Construction of an Iminoketenylidene

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Abstract: The new isonitrile-μ-carbido complexes [WPt(μ-C)Br(CNR)(PPh_3)$(CO)_2$(Tp*)] (R = $C_6H_2Me_3$-2,4,6, $C_6H_3Me_2$-2,6; Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate) rearrange irreversibly in polar solvents to provide the first examples of iminoketenylidene (CCNR) complexes.

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CCDC 2084966-2084969 and 2085626 contain the supplementary crystallographic data for this paper and are available free of charge from The Cambridge Crystallographic Data Centre.

Experimental Procedures

General Considerations

Experimental work was performed using standard Schlenk techniques using dried and pre-purified nitrogen or in an inert atmosphere glove-box charged with an argon atmosphere unless specified otherwise. Reactions employed dried and degassed solvents distilled over sodium and benzophenone (ethers, arenes and paraffins) or calcium hydride (CH_2Cl_2, MeCN). The compound [WPt(μ-C)Br(CO)$_2$(PPh$_3$)$_2$(Tp*)] (**1**)[1a] was prepared according to published procedures. The complex *triangulo*-[Pt$_3$(CNC$_6$H$_2$Me$_3$-2,4,6)$_6$] was prepared *in situ* in a manner analogous to that described for [Pt$_3$(CN^{t}Bu)$_6$][1b] from the reaction of [Pt(η^2-norbornene)$_3$] and CNC$_6$H$_2$Me$_3$. All other reagents were used as received from commercial suppliers.

NMR spectra were obtained on a Bruker Avance 400 (^{1}H at 400.1, ^{13}C{^{1}H} at 100.6, ^{31}P{^{1}H} at 162.0, ^{195}Pt{^{1}H} at 85.7 MHz), a Bruker Avance 600 (^{1}H at 600.0, ^{13}C{^{1}H} at 150.9 MHz) or a Bruker Avance 700 (^{1}H at 700.0, ^{13}C{^{1}H} at 176.1, ^{31}P{^{1}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 {$CFCl_3$ for ^{19}F{^{1}H}, 85% H_3PO_4 in H_2O for ^{31}P{^{1}H}, 1.2M Na_2PtCl_6 for ^{195}Pt}. 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 ^{1}H and ^{13}C{^{1}H} NMR spectra, but to the level of accuracy that is reportable (*i.e.*, 2 decimal places for ^{1}H NMR, 1 decimal place for ^{13}C{^{1}H} NMR) they are reported as having the same chemical shift.

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

Infrared spectra were obtained using a Shimadzu FTIR-8400 spectrometer (liquid) or Perkin Elmer FTIR Spectrum 2 (Solid State ATR, diamond anvil). Signals are denoted according to their absorption strength such as very sharp (vs), strong (s), medium (m), weak (w) or broad (br). Elemental microanalytical data were provided Macquarie University (Australia). 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 Xcalibur or SuperNova CCD diffractometers using Mo-Kα radiation (λ = 0.71073 Å) or Cu-Kα radiation (λ = 1.54184 Å) employing the *CrysAlis PRO* software.[2] The structures were solved iteratively (intrinsic phasing) using the SHELXT program and refined by full-matrix least-squares on F^2 using the SHELXL program.[3] Hydrogen atoms were located geometrically and refined using a riding model. Diagrams were produced using the CCDC visualisation program Mercury.[4] We gratefully acknowledge the assistance of Dr M. G. Gardiner with crystallographic analyses.

Computational Details

Computational studies were performed by using the *SPARTAN18* suite of programs.[5] Geometry optimisation (gas phase) for metal complexes was performed at the DFT level of theory using the exchange functionals ωB97X-D and ωB97X-V of Head-Gordon.[6] The Los Alamos effective core potential type basis set (LANL2Dζ) of Hay and Wadt[7] was used for Pt and W and Pople 6-31G* basis sets[8] were used for all other atoms. For the free iminoketenylidenes, geometries were optimised using the ωBP97X-V/6-31G* combination followed by the second order Møller Plesset method (RI-MP2) in combination with Dunning's cc-PVTζ basis set[9] for frequency and thermodynamics calculations based on these geometries. Frequency calculations were performed for all compounds to confirm that each optimized structure was a minimum and also to identify vibrational modes of interest (ν_{CCN}). Cartesian atomic coordinates are provided below.

Synthesis of [WPt(μ$_2$-C)Br(CNC$_6$H$_3$Me$_2$)(CO)$_2$(PPh$_3$)(Tp*)] (3a)

A sample of [WPt(μ-C)Br(CO)$_2$(PPh$_3$)$_2$(Tp*)] (**1**: 0.631 g, 0.462 mmol) and 2,6-dimethylphenylisonitrile (0.066 g, 0.503 mmol) was stirred in toluene (30 mL) for 16 hours at ambient temperature. The subsequent orange solution had solvent removed *via* rotary evaporation where the residue was sonicated in *n*-hexane (5 x 10 mL), decanted each time to remove excess phosphine. Now free of excess phosphine, flash column chromatography {silica gel, N_2, dry loaded, isocratic elution, 75% CH_2Cl_2/petroleum ether 60–80} first eluting the target as an orange band, followed by a minor band returning starting material and [WPt(μ-C)Br

$(CNC_6H_3Me_2)_2(CO)_2(Tp^*)]$ (**4a**). The product band was collected and crystallised from CH_2Cl_2 and EtOH to give an orange solid which was collected *via* vacuum filtration. The solid was washed with EtOH (2 x 5 mL) and *n*-hexane (10 mL) before drying in vacuo for 16 hours to afford compound **3a** as a pale yellow powder (0.220 g, 0.181 mmol, 40% yield). Crystals suitable for X-ray diffractometry were grown by vapour diffusion of *n*-hexane into a CH_2Cl_2 solution of the compound at 5 °C. Note: Spectra (*vide infra*) indicate a minor rotamer in a 1:4 ratio. Data presented are of the major component. IR (CH_2Cl_2, cm^{-1}): 2196 s ν_{CN}, 1943 vs ν_{CO}, 1852 vs ν_{CO}. IR (ATR, cm^{-1}): 2552 2532 w ν_{BH}, 2184 s ν_{CN}, 1939 vs ν_{CO}, 1846 vs ν_{CO}. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ_H = 7.49 [br, 6 H, C_6H_5], 7.25–7.17 [m, 4 H, C_6H_5], 7.12 [d, $^1J_{HH}$ = 8 Hz, C_6H_3], 7.03 [br, 5 H, C_6H_5], 5.64 [s, 1 H, pzCH], 5.62 [s, 2 H, pzCH], 2.71 [s, 6 H, XylCH_3], 2.40 [s, 6 H, pzCH_3], 2.37 [s, 6 H, pzCH_3], 2.31 [s, 3 H, pzCH_3], 2.25 [s, 3 H, pzCH_3]. ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 25°C): δ_C = 308.4 [d, $^2J_{CP}$ = 10 Hz, W≡C–Pt], 227.5 [$^1J_{CW}$ = 175 Hz, CO], 152.0, 151.3 [C^5(pz)], 144.3, 143.3 [C^3(pz)], 136.9 [$C^{2,6}(C_6H_3)$], 135.1 [d, $^2J_{CP}$ = 11 Hz, $C^{2,6}(C_6H_5)$], 130.6 [$C^4(C_6H_5)$], 129.4 [$C^4(C_6H_3)$], 129.2 [d, $^1J_{CP}$ = 59 Hz, $C^1(C_6H_5)$], 128.1 [$C^{3,5}(C_6H_3)$], 127.7 [d, $^2J_{CP}$ = 11 Hz, $C^{3,5}(C_6H_5)$], 126.4 [Pt*C*N], 106.6, 106.2 [C^4(pz)], 19.8 [XylCH_3], 16.7, 15.2, 12.8, 12.6 [pzCH_3]. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25°C): δ_P = 16.75 [s, $^1J_{PPt}$ = 3466 Hz]. ^{195}Pt{^{1}H} NMR (85.7 MHz, $CDCl_3$, 25°C): δ_P = –3761 [d.br., $^1J_{PtP}$ = 3489 Hz]. MS (ESI, +ve ion, *m/z*): Found: 1216.1874. Calcd for $C_{45}H_{46}{}^{11}B^{79}BrN_7O_2P^{195}Pt^{184}W$ $[M]^+$: 1216.1884. Anal. Found: C, 44.39; H, 3.92; N, 8.07%. Calcd for $C_{45}H_{46}BBrN_7O_2P_2PtW$: C, 44.39; H, 3.81; N, 8.05%. *Crystal data for* $C_{45}H_{46}BBrN_7O_2PPtW{\cdot}CH_2Cl_2$, M_w = 1302.44, triclinic, $P\bar{1}$ (No.2), *a* = 9.4191 (2) Å, *b* = 15.8501 (2) Å, *c* = 16.1962 (4) Å, α = 88.182 (2)°, β = 77.516 (2)°, γ = 82.340 (2)°, *V* = 2339.74 (10) Å^3, *Z* = 2, ρ_{calc} = 1.849 Mgm^{-3}, μ(Cu *K*α) = 12.73 mm^{-1}, *T* = 150(0) K, light orange plate, 0.18 × 0.06 × 0.04 mm, 8849 independent measured reflections (θ_{max} = 73.7), R_1 = 0.042, wR_2 = 0.112 for 7651 reflections [$I > 2\sigma(I)$], 571 parameters, 9 restraints. CDCC 2084969.

Synthesis of [WPt(μ$_2$-C)Br($CNC_6H_2Me_3$)$(CO)_2(PPh_3)(Tp^*)$] (3b)

A sample of [WPt(μ-C)Br$(CO)_2(PPh_3)_2(Tp^*)$] (**1**: 0.181 g, 0.134 mmol) and 2,4,6-trimethylphenylisonitrile (0.029 g, 0.199 mmol) was stirred in toluene (10 mL) for 16 hours at ambient temperature. The subsequent orange suspension had solvent removed *via* rotary evaporation where the residue was sonicated in *n*-hexane (5 x 10 mL), decanted each time to remove excess phosphine. Now free of excess phosphine, flash column chromatography {silica gel, N_2, dry loaded, isocratic elution, 75% CH_2Cl_2/petroleum ether 60–80} first eluted the product as an orange band, followed by a minor band returning starting material **1** and [WPt(μ-C)–Br$(CO)_2(CNC_6H_2Me_3)_2(Tp^*)$] (**4b**). The product-containing band was crystallised from CH_2Cl_2 and EtOH to give an orange solid which was collected *via* vacuum filtration. The solid was washed with EtOH (2 x 5 mL) and *n*-hexane (10 mL) before drying in vacuo to afford compound **3b** as a pale orange powder (0.077 g, 0.063 mmol, 47% yield). Crystals suitable for X-ray diffractometry were grown by vapour diffusion of *n*-hexane into a $CHCl_3$ solution of **3b** at 5 °C. Note: Spectra (*vide infra*) indicate the presence of a minor rotamer in a ratio of 1:6 with the major isomer. IR (CH_2Cl_2, cm^{-1}): 2197 s ν_{CN}, 1943 vs $\nu_{CO,}$ 1852 vs ν_{CO}. IR (ATR, cm^{-1}): 2544 2529 w ν_{BH}, 2180 s ν_{CN}, 1931 vs $\nu_{CO,}$ 1835 vs ν_{CO}. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ_H = 7.49 [m.br., 6 H, C_6H_5], 7.19 [m.br., 3 H, C_6H_5], 7.02 [m.br., 6 H, C_6H_5], 6.92 [s, 2 H, C_6H_2], 5.63 [s, 1 H, pzCH], 5.61 [s, 2 H, pzCH], 2.65 [s, 6 H, MesCH_3-2,6], 2.40 [s, 6 H, pzCH_3], 2.36 [s, 6 H, pzCH_3], 2.30 [overlapping 3 H singlets, MesCH_3-4 and pzCH_3], 2.24 [s, 3 H, pzCH_3]. ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$, 25°C, δ): 308.6 [m, W≡C–Pt], 227.4 [$^1J_{CW}$ = 175 Hz], 152.0, 151.3 [C^5(pz)], 144.3, 143.3 [C^3(pz)], 140.1 [$C^4(C_6H_2)$], 136.6 [$C^{2,6}(C_6H_2)$], 135.1 [d, $^2J_{CP}$ = 11 Hz, $C^{2,6}(C_6H_5)$], 130.6 [$C^4(C_6H_5)$], 129.2 [d, $^1J_{CP}$ = 55 Hz, $C^1(C_6H_5)$], 128.9 [$C^{3,5}(C_6H_2)$], 127.6 [d, $^3J_{CP}$ = 12 Hz, $C^{3,5}(C_6H_5)$], 123.8 [Pt*C*N], 106.6 106.2 [C^4(pz)], 21.5 [MesCH_3-2,6] 19.7 [MesCH_3-4], 16.7, 15.3, 12.8, 12.6 [pzCH_3]. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25°C): δ_P = 15.74 [s, $^1J_{PPt}$ = 3477 Hz]. This spectrum also indicates a minor isomer (ratio 1:7, δ_P = 16.52) co-existing with the major isomer. ^{195}Pt{^{1}H} NMR (150 MHz, $CDCl_3$, 25°C): δ_{Pt} = –3763 [d, $^1J_{PtP}$ = 3473 Hz]. MS (ESI, +ve ion, *m/z*): Found: 1232.2062. Calcd for $C_{46}H_{48}{}^{11}B^{81}BrN_7O_2P_1{}^{195}Pt^{184}W$ $[M]^+$: 1232.2020. Anal. Found: C, 44.84; H, 3.97; N, 7.84%. Calcd for $C_{46}H_{48}BBrN_7O_2PPtW$: C, 44.86; H, 3.93; N, 7.96%. *Crystal data for* $C_{46}H_{48}BBrN_7O_2PPtW.CHCl_3$, M_w = 1350.91, triclinic, $P\bar{1}$ (No. 2) *a* = 9.5314 (3) Å, *b* = 16.2298 (5) Å, *c* = 16.3030 (5) Å, α = 91.074 (2)°, β = 103.031 (2)º, γ = 93.835 (2), *V* = 2450.02 (13) Å^3, *Z* = 2, ρ_{calc} = 1.831 Mgm^{-3}, μ(Cu *K*α) = 12.67 mm^{-1}, *T* = 150(0) K, light yellow plate, 0.10 × 0.06 × 0.04 mm, 9597 independent measured reflections (θ_{max} = 73.5), R_1 = 0.033, wR_2 = 0.088 for 8386 reflections [$I > 2\sigma(I)$], 590 parameters without restraints. CDCC 2084966.

Synthesis of [WPt(μ-C)Br($C_6H_2Me_3$)$_2(CO)_2(Tp^*)$] (4b).

A sample of [WPt(μ-C)Br$(CO)_2(PPh_3)_2(Tp^*)$] (**1**: 502 mg, 0.372 mmol) was stirred in benzene (30 mL) with mesitylisocyanide (148 mg, 1.02 mmol). Upon solvent injection an orange suspension was noted. The reaction was stirred for 16 hours at 60°C during which precipitation of an orange solid occurred to provide a clear supernatant phase. The solvent was removed under reduced pressure to give a pale orange solid. Flash column chromatography (silica gel, N_2, CH_2Cl_2/THF/$CHCl_3$ gradient) was employed for purification, eluting a major orange band that was freed of volatiles to afford an orange solid. Ultrasonic trituration in Et_2O (10 mL) allowed for a very fine pale orange powder to form. This was collected by filtration, washed with *n*-hexane (3 x 10 mL) and *n*-pentane (3 x 10 mL) and dried in vacuo to afford the title compound (376 mg, 0.337 mmol, 91% isolated yield). Crystals suitable for X-ray diffractometry were obtained by the slow evaporation of $CDCl_3$ at ambient temperature. IR (CH_2Cl_2, cm^{-1}): 2194 vs ν_{CN}, 1951 vs ν_{CO}, 1859 vs ν_{CO}. IR (ATR, cm^{-1}): 2536 w ν_{BH}, 2190 vs ν_{CN}, 1940 vs ν_{CO}, 1850 vs ν_{CO}. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ_H = 7.36 [s, 2 H, C_6H_2], 6.85 [s, 4 H, C_6H_2], 5.76 [s, 2 H, pzCH], 5.69 [s, 1 H, pzCH], 2.81 [s, 6

H, MesCH$_3$], 2.35 [s, 6 H, pzCH$_3$], 2.33 [s, 3 H, pzCH$_3$], 2.29 [s, 3 H, pzCH$_3$], 2.28 [s, 6 H, pzCH$_3$], 2.15 [s, 12 H, MesCH$_3$]. ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$, 25°C): δ_C = 299.3 [W≡C–Pt], 226.7 [$^1J_{CW}$ = 174 Hz, CO], 152.1 151.7 [C^5(pz)], 144.8 143.7 [C^3(pz)], 140.7 [C^4(C$_6$H$_2$)], 136.5 [C^{2,6}(C$_6$H$_2$)], 128.8 [C^{3,5}(C$_6$H$_2$)], 128.5 [C^1(C$_6$H$_2$)], 122.8 [Pt*C*N], 106.3 106.2 [C^4(pz)], 21.5 18.1 [MesCH$_3$], 17.1 15.3 12.8 12.7 [pzCH$_3$]. ^{195}Pt{^{1}H} NMR (85.7 MHz, CDCl$_3$, 25°C): δ_{Pt} = –3656 [s.br.]. MS (ESI, +ve ion, *m/z*): Found: 1114.20745. Calcd for C$_{38}$H$_{45}$^{11}B^{79}BrN$_8$O$_2$^{195}Pt^{184}W [M+H]$^+$: 1114.20883. Anal. Found: C, 41.00; H, 3.82; N, 9.94%. Calcd for C$_{38}$H$_{44}$BBrN$_8$O$_2$PtW: C, 40.95; H, 3.98; N, 10.05%. *Crystal data for* C$_{38}$H$_{45}$BBrN$_8$O$_2$PtW, M_w = 1258.87, monoclinic, *I2/a*, *a* = 20.9197 (3) Å, *b* = 13.80583 (17) Å, *c* = 34.4091 (6) Å, β = 90.7607 (14)°, *V* = 9936.9 (4) Å^3, *Z* = 8, ρ_{calc} = 1.683 Mgm^{-3}, μ(Mo *K*α) = 12.15 mm^{-1}, *T* = 150(0) K, light orange block, 9812 independent measured reflections (θ_{max} = 73.0°), R_1 = 0.034, wR_2 = 0.087 for 8154 reflections [*I* >2σ(*I*)], 481 parameters without restraints. CDCC 2084968.

Synthesis of [WPt(μ$_2$-CCNC$_6$H$_3$Me$_2$)(CO)$_2$(PPh$_3$)$_2$(CO)$_2$(Tp*)]-[BPh$_4$] ([5a]BPh$_4$)

A solvent mixture of 1:5 MeOH/CH$_2$Cl$_2$ (15 mL) was injected to a flask charged with solid [WPt(μ-C)-Br(CNXyl)(CO)$_2$(PPh$_3$)(Tp*)] (**3a**: 0.102 g, 0.0838 mmol), triphenylphosphine (0.026 g, 0.099 mmol) and Na[BPh$_4$] (0.032 g, 0.094 mmol). With rapid stirring, this immediately turned from an orange to a pink/maroon coloured solution. This was stirred for 20 hours after which the solvent was removed. The resulting purple residue was chromatographed through a short silica gel column eluting with CH$_2$Cl$_2$ to remove excess NaBPh$_4$. This purple eluate was freed of volatiles and the residue was then be purified by flash column chromatography {silica gel, N$_2$, isocratic elution, neat CH$_2$Cl$_2$} eluting a major purple band, where 5 fractions of 40 mL were sampled across the band. Samples of each fraction were tested by ^{1}H NMR spectroscopy determining that fraction 1 was pure, fractions 2–4 could be purified by crystallisation and fraction 5 was an unidentified compound of similar colour and polarity. Crystallisation of relevant fractions was performed by the concentration of CH$_2$Cl$_2$ into EtOH by rotary evaporation. When solids began emerging, the flash was sonicated to encourage more precipitation before concentrating further. This resulting precipitate was collected via vacuum filtration to give a pastel purple powder and a pink/red supernatant after careful washing with EtOH (2 x 5 mL) and *n*-hexane (2 x 10 mL). The powders were dried *in vacuo* for 16 hours to afford compound [**5a**][BPh$_4$] as a purple powder (0.080 g total, 0.047 mmol total, 56% isolated yield). Crystals of a chloroform solvate suitable for X-ray diffractometry were grown by the vapour diffusion of *n*-hexane into a solution of [**5a**][BPh$_4$] in CHCl$_3$ at 5 °C. IR (CH$_2$Cl$_2$, cm^{-1}): 2104 s ν$_{CN}$, 1944 vs ν$_{CO}$, 1853 vs ν$_{CO}$. IR (ATR, cm^{-1}): 2556 w ν$_{BH}$, 2094 s ν$_{CN}$, 1936 vs ν$_{CO}$, 1855 vs ν$_{CO}$. UV-Vis [1.95(2) x 10^{-5} molL^{-1}, nm(ϵ), CH$_2$Cl$_2$]: 268 (36100), 276 (36000), 292 (36200), 365 (14000), 535 (6900). ^{1}H NMR (400 MHz, CDCl$_3$, 25°C): δ_H = 7.73 [m, 5 H, C$_6$H$_5$], 7.49 [m, 8 H, C$_6$H$_5$], 7.42 [m, 4 H, C$_6$H$_5$], 7.30 [m, 8 H, C$_6$H$_5$], 7.21 [m, 9 H, C$_6$H$_5$], 7.07 [m, 14 H, C$_6$H$_5$], 6.92 [m, 4 H, C$_6$H$_5$], 6.78 6.76 [d, $^1J_{HH}$ = 7 Hz, 2 H, H^{3,5}(C$_6$H$_3$)], 5.87 [s, 2 H, pzCH], 5.81 [s, 1 H, pzCH], 2.51 [s, 6 H, pzCH$_3$], 2.37 [s, 3 H, pzCH$_3$], 2.24 [s, 6 H, pzCH$_3$], 1.76 [s, 3 H, pzCH$_3$], 0.95 [s, 6 H, XylCH$_3$]. ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$, 25°C): δ_C = 226.5 [d, $^2J_{CP}$ = 6, $^2J_{CPt}$ = 48, $^2J_{CW}$ = 158 Hz, CO], 222.8 [dd, $^2J_{CP}$ = 73, 7 Hz, WPt(μ-*C*CN)], 164.5 [quart. + hept., $^1J_{C\text{-}11B}$ = 49.7, $^1J_{C\text{-}10B}$ = 17 Hz, γ(^{11}B)/γ(^{10}B) = 2.99, C^1(BC$_6$H$_5$)], 156.1, 151.2 [C^5(pz)], 147.3, 145.2 [C^3(pz)], 139.1 [t, $^3J_{CP}$ = 9, $^2J_{CPt}$ = 111 Hz, WPt(μ-C*C*N)], 136.5 [C^{2,6}(BC$_6$H$_5$)], 135.1, 134.5 [d, $^2J_{CP}$ = 12 Hz, C^{2,6}(C$_6$H$_5$)], 133.3 [d, $^1J_{CP}$ = 49 Hz, C^1(C$_6$H$_5$)], 132.9 [C^2(C$_6$H$_3$)], 132.3 [d, $^1J_{CP}$ = 50 Hz, C^1(PC$_6$H$_5$)], 131.0, 130.8 [C^4(C$_6$H$_5$)], 129.7 [C^4(C$_6$H$_3$)], 128.5 [d, $^3J_{CP}$ = 10 Hz, C^{3,5}(C$_6$H$_5$)], 128.4 [C^{3,5}(C$_6$H$_3$)], 128.2 [d, ^3J = 10 Hz, C^{3,5}(C$_6$H$_5$)], 127.2 [C^1(C$_6$H$_3$)], 125.6 [m, C^{3,5}(BC$_6$H$_5$)], 121.6 [C^4(BC$_6$H$_5$)], 108.6, 107.7 [C^4(pz)], 17.4 [pzCH$_3$], 17.0 [XylCH$_3$], 16.0, 13.2, 12.7 [pzCH$_3$]. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 25°C): δ_P = 44.46 [d, $^2J_{PP}$ = 20, $^1J_{PPt}$ = 3772 Hz], 25.60 [d, $^2J_{PP}$ = 20, $^1J_{PPt}$ = 3440 Hz]. ^{195}Pt{^{1}H} NMR (149.9 MHz, CDCl$_3$, 25°C): δ_{Pt} = –4174 [dd, $^1J_{PtP}$ = 3766, 3448 Hz]. MS (ESI, *m/z*): Found: 1399.3612. Calcd for C$_{63}$H$_{61}$^{11}BN$_7$O$_2$P$_2$^{195}Pt^{184}W [M]$^+$: 1399.3662. Anal. Found: C, 60.77; H, 4.63; N, 5.73%. Calcd for C$_{87}$H$_{81}$B$_2$N$_7$O$_2$P$_2$PtW: C, 60.78; H, 4.75; N, 5.70%. Calcd for C$_{87}$H$_{81}$B$_2$N$_7$O$_2$P$_2$PtW.2CHCl$_3$: C, 54.60; H, 4.27; N, 5.01%.

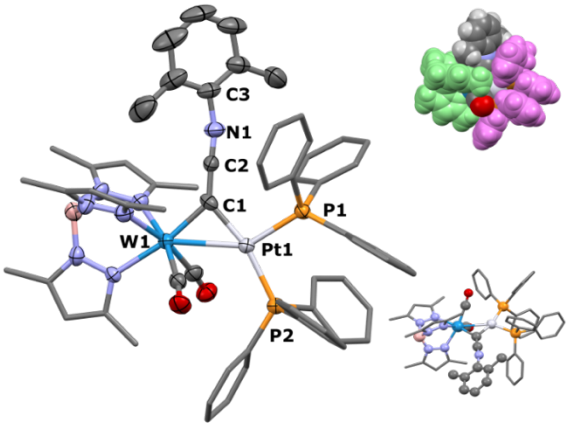


Figure S1. Molecular structure of [**5a**]$^+$ in a crystal of [**5a**].BPh$_4$.2CHCl$_3$ (50% displacement ellipsoids, pyrazolyl and aryl rings simplified, solvent and borate anion excluded). Selected bond lengths (Å) and and angles (°): W1–C1 2.024(6), Pt1–C1 1.982(7), C1–C2 1.34(1), C2–N1 1.18(1), N1–C3 1.39(1), Pt1–P1 2.298(1), Pt1–P2 2.310(2), W1–C1–Pt1 88.0(3), C1–Pt1–W1 46.6(2), Pt1–W1–C1 45.4(2), C3–N1–C2 162.2(8), P1–Pt1–P2 96.55(6). Inserts: a) space-filling representation with Tp* in green and phenyl rings in pink, b) ball and stick model showing bending at nitrogen.

Crystal data for C$_{63}$H$_{61}$BN$_7$O$_2$P$_2$PtW.2(CHCl$_3$).C$_{24}$H$_{20}$B, M_w = 1957.82, monoclinic, *P*2$_1$/*c* (No. 14), *a* = 20.9875 (3) Å, *b* = 15.7357 (2) Å, *c* = 26.1799 (5) Å, β = 105.436 (2)°, *V* = 8334.1 (2) Å^3, *Z* = 4, ρ_{calc} = 1.560 Mgm^{-3}, μ(Cu *K*α) = 8.15 mm^{-1}, *T* = 150(0) K, light red plate, 0.11 × 0.04 × 0.03 mm, 16087 independent measured reflections (θ_{max} = 72.8°), R_1 = 0.047, wR_2 = 0.128 for 12305 reflections [*I* >2σ(*I*)], 1003 parameters. CDCC 2084967. The cationic complex was also crystallised as a chloroform solvate with a PF$_6$ counter-anion. *Crystal data for* C$_{63}$H$_{61}$BN$_7$O$_2$P$_2$PtW·(CHCl$_3$)·PF$_6$, M_w = 1664.21, triclinic, *P*$\bar{1}$ (no. 2), *a* = 11.8143 (3) Å, *b* = 14.7029 (4) Å, *c* = 22.6429 (8) Å, α = 100.170 (3)°, β = 103.965 (3)°, γ = 107.433 (2)°, *V* = 3507.58 (19) Å^3, *Z* = 2,

ρ_{calc} = 1.576 Mgm^{-3}, μ(Mo $K\alpha$) = 3.88 mm^{-1}, T = 150(0) K, purple block, 0.23 × 0.13 × 0.04 mm, 19658 independent measured reflections (θ_{max} = 32.2°), R_1 = 0.044, wR_2 = 0.103 for 15114 reflections [I >2σ(I)], 805 parameters without restraints. CDCC 2085626.

