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Synthesis and Reactivity of an Anionic Allenylidene Complex

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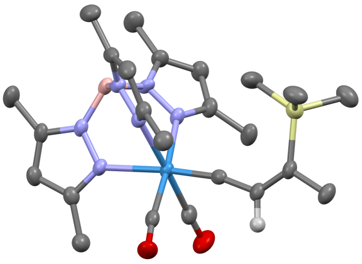
Experimental Procedures

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 recorded on a Bruker Avance 700 (^{1}H at 700.2 MHz, ^{13}C at 176.1 MHz) spectrometers or a Bruker Avance 800 with cryoprobe (^{1}H at 800.1 MHz, ^{13}C{^{1}H} at 201.2 MHz). Chemical shifts (δ) are reported in ppm and referenced to the solvent peak ($CHCl_3$: $\delta_H = 7.26$, $\delta_C = 77.0$) with coupling constants given in Hz. The multiplicities of NMR resonances are denoted by the abbreviations s (singlet), d (doublet), t (triplet), q (quartet), 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 (See actual spectra). Infrared spectra were obtained using a Perkin-Elmer FT-IR/FIR Frontier 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 obtained from the London Metropolitan University microanalytical service. High-resolution electrospray ionisation mass spectrometry (ESI-MS) was performed by the ANU Research School of Chemistry mass spectrometry service with acetonitrile 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-Kαradiation (λ= 1.54184 Å). CCDC 1559203 - 1559205 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. The synthesis of the complex [W(≡CCCSiMe$_3$)(CO)$_2$Tp*] (**1a**) has been described previously.[1] The abbreviation 'pz' is used to refer to the pyrazolyl rings on the hydridotris(3,4-dimethylpyrazolyl)borate (Tp*) ligand.

Synthesis of W(≡CCH=CMeSiMe$_3$)(CO)$_2$(Tp*) *E/Z*-3



A red solution of [W(≡CC≡CSiMe$_3$)(CO)$_2$(Tp*)] (**1a**: 200 mg, 0.309 mmol)[1] in tetrahydrofuran (10 mL) at 0°C and was treated with methyllithium (0.2 mL, 1.6 M solution in Et_2O, 0.320 mmol) and was stirred at 0°C for 10 minutes resulting in a deep green coloured solution. The dark green solution was quenched with distilled water (10 mL) at 0°C instantly turning the solution red, which is then warmed to r.t. and stirred for an additional 20 minutes yielding a red solution. The compound was extracted with dichloromethane (10 mL) and the organic layer collected and dried over $MgSO_4$. The extract was then filtered and all volatiles were removed to give a dark red residue that was purified by column chromatography on silica gel. Elution with dichloromethane:petroleum spirits (40-60°C) (1:9) provided an orange band that was collected and freed of volatiles to give an orange solid powder that was shown to be a mixture of {*E,Z*}-[W(≡CCH=CMeSiMe$_3$)(CO)$_2$(Tp*)] isomers in a E:Z::45:55 ratio. Yield 131 mg (0.198 mmol, 64 % Yield). Crystals suitable for single crystal X-ray crystallographic study were grown from a solution in ^{n}pentane stored at –20 °C.

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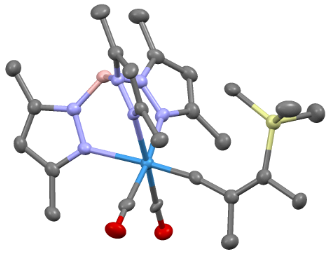
CCDC 1559203 - 1559205 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Crystal data for E-$C_{24}H_{35}BN_6O_2SiW$: M_w = 662.33, monoclinic, $P2_1/c$, a = 9.3555(3) Å, b = 14.6772(3) Å, c = 20.6011(4) Å, β = 89.688(2)°, V = 2828.74(12) Å^3, Z = 4, ρ_{calcd} = 1.555 Mg m^{-3}, μ = 4.16 mm^{-1}, T = 150(2) K, red block, 0.35 × 0.20 × 0.11 mm, 5791 independent reactions, F^2 refinement, R = 0.052, wR = 0.064 for 5791 reflections ($I > 2\sigma(I)$, $2\theta_{max}$ = 52.8°), 334 parameters (CCDC 1559203).

Data for ***{Z}*-[W(≡CCH=CMeSiMe$_3$)(CO)$_2$(Tp*)** ***Z*-3** - IR (DCM) ν_{CO} 1967 vs, 1875 vs cm^{-1}. ^{1}H NMR (CDCl$_3$, 25°C, 700.2 MHz): δ_H = 7.04 (q, 1 H, Hβ, $^4J_{HH}$ = 1.4 Hz), 5.87 (2 H), 5.75 (1 H) (s × 2, 3 H, pzH), 2.55 (6 H), 2.41 (3 H), 2.39 (6 H), 2.33 (3 H) (s × 4, 18 H, pzCH$_3$), 1.67 (d, 3 H, Meγ, $^4J_{HH}$ = 1.4 Hz), –0.02 (s, 9 H, SiCH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25°C, 176.1 MHz): δ_C = 280.2 (W≡C, $^1J_{WC}$ = 183.0), 224.5 (WCO, $^1J_{WC}$ = 166.4), 152.2 [C^5(pz)], 151.6 [C^5(pz)] 151.1 (Cβ, $^2J_{WC}$ = 46.1), 148.9 (Cγ, $^1J_{SiC}$ = 62.5 Hz), 145.0 [C^3(pz)], 144.2 [C^3(pz)], 106.5 [C^4(pz)], 106.3 [C^4(pz)], 23.8 (Meγ), 16.6 (pzCH$_3$), 15.3 (pzCH$_3$), 12.9 (pzCH$_3$), 12.7 (pz-CH$_3$) –0.72 (SiCH$_3$). MS (ESI, high resolution): m/z (%) 662.2225. Calcd for $C_{24}H_{35}{}^{11}B_1N_6O_2{}^{28}Si_1{}^{184}W_1$: 662.2193 [M]$^+$. Anal. found: C, 43.49; H, 5.46; N, 12.52%. Calcd for $C_{24}H_{35}B_1N_6O_2Si_1W_1$: 43.52; H, 5.33; N, 12.69%.

Data for ***E*-[W(≡CCH=CMeSiMe$_3$)(CO)$_2$Tp*** ***E*-3** - ^{1}H NMR (CDCl$_3$, 25°C, 700.2 MHz): δ_H = 6.43 (q, 1 H, Hβ, $^4J_{HH}$ = 1.4 Hz), 5.88 (2 H), 5.77 (1 H) (s × 2, 3 H, pzH), 2.53 (6 H), 2.42 (3 H), 2.38 (6 H), 2.34 (3 H) (s × 4, 18 H, pzCH$_3$), 1.96 (m, 3 H, Meγ, $^4J_{HH}$ = 1.4 Hz), -0.08 (s, 9 H, SiCH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25°C, 176.1 MHz): δ_C = 282.6 (WC, $^1J_{WC}$ = 183.7), 225.7 (WC, $^1J_{WC}$ = 167.3), 152.3, 152.0 [C^5(pz)], 149.9 (Cγ, $^1J_{SiC}$ = 69.0), 145.7 (Cβ, $^2J_{WC}$ = 42.4 Hz), 145.0, 144.4 [C^3(pz)], 106.6, 106.4 [C^3(pz)], 22.5 (Meγ), 16.4 (pzCH$_3$), 15.8 (pzCH$_3$), 12.7 (pzCH$_3$), –2.29 (SiCH$_3$).

Synthesis of W(≡CCMe=CMeSiMe$_3$)(CO)$_2$(Tp*) *E/Z*-4



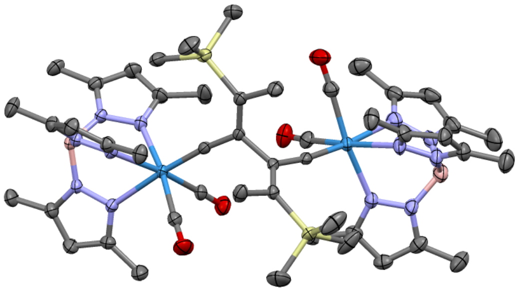
A red solution of [W(≡CCCSiMe$_3$)(CO)$_2$(Tp*)] (**1a**: 200 mg, 0.309 mmol) in tetrahydrofuran (10 mL) at 0°C was treated with methyl lithium (0.20 mL, 1.6 M solution in Et$_2$O, 0.32 mmol) and stirred at 0°C for 10 minutes resulting in a deep green coloured solution. The dark green solution was treated with iodomethane (0.02 mL, 2.28 g cm^{-1}, 0.320 mmol) at 0°C and was stirred for 10 minutes, then warmed up to r.t. and stirred for 20 minutes yielding an orange solution. All volatiles were removed to provide a dark orange solid residue. The residue was purified on silica gel with dichloromethane:petroleum spirits (40-60°C) (1:9) as the eluent providing an orange band that was collected and freed of volatiles to give an orange solid compound as a mixture of *E,Z*-[W(≡CCMe=CMeSiMe$_3$)(CO)$_2$(Tp*)] isomers in a E:Z::9:91 ratio. Yield 141 mg (0.207 mmol, 67% Yield). Crystals suitable for single x-ray crystallographic study were grown from a solution ^{n}pentane stored at -20˚C.

Crystal data for $C_{25}H_{37}BN_6O_2SiW$: M_w = 676.35, monoclinic, $P2_1/c$, a = 12.6360(4) Å, b = 14.8272(5) Å, c = 16.3046(6) Å, β = 109.839(4)°, V = 2873.47(18) Å^3, Z = 4, ρ_{calcd} = 1.563 Mg m^{-3}, μ = 4.09 mm^{-1}, T = 150(2) K, red plate, 0.48 × 0.17 × 0.05 mm, 5868 independent reactions, F^2 refinement, R = 0.033, wR = 0.071 for 4665 reflections ($I > 2\sigma(I)$, $2\theta_{max}$ = 58.2°), 340 parameters (CCDC 1559204).

Data for ***Z*-[W(≡CCMe=CMeSiMe$_3$)(CO)$_2$(Tp*)** - IR (DCM) ν_{CO} 1964 vs, 1871 vs cm^{-1}. ^{1}H NMR (CDCl$_3$, 25°C, 700.2 MHz): δ_H = 5.86 (2 H), 5.76 (1 H) (s × 2, 3 H, pzH), 2.52 (6 H), 2.41 (3 H), 2.37 (6 H), 2.31 (3 H) (s × 4, 18 H, pzCH$_3$), 2.06 (m, 3 H, Meβ), 1.57 (m, 3 H, Meγ), –0.16 (s, 9 H, SiCH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25°C, 176.0 MHz): δ_C = 287.3 (WC), 225.3 (WCO, $^1J_{WC}$ = 165.4 Hz), 156.0 (Cβ, $^2J_{WC}$ = 42.24 Hz), 152.2, 151.5 [C^5(pz)], 144.9, 144.1 [C^3(pz)], 140.7 (Cγ), 106.5, 106.2 [C^4(pz)], 19.2 (Meγ), 18.5 (Meβ), 16.5 (pzCH$_3$), 15.3 (pzCH$_3$), 12.9 (pzCH$_3$), 12.8 (pzCH$_3$) –0.4 (SiCH$_3$). MS (ESI, high resolution): *m/z* = 676.2342. Calcd. for $C_{25}H_{37}{}^{11}B_1N_6O_2Si_1{}^{184}W_1$: 676.2350 [M]$^+$. Anal. found: C, 44.38; H, 5.63; N, 12.35%. Calcd. for $C_{25}H_{37}B_1N_6O_2Si_1W_1$: 44.40; H, 5.51; N, 12.43%.

