Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPORTING INFORMATION

Heterobimetallic μ_2-carbido Complexes of Platinum and Tungsten

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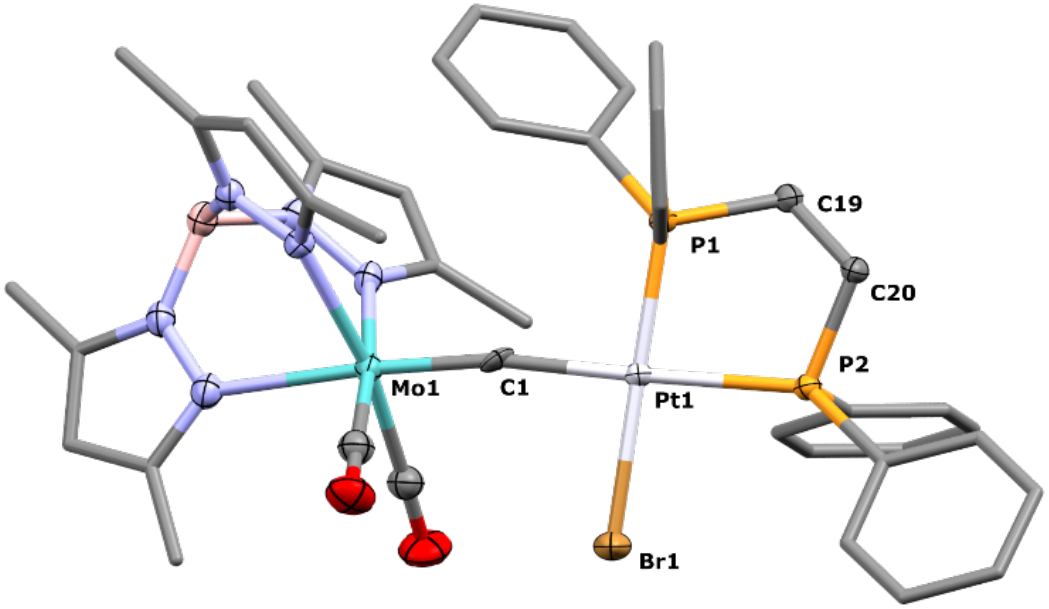


Figure S1. Molecular geometry of 6 in a crystal (50% displacement ellipsoids, hydrogen atoms removed, phenyl and pyrazolyly groups simplified for clarity). Selected bond lengths (Å), angles (°) and torsions (°): Mo1–C1 1.818(6), C1–Pt1 1.980(6), Mo1–C1–Pt1 167.9(3), Pt1–Br1 2.4734(7), Pt1–P1 2.121(1), Pt1–P2 2.342(1) P1–Pt1–P2 85.61(5), P1–C19–C20–P2 51.6(4).

Figure S2: ^{1}H NMR Spectrum of (8) [(Tp*)(CO)$_2$W≡C–Pt(terpy)][PF$_6$] (400 MHz, CD$_3$CN, 25 °C, δ):

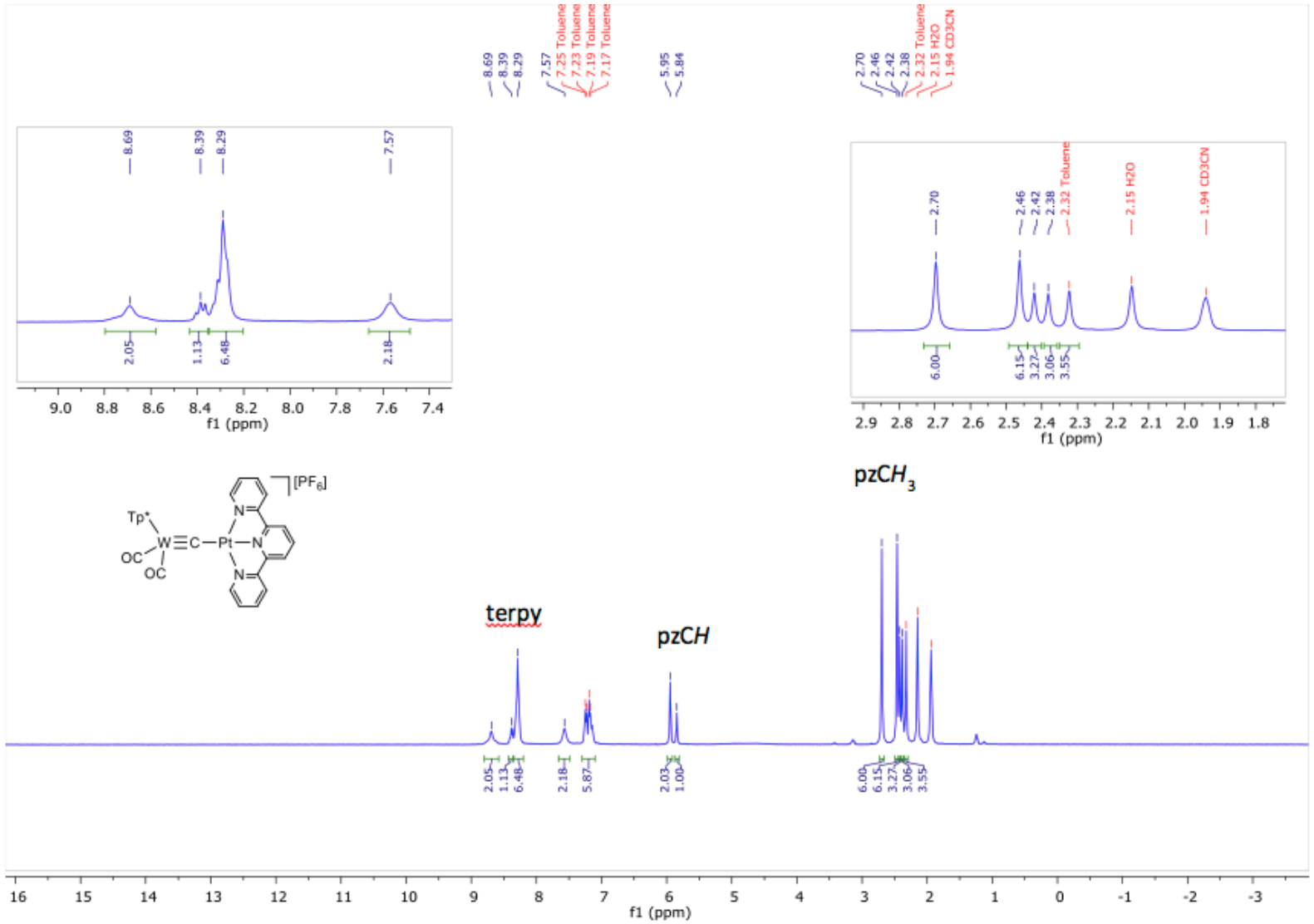


Figure S3: $^{113}C\{^{1}H\}$ NMR Spectrum of (8) [(Tp*)(CO)$_2$W≡C–Pt(terpy)][PF$_6$] (151 MHz, CD$_3$CN, 25 °C, δ):

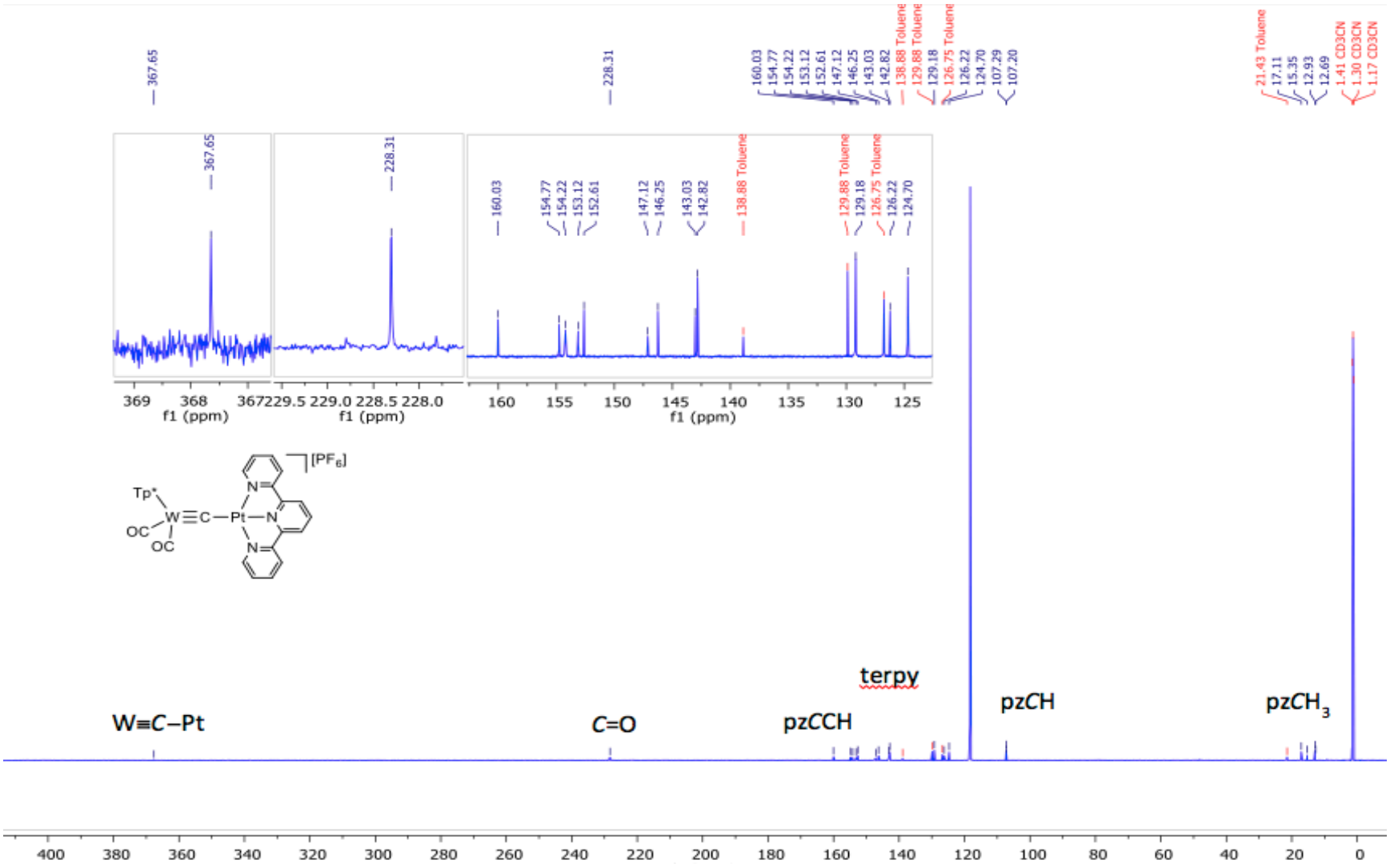


Figure S4: $^{119}F\{^{1}$ NMR Spectrum of (8) $[(Tp^*)(CO)_2W{\equiv}C{-}Pt(terpy)][PF_6]$ (376 MHz, CD_3CN, 25 °C, δ):

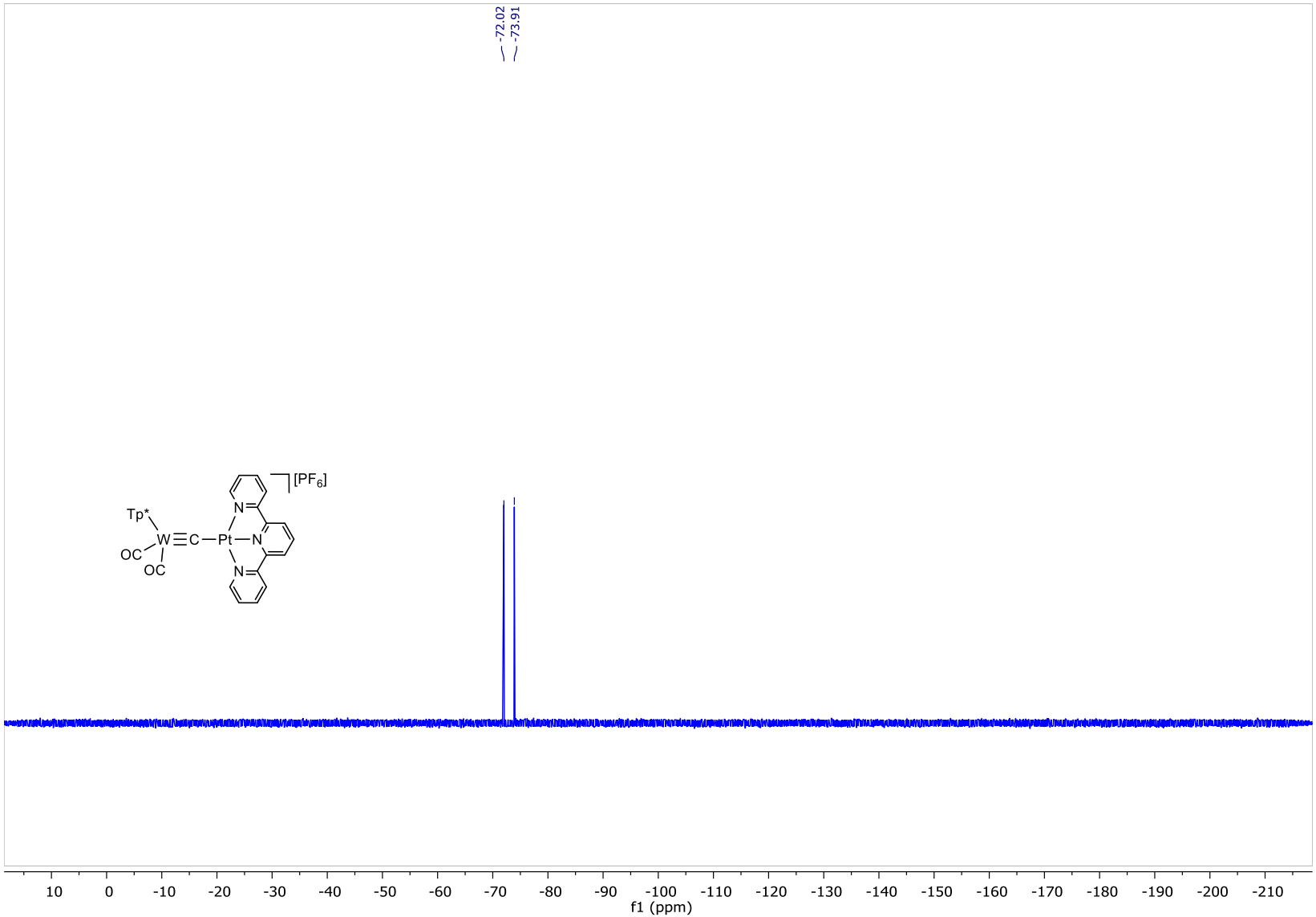


Figure S5: $^{131}P\{^{1}H\}$ NMR Spectrum of (5) [(Tp*)(CO)$_2$W≡C–Pt(terpy)][PF$_6$] (162 MHz, CD$_3$CN, 25 °C, δ):

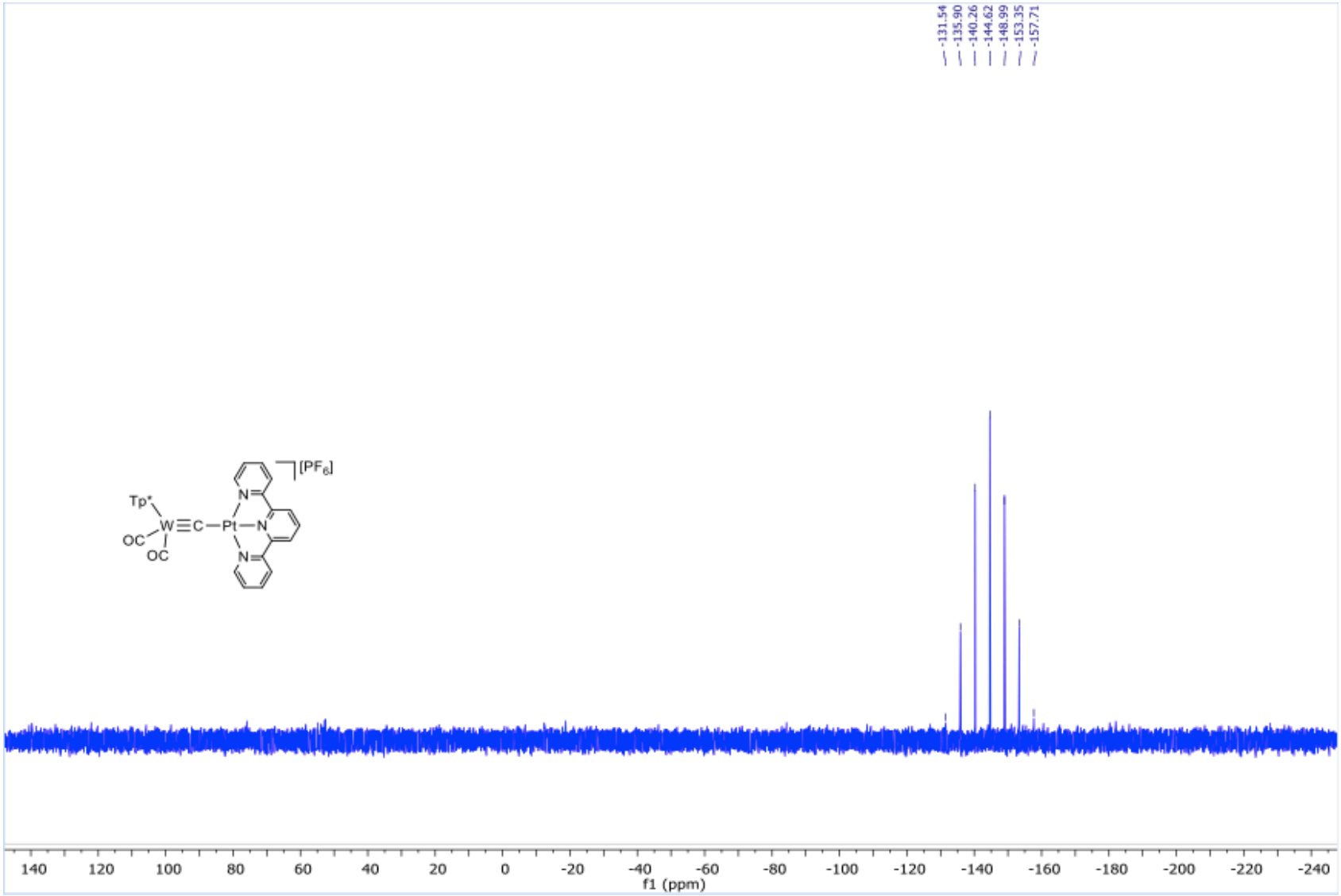


Figure S6: ^{11}H NMR Spectrum of (6) [(Tp*)(CO)$_2$Mo≡C–PtBr(dppe)] (400 MHz, $CDCl_3$, 25 °C, δ):

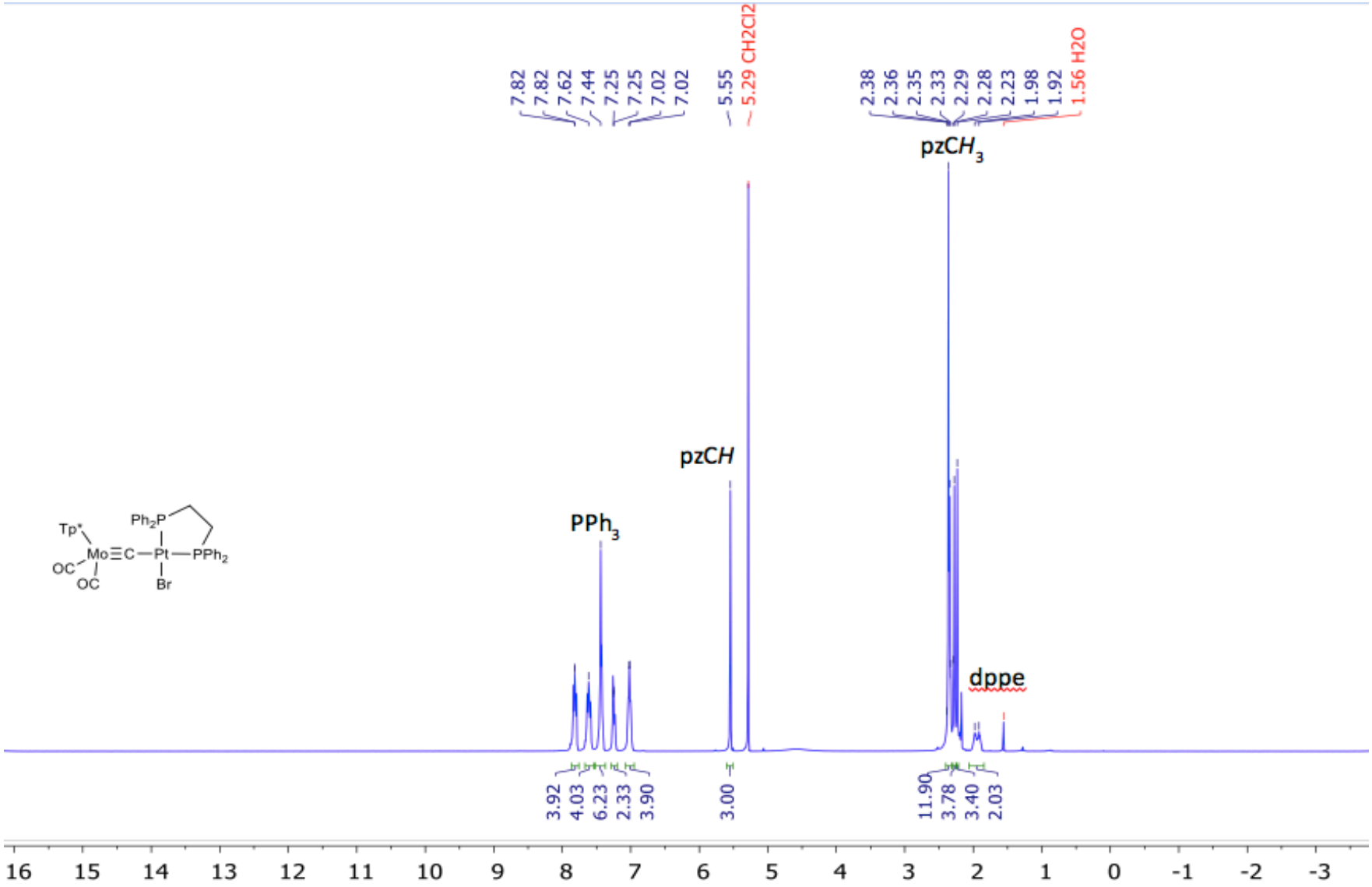


Figure S7: $^{13}C\{^{1}H\}$ NMR Spectrum of (6) [(Tp*)(CO)$_2$Mo≡C–PtBr(PPh$_3$)$_2$] (151 MHz, CD_2Cl_2, 25 °C, δ):

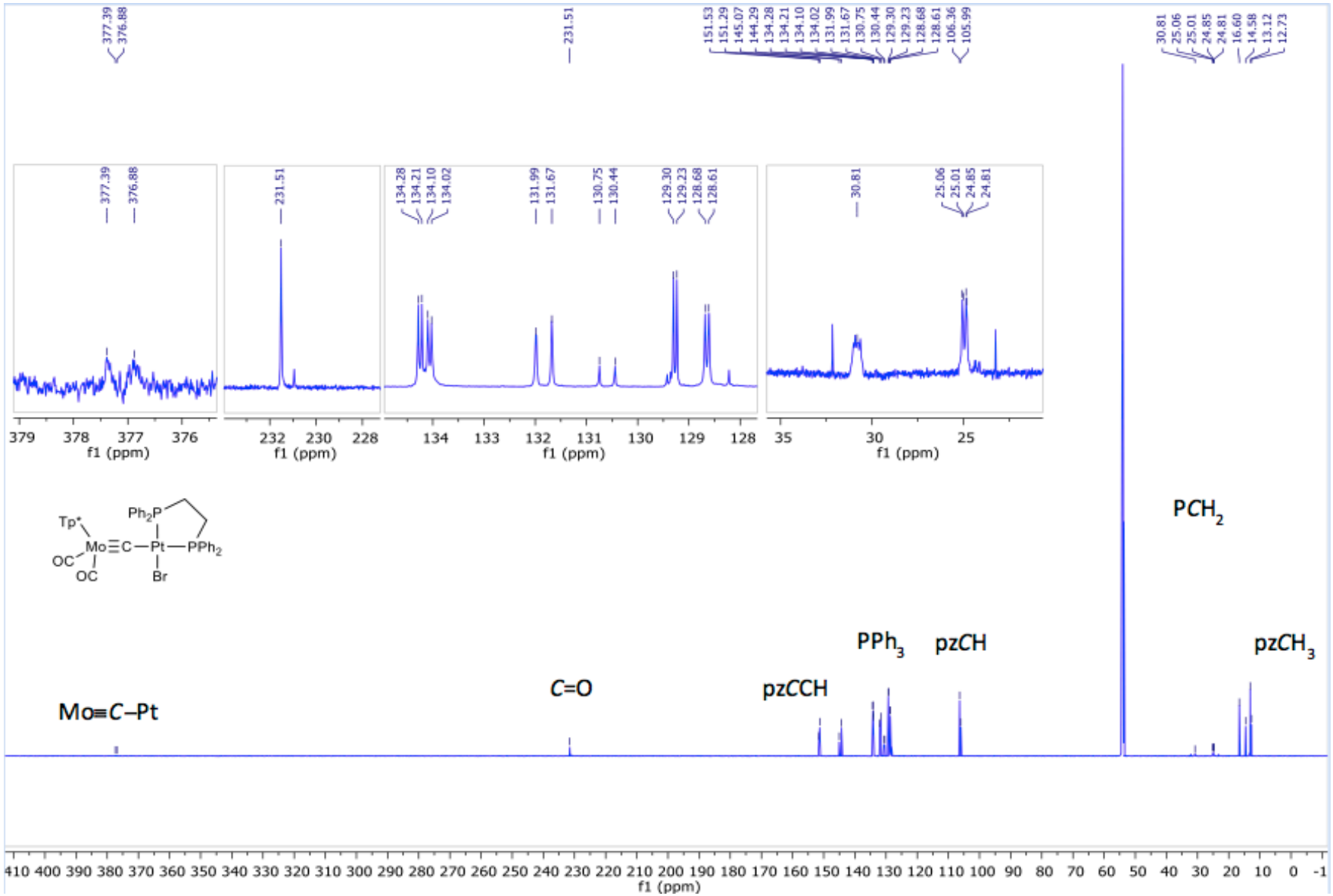


Figure S8: $^{131}P\{^{1}H\}$ NMR Spectrum of (6) [(Tp*)(CO)$_2$Mo≡C–PtBr(dppe)] (162 MHz, $CDCl_3$, 25 °C, δ):

