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Electronic Supporting Information for:

Bridging selenocarbonyl ligands: An open and shut case.

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Experimental

General Considerations

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

NMR spectra were obtained on a Bruker Avance 400 (^{1}H at 400.1 MHz, ^{13}C at 100.6 MHz, ^{19}F at 376.5 MHz), a Bruker Avance 600 (^{1}H at 600.0 MHz, ^{13}C at 150.9 MHz) or a Bruker Avance 700 (^{1}H at 700.0 MHz, ^{13}C at 176.1 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 peak, or external references ($(PhSe)_2$ for ^{77}Se, 1.2 M Na_2PtCl_6 in D_2O for ^{195}Pt). 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, ^{79}Se, ^{195}Pt or ^{183}W satellites. In some cases, distinct peaks were observed in the ^{1}H and ^{13}C{^{1}H} NMR spectra, but to the level of accuracy that is reportable (i.e. 2 decimal places for ^{1}H NMR, 1 decimal place for ^{13}C NMR) they are reported as having the same chemical shift. The abbreviation ‘pz’ is used to refer to the pyrazolyl rings on the hydrotris(3,5-dimethylpyrazol-1-yl)borate (Tp*) ligand. Spectra provided generally correspond to samples obtained directly from chromatography and may contain residual solvent as recrystallised samples often display reduced solubility.

Infrared spectra were obtained using a PerkinElmer Spectrum One FT-IR spectrometer. The strengths of IR absorptions are denoted by the abbreviations vs (very strong), s (strong), m (medium), w (weak), sh (shoulder) and br (broad). Elemental microanalytical data were provided the London Metropolitan University. High-resolution electrospray ionisation mass spectrometry (ESI-MS) was performed by the ANU Research School of Chemistry mass spectrometry service with acetonitrile or methanol as the matrix.

Data for X-ray crystallography were collected with an Agilent Xcalibur CCD diffractometer an Agilent SuperNova CCD diffractometer using Mo-Kα radiation (λ = 0.71073 Å) or Cu-Kα radiation (λ = 1.54184 Å) and the CrysAlis PRO software.[1] The structures were solved by direct or Patterson methods and refined by full-matrix least-squares on F^2 using the SHELXS or SHELXT and SHELXL programs.[2] Hydrogen atoms were located geometrically and refined using a riding model. Diagrams were produced using the CCDC visualisation program Mercury.[3]

The synthesis of the tungsten selenocarbonylate $[W(CSe)(CO)_2(Tp^*)]NEt_4$ [**1**]NEt_4 has been described previously.[4] The complexes $[PtCl_2(COD)]$ (COD = 1,5-cyclooctadiene),[5] $[PtCl_2(NBD)]$ (NBD = norbornadiene, bicyclo[2.2.1]hepta-2,5-diene)[6] and $[AuCl(SMe_2)]$[7] were prepared according to literature procedures.

Synthesis of $[W_2Pt(\mu_2\text{-}CSe)_2(COD)(CO)_4(Tp^*)_2]$ (2). A solution of [**1**]NEt_4 (200 mg, 0.276 mmol) and $[PtCl_2(COD)]$ (52 mg, 0.14 mmol) in CH_2Cl_2 (20 mL) was stirred at RT for 5 min. After this time, ethanol (20 mL) was added and the CH_2Cl_2 was removed under reduced pressure. The resulting precipitate was collected by filtration and washed with ethanol (50 mL) and petroleum spirits (40–60 °C, 60 mL) to give a brick red solid of pure **2** (156 mg, 0.0999 mmol, 72%). IR (CH_2Cl_2, cm^{-1}): 1964s, 1876s ν_{CO}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ_H = 5.85 (s, 4H, pzC*H*), 5.77 (br m, 4H, COD{=C*H*}), 5.70 (s, 2H, pzC*H*), 2.66 (s, 12H, pzCH_3), 2.45 (br m, 4H, COD{CH_2}), 2.34 (s, 18H, pzCH_3), 2.28 (s, 6H, pzCH_3), 2.11 (br m, 4H, COD{CH_2}). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$, 298 K): δ_C = 266.6 (W*C*Se), 226.6 (W*C*O), 152.9, 152.1, 145.0, 144.2 (pz*C*CH$_3$), 106.5 (pz*C*H), 100.3 (COD{=*C*H}, $^2J_{CPt}$ = 2230), 30.9 (COD{*C*H$_2$}, $^3J_{CPt}$ = 292), 16.8, 16.3, 12.8, 12.7 (pz*C*H$_3$). ^{195}Pt NMR (86 MHz, $CDCl_3$, 298 K): δ_{Pt} = –3839. ^{77}Se NMR (76 MHz, $CDCl_3$, 298 K): δ_{Se} = 597. MS (ESI, +ve ion, *m/z*): Found: 1582.1666. Calcd for $C_{44}H_{56}{}^{11}B_2N_{12}NaO_4{}^{195}Pt{}^{80}Se_2{}^{184}W_2$ $[M+Na]^+$: 1582.1654. Anal. Found: C, 34.02; H, 3.75; N, 10.82. Calcd for $C_{44}H_{56}B_2N_{12}O_4PtSe_2W_2$: C, 33.89; H, 3.62; N, 10.78%.

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CCDC 1949481–1949485 contain the supplementary crystallographic data for this paper, and are available free of charge from The Cambridge Crystallographic Data Centre.

Synthesis of $[W_2Pt(\mu_2\text{-}CSe)_2(NBD)(CO)_4(Tp^*)_2]$ (3). A solution of [**1**]NEt_4 (300 mg, 0.414 mmol) and $[PtCl_2(NBD)]$ (75 mg, 0.21 mmol) in CH_2Cl_2 (20 mL) was stirred at RT for 20 min. After this time, ethanol (20 mL) was added and the CH_2Cl_2 was removed under reduced pressure. The resulting precipitate was collected by filtration and washed with ethanol (20 mL) and petroleum spirits (40–60 °C, 40 mL) to give a brown solid of pure **3** (250 mg, 0.143 mmol, 69%). IR (CH_2Cl_2, cm^{-1}): 1972s, 1873s ν_{CO}. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ_H = 5.86 (s, 4H, pzC*H*), 5.71 (s, 2H, pzC*H*), 5.50 (br s, 2H, $^2J_{PtH}$ = 55, NBD{=C*H*}), 4.13 (br m, 2H, NBD{C*H*}), 2.64 (s, 12H, pzCH_3), 2.34 (s, 12H, pzCH_3), 2.34 (s, 6H, pzCH_3), 2.29 (s, 6H, pzCH_3), 1.62 (br m, 2H, NBD{CH_2}). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$, 298 K): δ_C = 268.8 (W*C*Se), 227.4 (W*C*O), 152.9, 152.1, 145.1, 144.2 (pz*C*CH_3), 106.6 (pz*C*H), 78.9 (NBD{=*C*H}), 70.2 (NBD{*C*H}), 50.0 (NBD{CH_2} 16.8, 16.3, 12.8, 12.7 (pzCH_3). ^{195}Pt NMR (86 MHz, $CDCl_3$, 298 K): $\delta_{Pt\,=}$ –3724. ^{77}Se NMR (76 MHz, $CDCl_3$, 298 K): δ_{Se} = 660. MS (ESI, +ve ion, *m/z*): Found: 1566.1343. Calcd for $C_{43}H_{52}{}^{11}B_2N_{12}NaO_4{}^{195}Pt^{80}Se_2{}^{184}W_2$ $[M+Na]^+$: 1566.1348. Anal. Found: C, 33.45; H, 3.28; N, 10.73. Calcd for $C_{43}H_{52}B_2N_{12}O_4PtSe_2W_2$: C, 33.47; H, 3.40; N, 10.89%. A crystal suitable for structure determination was grown by vapour diffusion of *n*-hexane into a CH_2Cl_2 solution at –20 °C. *Crystal data for* $C_{45}H_{56}B_2Cl_4N_{12}O_4PtSe_2W_2$ (*M* = 1713.14 g.mol^{-1}): monoclinic, space group C2/c (no. 15), *a* = 17.0574(3), *b* = 10.5308(3), *c* = 31.2176(8) Å, *β* = 91.680(2)°, *V* = 5605.1(2) Å^3, *Z* = 4, *T* = 150.0(1) K, μ(CuKα) = 15.658 mm^{-1}, *Dcalc* = 2.030 g.cm^{-3}, 13783 reflections measured (9.872° ≤ 2Θ ≤ 144.238°), 5488 unique (R_{int} = 0.0517, R_{sigma} = 0.0742) which were used in all calculations. The final R_1 was 0.0425 (I > 2σ(I)) and wR_2 was 0.0926 (all data) for 336 refined parameters with 0 restraints. CCDC 1949481.

Synthesis of $[W_2Pt(\mu_2\text{-}CSe)_2(CO)_4(Tp^*)_2]$ (4). A solution of **3** (142 mg, 0.0919 mmol) in toluene (50 mL) was heated under reflux for 90 mins. After cooling to RT, the volatiles were removed *in vacuo* to give a purple solid of pure **4** (113 mg, 0.0777 mmol, 85%). The same product can be obtained from **2** on refluxing in toluene for 5 h. Purification (if required) can be performed on a short (4 x 6 cm) silica plug, eluting the first red band with 20% v/v CH_2Cl_2/petroleum spirits (40–60 ˚C). IR (CH_2Cl_2, cm^{-1}): 1972s, 1895s ν_{CO}. ^1H NMR (700 MHz, $CDCl_3$, 298 K): δ_H = 5.83 (s, 4H, pzC*H*), 5.82 (s, 2H, pzC*H*), 2.43 (s, 12H, pzCH_3), 2.42 (s, 6H, pzCH_3), 2.32 (s, 6H, pzCH_3), 2.23 (s, 12H, pzCH_3). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$, 298 K): δ_C = 261.3 (W*C*Se), 218.6 (W*C*O), 153.8, 152.7, 145.5, 144.5 (pz*C*CH_3), 107.5, 107.4 (pz*C*H), 17.1, 15.9, 13.1, 12.9 (pzCH_3). The ^{195}Pt NMR resonance was not identified. ^{77}Se NMR (76 MHz, $CDCl_3$, 298 K): δ_{Se} = 501.8 (tentative). MS (ESI, +ve ion, *m/z*): Found: 1451.0798. Calcd. for $C_{36}H_{44}{}^{11}B_2N_{12}O_4{}^{195}Pt^{80}Se_2{}^{184}W_2$ $[M\text{–}e^-]^+$: 1451.0822. Anal. Found: C, 29.63; H, 2.91; N, 11.45. Calcd for $C_{36}H_{44}B_2N_{12}O_4PtSe_2W_2$: C, 29.80; H, 3.06; N, 11.58%. A crystal suitable for structure determination was grown by slow evaporation of a CH_2Cl_2 solution at –20 °C. *Crystal data for* $C_{38}H_{48}B_2Cl_4N_{12}O_4PtSe_2W_2$ (*M* = 1621.01 g.mol^{-1}): monoclinic, space group P2$_1$/n (no. 14), *a* = 12.4389(3), *b* = 13.8519(4), *c* = 14.2608(3) Å, *β* = 90.601(2)°, *V* = 2457.04(11) Å^3, *Z* = 2, *T* = 150.0(1) K, μ(CuKα) = 17.809 mm^{-1}, *Dcalc* = 2.191 g.cm^{-3}, 13477 reflections measured (8.9° ≤ 2Θ ≤ 141.6°), 4651 unique (R_{int} = 0.0365, R_{sigma} = 0.0416) which were used in all calculations. The final R_1 was 0.0434 (I > 2σ(I)) and wR_2 was 0.1229 (all data) for 305 refined parameters with 0 restraints. CCDC 1949482.

Synthesis of $[W_2Pt(\mu_2\text{-}CSe)_2(CN^tBu)_2(CO)_4(Tp^*)_2]$ (5). To a solution of **3** (50 mg, 0.032 mmol) in MeCN (10 mL) was added ^{t}BuNC (2 drops) and the resulting mixture was stirred for 1 h at RT. After this time, the resulting orange precipitate was collected by filtration, washed with MeCN (10 mL) and petroleum spirits (40–60°C, 20 mL) and dried *in vacuo* to give an orange solid of pure **5** (23 mg, 0.014 mmol, 44%). IR (CH_2Cl_2, cm^{-1}): 2205m, 2193sh ν_{CN}, 1951s, 1864s ν_{CO}. ^1H NMR (700 MHz, $CDCl_3$, 298 K): δ_H = 5.83 (s, 4H, pzC*H*), 5.71 (s, 2H, pzC*H*), 2.70 (s, 12H, pzCH_3), 2.40 (s, 6H, pzCH_3), 2.31 (s, 12H, pzCH_3), 2.28 (s, 6H, pzCH_3), 1.12 (s, 18H, C(CH_3)$_3$). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$, 298 K): δ_C = 289.0 (W*C*Se), 224.7 (W*C*O), 152.8, 152.4, 144.6, 143.9 (pz*C*CH_3), 106.5, 106.4 (pz*C*H), 58.7 (N*C*(CH_3)$_3$), 29.4 (NC(CH_3)$_3$), 17.1, 15.5, 12.7 (pzCH_3). The carbyne (W*C*Se) carbon assignment was confirmed by a correlation with pzCH_3 protons in the ^1H-^{13}C HMBC spectrum. ^{195}Pt and ^{77}Se NMR resonances could not be located, presumably due to the poor solubility of **5** in all common organic solvents. MS (ESI, +ve ion, *m/z*): Found: 1620.2314. Calcd. for $C_{46}H_{63}{}^{11}B_2N_{14}O_4{}^{195}Pt^{80}Se_2{}^{184}W_2$ $[M+H]^+$: 1620.2340. Anal. Found: C, 34.35; H, 3.76; N, 12.00. Calcd for $C_{46}H_{62}B_2N_{14}O_4PtSe_2W_2$: C, 34.16; H, 3.86; N, 12.12%. A crystal suitable for structure determination was grown by vapour diffusion of *n*-hexane into a CH_2Cl_2 solution at –20 °C. *Crystal data for* $C_{46}H_{62}B_2N_{14}O_4PtSe_2W_2$ (*M* = 1617.42 g.mol^{-}): monoclinic, space group P2$_1$/n (no. 14), *a* = 10.4524(6), *b* = 16.4733(10), *c* = 16.6029(12) Å, *β* = 99.080(6)°, *V* = 2823.0(3) Å^3, *Z* = 2, *T* = 150.0(1) K, μ(MoKα) = 7.879 mm^{-1}, *Dcalc* = 1.903 g.cm^{-3}, 14762 reflections measured (7.012° ≤ 2Θ ≤ 52.74°), 5771 unique (R_{int} = 0.0511, R_{sigma} = 0.0767) which were used in all calculations. The final R_1 was 0.0386 (I > 2σ(I)) and wR_2 was 0.0640 (all data) for 332 refined parameters with 0 restraints. CCDC 1949483.

Synthesis of $[W_2Pt(\mu_2\text{-}CSe)_2(CNMes)_2(CO)_4(Tp^*)_2]$ (6). A solution of **3** (20 mg, 0.013 mmol) and CNMes (5 mg, 0.03 mmol) in acetonitrile (5 mL) was stirred for 10 min. The resulting orange precipitate was collected by filtration, washed with MeCN (15 mL) and petroleum spirits (40–60 ˚C) (40 mL) to give an orange solid of pure **6** (13 mg, 0.0075 mmol, 58%). IR (CH_2Cl_2, cm^{-1}): 2184m ν_{NC}, 1954s, 1864s ν_{CO}. ^1H NMR (700 MHz, $CDCl_3$, 298 K): δ_H = 6.76 (s, 4H, Mes{C*H*}), 5.65 (s, 2H, pzC*H*), 5.59 (s, 4H, pzC*H*), 2.64 (s, 12H, pzCH_3), 2.32 (s, 6H, pzCH_3), 2.28 (s, 6H, pzCH_3), 2.27 (s, 12H, pzCH_3), 2.24 (s, 6H, Mes{*p*-CH_3}), 2.13 (s, 12H, Mes{*o*-CH_3}). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$, 298 K): δ_C = 224.9 (W*C*O), 152.6, 152.3, 144.6, 143.6 (pz*C*CH_3), 143.6 (*C*NMes), 140.0 (CN{*p-Mes*}), 136.3 (CN{*o-Mes*}), 128.4 (CN{*m-Mes*}), 123.5 (CN{*i-Mes*}, br, tentative), 106.3, 106.2 (pz*C*H), 21.5 (Mes{*p*-CH_3}), 18.3 (Mes{*o*-CH_3}), 17.1, 15.4, 12.7 (pzCH_3). Carbyne carbon (W*C*Se), platinum and selenium resonances were not unequivocally identified in the $^{13}C\{^1H\}$, ^{195}Pt and ^{77}Se NMR spectra respectively due to poor solubility of **6** in all common organic solvents. MS (ESI, +ve ion, *m/z*): Found: 1764.2493. Calcd. for $C_{56}H_{66}{}^{11}B_2N_{14}O_4{}^{195}Pt^{80}Se_2{}^{184}W_2Na$ $[M+Na]^+$: 1764.2487.

Synthesis of [$W_2PtAu_2(\mu_3\text{-}CSe)_2Cl_2(COD)(CO)_4(Tp^*)_2$] (7). A solution of **2** (100 mg, 0.0640 mmol) and [$AuCl(SMe_2)$] (34 mg, 0.12 mmol) in CH_2Cl_2 (15 mL) was stirred at RT for 5 min. After this time, the mixture was filtered through a pad of diatomaceous earth, which was washed with CH_2Cl_2 until the filtrate ran clear. To the filtrate was added petroleum spirits (40–60 °C, 10 mL) and the CH_2Cl_2 was removed under reduced pressure. The resulting precipitate was collected by filtration and washed with petrol (5 mL) to give an orange microcrystalline solid of pure **7** (82 mg, 0.041 mmol, 63%). IR (CH_2Cl_2, cm^{-1}): 1988s, 1904s ν_{CO}. ^1H NMR (700 MHz, $CDCl_3$, 298 K): δ_H = 6.10 (br m, 4H, COD{=C*H*}), 5.90 (s, 4H, pzC*H*), 5.86 (s, 2H, pzC*H*), 2.90 (br m, 4H, COD{C*H₂*}), 2.64 (s, 12H, pzCH_3), 2.45 (s, 6H, pzCH_3), 2.35 (s, 12H, pzCH_3), 2.35 (br m, 4H, COD{CH_2}), 2.31 (s, 6H, pzCH_3). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$, 298 K): δ_C = 257.1 (W*C*Se), 217.1 (W*C*O, $^1J_{WC}$ = 157), 153.1, 153.0, 145.6, 145.1 (pz*C*CH₃), 107.9, 107.5 (pz*C*H), 100.2 (COD{=*C*H}), 31.1 (COD{CH_2}), 18.2, 16.0 13.1, 12.9 (pzCH_3). ^{195}Pt NMR (150 MHz, $CDCl_3$, 298 K): $\delta_{Pt\,=}$ –3701. ^{77}Se NMR (134 MHz, $CDCl_3$, 298 K): δ_{Se} = 545. MS (ESI, +ve ion, *m/z*): Found: 1989.0758. Calcd for $C_{44}H_{56}Au_2{}^{11}B_2{}^{35}ClN_{12}O_4{}^{195}Pt^{80}Se_2{}^{184}W_2$ $[M–Cl]^+$: 1989.0776. Anal. Found: C, 26.45; H, 2.39; N, 7.94. Calcd for $C_{44}H_{56}Au_2B_2Cl_2N_{12}O_4PtSe_2W_2$: C, 26.11; H, 2.79; N, 8.30%. A crystal suitable for structure determination was grown by vapour diffusion of *n*-hexane into a CH_2Cl_2 solution at –20 °C. *Crystal data for* $C_{48}H_{64}Au_2B_2Cl_{10}N_{12}O_4PtSe_2W_2$ (*M* = 2363.87 g.mol^{-1}): monoclinic, space group $P2_1/c$ (no. 14), *a* = 20.1587(9) Å, *b* = 19.5305(6), *c* = 19.4821(8), *β* = 117.307(6)°, *V* = 6815.5(6) Å^3, *Z* = 4, *T* = 150.0(1) K, μ(MoKα) = 11.208 mm^{-1}, *Dcalc* = 2.304 g.cm^{-3}, 31925 reflections measured (6.46° ≤ 2Θ ≤ 50.052°), 12015 unique (R_{int} = 0.0480, R_{sigma} = 0.0668) which were used in all calculations. The final R_1 was 0.0358 (I > 2σ(I)) and wR_2 was 0.0695 (all data) for 756 refined parameters with 50 restraints. CCDC 1949484.

Synthesis of [$W_2PtAu_2(\mu_3\text{-}CSe)_2Cl_2(NBD)(CO)_4(Tp^*)_2$] (8). A solution of **3** (57 mg, 0.037 mmol) and [$AuCl(SMe_2)$] (23 mg, 0.078 mmol) in CH_2Cl_2 (10 mL) was stirred at RT for 5 min. After this time, the mixture was filtered through a pad of diatomaceous earth, which was washed with CH_2Cl_2 until the filtrate ran clear. To the filtrate was added ethanol (5 mL) and the CH_2Cl_2 was removed under reduced pressure. The resulting orange precipitate was collected by filtration, washed with ethanol (5 mL) and *n*-hexane (30 mL), and dried *in vacuo* to give an orange solid of pure **8** (24 mg, 0.012 mmol, 32%). A second crop of slightly reduced purity was collected by further reduction of the filtrate solvent volume under reduced pressure (29 mg, 0.014 mmol, 39%). IR (CH_2Cl_2, cm^{-1}): 2010m, 1932m ν_{CO}. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ_H = 6.21 (br m, 4H, NBD{=C*H*}), 5.94 (s, 4H, pzC*H*), 5.86 (s, 2H, pzC*H*), 4.37 (br m, 2H, NBD{C*H*}), 2.62 (s, 12H, pzCH_3), 2.55 (s, 6H, pzCH_3), 2.45 (s, 12H, pzCH_3), 2.31 (s, 6H, pzCH_3), 1.64 (br m, 2H, NBD{CH_2}). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$, 298 K): δ_C = 255.2 (W*C*Se), 217.0 (W*C*O, $^1J_{CW}$ = 162), 153.1, 153.0, 145.6, 145.1 (pz*C*CH₃), 107.9, 107.5 (pz*C*H), 87.2 (NBD{=*C*H}), 70.6 (NBD{*C*H}), 50.0 (NBD{CH_2}), 18.2, 16.0 13.1, 12.9 (pzCH_3). ^{195}Pt NMR (150 MHz, $CDCl_3$, 298 K): $\delta_{Pt\,=}$ –3594. ^{77}Se NMR (134 MHz, $CDCl_3$, 298 K): δ_{Se} = 587. MS (ESI, +ve ion, *m/z*): Found: 1847.0147 (z=2). Calcd for $C_{72}H_{88}Au_6{}^{11}B_4N_{24}O_8{}^{80}Se_4{}^{184}W_4$ $[4[\mathbf{1}]^-+6Au^+]^{2+}$: 1847.0180. MS (ESI, +ve ion, *m/z*): Found: 3497.0551 (z=1). Calcd for $C_{72}H_{88}Au_5{}^{11}B_4N_{24}O_8{}^{80}Se_4{}^{184}W_4$ $[4[\mathbf{1}]^-+5Au^+]^{2+}$: 3497.0693. NB: The complex apparently decomposes during ESI mass spectrometry conditions to give clusters comprised of the tungsten selenocarbonyls and gold(I) cations.

