



Electronic Supporting Information for:

Tungsten-Platinum μ -Carbido and μ -Methyldiyne Complexes

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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 $^{19}\text{F}\{^1\text{H}\}$, 85% H_3PO_4 in H_2O for $^{31}\text{P}\{^1\text{H}\}$), 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 $^{13}\text{C}\{^1\text{H}\}$ 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 hydridotris(3,5-dimethylpyrazol-1-yl)borate (Tp^*) ligand. Spectra provided generally correspond to samples obtained directly from chromatography and may contain residual solvent as recrystallised samples often display reduced solubility.

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-K α radiation ($\lambda = 0.71073 \text{ \AA}$) or Cu-K α radiation ($\lambda = 1.54184 \text{ \AA}$) and the CrysAlis PRO software.¹ Data for **5** were collected at the Australian Synchrotron on the MX1 beamline using silicon double crystal monochromated synchrotron radiation at 100 K. Raw frame data were collected using Bluelce² and data reduction, interframe scaling, unit cell refinement and absorption corrections were processed using XDS.³ 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.⁴ Hydrogen atoms were located geometrically and refined using a riding model. Diagrams were produced using the CCDC visualisation program Mercury.⁵

Synthesis of the bromocarbonyne $[\text{W}(\equiv\text{CBr})(\text{CO})_2(\text{Tp}^*)]$ has been described previously.⁶ The platinum complexes chloro(2,2':6',2''-terpyridine)platinum(II) chloride $[\text{PtCl}(\text{terpy})]\text{Cl}\cdot 2\text{H}_2\text{O}$,⁷ chloro(2,2':6',2''-terpyridine)platinum(II) hexafluorophosphate $[\text{PtCl}(\text{terpy})]\text{PF}_6$,⁸ dichloro(1,10-phenanthroline)platinum(II) $[\text{PtCl}_2(\text{phen})]$,⁹ dichloro(tetramethylcyclobutadiene)platinum(II), $[\text{PtCl}_2(\eta^4\text{-C}_4\text{Me}_4)]$,¹⁰ and dichloro(tetraethylcyclobutadiene)platinum(II) $[\text{PtCl}_2(\eta^4\text{-C}_4\text{Et}_4)]$ ¹⁰ were synthesised according to the literature methods.

$[\text{W}(\equiv\text{C}(\text{Pt}(\text{terpy}))(\text{CO})_2(\text{Tp}^*))]\text{PF}_6$ (4**).** A solution of $[\text{W}(\equiv\text{CBr})(\text{CO})_2(\text{Tp}^*)]$ (200 mg, 0.318 mmol) in THF (10 mL) at $-78 \text{ }^\circ\text{C}$ was treated with $n\text{BuLi}$ (200 μL , 1.6 M in hexanes, 0.32 mmol) and the mixture was stirred for 30 min at reduced temperature. After this time, $[\text{PtCl}(\text{terpy})]\text{PF}_6$ (194 mg, 0.318 mmol) was added, the mixture was warmed to RT and stirring continued for 2 h. The volatiles were then removed *in vacuo* and the residue was subjected to column chromatography (30 x 3 cm silica gel column), eluting first with CH_2Cl_2 and gradually increasing the polarity to 50% v/v $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$. A slow-moving red-purple band was collected and the volatiles were removed under reduced pressure to give a purple precipitate which was collected by filtration and washed with petroleum spirits (30–

40 °C) (3 x 5 mL) and ice-cold CH₂Cl₂ (3 x 5 mL) to give a purple solid of pure **4** (228 mg, 0.203 mmol, 64%). IR (CH₂Cl₂, cm⁻¹): 1954, 1858 ν_{CO}. ¹H NMR (400 MHz, CD₃CN, 25 °C): δ_H = 2.38 (s, 3 H, pzCH₃), 2.42 (s, 3 H, pzCH₃), 2.46 (s, 6 H, pzCH₃), 2.69 (s, 6 H, pzCH₃), 5.84 (s, 1 H, pzCH), 5.95 (s, 2 H, pzCH), 7.57 (br, 2 H, *terpy*), 8.25–8.42 (m, 7 H, *terpy*), 8.69 (br, 2 H, *terpy*). ¹³C{¹H} NMR (101 MHz, CD₃CN, 25 °C): δ_C = 12.7, 12.9, 15.3, 17.1 (pzCH₃), 107.2, 107.3 (pzCH), 124.7, 126.7, 129.2, 142.8, 143.0 (*terpy*), 146.2, 147.1, 152.6, 153.1 (pzCCH₃), 154.2, 154.8, 160.0 (*terpy*), 228.3 (WCO). W≡Cpt was not observed but is tentatively assigned at ca 368 ppm based on ¹H-¹³C HMBC correlations with pzCH₃ protons. ³¹P{¹H} NMR (162 MHz, CD₃CN, 25 °C): δ_P = -144.6 (heptet, ¹J_{PF} = 709, PF₆). ¹⁹F{¹H} NMR (376 MHz, CD₃CN, 25 °C): δ_F = -72.9 (d, ¹J_{FP} = 709, PF₆). MS (ESI, *m/z*): Found: 976.2018. Calcd for C₃₃H₃₃¹¹Bn₉O₂¹⁹⁵Pt¹⁸⁴W [M-PF₆]⁺: 976.1997. Anal. Found: C, 35.40; H, 3.08; N, 11.35. Calcd for C₃₃H₃₃BF₆N₉O₂PPTW: C, 35.31; H, 2.96; N, 11.23%. A crystal suitable for structure determination was grown by slow evaporation of an acetonitrile solution. *Crystal data for* C₃₃H₃₃BF₆N₉O₂PPTW (*M* = 1122.40 g.mol⁻¹): monoclinic, space group P2₁/n (no. 14), *a* = 19.2295(3), *b* = 7.9562(2), *c* = 27.8172(5) Å, β = 100.500(2)°, *V* = 4184.59(15) Å³, *Z* = 4, *T* = 150.0(1) K, μ(CuKα) = 12.117 mm⁻¹, *D*_{calc} = 1.782 g.cm⁻³, 30606 reflections measured (9.354° ≤ 2θ ≤ 147.584°), 8396 unique (*R*_{int} = 0.0445, *R*_{sigma} = 0.0428) which were used in all calculations. The final *R*₁ was 0.0406 (*I* > 2σ(*I*)) and *wR*₂ was 0.1026 (all data). CCDC 1945291.

