Dalton Transactions

SUPPORTING INFORMATION

Electronic Supporting Information for:

Metal coordination of phosphoniocarbynes

Chee S. Onn, Anthony F. Hill and Angus Olding

Cartesian coordinates for model complexes and Selected Spectra

Dalton Transactions

SUPPORTING INFORMATION

Figure S1. ^{1}H NMR Spectrum of [**1a**]PF_6

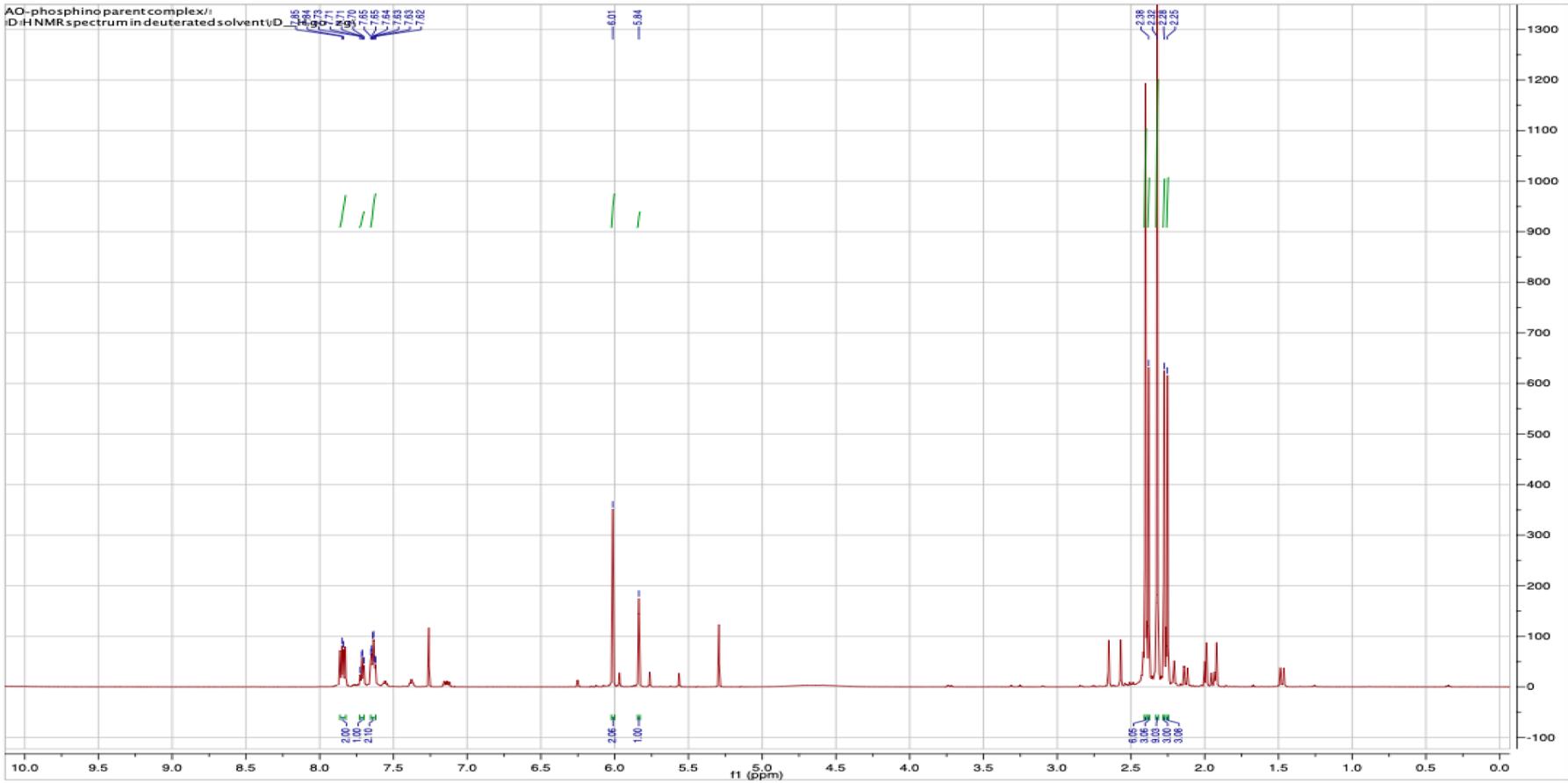


Figure S2. $^{13}C\{^{1}H\}$ NMR Spectrum of [**1a**]PF_6

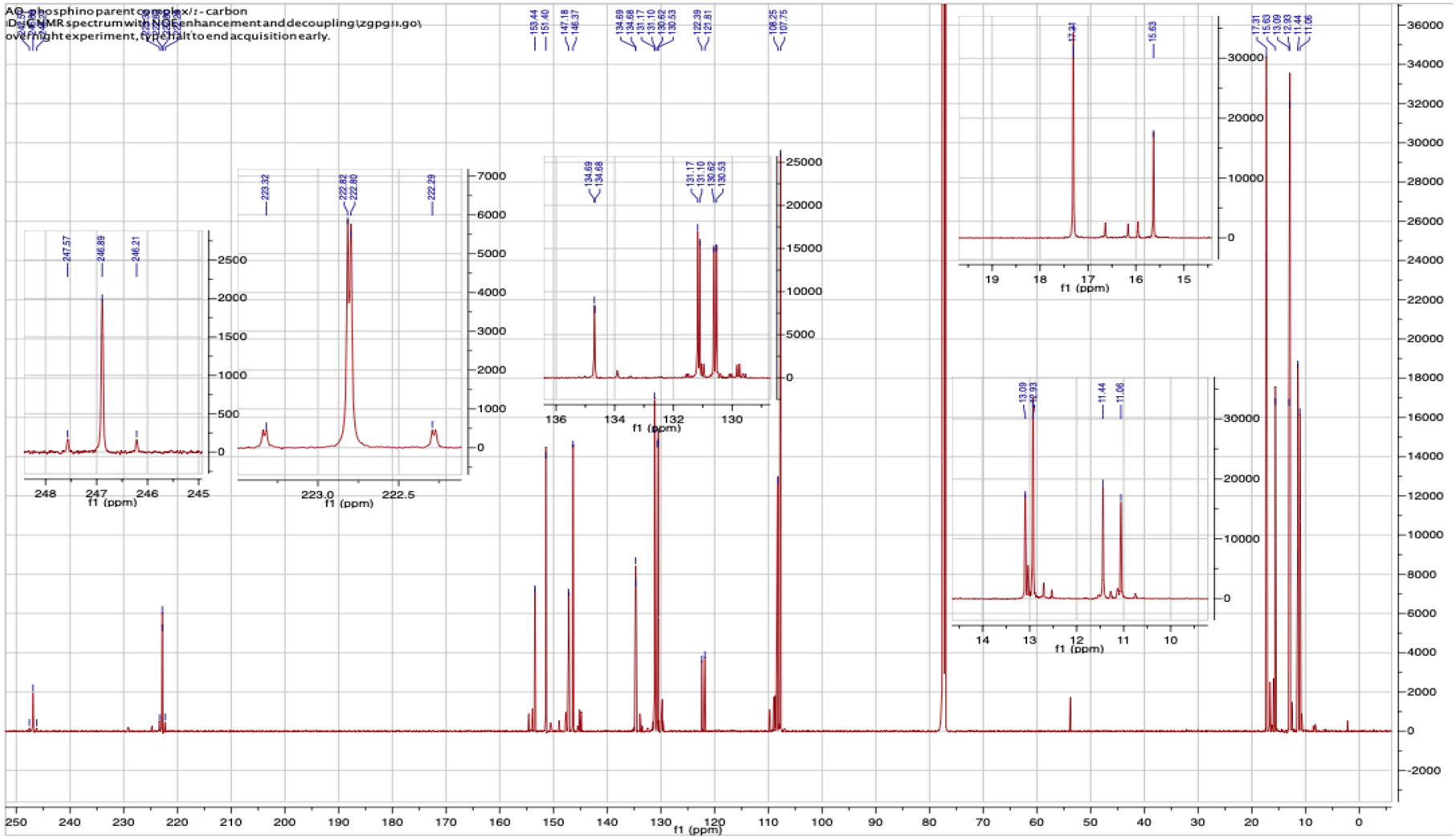


Figure S3. ^{31}P(proton coupled) NMR Spectrum of [**1a**]PF_6

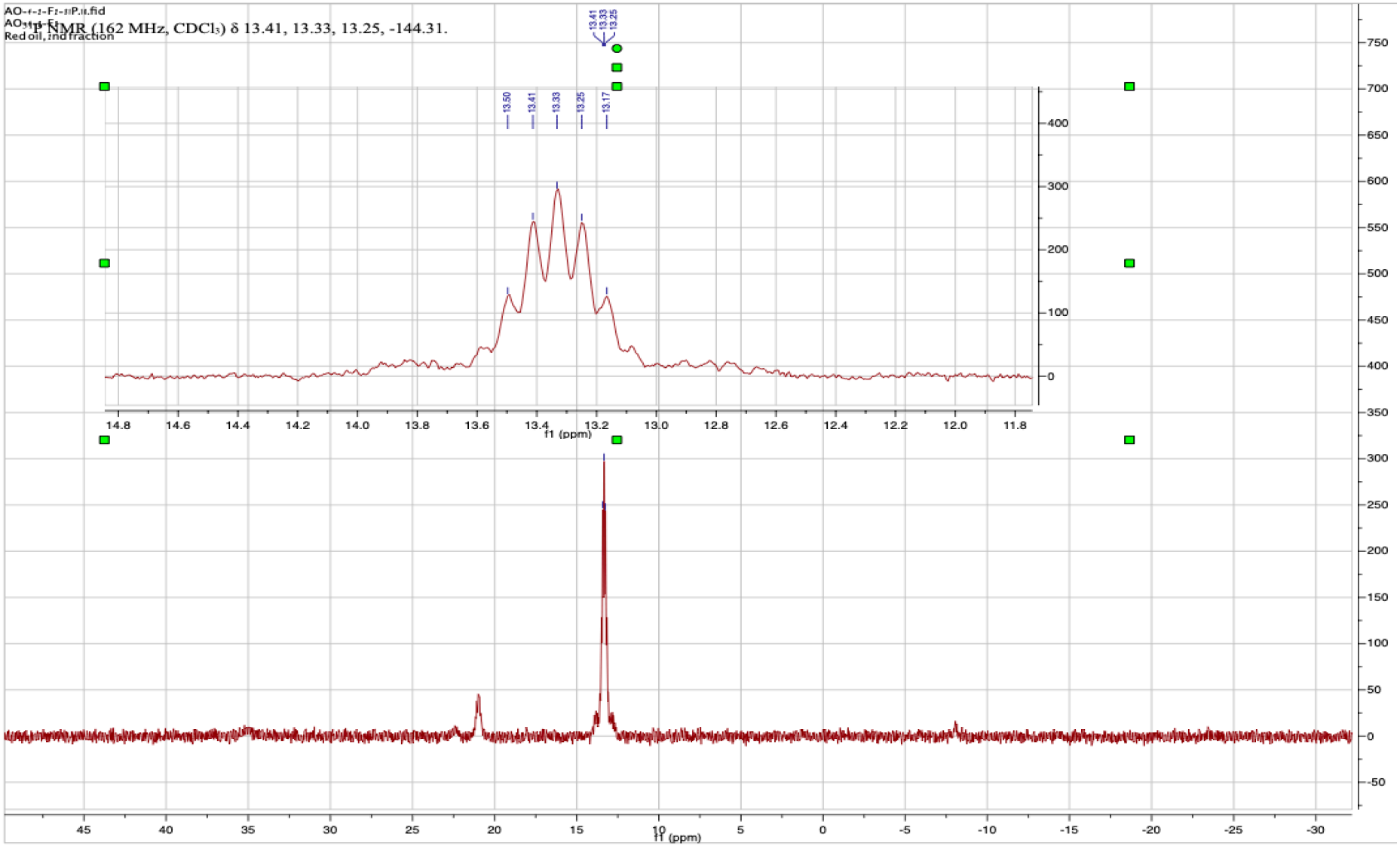


Figure S4. ^{1}H NMR Spectrum of [**4**]PF_6

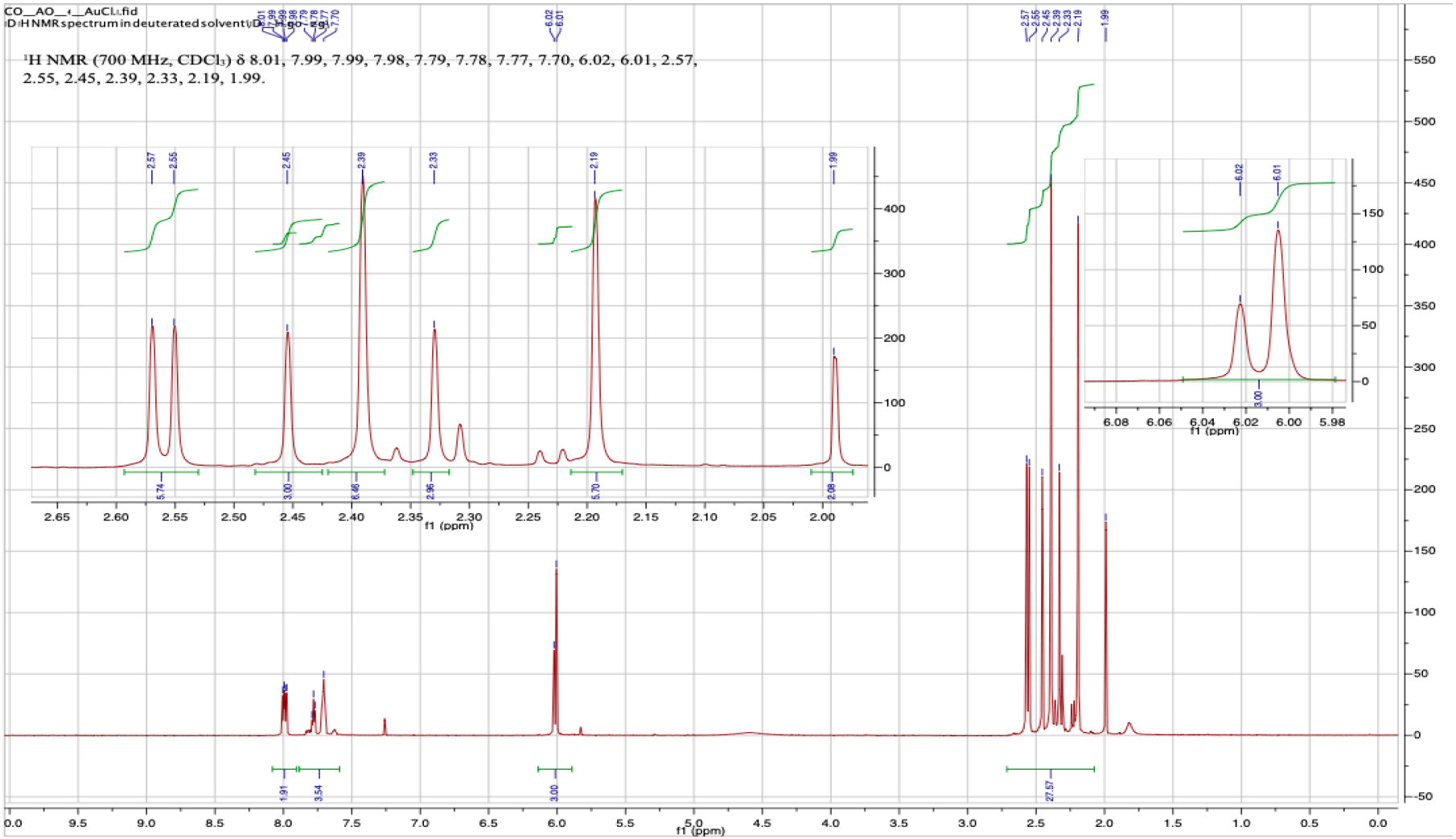


Figure S5. $^{13}C\{^{1}H\}$ NMR Spectrum of [**4**]PF_6

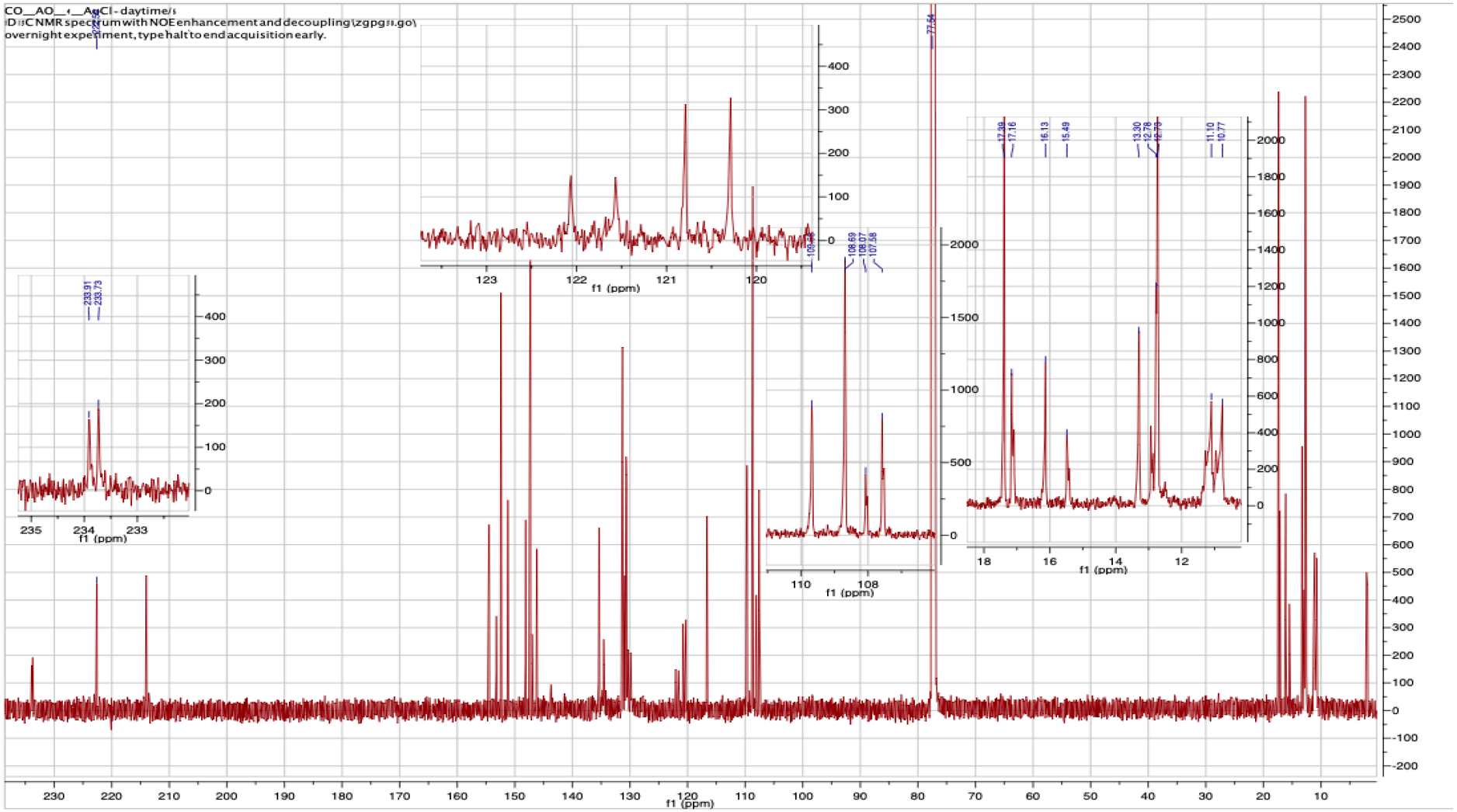


Figure S6. $^{31}P\{^{1}H\}$ NMR Spectrum of [**4**]PF_6 (δ_P = 13.7 = [**1a**]$^+$)

