

COMMUNICATION

Electronic Supporting Information for:

Bi- and Poly(carbyne) functionalised Polycyclic Aromatics

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Benjamin J. Frogley,^a Anthony F. Hill^{*a} and Antonia Seitz^a

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Experimental

Experimental work was carried out 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, ¹³C at 100.6 MHz, ¹⁹F at 376.5 MHz), a Bruker Avance 600 (¹H at 600.0 MHz, ¹³C at 150.9 MHz) or a Bruker Avance 700 (¹H at 700.0 MHz, ¹³C 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. 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 ¹⁸³W satellites. In some cases, distinct peaks were observed in the ¹H and ¹³C{¹H} NMR spectra, but to the level of accuracy that is reportable (i.e., 2 decimal places for ¹H NMR, 1 decimal place for ¹³C NMR) they are reported as having the same chemical shift. The abbreviation 'pz' is used to refer to the pyrazolyl rings on the hydridotris(3,5-dimethylpyrazol-1-yl)borate (Tp*) ligand. Spectra provided generally correspond to samples obtained directly from chromatography and may contain residual solvent as recrystallised samples often display reduced solubility. The BH protons give rise to very broad signals around 4–5 ppm in the ¹H NMR spectra due to coupling to the quadrupolar boron

nuclei. These are not listed in the experimental NMR data as their chemical shifts cannot be determined accurately.

Infrared spectra were obtained using a Shimadzu FTIR-8400 spectrometer. Electronic spectra were collected at room temperature as solution in 1 cm quartz cells using a PerkinElmer lambda 465 spectrophotometer. Fluorescence was measured on a Varian Cary Eclipse fluorescence spectrophotometer at room temperature. Elemental microanalytical data were provided the London Metropolitan University. Solvates evident from data were confirmed by NMR spectroscopy. High-resolution electrospray ionisation mass spectrometry (ESI-MS) was performed by the ANU Research School of Chemistry mass spectrometry service with acetonitrile or methanol as the matrix.

Cyclic voltammetry measurements were recorded using a e-corder 401 potentiostat system from eDAQ Pty Ltd. Measurements were carried out at room temperature using Pt disc working-, Pt wire auxiliary- and Ag/AgCl or SCE reference electrodes, such that the ferrocene/ferrocenium redox couple was located at 0.46 V (CH₂Cl₂) relative to saturated calomel electrode ($i_{pc}/i_{pa} = 1$, ΔE_p 0.09–0.12 V).¹ Scan rates were typically 100 mV s⁻¹. Electrochemical solutions contained 0.1 M [NBu₄][PF₆] and ca 10⁻³ M complex in dried and distilled solvent. Solutions were purged and maintained under a nitrogen atmosphere.

Data for X-ray crystallography were collected with Agilent Xcalibur or SuperNova CCD diffractometer using Mo-K α radiation ($\lambda = 0.71073$ Å) or Cu-K α radiation ($\lambda = 1.54184$ Å) employing the CrysAlis PRO software.² 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.³ Hydrogen atoms were located geometrically and refined using a riding model. Diagrams were produced using the CCDC visualisation program Mercury.⁴

The synthesis of [W(=CSnⁿBu₃)(CO)₂(Tp*)] (**1**)⁵ has been described previously. The complex [AuCl(SMe₂)]⁶ was prepared by literature methods. Commercially available haloarenes were used as received. 1,3,5,8-tetrabromopyrene was prepared by the literature methods.⁷ Petrol refers to petroleum spirits (40–

60 °C) and these terms are used interchangeably. Where appropriate, quoted yields relate to solvates as obtained.

[W(≡CSnⁿBu₃)(CO)₂(Tp*)] (2). A solution of [W(≡CSnⁿBu₃)(CO)₂(Tp*)] (500 mg, 0.596 mmol), 1,2-dibromobenzene (142 mg, 0.60 mmol), [Pd(PPh₃)₄] (69 mg, 0.060 mmol) and [AuCl(SMe₂)] (17 mg, 0.058 mmol) in toluene (20 mL) was heated under reflux for 6 h, during which time the solution turned red-brown. 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 10% v/v dichloromethane/petroleum spirits (40–60 °C). A red-orange band was collected and the volatiles were removed under reduced pressure to give **2**·0.5(C₆H₁₄) as an orange solid (344 mg, 0.460 mmol, 77% based on **1**). IR (CH₂Cl₂, cm⁻¹): 1976s, 1881s ν_{CO}. UV-Vis (CH₂Cl₂): λ_{max} = 495 (ε = 72 L⁻¹mol⁻¹cm⁻¹). ¹H NMR (700 MHz, CDCl₃, 25 °C): δ_H = 2.36 (s, 3H, pzCH₃), 2.40 (s, 6H, pzCH₃), 2.47 (s, 9H, pzCH₃), 5.80 (s, 1H, pzCH), 5.89 (s, 2H, pzCH), 7.14 (t'd, ³J_{HH} = 7.7, ⁴J_{HH} = 1.6, 1H, C₆H₁₄), 7.25 (t'd, ³J_{HH} = 7.7, ⁴J_{HH} = 1.2, 1H, C₆H₁₄), 7.44 (d, ³J_{HH} = 7.8, 1H, C₆H₁₄), 7.46 (dd, ³J_{HH} = 7.7, ⁴J_{HH} = 1.6, 1H, C₆H₁₄). ¹³C{¹H} NMR (176 MHz, CDCl₃, 25 °C): δ_C = 12.7, 12.9, 15.4, 16.7 (pzCH₃), 106.4, 106.8 (pzCH), 121.8, 127.1, 128.2, 132.5, 133.8 (C₆H₁₄), 144.5, 145.2 (pzCCH₃), 148.9 (W≡CC, ²J_{CW} = 43), 152.1, 152.5 (pzCCH₃), 224.7 (CO, ¹J_{CW} = 165), 274.8 (W≡C, ¹J_{CW} = 195). MS (ESI, *m/z*): Found: 705.09804. Calcd for C₂₄H₂₇¹¹B⁷⁹BrN₆O₂¹⁸⁴W [M+H]⁺: 705.09758. Anal. Found: C, 43.44; H, 4.55; N, 11.22%. Calcd for C₂₄H₂₆BBⁿBrN₆O₂W·0.5(C₆H₁₄): C, 43.34; H, 4.45; N, 11.23%. ¹H NMR spectroscopy indicated the presence of ca. 0.5 equivalents of C₆H₁₄ of solvation was present in the sample used for elemental analysis.

Crystals suitable for structure determination were grown by slow evaporation of a CH₂Cl₂/ethanol mixture at 4 °C and proved to be a dichloromethane solvate. *Crystal data for* C₂₅H₂₈BBⁿBrCl₂N₆O₂W (*M* = 790.00 g·mol⁻¹): monoclinic, space group P2₁/c (no. 14), *a* = 16.3710(6), *b* = 10.3034(5), *c* = 17.1373(6) Å, β = 94.539(4)°, *V* = 2881.6(2) Å³, *Z* = 4, *T* = 150.0(1) K, μ(MoKα) = 5.615 mm⁻¹, *D*_{calc} = 1.821 g·cm⁻³, 15174 reflections measured (6.626° ≤ 2θ ≤ 57.82°), 6031 unique (*R*_{int} = 0.0304, *R*_{sigma} = 0.0399) which were used in all calculations. The final *R*₁ was 0.0384 (*I* > 2σ(*I*)) and *wR*₂ was 0.0999 (all data) for 353 refined parameters with 36 restraints. CCDC 1963667.

[1,3-((Tp*)(CO)₂W≡C)₂C₆H₄] (3). A solution of [W(≡CSnⁿBu₃)(CO)₂(Tp*)] (500 mg, 0.596 mmol), 1,3-dibromobenzene (68 mg, 0.29 mmol), [Pd(PPh₃)₄] (69 mg, 0.060 mmol) and [AuCl(SMe₂)] (17 mg, 0.058 mmol) in toluene (20 mL) was heated under reflux for 14 h, during which time the solution turned red-brown. 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 10% v/v dichloromethane/petroleum spirits (40–60 °C). An orange band was collected, the volatiles were removed under reduced pressure and the residue was recrystallized from CH₂Cl₂/ethanol to **3** as an orange solid (212 mg, 0.181 mmol, 61% based on **1**). IR (CH₂Cl₂, cm⁻¹): 1973s, 1884s ν_{CO}. UV-Vis (CH₂Cl₂): λ_{max} = 471 (ε = 308 L⁻¹mol⁻¹cm⁻¹). ¹H NMR (700 MHz, CDCl₃, 25 °C): δ_H = 2.36 (s, 6H, pzCH₃), 2.40 (s, 12H, pzCH₃), 2.47 (s, 6H, pzCH₃), 2.55 (s, 12H, pzCH₃), 5.80 (s, 2H, pzCH), 5.91 (s,

4H, pzCH), 7.23 (t', ³J_{HH} = 7.7, 1H, C₆H₄), 7.41 (d, ³J_{HH} = 7.7, 2H, C₆H₄), 7.51 (s, 1H, C₆H₄). ¹³C{¹H} NMR (176 MHz, CDCl₃, 25 °C): δ_C = 12.7, 12.8, 15.4, 16.7 (pzCH₃), 106.6, 106.7 (pzCH), 128.0, 128.2, 129.5 (C₆H₄), 144.5, 145.1 (pzCCH₃), 150.0 (W≡CC, ²J_{CW} = 43), 152.1, 152.5 (pzCCH₃), 223.9 (CO, ¹J_{CW} = 165), 277.3 (W≡C, ¹J_{CW} = 187). MS (ESI, *m/z*): Found: 1175.31955. Calcd for C₄₂H₄₉¹¹B²N₁₂O₄¹⁸⁴W₂ [M+H]⁺: 1175.32060. Anal. Found: C, 42.85; H, 3.98; N, 14.27. Calcd for C₄₂H₄₈B²N₁₂O₄W₂: C, 42.96; H, 4.12; N, 14.31%.

[1,4-((Tp*)(CO)₂W≡C)₂C₆H₄] (4). A solution of [W(≡CSnⁿBu₃)(CO)₂(Tp*)] (500 mg, 0.596 mmol), 1,4-diiodobenzene (96 mg, 0.29 mmol), [Pd(PPh₃)₄] (69 mg, 0.060 mmol) and [AuCl(SMe₂)] (17 mg, 0.058 mmol) in toluene (20 mL) was heated under reflux for 6 h, during which time the solution turned red-brown. 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 10% v/v dichloromethane/petroleum spirits (40–60 °C). A red band was collected and the volatiles were removed under reduced pressure to give **4** as a red solid (270 mg, 0.230 mmol, 77% based on **1**). IR (CH₂Cl₂, cm⁻¹): 1969s, 1884s ν_{CO}. UV-Vis (CH₂Cl₂): λ_{max} = 521 (ε = 1399 L⁻¹mol⁻¹cm⁻¹). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ_H = 2.34 (s, 6H, pzCH₃), 2.38 (s, 12H, pzCH₃), 2.44 (s, 6H, pzCH₃), 2.50 (s, 12H, pzCH₃), 5.78 (s, 2H, pzCH), 5.89 (s, 4H, pzCH), 7.31 (s, 4H, C₆H₄). ¹³C{¹H} NMR (176 MHz, CDCl₃, 25 °C): δ_C = 12.8, 12.8, 15.4, 16.8 (pzCH₃), 106.6, 106.8 (pzCH), 128.9 (C₆H₄{CH}), 144.6, 145.2 (pzCCH₃), 148.8 (W≡CC), 152.1, 152.5 (pzCCH₃), 224.3 (CO), 278.2 (W≡C). MS (ESI, *m/z*): Found: 1175.32070. Calcd for C₄₂H₄₉¹¹B²N₁₂O₄¹⁸⁴W₂ [M+H]⁺: 1175.32061. Anal. Found: C, 43.06; H, 4.22; N, 14.07. Calcd for C₄₂H₄₈B²N₁₂O₄W₂: C, 42.96; H, 4.12; N, 14.31%.

A crystal suitable for structure determination were grown by slow evaporation of a cyclohexane solution at 4 °C and proved to be a cyclohexane pentasolvate. *Crystal data for* C₇₂H₁₀₈B²N₁₂O₄W₂ (*M* = 1595.02 g·mol⁻¹): monoclinic, space group P2₁/c (no. 14), *a* = 13.2449(8), *b* = 18.7892(6), *c* = 16.1898(7) Å, β = 107.336(6)°, *V* = 3846.0(3) Å³, *Z* = 2, *T* = 150.0(1) K, μ(CuKα) = 5.851 mm⁻¹, *D*_{calc} = 1.377 g·cm⁻³, 11888 reflections measured (6.992° ≤ 2θ ≤ 141.64°), 7133 unique (*R*_{int} = 0.0320, *R*_{sigma} = 0.0624) which were used in all calculations. The final *R*₁ was 0.0485 (*I* > 2σ(*I*)) and *wR*₂ was 0.1246 (all data) for 444 refined parameters with 102 restraints. CCDC 1963668.

[1,3,5-((Tp*)(CO)₂W≡C)₃C₆H₃] (5). A solution of [W(≡CSnⁿBu₃)(CO)₂(Tp*)] (500 mg, 0.596 mmol), 1,3,5-tribromobenzene (60 mg, 0.19 mmol), [Pd(PPh₃)₄] (69 mg, 0.060 mmol) and [AuCl(SMe₂)] (17 mg, 0.058 mmol) in toluene (20 mL) was heated under reflux for 14 h, during which time the solution turned red-brown. 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 20% v/v dichloromethane/petroleum spirits (40–60 °C). A red band was collected and the volatiles were removed under reduced pressure to give **5** as a red solid (168 mg, 0.0975 mmol, 49% based on **1**). IR (CH₂Cl₂, cm⁻¹): 1974s, 1889s ν_{CO}. UV-Vis (CH₂Cl₂): λ_{max} = 498 (ε = 974 L⁻¹mol⁻¹cm⁻¹). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ_H = 2.35 (s, 9H, pzCH₃), 2.38 (s, 18H, pzCH₃), 2.46

(s, 9H, pzCH₃), 2.56 (s, 18H, pzCH₃), 5.79 (s, 3H, pzCH), 5.91 (s, 6H, pzCH), 7.46 (s, 3H, C₆H₄). ¹³C{¹H} NMR (101 MHz, CDCl₃, 25 °C): δ_c = 12.8, 12.8, 15.4, 16.9 (pzCH₃), 106.6, 106.7 (pzCH), 128.3 (C₆H₄{CH}), 144.5, 145.1 (pzCCH₃), 149.7 (W≡CC, ²J_{CW} = 43), 152.1, 152.5 (pzCCH₃), 223.7 (CO, ¹J_{CW} = 165), 276.2 (W≡C, ¹J_{CW} = 189). MS (ESI, *m/z*): Found: 1723.45549. Calcd for C₆₀H₇₀¹¹B₃N₁₈O₆¹⁸⁴W₃ [M+H]⁺: 1723.45334. Anal. Found: C, 41.97; H, 4.12; N, 14.61. Calcd for C₆₀H₆₉B₃N₁₈O₆W₃: C, 41.84; H, 4.04; N, 14.64%.

A crystal suitable for structure determination was grown by slow evaporation of a chloroform/ethanol mixture. *Crystal data* for C₆₀H₆₉B₃N₁₈O₆W₃ (*M* = 1722.31 g.mol⁻¹): monoclinic, space group P2₁/n (no. 14), *a* = 14.1626(3), *b* = 36.3631(7), *c* = 14.8716(3) Å, β = 90.019(2)°, *V* = 7658.8(3) Å³, *Z* = 4, *T* = 150.0(1) K, μ(CuKα) = 8.586 mm⁻¹, *D*_{calc} = 1.494 g.cm⁻³, 43467 reflections measured (7.68° ≤ 2θ ≤ 142.16°), 14567 unique (*R*_{int} = 0.0547, *R*_{sigma} = 0.0605) which were used in all calculations. The final *R*₁ was 0.0546 (*I* > 2σ(*I*)) and *wR*₂ was 0.1535 (all data) for 841 refined parameters with 1 restraint. CCDC 1963669.

[1-{(Tp*)}(CO)₂W≡C]C₁₀H₇ (6). A solution of [W(≡CSnⁿBu₃)(CO)₂(Tp*)] (400 mg, 0.477 mmol), 1-bromonaphthalene (80 μL, 0.57 mmol), [Pd(PPh₃)₄] (55 mg, 0.048 mmol) and [AuCl(SMe₂)] (14 mg, 0.048 mmol) in toluene (30 mL) was heated under reflux for 18 h. After this time, the solvent was removed under reduced pressure and the residue was subjected to column chromatography (40 x 3 cm silica gel column), eluting initially with petroleum spirits (40–60 °C) followed by 10% v/v CH₂Cl₂/petrol. A red band was collected and the volatiles were removed under reduced pressure to give **6** as an orange-red solid (210 mg, 0.311 mmol, 65% based on **1**). IR (CH₂Cl₂, cm⁻¹): 1973s, 1882s *v*_{CO}. UV-Vis (CH₂Cl₂): λ_{max} = 492 (ε = 35 L⁻¹mol⁻¹cm⁻¹). ¹H NMR (700 MHz, CDCl₃, 25 °C): δ_H = 2.41 (s, 6H, pzCH₃), 2.41 (s, 3H, pzCH₃), 2.47 (s, 6H, pzCH₃), 2.55 (s, 3H, pzCH₃), 5.85 (s, 1H, pzCH), 5.92 (s, 2H, pzCH), 7.41–7.48 (m, 3H, C₁₀H₇), 7.71 (d, ³J_{HH} = 7.3 Hz, 1H, C₁₀H₇), 7.86 (d, ³J_{HH} = 8.0 Hz, 2H, C₁₀H₇), 8.59 (d, ³J_{HH} = 8.0 Hz, 1H, C₁₀H₇). ¹³C{¹H} NMR (176 MHz, CDCl₃, 25 °C): δ_c = 12.7, 12.9, 15.4, 16.4 (pzCH₃), 106.5, 106.8 (pzCH), 125.6, 126.1, 126.2, 126.8, 127.8, 128.3, 130.8, 133.0, 133.5 (C₁₀H₇), 144.6, 145.2 (pzCCH₃), 146.2 (W≡CC, ²J_{CW} = 42), 152.2, 152.5 (pzCCH₃), 224.6 (CO, ¹J_{CW} = 166), 278.9 (W≡C, ¹J_{CW} = 189). MS (ESI, *m/z*): Found: 677.20227. Calcd for C₂₈H₃₀¹¹BN₆O₂¹⁸⁴W [M+H]⁺: 677.20271. Anal. Found: C, 49.65; H, 4.45; N, 12.34. Calcd for C₂₈H₂₉BN₆O₂W: C, 49.73; H, 4.32; N, 12.43%.

A crystal suitable for structure determination was grown by slow evaporation of a CH₂Cl₂/ethanol solution. *Crystal data* for C₂₈H₂₉BN₆O₂W (*M* = 676.23 g/mol): monoclinic, space group P2₁/c (no. 14), *a* = 7.95010(10) Å, *b* = 17.9153(3) Å, *c* = 19.4550(2) Å, β = 100.4370(10)°, *V* = 2725.10(6) Å³, *Z* = 4, *T* = 150.0(1) K, μ(CuKα) = 8.150 mm⁻¹, *D*_{calc} = 1.648 g/cm³, 8551 reflections measured (9.244° ≤ 2θ ≤ 141.868°), 5082 unique (*R*_{int} = 0.0183, *R*_{sigma} = 0.0292) which were used in all calculations. The final *R*₁ was 0.0294 (*I* > 2σ(*I*)) and *wR*₂ was 0.0765 (all data) for 353 refined parameters with 0 restraints. CCDC 1963670.

[2-{(Tp*)}(CO)₂W≡C]C₁₀H₇ (7). A solution of [W(≡CSnⁿBu₃)(CO)₂(Tp*)] (295 mg, 0.351 mmol), 2-bromonaphthalene (75 mg, 0.36 mmol), [Pd(PPh₃)₄] (41 mg, 0.035 mmol) and [AuCl(SMe₂)] (10 mg, 0.034 mmol) in toluene (20 mL) was heated under reflux for 16 h. After this time, the solvent was removed under reduced pressure and the residue was subjected to column chromatography (25 x 3 cm silica gel column), eluting initially with petroleum spirits (40–60 °C) followed by 20% v/v dichloromethane/petrol. A red band was collected and the volatiles were removed under reduced pressure to give an orange-red solid of pure **7** (165 mg, 0.244 mmol, 70% based on **1**). IR (CH₂Cl₂, cm⁻¹): 1973s, 1882s *v*_{CO}. UV-Vis (CH₂Cl₂): λ_{max} = 495 (ε = 262 L⁻¹mol⁻¹cm⁻¹). ¹H NMR (700 MHz, CDCl₃, 25 °C): δ_H = 2.36 (s, 3H, pzCH₃), 2.40 (s, 6H, pzCH₃), 2.49 (s, 3H, pzCH₃), 2.53 (s, 6H, pzCH₃), 5.80 (s, 1H, pzCH), 5.91 (s, 2H, pzCH), 7.43–7.49 (m, 2H, C₁₀H₇), 7.53 (dd, ³J_{HH} = 8.4 Hz, ⁴J_{HH} = 1.6 Hz, 1H, C₁₀H₇), 7.72 (d, ³J_{HH} = 8.4 Hz, 1H, C₁₀H₇), 7.76 (d, ³J_{HH} = 7.6 Hz, 1H, C₁₀H₇), 7.80 (d, ³J_{HH} = 7.9 Hz, 1H, C₁₀H₇), 7.92 (s, 1H, C₁₀H₇). ¹³C{¹H} NMR (176 MHz, CDCl₃, 25 °C): δ_c = 12.8, 12.8, 15.4, 16.7 (pzCH₃), 106.6, 106.8 (pzCH), 126.5, 126.6, 126.7, 127.7, 128.0, 128.2, 128.9, 132.5, 133.1 (C₁₀H₇), 144.6, 145.2 (pzCCH₃), 147.9 (W≡CC, ²J_{CW} = 43), 152.2, 152.5 (pzCCH₃), 224.3 (CO, ¹J_{CW} = 165), 278.7 (W≡C, ¹J_{CW} = 187). MS (ESI, *m/z*): Found: 676.1947. Calcd for C₂₈H₂₉¹¹BN₆O₂¹⁸⁴W [M-e]⁺: 676.1954. Anal. Found: C, 49.66; H, 4.43; N, 12.32. Calcd for C₂₈H₂₉BN₆O₂W: C, 49.73; H, 4.32; N, 12.43%.

A crystal suitable for structure determination was grown by slow evaporation of a CH₂Cl₂/acetonitrile solution. *Crystal data* for C₂₈H₂₉BN₆O₂W (*M* = 676.23 g.mol⁻¹): monoclinic, space group P2₁/n (no. 14), *a* = 7.9431(4), *b* = 17.7548(8), *c* = 19.9617(9) Å, β = 99.821(4)°, *V* = 2773.9(2) Å³, *Z* = 4, *T* = 150.0(1) K, μ(CuKα) = 8.007 mm⁻¹, *D*_{calc} = 1.619 g.cm⁻³, 7988 reflections measured (8.992° ≤ 2θ ≤ 133.182°), 4854 unique (*R*_{int} = 0.0255, *R*_{sigma} = 0.0446) which were used in all calculations. The final *R*₁ was 0.0589 (*I* > 2σ(*I*)) and *wR*₂ was 0.1476 (all data) for 353 refined parameters with 0 restraints. CCDC 1963671.

[9-{(Tp*)}(CO)₂W≡C]C₁₄H₉ (8). A solution of [W(≡CSnⁿBu₃)(CO)₂(Tp*)] (400 mg, 0.477 mmol), 9-bromophenanthrene (129 mg, 0.502 mmol), [Pd(PPh₃)₄] (55 mg, 0.048 mmol) and [AuCl(SMe₂)] (14 mg, 0.048 mmol) in toluene (30 mL) was heated under reflux for 18 h. After this time, the solvent was removed under reduced pressure and the residue was subjected to column chromatography (25 x 3 cm silica gel column), eluting initially with petroleum spirits (40–60 °C) followed by 25% v/v CH₂Cl₂/petrol. A red band was collected and the volatiles were removed under reduced pressure to give **8**-(CH₂Cl₂)_{0.5} as a red solid (310 mg, 0.403 mmol, 85% based on **1**). IR (CH₂Cl₂, cm⁻¹): 1973s, 1883s *v*_{CO}. UV-Vis (CH₂Cl₂): λ_{max} = 498 (ε = 28 L⁻¹mol⁻¹cm⁻¹). ¹H NMR (600 MHz, CDCl₃, 25 °C): δ_H = 2.38 (s, 6H, pzCH₃), 2.38 (s, 3H, pzCH₃), 2.44 (s, 6H, pzCH₃), 2.53 (s, 3H, pzCH₃), 5.82 (s, 1H, pzCH), 5.90 (s, 2H, pzCH), 7.51 (t', ³J_{HH} = 7.8, 1H, C₁₄H₉), 7.57 (t', ³J_{HH} = 7.4, 1H, C₁₄H₉), 7.60 (t', ³J_{HH} = 7.4, 1H, C₁₄H₉), 7.66 (t', ³J_{HH} = 7.7, 1H, C₁₄H₉), 7.92 (d, ³J_{HH} = 7.9 Hz, 1H, C₁₄H₉), 7.95 (s, 1H, C₁₄H₉), 8.58 (d, ³J_{HH} = 8.3, 1H, C₁₄H₉), 8.66 (d, ³J_{HH} = 8.3, 2H, C₁₄H₉). ¹³C{¹H} NMR (151 MHz, CDCl₃, 25 °C): δ_c = 12.8, 12.9, 15.5, 16.4 (pzCH₃), 106.6, 106.8

(pzCH), 122.7, 122.8, 126.8, 126.8, 127.1, 127.1, 127.3, 129.0, 130.0, 130.2, 131.3, 131.9, 132.1 (C₁₄H₉), 144.5 (W≡CC, ²J_{CW} = 40), 144.6, 145.2, 152.3, 152.5 (pzCCH₃), 224.7 (CO, ¹J_{CW} = 166), 278.8 (W≡C, ¹J_{CW} = 188). MS (ESI, *m/z*): Found: 727.21706. Calcd for C₃₂H₃₂¹¹BN₆O₂¹⁸⁴W [M+H]⁺: 727.21836. Anal. Found: C, 50.70; H, 4.41; N, 10.17. Calcd for C₃₂H₃₁BN₆O₂W·(CH₂Cl₂)_{0.5}: C, 50.78; H, 4.20; N, 10.93%. ¹H NMR spectroscopy indicated the presence of ca. 0.5 equivalents of CH₂Cl₂ of solvation was present in the sample used for elemental analysis.

