Dalton Transactions

ELECTRONIC SUPPORTING INFORMATION

Figure S1. ^{13}C-^{1}H HSQC NMR spectrum (400-151 MHz, C_6D_6, 25 °C) extract showing correlation ($^{5}J_{CH}$) between the carbido resonance and those of the H^4(pz) methine protons.

Optimised Geometries and Cartesian Coordinates

[DFT:ωB97X-D/6-31G*/LANL2DZ]

$[PtH(CNH)_3]^+$

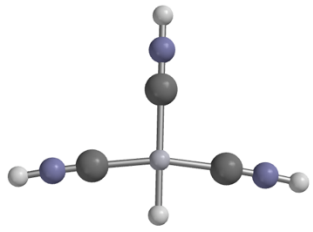

Figure S2: Optimised structure of $[PtH(CNH)_3]^+$ in the gas phase.

Table S1: Cartesian coordinates for $[PtH(CNH)_3]^+$

Atom	x	y	z
Pt	0.001595	0.000000	0.506381
H	0.001209	0.000000	2.110918
C	-1.952619	0.000000	0.717441
C	1.955913	0.000000	0.719244
C	-0.000841	0.000000	-1.550189
N	3.100280	0.000000	0.887687
N	-3.097216	0.000000	0.883820
N	-0.003926	0.000000	-2.708462
H	-4.083273	0.000000	1.068592
H	4.085556	0.000000	1.076451
H	-0.006677	0.000000	-3.711884

Table S2: Thermodynamic properties at 298.15 °K

Zero Point Energy :	164.60	kJ/mol	(ZPE)
Temperature Correction :	25.78	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	190.38	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-399.688494	au	(Electronic Energy + Enthalpy Correction)
Entropy :	386.65	J/mol•K	
Gibbs Energy :	-399.732402	au	(Enthalpy - T*Entropy)
C_v :	144.24	J/mol•K	

$[Pt(CH_2CH_3(CNH)_3]^+$

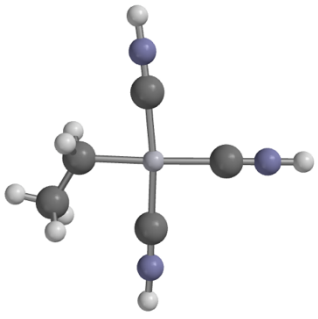

Figure S3: Optimised structure of $[Pt(CH_2CH_3)(CNH)_3]^+$ in the gas phase.

Table S3: Cartesian coordinates for $[PtH(CNH)_3]^+$

Atom	x	y	z
Pt	-0.281038	0.000000	-0.636140
C	-2.242739	0.000000	-0.428086
C	1.682411	-0.000000	-0.609482
C	-0.338961	-0.000000	-2.700540
N	2.839976	0.000000	-0.609842
N	-3.389112	0.000000	-0.268551
N	-0.366908	0.000000	-3.859817
H	-4.378824	-0.000000	-0.106991
H	3.841054	0.000000	-0.556543
H	-0.394932	-0.000000	-4.862381
C	-0.299693	0.000000	1.482927
H	-0.884053	-0.881761	1.769868
H	-0.884053	0.881761	1.769868
C	1.024222	-0.000000	2.242522
H	1.624942	-0.889354	2.026831
H	0.822767	0.000000	3.319524
H	1.624942	0.889353	2.026831

Table S4: Thermodynamic properties at 298.15 °K

Zero Point Energy :	308.57	kJ/mol	(ZPE)
Temperature Correction :	32.66	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	341.22	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-478.231287	au	(Electronic Energy + Enthalpy Correction)
Entropy :	433.29	J/mol•K	
Gibbs Energy :	-478.280491	au	(Enthalpy - T*Entropy)
C_v :	194.55	J/mol•K	

$[Pt(CH=CH_2)(CNH)_3]^+$

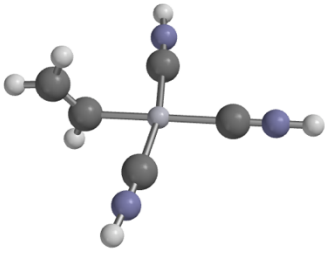

Figure S4: Optimised structure of $[Pt(CH=CH_2)(CNH)_3]^+$ in the gas phase.

Table S5: Cartesian coordinates for $[Pt(CH{=}CH_2)(CNH)_3]^+$

Atom	x	y	z
Pt	-0.025149	0.214939	-0.423445
C	-1.982595	0.190909	-0.177219
C	1.941286	0.204753	-0.295141
C	-0.088152	0.199200	-2.479162
N	3.092151	0.191936	-0.179766
N	-3.124416	0.170242	0.007611
N	-0.121700	0.188656	-3.637460
H	-4.104782	0.147720	0.217902
H	4.083309	0.178162	-0.028317
H	-0.145305	0.178705	-4.640331
C	0.041181	0.255326	1.634139
H	-0.010319	1.251253	2.074493
C	0.122542	-0.819444	2.411770
H	0.178145	-1.832052	2.019816
H	0.143804	-0.720305	3.495110

Table S6: Thermodynamic properties at 298.15 °K

Zero Point Energy :	248.52	kJ/mol	(ZPE)
Temperature Correction :	31.60	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	280.12	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-477.016136	au	(Electronic Energy + Enthalpy Correction)
Entropy :	427.17	J/mol•K	
Gibbs Energy :	-477.064646	au	(Enthalpy - T*Entropy)
C_V :	187.05	J/mol•K	

$[Pt(CCH)(CNH)_3]^+$

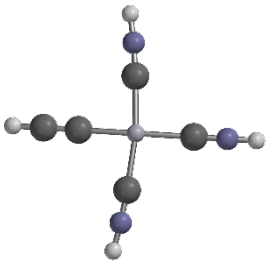

Figure S5: Optimised structure of $[Pt(CCH)(CNH)_3]^+$ in the gas phase.

Table S7: Cartesian coordinates for $[Pt(CCH)(CNH)_3]^+$

Atom	X	Y	Z
Pt	0.000109	-0.000903	0.147517
C	0.004706	-0.001146	-1.833234
C	-1.968985	0.002953	-0.010909
C	1.969928	-0.004381	-0.001393
C	-0.005347	0.000889	2.168635
C	0.00715	-0.000752	-3.044
H	0.009277	-0.000212	-4.112358
N	3.116084	-0.006888	-0.140832
N	-3.114365	0.005307	-0.156689
N	-0.008971	0.002533	3.326169
H	-4.099601	0.007001	-0.34675
H	4.102342	-0.008786	-0.325865
H	-0.012329	0.004385	4.329708

Table S8: Thermodynamic properties at 298.15 °K

Zero Point Energy:	192.31	kJ/mol	(ZPE)
Temperature Correction:	30.56	kJ/mol	(vibration+ gas law + rotation + translation)
Enthalpy Correction:	222.87	kJ/mol	(ZPE + temperature correction)
Enthalpy:	–475.787262	au	(Electronic Energy + Enthalpy Correction)
Entropy:	419.38	J/mol·K	
Gibbs Energy:	–475.834886	au	(Enthalpy + T×Entropy)
C_v:	178.98	J/mol·K	

$[Pt(CN)(CNH)_3]^+$

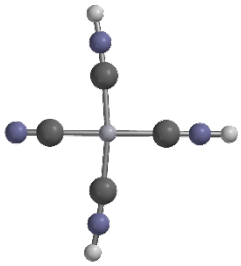

Figure S6: Optimised structure of $[Pt(CN)(CNH)_3]^+$ in the gas phase.

Table S9: Cartesian coordinates for $[Pt(CN)(CNH)_3]^+$

Atom	X	Y	Z
Pt	0.000242	-0.000272	-0.201959
C	0.000212	-0.003614	-2.186867
C	1.976827	0.000629	-0.343418
C	-1.976379	-0.000971	-0.342445
C	-0.000106	0.002247	1.812653
N	0.000399	-0.0062	-3.347575
N	-3.12044	-0.000814	-0.486984
N	3.120919	0.001576	-0.488064
N	-0.000887	0.003146	2.968504
H	-0.001194	0.003422	3.973165
H	4.107663	0.002147	-0.679306
H	-4.107256	-0.001296	-0.677704

Table S10: Thermodynamic properties at 298.15 °K

Zero Point Energy:	165.82	kJ/mol	(ZPE)
Temperature Correction:	29.65	kJ/mol	(vibration+ gas law + rotation + translation)
Enthalpy Correction:	195.47	kJ/mol	(ZPE + temperature correction)
Enthalpy:	–491.889321	au	(Electronic Energy + Enthalpy Correction)
Entropy:	414.89	J/mol·K	
Gibbs Energy:	–491.936436	au	(Enthalpy + T×Entropy)
C_v:	170.82	J/mol·K	

$[Pt(CP)(CNH)_3]^+$

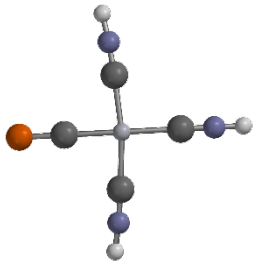

Figure S7: Optimised structure of $[Pt(CP)(CNH)_3]^+$ in the gas phase.

Table S11: Cartesian coordinates for $[Pt(CP)(CNH)_3]^+$

Atom	X	Y	Z
Pt	-0.000178	-0.007952	-0.181017
C	-0.000528	-0.068966	-2.158566
C	1.972094	-0.013004	-0.326619
C	-1.97233	-0.01031	-0.32645
C	0.000179	0.057505	1.851981
P	-0.000675	-0.113011	-3.705117
N	-3.119591	-0.010879	-0.457005
N	3.119331	-0.011649	-0.456732
N	0.000656	0.09612	3.008929
H	-4.108269	-0.023904	-0.631163
H	0.001172	0.130308	4.011918
H	4.108139	-0.024257	-0.630158

Table S12: Thermodynamic properties at 298.15 °K

Zero Point Energy:	158.62	kJ/mol	(ZPE)
Temperature Correction:	30.51	kJ/mol	(vibration+ gas law + rotation + translation)
Enthalpy Correction:	189.13	kJ/mol	(ZPE + temperature correction)
Enthalpy:	–778.458363	au	(Electronic Energy + Enthalpy Correction)
Entropy:	424.36	J/mol·K	
Gibbs Energy:	–778.506553	au	(Enthalpy + T×Entropy)
C_v:	174.45	J/mol·K	

$[Pt(CAs)(CNH)_3]^+$

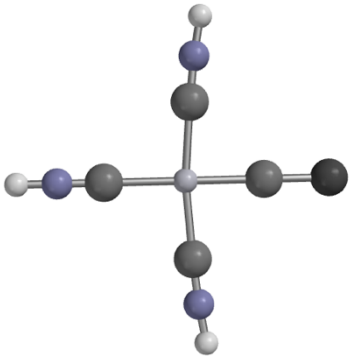

Figure S8: Optimised structure of $[Pt(CAs)(CNH)_3]^+$ in the gas phase.