Synthesis of [$W(\equiv CSeCH_2Cl)(CO)_2(Tp^*)$] (9). A solution of [**1**]NEt_4 (100 mg, 0.138 mmol) in CH_2Cl_2 (20 mL) was stirred for 5 h, during which time the initially yellow solution turned brown. After this time, the solvent was removed under reduced pressure, the residue was extracted with toluene and filtered through a pad of diatomaceous earth. The solvent was once more removed under reduced pressure to give a brown solid of pure **9** (91 mg, 0134 mmol, 97%). IR (CH_2Cl_2, cm^{-1}): 1983s, 1893s ν_{CO}. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ_H = 5.91 (s, 2H, pzC*H*), 5.78 (s, 1H, pzC*H*), 5.04 (s, $^2J_{HSe}$ = 13, 2H, SeCH_2Cl), 2.57 (s, 6H, pzCH_3), 2.41 (s, 3H, pzCH_3), 2.37 (s, 6H, pzCH_3), 2.32 (s, 3H, pzCH_3). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$, 298 K): δ_C = 247.3 (W*C*Se, $^1J_{CW}$ = 219, $^1J_{CSe}$ = 184), 224.0 (W*C*O, $^1J_{CW}$ = 166), 152.7, 152.2, 145.5, 144.6 (pz*C*CH₃), 106.9, 106.7 (pz*C*H), 37.7 (Se*C*H₂Cl, $^1J_{CSe}$ = 99.0), 16.8, 15.4, 12.8, 12.8 (pzCH_3). ^{77}Se NMR (76 MHz, $CDCl_3$, 298 K): δ_{Se} = 673 (t, $^2J_{SeH}$ = 13 Hz). MS (ESI, +ve ion, *m/z*): Found: 701.0294. Calcd for $C_{19}H_{24}{}^{11}B^{35}ClN_6NaO_2{}^{80}Se^{184}W$ $[M+Na]^+$: 701.0305. Anal. Found: C, 33.74; H, 3.29; N, 12.51. Calcd for $C_{19}H_{24}BClN_6O_2SeW$: C, 33.68; H, 3.57; N, 12.40%.

Synthesis of [$WAu(\mu\text{-}CSeCH_2Cl)Cl(CO)_2(Tp^*)$] (10). A solution of **9** (45 mg, 0.066 mmol) and [$AuCl(SMe_2)$] (22 mg, 0.077 mmol) in CH_2Cl_2 (10 mL) was stirred for 10 min with protection from light. After this time, the mixture filtered through a pad of diatomaceous earth, which was washed with CH_2Cl_2 until the filtrate ran clear. The solvent was removed under reduced pressure to give a brown solid of pure **10** (42 mg, 0.046 mmol, 70%). IR (CH_2Cl_2, cm^{-1}): 2008s, 1926s ν_{CO}. ^1H NMR (600 MHz, $CDCl_3$, 298 K): δ_H = 5.96 (s, 2H, pzC*H*), 5.93 (s, 1H, pzC*H*), 5.23 (s, $^2J_{HSe}$ = 15 Hz, 2H, SeCH_2Cl), 2.50 (s, 6H, pzCH_3), 2.46 (s, 3H, pzCH_3), 2.38 (s, 6H, pzCH_3), 2.35 (s, 3H, pzCH_3). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 298 K): δ_C = 245.4 (W*C*Se, $^1J_{WC}$ = 101), 216.2 (W*C*O, $^1J_{WC}$ = 156), 153.4, 152.8, 146.4, 145.8 (pz*C*CH₃), 108.4, 107.9 (pz*C*H), 42.8 (Se*C*H₂Cl, $^1J_{SeC}$ = 96), 17.5, 15.9, 13.2, 12.8 (pzCH_3). ^{77}Se NMR (76 MHz, $CDCl_3$, 298 K): δ_{Se} = 702 (t, $^2J_{SeH}$ = 15 Hz). MS (ESI, +ve ion, *m/z*): Found: 916.0346. Calcd. for $C_{21}H_{27}Au^{11}B^{35}N_7O_2{}^{80}Se^{184}WCH_3CN$ $[M–Cl+CH_3CN]^+$: 916.0342. Anal. Found: C, 25.12; H, 2.74; N 9.11. Calcd for $C_{19}H_{24}AuBClN_6O_2SeW\cdot CH_2Cl_2$: C, 24.93; H, 2.73; N, 8.76%. A crystal suitable for structure determination was grown by slow evaporation of a CH_2Cl_2 solution at –20 °C and proved to be a dichloromethane solvate. *Crystal data for* $C_{20}H_{26}AuBCl_4N_6O_2SeW$ (*M* = 994.85 g.mol^{-1}): monoclinic, space group $P2_1$ (no. 4), *a* = 14.1718(3), *b* = 15.5447(4), *c* = 15.4562(4) Å, *β* = 106.216(2)°, *V* = 3269.48(14) Å^3, *Z* = 4, *T* = 150.0(1) K, μ(CuKα) = 19.228 mm^{-1}, *Dcalc* = 2.021 g.cm^{-3}, 11885 reflections measured (7.488° ≤ 2Θ ≤ 133.184°), 8266 unique (R_{int} = 0.0343, R_{sigma} = 0.0581) which were used in all calculations. The final R_1 was 0.0438 (I > 2σ(I)) and wR_2 was 0.1211 (all data) for 664 refined parameters with 669 restraints. CCDC 1949485.

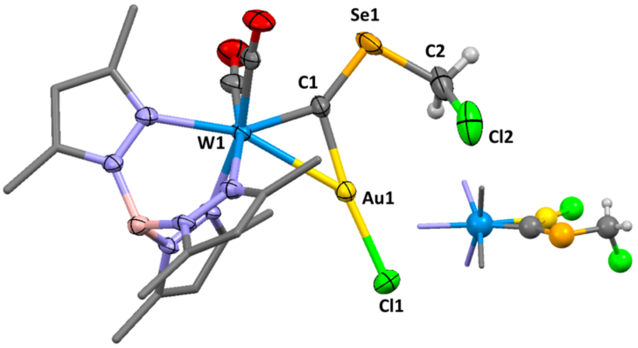

Figure ESI-1. Molecular structure of **10** in a crystal of **10**·CH_2Cl_2 showing 50% thermal probability ellipsoids. Pyrazolyl groups are simplified and solvent are not shown for clarity. Selected distances [Å] and angles [°]: W1–C1 1.933(17), W1–Au1 2.7737(7), C1–Au1 2.029(18), Au1–Cl1 2.283(5), C1–Se1 1.843(18), Se1–C4 1.92(2), W1–C1–Se1 145.8(10), C1–Se1–C4 99.5(9). Inset = alternative view of core.

Notes and references

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2. (a) G. Sheldrick, *Acta Crystallogr. Sect. A: Found. Crystallogr.*, 2008, **64**, 112-122; (b) G. M. Sheldrick, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.*, 2015, **71**, 3-8.
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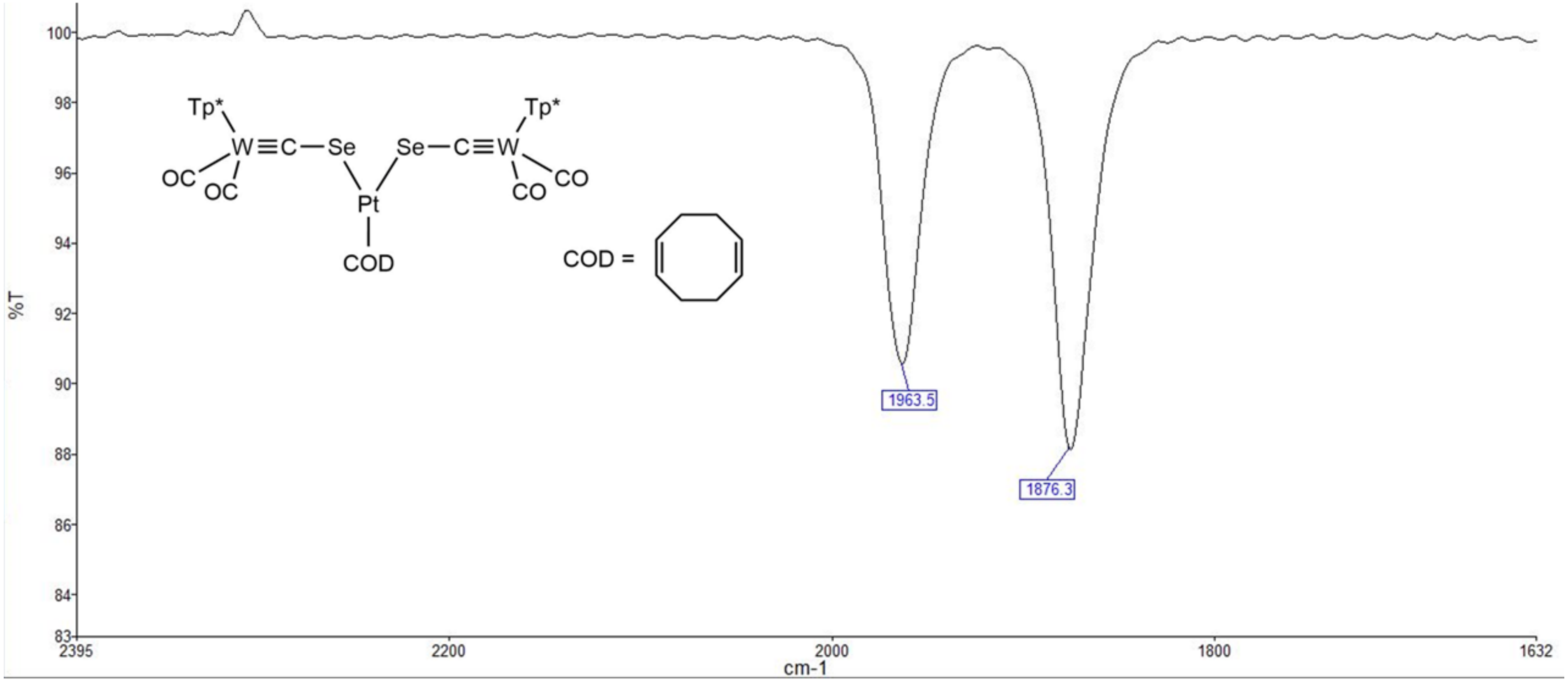
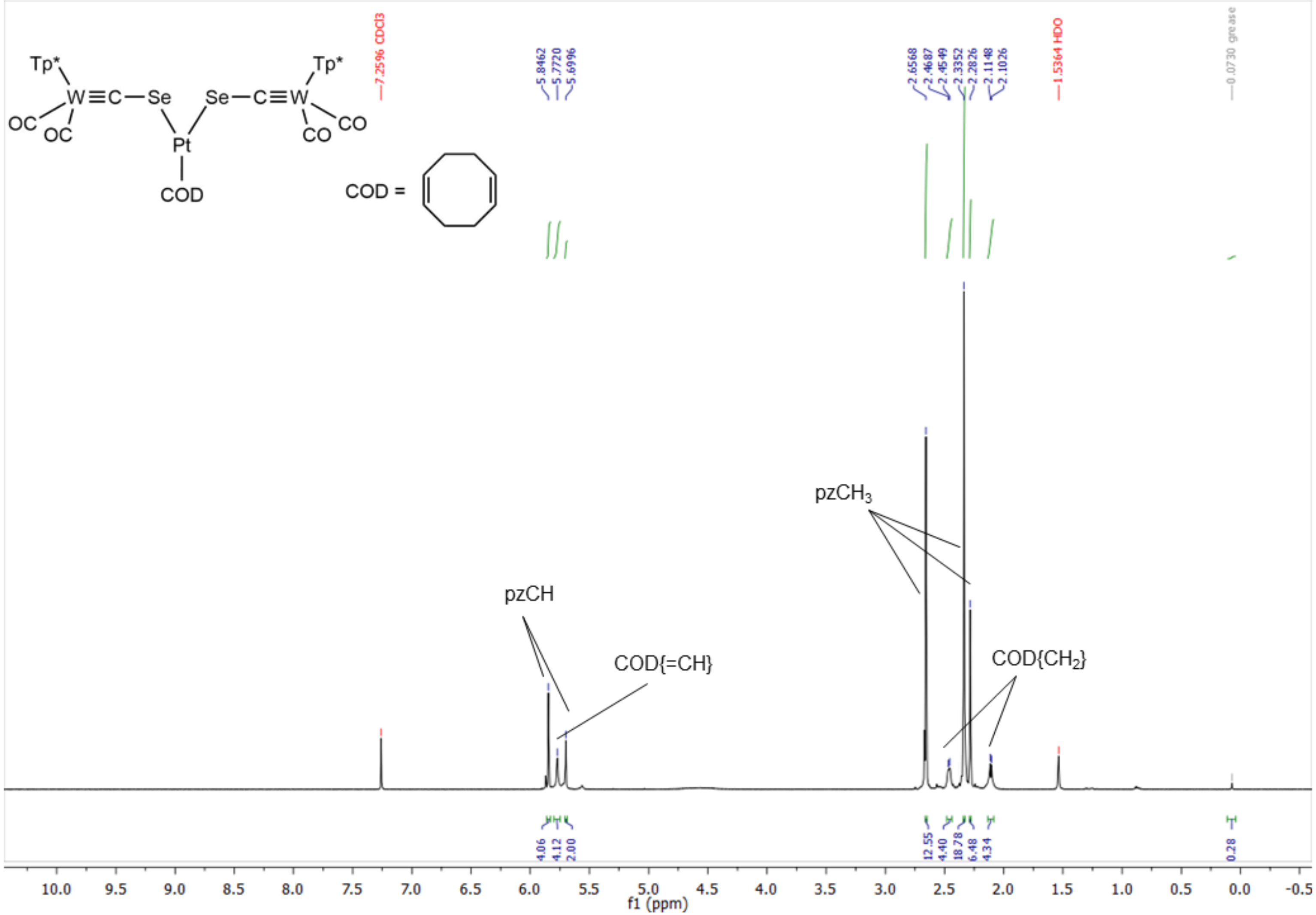
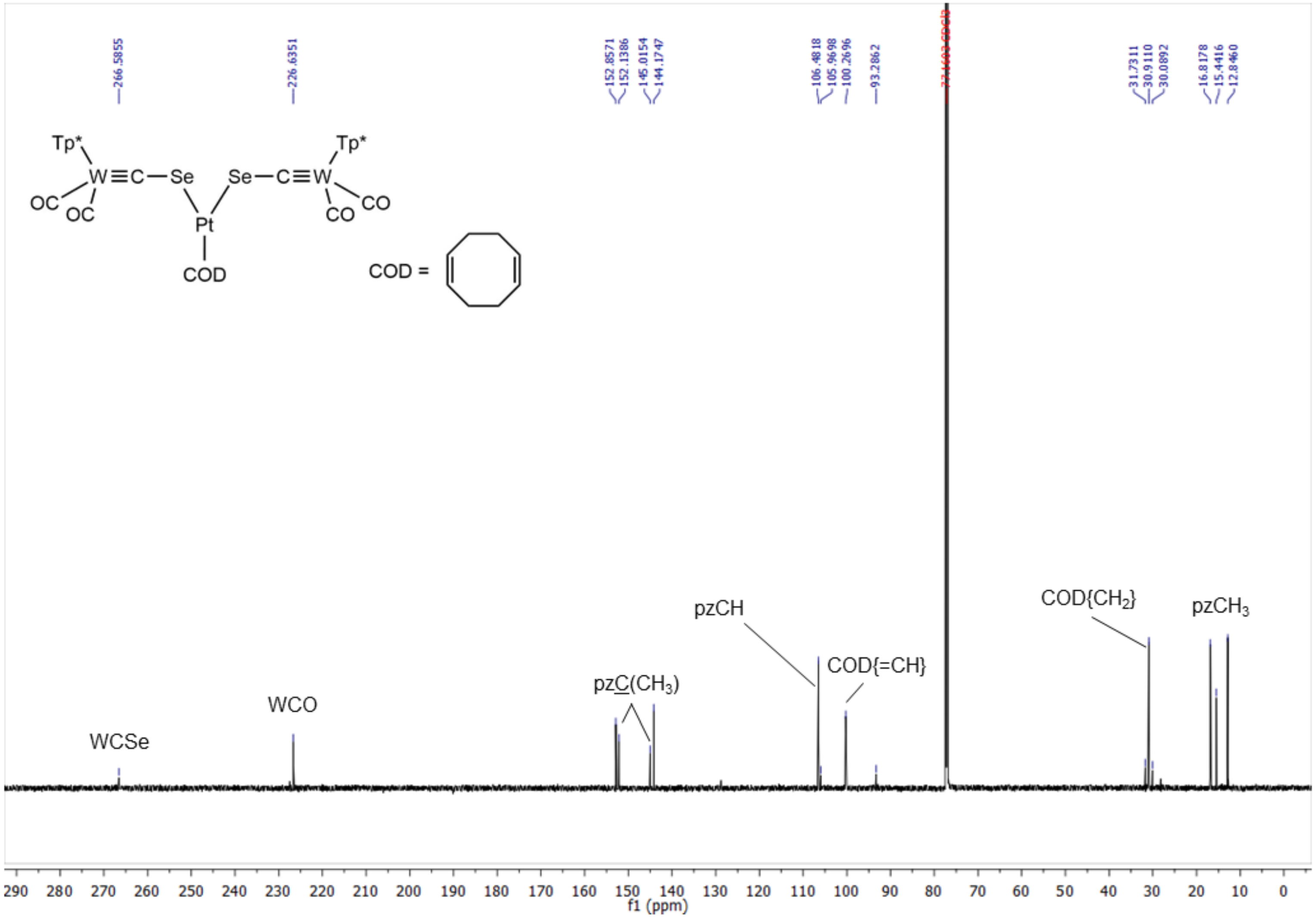


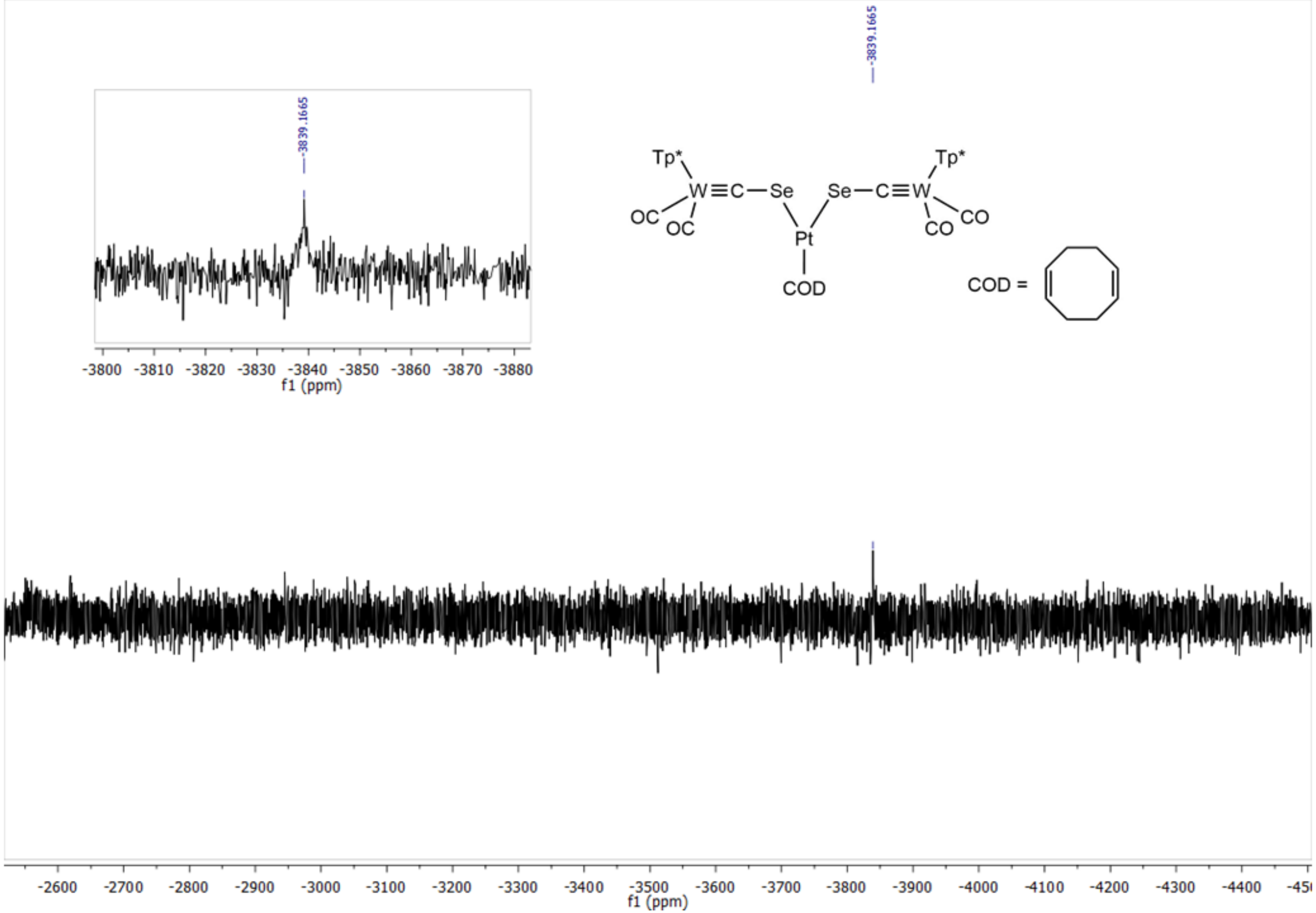
IR (CH_2Cl_2, cm^{-1}) for $[W_2Pt(\mu_2\text{-}CSe)_2(COD)_2(CO)_4(Tp^*)_2]$ (**2**).



