Chemical Communications

SUPPORTING INFORMATION

Electronic Supporting Information for:

Synthesis of pyridyl carbyne complexes and their conversion to *N*-heterocyclic vinylidenes

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Experimental

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

NMR spectra were obtained on a Bruker Avance 400 (^1H at 400.1 MHz, ^{13}C at 100.6 MHz, ^{19}F at 376.5 MHz), a Bruker Avance 600 (^1H at 600.0 MHz, ^{13}C at 150.9 MHz) or a Bruker Avance 700 (^1H at 700.0 MHz, ^{13}C at 176.1 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 peak, or external references ($CFCl_3$ for $^{19}F\{^1H\}$, 85% H_3PO_4 in H_2O for $^{31}P\{^1H\}$), 1.2M Na_2PtCl_6 in H_2O 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 satellites. In some cases, distinct peaks were observed in the ^1H and $^{13}C\{^1H\}$ NMR spectra, but to the level of accuracy that is reportable (i.e. 2 decimal places for ^1H NMR, 1 decimal place for ^{13}C NMR) they are reported as having the same chemical shift. The abbreviation 'pz' is used to refer to the pyrazolyl rings on the hydrotris(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.

Infrared spectra were obtained using a Shimadzu FTIR-8400 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). Elemental microanalytical data were provided the London Metropolitan University. High-resolution electrospray ionisation mass spectrometry (ESI-MS) was performed by the ANU Research School of Chemistry mass spectrometry service with acetonitrile or methanol as the matrix.

Data for X-ray crystallography were collected with an Agilent Xcalibur CCD diffractometer an Agilent SuperNova CCD diffractometer using Mo-Kα radiation (λ = 0.71073 Å) or Cu-Kα radiation (λ = 1.54184 Å) and the CrysAlis PRO software.[1] The structures were solved by direct or Patterson methods and refined by full-matrix least-squares on F^2 using the SHELXS or SHELXT and SHELXL programs.[2] Hydrogen atoms were located geometrically and refined using a riding model. Diagrams were produced using the CCDC visualisation program Mercury.[3]

The synthesis of $[W(\equiv CSn^nBu_3)(CO)_2(Tp^*)]$ (**2**)[4] has been described previously. The complexes $[AuCl(SMe_2)]$[5] and $K[PtCl_3(C_2H_4)].H_2O$[6] were prepared by literature methods. CAUTION: Methyl trifluoromethanesulfonate (MeO_3SCF_3) is highly toxic and should be handled with the utmost care by experienced synthetic chemists.

NB: The demonstration that some of the products form adducts with aurous halides under ambient conditions raises the question (noted by a reviewer) as to whether such adducts of AuCl or AuBr also form under the conditions of catalysis. This would seem entirely likely however adducts such as e.g. **9**, are not stable at the temperatures used for the C–C coupling reactions (toluene reflux ca 110 °C). Even under milder conditions, related adducts, *e.g.,* $[W_2Au_2(\mu\text{-}C_6)(CO)_4(Tp^*)_2]$ degrade in redox processes with deposition of elemental gold and formation of $[W_2Au_2(\mu\text{-}C_6)Cl_4(Tp^*)_2]$.[7] At the conclusion of the catalysis, the ultimate fate of the gold co-catalyst would appear to be (purple) colloidal gold, removed from glassware using *aqua regia*. Under chromatographic conditions, such gold adducts typically eliminate to gold to regenerate the free terminal carbyne.

$[NC_5H_4\{C\equiv W(CO)_2(Tp^*)\}\text{-}2]$ (2). A solution of $[W(\equiv CSn^nBu_3)(CO)_2(Tp^*)]$ (500 mg, 0.596 mmol), 2-bromopyridine (57 μL, 0.60 mmol), $[Pd(PPh_3)_4]$ (69 mg, 0.060 mmol) and $[AuCl(SMe_2)]$ (17 mg, 0.058 mmol) in toluene (20 mL) was heated under reflux for 6 h, during which time the solution turned dark red. After this time, the solvent was removed under reduced pressure and the residue was subjected to column chromatography (50 x 3 cm silica gel column), eluting with CH_2Cl_2. A slow-moving red band was collected and the volatiles were removed under reduced pressure. The residue was recrystallized from CH_2Cl_2 and *n*-hexane to give a red solid of pure **2** (266 mg, 0.424 mmol, 71%). IR (CH_2Cl_2, cm^{-1}): 1981s, 1889s ν_{CO}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ_H = 2.35 (s, 3H, pzCH_3), 2.37 (s, 6H, pzCH_3), 2.45 (s, 3H, pzCH_3), 2.53 (s, 6H, pzCH_3), 5.79 (s, 1H, pzC*H*), 5.89 (s, 2H, pzC*H*), 7.17 (ddd, $^3J_{HH}$ = 7.7, 4.8, $^4J_{HH}$ = 1.2, 1H, *Py-5*), 7.36 (dt', $^3J_{HH}$ = 7.8, 1H, *Py-3*), 7.62 (t'd, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.8, 1H, *Py-4*), 8.52 (ddd, $^3J_{HH}$ = 4.8, 1H, *Py-6*). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C): δ_C = 12.7, 15.3, 16.7 (pzCH_3), 106.6, 106.8 (pz*C*H), 121.5 (*Py-5)*, 124.3 (*Py-3)*, 135.7 *(Py-4)*, 144.4, 145.3 (pz*C*CH_3), 149.6 (*Py-6)*, 152.1, 152.5 (pz*C*CH_3), 165.2 (W≡C*C*, $^2J_{CW}$ = 45), 224.2 (*C*O, $^1J_{CW}$ = 164), 275.9 (W≡*C*, $^1J_{CW}$ = 190). MS (ESI, *m/z*): Found: 628.1817. Calcd for $C_{23}H_{27}{}^{11}BN_7O_2{}^{184}W$ $[M+H]^+$: 628.1823. Anal. Found: C, 44.05; H, 4.25; N, 15.59. Calcd for $C_{23}H_{26}BN_7O_2W$: C, 44.05; H, 4.18; N, 15.63%. A crystal suitable for structure determination was grown by slow evaporation of a CH_2Cl_2/acetonitrile solution at at 4 ˚C and proved to be an acetonitrile solvate. *Crystal data for* $C_{25}H_{29}BN_8O_2W$ (*M* = 668.22 $g.mol^{-1}$): monoclinic, space group $P2_1/c$ (no. 14), *a* = 15.3086(6), *b* = 9.8592(4), *c* = 17.7914(7) Å, *β* = 96.715(4)°, *V* = 2666.84(18) $Å^3$, *Z* = 4, *T* = 150.0(1) K, μ(MoKα) = 4.370 mm^{-1}, *Dcalc* = 1.664 $g.cm^{-3}$, 14443 reflections measured (6.65° ≤ 2Θ ≤ 50.052°), 4702 unique (R_{int} = 0.0600, R_{sigma} = 0.0587) which were used in all calculations. The final R_1 was 0.0455 (I > 2σ(I)) and wR_2 was 0.0865 (all data) for 345 refined parameters with 0 restraints. CCDC 1955818.

[NC_5H_3\{C≡W(CO)$_2$(Tp*)\}$_2$-2,6] (3). A solution of [W(≡CSn^{n}Bu$_3$)(CO)$_2$(Tp*)] (1.00 g, 1.19 mmol), 2,6-dibromopyridine (141 mg, 0.595 mmol), [Pd(PPh_3)$_4$] (138 mg, 0.119 mmol) and [AuCl(SMe_2)] (35 mg, 0.12 mmol) in toluene (25 mL) was heated under reflux for 14 h, during which time the solution turned dark red. After this time, the solvent was removed under reduced pressure and the residue was subjected to column chromatography (50 x 3 cm silica gel column), eluting with CH_2Cl_2. A slow-moving red band was collected and the volatiles were removed under reduced pressure to give a red solid of pure **3** (313 mg, 0.266 mmol, 45%). IR (CH_2Cl_2, cm^{-1}): 1980s, 1890s ν_{CO}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ_H = 2.34 (s, 6H, pzCH_3), 2.36 (s, 12H, pzCH_3), 2.45 (s, 6H, pzCH_3), 2.56 (s, 12H, pzCH_3), 5.78 (s, 2H, pzC*H*), 5.87 (s, 4H, pzC*H*), 7.28 (d, $^3J_{HH}$ = 7.8, 2H, *Py-3,5*), 7.56 (t, $^3J_{HH}$ = 7.8, 1H, *Py-4*). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C): δ_C = 12.8, 15.3, 17.0 (pzCH_3), 106.5, 106.8 (pz*C*H), 122.7 (*Py-3,5)*, 135.4 (*Py-4)*, 144.3, 145.2, 152.3, 152.4 (pz*C*CH_3), 164.7 (W≡C*C*, $^2J_{CW}$ = 45), 224.3 (*C*O, $^1J_{CW}$ = 164), 276.7 (W≡*C*, $^1J_{CW}$ = 191). MS (ESI, *m/z*): Found: 1176.3170. Calcd for $C_{41}H_{48}{}^{11}B_2N_{13}O_4{}^{184}W_2$ $[M+H]^+$: 1176.3160. Anal. Found: C, 41.88; H, 3.88; N, 15.36. Calcd for $C_{41}H_{47}B_2N_{13}O_4W_2$: C, 41.90; H, 4.03; N, 15.49%.

[HNC_5H_4\{C≡W(CO)$_2$(Tp*)\}-2]BF_4 (4). To a solution of **2** (50 mg, 0.080 mmol) in diethyl ether (5 mL) was added $HBF_4{\cdot}Et_2O$ (15 μL, 0.11 mmol), causing the initially red solution to immediately form a yellow-green precipitate. This precipitate was collected by filtration and washed with diethyl ether acidified with a few drops of $HBF_4{\cdot}Et_2O$ (5 x 5 mL) to give a yellow-green solid of pure **4** (52 mg, 0.073 mmol, 91%). This compound was found to deprotonate readily and so the spectral data was collected in the presence of a small amount of added $HBF_4{\cdot}Et_2O$. IR (CH_2Cl_2, cm^{-1}): 2010s, 1924s ν_{CO}. The IR spectrum was collected in the absence of added acid and contained a significant amount of the deprotonated **2**. ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ_H = 2.35 (s, 3H, pzCH_3), 2.37 (s, 3H, pzCH_3), 2.39 (s, 6H, pzCH_3), 2.41 (s, 6H, pzCH_3), 5.82 (s, 1H, pzC*H*), 5.84 (s, 2H, pzC*H*), 7.25–7.44 (m, 1 H, *Py-4*), 7.57 (d, $^3J_{HH}$ = 8.0, 1H, *Py-6*), 7.71 (m, 1H, *Py-5*), 8.34 (br, PyN*H*), 8.72 (d, $^3J_{HH}$ = 8.0, 1H, *Py-3*). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 25 °C): δ_C = 12.8, 12.8, 15.3, 16.7 (pzCH_3), 107.0, 107.3 (pz*C*H), 121.7 (br, *Py-3*), 128.0 (t, *J* = 5.2, *Py-6*), 130.5 (*Py-4*), 135.3 (t, *J* = 6.5, *Py-5*), 145.1, 146.1, 151.8, 152.9 (pz*C*CH_3), 159.4 (br, W≡C*C*), 223.2 (*C*O, $^1J_{CW}$ = 161), 260.3 (br, W≡*C*). We are uncertain why two of the pyridyl carbon nuclei appear as triplets but suspect ion-pairing with the BF_4^- counteranion may play a role. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, 25 °C): δ_F = –152.9 (s, B*F*$_4$). MS (ESI, *m/z*): Found: 628.1818. Calcd for $C_{23}H_{26}{}^{11}BN_7O_2{}^{184}W$ $[M–BF_4]^+$: 628.1826. Anal. Found: C, 38.75; H, 3.79; N, 13.59. Calcd for $C_{23}H_{27}B_2F_4N_7O_2W$: C, 38.64; H, 3.81; N, 13.71%.

[HNC_5H_4\{C≡W(CO)$_2$(Tp*)\}$_2$-2,6]BF_4 (5). To a solution of **3** (50 mg, 0.043 mmol) in diethyl ether (5 mL) was added $HBF_4{\cdot}Et_2O$ (10 μL, 0.073 mmol), causing the initially red solution to immediately form a yellow-green precipitate. This precipitate was collected by filtration and washed with diethyl ether acidified with a few drops of $HBF_4{\cdot}Et_2O$ (5 x 5 mL) to give a yellow-green solid of pure **5** (47 mg, 0.0037 mmol, 87%). This compound was found to deprotonate readily and so the spectral data was collected in the presence of a small amount of added $HBF_4{\cdot}Et_2O$. IR (CH_2Cl_2, cm^{-1}): 2010s, 1925s ν_{CO}. ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ_H = 2.35 (s, 6H, pzCH_3), 2.42 (s, 30H, pzCH_3), 5.83 (s, 2H, pzC*H*), 6.00 (s, 4H, pzC*H*), 7.62 (br, 2H, *Py-3*), 8.52 (br, 1H, *Py-4*). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 25 °C): δ_C = 12.8, 12.9, 15.5, 16.9 (pzCH_3), 107.4, 107.7 (pz*C*H), 125.2 (*Py-3*), 145.8, 146.6 (pz*C*CH_3), 146.8 (*Py-4*), 151.8, 153.0 (pz*C*CH_3), 154.6 (W≡C*C*), 223.5 (*C*O), 251.5 (br, W≡*C*). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, 25 °C): δ_F = –153.7 (s, B*F*$_4$). MS (ESI, *m/z*): Found: 1176.3163. Calcd for $C_{41}H_{48}{}^{11}B_2N_{13}O_4{}^{184}W_2$ $[M–BF_4]^+$: 1176.3160. Anal. Found: C, 37.70; H, 3.31; N, 13.81. Calcd for $C_{41}H_{48}B_3F_4N_{13}O_4W_2{\cdot}CH_2Cl_2$: C, 37.42; H, 3.74; N, 13.51%. A crystal suitable for single crystal X-ray crystallography was grown by vapour diffusion of *n*-pentane into a (wet) dichloromethane solution at 4 °C and proved to contain two equivalents of CH_2Cl_2 and one equivalent of H_2O for which the protons were not located. *Crystal data for* $C_{43}H_{54}B_3Cl_4F_4N_{13}O_5W_2$ (*M* =1450.92 $g.mol^{-1}$): orthorhombic, space group *Pnma* (no. 62), *a* = 15.8519(8), *b* = 24.1231(13), *c* = 14.0794(7) Å, *V* = 5383.9(5) $Å^3$, *Z* = 4, *T* = 150.0(1) K, μ(MoKα) = 4.538 mm^{-1}, *Dcalc* = 1.790 $g.cm^{-3}$, 22428 reflections measured (6.554° ≤ 2Θ ≤ 50.054°), 4868 unique (R_{int} = 0.0406, R_{sigma} = 0.0367) which were used in all calculations. The final R_1 was 0.0401 (I > 2σ(I)) and wR_2 was 0.0917 (all data) for 350 refined parameters with 33 restraints. CCDC 1955819.

[$MeNC_5H_4$\{C≡W(CO)$_2$(Tp*)\}-2]O_3SCF_3 (6). To a solution of **3** (50 mg, 0.080 mmol) in diethyl ether (5 mL) was added MeO_3SCF_3 (10 μL, 0.09 mmol), causing the initially red solution to immediately form a bright green precipitate. Stirring was continued for 5 min, after which time the solid was collected by filtration, washed with diethyl ether (5 x 5 mL) and *n*-hexane (10 x 5 mL) (CAUTION: filtrate may contain unreacted MeO_3SCF_3) and dried *in vacuo* to give a lime-green solid of pure **6** (57 mg, 0.072 mmol, 90%). IR (CH_2Cl_2, cm^{-1}): 2009s, 1922s ν_{CO}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ_H = 2.34 (s, 6H, pzC*H*$_3$), 2.35 (s, 3H, pzCH_3), 2.40 (s, 3H, pzCH_3), 2.45 (s, 6H, pzCH_3), 4.26 (s, 3H, PyCH_3), 5.83 (s, 1H, pzC*H*), 6.00 (s, 2H, pzC*H*), 7.68 (d, $^3J_{HH}$ = 8.0, 1H, *Py-3*), 7.88 (t', $^3J_{HH}$ = 6.8, 1H, *Py-5*), 8.25 (t', $^3J_{HH}$ = 7.9, 1H, *Py-4*), 8.84 (d, $^3J_{HH}$ = 6.2, 1H, *Py-6*). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$, 25 °C): δ_C = 12.7, 12.8, 15.4, 16.9 (pzCH_3), 45.5 (PyCH_3), 107.3, 107.6 (pz*C*H), 124.2 (*Py-3 or 5*), 130.7 (*Py-3 or 5*), 143.6 (*Py-4 or 6*), 145.9, 146.7 (pz*C*CH_3), 146.7 (*Py-4 or 6*), 151.6, 152.9 (pz*C*CH_3), 156.0 (W≡C*C*), 224.1 (*C*O, $^1J_{CW}$ = 158), 251.5 (W≡*C*, $^1J_{CW}$ = 190). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, 25 °C): δ_F = –78.3 (s, O_3SCF_3). MS (ESI, *m/z*): Found: 642.1981. Calcd for $C_{24}H_{29}{}^{11}BN_7O_2{}^{184}W$ $[M–O_3SCF_3]^+$: 642.1983. Anal. Found: C, 37.86; H, 3.50; N, 12.24. Calcd for $C_{25}H_{29}BF_3N_7O_5SW$: C, 37.95; H, 3.69; N, 12.39%. A crystal suitable for structure determination was grown by slow evaporation of a CH_2Cl_2/ethanol mixture at 4 °C. *Crystal data for* $C_{25}H_{29}BF_3N_7O_5SW$ (*M* =791.27 $g.mol^{-1}$): monoclinic, space group *C2*/c (no. 15), *a* = 33.2746(5) Å, *b* = 13.8436(2), *c* = 14.0874(2), *β* = 98.5290(10)°, *V* = 6417.46(16) $Å^3$, *Z* = 8, *T* = 150.0(1) K, μ(CuKα) = 7.829 mm^{-1}, *Dcalc* = 1.638 $g.cm^{-3}$, 17705 reflections measured (6.928° ≤ 2Θ ≤ 141.996°), 6075 unique (R_{int} = 0.0231, R_{sigma} = 0.0243) which were used in all calculations. The final R_1 was 0.0250 (I > 2σ(I)) and wR_2 was 0.0613 (all data) for 472 refined parameters with 114 restraints. CCDC 1955820.

$[MeNC_5H_4\{C≡W(CO)_2(Tp^*)\}_2\text{-}2,6]O_3SCF_3$ (7). To a solution of **4** (50 mg, 0.043 mmol) in diethyl ether (5 mL) was added MeO_3SCF_3 (10 μL, 0.09 mmol), causing the initially red solution to immediately form a dark green precipitate. Stirring was continued for 5 min, after which time the solid was collected by filtration, washed with diethyl ether (5 x 5 mL) and *n*-hexane (10 x 5 mL) (CAUTION: filtrate may contain unreacted MeO_3SCF_3) and dried *in vacuo* to give a green solid of pure **7** (50 mg, 0.037 mmol, 87%). IR (CH_2Cl_2, cm^{-1}): 2006s, 1923s ν_{CO}. ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ_H = 2.33 (s, 12H, pzCH_3), 2.35 (s, 6H, pzCH_3), 2.38 (s, 6H, pzCH_3), 2.43 (s, 12H, pzCH_3), 4.04 (s, 3H, PyCH_3), 5.82 (s, 2H, pzC*H*), 6.00 (s, 4H, pzC*H*), 7.64 (d, $^3J_{HH}$ = 7.9, 2H, *Py-3,5*), 8.28 (t, $^3J_{HH}$ = 7.9, 1H, *Py-4*). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 25 °C): δ_C = 12.7, 12.8, 15.4, 16.8 (pzCH_3), 40.7 (PyCH_3), 107.3, 107.6 (pz*C*H), 127.8 (*Py-3,5*), 142.9 (*Py-4*), 146.0, 146.8, 151.2, 152.9 (pz*C*CH_3), 155.6 (W≡C*C*, $^2J_{CW}$ = 45), 224.1 (*C*O, $^1J_{CW}$ = 157), 251.9 (W≡*C*, $^1J_{CW}$ = 199). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, 25 °C): δ_F = –78.0 (s, O_3SCF_3). MS (ESI, *m/z*): Found: 1190.3316. Calcd for $C_{42}H_{50}{}^{11}B_2N_{13}O_4{}^{184}W_2$ $[M–O_3SCF_3]^+$: 1190.3335. A crystal suitable for structure determination was grown by slow evaporation of a chloroform/ethanol mixture at 4 °C and proved to contain 2.5 equivalents of chloroform of solvation. *Crystal data for* $C_{45.5}H_{52.5}B_2Cl_{7.5}F_3N_{13}O_7SW_2$ (*M* =1637.76 $g.mol^{-1}$): triclinic, space group *P*-1 (no. 2), *a* = 13.6197(4), *b* = 18.3015(8), *c* = 26.9010(9) Å, *α* = 88.518(3)°, *β* = 76.527(3)°, *γ* = 70.518(3)°, *V* = 6137.7(4) $Å^3$, *Z* = 4, *T* = 150.0(1) K, μ(CuKα) = 10.717 mm^{-1}, *Dcalc* = 1.772 $g.cm^{-3}$, 34502 reflections measured (7.09° ≤ 2Θ ≤ 133.2°), 21463 unique (R_{int} = 0.0482, R_{sigma} = 0.0866) which were used in all calculations. The final R_1 was 0.0697 (I > 2σ(I)) and wR_2 was 0.1943 (all data) for 1487 refined parameters with 58 restraints. CCDC 1955821.

