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Alkynyltellurolato ligands including a solvatochromic rhenium(I) complex

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Experimental Section

General Considerations

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

NMR spectra were obtained at 25 °C on a Bruker Avance 400 (^{1}H at 400 MHz, ^{13}C at 101 MHz, ^{31}P at 162 MHz, ^{77}Se at 76 MHz, ^{125}Te at 126 MHz), a Bruker Avance 600 (^{1}H at 600 MHz, ^{13}C at 151 MHz) or a Bruker Avance 700 (^{1}H at 700 MHz, ^{13}C at 176.1 MHz, ^{77}Se at 134 MHz, ^{125}Te at 221 MHz) or Jeol FX270 (^{1}H at 270 MHz, ^{13}C at 68 MHz) spectrometers. Chemical shifts (δ) are reported in ppm and referenced to the residual solvent peak (^{1}H, ^{13}C) or an external reference (^{77}Se: Ph_2Se_2 $\delta_{Se} = 459.0$, ^{125}Te: Ph_2Te_2 $\delta_{Te} = 421.8$) 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 ^{77}Se or ^{125}Te isotopomer 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. 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). 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-Kα radiation(λ = 1.54184 Å) using the CrysAlis PRO software.[1] The structures were solved by direct or intrinsic phasing methods and refined by full- matrix least squares on F^2 using the SHELXL programs[2] and the WinGX3 or Olex2 software.[3] Hydrogen atoms were located geometrically and refined using a riding model. Diagrams were produced using the CCDC visualisation program Mercury.[5] The complexes $[FeCl(CO)_2(\eta^5\text{-}C_5H_5)]$,[5] and $[ReBr(CO)_3(bipy)]$[6] were prepared according to literature procedures. Remaining reagents were purchased from commercial sources and generally used as received.

Computational studies were performed by using the *SPARTAN20®* suite of programs.[7] Geometry optimisation was performed at the DFT level of theory using the exchange functionals ωB97X-D of Head-Gordon.[8] The Los Alamos effective core potential type basis set (LANL2Dζ) of Hay and Wadt[9] was used for rhenium and tellurium while Pople 6-31G* basis sets[10] were used for all other atoms. Frequency calculations were performed for all compounds to confirm that each optimized structure was a local minimum and also to identify vibrational modes of interest. Cartesian atomic coordinates are provided below.

Synthesis of $[Fe(TeC{\equiv}CPh)(CO)_2(\eta^5\text{-}C_5H_5)]$ (1-Te). A solution of ethynylbenzene (0.33 mL, 3.00 mmol) in THF (20 mL) was treated dropwise with *n*-butyllithium (1.9 mL, 3.04 mmol, 1.6 M in hexanes) at 0°C under N_2. The solution was warmed to ambient temperature and the resulting pale-yellow solution was treated with tellurium powder (0.38 g, 3.00 mg.atom) at 0°C, which was consumed over 1 h. The mixture was cooled (dry-ice/propanone) before the addition of a solution $[FeCl(CO)_2(\eta^5\text{-}C_5H_5)]$ (0.63 g, 3.0 mmol) in THF (10 mL). This caused a significant colour change from bright red to green as the mixture was allowed to slowly warm to room temperature. The volatiles were removed under reduced pressure to afford a dark residue that was purified via flash column chromatography (silica gel) eluting with 1:1 CH_2Cl_2/petroleum spirits 40-60. The

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solvent was evaporated from the major green fraction under reduced pressure to afford the title compound as a green oil. The complex is unstable in solution, compromising the acquisition of some spectroscopic data. Attempts to grow crystallographic grade crystals from pentane resulted in the deposition of brown insoluble material (ESI-MS indicated "$Fe_2Te_2(C_5H_5)_2$").

IR (CH_2Cl_2): 2026, 1979 ν_{CO} cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H = 7.37, 7.24 (m x 2, 5 H, C_6H_5), 5.03 (s, 5 H, C_5H_5) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ_C = 213.5 (CO), 132.1 {$C^{3,5}(C_6H_5)$], 128.0 [$C^{2,6}(C_6H_5)$], 127.4 [$C^4(C_6H_5)$], 124.6 [$C^1(C_6H_5)$], 99.7 ($\mathbf{C}{\equiv}C$–Te, $^2J_{TeC}$ = 144 Hz), 84.7 (C_5H_5), 35.4 ($C{\equiv}\mathbf{C}$–Te, $^1J_{TeC}$ = 314 Hz) ppm. ^{125}Te NMR (126.2 MHz, $CDCl_3$): δ –506.2 ppm. MS (ESI, +ve ion, MeCN, *m/z*): Found: 408.91. Calcd for $C_{15}H_{11}FeO_2Te$ [M+H]$^+$: 408.91709. Satisfactory elemental microanalytical data not acquired due to instability.

Synthesis of [Fe(TeC≡CPh)(CO)(PPh$_3$)(η^5-C$_5$H$_5$)] (2-Te) A solution of ethynylbenzene (0.33 mL, 3.00 mmol) in THF (20 mL) was treated dropwise with *n*-butyllithium (1.9 mL, 3.04 mmol, 1.6 M in hexanes) at 0°C under N_2. The solution was warmed to ambient temperature, whereupon tellurium powder (0.383 g, 3.00 mg.atom) was added to the mixture at 0°C resulting in a suspension. Stirring for 1 h allowed for complete consumption of tellurium. The mixture was cooled (dry-ice/propanone) before the addition of a solution comprised of [$FeCl(CO)_2(\eta^5\text{-}C_5H_5)$] (0.63 g, 2.97 mmol) in THF (10 mL). Subsequent addition of PPh_3 (0.80 g, 3.04 mmol) at –78°C gave a brown mixture that was allowed to warm slowly to room temperature and was stirred for a further 2 hours. Volatiles were removed under reduced pressure resulting in a brown residue which was ultrasonically titrated with EtOH (10 mL) and hexanes (3 x 10 mL), before recrystallisation from a mixture of CH_2Cl_2 and n-pentane. The title compound was obtained as a green solid (0.67 g, 1.05 mmol, 35 % yield).

IR (CH_2Cl_2): 2120, 1939 ν_{CO} cm^{-1}. ^{1}H NMR (400 MHz, 295 K, $CDCl_3$): δ_H 7.44 – 7.64 (m, 2 H, C_6H_5), 7.27 – 7.43 (m, 15H, aryl C–H), 7.07 – 7.18 (m, 3H, aryl C–H), 4.51 (s, 5H, Cp) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 220.4 (d, CO, $^2J_{PC}$ = 30 Hz), 135.4 [d, $^1J_{PC}$ = 44 Hz, $C^1(PC_6H_5)$], 133.1 [d, $^2J_{PC}$ = 9 Hz, $C^{3,5}(PC_6H_5)$], 130.3 [d, $^4J_{PC}$ = 2 Hz, $C^4(PC_6H_5)$], 128.4 [d, $^2J_{PC}$ = 10 Hz, $C^{2,6}(PC_6H_5)$] 96.8 (s, Te–$C{\equiv}\mathbf{C}$), 84.2 (C_5H_5), 41.8 (d, $^3J_{PC}$ = 9 Hz Te–$\mathbf{C}{\equiv}C$). ^{31}P NMR (283 MHz, $CDCl_3$): δ_P = 73.5 ($^2J_{PTe}$ = 139 Hz). ^{125}Te NMR (126.2 MHz, $CDCl_3$): δ_{Te} = –339.2. MS (ESI, m/z): Found: 642.0036. Calcd for $C_{32}H_{25}FeOPTe$ [M]$^+$: 642.0049.

Crystals for X-ray structure determination were grown by vapour diffusion of *n*-pentane into CH_2Cl_2 at –20 ºC. Crystal Data for $C_{32}H_{25}OPFeTe$ (*M* =639.94 g/mol): monoclinic, space group $P2_1/n$ (no. 14), *a* = 7.6985(2) Å, *b* = 19.2903(5) Å, *c* = 17.9591(5) Å, *β* = 92.031(3)°, *V* = 2665.37(12) Å^3, *Z* = 4, *T* = 149.97(18) K, μ(MoKα) = 1.722 mm^{-1}, *Dcalc* = 1.595 g/cm^3, 33012 reflections measured (6.732° ≤ 2Θ ≤ 52.738°), 5439 unique (R_{int} = 0.0363, R_{sigma} = 0.0252) which were used in all calculations. The final R_1 was 0.0259 (I > 2σ(I)) and wR_2 was 0.0630 (all data)

Synthesis of [Fe(SeC≡CC$_6$H$_4$Me-4)(CO)(PPh$_3$)(η^5-C$_5$H$_5$)] (4-Se). A mixture of [Fe(SeC≡CC$_6$H$_4$Me-4)(CO)$_2$(η^5-C$_5$H$_5$)]] (0.25 g, 0.67 mmol) and PPh_3 (0.18 g, 1 eq.) were dissolved together in diethyl ether (25mL). Irradiation with a tungsten lamp led to vigorous evolution of CO and a colour change to red/brown within 30 seconds. The solution was diluted with hexane then slowly concentrated under reduced pressure to give the title compound as a red/brown solid (0.30 g, 74%) after recrystallisation from dichloromethane/hexane.

IR (CH_2Cl_2): 2129 w $\nu_{C\equiv C}$, 1945 vs ν_{CO}. IR (Nujol): 2122 w $\nu_{C\equiv C}$, 1945, 1933 vs ν_{CO}, 816 m δC_6H_4. NMR ($CDCl_3$, 270 MHz, 298 K): δ_H = 2.30 (s, 3 H, CH_3), 4.50 (s, 5 H, C_5H_5), 7.22, 7.40, 7.71 (m x 3, 20 H, PC_6H_5 and CC_6H_5). ^{13}C{^{1}H} NMR ($CDCl_3$, 67 MHz, 298 K): δ_C = 219.8 (d, CO, $^2J_{PC}$ = 34 Hz), 136.0 [$C^1(C_6H_4)$], 135.0 [d, $C^1(C_6H_5)$, $^1J_{PC}$ = 44 Hz), 133.4 [d, $C^{2,6}(C_6H_5)$, $^2J_{PC}$ = 9.8 Hz], 131.6 [$C^3(C_6H_4)$], 130.3 [$C^4(C_6H_5)$], 128.8 [$C^2(C_6H_4)$], 128.4 [d, $C^{3,5}(C_6H_5)$), $^3J_{PC}$ = 9.9 Hz), 123.3 [$C^4(C_6H_4)$], 84.7 (C_5H_5), 82.7 ($C\underline{C}{\equiv}C$), 79.4 (d, $Se\underline{C}{\equiv}C$, $^3J_{PC}$ = 7.2 Hz), 21.6 (CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 109 MHz, 298 K): δ_P = 71.2. FAB MS (+ve ion) *m/z* 606 [M]$^+$, 578 [M-CO]$^+$, 513 [M-C_5H_5-CO]$^+$, 463 [M-CO-CCTol]$^+$, 411 [M-SeCCTol]$^+$, 399 [M-C_5H_5-CCTol-CO+H]$^+$, 383 [M-SeCCTol-CO]$^+$, 316 [M-PPh_3-CO]$^+$. Analysis found (S) (%) C; 65.51, H; 4.59. Calc for $C_{33}H_{27}OPFeSe$ requires (%) C; 65.48, H; 4.50%.

Syntheses of [Re(EC≡CSiMe$_3$)(CO)$_3$(bipy)] (E = Se 5-Se, Te 5-Te)

General procedure:

To a stirred solution of 0.15 mL HC≡CSiMe$_3$ (1.08 mmol) in 25 mL THF cooled to 0 °C was added 0.65 mL *n*-BuLi solution (1.08 mmol, 1.6 M in hexanes). The mixture was allowed to warm to ambient temperature and stirred for a further 30 minutes, after which time either 0.090 g Se or 0.140 g Te (1.1 mg·atom, 1.1 equiv.) was added resulting in dark yellow-orange (Se) or dark yellow-green (Te) mixtures over 90 minutes. Separately, to 0.500 g [ReBr(CO)$_3$(bipy)] (0.99 mmol) suspended in 25 mL THF was added 0.255 g AgOTf (0.99 mmol) with rapid stirring, resulting in formation of a grey precipitate and a light yellow solution. To the flask containing the LiEC≡CSiMe$_3$ reagent was fitted an argon-filled Schlenk column containing a plug of oven-dried diatomaceous earth (2.5 x 2.5 cm) and the receiving solution cooled to -78 °C; the solution of [Re(OTf)(CO)$_3$(bipy)] was then filtered through the plug directly into the chilled reaction mixture, rinsing with small portions of THF until washings were colourless. After stirring overnight at ambient temperature, the mixture was freed of volatile under reduced pressure, and the residue extracted into CH_2Cl_2, filtered, and absorbed onto a small quantity of silica gel under vacuum. Column chromatography on silica gel (30 x 2.5 cm) with 1:1 CH_2Cl_2/petroleum spirit afforded bright orange (Se) or red (Te) bands containing the products which were collected and dried, and then re-crystallised from CH_2Cl_2/*n*-hexane mixtures at 0 °C depositing orange (Se) or red (Te) needles.

[Re(SeC≡CSiMe$_3$)(CO)$_3$(bipy)] (5-Se)

Isolated yield: 0.210 g (0.36 mmol, 36% *w.r.t.* Re). The product is air stable and is readily soluble in polar organic and aromatic solvents, and poorly soluble in aliphatic hydrocarbons.

IR (CH_2Cl_2, 25 °C) ν_{CC} 2057(w) cm^{-1}, ν_{CO} 2019(vs), 1919(s), 1906(s) cm^{-1}; IR (ATR, 25 °C) ν_{CC} 2055(m) cm^{-1}, ν_{CO} 2021(s), 1911(vs), 1871(vs) cm^{-1}. ^{1}H ($CDCl_3$, 400 MHz, 25 °C) δ 9.06 (ddd, J_{HH} = 5.6, 1.6, 0.8 Hz, 2H, 3,3′-$C_{10}\mathit{H}_8N_2$), 8.20 (dt, J_{HH} = 8.2, 1.0 Hz, 2H, 6,6′-$C_{10}\mathit{H}_8N_2$), 8.03 (td, J_{HH} = 7.9, 1.6 Hz, 2H, 5,5′-$C_{10}\mathit{H}_8N_2$), 7.51 (ddd, J_{HH} = 7.5, 5.6, 1.3 Hz, 2H, 4,4′-$C_{10}\mathit{H}_8N_2$), –0.09 (s, 9H, $SiC\mathit{H}_3$) ppm; ^{13}C{^{1}H} ($CDCl_3$, 176 MHz, 25 °C) δ 197.5 ($\mathit{C}O_{eq}$), 189.5 ($\mathit{C}O_{ax}$), 155.5 (2,2′-$\mathit{C}_{10}H_8N_2$), 153.6 (3,3′- $C_{10}H_8N_2$), 138.2 (5,5′- $C_{10}H_8N_2$), 126.9 (4,4′-$\mathit{C}_{10}H_8N_2$), 123.0 (6,6′-$\mathit{C}_{10}H_8N_2$), 94.4 (Se-C≡*C*-Si), 90.9 (Se-*C*≡C-Si), 0.73 ($Si\mathit{C}H_3$) ppm; ^{77}Se{^{1}H} ($CDCl_3$, 133 MHz, 25 °C) δ –190.7 ppm. HR-MS (ESI, MeCN, +ve ion) found 626.9610 (calc. for $C_{18}H_{17}O_3N_2{}^{23}Na^{28}Si^{80}Se^{187}Re$ $[M + Na]^+$: 626.9623). Analysis found: C, 35.99; H, 2.80%. Calc. for $C_{18}H_{17}N_2O_3ReSeSi$: C, 35.88; H, 2.84%.

[Re(TeC≡CSiMe$_3$)(CO)$_3$(bipy)] (5-Te)

Isolated yield: 0.270 g (0.41 mmol, 41% *w.r.t.* Re). The product is air stable and is readily soluble in polar organic and aromatic solvents, and poorly soluble in aliphatic hydrocarbons.