Synthesis of [WPt(μ_2-CCNC$_6$H$_2$Me$_3$)(CNC$_6$H$_2$Me$_3$)(CO)$_2$(PPh$_3$) - (Tp*)][PF$_6$] ([5b]PF$_6$)

A mixture of [WPt(μ-C)Br(CNC$_6$H$_2$Me$_3$)-(CO)$_2$(PPh$_3$)(Tp*)] (**4b**: 0.178 g, 0.159 mmol), triphenylphosphine (56 mg, 0.21 mmol) and NaPF$_6$ (46 mg, 0.27 mmol) was dissolved in a mixture of MeOH and CH_2Cl_2 (15 mL, 1:5 v/v)—the colour immediately changed from orange to green and then slowly to a deep purple colour while stirring overnight. The solvent was removed to give a dark solid which was subjected to flash column chromatography {silica gel, N_2, isocratic elution, 2% THF/CH_2Cl_2} to provide a major purple band that was freed of volatiles under reduced pressure. Crystallisation of relevant fractions was performed by the concentration of CH_2Cl_2 into EtOH by rotary evaporation. When solids began emerging, the suspension was sonicated to encourage more precipitation before concentrating further. This resulting precipitate was collected via vacuum filtration to give a purple powder and a pink/red supernatant after careful washing with EtOH (2 x 5 mL) and *n*-hexane (2 x 10 mL) before drying *in vacuo* to give the title salt as a deep purple powder (77 mg, 0.053 mmol, 41% isolated yield). Single crystals suitable for conventional or synchrotron X-ray diffractometry were not successfully acquired. IR (CH_2Cl_2, cm^{-1}): 2558 w ν_{BH}, 2156* vs ν_{CN}, 2115* vs ν_{CN}, 1943 vs ν_{CO}, 1862 vs ν_{CO}. IR (ATR, cm^{-1}): 2553 w ν_{BH}, 2119 br vs ν_{CN}, 1933 vs ν_{CO}, 1844 vs ν_{CO}. *Computational analysis and spectra simulation indicates that the two CN stretches for the iminoketenylidene and Pt-isonitrile are strongly coupled rather than independent. UV-Vis [2.11(6) x 10^{-5} molL^{-1}, nm(ϵ), CH_2Cl_2]: 263 (35000), 320 (30300), 347 sh (17700), 550 (6800). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ_H = 7.58 [m, 6 H, C$_6$H$_5$], 7.36 [m, 9 H, C$_6$H$_5$], 7.17 [m, 2 H, C$_6$H$_5$], 6.90 [s, 2 H, C$_6$H$_2$], 6.67 [s, 2 H, C$_6$H$_2$], 5.95 [s, 1 H, pzCH], 5.91 [s, 2 H, pzCH], 2.62 [s, 3 H, pzCH$_3$], 2.55 [s, 6 H, pzCH$_3$], 2.41 [s, 3 H, pzCH$_3$], 2.33 [s, 3 H, MesCH$_3$], 2.15 [s, 6 H, MesCH$_3$], 2.11 [s, 3 H, MesCH$_3$], 1.02 [s, 6 H, MesCH$_3$]. ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 25°C): δ_C = 229.0, 228.9 [s x 2, CO], 217.9 [d, $^2J_{CP}$ = 6 Hz, WPt(μ-*C*CN)], 156.2, 151.2 [C^5(pz)], 147.4, 145.4 [C^3(pz)], 141.3 [C^1(C$_6$H$_2$)], 139.7 [C^1(C$_6$H$_2$)], 134.8 [C^4(C$_6$H$_2$)], 134.0 [d, $^2J_{CP}$ = 12 Hz, C^{2,6}(C$_6$H$_5$)], 133.8 [C^4(C$_6$H$_2$)], 132.3 [d, $^1J_{CP}$ = 53 Hz, C^1(C$_6$H$_5$)], 131.7 [C^4(C$_6$H$_5$)], 129.0 [d, $^3J_{CP}$ = 11 Hz, C^{3,5}(C$_6$H$_5$)], 129.5 [C^{3,5}(C$_6$H$_2$)], 128.8 [C^{3,5}(C$_6$H$_2$)], 124.3 WPt(μ-*C*CN)], 125.4 [C^1(C$_6$H$_2$)], 122.8 [C^1(C$_6$H$_2$)], 122.8 [Pt*C*NMes], 109.3, 107.8 [C^4(pz)], 21.6, 21.4 [MesCH$_3$], 18.5, 17.8 [MesCH$_3$], 16.9, 16.1, 13.2, 12.7 [pzCH$_3$]. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25°C): δ_P = 44.14 [s, $^1J_{PPt}$ = 3575 Hz]. ^{195}Pt{^{1}H} NMR (150 MHz, $CDCl_3$, 25°C) δ_{Pt} –4136 [d, $^1J_{PtP}$ = 3587 Hz]. MS (ESI, +ve ion, *m/z*): Found: 1296.3772. Calcd for C$_{56}$H$_{59}$^{11}BN$_8$O$_2$P^{195}Pt^{184}W [M]$^+$: 1296.3749. Anal. Found: C, 47.60; H, 4.29; N, 7.32%. Calcd for C$_{55}$H$_{59}$BF$_6$N$_8$O$_2$P$_2$PtW. ½C$_6$H$_{14}$: C, 47.30; H, 4.52; N, 7.61%.

Optimised Geometries and Cartesian Coordinates

(a) Singlet CCNMe *6$_s$Me*

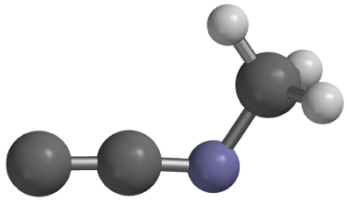


Figure S2. Optimised geometry for singlet CCNMe ***6$_s$Me***

Cartesian Coordinates

Atom	x	y	z
C	-1.048745	0.000000	2.455875
C	-0.909958	0.000000	1.147402
N	-0.846198	0.000000	-0.097344
C	0.468421	0.000000	-0.731103
H	1.299307	0.000000	-0.016034
H	0.518586	0.882244	-1.379398
H	0.518586	-0.882244	-1.379398

Thermodynamic properties (298.15 K; RI-MP2/cc-PVTζ): *ZPE* = 129.67 kJmol^{-1}, H^o = –170.247660 au, S^o = 283.96 Jmol^{-1}K^{-1}, G^o = –170.279907 au, C_v = 57.58 Jmol^{-1}K^{-1}.

(b) Triplet CCNMe *6$_t$Me*

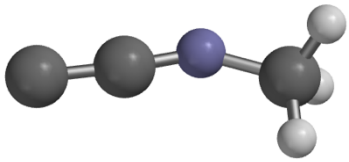


Figure S3. Optimised geometry for triplet CCNMe ***6$_t$Me***

Cartesian Coordinates (See attached .mol2 file)

Atom	x	y	z
C	-1.736731	0.792608	2.200168
C	-1.033154	0.294967	1.168965
N	-0.463593	-0.228505	0.237316
C	0.602453	-0.215781	-0.716319
H	1.567595	-0.215816	-0.196424
H	0.528651	0.678502	-1.346127
H	0.534779	-1.105975	-1.347579

Thermodynamic properties (298.15 K, RIMP2/cc-PVTζ): *ZPE* = 124.18 kJmol^{-1}, H^o = –170.244791 au, S^o = 253.24 Jmol^{-1}K^{-1}, G^o = –170.273548 au, C_v = 100.53 Jmol^{-1}K^{-1}.
G^o(triplet)-G^o (singlet) = – 0.006359 au (4.0 kcalmol^{-1})

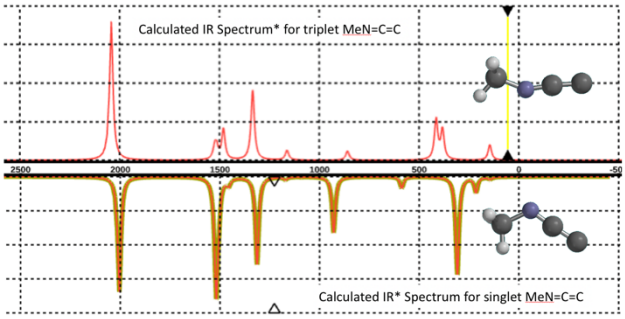


Figure S4. Calculated (ωBP97X-V/6-31G*) Infrared Spectra for singlet (***6$_s$Me*** orange) and triplet (***6$_t$Me*** red) CCNMe.

(c) Singlet CCNPh *6$_s$Ph*

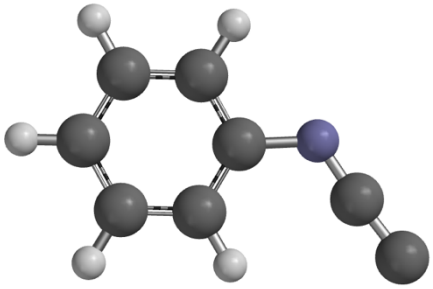


Figure S5. Optimised geometry for singlet CCNPh ***6$_s$Ph***

Cartesian Coordinates

Atom	x	y	z
C	0.212263	0.000000	-4.132084
C	-0.423417	0.000000	-2.989801
N	-1.107658	0.000000	-1.935170
C	-0.490447	0.000000	-0.667679
C	0.558110	0.000000	1.904461
C	0.902610	0.000000	-0.486217
C	-1.353174	0.000000	0.435786
C	-0.825904	0.000000	1.723813
C	1.420632	0.000000	0.801518
H	1.553186	0.000000	-1.359170
H	-2.425438	0.000000	0.254935
H	-1.490117	0.000000	2.585033
H	2.497832	0.000000	0.953291
H	0.971523	0.000000	2.911284

Thermodynamic properties (298.15 K, RIMP2/cc-PVTζ): *ZPE* = 266.41 kJmol^{-1}, H^o = –361.531325 au, S^o = 342.75 Jmol^{-1}K^{-1}, G^o = – 361.570247, C_v = 113.21 Jmol^{-1}K^{-1}.

(d) Triplet CCNPh *6$_t$Ph*

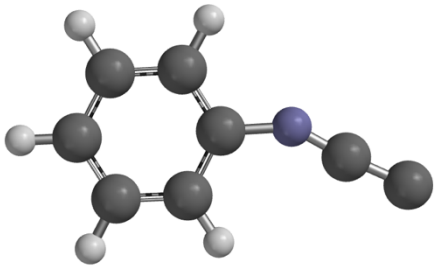


Figure S6. Optimised geometry for triplet CCNPh ***6$_t$Ph***

Cartesian Coordinates (See attached .mol2 file)

Atom	x	y	z
C	-0.362273	0.000000	-4.471052
C	-0.550812	0.000000	-3.148668
N	-0.821909	0.000000	-1.959963
C	-0.361862	0.000000	-0.654610
C	0.533603	0.000000	1.979583
C	1.017133	0.000000	-0.390503
C	-1.291601	0.000000	0.393424
C	-0.836024	0.000000	1.707877
C	1.454964	0.000000	0.929198
H	1.720398	0.000000	-1.220283
H	-2.353707	0.000000	0.161608
H	-1.554238	0.000000	2.524913
H	2.522538	0.000000	1.138971
H	0.883790	0.000000	3.009505

Thermodynamic properties (298.15 K, RIMP2/cc-PVTζ): *ZPE* = 269.98 kJmol^{-1}, H^o = –361.514664 au, S^o = 358.72 Jmol^{-1}K^{-1}, G^o = –361.555400 au, C_v = 113.35 Jmol^{-1}K^{-1}.

G^o(triplet)-G^o(singlet) = – 0.014847 au (–9.32 kcalmol^{-1})

(e) Singlet CCNH *6$_s$H*

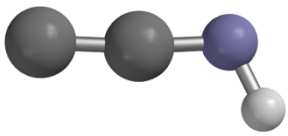


Figure S7. Optimised geometry for singlet CCNH ***6$_s$H***

Cartesian Coordinates

Atom	x	y	z
C	-0.350111	0.000000	1.703366
C	-0.215657	0.000000	0.386969
N	-0.196732	0.000000	-0.858987
H	0.762500	0.000000	-1.231349

Thermodynamic properties (298.15 K, RIMP2/cc-PVTζ): *ZPE* = 87.55 kJmol^{-1}, H^o = –131.046297 au, S^o = 233.85 Jmol^{-1}K^{-1}, G^o = –131.072853 au, C_v = 49.89Jmol^{-1}K^{-1}.

(f) Triplet CCNH *6$_t$H*

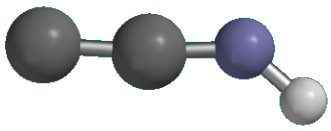


Figure S8. Optimised geometry for triplet CCNMe ***6$_t$H***

Cartesian Coordinates

Atom	x	y	z
C	-0.450542	0.000000	1.759545
C	-0.187004	0.000000	0.440261
N	-0.063136	0.000000	-0.770151
H	0.700682	0.000000	-1.429656

Thermodynamic properties (298.15 K, RIMP2/cc-PVTζ): *ZPE* = 77.30 kJmol^{-1}, H^o = –131.0147656 au, S^o = 231.02 Jmol^{-1}K^{-1}, G^o = –131.073890 au, C_v = 49.92 Jmol^{-1}K^{-1}.

(g) [Pt(CCNC$_6$H$_2$Me$_2$)(CO)$_2$(PMe$_3$)$_2$(Tp)]$^+$ (*7XylP*)

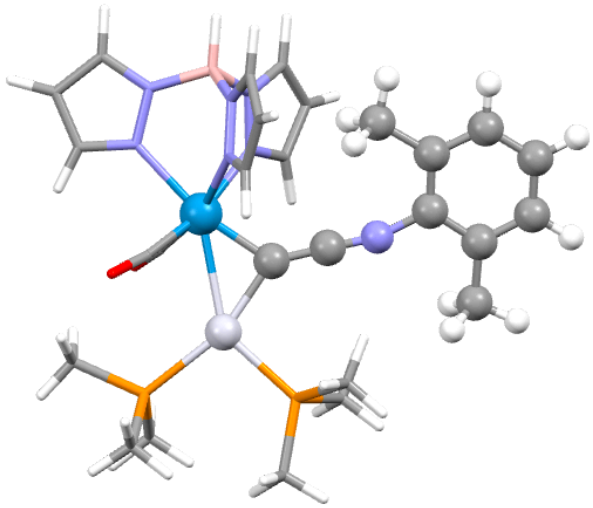


Figure S9. Optimised geometry for ***7XylP*** (Co-ligands simplified)

Cartesian Coordinates

Atom	x	y	z
Pt	0.146915	-1.401911	1.757412
W	-1.749535	-0.065262	0.189406
P	2.410271	-1.672059	2.066788
P	-0.669883	-2.903062	3.369666
N	-1.782586	2.138071	0.027259
O	-2.595424	-3.115922	0.175949
N	-3.901735	0.276864	-0.272261
O	-2.626038	0.112791	3.208593
N	-1.660532	0.118582	-2.038870
N	2.005614	0.763654	-1.336477
N	-4.317386	1.175283	-1.196487
N	-2.446000	2.796674	-0.948224
N	-2.360817	1.047069	-2.724682
C	1.166936	0.347588	-0.619666
C	0.222994	-0.167111	0.186242
C	-2.225909	-0.015328	2.125836
C	-2.233921	-2.017394	0.208477
C	-6.142927	0.268092	-0.326385
H	-7.173470	0.031211	-0.114068
C	-1.206346	3.061147	0.804684
C	-5.003134	-0.273406	0.258867
C	-0.971441	-0.591848	-2.937735
C	-5.656077	1.187148	-1.244023
C	-2.116583	0.924471	-4.040062
C	-1.221363	-0.115129	-4.225389
H	-0.818889	-0.480824	-5.156883
C	-1.492830	4.339044	0.324741
H	-1.175200	5.286097	0.731823
B	-3.289775	2.017814	-1.977229
C	-2.288868	4.119923	-0.787711
C	2.730530	1.532127	-2.227839
C	4.059141	1.168052	-2.495176
C	4.670092	-0.039751	-1.838631
H	4.622601	0.031545	-0.745872
H	5.718730	-0.149775	-2.123750
H	4.143494	-0.955582	-2.131231
C	0.670550	2.971871	-2.498076
H	0.004882	2.139698	-2.749194
H	0.340939	3.851270	-3.055671
H	0.538703	3.180731	-1.429842
C	2.098271	2.637710	-2.822982
C	2.854004	3.394429	-3.714395
H	2.397905	4.256600	-4.191510
C	4.174592	3.061494	-3.997131
H	4.745171	3.665884	-4.694792
C	4.769957	1.958319	-3.392496
H	5.800620	1.704715	-3.620977
H	-3.834496	2.767760	-2.739647
H	-0.622614	2.752096	1.659596
H	-2.758716	4.811194	-1.471618
H	-0.341312	-1.405570	-2.609209
H	-2.596705	1.584216	-4.747421
H	-4.910983	-1.023088	1.031339
H	-6.171481	1.849805	-1.923614
C	-0.186504	-2.596468	5.110009
H	0.898082	-2.639827	5.224126
H	-0.641847	-3.336768	5.775264
H	-0.526822	-1.598408	5.400122
C	-2.486310	-3.098616	3.529871
H	-2.706997	-3.880488	4.263532
H	-2.919480	-3.383848	2.569309
H	-2.937858	-2.161808	3.861132
C	-0.150632	-4.630120	3.040651
H	0.938435	-4.708613	2.999714
H	-0.550025	-4.933566	2.068538
H	-0.528856	-5.310296	3.810262
C	3.110918	-2.517039	3.534688
H	4.198586	-2.595605	3.437739
H	2.697192	-3.521351	3.650294
H	2.883358	-1.936167	4.432528
C	3.310760	-0.076256	2.123698
H	4.390632	-0.241122	2.199647
H	2.973918	0.498388	2.990842
H	3.097859	0.508694	1.226102
C	3.191103	-2.558452	0.667332
H	4.280987	-2.585177	0.770158
H	2.927028	-2.054104	-0.265722
H	2.806535	-3.581001	0.620716

Thermodynamic properties (298.15 K, ωBP97X-D/6-31G*/LANL2Dζ): *ZPE* = 1541.15 kJmol^{-1}, *H*^{o} = –2478.31654au, *S*^{o} = 1163.15 Jmol^{-1}K^{-1}, *G*^{o} = –2478.44862, C_v = 754.39 Jmol^{-1}K^{-1}.

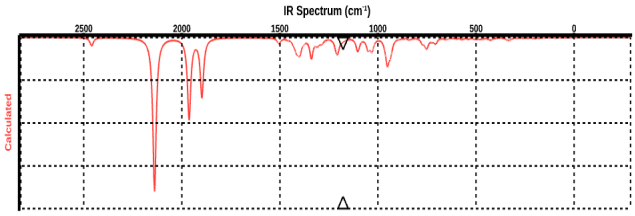


Figure S10. Calculated infrared spectrum for ***7XylP***

(h) [Pt(CCNMe)(CO)$_2$(PMe$_3$)$_2$(Tp)]$^+$ (*7MeP*)

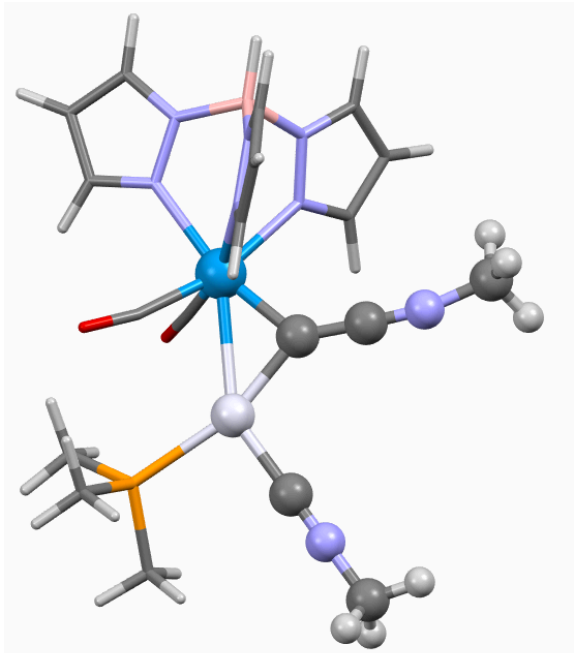


Figure S11. Optimised geometry for ***7MeP*** (Co-ligands simplified)

Cartesian Coordinates

Atom	x	y	z
Pt	0.869696	-1.100118	1.078577
W	-1.061646	0.300820	-0.423591
P	3.107770	-1.474040	1.421454
P	0.061281	-2.573435	2.727528
N	-1.041478	2.520678	-0.412973
O	-1.878224	-2.745164	-0.708232
N	-3.195532	0.732888	-0.890921
O	-2.076069	0.128191	2.549674
N	-0.940805	0.658780	-2.635004
N	2.323327	1.634924	-1.942969
N	-3.572776	1.705530	-1.754661
N	-1.681644	3.270692	-1.336937
N	-1.582310	1.674954	-3.249264
C	1.696350	0.969035	-1.205755
C	0.914420	0.238252	-0.385087
C	-1.608650	0.146931	1.484724
C	-1.531703	-1.651067	-0.579979
C	-5.434088	0.755859	-1.014049
H	-6.473204	0.516763	-0.851407
C	-0.440410	3.365703	0.430628
C	-4.318601	0.155821	-0.439402
C	-0.248538	0.008231	-3.575579
C	-4.909313	1.736785	-1.842231
C	-1.295826	1.670684	-4.560516
C	-0.432602	0.617526	-4.818532
H	-0.023134	0.318610	-5.770962
C	-0.687238	4.684367	0.048459
H	-0.345322	5.588500	0.527409
B	-2.516986	2.594791	-2.439670
C	-1.484130	4.573486	-1.078927
H	-3.035149	3.411603	-3.149764
H	0.131491	2.976218	1.260291
H	-1.930409	5.327633	-1.710294
H	0.337911	-0.858298	-3.305783
H	-1.735489	2.406316	-5.217850
H	-4.259256	-0.653343	0.274037
H	-5.396588	2.455525	-2.484610
C	0.013555	-1.817982	4.394175
H	1.017602	-1.505846	4.693504
H	-0.381041	-2.521635	5.134087
H	-0.627944	-0.933634	4.361016
C	-1.648839	-3.192890	2.503447
H	-1.938633	-3.808638	3.360870
H	-1.711087	-3.792380	1.592323
H	-2.343561	-2.355304	2.419824
C	0.961748	-4.150366	2.996597
H	1.991241	-3.971049	3.316927
H	0.979999	-4.722125	2.064248
H	0.461135	-4.746371	3.765963
C	3.697586	-1.393599	3.154797
H	4.781387	-1.541066	3.201548
H	3.213252	-2.159522	3.764707
H	3.450454	-0.414503	3.574516
C	4.213862	-0.271284	0.593835
H	5.261010	-0.474246	0.840374
H	3.959064	0.743984	0.909259
H	4.084747	-0.341351	-0.489499
C	3.749189	-3.074592	0.803900
H	4.829638	-3.147760	0.965402
H	3.538932	-3.153748	-0.266175
H	3.255139	-3.906940	1.309324
C	2.660159	2.477880	-3.036806
H	3.715427	2.356267	-3.287191
H	2.471720	3.518951	-2.761764
H	2.039132	2.209121	-3.897043

Thermodynamic properties (298.15 K, ωBP97X-D/6-31G*/LANL2Dζ): *ZPE* = 1270.06 kJmol^{-1}, *H*^{o} = –2208.12211 au, *S*^{o} = 1051.43 Jmol^{-1}K^{-1}, *G*^{o} = –2208.24151 au, C_v = 635.08 Jmol^{-1}K^{-1}.

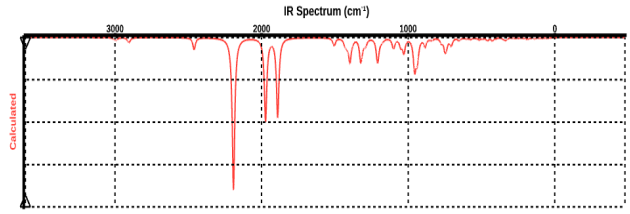


Figure S12. Calculated infrared spectrum for ***7MeP***

(i) [Pt(CCNMe)(CO)$_2$(PMe$_3$)(CNMe)(Tp)]$^+$ (*7MeC*)

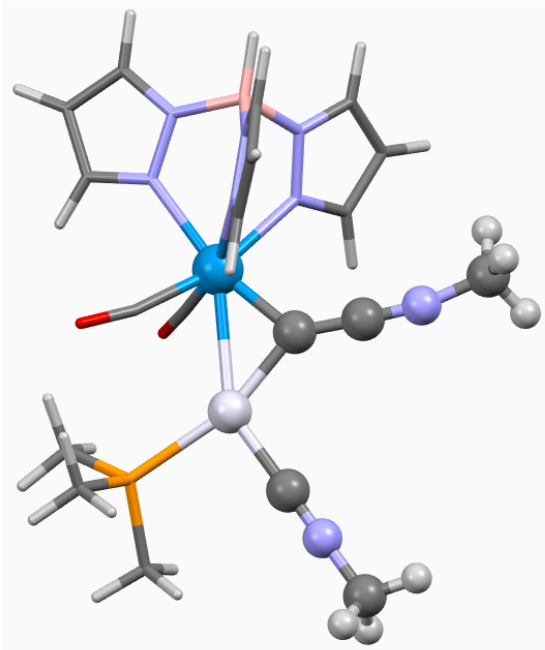


Figure S13. Optimised geometry for ***7MeC*** *(Co-ligands simplified)*

Cartesian Coordinates

Atom	x	y	z
Pt	1.223565	-1.140134	1.245756
W	-0.708000	0.136533	-0.340054
P	0.468247	-2.478764	3.040220
N	-0.737870	2.331762	-0.222788
O	-1.547284	-2.916291	-0.633781
N	-2.863272	0.549340	-0.780136
O	-1.751755	-0.051263	2.606560
N	-0.627512	0.565886	-2.543512
N	2.873762	0.954663	-2.067323
N	-3.254493	1.548633	-1.605897
N	-1.382228	3.113927	-1.117725
N	-1.274655	1.606686	-3.108278
C	2.141395	0.495278	-1.278218
C	1.251757	-0.008469	-0.390912
C	-1.240763	-0.043808	1.557610
C	-1.211064	-1.820106	-0.532196
C	-5.103009	0.577703	-0.862343
H	-6.139131	0.333353	-0.688995
C	-0.159756	3.145324	0.667978
C	-3.977497	-0.038437	-0.323611
C	0.010582	-0.076230	-3.527134
C	-4.592937	1.584748	-1.667083
C	-1.044586	1.626456	-4.430631
C	-0.213222	0.564318	-4.747589
H	0.150518	0.280452	-5.723023
C	-0.426280	4.475142	0.346138
H	-0.105040	5.360859	0.871309
B	-2.209674	2.481536	-2.251973
C	-1.212156	4.404591	-0.792664
H	-2.739358	3.326649	-2.919302
H	0.412940	2.724920	1.481849
H	-1.666490	5.181109	-1.390199
H	0.586848	-0.963008	-3.304662
H	-1.494881	2.386643	-5.051751
H	-3.907349	-0.864843	0.368967
H	-5.090459	2.327466	-2.273289
C	0.264626	-1.601274	4.630109
H	1.225561	-1.179214	4.937257
H	-0.095895	-2.282116	5.407647
H	-0.451759	-0.786719	4.502674
C	-1.133161	-3.322594	2.772793
H	-1.388366	-3.940314	3.639627
H	-1.071911	-3.956169	1.884305
H	-1.920294	-2.581421	2.621153
C	1.586620	-3.867345	3.460592
H	2.558153	-3.479007	3.778562
H	1.735063	-4.499755	2.580924
H	1.166116	-4.472065	4.269772
C	3.500972	1.529440	-3.202775
H	4.375524	0.937136	-3.480639
H	3.815303	2.549441	-2.969204
H	2.785454	1.546397	-4.029864
C	3.084609	-1.591028	1.561050
N	4.203149	-1.846320	1.769924
C	5.568381	-2.151538	2.016304
H	6.200534	-1.540135	1.369075
H	5.747273	-3.208650	1.808261
H	5.805153	-1.939375	3.061133

Thermodynamic properties (298.15 K, ωBP97X-D/6-31G*/LANL2Dζ): *ZPE* = 1099.16 kJmol^{-1}, H^o = –1879.81153 au, S^o = 1011.41 Jmol^{-1}K^{-1}, G^o = –1879.92638 au, C_v = 579.68 Jmol^{-1}K^{-1}.

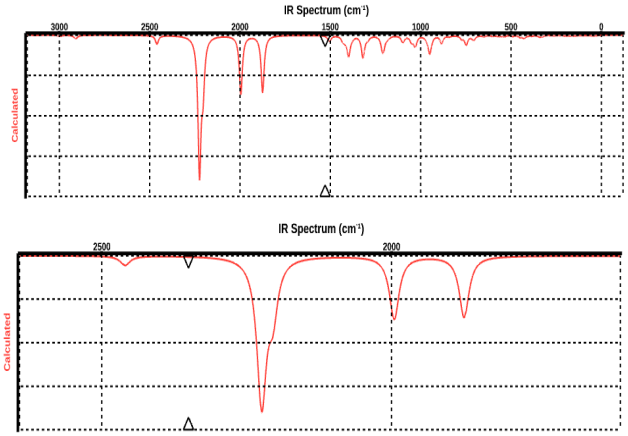


Figure S14. Calculated infrared spectrum for ***7MeC*** (Expansion showing ν_{CN}/ν_{CO} region)

Molecular Mechanics Modelling of Bent $CCNC_6H_3Me_2$ Ligand in $[5a]^+$.