[(Tp*)(CO)₂W≡CptCl(phen{C≡W(CO)₂(Tp*)-2})] (**5**). A solution of [W(≡CBr)(CO)₂(Tp*)] (200 mg, 0.318 mmol) in THF (10 mL) at -78 °C was treated with ⁿBuLi (200 μL, 1.6 M in THF, 0.32 mmol) and the mixture was stirred for 30 min at reduced temperature. After this time, [PtCl₂(phen)] (71 mg, 0.16 mmol) was added, the mixture was slowly warmed to RT and stirring was continued for 2 h. The volatiles were then removed under reduced pressure and the residue was subjected to column chromatography (50 x 3 cm silica gel column), eluting initially with petroleum ether (40–60 °C) and gradually increasing the ratio to 60% v/v CH₂Cl₂/petrol. An orange band was collected and the solvents were removed under reduced pressure to give an orange solid of pure **5** (136 mg, 0.0902 mmol, 57%). IR (CH₂Cl₂, cm⁻¹): 1977s, 1944s, 1886s, 1854s ν_{CO}. UV-Vis (CH₂Cl₂): λ_{max} = 395 nm (ε = 5250 Lmol⁻¹cm⁻¹). ¹H NMR (600 MHz, CDCl₃, 25 °C): δ_H = 2.32 (s, 3 H, pzCH₃), 2.36 (s, 3 H, pzCH₃), 2.39 (s, 3 H, pzCH₃), 2.41 (s, 3 H, pzCH₃), 2.42 (s, 6 H, pzCH₃), 2.46 (s, 3 H, pzCH₃), 2.70 (s, 3 H, pzCH₃), 2.72 (s, 6 H, pzCH₃), 2.79 (s, 6 H, pzCH₃), 5.69 (s, 1 H, pzCH), 5.78 (2 x s coincidental, 2 H, pzCH), 5.93 (s, 2 H, pzCH), 7.08 (br, 1 H, *phen*), 7.77 (d, ³J_{HH} = 8.6, 1 H, *phen*), 7.81 (d, ³J_{HH} = 8.6, 1 H, *phen*), 7.99 (d, ³J_{HH} = 8.6, 1 H, *phen*), 8.27 (d, ³J_{HH} = 8.5, 1 H, *phen*), 8.38 (d, ³J_{HH} = 8.5, 1 H, *phen*), 9.64 (br, 1 H, *phen*). ¹³C{¹H} NMR (151 MHz, CDCl₃, 25 °C): δ_C = 12.5, 12.7, 12.8, 13.0 (2 C), 15.0, 15.4, 15.5, 16.9 (2 C), 17.7 (2 C) (pzCH₃), 106.0, 106.1, 106.9, 107.0, 107.9, 108.0 (pzCH), 124.2, 125.9, 127.0, 127.6, 131.1, 133.6, 136.0, 136.2, 143.7, 144.3, 144.4, 144.8, 145.3, 146.5, 147.0, 147.8, 150.7, 152.0, 152.3, 152.4, 152.5, 154.6, 154.7, 168.7 (total of 24 C, pzCCH₃ & *phen*), 226.1, 227.3 (CO), 267.0 (W≡CC), 331.3 (br, W≡Cpt). MS (ESI, *m/z*): Found: 1508.2811. Calcd for

C₄₈H₅₂¹¹B₂CIN₁₄O₄¹⁹⁵Pt¹⁸⁴W₂ [M + H]⁺: 1508.2844. Found: 1531.2709. Calcd for C₄₈H₅₁¹¹B₂CIN₁₄O₄¹⁹⁵Pt¹⁸⁴W₂ [M + Na]⁺: 1531.2670. Anal. Found: C, 38.08; H, 3.46; N, 12.82. Calcd for C₄₈H₅₁B₂CIN₁₄O₄PtW₂: C, 38.23; H, 3.41; N, 13.00%. Crystals used for structure determination were grown by slow evaporation of a CHCl₃/ethanol mixture and proved to be a chloroform solvate. *Crystal data for* C₄₉H₅₂B₂Cl₄N₁₄O₄PtW₂ (*M* = 1627.25 g.mol⁻¹): monoclinic, space group P2₁/n (no. 14), *a* = 17.029(8), *b* = 20.850(9), *c* = 18.411(7) Å, β = 112.825(7)°, *V* = 6025(4) Å³, *Z* = 4, *T* = 100.033(2) K, μ(Synchrotron) = 6.355 mm⁻¹, *D*_{calc} = 1.794 g.cm⁻³, 47606 reflections measured (2.768° ≤ 2θ ≤ 52.738°), 11485 unique (*R*_{int} = 0.1946, *R*_{sigma} = 0.1316) which were used in all calculations. The final *R*₁ was 0.0782 (*I* > 2σ(*I*)) and *wR*₂ was 0.2202 (all data) for 697 refined parameters with 0 restraints. CCDC 1945292.

