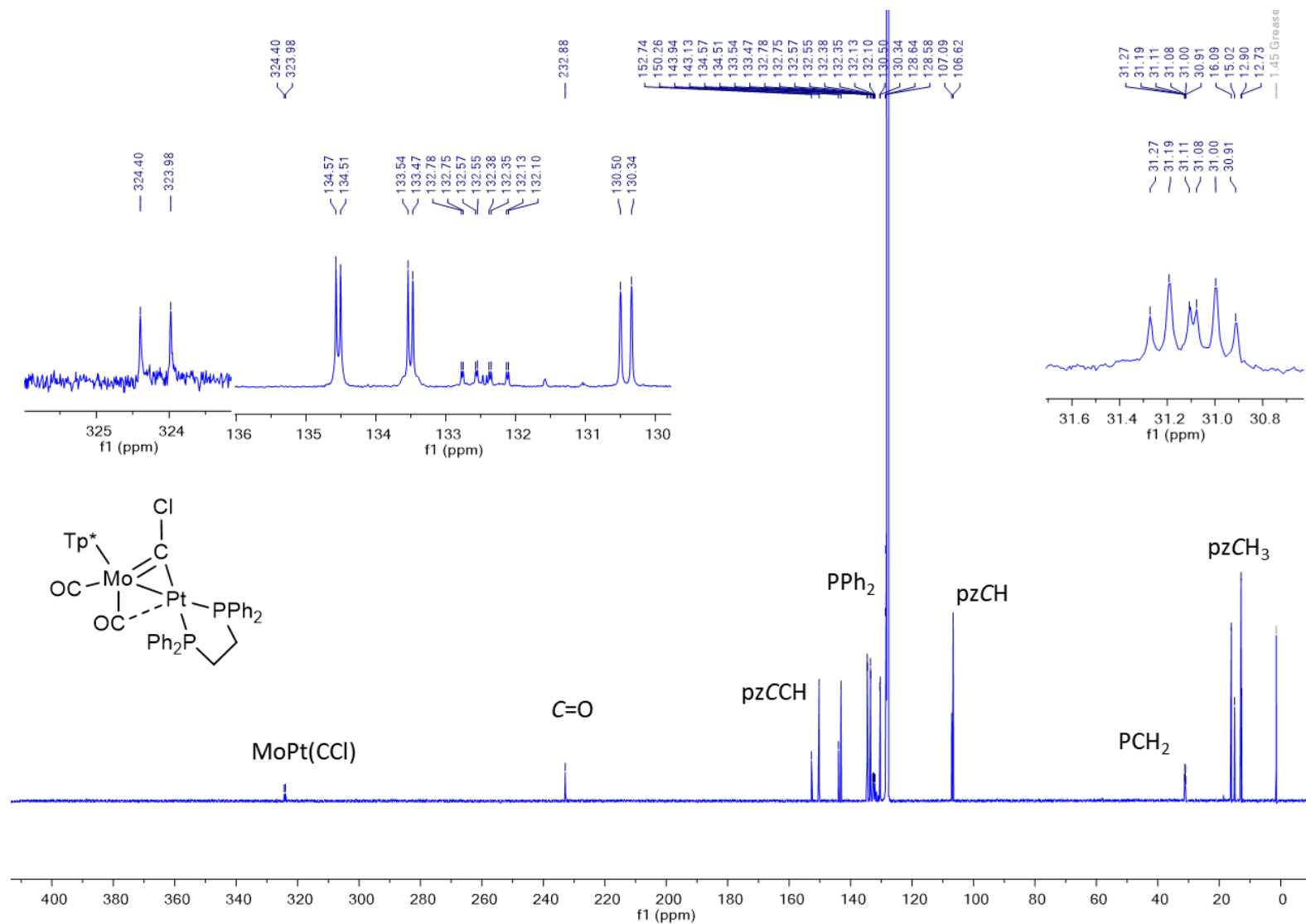
Figure S55. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of $[\text{MoPt}(\mu_2\text{-CCl})(\mu\text{-CO})(\text{dppe})(\text{CO})(\text{Tp}^*)]$ (4) (151 MHz, C_6D_6 , 25 °C, δ):

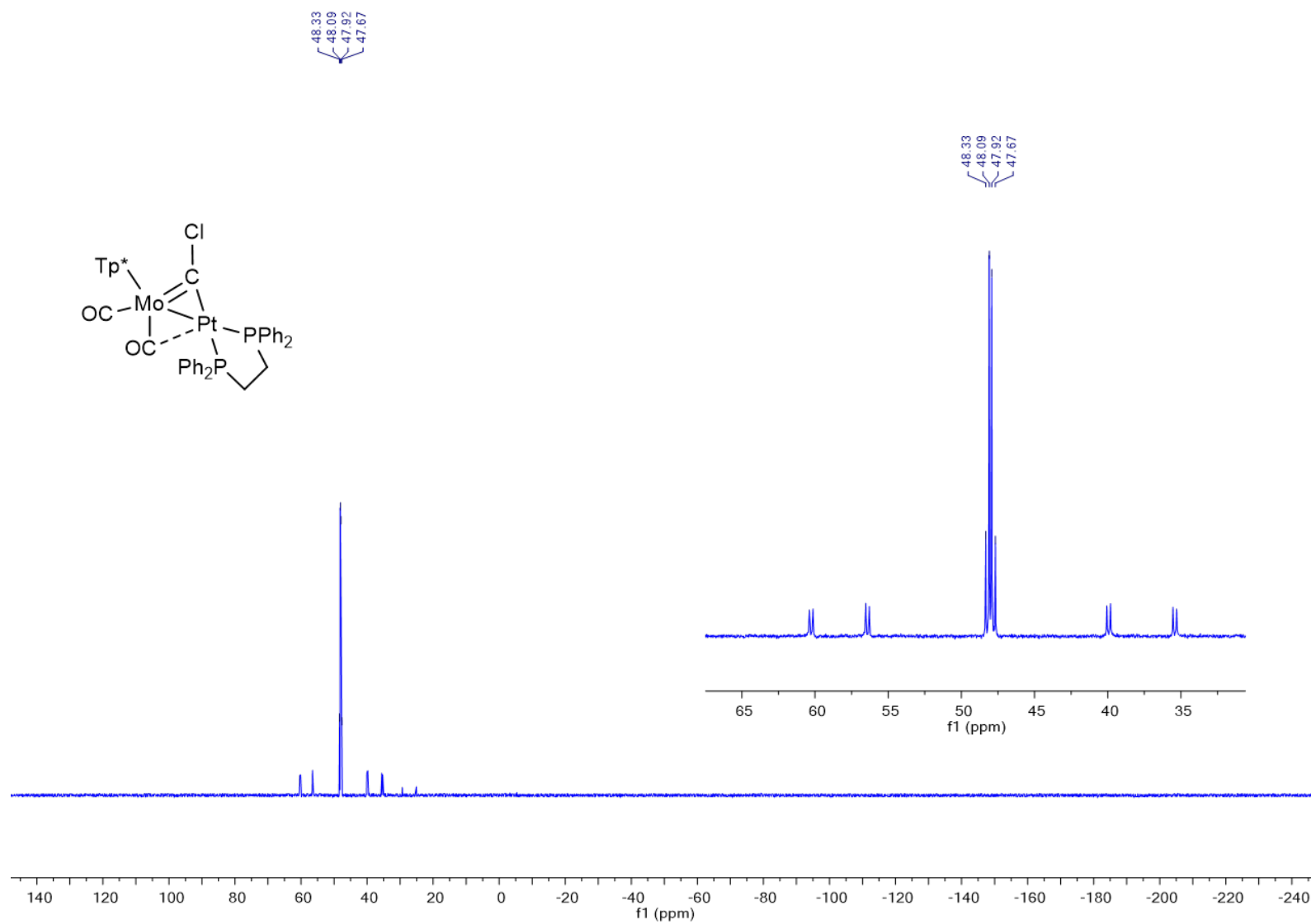
Figure S56. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of $[\text{MoPt}(\mu_2\text{-CCl})(\mu\text{-CO})(\text{dpppe})(\text{CO})(\text{Tp}^*)]$ (4) (162 MHz, C_6D_6 , 25 °C, δ):

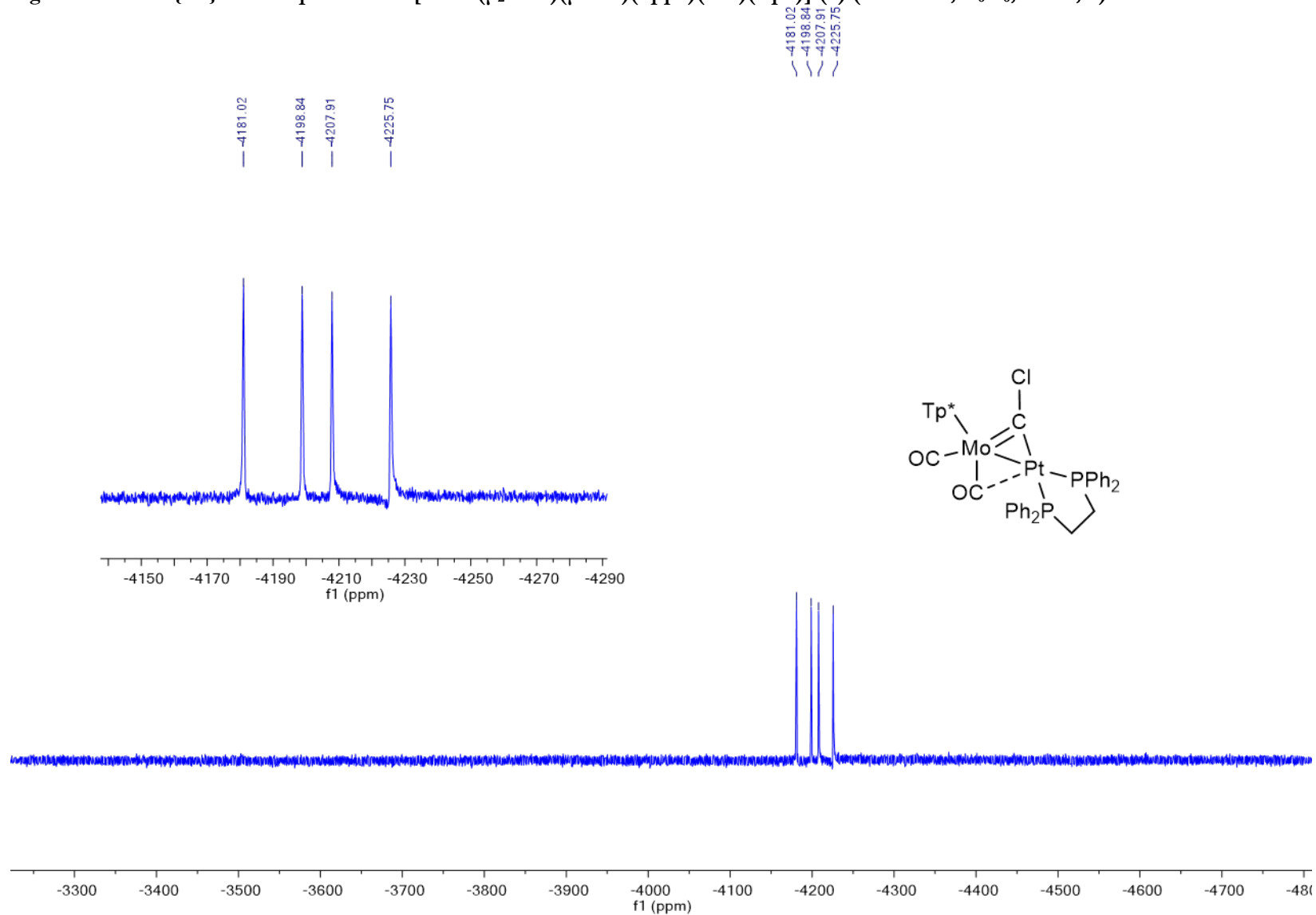
Figure S57. $^{195}\text{Pt}\{^1\text{H}\}$ NMR Spectrum of $[\text{MoPt}(\mu_2\text{-Cl})(\mu\text{-CO})(\text{dppe})(\text{CO})(\text{Tp}^*)]$ (4) (150 MHz, C_6D_6 , 25 °C, δ):

