COMMUNICATION

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Electronic Supporting Information for:
A Heterobimetallic Cumulenic μ-Carbido Complex

Anthony F. Hill*[a] Lachlan J. Watson[a]

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[a] *Research School of Chemistry, Australian National University, Canberra, Australian Capital Territory, ACT 2601, Australia.*
* Corresponding author. E-mail: a.hill@anu.edu.au

CCDC 1959089 and 1959090 contain the supplementary crystallographic data for this paper, and are available free of charge from The Cambridge Crystallographic Data Centre.

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) 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). 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, 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 using Mo-Kα radiation (λ = 0.71073 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]

Synthesis of [W(CSe)(CO)(NO)(Tp*)] (2). A solution of [**1**]NEt$_4$ (400 mg, 0.527 mmol) and N-methyl-N-nitroso-4-toluenesulfonamide (Diazald®, 118 mg, 0.551 mmol) in MeCN (30 mL) was stirred for 3.5 h, gradually turning dark green. After removing volatiles under reduced pressure, the product was extracted with benzene (15 mL) and filtered through a pad of diatomaceous earth (2 x 8 cm), washing with benzene until the filtrate ran clear. Volatiles were again removed under reduced pressure and the solid was then loaded onto a silica gel column with CH_2Cl_2, eluting the first green band with petroleum spirits (40–60 °C). Volatiles were removed under reduced pressure to give a light green solid. Yield: 241 mg (0.38 mmol, 72%). IR (CH_2Cl_2, cm^{-1}): 1992s, ν_{CO}, 1665br ν_{NO}, 1088s ν_{CSe}. IR (ATR, cm^{-1}): 1972s ν_{CO}, 1657s ν_{NO}, 1078s ν_{CSe}. ^{1}H NMR (700 MHz, $CDCl_3$, 298 K): δ_H = 5.91, 5.83, 5.82 (3 x s, 1H x 3, pzC*H*), 2.70, 2.64, 2.42, 2.39, 2.36, 2.35 (6 x s, 3H x 6, pzC*H*$_3$). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$, 298 K): δ_C = 367.2 ($^1J_{WC}$ = 176, W*C*Se), 215.9 ($^1J_{WC}$ = 158, W*C*O), 153.9, 153.5, 152.5, 145.4, 145.2, 144.9 (pz*C*CH$_3$), 107.3, 107.1, 106.8 (pz*C*H), 16.0, 14.9, 14.8, 13.0, 12.7, 12.6 (pz*C*H$_3$). ^{77}Se NMR (134 MHz, $CDCl_3$, 298 K): δ_{Se} = 1188. MS (ESI, +ve ion, *m/z*): Found: 631.0593. Calcd for $C_{17}H_{22}{}^{11}BN_7O_2{}^{80}Se{}^{184}W$ $[M]^+$: 631.0595. Anal. Found: C, 32.49; H, 3.22; N, 15.40. Calcd for $C_{17}H_{22}BN_7O_2SeW$: C, 32.41; H, 3.52; N, 15.56%.

Synthesis of [WRe(μ-C)(CO)$_3$(NO)(Tp*)(η-C$_5$H$_5$)] (5). A colourless solution of $[Re(CO)_3(\eta\text{-}C_5H_5)]$ (150 mg, 0.446 mmol) in THF (50 mL) was photolysed at 0 °C using an unfiltered mercury lamp until conversion was complete as determined by IR spectroscopy. The resultant light yellow $[Re(CO)_2(THF)(\eta\text{-}C_5H_5)]$ solution was added dropwise to a green solution of **2** (70 mg, 0.11 mmol) in THF (10 mL) and stirred for 3.5 hours during which time the mixture slowly turned yellow brown. After removing the volatiles under reduced pressure, the solid was dissolved in minimal CH_2Cl_2 and loaded onto a silica gel column (3 x 20 cm) and eluted with 100% petroleum spirits to collect a green band. The eluent was slowly changed to 30% CH_2Cl_2 in petroleum sprits (40-60 °C) to collect a yellow/green band then a dark yellow-brown band of pure **5**. Yield: 12 mg (0.014 mmol, 13%). IR (CH_2Cl_2, cm^{-1}): 1998s, 1944s, 1915s ν_{CO}, 1634s ν_{NO}. IR (ATR, cm^{-1}): 2022w, 1993m, 1949m, 1891s ν_{CO}, 1636s ν_{NO}, 968m ν_{WCRe}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ_H = 5.88, 5.81, 5.74 (3 x s, 1H x 3, pzC*H*), 5.59 (5H, Cp), 2.70, 2.64, 2.42, 2.39, 2.36, 2.35 (6 x s, 3H x 6, pzC*H*$_3$). ^{13}C{^{1}H} NMR (176

MHz, $CDCl_3$, 298 K): δ_C = 508.8 (*W*CRe), 224.7 (W*C*O), 200.2, 199.4 (Re*C*O), 152.9, 152.8, 152.2, 145.0, 144.6, 144.6 (pz*C*CH$_3$), 106.9, 106.6, 106.4 (pz*C*H), 88.4 (Cp), 16.6, 15.4, 14.9, 13.1, 12.9, 12.5 (pz*C*H$_3$). MS (ESI, +ve ion, *m/z*): Found: 859.12787. Calcd for $C_{24}H_{27}{}^{11}BN_7O_4{}^{187}Re{}^{184}W$ $[M]^+$: 859.12789. Crystals suitable for structural determination were grown by slow diffusion of *n*-hexane into a CH_2Cl_2 solution at -20 °C. *Crystal Data for* $C_{25}H_{29}BCl_2N_7O_4ReW$ (M_w =943.31 g.mol^{-1}): monoclinic, space group *P*2$_1$/c (no. 14), *a* = 8.0943(4), *b* = 21.8669(10), *c* = 17.3220(7) Å, *β* = 95.221(4)°, *V* = 3053.2(2) Å^3, *Z* = 4, *T* = 150.0(1) K, μ(Mo Kα) = 7.944 mm^{-1}, D_{calcd} = 2.052 Mg.m^{-3}, 31774 reflections measured (6.546° ≤ 2Θ ≤ 52.736°), 6229 unique (R_{int} = 0.0664, R_{sigma} = 0.0578) which were used in all calculations. The final R_1 was 0.0360 ($I > 2\sigma(I)$) and wR_2 was 0.0651 (all data) for 380 refined parameters with 0 restraints, CCDC 1959089.

Isolation of [Re$_2$(μ-Se)(CO)$_4$(η-C$_5$H$_5$)$_2$] (6). From the column above, elution of **5** was followed by an orange band which could not be unambiguously identified, followed closely by elution of a green band of pure **6**. Yield 8 mg (0.012 mmol, 10 % based on **2**). IR (CH_2Cl_2, cm^{-1}): 1955s, 1907m ν_{CO}. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ_H = 5.44 (Cp). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$, 298 K): δ_C = 201.5, 199.0 (*C*O), 88.4 (Cp). MS (ESI, +ve ion, *m/z*): Found: 693.8823. Calcd for $C_{14}H_{10}O_4{}^{185}Re_2{}^{81}Se$ $[M\text{-}e^-]^+$: 693.8835. Crystals suitable for structural determination were grown by slow diffusion of *n*-hexane into a CH_2Cl_2 solution at -20 °C. *Crystal Data for* $C_{14}H_{10}O_4Re_2Se$ (M_w =693.58 g.mol^{-1}): triclinic, space group *P*-1 (no. 2), *a* = 7.4306(5), *b* = 7.9327(6), *c* = 13.4641(11) Å, *α* = 103.629(6), *β* = 95.575(6), *γ* = 104.678(6)°, *V* = 735.66(10) Å^3, *Z* = 2, *T* = 150.0(1) K, μ(Mo Kα) = 18.924 mm^{-1}, $D_{calcd.}$ = 3.131 Mg.m^{-3}, 5879 reflections measured (6.734° ≤ 2Θ ≤ 52.74°), 2872 unique (R_{int} = 0.0378, R_{sigma} = 0.0554) which were used in all calculations. The final R_1 was 0.0310 ($I > 2\sigma(I)$) and wR_2 was 0.0504 (all data) for 190 refined parameters with 0 restraints, CCDC 1959090.