Table S13: Cartesian coordinates for $[Pt(CAs)(CNH)_3]^+$

Atom	x	y	z
Pt	0.000118	-0.000713	-0.172994
C	-0.000034	0.000948	-2.152080
C	-1.971879	-0.000637	-0.319201
C	1.972088	-0.000358	-0.319056
C	0.000126	-0.001426	1.862486
As	-0.000281	0.003171	-3.808170
N	3.119753	-0.000130	-0.448627
N	-3.119679	-0.000467	-0.448106
N	0.000141	-0.000821	3.020476
H	4.108686	0.000210	-0.619496
H	-0.000387	-0.000465	4.023826
H	-4.108652	0.000687	-0.619060

Table S14: Thermodynamic properties at 298.15 °K

Zero Point Energy :	156.25	kJ/mol	(ZPE)
Temperature Correction :	30.93	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	187.19	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-2672.781286	au	(Electronic Energy + Enthalpy Correction)
Entropy :	433.83	J/mol•K	
Gibbs Energy :	-2672.830552	au	(Enthalpy - T*Entropy)
C_V :	176.34	J/mol•K	

$[Pt(CSb)(CNH)_3]^+$

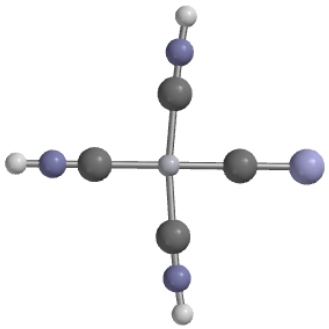

Figure S9: Optimised structure of $[Pt(CSb)(CNH)_3]^+$ in the gas phase.

Table S15: Cartesian coordinates for $[Pt(CSb)(CNH)_3]^+$

Atom	x	y	z
Pt	0.000454	-0.000231	-0.164460
C	0.000437	-0.001397	-2.139274
C	1.971832	0.000313	-0.308612
C	-1.971465	-0.001294	-0.308401
C	0.000468	0.000594	1.878066
Sb	0.000795	-0.000946	-3.991370
N	-3.120821	-0.001401	-0.428578
N	3.121072	0.001620	-0.429432
N	-0.000494	0.001347	3.036701
H	-4.110024	-0.000341	-0.590888
H	-0.002836	0.000821	4.039104
H	4.110580	0.000914	-0.592855

Table S16: Thermodynamic properties at 298.15 °K

Zero Point Energy :	154.50	kJ/mol	(ZPE)
Temperature Correction :	31.21	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	185.71	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-442.516120	au	(Electronic Energy + Enthalpy Correction)
Entropy :	440.58	J/mol•K	
Gibbs Energy :	-442.566152	au	(Enthalpy - T*Entropy)
C_V :	178.16	J/mol•K	

$[Pt(BNH)(CNH)_3]^+$

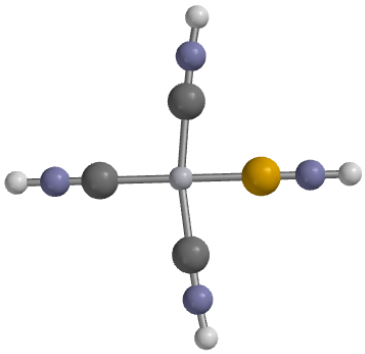

Figure S10: Optimised structure of $[Pt(BNH)(CNH)_3]^+$ in the gas phase.

Table S17: Cartesian coordinates for $[Pt(BNH)(CNH)_3]^+$

Atom	x	y	z
Pt	0.000000	0.000000	-0.168450
B	-0.000000	0.000000	1.875373
C	-1.958615	0.000000	0.028204
C	1.958615	0.000000	0.028204
C	0.000000	0.000000	-2.246627
N	-0.000000	0.000000	3.114923
H	0.000000	0.000000	4.111062
N	3.105450	0.000000	0.174908
N	-3.105450	0.000000	0.174908
N	0.000000	0.000000	-3.404431
H	-4.091452	0.000000	0.360062
H	4.091452	0.000000	0.360062
H	0.000000	0.000000	-4.408199

Table S18: Thermodynamic properties at 298.15 °K

Zero Point Energy :	189.51	kJ/mol	(ZPE)
Temperature Correction :	31.56	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	221.06	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-479.276803	au	(Electronic Energy + Enthalpy Correction)
Entropy :	419.50	J/mol•K	
Gibbs Energy :	-479.324441	au	(Enthalpy - T*Entropy)
C_V :	184.34	J/mol•K	

$[Pt(BO)(CNH)_3]^+$

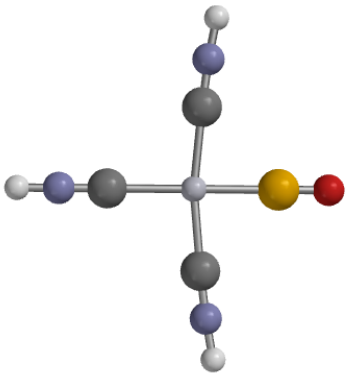

Figure S11: Optimised structure of $[Pt(BO)(CNH)_3]^+$ in the gas phase.

Table S19: Cartesian coordinates for $[Pt(BO)(CNH)_3]^+$

Atom	x	y	z
Pt	0.000000	0.000000	0.189257
B	0.000000	0.000000	2.224405
C	-1.964965	0.000000	0.366535
C	1.964965	0.000000	0.366535
C	0.000000	0.000000	-1.889448
O	0.000000	0.000000	3.429639
N	3.110949	0.000000	0.510290
N	-3.110949	0.000000	0.510290
N	0.000000	0.000000	-3.046054
H	-4.098497	0.000000	0.694609
H	4.098497	0.000000	0.694609
H	0.000000	0.000000	-4.050668

Table S20: Thermodynamic properties at 298.15 °K

Zero Point Energy :	162.72	kJ/mol	(ZPE)
Temperature Correction :	30.01	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	192.72	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-499.188737	au	(Electronic Energy + Enthalpy Correction)
Entropy :	411.84	J/mol•K	
Gibbs Energy :	-499.235505	au	(Enthalpy - T*Entropy)
C_V :	172.34	J/mol•K	

$[Pt(B{=}CH_2)(CNH)_3]^+$

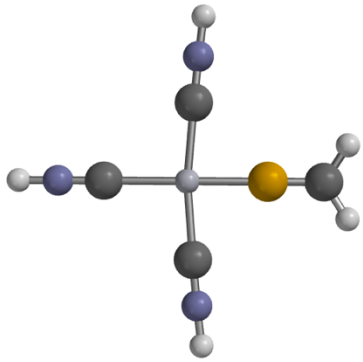

Figure S12: Optimised structure of $[Pt(B{=}CH_2)(CNH)_3]^+$ in the gas phase.

Table S21: Cartesian coordinates for $[Pt(B{=}CH_2)(CNH)_3]^+$

Atom	x	y	z
Pt	0.000000	0.000000	-0.383283
B	-0.000000	0.000000	1.625707
C	-1.963519	0.000000	-0.229572
C	1.963519	0.000000	-0.229572
C	0.000000	0.000000	-2.478135
N	3.115214	0.000000	-0.122734
N	-3.115214	0.000000	-0.122734
N	0.000000	0.000000	-3.636384
H	-4.111223	0.000000	-0.001177
H	4.111223	0.000000	-0.001177
H	0.000000	0.000000	-4.640050
C	-0.000000	0.000000	3.015217
H	0.916606	0.000000	3.601947
H	-0.916606	0.000000	3.601947

Table S22: Thermodynamic properties at 298.15 °K

Zero Point Energy :	211.62	kJ/mol	(ZPE)
Temperature Correction :	32.63	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	244.25	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-463.158582	au	(Electronic Energy + Enthalpy Correction)
Entropy :	427.82	J/mol•K	
Gibbs Energy :	-463.207165	au	(Enthalpy - T*Entropy)
C_V :	190.76	J/mol•K	

$[Pt(CNO)(CNH)_3]^+$

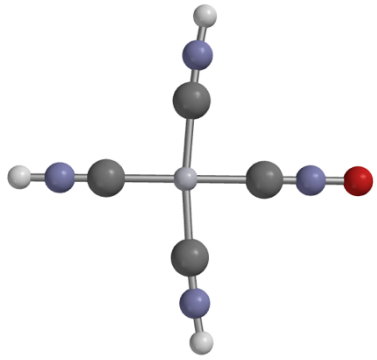

Figure S13: Optimised structure of $[Pt(CNO)(CNH)_3]^+$ in the gas phase.

Table S23: Cartesian coordinates for $[Pt(CNO)(CNH)_3]^+$

Atom	x	y	z
Pt	-0.001379	-0.002558	0.147065
C	-0.001171	0.019105	-1.839148
C	-1.976976	0.000532	0.015093
C	1.974076	-0.002117	0.013632
C	-0.000594	-0.023517	2.135517
N	3.119488	0.000194	-0.123280
N	-3.122430	0.003467	-0.121187
N	0.000303	-0.035491	3.292184
H	4.108341	0.000081	-0.300960
H	0.001626	-0.045351	4.296522
H	-4.111424	0.004335	-0.297534
N	0.003213	0.033400	-3.008409
O	0.006927	0.047920	-4.209494

Table S24: Thermodynamic properties at 298.15 °K

Zero Point Energy :	177.42	kJ/mol	(ZPE)
Temperature Correction :	31.52	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	208.94	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-567.009149	au	(Electronic Energy + Enthalpy Correction)
Entropy :	431.73	J/mol•K	
Gibbs Energy :	-567.058176	au	(Enthalpy - T*Entropy)
C_V :	185.03	J/mol•K	

$[Pt\{C{\equiv}W(CO)_2Tp\}(CNH)_3]^+$

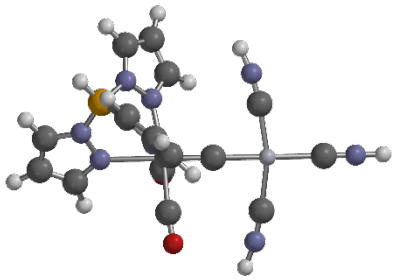

Figure S14: Optimised structure of $[Pt\{C{\equiv}W(CO)_2Tp\}(CNH)_3]^+$ in the gas phase.

