Electronic Supplementary Information for: Bis(alkylidynyl)phosphines and arsines

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Experimental

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

NMR spectra were obtained at 25 °C on a Bruker Avance 400 (^{1}H at 400.1 MHz, ^{13}C{^{1}H} at 100.6 MHz, ^{19}F{^{1}H} at 376.5 MHz), a Bruker Avance 600 (^{1}H at 600.0 MHz, ^{13}C{^{1}H} 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 solvent peak with coupling constants given in Hz, or external references ($CFCl_3$ for ^{19}F{^{1}H}, 85% H_3PO_4 for ^{31}P{^{1}H}). 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 hydridotris(3,5-dimethylpyrazol-1-yl)borate (Tp*) ligand. Spectra provided generally correspond to samples obtained directly from chromatography and may contain residual solvent as recrystallised samples often display reduced solubility.

Infrared spectra were obtained using a 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 SHELXS and SHELXL programs.[2] Hydrogen atoms were located geometrically and refined using a riding model. Diagrams were produced using the CCDC visualisation program Mercury.[3]

The bromocarbyne complexes [Mo(≡CBr)(CO)$_2$(Tp*)] (**1a**) and [W(≡CBr)(CO)$_2$(Tp*)] (**1b**), have been described previously.[4] The syntheses of PhP{C≡W(CO)$_2$(Tp*)}$_2$ (**2b**) and CyP{C≡W(CO)$_2$(Tp*)}$_2$ (**3b**) have also been previously reported.[5] CAUTION: the arsenic reagents ($AsCl_2Ph$, $AsCl_2Me$, $AsCl_3$) utilized herein are extremely toxic and can prove lethal if mishandled.

Synthesis of PhP{C≡Mo(CO)$_2$(Tp*)}$_2$ (2a). A solution of **1a** (200 mg, 0.370 mmol) in THF (10 mL) at –78 °C was treated with *n*-BuLi (230 μL, 1.6 M in hexanes, 0.37 mmol). The resulting orange solution was stirred for 30 min then treated with PCl_2Ph (25.0 μL, 0.184 mmol), causing the solution to immediately turn dark red. The mixture was slowly warmed to RT over the course of 1 h, after which time the volatiles were removed in vacuo. The residue was subjected to column chromatography (20 x 3 cm silica gel column), eluting initially with *n*-hexane followed by 20% v/v CH_2Cl_2/*n*-hexane. A red band was collected and the solvents were removed under reduced pressure. The resulting red powder was dried *in vacuo* to give a red solid of pure **2a** (136 mg, 0.132 mmol, 71%). This compound was previously reported but was not obtained analytically pure and only partial spectroscopic data were provided.[5] IR (CH_2Cl_2, cm^{-1}): 2001s, 1993s, 1916s ν(CO). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, δ): 2.30 (s, 12 H, pzC*H*$_3$), 2.32 (s, 6 H, pzC*H*$_3$), 2.33 (s, 6 H, pzC*H*$_3$), 2.38 (s, 12 H, pzC*H*$_3$), 5.71 (s, 2 H, pz*H*), 5.73 (s, 4 H, pz*H*), 7.34–7.45 (m, 3 H, P*Ph*), 7.83 (t, $^3J_{HH}$ = 8.1 Hz, 2 H, P*Ph*). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C, δ): 12.5, 12.7 (2 C, coincident) 14.3, 15.8 (2 C, coincident) (pz*C*H$_3$), 105.9, 106.2 (pz*C*H), 128.4 (d, $^3J_{CP}$ = 8.2, *m-Ph*)), 129.9 (*p-Ph*), 133.2 (d, $^1J_{CP}$ = 8.7, P(*i*-Ph)), 133.3 (d, $^2J_{CP}$ = 20.2, *o-Ph*)), 144.0, 144.9, 151.1, 151.3 (pz*C*CH$_3$), 227.2 (*C*O), 296.2 (d, $^1J_{CP}$ = 92 Hz, Mo≡*C*). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C, δ): 79.0 (s). MS (ESI, *m/z*): 1032.2064. Calcd for $C_{42}H_{50}{}^{11}B_2N_{12}O_4P^{98}Mo_2$ [M + H]$^+$: 1032.2113. Anal. Found: C, 48.88; H, 4.79; N, 16.25. Calcd for $C_{42}H_{49}B_2Mo_2N_{12}O_4P$: C, 48.96; H, 4.79; N, 16.31%.

Synthesis of CyP{C≡Mo(CO)$_2$(Tp*)}$_2$ (3a). A solution of **1a** (250 mg, 0.462 mmol) in THF (10 mL) at –78 °C was treated with *n*-BuLi (0.289 mL, 1.6 M in hexanes, 0.46 mmol). The resulting dark orange solution was stirred for 30 min then treated with PCl_2Cy (35.5 μL, 0.231 mmol), causing the solution to immediately turn 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 subjected to column chromatography (20 x 3 cm silica gel column), eluting initially with *n*-hexane and gradually increasing to 20% v/v CH_2Cl_2/*n*-hexane. A red band was collected and the solvents were removed under reduced pressure to give pure **3a** (129 mg, 0.124

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mmol, 54%) as red microcrystals. IR (CH_2Cl_2, cm^{-1}): 1998s, 1988s, 1911s ν(CO). ^1H NMR (400 MHz, $CDCl_3$, 25 °C, δ): 1.30–1.95 (m, 8 H, *Cy*), 2.20 – 2.29 (m, 2 H, *Cy*), 2.31 (s, 6 H, pzCH_3), 2.32 (s, 18 H, pzCH_3), 2.37 (s, 12 H, pzCH_3), 2.53 – 2.65 (m, 1 H, *Cy*), 5.64 (s, 4 H, pz*H*), 5.69 (s, 2 H, pz*H*). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C, δ): 12.7, 12.9, 14.6, 15.9 (pz*C*H_3), 26.2 (C^4(*Cy*)), 27.0 (d, $^{2,3}J_{CP}$ = 11.7, $C^{2,3,5,6}$(*Cy*)), 30.7 (d, $^{2,3}J_{CP}$ = 14.0 Hz, $C^{2,3,5,6}$(*Cy*)), 41.0 (d, $^1J_{CP}$ = 11.6, C^1(*Cy*)), 106.1, 106.4 (pz*C*H), 143.9, 145.1, 151.3, 151.4 (pz*C*CH_3), 228.1 (*C*O), 303.1 (d, $^1J_{CP}$ = 93 Hz, Mo≡*C*P). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C, δ): 91.6. MS (ESI, *m/z*): 1059.2402. Calcd for $C_{42}H_{55}N_{12}O_4{}^{11}B_2{}^{98}Mo_2PNa$ $[M + Na]^+$: 1059.2430. Anal. Found: C, 48.82; H, 5.43; N, 16.11. Calcd for $C_{42}H_{55}B_2Mo_2N_{12}O_4P$: C, 48.67; H, 5.25; N, 16.22%. Crystals used for X-ray structure determination were grown by slow evaporation of a dichloromethane/ethanol solution and that selected was found to contain 0.75 equivalents of dichloromethane of solvation. Crystal data for $C_{42}H_{55}B_2Mo_2N_{12}O_4P{\cdot}0.75CH_2Cl_2$ (M_w =1100.14 $gmol^{-1}$): triclinic, space group *P*-1 (no. 2), *a* = 10.6555(4), *b* = 12.0934(4), *c* = 21.6561(7) Å, *α* = 84.805(3), *β* = 77.532(3), *γ* = 67.728(3)°, *V* = 2521.42(16) $Å^3$, *Z* = 2, *T* = 150.0(2) K, μ(Mo Kα) = 0.661 mm^{-1}, D_{calc} = 1.449 Mgm^{-3}, 24,775 reflections measured (6.80° ≤ 2Θ ≤ 59.73°), 11,909 unique (R_{int} = 0.0254, R_{sigma} = 0.0426) which were used in all calculations. The final R_1 was 0.0376 ($I > 2\sigma(I)$) and wR_2 was 0.0888 (all data) for 615 refined parameters with 0 restraints. CCDC 1835465.

Synthesis of $CH_3P\{C{\equiv}W(CO)_2(Tp^*)\}_2$ (4). 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 (17.5 μL, 0. 201 mmol). The solution was warmed to RT and the resulting red solution stirred for 60 min, after which time the volatiles were removed i*n vacuo*. The residue was dissolved in THF (5 mL) and treated with MeLi (0.125 mL, 1.6 M in diethyl ether, 0.20 mmol), 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 40% v/v CH_2Cl_2/petrol and was dried under reduced pressure to give a bright orange solid of spectroscopically pure **4** (107 mg, 0.0944 mmol, 47%). A second chromatography step using the same conditions was necessary to provide an analytically pure product. IR (CH_2Cl_2, cm^{-1}): 1983s, 1972s, 1889s ν(CO). ^1H NMR (400 MHz, $CDCl_3$, 25 °C, δ): 1.69 (d, $^3J_{HP}$ = 2.3 Hz, 3 H, PCH_3), 2.30 (s, 6 H, pzCH_3), 2.36 (s, 24 H, pzCH_3), 2.37 (s, 6 H, pzCH_3), 5.73 (s, 6 H, pz*H*). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C, δ): 11.0 (d, $^1J_{CP}$ = 15, PCH_3), 12.7, 12.8, 15.2, 16.7 (pz*C*H_3), 106.3, 106.7 (pz*C*H), 144.0, 145.2, 152.1, 152.5 (pz*C*CH_3), 224.0, 225.4 (s, *C*O), 290.0 (d, $^1J_{CP}$ = 77, $^1J_{CW}$ = 188 Hz, W≡*C*P). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C, δ): 56.3 ($^2J_{PW}$ = 73 Hz). MS (ESI, *m/z*): 1145.2874. Calcd for $C_{37}H_{48}{}^{11}B_2N_{12}O_4P^{184}W_2$ $[M + H]^+$: 1145.2869. Anal. Found: C, 39.02; H, 4.03; N, 14.58. Calcd for $C_{37}H_{47}B_2N_{12}O_4PW_2$: C, 38.84; H, 4.14; N, 14.69%.

Synthesis of ^{n}BuP{C≡W(CO)$_2$(Tp*)}$_2$ (5). 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 (17.5 μL, 0.20 mmol). The solution was warmed to RT and the resulting red solution stirred for 60 min, after which time the volatiles were removed *in vacuo*. The residue was dissolved in THF (5 mL) and treated with *n*-BuLi (0.125 mL, 1.6 M in hexanes, 0.200 mmol), 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 freed of volatiles under reduced pressure to give and orange solid of pure **5** (168 mg, 0.142 mmol, 71%). IR (CH_2Cl_2, cm^{-1}): 1982s, 1971s, 1888s ν(CO). ^1H NMR (400 MHz, $CDCl_3$, 25 °C, δ): 0.99 (t, $^3J_{HH}$ = 7.3, 3 H, $PCH_2CH_2CH_2CH_3$), 1.55 (tq appearing as a sextet, $^3J_{HH}$ = 7.4 Hz, 2 H, $PCH_2CH_2CH_2CH_3$), 1.71–1.82 (m, 2 H, $PCH_2CH_2CH_3$), 2.22 (td, $^3J_{HH}$ = 7.2 , $^3J_{HP}$ = 1.5 Hz, 2 H, PCH_2CH_3), 2.31 (s, 6 H, pzCH_3), 2.32 (s, 12 H, pzCH_3), 2.38 (s, 18 H, pzCH_3), 5.70 (s, 4 H, pz*H*), 5.74 (s, 2 H, pz*H*). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C, δ): 12.7, 12.8 (pz*C*H_3), 13.9 ($P(CH_2)_3CH_3$), 15.2, 16.6 (pz*C*H_3), 24.3 (d, $^3J_{CP}$ = 14 Hz, $PCH_2CH_2CH_2CH_3$), 28.7 (d, $^1J_{CP}$ = 14 Hz, $PCH_2CH_2CH_2CH_3$), 29.2 (d, $^3J_{CP}$ = 15 Hz, $PCH_2CH_2CH_2CH_3$), 106.3, 106.7 (pz*C*H), 143.9, 145.2, 152.1, 152.4 (pz*C*CH_3), 225.5 (br, *C*O), 290.2 (d, $^1J_{CP}$ = 75.4, $^1J_{CW}$ = 188 Hz, W≡*C*P). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C, δ): 69.7 ($^2J_{PW}$ = 68 Hz). MS (ESI, *m/z*): 1187.3347. Calcd for $C_{40}H_{54}{}^{11}B_2N_{12}O_4P^{184}W_2$ $[M + H]^+$: 1187.3361. Anal. Found: C, 40.39; H, 4.67; N, 14.05. Calcd for $C_{40}H_{53}B_2N_{12}O_4PW_2$: C, 40.50; H, 4.50; N, 14.17%. A crystal suitable for X-ray structure determination was grown by slow evaporation of a CH_2Cl_2/ethanol solution and proved to be a dichloromethane solvate. Crystal data for $C_{41}H_{55}B_2Cl_2N_{12}O_4PW_2$ (M_w =1271.16 $gmol^{-1}$): monoclinic, space group $P2_1/n$ (no. 14), *a* = 11.4608(3), *b* = 19.9952(6), *c* = 21.5347(6) Å, *β* = 91.254(2)°, *V* = 4933.7(2) $Å^3$, *Z* = 4, *T* = 150.0(1) K, *μ*(Cu Kα) = 10.220 mm^{-1}, D_{calc} = 1.711 Mgm^{-3}, 38,238 reflections measured (8.21° ≤ 2Θ ≤ 133.17°), 8,724 unique (R_{int} = 0.0680, R_{sigma} = 0.0559) which were used in all calculations. The final R_1 was 0.0397 ($I > 2\sigma(I)$) and wR_2 was 0.1047 (all data) for 643 refined parameters with 120 restraints. CCDC 1835466.

Synthesis of PhAs{C≡Mo(CO)$_2$(Tp*)}$_2$ (6a). A solution of **1a** (250 mg, 0.462 mmol) in THF (10 mL) at –78 °C was treated with *n*-BuLi (0.290 mL, 1.6 M in hexanes, 0.46 mmol). The resulting dark orange solution was stirred for 30 min then treated with $AsCl_2Ph$ (31 μL, 51 mg, 0.23 mmol), causing the solution to turn orange-brown. The solution was slowly warmed to RT and stirring was continued for 3 h, after which time the volatiles were removed in vacuo. The residue was subjected to column chromatography (20 x 3 cm silica gel column), eluting initially with *n*-hexane and gradually increasing to 10% v/v CH_2Cl_2/*n*-hexane. An orange band was collected and the solvents were removed under reduced pressure to give pure **6a** (142 mg, 0.132 mmol, 57%) as orange microcrystals. IR (CH_2Cl_2, cm^{-1}): 2002s, 1995s, 1916s ν(CO). ^1H NMR (400 MHz, $CDCl_3$, 25 °C, δ): 2.24 (s, 6 H, pzCH_3), 2.30 (s, 6 H, pzCH_3), 2.31 (s, 6 H, pzCH_3), 2.32 (s, 6 H, pzCH_3), 2.36 (s, 12 H, pzCH_3), 5.68 (s, 2 H, pz*H*), 5.69 (s, 2 H, pz*H*), 5.71 (s, 2 H, pz*H*), 7.31–7.42 (m, 3 H, As*Ph*), 7.81–7.86 (m, 2 H, As*Ph*). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C, δ): 12.7, 12.9 (2 C, coincident) 14.6, 16.1 (2 C, coincident) (pz*C*H_3), 106.1, 106.1, 106.4 (pz*C*H), 128.7 (*p-Ph*), 128.8 (*o,m-Ph*), 133.7 (*o,m-Ph*), 140.1 (*i-Ph*), 144.2, 145.1, 151.3, 151.4 (pz*C*CH_3), 226.8, 227.6 (*C*O), 308.3 (Mo≡*C*As). MS (ESI, *m/z*): 1076.1538.

Calcd for $C_{42}H_{50}As^{11}B_2N_{12}O_4{}^{94}Mo_2$ [M + H]$^+$: 1076.1591. Anal. Found: C, 46.76; H, 4.68; N, 15.69. Calcd for $C_{42}H_{49}AsB_2N_{12}O_4Mo_2$: C, 46.95; H, 4.60; N, 15.65%. The crystal used for single crystal X-ray structure determination was grown by slow evaporation of a CH_2Cl_2/ethanol mixture. The structure was complicated by a small amount of full-molecule disorder, for which only the heaviest (molybdenum and arsenic) atoms could be identified from the minor component. These were refined to a partial occupancy of ca. 10%. Crystal data for $C_{42}H_{49}AsB_2Mo_2N_{12}O_4$ (M_w =1074.35 gmol^{-1}): triclinic, space group *P*-1 (no. 2), *a* = 11.5185(4), *b* = 13.0665(6), *c* = 17.5152(6) Å, *α* = 92.370(3), *β* = 100.329(3), *γ* = 108.935(4)°, *V* = 2439.02(17) Å^3, *Z* = 2, *T* = 150.0(1) K, μ(Cu Kα) = 5.385 mm^{-1}, D_{calc} = 1.463 Mgm^{-3}, 14,328 reflections measured (5.16° ≤ 2Θ ≤ 144.26°), 9,240 unique (R_{int} = 0.0263, R_{sigma} = 0.0527) which were used in all calculations. The final R_1 was 0.0435 ($I > 2\sigma(I)$) and wR_2 was 0.1170 (all data) for 607 refined parameters with 72 restraints. CCDC 1835467.

Synthesis of PhAs{C≡W(CO)$_2$(Tp*)}$_2$ (6b). Method 1: 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 yellow-orange solution was stirred for 30 min then treated with $AsCl_2Ph$ (27 μL, 45 mg, 0.20 mmol), causing the solution to turn orange-brown. The solution was slowly warmed to RT and stirring was continued for 3 h, after which time the volatiles were removed in vacuo. The residue was subjected to column chromatography (20 x 3 cm silica gel column), eluting initially with *n*-hexane and gradually increasing to 20% v/v CH_2Cl_2/*n*-hexane. A yellow band was collected from which the volatiles were removed under reduced pressure to give yellow microcrystals of pure **6b** (165 mg, 0.132 mmol, 66%). Method 2: A solution of **1b** (200 mg, 0.318 mmol) in THF (10 mL) at –78 °C was treated with *n*-BuLi (200 μL, 1.6 M in hexanes, 0.32 mmol). The resulting yellow-orange solution was stirred for 30 min then treated with $AsCl_3$ (13 μL, 28 mg, 0.16 mmol), causing the solution to turn orange-red. Stirring was continued for 30 min at reduced temperature, after which time PhLi (100 μL, 1.9 M in dibutyl ether, 0.16 mmol) was added, causing the solution to turn yellow-brown. Stirring was continued for 30 min at RT and then the volatiles were removed *in vacuo*. Column chromatography under the same conditions as Method 1 gave pure **6b** (49.0 mg, 0.0392 mmol, 25%). IR (CH_2Cl_2, cm^{-1}): 1986s, 1977s, 1892s ν(CO). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, δ): 2.19 (s, 6 H, pzC*H*$_3$), 2.30 (s, 6 H, pzC*H*$_3$), 2.31 (s, 6 H, pzC*H*$_3$), 2.37 (s, 6 H, pzC*H*$_3$), 2.38 (s, 6 H, pzC*H*$_3$), 2.39(s, 6 H, pzC*H*$_3$), 5.71 (s, 2 H, pz*H*), 5.73 (s, 2 H, pz*H*), 5.75 (s, 2 H, pz*H*), 7.29–7.32 (tt, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.3, 1 H, *p*-*Ph*), 7.39 (tt, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.3, 2 H, m-*Ph*), 7.83 (dt, $^3J_{HH}$ = 7.0, $^4J_{HH}$ = 1.3 Hz, 2 H, o-*Ph*). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C, δ): 12.7, 12.8 (2 C, coincident) 15.2, 16.7 (2 C, coincident) (pz*C*H$_3$), 106.3, 106.4, 106.7 (pz*C*H), 128.2 (*p*-*Ph*), 128.5 (*m*-*Ph*), 133.5 (*o*-*Ph*), 141.2 (*i*-*Ph*), 144.0, 144.1, 145.2, 152.2, 152.4 (pz*C*CH$_3$), 224.7 (*C*O, $^1J_{CW}$ = 159.9), 226.3 (*C*O, $^1J_{CW}$ = 160.3), 295.1 (W≡*C*As, $^1J_{CW}$ = 194 Hz). MS (ESI, *m/z*): 1251.2487. Calcd for $C_{42}H_{49}As^{11}B_2N_{12}O_4{}^{194}W_2$ [M + H]$^+$: 1251.2499. Anal. Found: C, 40.26; H, 3.97; N, 13.29. Calcd for $C_{42}H_{49}AsB_2N_{12}O_4W_2$: C, 40.35; H, 3.95; N, 13.44%. Crystals suitable for X-ray structure determination were grown by slow evaporation of a CH_2Cl_2/cyclohexane solution. The structure was complicated by a small amount of full-molecule disorder. Only the heaviest (tungsten) atoms could be identified from the minor component, which were refined to a partial occupancy of *ca*. 5.3%. Crystal data for $C_{42}H_{49}AsB_2N_{12}O_4W_2$ (*M* =1250.17 gmol^{-1}): triclinic, space group P-1 (no. 2), *a* = 11.5217(2) Å, *b* = 13.0117(2) Å, *c* = 17.5872(3) Å, *α* = 92.1520(10)°, *β* = 100.361(2)°, *γ* = 109.048(2)°, *V* = 2438.44(8) Å^3, *Z* = 2, *T* = 150.0(1) K, μ(CuKα) = 9.766 mm^{-1}, *Dcalc* = 1.703 Mgm^{-3}, 54807 reflections measured (5.136° ≤ 2Θ ≤ 144.06°), 9468 unique (R_{int} = 0.0503, R_{sigma} = 0.0345) which were used in all calculations. The final R_1 was 0.0369 ($I > 2\sigma(I)$) and wR_2 was 0.0939 (all data) for 597 refined parameters with 0 restraints. CCDC 1835468.