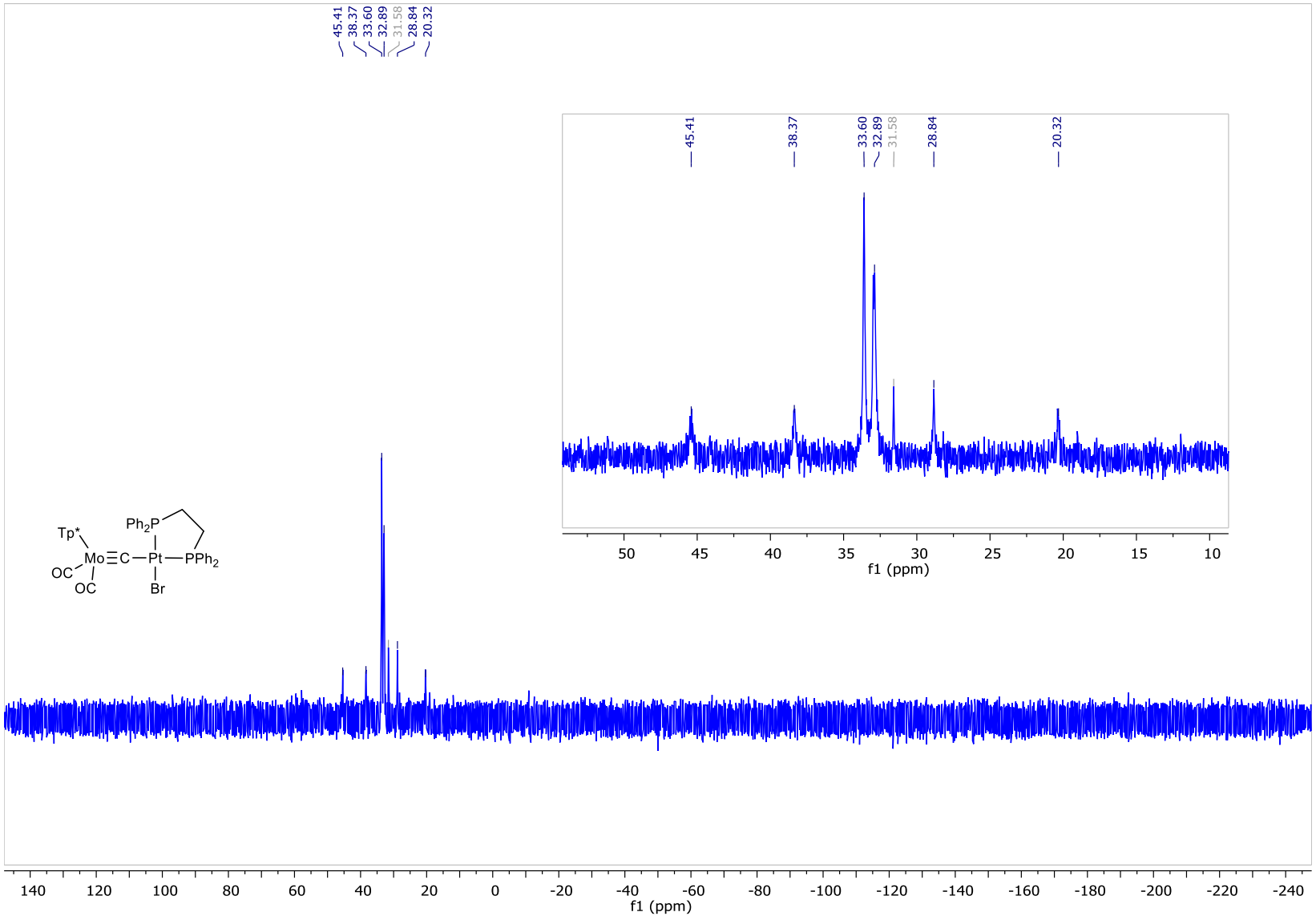


Figure S9: ^{1}Infrared Spectrum of (6) [(Tp*)(CO)$_2$Mo≡C–PtBr(PPh$_3$)$_2$] (CH_2Cl_2, 25 °C, ν):

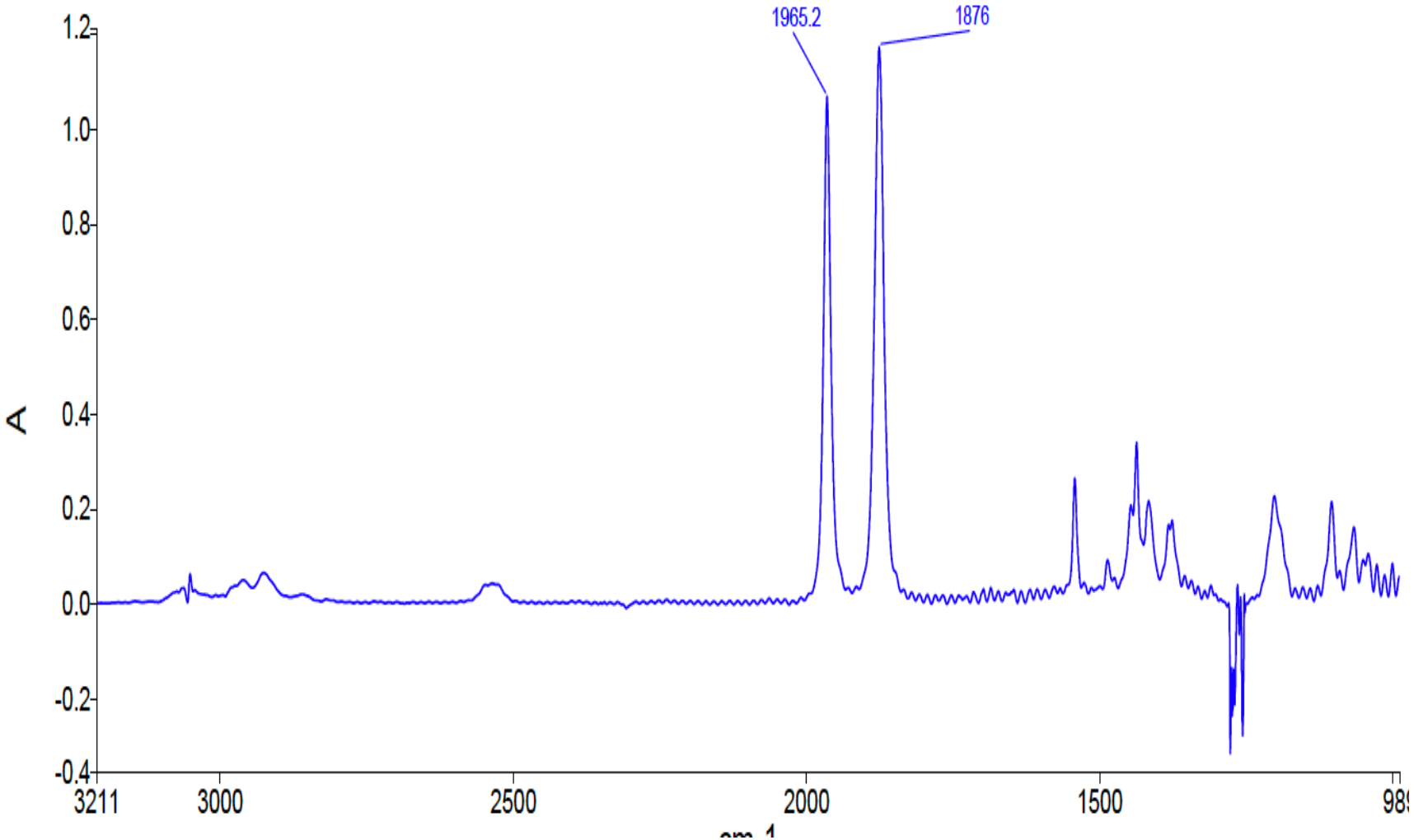
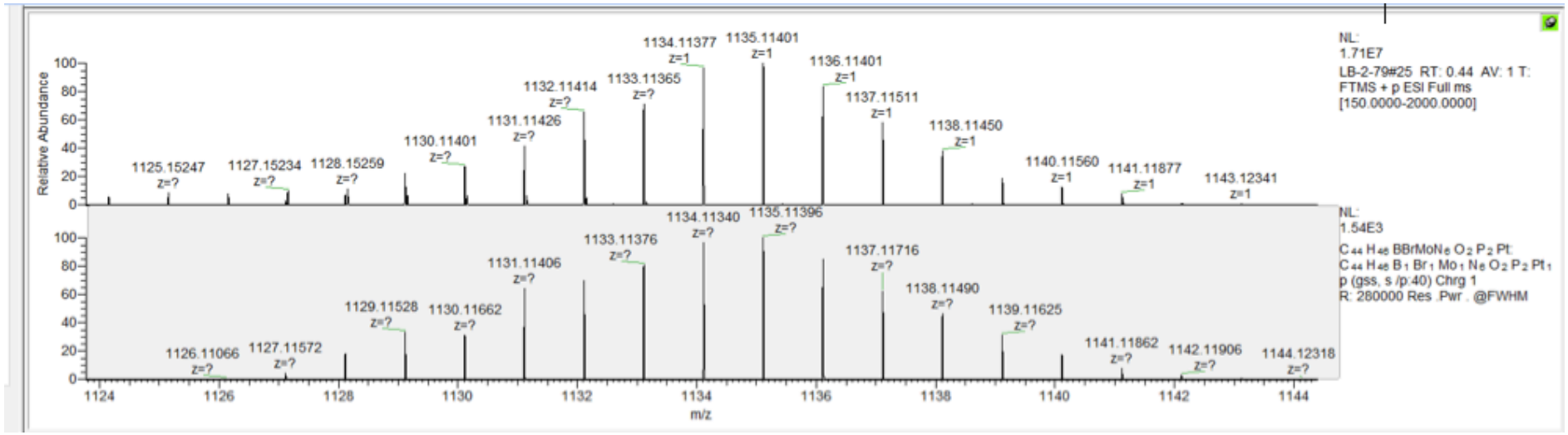


Figure S10: [1]Mass Spectrum of (6) [(Tp*)(CO)$_2$Mo≡C–PtBr(PPh$_3$)$_2$] (ESI):



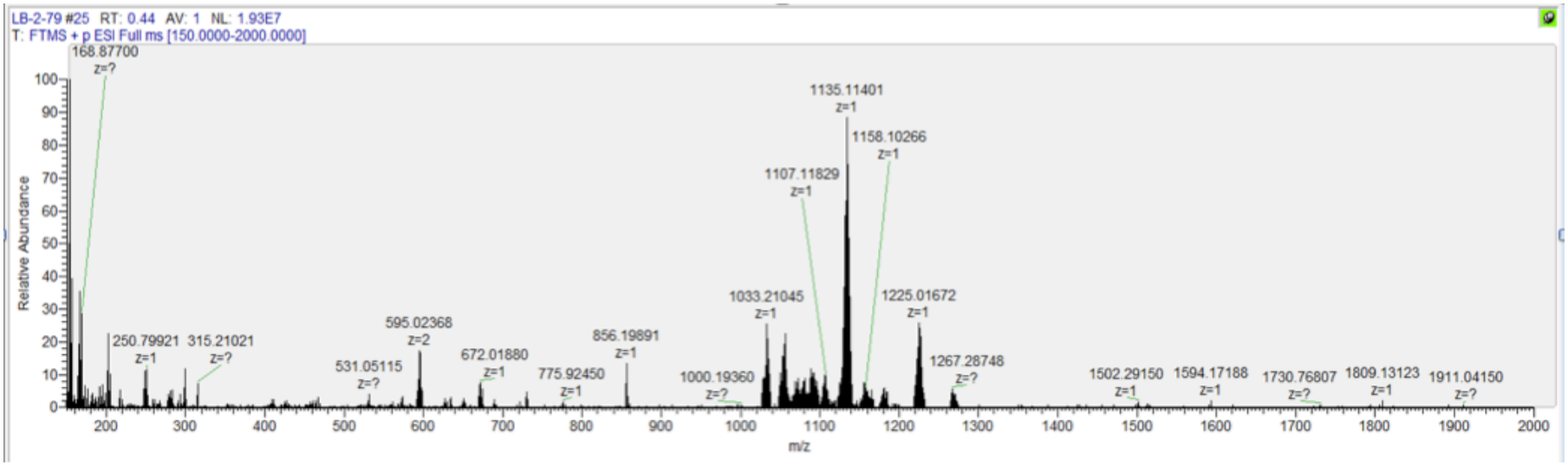


Figure S11: ^{11}H NMR Spectrum of (5) [(Tp*)(CO)$_2$W≡C–PtBr(dppe)] (400 MHz, $CDCl_3$, 25 °C, δ):

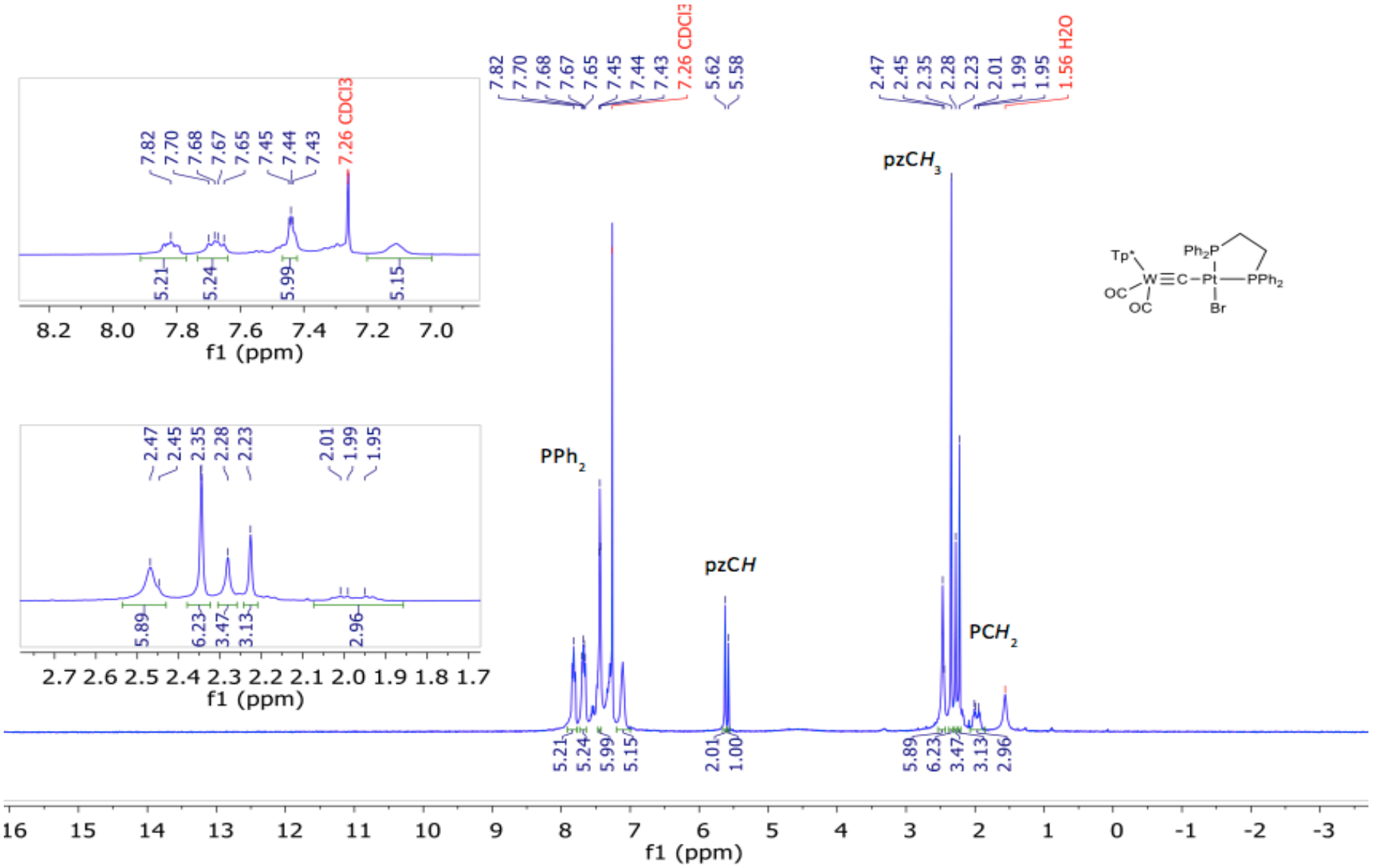


Figure S12: $^{13}C\{^{1}H\}$ NMR Spectrum (5) [(Tp*)(CO)$_2$W≡C–PtBr(dppe)] (151 MHz, $CDCl_3$, 25 °C, δ):

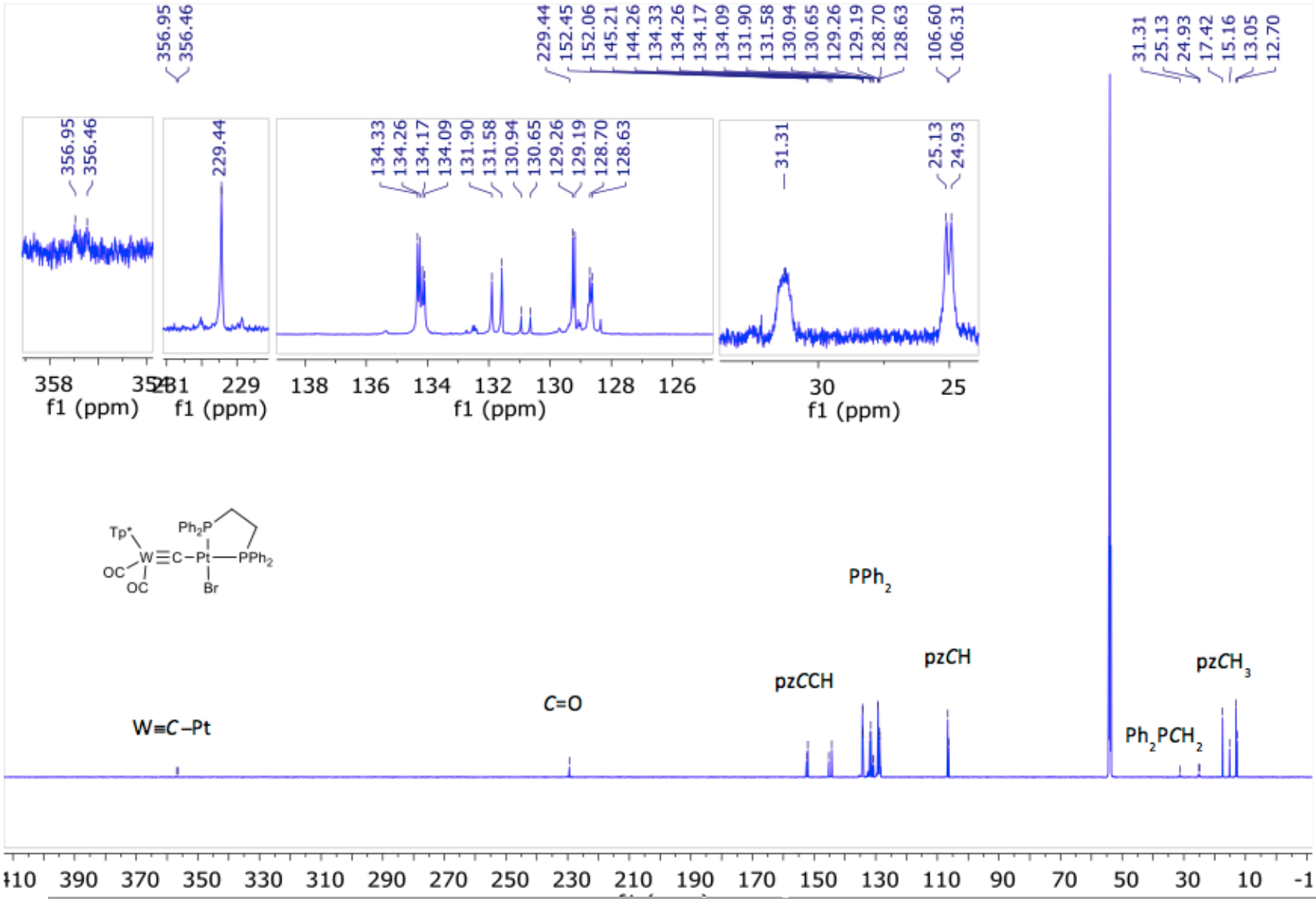


Figure S13: $^{31}P\{^{1}H\}$ NMR Spectrum (5) [(Tp*)(CO)$_2$W≡C–PtBr(dppe)] (284 MHz, CD_2Cl_2, –40 °C, δ):

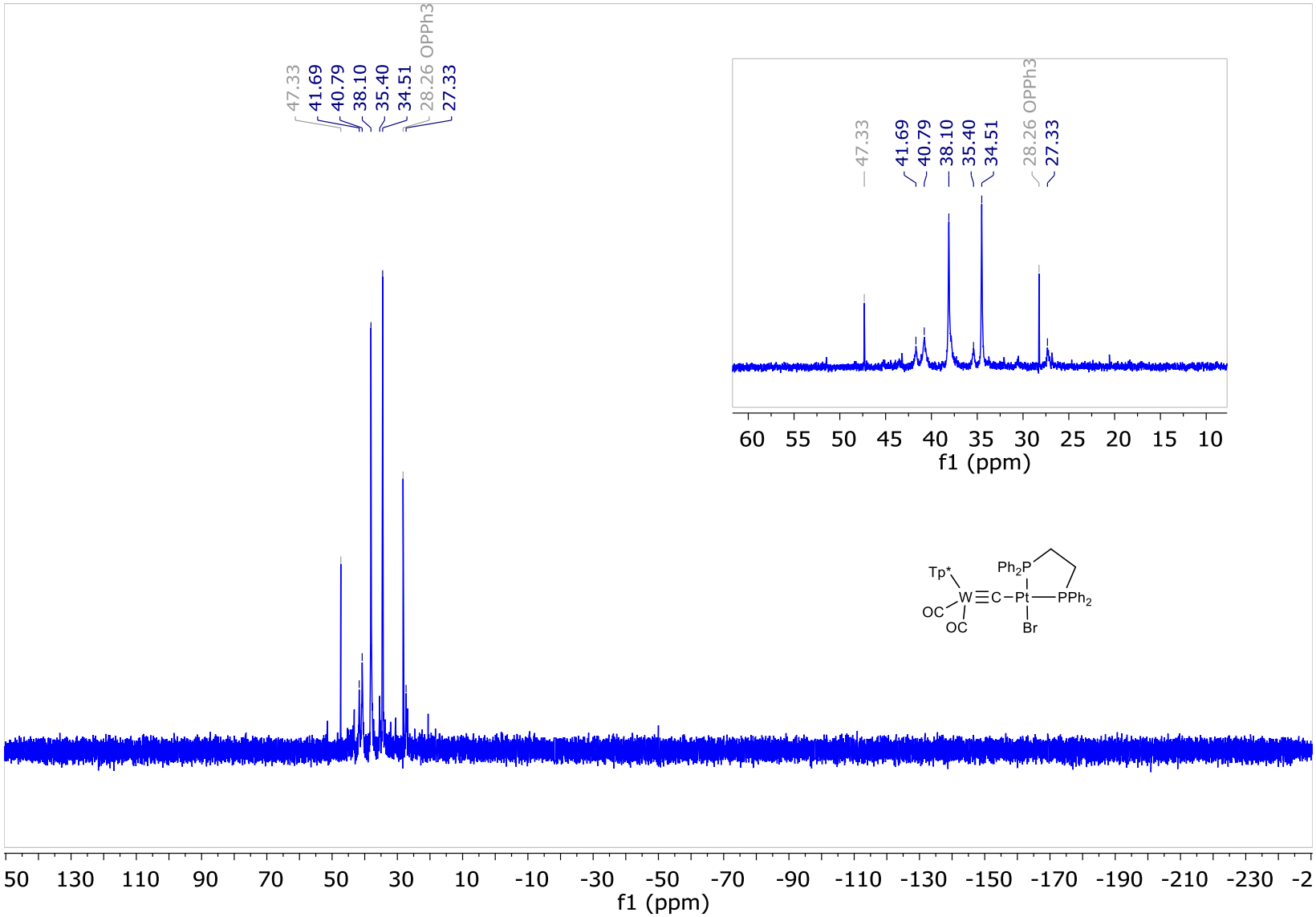


Figure S14: [1]Infrared Spectrum (5) [(Tp*)(CO)$_2$W≡C–PtBr(dppe)] (CH_2Cl_2, 25 °C, ν):

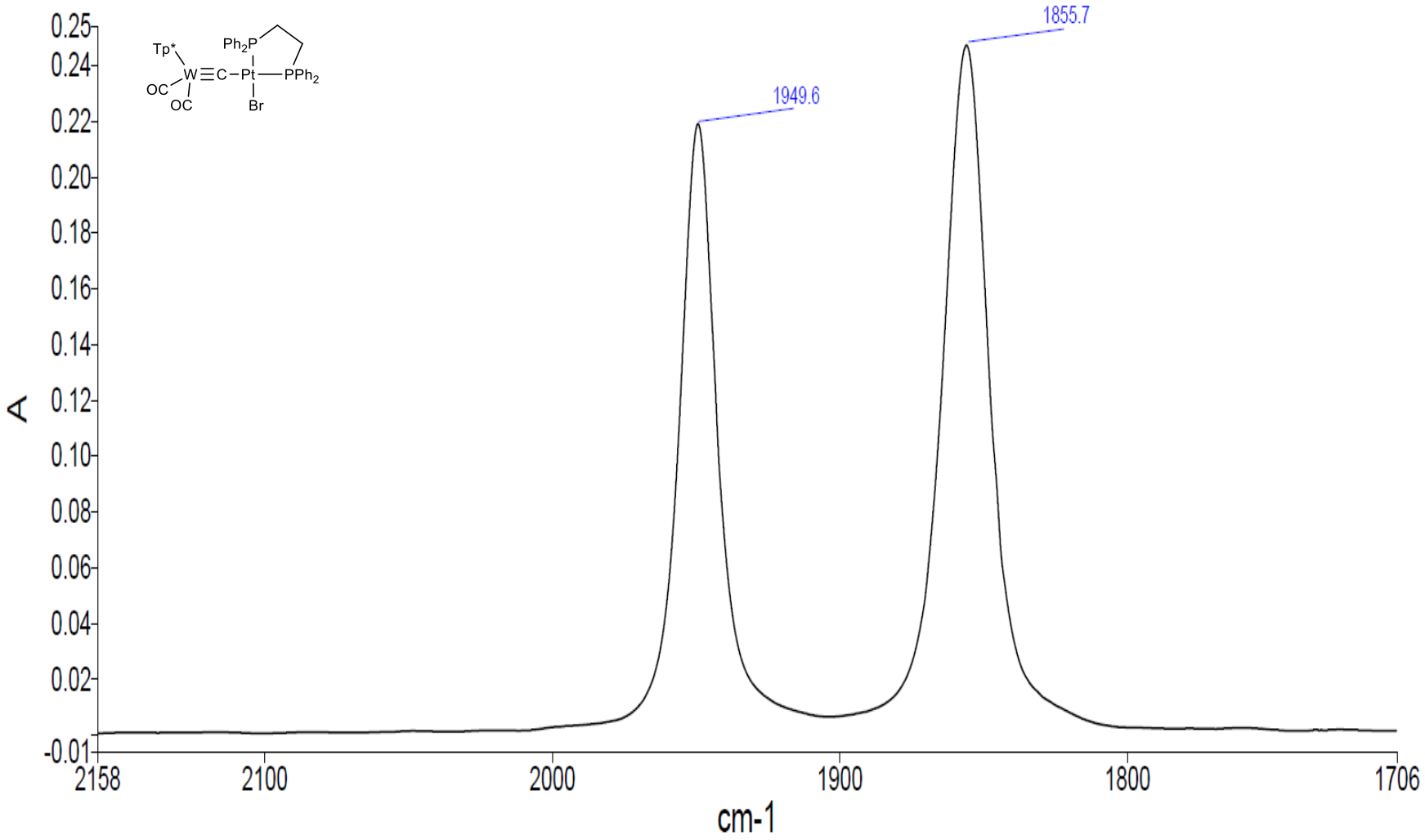


Figure S15: Mass Spectrum of (5) [(Tp*)W(CO$_2$)≡(μ–C)–PtBr(dppe)] (ESI):