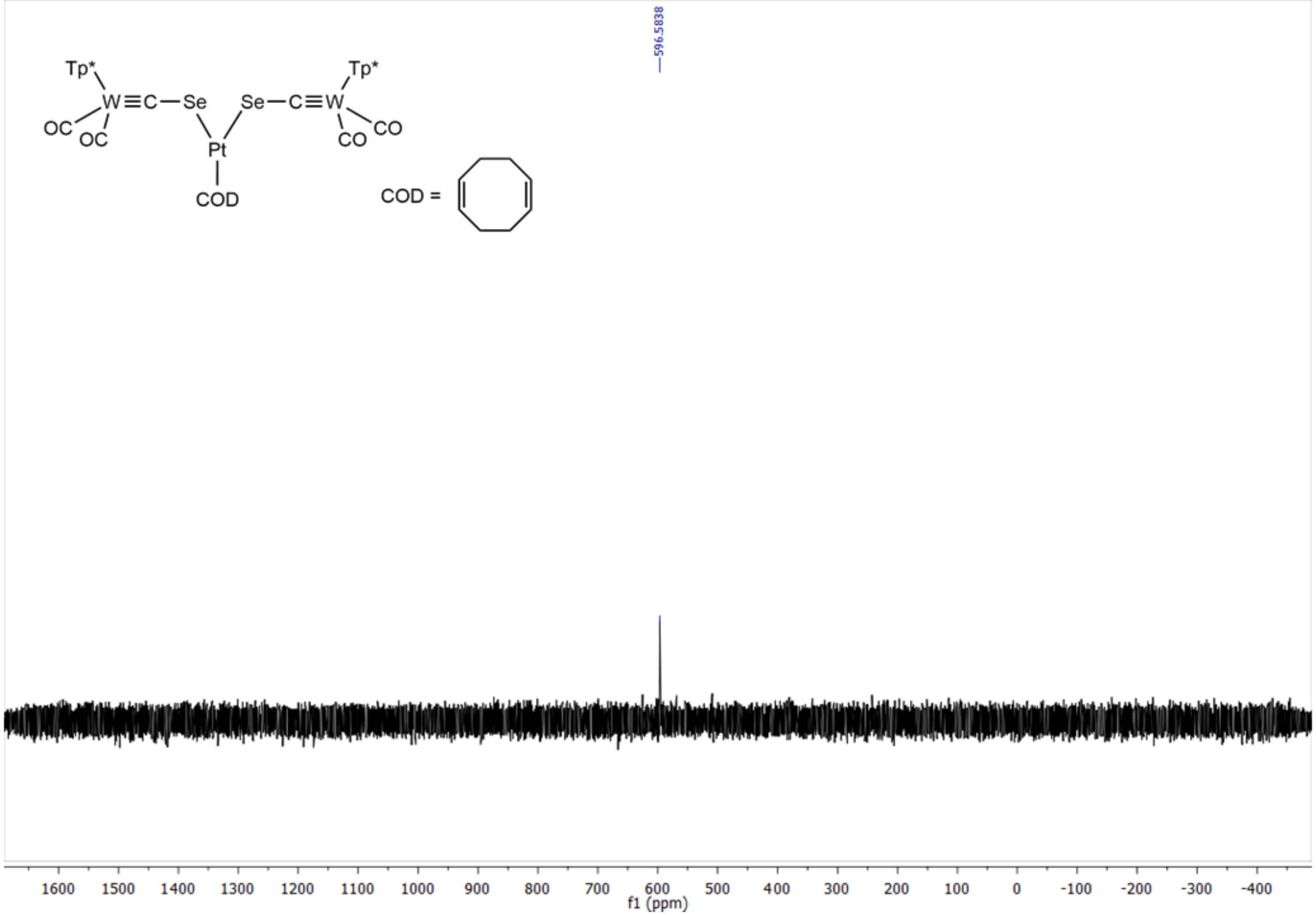
^1H NMR (400 MHz, $CDCl_3$, 298 K) for $[W_2Pt(\mu_2\text{-}CSe)_2(COD)_2(CO)_4(Tp^*)_2]$ (**2**).



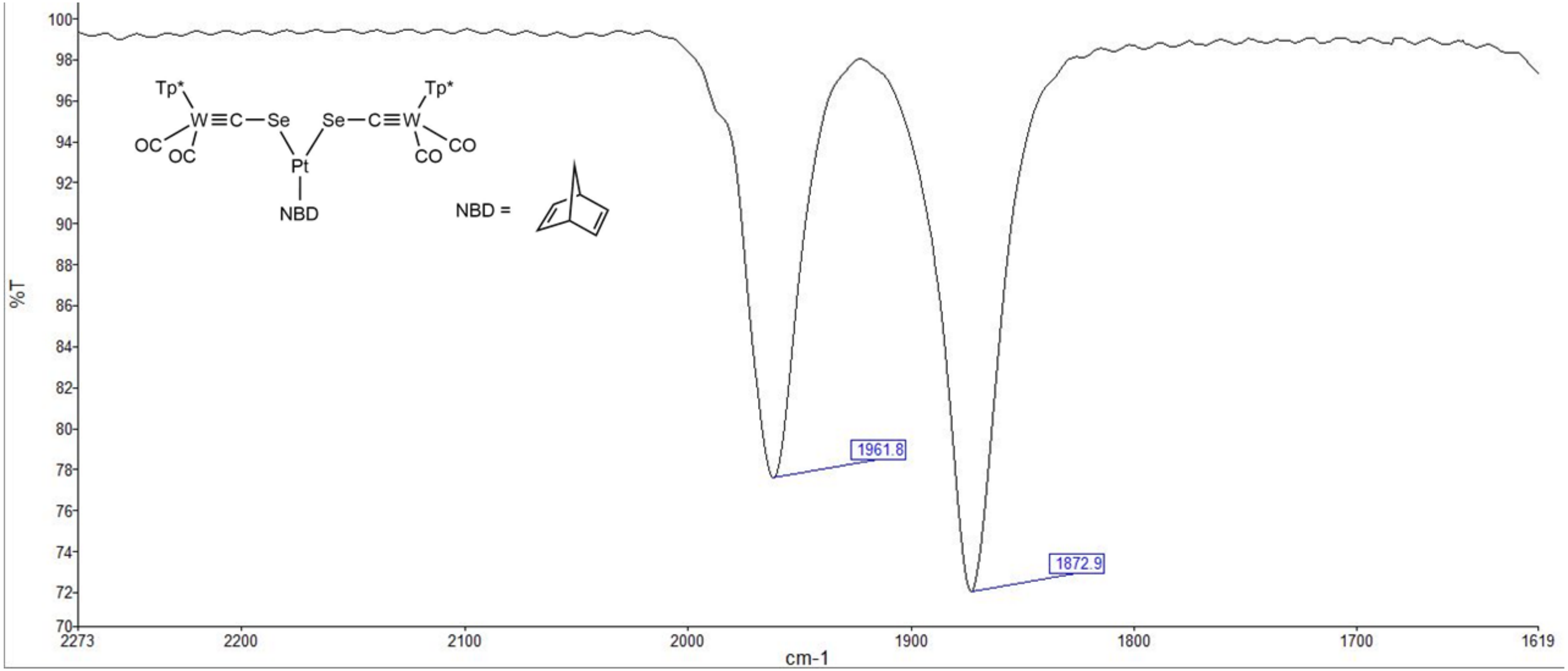
$^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$, 298 K) for $[W_2Pt(\mu_2\text{-}CSe)_2(COD)_2(CO)_4(Tp^*)_2]$ (**2**).



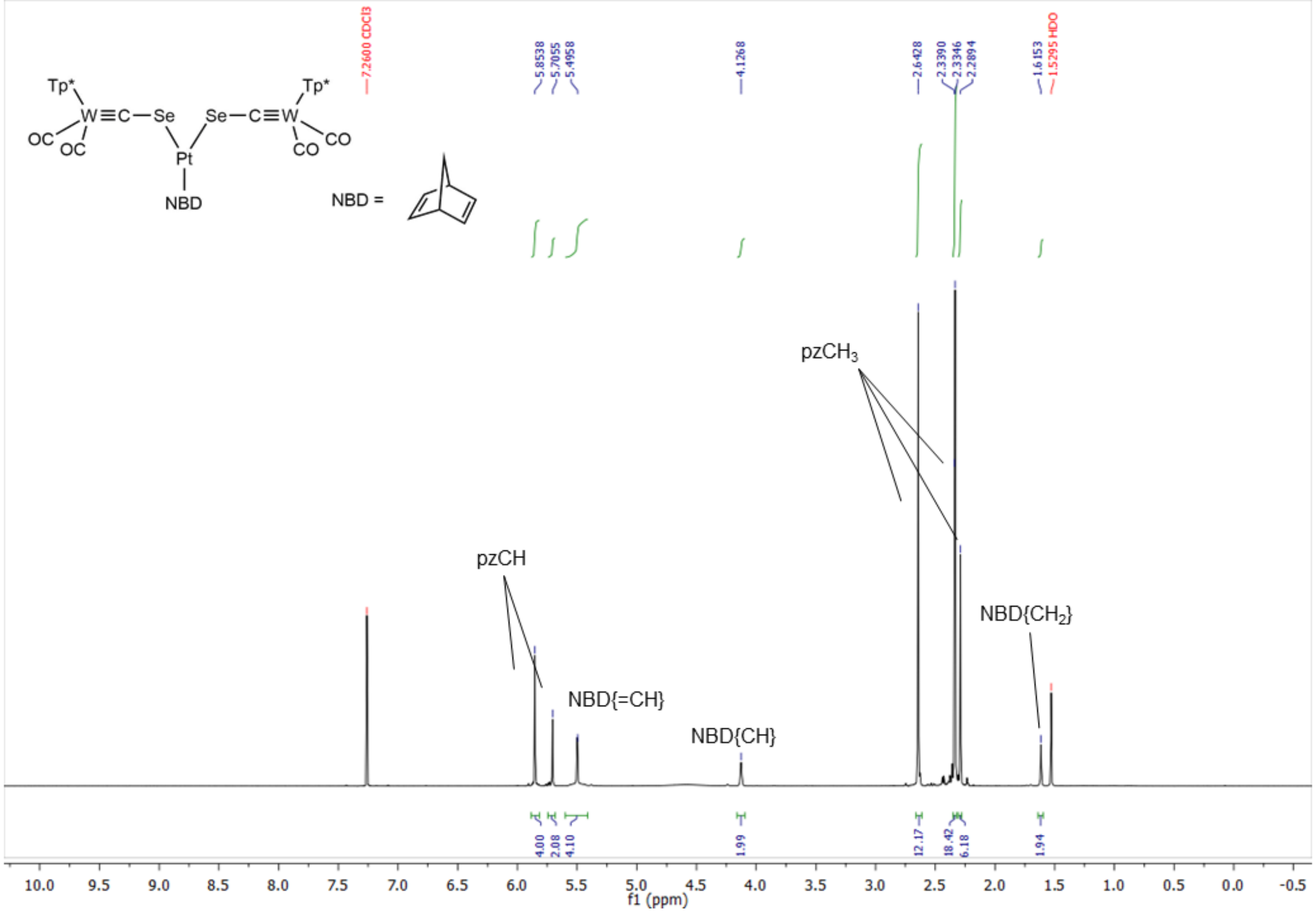
^{195}Pt NMR (86 MHz, $CDCl_3$, 298 K) for [$W_2Pt(\mu_2\text{-}CSe)_2(COD)_2(CO)_4(Tp^*)_2$] (**2**).



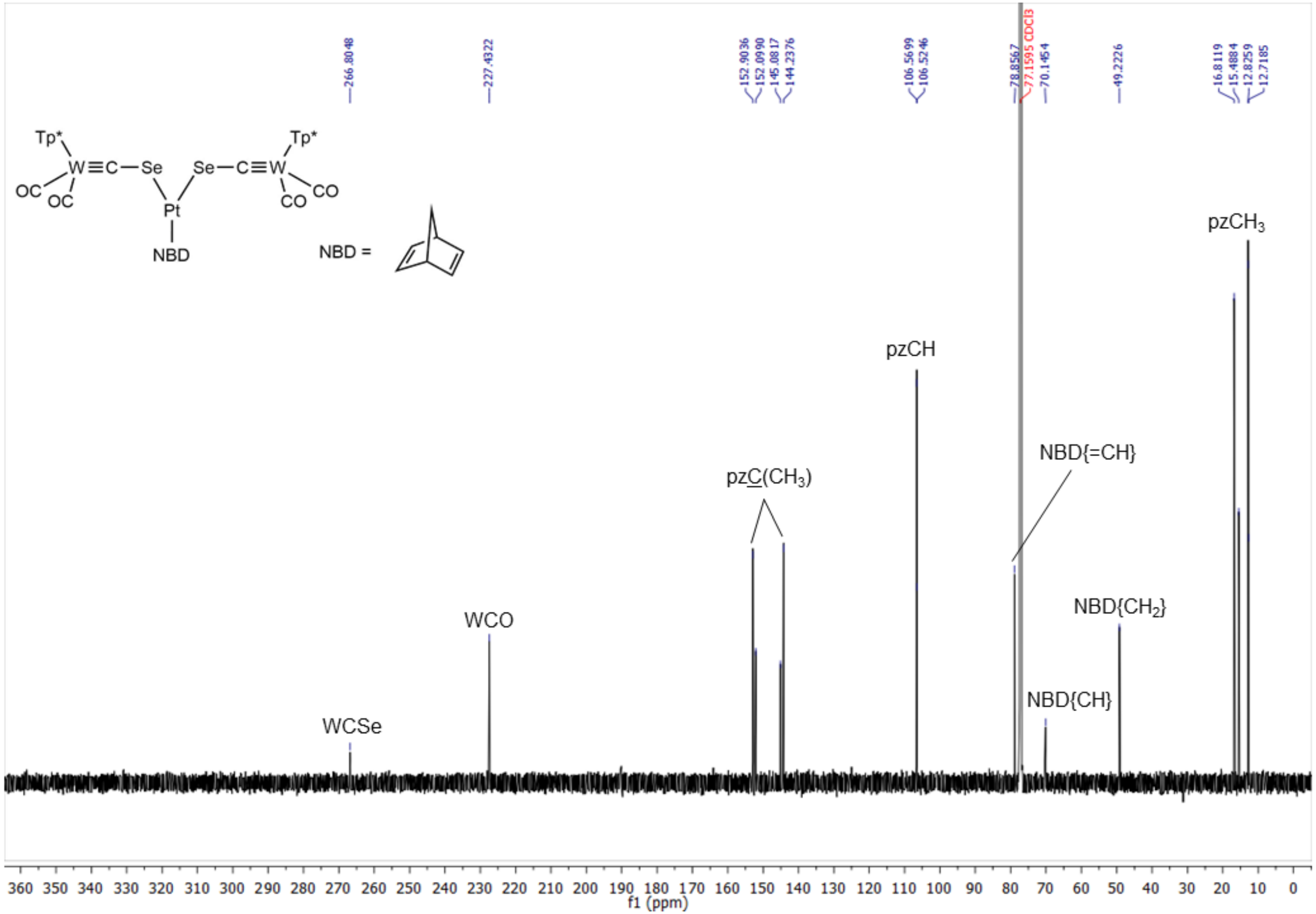
^{77}Se NMR (76 MHz, $CDCl_3$, 298 K) for $[W_2Pt(\mu_2\text{-}CSe)_2(COD)_2(CO)_4(Tp^*)_2]$ (**2**).



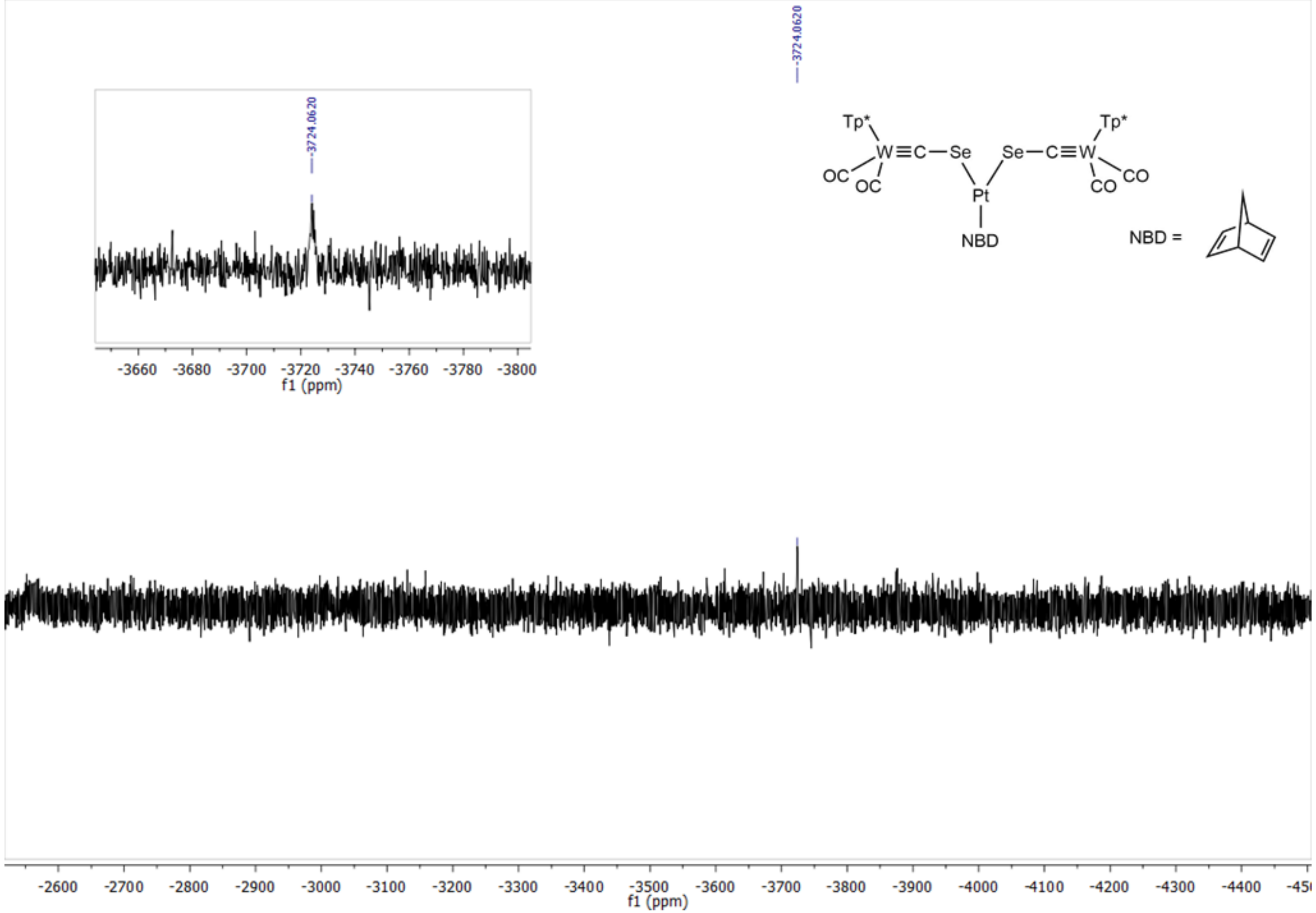
IR (CH_2Cl_2, cm^{-1}) for [$W_2Pt(\mu_2\text{-}CSe)_2(NBD)_2(CO)_4(Tp^*)_2$] (**3**).



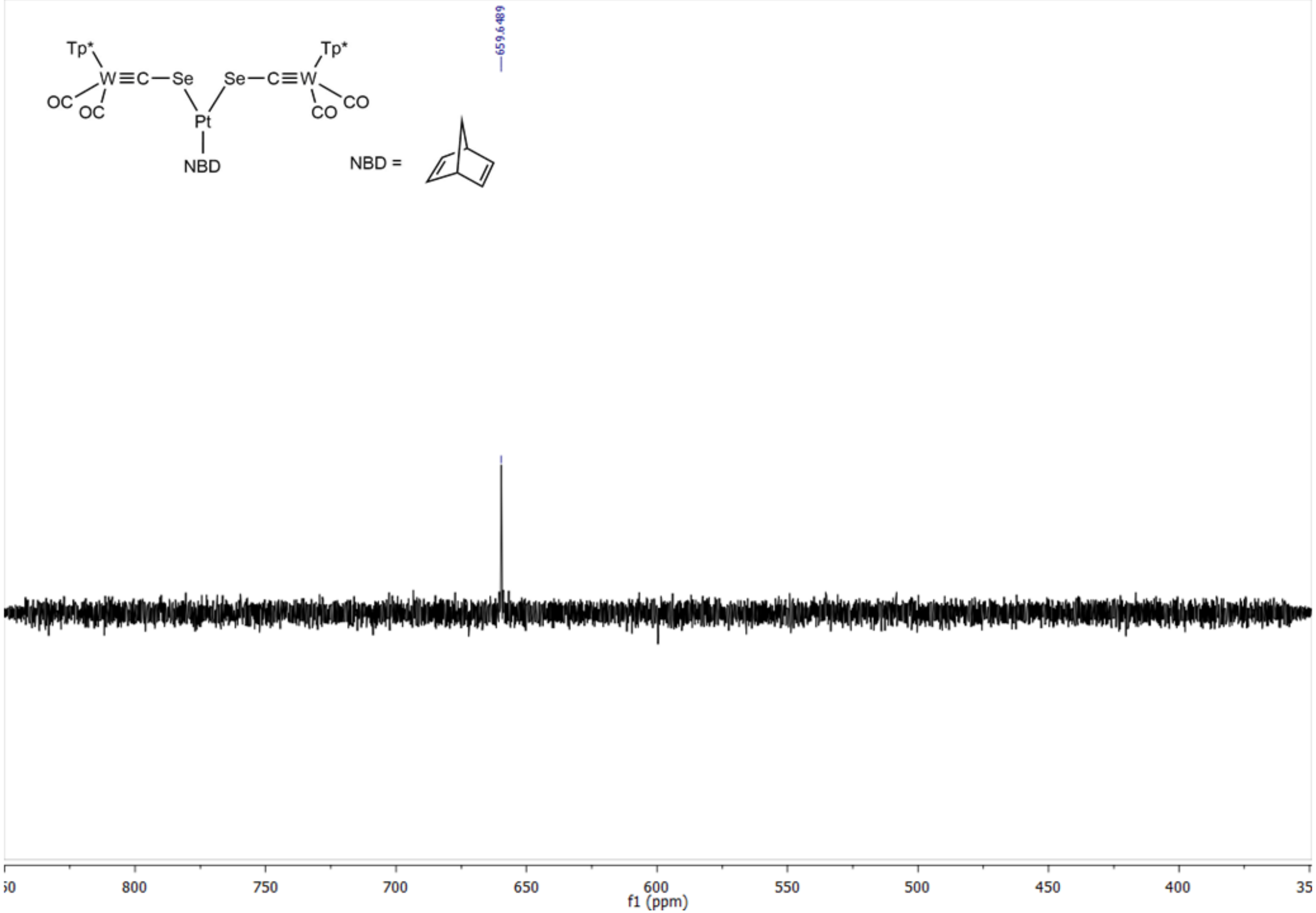
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) for $[W_2Pt(\mu_2\text{-}CSe)_2(NBD)_2(CO)_4(Tp^*)_2]$ (**3**).



