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Alkynylbis(alkylidynyl)phosphines: {LnMC}2PCCR

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Experimental section

General Considerations

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 at 25 °C on a Bruker Avance 400 (^{1}H at 400.1 MHz, ^{13}C at 100.6 MHz, ^{31}P at 162.0 MHz), a Bruker Avance 600 (^{1}H at 600.0 MHz, ^{13}C at 150.9 MHz) or a Bruker Avance 700 (^{1}H at 700.0 MHz, ^{13}C at 176.1 MHz) spectrometers. Chemical shifts (δ) are reported in ppm and referenced to the residual solvent peak (^{1}H, ^{13}C) or external 85% H_3PO_4 (^{31}P) with coupling constants given in Hz. The multiplicities of NMR resonances are denoted by the abbreviations s (singlet), d (doublet), t (triplet), m (multiplet), br (broad) and combinations thereof for more highly coupled systems. Where applicable, the stated multiplicity refers to that of the primary resonance exclusive of ^{183}W satellites. In some cases, distinct peaks were observed in the ^{1}H and ^{13}C{^{1}H} NMR spectra, but to the level of accuracy that is reportable (i.e. 2 decimal places for ^{1}H NMR, 1 decimal place for ^{13}C 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.

Infrared spectra were obtained using a Perkin-Elmer Spectrum One FT-IR spectrometer. The strengths of IR absorptions are denoted by the abbreviations vs (very strong), s (strong), m (medium), w (weak), sh (shoulder) and br (broad). 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 diffractomer using Mo-Kα radiation (λ = 0.71073 Å) or an Agilent SuperNova CCD diffractometer using Cu-Kα radiation (λ = 1.54184 Å) using 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 SHELXL programs[2] and the WinGX[3] or Olex2 software.[4] Hydrogen atoms were located geometrically and refined using a riding model. Diagrams were produced using the CCDC visualisation program Mercury.[5]

The complexes [Mo(≡CBr)(CO)$_2$(Tp*)] (**1a**) and [W(≡CBr)(CO)$_2$(Tp*)] (**1b**) have been described previously.[6] Chloro(tetrahydrothiophene)gold(I), AuCl(THT), was prepared by the literature method.[7] Bromodiphenylarsine was prepared by the literature method.[8]

Synthesis of (Tp*)(CO)$_2$Mo≡CP(Ph)C≡CSiMe$_3$ (2a). A solution of **1a** (1.00 g, 1.85 mmol) in THF (20 mL) at –78 °C was treated with *n*-BuLi (1.2 mL, 1.6 M in hexanes, 1.9 mmol). The resulting orange solution was stirred for 30 min then treated with PCl_2Ph (0.30 mL, 2.2 mmol), causing the solution to immediately turn dark orange-red. Stirring was continued for 30 min, after which time the solution was warmed to RT and the volatiles were removed *in vacuo*. The residue was dissolved in THF (20 mL) and a solution of LiC≡CSiMe$_3$ (prepared by treating HC≡CSiMe$_3$ (0.52 mL, 3.7 mmol) in THF (5 mL) with *n*-BuLi (1.2 mL, 1.6 M in hexanes, 1.9 mmol) at –78 °C) was added *via* cannula transfer. The resulting orange-brown solution was stirred for 1 h at –78 °C then warmed to RT at stirred for a further 1 h. After this time, the volatiles were removed *in vacuo* and the residue was subjected to column chromatography (40 x 3 cm silica gel column), eluting initially with *n*-hexane then with 10% v/v CH_2Cl_2/*n*-hexane. An orange band was collected and the solvents were removed under reduced pressure. The resulting orange oil was dissolved in *n*-pentane and slow removal of the solvent under reduced pressure gave pure **2a** (432 mg, 0.648 mmol, 35%) as orange microcrystals. IR (CH_2Cl_2,

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cm^{-1}): 2002s, 1919s ν(CO). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, δ): 0.26 (s, 9 H, Si*Me*$_3$), 2.28 (s, 3 H, pzC*H*$_3$), 2.31 (s, 3 H, pzC*H*$_3$), 2.31 (s, 3H, pzC*H*$_3$), 2.32 (s, 3H, pzC*H*$_3$), 2.33 (s, 3H, pzC*H*$_3$), 2.43 (s, 3 H, pzC*H*$_3$), 5.69 (s, 1 H, pz*H*), 5.79 (s, 1 H, pz*H*), 5.81 (s, 1 H, pz*H*), 7.36–7.44 (m, 3 H, P*Ph*), 7.73–7.80 (m, 2 H, P*Ph*). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C, δ): –0.1 (Si*Me*$_3$), 12.7, 12.8 (2 C, coincident), 14.6, 16.1, 16.3 (pz*C*H$_3$), 97.9 (d, $^1J_{CP}$ = 13.6 Hz, P*C*≡CTMS), 106.3, 106.3, 106.5 (pz*C*H), 116.9 (d, $^2J_{CP}$ = 3.8 Hz, PC≡*C*TMS), 128.8 (d, $^2J_{CP}$ = 8.9 Hz, *m-Ph*), 129.5 (*p-Ph*), 132.6 (d, $^1J_{CP}$ = 3.8 Hz, *i*-Ph), 133.2 (d, $^1J_{CP}$ = 22.1 Hz, *o-Ph*), 133.2 (*i-Ph*), 144.6 (2 C, coincident), 145.2, 151.3, 151.3, 151.5 (pz*C*CH$_3$), 225.8 (*C*O), 225.9 (*C*O), 295.5 (d, $^1J_{CP}$ = 88.8 Hz, Mo≡*C*). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C, δ): –2.8. MS (ESI, *m*/*z*): Found: 669.1629. Calcd for $C_{29}H_{37}{}^{11}B^{98}MoN_6O_2PSiNa$ [M + H]$^+$: 669.1627. Anal. Found: C, 52.39; H, 4.59; N, 12.34%. Calcd for $C_{29}H_{36}BMoN_6O_2PSi$: C, 52.26; H, 5.44; N, 12.61%. Crystals used for X-ray structure determination were grown by slow evaporation of a dichloromethane/ethanol solution. Crystal data for $C_{29}H_{36}BMoN_6O_2PSi$ (*M* =666.45 gmol^{-1}): orthorhombic, space group $Pna2_1$ (no. 33), *a* = 17.0572(4) , *b* = 10.5503(2) , *c* = 17.9411(4) Å, *V* = 3228.65(12)Å^3, *Z*= 4, *T*= 150.01(1)K, μ(MoKα) = 0.528 mm^{-1}, *Dcalc* = 1.371 Mgm^{-3}, 28899 reflections measured (6.55° ≤ 2Θ ≤ 57.784°), 6939 unique (R_{int} = 0.0333, R_{sigma} = 0.0323) which were used in all calculations. The final R_1 was 0.0305 (I > 2σ(I)) and wR_2 was 0.0696 (all data) for 383 refined parameters with 1 restraint.

Synthesis of [(Tp*)(CO)$_2$W≡CP(Ph)C≡CSiMe$_3$] (2b). A solution of **1b** (1.25 g, 1.99 mmol) in THF (20 mL) at –78 °C was treated with *n*-BuLi (1.3 mL, 1.6 M in hexanes, 2.1 mmol). The resulting orange solution was stirred for 30 min then treated with PCl_2Ph (0.30 mL, 2.2 mmol), causing the solution to immediately turn dark red. Stirring was continued for 30 min, after which time the solution was warmed to RT and the volatiles were removed *in vacuo*. The residue was dissolved in THF (20 mL) and a solution of LiC≡CSiMe$_3$ (prepared by treatment of HC≡CSiMe$_3$ (0.54 mL, 3.9 mmol) in THF (5 mL) with *n*-BuLi (2.0 mL, 1.6 M in hexanes, 3.2 mmol) at –78 °C) was added via cannula transfer. The resulting orange-brown solution was stirred for 1 h at –78 °C then warmed to RT at stirred for a further 1 h. After this time, the volatiles were removed in vacuo and the residue was subjected to column chromatography (40 x 3 cm silica gel column), eluting initially with *n*-hexane then with 10% v/v CH_2Cl_2/*n*-hexane. An orange band was collected and the solvents were removed under reduced pressure. The resulting orange oil was dissolved in *n*- pentane and slow removal of the solvent under reduced pressure gave pure **2b** (572 mg, 0.758 mmol, 38%) as orange microcrystals. A crystal suitable for X-ray structural analysis was grown by slow evaporation of a chloroform/cyclohexane solution. IR (CH_2Cl_2, cm^{-1}): 1986s, 1897s ν(CO). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, δ): 0.25 (s, 9 H, Si*Me*$_3$), 2.29 (s, 3 H, pzC*H*$_3$), 2.34 (s, 3 H, pzC*H*$_3$), 2.34 (s, 3 H, pzC*H*$_3$), 2.36 (s, 3 H, pzC*H*$_3$), 2.37 (s, 3 H, pzC*H*$_3$), 2.45 (s, 3 H, pzC*H*$_3$), 5.73 (s, 1 H, pz*H*), 5.85 (s, 1 H, pz*H*), 5.87 (s, 1 H, pz*H*), 7.33–7.43 (m, 3 H, P*Ph*), 7.74–7.80 (m, 2 H, P*Ph*). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C, δ): –0.1 (Si*Me*$_3$), 12.7, 12.8, 12.8, 15.2, 16.9, 17.0 (pz*C*H$_3$), 99.0 (d, $^1J_{CP}$ = 7.3 Hz, P*C*≡CTMS), 106.6, 106.6, 106.8 (pz*C*H), 115.9 (d, $^2J_{CP}$ = 1.6 Hz, PC≡*C*TMS), 128.7 (d, $^2J_{CP}$ = 4.4 Hz, *o-Ph*), 129.2 (*p-Ph*), 133.2 (d, $^3J_{CP}$ = 10.8 Hz, *m-Ph*), 133.6 (d, $^1J_{CP}$ = 1.5 Hz, *i-Ph*), 144.6, 144.6, 145.3, 152.2, 152.2, 152.6 (pz*C*CH$_3$), 224.0, 224.3 (*C*O), 280.8 (d, $^1J_{CP}$ = 76.2, $^1J_{CW}$ = 178 Hz, W≡*C*). ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C, δ): –4.0 ($^2J_{WP}$ = 84.4 Hz). MS (ESI, *m*/*z*): Found: 755.2088. Calcd for $C_{29}H_{37}{}^{11}BN_6OSiP^{184}W$ [M + H]$^+$: 755.2088. Anal. Found: C, 46.22; H, 4.92; N, 11.06. Calcd for $C_{29}H_{36}BN_6O_2SiPW$: C, 46.17; H, 4.81; N, 11.14%. Crystals used for X-ray structure determination were grown by slow evaporation of a dichloromethane/ethanol solution. Crystal data for $C_{29}H_{36}BN_6O_2PSiW$ (*M* =754.36 gmol^{-1}): orthorhombic, space group $Pna2_1$ (no. 33), *a* = 17.0998(2), *b* = 10.5256(2), *c* = 17.8373(3) Å, *V* = 3210.46(9) Å^3, *Z* = 4, *T* = 150.0(1) K, μ(MoKα) = 3.721 mm^{-1}, *Dcalc* = 1.561 Mgm^{-3}, 55398 reflections measured (6.444° ≤ 2Θ ≤ 60.19°), 8485 unique (R_{int} = 0.0387, R_{sigma} = 0.0312) which were used in all calculations. The final R_1 was 0.0235 (I > 2σ(I)) and wR_2 was 0.0467 (all data) for 376 refined parameters with 1 restraint.

Synthesis of [(Tp*)(CO)$_2$Mo≡CP(Cy)C≡CSiMe$_3$] (3a). A solution of **1a** (500 mg, 0.924 mmol) in THF (10 mL) at –78 °C was treated with *n*-BuLi (0.58 mL, 1.6 M in hexanes, 0.93 mmol). The resulting brown solution was stirred for 30 min then treated with PCl_2Cy (160 μL, 1.0 mmol), causing the solution to immediately turn orange-red. Stirring was continued for 30 min, after which time the solution was warmed to RT and the volatiles were removed in vacuo. The residue was dissolved in THF (10 mL) and a solution of LiC≡CSiMe$_3$ (prepared by treatment of HC≡CSiMe$_3$ (250 μL, 1.8 mmol) in THF (5 mL) with *n*-BuLi (1.0 mL, 1.6 M in hexanes, 1.6 mmol) at –78 °C) was added via cannula transfer. The resulting orange-brown solution was stirred for 1 h at –78 °C then warmed to RT at stirred for a further 1 h. After this time, the volatiles were removed in vacuo and the residue was subjected to column chromatography (30 x 3 cm silica gel column), eluting initially with *n*-hexane followed by 20% v/v CH_2Cl_2/*n*-hexane. An orange band was collected and the solvents were removed under reduced pressure. The resulting orange oil was dissolved in *n*- pentane and slow removal of the solvent under reduced pressure gave pure **3a** (334 mg, 0.497 mmol, 54%) as orange microcrystals. IR (CH_2Cl_2, cm^{-1}): 1999s, 1916s ν(CO). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, δ): 0.23 (s, 9 H, Si*Me*$_3$), 1.22–2.20 (m, 11 H, P*Cy*), 2.33 (s, 3 H, pzC*H*$_3$), 2.38 (s, 9 H, pzC*H*$_3$), 2.59 (s, 3 H, pzC*H*$_3$), 2.61 (s, 3H, pzC*H*$_3$), 5.72 (s, 2H, pz*H*), 5.87 (s, 2H, pz*H*). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C, δ): 0.0 (Si*Me*$_3$), 12.7, 12.9 (2 C, coincident), 14.6, 16.5, 16.6 (s, pz*C*H$_3$), 26.2 (C^4(*Cy*)), 27.1 (d, $^{2,3}J_{CP}$ = 9.1 Hz, C^{2,3,5,6}(*Cy*)), 27.1 (d, $^{2,3}J_{CP}$ = 14.8 Hz, C^{2,3,5,6}(*Cy*)), 30.1 (d, $^{2,3}J_{CP}$ = 11.8 Hz, C^{2,3,5,6}(*Cy*)), 30.2 (d, $^{2,3}J_{CP}$ = 10.0 Hz, C^{2,3,5,6}(*Cy*)), 39.4 (d, $^1J_{CP}$ = 6.2 Hz, C^1(*Cy*)), 98.1 (d, $^1J_{CP}$ = 23.4 Hz, P*C*≡CTMS), 106.3, 106.3, 106.5 (pz*C*H), 116.0 (d, $^2J_{CP}$ = 6.2 Hz, PC≡*C*TMS), 144.7, 144.7, 145.1, 151.3, 151.3, 151.5 (pz*C*CH$_3$), 226.1 (d, $^3J_{CP}$ = 2.5 Hz, *C*O), 227.2 (*C*O), 303.6 (d, $^1J_{CP}$ = 88.8 Hz, Mo≡*C*P). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C, δ): 10.0. MS (ESI, *m*/*z*): Found: 675.2098. Calcd for $C_{29}H_{42}{}^{11}B^{98}MoN_6O_2SiPNa$ [M + H]$^+$: 675.2102. Anal. Found: C, 51.72; H, 6.29; N, 12.36. Calcd for $C_{29}H_{42}BMoN_6O_2PSi$: C, 51.79; H, 6.29; N, 12.50%. Crystals used for X-ray structure determination were grown by slow evaporation of a $CHCl_3$/cyclohexane solution. Crystal data for

$C_{29}H_{42}BMoN_6O_2PSi$ (M =672.49 gmol^{-1}): orthorhombic, space group $Pna2_1$ (no. 33), a = 17.5232(3), b = 10.5308(2), c = 18.0406(3) Å, V = 3329.09(10) Å^3, Z = 4, T = 150.0(1) K, μ(MoKα) = 0.513 mm^{-1}, *Dcalc* = 1.342 Mgm^{-3}, 70511 reflections measured (6.482° ≤ 2Θ ≤ 59.786°), 8728 unique (R_{int} = 0.0338, R_{sigma} = 0.0227) which were used in all calculations. The final R_1 was 0.0318 (I > 2σ(I)) and wR_2 was 0.0720 (all data) for 410 refined parameters with 85 restraints.

Synthesis of [(Tp*)(CO)$_2$W≡CP(Cy)C≡CSiMe$_3$] (3b). A solution of **1b** (250 mg, 0.398 mmol) in THF (10 mL) at –78 °C was treated with *n*-BuLi (0.25 mL, 1.6 M in hexanes, 0.40 mmol). The resulting orange solution was stirred for 30 min then treated with PCl_2Cy (62 μL, 0.40 mmol), causing the solution to immediately turn dark red. Stirring was continued for 30 min, after which time the solution was warmed to RT and the volatiles were removed in vacuo. The residue was dissolved in THF (10 mL) and a solution of $LiC{\equiv}CSiMe_3$ (prepared by treatment of $HC{\equiv}CSiMe_3$ (55 μL, 0.40 mmol) in THF (5 mL) with *n*-BuLi (0.25 mL, 1.6 M in hexanes, 0.40 mmol) at –78 °C) was added via cannula transfer. The resulting orange-brown solution was stirred for 1 h at –78 °C then warmed to RT at stirred for a further 1 h. After this time, the volatiles were removed in vacuo and the residue was subjected to column chromatography (20 x 3 cm silica gel column), eluting initially with *n*-hexane followed by 10% v/v CH_2Cl_2/*n*-hexane. An orange band was collected and the solvents were removed under reduced pressure. The resulting orange oil was dissolved in *n*- pentane and slow removal of the solvent under reduced pressure gave pure **3b** (89.0 mg, 0.117 mmol, 29%) as yellow- orange microcrystals. IR (CH_2Cl_2, cm^{-1}): 1984s, 1893s ν(CO). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, δ): 0.21 (s, 9 H, Si*Me*$_3$), 1.20–2.20 (m, 11 H, *Cy*), 2.30 (s, 3H, pzC*H*$_3$), 2.37 (s, 6H, pzC*H*$_3$), 2.41 (s, 3 H, pzC*H*$_3$), 2.61 (s, 3 H, pzC*H*$_3$), 2.62 (s, 3 H, pzC*H*$_3$), 5.76 (s, 1 H, pz*H*), 5.92 (s, 2 H, pz*H*). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C, δ): 0.0 (Si*Me*$_3$), 12.7, 12.8, 15.3, 17.3, 17.4 (pz*C*H$_3$), 26.3 (C^4(*Cy*)), 27.2 (d, $^{2,3}J_{CP}$ = 8.9 Hz, C^{2,3,5,6}(*Cy*)), 27.3 (d, $^{2,3}J_{CP}$ = 14.1 Hz, C^{2,3,5,6}(*Cy*)), 30.1 (d, $^{2,3}J_{CP}$ = 8.6 Hz, C^{2,3,5,6}(*Cy*)), 30.2 (d, $^{2,3}J_{CP}$ = 14.1 Hz, C^{2,3,5,6}(*Cy*)), 39.3 (d, $^1J_{CP}$ = 6.2 Hz, C^1(*Cy*)), 99.3 (d, $^1J_{CP}$ = 23.2 Hz, P*C*≡CTMS), 106.6 (2 C, coincident), 106.8 (pz*C*H), 114.9 (d, $^2J_{CP}$ = 6.2 Hz, PC≡*C*TMS), 144.6, 144.7, 145.3, 152.2, 152.3, 152.6 (pz*C*CH$_3$), 224.2, 226.0 (*C*O), 288.0 (d, $^1J_{CP}$ = 77.6 Hz, W≡*C*). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C, δ): 6.6 ($^2J_{WP}$ = 78.0 Hz). MS (ESI, *m*/*z*): Found: 761.2550. Calcd for $C_{29}H_{43}{}^{11}BN_6O_2PSi^{184}W$ [M + H]$^+$: 761.2565. Anal. Found: C, 45.75; H, 5.50; N, 11.12. Calcd for $C_{29}H_{42}BN_6O_2PSiW$: C, 45.81; H, 5.57; N, 11.05%.

Synthesis of [(Tp*)(CO)$_2$Mo≡CP(Ph)C≡CH] (4a). A solution of **2a** (100 mg, 0.150 mmol) in CH_2Cl_2 (5 mL) was treated with TBAF (150 μL, 1.0 M in THF, 0.150 mmol) and the mixture was stirred at RT for 1 h, during which time the initially bright orange solution darkened. After this time, the solution was dried in vacuo and the residue was subjected to column chromatography (10 x 1 cm silica gel column), eluting with CH_2Cl_2. An orange band was collected, *n*-hexane was added and slow removal of the dichloromethane under reduced pressure gave an orange solid of pure **4a** (77.0 mg, 0.130 mmol, 86%). IR (CH_2Cl_2, cm^{-1}): 2003s, 1921s ν(CO). ^{1}H NMR (700 MHz, $CDCl_3$, 25 °C, δ): 2.29 (s, 3 H, pzC*H*$_3$), 2.32 (s, 3 H, pzC*H*$_3$), 2.33 (s, 3 H, pzC*H*$_3$), 2.34 (s, 6 H, pzC*H*$_3$), 2.42 (s, 3 H, pzC*H*$_3$), 3.34 (s, 1 H, C≡C*H*), 5.69 (s, 1 H, pz*H*), 5.80 (s, 1 H, pz*H*), 5.82 (s, 1 H, pz*H*), 7.36–7.46 (m, 3 H, P*Ph*), 7.77–7.82 (t, 3JHH = 8.3 Hz 2 H, P*Ph*). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$, 25 °C, δ): 12.7, 12.8 (2 C, coincident), 14.6, 16.1, 16.2 (pz*C*H$_3$), *ca.* 77.1 (P*C*≡CH, obscured by $CDCl_3$), 96.2 (PC≡*C*H), 106.3, 106.4, 106.5 (pz*C*H), 128.9 (d, $^2J_{CP}$ = 8.6 Hz, *o-Ph*), 129.6 (*p-Ph*), 131.0 (d, $^1J_{CP}$ = 11.8 Hz, P*C*≡CH), 132.0 (d, $^1J_{CP}$ = 3.4 Hz, *i-Ph*), 133.2 (d, $^3J_{CP}$ = 21.8 Hz, *m-Ph*), 144.7, 144.7, 145.2, 151.3, 151.3, 151.5 (pz*C*CH$_3$), 225.7, 225.7 (*C*O), 294.1 (d, $^1J_{CP}$ = 87.6 Hz, Mo≡*C*). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C, δ): –4.8. MS (ESI, *m*/*z*): Found: 597.1237. Calcd for $C_{26}H_{29}{}^{11}BN_6O_2P^{184}W$ [M + H]$^+$ 597.1231. Anal. Found: C, 52.42; H, 4.81; N, 14.05%. Calcd for $C_{26}H_{28}BMoN_6O_2P$: C, 52.55; H, 4.75; N, 14.14%.

Synthesis of [(Tp*)(CO)$_2$W≡CP(Ph)C≡CH] (4b). A solution of **2b** (25.0 mg, 0.0331 mmol) in THF (5 mL) was treated with TBAF (33.1 μL, 1.0 M in THF, 0.0331 mmol) and the mixture was stirred at RT for 2 h, during which time the initially bright orange solution darkened. After this time, the solution was dried in vacuo, the residue was dissolved in CH_2Cl_2 (10 mL) and washed with deionised water (3 x 10 mL). The CH_2Cl_2 layer was collected and dried under reduced pressure. The residue was redissolved in dichloromethane and subjected to column chromatography (10 x 1 cm silica gel column), eluting with CH_2Cl_2. An orange band was collected, *n*-hexane was added and slow removal of the dichloromethane under reduced pressure gave an orange solid of pure **4b** (19.0 mg, 0.0279 mmol, 84%). IR (CH_2Cl_2, cm^{-1}): 1999s, 1910s ν(CO). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, δ): 2.28 (s, 3H, pzC*H*$_3$), 2.33 (s, 3H, pzC*H*$_3$), 2.33 (s, 3H, pzC*H*$_3$), 2.35 (s, 3 H, pzC*H*$_3$), 2.37 (s, 6H, pzC*H*$_3$), 2.42 (s, 3H, pzC*H*$_3$), 3.28 (s, 1H, C≡C*H*), 5.73 (s, 1H, pz*H*), 5.85 (s, 1H, pz*H*), 5.86 (s, 1H, pz*H*), 7.34–7.43 (m, 3H, P*Ph*), 7.75–7.80 (m, 2H, P*Ph*). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C, δ): 12.8, 15.3, 16.8, 16.9 (pz*C*H$_3$), 78.3 (d, $^1J_{CP}$ = 13.0 Hz, P*C*≡CH), 95.5 (PC≡*C*H), 106.7, 106.9 (pz*C*H), 128.8 (d $^1J_{CP}$ = 8.8 Hz), 129.3, 133.1, 133.3 (*Ph*, could not be unambiguously assigned), 144.7, 145.4, 152.2, 152.2, 152.7 (pz*C*CH$_3$), 224.4, 224.4 (*C*O), 279.7 (d, $^1J_{CP}$ = 75.4 Hz, W≡*C*). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C, δ): –5.5 ($^2J_{WP}$ = 81.8 Hz). MS (ESI, *m*/*z*): Found: 683.1686. Calcd for $C_{26}H_{29}{}^{11}BN_6O_2P^{184}W$ [M + H]$^+$ 683.1687. Anal. Found: C, 46.51; H, 3.73; N, 12.15%. Calcd for $C_{26}H_{28}BN_6O_2WP$: C, 45.78; H, 4.14; N, 12.32%. Despite spectroscopic purity, results for this complex were consistently high in carbon (ca 0.7%).

Synthesis of [(Tp*)(CO)$_2$Mo≡CP(Cy)C≡CH] (5a). To a solution of **3a** (100 mg, 0.149 mmol) in THF (5 mL) was added TBAF (149 μL, 1.0 M in THF, 0.149 mmol) and the mixture was stirred at RT for 3 h. After this time, the volatiles were removed in vacuo and the residue subjected to column chromatography (10 x 1 cm silica gel column), eluting with *n*-hexane followed by 10% v/v CH_2Cl_2/*n*-hexane. An orange band was collected and the solvents were removed under reduced pressure and the residue recrystallized from *n*-pentane to furnish pure **5a** (78.0 mg, 0.130 mmol, 87%) as orange microcrystals. IR (CH_2Cl_2, cm^{-1}): 2000s, 1916s ν(CO). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, δ): 1.30–2.22 (m, 11 H, *Cy*), 2.30 (s, 3 H, pzC*H*$_3$), 2.37 (s, 9 H, pzC*H*$_3$), 2.59 (s, 3 H, pzC*H*$_3$), 2.60 (s, 3 H, pzC*H*$_3$), 3.15 (d, $^3J_{HP}$ = 0.9 Hz, 1 H, C≡C*H*), 5.72 (s, 1 H, pz*H*), 5.87 (s, 2 H, pz*H*). ^{13}C{^{1}H} NMR (101 MHz,

$CDCl_3$, 25 °C, δ): 12.7, 12.9 (2 C, coincident), 14.6, 16.4, 16.4 (pz*C*H_3), 26.1 (C^4(*Cy*)), 27.0 (d, $^{2,3}J_{CP}$ = 9.0 Hz, $C^{2,3,5,6}$(*Cy*)), 27.0 (d, $^{2,3}J_{CP}$ = 14.5 Hz, $C^{2,3,5,6}$(*Cy*)), 30.0 (d, $^{2,3}J_{CP}$ = 12.5 Hz, $C^{2,3,5,6}$(*Cy*)), 30.1 (d, $^{2,3}J_{CP}$ = 10.4 Hz, $C^{2,3,5,6}$(*Cy*)), 39.2 (d, $^{1}J_{CP}$ = 6.3 Hz, C^1(*Cy*)), *ca.* 77.1 (obs by CDCl3, P*C*≡CH), 95.7 (s, PC≡*C*H), 106.3 (2 C, coincident), 106.5 (pz*C*H), 144.7, 144.7, 145.2, 151.2, 151.3, 151.5 (pz*C*CH_3), 226.4, 226.9 (*C*O), 302.5 (d, $^{1}J_{CP}$ = 89.1, Mo≡*C*P). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C, δ): 8.0. MS (ESI, *m*/*z*): Found: 603.1705. Calcd for $C_{26}H_{35}{}^{11}BN_6O_2{}^{98}MoP$ $[M + H]^+$: 603.1701. Anal. Found: C, 51.89; H, 5.62; N, 13.93. Calcd for $C_{26}H_{34}BMoN_6O_2P$: C, 52.02; H, 5.71; N, 14.00%.

Synthesis of [(Tp*)(CO)$_2$W≡CP(Cy)C≡CH] (5b). To a solution of **3b** (100 mg, 0.138 mmol) in THF (5 mL) was added TBAF (14 μL, 1.0 M in THF, 0.14 mmol) and the mixture was stirred at RT for 3 h. After this time, the volatiles were removed in vacuo and the residue subjected to column chromatography (10 x 1 cm silica gel column), eluting with *n*-hexane followed by 10% v/v CH_2Cl_2/*n*-hexane. An orange band was collected and the solvents were removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and ethanol and on slow removal of the CH_2Cl_2 under reduced pressure, an orange precipitate formed, which was collected by filtration and washed with cold ethanol to give pure **5b** (69.0 mg, 0.100 mmol, 73%) as orange microcrystals. IR (CH_2Cl_2, cm^{-1}): 1984s, 1893s ν(CO). ^1H NMR (400 MHz, $CDCl_3$, 25 °C, δ): 1.30–1.50 (m, 5 H, *Cy*), 1.66–1.72 (m, 1 H, *Cy*), 1.79–1.87 (m, 2 H, *Cy*), 2.02–2.20 (m, 3 H, *Cy*), 2.32 (s, 3 H, pzC*H*$_3$), 2.37 (s, 6 H, pzC*H*$_3$), 2.41 (s, 3 H, pzC*H*$_3$), 2.61 (s, 3 H, pzC*H*$_3$), 2.63 (s, 3 H, pzC*H*$_3$), 3.08 (s, 1 H, integration varies between 0.4–0.8 H, PC≡C*H*), 5.76 (s, 1 H, pzC*H*), 5.91 (s, 2 H, pzC*H*). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C, δ): 12.7, 12.8, 15.3, 17.1, 17.1, 17.3 (pz*C*H_3), 26.2 (C^4(*Cy*)), 27.1 (d, $^{2,3}J_{CP}$ = 5.4 Hz, $C^{2,3,5,6}$(*Cy*)), 27.2 (d, $^{2,3}J_{CP}$ = 11.1 Hz, $C^{2,3,5,6}$*Cy*)), 30.0 ($C^{2,3,5,6}$(*Cy*)), 30.2 (d, $^{2,3}J_{CP}$ = 9.7 Hz, $C^{2,3,5,6}$(*Cy*)), 39.1 (d, $^{1}J_{CP}$ = 5.8 Hz, C^1(*Cy*)), 78.2 (d, $^{1}J_{CP}$ = 22.2 Hz, P*C*≡CH), 94.9 (d, $^{1}J_{CP}$ = 2.7 Hz, PC≡*C*H), 106.7, 106.9 (pz*C*H), 144.6, 144.7, 145.3, 152.2, 152.3, 152.6 (pz*C*CH_3), 224.7, 225.7 (*C*O), 286.9, 287.0 ($^{1}J_{CP}$ = 76.3 Hz, W≡*C*). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C, δ): 5.0 ($^{1}J_{CW}$ = 77 Hz), 5.1 ($^{1}J_{CW}$ = 77 Hz). The P and carbyne C atoms give rise to two slightly distinct signals in the $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ spectra, respectively, in a ratio of *ca.* 40:60. We suspect that this observation is a result of a large barrier to rotation about the phosphorus, a consequence of the bulky substituents, thus giving rise to distinct rotamers with slightly (a difference of 10 Hz in the $^{31}P\{^1H\}$ and 4 Hz in the $^{13}C\{^1H\}$ NMR). MS (ESI, *m*/*z*): Found: 689.2160. Calcd for $C_{26}H_{35}{}^{11}BN_6O_2P^{184}W$ $[M + H]^+$: 689.2162.

Anal. Found: C, 45.59; H, 5.16; N, 12.11%. Calcd for $C_{26}H_{34}BN_6O_2PW$: C, 45.38; H, 4.98; N, 12.21%. The crystal (of unfortunately less-than-ideal quality) used for X-ray structure determination was grown by slow evaporation of a $CHCl_3$/ethanol solution. The structure was found to contain diffuse solvent which could not be adequately modelled through disordered components and so the SQUEEZE algorithm was invoked. Crystal data for $C_{26}H_{34}BClN_6O_2PW$ (M = 688.22 $gmol^{-1}$): orthorhombic, space group Pbca (no. 61), a = 15.0730(4), b = 20.5330(5), c = 20.5731(5) Å, V = 6367.2(3) Å^3, Z = 8, T = 150.0(1) K, μ(CuKα) = 7.441 mm^{-1}, $Dcalc$ = 1.436 Mgm^{-3}, 9401 reflections measured (8.452° ≤ 2Θ ≤ 133.176°), 4874 unique (R_{int} = 0.0326, R_{sigma} = 0.0447) which were used in all calculations. The final R_1 was 0.0580 (I > 2σ(I)) and wR_2 was 0.1676 (all data) for 346 refined parameters with 0 restraints.

Synthesis of [{(Tp*)(CO)$_2$W≡C}$_2$PC≡CPh] (6). A solution of **1b** (250 mg, 0.398 mmol) in THF (10 mL) at –78 °C was treated with *n*-BuLi (0.249 mL, 1.6 M in hexanes, 0.398 mmol). The resulting orange solution was stirred for 30 min at reduced temperature then treated with PCl_3 (17 μL, 0.19 mmol). The solution was warmed to RT and the resulting red solution was stirred for 30 min, after which time the volatiles were removed *in vacuo*. The residue was dissolved in THF (5 mL) and a separately prepared solution of LiC≡CPh (prepared by treating HC≡CPh (100 μL, 0.91 mmol) in THF (5 mL) with *n*-BuLi (0.50 mL, 1.6 M in hexanes, 0.80 mmol) at –78 °C) was added *via* cannula, causing the mixture to turn dark orange. Stirring was continued for 1 h, the volatiles were removed *in vacuo* and the residue was subjected to column chromatography (30 x 1 cm silica gel column), eluting with petroleum ether (40–60 °C) with gradually increasing amounts of CH_2Cl_2. An orange band was collected with 30% v/v CH_2Cl_2/petrol and was dried under reduced pressure to give an orange solid of pure **6** (198 mg, 0.161 mmol, 81%). IR (CH_2Cl_2, cm^{-1}): 1990s, 1981s, 1898s ν(CO). ^1H NMR (400 MHz, $CDCl_3$, 25 °C, δ): 2.31 (s, 6 H, pzC*H*$_3$), 2.37 (s, 12 H, pzC*H*$_3$), 2.39 (s, 6 H, pzC*H*$_3$), 2.45 (s, 12 H, pzC*H*$_3$), 5.74 (s, 2 H, pz*H*), 5.78 (s, 4 H, pz*H*), 7.29–7.34 (m, 3 H, *Ph*), 7.47–7.53 (m, 2 H, *Ph*). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C, δ): 12.7, 12.8, 15.3, 16.8 (pz*C*H_3), 79.8 (d, $^{1}J_{CP}$ = 9.6 Hz, P*C*≡C), 106.4, 106.8 (pz*C*H), 107.7 (d, $^{1}J_{CP}$ = 2.8 Hz, PC≡*C*), 123.7 (*i*-*Ph*), 128.3 (*o*-*Ph*), 128.4 (*p*-*Ph*), 131.8 (*m*-*Ph*), 144.1, 145.3, 152.4, 152.6 (pz*C*CH_3), 224.7 (*C*O, $^{1}J_{CW}$ = 168 Hz), 274.6 (d, $^{1}J_{CP}$ = 76.5, W≡*C*P). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C, δ): 34.5 ($^{2}J_{PW}$ = 82 Hz). MS (ESI, *m*/*z*): Found: 1230.3019. Calcd for $C_{44}H_{50}{}^{11}B_2N_{12}O_4P^{184}W_2$ $[M + H]^+$: 1231.3049. Anal. Found: C, 43.10; H, 4.10; N, 13.55. Calcd for $C_{44}H_{49}B_2N_{12}O_4PW_2$: C, 42.96; H, 4.01; N, 13.66%. A crystal suitable for X-ray structure determination was grown by slow evaporation of a CH_2Cl_2/MeCN solution. Crystal data for $C_{44}H_{49}B_2N_{12}O_4PW_2$ (M = 1230.24 $gmol^{-1}$): monoclinic, space group C2/c (no. 15), a = 22.4317(10), b = 10.8744(3), c = 23.8394(10) Å, β = 117.336(5)°, V = 5165.8(4) Å^3, Z = 4, T = 150.0(1) K, μ(CuKα) = 8.815 mm^{-1}, $Dcalc$ = 1.582 Mgm^{-3}, 36085 reflections measured (8.876° ≤ 2Θ ≤ 144.506°), 5069 unique (R_{int} = 0.0666, R_{sigma} = 0.0342) which were used in all calculations. The final R_1 was 0.0516 (I > 2σ(I)) and wR_2 was 0.1409 (all data) for 324 refined parameters with 36 restraints.

Synthesis of [{(Tp*)(CO)$_2$W≡C}$_2$PC≡C(*p*-tolyl)] (7). A solution of **1b** (250 mg, 0.398 mmol) in THF (10 mL) at –78 °C was treated with *n*-BuLi (0.249 mL, 1.6 M in hexanes, 0.398 mmol). The resulting orange solution was stirred for 30 min at reduced temperature then treated with PCl_3 (17 μL, 0.19 mmol). The solution was warmed to RT and the resulting red solution was stirred for 30 min, after which time the volatiles were removed *in vacuo*. The residue was dissolved in THF (5 mL) and a separately prepared solution of LiC≡C(*p*-tolyl) (prepared by treating HC≡C(*p*-tolyl) (110 mg, 0.95 mmol) in THF (5 mL) with *n*-BuLi (0.50 mL, 1.6 M in hexanes, 0.80 mmol) at –78 °C) was added *via* cannula, causing the mixture to turn dark orange-red. Stirring was continued for 1 h, the volatiles were removed *in*

vacuo and the residue was subjected to column chromatography (30 x 1 cm silica gel column), eluting with petroleum ether (40–60 °C) with gradually increasing amounts of CH_2Cl_2. An orange band was collected with 50% v/v CH_2Cl_2/petrol and the solvents were removed under reduced pressure to give a bright red solid of pure **7** (132 mg, 0.106 mmol, 53%). IR (CH_2Cl_2, cm^{-1}): 1990s, 1980s, 1897s ν(CO). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, δ): 2.31 (s, 6 H, pzCH_3), 2.36 (s, 3 H, $C_6H_4CH_3$), 2.37 (s, 12 H, pzCH_3), 2.39 (s, 6 H, pzCH_3), 2.46 (s, 6 H, pzCH_3), 5.75 (s, 2 H pz$H$), 5.77 (s, 4 H, pz$H$), 7.13 (d, $^3J_{HH}$ = 7.8 Hz, 2 H, C^{2,6}{*p*-tolyl}), 7.40 (d, $^3J_{HH}$ = 7.8 Hz, 2 H, C^{3,5}{*p*-tolyl}). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C, δ): 12.7, 12.8, 15.3, 16.8 (pzCH_3), 21.7 ($C_6H_4CH_3$), 79.0 (d, $^1J_{CP}$ = 7.4 Hz, PC≡C), 106.4, 106.6 (pz$C$H), 107.9 (d, $^2J_{CP}$ = 3.6 Hz, PC≡C), 120.7 (C^4{*p*-tolyl}), 129.1 (C^{2,6}{*p*-tolyl}), 131.7 (C^{3,5}{*p*-tolyl}), 138.5 (C^1{*p*-tolyl}), 144.1, 145.3, 152.4, 152.6 (pz$C$CH$_3$), 224.7 (CO, $^1J_{CW}$ = 168 Hz), 275.1 (d, $^1J_{CP}$ = 75.3, W≡CP). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C, δ): 34.8 ($^2J_{PW}$ = 83 Hz). MS (ESI, *m*/*z*): Found: 1245.3196. Calcd for $C_{45}H_{52}{}^{11}B_2N_{12}O_4P^{184}W_2$ [M + H]$^+$: 1245.3182. Anal. Found: C, 43.38; H, 4.19; N, 13.48. Calcd for $C_{45}H_{51}B_2N_{12}O_4PW_2$: C, 43.44; H, 4.13; N, 13.51%. The crystal used for X-ray structure determination was grown by slow evaporation of a CH_2Cl_2/ethanol mixture. Crystal data for $C_{45}H_{51}B_2N_{12}O_4PW_2$ (M =1244.26 gmol^{-1}): triclinic, space group P-1 (no. 2), a = 10.7103(8), b = 12.8936(5), c = 19.5744(8) Å, α = 77.598(4)°, β = 78.252(5)°, γ = 70.388(5)°, V = 2461.3(2) Å^3, Z = 2, T = 150.0(1) K, μ(MoKα) = 4.757 mm^{-1}, $Dcalc$ = 1.679 gcm^{-3}, 35346 reflections measured (6.776° ≤ 2Θ ≤ 52.744°), 10039 unique (R_{int} = 0.0470, R_{sigma} = 0.0489) which were used in all calculations. The final R_1 was 0.0367 (I > 2σ(I)) and wR_2 was 0.0865 (all data) for 569 refined parameters with 0 restraints.