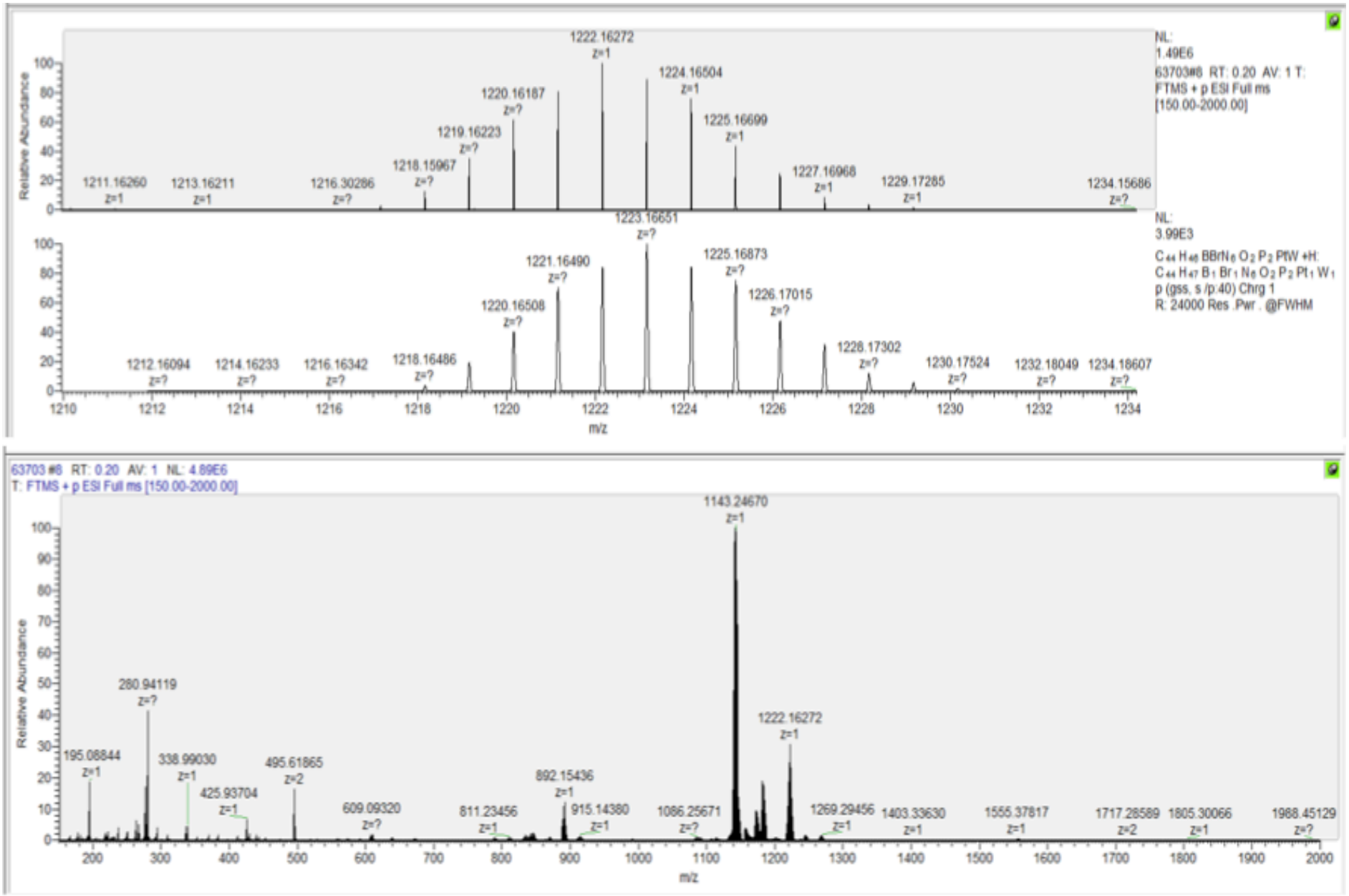


Figure S16: ^{1}H NMR Spectrum of (7) [(Tp*)(CO)$_2$W≡C–Pt(S$_2$CNEt$_2$)(PPh$_3$)] (700 MHz, CDCl$_3$, 25 °C, δ):

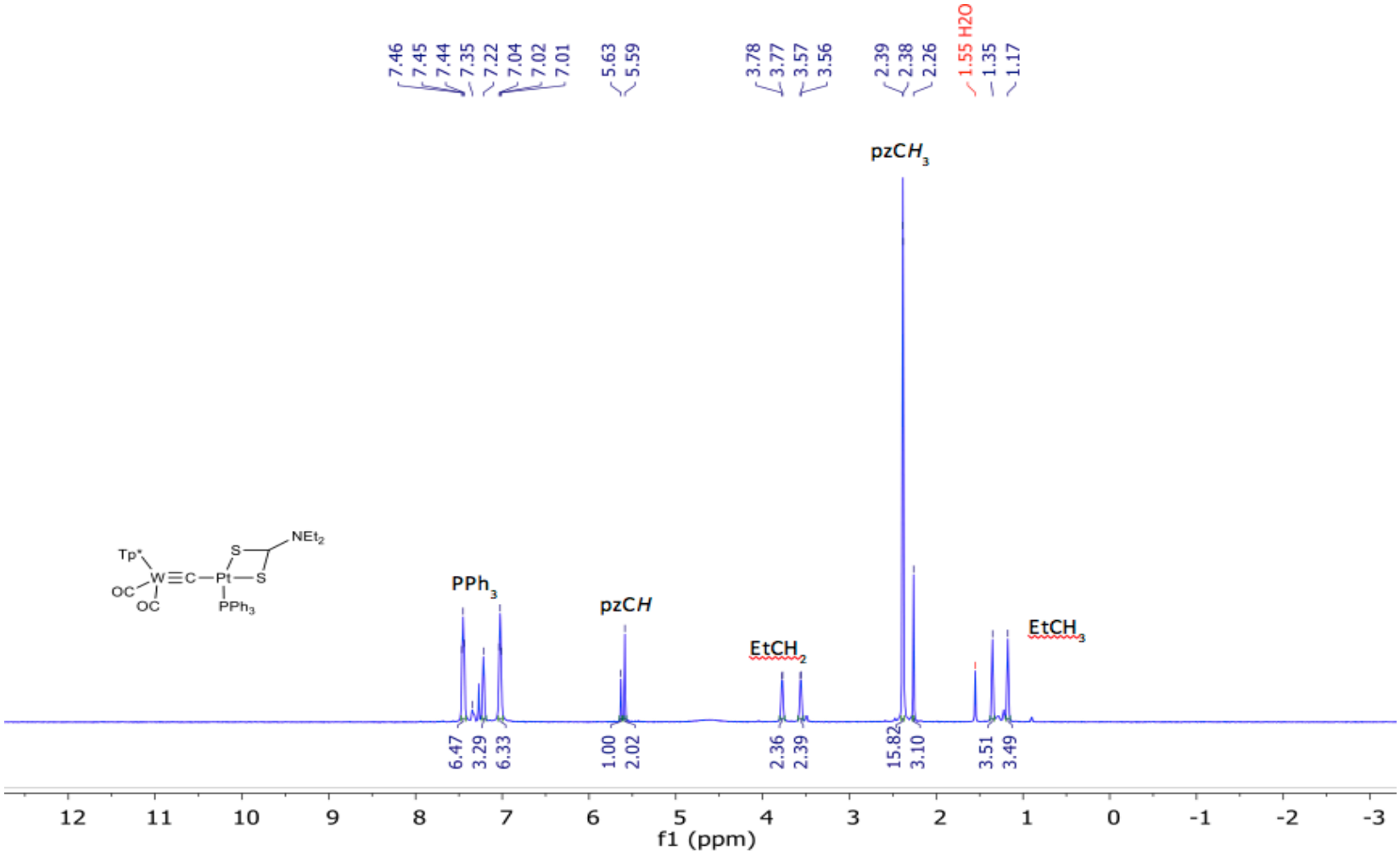


Figure S17: $^{13}C\{^{1}H\}$ NMR Spectrum of (7) [(Tp*)(CO)$_2$W≡C–Pt(S$_2$CNEt$_2$)(PPh$_3$)] (151 MHz, $CDCl_3$, 25 °C, δ):

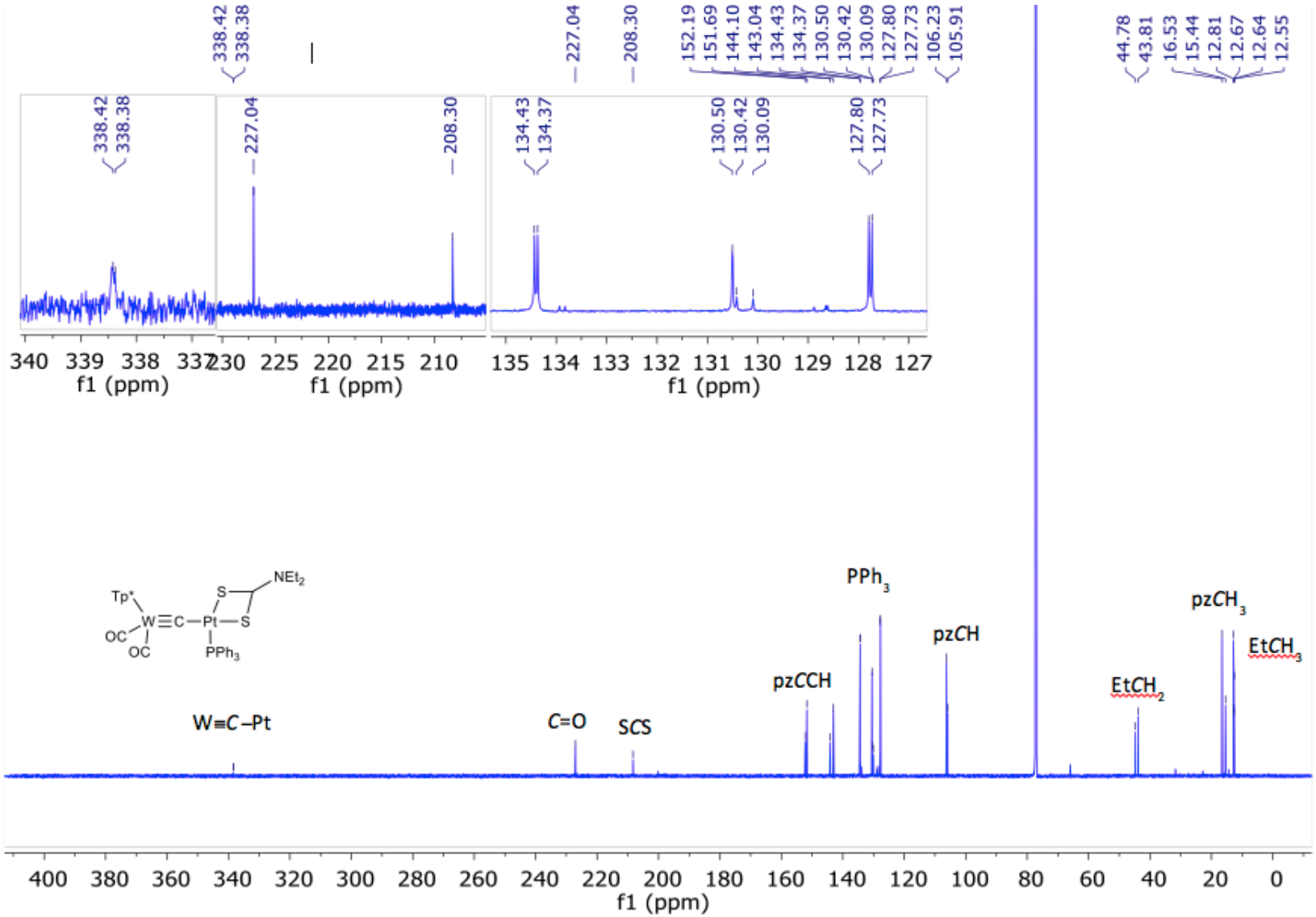


Figure S18: $^{31}P\{^{1}H\}$ NMR Spectrum of (7) [(Tp*)(CO)$_2$W≡C–Pt(S$_2$CNEt$_2$)(PPh$_3$)] (162 MHz, CDCl$_3$, 25 °C, δ):

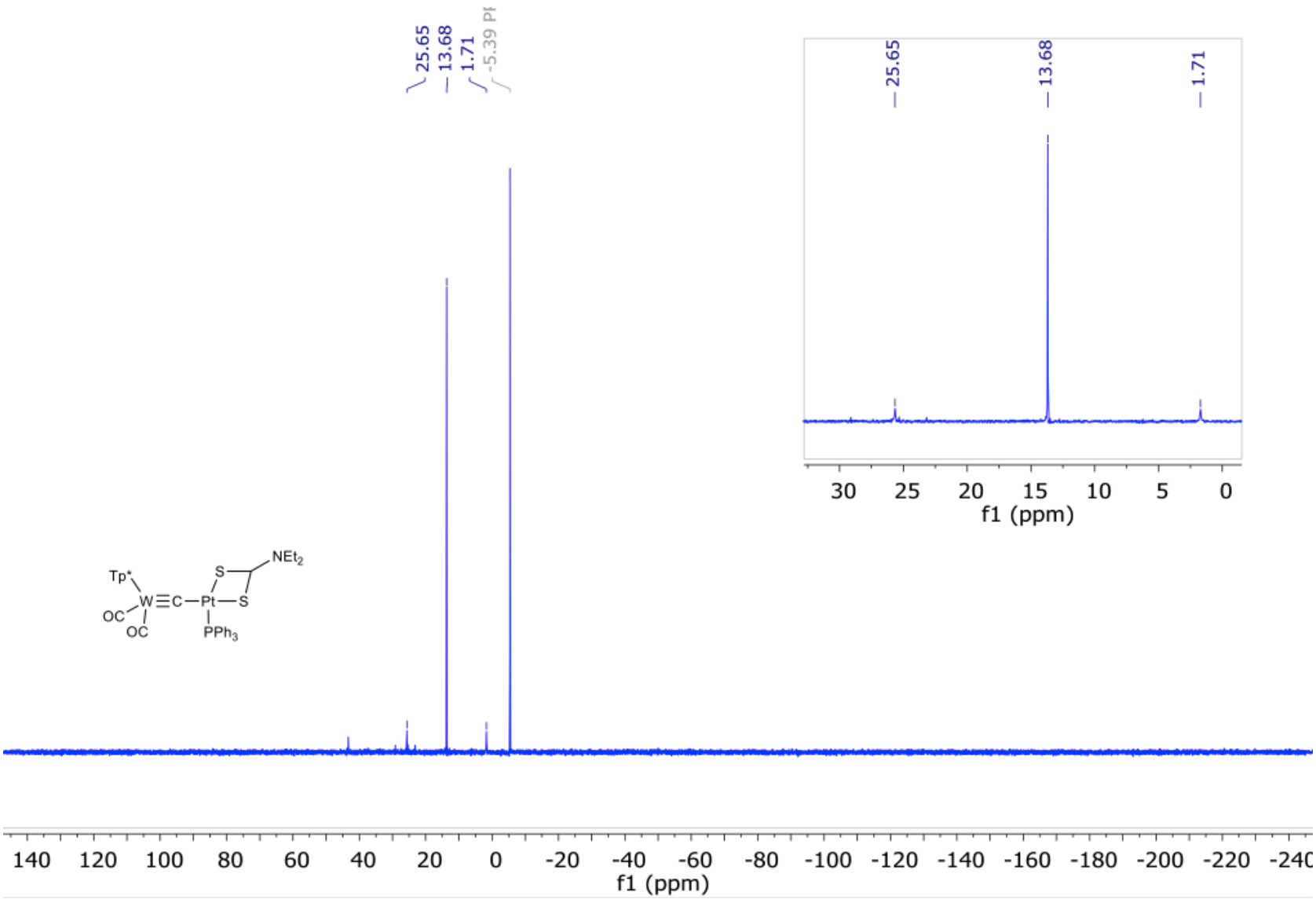


Figure S19: $^{195}Pt\{^{1}H\}$ NMR Spectrum of (9) [(Tp*)(CO)$_2$W≡C–Pt(S$_2$CNEt$_2$)(PPh$_3$)] 86 MHz, CDCl$_3$, 25 °C, δ):

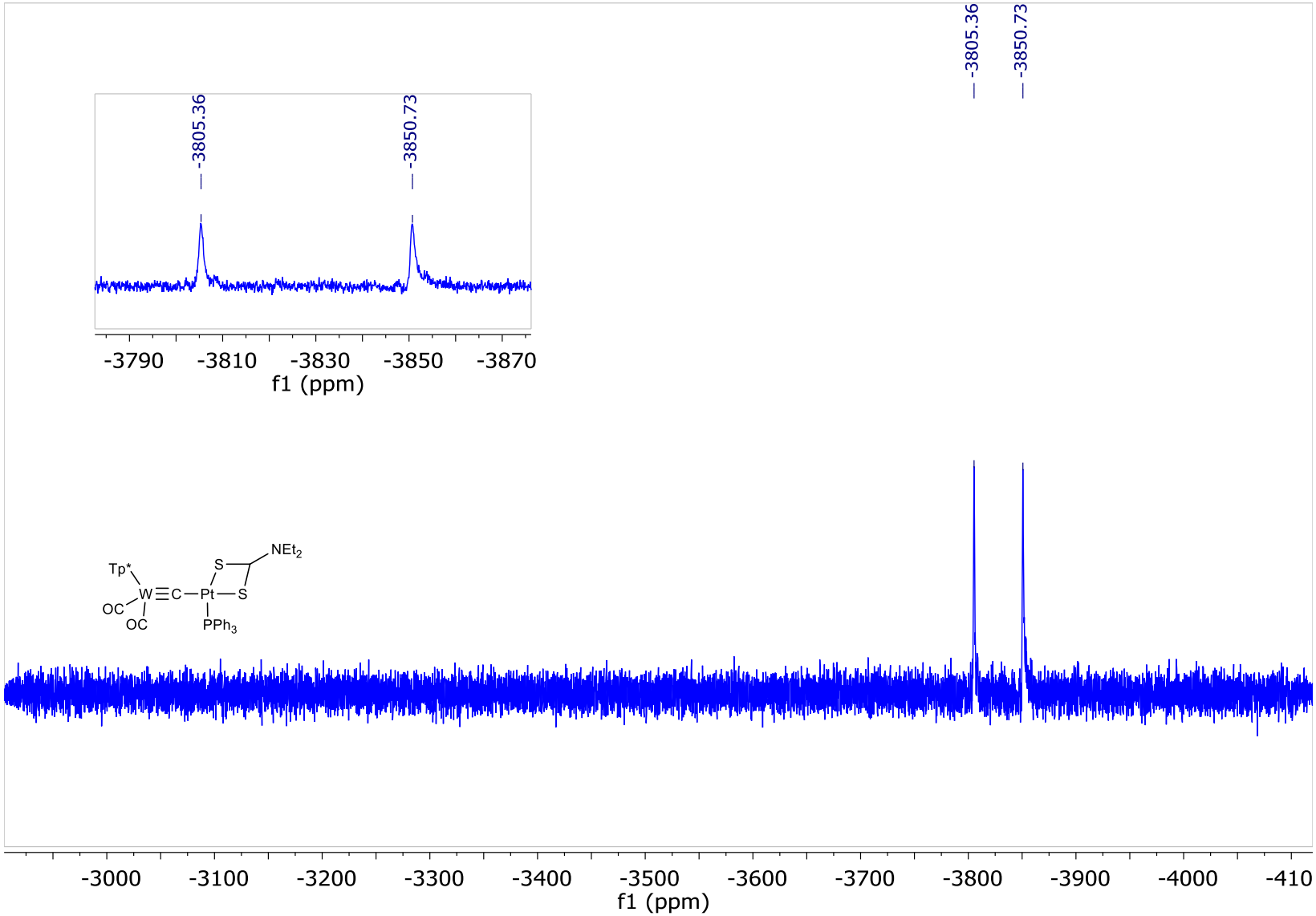


Figure S20: Infrared Spectrum of (9) [(Tp*)(CO)$_2$W≡C–Pt{SC(=S)NEt$_2$}(PPh$_3$)] (CH$_2$Cl$_2$, 25 °C, ν):

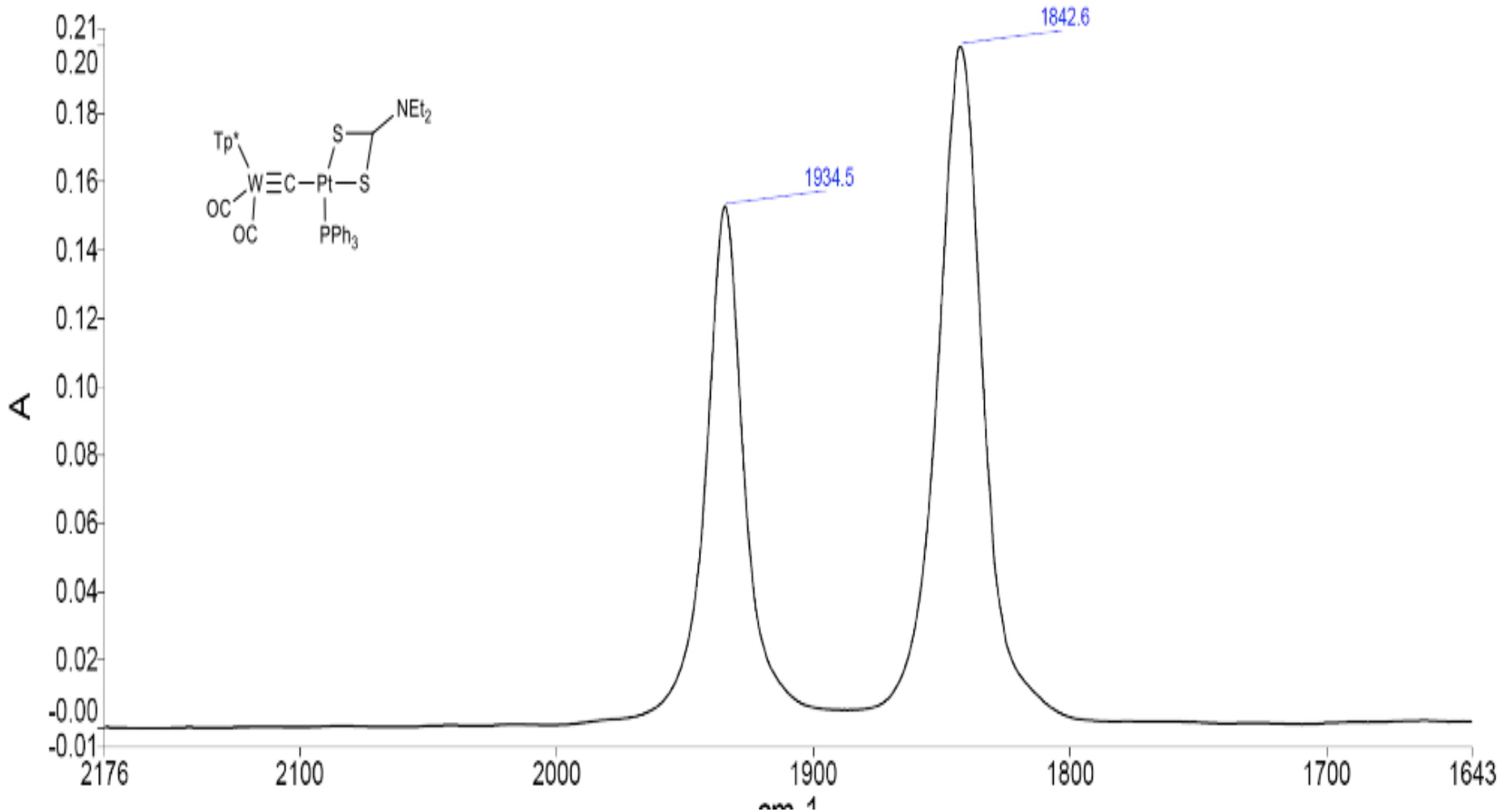


Figure S21: $^{13}C\{^{1}H\}$ NMR Spectrum of [9]PF_6 [(Tp*)(CO)$_2$W≡C–Pt(phen)(PPh_3)][PF_6] (151 MHz, $CDCl_3$, 25 °C, δ):

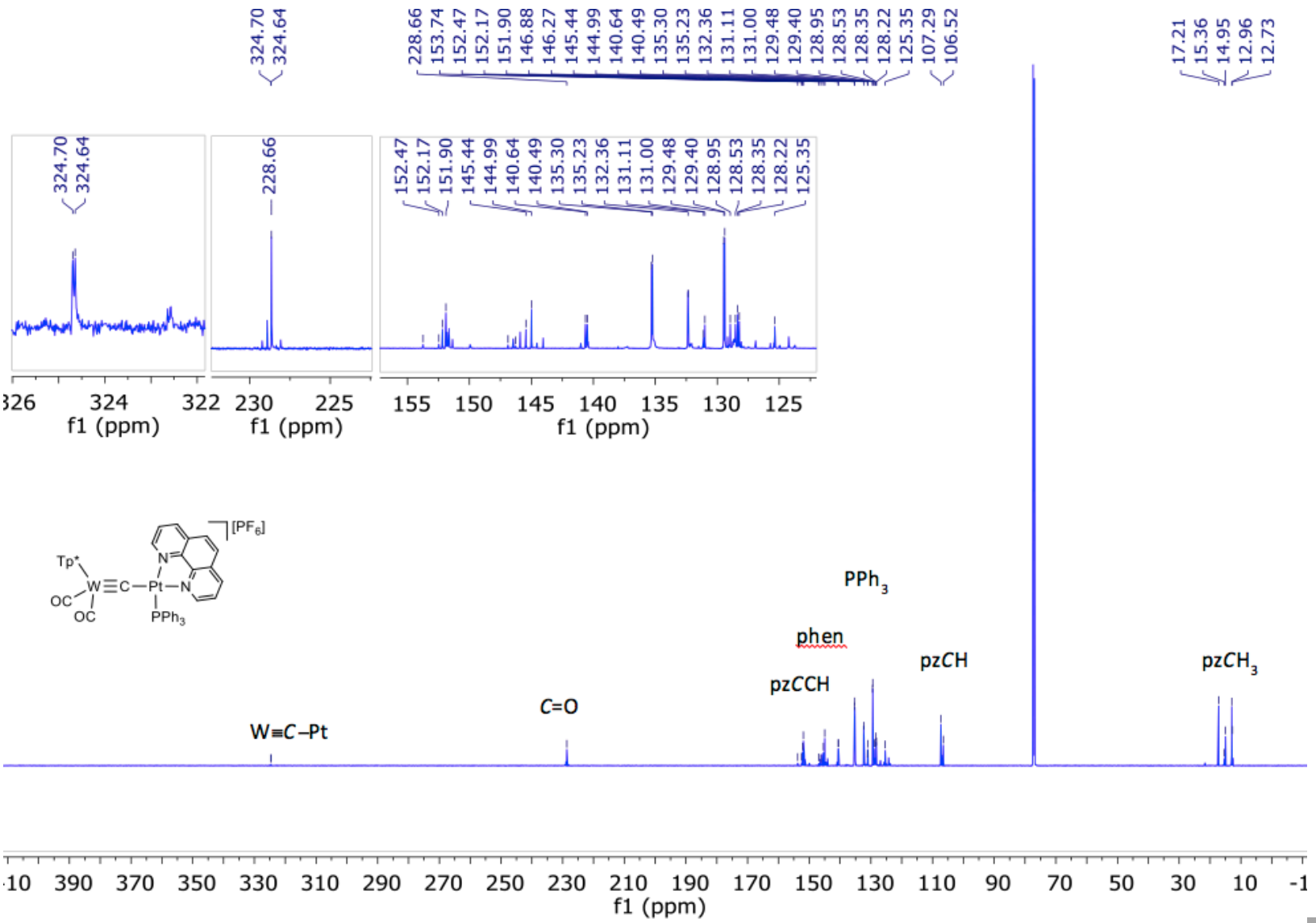


Figure S22: $^{31}P\{^{1}H\}$ NMR Spectrum of [9]PF_6 [(Tp*)$(CO)_2$W≡C–Pt(phen)(PPh_3)][PF_6](162 MHz, $CDCl_3$, 25 °C, δ):