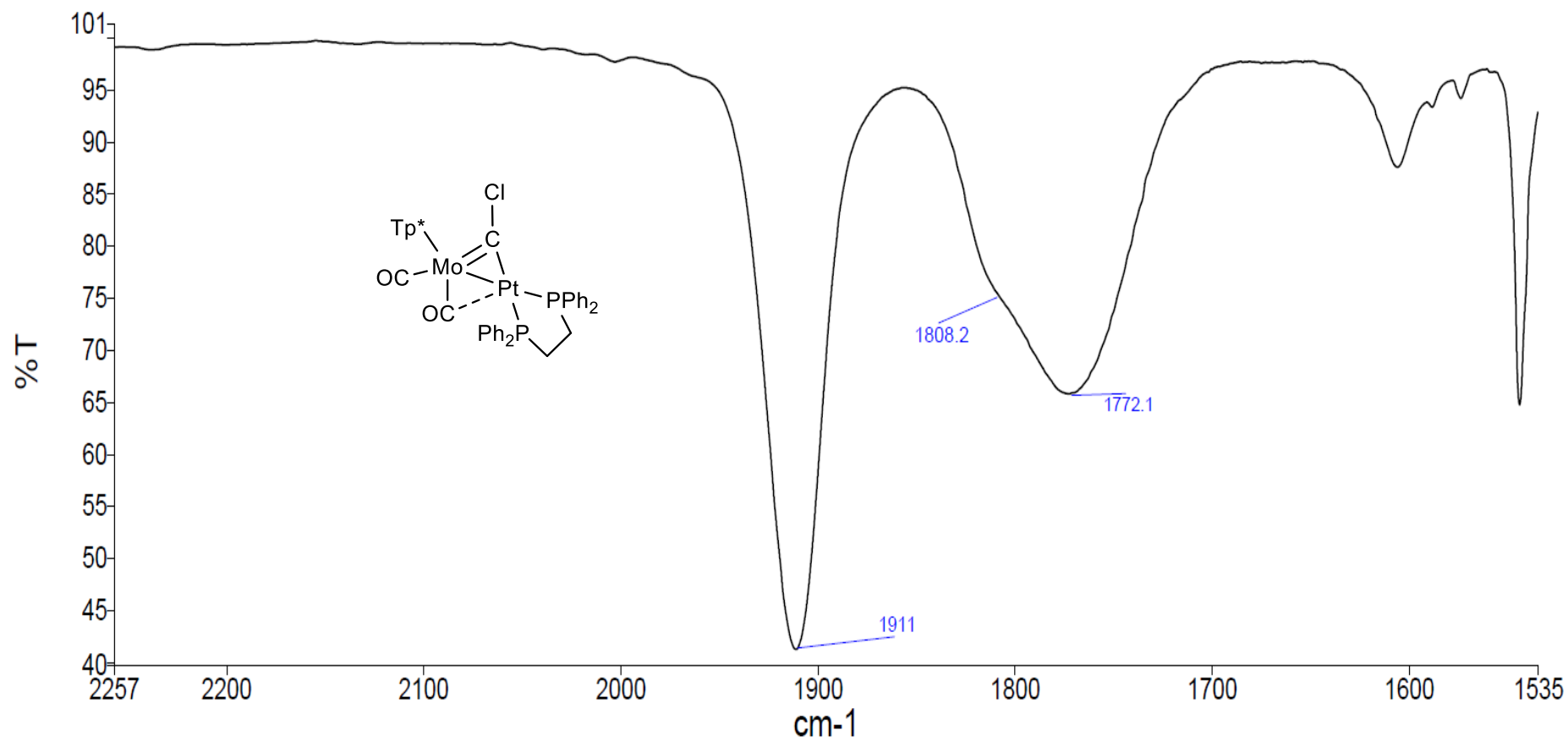
Figure S58. Infrared Spectrum of $[\text{MoPt}(\mu_2\text{-CCl})(\mu\text{-CO})(\text{dppe})(\text{CO})(\text{Tp}^*)]$ (4) (CH_2Cl_2 , 25 °C, ν):

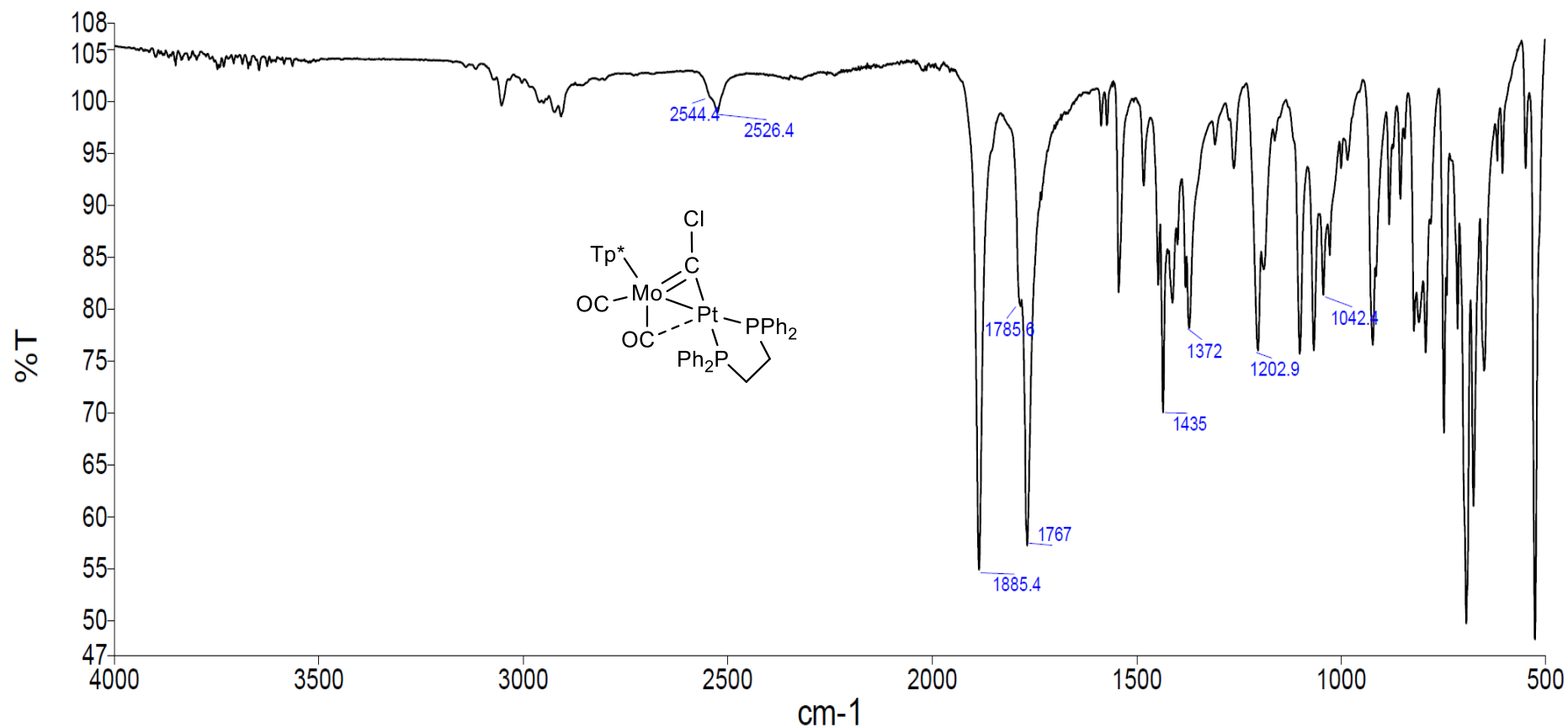
Figure S59. Infrared Spectrum of $[\text{MoPt}(\mu_2\text{-CCl})(\mu\text{-CO})(\text{dppe})(\text{CO})(\text{Tp}^*)]$ (4) (ATR, 25 °C, ν):

Figure S60. Mass Spectrum of $[\text{MoPt}(\mu_2\text{-CCl})(\mu\text{-CO})(\text{dppe})(\text{CO})(\text{Tp}^*)] (4)$:**Single Mass Analysis**

Tolerance = 3.0 PPM / DBE: min = -1.5, max = 26.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions

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

Elements Used:

C: 0-45 H: 0-50 11B: 0-1 N: 0-6 P: 0-2 35Cl: 0-1 37Cl: 0-1 98Mo: 0-1 195Pt: 0-1

LB-6-48/AJ

66727

0632.48 (0.113) Cm (48:55)

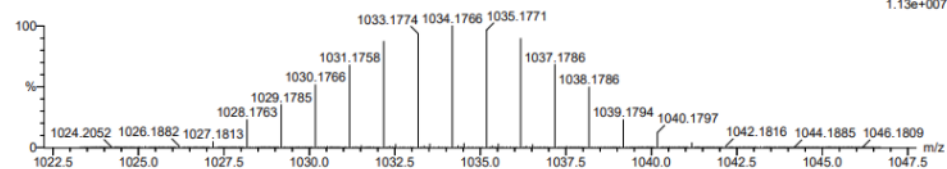
1: TOF MS ES+

SYNAPT G2-Si#NotSet

16-Jun-2021

12:45:21

1.13e+007



Minimum: -1.5
Maximum: 5.0 3.0 26.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
1035.1771	1035.1743	2.8	2.7	25.0	942.7	n/a	n/a	C42 H46 11B N6 P2 35Cl 98Mo 195Pt

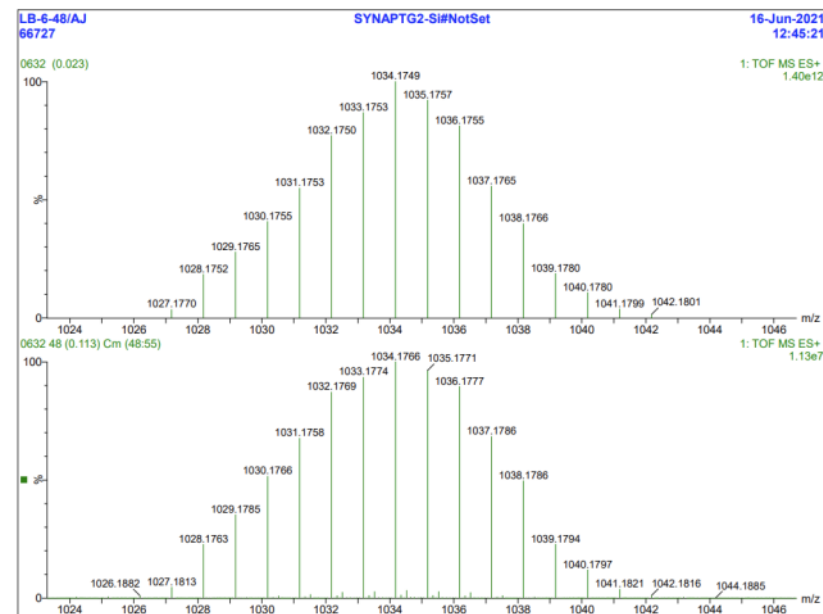


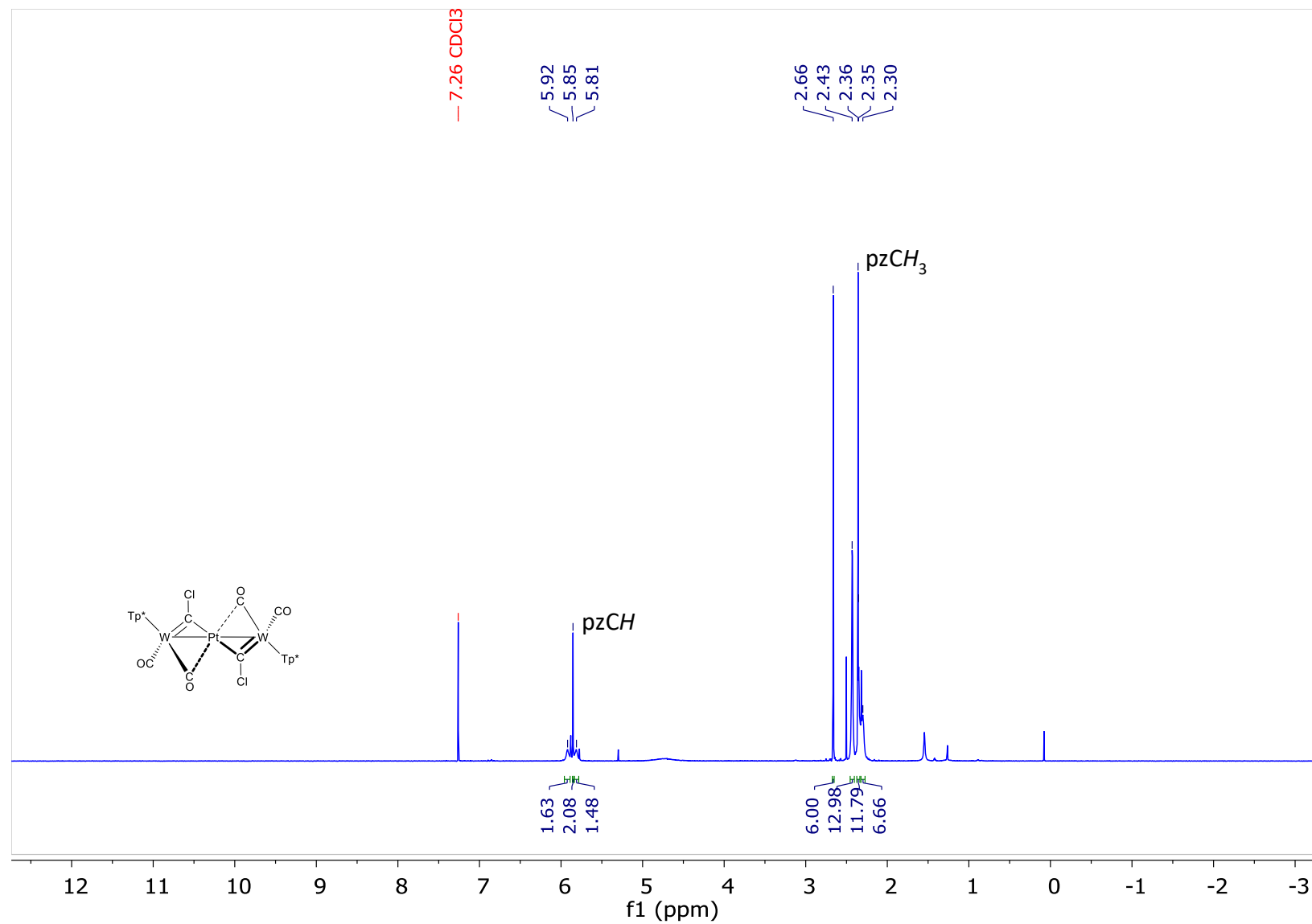
Figure S61. ^1H NMR Spectrum of $[\text{W}_2\text{Pt}(\mu_2\text{-CCl})_2(\mu_2\text{-CO})_2(\text{CO})_2(\text{Tp}^*)_2]$ (5) (700 MHz, CDCl_3 , 25 °C, δ):