IR (CH_2Cl_2, 25 °C) ν_{CC} 2051(w) cm^{-1}, ν_{CO} 2016(vs), 1916(s), 1905(s) cm^{-1}; IR (ATR, 25 °C) ν_{CC} 2044(w) cm^{-1}, ν_{CO} 2011(s), 1893(vs), 1871(s) cm^{-1}. ^{1}H ($CDCl_3$, 400 MHz, 25 °C) δ 9.14 (ddd, J_{HH} = 5.6, 1.6, 0.8 Hz, 2H, 3,3′-$C_{10}\mathit{H}_8N_2$), 8.20 (dt, J_{HH} = 8.1, 1.0 Hz, 2H, 6,6′-$C_{10}\mathit{H}_8N_2$), 7.99 (td, J_{HH} = 7.9, 1.5 Hz, 2H, 5,5′-$C_{10}\mathit{H}_8N_2$), 7.48 (ddd, J_{HH} = 7.5, 5.6, 1.3 Hz, 2H, 4,4′-$C_{10}\mathit{H}_8N_2$), –0.08 (s, 9H, $SiC\mathit{H}_3$) ppm; ^{13}C{^{1}H} ($CDCl_3$, 176 MHz, 25 °C) δ 197.8 ($\mathit{C}O_{eq}$), 189.4 ($\mathit{C}O_{ax}$), 155.3 (2,2′-$\mathit{C}_{10}H_8N_2$), 153.8 (3,3′- $C_{10}H_8N_2$), 137.8 (5,5′- $\mathit{C}_{10}H_8N_2$), 126.8 (4,4′-$\mathit{C}_{10}H_8N_2$), 123.1 (6,6′-$\mathit{C}_{10}H_8N_2$), 110.0 (Te-C≡*C*-Si), 55.0 (Te-*C*≡C-Si), 0.7 ($Si\mathit{C}H_3$) ppm; ^{125}Te{^{1}H} ($CDCl_3$, 220 MHz, 25 °C) δ –339.7 ppm. HR-MS (ESI, MeCN, +ve ion) found 676.9505 (calc. for $C_{18}H_{17}O_3N_2{}^{23}Na^{28}Si^{130}Te^{187}Re$ $[M + Na]^+$: 676.9520). Analysis found: C, 33.33; H, 2.52%. Calc. for $C_{18}H_{17}N_2O_3ReSiTe$: C, 33.20; H, 2.63%.

The somewhat less soluble complex [Re(TeC≡CSiMe$_3$)(CO)$_3$(phen)] was prepared similarly: NMR ^{1}H ($CDCl_3$, 25 °C, 400 MHz): δ_H = 0.19 (s, 9 H, $SiCH_3$, $^{5}J_{TeH}$ = 119.7 Hz), 7.82 [dd, 2 H, H^{3,8}(phen), $^{3}J_{HH}$ = 7.8, 5.1 Hz], 8.04 [s, 2 H, H^{5,6}(phen)], 8.48 [d, 2 H, H^{4,7}(phen), $^{3}J_{HH}$ = 7.8 Hz], 9.47 [d, 2 H, H^{2,9}(phen), $^{2}J_{HH}$ = 5.1 Hz]. ^{13}C{^{1}H} ($CDCl_3$, 25 °C, 100.6 MHz): δ_C = 223.6, 197.7 [br, tentative, ReCO], 153.4 [C^{1,9}(phen)], 146.7 [C^{10,11}(phen)], 137.1 [C^{4,7}(phen)], 130.8 [C^{11,12}(phen)], 127.7 [C^{5,6}(phen)], 125.6 [C^{3,8}(phen)], 109.4 [TeC≡***C***], 54.8 [Te***C***≡C], 0.6 [$SiCH_3$, $^{4}J_{TeC}$ = 110 Hz]. ^{125}Te{^{1}H} ($CDCl_3$, 25 °C, 126.2 MHz): δ_{Te} = –355.5.

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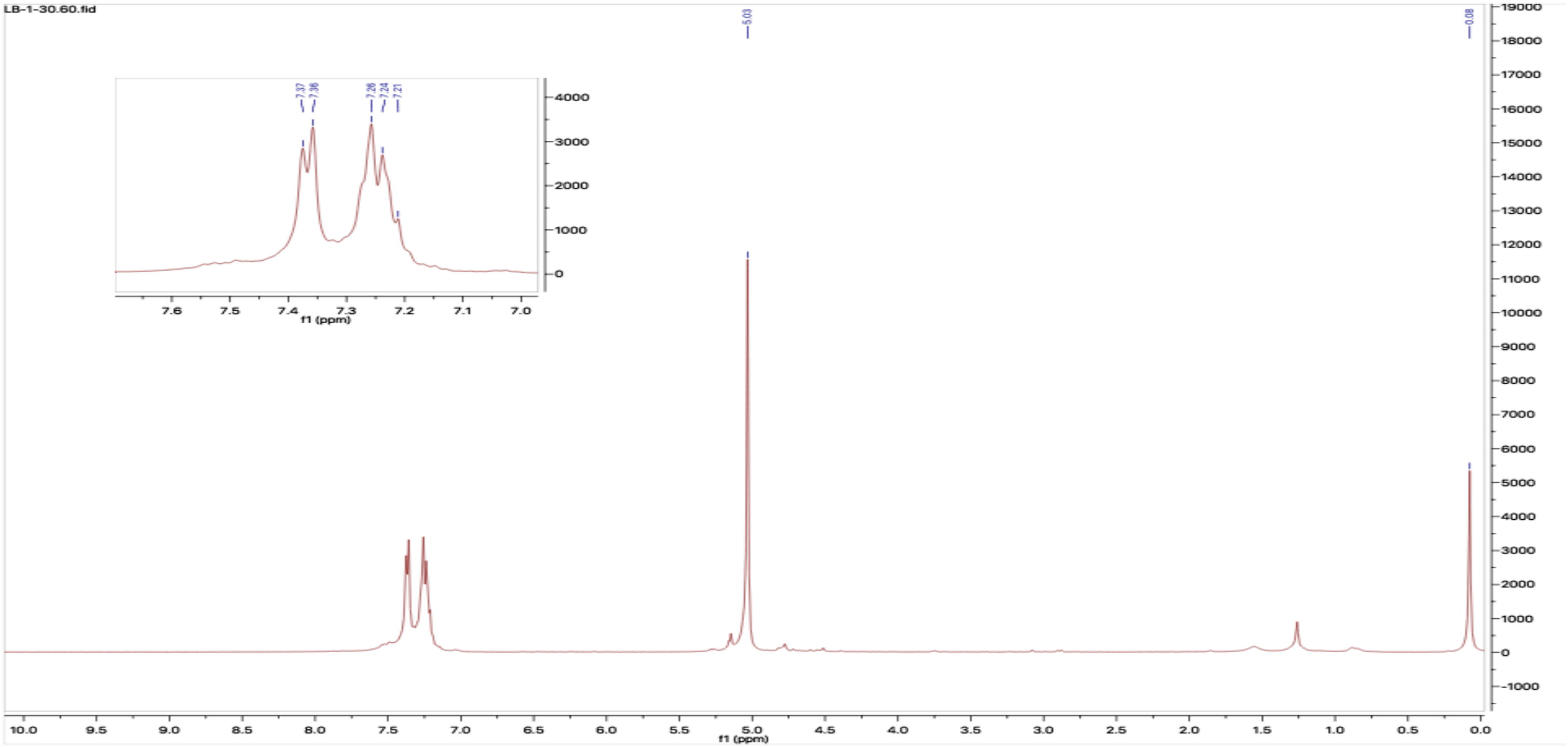

Figure S1. ^{1}H NMR spectrum of [Fe(TeC≡CPh)(CO)$_2$(η^5-C$_5$H$_5$)] (**1-Te**,295 K, CDCl$_3$, 400 MHz, δ$_H$).

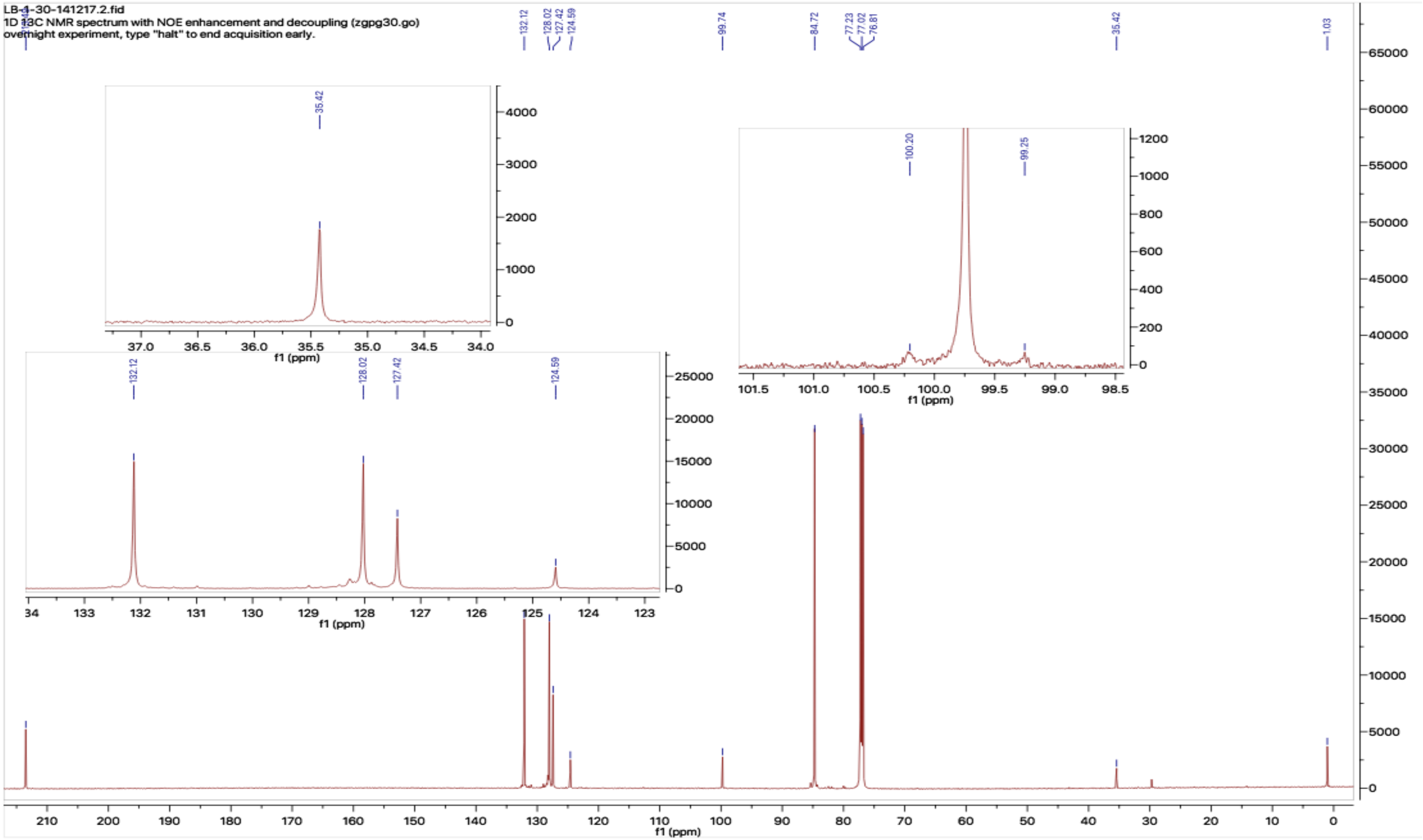

Figure S2. $^{13}C\{^1H\}$ NMR spectrum of [Fe(TeC≡CPh)(CO)$_2$(η^5-C$_5$H$_5$)] (**1-Te**, 295 K, CDCl$_3$, 151 MHz, δ_C).

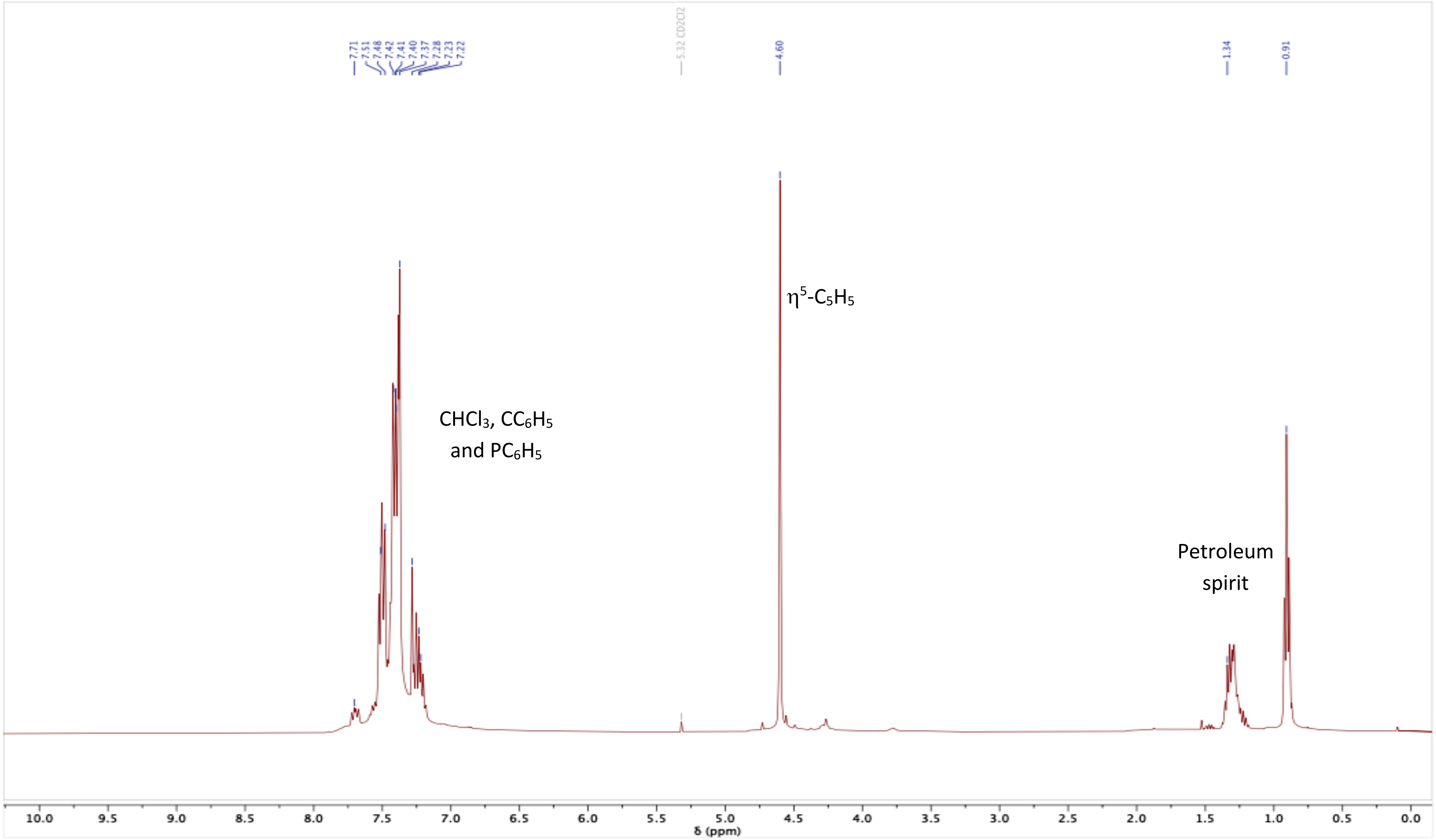

Figure S3. ^{1}H NMR spectrum of [Fe(TeC≡CPh)(CO)(PPh$_3$)(η^5-C$_5$H$_5$)] (**2-Te** 295 K, $CDCl_3$, 400 MHz, δ_H).