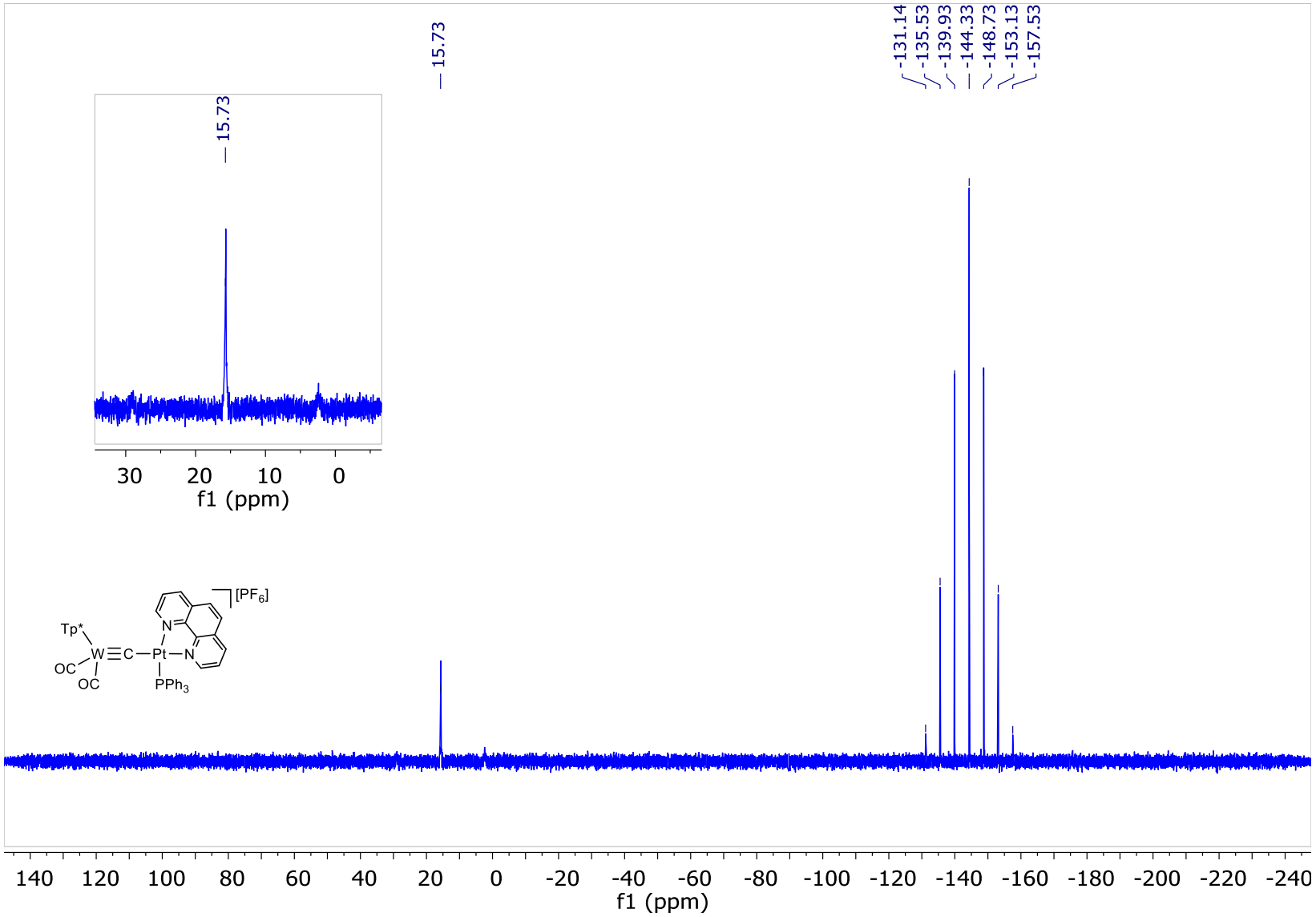


Figure S23: $^{195}Pt\{^{1}H\}$ NMR Spectrum of [9]PF_6 [(Tp*)$(CO)_2$W≡C–Pt(phen)(PPh_3)][PF_6] (86 MHz, $CDCl_3$, 25 °C, δ):

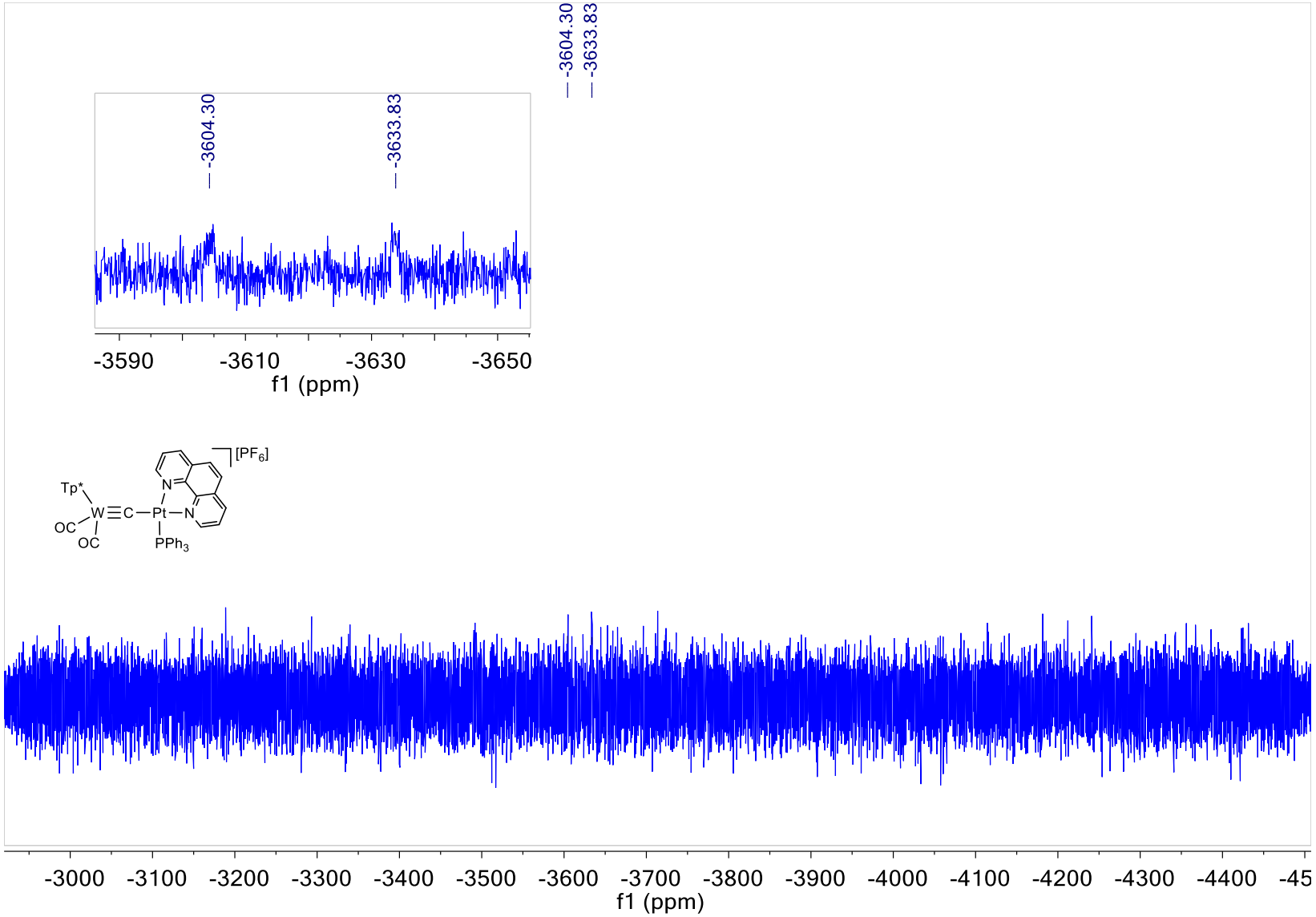


Figure S24: Infrared Spectrum of [89]PF_6 [(Tp*)$(CO)_2$W≡C–Pt(phen)(PPh_3)][PF_6] (CH_2Cl_2, 25 °C, ν):

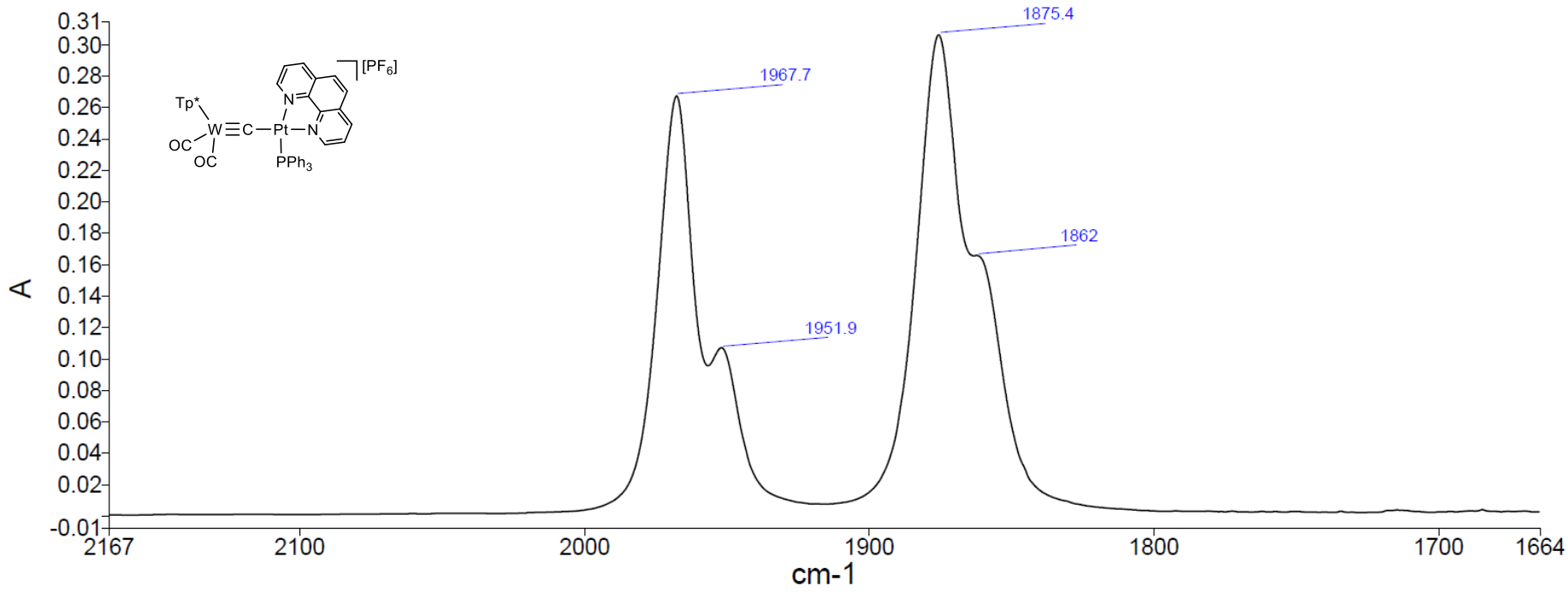


Figure S25: Mass Spectrum of [9]PF_6 [(Tp*)$(CO)_2$W≡C–Pt(phen)(PPh_3)][PF_6] (ESI):

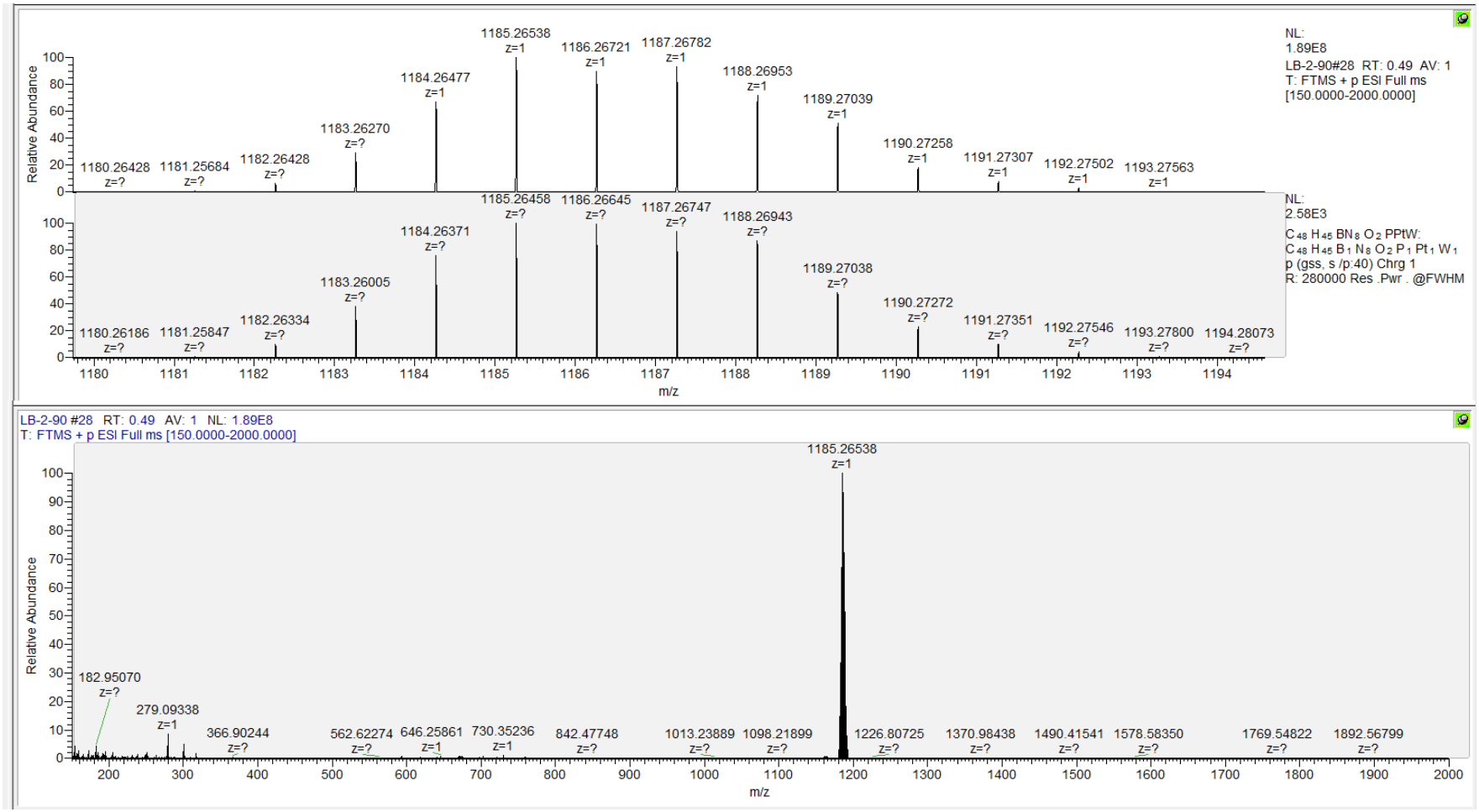


Figure S26: ^{1}H NMR Spectrum of [10a]PF_6 [(Tp*)(CO)$_2$W≡C–Pt(bpy)(PPh_3)][PF_6] (400 MHz, $CDCl_3$, 25 °C, δ):

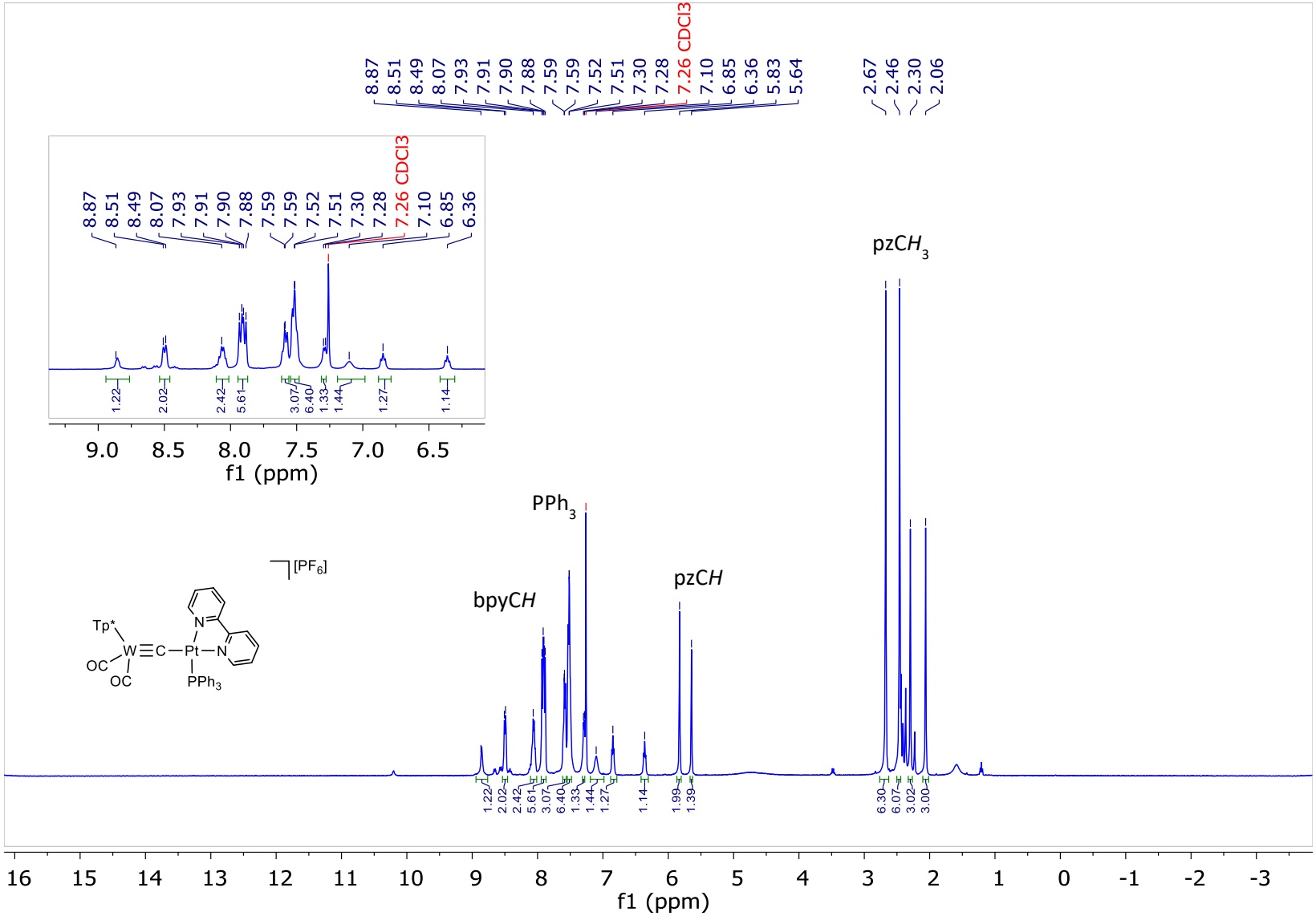


Figure S27: $^{13}C\{^{1}H\}$ NMR Spectrum of [10a]PF_6 [(Tp*)$(CO)_2$W≡C–Pt(bpy)(PPh_3)][PF_6] (151 MHz, $CDCl_3$, 25 °C, δ):

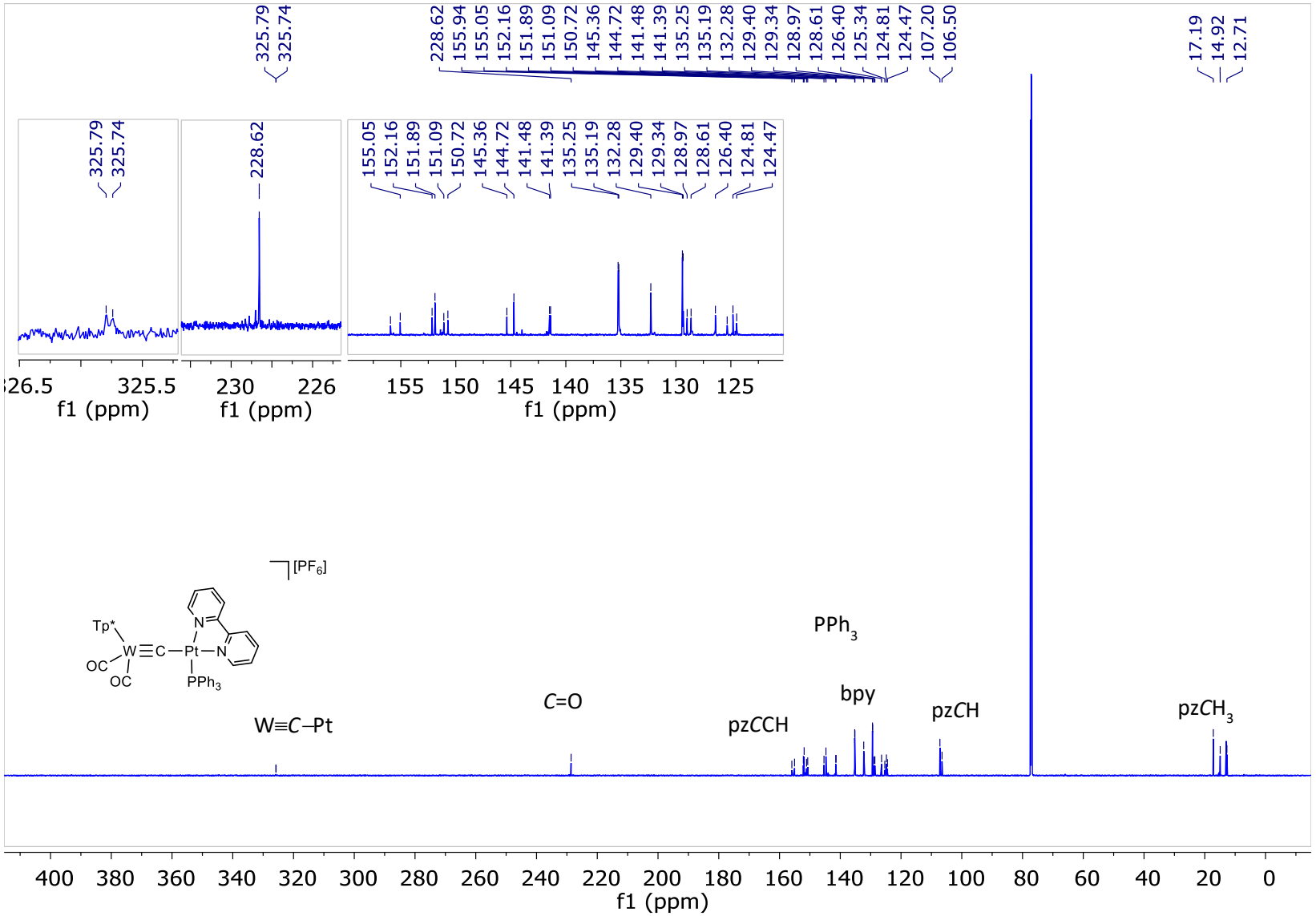


Figure S28: $^{19}F\{^{1}H\}$ NMR Spectrum of [10a]PF_6 [(Tp*)$(CO)_2$W≡C–Pt(bpy)(PPh_3)][PF_6] (377 MHz, $CDCl_3$, 25 °C, δ):

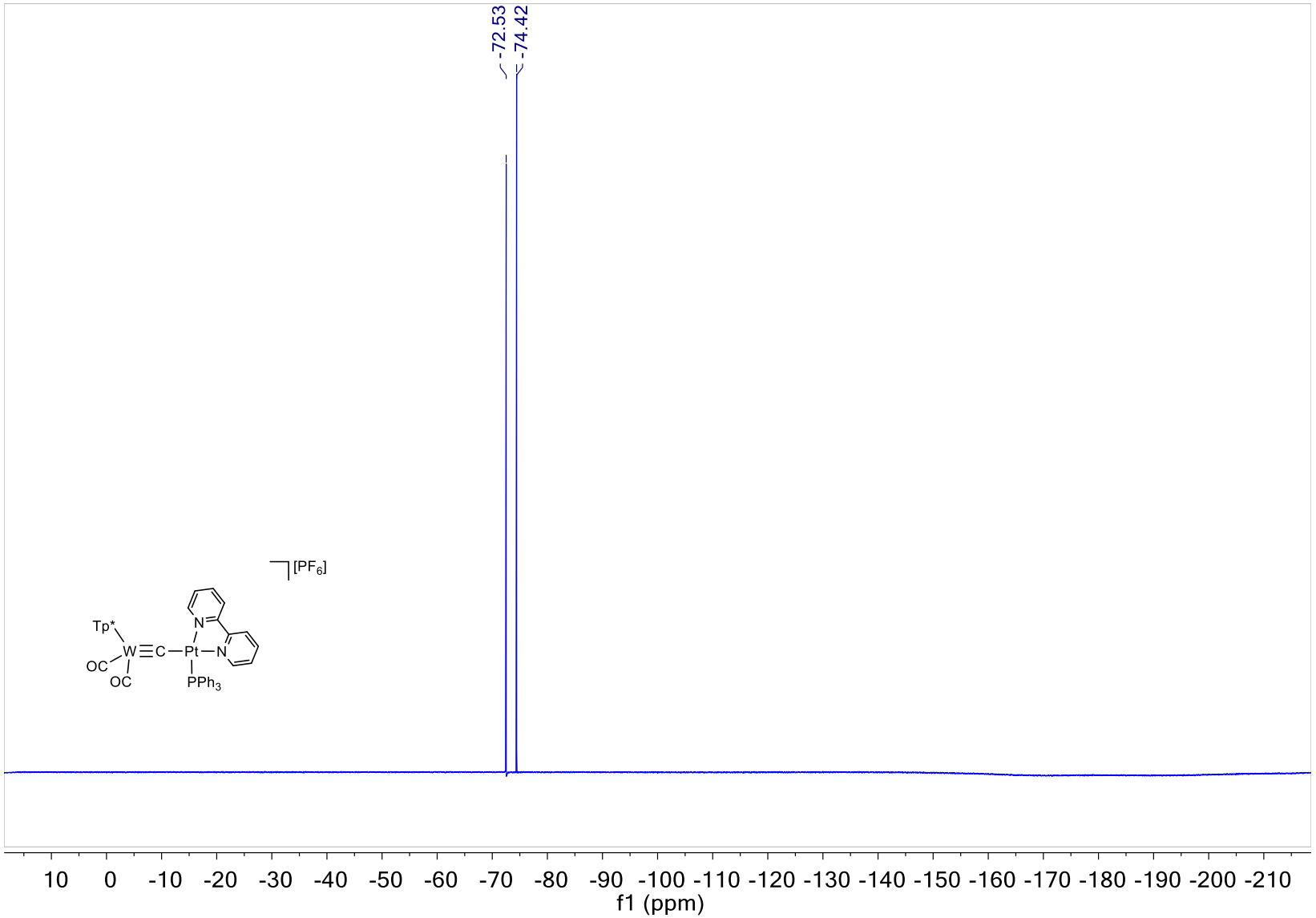


Figure S29: $^{31}P\{^{1}H\}$ NMR Spectrum of [10a]PF_6 [(Tp*)$(CO)_2$W≡C–Pt(bpy)(PPh_3)][PF_6] (162 MHz, $CDCl_3$, 25 °C, δ):