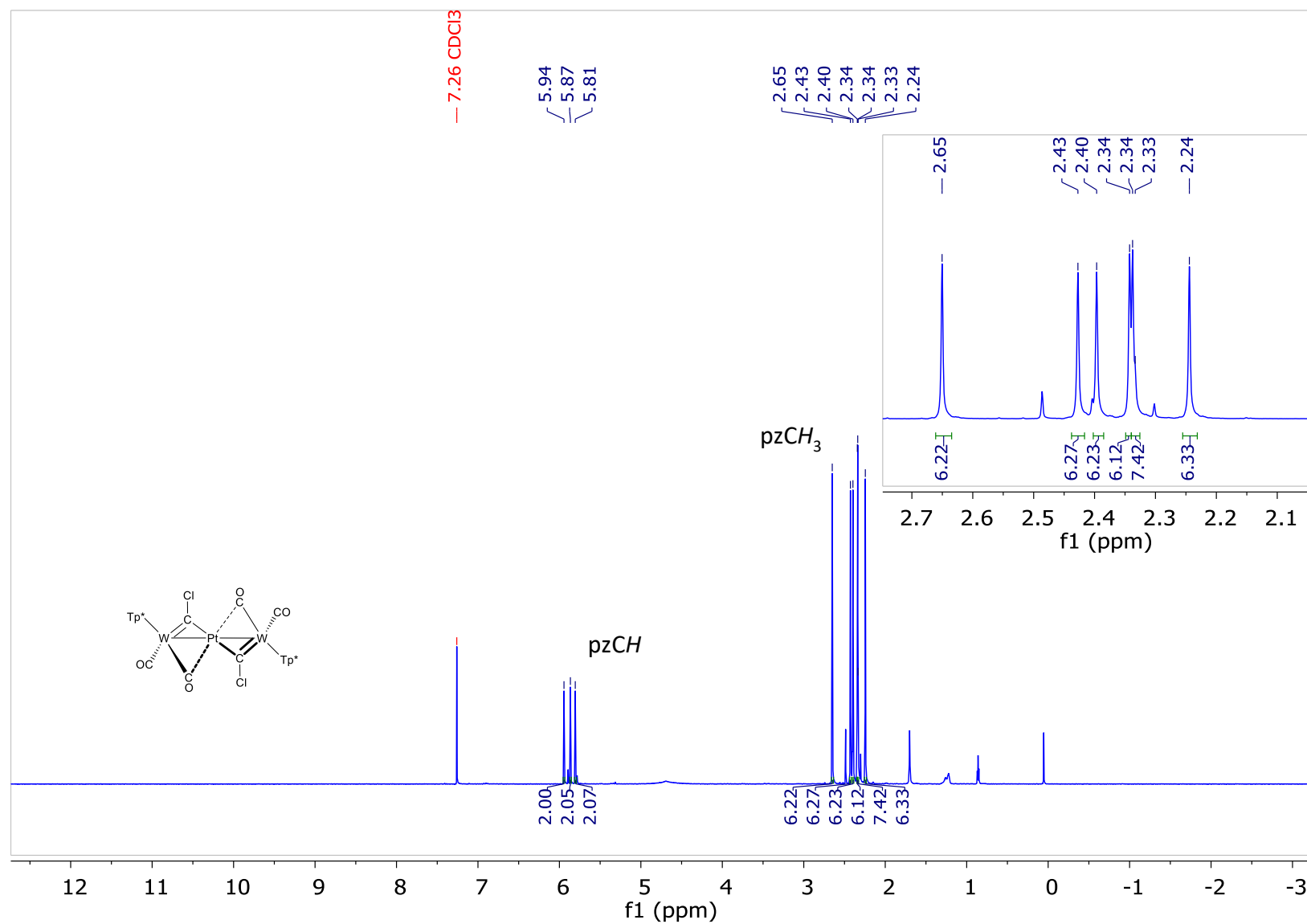
Figure S62. ^1H NMR Spectrum of $[\text{W}_2\text{Pt}(\mu_2\text{-CCl})_2(\mu_2\text{-CO})_2(\text{CO})_2(\text{Tp}^*)_2]$ (5) (700 MHz, CDCl_3 , -40°C , δ):

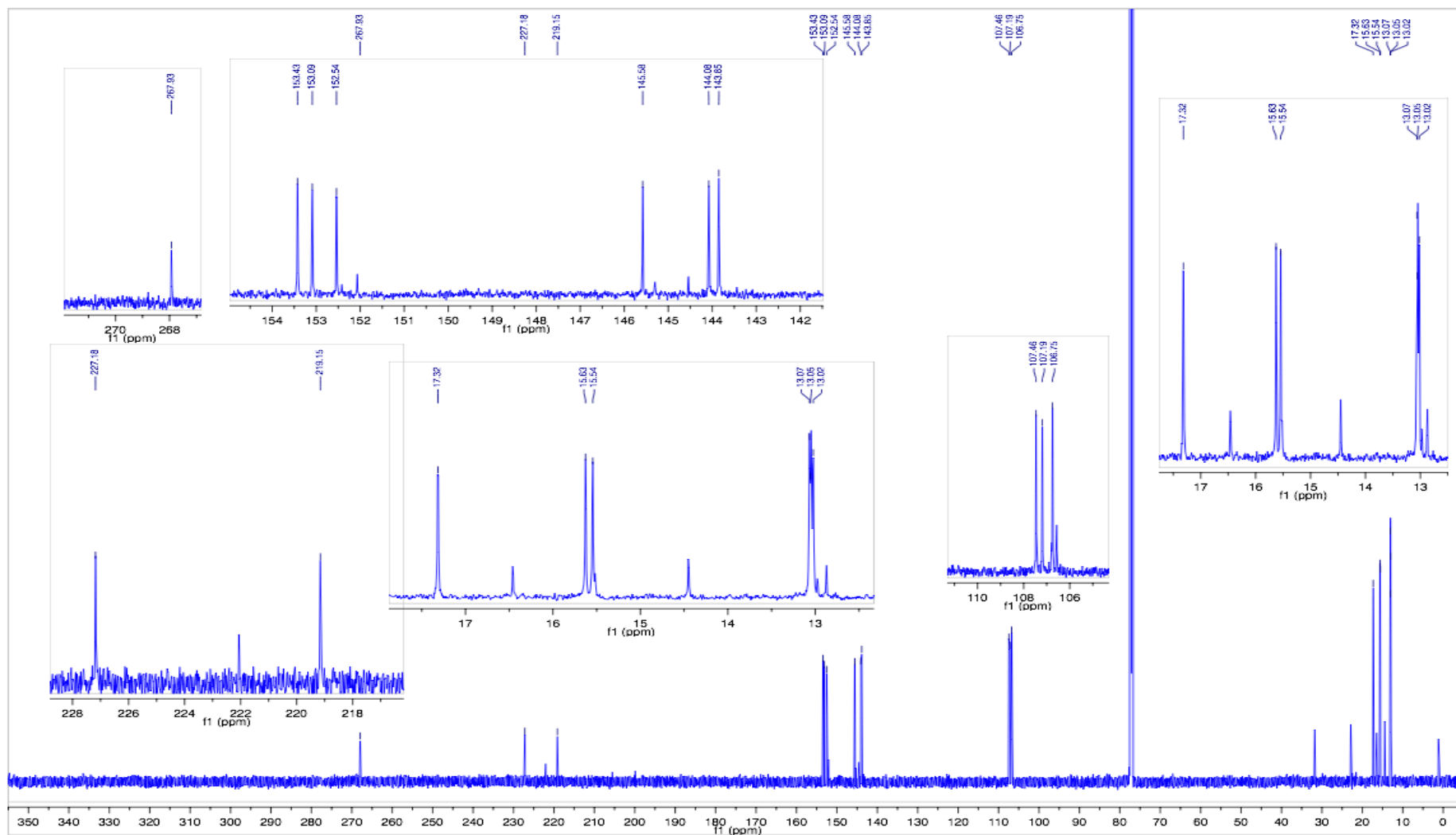
Figure S63. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of $[\text{W}_2\text{Pt}(\mu_2\text{-CCl})_2(\mu_2\text{-CO})_2(\text{CO})_2(\text{Tp}^*)_2]$ (5) (162 MHz, CDCl_3 , -40°C , δ):

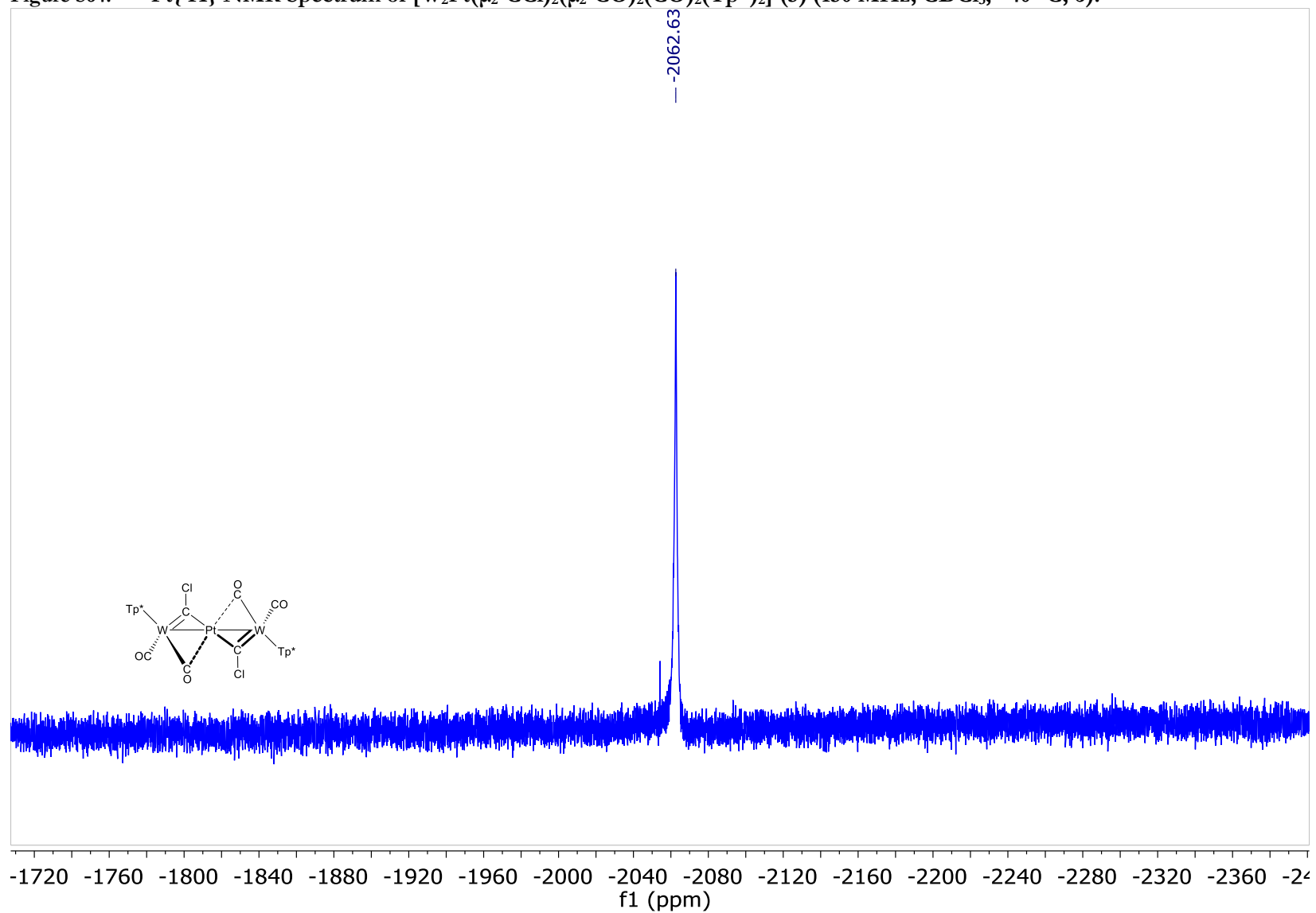
Figure S64. $^{195}\text{Pt}\{^1\text{H}\}$ NMR Spectrum of $[\text{W}_2\text{Pt}(\mu_2\text{-CCl})_2(\mu_2\text{-CO})_2(\text{CO})_2(\text{Tp}^*)_2]$ (5) (150 MHz, CDCl_3 , -40°C , δ):

Figure S65. Infrared Spectrum of $[\text{W}_2\text{Pt}(\mu_2\text{-CCl})_2(\mu_2\text{-CO})_2(\text{CO})_2(\text{Tp}^*)_2]$ (5) (CH_2Cl_2 , 25 °C, ν):