Synthesis of [{(Tp*)(CO)$_2$W≡C}$_2$PC≡CC(CH$_3$)$_3$] (8). A solution of **1b** (250 mg, 0.398 mmol) in THF (10 mL) at –78 °C was treated with *n*-BuLi (0.249 mL, 1.6 M in hexanes, 0.398 mmol). The resulting light brown solution was stirred for 1 h at reduced temperature then treated with PCl_3 (17 μL, 0.19 mmol). The resulting red solution was stirred for 30 min at reduced temperature then treated with a separately prepared solution of LiC≡CC(CH$_3$)$_3$ (prepared by treating HC≡CC(CH$_3$)$_3$ (100 μL, 0.81 mmol) in THF (5 mL) with *n*-BuLi (0.50 mL, 1.6 M in hexanes, 0.80 mmol) at –78 °C) was added *via* cannula, causing the mixture to turn dark orange. Stirring was continued for 1 h, the volatiles were removed *in vacuo* and the residue was subjected to column chromatography (30 x 1 cm silica gel column), eluting with *n*-pentane with a gradually increasing proportion of CH_2Cl_2. An orange band was collected with 50% v/v CH_2Cl_2/pentane and was dried under reduced pressure to give a red solid of pure **8** (48.0 mg, 0.0397 mmol, 20%). IR (CH_2Cl_2, cm^{-1}): 1989s, 1979s, 1896s ν(CO). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, δ): 1.28 (s, 9 H, ^{t}*Bu*), 2.30 (s, 9 H, pzCH_3), 2.36 (s, 12 H, pzCH_3), 2.37 (s, 6 H, pzCH_3), 2.39 (s, 9 H, pzCH_3), 5.73 (s, 2 H, pzCH), 5.75 (s, 4 H, pzCH). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 25 °C, δ): 12.7, 12.8, 15.2, 17.0 (pzCH_3), 29.1 (C(CH_3)$_3$), 30.8 (C(CH_3)$_3$), 67.7 (d, $^1J_{CP}$ = 3.2 Hz, PC≡C), 106.3, 106.8 (pz$C$H), 117.8 (d, $^2J_{CP}$ = 2.4 Hz, PC≡C), 144.0, 145.2, 152.4, 152.5 (pz$C$CH$_3$), 224.6 (CO), 277.9 (d, $^1J_{CP}$ = 74.2 Hz, W≡C). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C, δ): 36.0 ($^2J_{PW}$ = 80 Hz). MS (ESI, *m*/*z*): Found: 1227.3284. Calcd for $C_{42}H_{54}{}^{11}B_2N_{12}O_5P^{184}W_2$ [M + O + H]$^+$: 1227.3288. Anal. Found: C, 38.83; H, 4.22; N, 12.69. Calcd for $C_{42}H_{53}B_2N_{12}O_4PW_2{\cdot}CHCl_3$: C, 38.84; H, 4.09; N, 12.64%. The crystals used for elemental analysis and X-ray structure determination were grown by slow evaporation of a $CHCl_3$/ethanol mixture and proved to be a chloroform solvate. Crystal data for $C_{43}H_{54}B_2Cl_3N_{12}O_4PW_2$ (M =1329.62 gmol^{-1}): monoclinic, space group C2/c (no. 15), a = 21.4150(5), b = 10.8991(2), c = 24.0583(5) Å, β = 115.668(3)°, V = 5061.2(2) Å^3, Z = 4, T = 150.0(1) K, μ(MoKα) = 4.785 mm^{-1}, $Dcalc$ = 1.745 gcm^{-3}, 51216 reflections measured (6.76° ≤ 2Θ ≤ 52.742°), 5154 unique (R_{int} = 0.0238, R_{sigma} = 0.0107) which were used in all calculations. The final R_1 was 0.0198 (I > 2σ(I)) and wR_2 was 0.0441 (all data) for 349 refined parameters with 30 restraints.

Synthesis of [{(Tp*)(CO)$_2$W≡C}$_2$PC≡CSiMe$_3$] (9). A solution of **1b** (250 mg, 0.398 mmol) in THF (10 mL) at –78 °C was treated with *n*-BuLi (0.25 mL, 1.6 M in hexanes, 0.40 mmol). The resulting brown solution was stirred for 30 min at reduced temperature then treated with PCl_3 (17 μL, 0.19 mmol). The solution was warmed to RT and the resulting red solution stirred for 30 min, after which time the volatiles were removed *in vacuo*. The residue was dissolved in THF (5 mL) and a separately prepared solution of LiC≡CTMS (prepared from HC≡CTMS (290 μL, 2.0 mmol) and *n*-BuLi (1.00 mL, 1.6 M in hexanes, 1.60 mmol) in THF (5 mL)) was added *via* cannula, causing the mixture to turn dark orange. Stirring was continued for 1 h, the volatiles were removed in vacuo, and the residue was subjected to column chromatography (30 x 1 cm silica gel column), eluting with petroleum ether (40–60 °C) with gradually increasing amounts of CH_2Cl_2. At 40% v/v CH_2Cl_2/petrol an orange band was collected, which was dried under reduced pressure and recrystallized from CH_2Cl_2/ethanol to give pure **9** (153 mg, 0.125 mmol, 63%) as an orange–red solid. A small red band was also collected with 50% v/v CH_2Cl_2/petrol as the eluent, which was dried *in vacuo* to give a red solid which proved to be the desilylated product **10** (29.0 mg, 0.0251 mmol, 12%). IR (CH_2Cl_2, cm^{-1}): 1991s, 1982s, 1898s ν(CO). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, δ): 0.21 (s, 9 H, Si(CH_3)$_3$), 2.30 (s, 6 H, pzCH_3), 2.36 (s, 12 H, pzCH_3), 2.38 (s, 6 H, pzCH_3), 2.41 (s, 12 H, pzCH_3), 5.74 (s, 2 H, pzCH), 5.77 (s, 2 H, pzCH). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C, δ): –0.1 (Si(CH_3)$_3$), 12.7, 12.8, 15.2, 17.0 (pzCH_3), 95.3 (d, $^1J_{CP}$ = 15.8 Hz, PC≡C), 106.3, 106.8 (pz$C$H), 115.7 (PC≡C), 144.1, 145.3, 152.4, 152.6 (pz$C$CH$_3$), 224.5 (CO), 274.1 (d, $^1J_{CP}$ = 75.7, W≡CP). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C, δ): (s). 36.1 ($^2J_{PW}$ = 83 Hz). MS (ESI, *m*/*z*): Found: 1227.3109. Calcd for $C_{41}H_{53}{}^{11}B_2N_{12}O_4P^{184}W_2$ [M + H]$^+$: 1227.3103. Anal. Found: C, 39.98; H, 4.50; N, 13.62. Calcd for $C_{41}H_{53}B_2N_{12}O_4PSiW_2$: C, 40.16; H, 4.36; N, 13.71%. A crystal suitable for structure determination was grown by slow evaporation of a $CHCl_3$/ethanol mixture and was found to contain *ca*. 2/3 equivalents of chloroform of solvation. Crystal data for $C_{41.67}H_{53.67}B_2Cl_2N_{12}O_4PSiW_2$ (M =1305.92 gmol^{-1}): monoclinic, space group C2/c (no. 15), a = 21.7758(4), b = 10.9760(2), c = 24.1570(8) Å, β = 115.485(2)°, V = 5212.0(2) Å^3, Z = 4, T = 150.0(1) K, μ(CuKα) = 9.907 mm^{-1}, $Dcalc$ = 1.664 Mgm^{-3}, 51072 reflections measured (8.11° ≤ 2Θ ≤ 147.796°), 5275 unique (R_{int} = 0.0434, R_{sigma} = 0.0209) which were used in all calculations.

The final R_1 was 0.0389 ($I > 2\sigma(I)$) and wR_2 was 0.1076 (all data) for 317 refined parameters with 6 restraints.

Synthesis of [{(Tp*)(CO)$_2$W≡C}$_2$PC≡CH] (10). A solution of **9** (100 mg, 0.0815 mmol) in THF (10 mL) was treated with TBAF (85 μL, 1.0 M solution in THF, 0.085 mmol) and the mixture was stirred at RT for 1 h without visible colour change. After this time, the solvent was removed under reduced pressure and the residue was subjected to column chromatography (30 x 1 cm silica gel column), eluting initially with petroleum ether (40–60 °C) and gradually increasing the proportion of CH_2Cl_2. At 50% v/v CH_2Cl_2/petrol a red band was collected, which was dried under reduced pressure and recrystallized from CH_2Cl_2/ethanol to give a red solid of pure **10** (74.0 mg, 0.0641 mmol, 79%). IR (CH_2Cl_2, cm^{-1}): 1992s, 1982s, 1899s ν(CO). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, δ): 2.31 (s, 6 H, pzC*H$_3$*), 2.37 (s, 12 H, pzC*H$_3$*), 2.38 (s, 6 H, pzC*H$_3$*), 2.42 (s, 12 H, pzC*H$_3$*), 3.37 (s, 1 H, C≡C*H*), 5.74 (s, 2 H, pz*H*), 5.78 (s, 4 H, pz*H*). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C, δ): 12.7, 12.8, 15.3, 16.9 (pz*C*H$_3$), 75.1 (d, $^1J_{CP}$ = 14.8 Hz, P*C*≡C), 95.9 (PC≡*C*), 106.4, 106.8 (pz*C*H), 144.2, 145.4, 152.4, 152.6 (pz*C*CH$_3$), 224.6 (*C*O), 272.9 (d, $^1J_{CP}$ = 75.6, W≡*C*P). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C, δ): 33.8 ($^2J_{PW}$ = 84 Hz). MS (ESI, *m*/*z*): Found: 1155.2710. Calcd for $C_{40}H_{47}{}^{11}B_2N_{12}O_4P^{184}W_2$ [M + H]$^+$: 1155.2708. Anal. Found: C, 39.70; H, 3.99; N, 14.36. Calcd for $C_{38}H_{45}B_2N_{12}O_4PW_2$: C, 39.55; H, 3.93; N, 14.56%. Crystal data for $C_{38}H_{45}B_2N_{12}O_4PW_2$ (*M* =1154.15 gmol^{-1}): monoclinic, space group I2/a (no. 15), *a* = 15.2850(6), *b* = 10.7644(5), *c* = 27.3927(10) Å, *β* = 93.766(4)°, *V* = 4497.3(3) Å^3, *Z* = 4, *T* = 150.01(10) K, μ(MoKα) = 5.199 mm^{-1}, *Dcalc* = 1.705 Mgm^{-3}, 13126 reflections measured (6.636° ≤ 2Θ ≤ 50.052°), 3968 unique (R_{int} = 0.0334, R_{sigma} = 0.0362) which were used in all calculations. The final R_1 was 0.0282 ($I > 2\sigma(I)$) and wR_2 was 0.0687 (all data) for 290 refined parameters with 13 restraints. **Synthesis of [{(Tp*)(CO)$_2$W≡C}$_2$P(AuCl)(C≡C{*p*-tolyl})] (11).** A solution of **7** (50.0 mg, 0.0402 mmol) in CH_2Cl_2 (10 mL) was treated with AuCl(THT) (13.0 mg, 0.0406 mmol) and the mixture was stirred at RT for 15 min. After this time the mixture was filtered through diatomaceous earth, washed with CH_2Cl_2, and the filtrate dried under reduced pressure to give a red-orange solid of pure **11** (55.0 mg, 0.0372 mmol, 93%). IR (CH_2Cl_2, cm^{-1}): 2007s, 2001s, 1918s ν(CO). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, δ): 2.31 (s, 6 H, pzC*H$_3$*), 2.38 (overlapping s, 21 H, pzC*H$_3$* & $C_6H_4CH_3$), 2.50 (overlapping s, 12 H, pzC*H$_3$*), 5.76 (s, 2 H, pzC*H*), 5.83 (s, 2 H, pzC*H*), 5.84 (s, 2 H, pzC*H*), 7.18 (d, $^3J_{HH}$ = 7.9 Hz, 2 H, C^{3,5}{*p*- tolyl}), 7.46 (d, $^3J_{HH}$ = 7.9 Hz, 2 H, C^{2,6}{*p*-tolyl}). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 25 °C, δ): 12.8, 12.8, 15.3, 17.4, 17.6 (pz*C*H$_3$), 21.9 ($C_6H_4CH_3$), 74.9 (d, $^1J_{CP}$ = 118 Hz, P*C*≡C), 106.4 (d, $^2J_{CP}$ = 20 Hz, PC≡*C*), 106.7, 106.8, 107.2 (pz*C*H), 118.3 (d, $^3J_{CP}$ = 3.6 Hz, *C*^{1}{*p*- tolyl}), 129.4 (*C*^{3,5}{*p*-tolyl}), 132.4 (*C*^{2,6}{*p*-tolyl}), 140.6 (*C*^{4}{*p*- tolyl}), 144.7, 144.8, 145.8, 152.4, 152.4, 152.9 (pz*C*CH$_3$), 222.8, 224.3 (*C*O), 255.2 (d, $^1J_{CP}$ = 20.2 Hz, W≡*C*P). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C, δ): 9.7 ($^2J_{PW}$ = 159 Hz). MS (ESI, *m*/*z*): Found: 1477.25681. Calcd for $C_{45}H_{52}Au^{11}B_2ClN_{12}O_4P^{184}W_2$ [M + H]$^+$: 1477.25324. Anal. Found: C, 36.71; H, 3.71; N, 11.12%. Calcd for $C_{45}H_{51}AuB_2ClN_{12}O_4PW_2$: C, 36.60; H, 3.48; N, 11.38%.

Synthesis of [{(Tp*)(CO)$_2$W≡C}$_2$P(AuCl)(C≡CSiMe$_3$)] (12). A solution of **9** (50.0 mg, 0.0408 mmol) in CH_2Cl_2 (10 mL) was treated with AuCl(THT) (13.1 mg, 0.0409 mmol) and the mixture was stirred at RT for 30 min. After this time, the solution was filtered through diatomaceous earth, washed with CH_2Cl_2, and the filtrate dried under reduced pressure. The residue was then subjected to column chromatography (10 x 1 cm silica gel column), eluting with CH_2Cl_2. A red band was collected and dried under reduced pressure to give a red solid of pure **12** (39.0 mg, 0.0267 mmol, 66%). IR (CH_2Cl_2, cm^{-1}): 2002s, 1919s ν(CO). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, δ): 0.26 (s, 9 H, Si(C*H$_3$*)$_3$), 2.30 (s, 6 H, pzC*H$_3$*), 2.37 (s, 18 H, pzC*H$_3$*), 2.43 (s, 6 H, pzC*H$_3$*), 2.48 (s, 6 H, pzC*H$_3$*), 5.76 (s, 2 H, pzC*H*), 5.83 (s, 2 H, pzC*H*), 5.85 (s, 2 H, pzC*H*). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 25 °C, δ): –0.6 (Si(*C*H$_3$)$_3$), 12.8, 12.8, 15.3, 17.5, 17.6 (pz*C*H$_3$), 89.9 (d, $^1J_{CP}$ = 99 Hz, P*C*≡C), 106.6, 106.8, 107.3 (pz*C*H), 115.9 (d, $^1J_{CP}$ = 9.5 Hz, PC≡*C*), 144.7, 144.8, 145.8, 152.3, 152.4, 152.9 (pz*C*CH$_3$), 222.6, 224.0 (*C*O), 254.1 (d, $^1J_{CP}$ = 20 Hz, W≡*C*P). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C, δ): 9.7 ($^2J_{PW}$ = 158 Hz). MS (ESI, *m*/*z*): Found: 1459.24371. Calcd for $C_{41}H_{54}Au^{11}B_2ClN_{12}O_4PSi^{184}W_2$ [M + H]$^+$: 1459.24656. Found: 1481.22891. Calcd for $C_{41}H_{53}Au^{11}B_2ClN_{12}NaO_4PSi^{184}W_2$ [M + Na]$^+$: 1481.22851. Anal. Found: C, 33.82; H, 3.57; N, 11.42%. Calcd for $C_{41}H_{53}AuB_2ClN_{12}O_4PSiW_2$: C, 33.76; H, 3.66; N, 11.52%. A crystal suitable for X-ray structure determination was grown by slow evaporation of a CH_2Cl_2/ethanol mixture. The data quality is unfortunately rather poor and this structure is included primarily as evidence of connectivity. Crystal data for $C_{41}H_{53}AuB_2ClN_{12}O_4PSiW_2$ (*M* =1458.75 gmol^{-1}): monoclinic, space group C2/c (no. 15), *a* = 22.114(2), *b* = 11.0992(5), *c* = 23.9715(16) Å, *β* = 114.633(9)°, *V* = 5348.3(7) Å^3, *Z* = 4, *T* = 150.0(1) K, μ(MoKα) = 7.178 mm^{-1}, *Dcalc* = 1.812 Mgm^{-3}, 13179 reflections measured (6.744° ≤ 2Θ ≤ 50.05°), 4708 unique (R_{int} = 0.0546, R_{sigma} = 0.0771) which were used in all calculations. The final R_1 was 0.0838 ($I > 2\sigma(I)$) and wR_2 was 0.1791 (all data) for 319 refined parameters with 1 restraint.

Synthesis of [{(Tp*)(CO)$_2$W≡C}$_2$P(C≡CAsPh$_2$)] (13). A solution of **10** (50.0 mg, 0.0433 mmol) in THF (10 mL) was treated with *n*-BuLi (1.6 M, 30 μL, 0.048 mmol) and the mixture was stirred at reduced temperature for 15 min, causing the initially bright red solution to turn yellow-brown. After this time, $AsBrPh_2$ (30.0 mg, 0.0971 mmol) was added as a solid and the mixture was stirred at RT for 30 min, during which time the solution turned orange-red. The solvents were removed under reduced pressure and the residue was subjected to column chromatography (20 x 1 cm silica gel column), eluting with 1:1 *n*-pentane/CH_2Cl_2. An orange band was collected and the solvents were removed under reduced pressure to give a bright orange solid of pure **13** (41.0 mg, 0.0297 mmol, 69%). IR (CH_2Cl_2, cm^{-1}): 1991s, 1981s, 1899s ν(CO). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, δ): 2.30 (s, 6 H, pzC*H$_3$*), 2.34 (s, 12 H, pzC*H$_3$*), 2.36 (s, 12 H, pzC*H$_3$*), 2.37 (s, 6 H, pzC*H$_3$*), 5.73, 5.74 (2 x s overlapping, 6 H, pzC*H*), 7.26–7.31 (m, 6 H, As*Ph$_2$*), 7.61–7.67 (m, 4 H, As*Ph$_2$*). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 25 °C, δ): 12.7, 12.8, 15.3, 16.8 (pz*C*H$_3$), 97.9 (d, $^1J_{CP}$ = 21.8 Hz, P*C*≡CAs), 106.4, 106.8 (pz*C*H), 108.2 (d, $^2J_{CP}$ = 6.3 Hz, PC≡*C*As), 128.6 (*p*-*Ph*), 128.8 (*o*-*Ph*), 133.0 (*m*-*Ph*), 138.9 (*i*-*Ph*), 144.1, 145.3, 152.5, 152.6 (pz*C*CH$_3$), 224.8 (CO, $^1J_{CW}$ = 167 Hz), 273.5 (d, $^1J_{CP}$ = 76.5, $^1J_{CW}$ = 197 Hz, W≡*C*P). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C, δ): 37.0 ($^2J_{PW}$ = 84 Hz). MS (ESI, *m*/*z*): Found: 1383.2631. Calcd for $C_{50}H_{55}As^{11}B_2N_{12}O_4P^{184}W_2$ [M + H]$^+$: 1383.2629. Anal. Found: C,

43.44; H, 3.87; N, 11.99%. Calcd for $C_{50}H_{54}AsB_2N_{12}O_4PW_2$: C, 43.45; H, 3.94; N, 12.16%. Crystal data for $C_{50}H_{54}AsB_2N_{12}O_4PW_2$ (M =1382.26 gmol^{-1}): triclinic, space group P-1 (no. 2), a = 11.2582(3), b = 11.6958(4), c = 22.3488(6) Å, α = 83.656(3)°, β = 81.841(2)°, γ = 71.230(3)°, V = 2751.44(15) Å^3, Z = 2, T = 150.0(1) K, μ(CuKα) = 8.990 mm^{-1}, $Dcalc$ = 1.668 gcm^{-3}, 17344 reflections measured (8.004° ≤ 2Θ ≤ 133.198°), 9655 unique (R_{int} = 0.0298, R_{sigma} = 0.0446) which were used in all calculations. The final R_1 was 0.0502 (I > 2σ(I)) and wR_2 was 0.1423 (all data) for 669 parameters with 36 restraints.

Single crystal X-ray structures

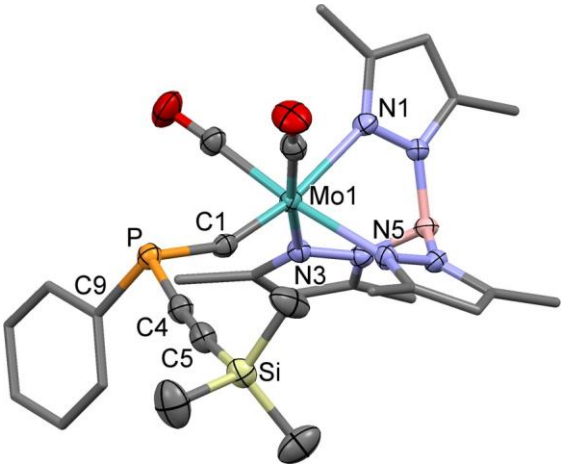

Figure S1. Molecular structure of **2a** showing 50% thermal probability ellipsoids. Pyrazolyl groups and phenyl rings are simplified and hydrogen atoms are not shown for clarity. Selected distances [Å] and angles [°]: Mo1–C1 1.807(4), Mo1– N1 2.308(3), Mo1–N3 2.218(3), Mo1–N5 2.223(3), C1–P 1.803(4), P–C4 1.770(4), P–C9 1.828(4), C4–C5 1.198(6), C5–Si 1.855(4), Mo1–C1–P 157.2(2), C1–P–C4 101.37(18), C1–P–C9 103.13(18), C4–P–C9 103.04(18), P–C4–C5 172.1(4), C4–C5–Si 174.0(4). ***TR*** = 2(Mo–N1)/(Mo–N3 + Mo–N5) = 1.039.[9]

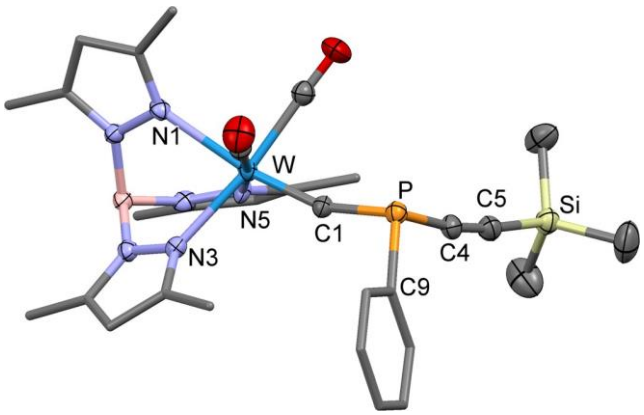

Figure S2. Molecular structure of **2b** showing 50% thermal probability ellipsoids. Pyrazolyl groups and phenyl rings are simplified and hydrogen atoms are not shown for clarity.

Selected distances [Å] and angles [°]: W–C1 1.827(4), W–N1 2.287(4), W–N3 2.209(4), W–N5 2.204(4), C1–P 1.790(4), P–C9 1.831(5), P–C4 1.767(5), C4–C5 1.204(6), C5–Si 1.851(5), W–C1–P 157.3(3), C1–P–C4 101.7(2), C1–P–C9 103.6(2), C4–P–C9 102.7(2), P–C4–C5 171.8(4), C4–C5–Si 174.1(4). ***TR*** = 2(W–N1)/(W–N3 + W–N5) = 1.036.

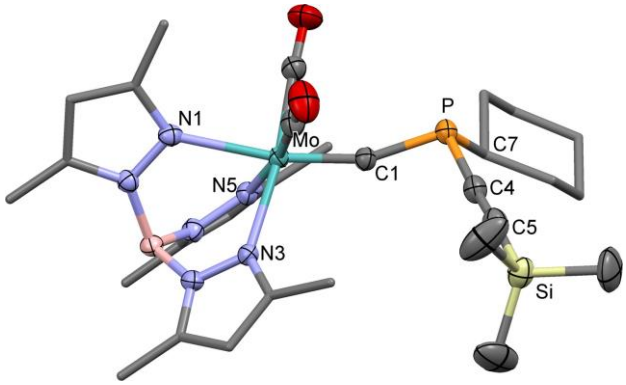

Figure S3. Molecular structure of **3a** showing 50% thermal probability ellipsoids. Pyrazolyl groups and phenyl rings are simplified, a minor disorder component and hydrogen atoms are not shown for clarity. Selected distances [Å] and angles [°]: Mo–C1 1.812(3), Mo–N1 2.311(3), Mo–N3 2.225(3), Mo–N5 2.228(3), C1–P 1.795(3), P–C4 1.768(4), P–C7 1.865(4), C4–C5 1.203(5), C5–Si 1.847(4), Mo–C1–P 159.0(2), C1–P–C4 101.77(16), C1–P–C7 101.14(16), C4–P–C7 104.57(16), P–C4–C5 172.9(3), C4–C5–Si 176.2(3). ***TR*** = 2(Mo–N1)/(Mo–N3 + Mo–N5) = 1.038.

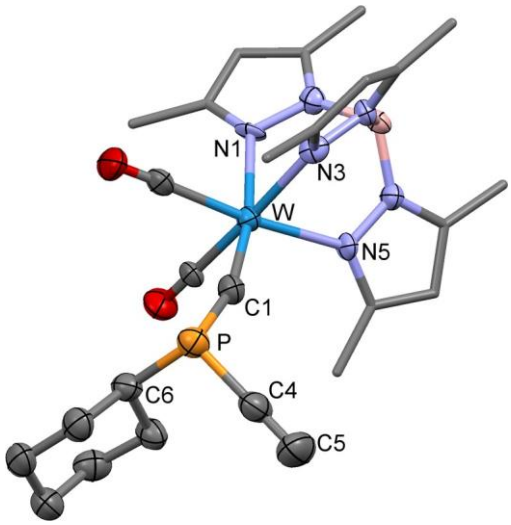

Figure S4. Molecular structure of **5b** showing 50% thermal probability ellipsoids. Pyrazolyl groups are simplified and hydrogen atoms are not shown for clarity. Selected distances [Å] and angles[°]: W–C1 1.850(8), C1–P1.764(8), P–C4 1.769(9), P–C6 1.854(8), C4–C5 1.182(14), W–N1 2.295(5), W–N3 2.194(8), W–N5 2.220(5), W–C1–P 163.4(5), C1–P–C4 101.4(4), C1–P–C6 102.7(4), C4–P–C6 101.3(4), P–C4–C5 174.2(10). ***TR*** = 2(W–N1)/(W–N3 + W–N5) = 1.040.

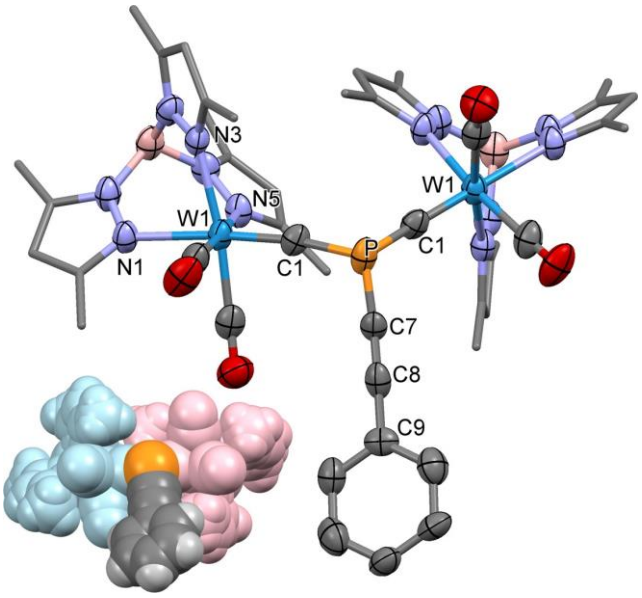

Figure S5. Molecular structure of **6** showing 50% thermal probability ellipsoids. Pyrazolyl groups are simplified and hydrogen atoms and a disorder component are not shown for clarity. Selected distances [Å] and angles [°]: W1–C1 1.831(7), W1–N1 2.280(6), W1–N3 2.226(6), W1–N5 2.201(6), C1–P 1.771(7), P–C7 1.608(14), C7–C8 1.24(2), C8–C9 1.382(18), W1–C1–P 170.8(5), C1–P–C1 102.0(5), C1–P–C7 107.2(5), P–C7–C8 171.6(13). ***TR*** = 2(W–N1)/(W–N3 + W–N5) = 1.030. Inset: space-filling diagram indicating steric bulk around the tungsten and phosphorus centers.

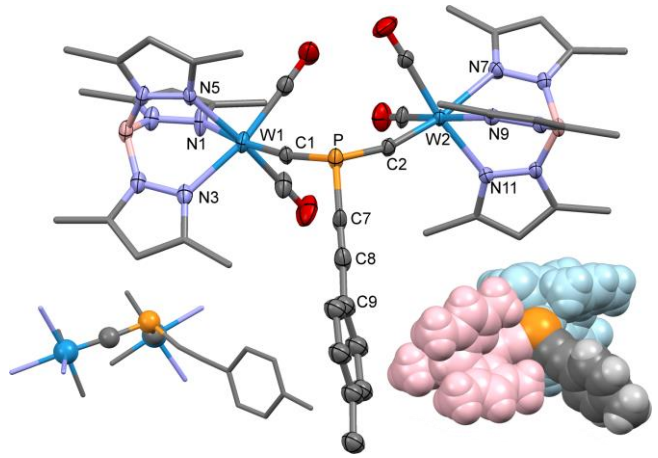

Figure S6. Molecular structure of **7** showing 50% thermal probability ellipsoids. Pyrazolyl groups are simplified and hydrogen atoms and a disorder component are not shown for clarity. Selected distances [Å] and angles [°]: W1–C1 1.813(5), C1–P 1.793(5), C2–W2 1.836(5), P–C2 1.781(5), P–C7 1.762(6), C7–C8 1.198(8), W1–N1 2.286(4), W1–N3 2.206(5), W1–N5 2.221(4), W2–N7 2.302(4), W2–N9 2.201(4), W2–N11 2.202(4), W1–C1–P 168.9(3), W2–C2–P 163.6(3), C1–P–C2 107.3(2), C1–P–C7 103.8(3), C2–P–C7 103.7(3), P–C7–C8 168.8(6). ***TR*** = 2(W1–N1)/(W1–N3 + W1–N5) = 1.033. ***TR*** = 2(W2–N7)/(W2–N9 + W2–N11) = 1.046. Inset: space-filling representation and view along the W2···C2 vector.

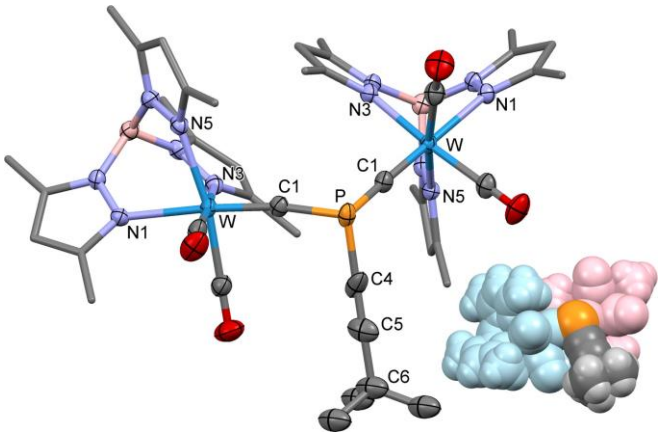

Figure S7. Molecular structure of **8** showing 50% thermal probability ellipsoids. Pyrazolyl groups are simplified and hydrogen atoms, solvent molecules and disorder components are not shown for clarity. Selected distances [Å] and angles [°]: W–C1 1.823(3), C1–P 1.788(3), P–C4 1.783(8), C4–C5 1.149(10), C5–C6 1.486(15), W–N1 2.279(2), W–N3 2.211(3), W–N5 2.219(2), W–C1–P 170.88(19), C1–P–C1 102.0(2), C1–P–C4 100.7(3), P–C4–C5 175.0(7). ***TR*** = 2(W–N1)/(W–N3 + W–N5) = 1.029.

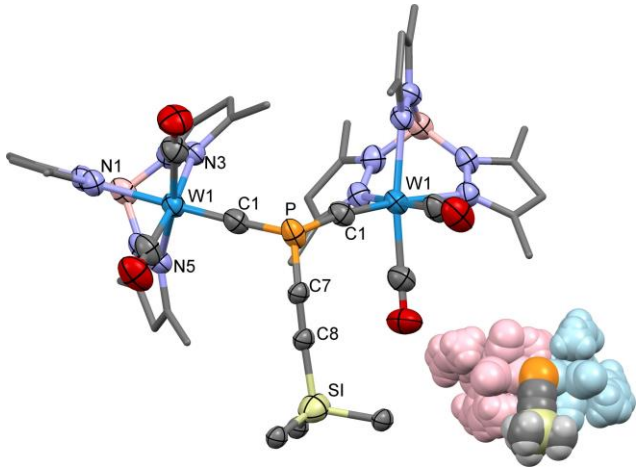

Figure S8. Molecular structure of **9** showing 50% thermal probability ellipsoids. Pyrazolyl groups are simplified and hydrogen atoms, solvent molecules and disorder components are not shown for clarity. Selected distances [Å] and angles [°]: W1–C1 1.827(5), W1–N1 2.274(4), W1–N3 2.204(4), W1–N5 2.219(4), C1–P 1.769(6), P–C7 1.590(9), C7–C8 1.232(13), C8–Si 1.826(13), W1–C1–P 171.3(4), C1–P–C1 103.8(4), C1–P–C7 109.2(4), P–C7–C8 165.2(9). ***TR*** = 2(W–N1)/(W–N3 + W–N5) = 1.028. Inset: space-filling representation.

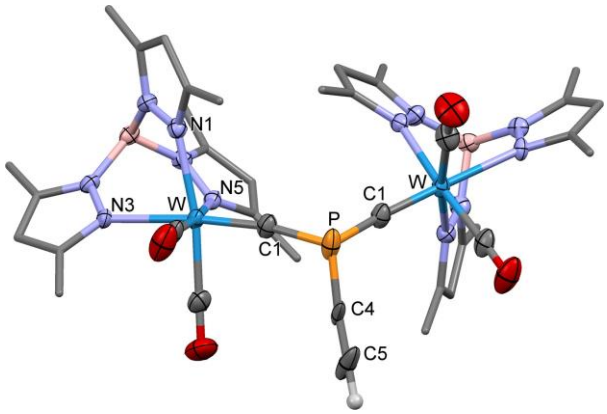

Figure S9. Molecular structure of **10** showing 50% thermal probability ellipsoids. Pyrazolyl groups are simplified and hydrogen atoms and disorder components are not shown for clarity. Selected distances [Å] and angles [°]: W–C1 1.827(5), C1– P 1.788(5), P–C4 1.660(10), C4–C5 1.221(17), W–N1 2.212(3), W–N3 2.291(3), W–N5 2.221(4), W–C1–P 168.8(3), C1–P–C1 101.1(3), C1–P–C4 106.7(4), P–C4–C5 173.0(16). ***TR*** = 2(W–N3)/(W–N1 + W–N5) = 1.034.

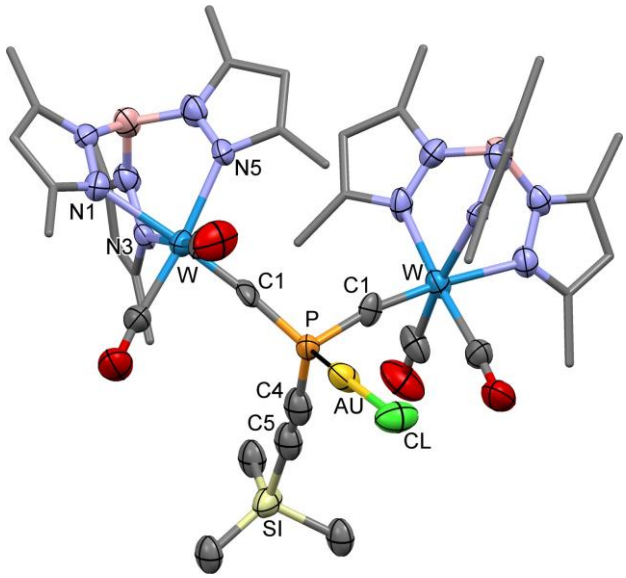

Figure S10. Molecular structure of **12** showing 50% thermal probability ellipsoids. Pyrazolyl groups are simplified and hydrogen atoms, solvent molecules and disorder components are not shown for clarity. Selected distances [Å] and angles [°]: W–C1 1.819(17), W–N1 2.282(14), W–N3 2.183(13), W–N5 2.231(13), C1–P 1.772(17), P–C4 1.726(19), P–Au 2.297(4), Au–Cl 2.285(18), C4–C5 1.10(5), W–C1–P 170.0(11), C1–P–C4 99.6(15), C1–P–Au 119.3(6), P–Au–Cl 167.3(7). ***TR*** = 2(W1–N1)/(W1–N3 + W1–N5) = 1.034.