$[NC_5H_4\{CWAuCl(CO)_2(Tp^*)\}\text{-}2]$ (8). To a flask containing **3** (50 mg, 0.080 mmol) and $[AuCl(SMe_2)]$ (24 mg, 0.081 mmol) was added CH_2Cl_2 (4 mL) and the solution was stirred at RT for 5 min. After this time, the mixture was filtered through a pad of diatomaceous earth (washed with CH_2Cl_2), the filtrate collected and the volatiles removed under reduced pressure to give an orange-red solid of pure **8** (61 mg, 0.071 mmol, 89%). IR (CH_2Cl_2, cm^{-1}): 2016s, 1933s ν_{CO}. ^1H NMR (700 MHz, $CDCl_3$, 25 °C): δ_H = 2.37 (s, 3H, pzCH_3), 2.41 (s, 6H, pzCH_3), 2.46 (s, 6H, pzCH_3), 2.61 (s, 3H, pzCH_3), 5.95 (s, 1H, pzC*H*), 5.96 (s, 2H, pzC*H*), 7.22 (dd, $^3J_{HH}$ = 6.9, 5.6, 1H, *Py-5*), 7.72 (t', $^3J_{HH}$ = 7.7, 1H, *Py-4*), 7.90 (d, $^3J_{HH}$ = 7.9, 1H, *Py-3*), 8.72 (d, $^3J_{HH}$ = 4.0, 1H, *Py-6*). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$, 25 °C): δ_C = 12.8, 13.2, 16.1, 17.6 (pzCH_3), 107.8, 108.3 (pz*C*H), 122.6 (br, *Py-3*), 123.6 (*Py-5*), 136.2 (br, *Py-4*), 145.8, 146.2 (pz*C*CH_3), 150.5 (*Py-6)*, 152.4, 153.7 (pz*C*CH_3), 164.2 (br, W≡C*C*), 216.3 (*C*O, $^1J_{CW}$ = 155), 262.1 (br, W≡*C*). MS (ESI, *m/z*): Found: 860.1184. Calcd for $C_{23}H_{26}Au{}^{11}B{}^{35}ClN_7O_2{}^{184}W$ $[M+H]^+$: 860.1181. Anal. Found: C, 30.68; H, 2.78; N, 10.37. Calcd for $C_{23}H_{26}AuBClN_7O_2W{\cdot}CH_2Cl_2$: C, 30.52; H, 2.99; N, 10.38%. A crystal suitable for structure determination was grown by slow evaporation of a CH_2Cl_2/ethanol mixture at 4 °C. *Crystal data for* $C_{23}H_{26}AuBClN_7O_2W$ (*M* = 859.58 $g.mol^{-1}$): orthorhombic, space group *Pna*2$_1$ (no. 33), *a* = 15.8904(3), *b* = 9.6054(2), *c* = 17.1964(3) Å, *V* = 2624.75(9) $Å^3$, *Z* = 4, *T* = 150.0(1) K, μ(CuKα) = 19.565 mm^{-1}, *Dcalc* = 2.175 $g.cm^{-3}$, 5099 reflections measured (10.288° ≤ 2Θ ≤ 142.034°), 3333 unique (R_{int} = 0.0356, R_{sigma} = 0.0456) which were used in all calculations. The final R_1 was 0.0383 (I > 2σ(I)) and wR_2 was 0.0984 (all data) for 332 refined parameters with 1 restraint. CCDC 1955822.

$[NC_5H_3\{CWAuCl(CO)_2(Tp^*)\}_2\text{-}2,6]$ (9). To a flask containing **4** (50 mg, 0.043 mmol) and $[AuCl(SMe_2)]$ (26 mg, 0.088 mmol) was added CH_2Cl_2 (4 mL) and the solution was stirred at RT for 5 min. After this time, the mixture was filtered through a pad of diatomaceous earth (washed with CH_2Cl_2), the filtrate collected and the volatiles removed under reduced pressure to give an orange-red solid of pure **8** (59 mg, 0.036 mmol, 84%). IR (CH_2Cl_2, cm^{-1}): 2015s, 1942s, 1927sh ν_{CO}. ^1H NMR (700 MHz, $CDCl_3$, 25 °C): δ_H = 2.37 (s, 6H, pzCH_3), 2.41 (s, 12H, pzCH_3), 2.48 (s, 12H, pzCH_3), 2.59 (s, 6H, pzCH_3), 5.92 (s, 2H, pzC*H*), 5.96 (s, 4H, pzC*H*), 7.81 (t, $^3J_{HH}$ = 7.9, 1H, *Py-4*), 7.90 (d, $^3J_{HH}$ = 7.9, 2H, *Py-3,5*). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$, 25 °C): δ_C = 12.8, 13.2, 16.4, 17.7 (pzCH_3), 107.9, 108.2 (pz*C*H), 123.2 (*Py-3,5*), 136.9 (*Py-4*), 145.7, 146.2, 152.6, 154.0 (pz*C*CH_3), 164.9 (W≡C*C*, $^1J_{CW}$ = 30), 215.7 (*C*O, $^1J_{CW}$ = 154), 260.8 (W≡*C*, $^1J_{CW}$ = 95). MS (ESI, *m/z*): Found: 1662.1689. Calcd for $C_{41}H_{47}Au_2{}^{11}B_2Cl_2N_{13}O_4{}^{184}W_2Na$ $[M+Na]^+$: 1662.1685. Anal. Found: C, 29.93; H, 2.89; N, 11.03. Calcd for $C_{41}H_{47}Au_2B_2Cl_2N_{13}O_4W_2$: C, 30.03; H, 2.90; N, 11.10%. A crystal suitable for structure determination was grown by slow evaporation of a dichloromethane and acetonitrile mixture at 4 °C and proved to be an acetonitrile solvate. *Crystal data for* $C_{43}H_{50}Au_2B_2Cl_2N_{14}O_4W_2$ (*M* = 1681.12 $g.mol^{-1}$): monoclinic, space group *P*2$_1$/c (no. 14), *a* = 12.7628(2), *b* = 40.5530(5), *c* = 11.33830(10) Å, *β* = 91.8980(10)°, *V* = 5865.14(13) $Å^3$, *Z* = 4, *T* = 150.0(1) K, μ(CuKα) = 17.493 mm^{-1}, *Dcalc* = 1.904 $g.cm^{-3}$, 43996 reflections measured (7.264° ≤ 2Θ ≤ 147.494°), 11741 unique

(R_{int} = 0.0498, R_{sigma} = 0.0428) which were used in all calculations. The final R_1 was 0.0634 (I > 2σ(I)) and wR_2 was 0.1363 (all data) for 637 refined parameters with 0 restraints. CCDC 1955823.

$[Cl_2(C_2H_4)PtNC_5H_4\{C{\equiv}W(CO)_2(Tp^*)\}\text{-}2]$ (10). A solution of **3** (50 mg, 0.080 mmol) and $K[PtCl_3(C_2H_4)]\cdot H_2O$ (31 mg, 0.080 mmol) in CH_2Cl_2 (4 mL) and ethanol (4 mL) was stirred at RT for 15 min. After this time, the mixture CH_2Cl_2 was removed under reduced pressure. The resulting green precipitate was collected by filtration, washed with ethanol (3 x 5 mL) and dried in vacuo to give an emerald green solid of pure **10** (54 mg, 0.059 mmol, 73%). IR (CH_2Cl_2, cm^{-1}): 2005s, 1988s, 1916s, 1897s ν_{CO}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ_H = 2.34 (s, 3H, pzC*H₃*), 2.44 (s, 9H, pzC*H₃*), 2.55 (s, 6H, pzC*H₃*), 4.63 (s, 4H, C_2H_4), 5.77 (s, 1H, pzC*H*), 5.93 (s, 2H, pzC*H*), 7.35 (t', $^3J_{HH}$ = 6.4, 1H, *Py-5*), 7.40 (d, $^3J_{HH}$ = 7.9, 1H, *Py-3*), 7.62 (t', $^3J_{HH}$ = 7.9, 1H, *Py-4*), 8.45 (d, $^3J_{HH}$ = 5.4, 1H, *Py-6*). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 25 °C): δ_C = 12.8, 12.9, 15.3, 17.6 (pzCH_3), 75.9 (C_2H_4), 106.7, 106.9 (pz*C*H), 122.4 (*Py-5*), 130.1 (*Py-3*), 137.8 (*Py-4*), 144.8, 145.6 (pz*C*CH₃), 149.5 (*Py-6)*, 152.3, 153.0 (pz*C*CH₃), 164.2 (W≡*C*C, $^2J_{CW}$ = 47), 226.9 (*C*O, $^1J_{CW}$ = 162), 265.8 (W≡*C*, $^1J_{CW}$ = 205). ^{195}Pt NMR (150 MHz, $CDCl_3$, 25 °C): δ_{Pt} = –2864. MS (ESI, *m/z*): Found: 628.1826. Calcd for $C_{23}H_{26}{}^{11}BN_7O_2{}^{184}W$ $[M–PtCl_2(C_2H_4)+H]^+$: 628.1823. Crystals suitable for structure determination were grown by slow evaporation of a CH_2Cl_2/ethanol mixture at 4 ˚C. *Crystal data for* $C_{25}H_{30}BCl_2N_7O_2PtW$ (*M* = 921.21 g.mol^{-1}): monoclinic, space group $P2_1/n$ (no. 14), a = 10.6485(4), b = 21.1039(9), c = 13.1797(5) Å, β = 91.758(4)°, V = 2960.4(2) Å^3, Z = 4, T = 150.0(1) K, μ(MoKα) = 8.819 mm^{-1}, $Dcalc$ = 2.067 g.cm^{-3}, 15169 reflections measured (6.944° ≤ 2Θ ≤ 57.928°), 6356 unique (R_{int} = 0.0320, R_{sigma} = 0.0484) which were used in all calculations. The final R_1 was 0.0416 (I > 2σ(I)) and wR_2 was 0.0892 (all data) for 362 refined parameters with 0 restraints. CCDC 1955824.

Selected X-ray structural data

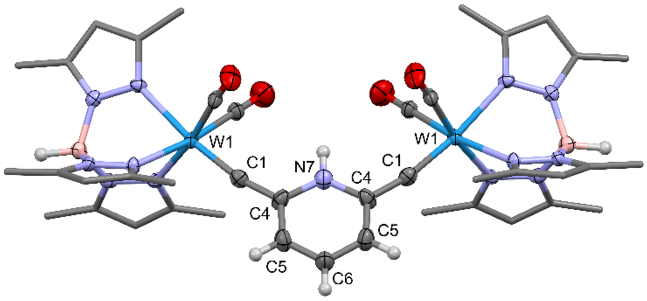

Figure S1. Molecular structure of the cation of [**5**]BF_4 in a crystal of **5**·$2CHCl_3\cdot H_2O$ showing 50% thermal probability ellipsoids. Only one-half of the molecule is crystallographically unique. Pyrazolyl groups are simplified for clarity. Selected distances [Å] and angles [°]: W1–C1 1.843(7), C1–C4 1.398(10), W1–C1–C4 168.9(6).

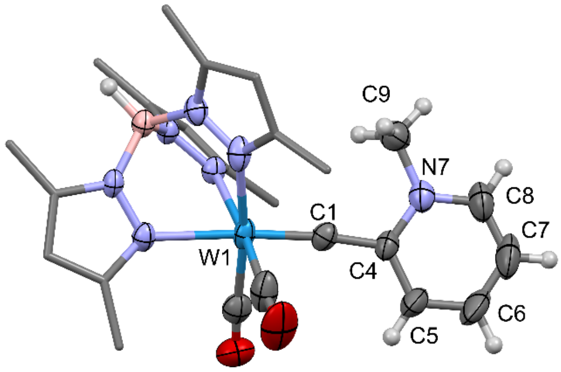

Figure S2. Molecular structure of the cation of [**6**]O_3SCF_3 showing 50% thermal probability ellipsoids. Pyrazolyl groups are simplified for clarity. Selected distances [Å] and angles [°]: W1–C1 1.820(3), C1–C4 1.425(4), C4–C5 1.400(5), C5–C6 1.379(6), C6–C7 1.371(7), C7–C8 1.346(7), C8–N7 1.347(5), N7–C4 1.365(4), N7–C9 1.472(5), W1–C1–C4 173.9(3).

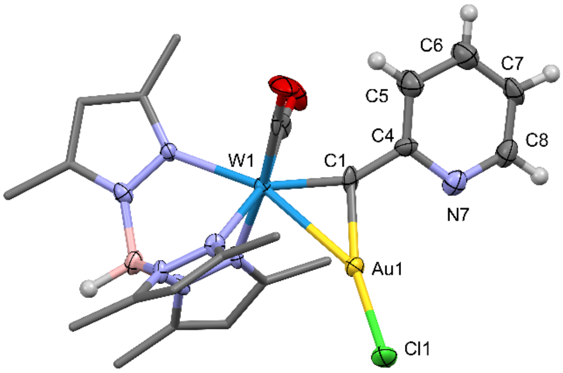

Figure S3. Molecular structure of **8** showing 50% thermal probability ellipsoids. Pyrazolyl groups are simplified for clarity. Selected distances [Å] and angles [°]: W1–C1 1.929(15), C1–C4 1.44(2), W1–Au1 2.7635(8), C1–Au1 2.046(16), Au1–Cl1 2.285(3), W1–C1–C4 151.9(12).

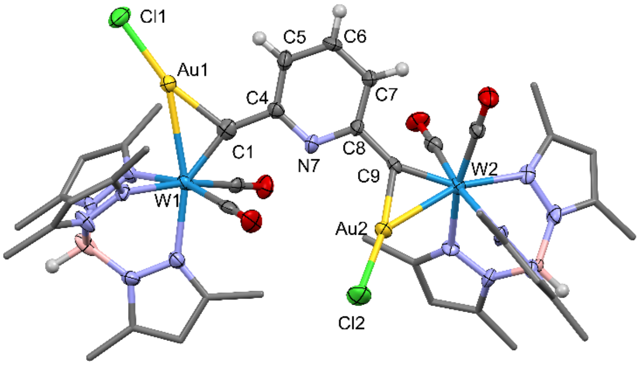

Figure S4. Molecular structure of **9** in a crystal of **9**·CH_3CN showing 50% thermal probability ellipsoids. Pyrazolyl groups are simplified for clarity. Selected distances [Å] and angles [°]: W1–C1 1.894(13), C1–C4 1.463(16), W1–Au1 2.8007(7), C1–Au1 2.046(13), Au1–Cl1 2.283(3), W2–C9 1.922(11), C9–C8 1.468(15), W2–Au2 2.7769(7), C9–Au2 2.015(10), W1–C1–C4 149.0(10), W2–C9–C8 149.2(8).

Notes and references

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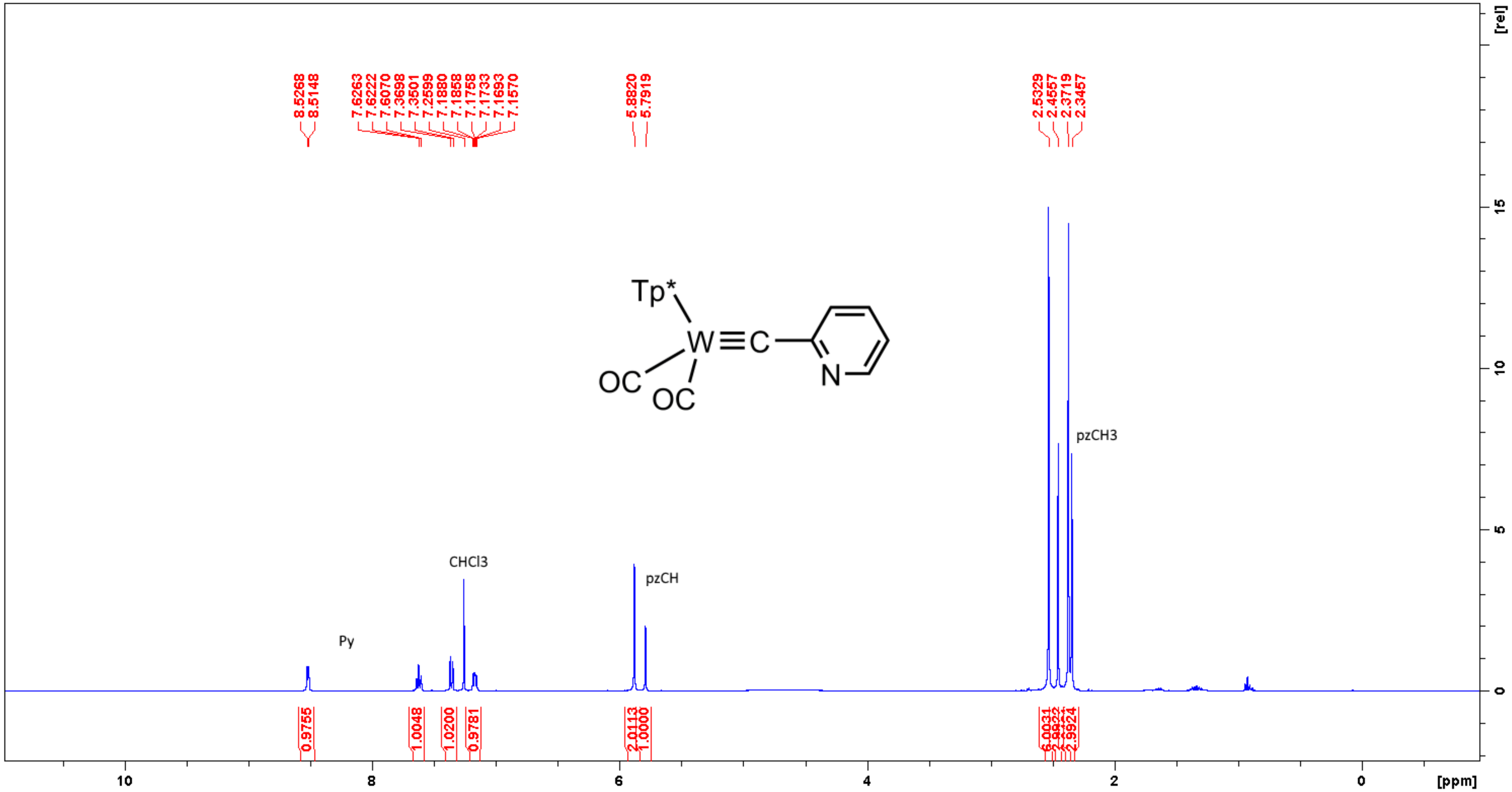
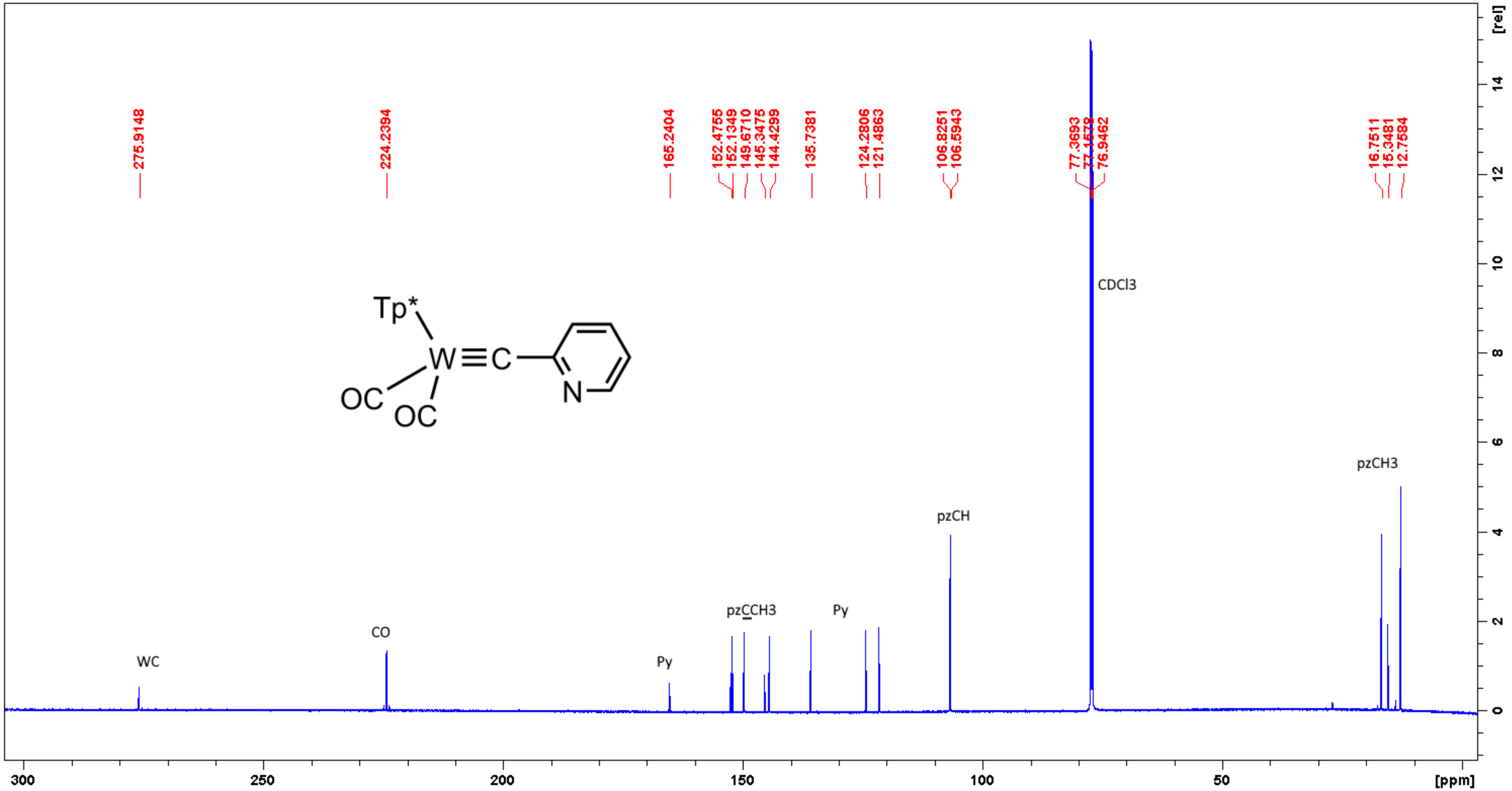
Chemical Communications

