ELECTRONIC SUPPORTING INFORMATION

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Electronic Supporting Information for: Organometallic Flow Chemistry: *Solvento* Complexes

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Experimental

General Considerations

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). NMR spectra were obtained on Varian 400 (^{1}H at 399.8, ^{13}C at 100.5), Bruker Avance 400 (^{1}H at 400.1 MHz, ^{13}C at 100.6 MHz, ^{31}P at 162.0 MHz), 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 (85% H_3PO_4 in H_2O for ^{31}P). 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 ^{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. High-resolution electrospray ionisation mass spectrometry (ESI-MS) was performed by the ANU Research School of Chemistry mass spectrometry service with acetonitrile, dichloromethane or methanol as the matrix.

The data for each complex are consistent with those previously reported for each complex: $[W(CO)_5(PPh_3)]$,[1] $[Mo(CO)_5(PPh_3)]$,[1] $[Cr(CO)_5(PPh_3)]$,[1] $[Mn(Cp')(CO)_2(PPh_3)]$[2] and $[Re(Cp^*)(CO)_2(PPh_3)]$[3]. Crude NMR spectra are provided along with the isolated products for context.

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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.

Computational Details

Computational studies were performed by using the *SPARTAN20*® suite of programs.[4] 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.[5,6] The Los Alamos effective core potential type basis set (LANL2Dζ) of Hay and Wadt [7-9] was used for I, Mo and W while Pople 6-31G* basis sets[10] were used for all other atoms. Frequency calculations were performed for all compounds to confirm that each optimized structure was a local minimum and also to identify vibrational modes of interest. Cartesian atomic coordinates are provided below.

General synthetic strategy

Following the quenching of *solvento* complexes with PPh_3, the solutions were worked with under atmospheric conditions. Mixtures were recrystallised from Et_2O/hexane or subjected to column chromatography for purification (neutral alumina, gradient elution with petroleum spirits (40-60 °C or 60-80 °C)/diethyl ether or petroleum spirits (40-60 °C/CH_2Cl_2).

Data for known compounds

$[W(CO)_5(PPh_3)]$: IR (THF, cm^{-1}): 2072 m, 1983 w, 1940 vs; ν_{CO}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ_H = 7.48 (m, 15 H, PPh_3). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K): δ_P = 20.85 ($^{1}J_{WP}$ = 244 Hz). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 298 K): δ_C = 199.32 (d, $^{2}J_{PC}$ = 7 Hz, $^{1}J_{WC}$ = 72 Hz, *trans*-W*C*O), 197.40 (d, $^{2}J_{PC}$ = 7 Hz, $^{1}J_{WC}$ = 63 Hz, *cis*-W*C*O), 135.4 (d, $^{1}J_{PC}$ = 41 Hz, *i*-PPh_3), 133.1 (d, $^{2}J_{PC}$ = 12 Hz, *o*-PPh_3), 130.5 (d, $^{4}J_{PC}$ = 2 Hz, *p*-PPh_3), 128.8 (d, $^{3}J_{PC}$ = 10 Hz, *m*-PPh_3). No discernible fragments were observed in the ESI-MS (+ve ion) spectrum other than $[PPh_3 + H]^+$.

[Mo(CO)$_5$(PPh$_3$)]: IR (THF, cm^{-1}): 2072 m, 1988 w, 1947 vs; ν_{CO}.^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ_H = 7.44 (m, 15 H, PPh_3). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K): δ_P = 37.68. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, 298 K): δ_C = 210.4 (d, $^2J_{PC}$ = 23 Hz, *trans*-Mo*C*O), 205.8 (d, $^2J_{PC}$ = 9 Hz, *cis*-Mo*C*O), 135.6 (d, $^1J_{PC}$ = 35 Hz, *i*-PPh_3), 133.0 (d, $^2J_{PC}$ = 13 Hz, *o*-PPh_3), 130.2 (d, $^4J_{PC}$ = 2 Hz, *p*-PPh_3), 128.7 (d, $^3J_{PC}$ = 9 Hz, *m*-PPh_3). This compound was not amenable to ESI-MS spectroscopic conditions.

[Cr(CO)$_5$(PPh$_3$)]: IR (THF, cm^{-1}): 2063 m, 1983 w, 1942 vs; ν_{CO}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ_H = 7.44 (m, 15 H, PPh_3). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K): δ_P = 55.89. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, 298 K): δ_C = 221.7 (d, $^2J_{PC}$ = 7 Hz, *trans*-Cr*C*O), 216.9 (d, $^2J_{PC}$ = 13 Hz, *cis*-Cr*C*O), 135.5 (d, $^1J_{PC}$ = 36 Hz, *i*-PPh_3), 132.9 (d, $^2J_{PC}$ = 11 Hz, *o*-PPh_3), 130.3 (s, *p*-PPh_3), 128.7 (d, $^3J_{PC}$ = 10 Hz, *m*-PPh_3). This compound was not amenable to ESI-MS spectroscopic conditions.

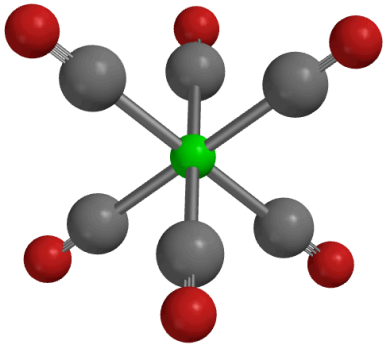
[Mn(Cp')(CO)$_2$(PPh$_3$)]: IR (THF, cm^{-1}): 1933, 1870 ν_{CO}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ_H = 7.47 (m, 15 H, PPh_3), 4.19, 4.05 (2 x brs, 2 x 2 H, $C_5H_4CH_3$), 1.95 (s, 3 H, $C_5H_4CH_3$). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K): δ_P = 92.73. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, 298 K): δ_C = 233.1 (d, $^2J_{PC}$ = 24 Hz, Mn*C*O), 138.4 (d, $^1J_{PC}$ = 40 Hz, *i*-PPh_3), 133.0 (d, $^2J_{PC}$ = 10 Hz, *o*-PPh_3), 129.5 (d, $^4J_{PC}$ = 2 Hz, *p*-PPh_3), 128.2 (d, $^3J_{PC}$ = 9 Hz, *m*-PPh_3), 99.1 ($C_4H_4CCH_3$), 83.2, 82.0 (2 x s, $C_4H_4CCH_3$), 13.9 ($C_4H_4CCH_3$). MS (ESI, +ve ion, *m/z*): Found: 452.0730. Calcd for $C_{26}H_{22}{}^{55}MnO_2P$ $[M+Na]^+$: 452.0738.

[Re(Cp*)(CO)$_2$(PPh$_3$)]: IR (THF, cm^{-1}): 1918, 1855 ν_{CO}. ^{1}H NMR (700 MHz, $CDCl_3$, 298 K): δ_H = 7.45, 7.35 (2 x m, 15 H, PPh_3), 1.82 (s, 15 H, Cp*). $^{31}P\{^1H\}$ NMR (283 MHz, $CDCl_3$, 298 K): δ_P = 33.50. $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$, 298 K): δ_C = 206.7 (d, $^2J_{PC}$ = 8 Hz, Re*C*O), 137.8 (d, $^1J_{PC}$ = 50 Hz, *i*-PPh_3), 133.5 (d, $^2J_{PC}$ = 11 Hz, *o*-PPh_3), 129.5 (d, $^4J_{PC}$ = 2 Hz, *p*-PPh_3), 128.0 (d, $^3J_{PC}$ = 10 Hz, *m*-PPh_3), 95.6 ($C_5(CH_3)_5$), 10.5 ($C_5(CH_3)_5$). MS (ESI, +ve ion, *m/z*): Found: 641.1621. Calcd for $C_{30}H_{31}O_2P^{187}Re$ $[M+H]^+$: 641.1620.

Optimised Geometries and Cartesian Coordinates

[W(CO)$_6$]

Optimised structure of **[W(CO)$_6$]** in the gas phase

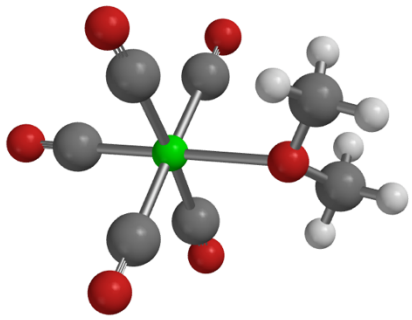


Cartesian coordinates of optimised [W(CO)$_6$]

Atom	X	Y	Z
W	-0.000002	-0.000020	-0.000000
C	0.000000	2.060635	0.000000
O	0.000002	3.206866	0.000000
C	2.060652	0.000002	0.000000
O	3.206883	0.000022	0.000000
C	-2.060656	0.000002	0.000000
O	-3.206887	0.000022	0.000000
C	0.000000	-2.060672	0.000000
O	0.000002	-3.206903	0.000000
C	0.000000	0.000002	2.060654
O	0.000002	0.000022	3.206885
C	0.000000	0.000002	-2.060654
O	0.000002	0.000022	-3.206885

$[W(CO)_5(OMe_2)]$

Optimised structure of **$[W(CO)_6]$** in the gas phase



Cartesian coordinates of optimised $[W(CO)_5(OMe_2)]$

Atom	X	Y	Z
W	-0.155744	0.000002	-1.108709
C	-0.793329	-0.000007	-2.979051
O	-1.170629	-0.000010	-4.073487
C	1.801128	0.000004	-1.739658
O	2.887040	0.000005	-2.114183
C	-2.086037	0.000001	-0.425154
O	-3.176044	-0.000000	-0.055193
C	-0.175110	2.046512	-1.184047
O	-0.202547	3.193268	-1.280630
C	-0.175115	-2.046508	-1.184049
O	-0.202554	-3.193264	-1.280632
O	0.627127	0.000000	1.127846
C	0.391755	-1.176305	1.895279
H	0.732339	-2.025689	1.305321
H	-0.677255	-1.282021	2.119333
H	0.964068	-1.128100	2.828536
C	0.391755	1.176305	1.895281
H	0.732339	2.025688	1.305323
H	0.964068	1.128098	2.828538
H	-0.677255	1.282020	2.119334

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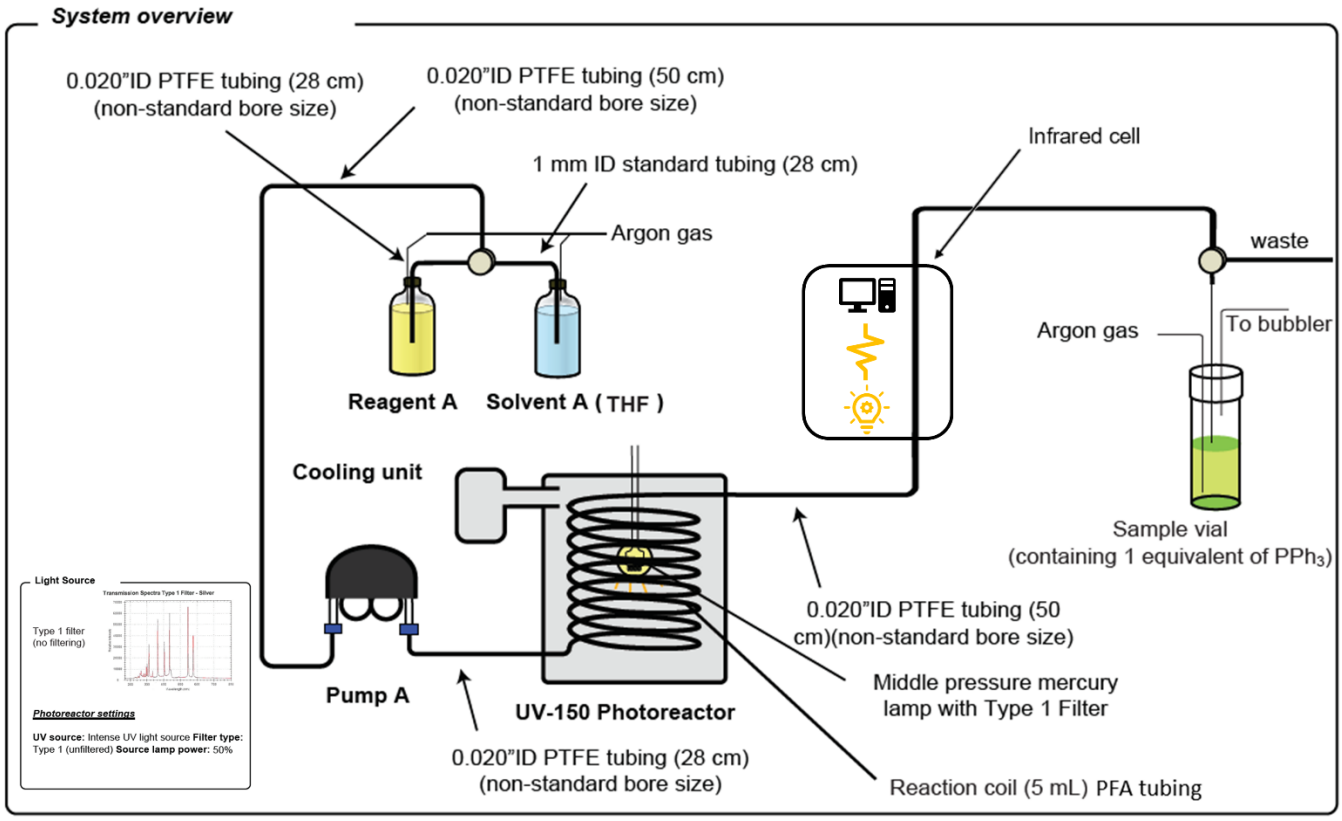

