



## Chemical Communications

### ELECTRONIC SUPPORTING INFORMATION

## Carbon-chalcogen Wires: Alkynyltellurolatocarbynes

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### General

Experimental work was performed using standard Schlenk techniques using dried and pre-purified nitrogen or in an inert atmosphere glovebox charged with an argon atmosphere unless specified otherwise. Reactions employed dried and degassed solvents distilled over sodium and benzophenone (ethers, arenes and paraffins) or calcium hydride (CH<sub>2</sub>Cl<sub>2</sub>, MeCN). The compounds [M(≡CBr)(CO)<sub>2</sub>(Tp\*)] (M = Mo, W)<sup>1</sup> has been described previously. All other reagents, including terminal alkynes, were used as received from commercial suppliers.

NMR spectra were obtained on a Bruker Avance 400 (<sup>1</sup>H at 400.1 MHz, <sup>13</sup>C{<sup>1</sup>H} at 100.6 MHz), a Bruker Avance 600 (<sup>1</sup>H at 600.0 MHz, <sup>13</sup>C{<sup>1</sup>H} at 150.9 MHz) or a Bruker Avance 700 (<sup>1</sup>H at 700.0 MHz, <sup>13</sup>C{<sup>1</sup>H} at 176.1 MHz, <sup>125</sup>Te{<sup>1</sup>H} at 126.4 MHz) spectrometers at the temperatures indicated. Chemical shifts (δ) are reported in ppm with coupling constants given in Hz and are referenced to the solvent resonance or external references (Te<sub>2</sub>Ph<sub>2</sub> for <sup>125</sup>Te{<sup>1</sup>H}, δ<sub>Te</sub> = 422.0 in CDCl<sub>3</sub>). 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 <sup>183</sup>W satellites. In select cases, distinct peaks were observed in the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra, but to the level of accuracy that is reportable (i.e., two decimal places for <sup>1</sup>H NMR, one decimal place for <sup>13</sup>C{<sup>1</sup>H} NMR) they are reported as having the same chemical shift.

The abbreviation 'pz' is used to refer to the pyrazolyl rings on the hydridotris(3,5-dimethylpyrazol-1-yl)borate (Tp\*) ligand. Spectra provided generally correspond to samples obtained directly from chromatography and may contain residual solvent as recrystallised samples often display reduced solubility. The BH protons give rise to very broad signals around 4–5 ppm in the <sup>1</sup>H NMR spectra due to coupling to the quadrupolar boron nuclei. These are generally not listed in the experimental NMR data as their chemical shifts and associated integrals are not determined accurately. The BH unit, being remote from the metal centre of interest is not particularly

responsive to variations and accordingly <sup>11</sup>B{<sup>1</sup>H} NMR spectra were not recorded.

Infrared spectra were obtained using a Shimadzu FTIR-8400 spectrometer (liquid) or Perkin Elmer FTIR Spectrum Two (solid state ATR, diamond anvil). Signals are denoted according to their absorption strength such as very sharp (vs), strong (s), medium (m), weak (w) or broad (br). Elemental microanalytical data were provided by Macquarie University, Australia, with the caveat that compounds containing B–N bonds are considered prone to incomplete oxidation in the combustion analysis (formation of refractory boron nitride materials). Solvates evident from data were confirmed where possible by NMR spectroscopy. High and low resolution electrospray ionisation mass spectrometry (ESI-MS) was performed by the ANU Research School of Chemistry mass spectrometry service with acetonitrile or dichloromethane as the matrix.

### Crystallographic Details

Data for X-ray crystallography were collected with Agilent Technologies Xcalibur or Supernova/EosS2-CCD diffractometers as indicated using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) or Cu-Kα radiation (λ = 1.54184 Å) employing the CrysAlis PRO-CCD and -RED software,<sup>2</sup> with Gaussian absorption corrections being applied. The structures were solved using intrinsic phasing and refined by full-matrix least-squares on F<sup>2</sup> in an anisotropic (for non-hydrogen atoms) approximation using the SHELXS or SHELXT and SHELXL programs,<sup>3,4</sup> implemented within the Olex2 suite of programs.<sup>5</sup> Hydrogen atoms were located geometrically and refined using a riding model. Diagrams were produced using the CCDC visualisation program Mercury.<sup>6,7</sup>

### Computational Details

Computational studies were performed by using the SPARTAN20<sup>®</sup> suite of programs.<sup>8</sup> Geometry optimisation (gas phase) for diatomics and metal complexes was performed at the DFT level of theory using the exchange functionals ωB97X-D of

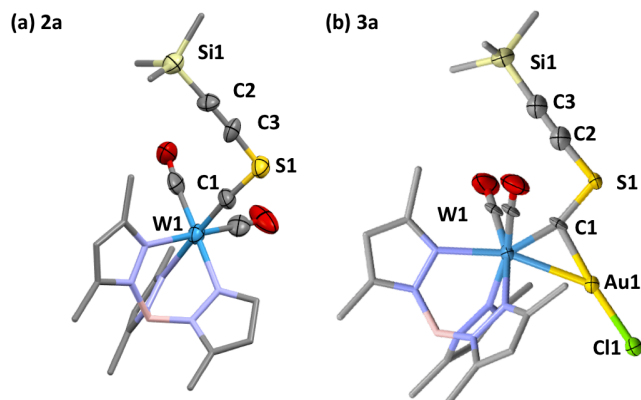
Head-Gordon.<sup>9,10</sup> The Los Alamos effective core potential type basis set (LANL2DZ) of Hay and Wadt<sup>11-12</sup> was used for W, Se and Te while Pople basis sets<sup>15</sup> were used for all other atoms. Frequency calculations were performed for all compounds to confirm that each optimized structure was a local minimum and also to identify vibrational modes of interest. Cartesian atomic coordinates and thermodynamic properties are provided below.

## Synthetic Procedures and Crystallographic Data

**Synthesis of  $[W(\equiv CSC\equiv CSiMe_3)(CO)_2(Tp^*)]$  (**2a**).** To a solution of ethynyltrimethylsilane (23  $\mu$ L, 0.163 mmol) in THF (5 mL) at  $-78$  °C was added <sup>n</sup>BuLi (0.10 mL, 1.6 M in hexanes, 0.16 mmol). The mixture was warmed to room temperature and stirring was continued for 30 min. Grey selenium (0.006 g, 0.187 mg.atom) was then added and the mixture stirred for 1 h, during which time the solution turned clear. The mixture was again cooled to  $-78$  °C and transferred *via* cannula to a similarly cooled solution of  $[W(\equiv CBr)(CO)_2(Tp^*)]$  (**1**: 0.100 g, 0.159 mmol) in THF (5 mL). The mixture was gradually warmed to room temperature and stirring was continued overnight, during which time the mixture turned orange-brown. Volatiles were removed *in vacuo* and the residue was extracted with the minimum dichloromethane and subjected to column chromatography (20 x 1 cm silica gel column), eluting first with petroleum spirits (40–60 °C) and gradually increasing the polarity to 3:1 v/v petrol/ $CH_2Cl_2$ . A bright orange band was collected and the volatiles were removed under reduced pressure to give an orange solid of pure **2a** (0.048 g, 0.071 mmol, 45%).

IR ( $CH_2Cl_2$ ,  $cm^{-1}$ ): 1988s, 1897s  $\nu_{CO}$ . 2092s  $\nu_{C\equiv C}$ . <sup>1</sup>H NMR (600 MHz,  $CDCl_3$ , 298 K):  $\delta_H$  = 0.22 (s, 9 H,  $SiCH_3$ ), 2.33 (s, 3 H,  $pzCH_3$ ), 2.38 (s, 6 H,  $pzCH_3$ ), 2.42 (s, 3 H,  $pzCH_3$ ), 2.54 (s, 6 H,  $pzCH_3$ ), 5.77 (s, 1 H,  $pzH$ ), 5.90 (s, 2 H,  $pzH$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz,  $CDCl_3$ , 298 K):  $\delta_C$  = 0.1 ( $Si(CH_3)_3$ ), 12.9, 13.0, 15.6, 17.1 ( $pzCH_3$ ), 82.8 ( $SC\equiv C$ ), 106.9, 107.2 ( $pzCH$ ), 107.3 ( $SC\equiv C$ ), 144.8, 145.7, 152.4, 153.1 ( $pzC^{3,5}CH_3$ ), 223.7 (CO, <sup>1</sup>J<sub>WC</sub> = 161.6 Hz), 233.5 ( $W\equiv C$ , <sup>1</sup>J<sub>WC</sub> = 225.0 Hz). MS (ESI, *m/z*): Found: 678.1600. Calcd for  $C_{23}H_{31}^{11}BN_6O_2SSi^{184}W$  [M]<sup>+</sup>: 678.1599. Anal. Found: C, 40.46; H, 4.50; N, 12.26%. Calcd for  $C_{23}H_{31}BN_6O_2^{32}S^{28}Si^{184}W$ : C, 40.73; H, 4.61; N, 12.39%.

Single crystals suitable for X-ray structure diffraction were grown by slow evaporation of a chloroform/ethanol mixture. *Crystal data* for  $C_{23}H_{31}BN_6O_2SSiW$  ( $M_w$  = 678.35  $g\cdot mol^{-1}$ ): orthorhombic, space group  $P2_12_12_1$  (no. 19),  $a$  = 8.0110(16) Å,  $b$  = 17.654(4) Å,  $c$  = 19.997(4) Å,  $V$  = 2828.1(10) Å<sup>3</sup>,  $Z$  = 4,  $T$  = 293(2) K,  $\mu$ (MoK $\alpha$ ) = 4.231  $mm^{-1}$ ,  $D_{calc}$  = 1.593  $Mgm^{-3}$ , 29140 reflections measured ( $2.04^\circ \leq 2\theta \leq 63.3^\circ$ ), 8132 unique ( $R_{int}$  = 0.0484,  $R_{sigma}$  = 0.0446) which were used in all calculations. The final  $R_1$  was 0.0686 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.1804 (all data) for 338 refined parameters with 1 restraints. For molecular geometry see Figure S1a. Because the data were acquired using synchrotron radiation on a minute crystal resulting in poor data leading to an imprecise structural model, the .cif was not deposited in the CCDC. The model does however confirm connectivity.



**Figure S1.** Molecular structures of alkynylthiolatocarbynes (a) **2a** and (b) **3a** (one of two similar but crystallographically independent molecules) in crystals (50% displacement ellipsoids, pyrazolyl groups simplified, hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): **2a**: W1–C1 1.842(17), C1–S1 1.728(17), S1–C4 1.691(17), C4–C5 1.22(2), W1–C1–S1 168.1(12), C1–S1–C4 102.0(8). **3a**: W1–C1 1.838(16), W1–Au1 2.7950(10), C1–Au1 2.126(17), C1–S1 1.736(15), S1–C4 1.69(2), C4–C5 1.21(3), W1–C1–S1 160.5(12), C1–Au1–C1 174.5(5), C1–S1–C4 99.4(10).

**Synthesis of  $[WAu(\mu-CSC\equiv CSiMe_3)Cl(CO)_2(Tp^*)]$  (**3a**).** To a flask containing  $[W(\equiv CSC\equiv CSiMe_3)(CO)_2(Tp^*)]$  (**2a**: 0.029 g, 0.043 mmol) and  $[AuCl(SMe_2)]$  (0.013 g, 0.044 mmol) was added  $CH_2Cl_2$  (5 mL) and the resulting mixture was stirred for 30 min, during which time the orange solution darkened. The mixture was filtered through diatomaceous earth and the filtrate was dried under reduced pressure to give an orange solid of pure **3a** (0.033 g, 0.036 mmol, 84%).

IR ( $CH_2Cl_2$ ,  $cm^{-1}$ ): 2015s, 1935s  $\nu_{CO}$ . <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ , 298 K):  $\delta_H$  = 0.24 (s, 9 H,  $SiCH_3$ ), 2.35 (s, 3 H,  $pzCH_3$ ), 2.38 (s, 6 H,  $pzCH_3$ ), 2.48 (s, 9 H,  $pzCH_3$ ), 5.93 (s, 1 H,  $pzCH$ ), 5.95 (s, 2 H,  $pzCH$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (176 MHz,  $CDCl_3$ , 298 K):  $\delta_C$  =  $-0.1$  ( $SiCH_3$ ), 13.0, 13.4, 16.2, 17.7 ( $pzCH_3$ ), 88.2 ( $SC\equiv C$ ), 108.1, 108.6 ( $pzCH$ ), 110.7 ( $SC\equiv C$ ), 146.0, 146.6, 153.1, 153.8 ( $pzC^{3,5}CH_3$ ), 215.7 (CO), 235.2 ( $W=C$ ). MS (ESI, *m/z*): Found: 933.0866. Calcd for  $C_{23}H_{31}Au^{11}B^{35}ClN_6O_2^{32}S^{28}Si^{184}WNa$  [M+Na]<sup>+</sup>: 933.0846. Anal. Found: C, 26.53; H, 2.99; N, 8.60%. Calcd for  $C_{23}H_{31}AuBClN_6O_2SSiW\cdot 2CHCl_3$ : C, 26.12; H, 2.89; N, 7.31%.

Single crystals suitable for X-ray structure diffraction were grown by slow evaporation of a dichloromethane/ethanol mixture. *Crystal data* for  $C_{23}H_{31}AuBClN_6O_2SSiW$  ( $M_w$  = 910.76  $g\cdot mol^{-1}$ ): monoclinic, space group  $P2_1/m$  (no. 11),  $a$  = 12.3181(4) Å,  $b$  = 24.9472(13) Å,  $c$  = 16.5061(6) Å,  $\beta$  = 108.592(4)°,  $V$  = 4807.6(4) Å<sup>3</sup>,  $Z$  = 6,  $T$  = 150.0(1) K,  $\mu$ (Cu K $\alpha$ ) = 16.992  $mm^{-1}$ ,  $D_{calc}$  = 1.887  $Mgm^{-3}$ , 15801 reflections measured ( $7.086^\circ \leq 2\theta \leq 133.202^\circ$ ), 8618 unique ( $R_{int}$  = 0.0399,  $R_{sigma}$  = 0.0637) which were used in all calculations. The final  $R_1$  was 0.0772 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.2006 (all data) for 482 refined parameters with 2 restraints (CCDC 2033073). For molecular geometry see Figure S1b.

**Synthesis of  $[W(\equiv CTeC\equiv CSiMe_3)(CO)_2(Tp^*)]$  (**4a**).** To a solution of ethynyltrimethylsilane (450  $\mu$ L, 3.18 mmol) in THF (10 mL) at  $-78$  °C was added <sup>n</sup>BuLi (2.0 mL, 1.6 M in hexane, 3.2 mmol). The mixture was warmed to room temperature and stirring was continued for 30 min. Powdered tellurium (0.406 g, 3.18 mg.atom) was then added and the mixture stirred for 1 h,

during which time the solution turned clear. The mixture was again cooled to  $-78\text{ }^{\circ}\text{C}$  and transferred *via* cannula to a similarly cooled solution of  $[\text{W}(\equiv\text{CBr})(\text{CO})_2(\text{Tp}^*)]$  (**1**: 2.00 g, 3.18 mmol) in THF (10 mL). The mixture was gradually warmed to room temperature and stirring was continued overnight, during which time the mixture turned orange-brown. Volatiles were removed *in vacuo* and the residue was extracted with the minimum dichloromethane and subjected to column chromatography (20 x 1 cm silica gel column), eluting first with petrol and gradually increasing the polarity to 3:1 v/v petrol/ $\text{CH}_2\text{Cl}_2$ . The first dark red band collected was  $[\text{W}(\equiv\text{CC}(\text{SiMe}_3)(\text{CO})_2(\text{Tp}^*))]$  (**6a**).<sup>16</sup> A bright orange band was then collected and the volatiles were removed under reduced pressure to give an orange solid of pure **4a** (1.618 g, 2.09 mmol, 66%).

IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ): 1988s, 1897s  $\nu_{\text{CO}}$ . 2077s  $\nu_{\text{C}=\text{C}}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{H}} = 0.21$  (s, 9 H,  $\text{SiMe}_3$ ), 2.31 (s, 3 H,  $\text{pzCH}_3$ ), 2.36 (s, 6 H,  $\text{pzCH}_3$ ), 2.40 (s, 3 H,  $\text{pzCH}_3$ ), 2.57 (s, 6 H,  $\text{pzCH}_3$ ), 5.76 (s, 1 H,  $\text{pzH}$ ), 5.91 (s, 2 H,  $\text{pzH}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{C}} = 0.4$  ( $\text{SiCH}_3$ ), 12.9, 13.0, 15.6, 17.3 ( $\text{pzCH}_3$ ), 59.6 ( $\text{TeC}\equiv\text{C}$ ), 106.9, 107.2 ( $\text{pzCH}$ ), 125.2 ( $\text{TeC}\equiv\text{C}$ ), 144.8, 145.8, 152.4, 153.1 [ $\text{C}^{3,5}(\text{pz})$ ], 223.7 ( $\text{CO}$ ,  $^1J_{\text{WC}} = 166.7$  Hz), 234.5 ( $\text{W}\equiv\text{C}$ ,  $^1J_{\text{WC}} = 214.5$  Hz).  $^{125}\text{Te}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{Te}} = 771$ . MS (ESI,  $m/z$ ): Found: 777.1016. Calcd for  $\text{C}_{23}\text{H}_{32}^{11}\text{BN}_6\text{O}_2^{28}\text{Si}^{130}\text{Te}^{184}\text{W}$  [ $\text{M}+\text{H}$ ] $^+$ : 777.1015. Anal. Found: C, 35.80; H, 4.13; N, 10.63%. Calcd for  $\text{C}_{23}\text{H}_{31}\text{BN}_6\text{O}_2\text{SeSiW}$ : C, 35.70; H, 4.04; N, 10.86%.

**Synthesis of  $[\text{W}(\equiv\text{CTeC}\equiv\text{CSi}^i\text{Pr}_3)(\text{CO})_2(\text{Tp}^*)]$  (**4b**).** A solution of ethynyltriisopropylsilane (72  $\mu\text{L}$ , 0.318 mmol) in THF (5 mL) at  $-78\text{ }^{\circ}\text{C}$  was treated with  $^n\text{BuLi}$  (0.20 mL, 1.6 M in hexane, 0.32 mmol). The mixture was warmed to room temperature and stirring was continued for 30 min. Powdered tellurium (0.041 g, 0.318 mg.atom) was then added and stirring continued for 1 h, during which time the solution became clear. The mixture was again cooled to  $-78\text{ }^{\circ}\text{C}$  and transferred *via* cannula into a similarly cooled solution  $[\text{W}(\equiv\text{CBr})(\text{CO})_2(\text{Tp}^*)]$  (**1**: 0.200 g, 0.318 mmol) in THF (10 mL). The mixture was warmed slowly to room temperature and stirred overnight. After this time, the volatiles were removed *in vacuo* and the residue was extracted with the minimum dichloromethane and subjected to column chromatography (20 x 1 cm silica gel column), eluting first with petrol and gradually increasing the polarity to 3:1 v/v petrol/ $\text{CH}_2\text{Cl}_2$ . The first dark red band collected was  $[\text{W}(\equiv\text{CC}(\text{Si}^i\text{Pr}_3)(\text{CO})_2(\text{Tp}^*))]$  (**6b**). A bright orange band was collected and the volatiles were removed under reduced pressure to give an orange solid of pure **4b** (0.158 g, 0.184 mmol, 58%).

IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ): 1987s, 1897s  $\nu_{\text{CO}}$ .  $^1\text{H}$  NMR (700 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{H}} = 1.10$  (d, 18 H,  $\text{SiCHCH}_3$ ), 2.33 (s, 3 H,  $\text{pzCH}_3$ ), 2.38 (s, 6 H,  $\text{pzCH}_3$ ), 2.41 (s, 3 H,  $\text{pzCH}_3$ ), 2.59 (s, 6 H,  $\text{pzCH}_3$ ), 5.77 (s, 1 H,  $\text{pzH}$ ), 5.92 (s, 2 H,  $\text{pzH}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (176 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{C}} = 11.9$  ( $\text{SiCH}$ ), 12.9, 13.0, 15.6, 17.2 ( $\text{pzCH}_3$ ), 18.9 ( $\text{SiCHCH}_3$ ), 60.5 ( $\text{TeC}\equiv\text{C}$ ), 106.9, 107.1 ( $\text{pzCH}$ ), 121.7 ( $\text{TeC}\equiv\text{C}$ ), 144.7, 145.8, 152.5, 153.0 ( $\text{pzC}^{3,5}\text{CH}_3$ ), 223.8 ( $\text{CO}$ ,  $^1J_{\text{WC}} = 165.4$  Hz), 235.7 ( $\text{W}\equiv\text{C}$ ,  $^1J_{\text{WC}} = 214.7$  Hz).  $^{125}\text{Te}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{Te}} = 764$ . MS (ESI,  $m/z$ ): Found: 860.1974. Calcd for  $\text{C}_{29}\text{H}_{43}^{11}\text{BN}_6\text{O}_2^{28}\text{Si}^{130}\text{Te}^{184}\text{W}$  [ $\text{M}$ ] $^+$ : 860.1976. Anal. Found: C,

40.58; H, 5.05; N, 9.77%. Calcd for  $\text{C}_{29}\text{H}_{43}\text{BN}_6\text{O}_2\text{SiTeW}$ : C, 40.59; H, 5.05; N, 9.79%.

Single crystals suitable for X-ray structure diffraction were grown by slow evaporation of a chloroform/ethanol mixture. *Crystal data* for  $\text{C}_{29}\text{H}_{43}\text{BN}_6\text{O}_2\text{SiTeW}$  ( $M_w = 858.04$  g.mol $^{-1}$ ): triclinic, space group  $P-1$  (no. 2),  $a = 10.6281(5)$   $\text{\AA}$ ,  $b = 11.0432(6)$   $\text{\AA}$ ,  $c = 15.1354(7)$   $\text{\AA}$ ,  $\alpha = 84.687(4)^\circ$ ,  $\beta = 87.521(4)^\circ$ ,  $\gamma = 75.938(4)^\circ$ ,  $V = 1715.38(15)$   $\text{\AA}^3$ ,  $Z = 2$ ,  $T = 150.0(1)$  K,  $\mu(\text{CuK}\alpha) = 13.419$  mm $^{-1}$ ,  $D_{\text{calc}} = 1.661$  Mg.m $^{-3}$ , 10111 reflections measured ( $8.284^\circ \leq 2\theta \leq 133.194^\circ$ ), 6019 unique ( $R_{\text{int}} = 0.0546$ ,  $R_{\text{sigma}} = 0.0898$ ) which were used in all calculations. The final  $R_1$  was 0.0604 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.1600 (all data) for 368 refined parameters with 0 restraints (CCDC 2033027). For molecular geometry see Figure 2.

**Synthesis of  $[\text{W}(\equiv\text{CTeC}\equiv\text{C}^i\text{Pr})(\text{CO})_2(\text{Tp}^*)]$  (**4c**).** To a solution of 3-methyl-1-butyne (40  $\mu\text{L}$ , 0.391 mmol) in THF (5 mL) at  $-78\text{ }^{\circ}\text{C}$  was added  $^n\text{BuLi}$  (0.20 mL, 1.6 M in hexane, 0.32 mmol). The mixture was warmed to room temperature and stirring was continued for 30 min. Powdered tellurium (0.041 g, 0.318 mg.atom) was then added and stirring continued for 1 h, during which time the solution became clear. The mixture was again cooled to  $-78\text{ }^{\circ}\text{C}$  and transferred *via* cannula into a similarly cooled solution of  $[\text{W}(\equiv\text{CBr})(\text{CO})_2(\text{Tp}^*)]$  (**1**: 0.200 g, 0.318 mmol) in THF (10 mL). The mixture was warmed slowly to room temperature and stirred overnight. After this time, the volatiles were removed *in vacuo* and the residue was extracted with the minimum dichloromethane and subjected to column chromatography (20 x 1 cm silica gel column), eluting first with petrol and gradually increasing the polarity to 3:1 v/v petrol/ $\text{CH}_2\text{Cl}_2$ . A bright orange band was collected and the volatiles were removed under reduced pressure to give an orange solid of pure **4c** (0.081 g, 0.109 mmol, 34%).

IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ): 1986s, 1896s  $\nu_{\text{CO}}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{H}} = 1.22$  (d,  $^3J_{\text{HH}} = 6.9$  Hz, 6 H,  $\text{CHCH}_3$ ), 2.31 (s, 3 H,  $\text{pzCH}_3$ ), 2.36 (s, 3 H,  $\text{pzCH}_3$ ), 2.40 (s, 6 H,  $\text{pzCH}_3$ ), 2.58 (s, 6 H,  $\text{pzCH}_3$ ), 2.93 (m,  $^3J_{\text{HH}} = 6.9$  Hz, 1 H,  $\text{CHMe}_2$ ), 5.76 (s, 1 H,  $\text{pzH}$ ), 5.90 (s, 2 H,  $\text{pzH}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{C}} = 13.0$ , 15.6, 17.2 ( $\text{pzCH}_3$ ), 23.1 ( $\text{CHMe}_2$ ), 23.5 ( $\text{CHCH}_3$ ), 77.6 ( $\text{TeC}\equiv\text{C}$ ), 106.9, 107.1 ( $\text{pzCH}$ ), 122.2 ( $\text{TeC}\equiv\text{C}$ ), 144.8, 145.7, 152.5, 153.1 ( $\text{pzC}^{3,5}\text{CH}_3$ ), 223.8 ( $\text{CO}$ ,  $^1J_{\text{WC}} = 167.7$  Hz), 237.4 ( $\text{W}\equiv\text{C}$ ,  $^1J_{\text{WC}} = 214.1$  Hz).  $^{125}\text{Te}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_{\text{Te}} = 747$ . MS (ESI,  $m/z$ ): Found: 746.1080. Calcd for  $\text{C}_{23}\text{H}_{29}^{11}\text{BN}_6\text{O}_2^{130}\text{Te}^{184}\text{W}$  [ $\text{M}$ ] $^+$ : 746.1114. MS (ESI,  $m/z$ ): Found: 769.0901. Calcd for  $\text{C}_{23}\text{H}_{29}^{11}\text{BN}_6\text{O}_2^{130}\text{Te}^{184}\text{WNa}$  [ $\text{M}+\text{Na}$ ] $^+$ : 769.0929. Anal. Found: C, 37.25; H, 3.99; N, 11.12%. Calcd for  $\text{C}_{23}\text{H}_{29}\text{BN}_6\text{O}_2\text{TeW}$ : C, 37.14; H, 3.93; N, 11.30%.

**Synthesis of  $[\text{W}(\equiv\text{CTeC}\equiv\text{C}^i\text{Bu})(\text{CO})_2(\text{Tp}^*)]$  (**4d**).** To a solution of 1-hexyne (37  $\mu\text{L}$ , 0.318 mmol) in THF (5 mL) at  $-78\text{ }^{\circ}\text{C}$  was added  $^n\text{BuLi}$  (0.20 mL, 1.6 M in hexane, 0.318 mmol). The mixture was brought to room temperature and stirred for 30 min. Powdered tellurium (0.041 g, 0.318 mg.atom) was then added and stirring was continued for 1 h, during which time the solution became clear. The mixture was again cooled to  $-78\text{ }^{\circ}\text{C}$  and transferred *via* cannula into a similarly cooled solution of  $[\text{W}(\equiv\text{CBr})(\text{CO})_2(\text{Tp}^*)]$  (**1**: 0.200 g, 0.318 mmol) in THF (10 mL). The mixture was warmed slowly to room temperature and stirred overnight, during which time the mixture turned orange-

brown. The volatiles were then removed *in vacuo* the residue was extracted with the minimum dichloromethane and subjected to column chromatography (20 x 1 cm silica gel column), eluting first with petrol and gradually increasing the polarity to 7:1 v/v petrol/CH<sub>2</sub>Cl<sub>2</sub>. A bright orange band was collected and the volatiles were removed under reduced pressure to give an orange solid of pure **4d** (0.129 g, 0.170 mmol, 54%).

IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1986s, 1895s  $\nu_{\text{CO}}$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{H}}$  = 0.92 (t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>), 1.44 (m, 2 H, CH<sub>2</sub>CH<sub>3</sub>), 1.53 (m, 2 H,  $\equiv\text{CCH}_2\text{CH}_2$ ), 2.32 (s, 3 H, pzCH<sub>3</sub>), 2.37 (s, 6 H, pzCH<sub>3</sub>), 2.40 (s, 3 H, pzCH<sub>3</sub>), 2.51 (m, 2 H,  $\equiv\text{CCH}_2$ ), 2.59 (s, 6 H, pzCH<sub>3</sub>), 5.76 (s, 1 H, pzCH), 5.91 (s, 2 H, pzCH). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{C}}$  = 12.9, 13.0 (pzCH<sub>3</sub>), 13.9 (CH<sub>2</sub>CH<sub>3</sub>), 15.6, 17.1 (pzCH<sub>3</sub>), 21.0 ( $\equiv\text{CCH}_2\text{CH}_2$ ), 22.3 (CH<sub>2</sub>CH<sub>3</sub>), 31.1 ( $\equiv\text{CCH}_2\text{CH}_2$ ), 77.6 (TeC $\equiv$ C), 106.9, 107.1 (pzCH), 116.9 (TeC $\equiv$ C), 144.8, 145.7, 152.5, 153.0 (pzC<sup>3,5</sup>CH<sub>3</sub>), 223.8 (CO, <sup>1</sup>J<sub>WC</sub> = 167.7 Hz), 238.4 (W $\equiv$ C, <sup>1</sup>J<sub>WC</sub> = 214.1 Hz). <sup>125</sup>Te{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{Te}}$  = 747. MS (ESI, *m/z*): Found: 759.1216. Calcd for C<sub>24</sub>H<sub>32</sub><sup>11</sup>BN<sub>6</sub>O<sub>2</sub><sup>128</sup>Te<sup>184</sup>W [M+H]<sup>+</sup>: 759.1245. Anal. Found: C, 37.05; H, 4.03; N, 11.21%. Calcd for C<sub>24</sub>H<sub>31</sub>BN<sub>6</sub>O<sub>2</sub>TeW: C, 38.04; H, 4.12; N, 11.09%.

**Synthesis of [W( $\equiv$ CTeC $\equiv$ C<sup>t</sup>Bu)(CO)<sub>2</sub>(Tp\*)] (4e) and [W( $\equiv$ CC $\equiv$ C<sup>t</sup>Bu)(CO)<sub>2</sub>(Tp\*)] (4g).** To a solution of 3,3-dimethyl-1-butyne (39  $\mu$ L, 0.318 mmol) in THF (5 mL) at -78 °C was added <sup>n</sup>BuLi (0.20 mL, 1.6 M in hexane, 0.32 mmol). The mixture was warmed to room temperature and stirred for 30 min. Powdered tellurium (0.041 g, 0.318 mg.atom) was then added and stirring continued for 1 h, during which time the solution became clear. The mixture was again cooled to -78 °C and transferred *via* cannula into a similarly cooled solution of [W( $\equiv$ CBr)(CO)<sub>2</sub>(Tp\*)] (**1**: 0.200 g, 0.318 mmol) in THF (10 mL). The mixture was warmed slowly to room temperature and stirred overnight. After this time, the volatiles were removed *in vacuo* and the residue was extracted with the minimum dichloromethane and subjected to column chromatography (20 x 1 cm silica gel column), eluting first with petrol and gradually increasing the polarity to 3:1 v/v petrol/CH<sub>2</sub>Cl<sub>2</sub>. The first dark red band collected was [W( $\equiv$ CC $\equiv$ C<sup>t</sup>Bu)(CO)<sub>2</sub>(Tp\*)].<sup>17</sup> A second bright orange band was collected and the volatiles were removed under reduced pressure to give an orange solid of pure **4e** (0.127 g, 0.168 mmol, 53%).

IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1986s, 1895s  $\nu_{\text{CO}}$ . <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{H}}$  = 1.29 (s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>), 2.33 (s, 3 H, pzCH<sub>3</sub>), 2.38 (s, 6 H, pzCH<sub>3</sub>), 2.42 (s, 3 H, pzCH<sub>3</sub>), 2.60 (s, 6 H, pzCH<sub>3</sub>), 5.77 (s, 1 H, pzCH), 5.92 (s, 2 H, pzCH). <sup>13</sup>C{<sup>1</sup>H} NMR (176 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{C}}$  = 13.0, 15.6, 17.3 (pzCH<sub>3</sub>), 31.5 (C(CH<sub>3</sub>)<sub>3</sub>), 41.7 (C(CH<sub>3</sub>)<sub>3</sub>), 68.3 (TeC $\equiv$ C), 106.9, 107.1 (pzCH), 124.8 (TeC $\equiv$ C), 144.8, 145.7, 152.4, 153.1 (pzC<sup>3,5</sup>CH<sub>3</sub>), 223.9 (CO, <sup>1</sup>J<sub>WC</sub> = 167.2 Hz), 238.9 (W $\equiv$ C, <sup>1</sup>J<sub>WC</sub> = 211.2 Hz). <sup>125</sup>Te{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{Te}}$  = 745. MS (ESI, *m/z*): Found: 759.1218. Calcd for C<sub>24</sub>H<sub>32</sub><sup>11</sup>BN<sub>6</sub>O<sub>2</sub><sup>128</sup>Te<sup>184</sup>W [M+H]<sup>+</sup>: 759.1239. Anal. Found: C, 37.93; H, 4.12; N, 10.93%. Calcd for C<sub>24</sub>H<sub>31</sub>BN<sub>6</sub>O<sub>2</sub>TeW: C, 38.04; H, 4.12; N, 11.09%.

**Synthesis of [W( $\equiv$ CTeC $\equiv$ CPh)(CO)<sub>2</sub>(Tp\*)] (4f).** To a solution of ethynylbenzene (35  $\mu$ L, 0.32 mmol) in THF (5 mL) at -78 °C was added <sup>n</sup>BuLi (0.20 mL, 1.6 M in hexane, 0.32 mmol). The

mixture was warmed to room temperature and stirred for 30 min. Powdered tellurium (0.041 g, 0.32 mg.atom) was then added and stirring continued for 1 h, during which time the solution became clear. The mixture was again cooled to -78 °C and transferred *via* cannula into a similarly cooled solution of [W( $\equiv$ CBr)(CO)<sub>2</sub>(Tp\*)] (**1**: 0.200 g, 0.318 mmol) in THF (10 mL). The mixture was warmed slowly to RT and stirred overnight. After this time, the volatiles were removed *in vacuo* and the residue was extracted with the minimum dichloromethane and subjected to column chromatography (20 x 1 cm silica gel column), eluting first with petrol and gradually increasing the polarity to 3:1 v/v petrol/CH<sub>2</sub>Cl<sub>2</sub>. The first dark red band collected is [W( $\equiv$ CC $\equiv$ CPh)(CO)<sub>2</sub>(Tp\*)]. A second bright orange band was collected and the volatiles were removed under reduced pressure to give an orange solid of pure **4f** (0.163 g, 0.210 mmol, 66%).

IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1989s, 1896s  $\nu_{\text{CO}}$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{H}}$  = 2.32 (s, 3 H, pzCH<sub>3</sub>), 2.36 (s, 6 H, pzCH<sub>3</sub>), 2.40 (s, 3 H, pzCH<sub>3</sub>), 2.61 (s, 6 H, pzCH<sub>3</sub>), 5.76 (s, 1 H, pzCH), 5.91 (s, 2 H, pzCH), 7.27 (m, 3 H, overlapping H<sup>3,5</sup>(C<sub>6</sub>H<sub>5</sub>)), 7.42 (m, 2 H, H<sup>2,6</sup>(C<sub>6</sub>H<sub>5</sub>)). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{C}}$  = 13.0, 15.6, 17.2 (pzCH<sub>3</sub>), 43.8 (TeC $\equiv$ C), 107.0, 107.2 (pzCH), 115.4 [C<sup>1</sup>(C<sub>6</sub>H<sub>5</sub>)], 123.8 (TeC $\equiv$ C), 128.5 [C<sup>3,5</sup>(C<sub>6</sub>H<sub>5</sub>)], 128.7 [C<sup>4</sup>(C<sub>6</sub>H<sub>5</sub>)], 132.1 [C<sup>2,6</sup>(C<sub>6</sub>H<sub>5</sub>)], 144.8, 145.8, 152.5, 153.1 (pzC<sup>3,5</sup>CH<sub>3</sub>), 223.8 (CO, <sup>1</sup>J<sub>WC</sub> = 169.0 Hz), 235.5 (W $\equiv$ C, <sup>1</sup>J<sub>WC</sub> = 213.0 Hz). <sup>125</sup>Te{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{Te}}$  = 759. MS (ESI, *m/z*): Found: 779.0926. Calcd for C<sub>26</sub>H<sub>28</sub><sup>11</sup>BN<sub>6</sub>O<sub>2</sub><sup>128</sup>Te<sup>184</sup>W [M+H]<sup>+</sup>: 779.0923. Anal. Found: C, 40.05; H, 3.61; N, 10.86%. Calcd for C<sub>26</sub>H<sub>27</sub>BN<sub>6</sub>O<sub>2</sub>TeW: C, 40.15; H, 3.50; N, 10.81%.

Single crystals suitable for X-ray structure diffraction were grown by slow evaporation of a dichloromethane/ethanol mixture. *Crystal data* for C<sub>26</sub>H<sub>27</sub>BN<sub>6</sub>O<sub>2</sub>TeW (*M*<sub>w</sub> = 777.79 g.mol<sup>-1</sup>): monoclinic, space group *P*2<sub>1</sub>/*n* (no. 14), *a* = 20.5319(5) Å, *b* = 14.2779(2) Å, *c* = 21.6073(4) Å,  $\beta$  = 117.804(3)°, *V* = 5602.9(2) Å<sup>3</sup>, *Z* = 8, *T* = 150.0(1) K,  $\mu$ (CuK $\alpha$ ) = 15.967 mm<sup>-1</sup>, *D*<sub>calc</sub> = 1.780 g.cm<sup>-3</sup>, 56411 reflections measured (7.728° ≤ 2 $\theta$  ≤ 133.202°), 9890 unique (*R*<sub>int</sub> = 0.0386, *R*<sub>sigma</sub> = 0.0207) which were used in all calculations. The final *R*<sub>1</sub> was 0.0524 (*I* > 2 $\sigma$ (*I*)) and *wR*<sub>2</sub> was 0.1380 (all data) for 696 refined parameters without restraints (CCDC 2033039). For molecular geometry see Figure 2.

**Synthesis of [W( $\equiv$ CTeC $\equiv$ CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>2</sub>(Tp\*)] (4g) and [W( $\equiv$ CC $\equiv$ CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>2</sub>(Tp\*)] (4g)** To a solution of 4-ethynyltoluene (41  $\mu$ L, 0.32 mmol) in THF (5 mL) at -78 °C was added <sup>n</sup>BuLi (0.20 mL, 1.6 M in hexane, 0.32 mmol). The mixture was warmed to room temperature and stirred for 30 min. Powdered tellurium (0.041 g, 0.32 mg.atom) was then added and stirring continued for 1 h, during which time the solution became clear. The mixture was again cooled to -78 °C and transferred *via* cannula into a similarly cooled solution of [W( $\equiv$ CBr)(CO)<sub>2</sub>(Tp\*)] (**1**: 0.200 g, 0.318 mmol) in THF (10 mL). The mixture was warmed slowly to RT and stirred overnight. After this time, the volatiles were removed *in vacuo* and the residue was extracted with the minimum dichloromethane and subjected to column chromatography (20 x 1 cm silica gel column), eluting first with petrol and gradually increasing the polarity to 3:1 v/v petrol/CH<sub>2</sub>Cl<sub>2</sub>. The first dark red band collected was [W( $\equiv$ CC $\equiv$ CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>2</sub>(Tp\*)]. A second bright

orange band was collected and the volatiles were removed under reduced pressure to give an orange solid of pure **4g** (0.145 g, 0.183 mmol, 58%). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1987s, 1897s  $\nu_{CO}$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_H$  = 2.34 (s, 3 H, pzCH<sub>3</sub>), 2.37 (s x 2 overlapping, 9 H, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub> and pzCH<sub>3</sub>), 2.42 (s, 3 H, pzCH<sub>3</sub>), 2.63 (s, 6 H, pzCH<sub>3</sub>), 5.78 (s, 1 H, pzCH), 5.92 (s, 2 H, pzCH), 7.14 (d, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, 2 H, H<sup>3,5</sup>(C<sub>6</sub>H<sub>5</sub>)), 7.36 (d, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 2 H, H<sup>2,6</sup>(C<sub>6</sub>H<sub>5</sub>)). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_C$  = 12.9, 13.0, 15.6, 17.1 (pzCH<sub>3</sub>), 21.8 (C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 42.6 (TeC≡C), 106.9, 107.2 [C<sup>4</sup>(pz)], 115.5 [C<sup>1</sup>(C<sub>6</sub>H<sub>4</sub>)], 120.9 (TeC≡C), 129.4 [C<sup>3,5</sup>(C<sub>6</sub>H<sub>4</sub>)], 132.2 [C<sup>2,6</sup>(C<sub>6</sub>H<sub>4</sub>)], 138.9 [C<sup>4</sup>(C<sub>6</sub>H<sub>4</sub>)], 144.8, 145.8, 152.5, 153.1 [C<sup>3,5</sup>(pz)], 223.8 (CO, <sup>1</sup>J<sub>WC</sub> = 166.7 Hz), 236.2 (W≡C, <sup>1</sup>J<sub>WC</sub> = 215.1 Hz). <sup>125</sup>Te{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{Te}$  = 758. MS (ESI, *m/z*): Found: 793.1080. Calcd for C<sub>27</sub>H<sub>30</sub><sup>11</sup>BN<sub>6</sub>O<sub>2</sub><sup>128</sup>Te<sup>184</sup>W [M+H]<sup>+</sup>: 793.1089. Anal. Found: C, 40.86; H, 3.63; N, 10.47%. Calcd for C<sub>27</sub>H<sub>29</sub>BN<sub>6</sub>O<sub>2</sub>TeW: C, 40.96; H, 3.69; N, 10.61%.

The first dark red band was also collected and the volatiles were removed under reduced pressure to give a dark-red solid of the pure tolylpropargylidyne **6g** (0.078 g, 0.117 mmol, 37%). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1981s, 1892s  $\nu_{CO}$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_H$  = 2.32 (s x 2 overlapping, 6 H, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub> and pzCH<sub>3</sub>), 2.37 (s, 9 H, pzCH<sub>3</sub>), 2.62 (s, 6 H, pzCH<sub>3</sub>), 5.75 (s, 1 H, pzCH), 5.91 (s, 2 H, pzCH), 7.09 (d, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, 2 H, H<sup>3,5</sup>(C<sub>6</sub>H<sub>5</sub>)), 7.37 (d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2 H, H<sup>2,6</sup>(C<sub>6</sub>H<sub>5</sub>)). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_C$  = 13.0, 15.6, 16.9 (pzCH<sub>3</sub>), 22.1 (C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 71.1 (C≡CAr), 106.9, 107.0 (overlapping pzCH and C≡CAr), 119.3 [C<sup>1</sup>(C<sub>6</sub>H<sub>4</sub>)], 129.6 [C<sup>3,5</sup>(C<sub>6</sub>H<sub>4</sub>)], 132.8 [C<sup>2,6</sup>(C<sub>6</sub>H<sub>4</sub>)], 139.2 [C<sup>4</sup>(C<sub>6</sub>H<sub>4</sub>)], 44.7, 145.5, 152.6, 152.7 (pzC<sup>3,5</sup>CH<sub>3</sub>), 226.6 (CO, <sup>1</sup>J<sub>WC</sub> = 163.6 Hz), 247.2 (W≡C, <sup>1</sup>J<sub>WC</sub> = 200.0 Hz). MS (ESI, *m/z*): Found: 665.2023. Calcd for C<sub>27</sub>H<sub>30</sub><sup>11</sup>BN<sub>6</sub>O<sub>2</sub><sup>184</sup>W [M+H]<sup>+</sup>: 665.2031. Anal. Found: C, 48.59; H, 4.26; N, 12.59%. Calcd for C<sub>27</sub>H<sub>29</sub>BN<sub>6</sub>O<sub>2</sub>W: C, 48.82; H, 4.40; N, 12.65%.