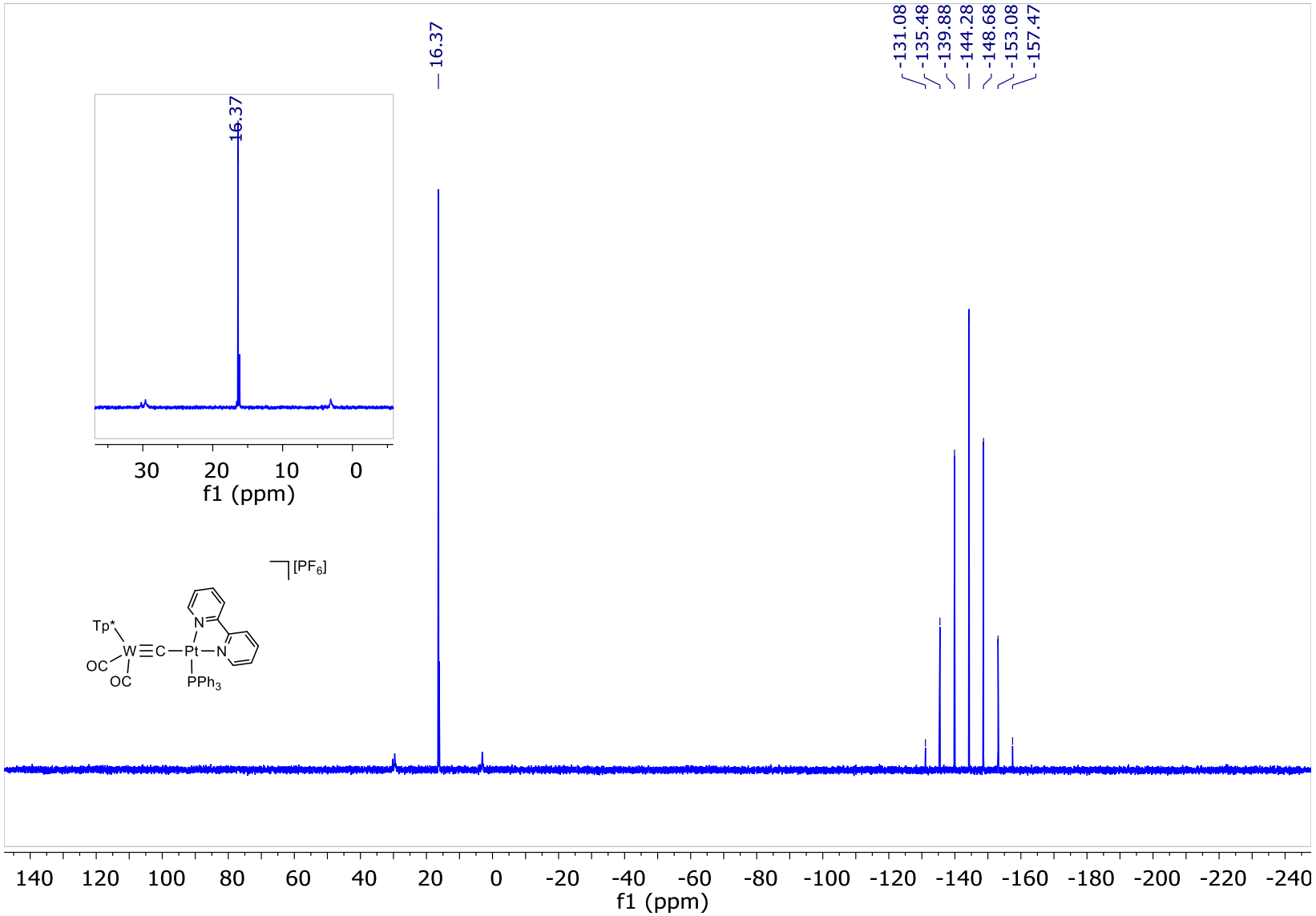


Figure S30: $^{195}Pt\{^{1}H\}$ NMR Spectrum of $[10a]PF_6$ [(Tp*)(CO)$_2$W≡C–Pt(bpy)(PPh$_3$)][PF$_6$] (86 MHz, $CDCl_3$, 25 °C, δ):

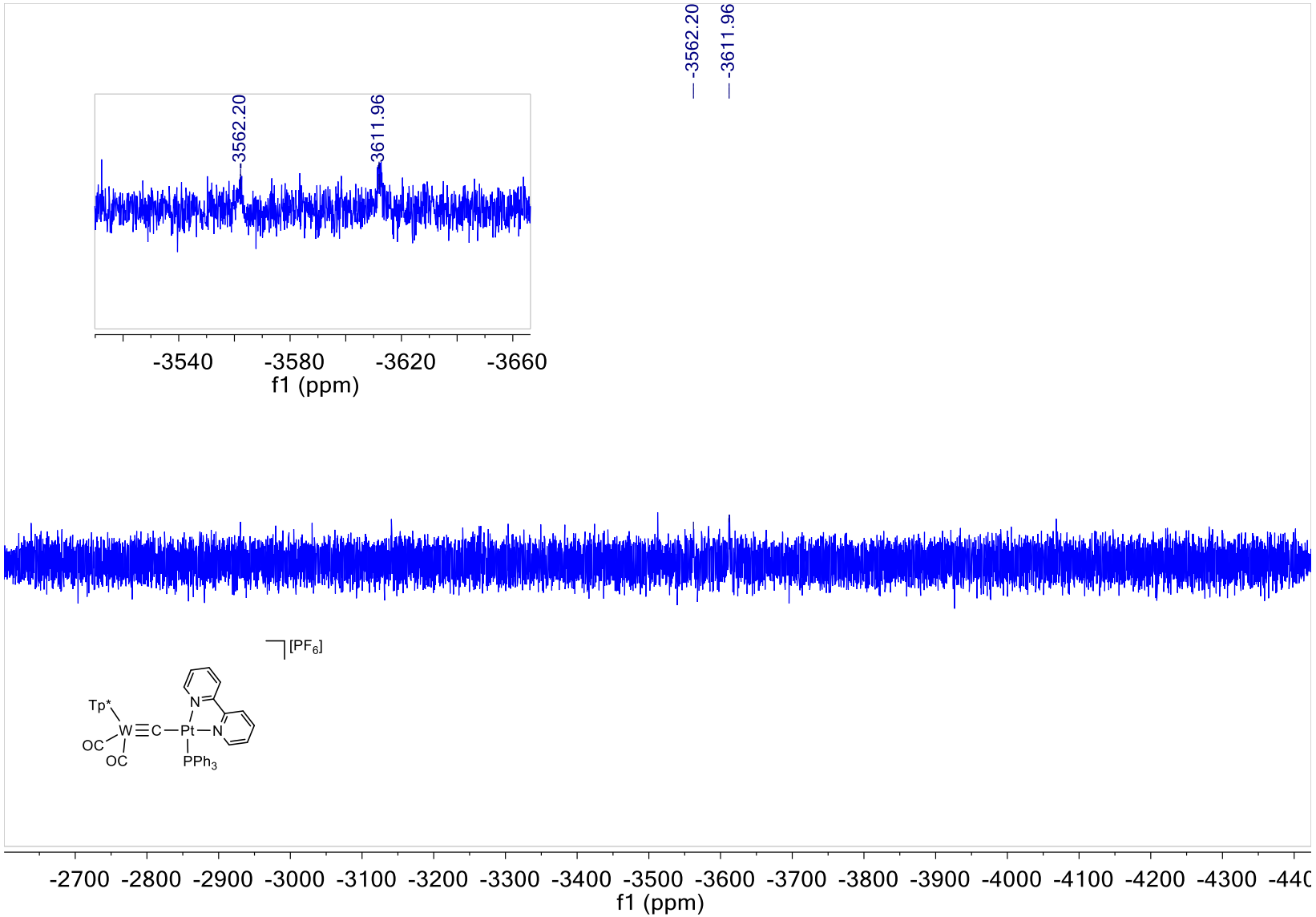


Figure S31: Infrared Spectrum of [10a]PF_6 [(Tp*)$(CO)_2$W≡C–Pt(bpy)(PPh_3)][PF_6] (CH_2Cl_2, 25 °C, ν):

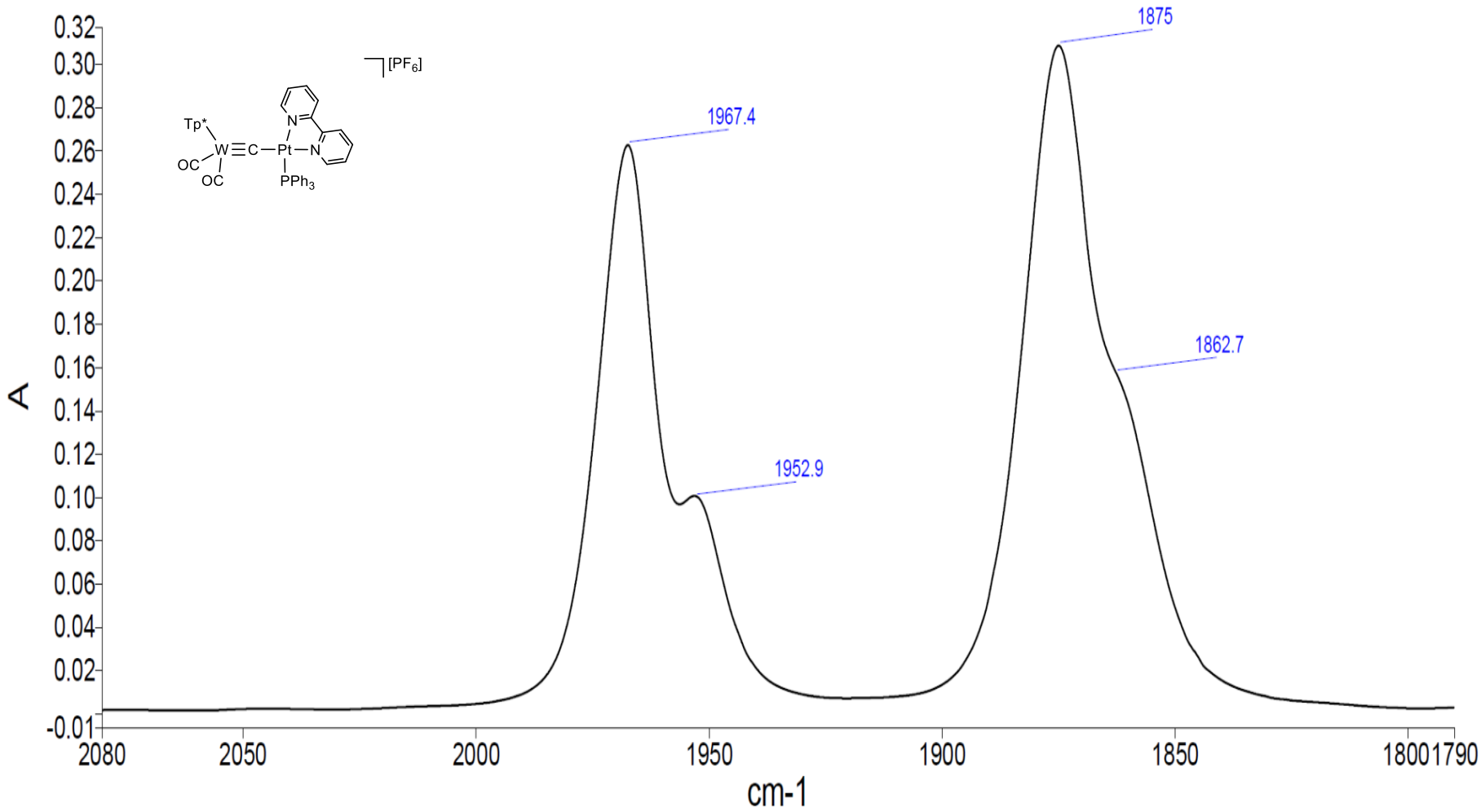


Figure S32: Mass Spectrum of [10a]PF_6 [(Tp*)$(CO)_2$W≡C–Pt(bpy)(PPh_3)][PF_6] (ESI):

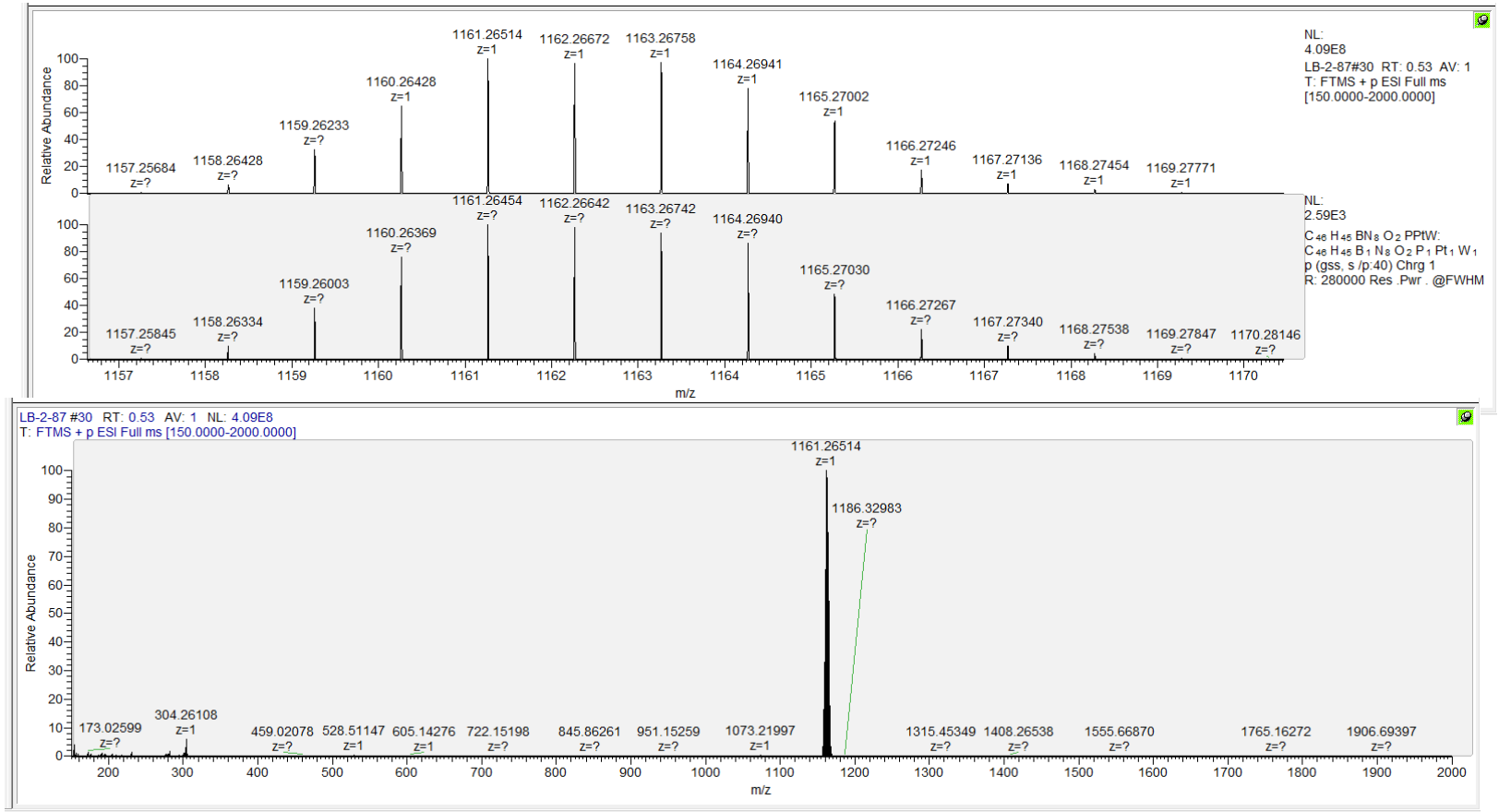


Figure S33: ^{1}H NMR Spectrum of [10b]PF_6 [(Tp*)(CO)$_2$W≡C–Pt(dtbbpy)(PPh_3)][PF_6] (400 MHz, $CDCl_3$, 25 °C, δ):

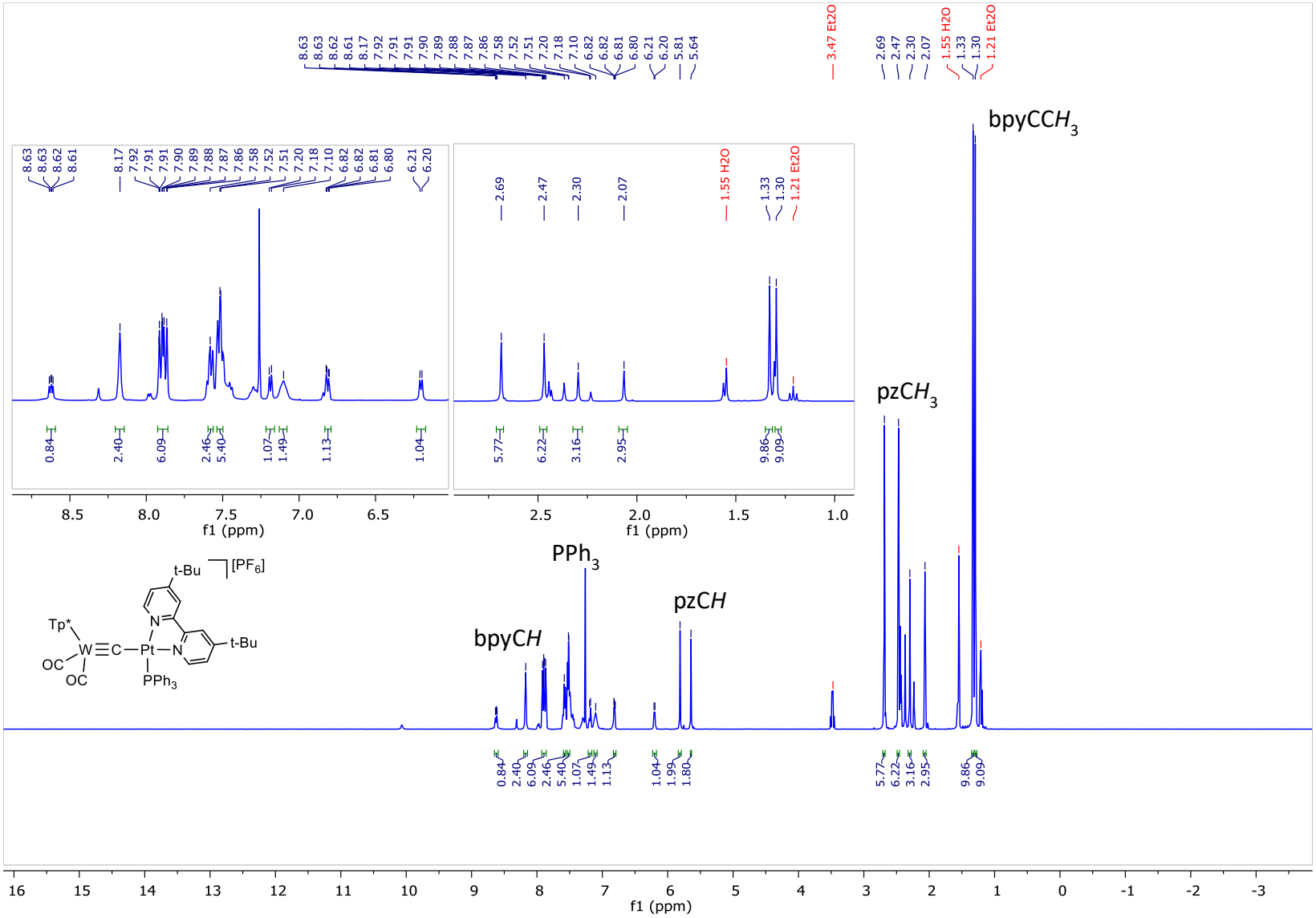


Figure S34: $^{13}C\{^{1}H\}$ NMR Spectrum of [10b]PF_6 [(Tp*)$(CO)_2$W≡C–Pt(dtbbpy)(PPh_3)][PF_6] (176 MHz, $CDCl_3$, 25 °C, δ):

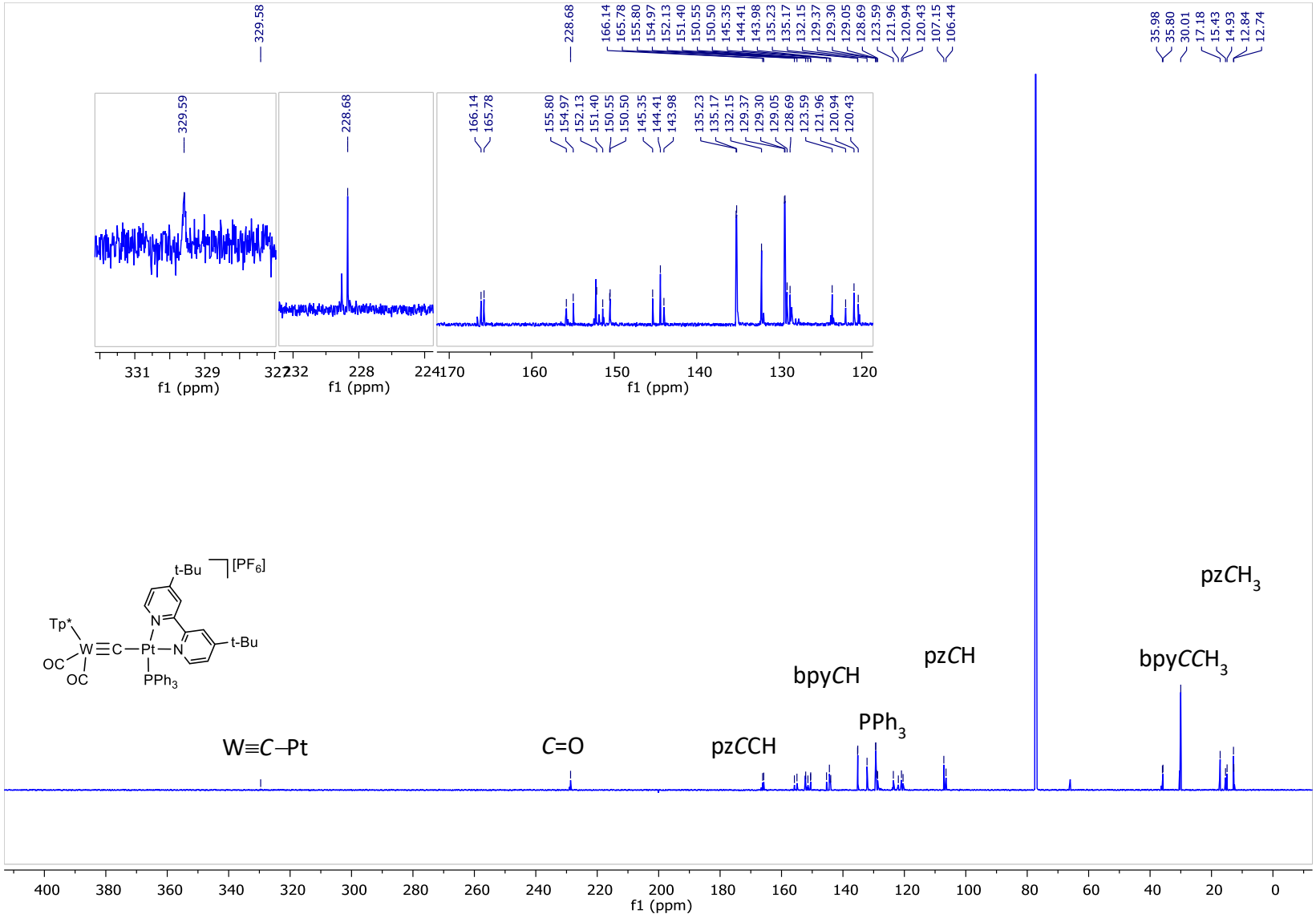


Figure S35: $^{19}F\{^{1}H\}$ NMR Spectrum of [10b]PF_6 [(Tp*)$(CO)_2$W≡C–Pt(dtbbpy)(PPh_3)][PF_6] (376 MHz, $CDCl_3$, 25 °C, δ):

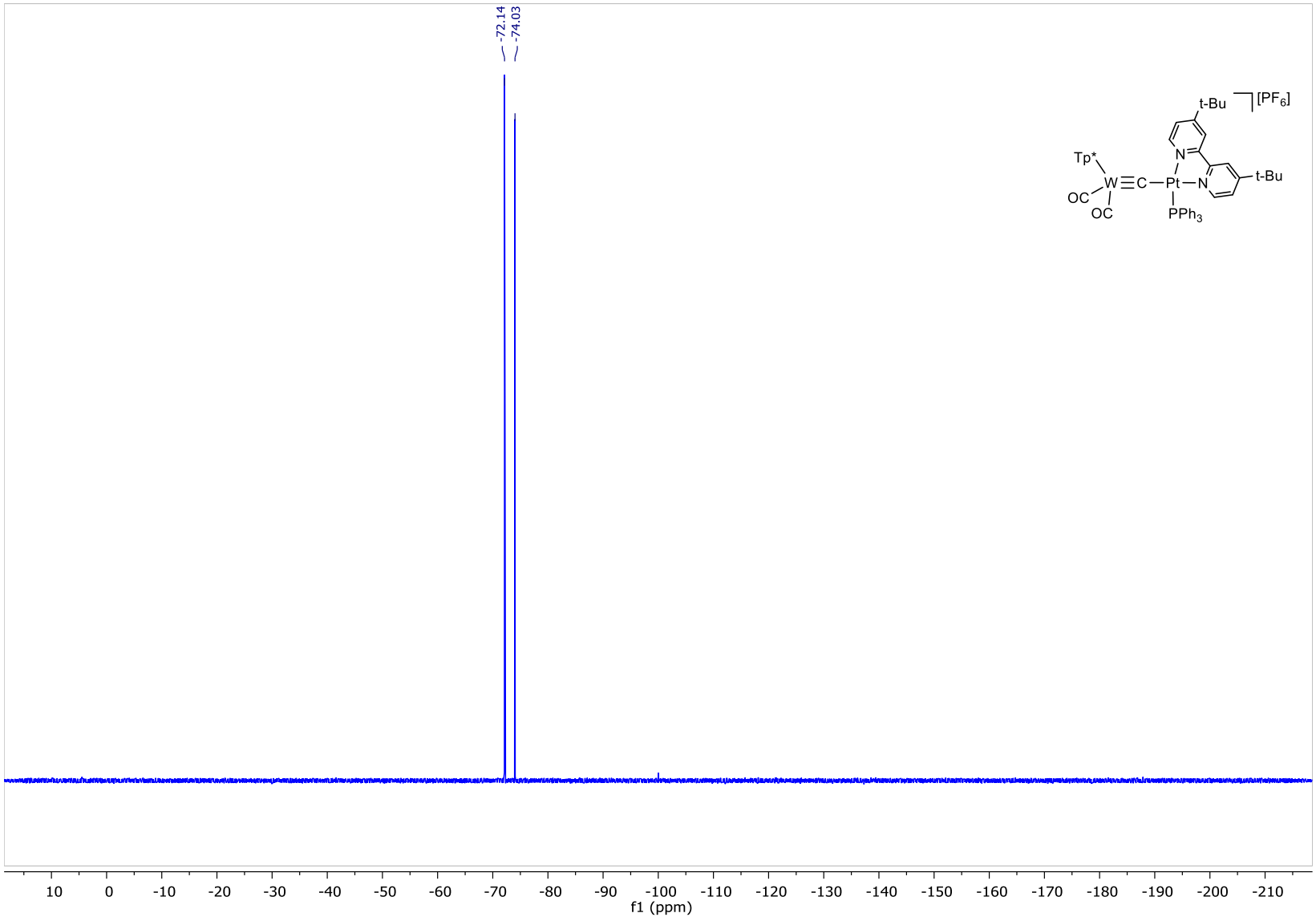


Figure S36: $^{31}P\{^{1}H\}$ NMR Spectrum of [10b]PF_6 [(Tp*)(CO)$_2$W≡C–Pt(dtbbpy)(PPh_3)][PF_6] (162 MHz, $CDCl_3$, 25 °C, δ):