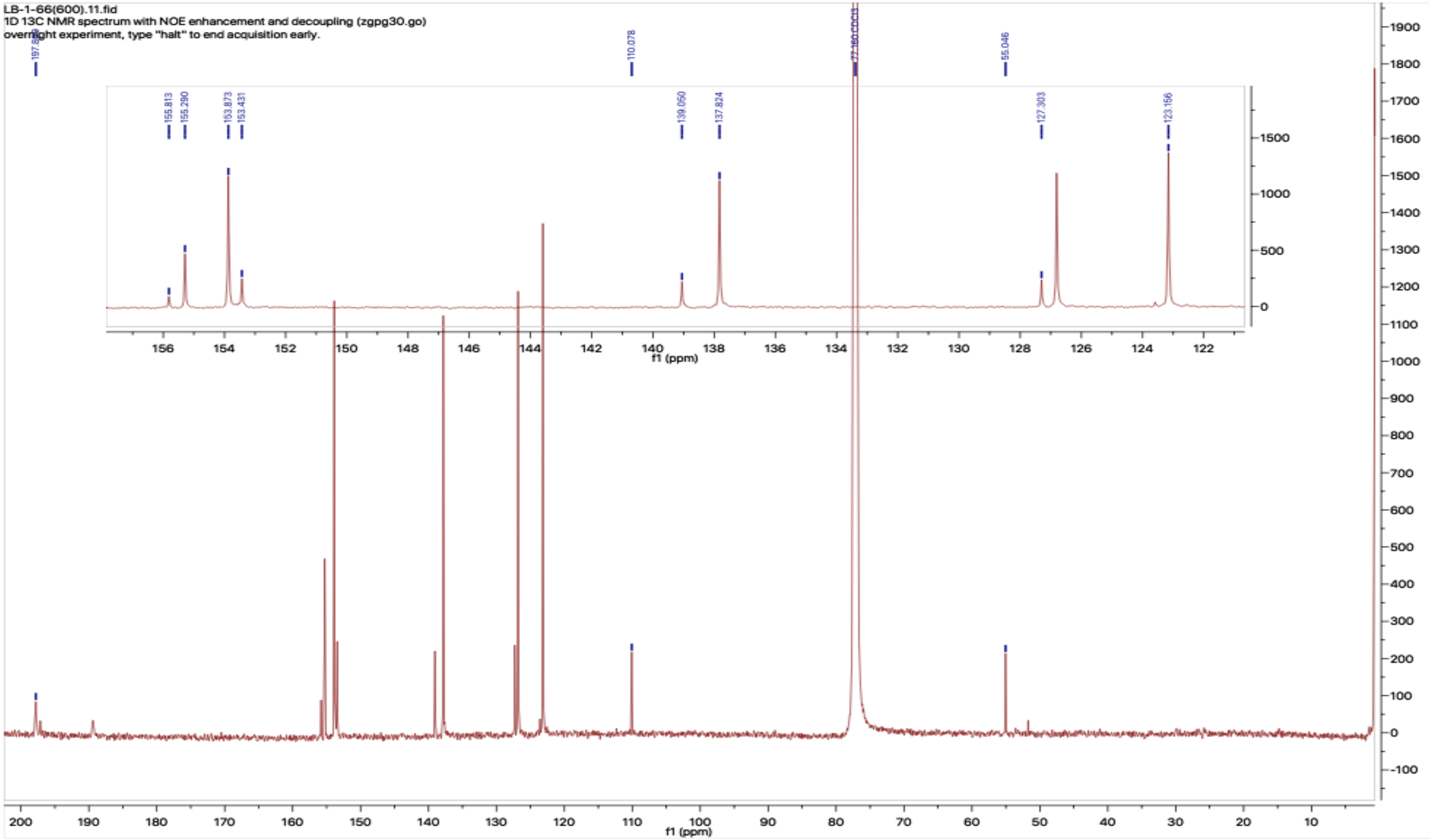

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of [Fe(TeC≡CPh)(CO)(PPh_3)(η^5-C_5H_5)] (**2-Te** 295 K, $CDCl_3$, 151 MHz, δ_C).

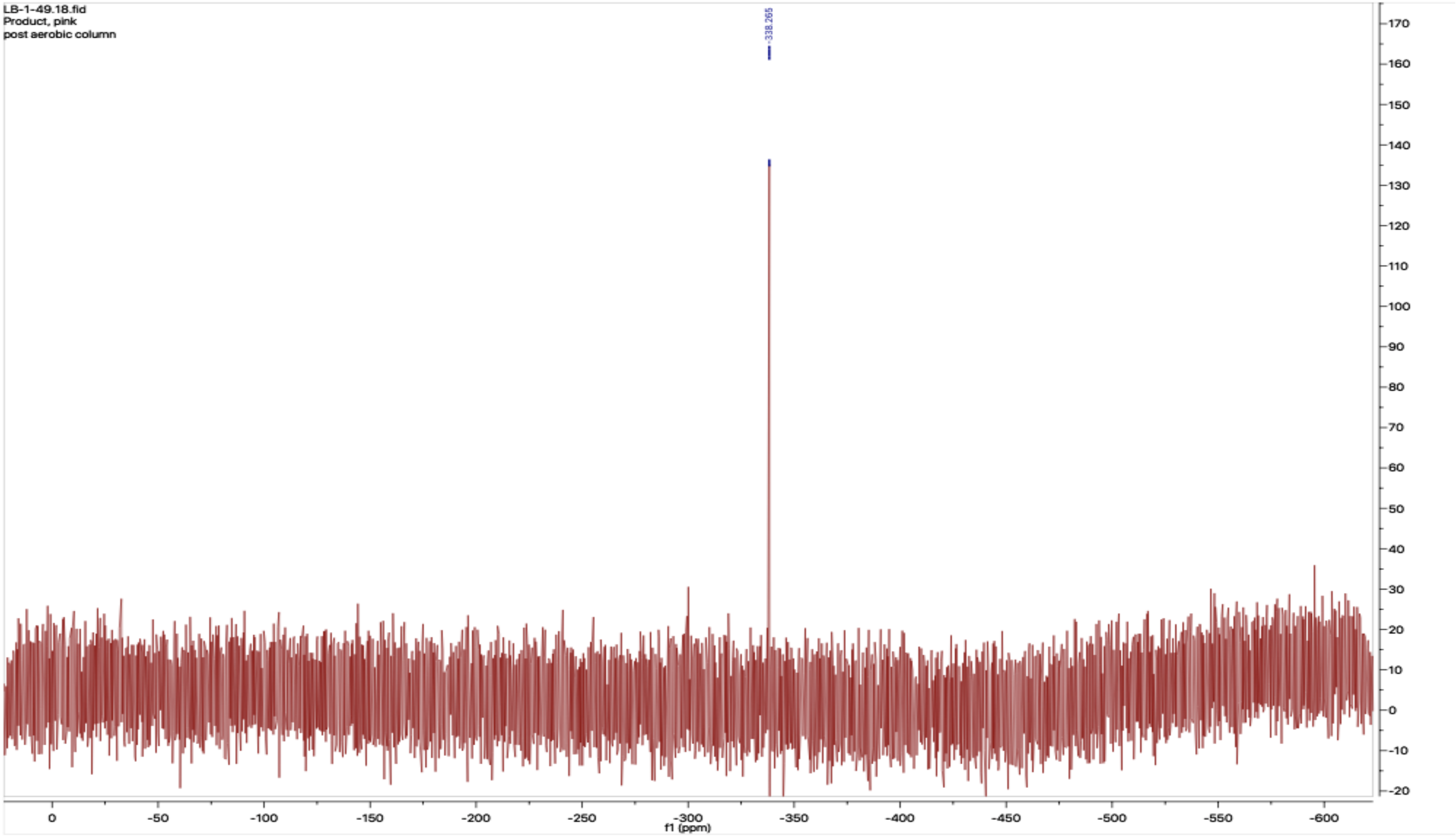

Figure S5. ^{125}Te{^{1}H} NMR Spectrum of [Fe(TeC≡CPh)(CO)(PPh$_3$)(η^5-C$_5$H$_5$)] (**2-Te** CDCl$_3$, 126.2 MHz, 25 °C, δ_{Te} *cf.* δ_{Te}(Ph$_2$Te$_2$) = 422)

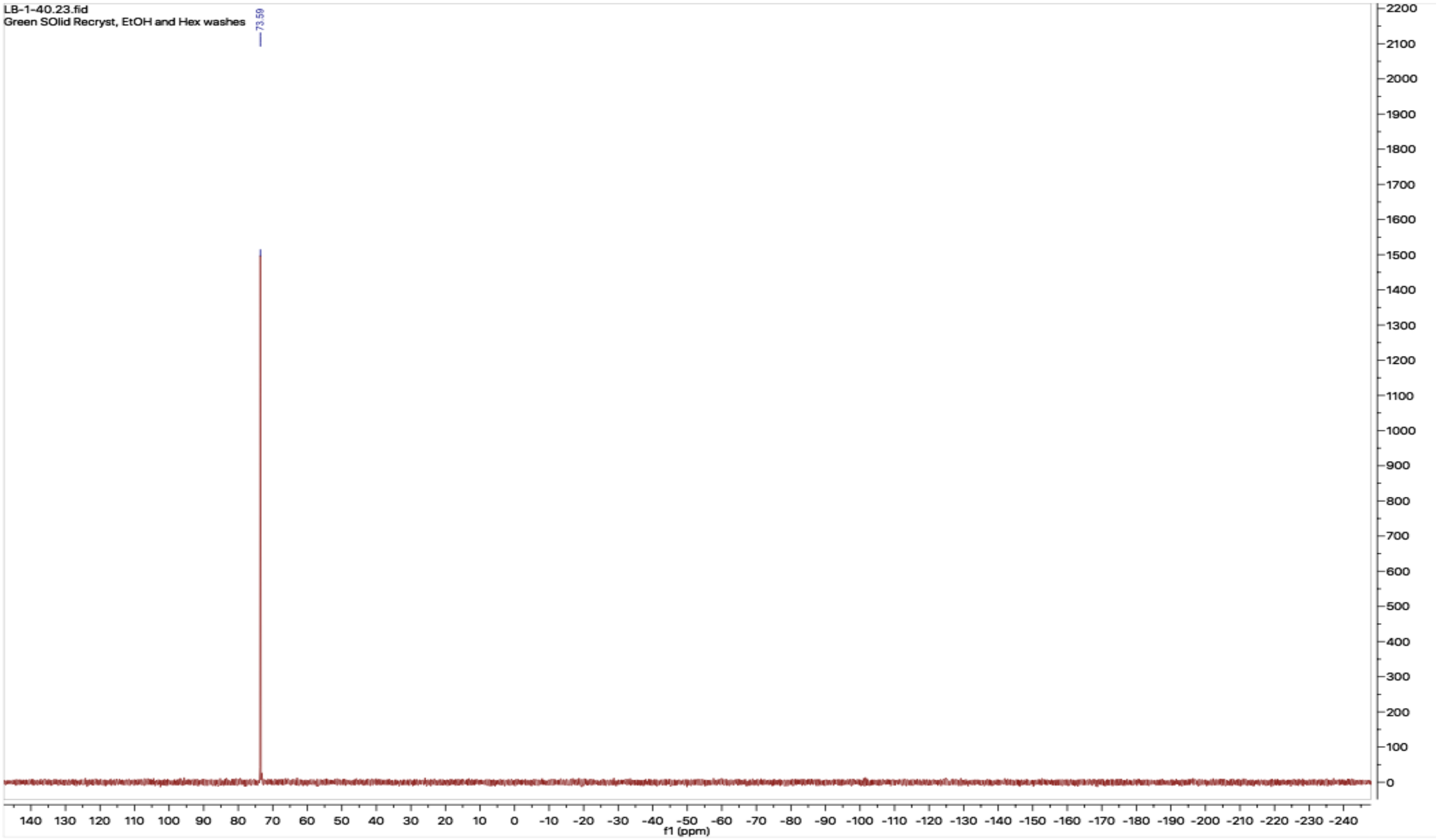

Figure S6. $^{31}P\{^{1}H\}$ NMR Spectrum of $[Fe(TeC{\equiv}CPh)(CO)(PPh_3)(\eta^5\text{-}C_5H_5)]$ (**2-Te**, $CDCl_3$, 162 MHz, 25 °C, δ_P)

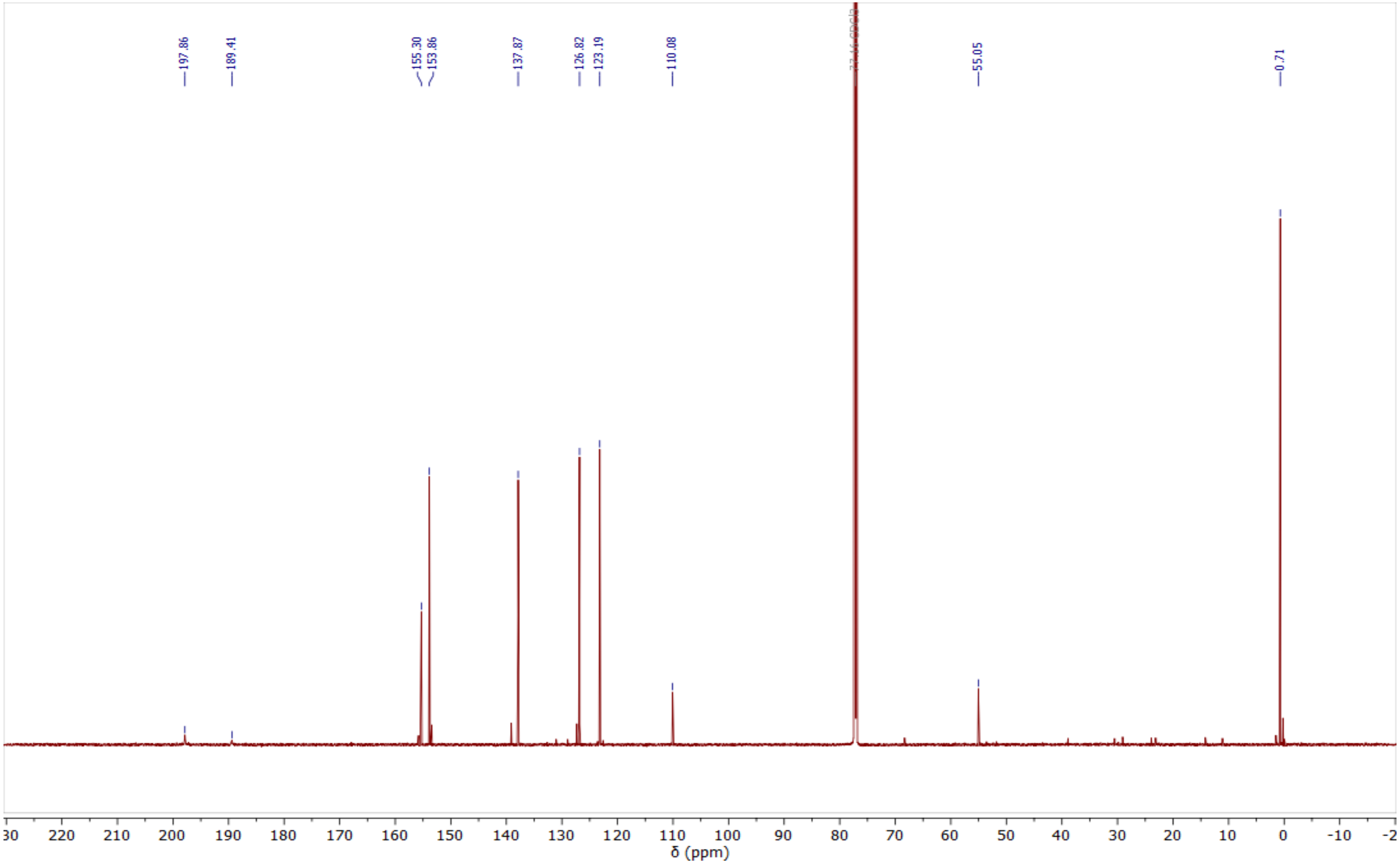

Figure S7. $^{13}C\{^1H\}$ NMR Spectrum of [Re(TeC≡CSiMe$_3$)(CO)$_3$(bipy)] (**5-Te**,CDCl$_3$, 176 MHz, 25 °C, δ_C)