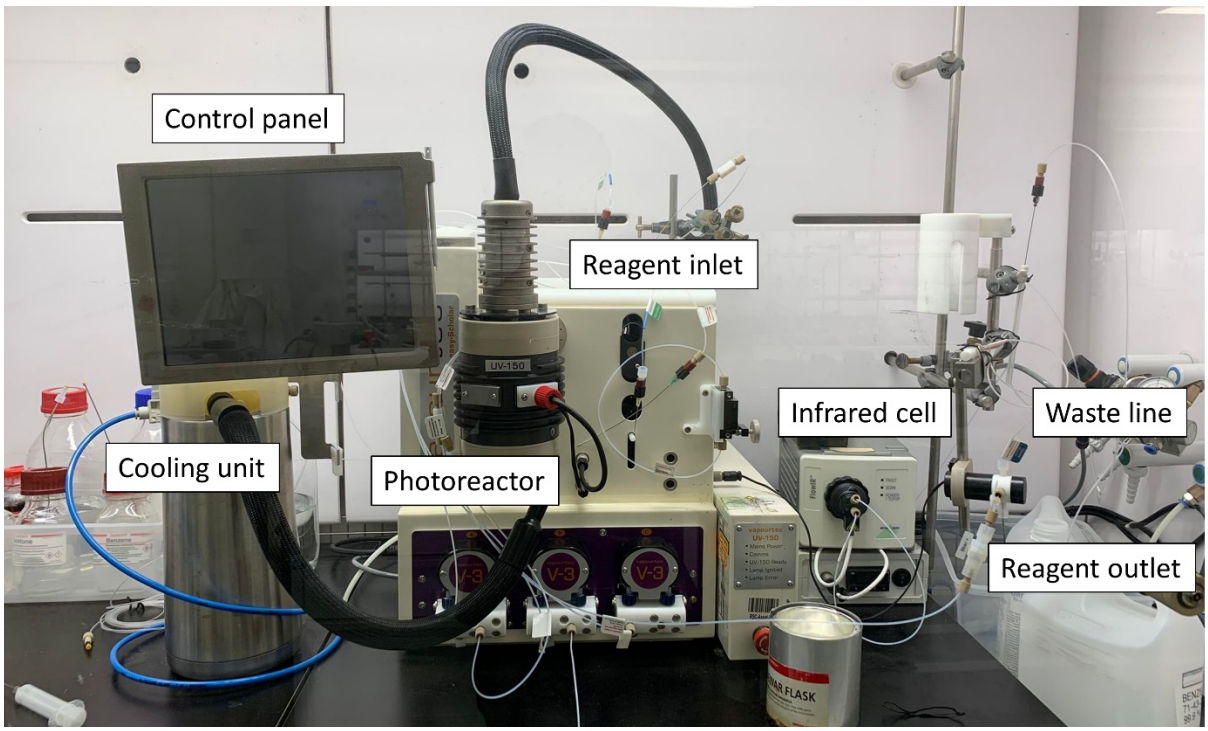

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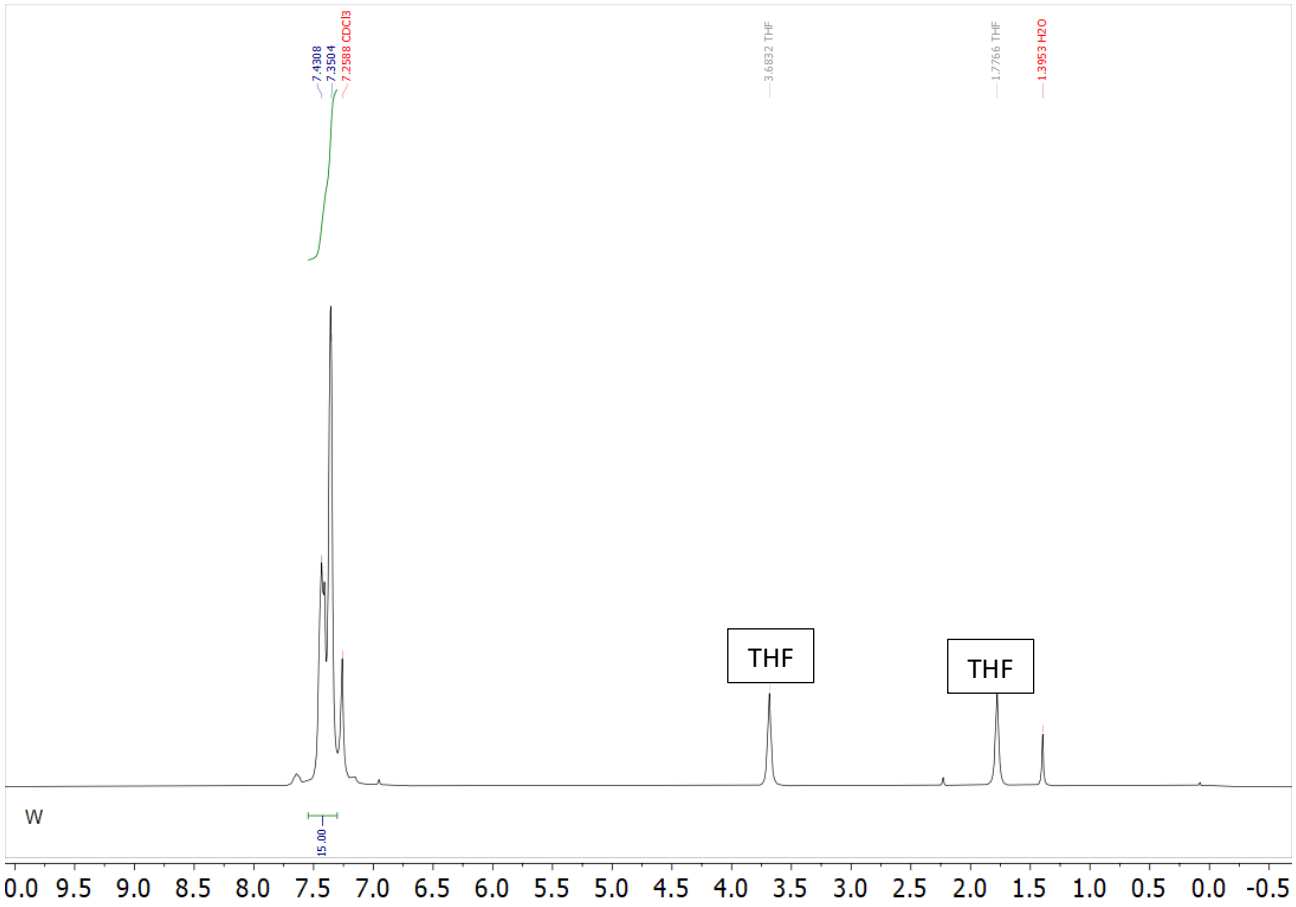
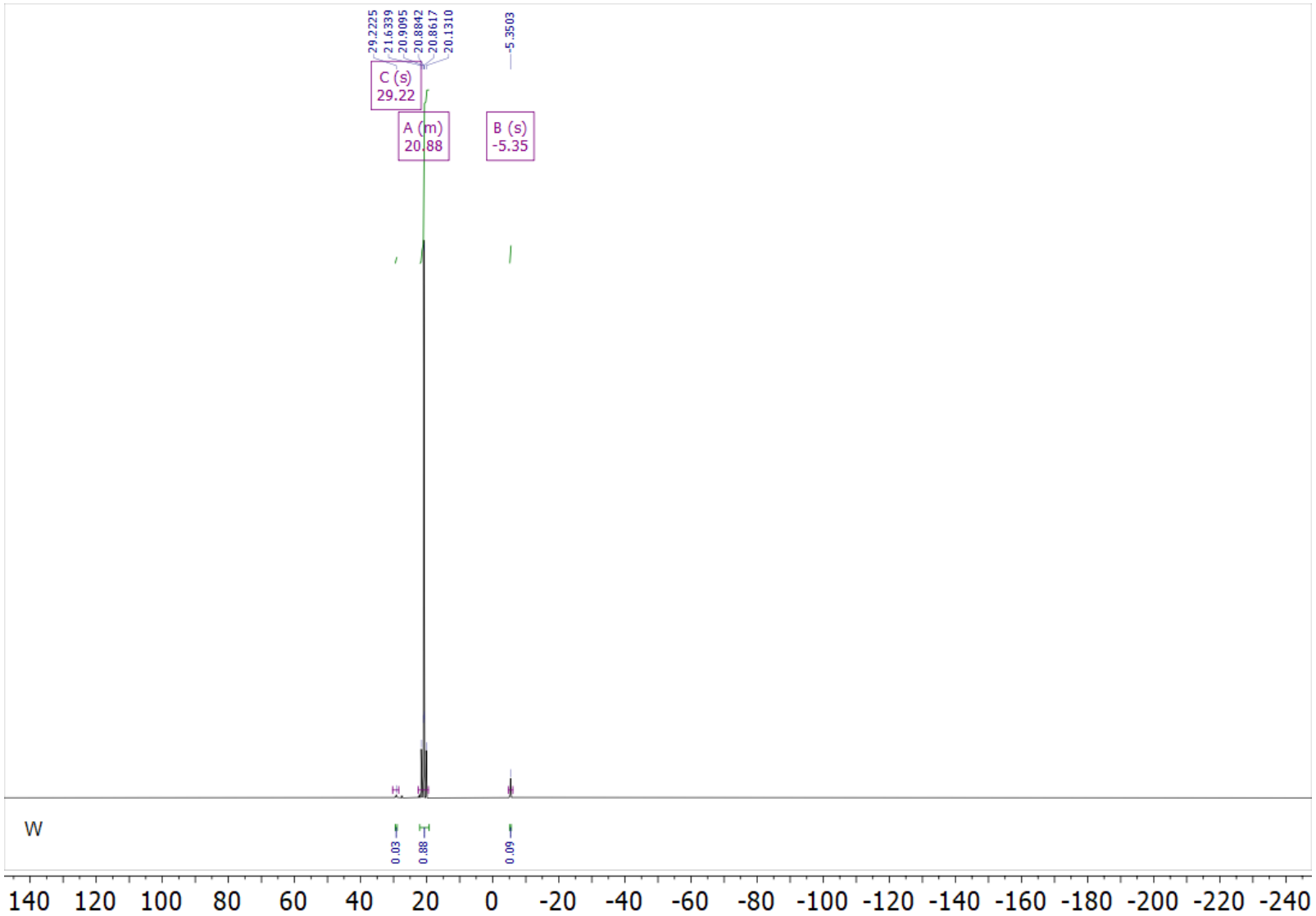


CRUDE ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) for $[W(CO)_5(PPh_3)]$.



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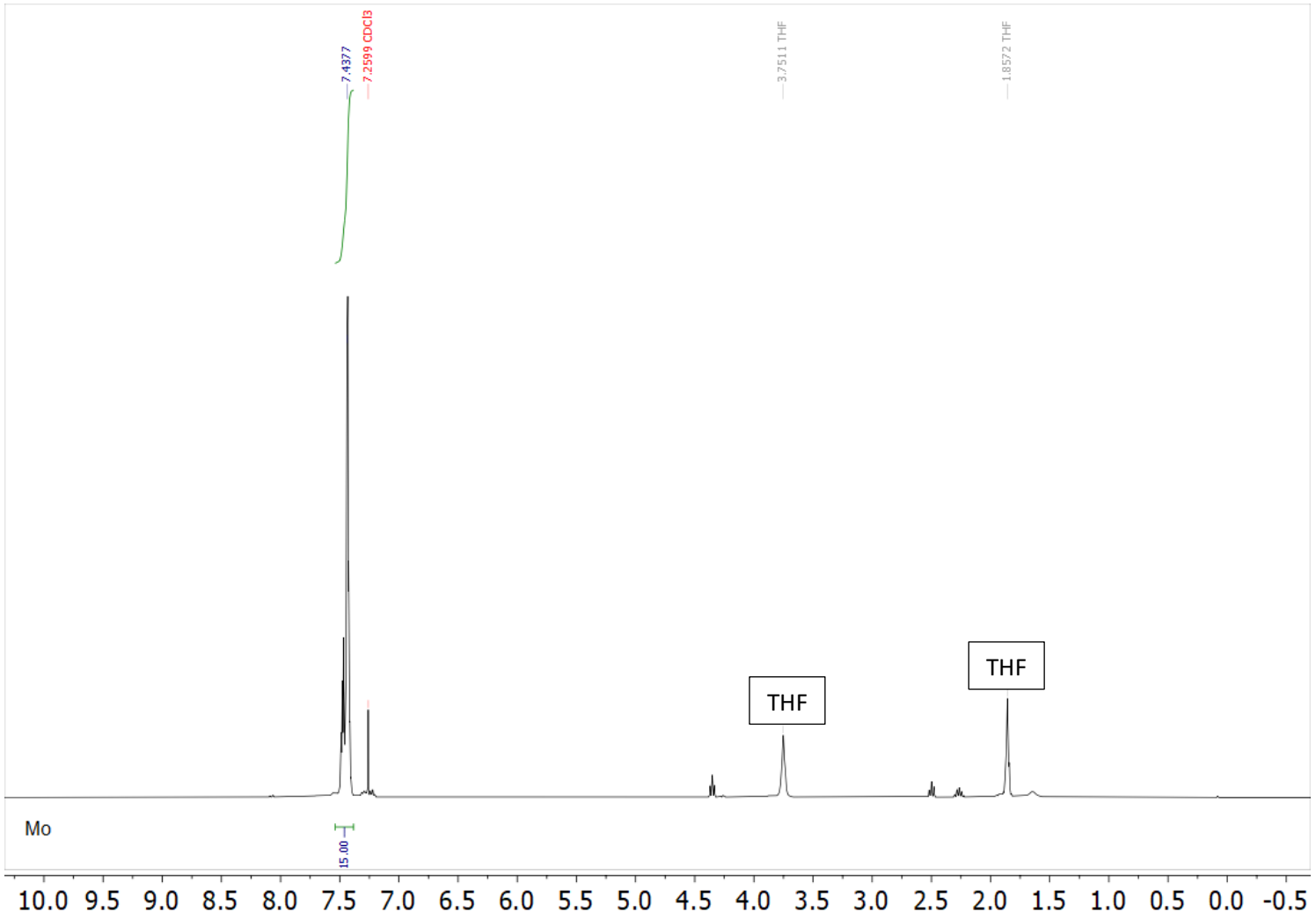

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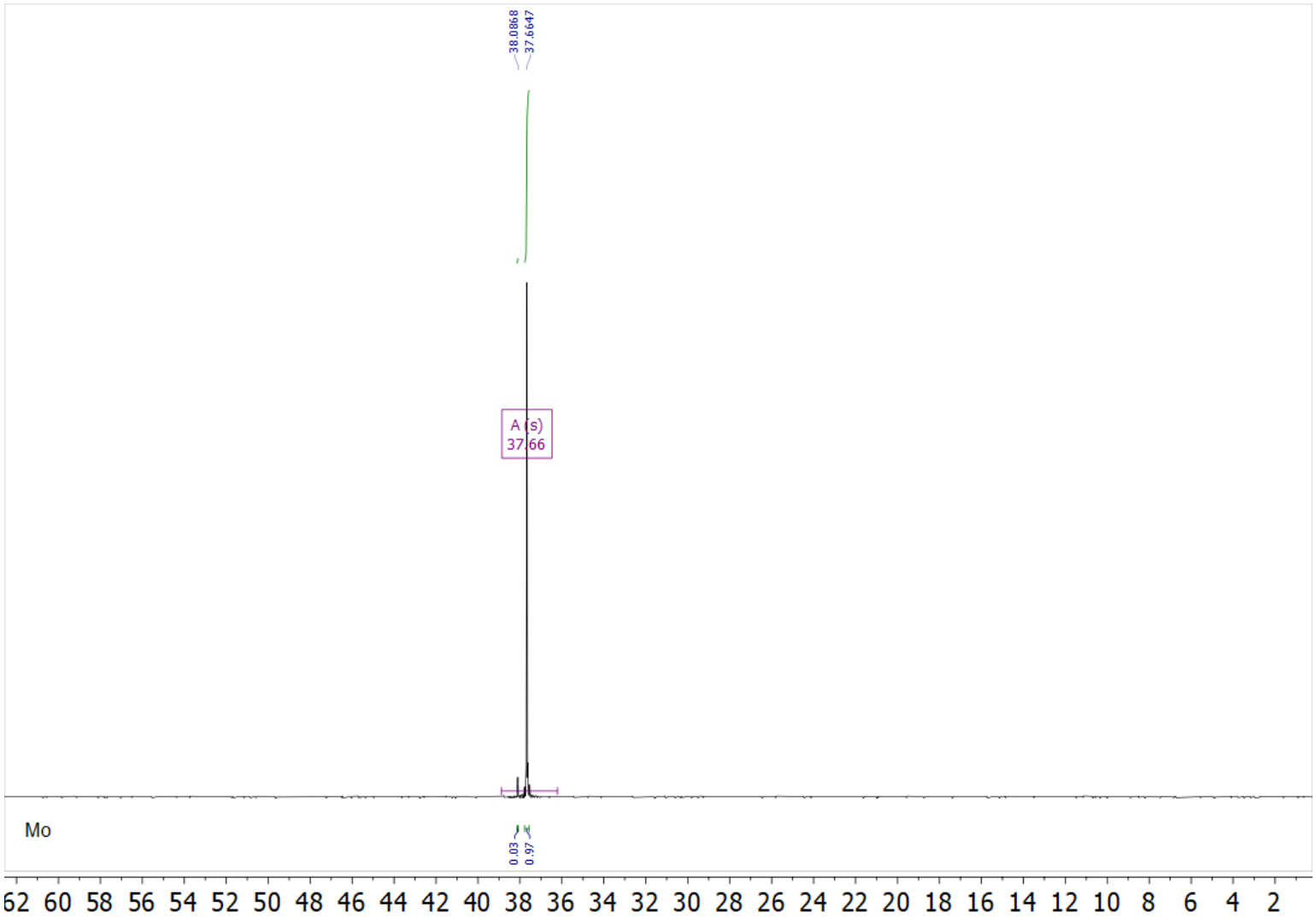
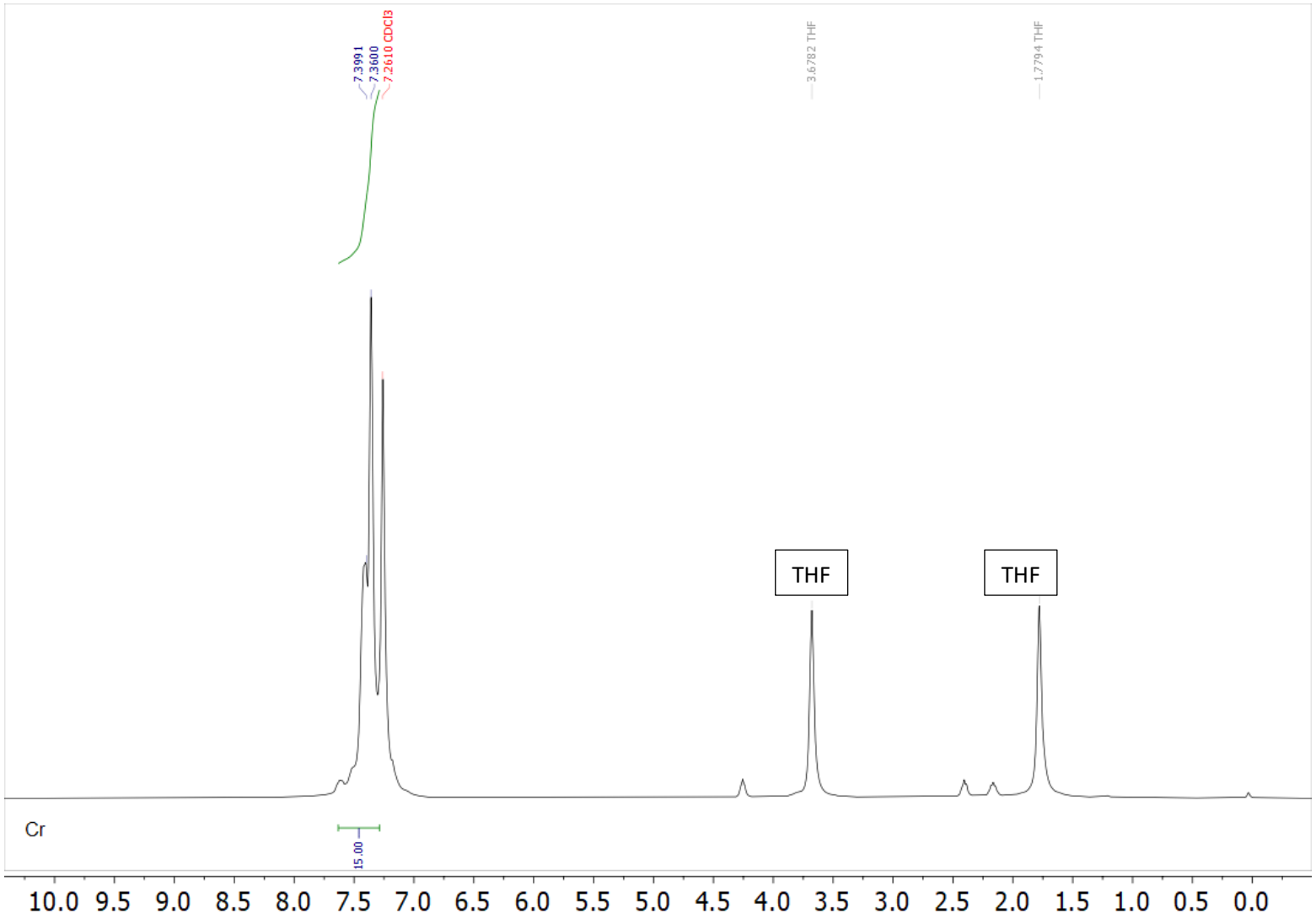


CRUDE $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) for $[Mo(CO)_5(PPh_3)]$.



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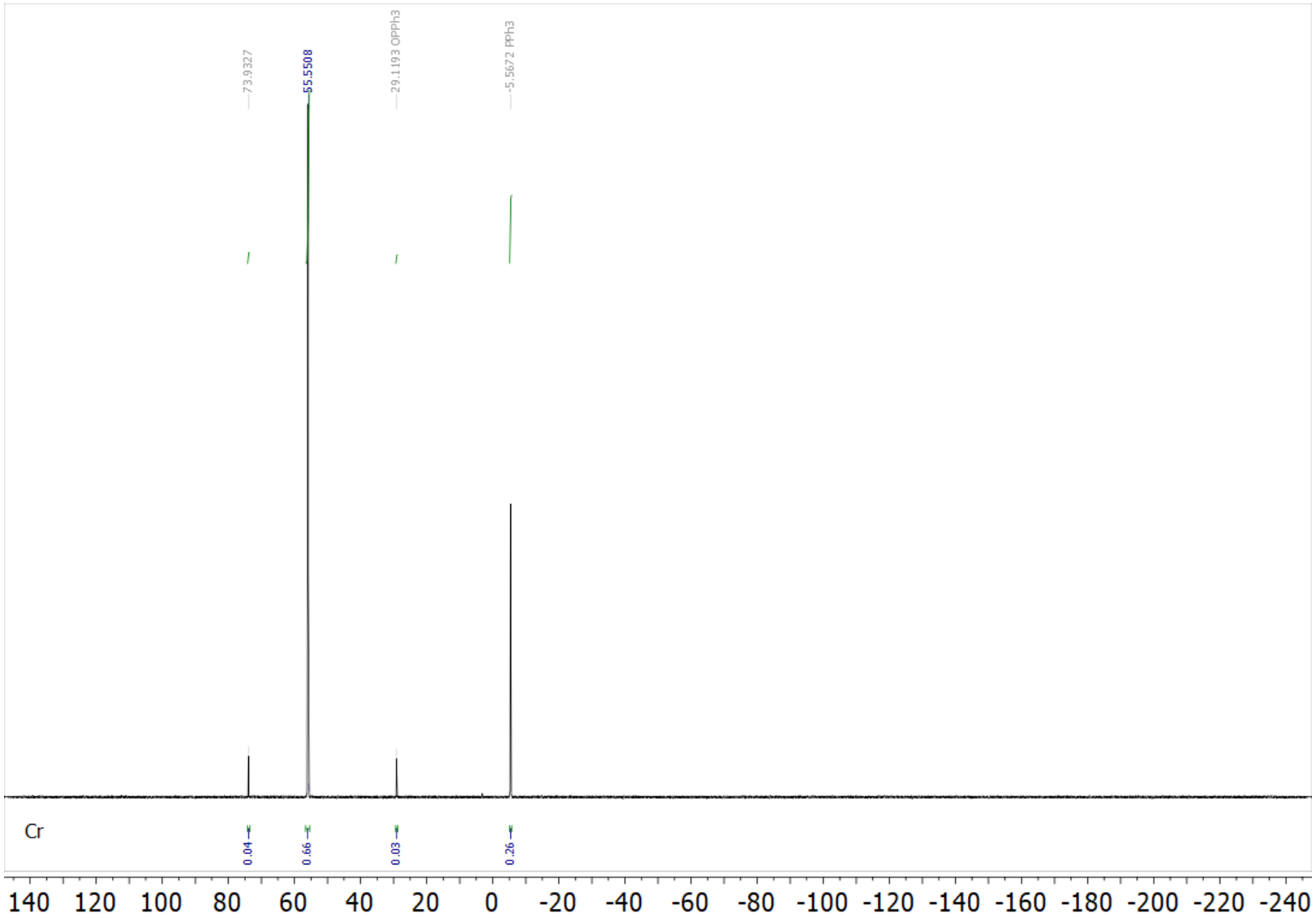