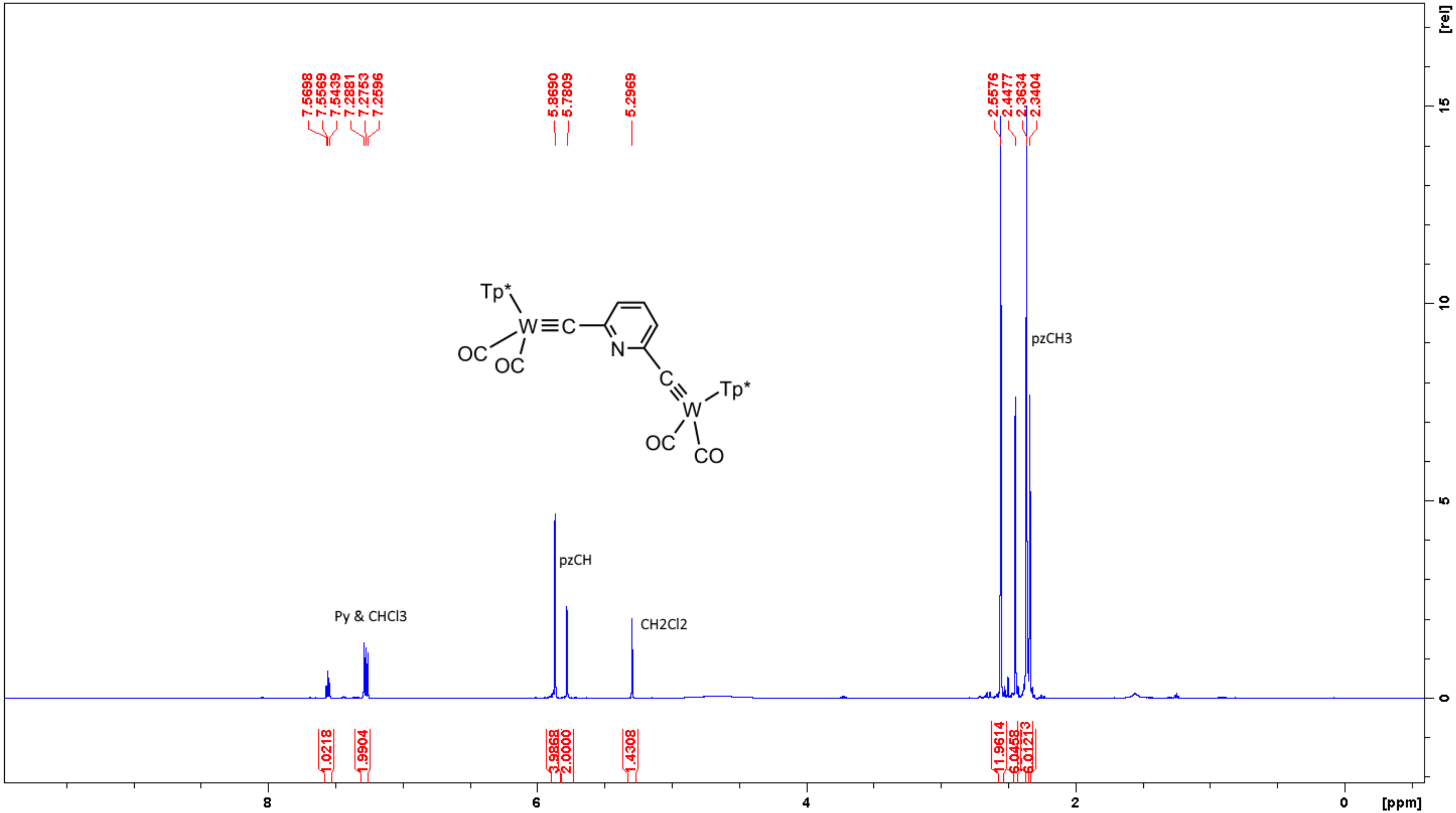
SUPPORTING INFORMATION



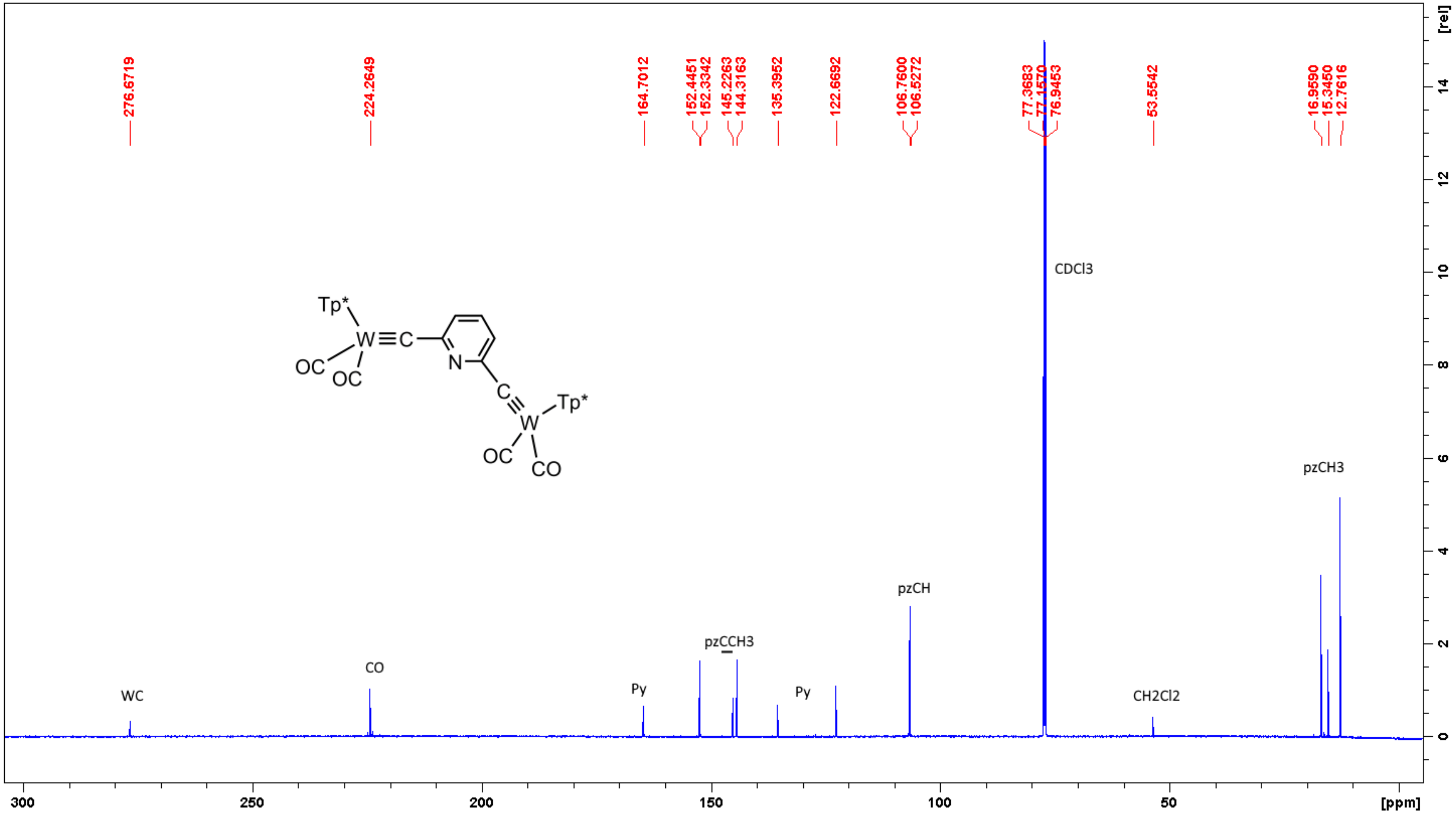
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of [W(≡C{2-Py})(CO)$_2$(Tp*)] (**2**).



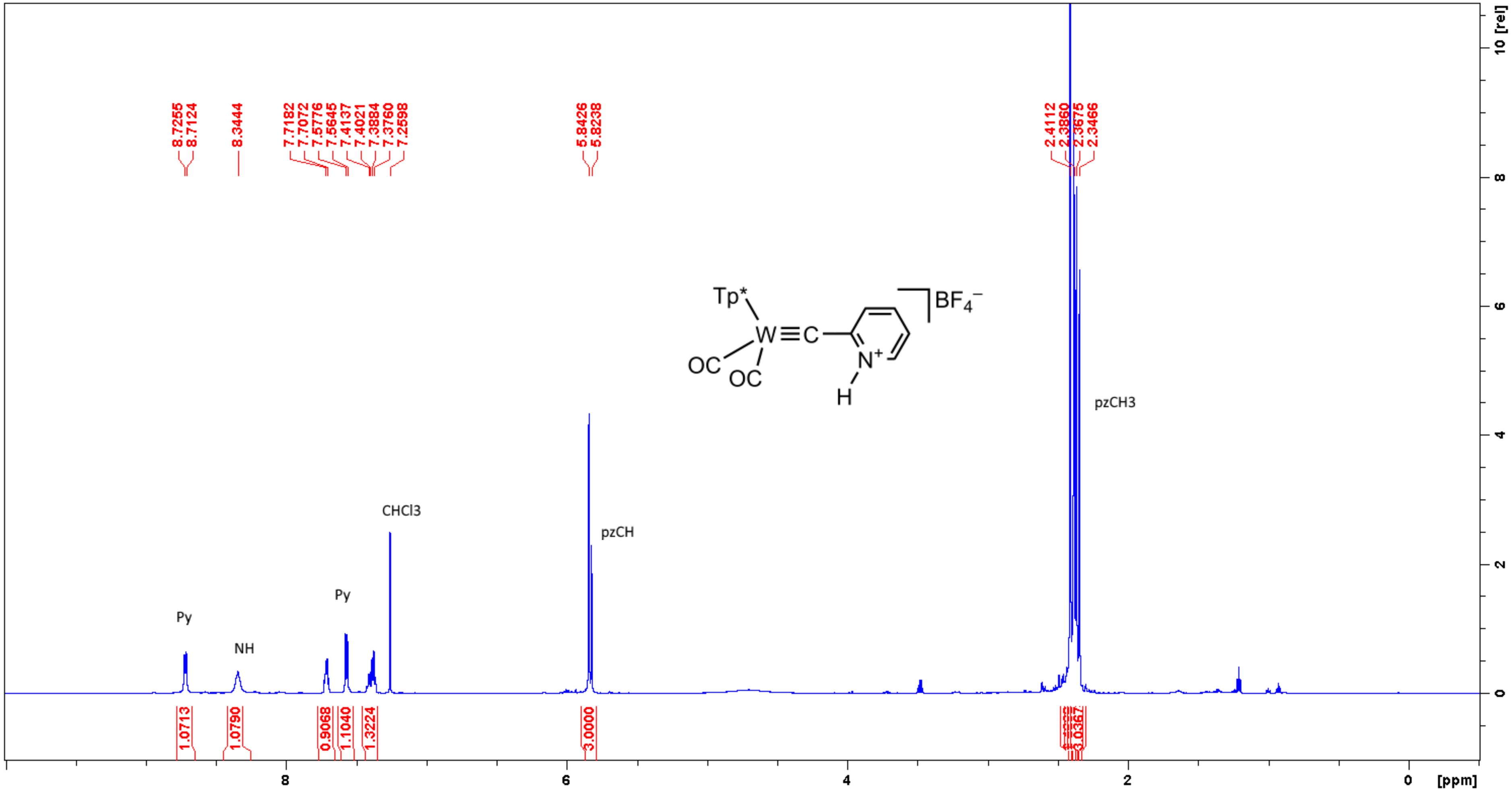
^{13}C{^{1}H} NMR spectrum (101 MHz, CDCl$_3$, 25 °C) of [W(≡C{2-Py})(CO)$_2$(Tp*)] (**2**).



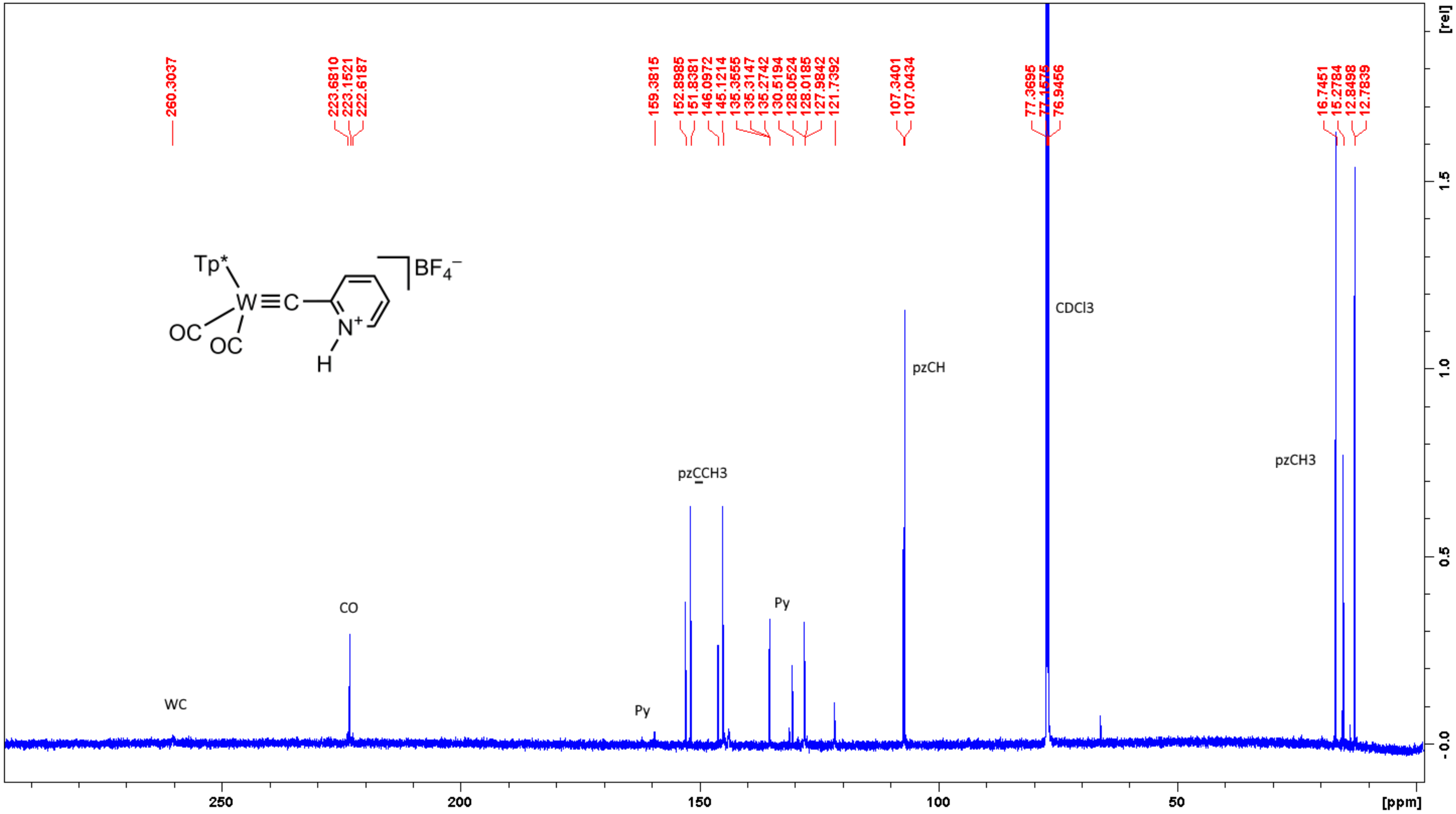
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of [2,6-{(Tp*)$(CO)_2$W≡C}$_2$Py] (**3**).



