Dalton Transactions

ELECTRONIC SUPPORTING INFORMATION

Two Approaches to Phosphaniminocarbyne Complexes

Lucas G. Foglia, Ryan M. Kirk and Anthony F. Hill

Experimental Section

General Considerations

Unless otherwise stated, experimental work was carried out at ambient temperature under a dry, oxygen-free nitrogen atmosphere utilising standard Schlenk techniques with dried and degassed solvents.

NMR spectra were obtained at 25 °C on a Bruker Avance 400 (^{1}H at 400 MHz, ^{13}C at 101 MHz, ^{31}P at 162 MHz,), or a Bruker Avance 700 (^{1}H at 700 MHz, ^{13}C at 176.1 MHz). Chemical shifts (δ) are reported in ppm and referenced to the residual solvent peak (^{1}H, ^{13}C) or an external reference (^{31}P: H_3PO_4 $\delta_P = 0$) with coupling constants given in Hz. 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 isotopomer satellites. In cases where distinct peaks were observed in the ^{1}H or ^{13}C{^{1}H} NMR spectra, but not to the level of accuracy that is reportable (i.e. 2 decimal places for ^{1}H NMR, 1 decimal place for ^{13}C NMR) they are reported as having the same chemical shift. Infrared spectra were obtained using a Perkin-Elmer Spectrum One FT-IR spectrometer. The strengths of IR absorptions are denoted by the abbreviations vs (very strong), s (strong), m (medium), w (weak), sh (shoulder) and br (broad). High-resolution electrospray ionisation mass spectrometry (ESI-MS) was performed by the ANU Research School of Chemistry mass spectrometry service with acetonitrile as the matrix. Data for *X*-ray crystallography were collected with an Agilent SuperNova CCD diffractometer employing Cu-Kα radiation(λ = 1.54184 Å) using the CrysAlis PRO software.[1] The structures were solved by intrinsic phasing (spin-flipping) methods and refined by full- matrix least squares on F^2 using the SHELXL programs[2] and the Olex2 software.[3] Hydrogen atoms were located geometrically and refined using a riding model. Diagrams were produced using the CCDC visualisation program Mercury.[4] We are grateful to Dr Fabian Kahlmeier for assistance with crystallographic data collection. The complexes $[W(\equiv CX)(CO)_2(Tp^*)]$ (X = F, Cl, Br), $[W(\equiv CF)Cl_2(Tp^*)]$ and $Na[W(CN)(CO)_5]$ were prepared according to literature procedures.[5] The reagents $Ph_3P{=}NR$ (R = H, $SiMe_3$, $SO_2C_6H_4Me$-4) have been described previously.[6] Remaining reagents were purchased from commercial sources and generally used as received.

Synthesis

Synthesis of $[W(\equiv CNPPh_3)(CO)_2(Tp^*)]$

To a dry two-necked flask under argon was added trimethylsilylimino triphenylphosphorane ($Me_3SiN{=}PPh_3$: 120 mg, 0.34 mmol) and $[W(\equiv CF)(CO)_2(Tp^*)]$[5b] (200 mg, 0.35 mmol) in THF (20 mL). The yellow solution was heated under reflux under argon for 60 hours. Volatiles from the resulting black solution were removed *in vacuo* affording the product as a crude black powder. The complex could be recrystallised as fine needles from a mixture of dichloromethane and hexane at -30°C in the dark but was not stable to anaerobic chromatography on either silica gel or alumina. Yield: 209 mg (73%, 0.25 mmol).

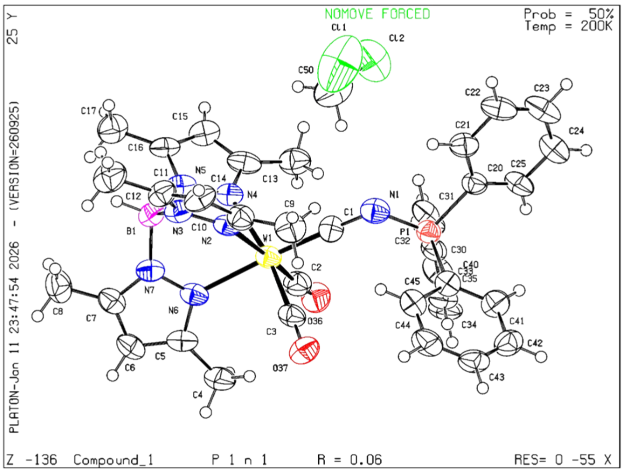
IR (THF, cm^{-1}): 1911 vs 1812 vs (ν_{CO}), 1544 (ν_{CN}). IR (CH_2Cl_2, cm^{-1}): 1907 vs, 1805 vs (ν_{CO}), 1514 br (ν_{CN}), 1543 sharp ($B(NN)_3W$ breathing mode). IR (ATR, cm^{-1}): 2542, 2525 (ν_{BH}), 1903 s, 1800 vs (ν_{CO}), 1542 s, sharp ($HB(NN)_3W$ breathing), 1507 s.br (ν_{CN}), 1075-1025 m.br (ν_{PN}) cm^{-1}. Fingerprint bands associated with the $CNPPh_3$ ligand were identified by comparison with a spectrum of $[W(\equiv CBr)(CO)_2(Tp^*)]$ and consideration of the IR spectrum calculated for $[W(\equiv CNPMe_3)(CO)_2(Tp)]$. ^{1}H NMR: (400 MHz, 298 K, d_8-toluene) δ_H = 7.67 (ddd, 12 H, J = 1.6, 7.0, 13.1 Hz, C_6H_5), 7.24 (m, 3 H, C_6H_5), 5.48 [s, 2 H, H^4(pz)], 5.35 [s, 1H, H^4(pz)] 2.61 (s, 3 H, $pzCH_3$) 2.43 (s, 6 H, $pzCH_3$) 2.14 (s, 6 H, $pzCH_3$) 2.09 (s, 3 H, $pzCH_3$). ^{1}H NMR: (700 MHz, 298 K, $CDCl_3$) δ_H =7.84 (ddd, J = 13.2, 8.2, 1.4 Hz, 4H), 7.70 – 7.62 (m, 2H), 7.64 – 7.59 (m, 2H), 7.52 (dd, J = 7.8, 3.2 Hz, 4H), 7.52 – 7.44 (td, 2H, J = 7.3, 1.9), 7.41 (td, J = 7.5, 2.7 Hz, 2H), 7.34 (dd, 1 H 2.3, 4.8), 7.31 (td, J = 7.3, 2.5, 1 H), 5.69 [s, 3 H, H^4(pz)], 2.46 (s, 3 H, pzMe), 2.30 (s, 12 H, $pzCH_3$), 2.29 (s, 3 H, $pzCH_3$). ^{13}C{^{1}H} NMR: (176 MHz, 298K, $CDCl_3$) δ_C = 239.7 (d, $^{2}J_{CP}$ = 15.4 Hz, WCNP), 226.2 (d, $^{4}J_{CP}$ = 3.2 Hz, CO), 152.0 [C^{3,5}(pz)], 151.9 [^{3,5}(pz)], 143.6 [C^{3,5}(pz)], 143.3 [C^{3,5}(pz)], 133.9 [d, $^{1}J_{PC}$ = 17.7 Hz, C^{1}(C_6H_5)], 133.1 [d, $^{3}J_{PC}$ = 10.8 Hz, C^{3,5}(C_6H_5)], 131.0 [s, C^{4}(C_6H_5)], 129.2 [d, $^{2}J_{PC}$ = 12.4, C^{2,6}(C_6H_5)], 105.9 [1 C, C^{4}(pz)], 105.8 [2 C, C^{4}(pz)], 16.21 (2C, $pzCH_3$) 16.18 (1 C, $pzCH_3$), 12.8 (2 C, $pzCH_3$) 12.7 (1 C, $pzCH_3$). ^{31}P{^{1}H} NMR: (162 MHz, 298

---

[a] *Research School of Chemistry, Australian National University, Canberra, Australian Capital Territory, Australia ACT 2601. Email. a.hill@anu.edu.au*

K, $CDCl_3$) $\delta_P = -3.67$ (NP, $3J_{WP} \approx 10$ Hz). $^{31}P\{^1H\}$ NMR: (162 MHz, 298 K, d_8-toluene) $\delta_P = -4.92$ (NP, $3J_{WP} \approx 11$ Hz), -1.28 (unreacted $Me_3SiN{=}PPh_3$). HR-MS (ESI, MeCN, +ve ion): found *m/z* 825.2377 (calc. for $C_{36}H_{37}{}^{11}BN_7O_2P^{184}W$ $[M]^+$: 825.2360). Attempts to recrystallise the complex for microanalysis were thwarted by the photoinstability in solution.

Crystal Data for $C_{37}H_{39}BCl_2N_7O_2PW$ (M_w =910.313 $gmol^{-1}$), orange plate 0.05 × 0.022 × 0.01 mm, monoclinic, space group *Pn* (no. 7), a = 10.1032(3) Å, b = 16.9852(5) Å, c = 11.3251(3) Å, β = 95.893(2)°, V = 1933.16(9) $Å^3$, Z = 2, T = 200.1(1) K, μ(Cu Kα) = 7.539 mm^{-1}, ρ_{calc} = 1.564 Mgm^{-3}, multi-scan correction T_{min}/T_{max} = 0.790/1.000, 11453 reflections measured (5.2° ≤ 2Θ ≤ 156.76°), 4792 unique (R_{int} = 0.0669, R_{sigma} = 0.0771) which were used in all calculations. The final R_1 was 0.0591 ($I \geq 2\sigma(I)$) and wR_2 was 0.1531 (all data), $GOF(F^2)$ = 1.065, D_{min}/D_{max} = -1.42/+3.77 $eÅ^{-3}$. CCDC 2504578, DOI: 10.5517/ccdc.csd.cc2q26vw.



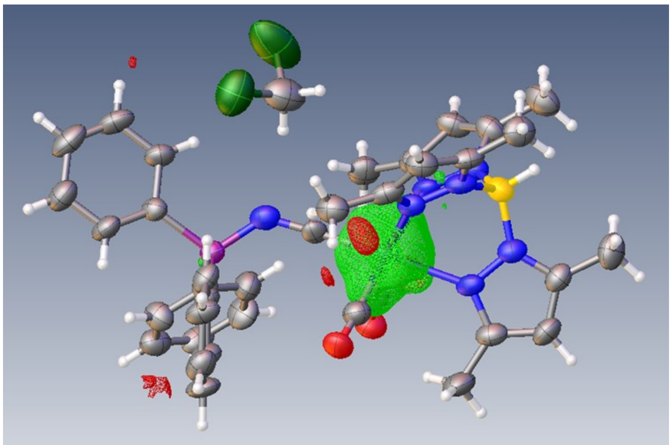


Figure S1. ORTEP representation (from CheckCif) of $[W(\equiv CNPPh_3)(CO)_2(Tp^*)].CH_2Cl_2$.

Figure S2. Residual electron density map (*Olex2*) following final refinement cycle for $[W(\equiv CNPPh_3)(CO)_2(Tp^*)].CH_2Cl_2$. NB: Unattributed electron density primarily associated with ripples surrounding heavy atom tungsten.

Synthesis of *trans*-$[WBr(\equiv CNPPh_3)(CO)_4]$

To a stirring solution of Br_2PPh_3 (282 mg, 0.67 mmol) in THF (15 mL) at –78 °C was added a solution of $Na[W(CO)_5(CN)]$[5c] (250 mg, 0.67 mmol) in THF (20 mL). After mixing for 30 minutes, the yellow solution was slowly warmed to room temperature, becoming brown then red. Volatiles were removed *in vacuo* and the dark black crude product dissolved in diethyl ether and filtered through a layer of diatomaceous earth. The removal of solvent *in vacuo* afforded a dark microcrystalline powder. Yield: 236 mg (54%, 0.36 mmol), IR: (THF, cm^{-1}): 1966 vs, 1946 vs 1925 vs (ν_{CO}), 1597 s (ν_{CN}). ^1H NMR (700 MHz, 298 K, $CDCl_3$). δ_H = 7.77 [t, 3 H, $^3J_{HH}$ = 7.4 Hz, $H^4(C_6H_5)$], 7.68 [dd, 6 H, $^3J_{HH}$ = 7.4, $^3J_{PH}$ = 13.4 Hz, $H^{2,6}(C_6H_5)$], 7.64 [dd, 6 H, $^3J_{HH}$ = 7.6 Hz, $^4J^{PH}$ = 3.5 Hz, $H^{3,5}(C^6H^5)$], 7.54 (m, unidentified impurity). $^{13}C\{^1H$ NMR: (176 MHz, $CDCl_3$) δ_C = 227.4 (d, ^2JPC = 11.0 Hz, WCNP), 195.8 (d, $^4J_{PC}$ = 3.5 Hz, $^1J_{WC}$ =126.5 Hz), 134.5 [d, $^4J_{PC}$ = 4.5 Hz, $C^4(C_6H_5)$], 134.3 [d, $^1J_{PC}$ = 11.3 Hz, $C^1(C_6H_5)$], 132.5 [d, $^3J_{PC}$ = 11.4 Hz, $C^{3,5}(C_6H_5)$], 129.8 [d, $^{2,6}J^{PC}$ = 13.9 Hz, $C^{2,6}(C_6H_5)$]. $^{31}P\{^1H\}$ NMR: (162 MHz, 298 K, $CDCl_3$) δ_P = 13.5 (WCNP, $^3J_{WP}$ = 10.7 Hz) HR-MS (ESI, MeCN, +ve ion): found *m/z* 472.0443 (calc. for $C_{19}H_{15}NP^{184}W$ $[M\text{-}Br\text{-}4CO]^+$: 472.0454. Attempts to recrystallise the complex for microanalysis were thwarted by the photosensitivity in solution.

Observation of $[Mo(\equiv CNPPh_3)(CO)_2(Tp^*)]$

To a Youngs NMR tube was added trimethylsilylimino triphenylphosphorane ($Me_3SiN{=}PPh_3$: 15 mg, 0.043 mmol) and $[Mo(\equiv CF)(CO)_2(Tp^*)]$[5b] (20 mg, 0.042 mmol) in $CDCl_3$ (0.5 mL). The NMR tube was sealed tightly and heated to 50 °C with exclusion of light for 15 days with periodic measurement of $^{31}P\{^1H\}$ and ^1H NMR spectra to monitor reaction progress. After 15 days there remained *ca* 18% unreacted $Me_3SiNPPh_3$ (δ_H = -0.03 and δ_P = 0.78 *cf* newly formed Me_3SiF δ_H = 0.25 $^3J_{FH}$ = 7.4 Hz), however it was apparent from the $^{31}P\{^1H\}$ NMR spectrum that decomposition of the product was also slowly occurring. Integrated ratio $[Mo(\equiv CNPPh_3)(CO)_2(Tp^*)]$: $Me_3SiNPPh_3$: $O{=}PPh_3$:PPh_3:others = 1.00:0.68:0.19:0.14:0.48. The presence of $[Mo(\equiv CNPPh_3)(CO)_2(Tp^*)]$ appears to reach a maximum around 17 days with the corresponding ratio being 1.00:0.75:0.11:0:0.18. Arithmetic subtraction of the spectra for the starting materials from that measured at 24 days provided limted characterisational data: ^1H NMR ($CDCl_3$, 400 MHz, 295 K): δ_H = 7.84 [dd, 3 H, $^3J_{HH}$ = 8.0, $^3J_{PH}$ = 13.5 Hz, $H^{2,6}(C_6H_5)$], 7.66 (m, 6 H, C_6H_5), 7.52 (m ≈ dt, 3 H, C_6H_5), 5.67 [s, 1 H, H^4(pz)], 5.66 [s, 2 H, H^4(pz)], 2.45 (s, 3 H, $pzCH_3$), 2.32 (s, 6 H, $pzCH_3$), 2.30 (s, 3 H, $pzCH_3$), 2.27 (s, 6 H, $pzCH_3$). $^{31}P\{^1H\}$ NMR: (162 MHz, 298 K, $CDCl_3$) δ_P = -2.49.

The following exploratory procedures do not provide definitive proof that the intended transformation might not be viable. They are provided to indicate which conditions did not, in our hands, result in success.

Attempted Synthesis of $[W(\equiv CNPPh_3)Cl_2(Tp^*)]$

To a Youngs NMR tube was added trimethylsilylimino triphenylphosphorane ($Me_3SiNPPh_3$: 12 mg, 0.034 mmol) and [W(≡CF)Cl_2(Tp*)][5b] (20 mg, 0.034 mmol) in d_8-toluene. The NMR tube was sealed tightly and heated to 50 °C for 48 hours with $^{31}P\{^1H\}$ and ^1H NMR spectra being measured at *t* = 1, 4 and 48 hours to monitor reaction progress. These showed only unreacted reagents.

Conditions Explored for Unsuccessful Synthetic Approaches to [W(≡CNPPh$_3$)(CO)$_2$(Tp*)] from [W(≡CCl)(CO)$_2$(Tp*)]

Method 1. To a Youngs NMR tube was added trimethylsilylimino triphenylphosphorane (15 mg, 0.04 mmol) and [W(≡CCl)$(CO)_2$(Tp*)][5a] (25 mg, 0.04 mmol) in $CDCl_3$ (0.5 mL). The NMR tube was sealed tightly and mixed for 1 hour before an NMR was taken to monitor reaction progress, with only decomposition products seen.

Method 2. To a Youngs NMR tube was added trimethylsilylimino(triphenyl)phosphorane (15 mg, 0.04 mmol) and [W(≡CCl)$(CO)_2$(Tp*)] (25 mg, 0.04 mmol) and tetrabutyl ammonium fluoride (TBAF: 0.05 mL, 1 M solution in THF, 2-3% H_2O) in $CDCl_3$ (0.5 mL). The NMR tube was sealed tightly and mixed for 1 hour before an NMR was taken to monitor reaction progress, with only unidentified decomposition products seen.

Method 3. To a dry Schlenk flask under argon was added [Ph_3PNH_2]Cl (250 mg, 0.80 mmol) in THF (15 mL). To the mixing solution *n*-BuLi (1.6 mL, 2M) was added and the mixture stirred for 20 minutes. A solution of [W(≡CCl)$(CO)_2$(Tp*)] (460 mg, 0.79 mmol) in THF (20 mL) was then added and the mixture stirred for three hours before *in situ* FTIR analysis showed only unreacted [W(≡CCl)$(CO)_2$(Tp*)].

Conditions Explored for Unsuccessful Syntheses of [W(≡CNEPh$_3$)(CO)$_2$(Tp*)] from [W(≡CBr)(CO)$_2$(Tp*)] (E = P, As)

Method 1. To a Youngs NMR tube was added $HNPPh_3$ (28 mg, 0.10 mmol) and [W(≡CBr)(CO)2(Tp*)][5a] (25 mg, 0.039 mmol) in $CDCl_3$ (0.5 mL). The NMR tube was sealed tightly and heated to 50 °C for 1 hour before a ^1H and $^{31}P\{^1H\}$ NMR spectra were measured to monitor reaction progress, with only unreacted [W(≡CBr)$(CO)_2$(Tp*)] and $HNPPh_3$ being observed.

Method 2. To a Youngs NMR tube was added $HNPPh_3$ (28 mg, 0.10 mmol) and [W(≡CBr)$(CO)_2$(Tp*)] (25 mg, 0.04 mmol) in $CDCl_3$ (0.5 mL). The NMR tube was sealed tightly and heated to 50 °C for 1 hour, with no visible change. Triethylamine (0.1 mL, 0.01 mmol) was added and after mixing for 15 minutes NMR spectra were measured to monitor reaction progress, with only unreacted [W(≡CBr)$(CO)_2$(Tp*)] being observed.

Method 3. To a dry Schlenk flask under argon was added [Ph_3PNH_2]Cl (50 mg, 0.16 mmol), [W(≡CBr)$(CO)_2$(Tp*)] (100 mg, 0.16 mmol) and triethylamine (1 mL, 7.2 mmol) in toluene (10 mL). The yellow solution was heated to 80 °C under argon for 20 hours, after which FTIR and NMR analysis of the resulting dark black solution showed only the [W(≡CBr)$(CO)_2$(Tp*)] starting material.

Method 4. To a dry Schlenk flask under argon was added [Ph_3AsNH_2]Cl (50 mg, 0.14 mmol) suspended in diethyl ether (15 mL). Upon cooling to 0 °C a solution of Na[N$(SiMe_3)_2$] (NaHMDS: 0.53 mL, 0.6 M) was then added and the solution was allowed to stir for 1.5 hours whilst warming. At room temperature, a solution of [W(≡CBr)(CO)2(Tp*)][5a] (100 mg, 0.16 mmol) in diethyl ether (10 mL) was added and the reaction mixed was stirred for 60 hours. Volatiles were removed *in vacuo* and NMR analysis of the resulting crude powder in $CDCl_3$ showed only unreacted [W(≡CBr)$(CO)_2$(Tp*)].

Method 5. To a dry Schlenk flask under argon was added [W(≡CBr)$(CO)_2$(Tp*)] (250 mg, 0.399 mmol) in THF (15 mL) and the solution was cooled to -78 °C. At this temperature, a solution of *n*-Buli (0.2 mL, 2M) was added and the mixture was then stirred for 30 minutes before addition of a solution tosylimino triphenylphosphorane (172 mg, 0.399 mmol) in THF (10 mL). The vibrant yellow solution was mixed for two hours before warming to 0 °C, then stirred for a further two hours before being allowed to warm to room temperature gradually over 12 hours. FTIR analysis showed the presence of only known lithiocarbyne decomposition products, *viz.* [W(≡CH)$(CO)_2$(Tp*)], [W(≡C^{n}Bu)$(CO)_2$(Tp*)] and [W_2(μ-CCH_2)$(CO)_4$$(Tp^*)_2$], while the $^{31}P\{^1H\}$ NMR indicated only unchanged $Ph_3P{=}NSO_2C_6H_4Me$ (δ_P = 14.4) was present.

Conditions Explored for Unsuccessful Synthesis of [W(≡CN=CHPh)-(CO)$_2$(Tp*)]

To a Young NMR tube was added [W(≡CNPPh$_3$)$(CO)_2$(Tp*)] (20 mg, 0.024 mmol) and benzaldehyde (0.05 mL, excess) in CDCl3 (0.5 mL). The NMR tube was sealed tightly and heated to 50 C for 48 hours before an NMR spectrum was measured to monitor reaction progress, which however showed only unreacted reagents.

Conditions Explored for Unsuccessful Synthesis of [W(≡CN=CHPh)-Br(CO)$_4$]

To a Young NMR tube was added [W(≡CNPPh$_3$)Br$(CO)_4$] (25 mg, 0.037 mmol) and benzaldehyde (0.05 mL, excess) in $CDCl_3$ (0.5 mL). The NMR tube was sealed tightly and heated to 50 C for 48 hours before an NMR spectrum was measured to monitor reaction progress, which however showed only unreacted reagents.

Computational Results

Computational studies were performed using the *SPARTAN24®* suite of programs.[7] In the first instance, geometry optimisations (gas phase) were performed at the DFT level of theory using the exchange functional (ωB97X-D) of Head-Gordon.[8] The Los Alamos effective core potential type basis set (LANL2Dζ) of Hay and Wadt[9] was used for transition metals; the Pople 6-31G* basis sets[10] were used for all other atoms. Geometry optimisations and single-point energy calculations were performed at the ωB97X-D/6-31G*/LANL2Dζ level; frequency calculations were performed to confirm that the optimized structures were local minima and to identify vibrational modes of interest. For the method's typical reflection of phenomenological Lewis bonds, Löwden bond orders,[11] which emphasise covalency were also calculated. The calculations follow a very similar form to the Wiberg indices, except using Löwden's symmetrically orthogonalized basis set instead of the natural basis, as implemented in the *SPARTAN24®* suite of programs.

[W(≡CN=PMe$_3$)(CO)$_2$(Tp)]

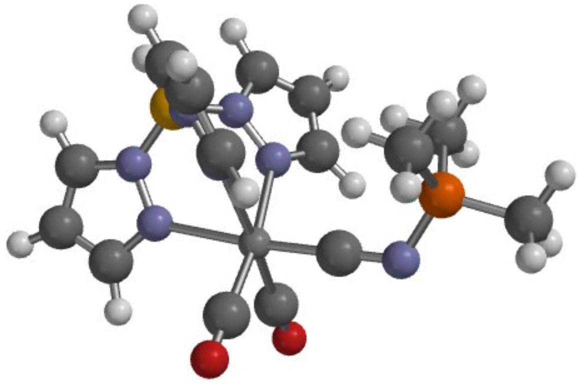


Figure S3. Optimised geometry for [W(≡CN=PMe$_3$)(CO)$_2$(Tp)] at the ωB97X-D/6-31G*/LANL2Dζ(W) level of DFT.