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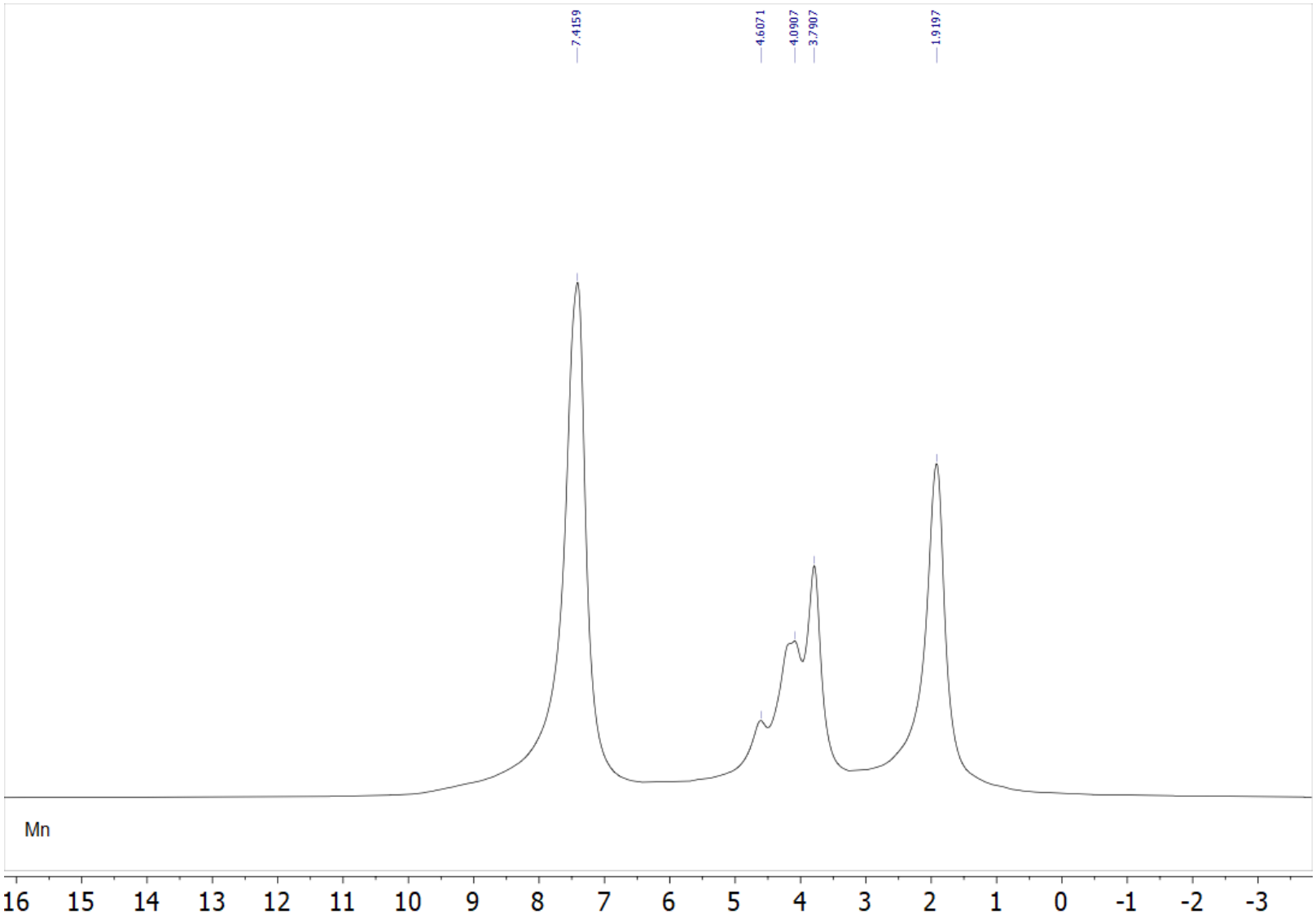

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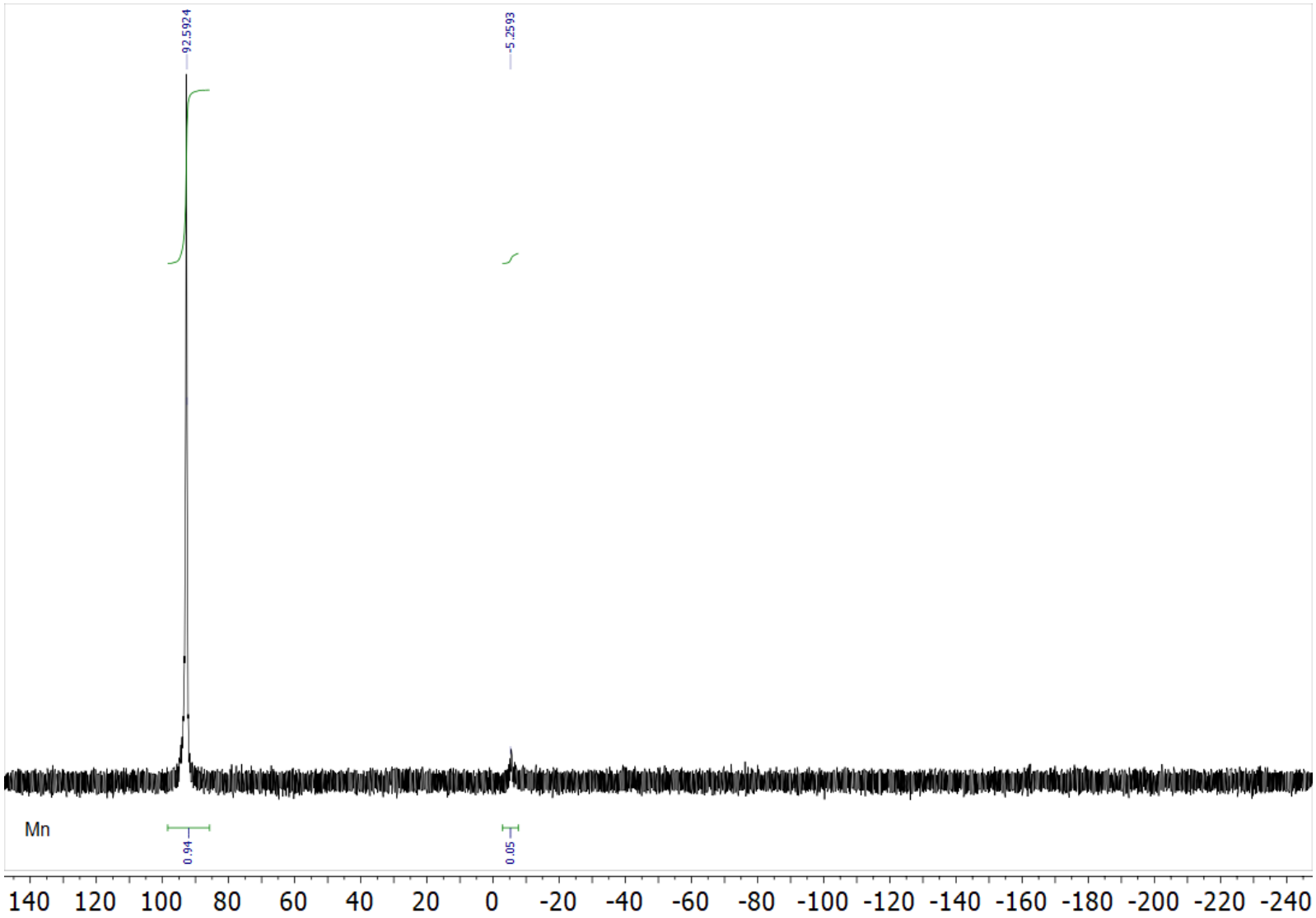
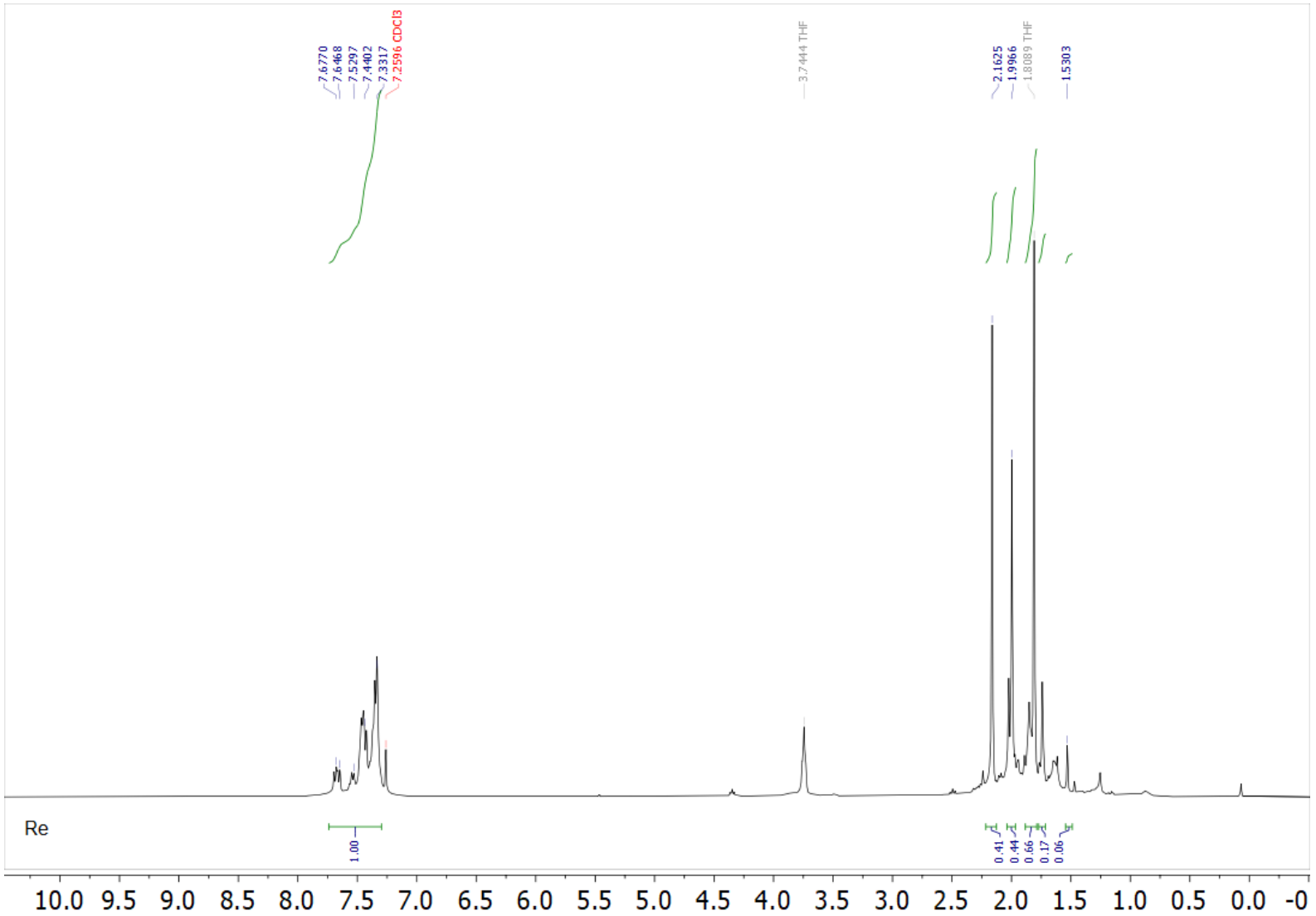


CRUDE $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) for $[Mn(Cp')(CO)_2(PPh_3)]$.



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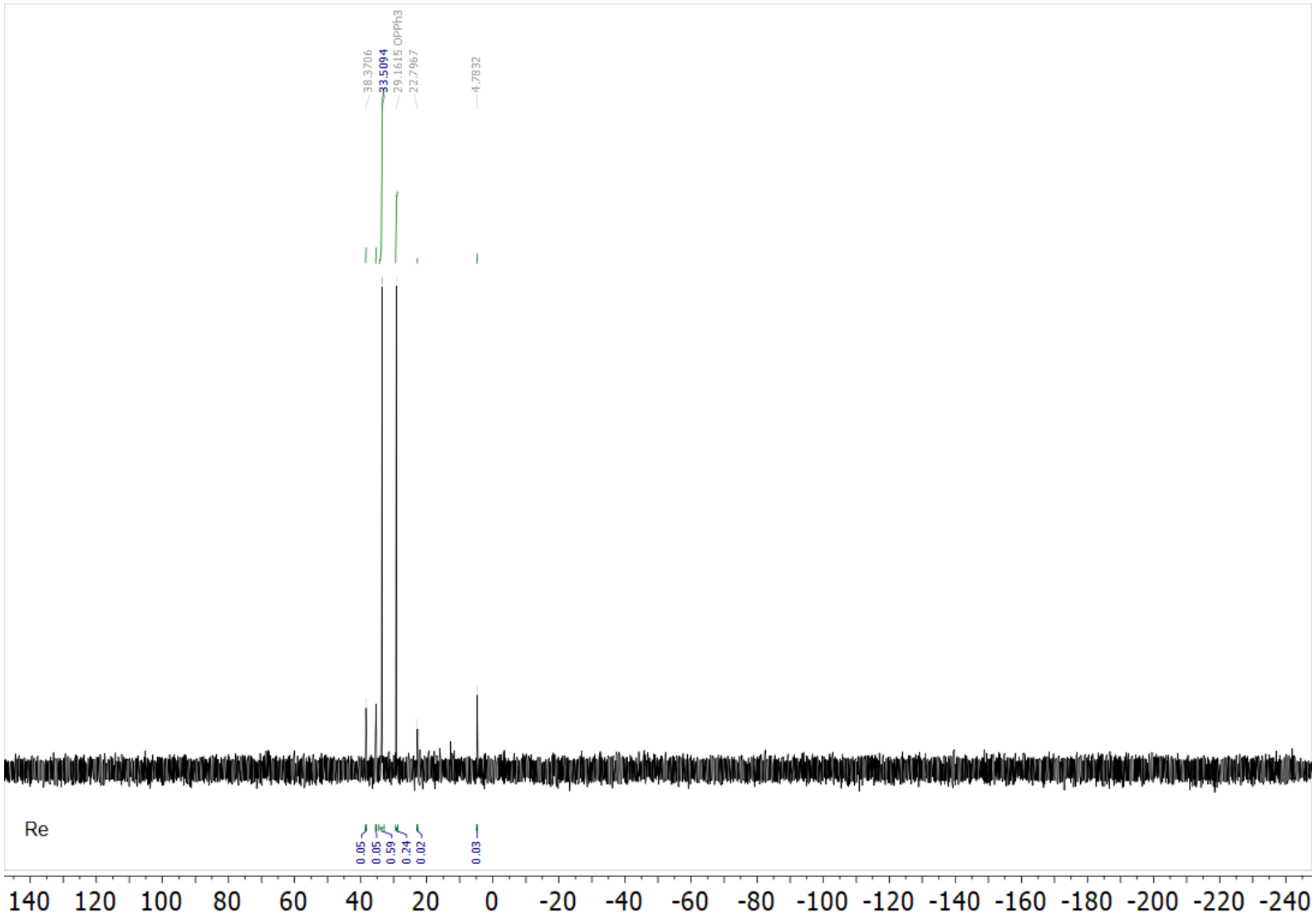
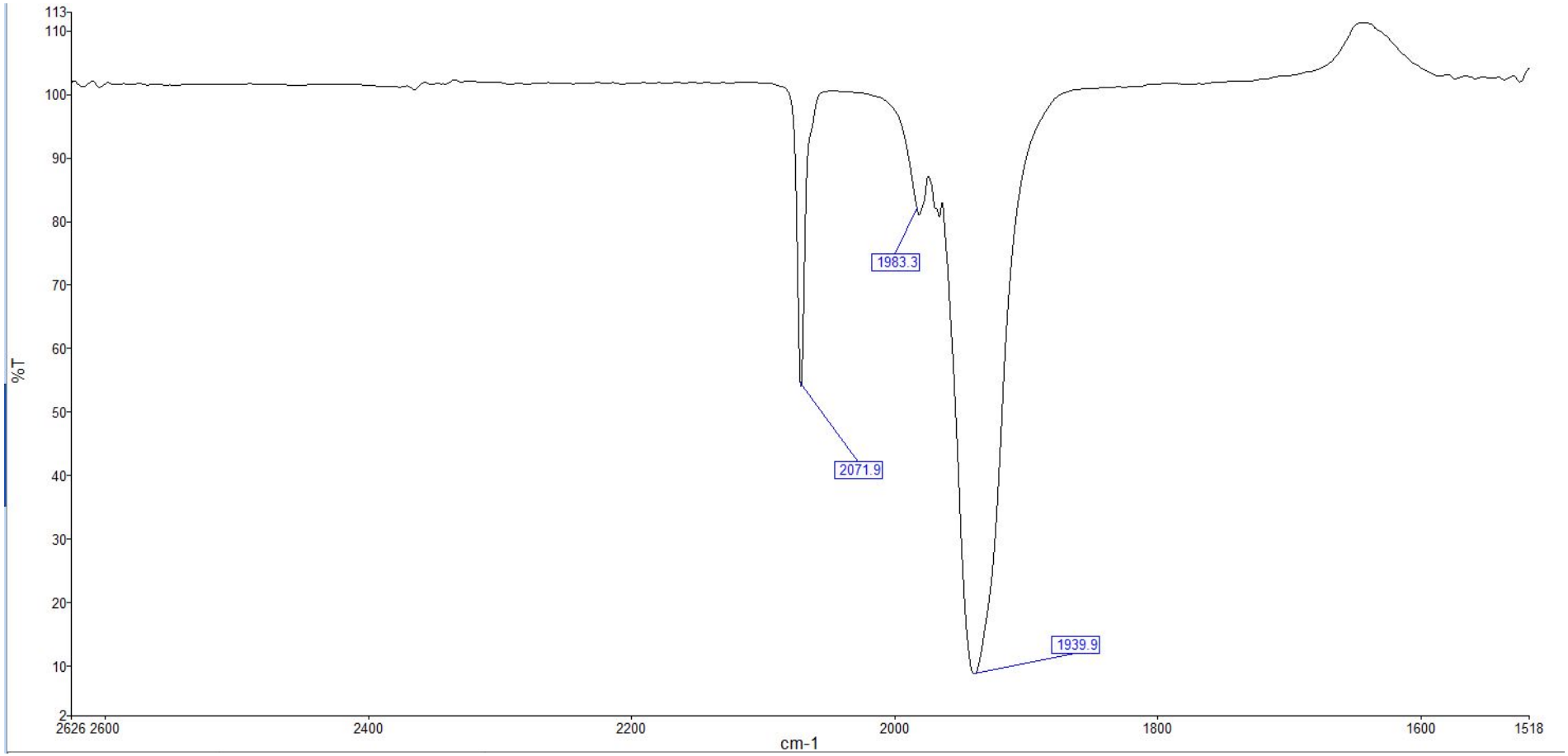
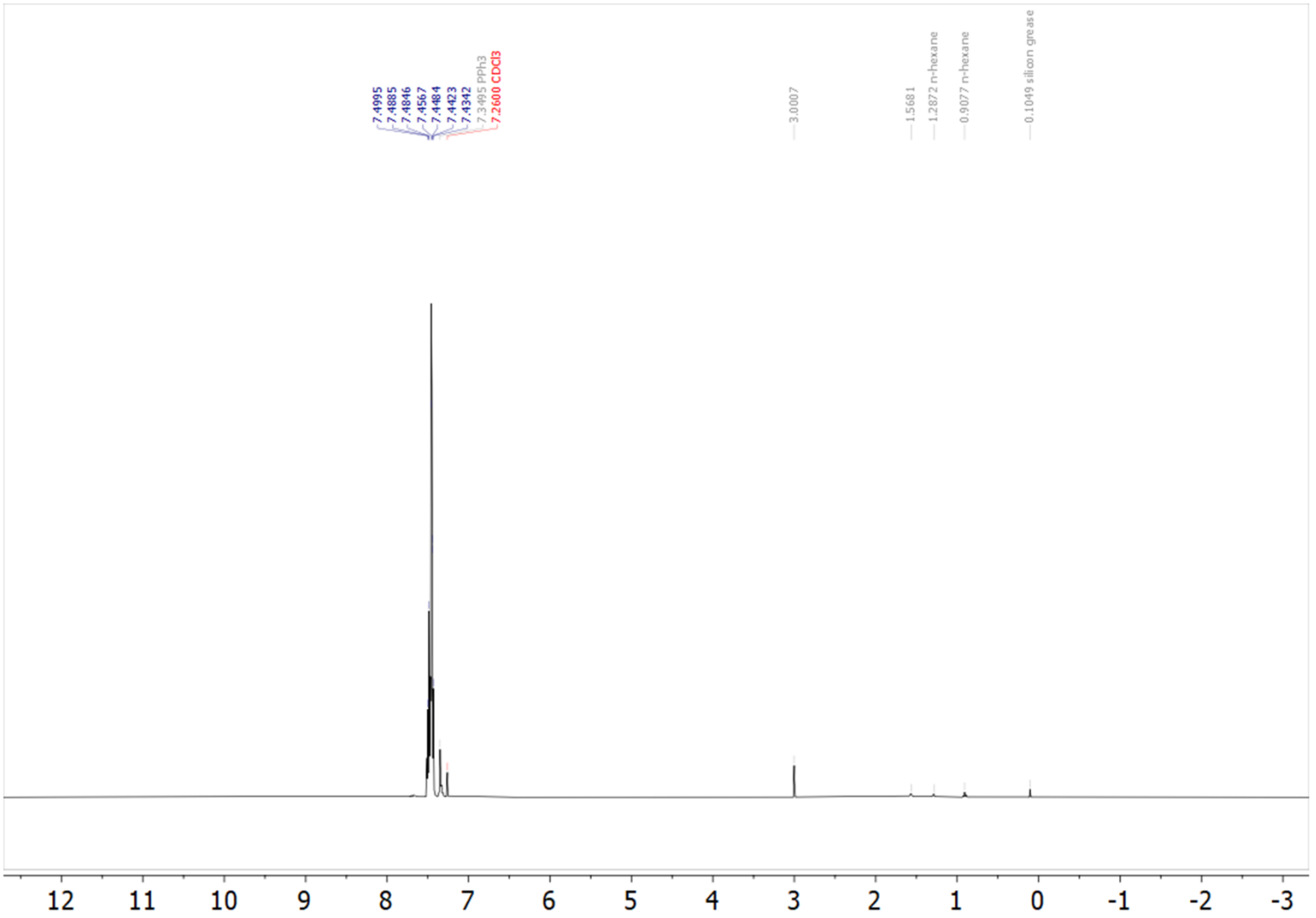


CRUDE $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) for $[Re(Cp^*)(CO)_2(PPh_3)]$.