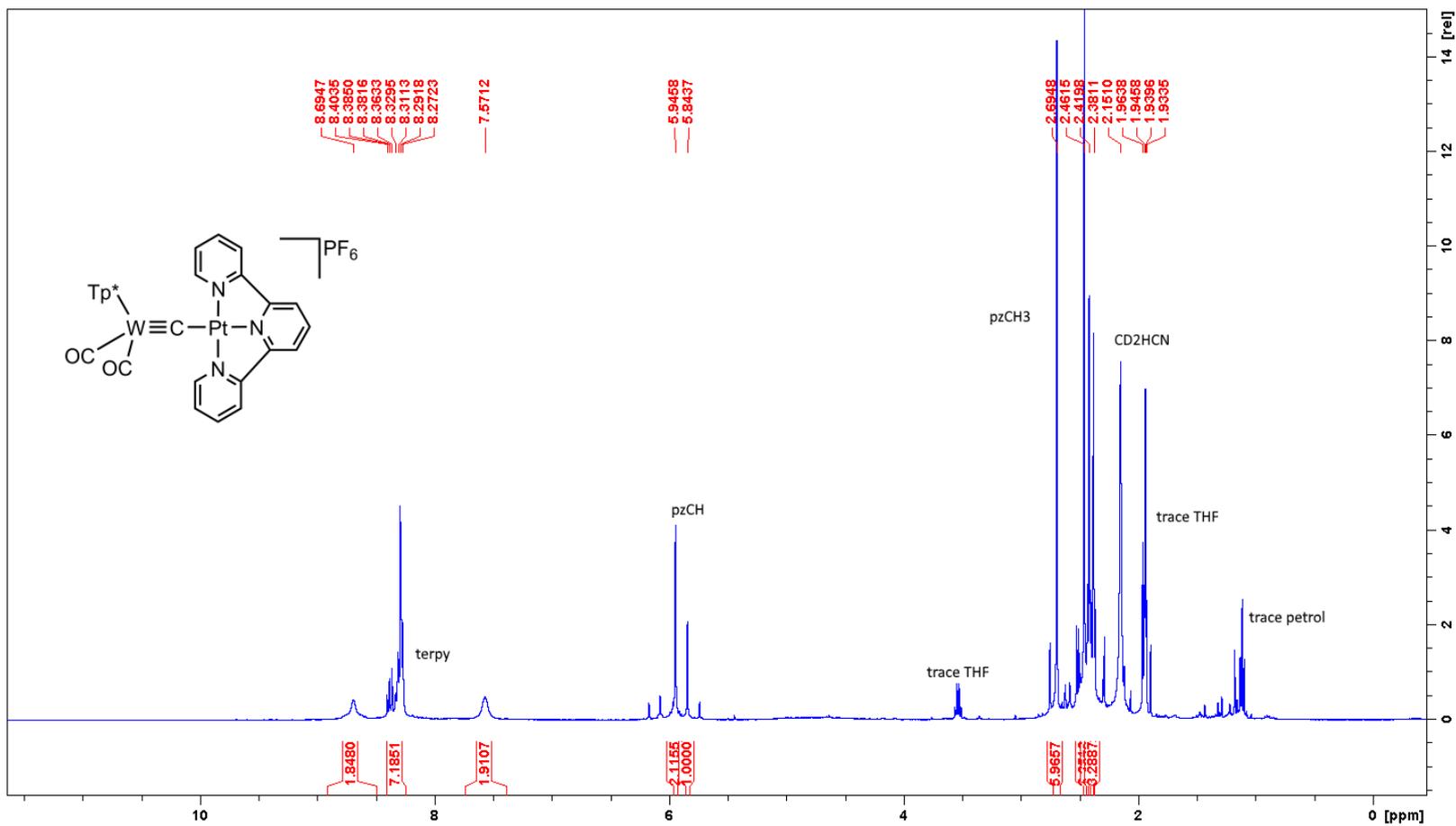
[W₂Pt(μ-CH)₂(CO)₄(Tp*)₂] (**7**). A solution of [W(≡CBr)(CO)₂(Tp*)] (200 mg, 0.318 mmol) in THF (10 mL) at -78 °C was treated with ⁿBuLi (200 μL, 1.6 M in THF, 0.32 mmol) and the mixture was stirred for 30 min at reduced temperature. After this time, [PtCl₂(η⁴-C₄Me₄)] (60 mg, 0.16 mmol) was added, the mixture was slowly warmed to RT and stirring was continued for 1 h. The volatiles were removed under reduced pressure and the residue was subjected to column chromatography (40 x 3 cm silica gel column), eluting initially with petroleum ether (40–60 °C) and gradually increasing the polarity to 60% v/v CH₂Cl₂/petrol. A bright orange band was collected and the solvents were removed under reduced pressure to give an orange solid of pure **7** (111 mg, mmol, 0.0857 mmol, 53%). IR (CH₂Cl₂, cm⁻¹): 1976s, 1943s ν_{CO}, 1811 ν_{μCO}. UV-Vis (CH₂Cl₂): λ_{max} = 321 (ε = 10,960 Lmol⁻¹cm⁻¹). ¹H NMR (700 MHz, CDCl₃, 25 °C): δ_H = 2.20–2.52 (br, 12 H, pzCH₃), 2.37 (s, 6 H, pzCH₃), 2.41 (s, 12 H, pzCH₃), 2.59 (s, 6 H, pzCH₃), 5.80–5.95 (br, 4 H, pzCH), 5.84 (s, 2 H, pzCH), 12.09 (s, ²J_{HW} = 44, 2 H, W≡CH). ¹H NMR (700 MHz, CDCl₃, -40 °C): δ_H = 2.17 (s, 6 H, pzCH₃), 2.34 (s, 6 H, pzCH₃), 2.35 (s, 6 H, pzCH₃), 2.37 (s, 6 H, pzCH₃), 2.42 (s, 6 H, pzCH₃), 2.57 (s, 6 H, pzCH₃), 2.65 (s, 6 H, pzCH₃), 5.77 (s, 2 H, pzCH), 5.84 (s, 2 H, pzCH), 5.99 (s, 2 H, pzCH), 12.09 (s, ²J_{HW} = 44, 2 H, W≡CH). ¹³C{¹H} NMR (176 MHz, CDCl₃, -40 °C): δ_C = 13.0, 13.0, 13.1, 15.6, 17.3, 19.0 (pzCH₃), 107.1, 107.2, 107.6 (pzCH), 144.2, 144.5, 145.2, 151.0, 153.2, 154.0 (pzCCH₃), 218.6, 229.9 (WCO), 293.8 (W≡CH). ¹⁹⁵Pt NMR (86 MHz, CDCl₃, 25 °C): δ_{Pt} = -3084 (¹J_{PtW} = 209). MS (ESI, *m/z*): Found: 1295.2706. Calcd for C₃₆H₄₆¹¹B₂N₁₂O₄¹⁹⁵Pt¹⁸⁴W₂ [M-e]⁺: 1295.2624. Found: 1318.2582. Calcd for C₃₆H₄₆¹¹B₂NaN₁₂O₄¹⁹⁵Pt¹⁸⁴W₂ [M+Na]⁺: 1318.2522. Anal. Found: C, 33.41; H, 3.59; N, 12.88%. Calcd for C₃₆H₄₆B₂N₁₂O₄PtW₂: C, 33.38; H, 3.58; N, 12.98%. A crystal suitable for structure determination was grown by slow evaporation of an acetonitrile solution. *Crystal data for* C₃₈H₄₉B₂N₁₃O₄PtW₂ (*M* = 1336.31 g.mol⁻¹): tridinic, space group P-1 (no. 2), *a* = 10.5256(5) Å, *b* = 12.7095(7), *c* = 17.9699(8), α = 70.976(5)°, β = 89.192(4)°, γ = 80.546(4)°, *V* = 2239.8(2) Å³, *Z* = 2, *T* = 150.0(1) K, μ(CuKα) = 15.448 mm⁻¹, *D*_{calc} = 1.981 g.cm⁻³, 12461 reflections measured (7.464° ≤ 2θ ≤ 133.192°), 7842 unique (*R*_{int} = 0.0233, *R*_{sigma} = 0.0381) which were used in all calculations. The final *R*₁ was 0.0390 (*I* > 2σ(*I*)) and *wR*₂ was 0.0959 (all data) for 554 refined parameters with 0 restraints. CCDC 1945293.

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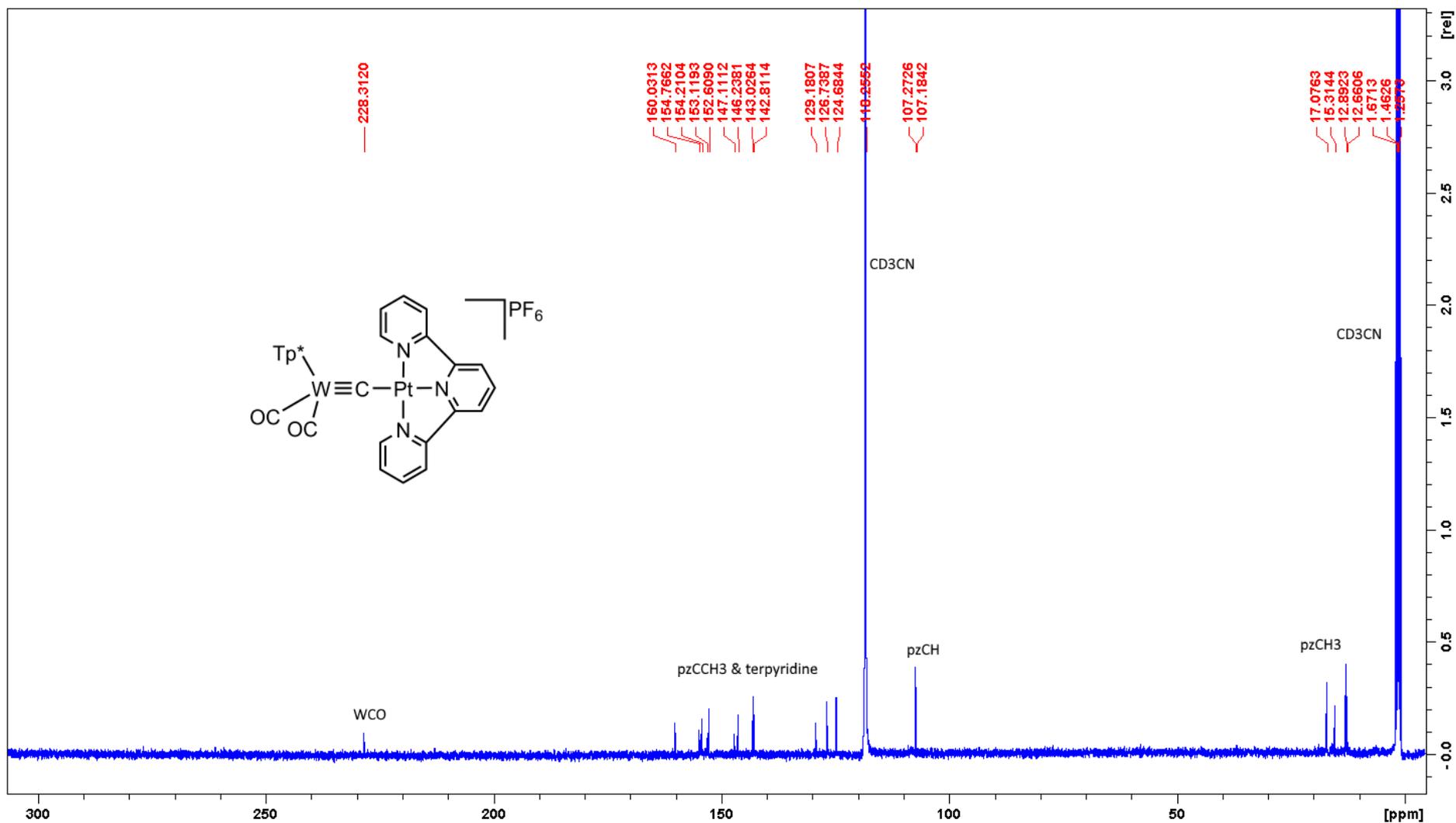
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Chemical Communications