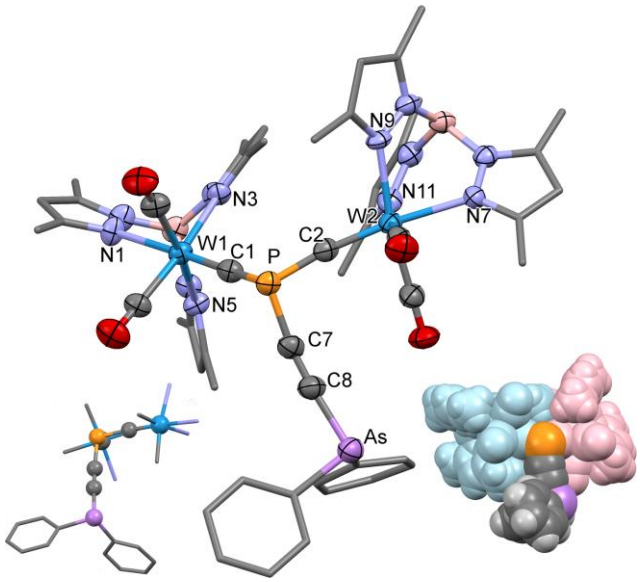

Figure S11. Molecular structure of **13** showing 50% thermal probability ellipsoids. Pyrazolyl and phenyl groups are simplified and hydrogen atoms are not shown for clarity. Selected distances [Å] and angles [°]: W1–C1 1.831(6), C1–P 1.783(6), P– C2 1.779(7), C2–W2 1.830(7), W1–N1 2.295(5), W1–N3 2.206(5), W1–N5 2.208(5), W2–N7 2.294(5), W2–N9 2.205(5), W2–N11 2.209(6), P–C7 1.770(7), C7–C8 1.188(10), C8–As 1.919(7), As–C9 1.972(7), As–C15 1.969(9), W1–C1–P 167.2(4), W2–C2–P 170.8(4), C1–P–C2 101.7(3), C1–P–C7 104.8(3), C2–P–C7 98.6(3), P–C7–C8 170.0(6), C7–C8–As 174.6(6), C8–As–C9 96.7(3), C8–As–C15 99.3(4), C9–As–C15 102.8(3). ***TR*** = 2(W1–N1)/(W1–N3 + W1–N5) = 1.040. ***TR*** = 2(W2–N7)/(W2–N9 + W2–N11) = 1.039. Inset: space-filling representation and view along the W1···C1 vector.

Notes and references

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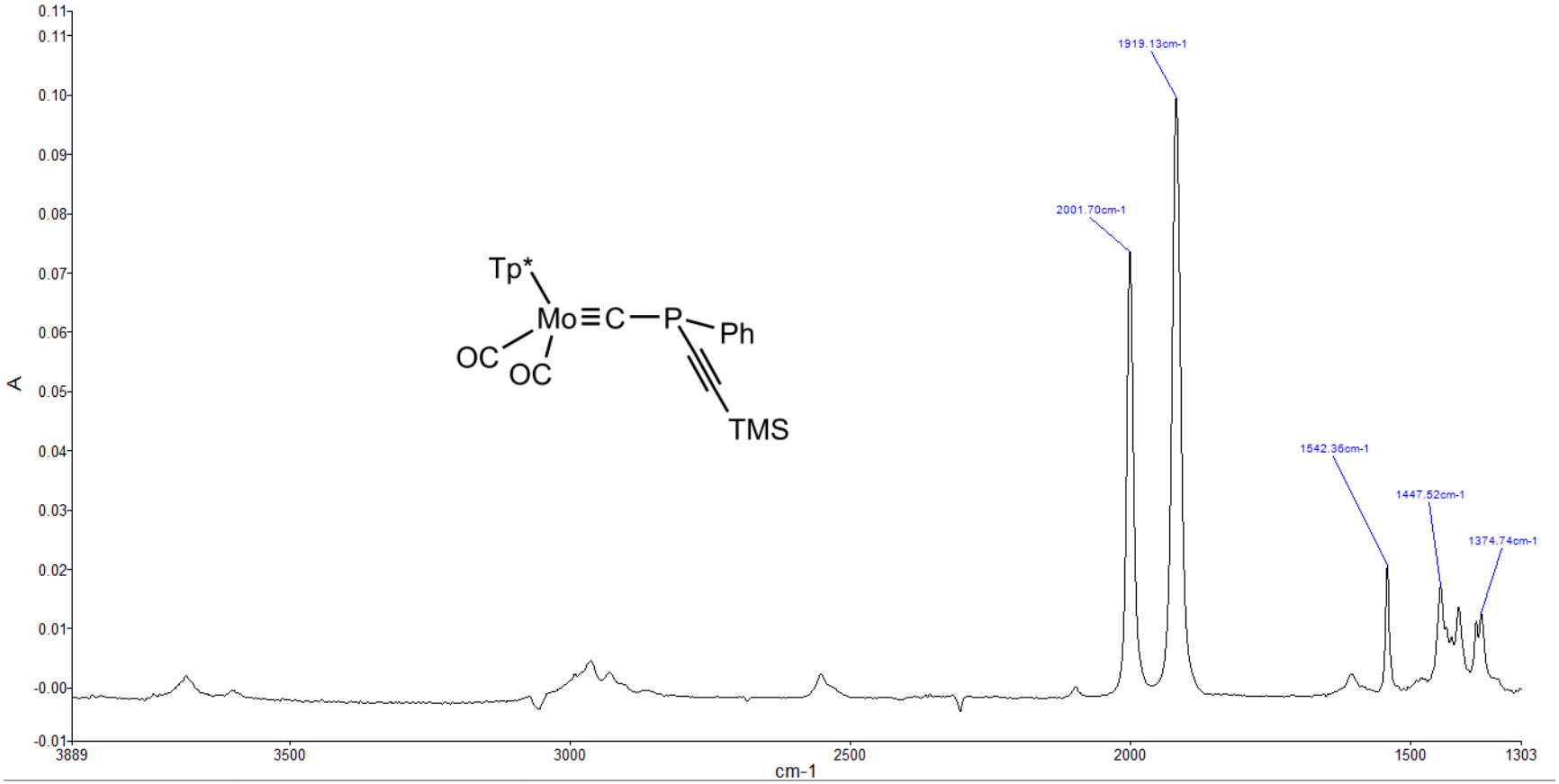
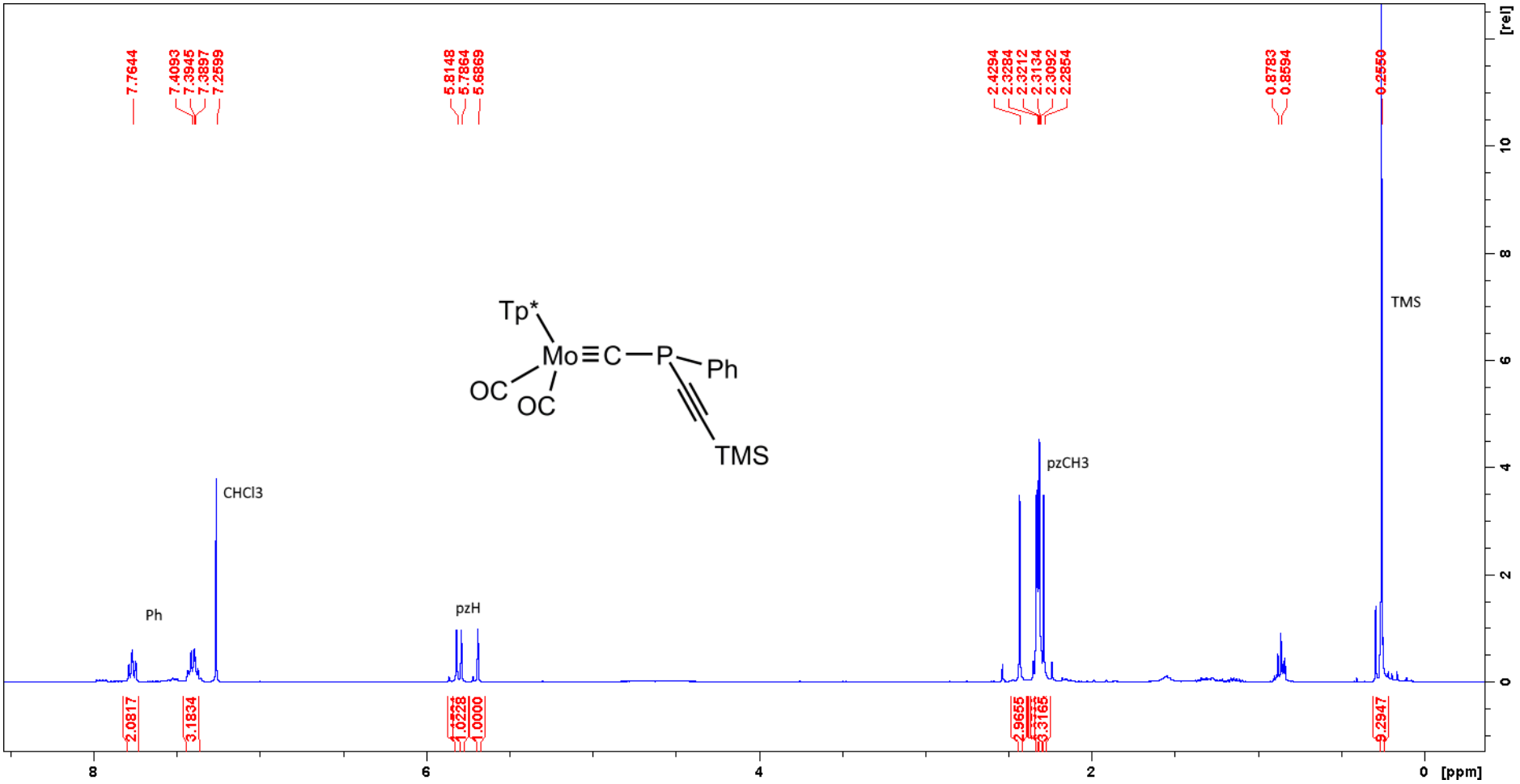
Chemical Communications

ELECTRONIC SUPPORTING INFORMATION

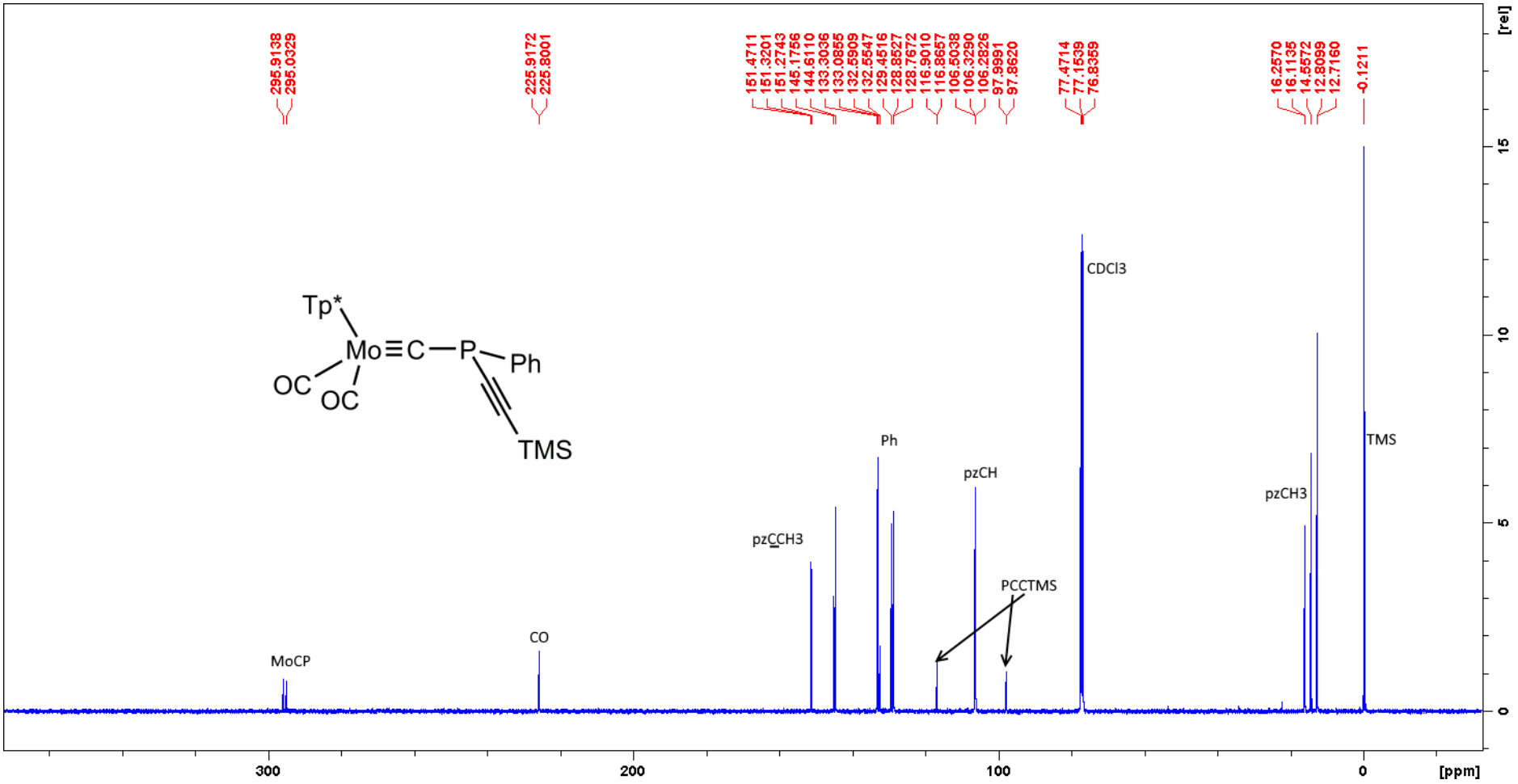
FTIR spectrum of **2a**.



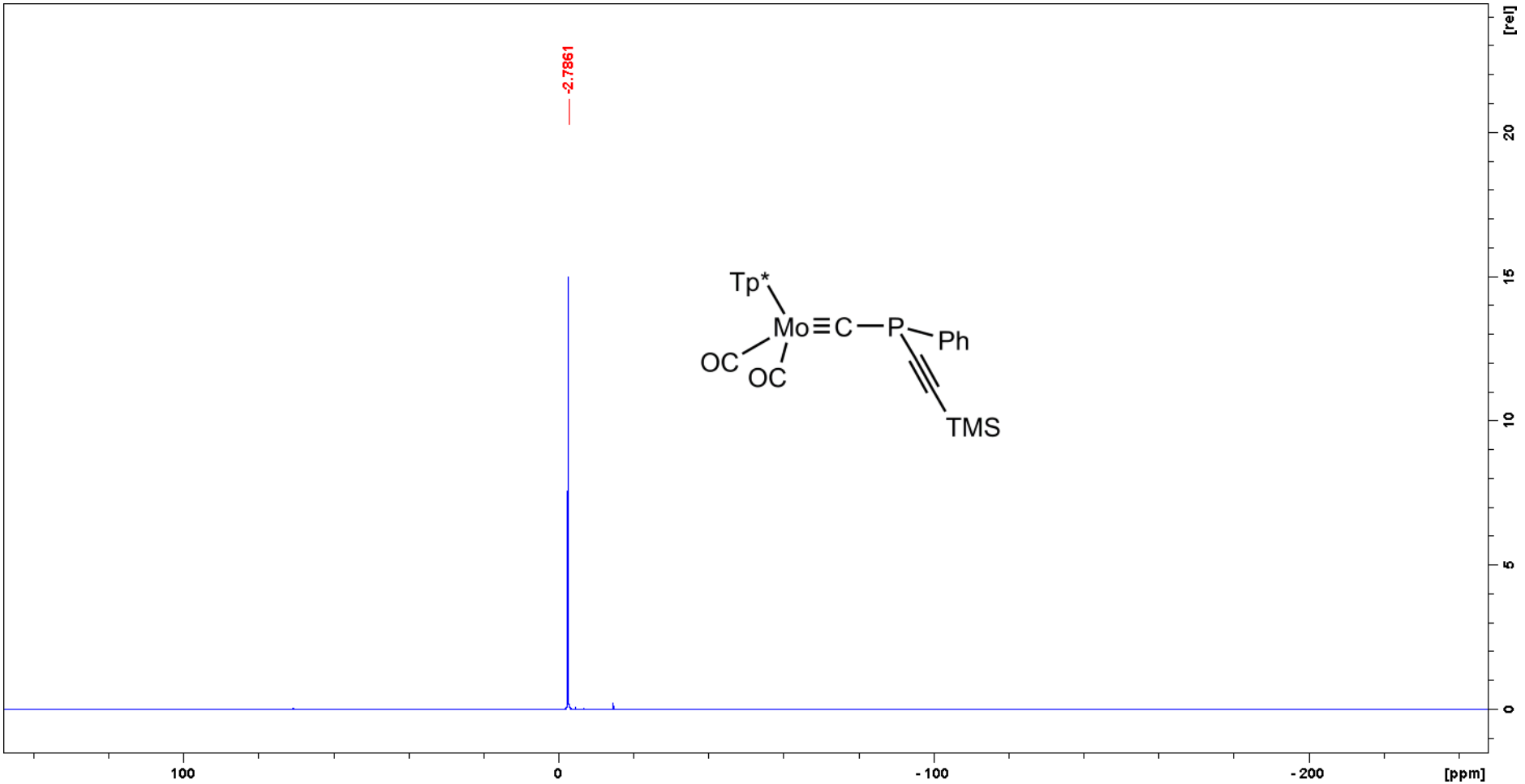
^{1}H NMR spectrum of **2a**.



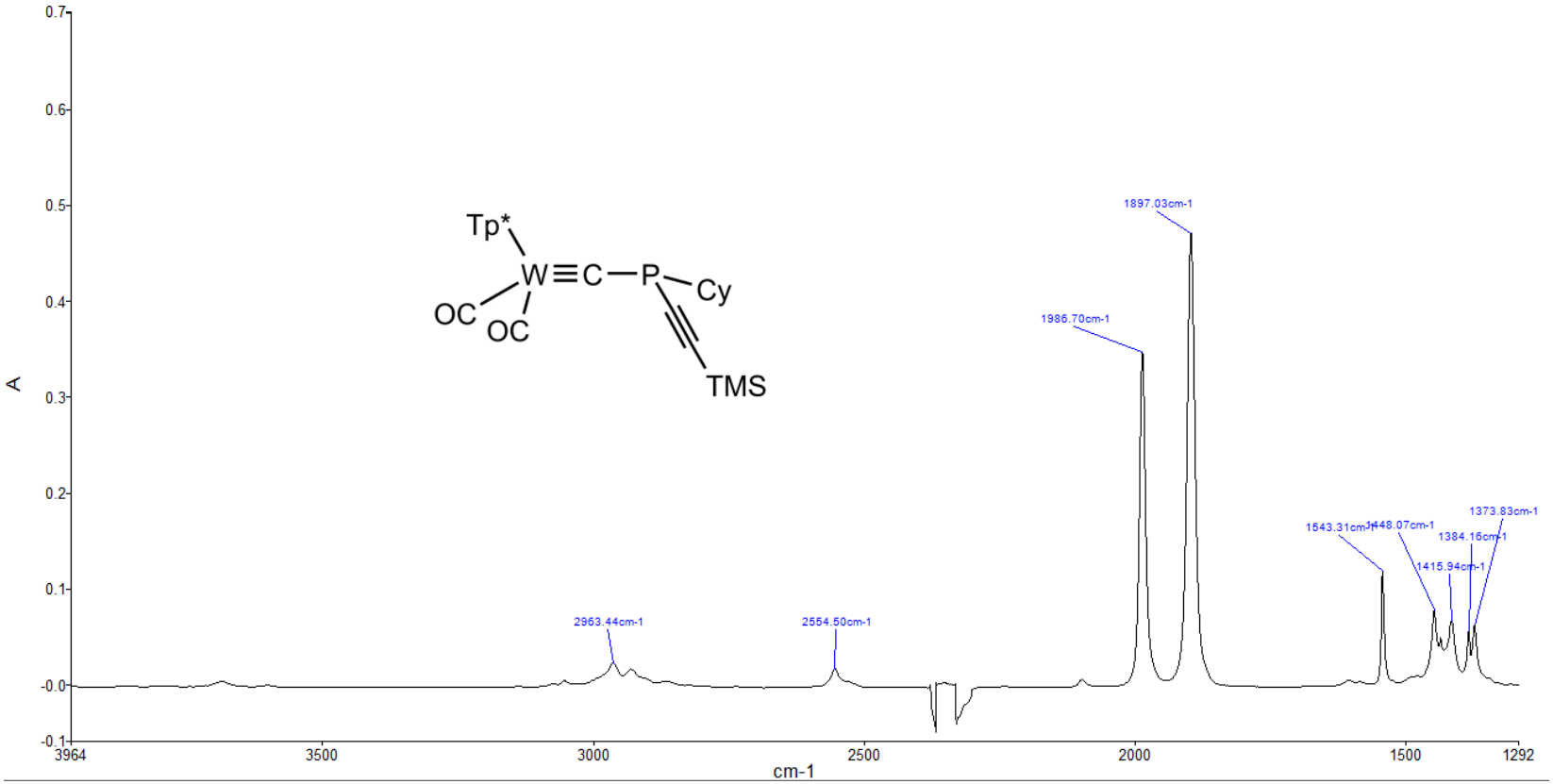
$^{13}C\{^{1}H\}$ NMR spectrum of **2a**.



$^{31}P\{^{1}H\}$ NMR spectrum of **2a**.



FTIR spectrum of **2b**.



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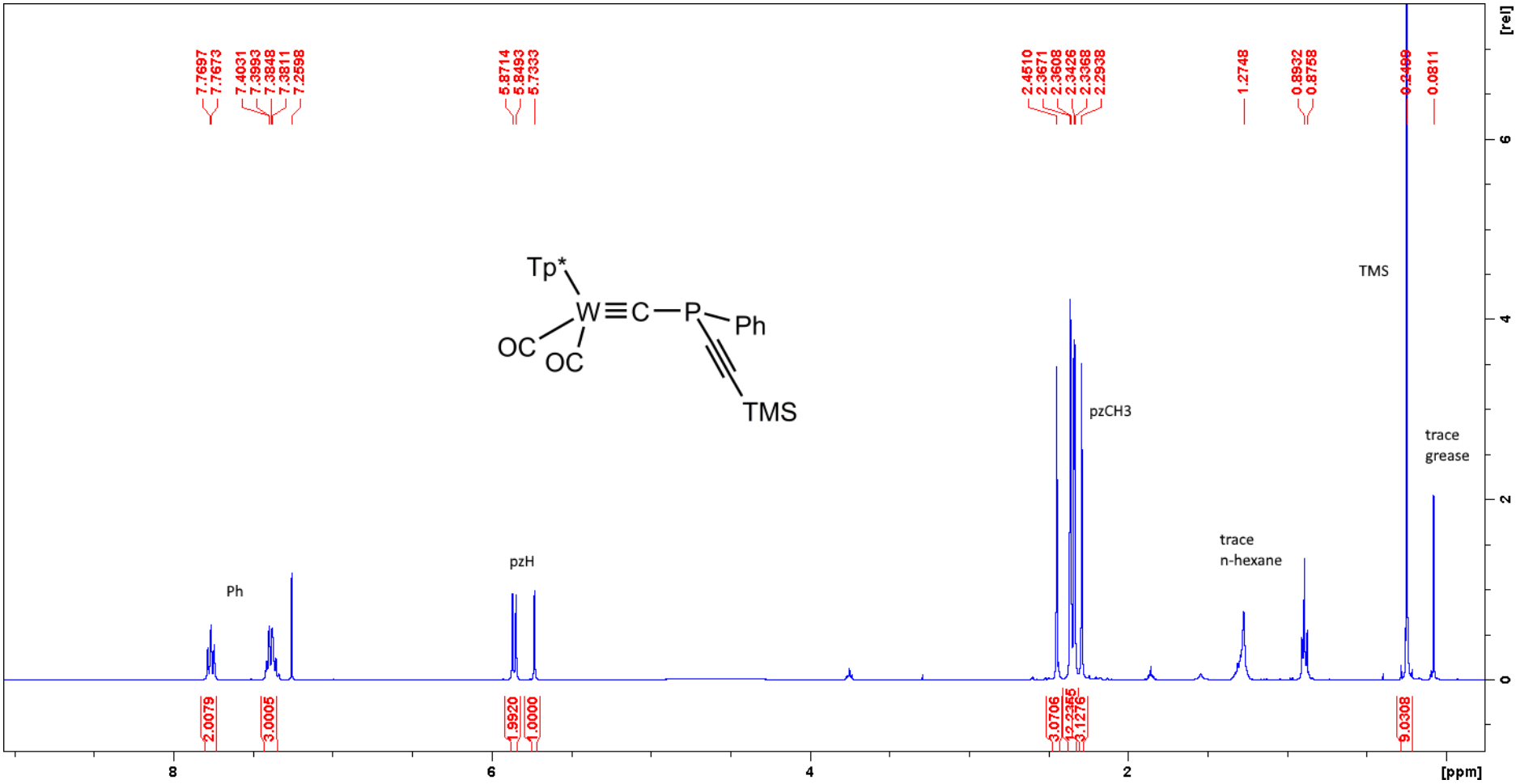

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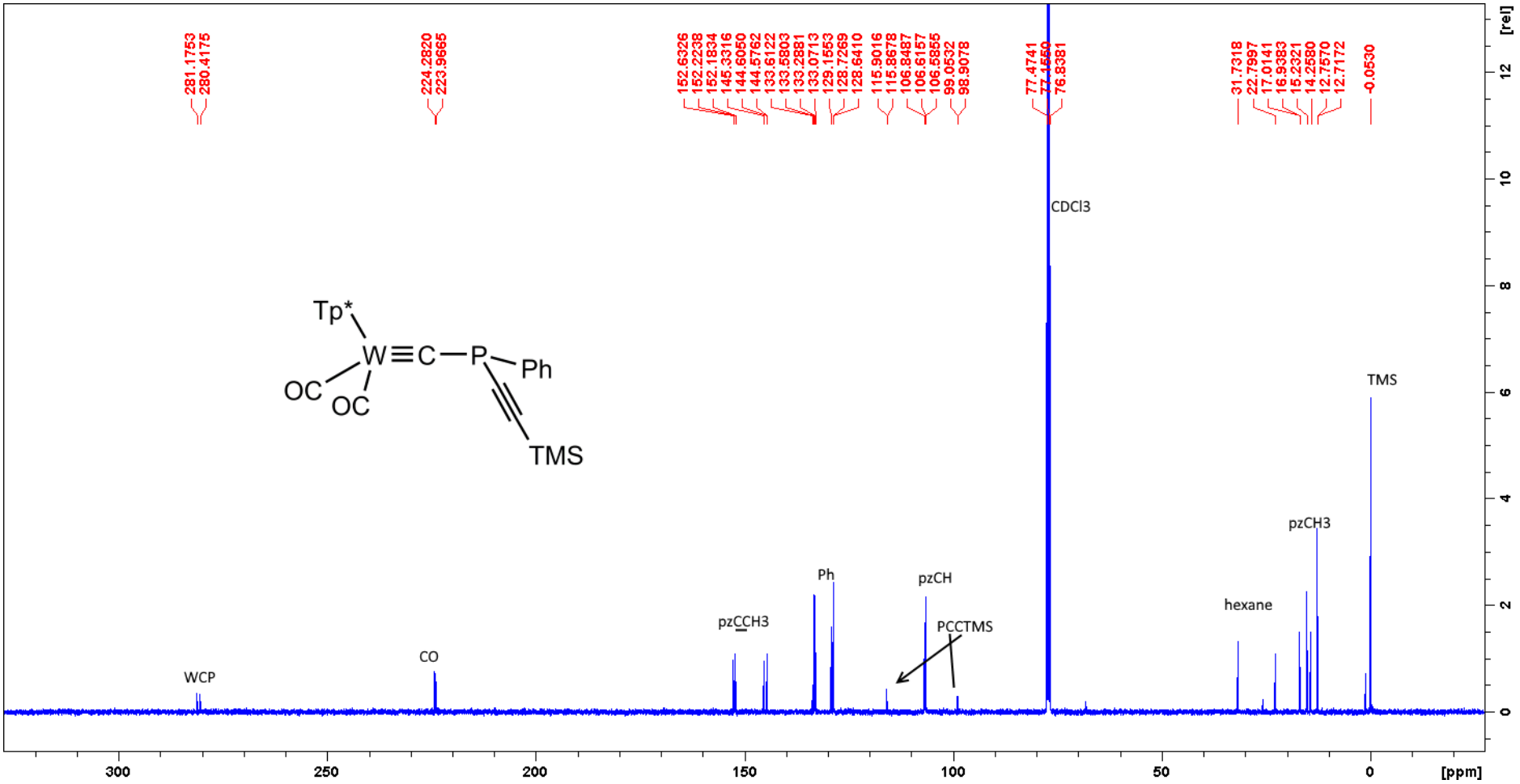

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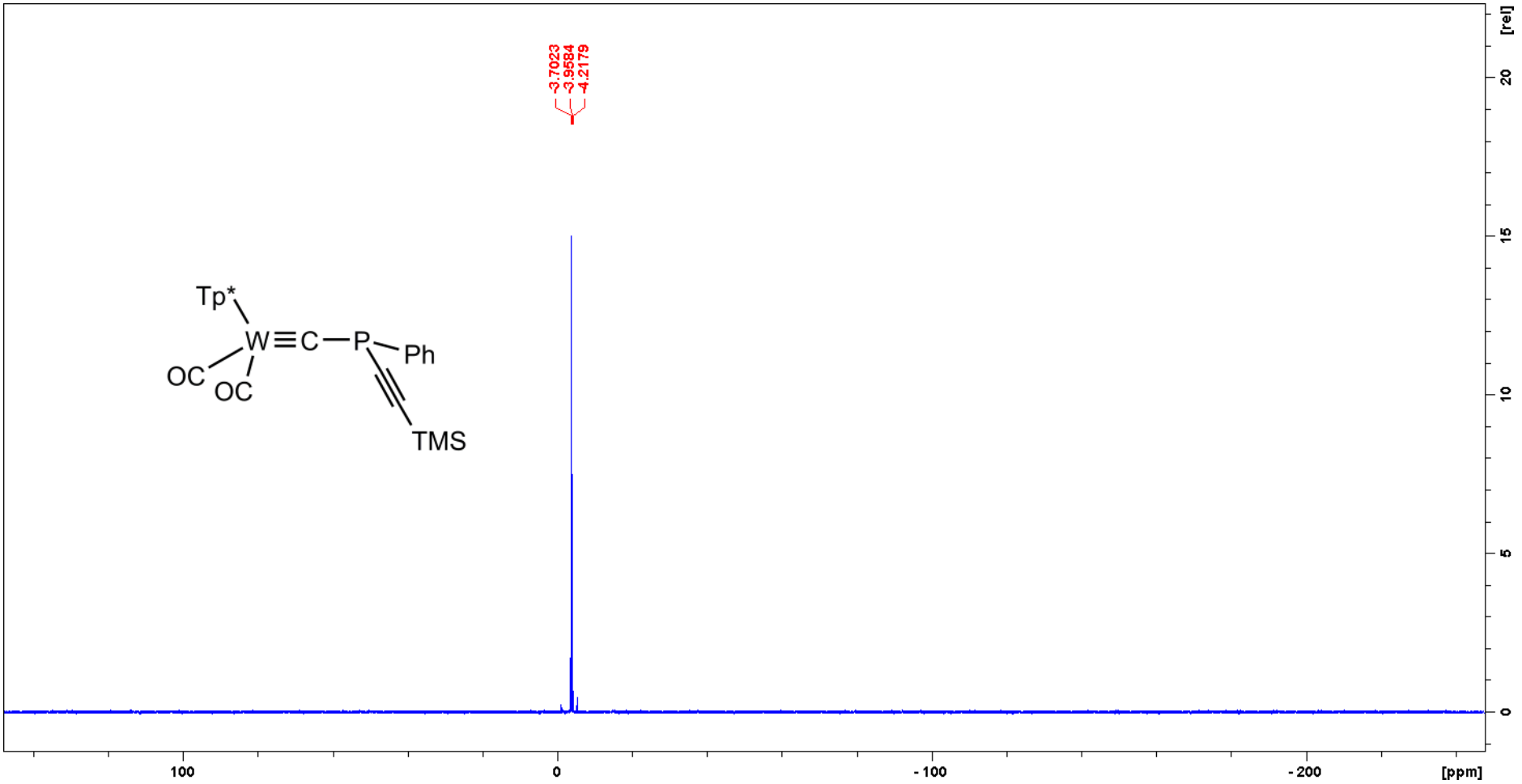

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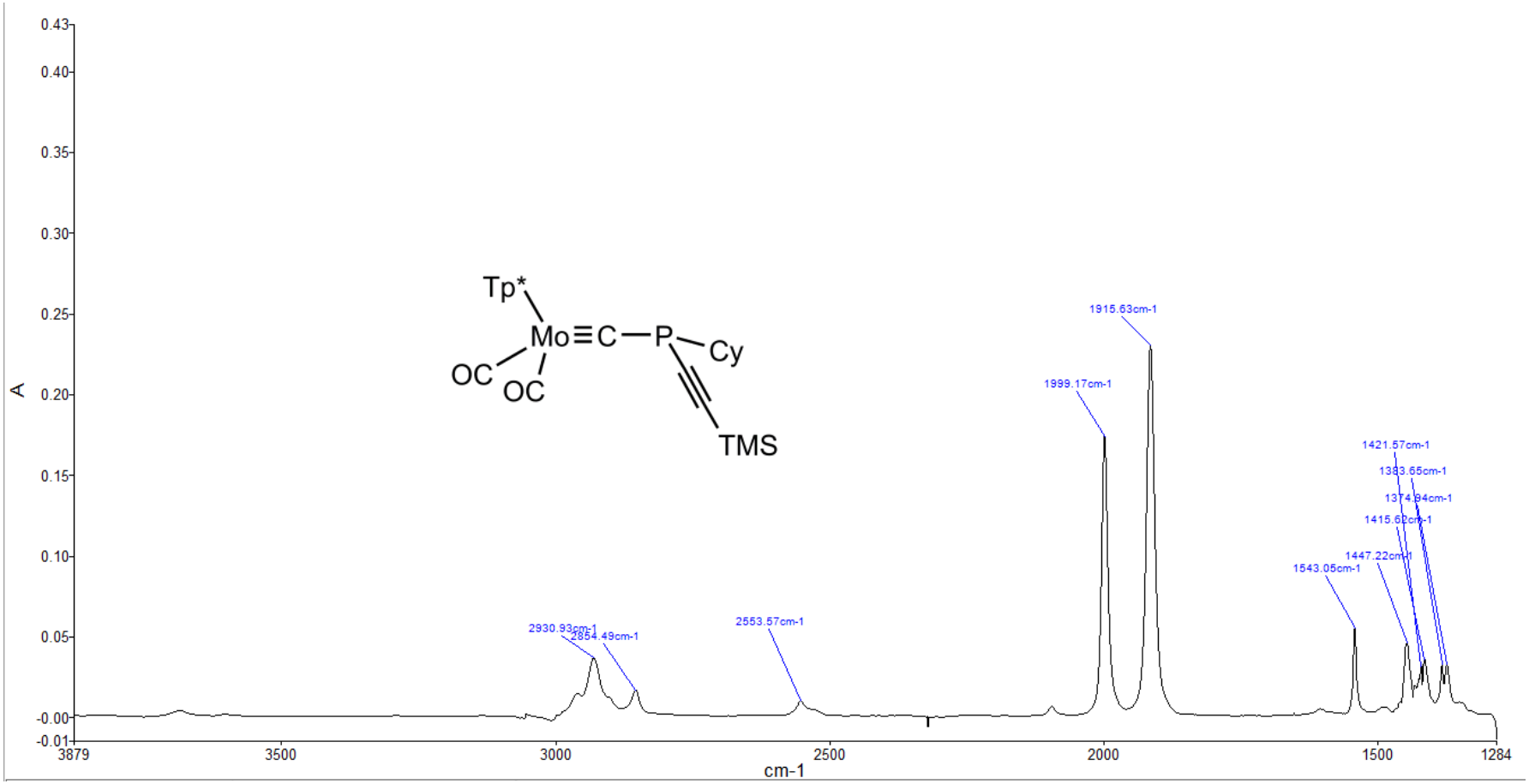

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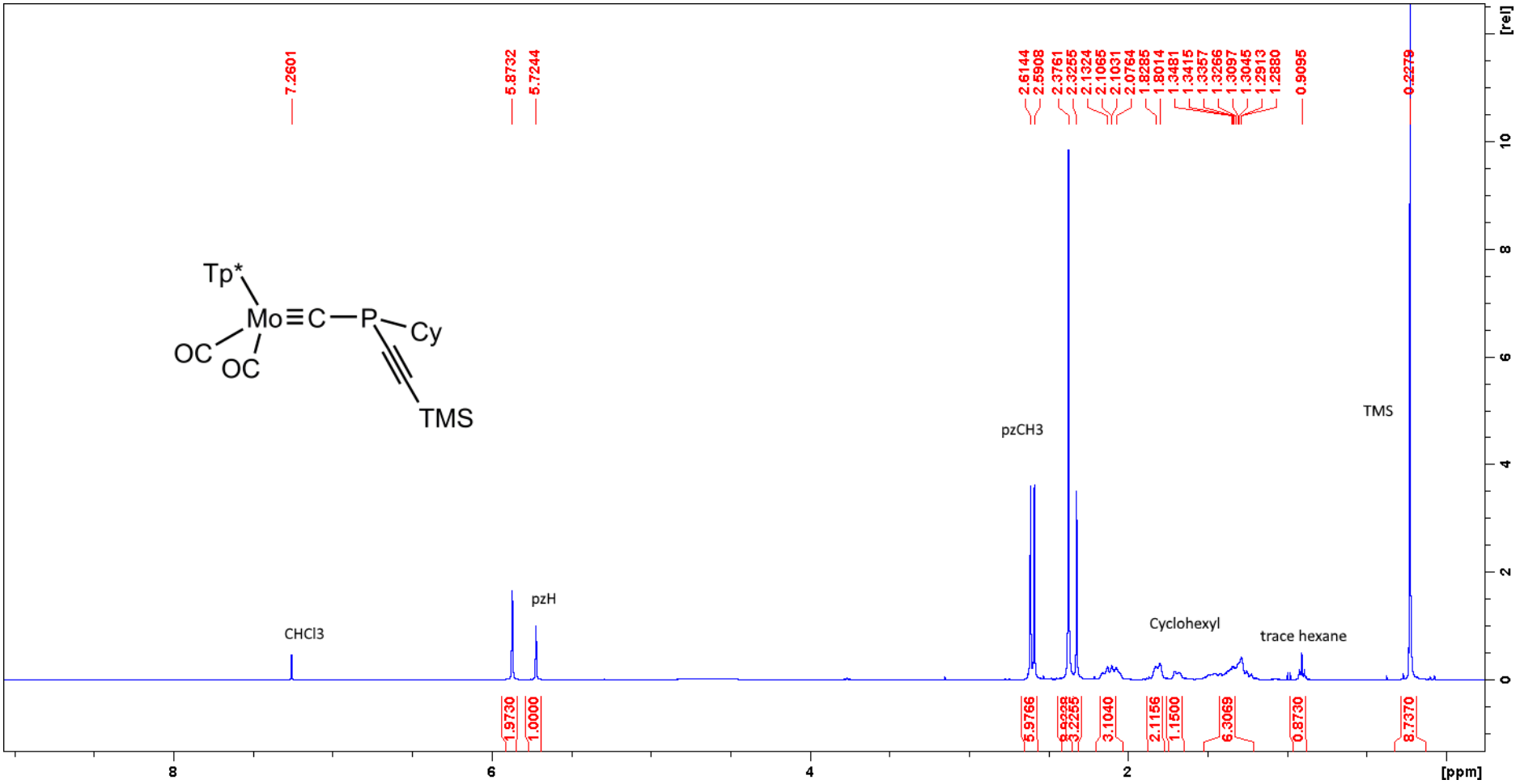