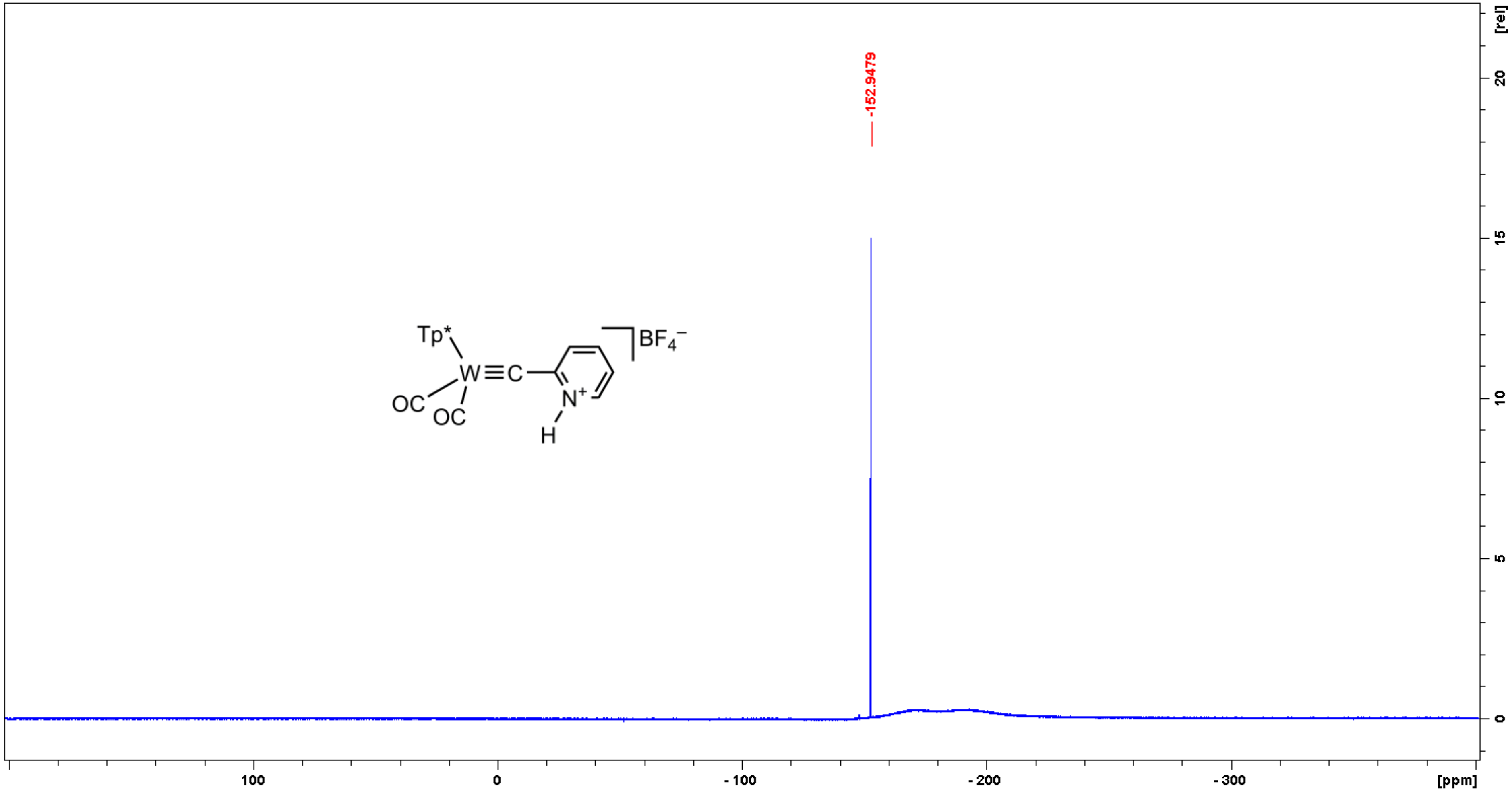
$^{13}C\{^1H\}$ NMR spectrum (101 MHz, $CDCl_3$, 25 °C) of [2,6-{(Tp*)(CO)$_2$W≡C}$_2$Py] (**3**).



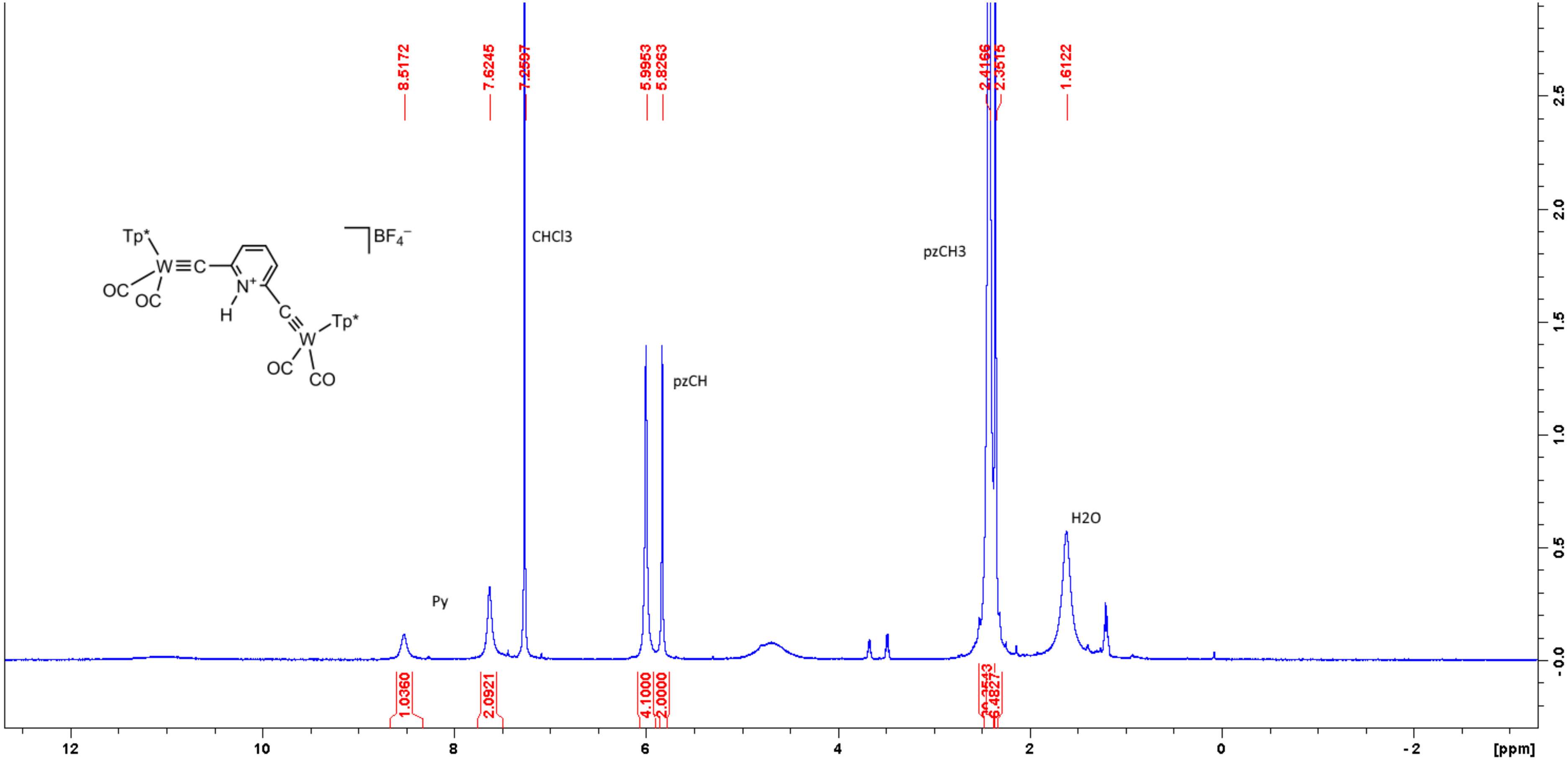
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 25 °C) of [W(≡C{2-PyH})$(CO)_2$(Tp*)]BF_4 (**4**).



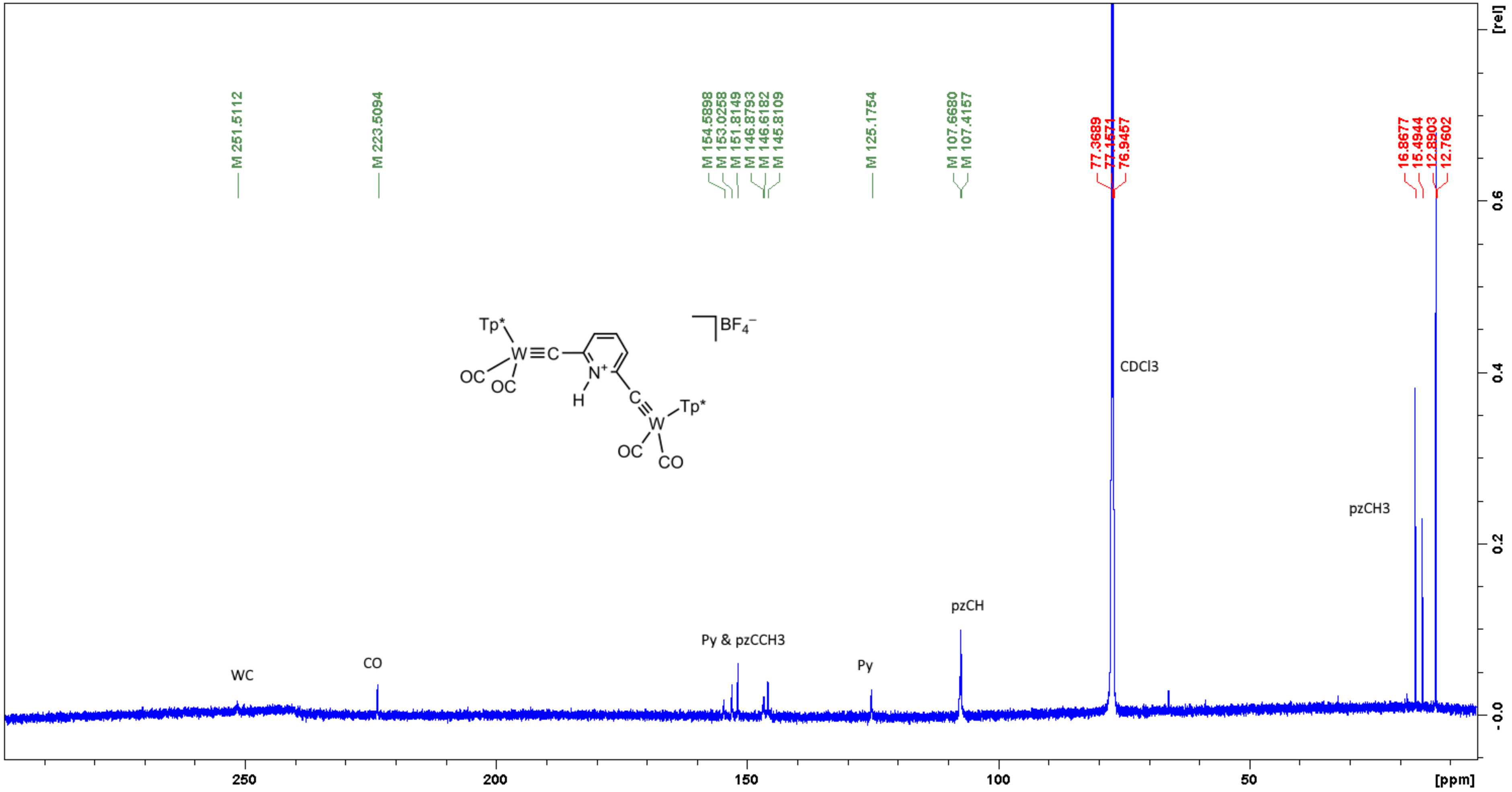
$^{13}C\{^1H\}$ NMR spectrum (151 MHz, $CDCl_3$, 25 °C) of $[W(\equiv C\{2\text{-}PyH\})(CO)_2(Tp^*)]BF_4$ (**4**).



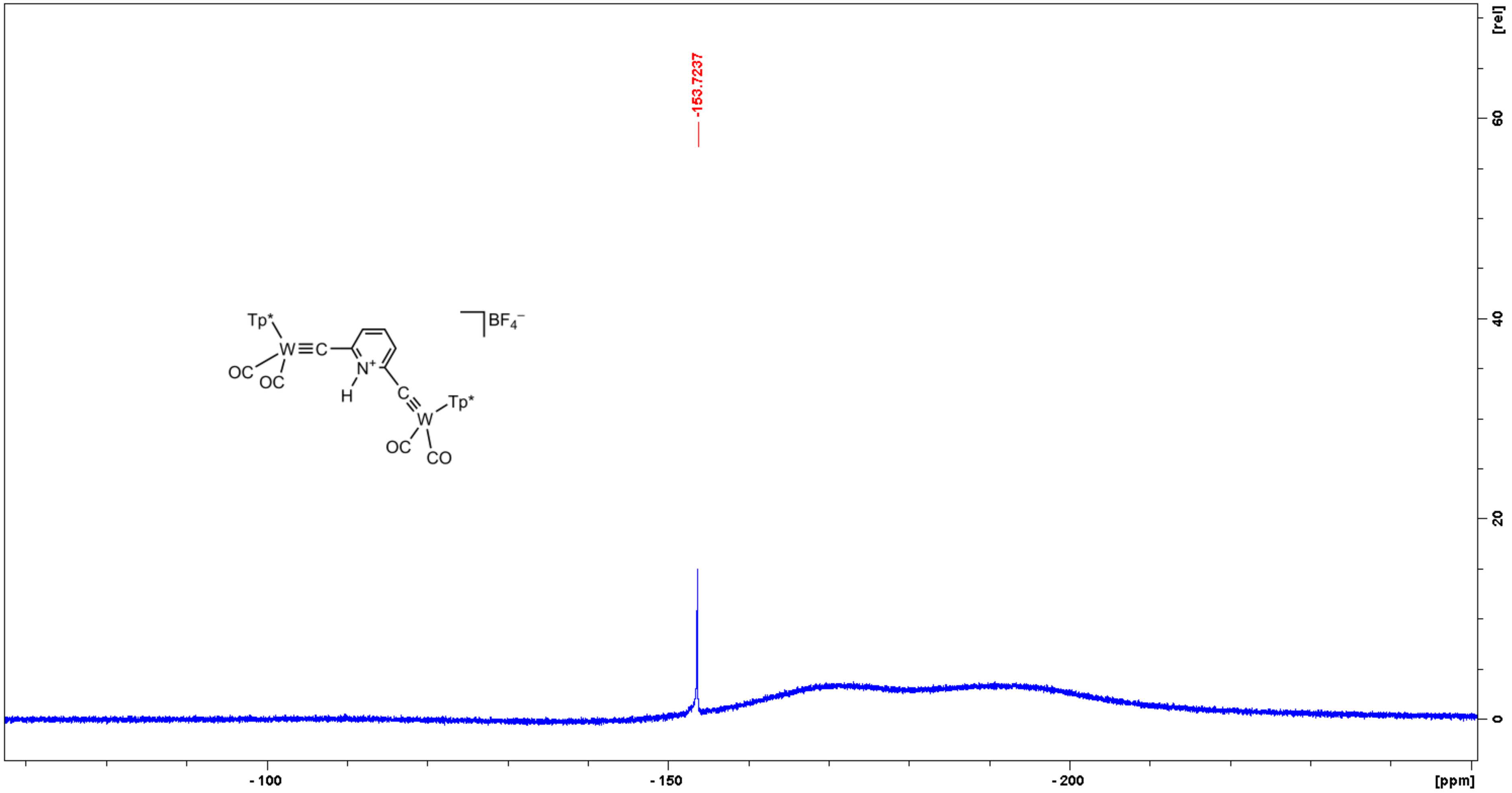
$^{19}F\{^1H\}$ NMR spectrum (376 MHz, $CDCl_3$, 25 °C) of [W(≡C{2-PyH})(CO)$_2$(Tp*)]BF_4 (**4**).



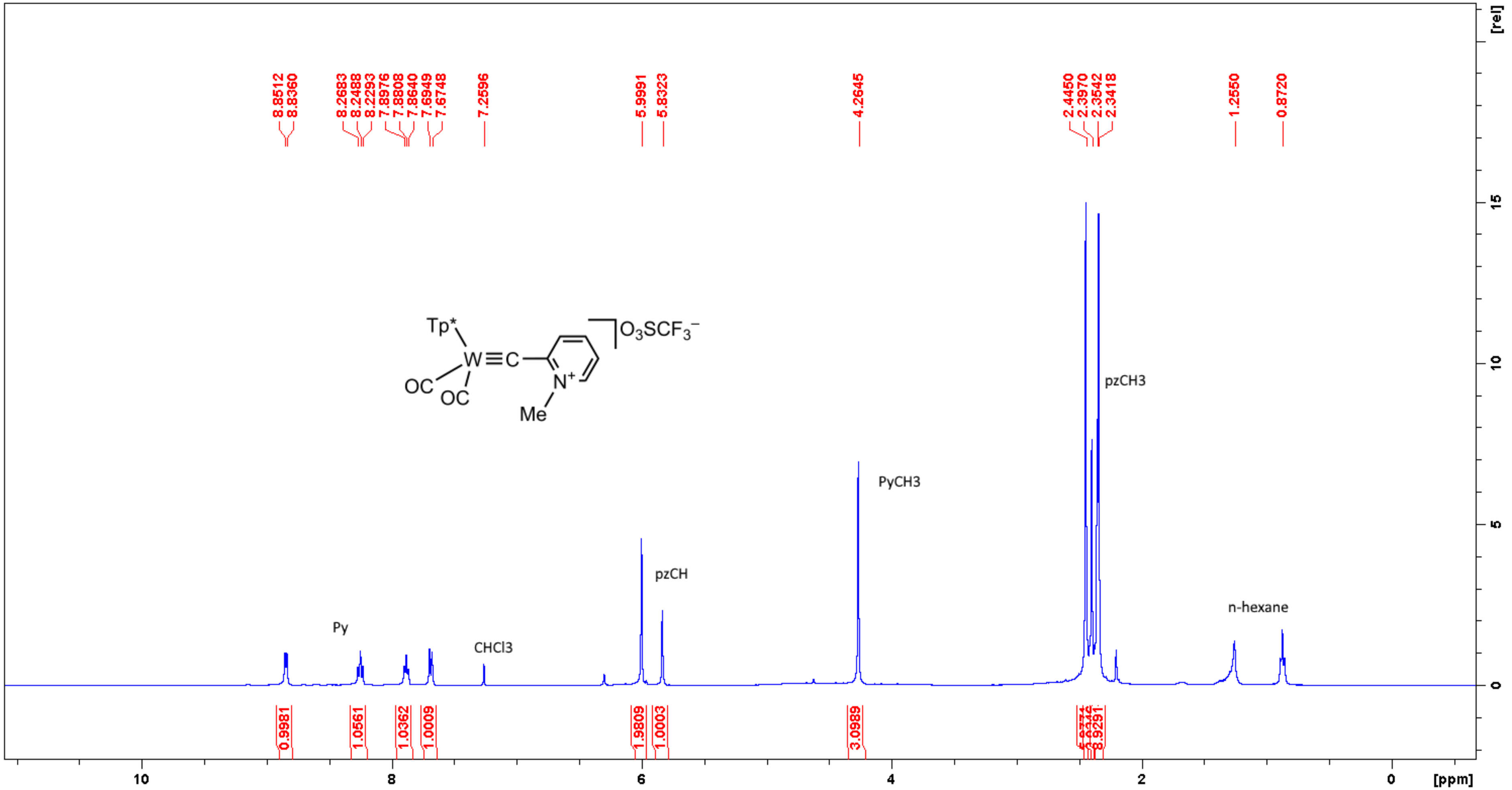
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 25 °C) of [2,6-{(Tp*)$(CO)_2W≡C$}$_2$PyH]BF_4 (**5**).



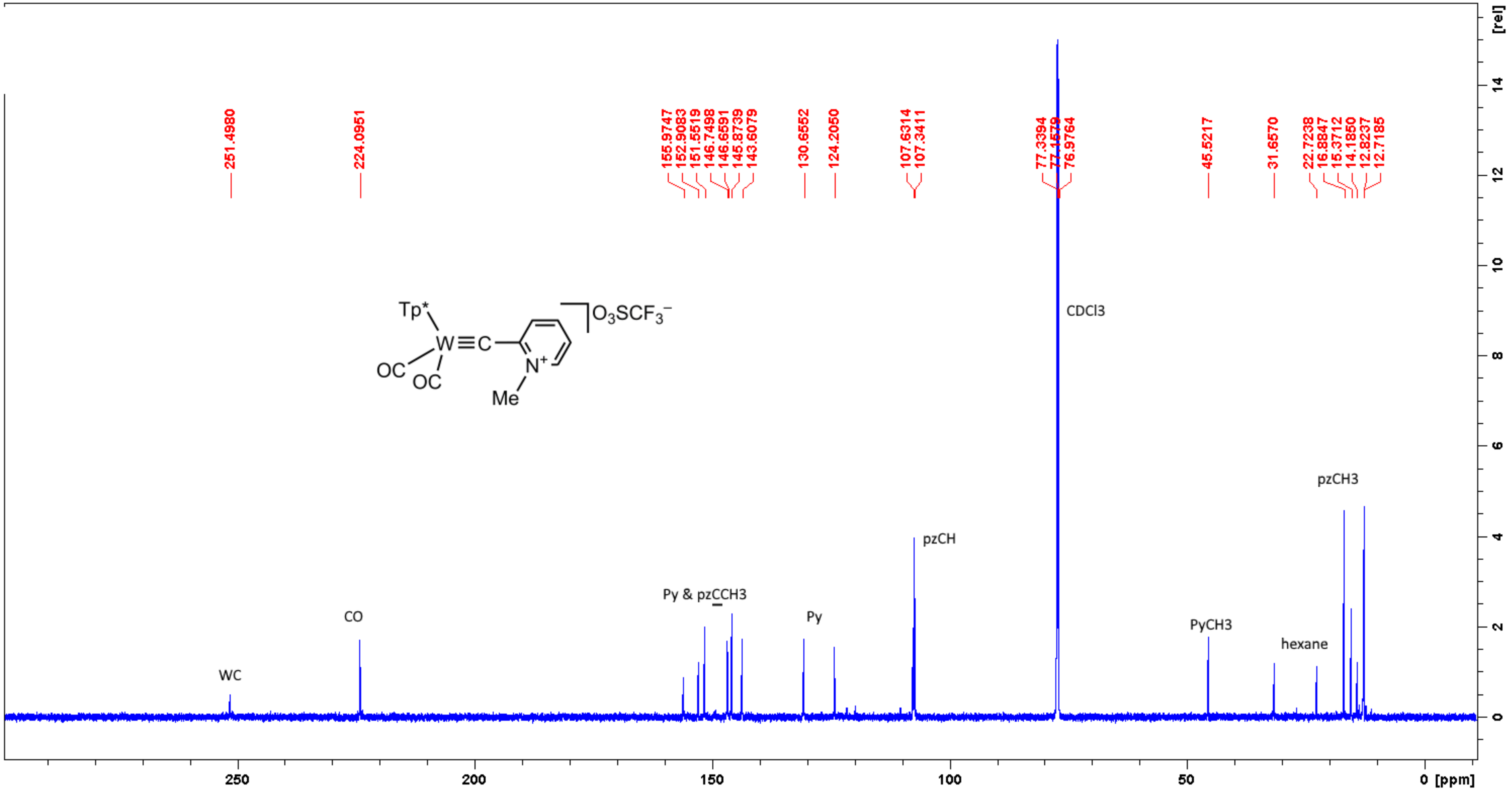
$^{13}C\{^1H\}$ NMR spectrum (151 MHz, $CDCl_3$, 25 °C) of [2,6-{(Tp*)(CO)$_2$W≡C}$_2$PyH]BF_4 (**5**).