Table S25: Cartesian coordinates for $[Pt\{C\equiv W(CO)_2Tp\}(CNH)_3]^+$

Atom	X	Y	Z
Pt	-1.23012	-3.581932	0.936207
W	0.433257	-0.571841	-0.65766
O	3.150254	-2.207177	-0.635296
O	-0.311631	-1.963001	-3.390791
N	1.518678	1.23356	-1.620503
N	1.320797	2.483568	-1.140291
N	0.972236	0.590791	1.172166
N	0.819784	1.928927	1.25092
N	-1.223194	0.902969	-0.704895
N	-1.047431	2.203418	-0.380878
C	-0.365774	-2.000404	0.107355
C	2.1712	-1.601764	-0.652515
C	-0.027523	-1.404639	-2.416678
C	2.4042	1.335376	-2.615166
C	2.788606	2.665431	-2.790204
H	3.483583	3.06579	-3.511471
C	2.073219	3.358192	-1.828873
C	1.441221	0.179804	2.353907
C	1.58096	1.264889	3.222135
H	1.957754	1.26499	4.233539
C	1.179011	2.358641	2.470667
C	-2.510343	0.752804	-1.030814
C	-3.184824	1.968543	-0.914955
H	-4.226514	2.171007	-1.108668
C	-2.211489	2.862381	-0.502136
B	0.34113	2.736482	0.020488
H	0.28583	3.906321	0.285894
H	1.133906	3.409715	2.714522
H	1.670894	-0.866026	2.501971
H	2.044054	4.410846	-1.588731
H	2.715776	0.450646	-3.152727
H	-2.262831	3.920196	-0.290796
H	-2.875503	-0.219073	-1.329065
C	-1.007176	-4.366275	-0.860503
C	-2.14959	-5.200365	1.812465
C	-1.251685	-2.396357	2.515527
N	-1.205059	-1.613933	3.366737
N	-2.672316	-6.108824	2.30864
N	-0.847652	-4.716081	-1.951103
H	-0.669494	-4.875082	-2.925864
H	-3.122507	-6.895305	2.737316
H	-1.083695	-0.837208	3.990128

Table S26: Thermodynamic properties at 298.15 °K

Zero Point Energy:	706.01	kJ/mol	(ZPE)
Temperature Correction:	67.77	kJ/mol	(vibration+ gas law + rotation + translation)
Enthalpy Correction:	773.78	kJ/mol	(ZPE + temperature correction)
Enthalpy:	–1433.621619	au	(Electronic Energy + Enthalpy Correction)
Entropy:	677.90	J/mol·K	
Gibbs Energy:	–1433.698601	au	(Enthalpy + T×Entropy)
C_v:	471.99	J/mol·K	

$[Pt\{C\equiv W(CO)_2Tp\}(CNMe)_3]^+$

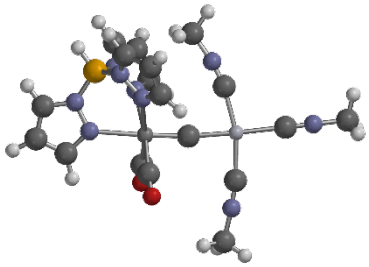

Figure S15: Optimised structure of $[Pt\{C\equiv W(CO)_2Tp\}(CNMe)_3]^+$ in the gas phase.

Table S27: Cartesian coordinates for $[Pt\{C\equiv W(CO)_2Tp\}(CNMe)_3]^+$

Atom	X	Y	Z
Pt	-0.987968	-2.762342	0.632401
W	0.859177	0.107293	-0.979122
O	3.509773	-1.607805	-1.17095
O	0.010813	-1.077232	-3.782594
N	1.822268	2.023144	-1.871557
N	1.615912	3.234342	-1.305309
N	1.445066	1.164067	0.911295
N	1.305695	2.497256	1.073551
N	-0.850397	1.546638	-0.776899
N	-0.681051	2.827721	-0.384446
C	0.045741	-1.329648	-0.254686
C	2.557349	-0.958762	-1.110756
C	0.327383	-0.605995	-2.775513
C	2.621866	2.218576	-2.922505
C	2.942683	3.571764	-3.046356
H	3.56488	4.040976	-3.792249
C	2.278976	4.178685	-1.994866
C	1.924326	0.677909	2.058876
C	2.093355	1.708143	2.988382
H	2.478035	1.638634	3.994133
C	1.691783	2.849282	2.311592
C	-2.161531	1.359732	-0.946602
C	-2.860551	2.533878	-0.652278
H	-3.924271	2.705527	-0.709745
C	-1.873463	3.442474	-0.30464
B	0.728141	3.374637	-0.061003
H	0.660318	4.521334	0.292002
H	1.663037	3.88455	2.618279
H	2.123601	-0.380252	2.147645
H	2.23105	5.213551	-1.689365
H	2.924425	1.379013	-3.532755
H	-1.93311	4.481288	-0.015018
H	-2.524298	0.39603	-1.273716
C	-0.268991	-3.934819	-0.784375
C	-2.100862	-4.198936	1.601786
C	-1.4692	-1.216888	1.781577
N	-1.627957	-0.193236	2.295077
N	-2.730245	-5.005009	2.148122
N	0.202865	-4.494604	-1.679402
C	-1.693662	1.152823	2.750826
H	-2.330565	1.207682	3.63473
H	-2.107131	1.765085	1.944601
H	-0.679226	1.4821	2.991668
C	-3.501647	-5.994417	2.819698
H	-2.833111	-6.766993	3.203705
H	-4.210419	-6.432649	2.114678
H	-4.040744	-5.526446	3.645088
C	0.823748	-5.070388	-2.823228
H	1.860498	-5.307677	-2.578006
H	0.789545	-4.342293	-3.635922
H	0.288092	-5.977742	-3.105847

Table S28: Thermodynamic properties at 298.15 °K

Zero Point Energy:	927.85	kJ/mol	(ZPE)
Temperature Correction:	75.91	kJ/mol	(vibration+ gas law + rotation + translation)
Enthalpy Correction:	1003.77	kJ/mol	(ZPE + temperature correction)
Enthalpy:	–1551.482936	au	(Electronic Energy + Enthalpy Correction)
Entropy:	740.57	J/mol·K	
Gibbs Energy:	–1551.567034	au	(Enthalpy + T×Entropy)
C_v:	526.31	J/mol·K	

$[Pt(H)Br(CNH)_2]$

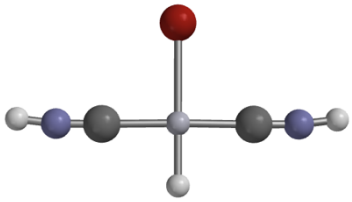

Figure S16: Optimised structure of $[Pt(H)Br(CNH)_2]$ in the gas phase.

Table S29: Cartesian coordinates for $[Pt(H)Br(CNH)_2]$

Atom	x	y	z
Pt	-0.000182	0.000000	0.121901
H	-0.000886	0.000000	1.712199
C	-1.943795	0.000000	0.144204
C	1.943579	0.000000	0.145815
N	3.105965	0.000000	0.141705
N	-3.106246	0.000000	0.139905
H	-4.096386	0.000000	0.018107
H	4.096554	0.000000	0.023755
Br	0.001398	0.000000	-2.447591

Table S30: Thermodynamic properties at 298.15 °K

Zero Point Energy :	114.55	kJ/mol	(ZPE)
Temperature Correction :	24.19	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	138.74	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-2880.477679	au	(Electronic Energy + Enthalpy Correction)
Entropy :	387.16	J/mol•K	
Gibbs Energy :	-2880.521645	au	(Enthalpy - T*Entropy)
C_V :	127.67	J/mol•K	

$[Pt(CH_2CH_3)Br(CNH)_2]$

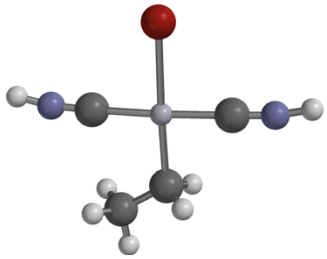

Figure S17: Optimised structure of $[Pt(CH_2CH_3)Br(CNH)_2]$ in the gas phase.

Table S31: Cartesian coordinates for $[Pt(CH_2CH_3)Br(CNH)_2]$

Atom	x	y	z
Pt	-0.336800	0.000000	-1.013234
C	-2.280831	0.000000	-0.975777
C	1.601319	0.000000	-1.151451
N	2.758262	-0.000000	-1.275831
N	-3.444223	-0.000000	-0.970359
H	-4.429461	-0.000000	-1.128195
H	3.719427	-0.000000	-1.543061
C	-0.348428	0.000000	1.081332
H	-0.925008	-0.881192	1.390373
H	-0.925007	0.881192	1.390373
C	0.997382	-0.000000	1.801485
H	1.591896	-0.885787	1.552192
H	0.850012	-0.000000	2.889474
H	1.591896	0.885786	1.552192
Br	-0.420434	0.000000	-3.599513

Table S32: Thermodynamic properties at 298.15 °K

Zero Point Energy :	259.89	kJ/mol	(ZPE)
Temperature Correction :	30.78	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	290.67	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-2959.017210	au	(Electronic Energy + Enthalpy Correction)
Entropy :	431.67	J/mol•K	
Gibbs Energy :	-2959.066230	au	(Enthalpy - T*Entropy)
C_V :	175.80	J/mol•K	

$[Pt(CH{=}CH_2)Br(CNH)_2]$

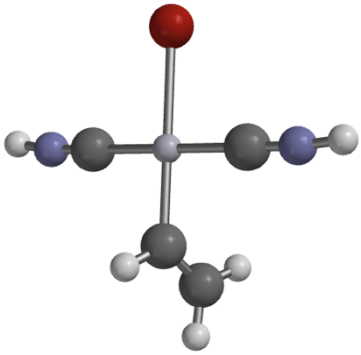

Figure S18: Optimised structure of $[Pt(CH{=}CH_2)Br(CNH)_2]$ in the gas phase.