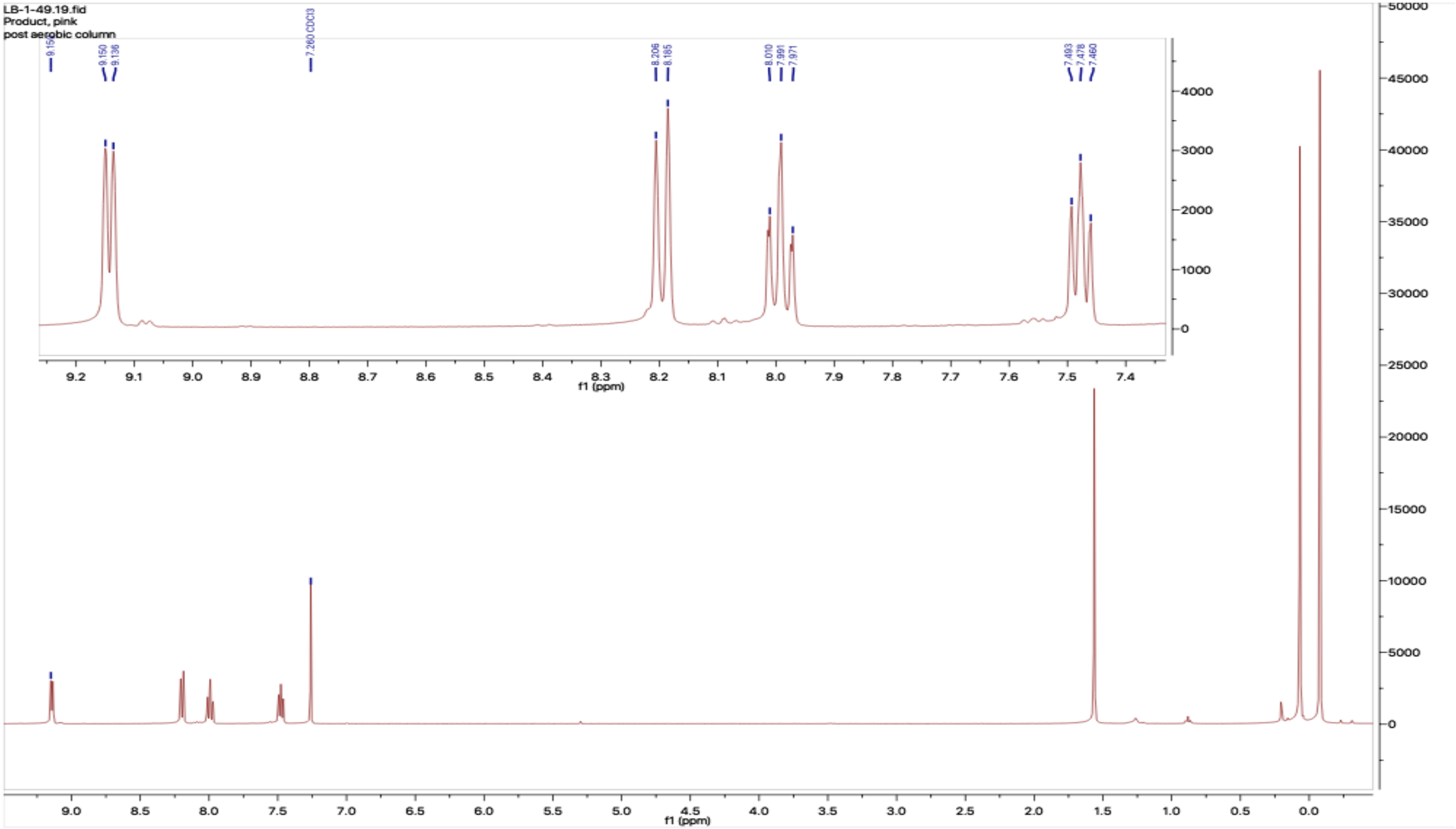

Figure S8. ^{1}H NMR Spectrum of [Re(TeC≡CSiMe$_3$)(CO)$_3$(bipy)] (**5-Te**, CDCl$_3$, 400 MHz, 25 °C, δ_H)

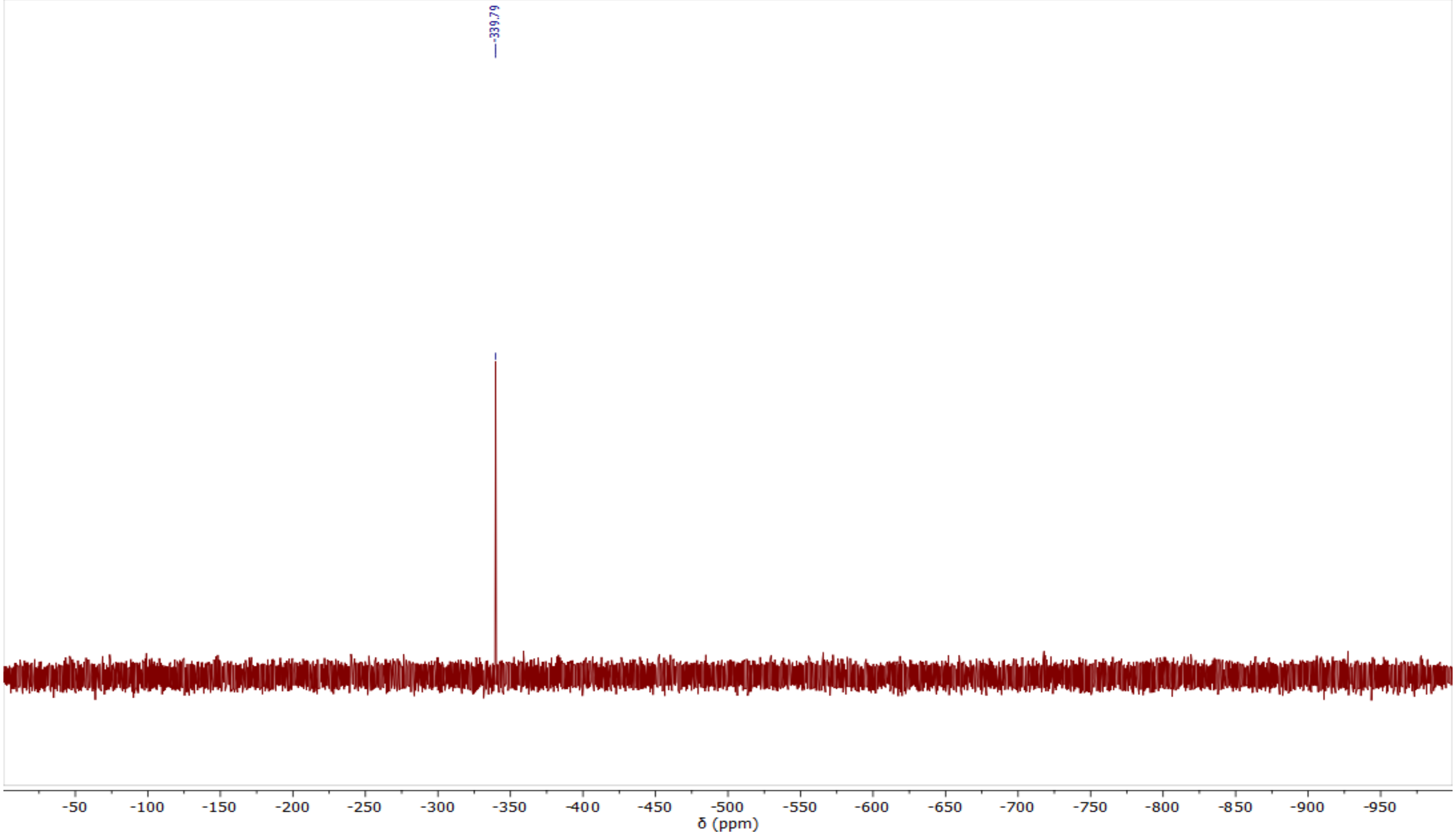

Figure S9. ^{125}Te{^{1}H} NMR Spectrum of [Re(TeC≡CSiMe$_3$)(CO)$_3$(bipy)] (**5-Te**, CDCl$_3$, 220 MHz, 25 °C, δ_{Te} *cf.* δ_{Te}(Ph$_2$Te$_2$) = 422)

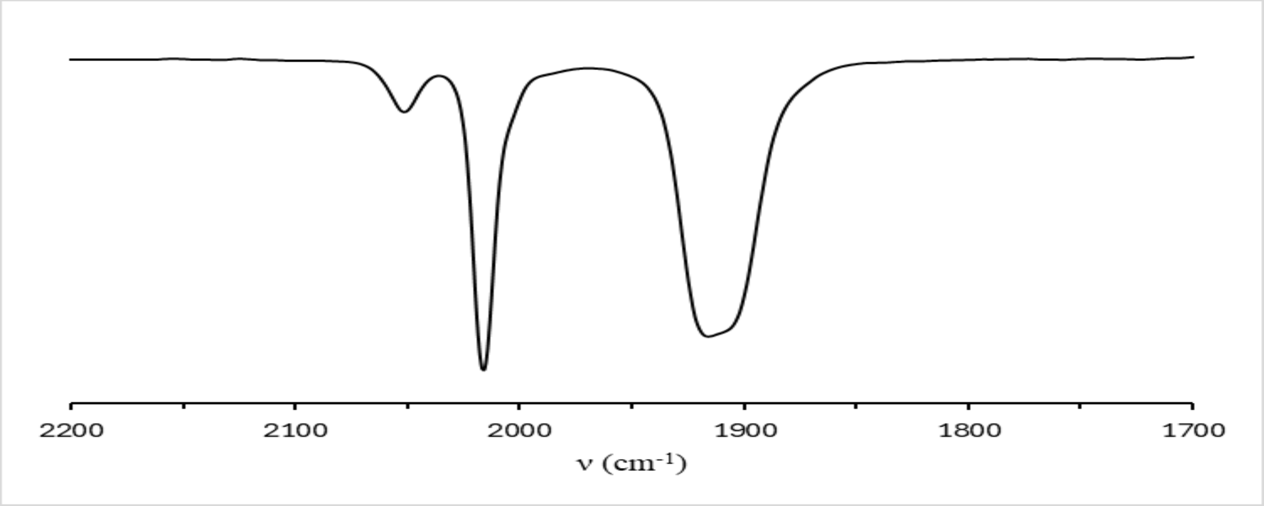

Figure S10. Infrared Spectrum of [Re(TeC≡CSiMe$_3$)(CO)$_3$(bipy)] (**5-Te**, CH$_2$Cl$_2$)

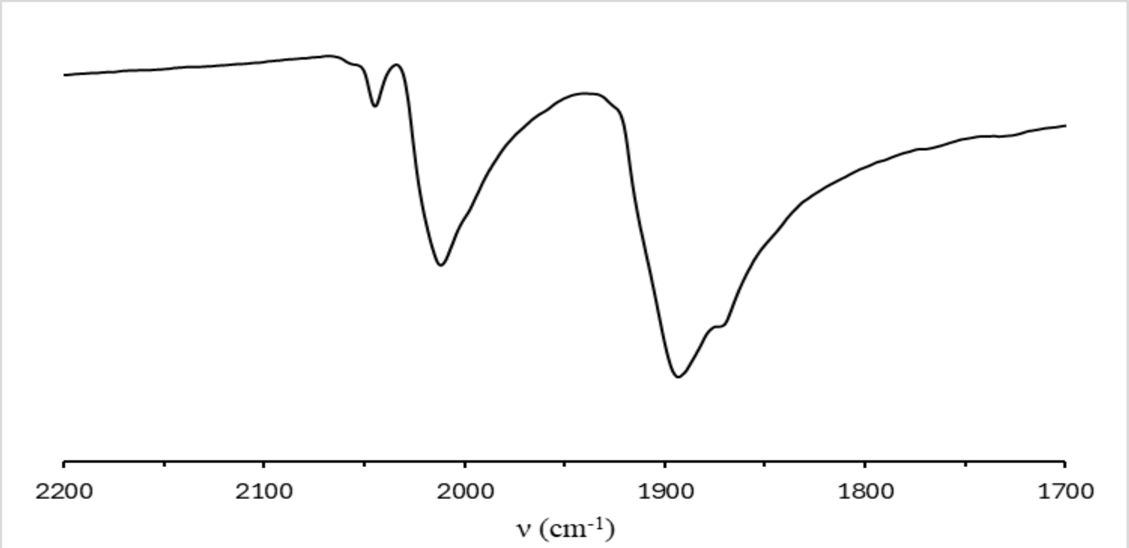

Figure S11. Infrared Spectrum of [Re(TeC≡CSiMe$_3$)(CO)$_3$(bipy)] (**5-Te**, ATR)

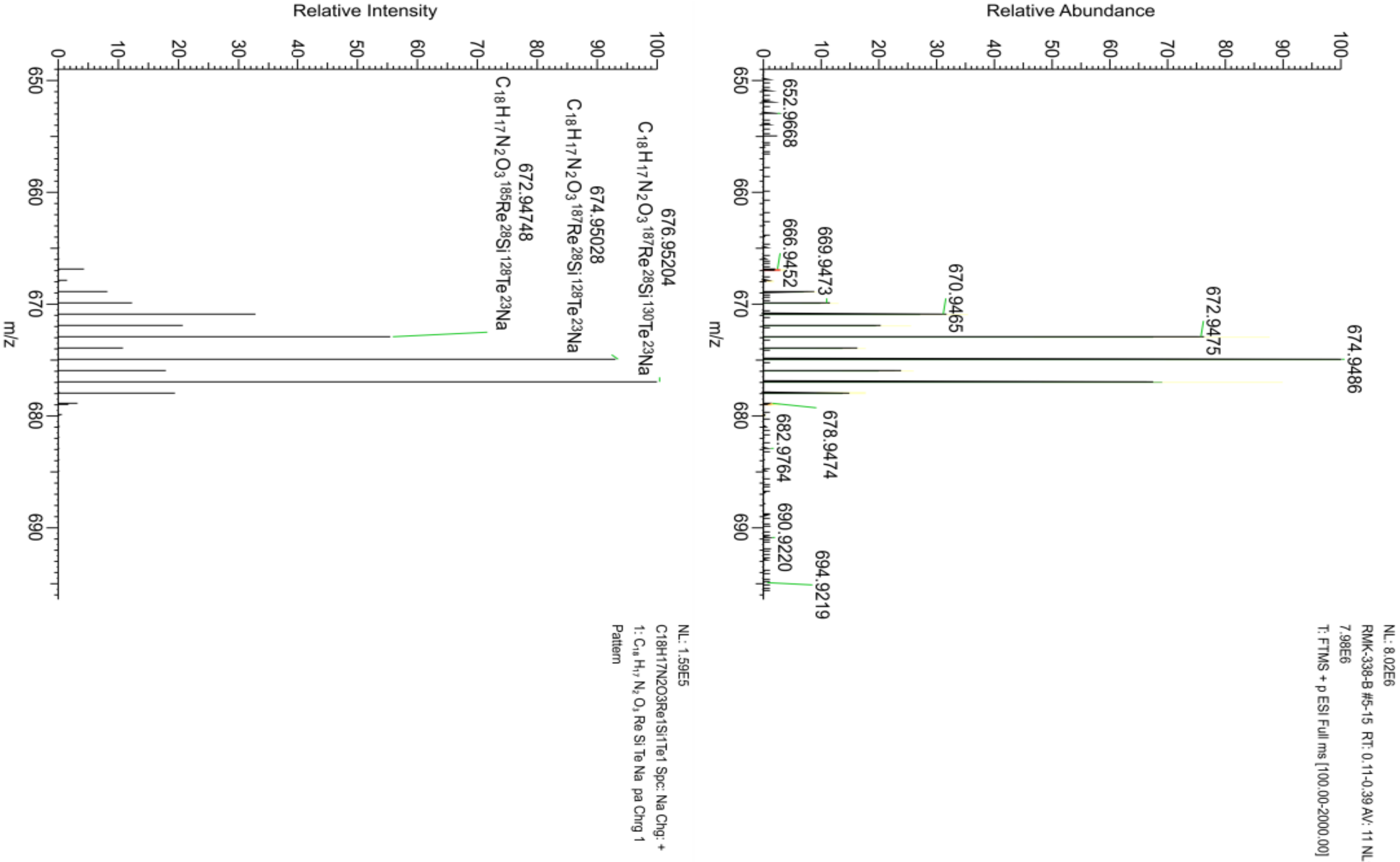

Figure S12. Observed and Calculated ESI-MS of [Re(TeC≡CSiMe$_3$)(CO)$_3$(bipy)] (**5-Te**, +ve ion, MeCN)

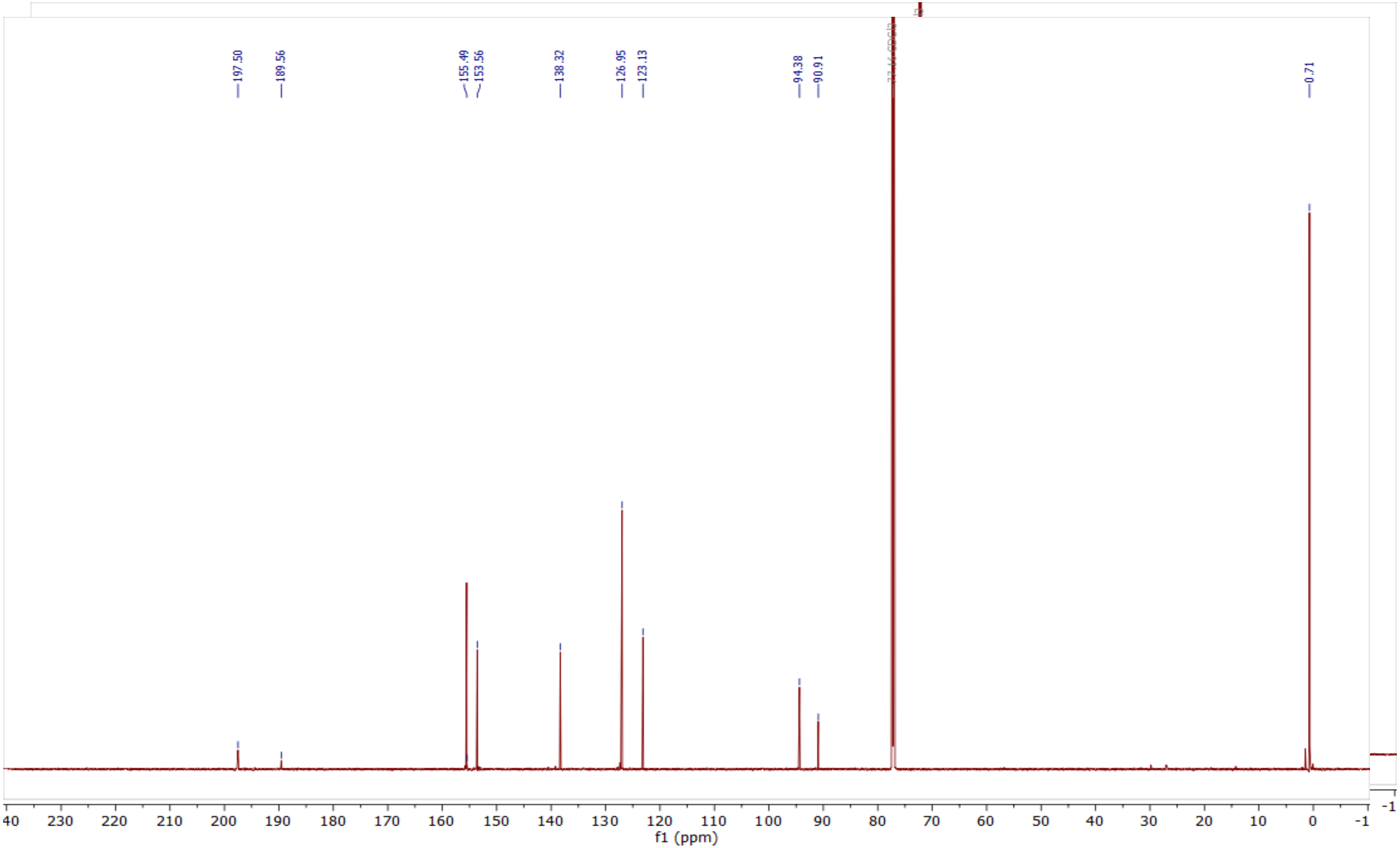

Figure S13. $^{13}C\{^1H\}$ NMR Spectrum of [Re(SeC≡CSiMe$_3$)(CO)$_3$(bipy)] (**5-Se**, CDCl$_3$, 176 MHz, 25 °C, δ_C)