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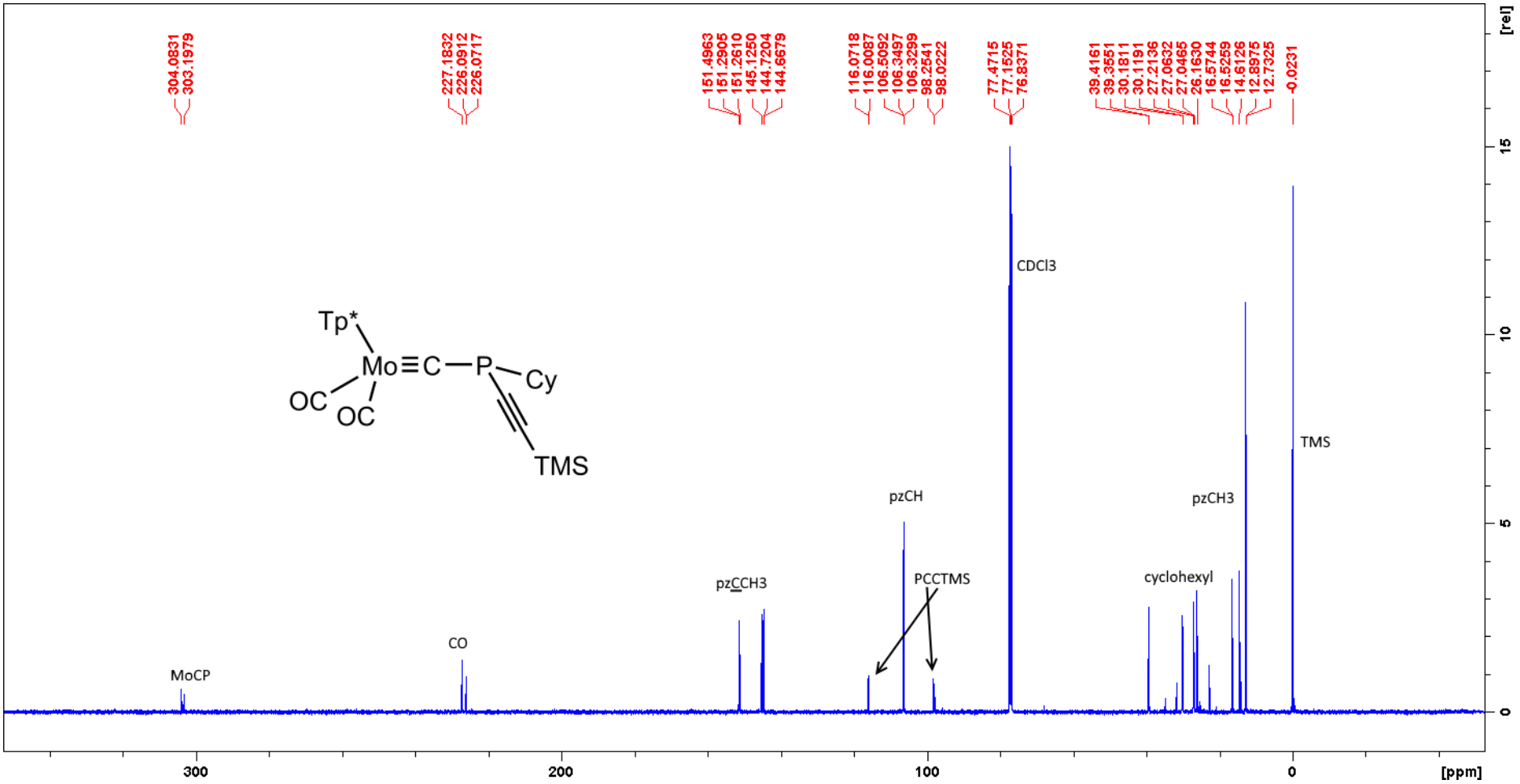

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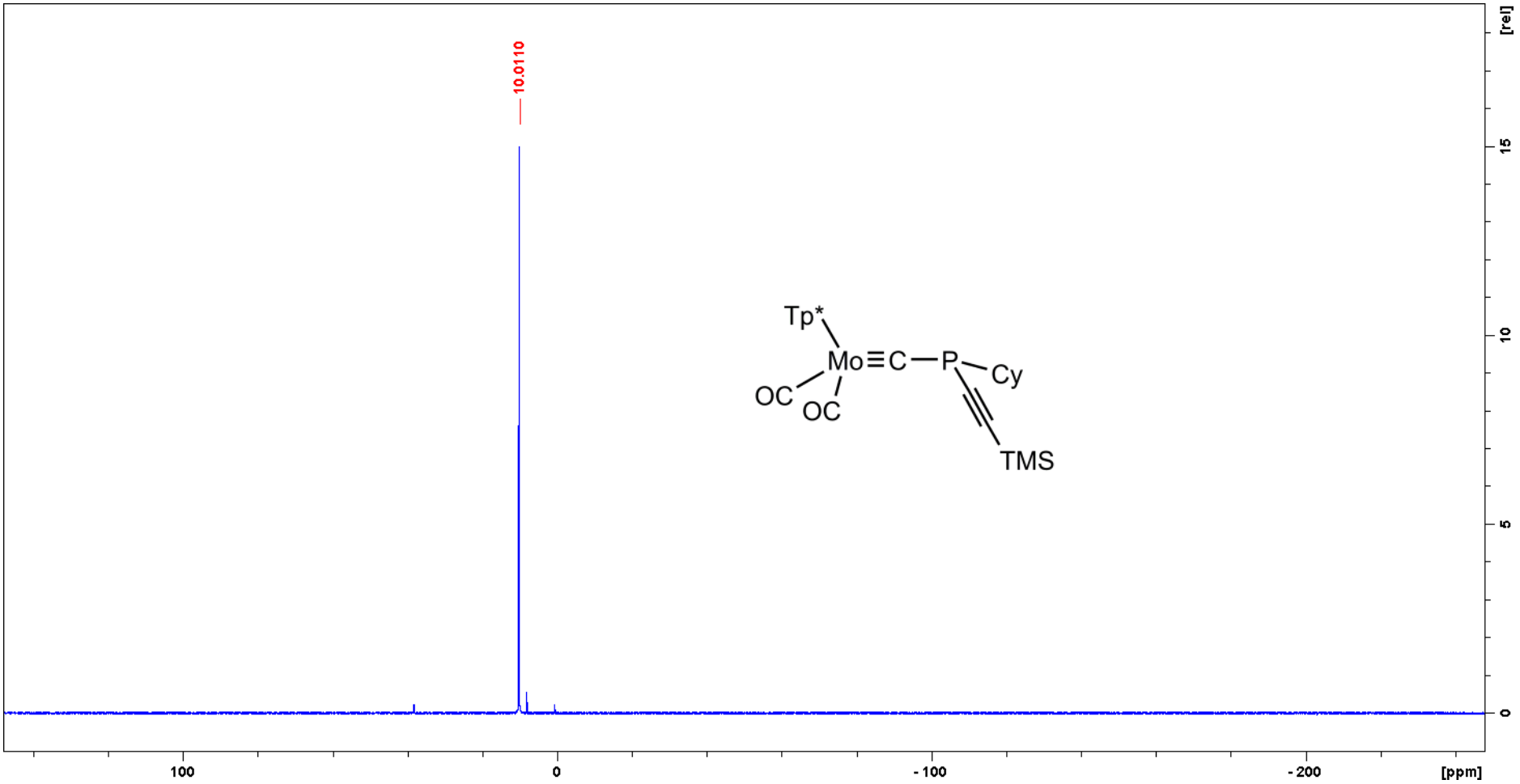

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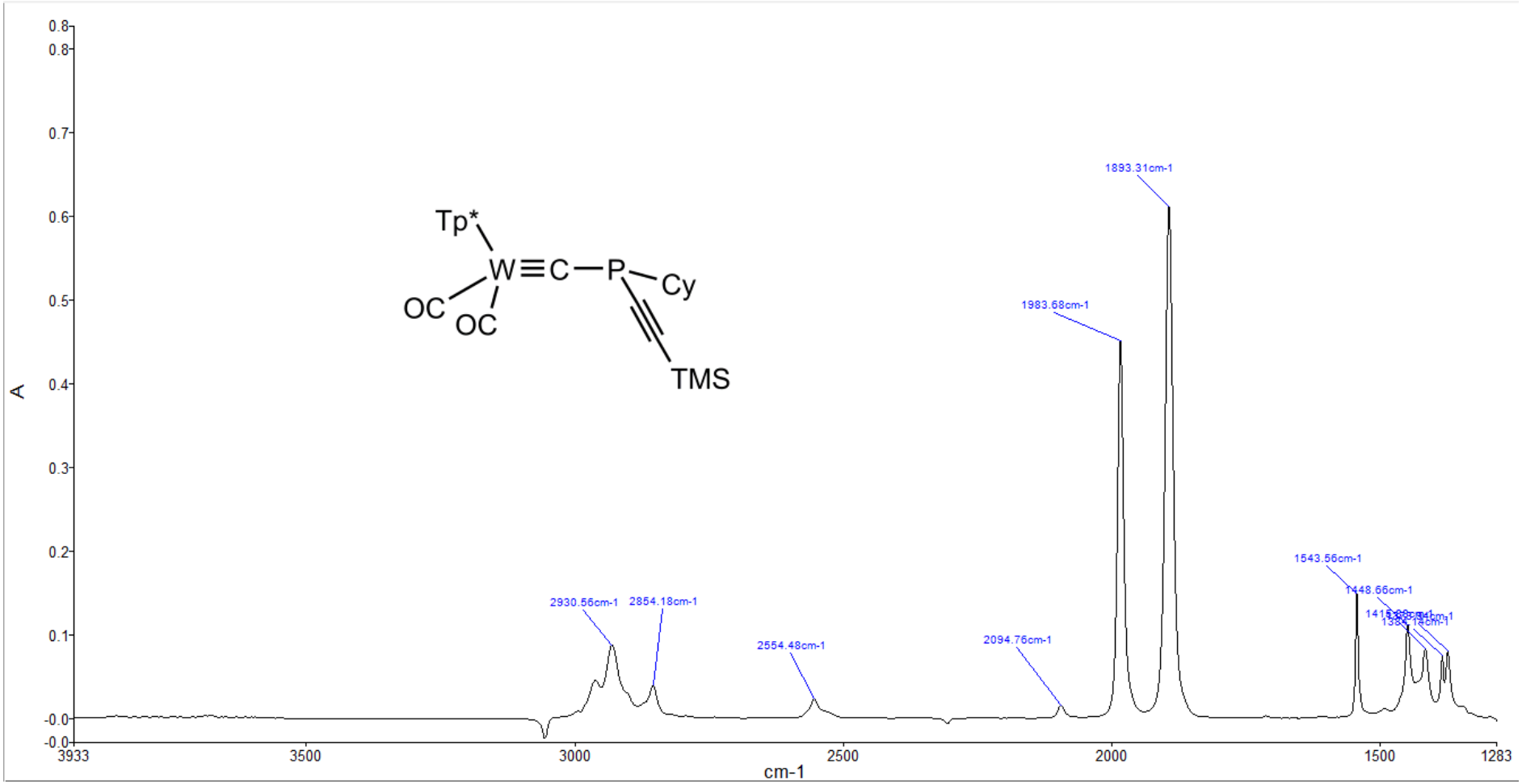

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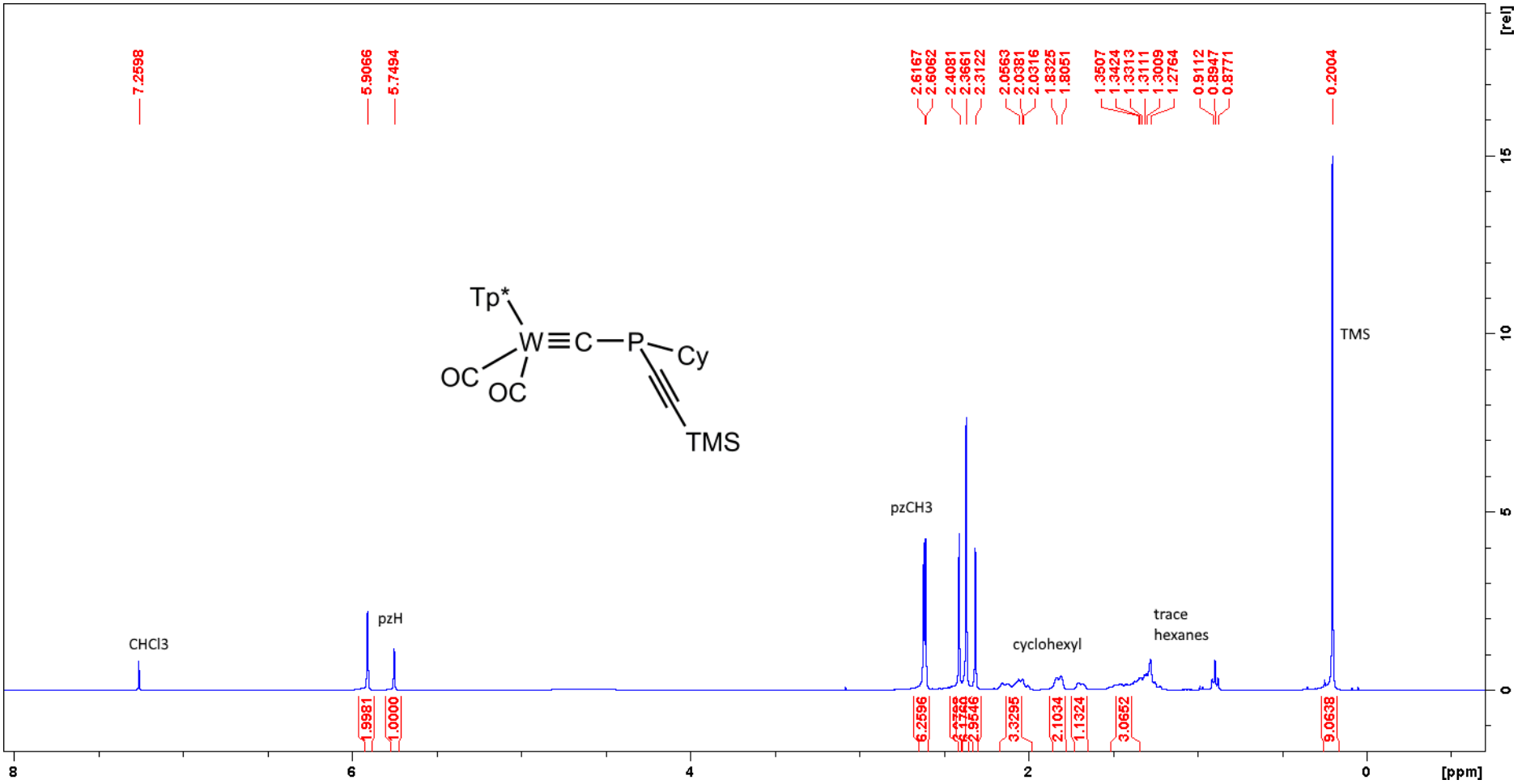

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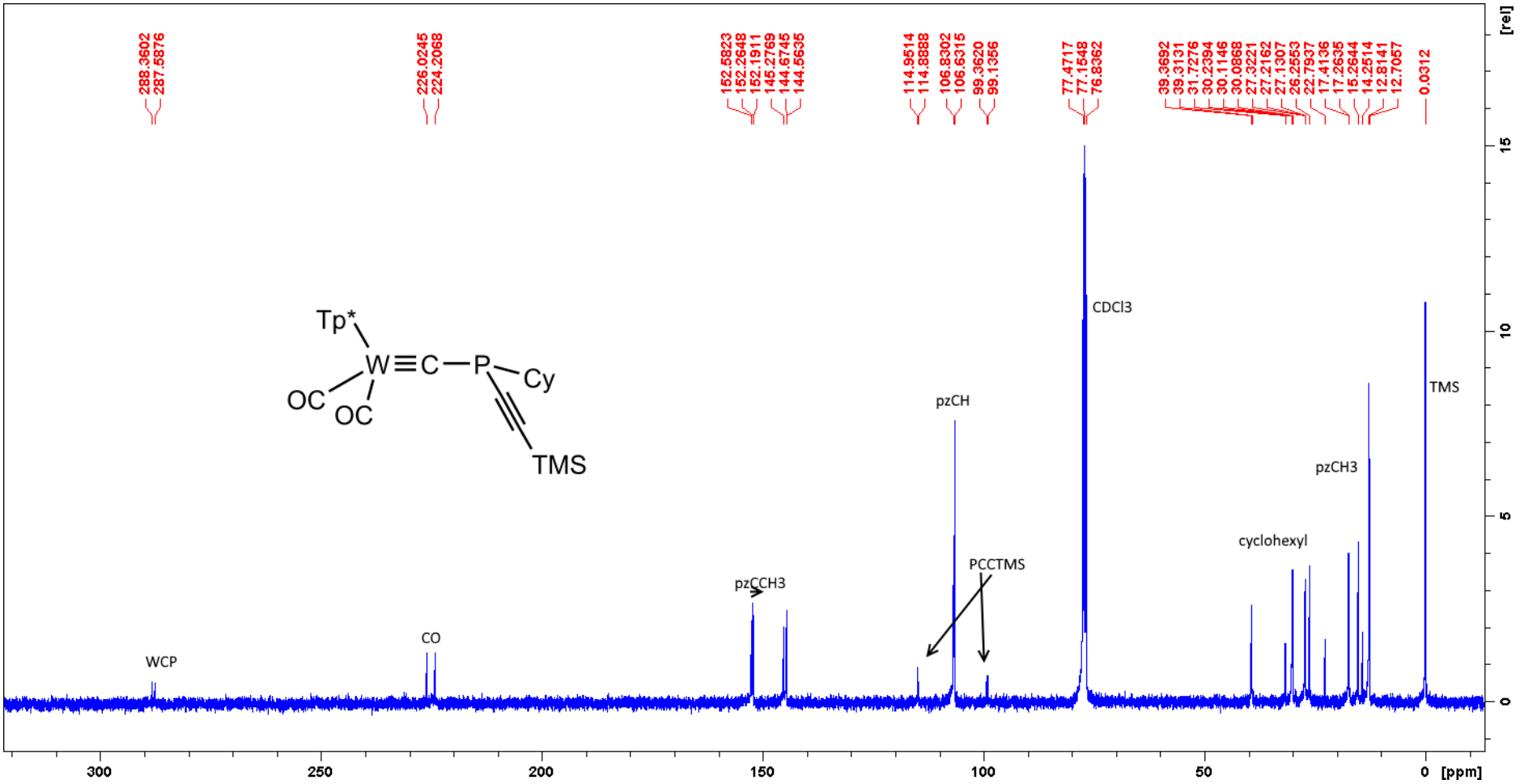

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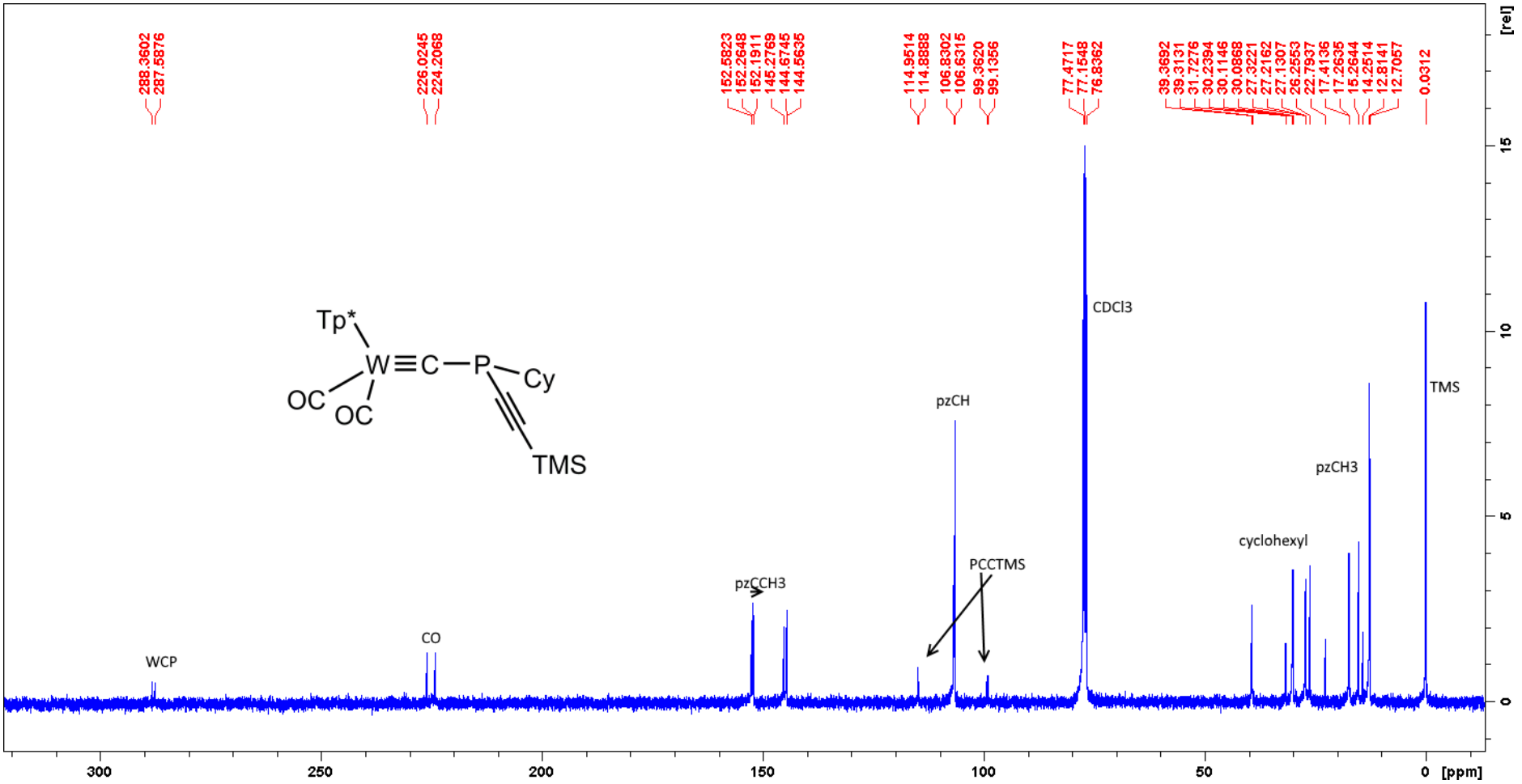

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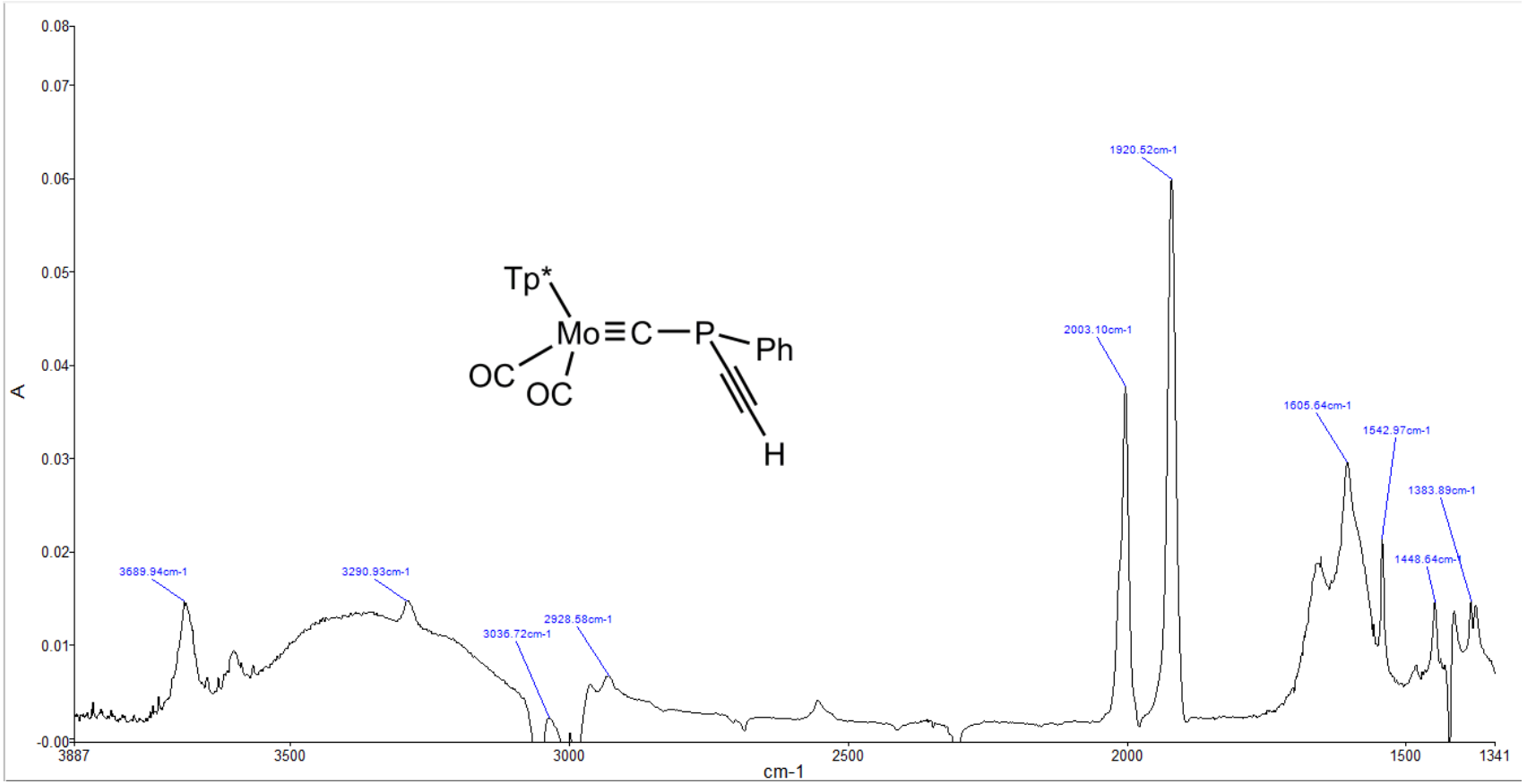

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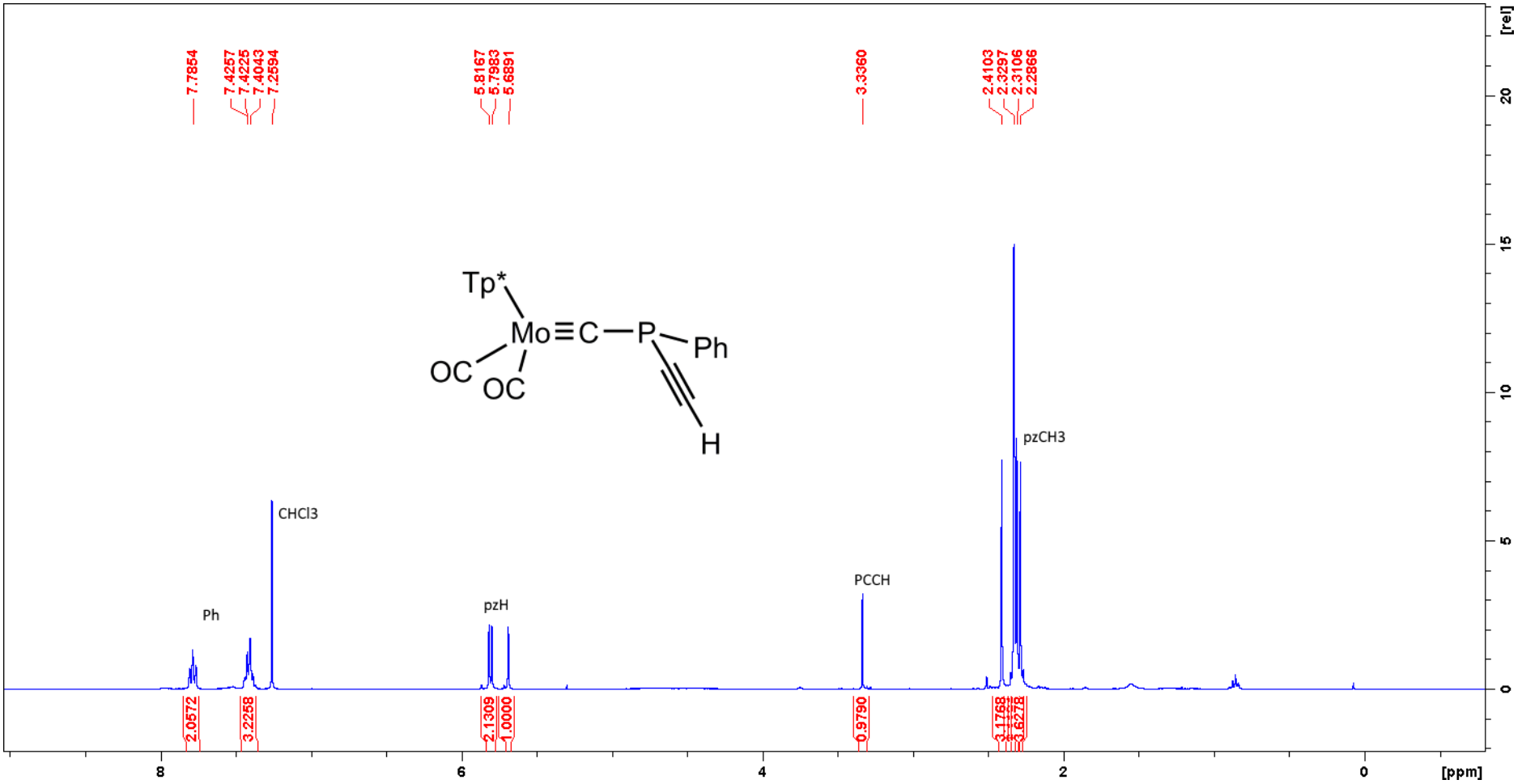

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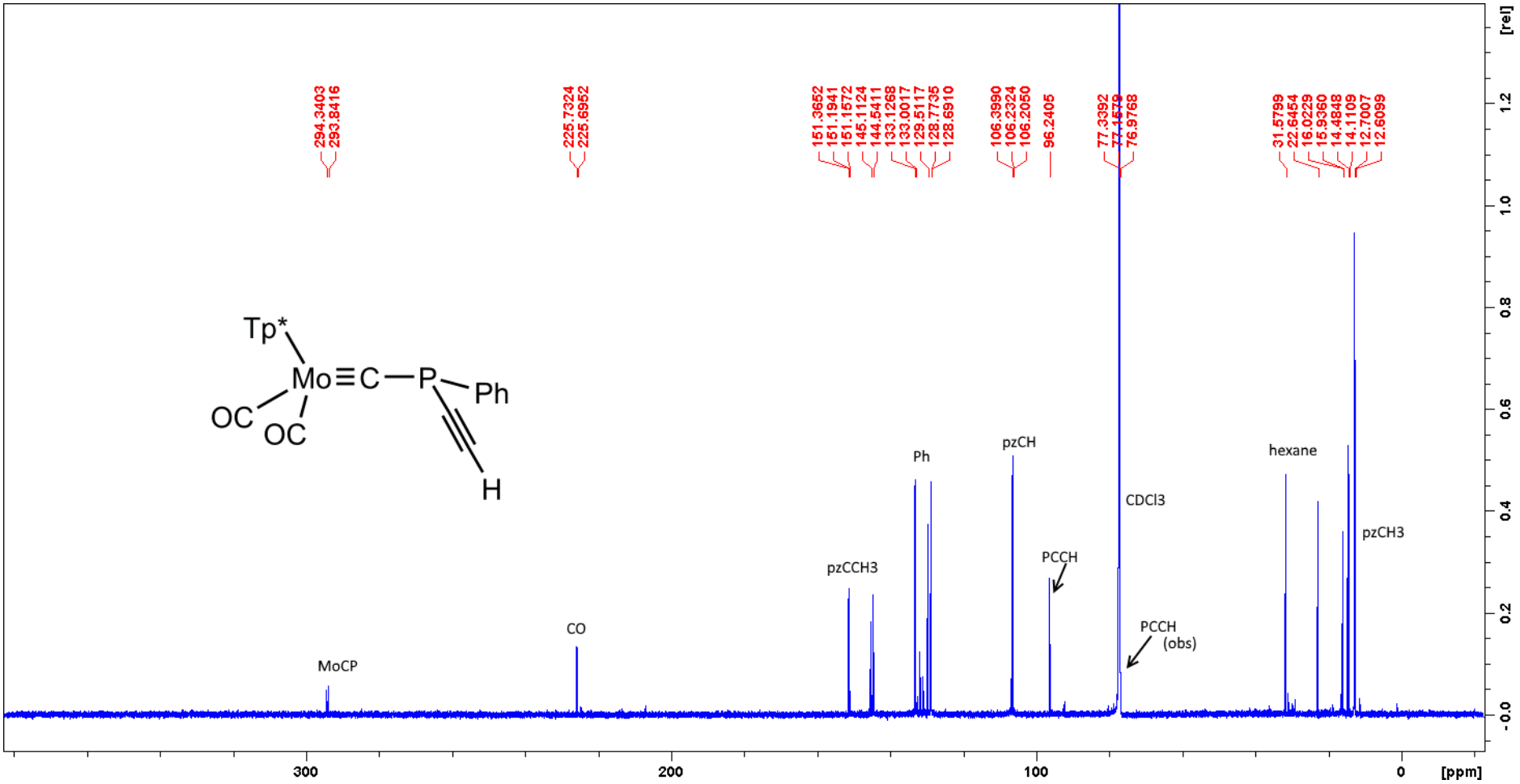

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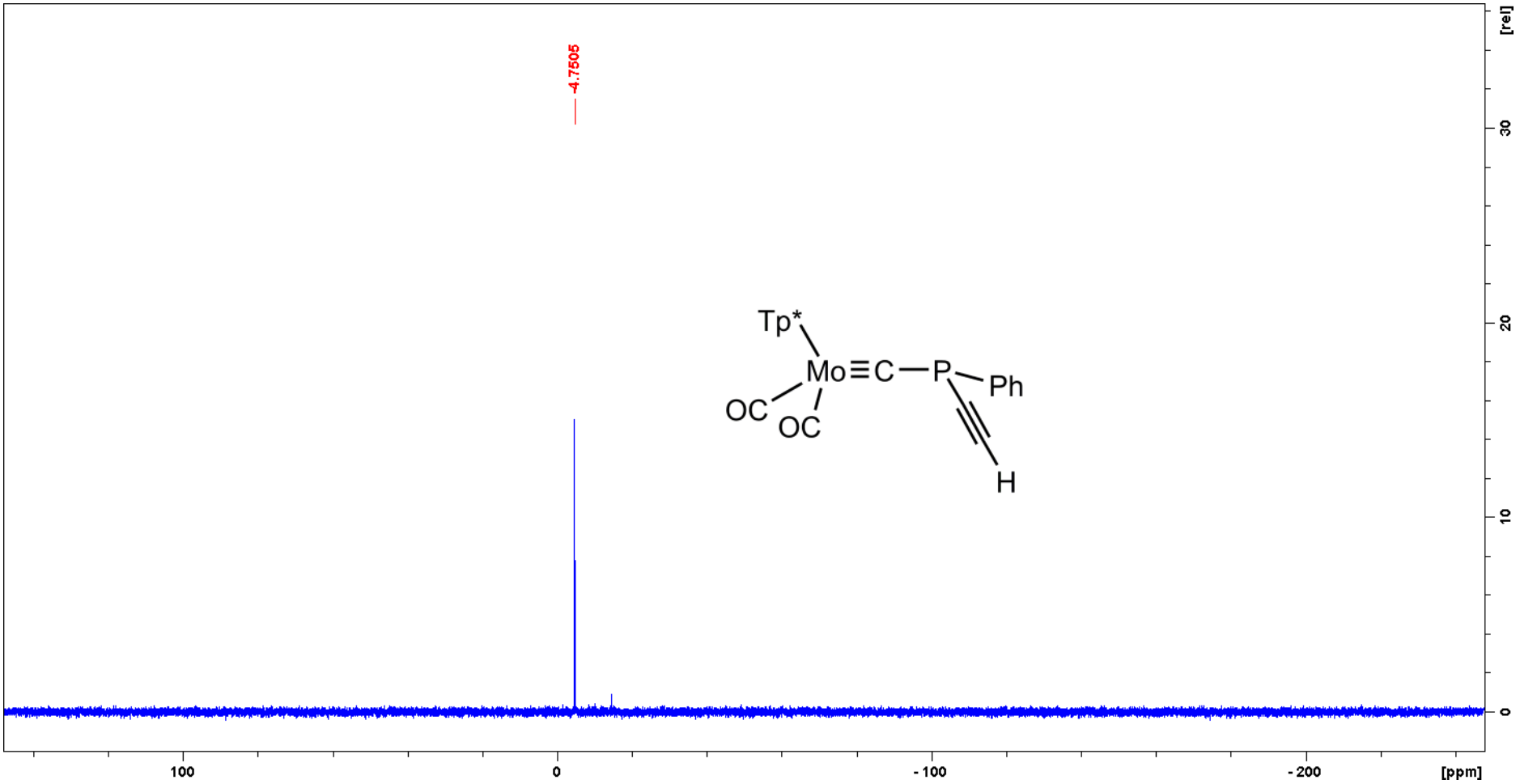

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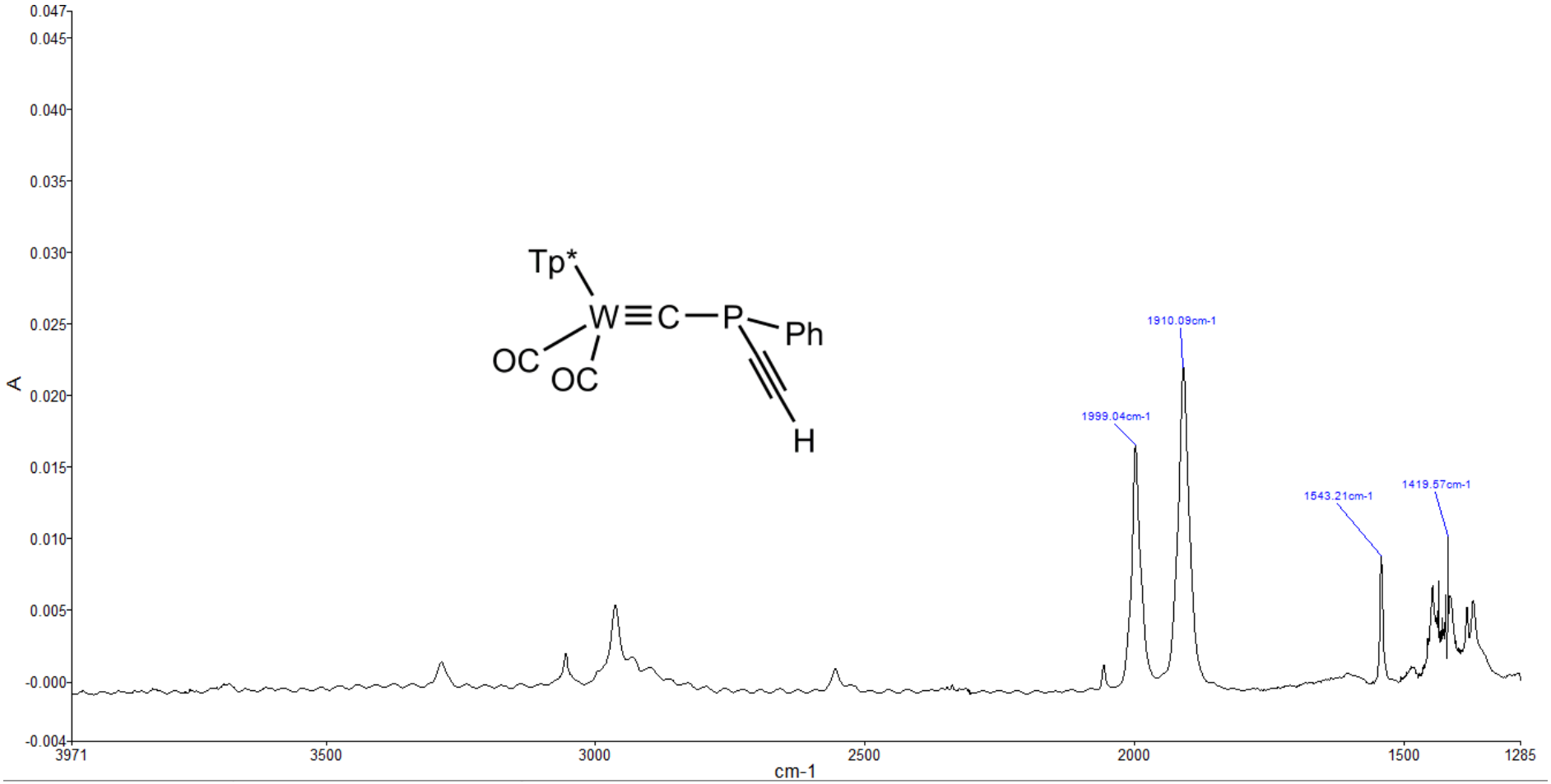