Table S33: Cartesian coordinates for $[Pt(CH{=}CH_2)Br(CNH)_2]$

Atom	x	y	z
Pt	0.105831	-0.140037	-0.849626
C	-1.833237	-0.303426	-0.897404
C	2.045505	0.053732	-0.806884
N	3.200929	0.180225	-0.799021
N	-2.990486	-0.398562	-0.936497
H	-3.977994	-0.467064	-1.060970
H	4.184701	0.307417	-0.906420
C	0.069164	-0.374840	1.170209
H	0.434065	-1.337120	1.537425
C	-0.344230	0.526270	2.059228
H	-0.719257	1.505173	1.768626
H	-0.320846	0.315450	3.127722
Br	0.145855	0.132781	-3.406387

Table S34: Thermodynamic properties at 298.15 °K

Zero Point Energy :	200.83	kJ/mol	(ZPE)
Temperature Correction :	29.54	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	230.37	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-2957.802777	au	(Electronic Energy + Enthalpy Correction)
Entropy :	424.17	J/mol•K	
Gibbs Energy :	-2957.850945	au	(Enthalpy - T*Entropy)
C_V :	167.67	J/mol•K	

$[PtBr(CCH)(CNH)_2]$

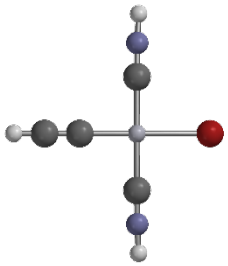

Figure S19: Optimised structure of $[PtBr(CCH)(CNH)_2]$ in the gas phase.

Table S35: Cartesian coordinates for [PtBr(CCH)(CNH)$_2$]

Atom	X	Y	Z
Pt	-0.00052	0.0	0.611934
C	-0.000777	0.0	-1.364526
C	-1.951059	0.0	0.617911
C	1.950617	0.0	0.61747
Br	-0.000766	0.0	3.143306
C	0.000628	0.0	-2.577444
H	0.002322	0.0	-3.644086
N	3.110523	0.0	0.624987
N	-3.110917	0.0	0.626706
H	-4.107799	0.0	0.67318
H	4.107747	0.0	0.670562

Table S36: Thermodynamic properties at 298.15 °K

Zero Point Energy:	144.11	kJ/mol	(ZPE)
Temperature Correction:	28.67	kJ/mol	(vibration+ gas law + rotation + translation)
Enthalpy Correction:	172.78	kJ/mol	(ZPE + temperature correction)
Enthalpy:	–2956.579354	au	(Electronic Energy + Enthalpy Correction)
Entropy:	417.23	J/mol·K	
Gibbs Energy:	–2956.626734	au	(Enthalpy + T×Entropy)
C_v:	160.90	J/mol·K	

[PtBr(CN)(CNH)$_2$]

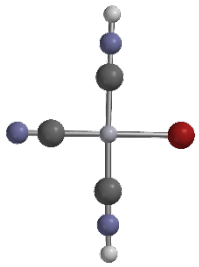

Figure S20: Optimised structure of [PtBr(CN)(CNH)$_2$] in the gas phase.

Table S37: Cartesian coordinates for [PtBr(CN)(CNH)$_2$]

Atom	X	Y	Z
Pt	3.1e-05	0.00034	-0.231274
C	-0.00188	-0.000789	1.741521
C	1.956376	7.5e-05	-0.250594
C	-1.95591	0.000598	-0.2545
Br	0.003634	0.001635	-2.749154
N	-0.003097	-0.000948	2.904516
N	-3.114303	-0.000146	-0.273768
N	3.11475	-0.000609	-0.266668
H	4.112851	-0.000159	-0.307257
H	-4.112451	1e-06	-0.312821

Table S38: Thermodynamic properties at 298.15 °K

Zero Point Energy:	118.06	kJ/mol	(ZPE)
Temperature Correction:	27.68	kJ/mol	(vibration+ gas law + rotation + translation)
Enthalpy Correction:	145.74	kJ/mol	(ZPE + temperature correction)
Enthalpy:	–2972.694972	au	(Electronic Energy + Enthalpy Correction)
Entropy:	412.27	J/mol·K	
Gibbs Energy:	–2972.741788	au	(Enthalpy + T×Entropy)
C_v:	152.30	J/mol·K	

[PtBr(CP)(CNH)$_2$]

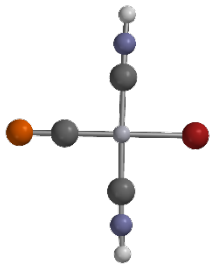

Figure S21: Optimised structure of [PtBr(CP)(CNH)$_2$] in the gas phase.

Table S39: Cartesian coordinates for [PtBr(CP)(CNH)$_2$]

Atom	X	Y	Z
Pt	0.000203	-0.042057	-0.253262
C	-0.001152	0.282189	1.676799
C	-1.955786	-0.048547	-0.275843
C	1.956337	-0.042713	-0.275218
Br	0.00186	-0.461932	-2.757655
P	-0.002742	0.536102	3.210369
N	3.115363	-0.044577	-0.299422
N	-3.114815	-0.053769	-0.299619
H	4.111539	-0.056817	-0.364167
H	-4.110806	-0.067877	-0.361982

Table S40: Thermodynamic properties at 298.15 °K

Zero Point Energy:	111.29	kJ/mol	(ZPE)
Temperature Correction:	28.44	kJ/mol	(vibration+ gas law + rotation + translation)
Enthalpy Correction:	139.73	kJ/mol	(ZPE + temperature correction)
Enthalpy:	–3259.255337	au	(Electronic Energy + Enthalpy Correction)
Entropy:	420.11	J/mol·K	
Gibbs Energy:	–3259.303405	au	(Enthalpy + T×Entropy)
C_v:	155.36	J/mol·K	

[Pt(CAs)Br(CNH)$_2$]

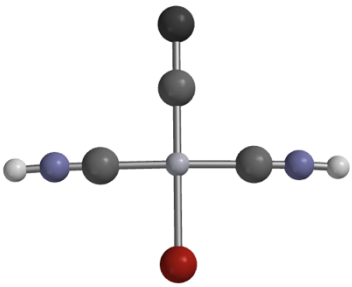

Figure S22: Optimised structure of [Pt(CAs)Br(CNH)$_2$] in the gas phase.

Table S41: Cartesian coordinates for [Pt(CAs)Br(CNH)$_2$]

Atom	x	y	z
Pt	-0.000127	0.000000	0.265976
C	0.000920	0.000000	-1.691627
C	1.955847	0.000000	0.288890
C	-1.956344	0.000000	0.288916
As	0.002280	0.000000	-3.353889
N	-3.115267	0.000000	0.315550
N	3.114852	0.000000	0.314242
H	-4.111361	0.000000	0.382977
H	4.111093	0.000000	0.380143
Br	-0.001893	0.000000	2.807717

Table S42: Thermodynamic properties at 298.15 °K

Zero Point Energy :	109.17	kJ/mol	(ZPE)
Temperature Correction :	28.85	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	138.02	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-5153.576483	au	(Electronic Energy + Enthalpy Correction)
Entropy :	428.10	J/mol•K	
Gibbs Energy :	-5153.625098	au	(Enthalpy - T*Entropy)
C_V :	156.83	J/mol•K	

[Pt(CSb)Br(CNH)$_2$]

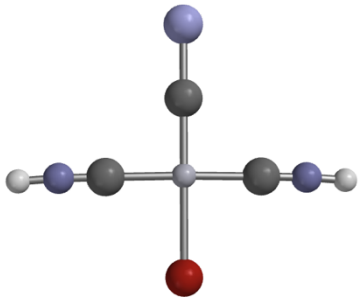

Figure S23: Optimised structure of [Pt(CSb)Br(CNH)$_2$] in the gas phase.

Table S43: Cartesian coordinates for [Pt(CSb)Br(CNH)$_2$]

Atom	x	y	z
Pt	0.000225	0.000000	0.280468
C	-0.000536	0.000000	-1.669807
C	1.957010	0.000000	0.305012
C	-1.956543	0.000000	0.304973
Sb	-0.001769	0.000000	-3.531158
N	-3.115717	0.000000	0.332949
N	3.116167	0.000000	0.334470
H	-4.111495	0.000000	0.404459
H	4.111663	0.000000	0.408009
Br	0.000996	0.000000	2.830623

Table S44: Thermodynamic properties at 298.15 °K

Zero Point Energy :	107.84	kJ/mol	(ZPE)
Temperature Correction :	28.97	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	136.81	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-2923.307738	au	(Electronic Energy + Enthalpy Correction)
Entropy :	433.70	J/mol•K	
Gibbs Energy :	-2923.356989	au	(Enthalpy - T*Entropy)
C_V :	157.89	J/mol•K	

[Pt(BNH)Br(CNH)$_2$]

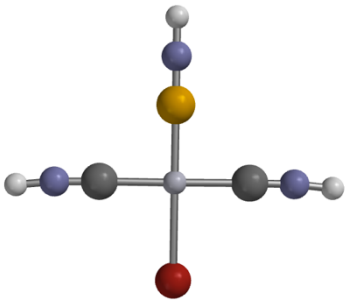

Figure S24: Optimised structure of [Pt(BNH)Br(CNH)$_2$] in the gas phase.