Table S1. Thermodynamic data (298.15 K) [W(≡CN=PMe$_3$)(CO)$_2$(Tp)] ωB97X-D/6-31G*/LANL2Dζ (W)

Zero Point Energy : 916.77 kJ/mol
Temperature Correction : 60.21 kJ/mol
Enthalpy Correction : 976.99 kJ/mol
Enthalpy : -1550.171239 au
Entropy : 632.41 J/mol.K
Gibbs Energy : -1550.243055 au
Cv : 420.39 J/mol.K

ν_{CO} 1937, 1860 cm^{-1} (λ = 0.9297).[12]
ν_{CN} 1467 cm^{-1} (λ = 0.9297).[12]
Lowest frequency real vibrational mode (uncorrected): 19 cm^{-1}

Table S2. Cartesian Coordinates for [W(≡CN=PMe$_3$)(CO)$_2$(Tp)]

Atom	x	y	z
W	1.077927	1.052362	0.530358
P	-2.028998	-0.455614	2.859797
O	0.919160	4.126197	1.152395
O	3.502999	0.677361	2.486660
N	2.362483	1.306184	-1.385403
N	2.059741	0.650000	-2.527592
N	-0.526294	1.152686	-1.076079
N	-0.422217	0.495871	-2.250468
N	1.207402	-1.085212	-0.226405
N	1.047312	-1.405920	-1.526860
B	0.851625	-0.303621	-2.589333
H	0.754904	-0.795804	-3.685586
C	3.446069	2.038755	-1.637033
C	3.862481	1.859204	-2.961329
H	4.704682	2.313283	-3.460125
C	2.949304	0.964382	-3.487320
C	-1.687206	1.808371	-1.101455
C	-2.357573	1.567844	-2.306299
H	-3.311675	1.957967	-2.625641
C	-1.508796	0.730695	-3.008238
C	1.460439	-2.221198	0.424423
C	1.454364	-3.303623	-0.462507
H	1.630539	-4.344950	-0.241232
C	1.193252	-2.732546	-1.695322
C	0.996213	2.989634	0.921324
C	2.611124	0.834322	1.756309
C	-0.050585	0.801359	1.975512
N	-0.871195	0.643516	2.979741
C	-1.427397	-2.156286	2.628513
H	-0.889378	-2.211229	1.677062
H	-2.257025	-2.869551	2.619841
H	-0.735098	-2.407208	3.436644
C	-2.991962	-0.429405	4.387333
H	-2.335230	-0.656474	5.230817
H	-3.802376	-1.162410	4.346406
H	-3.409180	0.570456	4.530159
C	-3.182232	-0.181383	1.482677
H	-3.658622	0.795902	1.597146
H	-3.949272	-0.960949	1.446236
H	-2.615450	-0.181491	0.546287
H	-1.967409	2.418428	-0.254726
H	-1.593929	0.290319	-3.990725
H	2.865185	0.528578	-4.472033
H	1.106429	-3.169501	-2.679078
H	3.868399	2.651670	-0.853435
H	1.647066	-2.190974	1.488585

[W(≡CN=SMe$_2$)(CO)$_2$(Tp)]

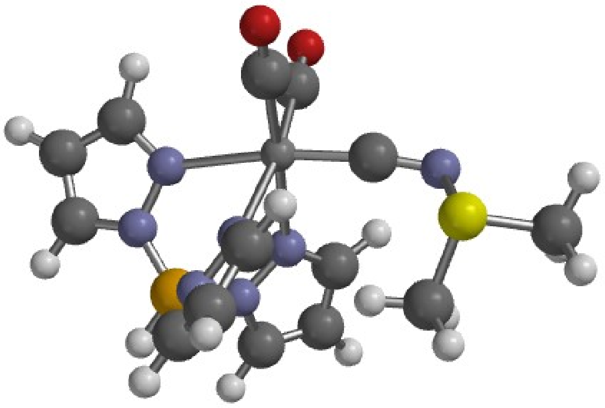


Figure S4. Optimised geometry for [W(≡CN=SMe$_2$)(CO)$_2$(Tp)]at the ωB97X-D/6-31G*/LANL2Dζ(W) level of DFT.

Table S3. Thermodynamic data (298.15 K) [W(≡CN=SMe$_2$)(CO)$_2$(Tp)] ωB97X-D/6-31G*/LANL2Dζ (W)

Zero Point Energy : 816.52 kJ/mol
Temperature Correction : 55.94 kJ/mol
Enthalpy Correction : 872.45 kJ/mol
Enthalpy : -1567.065296 au
Entropy : 604.52 J/mol.K
Gibbs Energy : -1567.133945 au (
Cv : 388.94 J/mol.K

ν_{CO} 1943, 1873 cm^{-1} (λ = 0.9297).[12]
ν_{CN} 1418 cm^{-1} (λ = 0.9297).[12]
Lowest frequency real vibrational mode (uncorrected): 29 cm^{-1}

Table S4. Cartesian Coordinates for [W(≡CN=SMe$_2$)(CO)$_2$(Tp)]

Atom	x	y	z
W	0.872757	1.109830	0.727959
S	-2.281454	0.029137	3.017582
O	0.345722	4.128185	1.358385
O	3.514410	1.316696	2.428773
N	2.024865	1.326649	-1.248630
N	1.757226	0.555543	-2.327628
N	-0.804907	1.002457	-0.795948
N	-0.710539	0.293161	-1.940086
N	1.032851	-1.069965	0.109403
N	0.866194	-1.489215	-1.162703
B	0.599218	-0.464197	-2.281018
H	0.486773	-1.020664	-3.343473
C	3.053031	2.113569	-1.591775
C	3.453390	1.844754	-2.909867
H	4.252602	2.321391	-3.456721
C	2.588907	0.845753	-3.325406
C	-2.017896	1.576401	-0.800234
C	-2.714621	1.221026	-1.960765
H	-3.707151	1.533650	-2.245840
C	-1.835087	0.409889	-2.652014
C	1.199489	-2.167217	0.855771
C	1.139562	-3.311732	0.055864
H	1.250630	-4.339666	0.364281
C	0.926275	-2.829282	-1.221450
C	0.564617	3.017329	1.121639
C	2.548337	1.236626	1.800353
C	0.003691	0.623357	2.210832
N	-0.648323	0.021947	3.312422
C	-2.519164	-1.225403	1.731693
H	-2.073196	-0.816873	0.820486
H	-3.590206	-1.428007	1.649174
H	-1.950958	-2.125594	1.984031
C	-2.797552	-0.898589	4.464545
H	-2.188180	-1.800255	4.561781
H	-3.854690	-1.151708	4.358985
H	-2.613638	-0.273140	5.339532
H	-2.294409	2.213425	0.028595
H	-1.936310	-0.085163	-3.605837
H	2.527470	0.337542	-4.276032
H	0.818040	-3.339225	-2.167112
H	3.437209	2.823632	-0.871790
H	1.353924	-2.052564	1.919225

$[W(\equiv CN{=}CMe_2)(CO)_2(Tp)]$

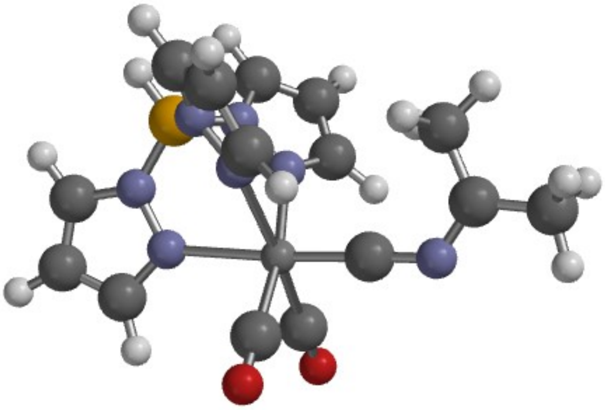


Figure S5. Optimised geometry for $[W(\equiv CN{=}CMe_2)(CO)_2(Tp)]$at the ωB97X-D/6-31G*/LANL2Dζ(W) level of DFT.

Table S5. Thermodynamic data (298.15 K) $[W(\equiv CN{=}CMe_2)(CO)_2(Tp)]$ ωB97X-D/6-31G*/LANL2Dζ (W)

Zero Point Energy : 828.41 kJ/mol
Temperature Correction : 54.30 kJ/mol
Enthalpy Correction : 882.71 kJ/mol
Enthalpy : -1207.040022 au
Entropy : 594.30 J/mol.K
Gibbs Energy : -1207.107510 au
Cv : 379.02 J/mol.K

ν_{CO} 1947, 1883 cm^{-1} (λ = 0.9297).[12]
ν_{CN} 1607 m cm^{-1} (λ = 0.9297).[12]
Lowest frequency real vibrational mode (uncorrected): 22 cm^{-1}

Table S6. Cartesian Coordinates for $[W(\equiv CN{=}CMe_2)(CO)_2(Tp)]$

Atom	x	y	z
W	0.346016	0.446579	0.307569
C	-1.213692	0.577136	4.125514
O	0.128656	3.535851	0.897607
O	2.904345	0.440748	2.151829
N	1.602024	0.789067	-1.590204
N	1.355859	0.107338	-2.730238
N	-1.265483	0.400764	-1.254164
N	-1.106396	-0.224057	-2.441369
N	0.577293	-1.668264	-0.411155
N	0.484233	-2.005910	-1.715067
B	0.216923	-0.932492	-2.786047
H	0.157741	-1.432760	-3.879836
C	2.631397	1.599341	-1.835350
C	3.065896	1.449695	-3.154414
H	3.874284	1.963395	-3.650954
C	2.222414	0.486791	-3.683307
C	-2.497450	0.912424	-1.245414
C	-3.154146	0.617418	-2.443078
H	-4.156053	0.891741	-2.734332
C	-2.228516	-0.106818	-3.172295
C	0.804175	-2.793071	0.268722
C	0.858208	-3.883716	-0.603115
H	1.025813	-4.920951	-0.357861
C	0.650224	-3.332681	-1.854940
C	0.210594	2.394442	0.666109
C	1.963303	0.438119	1.460054
C	-0.674277	0.160231	1.844398
N	-1.380986	-0.074065	2.823238
C	-0.152858	1.557065	4.262507
H	0.844266	1.140483	4.072398
H	-0.195890	1.925378	5.291200
H	-0.263437	2.404854	3.574497
C	-2.132873	0.177845	5.163845
H	-1.531398	-0.179313	6.010769
H	-2.849610	-0.604034	4.913503
H	-2.704896	1.067662	5.462079
H	-2.839046	1.459902	-0.379183
H	-2.284083	-0.546417	-4.157144
H	2.176301	0.045142	-4.667850
H	0.607563	-3.785123	-2.834615
H	3.003857	2.245520	-1.053423
H	0.910725	-2.752964	1.342893

[W(≡CN=NMe)(CO)$_2$(Tp)]

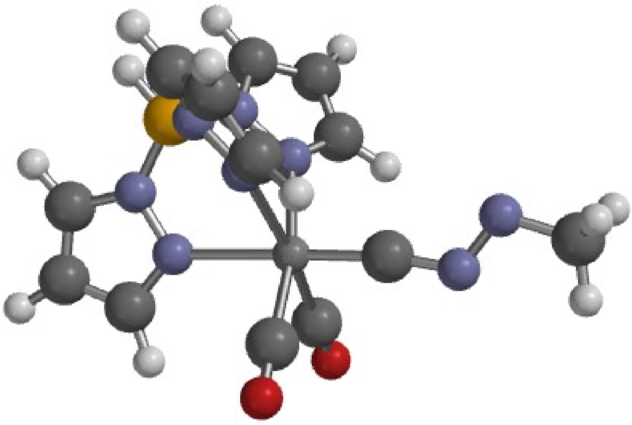


Figure S6. Optimised geometry for [W(≡CN=NMe)(CO)$_2$(Tp)]at the ωB97X-D/6-31G*/LANL2Dζ(W) level of DFT.

Table S7. Thermodynamic data (298.15 K) [W(≡CN=NMe)(CO)$_2$(Tp)] ωB97X-D/6-31G*/LANL2Dζ (W)

Zero Point Energy : 721.15 kJ/mol
Temperature Correction : 51.29 kJ/mol
Enthalpy Correction : 772.44 kJ/mol
Enthalpy : -1183.758411 au
Entropy : 576.39 J/mol.K
Gibbs Energy : -1183.823865 au
Cv : 353.37 J/mol.K

ν_{CO} 1980, 1917 cm^{-1} (λ = 0.9297).[12]
ν_{CN} 1507 vw cm^{-1} (λ = 0.9297).[12]
Lowest frequency real vibrational mode (uncorrected): 10 cm^{-1}

Table S8. Cartesian Coordinates for [W(≡CN=NMe)(CO)$_2$(Tp)]

Atom	x	y	z
W	0.386616	0.693118	0.880464
N	-2.286476	-0.556526	3.646416
O	0.149807	3.777822	1.510173
O	2.919594	0.655714	2.766044
N	1.706544	1.131511	-0.952587
N	1.516530	0.484594	-2.122494
N	-1.160717	0.689087	-0.730994
N	-0.951268	0.113593	-1.934901
N	0.674676	-1.381686	0.103314
N	0.632710	-1.674223	-1.214346
B	0.393373	-0.566071	-2.258017
H	0.379343	-1.025753	-3.370011
C	2.728218	1.969265	-1.130546
C	3.215486	1.870311	-2.437223
H	4.032329	2.414449	-2.885496
C	2.408275	0.910216	-3.028321
C	-2.399294	1.181375	-0.743281
C	-3.011015	0.925202	-1.973275
H	-4.006953	1.195502	-2.288031
C	-2.048252	0.243987	-2.698494
C	0.884750	-2.526934	0.751978
C	0.980936	-3.586642	-0.153894
H	1.146960	-4.630708	0.061260
C	0.814978	-2.992593	-1.393444
C	0.236856	2.650706	1.274472
C	1.996045	0.667497	2.072849
C	-0.649268	0.369715	2.354845
N	-1.248586	0.314520	3.514424
C	-2.831007	-0.491692	4.969275
H	-2.720135	-1.507837	5.369572
H	-3.884454	-0.218544	4.826577
H	-2.350385	0.225723	5.642063
H	-2.781498	1.687139	0.131333
H	-2.065199	-0.154800	-3.702008
H	2.410030	0.504994	-4.029537
H	0.814945	-3.413069	-2.388167
H	3.061398	2.598189	-0.316966
H	0.950140	-2.525193	1.830186

[W(≡CN=NO)(CO)$_2$(Tp)]

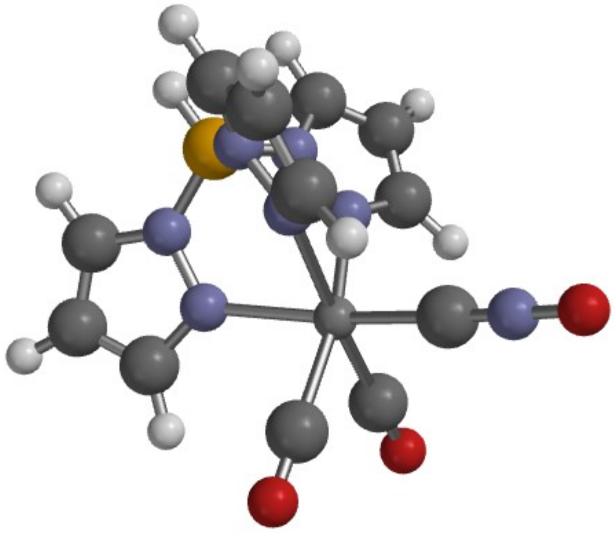


Figure S7. Optimised geometry for [W(≡CN=NO)(CO)$_2$(Tp)]at the ωB97X-D/6-31G*/LANL2Dζ(W) level of DFT.

Table S9. Thermodynamic data (298.15 K) [W(≡CN=NO)(CO)$_2$(Tp)] ωB97X-D/6-31G*/LANL2Dζ (W)

Zero Point Energy : 617.96 kJ/mol
Temperature Correction : 48.27 kJ/mol
Enthalpy Correction : 666.23 kJ/mol
Enthalpy : -1164.346368 au
Entropy : 553.62 J/mol.K
Gibbs Energy : -1164.409237 au
Cv : 328.40 J/mol.K

ν_{CO} 1961, 1878 cm^{-1} (λ = 0.9297).[12]
ν_{NN} 2107 vs cm^{-1} (λ = 0.9297).[12]
Lowest frequency real vibrational mode (uncorrected): 23 cm^{-1}

Table S10. Cartesian Coordinates for [W(≡CN=NO)(CO)$_2$(Tp)]

Atom	x	y	z
W	0.057693	0.778568	1.363604
O	-1.868781	-1.038599	4.925303
O	-0.352294	3.744077	2.271203
O	2.662628	1.430119	3.023809
N	1.356280	1.011195	-0.383514
N	1.154153	0.292202	-1.516895
N	-1.463905	0.779071	-0.200026
N	-1.325092	0.061513	-1.340093
N	0.249023	-1.398406	0.760648
N	0.171619	-1.775047	-0.533562
B	-0.014649	-0.713390	-1.620137
H	-0.049322	-1.209477	-2.715451
C	2.399096	1.821041	-0.619736
C	2.881279	1.626006	-1.909797
H	3.707085	2.125243	-2.391631
C	2.052591	0.648991	-2.442362
C	-2.654397	1.390918	-0.262969
C	-3.303152	1.057152	-1.448005
H	-4.272849	1.384361	-1.788599
C	-2.414418	0.216005	-2.102745
C	0.407714	-2.510883	1.478167
C	0.438625	-3.629409	0.639648
H	0.554897	-4.664031	0.922196
C	0.283087	-3.111734	-0.632424
C	-0.202628	2.648810	1.917033
C	1.709883	1.137462	2.439553
C	-0.865315	0.007324	3.023952
N	-1.354590	-0.507234	3.969517
H	-2.969935	2.030842	0.548347
H	-2.480815	-0.274072	-3.063053
H	2.037834	0.189281	-3.419665
H	0.243357	-3.592497	-1.598605
H	2.738374	2.495604	0.152554
H	0.486924	-2.451005	2.553735

[W(≡CP=PMe$_3$)(CO)$_2$(Tp)]

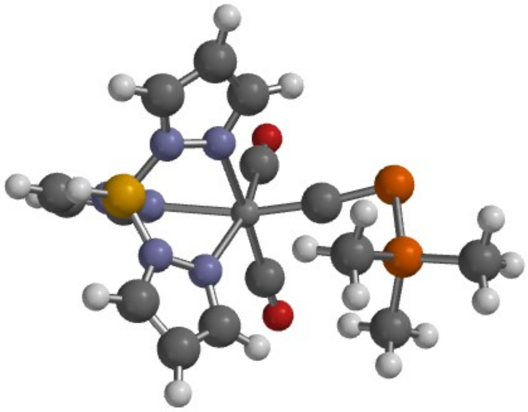


Figure S8. Optimised geometry for [W(≡CP=PMe$_3$)(CO)$_2$(Tp)] at the ωB97X-D/6-31G*/LANL2Dζ(W) level of DFT.

Table S11. Thermodynamic data (298.15 K) [W(≡CP=PMe$_3$)(CO)$_2$(Tp)] ωB97X-D/6-31G*/LANL2Dζ (W)

Zero Point Energy : 907.50 kJ/mol
Temperature Correction : 62.01 kJ/mol
Enthalpy Correction : 969.51 kJ/mol
Enthalpy : -1836.756077 au
Entropy : 643.78 J/mol.K
Gibbs Energy : -1836.829184 au
Cv : 430.59 J/mol.K

ν_{CO} 1952, 1874 cm^{-1} (λ = 0.9297).[12]
ν_{CP} 1059, 1051 w cm^{-1} (λ = 0.9297).[12]
Lowest frequency real vibrational mode (uncorrected): 16 cm^{-1}

Table S12. Cartesian Coordinates for [W(≡CP=PMe$_3$)(CO)$_2$(Tp)]

Atom	x	y	z
W	0.930655	1.061093	0.436257
P	-2.002166	-0.510160	3.040212
O	1.702260	4.040040	1.126543
O	2.881489	0.084132	2.685161
N	2.377529	1.206672	-1.396220
N	2.027163	0.686249	-2.597954
N	-0.558077	1.445325	-1.233363
N	-0.474205	0.889103	-2.440343
N	0.790068	-1.019303	-0.432519
N	0.678702	-1.229598	-1.772578
B	0.693384	-0.054389	-2.775235
H	0.703264	-0.570147	-3.873046
C	3.571554	1.776969	-1.554948
C	4.009963	1.638277	-2.860871
H	4.936430	2.000656	-3.276676
C	3.004067	0.940165	-3.491110
C	-1.672053	2.175743	-1.201111
C	-2.336058	2.084768	-2.453332
H	-3.257560	2.558396	-2.760006
C	-1.507876	1.237224	-3.206147
C	0.846236	-2.225425	0.141248
C	0.757901	-3.223548	-0.805190
H	0.776236	-4.287123	-0.629991
C	0.660331	-2.557686	-2.003972
C	1.413228	2.950272	0.868995
C	2.196134	0.480617	1.832185
C	-0.360081	1.247600	1.720483
P	-1.647471	1.591753	2.861471
C	-0.606480	-1.448398	3.747645
H	0.305575	-1.174502	3.211505
H	-0.774539	-2.527958	3.677419
H	-0.485289	-1.161287	4.795364
C	-3.410087	-0.841247	4.151633
H	-3.207368	-0.415864	5.137986
H	-3.572665	-1.918609	4.250535
H	-4.313502	-0.376252	3.748537
C	-2.423954	-1.342904	1.473522
H	-3.367548	-0.935053	1.101345
H	-2.517156	-2.424534	1.614654
H	-1.641043	-1.132568	0.740266
H	-1.878914	2.686984	-0.266518
H	-1.482524	0.806784	-4.206972
H	2.951787	0.616893	-4.521240
H	0.590561	-2.995456	-2.991319
H	4.075392	2.266850	-0.733619
H	0.957900	-2.352117	1.209016

[W(≡CP=CMe$_2$)(CO)$_2$(Tp)]

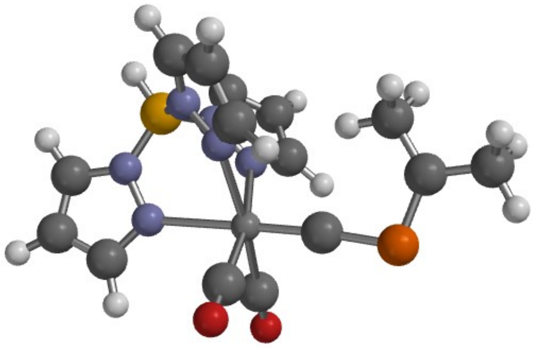


Figure S9. Optimised geometry for [W(≡CP=CMe$_2$)(CO)$_2$(Tp)] at the ωB97X-D/6-31G*/LANL2Dζ(W) level of DFT.

Table S13. Thermodynamic data (298.15 K) [W(≡CP=CMe$_2$)(CO)$_2$(Tp)] ωB97X-D/6-31G*/LANL2Dζ (W)

Zero Point Energy : 817.79 kJ/mol
Temperature Correction : 55.89 kJ/mol
Enthalpy Correction : 873.68 kJ/mol
Enthalpy : -1493.614151 au
Entropy : 604.38 J/mol.K
Gibbs Energy : -1493.682784 au
Cv : 388.02 J/mol.K

ν_{CO} 1981, 1918 cm^{-1} (λ = 0.9297).[12]
ν_{CP} 1231 w cm^{-1} (λ = 0.9297).[12]
Lowest frequency real vibrational mode (uncorrected): 15 cm^{-1}

Table S14. Cartesian Coordinates for [W(≡CP=CMe$_2$)(CO)$_2$(Tp)]

Atom	x	y	z
W	0.781689	1.070170	0.647743
C	-2.098182	-0.552473	3.586939
O	0.535267	4.195665	1.047278
O	3.414515	0.999895	2.392225
N	2.069211	1.338368	-1.301370
N	1.790196	0.613164	-2.403167
N	-0.826744	1.001619	-0.900189
N	-0.683160	0.346183	-2.073586
N	0.968640	-1.058838	-0.003141
N	0.868914	-1.440728	-1.295977
B	0.625734	-0.399632	-2.406096
H	0.537263	-0.941450	-3.477159
C	3.112631	2.108800	-1.597858
C	3.525714	1.886269	-2.914821
H	4.340207	2.358846	-3.441057
C	2.653116	0.925278	-3.388134
C	-2.057330	1.520294	-0.890235
C	-2.727446	1.198395	-2.072683
H	-3.730122	1.469607	-2.364193
C	-1.811079	0.452644	-2.794142
C	1.141367	-2.167125	0.720257
C	1.152907	-3.290587	-0.110893
H	1.275411	-4.324747	0.171178
C	0.977080	-2.776807	-1.384384
C	0.637166	3.055481	0.902000
C	2.455126	1.035669	1.751853
C	-0.134629	0.857688	2.164187
P	-0.943450	0.682931	3.768368
C	-2.292766	-1.296735	2.166846
H	-1.796112	-0.976213	1.239054
H	-3.383498	-1.316106	1.996757
H	-2.080177	-2.365335	2.345278
C	-2.909056	-0.976211	4.610324
H	-2.768635	-2.045357	4.814181
H	-3.966480	-0.798618	4.375618
H	-2.628652	-0.393987	5.494378
H	-2.390308	2.090814	-0.035454
H	-1.875303	-0.010270	-3.767703
H	2.587451	0.445501	-4.353533
H	0.922267	-3.260647	-2.348345
H	3.507853	2.780099	-0.848441
H	1.243710	-2.092156	1.793113

[W(≡CP=CMe$_2$)(CO)$_2$(Tp)]

Figure S10. Optimised geometry for [W(≡CP=CMe$_2$)(CO)$_2$(Tp)] at the ωB97X-D/6-31G*/LANL2Dζ(W) level of DFT.

Table S15. Thermodynamic data (298.15 K) [W(≡CP=CMe$_2$)(CO)$_2$(Tp)] ωB97X-D/6-31G*/LANL2Dζ (W)

Zero Point Energy : 817.79 kJ/mol
Temperature Correction : 55.89 kJ/mol
Enthalpy Correction : 873.68 kJ/mol
Enthalpy : -1493.614151 au
Entropy : 604.38 J/mol.K
Gibbs Energy : -1493.682784 au
Cv : 388.02 J/mol.K

ν_{CO} 1981, 1918 cm^{-1} (λ = 0.9297).[12]
ν_{CP} 1231 w cm^{-1} (λ = 0.9297).[12]
Lowest frequency real vibrational mode (uncorrected): 15 cm^{-1}

Table S16. Cartesian Coordinates for [W(≡CP=CMe$_2$)(CO)$_2$(Tp)]

Atom	x	y	z
W	0.781689	1.070170	0.647743
C	-2.098182	-0.552473	3.586939
O	0.535267	4.195665	1.047278
O	3.414515	0.999895	2.392225
N	2.069211	1.338368	-1.301370
N	1.790196	0.613164	-2.403167
N	-0.826744	1.001619	-0.900189
N	-0.683160	0.346183	-2.073586
N	0.968640	-1.058838	-0.003141
N	0.868914	-1.440728	-1.295977
B	0.625734	-0.399632	-2.406096
H	0.537263	-0.941450	-3.477159
C	3.112631	2.108800	-1.597858
C	3.525714	1.886269	-2.914821
H	4.340207	2.358846	-3.441057
C	2.653116	0.925278	-3.388134
C	-2.057330	1.520294	-0.890235
C	-2.727446	1.198395	-2.072683
H	-3.730122	1.469607	-2.364193
C	-1.811079	0.452644	-2.794142
C	1.141367	-2.167125	0.720257
C	1.152907	-3.290587	-0.110893
H	1.275411	-4.324747	0.171178
C	0.977080	-2.776807	-1.384384
C	0.637166	3.055481	0.902000
C	2.455126	1.035669	1.751853
C	-0.134629	0.857688	2.164187
P	-0.943450	0.682931	3.768368
C	-2.292766	-1.296735	2.166846
H	-1.796112	-0.976213	1.239054
H	-3.383498	-1.316106	1.996757
H	-2.080177	-2.365335	2.345278
C	-2.909056	-0.976211	4.610324
H	-2.768635	-2.045357	4.814181
H	-3.966480	-0.798618	4.375618
H	-2.628652	-0.393987	5.494378
H	-2.390308	2.090814	-0.035454
H	-1.875303	-0.010270	-3.767703
H	2.587451	0.445501	-4.353533
H	0.922267	-3.260647	-2.348345
H	3.507853	2.780099	-0.848441
H	1.243710	-2.092156	1.793113

[W(≡CP=NMe)(CO)$_2$(Tp)]

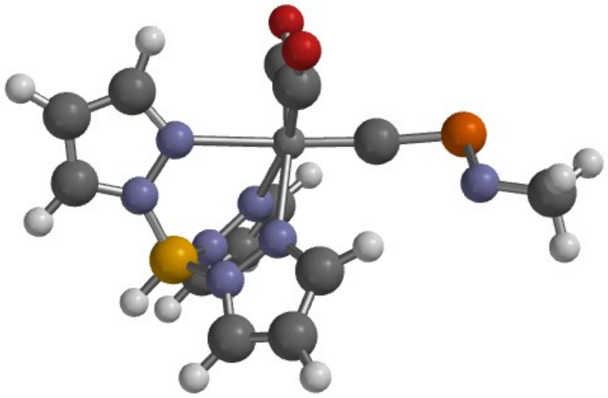


Figure S11. Optimised geometry for [W(≡CP=NMe)(CO)$_2$(Tp)] at the ωB97X-D/6-31G*/LANL2Dζ(W) level of DFT.