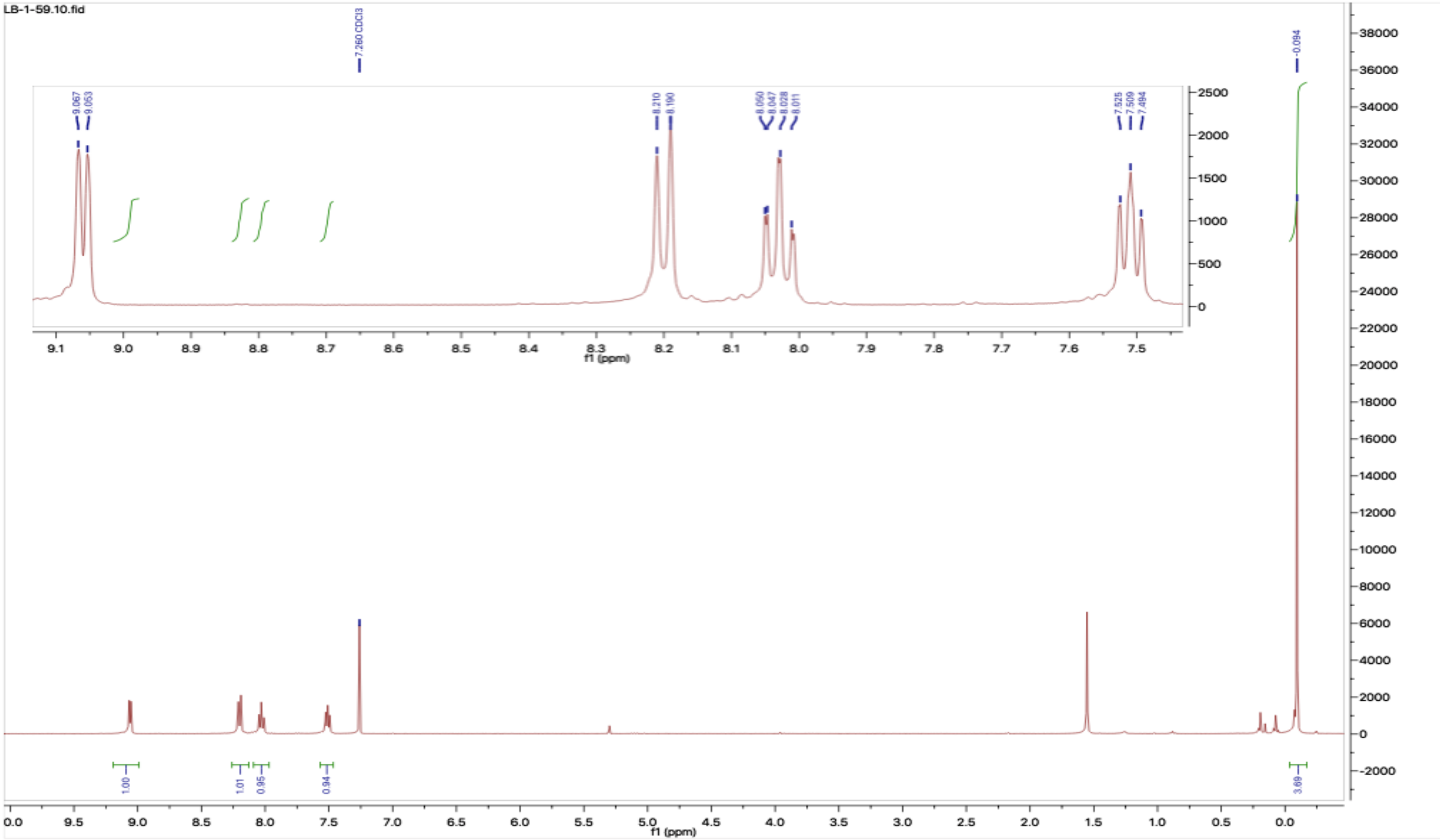

Figure S14. ^{1}H NMR Spectrum of [Re(SeC≡CSiMe$_3$)(CO)$_3$(bipy)] (**5-Se** CDCl$_3$, 400 MHz, 25 °C, δ_H)

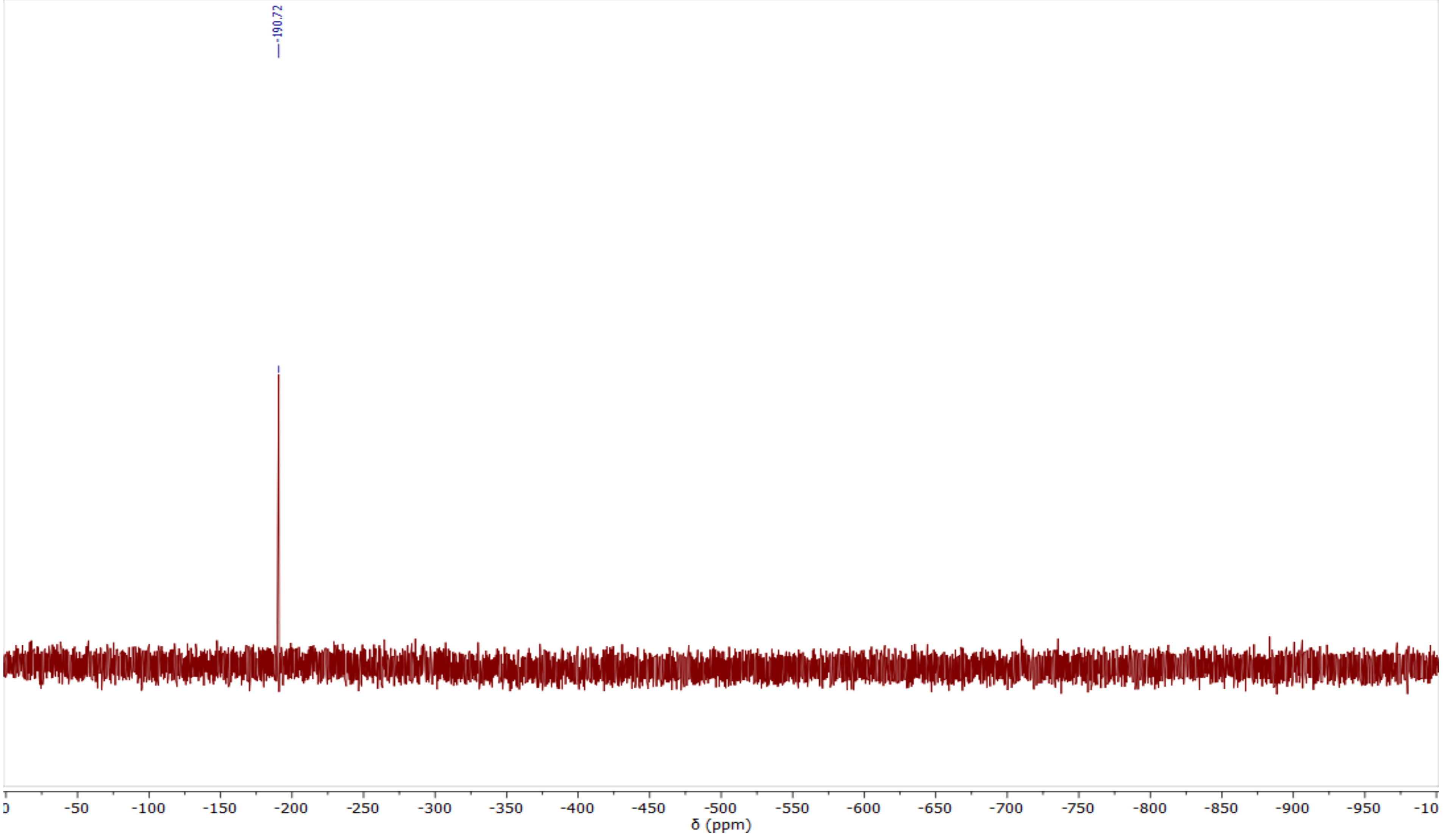

Figure S15. ^{77}Se{^{1}H} NMR Spectrum of [Re(SeC≡CSiMe$_3$)(CO)$_3$(bipy)] (**5-Se** CDCl$_3$, 133 MHz, 25 °C, δ_{Se})

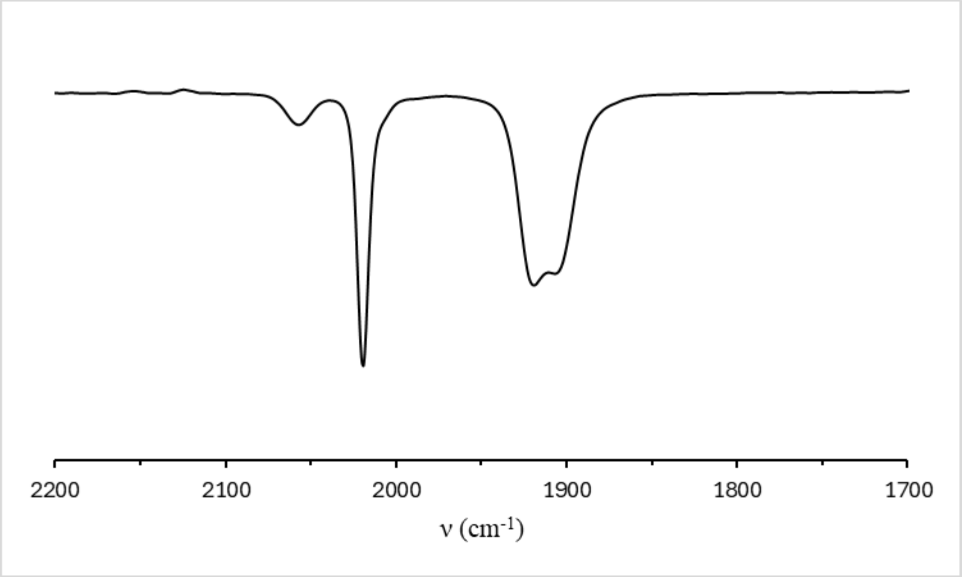

Figure S16 Infrared Spectrum of [Re(SeC≡CSiMe3)(CO)$_3$(bipy)] (**5-Se** CH_2Cl_2)

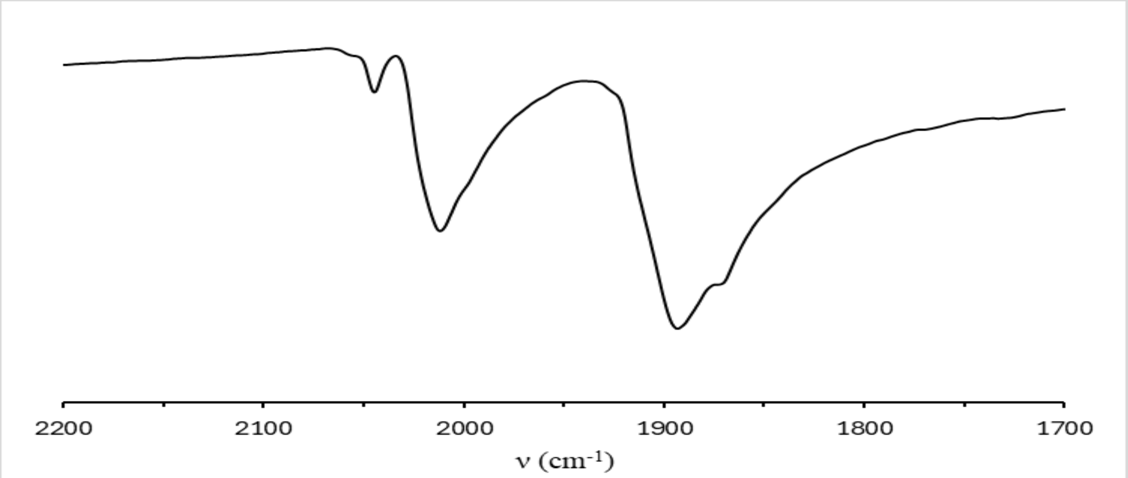

Figure S17. Infrared Spectrum of [Re(SeC≡CSiMe$_3$)(CO)$_3$(bipy)] (**5-Se** ATR)

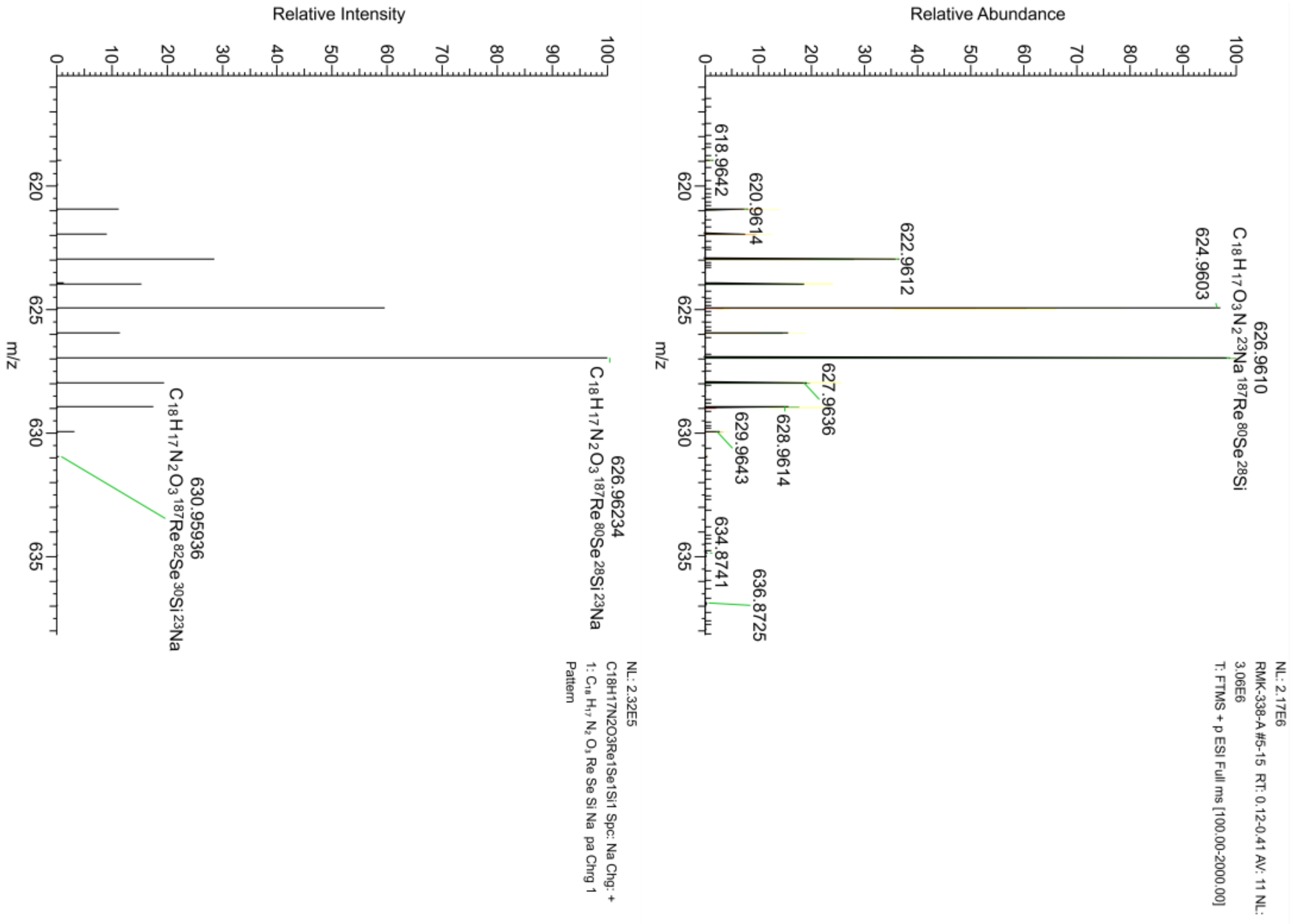

Figure S18. Observed and Calculated ESI-MS of of [Re(SeC≡CSiMe$_3$)(CO)$_3$(bipy)] (**5-Se**, +ve ion, MeCN)