**Synthesis of [W(≡CTeC≡C-(N-methylimidazol-4))(CO)<sub>2</sub>(Tp\*)] (4h).** To a solution of 5-ethynyl-1-methyl-1H-imidazole (33  $\mu$ L, 0.32 mmol) in THF (5 mL) at -78 °C was added <sup>n</sup>BuLi (0.20 mL, 1.6 M in hexane, 0.32 mmol). The mixture was brought to room temperature and stirred for 30 min. Powdered tellurium (0.041 g, 0.32 mg.atom) was then added and stirring was continued for 1 h, during which time the solution became clear. The mixture was again cooled to -78 °C and transferred *via* cannula into a similarly cooled solution of [W(≡CBr)(CO)<sub>2</sub>(Tp\*)] (**1**: 0.200 g, 0.318 mmol) in THF (10 mL). The mixture was warmed slowly to room temperature and stirred overnight, during which time the mixture turned orange-brown. The volatiles were then removed *in vacuo* the residue was extracted with the minimum dichloromethane and subjected to column chromatography (20 x 1 cm silica gel column), eluting first with 2:1 v/v petrol/CH<sub>2</sub>Cl<sub>2</sub> and gradually increasing the polarity to 2:1 v/v CH<sub>2</sub>Cl<sub>2</sub>/acetonitrile. An orange-brown band was collected and the volatiles were removed under reduced pressure to give an orange solid of pure **4h** (0.073 g, 0.093 mmol, 29%). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1987s, 1897s  $\nu_{CO}$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_H$  = 2.32 (s, 3 H, pzCH<sub>3</sub>), 2.37 (s, 6 H, pzCH<sub>3</sub>), 2.39 (s, 3 H, pzCH<sub>3</sub>), 2.58 (s, 6 H, pzCH<sub>3</sub>), 3.67 (s, 3H, NMe), 5.77 (s, 1 H, pzCH), 5.91 (s, 2 H, pzCH), 7.29 (s, 1H, C-CH-N), 7.45 (s, 1H, N-CH-N). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_C$  = 12.9, 13.0, 15.6, 17.0 (pzCH<sub>3</sub>), 32.3 (N-Me), 52.5 (TeC≡C),

102.8 (TeC≡C), 106.9, 107.2 (pzCH), 116.9 (C-CH-N), 135.9 (C-CH-N), 138.6 (N-CH-N), 144.9, 145.8, 152.3, 153.0 (pzC<sup>3,5</sup>CH<sub>3</sub>), 223.7 (CO, <sup>1</sup>J<sub>WC</sub> = 166.1 Hz), 234.1 (W≡C, <sup>1</sup>J<sub>WC</sub> = 214.4 Hz). <sup>125</sup>Te{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{Te}$  = 761. MS (ESI, *m/z*): Found: 783.0972. Calcd for C<sub>24</sub>H<sub>28</sub><sup>11</sup>BN<sub>8</sub>O<sub>2</sub><sup>128</sup>Te<sup>184</sup>W [M+H]<sup>+</sup>: 783.0987. Anal. Found: C, 33.41; H, 3.57; N, 12.06%. Calcd for C<sub>24</sub>H<sub>27</sub>BN<sub>8</sub>O<sub>2</sub>TeW.CHCl<sub>3</sub>: C, 33.32; H, 3.13; N, 12.43%. Single crystals suitable for X-ray structure diffraction were grown by slow evaporation of a dichloromethane/ethanol mixture. *Crystal data* for C<sub>24</sub>H<sub>27</sub>BN<sub>8</sub>O<sub>2</sub>TeW (*M<sub>w</sub>* = 781.79 g.mol<sup>-1</sup>): monoclinic, space group *P*2<sub>1</sub> (no. 4), *a* = 7.9095(2) Å, *b* = 18.2594(4) Å, *c* = 9.7522(3) Å,  $\beta$ [W(≡CBr)(CO)<sub>2</sub>(Tp\*)] (**1**): = 99.742(2)°, *V* = 1388.13(6) Å<sup>3</sup>, *Z* = 2, *T* = 150.0(1) K,  $\mu$ (Cu K $\alpha$ ) = 16.138 mm<sup>-1</sup>, *D<sub>calc</sub>* = 1.870 Mg m<sup>-3</sup>, 14026 reflections measured (9.2° ≤ 2 $\theta$  ≤ 136.492°), 3673 unique (*R<sub>int</sub>* = 0.0524, *R<sub>sigma</sub>* = 0.0513) which were used in all calculations. The final *R<sub>1</sub>* was 0.0521 (*I* > 2 $\sigma$ (*I*)) and *wR<sub>2</sub>* was 0.1359 (all data) for 323 refined parameters with 1 restraint (CCDC 2033028, for molecular geometry see Figure 2c).

**Synthesis of [W(≡CTeC≡CH)(CO)<sub>2</sub>(Tp\*)] (A.11).** To a stirred solution of **A.3** (1.000 g, 1.29 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.230 g, 1.66 mmol) in THF (15 mL) and MeOH (5 mL) was added deionised H<sub>2</sub>O (5 mL). Stirring was continued for 30 min, after which time the mixture was extracted with dichloromethane. The organic phase was collected and volatiles removed under reduced pressure. The residue was subjected to column chromatography (20 x 4 cm silica gel column), eluting with 3:1 v/v petrol/CH<sub>2</sub>Cl<sub>2</sub>. A bright orange band was collected and removal of the solvents under reduced pressure gave an orange-brown solid of pure **A.11** (0.819 g, 1.17 mmol, 91%). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1988s, 1899s  $\nu_{CO}$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_H$  = 2.31 (s, 3 H, pzCH<sub>3</sub>), 2.36 (s, 6 H, pzCH<sub>3</sub>), 2.40 (s, 3 H, pzCH<sub>3</sub>), 2.57 (s, 6 H, pzCH<sub>3</sub>), 3.17 (s, 1 H, C≡CH), 5.76 (s, 1 H, pzCH), 5.91 (s, 2 H, pzCH). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_C$  = 12.9, 13.0, 15.6, 17.1 (pzCH<sub>3</sub>), 68.3 (TeC≡C), 103.5 (TeC≡C), 107.0, 107.2 (pzCH), 144.9, 145.8, 152.5, 153.1 (pzC<sup>3,5</sup>CH<sub>3</sub>), 223.6 (CO), 232.6 (W≡C). <sup>125</sup>Te{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{Te}$  = 762. MS (ESI, *m/z*): Found: 702.05263. Calcd for C<sub>20</sub>H<sub>23</sub><sup>11</sup>BN<sub>6</sub>O<sub>2</sub><sup>128</sup>Te<sup>184</sup>W [M]<sup>+</sup>: 702.05332. Anal. Found: C, 34.37; H, 3.40; N, 11.75%. Calcd for C<sub>20</sub>H<sub>23</sub>BN<sub>6</sub>O<sub>2</sub>TeW: C, 34.23; H, 3.30; N, 11.98%.

**Synthesis and decomposition (to 8) of [WAuCl( $\mu$ -CTeC≡CSiMe<sub>3</sub>)(CO)<sub>2</sub>(Tp\*)] (6b).** To a flask containing [W(≡CTeC≡CSiMe<sub>3</sub>)(CO)<sub>2</sub>(Tp\*)] (**4a**: 0.050 g, 0.065 mmol) and [AuCl(SMe<sub>2</sub>)] (0.021 g, 0.065 mmol) was added CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and the resulting mixture was stirred for 30 min. The mixture was filtered through diatomaceous earth and concentrated under reduced pressure. Upon adding hexane, a precipitate formed that was collected by filtration, washed with pentane and dried to give an orange solid of pure **6b** (0.046 g, 0.046 mmol, 71%).

IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2015s, 1935s  $\nu_{CO}$ . <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_H$  = 0.23 (s, 9 H, SiCH<sub>3</sub>), 2.34 (s, 3 H, pzCH<sub>3</sub>), 2.38 (s, 6 H, pzCH<sub>3</sub>), 2.50 (s, 9 H, pzCH<sub>3</sub>), 5.93 (s, 1 H, pzCH), 5.96 (s, 2 H, pzCH). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_C$  = 0.2 (SiCH<sub>3</sub>), 13.0, 13.4, 16.3, 17.7 (pzCH<sub>3</sub>), 66.7 (TeC≡C), 108.1, 108.6 (pzCH), 128.3 (TeC≡C), 145.9, 146.7, 152.9, 153.8 (pzC<sup>3,5</sup>CH<sub>3</sub>), 215.7 (CO,

$^1J_{WC} = 158.0$  Hz), 228.3 (W=C,  $^1J_{WC} = 95.7$  Hz). Multiple new carbon resonances appear after overnight  $^{13}C$  NMR, complicating absolute assignments. Tellurium resonance was not able to be observed due to rapid decomposition of the complex. MS (ESI,  $m/z$ ): Found: 1012.0866. Calcd for  $C_{25}H_{34}Au^{11}BN_7O_2^{28}Si^{128}Te^{184}W$  [M-Cl+CH<sub>3</sub>CN]<sup>+</sup>: 1012.0919. Elemental analyses could not be obtained due to its tendency to decompose rapidly. Single crystals suitable for X-ray structure diffraction were grown by slow evaporation of a dichloromethane/hexane mixture and proved to be a decomposition product (**A.14a**). *Crystal data* for  $C_{20}H_{28}AuB_2Cl_4N_6O_2STeW.CH_2Cl_2$  (**A.14a**):  $M_w = 1162.49$  g.mol<sup>-1</sup>; triclinic, space group P-1 (no. 2),  $a = 11.1523(4)$  Å,  $b = 11.1610(5)$  Å,  $c = 14.3505(6)$  Å,  $\alpha = 89.093(4)^\circ$ ,  $\beta = 89.186(3)^\circ$ ,  $\gamma = 77.275(3)^\circ$ ,  $V = 1742.02(13)$  Å<sup>3</sup>,  $Z = 2$ ,  $T = 150.01(10)$  K,  $\mu(Cu K\alpha) = 25.339$  mm<sup>-1</sup>,  $D_{calc} = 2.216$  g.cm<sup>-3</sup>, 9740 reflections measured ( $8.122^\circ \leq 2\theta \leq 142.078^\circ$ ), 6466 unique ( $R_{int} = 0.0452$ ,  $R_{\sigma} = 0.0833$ ) which were used in all calculations. The final  $R_1$  was 0.0632 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.1831 (all data) for 339 refined parameters with 0 restraints (CCDC 2033082).

**Synthesis of [W<sub>2</sub>Cu<sub>4</sub>Cl(μ-CTeC≡CSi<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub>(CO)<sub>4</sub>(Tp\*)<sub>2</sub>] (**6a<sub>2</sub>** = **7**).** To a flask containing [W(≡CTeC≡CSi<sup>i</sup>Pr<sub>3</sub>)(CO)<sub>2</sub>(Tp\*)] (**4a**; 0.018 g, 0.021 mmol) and excess [CuCl(SMe<sub>2</sub>)] (0.008 g, 0.050 mmol) was added CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and the resulting mixture was stirred for 30 min. The mixture was filtered through diatomaceous earth and the filtrate was dried under reduced pressure to give an orange solid of pure **6a<sub>2</sub>** (0.019 g, 0.018 mmol, 86%). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2001s, 1918s  $\nu_{CO}$ .  $^1H$  NMR (600 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_H = 1.09$  (2 x overlapping s, 42 H, Si(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), 2.32 (s, 6 H, pzCH<sub>3</sub>), 2.36 (s, 18 H, pzCH<sub>3</sub>), 2.46 (s, 12 H, pzCH<sub>3</sub>), 5.85 (s, 2 H, pzH), 5.92 (s, 4 H, pzH).  $^{13}C\{^1H\}$  NMR (151 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_C = 12.0$  (SiCH), 13.0, 13.3, 16.0, 17.9 (pzCH<sub>3</sub>), 19.1 (SiCHCH<sub>3</sub>), 95.5 (TeC≡C), 107.5, 108.0 (pzCH), 119.2 – 120.1 (bm, TeC≡C), 144.9, 146.2, 152.3, 153.4 (pzC<sup>3-5</sup>CH<sub>3</sub>), 218.3 (CO,  $^1J_{WC} = 158.6$  Hz), 229.9 – 230.6 (bm, W≡C). Tellurium resonance could not be identified. MS (ESI,  $m/z$ ): Found: 1021.0117. Calcd for  $C_{29}H_{43}^{11}B^{35}Cl^{63}Cu_2N_6O_2^{28}Si^{130}Te^{184}W$  [M]<sup>+</sup>: 1021.0136. Anal. Found: C, 33.06; H, 4.40; N, 7.90%. Calcd for  $C_{29}H_{43}B_2Cl_2Cu_2N_6O_2SiTeW$ : C, 32.98; H, 4.10; N, 7.96%. Single crystals suitable for X-ray structure diffraction were grown by slow evaporation of a dichloromethane/hexane mixture. *Crystal data* for  $C_{58}H_{86}B_2Cl_4Cu_4N_{12}O_4Si_2Te_2W_2.C_6H_{14}$  ( $M_w = 2198.21$  g.mol<sup>-1</sup>): monoclinic, space group P2<sub>1</sub>/n (no. 14),  $a = 10.9539(2)$  Å,  $b = 18.7716(4)$  Å,  $c = 20.4333(4)$  Å,  $\beta = 102.630(2)^\circ$ ,  $V = 4099.87(14)$  Å<sup>3</sup>,  $Z = 2$ ,  $T = 150.01(10)$  K,  $\mu(CuK\alpha) = 13.541$  mm<sup>-1</sup>,  $D_{calc} = 1.781$  g.cm<sup>-3</sup>, 13081 reflections measured ( $8.488^\circ \leq 2\theta \leq 133.202^\circ$ ), 7171 unique ( $R_{int} = 0.0349$ ,  $R_{\sigma} = 0.0586$ ) which were used in all calculations. The final  $R_1$  was 0.0372 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.0954 (all data) for 450 refined parameters with 1 restraints (CCDC 2033029).

## Notes and references

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## Chemical Communications

## ELECTRONIC SUPPORTING INFORMATION

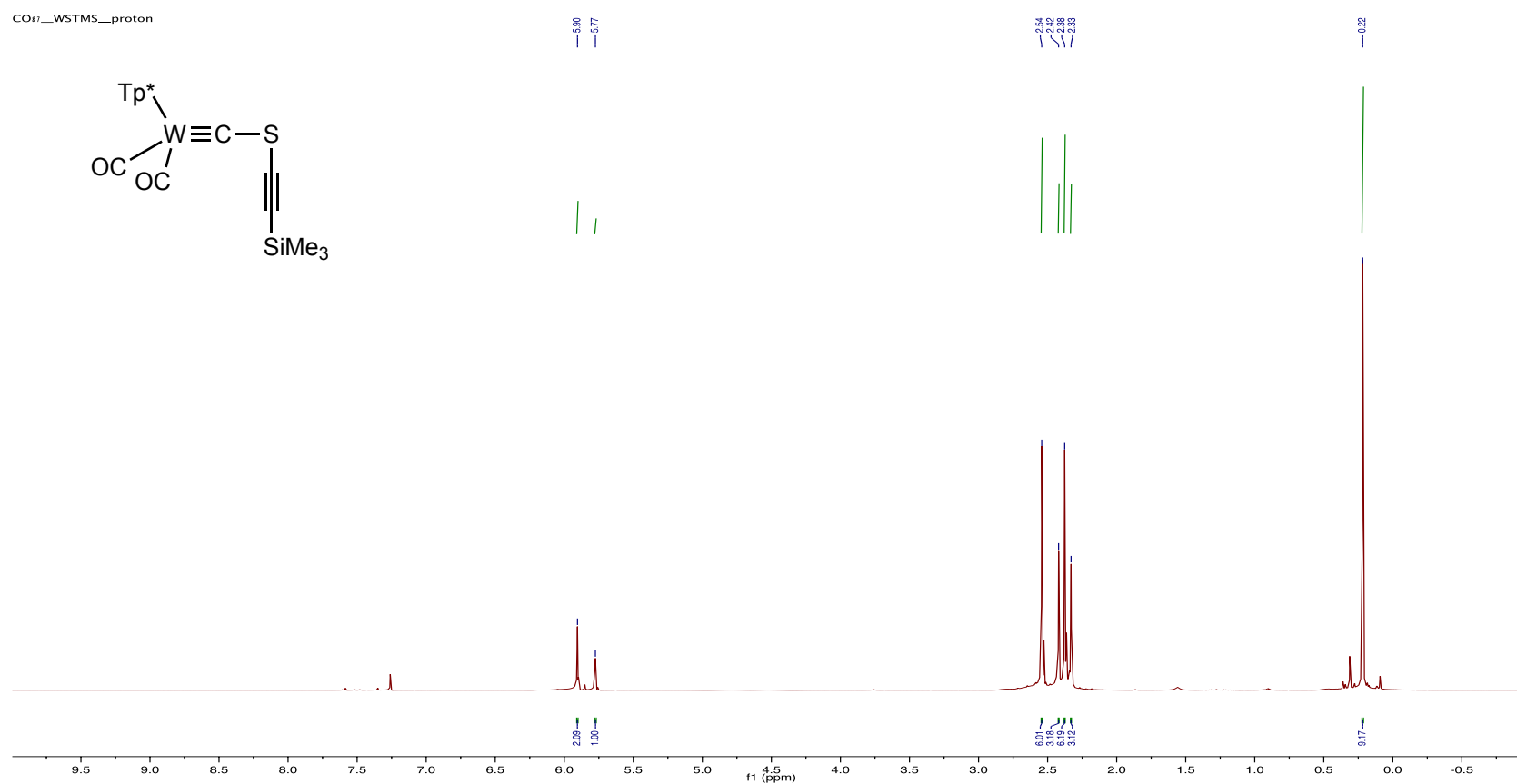


Figure S2.  $^1\text{H}$  NMR spectrum (600 MHz,  $\text{CDCl}_3$ , 25°C,  $\delta$ ) of compound **2a**.



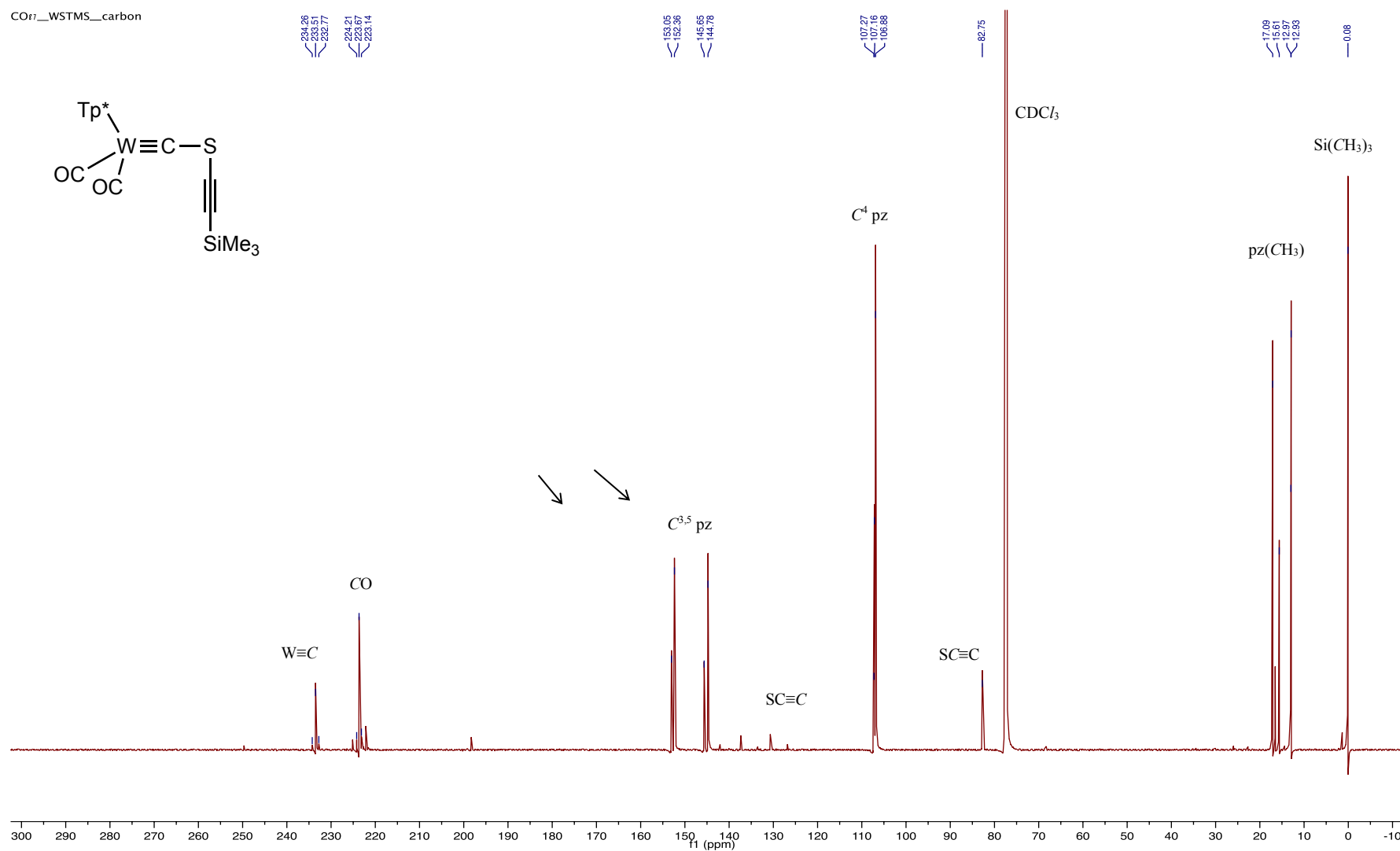
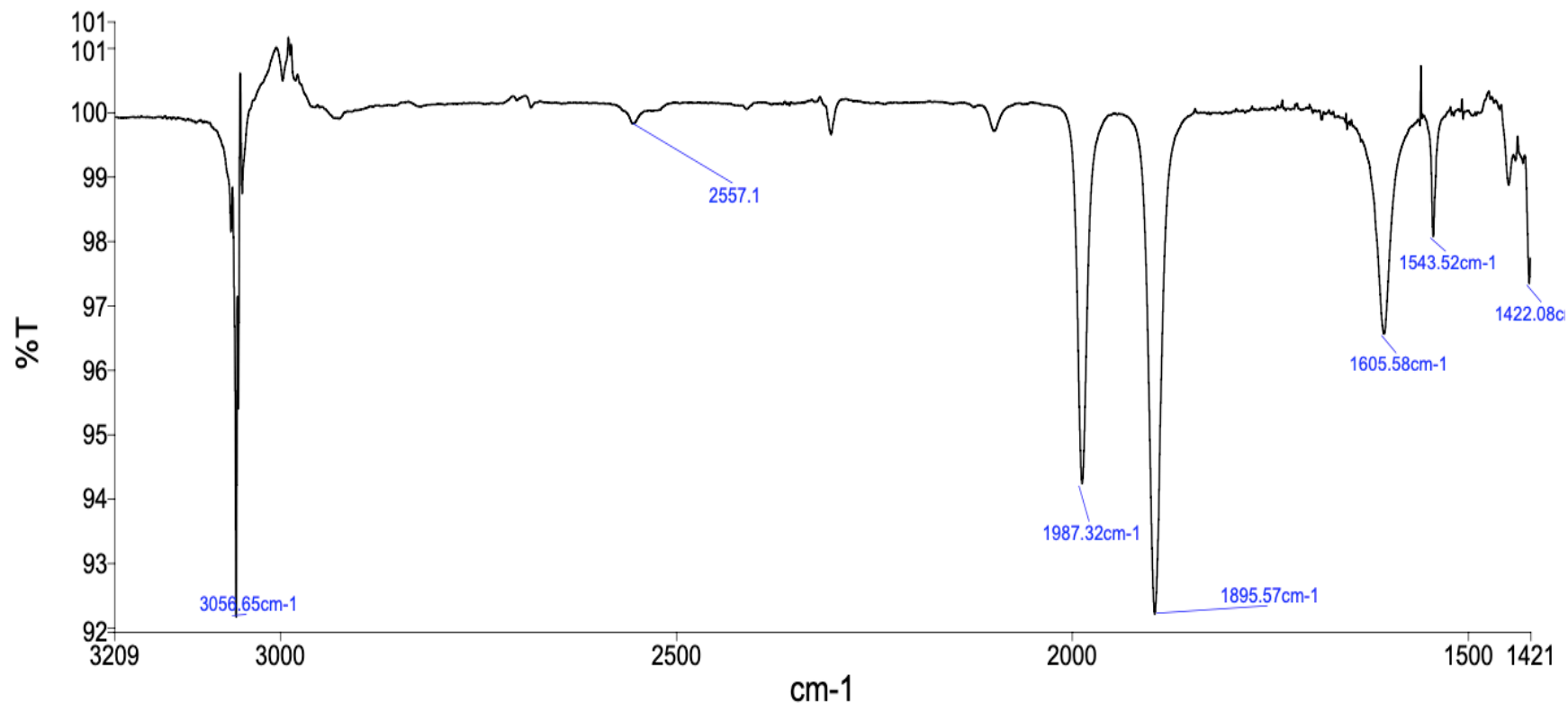


Figure S3.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (151 MHz,  $\text{CDCl}_3$ , 25°C,  $\delta$ ) of compound **2a**.



PerkinElmer Spectrum Version 10.4.3  
Wednesday, 25 November 2020 3:48 PMAnalyst Administrator  
Date Wednesday, 25 November 2020 3:48 PM

Sample Name	Description	Quality Checks
CO_WSulfur_TMS	Sample 068 By Administrator Date Friday, January 25 2019	The Quality Checks give rise to multiple warnings for the sample.

Figure S4. Infrared spectrum ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ) of Compound 2a

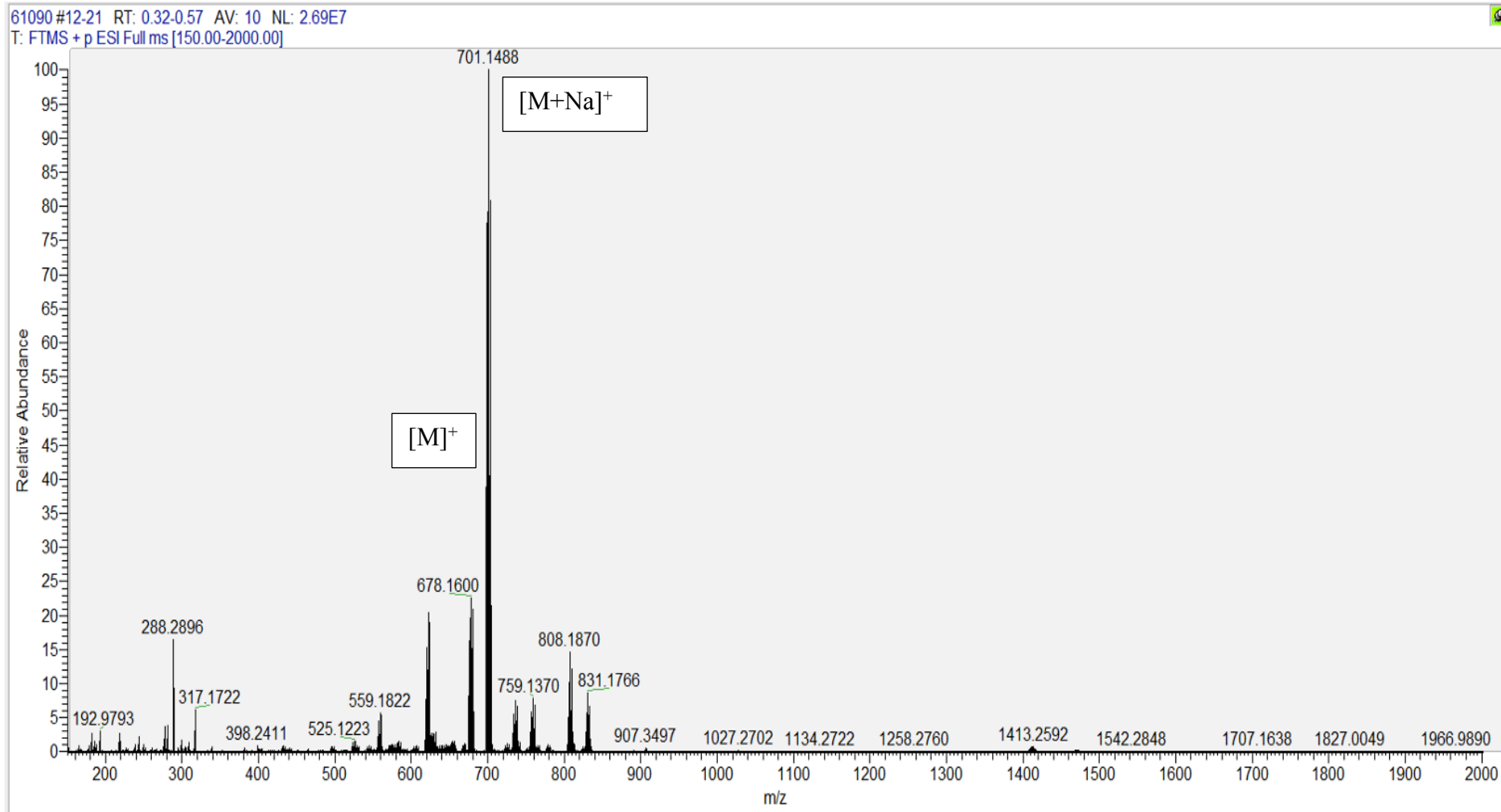
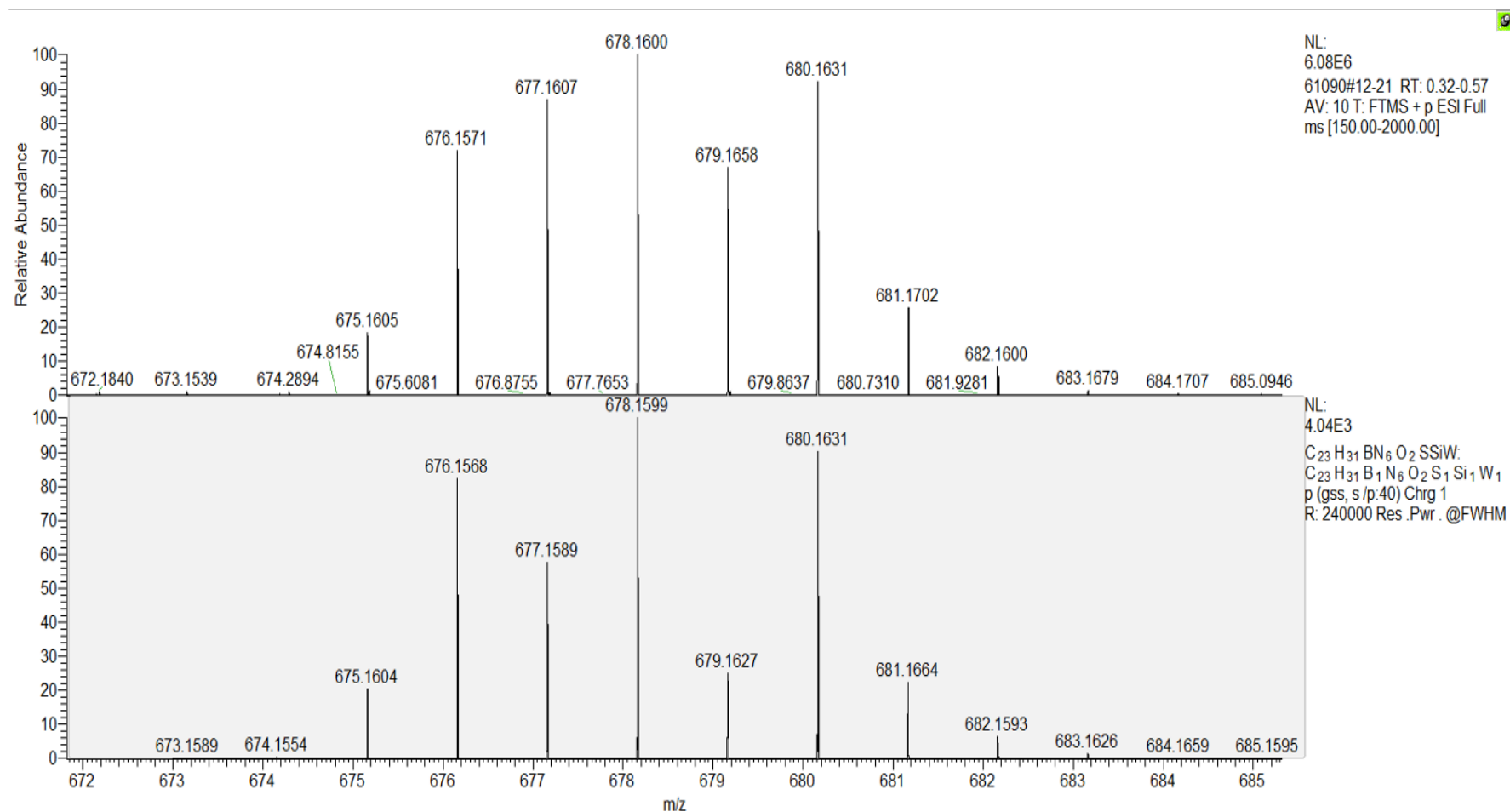
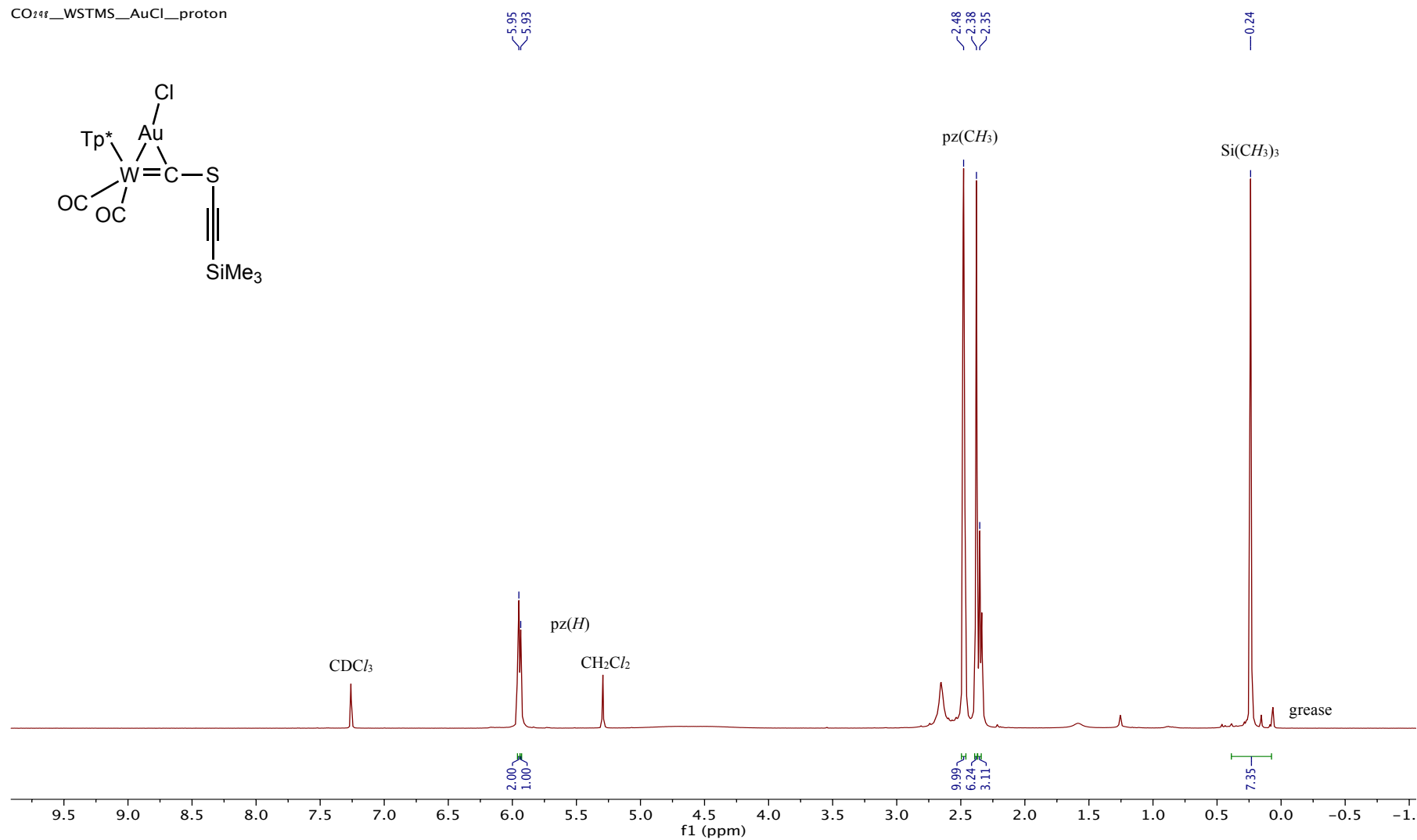


Figure S5. ESI-MS Spectrum of Compound 2a

Observed versus simulated spectrum for detected target formulas [M]<sup>+</sup> ionFigure S6. Isotopic analysis of [M]<sup>+</sup> ion for Compound 2a

CO<sub>2</sub>d<sub>8</sub>\_WSTMS\_AuCl\_protonFigure S7. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 25°C, δ) of compound 3a.

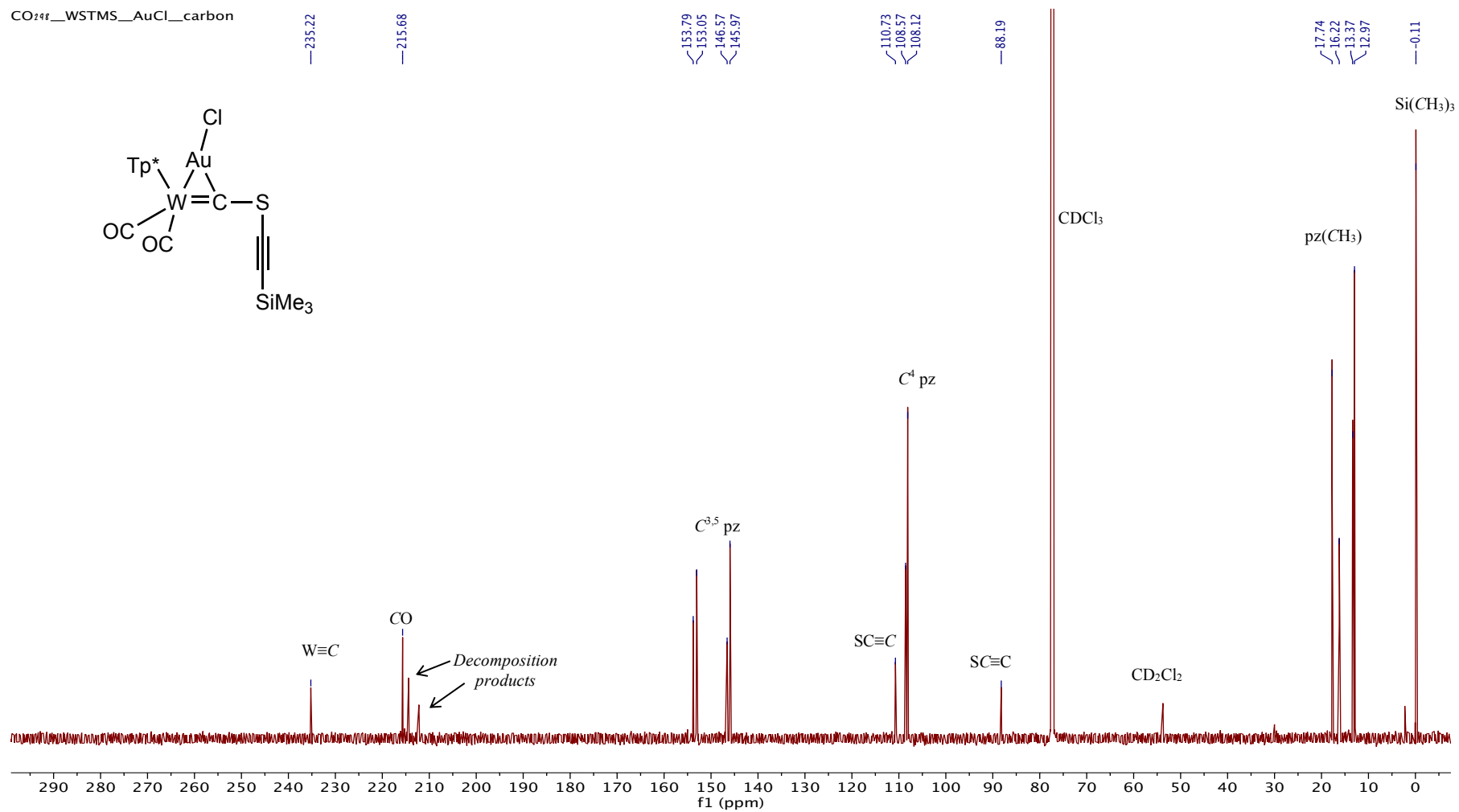


Figure S8. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (176 MHz, CDCl<sub>3</sub>, 25 °C, δ) of compound **3a**.

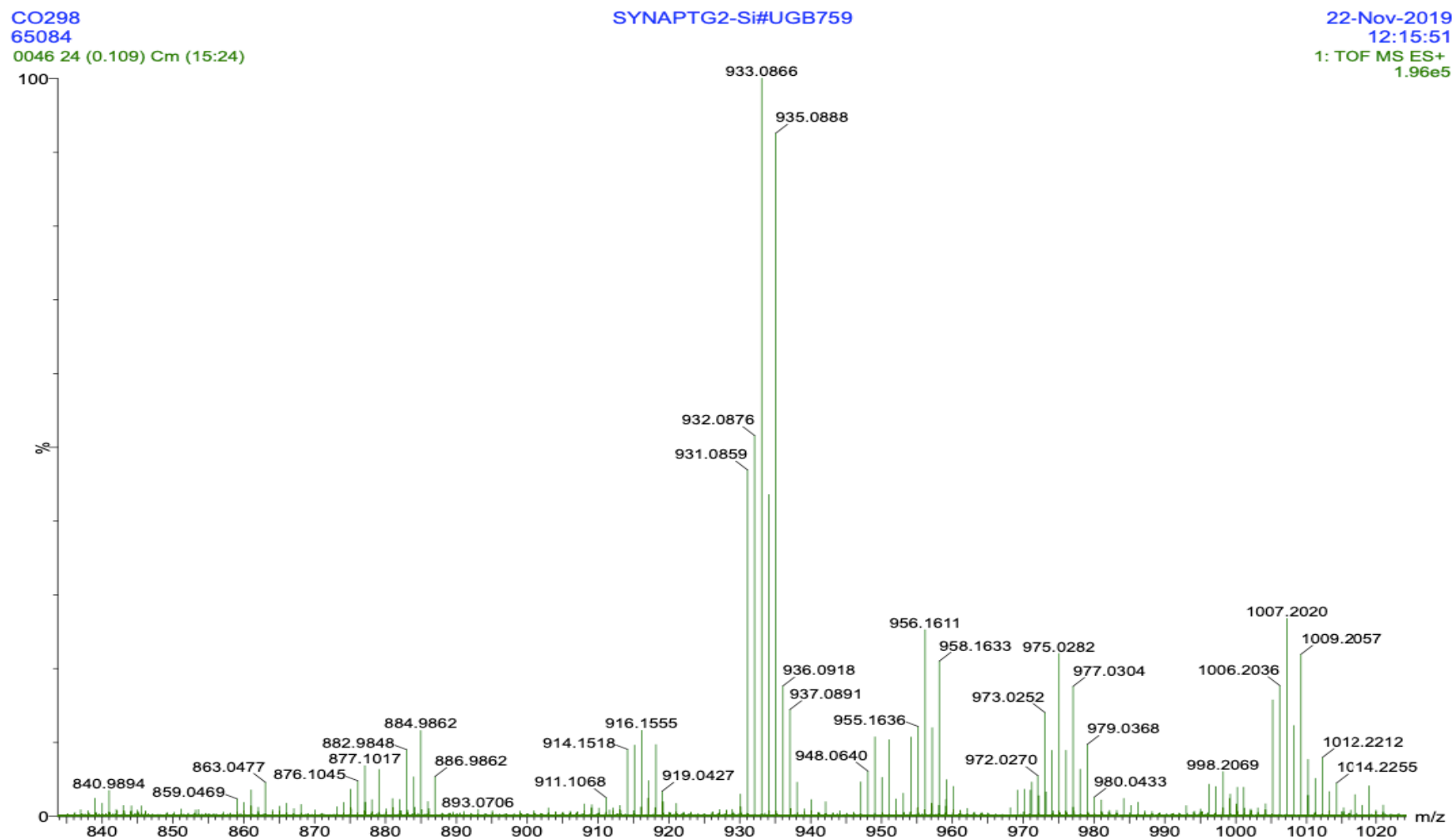
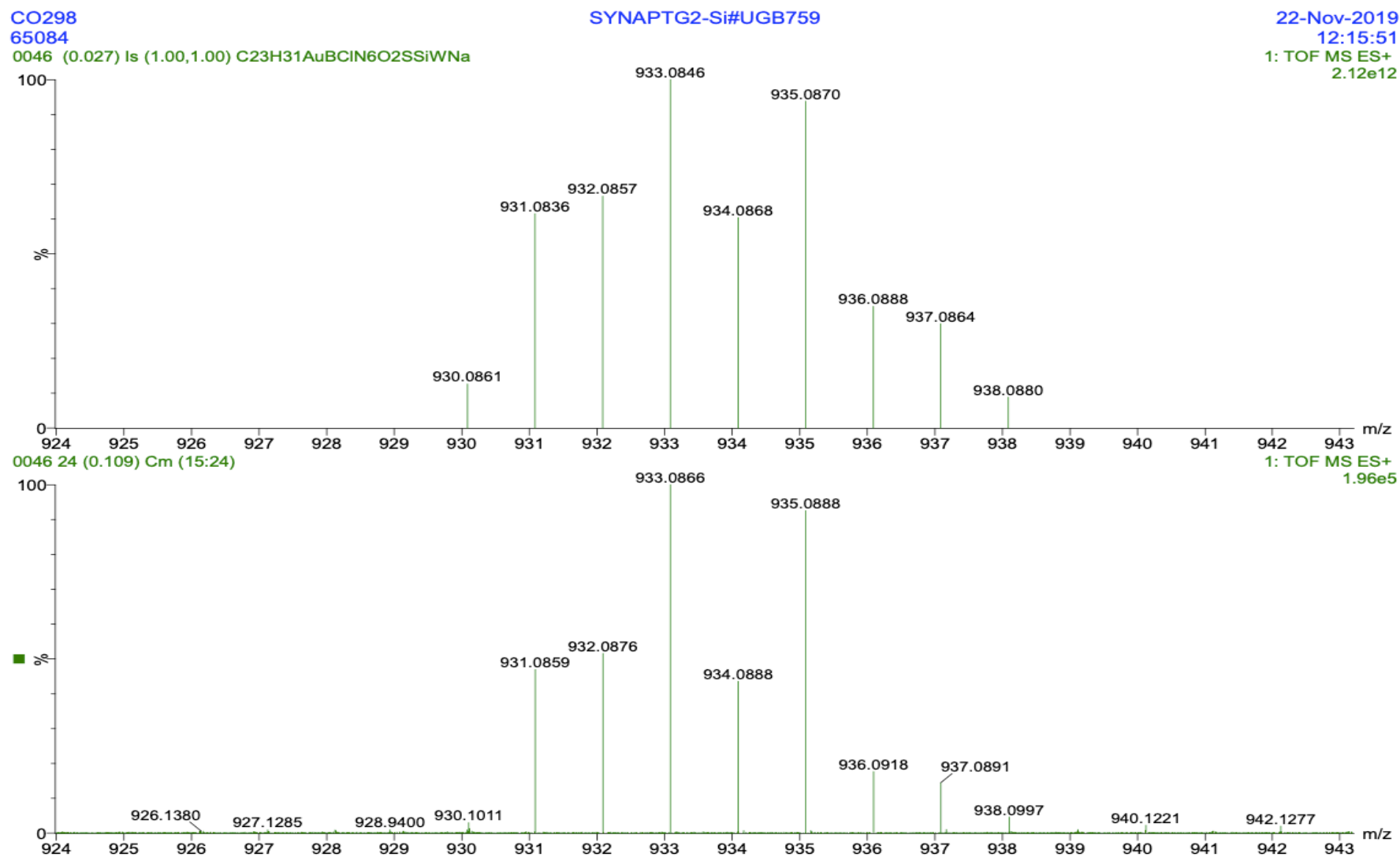


Figure S9. ESI-MS Spectrum of Compound 3a [M+Na]<sup>+</sup>.