Table S45: Cartesian coordinates for [Pt(BNH)Br(CNH)$_2$]

Atom	x	y	z
Pt	-0.000248	0.000000	-0.612771
B	0.000609	0.000000	1.396200
C	-1.947591	0.000000	-0.604395
C	1.947129	0.000000	-0.603833
N	0.001069	0.000000	2.644303
H	0.001472	0.000000	3.637511
N	3.107900	0.000000	-0.620106
N	-3.108339	0.000000	-0.621761
H	-4.101914	0.000000	-0.716474
H	4.101337	0.000000	-0.713035
Br	-0.001425	0.000000	-3.185639

Table S46: Thermodynamic properties at 298.15 °K

Zero Point Energy :	140.78	kJ/mol	(ZPE)
Temperature Correction :	29.95	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	170.73	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-2960.071659	au	(Electronic Energy + Enthalpy Correction)
Entropy :	424.69	J/mol•K	
Gibbs Energy :	-2960.119886	au	(Enthalpy - T*Entropy)
C_V :	167.16	J/mol•K	

[Pt(BO)Br(CNH)$_2$]

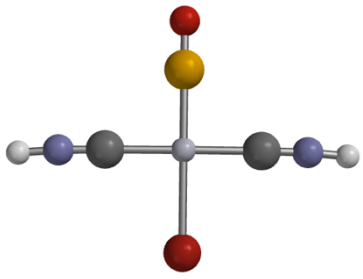

Figure S25: Optimised structure of [Pt(BO)Br(CNH)$_2$] in the gas phase.

Table S47: Cartesian coordinates for [Pt(BO)Br(CNH)$_2$]

Atom	x	y	z
Pt	-0.000279	0.000000	-0.234824
B	0.000187	0.000000	1.762846
C	-1.951951	0.000000	-0.240622
C	1.951608	0.000000	-0.241281
O	0.001145	0.000000	2.975965
N	3.110909	0.000000	-0.266806
N	-3.111331	0.000000	-0.265380
H	-4.106561	0.000000	-0.348703
H	4.106500	0.000000	-0.346407
Br	-0.000228	0.000000	-2.794789

Table S48: Thermodynamic properties at 298.15 °K

Zero Point Energy :	115.26	kJ/mol	(ZPE)
Temperature Correction :	27.83	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	143.10	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-2979.994922	au	(Electronic Energy + Enthalpy Correction)
Entropy :	413.59	J/mol•K	
Gibbs Energy :	-2980.041889	au	(Enthalpy - T*Entropy)
C_V :	153.17	J/mol•K	

[Pt(B=CH$_2$)Br(CNH)$_2$]

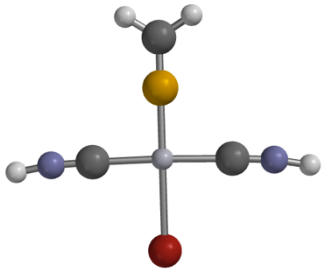

Figure S26: Optimised structure of [Pt(B=CH$_2$)Br(CNH)$_2$] in the gas phase.

Table S49: Cartesian coordinates for [Pt(B=CH$_2$)Br(CNH)$_2$]

Atom	x	y	z
Pt	0.000000	0.000000	-0.822574
B	0.000000	0.000000	1.158289
C	-1.948014	0.000000	-0.861824
C	1.948014	0.000000	-0.861824
N	3.107794	0.000000	-0.920790
N	-3.107794	0.000000	-0.920790
H	-4.090877	0.000000	-1.094797
H	4.090877	0.000000	-1.094797
Br	0.000000	0.000000	-3.411610
C	0.000000	0.000000	2.554715
H	0.918371	0.000000	3.138000
H	-0.918371	0.000000	3.138000

Table S50: Thermodynamic properties at 298.15 °K

Zero Point Energy :	163.83	kJ/mol	(ZPE)
Temperature Correction :	30.47	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	194.30	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-2943.954520	au	(Electronic Energy + Enthalpy Correction)
Entropy :	423.58	J/mol•K	
Gibbs Energy :	-2944.002622	au	(Enthalpy - T*Entropy)
C_V :	171.88	J/mol•K	

[Pt(CNO)Br(CNH)$_2$]

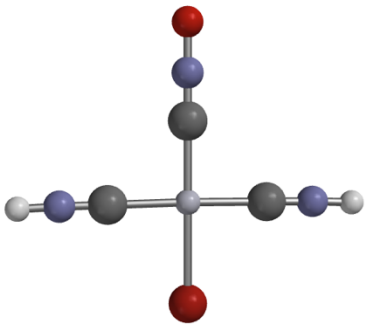

Figure S27: Optimised structure of [Pt(CNO)Br(CNH)$_2$] in the gas phase.

Table S51: Cartesian coordinates for [Pt(CNO)Br(CNH)$_2$]

Atom	x	y	z
Pt	-0.000495	0.000000	-0.608509
C	0.001922	0.000000	1.375403
C	1.954706	0.000000	-0.635789
C	-1.955658	0.000000	-0.631740
N	-3.113953	0.000000	-0.648267
N	3.112986	0.000000	-0.653090
H	-4.112150	0.000000	-0.687967
H	4.110846	0.000000	-0.698366
N	0.001174	0.000000	2.542395
O	0.002222	0.000000	3.761430
Br	-0.001599	0.000000	-3.115501

Table S52: Thermodynamic properties at 298.15 °K

Zero Point Energy :	129.02	kJ/mol	(ZPE)
Temperature Correction :	29.91	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	158.94	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-3047.812192	au	(Electronic Energy + Enthalpy Correction)
Entropy :	430.57	J/mol•K	
Gibbs Energy :	-3047.861087	au	(Enthalpy - T*Entropy)
C_V :	167.16	J/mol•K	

[PtBr{C≡W(CO)$_2$Tp}(CNH)$_2$]

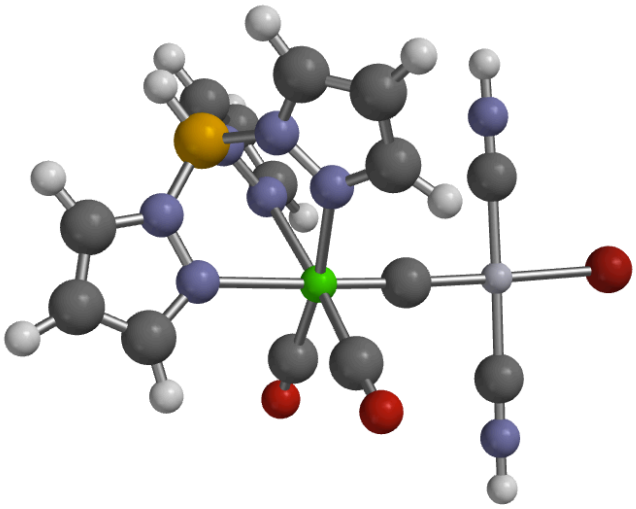

Figure S28: Optimised structure of [PtBr{C≡W(CO)$_2$Tp}(CNH)$_2$] in the gas phase.

Table S53: Cartesian coordinates for [PtBr{C≡W(CO)$_2$Tp}(CNH)$_2$]

Atom	X	Y	Z
Pt	-1.320992	-3.858599	0.9879
W	0.324585	-0.849468	-0.558341
O	2.974028	-2.561671	-0.497801
O	-0.452901	-2.235686	-3.276204
N	1.416231	0.979435	-1.542397
N	1.214802	2.231638	-1.077881
N	0.864152	0.349411	1.267628
N	0.738228	1.691964	1.322461
N	-1.336133	0.652711	-0.589083
N	-1.148401	1.955971	-0.288426
C	-0.489334	-2.271485	0.213434
C	2.008025	-1.924806	-0.528624
C	-0.15554	-1.692769	-2.293746
C	2.291682	1.072465	-2.542623
C	2.669861	2.404346	-2.737246
H	3.357512	2.799634	-3.468606
C	1.95772	3.104762	-1.7798
C	1.308694	-0.050988	2.459045
C	1.474173	1.047318	3.308181
H	1.827503	1.052175	4.32768
C	1.100189	2.135298	2.538541
C	-2.632342	0.495967	-0.859049
C	-3.304131	1.71485	-0.732978
H	-4.353325	1.912123	-0.88751
C	-2.317889	2.614091	-0.368721
B	0.246887	2.485875	0.093061
H	0.195807	3.660887	0.349097
H	1.069907	3.191022	2.76438
H	1.489187	-1.10213	2.632361
H	1.923614	4.159228	-1.547902
H	2.601457	0.180172	-3.068244
H	-2.360463	3.673554	-0.163899
H	-3.004794	-0.482918	-1.123595
C	-1.109196	-4.744136	-0.744543
Br	-2.426657	-5.930887	2.00649
C	-1.508009	-2.907977	2.686488
N	-1.606536	-2.323998	3.684249
N	-0.974705	-5.227219	-1.789389
H	-0.845382	-5.579456	-2.715247
H	-1.707511	-1.820706	4.540858

Table S54: Thermodynamic properties at 298.15 °K

Zero Point Energy:	658.36	kJ/mol	(ZPE)
Temperature Correction:	65.34	kJ/mol	(vibration+ gas law + rotation + translation)
Enthalpy Correction:	723.70	kJ/mol	(ZPE + temperature correction)
Enthalpy:	–3914.405567	au	(Electronic Energy + Enthalpy Correction)
Entropy:	670.26	J/mol·K	
Gibbs Energy:	–3914.481681	au	(Enthalpy + T×Entropy)
C_v:	451.72	J/mol·K	

[PtBr{C≡W(CO)$_2$Tp}(CNMe)$_2$]

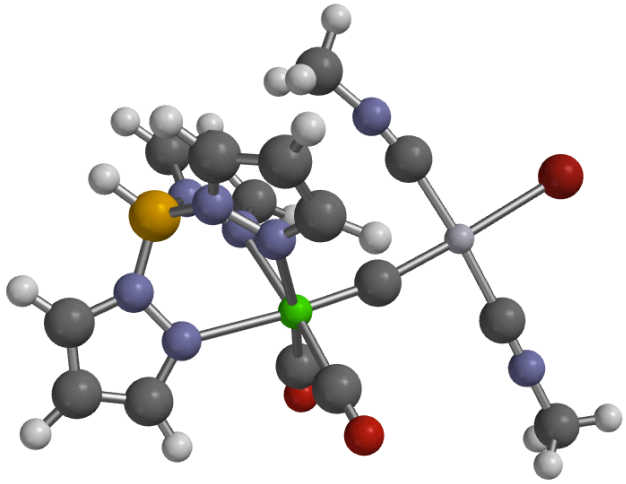

Figure S29: Optimised structure of [PtBr{C≡W(CO)$_2$Tp}(CNMe)$_2$] in the gas phase.