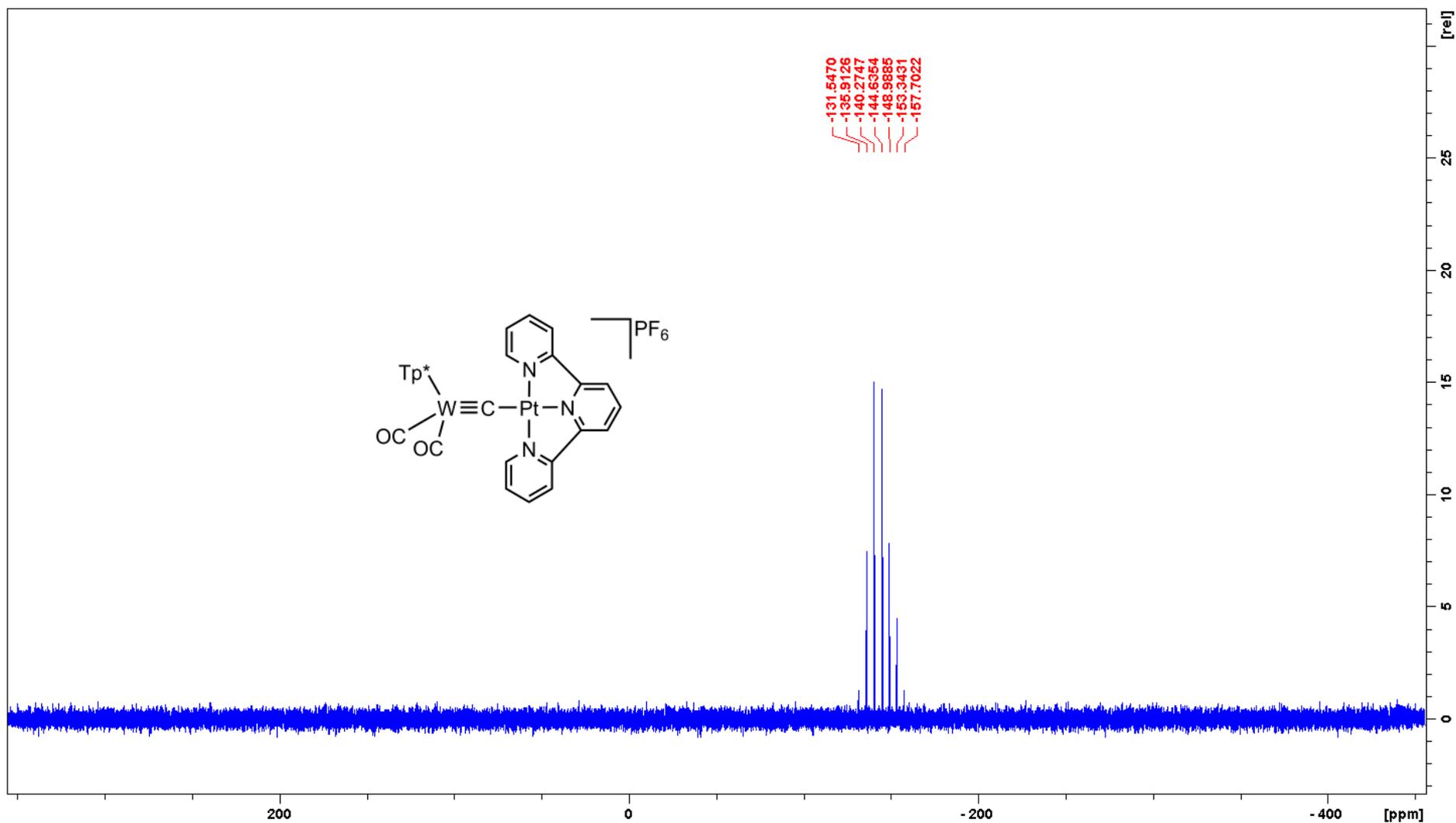
COMMUNICATION



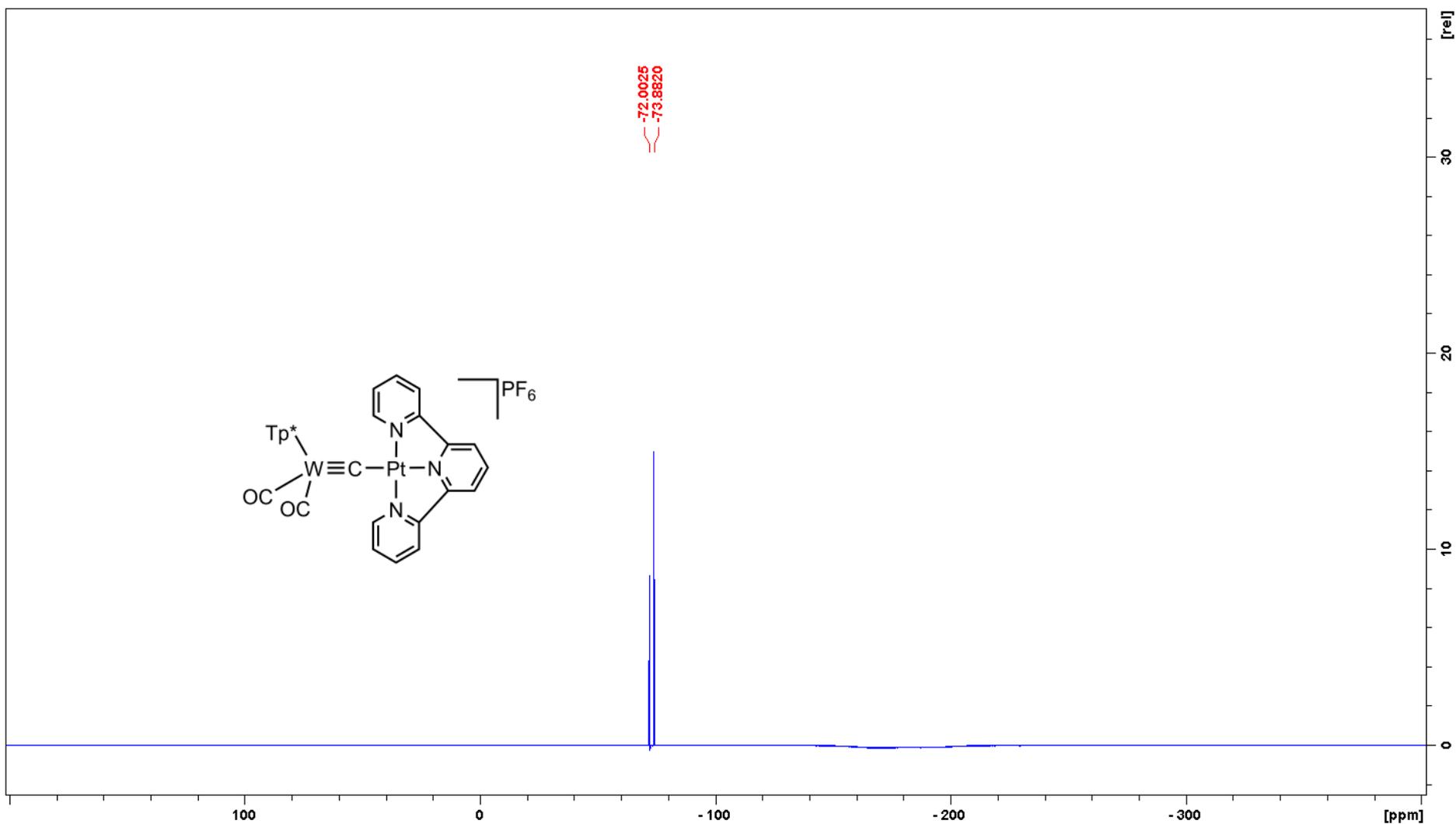
¹H NMR spectrum (400 MHz, CD₃CN, 25 °C, δ) of $[W\{\equiv C\}Pt(terpy)](CO)_2(Tp^*)PF_6$ (4).