IR (THF) for $[W(CO)_5(PPh_3)]$.



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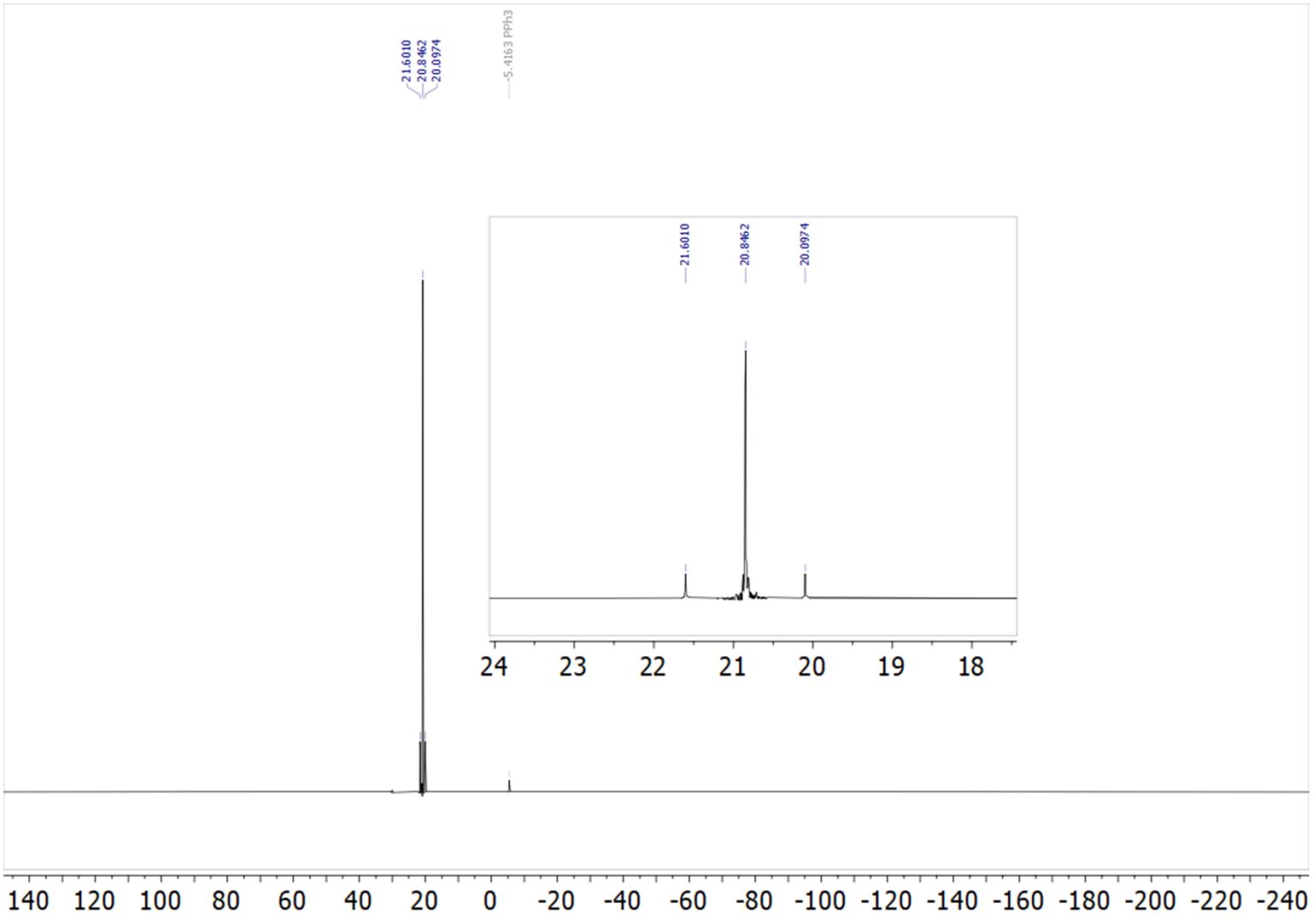

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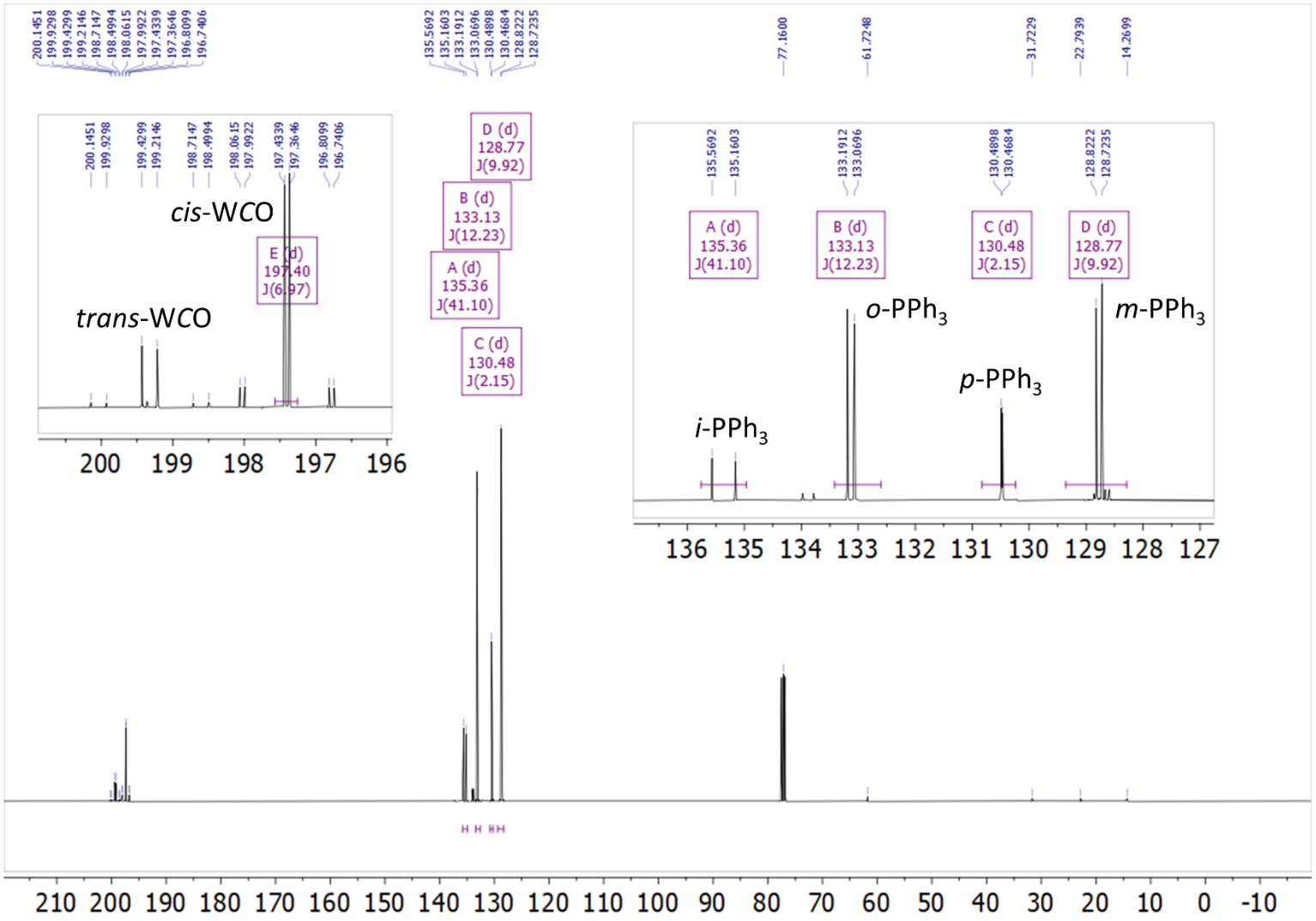
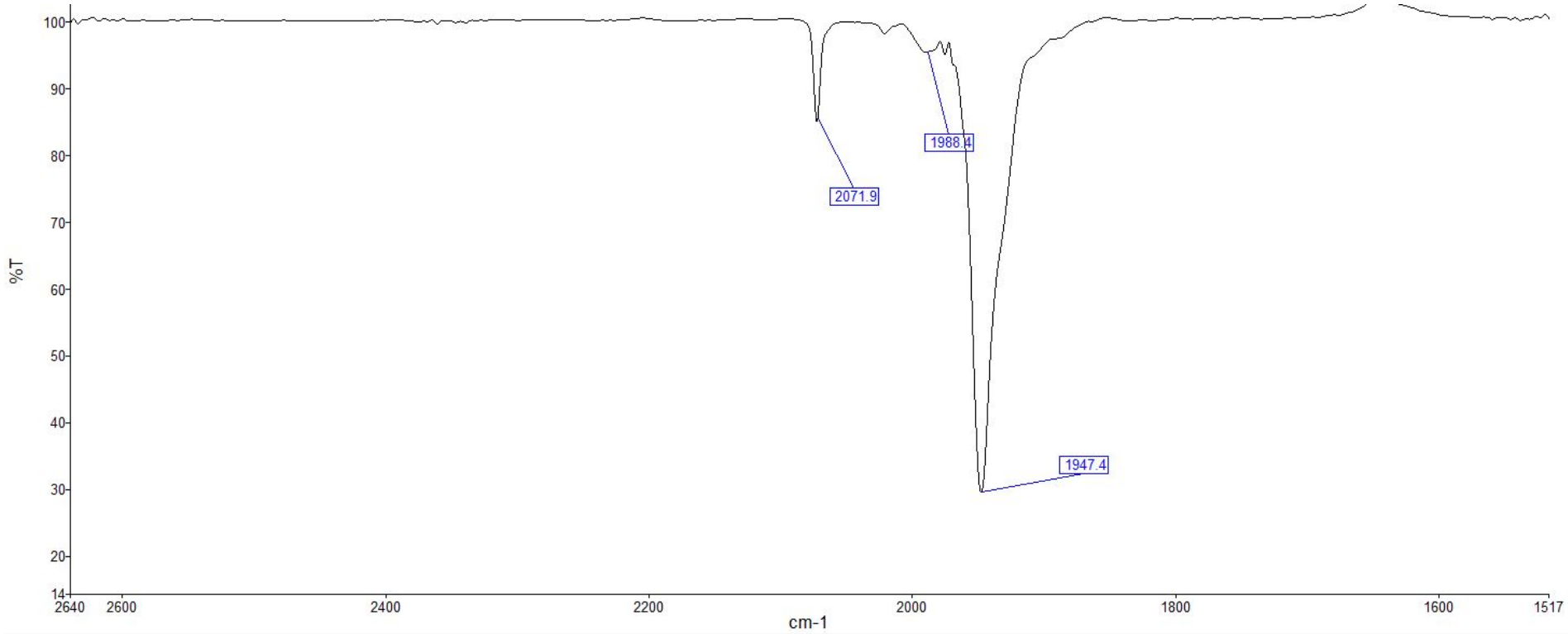
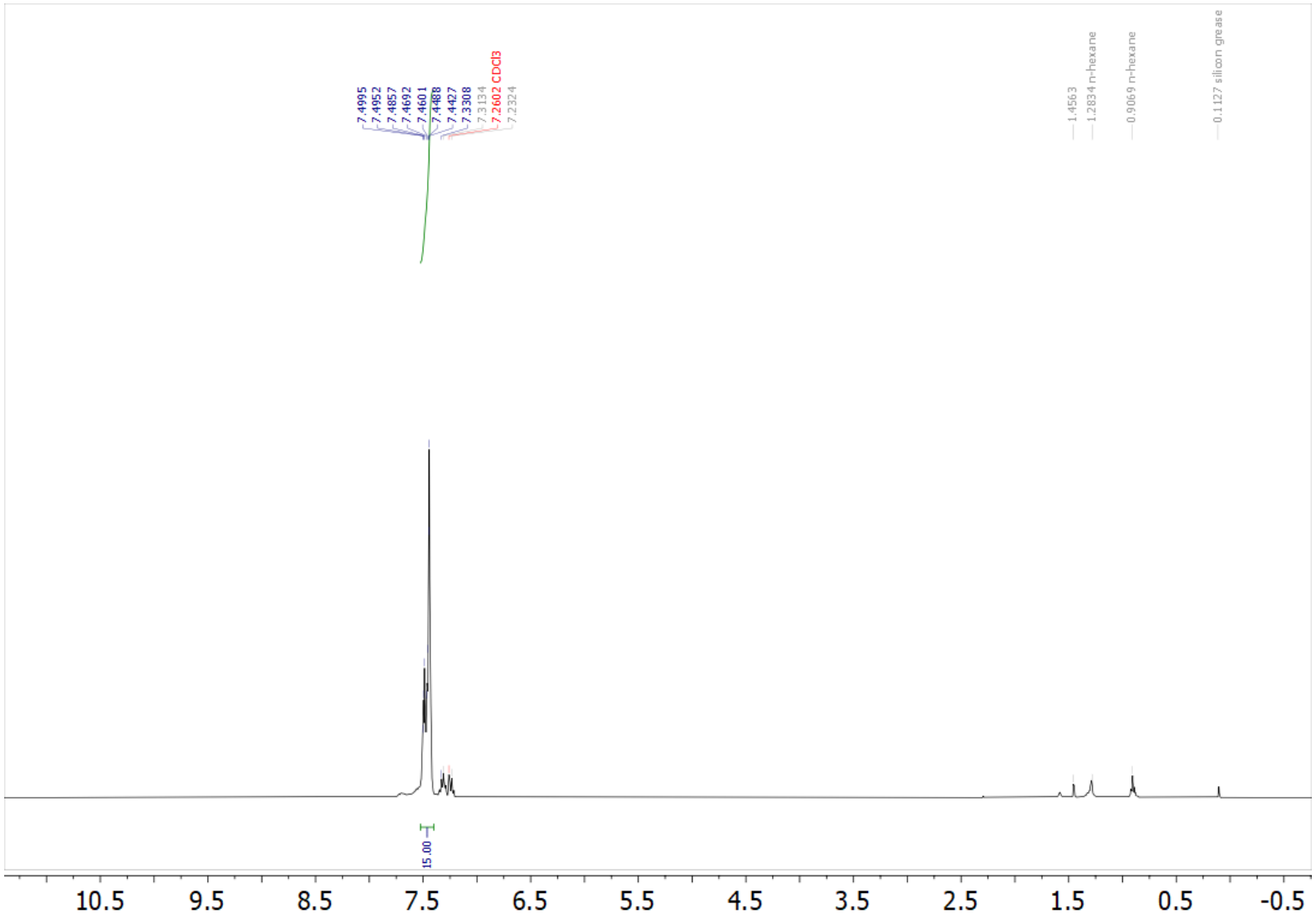


$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, 298 K) for $[W(CO)_5(PPh_3)]$.



IR (THF) for $[Mo(CO)_5(PPh_3)]$.



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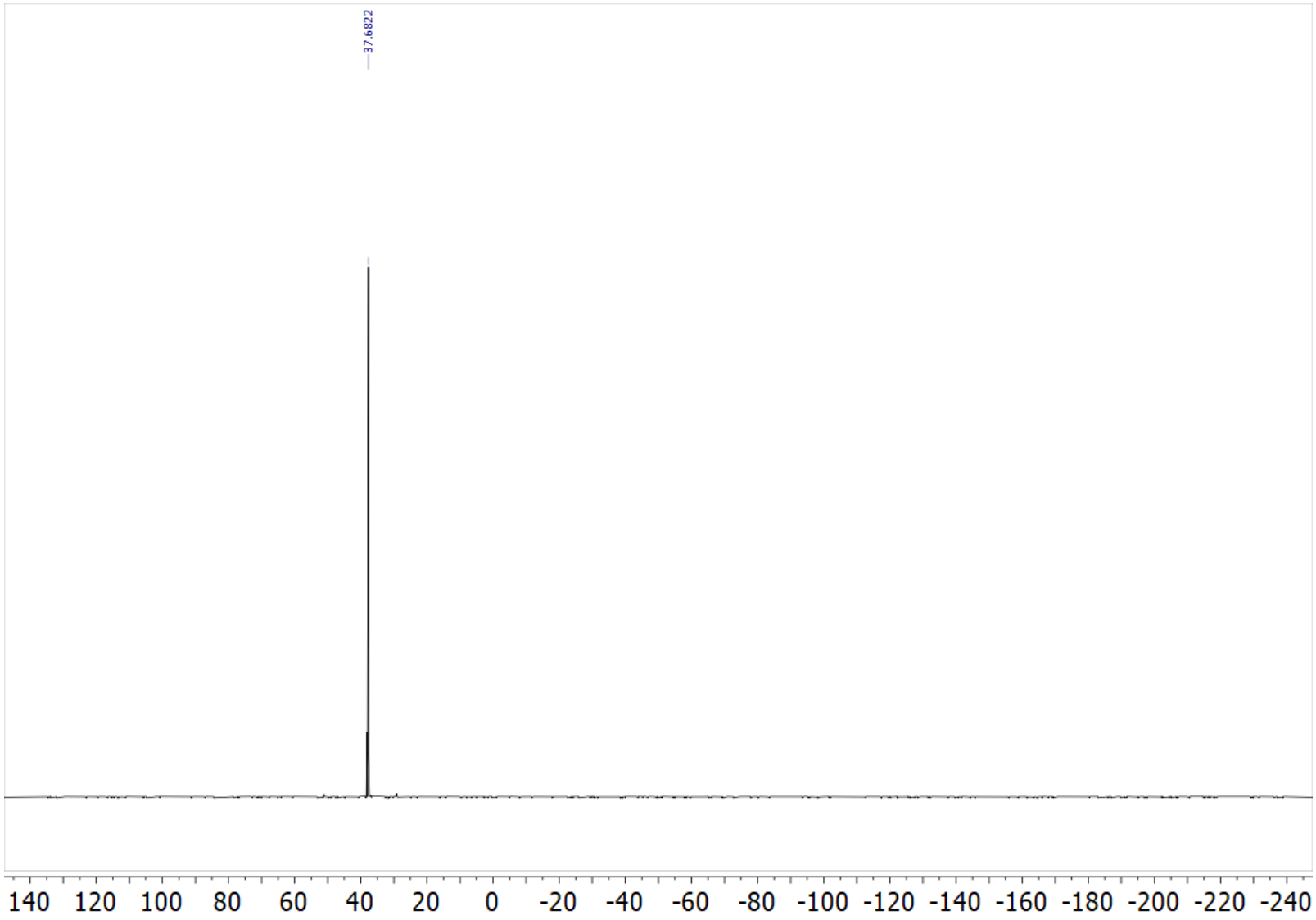