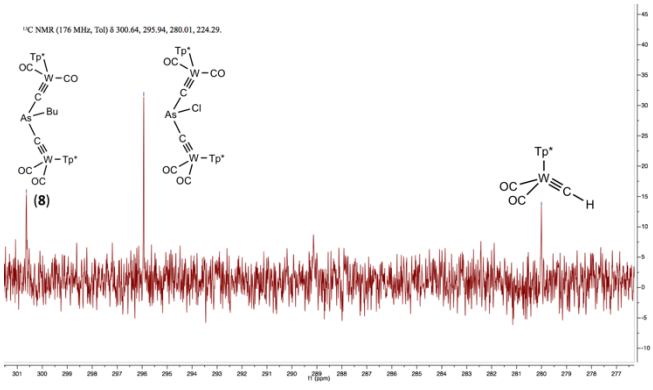
Synthesis of CH$_3$As{C≡Mo(CO)$_2$(Tp*)}$_2$ (7a). A solution of **1a** (200 mg, 0.370 mmol) in THF (10 mL) at –78 °C was treated with *n*-BuLi (230 μL, 1.6 M in hexanes, 0.37 mmol). The resulting orange solution was stirred for 30 min then treated with $AsCl_2Me$ (16 μL, 29 mg, 0.18 mmol), causing the solution to turn orange-brown. The solution was slowly warmed to RT and stirring was continued for 2 h, after which time the volatiles were removed in vacuo. The residue was subjected to column chromatography (20 x 3 cm silica gel column), eluting initially with petroleum ether (40–60 °C) and gradually increasing to 20% v/v CH_2Cl_2/petroleum ether. A yellow band was collected and the solvents were removed under reduced pressure to give pure **7a** (113 mg, 0.112 mmol, 60%) as yellow-orange microcrystals. IR (CH_2Cl_2, cm^{-1}): 1999s, 1991s, 1911s ν(CO). ^{1}H NMR (700 MHz, $CDCl_3$, 25 °C, δ): 1.72 (s, 3 H, AsC*H*$_3$), 2.30 (s, 6 H, pzC*H*$_3$), 2.34 (s, 6 H, pzC*H*$_3$), 2.36 (2 x s overlapping, 18 H, pzC*H*$_3$), 2.39 (s, 6 H, pzC*H*$_3$), 5.70 (s, 4 H, pz*H*), 5.72 (s, 2 H, pz*H*). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$, 25 °C, δ): 12.0 (As*C*H$_3$), 12.7, 12.9 (2 C, coincident), 14.6, 16.1 (2 C, coincident) (pz*C*H$_3$), 106.0, 106.1, 106.4 (pz*C*H), 144.1, 144.2, 145.1, 151.0, 151.2, 151.4 (pz*C*CH$_3$), 226.4, 227.3 (*C*O), 313.0 (Mo≡*C*). MS (ESI, *m/z*): 1013.1473. Calcd for $C_{37}H_{47}As^{11}B_2N_{12}O_4{}^{94}Mo_2$ [M + H]$^+$: 1013.1461. Anal. Found: C, 43.78; H, 4.67; N, 16.49. Calcd for $C_{37}H_{47}AsB_2N_{12}O_4Mo_2$: C, 43.90; H, 4.68; N, 16.60%.

Synthesis of CH$_3$As{C≡W(CO)$_2$(Tp*)}$_2$ (7b). Method 1: A solution of **1b** (200 mg, 0.318 mmol) in THF (10 mL) at –78 °C was treated with *n*-BuLi (200 μL, 1.6 M in hexanes, 0.32 mmol). The resulting yellow-orange solution was stirred for 30 min then treated with $AsCl_2Me$ (14 μL, 26 mg, 0.16 mmol), causing the solution to turn orange-brown. The solution was slowly warmed to RT and stirring was continued for 2 h, after which time the volatiles were removed in vacuo. The residue was subjected to column chromatography (20 x 3 cm silica gel column), eluting initially with petroleum ether (40–60 °C) and gradually increasing to 40% v/v CH_2Cl_2/petroleum ether. A yellow band was collected and the solvents were removed under reduced pressure to give pure **7b** (146 mg, 0.123 mmol, 77%) as yellow microcrystals. Method 2: A solution of **1b** (200 mg, 0.318 mmol) in THF (10 mL) at –78 °C was treated with *n*-BuLi (200 μL, 1.6 M in hexanes, 0.32 mmol). The resulting yellow-orange solution was stirred for 30 min then treated with $AsCl_3$ (13 μL, 28 mg, 0.16 mmol), causing the solution to turn orange-red. Stirring was continued for 30 min at reduced temperature, after which time MeLi (100 μL, 1.6 M in diethyl ether, 0.16 mmol) was added, causing the solution to turn yellow-brown. Stirring was continued for 30 min at RT and the volatiles were then removed *in vacuo*. Column chromatography under the same conditions as method 1 gave pure **7b** (41.5 mg, 0.0350 mmol, 22%). IR (CH_2Cl_2, cm^{-1}): 1983s,

1974s, 1888s ν(CO). ^{1}H NMR (700 MHz, $CDCl_3$, 25 °C, δ): 1.63 (s, 3 H, AsCH_3), 2.29 (s, 6 H, pzCH_3), 2.36 (2 x s overlapping, 18 H, pzCH_3), 2.38 (s, 12 H, pzCH_3), 5.72 (s, 4 H, pz*H*), 5.74 (s, 2 H, pz*H*). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$, 25 °C, δ): 11.8 (As*C*H$_3$), 12.7, 12.8, (2 C, coincident), 15.2, 16.8, 17.0 (pz*C*H$_3$), 106.2, 106.4, 106.7 (pz*C*H), 144.0, 144.1, 145.2, 151.8, 152.0, 152.5 (pz*C*CH$_3$), 224.4, 225.6 (*C*O), 299.8 ($^{1}J_{CW}$ = 188 Hz, W≡*C*). MS (ESI, *m/z*): 1189.2374. Calcd for $C_{37}H_{48}As^{11}B_2N_{12}O_4{}^{184}W_2$ [M + H]$^+$: 1189.2369. Anal. Found: C, 37.36; H, 4.00; N, 14.12. Calcd for $C_{37}H_{47}AsB_2N_{12}O_4W_2$: C, 37.40; H, 3.99; N, 14.15%.

Synthesis of ^{n}BuAs{C≡W(CO)$_2$(Tp*)}$_2$ (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, 0.40 mmol). The resulting brown solution was stirred for 30 min at reduced temperature then treated with $AsCl_3$ (17 μL, 37 mg, 0.20 mmol). The solution was warmed to RT and the resulting orange-red solution stirred for 1 h, after which time additional *n*-BuLi (0.125 mL, 1.6 M in hexanes, 0.20 mmol) was added, 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. A yellow-orange band was collected with 20% v/v CH_2Cl_2/petrol and was dried under reduced pressure to give a yellow-orange solid. A second chromatography step under the same conditions was typically required, from which pure **8** (66.0 mg, 0.0537 mmol, 27%) was isolated. IR (CH_2Cl_2, cm^{-1}): 1982, 1973s, 1888s ν(CO). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, δ): 0.97 (t, $^{3}J_{HH}$ = 7.2, 3 H, As(CH$_2$)$_3$CH_3), 1.51 (p, $^{3}J_{HH}$ = 7.2, 3 H, As(CH$_2$)$_2$CH_2), 1.78 (p, $^{3}J_{HH}$ = 7.2 Hz, 3 H, AsCH$_2$CH_2), 2.25–2.40 (obscured, 2 H, AsCH_2, 2.29 (s, 6 H, pzCH_3), 2.30 (s, 6 H, pzCH_3), 2.33 (s, 6 H, pzCH_3), 2.36 (2 x s overlapping, 12 H, pzCH_3), 2.37 (s, 6 H, pzCH_3), 5.67 (s, 2 H, pz*H*), 5.68 (s, 2 H, pz*H*), 5.72 (s, 2 H, pz*H*). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C, δ): 12.7, 12.8 (pzCH$_3$), 13.9 (As(CH$_2$)$_3$CH$_3$), 15.2, 16.6, 16.8 (pzCH$_3$), 24.7 (As(CH$_2$)$_2$CH$_2$), 29.4 (AsCH$_2$CH$_2$), 30.8 (AsCH$_2$), 106.2, 106.4, 106.7 (pz*C*H), 143.8, 143.9, 145.2, 151.8, 152.1, 152.4 (pz*C*CH$_3$), 224.4, 226.2 (*C*O), 300.4 (W≡*C*As, $^{1}J_{CW}$ = 190 Hz). MS (ESI, *m/z*): 1231.2813. Calcd for $C_{40}H_{54}As^{11}B_2N_{12}O_4{}^{184}W_2$ [M + H]$^+$: 1231.2817. Anal. Found: C, 38.95; H, 4.28; N, 13.55. Calcd for $C_{40}H_{53}AsB_2N_{12}O_4W_2$: C, 39.05; H, 4.34; N, 13.66%. Crystals suitable for X-ray structure determination were grown by slow evaporation of a CH_2Cl_2/ethanol solution. The asymmetric unit was found to contain four independent molecules, with significant disorder characteristics in each As^{n}Bu moiety. Hydrogen atoms were excluded and the extensive use of distance and thermal displacement parameter restraints were required. Crystal data for $C_{40}H_{53}AsB_2N_{12}O_4W_2$ (*M* =1230.18 gmol^{-1}): triclinic, space group P-1 (no. 2), *a* = 10.7560(3) Å, *b* = 29.5247(8) Å, *c* = 32.3562(8) Å, *α* = 68.469(2)°, *β* = 86.621(2)°, *γ* = 85.103(2)°, *V* = 9519.1(5) Å^3, *Z* = 8, *T* = 150.0(1) K, μ(CuKα) = 9.992 mm^{-1}, *Dcalc* = 1.717 Mgm^{-3}, 52125 reflections measured (6.968° ≤ 2Θ ≤ 133.202°), 33274 unique (R_{int} = 0.0395, R_{sigma} = 0.0716) which were used in all calculations. The final R_1 was 0.0641 (I > 2σ(I)) and wR_2 was 0.1414 (all data) for 2310 refined parameters with 457 restraints. CCDC 1835469.

General Observations on the Synthesis of arsinidine bridged bis(carbyne) complexes via the chloroarsinidines "[W$_2$(μ-C$_2$AsCl)(CO)$_4$(Tp*)$_2$]. - Room-temperature ^{1}H NMR and IR spectroscopy on the bromocarbyne/^{n}BuLi/$AsCl_3$ crude mixture (before a nucleophile is added) is dominated by signatures for **8** and the methylidyne [W(≡CH)(CO)$_2$(Tp*)] and its dimer [W$_2$(μ-C=CH$_2$)(CO)$_4$(Tp*)$_2$]. Other (unidentified) Tp*-containing species are present only in much smaller quantities, and the region is too cluttered for us to be confident in assigning any resonances to the purported chloroarsinidine intermediate. We presume that the key chloroarsinidine intermediate is thermally unstable based on the observation that the solution is bright red at -78°C but quickly turns a brown-orange when warmed to ambient temperature, i.e., under the conditions required for spectroscopy, the intermediate is short-lived. Because each of these products has 6 ^{1}H NMR pyrazolyl resonances over narrow frequency ranges, it is not viable to use these as spectroscopic handles. When the reaction (without added nucleophile) is carried out at -78°C, freed of solvent at -10°C and then the ^{13}C{^{1}H} NMR spectrum of the residue acquired in d_8-toluene at -10 °C (a compromise between thermal sensitivity and ensuring that all products are in solution), a major resonance is observed at δ_C = 296.0 tentatively assigned to the chloroarsinidine, flanked by weaker resonances at 300.7 (**8**) and 280.1 ([W(≡CH)(CO)$_2$(Tp*)], which only begins to dimerise at room temperature).



The measured intensities are *ca* 3:1:1, respectively, however given the thermal sensitivity of the chloroarsinidine intermediate, this will have progressively decomposed to **8** and the methylidyne during extended NMR data acquisition, *i.e.,* the apparent 60% formation of the chloroarsine is most likely a conservative estimate. The eventual low yield of the product of nucleophilic attack will thus in part be due to competition with these concurrent decomposition processes. It would therefore however appear that neither IR, ^{1}H nor ^{13}C{^{1}H} NMR spectroscopies provide convenient spectroscopic handles that might be used to monitor the progress of these reactions in contrast to the phosphorus derivatives where ^{31}P{^{1}H} NMR is both rapid and quantitative.

Selected X-ray crystallographic data

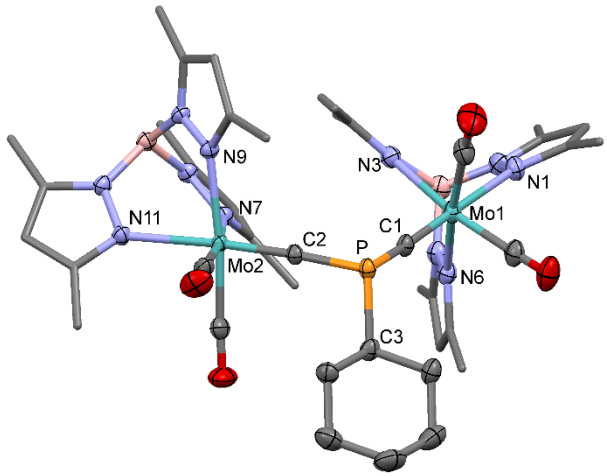


Figure S1. Molecular structure of **3b** in a crystal of **3b**·0.75CH_2Cl_2 (50% thermal probability ellipsoids, hydrogen atoms and solvent molecules not shown and pyrazolyl rings are simplified for clarity). Selected bold lengths (Å) and angles (°): Mo1–C1 1.813(2), Mo2–C2 1.806(2), C1–P 1.795(2), C2–P 1.794(2), P–C3 1.865(3), Mo1–N1 2.319(2), Mo1–N3 2.228(2), Mo1–N6 2.229(2), Mo2–N7 2.216(2), Mo2–N9 2.216(2), Mo2–N11 2.322(2), Mo1–C1–P 168.06(17), C1–P–C2 99.14(11), Mo2–C2–P 174.55(14), C1–P–C3 106.29(12), C2–P–C3 102.51(12). ***TR*** = 2(Mo1–N1)/(Mo1–N3 + Mo1–N6) = 1.041. ***TR*** = 2(Mo2–N11)/(Mo2–N7 + Mo2–N9) = 1.048.

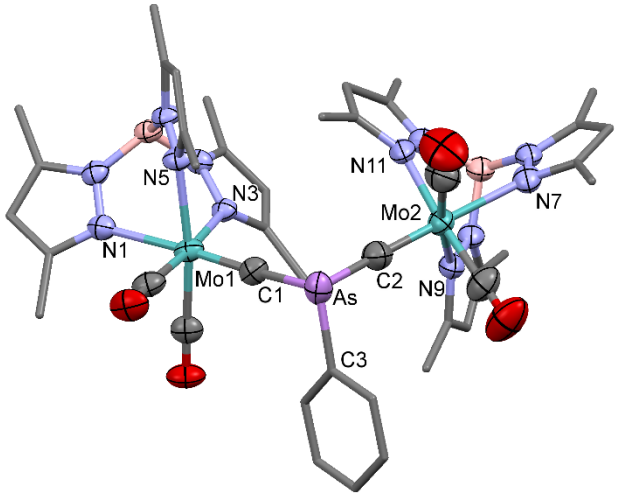


Figure S3. Molecular structure of **6a** showing 50% displacement ellipsoids. Hydrogen atoms are omitted and the phenyl and pyrazolyl rings are simplified for clarity. Selected bond distances (Å) and angles (°): Mo1–C1 1.790(4), C1–As 1.931(4), As–C2 1.924(5), C2–Mo2 1.809(5), As–C3 1.953(6), Mo1–N1 2.334(4), Mo1–N3 2.220(3), Mo1–N5 2.230(3), Mo2–N7 2.327(4), Mo2–N9 2.235(4), Mo2–N11 2.234(4), Mo1–C1–As 171.3(3), C1–As–C2 95.7(2), As–C2–Mo2 166.4(3). ***TR*** = 2(Mo1–N1)/(Mo1–N3 + Mo1–N5) = 1.046. ***TR*** = 2(Mo2–N7)/(Mo2–N9 + Mo2–N11) = 1.041.

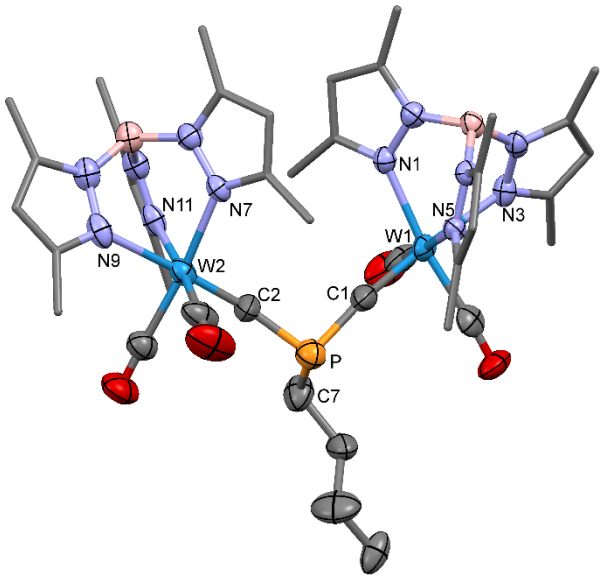


Figure S2. Molecular structure of **5** in a crystal of **5**·CH_2Cl_2 showing 50% displacement ellipsoids. Hydrogen atoms and minor disorder component are omitted and the phenyl and pyrazolyl rings are simplified for clarity. Selected bond distances (Å) and angles (°): W1–C1 1.833(6), C1–P 1.857(6), P–C2 1.825(6), C2–W2 1.822(6), P–C7 1.858(17), W1–N1 2.207(5), W1–N3 2.311(5), W1–N5 2.234(5), W2–N7 2.197(5), W2–N9 2.295(6), W2–N11 2.223(6), W1–C1–P 170.0(4), W2–C2–P 151.6(5), C1–P–C2 95.6(3), C1–P–C7 99.1(7), C2–P–C7 94.2(6). ***TR*** = 2(W1–N3)/(W1–N1 + W1–N5) = 1.041. ***TR*** = 2(W2–N9)/(W2–N7 + W2–N11) = 1.038.

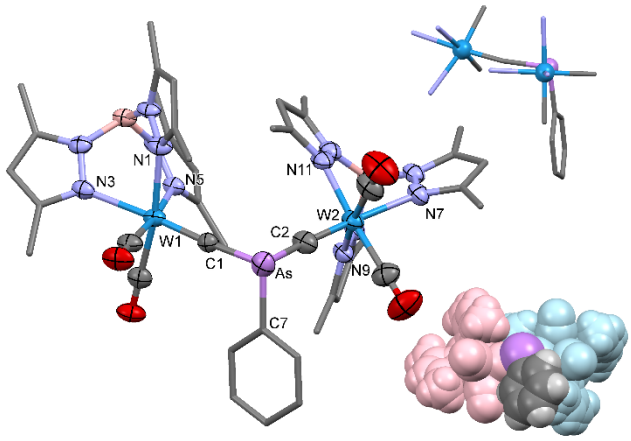


Figure S4. Molecular structure of **6b** showing 50% displacement ellipsoids. Hydrogen atoms are omitted and the phenyl and pyrazolyl rings are simplified for clarity. Selected bond distances (Å) and angles (°): W1–C1 1.808(5), C1–As 1.921(5), As–C2 1.927(5), C2–W2 1.819(5), As–C7 1.954(7), W1–N1 2.222(4), W1–N3 2.325(4), W1–N5 2.214(4), W2–N7 2.316(4), W2–N9 2.208(4), W2–N11 2.211(5), W1–C1–As 171.3(3), C1–As–C2 96.4(2), As–C2–W2 168.0(4). ***TR*** = 2(W1–N3)/(W1–N1 + W1–N5) = 1.048 ***TR*** = 2(W2–N7)/(W2–N9 + W2–N11) = 1.048. Insets: view along the W1···C1 vector and space-filling representation.