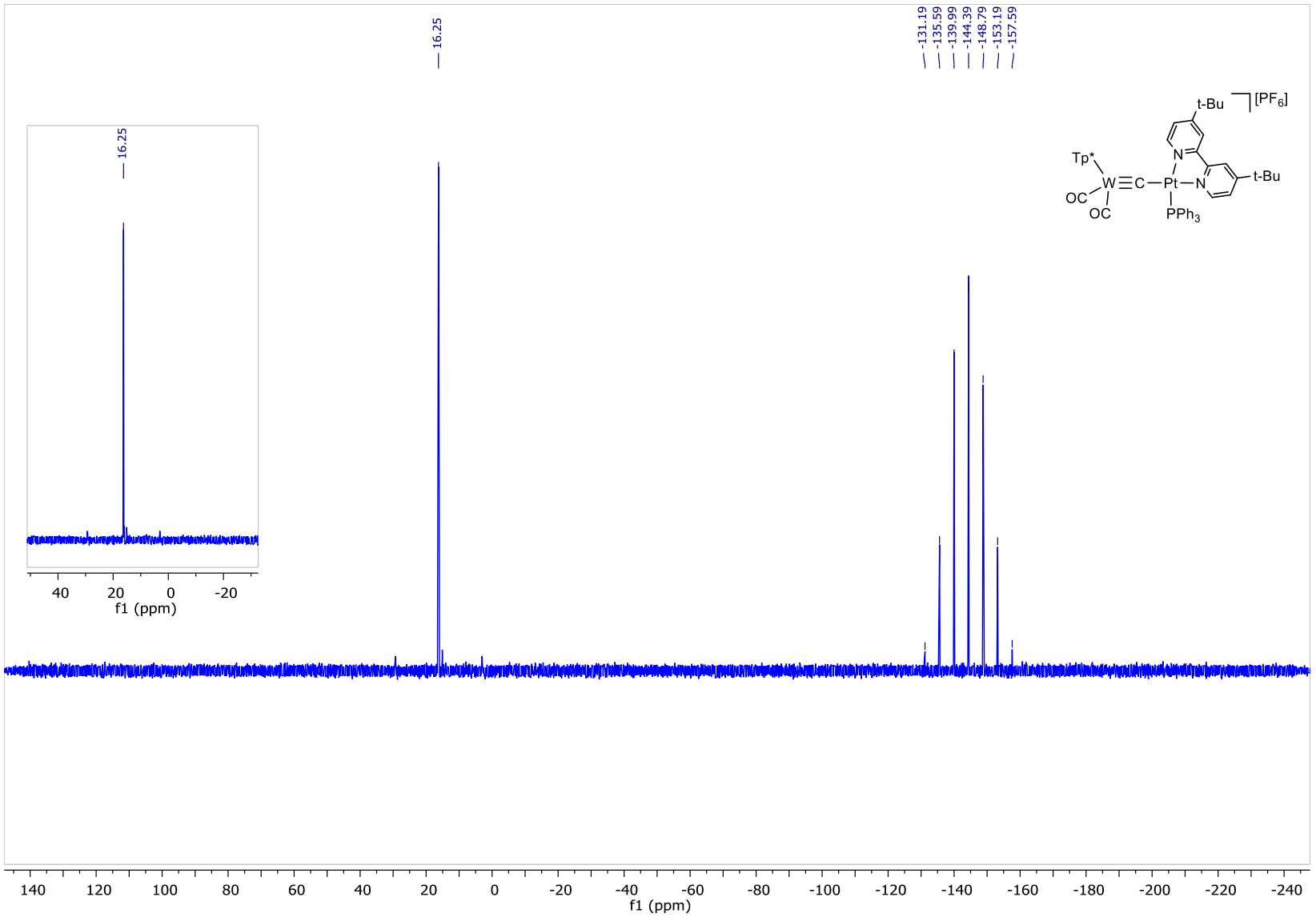


Figure S37: $^{195}Pt\{^{1}H\}$ NMR Spectrum of $[10b]PF_6$ [(Tp*)(CO)$_2$W≡C–Pt(dtbbpy)(PPh$_3$)][PF$_6$] (86 MHz, $CDCl_3$, 25 °C, δ):

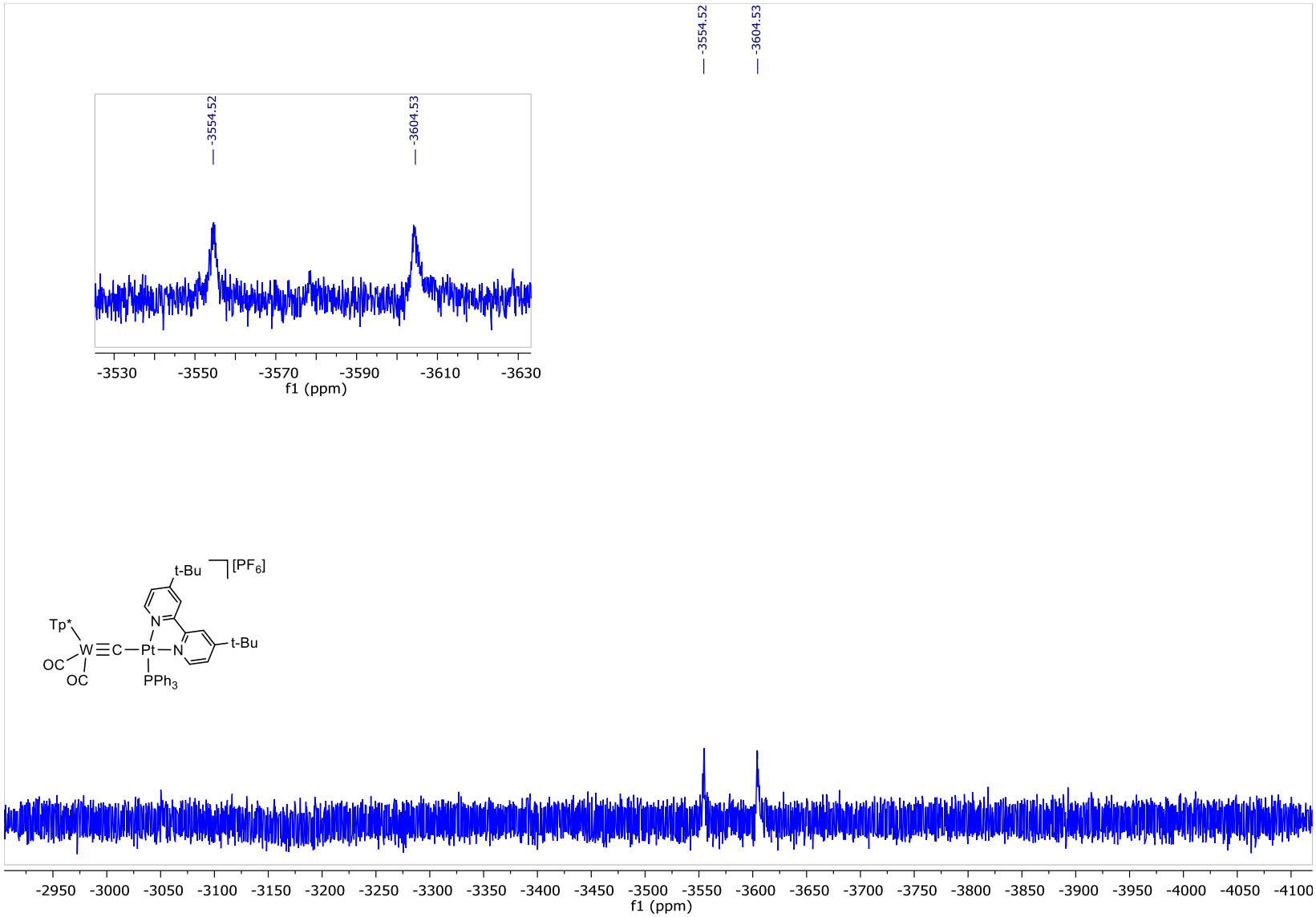


Figure S38: ^{1}H NMR Spectrum of (11) [(Tp*)(CO)$_2$W≡C–Pt(Bp*)(PPh$_3$)] (400 MHz, CDCl$_3$, 25 °C, δ):

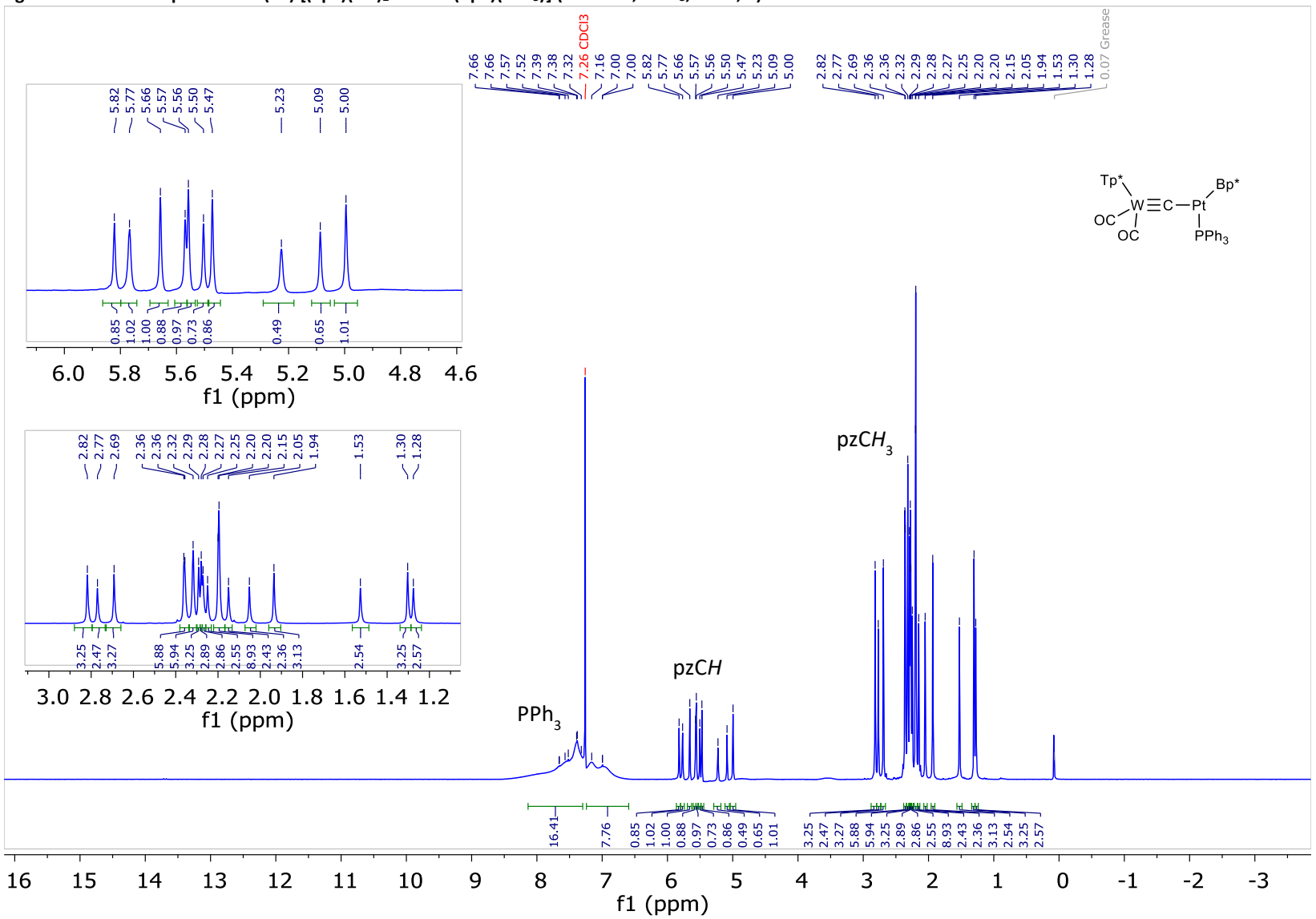


Figure S39: $^{13}C\{^{1}H\}$ NMR Spectrum of (11) [(Tp*)(CO)$_2$W≡C–Pt(Bp*)(PPh$_3$)] (151 MHz, CDCl$_3$, 25 °C, δ):

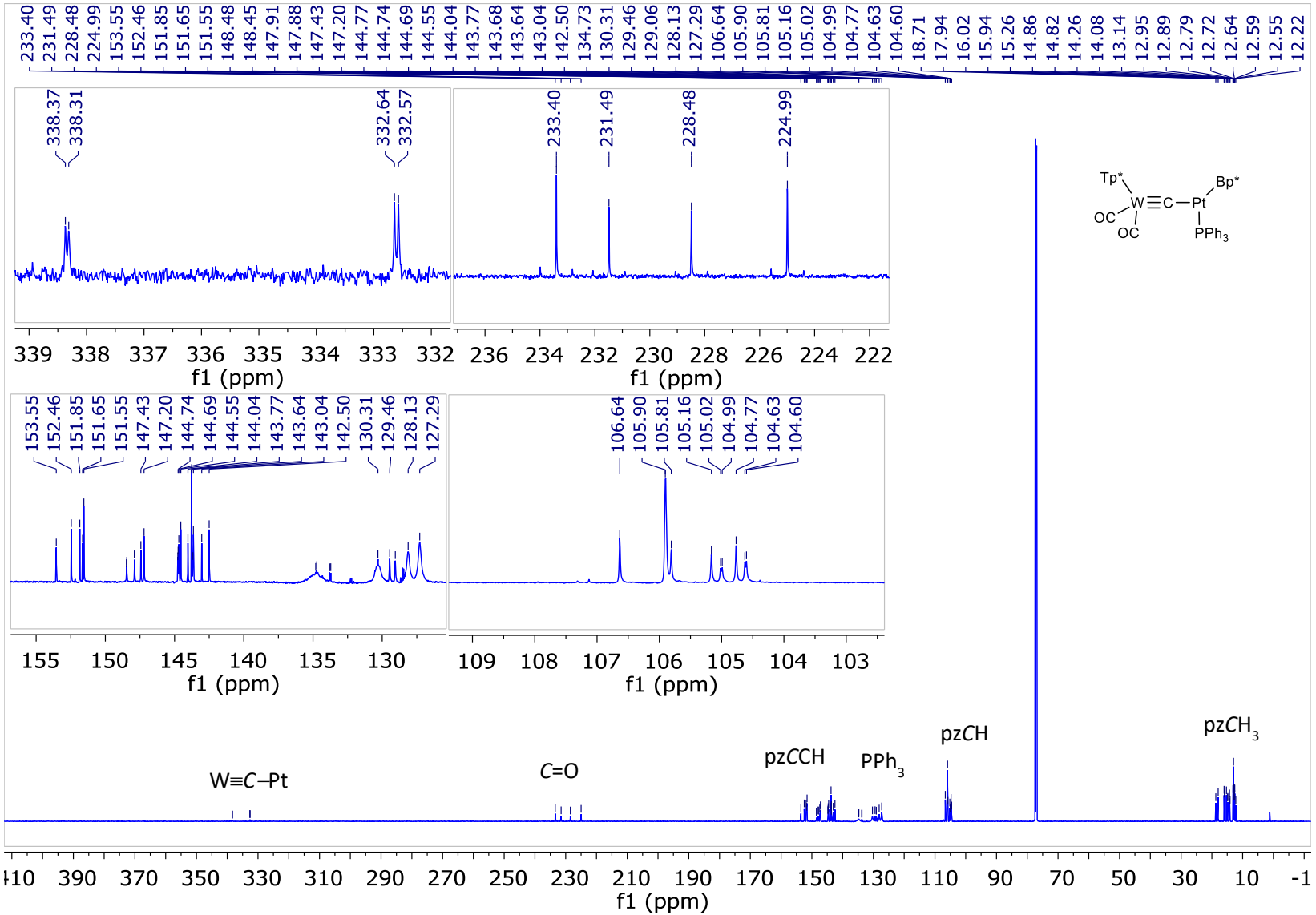


Figure S40: $^{31}P\{^{1}H\}$ NMR Spectrum of (11) [(Tp*)(CO)$_2$W≡C–Pt(Bp*)(PPh$_3$)] (283 MHz, CDCl$_3$, 25 °C, δ):

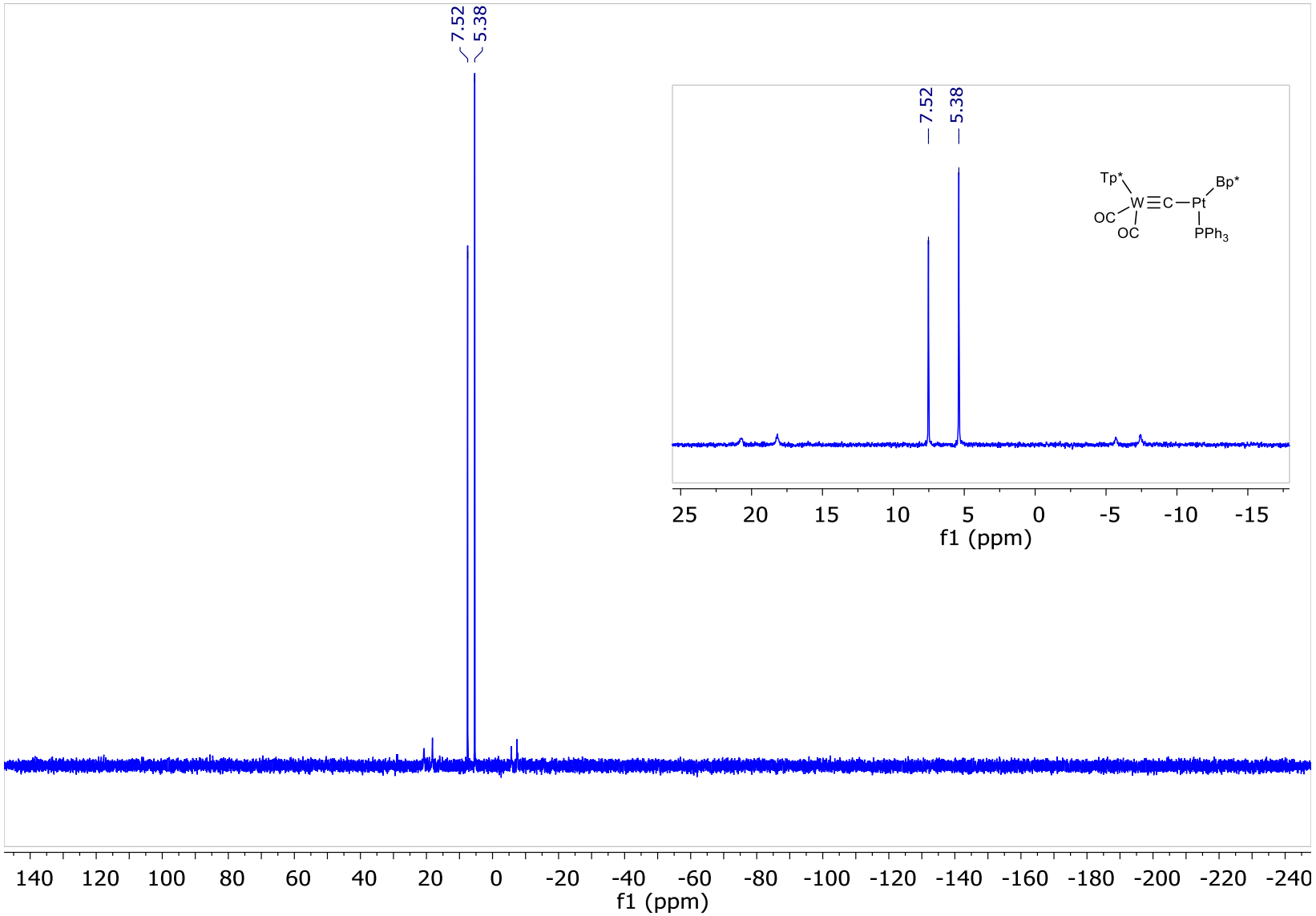


Figure S41: $^{195}Pt\{^{1}H\}$ NMR Spectrum of (11) [(Tp*)(CO)$_2$W≡C–Pt(Bp*)(PPh$_3$)] (283 MHz, $CDCl_3$, 25 °C, δ):

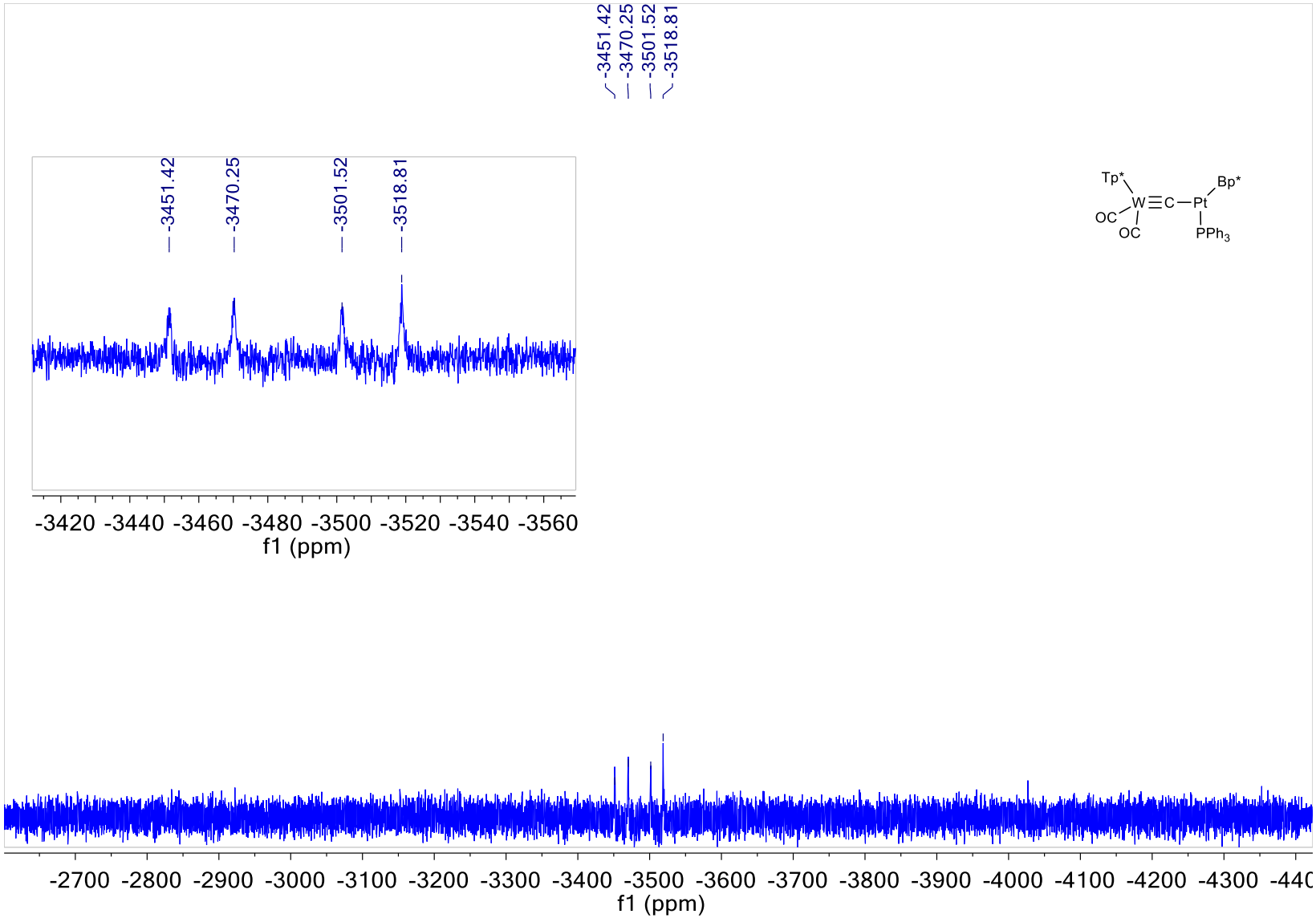


Figure S42: Infrared Spectrum of (11) [(Tp*)(CO)$_2$W≡C–Pt(Bp*)(PPh$_3$)] (CH$_2$Cl$_2$, 25 °C, ν):

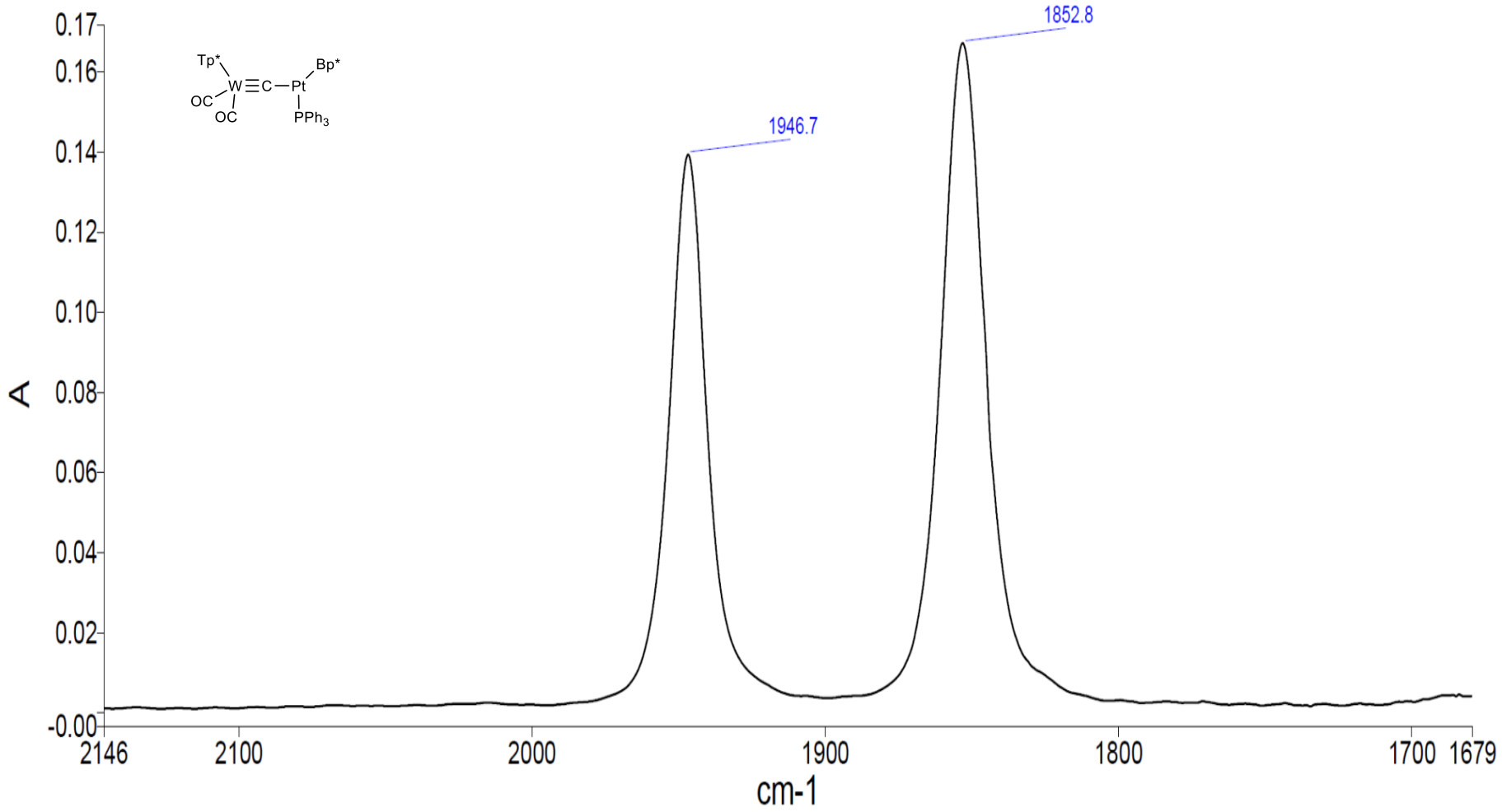


Figure S43: ^{1}H NMR Spectrum of (12) [(Tp*)(CO)$_2$W≡C–Pt(κ$_2$-Tp*)(PPh$_3$)] (400 MHz, CDCl$_3$, 25 °C, δ):