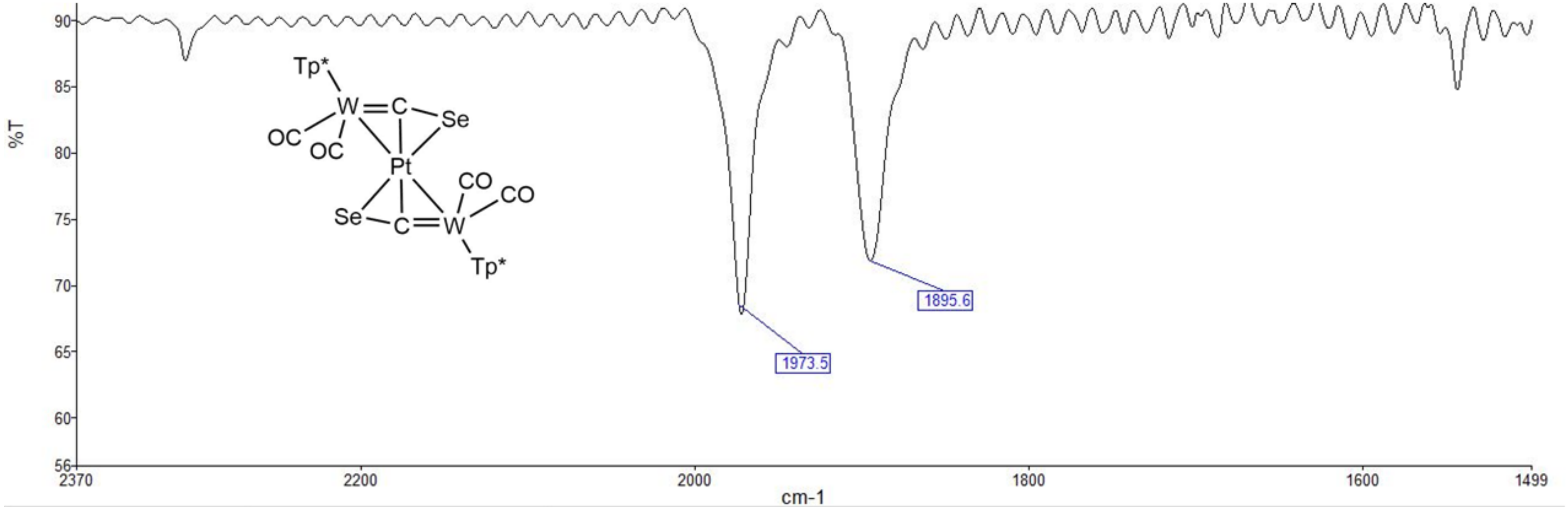
$^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$, 298 K) for $[W_2Pt(\mu_2\text{-}CSe)_2(NBD)_2(CO)_4(Tp^*)_2]$ (**3**).



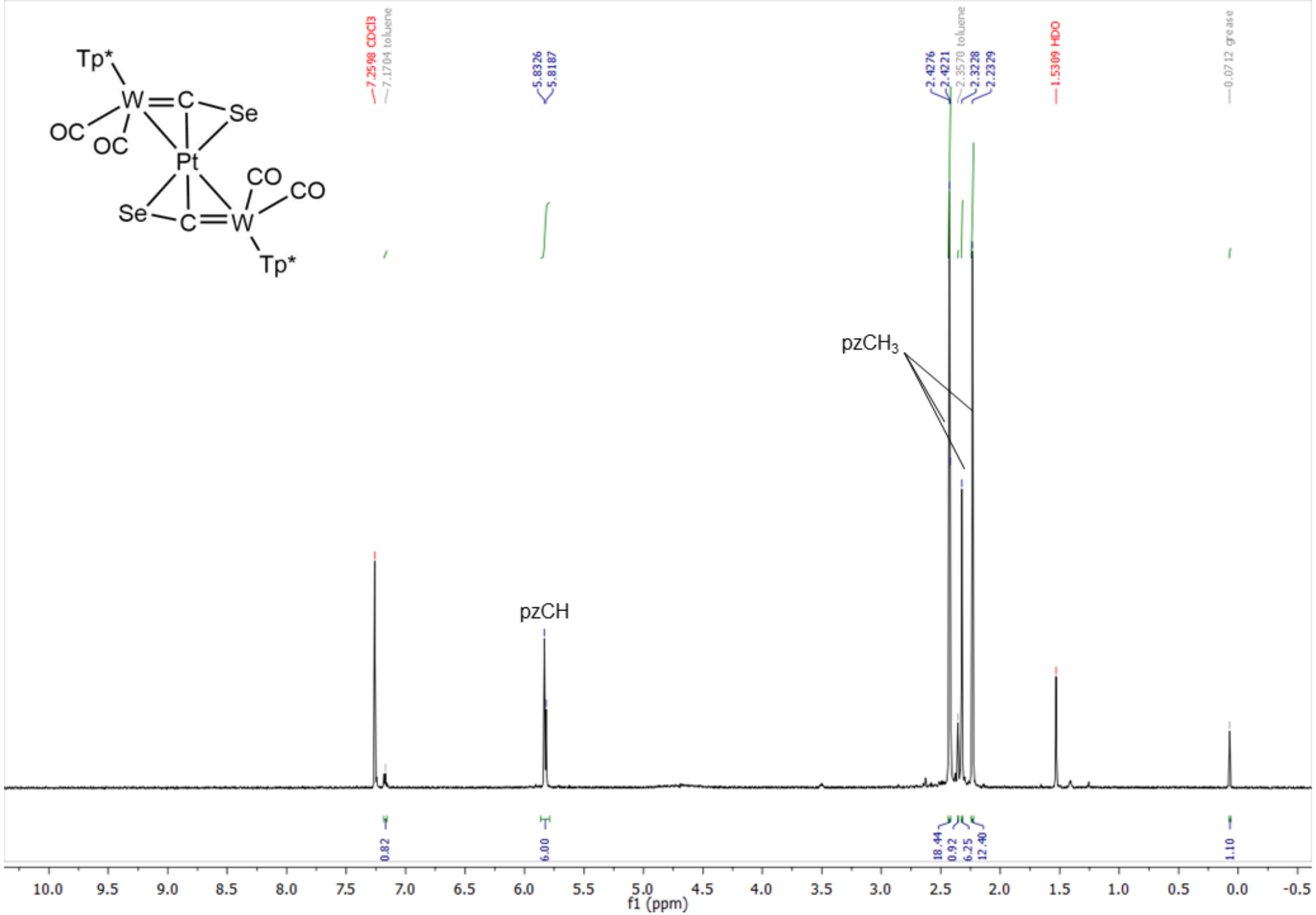
^{195}Pt NMR (86 MHz, $CDCl_3$, 298 K) for [$W_2Pt(\mu_2\text{-}CSe)_2(NBD)_2(CO)_4(Tp^*)_2$] (**3**).



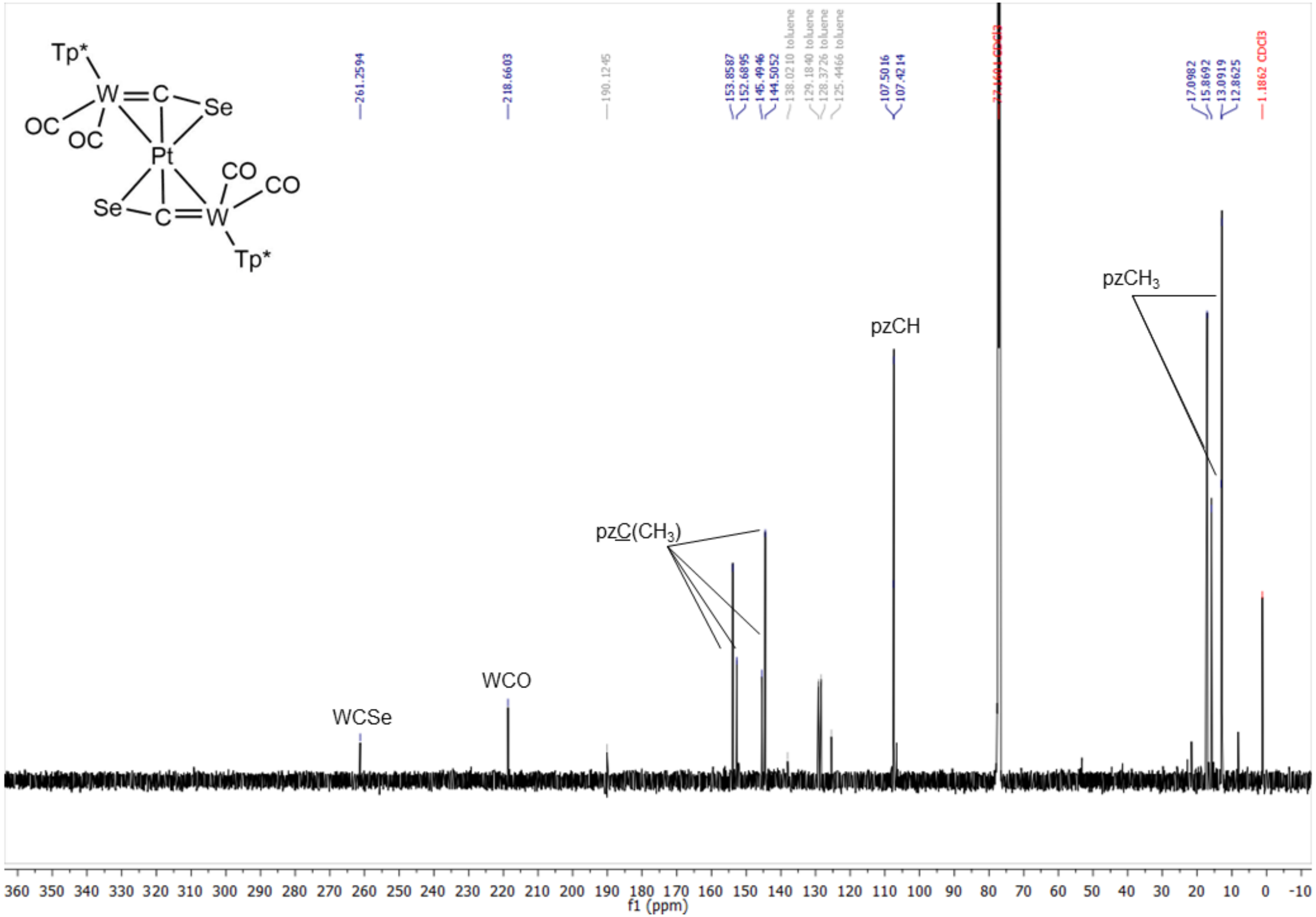
^{77}Se NMR (76 MHz, $CDCl_3$, 298 K) for [$W_2Pt(\mu_2\text{-}CSe)_2(NBD)_2(CO)_4(Tp^*)_2$] (**3**).



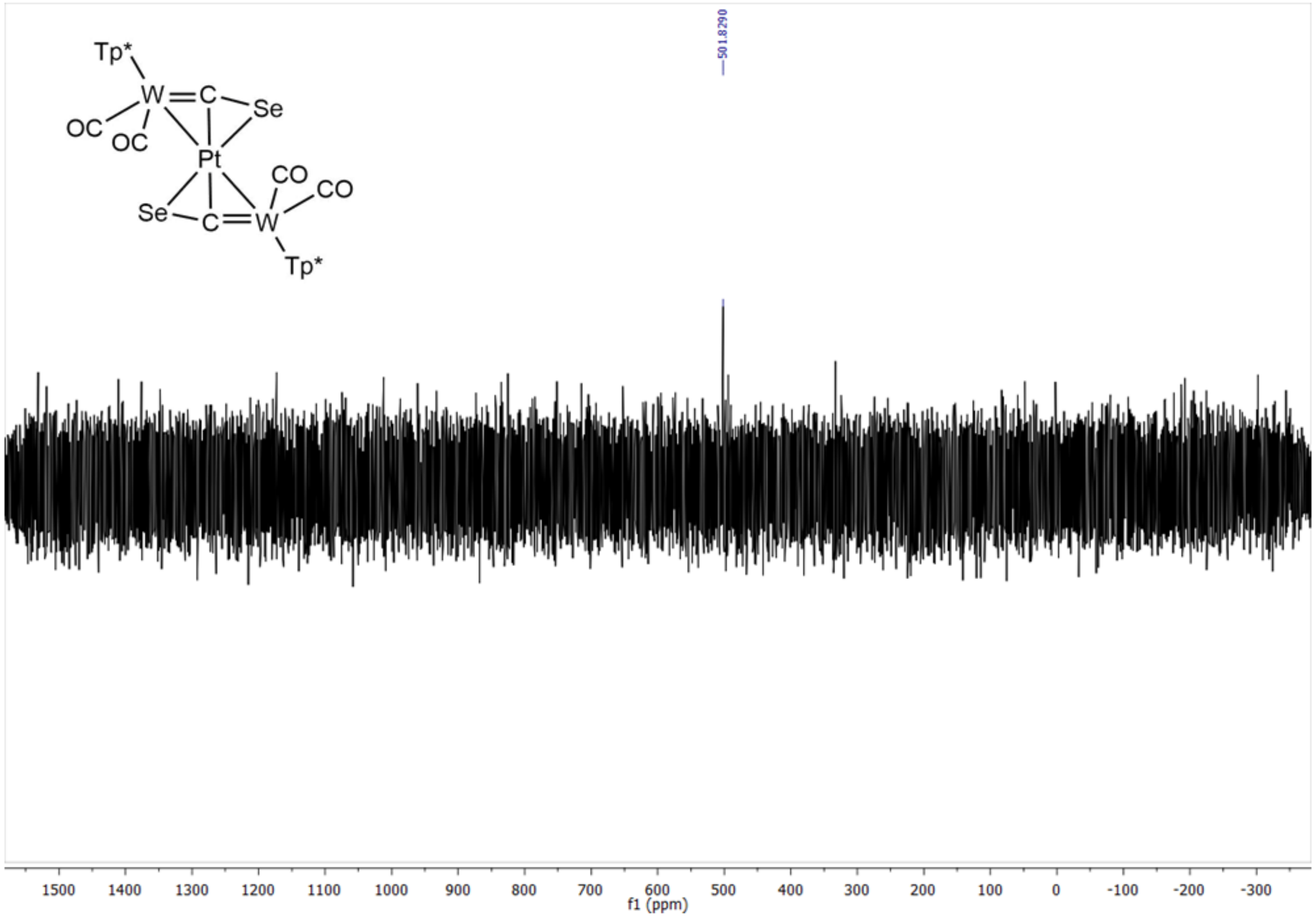
IR (CH_2Cl_2, cm^{-1}) for [$W_2Pt(\mu_2\text{-}CSe)_2(CO)_4(Tp^*)_2$] (**4**).



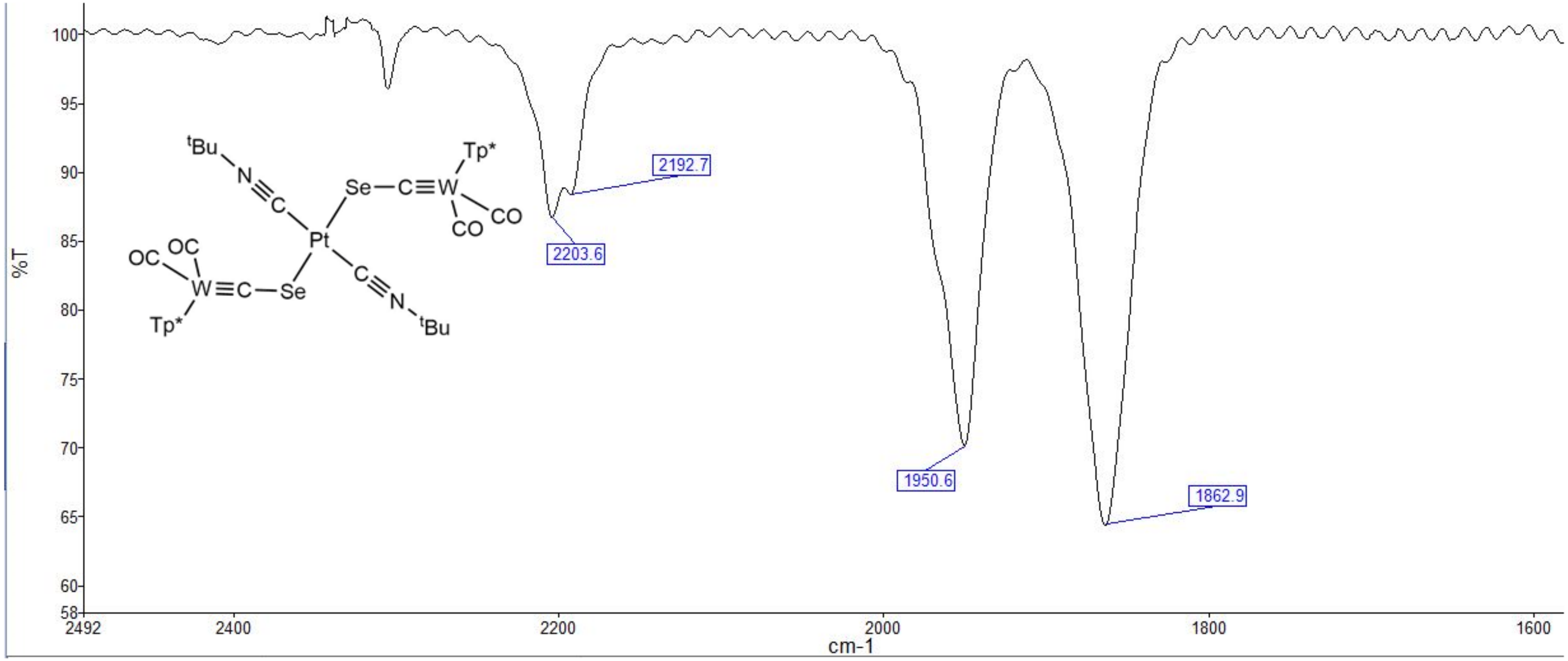
^{1}H NMR (700 MHz, $CDCl_3$, 298 K) for $[W_2Pt(\mu_2\text{-}CSe)_2(CO)_4(Tp^*)_2]$ (**4**).



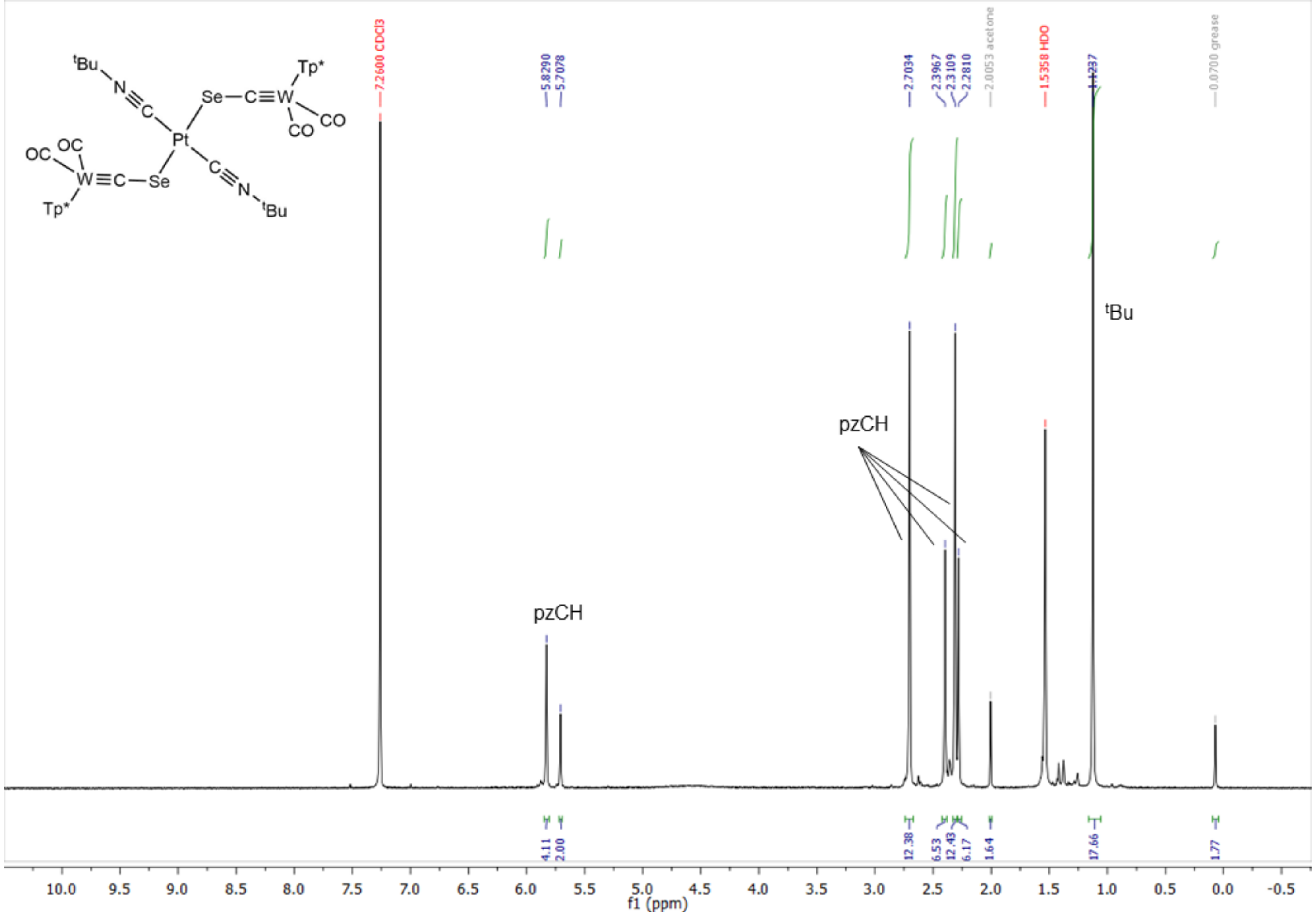
$^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$, 298 K) for $[W_2Pt(\mu_2\text{-}CSe)_2(CO)_4(Tp^*)_2]$ (**4**).