Figure S10. Isotopic analysis of [M]<sup>+</sup> ion for Compound 3a



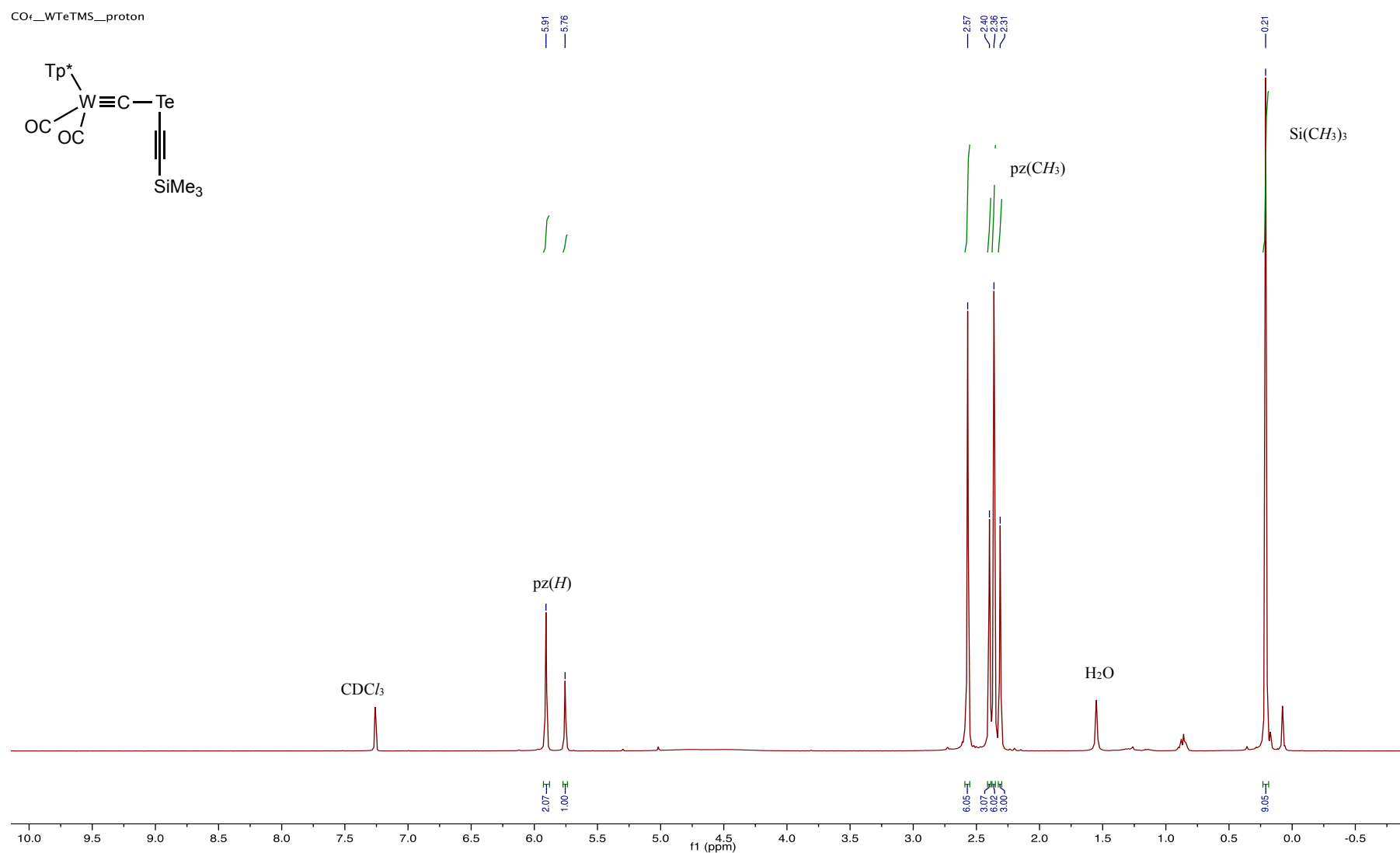


Figure S11. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 25 °C, δ) of compound 4a.

CO<sub>r</sub>\_WTeTMS\_carbon235.59  
233.52  
233.46224.47  
223.64  
222.81153.07  
152.42145.76  
144.81

125.21

107.16  
106.92

-59.58

17.25  
13.96  
13.94

-0.36

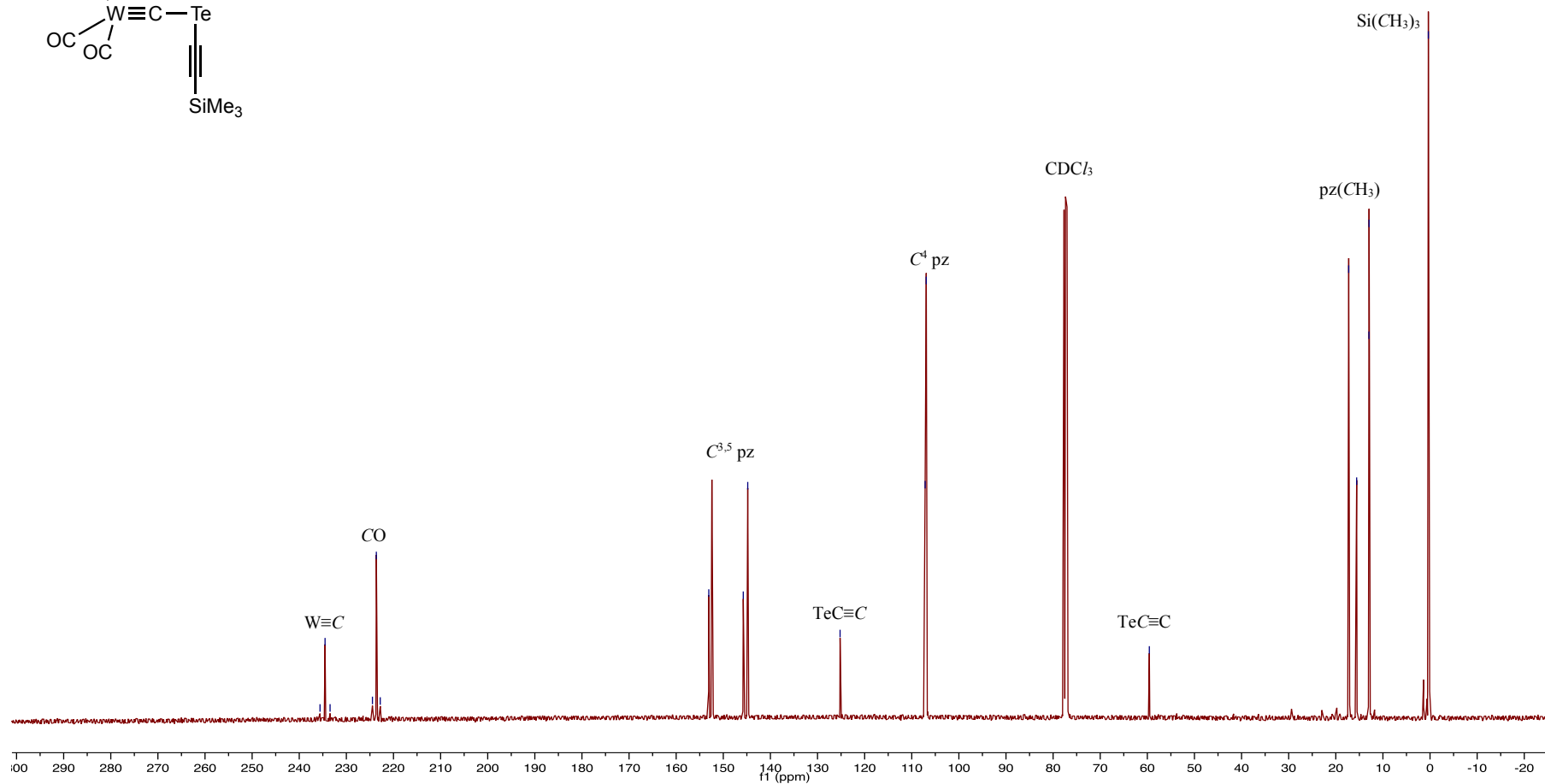
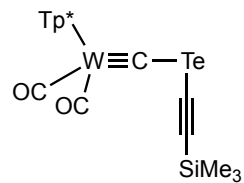


Figure S12.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ , 25 °C,  $\delta$ ) of compound **4a**.

CO<sub>2</sub>\_WTeTMS\_tellurium

—771.16

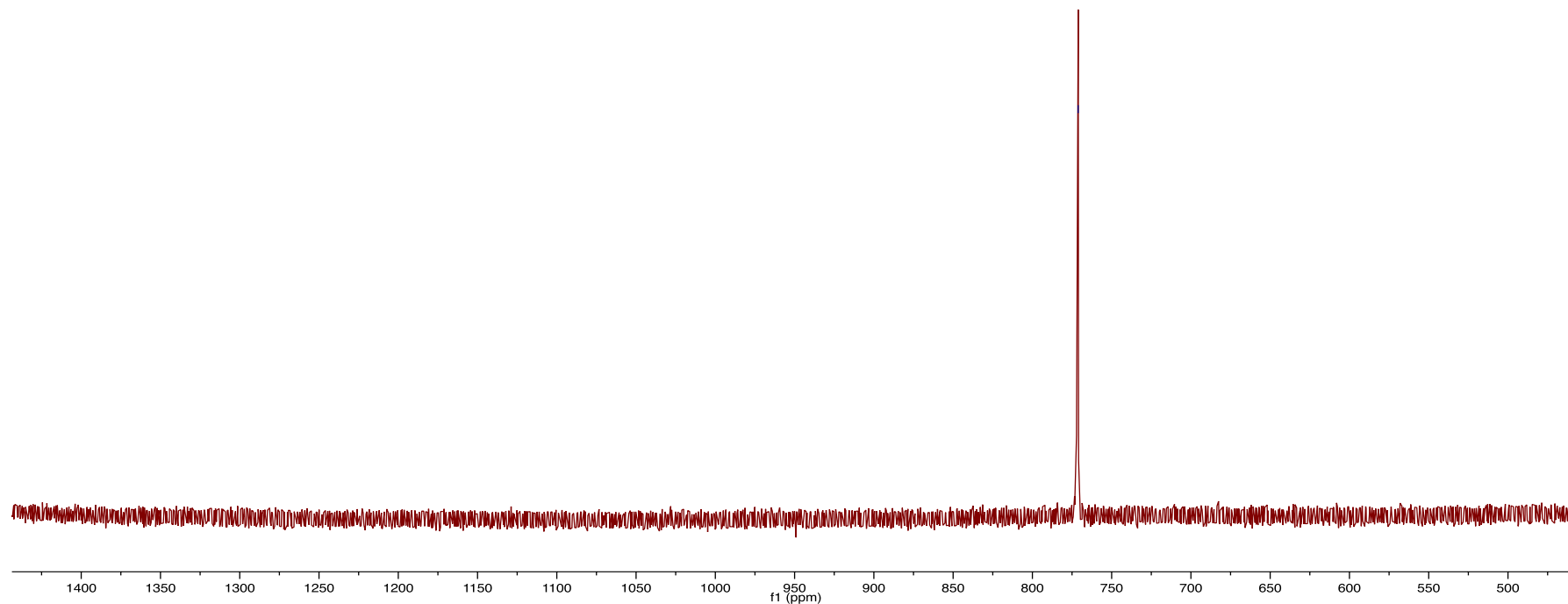
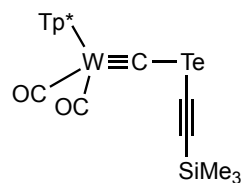
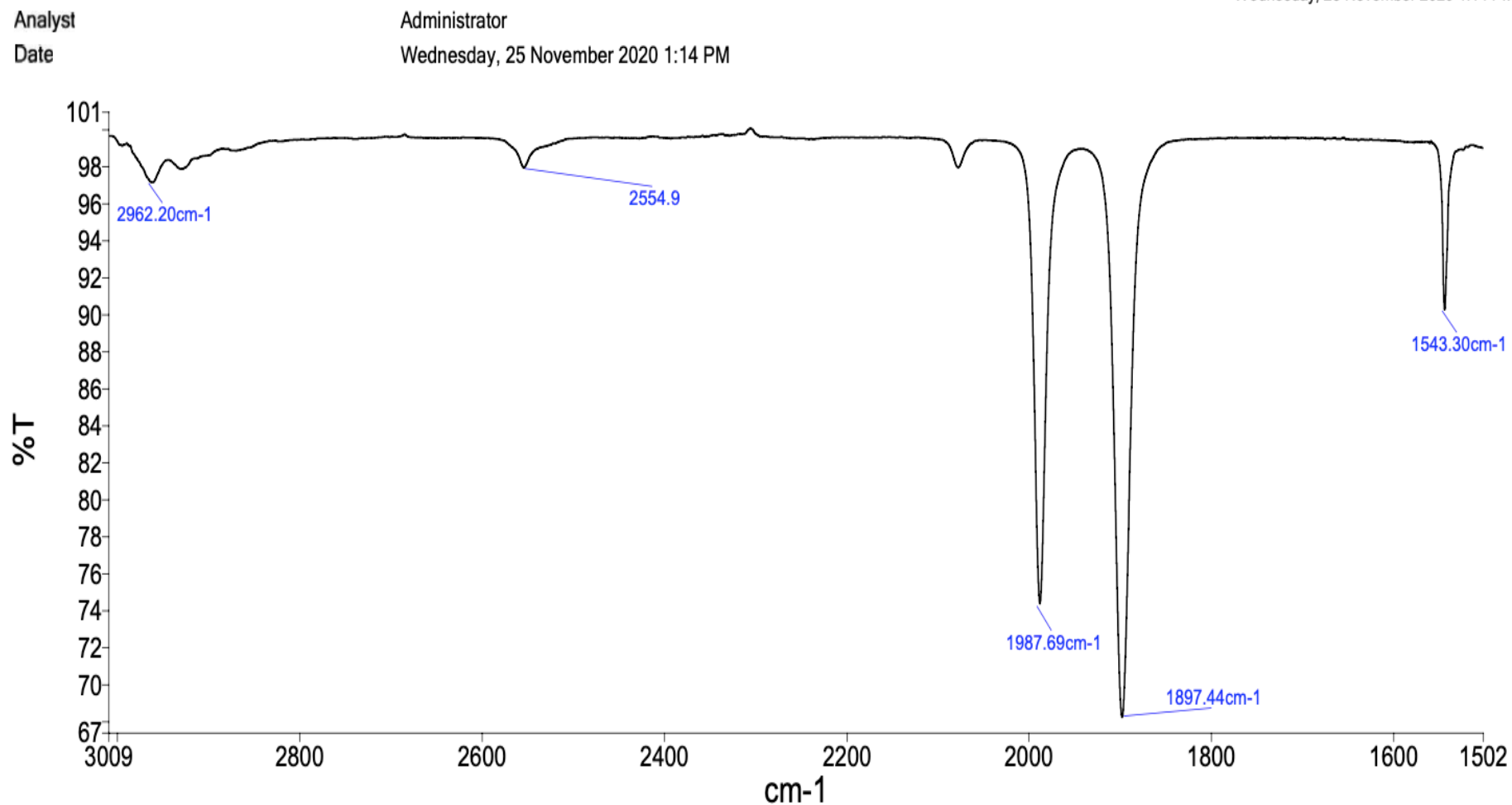
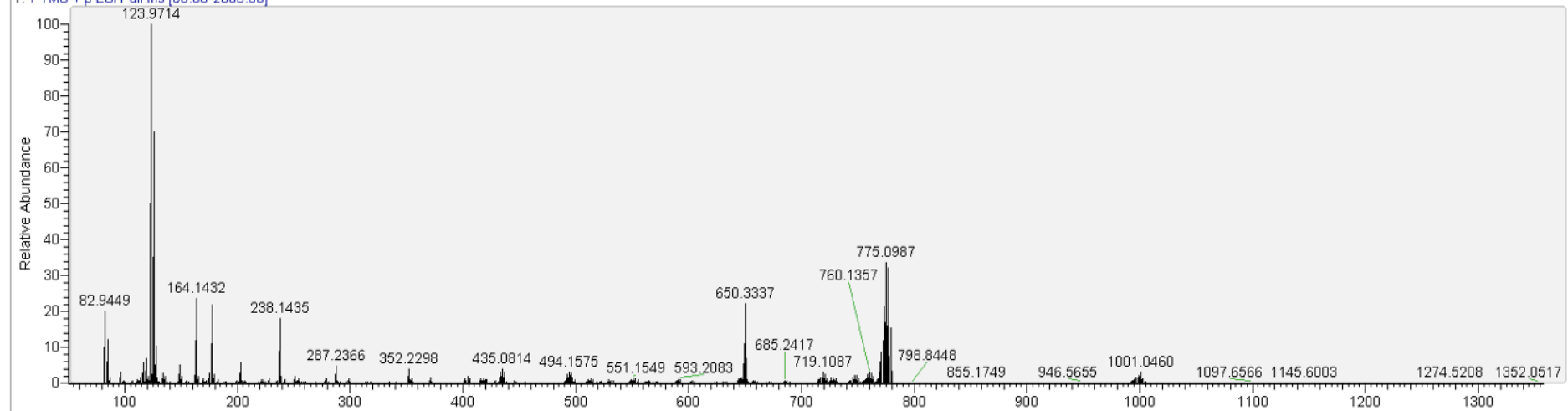


Figure 13. <sup>125</sup>Te{<sup>1</sup>H} NMR spectrum (126 MHz, CDCl<sub>3</sub>, 25°C, δ) of compound 4a.

PerkinElmer Spectrum Version 10.4.3  
Wednesday, 25 November 2020 1:14 PMFigure S14. Infrared spectrum ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ) of Compound 4a

CO\_4\_AJ #10-12 RT: 0.29-0.35 AV: 3 NL: 1.24E6  
T: FTMS + p ESI Full ms [50.00-2000.00]



CO\_4\_AJ #10-12 RT: 0.29-0.35 AV: 3 NL: 4.17E5  
T: FTMS + p ESI Full ms [50.00-2000.00]

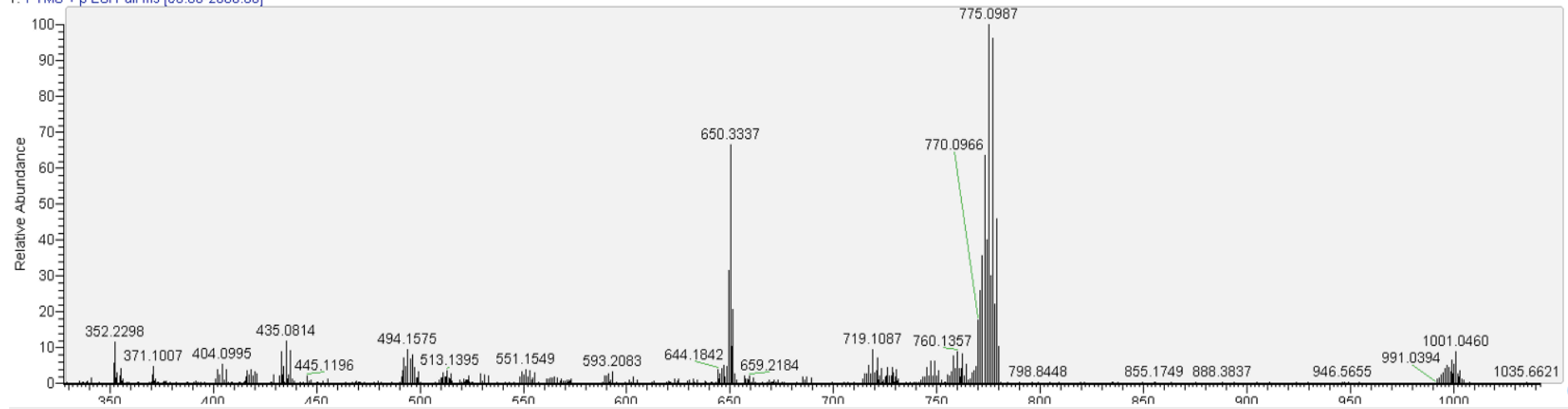
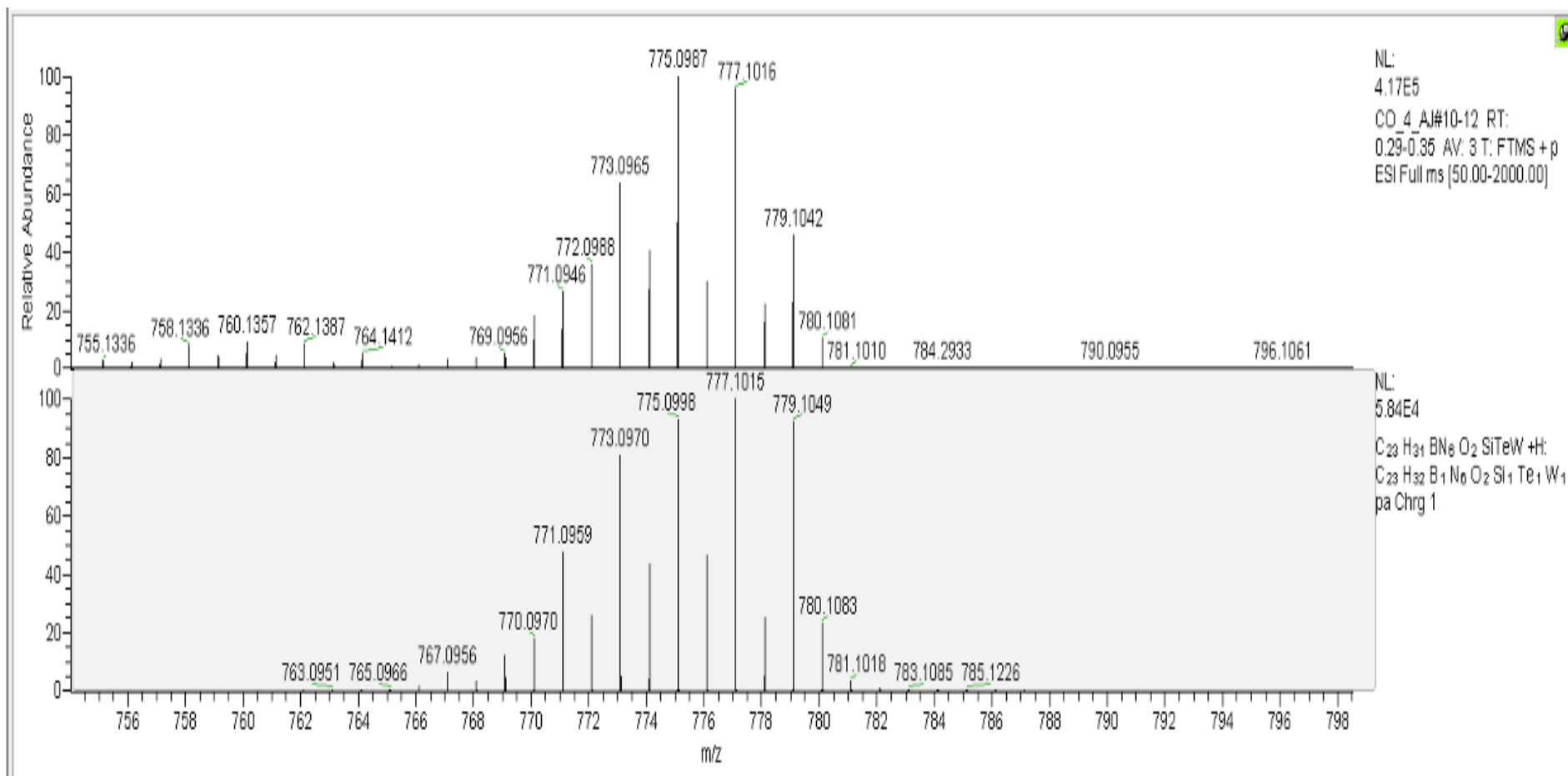


Figure S15. ESI-MS Spectrum of Compound 4a

Figure S16. Isotopic analysis of  $[M]^+$  ion for Compound 4a

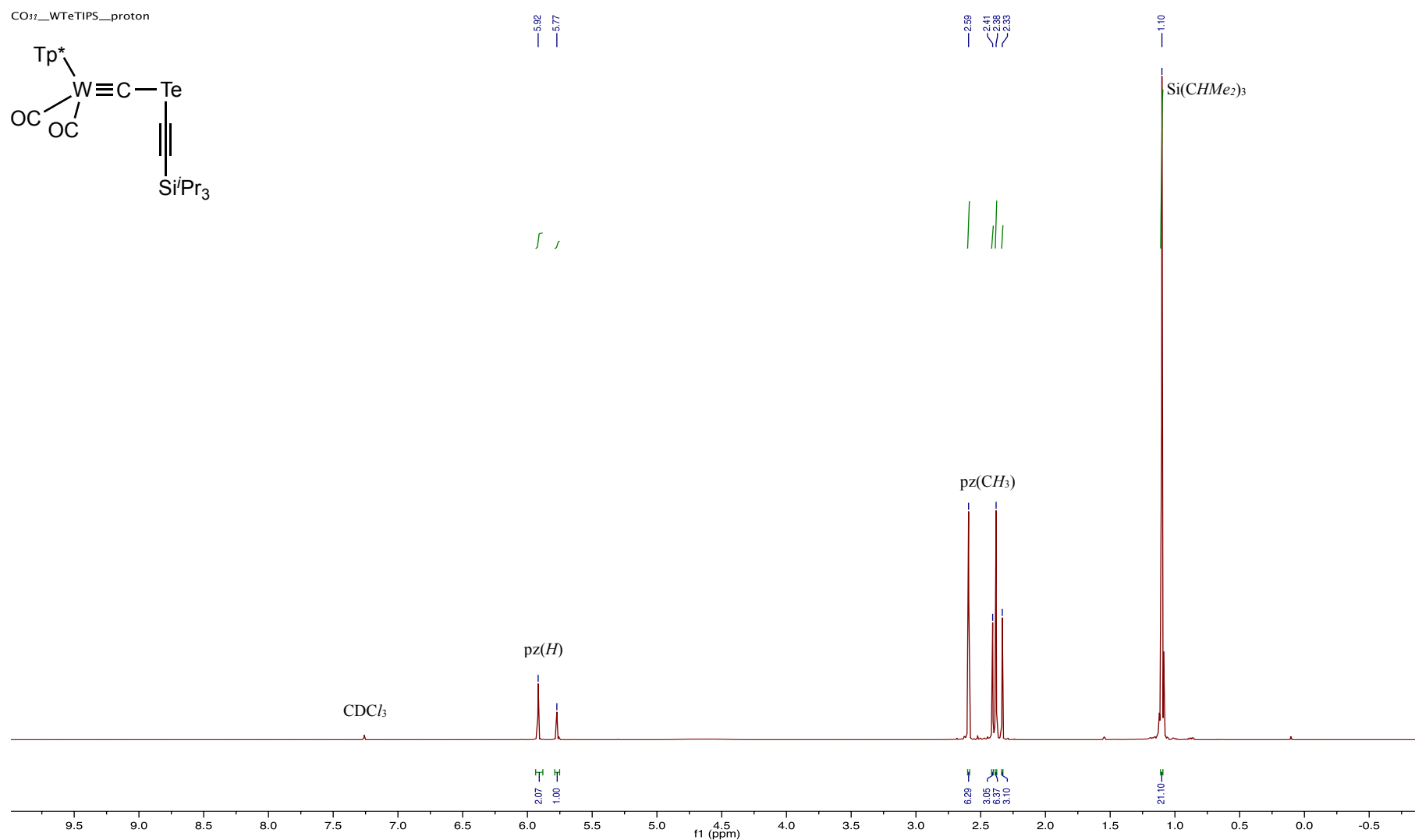


Figure S17. <sup>1</sup>H NMR spectrum (700 MHz, CDCl<sub>3</sub>, 25 °C, δ) of compound **4b**.



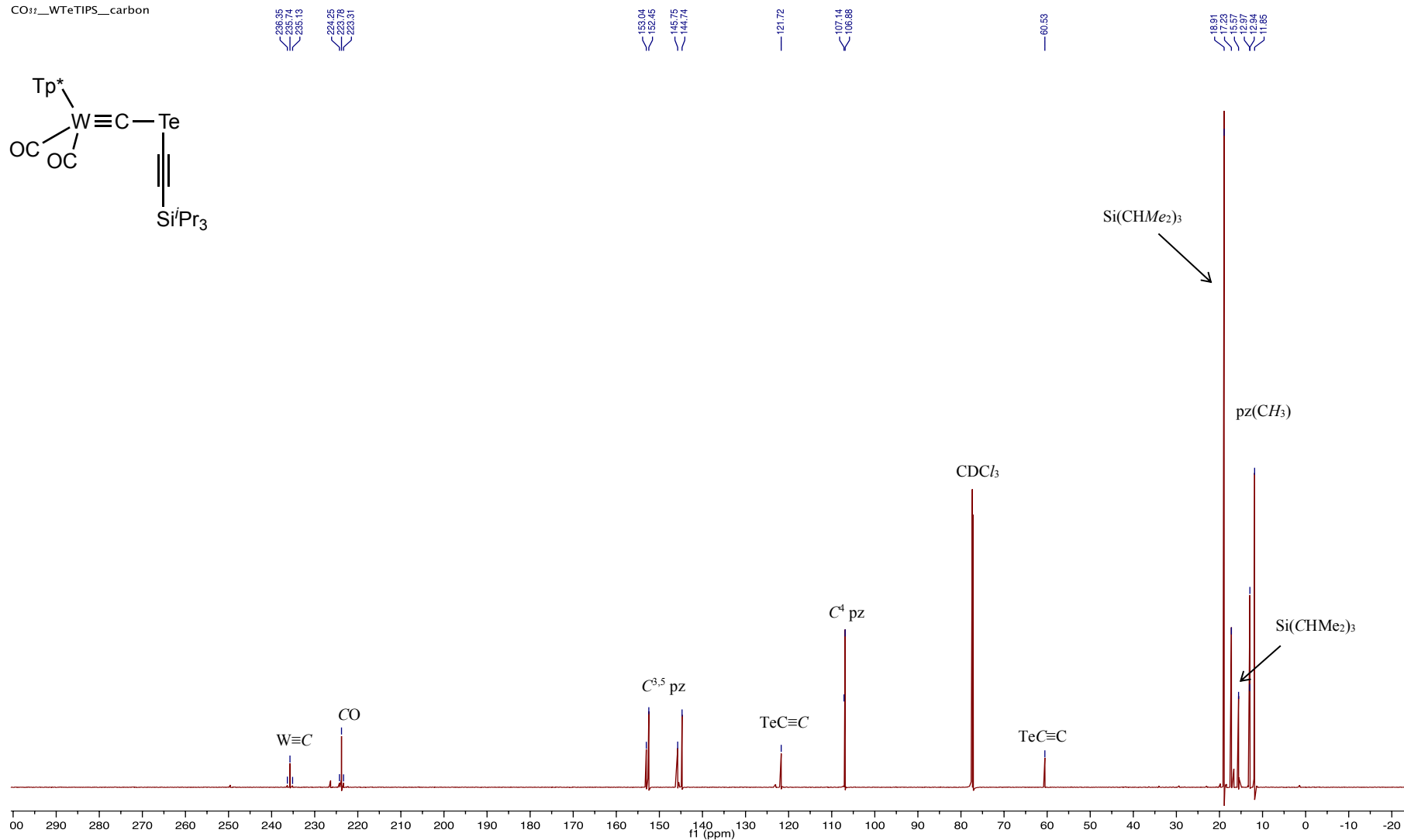
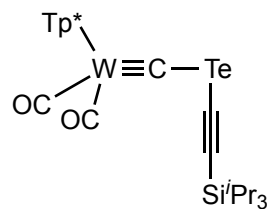
CO<sub>3</sub>\_WTeTIPS\_carbon

Figure S18.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (176 MHz,  $\text{CDCl}_3$ , 25°C,  $\delta$ ) of compound **4b**.

CO<sub>3</sub>\_WTeTIPS\_tellurium

763.54

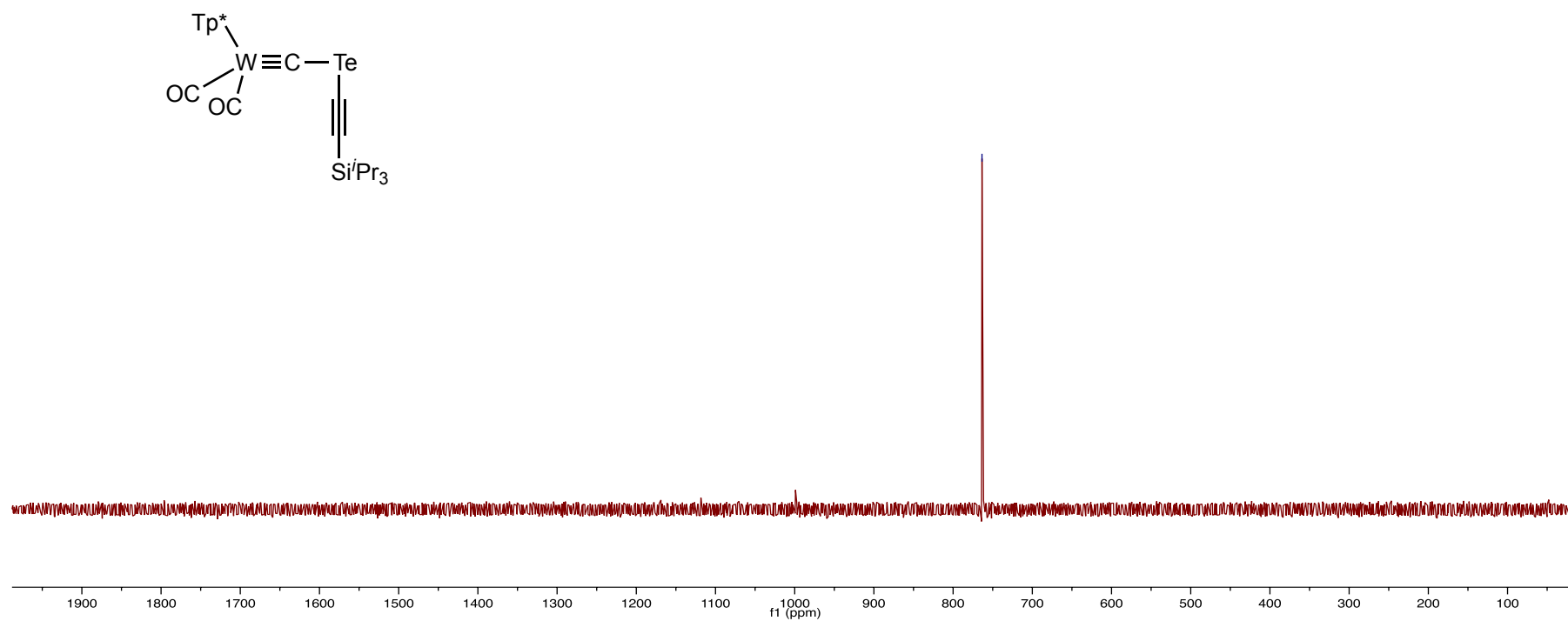


Figure 19. <sup>125</sup>Te{<sup>1</sup>H} NMR spectrum (126 MHz, CDCl<sub>3</sub>, 25°C, δ) of compound 4b.