Crystals suitable for structure determination were grown by slow evaporation of a CH₂Cl₂/methanol solution at 4 °C and was found to be a dichloromethane hemisolvate. *Crystal data for* C_{32.5}H₃₂BCIN₆O₂W (*M* = 768.75 g·mol⁻¹): monoclinic, space group I2/a (no. 15), *a* = 37.5930(3), *b* = 10.45550(10), *c* = 32.1962(3) Å, *β* = 96.4830(10)°, *V* = 12573.9(2) Å³, *Z* = 16, *T* = 150.0(1) K, *μ*(CuKα) = 7.911 mm⁻¹, *D*_{calc} = 1.624 g·cm⁻³, 32434 reflections measured (7.672° ≤ 2θ ≤ 133.196°), 11119 unique (*R*_{int} = 0.0276, *R*_{sigma} = 0.0286) which were used in all calculations. The final *R*₁ was 0.0295 (*I* > 2σ(*I*)) and *wR*₂ was 0.0732 (all data) for 804 refined parameters with 0 restraints. CCDC 1963673.

[9-{(Tp*)(CO)₂W≡C}C₁₄H₉] (9). A solution of [W(≡CSnⁿBu₃)(CO)₂(Tp*)] (400 mg, 0.477 mmol), 9-bromoanthracene (125 mg, 0.486 mmol), [Pd(PPh₃)₄] (55 mg, 0.048 mmol) and [AuCl(SMe₂)] (14 mg, 0.048 mmol) in toluene (20 mL) was heated under reflux for 16 h. After this time, the solvent was removed under reduced pressure and the residue was subjected to column chromatography (25 x 3 cm silica gel column), eluting initially with petroleum spirits (40–60 °C) followed by 25% v/v CH₂Cl₂/petrol. A yellow-green band was collected and the volatiles were removed under reduced pressure to give **9**·(CH₂Cl₂)_{0.33} as a yellow-green solid (133 mg, 0.176 mmol, 37% based on **1**). IR (CH₂Cl₂, cm⁻¹): 1973s, 1884s *v*_{CO}. UV-Vis (CH₂Cl₂): λ_{max} = 418 (ε = 2895 L⁻¹mol⁻¹cm⁻¹), 443 (ε = 6089 L⁻¹mol⁻¹cm⁻¹), 470 (ε = 7408 L⁻¹mol⁻¹cm⁻¹). ¹H NMR (700 MHz, CDCl₃, 25 °C): δ_H = 2.25 (s, 6H, pzCH₃), 2.40 (s, 3H, pzCH₃), 2.47 (s, 6H, pzCH₃), 2.56 (s, 3H, pzCH₃), 5.83 (s, 1H, pzCH), 5.86 (s, 2H, pzCH), 7.40 (br, 2H, C₁₄H₉), 7.36–7.53 (br, 2H, C₁₄H₉), 8.50 (s, 1H, C₁₄H₉), 8.64–9.00 (br, 2H, C₁₄H₉). ¹H NMR (700 MHz, CDCl₃, -50 °C): δ_H = 2.21 (s, 6H, pzCH₃), 2.38 (s, 3H, pzCH₃), 2.45 (s, 6H, pzCH₃), 2.55 (s, 3H, pzCH₃), 5.84 (s, 1H, pzCH), 5.86 (s, 2H, pzCH), 7.23 (t', ³J_{HH} = 7.3, 1H, C₁₄H₉), 7.34 (t', ³J_{HH} = 7.3, 1H, C₁₄H₉), 7.51 (t', ³J_{HH} = 7.3, 1H, C₁₄H₉), 7.76 (t', ³J_{HH} = 7.3, 1H, C₁₄H₉), 7.98 (d, ³J_{HH} = 7.8, 1H, C₁₄H₉), 8.05 (d, ³J_{HH} = 8.0, 1H, C₁₄H₉), 8.43 (d, ³J_{HH} = 8.0, 1H, C₁₄H₉), 8.54 (s, 1H, C₁₄H₉), 9.17 (d, ³J_{HH} = 8.0, 1H, C₁₄H₉). ¹³C{¹H} NMR (176 MHz, CDCl₃, -50 °C): δ_C = 12.9, 13.2, 15.6, 16.2 (pzCH₃), 106.2, 106.7 (pzCH), 125.4, 125.8, 126.0, 126.9, 127.0 (2C), 127.5, 128.8, 128.9, 131.0, 131.1, 131.5, 134.2 (C₁₄H₉), 140.4 (W≡CC), 144.5, 145.2 (pzCCH₃), 152.0, 152.2 (pzCCH₃), 227.0 (CO), 280.1 (W≡C). MS (ESI, *m/z*): Found: 727.21805. Calcd for C₃₂H₃₂¹¹BN₆O₂¹⁸⁴W [M+H]⁺: 727.21836. Anal. Found: C, 51.43; H, 4.12; N, 11.06. Calcd for C₃₂H₃₁BN₆O₂W·(CH₂Cl₂)_{0.33}: C, 51.46; H, 4.23; N, 11.14%. ¹H NMR spectroscopy indicated the presence of ca. 0.33 equivalents of CH₂Cl₂ of solvation was present in the sample used for elemental analysis.

Crystals suitable for structure determination were grown by slow evaporation of a CH₂Cl₂/acetonitrile solution at 4 °C and was found to be an acetonitrile solvate. *Crystal data for* C₃₄H₃₄BN₇O₂W (*M* = 767.34 g·mol⁻¹): monoclinic, space group P2₁/n (no. 14), *a* = 10.2667(4), *b* = 23.1598(12), *c* = 13.5771(6) Å, *β* = 92.406(4)°, *V* = 3225.4(3) Å³, *Z* = 4, *T* = 150.0(1) K, *μ*(MoKα) = 3.624 mm⁻¹, *D*_{calc} = 1.580 g·cm⁻³, 15366 reflections measured (6.962° ≤ 2θ ≤ 50.052°), 5678 unique (*R*_{int} = 0.0290, *R*_{sigma} = 0.0386) which were used in all calculations. The final *R*₁ was 0.0432 (*I* > 2σ(*I*)) and *wR*₂ was 0.0802 (all data) for 417 refined parameters with 36 restraints. CCDC 1963672.

[9,10-{(Tp*)(CO)₂W≡C}C₁₄H₈] (10). A solution of [W(≡CSnⁿBu₃)(CO)₂(Tp*)] (630 mg, 0.751 mmol), 9,10-dibromoanthracene (121 mg, 0.360 mmol), [Pd(PPh₃)₄] (83 mg, 0.072 mmol) and [AuCl(SMe₂)] (23 mg, 0.078 mmol) in toluene (30 mL) was heated under reflux for 17 h. After this time, the solvent was removed under reduced pressure and the residue was subjected to column chromatography (25 x 3 cm silica gel column), eluting initially with petroleum spirits (40–60 °C), followed thereafter by CH₂Cl₂, and finally with CHCl₃. A red-purple band was collected and the volatiles were removed under reduced pressure to give **10**·2.5(CHCl₃) as a dark red-purple solid (50 mg, 0.032 mmol, 9% based on **1**). IR (CH₂Cl₂, cm⁻¹): 1972s, 1887s *v*_{CO}. UV-Vis (CH₂Cl₂): λ_{max} = 492 (ε = 14500 L⁻¹mol⁻¹cm⁻¹), 525 (ε = 16700 L⁻¹mol⁻¹cm⁻¹), 565 (ε = 14100 L⁻¹mol⁻¹cm⁻¹). ¹H NMR (700 MHz, CDCl₃, 25 °C): δ_H = 2.25 (s, 12H, pzCH₃), 2.39 (s, 6H, pzCH₃), 2.47 (s, 12H, pzCH₃), 2.53 (s, 6H, pzCH₃), 5.82 (s, 2H, pzCH), 5.85 (s, 4H, pzCH), 7.20–9.20 (br m, 8H, C₁₄H₈). ¹H NMR (700 MHz, CDCl₃, -50 °C): δ_H = 2.20 (s, 6H, pzCH₃), 2.23 (s, 6H, pzCH₃), 2.39 (s, 6H, pzCH₃), 2.46 (s, 12H, pzCH₃), 2.52 (s, 6H, pzCH₃), 5.84 (s, 4H, pzCH), 5.87 (s, 2H, pzCH), 7.06 (br, 1H, C₁₄H₈), 7.51 (br, 1H, C₁₄H₈), 7.59 (br, 1H, C₁₄H₈), 7.81 (br, 1H, C₁₄H₈), 8.42 (br, 1H, C₁₄H₈), 8.49 (br, 1H, C₁₄H₈), 9.14 (br, 1H, C₁₄H₈), 9.27 (br, 1H, C₁₄H₈). ¹³C{¹H} NMR (176 MHz, CDCl₃, 25 °C): δ_C = 12.9, 13.2, 15.6, 16.3 (pzCH₃), 106.2, 106.7 (pzCH), 126.6, 127.1, 127.4, 130.3, 132.8 (C₁₄H₈), 144.5, 145.3, 152.0, 152.2 (pzCCH₃). Poor solubility in all common organic solvents, including CDCl₃, and broadening of signals prevented unequivocal assignment of the remaining carbon resonances. MS (ESI, *m/z*): Found: 1274.3453. Calcd for C₅₀H₅₂¹¹B₂N₁₂O₄¹⁸⁴W₂ [M-e]⁺: 1274.3463. Anal. Found: C, 40.12; H, 4.12; N, 10.13%. Calcd for C₅₀H₅₂B₂N₁₂O₄W₂·2.5(CHCl₃): C, 40.09; H, 3.49; N, 10.69%.

A crystal suitable for structure determination was grown by slow evaporation of a CHCl₃/cyclohexane solution at 4 °C. *Crystal data for* C₅₀H₅₂B₂N₁₂O₄W₂ (*M* = 1274.35 g·mol⁻¹): monoclinic, space group P2₁/c (no. 14), *a* = 13.8341(4), *b* = 10.1106(3), *c* = 20.5773(6) Å, *β* = 106.771(3)°, *V* = 2755.75(15) Å³, *Z* = 2, *T* = 150.0(1) K, *μ*(CuKα) = 8.020 mm⁻¹, *D*_{calc} = 1.536 g·cm⁻³, 9063 reflections measured (8.976° ≤ 2θ ≤ 141.718°), 5147 unique (*R*_{int} = 0.0361, *R*_{sigma} = 0.0606) which were used in all calculations. The final *R*₁ was 0.0350 (*I* > 2σ(*I*)) and *wR*₂ was 0.0850 (all data) for 326 refined parameters with 0 restraints. CCDC 1963674.

[1,3,6,8-{(Tp*)(CO)₂W≡C}C₁₆H₆] (11). A solution of [W(≡CSnⁿBu₃)(CO)₂(Tp*)] (750 mg, 0.894 mmol), 1,3,6,8-

tetrabromopyrene (90 mg, 0.174 mmol), [Pd(PPh₃)₄] (80 mg, 0.070 mmol) and [AuCl(SMe₂)] (21 mg, 0.070 mmol) in toluene (30 mL) was heated under reflux for 21 h. After this time, the solvent was removed under reduced pressure and the residue was subjected to column chromatography (35 x 3 cm silica gel column), eluting initially with petroleum spirits (40–60 °C) followed by 50% v/v CH₂Cl₂/petrol. A purple band was collected and the volatiles were removed under reduced pressure to give **11** as a dark purple solid (118 mg, 0.049 mmol, 28% based on **1**). IR (CH₂Cl₂, cm⁻¹): 1975s, 1889s ν_{CO}. UV-Vis (CH₂Cl₂): λ_{max} = 407 (ε = 27900 L⁻¹mol⁻¹cm⁻¹), 530 (ε = 13600 L⁻¹mol⁻¹cm⁻¹), 568 (ε = 21500 L⁻¹mol⁻¹cm⁻¹). ¹H NMR (600 MHz, CDCl₃, 25 °C): δ_H = 2.36 (s, 24H, pzCH₃), 2.37 (s, 12H, pzCH₃), 2.42 (s, 24H, pzCH₃), 2.54 (s, 12H, pzCH₃), 5.81 (s, 4H, pzCH), 5.87 (s, 8H, pzCH), 8.03 (s, 2H, C₁₆H₆), 8.53 (s, 4H, C₁₆H₆). ¹³C{¹H} NMR (151 MHz, CDCl₃, 25 °C): δ_C = 12.8, 12.9, 15.7, 16.5 (pzCH₃), 106.7 (pzCH), 124.6, 126.7, 131.1, 133.2 (C₁₆H₆), 143.3 (W≡CC), 144.5, 145.1 (pzCCH₃), 152.3, 152.7 (pzCCH₃), 224.1 (CO), 278.0 (W≡C). MS (ESI, *m/z*): Found: 2395.61710. Calcd for C₈₈H₉₅¹¹B₄N₂₄O₈¹⁸⁴W₄ [M+H]⁺: 2395.62434. Anal. Found: C, 44.04; H, 3.98; N, 13.99. Calcd for C₈₈H₉₄B₄N₂₄O₈W₄: C, 44.14; H, 3.96; N, 14.04%.

Crystals suitable for structure determination were grown by slow evaporation of a CH₂Cl₂/cyclohexane solution at 4 °C and was found to be a cyclohexane pentasolvate, although two of these were found to be highly disordered and were removed from the refinement using the solvent mask implementation in Olex².⁸ These are not included in the molecular weight calculations. *Crystal data* for C₁₀₆H₁₃₀B₄N₂₄O₈W₄ (*M* = 2646.97 g.mol⁻¹): monoclinic, space group I2/m (no. 12), *a* = 23.8078(8), *b* = 25.2600(6), *c* = 25.4589(9) Å, β = 114.840(4)°, *V* = 13894.1(9) Å³, *Z* = 4, *T* = 150.0(1) K, μ(CuKα) = 6.379 mm⁻¹, *D*_{calc} = 1.265 g.cm⁻³, 36913 reflections measured (7.654° ≤ 2θ ≤ 141.49°), 13503 unique (*R*_{int} = 0.0293, *R*_{sigma} = 0.0321) which were used in all calculations. The final *R*₁ was 0.0523 (*I* > 2σ(*I*)) and *wR*₂ was 0.1497 (all data) for 687 refined parameters with 0 restraints. CCDC 1963675.

Selected crystallographic data

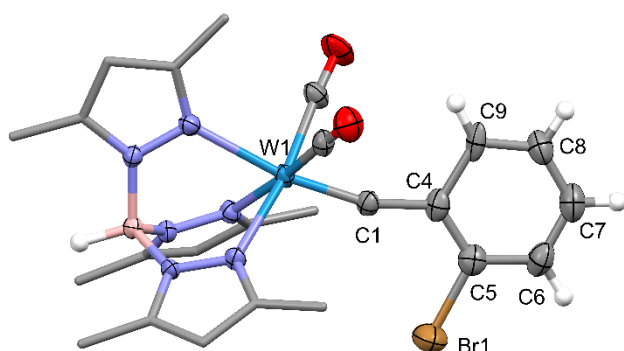


Figure S1. Molecular structure of **2** in a crystal of 2-CH₂Cl₂ showing 50% displacement ellipsoids. Pyrazolyl groups are simplified and solvent is not shown for clarity. Selected distances [Å] and angles [°]: W1–C1 1.826(6), C1–C4 1.440(8), C5–Br1 1.872(7), W1–C1 C4 162.6(5).

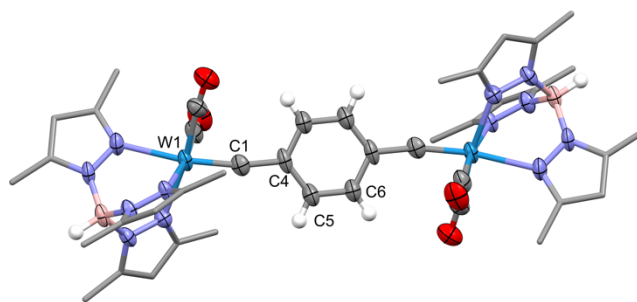


Figure S2. Molecular structure of **4** in a crystal of 4-5C₆H₁₂ showing 50% displacement ellipsoids. Only one-half of the molecule is unique with a crystallographic mirror plane present through the benzene ring. Pyrazolyl groups are simplified and solvent is not shown for clarity. Selected distances [Å] and angles [°]: W1–C1 1.799(6), C1–C4 1.462(8), W1–C1–C4 169.2(6).

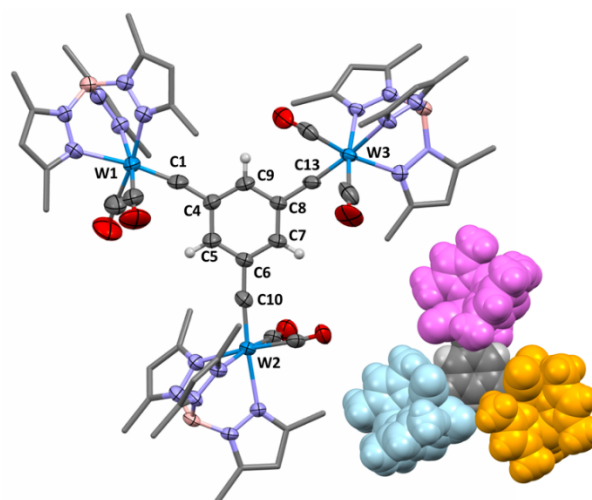


Figure S3. Molecular structure of **5** in a crystal (50% displacement ellipsoids, pyrazolyl groups simplified and most hydrogen atoms omitted for clarity). Selected distances [Å] and angles [°]: W1–C1 1.832(9), C1–C4 1.455(11), W2–C10 1.822(8), C10–C6 1.450(11), W3–C13 1.822(8), C13–C8 1.458(10), W1–C1–C4 166.7(8), W2–C10–C6 174.3(7), W3–C13–C8 164.9(6). Inset: space-filling representation with each 'W(=C)(CO)₂(Tp*)' group distinctly coloured.

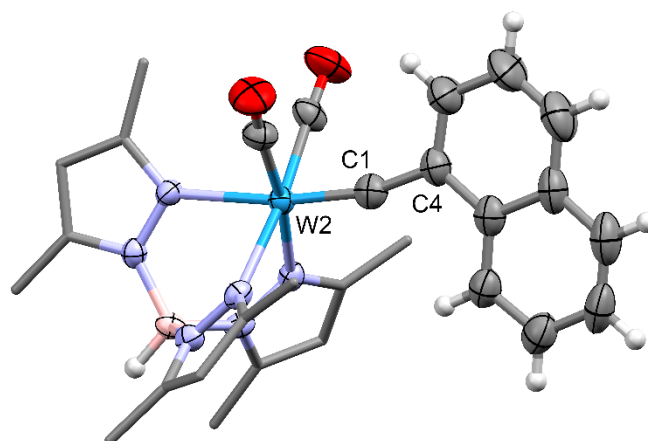


Figure S4. Molecular structure of **6** showing 50% displacement ellipsoids. Pyrazolyl groups are simplified for clarity. Selected distances [Å] and angles [°]: W1–C1 1.823(4), C1–C4 1.445(6), W1–C1–C4 165.9(4).

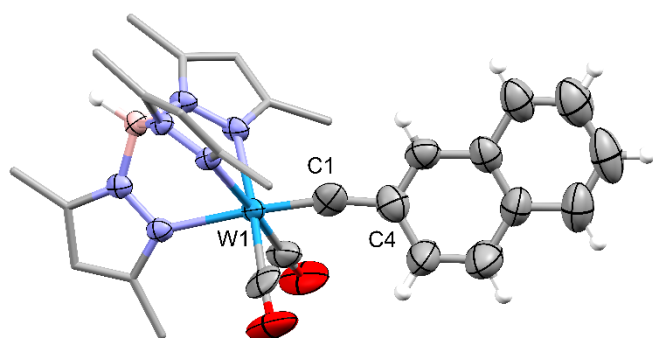


Figure S5. Molecular structure of **7** showing 50% displacement ellipsoids. Pyrazolyl groups are simplified for clarity. Selected distances [Å] and angles [°]: W1–C1 1.817(13), C1–C4 1.455(18), W1–C1–C4 166.9(11).

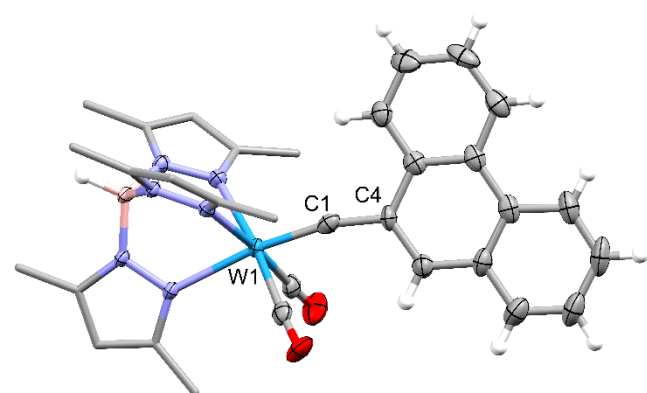


Figure S6. Molecular structure of **8** in a crystal of $8 \cdot \frac{1}{2} \text{CH}_2\text{Cl}_2$ showing 50% displacement ellipsoids (one of two crystallographically independent molecules). Pyrazolyl groups are simplified and solvent is not shown for clarity. Selected distances [Å] and angles [°]: W1–C1 1.825(4), C1–C4 1.437(5), W1–C1–C4 167.0(3); W2–C34 1.816(4), C34–C37 1.445(5), W2–C34–C37 172.2(3).

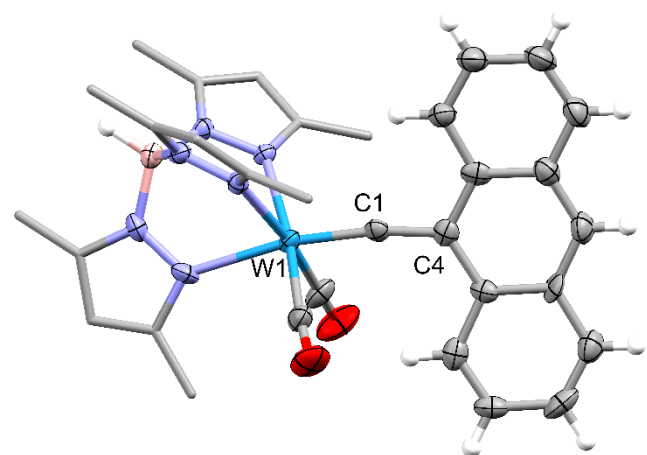


Figure S7. Molecular structure of **9** in a crystal of $9 \cdot \text{CH}_3\text{CN}$ showing 50% displacement ellipsoids. Pyrazolyl groups are simplified and solvent is not shown for clarity. Selected distances [Å] and angles [°]: W1–C1 1.834(6), C1–C4 1.433(8), W1–C1–C4 171.1(5).

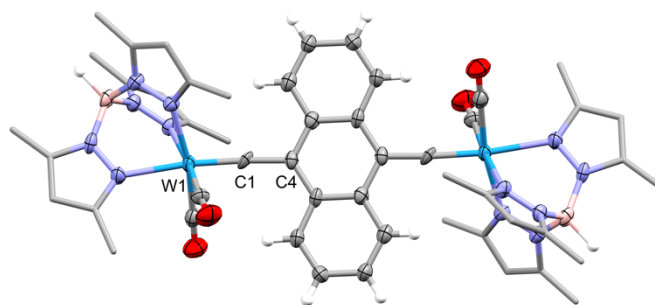


Figure S8. Molecular structure of **10** showing 50% displacement ellipsoids. Only one-half of the molecule is crystallographically unique with a crystallographic mirror plane orthogonal to the anthracene plane and running through the centre of all three anthracene rings. Pyrazolyl groups are simplified for clarity. Selected distances [Å] and angles [°]: W1–C1 1.792(5), C1–C4 1.466(7), W1–C1–C4 176.6(4).

Comments on the stability, optical and electronic properties of complexes **2–11**

All the compounds reported herein are stable to air and moisture for at least one week in CDCl_3 solutions (monitored by ^1H NMR spectroscopy) and several months in the solid state. We have not observed reactions with any common organic solvents.

The UV-Vis spectra of **2–11** have been obtained. Complexes **2–8** are generally orange and red solids and exhibit weak absorption in the visible region at $\lambda_{\text{max}} = 471\text{--}521$ nm. The yellow-green, singly substituted anthracene complex **9** exhibits two strong absorbances, at $\lambda_{\text{max}} = 443$ and 470 nm, intensely red-purple, disubstituted anthracene complex **10** has several broad, strong absorptions below 600 nm ($\lambda_{\text{max}} = 492, 525, 565$ nm), and finally the tetrasubstituted complex **11** absorbs strongly at $\lambda_{\text{max}} = 407, 530, 568$ nm, providing its deep, royal purple colour.

Fluorescence has been noted for a number of arylcarbyne complexes,⁹ but is seemingly rather variable, being highly dependent on the nature of the ancillary ligands and carbyne substituent, and readily quenched by addition of electron acceptors. The related 2-naphthylcarbyne complex $[\text{W}(\equiv\text{CC}_{10}\text{H}_7-2)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ absorbs moderately strongly in the UV (at 348 nm) and weakly in the visible region at 490 nm, with only very weak emission being observed beyond 780 nm.¹⁰ A number of Mo and W arylcarbynes with tripodal poly(pyridyl) ligands are strongly red emissive with 330 nm excitation.^{9e,9f} Confounding expectations, excitation of the complexes prepared herein at 350 nm or their visible-region λ_{max} values (see Table 1) either did not give rise to any observable emission below 800 nm, or these were too broad and weak to be convincingly identified. This was an especially surprising (and rather disappointing) result given the typically strong emission observed for the polycyclic aromatic hydrocarbon appendages. We credit this to quenching by the ‘ $\text{W}(\text{CO})_2(\text{Tp}^*)$ ’ fragment and, in light of the previously noted dependence on the identity of ancillary ligands, expect that co-ligand variation would provide a worthy avenue of future investigation.