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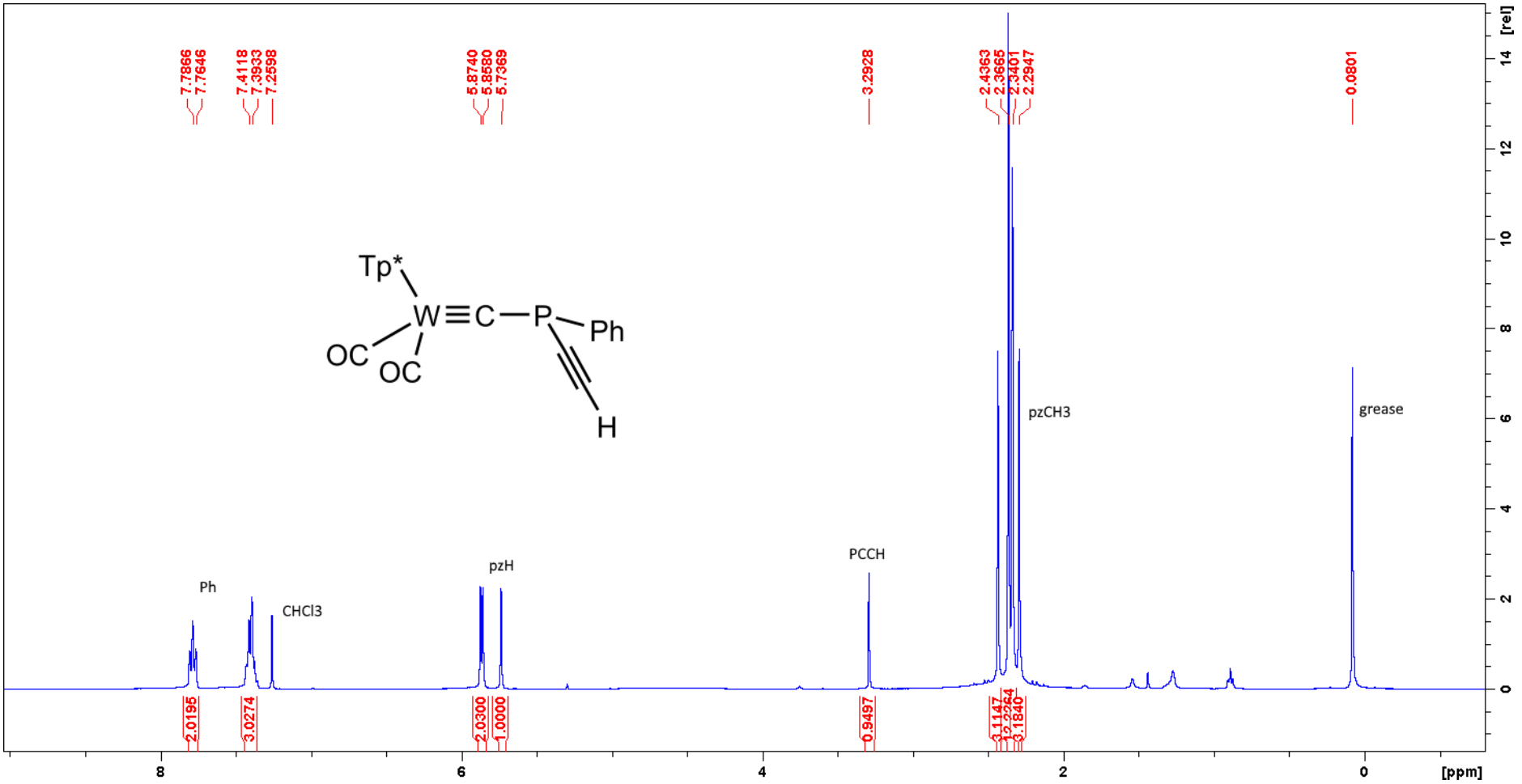

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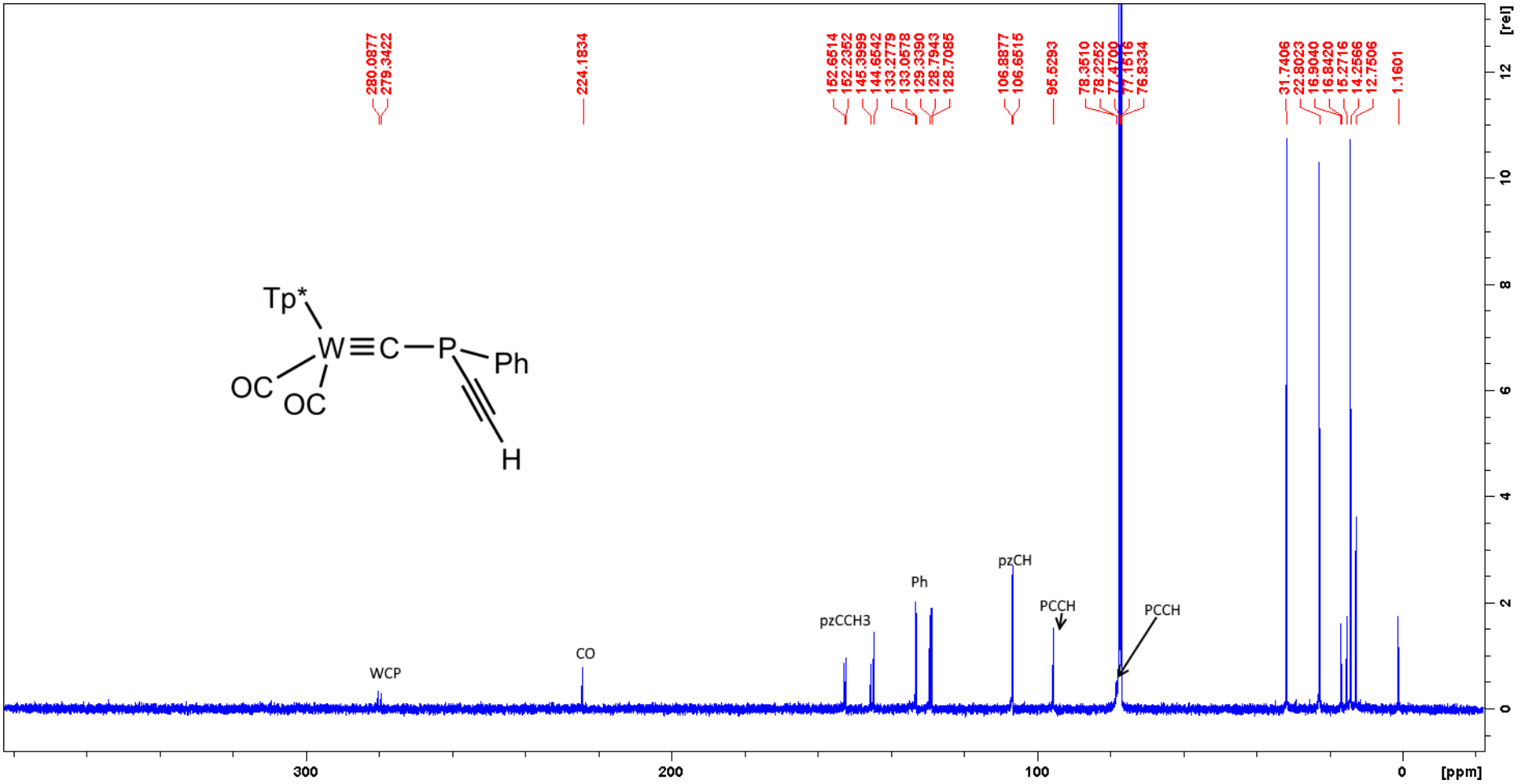

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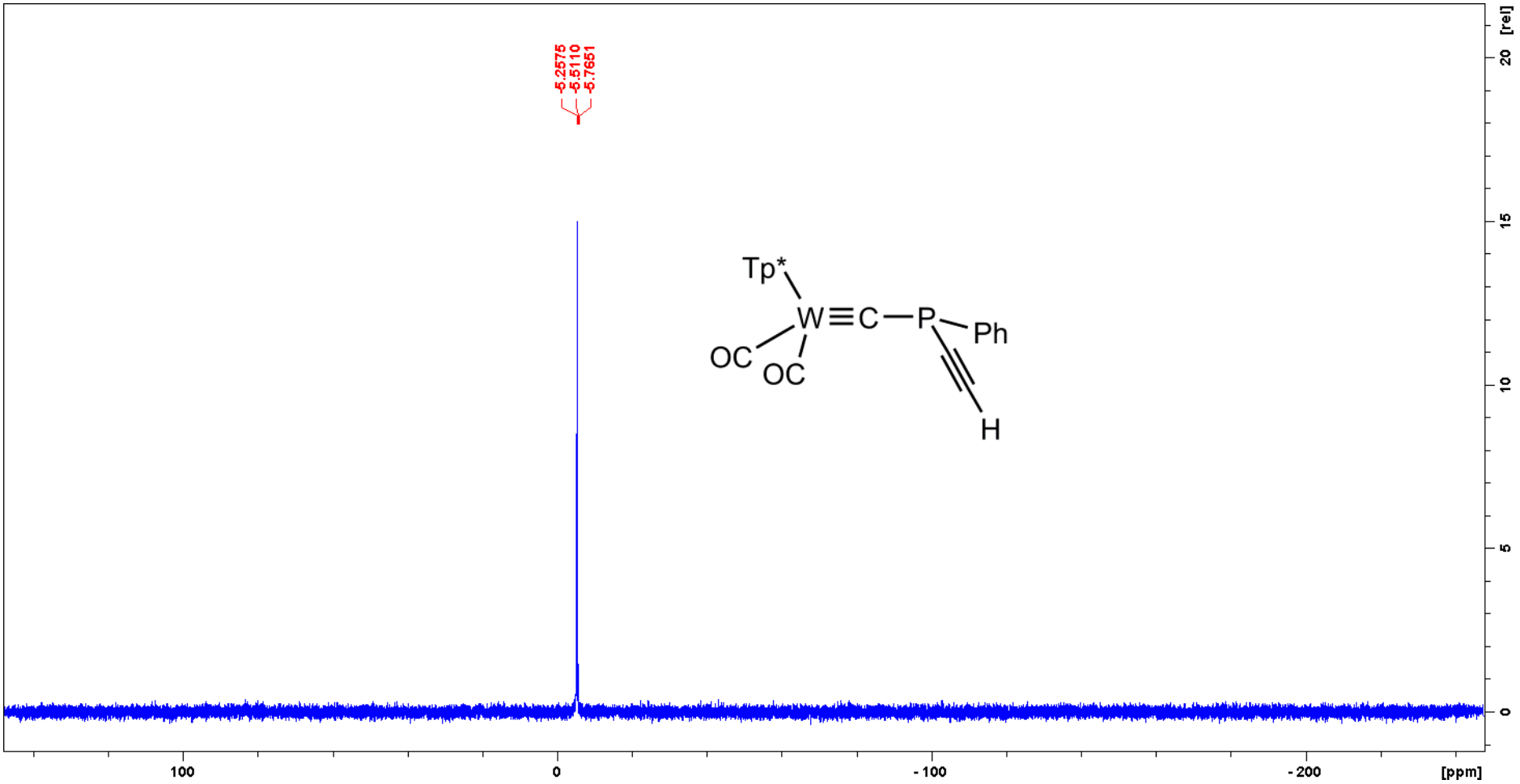

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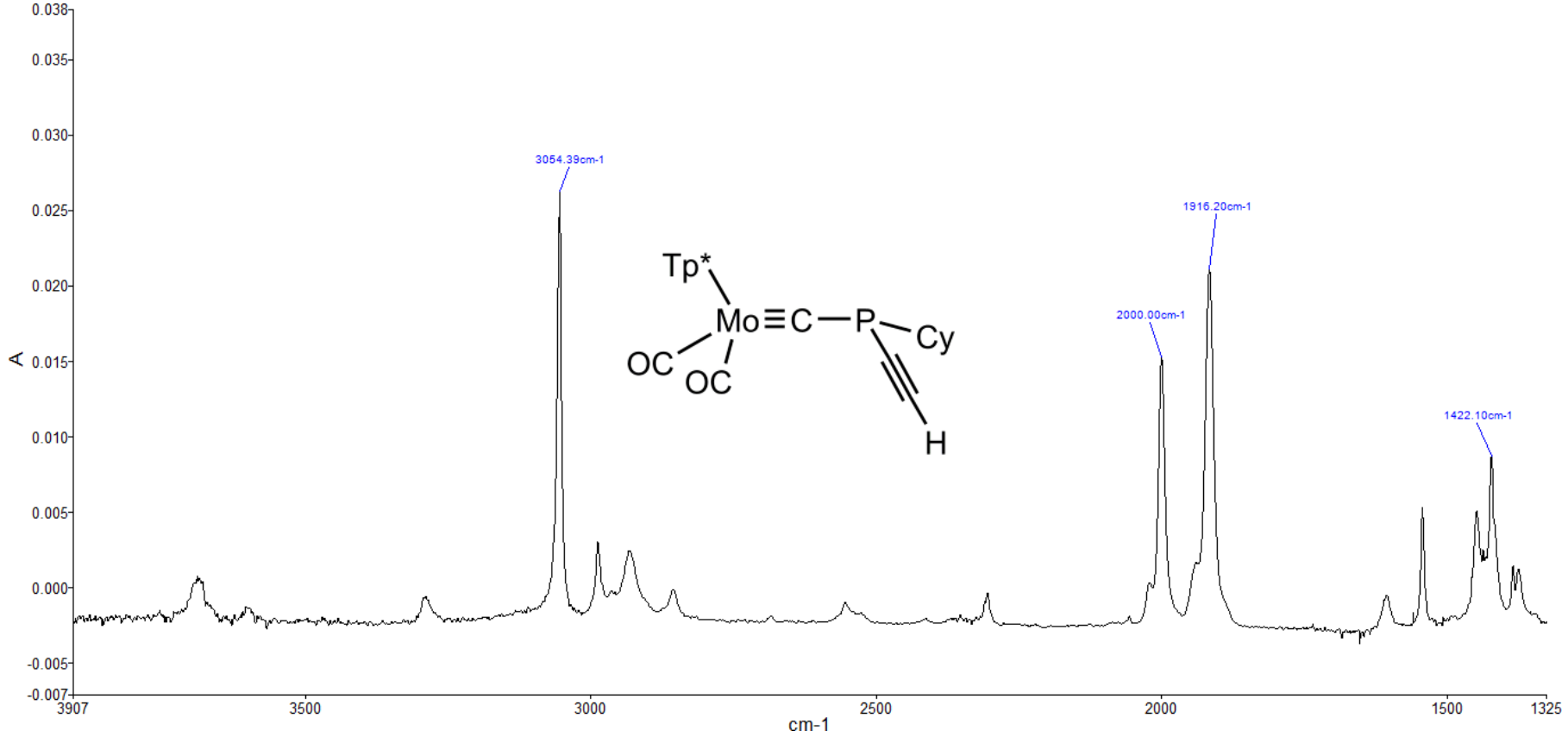

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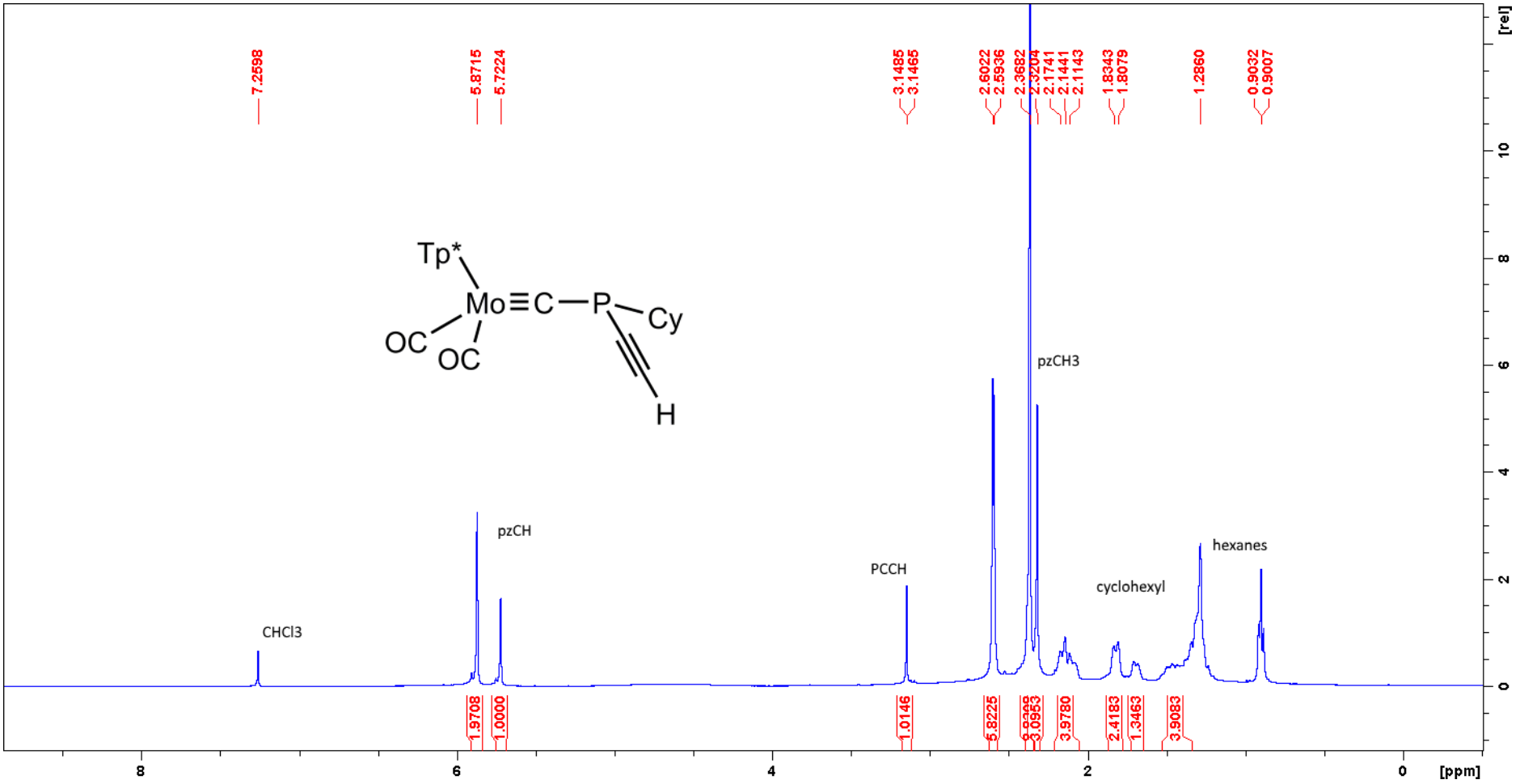
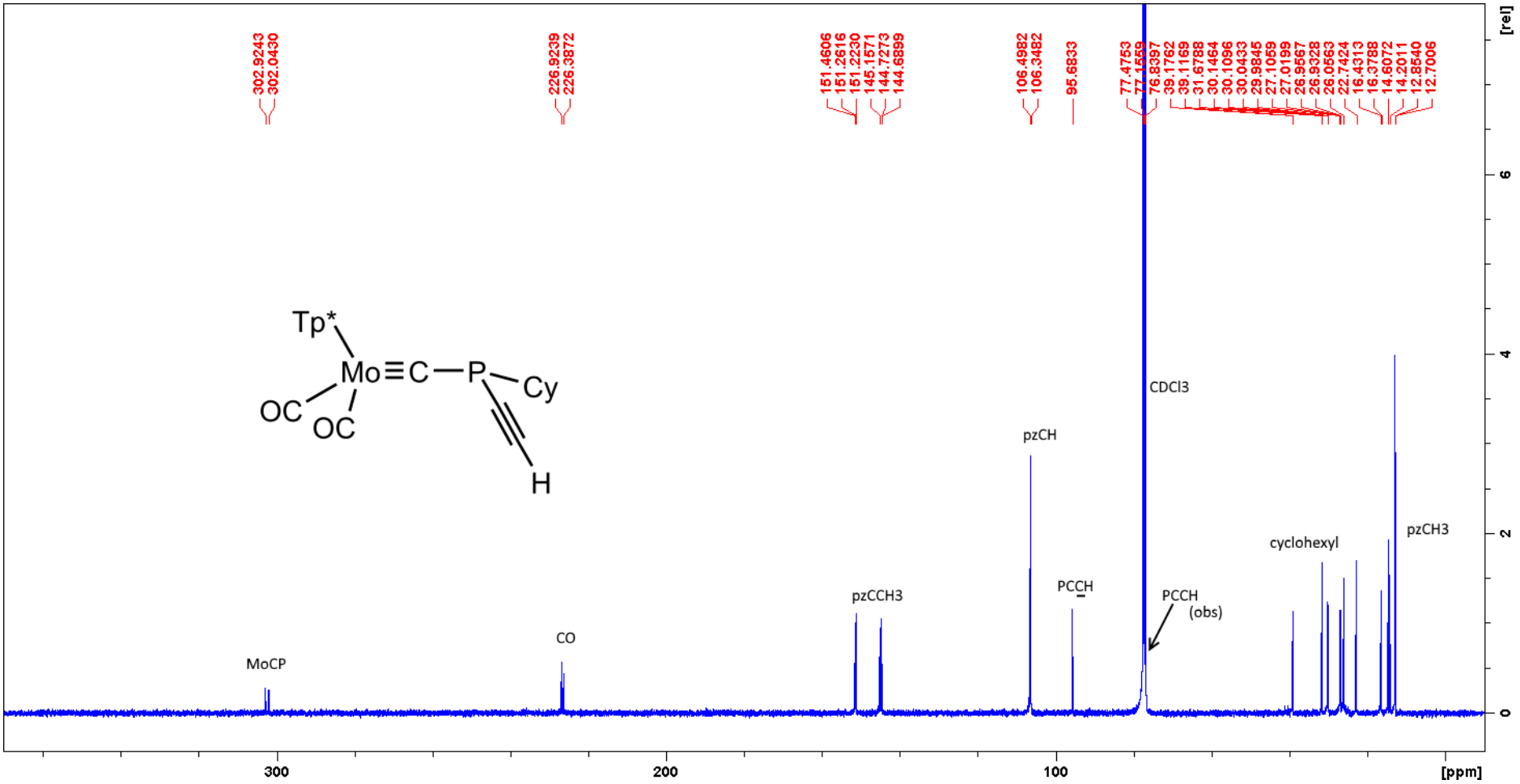
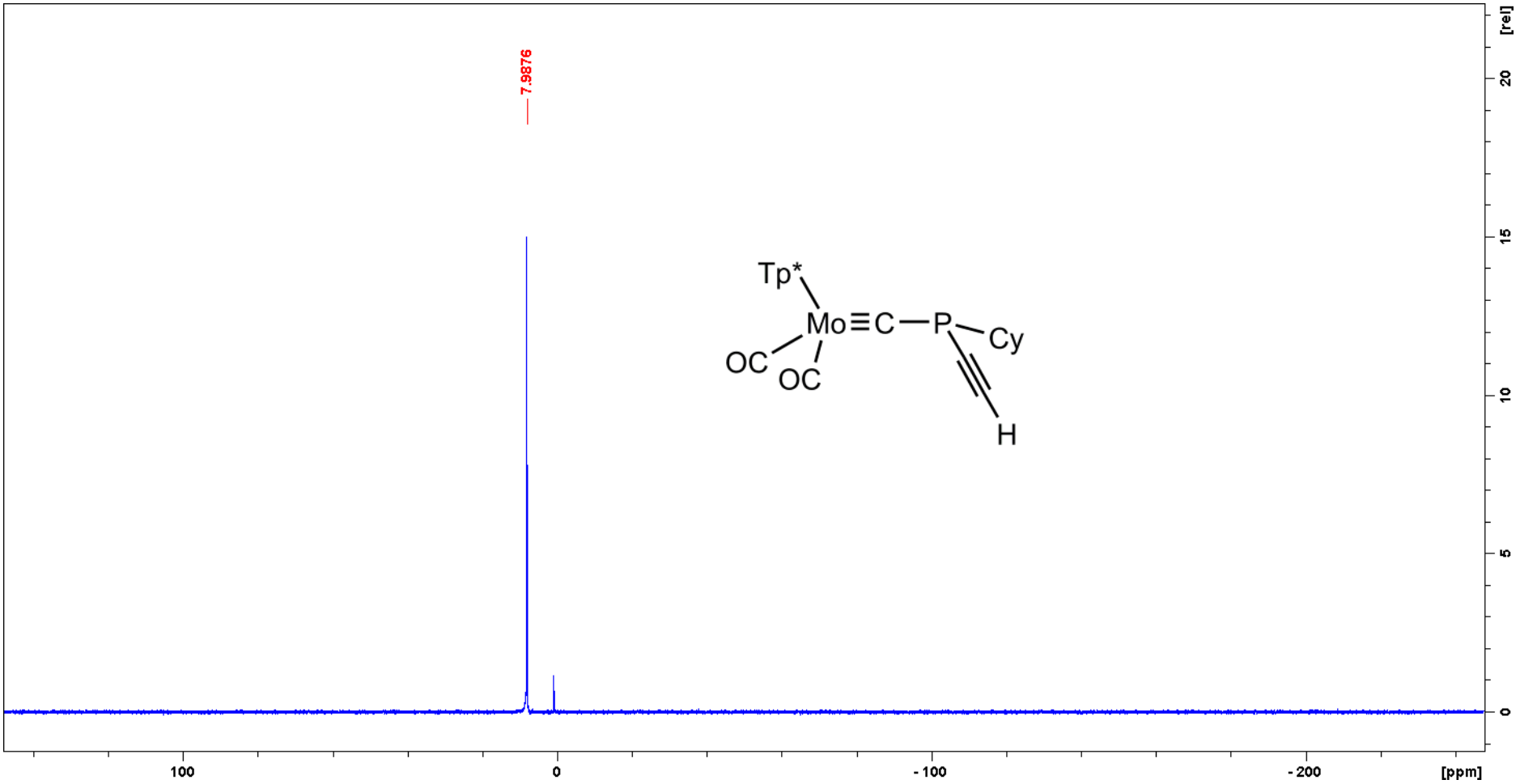


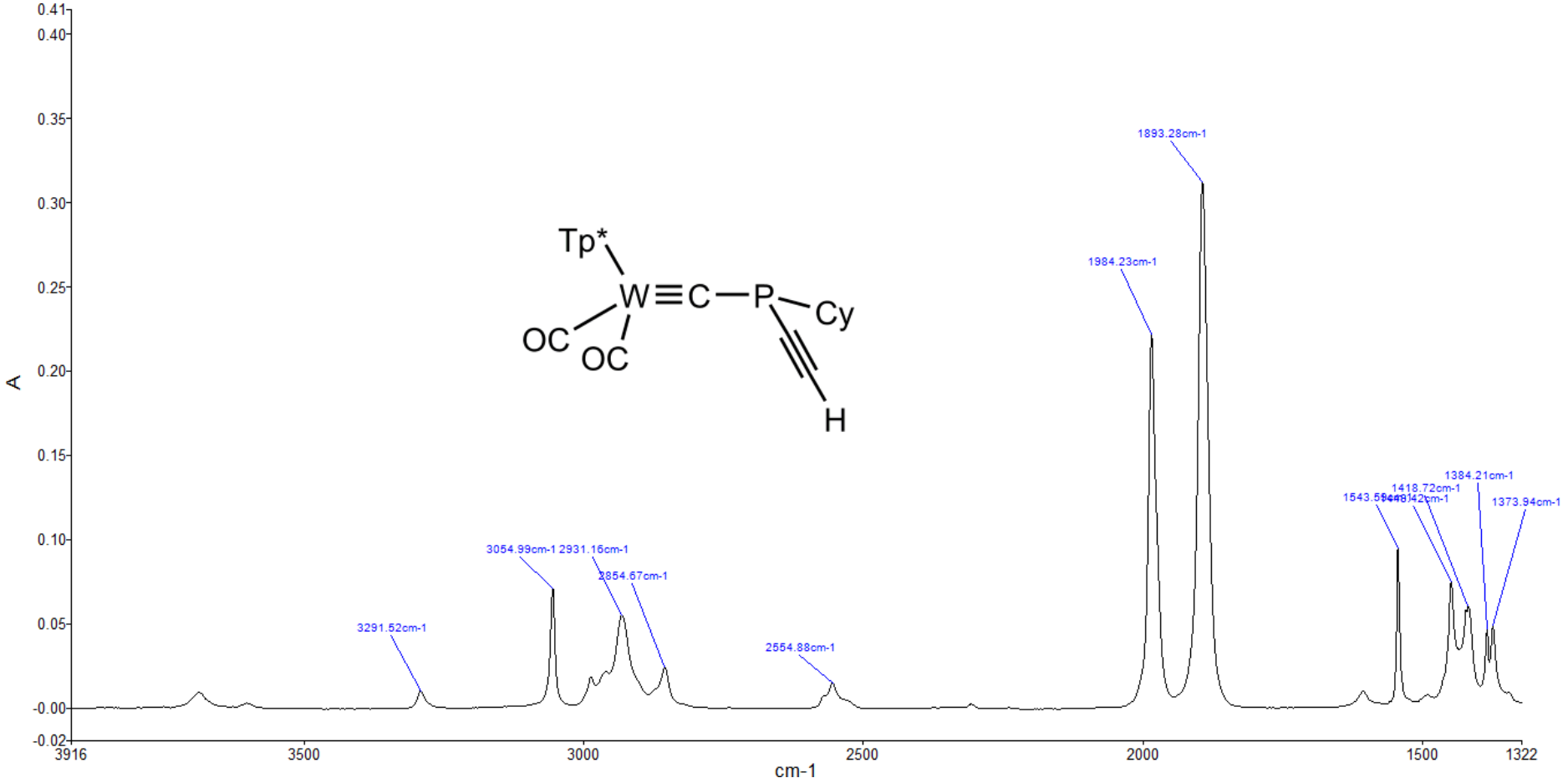
$^{13}C\{^{1}H\}$ NMR spectrum of **5a**.



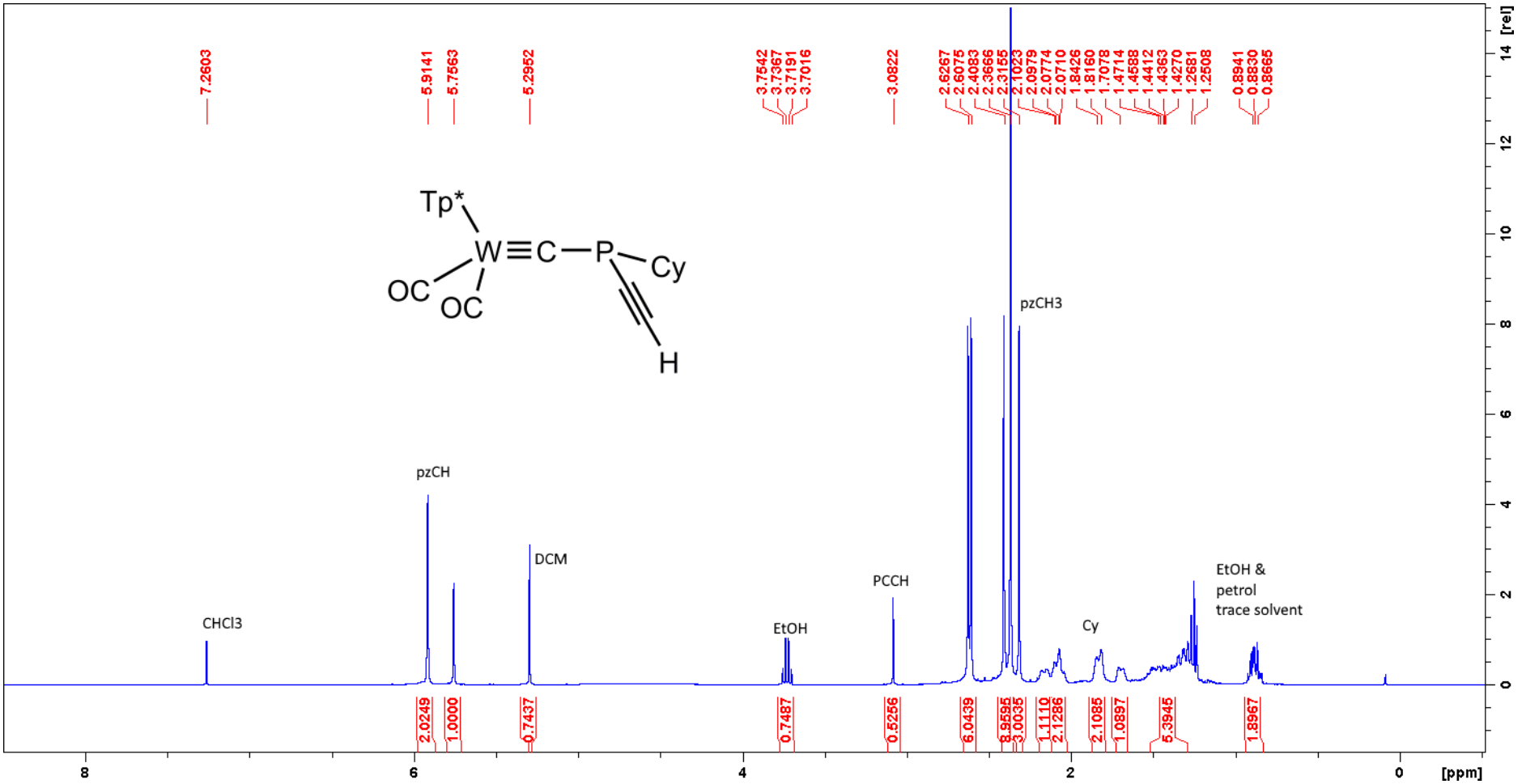
$^{31}P\{^{1}H\}$ NMR spectrum of **5a**.



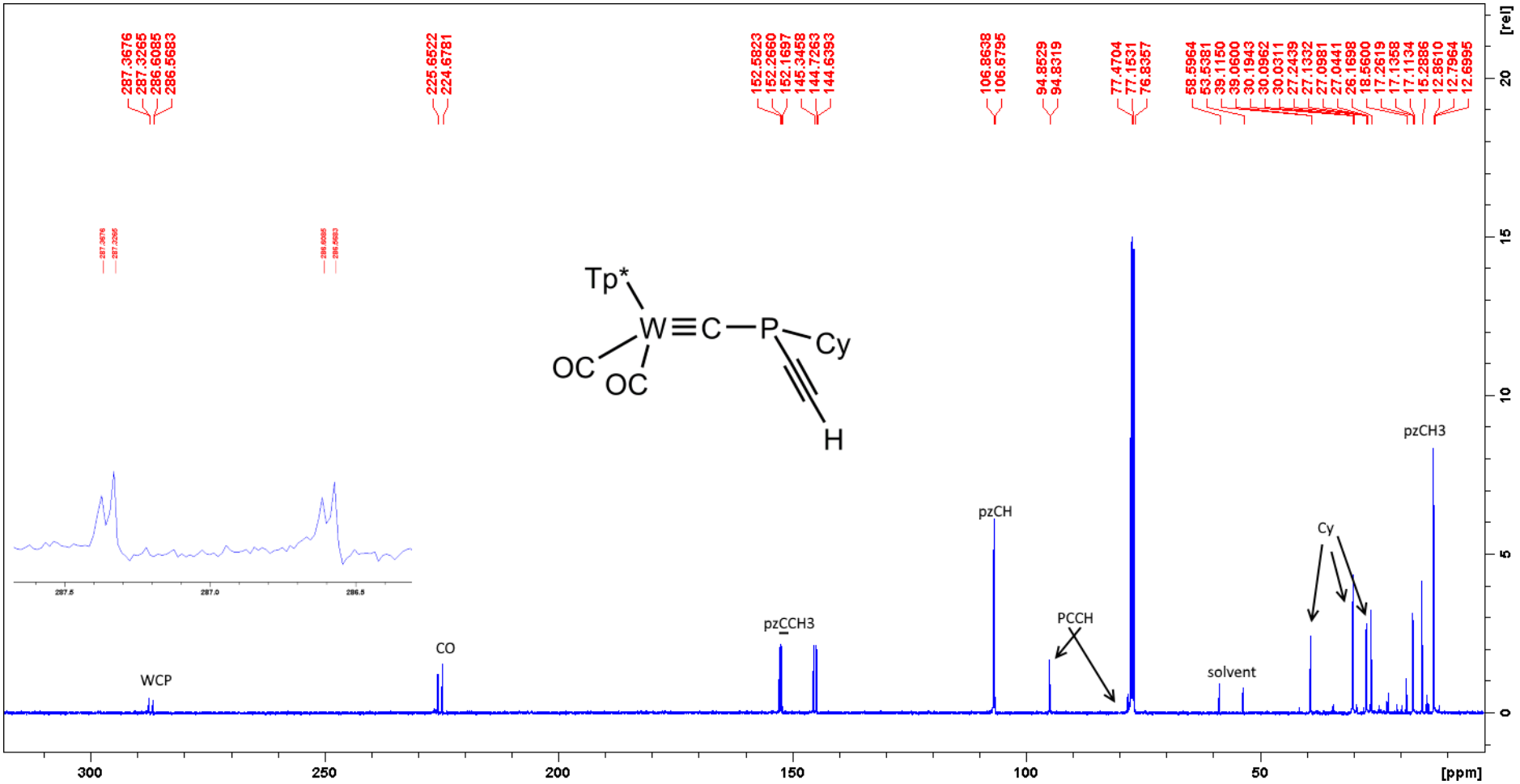
FTIR spectrum of **5b**.



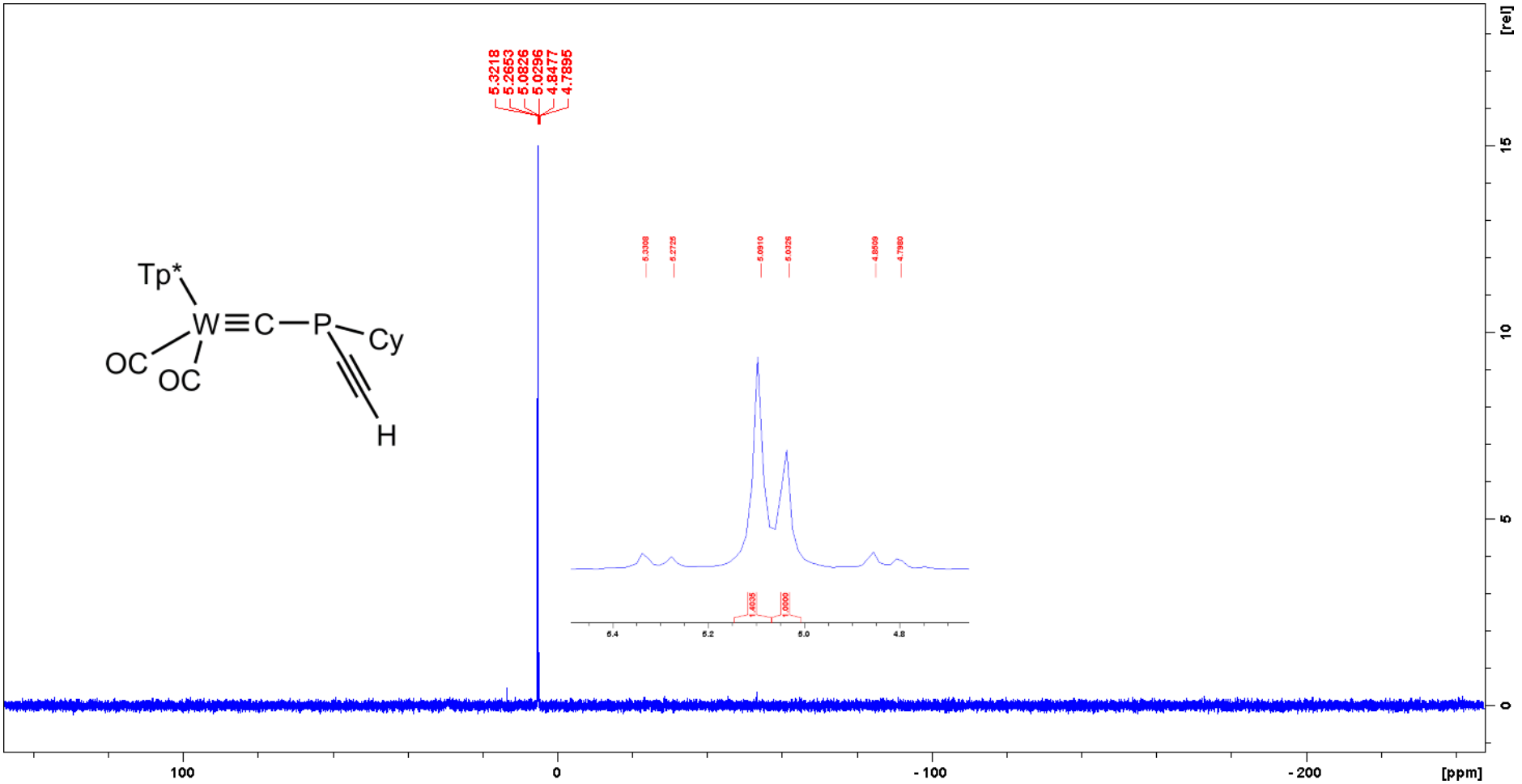
^{1}H NMR spectrum of **5b**.