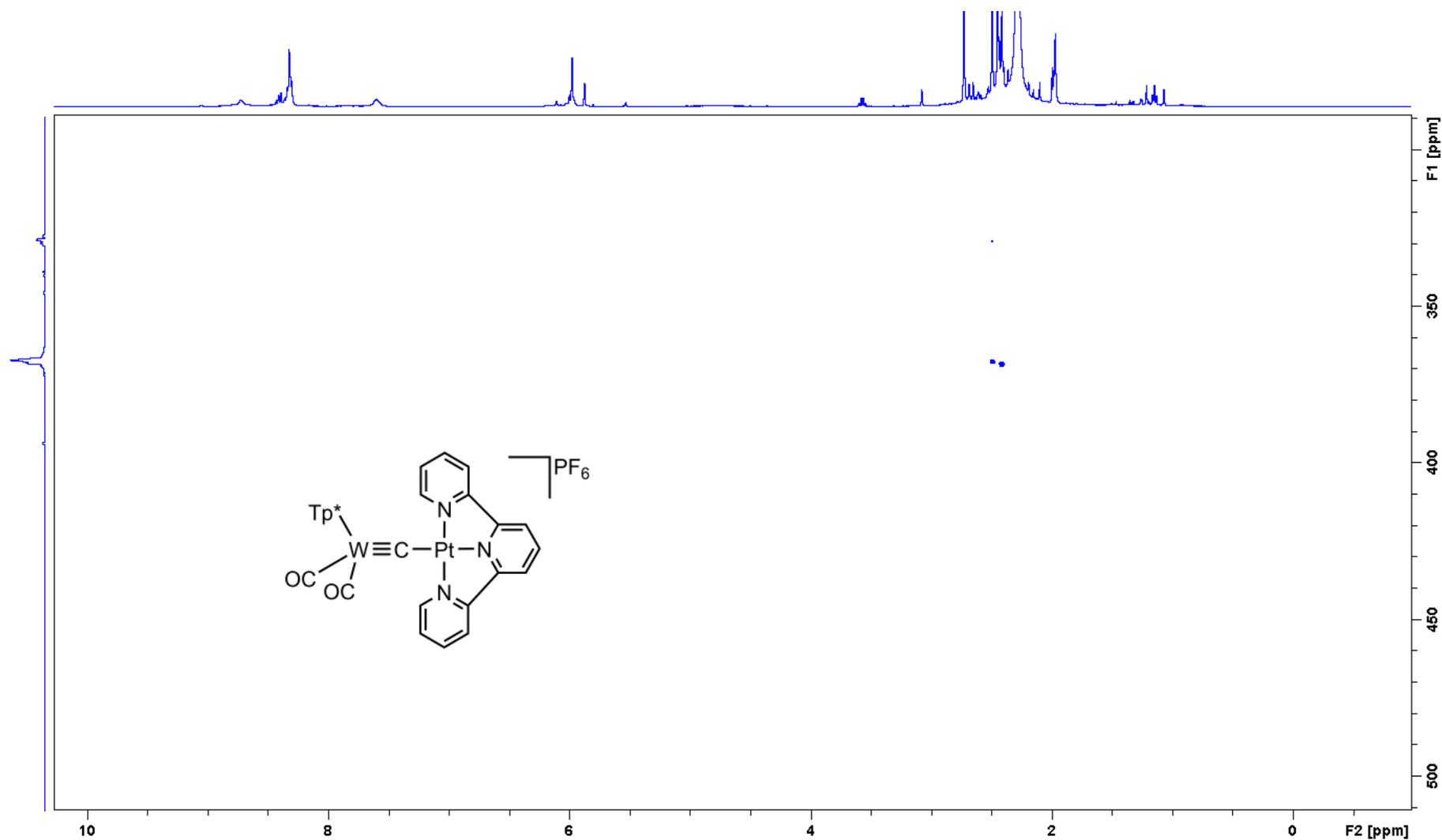
$^{13}C\{^1H\}$ NMR spectrum (101 MHz, CD_3CN , 25 °C, δ) of $[W\{\equiv C Pt(terpy)\}(CO)_2(Tp^*)]PF_6$ (**4**).



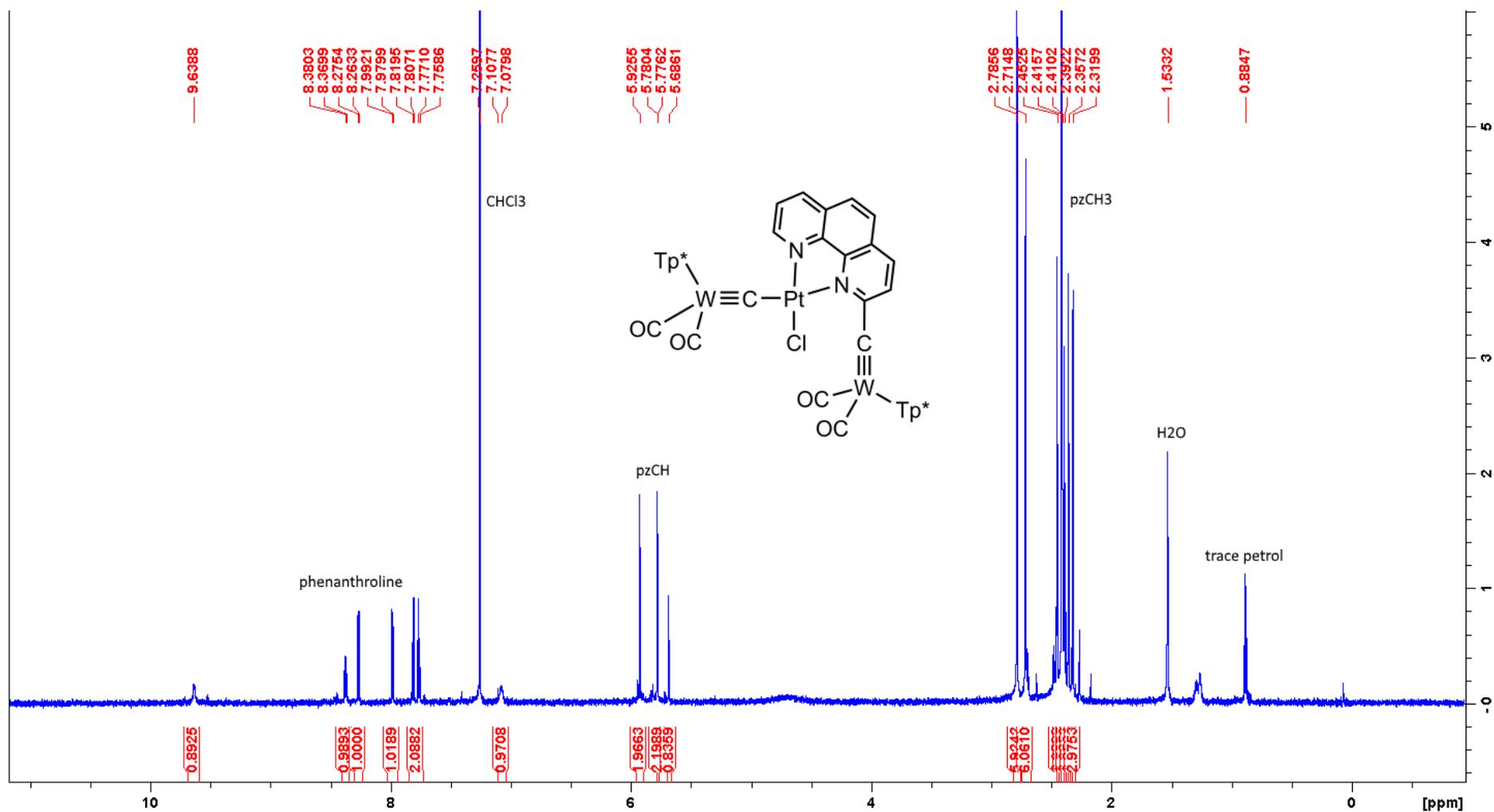
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, CD_3CN , 25 °C, δ) of $[\text{W}\{\equiv\text{C Pt}(\text{terpy})\}(\text{CO})_2(\text{Tp}^*)]\text{PF}_6$ (4).