Data for ***E*-[W(≡CCMe=CMeSiMe$_3$)(CO)$_2$(Tp*)** - ^{1}H NMR (CDCl$_3$, 25°C, 700.2 MHz): δ_H = 5.85 (2 H), 5.76 (1 H) (s × 2, 3 H, pzH), 2.47 (6 H), 2.41 (3 H), 2.37 (6 H), 2.33 (3 H) (s × 4, 18 H, pzCH$_3$), 2.00 (m, 3 H, Meβ), 1.86 (m, 3 H, Meγ), 0.12 (s, 9 H, SiCH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25°C, 176.0 MHz): δ_C = 286.1 (WC), 225.5, 153.4, 152.3 [C^5(pz)], 151.9, 144.9, 144.2 [C^3(pz)], 140.5 (Cγ), 106.6, 106.2 [C^4(pz)], 19.6 (Meγ), 19.5 (Meβ), 16.1 (pzCH$_3$), 14.2 (pzCH$_3$), 12.9 (pzCH$_3$), 12.7 (pzCH$_3$) –0.3 (SiCH$_3$).

Synthesis of {C(=CMeSiMe$_3$)C≡W(CO)$_2$(Tp*)}$_2$ (6)



A red solution of [W(≡CCCSiMe$_3$)(CO)$_2$(Tp*)] (**1a**: 200 mg, 0.309 mmol) in tetrahydrofuran (10 mL) at 0°C and was treated with methyl lithium (0.20 mL, 1.6 M solution in Et$_2$O, 0.32 mmol) and was stirred at 0°C for 10 minutes resulting in a deep green coloured solution. The dark green solution was treated with bromine (0.016 mL, 3.103 g cm^{-1}, 0.320 mmol) at 0°C and was stirred for 10 minutes, then allowed to warm to r.t. Stirring for a further 20 minutes yielded a dark orange solution. All volatiles are removed under reduced pressure providing a brown solid residue. The residue was purified by column chromatography on silica gel commencing with dichlorometane:petroleum spirits (40-60°C) (1:9) as the eluent followed by a gradual change to (1:1). The third orange band was collected and freed of volatiles to give an orange microcrystalline solid identified as {C(=CMeSiMe$_3$)C≡W(CO)$_2$(Tp*)}$_2$ (**6**). Yield 39 mg (19% Yield). Crystal suitable for single crystal *X*-ray crystallographic study were grown from a solution in ^{n}pentane and dichloromethane stored at –20˚C. IR (DCM) ν_{CO} 1980 sh, 1972 vs, 1892 s, 1871 s cm^{-1}. ^{1}H NMR (CDCl$_3$, 25°C, 800 MHz): δ_H = 5.87, 5.84, 5.71 (s x 3, 1 H x 3, pzH), 2.76, 2.50, 2.40, 2.39, 2.37, 2.30 (s x 6, 3 H x 6, pzCH$_3$), 1.74 (s, 3 H, =CCH$_3$), –0.15 (s, 9 H, SiCH$_3$). Minor stereoisomer (14%): 5.80, 5.69, 5.65 (s x 3, 1 H x 3, pzH), 2.34, 2.33, 2.32, 2.28, 2.25 (s x 5, 3 H x 5, pzCH$_3$, equivocal assignments due to peak overlap with major stereoisomer), 1.79 (s, 3 H, =CCH$_3$), 0.17 (s, 9 H, SiCH$_3$). ^{13}C{^{1}H} (201 MHz, CDCl$_3$, resonances for minor isomer in italics) 281.9 (W≡C), 227.0, 226.4 (diastereotopic CO), 159.0 (Cβ, $^2J_{WC}$ = 23), 152.5, *152.14*, 152.1, *151.9*, 151.3 [C^5(pz)], 145.0 (Cγ), 144.4, *144.4*, *144.2*, 144.1, 143.9 [C^3(pz)], 106.5, 106.4, *106.4, 106.1*, 106.0, 106.0, *105.6* [C^4(pz)], 31.60, *29.7*, 22.7 [pzCH$_3$], 20.9 (CCH$_3$, HSQC with δ_H = 1.74), *17.7*, 17.4, 17.1, *15.1*, 15.0, 14.1 [C^3(pz)], *12.9*, 12.9(2C), *12.8*, 12.8(2C), *12.8*, *12.7*, 12.6(2C), *12.6*, *12.5*, *0.3*, –0.2 (SiCH$_3$). MS (ESI, high resolution): *m/z* = 1322.4226. Calcd. for $C_{48}H_{68}{}^{11}B_2N_{12}O_4Si_2{}^{184}W_2$: 1322.4230 [M]$^+$. Anal. found: C, 43.74; H, 5.23; N, 12.61%. Calcd. for $C_{48}H_{68}B_2N_{12}O_4Si_2W_2$: 43.59; H, 5.18; N, 12.71%. *Crystal data for* $C_{48}H_{68}B_2N_{12}O_4Si_2W_2{\cdot}C_5H_{12}$: M_w = 1394.79, triclinic, *P*-1, *a* = 11.0937(3) Å, *b* = 13.1532(3) Å, *c* = 22.7516(4) Å, α = 91.059(2)°, β = 98.161(4)°, γ = 108.441(2)°, *V* = 3110.38(13) Å^3, Z = 2, ρ_{calcd} = 1.489 Mg m^{-3}, μ = 3.79 mm^{-1}, *T* = 150 K, orange block, 0.36 × 0.17 × 0.11 mm, 12726 independent reactions, F^2 refinement, *R* = 0.029, *wR* = 0.062 for 10868 reflections ($I > 2\sigma(I)$, $2\theta_{max}$ = 52.8°), 725 parameters, 65 restraints (CCDC 1559204).

In Situ* Observation of Li[W(=C=C=CMeSiMe$_3$)(CO)$_2$(Tp*)] 2 –** A red solution of [W(≡CCCSiMe$_3$)(CO)$_2$(Tp*)] (**1a**: 10 mg, 0.015 mmol) in *d*$_6$-tetrahydrofuran (*ca* 0.4 mL) at 0°C and was treated with methyl lithium (0.1 mL, 1.6 M solution in Et$_2$O, 0.016 mmol) and was stirred at 0°C for 10 minutes resulting in a deep green coloured solution. IR (THF) ν_{CO} 1853vs, 1676vs, $\nu_{C=C=C}$ 1928w (tentative) cm^{-1}. A second minor (ca 15%) species believed to be the alternative rotamer (Me syn to Tp*) gives rise to absorptions at ν_{CO} 1830m, 1728w, $\nu_{C=C=C}$ 1933sh cm^{-1} (k***$_{CO}$ = 12.79 Ncm^{-1}). On the ^{1}H and ^{13}C NMR timescale, however, only a single species is apparent suggesting rapid rotation about the allenylidene spine. Partial hydrolysis (*ca* 5%) during data acquisition corresponds to formation of **3** (THF: ν_{CO} = 1961 cm^{-1}). ^{1}H NMR (d$_6$-THF, –10°C, 700 MHz): δ_H = 5.87 (1 H), 5.62 (2 H) (s × 2, 3 H, pzH), 2.48 (3 H), 2.41 (3 H), 2.40 (6 H), 2.10 (6 H) (s × 4, 18 H, pzCH$_3$), 0.70 (s, 3 H, Meγ), –0.3 (s, 9 H, SiCH$_3$). ^{13}C{^{1}H} NMR (d$_6$-THF, –10°C, 176.1 MHz): δ_C = 286.8 (W=C, $^1J_{WC}$ = 165.4), 252.8 (WCO, $^1J_{WC}$ = 176.0 Hz), 241.8 (Cβ, br. HMBC with δ_H = 0.70) 154.7, 151.3 [C^5(pz)], 143.5, 142.1 [C^3(pz)], 120.1 (Cγ, HMBC with δ_H = 0.70, –0.3), 106.1, 105.2 [C^4(pz)], 29.0 (Cγ-**C**H$_3$, HSQC with δ_H = 0.70), 16.9, 16.5(pzCH$_3$), 12.5 (2 overlapping, pz-CH$_3$), –2.4 (SiMe$_3$). From the ^{13}C-^{1}H HMBC spectrum it is clear that a second compound is also present with δ_H = 0.81 correlating with δ_C = 269, 218 and 98 resonances.

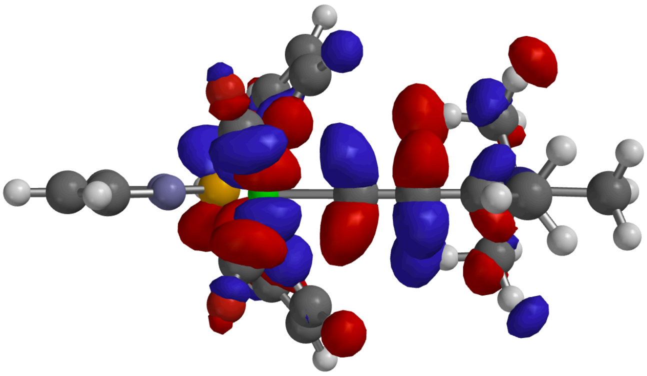


Figure S1. HOMO-2 Calculated (DFT: B3LYP-LANL2DZ) for the [W(C=C=CSiMe$_3$Me)(CO)$_2$(Tp)]$^-$ anion. HOMO-3 also has appreciable Cβ character.

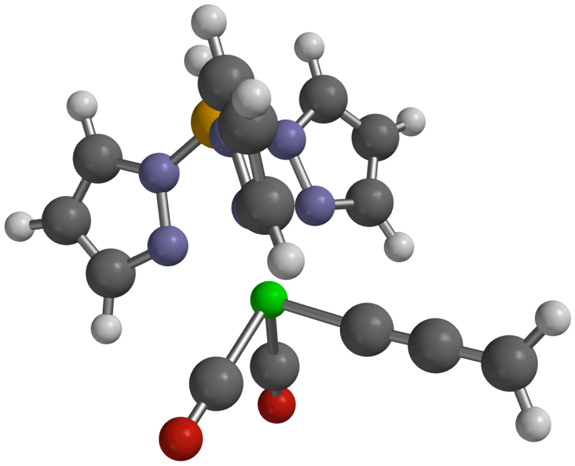


Figure S2. Optimised Geometry (B3LYP-LANL2DZ) for [(Tp)(OC)$_2$W=C=C=CH$_2$]$^-$.

Table S1. Cartesian Coordinates (Å) (B3LYP-LANL2DZ) for [(Tp)(OC)$_2$W=C=C=CH$_2$]$^-$.