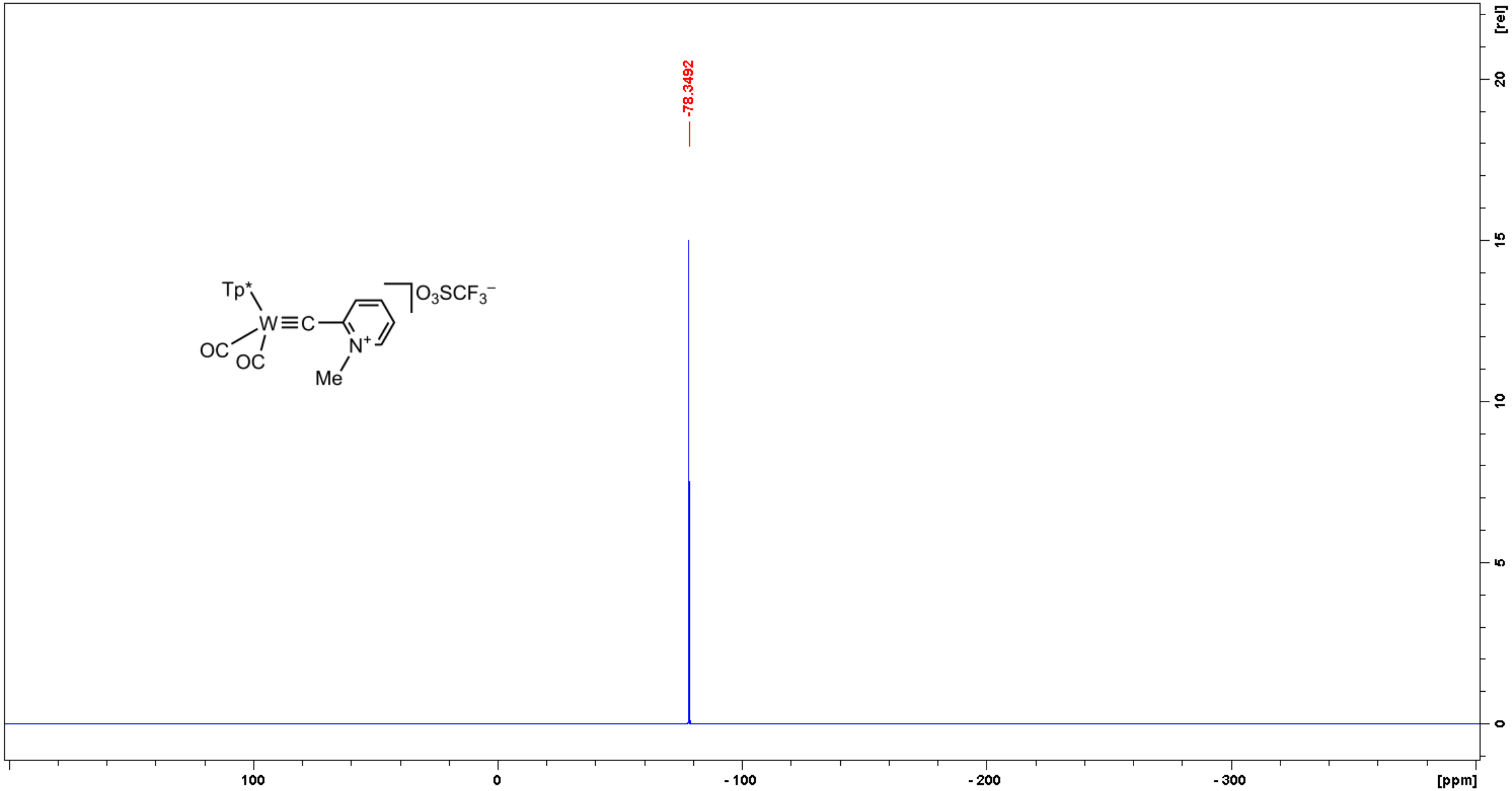
^{19}F{^{1}H} NMR spectrum (376 MHz, $CDCl_3$, 25 °C) of [2,6-{(Tp*)$(CO)_2$W≡C}$_2$PyH]BF_4 (**5**).



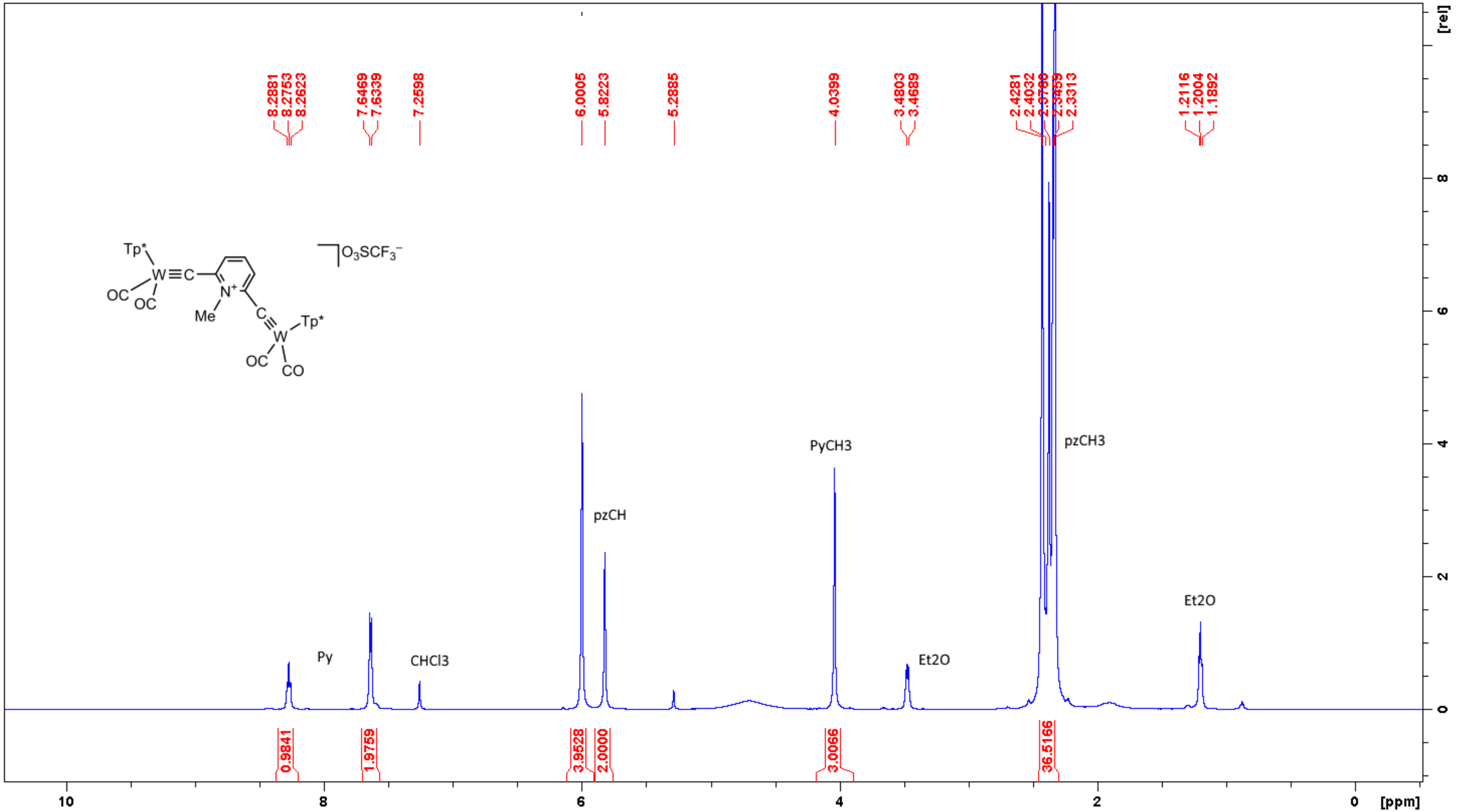
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of [W(≡C{2-PyCH$_3$})(CO)$_2$(Tp*)]O$_3$SCF$_3$ (**6**).



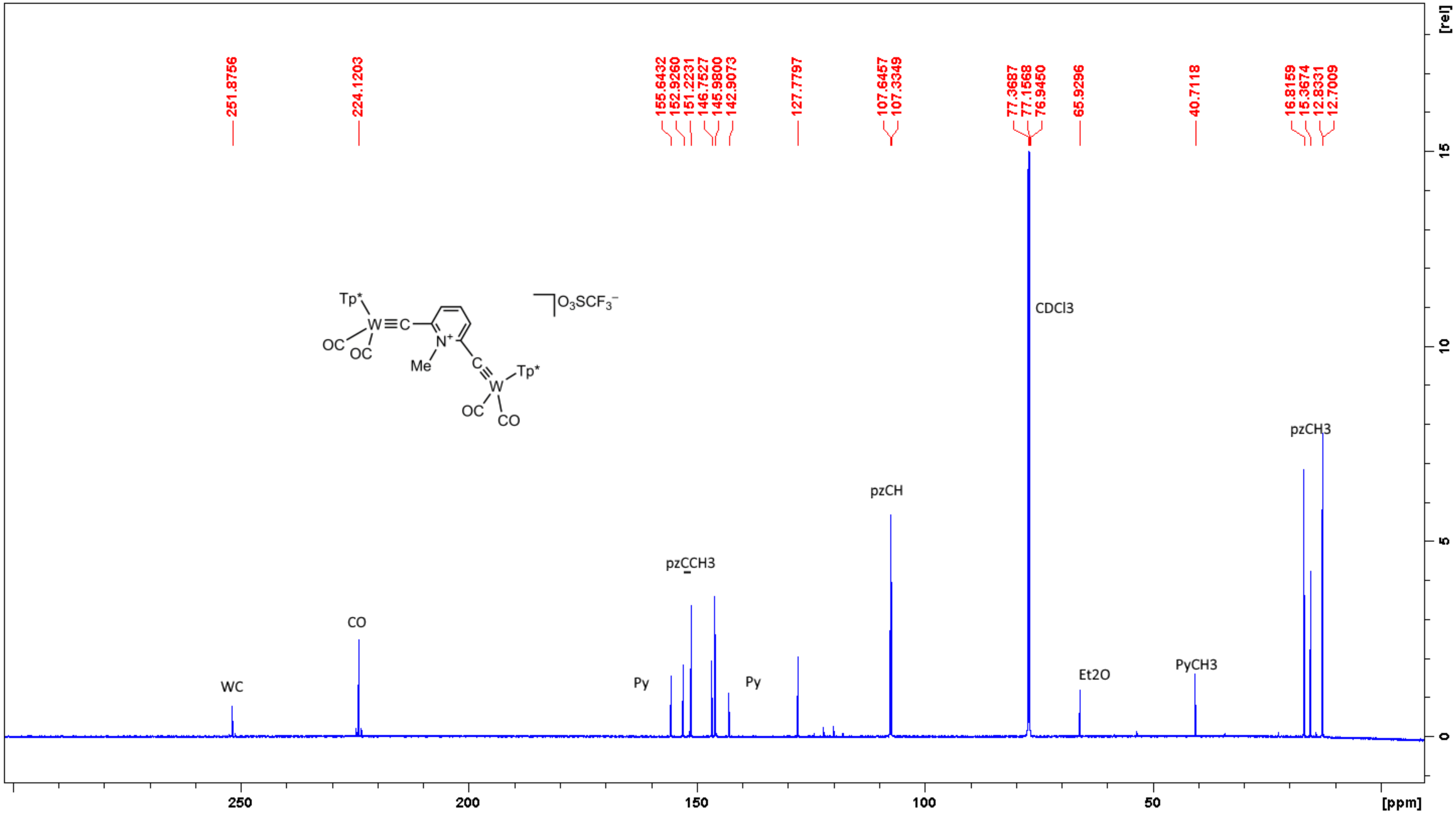
$^{13}C\{^1H\}$ NMR spectrum (101 MHz, $CDCl_3$, 25 °C) of $[W(\equiv C\{2\text{-}PyCH_3\})(CO)_2(Tp^*)]O_3SCF_3$ (**6**).



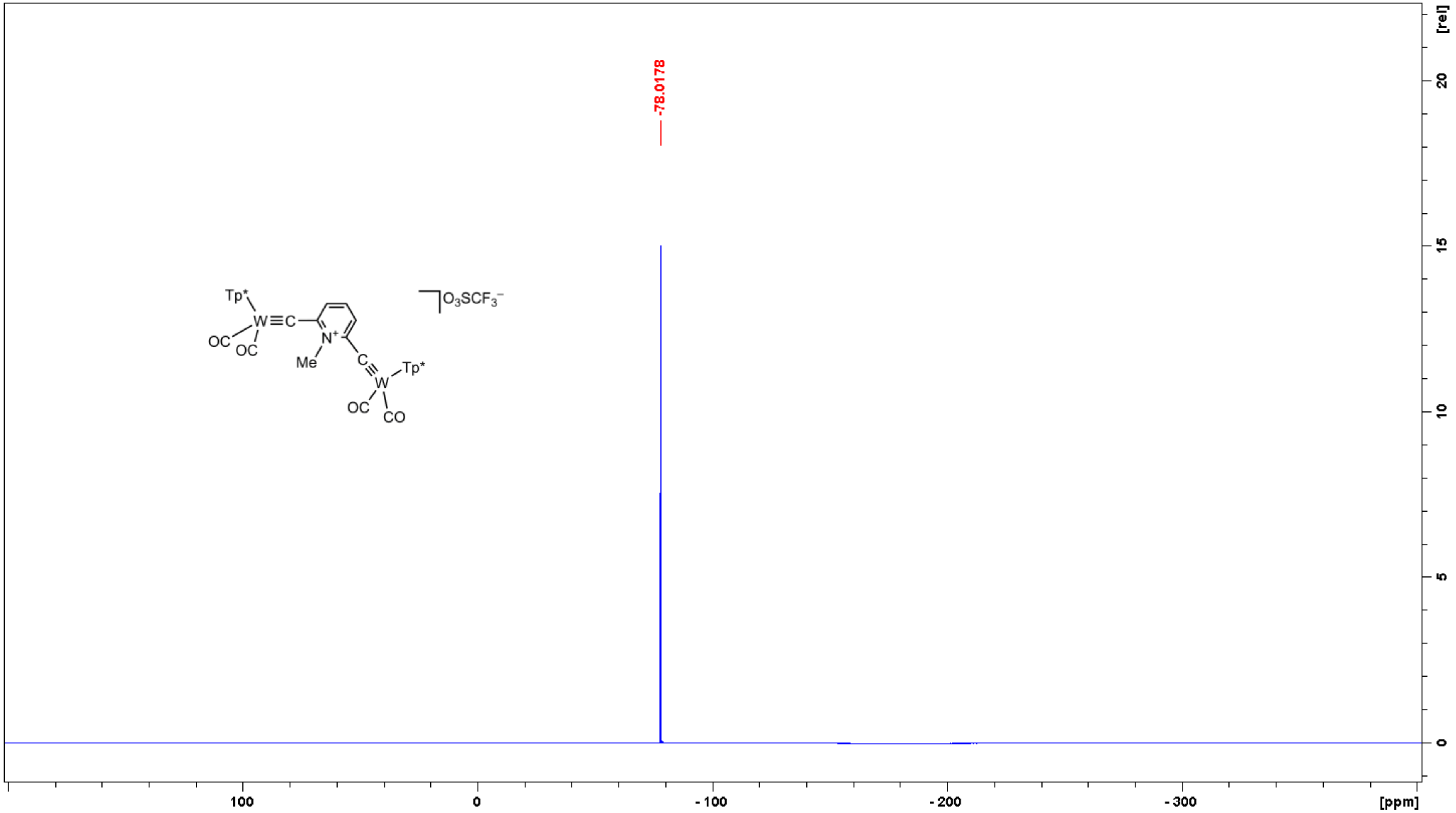
$^{19}F\{^1H\}$ NMR spectrum (376 MHz, $CDCl_3$, 25 °C) of [W(≡C{2-$PyCH_3$})$(CO)_2$(Tp*)]O_3SCF_3 (**6**).



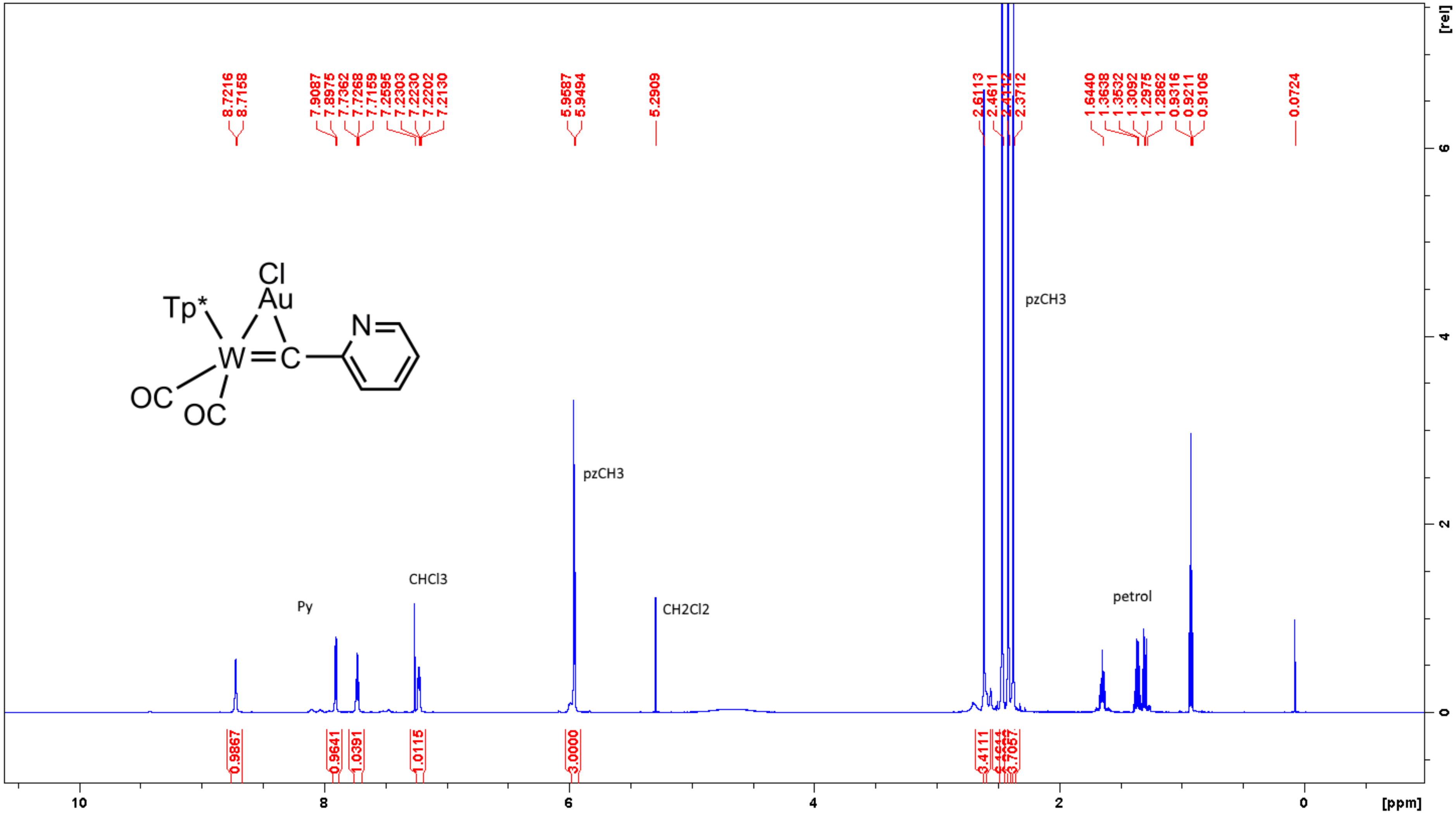
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 25 °C) of $[2,6\text{-}\{(Tp^*)(CO)_2W{\equiv}C\}_2PyCH_3]O_3SCF_3$ (**7**).