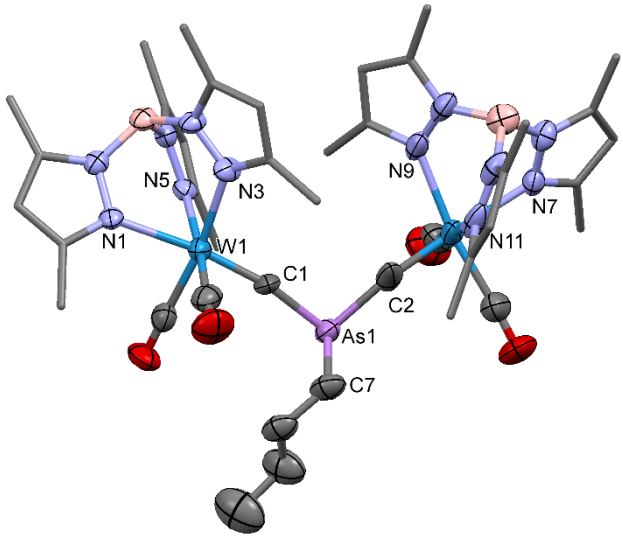


Figure S5. Molecular structure of **8** showing 50% displacement ellipsoids (one of four independent molecules). Hydrogen atoms and minor disorder components are omitted, and the phenyl and pyrazolyl rings are simplified for clarity. Selected bond distances (Å) and angles (°): W1–C1 1.835(11), C1–As1 1.962(11), As1–C2 2.046(16), C2–W2 1.784(13), As1–C7 2.019(16), W1–N1 2.297(7), W1–N3 2.222(8), W1–N5 2.208(8), W2–N7 2.280(8), W2–N9 2.214(9), W2–N11 2.221(12), W1–C1–As1 167.3(8), C1–As1–C2 91.3(5), As1–C2–W2 156.2(11). ***TR*** = 2(W1–N1)/(W1–N3 + W1–N5) = 1.037. ***TR*** = 2(W2–N7)/(W2–N9 + W2–N11) = 1.028.

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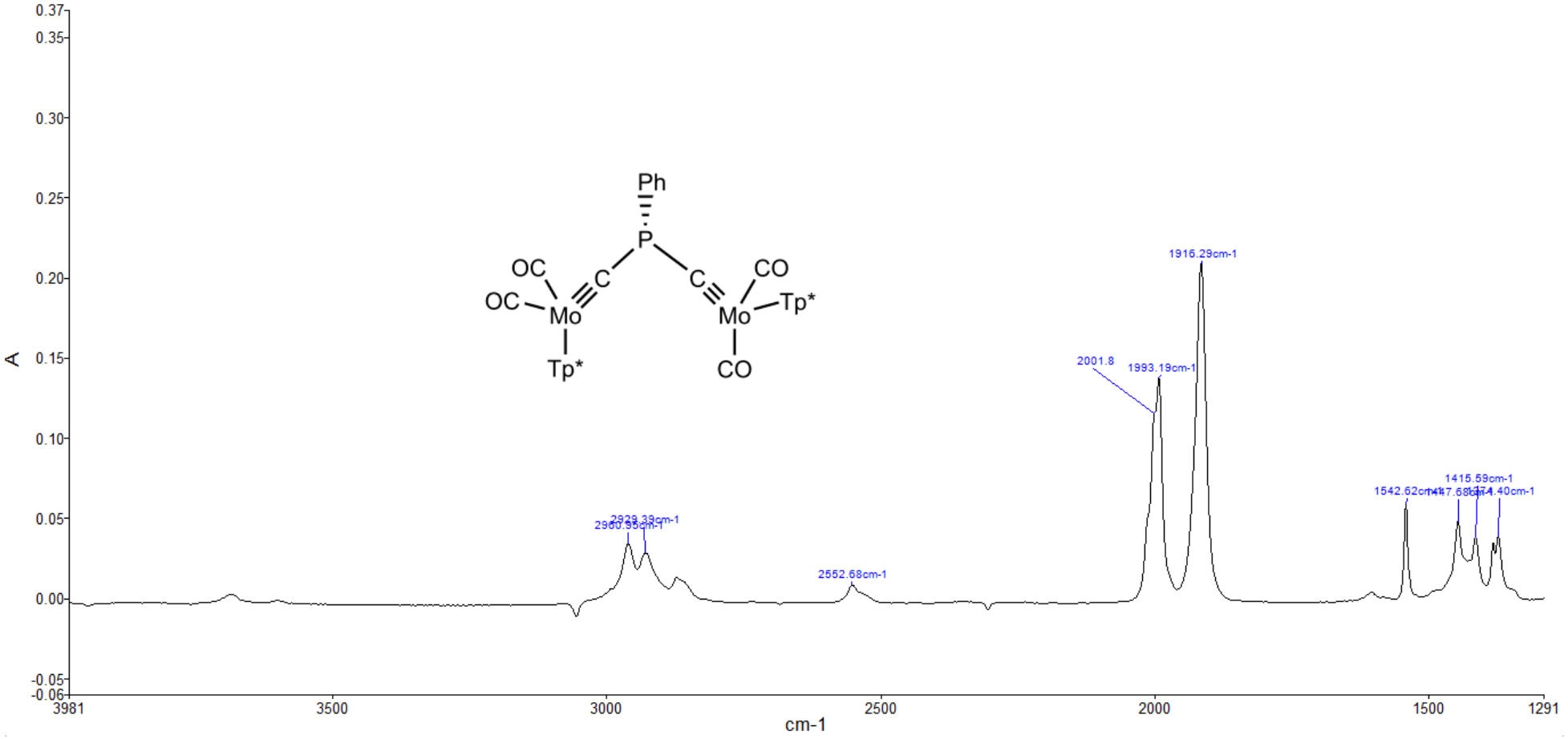
Table S1. Selected spectroscopic and structural data for complexes [RA{C≡M(CO)$_2$(Tp*)] (**2**–**8**).

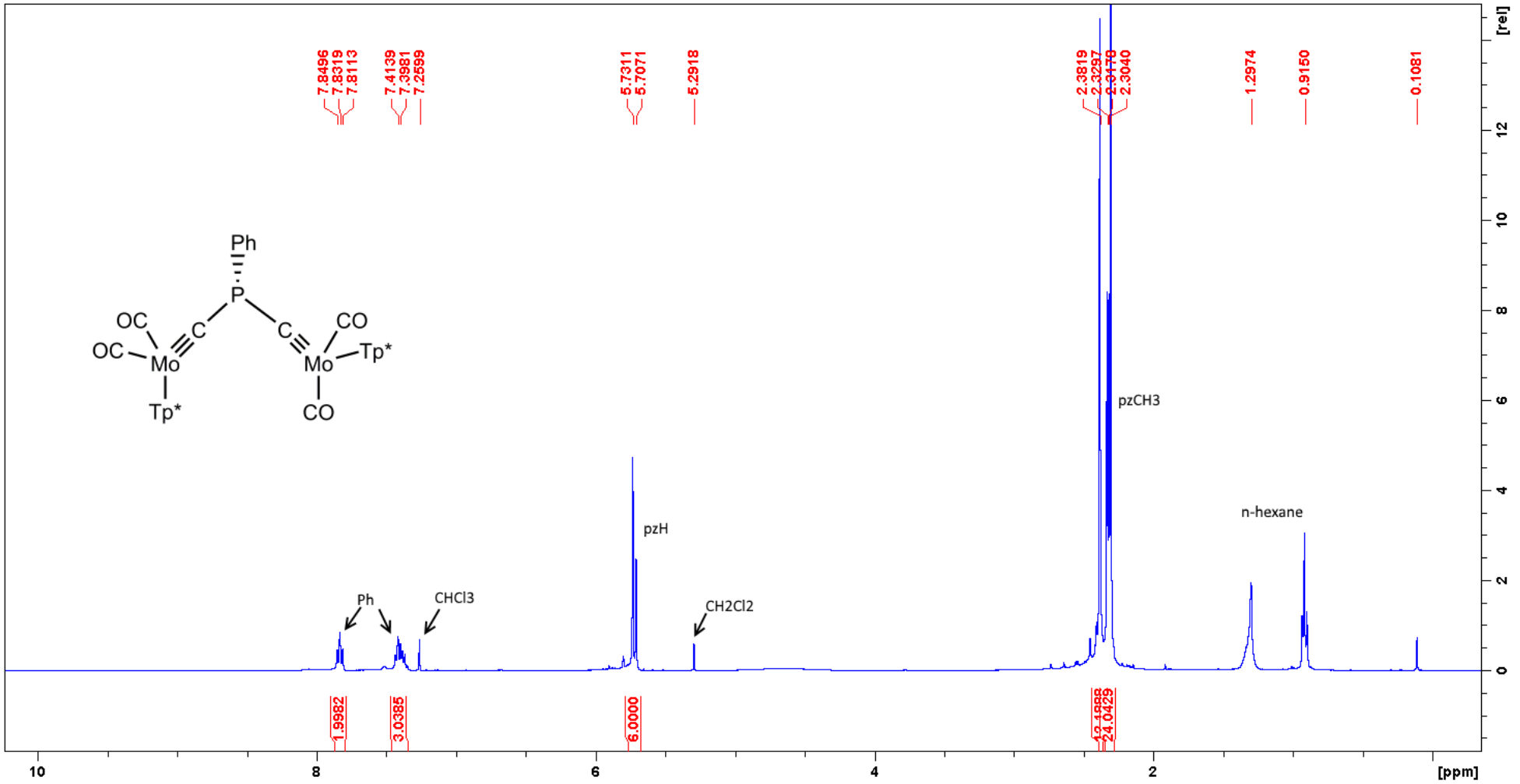
	M	A	R	$\delta_{\equiv C}$[a]	$^1J_{CP}$[b]	$^1J_{CW}$[b]	δ_P[a]	$^2J_{PW}$[b]	ν_{CO}[c]	$d_{M\equiv C}$ (Å)	d_{C-A} (Å)
2a	Mo	P	Ph	296.2	92		79.0		2001, 1993, 1916		
2b[8g]	W	P	Ph	285.0	79	192	80.4	76	1984, 1970, 1892	1.821(9), 1.832(9)	1.810(10), 1.780(10)
3a	Mo	P	Cy	303.1	93		91.6		1998, 1988, 1911	1.813(2), 1.806(2)	1.795(2), 1.794(2)
3b[8g]	W	P	Cy	291.1	80	190	87.8	68	1980, 1969, 1888	1.832(5), 1.836(5)	1.784(6), 1.789(6)
4	W	P	Me	290.0	77	188	56.3	73	1983, 1972, 1889		
5	W	P	^{n}Bu	290.2	75	188	69.7	68	1982, 1971, 1888	1.833(6), 1.822(6)	1.857(6), 1.825(6)
6a	Mo	As	Ph	308.3					2002, 1995, 1916	1.790(4), 1.809(5)	1.931(4), 1.924(5)
6b	W	As	Ph	295.1		194			1986, 1977, 1892	1.808(5), 1.819(5)	1.921(5), 1.927(5)
7a	Mo	As	Me	313.0					1999, 1991, 1911		
7b	W	As	Me	299.8		188			1983, 1974, 1888		
8	W	As	^{n}Bu	300.4		190			1982, 1973, 1888	1.835(11), 1.784(13)	1.961(11), 2.046(16)

[a] ppm, measured in a solution of $CDCl_3$ or C_6D_6 (for **2b** and **3b**). [b] Hz, measured in a solution of $CDCl_3$ or C_6D_6 (**2b** and **3b**).
[c] cm^{-1}, measured in a solution of CD_2Cl_2 or THF (**2b** and **3b**

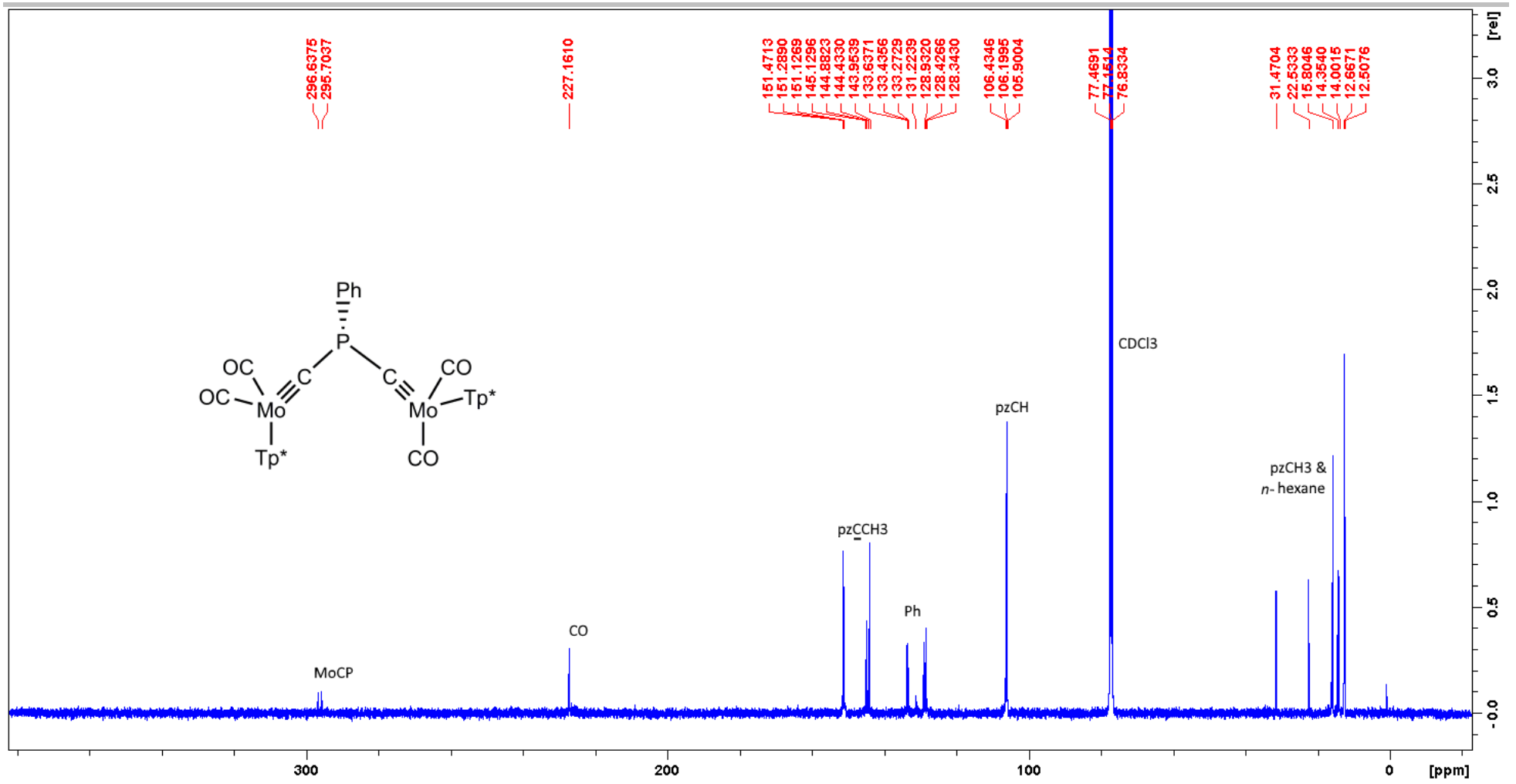
Infrared Spectrum (CH_2Cl_2) of **2a**.



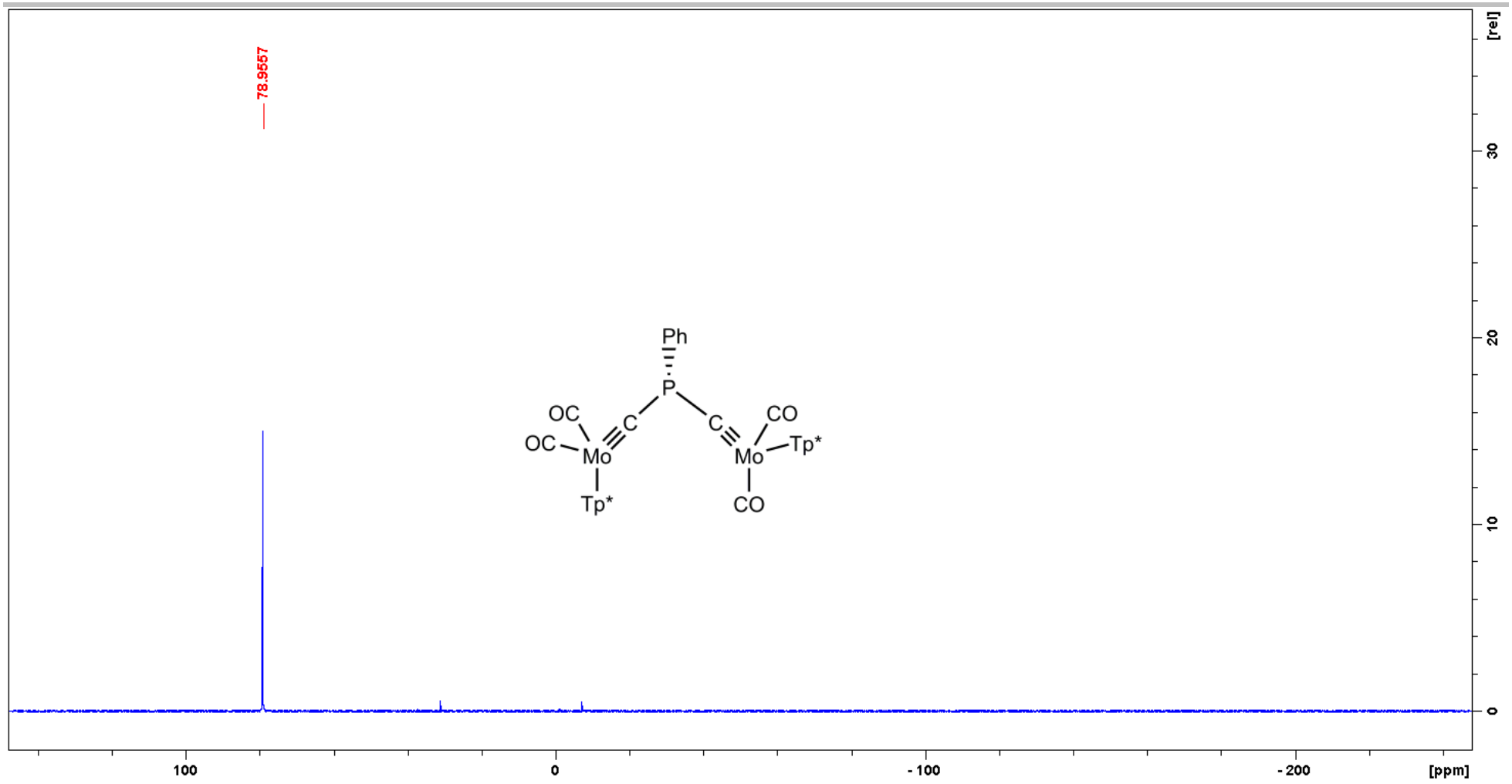
^{1}H NMR of **2a**.