Computational Details

Computational studies were performed by using the SPARTAN18® suite of programs.[5] Geometry optimisation (gas phase) was performed at the DFT level of theory using either (i) the ωB97X-D range separated hybrid generalized gradient approximation functional with empirical corrections for long-range non-bonded (dispersive) interactions,[6] or (ii) the Minnesota functional MO6-2.[7] The Los Alamos effective core potential type basis set (LANL2DZ) of Hay and Wadt[8] was used for tungsten and rhenium; the Pople 6-31G* basis sets[9] were used for all other atoms. Frequency calculations were performed to confirm that the optimized structure was a minimum and also to identify vibrational modes of interest.

Thermodynamic properties (298.15 K): *ZPE* = 816.32 kJmol^{-1}, H^o = –1550.237889 au, S^o = 864.11 Jmol^{-1}K^{-1}, G^o = –1550.336017 au, C_v = 479.17 Jmol^{-1}K^{-1}.

Cartesian Coordinates (See attached .mol2 file)

Atom	x	y	z
W1	0.205622342	-0.446470381	1.016487378
N2	1.524012868	-1.456568843	1.710871269
N3	-1.345444718	0.905810197	0.064831636
O4	-1.811040152	-2.878019306	1.212920873
N5	1.419350000	1.430290477	0.772036488
C6	-2.941603776	1.823685850	-1.213064228
H7	-3.717273702	1.949825329	-1.951438474
N8	-0.507759756	0.757421562	2.863406814
C9	-1.095559388	-1.977022188	1.191320965
N10	-0.746001121	2.080896688	2.792832704
N11	-1.464457448	2.206802959	0.393578310
C12	3.008155767	2.947077745	0.331395578
H13	3.946094810	3.395431469	0.043837688
C14	2.677519506	1.587881242	0.360079531
C15	-2.229801113	0.661801805	-0.903850019
C16	-2.415472199	2.781256209	-0.361281769
C17	1.855060776	3.587899309	0.750585384
N18	0.918833411	2.658188551	1.009713591
O19	2.414271284	-2.113149625	2.112946527
C20	-1.148600635	2.539661553	3.990668107
C21	-0.759850380	0.381476447	4.117013383
C22	-1.172091188	1.479581761	4.880636956
H23	-1.444419036	1.499064219	5.924121165
B24	-0.544795928	2.842374554	1.466285015
C25	0.575816622	-1.179121998	-0.734964015
H26	-0.801984646	4.006037164	1.602200782
H27	-2.294336462	-0.331086644	-1.329779269
H28	-2.646042608	3.829343096	-0.237888138
H29	-1.385890009	3.585586645	4.120365986
H30	1.629356312	4.636060440	0.882240003
H31	-0.629751649	-0.653523143	4.402619878
H32	3.269385760	0.720297283	0.101662221
Re33	0.770887962	-2.005731489	-2.369103350
H34	2.128953931	-4.752542326	-2.272741369
C35	1.150983415	-4.342086168	-2.484263457
C36	0.650988860	-3.979248618	-3.772307195
H37	0.186149727	-4.301749677	-0.464572533
H38	1.192428427	-4.043321307	-4.705829723
C39	-0.667475804	-3.488198907	-3.596185591
H40	-1.314815298	-3.120011585	-4.381263074
C41	-1.007528353	-3.581632579	-2.212849339
H42	-1.954880772	-3.316390310	-1.763597020
C43	0.120117864	-4.117465459	-1.528442612
C44	0.248483275	-0.371133623	-3.232585814
O45	-0.100040240	0.595772112	-3.749046940
C46	2.579063094	-1.395060494	-2.422122159
O47	3.675380318	-1.039989944	-2.427482038