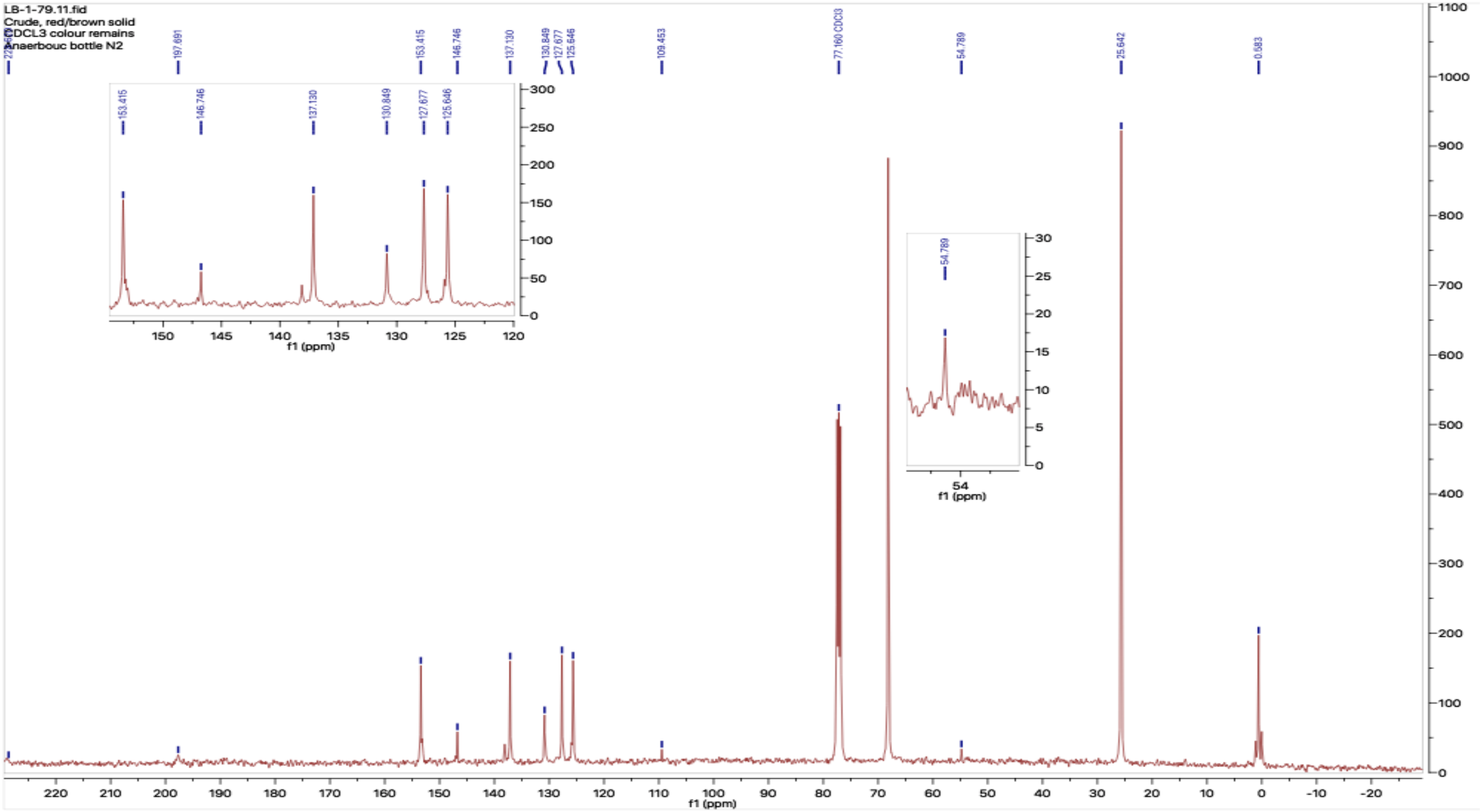

Figure S19. $^{13}C\{^{1}H\}$ NMR Spectrum of $[Re(TeC{\equiv}CSiMe_3)(CO)_3(phen)]$ (**6-Te** $CDCl_3$, 101 MHz, 25 °C, δ_C)

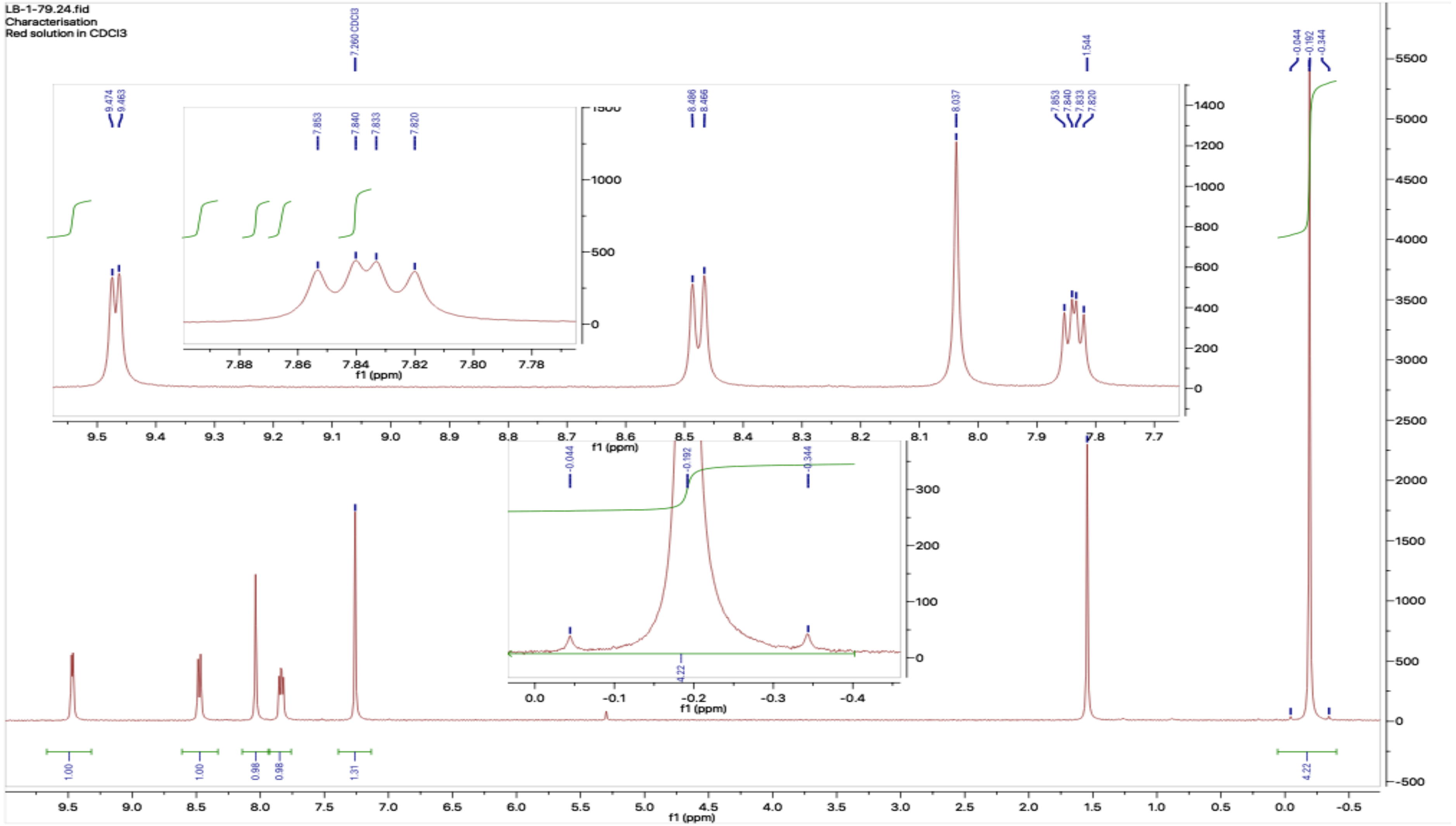

Figure S20. ^{1}H NMR Spectrum of $[Re(TeC{\equiv}CSiMe_3)(CO)_3(phen)]$ (**6-Te** $CDCl_3$, 400 MHz, 25 °C, δ_H)

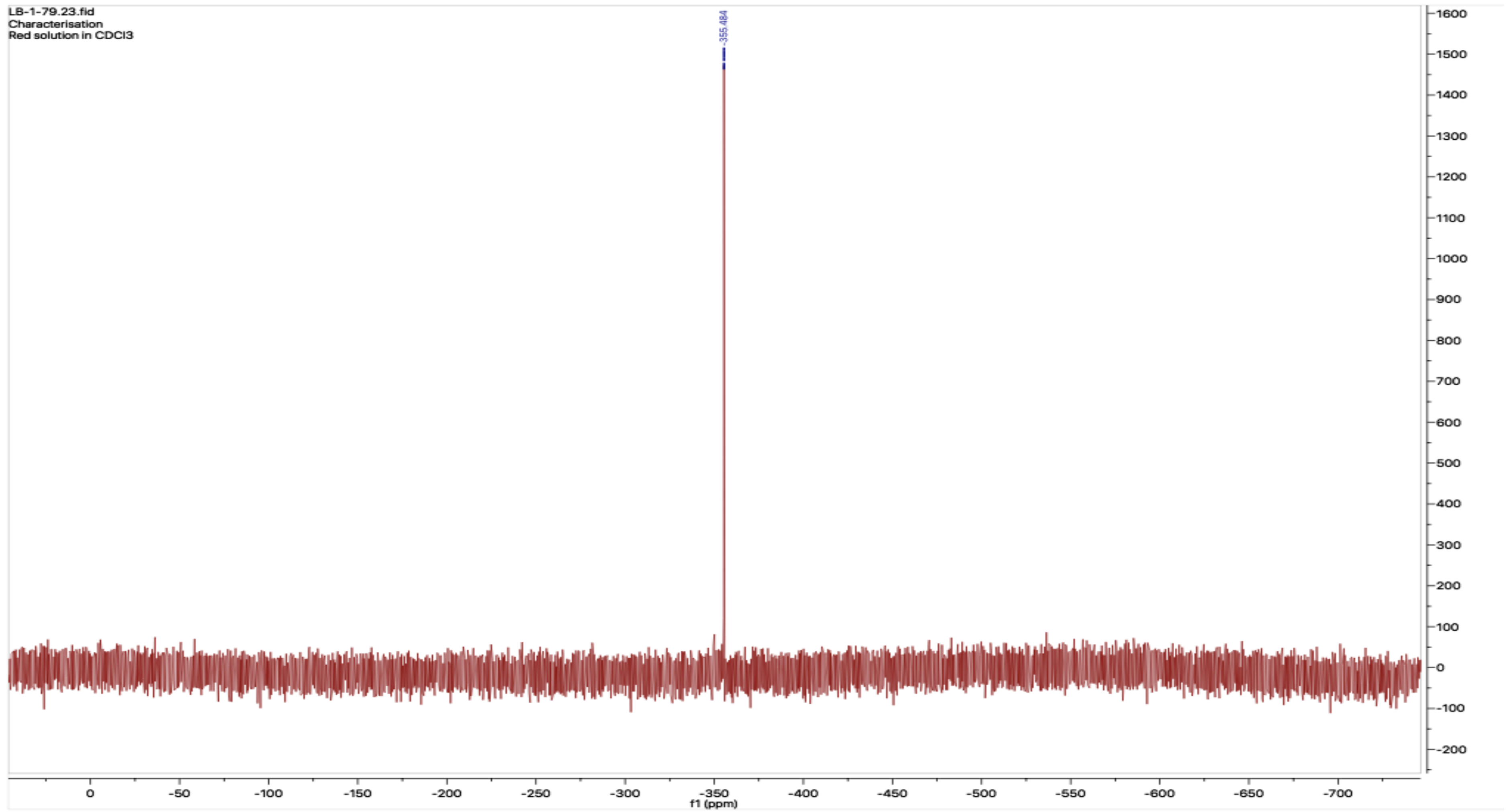

Figure S21. ^{125}Te{^{1}H} NMR Spectrum of [Re(TeC≡CSiMe$_3$)(CO)$_3$(phen)] (**6-Te** CDCl$_3$, 126.2 MHz, 25 °C, δ_{Te} *cf.* δ_{Te}(Ph$_2$Te$_2$) = 422)

Chemical Communications

ELECTRONIC SUPPORTING INFORMATION

Optimised Geometries and Cartesian Coordinates

[OCα≡CβMe]$^{-}$

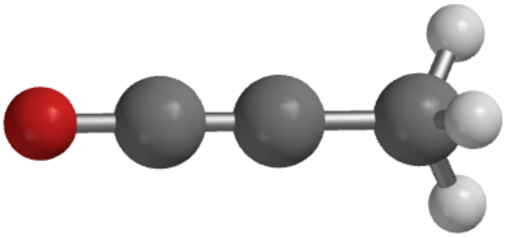

Figure S22: Optimised structure of [OCα≡CβMe]$^{-}$ (ωB97X-D/6-31G*/LANL2Dζ(W)/gas phase). Bond lengths (Å) and angles (°) of interest: OCα 1.327, Cα≡Cβ 1.237

Infrared absorptions of interest (cm^{-1}, scaled by 0.9297): 2185 ν_{CCO}.
Natural atomic charges of note: Cβ (–0.533), Cα (0.407), O(–0.764).
Löwden bond orders of interest: Cα–O (1.92), Cα≡Cβ (2.47).

Table S1. Cartesian Coordinates for [OCα≡CβMe]$^{-}$

Atom	x	y	z
C	-0.000073	-0.000313	1.833347
C	0.000278	0.001701	0.409143
C	0.000006	0.000445	-0.951102
H	0.516804	-0.895346	-1.398759
H	0.516878	0.895011	-1.400907
H	-1.033909	-0.000518	-1.399449
O	-0.000062	-0.000986	2.942355

Table S2: Thermodynamic Properties at 298.15 K

Zero Point Energy :	120.07 kJ/mol (ZPE)
Temperature Correction :	13.98 kJ/mol (vibration + gas law + rotation + translation)
Enthalpy Correction :	134.05 kJ/mol (ZPE + temperature correction)
Enthalpy :	-191.174054 au (Electronic Energy + Enthalpy Correction)
Entropy :	276.56 J/mol•K
Gibbs Energy :	-191.205460 au (Enthalpy - T*Entropy)
C_v :	59.23 J/mol•K

[SCα≡CβMe]$^{-}$

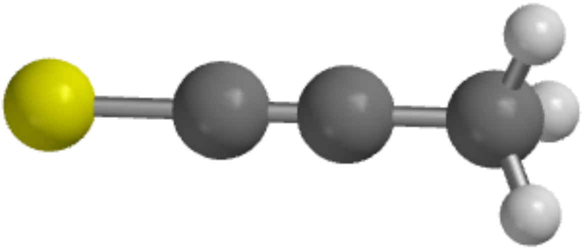

Figure S23: Optimised structure of [SCα≡CβMe]$^{-}$ (ωB97X-D/6-31G*/LANL2Dζ(W,S)/gas phase). Bond lengths (Å) and angles (°) of interest: SCα 1.683, Cα≡Cβ 1.223

Infrared absorptions of interest (cm^{-1}, scaled by 0.9297): 2118 ν_{CC}.
Natural atomic charges of note:
Cβ (–0.533), Cα (–0.179), S (–0.256).
Löwden bond orders of interest:
Cα–S (1.46), Cα≡Cβ (2.68).