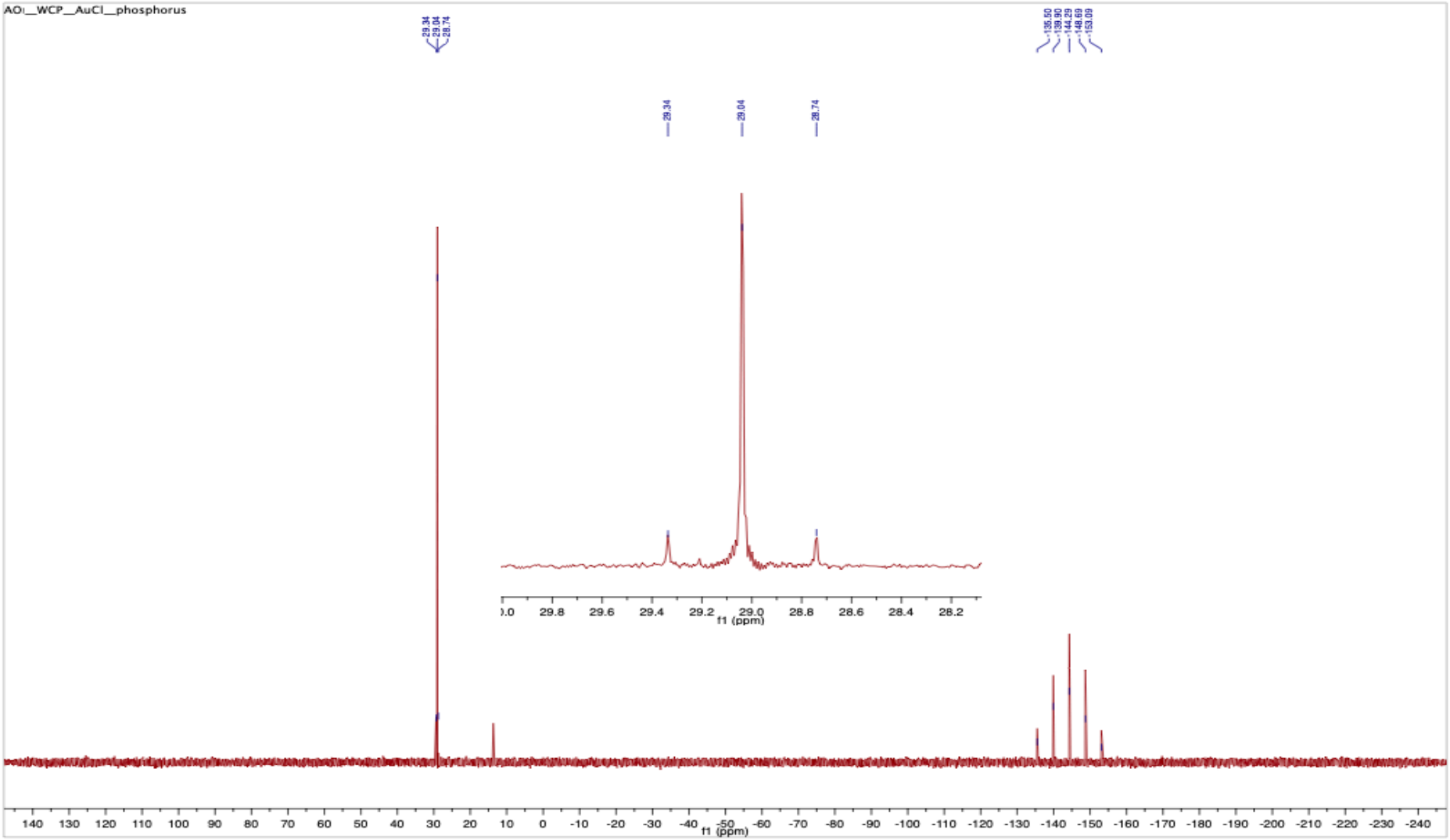


Figure S7. ^{1}H NMR Spectrum (400 MHz) of [**5**]PF_6

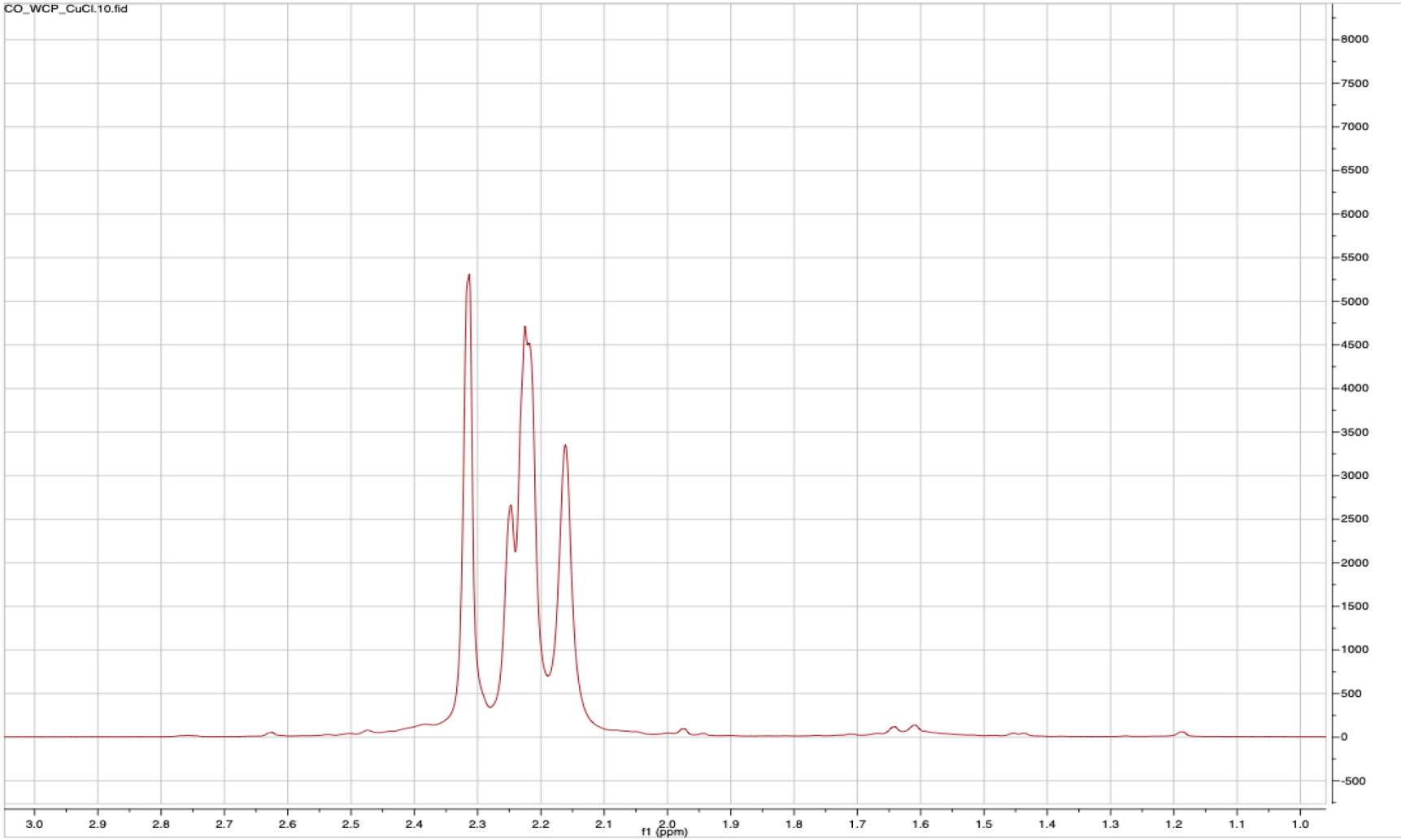


Figure S8. ^{1}H NMR Spectrum (700 MHz) of [**5**]PF_6

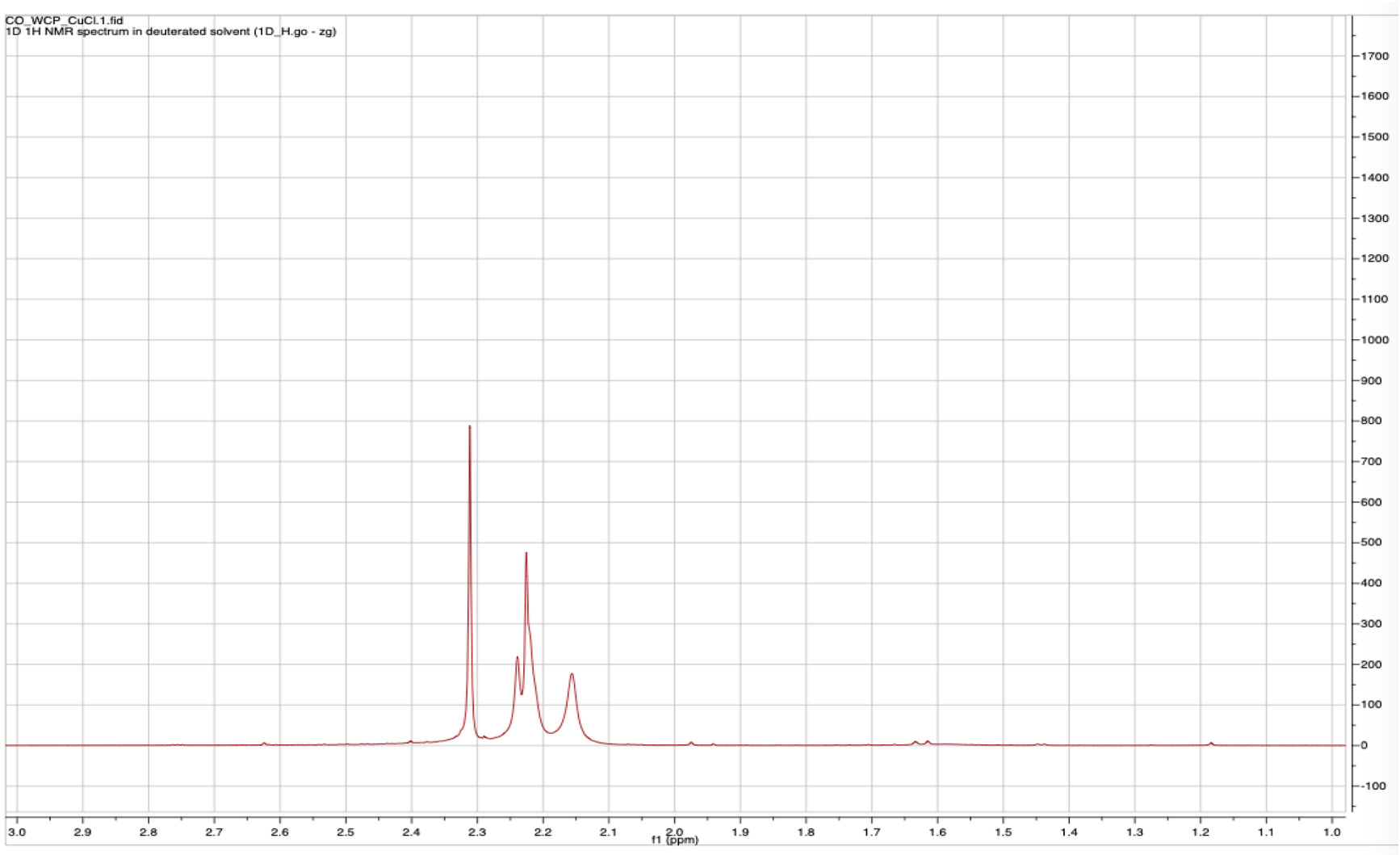


Figure S9. ^{1}H NMR Spectrum (Full, 400 MHz) of [**5**]PF_6

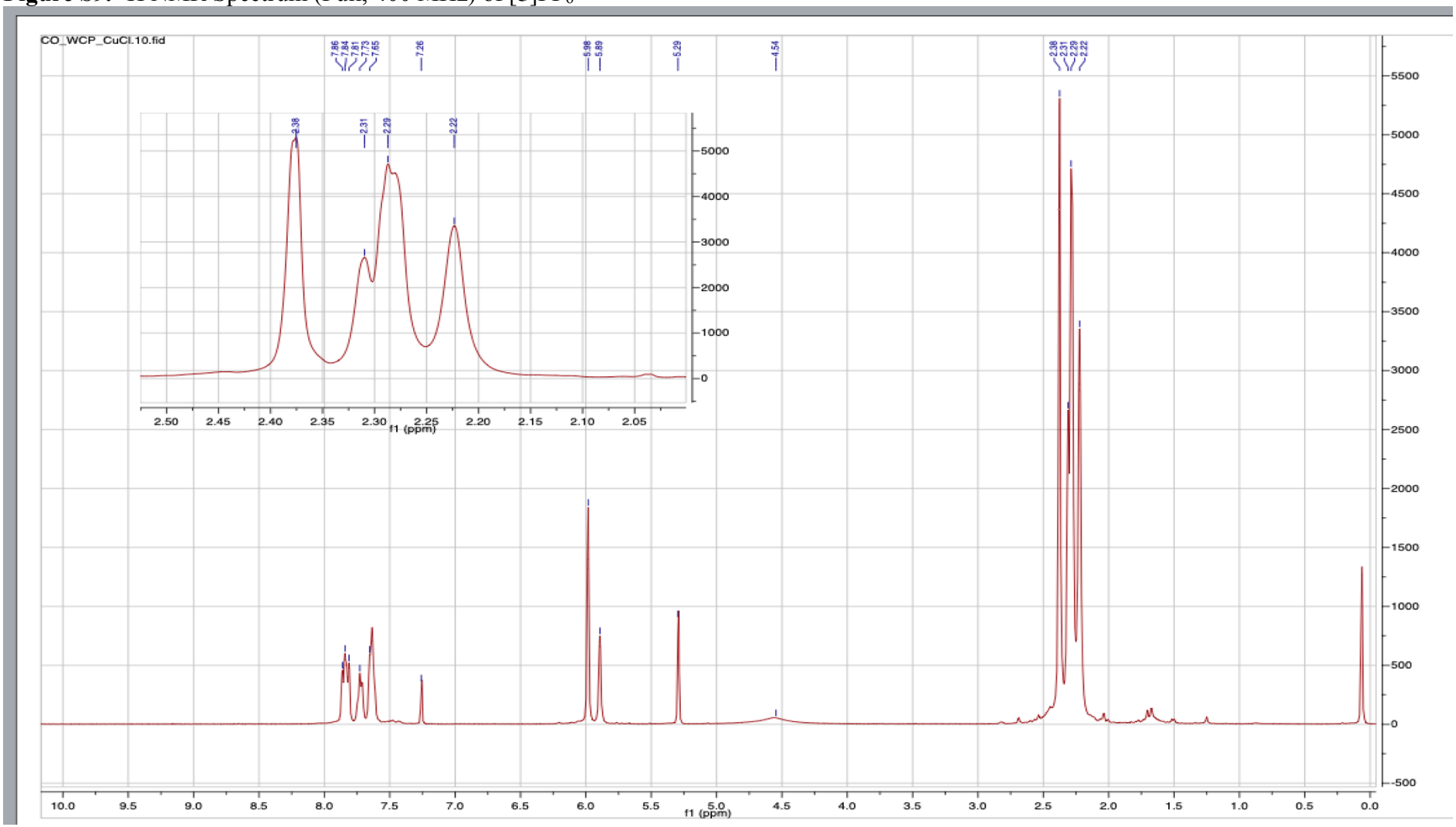


Figure S10. $^{13}C\{^{1}H\}$ NMR Spectrum of [**5**]PF_6

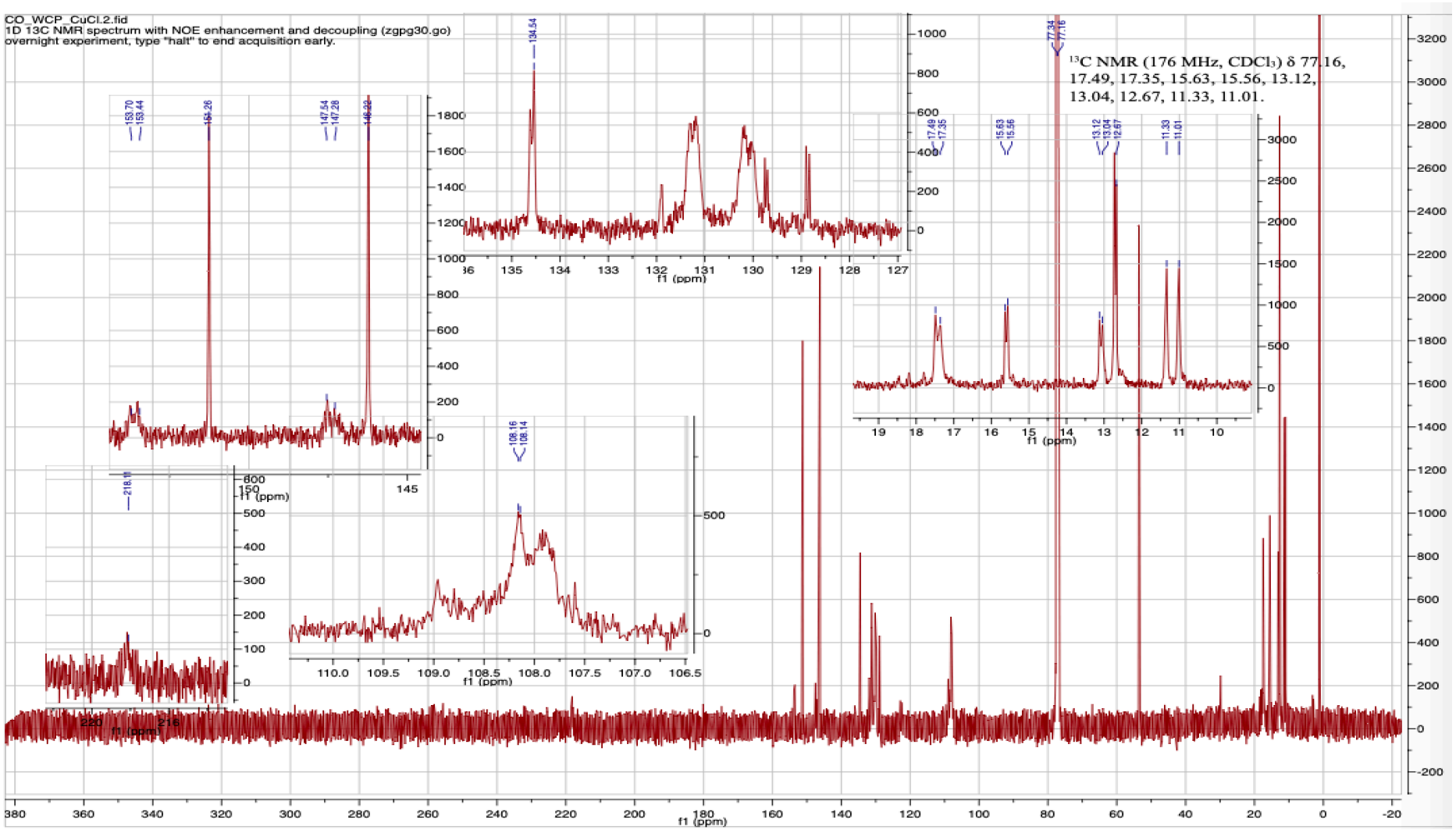


Figure S11. $^{31}P\{^{1}H\}$ NMR Spectrum of [**5**]PF_6

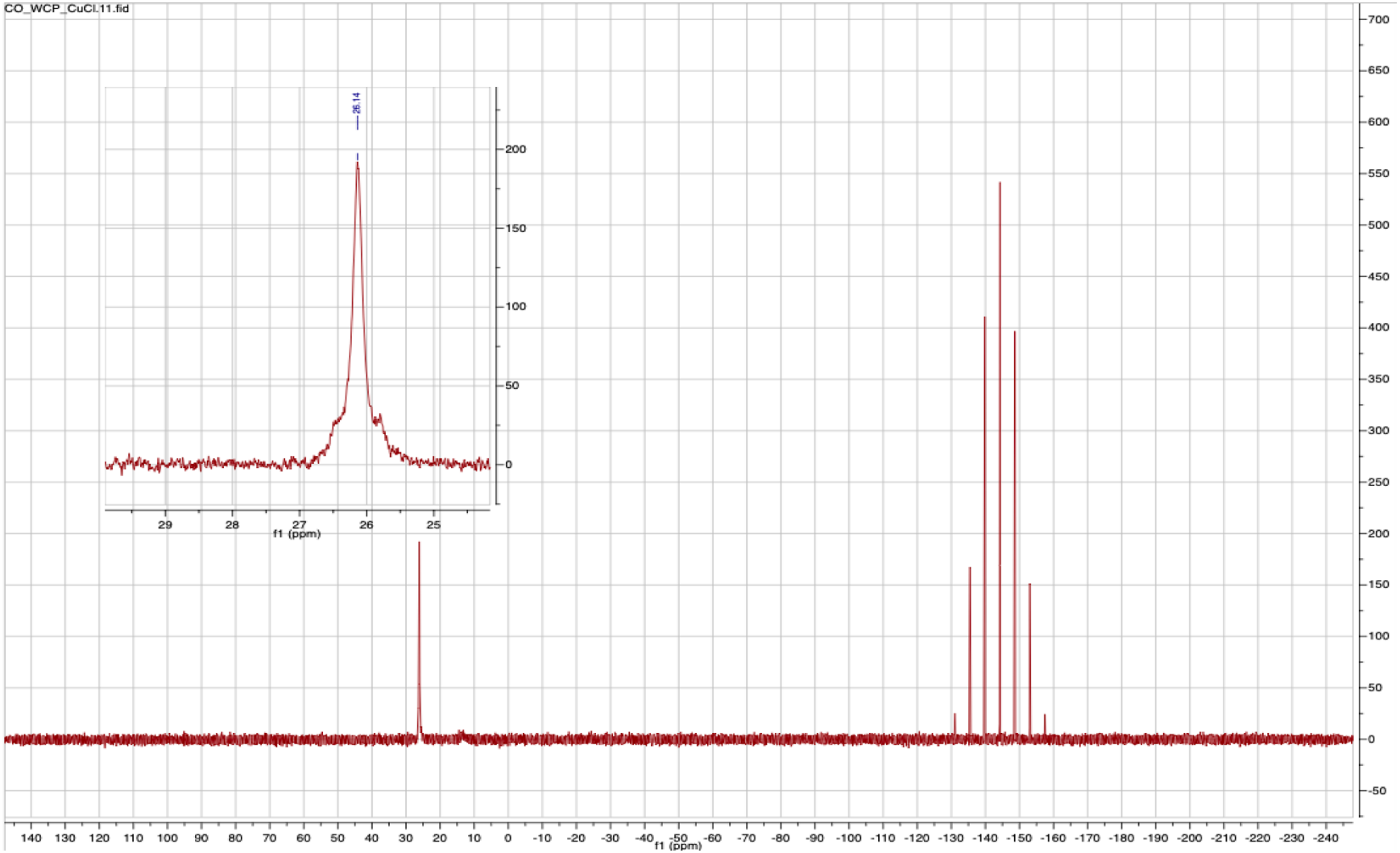
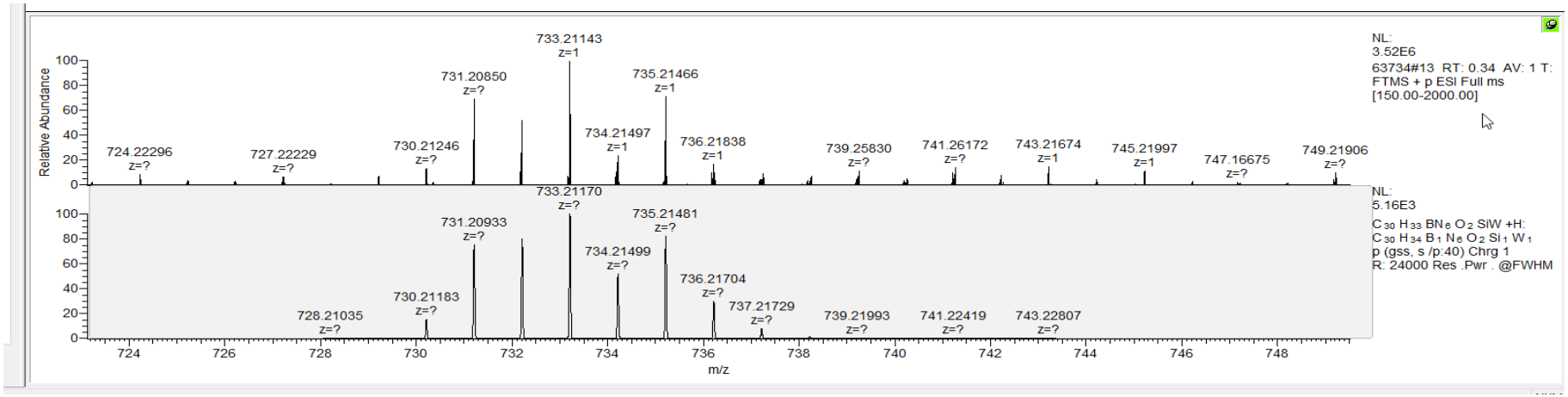
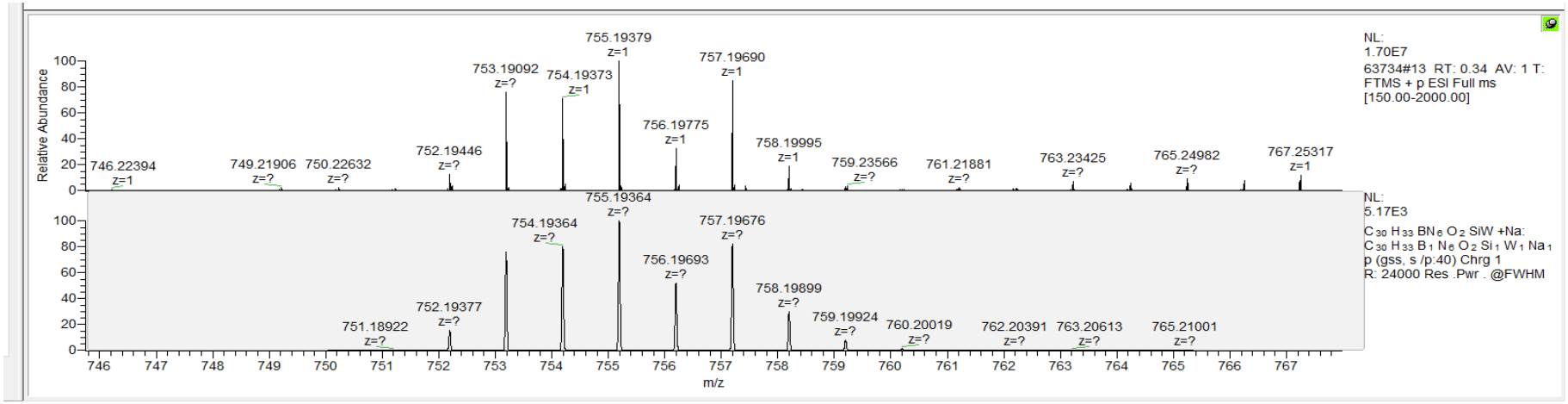


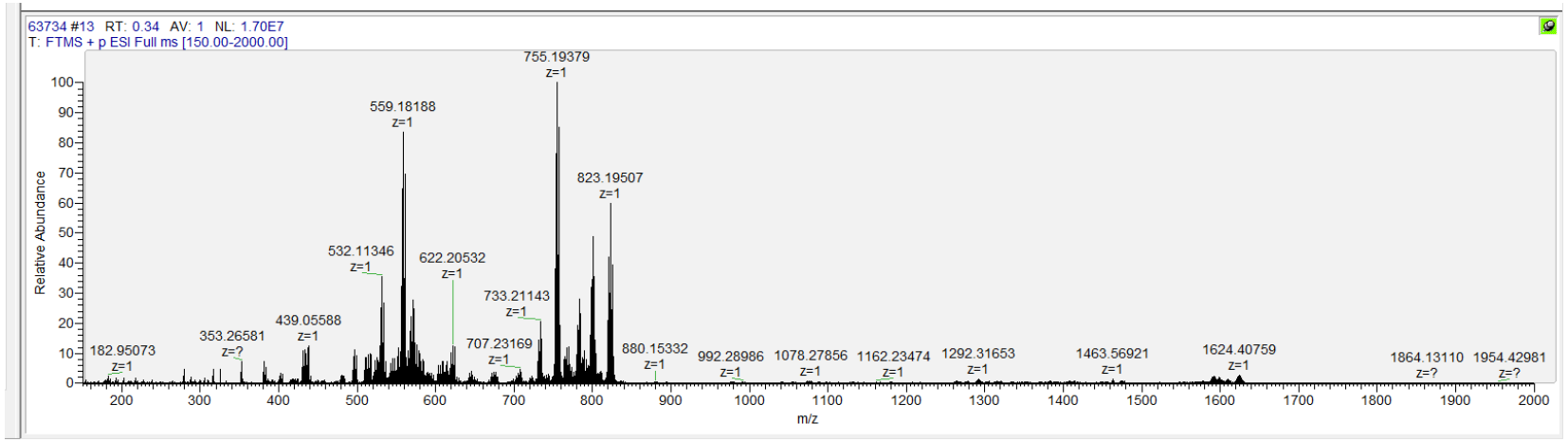
Figure S12. ESI Mass Spectra of [**5**]PF_6



(a) Observed versus simulated spectrum for detected target formulas [M+H]+ & (M+Na)+ ions



(b) Full Spectra:



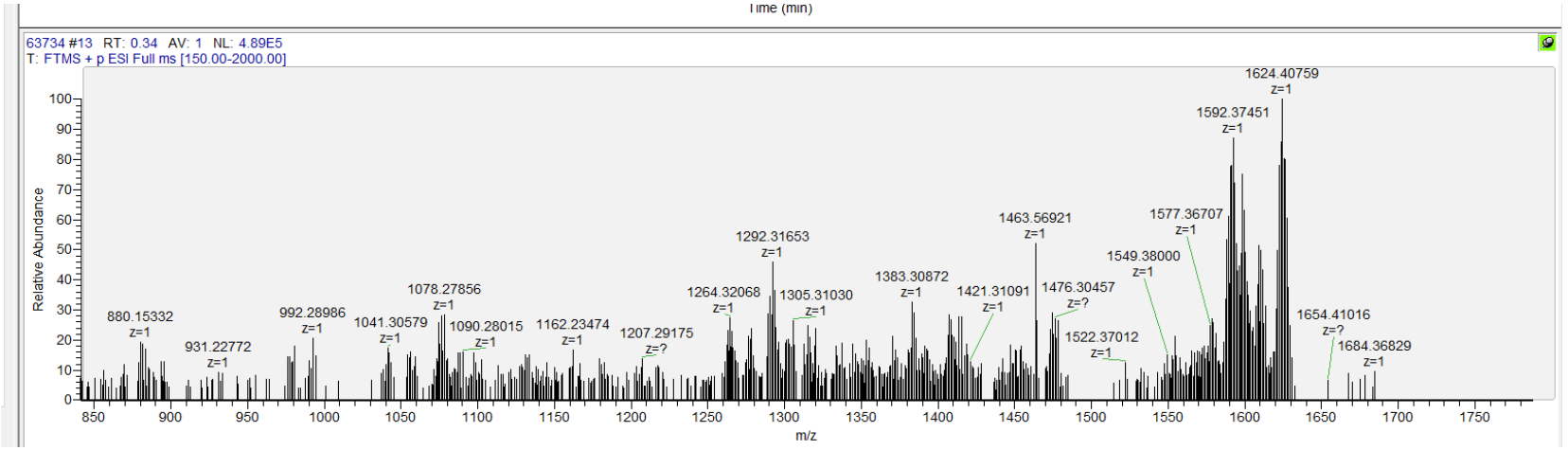


Figure S13. ^{1}H NMR Spectrum of [**6**]PF_6

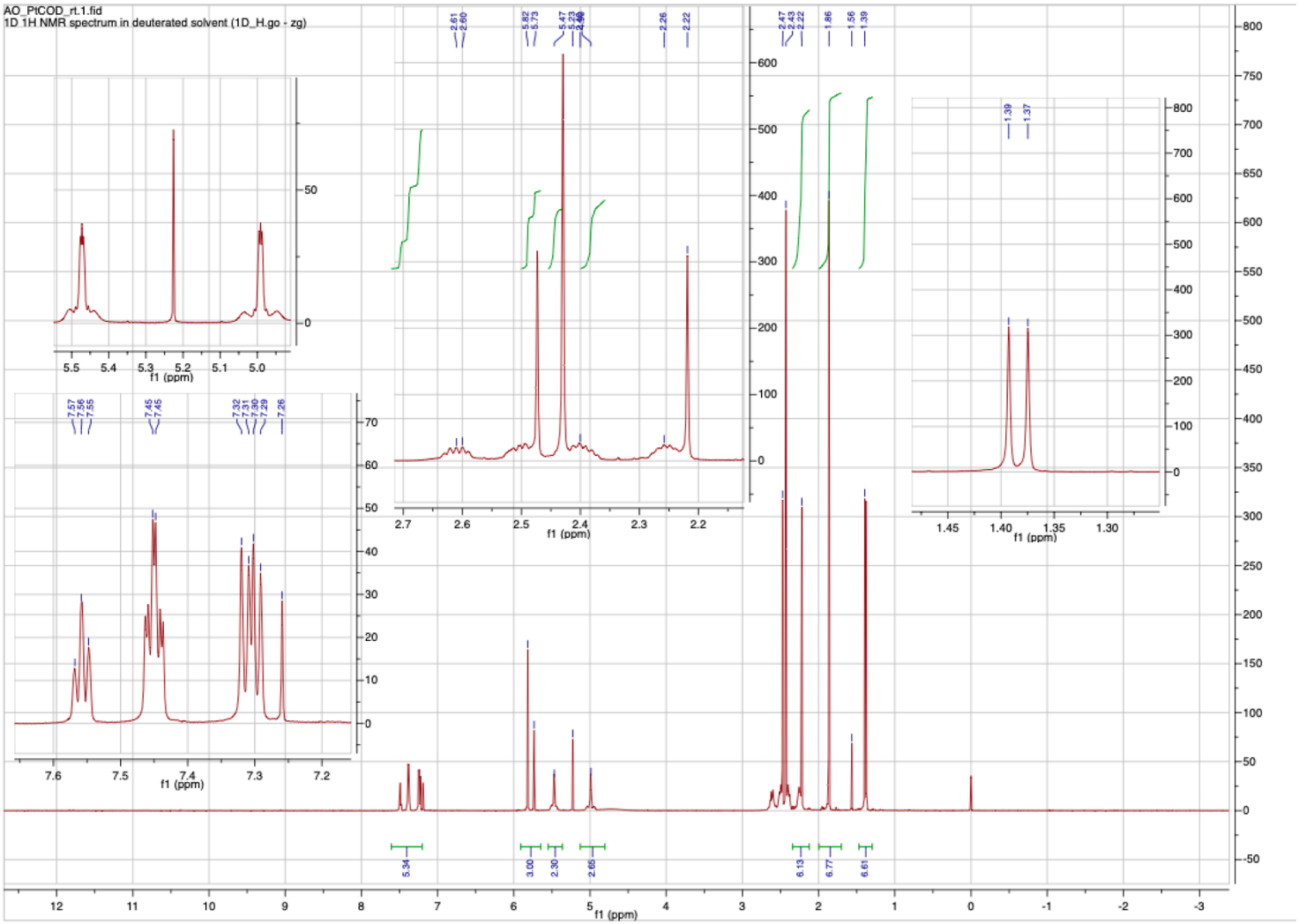


Figure S14. $^{13}C\{^{1}H\}$ NMR Spectrum of [**6**]PF_6

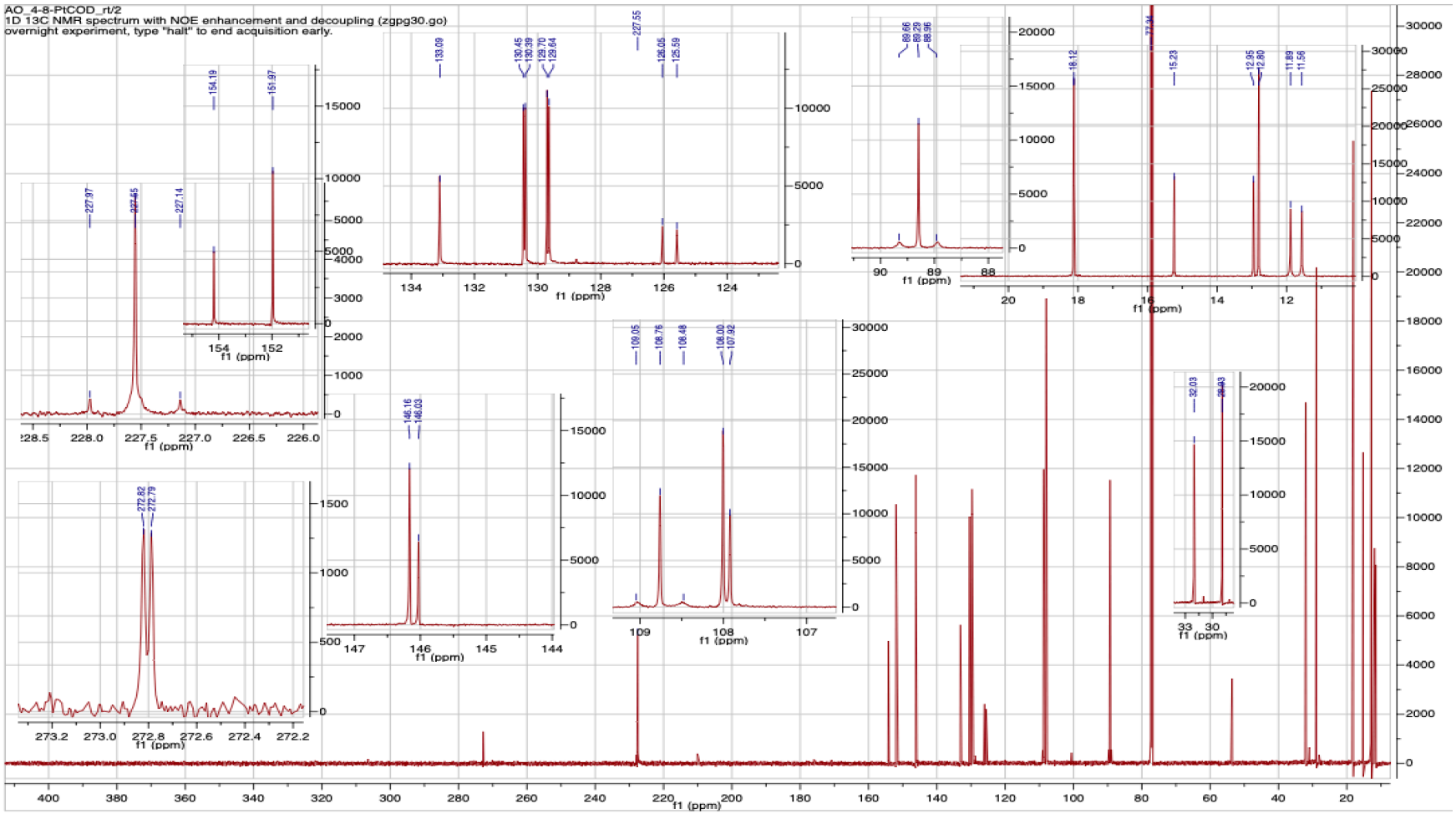


Figure S15. ^{31}P (proton coupled) NMR Spectrum of [**6**]PF_6

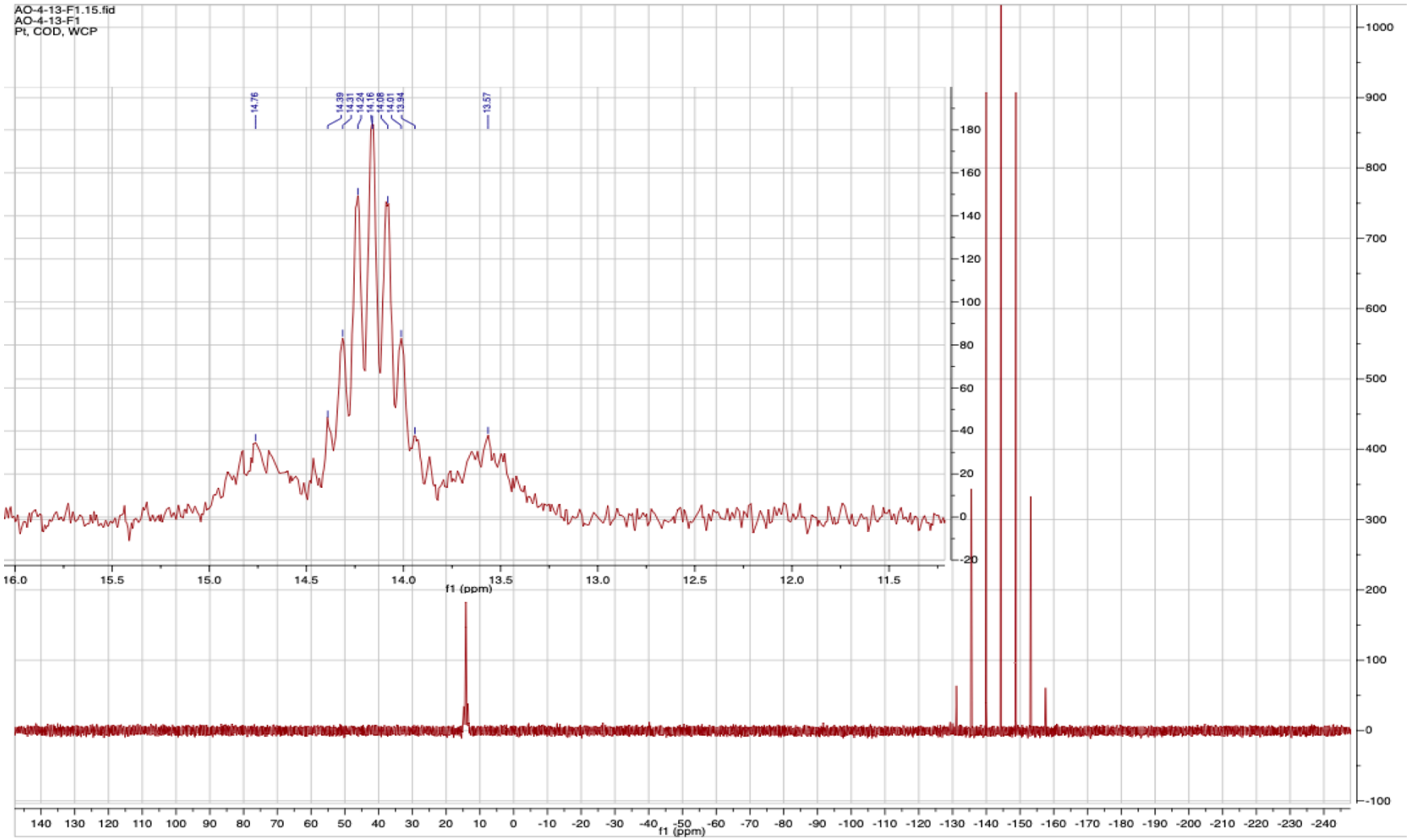


Figure S16. $^{31}P\{^{1}H\}$ NMR Spectrum of [**6**]PF_6

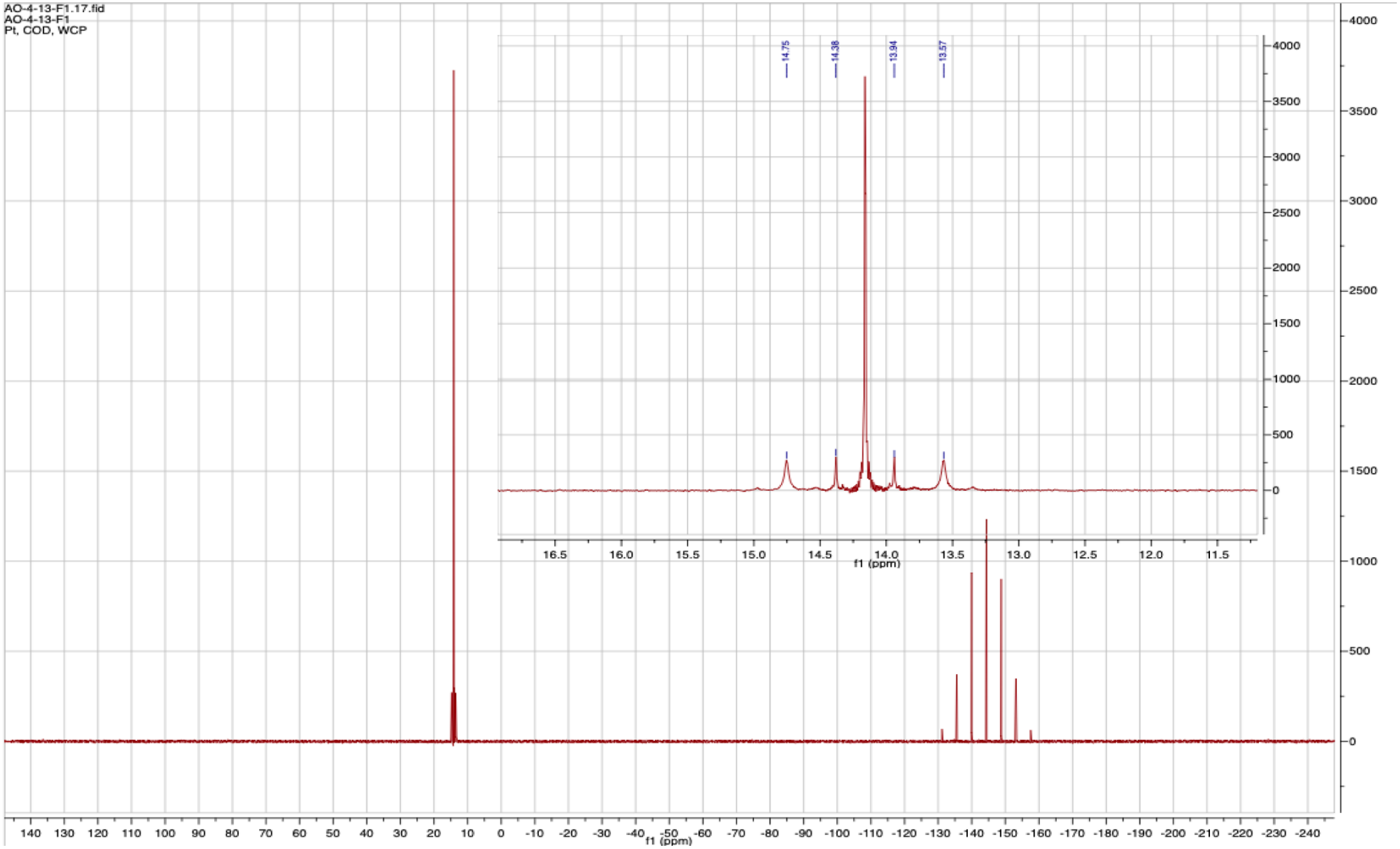


Figure S17. ^{13}C-^{1}H HSQC NMR Spectrum of [**6**]PF_6

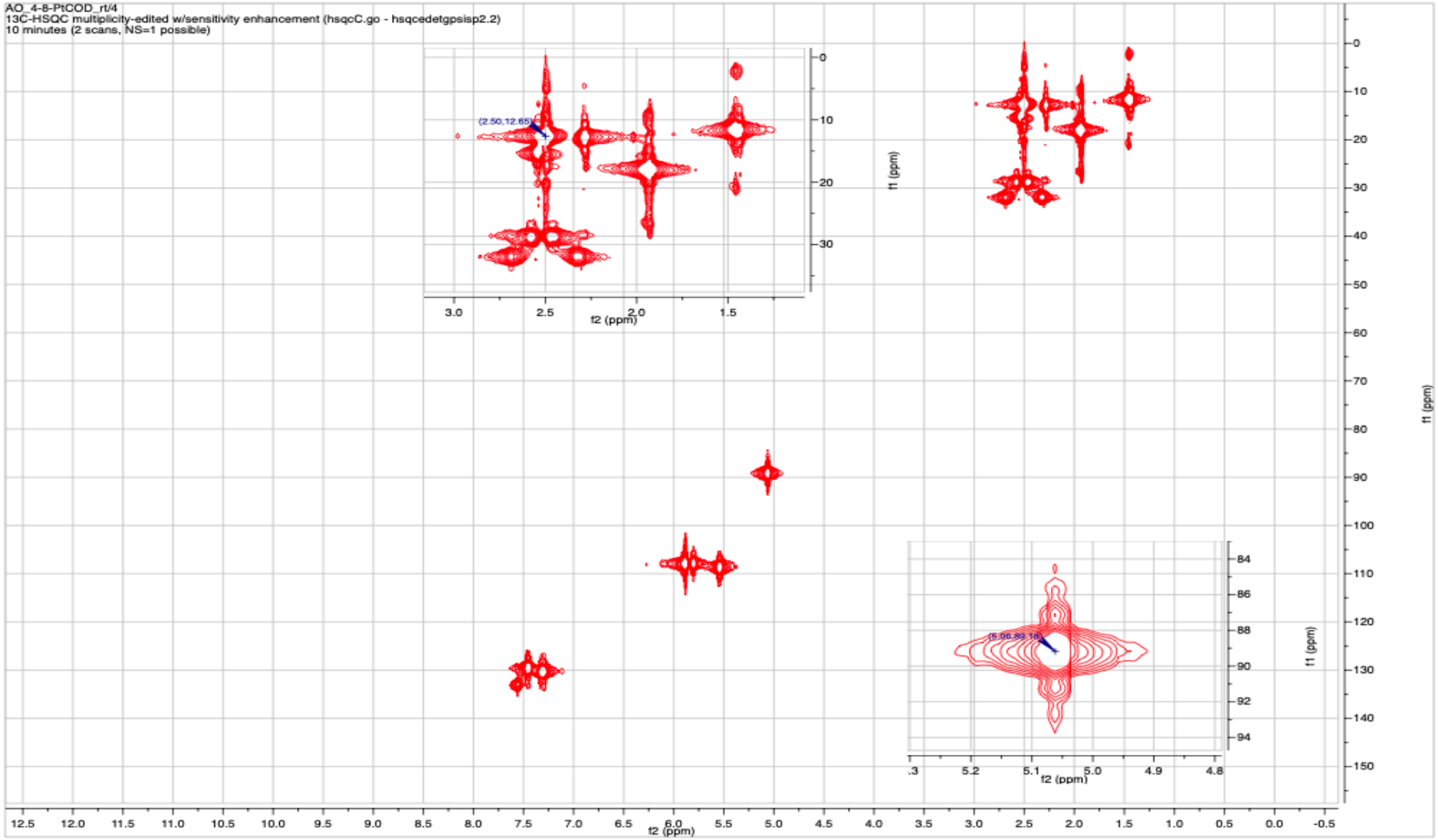


Figure S18. ^{13}C-^{1}H HMBC NMR Spectrum of [**6**]PF_6