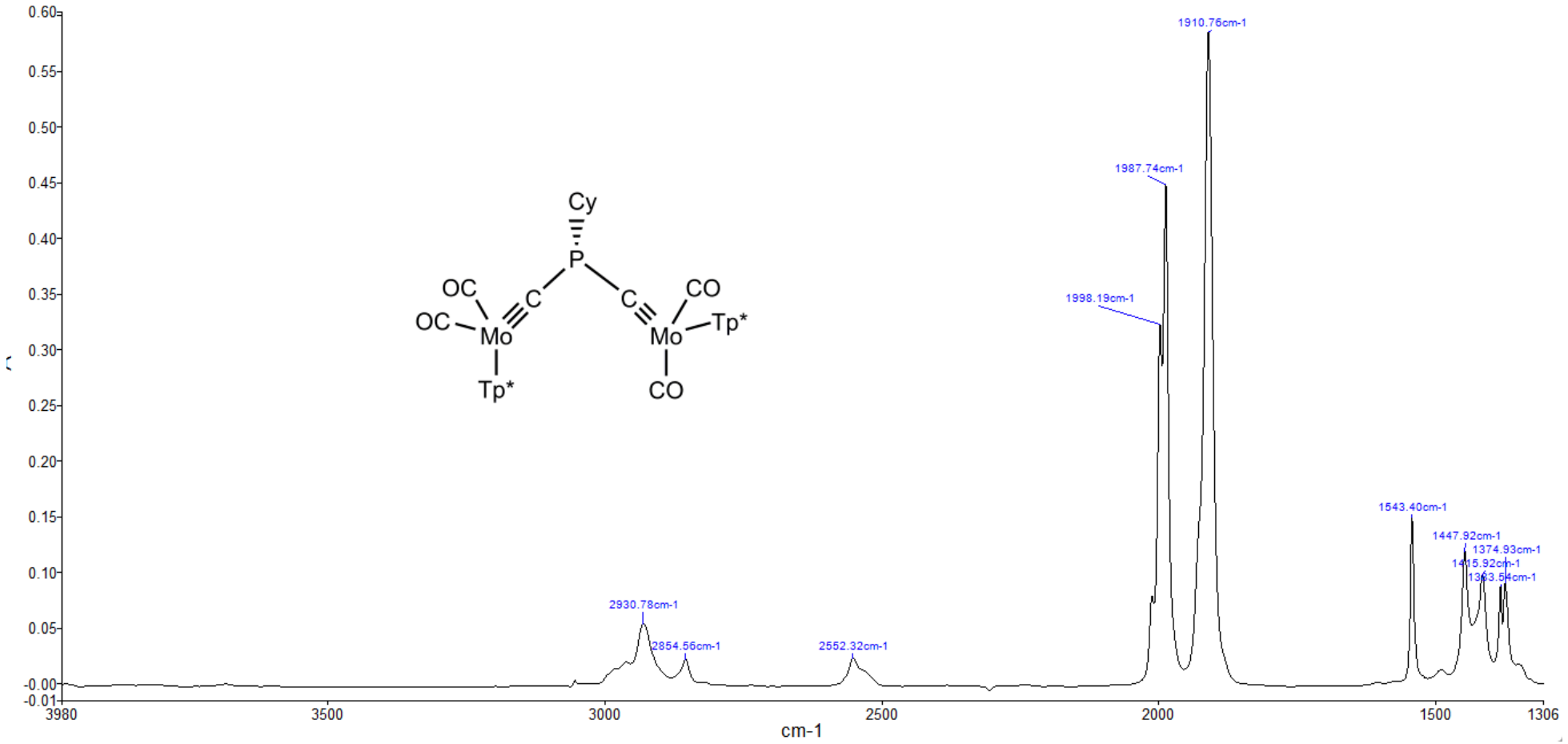
^{13}C{^{1}H} NMR of **2a**.



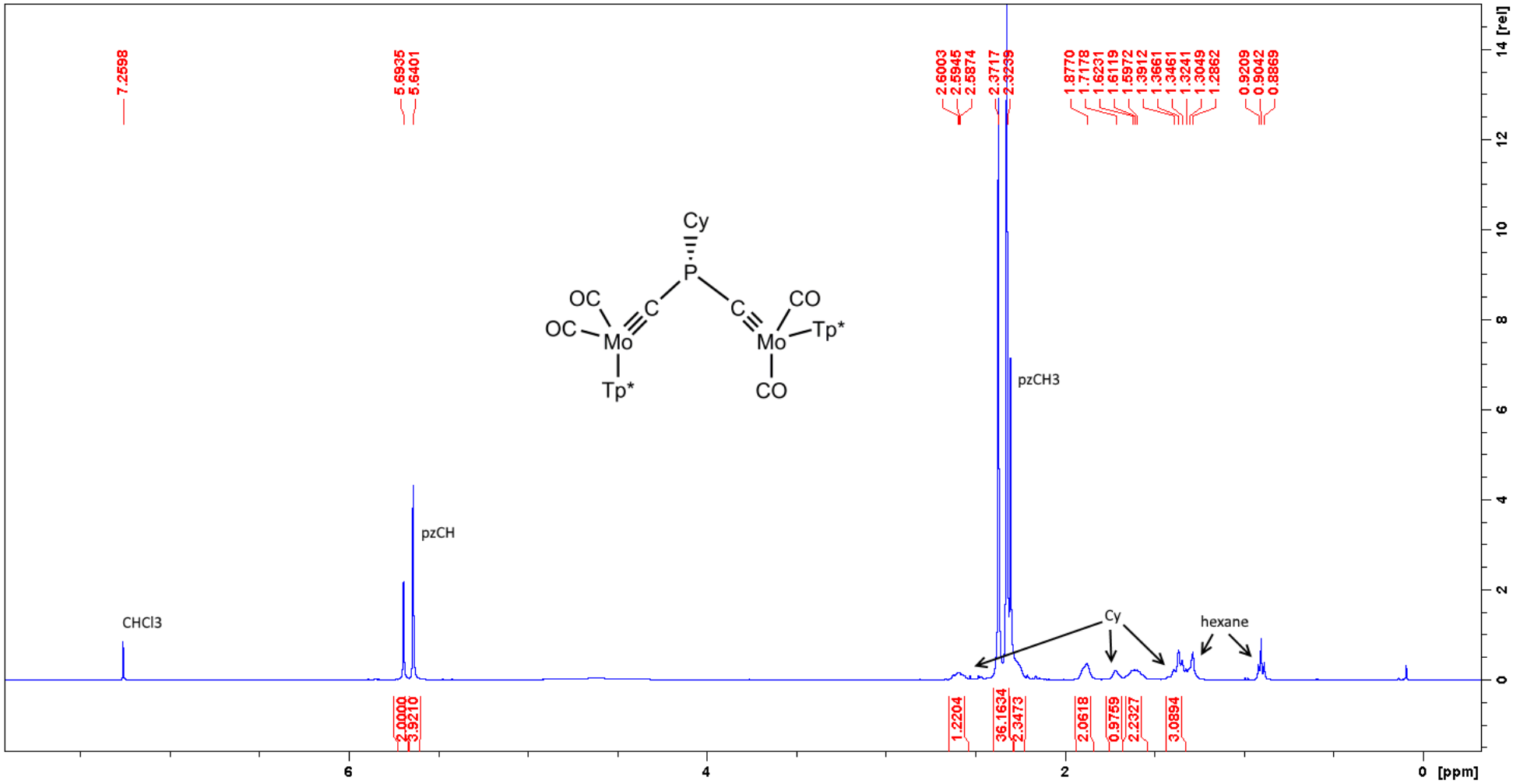
$^{31}P\{^{1}H\}$ NMR of **2a**.



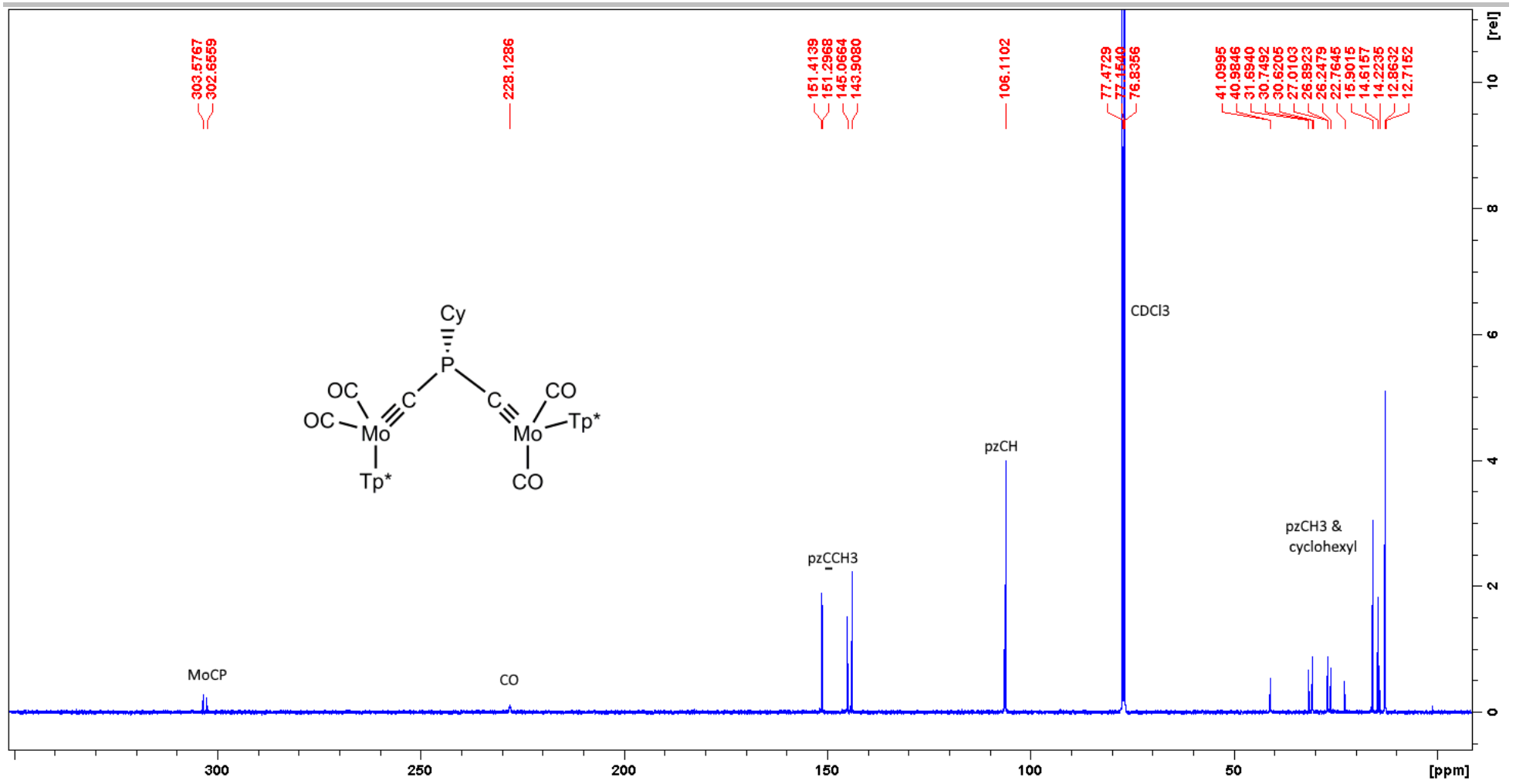
Infrared Spectrum (CH_2Cl_2) of **3a**.


Cy
P
OC
OC
C
C
CO
Mo
Mo
Tp*
Tp*
CO
1910.76cm-1
1987.74cm-1
1998.19cm-1
1543.40cm-1
1447.92cm-1
1374.93cm-1
1415.92cm-1
1363.54cm-1
2930.78cm-1
2854.56cm-1
2552.32cm-1
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
-0.00
-0.01
3980
3500
3000
2500
2000
1500
1306
cm-1

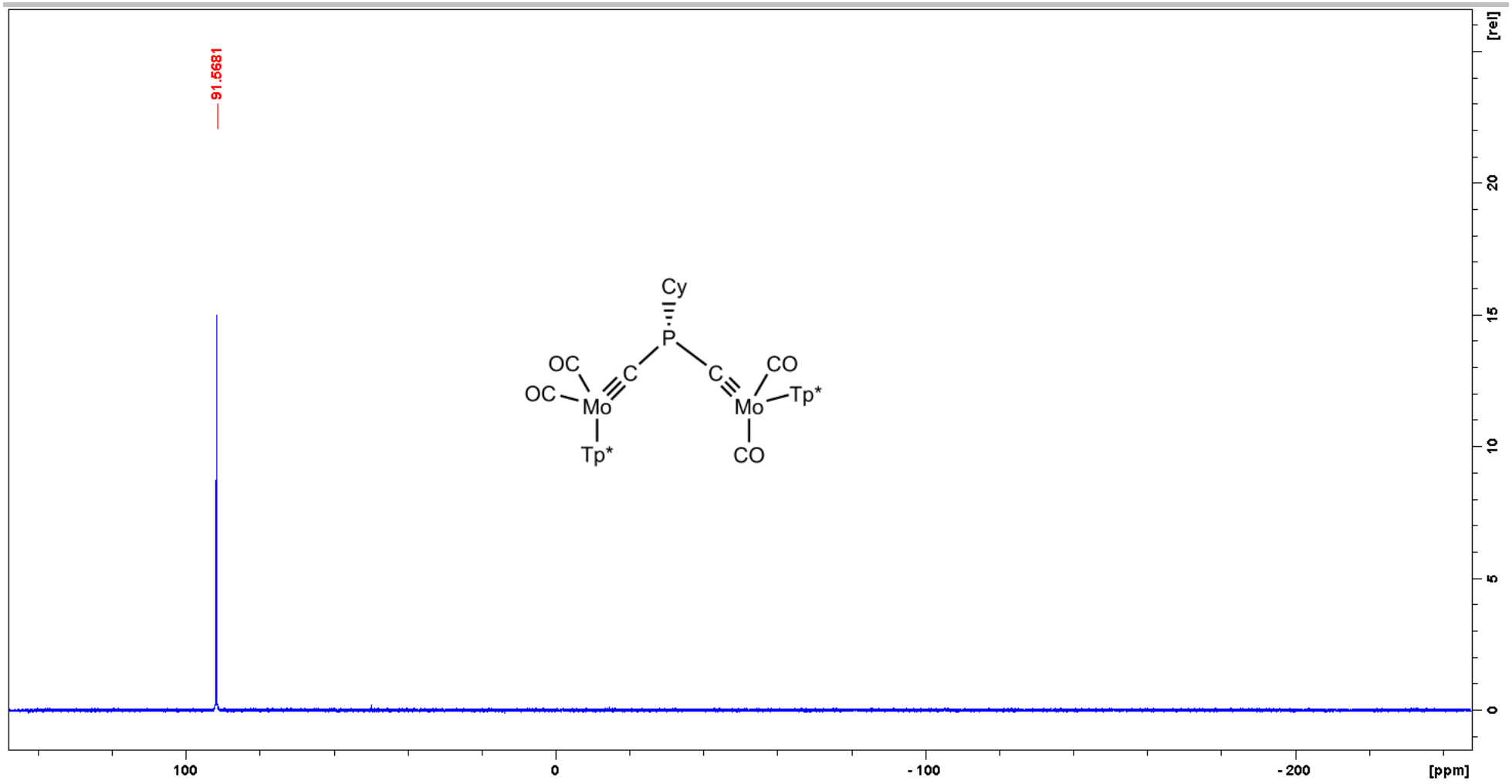
^{1}H NMR of **3a**.



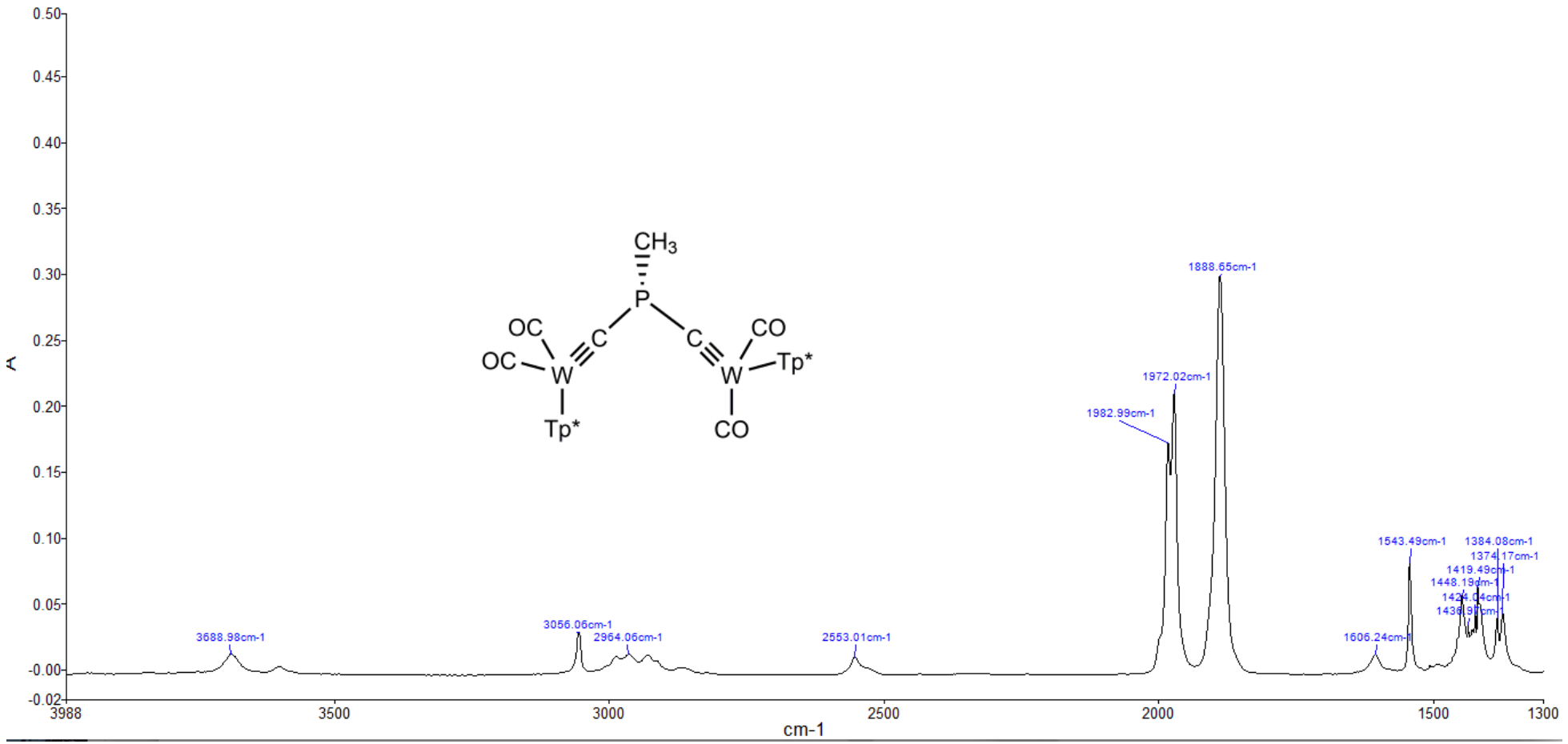
^{13}C{^{1}H} NMR of **3a**.



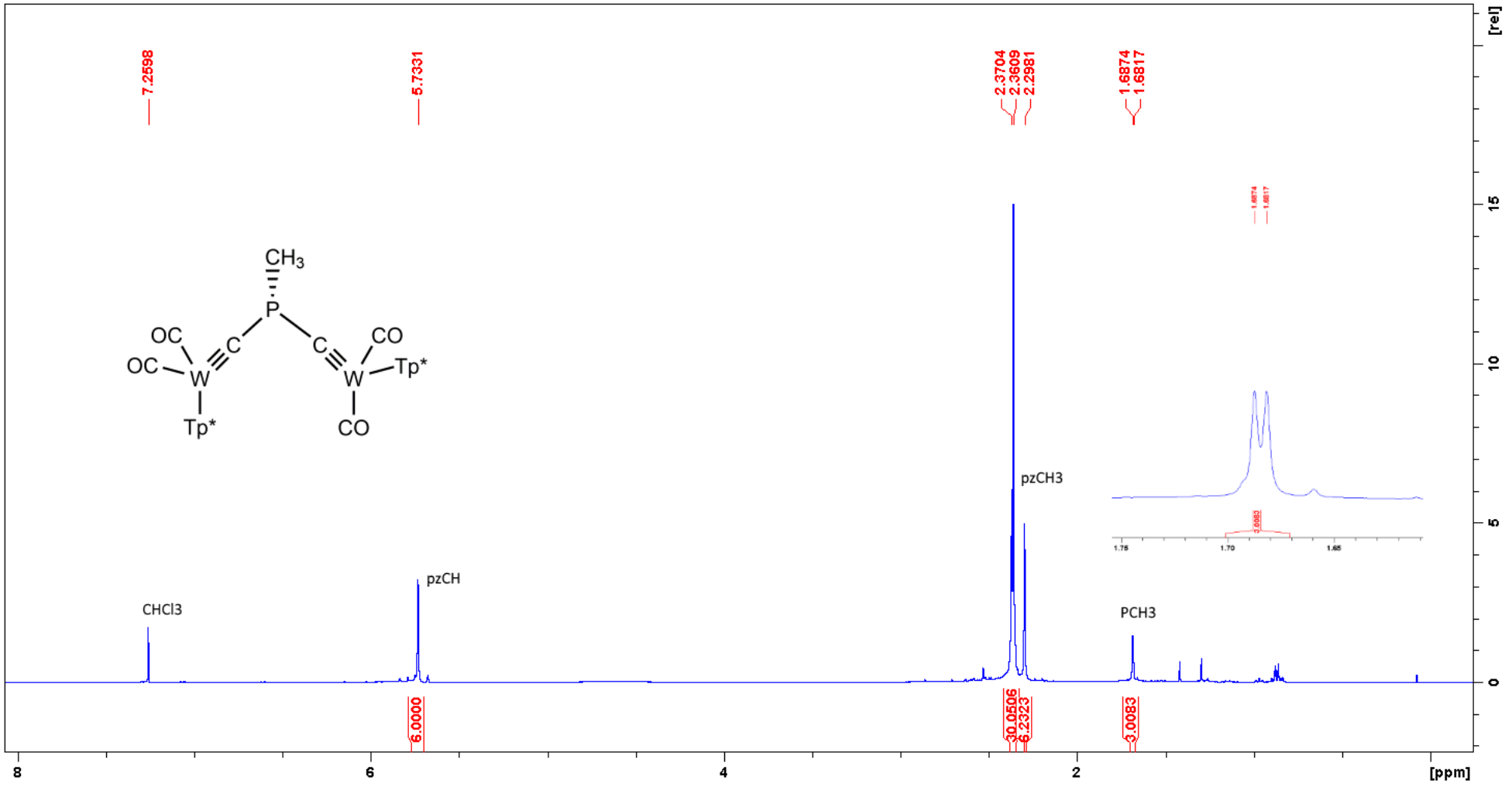
$^{31}P\{^{1}H\}$ NMR of **3a**.