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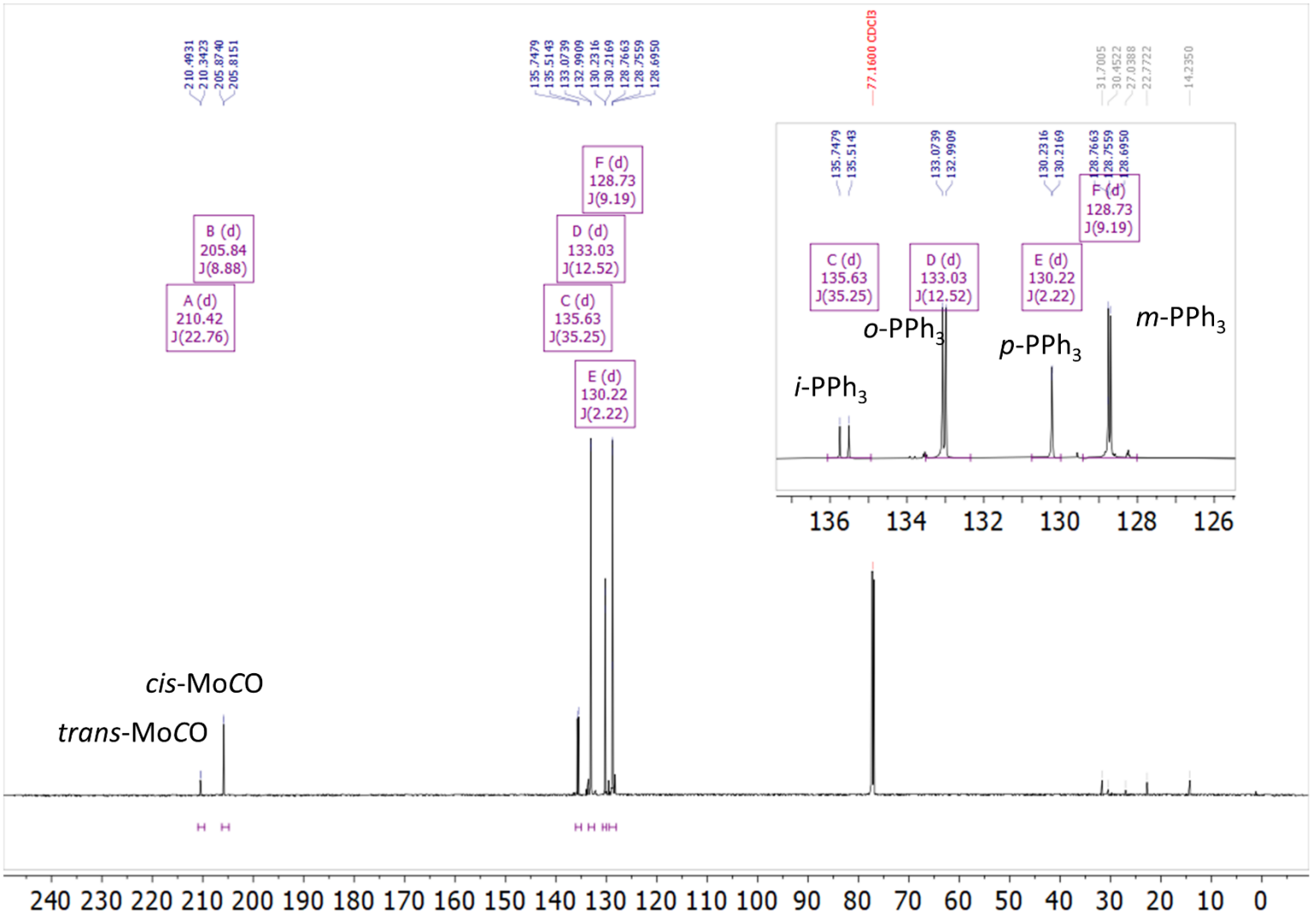
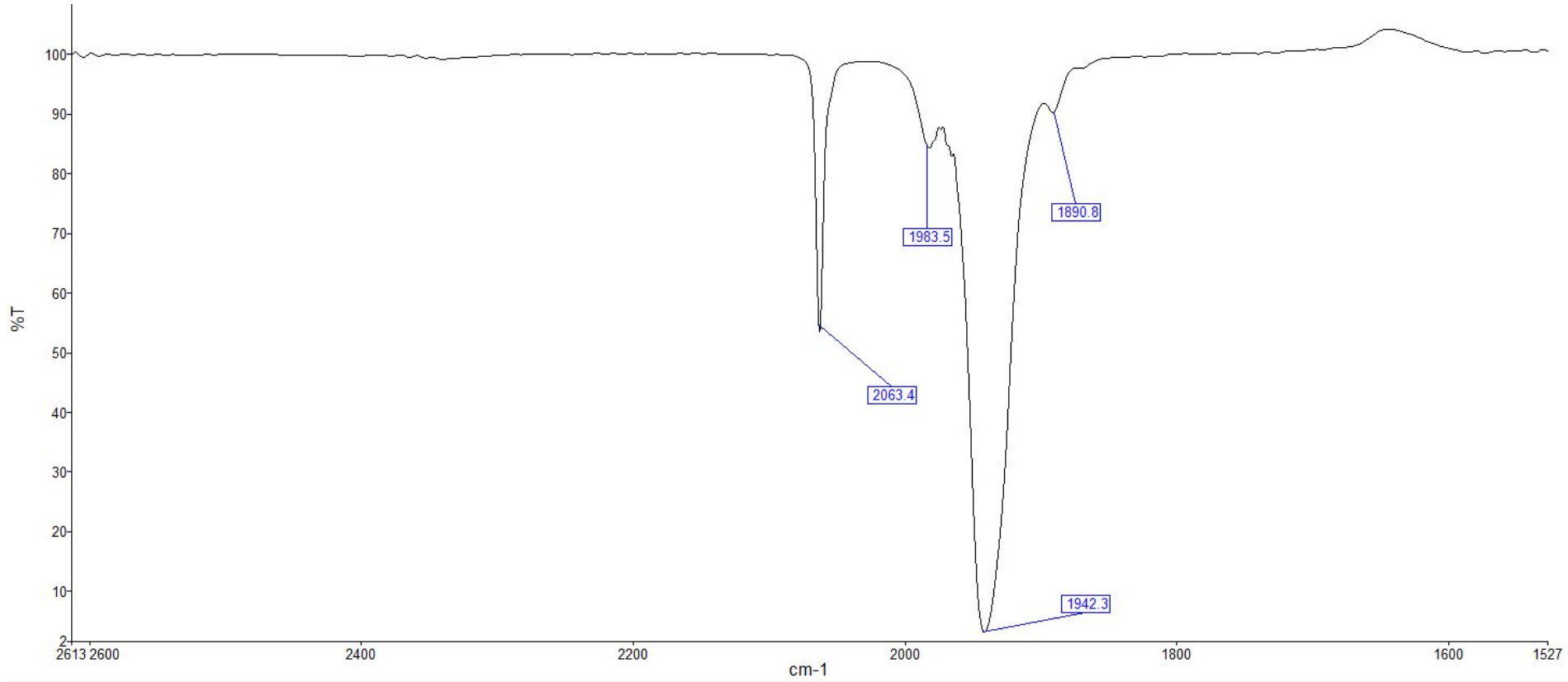
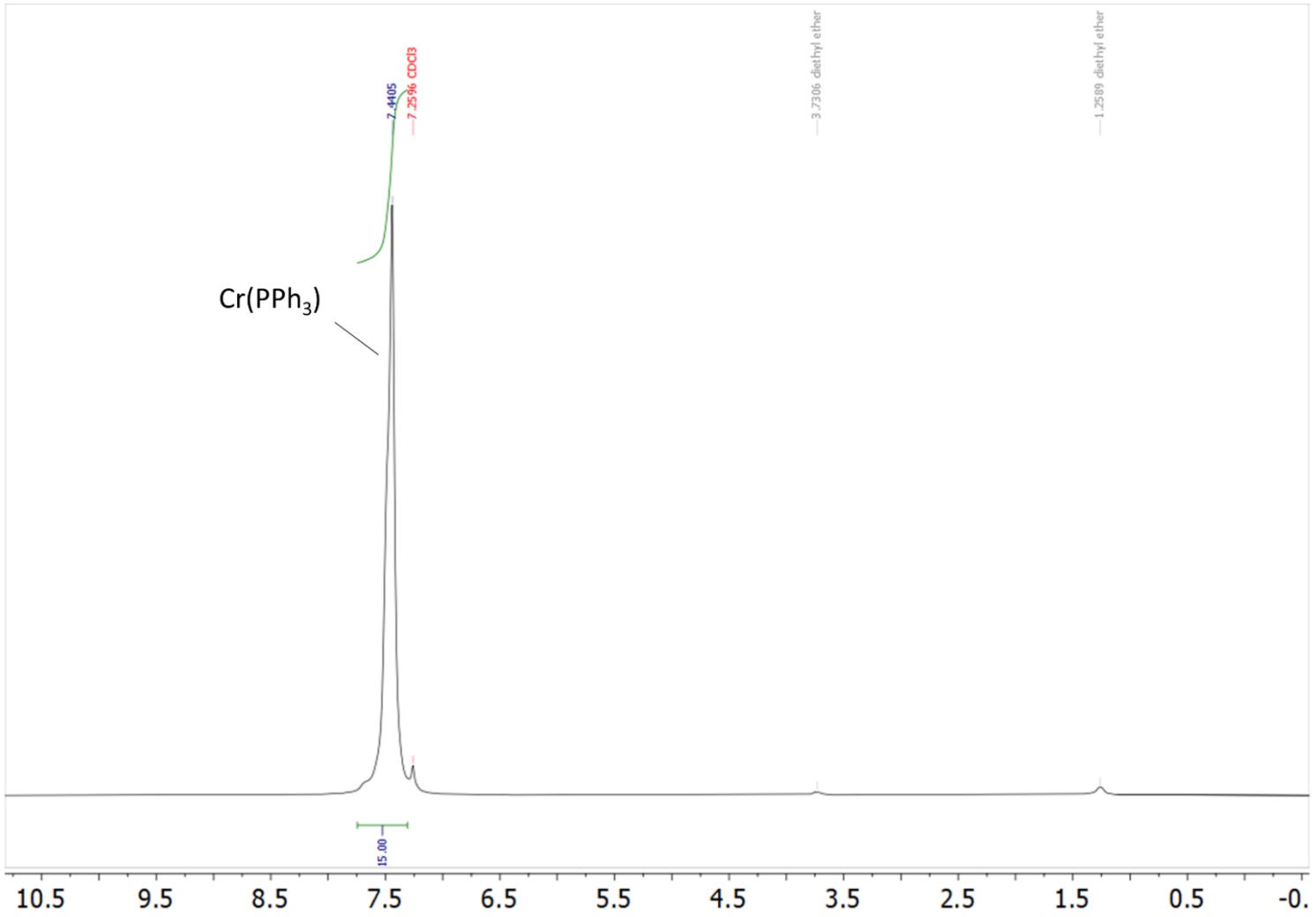


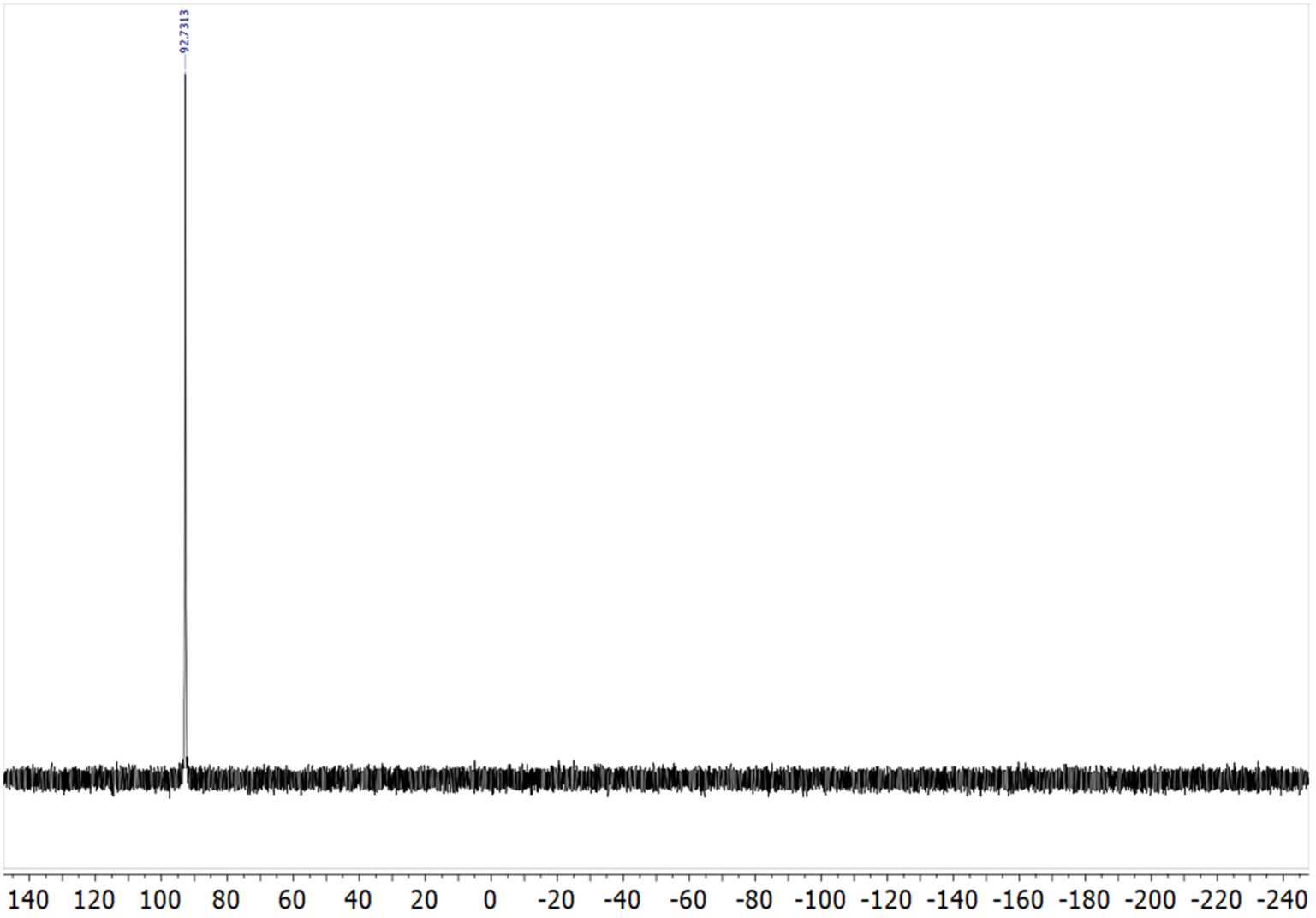
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, 298 K) for $[Mo(CO)_5(PPh_3)]$.



IR (THF) for $[Cr(CO)_5(PPh_3)]$.



^{1}H NMR (400 MHz, $CDCl_3$, 298 K) for $[Cr(CO)_5(PPh_3)]$.