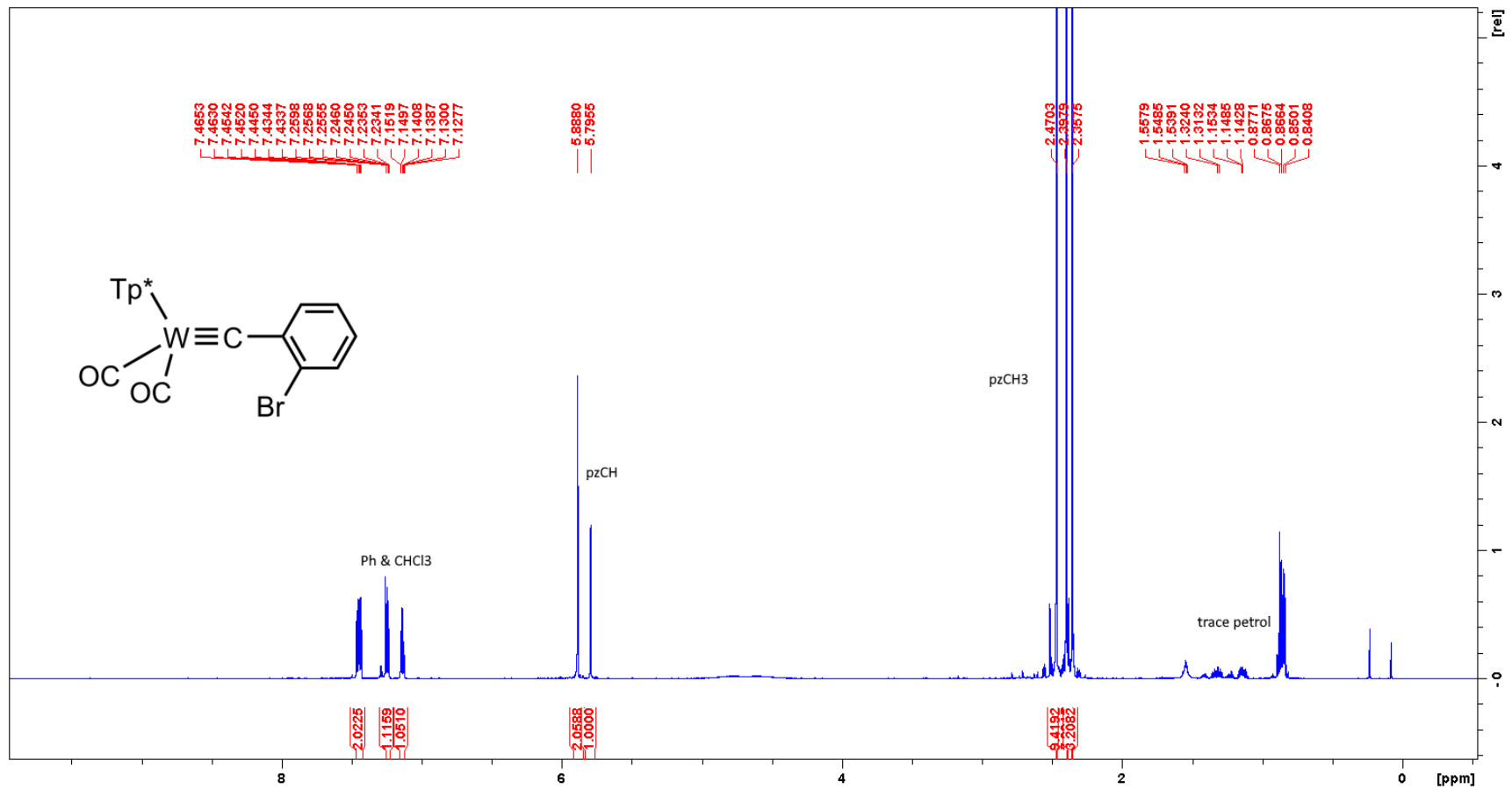
The cyclic voltammograms of **2–11** have also been obtained. The monometallic complexes **2, 6–9** exhibit one simple, reversible oxidation event ($E_{1/2} = 0.63\text{--}0.72$ V) related to

tungsten. Since for simple carbynes of the form $[W(\equiv CR)(CO)_2(Tp^*)]$ the HOMO is the metal-based orbital associated with retrodonative carbonyl binding,¹¹ it is orthogonal to the $W\equiv C$ bond and therefore accordingly the oxidation potential is unlikely to be directly responsive to minor variations in carbyne substituents. The polysubstituted complexes **3–5**, **10** and **11** feature two or more events with significant overlap/broadening which due to rather poor resolution are cautiously identified at $E_{1/2} = 0.61–0.74$ V for the first oxidation and 0.73–0.88 V for the subsequent processes. While, due to poor separation of oxidation potentials, these data are given with some reservations, the results nevertheless indicate that there must be at least a small degree of communication occurring between tungsten centres.

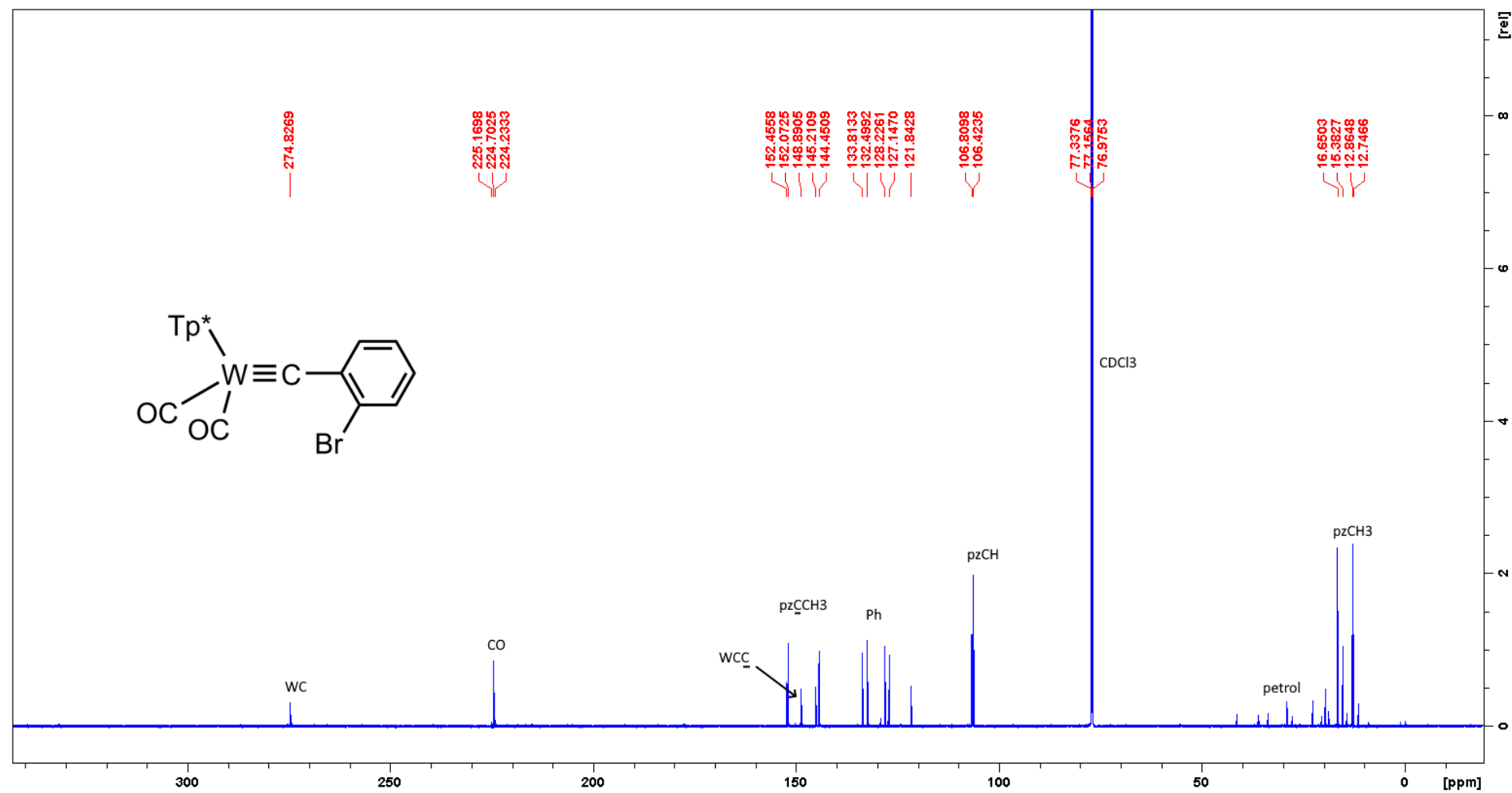
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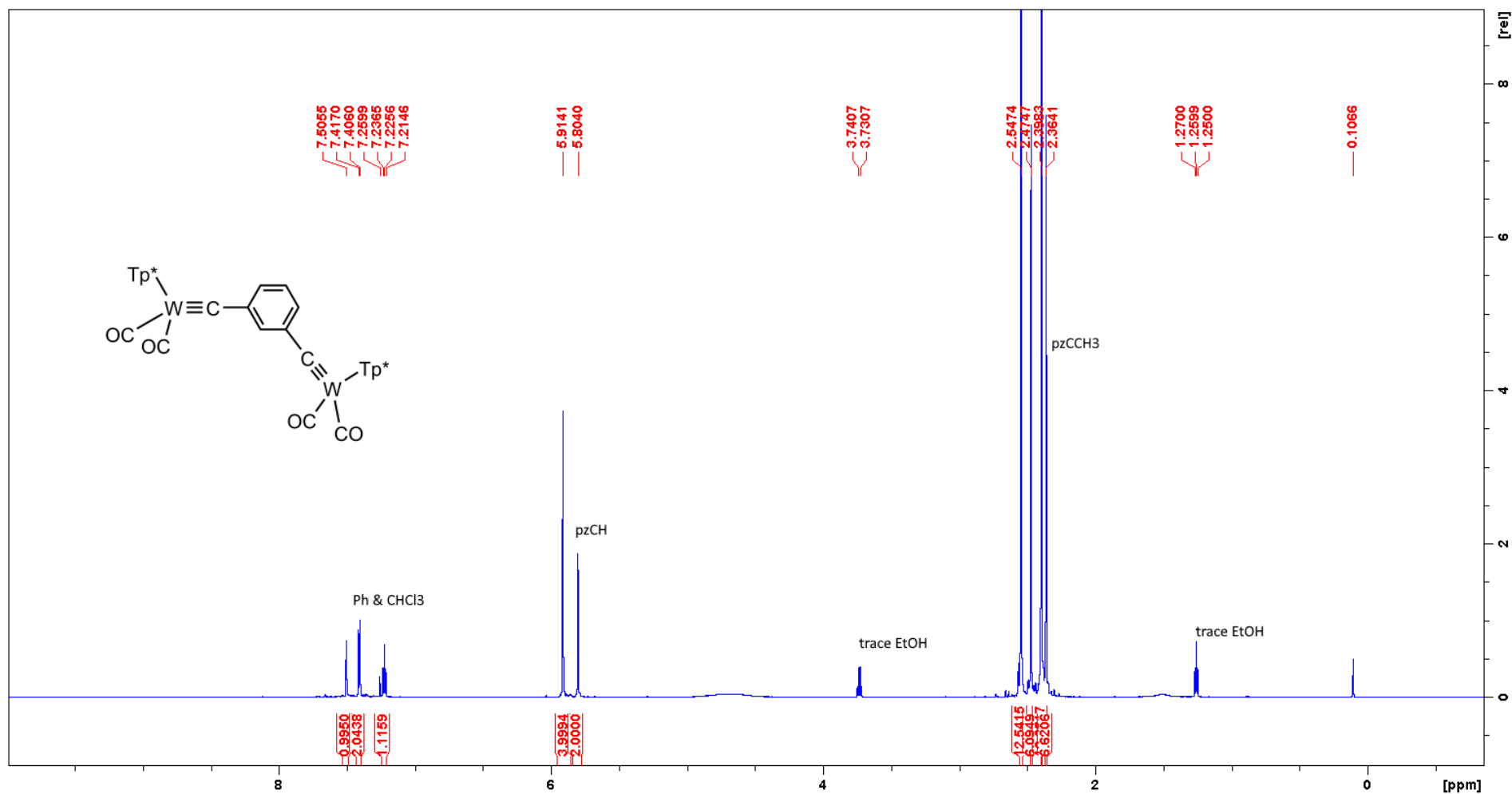
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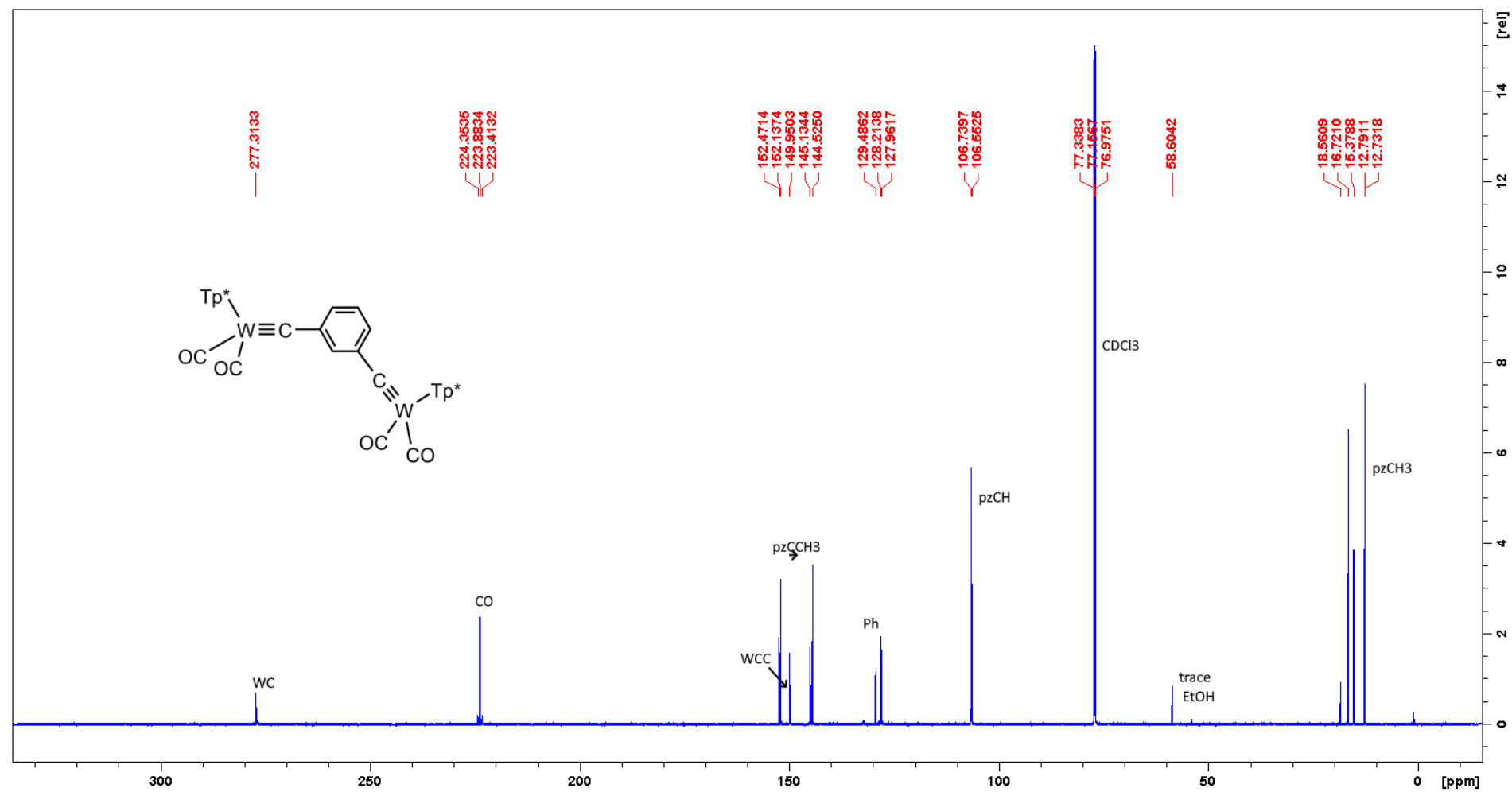
^1H NMR spectrum (700 MHz, CDCl_3 , 298 K) for $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Br-2})(\text{CO})_2(\text{Tp}^*)] \cdot 2 \cdot 0.5(\text{C}_6\text{H}_{14})$.



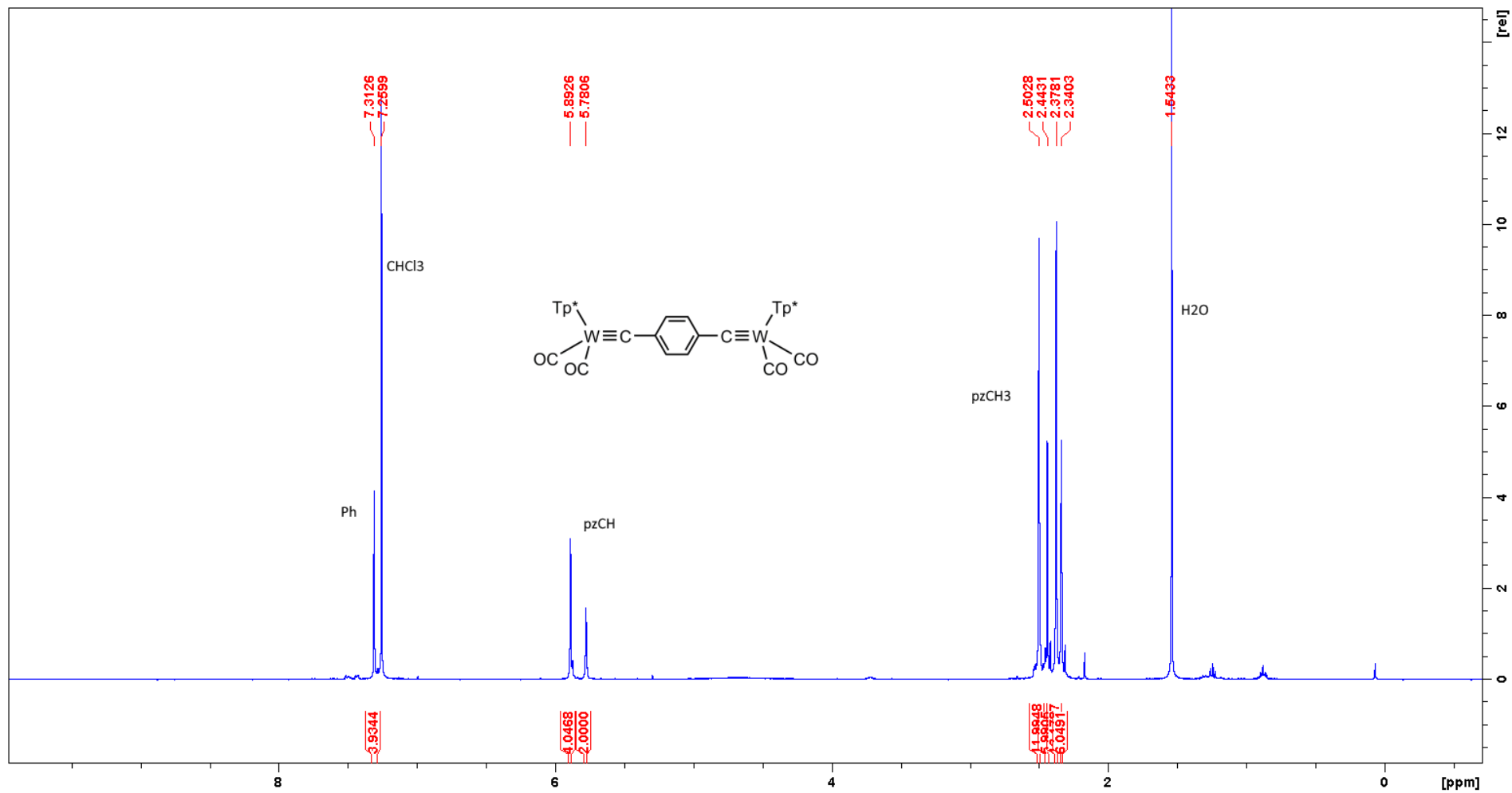
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (176 MHz, CDCl_3 , 298 K) for $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Br-2})(\text{CO})_2(\text{Tp}^*)] \cdot 2 \cdot 0.5(\text{C}_6\text{H}_{14})$.



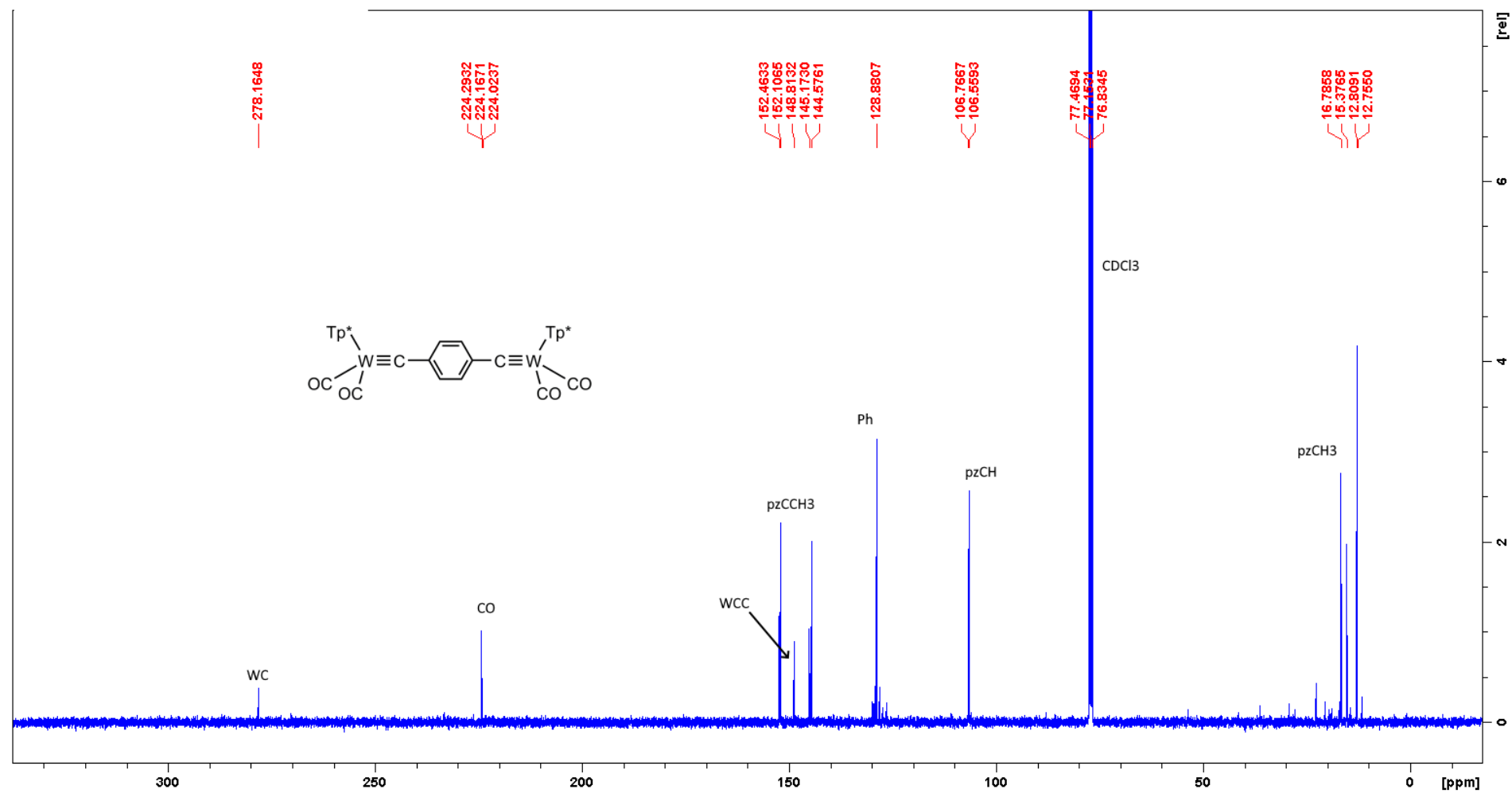
1H NMR spectrum (700 MHz, $CDCl_3$, 298 K) for $[1,3-\{(Tp^*)(CO)_2W \equiv C\}_2C_6H_4]$ (**3**).



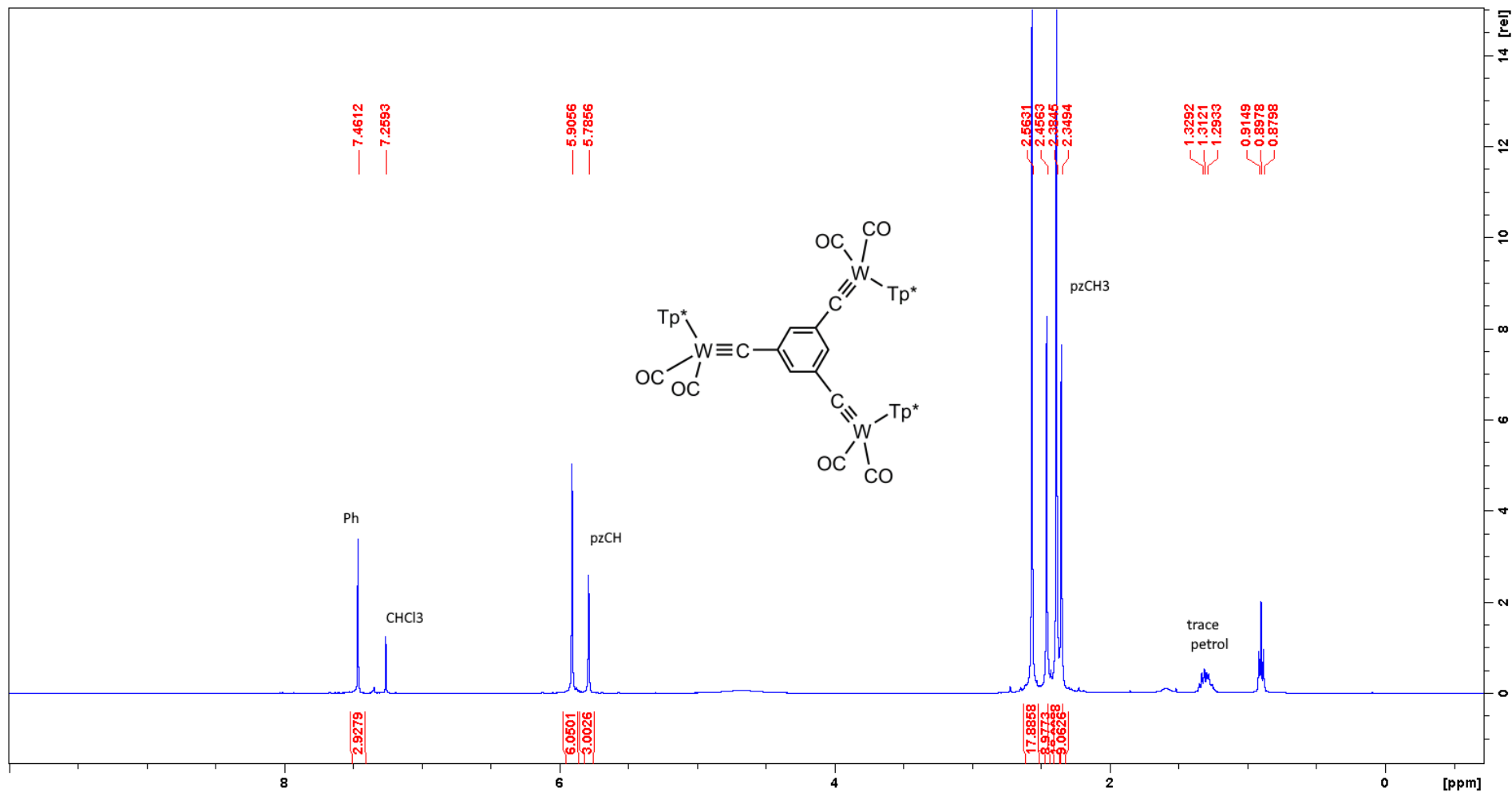
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (176 MHz, CDCl_3 , 298 K) for $[1,3-((\text{Tp}^*)(\text{CO})_2)\text{W}\equiv\text{C}]_2\text{C}_6\text{H}_4$ (3).