Table S17. Thermodynamic data (298.15 K) [W(≡CP=NMe)(CO)$_2$(Tp)] ωB97X-D/6-31G*/LANL2Dζ (W)

Zero Point Energy :	713.52	kJ/mol
Temperature Correction :	52.61	kJ/mol
Enthalpy Correction :	766.12	kJ/mol
Enthalpy :	-1470.373303	au
Entropy :	585.20	J/mol.K
Gibbs Energy :	-1470.439758	au (
Cv :	360.18	J/mol.K

ν_{CO} 1990, 1926 cm^{-1} (λ = 0.9297).[12]

ν_{CP} 1171 vw cm^{-1} (λ = 0.9297).[12]

Lowest frequency real vibrational mode (uncorrected): 24 cm^{-1}

Table S18. Cartesian Coordinates for [W(≡CP=NMe)(CO)$_2$(Tp)]

Atom	x	y	z
W	0.703278	0.351044	1.004438
N	-2.515127	0.427116	3.530459
O	0.339517	3.397994	1.766053
O	3.439207	0.187317	2.588789
N	1.721108	1.147694	-0.951244
N	1.390431	0.602550	-2.146274
N	-1.052579	0.303992	-0.352222
N	-0.968663	-0.071396	-1.651534
N	1.089327	-1.571628	-0.041719
N	0.875086	-1.715704	-1.371591
B	0.370050	-0.541696	-2.238939
H	0.226732	-0.895174	-3.379952
C	2.618850	2.099328	-1.187172
C	2.890181	2.187809	-2.556624
H	3.576762	2.868986	-3.035589
C	2.083944	1.214873	-3.125998
C	-2.335802	0.564870	-0.093367
C	-3.105174	0.364035	-1.245623
H	-4.171194	0.493281	-1.351959
C	-2.194320	-0.040510	-2.207447
C	1.526349	-2.743257	0.416975
C	1.598270	-3.675365	-0.621188
H	1.914317	-4.704554	-0.549750
C	1.177874	-2.974502	-1.739719
C	0.478370	2.286604	1.493688
C	2.445820	0.263522	2.006117
C	-0.219481	0.012380	2.553682
P	-1.158532	-0.037152	4.035412
C	-3.685338	0.529540	4.494957
H	-3.376555	0.234661	5.511302
H	-4.494117	-0.145744	4.194996
H	-4.046312	1.562099	4.553351
H	-2.619119	0.852547	0.911930
H	-2.334600	-0.310534	-3.244003
H	1.972934	0.932595	-4.163225
H	1.081513	-3.298654	-2.765760
H	3.003396	2.652168	-0.340767
H	1.754323	-2.826213	1.469876

[W(≡CP=O)(CO)$_2$(Tp)]

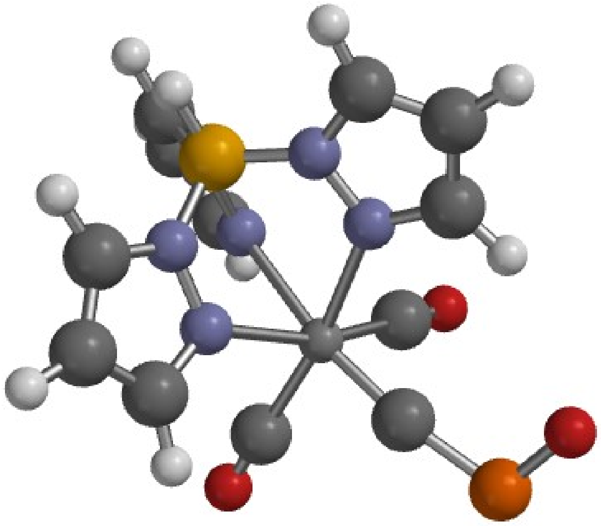


Figure S12. Optimised geometry for [W(≡CP=O)(CO)$_2$(Tp)] at the ωB97X-D/6-31G*/LANL2Dζ(W) level of DFT.

Table S19. Thermodynamic data (298.15 K) [W(≡CP=O)(CO)$_2$(Tp)] ωB97X-D/6-31G*/LANL2Dζ (W)

Zero Point Energy : 607.56 kJ/mol
Temperature Correction : 49.17 kJ/mol
Enthalpy Correction : 656.73 kJ/mol
Enthalpy : -1450.999580 au
Entropy : 562.61 J/mol.K
Gibbs Energy : -1451.063470 au
Cv : 333.64 J/mol.K

ν_{CO} 1999,1935 cm^{-1} (λ = 0.9297).[12]
ν_{PO} 1138 vw cm^{-1} (λ = 0.9297).[12]
Lowest frequency real vibrational mode (uncorrected): 34 cm^{-1}

Table S20. Cartesian Coordinates for [W(≡CP=O)(CO)$_2$(Tp)]

Atom	x	y	z
W	0.177735	0.603226	1.495538
O	-3.337555	1.249682	3.787315
O	0.215522	3.764262	1.729204
O	2.756341	0.359507	3.313962
N	1.415810	1.011448	-0.456879
N	1.102868	0.354165	-1.592428
N	-1.482193	0.541946	0.025499
N	-1.353171	-0.005605	-1.204816
N	0.421620	-1.462185	0.749247
N	0.277892	-1.773216	-0.558412
B	-0.039692	-0.685184	-1.616262
H	-0.140116	-1.181851	-2.707105
C	2.443232	1.806115	-0.737678
C	2.812603	1.672130	-2.078335
H	3.606535	2.184822	-2.598127
C	1.933062	0.733413	-2.581693
C	-2.751252	0.939361	0.151584
C	-3.460294	0.650807	-1.018521
H	-4.500612	0.848359	-1.224740
C	-2.533221	0.046477	-1.848081
C	0.706923	-2.594976	1.394706
C	0.744379	-3.662684	0.499295
H	0.943920	-4.700568	0.714168
C	0.472522	-3.089410	-0.730649
C	0.201398	2.616777	1.646748
C	1.828322	0.463130	2.639027
C	-0.841040	0.632573	2.944139
P	-1.894136	1.007702	4.383923
H	-3.086112	1.381972	1.080422
H	-2.623111	-0.350319	-2.848537
H	1.844924	0.313479	-3.572842
H	0.404365	-3.525299	-1.716221
H	2.856123	2.430433	0.042087
H	0.862322	-2.574974	2.463433

Trans-[W(≡CN=PMe$_3$)Br(CO)$_4$]

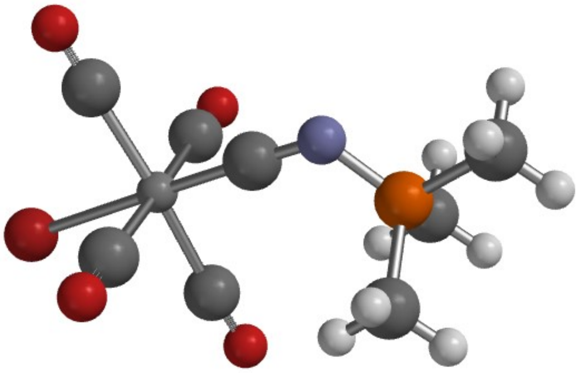


Figure S13. Optimised geometry for *trans*-[W(≡CN=PMe$_3$)Br(CO)$_4$] at the ωB97X-D/6-31G*/LANL2Dζ(W) level of DFT.

Table S21. Thermodynamic data (298.15 K) *trans*-[W(≡CN=PMe$_3$)Br(CO)$_4$] ωB97X-D/6-31G*/LANL2Dζ (W)

Zero Point Energy : 424.10 kJ/mol
Temperature Correction : 46.78 kJ/mol
Enthalpy Correction : 470.88 kJ/mol

Enthalpy : -3648.707686 au
Entropy : 548.25 J/mol.K
Gibbs Energy : -3648.769945 au
Cv : 296.69 J/mol.K

ν_{CO} 2057, 2002, 1966, 1950 cm^{-1} (λ = 0.9297).[12]
ν_{PO} 1524 vs cm^{-1} (λ = 0.9297).[12]
Lowest frequency real vibrational mode (uncorrected): 20 cm^{-1}

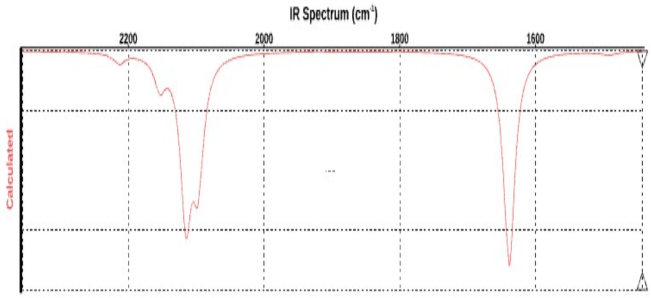


Figure S14. Calculated infrared spectrum (carbonyl region, uncorrected) for *trans*-[W(≡CN=PMe$_3$)Br(CO)$_4$] at the ωB97X-D/6-31G*/LANL2Dζ(W) level of DFT.

Table S22. Cartesian Coordinates for *trans*-[W(≡CN=PMe$_3$)Br(CO)$_4$]

Atom	x	y	z
W	-2.238705	0.000919	-1.220547
Br	-4.932436	0.000042	-1.392721
C	-0.300226	-0.001418	-1.074948
N	0.867560	0.000511	-0.972301
P	1.605314	0.000254	0.497397
C	1.166487	-1.451136	1.491661
H	0.088723	-1.445744	1.679054
H	1.681343	-1.449268	2.457068
H	1.429973	-2.356368	0.938792
C	3.392356	0.000624	0.261271
H	3.674526	-0.888725	-0.308577
H	3.920031	-0.000127	1.219467
H	3.674216	0.891022	-0.306958
C	1.166132	1.450479	1.493441
H	0.088249	1.444372	1.681706
H	1.429154	2.356396	0.941290
H	1.681876	1.447842	2.458698
C	-2.292367	-2.059414	-1.217477
O	-2.276978	-3.212245	-1.195667
C	-2.420756	-0.002390	0.819330
O	-2.441329	-0.006683	1.978291
C	-2.213333	0.001862	-3.307937
O	-2.170102	0.004109	-4.453418
C	-2.290622	2.061125	-1.226037
O	-2.274066	3.213944	-1.212986

[W(≡CN=PMe$_3$)(CO)$_5$]$^+$

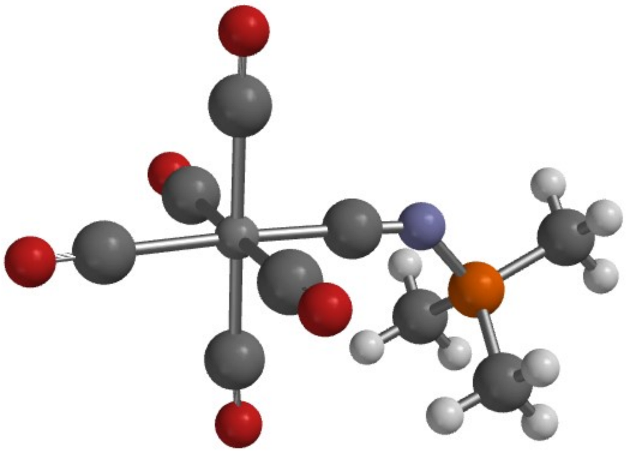


Figure S15. Optimised geometry for [W(≡CN=PMe$_3$)(CO)$_5$]$^+$ at the ωB97X-D/6-31G*/LANL2Dζ(W) level of DFT.

Table S23. Thermodynamic data (298.15 K) [W(≡CN=PMe$_3$)(CO)$_5$]$^+$ ωB97X-D/6-31G*/LANL2Dζ (W)

Zero Point Energy : 442.83 kJ/mol
Temperature Correction : 48.50 kJ/mol
Enthalpy Correction : 491.33 kJ/mol
Enthalpy : -1187.838439 au
Entropy : 553.22 J/mol.K
Gibbs Energy : -1187.901263 au
Cv : 309.44 J/mol.K

∴ ν_{CO} 2096, 2046, 2025, 1992, 1978 cm^{-1} (λ = 0.9297).[12]
ν_{PO} 1719 vs cm^{-1} (λ = 0.9297).[12]
Lowest frequency real vibrational mode (uncorrected): 20 cm^{-1}

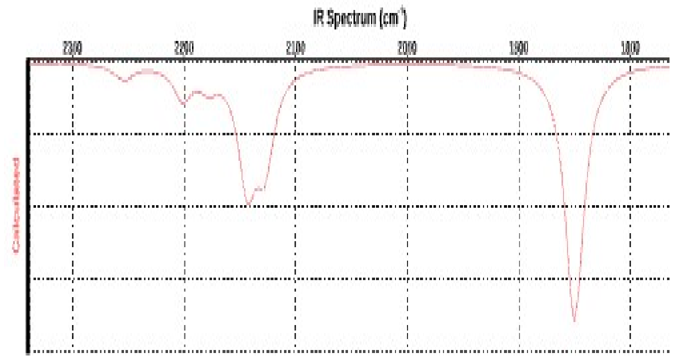


Figure S16. Calculated infrared spectrum (carbonyl region, uncorrected) for *trans*-[W(≡CN=PMe$_3$)(CO)$_5$]$^+$ at the ωB97X-D/6-31G*/LANL2Dζ(W) level of DFT.

Table S24. Cartesian Coordinates for [W(≡CN=PMe$_3$)(CO)$_5$]$^+$

Atom	x	y	z
W	-2.218179	0.000141	-1.214721
C	-2.204670	-2.069531	-1.227469
O	-2.161278	-3.211451	-1.223262
C	-4.336604	-0.003595	-1.463179
O	-5.466771	-0.008102	-1.583008
C	-2.459134	0.003019	0.825975
O	-2.505213	0.005717	1.972249
C	-1.957740	0.001005	-3.288026
O	-1.787187	0.002960	-4.414736
C	-2.201376	2.069815	-1.229956
O	-2.154708	3.211612	-1.227321
C	-0.278746	-0.003209	-0.895638
N	0.927428	-0.001336	-0.656314
P	1.859442	-0.000186	0.693801
C	1.506053	-1.468944	1.676621
H	0.457229	-1.456454	1.987721
H	2.143030	-1.485819	2.566352
H	1.693655	-2.367045	1.081990
C	1.505413	1.469047	1.675663
H	0.456659	1.456402	1.986836
H	1.692489	2.366939	1.080552
H	2.142290	1.486902	2.565465
C	3.573338	0.000364	0.161765
H	3.770609	-0.889260	-0.442419
H	4.234146	0.000745	1.033463
H	3.769802	0.890258	-0.442355

Free Carbyne Cations

Linear [CN=PMe$_3$]$^+$

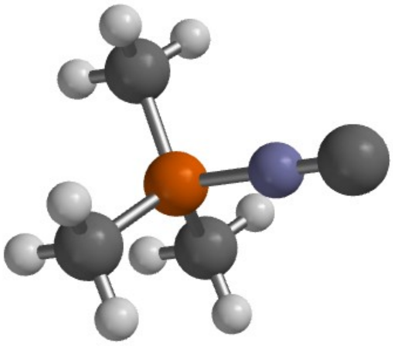


Figure S17. Optimised geometry for linear [CN=PMe$_3$]$^+$ at the ωB97X-D/6-31G*/LANL2Dζ level of DFT.

Table S25. Thermodynamic data (298.15 K) for linear [CN=PMe$_3$]$^+$ at the ωB97X-D/6-31G*/LANL2Dζ level of DFT.

Zero Point Energy : 306.91 kJ/mol
Temperature Correction : 24.12 kJ/mol
Enthalpy Correction : 331.04 kJ/mol
Enthalpy : -553.465339 au
Entropy : 365.80 J/mol.K
Gibbs Energy : -553.506879 au
Cv : 132.16 J/mol.K

ν_{CN} 1997 vs cm^{-1} (λ = 0.9297).[12]
Lowest frequency real vibrational mode (uncorrected): 130 cm^{-1}

Natural Charges (a.u.)

C (+0.540) N (–0.978) P (1.867)

Löwden Bond Orders

C–N (2.72) N–P (1.03)

Table S26. Cartesian Coordinates for linear [CN=PMe$_3$]$^+$

Atom	x	y	z
C	-1.264141	0.000000	-2.663558
N	-0.835171	0.000000	-1.755555
P	-0.081181	-0.000000	-0.168253
C	0.921582	-1.485129	-0.059943
H	1.410198	-1.525454	0.919908
H	1.684708	-1.473399	-0.843335
H	0.288714	-2.368628	-0.183872
C	-1.403306	-0.000000	1.045472
H	-0.975133	-0.000001	2.054213
H	-2.022836	-0.892017	0.917194
H	-2.022836	0.892017	0.917194
C	0.921582	1.485129	-0.059943
H	1.410198	1.525454	0.919908
H	0.288714	2.368628	-0.183872
H	1.684708	1.473398	-0.843335

Linear [CN=CMe$_2$]$^+$

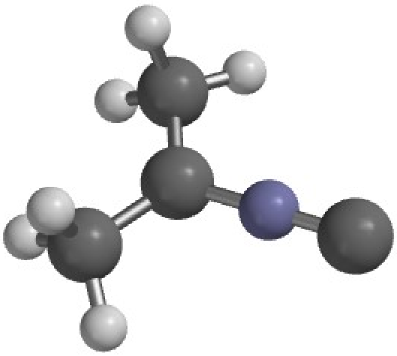


Figure S18. Optimised geometry for linear [CN=CMe$_2$]$^+$ at the ωB97X-D/6-31G*/LANL2Dζ level of DFT.

Table S27. Thermodynamic data (298.15 K) for linear [CN=CMe$_2$]$^+$ at the ωB97X-D/6-31G*/LANL2Dζ level of DFT.

Zero Point Energy : 219.71 kJ/mol
Temperature Correction : 17.93 kJ/mol
Enthalpy Correction : 237.64 kJ/mol
Enthalpy : -210.253441 au
Entropy : 315.11 J/mol.K
Gibbs Energy : -210.289225 au
Cv : 89.26 J/mol.K

ν_{CN} 1967 vs cm^{-1} (λ = 0.9297).[12]
Lowest frequency real vibrational mode (uncorrected): 55 cm^{-1}

Natural Charges (a.u.)

C (+0.628) N (–0.643) C (0.615)

Löwden Bond Orders

C–N (2.52) N–C (1.39)

Table S28. Cartesian Coordinates for linear [CN=CMe$_2$]$^+$.

Atom	x	y	z
C	-2.464784	1.223514	0.417097
N	-1.394015	0.710268	0.227824
C	-0.211836	0.157741	0.003225
C	-0.072824	-0.753314	-1.138713
H	0.935819	-0.716246	-1.558932
H	-0.845634	-0.604246	-1.894925
H	-0.200093	-1.773165	-0.725420
C	0.870233	0.421623	0.960331
H	1.854516	0.288418	0.507699
H	0.765275	-0.347029	1.750625
H	0.763342	1.392435	1.451188

Linear [CN=SMe$_2$]$^+$

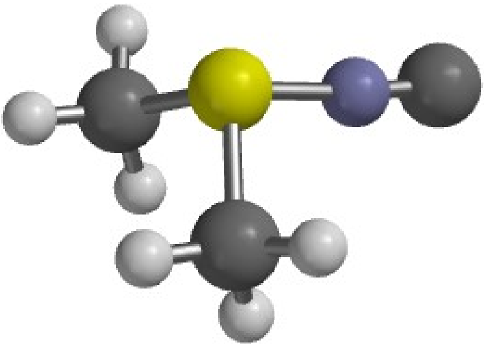


Figure S19. Optimised geometry for linear [CN=SMe$_2$]$^+$ at the ωB97X-D/6-31G*/LANL2Dζ level of DFT.

Table S29. Thermodynamic data (298.15 K) for linear [CN=SMe$_2$]$^+$ at the ωB97X-D/6-31G*/LANL2Dζ level of DFT.

Zero Point Energy : 213.05 kJ/mol
Temperature Correction : 19.70 kJ/mol
Enthalpy Correction : 232.75 kJ/mol
Enthalpy : -570.336012 au
Entropy : 331.65 J/mol•K
Gibbs Energy : -570.373674 au (
Cv : 98.59 J/mol•K

ν_{CN} 1975 vs cm^{-1} (λ = 0.9297).[12]
Lowest frequency real vibrational mode (uncorrected): 133 cm^{-1}

Natural Charges (a.u.)

C (+0.542) N (–0.862) S (1.204)

Löwden Bond Orders

C–N (2.71) N–P (1.08)

Table S30. Cartesian Coordinates for linear [CN=SMe$_2$]$^+$.

Atom	x	y	z
C	-2.631254	0.927394	0.735871
N	-1.562426	0.800931	0.221638
S	-0.062009	0.754566	-0.438664
C	-0.064423	-0.871199	-1.228817
H	0.941243	-1.022151	-1.631615
H	-0.788733	-0.832078	-2.045180
H	-0.324721	-1.640886	-0.500213
C	0.970001	0.495969	1.023017
H	1.993546	0.364062	0.660544
H	0.623726	-0.379339	1.575246
H	0.905049	1.402731	1.628173

Bent [CN=PMe$_3$]$^+$

(Constraint: P–N–C = 120 °)

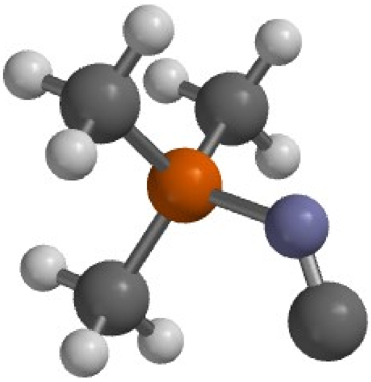


Figure S20. Optimised geometry for bent [CN=PMe$_3$]$^+$ at the ωB97X-D/6-31G*/LANL2Dζ level of DFT.

Table S31. Thermodynamic data (298.15 K) for bent [CN=PMe$_3$]$^+$ at the ωB97X-D/6-31G*/LANL2Dζ level of DFT.

Zero Point Energy : 307.04 kJ/mol
Temperature Correction : 24.24 kJ/mol
Enthalpy Correction : 331.28 kJ/mol
Enthalpy : -553.449451 au
Entropy : 365.82 J/mol.K
Gibbs Energy : -553.490993 au
Cv : 131.43 J/mol.K

ν_{CN} 1871 vs cm^{-1} (λ = 0.9297).[12]
Lowest frequency real vibrational mode (uncorrected): 124 cm^{-1}

Natural Charges (a.u.)

C (+0.510) N (–0.900) P (1.838)

Löwden Bond Orders

C–N (2.65) N–P (0.98)

Table S32. Cartesian Coordinates for bent [CN=PMe$_3$]$^+$

Atom	x	y	z
C	-0.630360	0.129707	-2.657565
N	0.294063	-0.095680	-1.918851
P	0.077152	-0.018031	-0.236320
C	0.883244	1.480398	0.338001
H	0.815201	1.522970	1.430246
H	0.390319	2.359043	-0.087546
H	1.935491	1.476293	0.040831
C	0.875555	-1.486752	0.416077
H	0.785999	-1.506386	1.506365
H	1.932788	-1.482522	0.135795
H	0.399394	-2.378201	-0.002533
C	-1.672372	-0.001745	0.187020
H	-1.765259	-0.014864	1.278077
H	-2.169372	-0.884232	-0.225419
H	-2.151843	0.900001	-0.204179

Bent [CN=CMe$_2$]$^+$

(Constraints: C–N≡C = 120°, C–C–N–C = 180°)

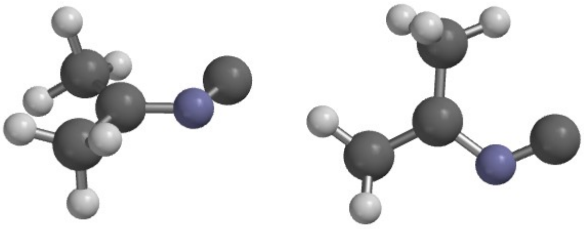


Figure S21. Optimised geometry for bent [CN=CMe$_2$]$^+$ at the ωB97X-D/6-31G*/LANL2Dζ level of DFT.

Table S33. Thermodynamic data (298.15 K) for bent [CN=CMe$_2$]$^+$ at the ωB97X-D/6-31G*/LANL2Dζ level of DFT.

Zero Point Energy : 218.42 kJ/mol
Temperature Correction : 18.04 kJ/mol
Enthalpy Correction : 236.46 kJ/mol
Enthalpy : -210.229280 au
Entropy : 314.66 J/mol.K
Gibbs Energy : -210.265012 au
Cv : 89.52 J/mol.K

ν_{CN} 1767 vs cm^{-1} (λ = 0.9297).[12]
Lowest frequency real vibrational mode (uncorrected): 62 cm^{-1}

Natural Charges (a.u.)

C (+0.581) N (–0.619) C (0.615)

Löwden Bond Orders

C–N (2.41) N–C (1.32)

Table S34. Cartesian Coordinates for bent [CN=CMe$_2$]$^+$.