Table S3. Cartesian Coordinates for [SCα≡CβMe]$^{-}$

Atom	x	y	z
C	-0.000534	0.000213	1.556780
C	-0.002876	0.000570	0.525891
C	-0.000059	-0.000033	-1.048955
H	-0.515716	-0.867523	-1.468270
H	1.009349	-0.013923	-1.467817
H	-0.492444	0.880065	-1.470211
S	0.002338	0.000624	3.334926

Table S4: Thermodynamic Properties at 298.15 K

Zero Point Energy :	117.35 kJ/mol (ZPE)
Temperature Correction :	14.81 kJ/mol (vibration + gas law + rotation + translation)
Enthalpy Correction :	132.16 kJ/mol (ZPE + temperature correction)
Enthalpy :	-514.178469 au (Electronic Energy + Enthalpy Correction)
Entropy :	288.30 J/mol•K
Gibbs Energy :	-514.211208 au (Enthalpy - T*Entropy)
C_v :	63.58 J/mol•K

[SeCα≡CβMe]$^-$

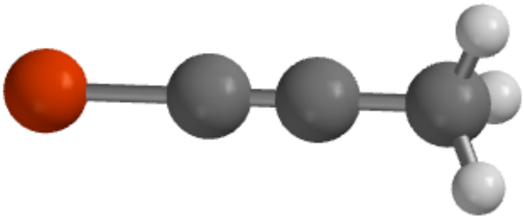

Figure S24: Optimised structure of [SeCα≡CβMe]$^-$ (ωB97X-D/6-31G*/LANL2Dζ(W,Se)/gas phase). Bond lengths (Å) and angles (°) of interest: SeCα 1.833, Cα≡Cβ 1.220

Infrared absorptions of interest (cm^{-1}, scaled by 0.9297): 2127 ν_{CC}.
Natural atomic charges of note:
Cβ (–0.230), Cα (–0.221), Se (–0.505).
Löwden bond orders of interest:
Cα–Se (1.34), Cα≡Cβ (2.74).

Table S5. Cartesian Coordinates for [SeCα≡CβMe]$^-$

Atom	**x**	**y**	**z**
C	0.000055	-0.000937	1.622944
C	-0.001307	-0.000683	0.402899
C	-0.000371	0.000136	-1.057217
H	-0.508275	-0.882793	-1.475843
H	1.019021	0.001412	-1.473880
H	-0.510477	0.882063	-1.475072
Se	0.001353	0.000802	3.456169

Table S6: Thermodynamic Properties at 298.15 K

Zero Point Energy :	116.40 kJ/mol (ZPE)
Temperature Correction :	15.19 kJ/mol (vibration + gas law + rotation + translation)
Enthalpy Correction :	131.59 kJ/mol (ZPE + temperature correction)
Enthalpy :	-2517.337121 au (Electronic Energy + Enthalpy Correction)
Entropy :	300.14 J/mol•K
Gibbs Energy :	-2517.371205 au (Enthalpy - T*Entropy)
C$_v$:	65.34 J/mol•K

[TeCα≡CβMe]$^-$

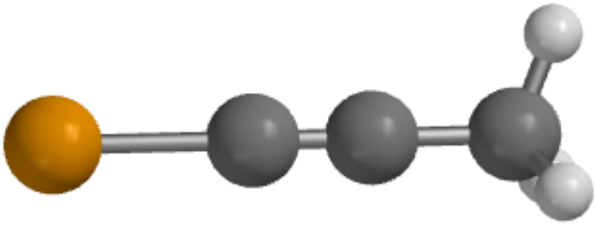

Figure S25: Optimised structure of [SCα≡CβMe]$^-$ (ωB97X-D/6-31G*/LANL2Dζ(W,Te)/gas phase). Bond lengths (Å) and angles (°) of interest: Te–Cα 2.047, Cα≡Cβ 1.219

Infrared absorptions of interest (cm^{-1}, scaled by 0.9297): 2125 ν_{CC}.
Natural atomic charges of note:
Cβ (–0.201), Cα (–0.324), Te (–0.441).
Löwden bond orders of interest:
Cα–Te (1.21), Cα≡Cβ (2.81).

Table S7. Cartesian Coordinates for [TeCα≡CβMe]$^-$]

Atom	**x**	**y**	**z**
C	-0.000707	-0.000000	1.589938
C	-0.001264	-0.000000	0.370945
C	-0.000205	-0.000000	-1.089947
H	1.019932	0.000000	-1.501582
H	-0.509498	0.883081	-1.503329
H	-0.509498	-0.883080	-1.503330
Te	0.001239	0.000000	3.637305

Table S8: Thermodynamic Properties at 298.15 K

Zero Point Energy :	115.36 kJ/mol (ZPE)
Temperature Correction :	15.64 kJ/mol (vibration + gas law + rotation + translation)
Enthalpy Correction :	130.99 kJ/mol (ZPE + temperature correction)
Enthalpy :	-124.074824 au (Electronic Energy + Enthalpy Correction)
Entropy :	309.16 J/mol•K
Gibbs Energy :	-124.109932 au (Enthalpy - T*Entropy)
C$_v$:	67.02 J/mol•K

[Fe(TeCα≡CβH)(CO)$_2$(η^5-C$_5$H$_5$)]

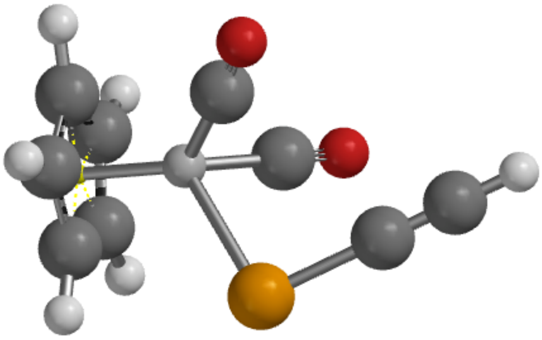

Figure S26: Optimised structure of [Fe(TeCα≡CβH)(CO)$_2$(η^5-C$_5$H$_5$)] (ωB97X-D/6-31G*/LANL2Dζ(Fe,Te)/gas phase). Bond lengths (Å) and angles (°) of interest: Fe–Te 2.610, Te–Cα 2.032, Cα≡Cβ 1.211, Fe–Te–Cα 98.5.

Infrared absorptions of interest (cm^{-1}, scaled by 0.9297): 2015w ν_{CC}. 2033s, 2008vs ν_{CO}
Natural atomic charges of note:
Cβ (–0.252), Cα (–0.449), Te (0.123), Fe (0.809).
Löwden bond orders of interest:
Cα–Te (1.12), Cα≡Cβ (2.96), Fe–Te (1.03).

Table S9. Cartesian Coordinates for [Fe(TeCα≡CβH)(CO)$_2$(η^5-C$_5$H$_5$)]

Atom	x	y	z
Fe	0.013888	0.102457	-0.039532
C	-1.214974	0.819990	1.016207
O	-2.036549	1.322104	1.635502
C	1.347778	0.277960	1.114921
O	2.254478	0.419323	1.799270
H	2.087701	-0.889481	-1.728979
C	1.160032	-0.335010	-1.723332
C	1.019366	1.080086	-1.566156
H	-0.373766	-1.922601	-2.036236
H	1.826338	1.785178	-1.419750
C	-0.357202	1.394130	-1.614375
H	-0.788628	2.380881	-1.514546
C	-1.085322	0.177419	-1.804771
H	-2.158626	0.079272	-1.884635
C	-0.140043	-0.875716	-1.890623
Te	-0.517421	-2.197753	1.073371
C	-0.425465	-1.619446	3.018665
C	-0.366493	-1.265704	4.175849
H	-0.316670	-0.961971	5.197534

Table S10: Thermodynamic Properties at 298.15 K

Zero Point Energy :	306.77	kJ/mol	(ZPE)
Temperature Correction :	33.64	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	340.41	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-1768.345137	au	(Electronic Energy + Enthalpy Correction)
Entropy :	450.95	J/mol•K	
Gibbs Energy :	-1768.396347	au	(Enthalpy - T*Entropy)
C_v :	212.20	J/mol•K	

[Fe(TeCα≡CβH)(CO)(PMe$_3$)(η^5-C$_5$H$_5$)]

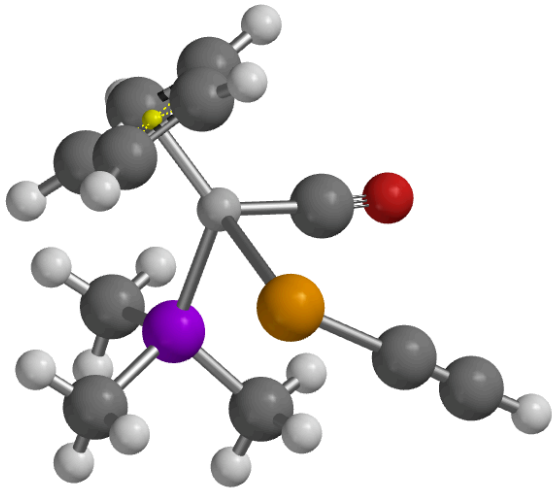

Figure S27: Optimised structure of [Fe(TeCα≡CβH)(CO)(PMe$_3$)(η-C$_5$H$_5$)] (ωB97X-D/6-31G*/LANL2Dζ(Fe,Te,P)/gas phase). Bond lengths (Å) and angles (°) of interest: Fe–Te 2.621, Te–Cα 2.034, Cα≡Cβ 1.213, Re–S–Cα 102.7.

Infrared absorptions of interest (cm^{-1}, scaled by 0.9297): 2009w ν_{CC}, 1971vs ν_{CO}.
Natural atomic charges of note: Cβ (–0.281), Cα (–0.438), Te (0.025), Fe (0.820).
Löwden bond orders of interest: Cα–Te (1.12), Cα≡Cβ (2.95), Fe–Te (1.01).

Table S11. Cartesian Coordinates for [Fe(TeCα≡CβH)(CO)(PMe$_3$)(η-C$_5$H$_5$)]

Atom	x	y	z
Fe	-0.673638	-0.133081	-0.743092
H	1.777202	-0.913074	-1.992203
C	0.731912	-0.702558	-2.177335
C	0.184646	0.575336	-2.490981
H	-0.214264	-2.703218	-1.929528
H	0.736966	1.497595	-2.604614
C	-1.215951	0.395378	-2.680596
H	-1.923533	1.176588	-2.924838
C	-1.533999	-0.961999	-2.456519
H	-2.520511	-1.400986	-2.494965
C	-0.318491	-1.647652	-2.142851
C	-1.615177	1.186558	-0.086134
O	-2.232115	2.093299	0.264361
Te	-1.883954	-1.862296	0.811331

C	-2.695316	-0.675876	2.250939
C	-3.164878	0.027050	3.120664
H	-3.600110	0.647264	3.871760
P	0.946962	0.161959	0.735635
C	2.240402	1.349434	0.192268
H	3.004477	1.481439	0.965249
H	1.775871	2.317932	-0.015259
H	2.725076	0.999239	-0.723486
C	0.479620	0.852536	2.362518
H	1.357996	0.953718	3.007938
H	-0.259244	0.208432	2.845704
H	0.022665	1.836443	2.221830
C	1.932658	-1.312686	1.193273
H	2.745494	-1.044850	1.875977
H	2.358579	-1.776605	0.298620
H	1.272619	-2.037618	1.676490
Lig	-0.430377	-0.468299	-2.389656

Table S12: Calculated Electronic Transitions (gas phase)

nm ▼	strength	MO Component	%
318.53	0.0117	HOMO-3 -> LUMO	64%
		HOMO-4 -> LUMO	22%
325.12	0.0549	HOMO-2 -> LUMO	72%
334.36	0.0010	HOMO -> LUMO+2	85%
349.36	0.0028	HOMO -> LUMO+1	97%
360.31	0.0455	HOMO-1 -> LUMO	93%
525.46	0.0001	HOMO -> LUMO	98%
318.53	0.0117	HOMO-3 -> LUMO	64%

Table S13: Thermodynamic Properties at 298.15 K

Zero Point Energy :	574.42	kJ/mol	(ZPE)
Temperature Correction :	46.01	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	620.43	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-2116.013829	au	(Electronic Energy + Enthalpy Correction)
Entropy :	533.35	J/mol•K	
Gibbs Energy :	-2116.074396	au	(Enthalpy - T*Entropy)
C_v :	301.39	J/mol•K	

***anti*-[Re(TeCα≡CβMe)(CO)$_3$(bipy)]**

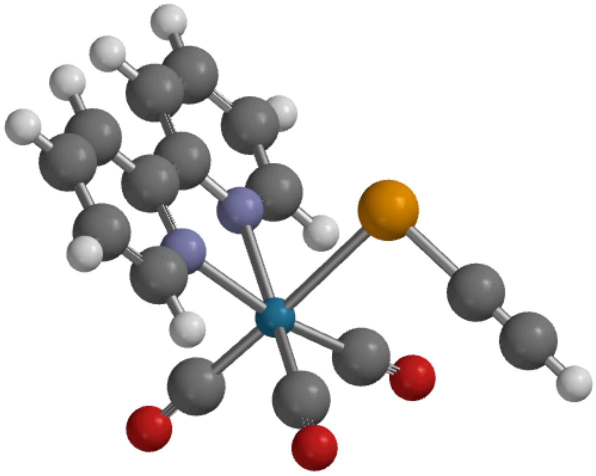

Figure S28. Optimised structure of *anti*-[Re(TeCα≡CβMe)(CO)$_3$(bipy)] (ωB97X-D/6-31G*/LANL2Dζ(Re,Te)/gas phase). Bond lengths (Å) and angles (°) of interest: Re–Te 2.840, Te–Cα 2.033, Cα≡Cβ 1.211, Re–Te–Cα 99.1.

Infrared absorptions of interest (cm^{-1}, scaled by 0.9297): 2015w ν_{CC}, 1998s, 1929vs, 1914vs. ν_{CO}.
Natural atomic charges of note: Cβ (–0.275), Cα (–0.416), Te (0.003), Re (0.452).
Löwden bond orders of interest: Cα–Te (1.12), Cα≡Cβ (2.97), Re–Te (1.06).

Table S14. Cartesian Coordinates for *anti*-[Re(TeCα≡CβMe)(CO)$_3$(bipy)

Atom	x	y	z
Re	-1.030262	1.081774	0.346992
N	1.149159	0.769763	0.335529
C	3.879587	0.260449	0.368171
C	1.601599	-0.502867	0.345443
C	2.037106	1.776286	0.321714
C	3.405140	1.566790	0.337683
C	2.967331	-0.782849	0.368653
H	1.619002	2.774737	0.293020
H	4.077849	2.416076	0.325739
H	3.320489	-1.806786	0.386001
H	4.944977	0.055398	0.386303
N	-0.715405	-1.097437	0.301697
C	-0.199464	-3.824671	0.191006
C	-1.719077	-1.985151	0.232450
C	0.557136	-1.548316	0.306725
C	0.841366	-2.911805	0.252554
C	-1.506311	-3.351982	0.179161
H	-2.718359	-1.569473	0.212420
H	1.865737	-3.262073	0.250091
H	-2.353850	-4.024978	0.123904
H	0.007644	-4.888406	0.147318
C	-1.115933	1.142515	2.262655
O	-1.175929	1.190104	3.419406
C	-1.031874	2.995729	0.213808
O	-0.977730	4.146980	0.127962

C	-2.944152	1.074807	0.195090
O	-4.093912	1.012245	0.101950
Te	-0.816880	0.931213	-2.480812
C	-2.390248	2.116197	-2.985699
C	-3.328682	2.814591	-3.299266
H	-4.156053	3.431140	-3.567668

Table S15: Calculated Electronic Transitions (gas phase)

nm ▼	strength	MO Component	%
349.53	0.0026	HOMO-4 → LUMO	50%
		HOMO-2 → LUMO	26%
		HOMO-3 → LUMO	17%
351.40	0.0021	HOMO-3 → LUMO	66%
		HOMO-2 → LUMO	14%
364.34	0.0061	HOMO → LUMO+2	95%
380.55	0.0018	HOMO → LUMO+1	95%
400.51	0.1180	HOMO-1 → LUMO	84%
618.27	0.0001	HOMO → LUMO	96%

Table S16: Thermodynamic Properties at 298.15 K

Zero Point Energy :	517.15	kJ/mol	(ZPE)
Temperature Correction :	49.64	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	566.79	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-998.906401	au	(Electronic Energy + Enthalpy Correction)
Entropy :	565.02	J/mol•K	
Gibbs Energy :	-998.970564	au	(Enthalpy - T*Entropy)
C_v :	336.50	J/mol•K	

syn-[Re(TeCα≡CβMe)(CO)$_3$(bipy)]

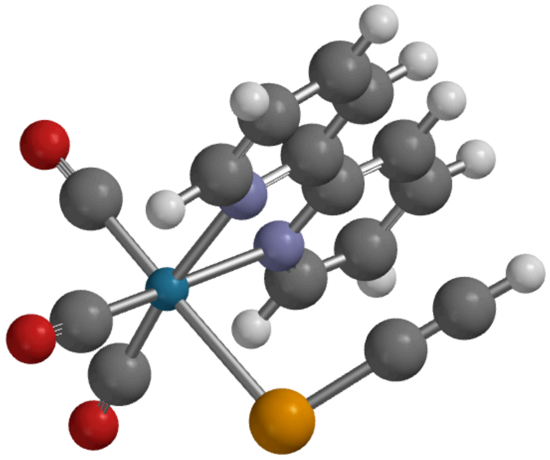

Figure S29: Optimised structure of *syn*-[Re(TeCα≡CβMe)(CO)$_3$(bipy)] (ωB97X-D/6-31G*/LANL2Dζ(Re,Te)/gas phase). Bond lengths (Å) and angles (°) of interest: Re–Te 2.852, Te–Cα 2.037, Cα≡Cβ 1.214, Re–Te–Cα 98.8.