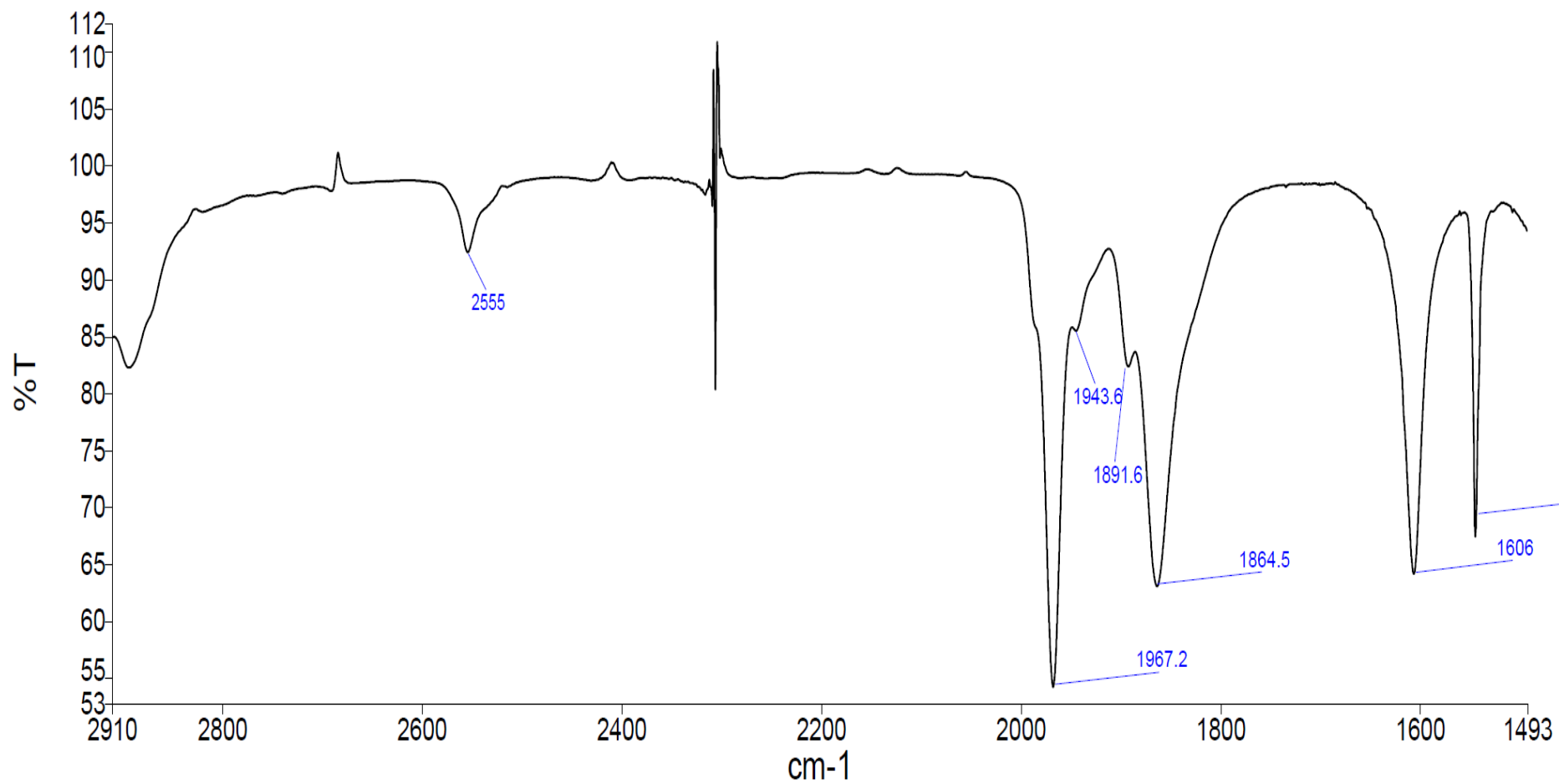


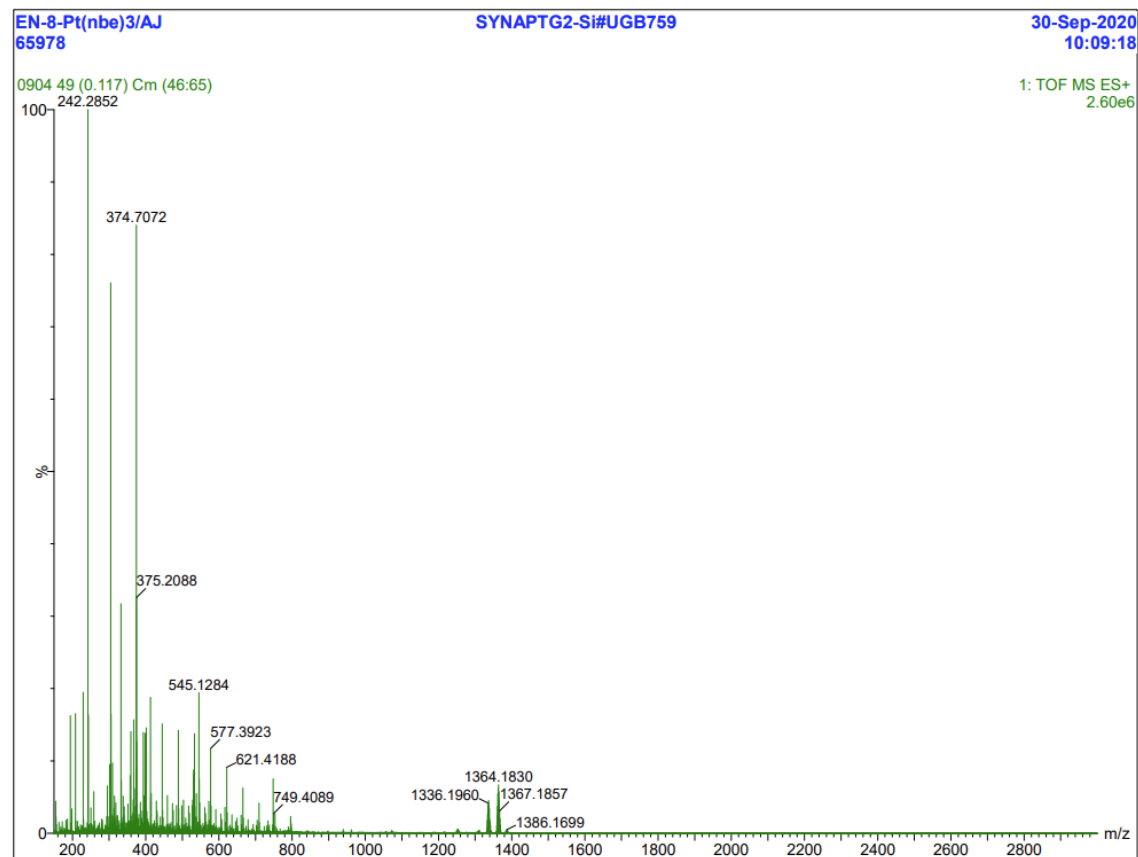
Figure S66. Mass Spectrum of $[\text{W}_2\text{Pt}(\mu_2\text{-CCl})_2(\mu_2\text{-CO})_2(\text{CO})_2(\text{Tp}^*)_2]$ (5) (ESI):

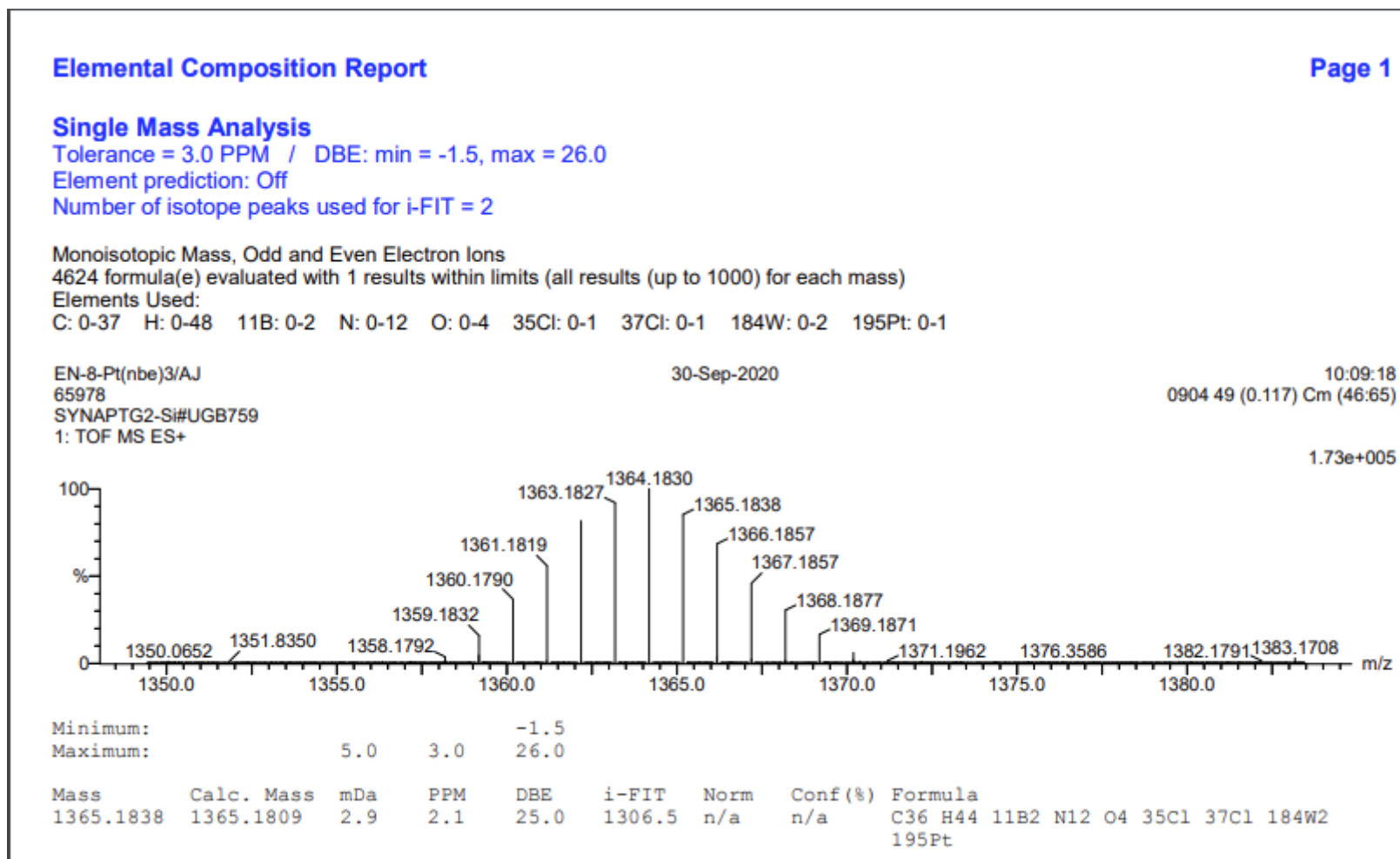
Figure S67. Mass Spectrum of $[\text{W}_2\text{Pt}(\mu_2\text{-CCl})_2(\mu_2\text{-CO})_2(\text{CO})_2(\text{Tp}^*)_2](5)$ (ESI):