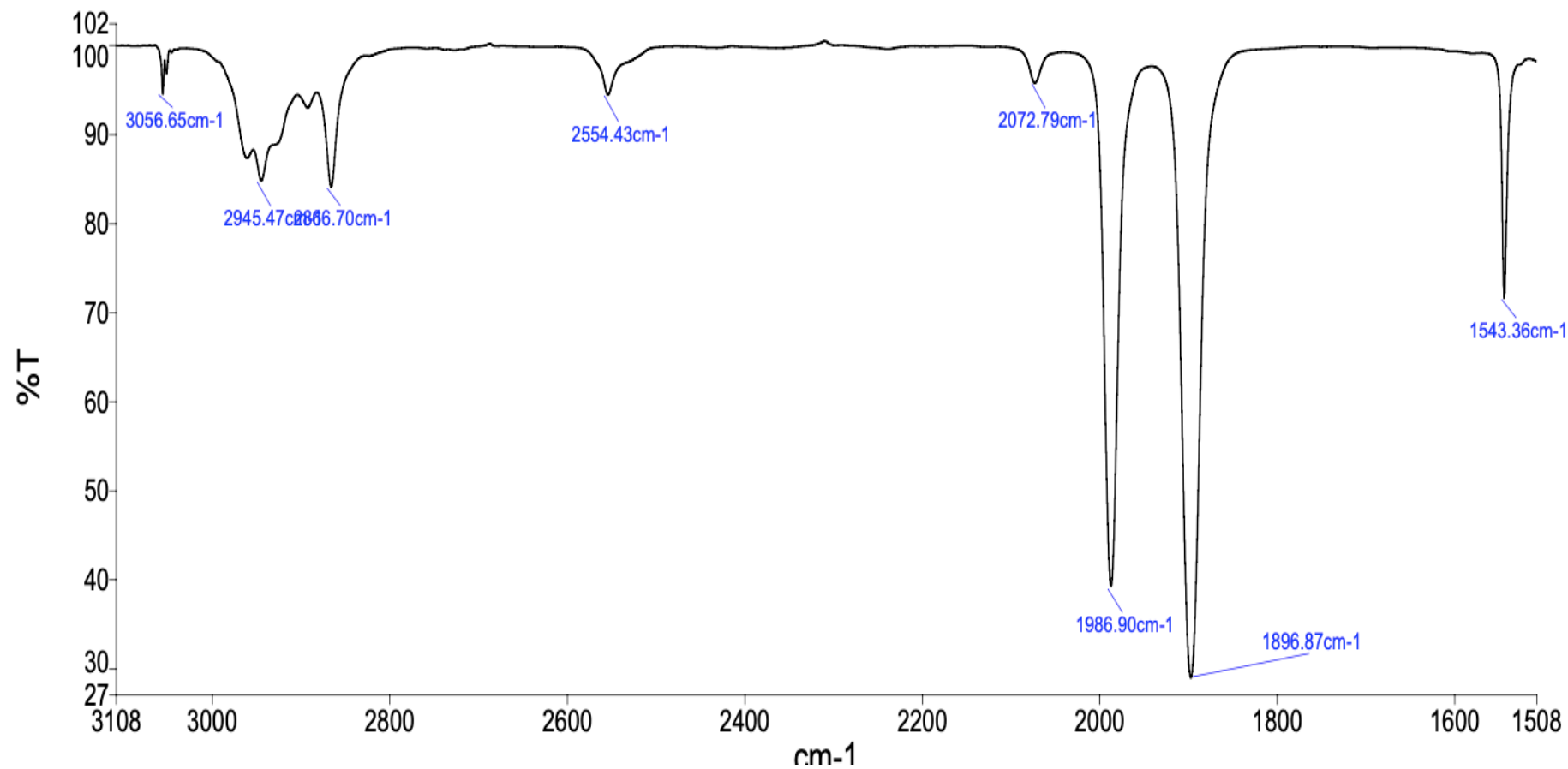
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Figure S20. Infrared spectrum (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>) of Compound 4b

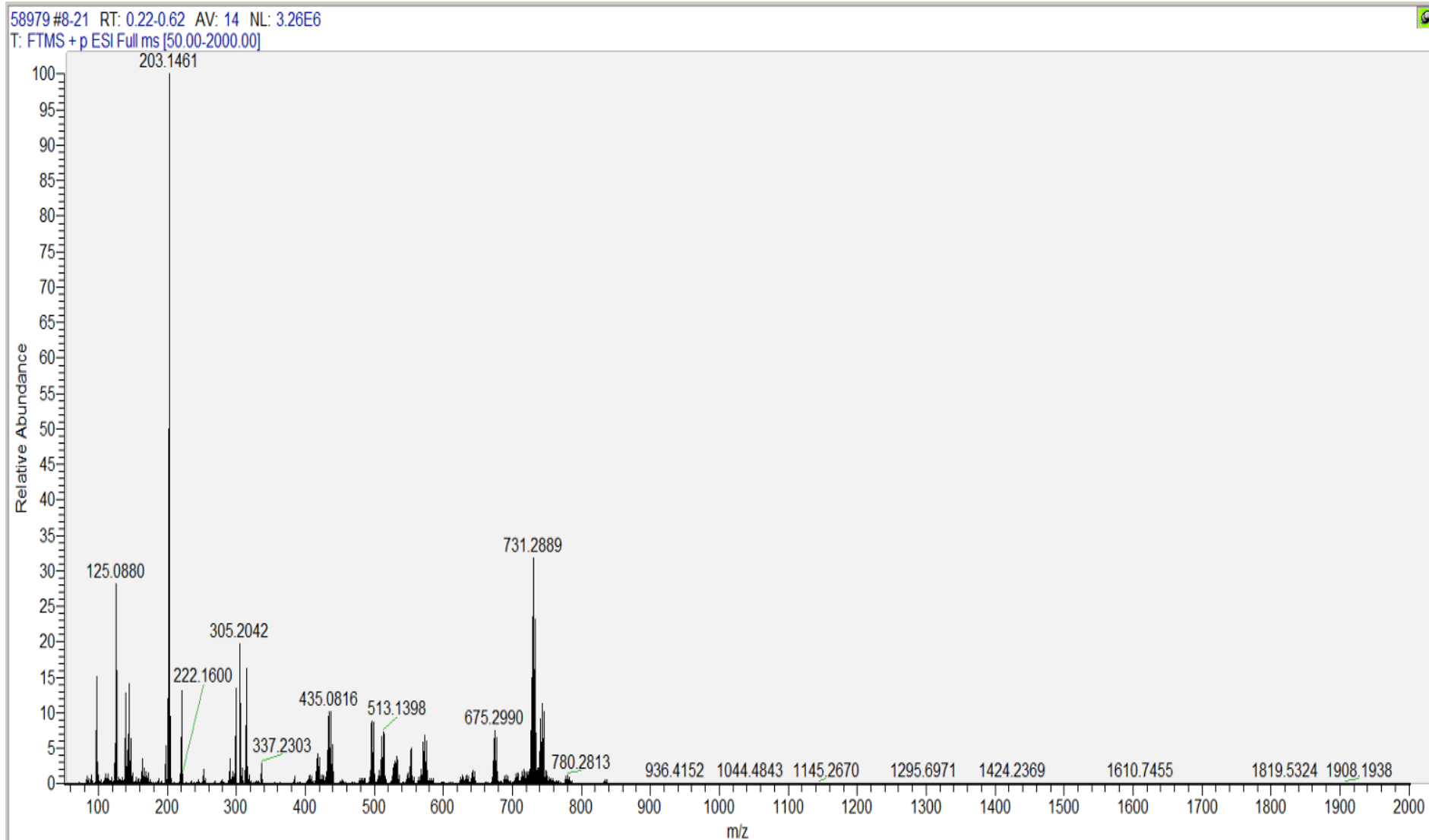
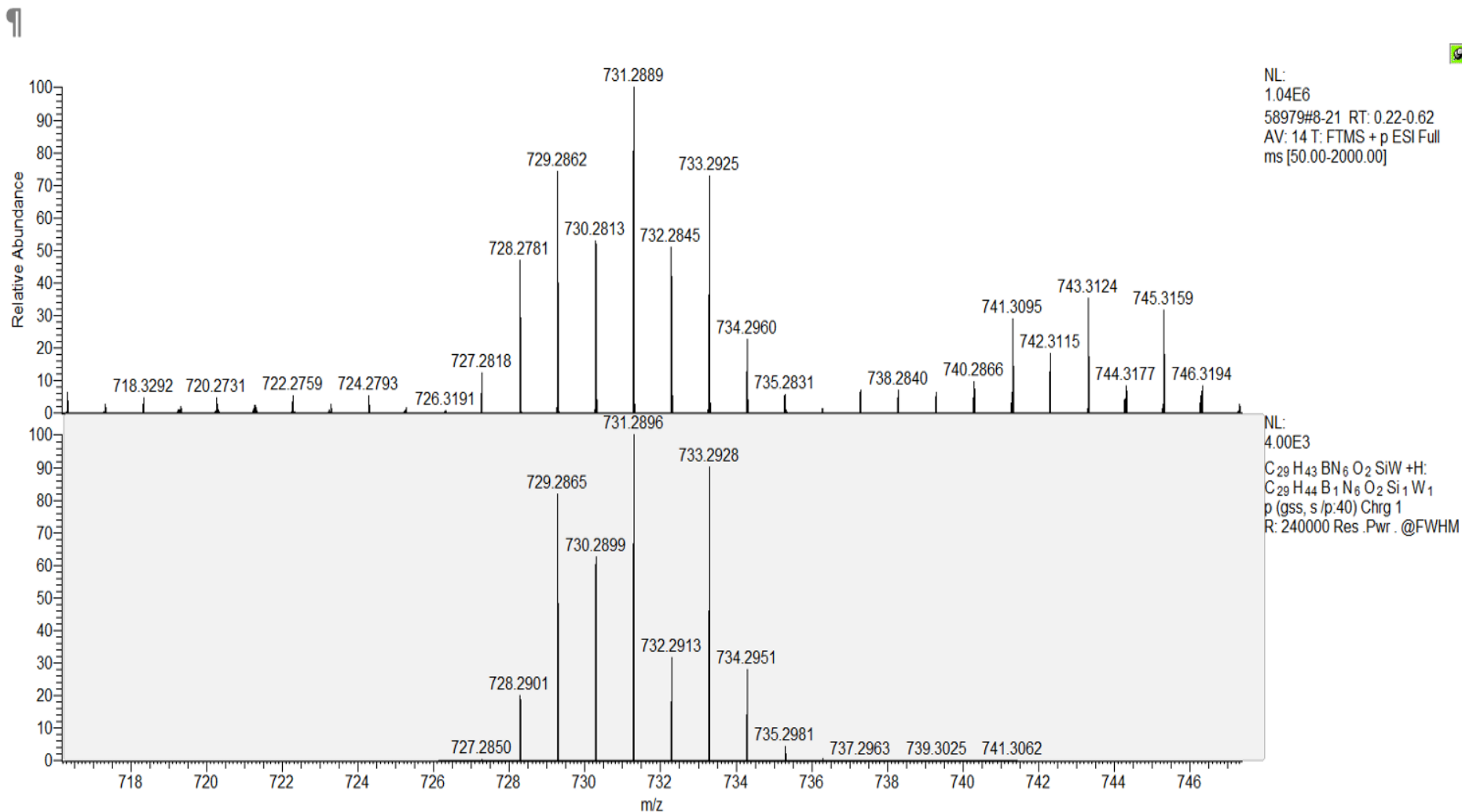
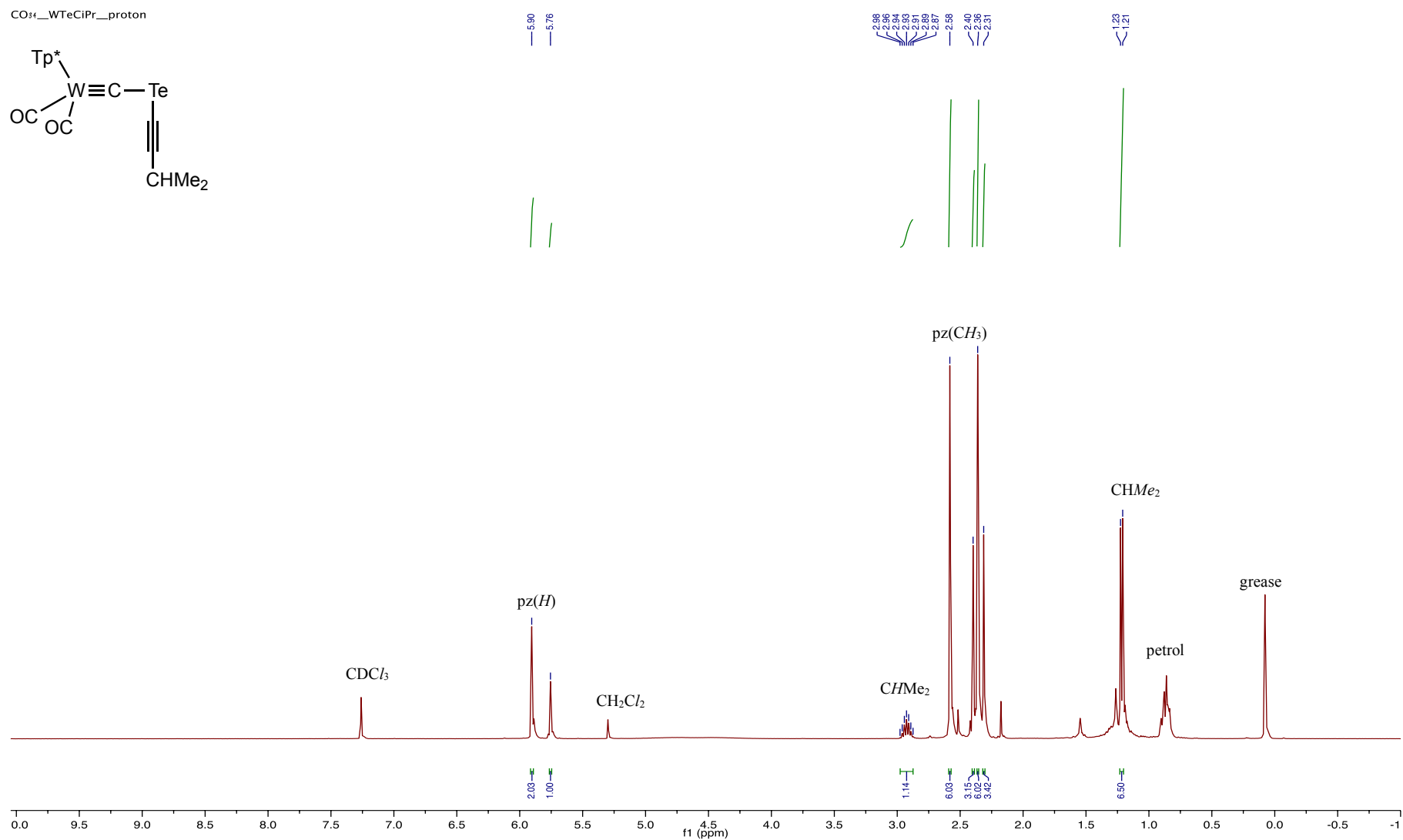
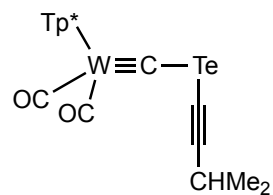


Figure S21. ESI-MS Spectrum of Compound 4b

Observed versus simulated spectrum for detected target formulas ([M+H]<sup>+</sup> ion)Figure S22. Isotopic analysis of [M]<sup>+</sup> ion for Compound 4b

CO34\_WTeCiPr\_proton

Figure S23.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 25°C,  $\delta$ ) of compound 4c.

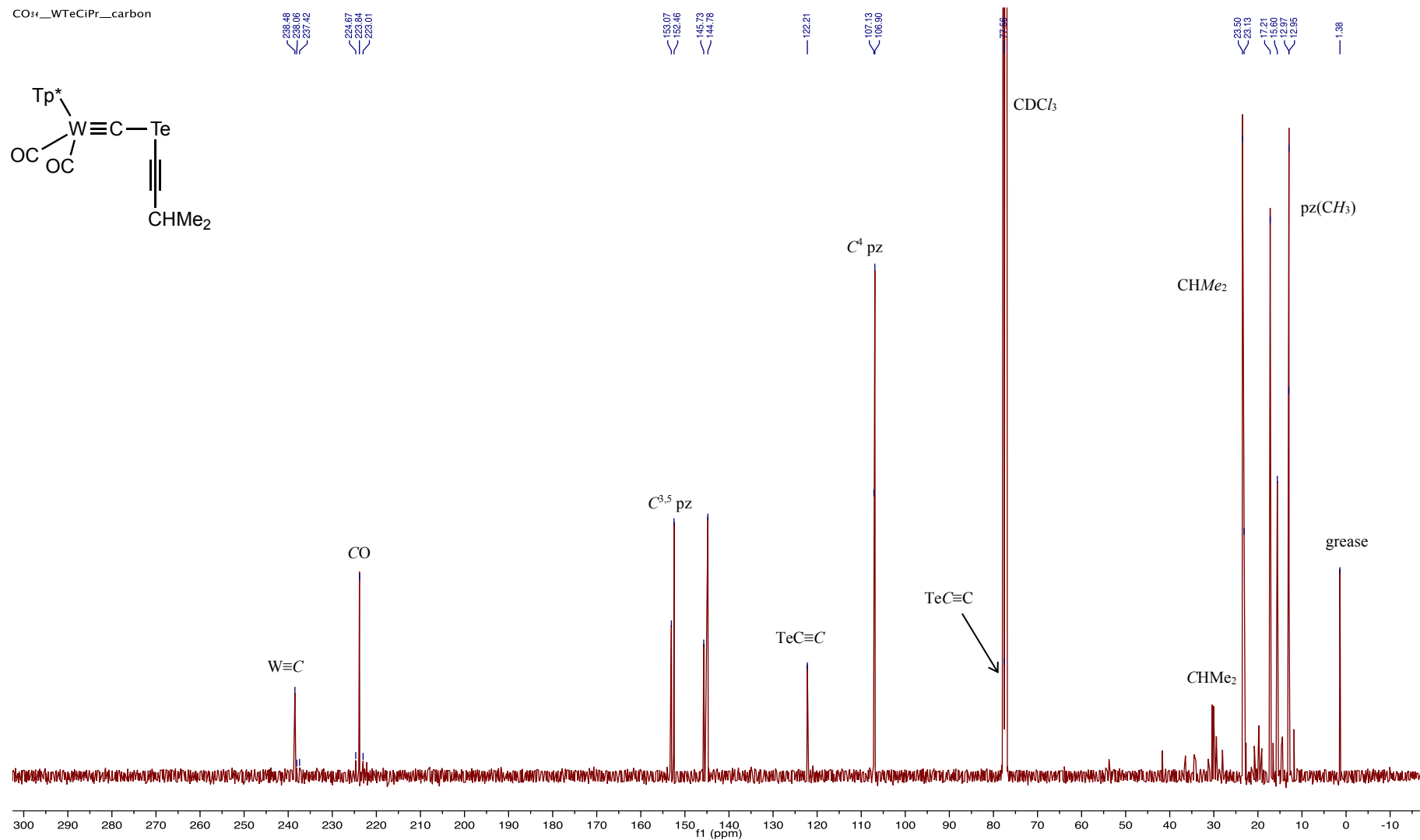


Figure 24. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (101 MHz, CDCl<sub>3</sub>, 25°C, δ) of compound **4c**.



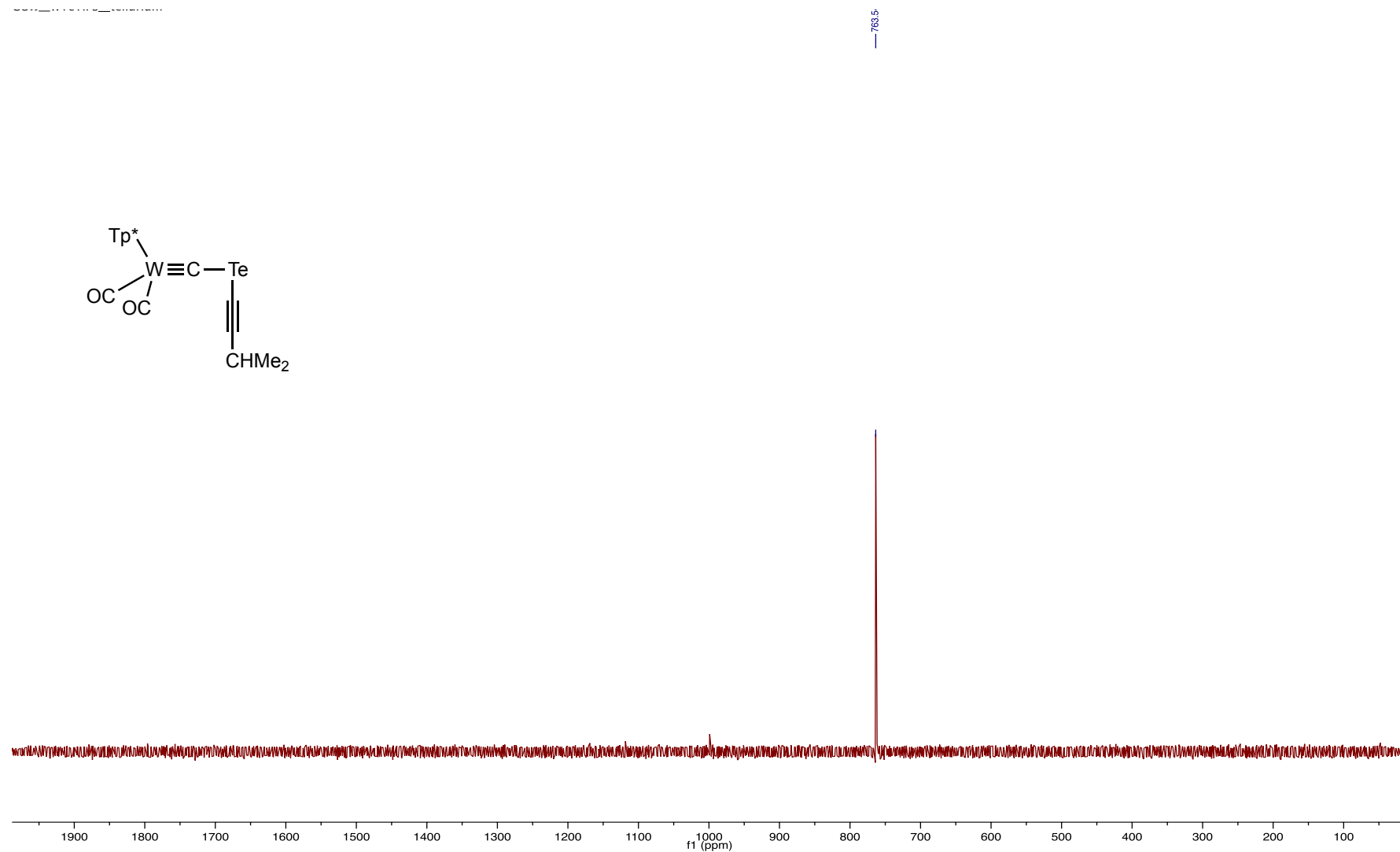


Figure 25.  $^{125}\text{Te}\{^1\text{H}\}$  NMR spectrum (126 MHz,  $\text{CDCl}_3$ , 25°C,  $\delta$ ) of compound 4c.

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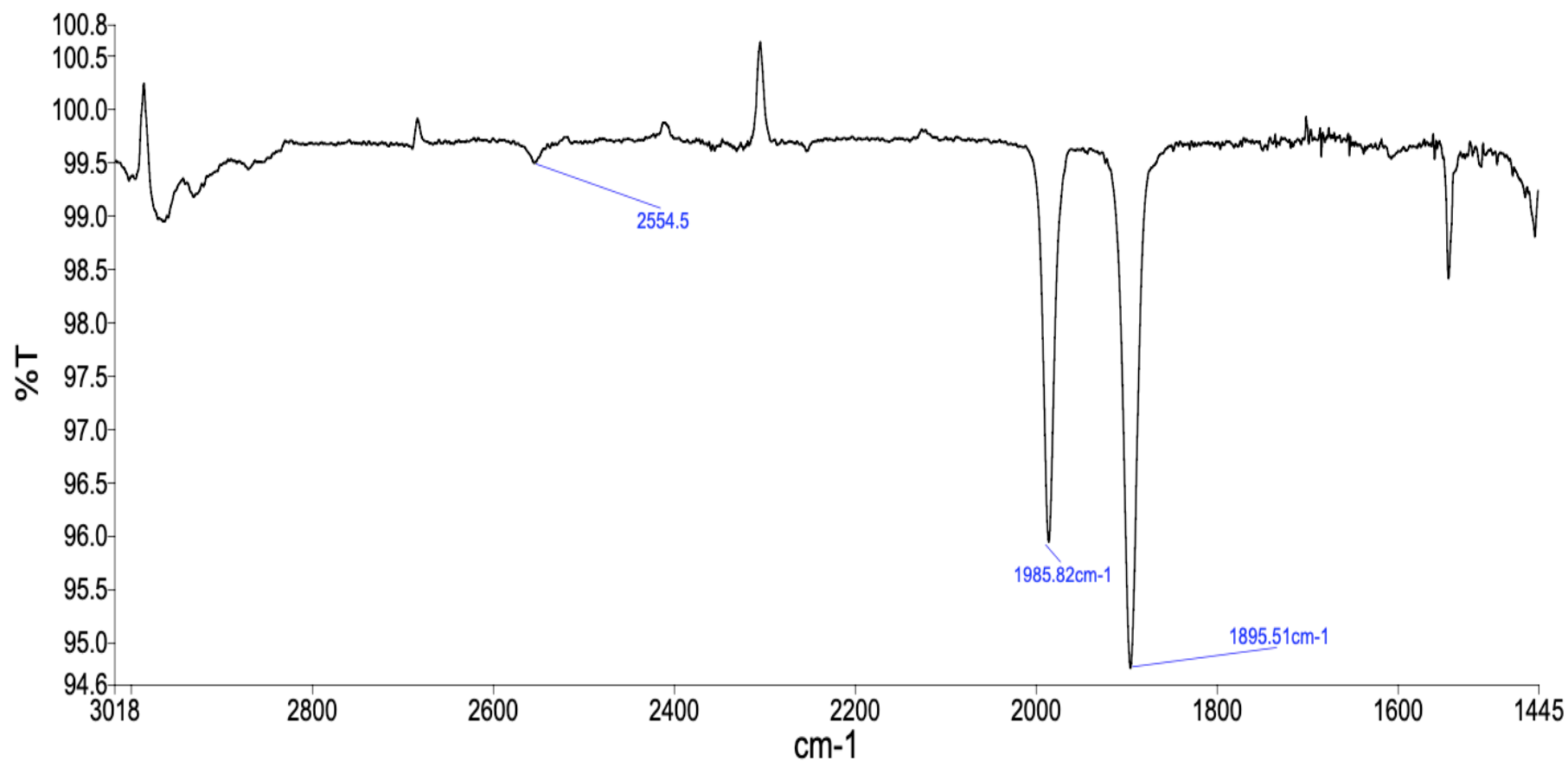


Figure S26. Infrared spectrum ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ) of Compound 4c

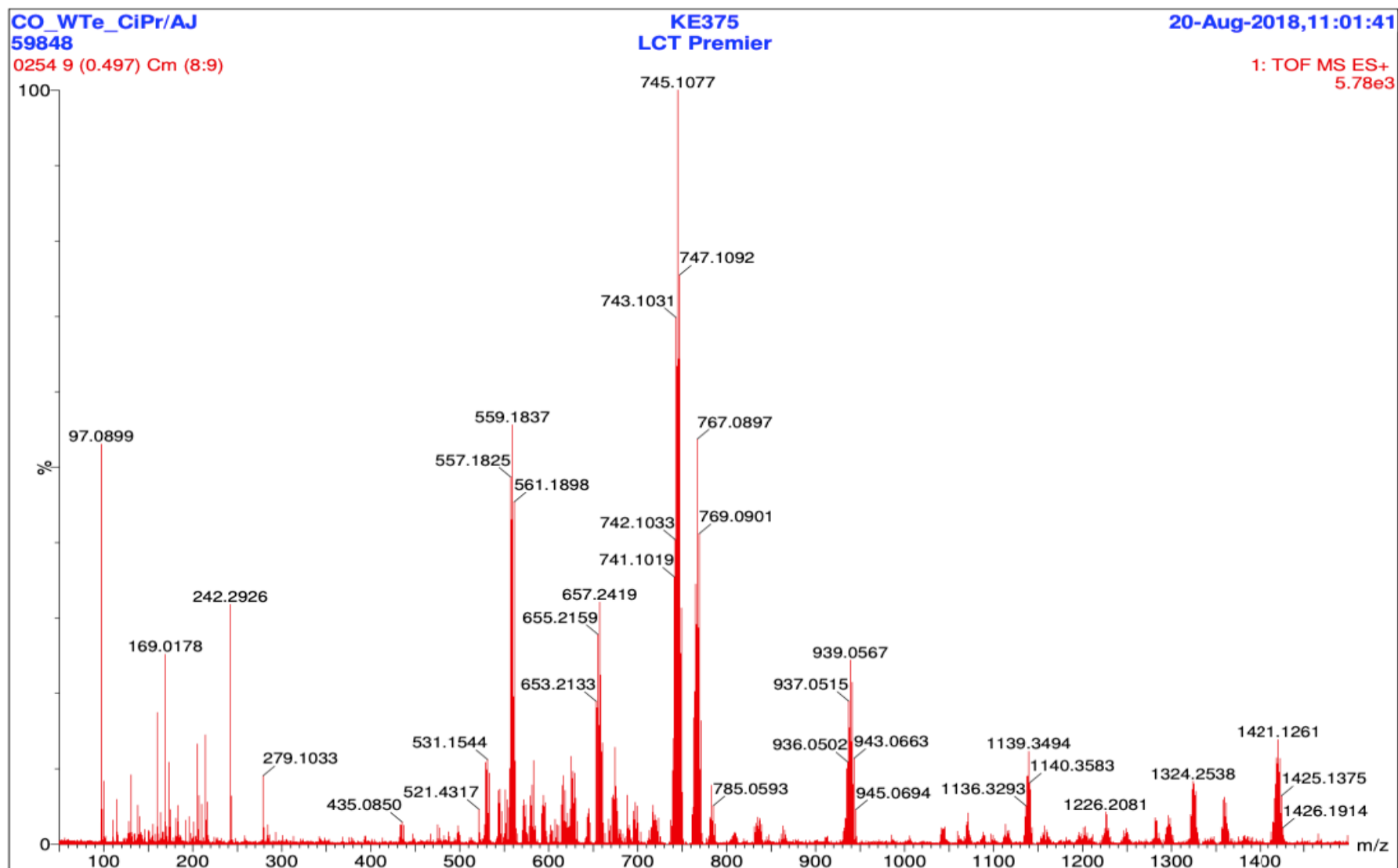
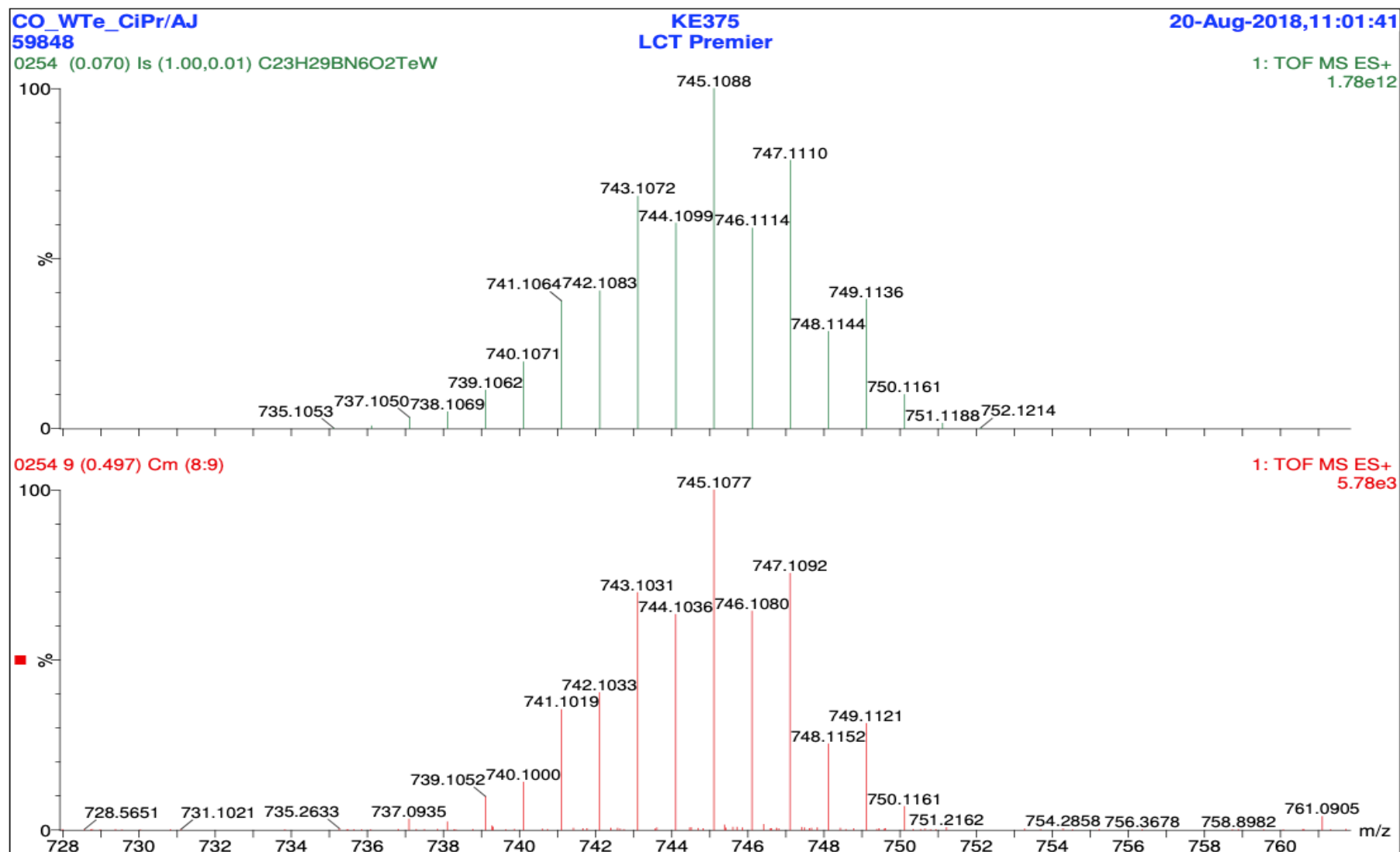


Figure S27. ESI-MS Spectrum of Compound 4c

Figure S28. Isotopic analysis of [M]<sup>+</sup> ion for Compound 4c

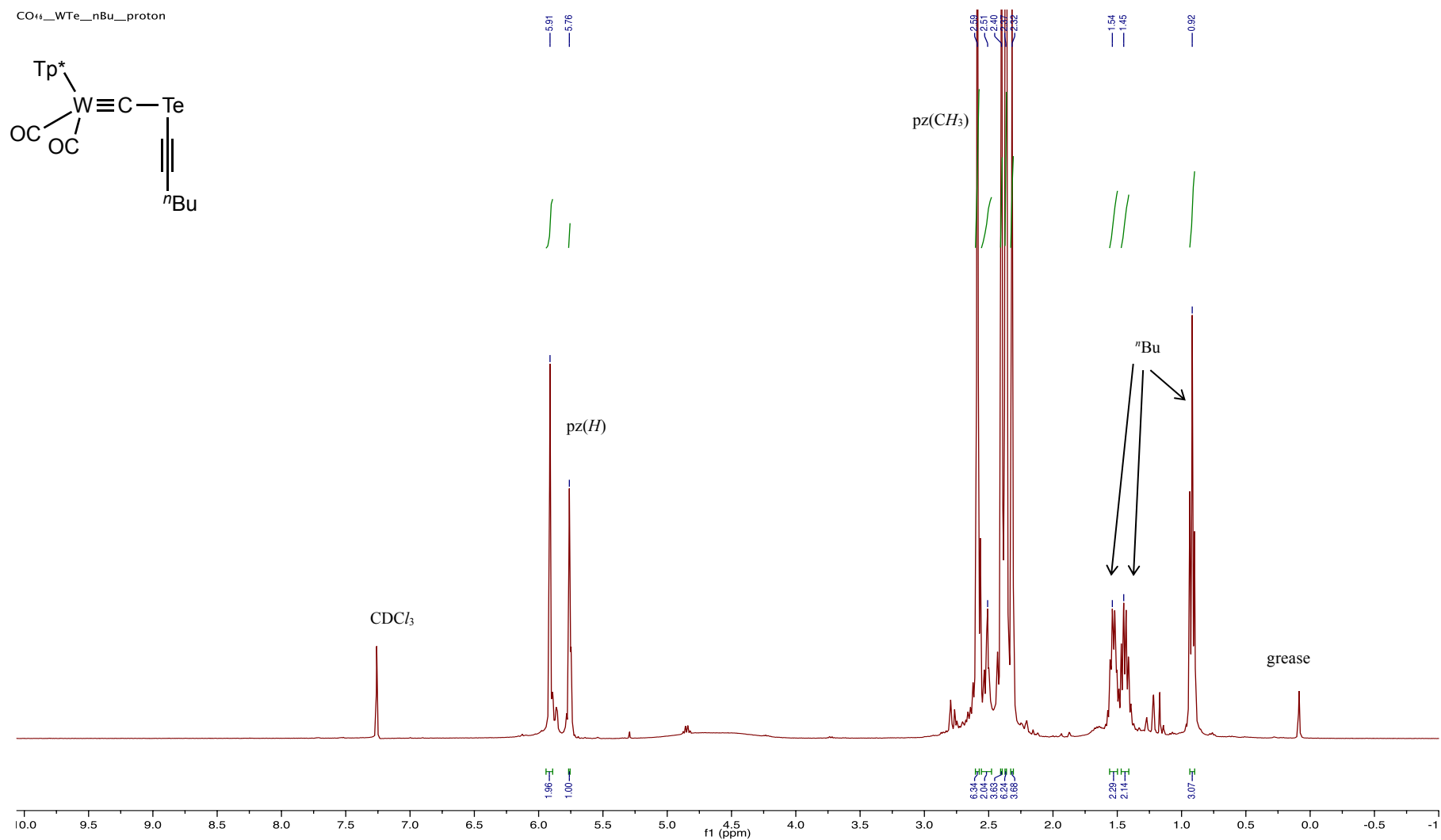


Figure S29. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 25 °C, δ) of compound **4d**.

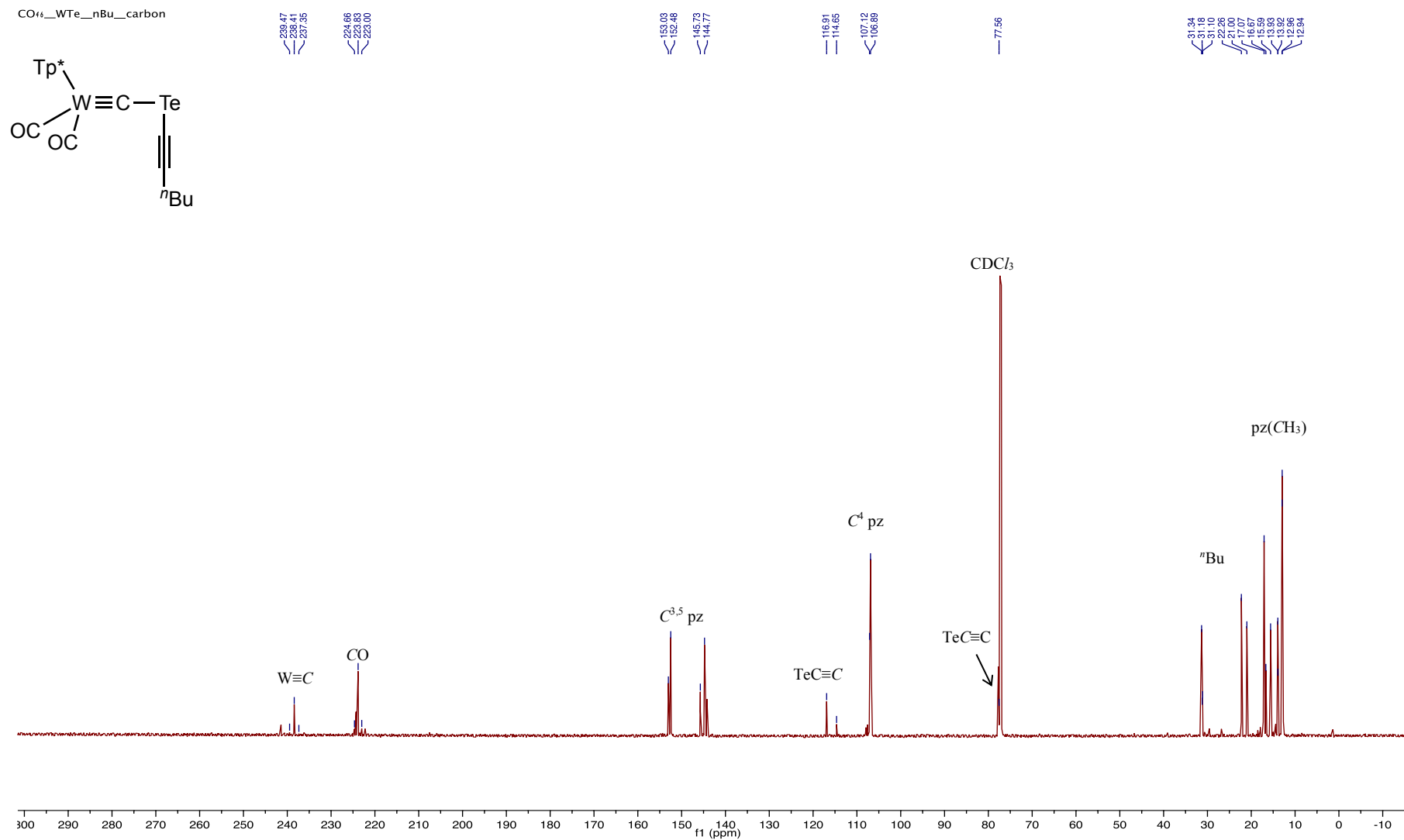
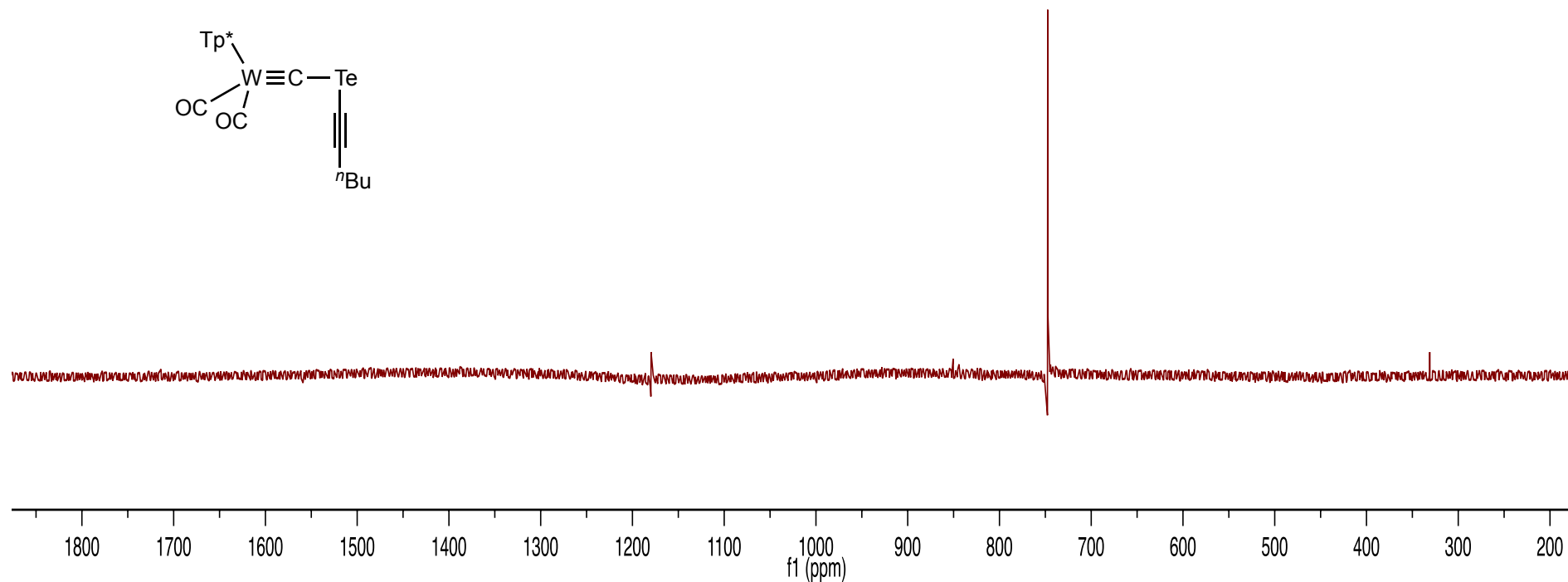


Figure S30. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (101 MHz, CDCl<sub>3</sub>, 25 °C, δ) of compound 4d.



**Figure S31.**  $^{125}\text{Te}\{^1\text{H}\}$  NMR spectrum (126 MHz,  $\text{CDCl}_3$ , 25°C,  $\delta$ ) of compound **4d**.



