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Bis(alkylidynyl)telluride and Ditellurides

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Experimental

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 Bruker Avance 400 (^{1}H at 400.1 MHz, ^{13}C{^{1}H} at 100.6 MHz, ^{125}Te{^{1}H} at 126.3 MHz) or Bruker Avance 700 (^{1}H at 700.0 MHz, ^{13}C at 150.9 MHz) spectrometers. Chemical shifts (δ) are reported in ppm and referenced to the solvent peak (^{1}H, ^{13}C) or externally referenced to diphenyl ditelluride (^{125}Te, $\delta_{Te} = 422$), 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 hydridotris(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] A summary of the X-ray crystal structure data for compounds all compounds described in this work is provided in Table S1. 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,[2,3] or with the CRYSTALS software.[4] Hydrogen atoms were located geometrically and refined using a riding model. Diagrams were produced using the CCDC visualisation program Mercury.[5,6]

The complexes [Mo(≡CBr)(CO)$_2$(Tp*)] (**1a**) and [W(≡CBr)(CO)$_2$(Tp*)] (**1b**) have been described previously.[6-8]

Synthesis of [Et$_4$N][Mo(≡CTe)(CO)$_2$(Tp*)] Et$_4$N[**2a**]

This salt has been described previously[6] from the reaction of the chlorocarbyne complex [Mo(≡CCl)(CO)$_2$(Tp*)] and an aqueous/methanol solution of 'Na$_2$Te' however, no experimental details were provided and only limited spectroscopic data (ν_{CO}, ν_{CTe}) were reported. The following high yield synthesis involves anhydrous conditions and the use of Li$_2$Te. Further charactersational data are also included

To a solution of elemental tellurium (59.1 mg, 0.463 mg.atom) in THF (5 mL) at –78 °C was added lithium triethylborohydride (463 µL, 1.0 M in THF, 0.46 mmol). The mixture was stirred at reduced temperature for 1 h before being warmed to room temperature and stirred for a further 1 h. After this time the solution was transferred by cannula into a solution of **1a** (250 mg, 0.463 mmol) in THF (10 mL) at –78 °C. The mixture was warmed to room temperature and stirred for 1 h, during which time the mixture turned light brown. After this time, Et$_4$NBr (97.3 mg, 0.463 mmol) was added as a solid and the mixture was stirred for 4 h, during which time a yellow precipitate formed. The precipitate was collected by filtration, washed with THF (3 x 10 mL), deionized water (3 x 10 mL) and diethyl ether (5 x 10 mL), and dried in vacuo to give pure Et$_4$N[**2a**] (268 mg, 0.373 mmol, 81%) as a yellow (sometimes yellow-green) solid. IR (CH$_2$Cl$_2$, cm^{-1}): 1927s, 1843s ν_{CO}. 1925s, 1840s ν_{CO}, 952s ν_{CTe} ^{1}H NMR (400 MHz, DMSO-d_6, 298 K, δ): 1.15 (t, $^3J_{HH}$ = 7.2 Hz, 12 H, CH$_2$C*H$_3$*), 2.22 [s, 6 H, pz(C*H$_3$*)], 2.28 [s, 6 H, pz(C*H$_3$*)], 2.62 [s, 6 H, pz(C*H$_3$*)], 3.19 (q, $^3J_{HH}$ = 6.9 Hz, 8 H, NC*H$_2$*), 5.70 (s, 1 H, pz*H*), 5.83 (s, 2 H, pz*H*). Satisfactory ^{13}C{^{1}H} NMR have not been acquired due to the very poor solubility in a range of common deuterated organic solvents. ^{125}Te NMR (126 MHz, DMSO, 298 K, δ): 1248. MS (ESI, –ve ion, *m/z*): Calcd for $C_{18}H_{22}N_6O_2BMoTe$ [M – NEt$_4$]$^-$: 589.0007. Found: 589.0003. Anal. Calcd for $C_{26}H_{42}N_7O_2BMoTe$: C, 43.43; H, 5.89; N, 13.46%. Found: C, 41.65; H, 6.02; N, 13.57%.

Synthesis of [Et$_4$N][W(≡CTe)(CO)$_2$(Tp*)] Et$_4$N[**2b**]

To a solution of **1b** (100 mg, 0.159 mmol) in THF (10 mL) was added Li$_2$Te (2.02 mL, 0.078 M in THF, 0.158 mmol, prepared as described above) and the resulting mixture was stirred at room temperature overnight, during which time the solution turned light brown. After this time, Et$_4$NBr (33.6 mg, 0.160 mmol) was added as a solid and the mixture stirred at 0 °C for 4 h, during which time a yellow precipitate formed. The solvent was removed by cannula filtration and the precipitate was collected by filtration, washed with deionized water (2 x 10 mL) and diethyl ether (5 x 10 mL), and dried in vacuo to give pure **2b** (109 mg, 0.135 mmol, 85%) as a yellow (sometimes yellow-green) solid. A crystal suitable for X-ray crystallographic analysis was grown by slow evaporation of an acetonitrile solution at –20 °C.

IR (CH$_2$Cl$_2$, cm^{-1}): 1978, 1891 ν_{CO}. (KBr, cm^{-1}): 1971, 1885 ν_{CO}. 1912s, 1923s ν_{CO}, 982s $\nu_{CTe.}$ ^{1}H NMR (600 MHz, CD$_3$CN, 298 K, δ): 1.18 (t, $^3J_{HH}$ = 7.2 Hz, 12 H CH$_2$C*H$_3$*), 2.31 [s, 3 H, pz(C*H$_3$*)], 2.37 [s, 3 H, pz(C*H$_3$*)], 2.37 [s, 6 H, pz(C*H$_3$*)], 2.77 [s, 6 H, pz(C*H$_3$*)], 3.10 (q, $^3J_{HH}$ = 7.2 Hz, 8 H, NC*H$_2$*), 5.73 (s, 1 H, pz*H*), 5.86 (s, 2 H, pz*H*). ^{13}C{^{1}H} NMR (150 MHz, CD$_3$CN/toluene-d_6, 298 K, δ): 7.6 (CH$_2$CH$_3$), 12.7 12.8 15.6 16.5 (pzCH$_3$), 52.9 (N*C*H$_2$), 106.6, 106.8 [*C*^{4}(pz)], 145.0 145.9 152.7 153.8 [*C*^{3,5}(pz)], 227.7 (*C*O), 302.3 (W≡*C*Te). Low solubility precluded the measurement of $^1J_{WC}$ or $^1J_{TeC}$. This resonance is tentatively attributed to the tellurocarbonyl ligand, however it is to higher frequency than might be expected and is unusually broad when compared to the rest of the spectrum. We suggest that this reflects a dynamic process that possibly involves the solvent or ion pairing, in which case the apparent chemical shift may well represent a weighted average. In any event, the assignment of this resonance should be taken as speculative. CD_3CN. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K, δ): 1.24 (t, 12 H, CH_2CH_3), 2.30 [s, 3 H, pz(CH_3)], 2.34 [s, 3 H, pz(CH_3)], 2.36 [s, 6 H, pz(CH_3)], 2.76 [s, 6 H, pz(CH_3)], 3.24 (q, 8 H, NCH_2), 5.71 (s, 1 H, pzH), 5.85 (s, 2 H, pzH). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, 298 K, δ): 12.5, 12.6, 15.4, 16.3 ($pzCH_3$), 106.3, 106.6 [C(pz)], 144.8, 145.7, 152.5, 153.6 [C(pz)], 227.5 (CO), 302.3 (CTe). ^{125}Te NMR (126 MHz, CD_3CN, 298 K, δ): 1031. MS (ESI, –ve ion, *m/z*): Calcd for $C_{18}H_{22}BN_6O_2TeW$ $[M - NEt_4]^-$: 677.0460. Found: 677.0466. Anal. Calcd for $C_{26}H_{42}BN_7O_2TeW$: C, 38.70; H, 5.25; N, 12.15%. Found: C, 38.64; H, 5.12; N, 12.06%.

Formation of [W(≡CTeLi)(CO)$_2$(Tp*)] *in situ* Li[**2b**].

A yellow solution of [W(≡CBr)(CO)$_2$(Tp*)] (**1b**: 0.472 g, 0.795 mmol) in tetrahydrofuran (20 mL) was treated with Li_2Te in tetrahydrofuran (0.048 M, 16.69 mL,0.799 mmol) and was stirred for 17 hours to yield a clear dark brown solution of [W(≡CTeLi)(CO)$_2$(Tp*)] Li[**2b**]. IR (KBr, cm^{-1}): 1969, 1879 ν_{CO}. IR (THF, cm^{-1}): 1906, 1819 ν_{CO}. ^{1}H NMR (600 MHz, acetone-d_6, 298 K, δ): 2.41 [s, 3 H, pz(CH_3)], 2.42 [s, 3 H, pz(CH_3)], 2.48 [s, 6 H, pz(CH_3)], 2.86 [s, 6 H, pz(CH_3)], 5.85 (s, 1 H, pzH), 5.97 (s, 2 H, pzH). $^{13}C\{^1H\}$ NMR (150 MHz, acetone-d_6, 298 K, δ): 34.6, 34.7, 35.6, 35.8 [C^4(pz)], 125.7, 125.9 [C^4(pz)], 164.2, 165.1, 171.9, 173.0 [$C^{3,5}$(pz)], 246.9 (CO), 322.9 (CTe).

Synthesis of Mo(≡CTe^{n}Bu)(CO)$_2$(Tp*) **3a**

To a solution of tellurium (35.4 mg, 0.277 mmol) in THF (5 mL) at –78 °C was added *n*BuLi (173 uL, 1.6 M in hexanes, 0.277 mmol) and the mixture was stirred at this temperature for 30 min. After this time, the solution was transferred by cannula into a solution of **1a** (100 mg, 0.185 mmol) in THF (5 mL) at –78 °C, causing the initially yellow solution to turn dark green. Stirring was continued for 30 min at reduced temperature before the solution was warmed to room temperature and the solvents removed in vacuo. The residue was subjected to column chromatography (10 x 1 cm silica gel column), eluting first 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 to afford pure **3a** (89.1 mg, 0.138 mmol, 75%) as orange microcrystals. IR (CH_2Cl_2, cm^{-1}): 1992s, 1908s ν_{CO}. ^{1}H NMR (400 MHz, $CDCl_3$, 278 K, δ): 0.96 (t, $^3J_{HH}$ = 7.9 Hz, 3 H, CH_2CH_3), 1.44 (sextet, $^3J_{HH}$ = 7.6 Hz, 2 H, CH_2CH_3), 1.98 (q, $^3J_{HH}$ = 7.6 Hz, 2 H, $TeCH_2CH_2$), 2.31 [s, 3 H, pz(CH_3)], 2.36 [s, 9 H, pz(CH_3)], 2.59 [s, 6 H, pz(CH_3)], 3.16 (t, $^3J_{HH}$ = 7.6 Hz, 2 H, $TeCH_2$), 5.71 (s, 1 H, pz*H*), 5.86 (s, 2 H, pz*H*). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 278 K, δ): 12.2 ($TeCH_2$), 12.8 12.8 ($pzCH_3$), 13.5 (CH_2CH_3), 14.7 16.0 ($pzCH_3$), 25.2 (CH_2CH_3), 34.6 ($TeCH_2CH_2$), 106.4 106.5 [C^4(pz)], 144.6 145.2 151.4 151.6 [$C^{3,5}$(pz)], 226.5 (CO), 267.7 (Mo≡*C*Te). $^{125}Te\{^1H\}$ NMR (126 MHz, $CDCl_3$, 298 K, δ): 908. MS (ESI, +ve ion, *m/z*): Calcd for $C_{22}H_{31}N_6O_2BMoTe$ $[M+H]^+$: 649.0778. Found: 649.0763. Anal. Calcd for $C_{22}H_{31}N_6O_2BMoTe$: C, 40.91; H, 4.84; N, 13.01%. Found: C, 40.84; H, 4.75; N, 13.02 %.

Synthesis of W(≡CTe^{n}Bu)(CO)$_2$(Tp*) (**3b**)

Method a. To a solution of tellurium (30.4 mg, 0.239 mg.atom) in THF (5 mL) at –78 °C was added *n*BuLi (149 μL, 1.6 M in hexanes, 0.239 mmol) and the mixture was stirred at reduced temperature for 30 min. After this time, the solution was transferred by cannula into a solution of **1b** (100 mg, 0.159 mmol) in THF (5 mL) at –78 °C, causing the initially yellow solution to turn dark green-brown. Stirring was continued for 30 min at reduced temperature before the solution was warmed to room temperature and the solvents removed in vacuo. The residue was then subjected to column chromatography (10 x 3 cm silica gel column), eluting first 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 to afford pure **3b** (87.9 mg, 0.120 mmol, 75%) as orange microcrystals.

Method b. A yellow solution of **1b** (0.200 g, 0.318 mmol) in tetrahydrofuran (20 mL) was cooled to –78 °C for 10 minutes and then treated with *n*BuLi in hexane (2.50 M, 0.17 mL, 0.425 mmol) and left to stir for 15 minutes. Elemental tellurium (0.046g, 0.361 mmol) was added to the cooled yellow solution via a solid addition tube. The mixture was allowed to warm up slowly with stirring. The mixture was left to react overnight to provide a clear brown solution. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (–40 °C), firstly eluting with 500 mL of hexane and finally eluting with hexane/dichloromethane (9:2) to afford a yellow band that was collected to provide a microcrystalline powder after the solvent was removed under reduced pressure. Yield (0.206 g, 0.280 mmol, 88%). IR (CH_2Cl_2, cm^{-1}): 1976, 1886 ν_{CO}. (KBr, cm^{-1}): 1969, 1880 ν_{CO}. (THF, cm^{-1}): 1971, 1885 ν_{CO}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, δ): 0.94 (t, $^3J_{HH}$ = 7.9 Hz, 3 H, CH_2CH_3), 1.42 (sextet, $^3J_{HH}$ = 7.4 Hz, 2 H, CH_2CH_3), 1.95 (q, $^3J_{HH}$ = 7.6 Hz, 2 H, $TeCH_2CH_2$), 2.30 [s, 3 H, pz(CH_3)], 2.34 [s, 6 H, pz(CH_3)], 2.39 [s, 3 H, pz(CH_3)], 2.59 [s, 6 H, pz(CH_3)], 3.11 (t, $^3J_{HH}$ = 7.6 Hz, 2 H, $TeCH_2$), 5.74 (s, 1 H, pz*H*), 5.89 (s, 2 H, pz*H*). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 278 K, δ): 10.5 ($TeCH_2$), 12.7 12.8 (s, $pzCH_3$), 13.6 (CH_2CH_3), 15.4 16.7 ($pzCH_3$), 25.2 (CH_2CH_3), 34.7 ($TeCH_2CH_2$), 106.6 106.8 [C^4(pz)], 144.5 145.4 152.2 152.7 [$C^{3,5}$(pz)], 224.6 (*C*O, $^1J_{CW}$ = 169.7 Hz), 252.0 (W≡*C*Te). $^{125}Te\{^1H\}$ NMR (126 MHz, $CDCl_3$, 278 K, δ): 756. MS (ESI, +ve ion, *m/z*): Calcd for $C_{22}H_{32}N_6O_2BWTe$ $[M + H]^+$: 735.1251. Found: 735.1252. Anal. Calcd for $C_{22}H_{31}BN_6O_2MoTe.CHCl_3$: C, 36.10; H, 4.21; N, 10.98%. Found: C, 36.14; H, 4.31; N, 11.39 %.