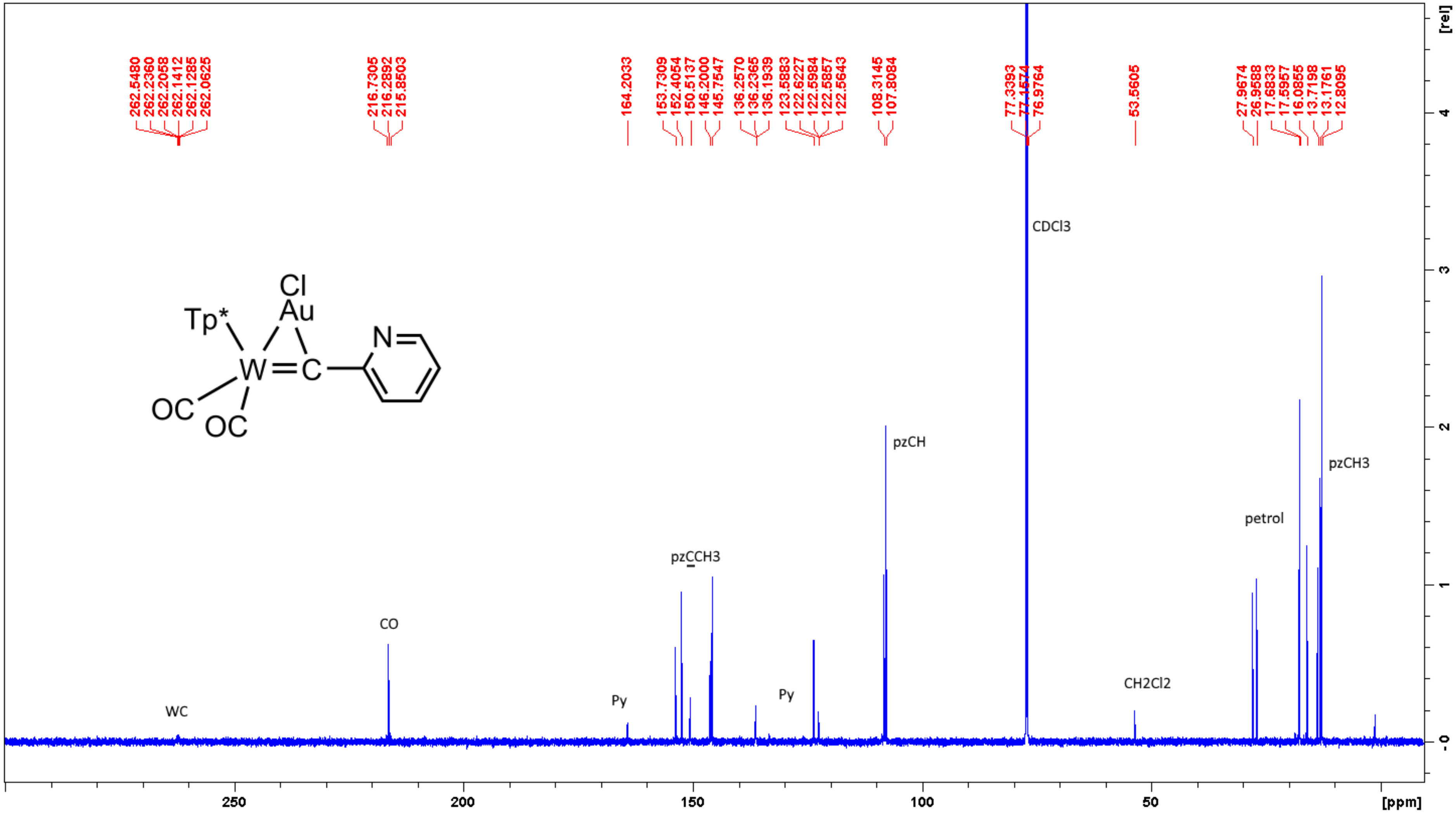
$^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$, 25 °C) of $[2,6\text{-}\{(Tp^*)(CO)_2W{\equiv}C\}_2PyCH_3]O_3SCF_3$ (**7**).



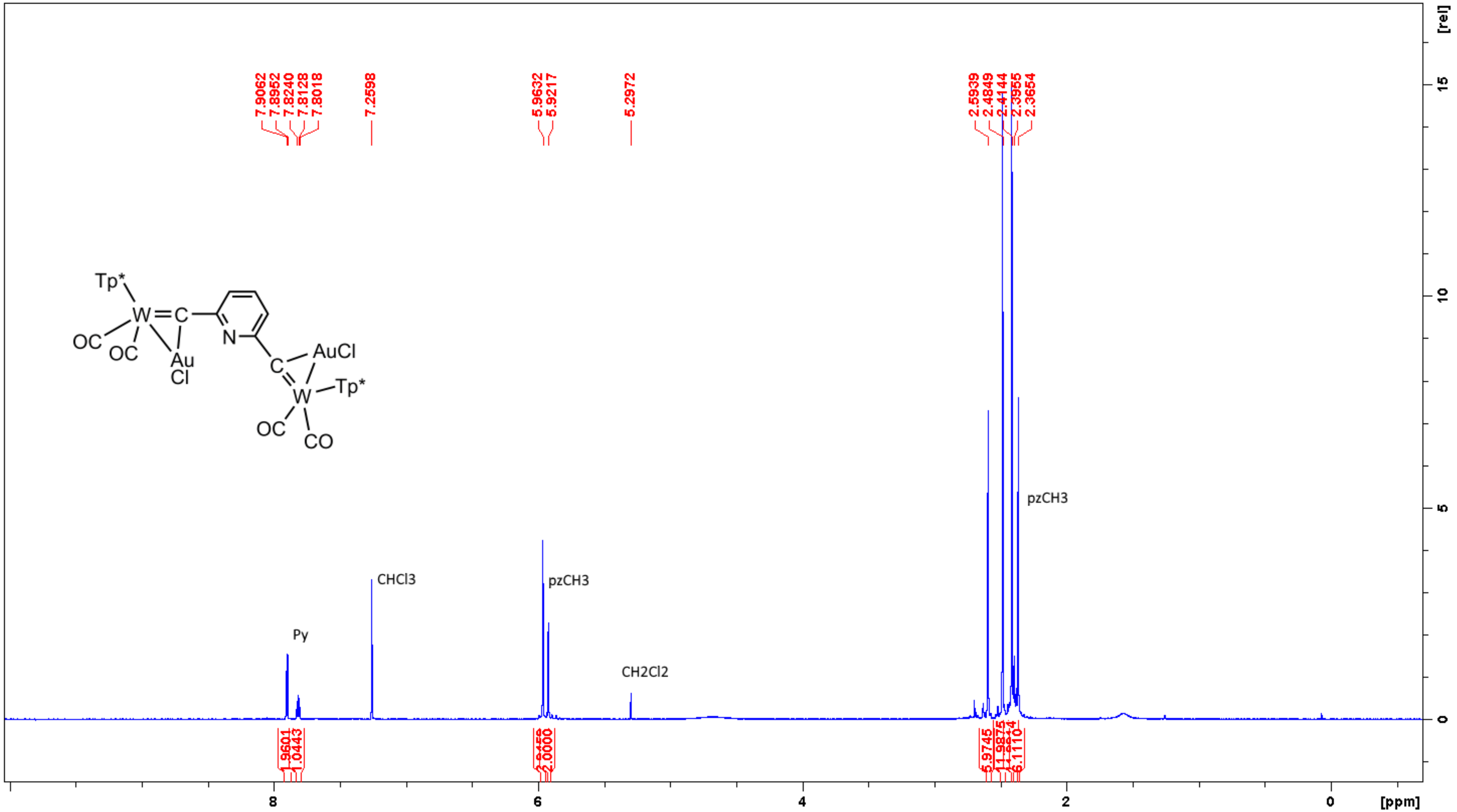
^{19}F{^{1}H} NMR spectrum (376 MHz, $CDCl_3$, 25 °C) of [2,6-{(Tp*)$(CO)_2W{\equiv}C$}$_2PyCH_3$]O_3SCF_3 (**7**).



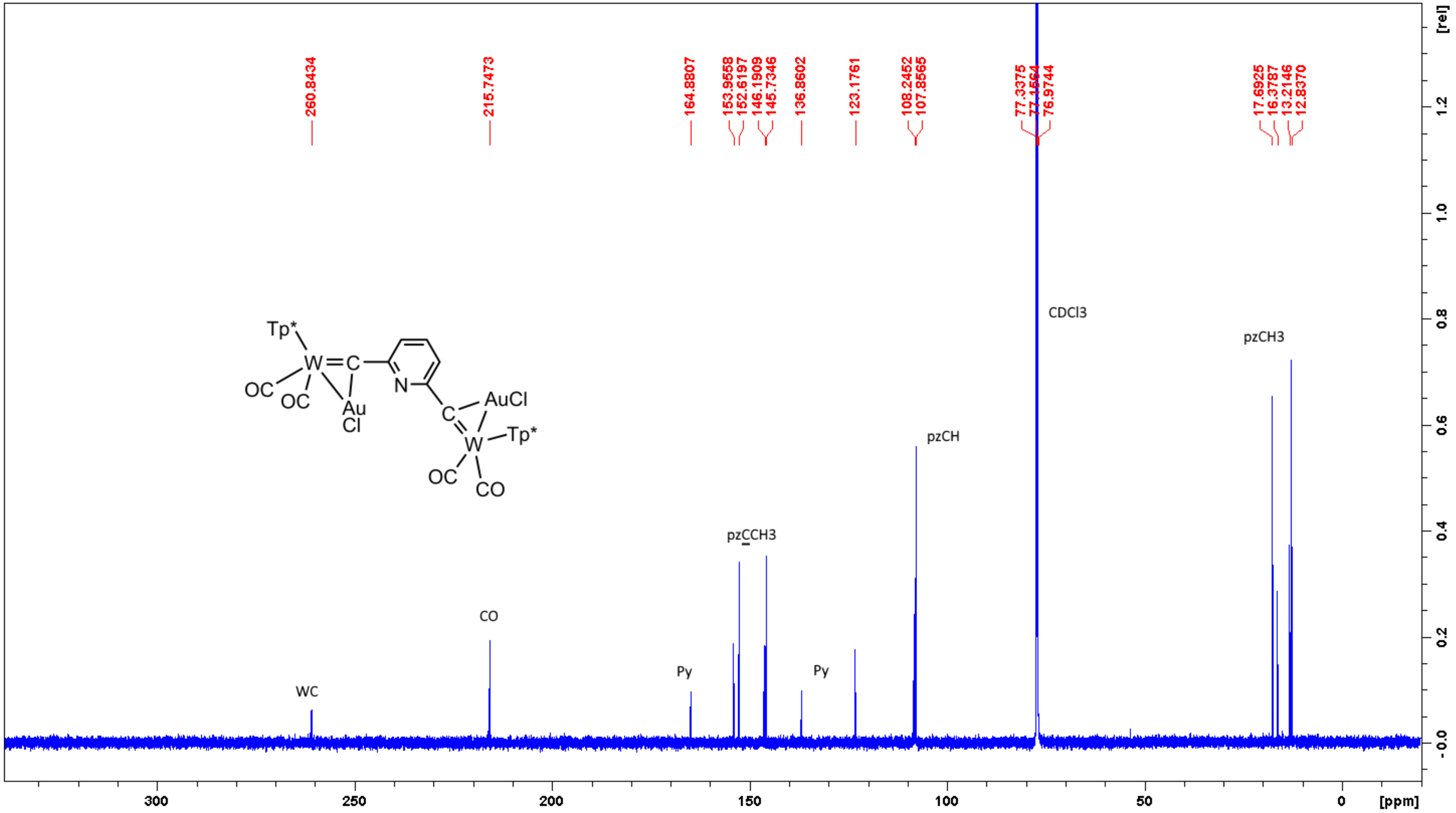
^{1}H NMR spectrum (700 MHz, $CDCl_3$, 25 °C) of [WAu{μ-C(2-Py)}Cl(CO)$_2$(Tp*)] (**8**).



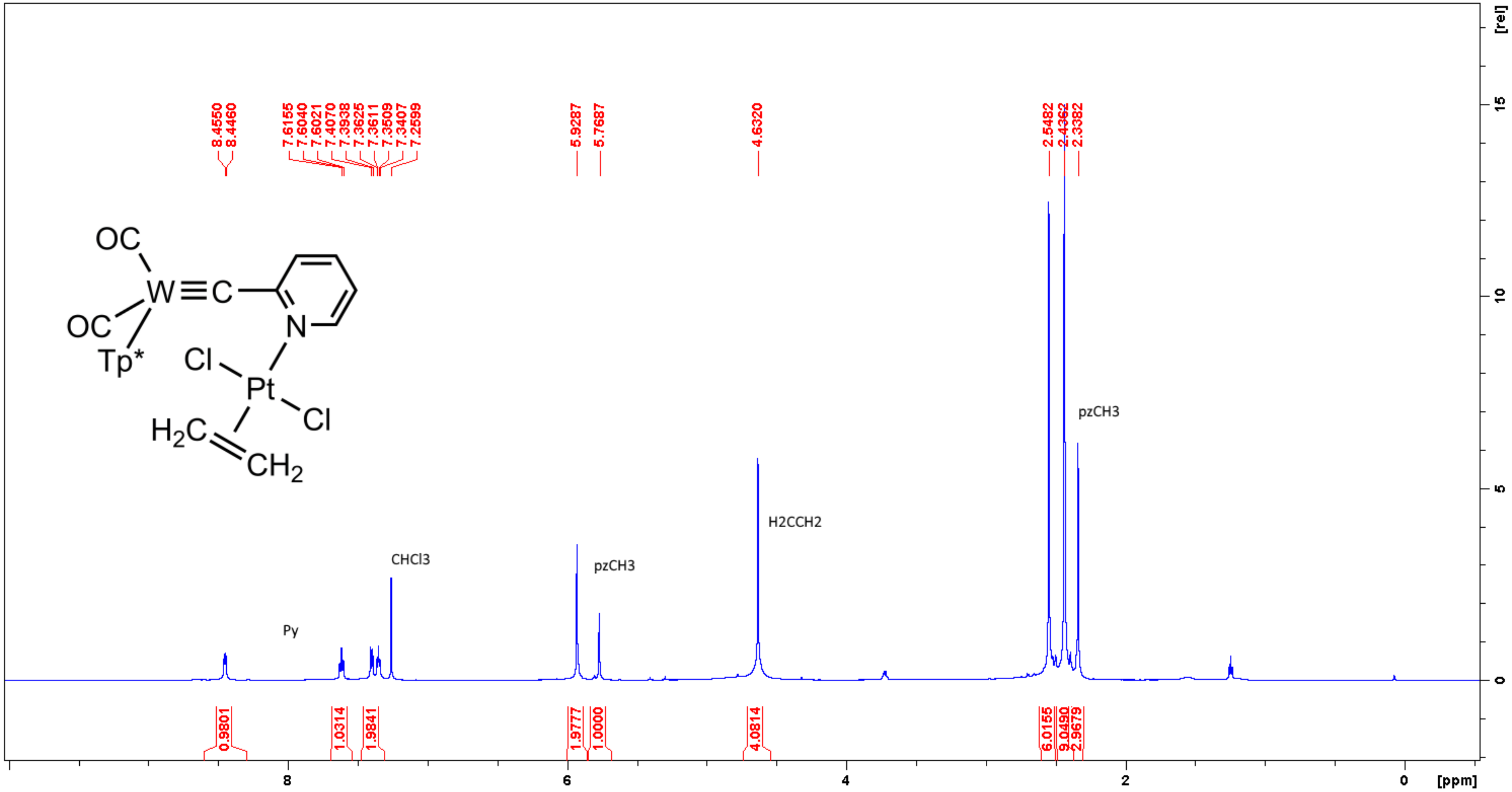
^{13}C{^{1}H} NMR spectrum (176 MHz, CDCl$_3$, 25 °C) of [WAu{μ-C(2-Py)}Cl(CO)$_2$(Tp*)] (**8**).



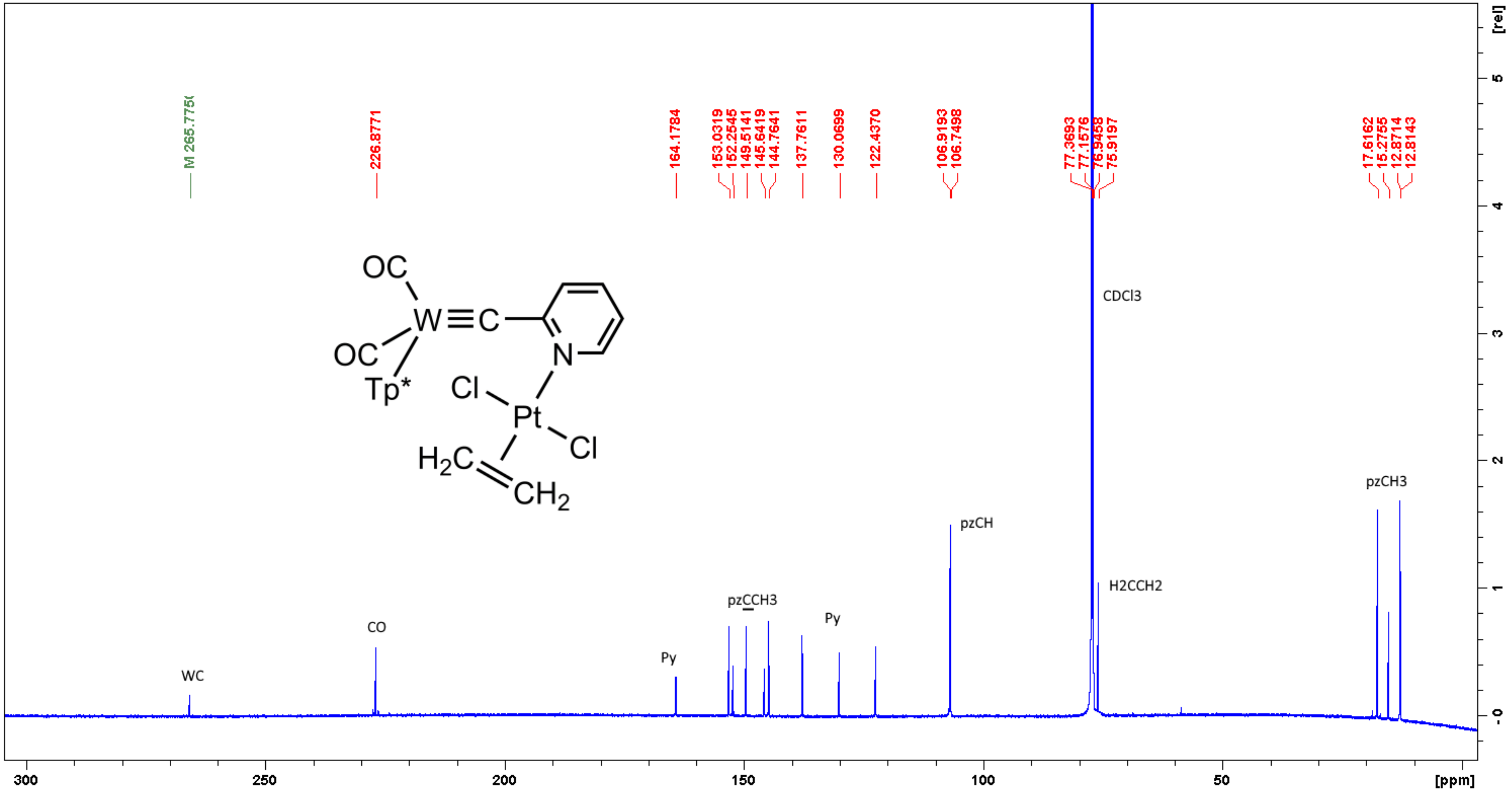
^{1}H NMR spectrum (700 MHz, $CDCl_3$, 25 °C) of [2,6-{(Tp*)$(CO)_2Cl_2WAu_2$(μ-C)}$_2$Py] (**9**).