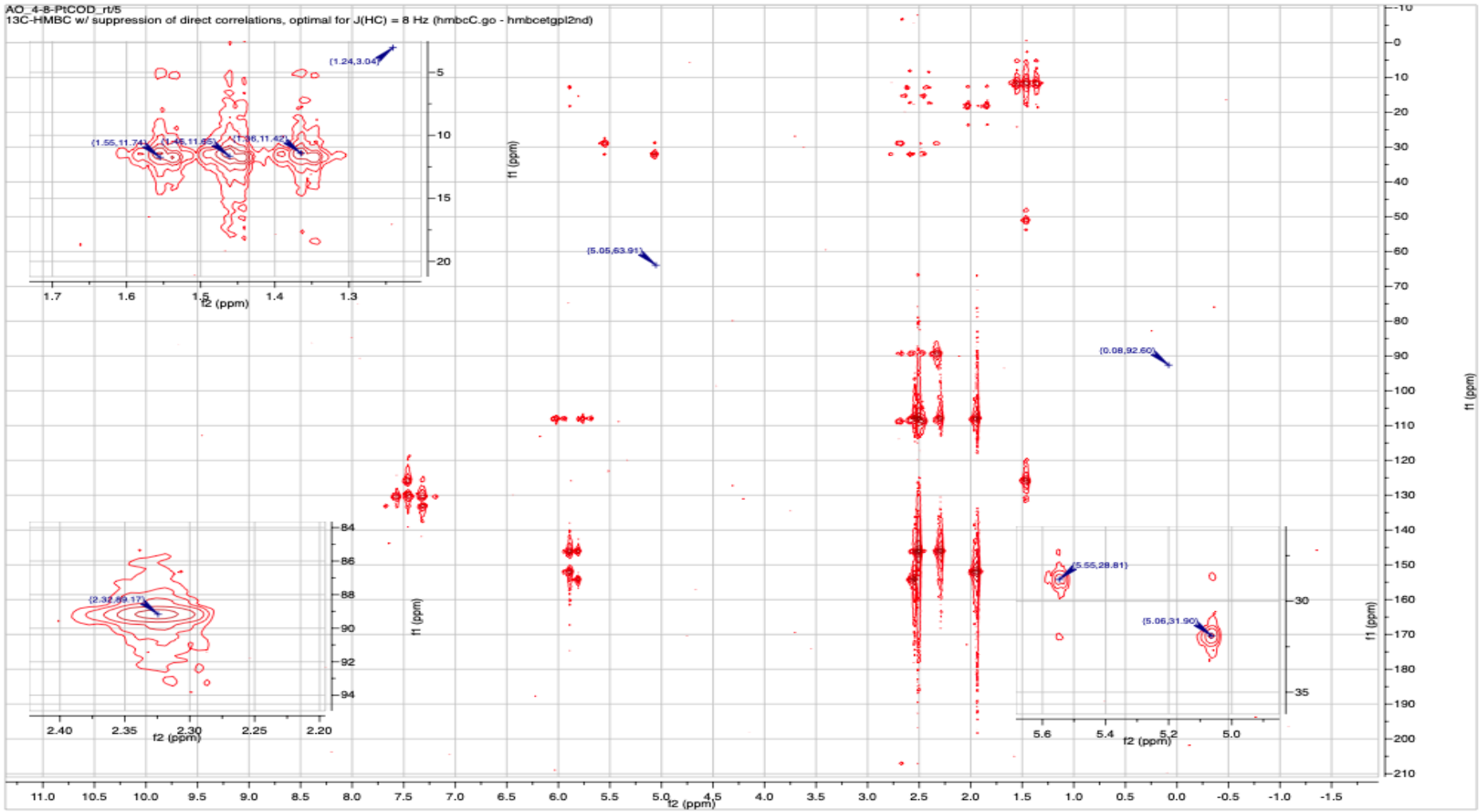


Figure S19. ^{1}H-^{1}H DQF-COSY NMR Spectrum of [**6**]PF_6

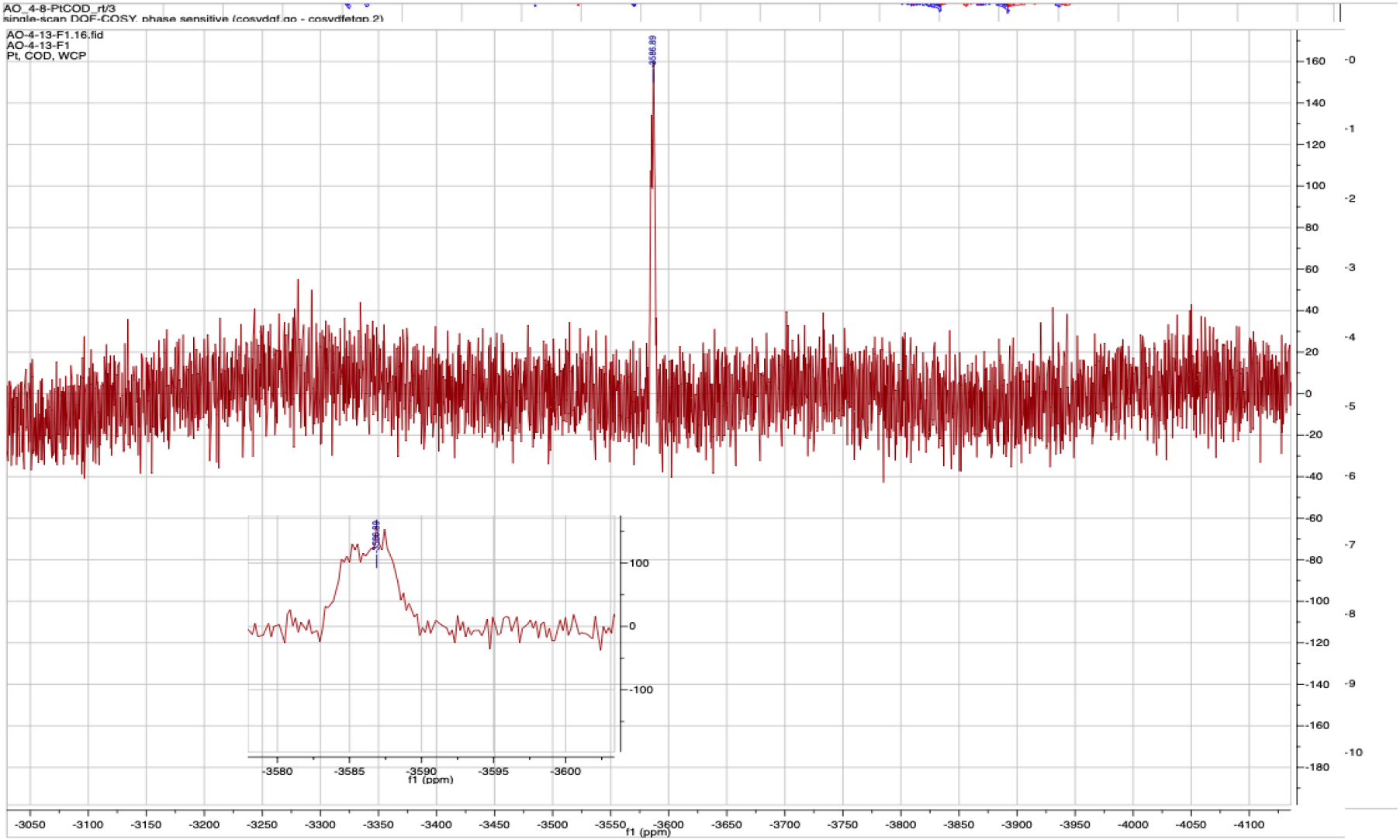


Figure S19. ^{195}Pt{^{1}H} NMR Spectrum of [**6**]PF_6

Figure S20. ^{1}H NMR Spectrum of [**7**]PF_6

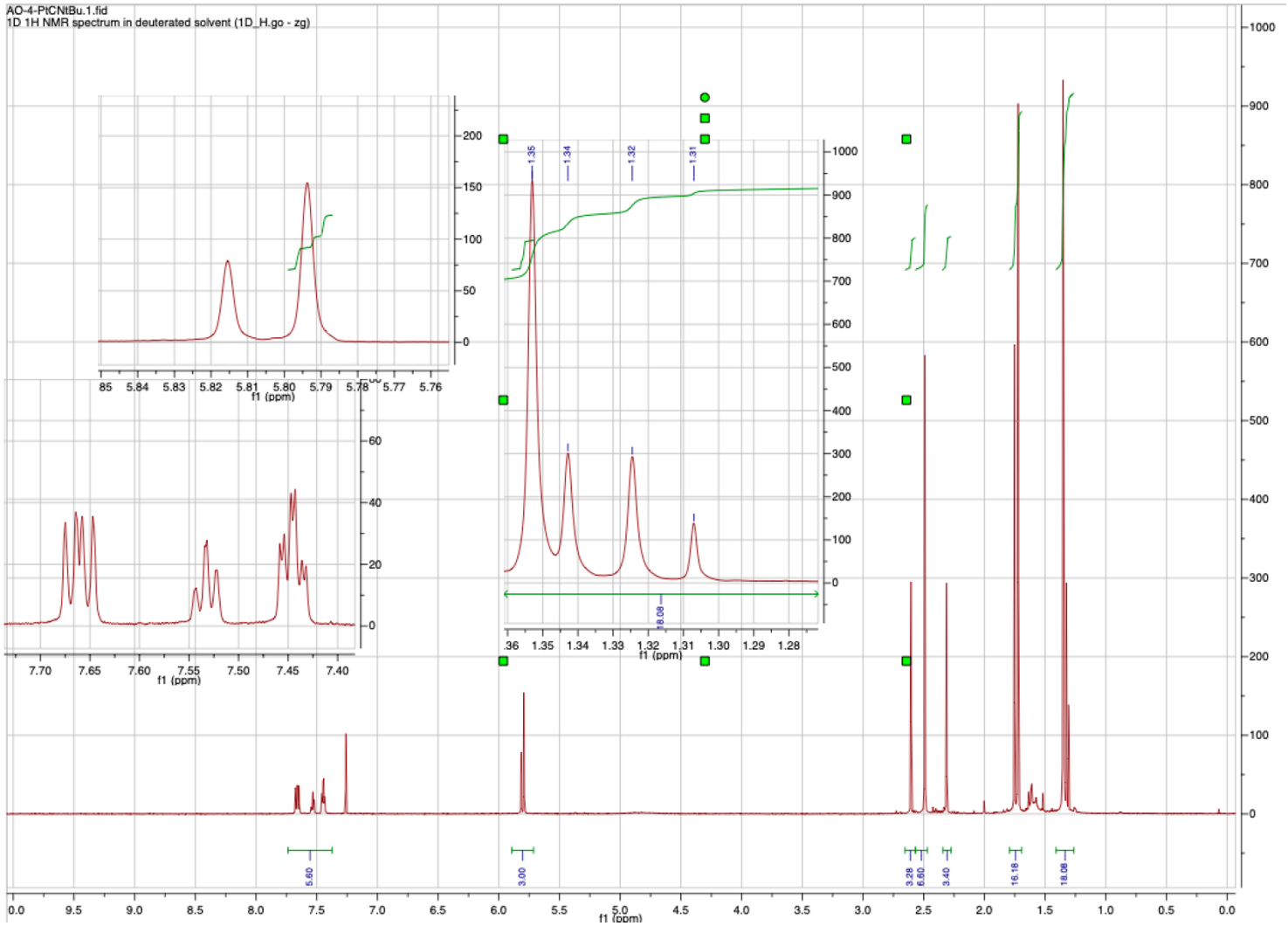


Figure S21. $^{13}C\{^{1}H\}$ NMR Spectrum of [**7**]PF_6 (176.1 MHz, 25 °C)

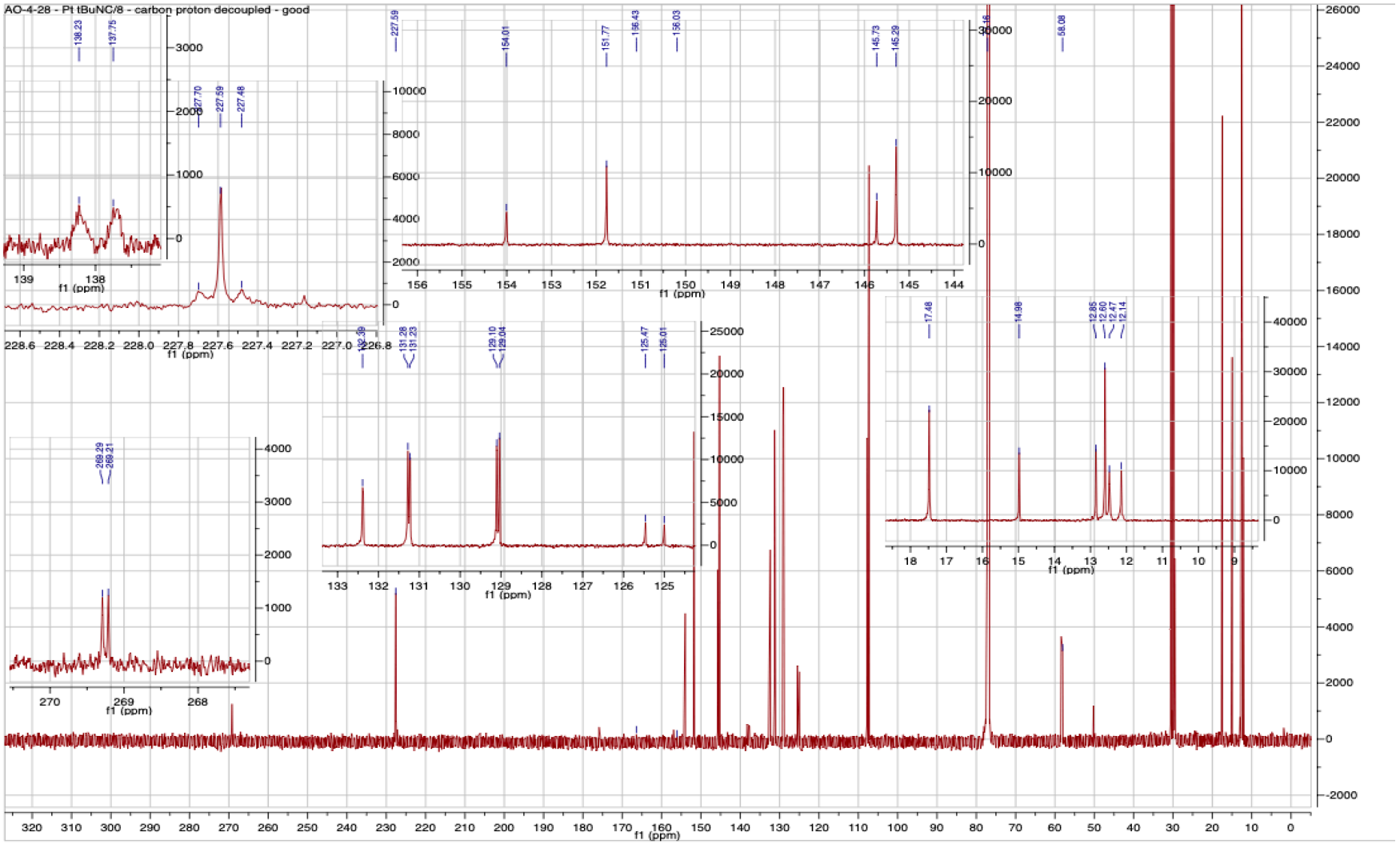


Figure S22. $^{31}P\{^{1}H\}$ NMR Spectrum of [**7**]PF_6 (283 MHz, 25 °C)

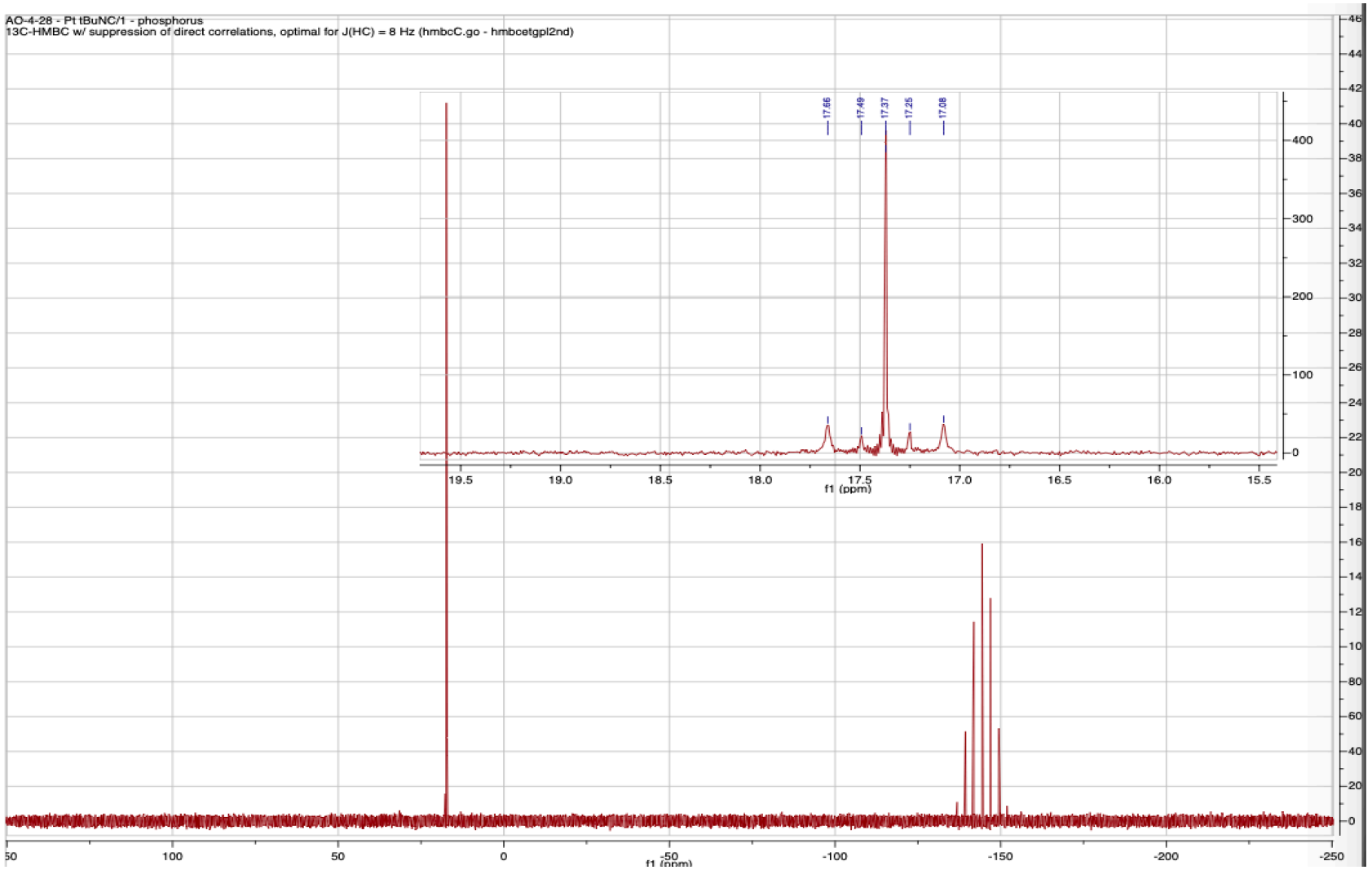


Figure S23. $^{195}Pt\{^{1}H\}$ NMR Spectrum of [**7**]PF_6 (150 MHz, 25 °C)