Table S55: Thermodynamic properties at 298.15 °K

Zero Point Energy :	808.16	kJ/mol	(ZPE)
Temperature Correction	70.19	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	878.34	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-3992.973669	au	(Electronic Energy + Enthalpy Correction)
Entropy :	708.15	J/mol•K	
Gibbs Energy :	-3993.054086	au	(Enthalpy - T*Entropy)
C_V :	485.11	J/mol•K	

Table S56: Cartesian coordinates for [PtBr{C≡W(CO)$_2$Tp}(CNMe)$_2$]

Atom	x	y	z
Pt	-1.195090	-3.289053	0.725338
W	0.589599	-0.403559	-0.850873
O	3.274444	-2.037977	-1.094348
O	-0.248240	-1.382266	-3.728282
N	1.510978	1.629995	-1.585778
N	1.255400	2.788393	-0.941302
N	1.113595	0.556124	1.127849
N	0.938004	1.872235	1.374879
N	-1.169869	0.987907	-0.561345
N	-1.041560	2.245521	-0.085504
C	-0.198963	-1.892311	-0.192772
C	2.294750	-1.424668	-1.016882
C	0.070420	-1.006375	-2.679517
C	2.316103	1.924589	-2.605881
C	2.591536	3.295864	-2.631533
H	3.206557	3.837384	-3.333433
C	1.893735	3.803371	-1.550445
C	1.568108	0.004542	2.253453
C	1.692116	0.975398	3.254134
H	2.044821	0.843394	4.265394
C	1.282432	2.149734	2.645137
C	-2.473160	0.763518	-0.728680
C	-3.210954	1.892881	-0.355482
H	-4.281475	2.024760	-0.387903
C	-2.254870	2.811760	0.044065
B	0.345652	2.806292	0.296157
H	0.237055	3.924635	0.728936
H	1.215301	3.160873	3.019130
H	1.777074	-1.055210	2.278565
H	1.803232	4.810897	-1.171590
H	2.653527	1.138443	-3.266764
H	-2.347091	3.825881	0.404416
H	-2.803851	-0.194710	-1.102590
C	-0.601124	-4.661719	-0.539647
C	-1.718764	-1.796069	1.897656
N	-1.935447	-0.813943	2.472303
N	-0.245006	-5.459644	-1.300907
C	-2.081996	0.480741	3.030457
H	-2.737465	0.432626	3.901856
H	-2.512020	1.140395	2.271691
H	-1.092920	0.845392	3.321208
C	0.176001	-6.444134	-2.228861
H	1.212492	-6.715248	-2.019915
H	0.099804	-6.037337	-3.239468
H	-0.462776	-7.324158	-2.132060
Br	-2.550097	-5.035164	2.019134

[PtBr{C≡W(CO)$_2$Tp}(CN^{t}Bu)$_2$]

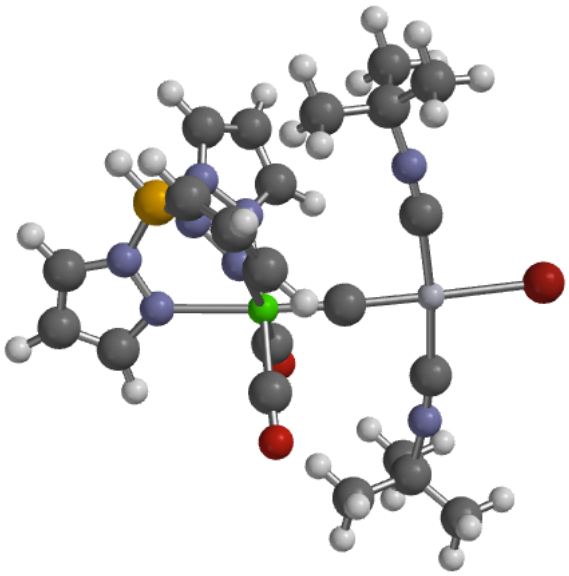

Figure S30: Optimised structure of [PtBr{C≡W(CO)$_2$Tp}(CN^{t}Bu)$_2$] in the gas phase.

Table S57: Thermodynamic properties at 298.15 °K

Zero Point Energy:	1231.63	kJ/mol	(ZPE)
Temperature Correction:	88.04	kJ/mol	(vibration+ gas law + rotation + translation)
Enthalpy Correction:	1319.68	kJ/mol	(ZPE + temperature correction)
Enthalpy:	–4228.655783	au	(Electronic Energy + Enthalpy Correction)
Entropy:	811.59	J/mol·K	
Gibbs Energy:	–4228.747947	au	(Enthalpy + T×Entropy)
C_v:	624.96	J/mol·K	

Table S58: Cartesian coordinates for [PtBr{C≡W(CO)$_2$Tp}(CN^{t}Bu)$_2$]

Atom	X	Y	Z
Pt	2.155501	1.860762	0.581007
W	-0.286383	-0.980869	0.560744
Br	3.835884	3.786385	0.46626
N	-0.617956	-0.954207	-1.668101
C	0.871445	0.408903	0.634912
O	2.303477	-2.76804	0.536058
O	-0.19007	-1.040335	3.710073
N	-1.825839	-1.16432	-2.233761
C	3.239535	0.827187	1.849817
N	-3.244307	-0.251759	-0.390274
N	-2.25957	0.098201	0.46444
N	-1.769226	-2.791468	0.31478
N	3.79793	0.112332	2.570489
C	-0.238368	-1.037714	2.551222
N	-2.817139	-2.718031	-0.534127
C	1.330786	-2.130953	0.530734
C	0.962658	2.702057	-0.734853
N	0.20199	3.08374	-1.521559
C	-4.302138	0.561392	-0.224338
C	-2.703484	1.139287	1.169066
C	-4.000891	1.47644	0.769649
H	-4.629322	2.265466	1.15325
C	0.240383	-0.706015	-2.657706
C	-1.729985	-1.051913	-3.570492
C	-1.810811	-3.998662	0.877463
C	-3.511511	-3.868866	-0.505464
C	-0.416449	-0.756173	-3.892451
H	0.00648	-0.612187	-4.874988
C	-2.900956	-4.727561	0.391397
H	-3.199744	-5.730878	0.6543
C	4.386814	-0.887409	3.428354
C	5.313716	-1.745082	2.559278
H	4.747449	-2.230623	1.760254
H	5.772509	-2.517801	3.183775
H	6.107942	-1.135297	2.118148
B	-3.066446	-1.442069	-1.3578
H	-4.045148	-1.566816	-2.047783
C	5.159997	-0.162113	4.533564
H	4.490955	0.470324	5.123963
H	5.94983	0.463936	4.110132
H	5.615947	-0.903366	5.196208
C	-0.8009	3.431272	-2.498188
C	3.237021	-1.725353	4.000052
H	2.537634	-1.101415	4.56281
H	3.650718	-2.486716	4.666549
H	2.689535	-2.221044	3.195329
C	-0.203341	3.166742	-3.884935
H	0.701581	3.760706	-4.039086
H	-0.93693	3.44101	-4.648541
H	0.038149	2.106388	-3.998825
C	-1.144082	4.912267	-2.310769
H	-1.53451	5.094858	-1.3058
H	-1.907171	5.198827	-3.040193
H	-0.260673	5.538681	-2.462591
C	-2.014132	2.531808	-2.238209
H	-1.733301	1.478016	-2.309197
H	-2.785236	2.742689	-2.985423
H	-2.432651	2.711782	-1.244096
H	-5.191216	0.426356	-0.82243
H	-2.064816	1.584487	1.918464
H	-1.05752	-4.279051	1.599938
H	-4.388098	-3.992265	-1.124082
H	1.27619	-0.504367	-2.424023
H	-2.601735	-1.191564	-4.192391

[PtBr{C≡W(CO)$_2$Tp}(CNPh)$_2$]

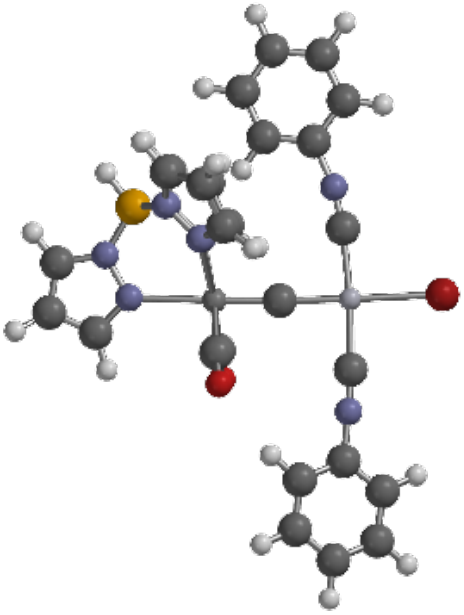

Figure S31: Optimised structure of [PtBr{C≡W(CO)$_2$Tp}(CNPh)$_2$] in the gas phase.