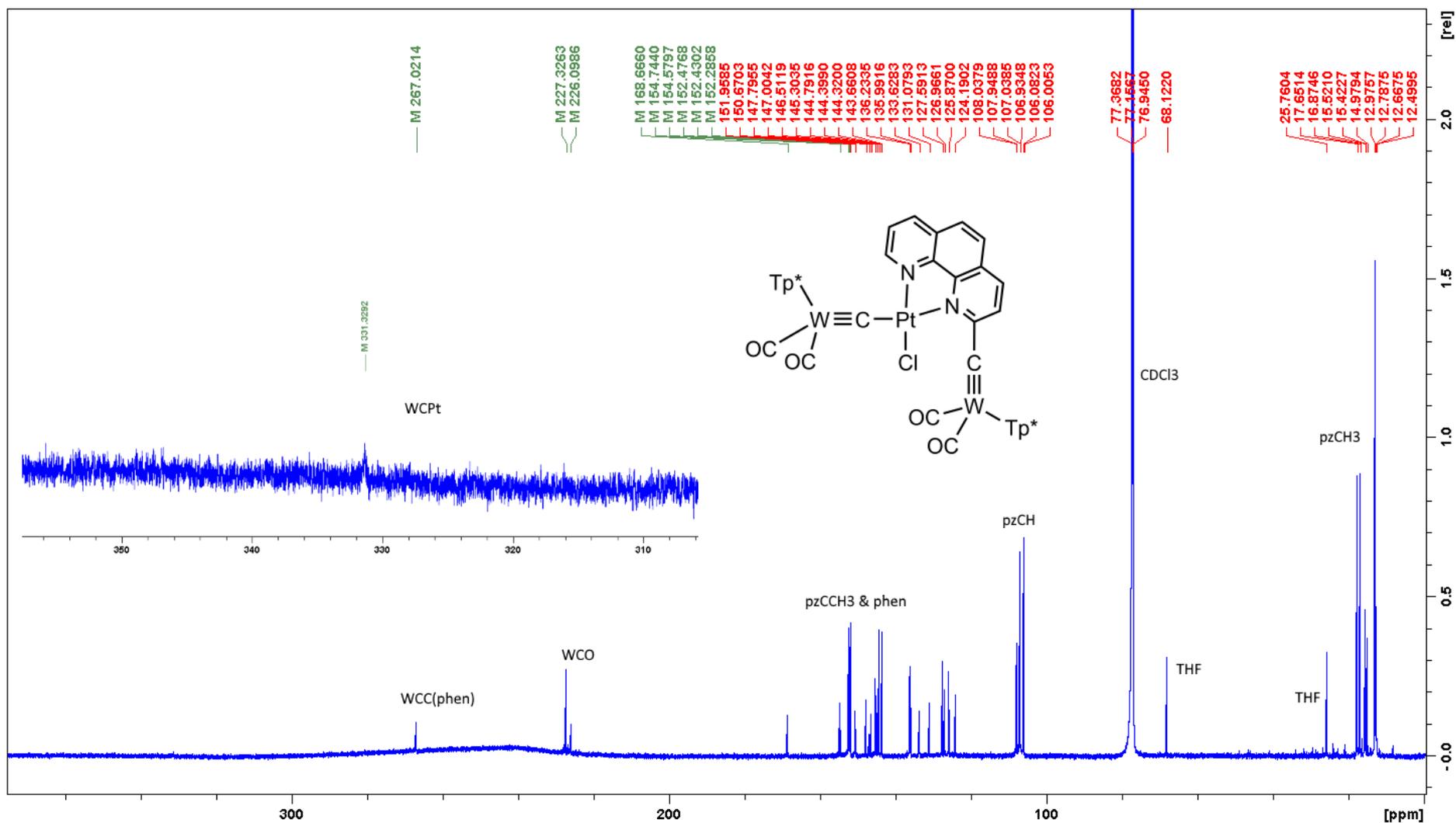
$^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (376 MHz, CD_3CN , 25 °C, δ) of $[\text{W}\{\equiv\text{C}(\text{Pt}(\text{terpy}))\}(\text{CO})_2(\text{Tp}^*)]\text{PF}_6$ (4).