Synthesis of Mo(≡CTeMe)(CO)$_2$(Tp*) **4a**.

This synthesis of this complex has been described previously, via the reaction of [Mo(≡CLi)(CO)$_2$(Tp*)] with tellurium and iodomethane.[8] The following procedure provides comparable yields.

To a solution of tellurium (35.4 mg, 0.277 mg.atom) in THF (5 mL) at –78 °C was added MeLi (173 μL, 1.6 M in diethyl ether, 0.277 mmol) and the mixture was stirred at reduced temperature for 1 h. After this time, the solution was transferred by cannula into a solution of **1a** (100 mg, 0.185 mmol) in THF (5 mL) at –78 °C, causing the initially yellow solution to turn bright orange. The mixture was slowly warmed to room temperature and stirring was continued for 1 h. The solvents were then removed in vacuo and the residue was subjected to column chromatography (10 x 3 cm silica gel column), eluting first 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 to afford pure **4a** (96.6 mg, 0.160 mmol, 86%) as an orange solid. The characterization data for this species matched those reported in the literature.[8]

Synthesis of W(≡CTeMe)(CO)$_2$(Tp*) **4b**

Method a. A solution of **1b** (0.050 g, 0.0795 mmol) in tetrahydrofuran (20 mL) was treated with a solution of Li_2Te in tetrahydrofuran (0.047 M, 1.89 mL, 0.089 mmol) and was left to stir for 17 hours to yield a clear dark brown solution of Li[**2b**] (*vide supra*). To the brown solution 1 drop of MeI (excess) was added and the mixture was left to stir for 17 hours turning the solution slightly red. The solvent was concentrated to a few mL under reduced pressure. Hexane was then added to the concentrate which was left to stand for a 24 hours producing microcrystals of **4b**. The crystals were washed with ether and hexane. Yield 0.0397g (0.057 mmol, 72%).

Method b. To a solution of tellurium (30.4 mg, 0.239 mg.atom) in THF (5 mL) at –78 °C was added MeLi (149 μL, 1.6 M in diethyl ether, 0.239 mmol) and the mixture was stirred at reduced temperature for 1 h. After this time, the solution was transferred by cannula into a solution of **1b** (100 mg, 0.159 mmol) in THF (5 mL) at –78 °C, causing the initially yellow solution to turn orange-brown. The mixture was slowly warmed to room temperature and stirring was continued for 1 h. The solvents were then removed in vacuo and the residue was subjected to column chromatography (10 x 3 cm silica gel column), eluting first 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 to afford pure **4b** (79.8 mg, 0.115 mmol, 73%) as an orange solid. IR (CH_2Cl_2, cm^{-1}): 1977s, 1886s ν_{CO}. (KBr, cm^{-1}): 1968s, 1877s ν_{CO}. ^{1}H NMR (700 MHz, $CDCl_3$, 298 K, δ): 2.30 [s, 3 H, pz(CH_3)], 2.35 [s, 6 H, pz(CH_3)], 2.36 [s, 3 H, pz(CH_3)], 2.39 (s, 3 H, TeCH_3), 2.59 [s, 6 H, pz(CH_3)], 5.74 (s, 1 H, pz*H*), 5.90 (s, 2 H, pz*H*). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$, 298 K, δ): –16.1 (Te*C*H$_3$), 12.8 15.4 16.8 (pz*C*H$_3$), 106.7 106.8 [C^4(pz)], 144.6 145.4 152.1 152.7 [$C^{3,5}$(pz)], 224.3 (*C*O, $^1J_{CW}$ = 85.0 Hz), 250.8 (W≡*C*Te). ^{125}Te{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K, δ): 634. MS (ESI, +ve ion, *m/z*): Calcd for $C_{19}H_{25}BN_6O_2TeW$ [M+H]$^+$: 693.0768. Found: 693.0736. Anal. Calcd for $C_{19}H_{25}BN_6O_2TeW$: C, 32.99; H, 3.64; N, 12.15%. Found: C, 33.06; H, 3.63; N, 12.04 %.

Synthesis of Mo(≡CTePh)(CO)$_2$(Tp*) (**5a**)

To a solution of tellurium (35.4 mg, 0.277 mg.atom) in THF (5 mL) at –78 °C was added PhLi (146 μL, 1.9 M in di-*n*-butyl ether, 0.277 mmol) and the mixture was stirred at reduced temperature for 30 min. After this time, the solution was transferred by cannula into a solution of **1a** (100 mg, 0.185 mmol) in THF (5 mL) at –78 °C, causing the initially yellow solution to turn dark green. Stirring was continued for 30 min at reduced temperature before the solution was warmed to room temperature and the solvents removed in vacuo. The residue was extracted with *n*-hexane (2 x 10 mL), the solvent volume was reduced to ca. 2 mL and subjected to column chromatography (10 x 1 cm silica gel column), eluting first 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 to afford pure **5a** (76.0 mg, 0.991 mmol, 62%) as red microcrystals. IR (CH_2Cl_2, cm^{-1}): 1988s, 1911s ν_{CO}. ^{1}H NMR (700 MHz, $CDCl_3$, 298 K, δ): 2.30 [s, 3 H, pz(CH_3)], 2.33 [s, 3 H, pz(CH_3)], 2.34 [s, 6 H, pz(CH_3)], 2.40 [s, 6 H, pz(CH_3)], 5.70 (s, 1 H, pz*H*), 5.81 (s, 2 H, pz*H*), 7.26–7.37 [m, 3 H, H$^{3-5}$(Ph)], 7.92 [d, $^3J_{HH}$ = 7.5 Hz, 2 H, H^{2,6}(Ph)]. ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$, 298 K, δ): 12.8 12.8 14.8 15.9 (pz*C*H$_3$), 106.4 106.5 [C^4(pz)], 114.9 [C^1(Ph)], 128.5 [C^4(Ph)], 129.7 [$C^{3,5}$(Ph)], 138.9 [$C^{2,6}$(Ph)], 144.6 145.3 151.5 151.6 [$C^{3,5}$(pz)], 226.1 (*C*O), 262.0 (Mo≡*C*Te). ^{125}Te{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K, δ): 1108. MS (ESI, +ve ion, *m/z*): Calcd for $C_{24}H_{27}N_6O_2BMoTeNa$ [M + Na]$^+$: 691.0286. Found: 691.0332. Anal. Calcd for $C_{24}H_{27}N_6O_2BMoTe$: C, 43.29; H, 4.09; N, 12.62%. Found: C, 43.30; H, 3.98; N, 12.52 %.

Synthesis of W(≡CTePh)(CO)$_2$(Tp*) (**5b**)

To a solution of tellurium (30.4 mg, 0.239 mg.atom) in THF (5 mL) at –78 °C was added PhLi (126 μL, 1.9 M in di-*n*-butyl ether, 0.239 mmol) and the mixture was stirred at reduced temperature for 30 min. After this time, the solution was transferred by cannula into a solution of **1b** (100 mg, 0.159 mmol) in THF (5 mL) at –78 °C, causing the initially yellow solution to turn dark green. Stirring was continued for 30 min at reduced temperature before the solution was warmed to room temperature and the solvents removed in vacuo. The residue was extracted with *n*-hexane (2 x 10 mL), the solvent volume was reduced to ca. 2 mL and subjected to column chromatography (10 x 1 cm silica gel column), eluting first 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 to afford pure **5b** (65.3 mg, 0.0866 mmol, 54%) as orange crystals. IR (CH_2Cl_2, cm^{-1}): 1980s, 1890s ν_{CO}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, δ): 2.30 [s, 3 H, pz(CH_3)], 2.34 [s, 6 H, pz(CH_3)], 2.38 [s, 3 H, pz(CH_3)], 2.41 [s, 6 H, pz(CH_3)], 5.74 (s, 1 H, pz*H*), 5.85 (s, 2 H, pz*H*), 7.21–7.32 [m, 3 H, H$^{3-5}$(Ph)], 7.85–7.90 [m, 2 H, H2,6(Ph)]. ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, 298 K, δ): 12.7 12.8 15.4 16.5 (pz*C*H$_3$), 106.6 106.9 [C^4(pz)], 114.2 [C^1(Ph)], 128.1 [C^4(Ph)], 129.5 [$C^{3,5}$(Ph)], 138.4 [$C^{2,6}$(Ph)], 144.5 145.4 152.3 152.8 [$C^{3,5}$(pz)], 224.6 ($^1J_{CW}$ = 165 Hz, *C*O), 247.7 (W≡*C*Te). ^{125}Te{^{1}H} NMR (126 MHz, CDCl$_3$, 298 K, δ): 634. MS (ESI, +ve ion, *m/z*): Calcd for $C_{24}H_{27}BN_6O_2TeW$ [M + H]$^+$: 755.0931. Found: 755.0942. Anal. Calcd for $C_{24}H_{27}BN_6O_2WTe$: C, 38.24; H, 3.61; N, 11.15%. Found: C, 38.17; H, 3.62; N, 11.05 %.

Synthesis of [(Tp*)(CO)$_2$Mo(≡C)]$_2$Te (**6a**)

To a solution of **1a** (100 mg, 0.185 mmol) in THF (10 mL) was added a solution of Li$_2$Te in THF (2.35 mL, 0.078 M, 0.19 mmol) and the resulting mixture was stirred for 3 h, during which time the solution turned brown. After this time, additional **1a** (100 mg, 0.185 mmol) was added as a solid and the mixture was stirred for a further 48 h. After this time, the solvent was removed in vacuo and the residue was subjected to column chromatography (20 x 1 cm silica gel column), eluting initially with *n*-hexane followed by 10% v/v CH$_2$Cl$_2$/*n*-hexane. An orange-red band was collected and the solvents were removed under reduced pressure to give pure **6a** (121 mg, 0.115 mmol, 31%) as an orange solid. IR (CH$_2$Cl$_2$, cm^{-1}): 1992s, 1916s ν_{CO}. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K, δ): 2.30 [s, 6 H, pz(CH_3)], 2.31 [s, 6 H, pz(CH_3)], 2.35 [s, 12 H, pz(CH_3)], 2.39 [s, 12 H, pz(CH_3)], 5.70 (s, 2 H, pz*H*), 5.72 (s, 4 H, pz*H*). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, 298 K, δ): 12.8 12.8 14.7 15.2 (pz*C*H$_3$), 106.3 106.6 [C^4(pz)], 144.2 145.4 151.6 151.8 [$C^{3,5}$(pz)], 226.0 (*C*O), 252.3 (Mo≡*C*Te). ^{125}Te{^{1}H} NMR (126 MHz, CDCl$_3$, 298 K, δ): 1426. MS (ESI, +ve ion, *m/z*): Calcd for $C_{36}H_{44}N_{12}O_4B_2Mo_2Te$ [M]$^+$: 1050.0980. Found: 1050.1000. Anal. Calcd for $C_{36}H_{44}N_{12}O_4B_2Mo_2Te$: C, 41.18; H, 4.22; N, 16.01%. Found: C, 41.09; H, 4.30; N, 15.76 %.

Synthesis of [(Tp*)(CO)$_2$W(≡C)]$_2$Te (**6b**)

To a solution of **1b** (100 mg, 0.159 mmol) in THF (10 mL) at –78 °C was added Li$_2$Te (2.35 mL, 0.078 M in THF, 0.19 mmol). The solution was warmed to room temperature and stirring continued for 2 h, during which time the solution turned light brown. After this time, additional **1b** (100 mg, 0.159 mmol) was added as a solid and the mixture was stirred for a further 48 h. After this time, the solvent was removed in vacuo and the residue was subjected to column chromatography (20 x 1 cm silica gel column), eluting initially with *n*-hexane followed by 10% v/v CH$_2$Cl$_2$/*n*-hexane. An orange-red band was collected and the solvents were removed under reduced pressure to give pure **6b** (155 mg, 0.126 mmol, 40%) as an orange solid. A crystal suitable for X-ray structure determination was grown by slow evaporation of a CHCl$_3$/ethanol mixture. IR (CH$_2$Cl$_2$, cm^{-1}): 1975s, 1892s ν_{CO}. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K, δ): 2.31 [s, 6 H, pz(CH_3)], 2.37 [s, 18 H, pz(CH_3)], 2.40 [s, 12 H, pz(CH_3)], 5.75 (s, 2 H, pz*H*), 5.76 (s, 4 H, pz*H*). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, 298 K, δ): 12.6 15.4 16.5 (s, pz*C*H$_3$), 106.5 106.8 [C^4(pz)], 144.0 145.4 152.7 [$C^{3,5}$(pz)], 244.1 (*C*O, $^1J_{CW}$ = 168.3), 241.3 (W≡*C*Te, $^1J_{CW}$ = 212.2 Hz). ^{125}Te{^{1}H} NMR (126 MHz, CDCl$_3$, 298 K, δ): 1181. MS (ESI, +ve ion, *m/z*): Calcd for $C_{36}H_{44}N_{12}O_4B_2W_2Te$ [M]$^+$: 1226.1863. Found: 1226.1857. Anal. Calcd for $C_{36}H_{44}N_{12}B_2O_4W_2Te$: C, 35.28; H, 3.62; N, 13.71%. Found: C, 35.19; H, 3.60; N, 13.53%.

Synthesis of [(Tp*)(CO)$_2$Mo(≡C)]$_2$Te$_2$ (**7a**)

To a flask containing Et$_4$N[**2a**] (50.0 mg, 0.070 mmol) and ferrocenium hexafluorophosphate (23.0 mg, 0.070 mmol) was added MeCN (10 mL) and the suspension was stirred vigorously for 2 h, during which time a dark purple precipitate formed. The mixture was filtered and the purple solid was washed with a large volume (10 x 10 mL) of MeCN then dried in vacuo to give pure **7a** (22.4 mg, 0.0190 mmol, 55%) as a dark purple powder. IR (CH$_2$Cl$_2$, cm^{-1}): 1995s, 1916s ν_{CO}. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K, δ): 2.30 [s, 6 H, pz(CH_3)], 2.33 [s, 6 H, pz(CH_3)], 2.35 [s, 12 H, pz(CH_3)], 2.54 [s, 12 H, pz(CH_3)], 5.70 (s, 2 H, pz*H*), 5.82 (s, 4 H, pz*H*). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, 298 K, δ): 12.8 12.8 14.8 16.3 (pz*C*H$_3$), 106.4 106.5 [C^4(pz)], 144.5 145.3 151.7 151.8 [$C^{3,5}$(pz)], 225.9 (*C*O), 248.9 (Mo≡*C*Te). ^{125}Te{^{1}H} NMR (126 MHz, CDCl$_3$, 298 K, δ): 992. MS (ESI, +ve ion, *m/z*): Calcd for $C_{36}H_{45}N_{12}O_4B_2Mo_2Te_2$ [M + H]$^+$: 1180.0082. Found: 1180.0062. Anal. Calcd for $C_{36}H_{44}N_{12}O_4B_2Mo_2Te_2$: C, 36.72; H, 3.77; N, 14.27%. Found: C, 36.80; H, 3.64; N, 14.18 %.