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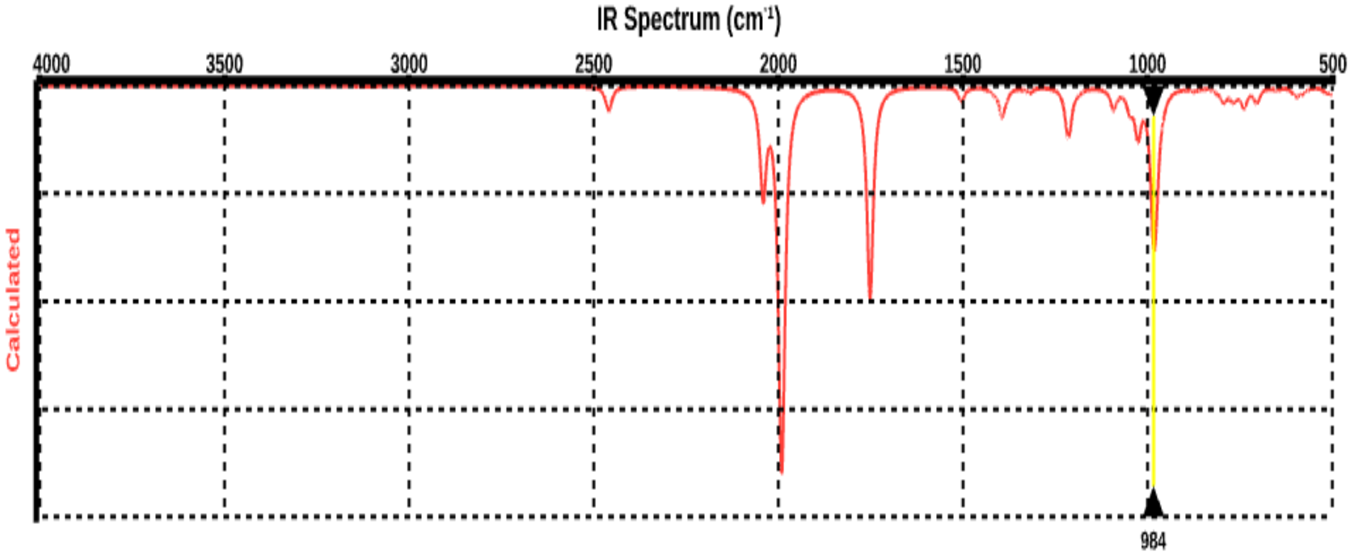
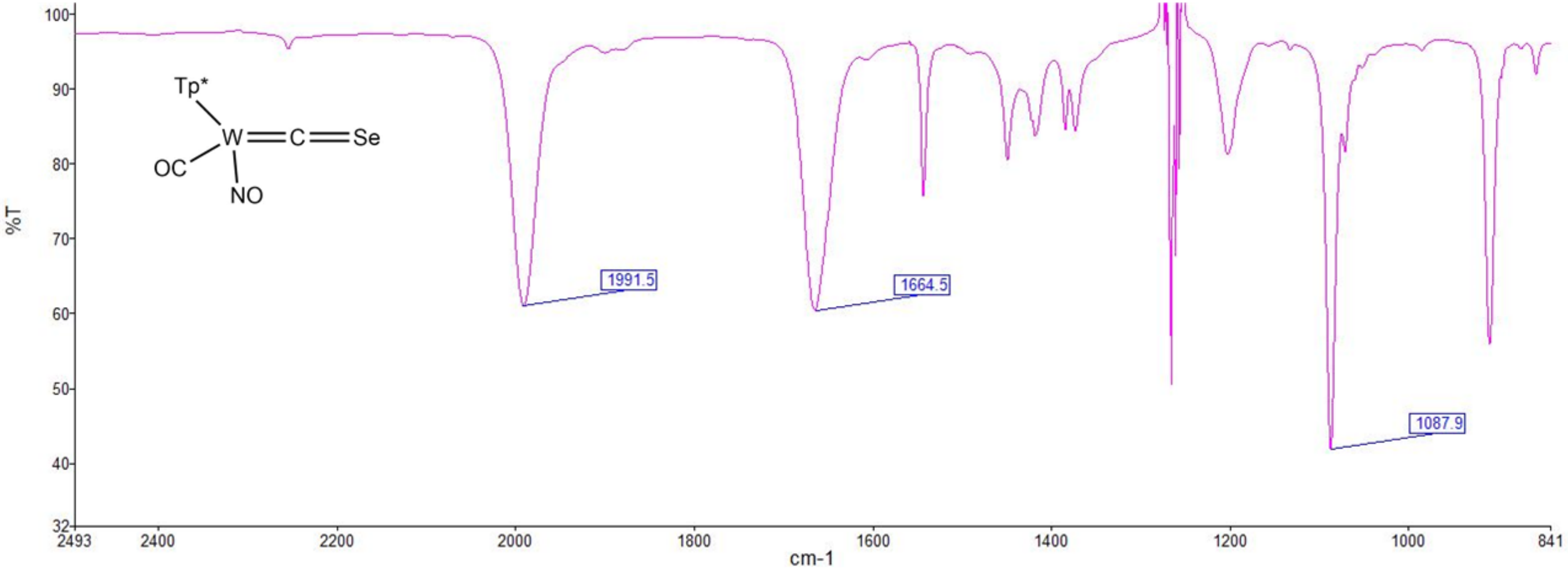
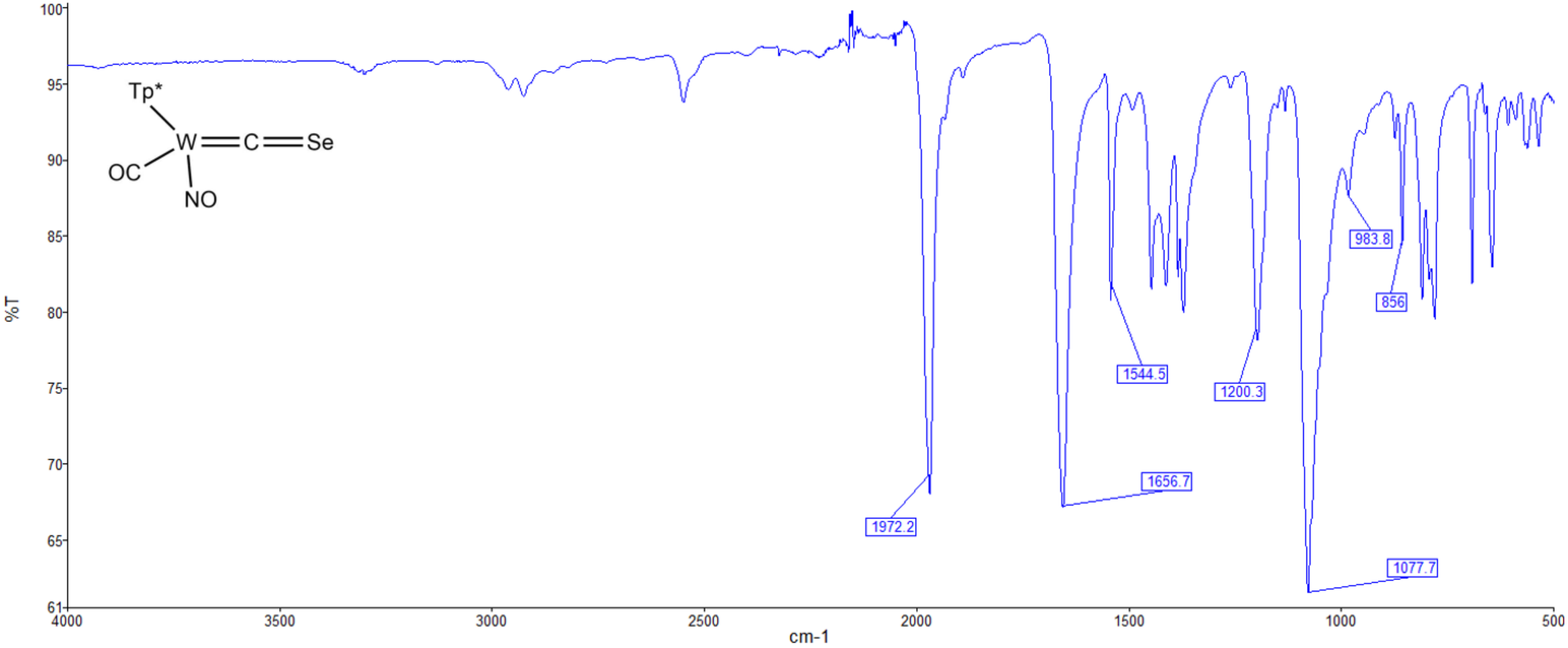


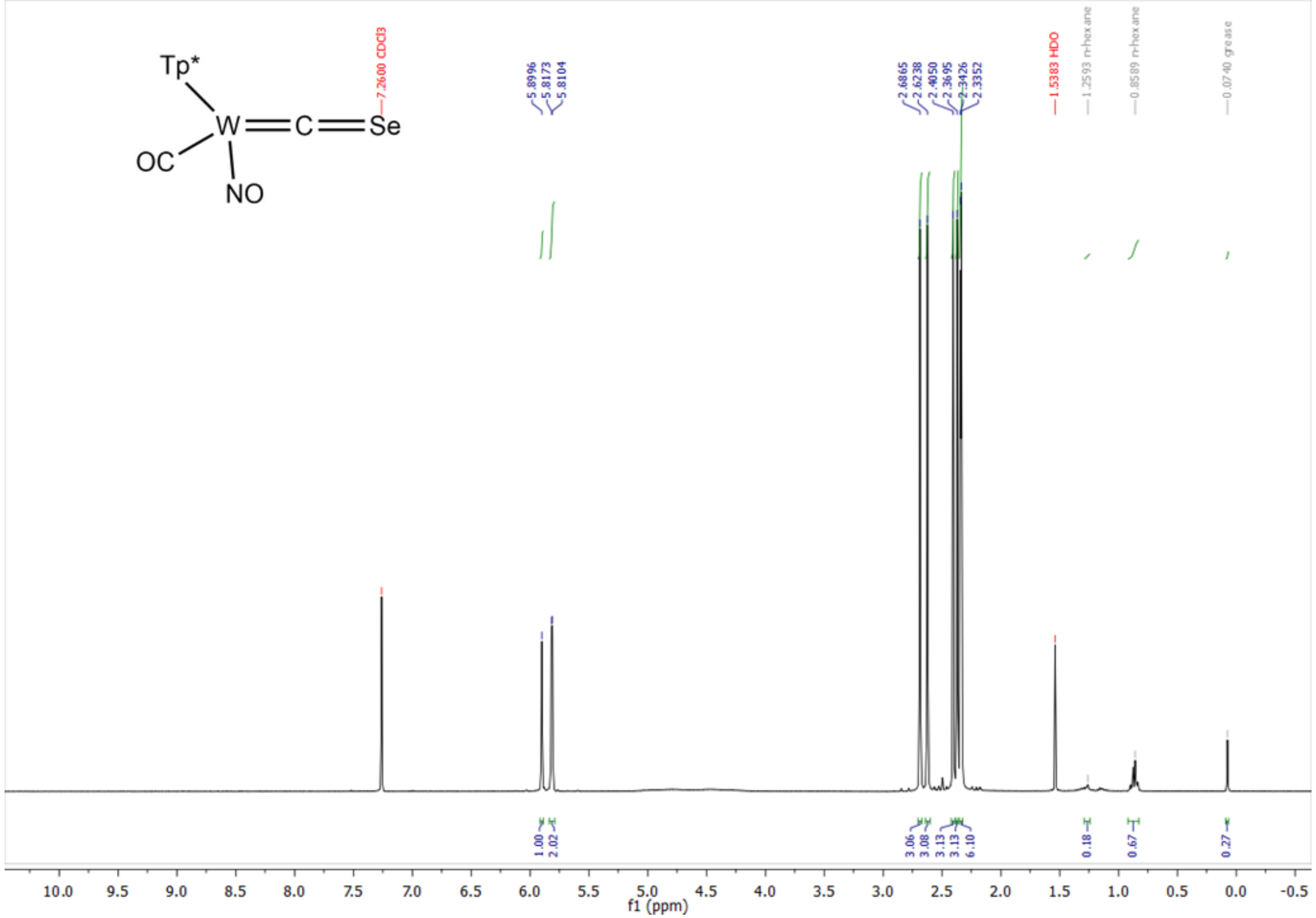
Calculated Infrared Spectrum of [WRe(μ-C)(CO)$_3$(NO)(Tp)] with location of primarily ν_{as}(W=C=Re) at 984 cm^{-1} (Obs.: 968 cm^{-1}).