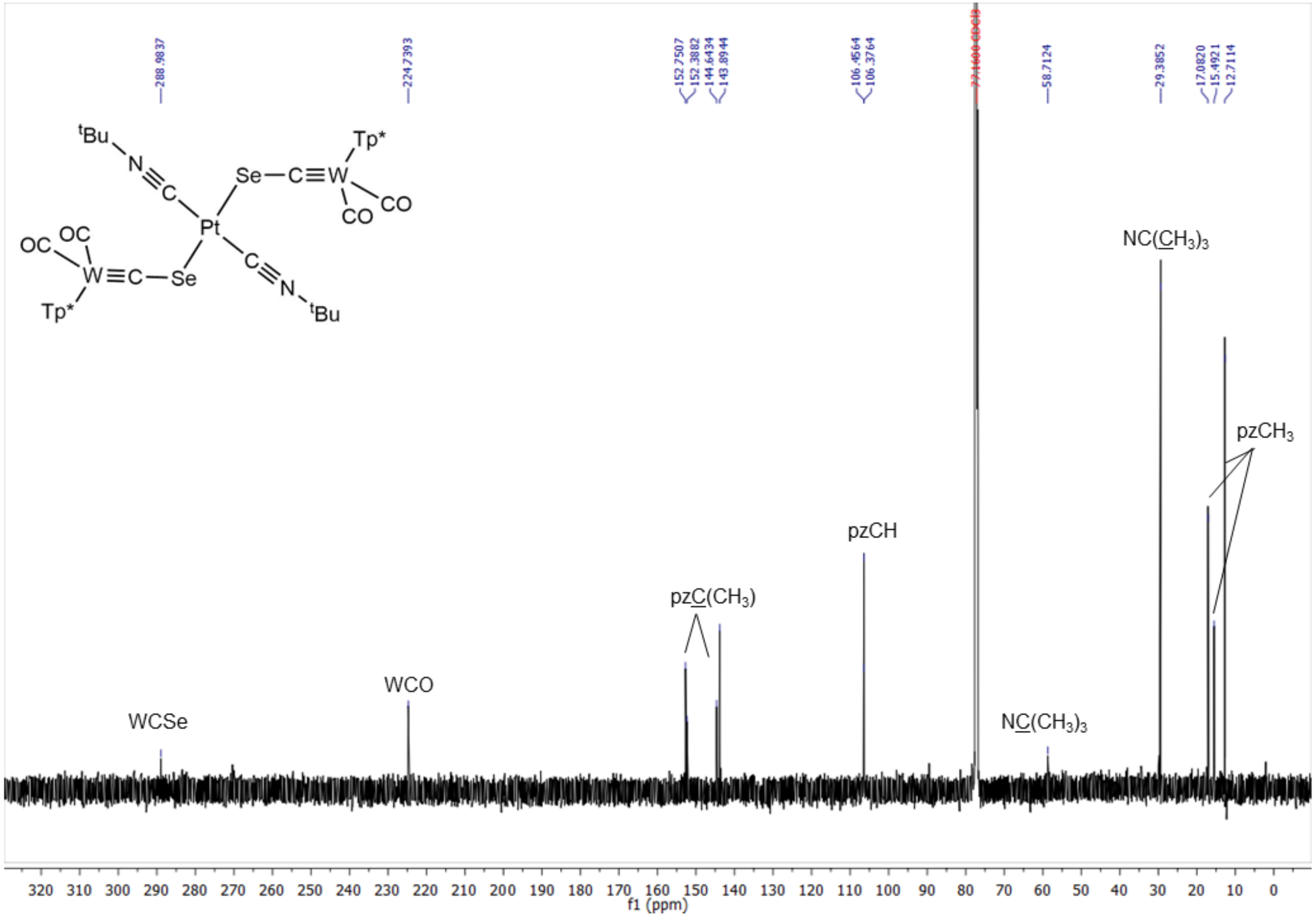
^{77}Se NMR (76 MHz, $CDCl_3$, 298 K) for [$W_2Pt(\mu_2\text{-}CSe)_2(CO)_4(Tp^*)_2$] (**4**).



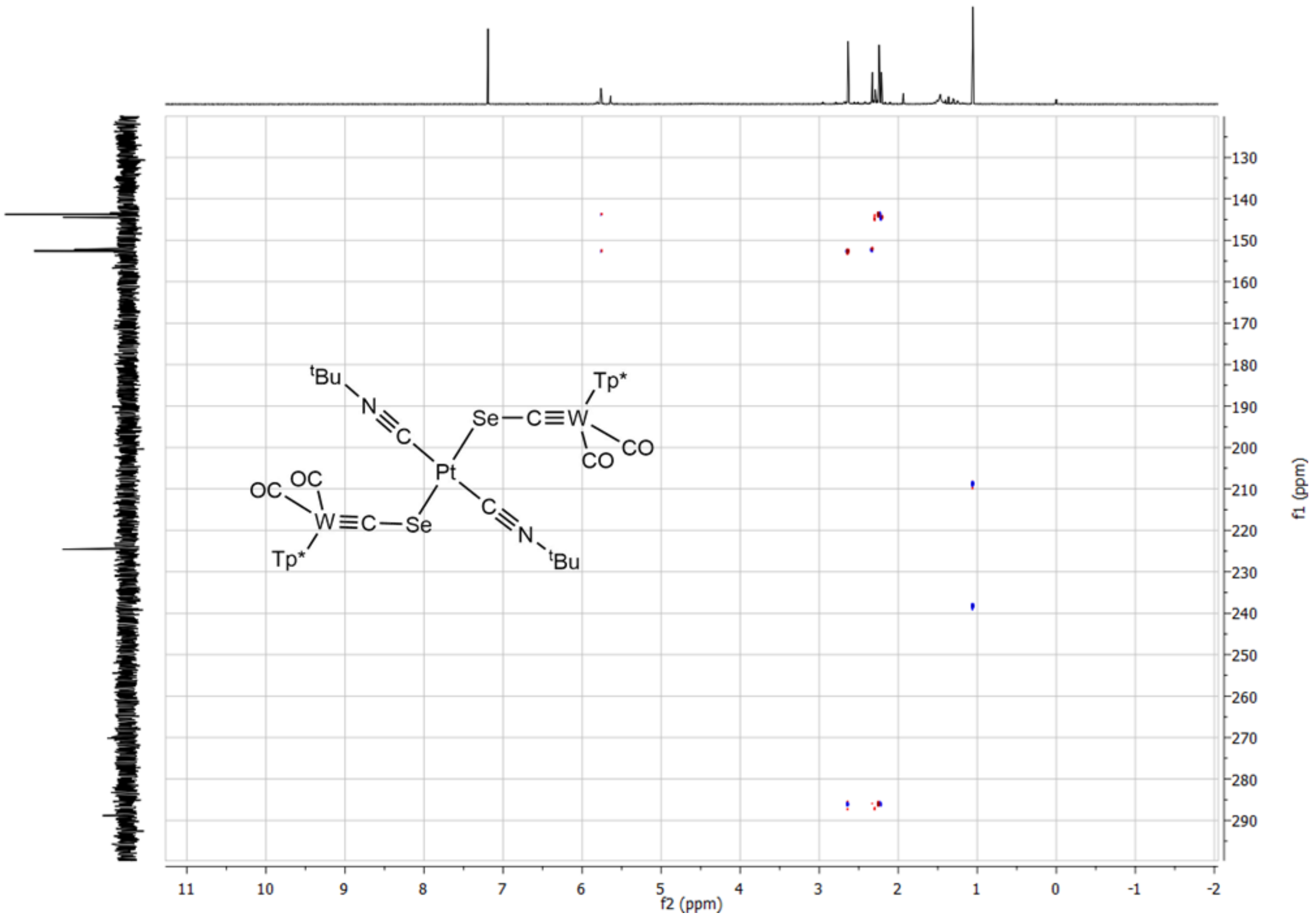
IR (CH_2Cl_2, cm^{-1}) for [$W_2Pt(\mu_2\text{-}CSe)_2(CN^tBu)_2(CO)_4(Tp^*)_2$] (**5**).



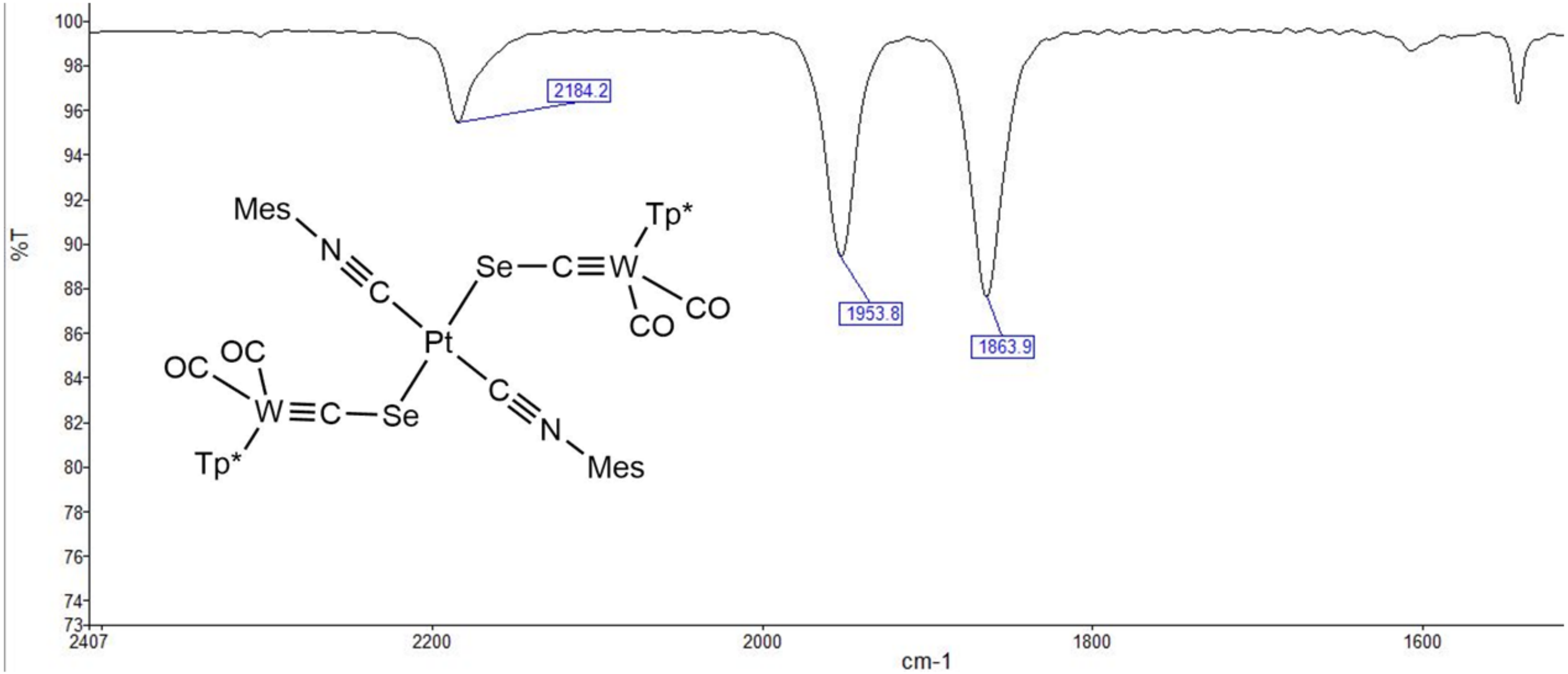
^{1}H NMR (700 MHz, $CDCl_3$, 298 K) for $[W_2Pt(\mu_2\text{-}CSe)_2(CN^tBu)_2(CO)_4(Tp^*)_2]$ (**5**).



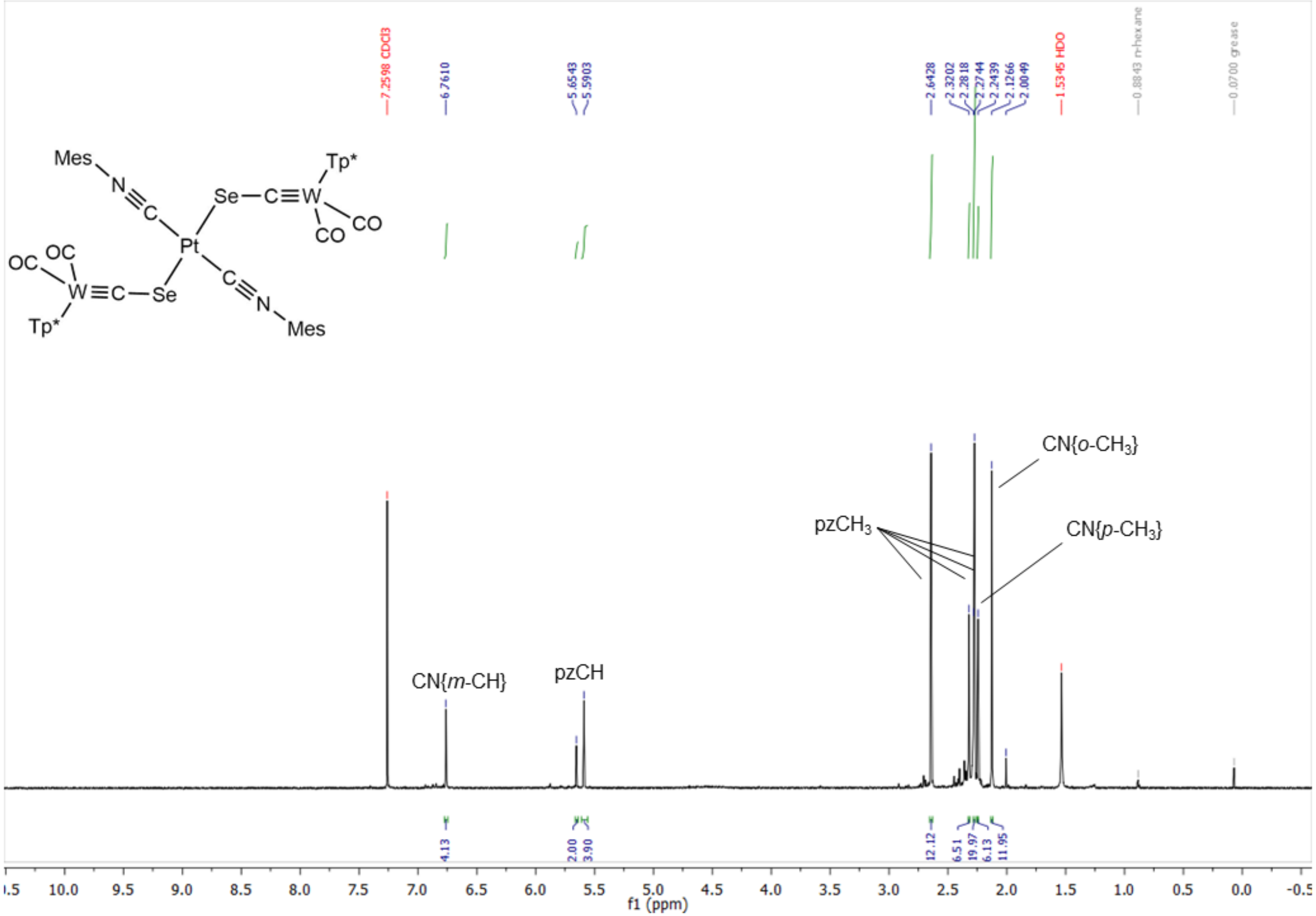
$^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$, 298 K) for $[W_2Pt(\mu_2\text{-}CSe)_2(CN^tBu)_2(CO)_4(Tp^*)_2]$ (**5**).



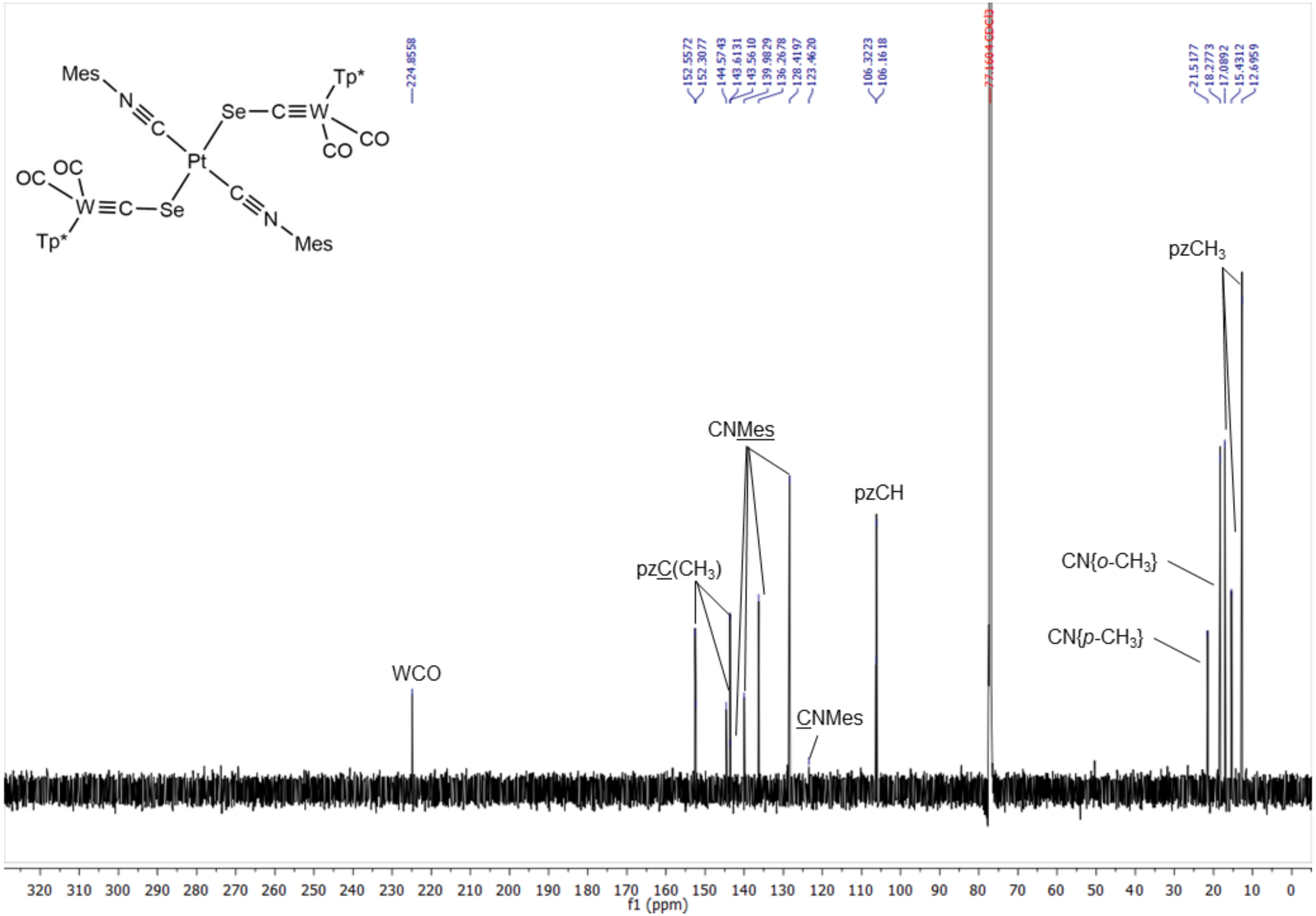
^{1}H-^{13}C HMBC (700, 176 MHz, CDCl$_3$, 298 K) for [W$_2$Pt(μ$_2$-CSe)$_2$(CN^{t}Bu)$_2$(CO)$_4$(Tp*)$_2$] (**5**).



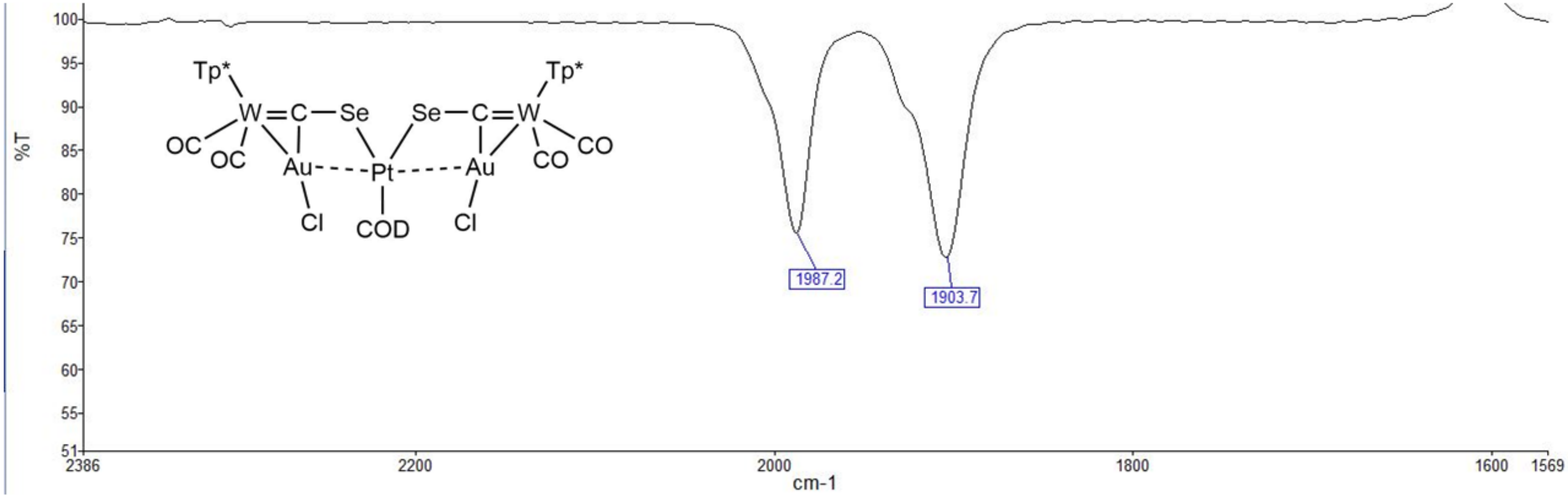
IR (CH_2Cl_2, cm^{-1}) for $[W_2Pt(\mu_2\text{-}CSe)_2(CNMes)_2(CO)_4(Tp^*)_2]$ (**6**).