Atom	*z*	*y*	*z*
W1	-0.7621884	-0.0043861	1.2635906
N2	1.5221080	-0.0608764	1.3917838
N3	2.3270185	-0.0504770	0.2646467
N4	-0.2217046	1.4889126	-0.3628101
N5	0.8240783	1.2792927	-1.2450294
N6	-0.2927053	-1.4313574	-0.4454457
N7	0.7681363	-1.2300739	-1.3116225
O8	-1.1885941	-2.1078727	3.5832880
O9	-1.1350598	2.0243962	3.6555181
C10	-2.6653029	0.0184519	0.7843419
C11	-1.0375621	-1.3168981	2.6873960
C12	-1.0025276	1.2587623	2.7341458
C13	2.3545674	-0.1081855	2.4552967
C14	3.6968159	-0.1288528	2.0264864
C15	3.6364890	-0.0895584	0.6344366
C16	-0.7856299	2.6661246	-0.7061404
C17	-0.1106760	3.2274142	-1.8099432
C18	0.8996981	2.3214748	-2.1220244
C19	-0.9180723	-2.5546740	-0.8559834
C20	-0.2670240	-3.0899533	-1.9869307
C21	0.7933599	-2.2252991	-2.2448107
B22	1.6853500	0.0002876	-1.1419486
H23	4.5806425	-0.1662433	2.6423253
H24	-0.3313123	4.1581028	-2.3071653
H25	-0.5348133	-3.9783705	-2.5356622
H26	2.5416906	0.0037201	-1.9875703
C27	-3.8946335	0.0191430	0.3857340
C28	-5.1665260	0.0194046	-0.0185055
H29	1.6551737	2.3436836	-2.8905416
H30	-1.6352306	3.0260462	-0.1510271
H31	-1.7900726	-2.8966025	-0.3248949
H32	1.5508625	-2.2457941	-3.0114464
H33	4.4203660	-0.0868574	-0.1056185
H34	1.9405931	-0.1234036	3.4494345
H35	-5.4507722	0.0167086	-1.0742659
H36	-6.0065427	0.0238105	0.6809624

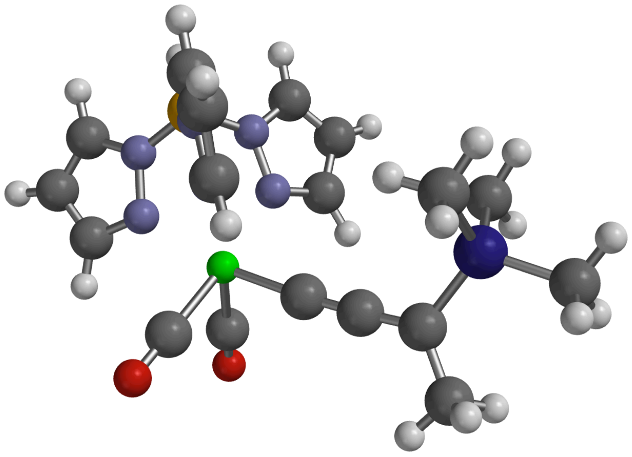


Figure S3. Optimised Geometry (B3LYP-LANL2DZ) for *syn*-$[(Tp)(OC)_2W{=}C{=}C{=}C(SiMe_3)Me]^-$.

Table S2. Cartesian Coordinates (Å) (B3LYP-LANL2DZ) for *syn*-$[(Tp)(OC)_2W{=}C{=}C{=}C(SiMe_3)Me]^-$.

Atom	***z***	***y***	***z***
W1	-0.9960384	0.0332673	1.8366938
N2	-3.2787618	0.0515686	1.8824066
N3	-4.0427022	0.0353298	0.7269431
N4	-1.4470920	-1.4542976	0.1795286
N5	-2.4657802	-1.2588612	-0.7369892
N6	-1.4248804	1.4633297	0.1226237
N7	-2.4473856	1.2497992	-0.7852508
O8	-0.6742563	2.1382513	4.1702312
O9	-0.7013442	-1.9858502	4.2479899
C10	0.9239457	0.0149400	1.4201707
C11	-0.7853373	1.3459377	3.2699751
C12	-0.8025822	-1.2265698	3.3184790
C13	-4.1495164	0.0777357	2.9159113
C14	-5.4753041	0.0782174	2.4392653
C15	-5.3648970	0.0513515	1.0499592
C16	-0.8400597	-2.6117970	-0.1597723
C17	-1.4606836	-3.1738953	-1.2948746
C18	-2.4829409	-2.2900067	-1.6300844
C19	-0.7996331	2.5973050	-0.2600462
C20	-1.4120856	3.1258087	-1.4155658
C21	-2.4489919	2.2466646	-1.7166829
B22	-3.3517649	0.0040255	-0.6564590
H23	-6.3810505	0.0962328	3.0232284
H24	-1.1977022	-4.0908276	-1.7967709
H25	-1.1348468	4.0188835	-1.9516519
H26	-4.1766977	-0.0070148	-1.5321031
C27	2.1654664	0.0049557	1.0641621
C28	3.4369775	-0.0063600	0.6271341
H29	-3.2088946	-2.3197879	-2.4262627
H30	-0.0021384	-2.9599108	0.4200821
H31	0.0434608	2.9533824	0.3073376
H32	-3.1751261	2.2583408	-2.5131890
H33	-6.1216462	0.0426106	0.2822916
H34	-3.7729799	0.0944586	3.9249245
C1	4.6211851	0.0064045	1.5874585
H2	4.2712920	0.0170959	2.6254968
H3	5.2648813	0.8879502	1.4350153
H4	5.2680225	-0.8755502	1.4532555
Si1	3.7313070	-0.0364684	-1.2392980
C2	3.0144415	1.5199392	-2.0788830
H6	1.9543444	1.6265647	-1.8222351
H7	3.1031241	1.4645828	-3.1719110
H8	3.5338395	2.4243894	-1.7393165
C3	2.9096022	-1.5607201	-2.0392788
H5	1.8500938	-1.6006717	-1.7620076
H9	3.3822117	-2.4877223	-1.6920064
H10	2.9824146	-1.5296386	-3.1344709
C4	5.6024590	-0.1030347	-1.6315413
H1	5.7713303	-0.1215803	-2.7160517
H11	6.0667581	-0.9997139	-1.2031302
H12	6.1259625	0.7709562	-1.2247306

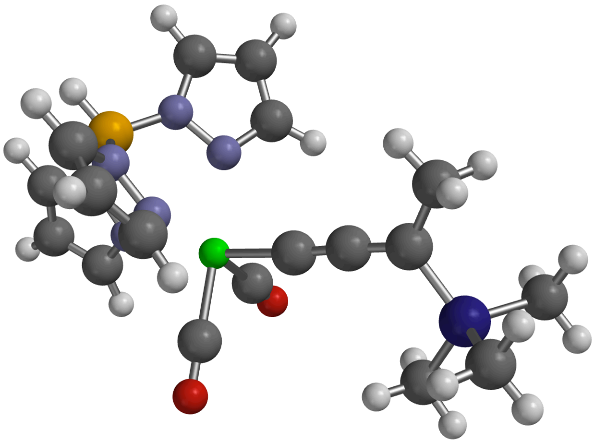


Figure S4. Optimised Geometry (B3LYP-LANL2DZ) for anti-[(Tp)(OC)$_2$W=C=C=C(SiMe$_3$)Me]$^-$.

Table S3. Cartesian Coordinates (Å) (B3LYP-LANL2DZ) for *anti*-[(Tp)(OC)$_2$W=C=C=C(SiMe$_3$)Me]$^-$.

Atom	z	y	z
W1	1.2508426	-0.0482529	0.9145673
N2	3.5310449	-0.0064837	1.0710443
N3	4.3480668	0.0094990	-0.0475937
N4	1.7422893	1.4083075	-0.7648104
N5	2.8088994	1.2125375	-1.6255491
N6	1.8051895	-1.5170395	-0.7224109
N7	2.8610704	-1.2981946	-1.5899151
O8	0.7519700	-2.1932651	3.1755657
O9	0.8948756	1.9388633	3.3489853
C10	-0.6502147	0.0451458	0.4271961
C11	0.9391193	-1.3764282	2.3083846
C12	1.0157145	1.2003265	2.4066969
C13	4.3515937	0.0265475	2.1443940
C14	5.6979115	0.0651568	1.7306140
C15	5.6531486	0.0511307	0.3374448
C16	1.1208340	2.5354156	-1.1715664
C17	1.7803191	3.0787926	-2.2938383
C18	2.8408585	2.2145391	-2.5513695
C19	1.2512899	-2.6958454	-1.0771058
C20	1.9415866	-3.2479936	-2.1754154
C21	2.9523672	-2.3360635	-2.4696810
B22	3.7220835	-0.0205694	-1.4619367
H23	6.5747938	0.0959587	2.3566440
H24	1.5173050	3.9717971	-2.8373637
H25	1.7316558	-4.1773240	-2.6796093
H26	4.5872295	-0.0156681	-2.2982648
C27	-1.8747068	0.1367184	0.0276482
C28	-3.1696649	0.2127457	-0.3242087
H29	3.6030065	2.2395726	-3.3132037
H30	0.2447060	2.8745484	-0.6456610
H31	0.3995633	-3.0644104	-0.5309279
H32	3.7179927	-2.3520495	-3.2281759
H33	6.4451968	0.0645901	-0.3937100
H34	3.9274051	0.0180326	3.1342907
C2	-3.5980865	0.4326007	-1.7722226
H1	-4.2166800	1.3380116	-1.8827649
H5	-4.2036762	-0.4069618	-2.1523952
H6	-2.7215532	0.5373005	-2.4215214
Si1	-4.5146109	0.0078828	0.9855175
C1	-3.7535158	-0.1404801	2.7148649
H2	-4.5228581	-0.3051831	3.4804389
H7	-3.1956046	0.7661748	2.9731270
H8	-3.0395516	-0.9700129	2.7523232
C3	-5.5643272	-1.5544510	0.6296701
H4	-6.3826581	-1.6597586	1.3541977
H9	-4.9401047	-2.4539395	0.6878053
H10	-6.0054429	-1.5160483	-0.3743277
C4	-5.7285618	1.4901266	0.9630795
H3	-6.5373478	1.3449861	1.6911050
H11	-6.1842620	1.6186397	-0.0266550
H12	-5.2065017	2.4204754	1.2165988

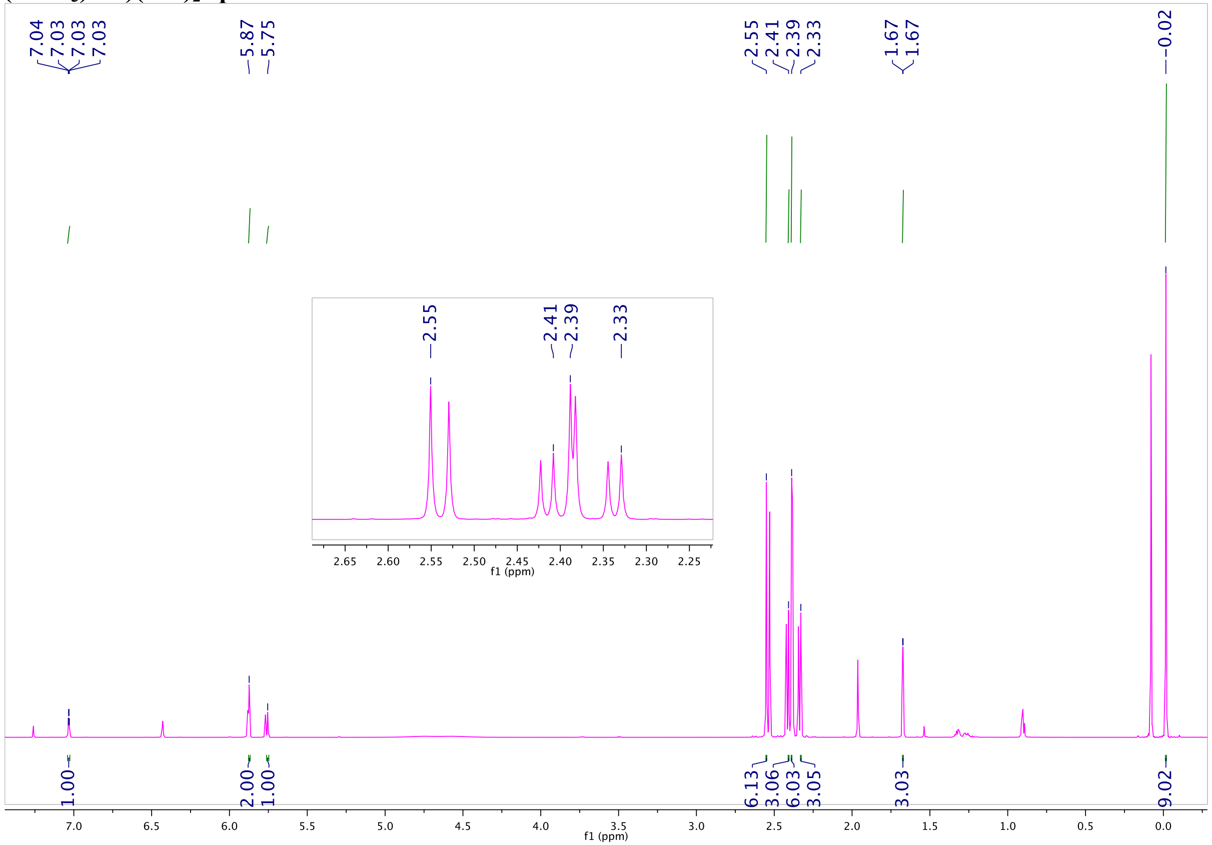
Notes and references

1 B. Schwenzer, J. Schleu, N. Burzlaff, C. Karl and H. Fischer, *J. Organomet. Chem.,* 2002, **641**, 134–141. (b) I. J. Hart, A. F. Hill and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.,* 1989, 2261–2267.