Atom	x	y	z
C	-1.884899	1.571198	-0.548231
N	-1.626584	0.468131	-0.087016
C	-0.326891	0.051854	0.003122
C	-0.107429	-1.278646	0.565861
H	0.888771	-1.671666	0.357491
H	-0.905373	-1.975500	0.289782
H	-0.195301	-1.147807	1.663306
C	0.807318	0.874750	-0.444354
H	1.684738	0.685461	0.182265
H	0.596119	1.940258	-0.537140
H	1.069530	0.481969	-1.445085

Linear $[NC\text{-}PMe_3]^+$

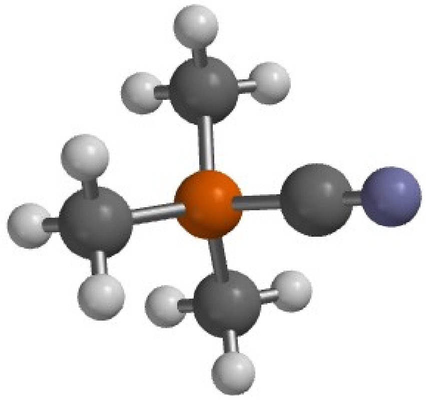


Figure S22. Optimised geometry for $[NC\text{-}PMe_3]^+$ at the ωB97X-D/6-31G*/LANL2Dζ level of DFT.

Table S35. Thermodynamic data (298.15 K) for $[NC\text{-}PMe_3]^+$ at the ωB97X-D/6-31G*/LANL2Dζ level of DFT.

Zero Point Energy : 308.92 kJ/mol
Temperature Correction : 23.92 kJ/mol
Enthalpy Correction : 332.84 kJ/mol
Enthalpy : -553.476039 au
Entropy : 365.18 J/mol.K
Gibbs Energy : -553.517509 au
Cv : 131.71 J/mol.K

ν_{CN} 2214 vs cm^{-1} (λ = 0.9297).[12]
Lowest frequency real vibrational mode (uncorrected): 136 cm^{-1}

Natural Charges (a.u.)

N (–0.103) C (–0.144) P (1.613)

Löwden Bond Orders

C–N (3.16) N–P (0.99)

Table S36. Cartesian Coordinates for $[NC\text{-}PMe_3]^+$

Atom	x	y	z
N	-0.000429	0.000021	3.103419
C	-0.000071	-0.000021	1.945524
P	-0.000381	-0.000002	0.180384
C	-1.722020	0.000000	-0.351753
H	-2.227949	0.891908	0.027651
H	-2.227949	-0.891908	0.027650
H	-1.756562	0.000001	-1.445599
C	0.860946	1.490572	-0.352025
H	1.886306	1.482620	0.027484
H	0.341887	2.375110	0.026830
H	0.878543	1.520136	-1.445923
C	0.860946	-1.490573	-0.352028
H	1.886306	-1.482620	0.027482
H	0.878543	-1.520135	-1.445925
H	0.341887	-2.375110	0.026827

Transition State (TS) for isocyano-cyano phosphonium cation interconversion

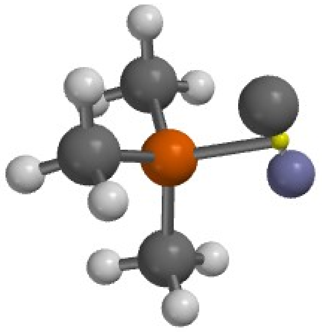
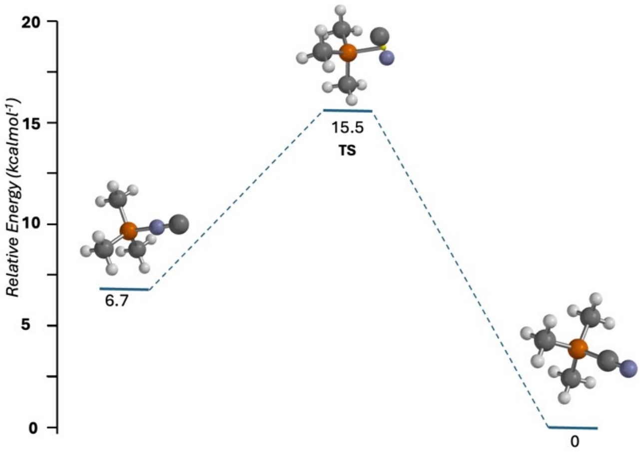


Figure S23 Optimised geometry for transition state for isocyano-cyano phosphonium cation interconversion the ωB97X-D/6-31G*/LANL2Dζ level of DFT.

The single imaginary frequency (–363 cm^{-1}) corresponds to oscillation of the C-N unit in the P-C-N plane in the direction of isocyano or cyano isomers (see Figs. S22 ad S23).



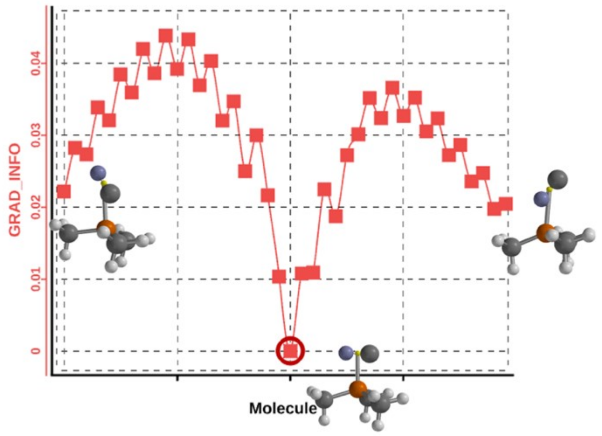


Figure S24. Reaction coordinate for isocyano-cyano phosphonium cation interconversion the ωB97X-D/6-31G*/LANL2Dζ level of DFT.

Figure S25. Intrinsic Reaction coordinate (Energy gradient) for isocyano-cyano phosphonium cation interconversion the ωB97X-D/6-31G*/LANL2Dζ level of DFT.

Table S37. Calculated Löwden bond orders for [W(≡C-A=X)(CO)$_2$(Tp)]

A=X	W–C	C–A	A–X
N=CMe$_2$	2.18	1.50	1.82
N=PMe$_3$	2.12	1.59	1.37
N=SMe$_2$	2.09	1.67	1.20
N=NMe	2.27	1.42	1.99
N=O	1.20	2.38	1.89
P=CMe$_2$	2.50	1.13	1.81
P=PMe$_3$	2.28	1.33	1.08
P=SMe$_2$	2.23	1.46	0.70
P=NMe	2.51	1.12	1.95
P=O	2.49	1.13	2.05

[a] ωB97X-D/6-31G*/LANL2Dζ(W)/gas phase.

Table S38. Calculated Natural Charges [a.u.] for [W(≡C-A=X)(CO)$_2$(Tp)]

A=X	W	C	A	X
N=CMe$_2$	0.920	–0.068	–0.516	0.361
N=PMe$_3$	0.787	–0.029	–1.053	1.897
N=SMe$_2$	0.820	–0.097	–0.864	1.111
N=NMe	0.970	–0.116	–0.256	–0.150
N=O	1.201	–0.271	0.143	–0.378
P=CMe$_2$	0.981	–0.664	0.600	–0.352
P=PMe$_3$	0.938	–0.709	–0.031	1.271
P=SMe$_2$	0.951	–0.756	0.097	0.548
P=NMe	1.040	–0.713	0.917	–0.834
P=O	1.075	–0.801	1.203	–0.925

[a] ωB97X-D/6-31G*/LANL2Dζ(W)/gas phase.

Table S39. Calculated Bond Lengths [Å] for [W(≡C-A=X)(CO)$_2$(Tp)]

A=X	W–C	C–A	A–X
N=CMe$_2$	1.843	1.313	1.287
N=PMe$_3$	1.851	1.306	1.601
N=SMe$_2$	1853	1.307	1.670
N=NMe	1.827	1.338	1.254
N=O	2.050	1.182	1.208
P=CMe$_2$	1.805	1.786	1.689
P=PMe$_3$	1.836	1.748	2.139
P=SMe$_2$	1.842	1.718	2.229
P=NMe	1.804	1.786	1.587
P=O	1.810	1.788	1.501

[a] ωB97X-D/6-31G*/LANL2Dζ(W)/gas phase.

[W(≡CN=PPh$_3$)(CO)$_2$(Tp*)] (1)

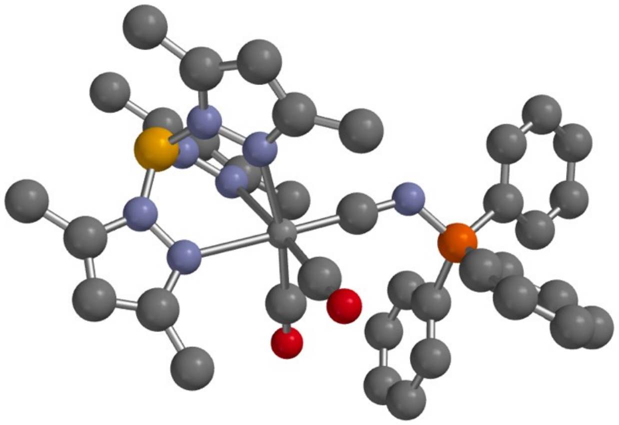


Figure S26. Optimised geometry for [W(≡CN=PPh$_3$)(CO)$_2$(Tp*)] (**1**) at the ωB97X-D/6-31G*/LANL2Dζ(W) level of DFT (Hydrogen atoms omitted for clarity).

Table S40. Thermodynamic data (298.15 K) [W(≡CN=PPh$_3$)(CO)$_2$(Tp*)] (**1**) ωB97X-D/6-31G*/LANL2Dζ (W)

Zero Point Energy :	1792.24	kJ/mol
Enthalpy Correction :	1915.15	kJ/mol
Enthalpy :	-2360.667049	au
Entropy :	1134.8	J/mol•K
Gibbs Energy :	-2360.795917	au
Cv:	728.23	J/mol•K

ν_{CO} 1908, 1823 cm^{-1} (λ = 0.9297).[12]

ν_{PO} 1459 vs cm^{-1} (λ = 0.9297).[12]

Lowest frequency real vibrational mode (uncorrected): 12 cm^{-1}

Table S41. Cartesian Coordinates for [W(≡CN=PPh$_3$)(CO)$_2$(Tp*)] (1)

Atom	x	y	z
W	0.214912	0.534673	-1.012590
P	-1.936039	-0.469357	2.582088
N	1.572911	-1.219296	-1.491207
C	-2.716216	1.101132	3.040833
N	3.277474	1.273049	-1.489899
C	1.753896	2.801460	1.398002
H	1.359728	1.956683	1.971292
H	0.899609	3.355991	0.997458
H	2.309148	3.459381	2.072354
C	-1.744380	-1.459400	4.079642
N	2.709375	-1.059099	-2.214599
C	5.687960	1.890531	-1.748289
H	5.616921	2.253015	-2.778778
H	6.084480	0.870806	-1.785193
H	6.405361	2.517471	-1.213122
C	-2.813708	3.497211	2.783565
H	-2.418865	4.406186	2.342087
C	-0.202173	0.072800	0.737609
C	3.331309	-2.245213	-2.374689
C	-2.201451	2.279807	2.500367
H	-1.332201	2.248019	1.853822
C	-3.926864	3.538662	3.616132
H	-4.403470	4.488972	3.837269
N	-0.472363	-0.253893	1.967992
C	-3.643522	-3.353967	0.293373
H	-3.441185	-4.394487	0.060207
C	4.612989	-2.401338	-3.127595
H	5.421001	-1.819113	-2.673003
H	4.513979	-2.070455	-4.166328
H	4.910231	-3.452937	-3.130321
C	-4.698220	-2.687955	-0.327788
H	-5.318245	-3.211787	-1.048630
C	0.057989	1.572112	-4.207855
C	-1.418823	-0.405545	-1.605405
C	0.345840	-3.066309	-0.380049
H	-0.615591	-2.893155	-0.872904
H	0.301447	-2.583222	0.600853
H	0.478011	-4.142828	-0.236871
C	-4.951980	-1.352127	-0.037656
H	-5.765357	-0.831552	-0.532480
C	-4.434390	2.363107	4.169428
H	-5.300271	2.397598	4.823405
N	2.224493	1.506396	-0.666284
C	0.885796	1.726111	-5.327318
H	0.606850	2.107876	-6.298928
C	-0.512049	-1.451640	4.737807
H	0.316111	-0.896251	4.308832
C	4.364977	1.941720	-1.054778
C	-2.811179	-2.197614	4.600313

H	-3.760867	-2.233553	4.073281
C	2.137357	1.287877	-4.931035
C	-2.841509	-2.681282	1.204222
H	-2.013568	-3.197208	1.682972
C	2.568966	-3.203749	-1.730248
H	2.777258	-4.261726	-1.660005
C	3.410166	1.227378	-5.712375
H	3.234544	1.594448	-6.726525
H	3.793653	0.204272	-5.779364
H	4.192241	1.843592	-5.257424
C	-4.149869	-0.670941	0.871874
H	-4.339293	0.376634	1.083234
C	1.475155	-2.516473	-1.188406
N	2.040143	0.896893	-3.644071
C	-2.648241	-2.912004	5.782541
H	-3.476576	-3.488011	6.182966
C	3.999791	2.629302	0.089430
H	4.628924	3.266083	0.694533
C	2.647673	2.328296	0.298075
C	-0.355384	-2.169475	5.918270
H	0.603347	-2.165437	6.427161
B	3.126296	0.339530	-2.706388
H	4.169841	0.268962	-3.295475
C	-1.395919	1.898885	-4.087933
H	-1.989448	1.004358	-3.878246
H	-1.755648	2.337197	-5.022849
H	-1.575822	2.610747	-3.277431
N	0.770522	1.068298	-3.195972
O	-2.364059	-0.974108	-1.982918
O	-1.408138	3.173922	-0.560731
C	-0.807405	2.185769	-0.747255
C	-3.094562	-1.336148	1.499207
C	-3.833195	1.144459	3.882522
H	-4.232081	0.231357	4.315538
C	-1.422346	-2.895037	6.442588
H	-1.296205	-3.455338	7.364067

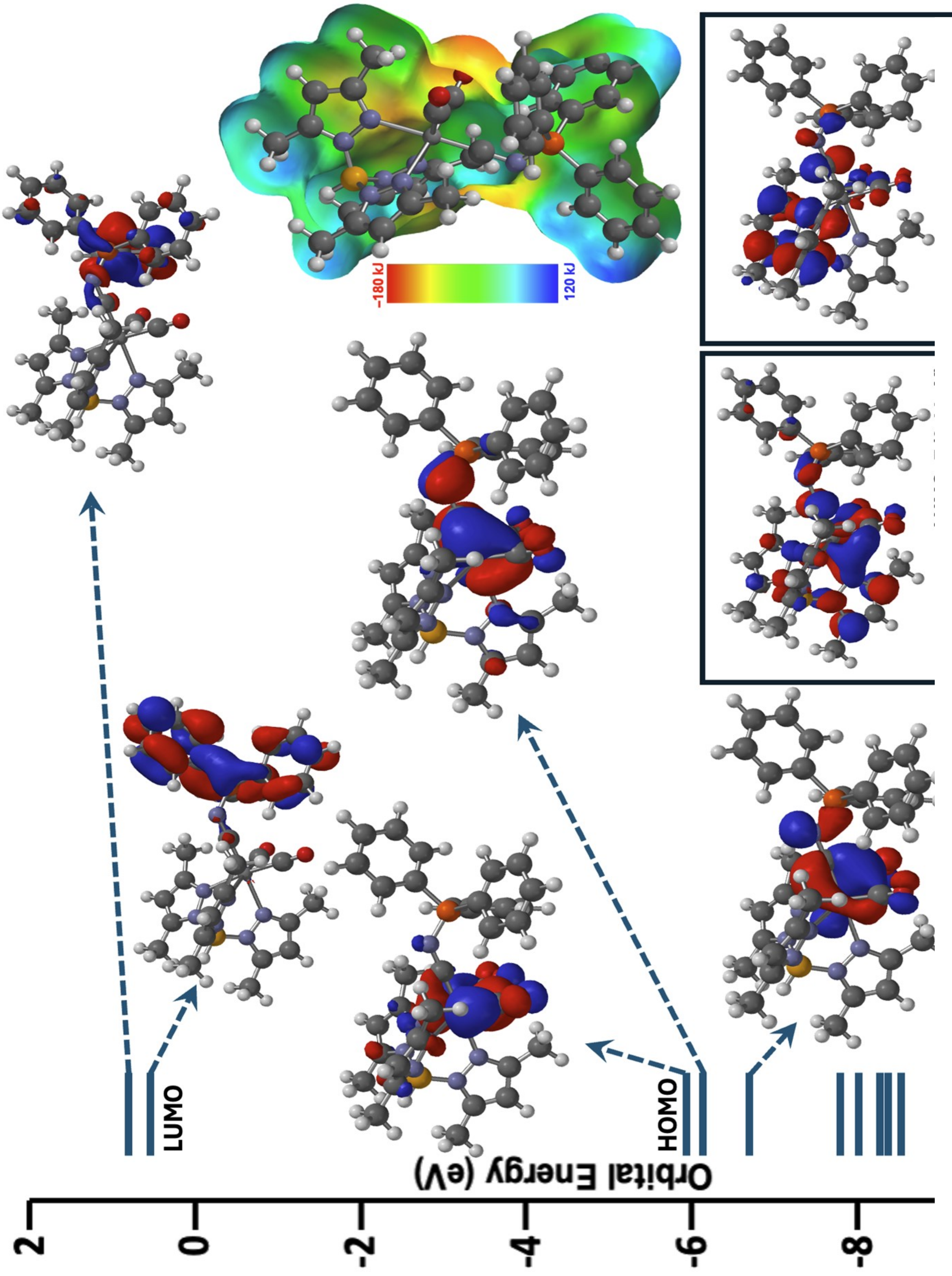


Figure S27. Frontier orbitals of interest for the model complex [W(≡CN=PPh$_3$)(CO)$_2$(Tp*)] (DFT:ωB97X-D/6-31G*/LANL2Dζ(W)/gas phase). Insets = LUMO+7, LUMO+8 and electrostatic potential (kJ on a 0.002 e/au^3 isosurface).

[W(≡CN=PPh$_3$)(CO)$_2$(Tp)]

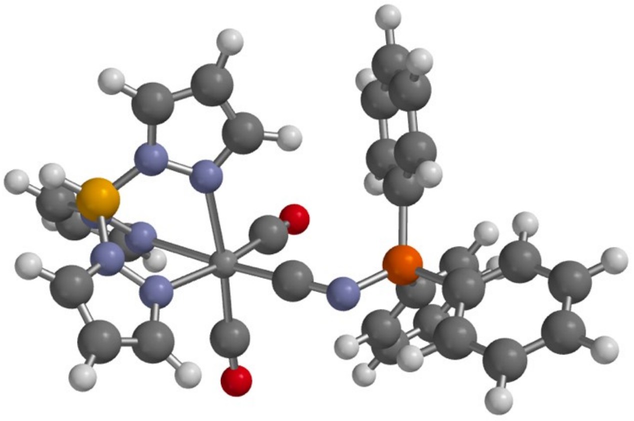


Figure S28. Optimised geometry for [W(≡CN=PPh$_3$)(CO)$_2$(Tp)] at the ωB97X-D/6-31G*/LANL2Dζ(W) level of DFT.

Table S42. Thermodynamic data (298.15 K) [W(≡CN=PPh$_3$)(CO)$_2$(Tp)] ωB97X-D/6-31G*/LANL2Dζ (W)

Zero Point Energy : 1346.23 kJ/mol
Temperature Correction : 78.19 kJ/mol
Enthalpy Correction : 1424.42 kJ/mol
Enthalpy : -2125.012518 au
Entropy : 743.47 J/mol•K
Gibbs Energy : -2125.096947 au
Cv : 582.10 J/mol•K

Lowest frequency real vibrational mode (uncorrected): 10 cm^{-1}

Table S43. Cartesian Coordinates for [W(≡CN=PPh$_3$)(CO)$_2$(Tp)]

Atom	x	y	z
W	1.018570	1.274540	-1.239781
P	-1.078427	-0.321115	2.059751
N	1.294659	-0.745261	-2.245736
C	-2.300641	1.014761	2.023074
N	3.957070	0.661393	-2.342240
C	-0.955301	-0.970514	3.739982
N	2.252154	-0.966820	-3.171014
C	-2.776231	3.363475	1.757373
H	-2.426284	4.371983	1.563252
C	0.666671	0.627183	0.467534
C	2.215294	-2.250220	-3.571149
C	-1.857496	2.319219	1.798189
H	-0.803766	2.519460	1.637968
C	-4.129289	3.109721	1.952012
H	-4.844531	3.925897	1.915986
N	0.390796	0.206373	1.664643
C	-1.635270	-3.966963	0.326511
H	-1.279954	-4.980322	0.484665
C	-2.454828	-3.672577	-0.762251
H	-2.738750	-4.459737	-1.454195
C	0.903444	2.900948	-4.155347
C	-0.927353	1.414847	-1.500195
C	-2.899185	-2.370645	-0.971047
H	-3.519589	-2.133693	-1.829201
C	-4.573194	1.808824	2.186348
H	-5.630245	1.610844	2.334394
N	3.277778	1.148226	-1.281902
C	1.489883	2.917783	-5.425041
H	1.268436	3.576371	-6.250577
C	0.164968	-0.649634	4.508761
H	0.957471	-0.053120	4.068547
C	5.278235	0.699858	-2.095668
C	-1.978694	-1.752292	4.285152
H	-2.841801	-2.024517	3.683666
C	2.423534	1.897343	-5.382573
C	-1.264711	-2.959550	1.208639
H	-0.615963	-3.189985	2.048823
C	1.199350	-2.892292	-2.886207
H	0.897465	-3.925234	-2.966264
C	-2.533384	-1.356633	-0.090399
H	-2.862883	-0.340221	-0.277877
C	0.654911	-1.899469	-2.065070
N	2.377155	1.328135	-4.165781
C	-1.880462	-2.208472	5.594155
H	-2.673193	-2.819624	6.014101
C	5.473256	1.227779	-0.831870
H	6.410402	1.396019	-0.324137
C	4.181600	1.493228	-0.365727
C	0.257271	-1.109702	5.818740
H	1.129671	-0.861767	6.415149
B	3.208909	0.163076	-3.594608
H	3.991842	-0.236953	-4.418955
N	1.444341	1.940713	-3.406244
O	-2.084106	1.511900	-1.636322
O	0.865873	4.123432	0.056688
C	0.943446	3.077895	-0.456737
C	-1.721710	-1.650884	1.009808
C	-3.662742	0.761347	2.219357
H	-4.017347	-0.253470	2.378243
C	-0.763090	-1.885183	6.361358
H	-0.688304	-2.241570	7.384335
H	-0.160860	-1.950533	-1.360128
H	2.913722	-2.609555	-4.312496
H	3.849768	1.909874	0.573980
H	5.980488	0.347075	-2.836535
H	0.124851	3.525088	-3.740583
H	3.116300	1.533914	-6.127327

[W(≡CN=PMe$_3$)(CO)$_2$(Tp*)]

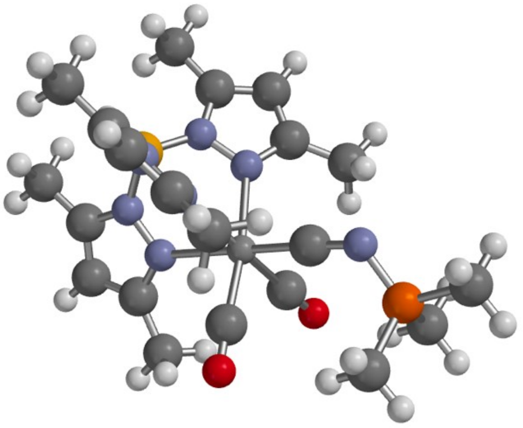


Figure S29. Optimised geometry for [[W(≡CN=PMe$_3$)(CO)$_2$(Tp*)] (**1**) at the ωB97X-D/6-31G*/LANL2Dζ(W) level of DFT.