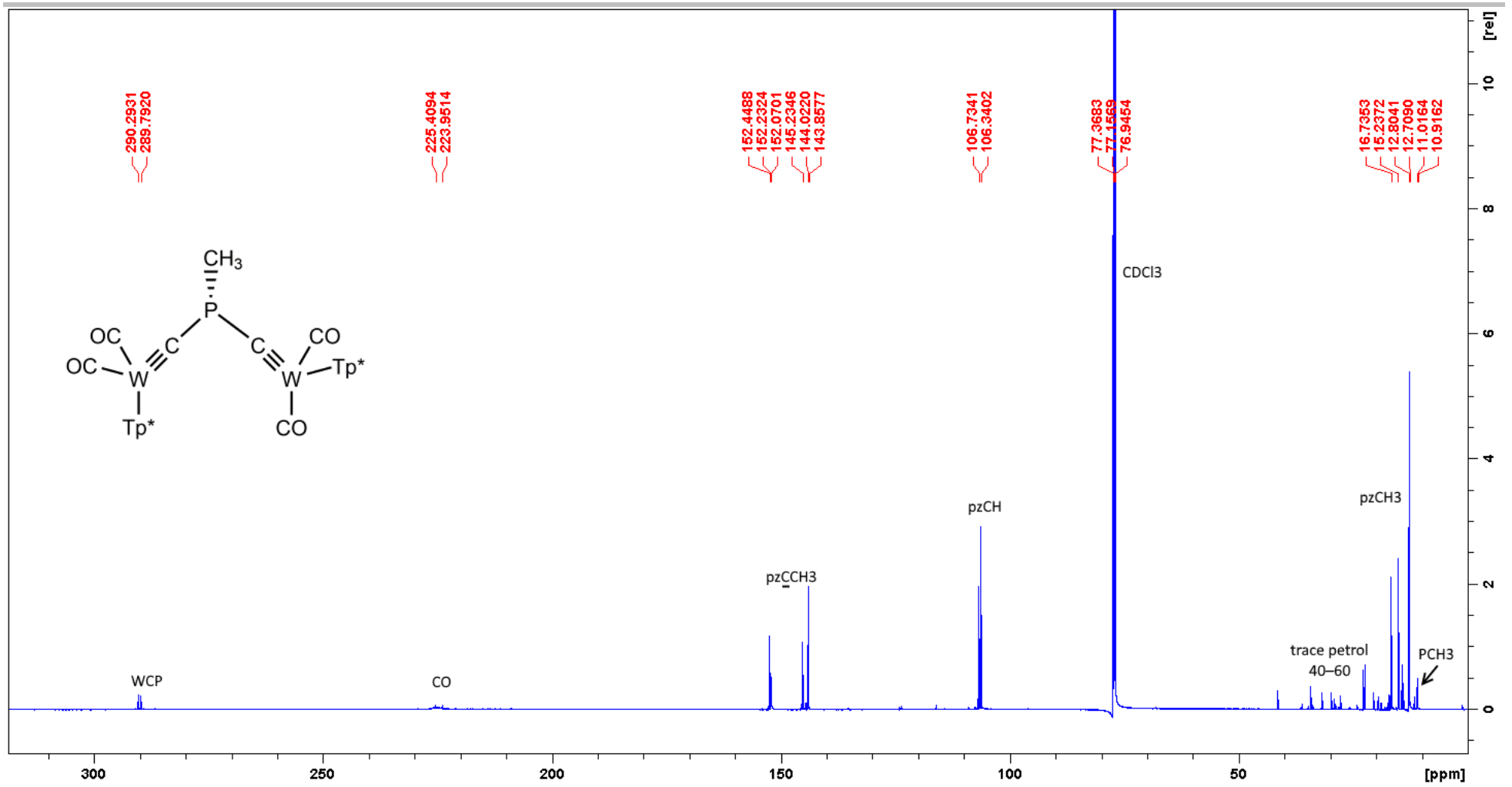
Infrared Spectrum (CH_2Cl_2) of **4**.


0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
-0.00
-0.02
A
3988
3500
3000
2500
2000
1500
1300
cm-1
CH3
P
OC
OC
C
C
CO
W
W
Tp*
Tp*
CO
3688.98cm-1
3056.06cm-1
2964.06cm-1
2553.01cm-1
1982.99cm-1
1972.02cm-1
1888.65cm-1
1606.24cm-1
1543.49cm-1
1384.08cm-1
1374.17cm-1
1419.49cm-1
1448.19cm-1

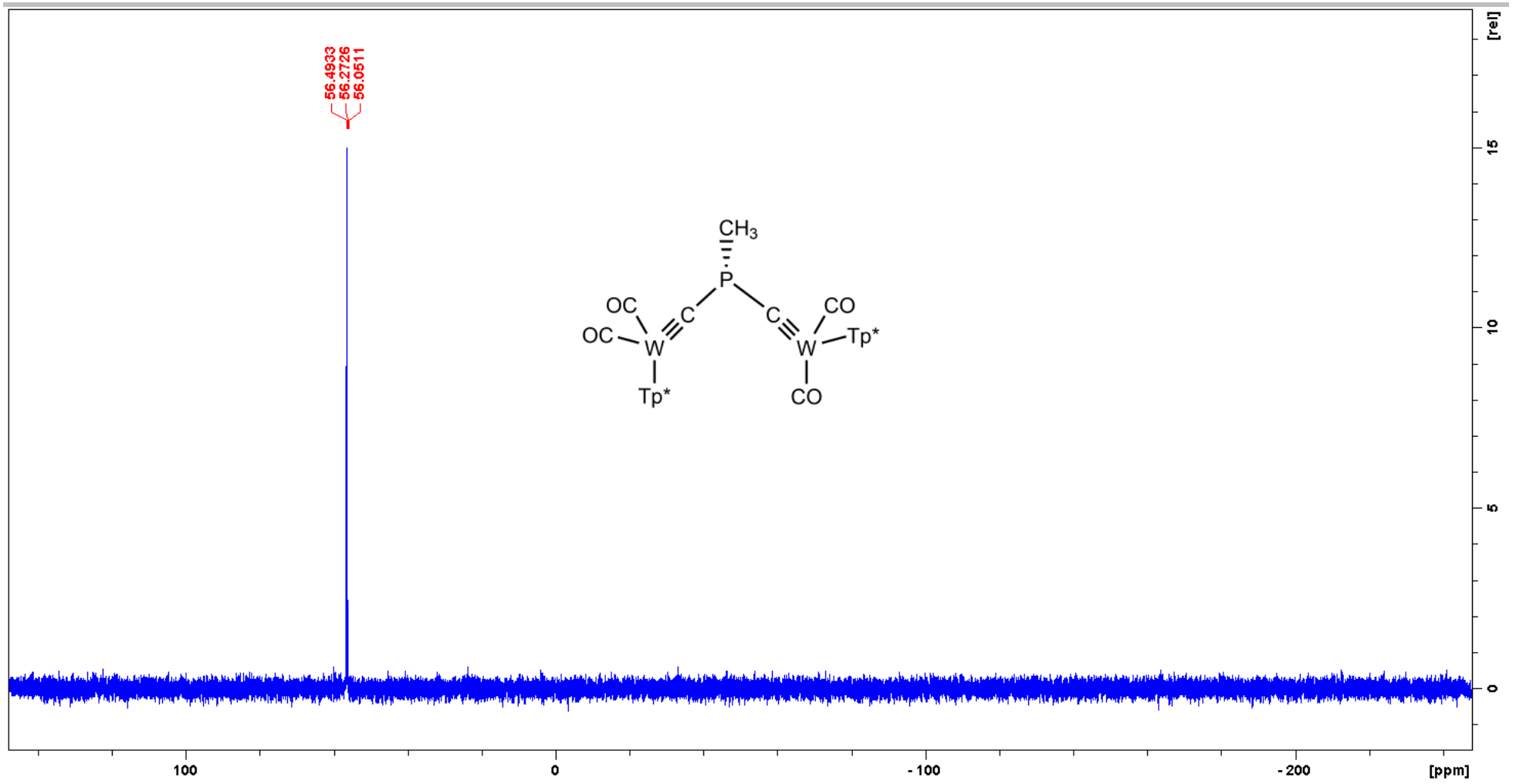
^{1}H NMR of **4**.



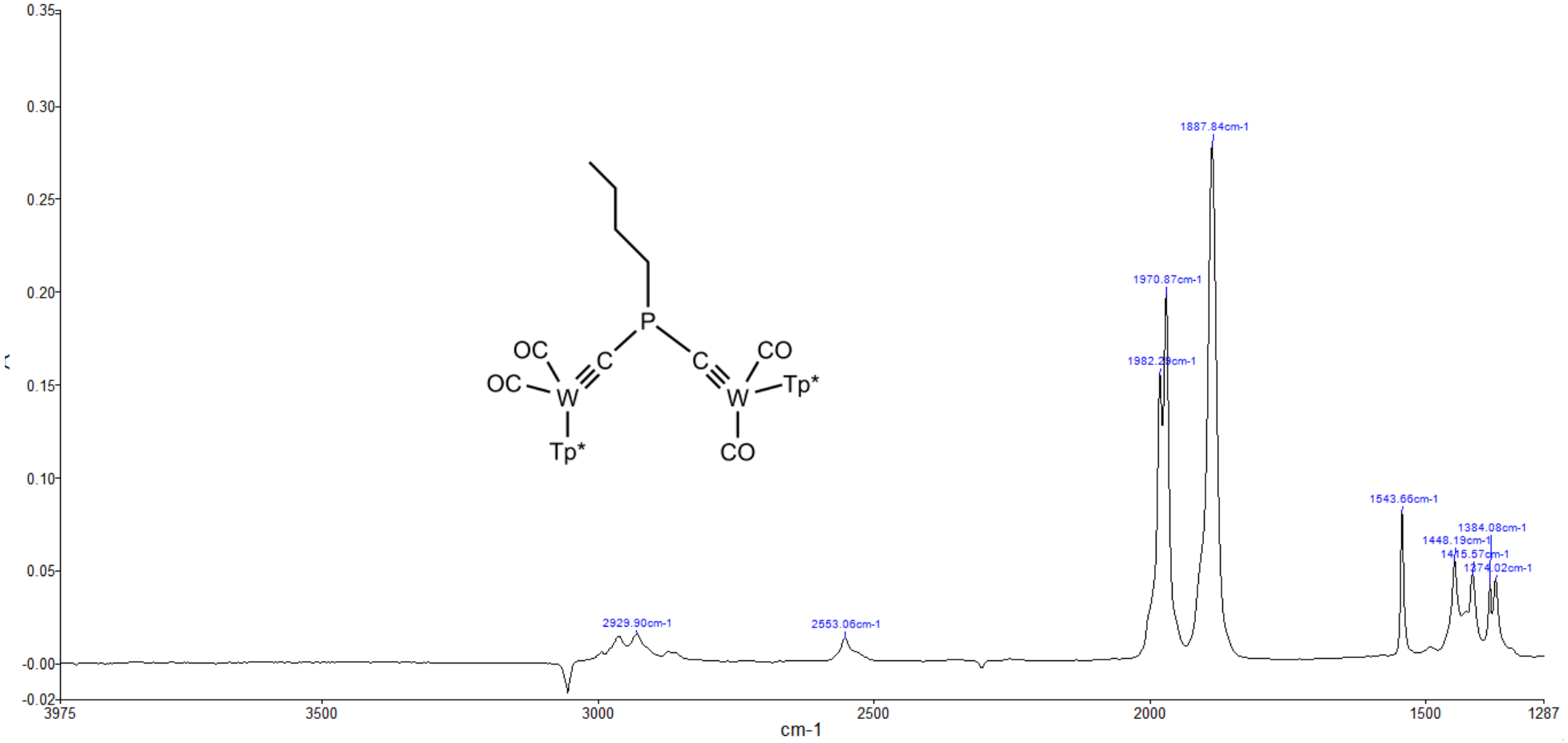
^{13}C{^{1}H} NMR of **4**.



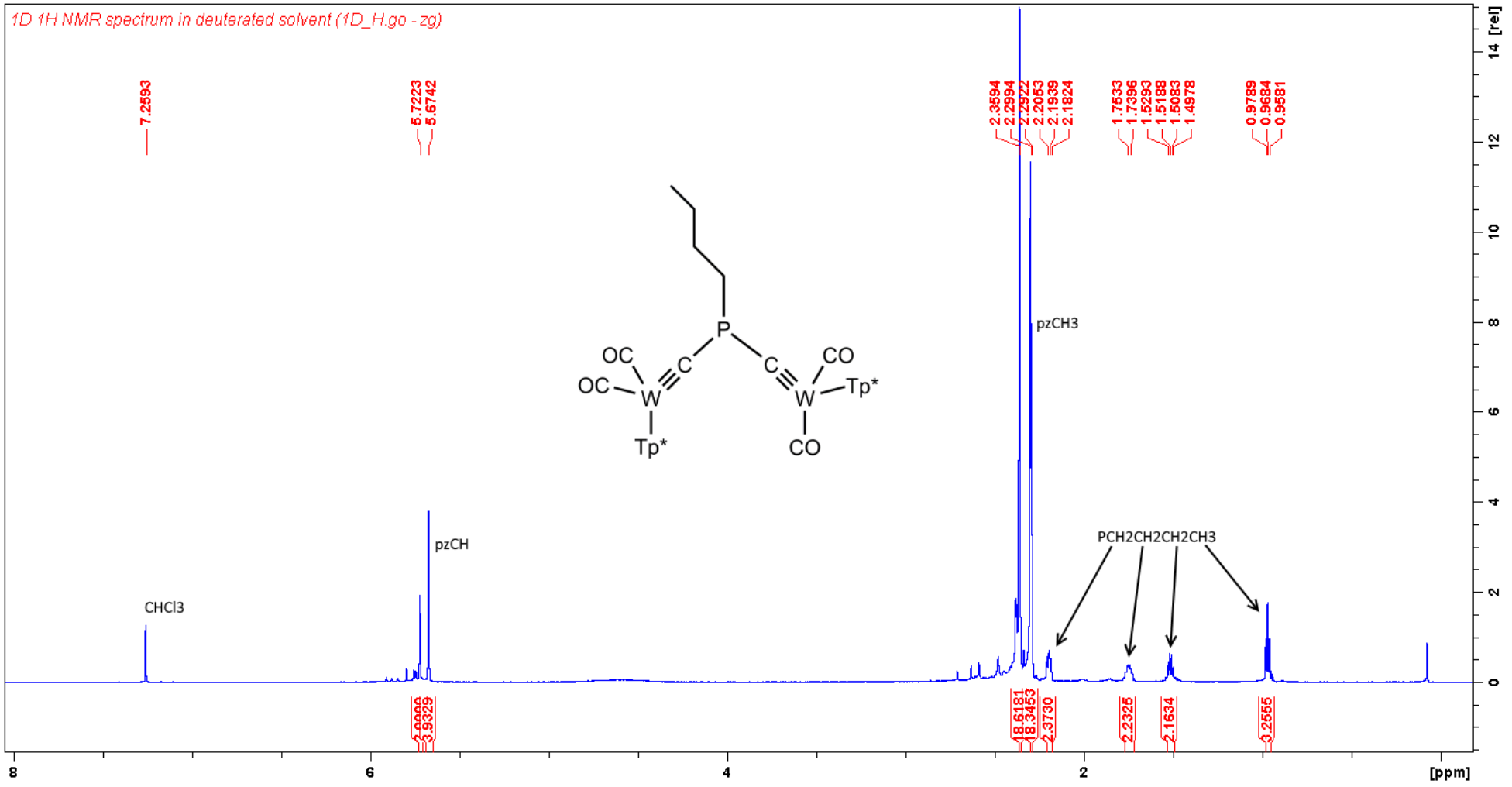
$^{31}P\{^{1}H\}$ NMR of **4**.



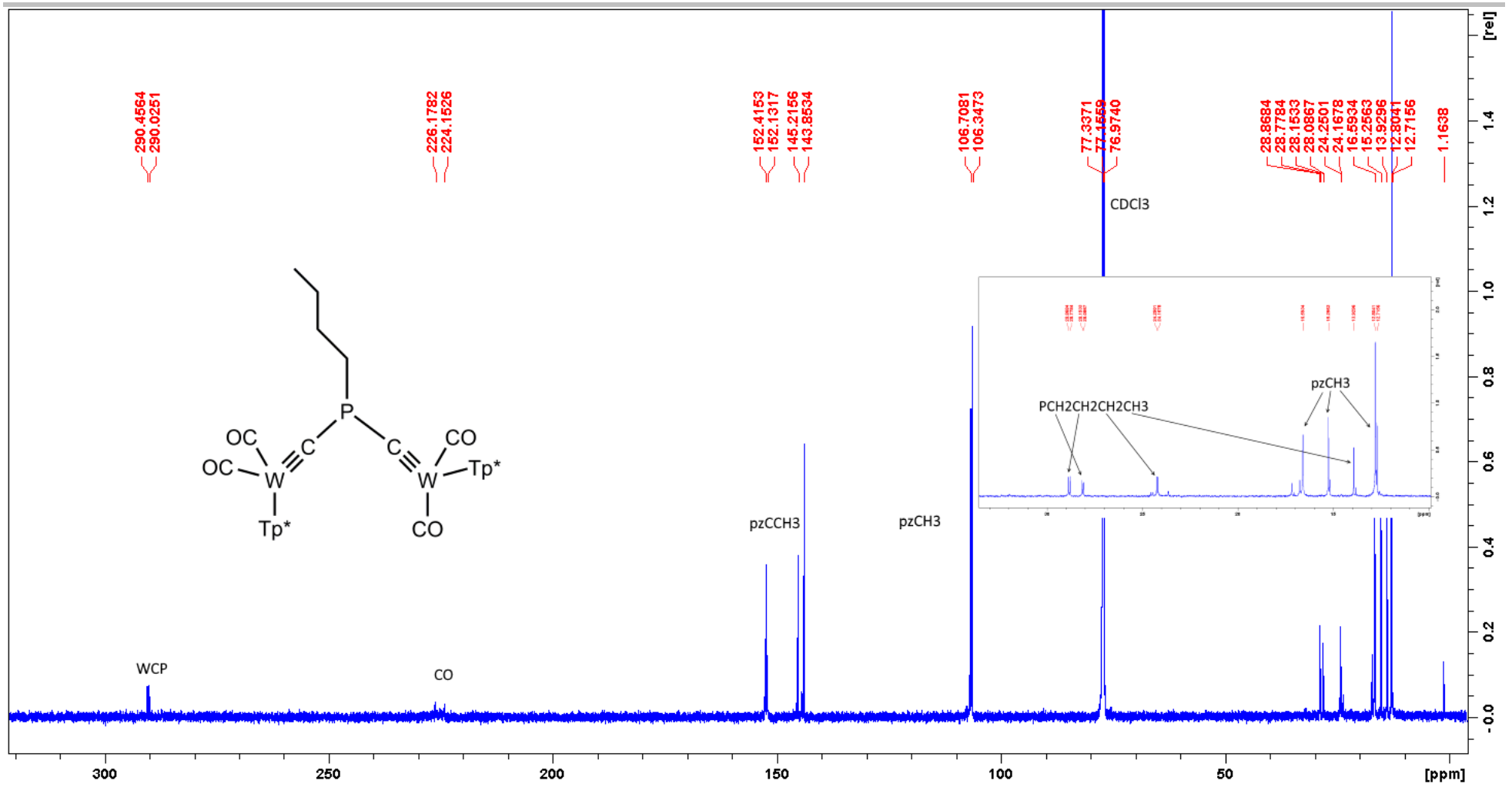
Infrared Spectrum (CH_2Cl_2) of **5**.