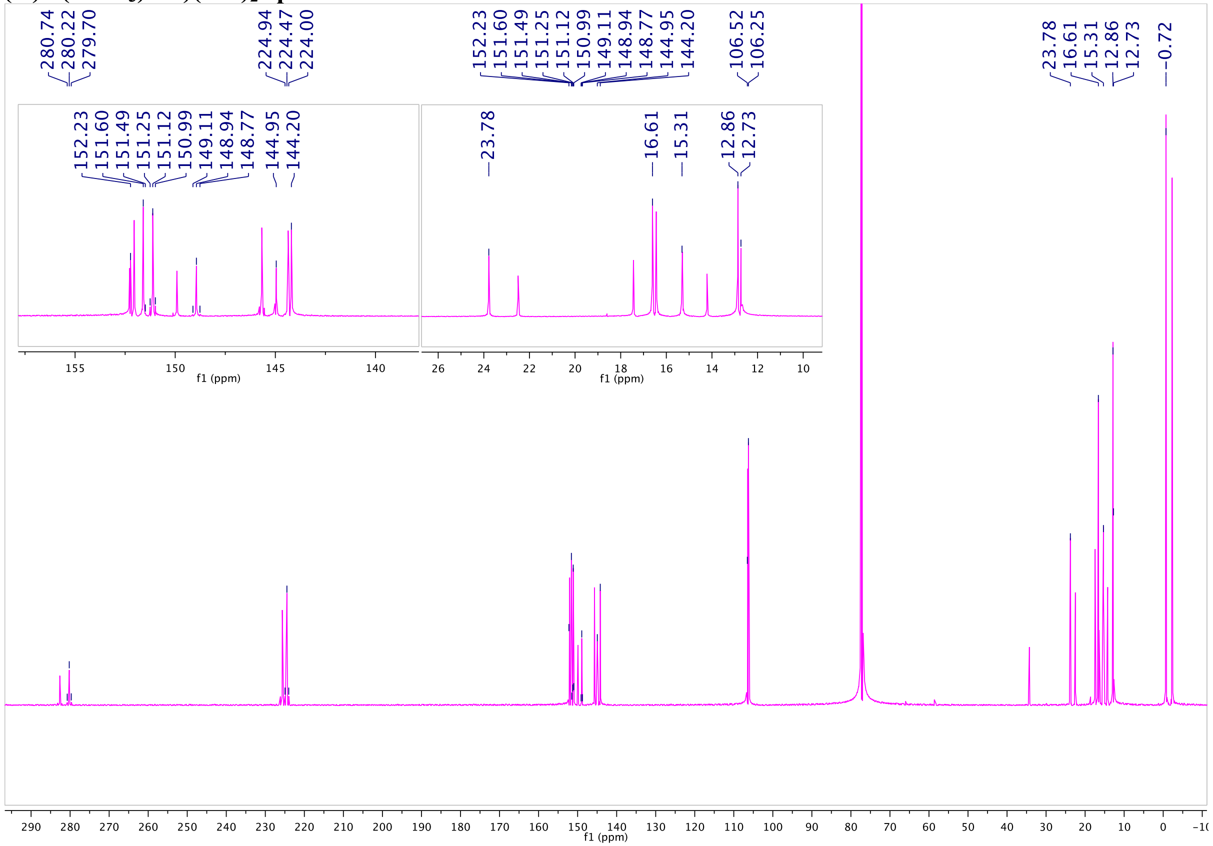
Dalton Transactions

ELECTRONIC SUPPORTING INFORMATION

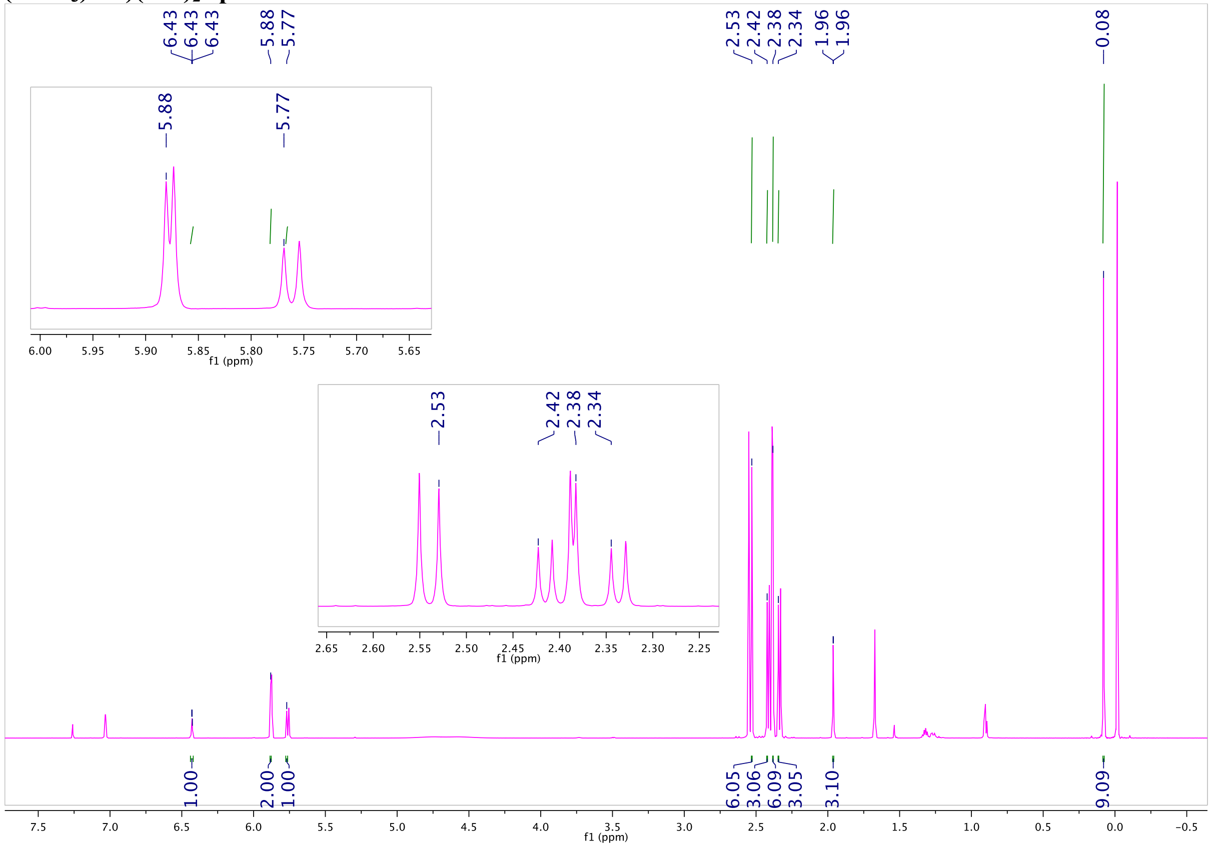
^{1}H NMR of E/Z-W(≡CC(H)C(SiMe$_3$)Me)(CO)$_2$Tp* Resonances for *Z*-isomer indicated.



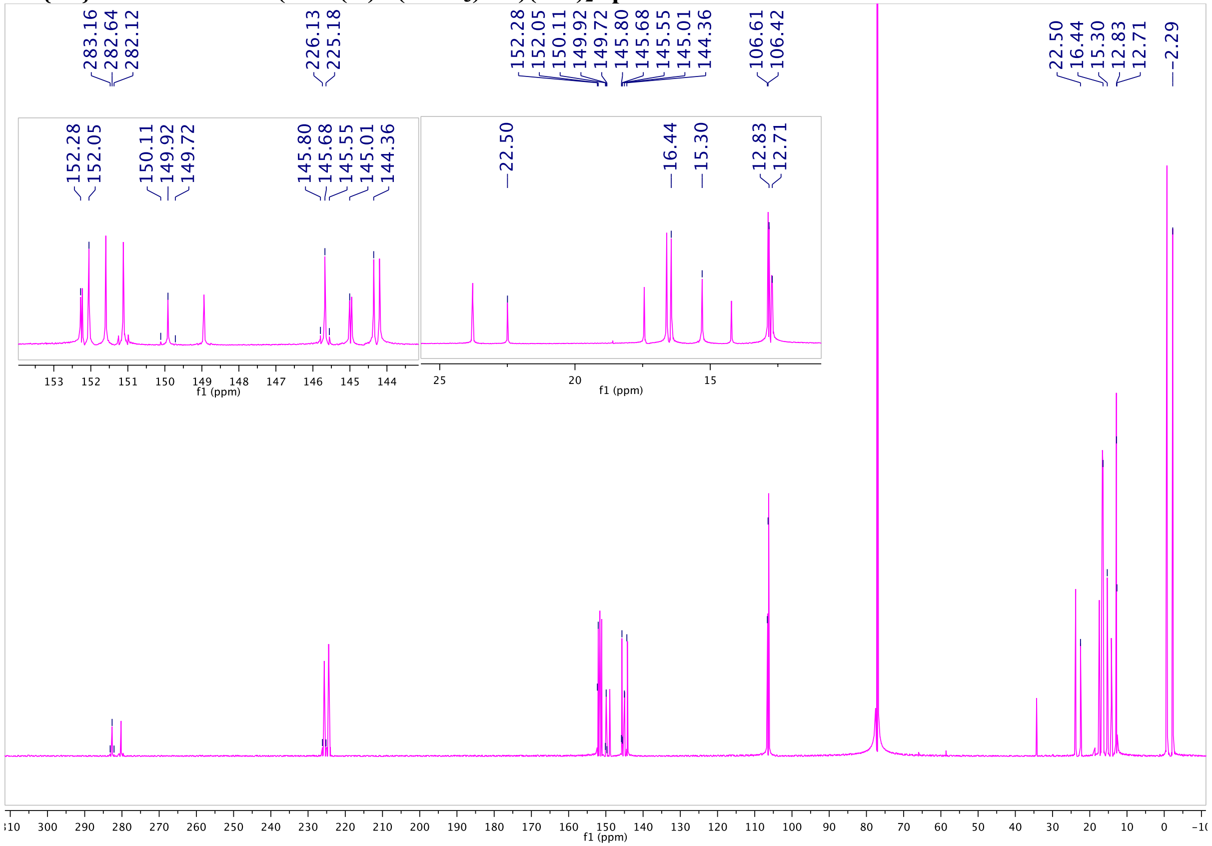
^{13}C{^{1}H} NMR of E/Z-W(≡CC(H)C(SiMe$_3$)Me)(CO)$_2$Tp* Resonances for *Z*-isomer indicated.