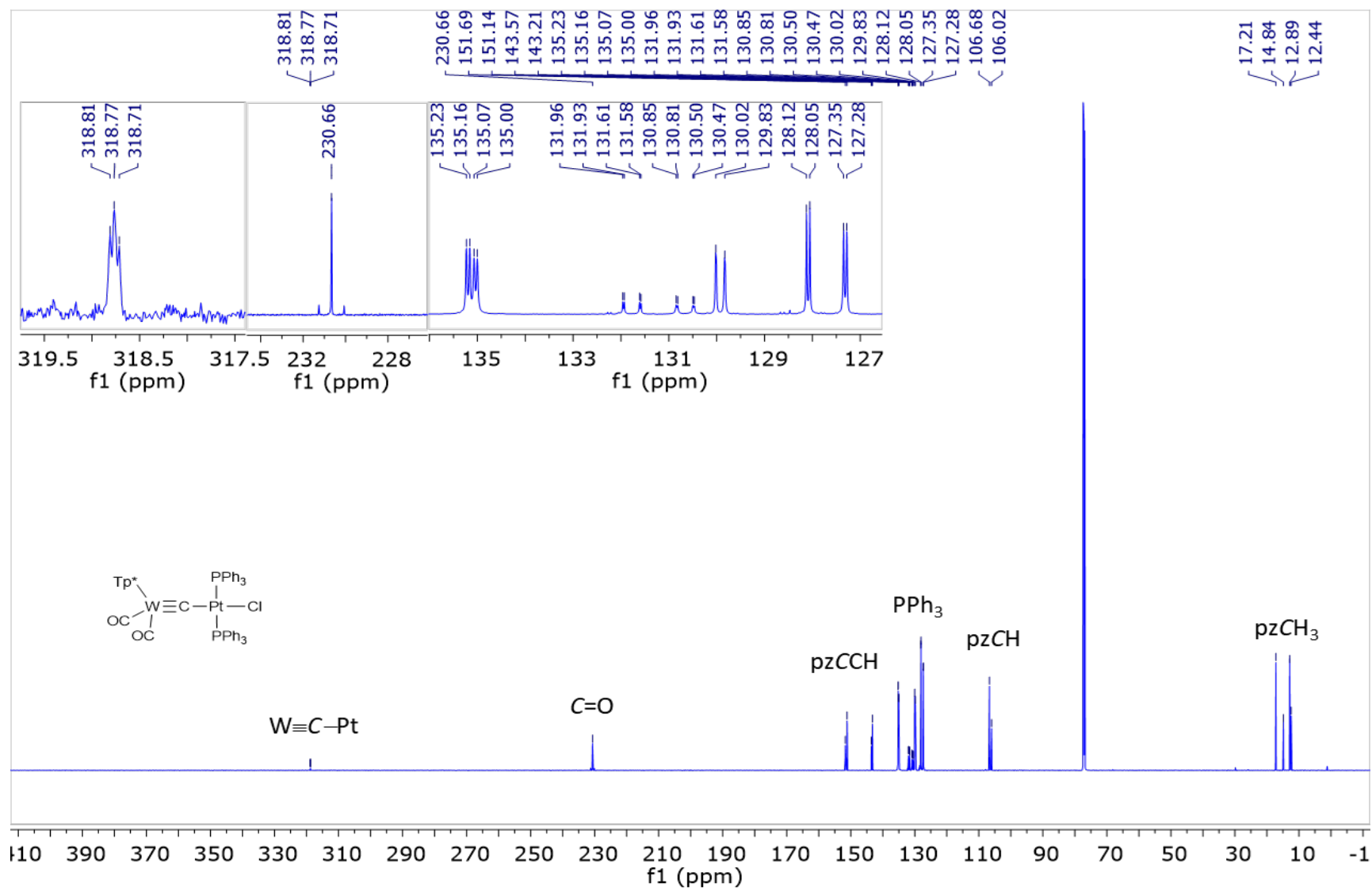
Figure S69. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of $[(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}-\text{PtCl}(\text{PPh}_3)_2]$ (6) (151 MHz, CDCl_3 , 25 °C, δ):

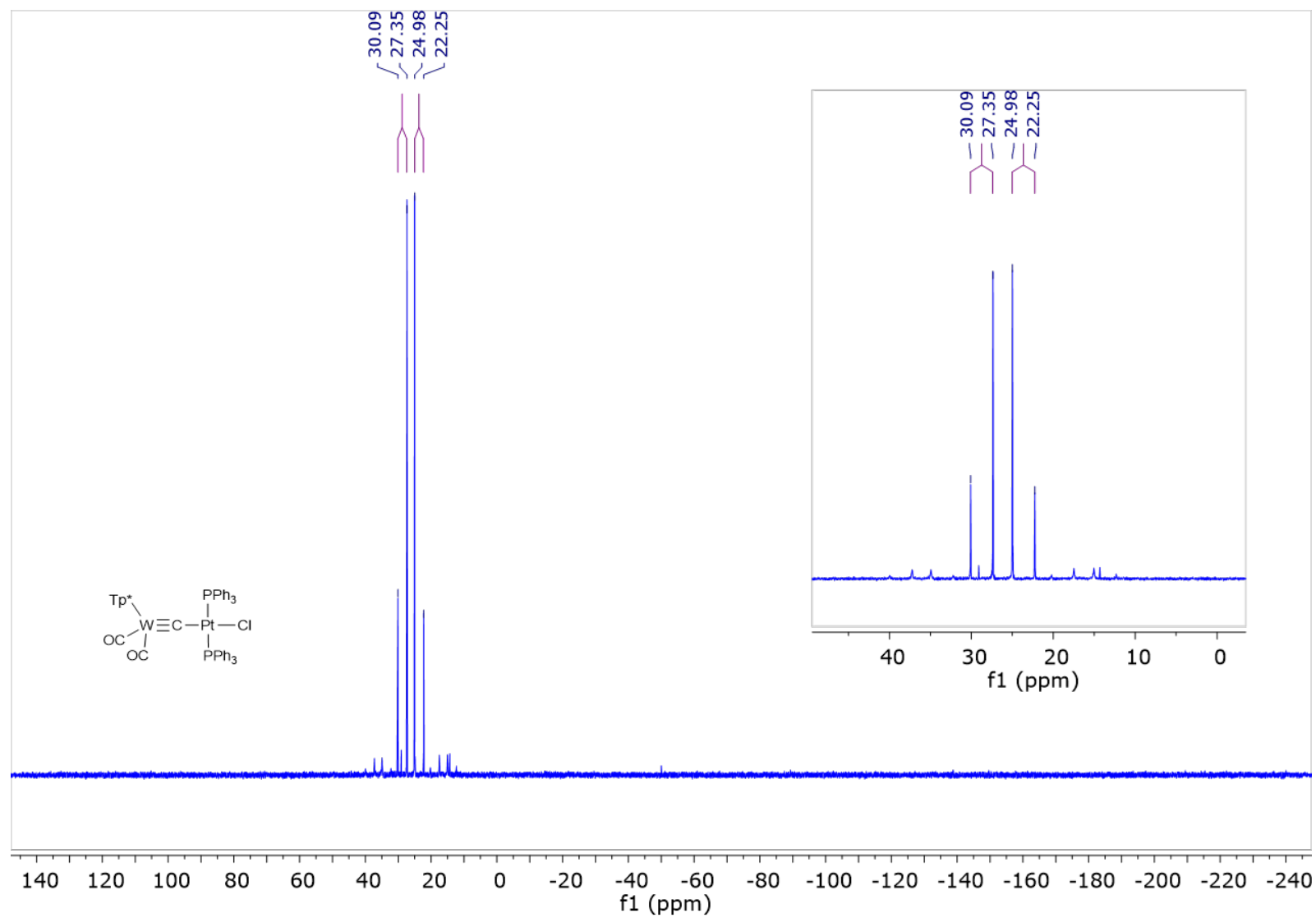
Figure S70. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of $[(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}-\text{PtCl}(\text{PPh}_3)_2]$ (**6**) (162 MHz, CDCl_3 , 25 °C, δ):

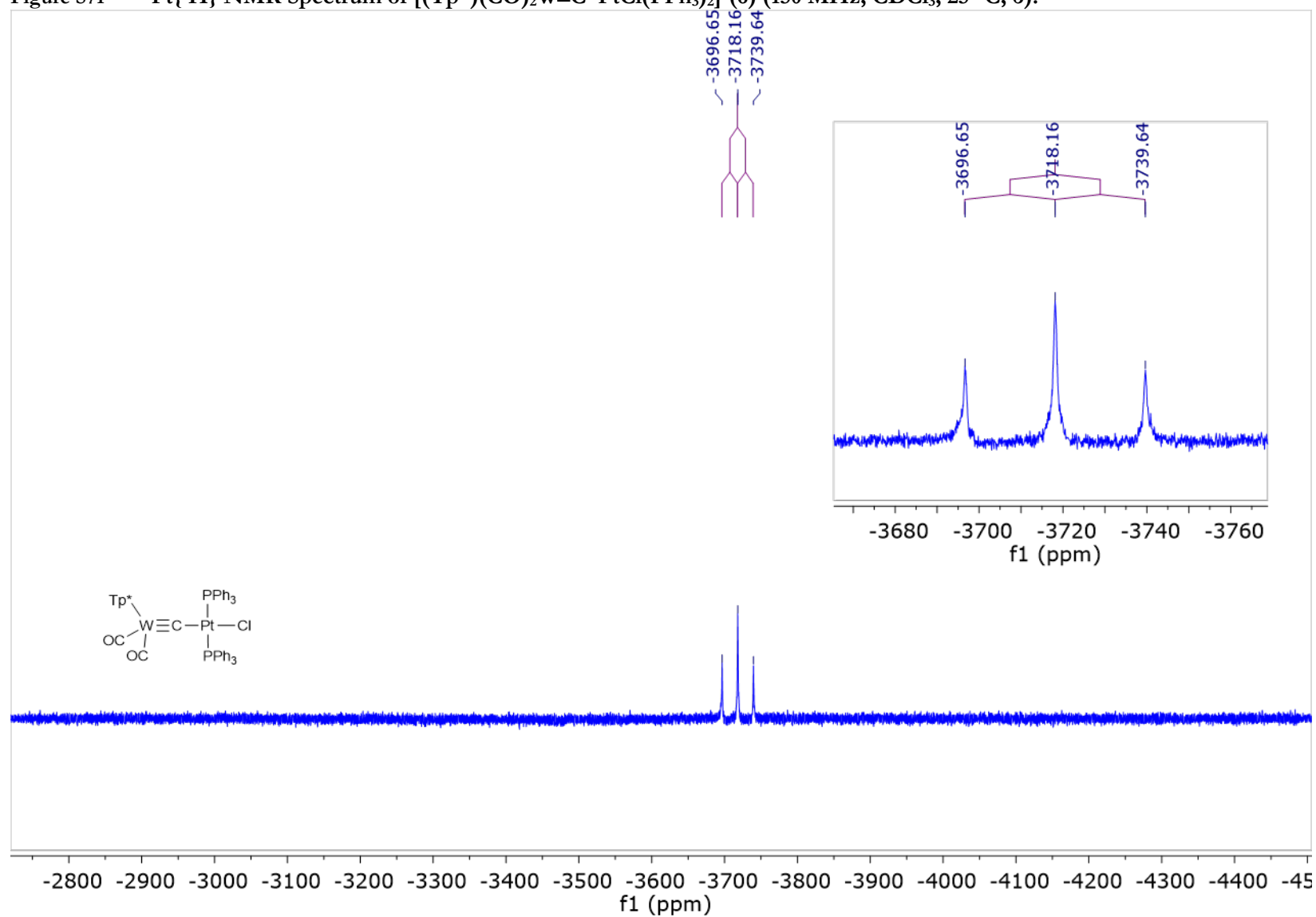
Figure S71 $^{195}\text{Pt}\{^1\text{H}\}$ NMR Spectrum of $[(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}-\text{PtCl}(\text{PPh}_3)_2]$ (**6**) (150 MHz, CDCl_3 , 25 °C, δ):

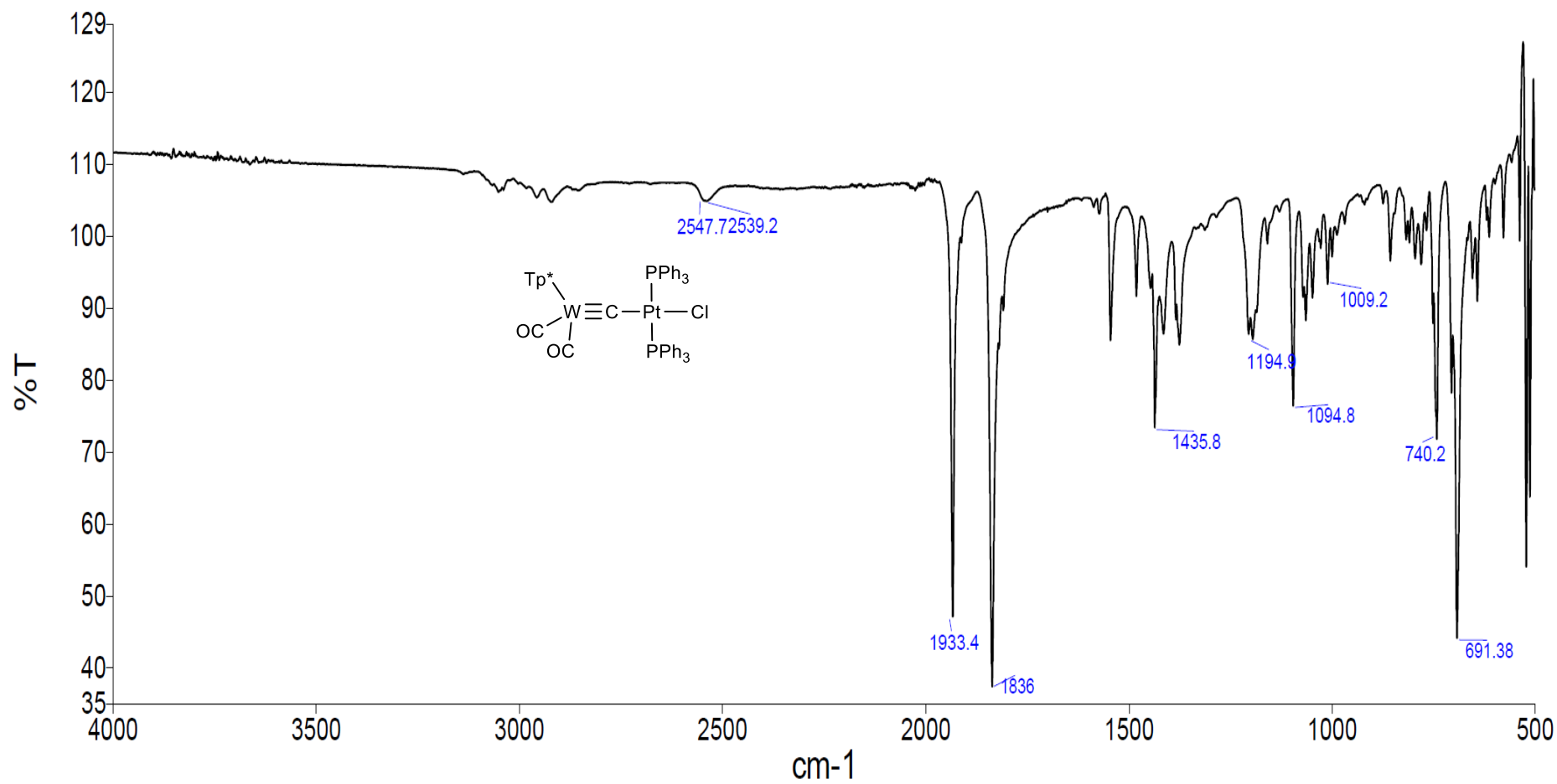
Figure S73. Infrared Spectrum of $[(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}-\text{PtCl}(\text{PPh}_3)_2]$ (6) (ATR, 25 °C, ν):