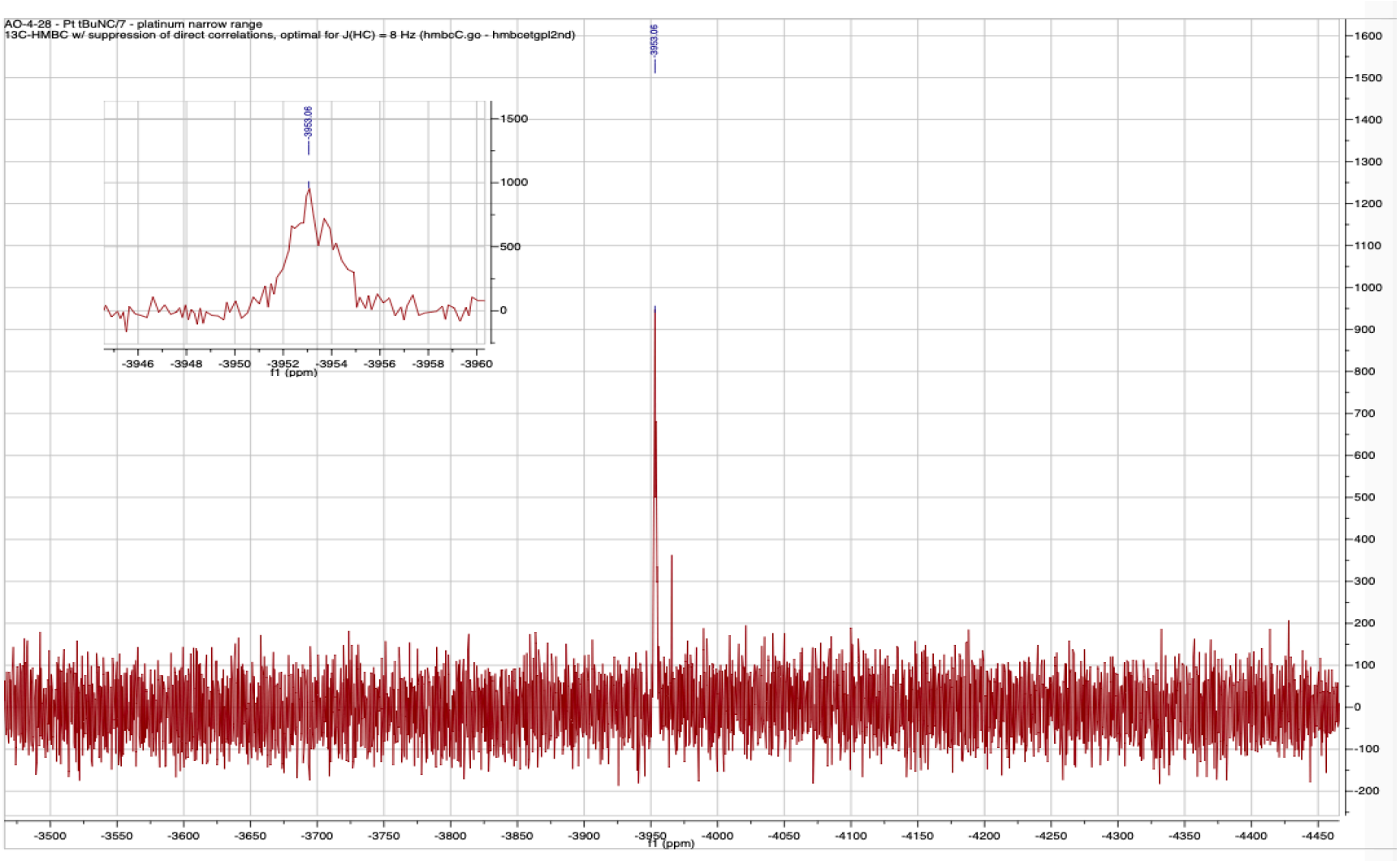
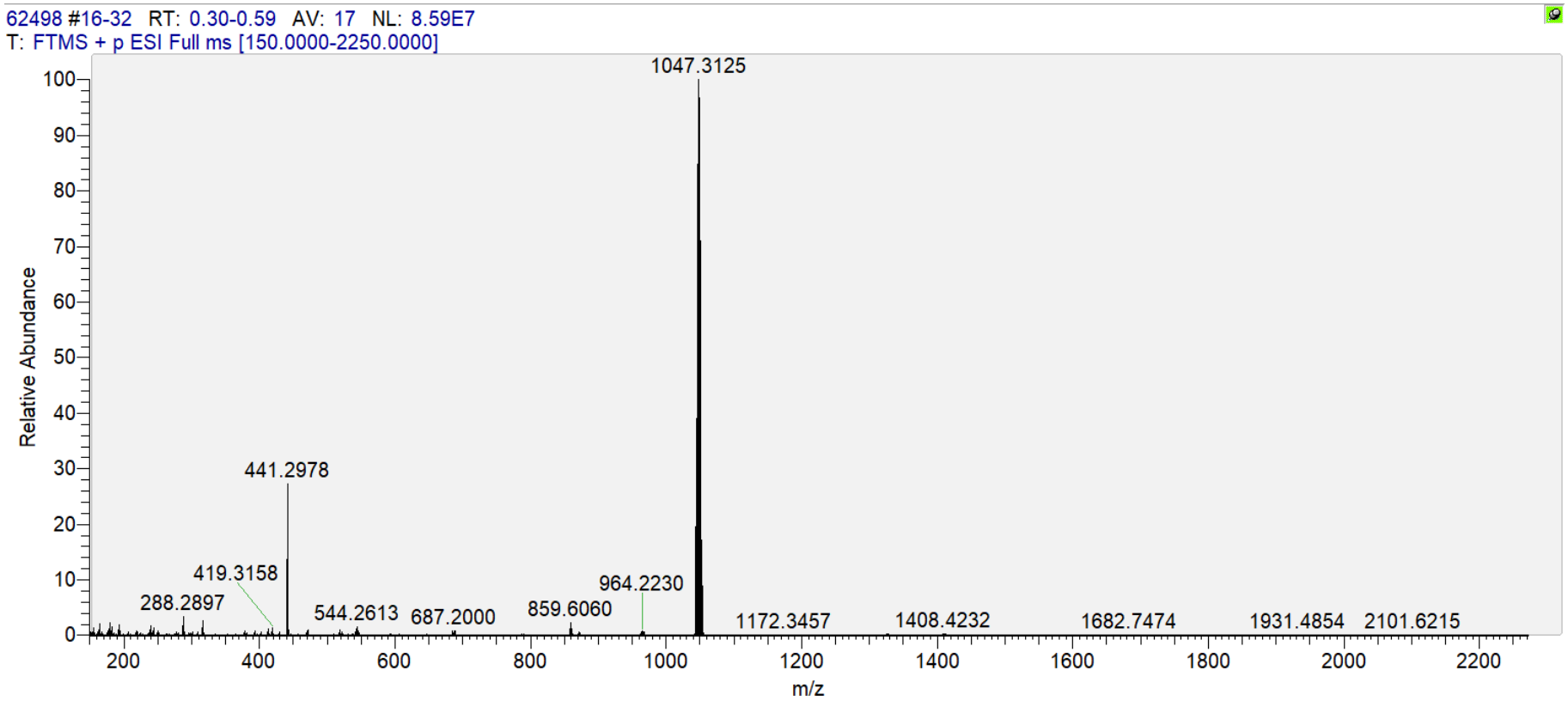
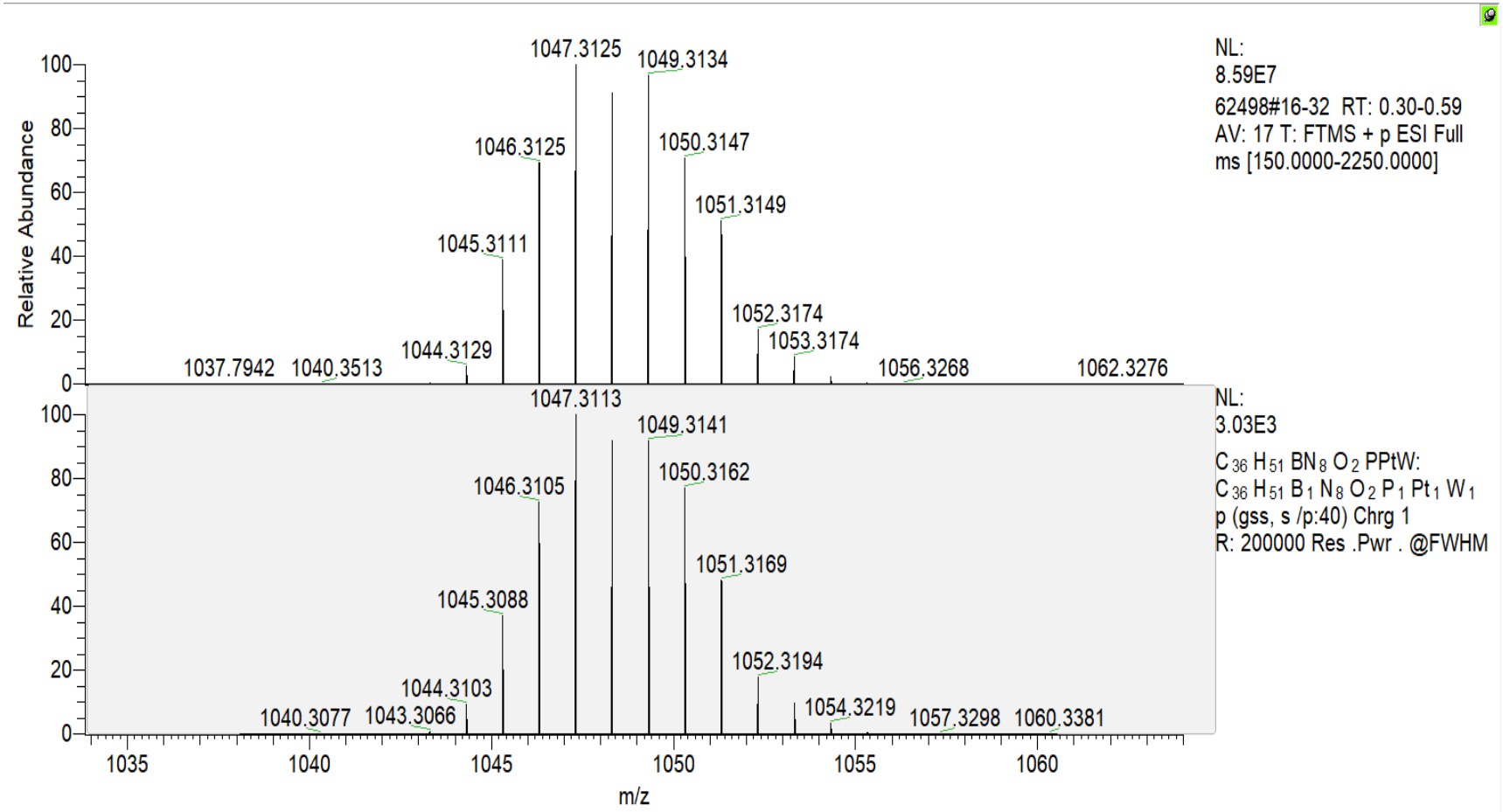