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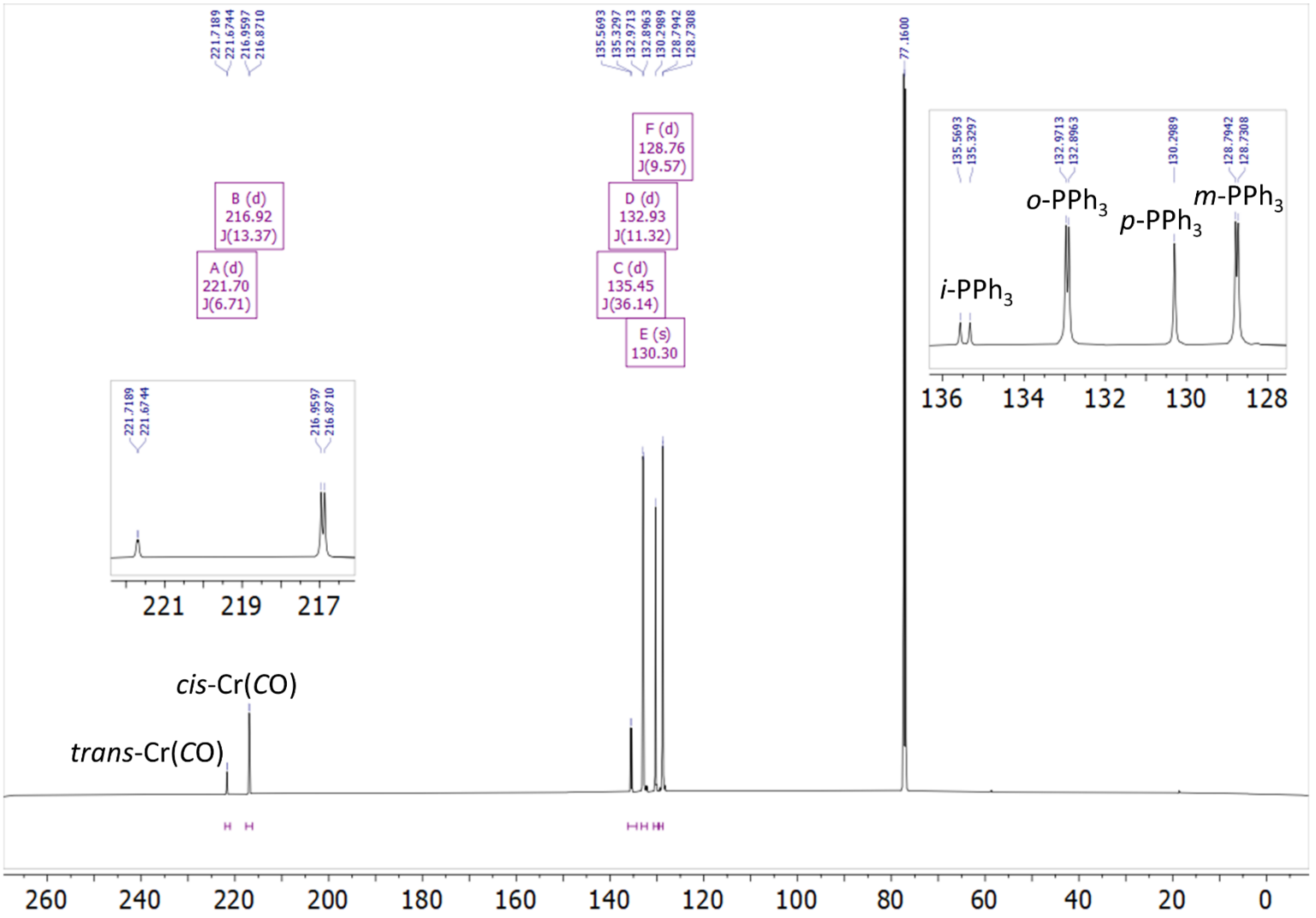
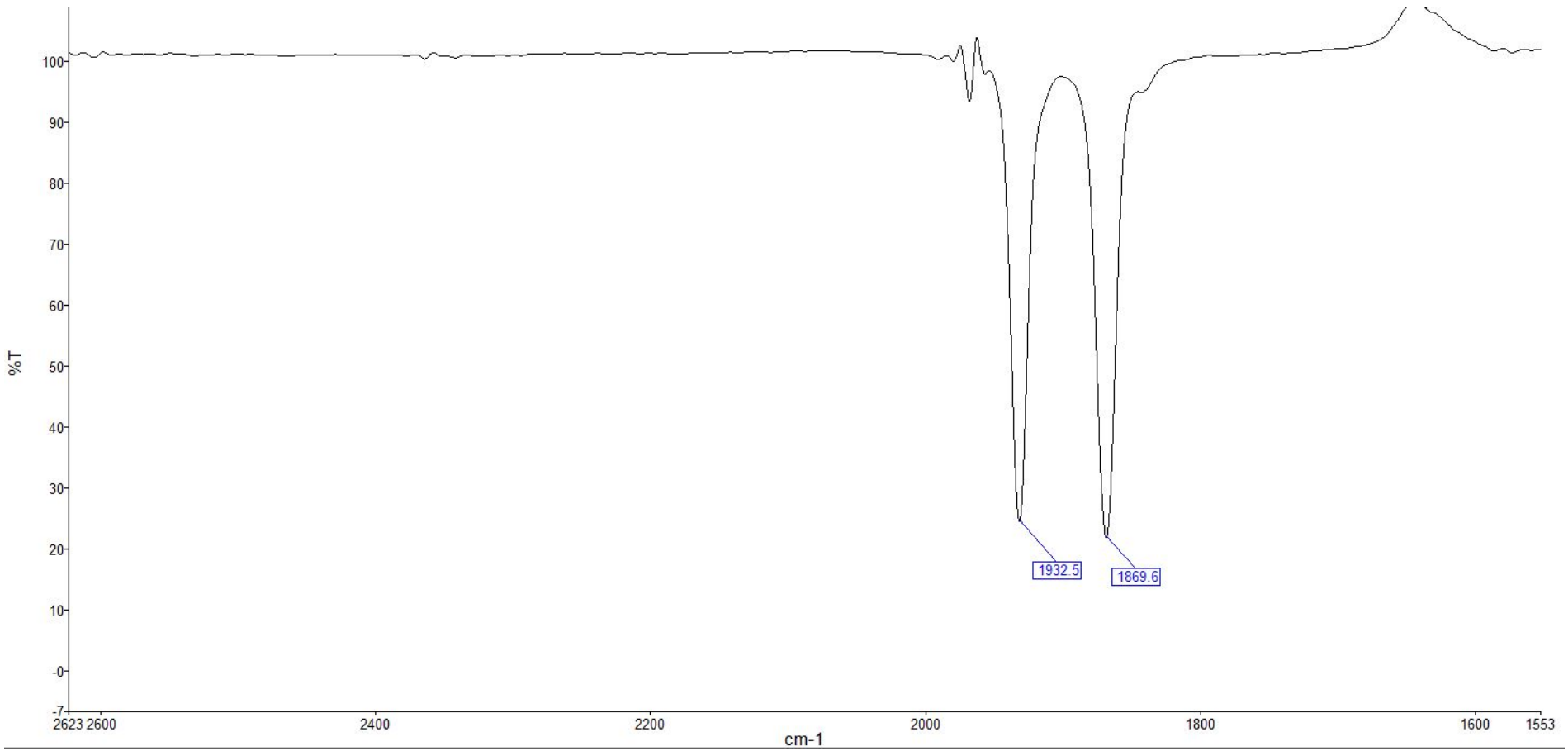
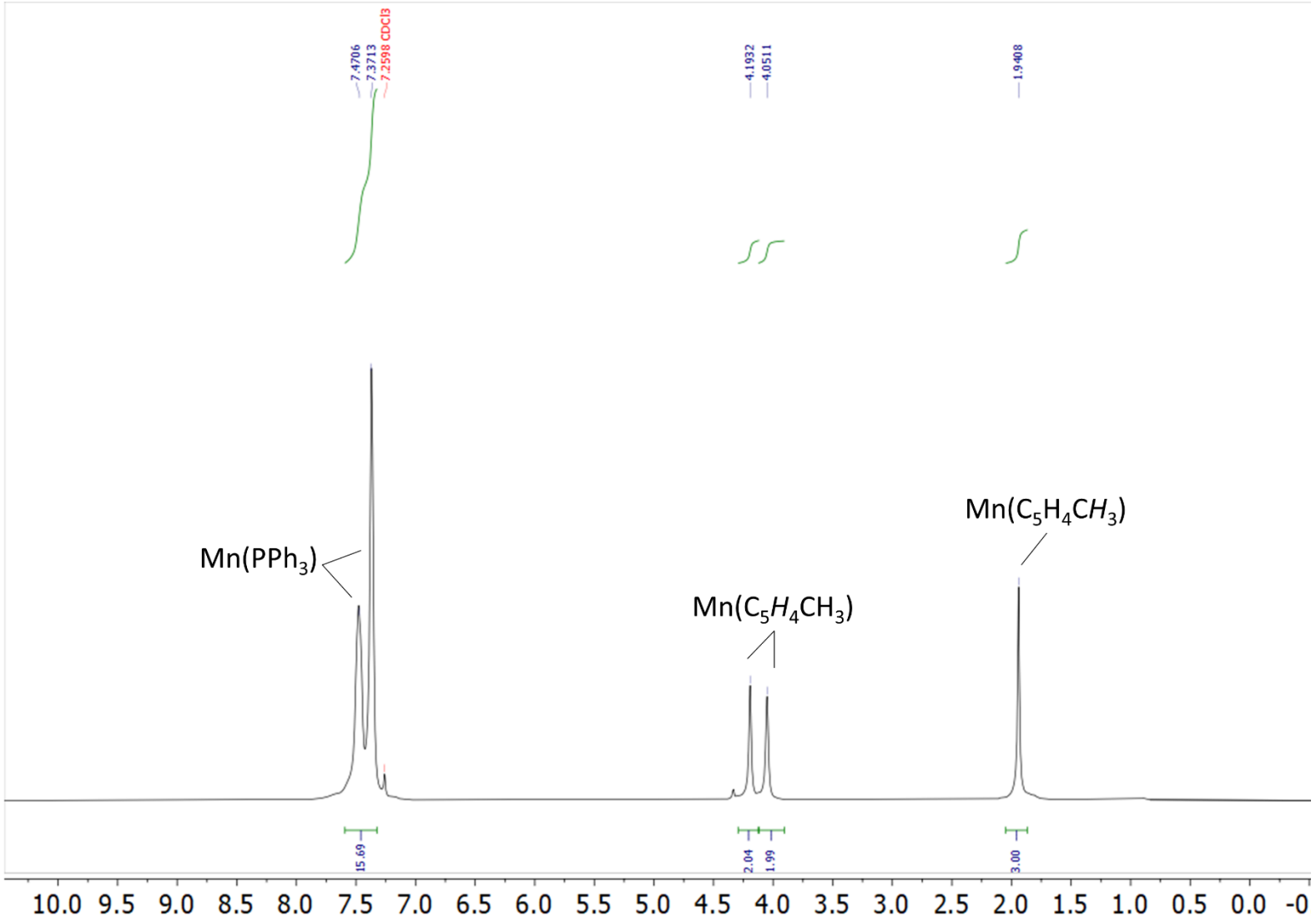


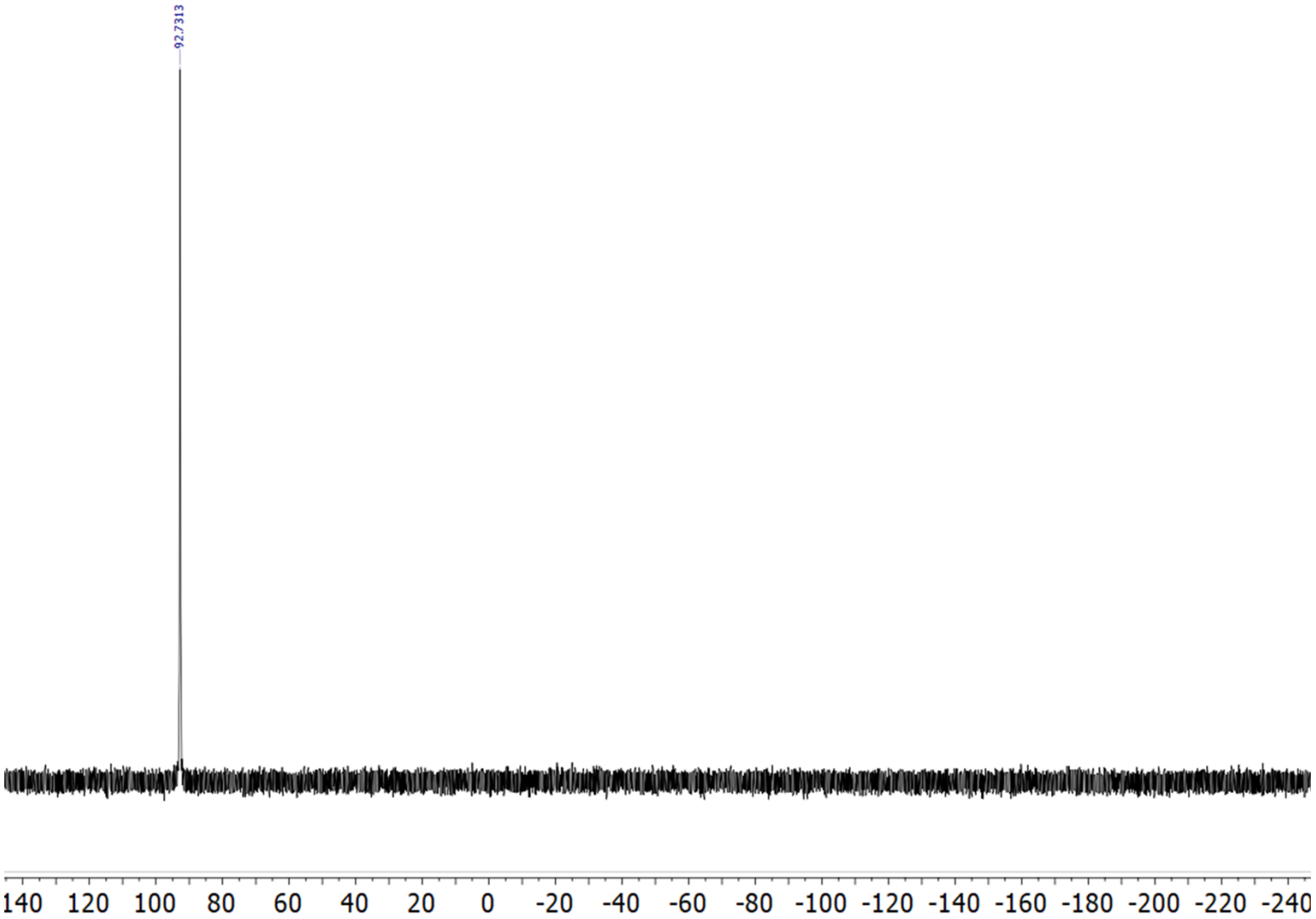
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, 298 K) for $[Cr(CO)_5(PPh_3)]$.



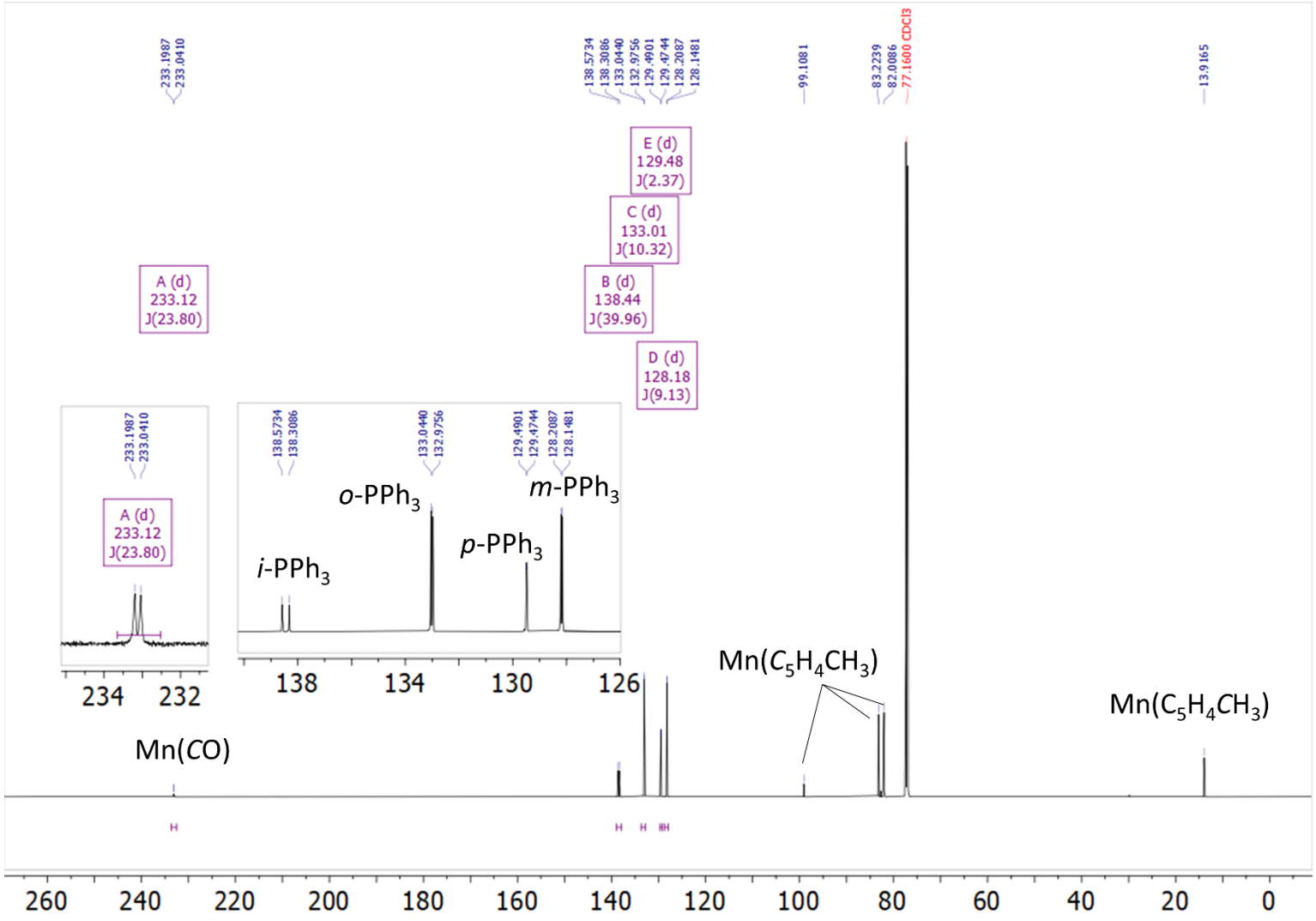
IR (THF) for [Mn(Cp')$(CO)_2(PPh_3)$].



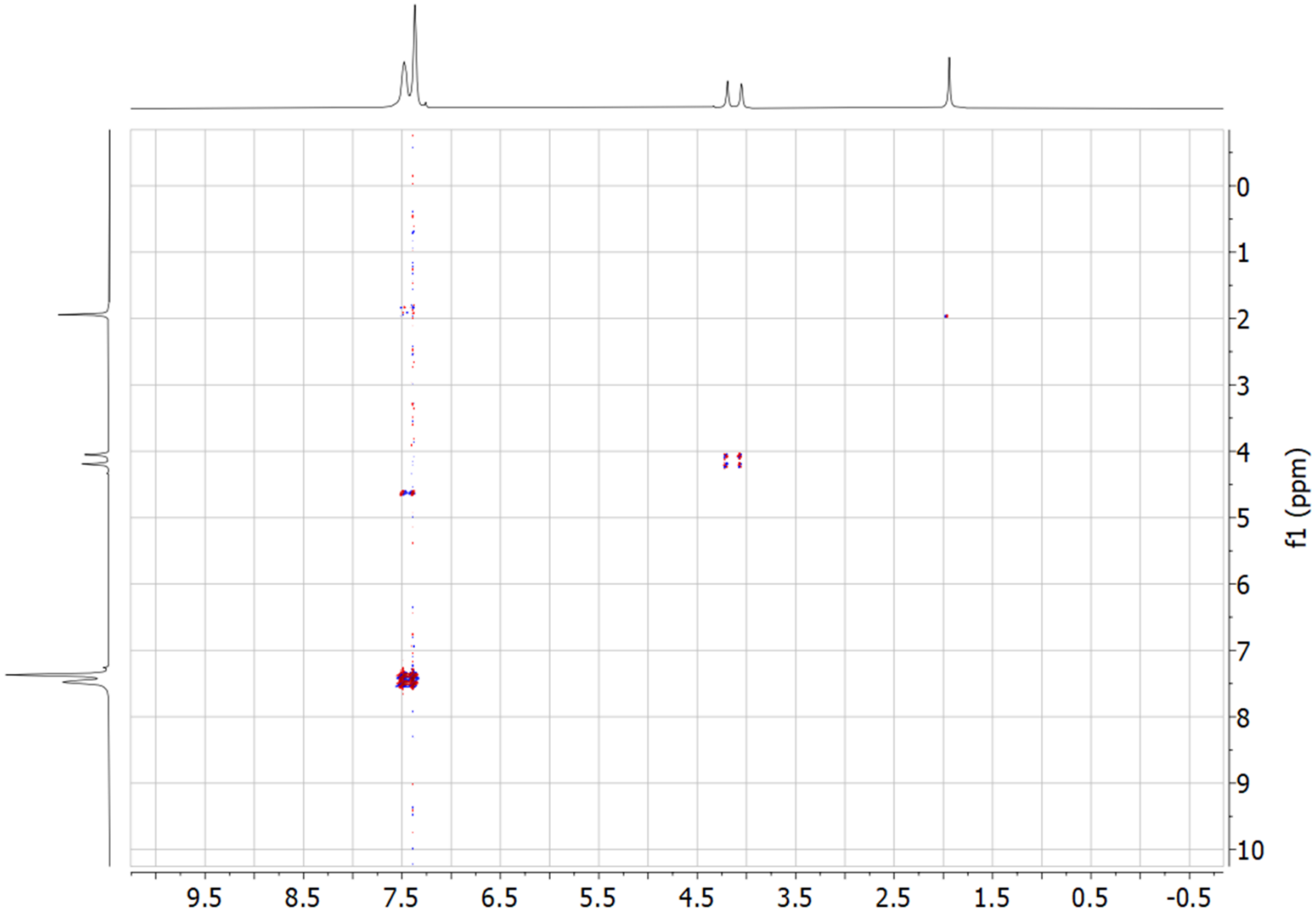
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) for $[Mn(Cp')(CO)_2(PPh_3)]$.



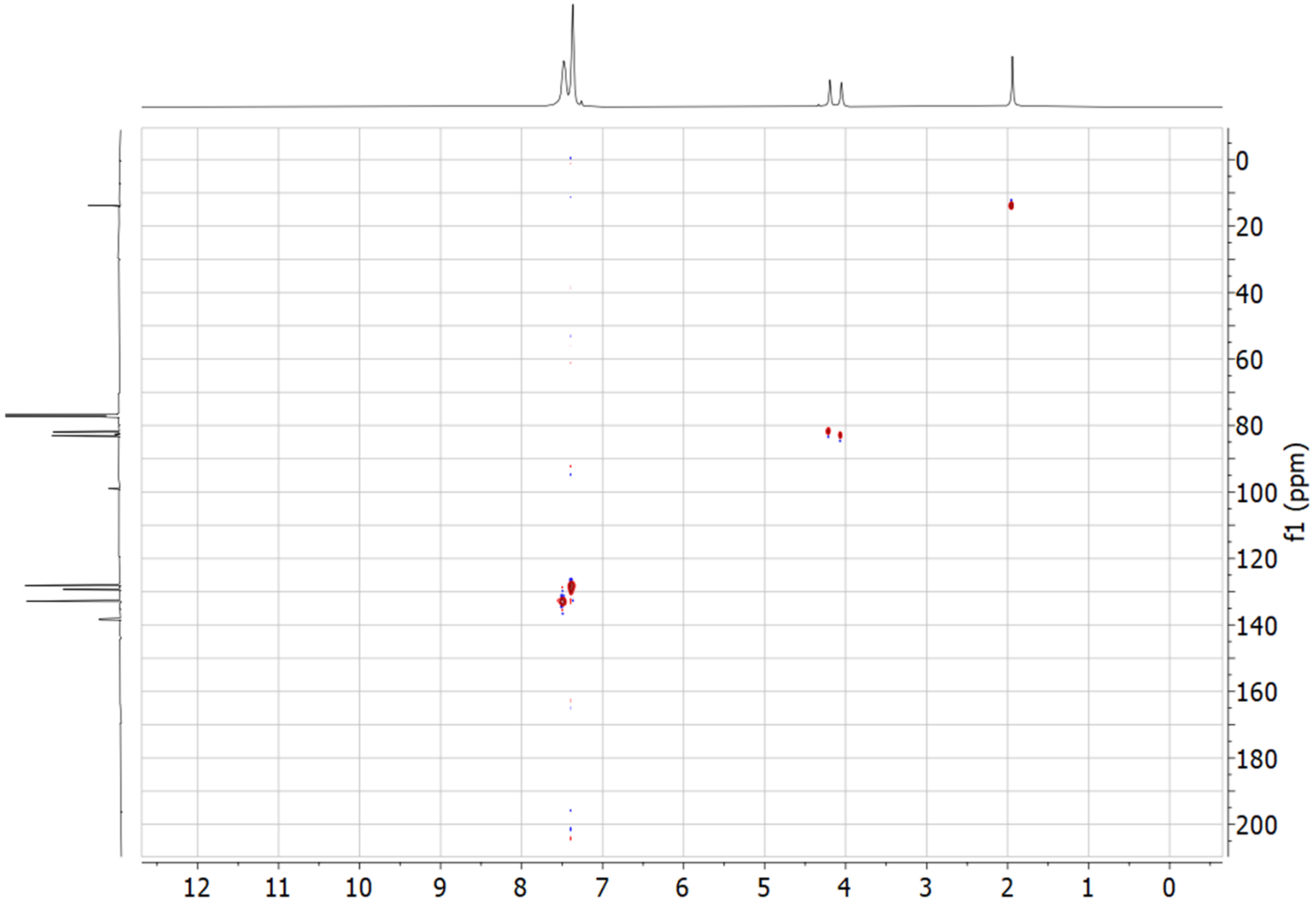
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) for $[Mn(Cp')(CO)_2(PPh_3)]$.