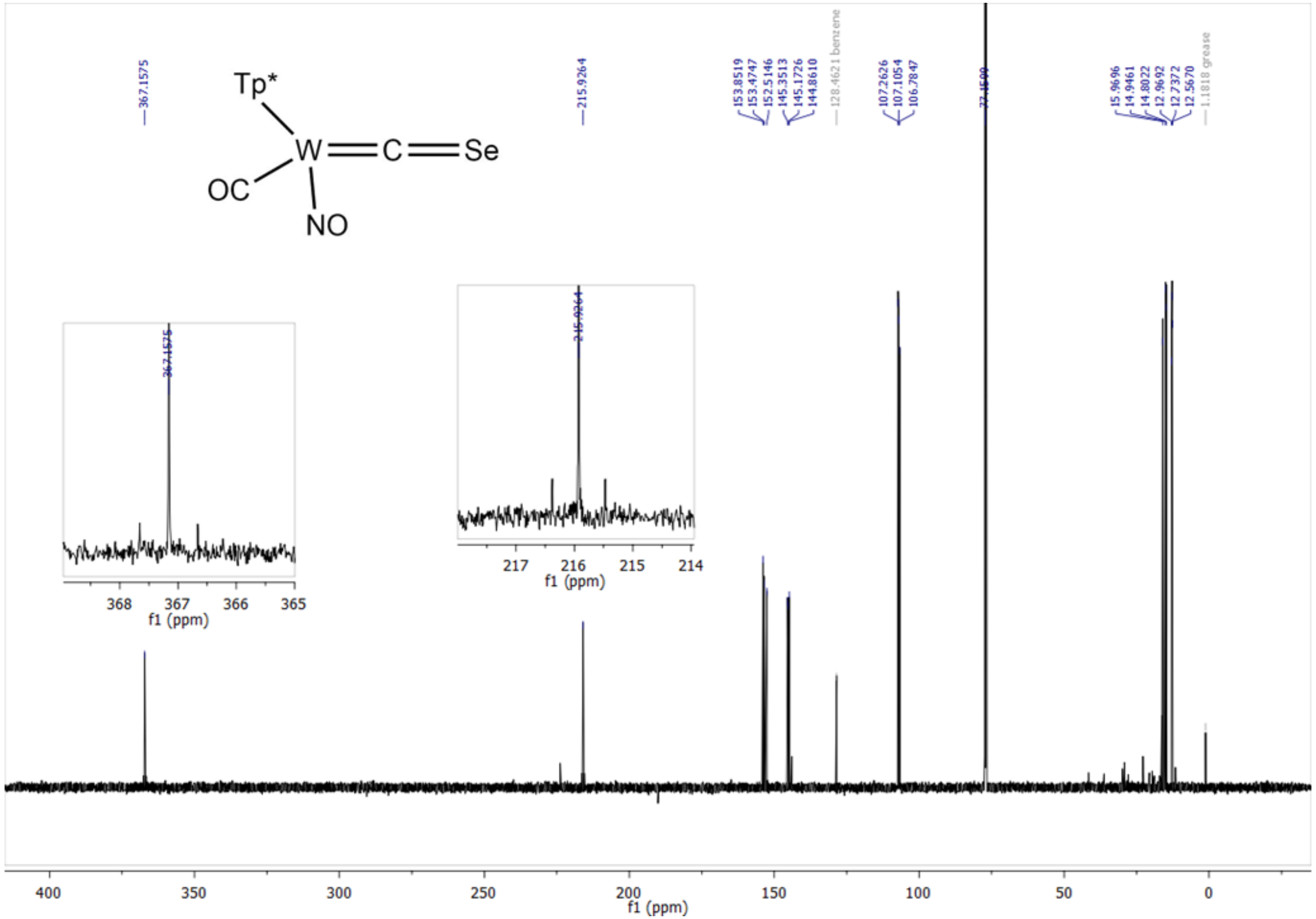
IR (CH_2Cl_2, cm^{-1}) for $[W(CSe)(CO)_2(Tp^*)]NEt_4$ (**2**)