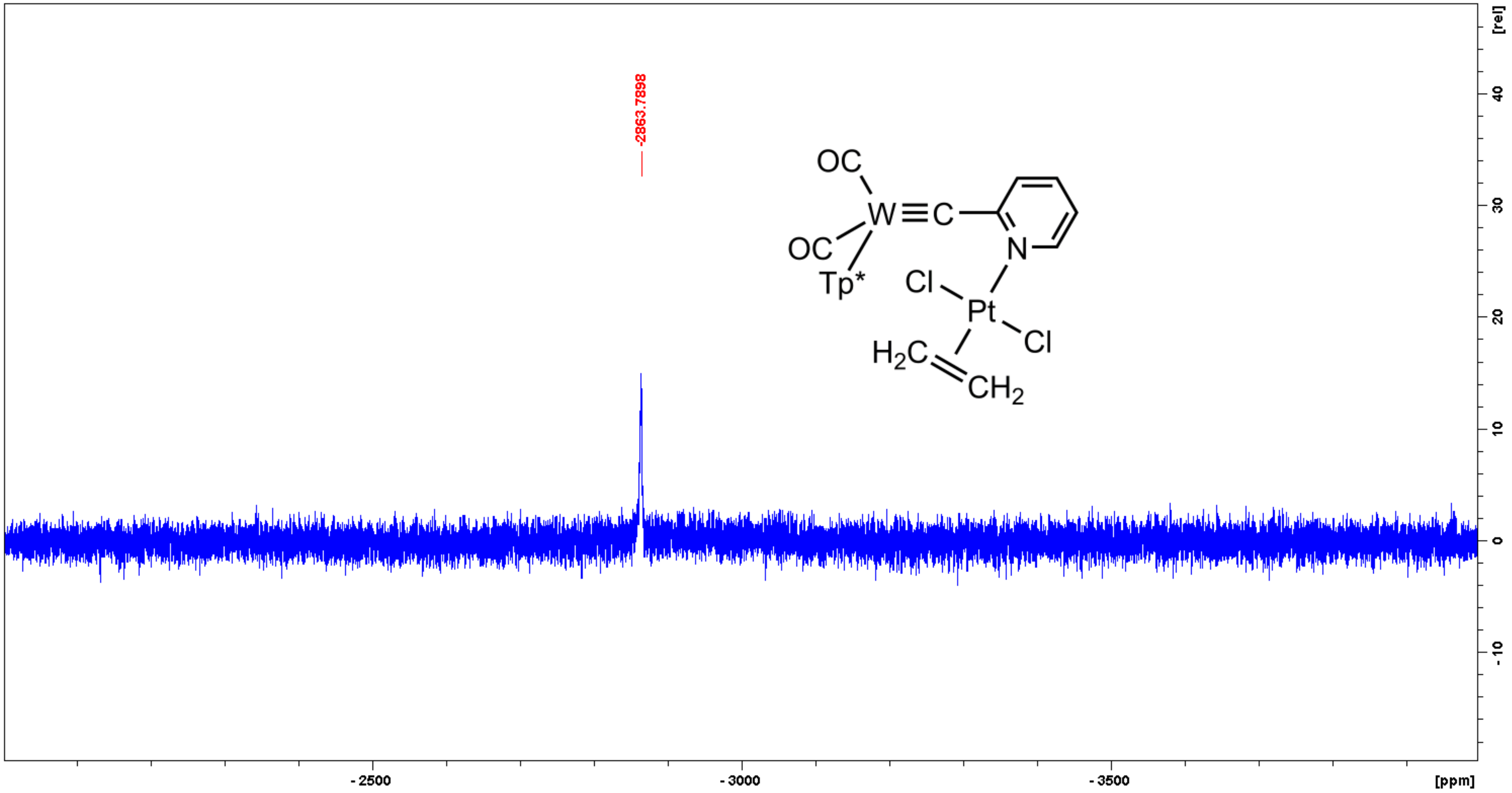
$^{13}C\{^1H\}$ NMR spectrum (176 MHz, $CDCl_3$, 25 °C) of [2,6-{(Tp*)$(CO)_2Cl_2WAu_2$(μ-C)}$_2$Py] (**9**).



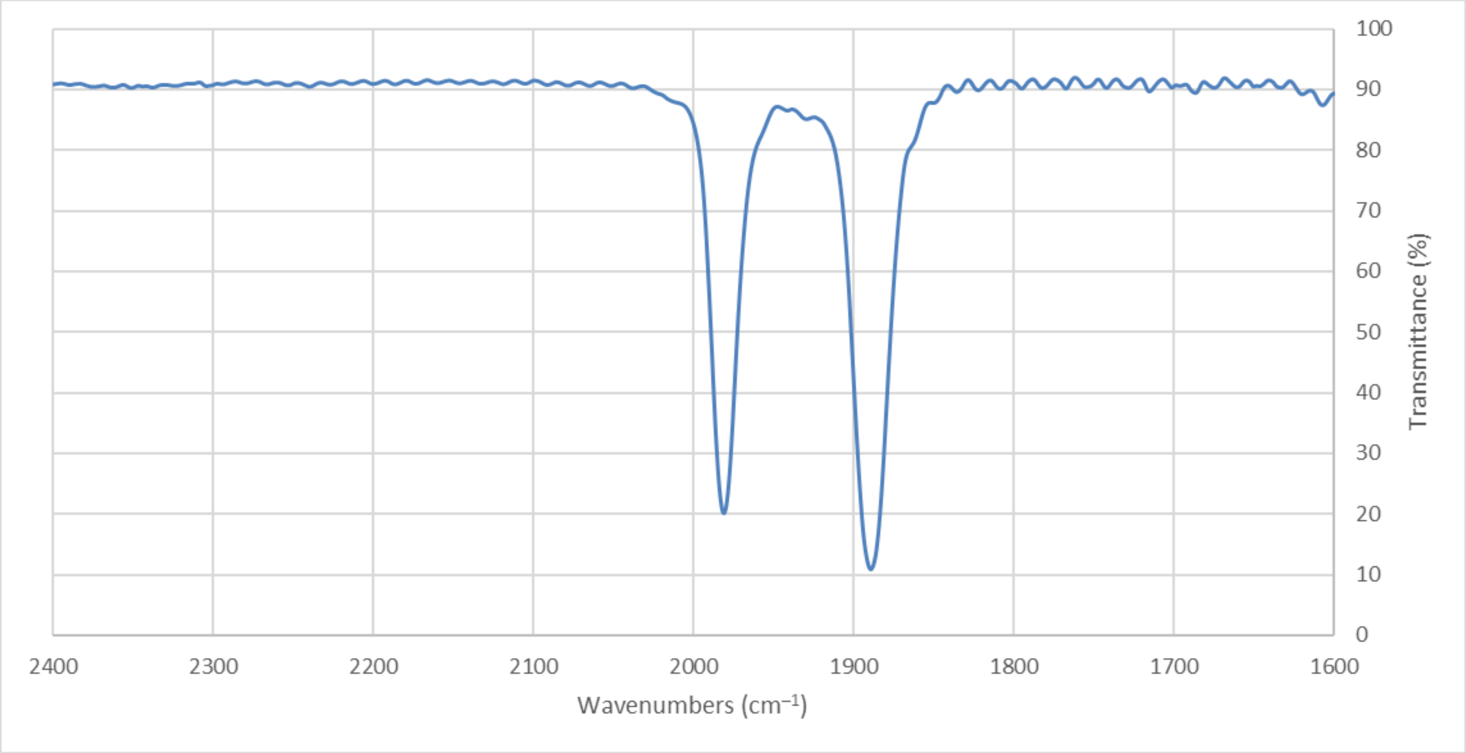
^1H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of [WPt{μ-C(2-Py)}$Cl_2(C_2H_4)(CO)_2$(Tp*)] (**10**).



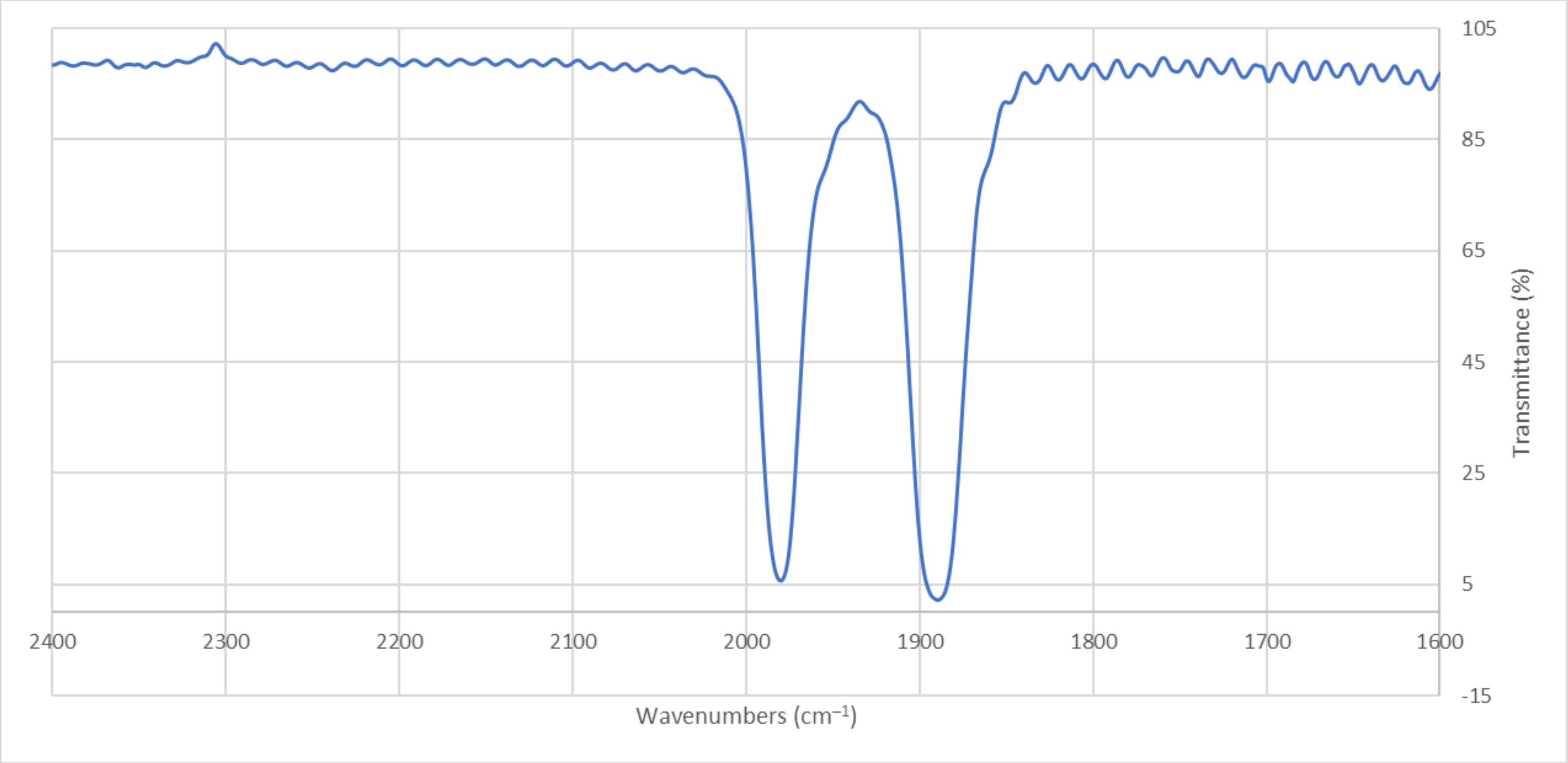
^{13}C{^{1}H} NMR spectrum (151 MHz, CDCl$_3$, 25 °C) of [WPt{μ-C(2-Py)}Cl$_2$(C$_2$H$_4$)(CO)$_2$(Tp*)] (**10**).



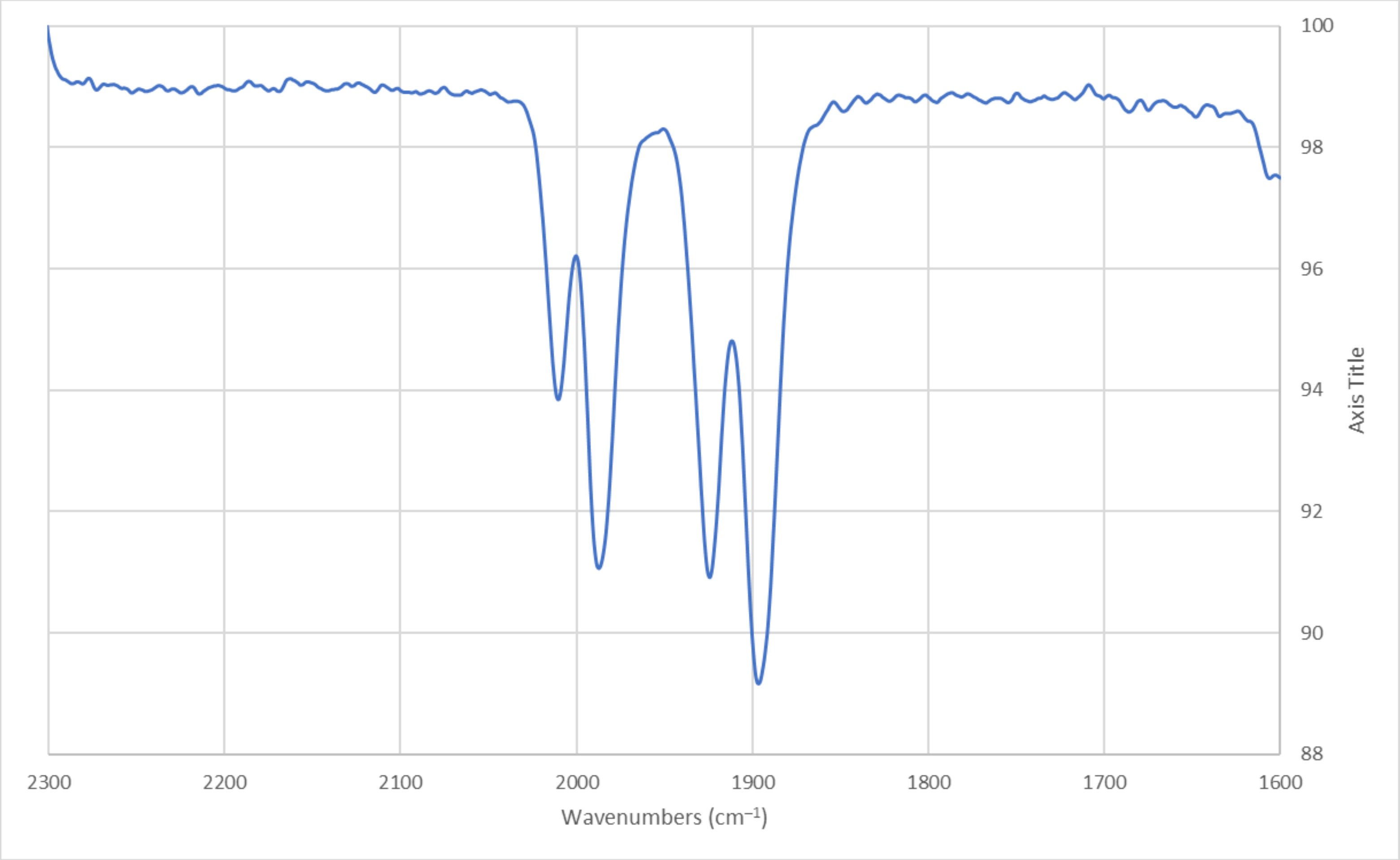
^{195}Pt NMR spectrum (150 MHz, $CDCl_3$, 25 °C) of [WPt{μ-C(2-Py)}$Cl_2(C_2H_4)(CO)_2$(Tp*)] (**10**).



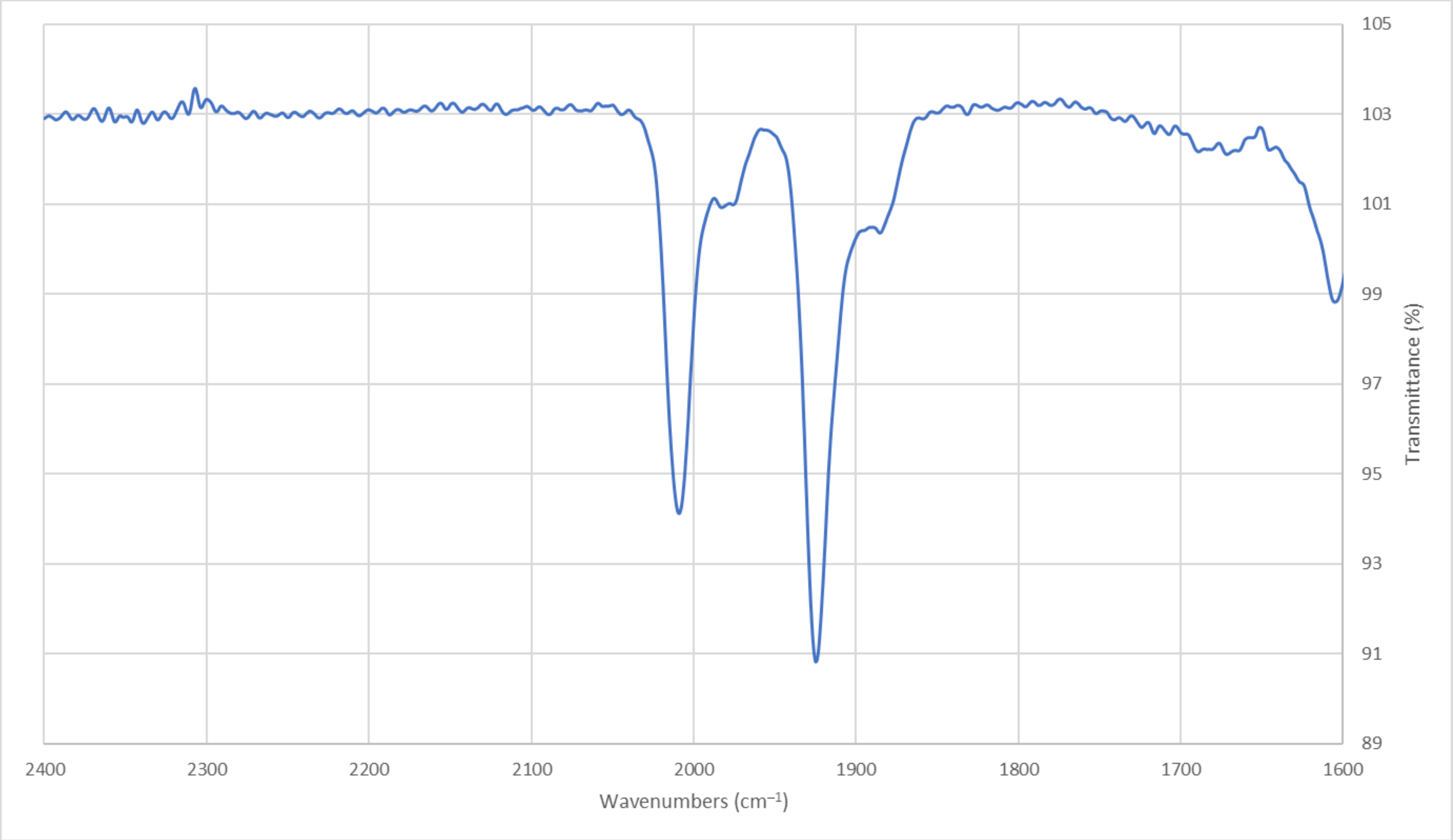
Infrared spectrum of [W(≡C{2-Py})$(CO)_2$(Tp*)] (**2**).