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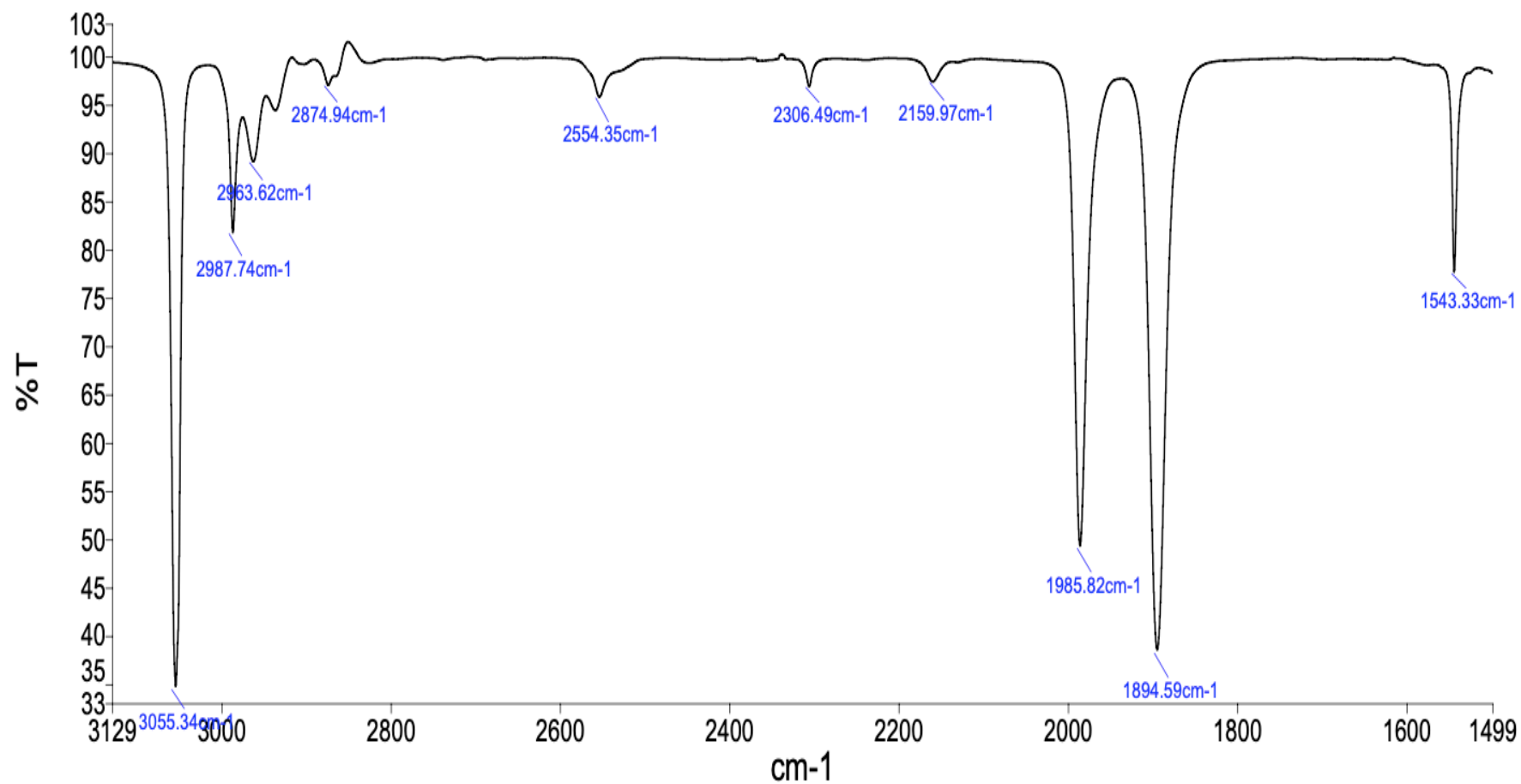


Figure S32. Infrared spectrum ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ) of Compound 4d

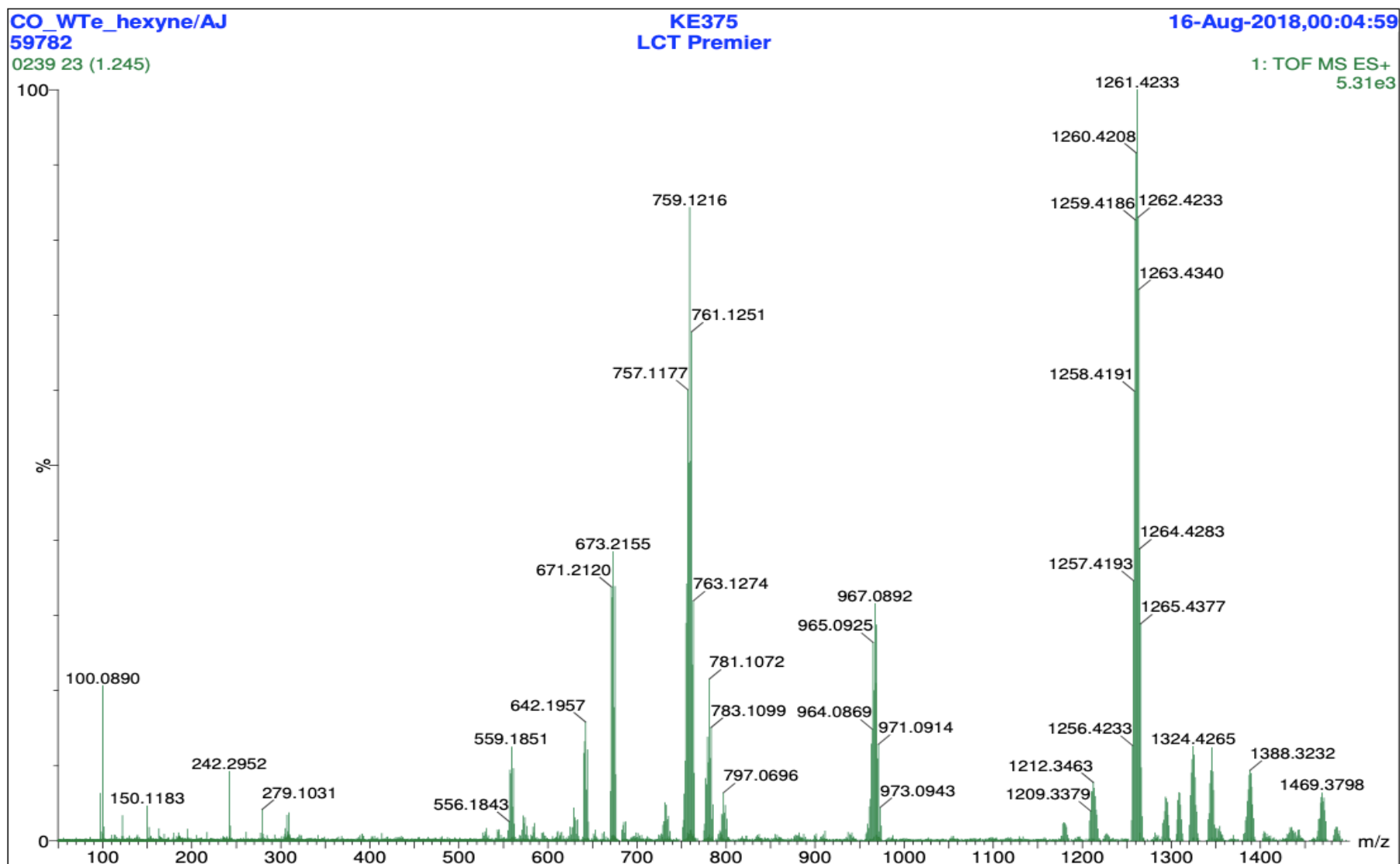
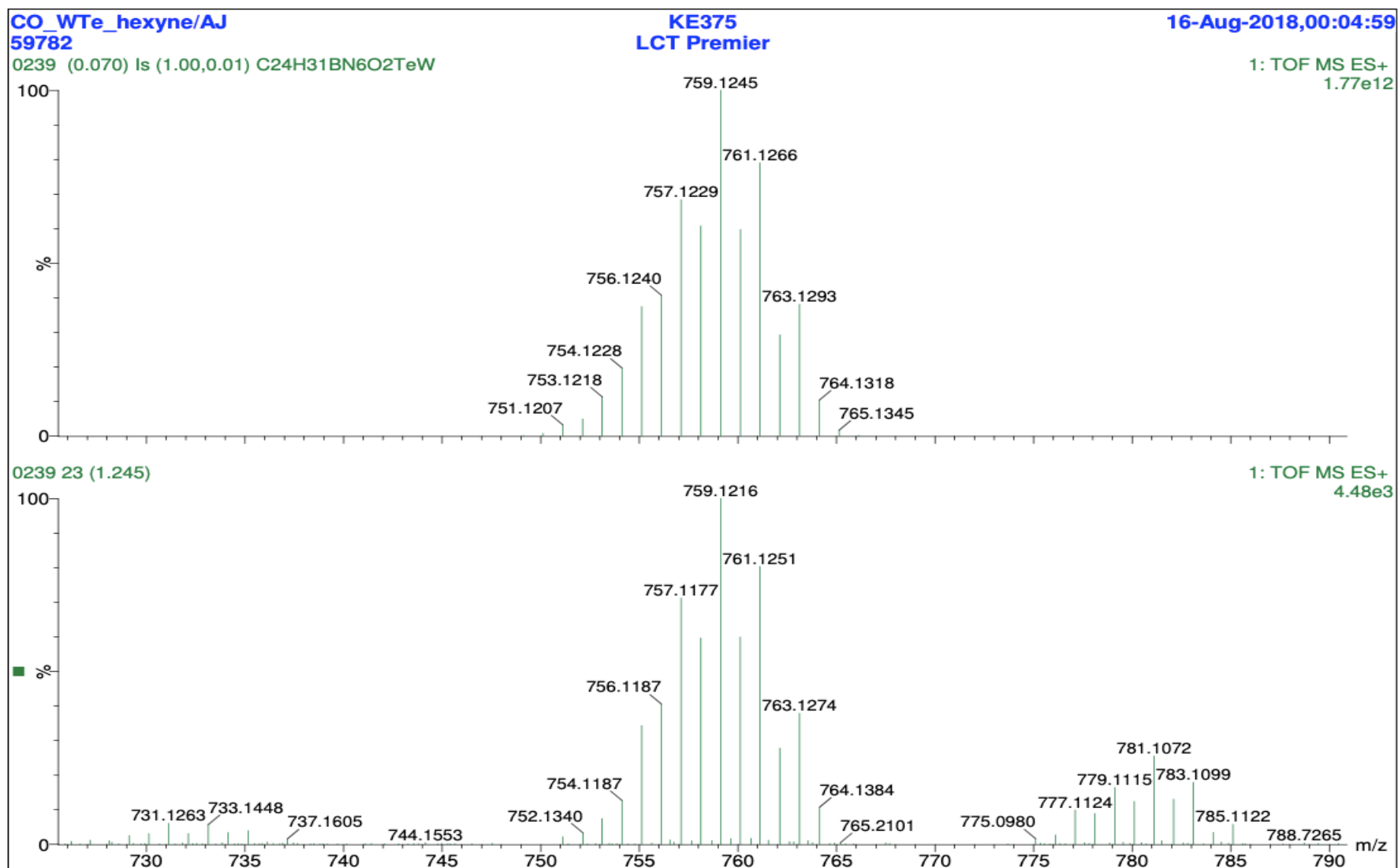


Figure S33. ESI-MS Spectrum of Compound 4d

Figure S34. Isotopic analysis of [M]<sup>+</sup> ion for Compound 4d

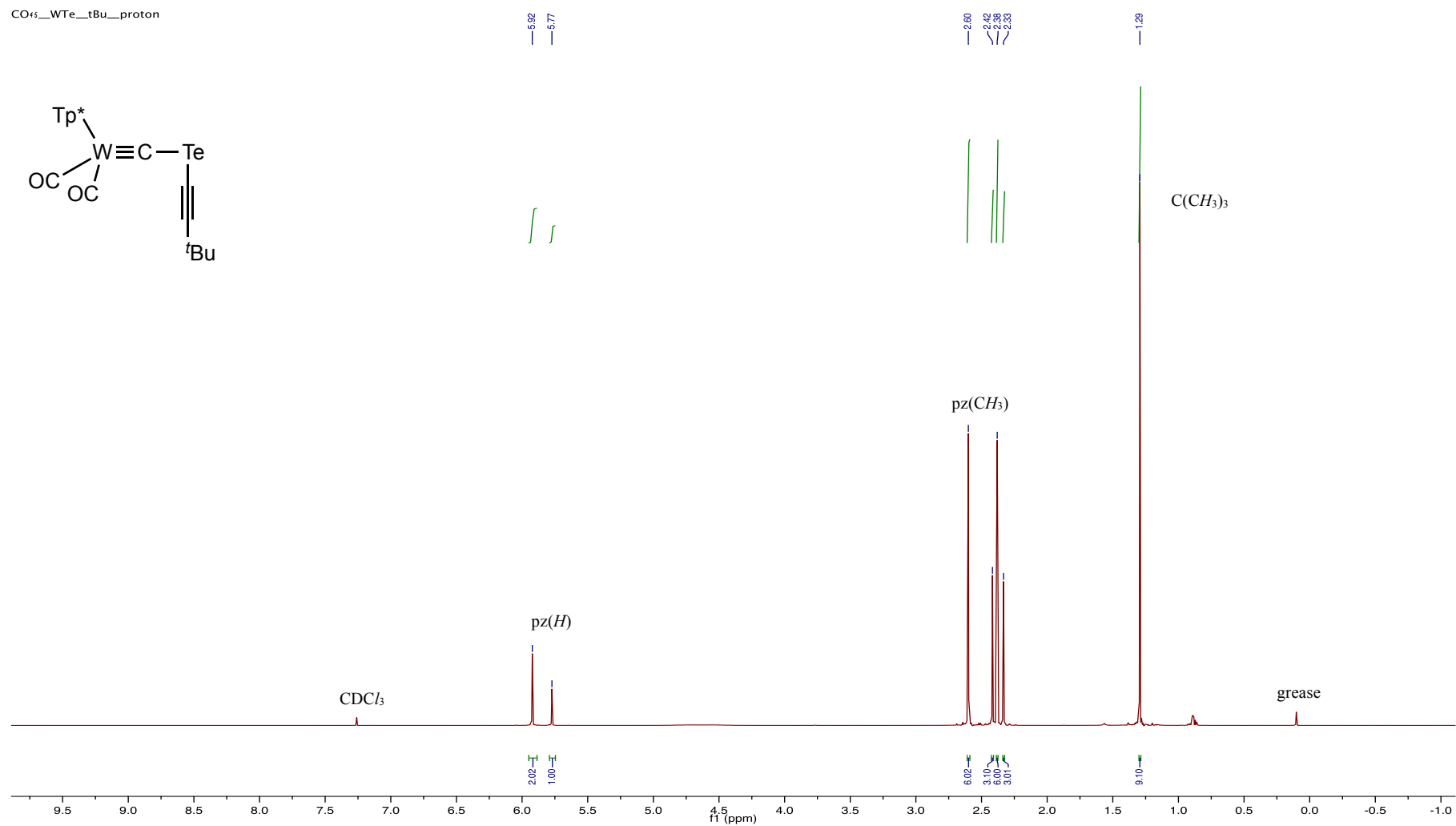


Figure S35.  $^1\text{H}$  NMR spectrum (700 MHz,  $\text{CDCl}_3$ , 25 °C,  $\delta$ ) of compound **4e**.

CO<sub>2</sub>\_WTe\_tBu\_carbon239.45  
238.85  
238.25224.82  
223.86  
223.37153.05  
152.35145.71  
144.77

124.81

107.12  
106.89

-68.31

-41.70

-31.48

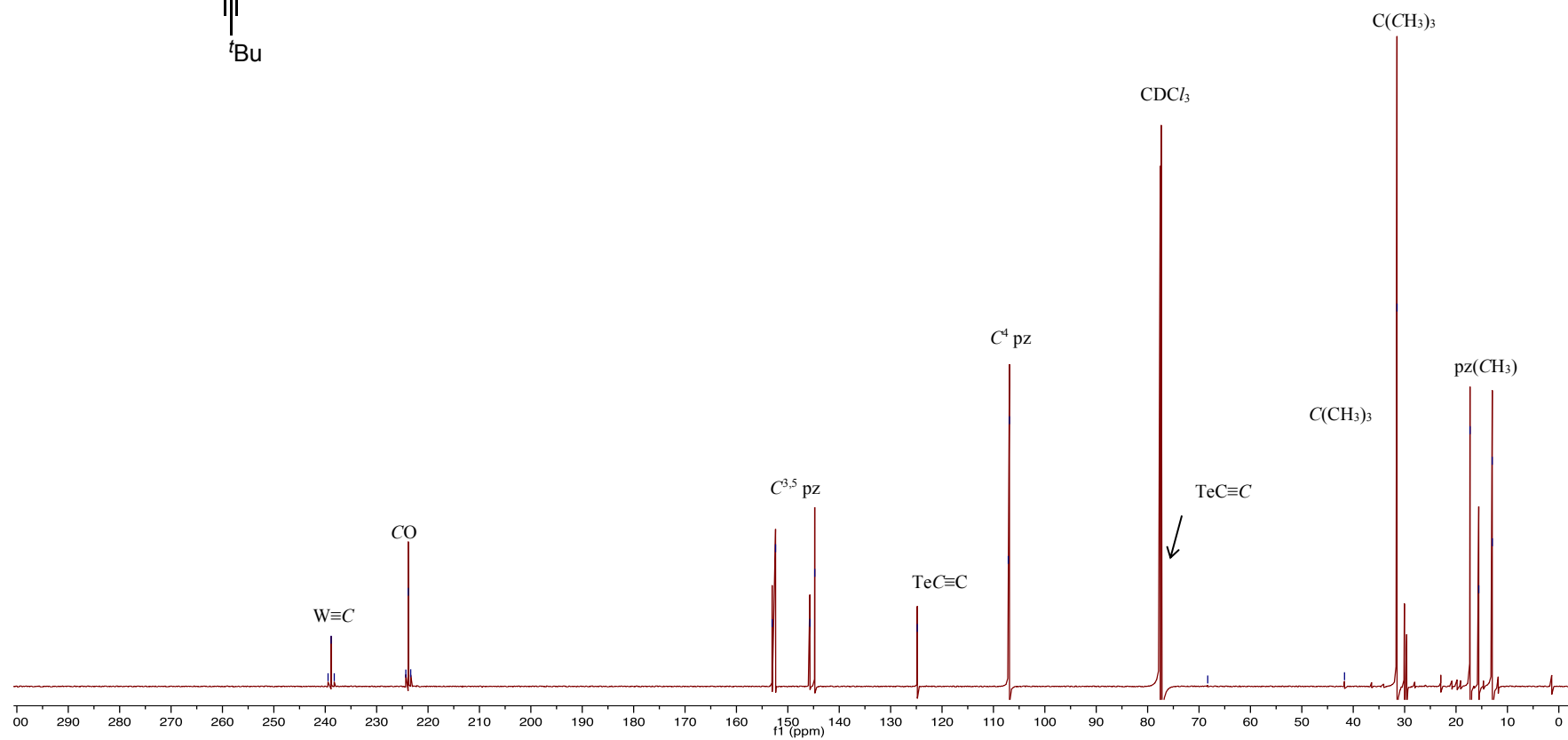
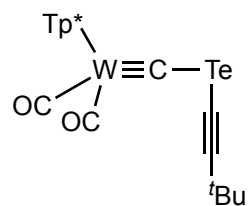
17.29  
15.57  
13.97  
12.95

Figure S36.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (176 MHz,  $\text{CDCl}_3$ , 25 °C,  $\delta$ ) of compound **4e**.

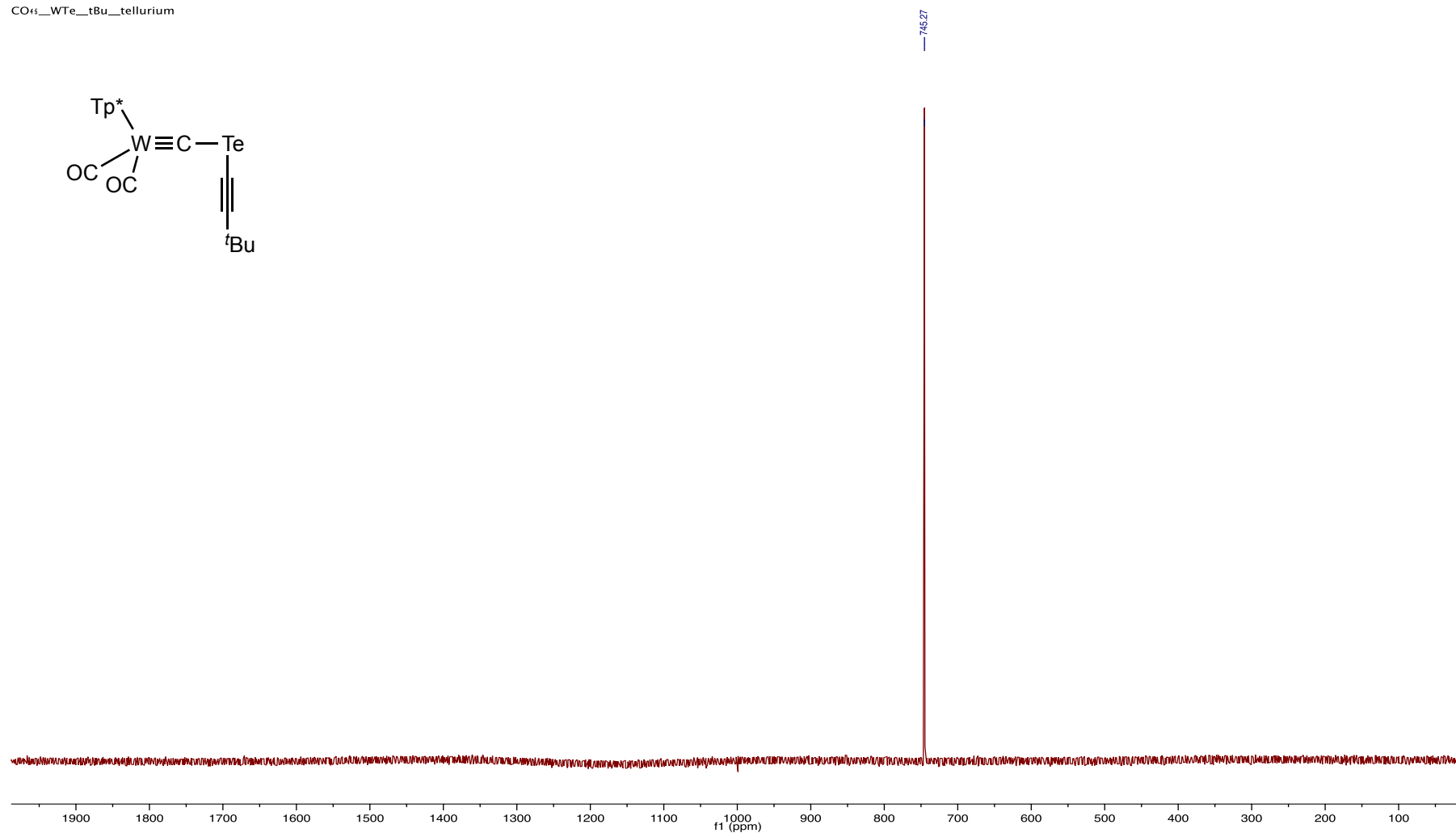
CO<sub>2</sub>\_WTe\_tBu\_tellurium

Figure S37.  $^{125}\text{Te}\{^1\text{H}\}$  NMR spectrum (126 MHz,  $\text{CDCl}_3$ , 25°C,  $\delta$ ) of compound 4e.

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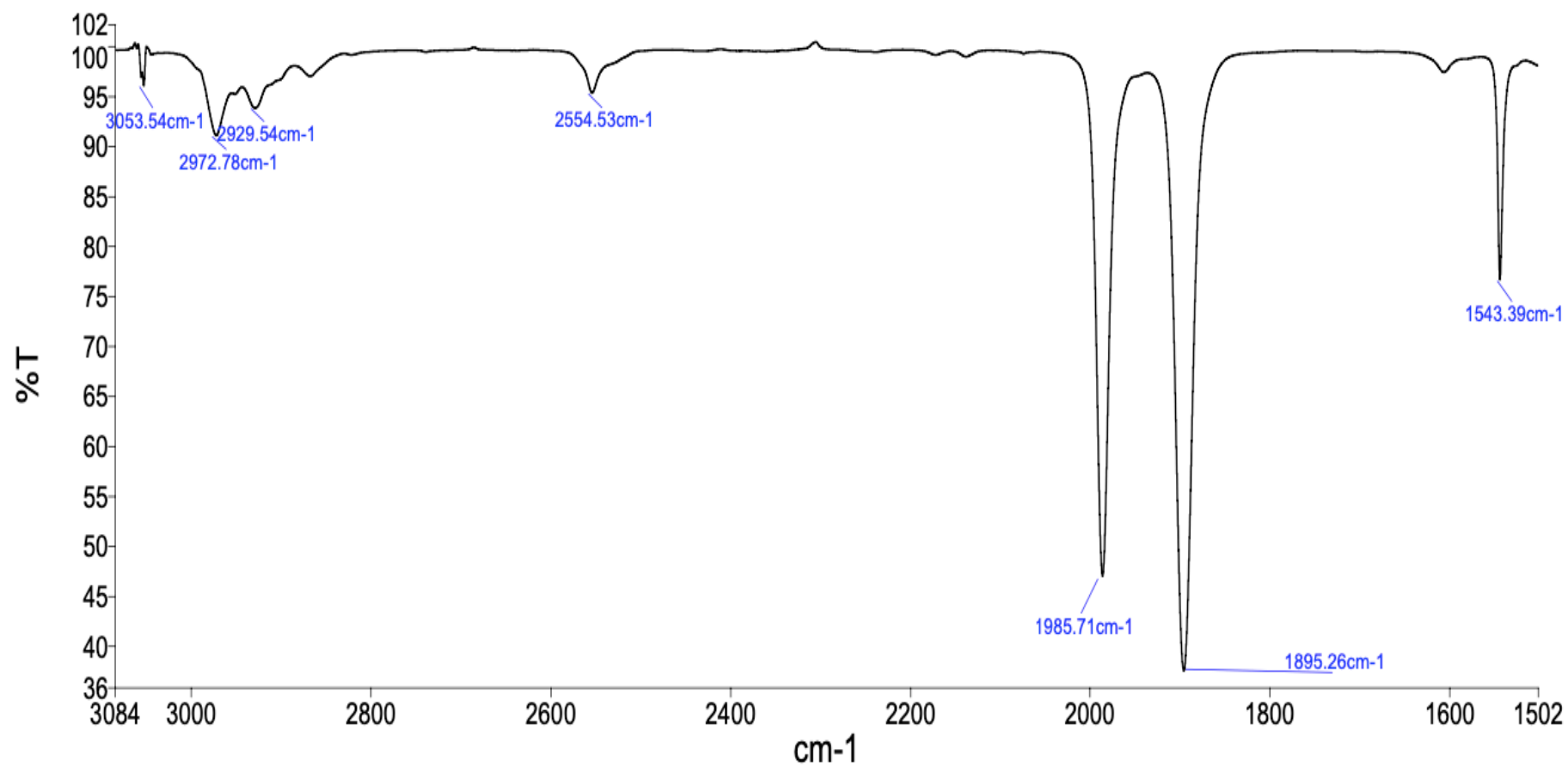


Figure S38. Infrared spectrum ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ) of Compound 4e

59963 #22-40 RT: 0.38-0.70 AV: 19 NL: 2.11E7  
T: FTMS + p ESI Full ms [150.0000-2000.0000]

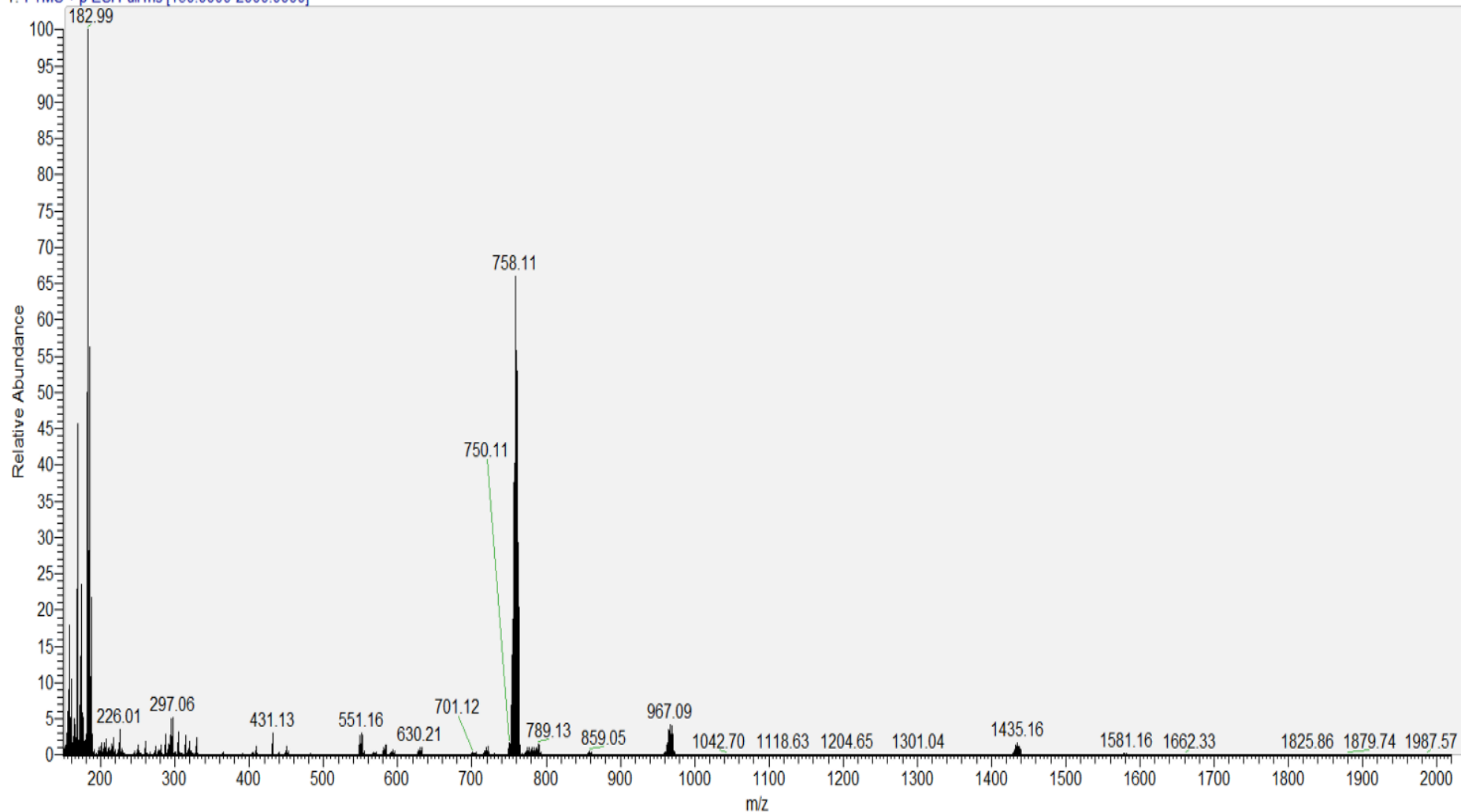
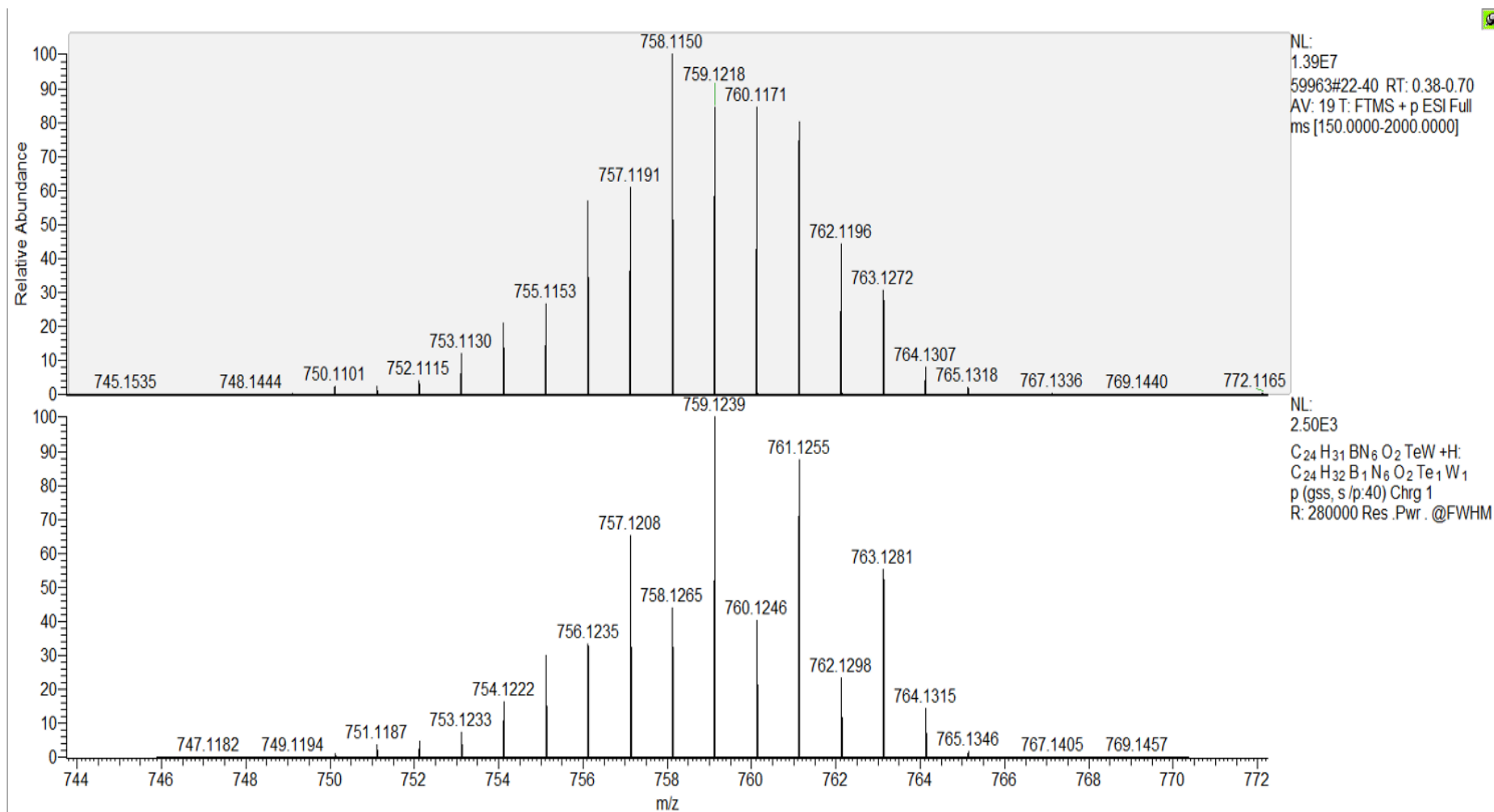


Figure S39. ESI-MS Spectrum of Compound 4e



Observed versus simulated spectrum for detected target formulas ( $[M+H]^+$  ion)Figure S40. Isotopic analysis of  $[M]^+$  ion for Compound 4e

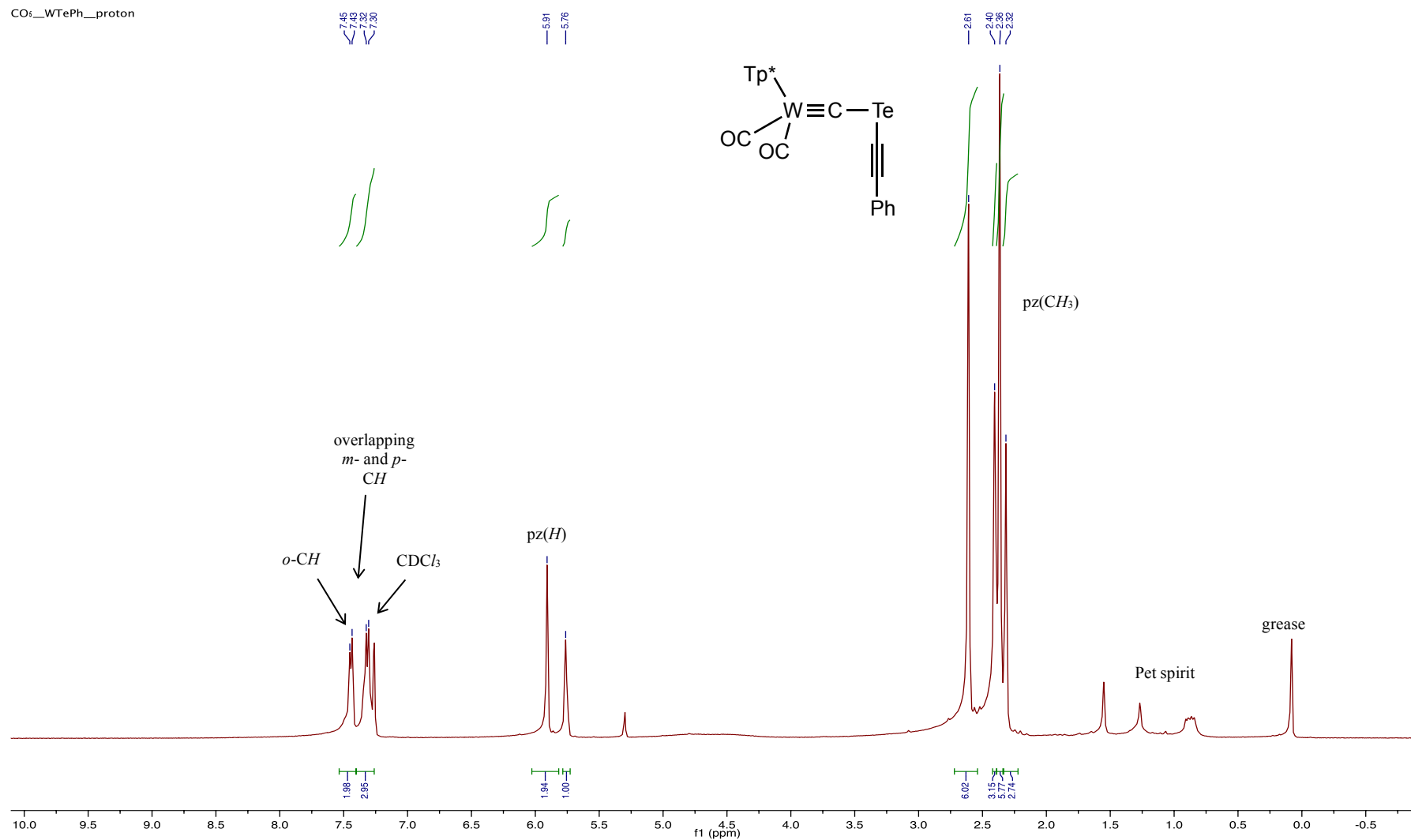


Figure S41. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 25°C, δ) of compound 4f.

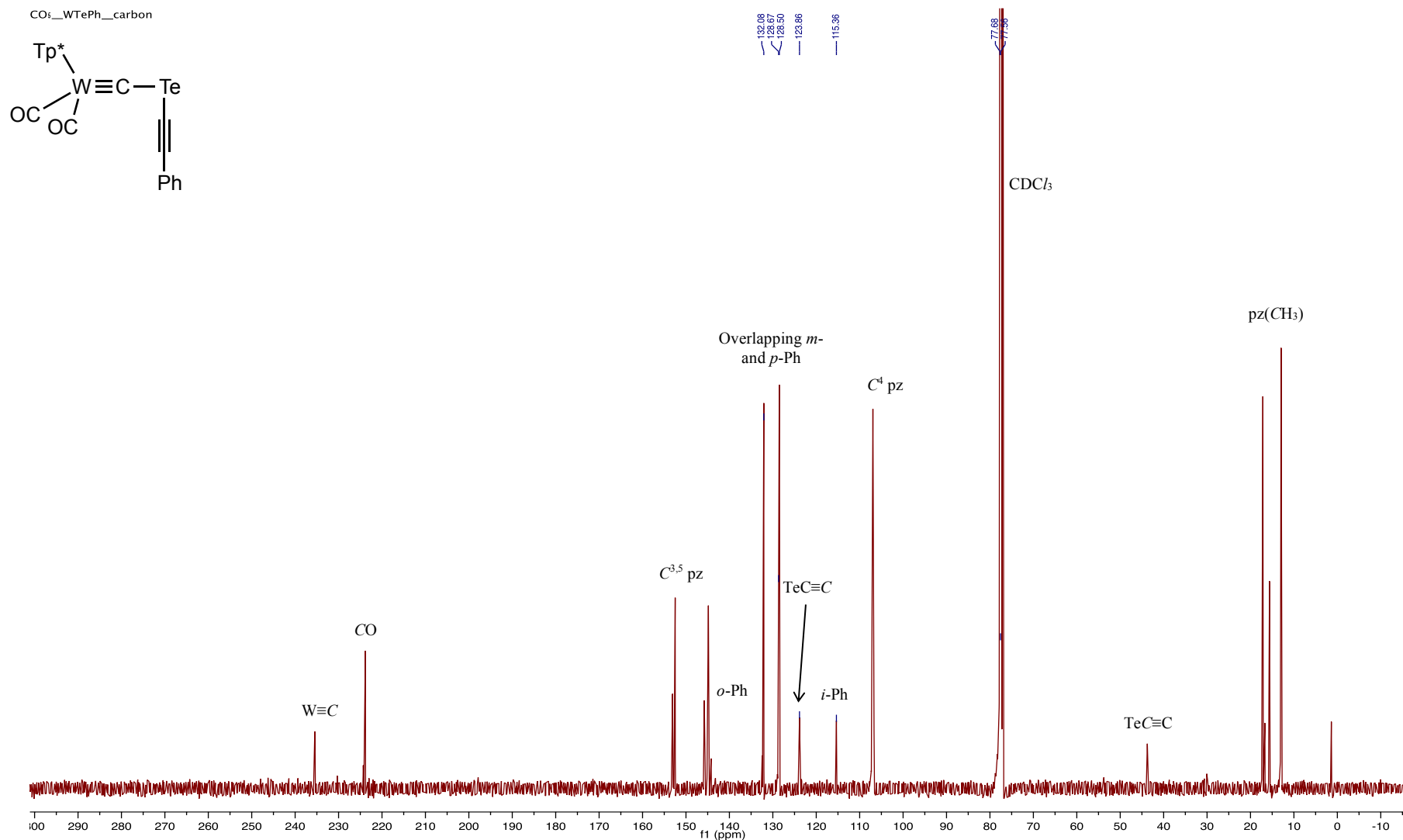


Figure S42. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (101 MHz, CDCl<sub>3</sub>, 25 °C, δ) of compound **4f**.

CO<sub>2</sub>\_WTePh\_tellurium

758.95

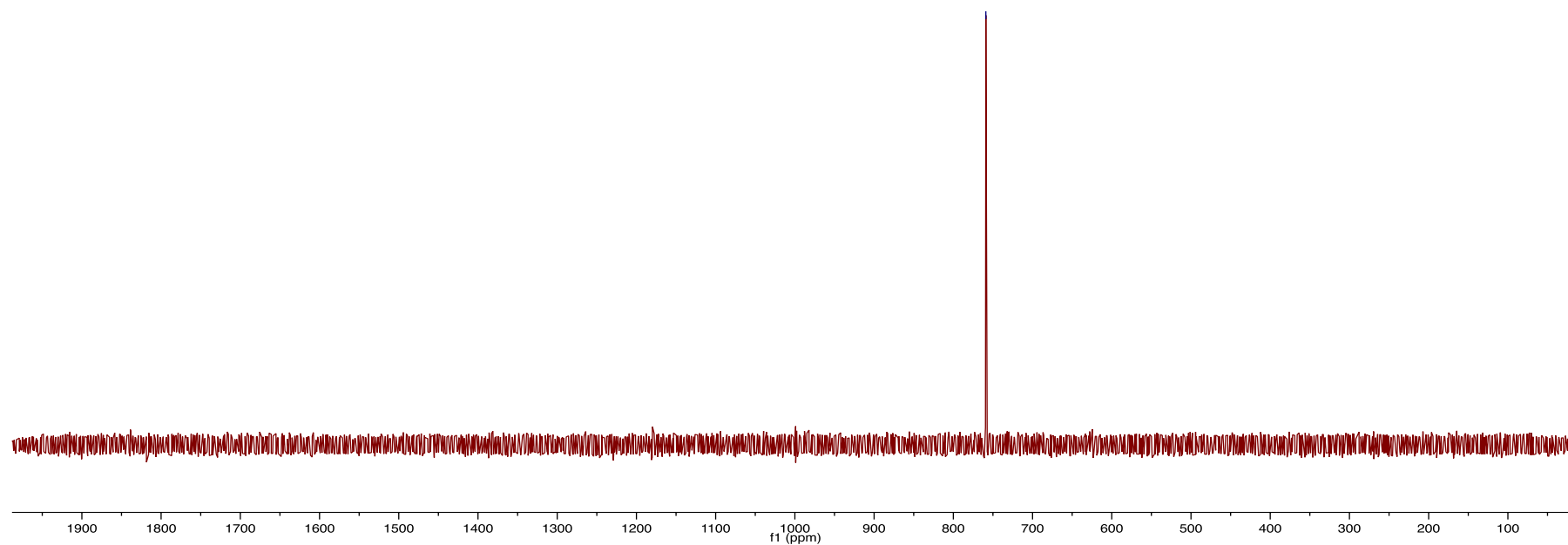
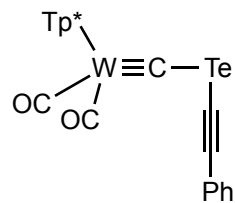


Figure S43. <sup>125</sup>Te{<sup>1</sup>H} NMR spectrum (126 MHz, CDCl<sub>3</sub>, 25 °C, δ) of compound 4f.