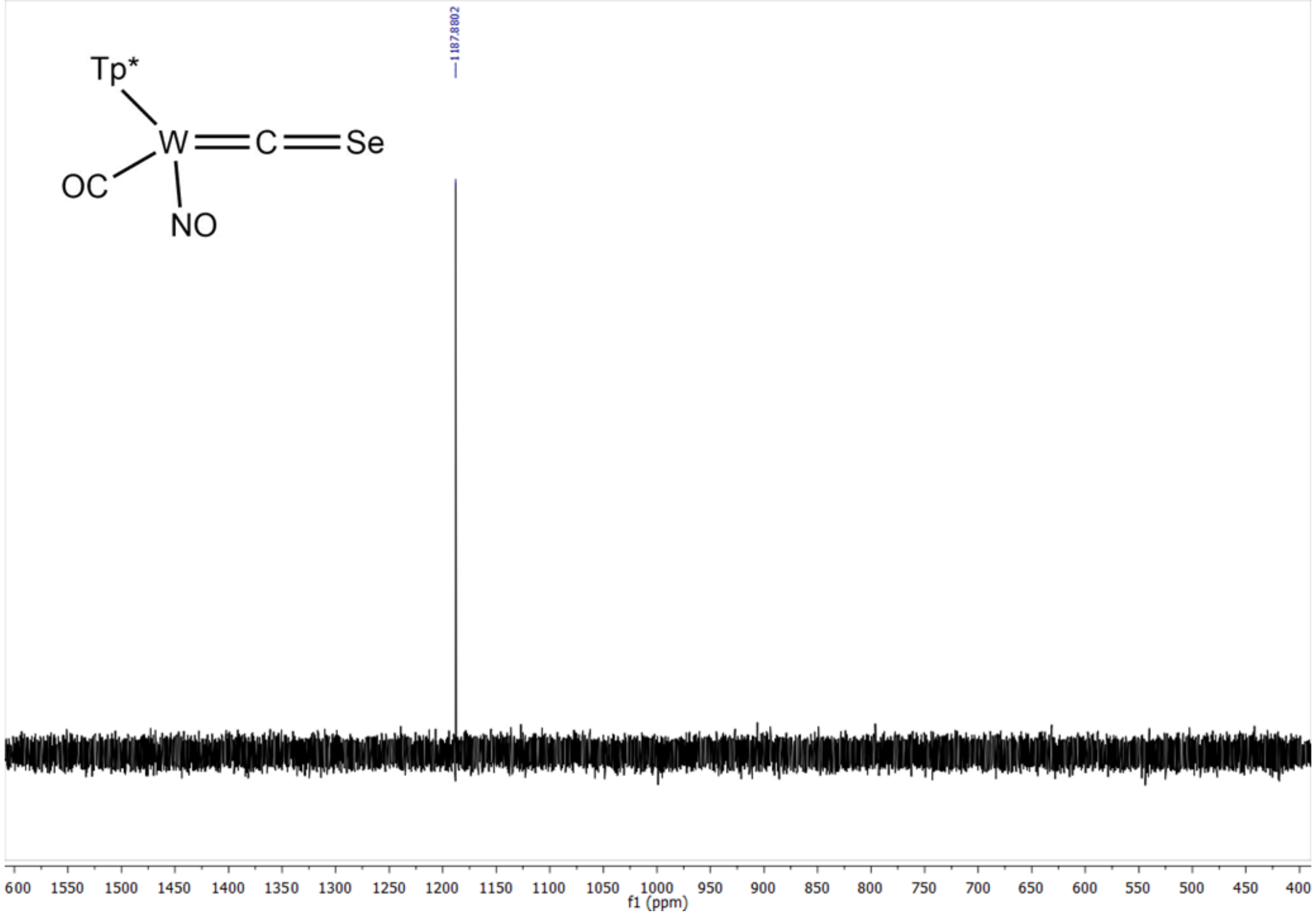
IR (ATR, cm^{-1}) for [W(CSe)(CO)$_2$(Tp*)]NEt$_4$ (**2**)



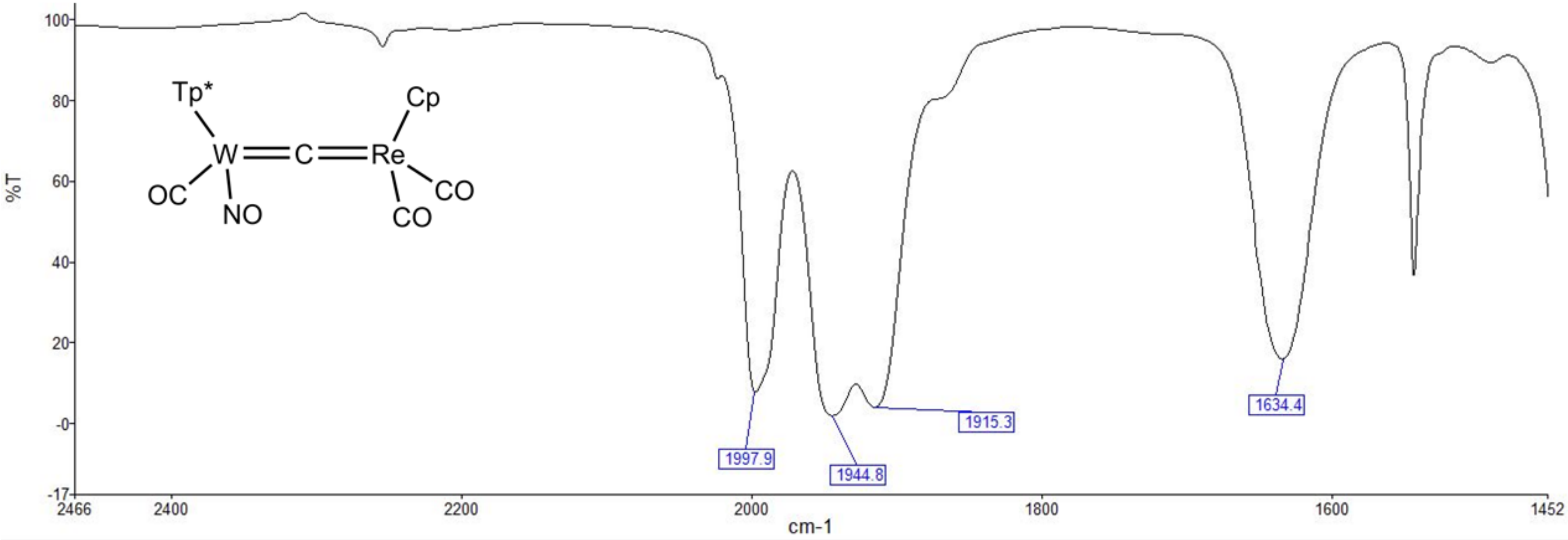
^{1}H NMR (700 MHz, $CDCl_3$, 298 K) for $[W(CSe)(CO)_2(Tp^*)]NEt_4$ (**2**)



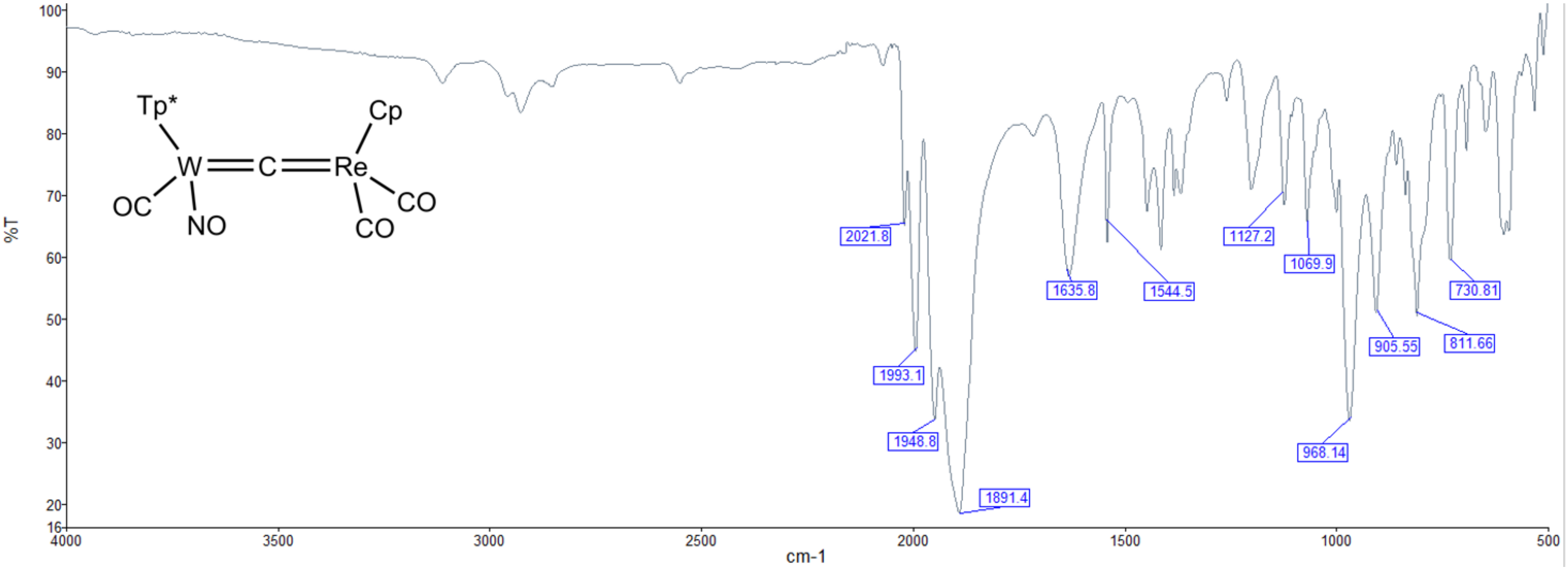
$^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$, 298 K) for $[W(CSe)(CO)_2(Tp^*)]NEt_4$ (**2**)