Table S44. Thermodynamic data (298.15 K) [W(≡CN=PMe$_3$)(CO)$_2$(Tp*)] ωB97X-D/6-31G*/LANL2Dζ (W)

Zero Point Energy : 1362.99 kJ/mol
Temperature Correction : 80.88 kJ/mol
Enthalpy Correction : 1443.88 kJ/mol
Enthalpy : -1785.865021 au
Entropy : 764.50 J/mol•K
Gibbs Energy : -1785.951837 au
Cv : 558.60 J/mol•K

Table S45. Cartesian Coordinates for [W(≡CN=PMe$_3$)(CO)$_2$(Tp*)]

Atom	**x**	**y**	**z**
W	0.344841	0.459589	0.575411
P	-1.101964	0.900673	4.491454
O	0.202851	3.510467	1.279932
O	2.764453	0.167962	2.546410
N	1.667185	0.772375	-1.290710
N	1.386004	0.122783	-2.448964
N	-1.265824	0.545880	-1.006314
N	-1.108719	-0.055996	-2.212422
N	0.440785	-1.670298	-0.174266
N	0.354784	-1.960776	-1.497198
B	0.181929	-0.833284	-2.532240
H	0.111038	-1.301688	-3.634879
C	2.752539	1.520262	-1.509020
C	3.176750	1.348115	-2.832618
H	4.023671	1.815548	-3.313993
C	2.284774	0.453527	-3.398490
C	-2.472640	1.118719	-1.001505
C	-3.103043	0.881520	-2.229368
H	-4.085031	1.212721	-2.535160
C	-2.206950	0.132773	-2.972490
C	0.564540	-2.828080	0.480539
C	0.559263	-3.883639	-0.440058
H	0.641856	-4.939360	-0.225221
C	0.424370	-3.294549	-1.685386
C	0.267441	2.376735	0.990979
C	1.879098	0.273991	1.787005
C	-0.722444	0.211418	2.080823
N	-1.436534	0.070117	3.160456
C	-1.241886	2.700388	4.297039
H	-0.533166	3.043507	3.538130
H	-1.040620	3.210235	5.244397
H	-2.251792	2.945689	3.957320
C	-2.289205	0.404788	5.760305
H	-3.301573	0.622962	5.411404
H	-2.101648	0.940733	6.694876
H	-2.202707	-0.670825	5.932637
C	0.559238	0.592351	5.155637
H	0.674100	-0.477561	5.348992
H	0.718293	1.152165	6.082374
H	1.309068	0.885875	4.416001
C	3.361748	2.382922	-0.451257
H	4.241938	2.894318	-0.850017
H	3.669049	1.789979	0.415256
H	2.653539	3.138150	-0.097753
C	2.247817	-0.095839	-4.788087
H	3.077914	0.317278	-5.366224
H	1.313811	0.160640	-5.298177
H	2.336393	-1.186936	-4.792561
C	-2.997103	1.872686	0.176956
H	-2.364996	2.736120	0.406075
H	-3.018664	1.236385	1.066952
H	-4.010509	2.228141	-0.029609
C	-2.346041	-0.409566	-4.358302
H	-1.566936	-0.022548	-5.022854
H	-3.317831	-0.122012	-4.766910
H	-2.277661	-1.502056	-4.372225
C	0.356078	-3.934845	-3.034280
H	1.165970	-3.590473	-3.685295
H	-0.589354	-3.711616	-3.539077
H	0.439750	-5.019241	-2.928586
C	0.678348	-2.897453	1.968425
H	1.582279	-2.389621	2.318832
H	0.718688	-3.941612	2.291050
H	-0.177352	-2.410610	2.445847

Table S46. Comparison of parameters of interest calculated for the complexes [W(CNPR$_3$)(CO)$_2$(L)] (L = Tp, Tp*; R = Me, Ph).[a]

	Tp*	**Tp**	**Tp***	**Tp**
PR$_3$	**PMe$_3$**	**PMe$_3$**	**PPh$_3$**	**PPh$_3$**
N	64	46	85	67
N^2/N(TpPMe$_3$)^2	1.94	1	2.12	3.41
Parameter				
Z(W) [a.u.]	0.861	0.787	0.849	0.835
Z(C) [a.u.]	-0.010	-0.029	-0.015	-0.009
Z(N) [a.u.]	-1.059	-1.053	-1.065	-1.045
Z(P) [a.u.]	1.895	+1.897	1.946	1.939
LBO (WC)	2.04	2.12	2.06	2.05
LBO (CN)	1.61	1.59	1.62	1.64
LBO (NP)	1.35	1.37	1.33	1.31
r(WC) [Å]	1.862	1.851	1.858	1.860
r(CN) [Å]	1.302	1.306	1.301	1.299
r(NP) [Å]	1.604	1.601	1.602	1.610
<WCN [°]	177.7	178.5	179.0	178.1
<CNP [°]	121.2	118.9	125.9	121.8
<CWC(O) [°][b]	86.4	87.9	88.4	87.3
<CWN(pz) [°][b]	99.5	98.5	98.7	98.8
LUMO+1 [eV]	1.91	+1.80	+0.80	2.01k
LUMO [eV]	1.75	+1.67	+0.58	1.91k
HOMO [eV]	-6.30	-6.12	-5.92	-6.05
HOMO-1 [eV]	-6.94	-6.31	-6.13	-6.40
HOMO-2 [eV]	-7.86	-6.86	-6.67	-6.69
f^-(C) [a.u.][c]	0.168	0.172	0.028	0.029
f^-(N) [a.u.][c]	0.041	0.037	0.026	0.016
f^-(P) [a.u.][c]	0.028	0.003	0.048	0.064
f^+(C) [a.u.][d]	0.046	0.048	0.056	0.046
f^+(N) [a.u.][d]	0.059	0.059	0.055	0.069
f^+(P) [a.u.][d]	0.010	0.009	0.000	0.001
ν_T[e]	2.064.1	2.064.1	2068.9	2068.9
θ_T[f]	118	118	145	145
ν_{CO}[g]	1890	1937	1908	1910
	1810	1869	1823	1835
k_{CO} [Ncm^{-1}][h]	13.83	14.62	14.07	14.16

[a] DFT:ωBP7X-D/6-31G*/LANL2Dζ/gas phase. [b] Average of two values. [c] Atom-condensed Fukui function for nucleophilic attack.[15] [d] Atom-condensed Fukui function for electrohilic attack.[15] [e] ν_T = Tolman electronic parameter for PR$_3$. [f] θ_T = Tolman cone angle for PR$_3$. [g] Anharmonic scaling factor λ = 0.9297.[12] [h] Cotton-Kraihanzel force constant.

Table S47. Comparison of parameters of interest calculated for the complexes [W(CNPR$_3$)(CO)$_2$(Tp)] (R = F, H, OMe, NMe$_2$, atran, Me, Ph).[a]

Parameter R =	**F**	**H**	**OMe**	**Ph**	**Me**	**NMe$_2$**	**atran**[b]
Z(W) [a.u.]	0.906	0.852	0.845	0.835	0.787	0.825	0.839
Z(C) [a.u.]	-0.073	-0.056	-0.022	-0.009	-0.029	0.011	-0.014
Z(N) [a.u.]	-1.116	-1.013	-1.113	-1.045	-1.053	-1.085	-1.064
Z(P) [a.u.]	2.618	1.081	2.608	1.939	+1.897	2.447	2.598[j]
LBO (WC)	2.28	2.14	2.10	2.05	2.12	2.02	2.09
LBO (CN)	1.39	1.54	1.56	1.64	1.59	1.65	1.56
LBO (NP)	1.74	1.44	1.43	1.31	1.37	1.32	1.44
r(WC) [Å]	1.826	1.848	1.854	1.860	1.851	1.866	1.853
r(CN) [Å]	1.331	1.320	1.307	1.299	1.306	1.291	1.313
r(NP) [Å]	1.507	1.588	1.569	1.610	1.601	1.597	1.569[j]
<WCN [°]	175.9	175.1	177.0	178.1	178.5	176.2	173.7
<CNP [°]	138.2	117.2	128.3	121.8	118.9	129.4	115.9
<CWC(O) [°][c]	86.9	87.0	86.8	87.3	87.9	86.0	86.0
<CWN(pz) [°][c]	101.8	101.3	100.7	98.8	98.5	100.6	101.0
LUMO+1 [eV]	1.12	1.45	1.59	2.01k	1.80	1.87	1.94
LUMO [eV]	1.02	1.23	1.50	1.91k	1.67	1.81	1.83
HOMO [eV]	-6.78	-6.44	-6.43	-6.05	-6.12	-6.10	-6.09
HOMO-1 [eV]	-7.50	-6.76	-6.78	-6.40	-6.31	-6.36	-6.36
HOMO-2 [eV]	-7.83	-7.34	-7.19	-6.69	-6.86	-6.74	-6.94
ν_T[d] [cm^{-1}]	2110.8	2083.2	2079.5	2068.9	2.064.1	2061.9	n.a.
θ_T[e] [°]	104	87	107	145	118	157	n.a.
σ^I(R)[f]	-0.52	0	-0.27	0.10	-0.04	0.06	n.a.
σ^P(R)[g]	0.06	0	-0.27	0.06	-0.17	-0.16	n.a.
ν_{CO}[h] [cm^{-1}]	1961	1931	1921	1910	1937	1905	1919
	1892	1862	1847	1835	1869	1824	1843
k_{CO}[i] [Ncm^{-1}]	14.99	14.53	14.34	14.16	14.62	14.05	14.29

[a] DFT:ωBP7X-D/6-31G*/LANL2Dζ/gas phase. [b] atran: PR$_3$ = P(OCH$_2$CH$_2$)$_3$N. [c] Average of two values. [d] ν_T = Tolman electronic parameter for PR$_3$.[13] [e] θ_T = Tolman cone angle for PR$_3$.[13] [f] Hammett inductive parameter. [g] Hammett para mesomeric parameter. [h] Anharmonic scaling factor λ = 0.9297.[12] [i] Cotton-Kraihanzel force constant.[14] [j] transannular N···P = 3.012 Å, Σ<CNC = 359.9°, Σ°<POP = 319.0°. [k] These values correspond to LUMO+6/7 as LUMO to LUMO+5 are associated with the PPh$_3$ ligand. n.a. = not available.

References

1 *CrysAlis PRO*, Agilent Technologies Ltd, Yarnton, Oxfordshire, England, 2014.

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

3 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallog.,* 2009, **42**, 339-341.

4 (*a*) C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Crystallogr.*, 2006, **39**, 453-457. (*b*) C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Crystallogr.*, 2008, **41**, 466-470.

5 (*a*) T. Desmond, F. J. Lalor, G. Ferguson and M. Parvez, *J. Chem. Soc., Chem. Commun.*, 1984, 75-77 (*b*) R. A. Manzano and A. F. Hill, *Chem. Sci.*, 2023, **14**, 3776-3781. (c) R. M. Kirk and A. F. Hill, *Dalton Trans.*, 2025, **54**, 8881-8887.

6 (*a*) R. Appel and A. Hauss, *Chem. Ber.*, 1960, **93**, 405-411. (*b*) A. Eckart, K. Lux and K. Karaghiosoff, *Z. Anorg. Allg. Chem.*, 2014,

640, 962-967. (c) Q. Ma, C. Liu and C. G. Tsui, *Org. Lett.*, 2020, **22**, 5193-5197.

7 *Spartan24*® (2024) Wavefunction, Inc., 18401 Von Karman Ave., Suite 370 Irvine, CA 92612 U.S.A.

8 (*a*) J. D. Chai and M. Head-Gordon, *J. Chem. Phys.*, 2008, **128**, 084106. (*b*) J. D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615-6620.

9 (*a*) P. J. Hay and W. R. Wadt, *J. Chem. Phys*., 1985, **82**, 270-283. (*b*) P. J. Hay and W. R. Wadt, *J. Chem. Phys*., 1985, **82**, 299-310. (*c*) W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284-298.

10 W. J. Hehre, R. Ditchfeld and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257–2261.

11 (*a*) P.-O. Löwden, *J. Mol. Spec.*, 1963, **10**, 12-33. (*b*) P.-O. Löwden, *J. Mol. Spec.*, 1964, **13**, 320-337. (*c*) P.-O. Löwden, *J. Math. Phys.*, 1962, **3**, 969–982. (*d*) P.-O. Löwden, *J. Mol. Spec.*, 1964, **14**, 112-118.

12 C. M. Inglis, R. A. Manzano, R. M. Kirk, M. Sharma, M. D. Stewart, L. J. Watson and A. F. Hill, *Molecules*, 2023, **28**, 7761.

13 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313-348.

14 F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, 1962, **84**, 4432-4438.

15 (a) R. G. Parr, W. Yang, *J. Am. Chem. Soc.*, 1984, **106**, 4049-4050; b) W. Yang, W. J. Mortier, *J. Am. Chem. Soc.*, 1986, **108**, 5708-5711.

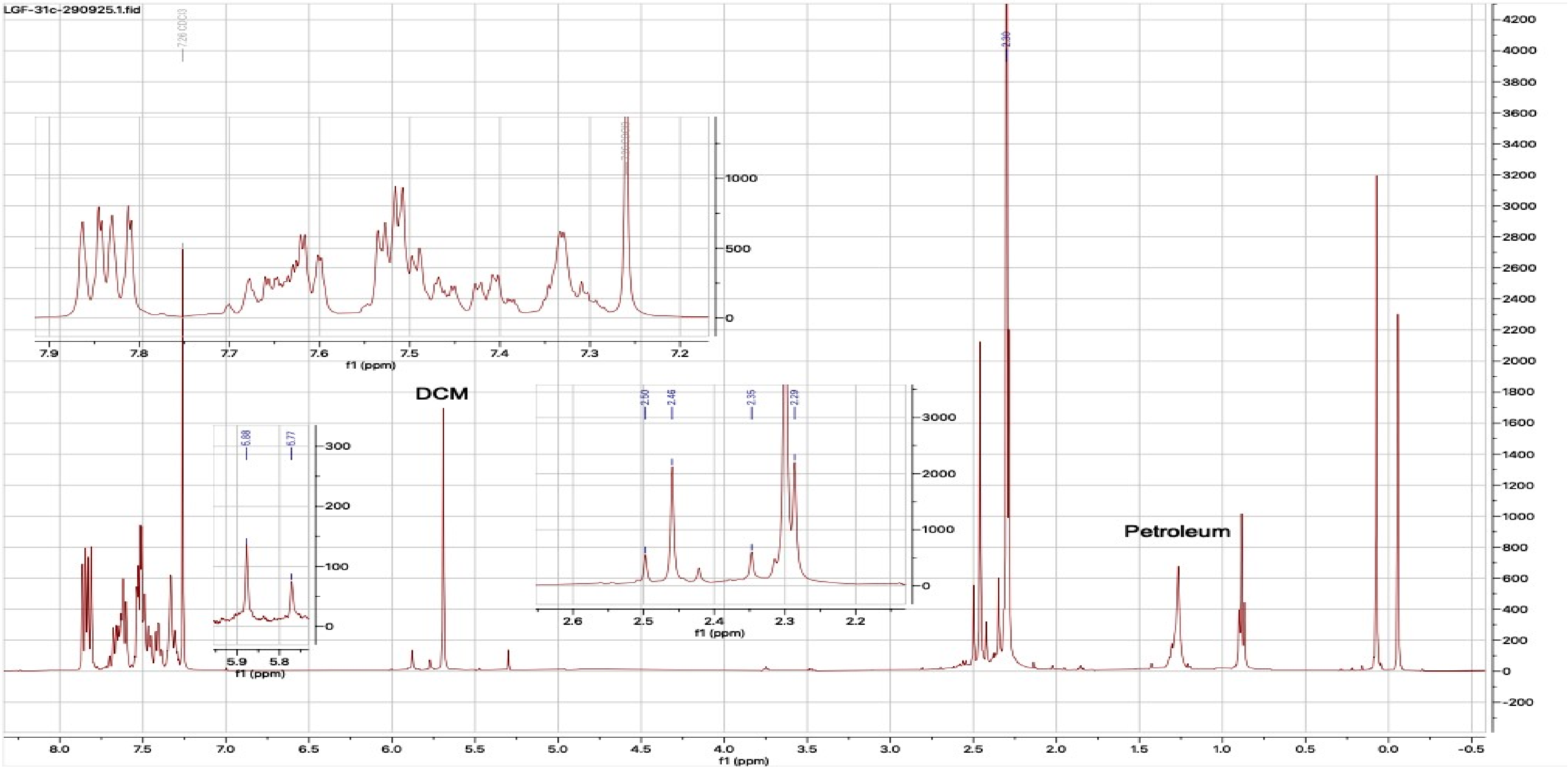


Figure S30. ^{1}H NMR spectrum of $[W(\equiv CN{=}PPh_3)(CO)_2(Tp^*)]$ (**1**, 295 K, $CDCl_3$, 400 MHz, δ_H)

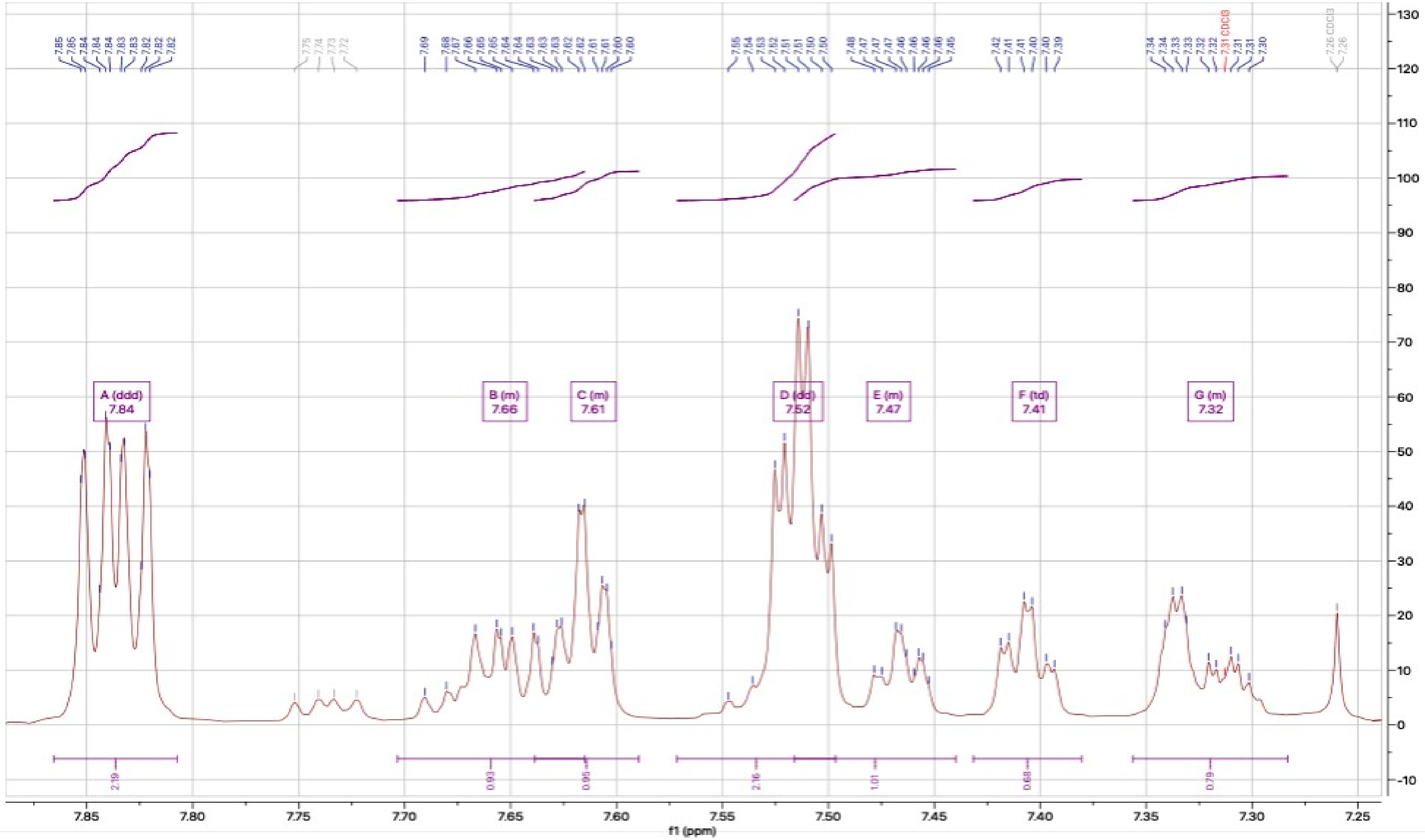


Figure S31. ^{1}H NMR spectrum of [W(≡CN=PPh$_3$)(CO)$_2$(Tp*)] (**1**, 295 K, CDCl$_3$, 700 MHz, δ_H). Aromatic region.

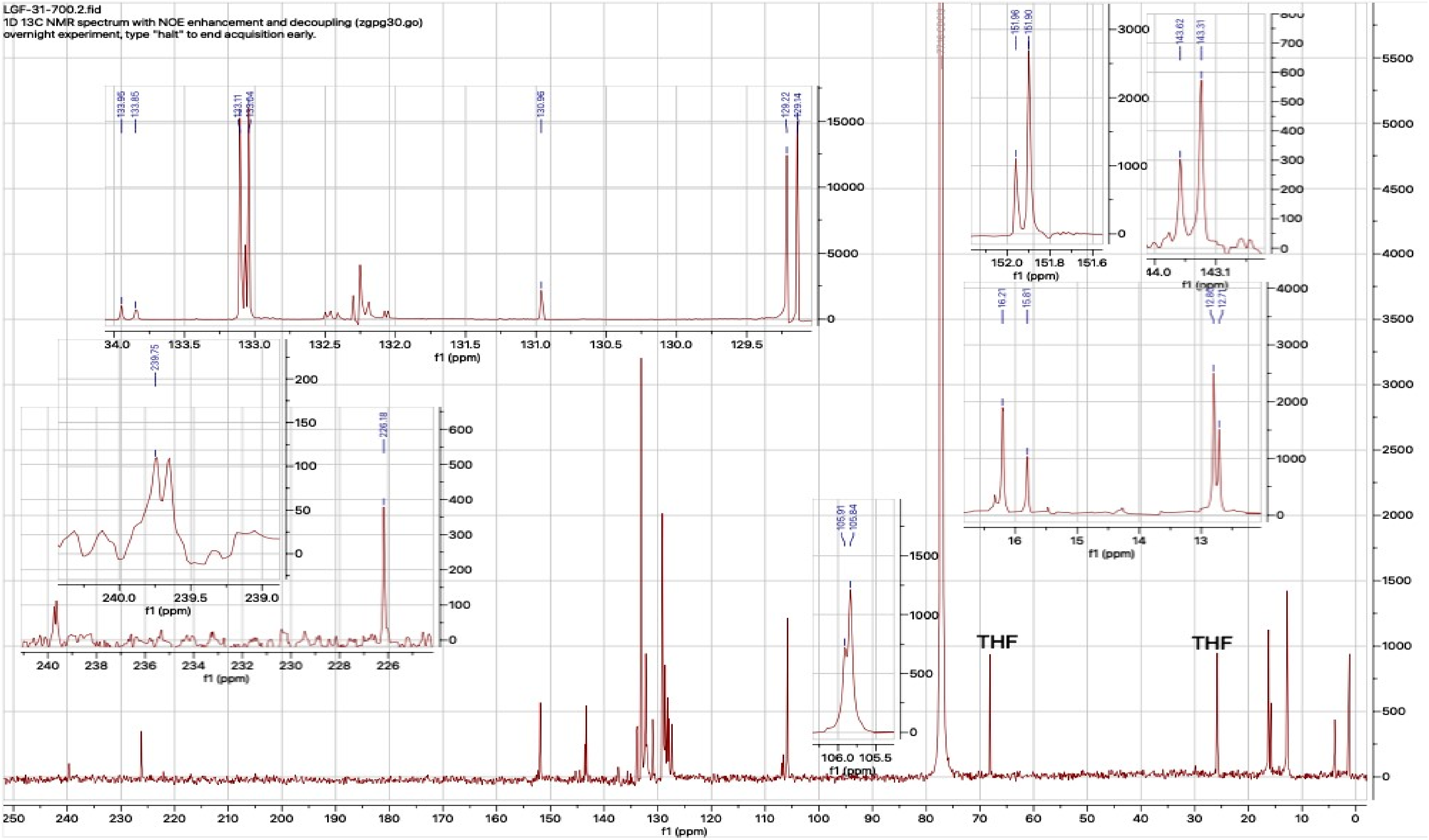


Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum of [W(≡CN=PPh$_3$)(CO)$_2$(Tp*)] (**1**, 295 K, CDCl$_3$, 151 MHz, δ_C).

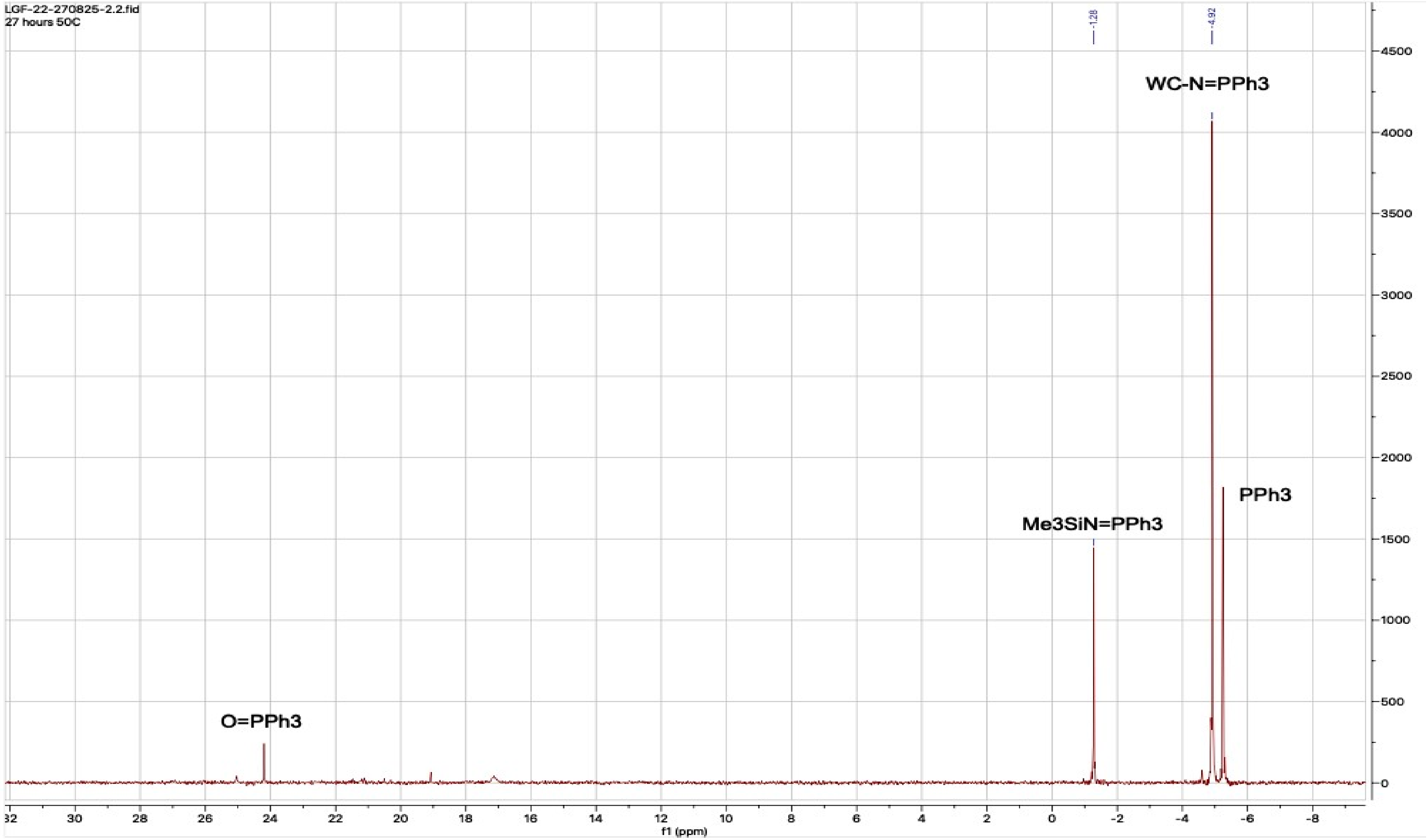


Figure S33. $^{31}P\{^1H\}$ NMR spectrum of [W(≡CN=PPh$_3$)(CO)$_2$(Tp*)] (**1**, 295 K, δ_8-toluene, 162 MHz, δ_P).