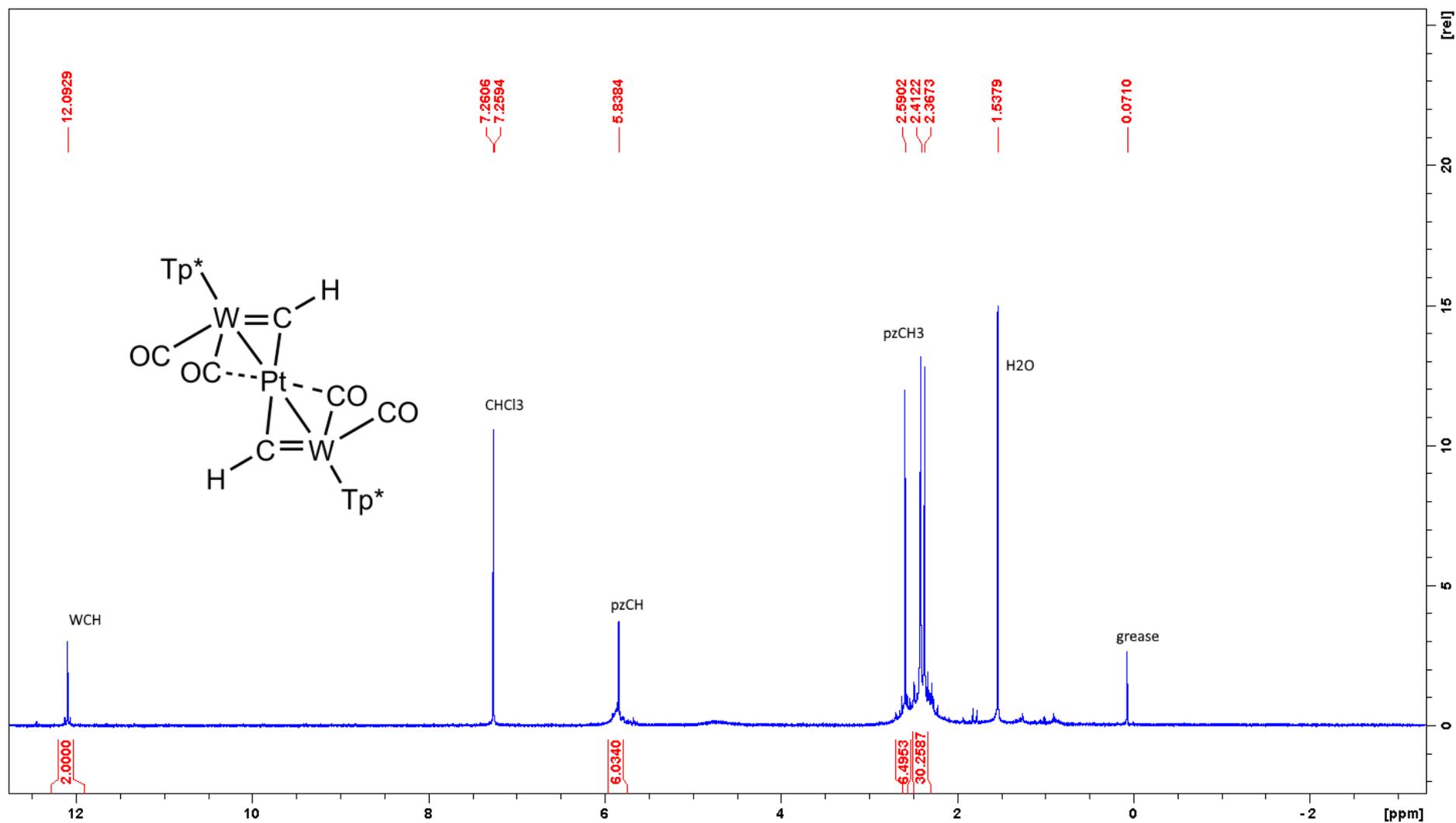
^1H - ^{13}C HMBC NMR spectrum (400 & 101 MHz, CD_3CN , 25 °C, δ) of $[\text{W}\{\equiv\text{Cpt}(\text{terpy})\}(\text{CO})_2(\text{Tp}^*)]\text{PF}_6$ (**4**).



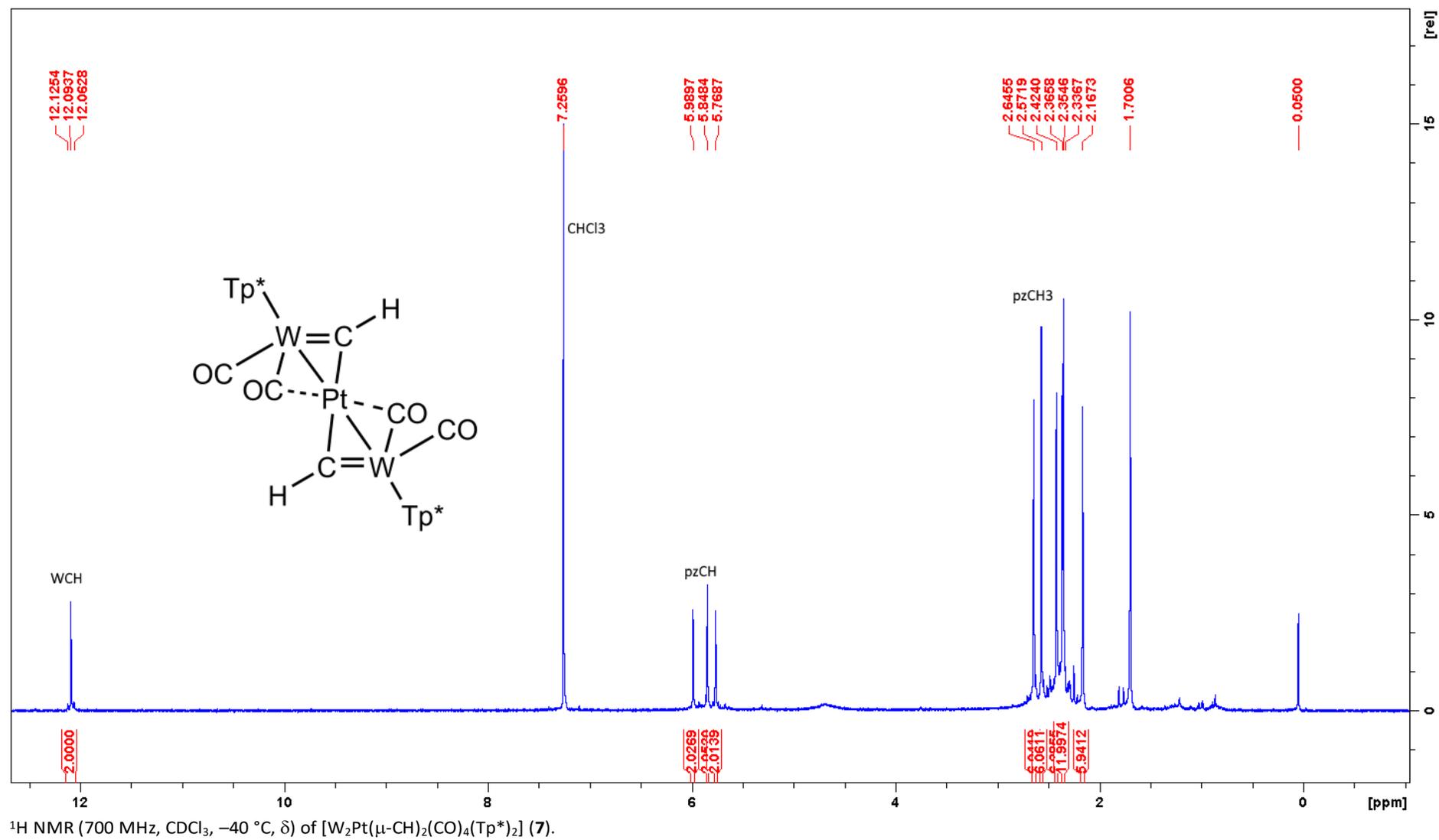
^1H NMR (600 MHz, CDCl_3 , 25 °C, δ) of $[(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}\text{PtCl}(\text{phen}\{\text{C}\equiv\text{W}(\text{CO})_2(\text{Tp}^*)-2\})]$ (5).