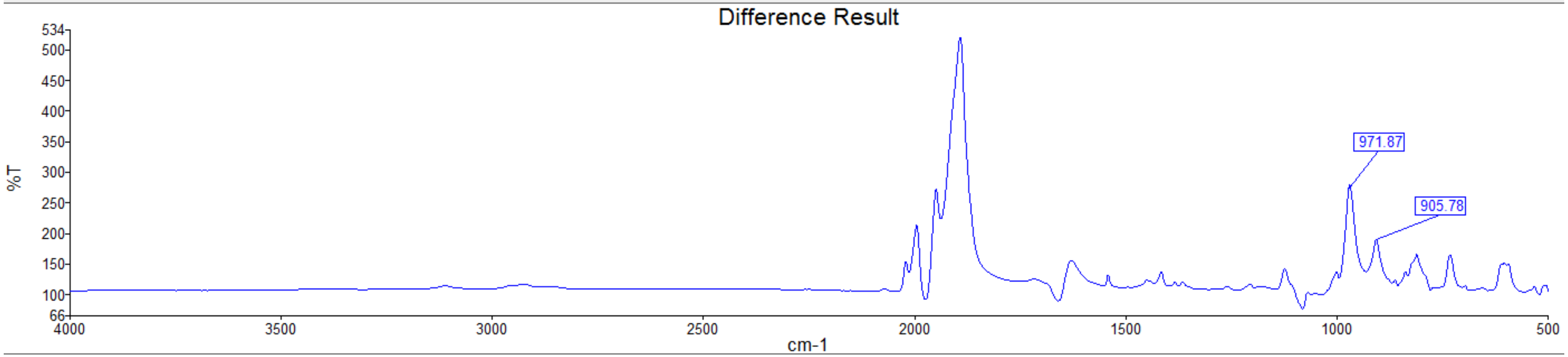
^{77}Se NMR (134 MHz, $CDCl_3$, 298 K) for $[W(CSe)(CO)_2(Tp^*)]NEt_4$ (**2**)



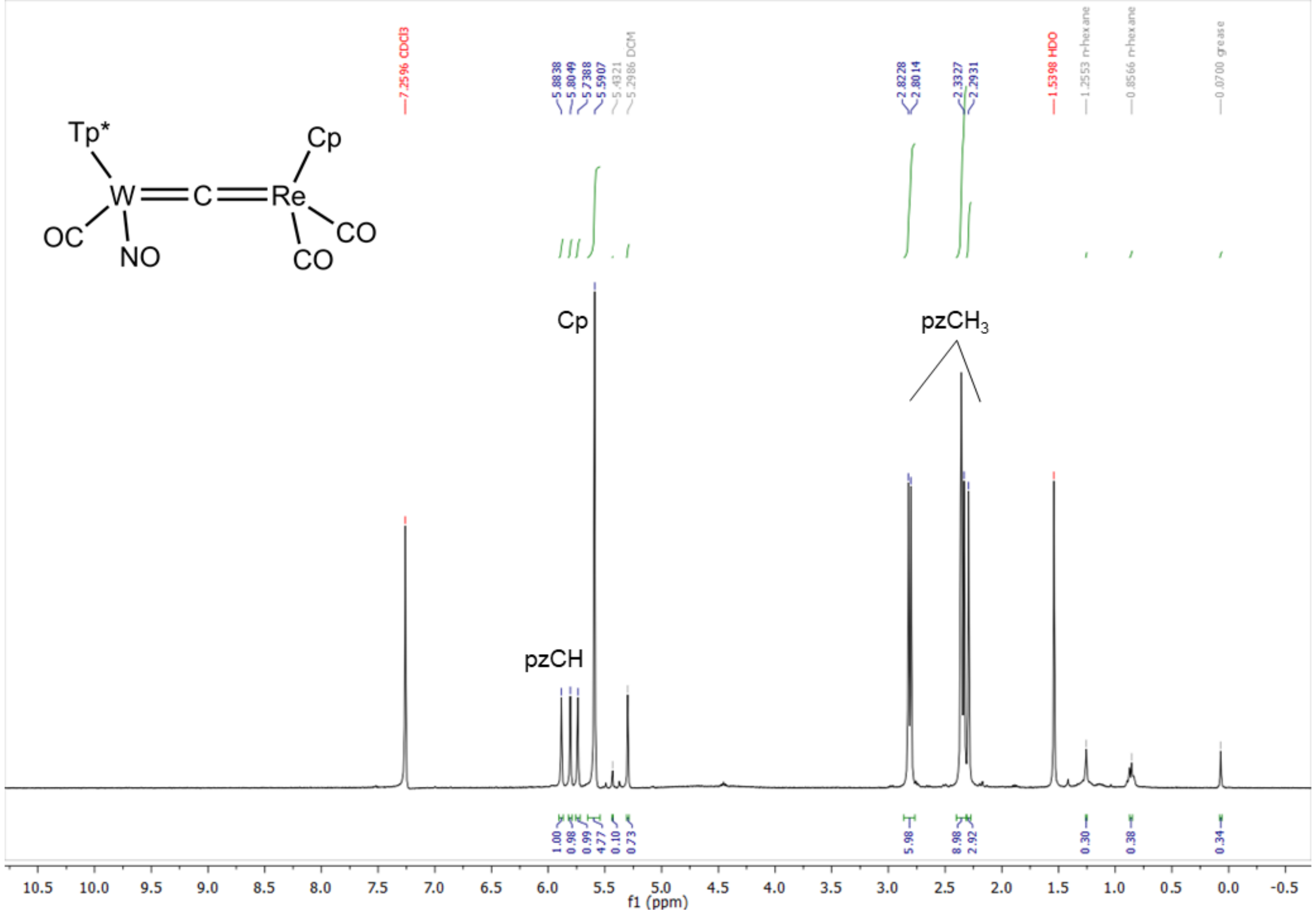
IR (CH_2Cl_2, cm^{-1}) for [$WRe(\mu\text{-}C)(CO)_3(NO)(Tp^*)(\eta\text{-}C_5H_5)$] (**5**)