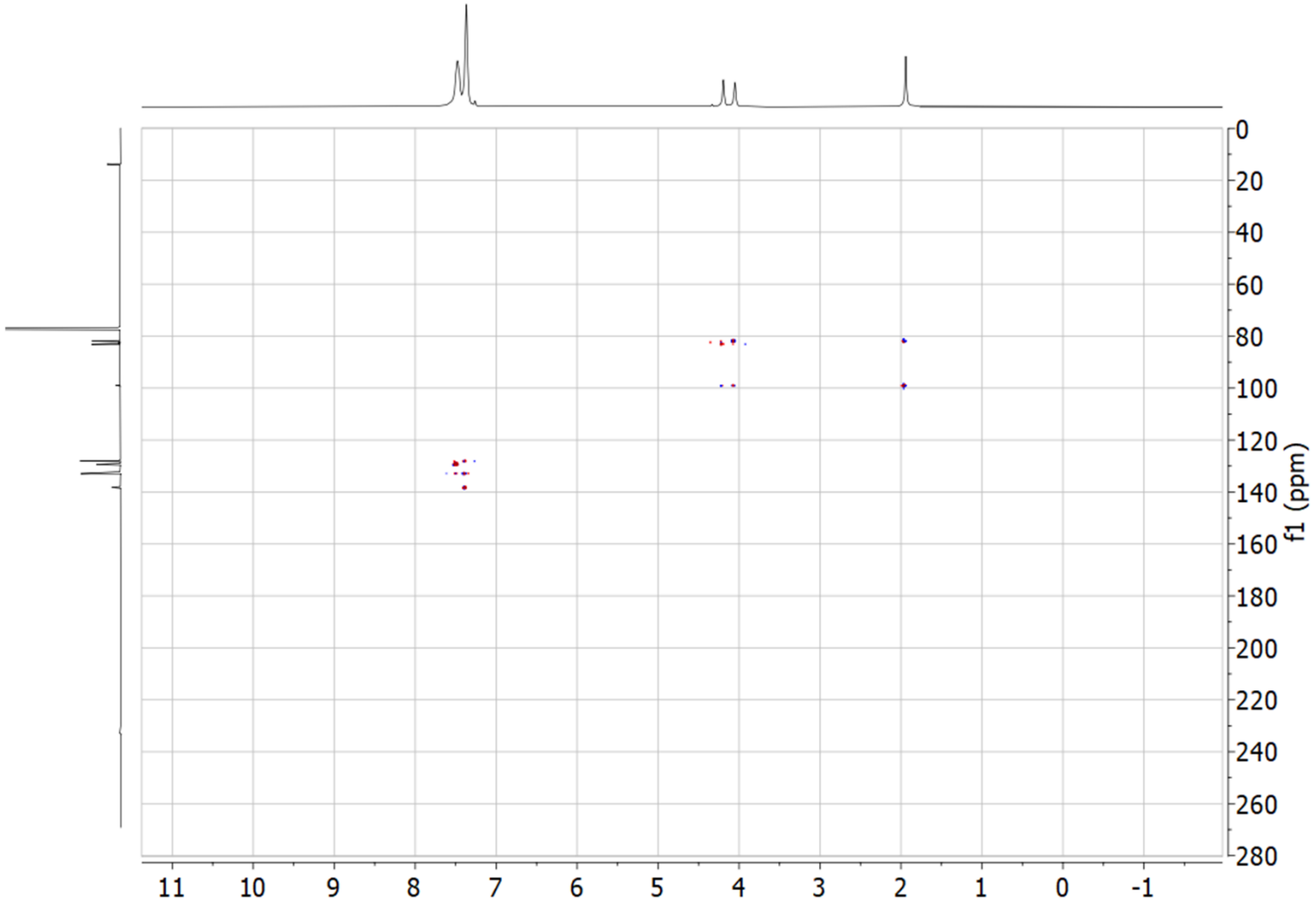
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, 298 K) for $[Mn(Cp')(CO)_2(PPh_3)]$.



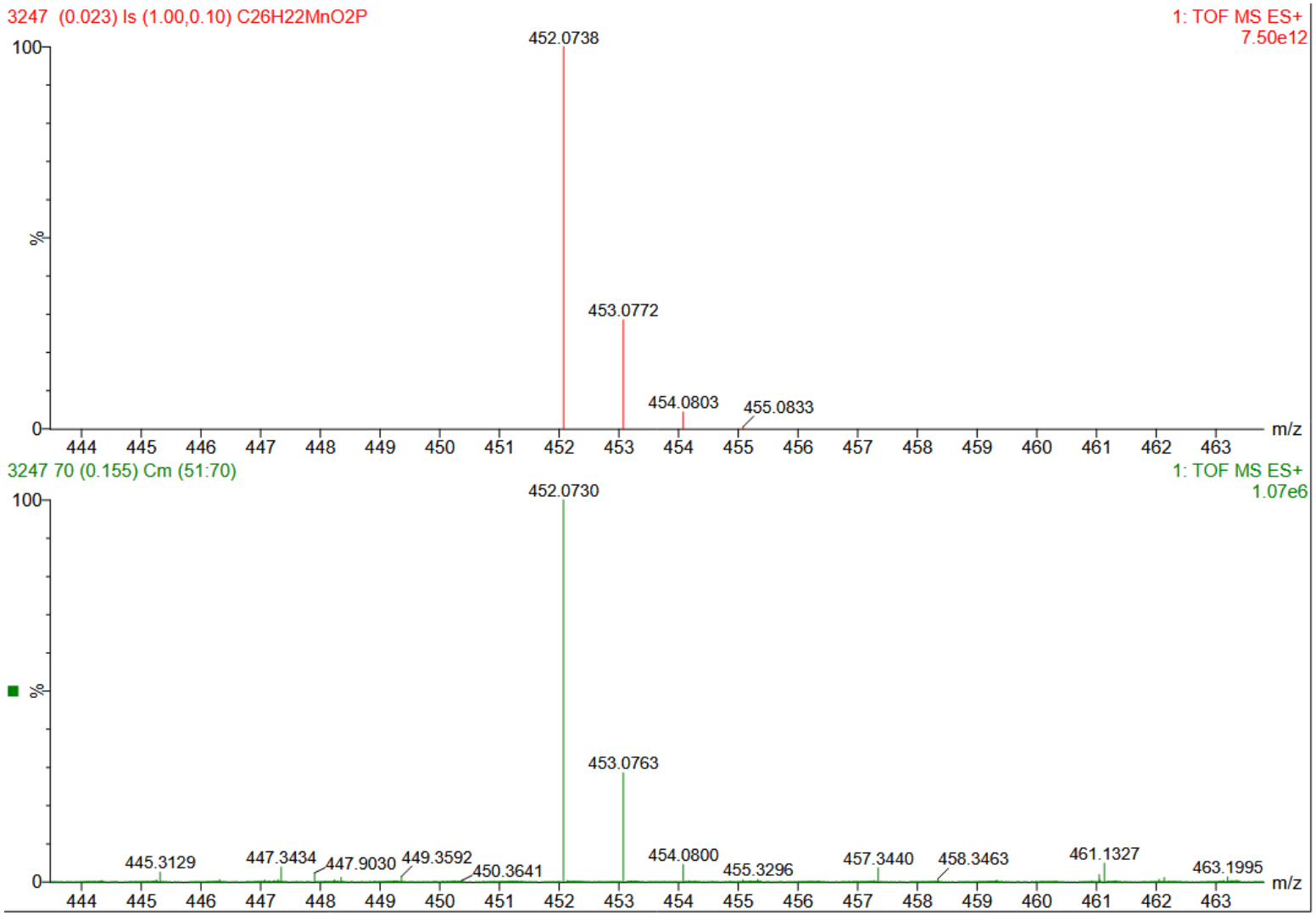
COSY NMR (600 MHz, $CDCl_3$, 298 K) for $[Mn(Cp')(CO)_2(PPh_3)]$.



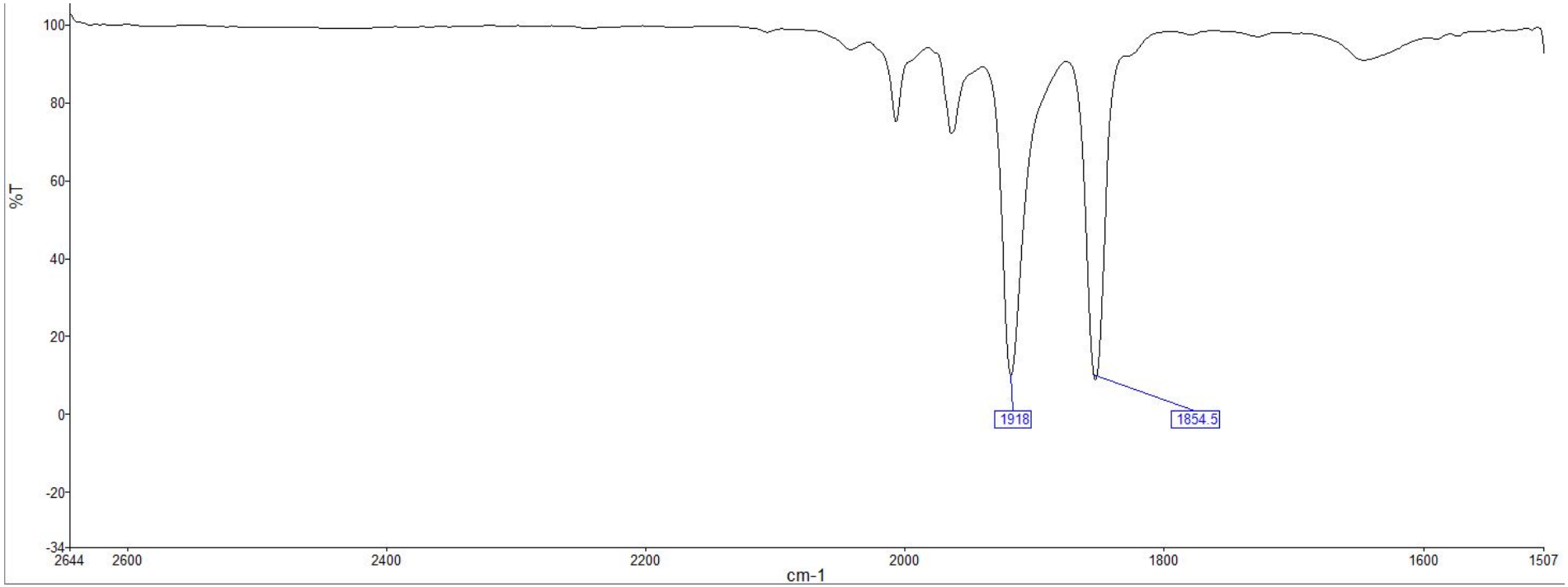
HSQC NMR (600, 150 MHz, $CDCl_3$, 298 K) for $[Mn(Cp')(CO)_2(PPh_3)]$.



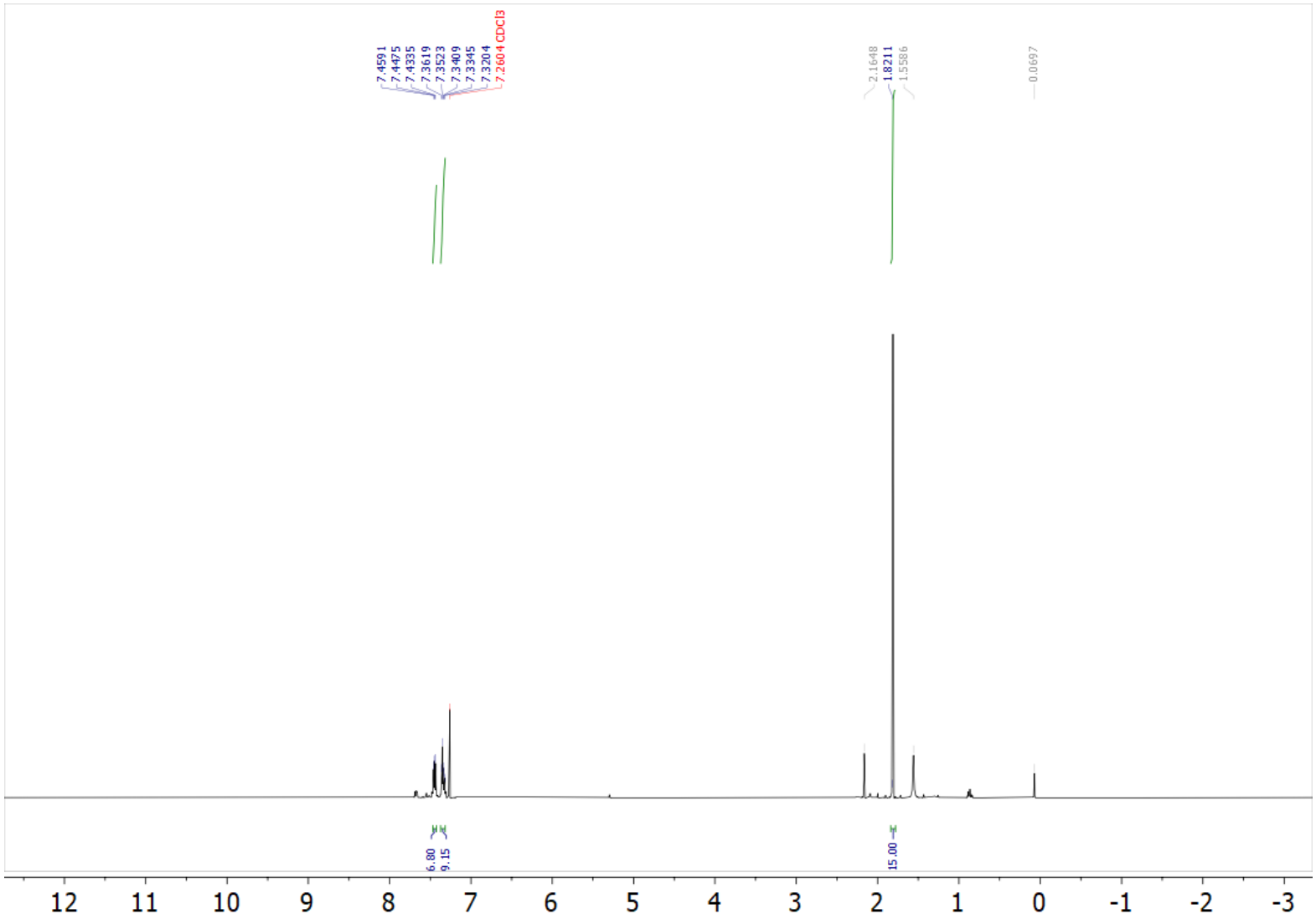
HMBC NMR (600, 150 MHz, $CDCl_3$, 298 K) for [Mn(Cp')$(CO)_2(PPh_3)$].



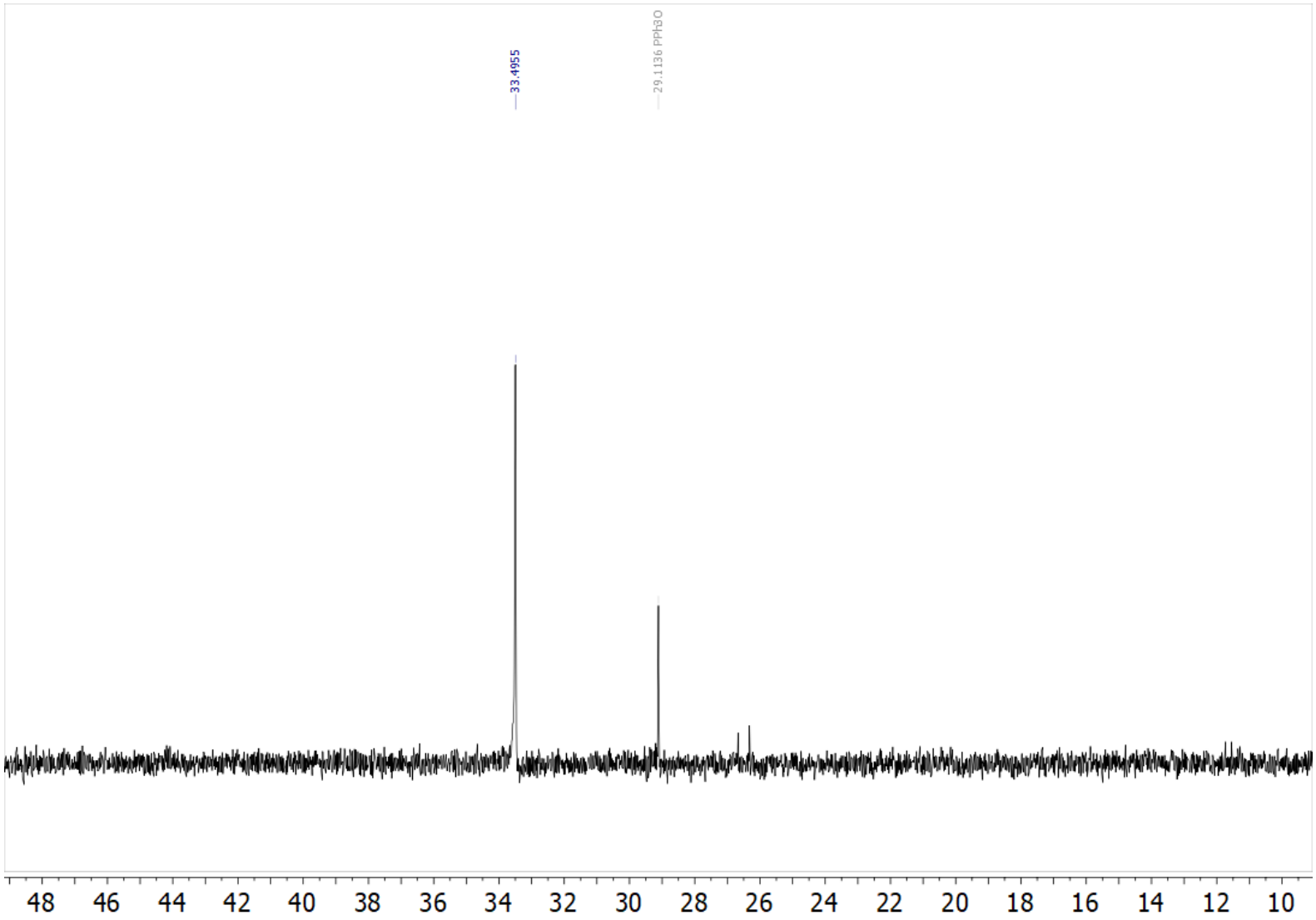
High Resolution ESI-MS (+ve ion) for $[Mn(Cp')(CO)_2(PPh_3)]$.