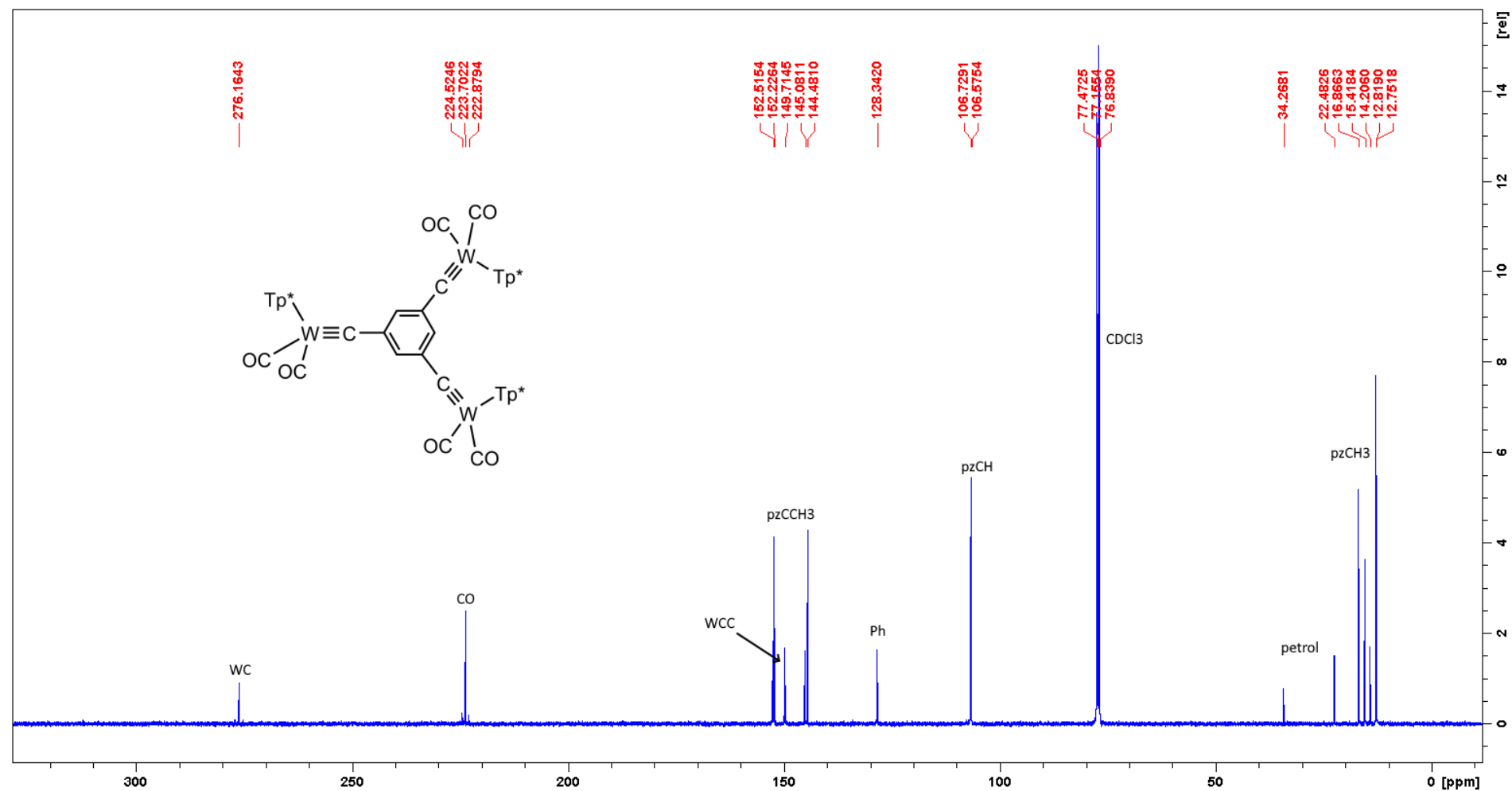
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) for [1,4-((Tp*)(CO)₂W=C)₂C₆H₄] (4).



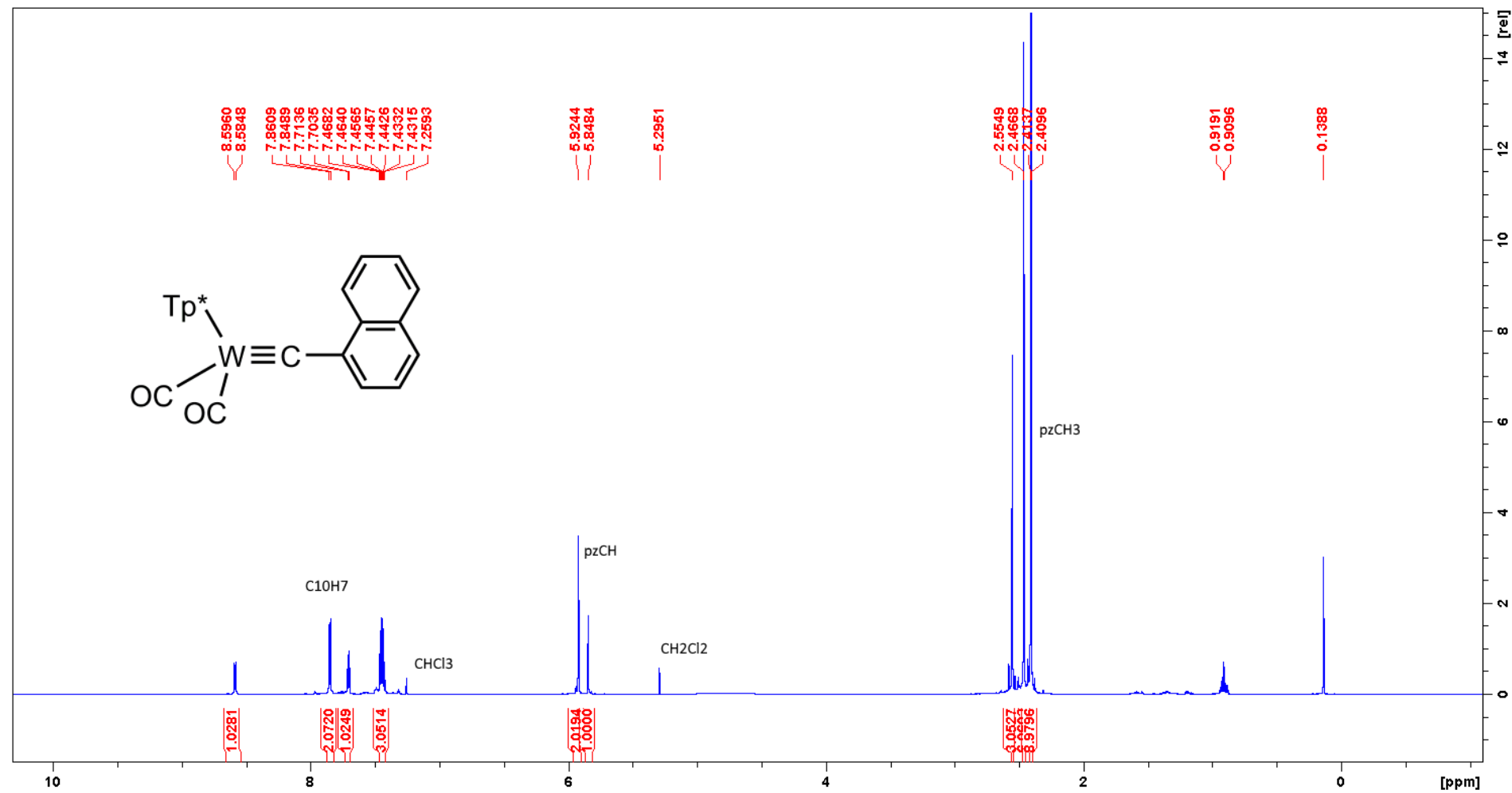
¹³C{¹H} NMR spectrum (176 MHz, CDCl₃, 298 K) for [1,4-((Tp*)(CO)₂W≡C)₂C₆H₄] (4).



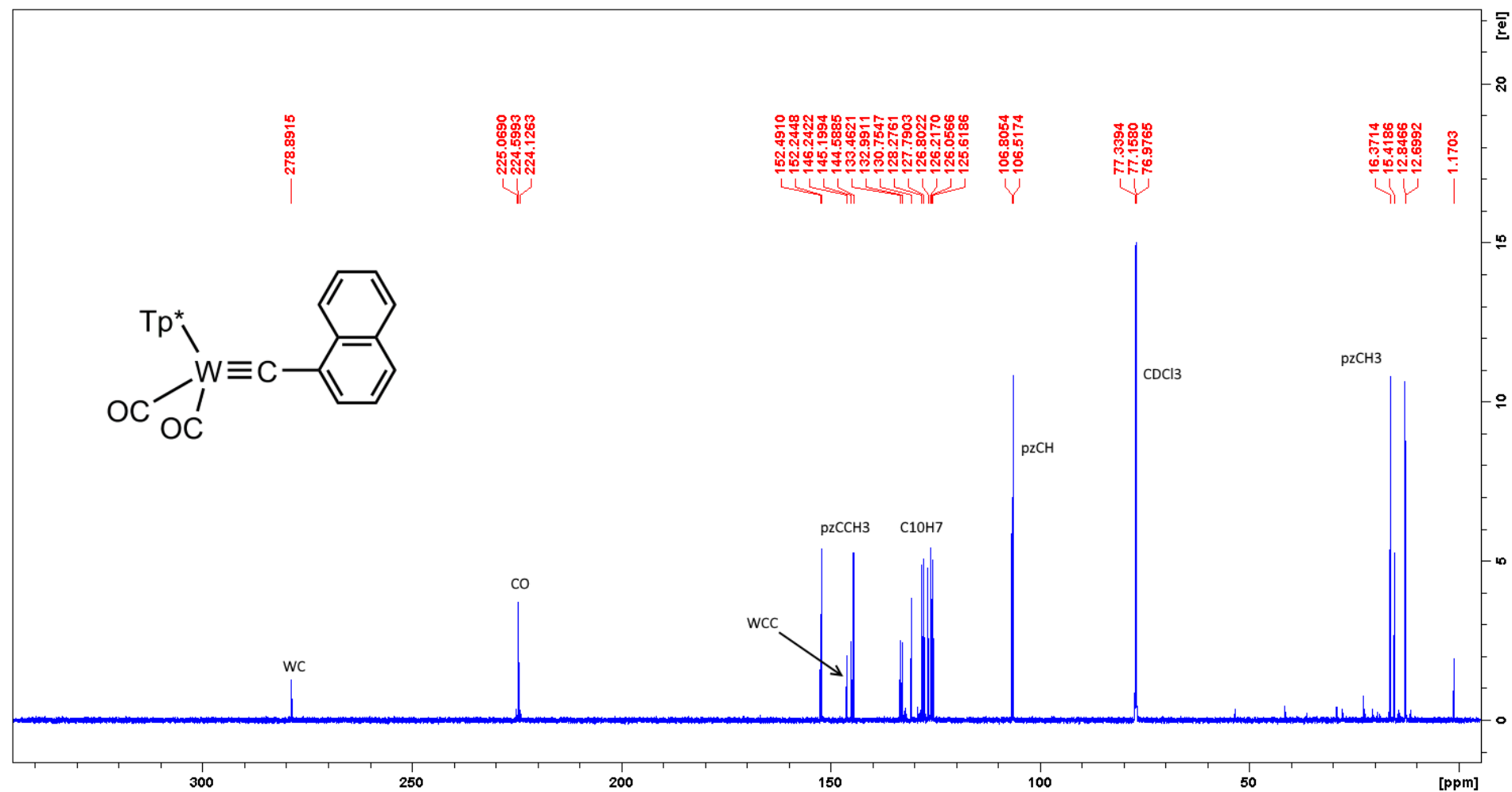
^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) for $[1,3,5\text{-}((\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C})_3\text{C}_6\text{H}_4]$ (**5**).



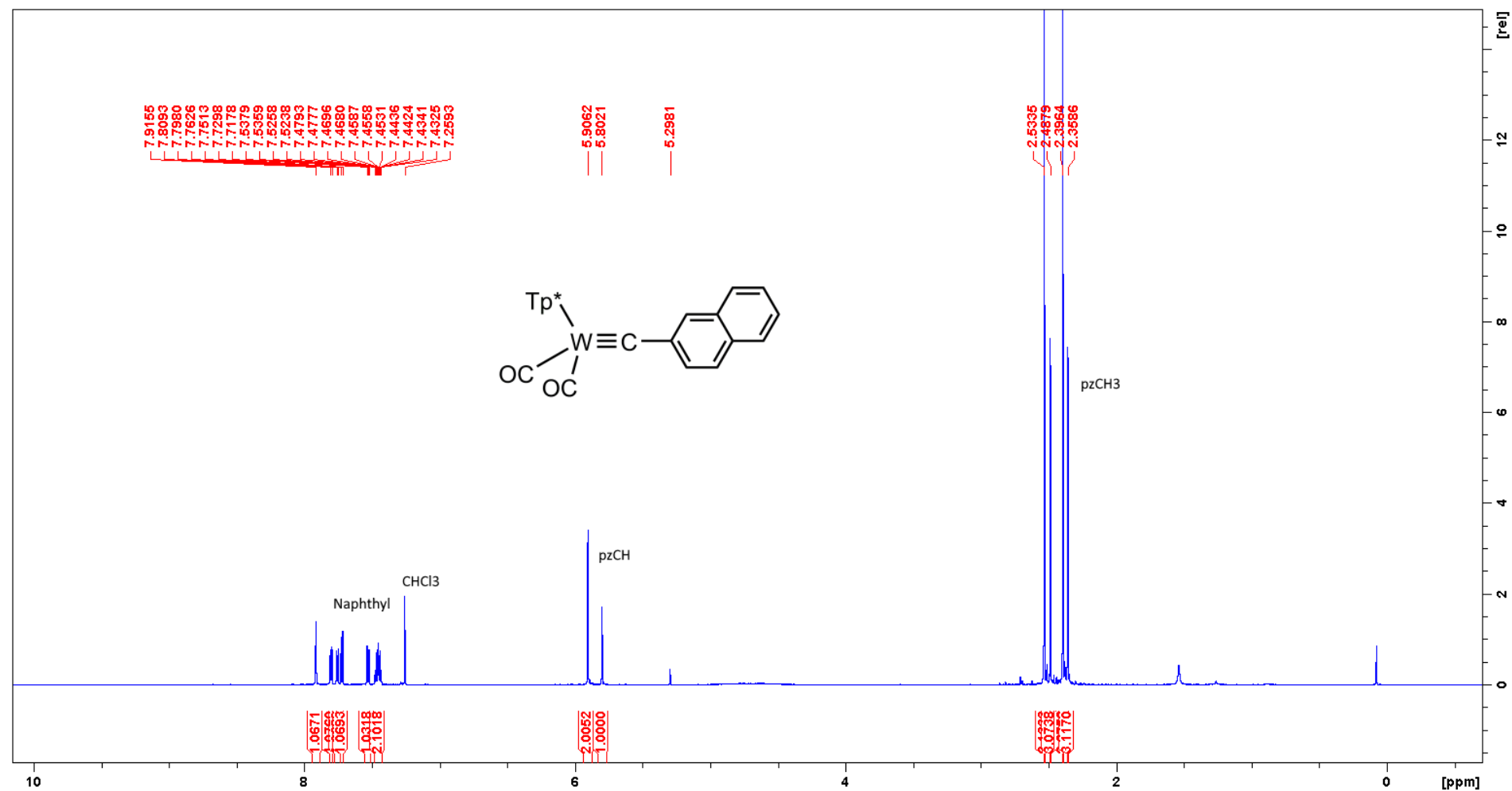
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 298 K) for $[1,3,5\text{-}(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}]_3\text{C}_6\text{H}_4$ (**5**).



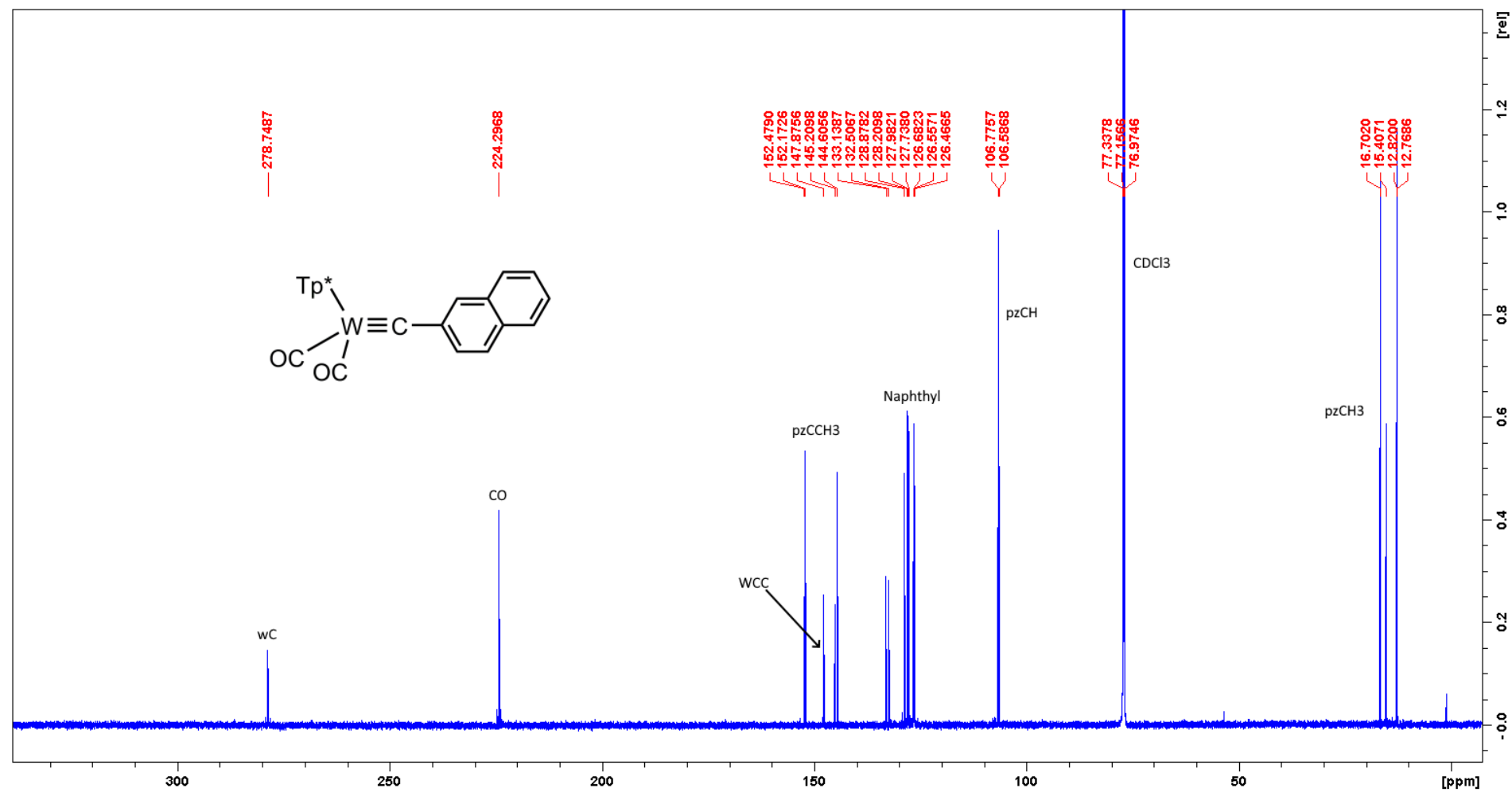
^1H NMR spectrum (700 MHz, CDCl_3 , 298 K) for $[1-\{(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}\}\text{C}_{10}\text{H}_7]$ (**6**).



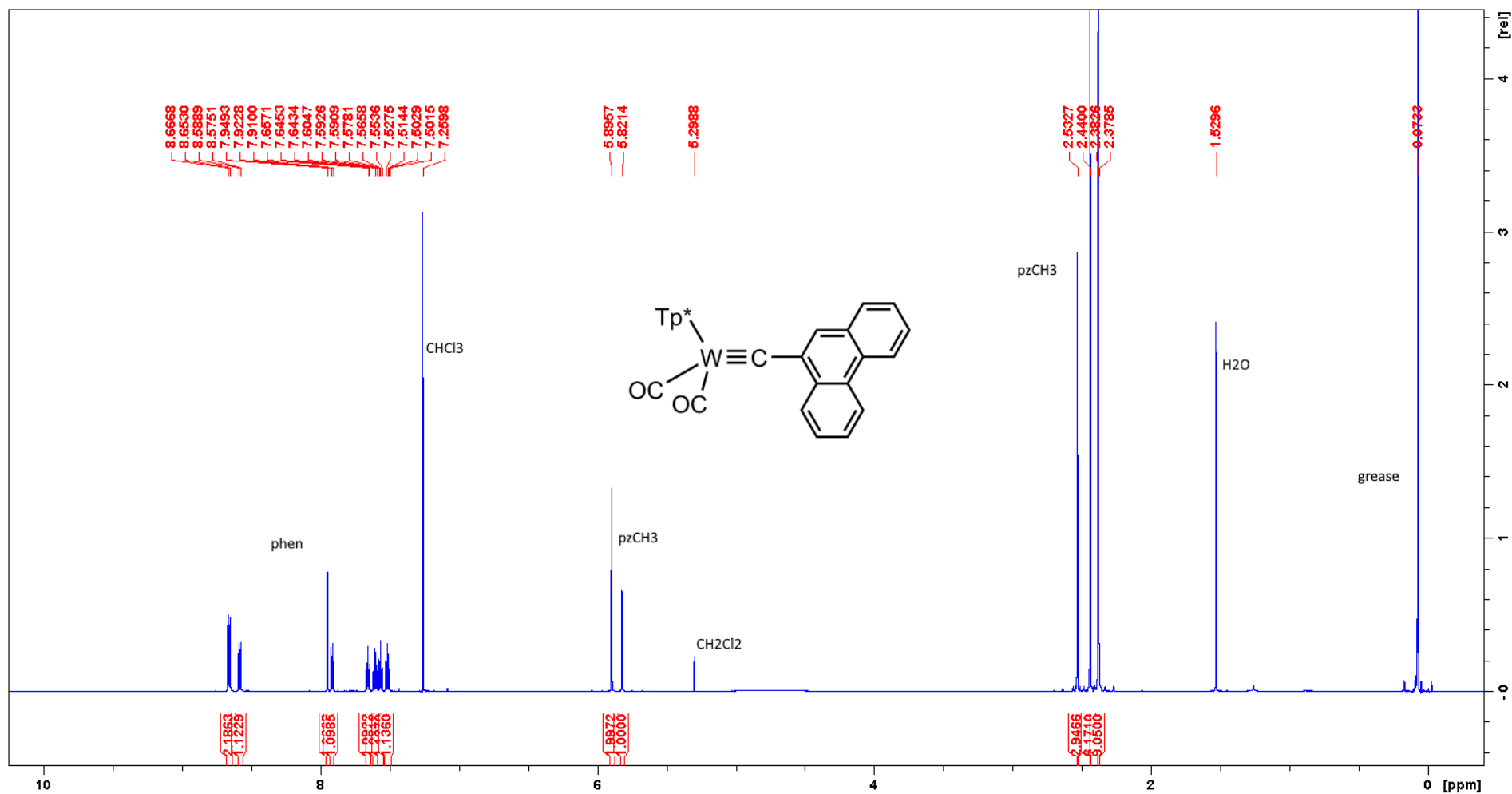
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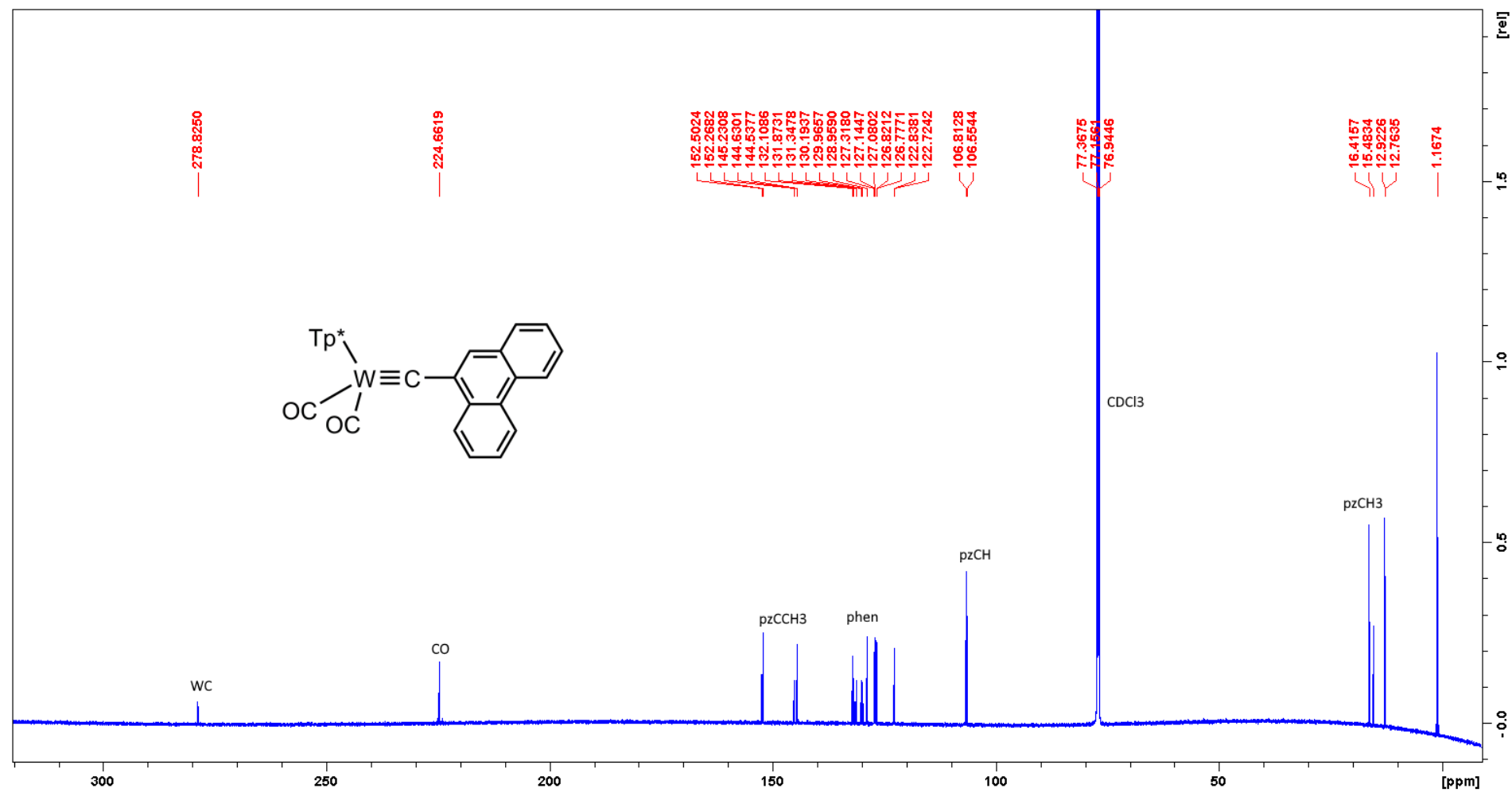
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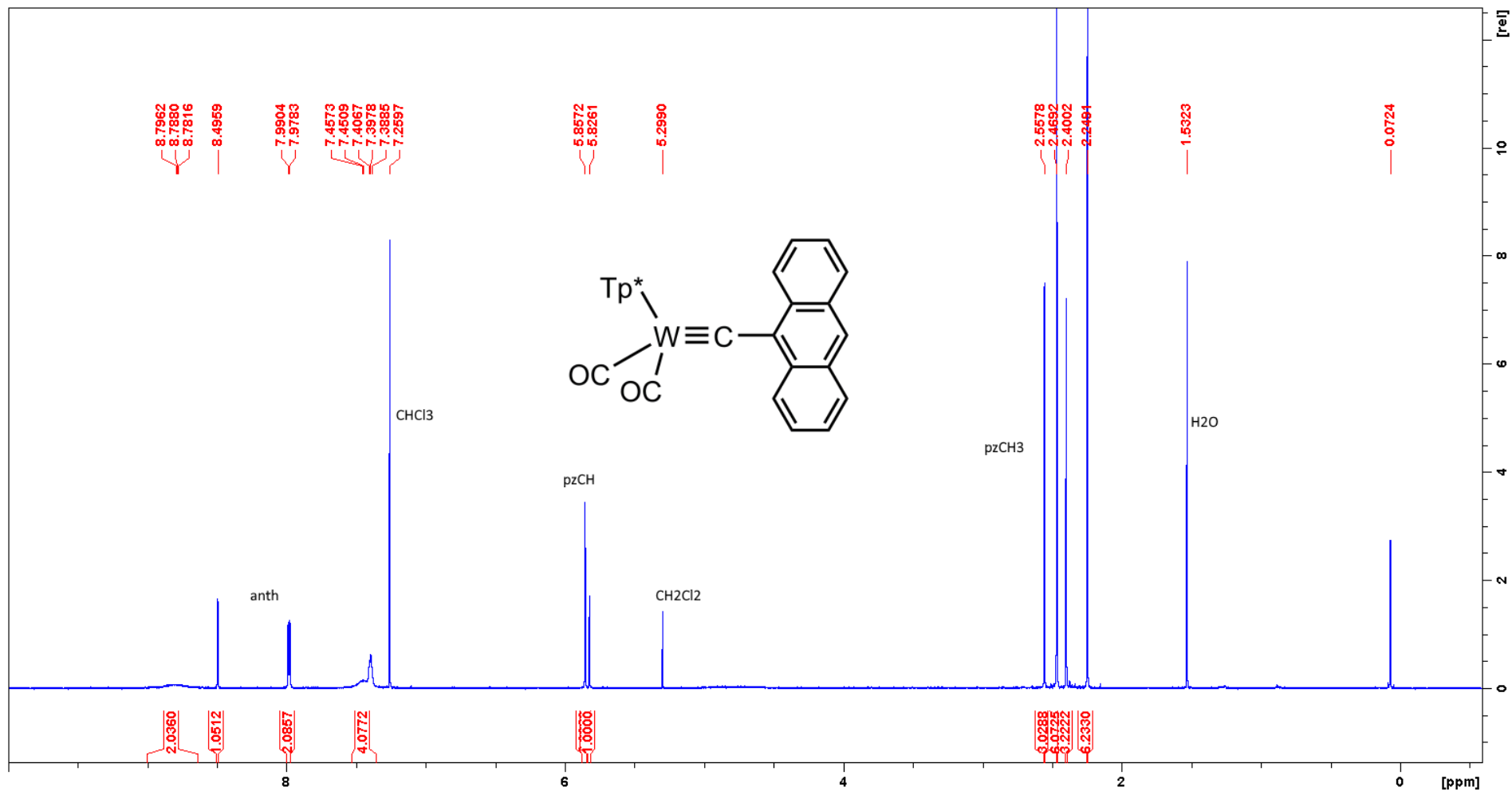
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (176 MHz, CDCl_3 , 298 K) for $[2-((\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C})\text{C}_{10}\text{H}_7]$ (7).