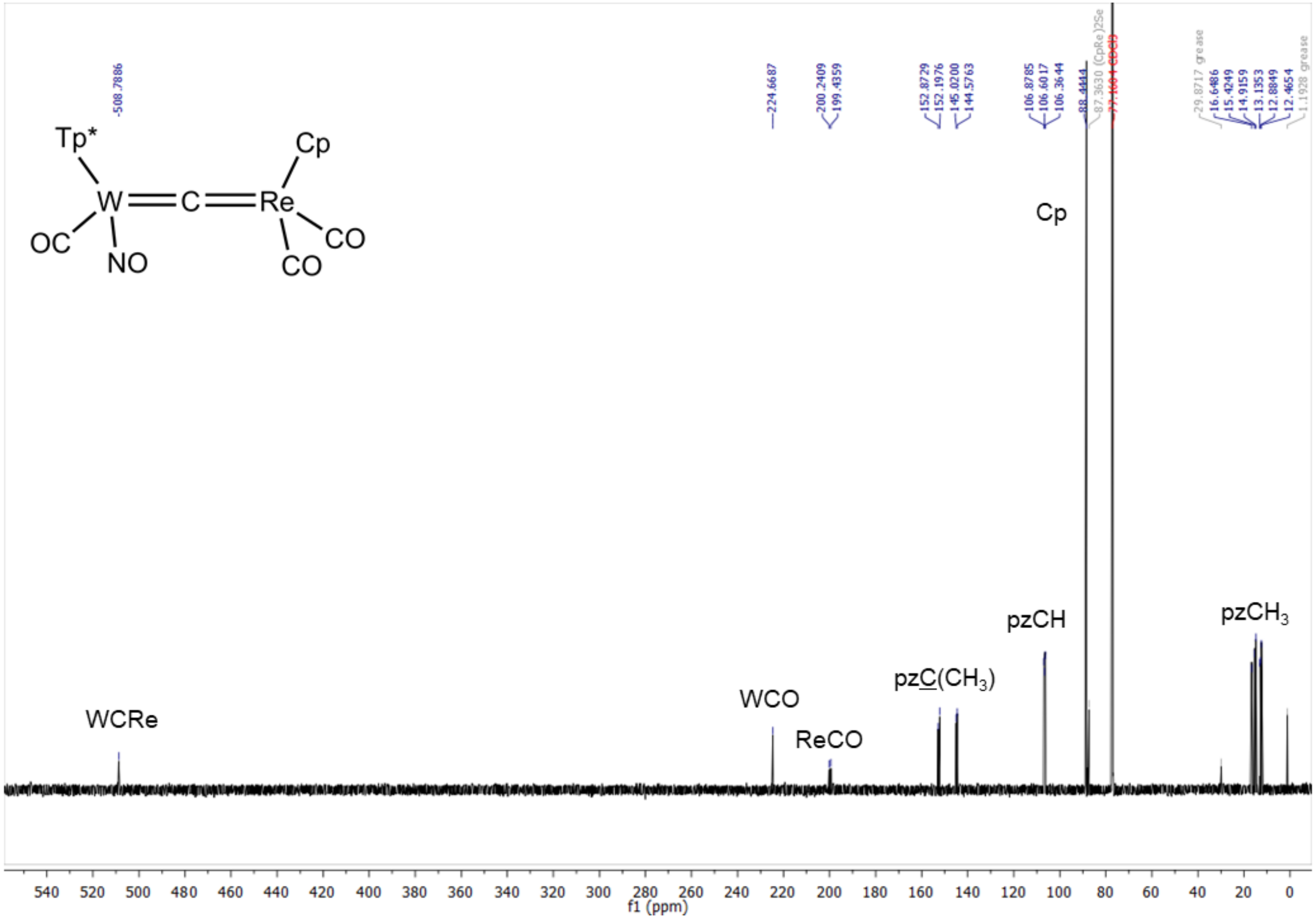
IR (ATR, cm^{-1}) for $[WRe(\mu\text{-}C)(CO)_3(NO)(Tp^*)(\eta\text{-}C_5H_5)]$ (**5**)



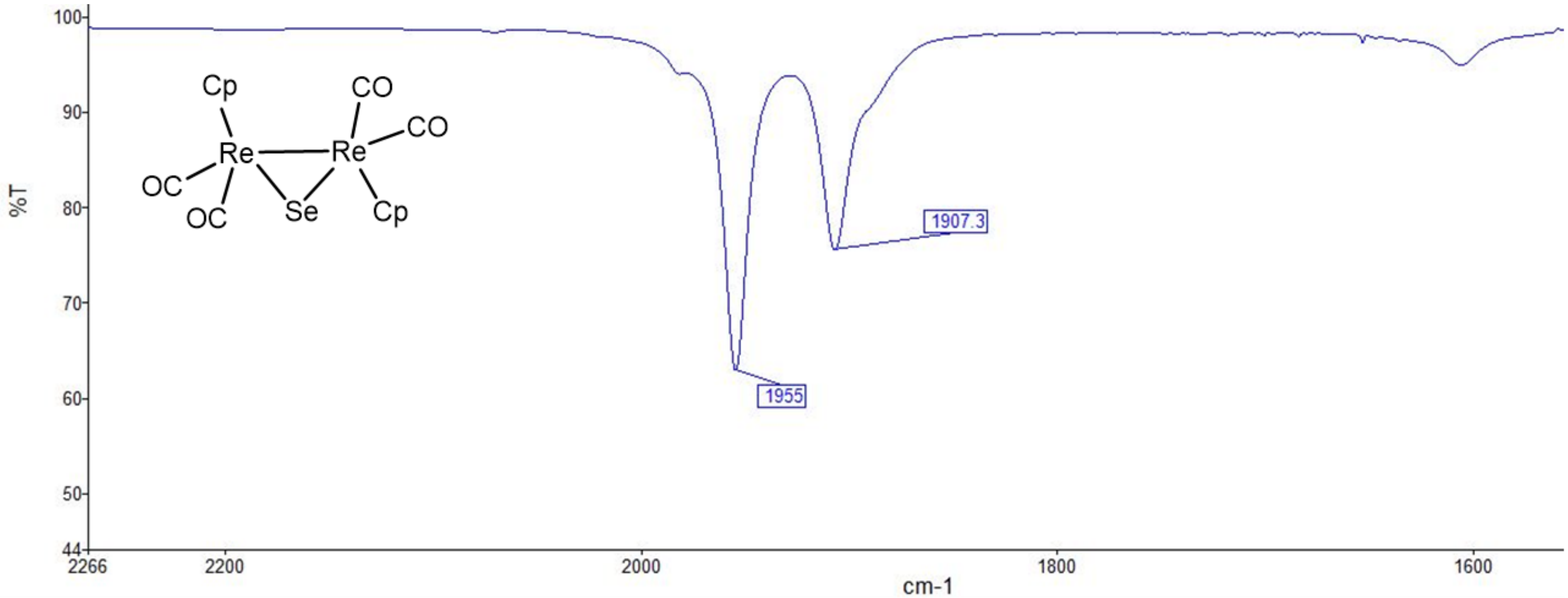
Difference IR (ATR, cm^{-1}) of [W(CSe)(CO)$_2$(Tp*)]NEt$_4$ (**2**) and [WRe(μ-C)(CO)$_3$(NO)(Tp*)(η-C$_5$H$_5$)] (**5**)