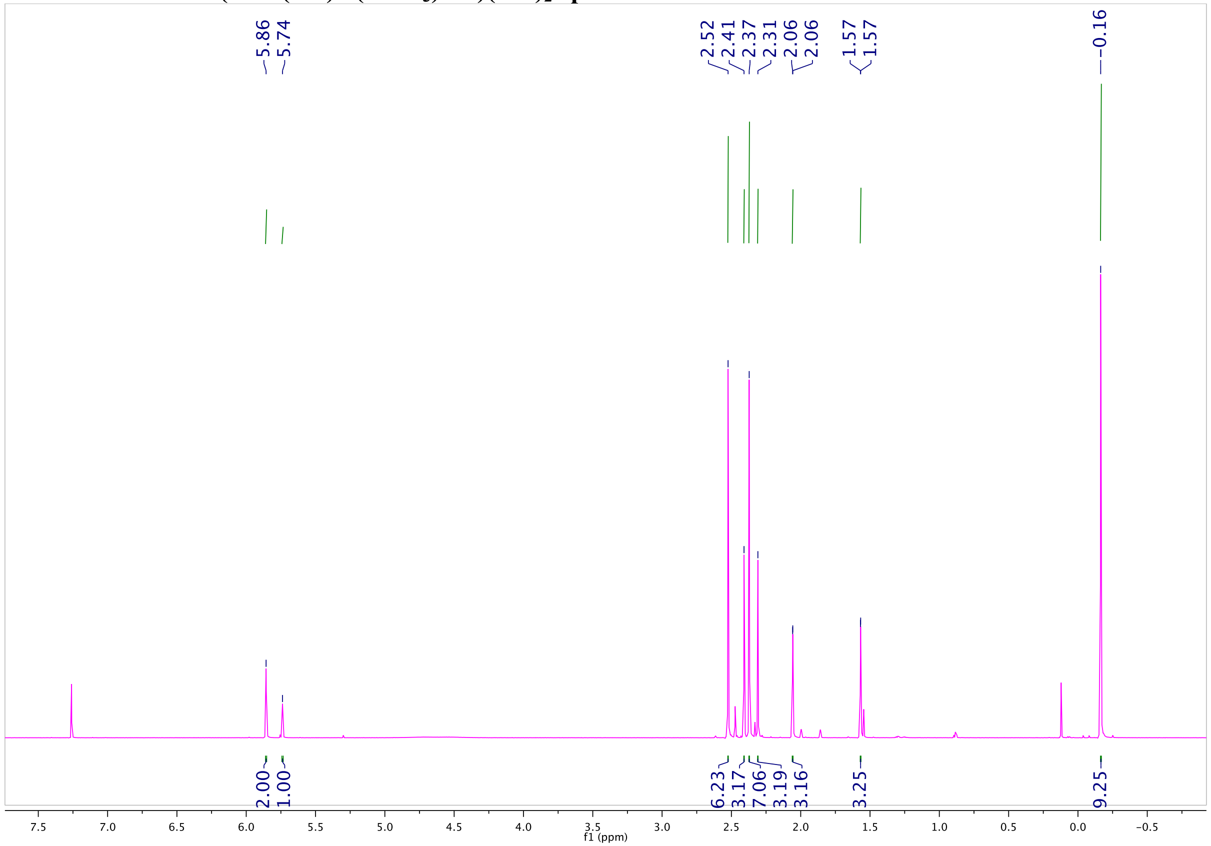
^{1}H NMR of E/Z-W(≡CC(H)C(SiMe$_3$)Me)(CO)$_2$Tp* Resonances for *E*-isomer indicated.



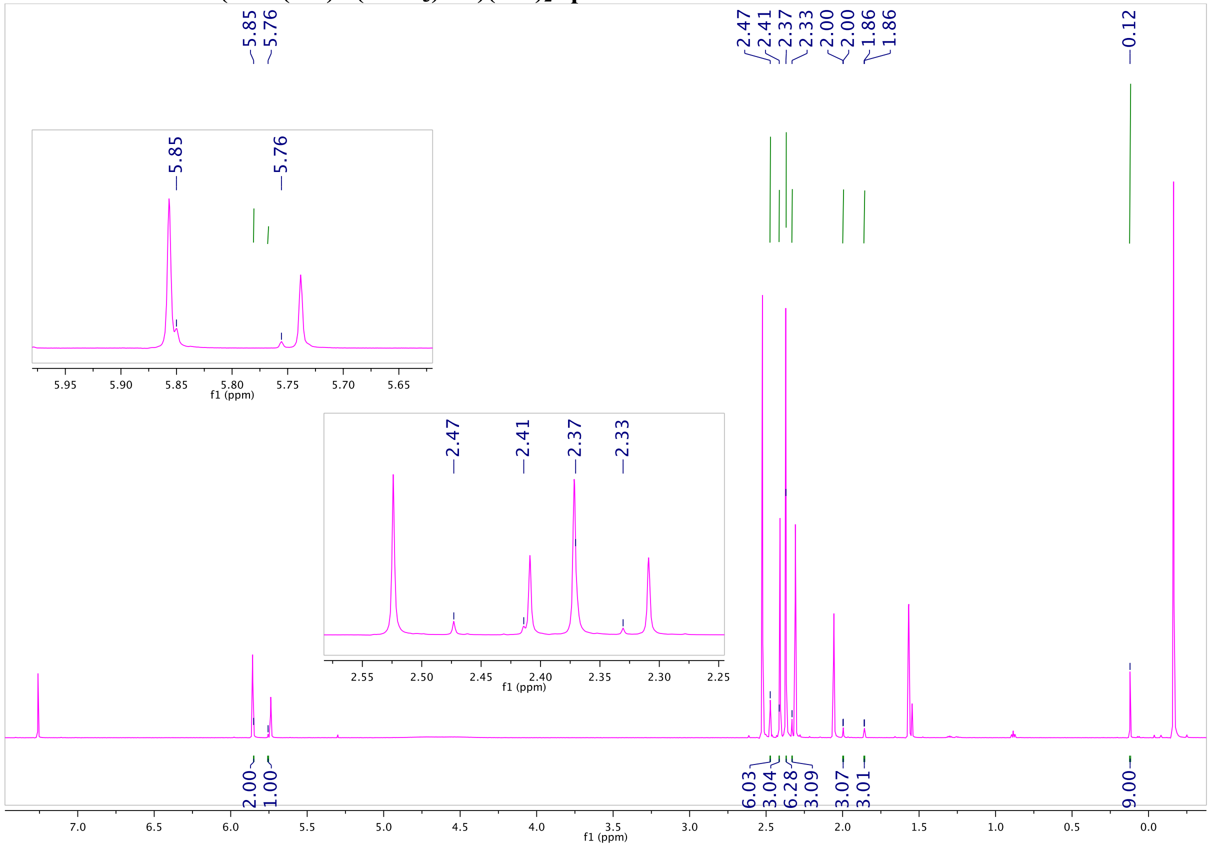
$^{13}C\{^{1}H\}$ NMR of E/Z-W(≡CC(H)C(SiMe$_3$)Me)(CO)$_2$Tp* Resonances for *E*-isomer indicated.



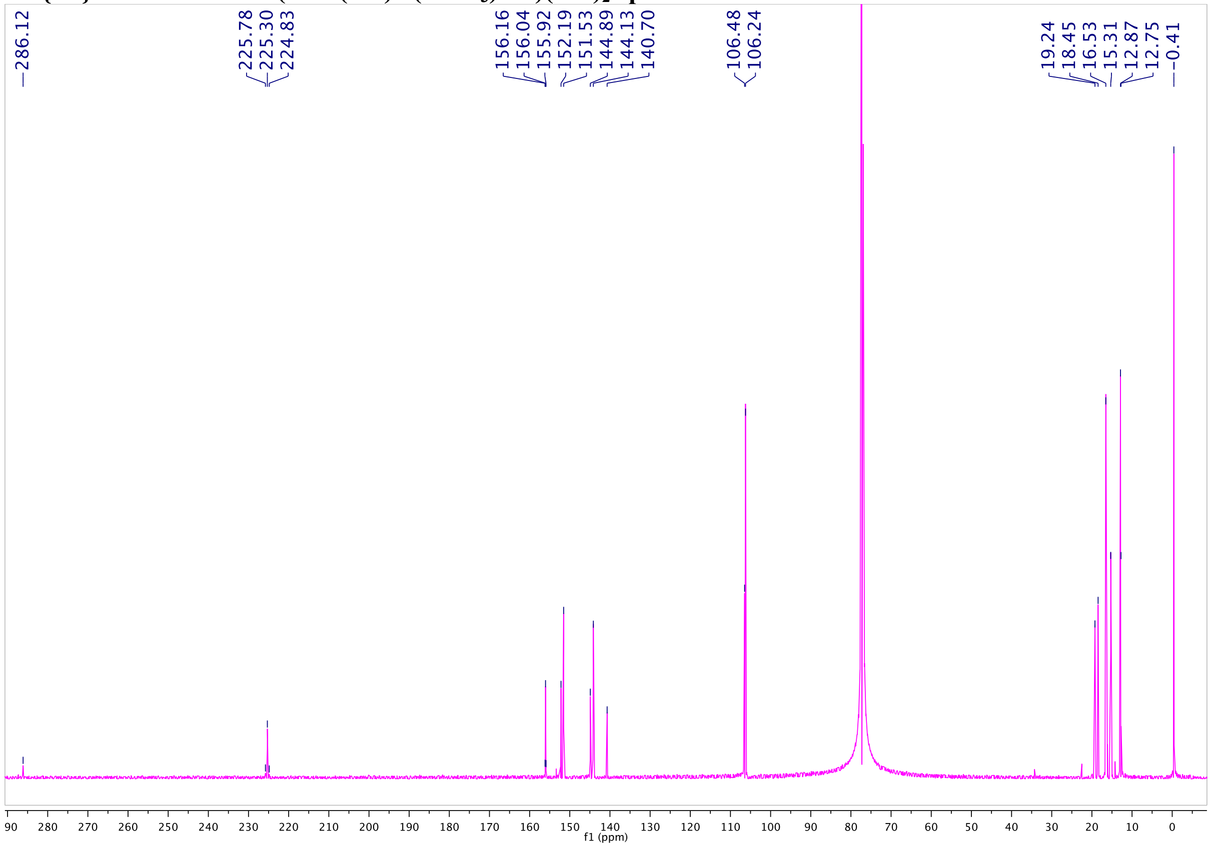
^{1}H NMR of E/Z-W($\equiv$CC(Me)C(SiMe$_3$)Me)(CO)$_2$Tp* Resonances for *Z*-isomer indicated.