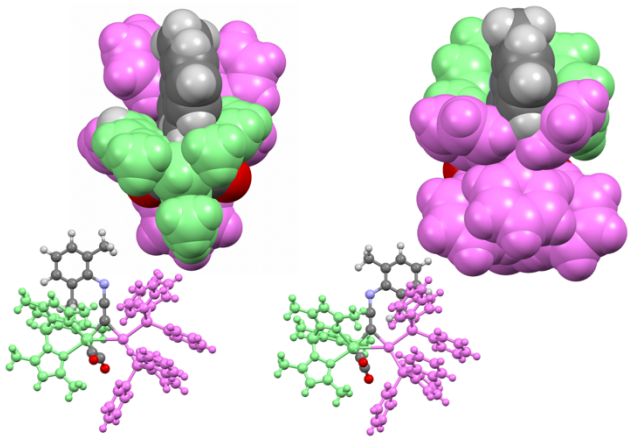


Figure S15. Illustration of non-viability of C–N–C binding of the $CCNC_6H_3Me_2$-2,6 ligand in [**5a**]$^+$ (Tp* ligand green, PPh_3 ligand pink).

Molecular Orbitals of Free Iminoketenylidenes

In contrast to CCO and CCS which have cylindrical $C_{\infty v}$ symmetry, hypothetical iminoketenylidenes have C_s symmetry due to bending at nitrogen thereby lifting the π-orbital degeneracy and, upon coordination, possibly giving rise to conformational preferences. We consider here the valence orbitals and geometries of the free iminoketenylidenes CCNMe (***6$_s$Me***) and CCNPh (***6$_s$Ph***) which are depicted in Figure S16 (ωB97X-V/6-31G*). The singlet geometries of both derivatives have conventional sp^2-N angles (***6$_s$Me***: 118.7°, ***6$_s$Ph***: 121.1°) and short C=N and C=C (Ph: 1.307, Me: 1.316 Å) bonds. The triplet optimised geometries ***6$_t$Me*** and ***6$_t$Ph*** lie, respectively, 1.5 and 10.1 kcalmol^{-1} (RI-MP2/cc-pVTζ) above the corresponding singlet geometries at this level of theory, the latter reflecting the clear and quite substantial involvement of arene-based orbitals. The most dramatic change in geometry in proceeding from singlet to triplet spin multiplicities is the opening of the C–N–C angle to 149.3° for ***6$_t$Me*** and 147.7° for ***6$_t$Ph*** and attended by a modest increase in the negative charge at the terminal carbon, consistent with increased *sp*-character in the nitrogen hybridisation. The frontier orbitals for ***6$_s$Ph*** comprise *one* energetically accessible π-acceptor orbital (LUMO) and a low lying σ-donor orbital (HOMO-3) straddled by two occupied orbitals of π-symmetry (HOMO, HOMO-1).

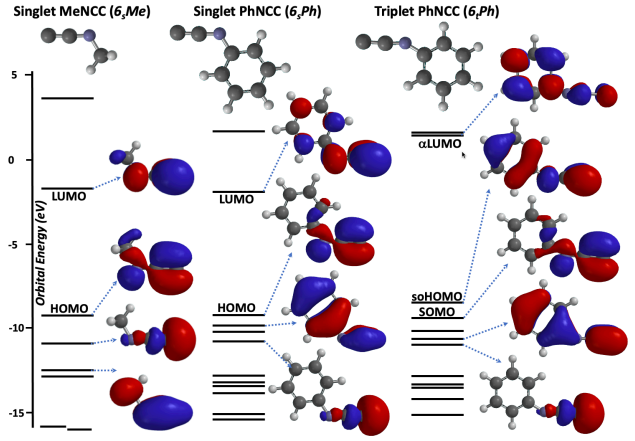
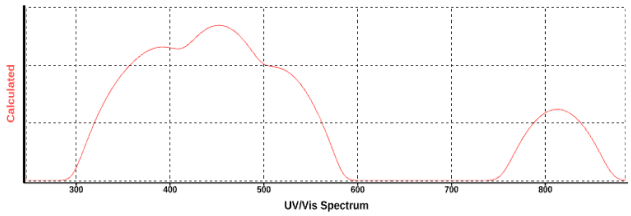


Figure S16. Frontier orbitals of interest for optimised geometries (DFT: ωB97X-V/6-31G*) of (a) singlet CCNMe ***6$_s$Me*** and CCNPh ***6$_s$Ph*** and (b) triplet CCNPh ***6$_t$Ph***.

Calculated[a] Electronic Spectrum for *7MesP*

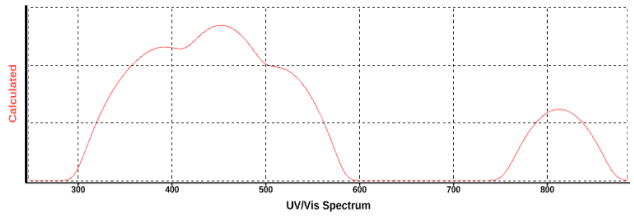


Wavelength nm	Intensity (relative)	Origin	Contribution %
368.78	0.0066	HOMO-4 → LUMO	62%
391.74	0.0378	HOMO → LUMO+1	57%
		HOMO-1 → LUMO+1	30%
414.13	0.0050	HOMO-1 → LUMO+1	58%
		HOMO → LUMO+1	31%
452.18	0.2419	HOMO-1 → LUMO	80%
511.54	0.0082	HOMO-2 → LUMO	82%
812.67	0.0003	HOMO → LUMO	87%

TD-DFT: ωB97X-V/6-31G*/LANL2Dz(W,Pt)

Calculated[a] Electronic Spectrum for [5a]$^+$

Due to the large number of atoms in the real complex [**5a**]$^+$, the following data were calculated based on the non-optimised crystallographically determined geometry for [5a]+ and are only provided for



Wavelength nm	Intensity (relative)	Origin	Contribution %
368.78	0.0066	HOMO-4 → LUMO	62%
391.74	0.0378	HOMO → LUMO+1	57%
		HOMO-1 → LUMO+1	30%
414.13	0.0050	HOMO-1 → LUMO+1	58%
		HOMO → LUMO+1	31%
452.18	0.2419	HOMO-1 → LUMO	80%
511.54	0.0082	HOMO-2 → LUMO	82%
812.67	0.0003	HOMO → LUMO	87%

TD-DFT: ωB97X-V/6-31G*/LANL2Dz(W,Pt)

Author Contributions

Both LKB and AFH contributed equally to the conceptualization, experimental design, interpretation of experimental results and manuscript compilation. All experimental procedures and data acquisition, including structural analysis, were executed by LKB. AFH was responsible for overall project administration.

Notes and references

1 (a) L. K. Burt, R. L. Cordiner, A. F. Hill, R. A. Manzano and J. Wagler, *Chem. Commun.*, **2020**, 56, 5673–5676. (b) M. Green, J. A. K. Howard, M. Murray, J. L. Spencer and F. G. A. Stone, J. Chem. Soc., Dalton Trans., **1977**, 1509-1514.

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3 (*a*) G. Sheldrick, *Acta Crystallogr.*, *Sect A: Found Crystallogr.,* 2008, **64**, 112–122; (*b*) G. M. Sheldrick, *Acta Crystallogr., Sect C: Cryst. Struct. Commun.,* 2015, **71**, 3–8.

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5 *Spartan18®*, Wavefunction, Inc., 18401 Von Karman Ave., Suite 370, Irvine, CA 92612 U.S.A., 2018

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Selected Spectra

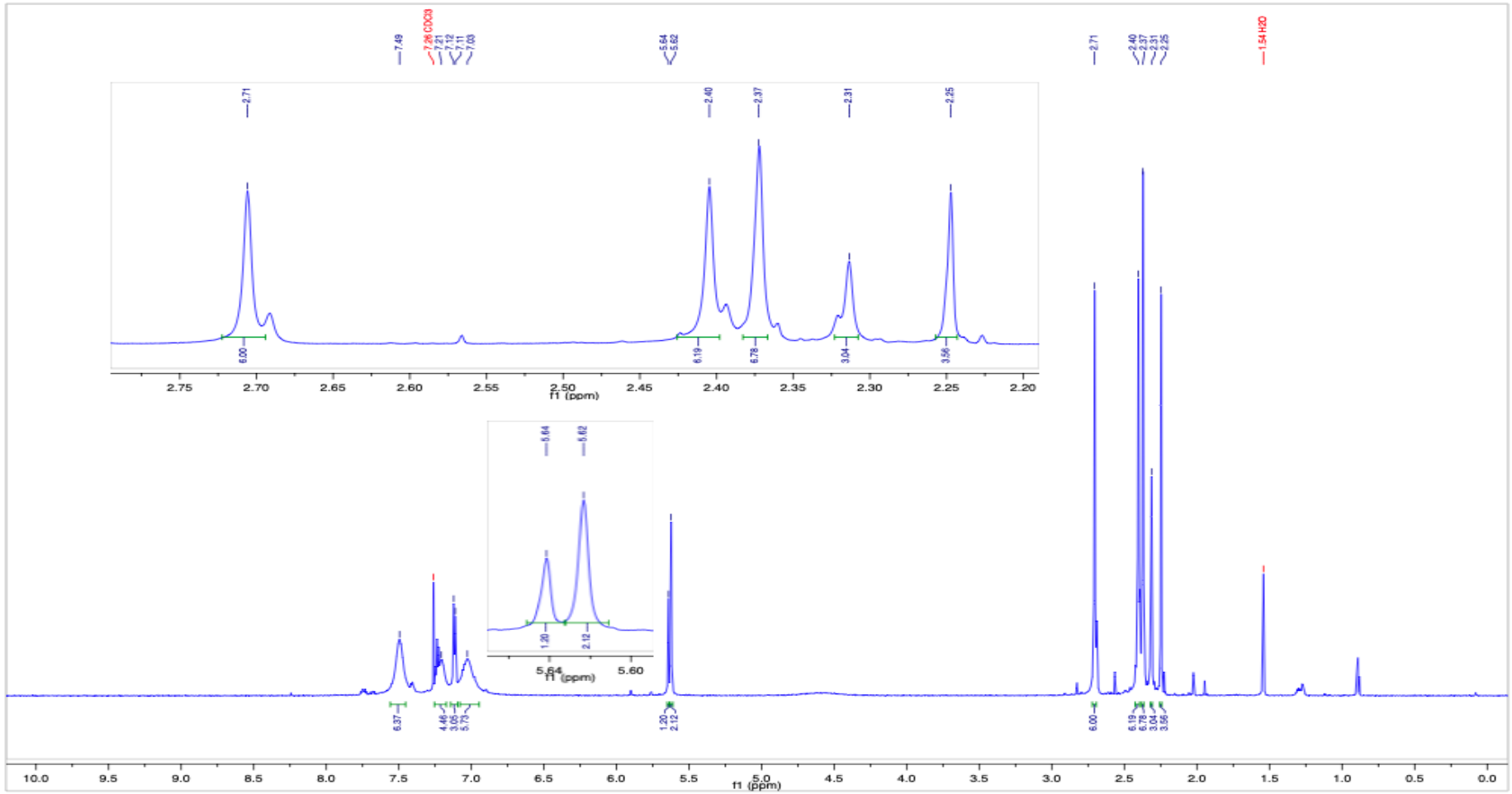

Figure S17. ^{1}H NMR Spectrum (700 MHz, $CDCl_3$, 298 K, δ) of [$WPt(\mu\text{-}C)Br(CO)_2(CNC_6H_3Me_2)(PPh_3)(Tp^*)$] (**3a**).

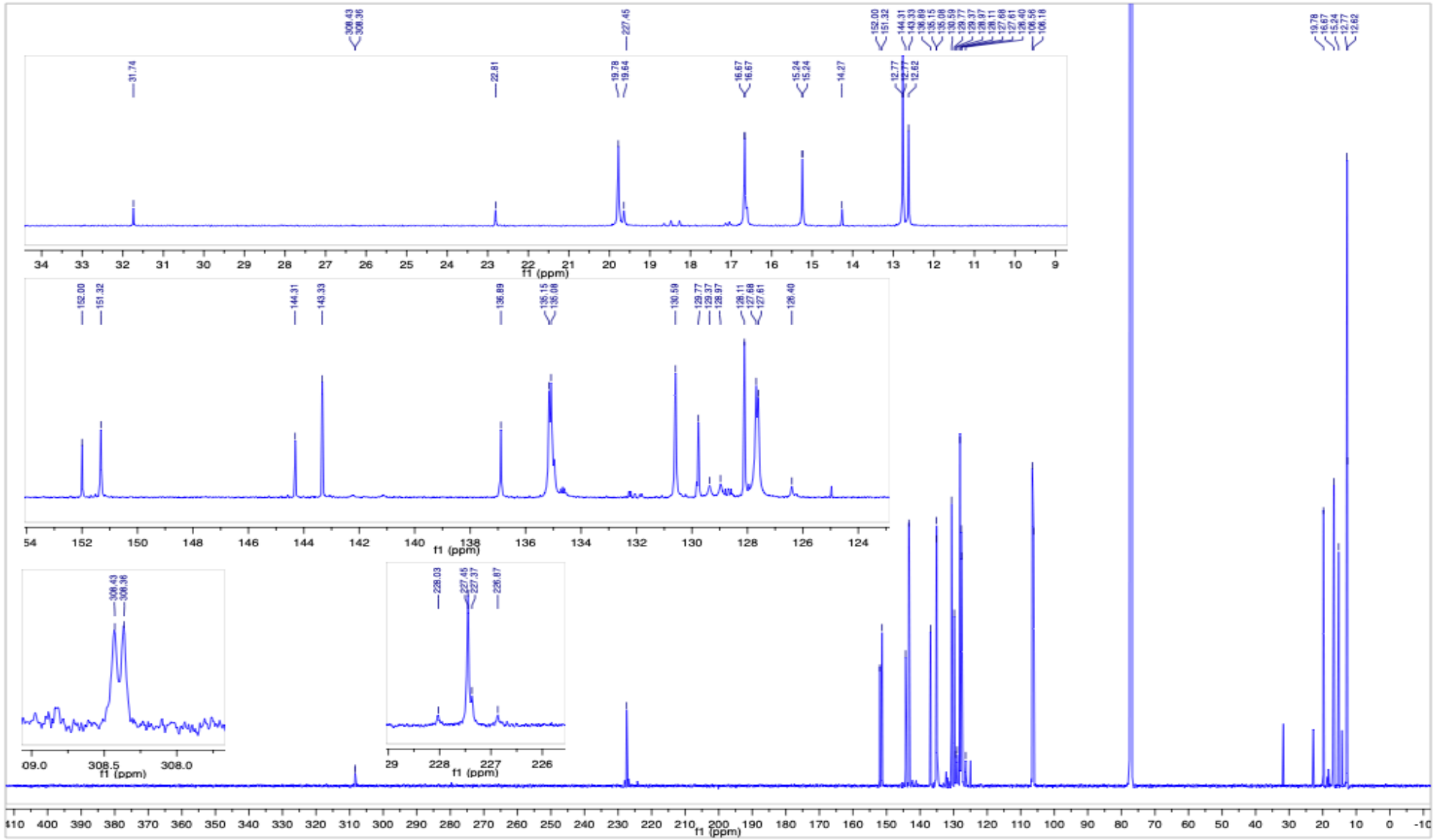

Figure S18. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, $CDCl_3$, 298 K, δ) of $[WPt(\mu\text{-}C)Br(CO)_2(CNC_6H_3Me_2)(PPh_3)(Tp^*)]$ (**3a**).

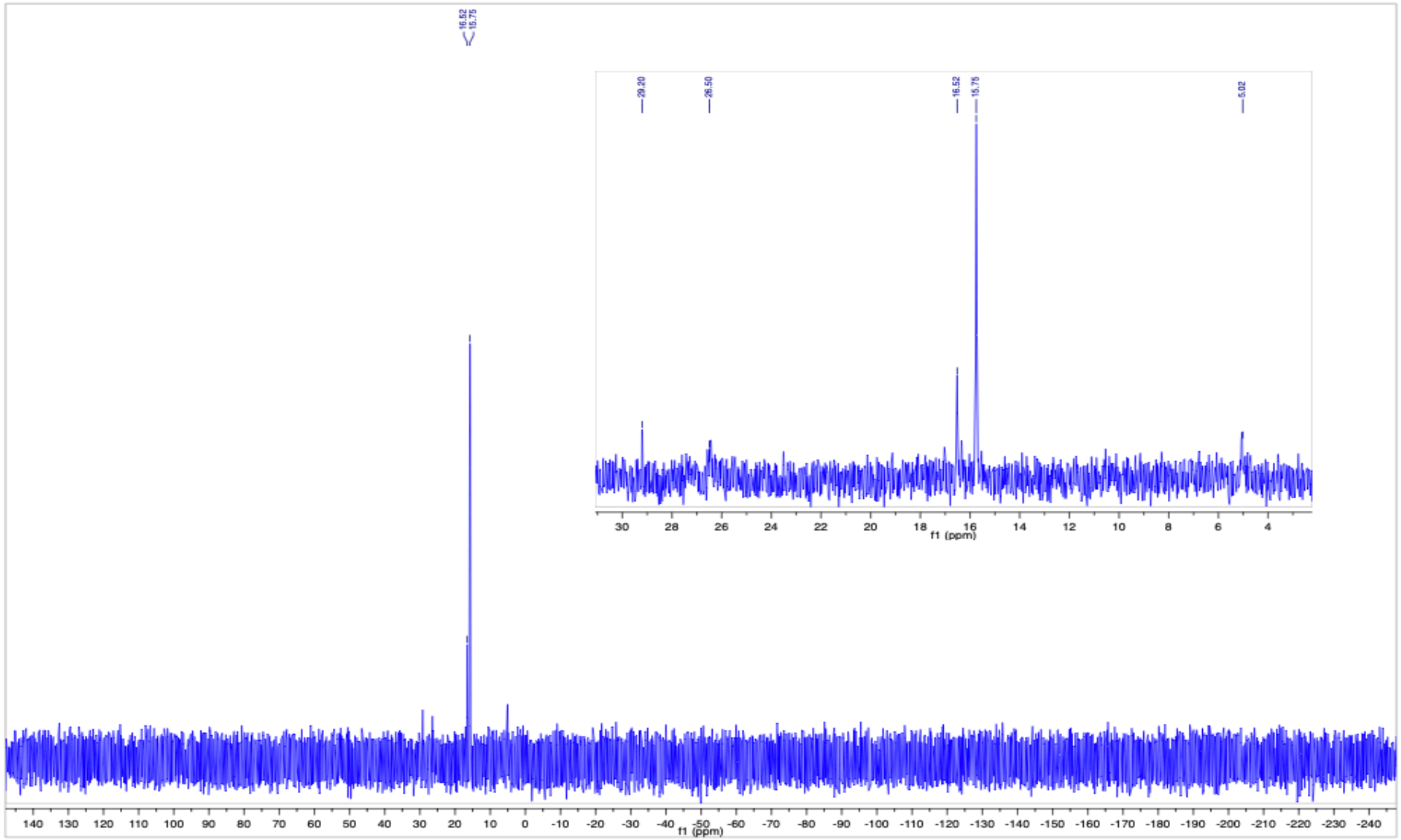

Figure S19. $^{31}P\{^{1}H\}$ NMR Spectrum (162 MHz, $CDCl_3$, 298 K, δ) of $[WPt(\mu\text{-}C)Br(CO)_2(CNC_6H_3Me_2)(PPh_3)(Tp^*)]$ (**3a**).

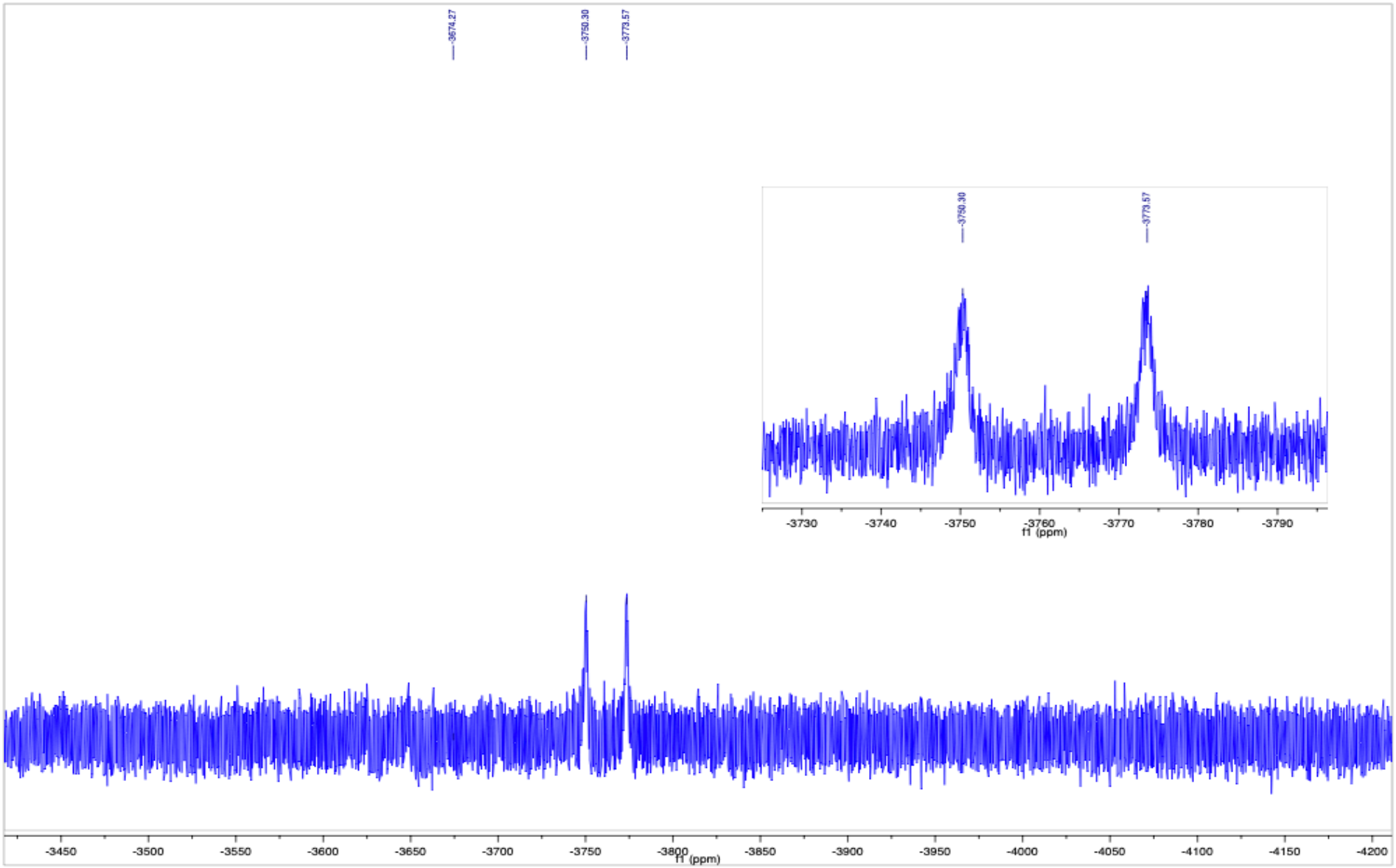

Figure S20. $^{195}Pt\{^{1}H\}$ NMR Spectrum (149.9 MHz, $CDCl_3$, 298 K, δ) of $[WPt(\mu\text{-}C)Br(CO)_2(CNC_6H_3Me_2)(PPh_3)(Tp^*)]$ (**3a**)

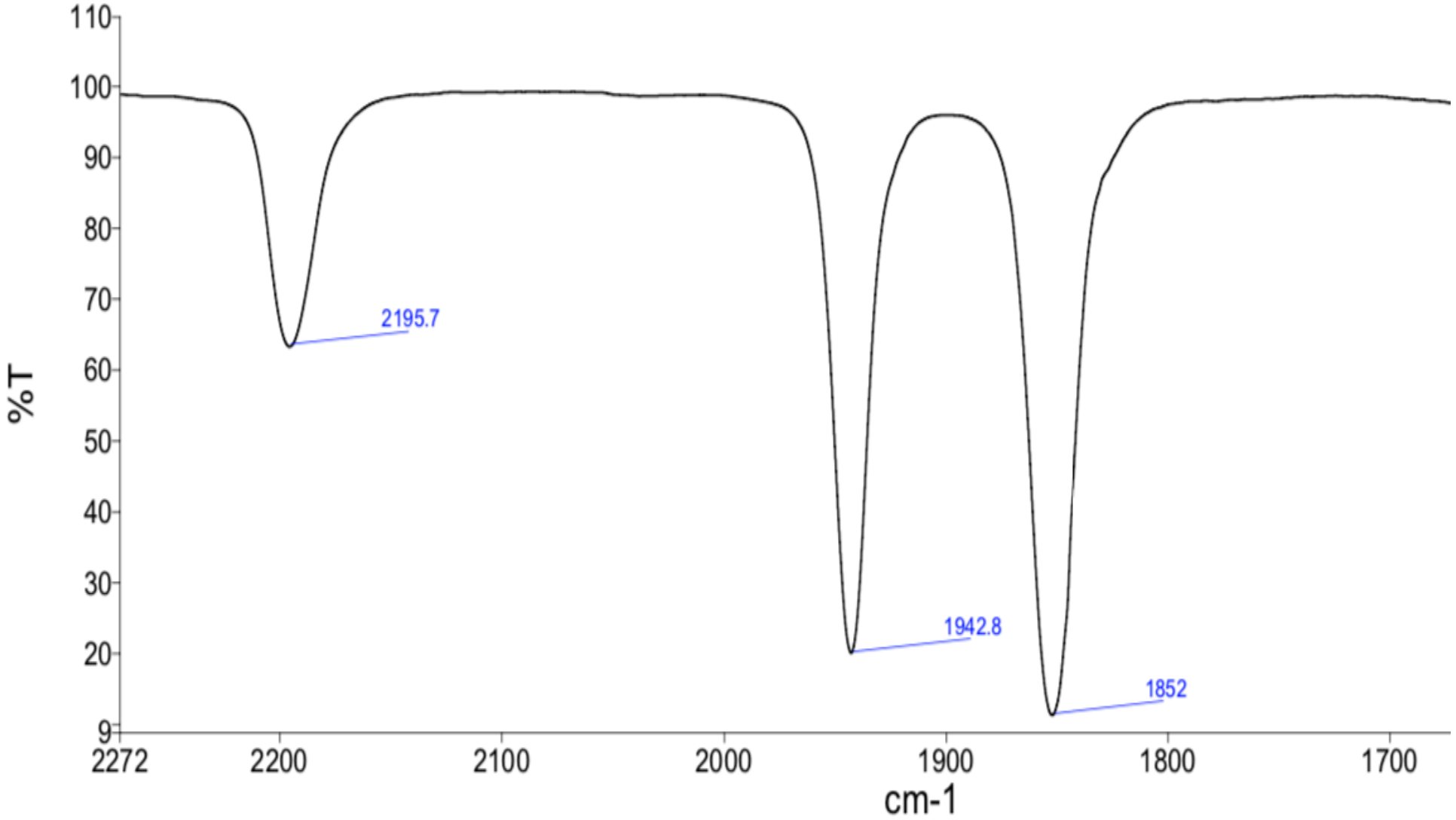

Figure S21. Infrared Spectrum (CH_2Cl_2, 298 K, cm^{-1}) of [WPt(μ-C)Br(CO)$_2$($CNC_6H_3Me_2$)(PPh_3)(Tp*)] (**3a**)