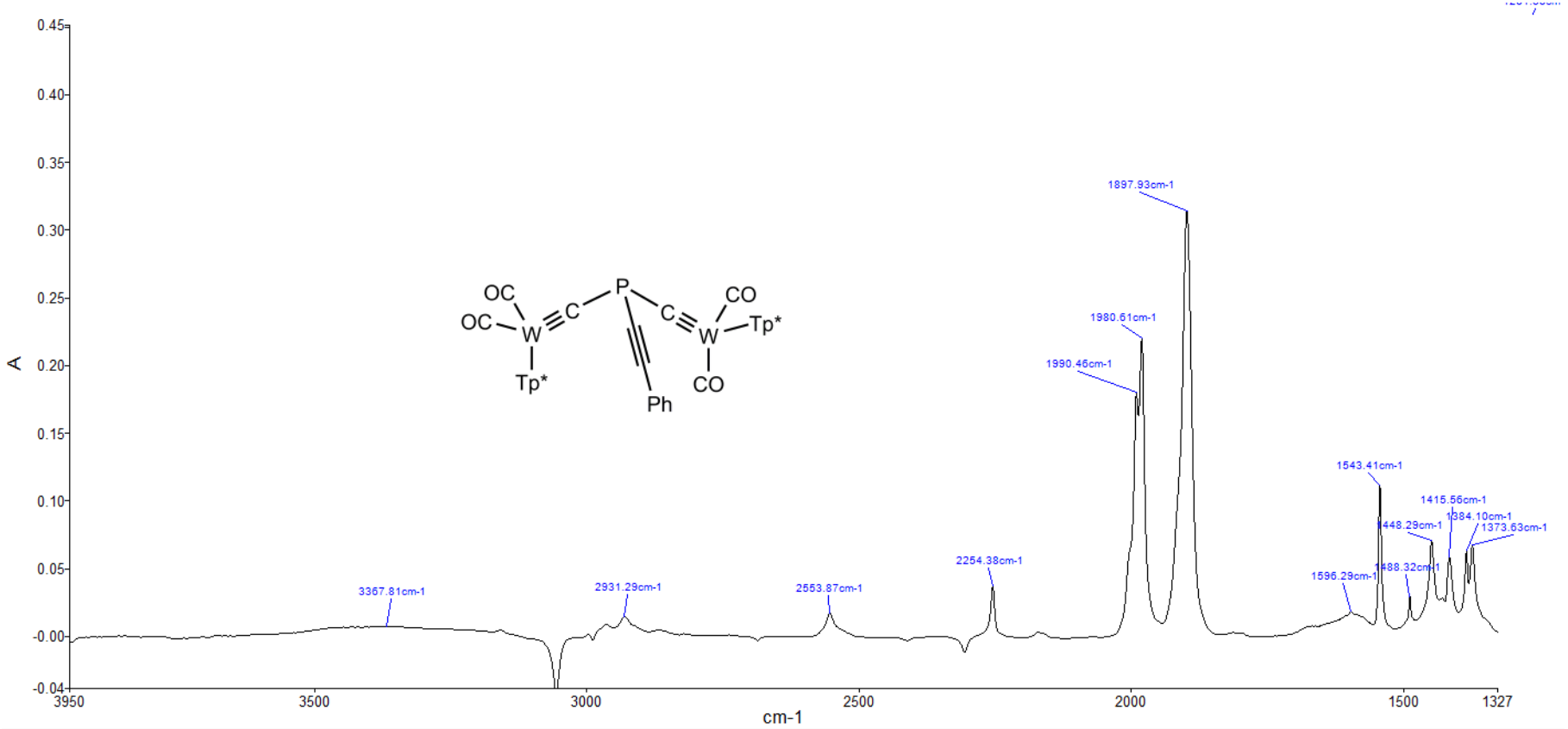
$^{13}C\{^{1}H\}$ NMR spectrum of **5b**.



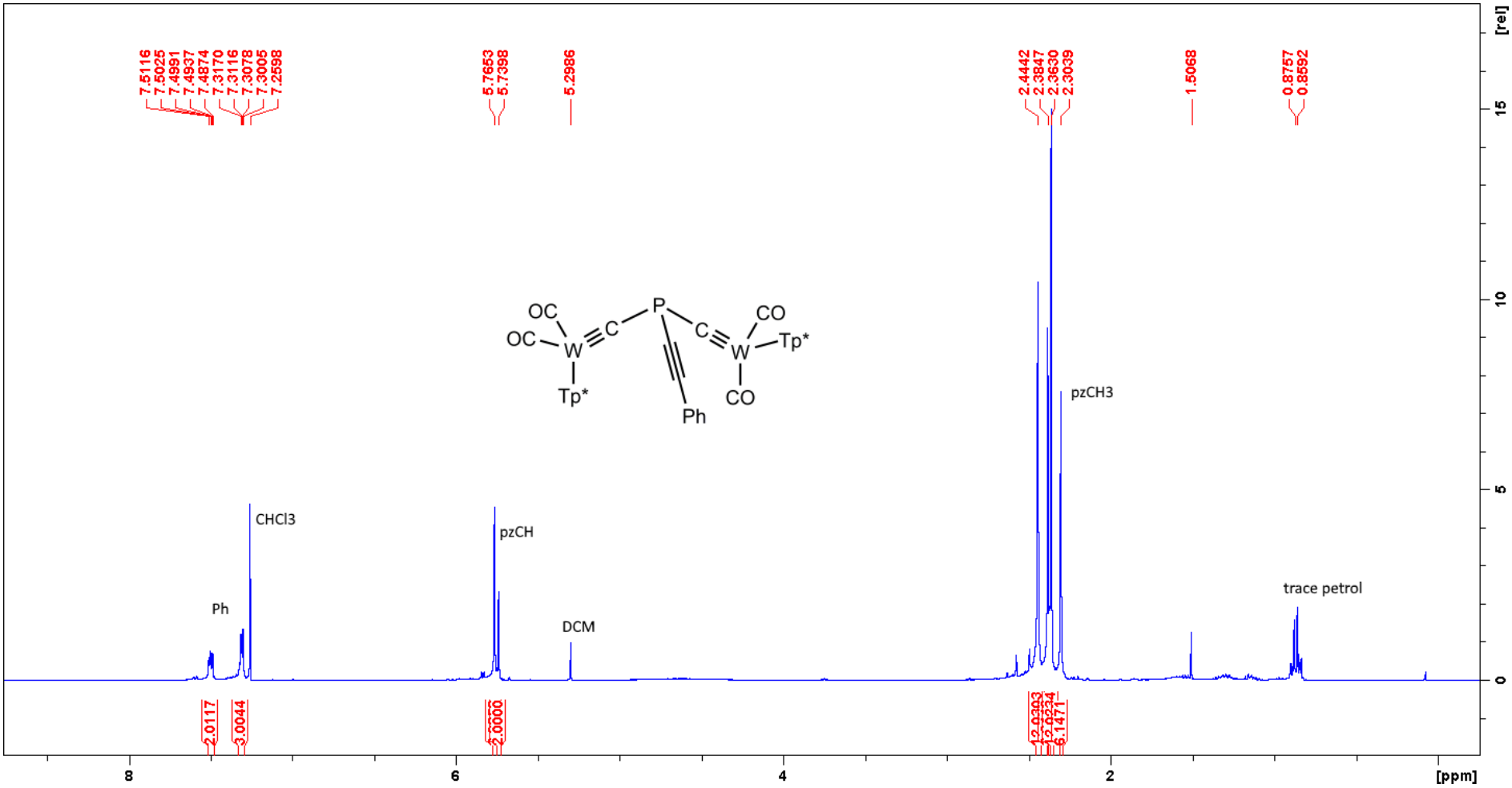
$^{31}P\{^{1}H\}$ NMR spectrum of **5b**.



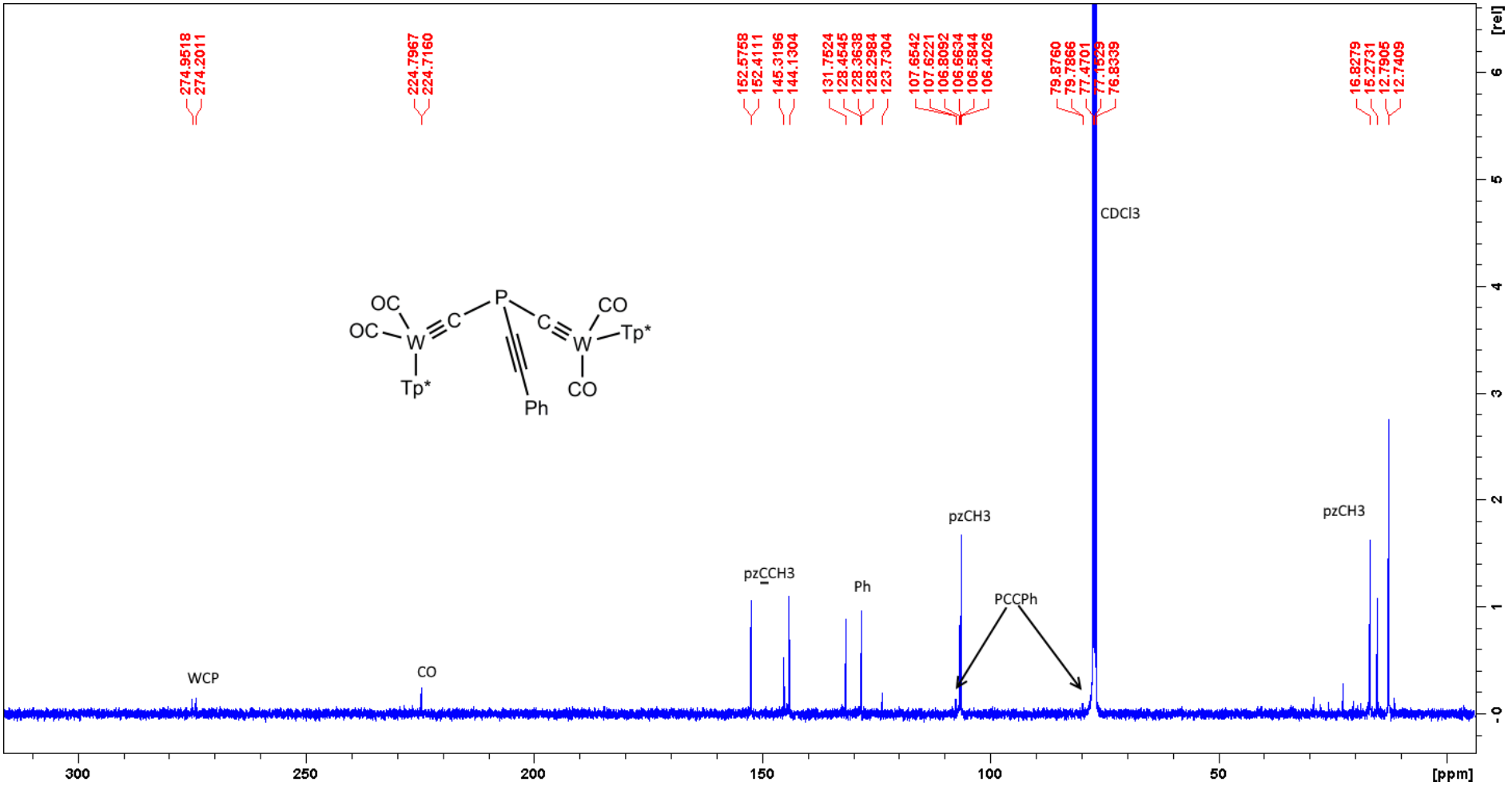
FTIR spectrum of **6**.



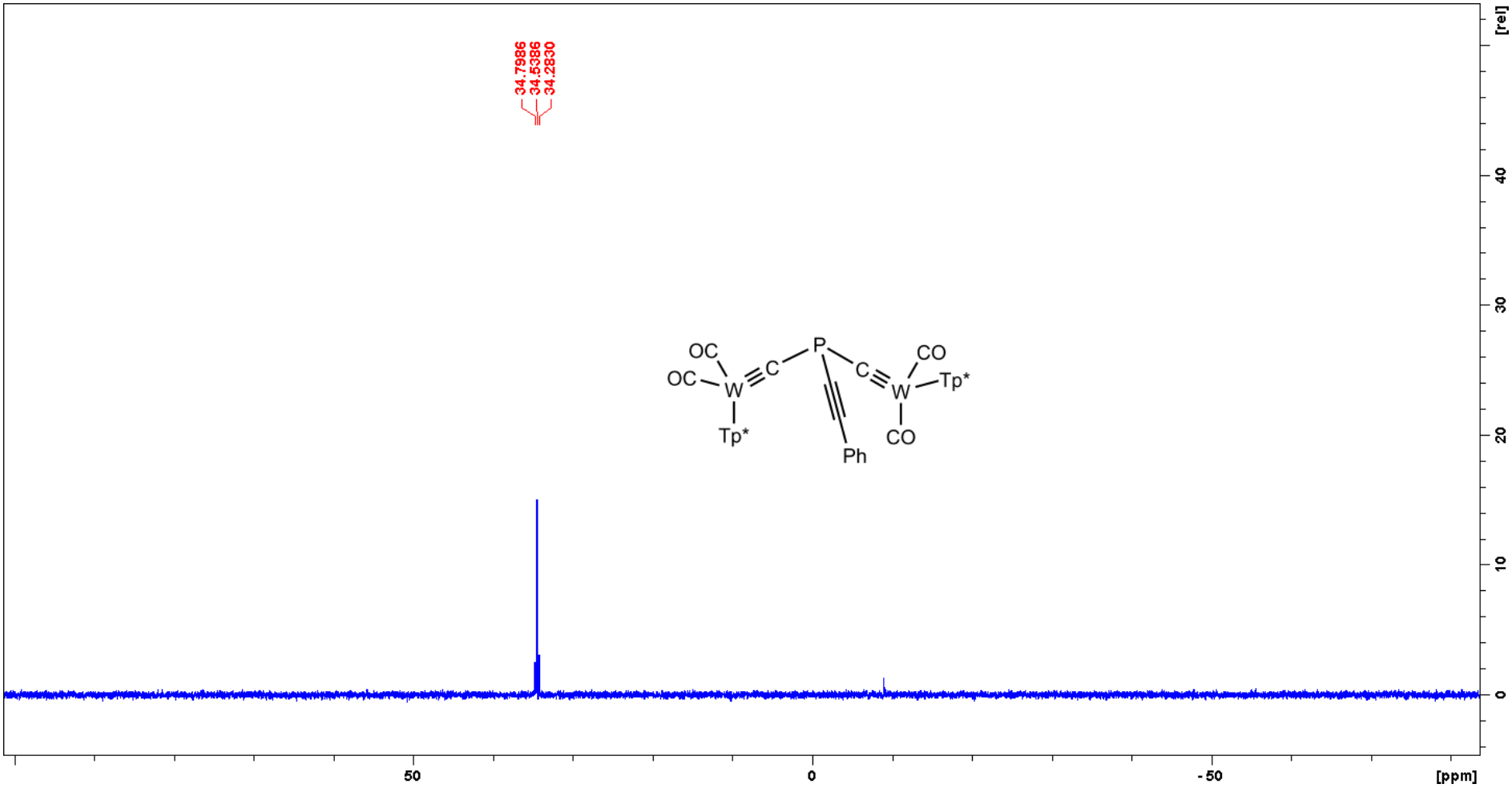
^{1}H NMR spectrum of **6**.



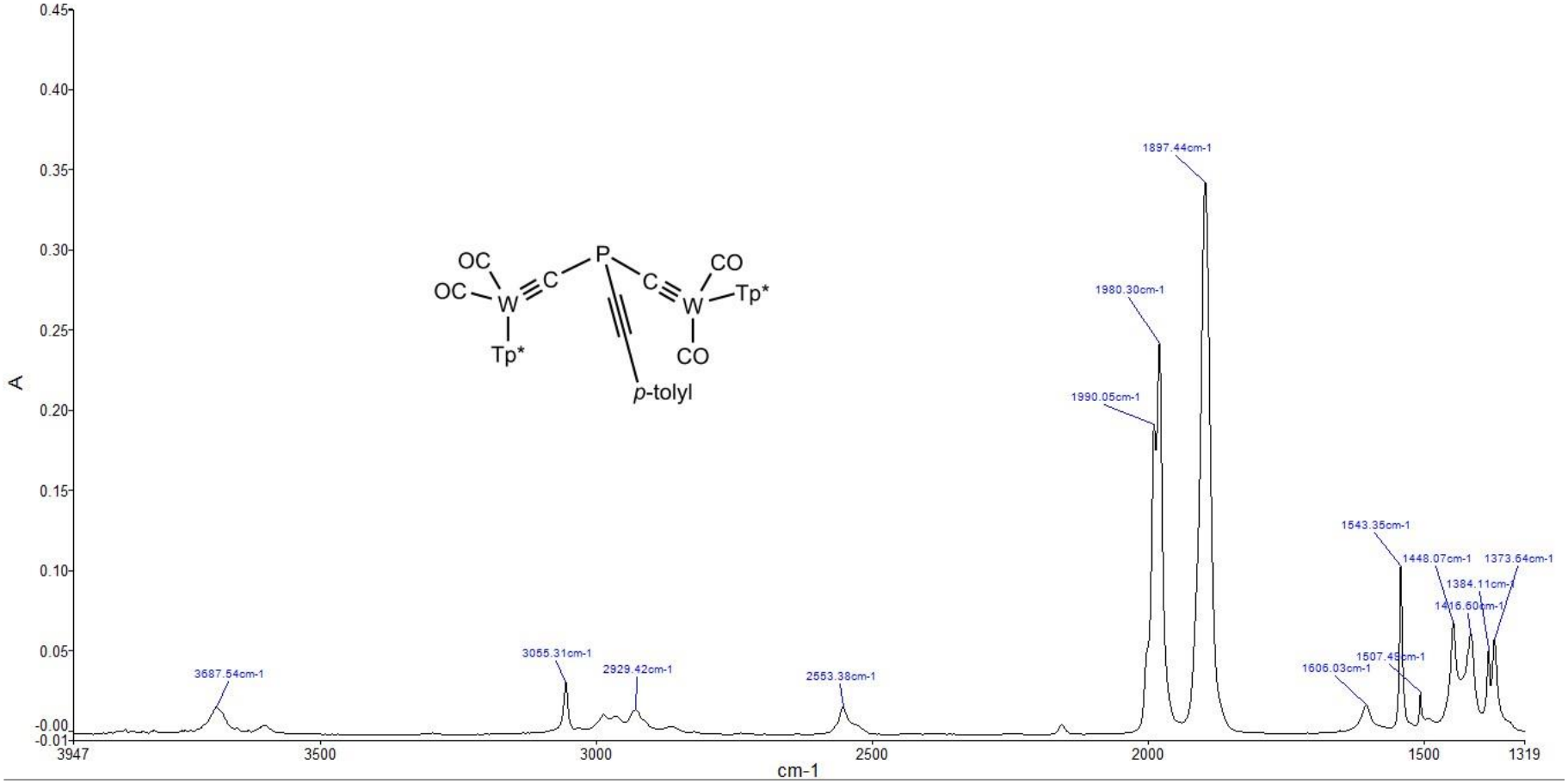
$^{13}C\{^{1}H\}$ NMR spectrum of **6**.



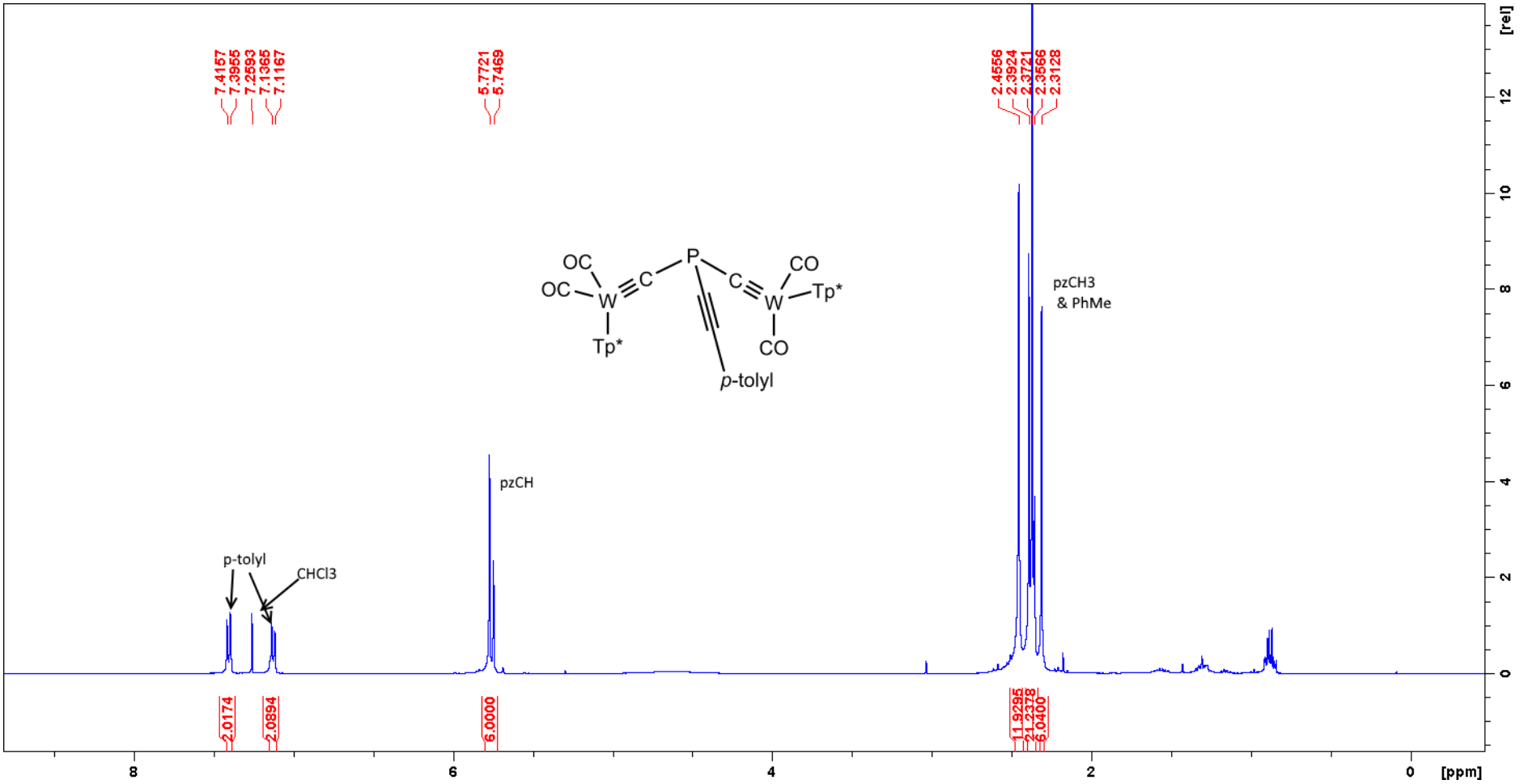
$^{31}P\{^{1}H\}$ NMR spectrum of **6**.



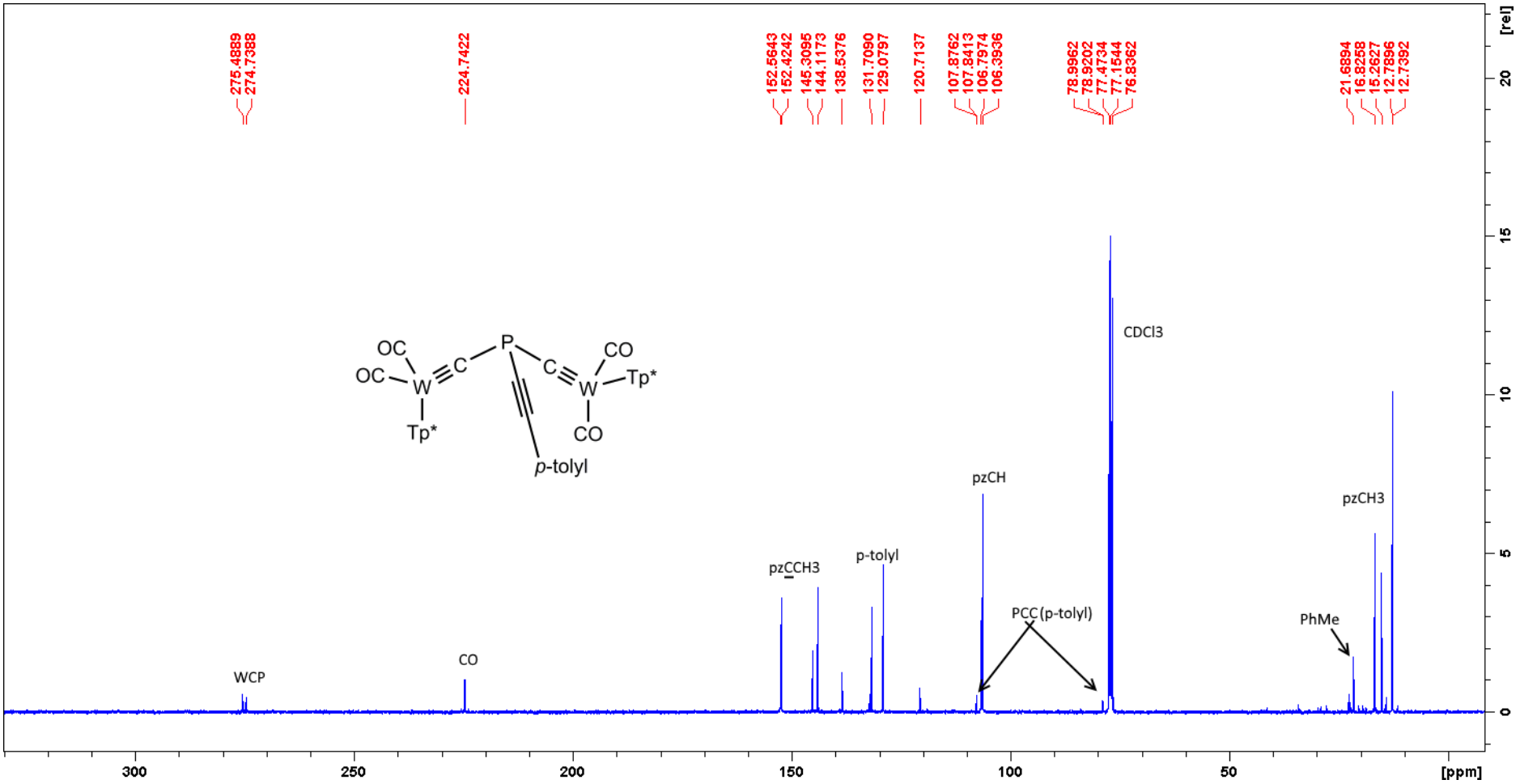
FTIR spectrum of **7**.



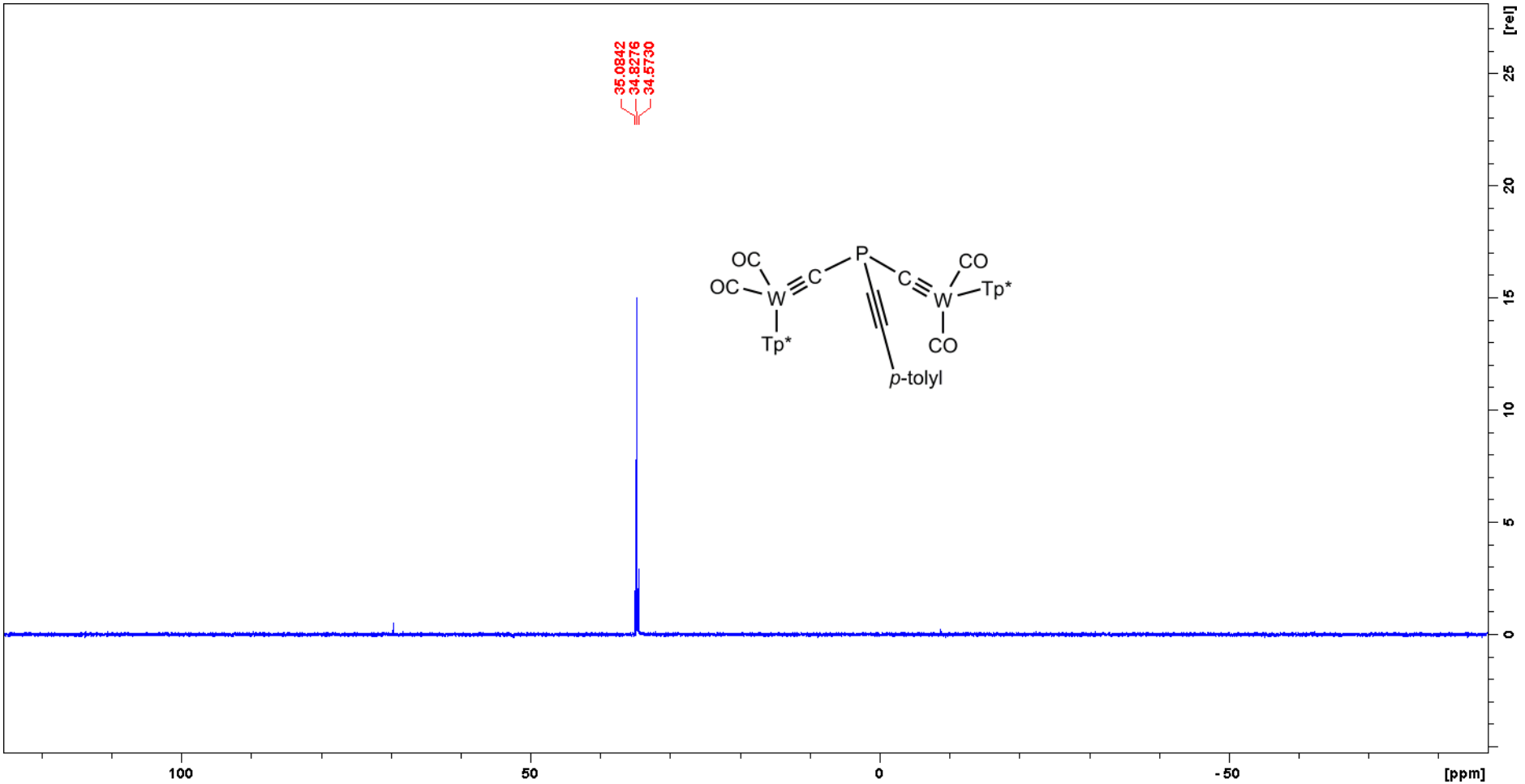
^{1}H NMR spectrum of **7**.



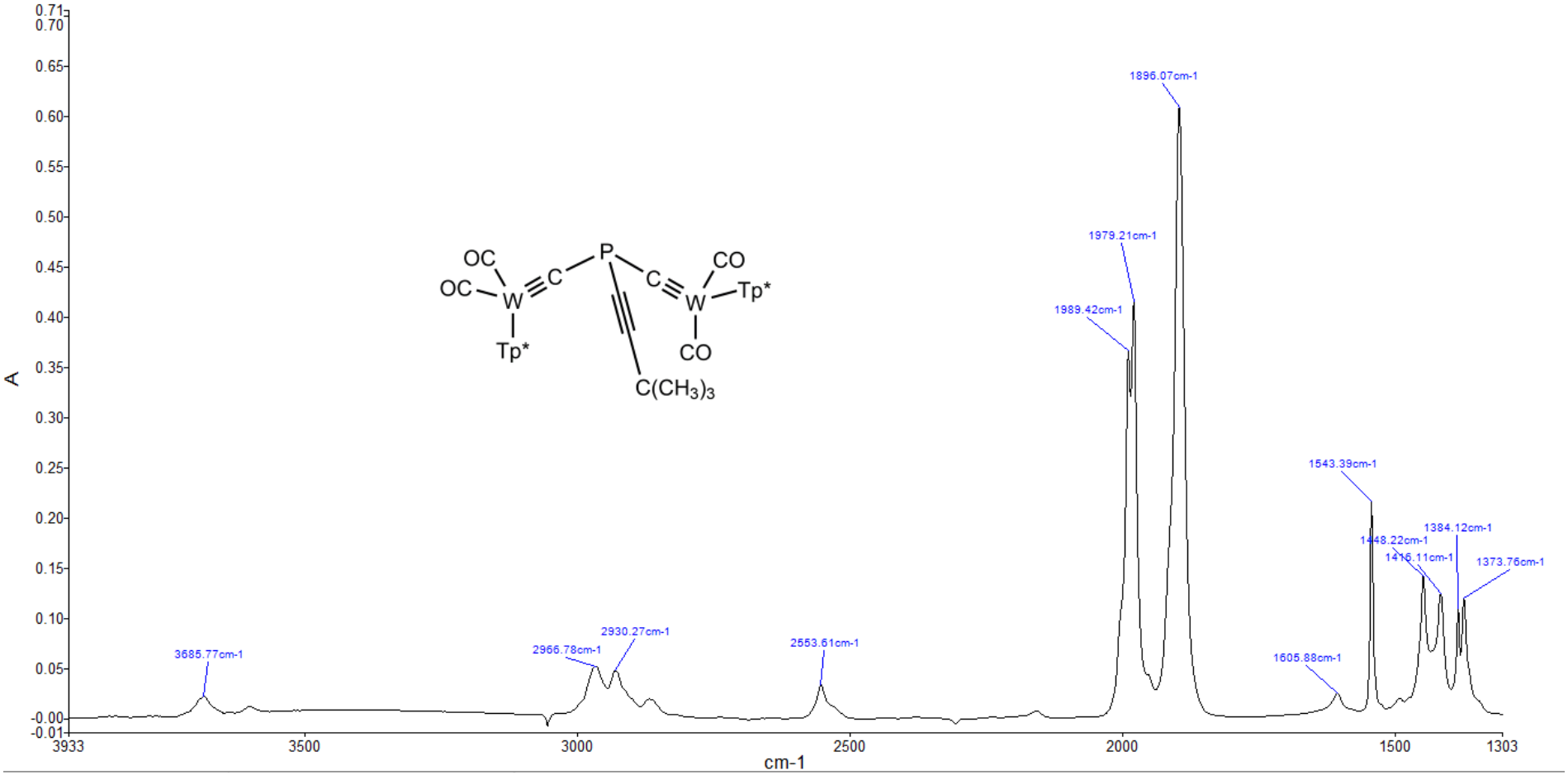
$^{13}C\{^{1}H\}$ NMR spectrum of **7**.



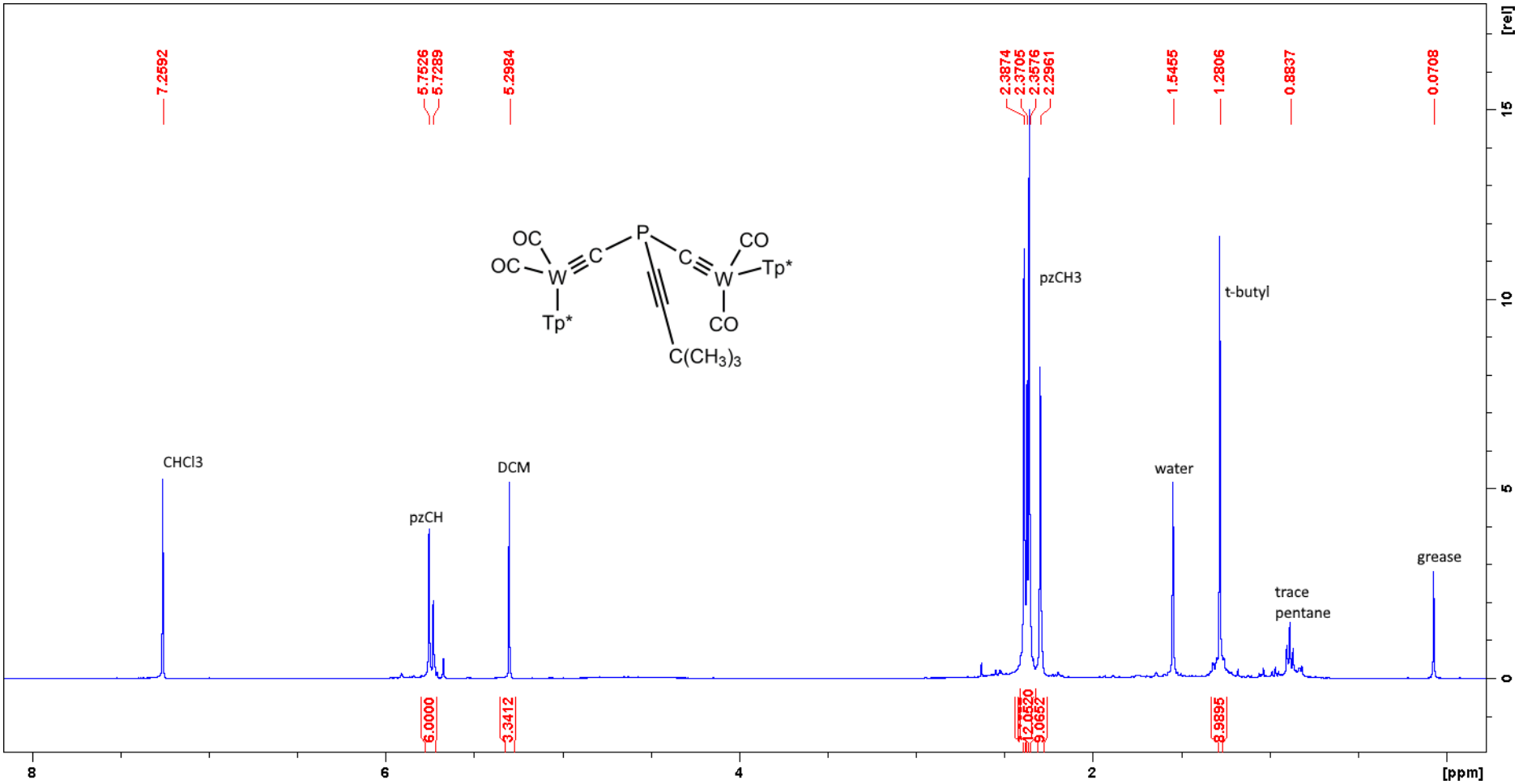
$^{31}P\{^{1}H\}$ NMR spectrum of **7**.