0.35
0.30
0.25
0.20
0.15
0.10
0.05
-0.00
-0.02
3975
3500
3000
2500
2000
1500
1287
cm-1
P
C
C
OC
OC
W
Tp*
CO
W
Tp*
CO
1887.84cm-1
1970.87cm-1
1982.29cm-1
1543.66cm-1
1384.08cm-1
1448.19cm-1
1415.57cm-1
1274.02cm-1
2929.90cm-1
2553.06cm-1

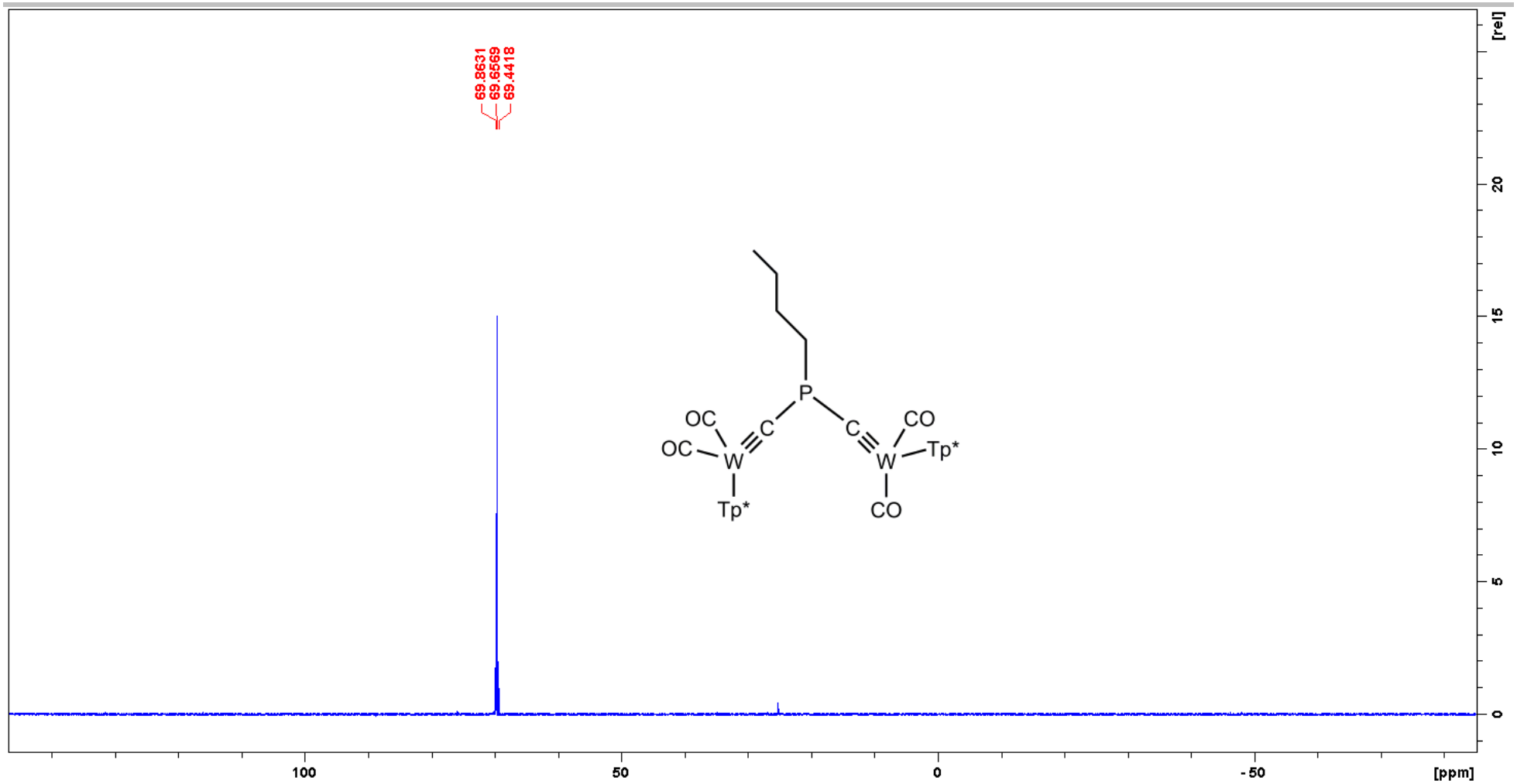
^{1}H NMR of **5**.



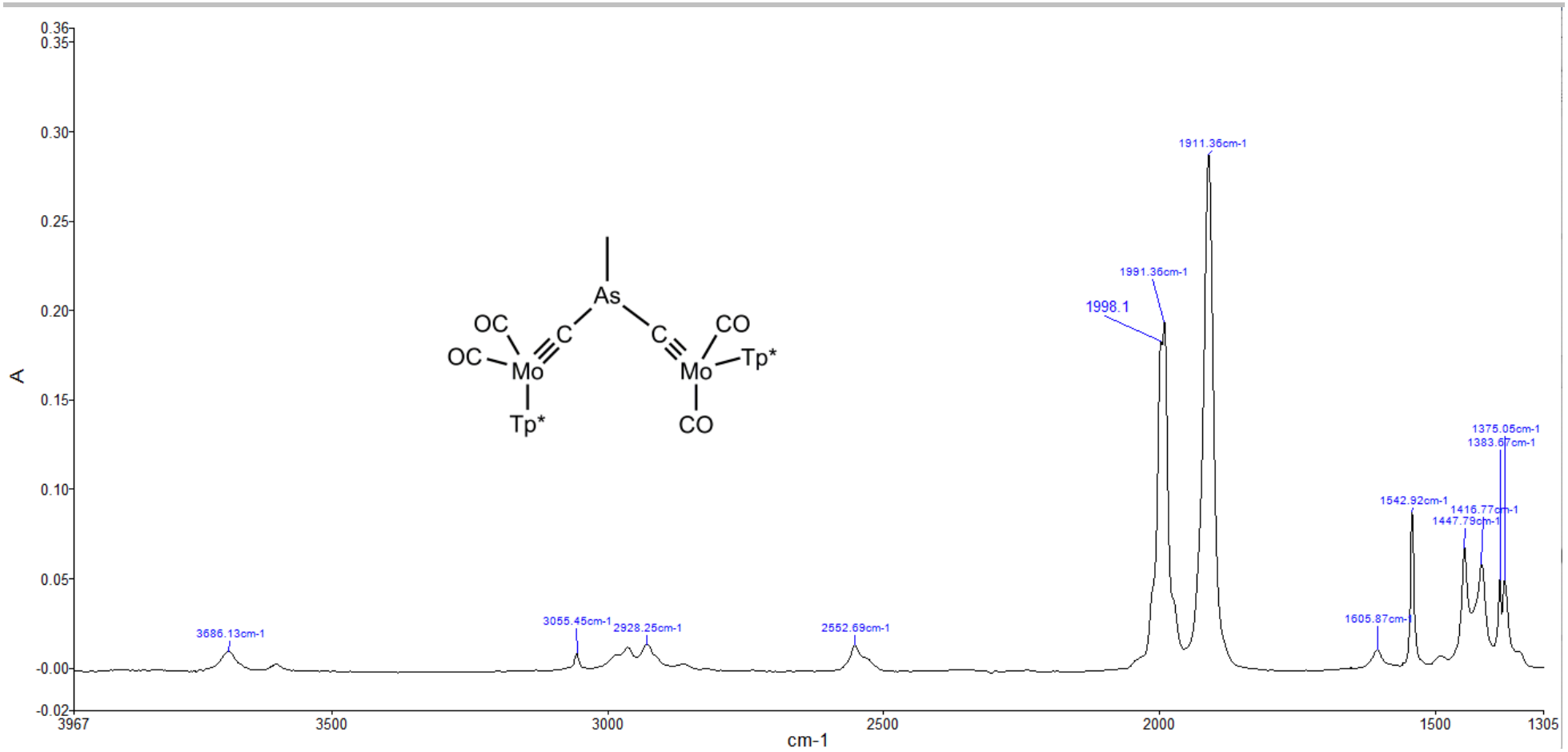
^{13}C{^{1}H} NMR of **5**.



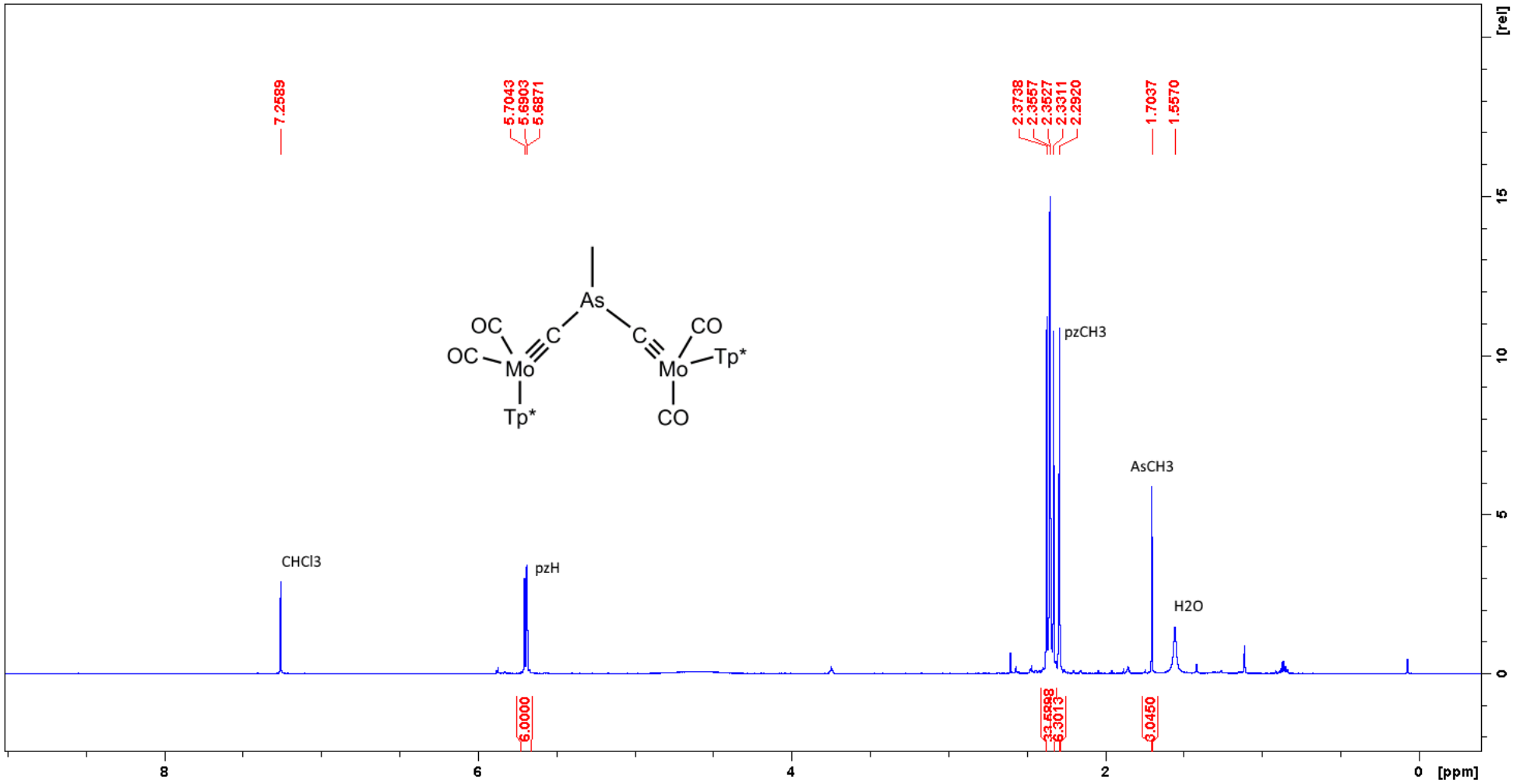
$^{31}P\{^{1}H\}$ NMR of **5**.



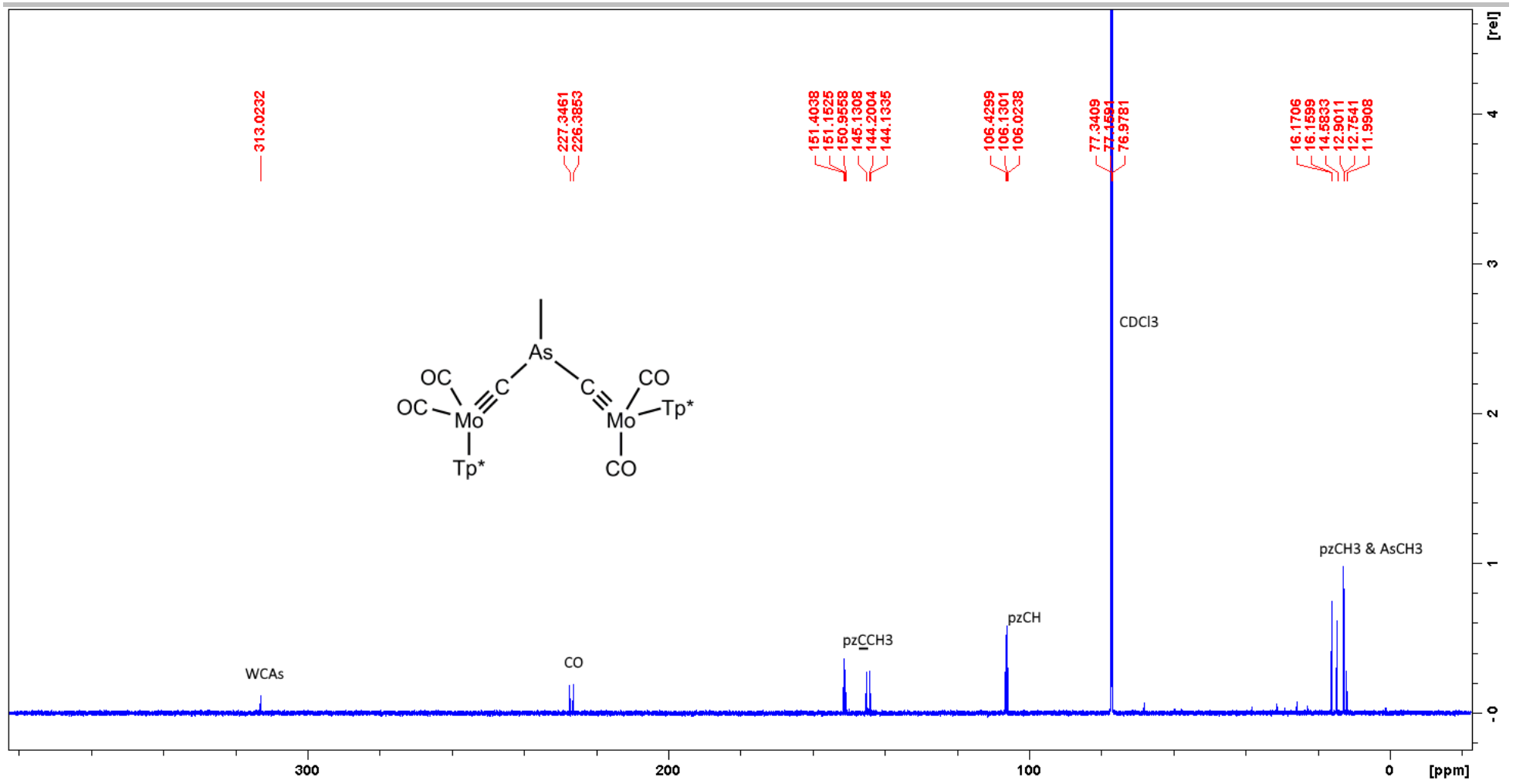
Infrared Spectrum (CH_2Cl_2) of **6a**.


0.36
0.35
0.30
0.25
0.20
0.15
0.10
0.05
-0.00
-0.02
A
3967
3500
3000
2500
2000
1500
1305
cm-1
As
OC
OC
C
C
CO
Mo
Mo
Tp*
Tp*
CO
3686.13cm-1
3055.45cm-1
2928.25cm-1
2552.69cm-1
1998.1
1991.36cm-1
1911.36cm-1
1605.87cm-1
1542.92cm-1
1447.79cm-1
1416.77cm-1
1383.67cm-1
1375.05cm-1

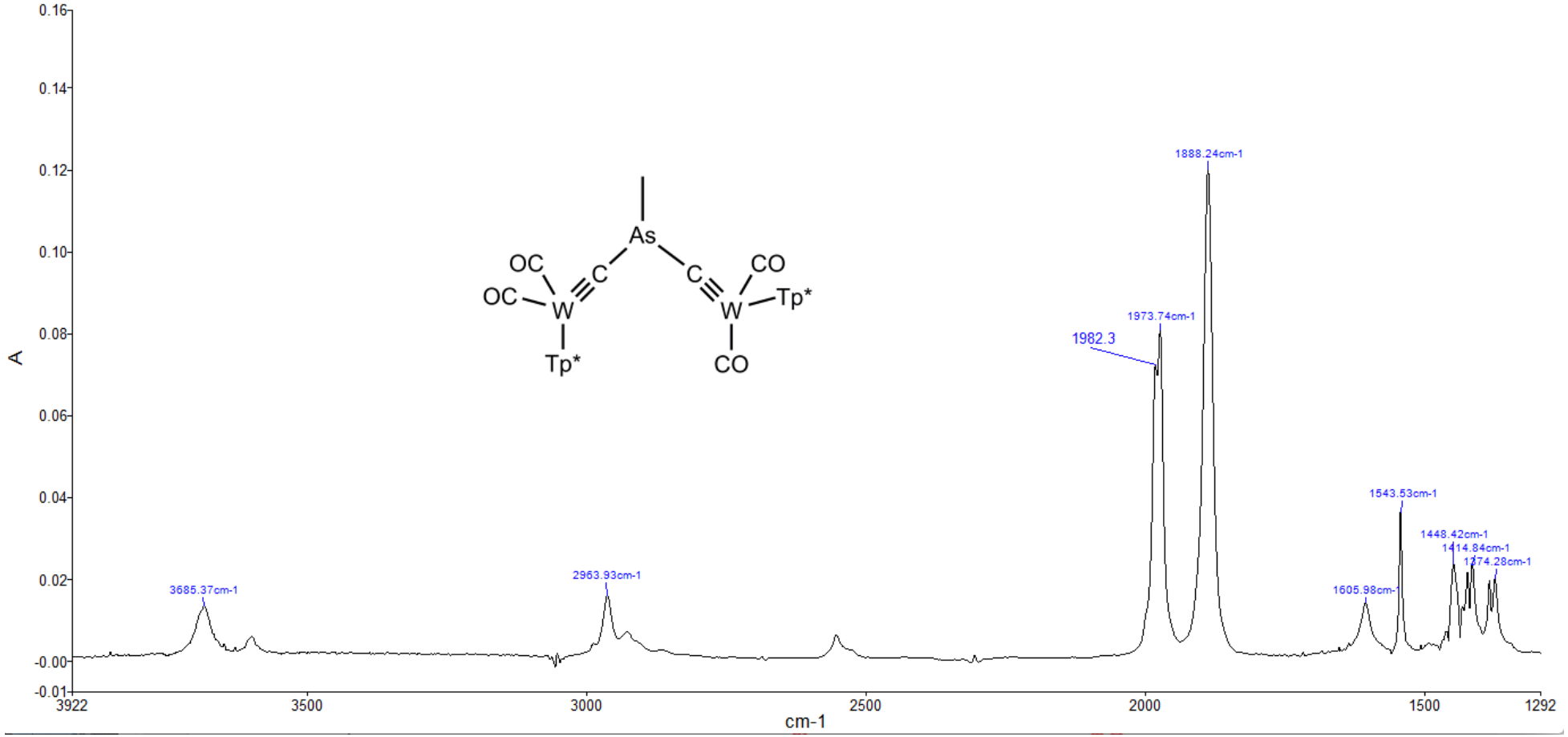
^{1}H NMR of **6a**.



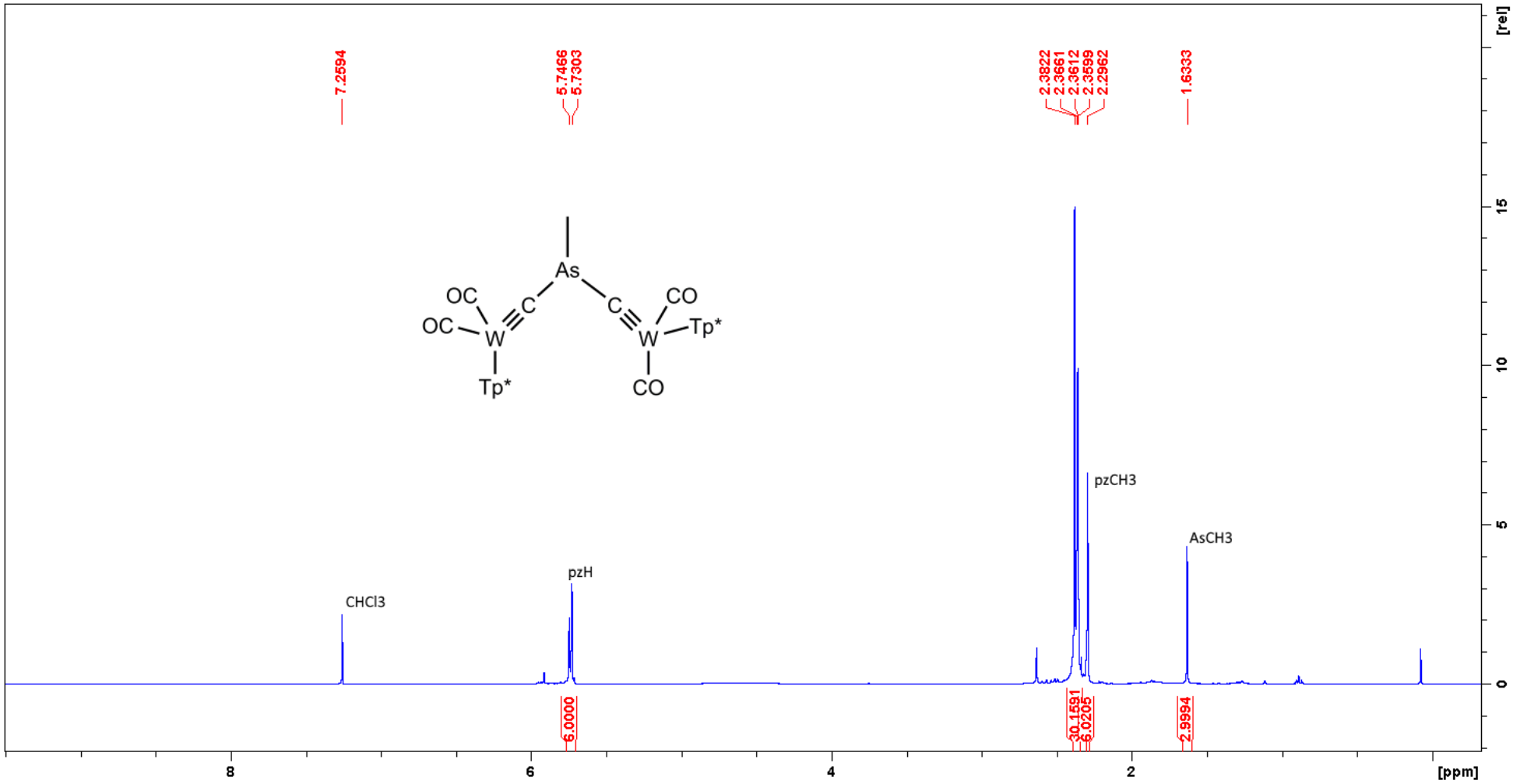
^{13}C{^{1}H} NMR of **6a**.