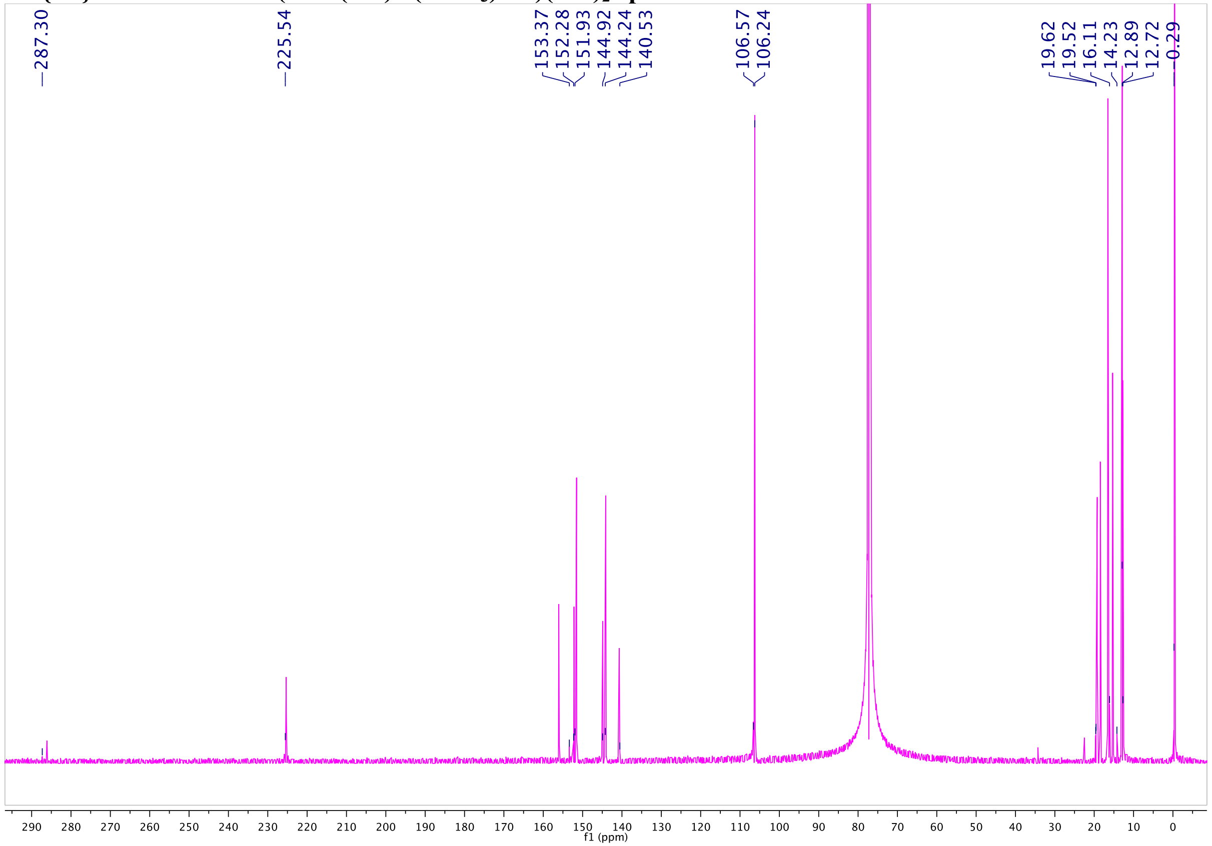
^{1}H NMR of E/Z-W(≡CC(Me)C(SiMe$_3$)Me)(CO)$_2$Tp* Resonances for *E*-isomer indicated.



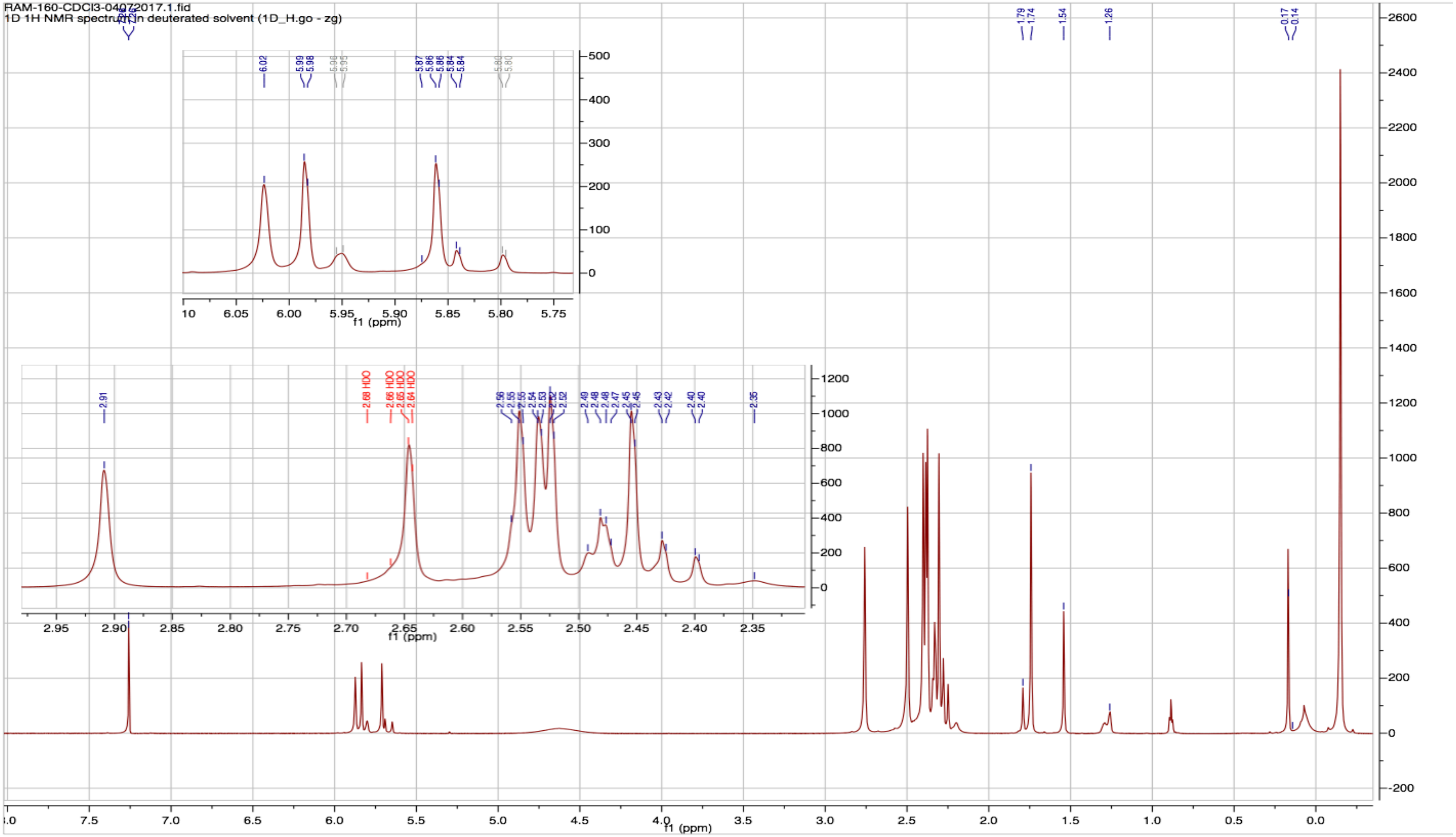
^{13}C{^{1}H} NMR of E/Z-W(≡CC(Me)C(SiMe$_3$)Me)(CO)$_2$Tp* Resonances for *Z*-isomer indicated.



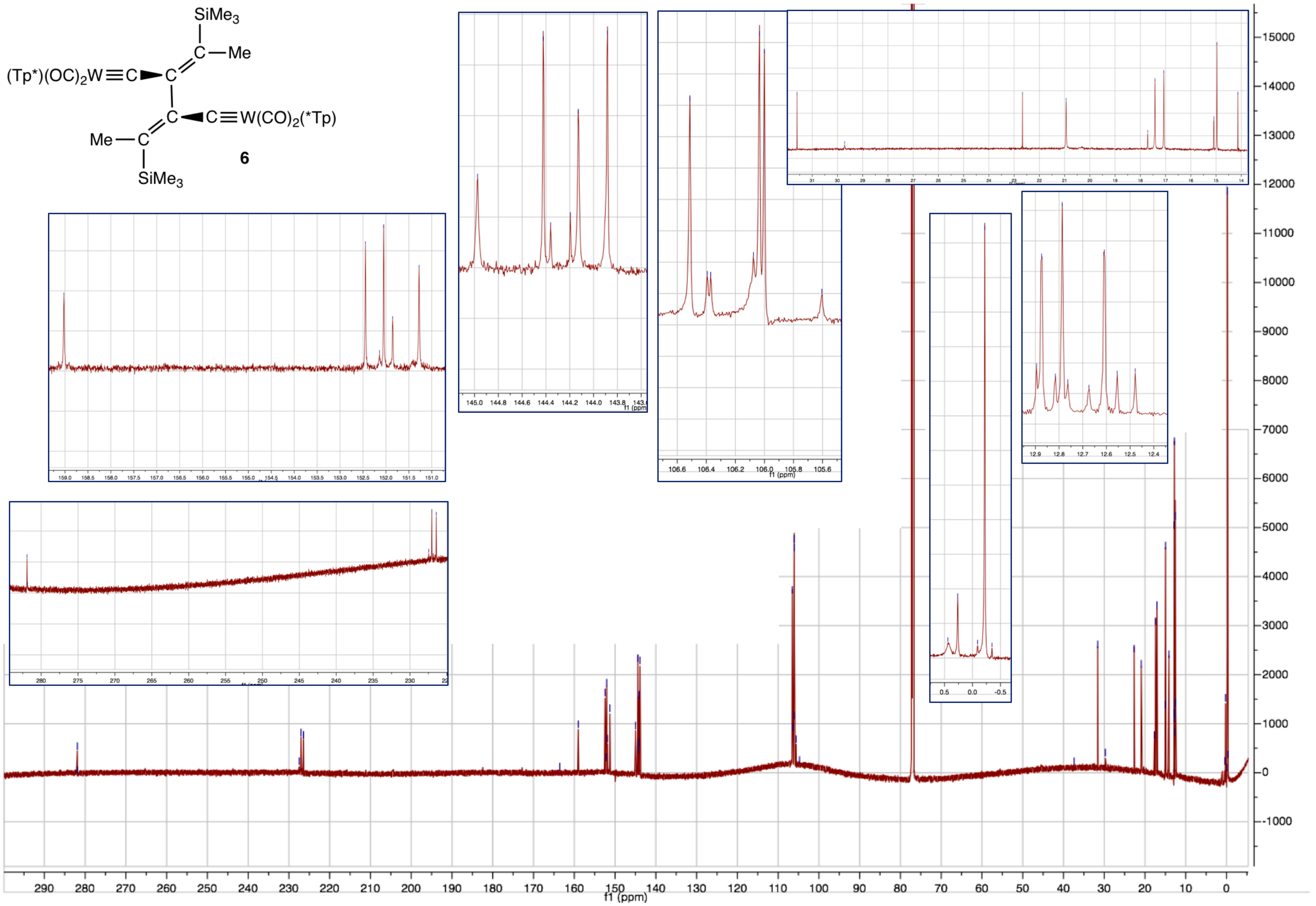
^{13}C{^{1}H} NMR of E/Z-W(≡CC(Me)C(SiMe$_3$)Me)(CO)$_2$Tp* Resonances for *E*-isomer indicated.