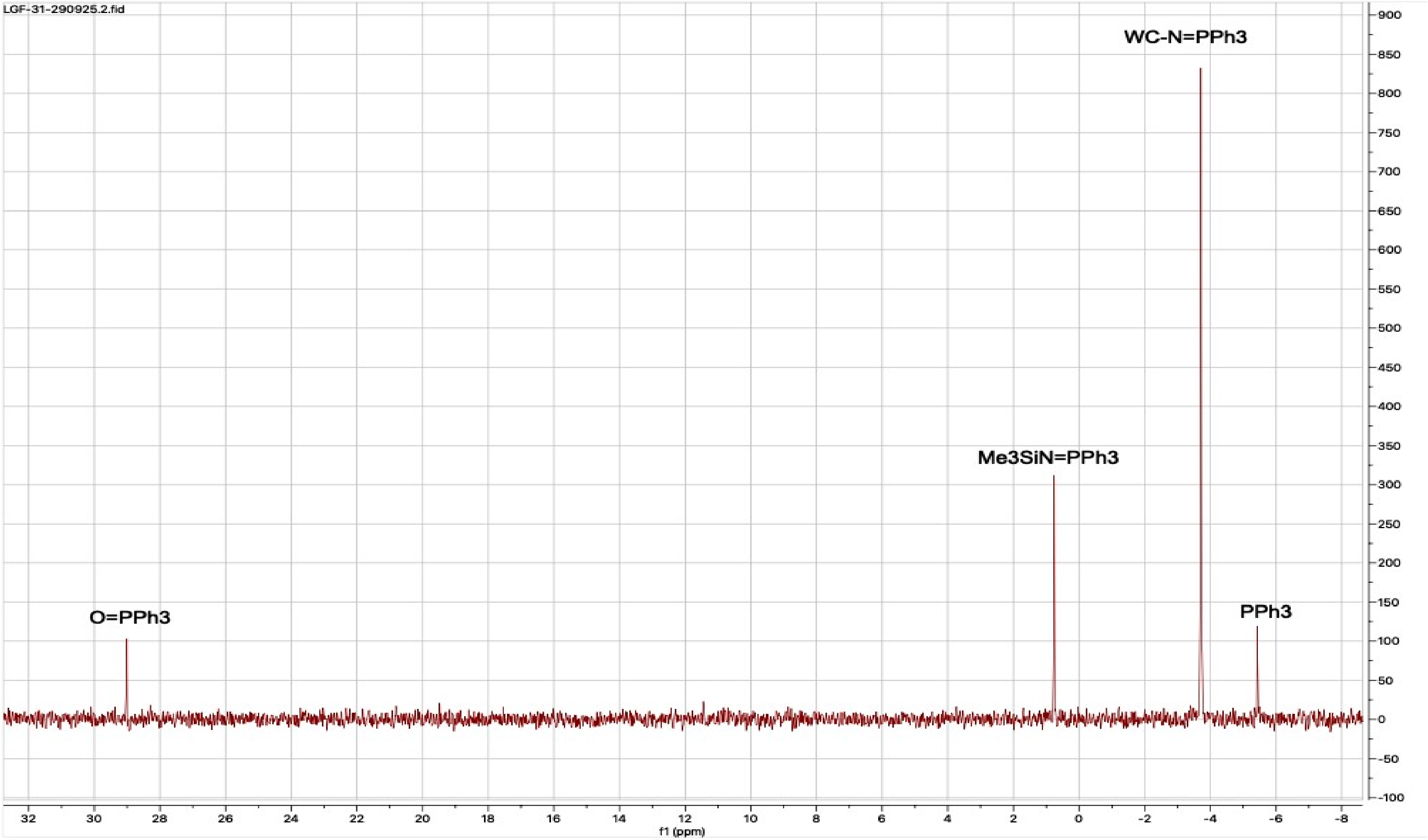


Figure S34. $^{31}P\{^1H\}$ NMR spectrum of [W(≡CN=PPh$_3$)(CO)$_2$(Tp*)] (**1**, 295 K, CDCl$_3$, 162 MHz, δ_P).

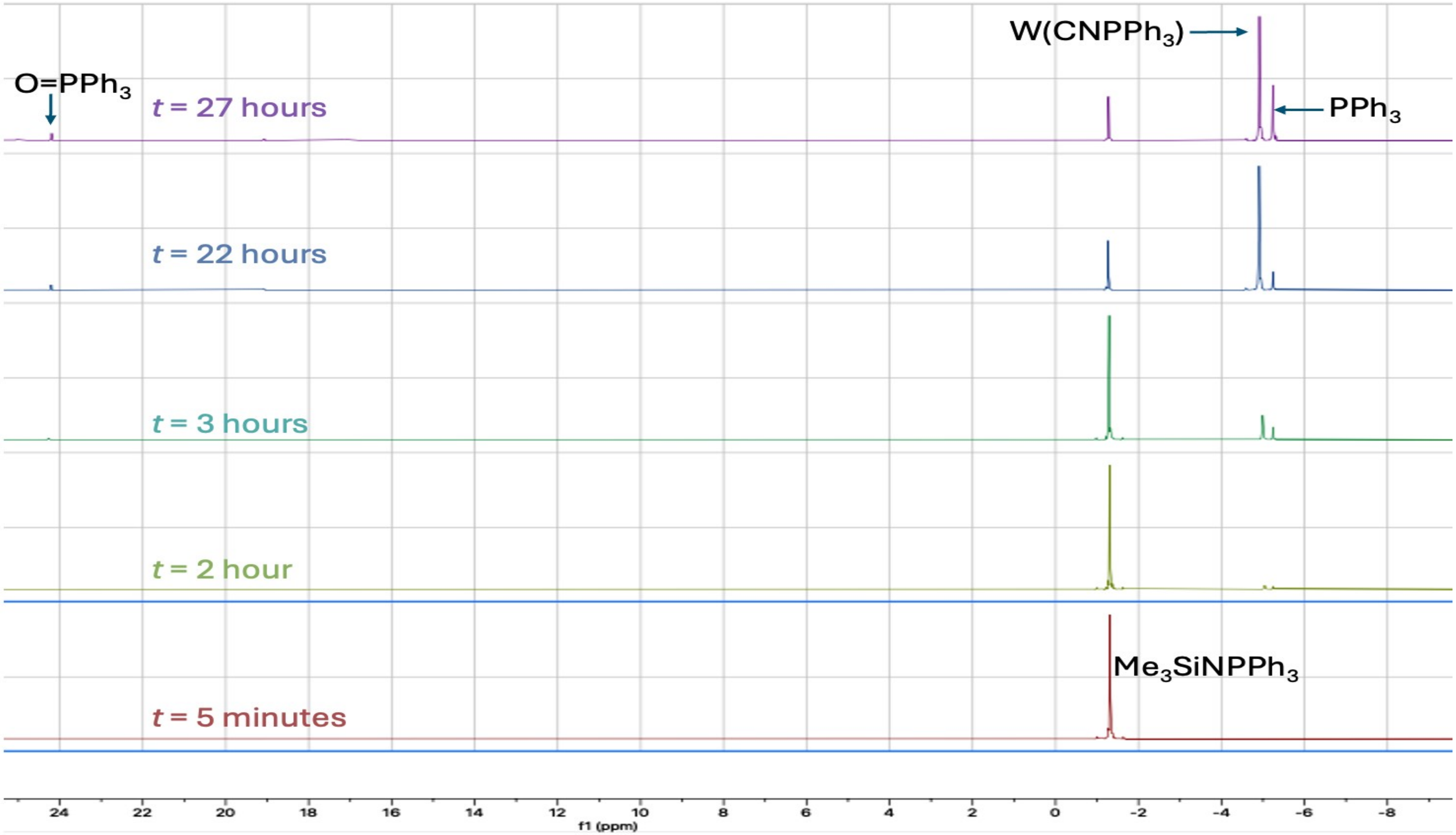


Figure S35. Time course for the reaction of [W(≡CF)(CO)$_2$(Tp*)] with Me$_3$SiN=PPh$_3$ over 27 hours (d_6-toluene, 50 °C) as monitored by ^{31}P{^{1}H} NMR (295 K, CDCl$_3$, 162 MHz, δ$_P$).

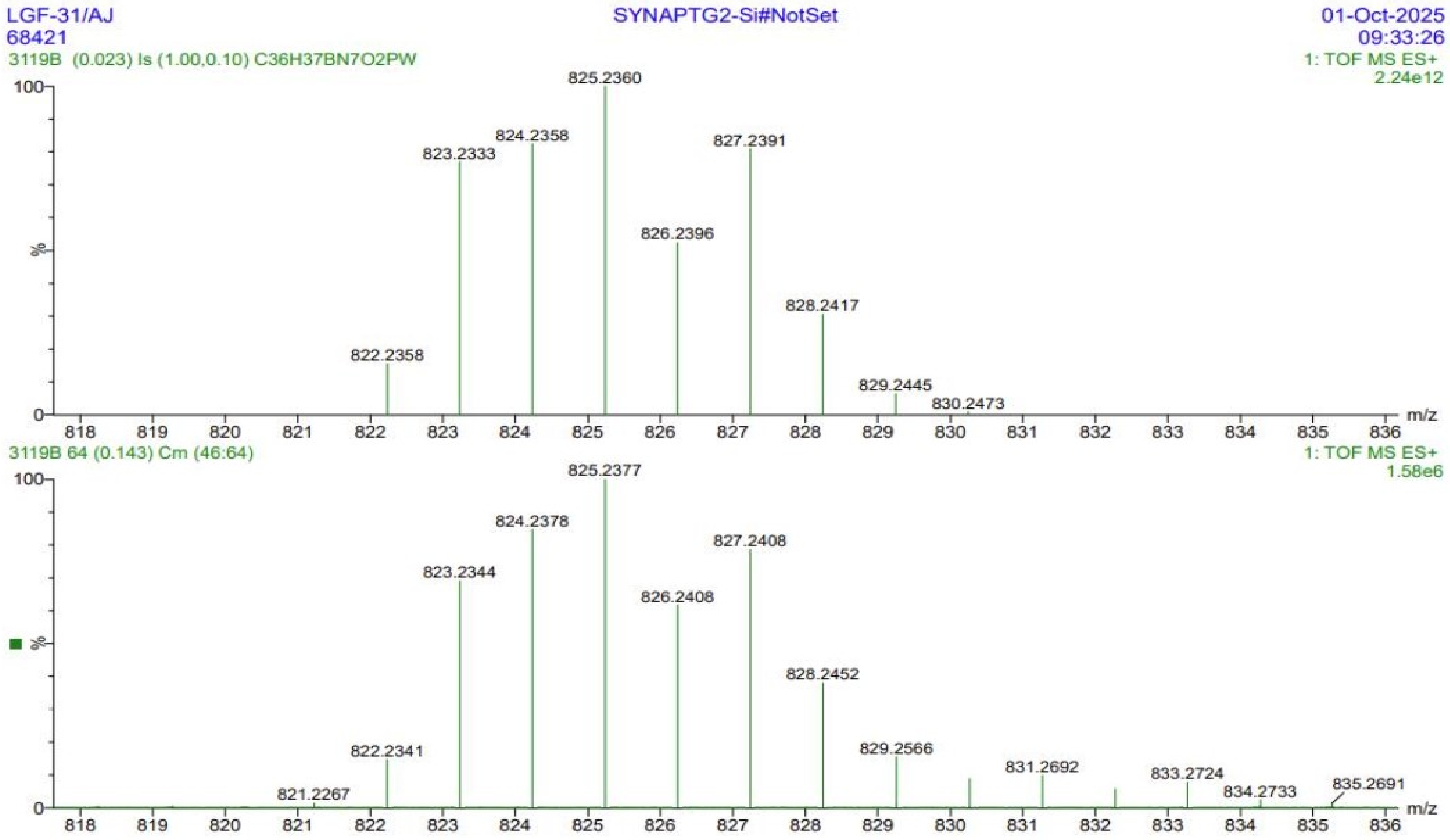


Figure S36. High Resolution Mass Spectrum of [W(≡CNPPh$_3$)(CO)$_2$(Tp*)] (ESI, MeCN, +ve ion).

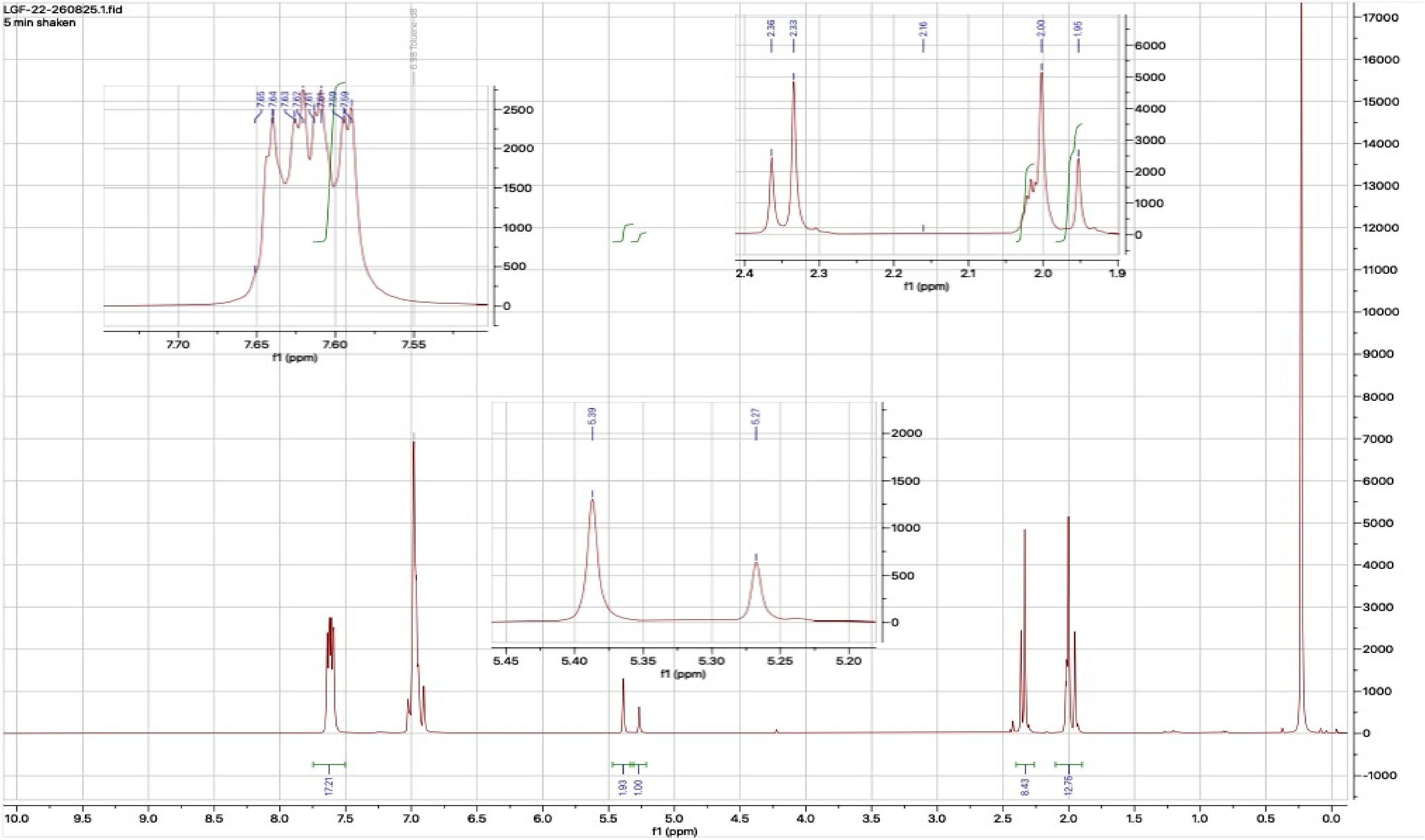


Figure S37. ^{1}H NMR spectrum of [W(≡CN=PPh$_3$)(CO)$_2$(Tp*)] (**1**) from [W(≡CF)(CO)$_2$(Tp*)] + Me$_3$SiF (in situ, *t* = 27 hours @ 50 °C, 295 K, δ_8-toluene, 400 MHz, δ_H).

Figure S38. Infrared Spectrum of [W($\equiv$CN=PPh$_3$)(CO)$_2$(Tp*)] (**1**, THF, cm^{-1}).

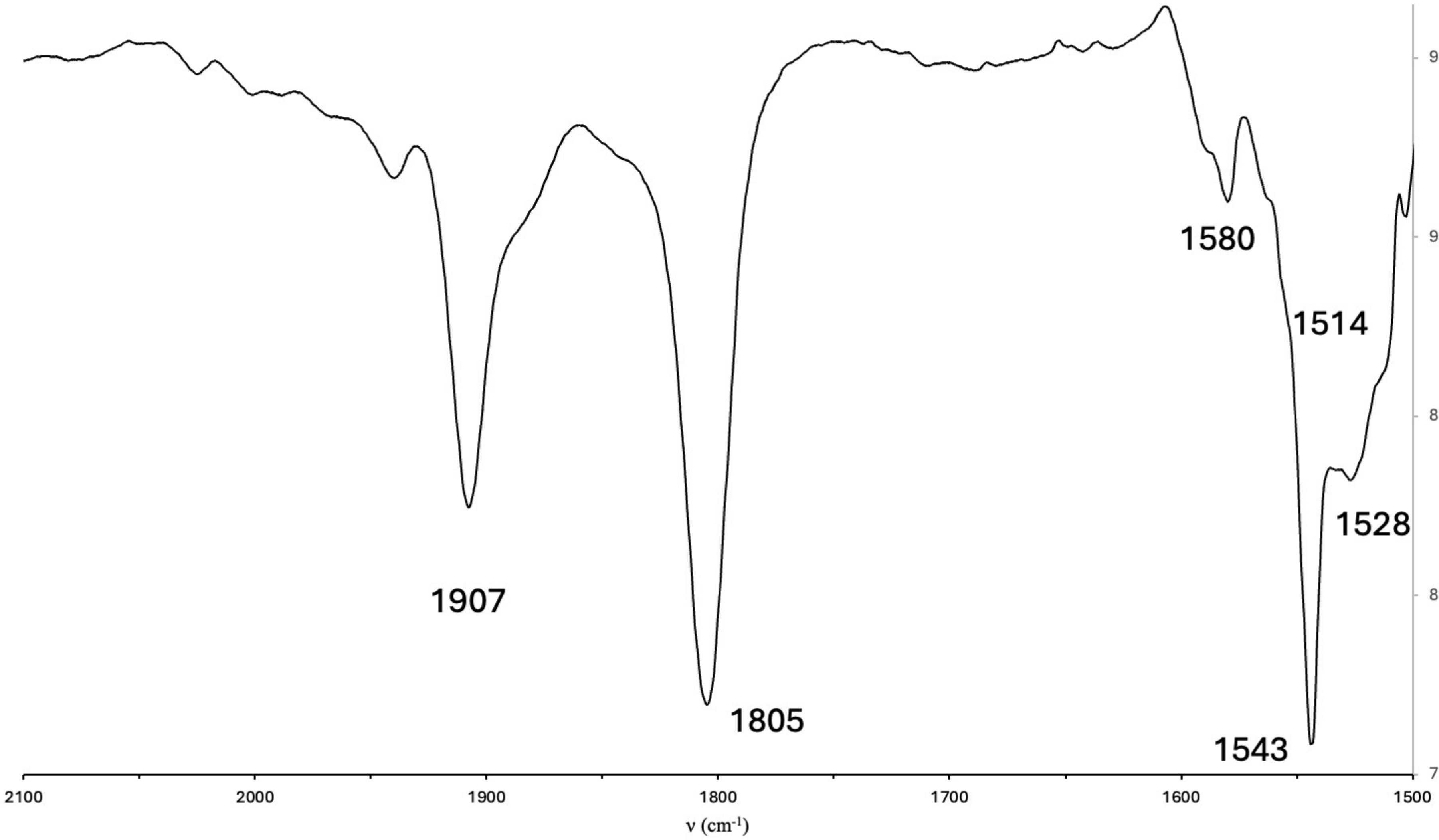


Figure S39. Infrared Spectrum of [W(≡CN=PPh$_3$)(CO)$_2$(Tp*)] (**1**, CH$_2$Cl$_2$, cm^{-1}).

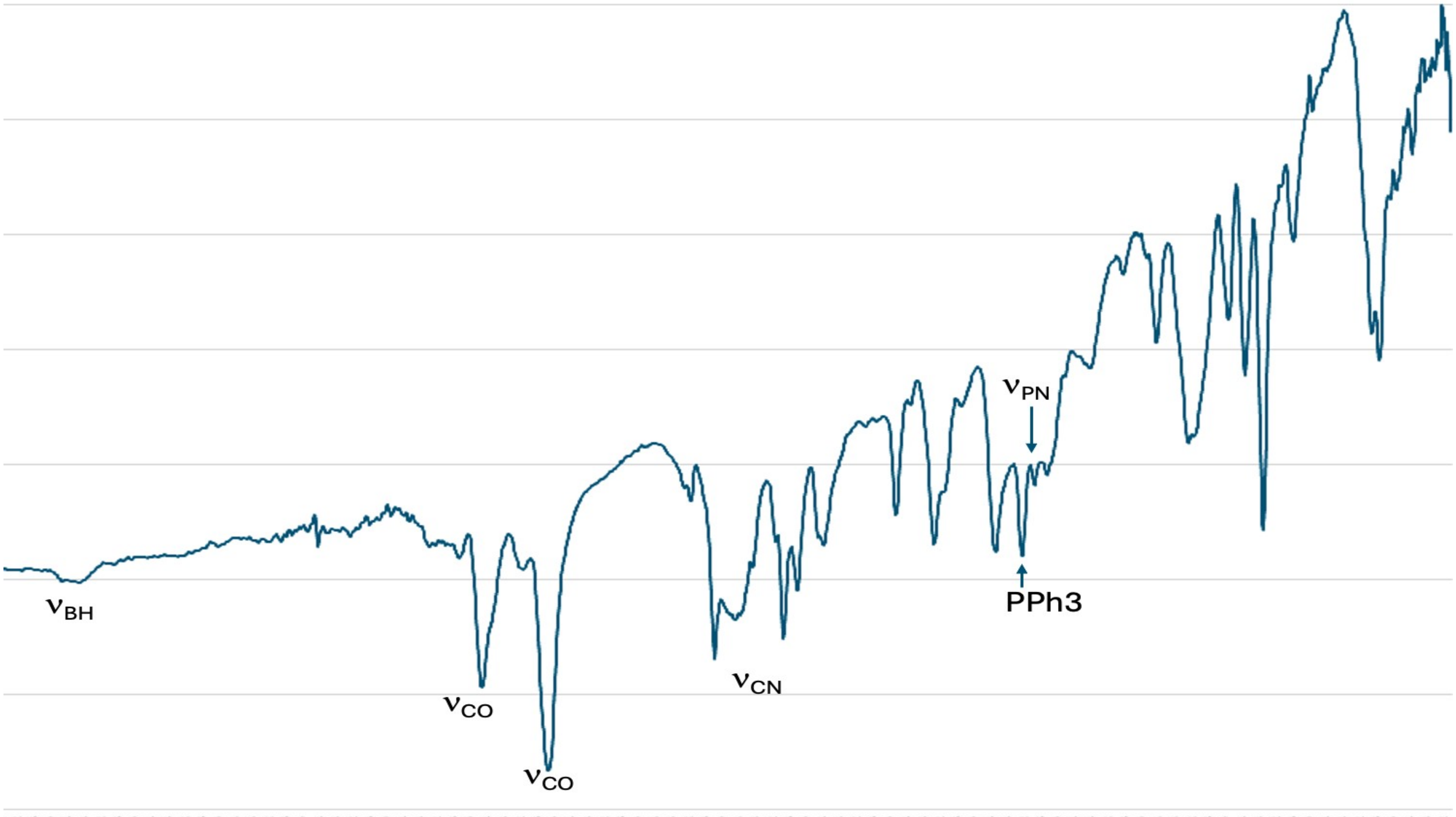


Figure S40. Infrared Spectrum of [W(≡CN=PPh$_3$)(CO)$_2$(Tp*)] (**1**, ATR, cm^{-1}).

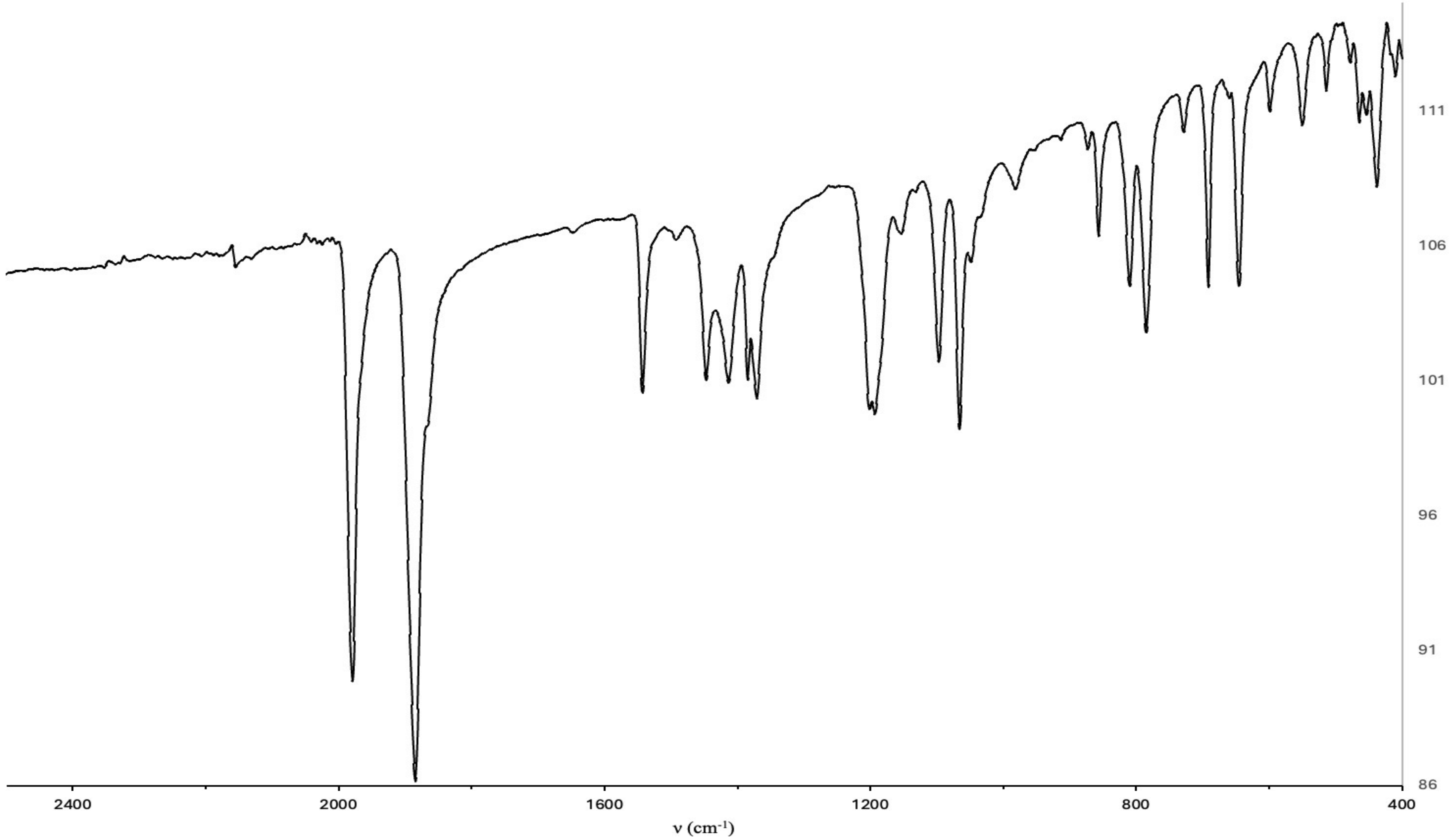


Figure S41. Infrared Spectrum of [W(≡CBr)(CO)$_2$(Tp*)] (ATR, cm^{-1}) – for reference.