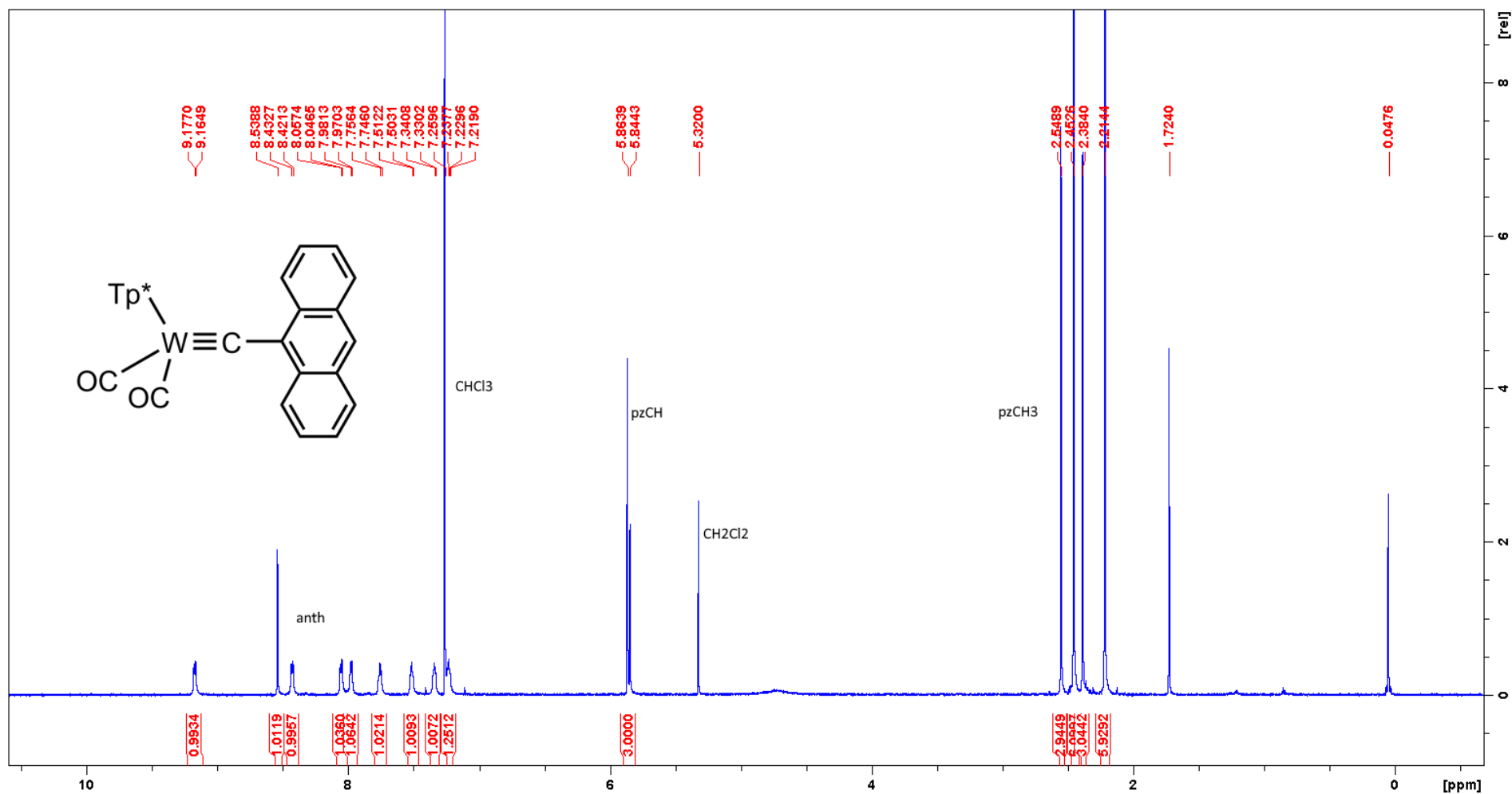
^1H NMR spectrum (600 MHz, CDCl_3 , 298 K) for $[9-\{(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}\}\text{C}_{14}\text{H}_9] \mathbf{8} \cdot (\text{CH}_2\text{Cl}_2)_{0.5}$.



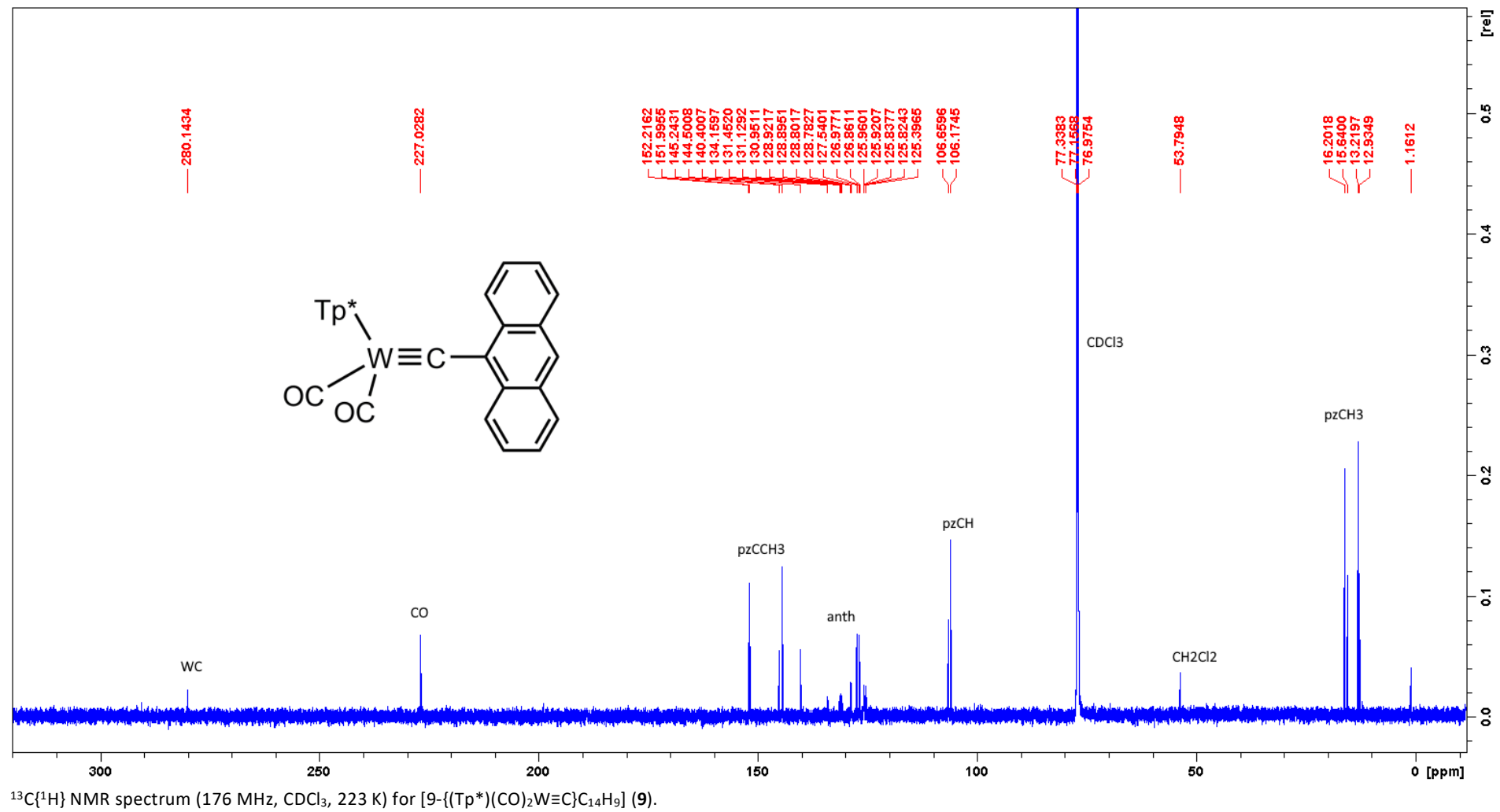
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (151 MHz, CDCl_3 , 298 K) for $[9\text{-}(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}]_{\text{C}_{14}\text{H}_9} \mathbf{8} \cdot (\text{CH}_2\text{Cl}_2)_{0.5}$.

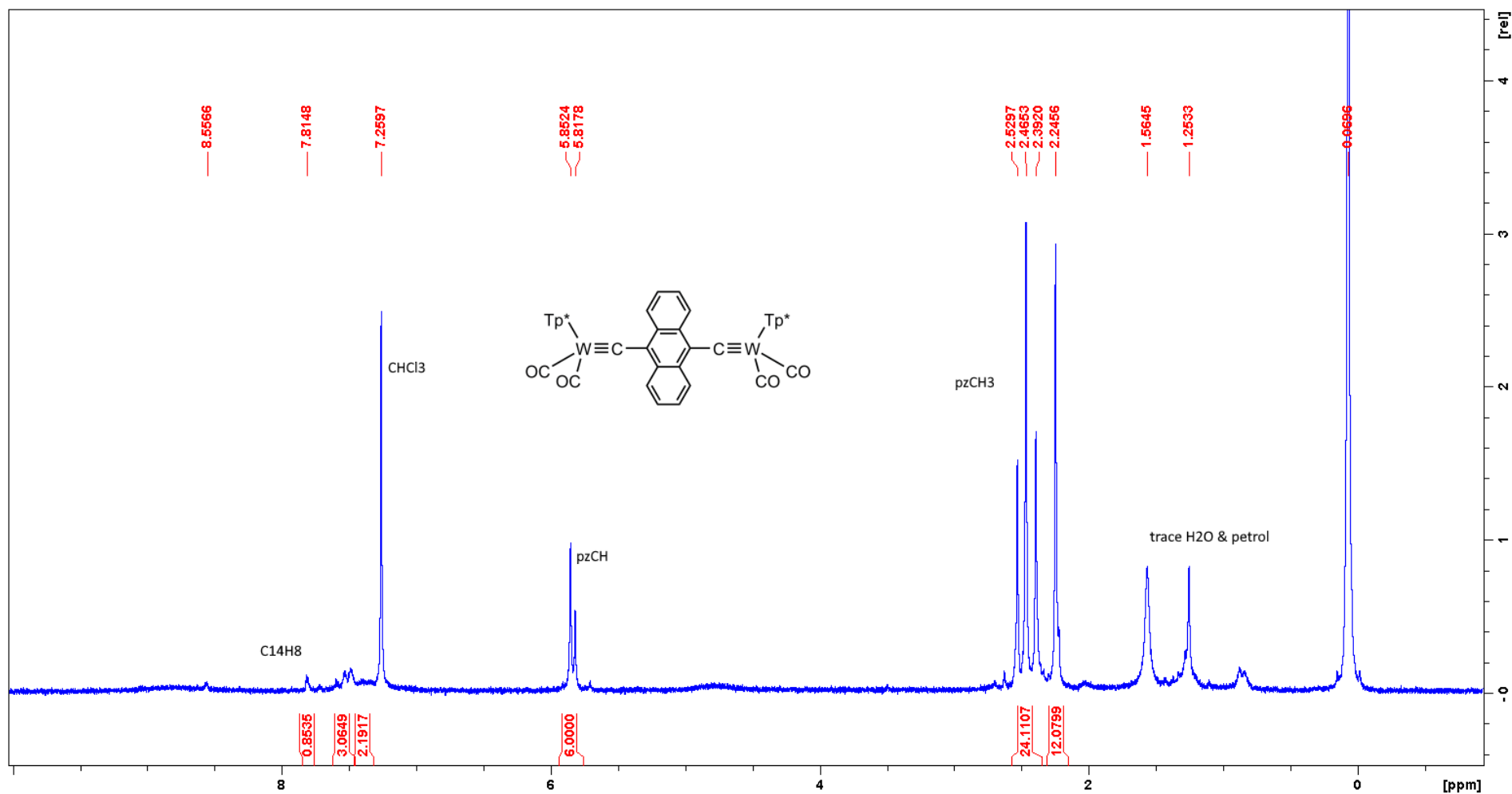


^1H NMR spectrum (700 MHz, CDCl_3 , 298 K) for $[9\text{-}(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}]_{\text{C}_{14}\text{H}_9}$ $9\text{-}(\text{CH}_2\text{Cl})_{0.33}$.

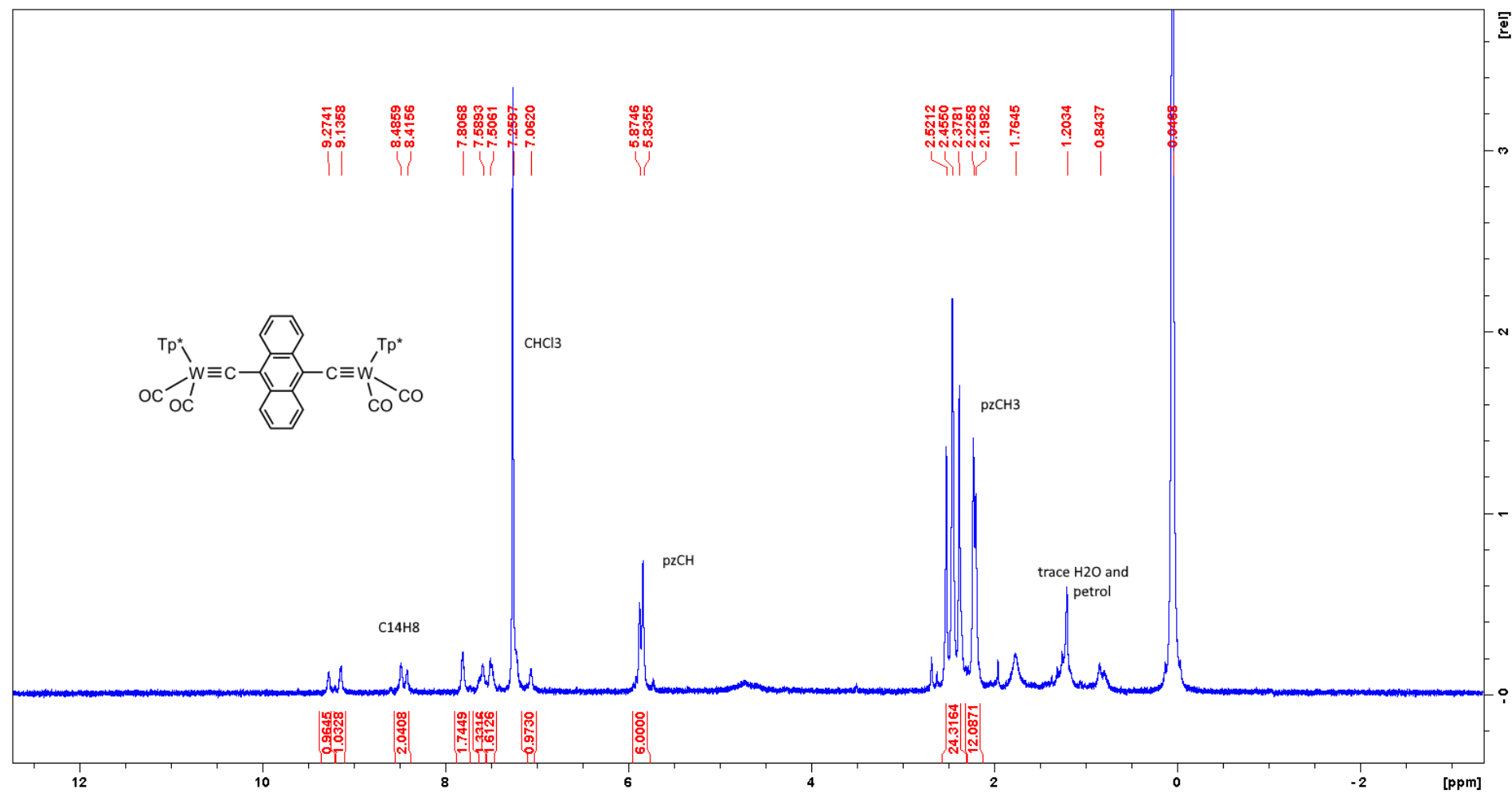


^1H NMR spectrum (700 MHz, CDCl_3 , 223 K) for $[9-(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}]_{\text{C}_{14}\text{H}_9}$ $\mathbf{9} \cdot (\text{CH}_2\text{Cl}_2)_{0.33}$.

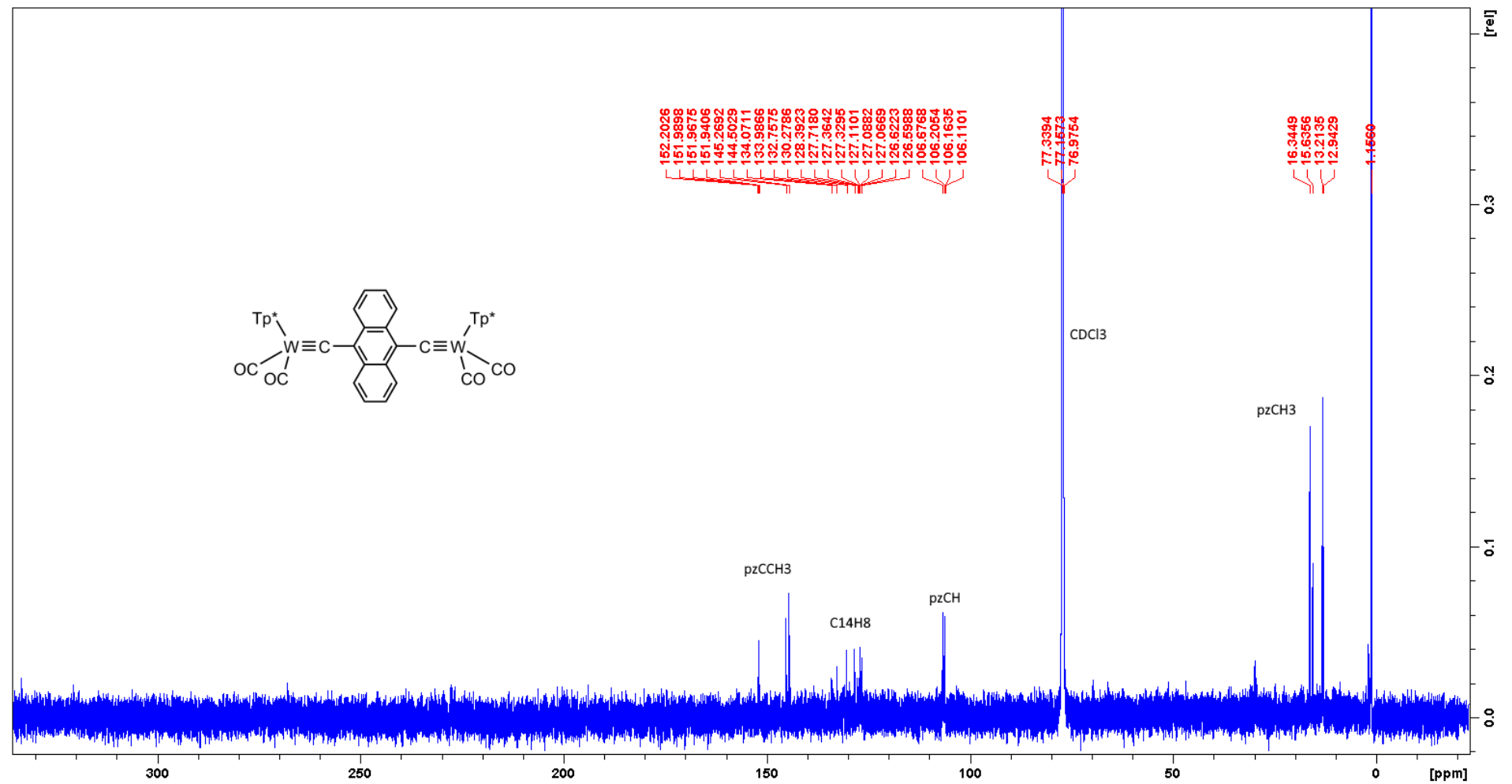




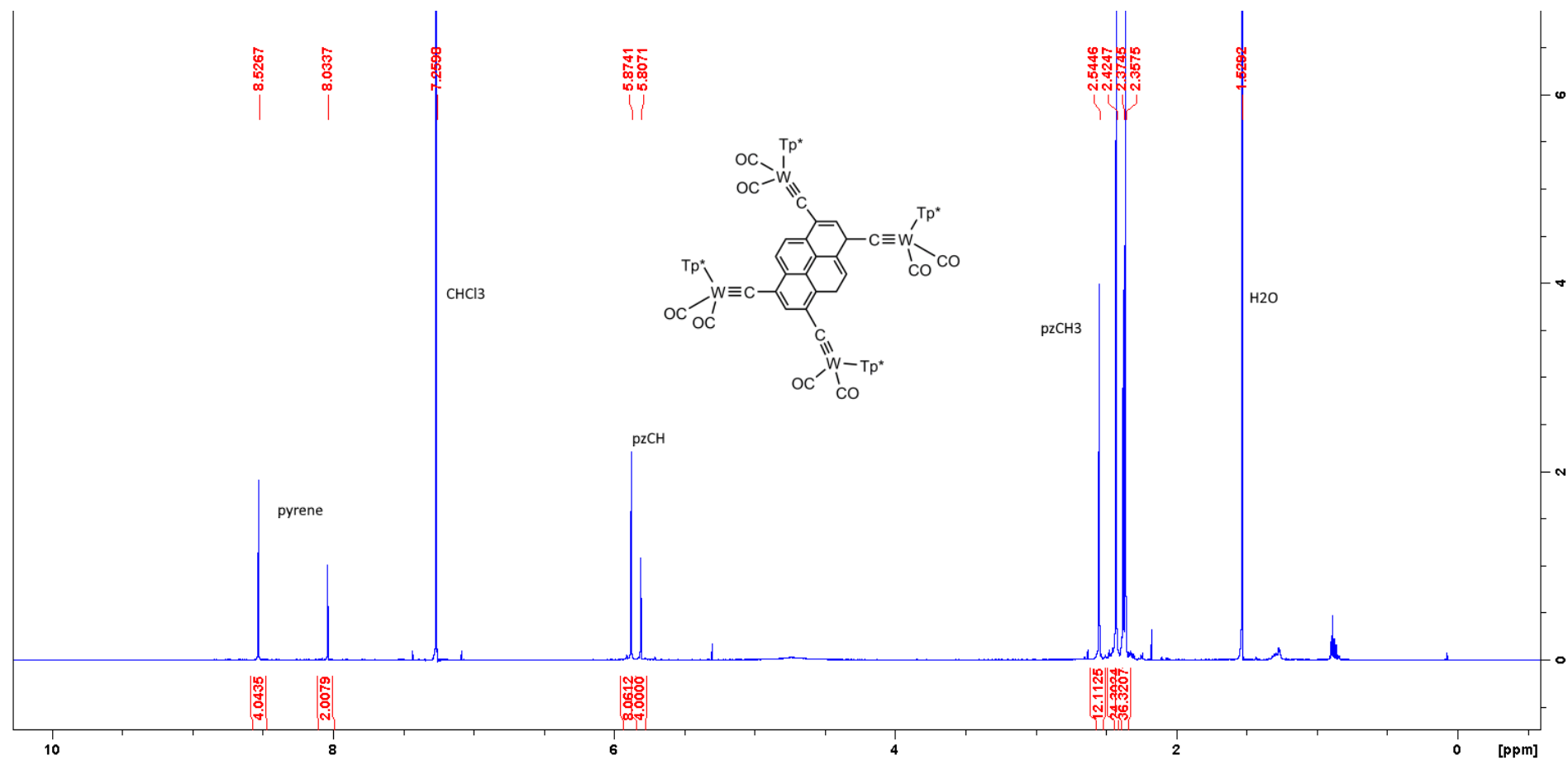
^1H NMR spectrum (700 MHz, CDCl_3 , 298 K) for $[9,10\text{-}(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}]_2\text{C}_{14}\text{H}_8$ (**10**).