Synthesis of [(Tp*)(CO)$_2$W(≡C)]$_2$Te$_2$ (**7b**)

To a flask containing Et$_4$N[**2b**] (50.0 mg, 0.062 mmol) and ferrocenium hexafluorophosphate (20.5 mg, 0.062 mmol) was added MeCN (10 mL) and the suspension was stirred vigorously for 2 h, during which time a dark purple precipitate formed. The mixture was filtered and the purple solid was washed with a large volume (10 x 10 mL) of MeCN then dried in vacuo to give pure **7b** (19.2 mg, 0.0142 mmol, 46%) as a dark purple powder. The crystal selected for X-ray structure determination was grown by slow evaporation of a diethyl ether solution. IR (CH$_2$Cl$_2$, cm^{-1}): 1978s, 1894s ν_{CO}. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K, δ): 2.31 (s, 6 H, pzCH_3), 2.36 (s, 12 H, pzCH_3), 2.38 (s, 6 H, pzCH_3), 2.55 (s, 12 H, pzCH_3), 5.73 (s, 2 H, pz*H*), 5.85 (s, 4 H, pz*H*). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, 298 K, δ): 12.8 (2 C, coincident) 15.4 17.1 (pz*C*H$_3$), 106.7 106.8 [C^4(pz)], 144.4 145.4 152.7 152.8 [$C^{3,5}$(pz)], 224.2 (*C*O), 236.0 (W≡*C*Te). ^{125}Te{^{1}H} NMR (126 MHz, CDCl$_3$, 298 K, δ): 851. MS (ESI, *m/z*): Calcd for $C_{36}H_{45}N_{12}O_4B_2W_2Te_2$ [M + H]$^+$: 1355.0988. Found: 1355.1069. Anal. Calcd for $C_{36}H_{44}N_{12}O_4B_2W_2Te_2$: C, 31.95; H, 3.28; N, 12.42%. Found: C, 35.01; H, 3.28; N, 12.41%. NB: The crystallographic analysis suggested solvent accessible voids which may account for the low %carbon value.

X-Ray Crystallography

Refinement details

The crystal structure determination of **4b** was complicated by significant positional disorder characteristics. Two molecules of **4b** were present per asymmetric unit. One of these molecules was fairly well defined, although the tellurium atom was located over two positions and was refined to a relative ratio of *ca* 92:8, the minor component was treated isotropically. In the second molecule, the C–Te–Me moiety was heavily disordered and was modelled over four positions and was refined to a relative ratio of *ca*. 57:20:8:6 with the liberal use of distance and thermal parameter restraints. There was also a small amount of full-molecule disorder (*ca*. 10%) for which only the heavy W and Te atoms could be located in the difference map. These disorder characteristics were present in four distinct data sets for which crystals were obtained from different solvent combinations. For this reason, we have included this structure only as evidence of the connectivity, but eschew more detailed interpretation.

The crystal of **4b** was found to contain two parent molecules per asymmetric unit. In one of these molecules a carbonyl group and the phenyltellurocarbyne exhibited positional disorder, the components of which were refined to a relative ratio of *ca* 89:11. The minor component was refined with restrained, isotropic thermal parameters. Hydrogen atoms were not located for the minor component.

The crystal of **6b** was grown by slow evaporation of a chloroform/ethanol solution and was found to contain regions of highly disordered solvent which could not be modelled effectively. The SQUEEZE algorithm[9] was invoked, the calculations for which indicated that the two solvent accessible voids contained approximately 237 electrons, consistent with four molecules of chloroform (232 electrons), or two molecules of chloroform of solvation per molecule of **6b**. The data precision is less than ideal and so is not suitable for distance and angle comparisons, but is included as confirmation of the atom connectivity.

The crystal of **7b**, grown by slow evaporation of a diethyl ether solution, was found to contain a region of significantly disordered solvent which could not be modelled effectively and so the SQUEEZE algorithm[9] was invoked. The calculations determined that the two solvent accessible voids in the unit cell contained approximately 244 electrons each, consistent with 6 diethyl ether molecules (252 electrons) in total, or 1.5 molecules of diethyl ether per molecule of **7b**.

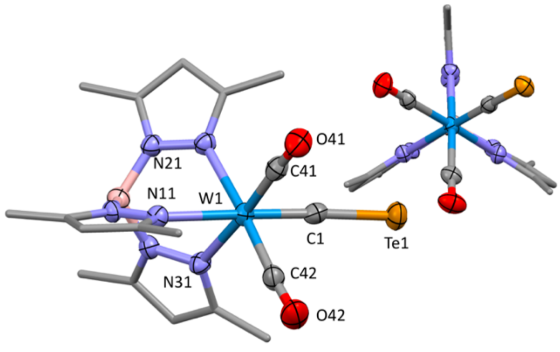

Figure ESI-1. Molecular structure of the [**2b**]$^-$ anion in a crystal of [Et$_4$N][**2b**] (50% displacement ellipsoids, pyrazolyl groups simplified, hydrogen atoms and Et$_4$N cation omitted for clarity). Selected bold lengths (Å) and angles (°) Te1–C1 2.018(7), W1–N11 2.308(5), W1–N21 2.234(5), W1–N31 2.240(5), W1–C1 1.855(7), W1–C41 1.975(7), W1–C42 1.961(7), C1–W1–C41 82.5(3), C1–W1–C42 80.9(3), C41–W1–C42 86.5(3). ***TR*** = 2(W1–N11)/(W1–N21 + W1–N31) = 1.032. Inset = view along W1···B1 vector.

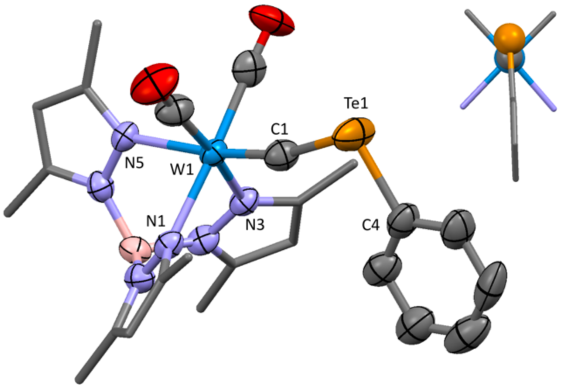

Figure ESI-2. Molecular structure of **5b** in a crystal of **5b** (50% displacement ellipsoids, pyrazolyl groups simplified and hydrogen atoms omitted for clarity; one of two crystallographically independent molecules shown). Selected bold lengths (Å) and angles (°) W1–C1 1.805(8), Te1–C1 2.078(8), Te1–C4 2.119(9), W1–N1 2.207(6), W1–N3 2.222(6), W1–N5 2.287(6), C1–Te1–C4 97.2(3), W1–C1–Te1 165.5(5). Inset: View along C1···W1 vector.

ChemComm

Electronic Supporting Information

Table S1. X-ray Structure Summary

	Et_4N[**2b**]	**4b**	**5b**	**6b**·$2.5C_6H_{12}$	**7b**
formula	$C_{26}H_{42}BN_7O_2TeW$	$C_{19}H_{25}BN_6O_2TeW$	$C_{24}H_{27}BN_6O_2TeW$	$C_{36}H_{44}B_2N_{12}O_4TeW_2$ $\cdot 2.5C_6H_{12}$	$C_{36}H_{44}B_2N_{12}O_4Te_2W_2$
M_w	806.93	691.71	753.77	1436.14	1353.35
cryst syst	triclinic	triclinic	triclinic	monoclinic	monoclinic
space group	P-1	P-1	P-1	$P2_1/c$	I2/a
***a*, Å**	10.0038(6)	10.28500(10)	11.1515(3)	10.4143(4)	20.1187(4)
***b*, Å**	10.0481(6)	11.7366(2)	14.7348(4)	25.0854(9)	13.9835(3)
c, Å	16.8445(11)	20.8637(4)	17.8819(4)	22.5482(14)	36.0701(10)
α, °	96.049(4)	90.500(2)	70.872(2)	90	90
β, °	93.448(3)	100.717(2)	89.962(2)	102.335(5)	104.180(2)
γ, °	111.328(4)	103.866(2)	75.377(2)	90	90
V, Å^3	1559.56(17)	2398.68(7)	2675.28(12)	5754.7(5)	9838.4(4)
T, K	200.0(1)	150.0(1)	150.0(1)	150.0(1)	150.0(1)
Z	2	4	4	4	8
D_{calcd}, Mg m^{-3}	1.718	1.915	1.871	1.658	1.827
F(000)	788	1312	1440	2824	5104
μ, mm^{-1}	4.654	18.545	16.696	4.544	5.882
crystal size, mm	0.080 x 0.124 x 0.260	0.049 x 0.142 x 0.166	0.088 x 0.197 x 0.658	0.036 x 0.082 x 0.222	0.032 x 0.043 x 0.155
2θ (min., max.), deg	2.627, 28.030	2.159, 73.763	2.626, 66.599	3.672, 27.074	3.366, 25.027
no. rflns collect	28686	48748	47991	31005	55006
no. indep rflns	7381	9680	9451	12172	8664
T (min., max.)	0.56, 0.69	0.102, 0.552	0.082, 0.18	0.98, 1.0	0.74, 1.0
goof on F^2	1.038	1.204	1.099	1.018	1.023
R_1, wR_2 (obsd data)	0.0470, 0.1009	0.0456, 0.1009	0.0514, 0.1453	0.0498, 0.0698	0.0253, 0.0541
R_1, wR_2 (all data)	0.0681, 0.1168	0.0473, 0.1017	0.0535, 0.1477	0.0946, 0.0825	0.0343, 0.0568
CCDC Number	1576983	1580612	1576984	1576985	1576986

Notes and references

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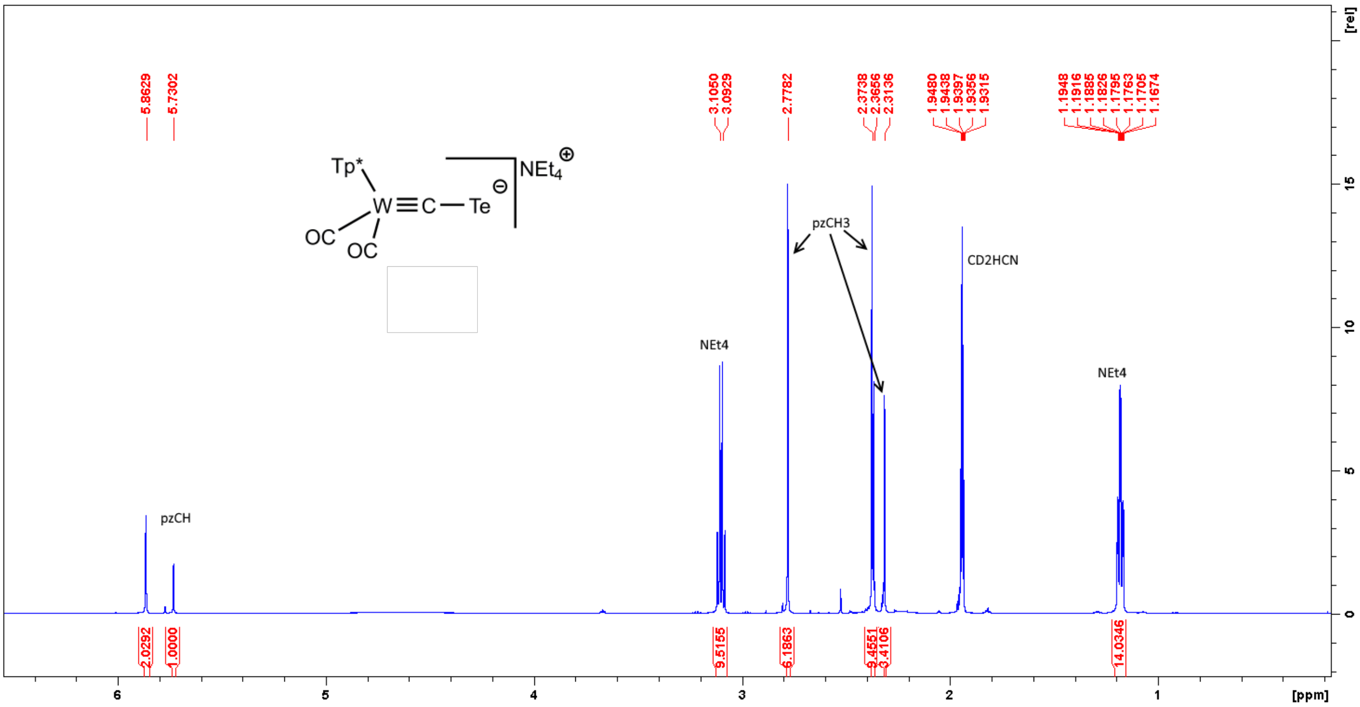
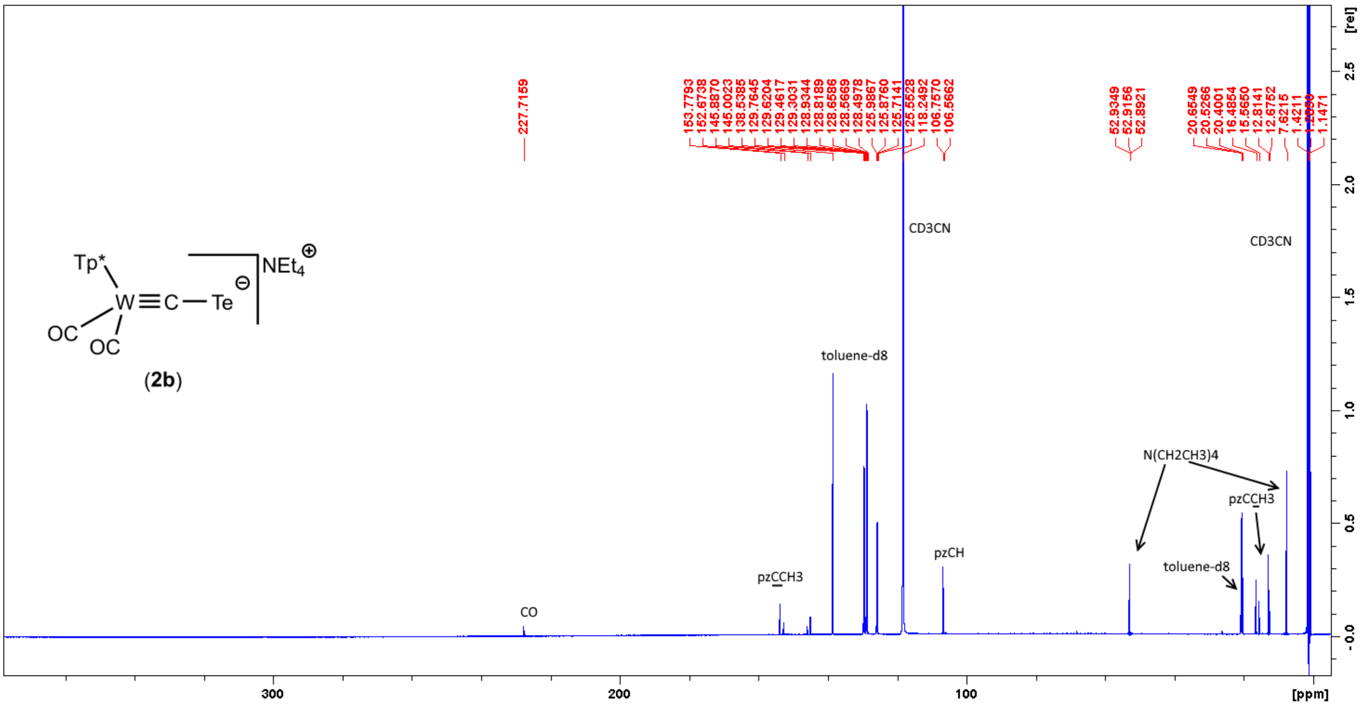
9