Figure S24. ESI Mass Spectra for [**7**]PF_6





Please do not adjust margins

Figure S25. ^{1}H NMR Spectrum of [**8**]PF_6

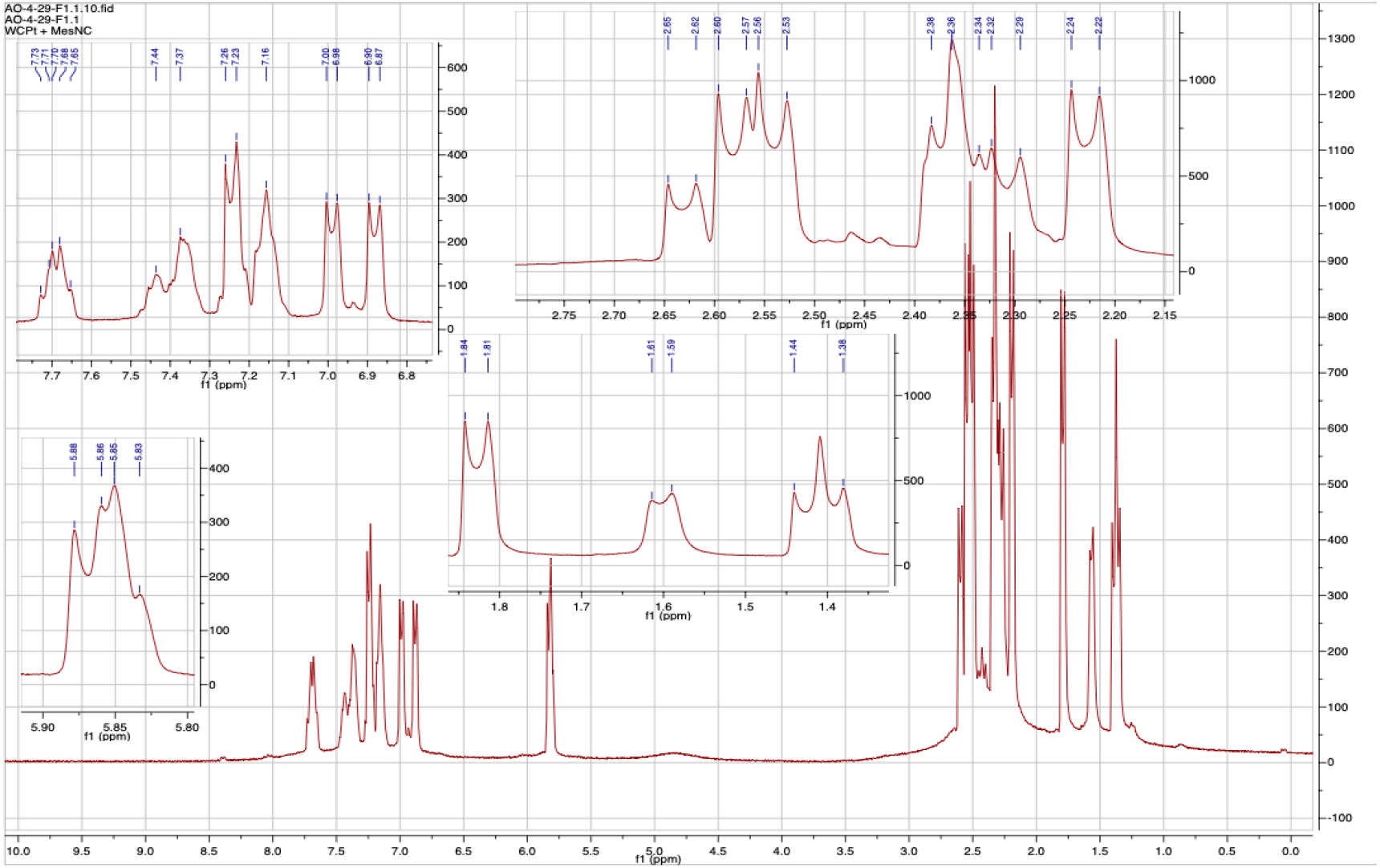


Figure S26. $^{13}C\{^{1}H\}$ NMR Spectrum of [**8**]PF_6

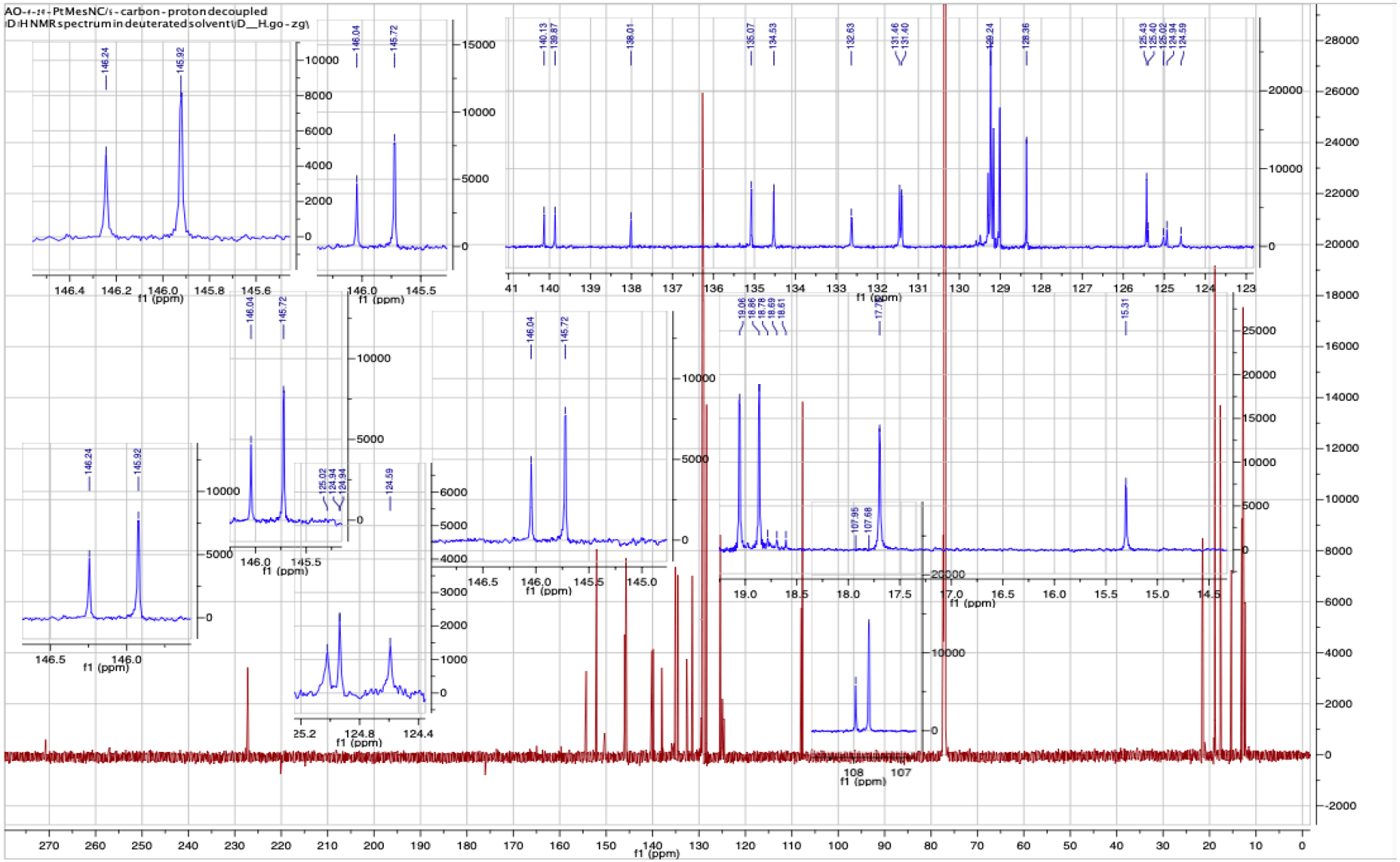


Figure S27. $^{31}P\{^{1}H\}$ NMR Spectrum of [**8**]PF_6

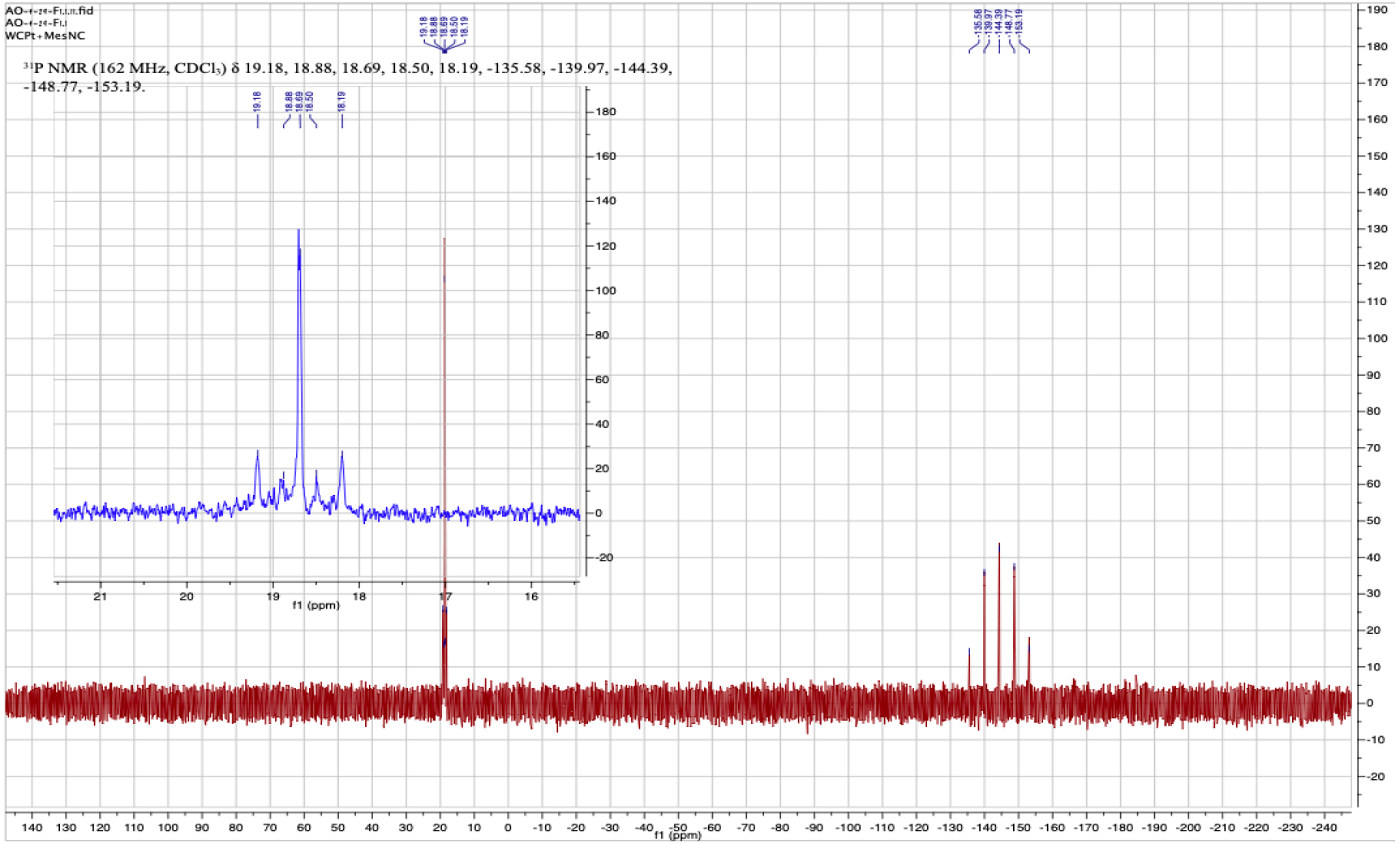


Figure S28. $^{195}Pt\{^{1}H\}$ NMR Spectrum of [**8**]PF_6

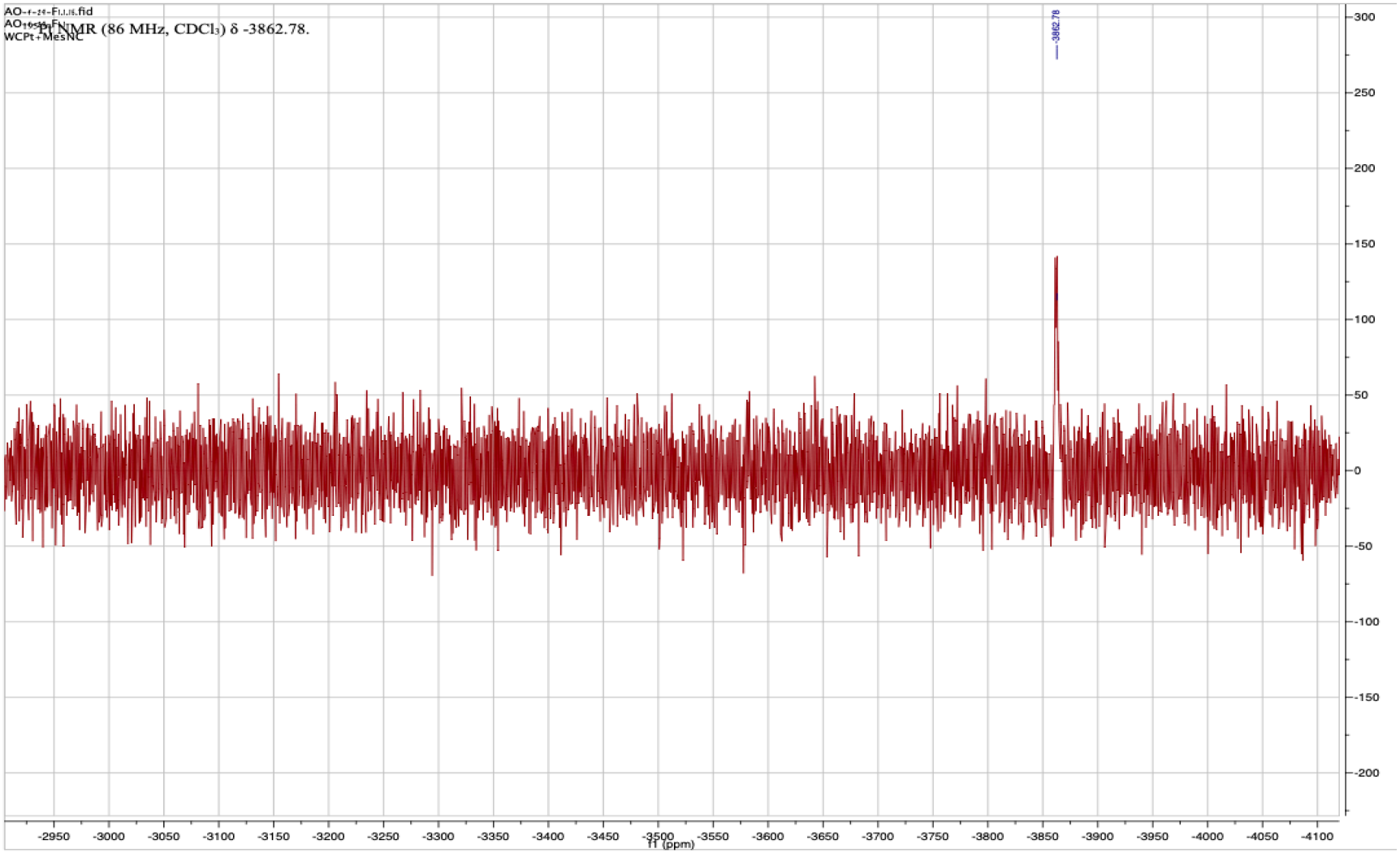
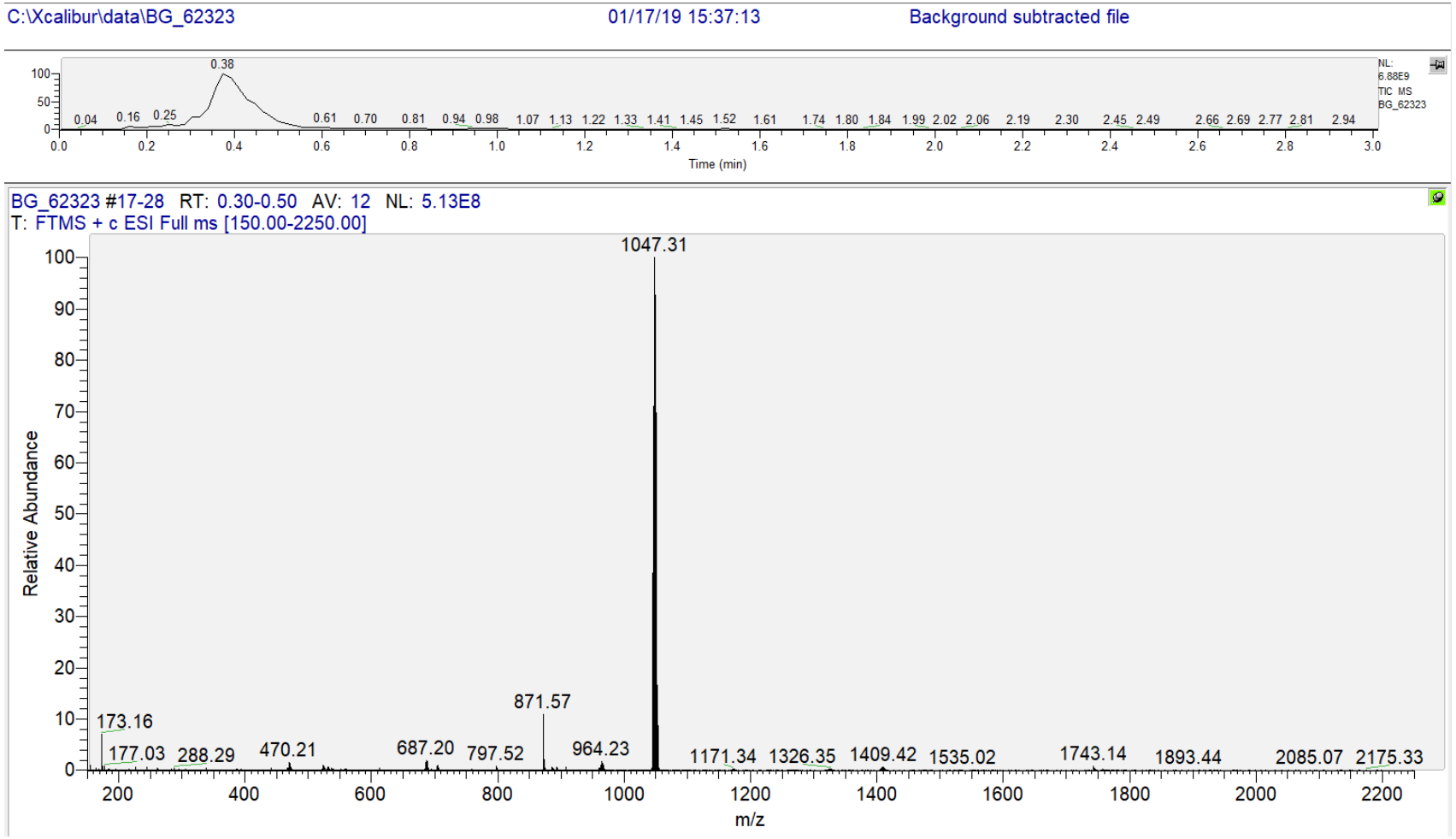
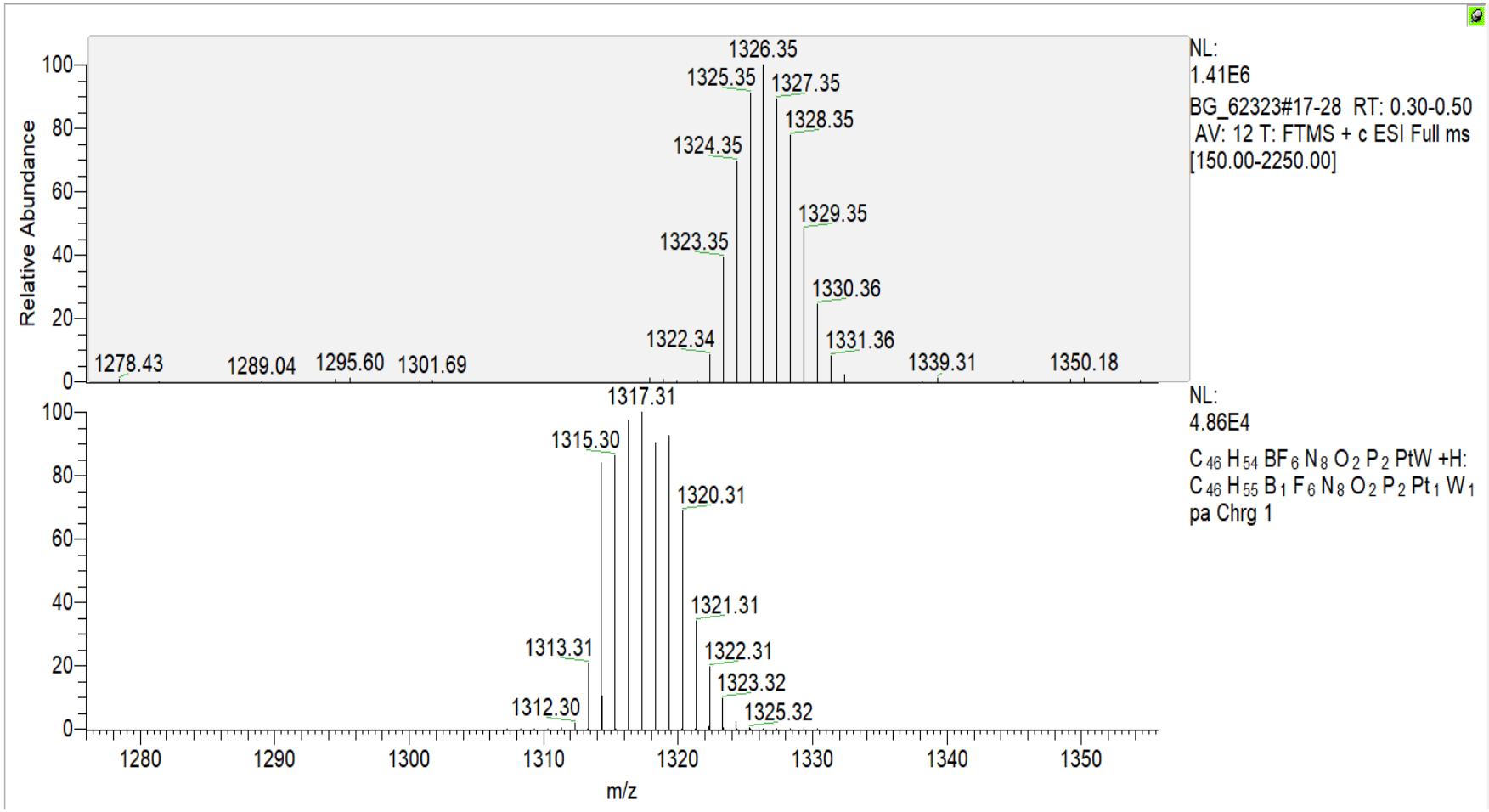


Figure S29. ESI Mass Spectra for [**8**]PF_6



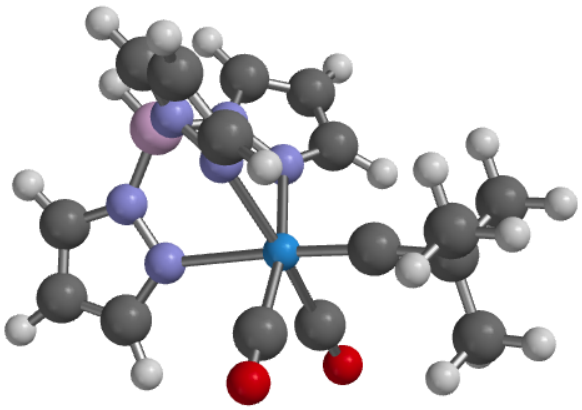


Dalton Transactions

SUPPORTING INFORMATION

Geometry Optimisation for [W(≡CCMe$_3$)(CO)$_2$(Tp)] (WC)

Method: DFT/ωB97X-D/6-31G*/LANL2Dζ, gas phase.

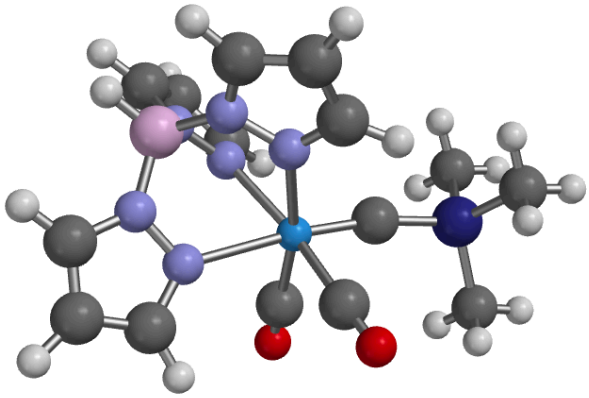


Cartesian Coordinates

Atom	x	y	z
W	0.503680	0.060885	0.651349
C	1.683413	2.763932	-0.779549
N	-1.701542	0.179812	0.267616
N	-0.710906	-2.337773	-1.041961
N	0.318989	-1.466413	-0.978226
N	-0.237354	-1.779794	1.888760
N	-2.456960	-0.913922	0.029358
O	0.397208	1.922414	3.192750
N	-1.200109	-2.591889	1.402919
C	1.118600	1.523097	-0.206458
O	3.530869	-0.611033	1.225481
C	2.414656	-0.375159	1.031719
C	1.108857	-1.718879	-2.022951
C	0.584744	-2.764930	-2.786418
H	0.990679	-3.195899	-3.688234
C	0.435842	1.221524	2.272261
C	-0.643371	-3.396142	3.389522
H	-0.597454	-4.003302	4.280057
C	-2.512689	1.236223	0.201621
C	-0.574155	-3.125732	-2.122159
C	-3.732519	-0.548676	-0.185120
C	-3.817992	0.828675	-0.085732
H	-4.694765	1.446319	-0.202091
C	0.106283	-2.256322	3.085201
C	2.085596	2.495570	-2.241376
H	2.850357	1.713773	-2.295812
H	2.494209	3.406615	-2.694419
H	1.221790	2.174016	-2.832208
C	-1.461818	-3.569508	2.287127
C	2.915719	3.178944	0.044802
H	2.643934	3.350840	1.091084
H	3.345876	4.103380	-0.358602
H	3.684073	2.400036	0.015611
B	-1.827082	-2.321515	0.021008
H	-2.659585	-3.153947	-0.231762
H	-2.110112	2.225637	0.362554