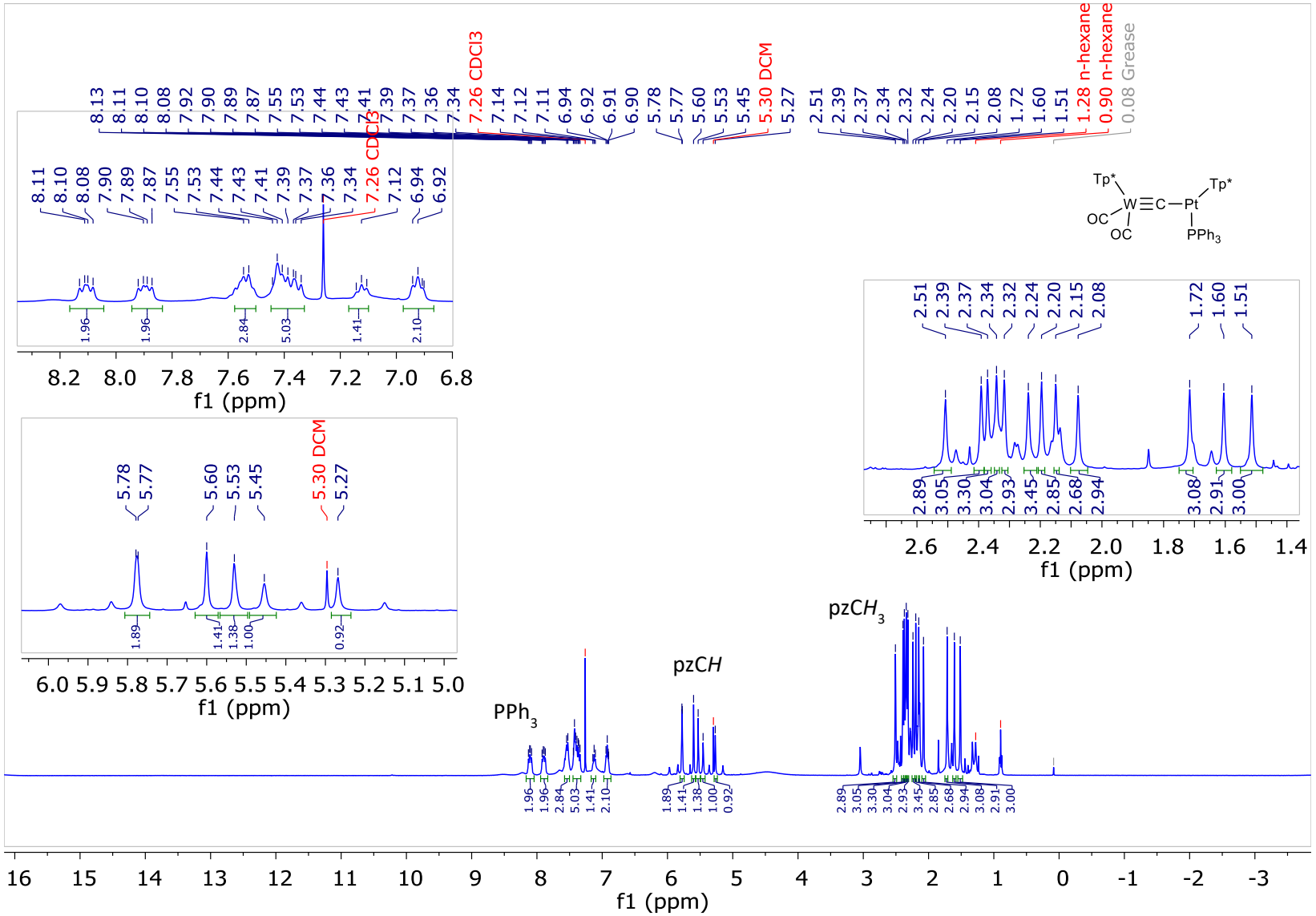


Figure S44: $^{13}C\{^{1}H\}$ NMR Spectrum of (12) [(Tp*)(CO)$_2$W≡C–Pt(κ$_2$-Tp*)(PPh$_3$)] (151 MHz, $CDCl_3$, 25 °C, δ):

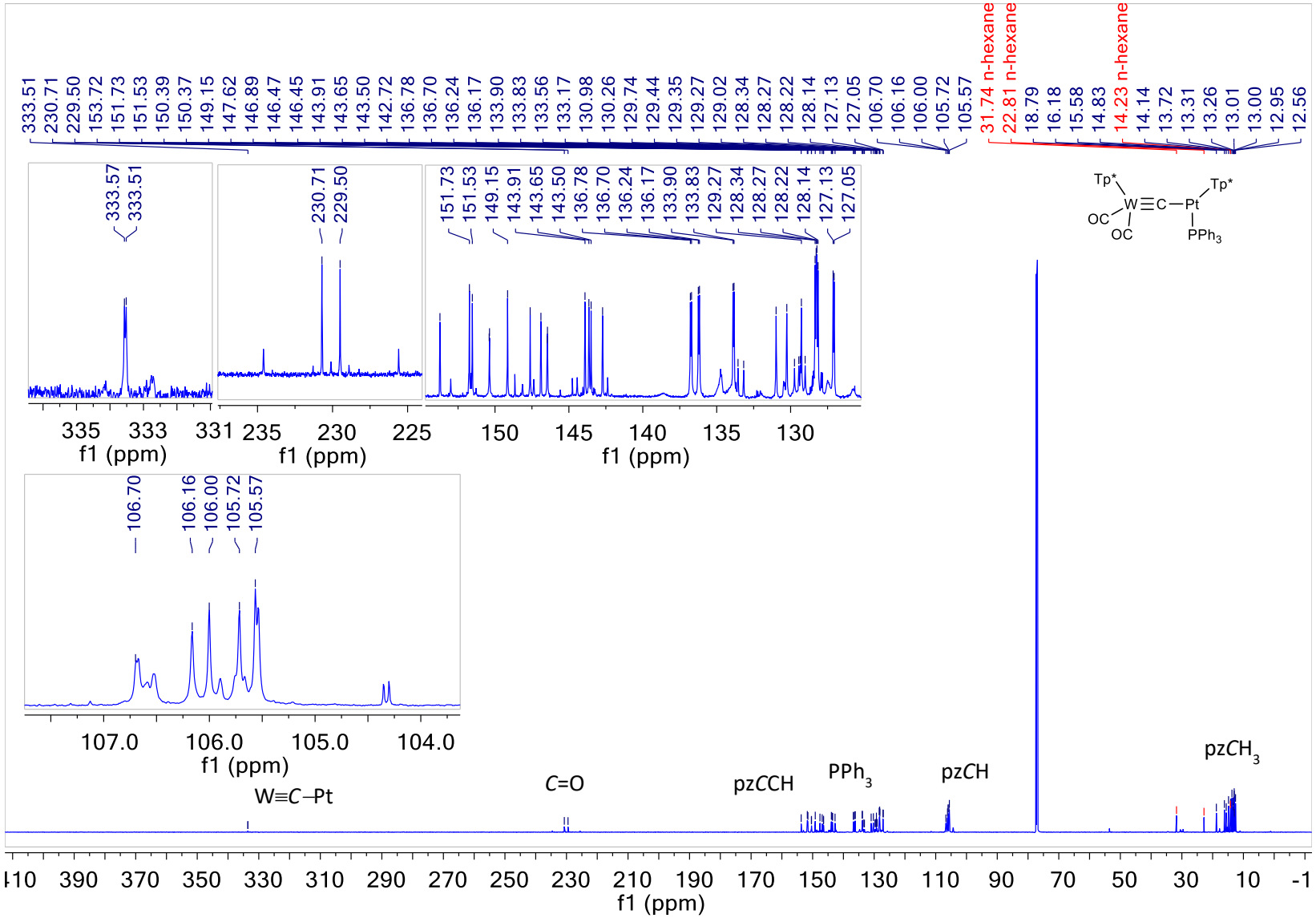


Figure S45: $^{31}P\{^{1}H\}$ NMR Spectrum of (12) [(Tp*)(CO)$_2$W≡C–Pt(κ$_2$-Tp*)(PPh$_3$)] (162 MHz, CDCl$_3$, 25 °C, δ):

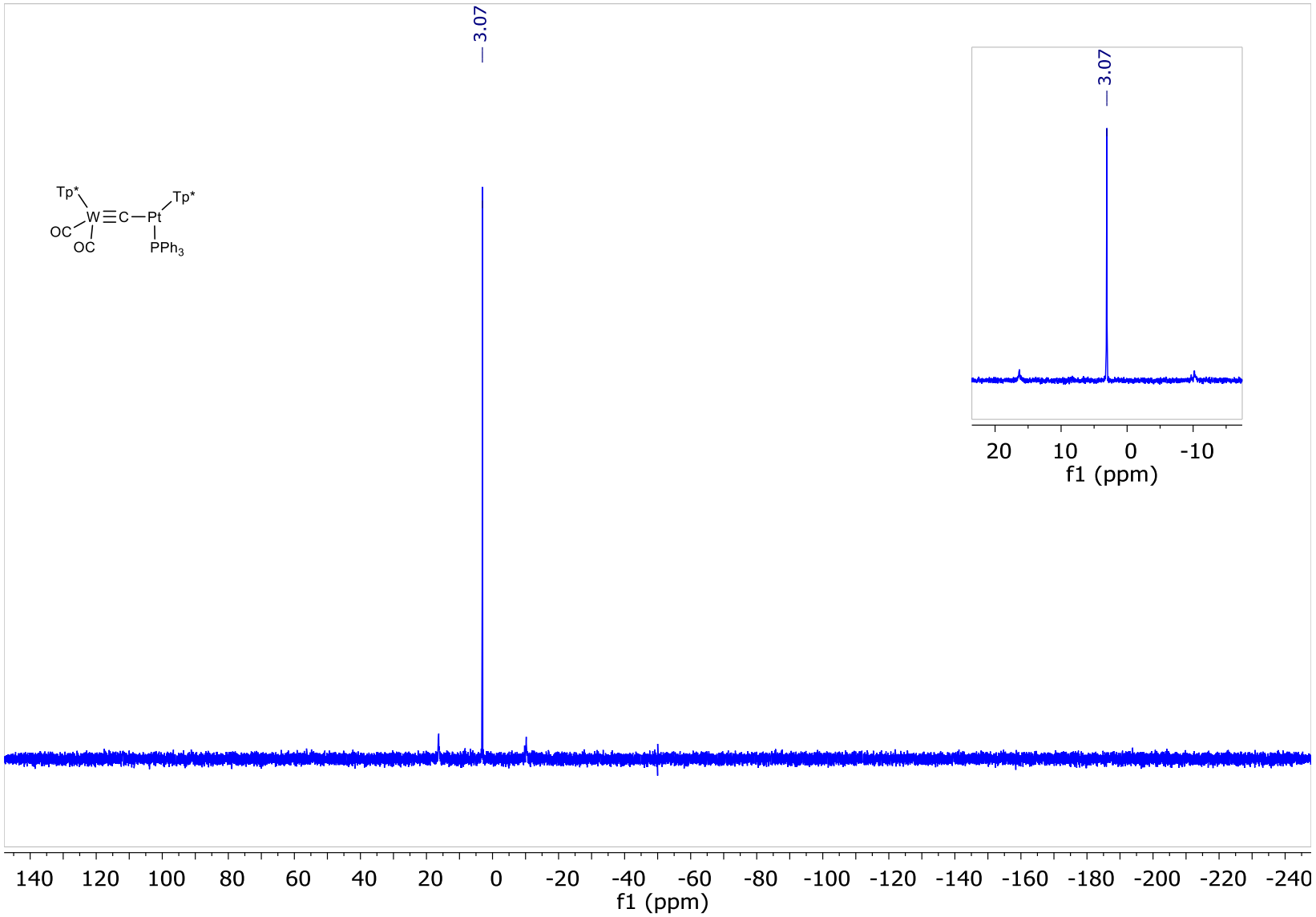


Figure S46: $^{195}Pt\{^{1}H\}$ NMR Spectrum of (12) [(Tp*)(CO)$_2$W≡C–Pt(κ$_2$-Tp*)(PPh$_3$)] (86 MHz, CDCl$_3$, 25 °C, δ):

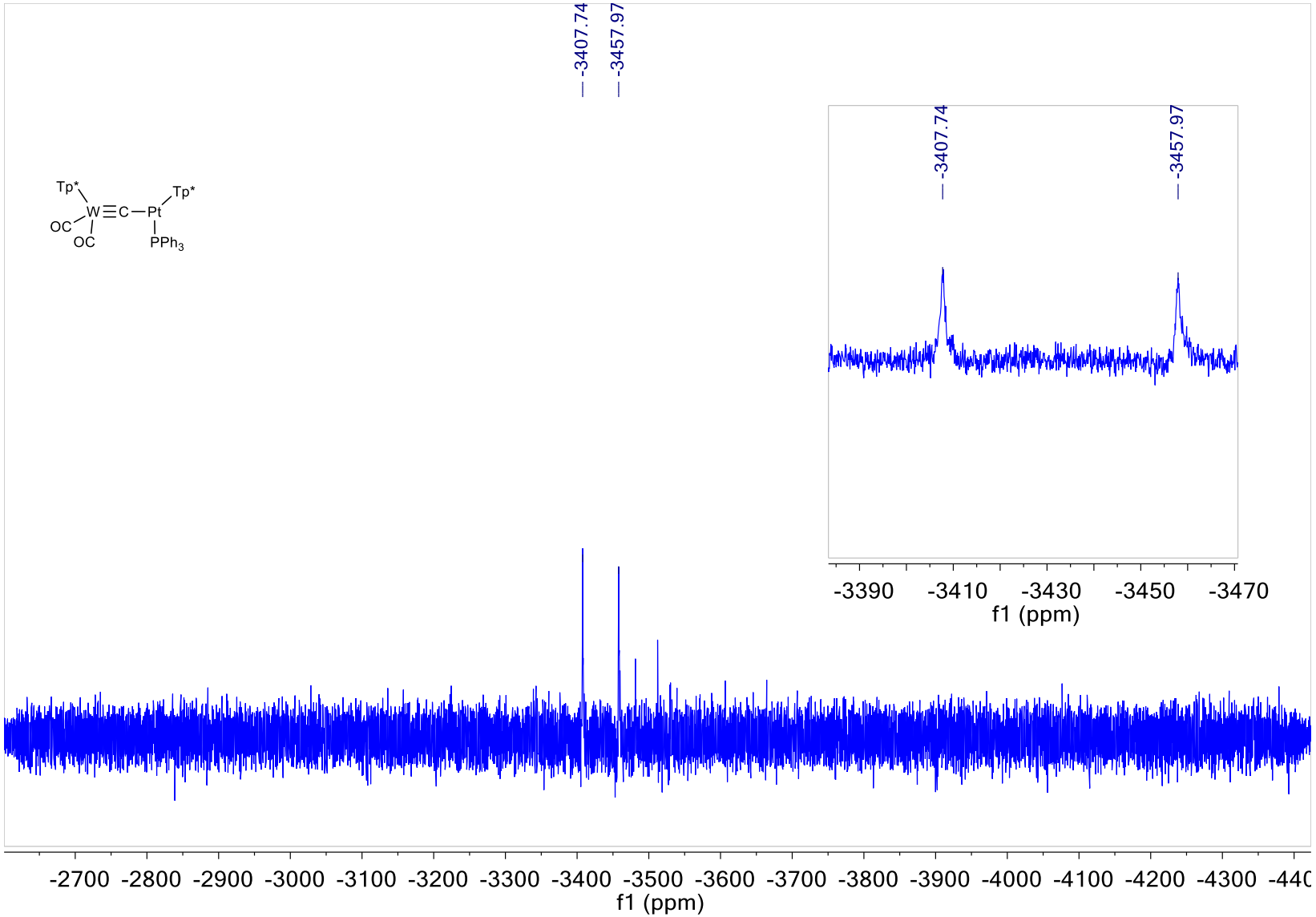


Figure S47: Infrared Spectrum of (12) [(Tp*)(CO)$_2$W≡C–Pt(κ$_2$-Tp*)(PPh$_3$)] (CH$_2$Cl$_2$, 25 °C, ν):

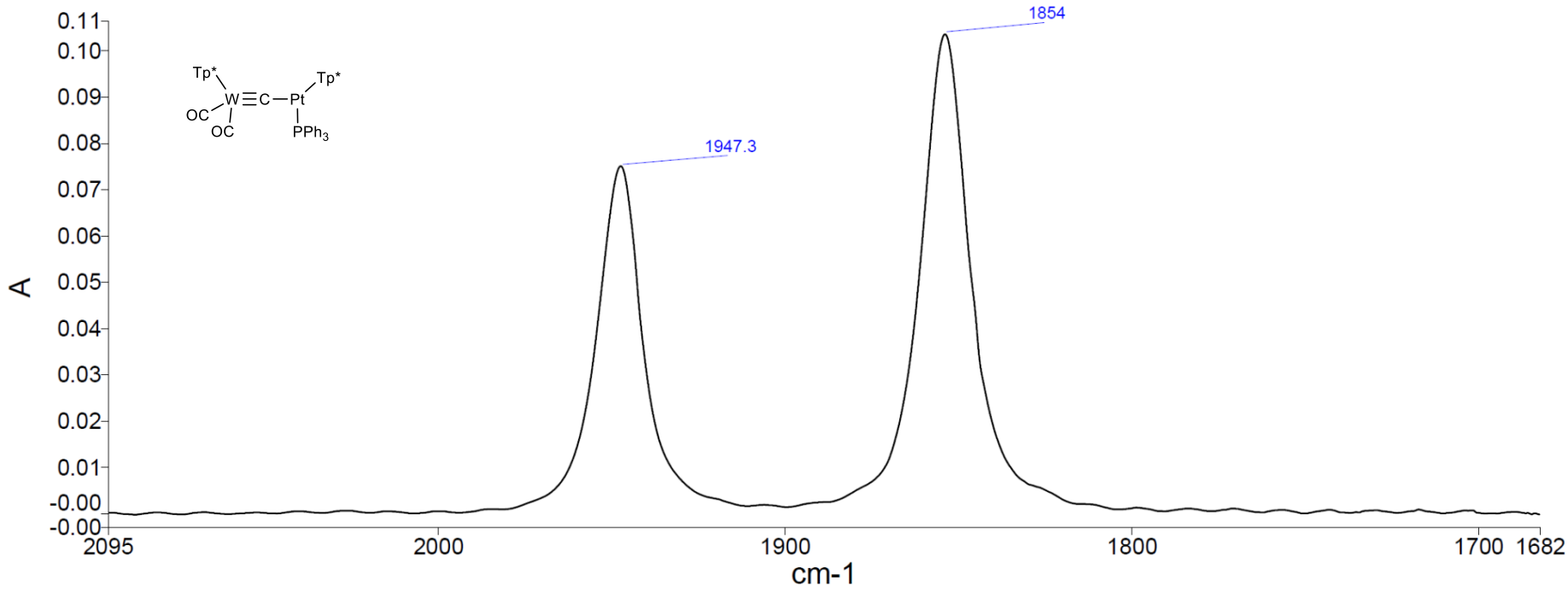
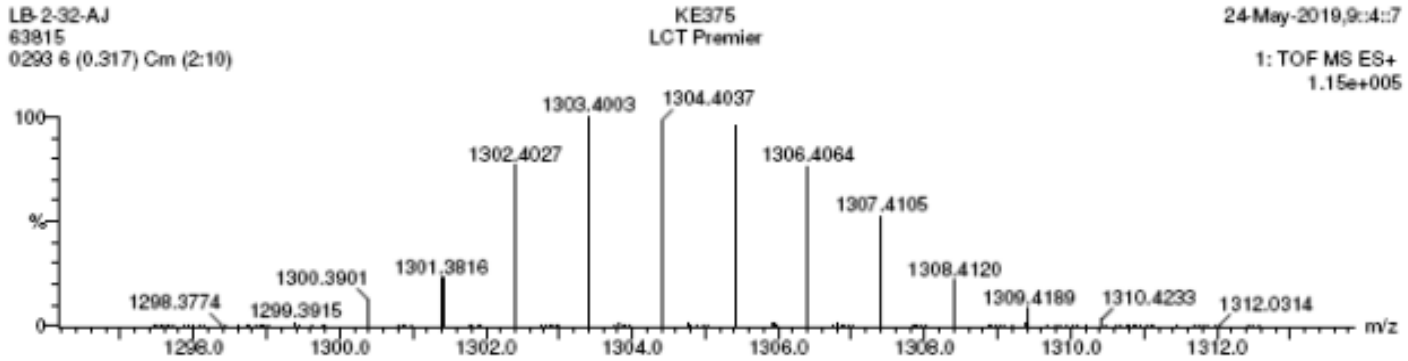


Figure S48: Mass Spectrum of (12) [(Tp*)(CO)$_2$W≡C–Pt(κ$_2$-Tp*)(PPh$_3$)] (ESI):

Single Mass Analysis
Tolerance = 3.0 PPM / DBE: min = -1.5, max = 32.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
1198 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-55 H: 0-60 11B: 0-2 N: 0-15 O: 0-2 P: 0-1 184W: 0-1 195Pt: 0-1



Minimum:				-1.5		
Maximum:		5.0	3.0	32.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
1304.4037	1304.4043	-0.6	-0.5	32.0	26501.1	C51 H60 11B2 N12 O2 P 184W 195Pt

Figure S49: ^{1}H NMR Spectrum of (13) [(Tp*)W≡C–Pt(Bm^{Me})(PPh$_3$)] (400 MHz, CDCl$_3$, 25 °C, δ):

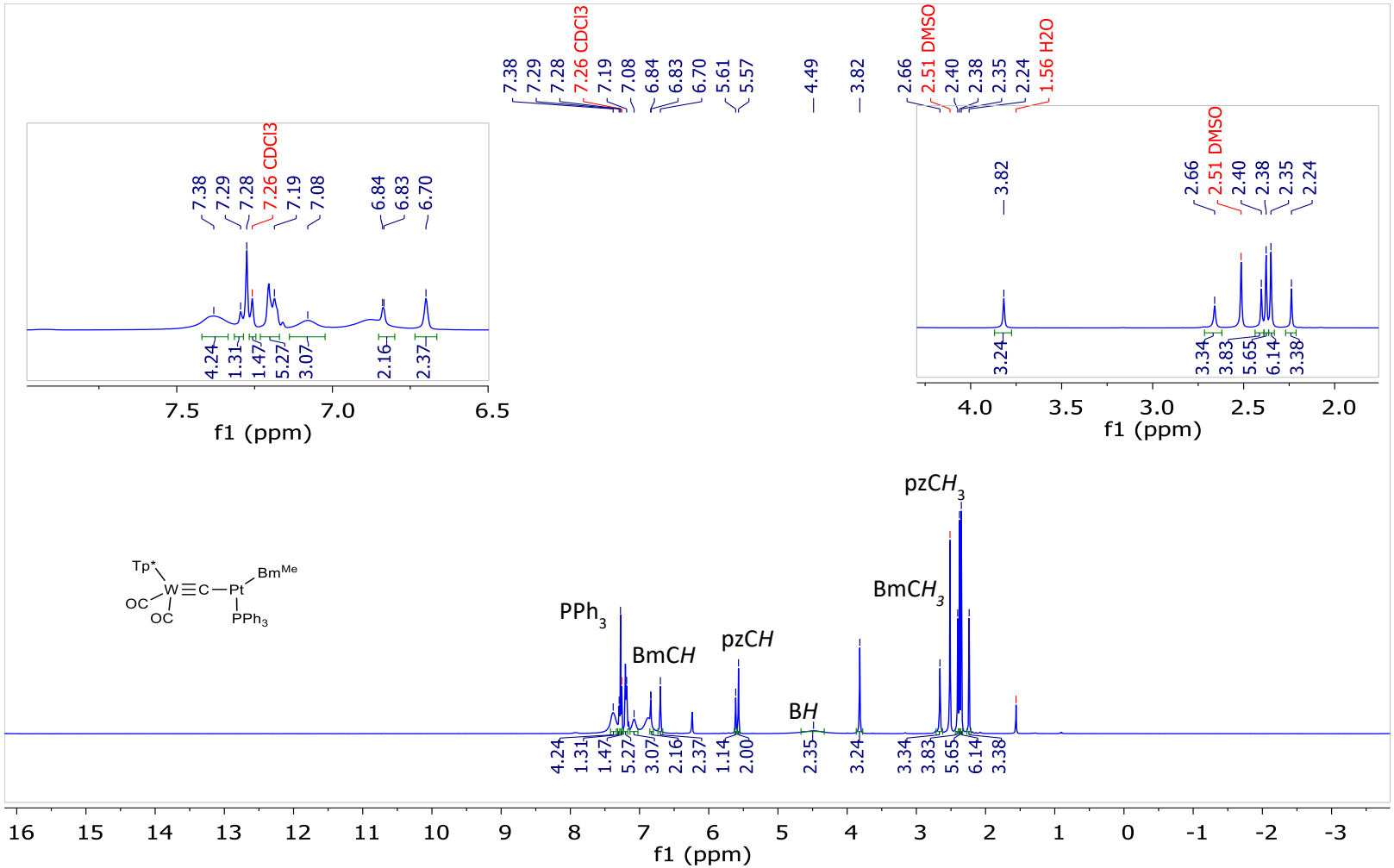


Figure S50: $^{13}C\{^{1}H\}$ NMR Spectrum of (13) [(Tp*)W≡C–Pt(Bm^{Me})(PPh$_3$)] (151 MHz, $CDCl_3$, 25 °C, δ):