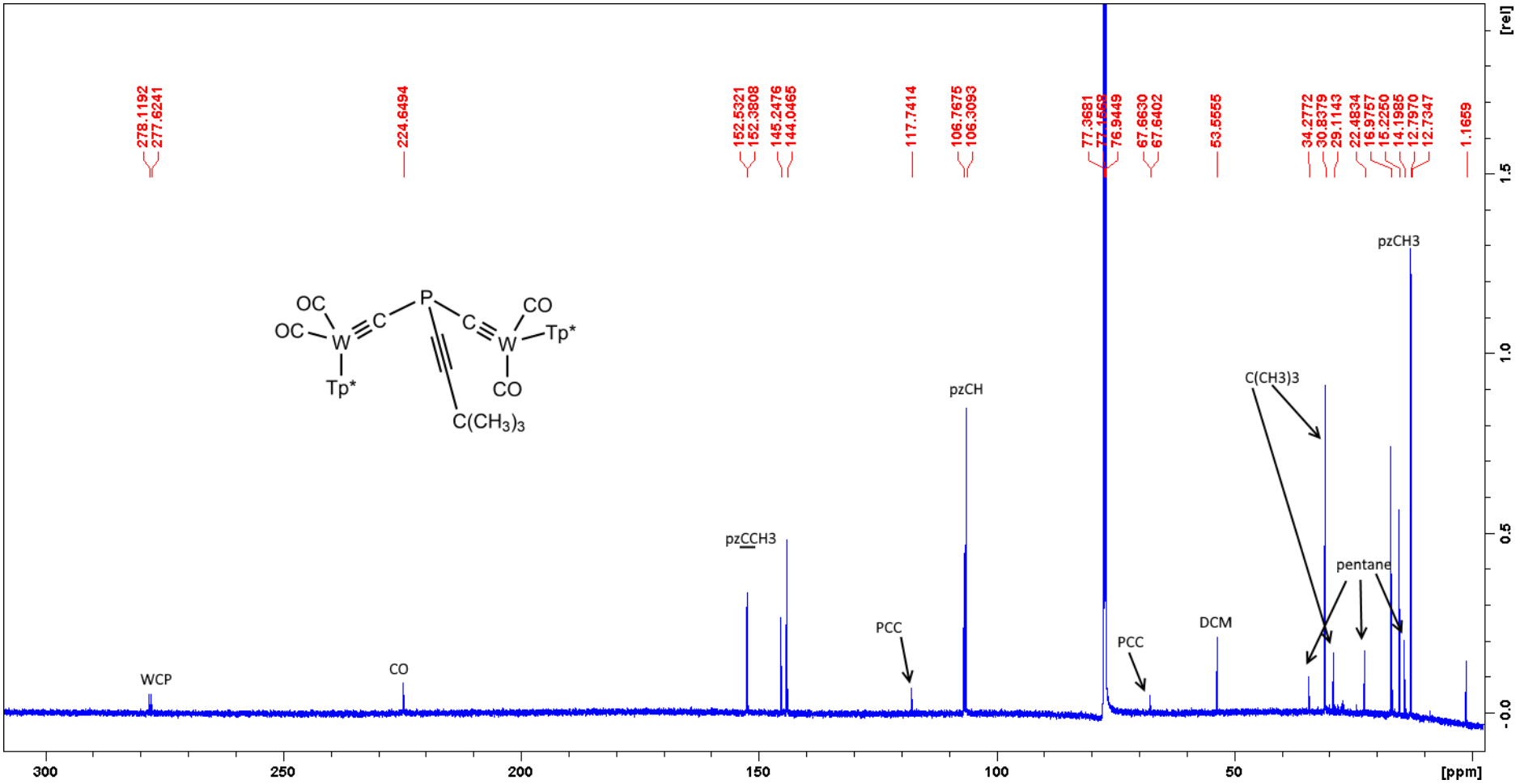
FTIR spectrum of **8**.



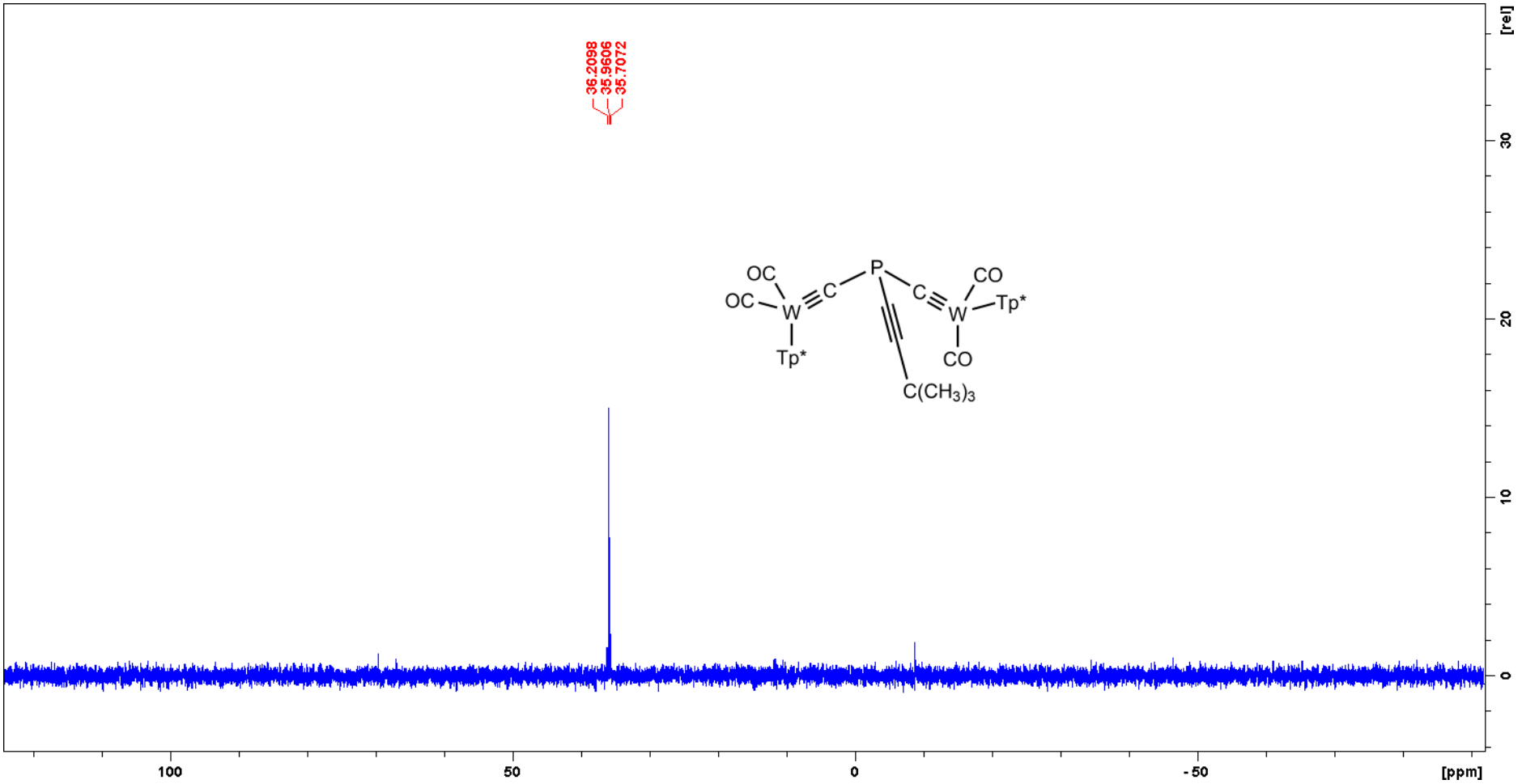
^{1}H NMR spectrum of **8**.



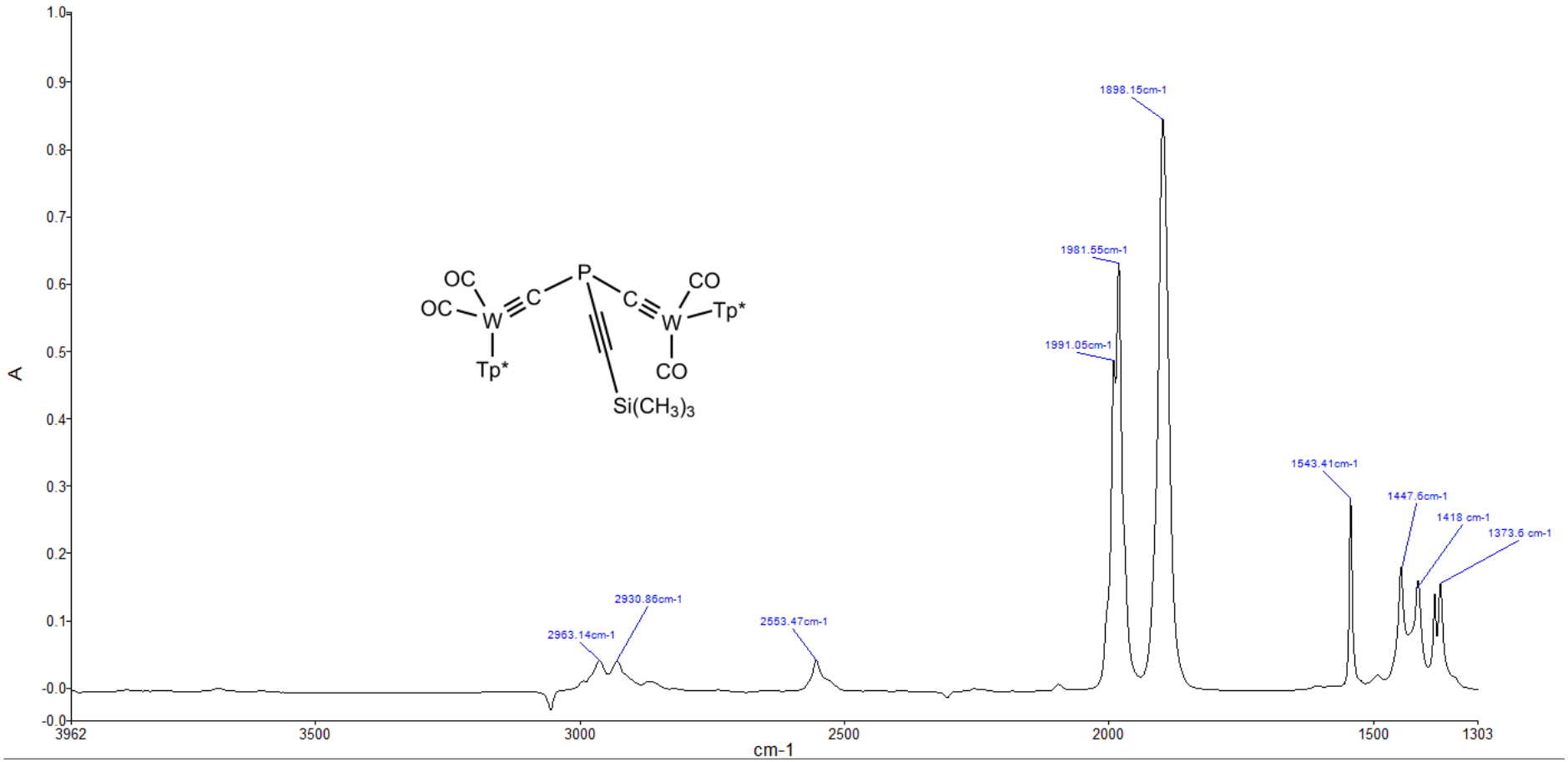
$^{13}C\{^{1}H\}$ NMR spectrum of **8**.



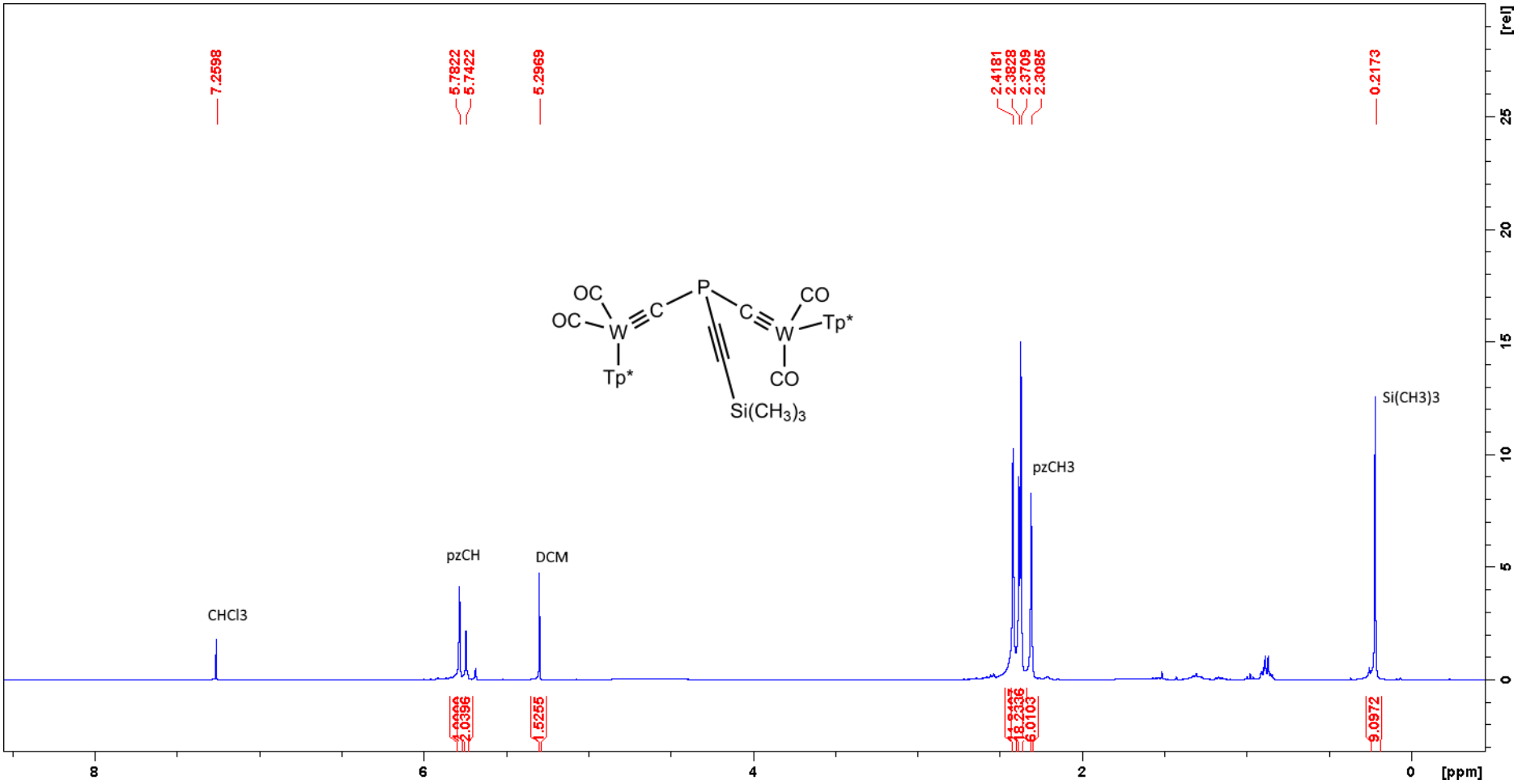
$^{31}P\{^{1}H\}$ NMR spectrum of **8**.



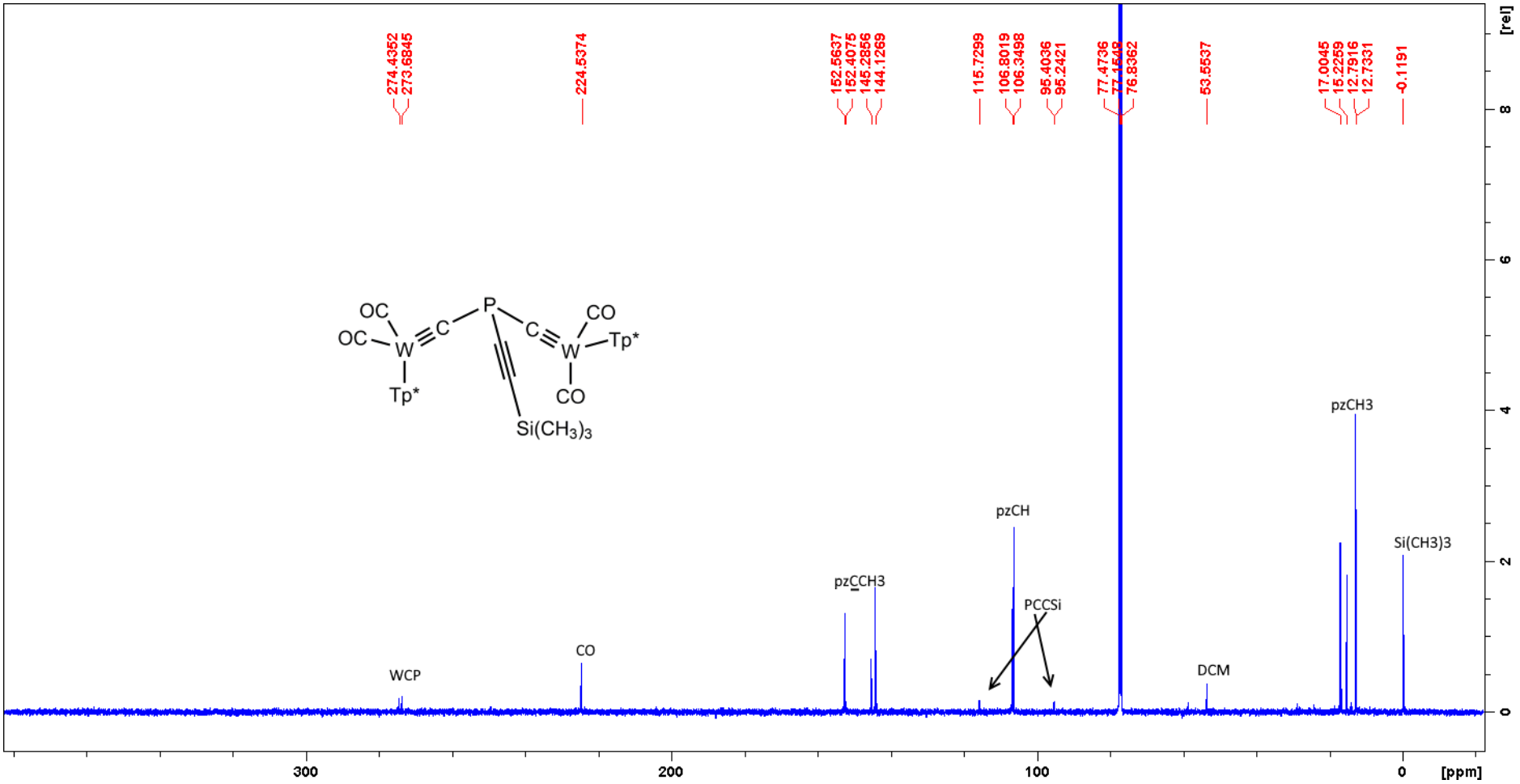
FTIR spectrum of **9**.



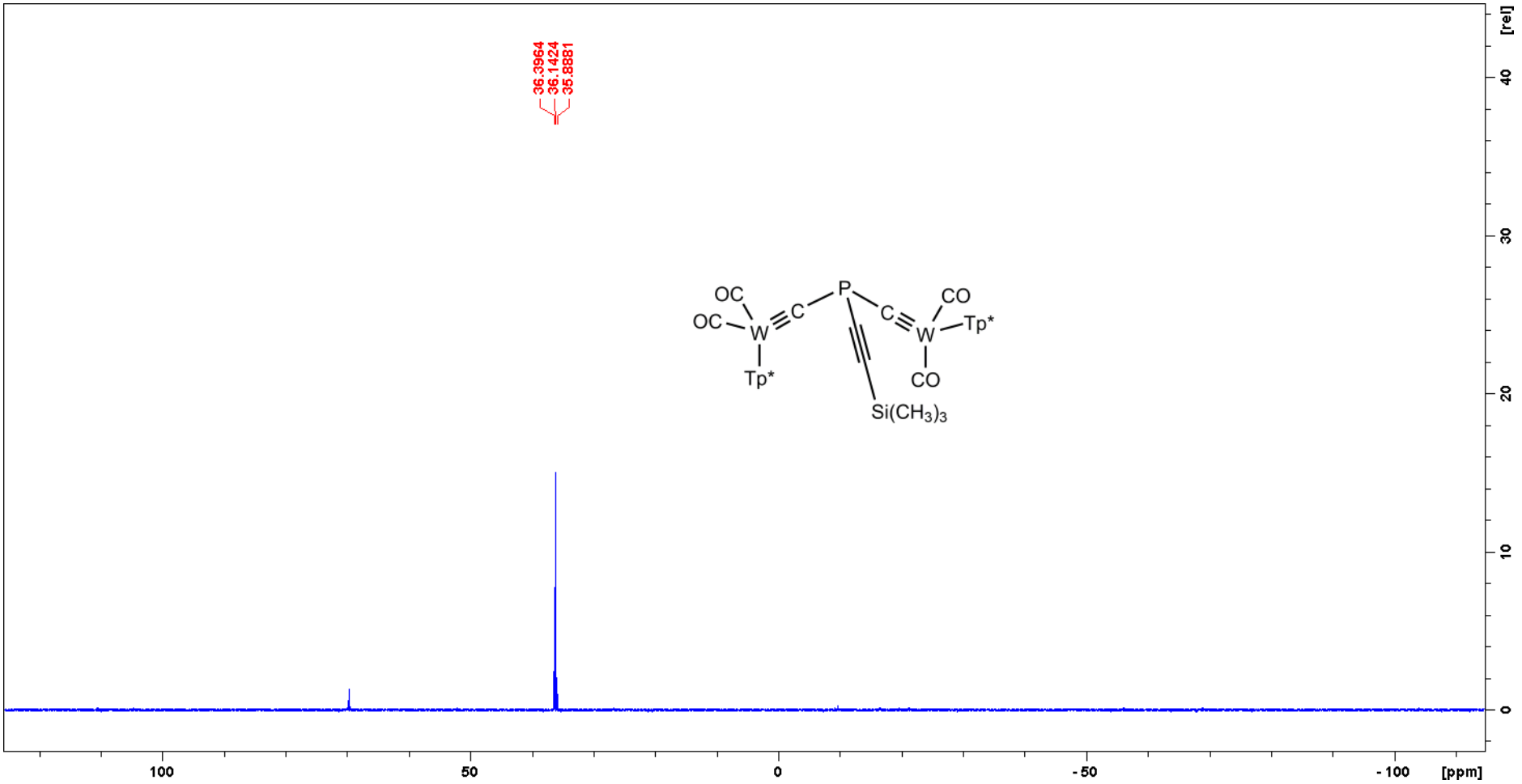
^{1}H NMR spectrum of **9**.



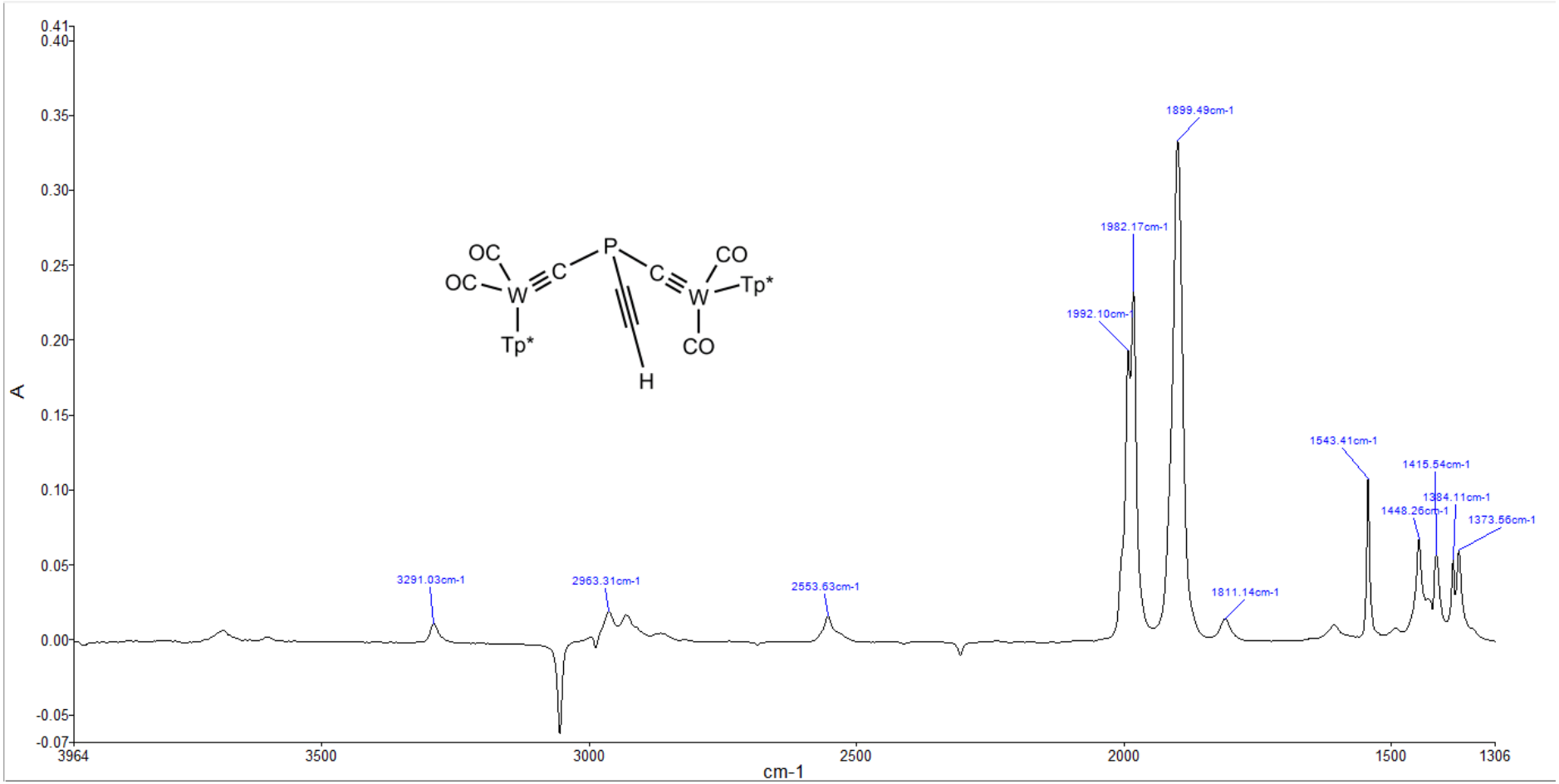
$^{13}C\{^{1}H\}$ NMR spectrum of **9**.



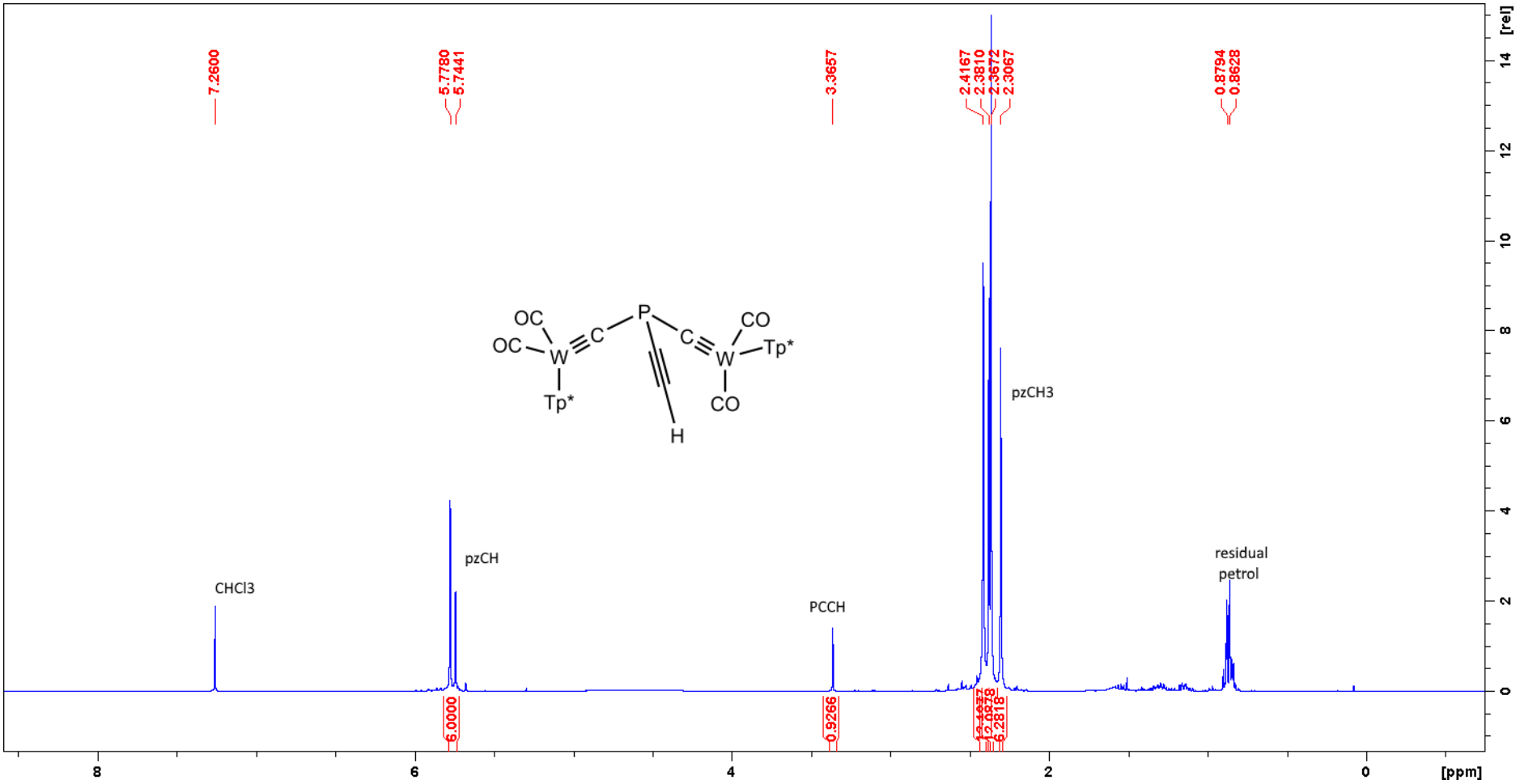
$^{31}P\{^{1}H\}$ NMR spectrum of **9**.



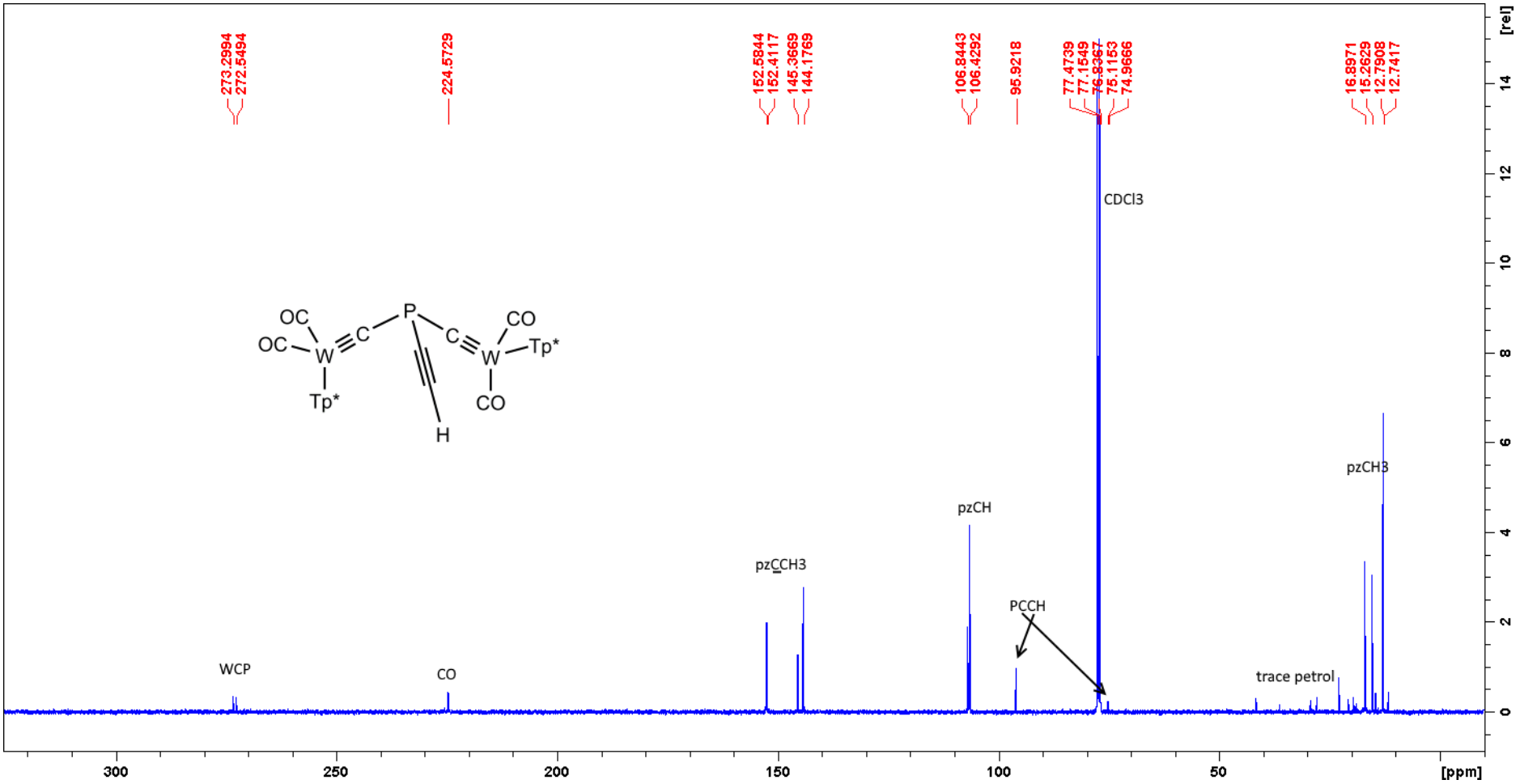
FTIR spectrum of **10**.



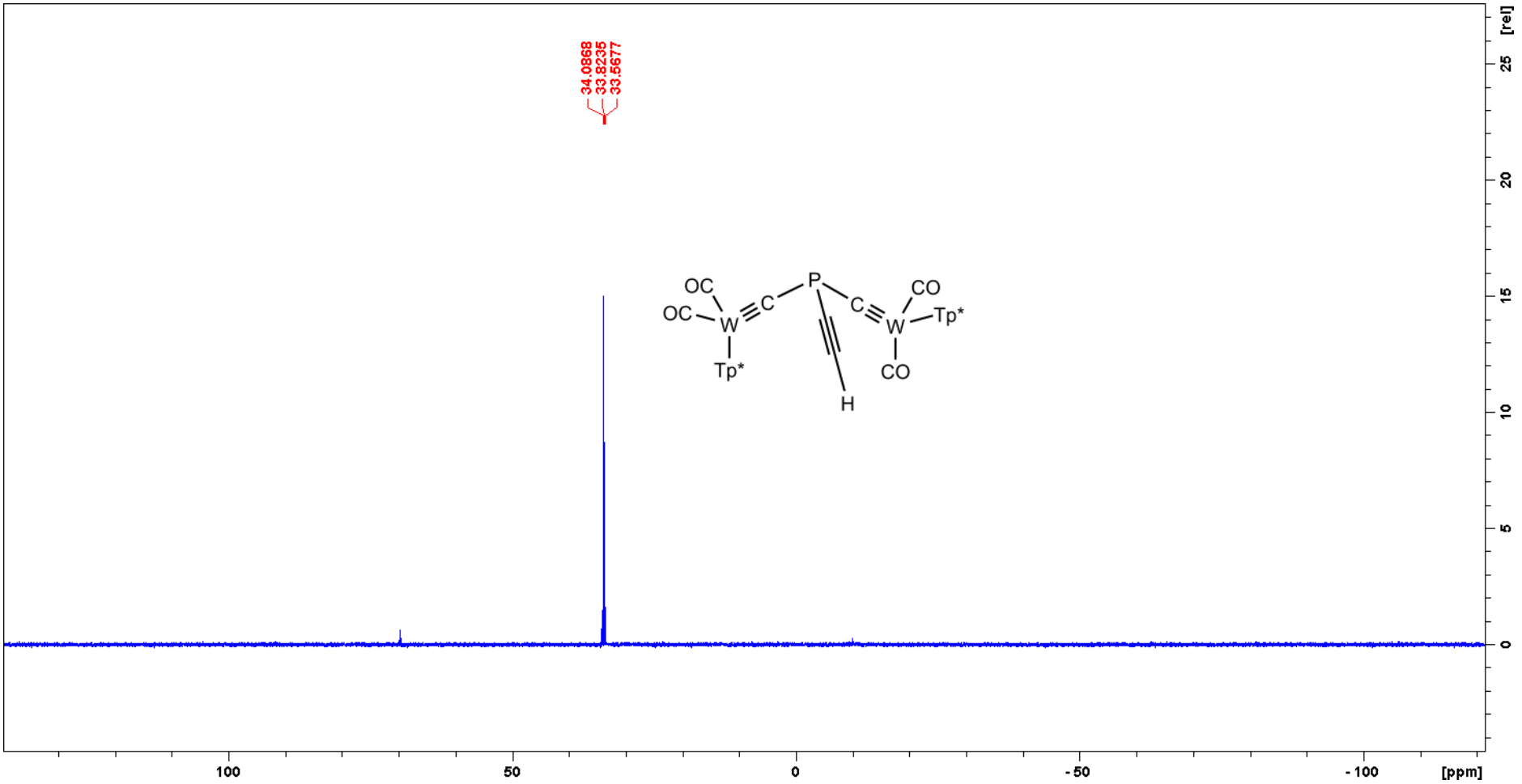
^{1}H NMR spectrum of **10**.



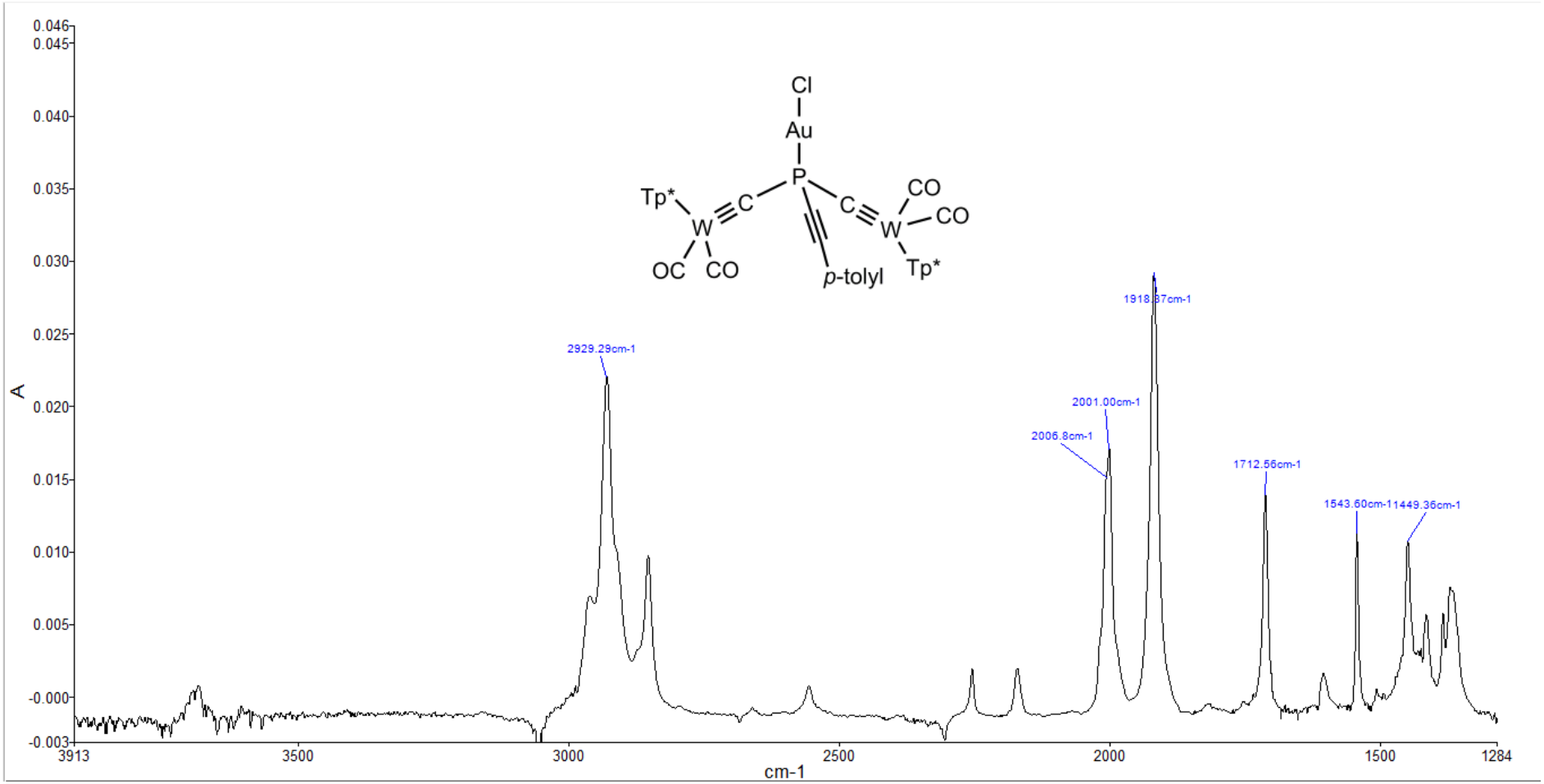
$^{13}C\{^{1}H\}$ NMR spectrum of **10**.