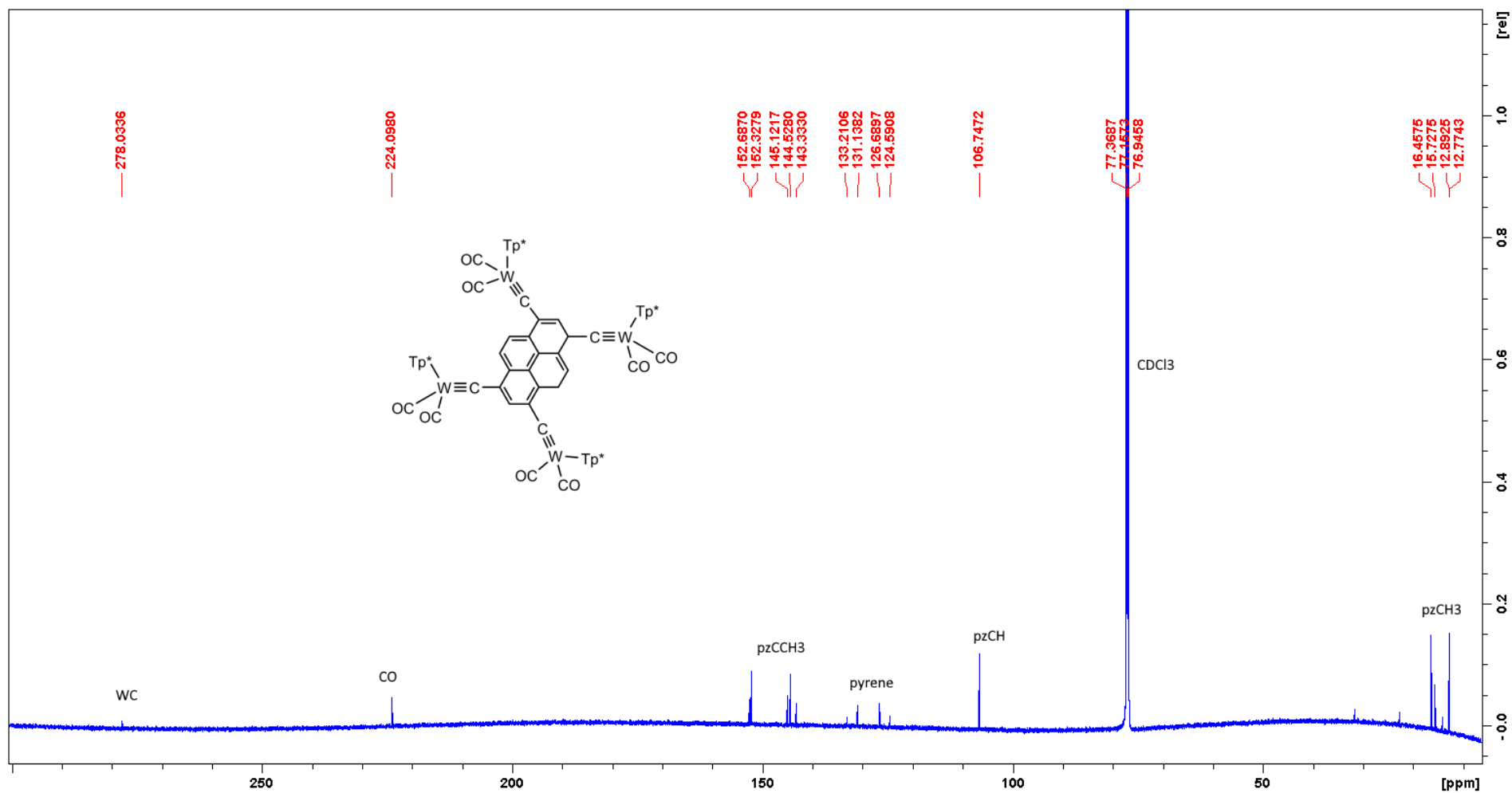
¹H NMR spectrum (700 MHz, CDCl₃, 223 K) for [9,10-((Tp*)(CO)₂W≡C)₂C₁₄H₈] **10**·2.5(CHCl₃).



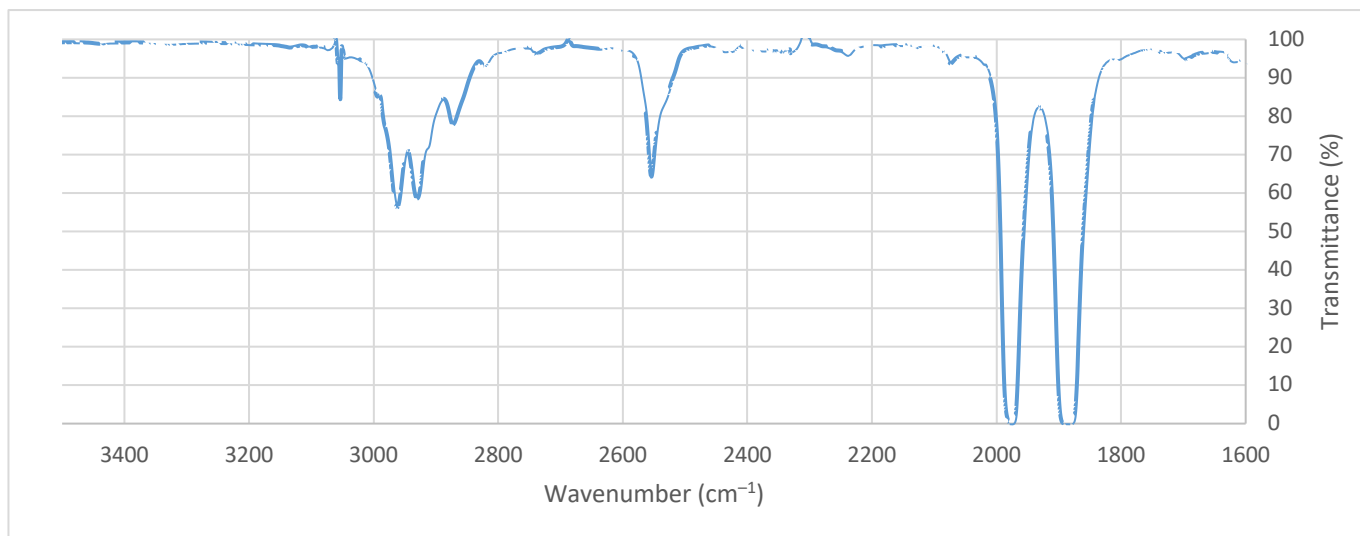
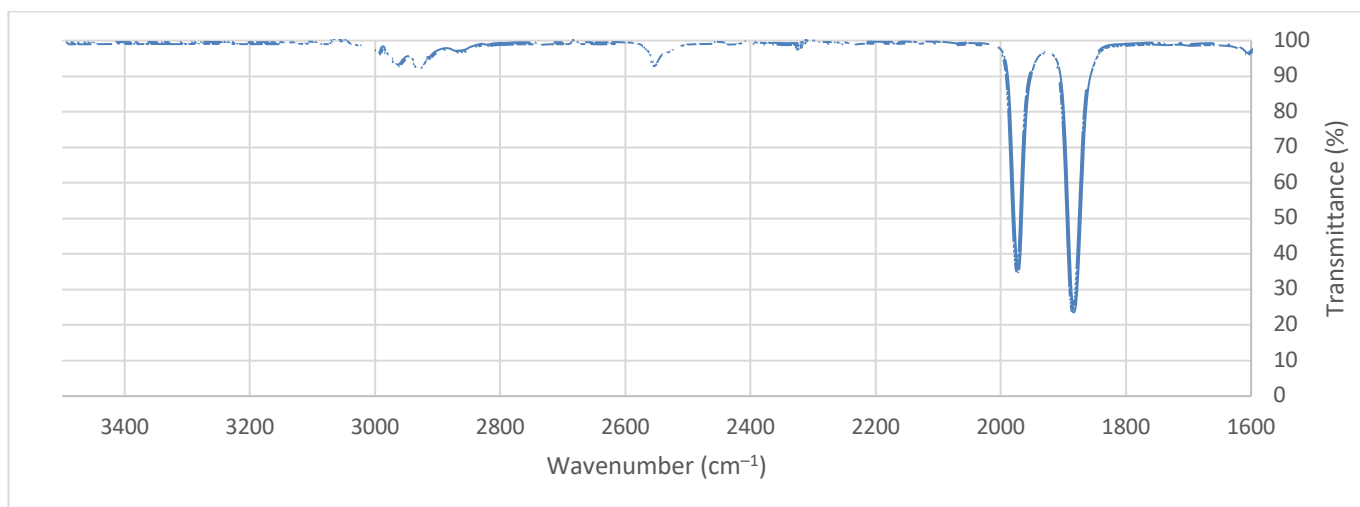
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (176 MHz, CDCl_3 , 298 K) for $[9,10\text{-}(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}]_2\text{C}_{14}\text{H}_8$ **10**·2.5(CHCl_3).

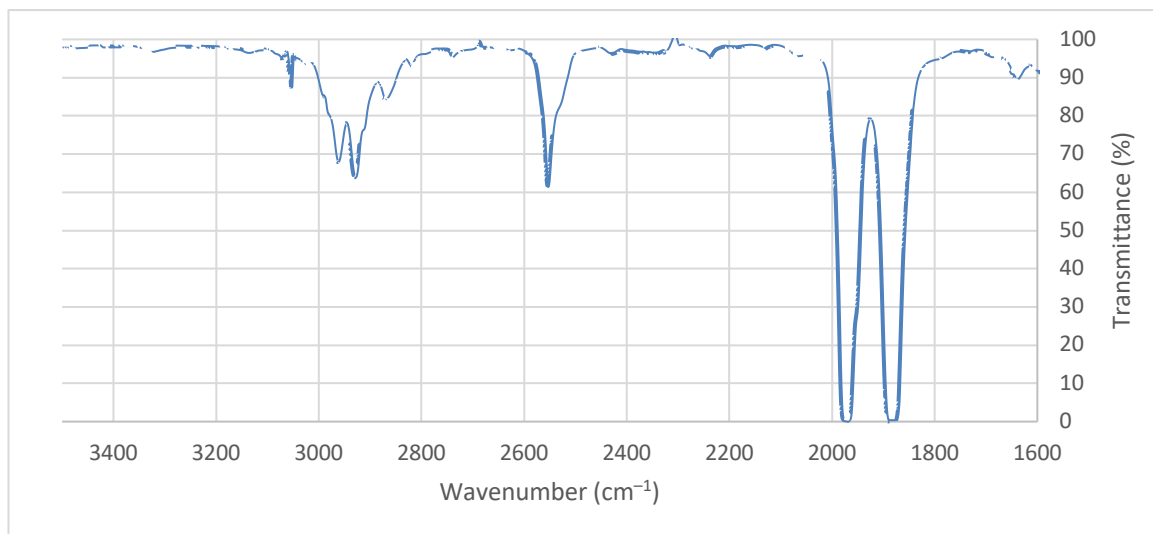


^1H NMR spectrum (600 MHz, CDCl_3 , 298 K) for $[1,3,6,8-((\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C})_4\text{C}_{16}\text{H}_6]$ (**11**).

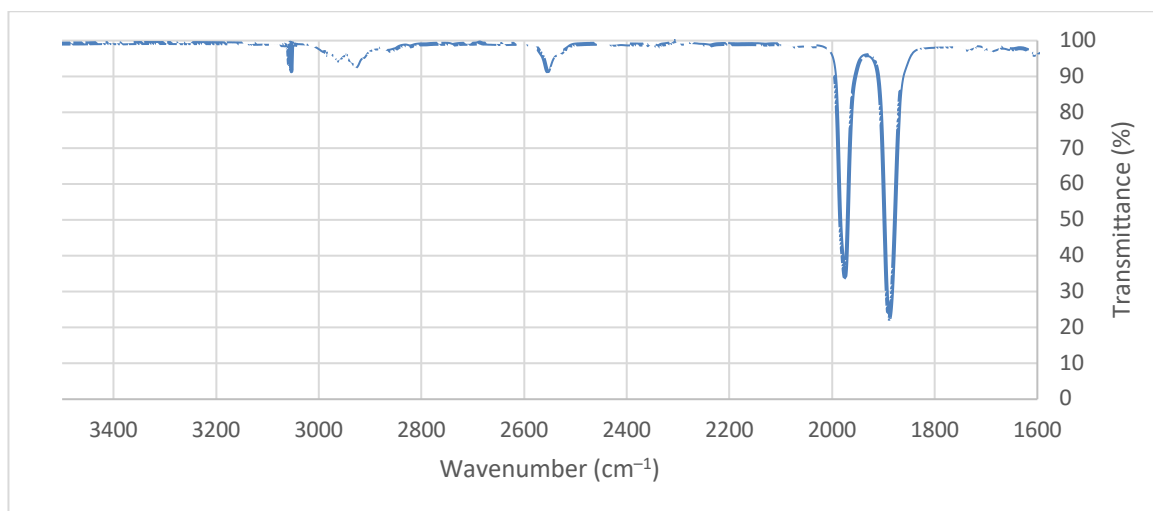


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (151 MHz, CDCl_3 , 298 K) for [1,3,6,8- $\{(\text{Tp}^*)(\text{CO})_2\text{W}=\text{C}\}_4\text{C}_{16}\text{H}_6$] (**11**).

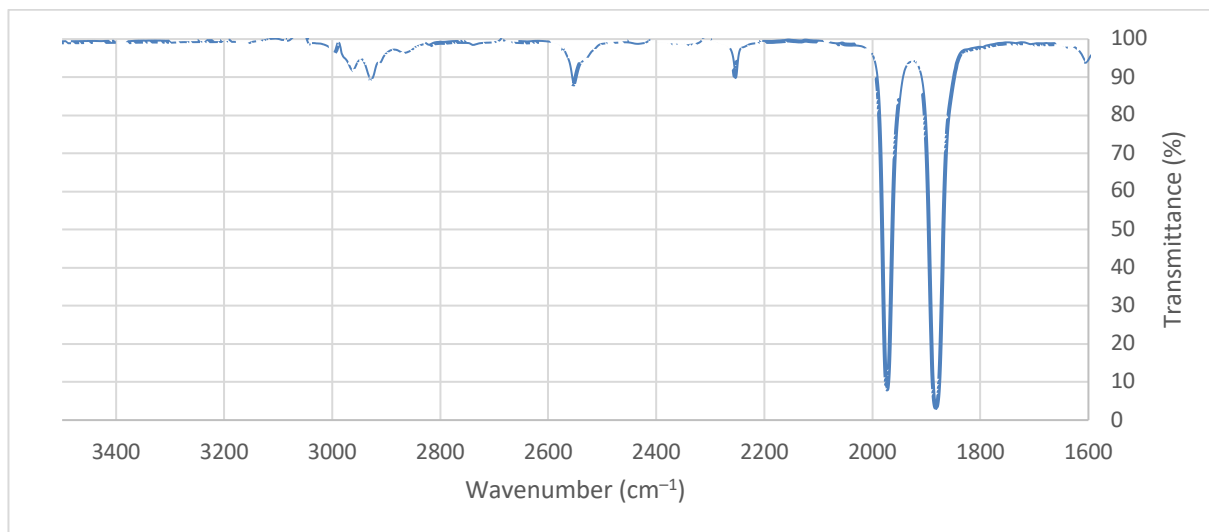
IR spectrum (CH₂Cl₂, cm⁻¹) for [W(≡CC₆H₄Br-2)(CO)₂(Tp^{*})] (**2**).IR spectrum (CH₂Cl₂, cm⁻¹) for [1,3-((Tp^{*})(CO)₂W≡C)₂C₆H₄] (**3**).



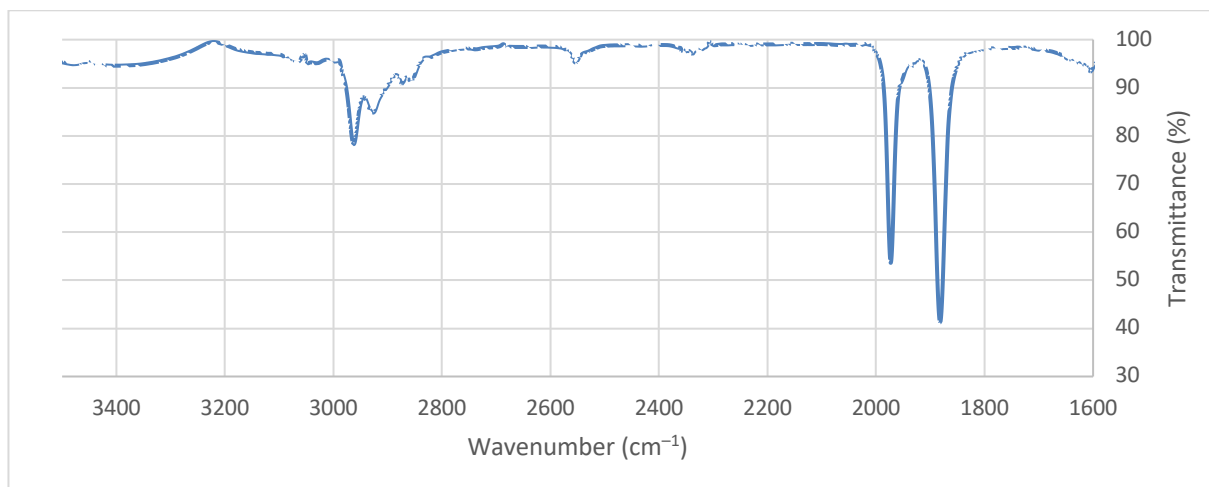
IR spectrum (CH₂Cl₂, cm⁻¹) for [1,4-((Tp*)₂(CO)₂W≡C)₂C₆H₄] (**4**).



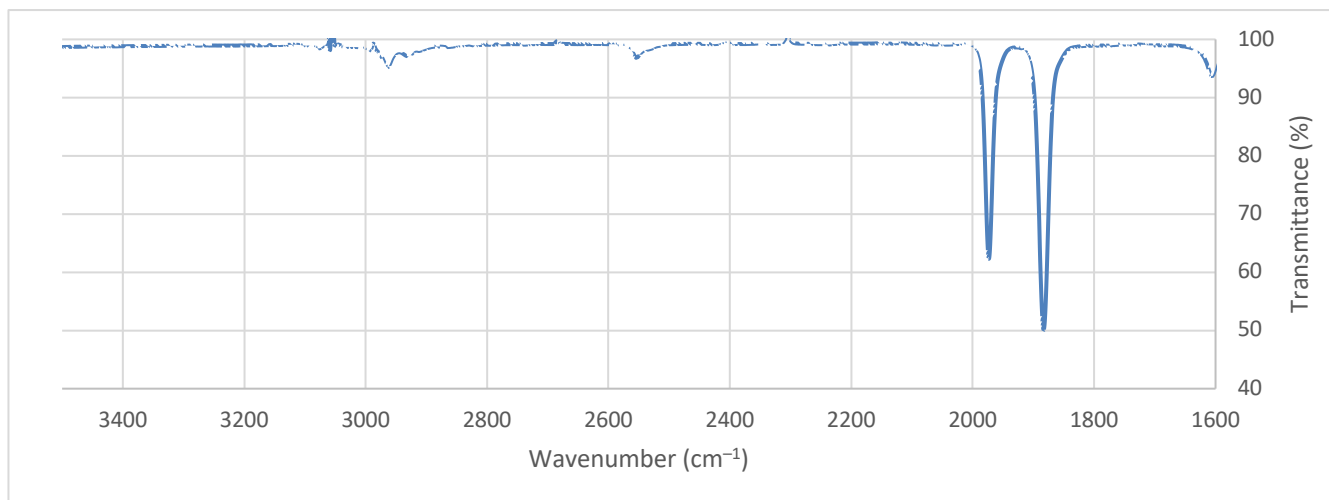
IR spectrum (CH₂Cl₂, cm⁻¹) for [1,3,5-((Tp*)₂(CO)₂W≡C)₃C₆H₄] (**5**).



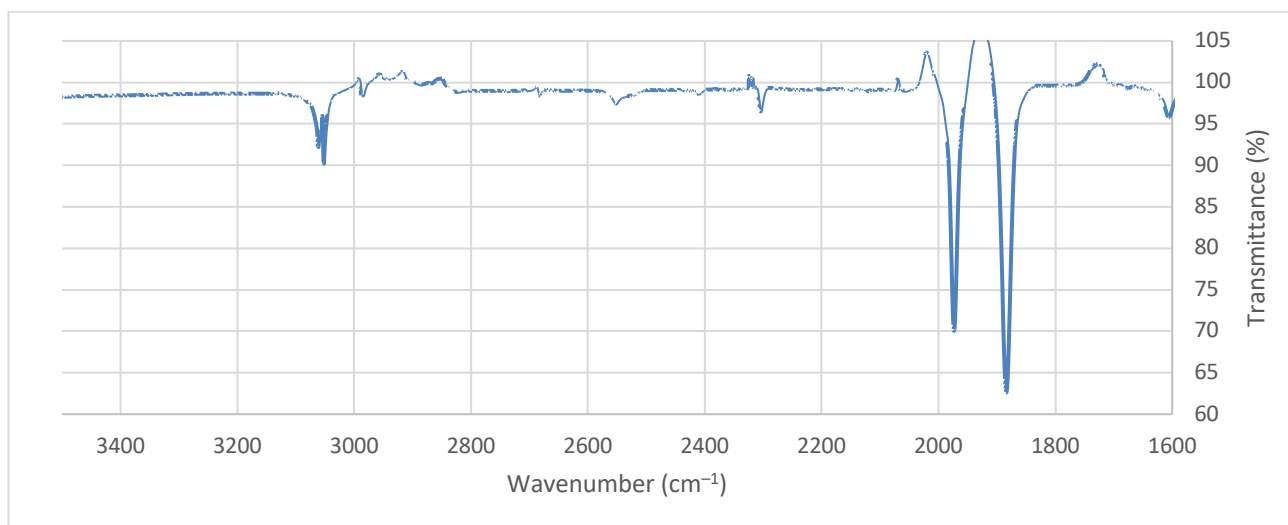
IR spectrum (CH₂Cl₂, cm⁻¹) for [1-((Tp*)₂(CO)₂W≡C)C₁₀H₇] (**6**).



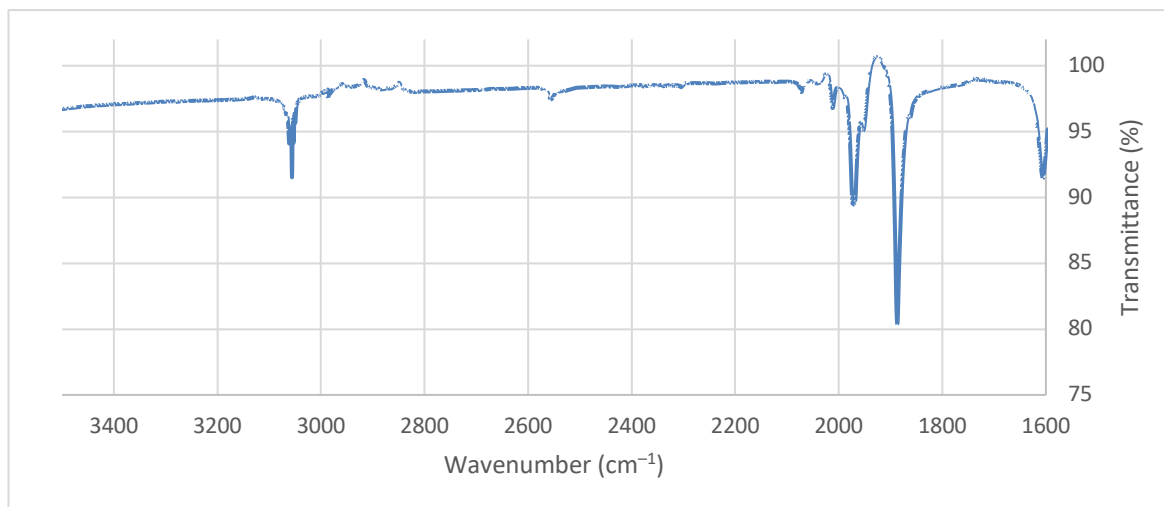
IR spectrum (CH₂Cl₂, cm⁻¹) for [2-((Tp*)₂(CO)₂W≡C)C₁₀H₇] (**7**).