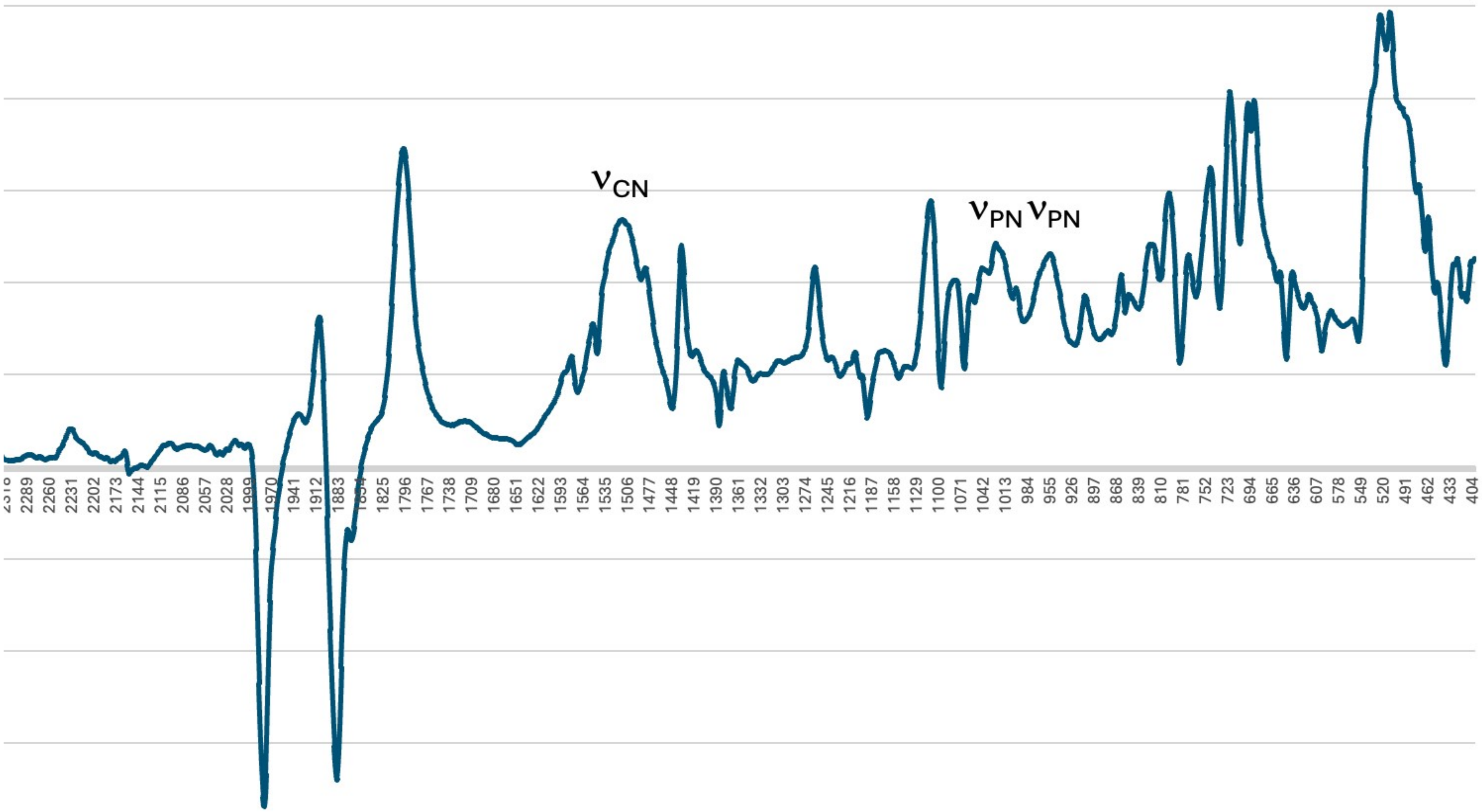


Figure S42. Infrared Spectrum subtraction of [W(≡CBr)(CO)$_2$(Tp*)] from [W(≡CNPPh$_3$)(CO)$_2$(Tp*)] to identify bans associated with the CNPPh$_3$ ligand (ATR, cm^{-1})

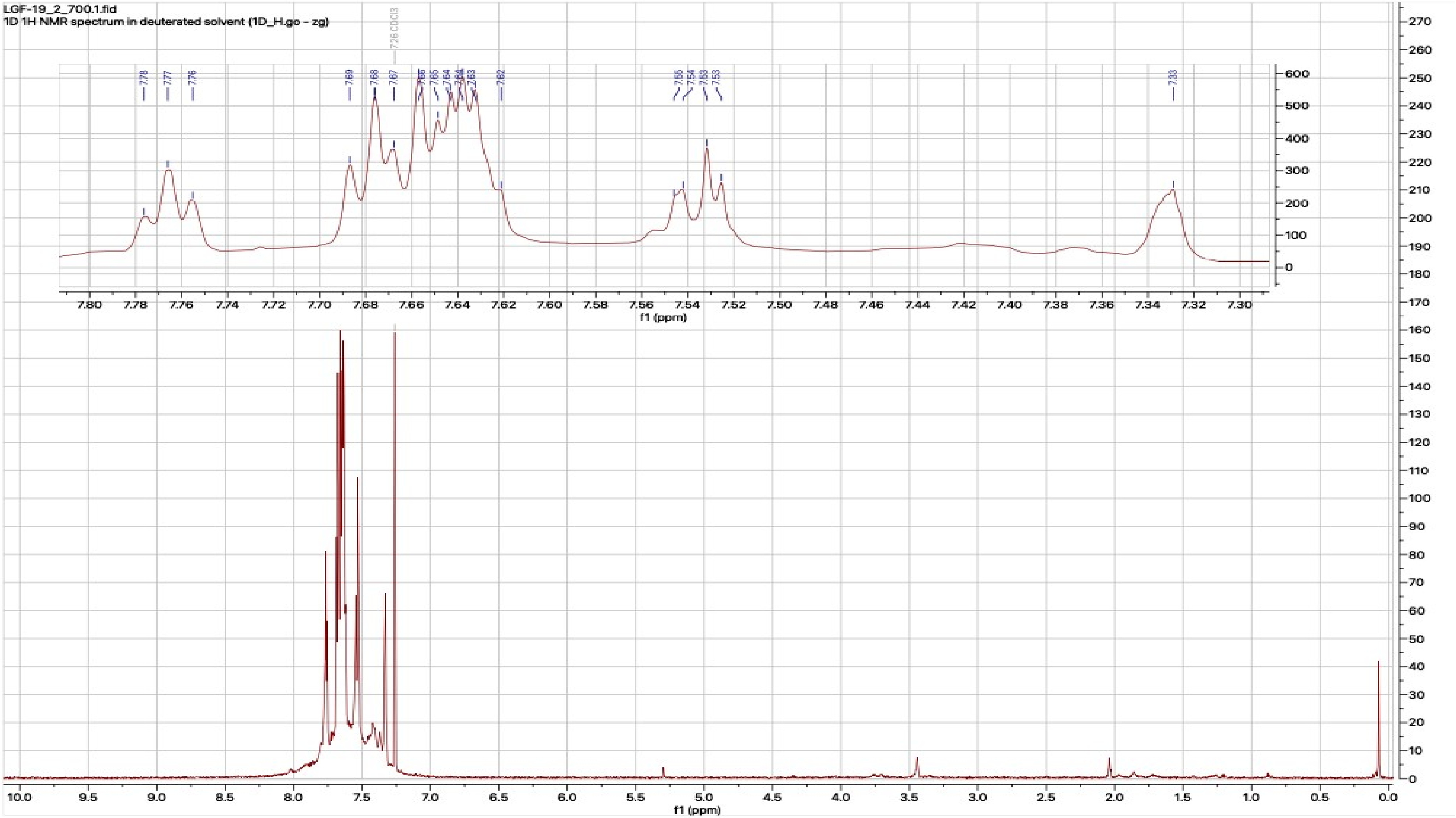


Figure S43. ^{1}H NMR spectrum of [W(≡CN=PPh$_3$)Br(CO)$_4$] (**2**, 295 K, CDCl$_3$, 700 MHz, δ_H).

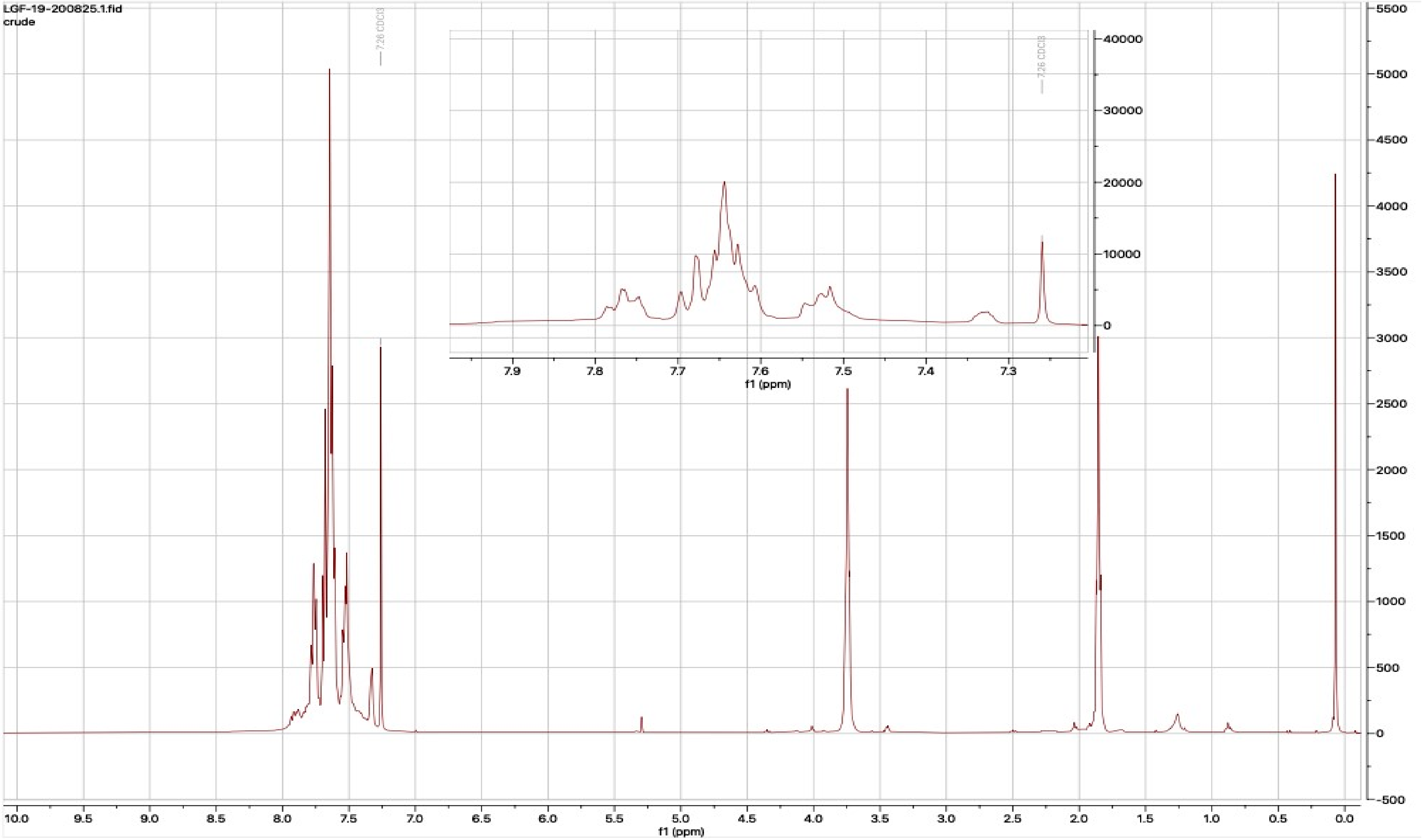


Figure S44. ^1H NMR spectrum of crude product [W(≡CN=PPh$_3$)Br(CO)$_4$] (**2**, 295 K, CDCl3/THF, 400 MHz, δ_H).

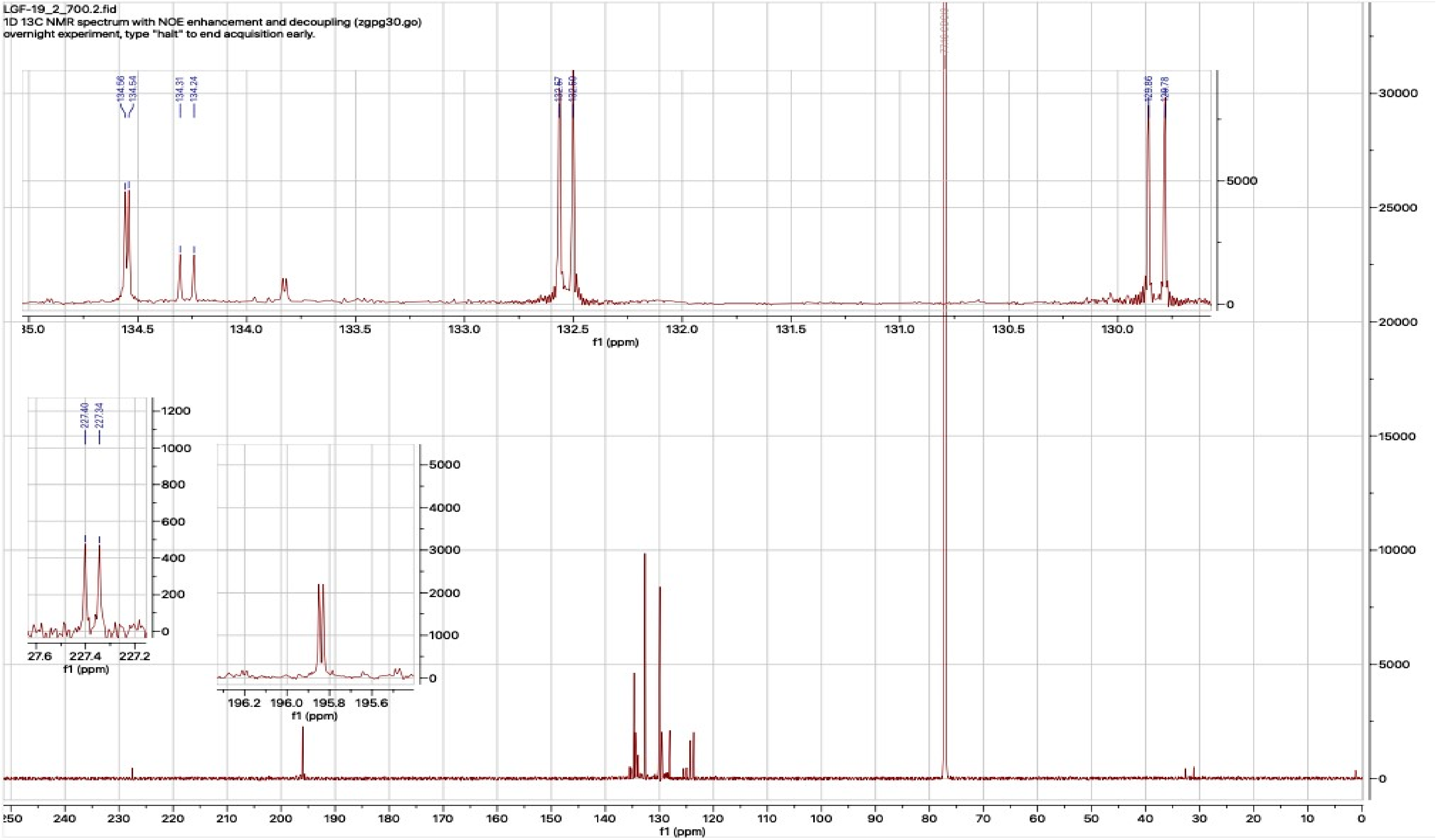


Figure S45. $^{13}C\{^{1}H\}$ NMR spectrum of [W(≡CN=PPh$_3$)Br(CO)$_4$] (**2**, 295 K, CDCl$_3$, 176 MHz, δ_C).

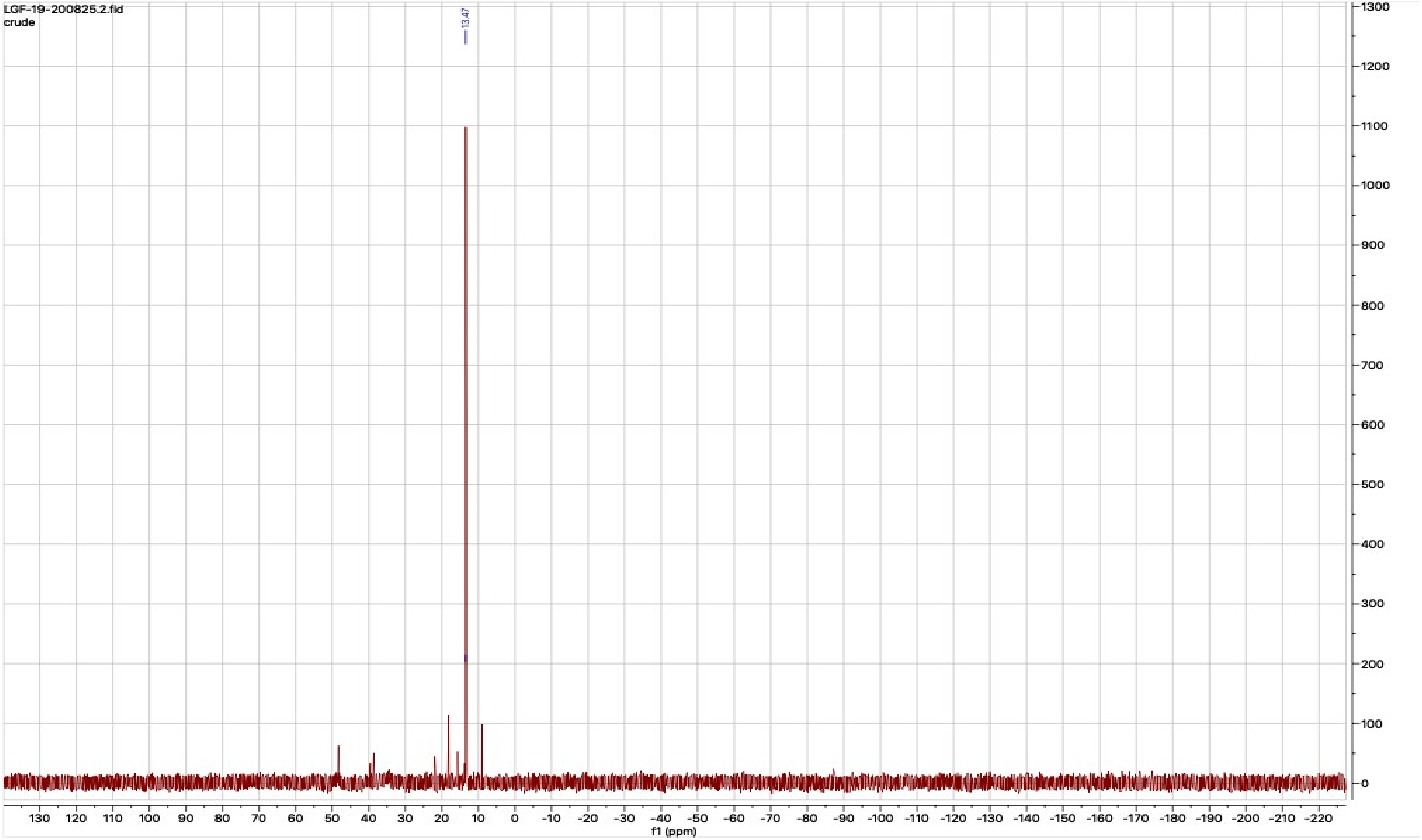


Figure S46. $^{31}P\{^1H\}$ NMR spectrum of crude [W(≡CN=PPh$_3$)Br(CO)$_4$] (**2**, 295 K, CDCl$_3$, 162 MHz, δ_P).

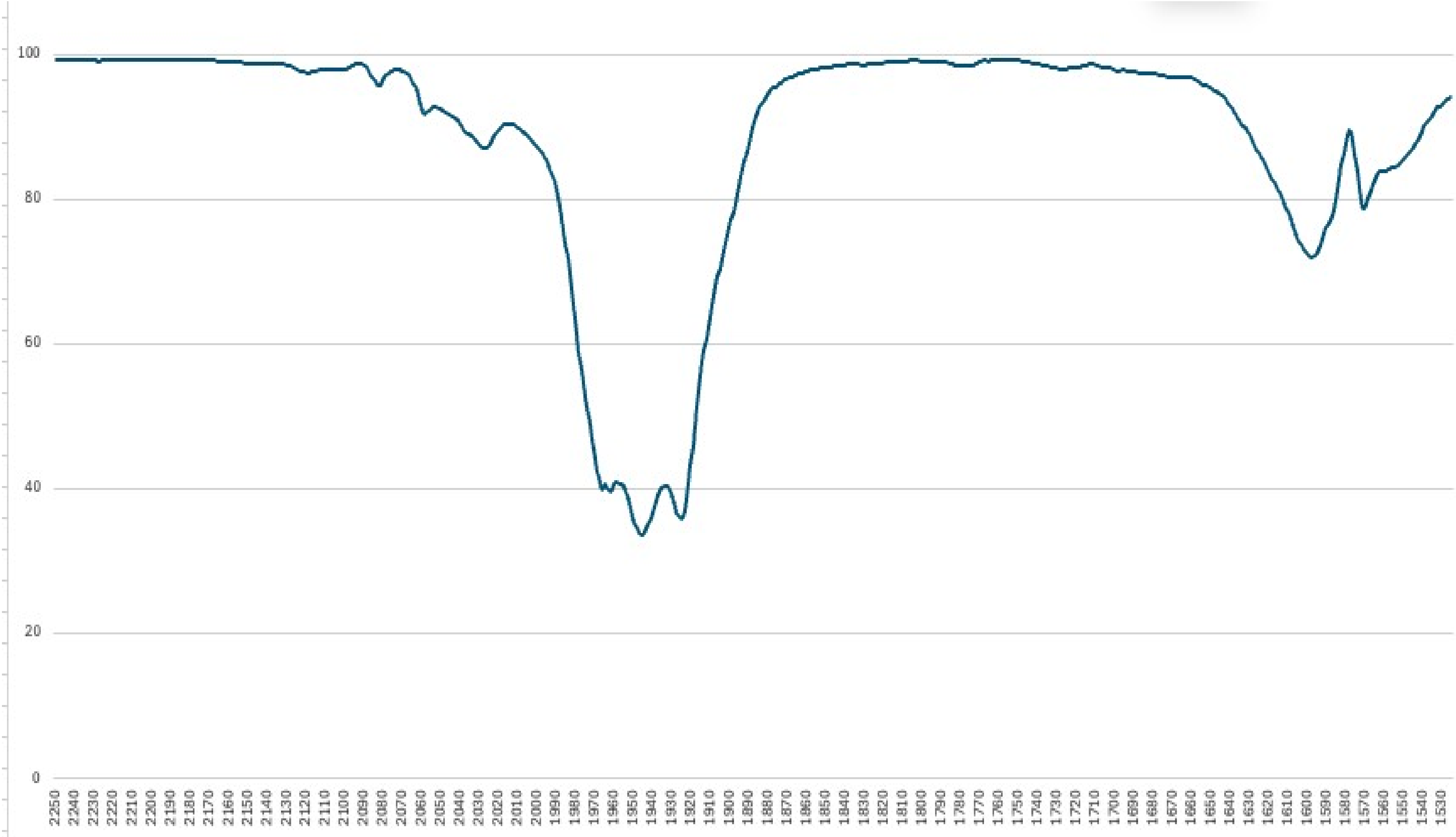


Figure S47. Infrared Spectrum of [W(≡CN=PPh$_3$)Br(CO)$_4$] (**2**, THF, cm^{-1}).