Spectra

^{1}H NMR Spectrum of Et$_4$N[**2b**]

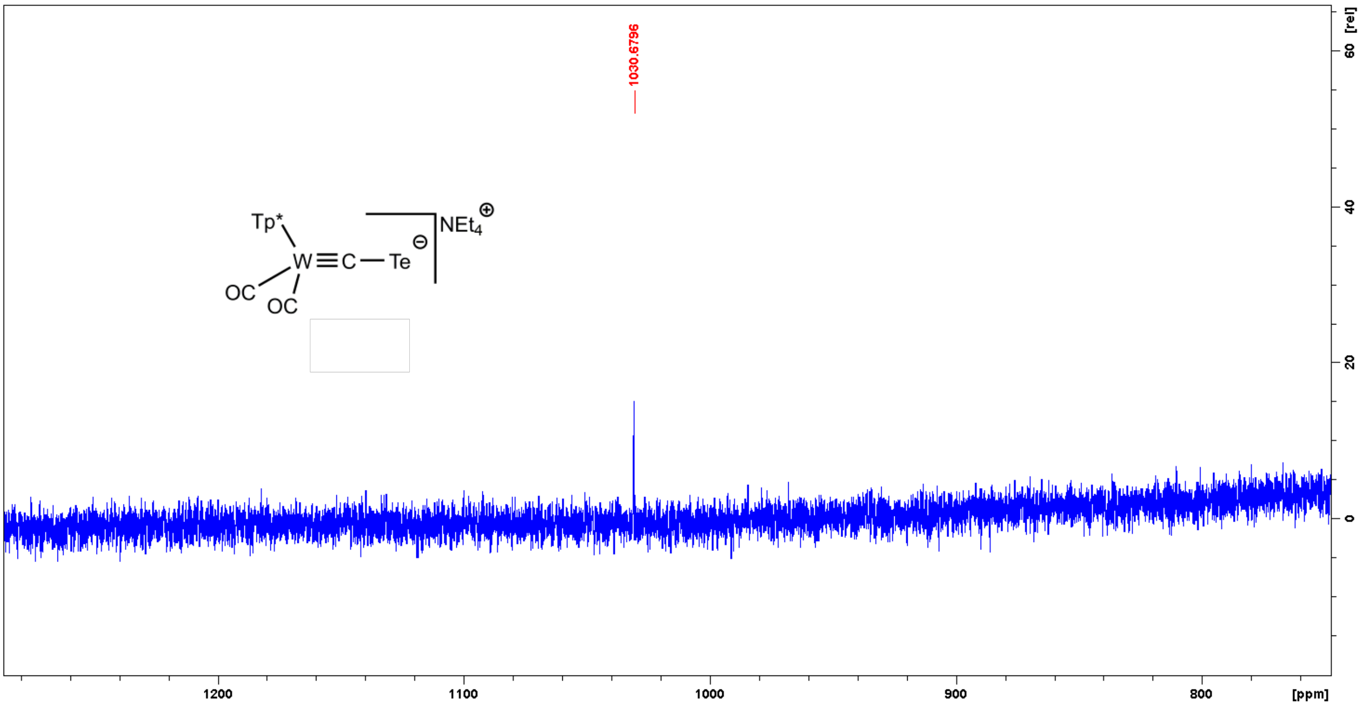


^{13}C{^{1}H} NMR Spectrum of Et$_4$N[**2b**]

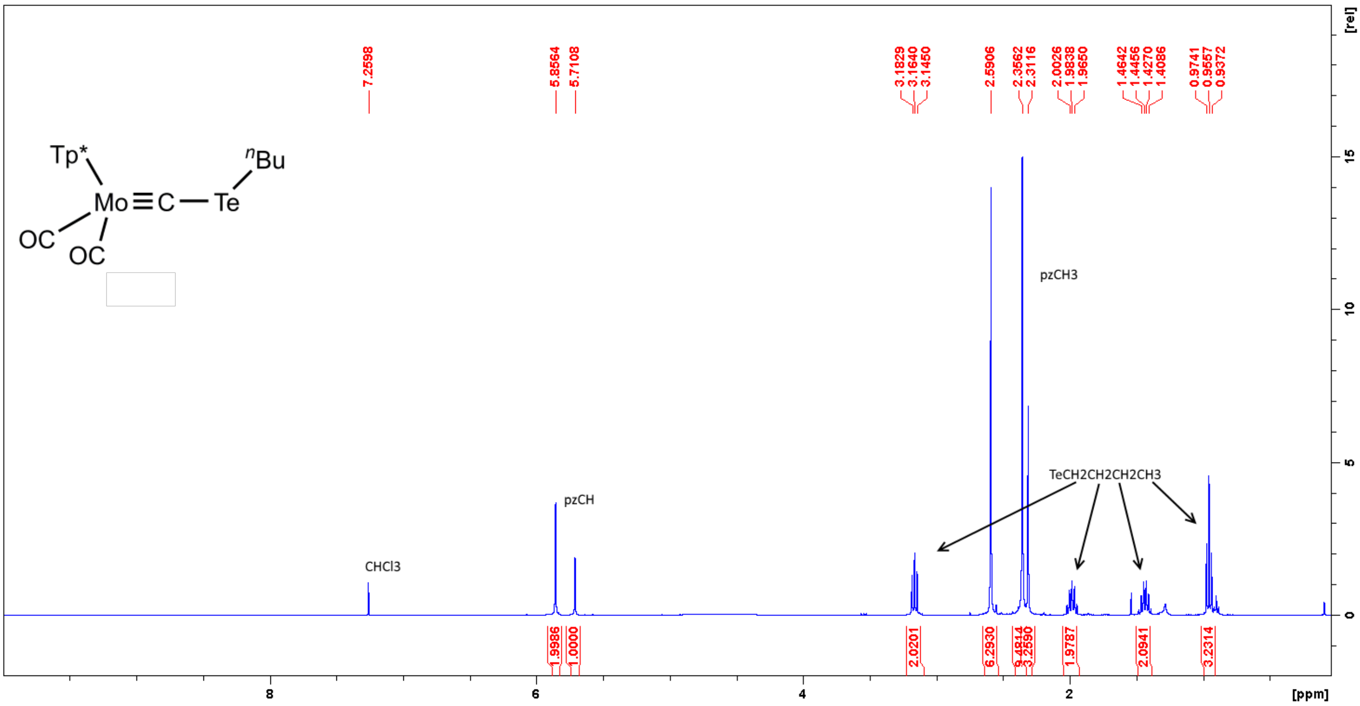


See caveat discussed in experimental procedure regarding tentative observation of δ(CTe).

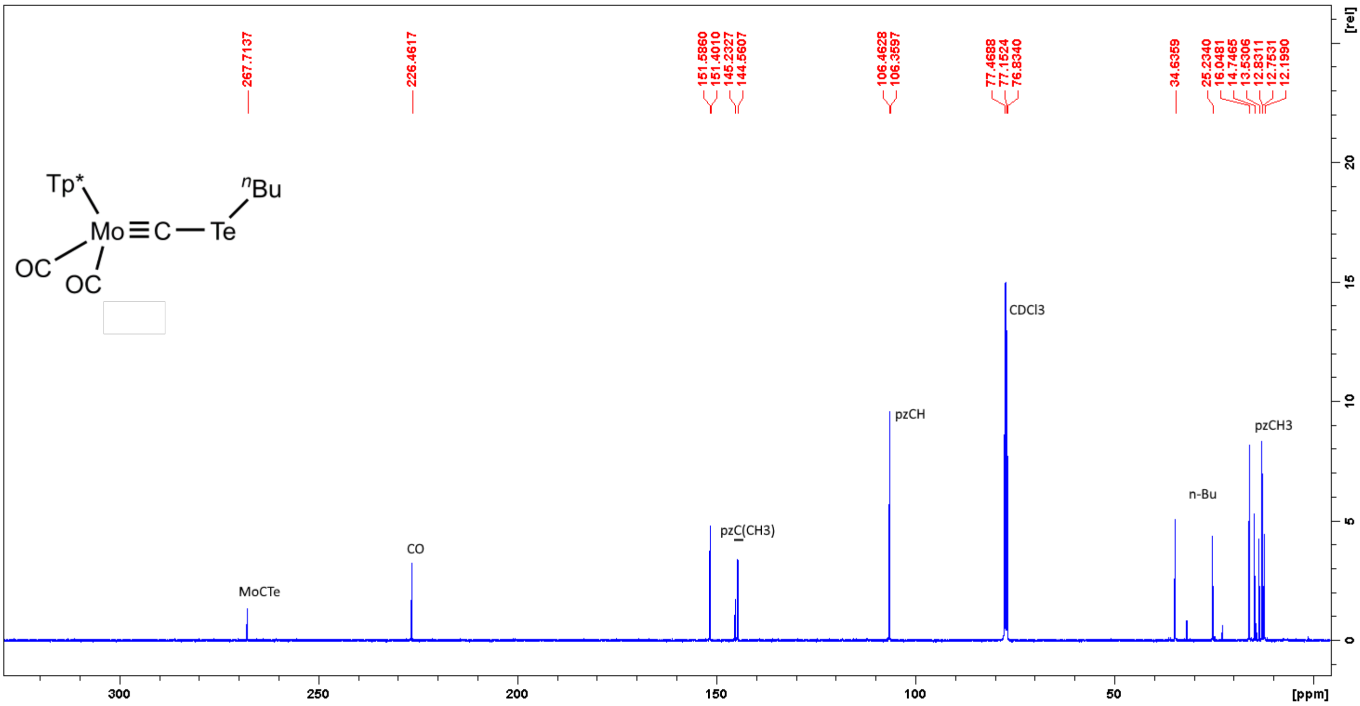
^{125}Te{^{1}H} NMR Spectrum of Et$_4$N[**2b**]