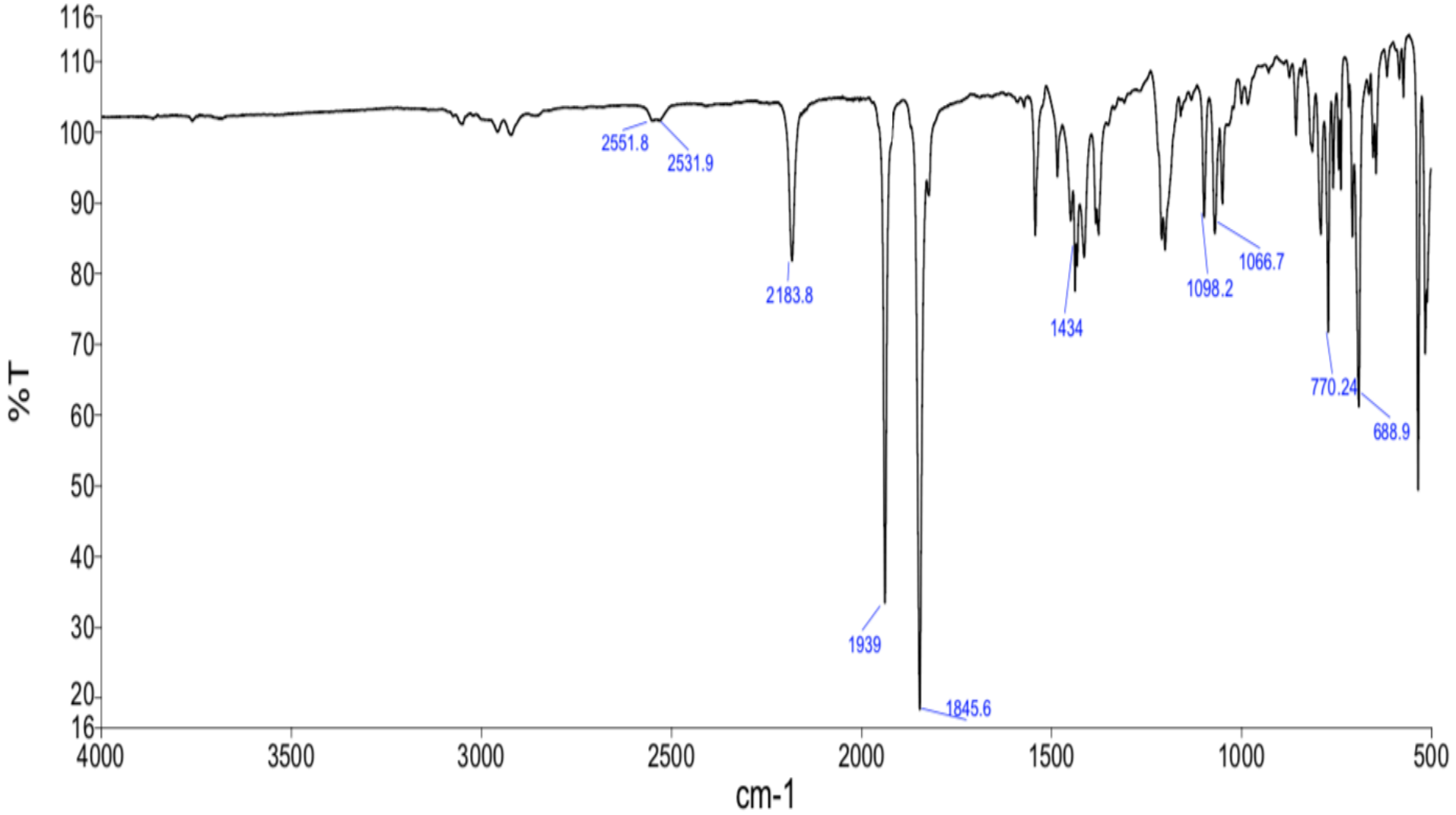

Figure S22. Infrared Spectrum (ATR Diamond anvil,, 298 K, cm^{-1}) of [WPt(μ-C)Br(CO)$_2$(CNC$_6$H$_3$Me$_2$)(PPh$_3$)(Tp*)] (**3a**)

Elemental Composition Report

Single Mass Analysis

Tolerance = 3.0 PPM / DBE: min = -1.5, max = 30.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
872 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-50 H: 0-50 11B: 1-1 N: 0-7 O: 0-2 P: 0-1 79Br: 0-1 81Br: 0-1 184W: 0-1 195Pt: 0-1

LB-5-90/AJ
66373
0127 55 (0.126) Cm (53:77)

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11-Feb-2021
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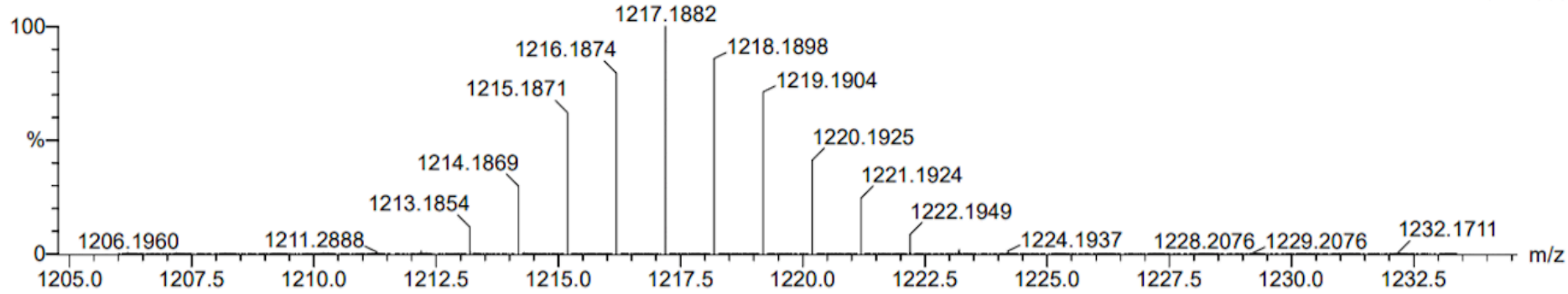

Minimum:				-1.5				
Maximum:		5.0	3.0	30.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
1216.1874	1216.1884	-1.0	-0.8	29.5	1165.8	n/a	n/a	C45 H46 11B N7 O2 P 79Br 184W 195Pt

Figure S23. ESI Mass Spectrum (+ve ion) of [WPt(μ-C)Br(CO)$_2$(CNC$_6$H$_3$Me$_2$)(PPh$_3$)(Tp*)] (**3a**).

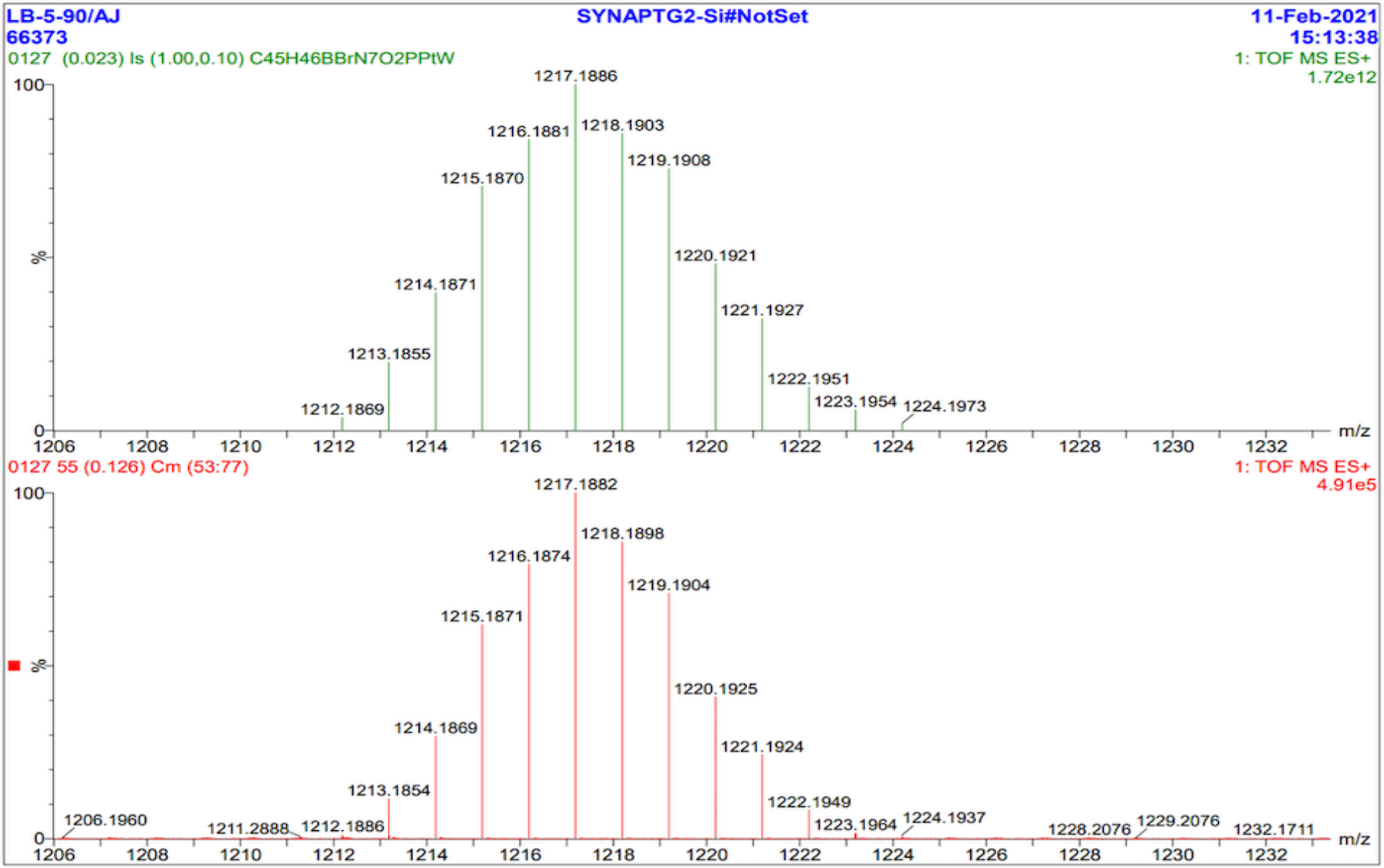

Figure S24. ESI Mass Spectrum (Red = measured; green = isotopic simulation) of [WPt(μ-C)Br(CO)$_2$(CNC$_6$H$_3$Me$_2$)(PPh$_3$)(Tp*)] (**3a**).

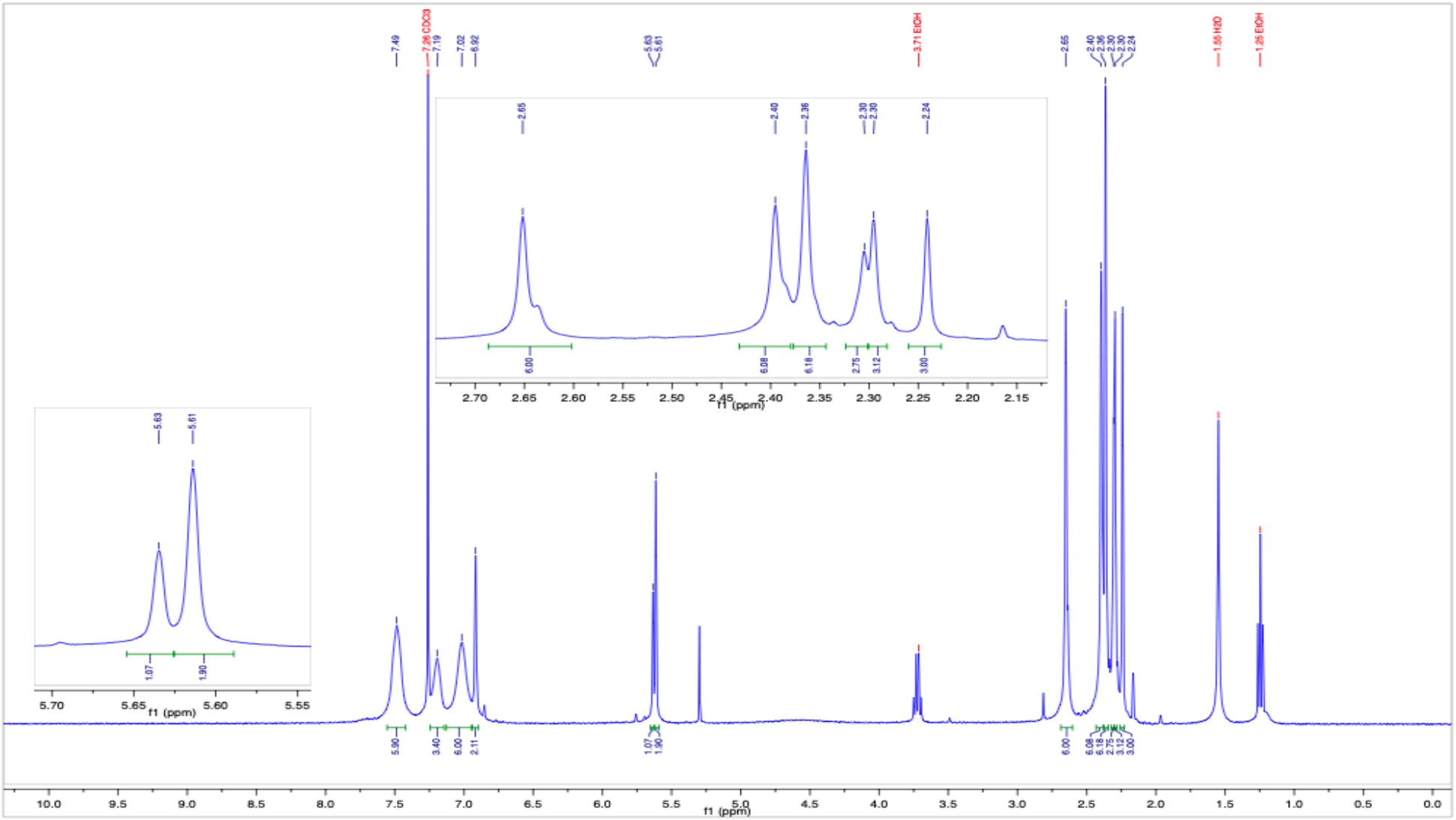

Figure S25. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$, 298 K, δ) of [WPt(μ-C)Br(CO)$_2$($CNC_6H_2Me_3$)(PPh_3)(Tp*)] (**3b**).

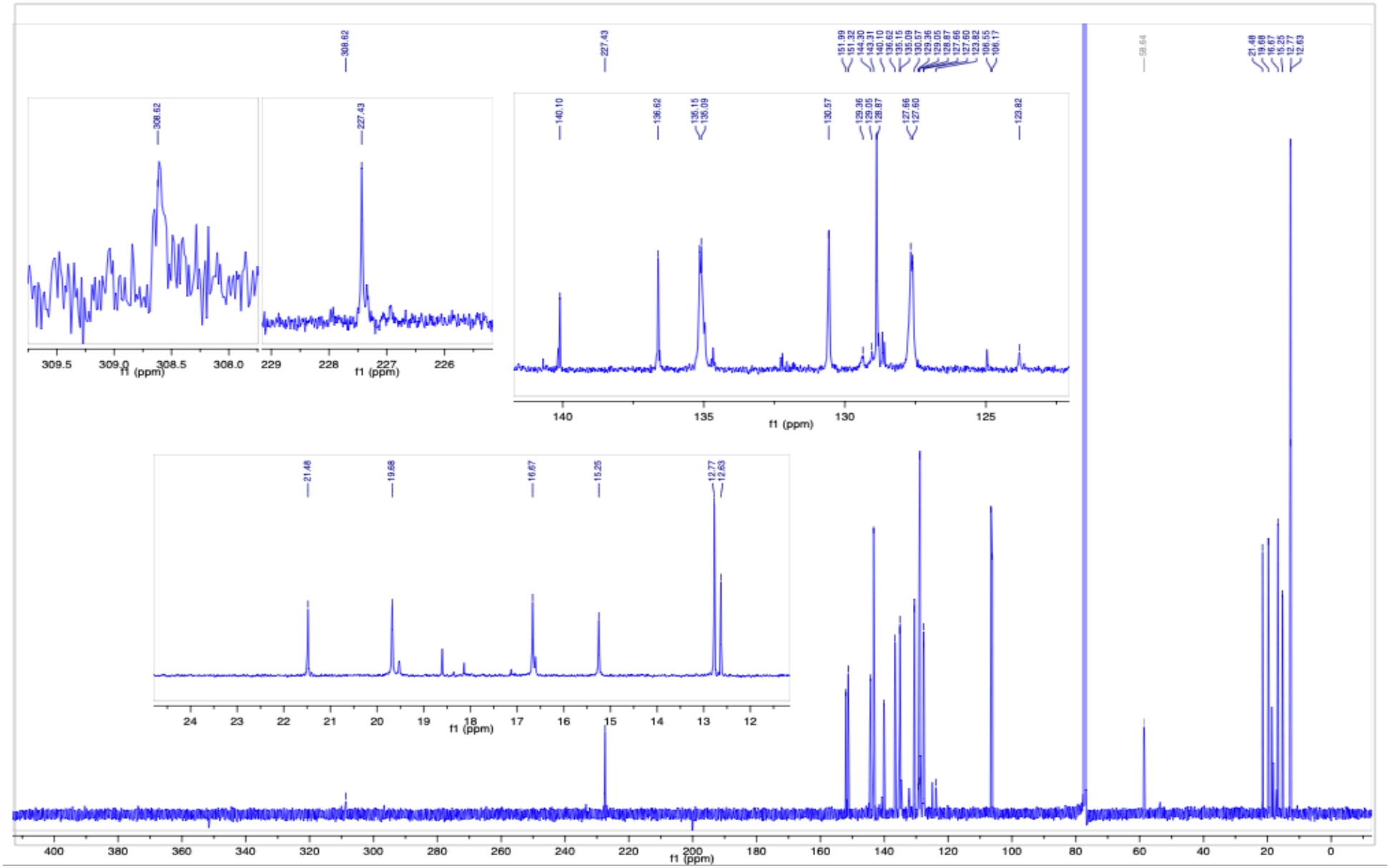

Figure S26. $^{13}C\{^{1}H\}$ NMR Spectrum (176 MHz, $CDCl_3$, 298 K, δ) of $[WPt(\mu\text{-}C)Br(CO)_2(CNC_6H_2Me_3)(PPh_3)(Tp^*)]$ (**3b**).

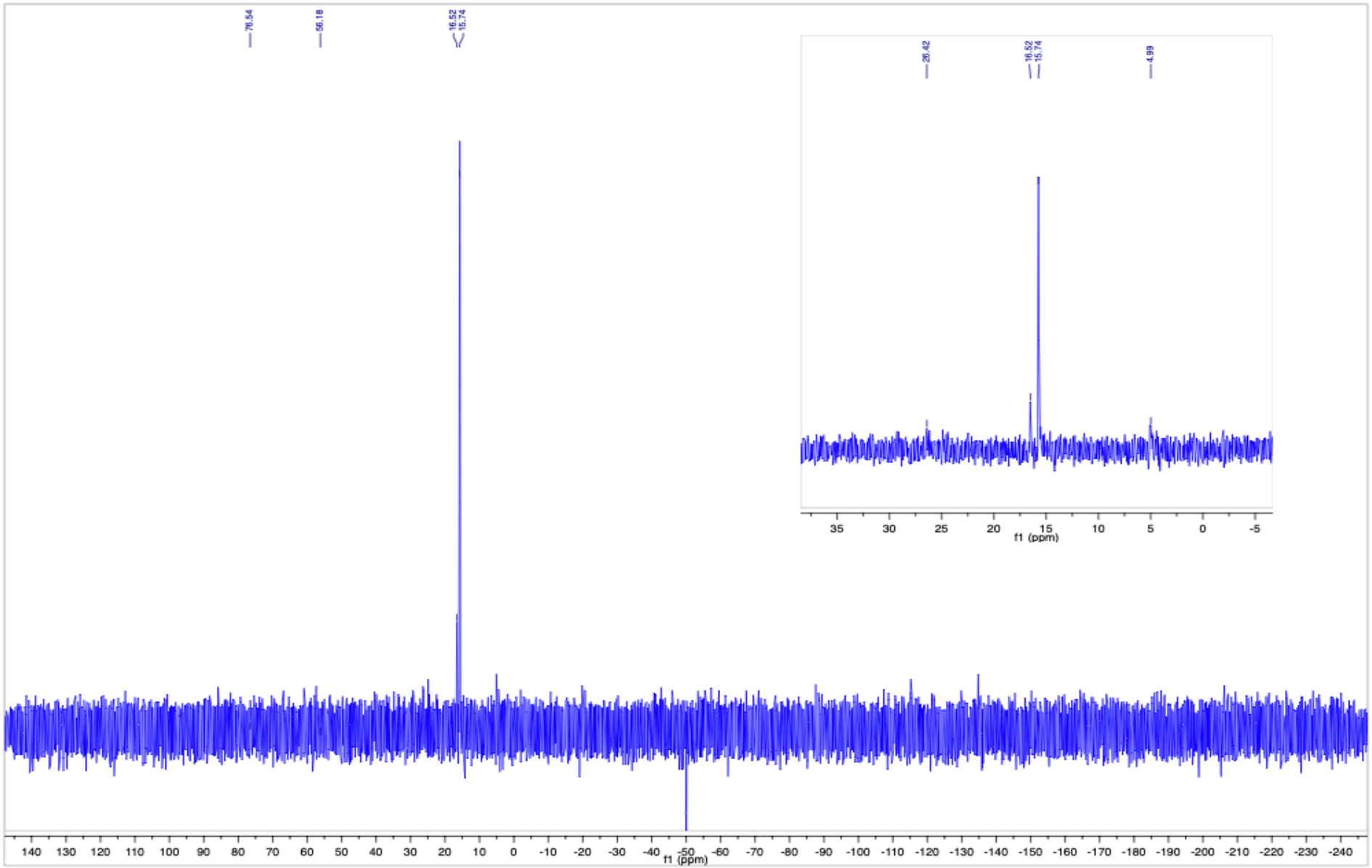

Figure S27. $^{31}P\{^{1}H\}$ NMR Spectrum (162 MHz, $CDCl_3$, 298 K, δ) of $[WPt(\mu\text{-}C)Br(CO)_2(CNC_6H_2Me_3)(PPh_3)(Tp^*)]$ (**3b**).

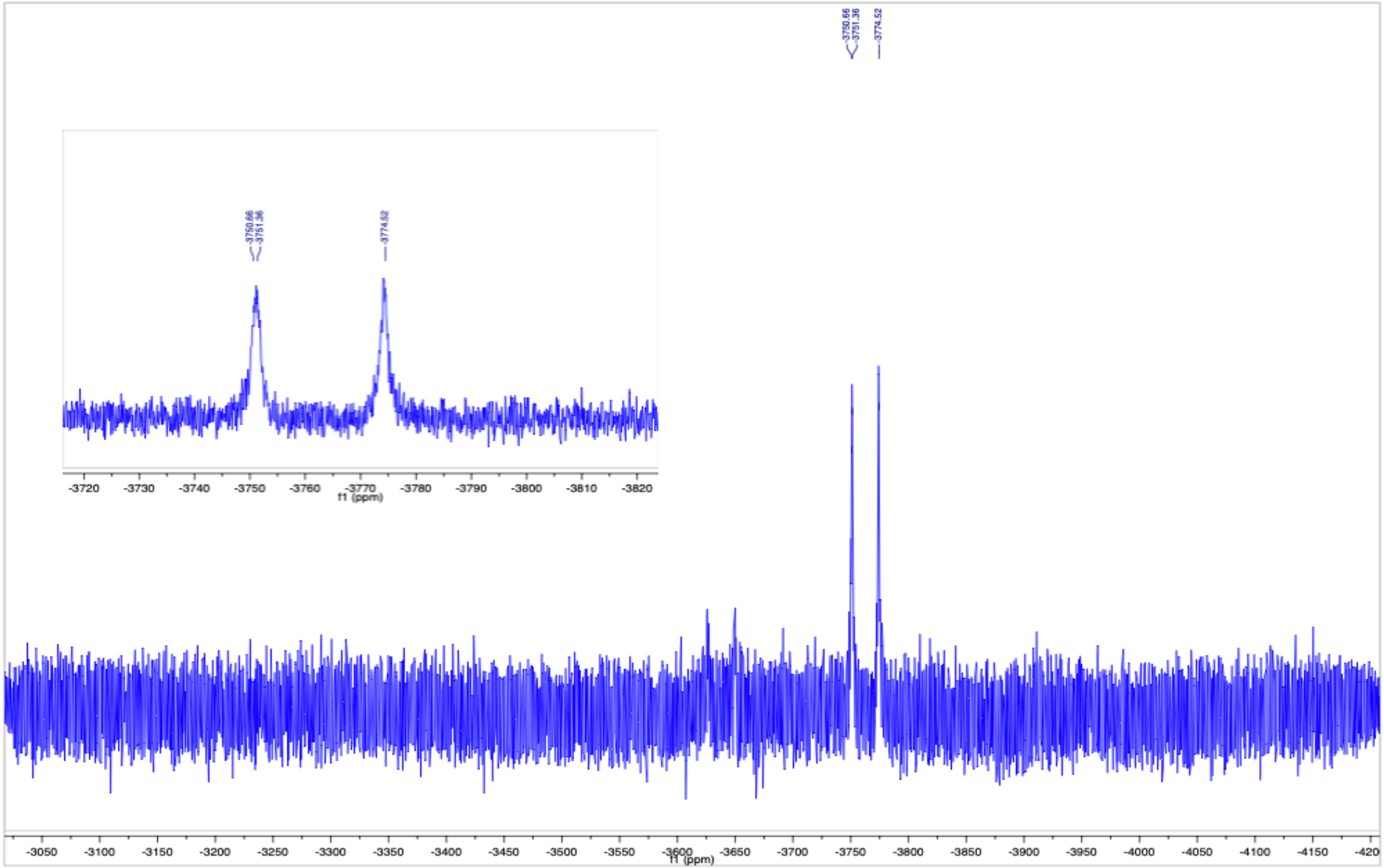

Figure S28. $^{195}Pt\{^{1}H\}$ NMR Spectrum (149.9 MHz, $CDCl_3$, 298 K, δ) of $[WPt(\mu\text{-}C)Br(CO)_2(CNC_6H_2Me_3)(PPh_3)_2(Tp^*)]$ (**3b**)

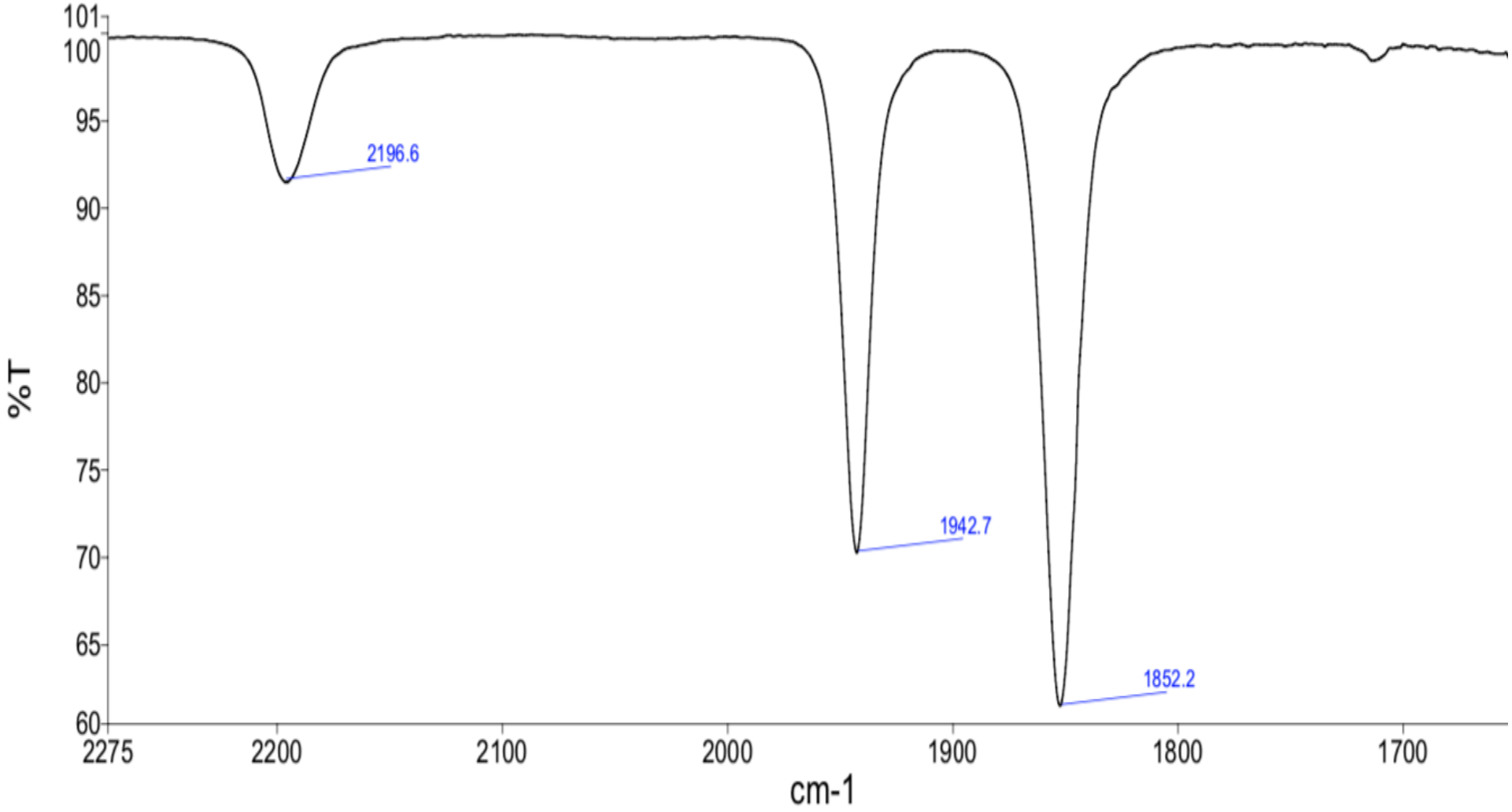

Figure S29. Infrared Spectrum (CH_2Cl_2, 298 K, cm^{-1}) of [WPt(μ-C)Br$(CO)_2(CNC_6H_2Me_3)(PPh_3)$(Tp*)] (**3b**)