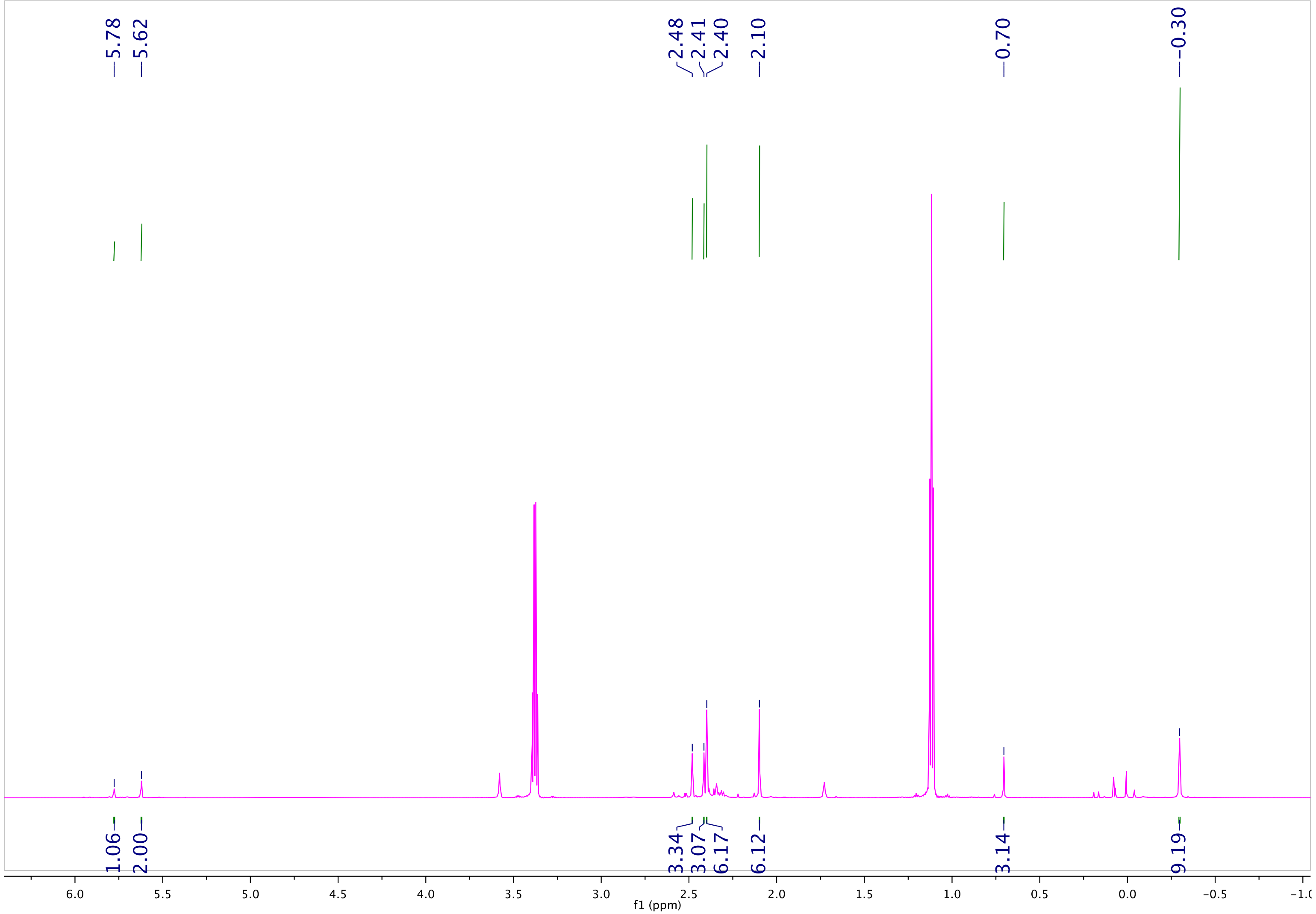
^{1}H NMR Spectrum of {C(=CMeSiMe$_3$)C≡W(CO)$_2$(Tp*)}$_2$ 6



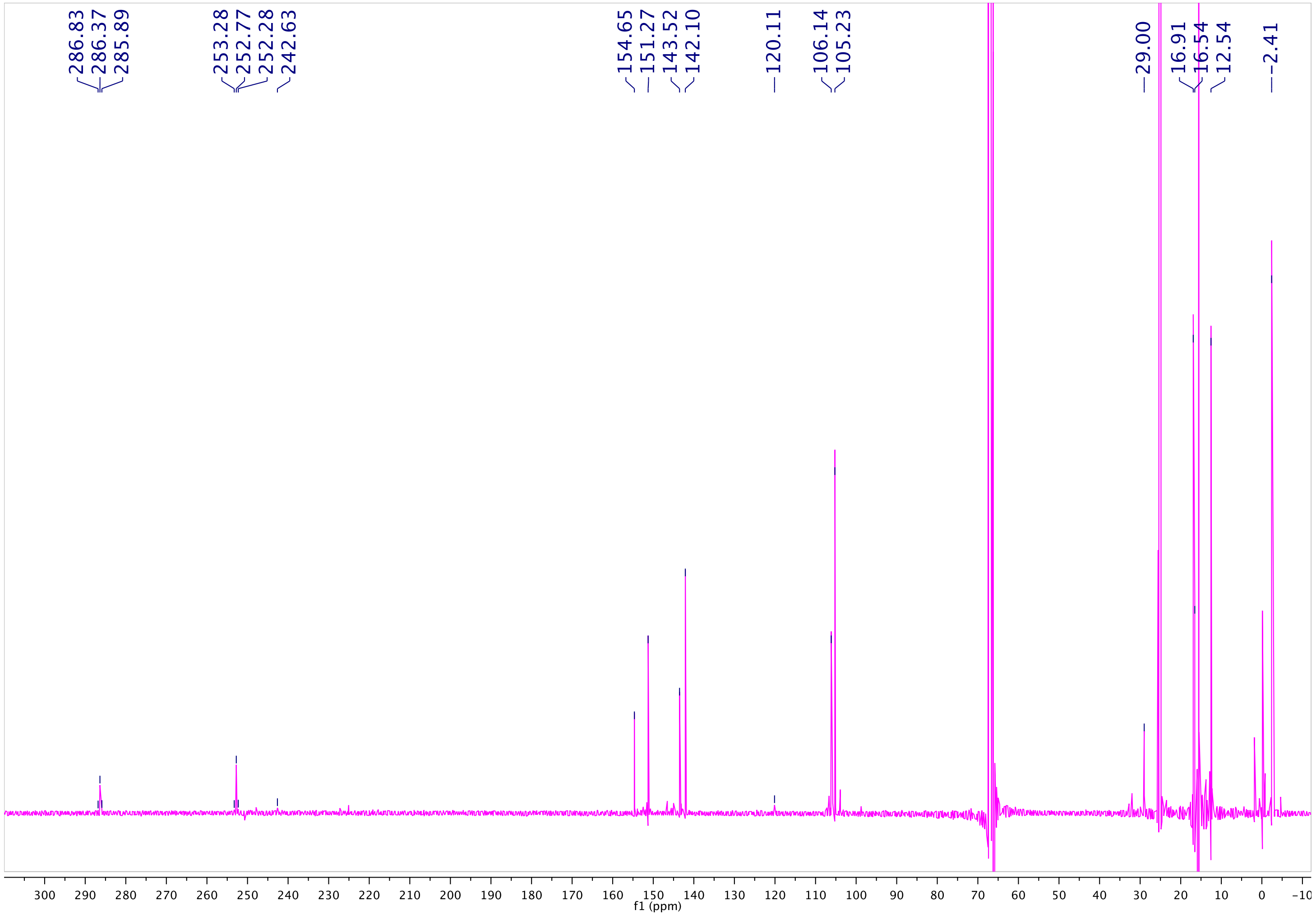
$^{13}C\{^1H\}$ NMR Spectrum of $\{C(=CMeSiMe_3)C\equiv W(CO)_2(Tp^*)\}_2$ 6



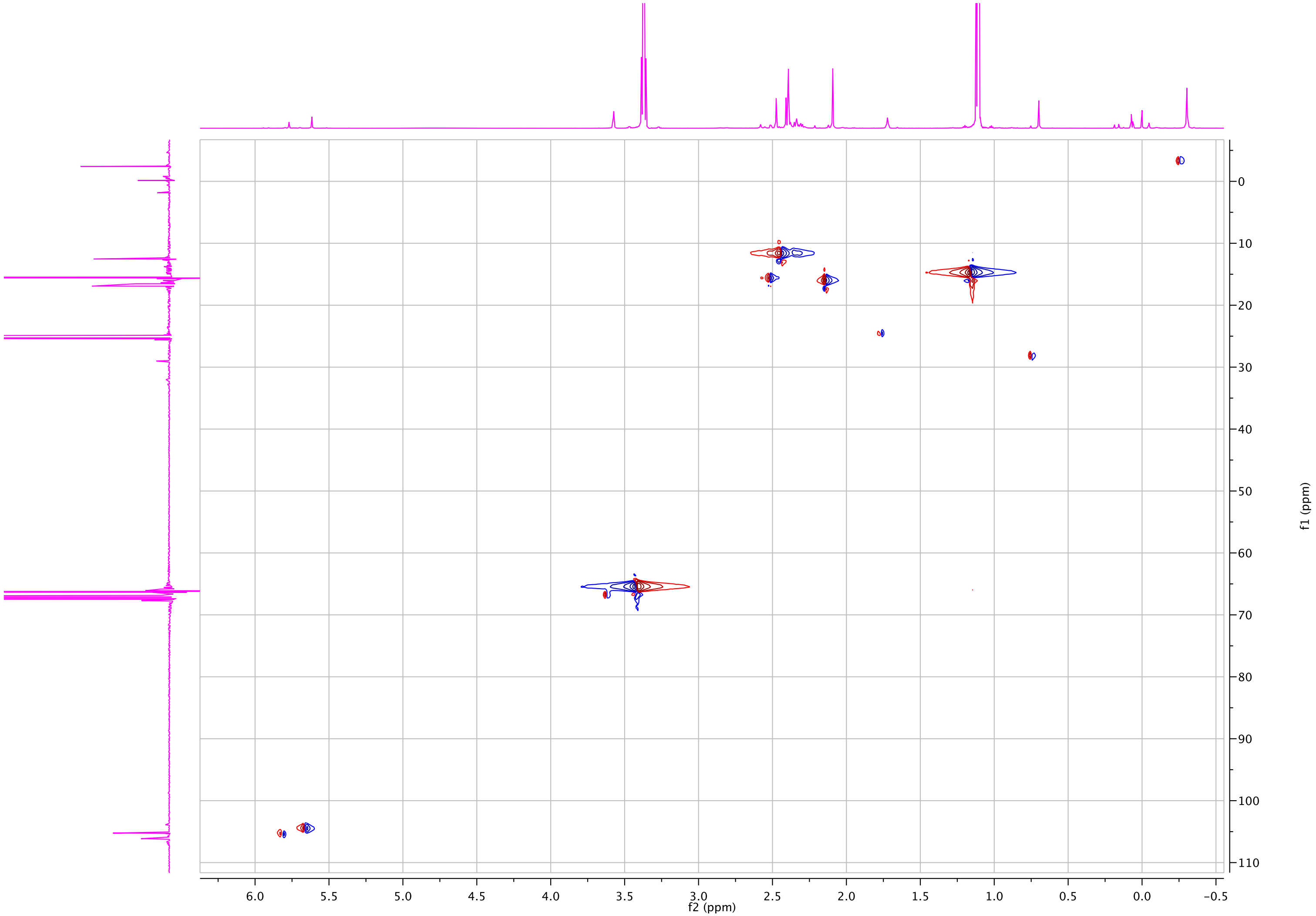
^{1}**H NMR (very large peaks are THF and Et$_2$O) of Li[W(=C=C=CMeSiMe$_3$)(CO)$_2$(Tp*)]**



^{13}C{^{1}H} NMR (very large peaks are THF and Et$_2$O) Spectrum of Li[W(=C=C=CMeSiMe$_3$)(CO)$_2$(Tp*)]