Infrared absorptions of interest (cm^{-1}, scaled by 0.9297): 1990w ν_{CC}, 1998s, 1921vs, 1916vs. ν_{CO}.
Natural atomic charges of note: Cβ (–0.319), Cα (–0.409), Te (0.038), Re (0.464).
Löwden bond orders of interest: Cα–Te (1.13), Cα≡Cβ (2.93), Re–Te (1.03).

Table S17. Cartesian Coordinates for *syn*-[Re(TeCα≡CβMe)(CO)$_3$(bipy)

Atom	x	y	z
Re	-1.477970	1.473495	0.273756
N	0.698130	1.162501	0.274888
C	3.425190	0.647791	0.329009
C	1.146374	-0.107809	0.317399
C	1.588894	2.165702	0.232962
C	2.955126	1.954358	0.255433
C	2.510643	-0.391011	0.358988
H	1.175097	3.164572	0.175296
H	3.630138	2.801048	0.216207
H	2.859029	-1.415207	0.399387
H	4.489818	0.440751	0.354461
N	-1.167945	-0.702718	0.233959
C	-0.653326	-3.430473	0.223538
C	-2.169611	-1.591467	0.142879
C	0.101286	-1.152603	0.291988
C	0.384027	-2.517521	0.303010
C	-1.958095	-2.957922	0.132174
H	-3.166798	-1.175356	0.073863
H	1.407219	-2.867137	0.356582
H	-2.803099	-3.631645	0.053911
H	-0.446452	-4.495457	0.224190
C	-1.560907	1.515209	2.190597
O	-1.616001	1.546794	3.346982
C	-1.461786	3.388855	0.185414
O	-1.398936	4.542739	0.126479
C	-3.390878	1.464890	0.140940
O	-4.543268	1.405841	0.054986

Atom	x	y	z
Te	-1.325333	1.382031	-2.572788
C	0.106325	-0.054270	-2.760488
C	0.958519	-0.909285	-2.893089
H	1.704588	-1.656695	-3.042909

Table S18: Calculated Electronic Transitions (gas phase)

nm ▼	strength	MO Component	%
337.51	0.0014	HOMO-4 -> LUMO	34%
351.77	0.0014	HOMO-4 -> LUMO+1	42%
		HOMO-2 -> LUMO	15%
		HOMO -> LUMO	12%
		HOMO-4 -> LUMO	10%
379.74	0.0002	HOMO-2 -> LUMO+1	60%
438.06	0.0004	HOMO-2 -> LUMO	43%
		HOMO-4 -> LUMO	25%
		HOMO-3 -> LUMO	12%
59	0.0045	HOMO -> LUMO+1	39%
		HOMO-3 -> LUMO+1	38%
623.19	0.0005	HOMO -> LUMO	44%
		HOMO-3 -> LUMO	27%

Table S19: Thermodynamic Properties at 298.15 K

Zero Point Energy :	574.42	kJ/mol	(ZPE)
Temperature Correction :	46.01	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	620.43	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-2116.013829	au	(Electronic Energy + Enthalpy Correction)
Entropy :	533.35	J/mol•K	
Gibbs Energy :	-2116.074396	au	(Enthalpy - T*Entropy)
C_v :	301.39	J/mol•K	

syn-[Re(SeCα≡CβMe)(CO)$_3$(bipy)]

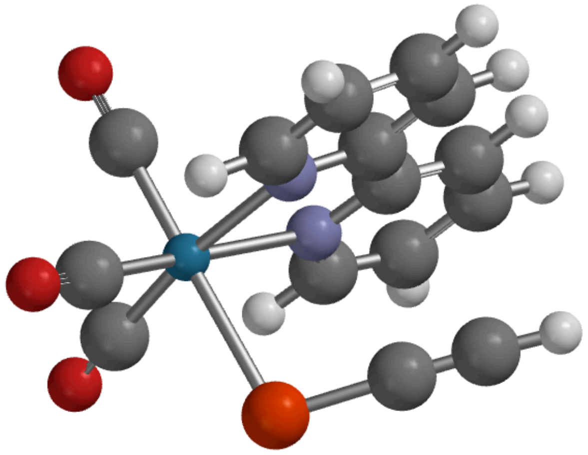

Figure S30: Optimised structure of *syn*-[Re(SeCα≡CβMe)(CO)$_3$(bipy)] (ωB97X-D/6-31G*/LANL2Dζ(Re,Se)/gas phase). Bond lengths (Å) and angles (°) of interest: Re–Se 2.668, Se–Cα 1.833, Cα≡Cβ 1.214, Re–Se–Cα 102.2.

Infrared absorptions of interest (cm^{-1}, scaled by 0.9297): 2003w ν_{CC}, 2000s, 1924vs, 1915vs. ν_{CO}.

Natural atomic charges of note: Cβ (–0.341), Cα (–0.289), Se (–0.127), Re (0.498).

Löwden bond orders of interest: Cα–Se (1.22), Cα≡Cβ (2.87), Re–Se (0.95).

Table S20. Cartesian Coordinates for *syn*-[Re(SeCα≡CβMe)(CO)$_3$(bipy)

Atom	x	y	z
Re	1.452491	1.450892	0.344176
C	1.442605	3.367014	0.284096
O	1.380977	4.521143	0.237391
C	3.368088	1.442832	0.269372
O	4.521901	1.383327	0.213143
C	1.480205	1.463780	2.262036
O	1.498700	1.472022	3.420398
N	-0.724539	1.141788	0.276697
C	-3.450037	0.626981	0.200166
C	-1.172785	-0.128875	0.271267
C	-1.611760	2.145762	0.211740
C	-2.978377	1.934314	0.169269
C	-2.537030	-0.412898	0.250713
H	-1.196142	3.145441	0.193124
H	-3.651794	2.781443	0.114735
H	-2.886704	-1.437489	0.257190
H	-4.514664	0.419545	0.176726
N	1.143877	-0.725721	0.263208
C	0.629750	-3.451001	0.176289
C	-0.126638	-1.174552	0.264329
C	2.147777	-1.612037	0.186464
C	1.936626	-2.978524	0.138285
C	-0.410174	-2.538801	0.239042
H	3.147085	-1.195718	0.163195
H	2.783604	-3.651283	0.074207
H	-1.434515	-2.889032	0.251849
H	0.422652	-4.515605	0.149166
Se	1.393589	1.412344	-2.323268
C	0.118722	0.139978	-2.664316
C	-0.721636	-0.702091	-2.906762
H	-1.451855	-1.434977	-3.163925

Table S21: Calculated Electronic Transitions (gas phase)

nm ▼	strength	MO Component	%
316.73	0.0162	HOMO-3 -> LUMO	73%
		HOMO-2 -> LUMO	20%
322.89	0.0334	HOMO-2 -> LUMO	65%
		HOMO-3 -> LUMO	21%
336.71	0.0027	HOMO -> LUMO+2	94%
353.05	0.0025	HOMO -> LUMO+1	97%
357.21	0.0609	HOMO-1 -> LUMO	89%
532.01	0.0002	HOMO -> LUMO	98

Table S22: Thermodynamic Properties at 298.15 K

Zero Point Energy :	519.22	kJ/mol	(ZPE)
Temperature Correction :	49.17	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	568.39	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-3392.178811	au	(Electronic Energy + Enthalpy Correction)
Entropy :	558.66	J/mol•K	
Gibbs Energy :	-3392.242251	au	(Enthalpy - T*Entropy)
C_V :	334.69	J/mol•K	

syn-[Re(SCα≡CβMe)(CO)$_3$(bipy)]

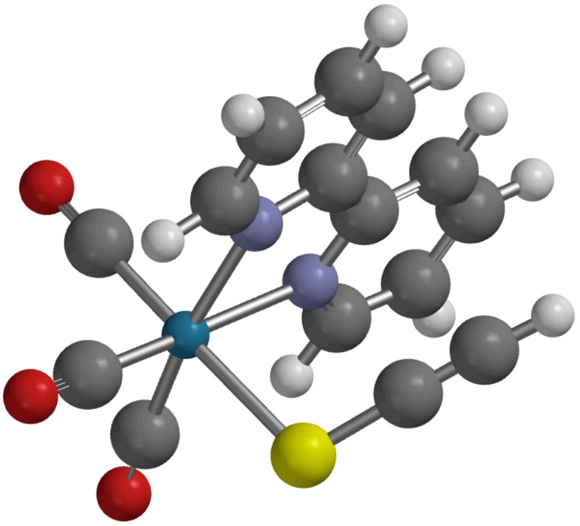

Figure S31: Optimised structure of *syn*-[Re(SCα≡CβMe)(CO)$_3$(bipy)] (ωB97X-D/6-31G*/LANL2Dζ(Re,Te)/gas phase). Bond lengths (Å) and angles (°) of interest: Re–S 2.559, S–Cα 1.688, Cα≡Cβ 1.215, Re–S–Cα 105.1.

Infrared absorptions of interest (cm^{-1}, scaled by 0.9297): 2011w ν_{CC}, 2002s, 1924vs, 1915vs. ν_{CO}.
Natural atomic charges of note: Cβ (–0.353), Cα (–0.228), S (–0.215), Re (0.515).
Löwden bond orders of interest: Cα–S (1.30), Cα≡Cβ (2.83), Re–S (0.94).

Table S23. Cartesian Coordinates for *syn*-[Re(SCα≡CβMe)(CO)$_3$(bipy)

Atom	x	y	z
Re	1.441948	1.441583	0.319906
C	1.439728	3.357387	0.240990
O	1.383391	4.510977	0.183294
C	3.357166	1.435803	0.226378
O	4.510268	1.378470	0.160368
C	1.488450	1.476143	2.235897
O	1.512415	1.493727	3.394283
N	-0.733442	1.134039	0.273451
C	-3.458580	0.618811	0.207169
C	-1.181138	-0.136864	0.264200
C	-1.620905	2.137966	0.221538
C	-2.987853	1.926514	0.183905
C	-2.545162	-0.421391	0.247886
H	-1.205619	3.137926	0.209400
H	-3.661891	2.773699	0.139259
H	-2.894761	-1.445979	0.250348
H	-4.523217	0.410981	0.186649
N	1.136167	-0.734153	0.261330
C	0.622857	-3.459306	0.180735
C	-0.134371	-1.182861	0.257294
C	2.140409	-1.620496	0.197112
C	1.929970	-2.987319	0.152063
C	-0.417782	-2.547044	0.234066
H	3.140027	-1.204579	0.181490
H	2.777513	-3.660220	0.097855
H	-1.442007	-2.897614	0.241081
H	0.415899	-4.523988	0.154852
S	1.351980	1.367803	-2.236255
C	0.183791	0.205653	-2.602183
C	-0.653124	-0.629418	-2.882164
H	-1.372129	-1.356249	-3.182197

Table S24: Calculated Electronic Transitions (gas phase)

nm ▼	strength	MO Component	%
318.53	0.0117	HOMO-3 -> LUMO	64%
		HOMO-4 -> LUMO	22%
325.12	0.0549	HOMO-2 -> LUMO	72%
334.36	0.0010	HOMO -> LUMO+2	85%
349.36	0.0028	HOMO -> LUMO+1	97%
360.31	0.0455	HOMO-1 -> LUMO	93%
525.46	0.0001	HOMO -> LUMO	98%
318.53	0.0117	HOMO-3 -> LUMO	64%

Table S25: Thermodynamic Properties at 298.15 K

Zero Point Energy :	521.05	kJ/mol	(ZPE)
Temperature Correction :	48.87	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	569.92	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-1389.022397	au	(Electronic Energy + Enthalpy Correction)
Entropy :	553.72	J/mol•K	
Gibbs Energy :	-1389.085277	au	(Enthalpy - T*Entropy)
C_V :	332.63	J/mol•K	

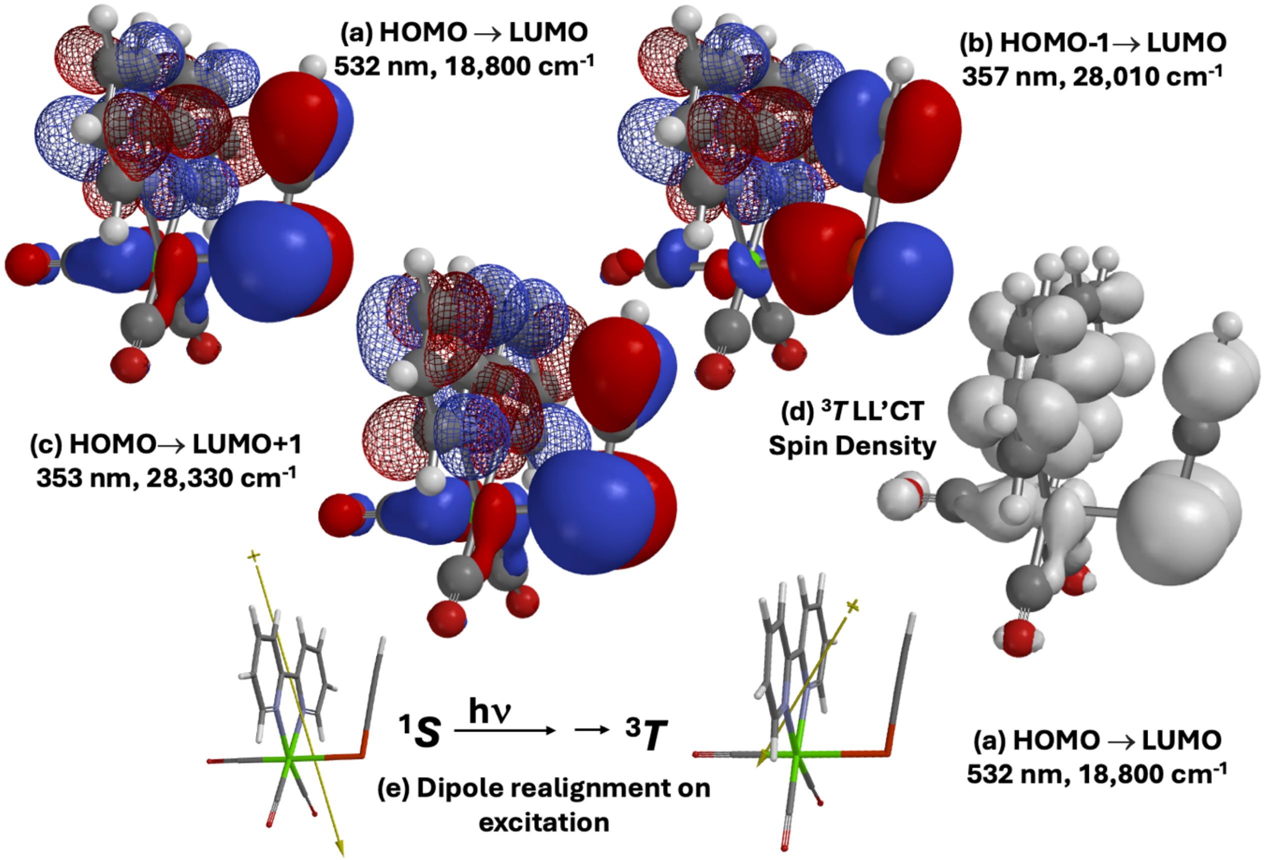

Figure 32. LL'CT electronic transitions of interest between occupied (solid) and virtual (mesh) orbitals for [Re(SeCCH)(CO)3(bipy). (a) HOMO→LUMO; (b) HOMO-1→LUMO; (c) HOMO→LUMO+1; (d) Spin density for excited LL'CT triplet state.