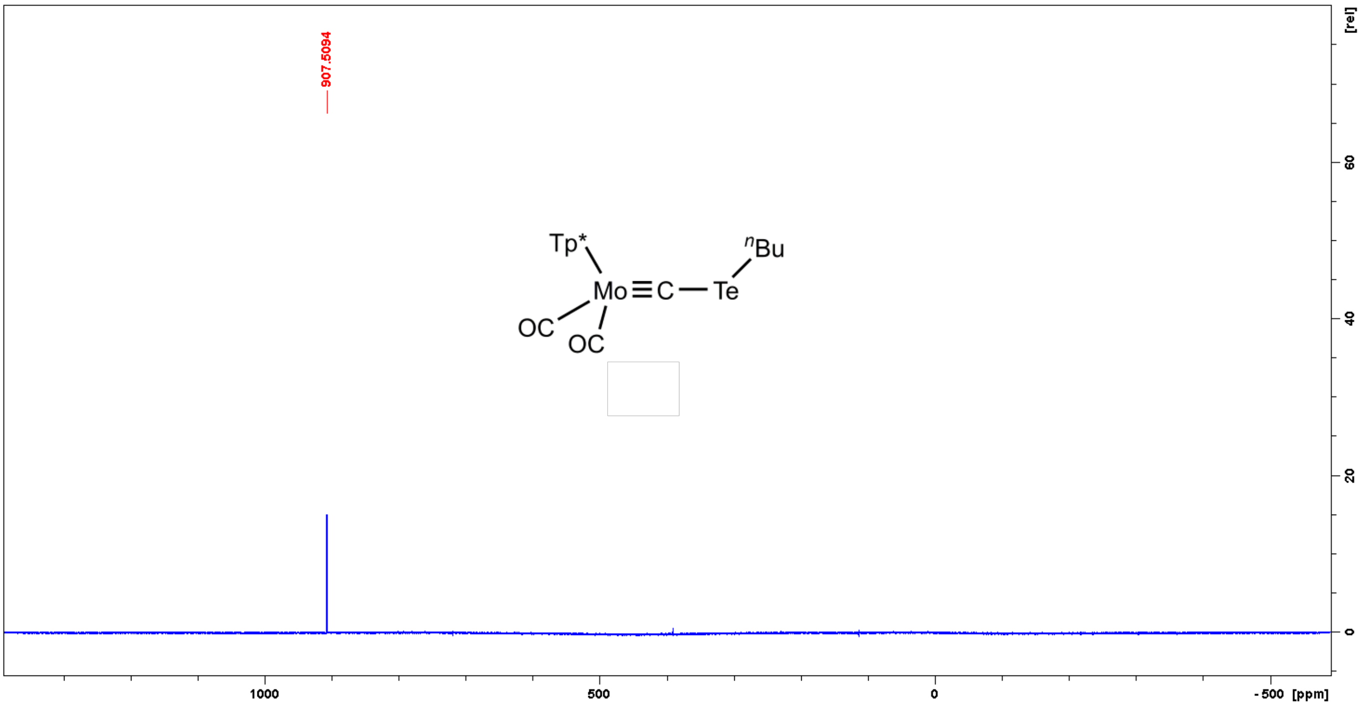
^{1}H NMR Spectrum of **3a**



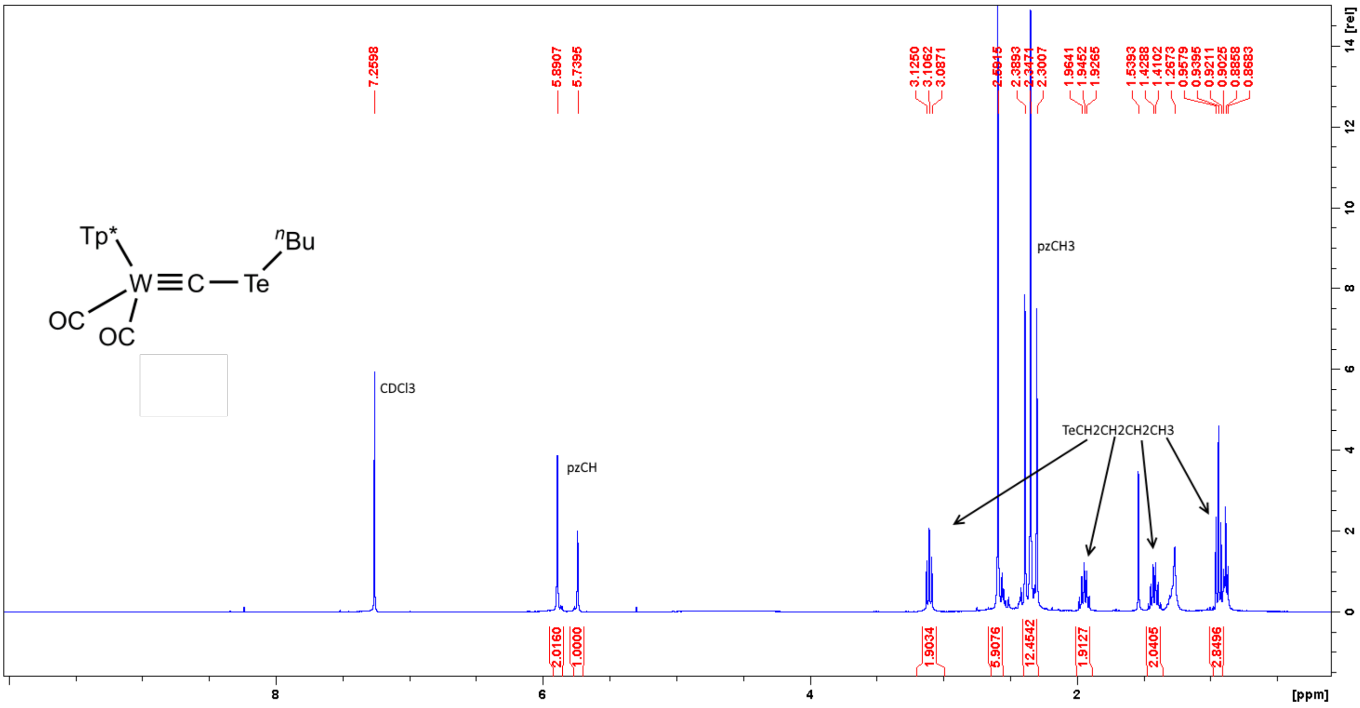
$^{13}C\{^1H\}$ NMR Spectrum of **3a**



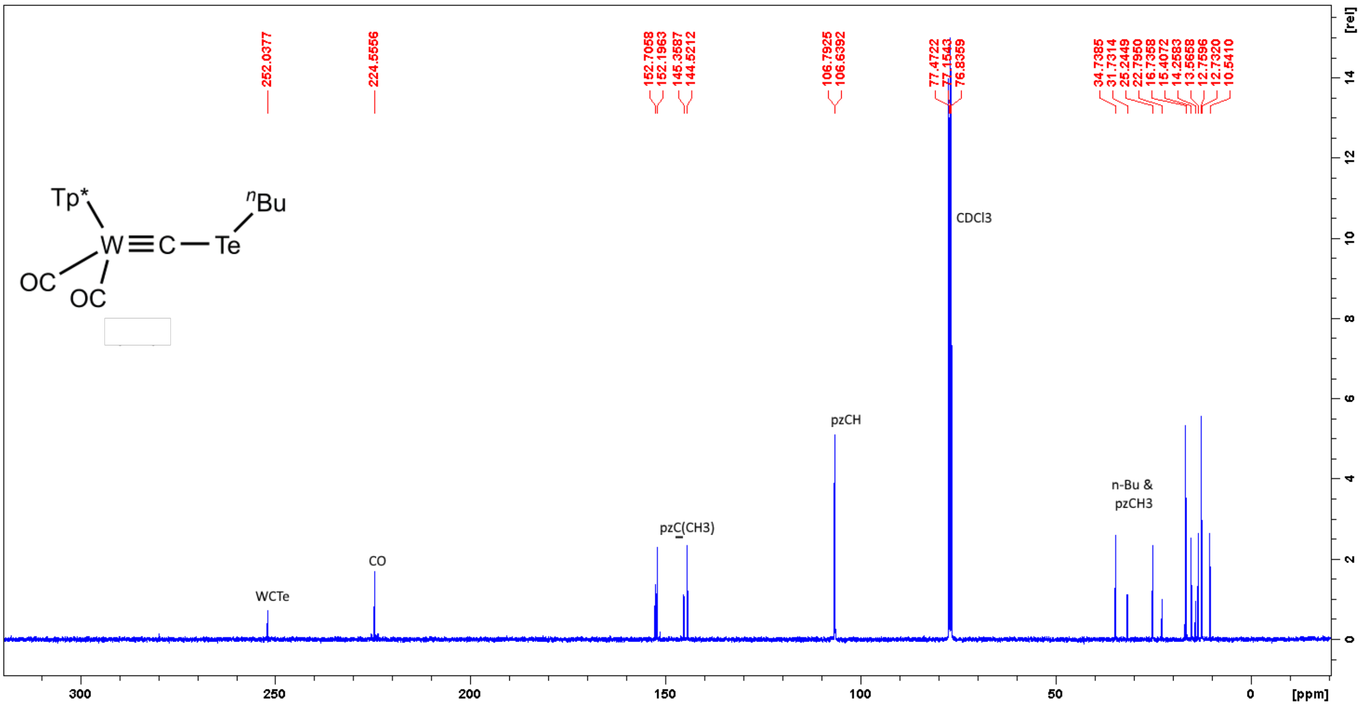
$^{125}Te\{^1H\}$ NMR Spectrum of **3a**



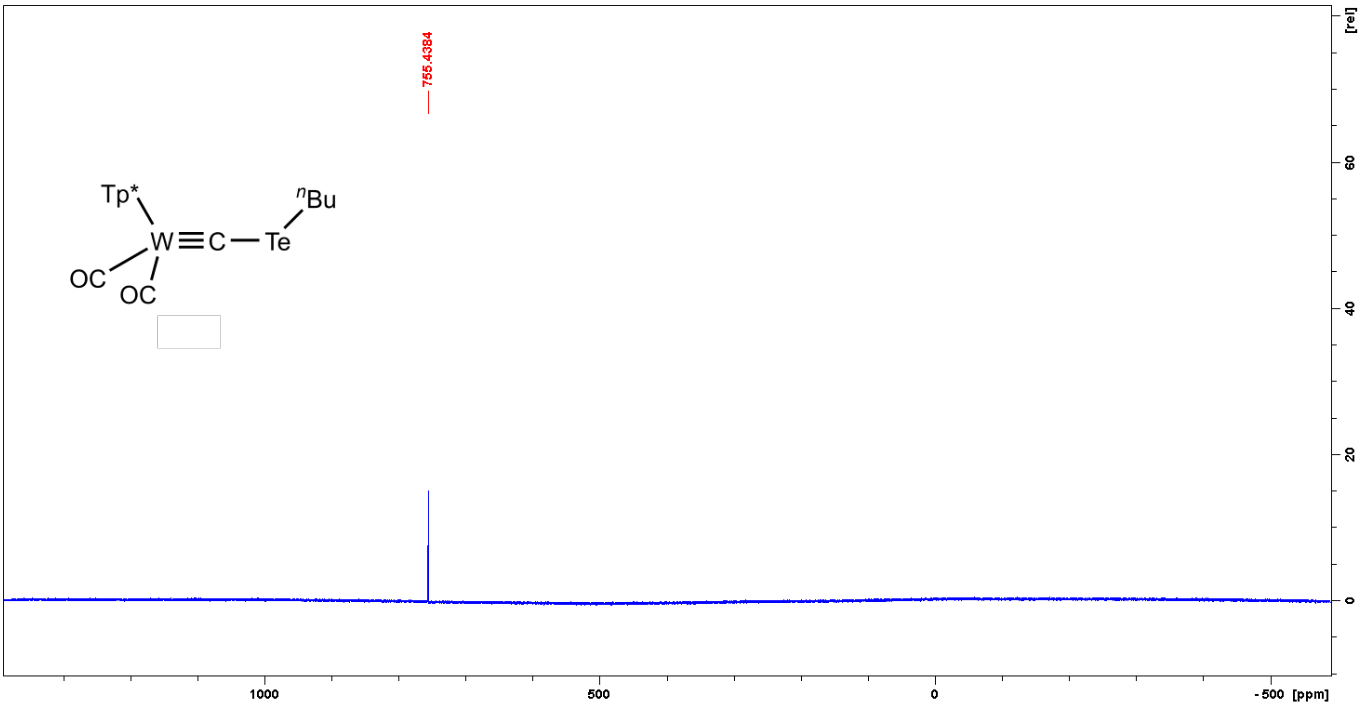
^{1}H NMR Spectrum of **3b**



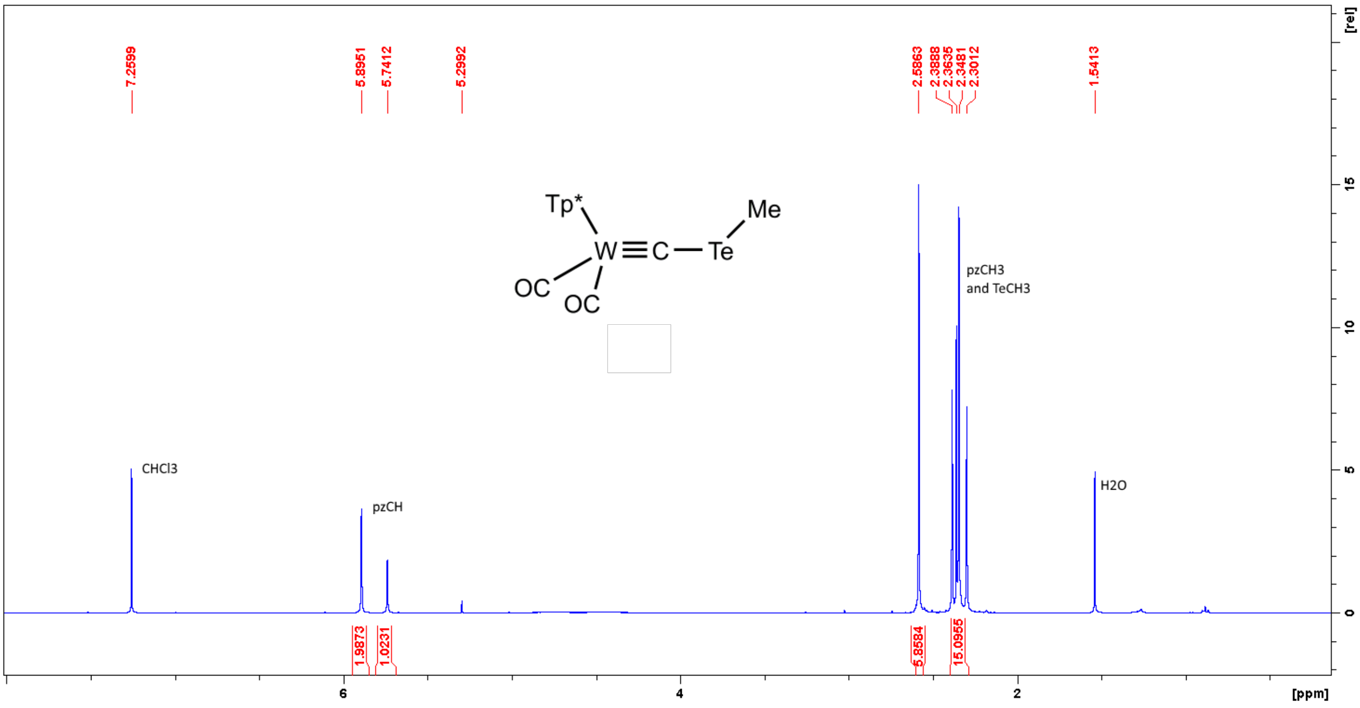
^{13}C{^{1}H} NMR Spectrum of **3b**



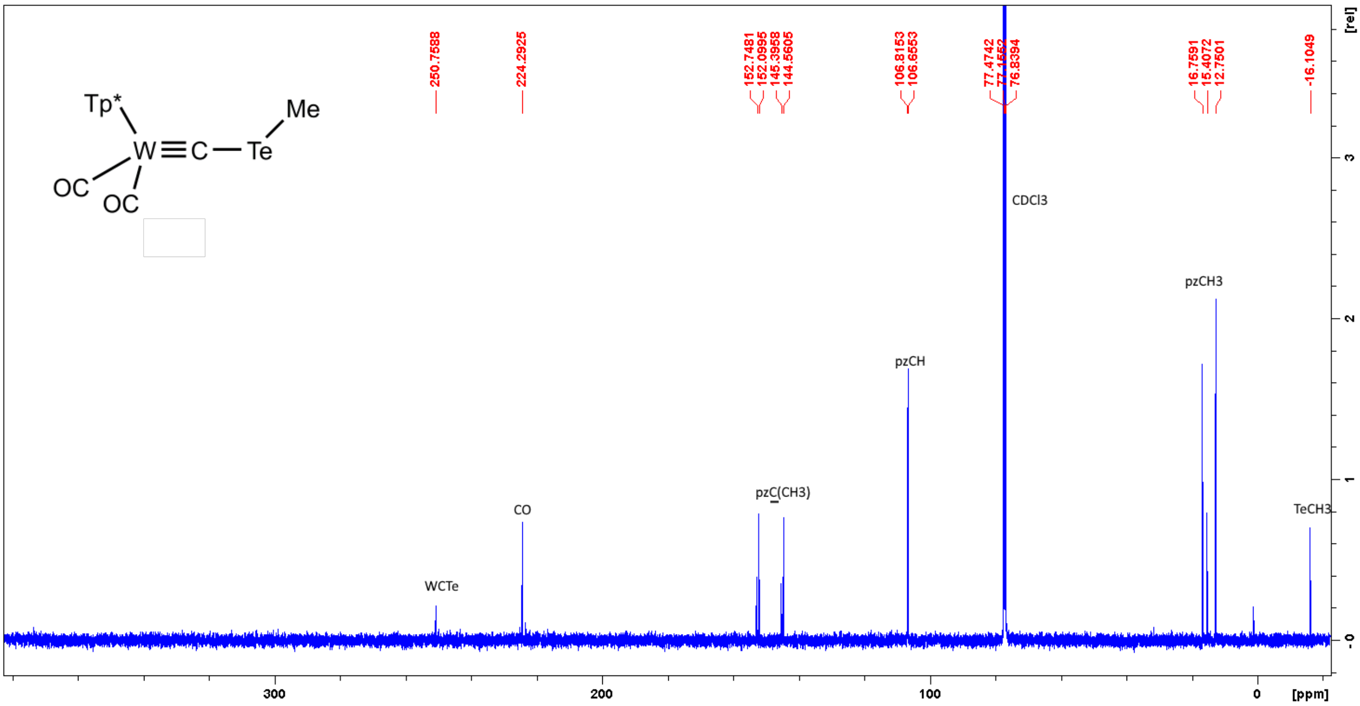
$^{125}Te\{^1H\}$ NMR Spectrum of **3b**