Table S59: Thermodynamic properties at 298.15 °K

Zero Point Energy:	1072.50	kJ/mol	(ZPE)
Temperature Correction:	82.45	kJ/mol	(vibration+ gas law + rotation + translation)
Enthalpy Correction:	1154.95	kJ/mol	(ZPE + temperature correction)
Enthalpy:	–4376.220141	au	(Electronic Energy + Enthalpy Correction)
Entropy:	779.72	J/mol·K	
Gibbs Energy:	–4376.308685	au	(Enthalpy + T×Entropy)
C_v:	602.23	J/mol·K	

Table S60: Cartesian coordinates for [PtBr{C≡W(CO)$_2$Tp}(CNPh)$_2$]

Atom	X	Y	Z
Pt	-0.714405	0.132281	-3.012096
W	-0.696452	0.110235	0.745147
Br	-0.633233	0.14211	-5.569484
O	-3.062431	-1.955913	0.533711
O	-2.829759	2.431898	0.675333
N	-0.595153	0.038432	3.09347
N	0.59126	-0.017688	3.73589
N	1.054611	1.481217	1.117789
N	1.98511	1.239548	2.068019
N	0.962034	-1.385852	1.039856
N	1.911213	-1.249148	1.992507
N	2.374965	0.164785	-2.604123
N	-3.826413	-0.039217	-2.938903
C	-0.734633	0.13542	-1.064703
C	-2.181904	-1.2045	0.637331
C	-2.048686	1.578437	0.717858
C	-1.543127	0.028976	4.029861
C	-0.97029	-0.033725	5.304399
C	0.391696	-0.062041	5.064715
C	1.422257	2.597028	0.485654
C	2.611531	3.092204	1.028128
H	3.157636	3.974403	0.732809
C	2.930155	2.196252	2.032707
C	1.268873	-2.475992	0.33523
C	2.436906	-3.061652	0.832411
H	2.935866	-3.949737	0.477244
C	2.807661	-2.247044	1.887152
C	1.236503	0.171618	-2.840009
C	3.653087	0.150646	-2.067112
C	3.77706	0.058149	-0.681636
C	5.049142	0.03834	-0.127214
H	5.155299	-0.030771	0.950566
C	6.173409	0.109802	-0.946717
C	6.029785	0.201498	-2.330069
H	6.906476	0.255937	-2.967043
C	4.764335	0.222627	-2.904077
C	-2.669714	0.036757	-3.009283
C	-5.199304	-0.153844	-2.791566
C	-6.032033	0.24857	-3.834275
C	-7.406718	0.133783	-3.66962
H	-8.069006	0.442545	-4.471636
C	-7.931108	-0.375572	-2.483683
C	-7.082262	-0.775559	-1.453829
H	-7.491303	-1.175501	-0.531909
C	-5.70476	-0.668361	-1.597718
B	1.907134	-0.03115	2.942207
H	2.852533	-0.081036	3.68708
H	0.635407	-2.770067	-0.489181
H	3.641959	-2.303128	2.570796
H	3.758534	2.168671	2.725176
H	0.812158	2.974779	-0.32215
H	1.232434	-0.109504	5.741203
H	-2.583645	0.067211	3.739344
H	-1.471093	-0.058482	6.260158
H	7.166003	0.095718	-0.507649
H	4.628482	0.289376	-3.977928
H	2.885311	0.005896	-0.067834
H	-5.600084	0.64214	-4.747909
H	-9.006039	-0.463416	-2.36213
H	-5.023269	-0.97839	-0.812263

[PtBr{C≡W(CO)$_2$Tp}(CNPhMe-2)$_2$]

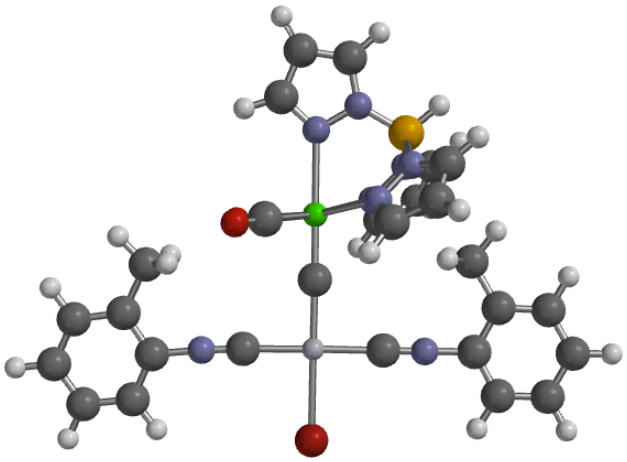

Figure S32: Optimised structure of [PtBr{C≡W(CO)$_2$Tp}(CNPhMe-2)$_2$] in the gas phase.

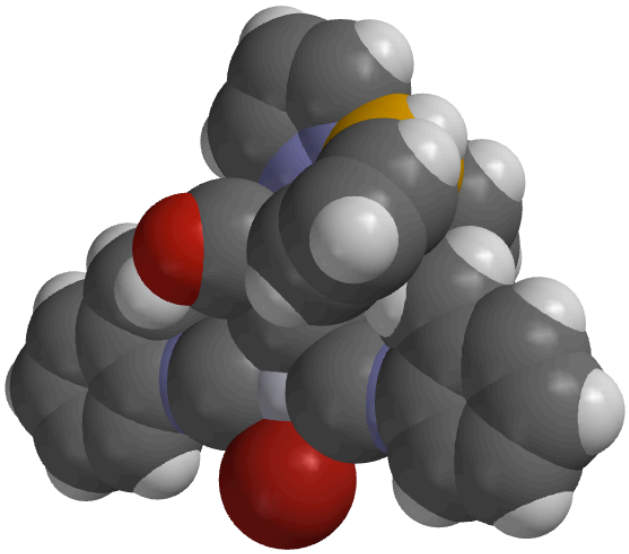

Figure S33: Optimised structure of [PtBr{C≡W(CO)$_2$Tp}(CNPhMe-2)$_2$] – Space-filling representation to demonstrate nestling of 2-tolylsubstituent between pyrazolyl wings.

Table S61: Thermodynamic properties at 298.15 °K

Zero Point Energy:	1212.27	kJ/mol	(ZPE)
Temperature Correction:	89.55	kJ/mol	(vibration+ gas law + rotation + translation)
Enthalpy Correction:	1301.82	kJ/mol	(ZPE + temperature correction)
Enthalpy:	–4454.786262	au	(Electronic Energy + Enthalpy Correction)
Entropy:	824.22	J/mol·K	
Gibbs Energy:	–4454.879859	au	(Enthalpy + T×Entropy)
C_v:	652.96	J/mol·K	

Table S62: Cartesian coordinates for [PtBr{C≡W(CO)$_2$Tp}(CNPhMe-2)$_2$]

Atom	X	Y	Z
Pt	0.573872	-0.082648	-2.649643
W	0.637179	0.09757	1.102155
Br	0.5353	-0.234618	-5.214384
O	2.68593	2.46524	0.760677
O	2.98643	-1.987011	0.897425
N	0.68764	0.157998	3.455551
N	-0.456003	0.100056	4.171644
N	-0.911298	-1.451275	1.604569
N	-1.817537	-1.287673	2.591488
N	-1.105464	1.451372	1.538221
N	-1.98872	1.207466	2.52956
N	-2.546508	-0.180757	-2.606967
N	3.690532	0.023653	-2.77978
C	0.587932	0.026102	-0.709701
C	1.936816	1.590747	0.904628
C	2.125407	-1.213965	0.991343
C	1.687777	0.25467	4.330526
C	1.1937	0.260015	5.639027
C	-0.177659	0.159732	5.485712
C	-1.145818	-2.641742	1.050619
C	-2.224067	-3.266871	1.68532
H	-2.651882	-4.233143	1.467803
C	-2.616045	-2.367387	2.66111
C	-1.499105	2.572161	0.930562
C	-2.660241	3.067228	1.531875
H	-3.217429	3.95276	1.268564
C	-2.930822	2.166704	2.547054
C	-1.385065	-0.147972	-2.61907
C	-3.931442	-0.206332	-2.570854
C	-4.567456	-0.223931	-1.321039
C	-5.961337	-0.242732	-1.331608
H	-6.4901	-0.255089	-0.382855
C	-6.680402	-0.245391	-2.523348
C	-6.017602	-0.229155	-3.747895
H	-6.576736	-0.230955	-4.677458
C	-4.630282	-0.209364	-3.776993
C	2.532005	-0.014239	-2.707647
C	5.066407	0.06006	-2.944088
C	5.578283	-0.079646	-4.233831
C	6.953169	-0.046632	-4.416735
H	7.367467	-0.15462	-5.413451
C	7.789498	0.124226	-3.316436
C	7.255478	0.262369	-2.038721
H	7.918803	0.396268	-1.189171
C	5.879304	0.234495	-1.815752
B	-1.816946	-0.012366	3.459258
H	-2.713222	-0.05403	4.26253
H	-0.928141	2.951911	0.095692
H	-3.721867	2.138377	3.281782
H	-3.40154	-2.416615	3.40061
H	-0.52967	-2.975203	0.228093
H	-0.974457	0.12602	6.214208
H	2.706556	0.3152	3.974078
H	1.751837	0.32769	6.559914
H	-7.76552	-0.25974	-2.49513
H	-4.078833	-0.195246	-4.711092
H	4.893573	-0.211007	-5.065122
H	8.866107	0.150978	-3.45324
C	-3.767815	-0.228162	-0.050383
H	-4.419937	-0.162031	0.823586
H	-3.068036	0.612431	-0.018856
H	-3.171907	-1.143071	0.036637
C	5.283232	0.380798	-0.444526
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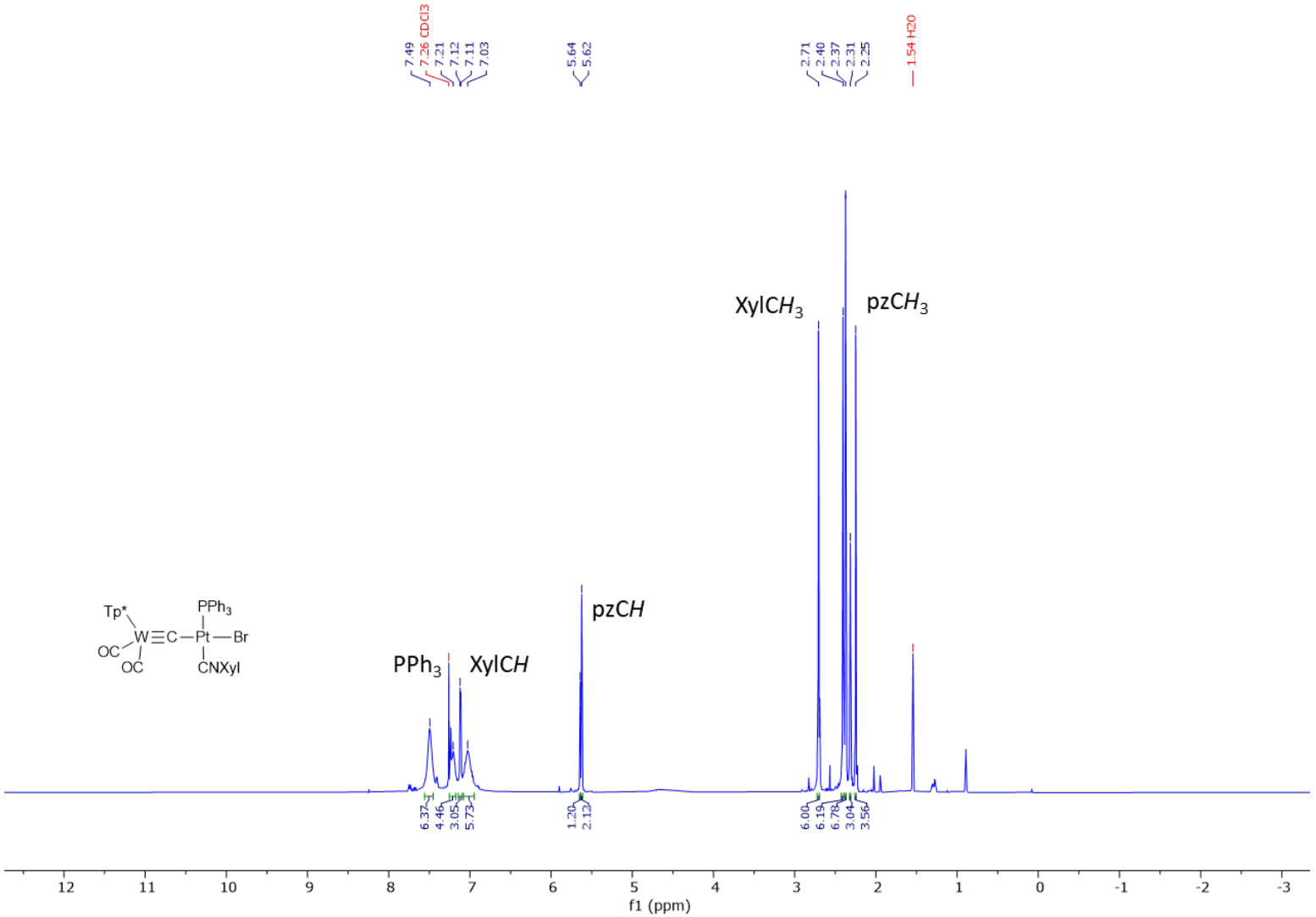