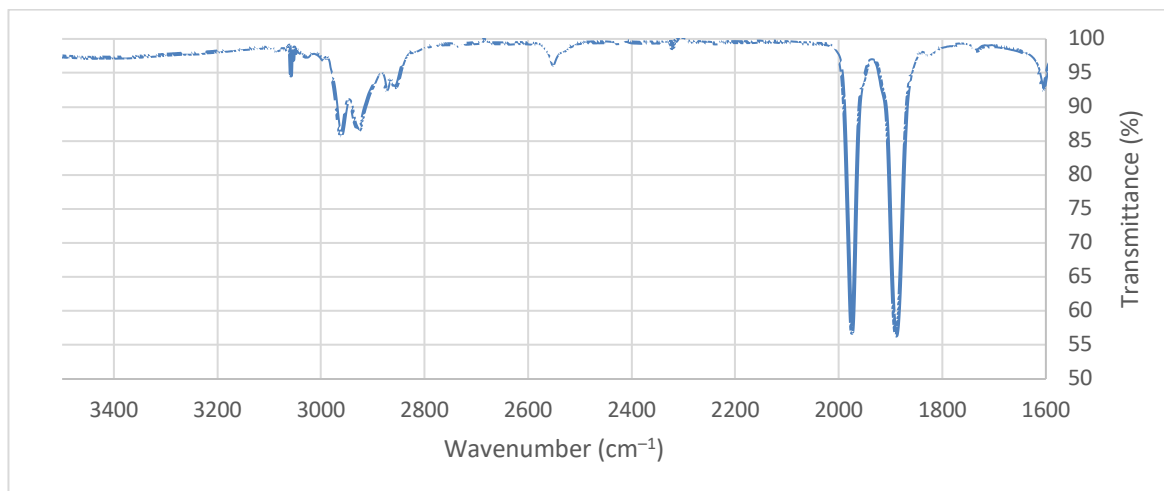
IR spectrum (CH₂Cl₂, cm⁻¹) for [9-((Tp*)₂(CO)₂W≡C)C₁₄H₉] (**8**).



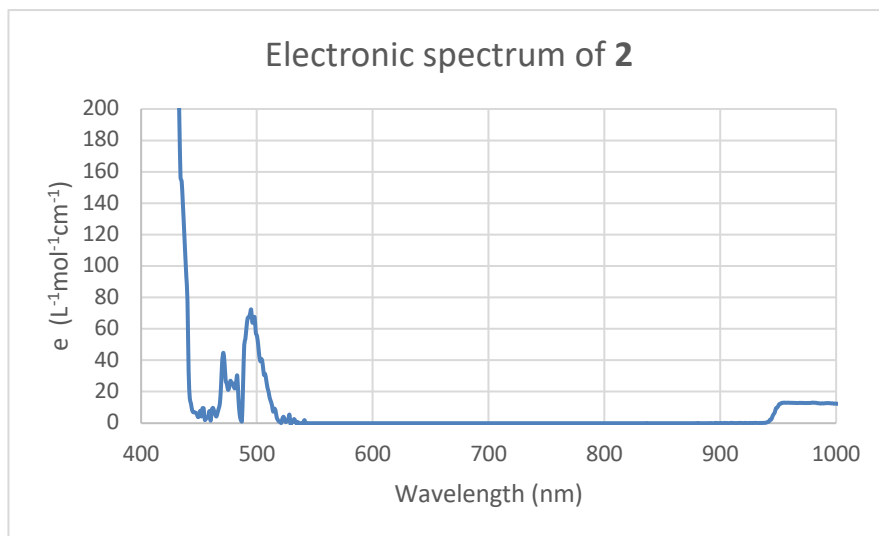
IR spectrum (CH₂Cl₂, cm⁻¹) for [9-((Tp*)₂(CO)₂W≡C)C₁₄H₉] (**9**).



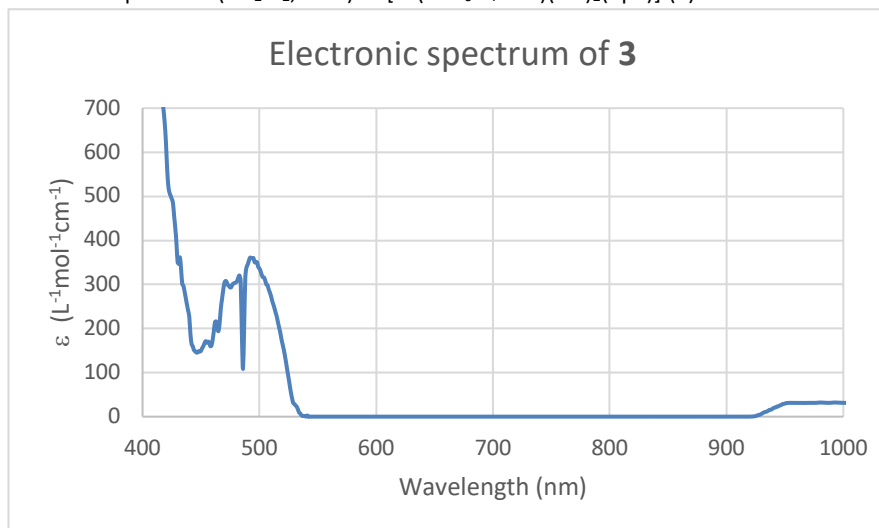
IR spectrum (CH₂Cl₂, cm⁻¹) for [9,10-((Tp*)₂(CO)₂W≡C)₂C₁₄H₈] (**10**).



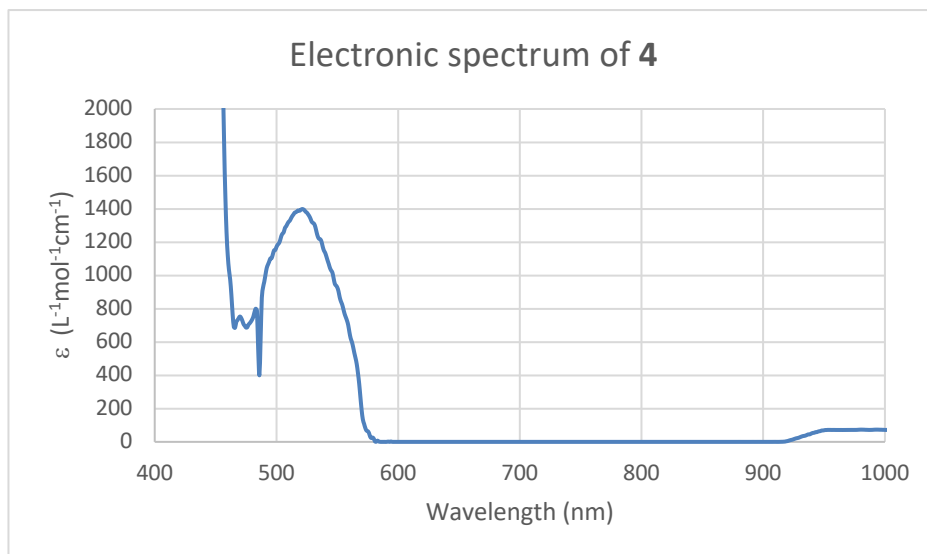
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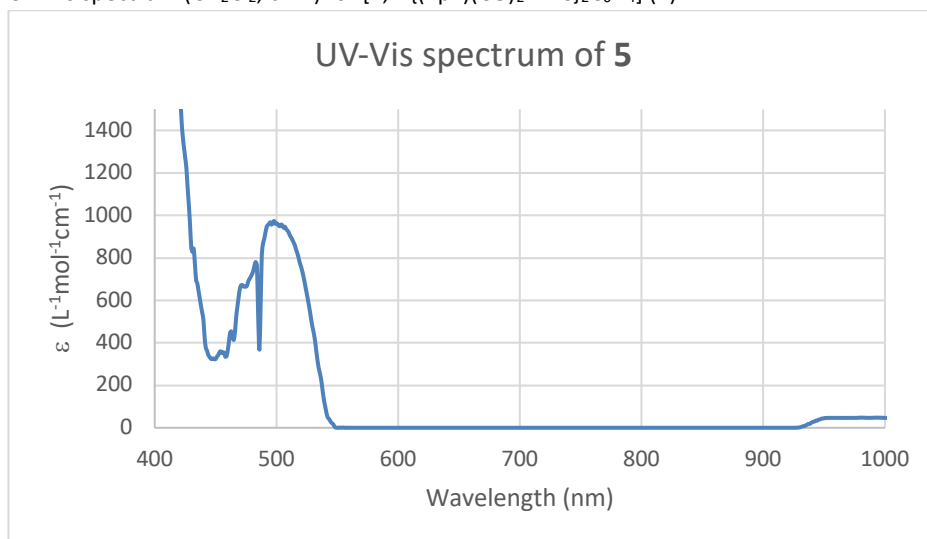
Electronic spectrum (CH_2Cl_2 , cm^{-1}) of $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Br}-2)(\text{CO})_2(\text{Tp}^*)]$ (**2**).



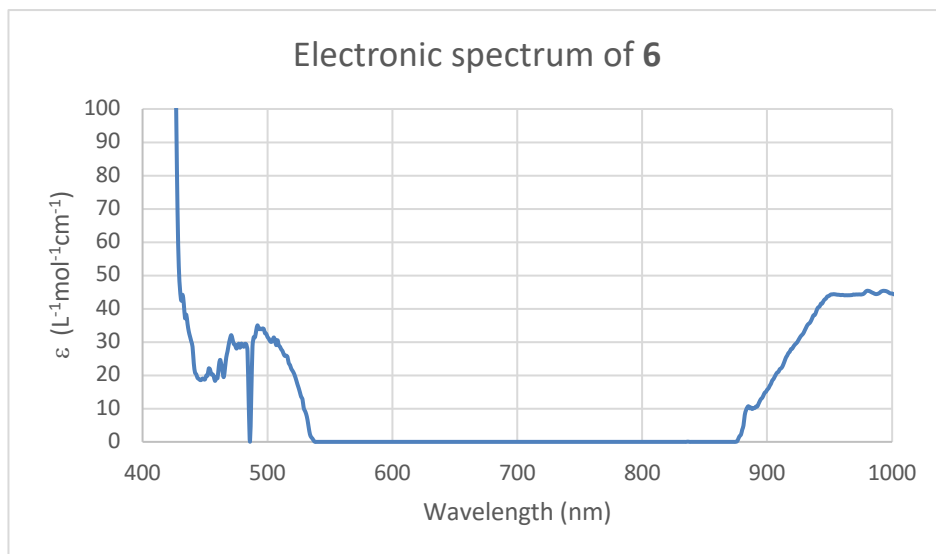
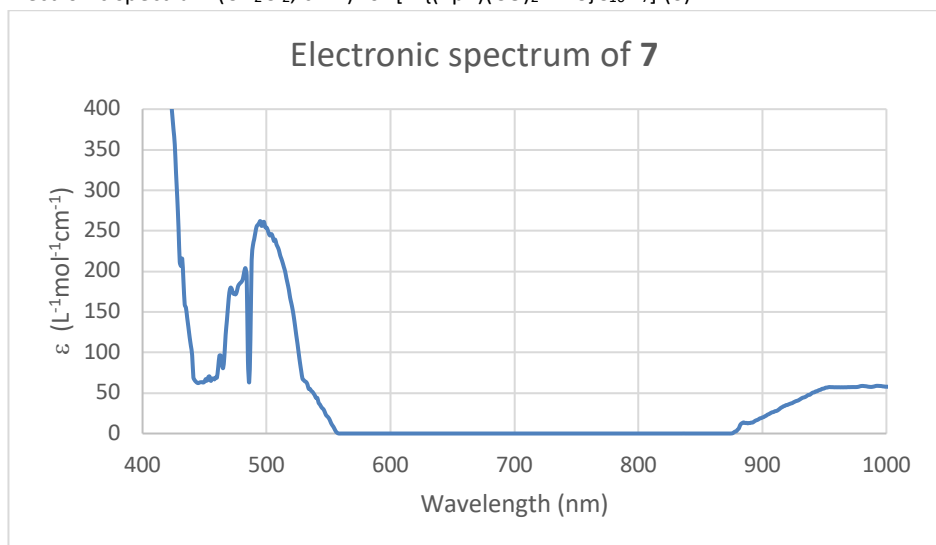
Electronic spectrum (CH_2Cl_2 , cm^{-1}) of $[1,3\text{-}(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}]_2\text{C}_6\text{H}_4$ (**3**).

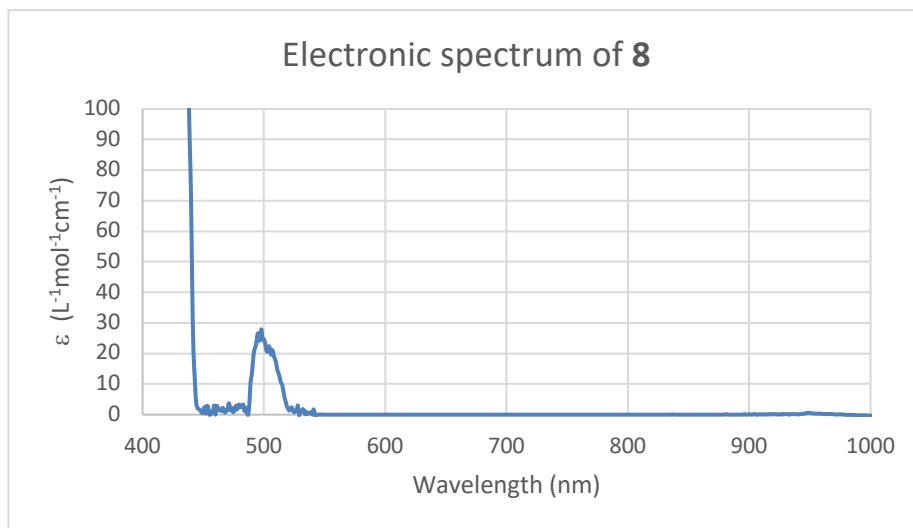


UV-Vis spectrum (CH_2Cl_2 , cm^{-1}) for [1,4- $\{(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}\}_2\text{C}_6\text{H}_4$] (**4**).

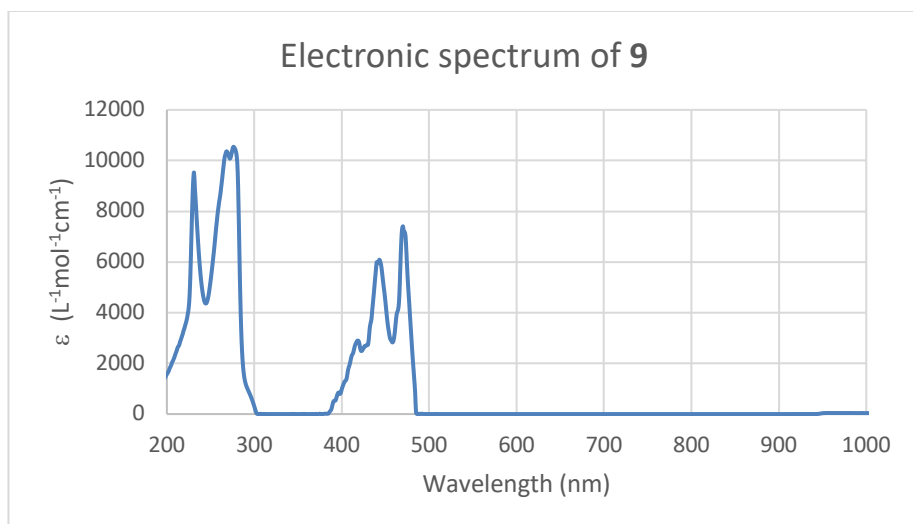


Electronic spectrum (CH_2Cl_2 , cm^{-1}) of [1,3,5- $\{(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}\}_3\text{C}_6\text{H}_4$] (**5**).

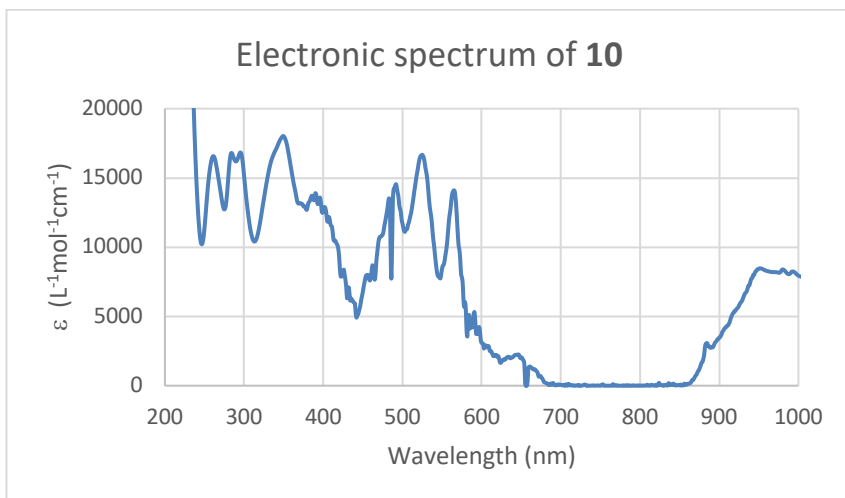
Electronic spectrum (CH_2Cl_2 , cm^{-1}) for [1- $\{(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}\}$]C₁₀H₇] (**6**).Electronic spectrum (CH_2Cl_2 , cm^{-1}) for [2- $\{(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}\}$]C₁₀H₇] (**7**).



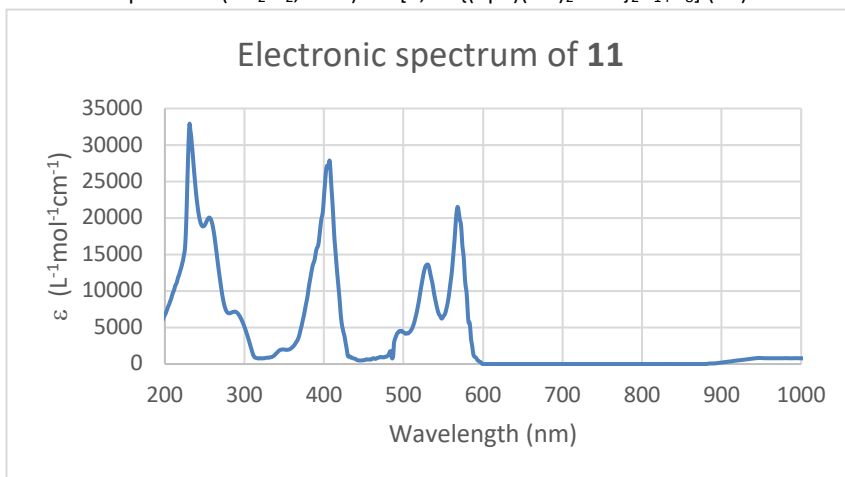
Electronic spectrum (CH_2Cl_2 , cm^{-1}) for $[9\text{-}\{\text{Tp}^*\}(\text{CO})_2\text{W}\equiv\text{C}\}\text{C}_{14}\text{H}_9]$ (**8**).



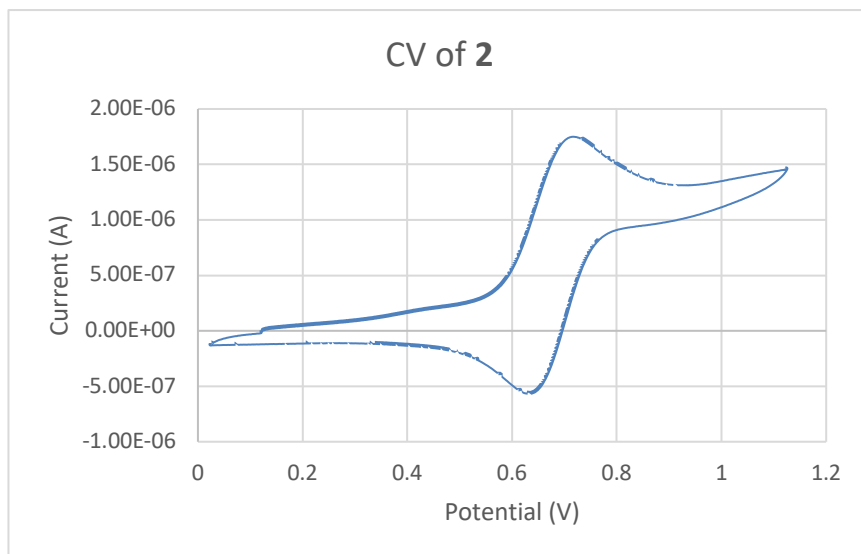
Electronic spectrum (CH_2Cl_2 , cm^{-1}) for $[9\text{-}\{\text{Tp}^*\}(\text{CO})_2\text{W}\equiv\text{C}\}\text{C}_{14}\text{H}_9]$ (**9**).



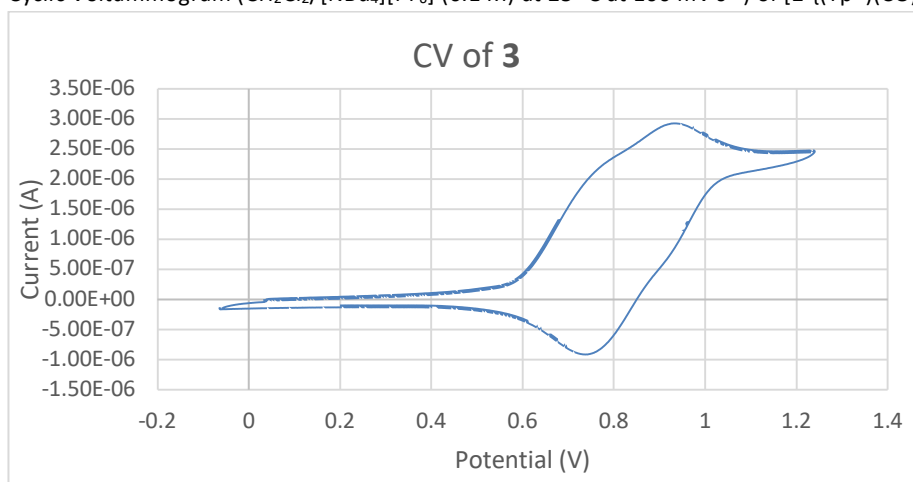
Electronic spectrum (CH_2Cl_2 , cm^{-1}) for [9,10- $\{(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}\}_2\text{C}_{14}\text{H}_8$] (**10**).



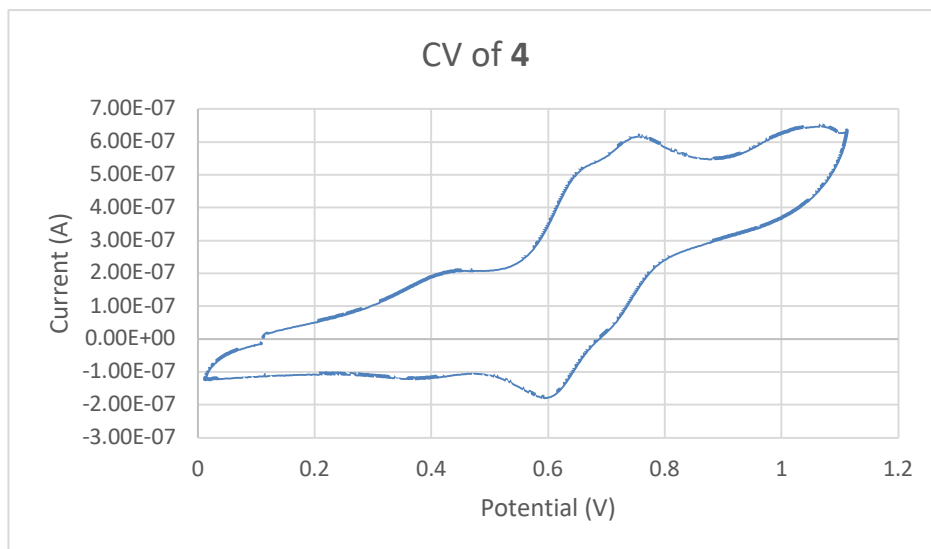
Electronic spectrum (CH_2Cl_2 , cm^{-1}) for [1,3,6,8- $\{(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}\}_4\text{C}_{16}\text{H}_6$] (**11**).



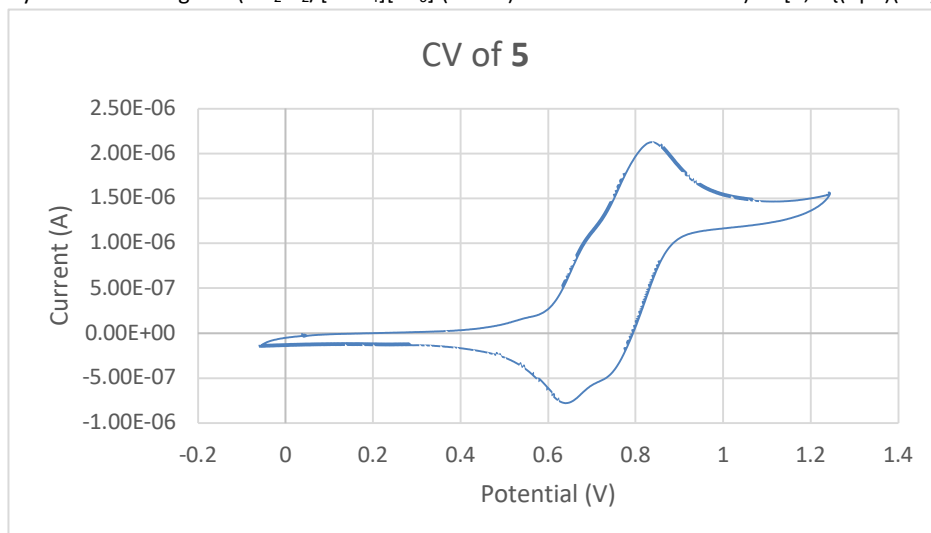
Cyclic Voltammogram ($\text{CH}_2\text{Cl}_2/[\text{NBu}_4][\text{PF}_6]$ (0.1 M) at 25°C at 100 mV s^{-1}) of $[2\text{-}\{(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}\}_2\text{C}_6\text{H}_4\text{Br}]$ (**2**) relative to $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]^{0/+} = 0.460\text{ V}$.



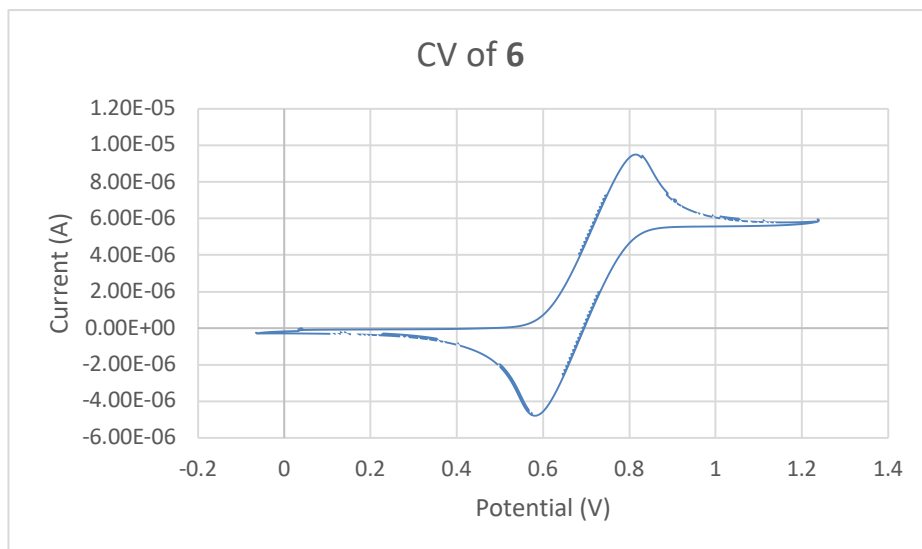
Cyclic Voltammogram ($\text{CH}_2\text{Cl}_2/[\text{NBu}_4][\text{PF}_6]$ (0.1 M) at 25°C at 100 mV s^{-1}) of $[1,3\text{-}\{(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}\}_2\text{C}_6\text{H}_4]$ (**3**) relative to $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]^{0/+} = 0.460\text{ V}$.