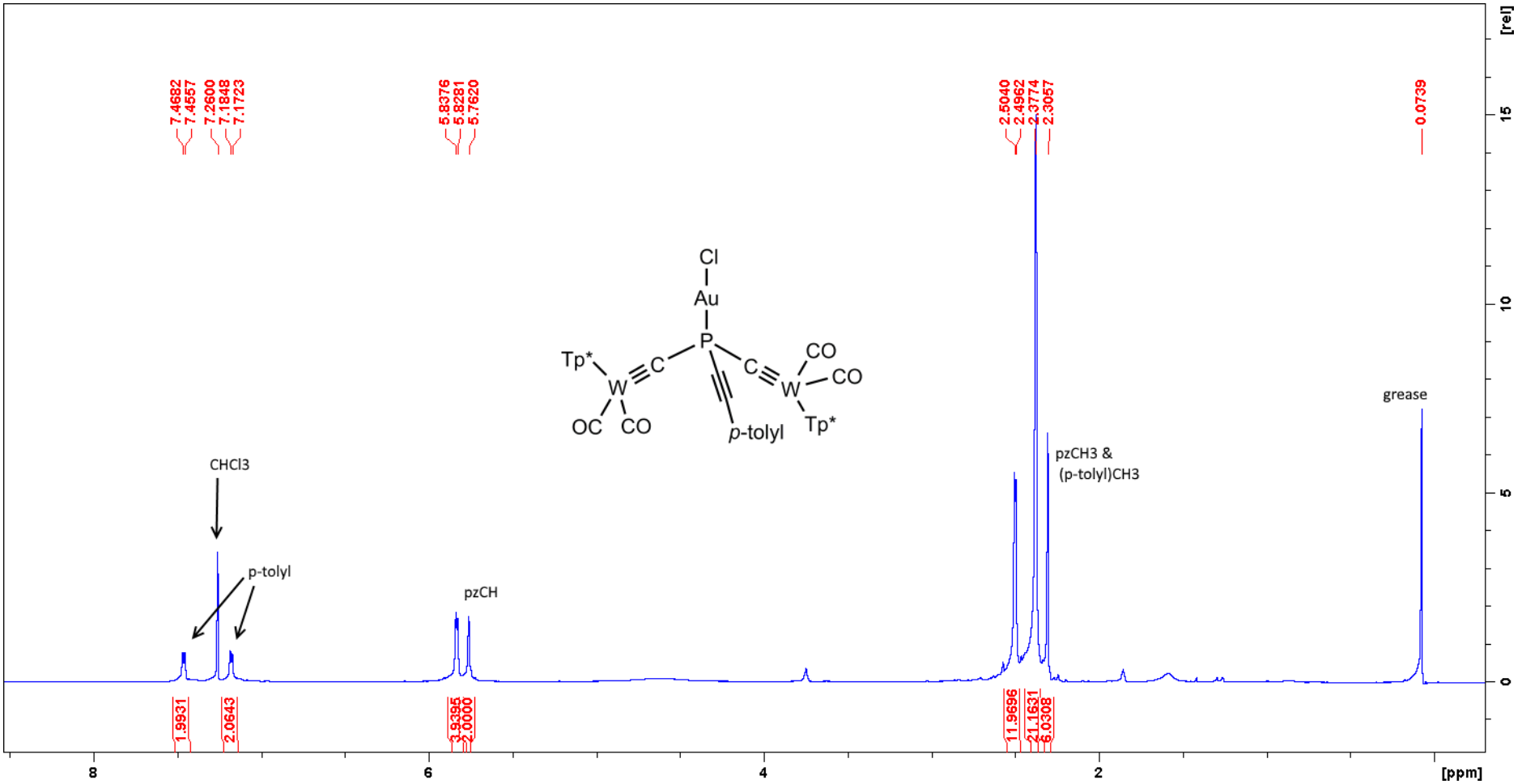
$^{31}P\{^{1}H\}$ NMR spectrum of **10**.



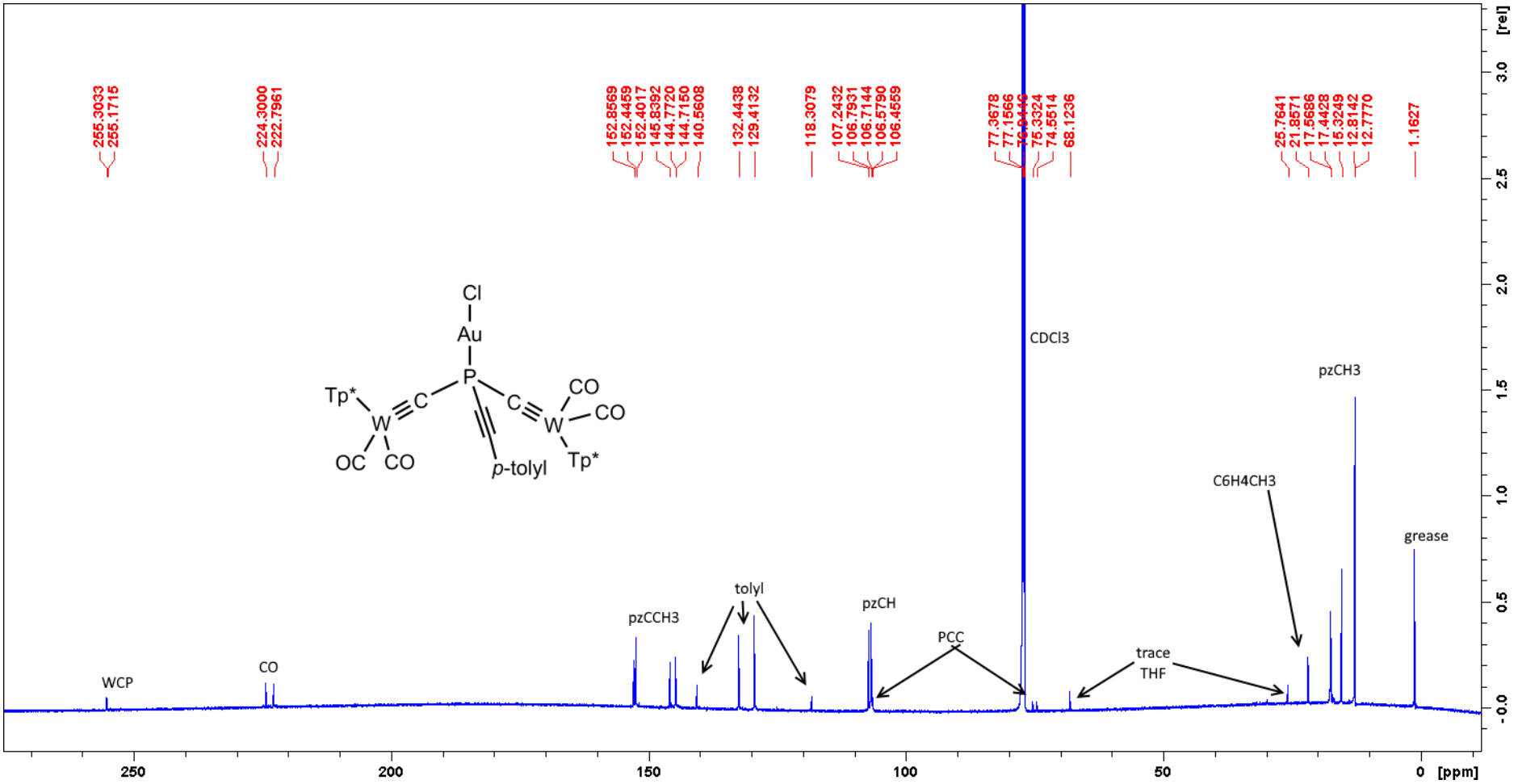
FTIR spectrum of **11**.



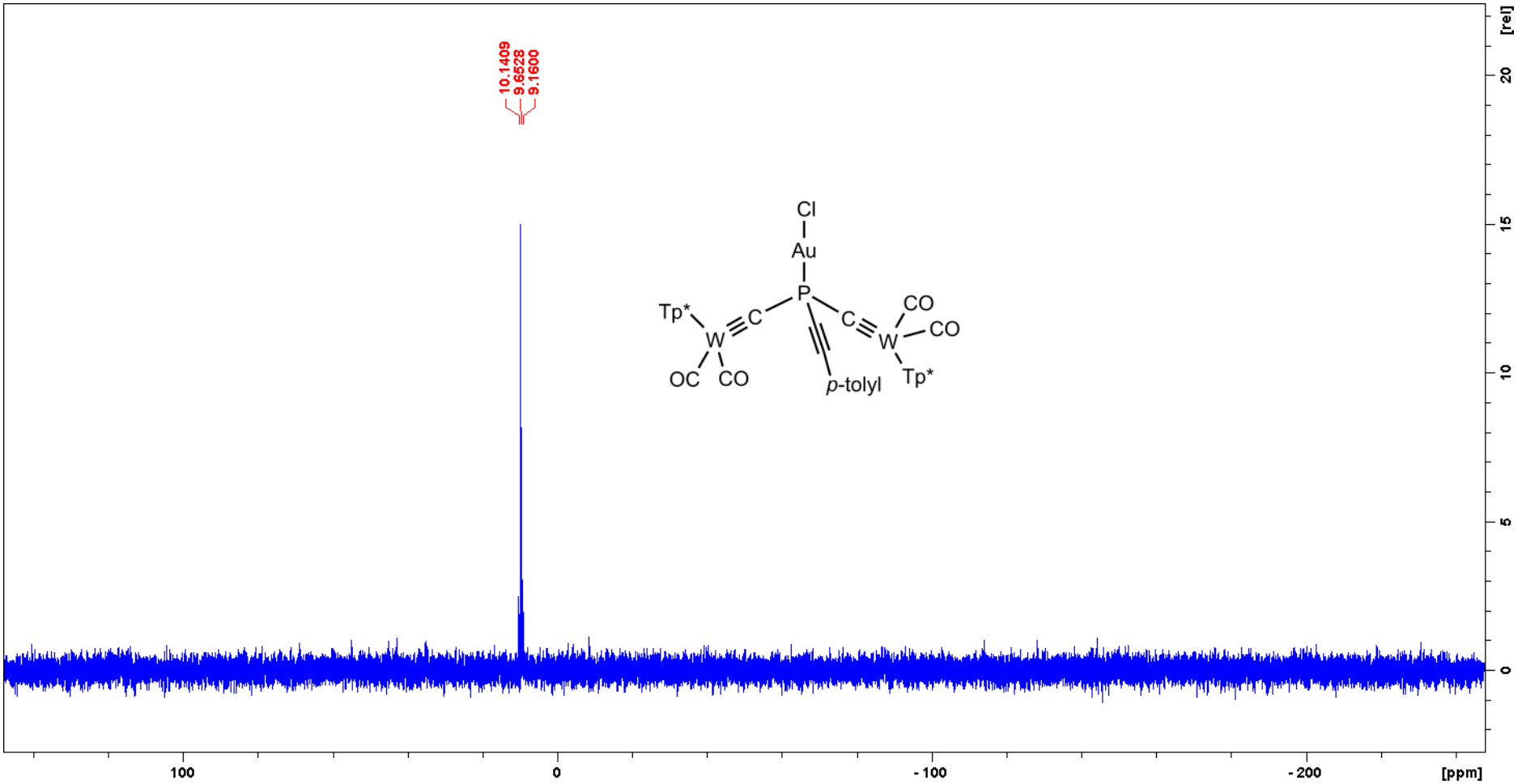
^{1}H NMR spectrum of **11**.



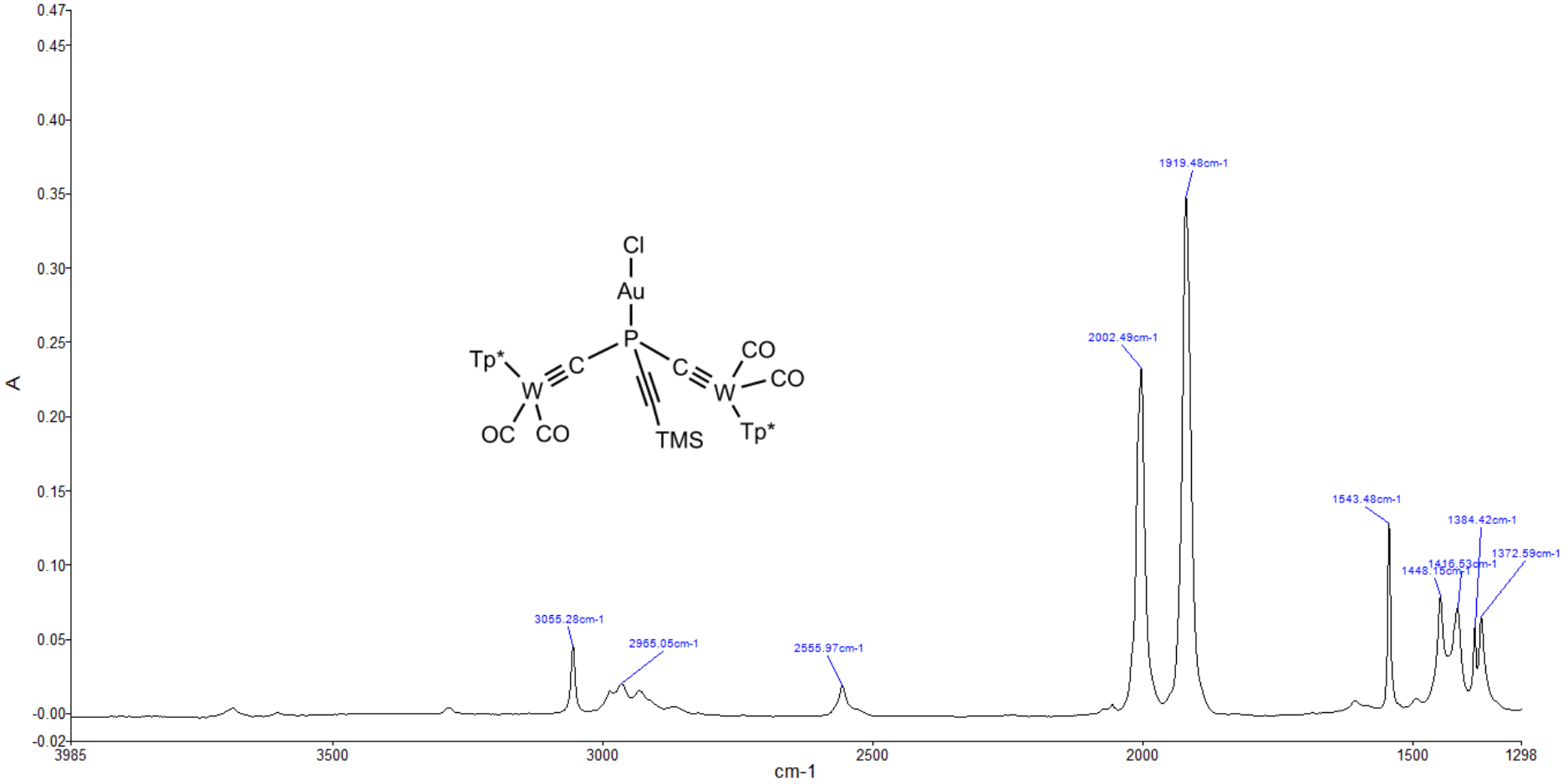
$^{13}C\{^{1}H\}$ NMR spectrum of **11**.



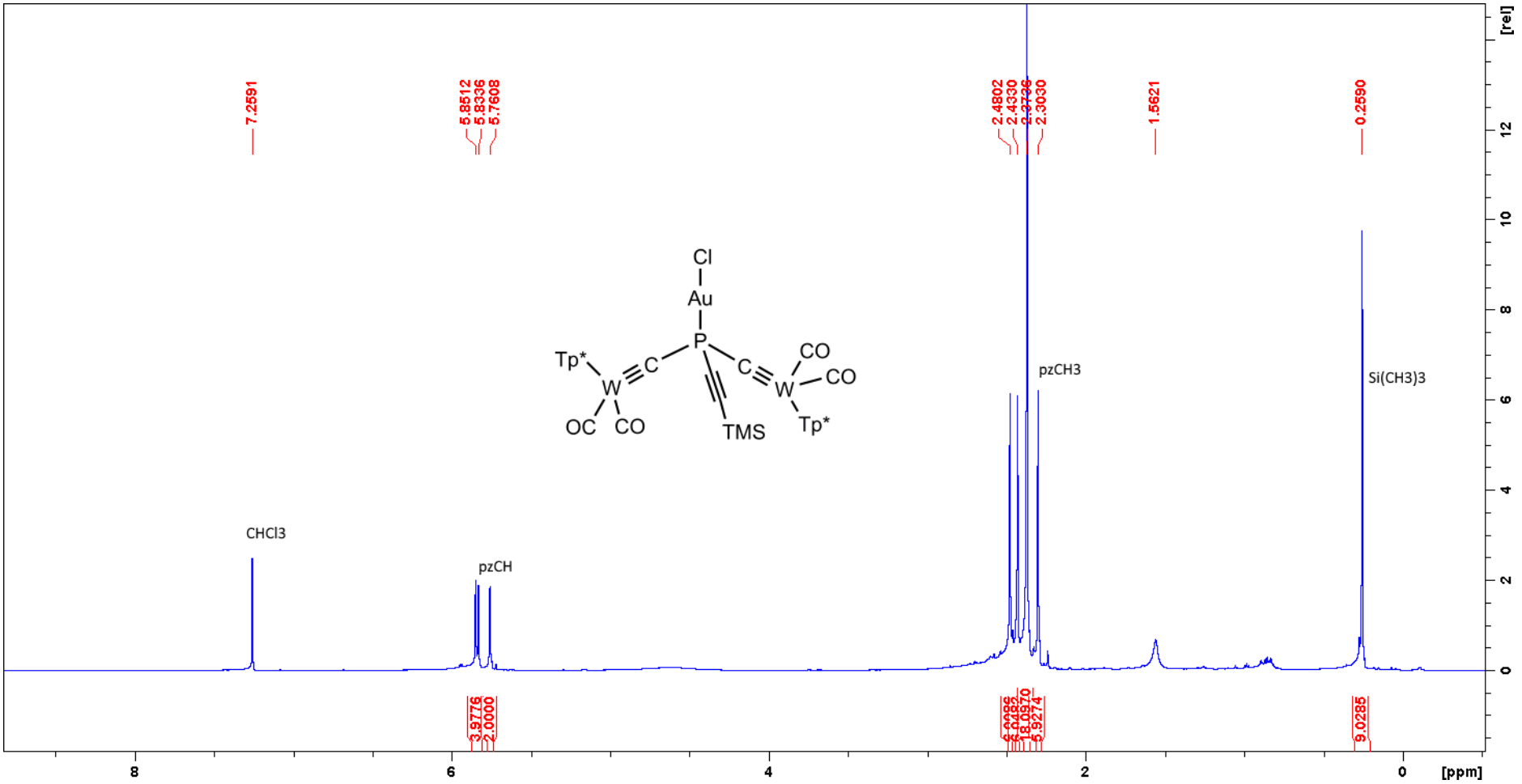
$^{31}P\{^{1}H\}$ NMR spectrum of **11**.



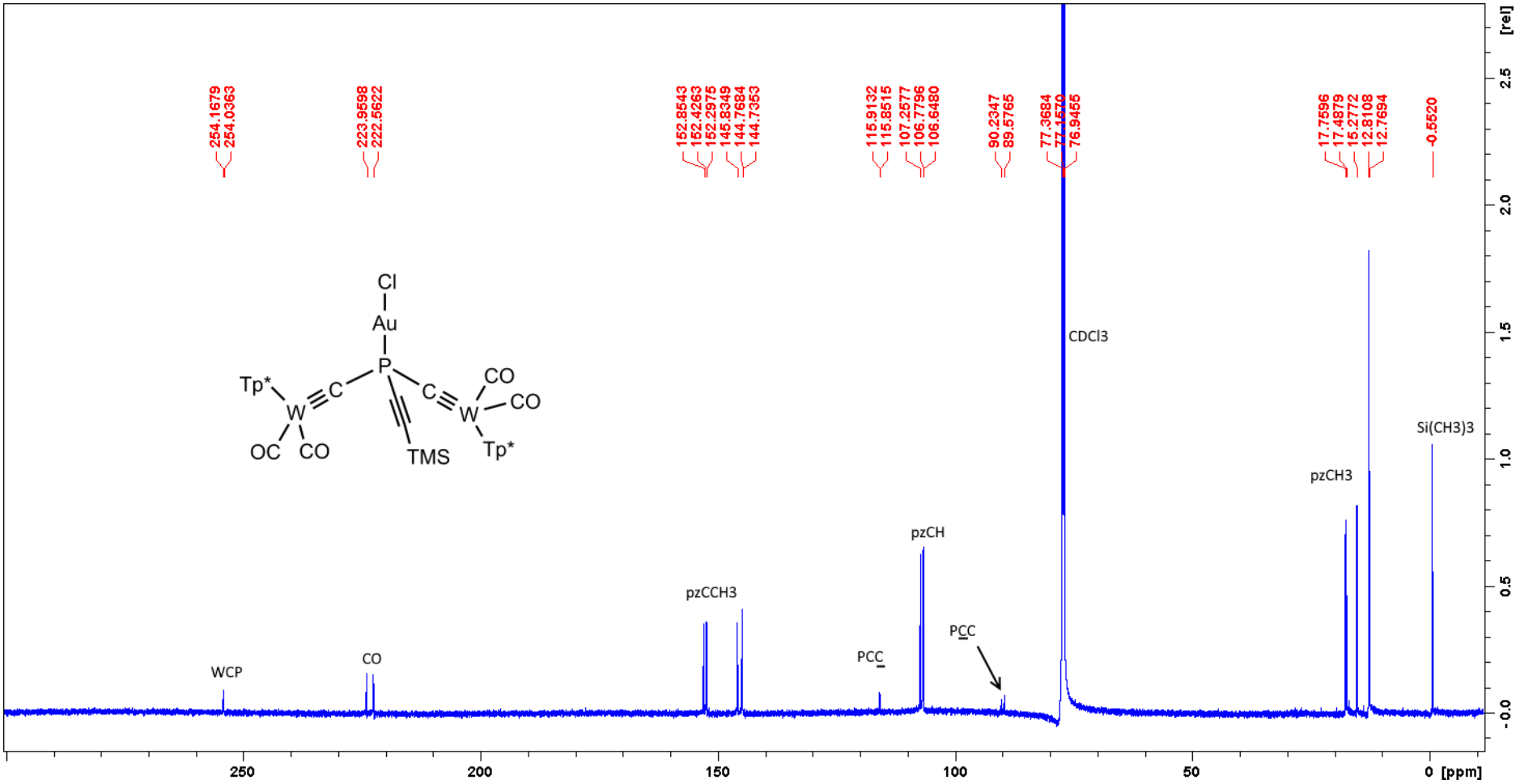
FTIR spectrum of **12**.



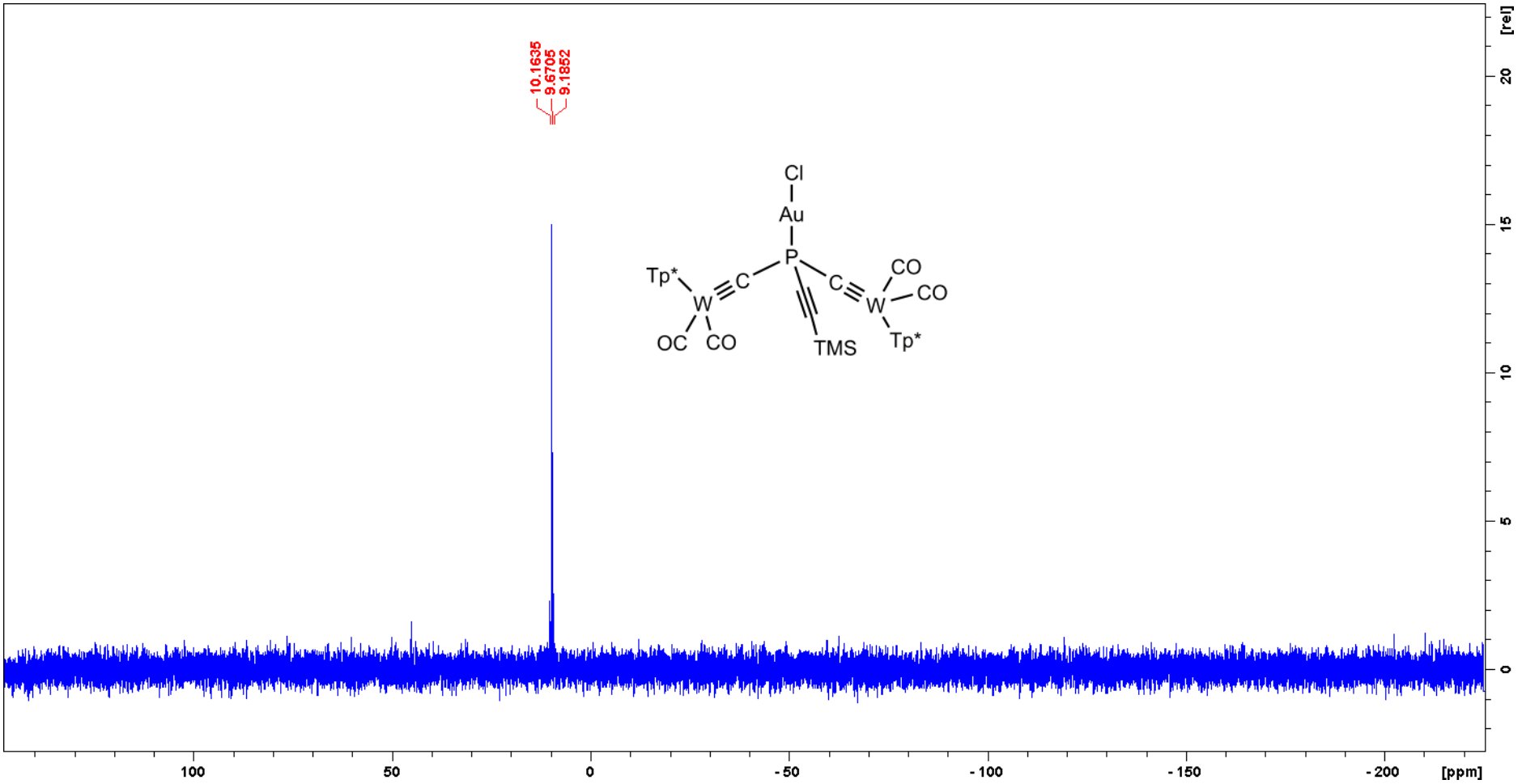
^{1}H NMR spectrum of **12**.



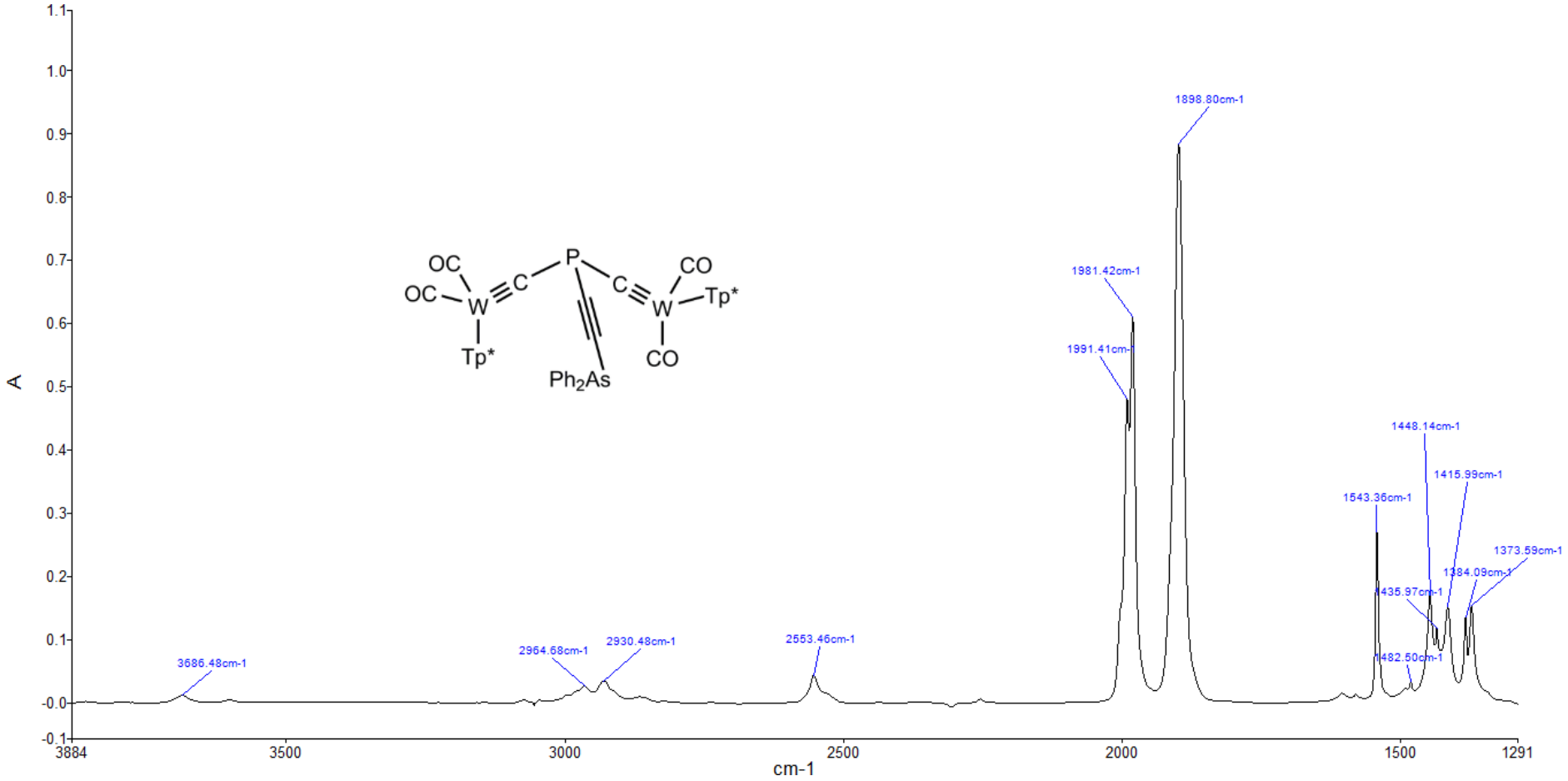
$^{13}C\{^{1}H\}$ NMR spectrum of **12**.



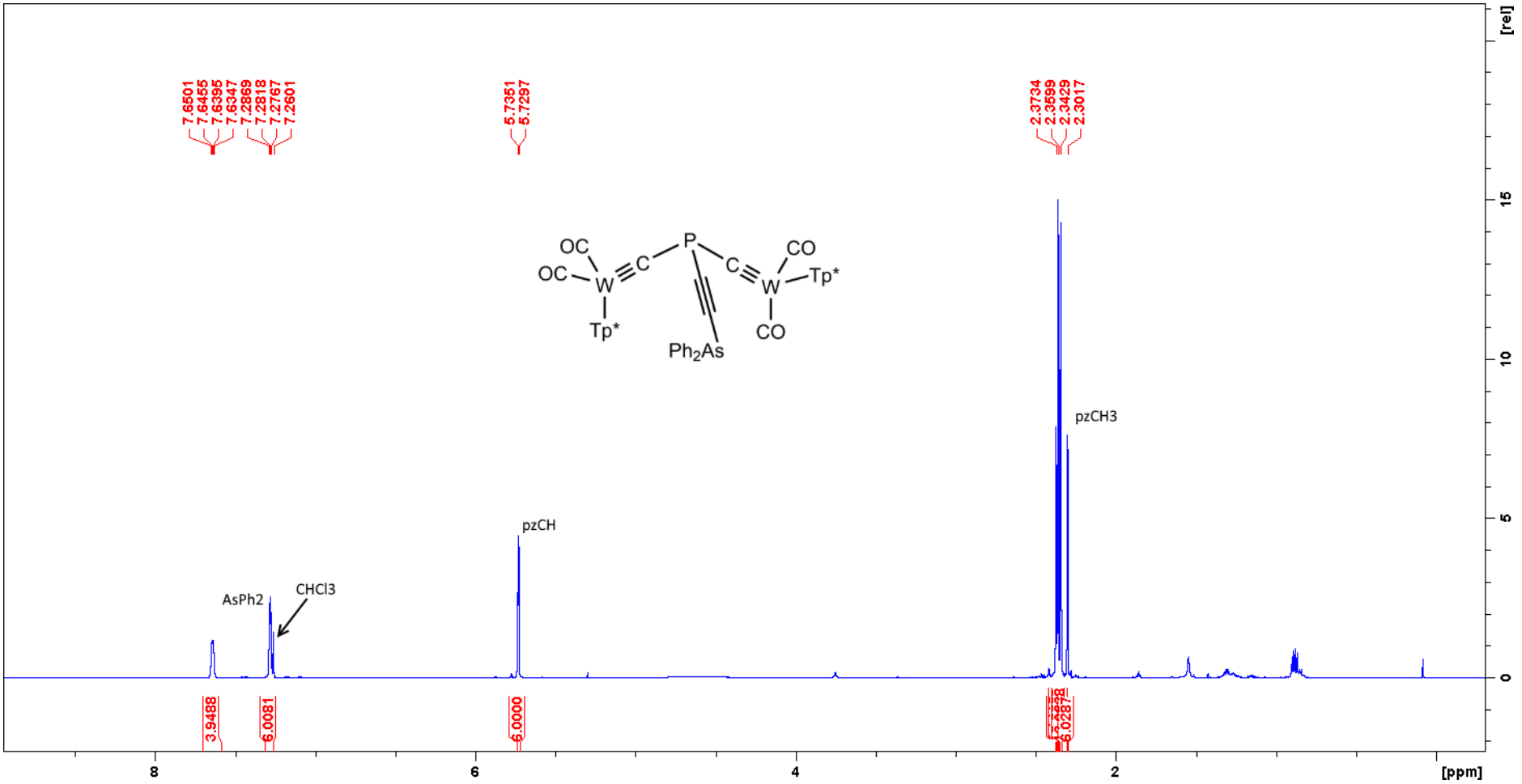
$^{31}P\{^{1}H\}$ NMR spectrum of **12**.



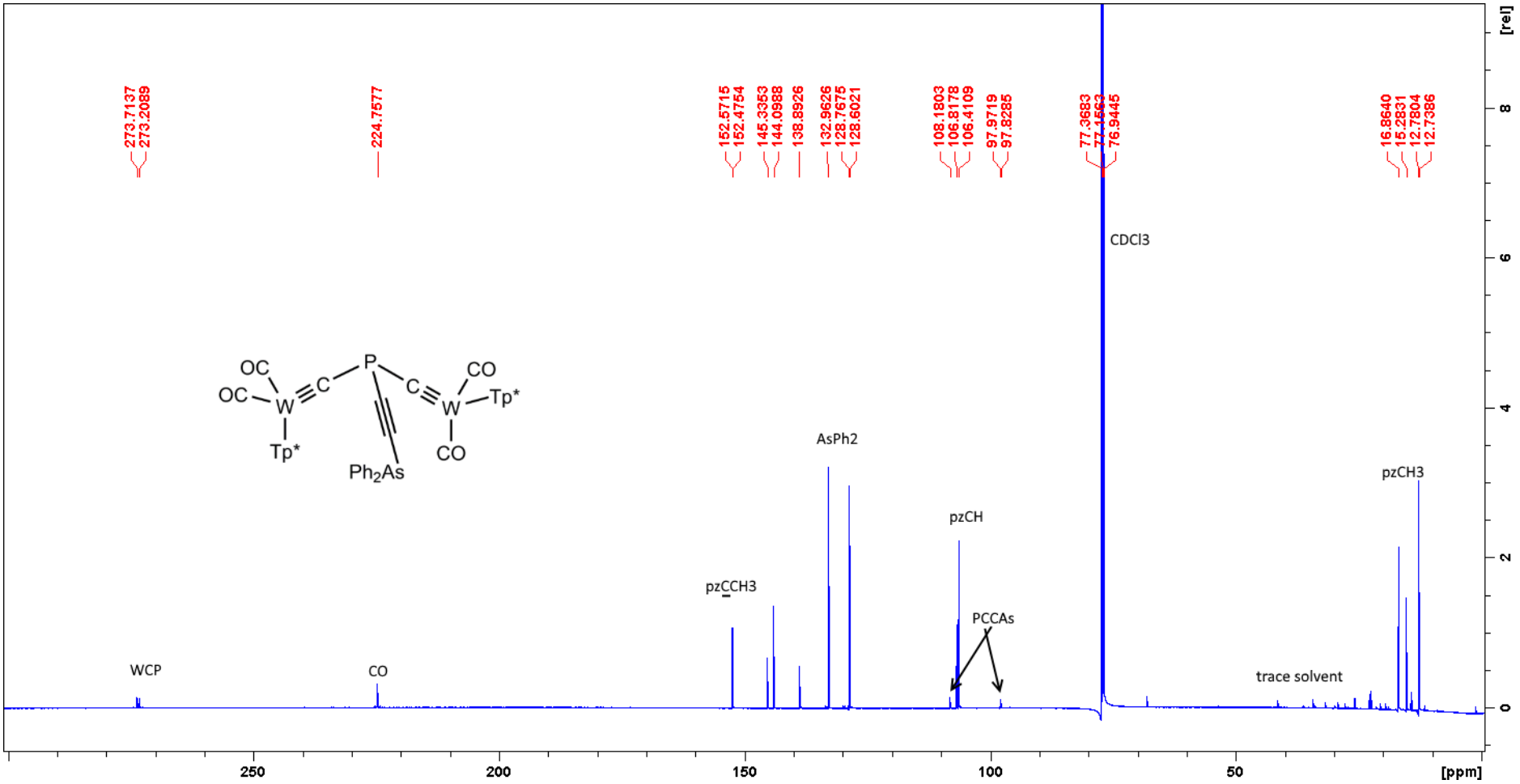
FTIR spectrum of **13**.



^{1}H NMR spectrum of **13**.



$^{13}C\{^{1}H\}$ NMR spectrum of **13**.



$^{31}P\{^{1}H\}$ NMR spectrum of **13**.