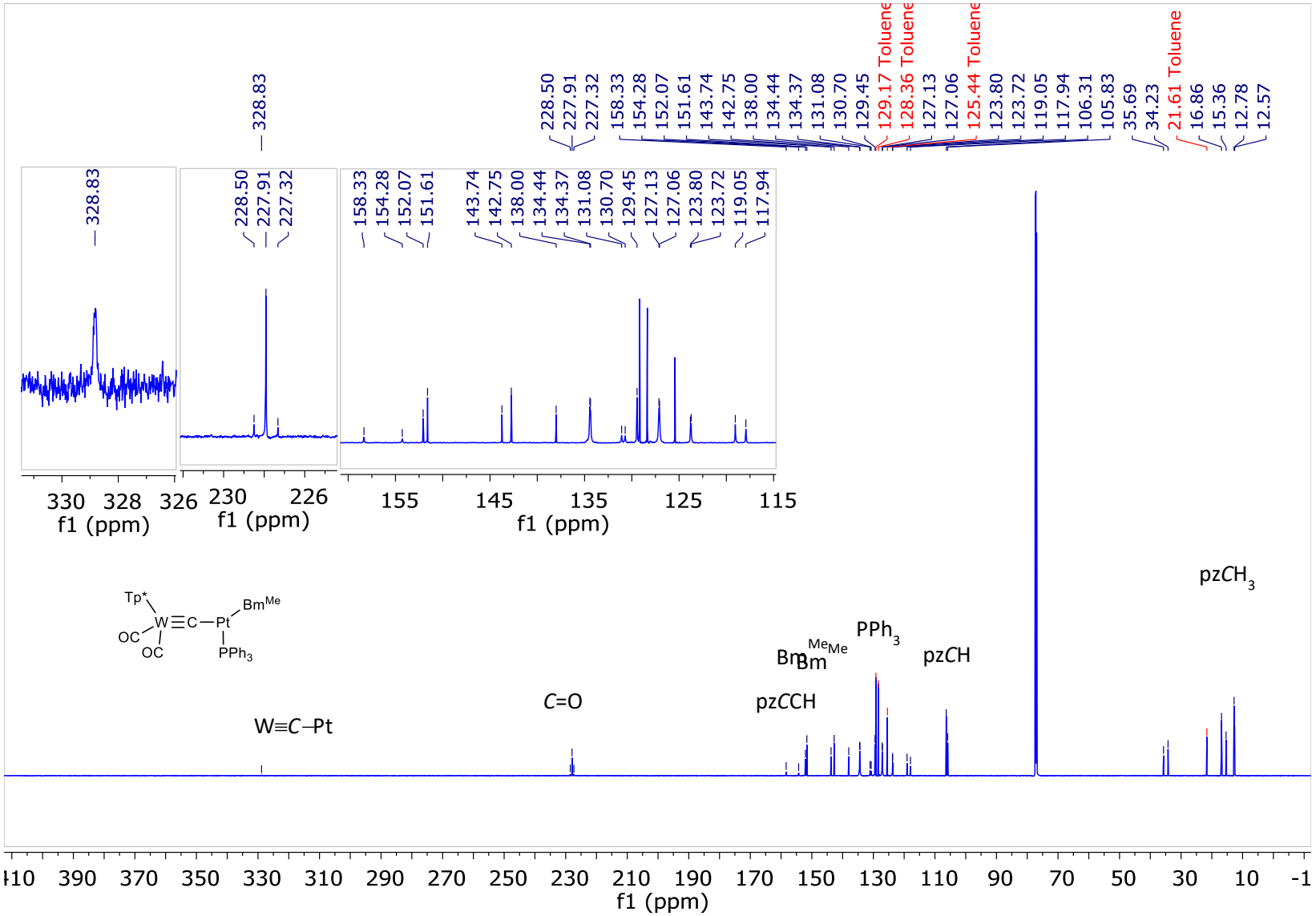


Figure S51: $^{31}P\{^{1}H\}$ NMR Spectrum of (13) [(Tp*)W≡C–Pt(Bm^{Me})(PPh_3)] (162 MHz, $CDCl_3$, 25 °C, δ):

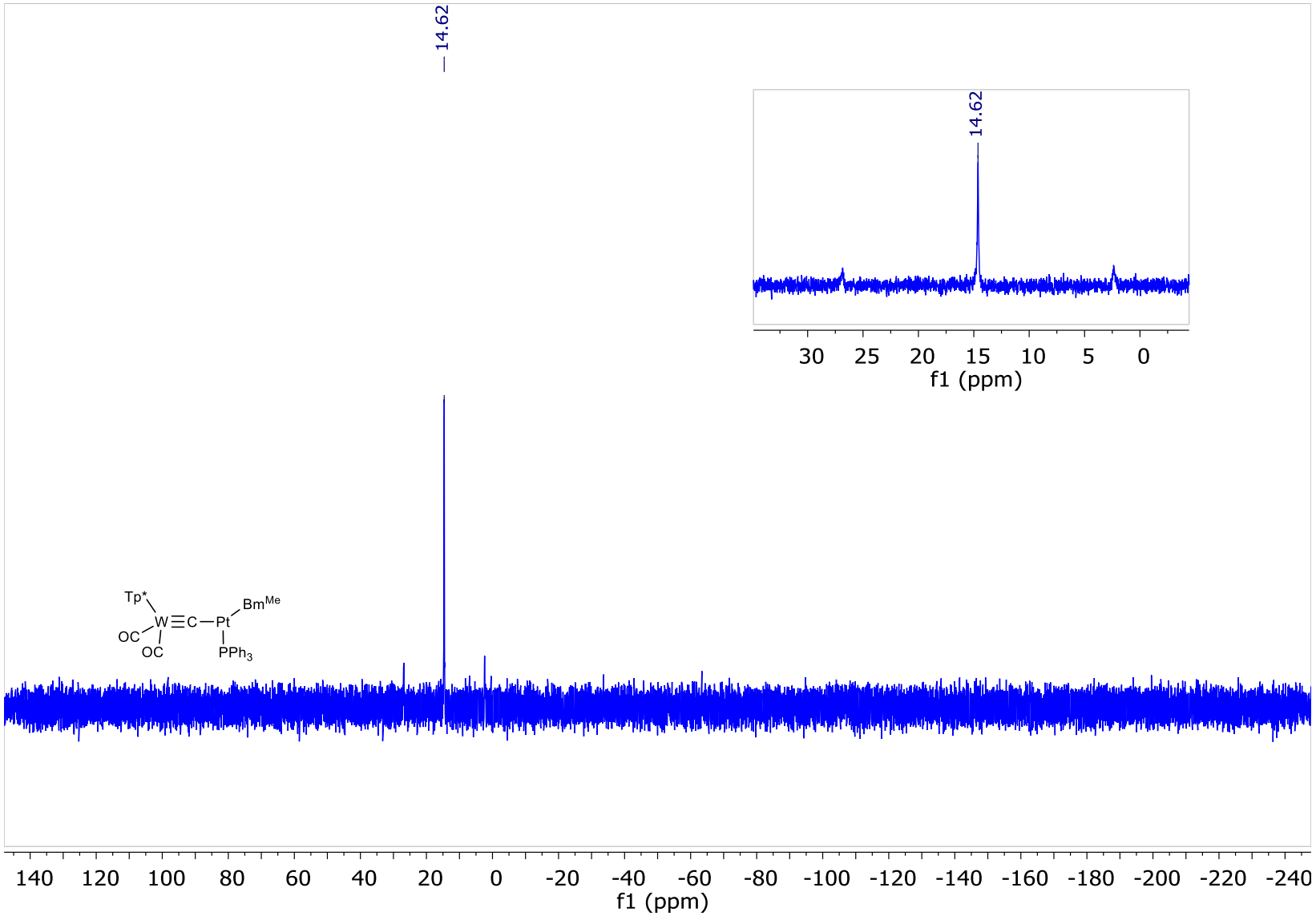


Figure S52: $^{195}Pt\{^{1}H\}$ NMR Spectrum of (13) [(Tp*)W≡C–Pt(Bm^{Me})(PPh_3)] (86 MHz, $CDCl_3$, 25 °C, δ):

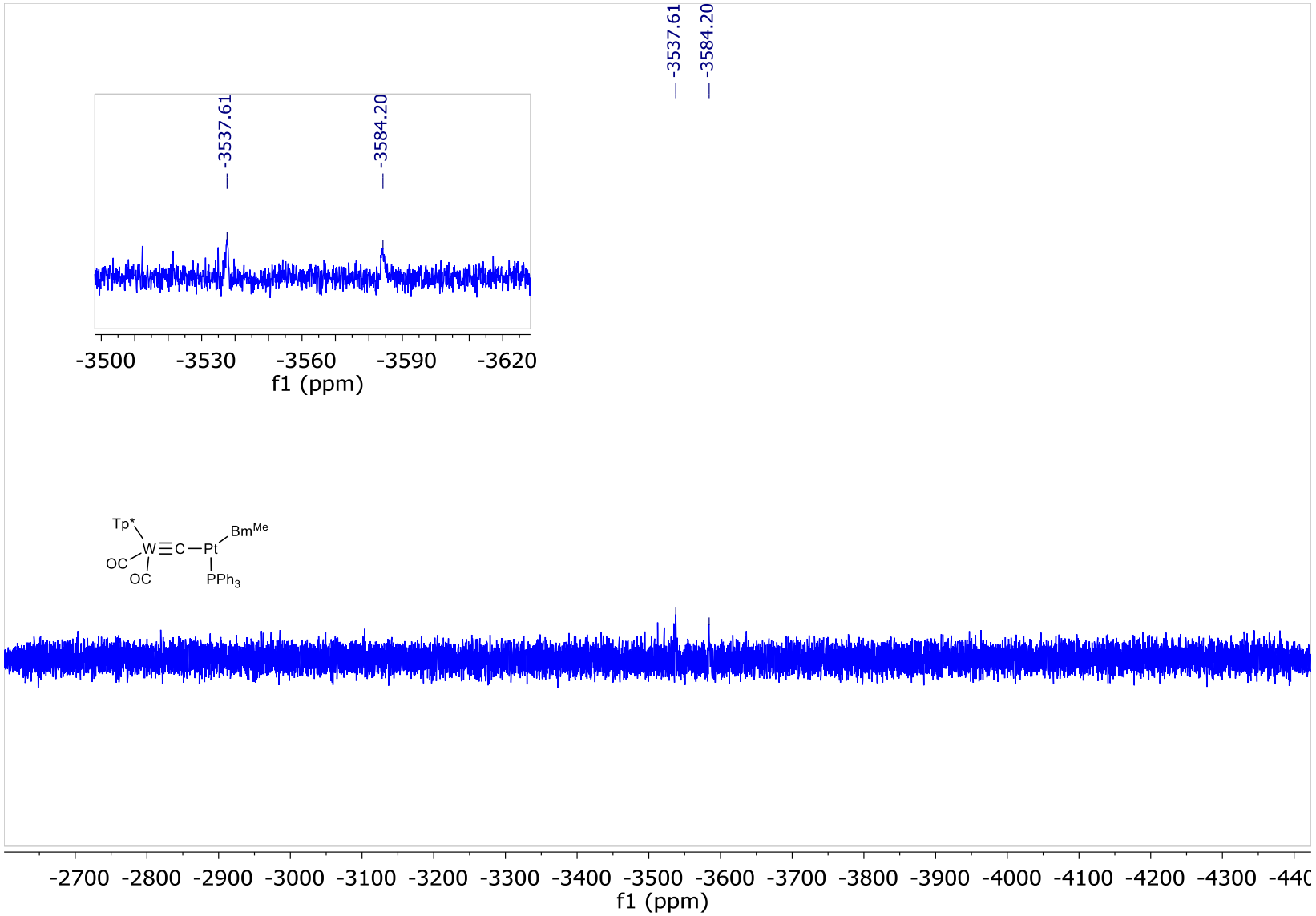


Figure S53: Infrared Spectrum of (13) [(Tp*)W≡C–Pt(Bm^{Me})(PPh$_3$)] (CH_2Cl_2, 25 °C, ν):

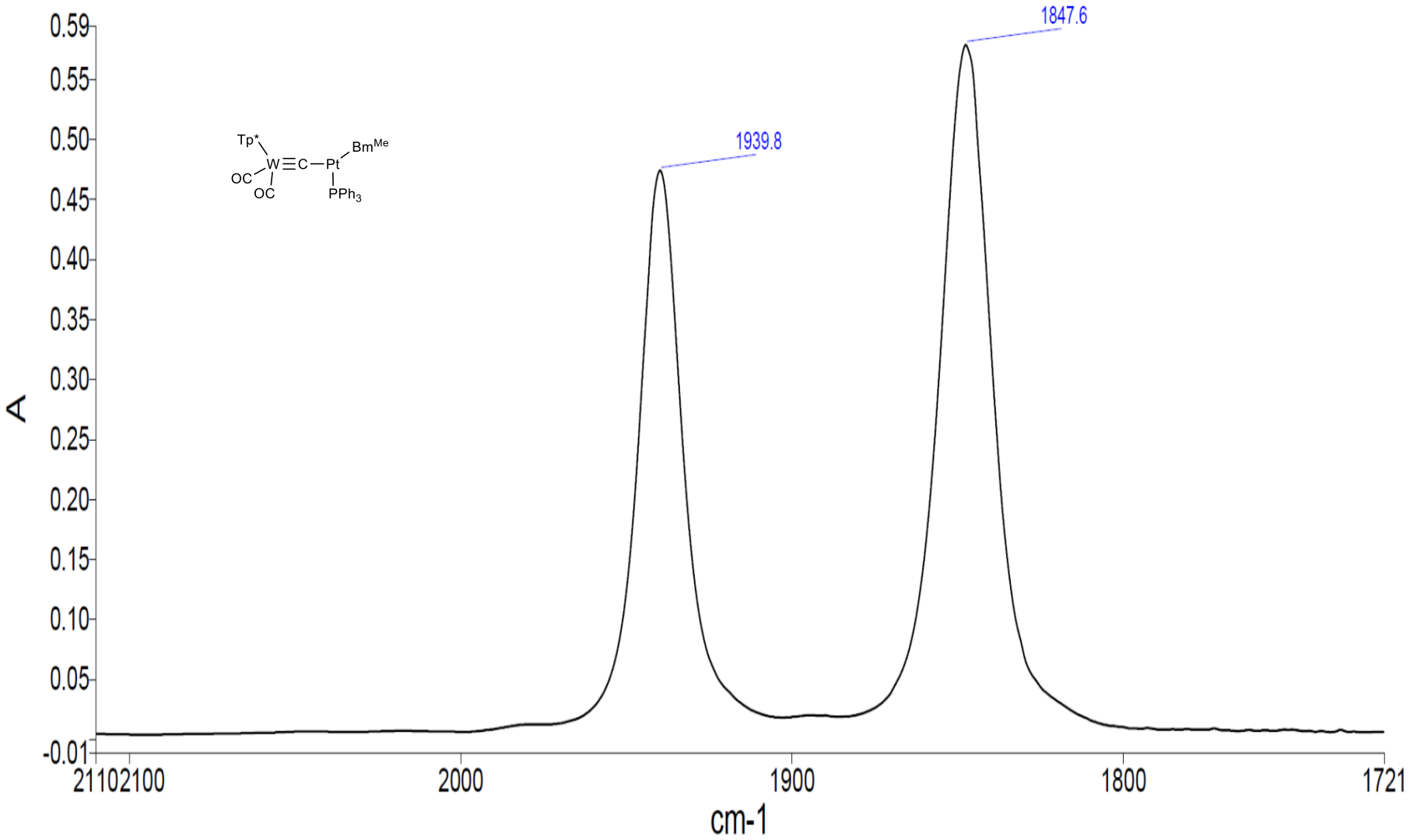
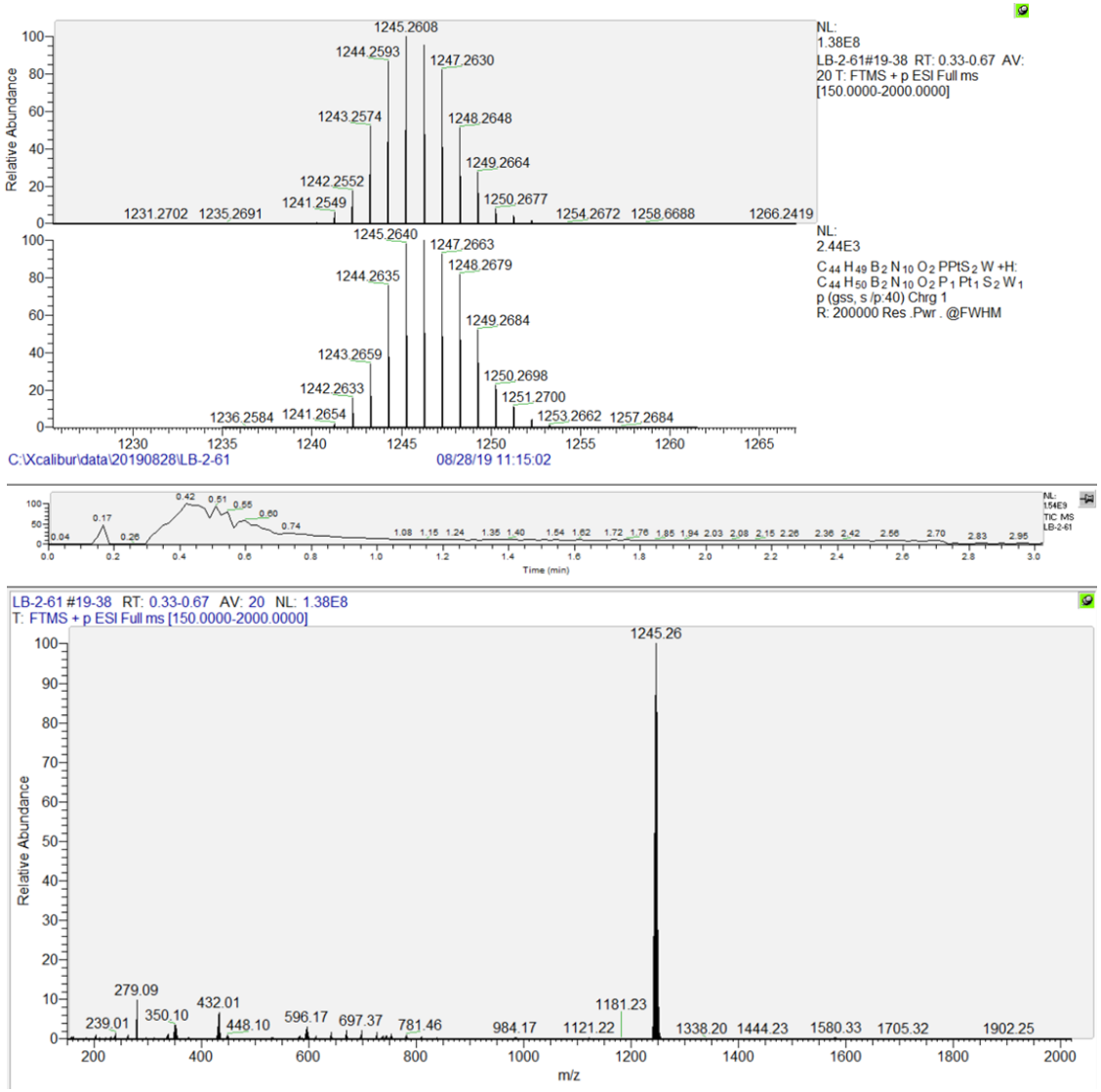


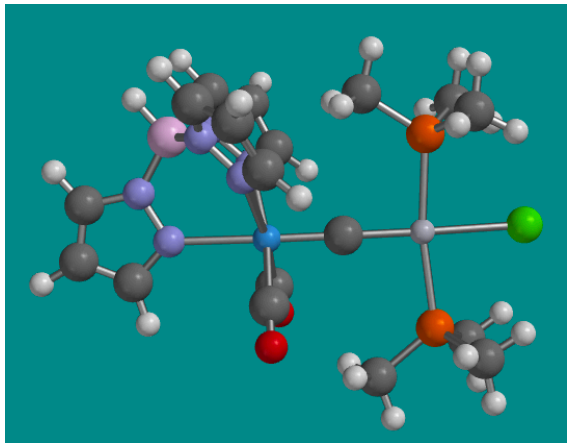
Figure S54: Mass Spectrum of (13) [(Tp*)W≡C–Pt(Bm^{Me})(PPh$_3$)] (ESI):



Computational Details

Computational studies were performed by using the *SPARTAN18* suite of programs.[1] Geometry optimisation (gas phase) was performed at the DFT level of theory using the exchange functional of Becke[2] for **1Cl*** (for consistency with reference 6) and the ωB97X-D functional of Head-Gordon[3] for **1Br***. The Los Alamos effective core potential type basis set (LANL2Dζ) of Hay and Wadt[4] was used for Pt and W Pople 6-31G* basis sets[5] 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 (ν_{WCPt}).

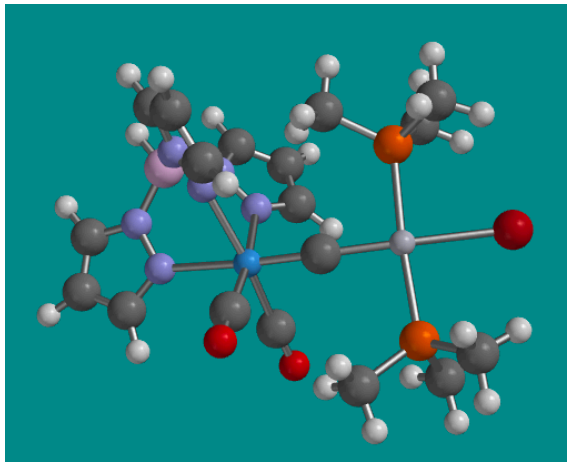
[WPt(μ-C)Cl(CO)$_2$(PMe$_3$)$_2$(Tp)] 1Cl*



Cartesian Coordinates

Atom	x	y	z
Pt	1.074876	2.352687	0.574721
W	-0.837563	-0.471792	-1.027986
Cl	2.255928	4.242487	1.745010
P	0.409132	3.995586	-0.999227
P	1.971817	0.988337	2.288612
O	-3.265457	1.541316	-1.183212
O	0.206362	0.451700	-3.861932
N	-2.122251	-2.229117	-1.943237
N	-2.083203	-3.468788	-1.384095
N	-1.615553	-1.460938	0.853115
N	-1.642091	-2.813038	1.000142
N	0.642527	-2.173616	-0.919559
N	0.277683	-3.421131	-0.516254
C	0.140352	0.902738	-0.267504
C	-2.369575	0.792790	-1.136801
C	-0.191160	0.112807	-2.817375
C	-2.986768	-2.294509	-2.963307
C	-3.519514	-3.586569	-3.075623
H	-4.237440	-3.948656	-3.796456
C	-2.915947	-4.298245	-2.049553
C	-2.129482	-0.938154	1.975931
C	-2.487757	-1.956754	2.869674
H	-2.926207	-1.854411	3.851190
C	-2.164559	-3.131300	2.204806
C	1.948900	-2.228348	-1.217387
C	2.446585	-3.520238	-0.998077
H	3.455273	-3.876232	-1.145665
C	1.347935	-4.244164	-0.556809
B	-1.191333	-3.744258	-0.152050
H	-1.288455	-4.892998	0.184653
H	-3.016739	-5.330509	-1.745804
H	-3.182082	-1.414489	-3.560637
H	-2.272231	-4.166116	2.496096
H	-2.210765	0.135187	2.075633
H	1.247950	-5.282871	-0.276989
C	1.658675	-0.822486	2.298541
H	0.585114	-1.016229	2.344857
H	2.153351	-1.279186	3.162857
H	2.041885	-1.273616	1.380582
C	1.422277	1.539335	3.956433
H	0.344719	1.377169	4.053055
H	1.627771	2.607855	4.054764
H	1.942425	0.982469	4.744136
C	3.808727	1.106875	2.345050
H	4.091843	2.160016	2.410804
H	4.225712	0.688140	1.424309
H	4.206337	0.555683	3.204796
C	1.888957	4.784379	-1.756022
H	1.598287	5.609432	-2.415742
H	2.433119	4.032227	-2.335056
H	2.537123	5.151615	-0.957319
C	-0.645241	3.588267	-2.449423
H	-1.605920	3.187709	-2.119334
H	-0.157888	2.841479	-3.079770
H	-0.818631	4.497934	-3.035670
C	-0.503051	5.364624	-0.176369
H	-1.470851	4.990609	0.171099
H	-0.664927	6.198021	-0.868790
H	0.079089	5.697285	0.685805
H	2.451911	-1.338001	-1.567635

[WPt(μ-C)Br(CO)$_2$(PMe$_3$)$_2$(Tp)] 1Br*



Cartesian Coordinates

Atom	x	y	z
Pt	1.063511	2.322691	0.581614
W	-0.753007	-0.417685	-1.172536
Br	1.843811	4.234028	2.165306
P	0.426290	3.957386	-0.975599
P	1.915117	0.804784	2.167343
O	-2.970019	1.803661	-1.317771
O	0.254696	0.357730	-4.053367
N	-2.184288	-2.170256	-1.813914
N	-2.164671	-3.350010	-1.155357
N	-1.456799	-1.204244	0.819641
N	-1.514143	-2.519892	1.113397
N	0.609860	-2.202975	-1.053303
N	0.241857	-3.361741	-0.466512
C	0.274376	0.912374	-0.456603
C	-2.170841	0.958376	-1.276780
C	-0.131728	0.064175	-2.998691
C	-3.104722	-2.276633	-2.770793
C	-3.697861	-3.543405	-2.740880
H	-4.471236	-3.930484	-3.385971
C	-3.065662	-4.190573	-1.694759
C	-1.814310	-0.540971	1.920505
C	-2.103148	-1.438712	2.953448
H	-2.424525	-1.212327	3.958394
C	-1.901230	-2.687123	2.390239
C	1.875637	-2.349114	-1.446733
C	2.346909	-3.619874	-1.104138
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C	1.268765	-4.229175	-0.486282
B	-1.205086	-3.572941	0.028740
H	-1.333380	-4.682792	0.477294
H	-3.190272	-5.186213	-1.294876
H	-3.291330	-1.439474	-3.428801
H	-2.010964	-3.679860	2.801068
H	-1.832150	0.539930	1.905882
H	1.154002	-5.218146	-0.067814
C	1.864092	-0.987540	1.823608
H	0.832892	-1.317694	1.692456
H	2.322537	-1.535150	2.653399
H	2.406693	-1.205467	0.901275
C	1.136430	0.946580	3.814680
H	0.099679	0.605926	3.750536
H	1.151615	1.993812	4.125764
H	1.670403	0.331271	4.546251
C	3.692089	1.109422	2.474846
H	3.825961	2.145458	2.793741
H	4.248187	0.956522	1.545806
H	4.071540	0.426545	3.242174
C	1.749045	5.179346	-1.290284
H	1.392787	5.954975	-1.976213
H	2.608853	4.670286	-1.734653
H	2.061393	5.626378	-0.344496
C	-0.042152	3.433183	-2.660068
H	-0.940921	2.816389	-2.628734
H	0.762604	2.842725	-3.103451
H	-0.232294	4.314660	-3.281034
C	-1.000529	4.940410	-0.400460
H	-1.873624	4.286311	-0.326735
H	-1.216990	5.756996	-1.096943
H	-0.772803	5.345599	0.588755
H	2.374370	-1.529956	-1.944431

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1 *Spartan18®* (2018) Wavefunction, Inc., 18401 Von Karman Ave., Suite 370 Irvine, CA 92612 U.S.A

2 (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652. (b) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623-11627.

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4 (a) P. J. Hay and W.R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270-283. (b) W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284-298. (c) P. J. Hay, W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299-310.

5 W. J. Hehre, R. Ditchfeld and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257-2261.