H	-4.484805	-1.295841	-0.390033
H	-1.308383	-3.888537	-2.334951
H	2.005934	-1.133868	-2.163474
H	0.870734	-1.754738	3.661966
H	-2.210117	-4.316855	2.067865
C	0.607564	3.864591	-0.717899
H	0.997361	4.799964	-1.136731
H	0.303616	4.050354	0.317586
H	-0.278861	3.574071	-1.292049

Geometry Optimisation for [W(≡CSiMe$_3$)(CO)$_2$(Tp)] (WSi)

Method: DFT/ωB97X-D/6-31G*/LANL2Dζ, gas phase.

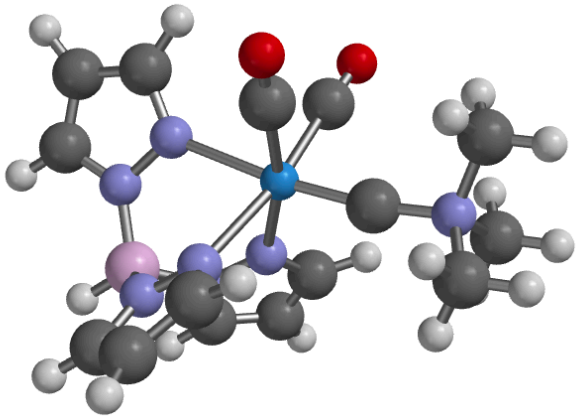


Cartesian Coordinates

Atom	x	y	z
W	0.423035	-0.053981	0.612696
Si	1.834158	3.000290	-0.810655
N	-1.780250	0.054192	0.265583
N	-0.808270	-2.468441	-1.030705
N	0.218397	-1.591620	-0.990432
N	-0.303782	-1.909394	1.899904
N	-2.540146	-1.042775	0.055562
O	0.323077	1.788159	3.175750
N	-1.271344	-2.721617	1.422754
C	1.054772	1.411684	-0.216943
O	3.445549	-0.749501	1.212408
C	2.335806	-0.505443	1.002573
C	0.989573	-1.840968	-2.049743
C	0.459545	-2.895947	-2.795732
H	0.850592	-3.328021	-3.703471
C	0.359686	1.098945	2.248487
C	-0.692441	-3.530935	3.400529
H	-0.635632	-4.141306	4.288261
C	-2.591246	1.111290	0.201473
C	-0.683078	-3.263431	-2.106580
C	-3.819079	-0.678094	-0.138829
C	-3.901514	0.700781	-0.055581
H	-4.779971	1.317573	-0.163321
C	0.052078	-2.388397	3.091629
C	2.415693	2.773838	-2.588861
H	3.170048	1.982352	-2.656279
H	2.859827	3.696496	-2.979864
H	1.580079	2.497936	-3.241018
C	-1.522085	-3.702950	2.306494
C	3.287490	3.384241	0.324554
H	2.946716	3.508119	1.358265
H	3.800137	4.304958	0.023163
H	4.016402	2.566757	0.312819
B	-1.911702	-2.450958	0.047365
H	-2.748755	-3.281074	-0.195435
H	-2.185027	2.102673	0.339574
H	-4.575865	-1.426948	-0.319909
H	-1.415380	-4.032941	-2.301109
H	1.875406	-1.245624	-2.215004
H	0.821694	-1.888110	3.662686
H	-2.271164	-4.451274	2.092925
C	0.533539	4.361313	-0.713050
H	0.934045	5.324044	-1.051246
H	0.181851	4.485836	0.317106
H	-0.332463	4.118276	-1.338788

Geometry Optimisation for $[W(\equiv CNMe_3)(CO)_2(Tp)]^+$ (WN)

Method: DFT/ωB97X-D/6-31G*/LANL2Dζ, gas phase.