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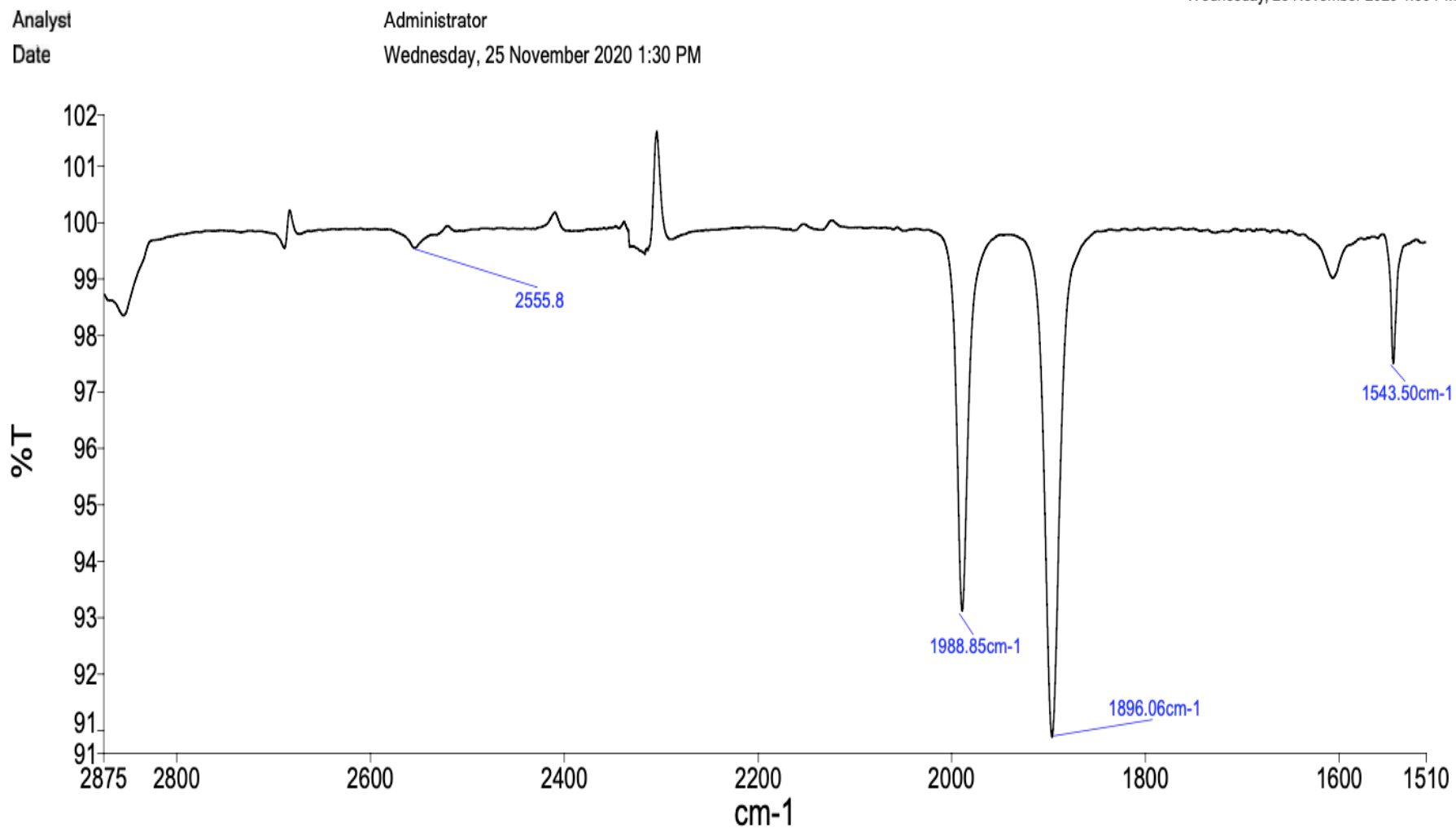


Figure S44. Infrared spectrum ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ) of Compound 4f

58912 #8-13 RT: 0.22-0.38 AV: 6 NL: 1.15E6

T: FTMS + p ESI Full ms [50.00-2000.00]

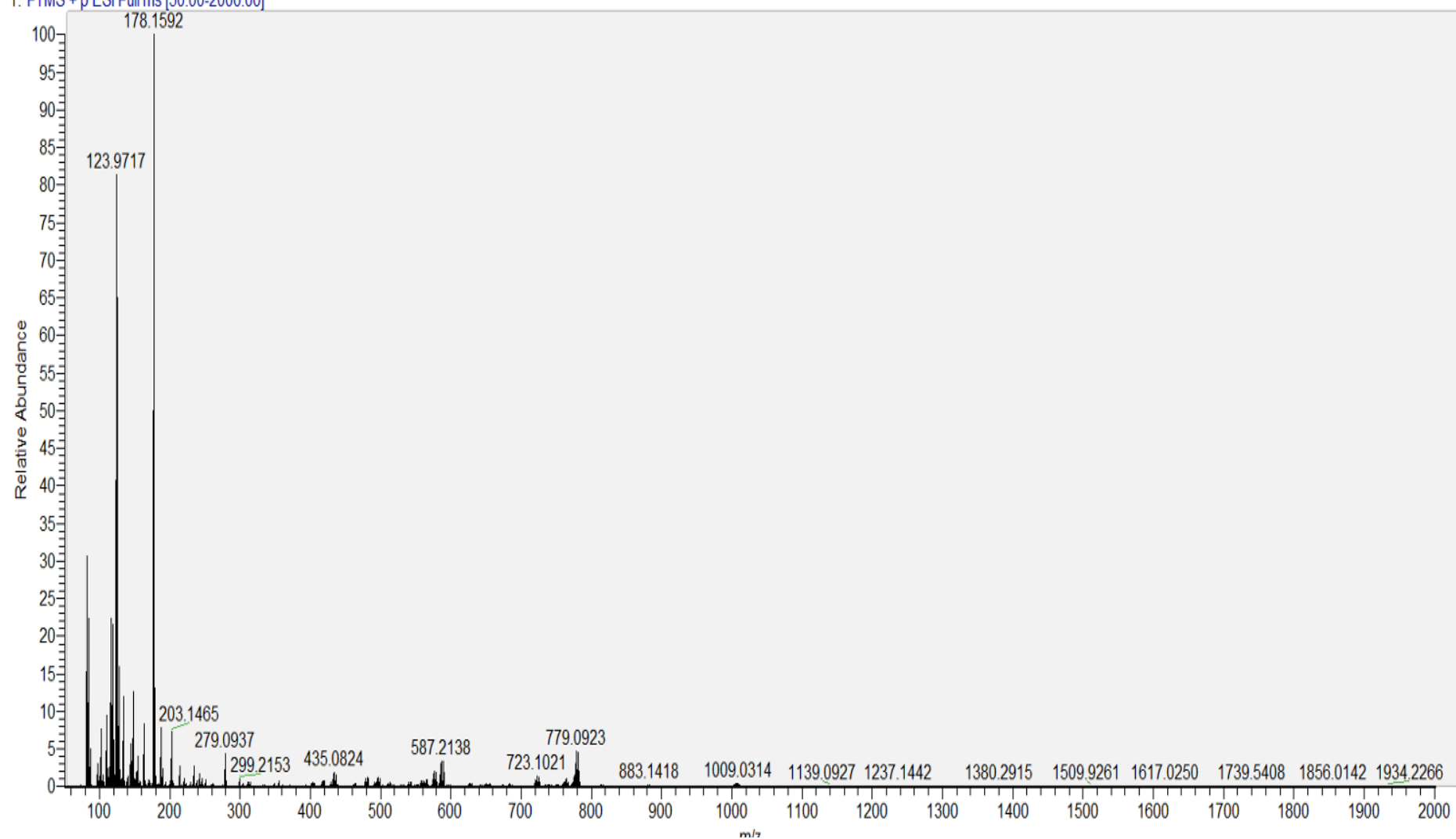
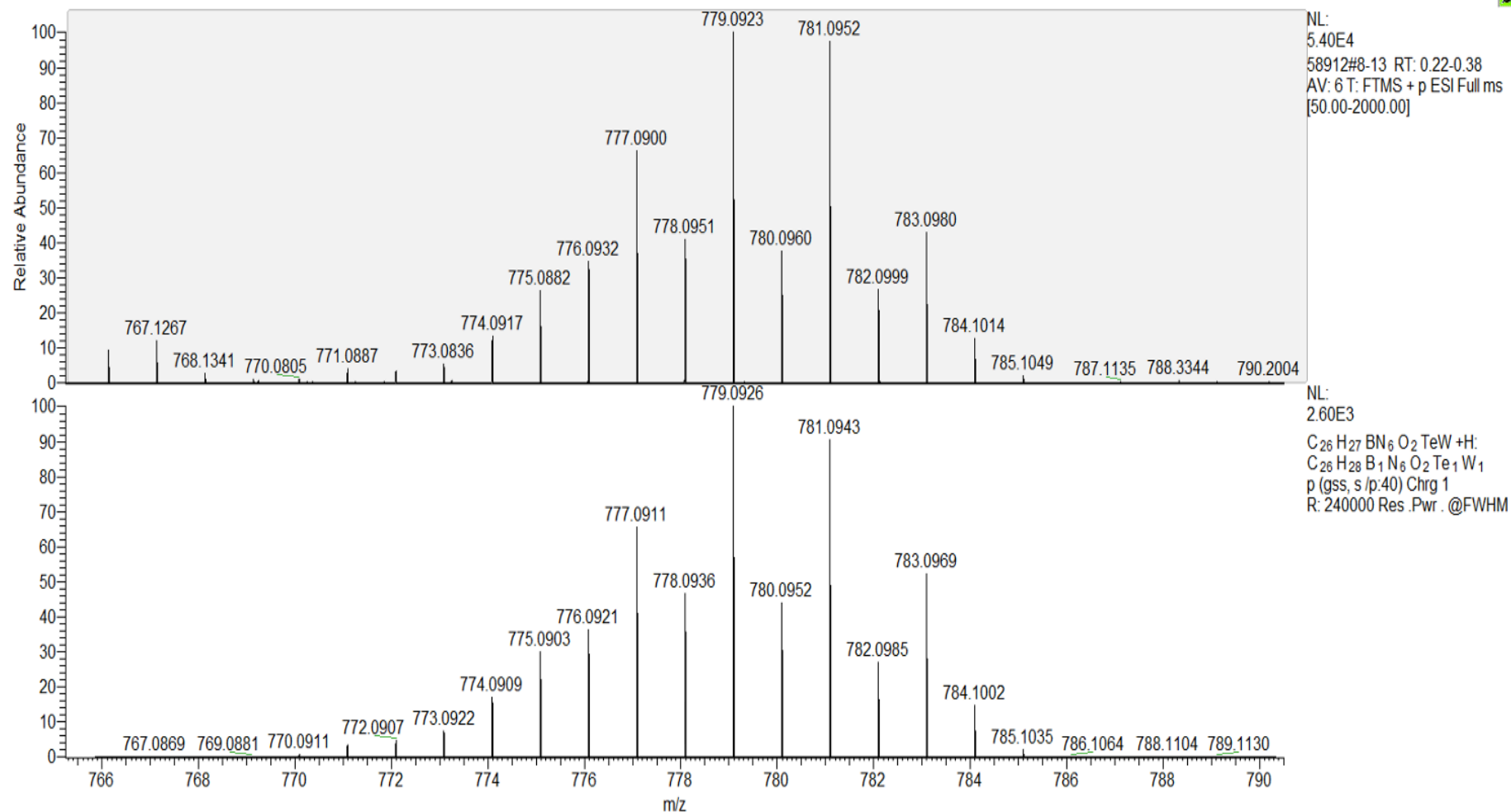
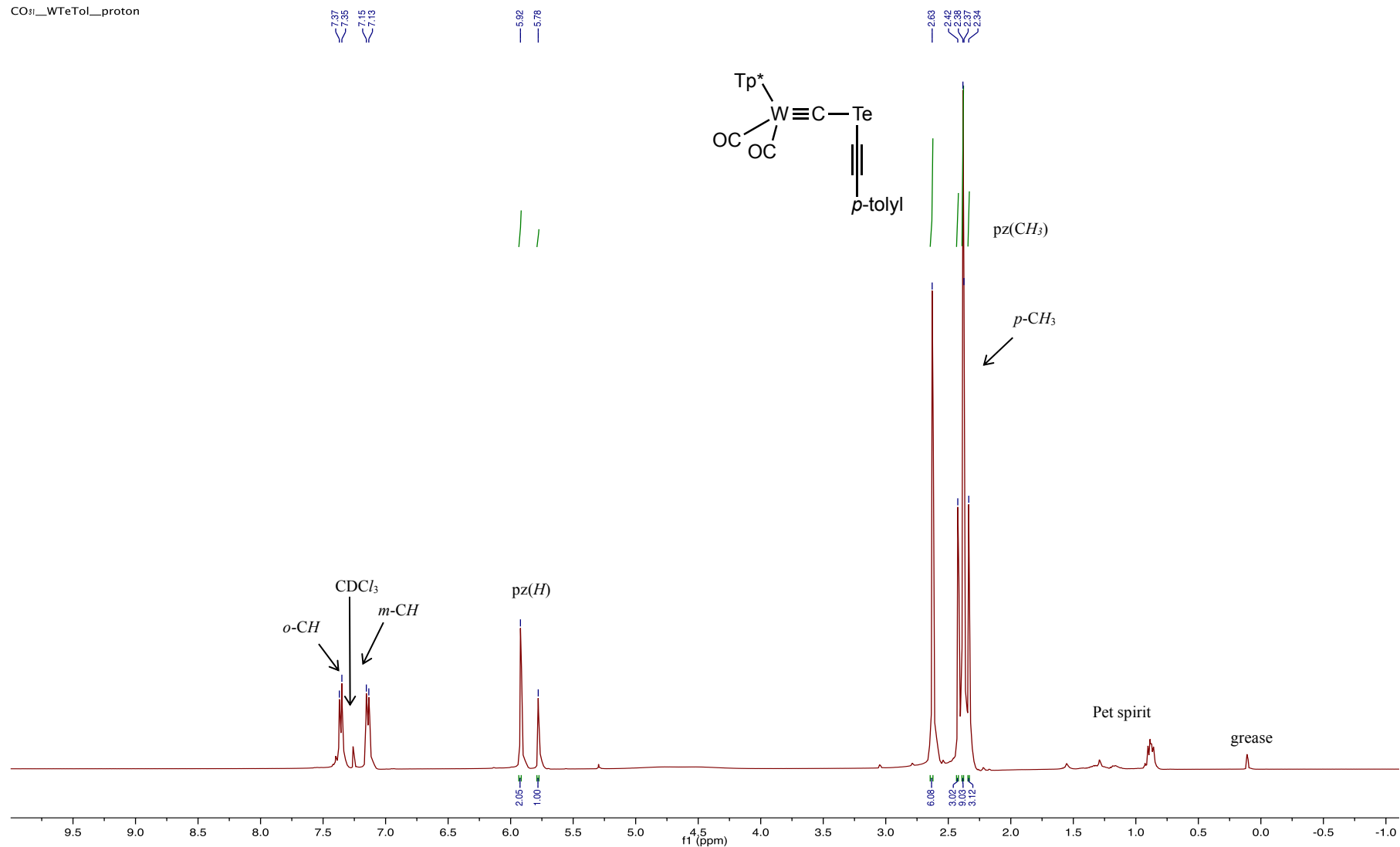


Figure S45. ESI-MS Spectrum of Compound 4f

Observed versus simulated spectrum for detected target formulas ([M+H]<sup>+</sup> ion)Figure S46. Isotopic analysis of [M]<sup>+</sup> ion for Compound 4f

CO<sub>2</sub>\_WTeTol\_proton**Figure S47.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 25 °C, δ) of compound **4g**.



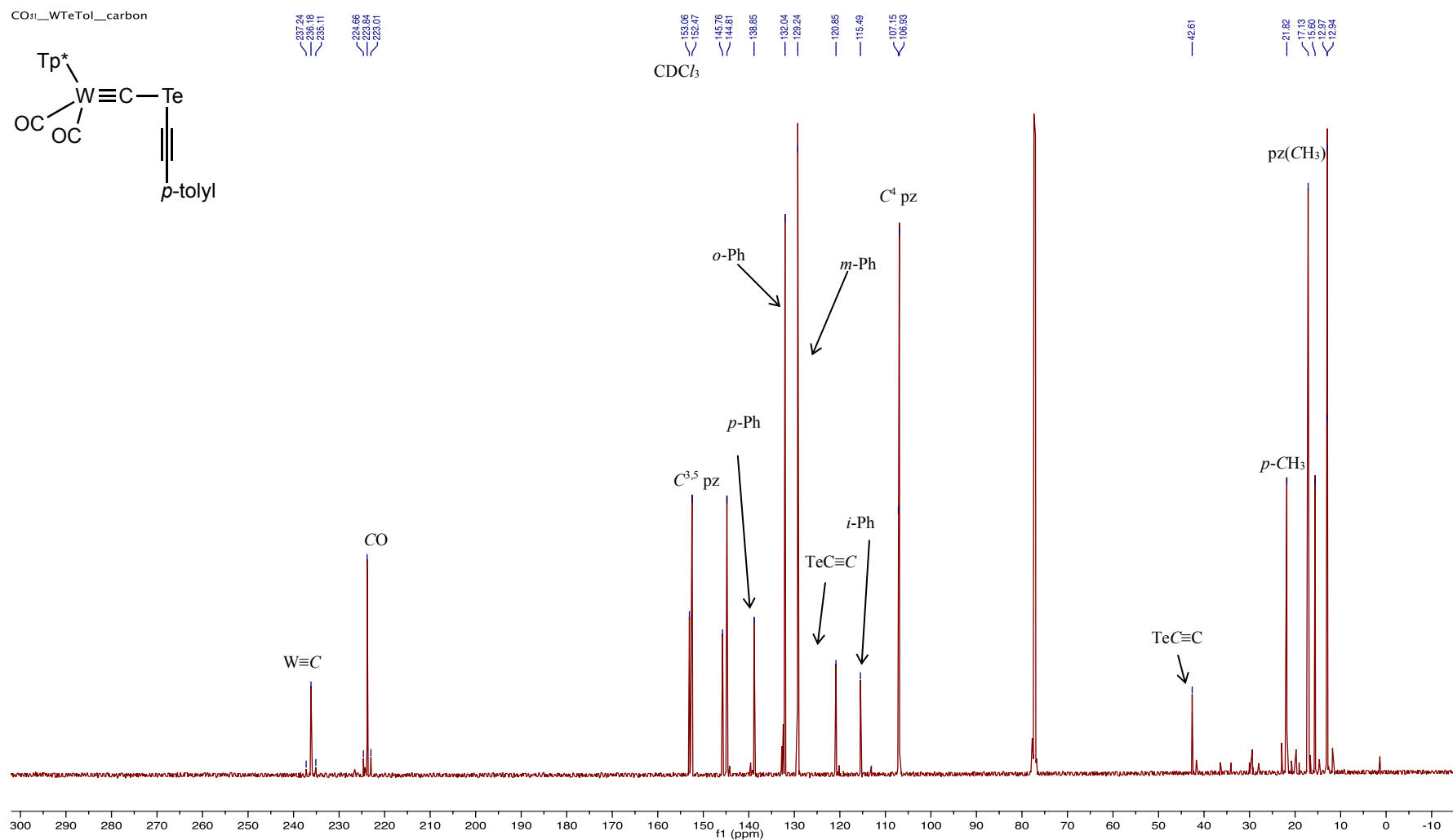


Figure 48. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (101 MHz, CDCl<sub>3</sub>, 25°C, δ) of compound 4g.

CO<sub>2</sub>\_WTeTo\_tellurium

798.27

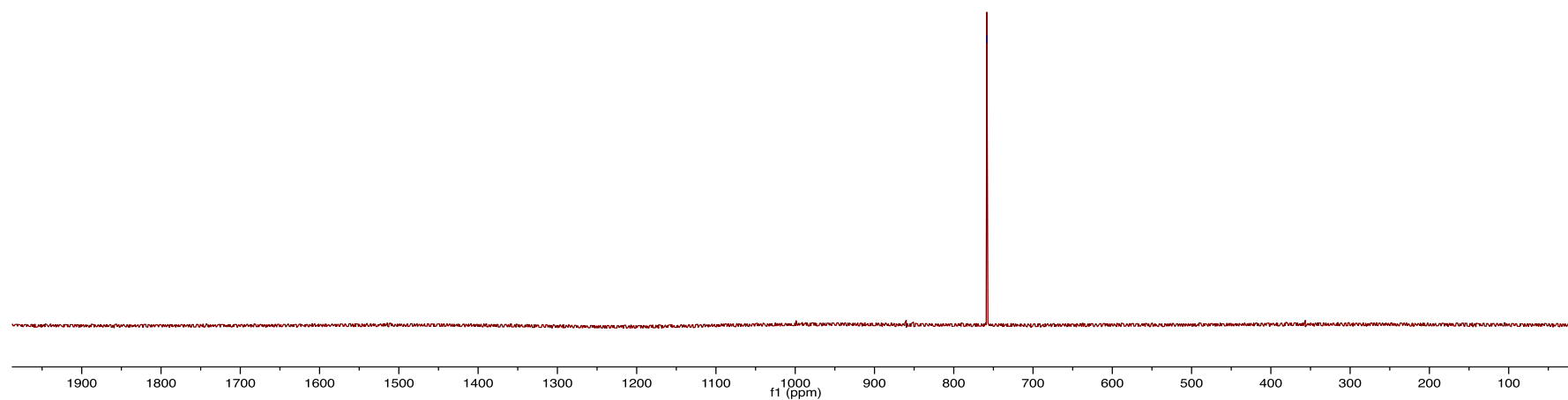
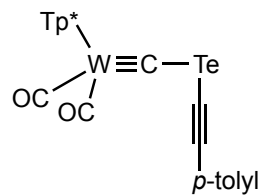


Figure S49. <sup>125</sup>Te{<sup>1</sup>H} NMR spectrum (126 MHz, CDCl<sub>3</sub>, 25 °C, δ) of compound 4g.

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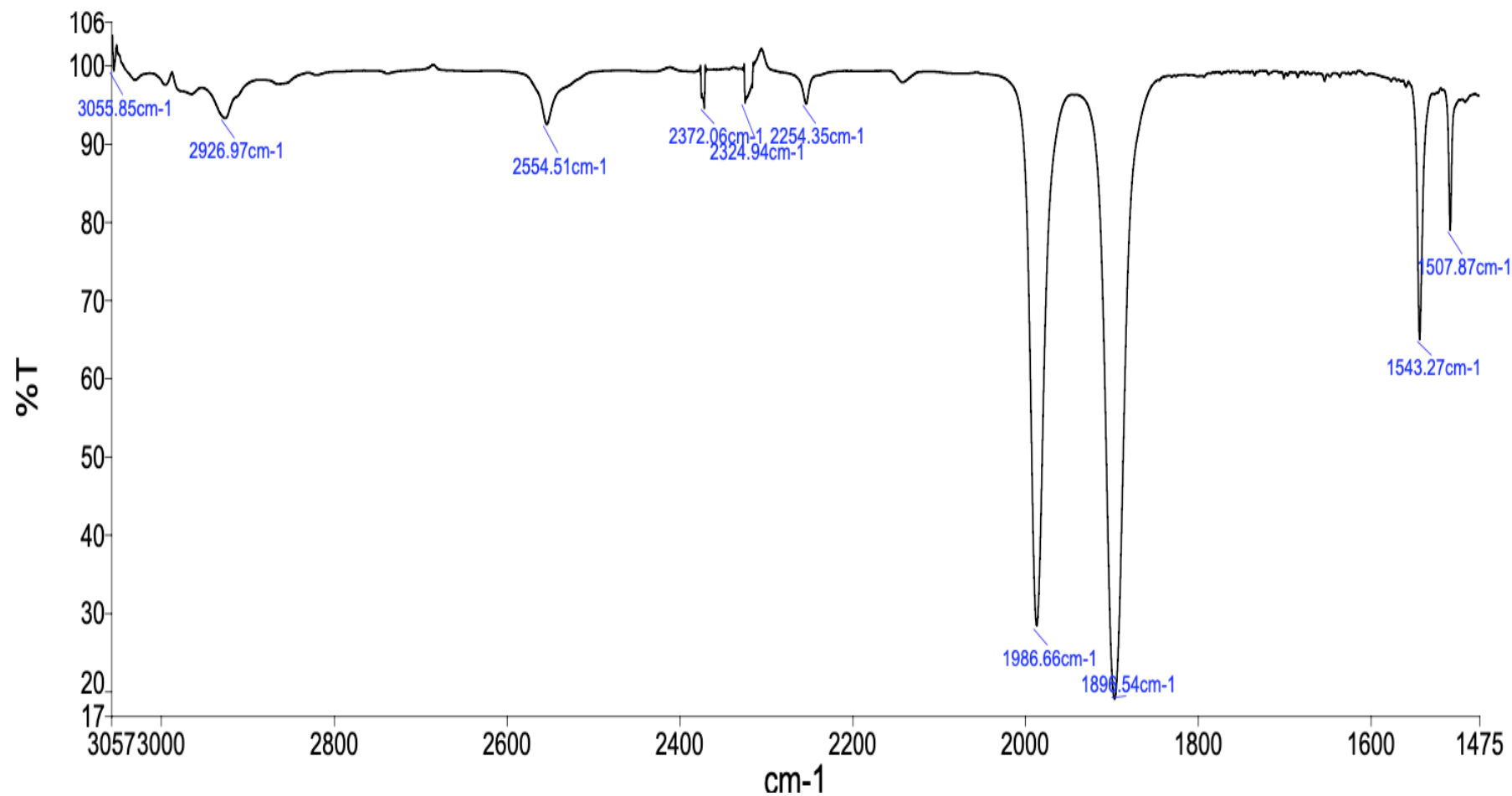


Figure S50. Infrared spectrum (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>) of Compound 4g

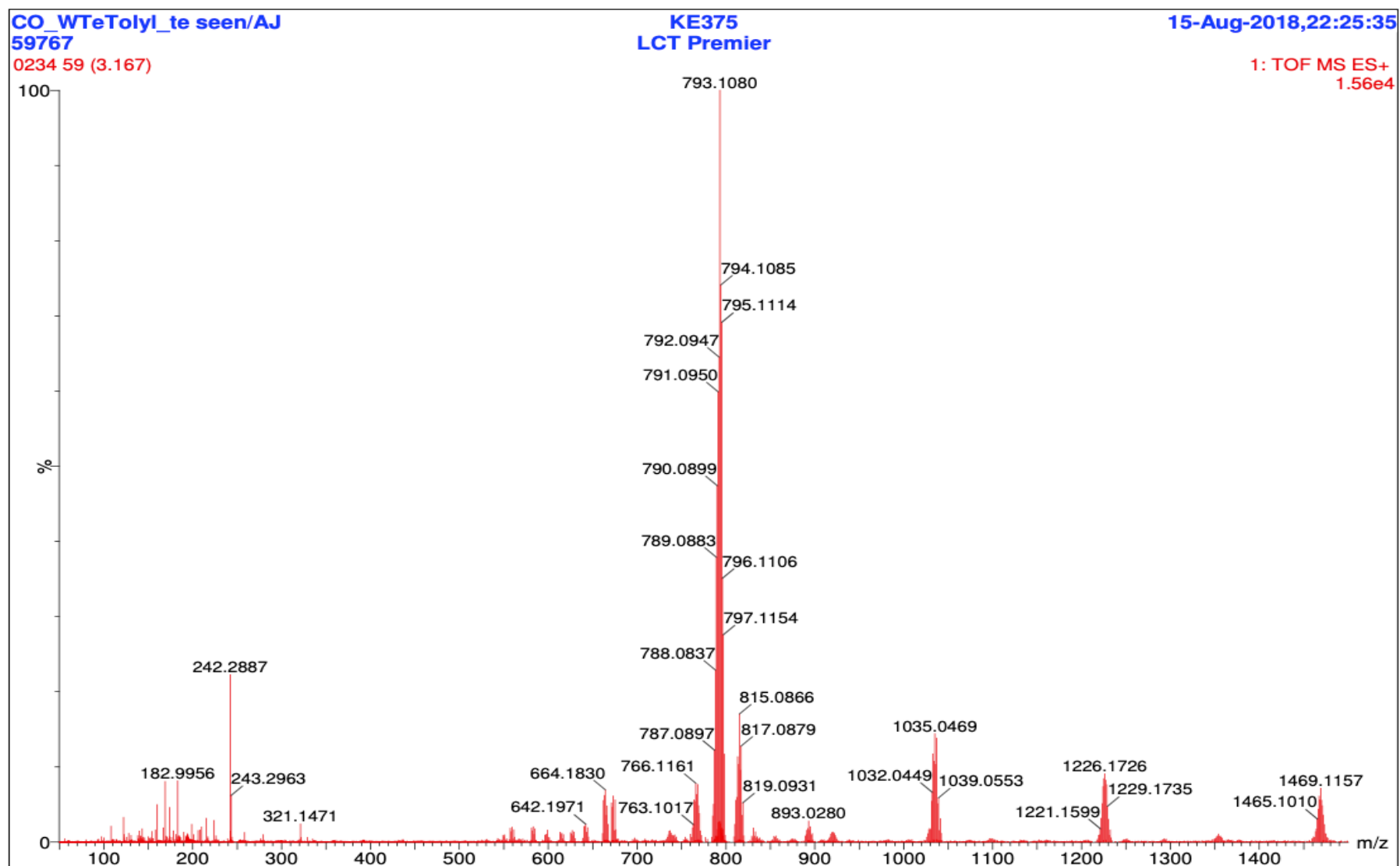
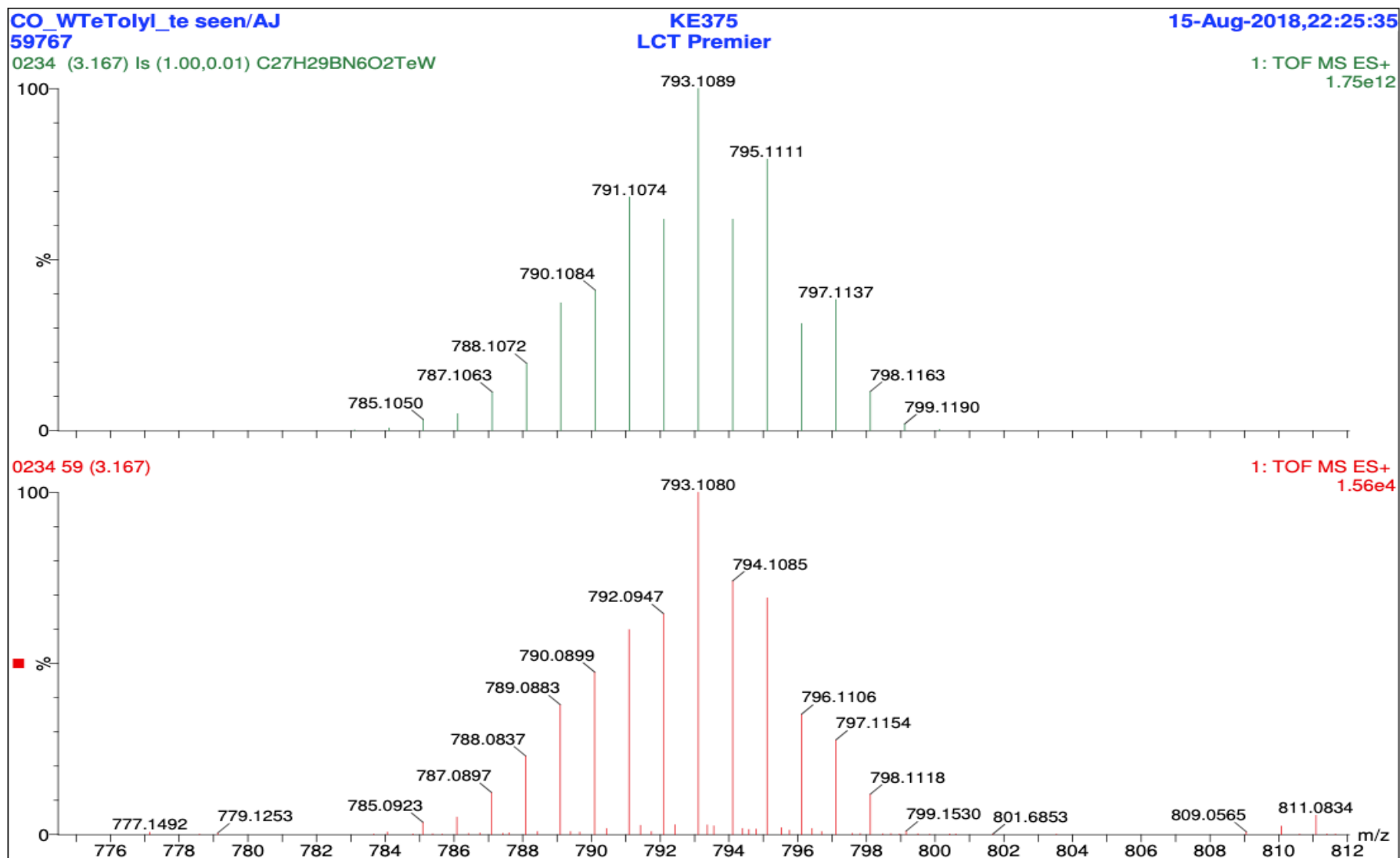


Figure S51. ESI-MS Spectrum of Compound 4g

Figure S52. Isotopic analysis of [M]<sup>+</sup> ion for Compound 4g

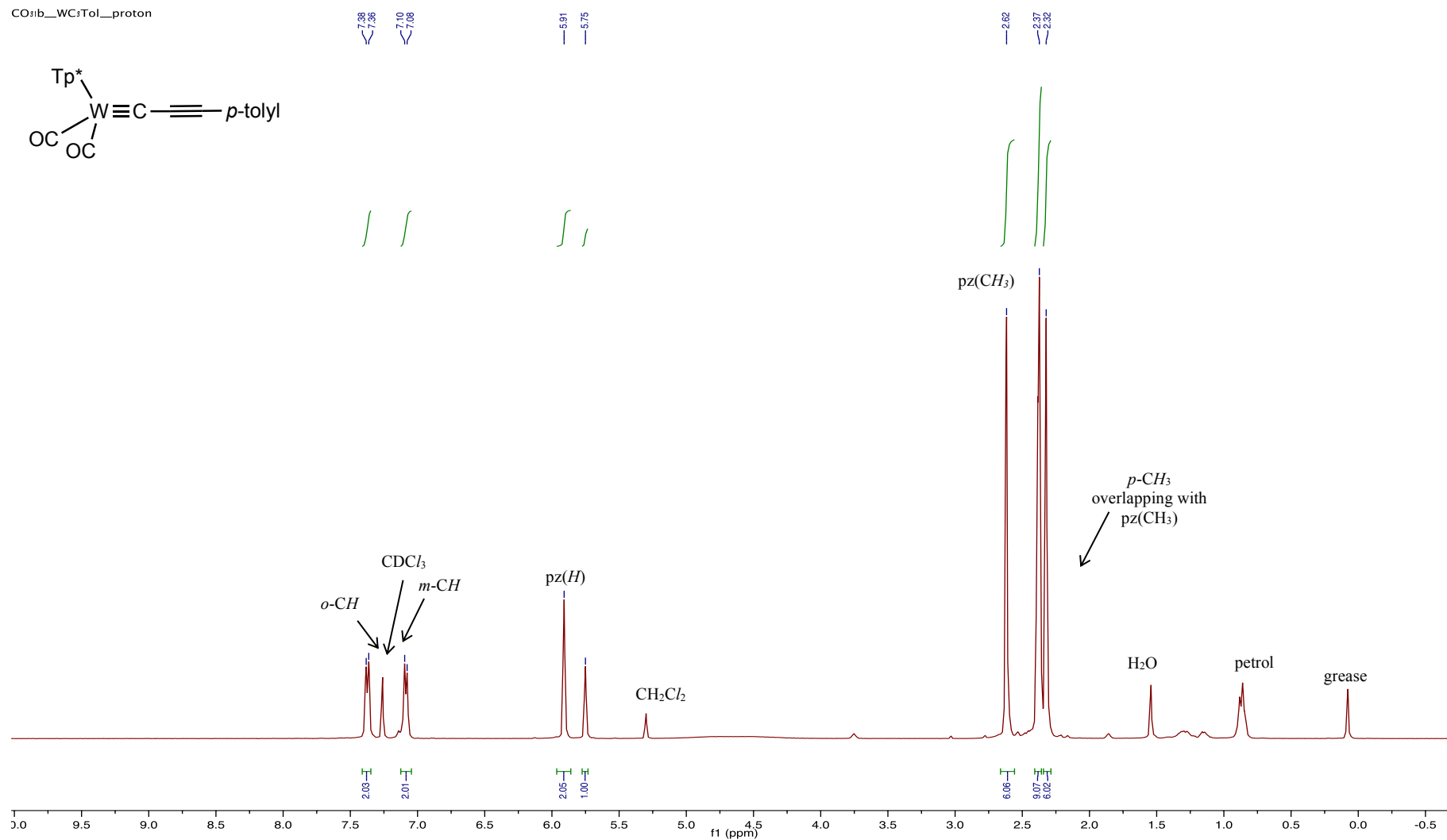


Figure S53.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 25 °C,  $\delta$ ) of compound **6g**.

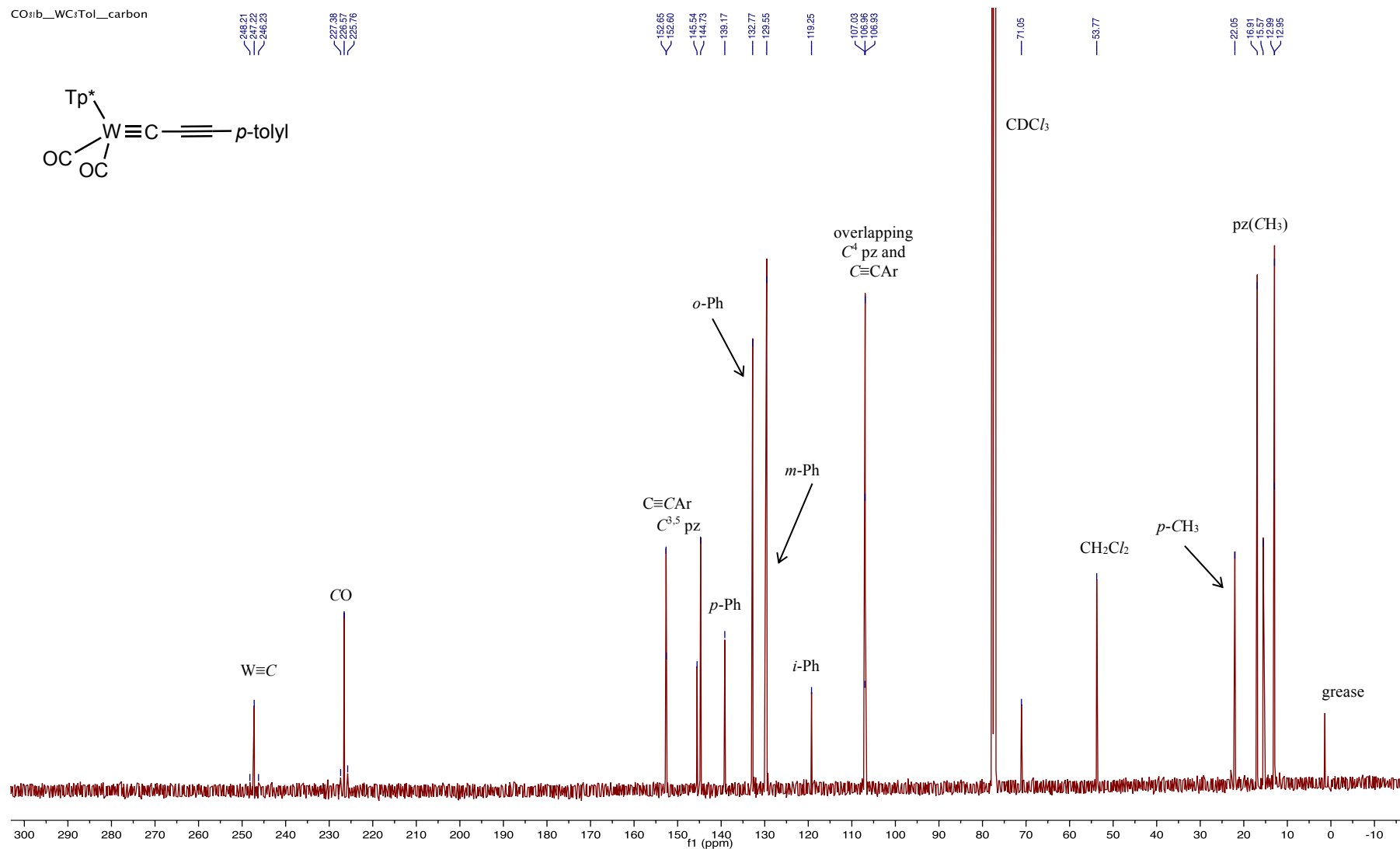
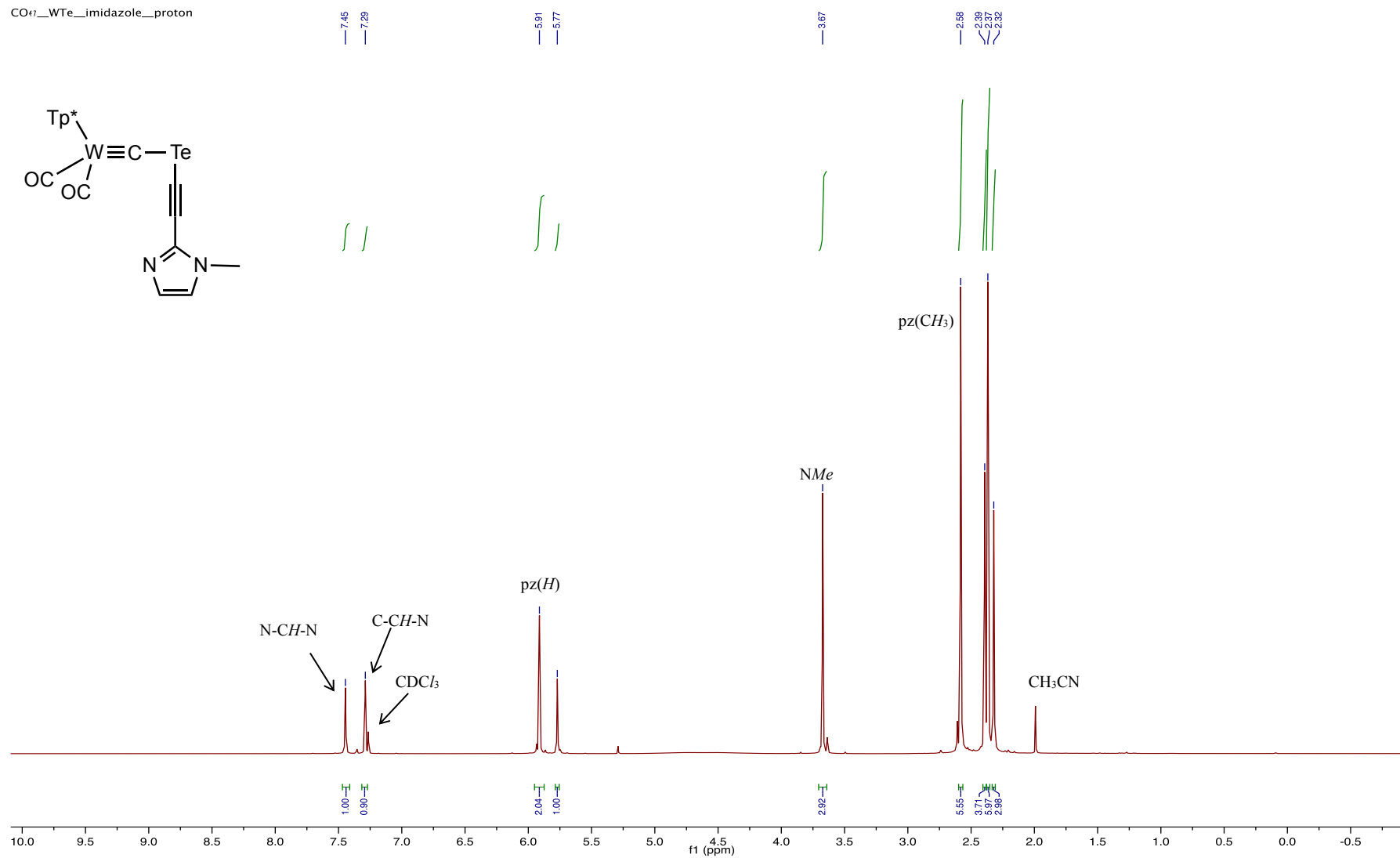
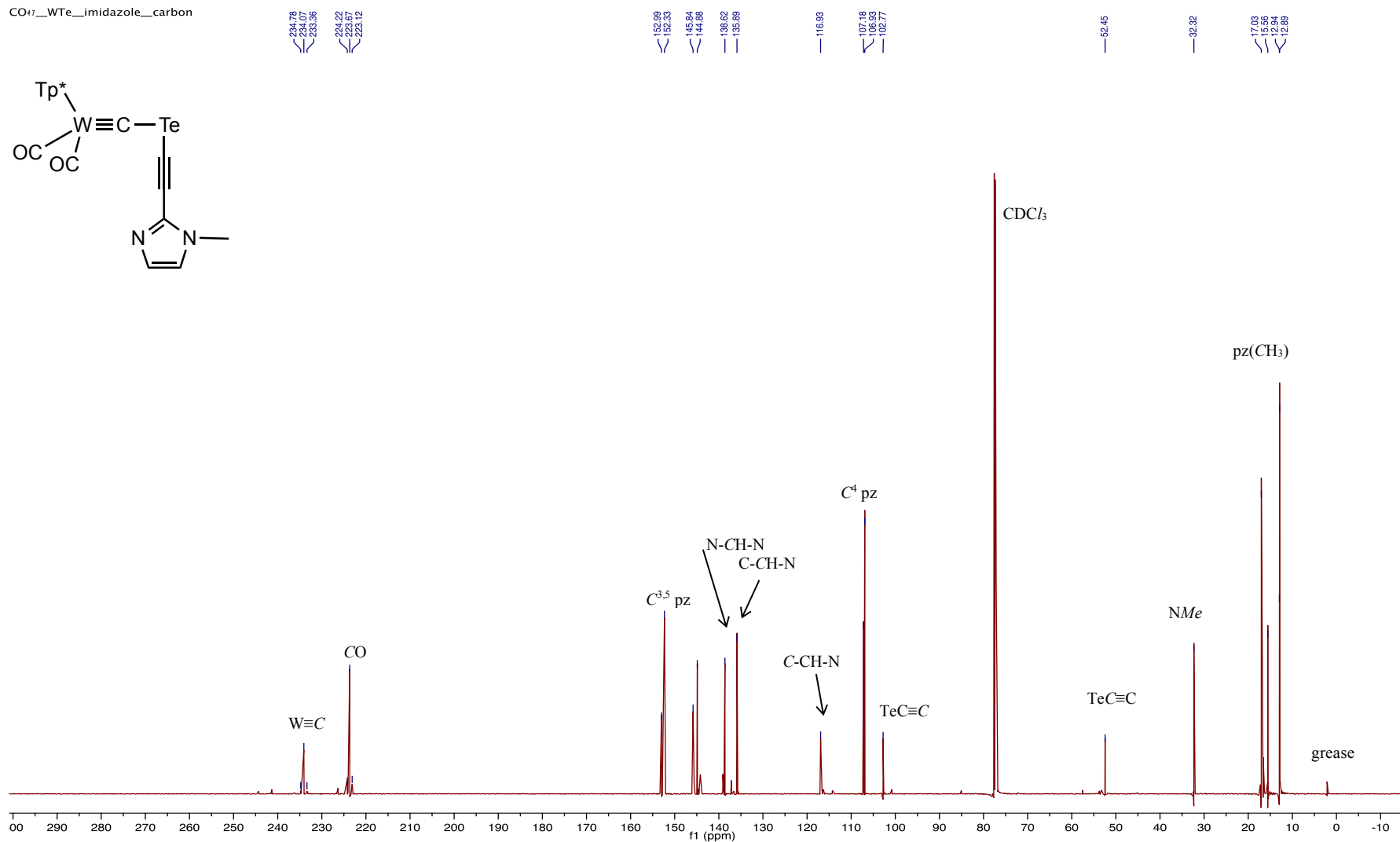


Figure S54. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (101 MHz, CDCl<sub>3</sub>, 25°C, δ) of compound **6g**.

CO<sub>2</sub>\_WTe\_imidazole\_protonFigure S55. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 25 °C, δ) of compound 4h.



CO17\_WTe\_imidazole\_carbon

Figure S56.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (151 MHz,  $\text{CDCl}_3$ , 25°C,  $\delta$ ) of compound 4h.