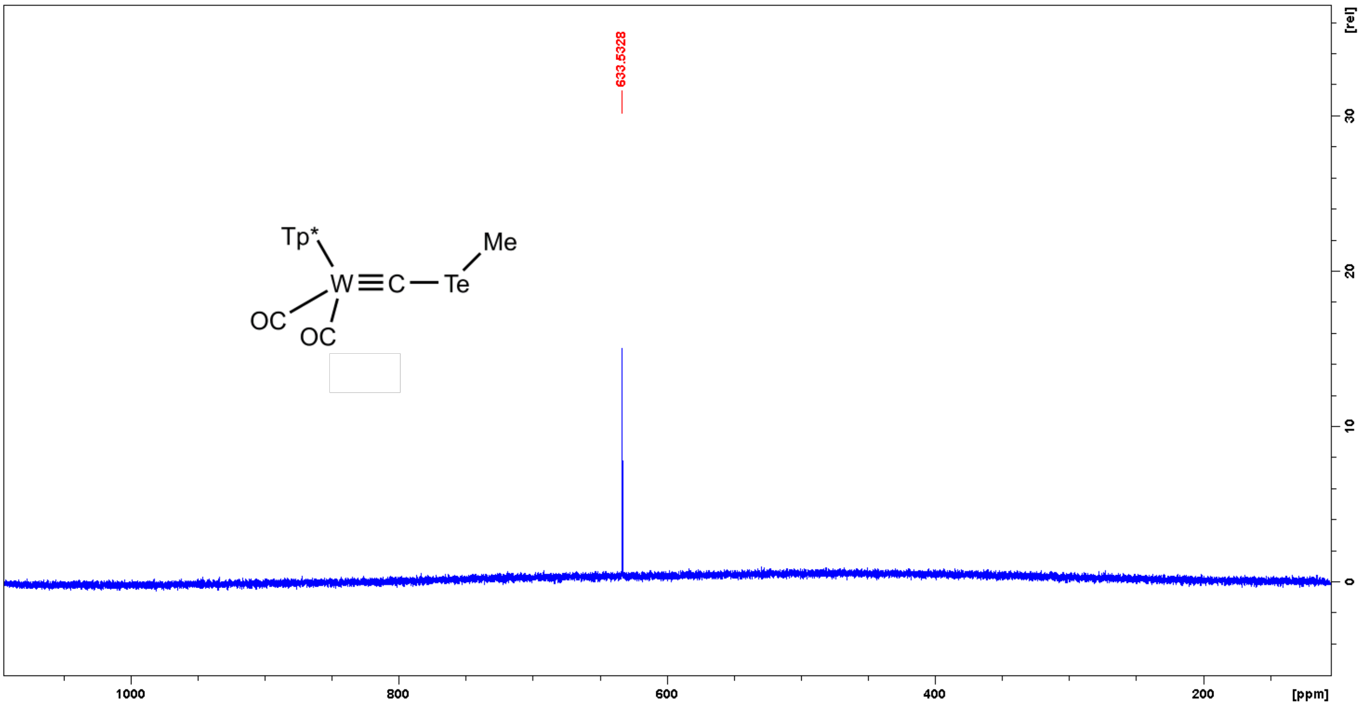
^1H NMR Spectrum of **4b**



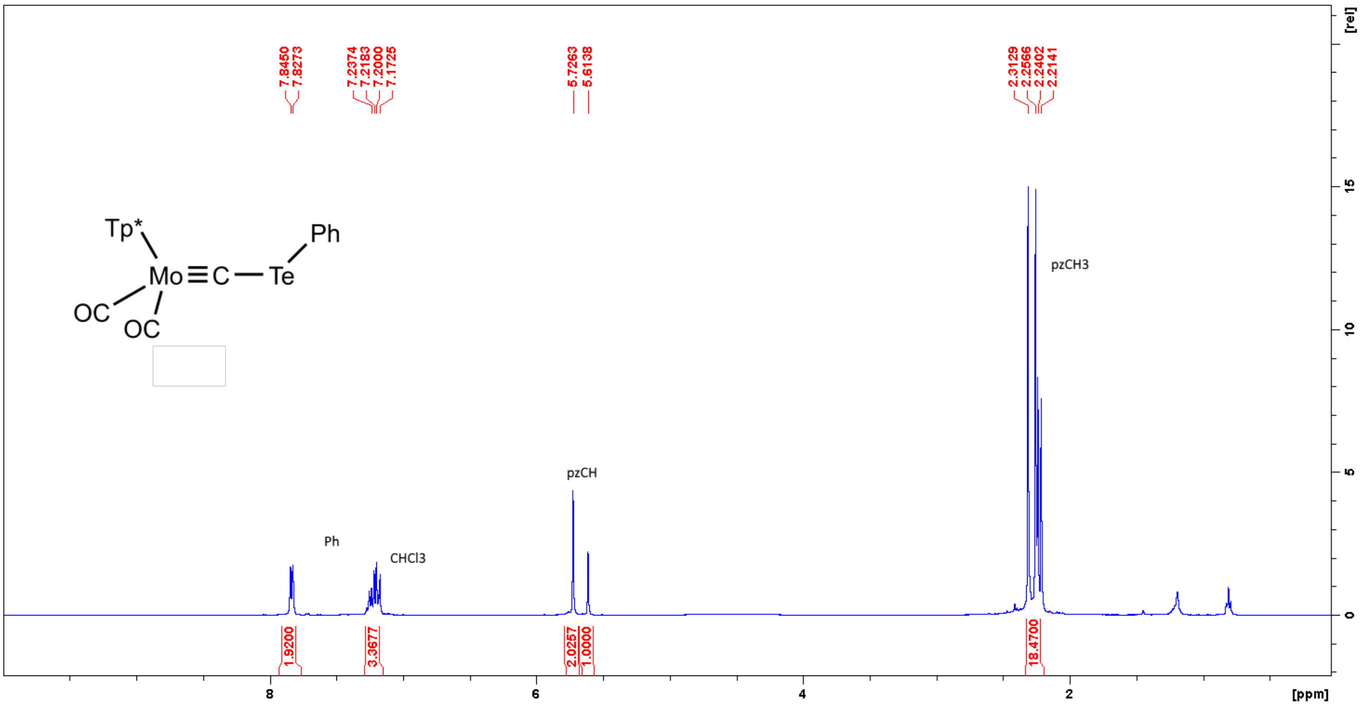
$^{13}C\{^1H\}$ NMR Spectrum of **4b**



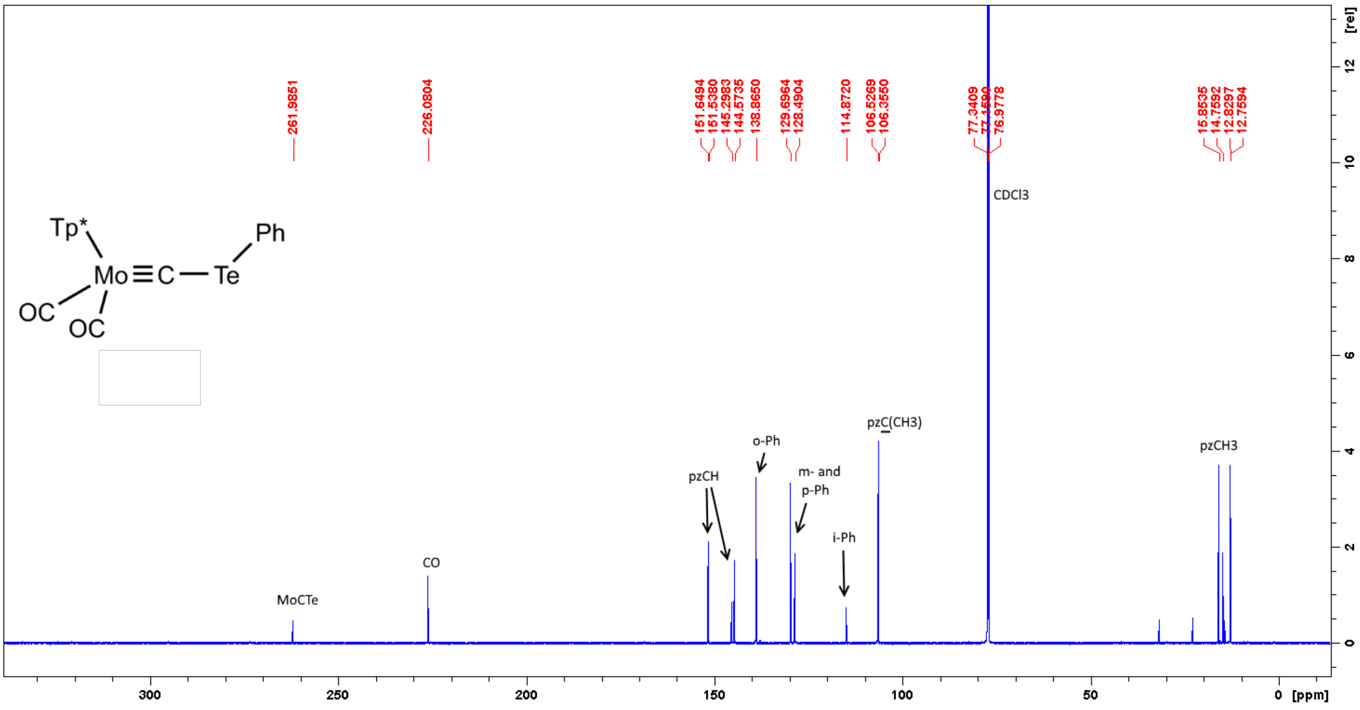
$^{125}Te\{^1H\}$ NMR Spectrum of **4b**