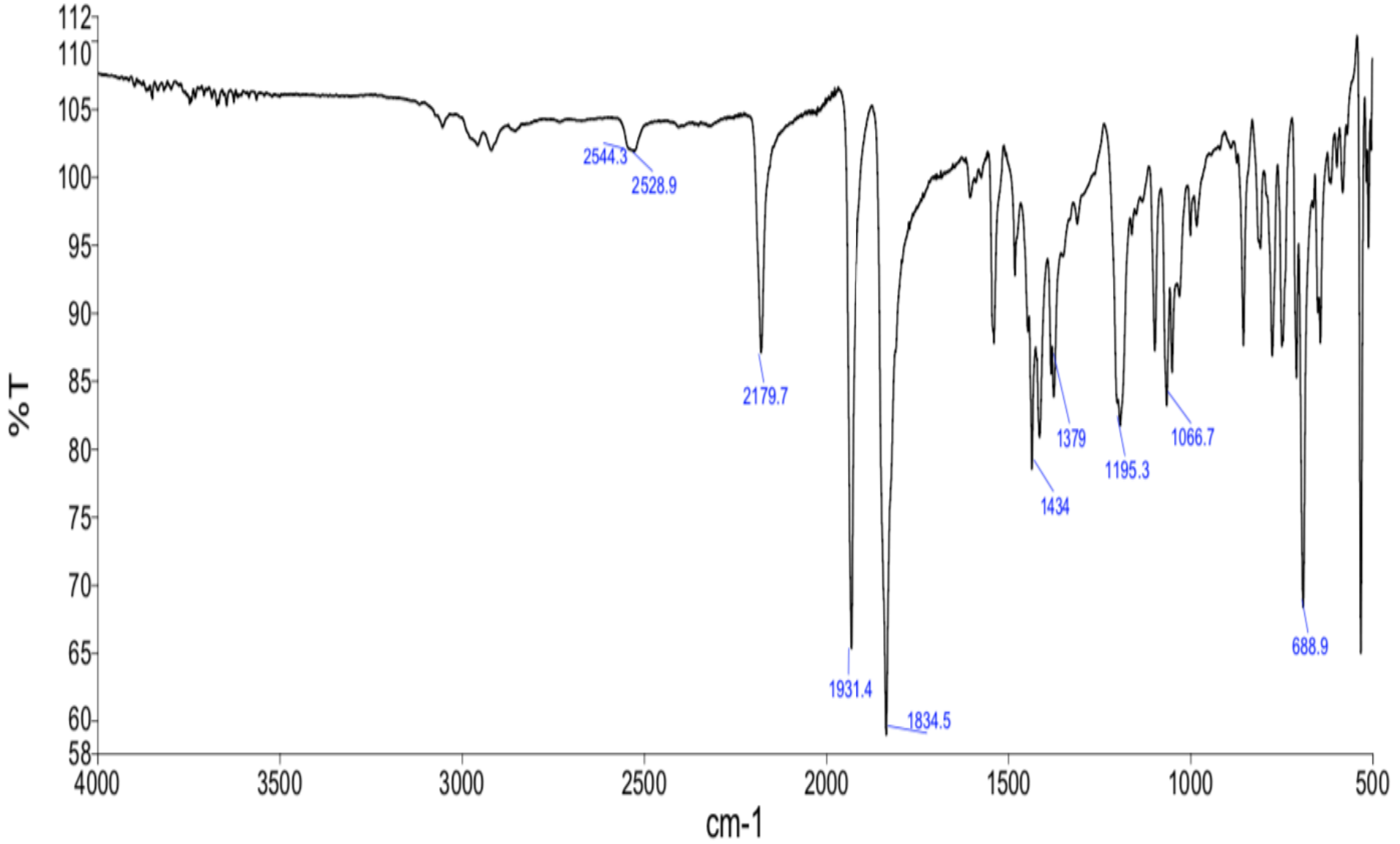

Figure S30. Infrared Spectrum (ATR, Diamond anvil, 298 K, cm^{-1}) of [WPt(μ-C)Br(CO)$_2$(CNC$_6$H$_2$Me$_3$)(PPh$_3$)(Tp*)] (**3b**)

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 30.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
961 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-50 H: 0-50 11B: 1-1 N: 0-8 O: 0-2 P: 0-1 79Br: 0-1 81Br: 0-1 184W: 0-1 195Pt: 0-1

LB-5-18[2]-MeOH/AJ 21-Oct-2020 10:09:31
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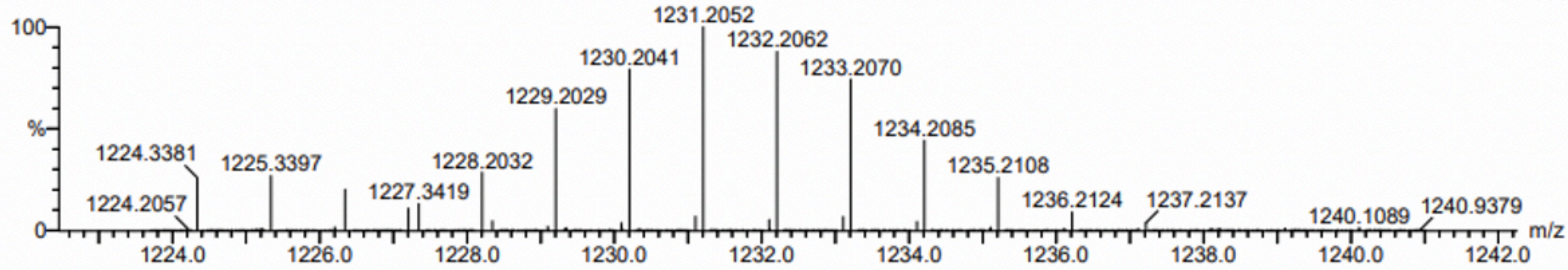
SYNAPTG2-Si#UGB759
1: TOF MS ES+
4.75e+005



Minimum:				-1.5				
Maximum:		5.0	5.0	30.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
1232.2062	1232.2020	4.2	3.4	29.5	1059.6	n/a	n/a	C46 H48 11B N7 O2 P 81Br 184W 195Pt

Figure S31. ESI Mass Spectrum (+ve ion) of [WPt(μ-C)Br(CO)$_2$(CNC$_6$H$_2$Me$_3$)(PPh$_3$)(Tp*)] (**3b**)

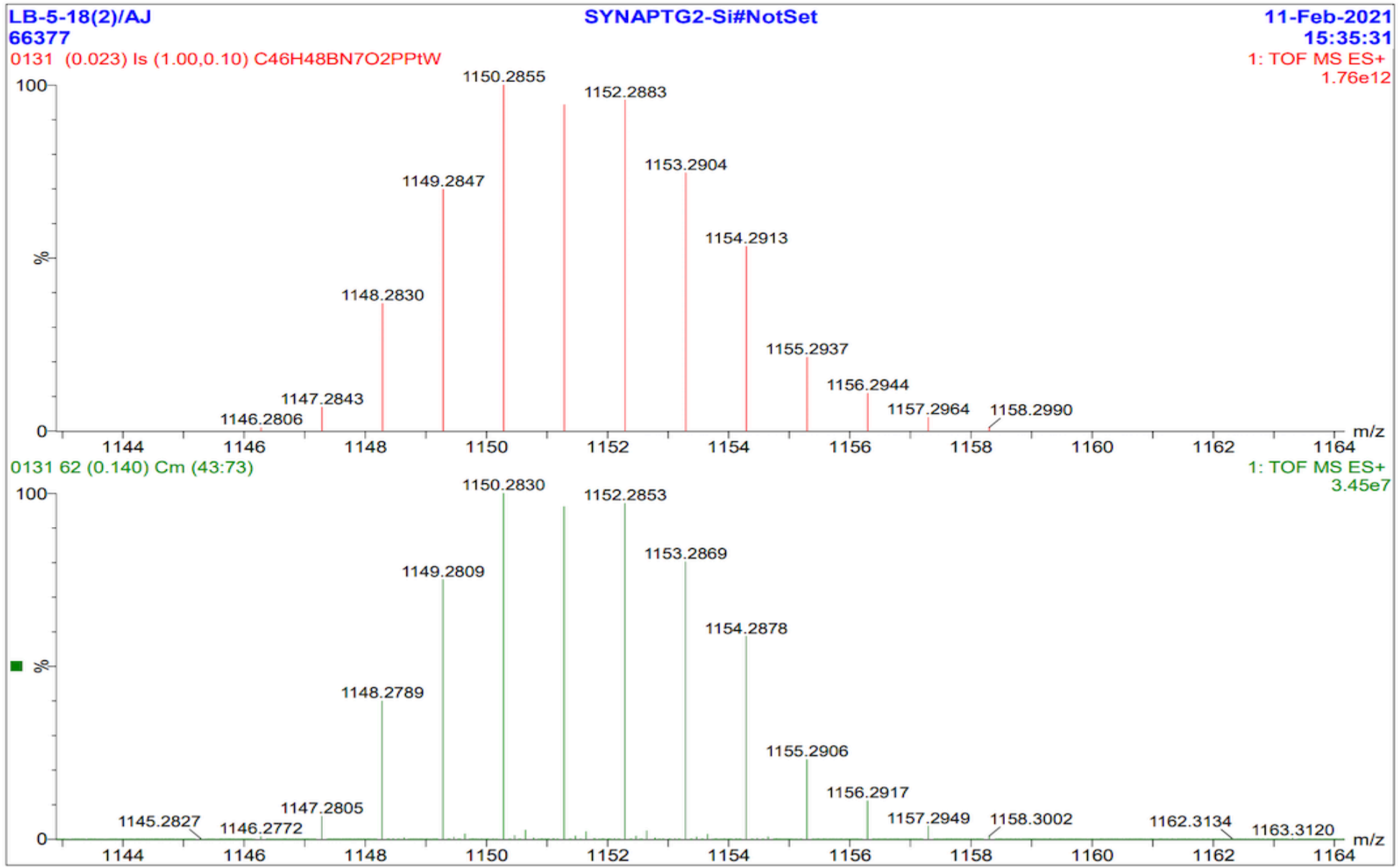


Figure S32. ESI Mass Spectrum (Red = measured; green = isotopic simulation) of [WPt(μ-C)Br(CO)$_2$(CNC$_6$H$_2$Me$_3$)(PPh$_3$)(Tp*)] (**3b**)

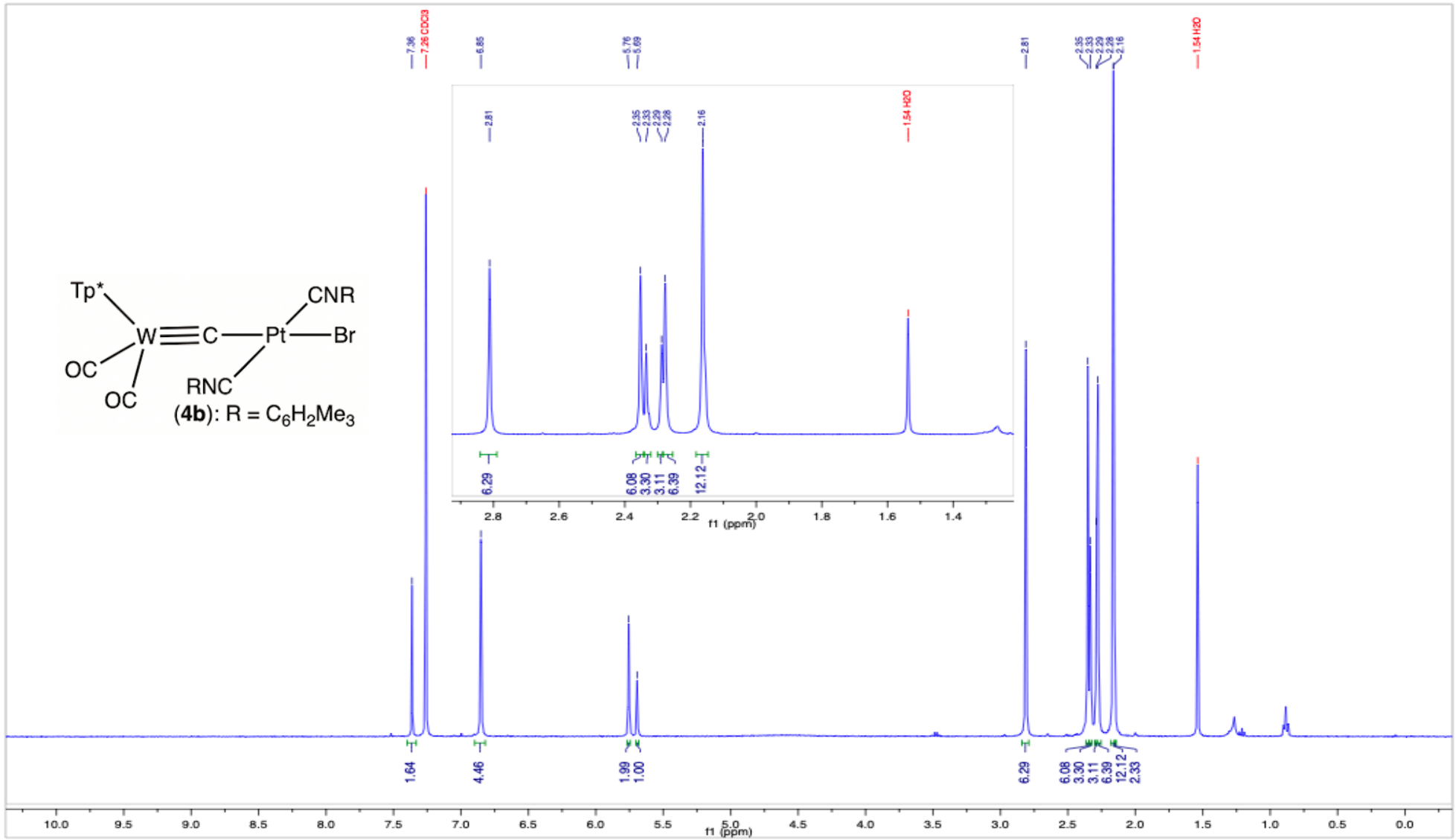


Figure S33. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$, 298 K, δ) of [WPt(μ-C)Br(CO)$_2$(CNC$_6$H$_2$Me$_3$)$_2$(Tp*)] (**4b**).

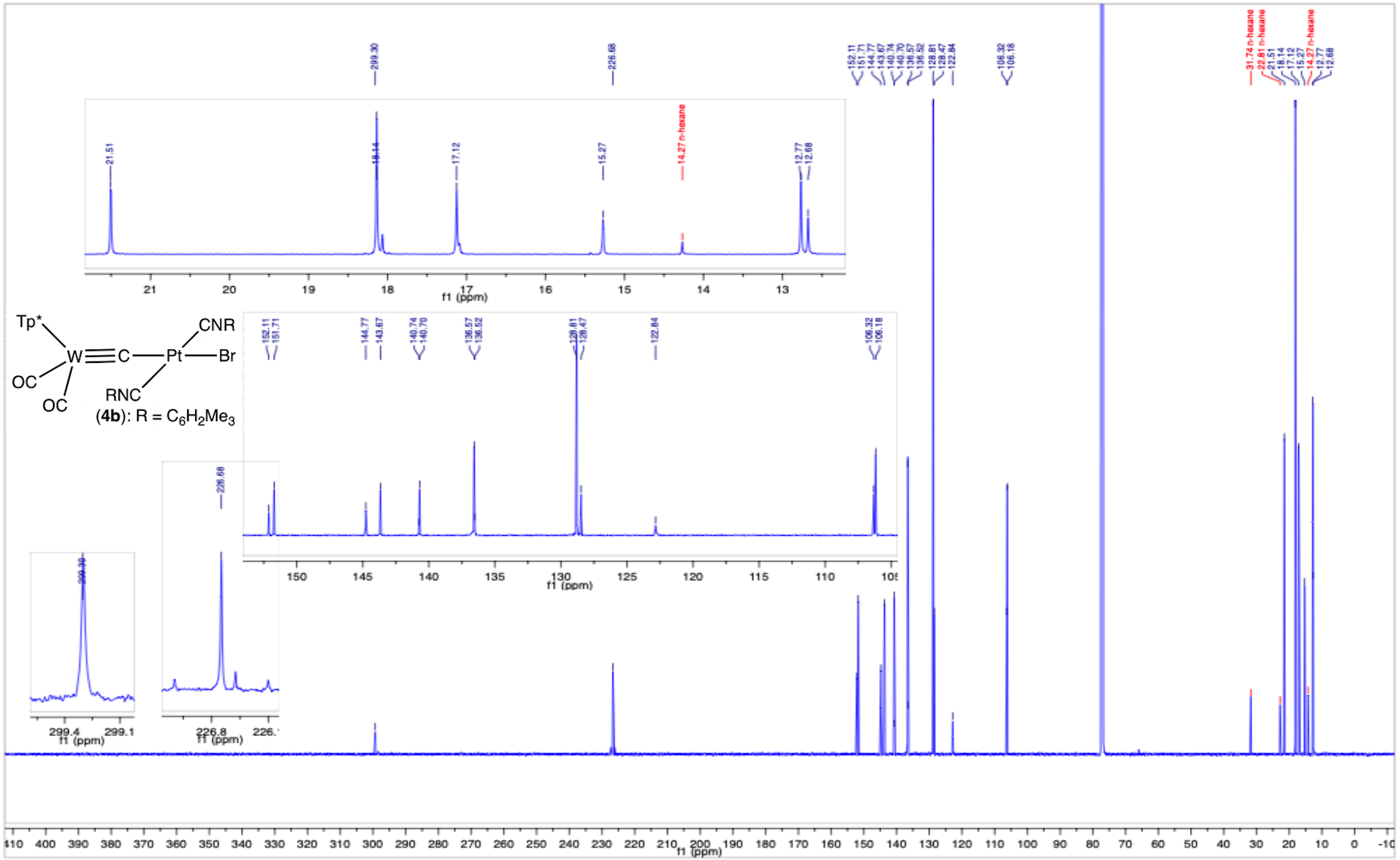


Figure S34. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, $CDCl_3$, 298 K, δ) of $[WPt(\mu\text{-}C)Br(CO)_2(CNC_6H_2Me_3)_2(Tp^*)]$ (**4b**).

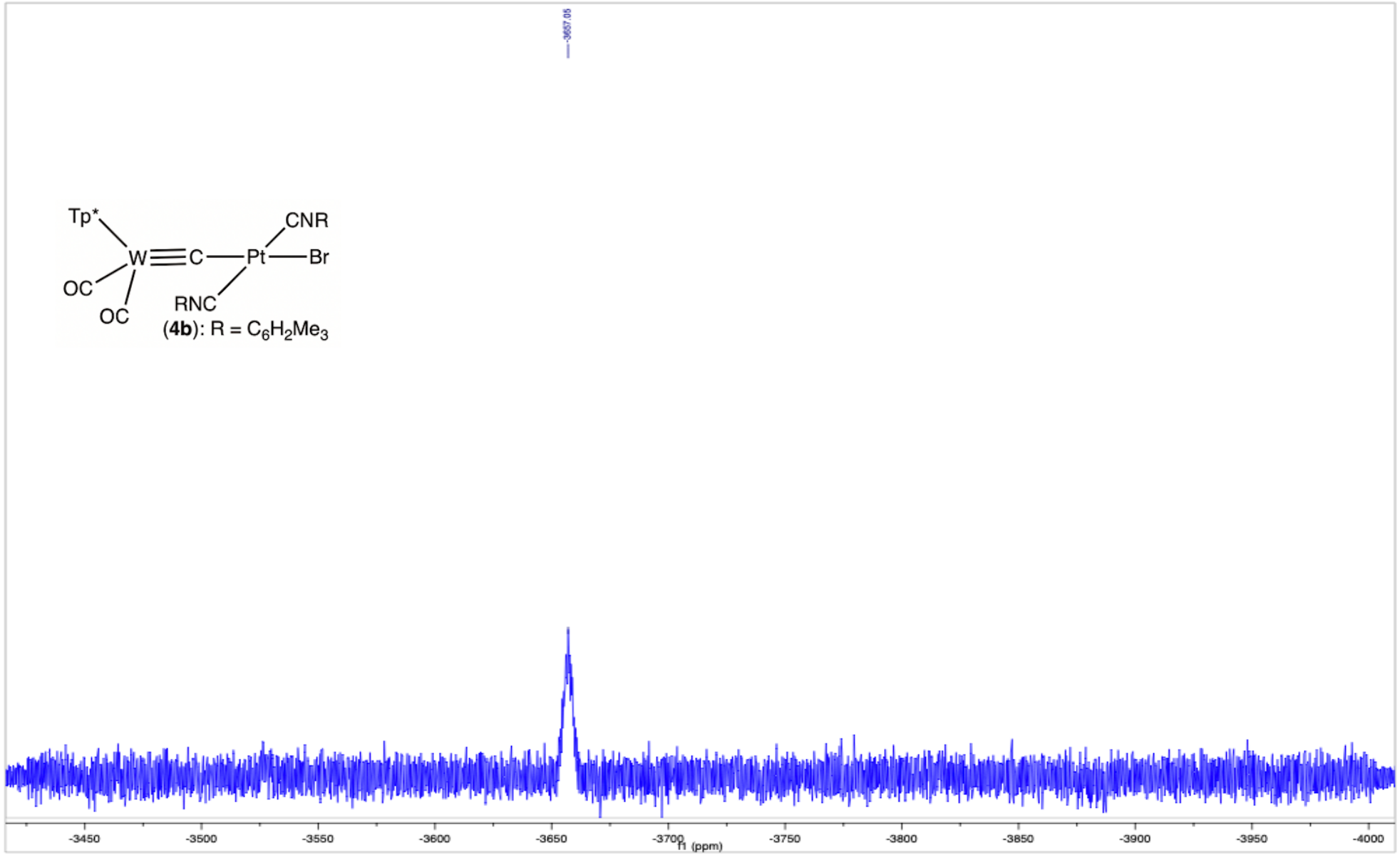


Figure S35. $^{195}Pt\{^{1}H\}$ NMR Spectrum (85.7 MHz, $CDCl_3$, 298 K, δ) of $[WPt(\mu\text{-}C)Br(CO)_2(CNC_6H_2Me_3)_2(Tp^*)]$ (**4b**).

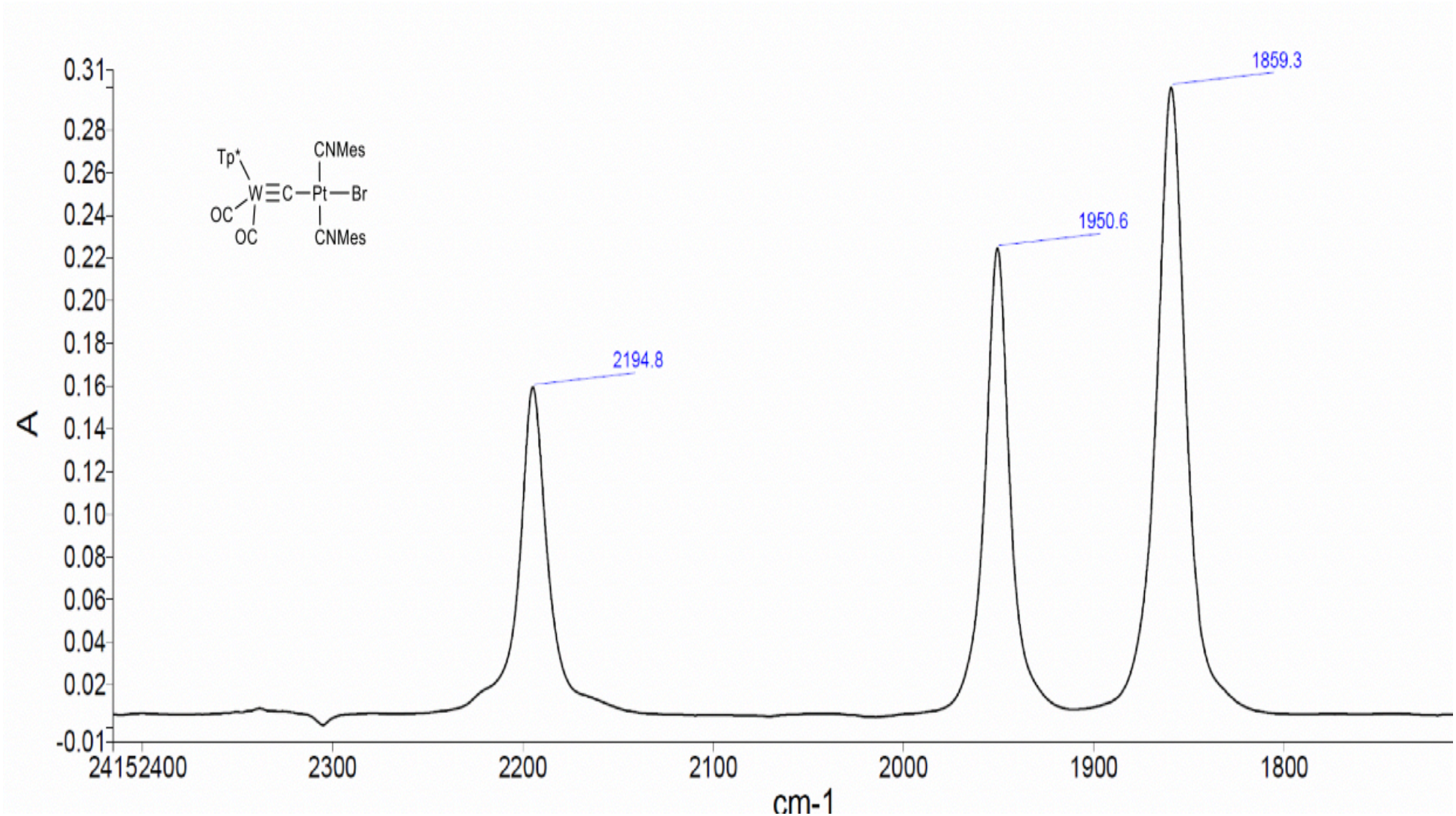


Figure S36. Infrared Spectrum (CH_2Cl_2, 298 K, cm^{-1}) of [WPt(μ-C)Br$(CO)_2(CNC_6H_2Me_3)_2$(Tp*)] (**4b**)

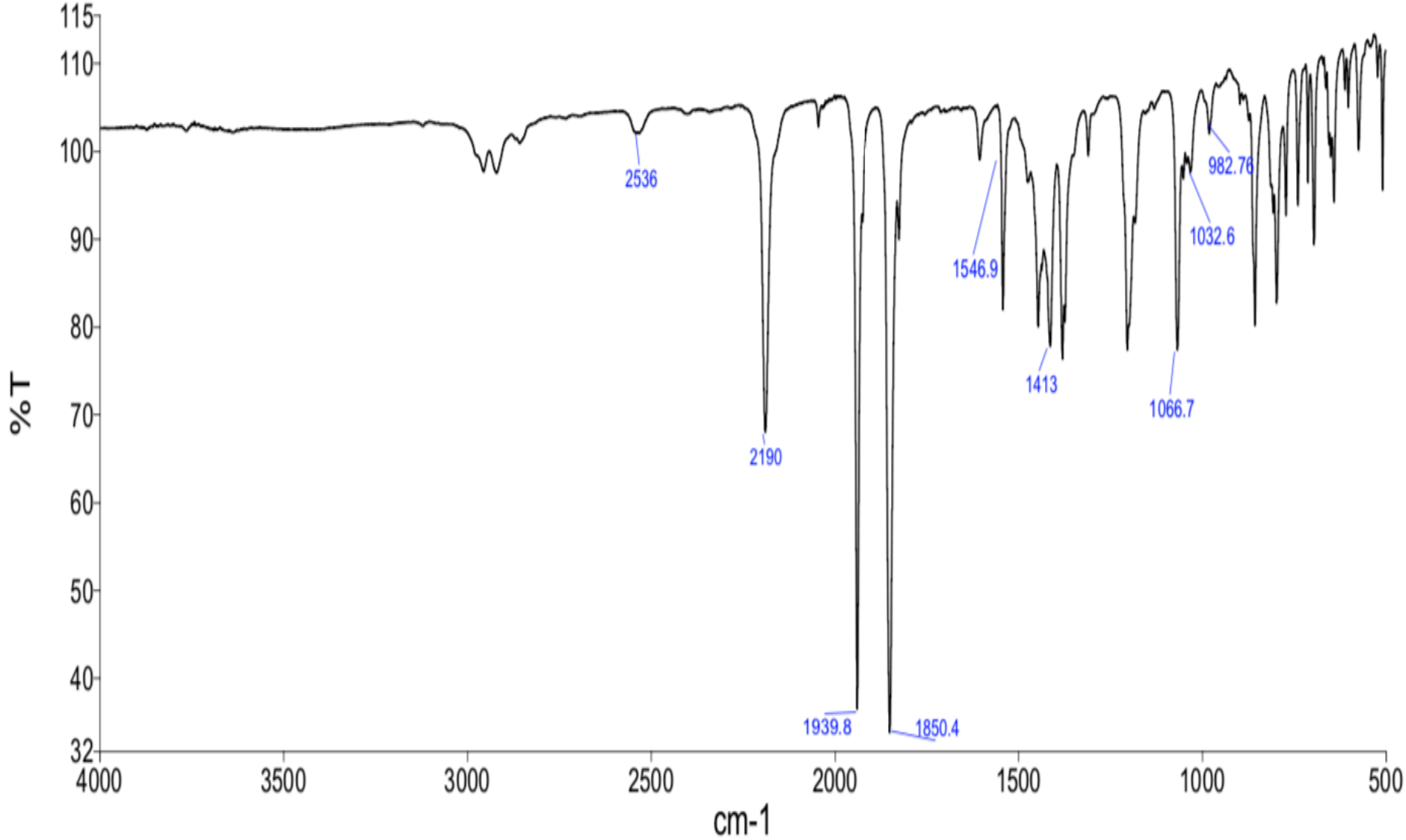


Figure S37. Infrared Spectrum (ATR, diamond anvil, 298 K, cm^{-1}) of [WPt(μ-C)Br$(CO)_2(CNC_6H_2Me_3)_2$(Tp*)] (**4b**)