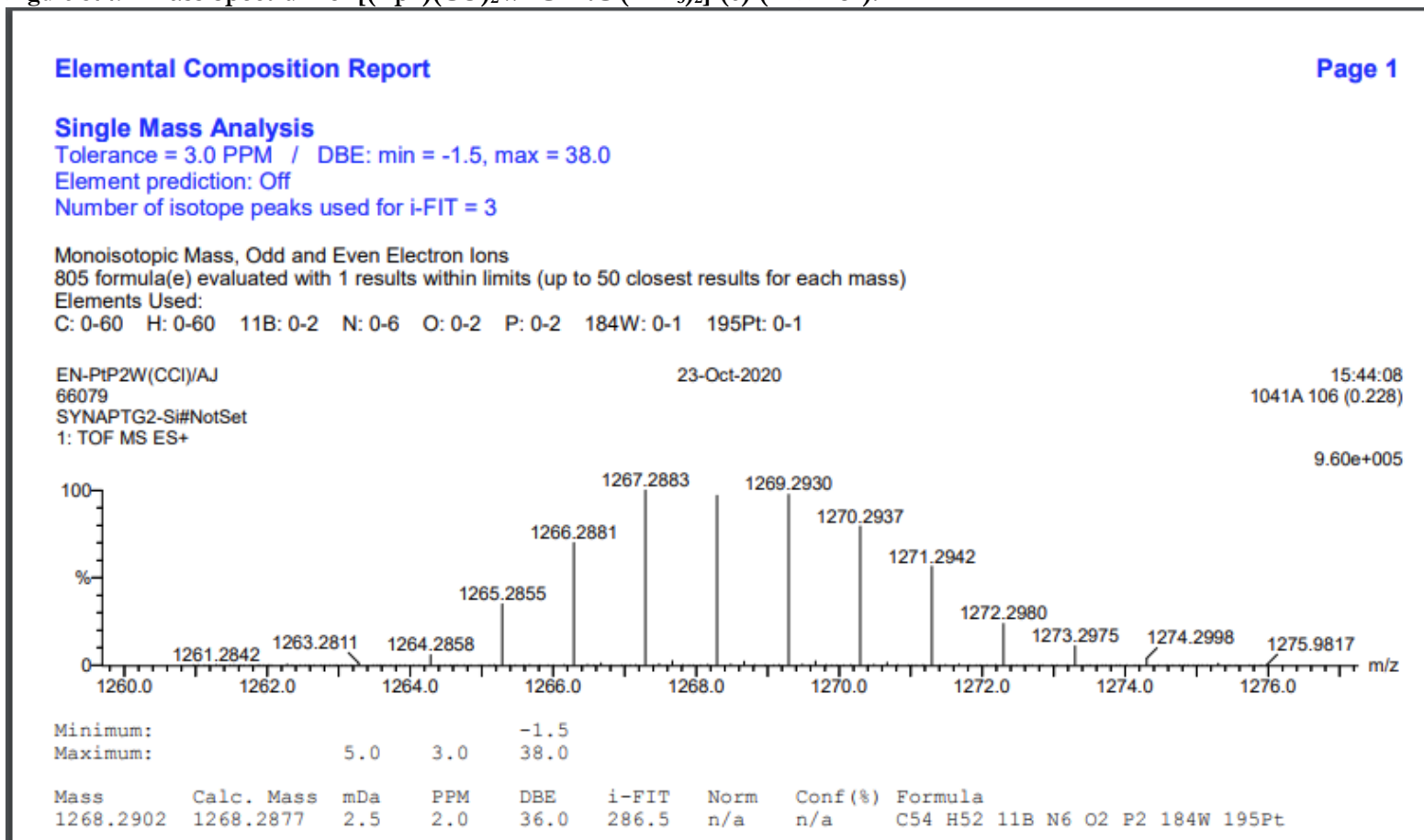
Figure S74. Mass Spectrum of [(Tp*)(CO)₂W≡C–PtCl(PPh₃)₂] (6) (HR-ESI):

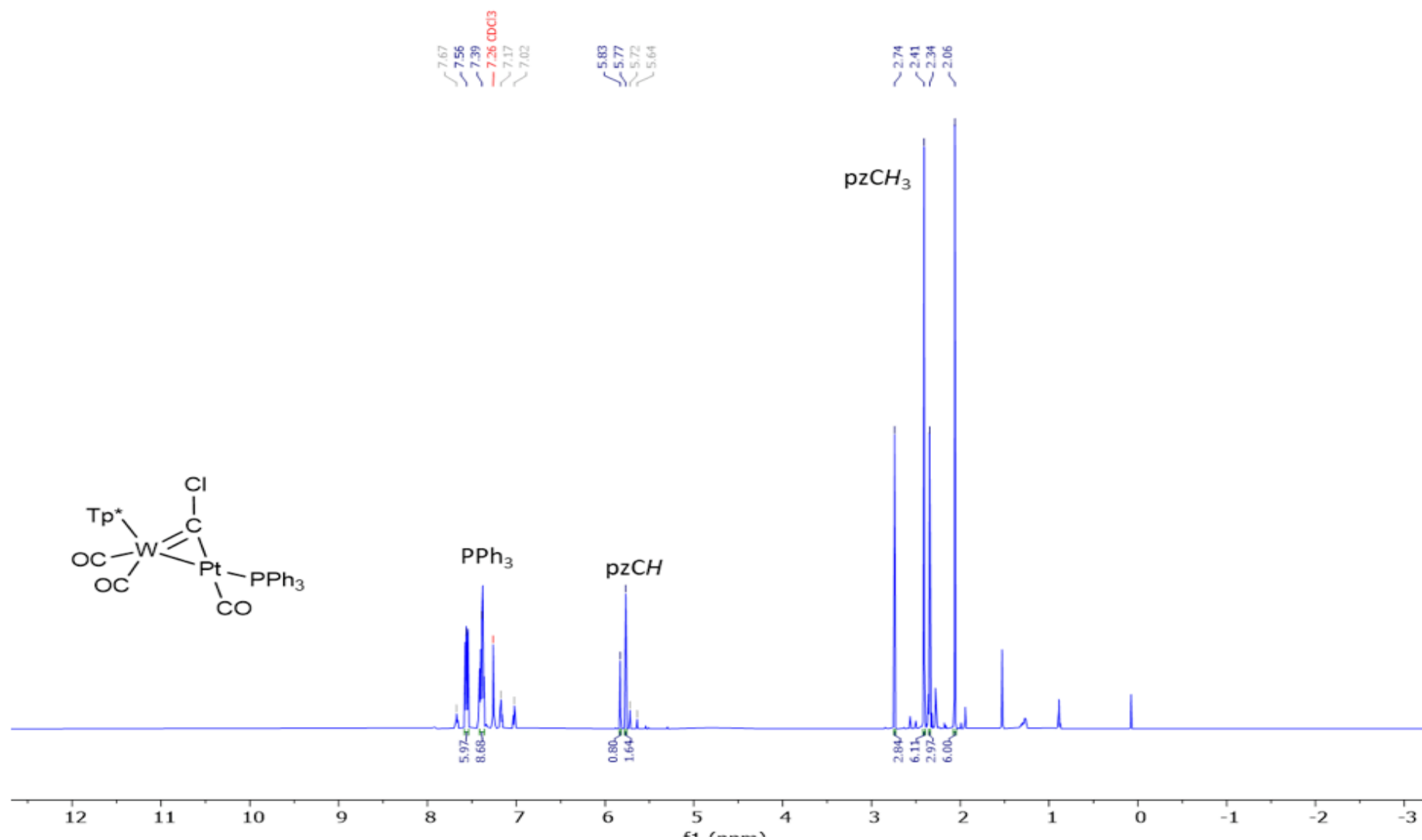
Figure S75. ^1H NMR Spectrum of $[\text{WPt}(\mu\text{-CCl})(\text{CO})_3(\text{PPh}_3)(\text{Tp}^*)]$ (7) (600 MHz, CDCl_3 , 25 $^\circ\text{C}$, δ):

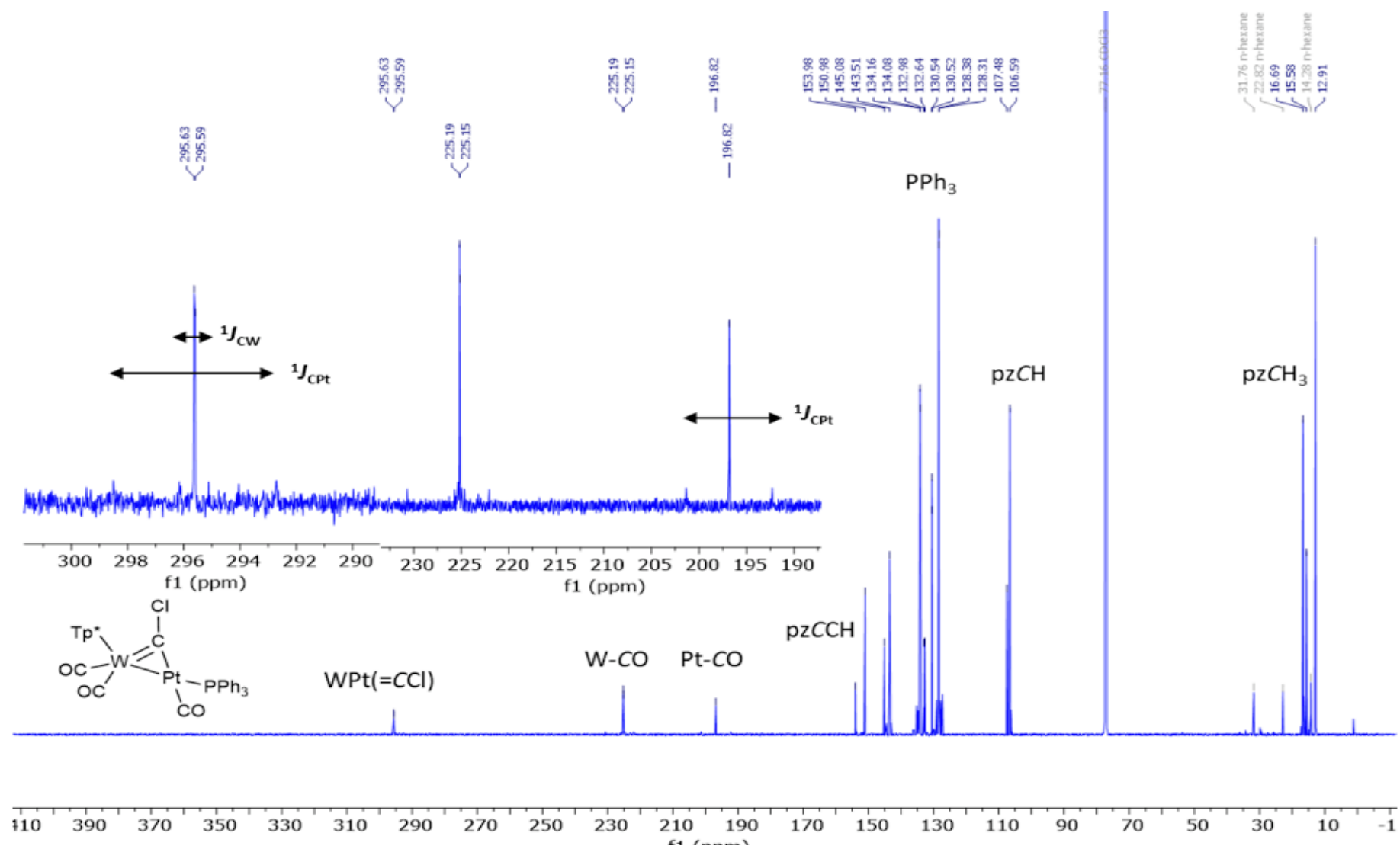
Figure S76. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of $[\text{WPt}(\mu\text{-CCl})(\text{CO})_3(\text{PPh}_3)(\text{Tp}^*)]$ (7) (151 MHz, CDCl_3 , 25 °C, δ):