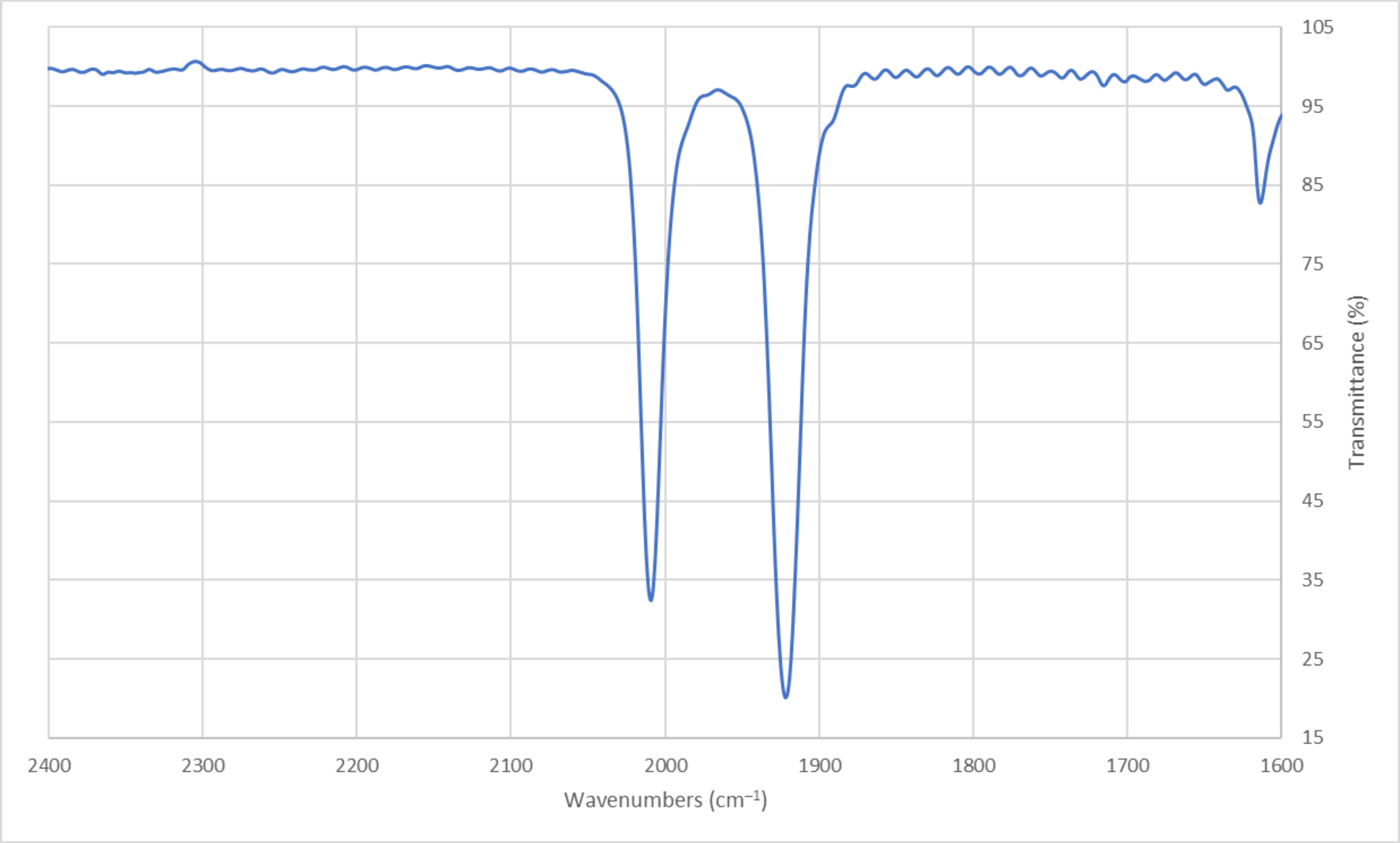
Infrared spectrum of [2,6-{(Tp*)(CO)$_2$W≡C}$_2$Py] (**3**).



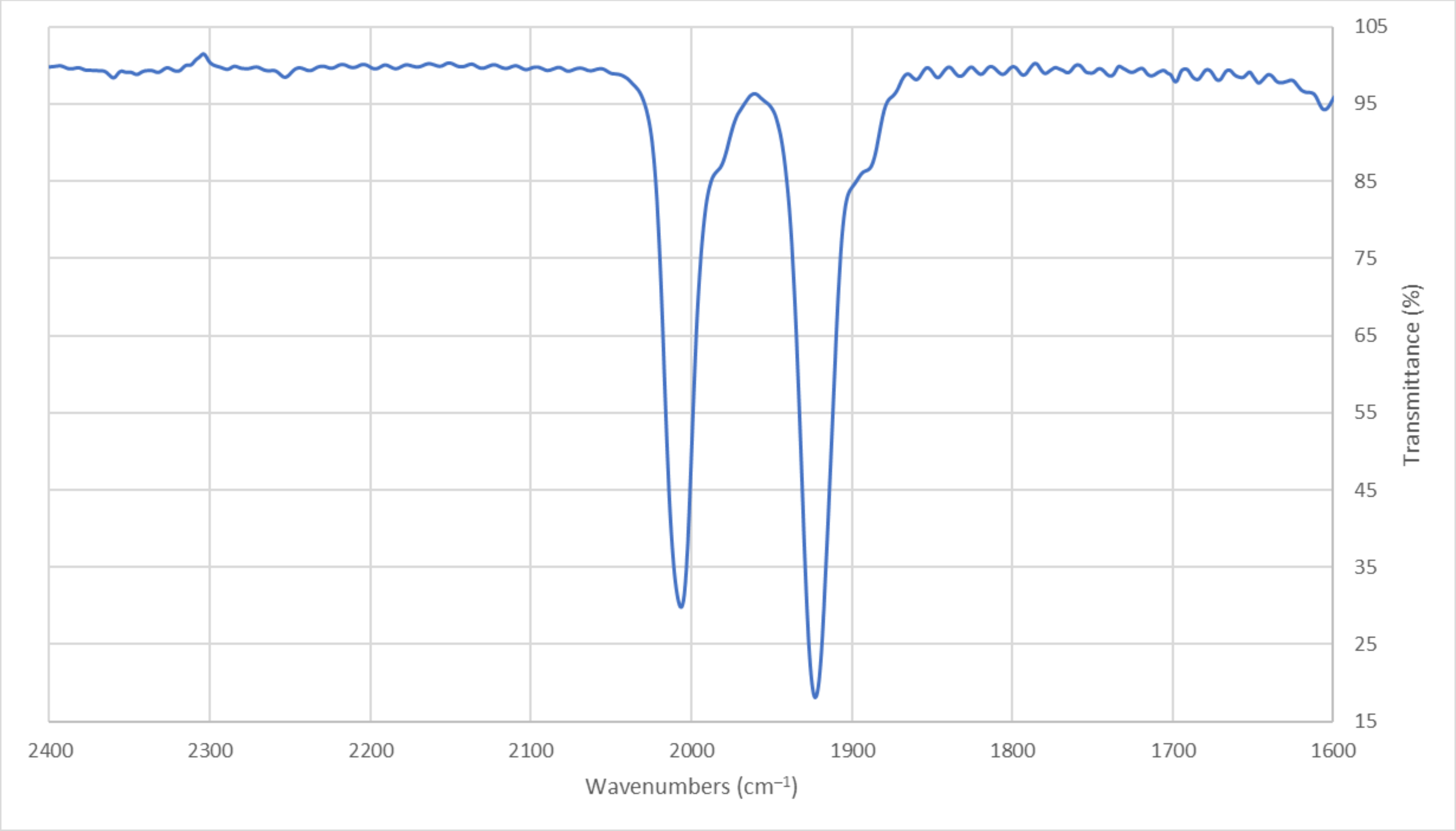
Infrared spectrum of [W(≡C{2-PyH})(CO)$_2$(Tp*)]BF$_4$ (**4**) (mixed with **2** due to rapid deprotonation).



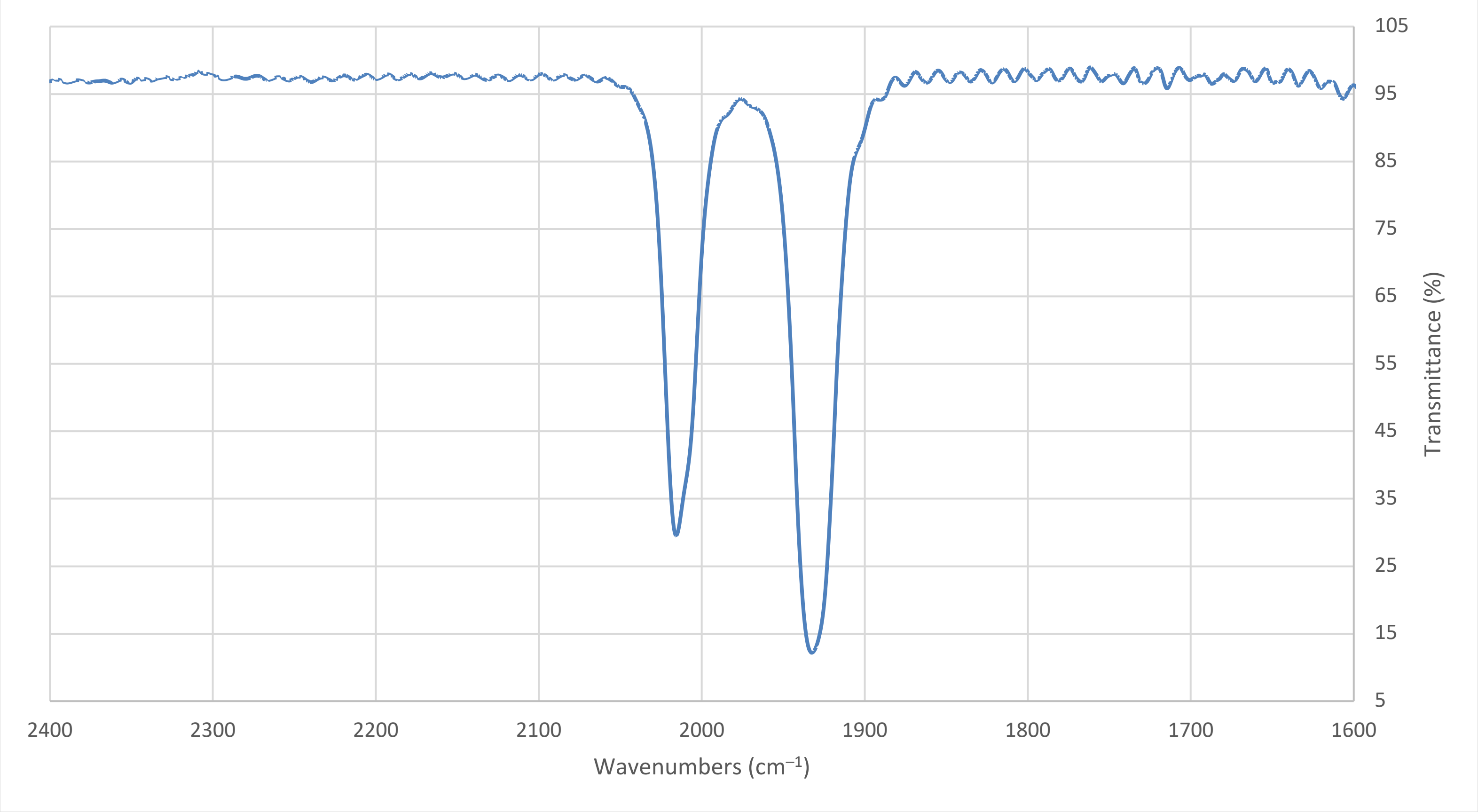
Infrared spectrum of [2,6-{(Tp*)(CO)$_2$W≡C}$_2$PyH]BF$_4$ (**5**).



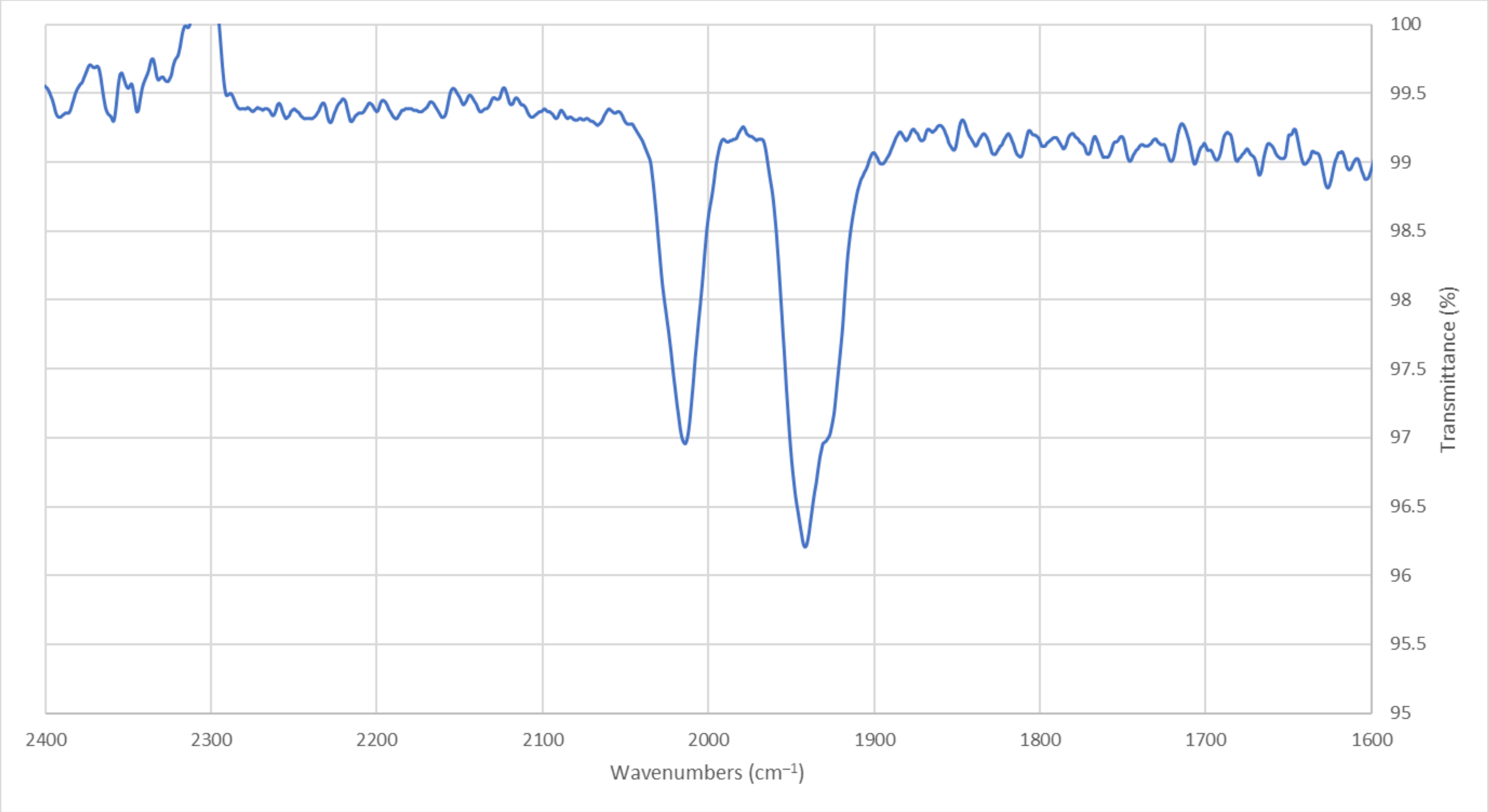
Infrared spectrum of $[W(\equiv C\{2\text{-}PyCH_3\})(CO)_2(Tp^*)]O_3SCF_3$ (**6**).



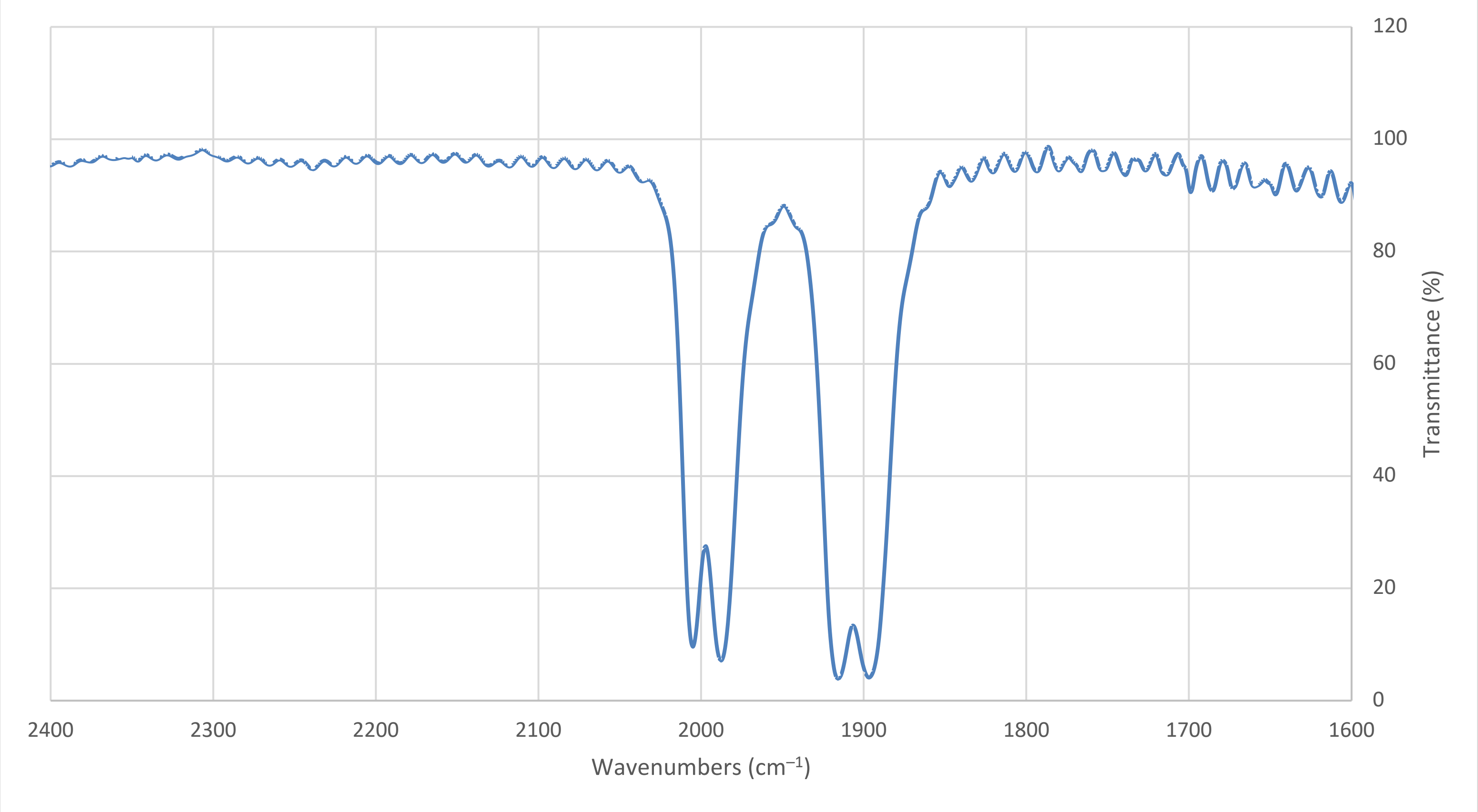
Infrared spectrum of [2,6-{(Tp*)(CO)$_2$W≡C}$_2$PyCH$_3$]O$_3$SCF$_3$ (**7**).



Infrared spectrum of [WAu{μ-C(2-Py)}Cl(CO)$_2$(Tp*)] (**8**).



Infrared spectrum of [2,6-{(Tp*)(CO)$_2$Cl$_2$WAu$_2$(μ-C)}$_2$Py] (**9**).



Infrared spectrum of [WPt{μ-C(2-Py)}$Cl_2(C_2H_4)(CO)_2$(Tp*)] (**10**, presumed to involve two rotamers of the W$(CO)_2$(Tp*) unit).