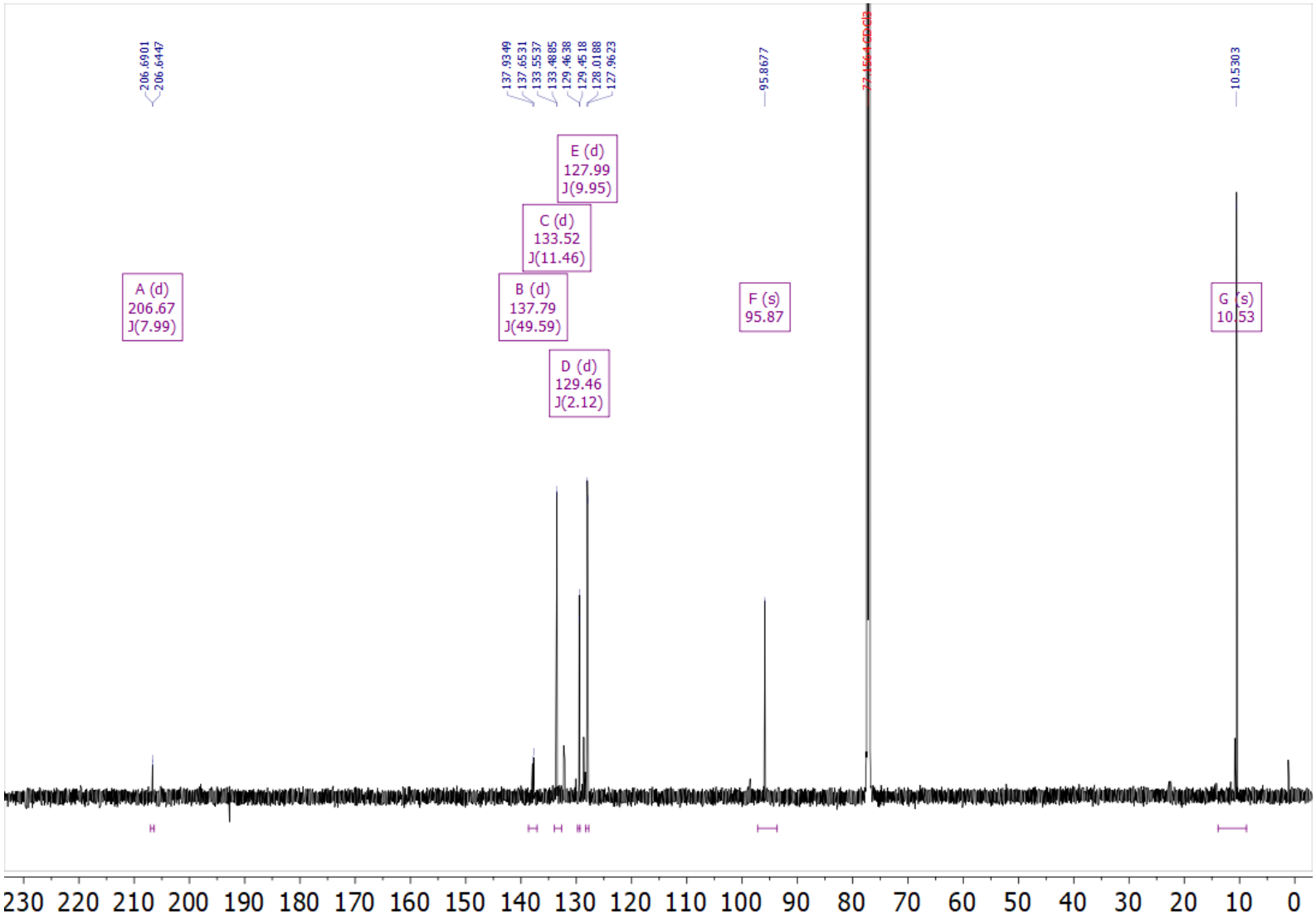
IR (THF) for [Re(Cp*)$(CO)_2(PPh_3)$].



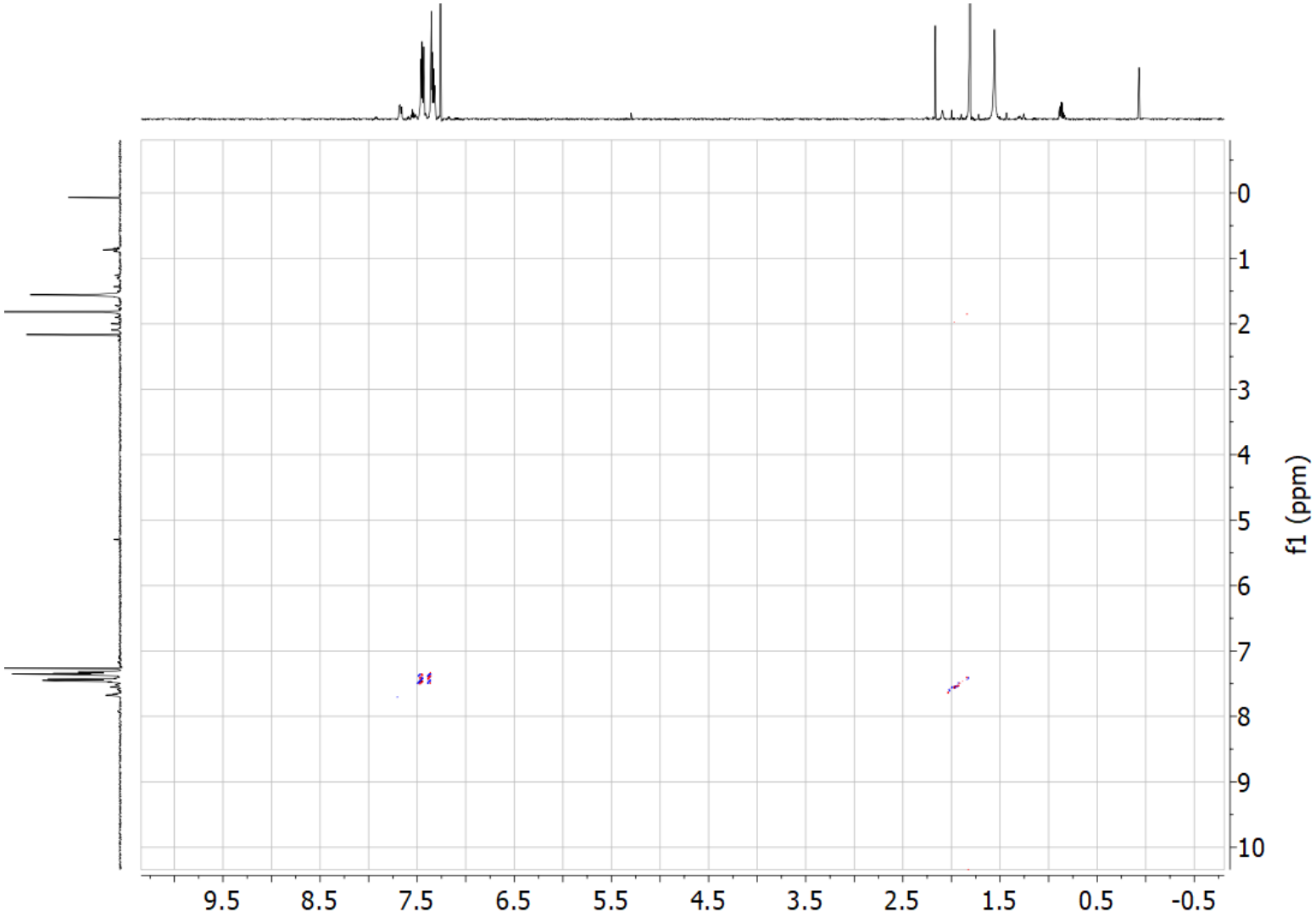
^{1}H NMR ($CDCl_3$, 700 MHz) for [Re(Cp*)$(CO)_2(PPh_3)$].



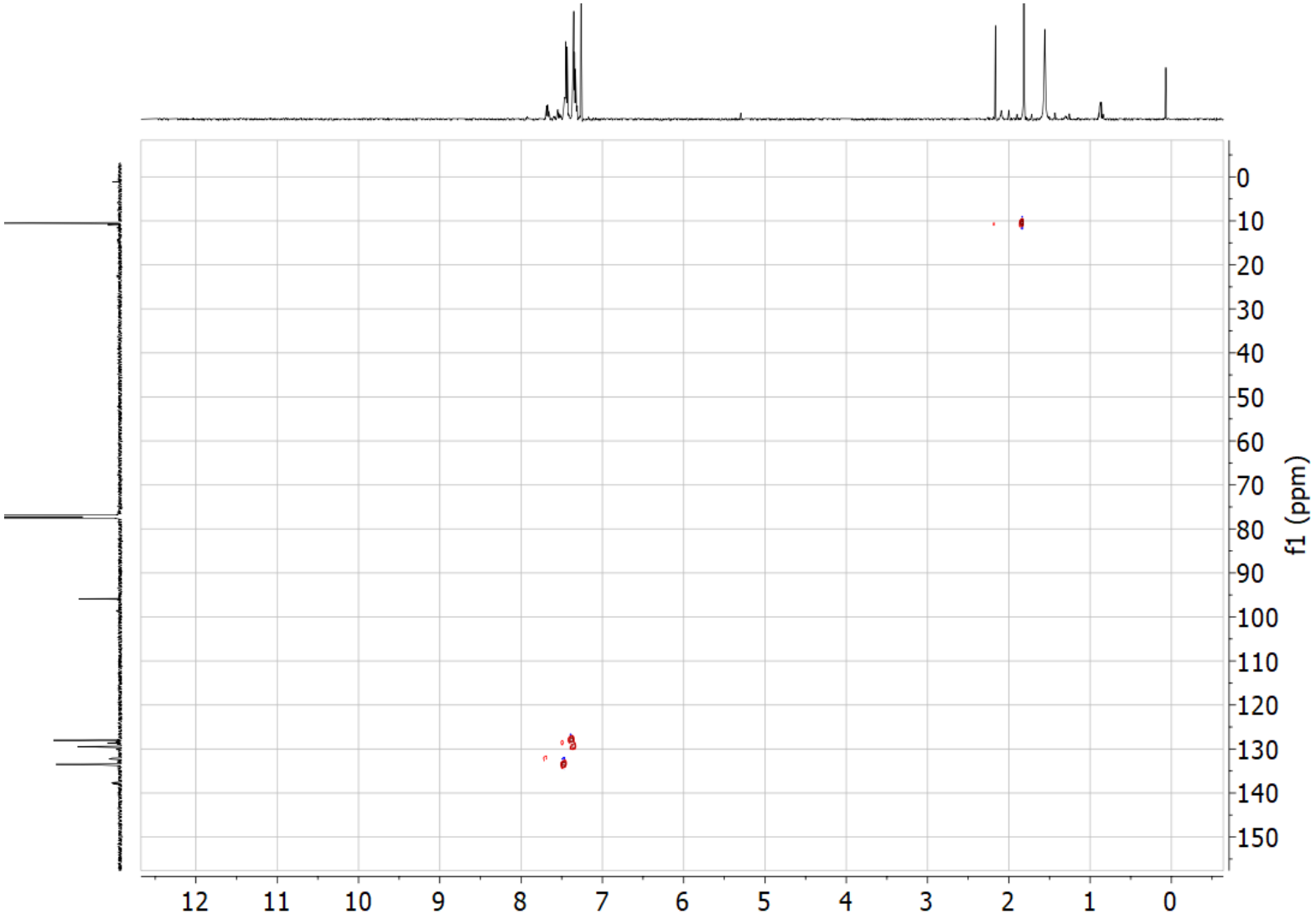
$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 283 MHz) for [$Re(Cp^*)(CO)_2(PPh_3)$].



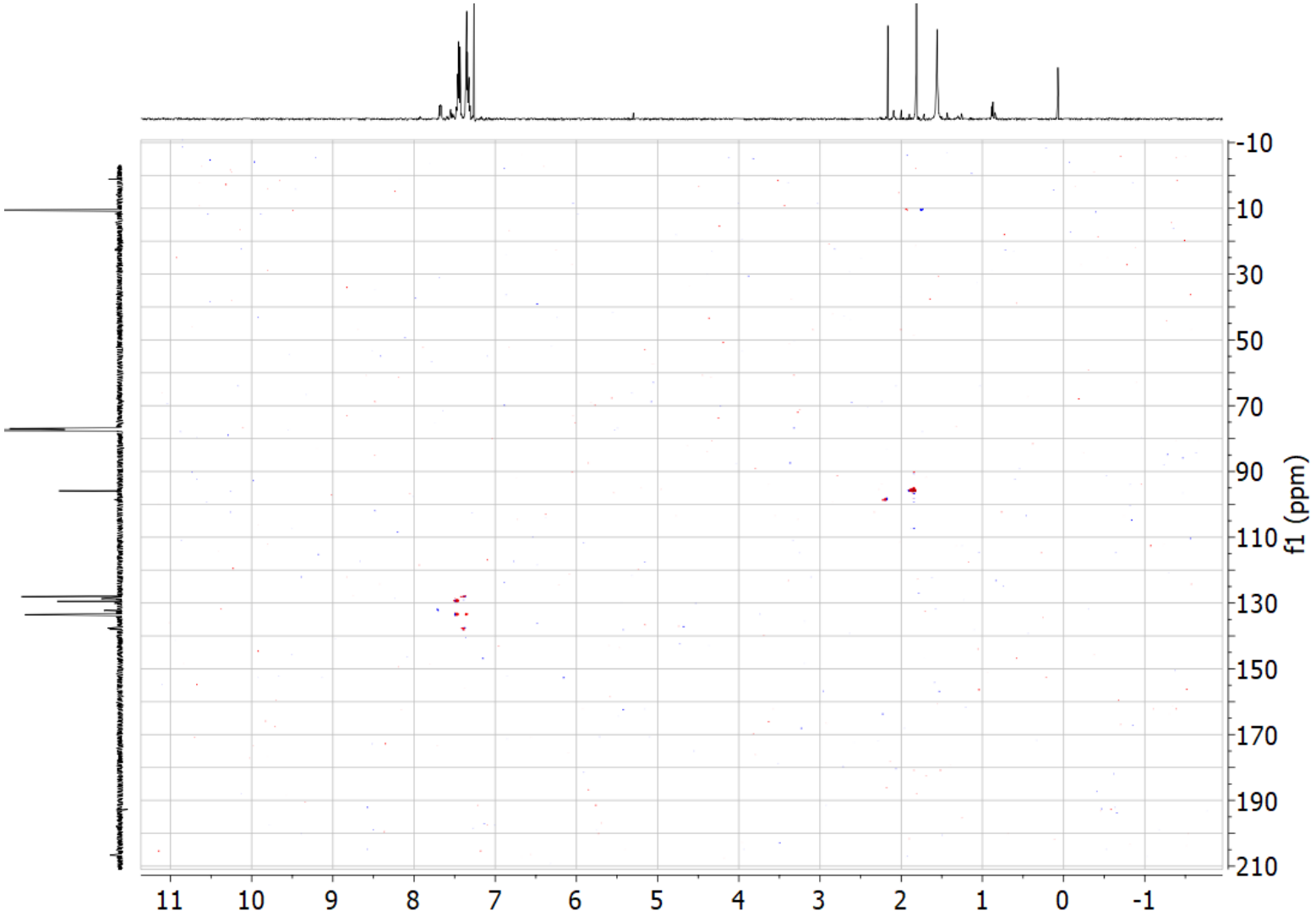
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 176 MHz) for [$Re(Cp^*)(CO)_2(PPh_3)$].



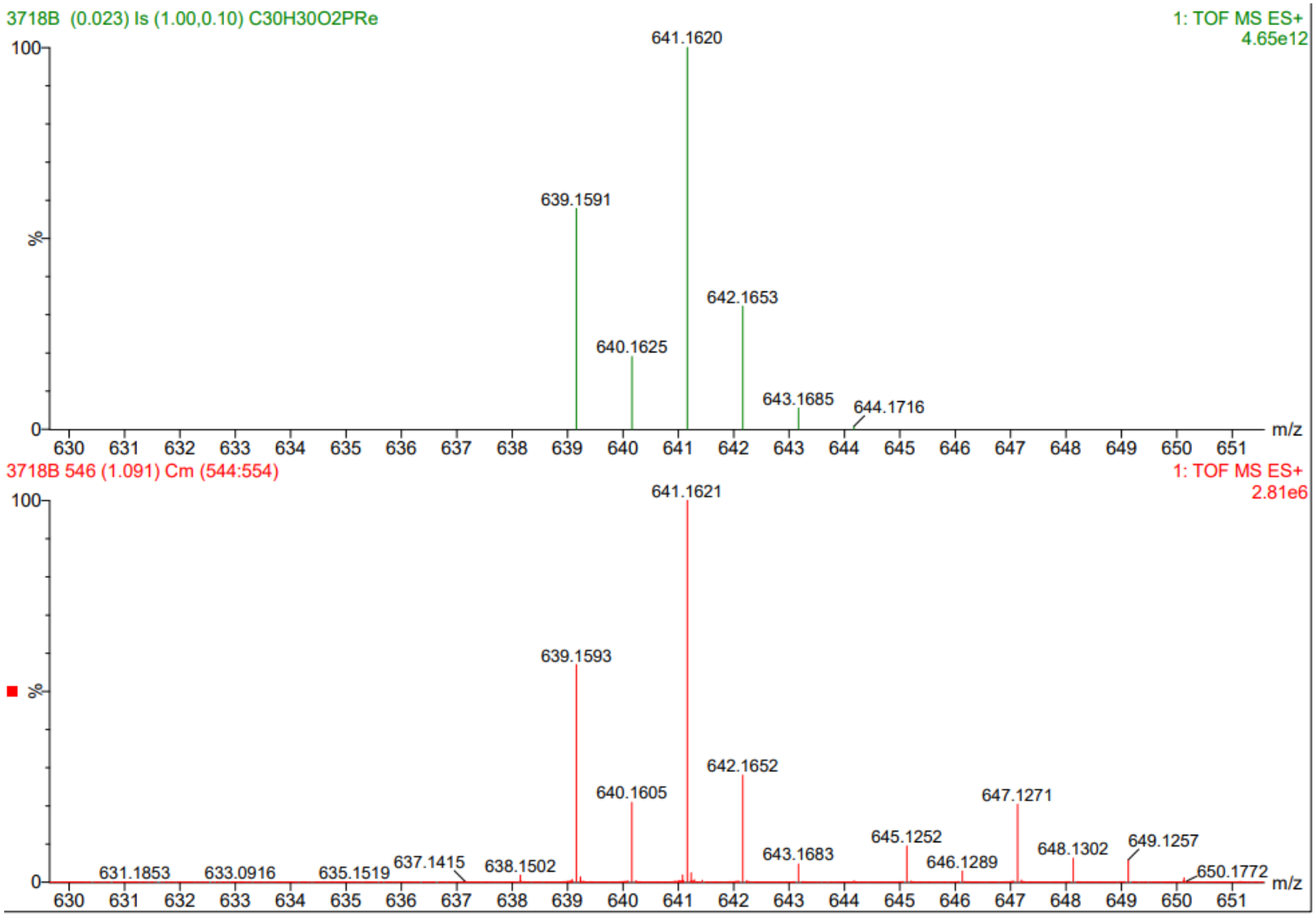
COSY ($CDCl_3$) for [Re(Cp*)$(CO)_2(PPh_3)$].



HSQC ($CDCl_3$) for [Re(Cp*)$(CO)_2(PPh_3)$].



HMBC ($CDCl_3$) for [Re(Cp*)$(CO)_2(PPh_3)$].



High Resolution ESI-MS (+ve ion) for $[Re(Cp^*)(CO)_2(PPh_3)]$.