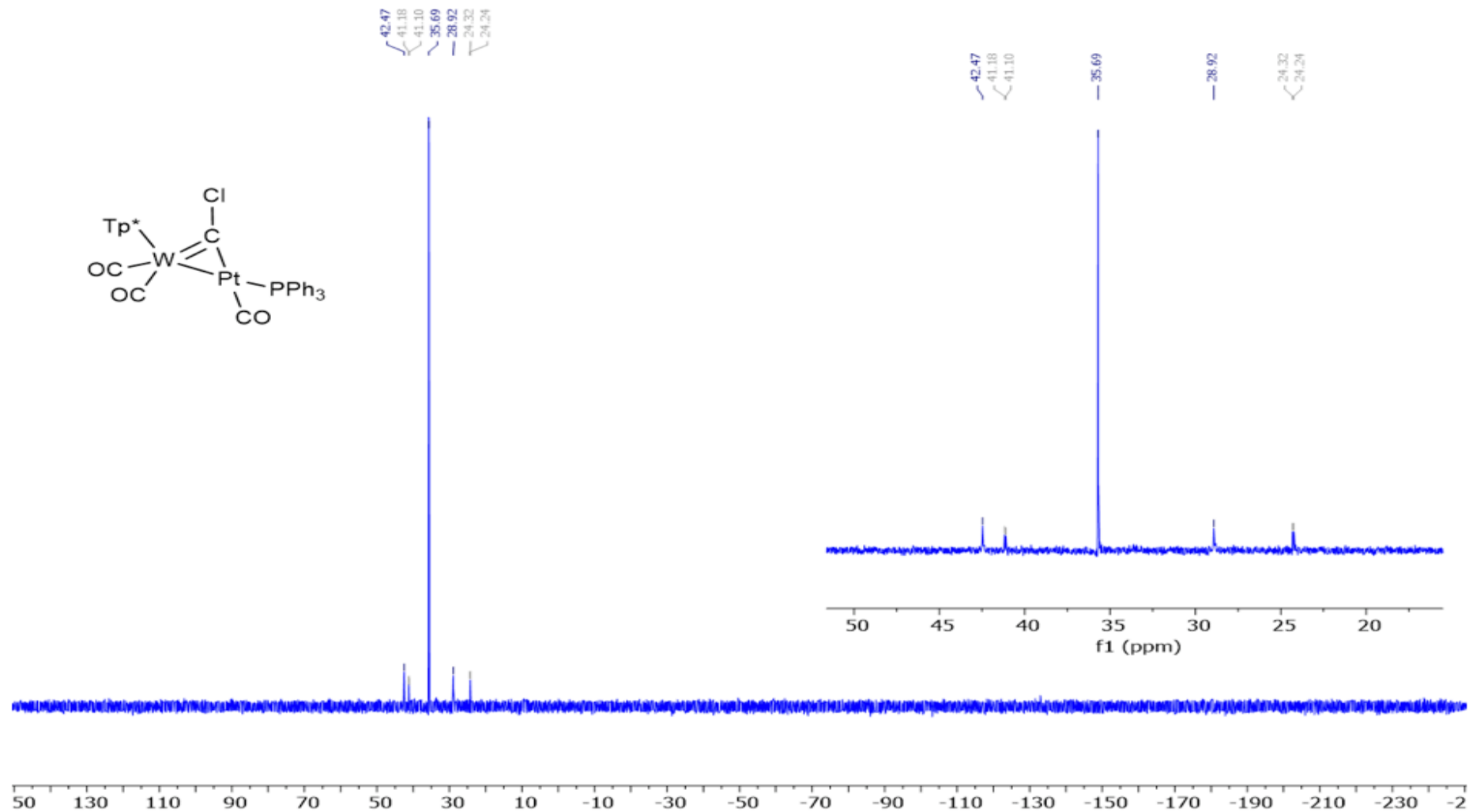
Figure S77. $^3\text{P}\{^1\text{H}\}$ NMR Spectrum of $[\text{WPt}(\mu\text{-CCl})(\text{CO})_3(\text{PPh}_3)(\text{Tp}^*)]$ (7) (283 MHz, CDCl_3 , 25 °C, δ):

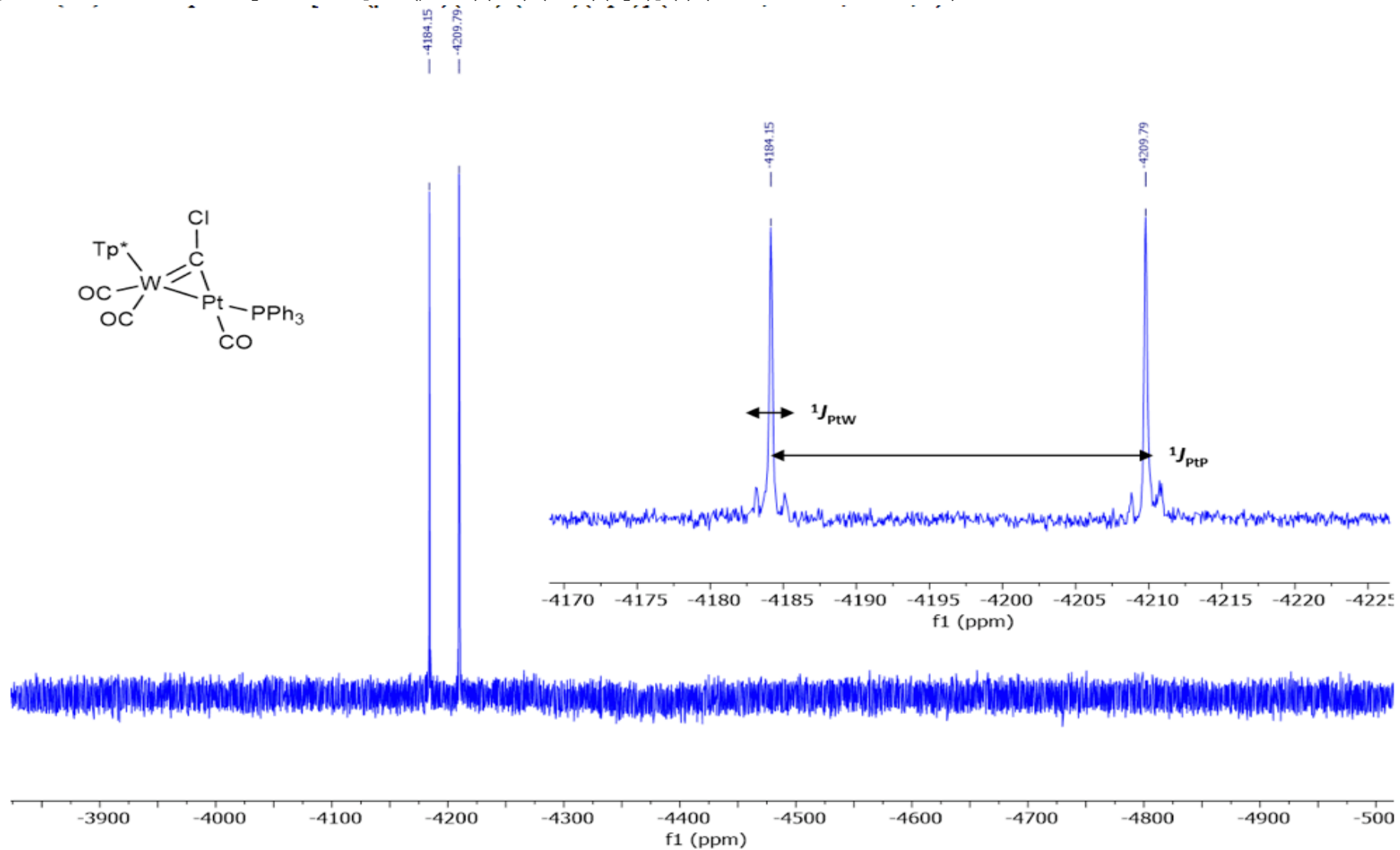
Figure S78. $^{195}\text{Pt}\{^1\text{H}\}$ NMR Spectrum of $[\text{WPt}(\mu\text{-Cl})(\text{CO})_3(\text{PPh}_3)(\text{Tp}^*)]$ (7) (150 MHz, CDCl_3 , 25 °C, δ):

Figure S79. Mass Spectrum of $[\text{WPt}(\mu\text{-CCl})(\text{CO})_3(\text{PPh}_3)(\text{Tp}^*)] (7)$ (ESI):**Single Mass Analysis**

Tolerance = 3.0 PPM / DBE: min = -1.5, max = 25.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

1308 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-40 H: 0-40 11B: 0-1 N: 0-6 O: 0-2 P: 0-1 35Cl: 0-1 37Cl: 0-1 184W: 0-1 195Pt: 0-1

LB-8-18/AJ

87018

2389 193 (0.399)

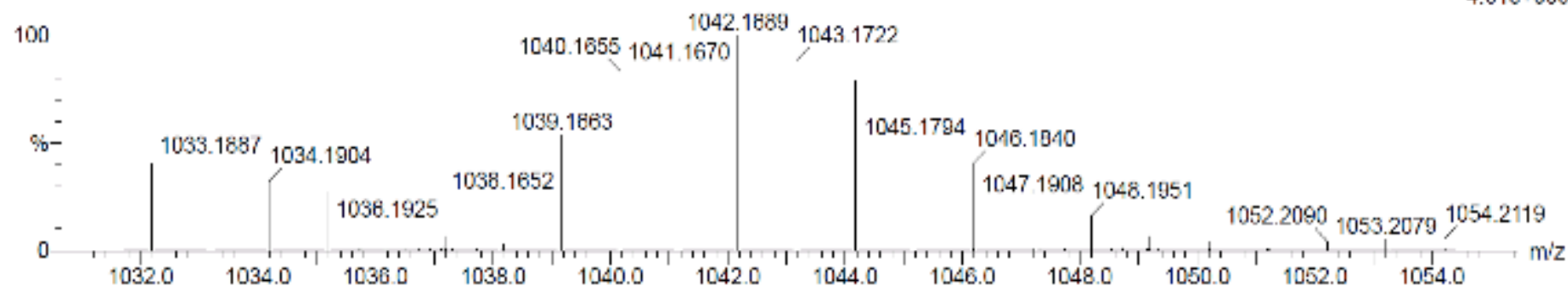
1: TOF MS ES+

SYNAPT-G2-Si#NotSet

09-May-2022

14.09.12

4.81e+006



Minimum: -1.5
 Maximum: 25.0 3.0 25.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
1041.1670	1041.1654	1.6	1.5	24.5	2269.4	C36 H37 11B N6 O2 P 35Cl 184W 195Pt

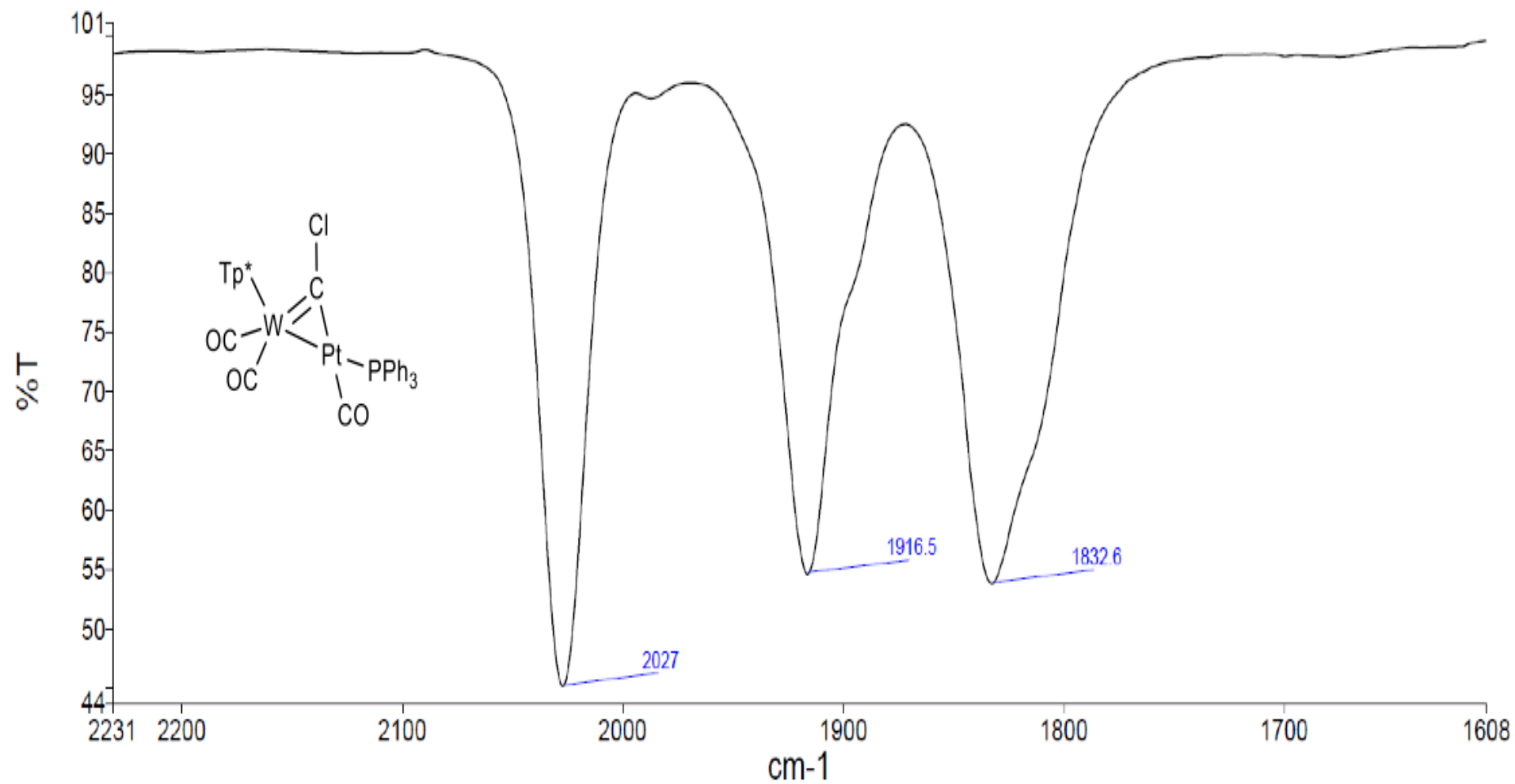
Figure S80. Infrared Spectrum of $[\text{WPt}(\mu\text{-Cl})(\text{CO})_3(\text{PPh}_3)(\text{Tp}^*)]$ (7) (CH_2Cl_2 , 25 °C, ν):