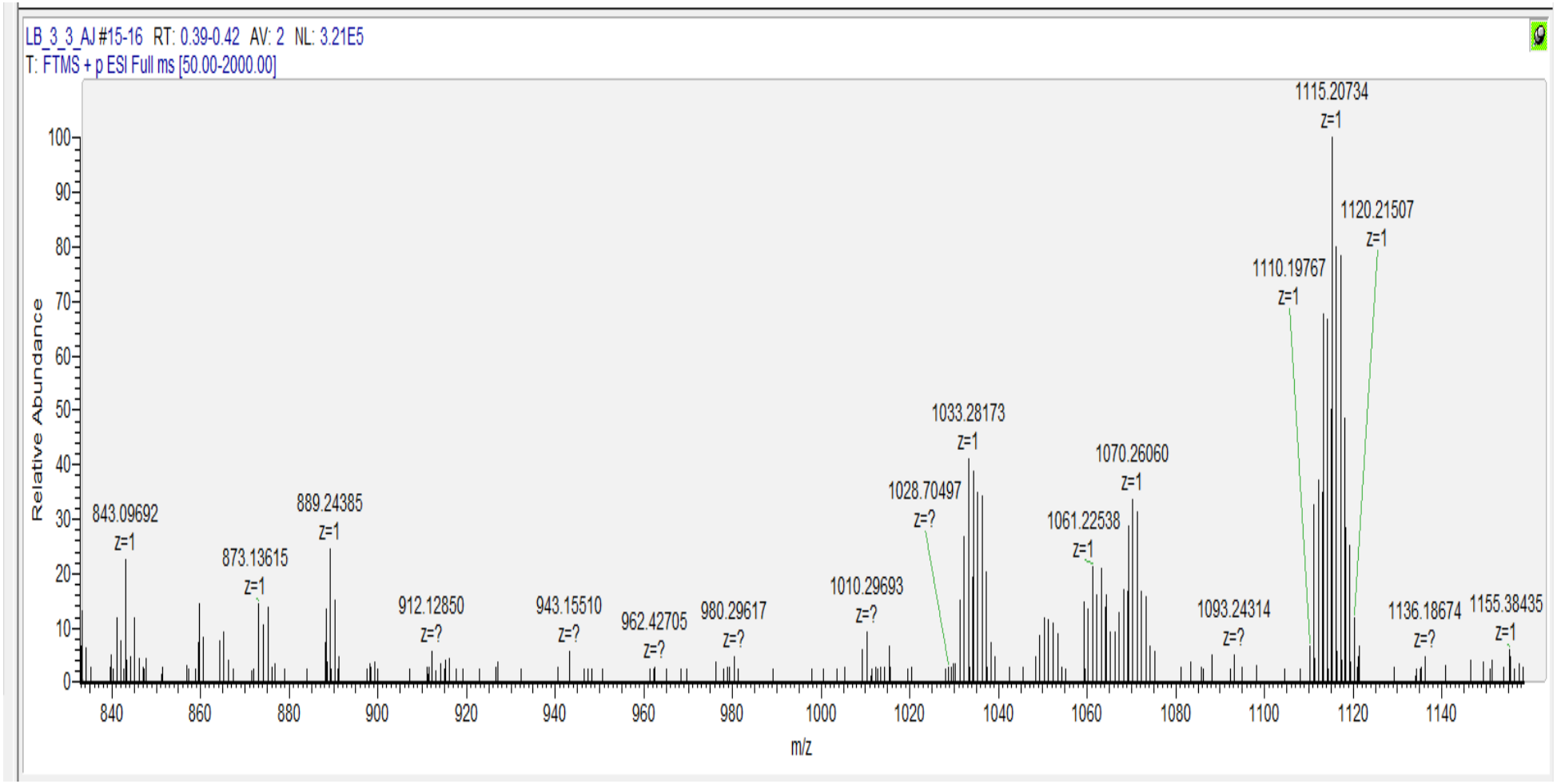


Figure S38. ESI Mass Spectrum (+ve ion) of [WPt(μ-C)Br(CO)$_2$(CNC$_6$H$_2$Me$_3$)$_2$(Tp*)] (**4b**)

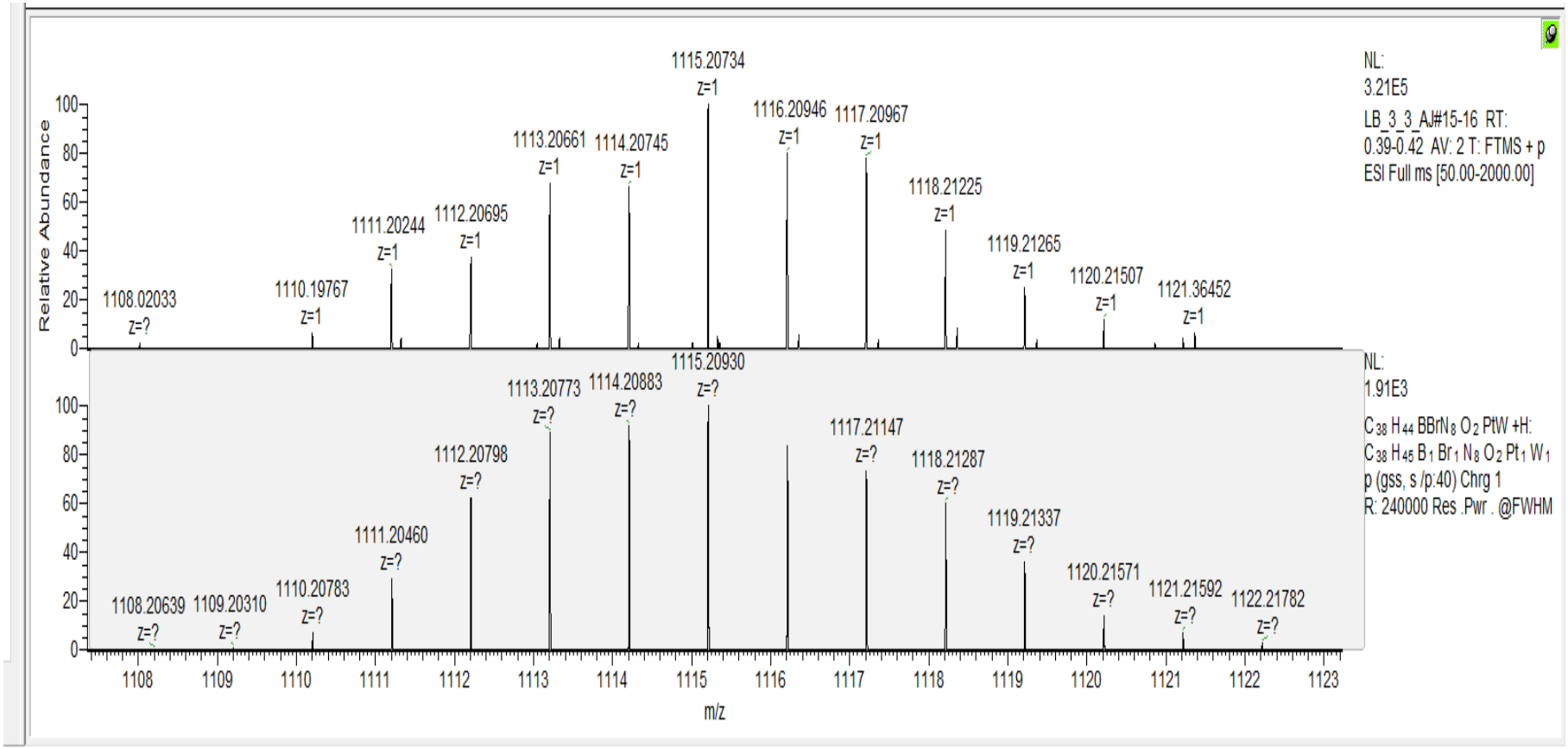


Figure S39. ESI Mass Spectrum (top = measured; bottom = isotopic simulation) of [WPt(μ-C)Br(CO)$_2$(CNC$_6$H$_2$Me$_3$)$_2$(Tp*)] (**4b**)

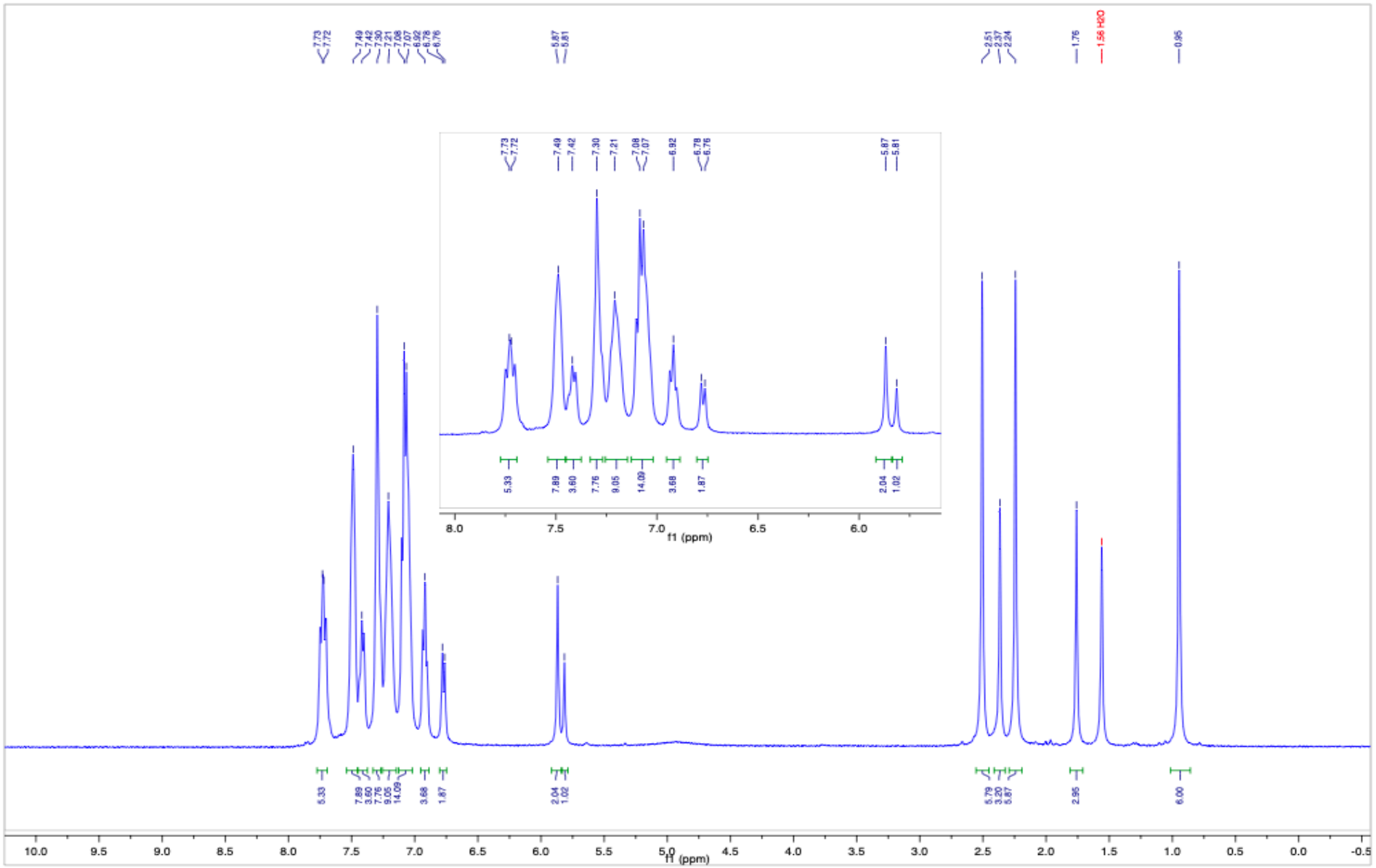


Figure S40. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$, 298 K, δ) of $[WPt(\mu\text{-}CCNC_6H_3Me_2)(CO)_2(PPh_3)_2(Tp^*)]PF_6$ [**5a**]BPh_4.

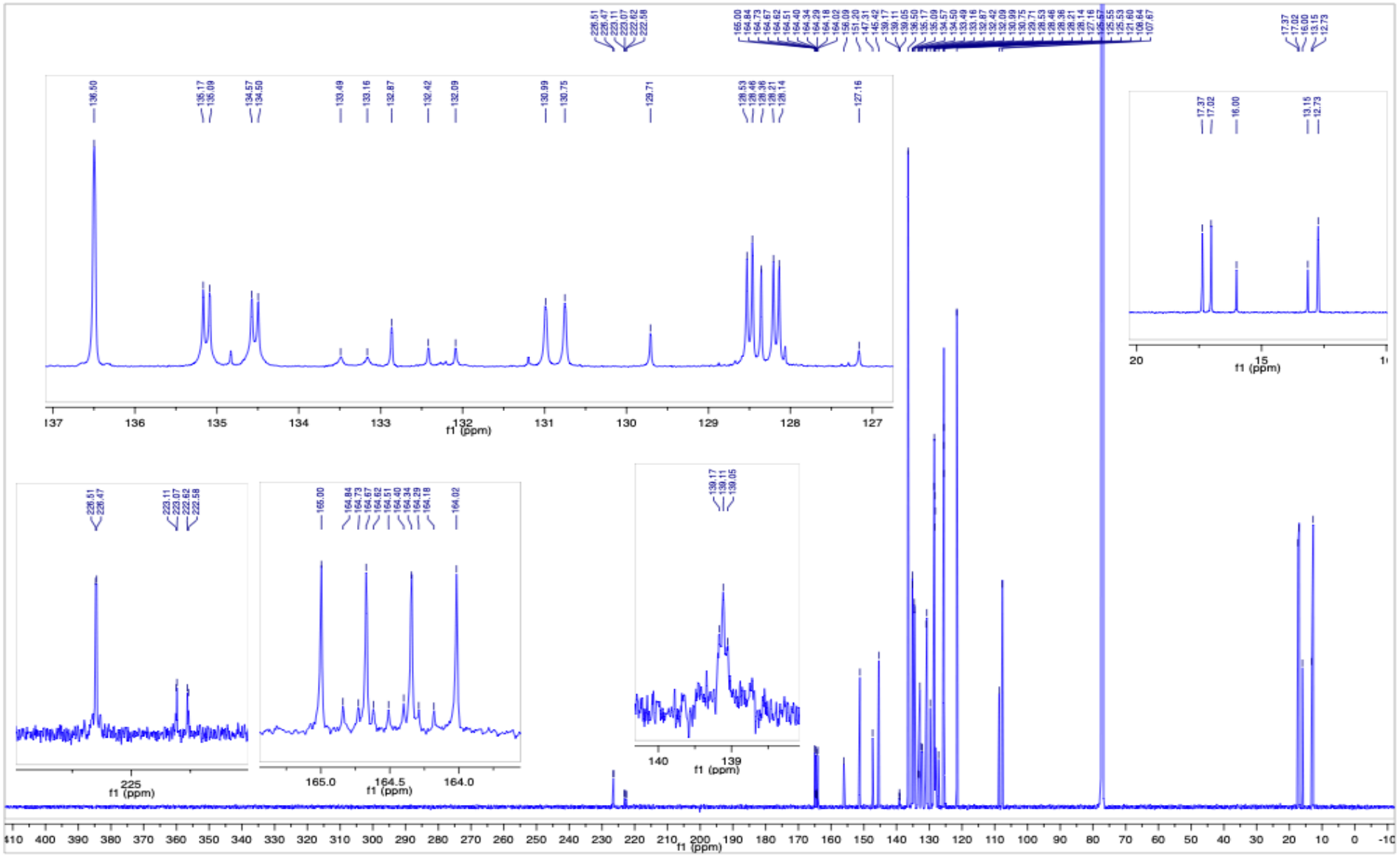


Figure S41. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, $CDCl_3$, 298 K, δ) of $[WPt(\mu\text{-}CCNC_6H_3Me_2)(CO)_2(PPh_3)_2(Tp^*)]PF_6$ **[5a]**BPh_4.

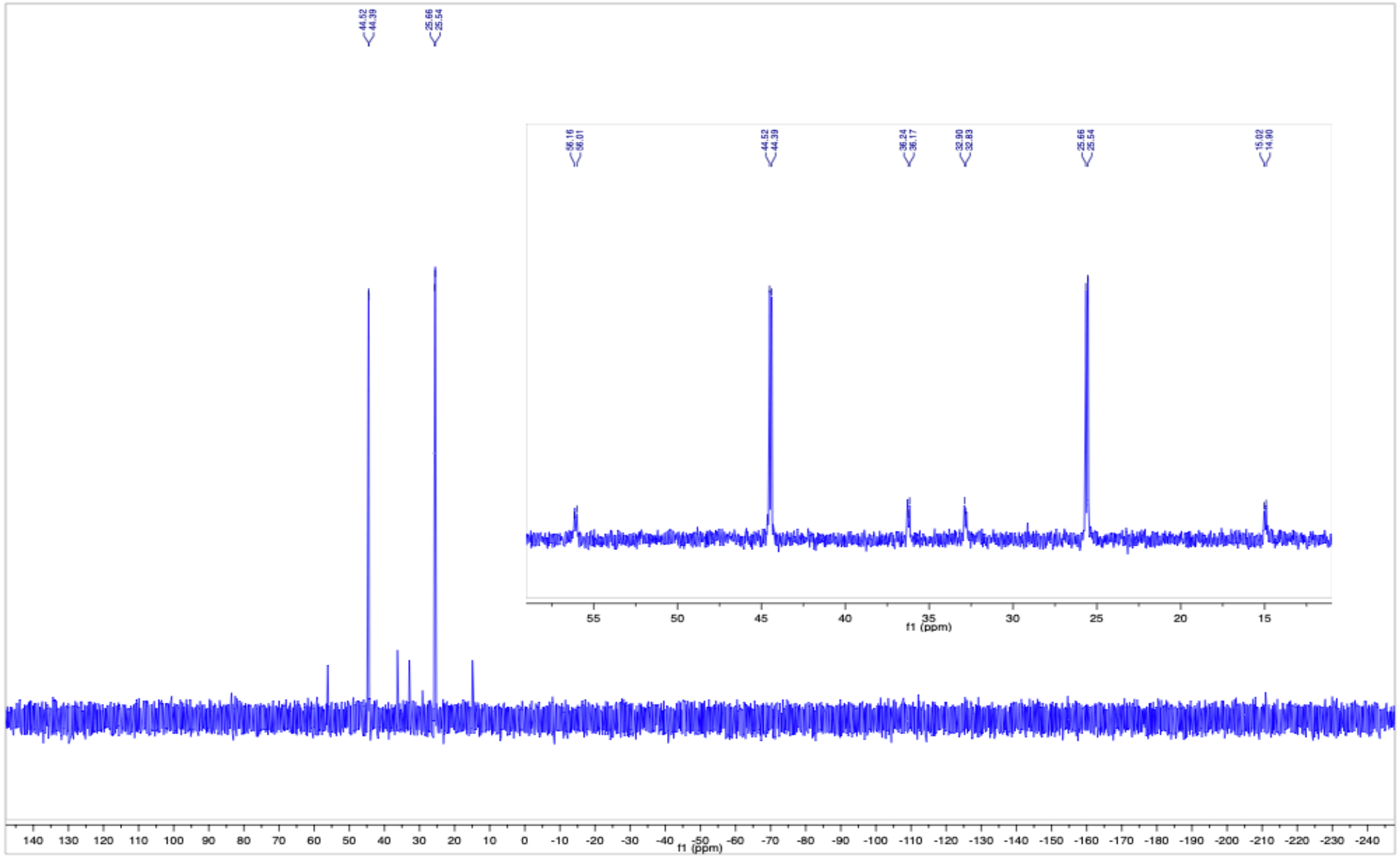


Figure S42. $^{31}P\{^{1}H\}$ NMR Spectrum (162 MHz, $CDCl_3$, 298 K, δ) of $[WPt(\mu\text{-}CCNC_6H_3Me_2)(CO)_2(PPh_3)_2(Tp^*)]PF_6$ [**5a**]BPh_4.

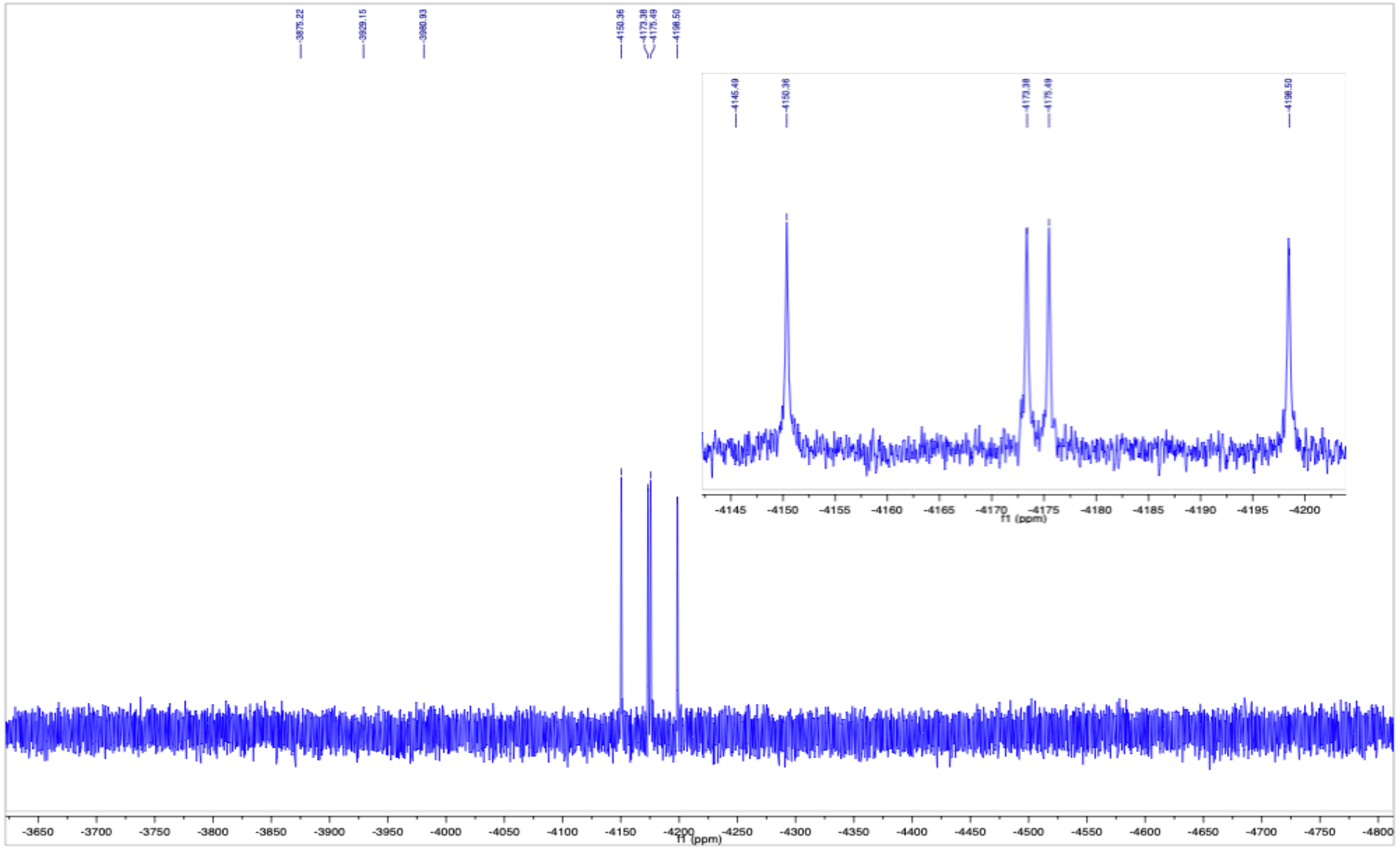


Figure S43. $^{195}Pt\{^{1}H\}$ NMR Spectrum (150 MHz, $CDCl_3$, 298 K, δ) of $[WPt(\mu\text{-}CCNC_6H_3Me_2)(CO)_2(PPh_3)_2(Tp^*)]PF_6$ [**5a**]BPh_4

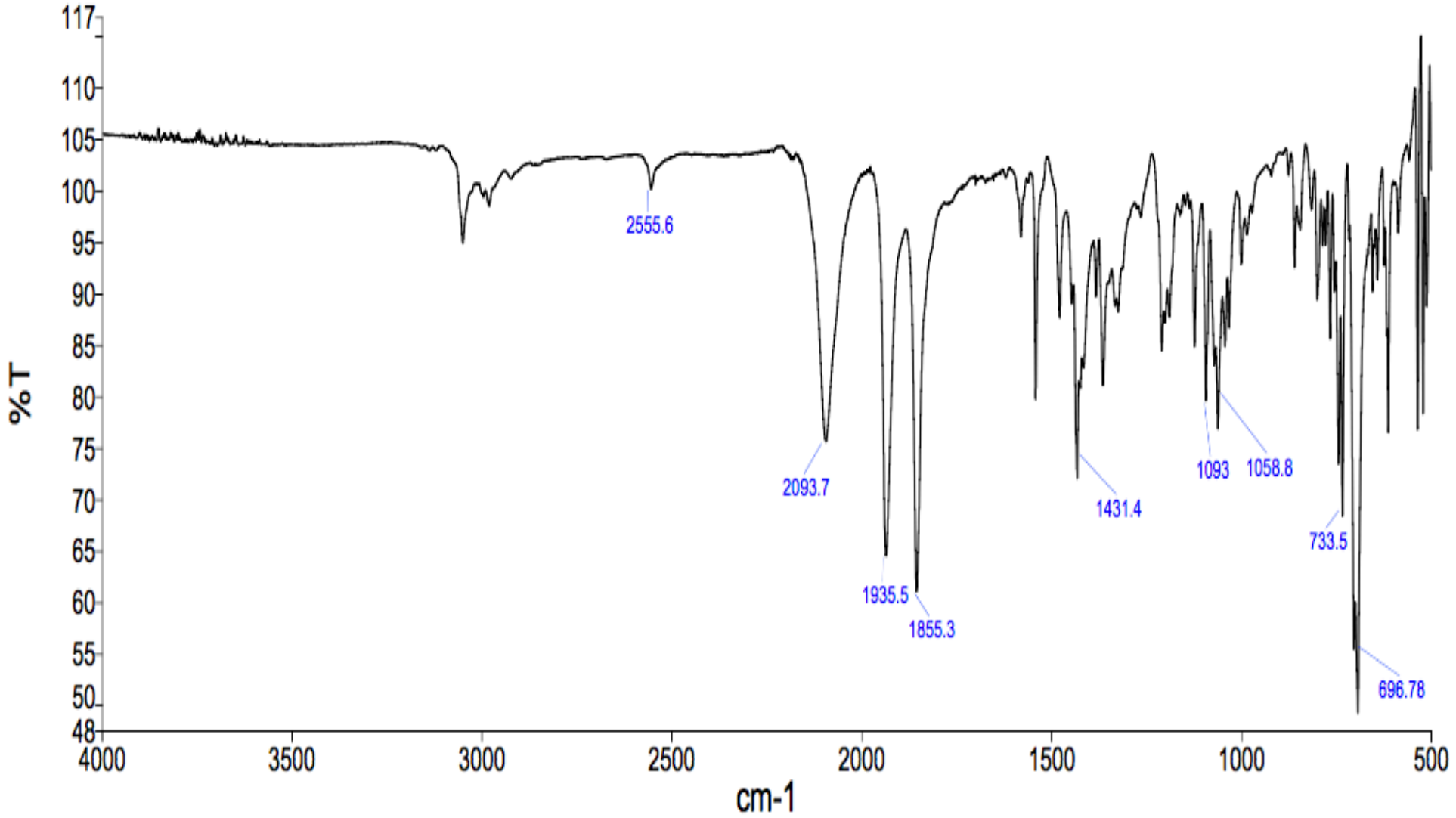


Figure S44. Infrared Spectrum (CH_2Cl_2, 298 K, cm^{-1}) of [WPt(μ-$CCNC_6H_2Me_3$)$(CO)_2(PPh_3)_2$(Tp*)] ([**5a**]BPh_4)