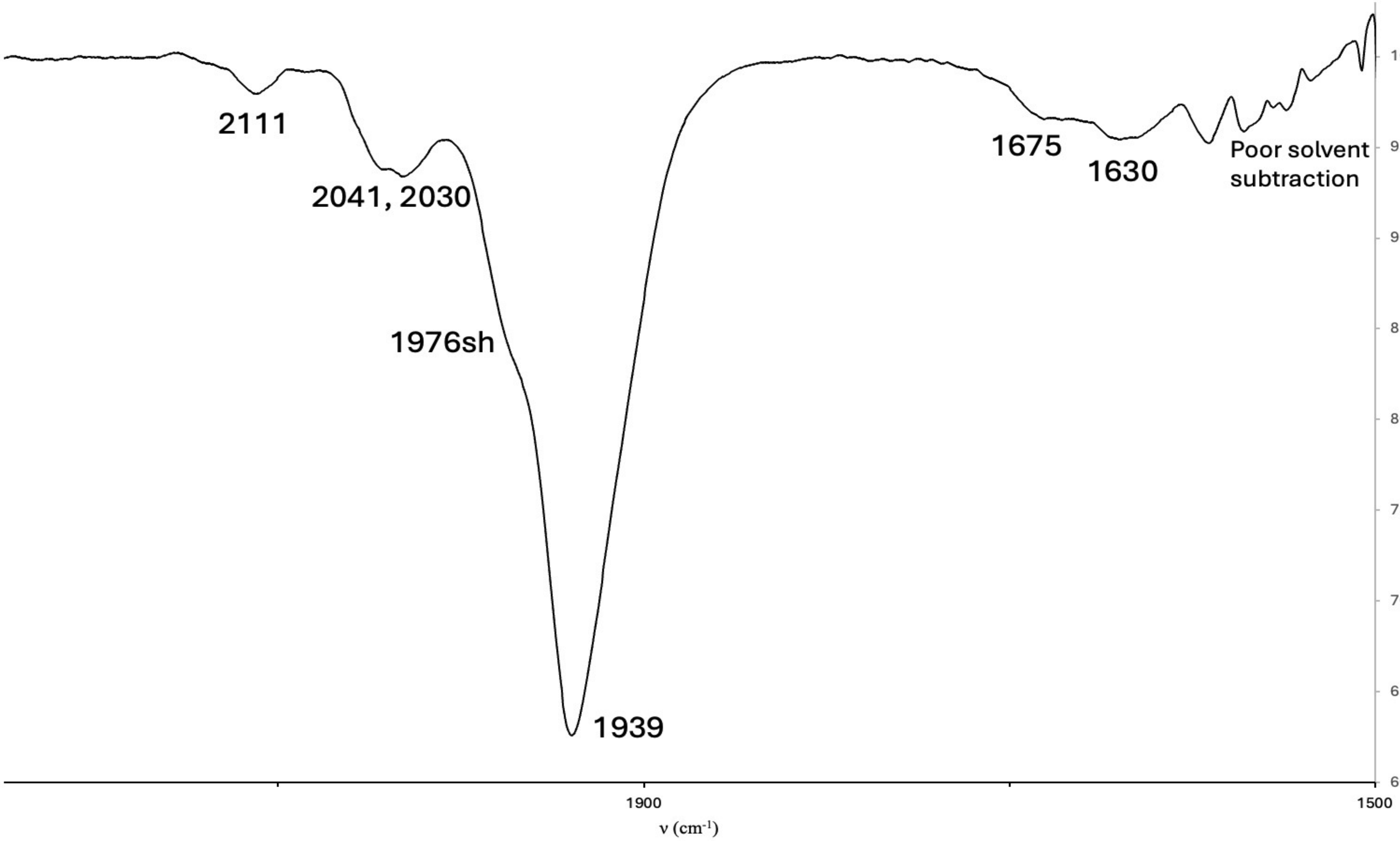


Figure S48. Infrared Spectrum of [W(≡CN=PPh$_3$)Br(CO)$_4$] (**2**, CH$_2$Cl$_2$, cm^{-1}).

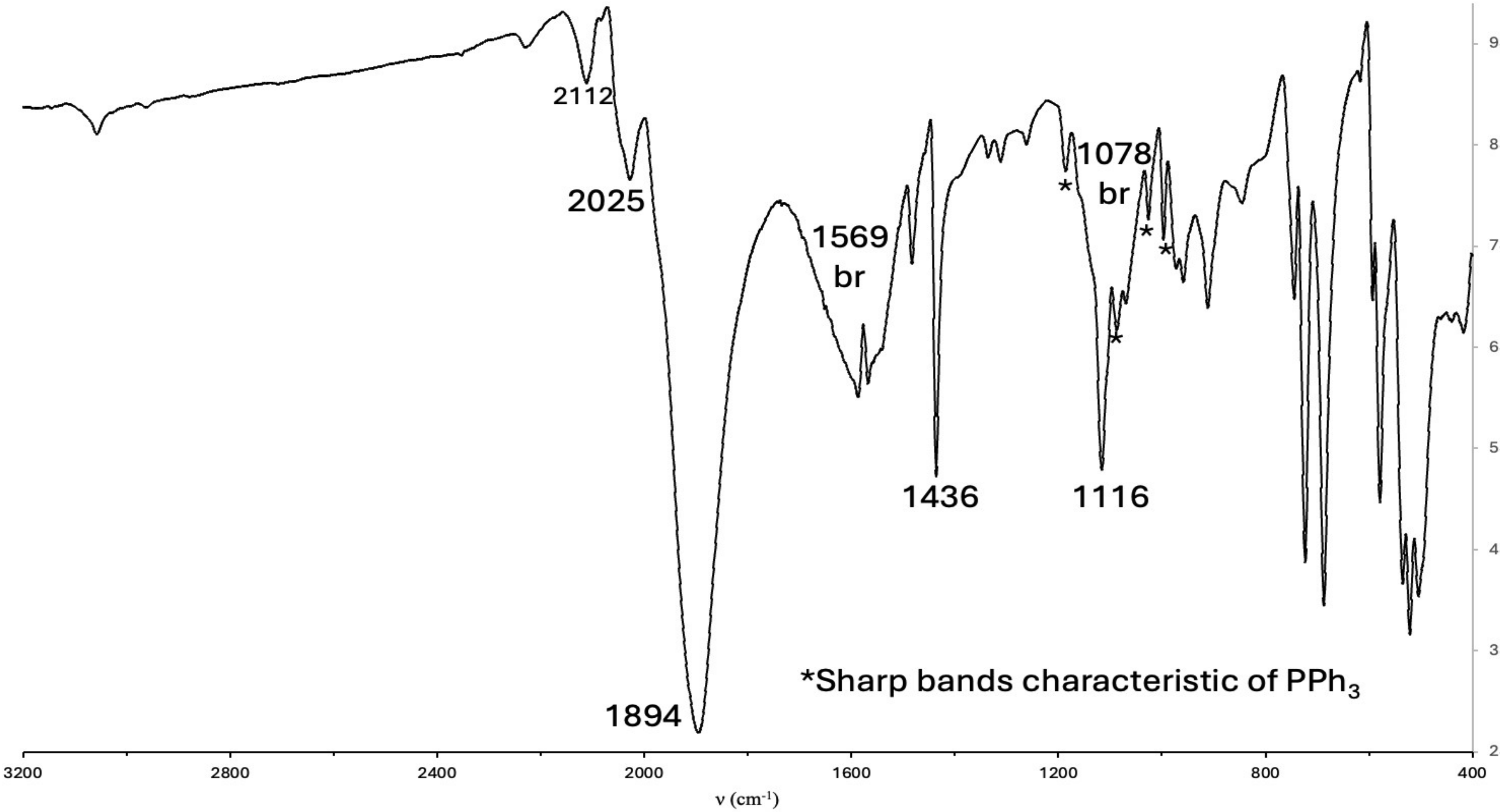


Figure S49. Infrared Spectrum of [W(≡CN=PPh$_3$)Br(CO)$_4$] (**2**, ATR, cm^{-1}).

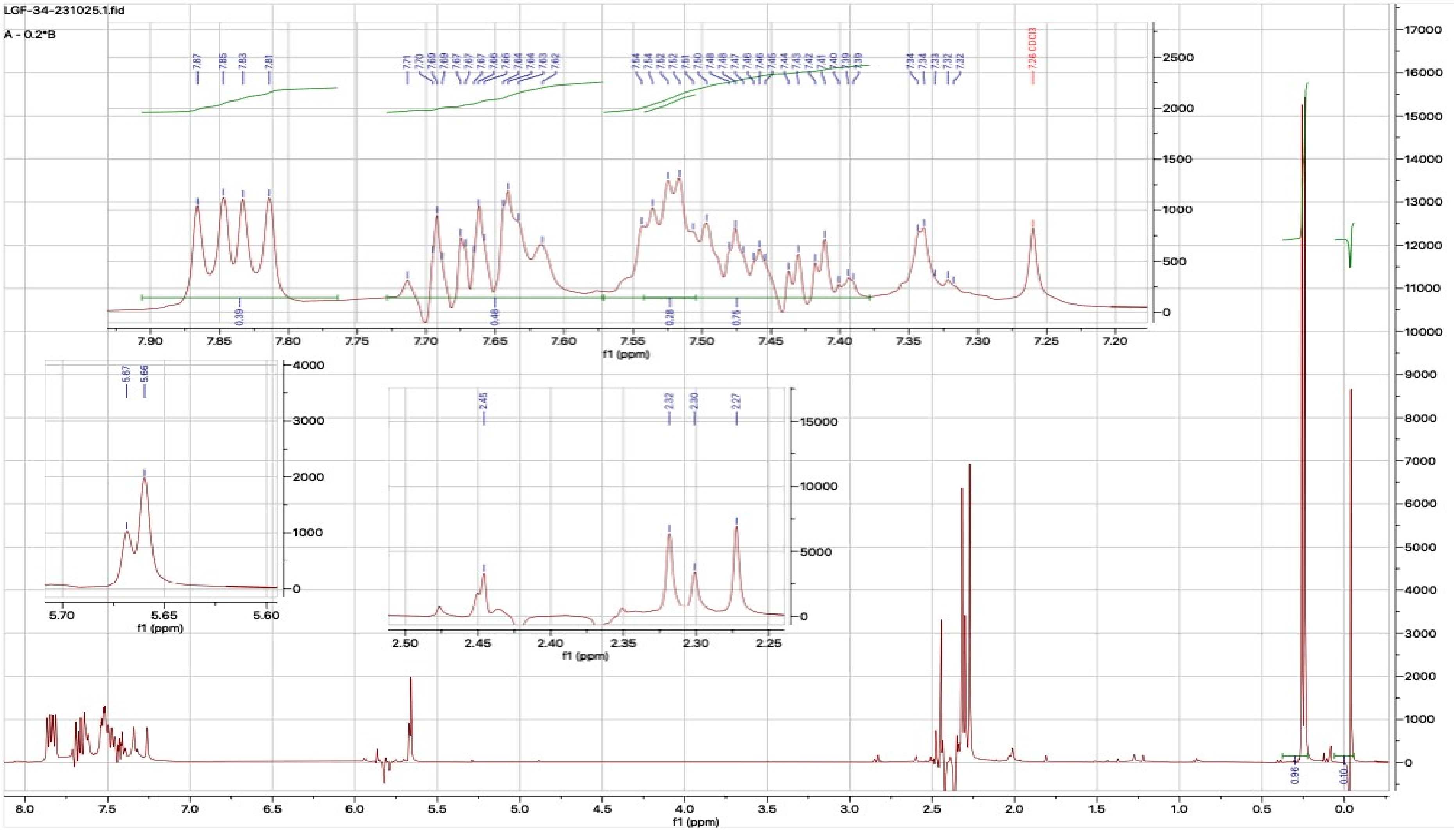


Figure S50. ^{1}H NMR spectrum of the reaction of [Mo(≡CF)(CO)$_2$(Tp*)] with Me3SiN=PPh3 (15 days, 50 °C) with 0.18 x the spectrum of [Mo(≡CF)(CO)$_2$(Tp*)] (see Fig. 45) corresponding primarily to the spectrum of [Mo(≡CN=PPh$_3$)(CO)$_2$(Tp*)] (**3**, 295 K, CDCl$_3$, 400 MHz, δ_H).

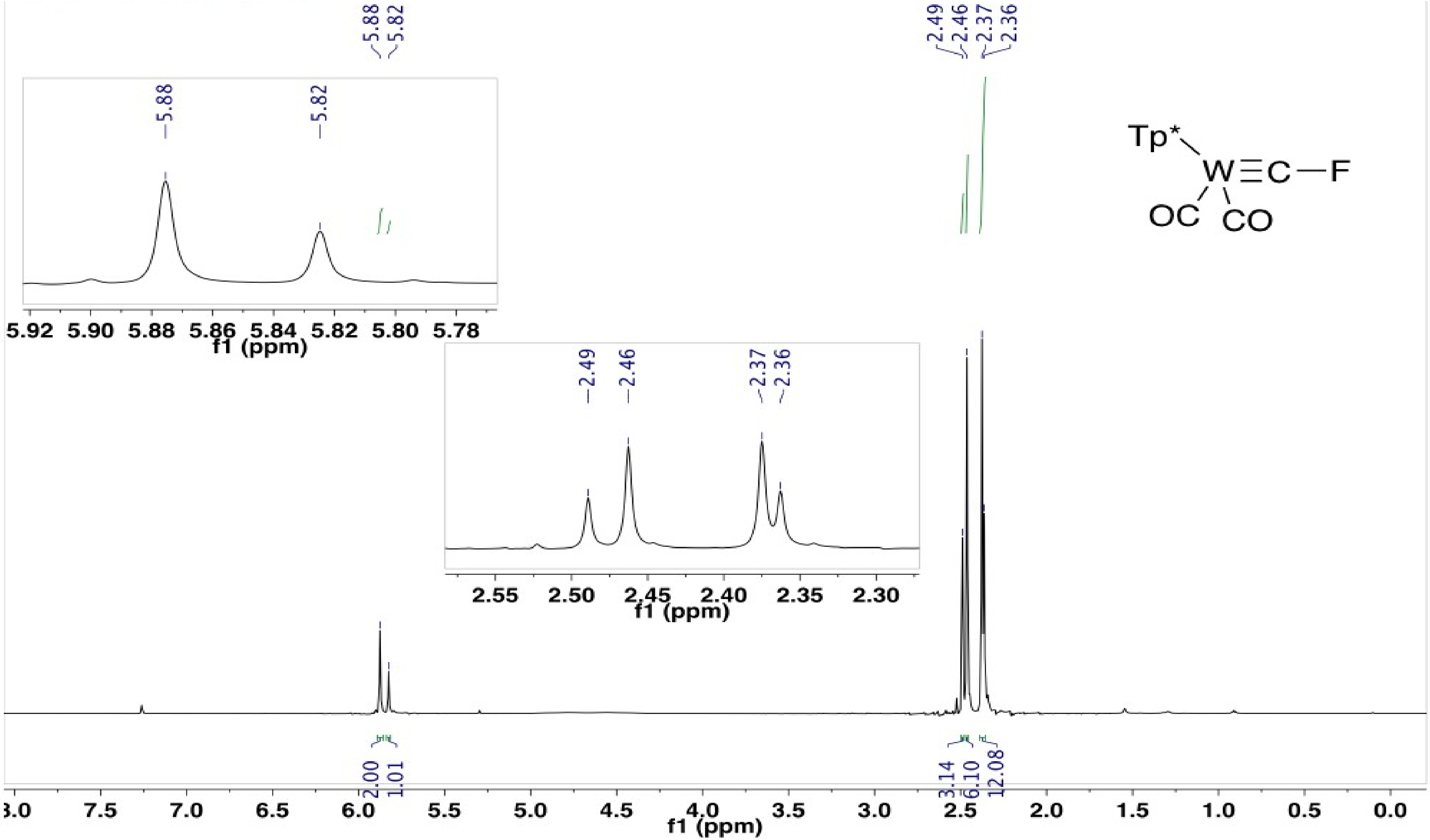


Figure S51. ^{1}H NMR spectrum of [Mo(≡CF)(CO)$_2$(Tp*)] (295 K, CDCl$_3$, 600 MHz, δ_H, for reference[5]).

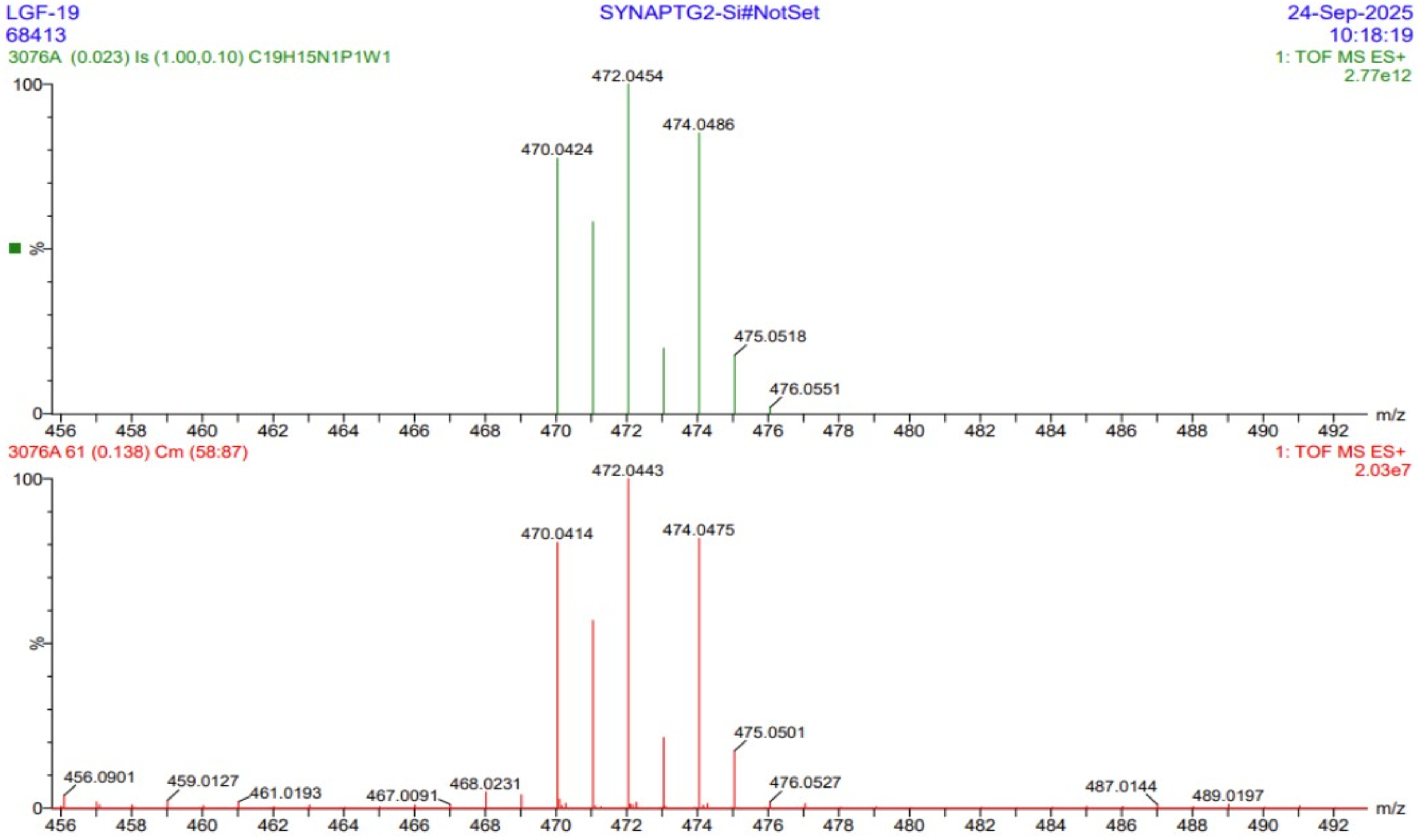


Figure S52. High Resolution Mass Spectrum of $[W(\equiv CNPPh_3)(CO)_4]$ (ESI, MeCN, +ve ion, $[M-Br-4CO]^+$).

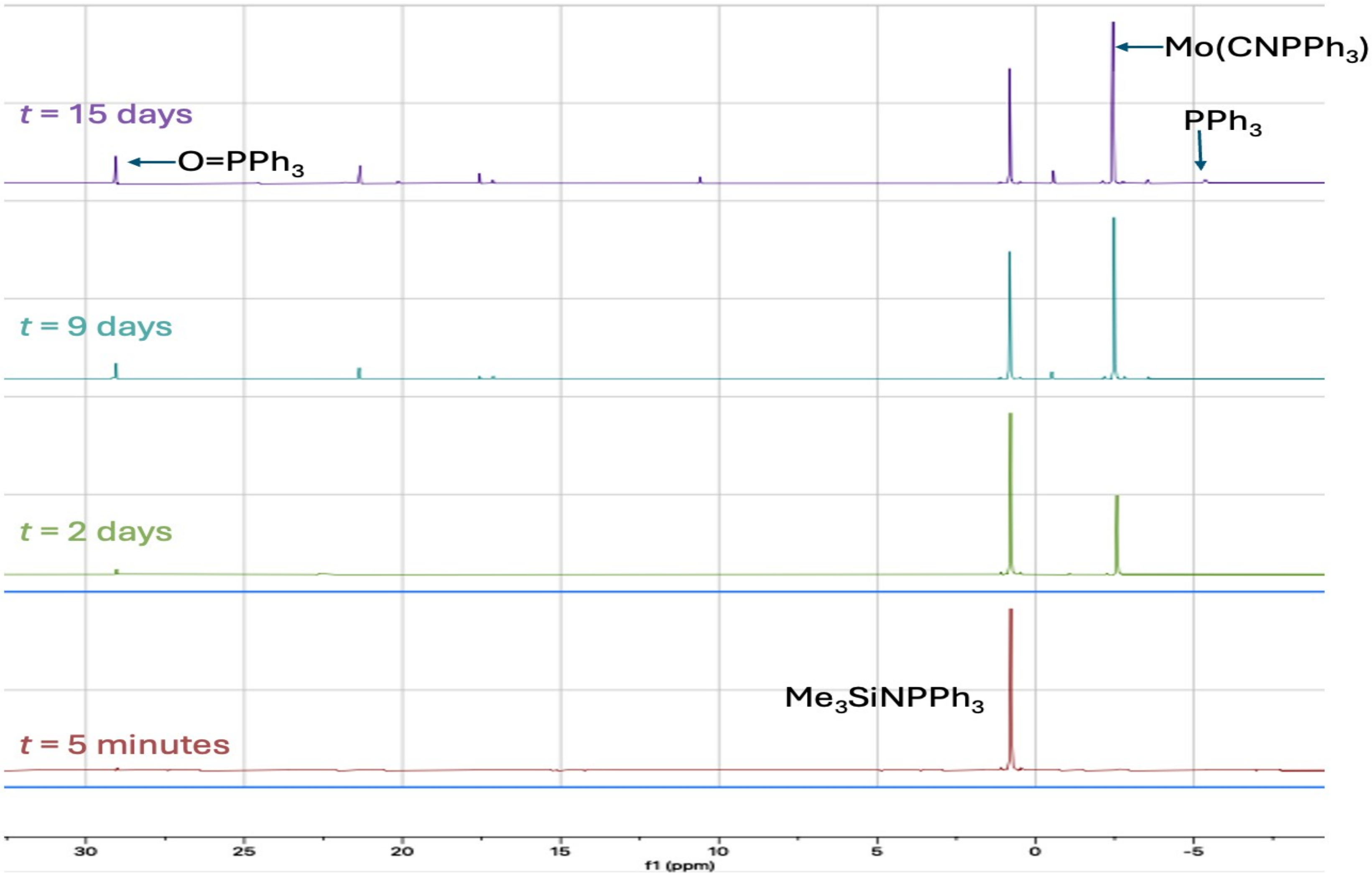


Figure S53. Time course for the reaction of [Mo(≡CF)(CO)$_2$(Tp*)] with Me$_3$SiN=PPh$_3$ over 15 days (CDCl$_3$, 50 °C) as monitored by ^{31}P{^{1}H} NMR (295 K, CDCl$_3$, 162 MHz, δ_P).

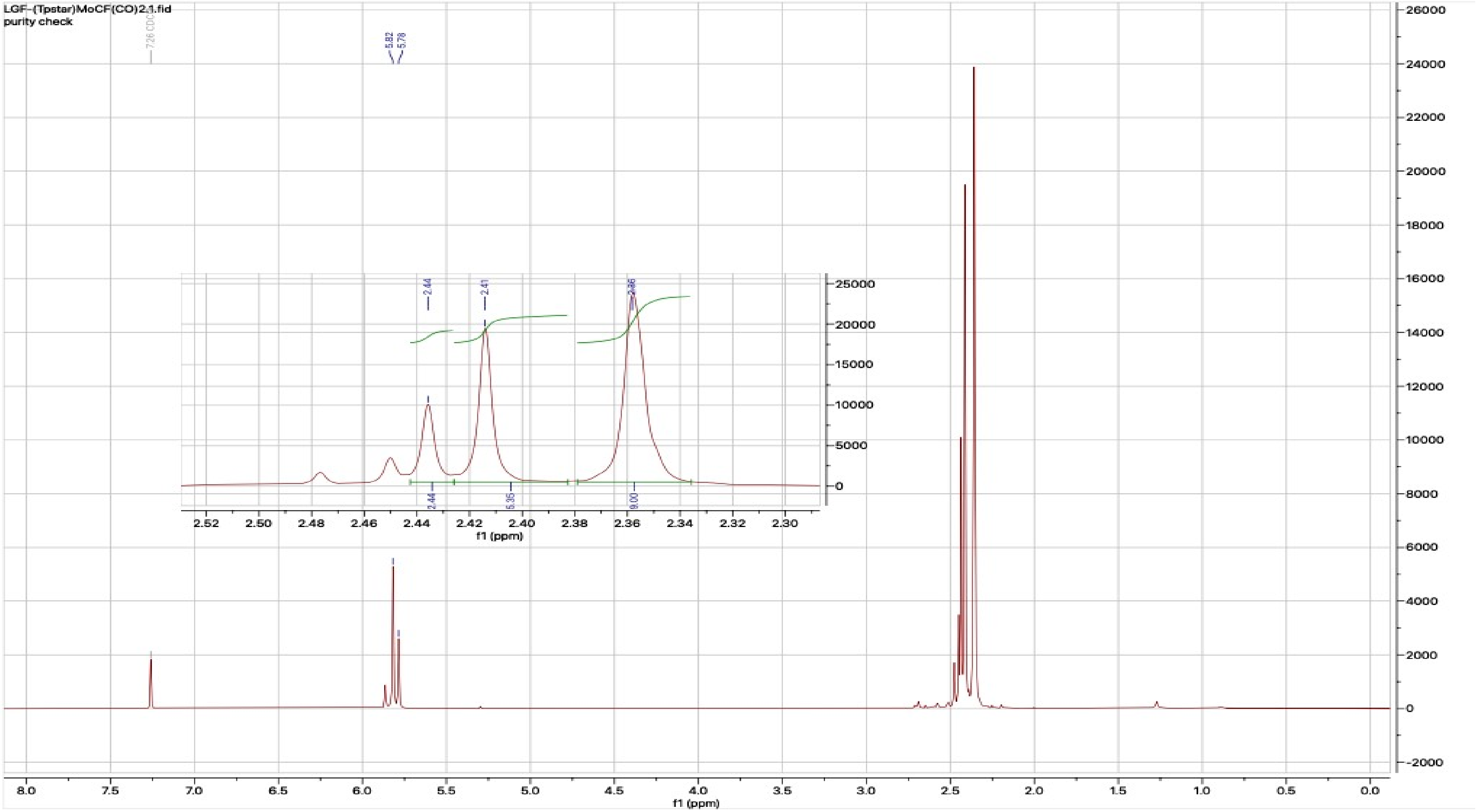


Figure S54. Reference ^{1}H NMR spectrum of [Mo(≡CF)(CO)$_2$(Tp*)] (295 K, CDCl$_3$, 400 MHz, δ_H).