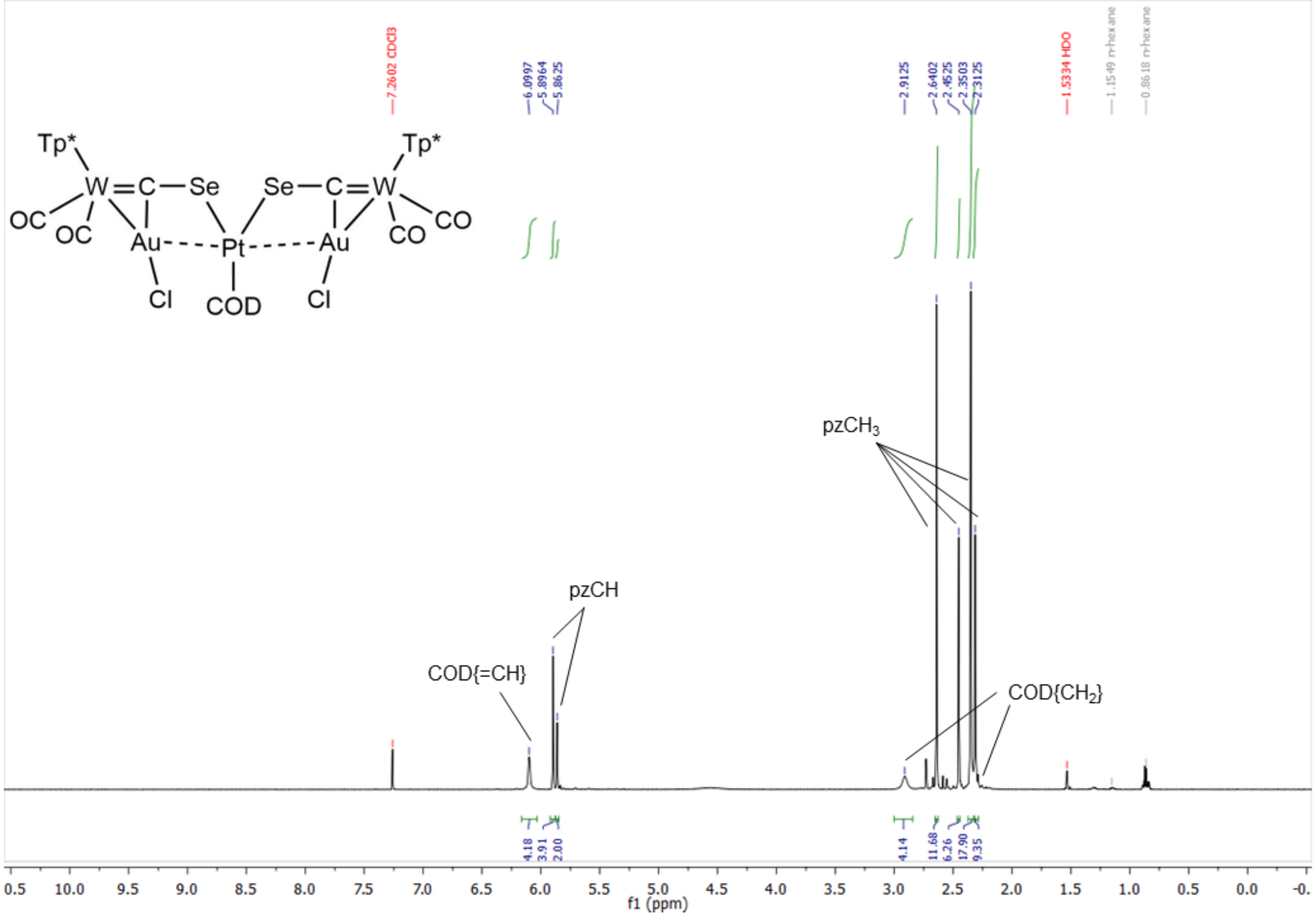
^{1}H NMR (700 MHz, $CDCl_3$, 298 K) for [$W_2Pt(\mu_2\text{-}CSe)_2(CNMes)_2(CO)_4(Tp^*)_2$] (**6**).



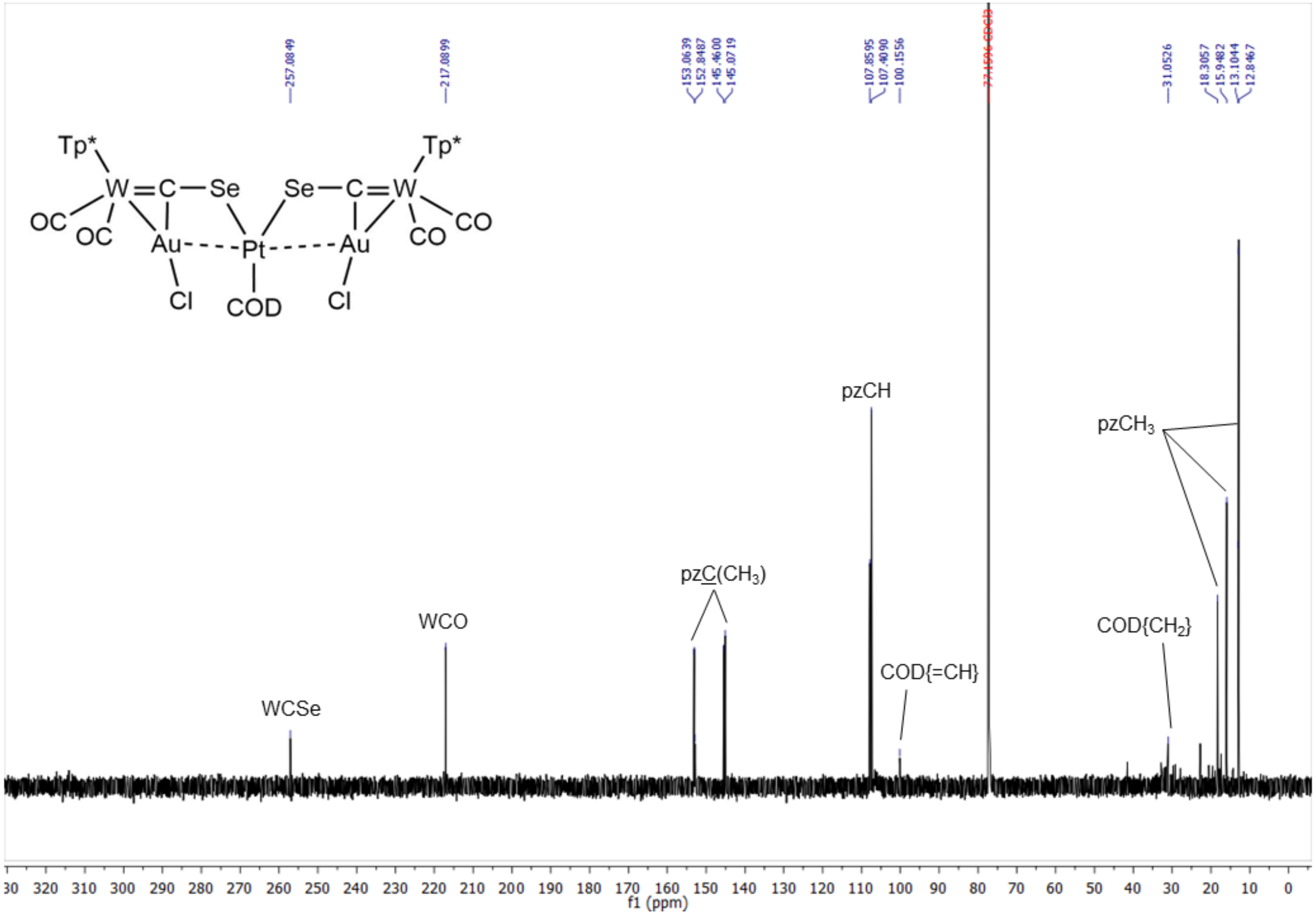
$^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$, 298 K) for $[W_2Pt(\mu_2\text{-}CSe)_2(CNMes)_2(CO)_4(Tp^*)_2]$ (**6**).



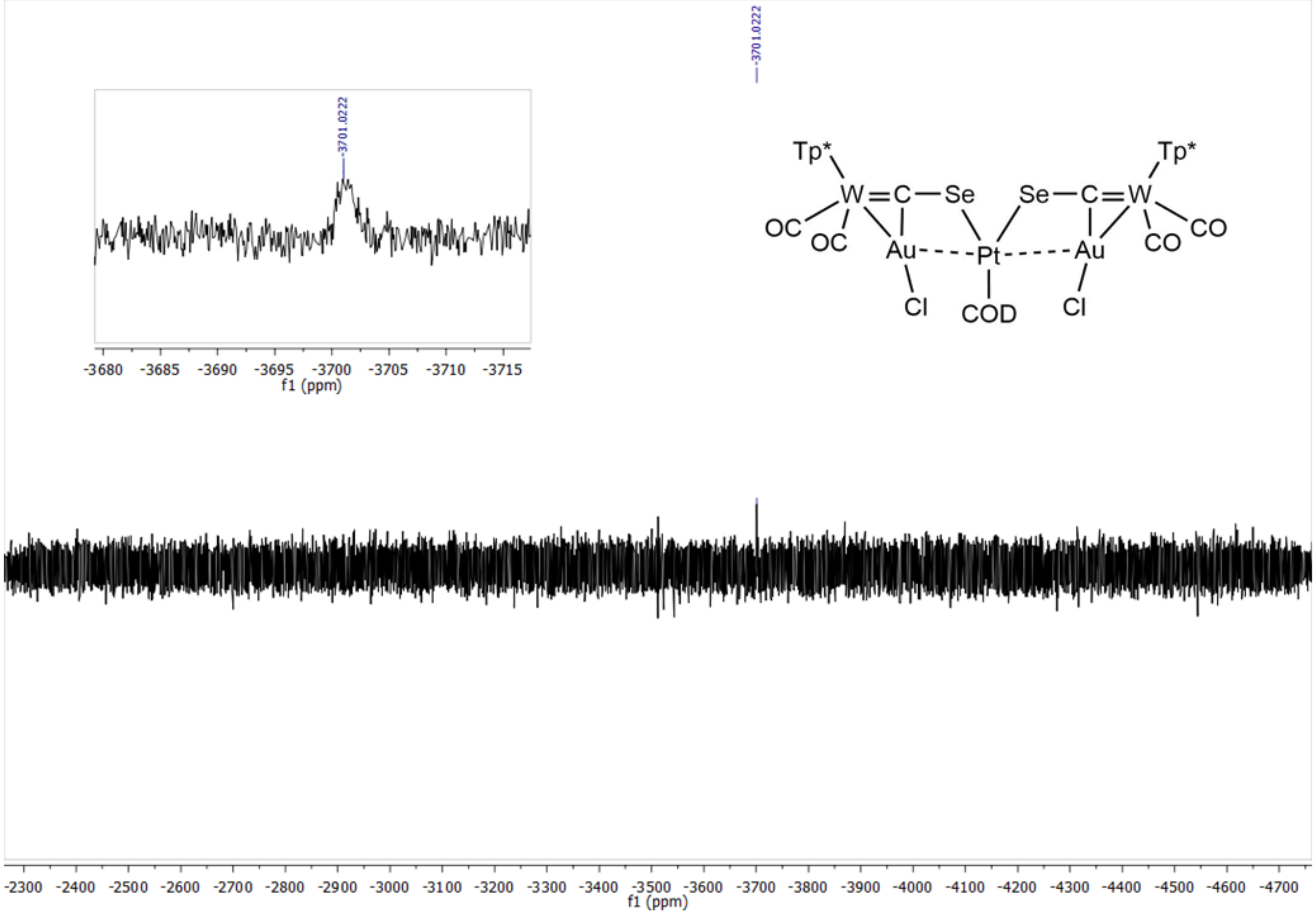
IR (CH_2Cl_2, cm^{-1}) for [$W_2PtAu_2(\mu_3\text{-}CSe)_2Cl_2(COD)(CO)_4(Tp^*)_2$] (**7**).



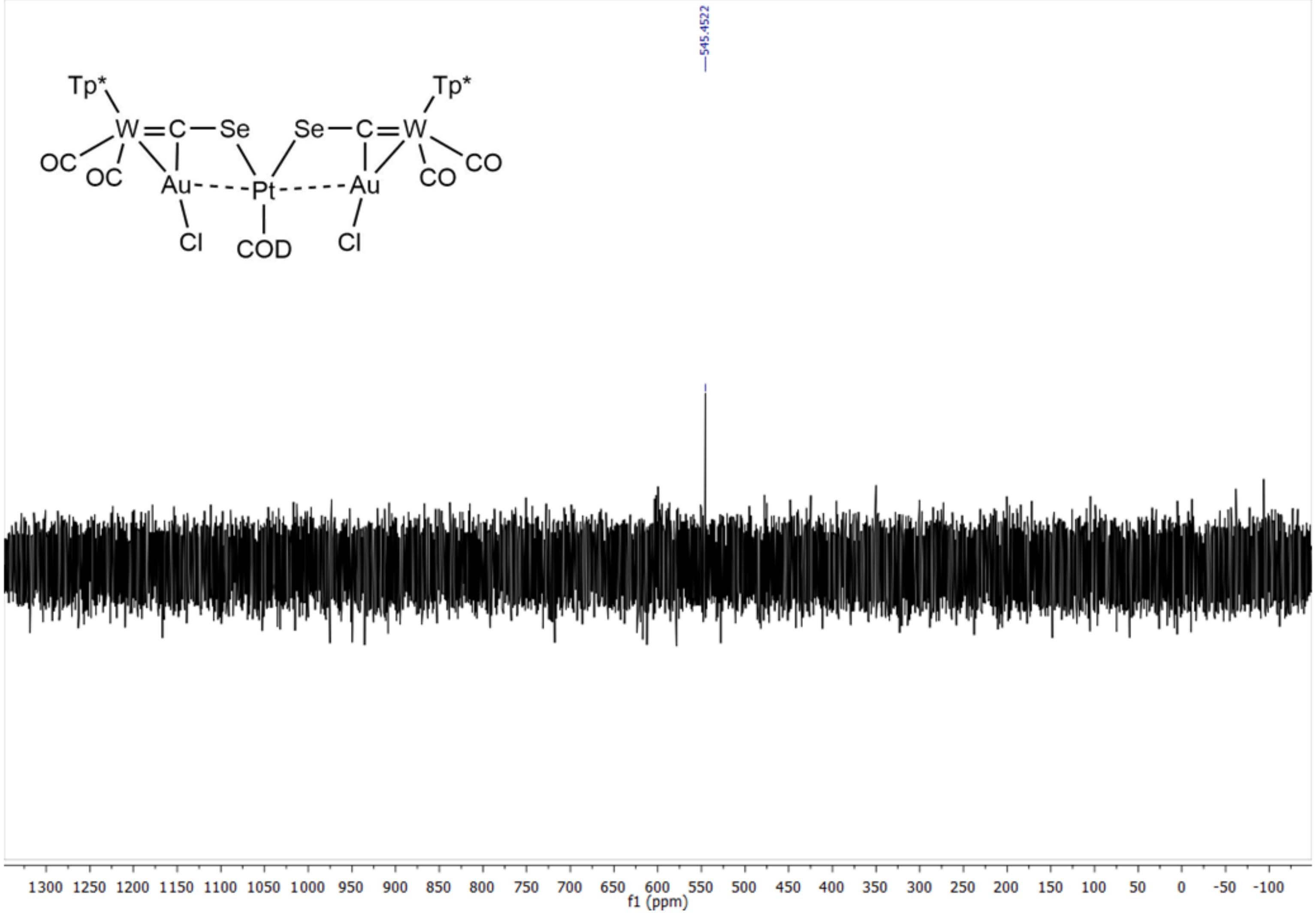
^{1}H NMR (700 MHz, $CDCl_3$, 298 K) for $[W_2PtAu_2(\mu_3\text{-}CSe)_2Cl_2(COD)(CO)_4(Tp^*)_2]$ (**7**).



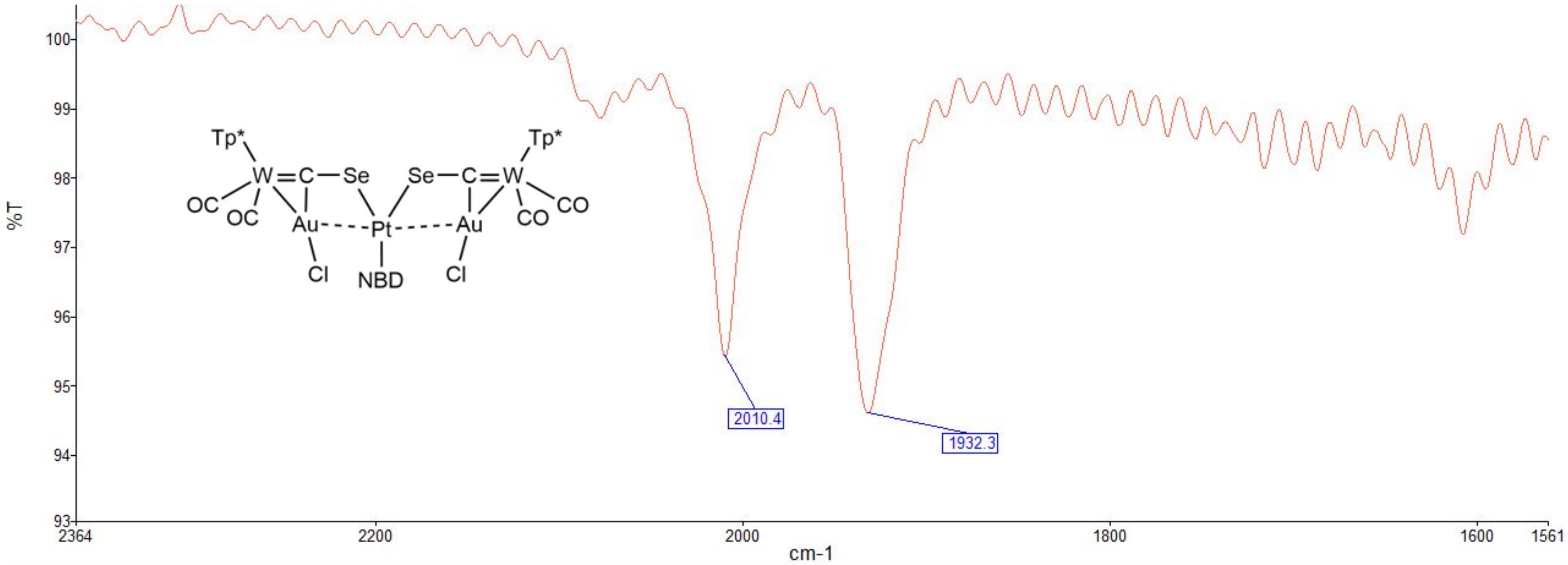
$^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$, 298 K) for $[W_2PtAu_2(\mu_3\text{-}CSe)_2Cl_2(COD)(CO)_4(Tp^*)_2]$ (**7**).



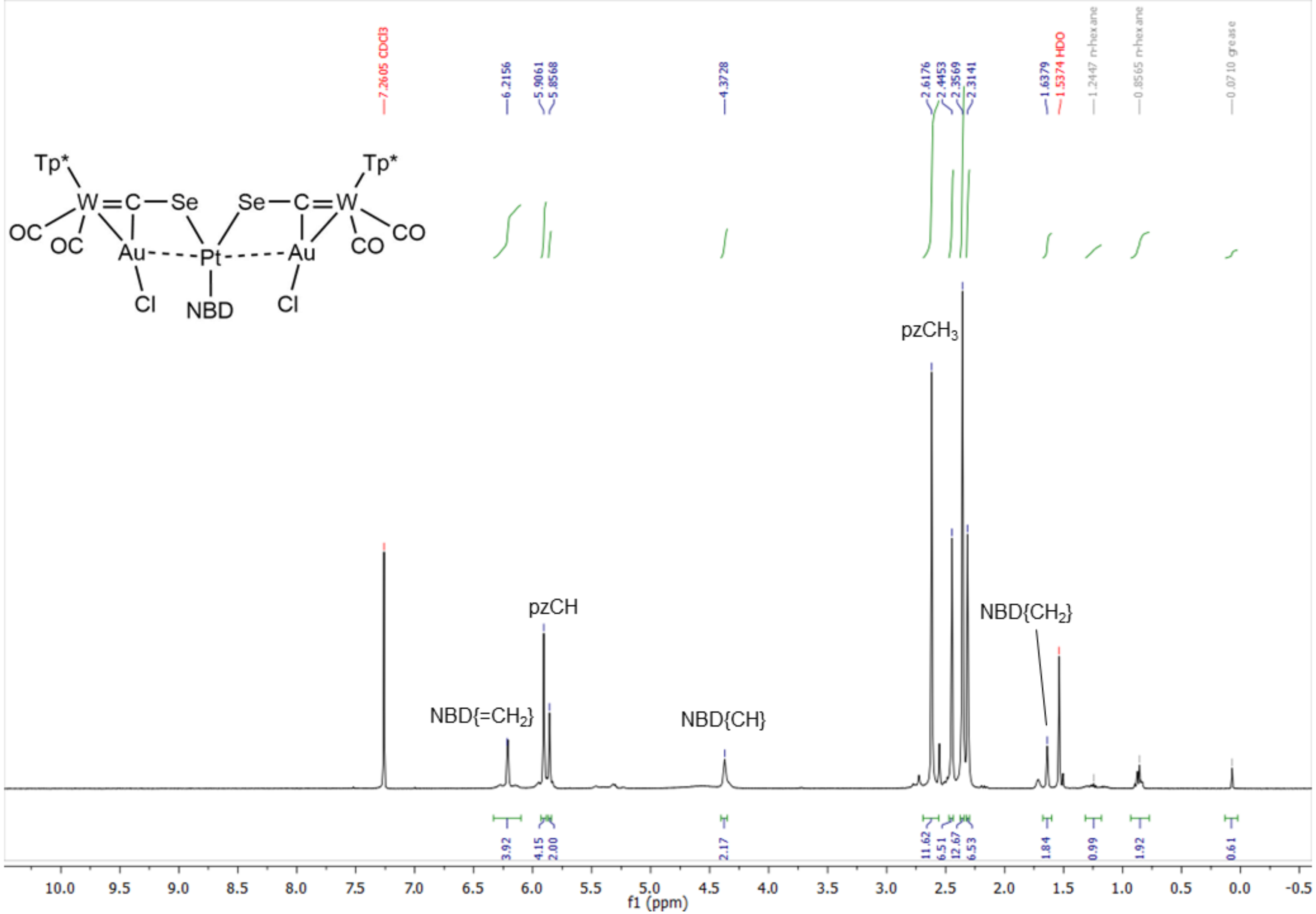
^{195}Pt NMR (150 MHz, $CDCl_3$, 298 K) for [$W_2PtAu_2(\mu_3\text{-}CSe)_2Cl_2(COD)(CO)_4(Tp^*)_2$] (**7**).