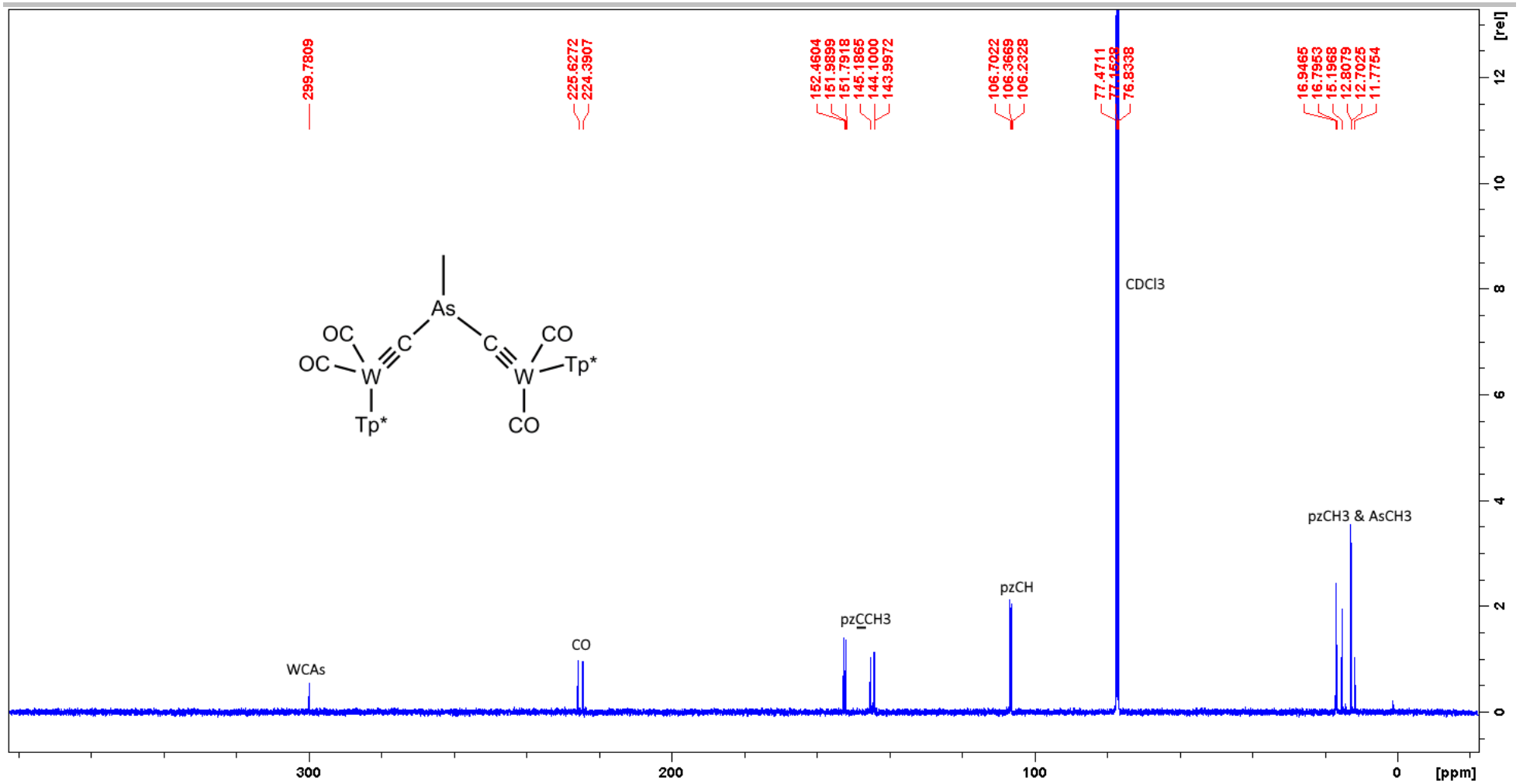
Infrared Spectrum (CH_2Cl_2) of **6b**.


0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
-0.00
-0.01
A
3922
3500
3000
2500
2000
1500
1292
cm-1
As
OC
OC
C
W
Tp*
C
CO
W
Tp*
CO
1888.24cm-1
1973.74cm-1
1982.3
1543.53cm-1
1448.42cm-1
1414.84cm-1
1374.28cm-1
1605.98cm-1
3685.37cm-1
2963.93cm-1

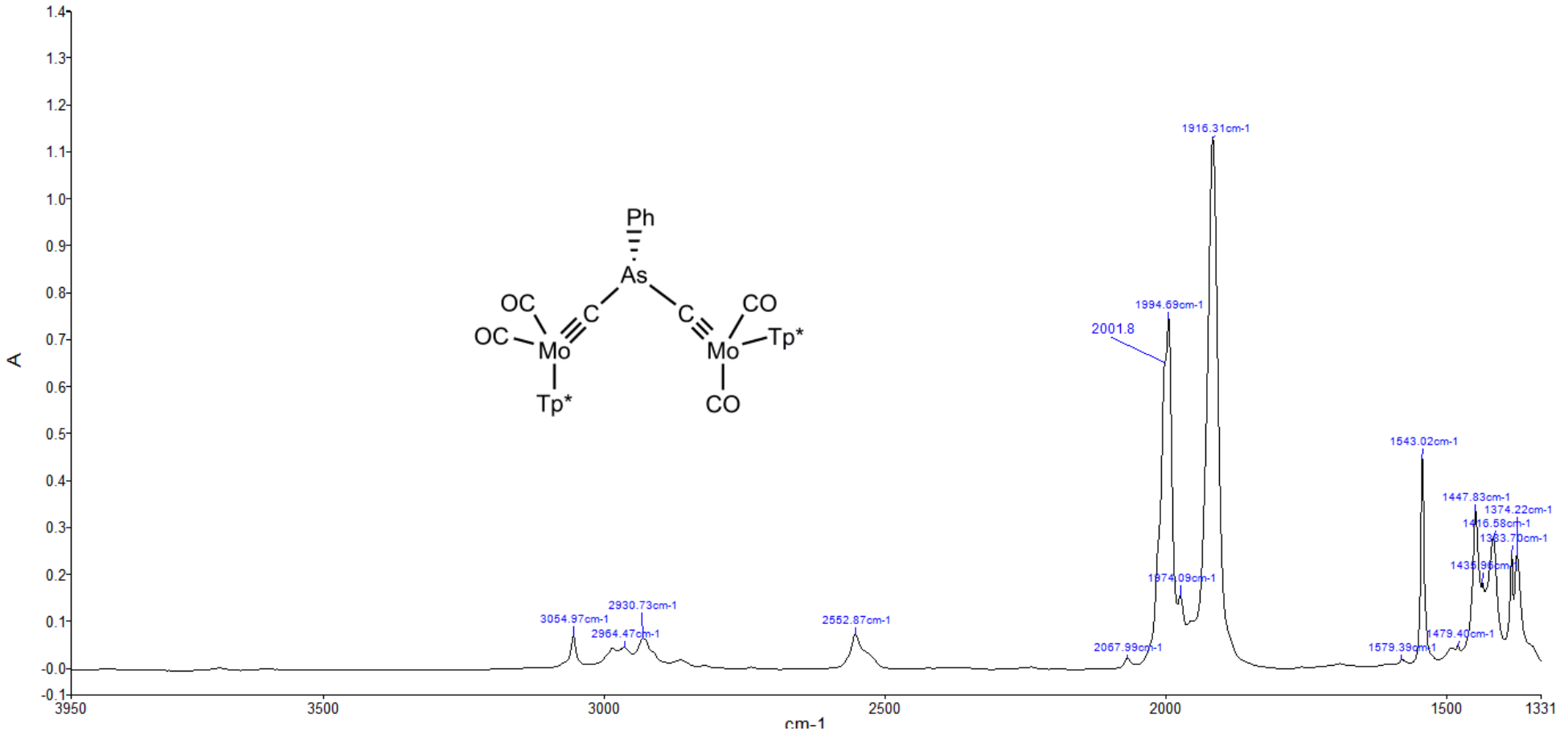
^{1}H NMR of **6b**.



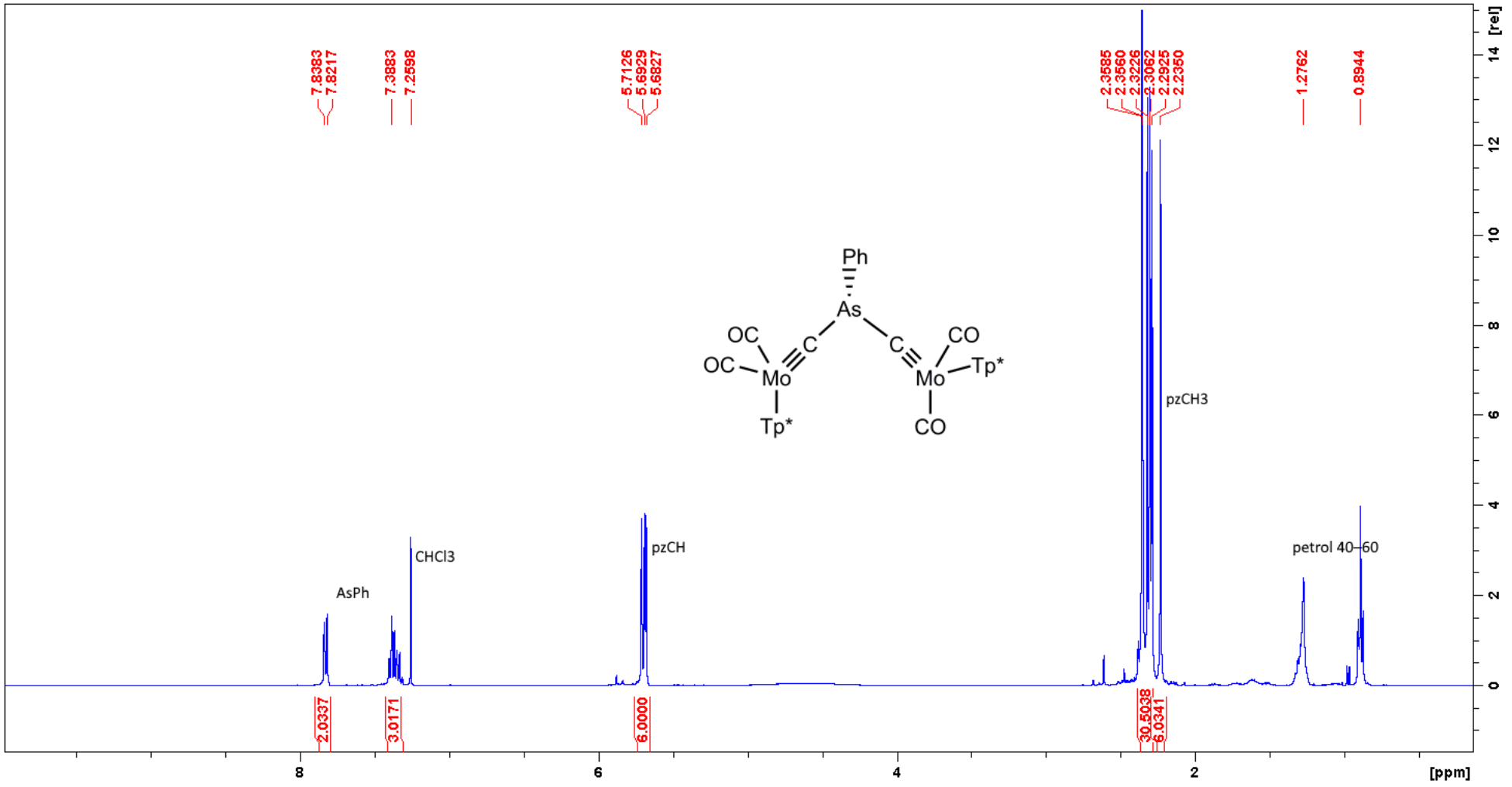
^{13}C{^{1}H} NMR of **6b**.



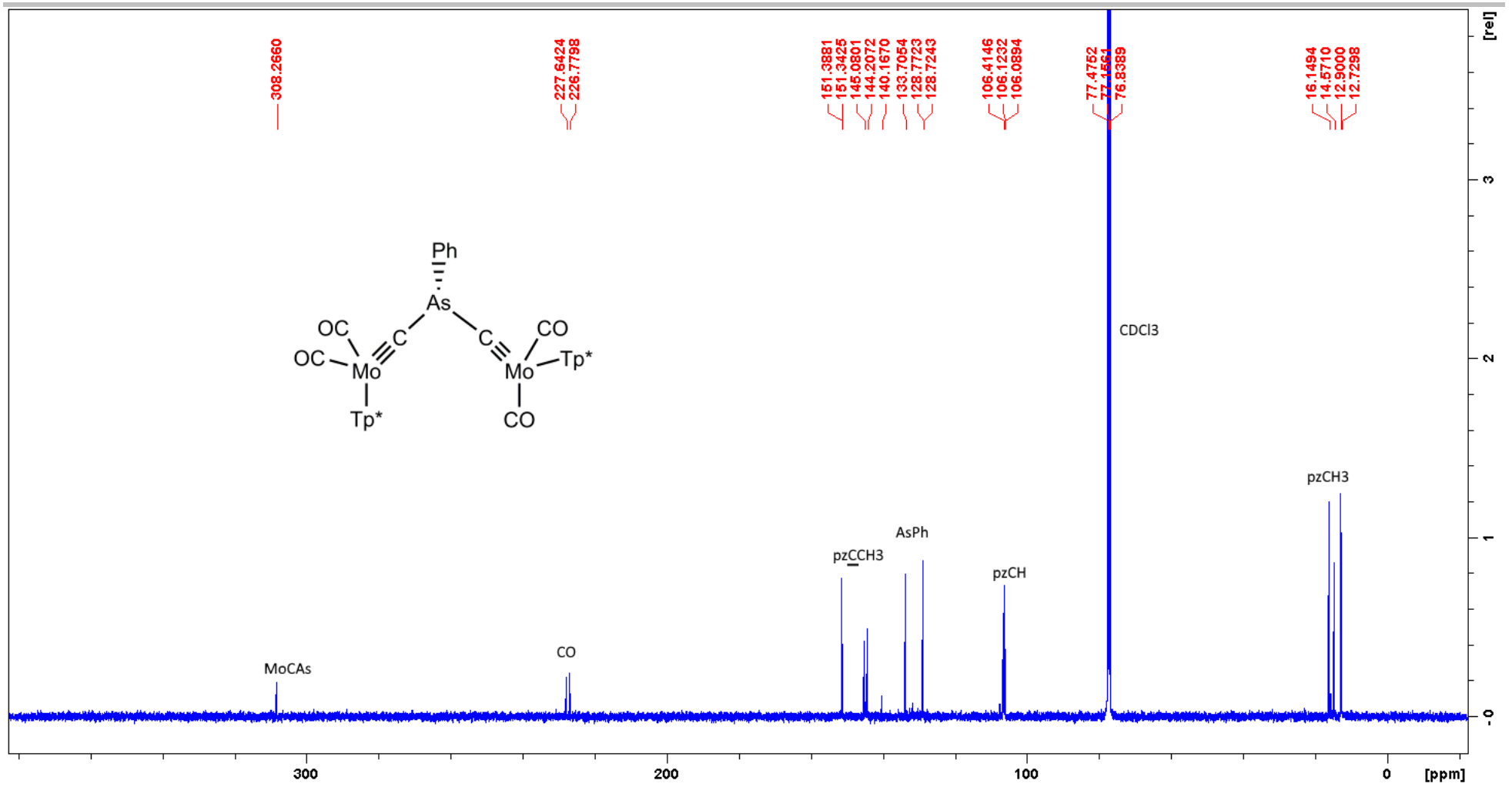
Infrared Spectrum (CH_2Cl_2) of **7a**.


Ph
As
OC
OC
C
C
CO
Mo
Mo
Tp*
Tp*
CO
A
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
-0.0
-0.1
3950
3500
3000
2500
2000
1500
1331
cm-1
1916.31cm-1
1994.69cm-1
2001.8
1543.02cm-1
1447.83cm-1
1374.22cm-1
1416.58cm-1
1383.70cm-1
1435.96cm-1
1974.09cm-1
2930.73cm-1
3054.97cm-1
2964.47cm-1
2552.87cm-1
2067.99cm-1
1579.39cm-1
1479.40cm-1

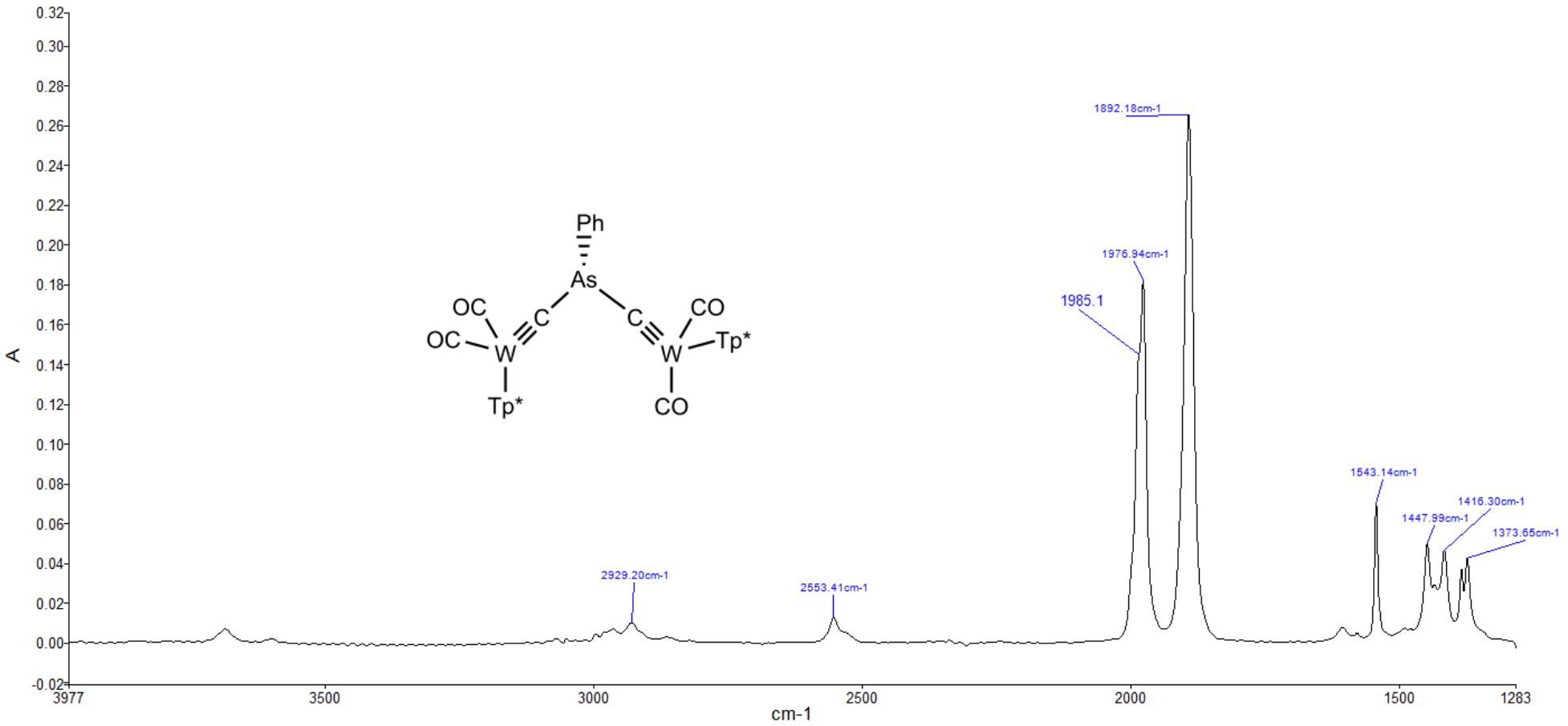
^{1}H NMR of **7a**.