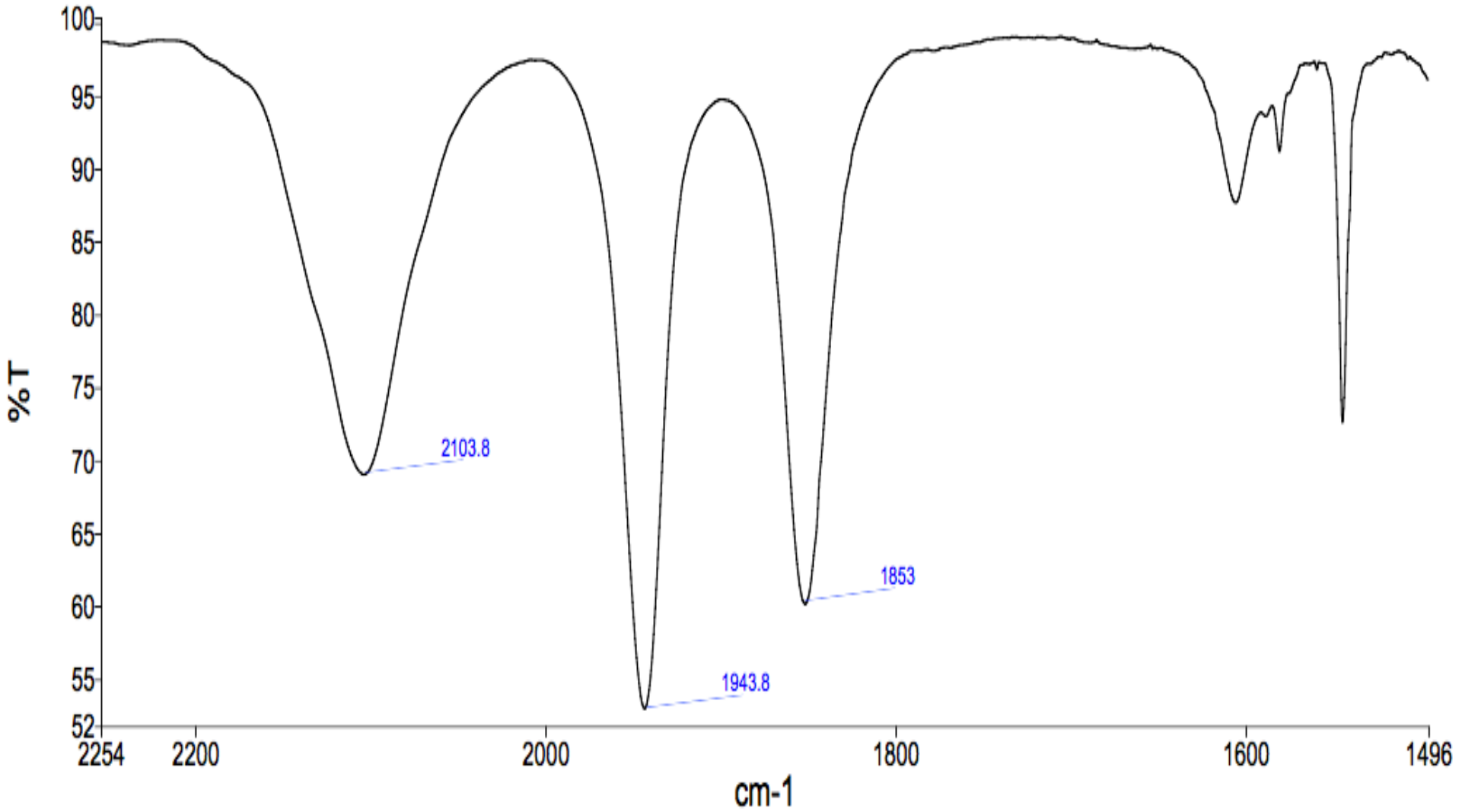


Figure S45. Infrared Spectrum (ATR, diamond anvil, 298 K, cm^{-1}) of [WPt(μ-$CCNC_6H_2Me_3$)$(CO)_2(PPh_3)_2$(Tp*)] ([**5a**]BPh_4)

Elemental Composition Report

Single Mass Analysis

Tolerance = 3.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
250 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-70 H: 0-70 11B: 0-1 N: 7-8 O: 0-2 P: 0-2 184W: 0-1 195Pt: 0-1

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11-Feb-2021
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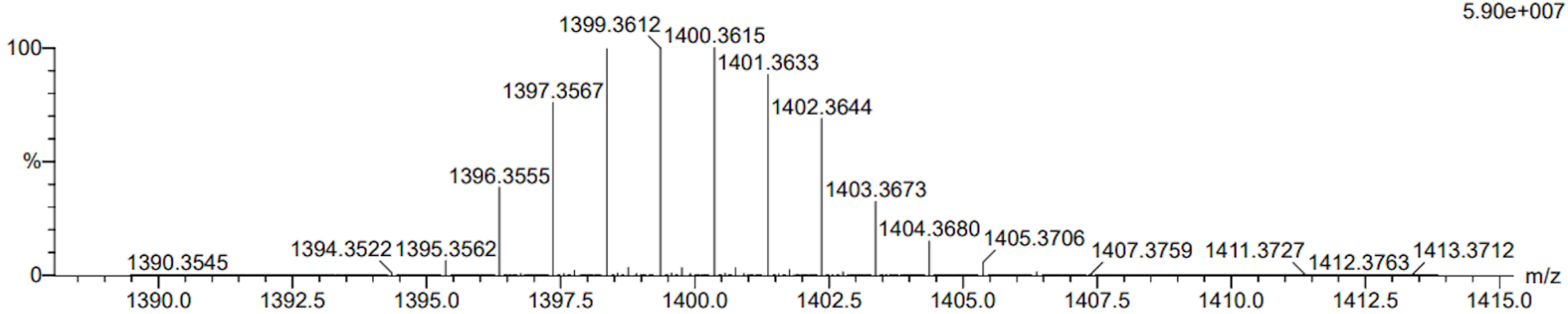

Minimum:				-1.5				
Maximum:		5.0	3.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
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Figure S46. ESI Mass Spectrum (+ve ion) of [WPt(μ-CCNC$_6$H$_2$Me$_3$)(CO)$_2$(PPh$_3$)$_2$(Tp*)] (**[5a]**BPh$_4$)

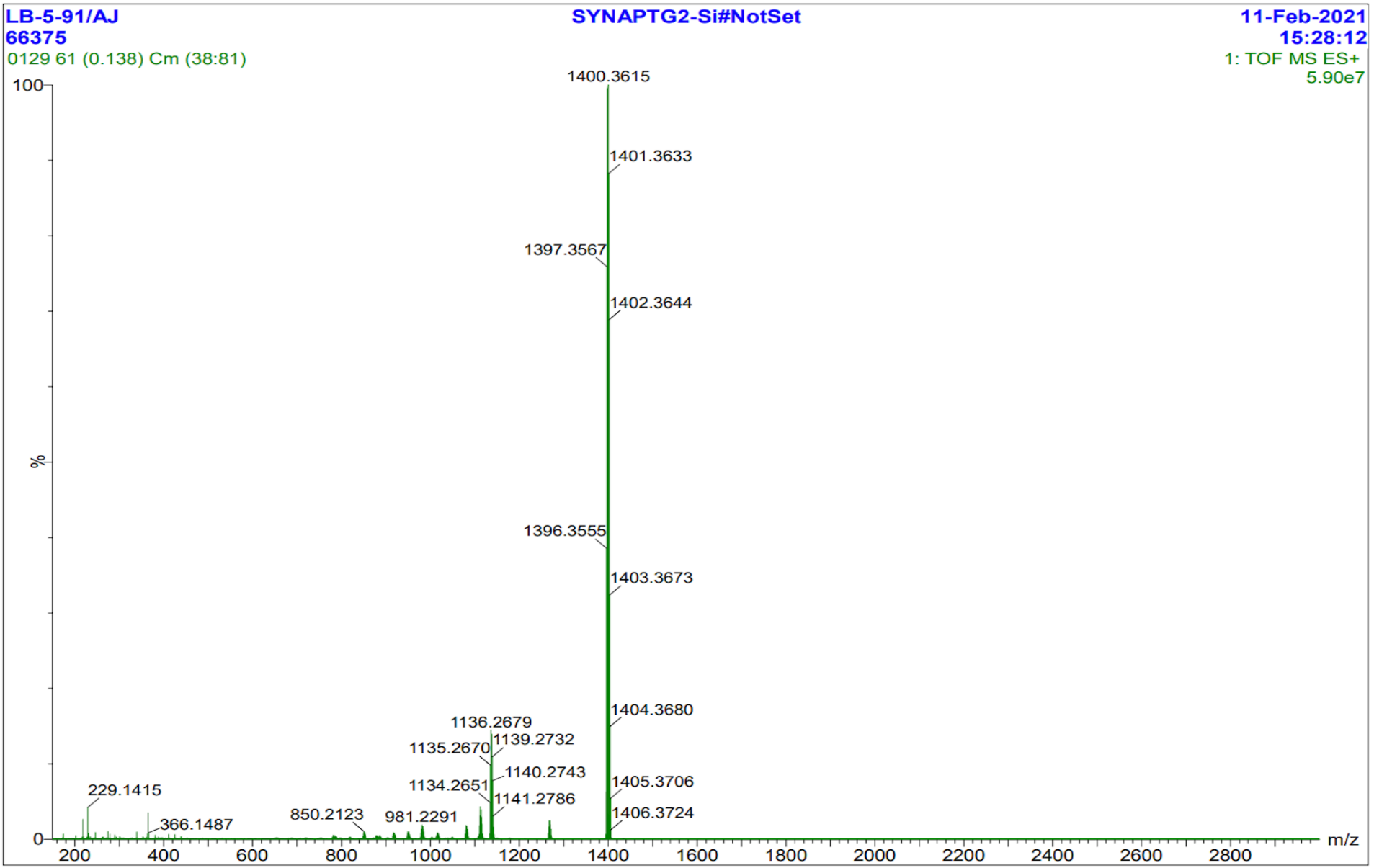

Figure S47. ESI Mass Spectrum (+ve ion) of [WPt(μ-CCNC$_6$H$_2$Me$_3$)(CO)$_2$(PPh$_3$)$_2$(Tp*)] ([**5a**]BPh$_4$) (cont.).

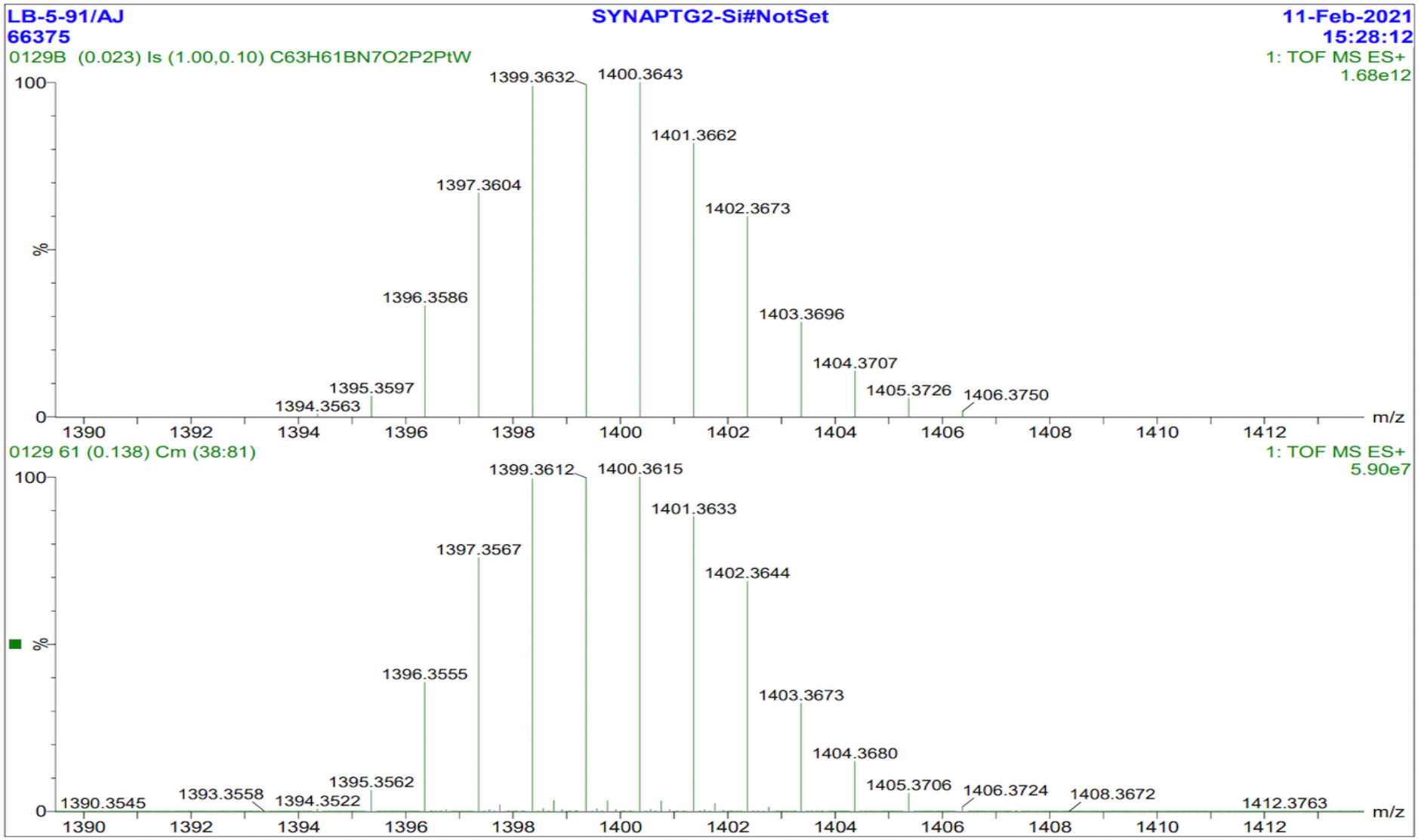

Figure S48. ESI Mass Spectrum (top = measured; bottom = isotopic simulation) of [WPt(μ-CCNC$_6$H$_2$Me$_3$)(CO)$_2$(PPh$_3$)$_2$(Tp*)] ([**5a**]BPh$_4$)

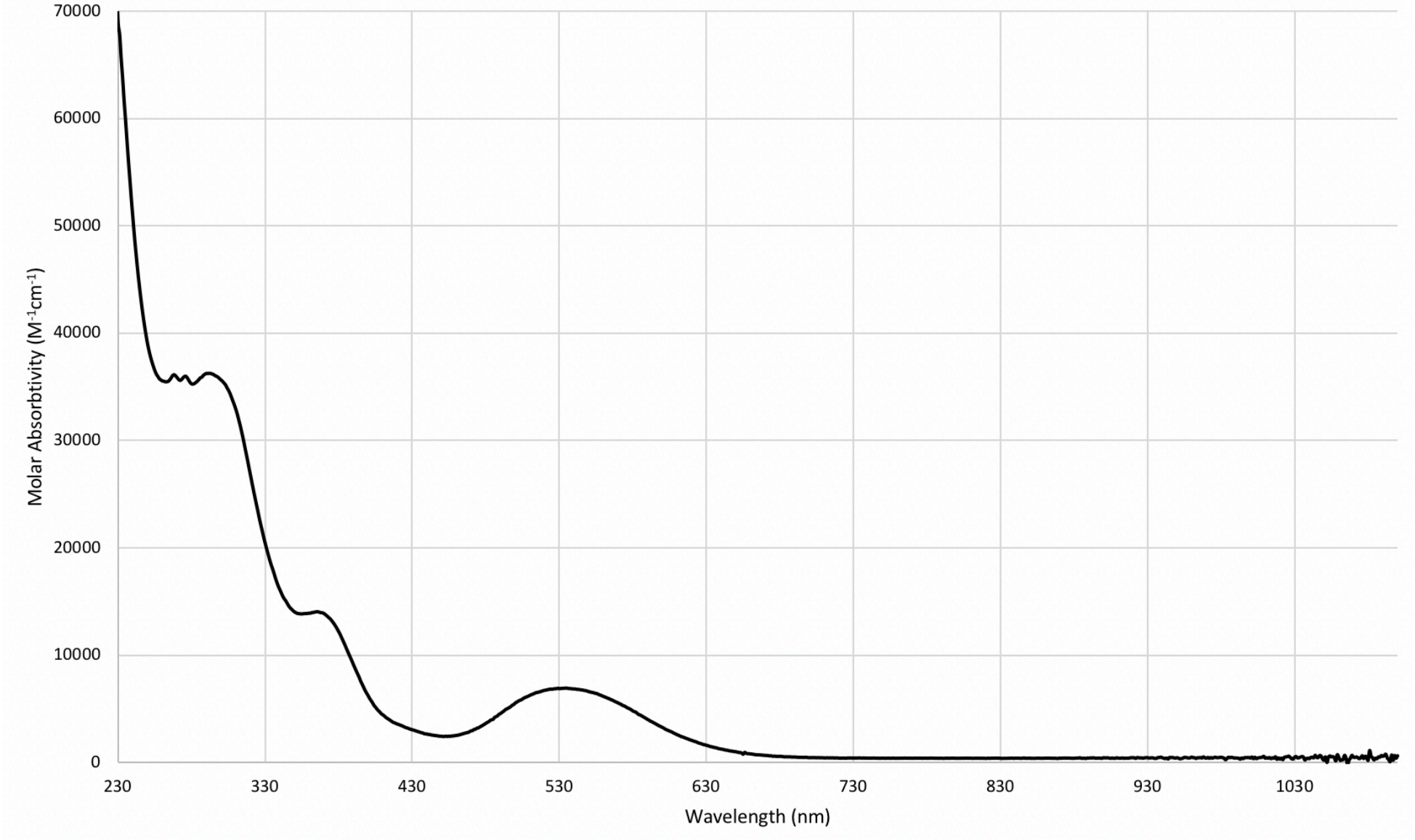

Figure 49. Electronic Spectrum of [WPt(μ-CCNC$_6$H$_2$Me$_3$)(CO)$_2$(PPh$_3$)$_2$(Tp*)] ([**5a**]BPh$_4$)

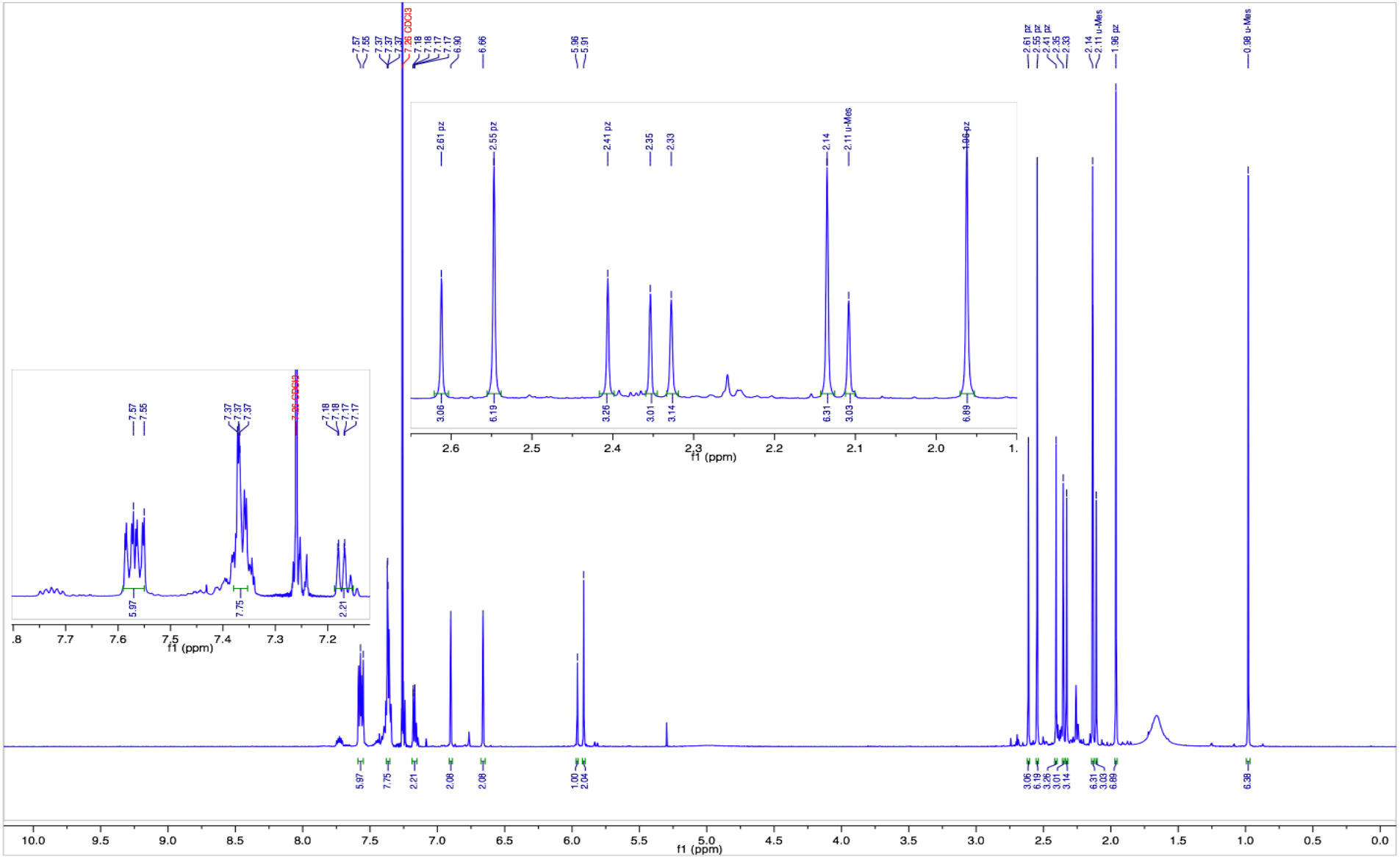

Figure S50. ^{1}H NMR Spectrum (600 MHz, $CDCl_3$, 298 K, δ) of $[WPt(\mu\text{-}CCNC_6H_2Me_3)(CO)_2(CNC_6H_2Me_3)(PPh_3)(Tp^*)]PF_6$ [**5b**]PF_6.

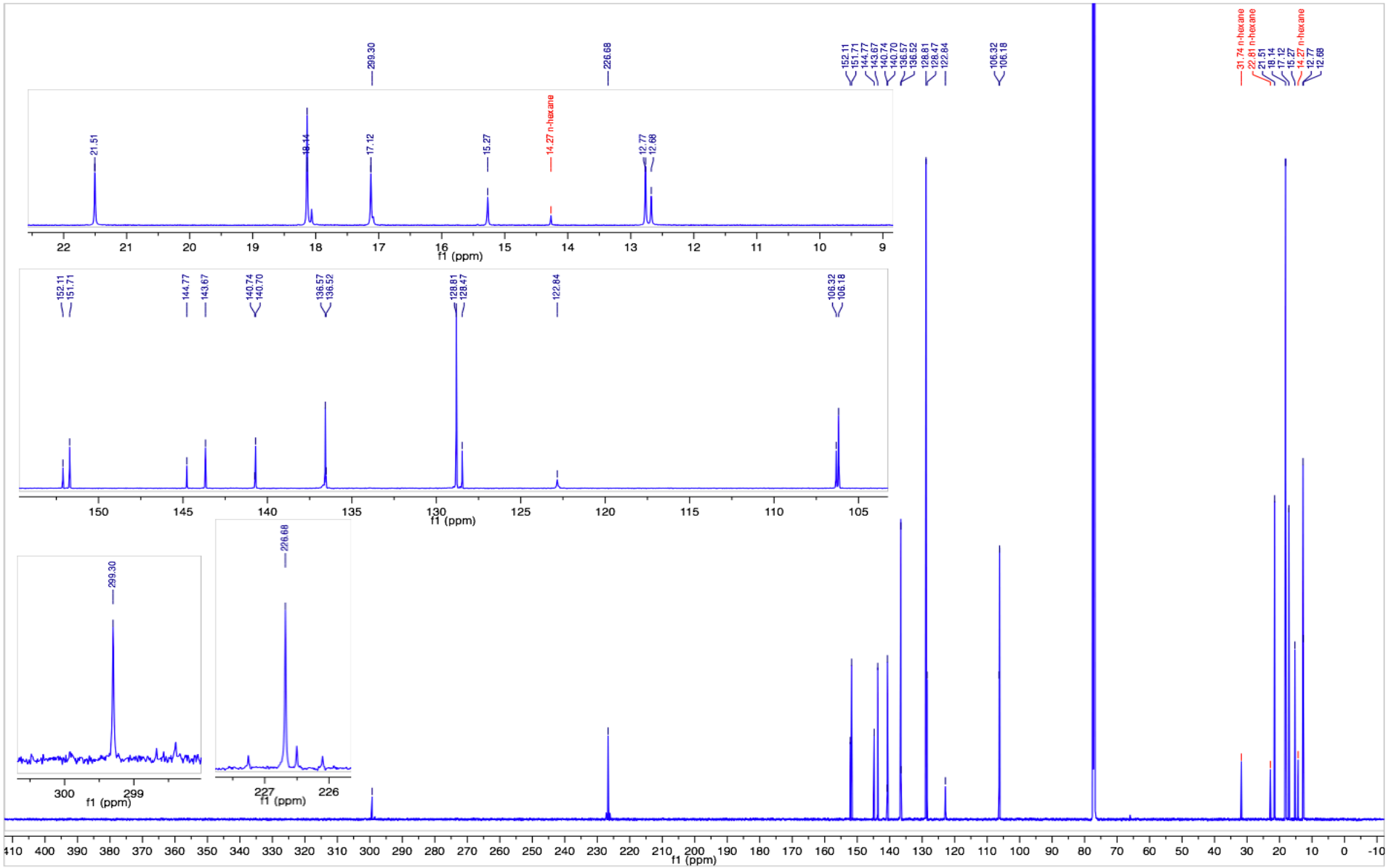

Figure S51. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, $CDCl_3$, 298 K, δ) of $[WPt(\mu\text{-}CCNC_6H_2Me_3)(CO)_2(CNC_6H_2Me_3)(PPh_3)(Tp^*)]PF_6$ [**5b**]PF_6.