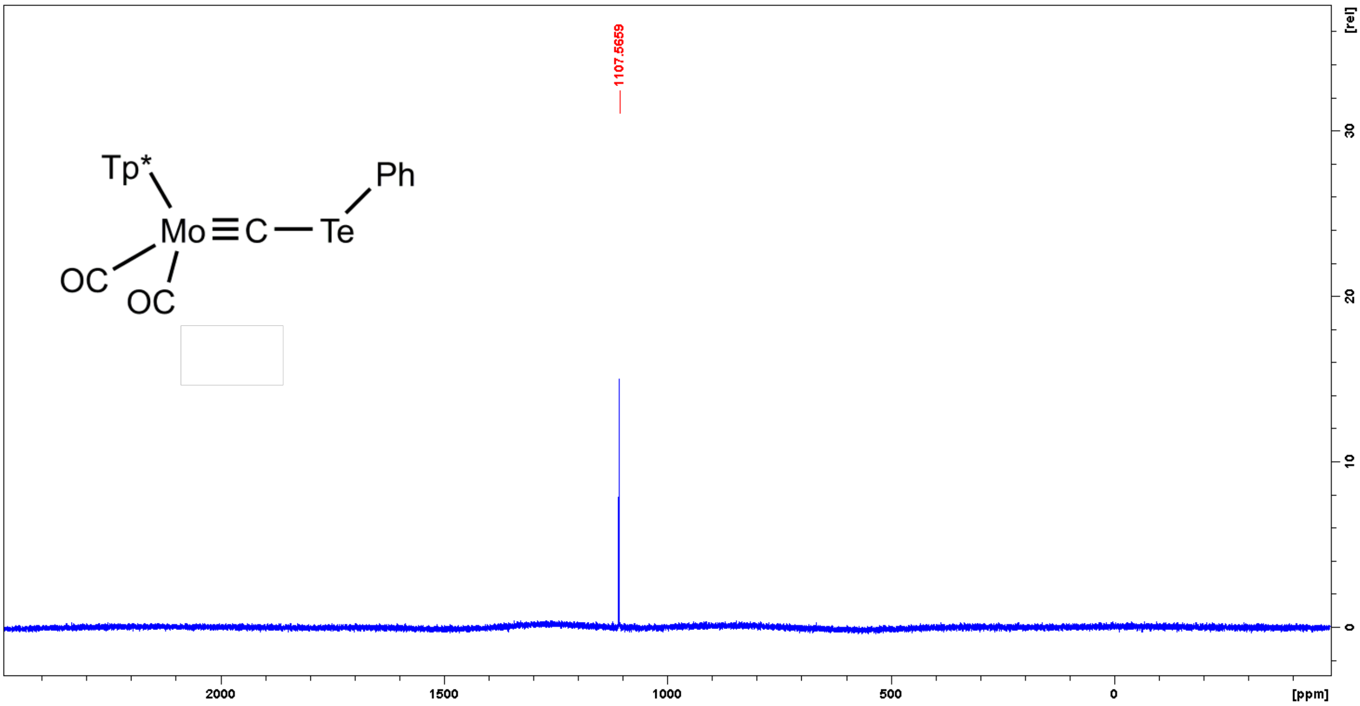
^{1}H NMR Spectrum of **5a**



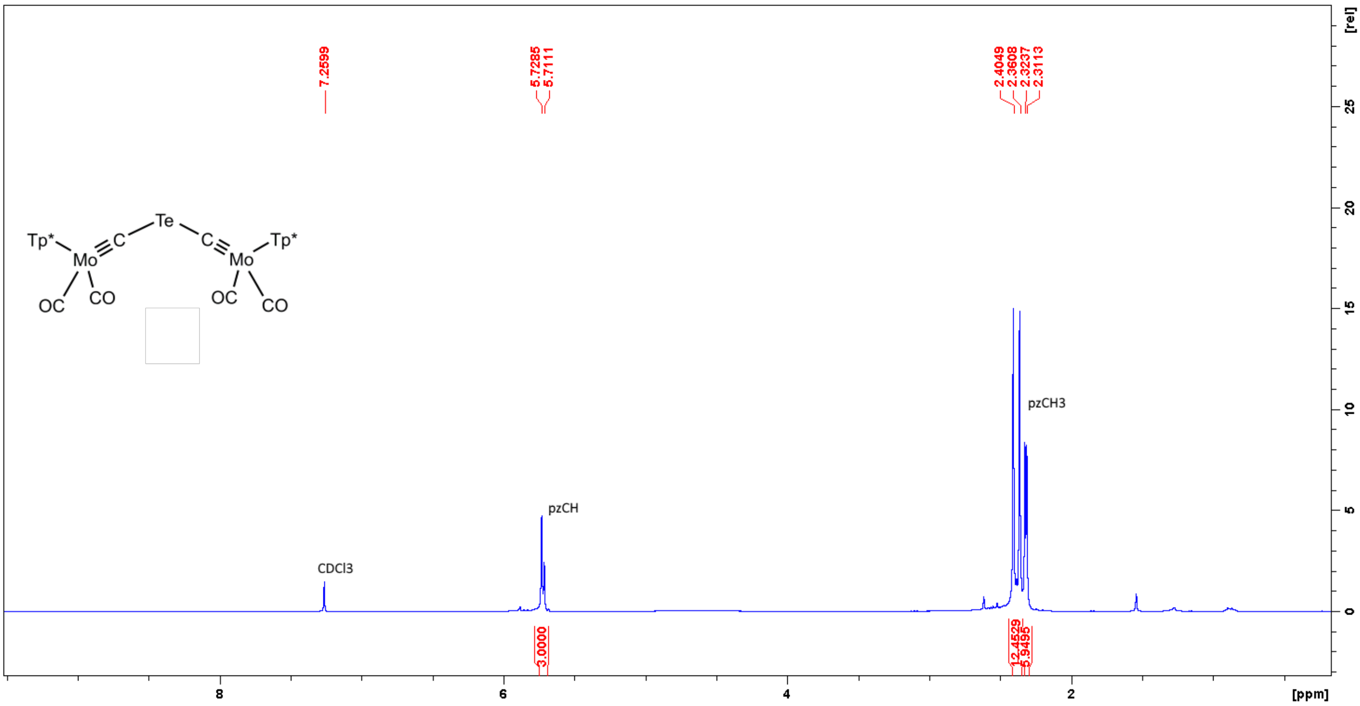
^{13}C{^{1}H} NMR Spectrum of **5a**



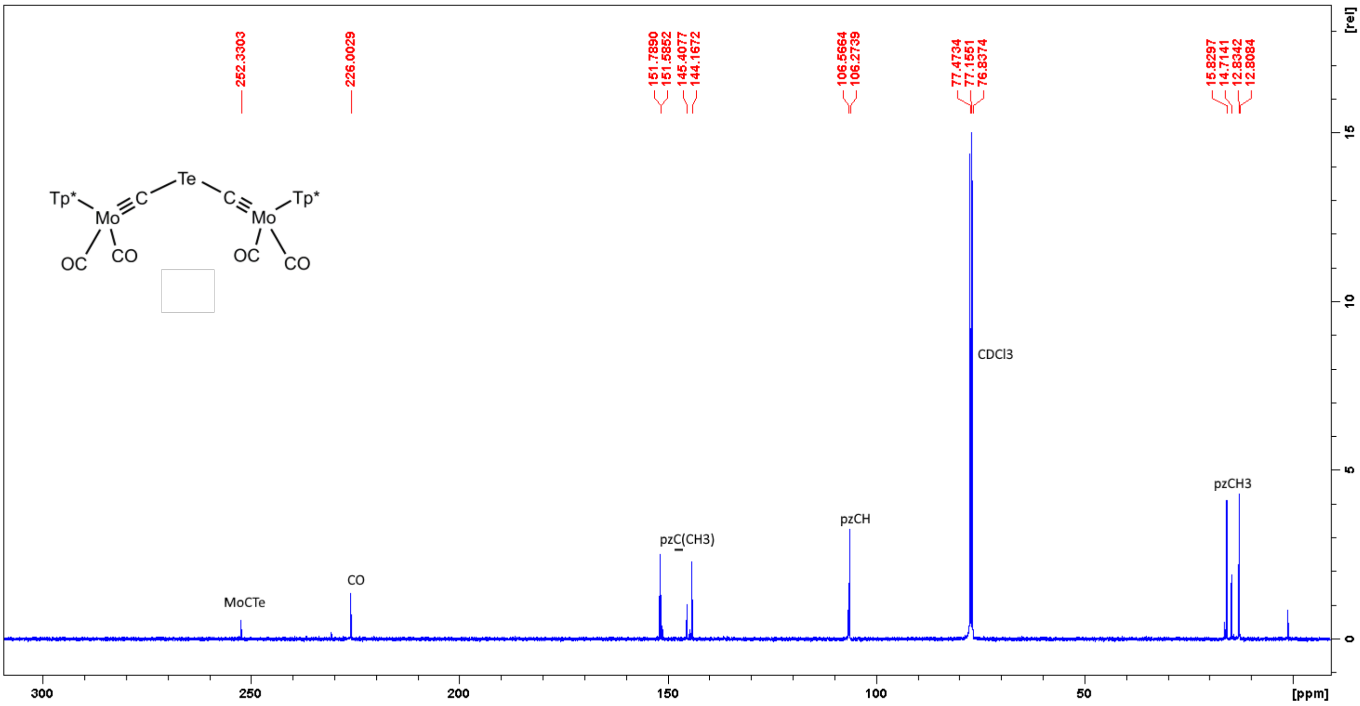
^{125}Te{^{1}H} NMR Spectrum of **5a**



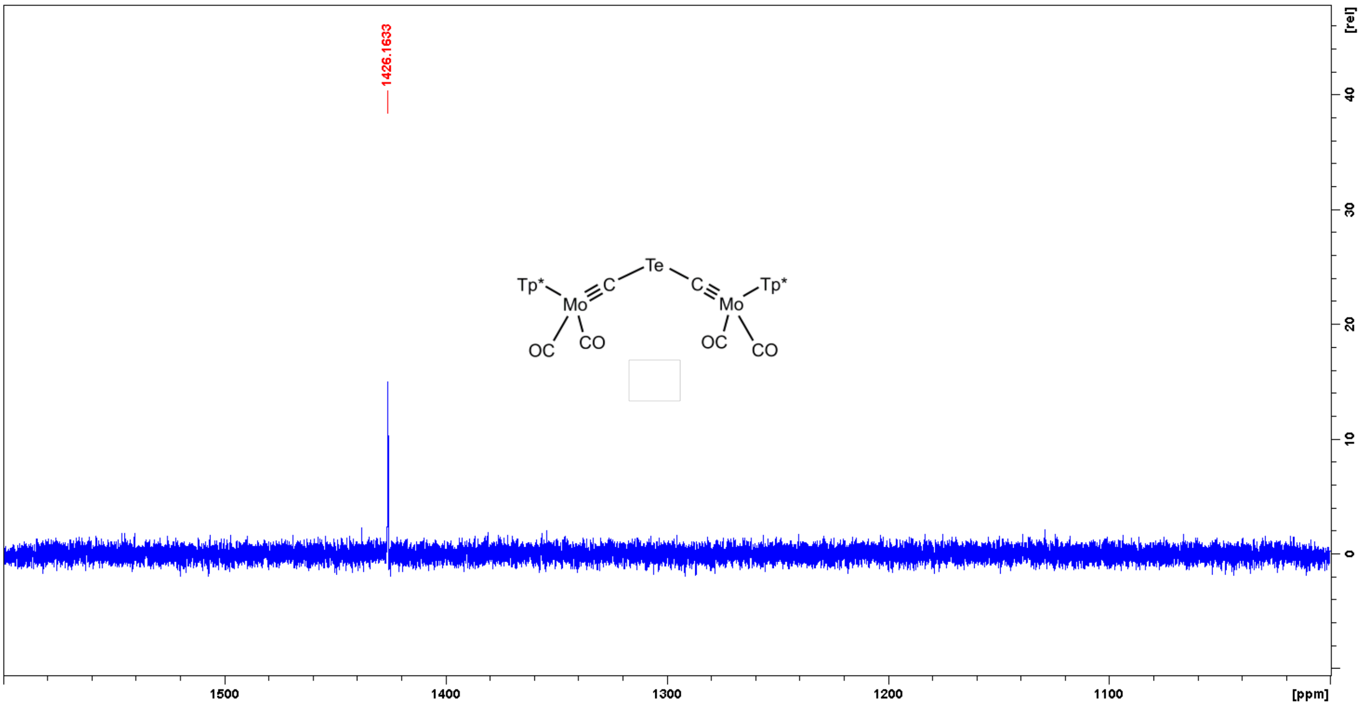
^{1}H NMR Spectrum of **6a**



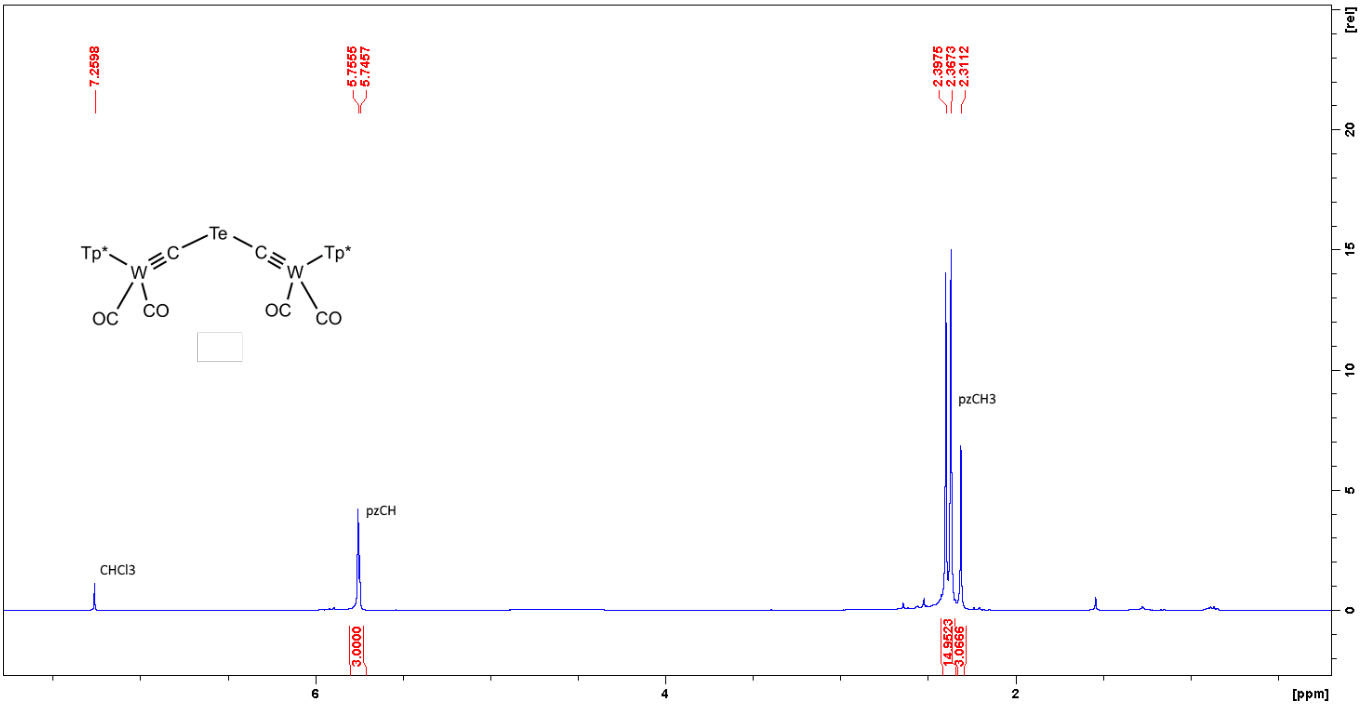
$^{13}C\{^{1}H\}$ NMR Spectrum of **6a**



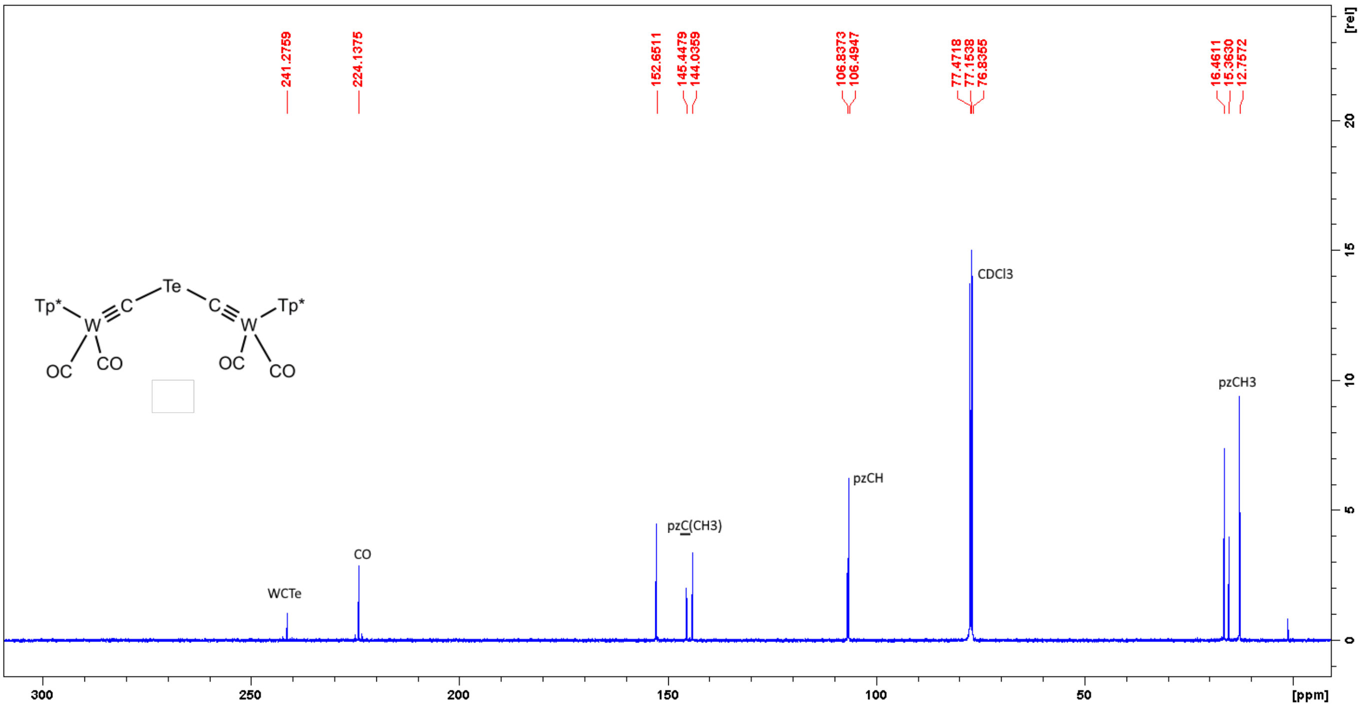
$^{125}Te\{^{1}H\}$ NMR Spectrum of **6a**