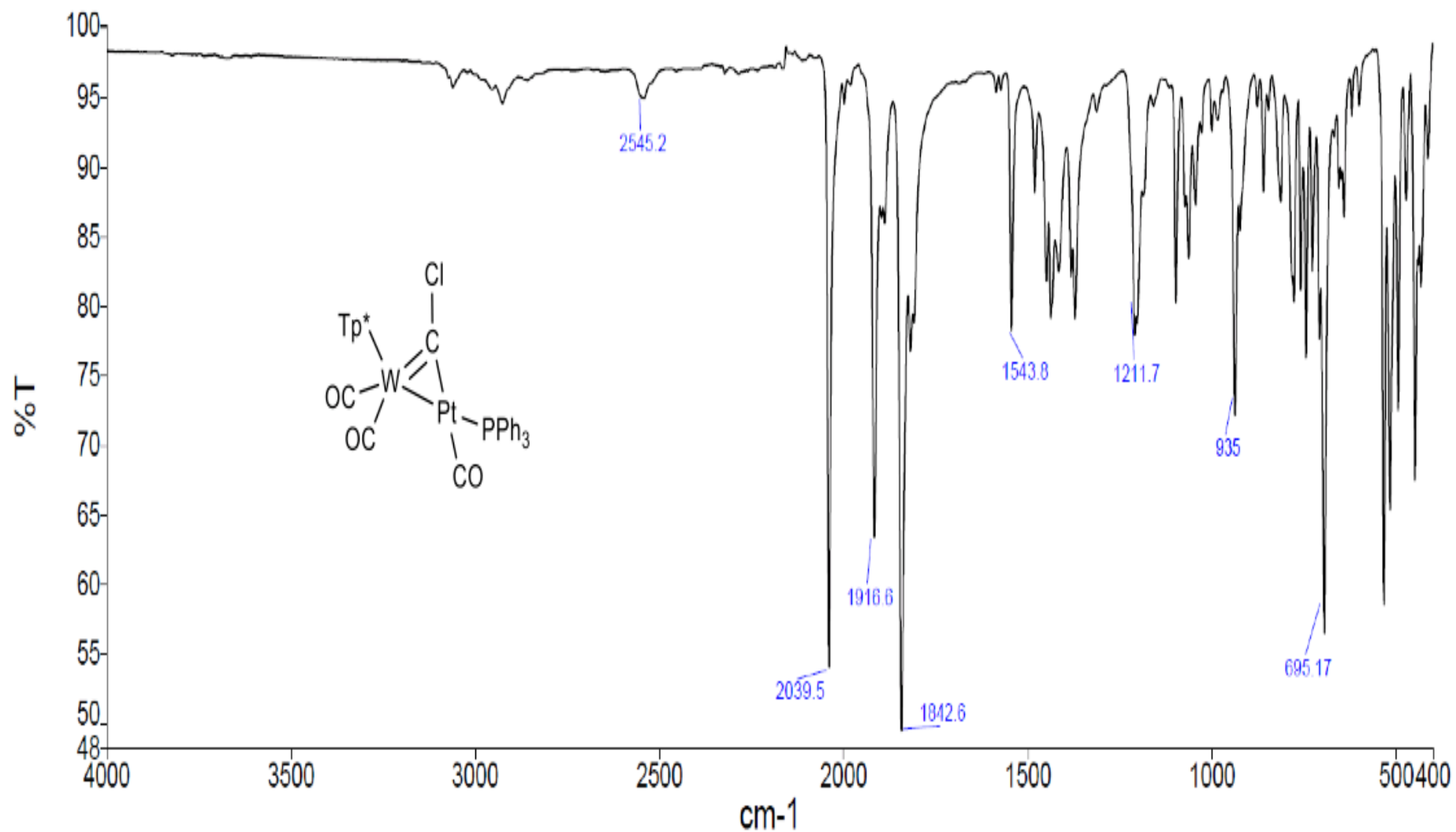
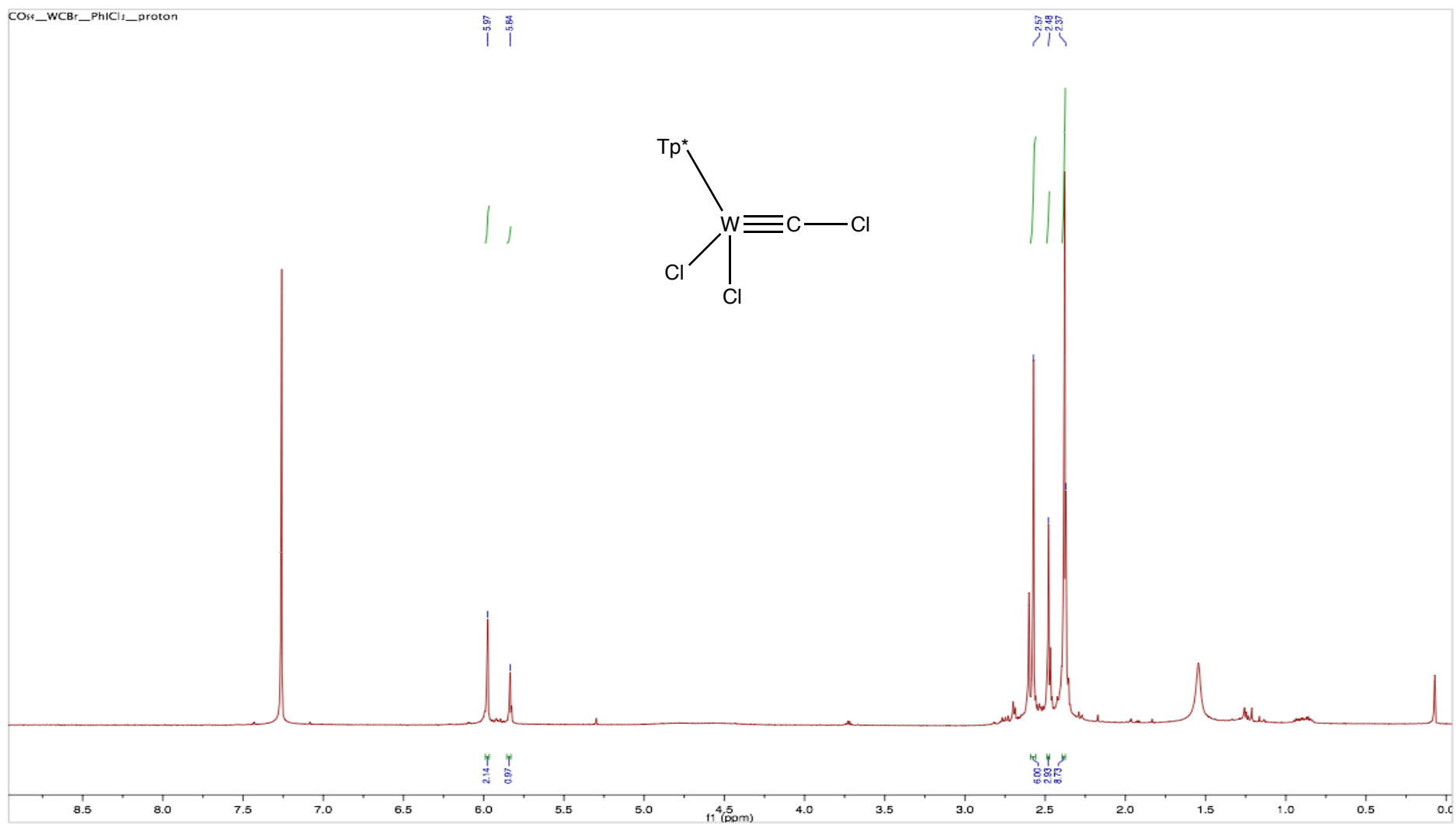
Figure S81. Infrared Spectrum of $[\text{WPt}(\mu\text{-Cl})(\text{CO})_3(\text{PPh}_3)(\text{Tp}^*)]$ (7) (ATR, 25 °C, ν):

Figure S82. ^1H NMR Spectrum of $[\text{W}(\text{CCl})\text{Cl}_2(\text{Tp}^*)]$ (9) (600 MHz, CDCl_3 , 25 °C, δ):Figure S83. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of $[\text{W}(\text{CCl})\text{Cl}_2(\text{Tp}^*)]$ (9) (151 MHz, CDCl_3 , 25 °C, δ):

80

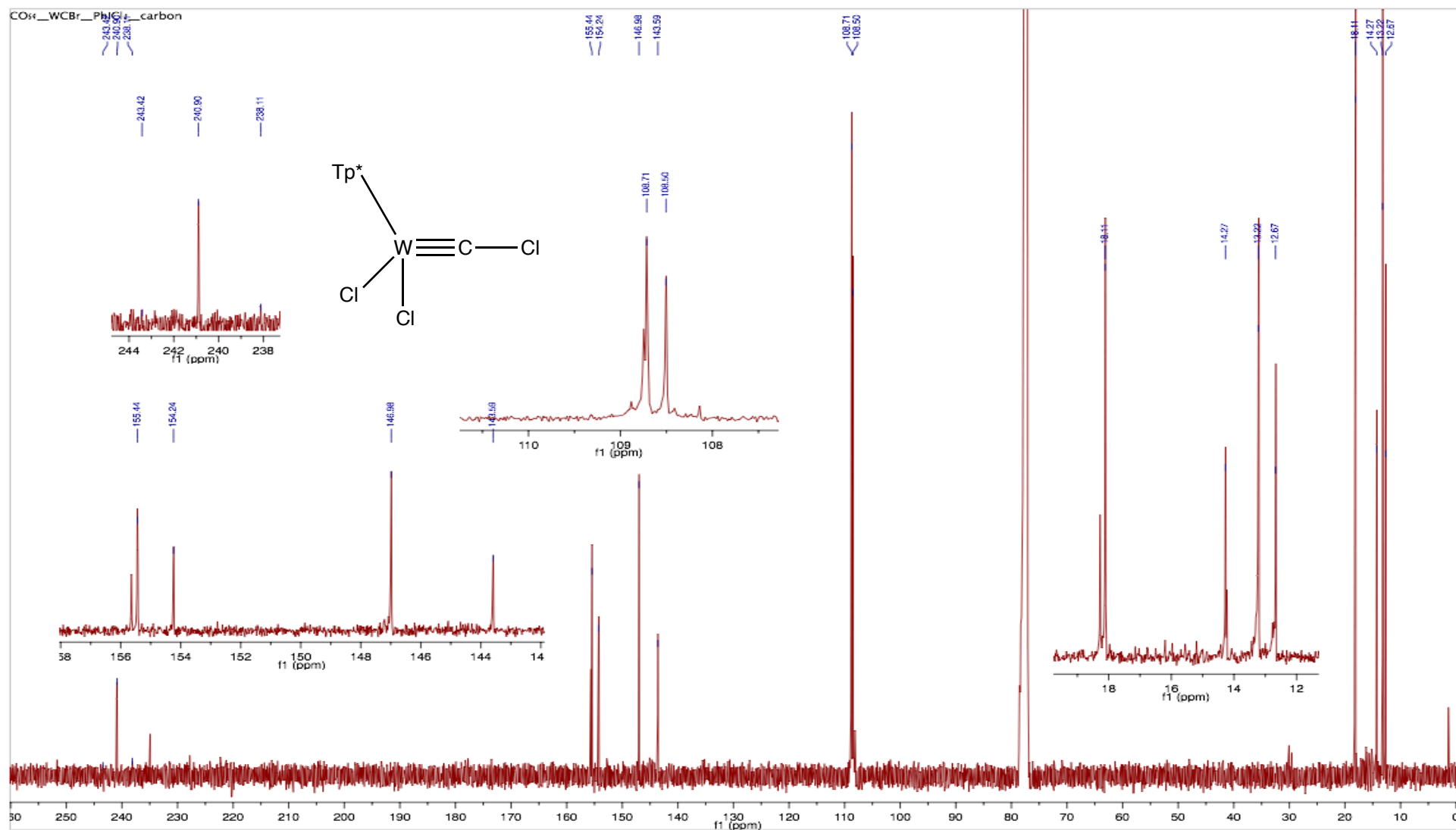


Figure S84. Mass Spectrum of $[\text{W}(\text{CCl})\text{Cl}_2(\text{Tp}^*)]$ (9) (ESI):

Observed versus simulated spectrum for detected target formulas $[M+H]^+$ ion