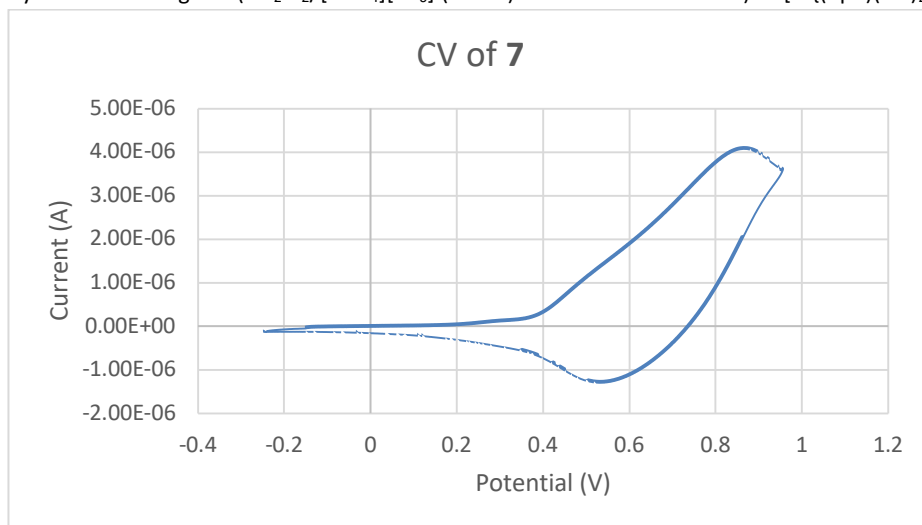
Cyclic Voltammogram (CH_2Cl_2 /[NBu₄][PF₆] (0.1 M) at 25 °C at 100 mV s⁻¹) of [1,4-((Tp*)₂(CO)₂W≡C)₂C₆H₄] (**4**) relative to [Fe(η-C₅H₅)₂]^{0/+} = 0.460 V.



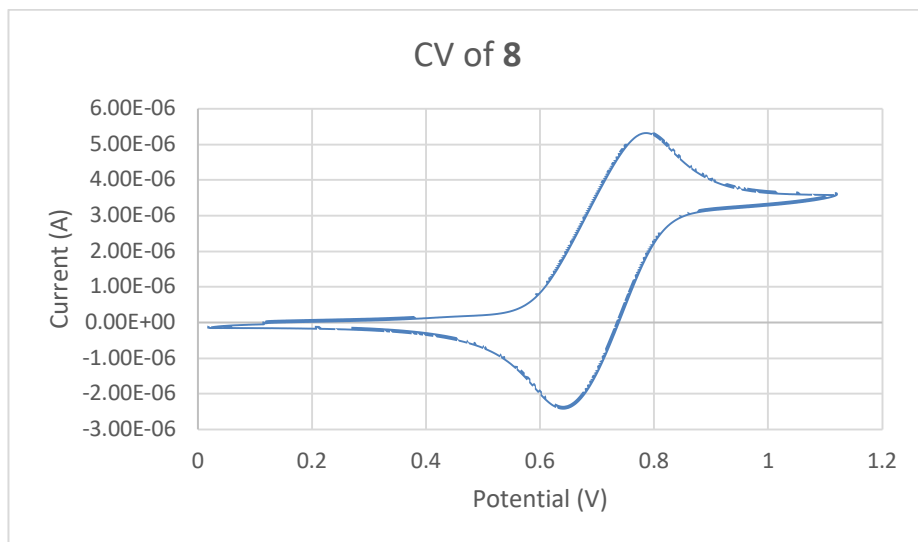
Cyclic Voltammogram (CH_2Cl_2 /[NBu₄][PF₆] (0.1 M) at 25 °C at 100 mV s⁻¹) of [1,3,5-((Tp*)₂(CO)₂W≡C)₃C₆H₄] (**5**) relative to [Fe(η-C₅H₅)₂]^{0/+} = 0.460 V.



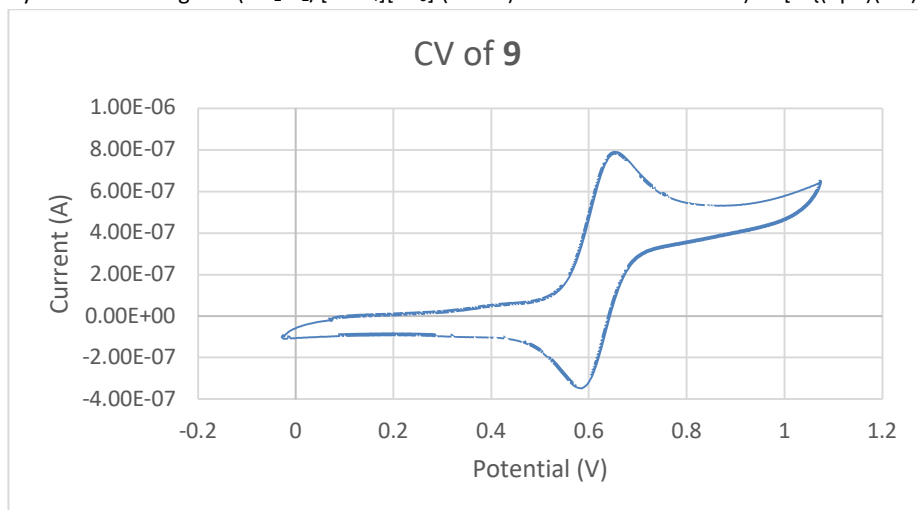
Cyclic Voltammogram (CH_2Cl_2 /[NBu₄][PF₆] (0.1 M) at 25 °C at 100 mV s⁻¹) of [1-(Tp*)(CO)₂W≡C]C₁₀H₇] (**6**) relative to [Fe(η-C₅H₅)₂]^{0/+} = 0.460 V.



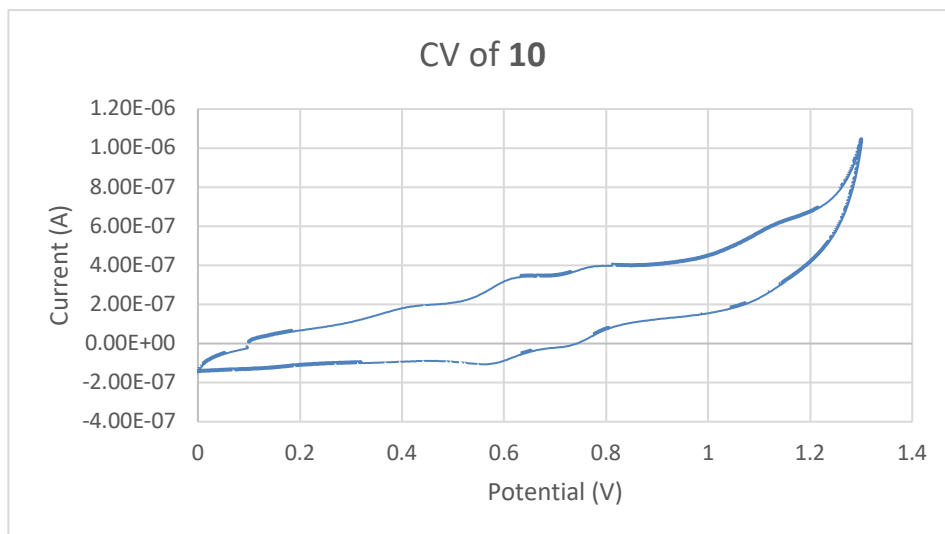
Cyclic Voltammogram (CH_2Cl_2 /[NBu₄][PF₆] (0.1 M) at 25 °C at 100 mV s⁻¹) of [2-(Tp*)(CO)₂W≡C]C₁₀H₇] (**7**) relative to [Fe(η-C₅H₅)₂]^{0/+} = 0.460 V.



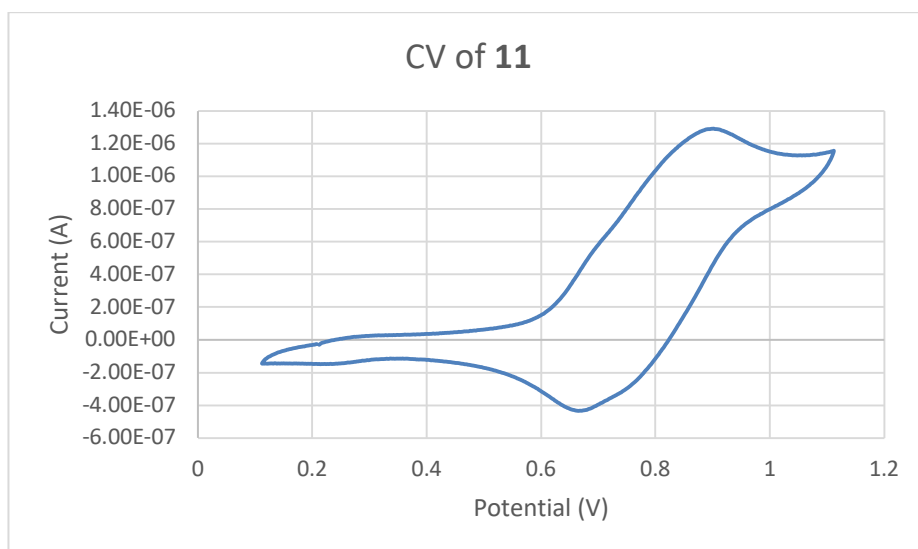
Cyclic Voltammogram (CH_2Cl_2 /[NBu₄][PF₆] (0.1 M) at 25 °C at 100 mV s⁻¹) of [9-{(Tp*)(CO)₂W≡C}C₁₄H₉] (**8**) relative to [Fe(η-C₅H₅)₂]^{0/+} = 0.460 V.



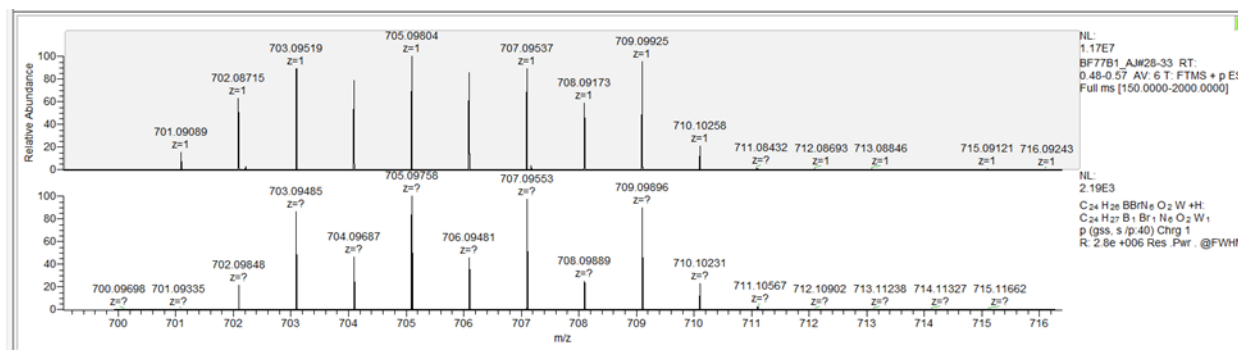
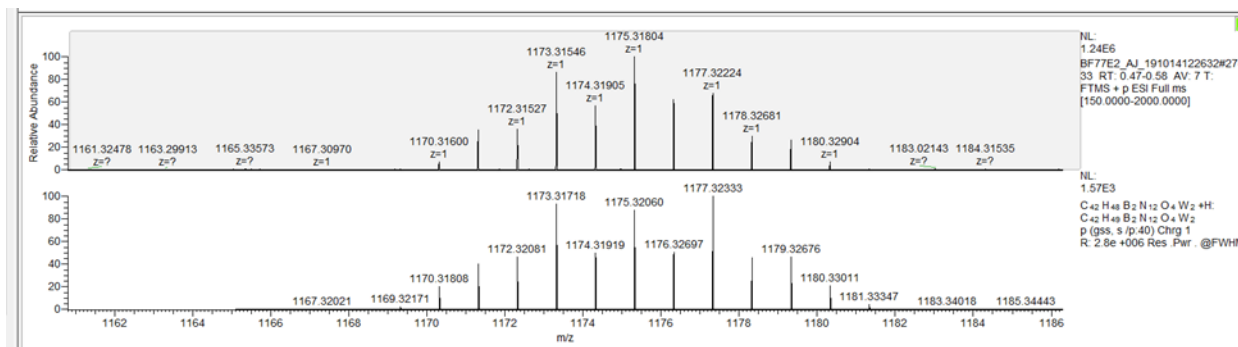
Cyclic Voltammogram (CH_2Cl_2 /[NBu₄][PF₆] (0.1 M) at 25 °C at 100 mV s⁻¹) of [9-{(Tp*)(CO)₂W≡C}C₁₄H₉] (**9**) relative to [Fe(η-C₅H₅)₂]^{0/+} = 0.460 V.

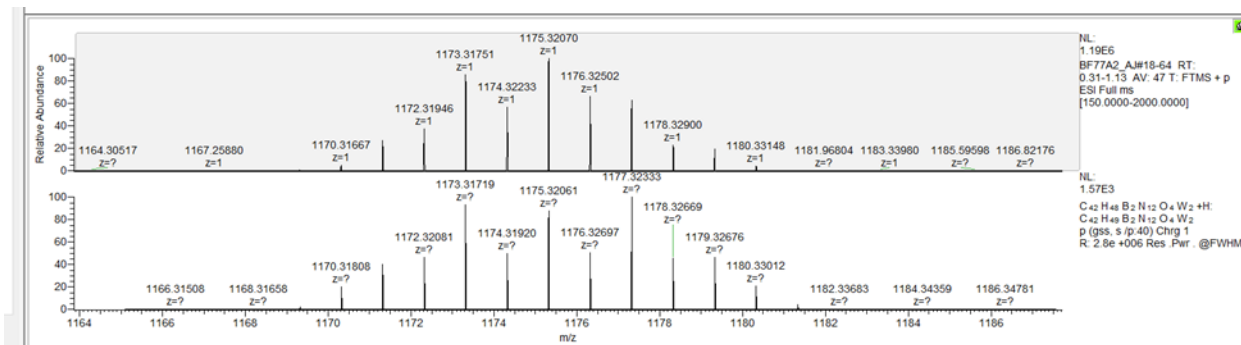


Cyclic Voltammogram ($\text{CH}_2\text{Cl}_2/[\text{NBu}_4][\text{PF}_6]$ (0.1 M) at 25°C at 100 mV s^{-1}) of $[9,10\text{-}(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}_2\text{C}_{14}\text{H}_8]$ (**10**) relative to $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]^{0/+} = 0.460\text{ V}$.

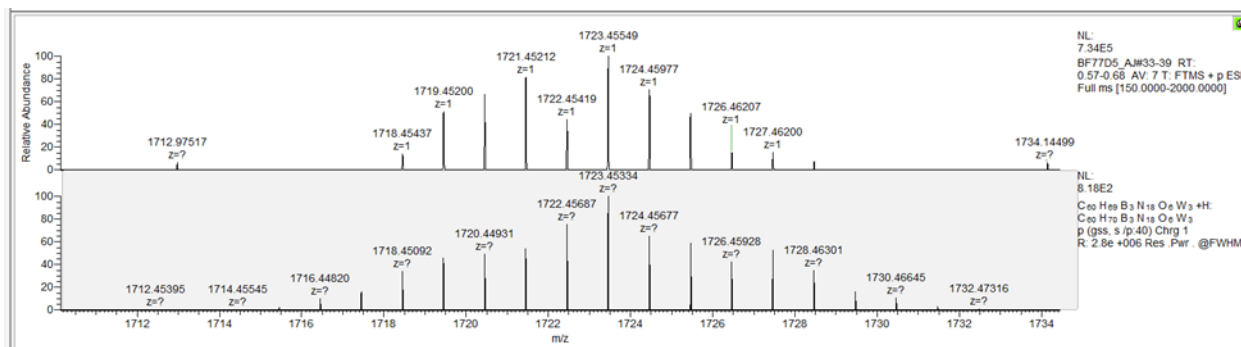


Cyclic Voltammogram ($\text{CH}_2\text{Cl}_2/[\text{NBu}_4][\text{PF}_6]$ (0.1 M) at 25°C at 100 mV s^{-1}) of $[1,3,6,8\text{-}(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}_4\text{C}_{16}\text{H}_6]$ (**11**) relative to $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]^{0/+} = 0.460\text{ V}$.

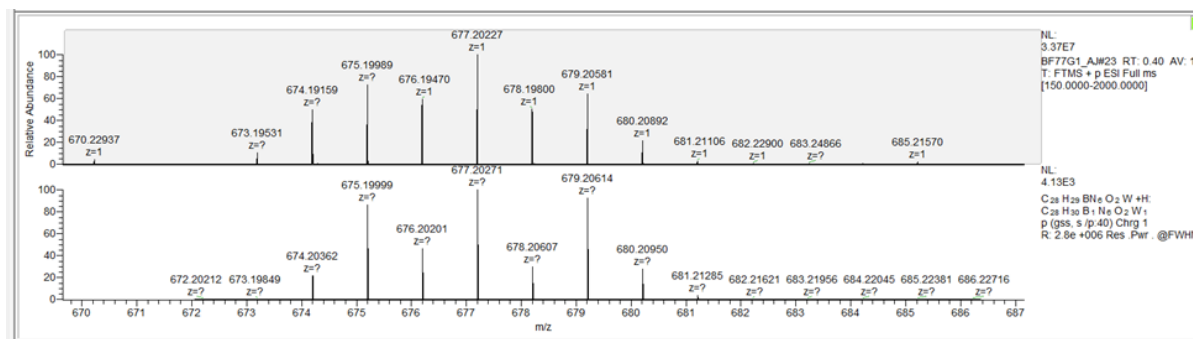
Mass spectrum (ESI, m/z, +ve ion) of **2**.Mass spectrum (ESI, m/z, +ve ion) of **3**.



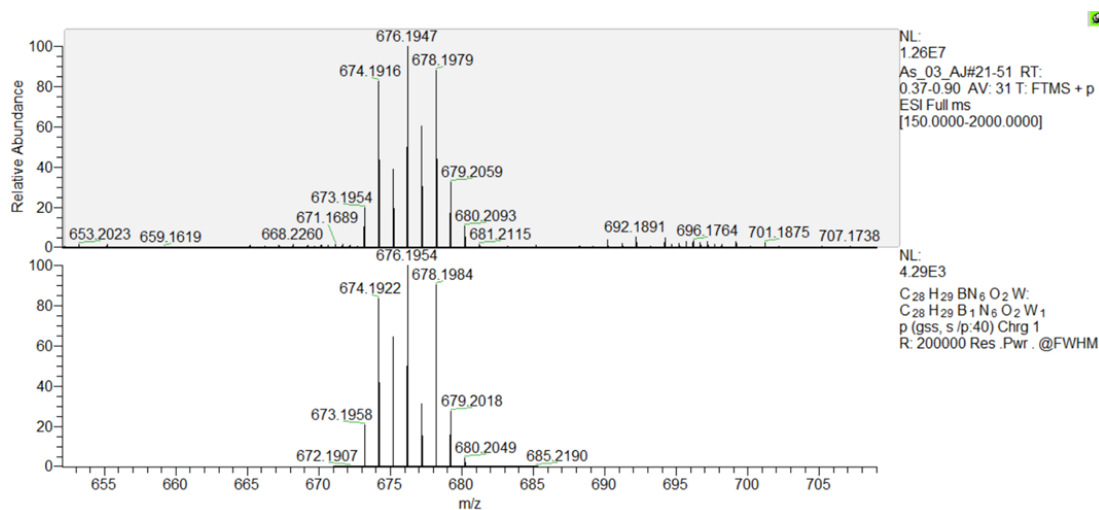
Mass spectrum (ESI, m/z, +ve ion) of 4.



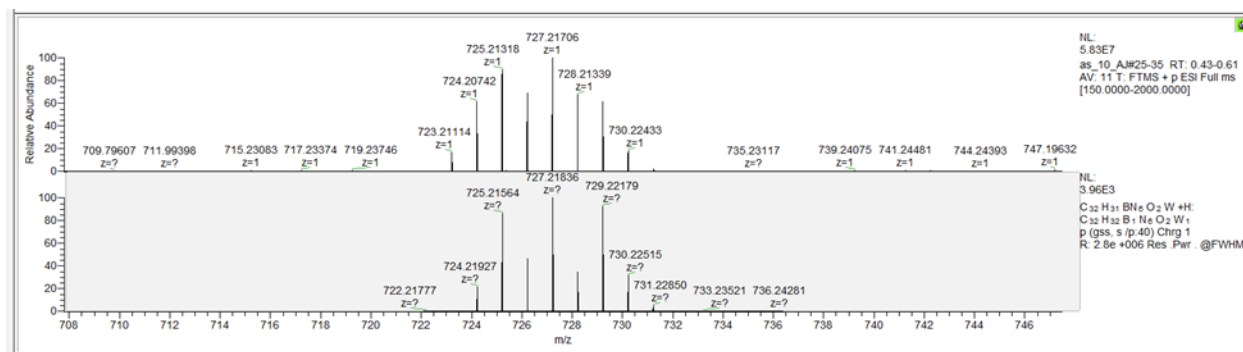
Mass spectrum (ESI, m/z, +ve ion) of 5.



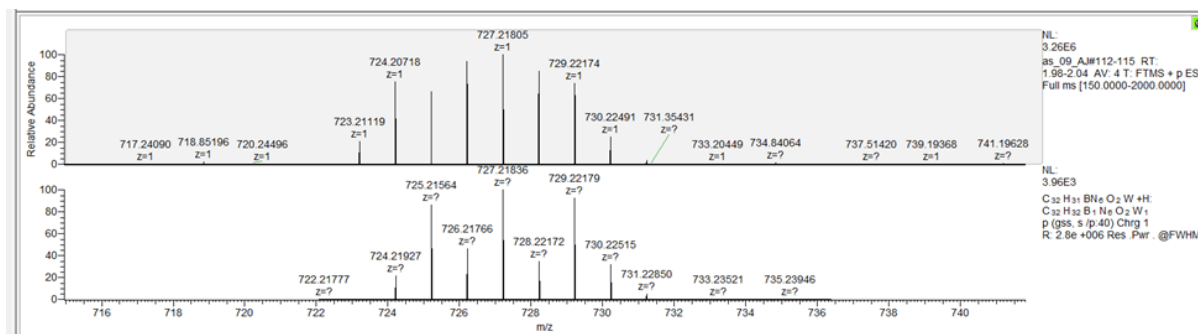
Mass spectrum (ESI, m/z, +ve ion) of 6.



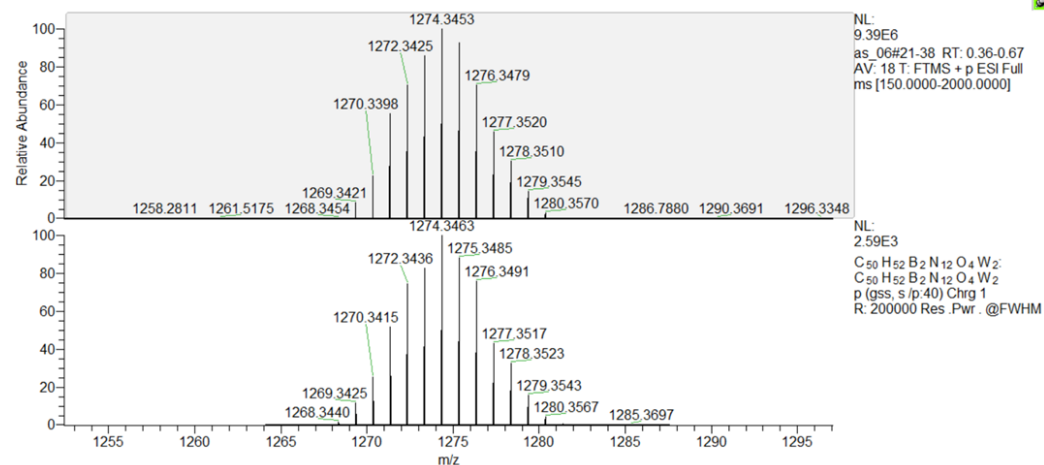
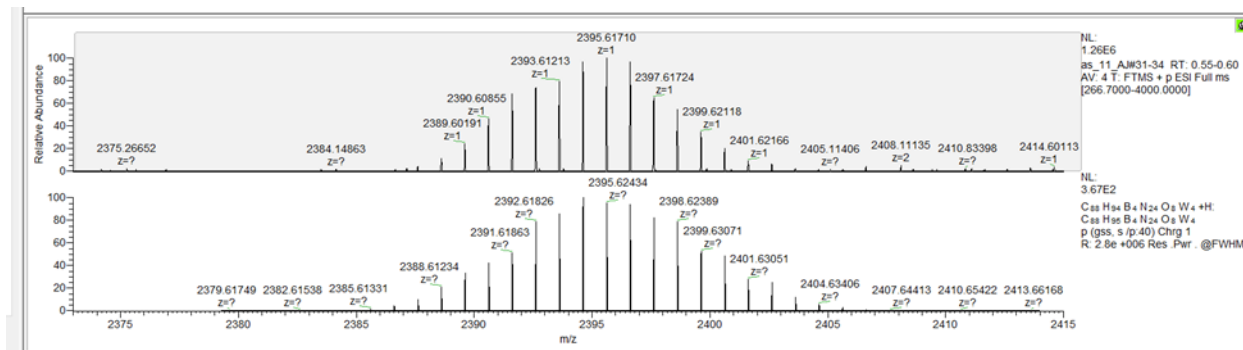
Mass spectrum (ESI, m/z, +ve ion) of 7.



Mass spectrum (ESI, m/z, +ve ion) of 8.



Mass spectrum (ESI, m/z, +ve ion) of 9.

Mass spectrum (ESI, m/z, +ve ion) of **10**.Mass spectrum (ESI, m/z, +ve ion) of **11**.