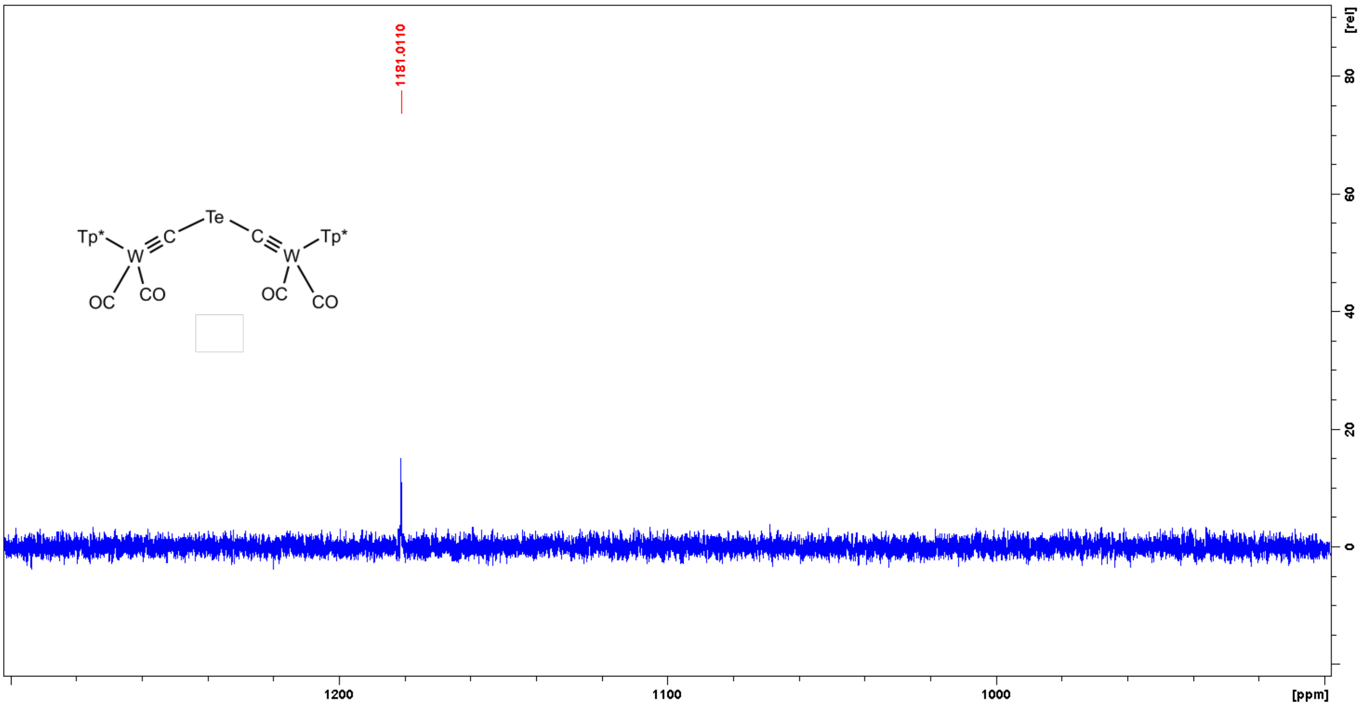
^{1}H NMR Spectrum of **6b**



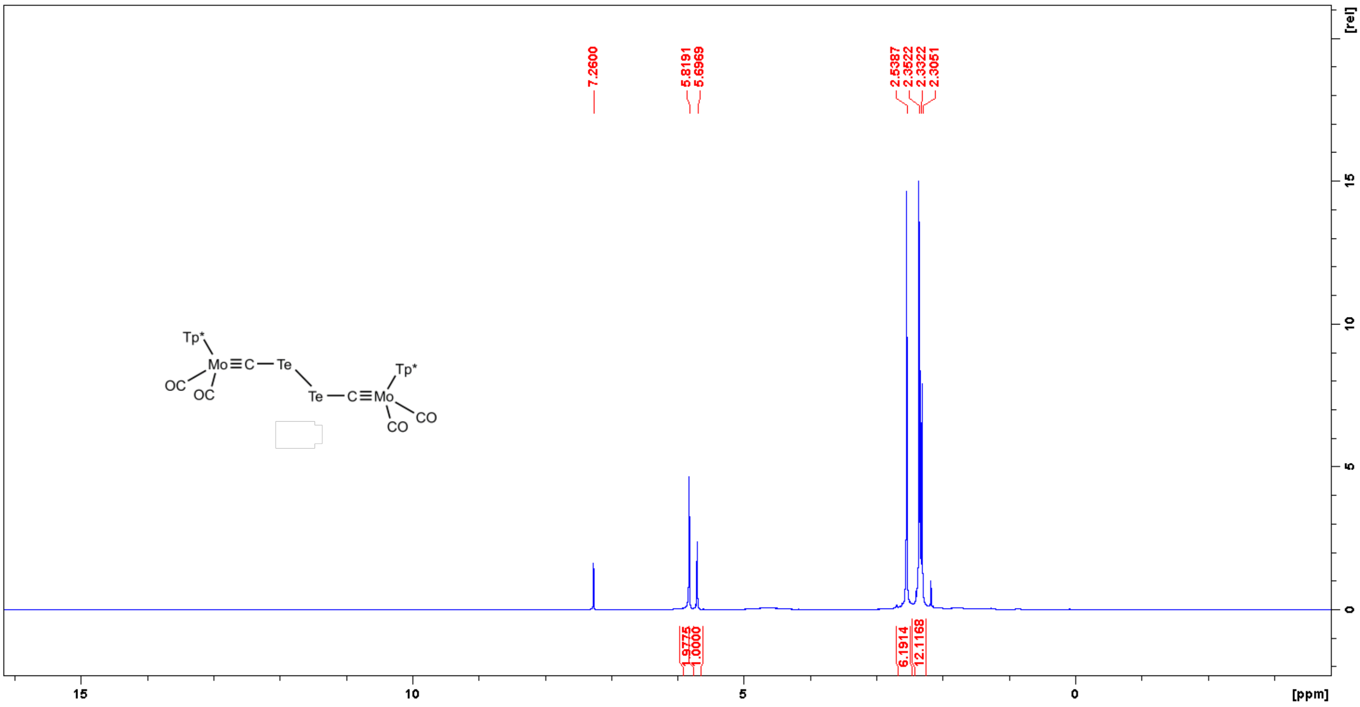
^{13}C{^{1}H} NMR Spectrum of **6b**



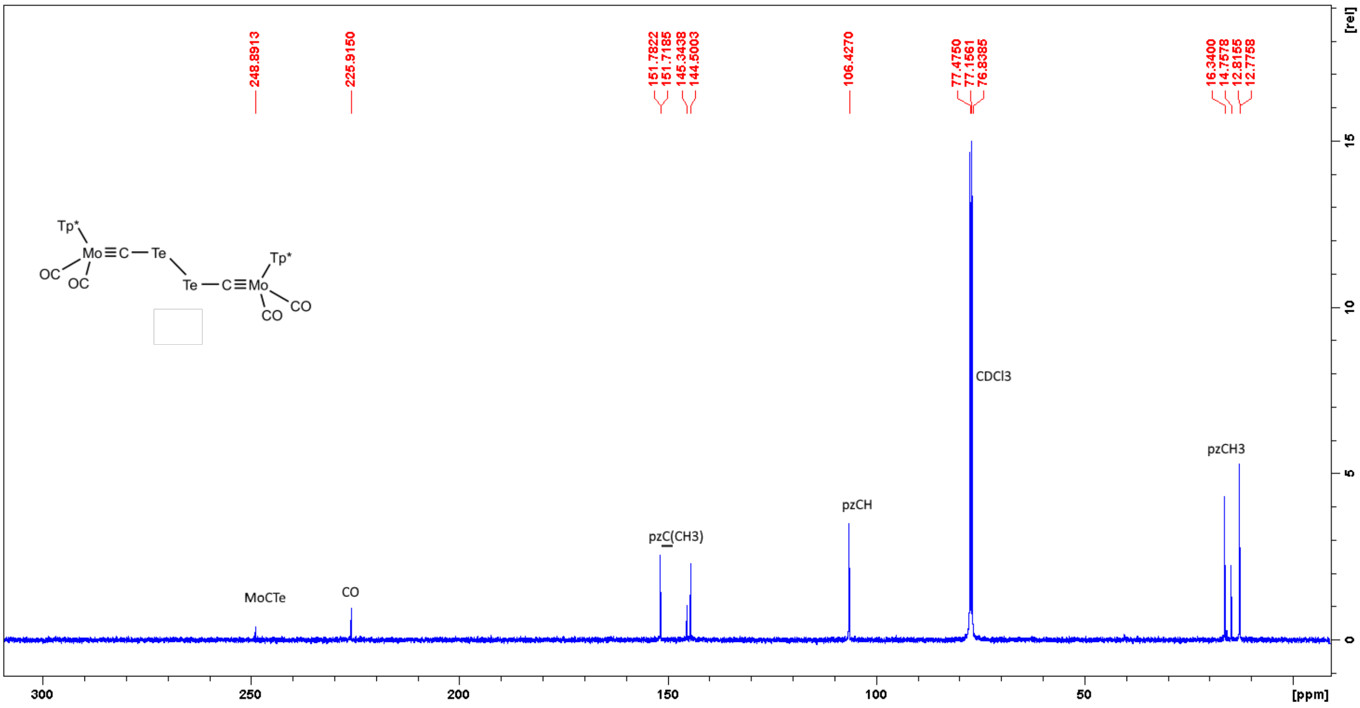
^{125}Te{^{1}H} NMR Spectrum of **6b**



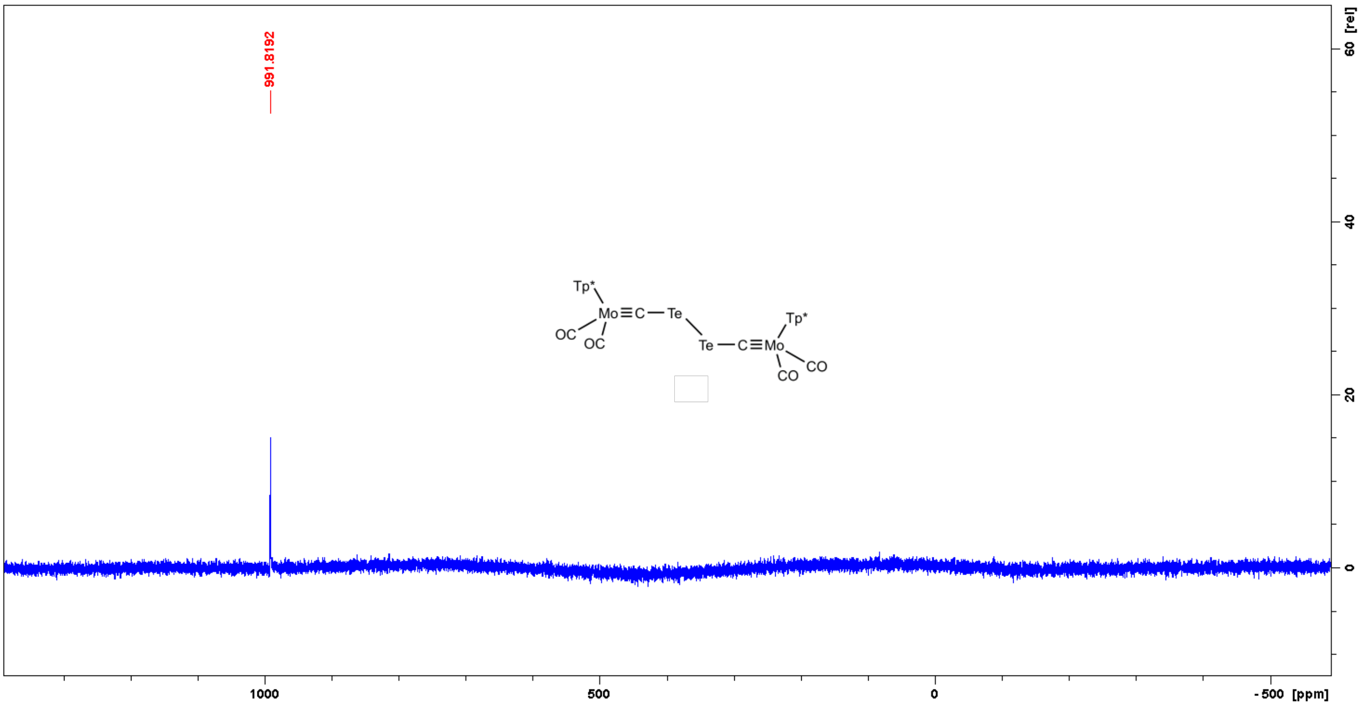
^{1}H NMR Spectrum of **7a**



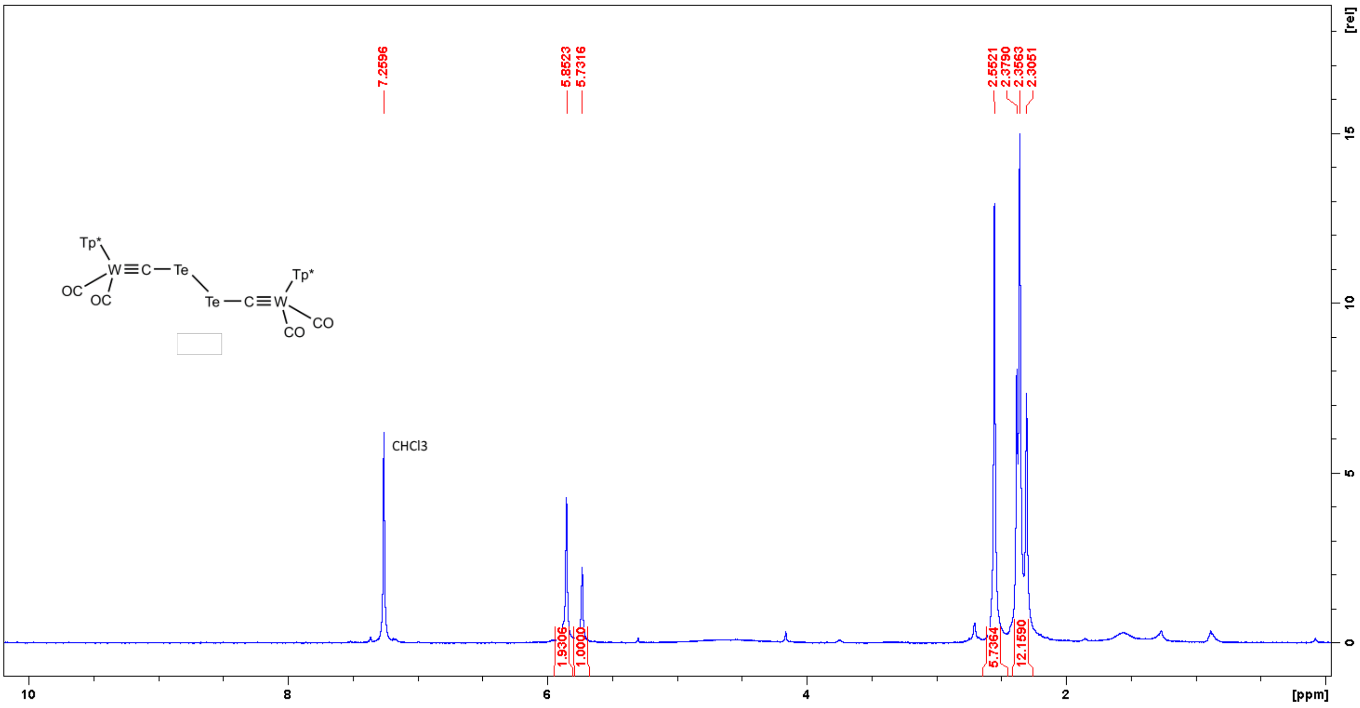
$^{13}C\{^{1}H\}$ NMR Spectrum of **7a**



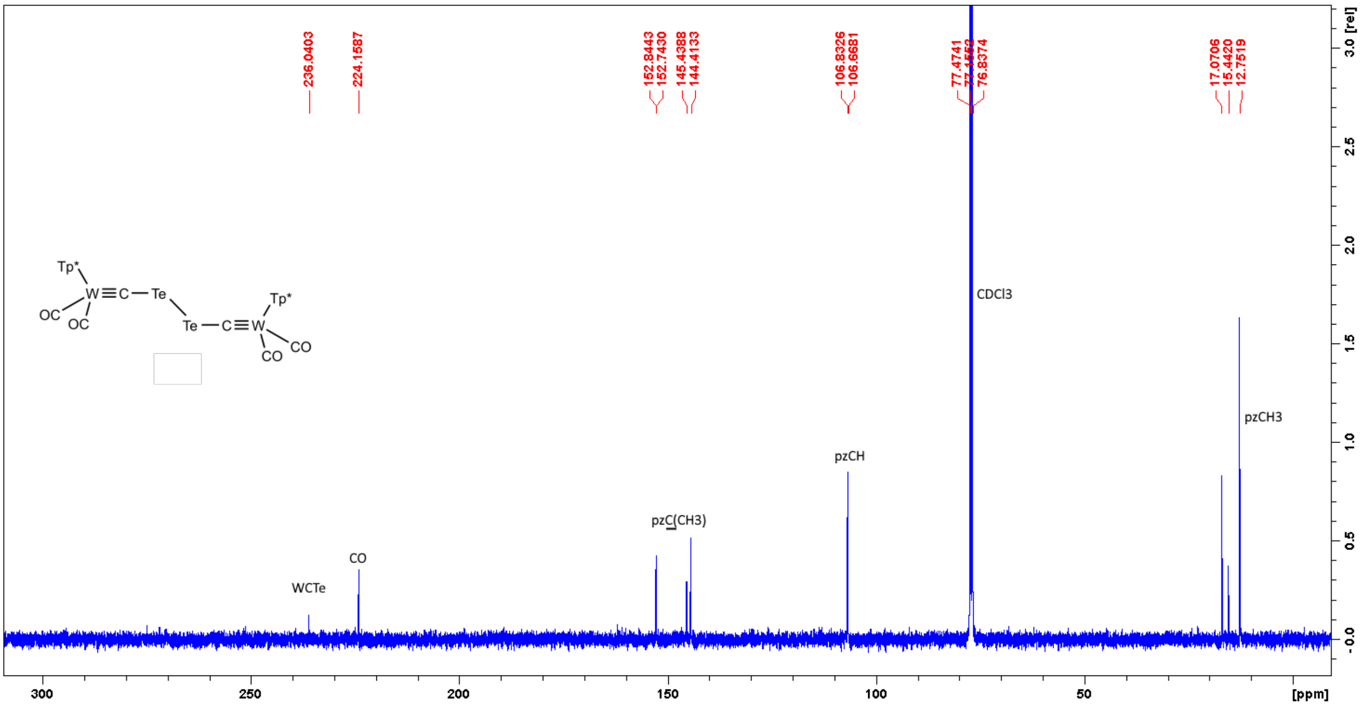
$^{125}Te\{^{1}H\}$ NMR Spectrum of **7a**



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



^{13}C{^{1}H} NMR Spectrum of **7b**



^{125}Te{^{1}H} NMR Spectrum of **7b**