CO<sub>2</sub>\_WTe\_imidazole\_tellurium

— 761.30

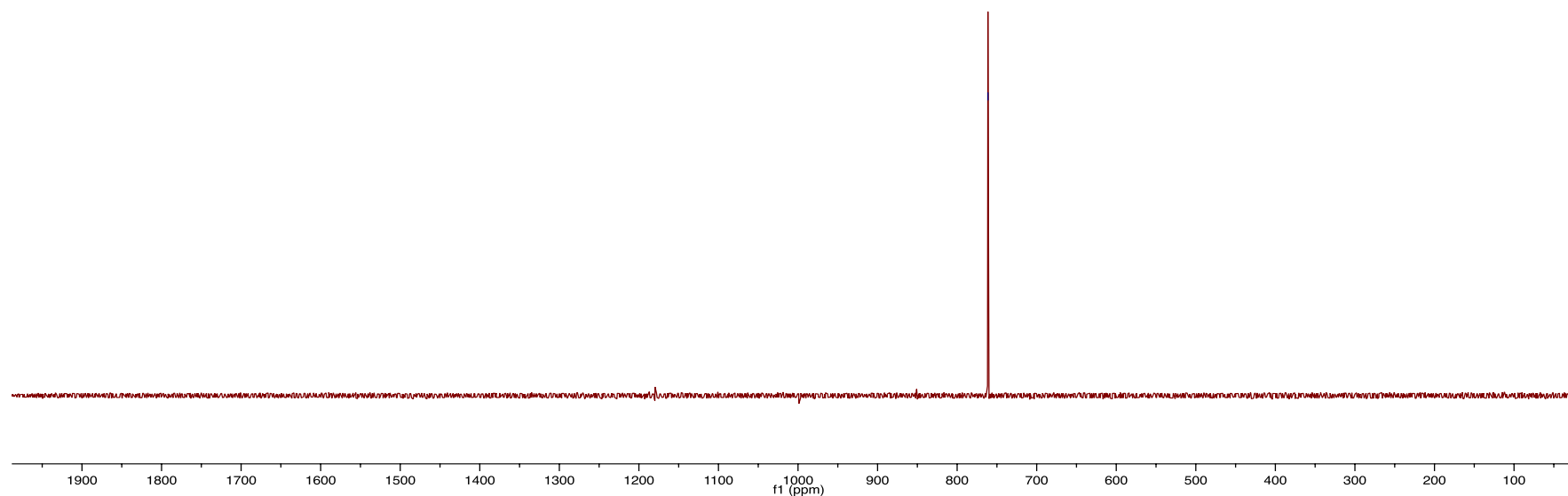
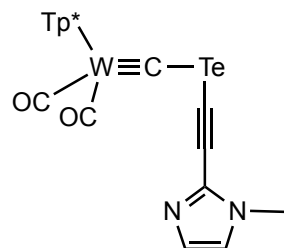


Figure S57. <sup>125</sup>Te(<sup>1</sup>H) NMR spectrum (126 MHz, CDCl<sub>3</sub>, 25 °C, δ) of compound 4h.

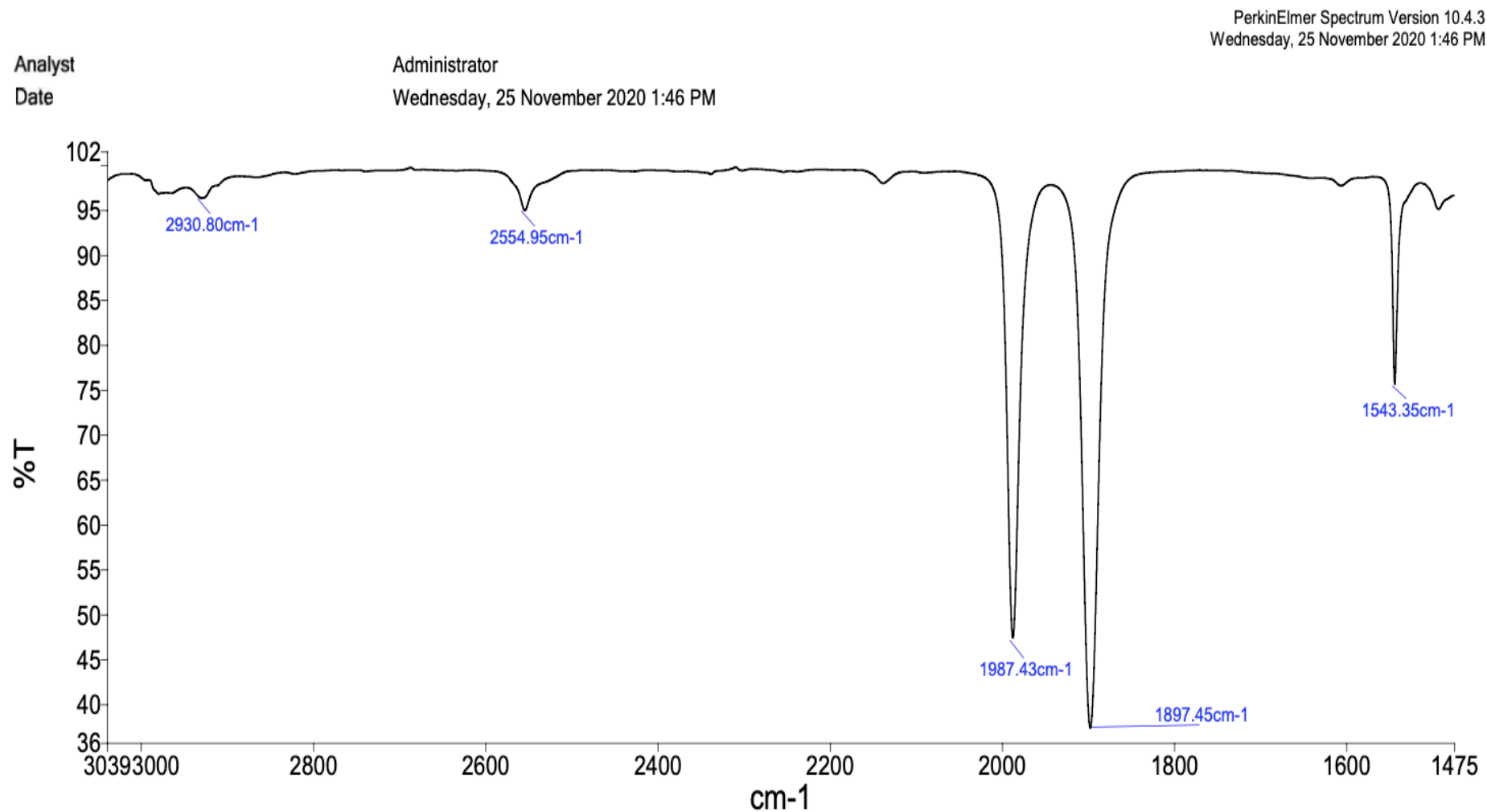


Figure S58. Infrared spectrum (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>) of Compound 4h

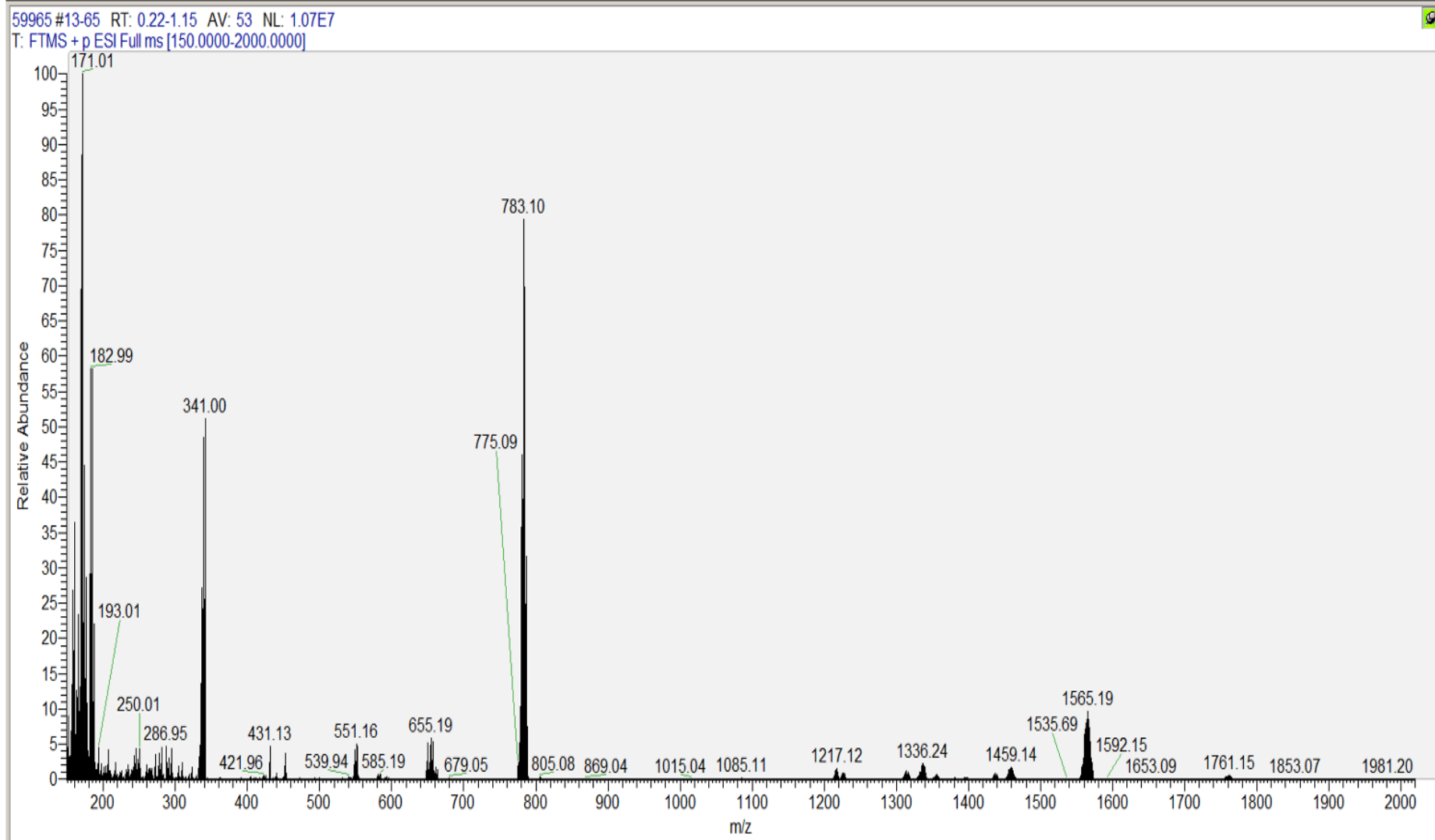
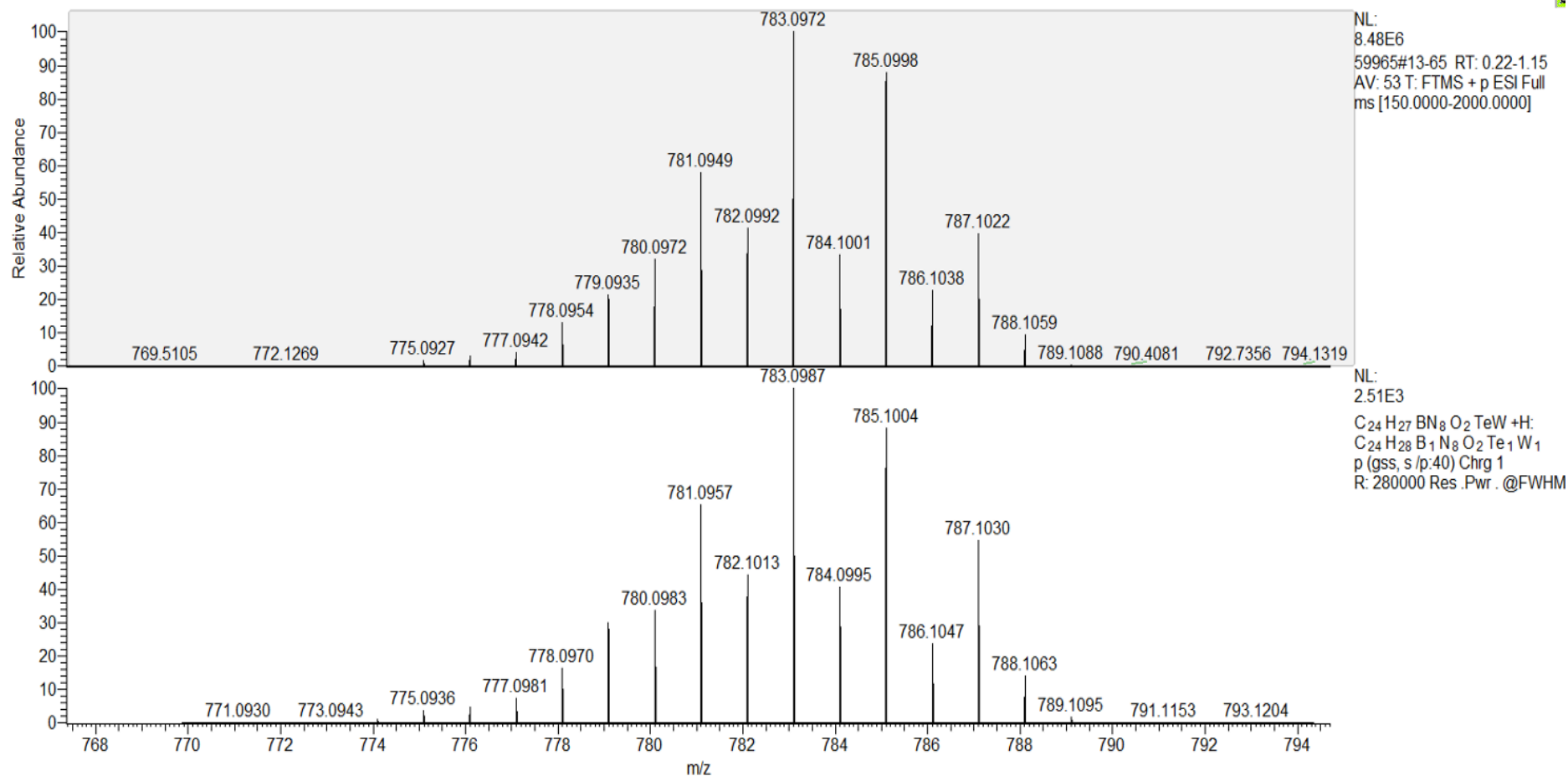


Figure S59. ESI-MS Spectrum of Compound 4h

Observed versus simulated spectrum for detected target formulas ( $[M+H]^+$  ion)Figure S60. Isotopic analysis of  $[M]^+$  ion for Compound 4h

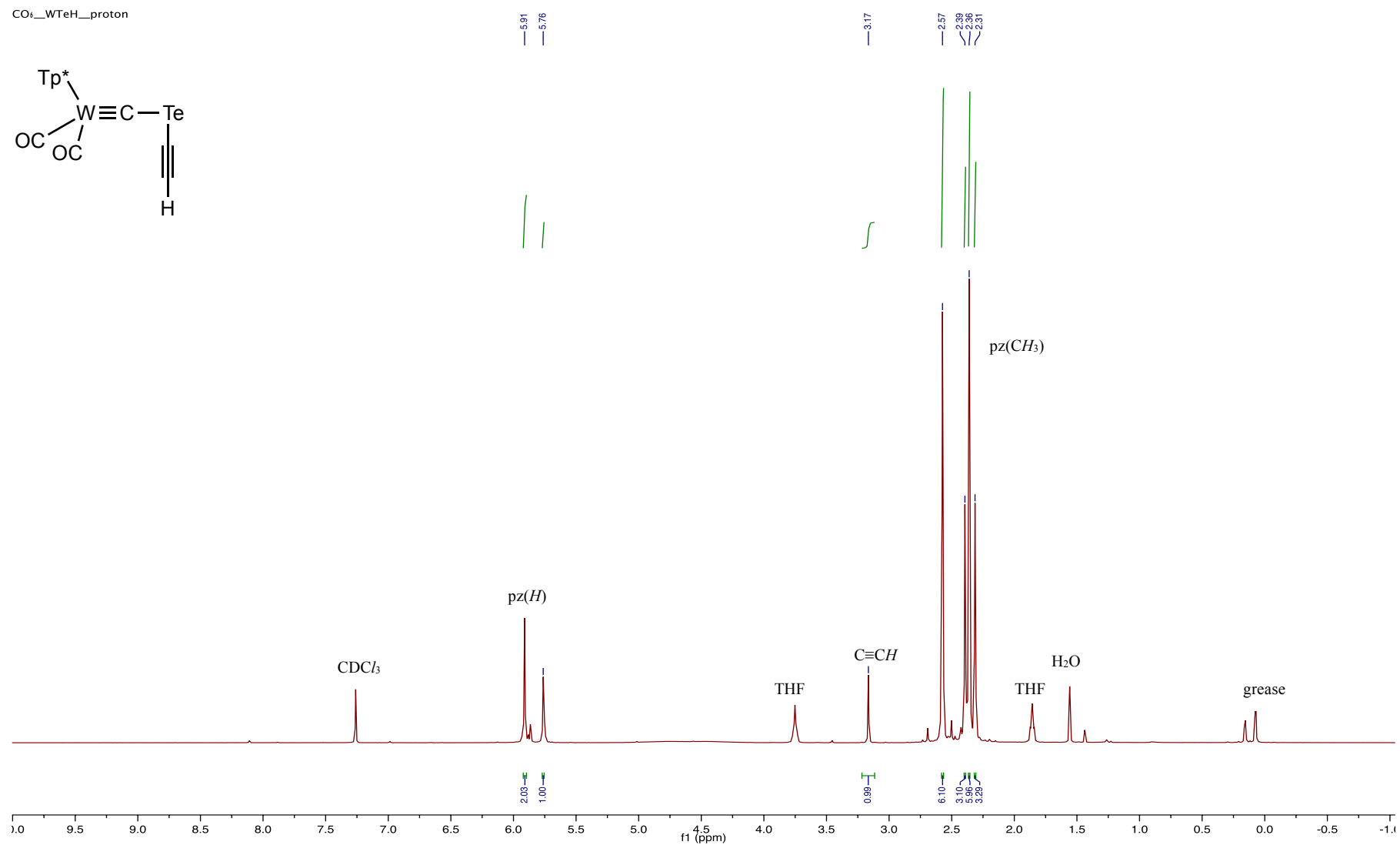
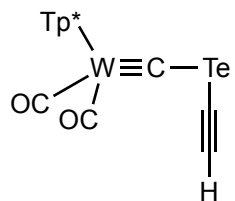
CO<sub>2</sub>\_WTeH\_\_proton

Figure 61. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 25 °C, δ) of compound 4i.

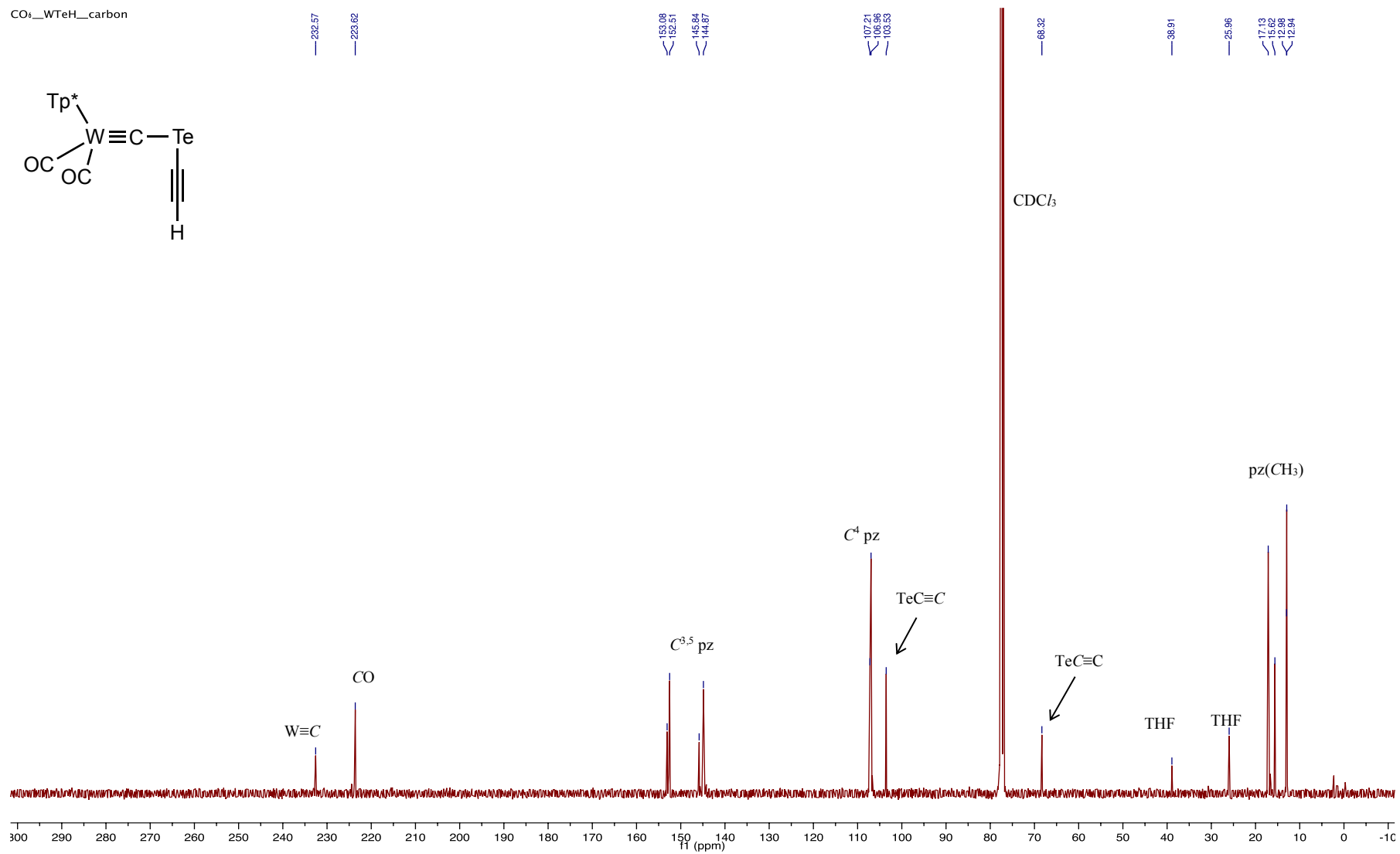


Figure 62. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (101 MHz, CDCl<sub>3</sub>, 25°C, δ) of compound 4i.

CO<sub>2</sub>\_WTeH\_\_tellurium

— 761.92

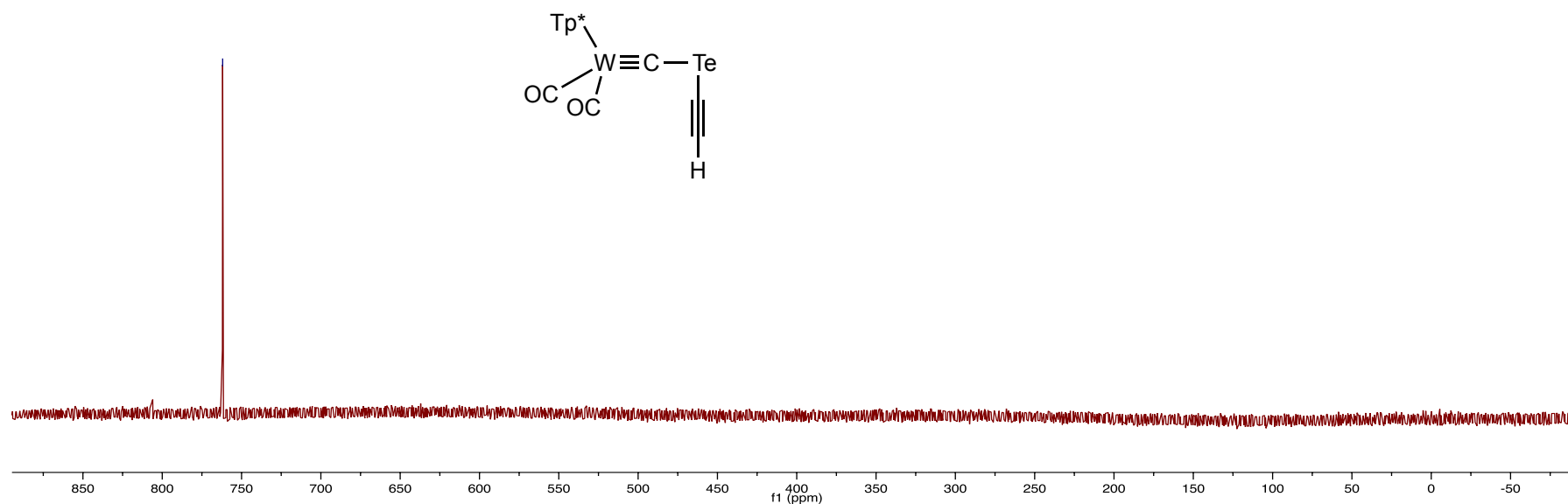
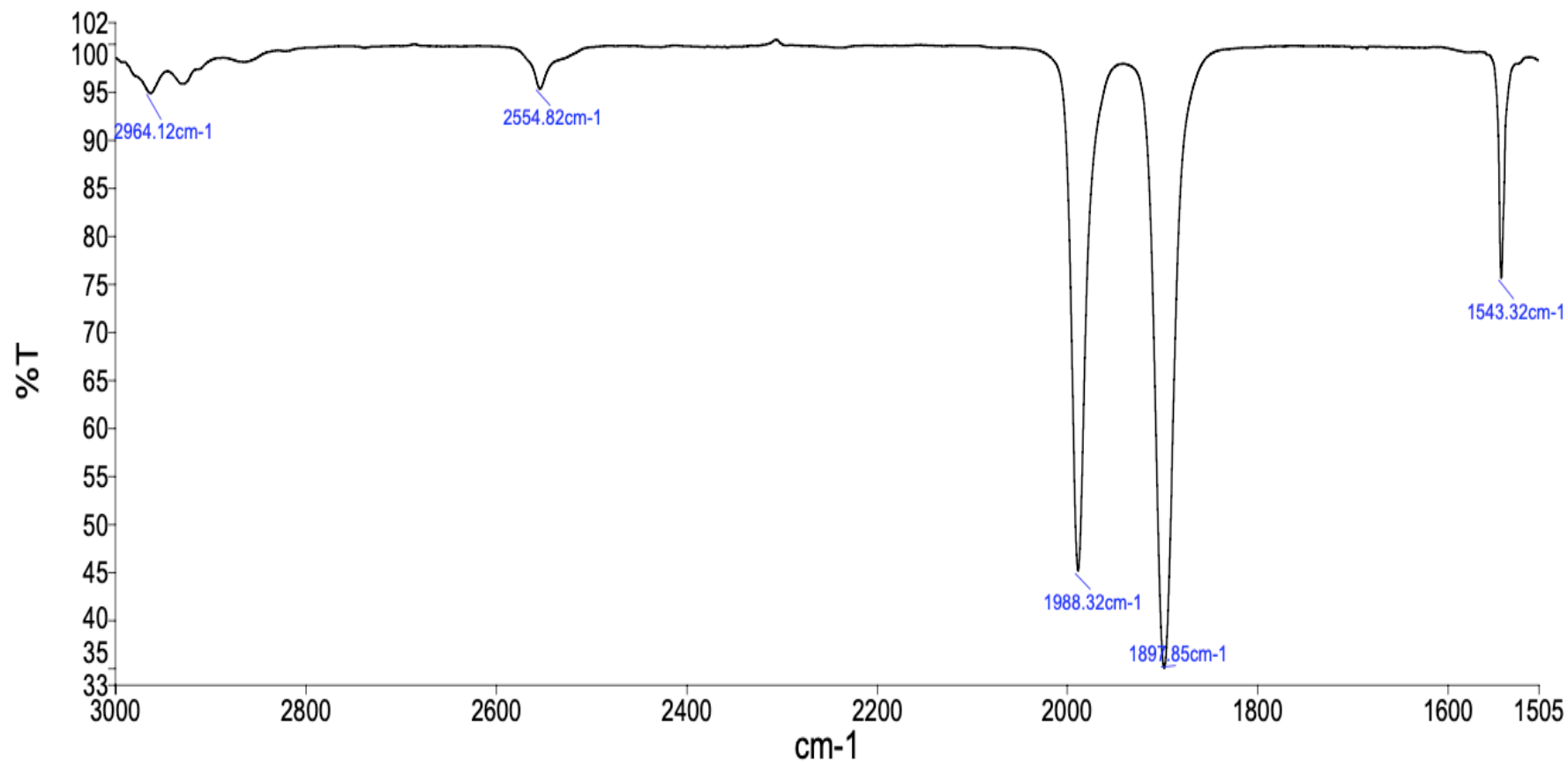


Figure 63. <sup>125</sup>Te{<sup>1</sup>H} NMR spectrum (126 MHz, CDCl<sub>3</sub>, 25°C, δ) of compound 4i.



PerkinElmer Spectrum Version 10.4.3  
Wednesday, 25 November 2020 1:12 PMAnalyst  
DateAdministrator  
Wednesday, 25 November 2020 1:12 PMFigure S64. Infrared spectrum ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ) of Compound 4i

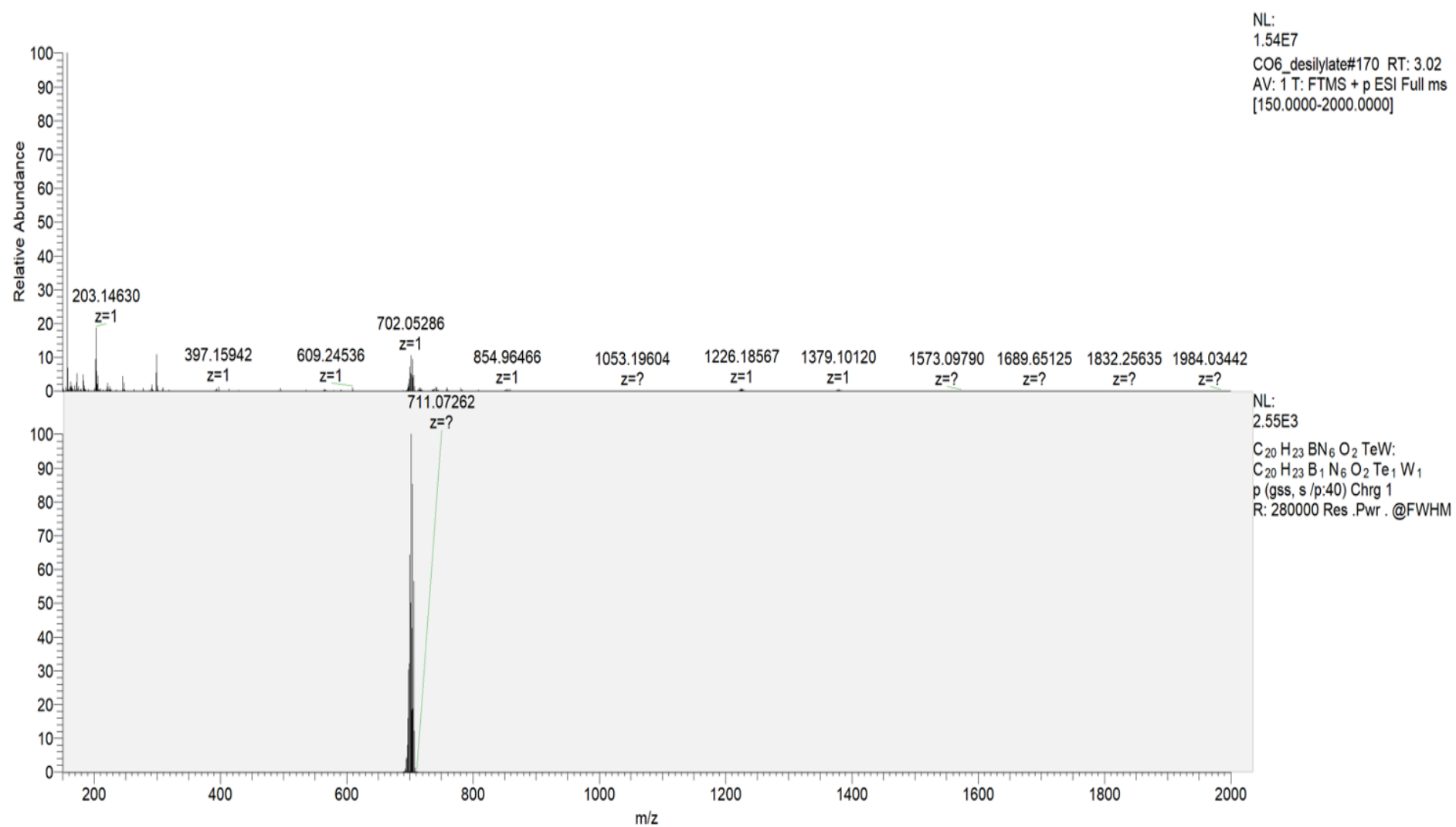
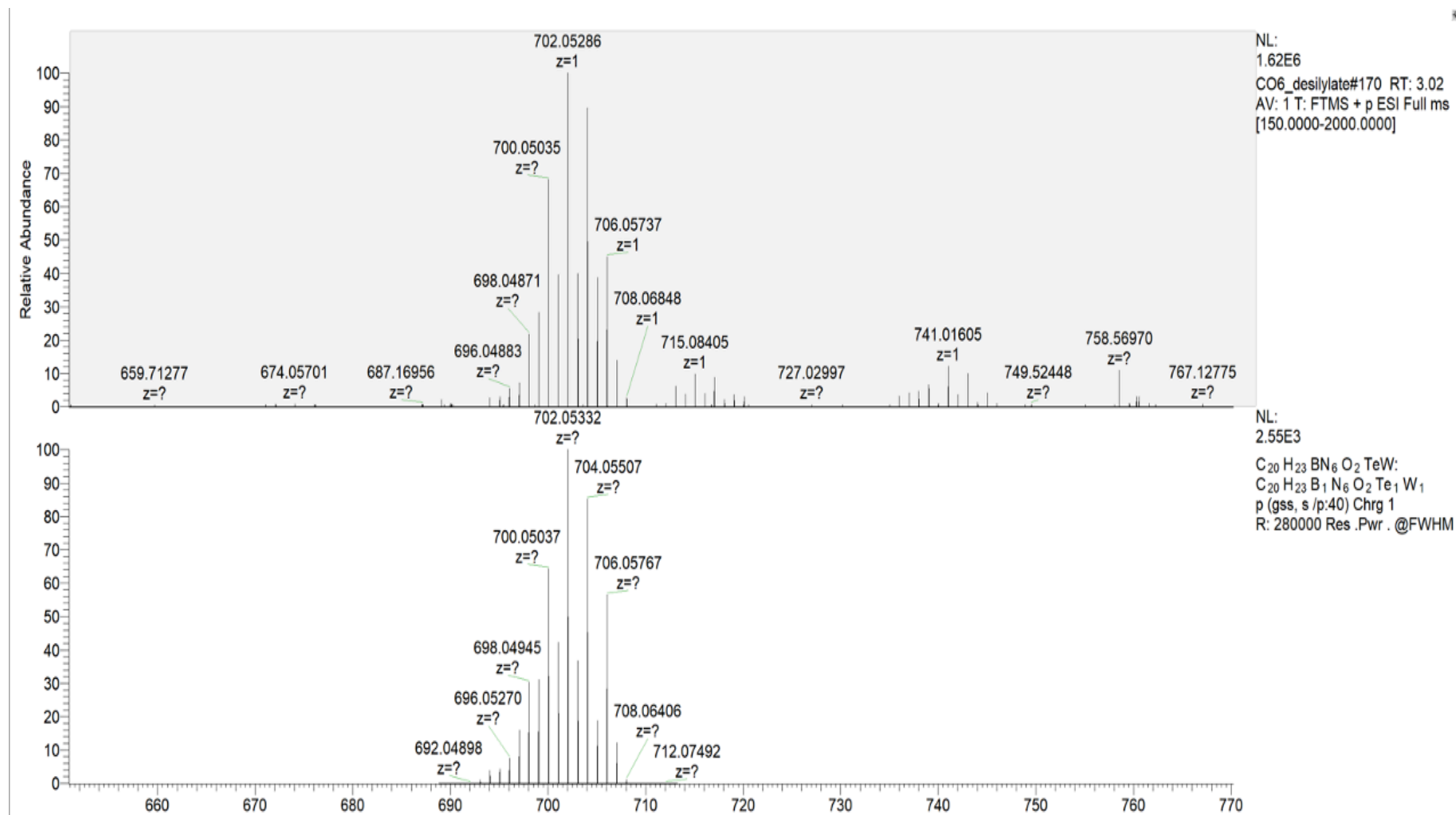


Figure S65. ESI-MS Spectrum of Compound 4i

Observed versus simulated spectrum for detected target formulas ( $M^+$  ion)Figure S66. Isotopic analysis of  $[M]^+$  ion for Compound 4i

CO144\_WTeTIPS\_excess CuCl\_proton

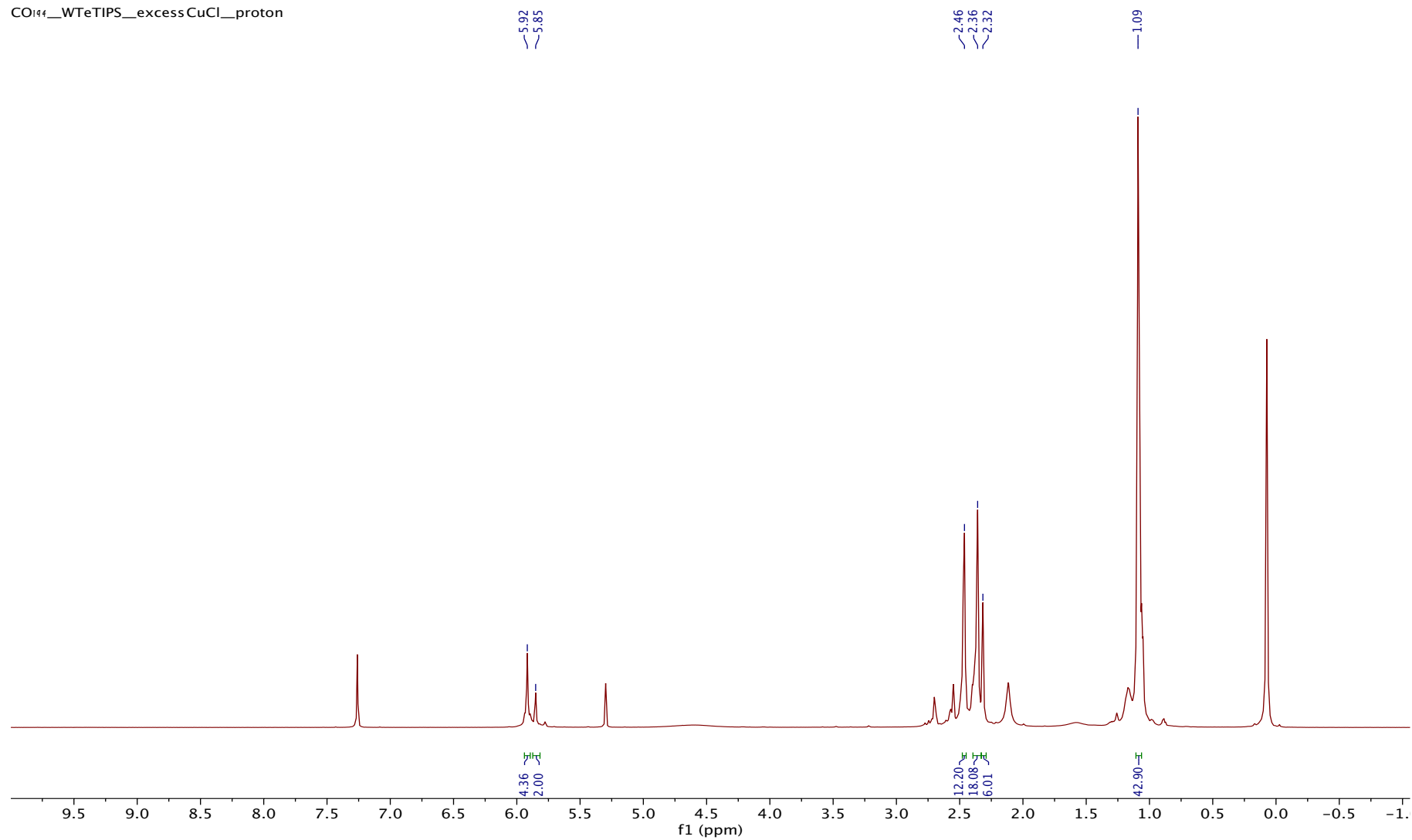


Figure 67.  $^1\text{H}$  NMR spectrum (600 MHz,  $\text{CDCl}_3$ , 25°C,  $\delta$ ) of compound **7a<sub>2</sub>**.

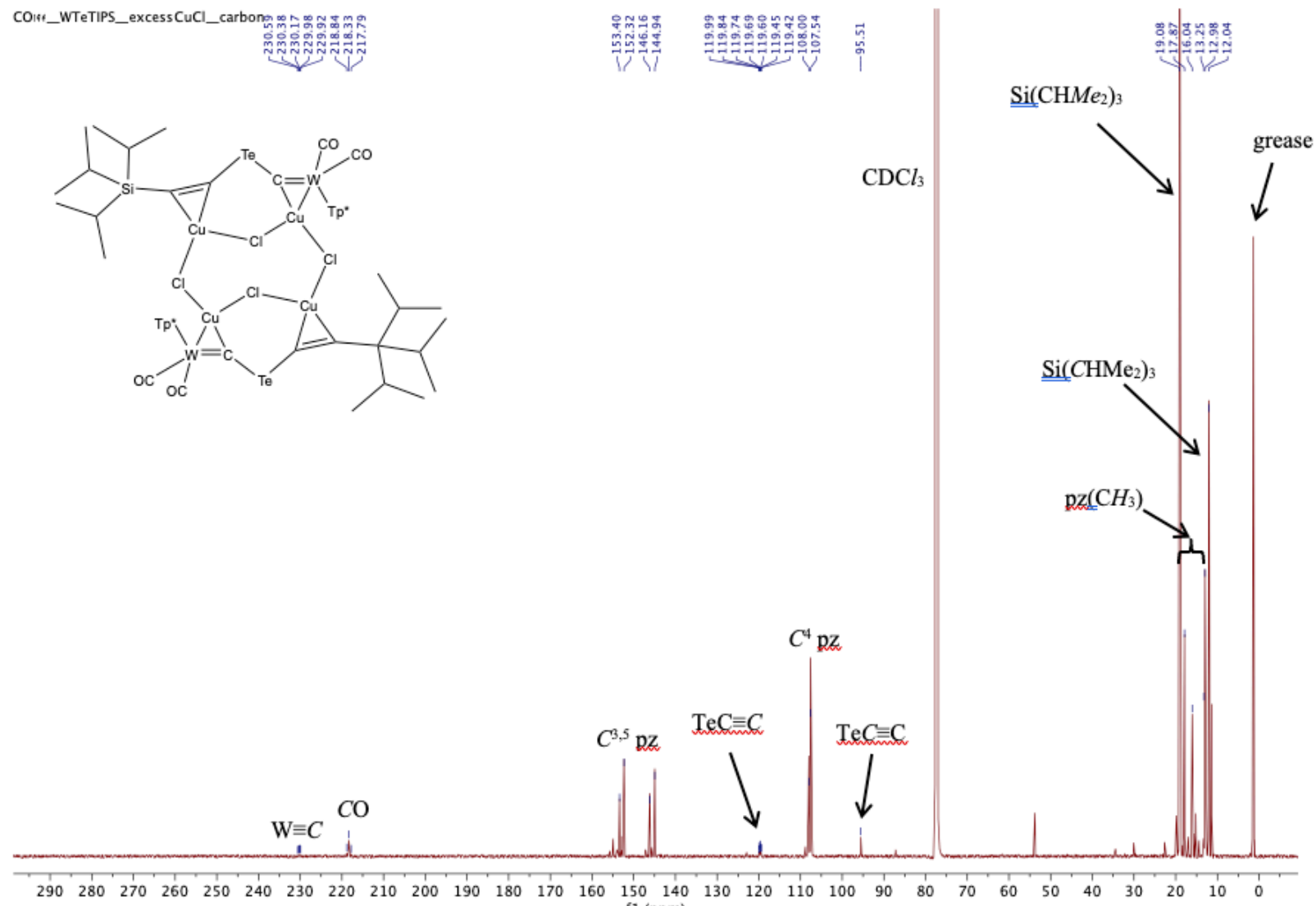


Figure S68. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (151 MHz, CDCl<sub>3</sub>, 25 °C, δ) of compound **7a<sub>2</sub>**.