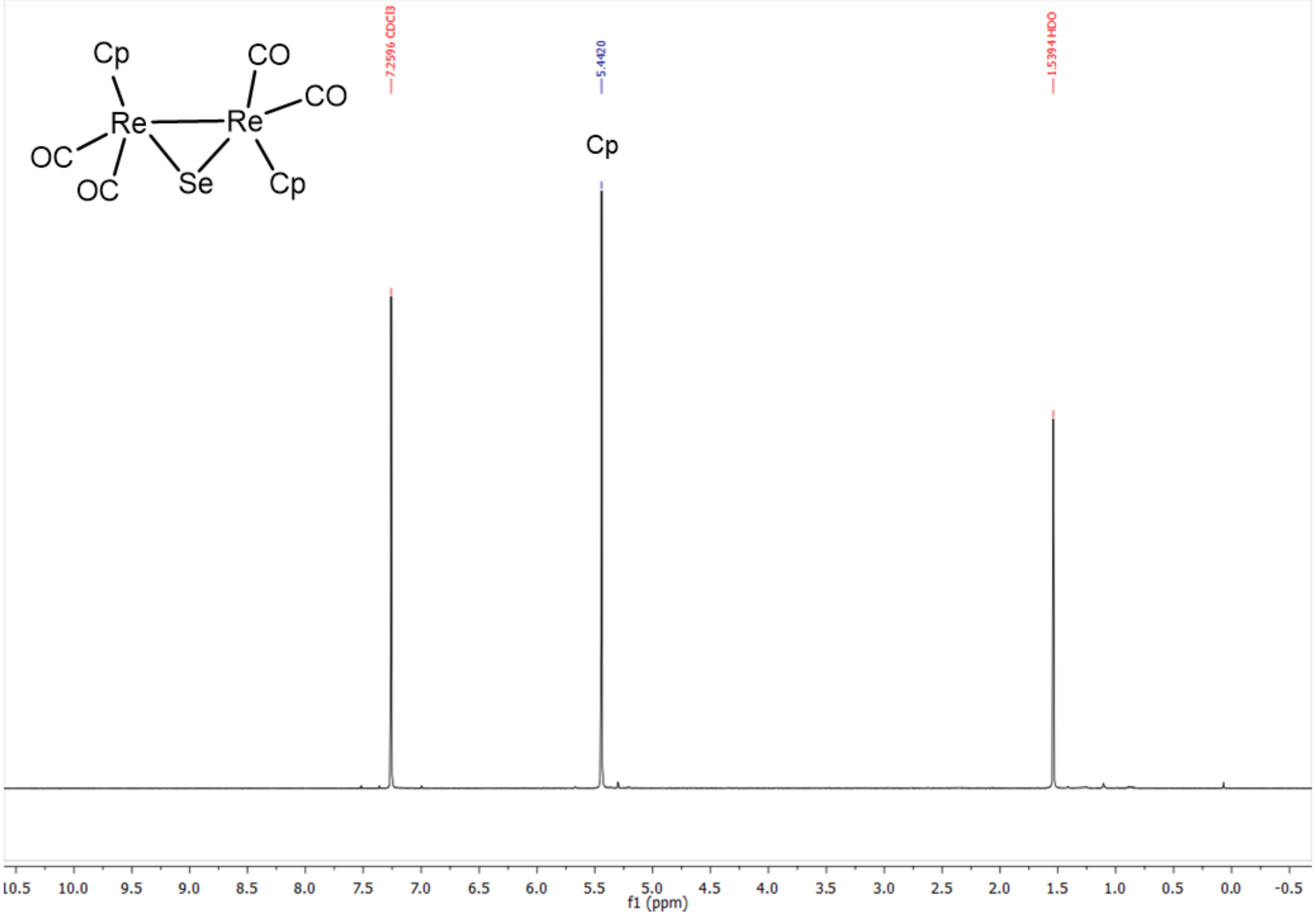
^{1}H NMR (400 MHz, CDCl$_3$, 298 K, δ) for [WRe(μ-C)(CO)$_3$(NO)(Tp*)(η-C$_5$H$_5$)] (**5**)



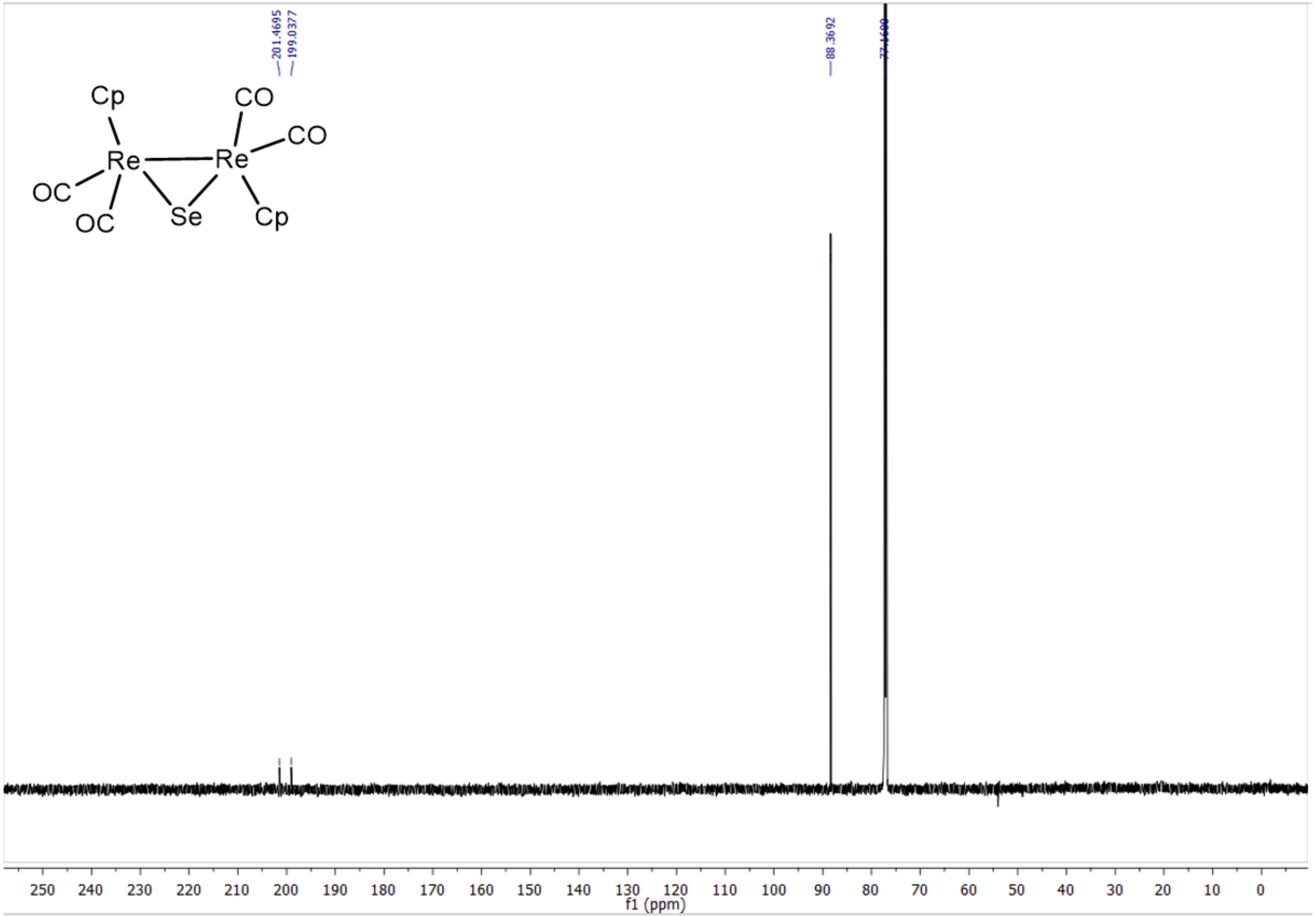
$^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$, 298 K) for [WRe(μ-C)$(CO)_3$(NO)(Tp*)(η-C_5H_5)] (**5**)



IR (CH_2Cl_2, cm^{-1}) for $[Re_2(\mu\text{-}Se)(CO)_4(\eta\text{-}C_5H_5)_2]$ (**6**)



^{1}H NMR (400 MHz, $CDCl_3$, 298 K) for $[Re_2(\mu\text{-}Se)(CO)_4(\eta\text{-}C_5H_5)_2]$ (**6**)



$^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$, 298 K) for [$Re_2(\mu\text{-}Se)(CO)_4(\eta\text{-}C_5H_5)_2$] (**6**)