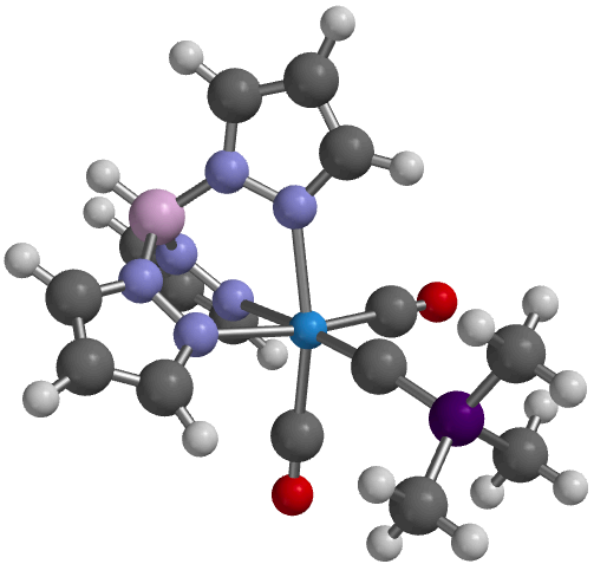


Cartesian Coordinates

Atom	x	y	z
W	0.462750	0.067389	0.559296
N	1.676748	2.751174	-0.773759
N	-1.715182	0.191845	0.212753
N	-0.722024	-2.336245	-1.074586
N	0.307488	-1.461471	-1.024527
N	-0.204442	-1.684252	1.828945
N	-2.467098	-0.907602	-0.015112
O	0.287212	1.846560	3.176311
N	-1.167791	-2.523836	1.379331
C	1.088612	1.528871	-0.281795
O	3.461509	-0.729755	1.218555
C	2.367928	-0.457903	0.994401
C	1.118075	-1.753877	-2.047521
C	0.608714	-2.826217	-2.776899
H	1.031184	-3.293414	-3.652535
C	0.346782	1.178607	2.242438
C	-0.566413	-3.256562	3.383854
H	-0.500413	-3.837290	4.290363
C	-2.543301	1.241775	0.191640
C	-0.560653	-3.165991	-2.116921
C	-3.750908	-0.552706	-0.179234
C	-3.848498	0.823723	-0.059795
H	-4.737042	1.430518	-0.135420
C	0.163734	-2.121980	3.039394
C	2.085381	2.546942	-2.205670
H	2.827602	1.749860	-2.237076
H	2.504782	3.479346	-2.588783
H	1.202802	2.255613	-2.774801
C	-1.399091	-3.473653	2.297816
C	2.878908	3.102030	0.058646
H	2.554348	3.232535	1.090750
H	3.316565	4.024093	-0.328820
H	3.591692	2.280209	-0.004350
B	-1.827187	-2.310106	-0.000691
H	-2.649692	-3.156724	-0.212836
H	-2.156996	2.235224	0.366701
H	-4.504523	-1.303815	-0.363639
H	-1.285712	-3.941974	-2.312475
H	2.022843	-1.183076	-2.196983
H	0.930483	-1.599969	3.594679
H	-2.140032	-4.238235	2.116197
C	0.655603	3.850621	-0.686053
H	1.092613	4.770917	-1.078744
H	0.376506	3.973408	0.360258
H	-0.213865	3.555394	-1.273307

Geometry Optimisation for $[W(\equiv CPMe_3)(CO)_2(Tp)]^+$ (WP)

Method: DFT/ωB97X-D/6-31G*/LANL2Dζ, gas phase

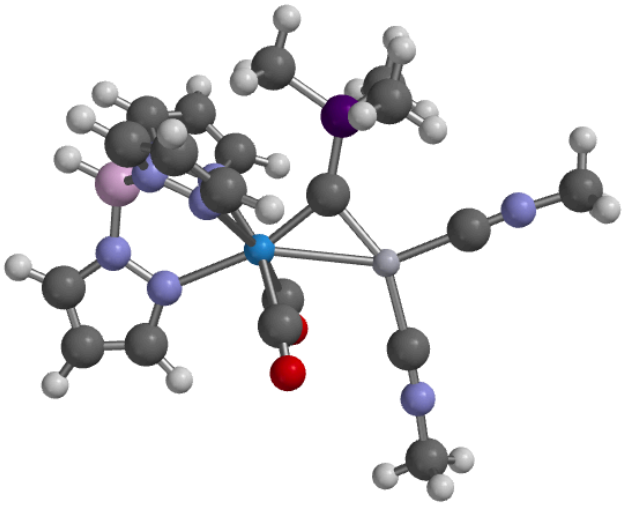


Cartesian Coordinates

Atom	x	y	z
W	0.346467	-0.025606	0.488820
P	1.806889	2.927879	-0.772979
N	-1.826366	0.051597	0.164170
N	-0.812984	-2.491882	-1.052244
N	0.199500	-1.595481	-1.040196
N	-0.274575	-1.767098	1.836930
N	-2.566066	-1.066368	-0.010453
O	0.151005	1.768200	3.100781
N	-1.228627	-2.631310	1.413320
C	1.001079	1.444516	-0.338082
O	3.346745	-0.807079	1.179939
C	2.256637	-0.538906	0.940641
C	0.999011	-1.892363	-2.071342
C	0.498980	-2.990326	-2.767306
H	0.914667	-3.466492	-3.641326
C	0.216761	1.101705	2.167870
C	-0.594362	-3.316309	3.424642
H	-0.509199	-3.878711	4.341116
C	-2.667513	1.090733	0.111882
C	-0.651237	-3.340222	-2.079013
C	-3.855632	-0.733274	-0.172284
C	-3.969335	0.645778	-0.106117
H	-4.866110	1.238132	-0.197187
C	0.112761	-2.176181	3.051114
C	2.336702	2.891757	-2.504765
H	3.042940	2.070553	-2.651804
H	2.818605	3.836295	-2.773295
H	1.467391	2.730561	-3.147404
C	-1.434653	-3.567511	2.351901
C	3.265877	3.186034	0.270719
H	2.955308	3.246007	1.317268
H	3.778050	4.110791	-0.010590
H	3.949961	2.341382	0.154275
B	-1.905078	-2.458649	0.035588
H	-2.716692	-3.322054	-0.148169
H	-2.288762	2.094838	0.233954
H	-4.601932	-1.499960	-0.318408
H	-1.362932	-4.135236	-2.245284
H	1.884452	-1.301012	-2.252502
H	0.876245	-1.631227	3.588738
H	-2.164761	-4.347498	2.192885
C	0.690622	4.338818	-0.551675
H	1.197634	5.270823	-0.817876
H	0.370473	4.385323	0.492615
H	-0.187948	4.209033	-1.188865

Geometry Optimisation for [WPt(μ-CPMe$_3$)(CNMe)$_2$(CO)$_2$(Tp)]$^+$ [10]$^+$

Method: DFT/ωB97X-D/6-31G*/LANL2Dζ, gas phase



Cartesian Coordinates

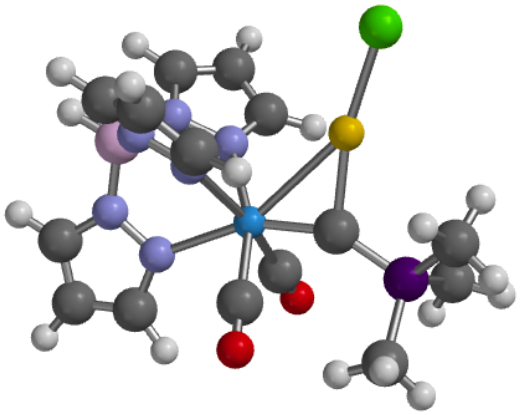
Atom	x	y	z
Pt	-2.426998	0.022790	0.547092
W	-0.048260	-0.730789	-0.697796
P	0.241750	1.775644	1.656866
C	-0.527390	0.571754	0.654066
N	1.773540	-1.259546	0.477679
C	-1.043900	-2.398667	-0.187157
O	-1.567076	-3.408526	0.022520
N	1.323746	0.766319	-1.629043
N	1.110028	-1.997650	-2.162910
O	-2.209924	-0.486057	-2.993349
C	-1.455657	-0.531630	-2.118541
N	3.024996	-1.165172	-0.017283
N	2.447718	-1.872365	-2.330625
C	-3.432861	1.129135	1.802212
N	2.644037	0.550180	-1.801957
C	-3.961430	-1.063431	-0.144479
N	-4.033977	1.797021	2.549101
N	-4.804597	-1.733015	-0.586630
C	2.871270	-2.747083	-3.255797
C	1.069230	2.005230	-2.060752

Cartesian Coordinates (cont.)

Atom	x	y	z
C	0.702061	-2.962396	-2.995496
C	1.782634	-3.471307	-3.713003
H	1.775548	-4.252376	-4.456789
C	1.883145	-1.662427	1.747247
C	2.245462	2.611245	-2.507493
H	2.367294	3.600016	-2.921525
C	3.220163	1.642465	-2.331008
C	3.917295	-1.497284	0.930740
C	2.033121	1.943962	1.422735
H	2.528215	0.997472	1.652224
H	2.414658	2.721260	2.091769
H	2.249955	2.221231	0.388313
C	3.228188	-1.817117	2.089469
H	3.639943	-2.138880	3.033304
C	-0.471626	3.418600	1.356961
H	-0.264707	3.713205	0.324974
H	-0.039977	4.158262	2.037603
H	-1.553931	3.370935	1.497636
B	3.242654	-0.840513	-1.509649
H	4.410497	-0.868257	-1.785546
H	4.276528	1.648191	-2.555682
H	3.916442	-2.793358	-3.524233
H	4.974517	-1.495667	0.710106
H	0.989898	-1.822239	2.333989
H	0.057148	2.382451	-2.028558
H	-0.342436	-3.236759	-3.032658
C	-5.791360	-2.583000	-1.150505
H	-5.301784	-3.443686	-1.610799
H	-6.352862	-2.032323	-1.907877
H	-6.469249	-2.923832	-0.365486
C	-4.854034	2.565760	3.417741
H	-4.227384	3.183454	4.064686
H	-5.460309	1.896106	4.031507
H	-5.507952	3.208071	2.823827
C	-0.012749	1.399122	3.415029
H	0.406334	2.188015	4.046324
H	0.477673	0.450710	3.648913
H	-1.083258	1.296745	3.607996

Geometry Optimisation for [WAu(μ-CPMe$_3$)Cl(CO)$_2$(Tp)]$^+$ [10]$^+$

Method: DFT/ωB97X-D/6-31G*/LANL2Dζ, gas phase



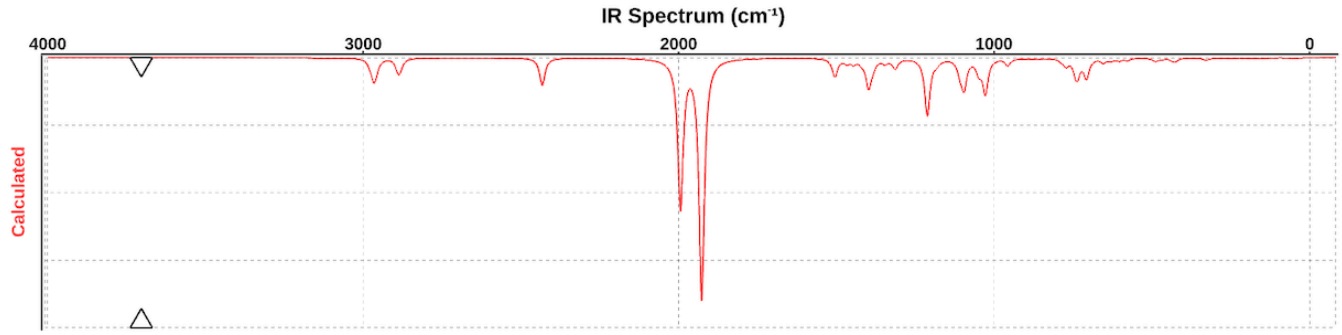
Cartesian Coordinates

Atom	x	y	z
Au	0.645218	-0.147535	-2.540208
W	0.088005	0.109975	0.258995
Cl	0.424667	-1.255130	-4.547195
P	2.098269	2.516102	-1.385194
N	-1.926684	-0.369852	-0.460220
N	-0.653735	-2.904623	0.513035
N	0.336100	-2.063068	0.134923
N	-0.794531	-0.394233	2.221940
N	-2.600459	-1.444587	0.005638
O	-0.882959	3.014572	1.059765
N	-1.625695	-1.462898	2.310260
C	1.099557	1.116927	-0.971913
O	2.758039	0.304871	1.957996
C	1.786433	0.230676	1.352759
C	1.356543	-2.819298	-0.293650
C	1.022797	-4.166707	-0.199265
H	1.624680	-5.016682	-0.478843
C	-0.536304	1.954740	0.784351
C	-1.478236	-0.583473	4.344303
H	-1.610965	-0.405470	5.399767
C	-2.713994	0.228438	-1.364567
C	-0.260617	-4.172748	0.322080
C	-3.794754	-1.523503	-0.599976
C	-3.910636	-0.470657	-1.492308
H	-4.739314	-0.246828	-2.145055
C	-0.703409	0.141413	3.448282
C	3.851069	2.094025	-1.244446
H	4.151959	2.125953	-0.193995
H	4.451730	2.806424	-1.817641
H	4.016263	1.083323	-1.628893
C	-2.044349	-1.590526	3.576093
C	1.751910	3.922388	-0.299743
H	1.002272	4.572493	-0.757355
H	2.670100	4.495396	-0.139815
H	1.381438	3.567289	0.665091
B	-1.969215	-2.346584	1.079856
H	-2.713985	-3.230116	1.397751
H	-2.371520	1.113217	-1.881475
H	-4.479005	-2.321289	-0.352085
H	-0.086455	1.012615	3.617322
H	-2.716903	-2.391335	3.846353
H	-0.920341	-4.990663	0.570804
H	2.261220	-2.355287	-0.659309
C	1.743578	2.996235	-3.093261
H	2.119301	4.005328	-3.286292
H	0.663658	2.971297	-3.262393
H	2.229257	2.289393	-3.772264

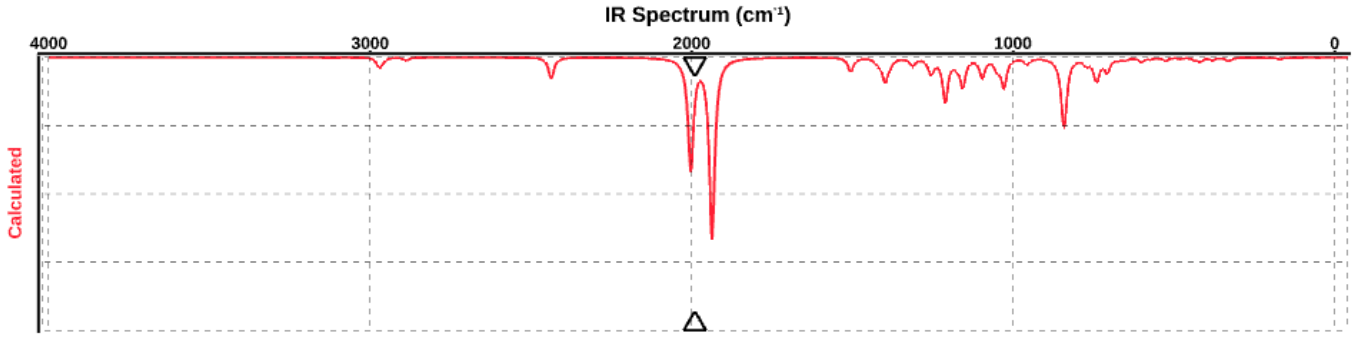
Dalton Transactions

SUPPORTING INFORMATION

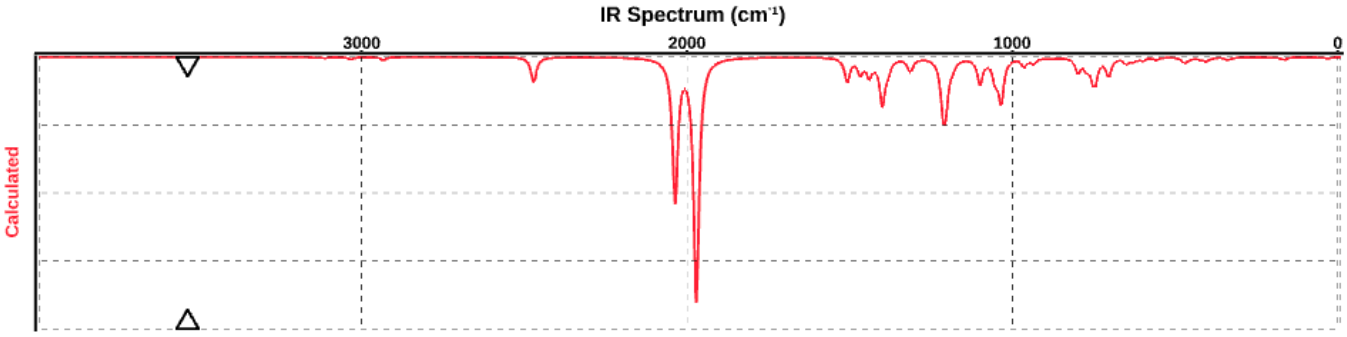
Calculated Infrared Spectrum for [W(≡CCMe$_3$)(CO)$_2$(Tp)] (WC) (DFT/ωB97X-D/6-31G*/LANL2Dζ, gas phase)



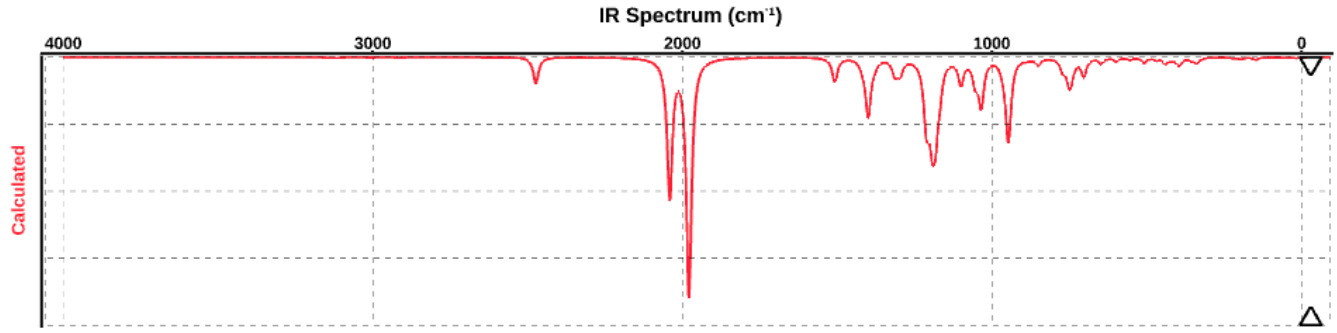
Calculated Infrared Spectrum for [W(≡CSiMe$_3$)(CO)$_2$(Tp)] (WSi) (DFT/ωB97X-D/6-31G*/LANL2Dζ, gas phase)



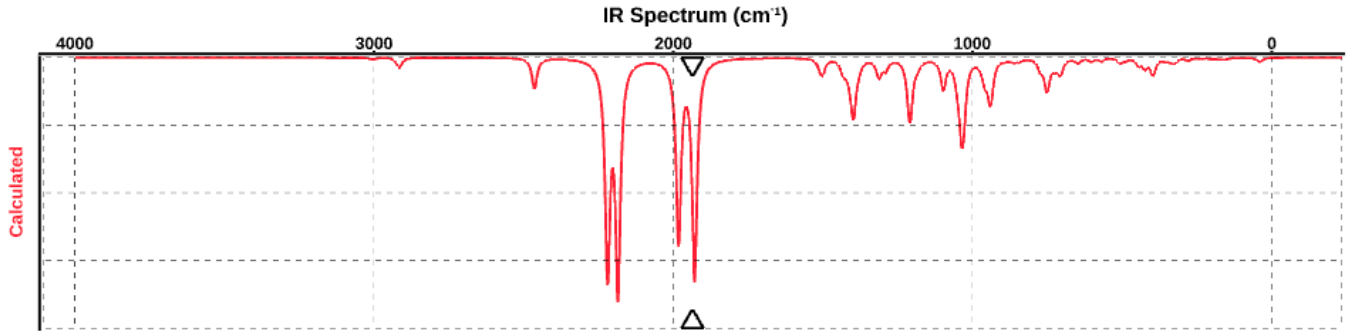
Calculated Infrared Spectrum for [W(≡CNMe$_3$)(CO)$_2$(Tp)]$^+$ (WN) (DFT/ωB97X-D/6-31G*/LANL2Dζ, gas phase)



Calculated Infrared Spectrum for $[W(\equiv CPMe_3)(CO)_2(Tp)]^+$ (WP) (DFT/ωB97X-D/6-31G*/LANL2Dζ, gas phase)



Calculated Infrared Spectrum for $[WPt(\mu CPMe_3)(CNMe)_2(CO)_2(Tp)]^+$ [10]$^+$ (DFT/ωB97X-D/6-31G*/LANL2Dζ, gas phase)



Calculated Infrared Spectrum for $[WAu(\mu CPMe_3)Cl(CO)_2(Tp)]^+$ [11]$^+$ (DFT/ωB97X-D/6-31G*/LANL2Dζ, gas phase)