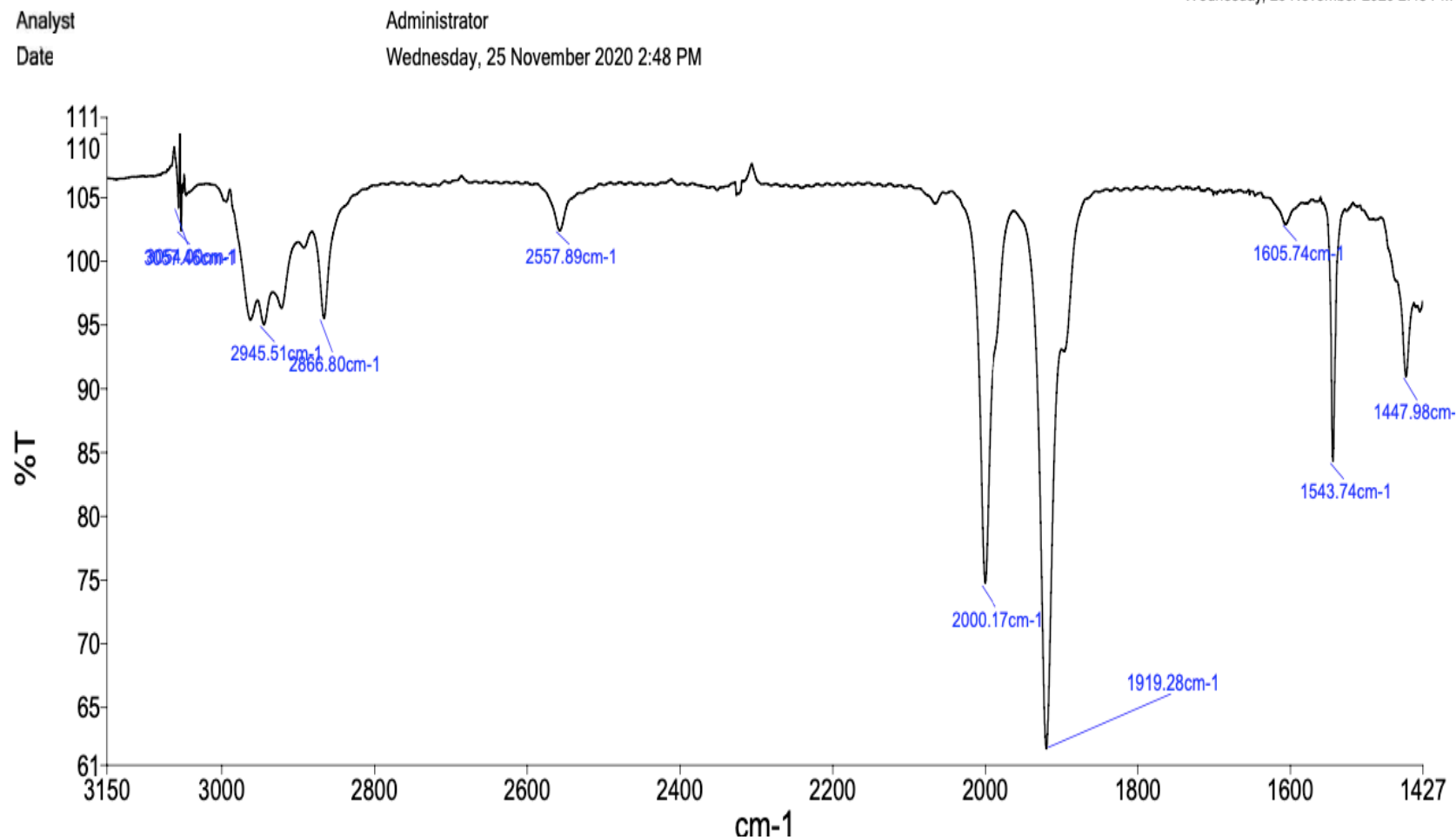
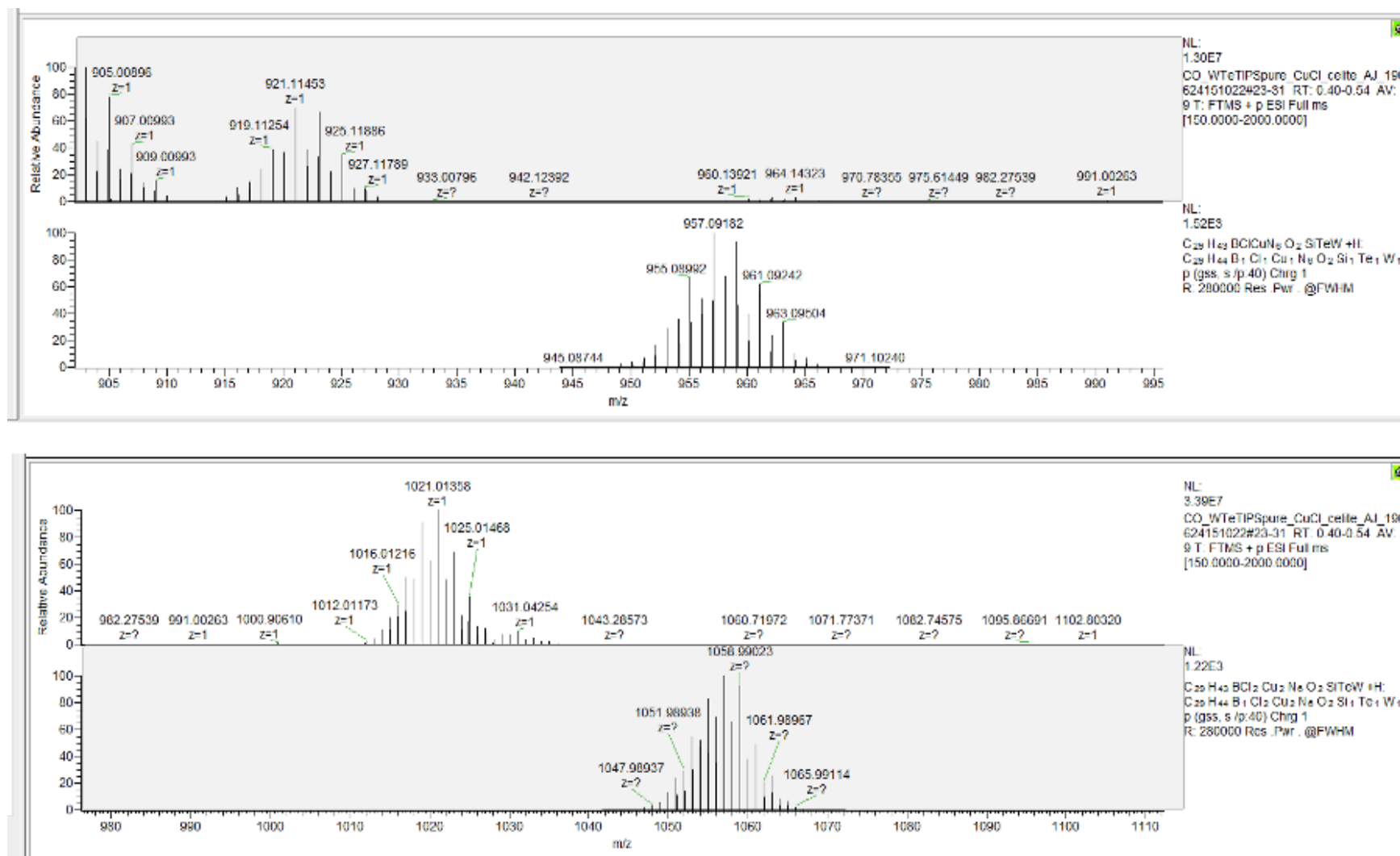
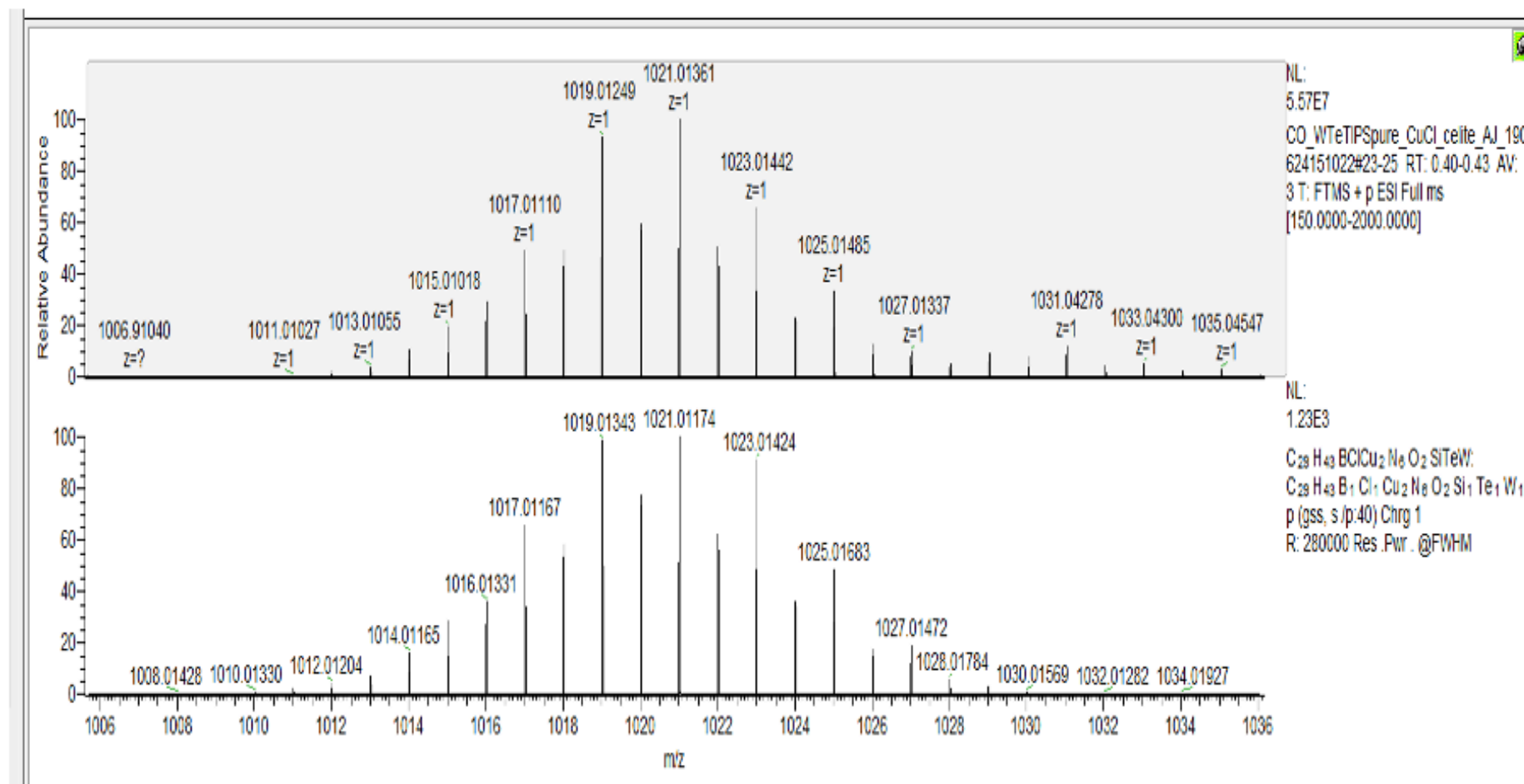


Figure S69. Infrared spectrum (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>) of Compound 7a<sub>2</sub>

Figure S70. ESI-MS Spectrum of Compound 7a<sub>2</sub>

Observed versus simulated spectrum for detected target formulas ( $[M-Cl]^+$  ion)Figure S71. Isotopic analysis of  $[M]^+$  ion for Compound **7a<sub>2</sub>**



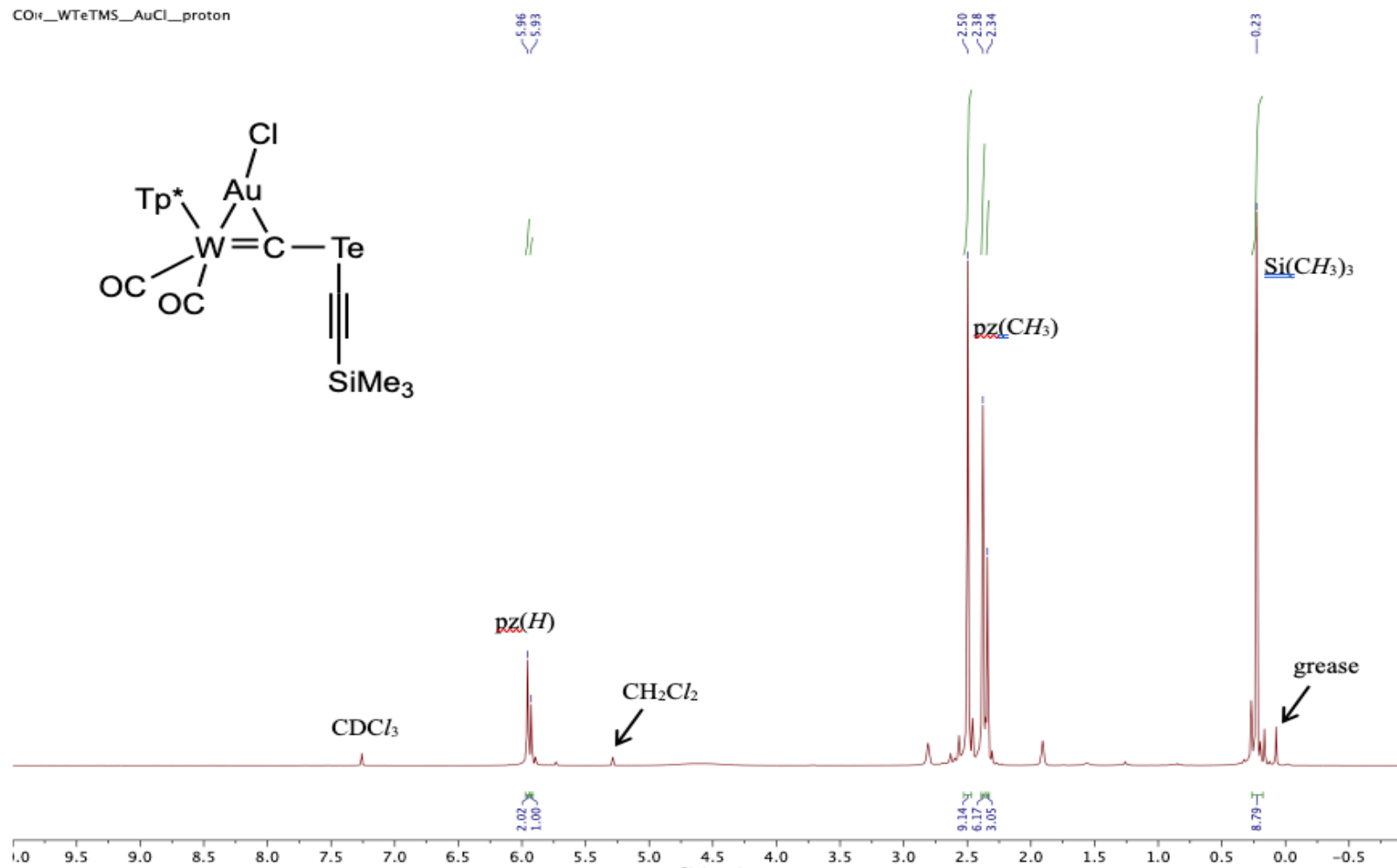


Figure S72. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>, 25 °C, δ) of compound **7b**.

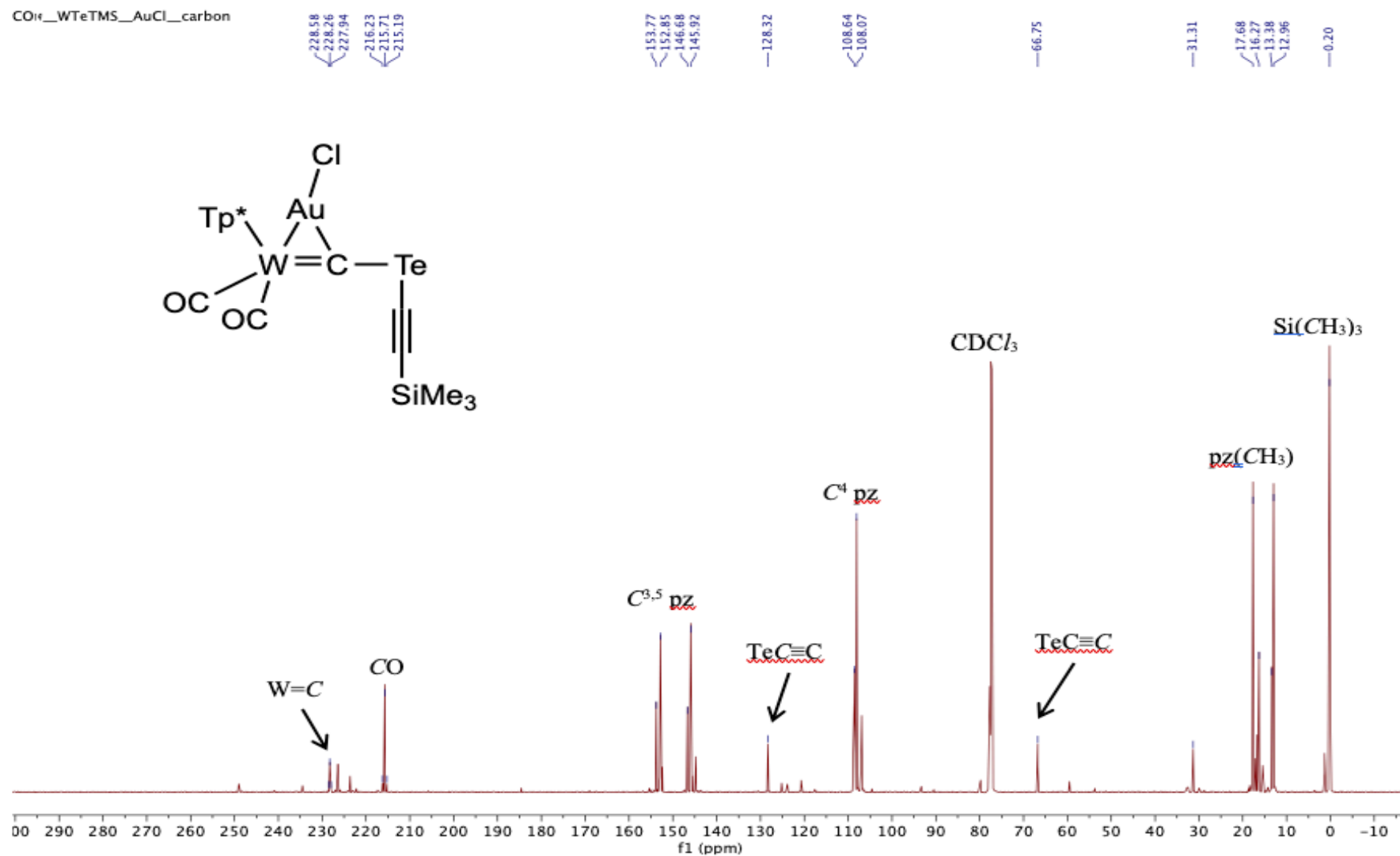


Figure S73.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (151 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ,  $\delta$ ) of compound 7b.

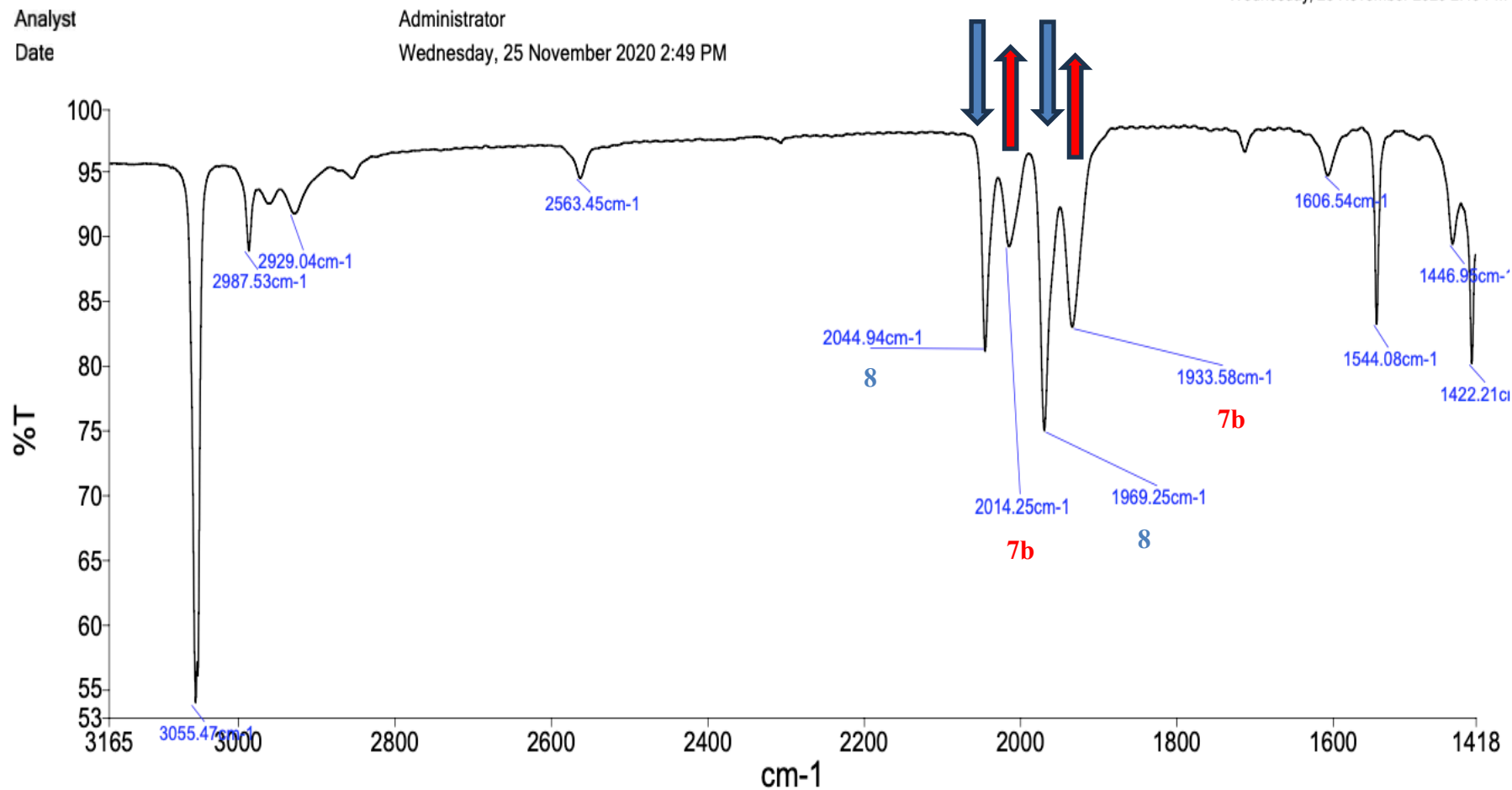
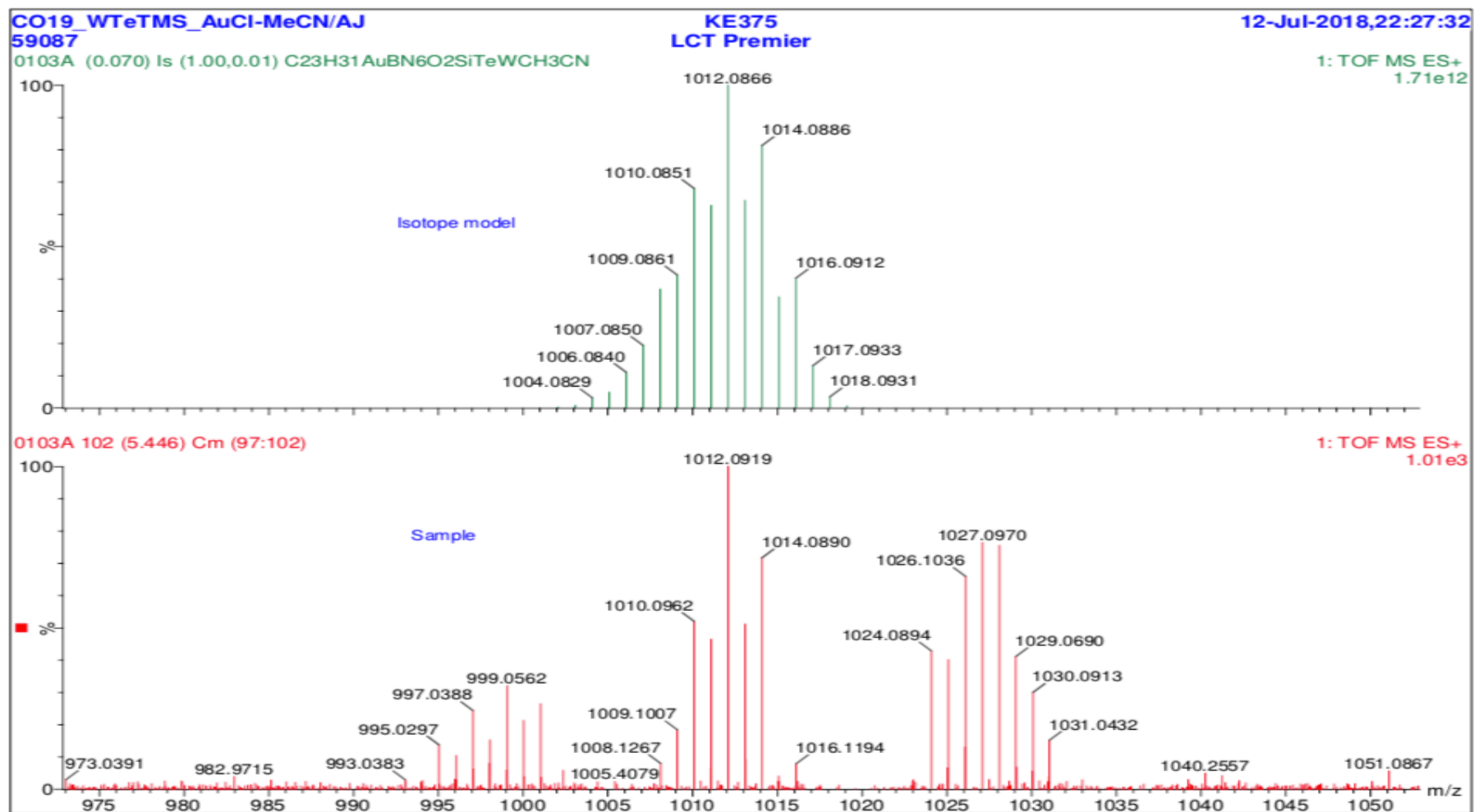
PerkinElmer Spectrum Version 10.4.3  
Wednesday, 25 November 2020 2:49 PM

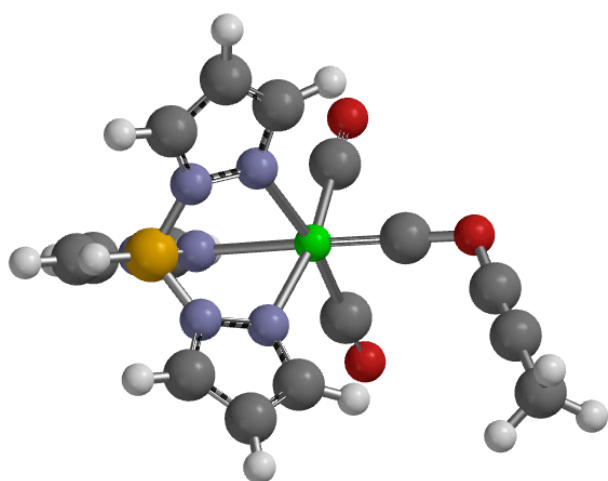
Figure S74. Infrared spectrum ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ) of Compound **7b** showing evolution to Compound **8**.

Observed versus simulated spectrum for detected target formulas ( $M^+$  ion)Figure S75. Isotopic analysis of  $[M-Cl+MeCN]^+$  ion for Compound 7b

## Chemical Communications

## ELECTRONIC SUPPORTING INFORMATION

## Optimised Geometries and Cartesian Coordinates

(a)  $[W(=COC\equiv CMe)(CO)_2(Tp)]$ 

**Figure S76:** Optimised structure of  $[W(=COC\equiv CMe)(CO)_2(Tp)]$  ( $\omega$ B97X-D/6-31G\*/LANL2DZ(W)/gas phase). Bond lengths (Å) and angles (°) of interest: W=C 1.181, WC-O 1.325, O-CC 1.325 Å, C=C 1.201, W-C-O 177.8, C-O-C 115.4.

Infrared absorptions of interest ( $\text{cm}^{-1}$ , scaled by 0.9297): 1982, 1914  $\nu_{\text{CO}}$ .

Natural atomic charges of note: W (0.877), C $\alpha$  (0.041), O(-0.496).

Löwden bond orders of interest: W-C (2.39), WC-O (1.29), C-OCC (1.24).

**Table S1.** Cartesian Coordinates for  $[W(=COC\equiv CMe)(CO)_2(Tp)]$

Atom	x	y	z
W	0.150984	1.384495	0.338629
O	1.374346	3.642613	2.182281
O	-2.121137	3.351643	-0.606214
N	-1.154017	0.640474	2.067780
N	-1.267282	-0.676532	2.344919
N	-0.791545	-0.398021	-0.627635
N	-0.972176	-1.566963	0.024162
N	1.474600	-0.235618	1.152560
N	0.987145	-1.427632	1.561222
C	1.161301	1.973776	-1.044247
C	0.920843	2.820603	1.510302
C	-2.081973	-0.850744	3.398064

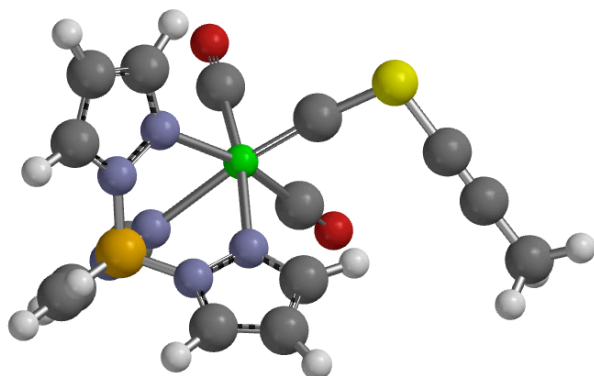
Atom	x	y	z
C	-2.517868	0.390654	3.829109
C	-1.905280	1.293206	2.956953
C	-1.284741	2.636716	-0.250924
C	-1.517884	-2.470984	-0.807196
C	-1.702754	-1.876467	-2.042975
C	-1.228759	-0.572665	-1.875456
C	1.996009	-2.216914	1.968322
C	3.183713	-1.523000	1.821865
C	2.798375	-0.282756	1.305889
B	-0.522926	-1.723015	1.490491
H	-0.756623	-2.834263	1.888475
H	-3.180498	0.608981	4.651940
H	-2.120990	-2.320530	-2.932848
H	4.180613	-1.863881	2.053918
H	-2.293212	-1.844743	3.763814
H	-1.963738	2.371913	2.921349
H	1.793815	-3.213323	2.332458
H	3.396464	0.575555	1.036783
H	-1.735765	-3.469360	-0.457829
H	-1.168123	0.245042	-2.579172
O	1.879789	2.450427	-2.050693
C	1.583620	1.956927	-3.244525
C	1.347563	1.520309	-4.338159
C	1.069866	0.983661	-5.669175
H	1.893052	0.348243	-6.012182
H	0.939701	1.790915	-6.397504
H	0.155493	0.381257	-5.664550

**Table S2:** Thermodynamic Properties at 298.15 K

Zero Point Energy :	692.54	kJ/mol	(ZPE)
Temperature Correction :	55.72	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	748.25	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-		(Electronic Energy + Enthalpy Correction)
Entropy :	1225.641653	au	
Gibbs Energy :	601.42	J/mol*K	
$C_V$ :	-		(Enthalpy - T*Entropy)
	1225.709950	au	
	379.39	J/mol*K	

## Optimised Geometries and Cartesian Coordinates

### (b) $[W(=CSC=CMe)(CO)_2(Tp)]$



**Figure S77:** Optimised structure of  $[W(=CSC=CMe)(CO)_2(Tp)]$  ( $\omega$ B97X-D/6-31G\*/LANL2DZ(W)/gas phase). Bond lengths (Å) and angles ( $^\circ$ ) of interest: W=C 1.813, WC-S 1.711, S-CC 1.706, C=C 1.209, W-C-S 173.8, C-S-C 100.1.

Infrared absorptions of interest ( $\text{cm}^{-1}$ , scaled by 0.9297): 1979, 1916  $\nu_{CO}$ .

Natural atomic charges of note: W (0.986), C $\alpha$  (-0.544), S (0.408).

Löwden bond orders of interest: W-C (2.41), WC-S (1.26), C-SCC (1.18).

**Table S3.** Cartesian Coordinates for  $[W(=CSC=CMe)(CO)_2(Tp)]$

Atom	x	y	z
W	0.555885	1.149659	0.261997
O	1.572019	3.642632	1.916000
O	-1.480654	3.067771	-1.199383
N	-1.109782	0.627983	1.777138
N	-1.322346	-0.648371	2.164418
N	-0.241259	-0.725508	-0.658784
N	-0.591396	-1.806690	0.070183
N	1.622872	-0.358192	1.514620
N	1.025168	-1.491981	1.944312
C	1.711478	1.558147	-1.073679
C	1.193164	2.729317	1.318954
C	-2.338608	-0.695051	3.040518
C	-2.810415	0.591898	3.237390
C	-2.002678	1.384205	2.418978
C	-0.735909	2.368682	-0.661070
C	-1.006052	-2.790454	-0.746622
C	-0.926063	-2.339757	-2.052208
C	-0.437120	-1.034982	-1.941308
C	1.900773	-2.225384	2.651151
C	3.112286	-1.556919	2.683593
C	2.881072	-0.386596	1.957613
B	-0.449634	-1.790193	1.602555
H	-0.785829	-2.845931	2.072507
H	-3.618942	0.907861	3.877846
H	-1.180857	-2.878004	-2.951852

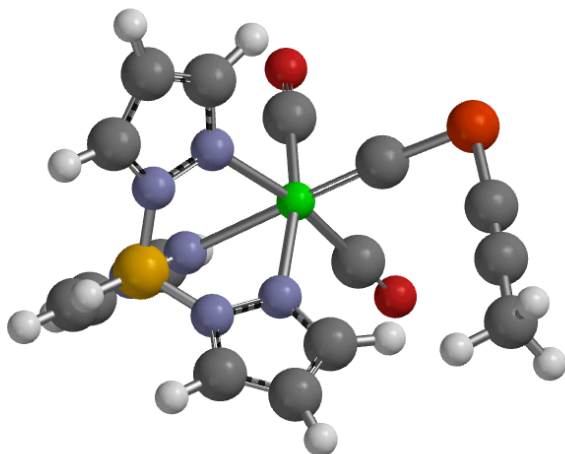
Atom	x	y	z
H	4.025922	-1.869361	3.164573
H	-2.652472	-1.639037	3.461140
H	-2.015343	2.453070	2.258095
H	1.596991	-3.168761	3.080043
H	3.546075	0.432056	1.724525
H	-1.328093	-3.737021	-0.338589
H	-0.205380	-0.305338	-2.705118
S	2.654203	1.990275	-2.434673
C	1.476569	1.941178	-3.667399
C	0.637903	1.905761	-4.537494
C	-0.368858	1.889346	-5.594047
H	-0.929065	0.948553	-5.590409
H	0.106138	1.994215	-6.574847
H	-1.081762	2.710923	-5.470669

**Table S4:** Thermodynamic Properties at 298.15 K

Zero Point Energy :	684.63	kJ/mol	(ZPE)
Temperature Correction :	56.92	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	741.56	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-		(Electronic Energy + Enthalpy Correction)
	1548.641295	au	
Entropy :	609.83	J/mol*K	
Gibbs Energy :	-		(Enthalpy - T*Entropy)
	1548.710547	au	
C <sub>v</sub> :	395.07	J/mol*K	

## Optimised Geometries and Cartesian Coordinates

### [W(≡CSeC≡CMe)(CO)<sub>2</sub>(Tp)]



**Figure S78:** Optimised structure of [W(≡CSeC≡CMe)(CO)<sub>2</sub>(Tp)] (ωB97X-D/6-31G\*/LANL2DZ(W,Se)/gas phase). Bond lengths (Å) and angles (°) of interest: W=C 1.806, WC-Se 1.858, Se-CC 1.841, C=C 1.210, W-C-Se 177.3, C-Se-C 96.3.

Infrared absorptions of interest (cm<sup>-1</sup>, scaled by 0.9297): 1982, 1918 ν<sub>CO</sub>.

Natural atomic charges of note: W (0.973), C<sub>α</sub> (-0.585), Se (0.519).

Löwden bond orders of interest: W-C (2.47), WC-Se (1.18), C-SeCC (1.15).

**Table S5.** Cartesian Coordinates for [W(≡CSeC≡CMe)(CO)<sub>2</sub>(Tp)]

Atom	x	y	z
W	0.221509	1.524505	0.465992
O	1.283753	3.646000	2.566981
O	-2.008891	3.536802	-0.488698
N	-1.175950	0.606064	2.080225
N	-1.265361	-0.732931	2.234304
N	-0.649282	-0.175929	-0.672602
N	-0.827199	-1.403232	-0.137433
N	1.529518	-0.130312	1.216480
N	1.048414	-1.359354	1.505139
C	1.290387	2.241620	-0.801165
C	0.888587	2.876233	1.804273
C	-2.138445	-1.021577	3.213285
C	-2.636773	0.165012	3.723143
C	-1.999329	1.156905	2.973747
C	-1.196919	2.801105	-0.122118
C	-1.342196	-2.230289	-1.062085
C	-1.504634	-1.524658	-2.241947
C	-1.056243	-0.235832	-1.941421
C	2.053366	-2.159259	1.900958
C	3.231072	-1.433839	1.870876
C	2.844834	-0.164186	1.434015

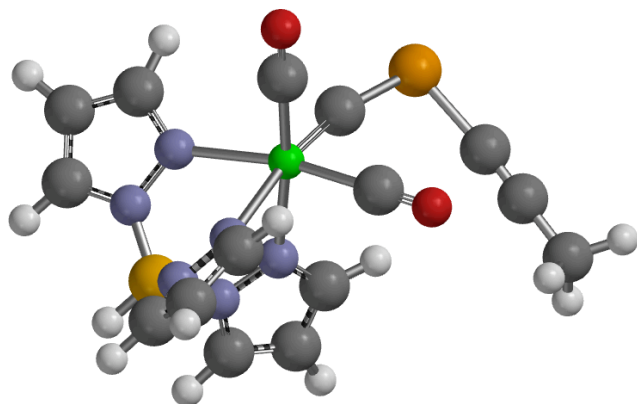
Atom	x	y	z
B	-0.447809	-1.680160	1.331781
H	-0.671154	-2.827905	1.616002
H	-3.355896	0.292276	4.517166
H	-1.899100	-1.888448	-3.178060
H	4.222401	-1.773266	2.127499
H	-2.342499	-2.049212	3.475728
H	-2.090143	2.232677	3.028468
H	1.855727	-3.184810	2.175367
H	3.436260	0.722467	1.258591
H	-1.557086	-3.258762	-0.812489
H	-0.987683	0.645067	-2.563216
Se	2.324169	2.974225	-2.160360
C	1.633866	1.941221	-3.518630
C	1.181806	1.229113	-4.385607
C	0.634915	0.342751	-5.407737
H	0.187747	-0.539817	-4.936700
H	1.420893	-0.002826	-6.087130
H	-0.136635	0.842563	-6.002623

**Table S6:** Thermodynamic Properties at 298.15 K

Zero Point Energy :	682.43	kJ/mol	(ZPE)
Temperature Correction :	57.72	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	740.15	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-	au	(Electronic Energy + Enthalpy Correction)
Entropy :	617.51	J/mol*K	
Gibbs Energy :	-	au	(Enthalpy - T*Entropy)
C <sub>v</sub> :	398.10	J/mol*K	

## Optimised Geometries and Cartesian Coordinates

### [W(≡CTeC≡CMe)(CO)<sub>2</sub>(Tp)]



**Figure S79:** Optimised structure of [W(≡CTeC≡CMe)(CO)<sub>2</sub>(Tp)] (ωB97X-D/6-31G\*/LANL2DZ(W,Te)/gas phase). Bond lengths (Å) and angles (°) of interest: W=C 1.807, WC-Te 2.043, Te-CC 2.029, C≡C 1.212, W-C-Te 168.3, C-Te-C 93.9.

Infrared absorptions of interest (cm<sup>-1</sup>, scaled by 0.9297): 1977, 1915 ν<sub>CO</sub>.

Natural atomic charges of note: W (0.985), C<sub>α</sub> (-0.725), Te (0.775).

Löwden bond orders of interest: W-C (2.50), WC-Te (1.13), C-TeCC (1.10).

**Table S7.** Cartesian Coordinates for [W(≡CTeC≡CMe)(CO)<sub>2</sub>(Tp)]

Atom	x	y	z
W	-0.632253	0.850929	-0.780512
O	0.164916	3.323979	1.019395
O	-3.150985	2.448605	-1.829192
N	-1.721267	-0.045494	1.074482
N	-1.575322	-1.350975	1.389623
N	-1.305400	-1.095572	-1.620728
N	-1.228084	-2.249872	-0.921779
N	0.976200	-0.460509	0.043853
N	0.741243	-1.704676	0.512203
C	0.390180	1.631750	-2.049400
C	-0.140205	2.424269	0.363766
C	-2.288256	-1.636439	2.491447
C	-2.923109	-0.481884	2.916801
C	-2.532610	0.487468	1.989599
C	-2.238602	1.860901	-1.434116
C	-1.690323	-3.263877	-1.670993
C	-2.081256	-2.762940	-2.900885
C	-1.820834	-1.394194	-2.815192
C	1.896486	-2.266100	0.909540
C	2.920493	-1.361176	0.693996
C	2.288043	-0.241192	0.146419
B	-0.688448	-2.271030	0.524154
H	-0.698692	-3.393607	0.958046
H	-3.572616	-0.361591	3.769772
H	-2.495491	-3.308025	-3.734506

Atom	x	y	z
H	3.971367	-1.493653	0.899081
H	-2.293233	-2.639383	2.892366
H	-2.791770	1.535379	1.932400
H	1.903542	-3.266617	1.316072
H	2.697874	0.704571	-0.181782
H	-1.710223	-4.267778	-1.273493
H	-1.970120	-0.609177	-3.541938
Te	1.769770	2.649329	-3.160627
C	2.778475	3.332714	-1.538397
C	3.273980	3.697359	-0.494023
C	3.837891	4.152548	0.772092
H	3.086004	4.062214	1.562958
H	4.139379	5.203251	0.710380
H	4.713257	3.560492	1.059120

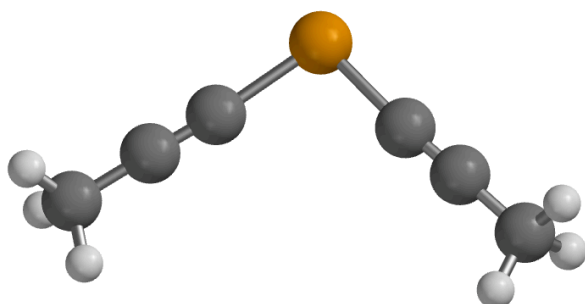
**Table S8:** Thermodynamic Properties at 298.15 K

Zero Point Energy :	680.76	kJ/mol	(ZPE)
Temperature Correction :	58.10	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	738.86	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-	au	(Electronic Energy + Enthalpy Correction)
Entropy :	623.15	J/mol*K	
Gibbs Energy :	-	au	(Enthalpy - T*Entropy)
C <sub>v</sub> :	400.07	J/mol*K	



## Optimised Geometries and Cartesian Coordinates

### Te(C≡CMe)<sub>2</sub>



**Figure S80:** Optimised structure of Te(C≡CMe)<sub>2</sub> (ωB97X-D/6-31G\*/LANL2Dζ(Te)/gas phase). (Mean) Bond lengths (Å) and angles (°) of interest: C=C 1.211, C-Te 2.023, C-Te-C 97.7.

Infrared absorptions of interest (cm<sup>-1</sup>, scaled by 0.9297):  
2171, 2165 ν<sub>CO</sub>. 967 ν<sub>CSe</sub>.

Natural atomic charges of note: C<sub>α</sub> (-0.468), Te (0.818).

Löwden bond orders of interest: C-Te (1.12), CC (2.84).

**Table S7.** Cartesian Coordinates for Te(C≡CMe)<sub>2</sub>

Atom	x	y	z
C	-1.760073	-0.003512	1.808441
C	-1.793964	-0.011459	0.597635
Te	-2.001328	-0.028310	-1.415191
C	-1.694030	0.005977	3.265975
H	-0.655430	-0.093262	3.598351
H	-2.264349	-0.826167	3.691653
H	-2.091945	0.940575	3.674919
C	-0.034542	-0.010492	-1.888892
C	1.117586	-0.002724	-2.262625
C	2.513485	0.005843	-2.687039
H	3.173845	0.000755	-1.813521
H	2.742474	0.898984	-3.277710
H	2.748271	-0.876206	-3.291996

**Table S8:** Thermodynamic Properties at 298.15 K

Zero Point Energy :	235.78	kJ/mol	(ZPE)
Temperature Correction :	24.84	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	260.62	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-		(Electronic Energy + Enthalpy Correction)
	239.980696	au	
Entropy :	390.82	J/mol•K	
Gibbs Energy :	-		(Enthalpy - T*Entropy)
	240.025077	au	
C <sub>v</sub> :	132.44	J/mol•K	

**ENDS**