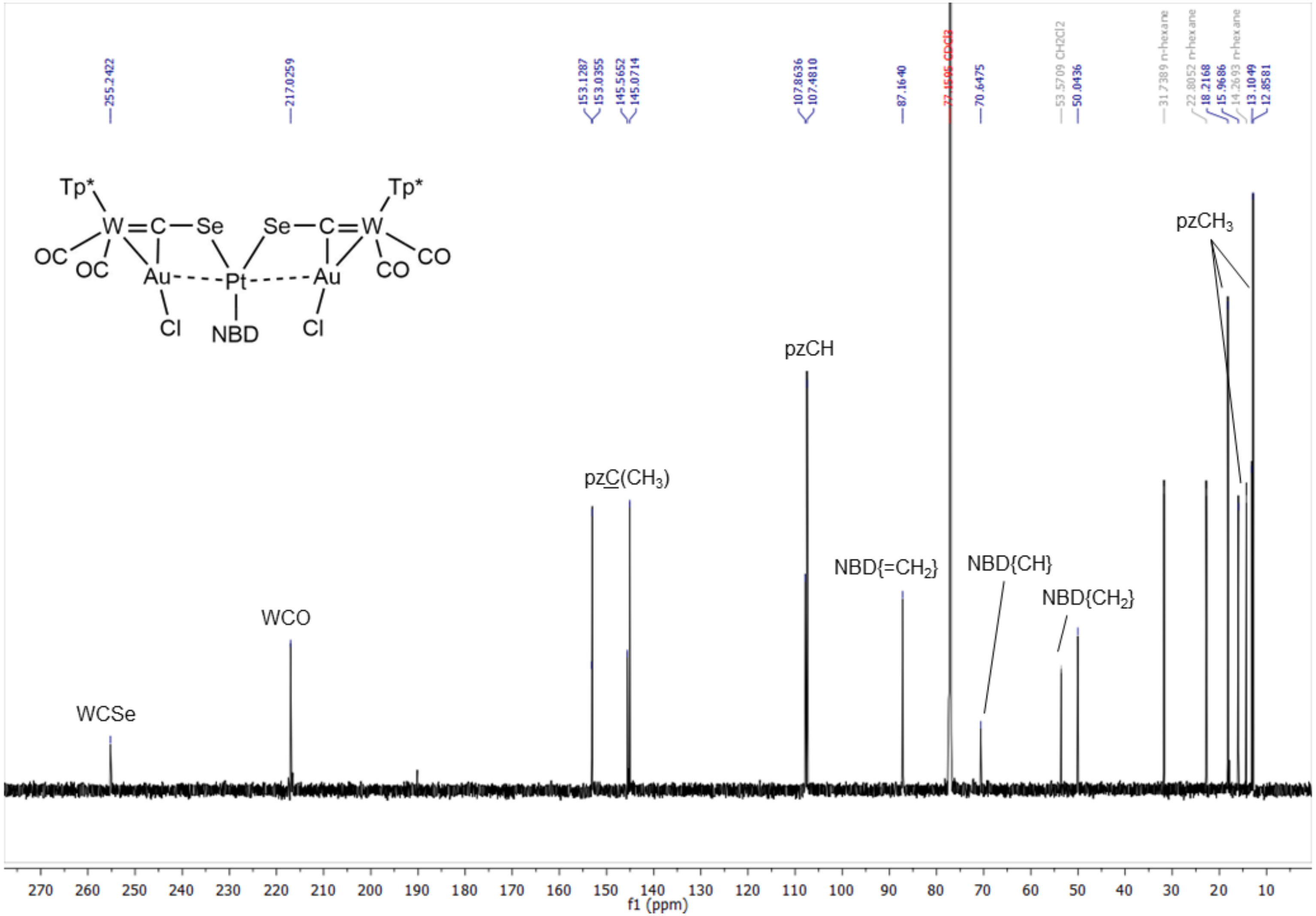
^{77}Se NMR (134 MHz, $CDCl_3$, 298 K) for [$W_2PtAu_2(\mu_3\text{-}CSe)_2Cl_2(COD)(CO)_4(Tp^*)_2$] (**7**).



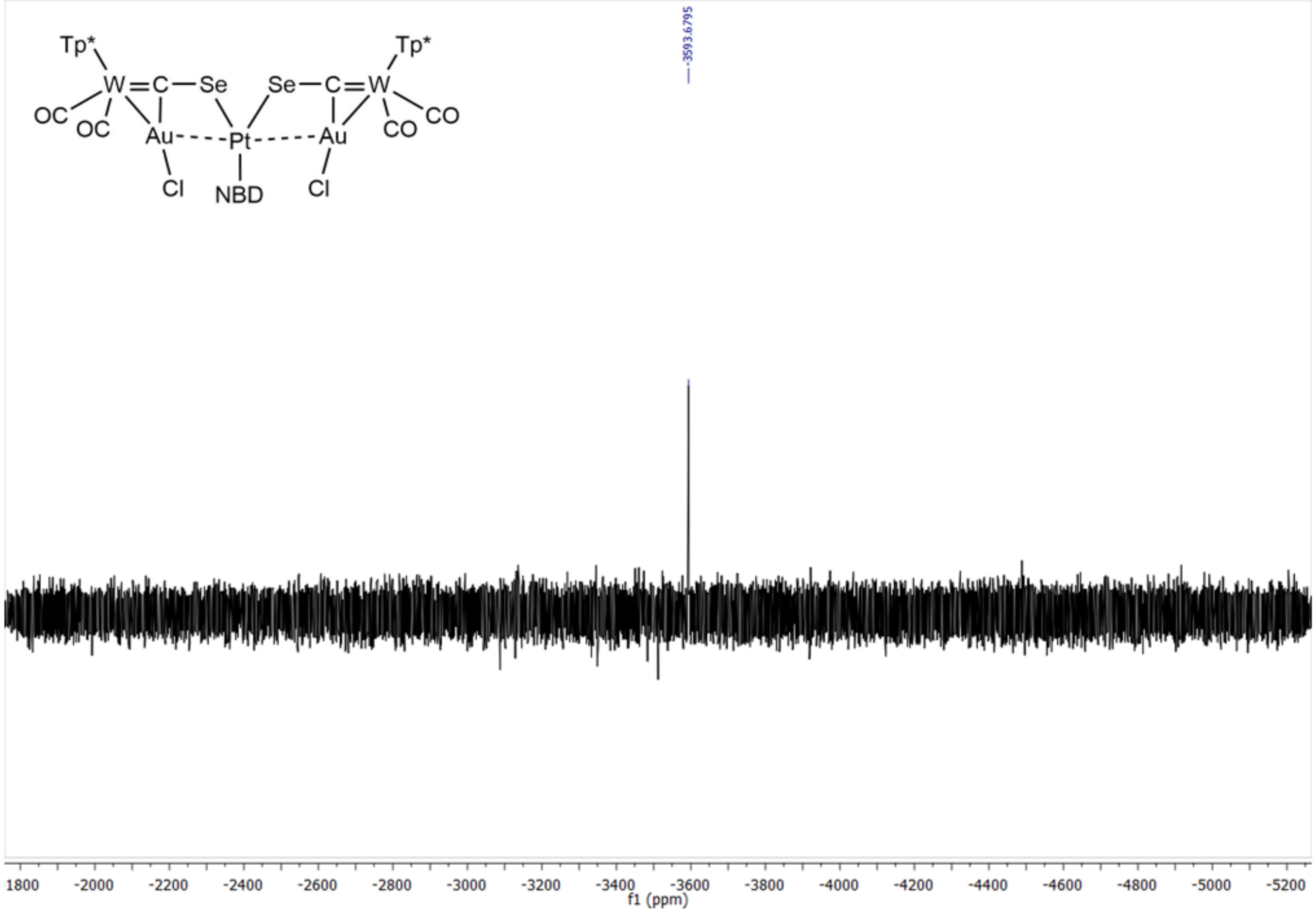
IR (CH_2Cl_2, cm^{-1}) for [$W_2PtAu_2(\mu_3\text{-}CSe)_2Cl_2(NBD)(CO)_4(Tp^*)_2$] (**8**).



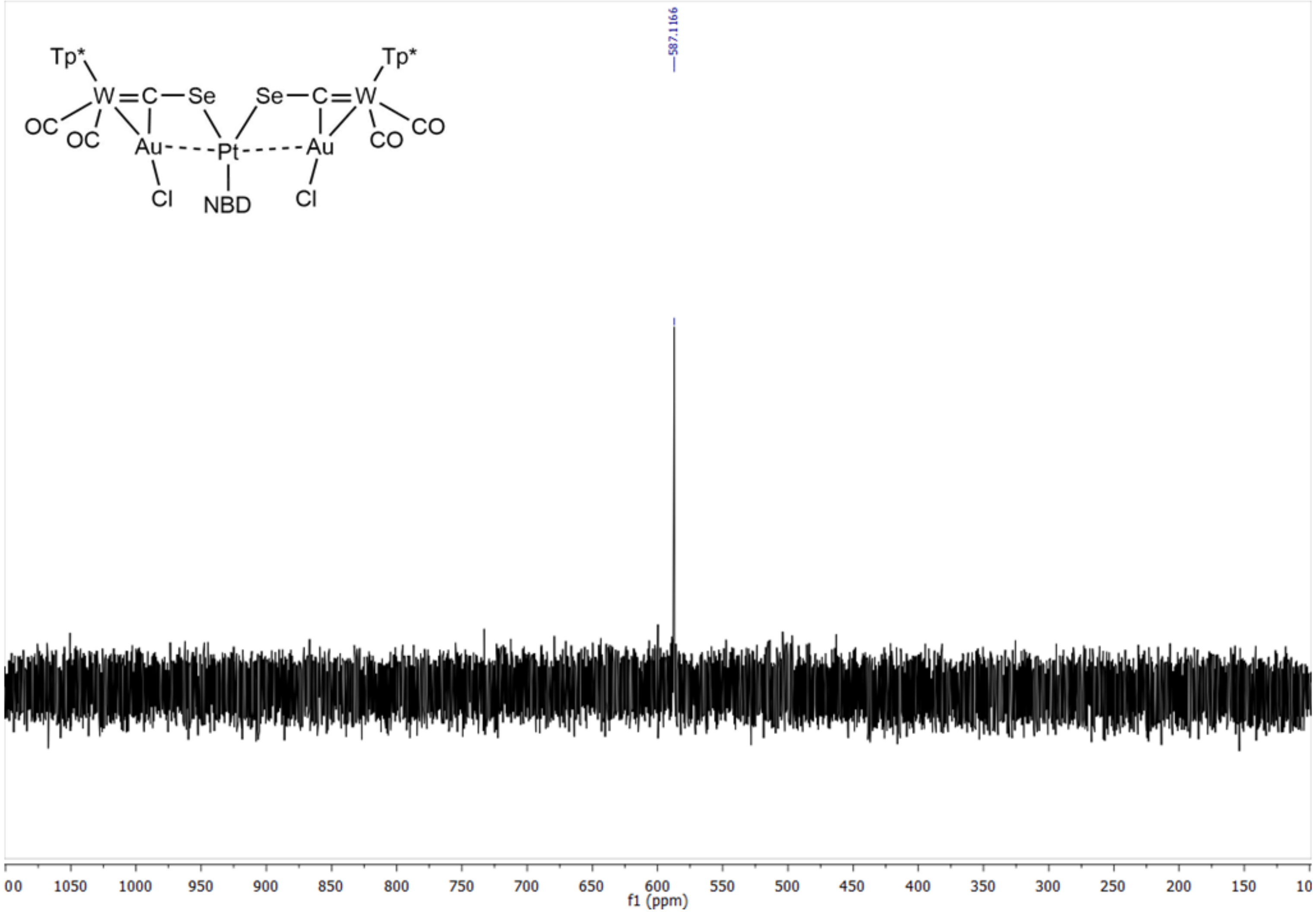
^{1}H NMR (700 MHz, CDCl$_3$, 298 K) for [$W_2PtAu_2(\mu_3\text{-}CSe)_2Cl_2(NBD)(CO)_4(Tp^*)_2$] (**8**).



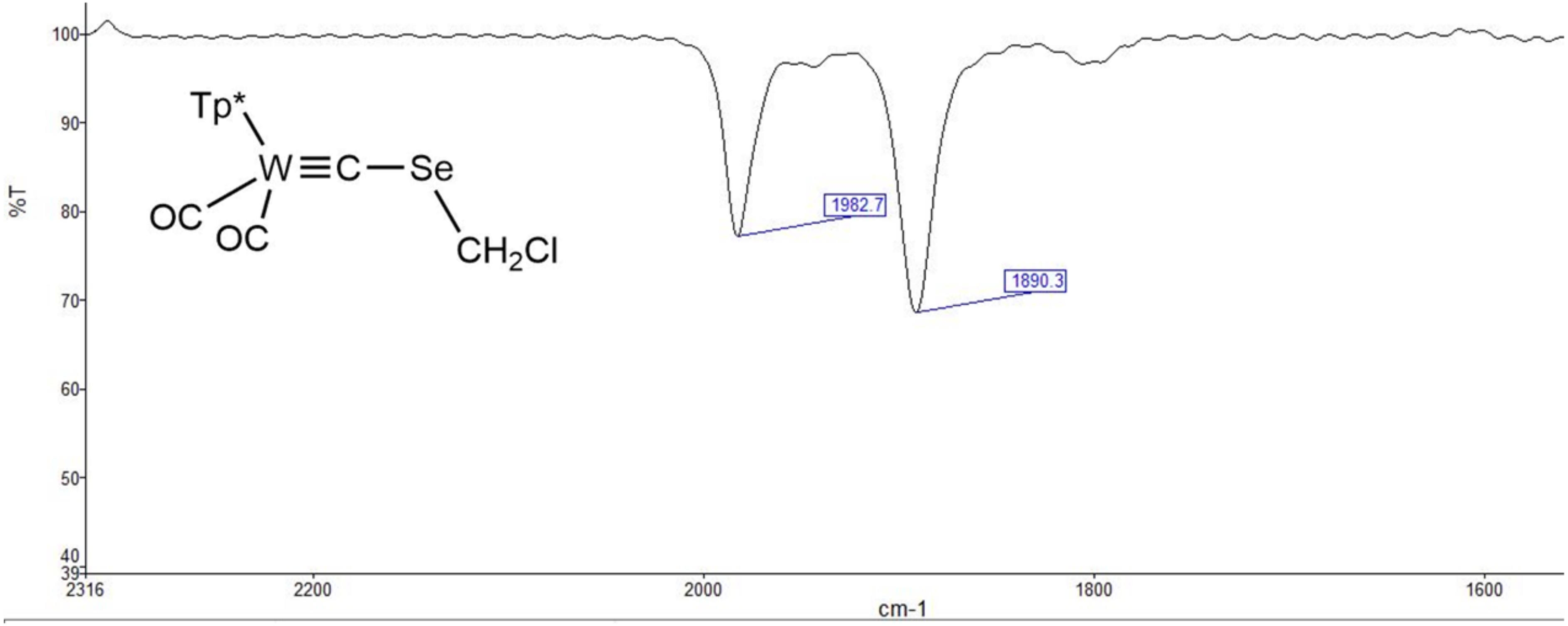
^{13}C{^{1}H} NMR (176 MHz, CDCl$_3$, 298 K) for [$W_2PtAu_2(\mu_3\text{-}CSe)_2Cl_2(NBD)(CO)_4(Tp^*)_2$] (**8**).



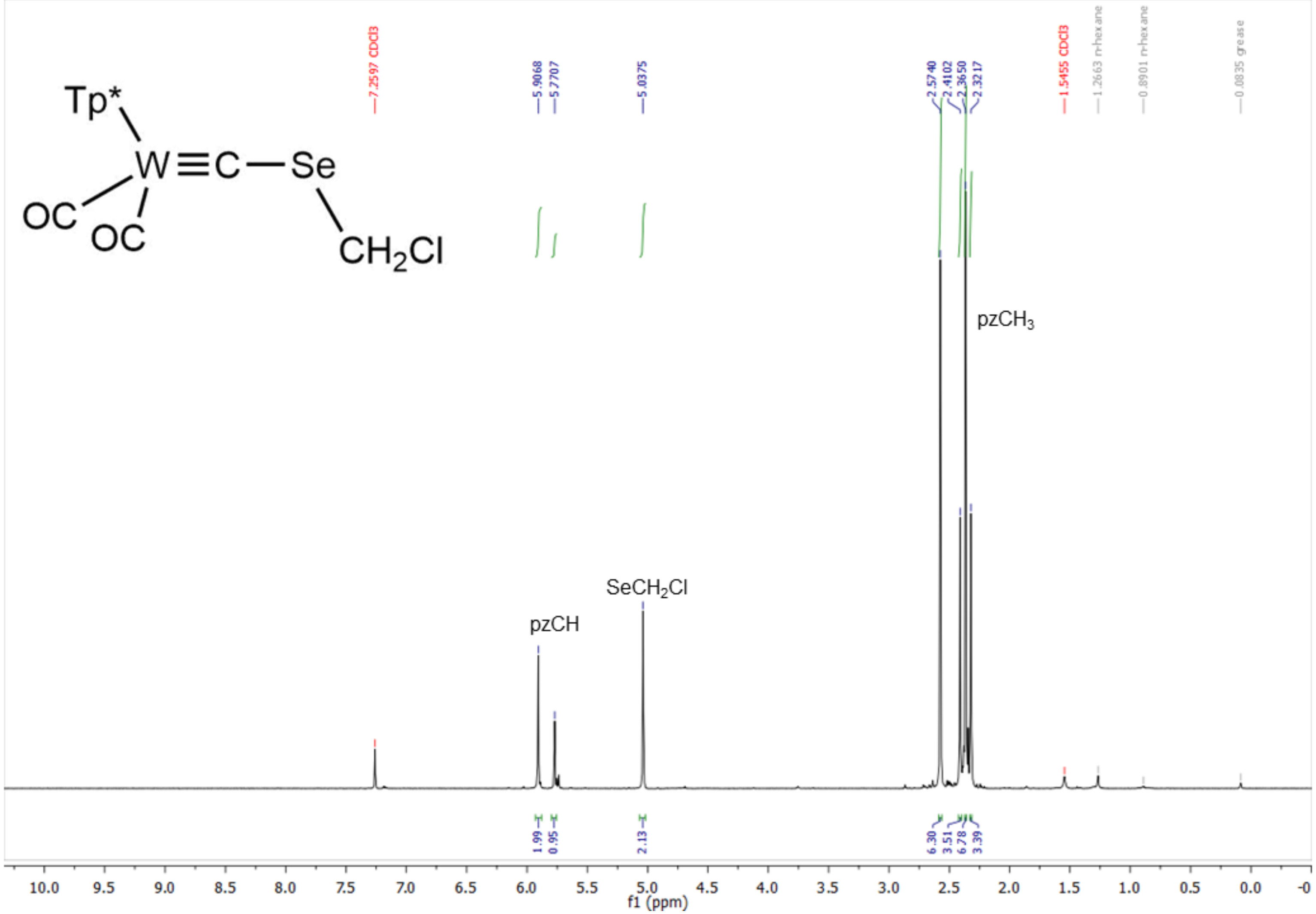
^{195}Pt NMR (150 MHz, $CDCl_3$, 298 K) for [$W_2PtAu_2(\mu_3\text{-}CSe)_2Cl_2(NBD)(CO)_4(Tp^*)_2$] (**8**).