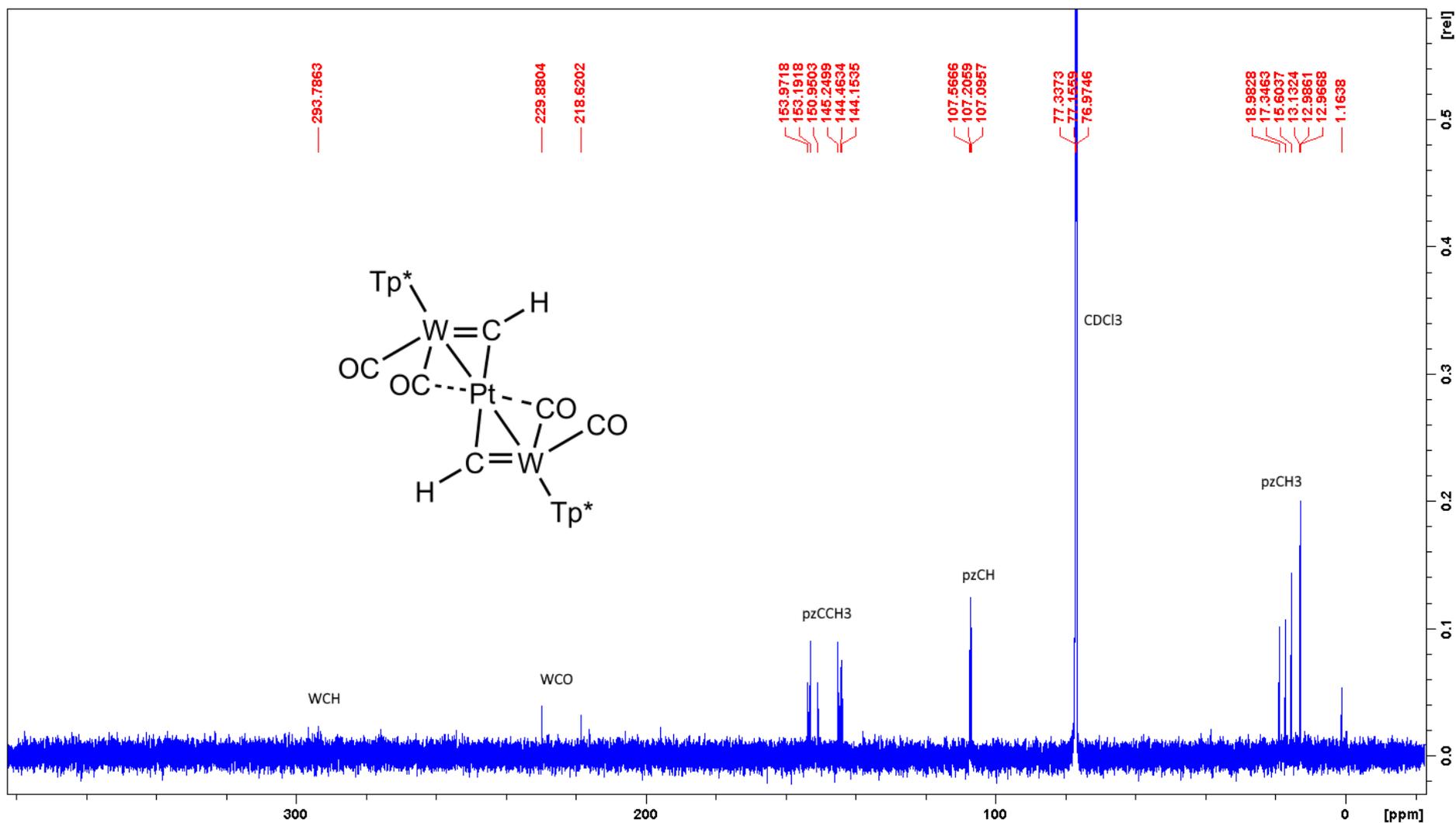


$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 25 °C, δ) of $[(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}\text{PtCl}(\text{phen}\{\text{C}\equiv\text{W}(\text{CO})_2(\text{Tp}^*)-2\})]$ (5).

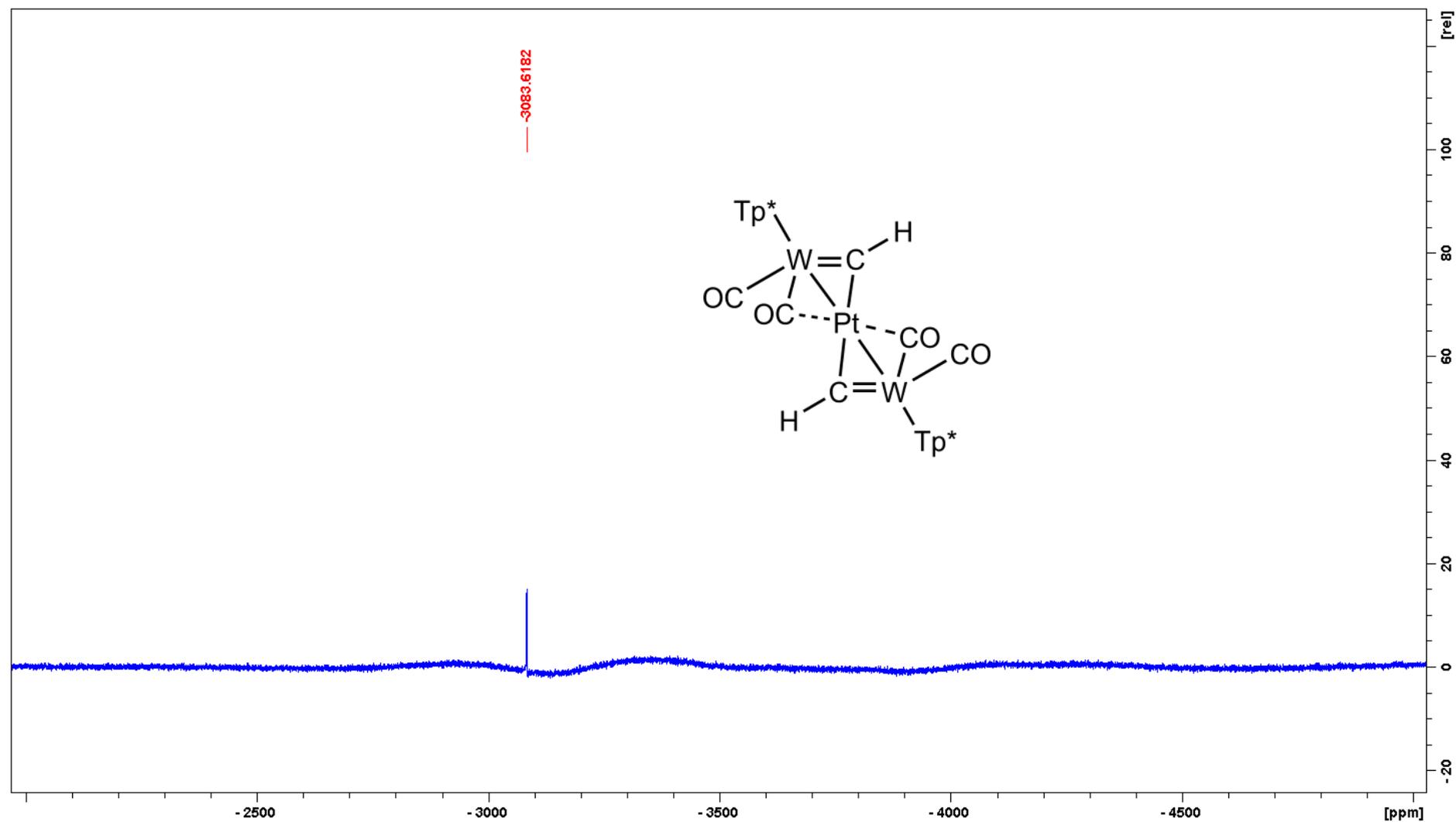


^1H NMR (700 MHz, CDCl_3 , 25°C , δ) of $[\text{W}_2\text{Pt}(\mu\text{-CH})_2(\text{CO})_4(\text{Tp}^*)_2]$ (7).





$^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, CDCl_3 , -40°C , δ) of $[\text{W}_2\text{Pt}(\mu\text{-CH})_2(\text{CO})_4(\text{Tp}^*)_2]$ (7).



^{195}Pt NMR (86 MHz, CDCl_3 , 25 °C, δ) of $[\text{W}_2\text{Pt}(\mu\text{-CH})_2(\text{CO})_4(\text{Tp}^*)_2]$ (7).