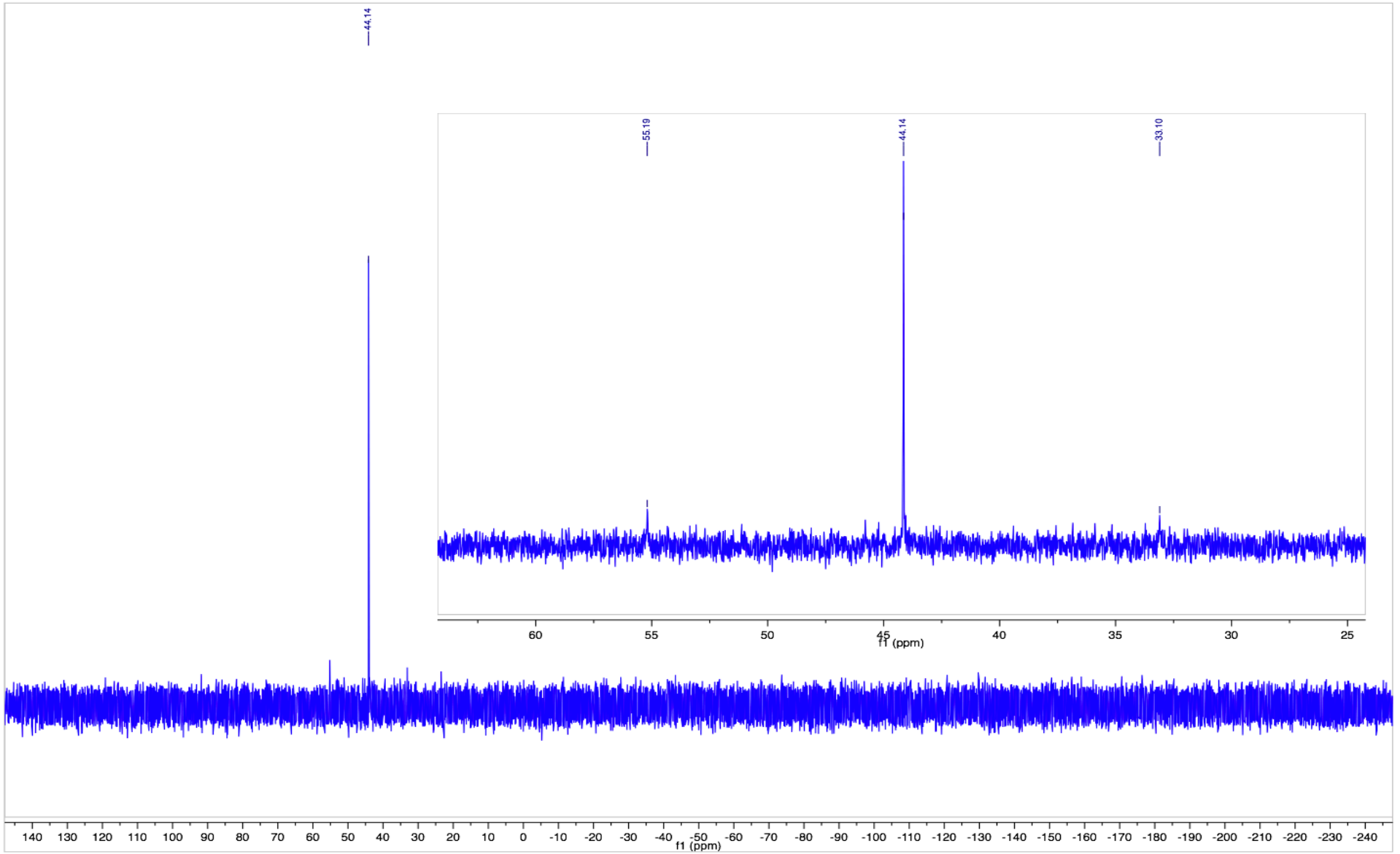

Figure S52. $^{31}P\{^{1}H\}$ NMR Spectrum (162 MHz, $CDCl_3$, 298 K, δ) of $[WPt(\mu\text{-}CCNC_6H_2Me_3)(CO)_2(CNC_6H_2Me_3)(PPh_3)(Tp^*)]PF_6$ [**5b**]PF_6.

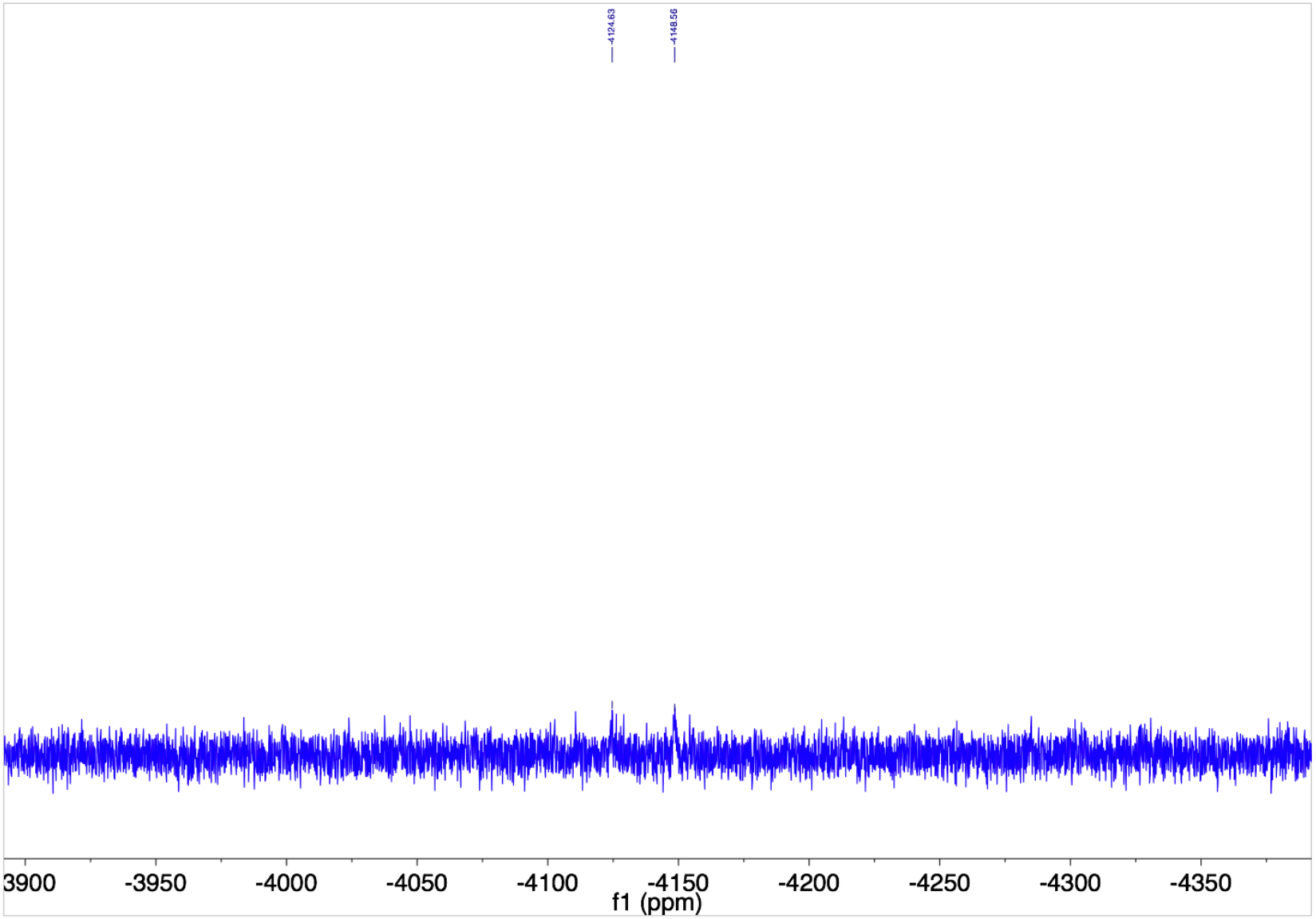

Figure S53. $^{195}Pt\{^{1}H\}$ NMR Spectrum (150 MHz, $CDCl_3$, 298 K, δ) of $[WPt(\mu\text{-}CCNC_6H_2Me_3)(CO)_2(CNC_6H_2Me_3)(PPh_3)(Tp^*)]PF_6$ [**5b**]PF_6.

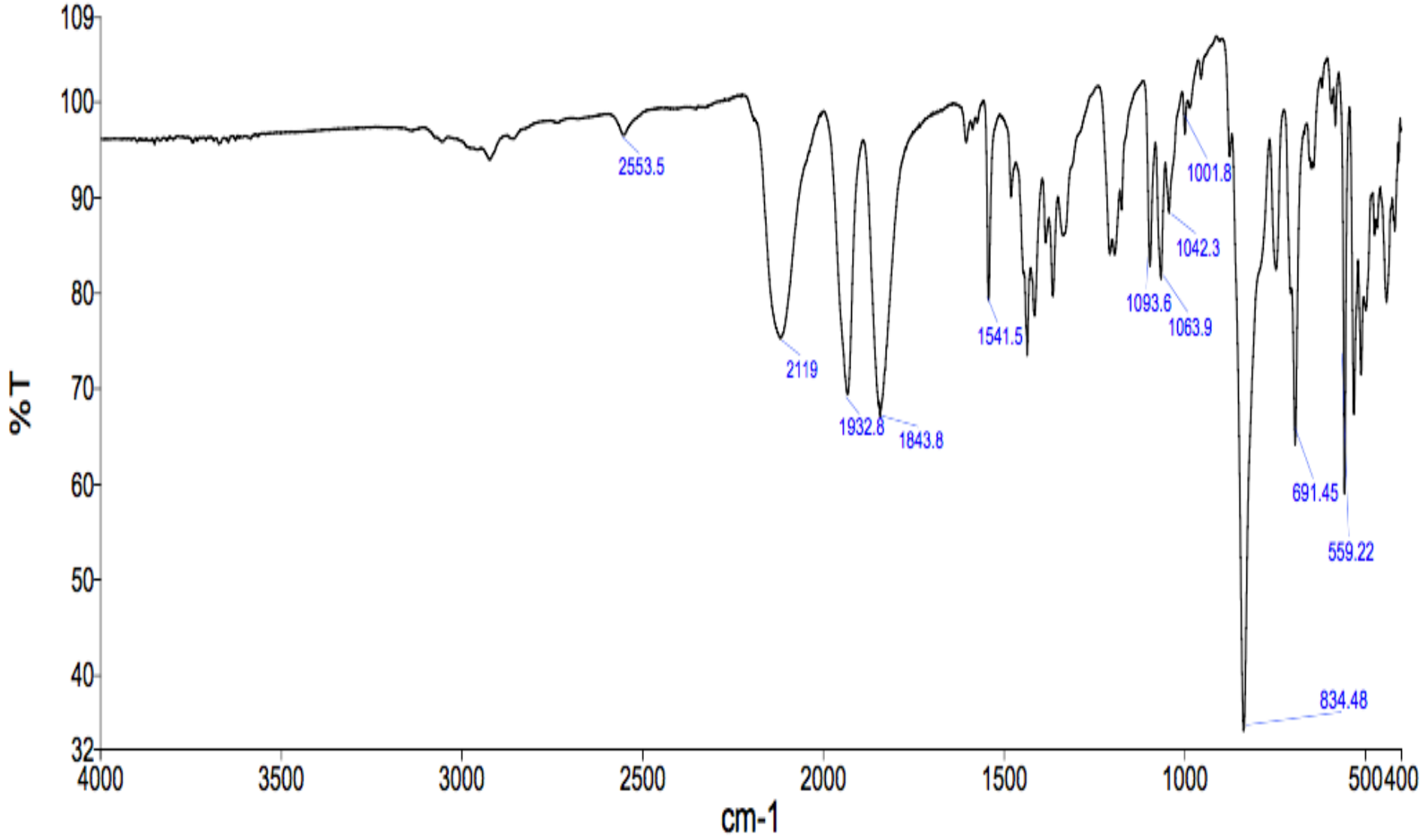

Figure S54. Infrared Spectrum (CH_2Cl_2, 298 K, cm^{-1}) of [WPt(μ-$CCNC_6H_2Me_3$)$(CO)_2$($CNC_6H_2Me_3$)(PPh_3)(Tp*)]PF_6 [**5b**]PF_6.

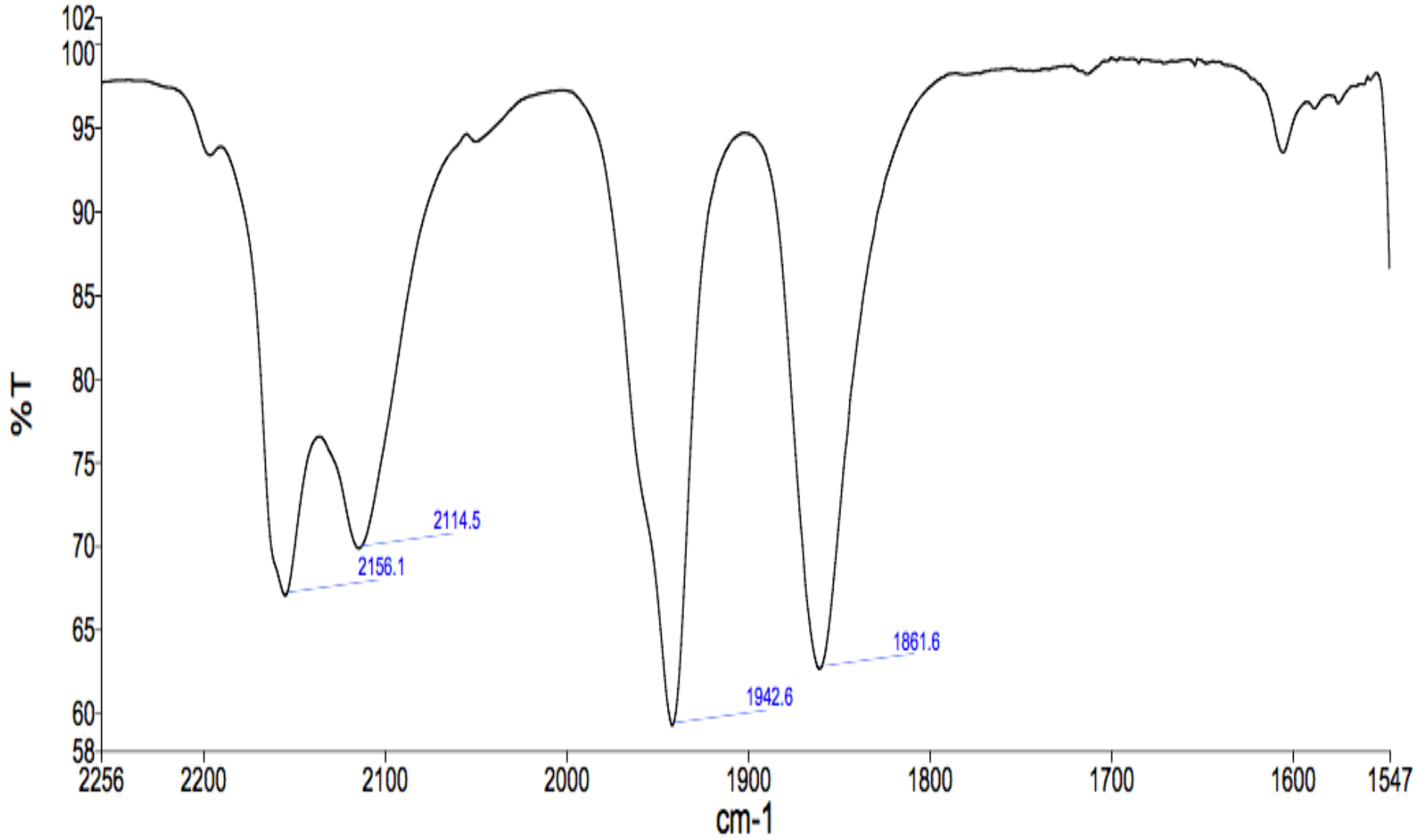

Figure S55. Infrared Spectrum (ATR, diamond anvil, 298 K, cm^{-1}) of [WPt(μ-CCNC$_6$H$_2$Me$_3$)(CO)$_2$(CNC$_6$H$_2$Me$_3$)(PPh$_3$)(Tp*)]PF$_6$ [**5b**]PF$_6$.

Elemental Composition Report

Single Mass Analysis

Tolerance = 3.0 PPM / DBE: min = -1.5, max = 36.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
988 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-60 H: 0-60 11B: 0-2 N: 0-8 O: 0-2 P: 0-2 184W: 0-1 195Pt: 0-1

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66376
0130A 100 (0.217) Cm (99:105)

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12-Feb-2021
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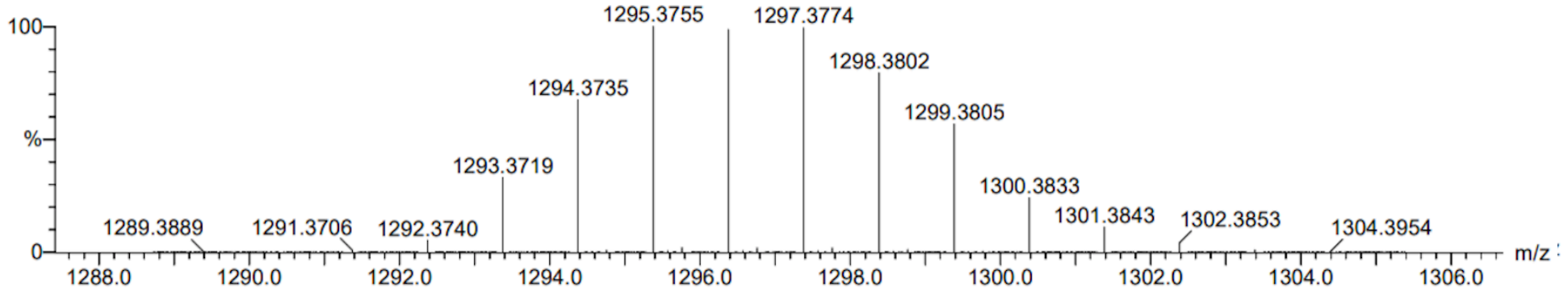

Minimum:				-1.5				
Maximum:		5.0	3.0	36.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
1296.3772	1296.3749	2.3	1.8	35.0	919.0	n/a	n/a	C56 H59 11B N8 O2 P 184W 195Pt

Figure S56. ESI Mass Spectrum (+ve ion) of [WPt(μ-CCNC$_6$H$_2$Me$_3$)(CO)$_2$(CNC$_6$H$_2$Me$_3$)(PPh$_3$)(Tp*)]PF$_6$ [**5b**]PF$_6$.

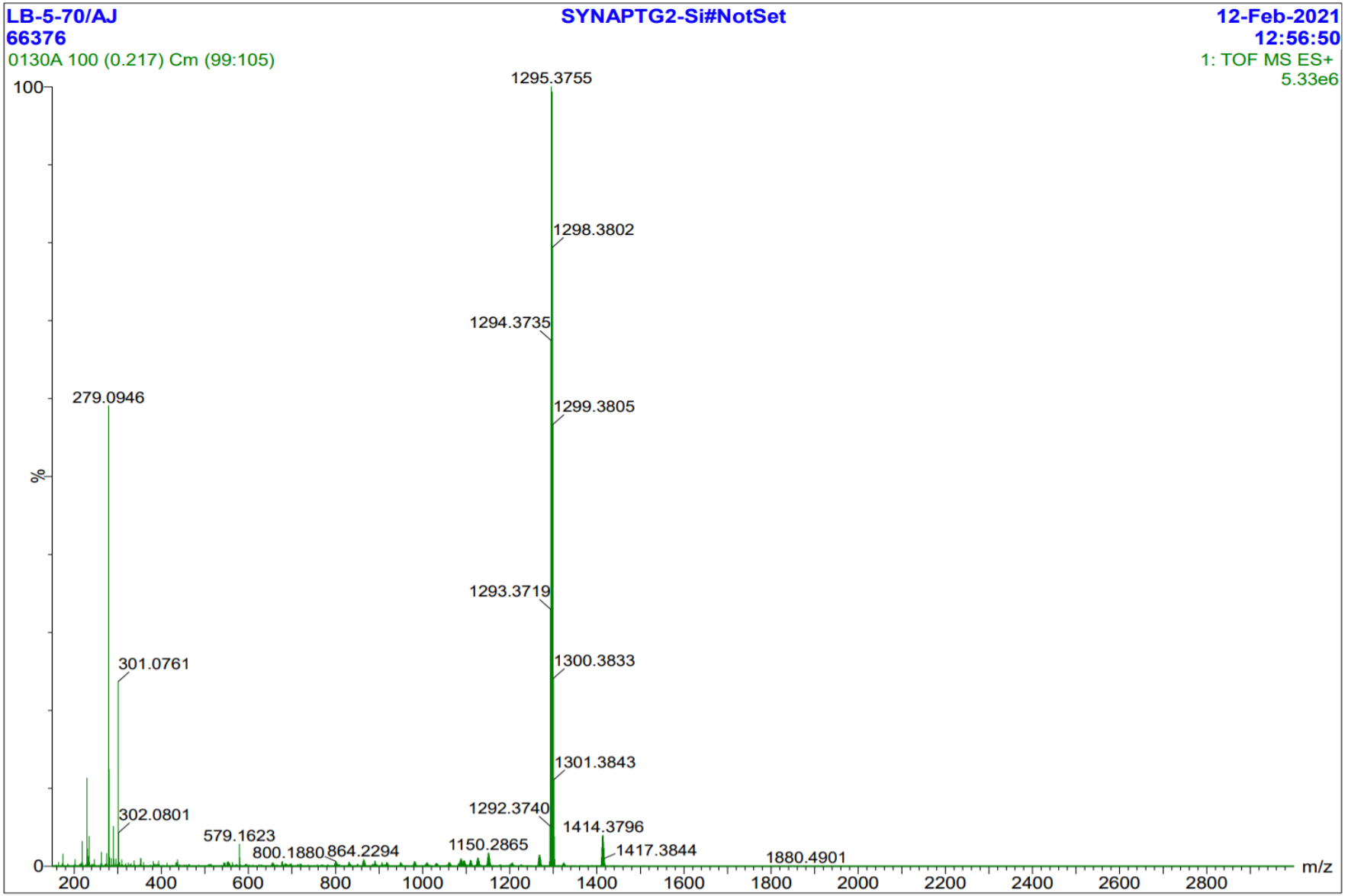

Figure S57. ESI Mass Spectrum (+ve ion) of [WPt(μ-CCNC$_6$H$_2$Me$_3$)(CO)$_2$(CNC$_6$H$_2$Me$_3$)(PPh$_3$)(Tp*)]PF$_6$ [**5b**]PF$_6$ (cont.)

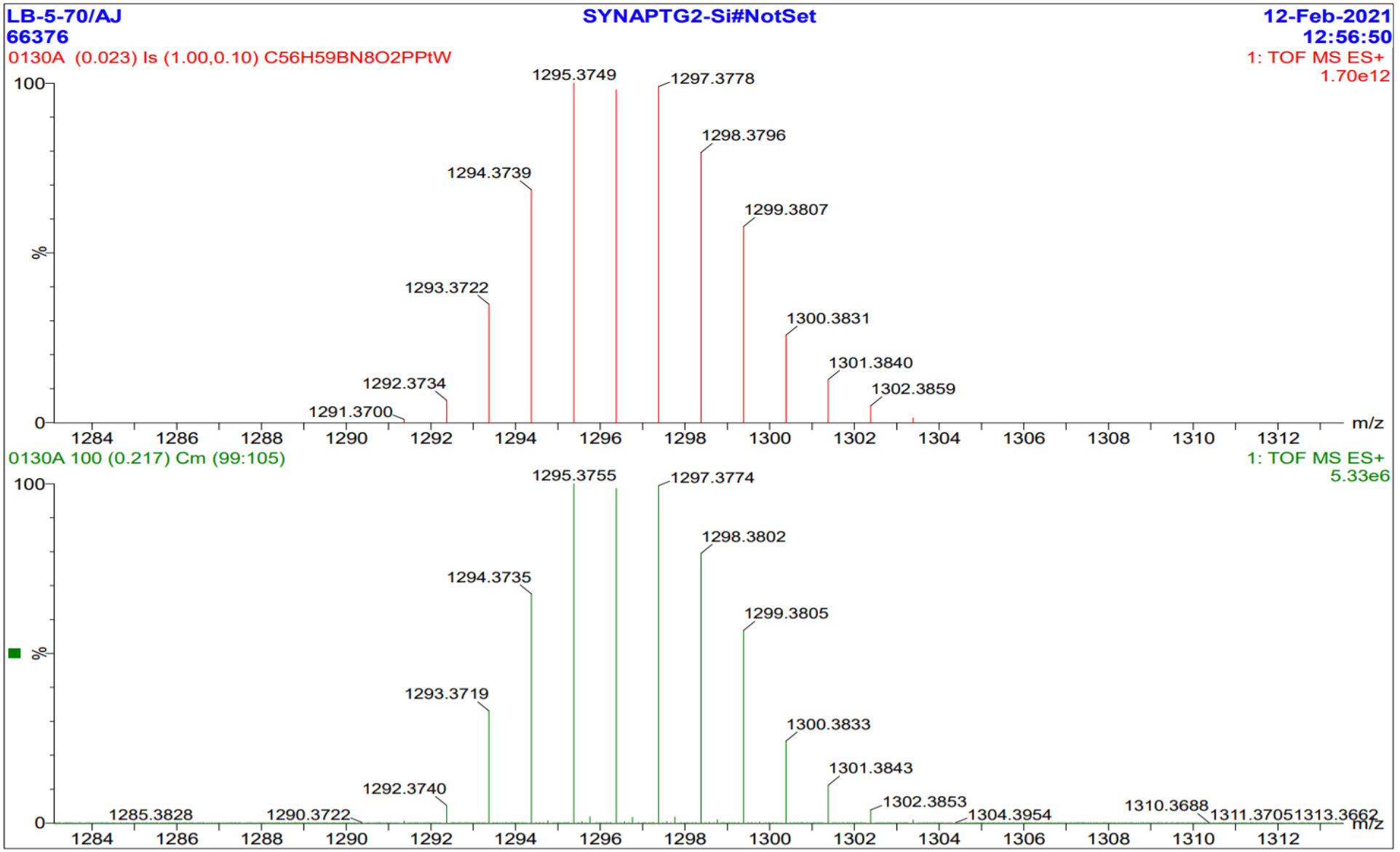

Figure S58. ESI Mass Spectrum (top = measured; bottom = isotopic simulation) of [WPt(μ-CCNC$_6$H$_2$Me$_3$)(CO)$_2$(PPh$_3$)$_2$(Tp*)] ([**5a**]BPh$_4$)

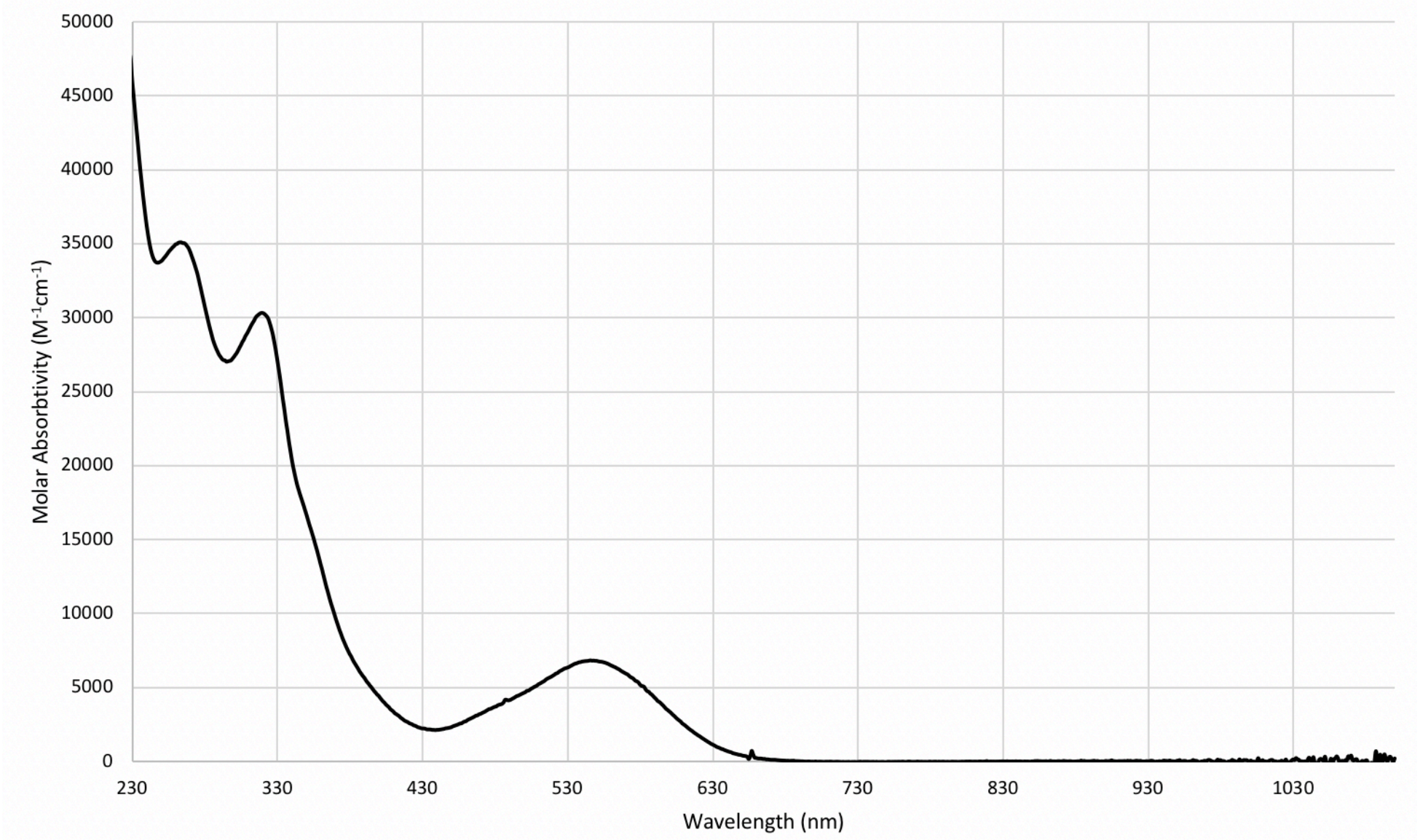

Figure 59. Electronic spectrum of [WPt(μ-CCNC$_6$H$_2$Me$_3$-2,4,6)(PPh$_3$)(CNC$_6$H$_2$Me$_3$-2,4,6)(CO)$_2$(Tp*)].BPh$_4$ ([**5b**]PF$_6$) in CH_2Cl_2