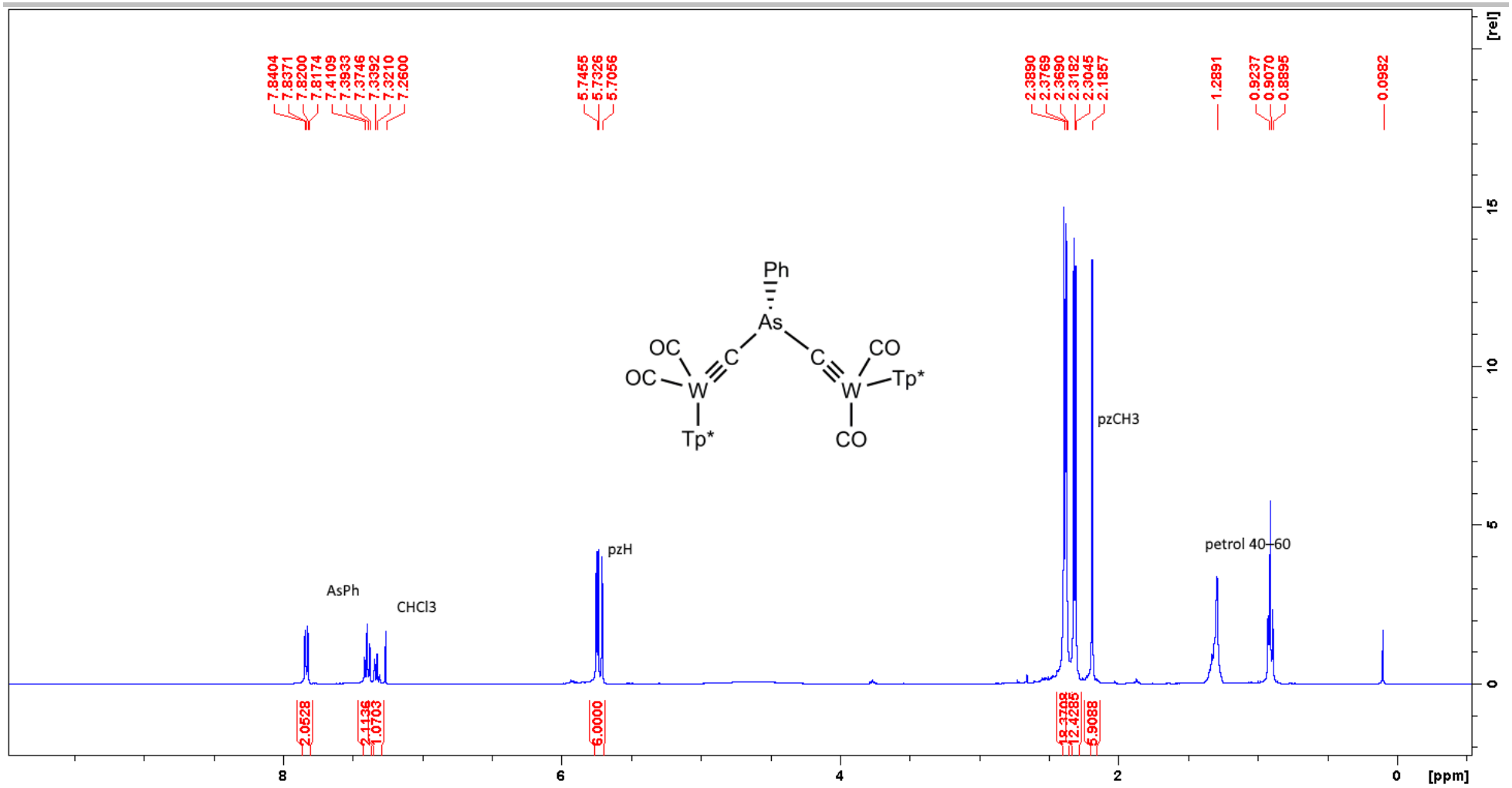
^{13}C{^{1}H} NMR of **7a**.



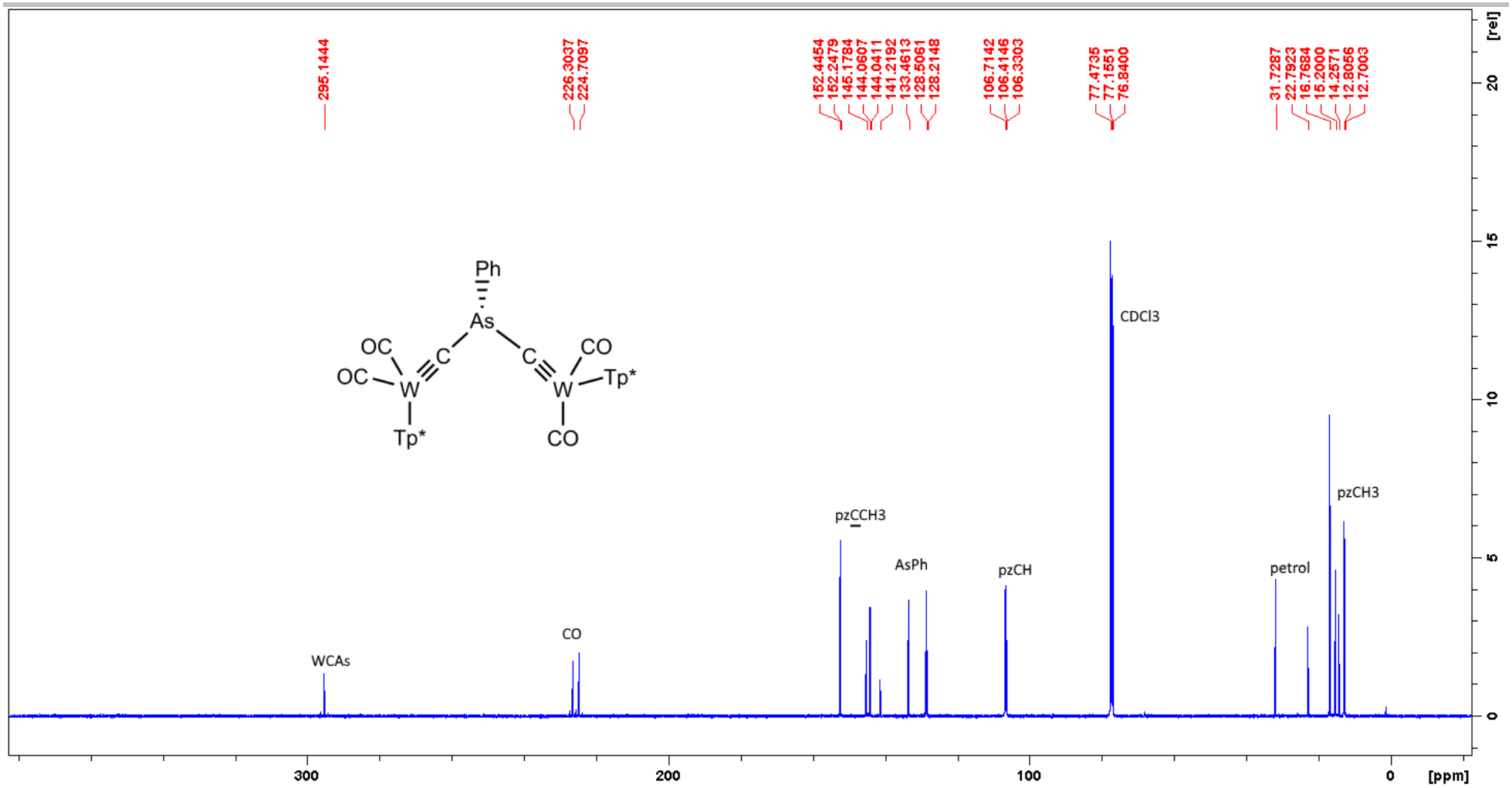
Infrared Spectrum (CH_2Cl_2) of **7b**.


A
cm-1
0.32
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
3977
3500
3000
2500
2000
1500
1283
1892.18cm-1
1976.94cm-1
1985.1
1543.14cm-1
1416.30cm-1
1447.99cm-1
1373.65cm-1
2929.20cm-1
2553.41cm-1
Ph
As
OC
OC
C
C
CO
W
W
Tp*
Tp*
CO

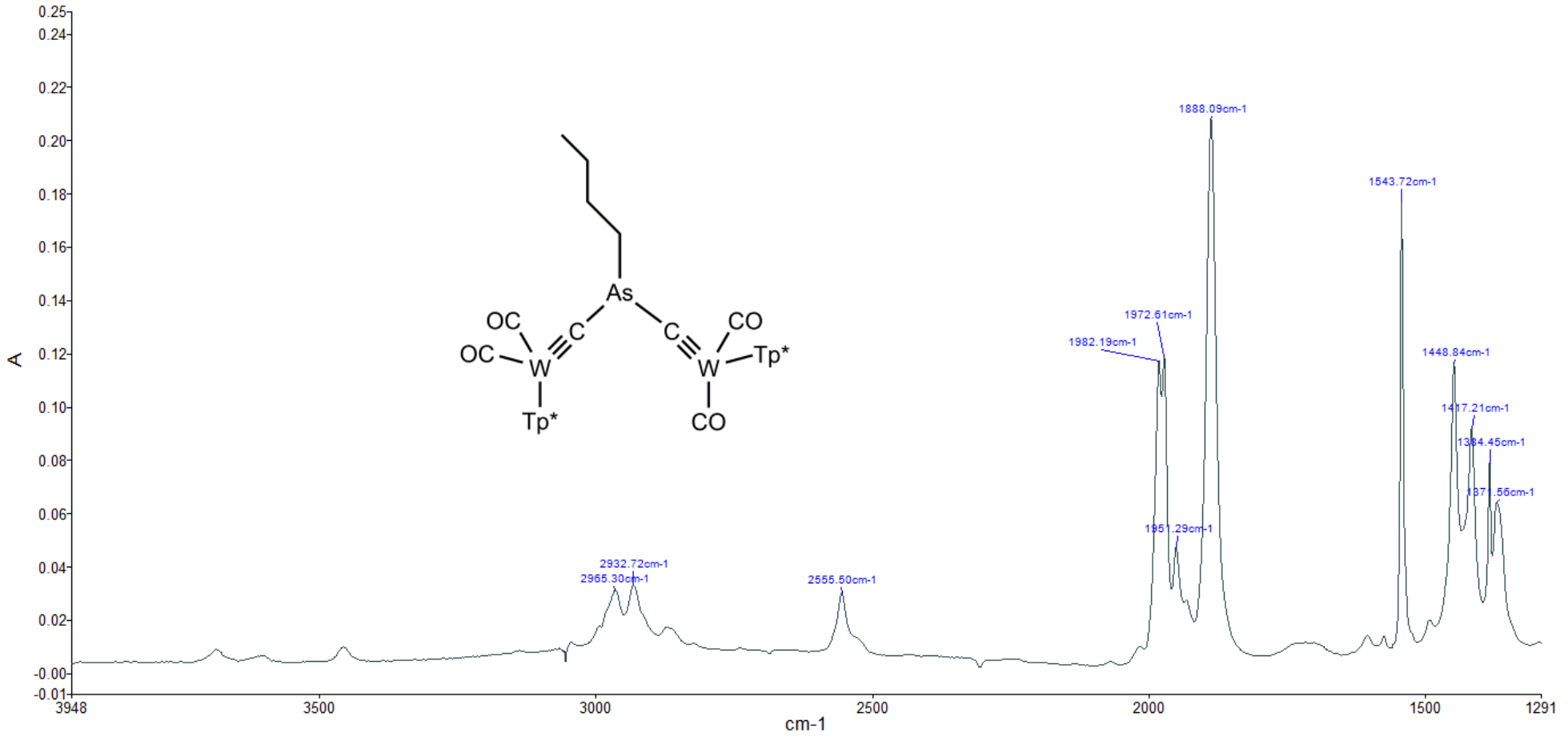
^{1}H NMR of **7b**.



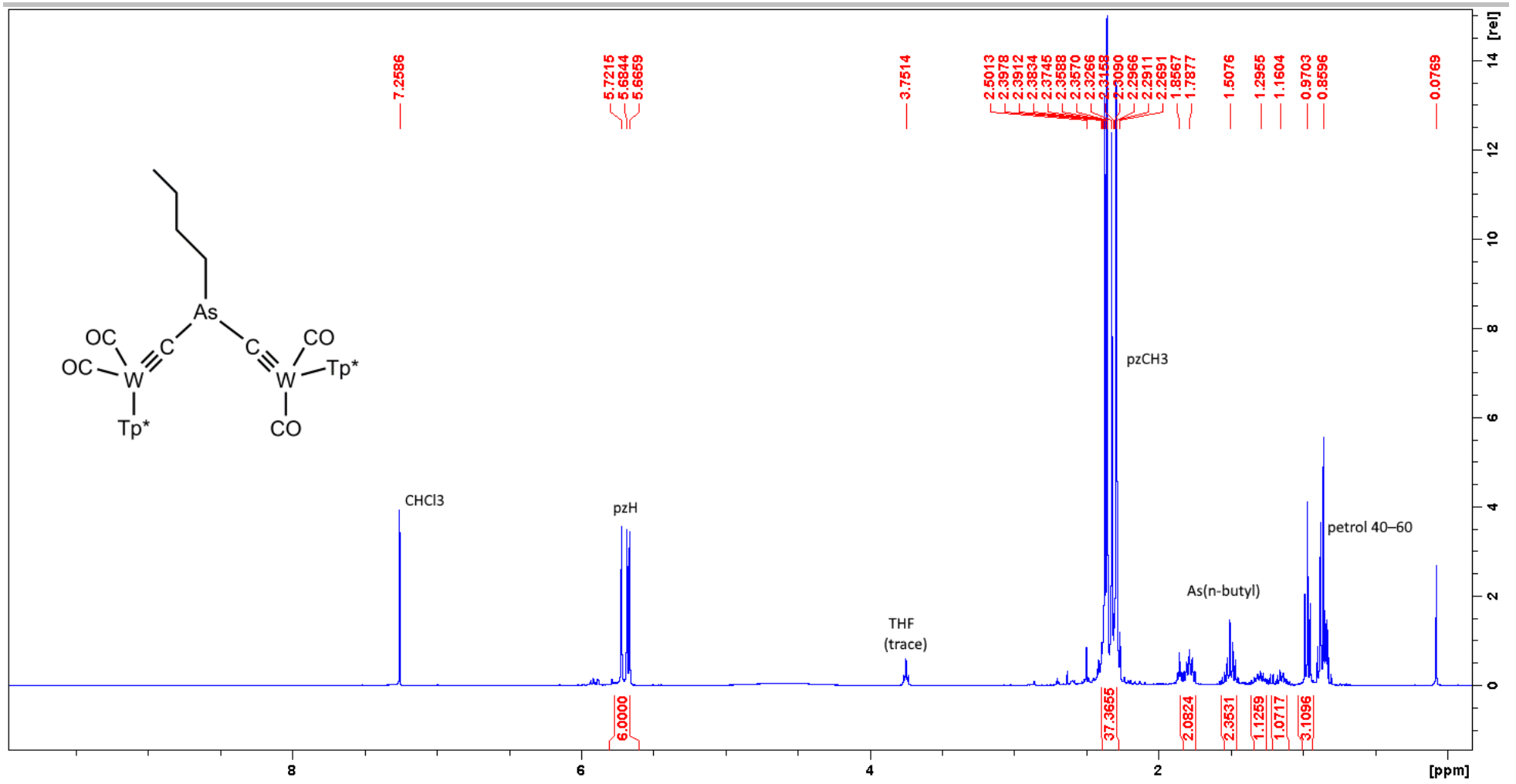
$^{13}C\{^{1}H\}$ NMR of **7b**.



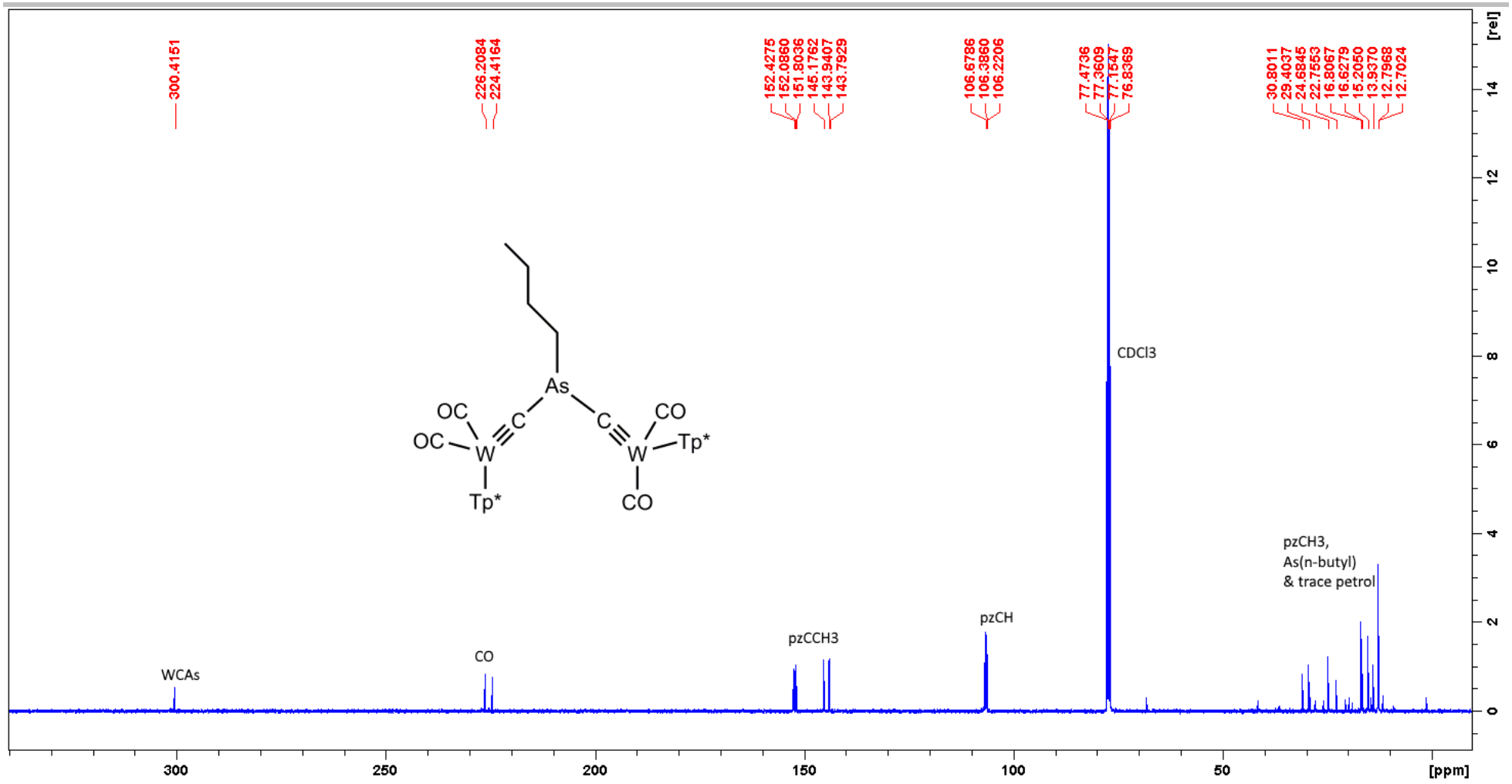
Infrared Spectrum (CH_2Cl_2) of **8**.


A
cm-1
0.25
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
-0.00
-0.01
3948
3500
3000
2500
2000
1500
1291
As
OC
OC
C
W
Tp*
C
CO
W
Tp*
CO
1888.09cm-1
1543.72cm-1
1972.61cm-1
1982.19cm-1
1448.84cm-1
1417.21cm-1
1384.45cm-1
1371.56cm-1
1951.29cm-1
2932.72cm-1
2965.30cm-1
2555.50cm-1

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



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


300.4151
226.2084
224.4164
152.4275
152.0860
151.8036
145.1762
143.9407
143.7929
106.6786
106.3860
106.2206
77.4736
77.3609
77.1547
76.8369
30.8011
29.4037
24.6845
22.7553
16.8067
16.6279
15.2050
13.9370
12.7968
12.7024
CDCl3
pzCH3,
As(n-butyl)
& trace petrol
pzCH
pzCCH3
CO
WCAs
As
OC
OC
C
W
Tp*
C
CO
W
Tp*
CO
[rel]
[ppm]