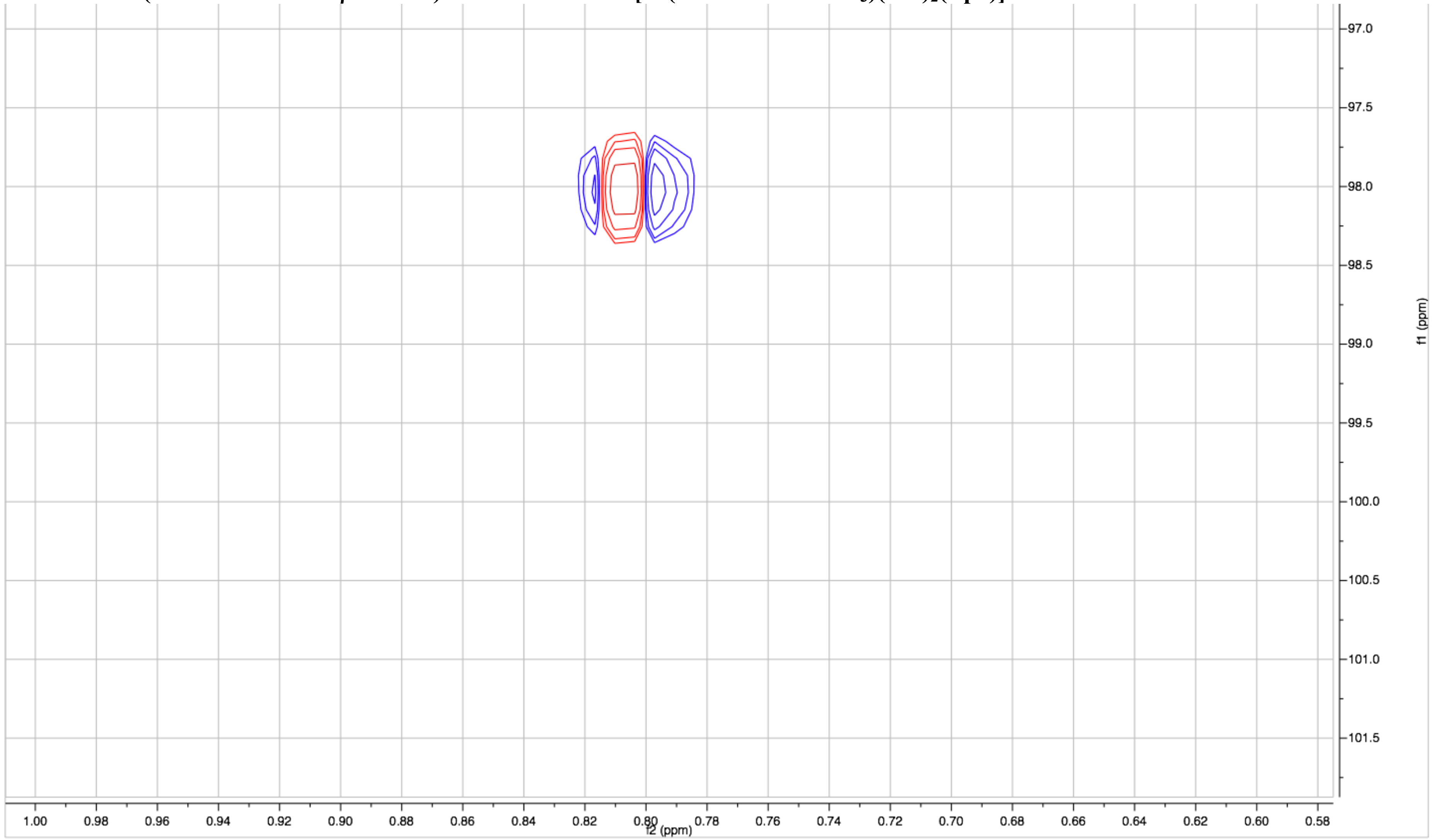


^{13}C-^{1}H HSQC Spectrum for Li[W(=C=C=CMeSiMe$_3$)(CO)$_2$(Tp*)] (3)

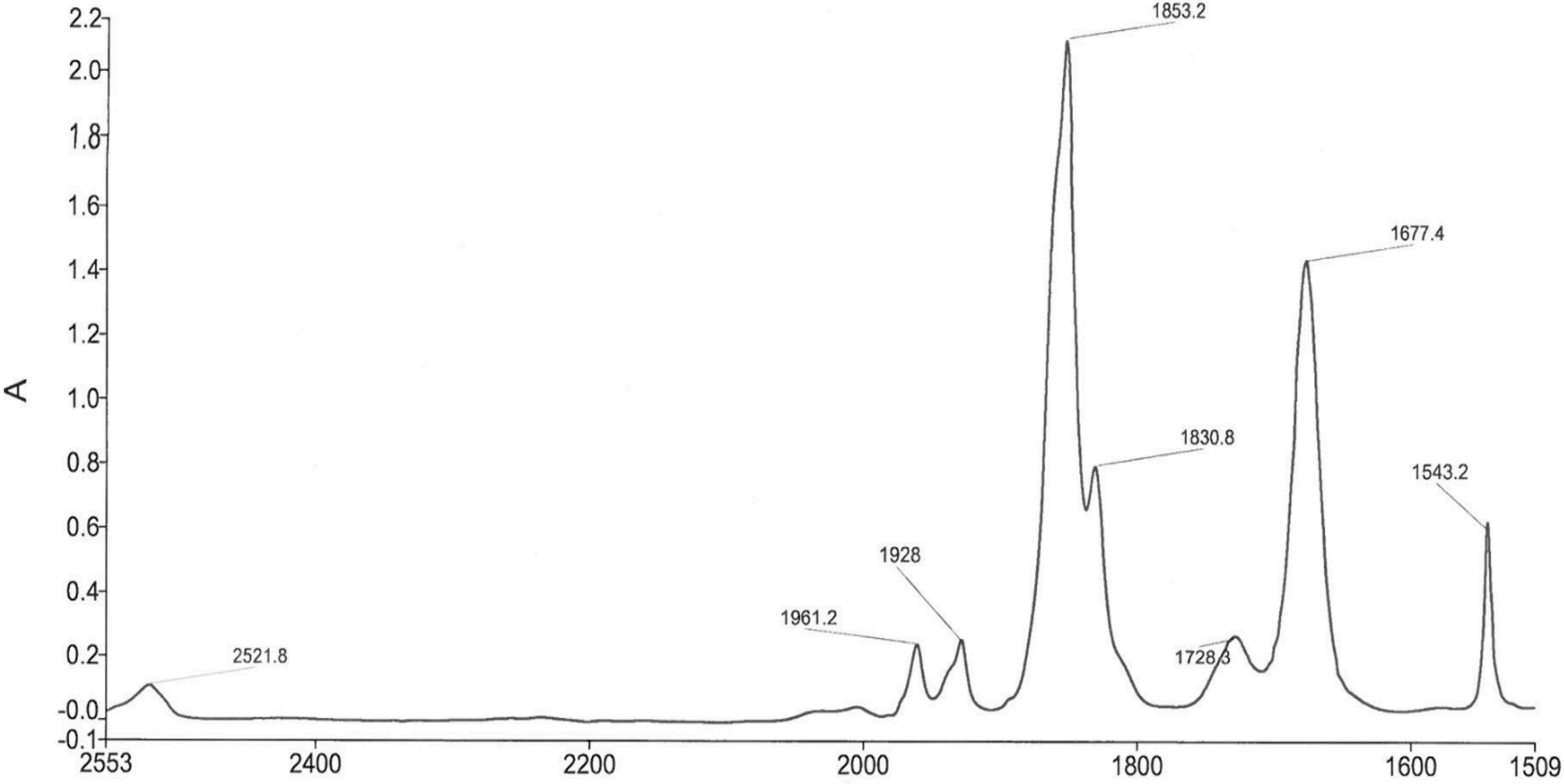


^{13}C-^{1}H HMBC (correlation to the γ carbon) from $SiMe_3$ and Me for Li[W(=C=C=CMeSiMe$_3$)(CO)$_2$(Tp*)]

^{13}C-^{1}H HMBC (correlation to the β carbon) from C-Me for Li[W(=C=C=CMeSiMe$_3$)(CO)$_2$(Tp*)]



Infrared Spectrum (THF) of Li[W(=C=C=CMeSiMe$_3$)(CO)$_2$(Tp*)] (cm^{-1})

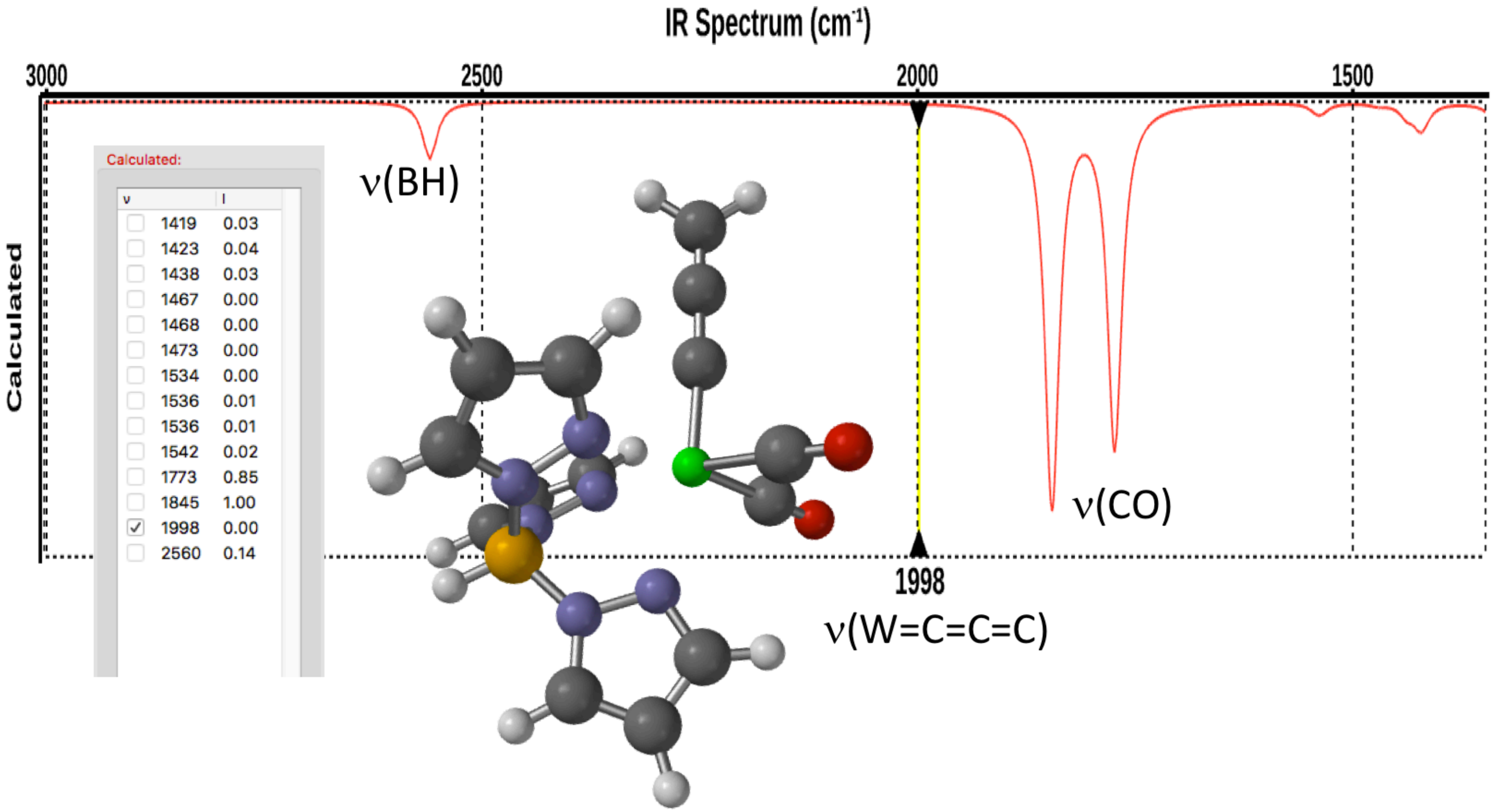


SiMe$_3$ *anti* to Tp* (major): 1928 ($\nu_{C=C=C}$), 1853, 1677 (ν_{CO}) SiMe$_3$ syn to Tp* (minor): 1933sh ($\nu_{C=C=C}$), 1830, 1728 (ν_{CO})

Both: 2521 ν_{BH}, 1543 Tp* mode

Calculated Infrared Spectrum (cm^{-1}, gas phase) of *anti*-[W(=C=C=CH_2)$(CO)_2$(Tp)]– (DFT: B3LYP-LANL2DZ)

The mode at 1998 cm^{-1} with zero IR intensity corresponds to the asymmetric C=C=C stretch that is usually characteristic of allenylidenes.



	ν	I
☐	1419	0.03
☐	1423	0.04
☐	1438	0.03
☐	1467	0.00
☐	1468	0.00
☐	1473	0.00
☐	1534	0.00
☐	1536	0.01
☐	1536	0.01
☐	1542	0.02
☐	1773	0.85
☐	1845	1.00
☑	1998	0.00
☐	2560	0.14

NB: Closer correlation between calculated (gas phase) and measured (THF) spectra are not to be expected due to the inestimable effect of ion pairing with lithium.