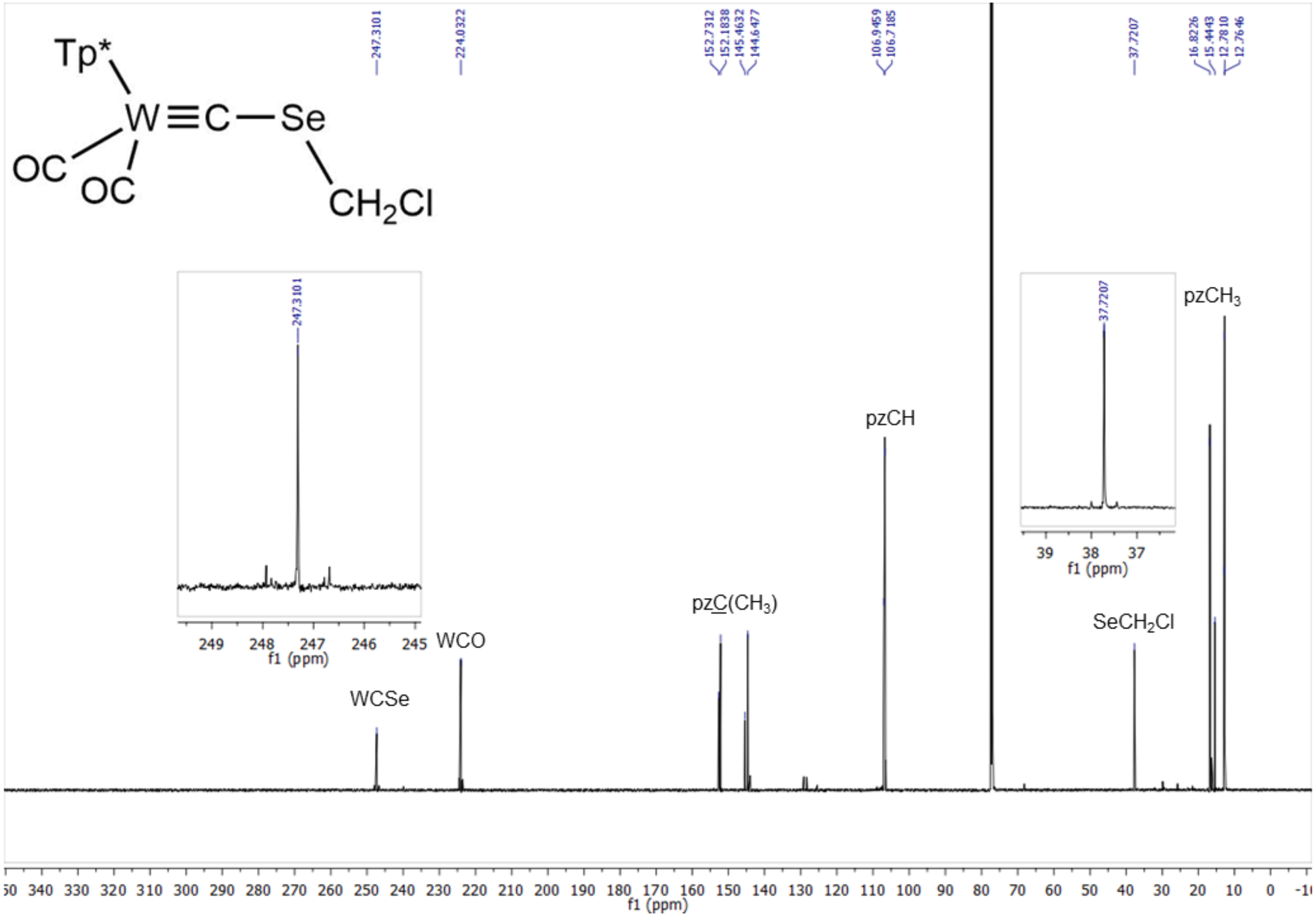
^{77}Se NMR (76 MHz, $CDCl_3$, 298 K) for $[W_2PtAu_2(\mu_3\text{-}CSe)_2Cl_2(NBD)(CO)_4(Tp^*)_2]$ (**8**).



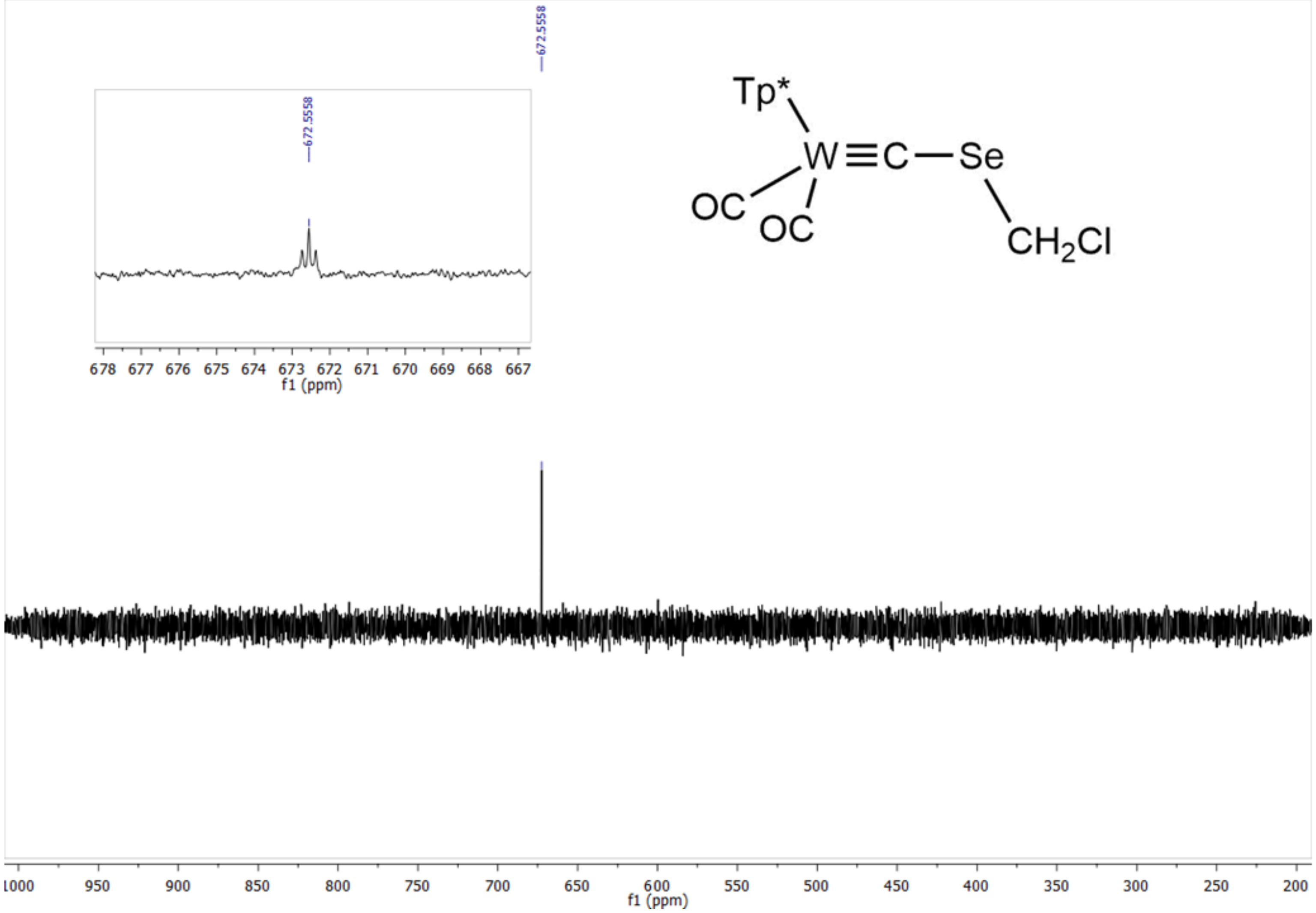
IR (CH_2Cl_2, cm^{-1}) for [W(≡$CSeCH_2Cl$)$(CO)_2$(Tp*)] (**9**).



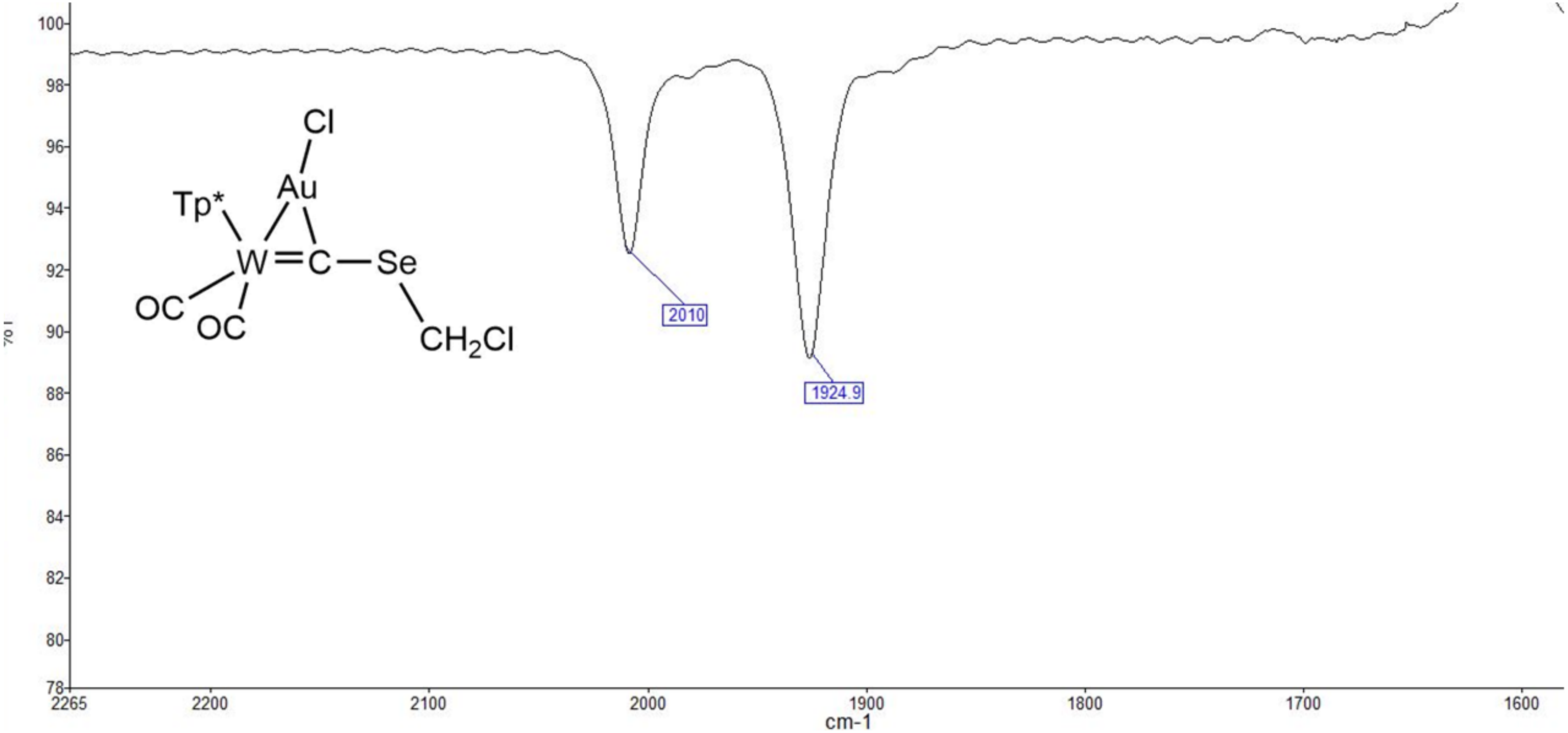
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) for [W(≡$CSeCH_2Cl$)$(CO)_2$(Tp*)] (**9**).



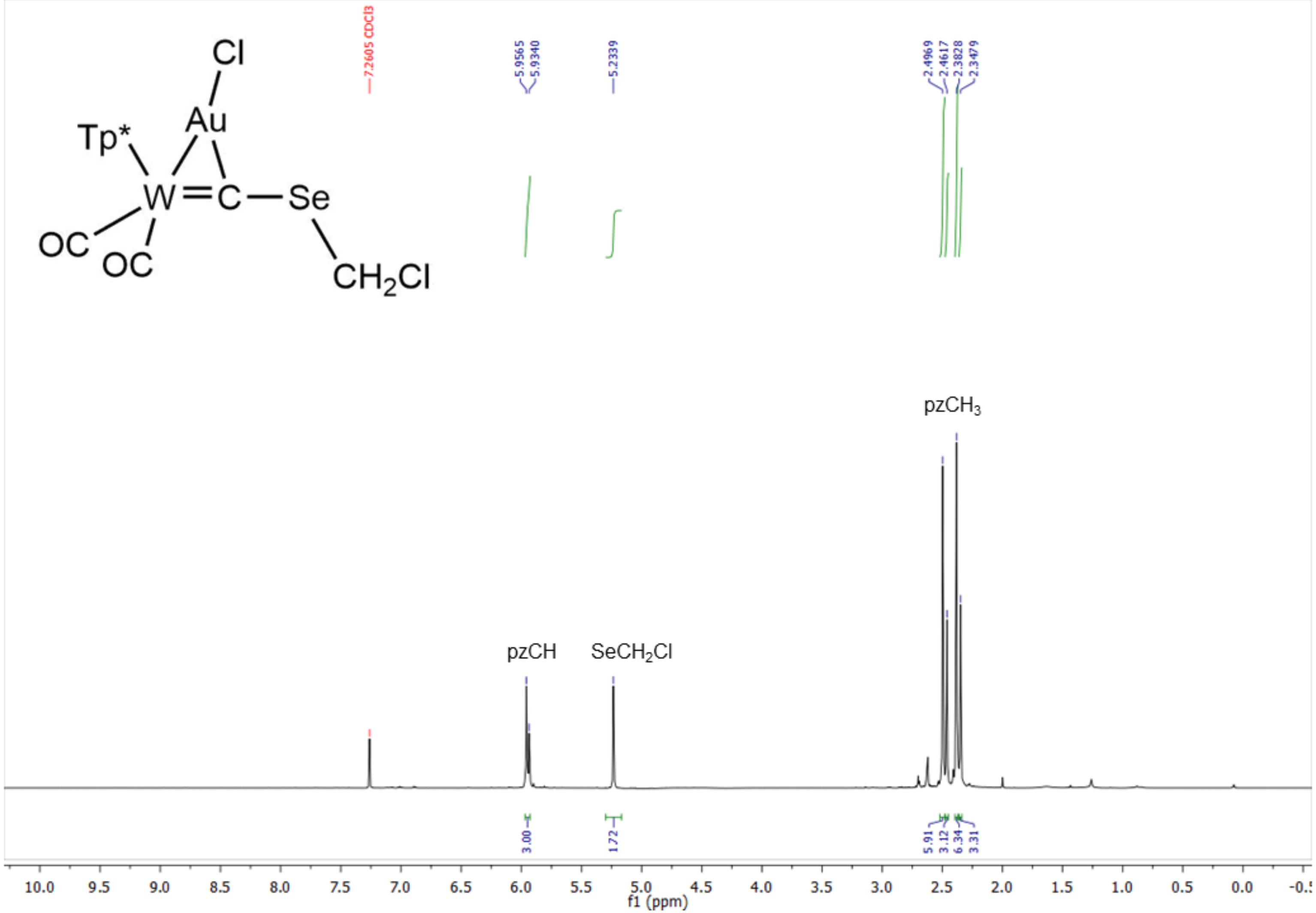
$^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$, 298 K) for [W(≡CSeCH$_2$Cl)(CO)$_2$(Tp*)] (**9**).



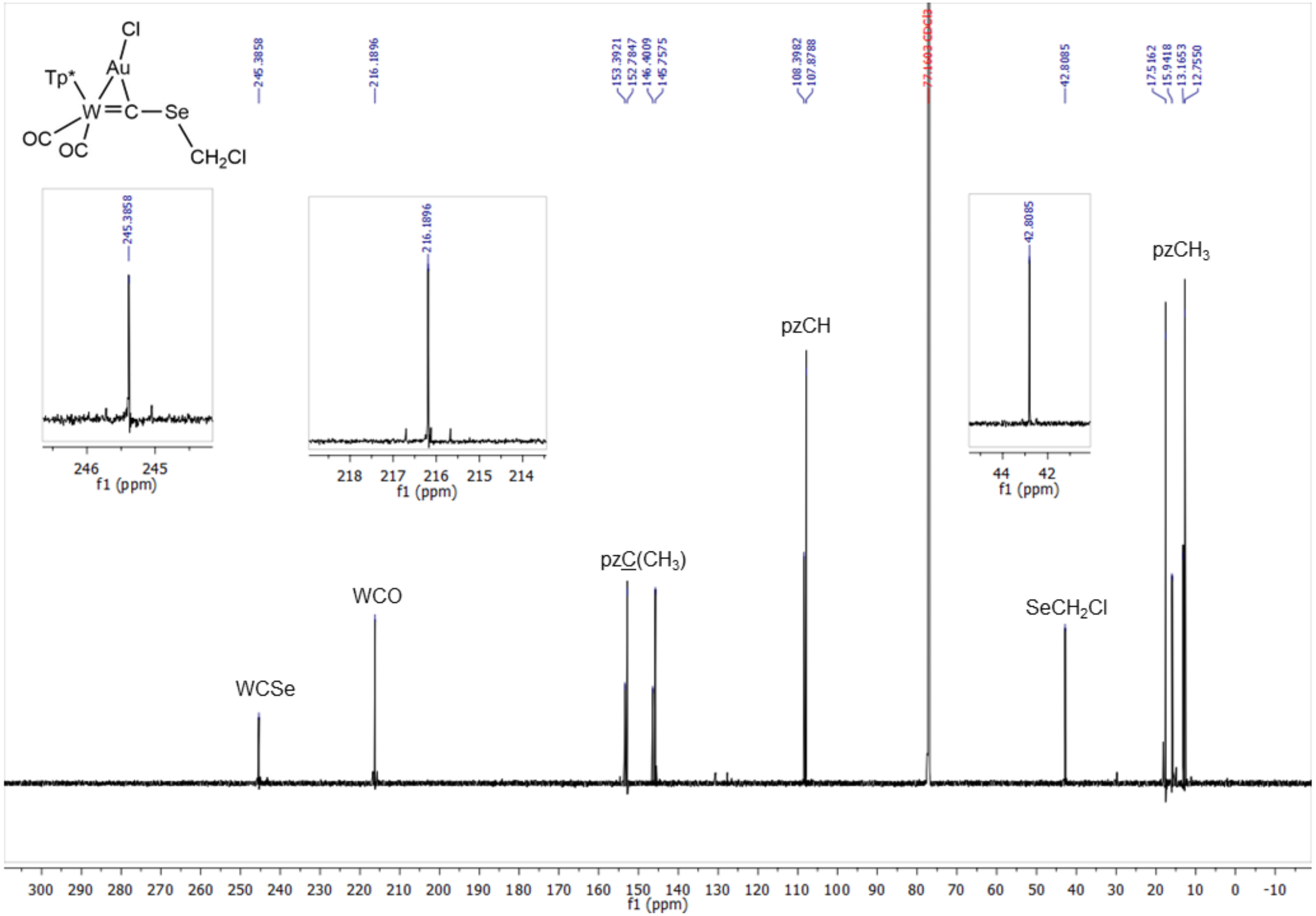
^{77}Se NMR (76 MHz, $CDCl_3$, 298 K) for [W(≡$CSeCH_2Cl$)$(CO)_2$(Tp*)] (**9**).



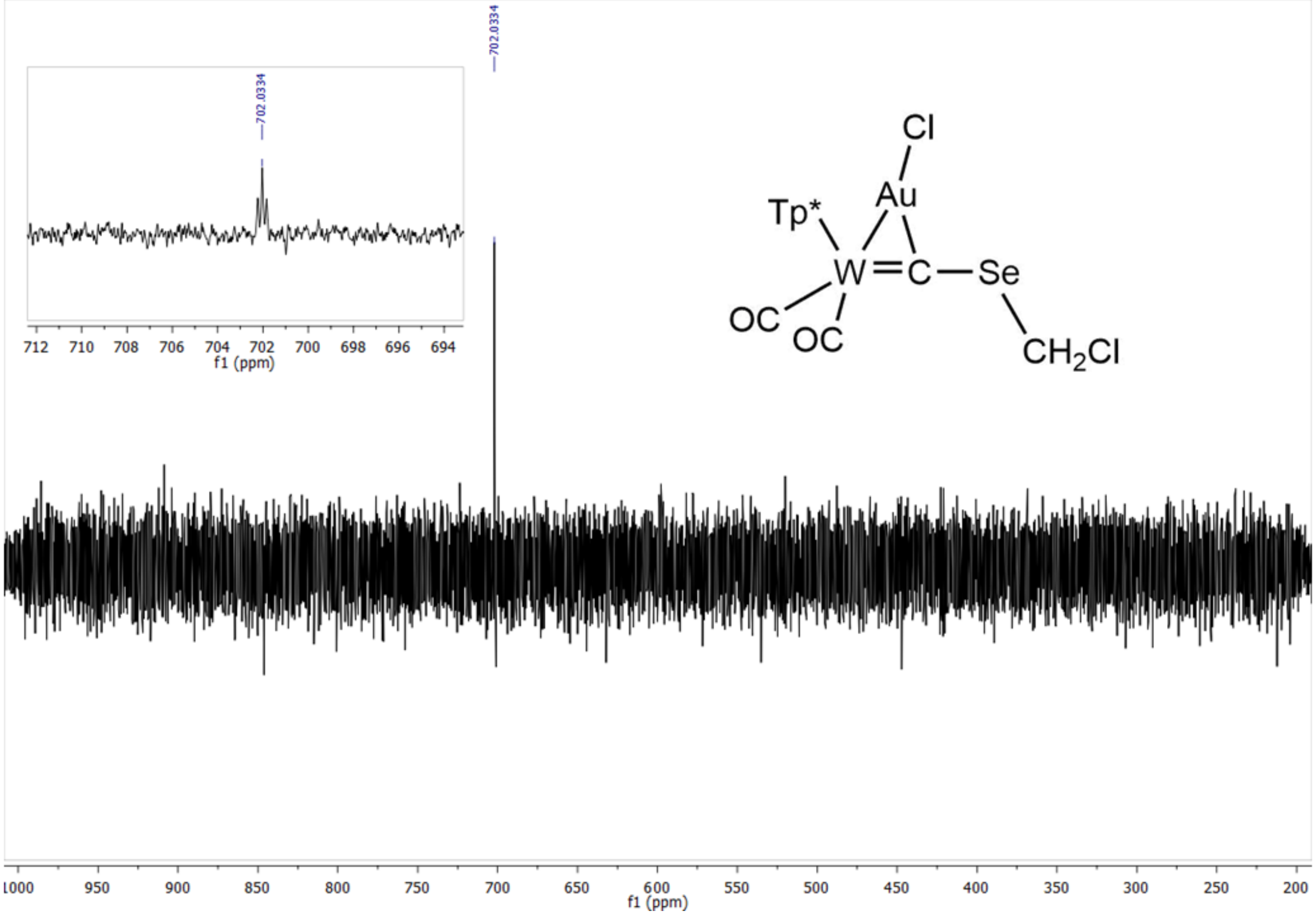
IR (CH_2Cl_2, cm^{-1}) for [WAu(μ-CSeCH$_2$Cl)Cl(CO)$_2$(Tp*)] (**10**).



^{1}H NMR (600 MHz, CDCl$_3$, 298 K) for [WAu(μ-CSeCH$_2$Cl)Cl(CO)$_2$(Tp*)] (**10**).



^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$, 298 K) for [WAu(μ-CSeCH$_2$Cl)Cl(CO)$_2$(Tp*)] (**10**).



^{77}Se NMR (76 MHz, CDCl$_3$, 298 K) for [WAu(μ-CSeCH$_2$Cl)Cl(CO)$_2$(Tp*)] (**10**).