Figure S34: ^{1}H NMR Spectrum of [WPt(μ_2-C)Br($CNC_6H_3Me_2$-2,6)$(CO)_2(PPh_3)$(Tp*)] (**4a**) (400 MHz, $CDCl_3$, 25 °C, δ)

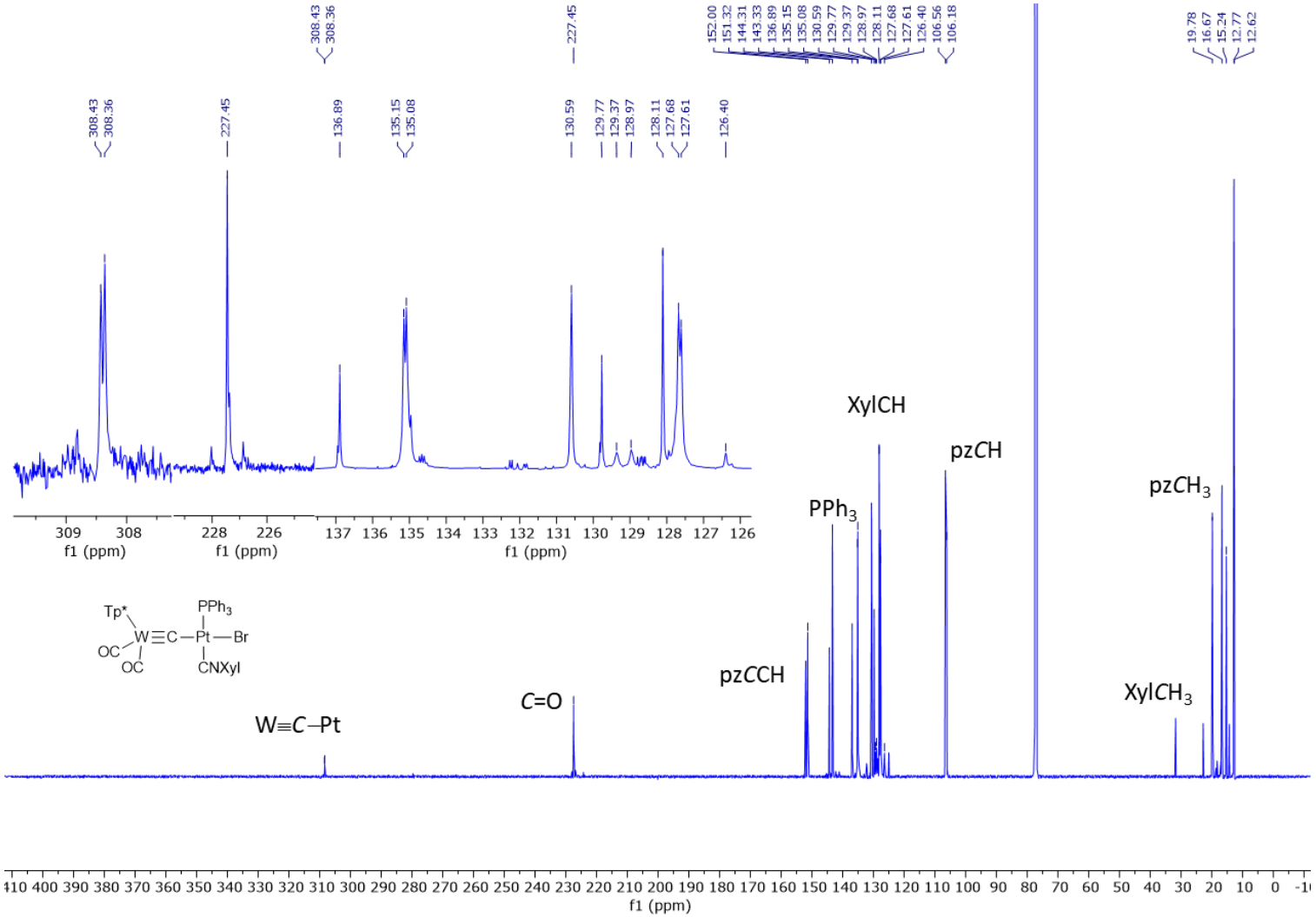

Figure S35: $^{13}C\{^{1}H\}$ NMR Spectrum of [WPt(μ_2-C)Br($CNC_6H_3Me_2$-2,6)$(CO)_2(PPh_3)$(Tp*)] (**4a**) (151 MHz, $CDCl_3$, 25 °C, δ)

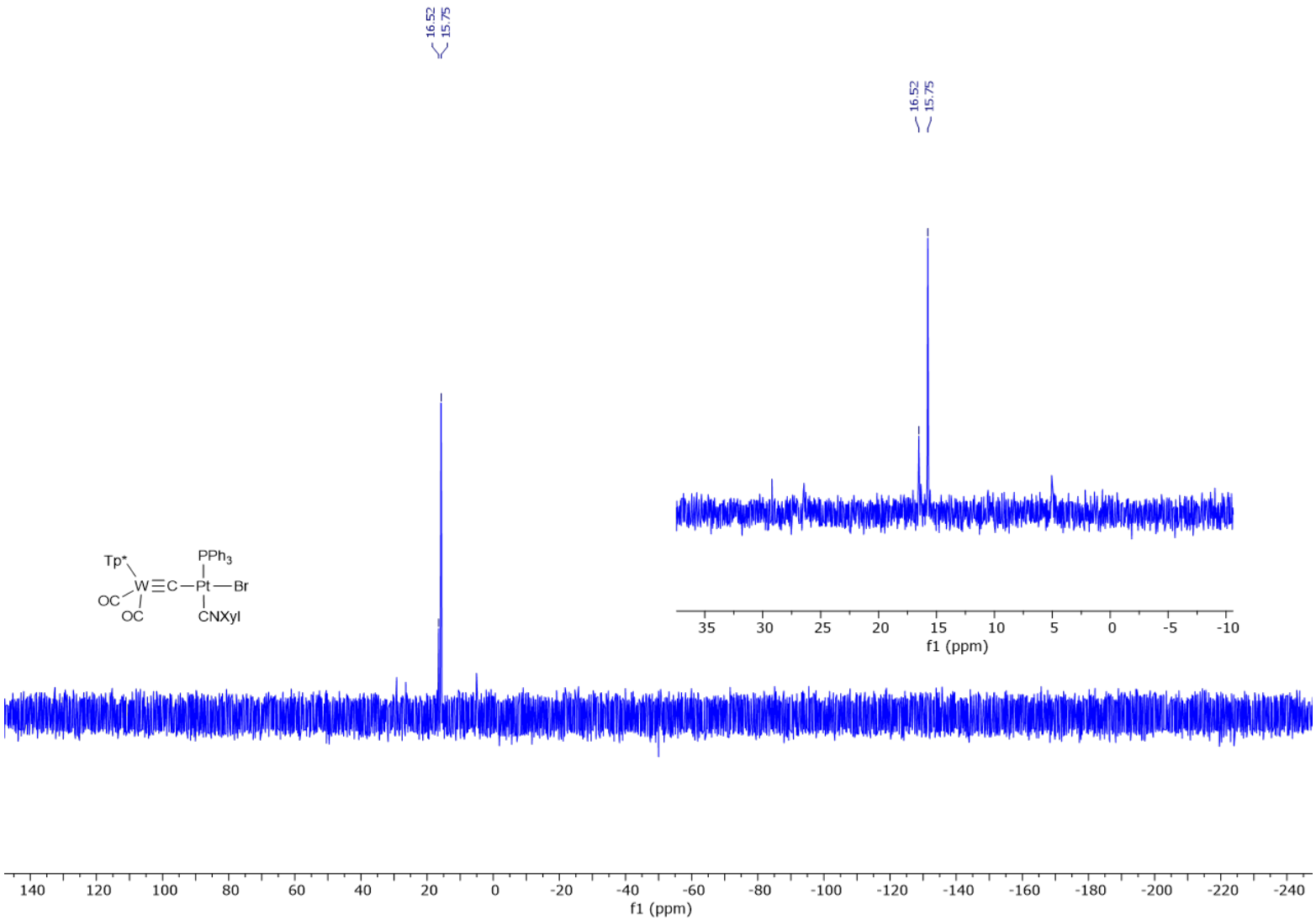

Figure S36: $^{31}P\{^{1}H\}$ NMR Spectrum of [WPt(μ_2-C)Br($CNC_6H_3Me_2$-2,6)$(CO)_2(PPh_3)$(Tp*)] (**4a**) (162 MHz, $CDCl_3$, 25 °C, δ)

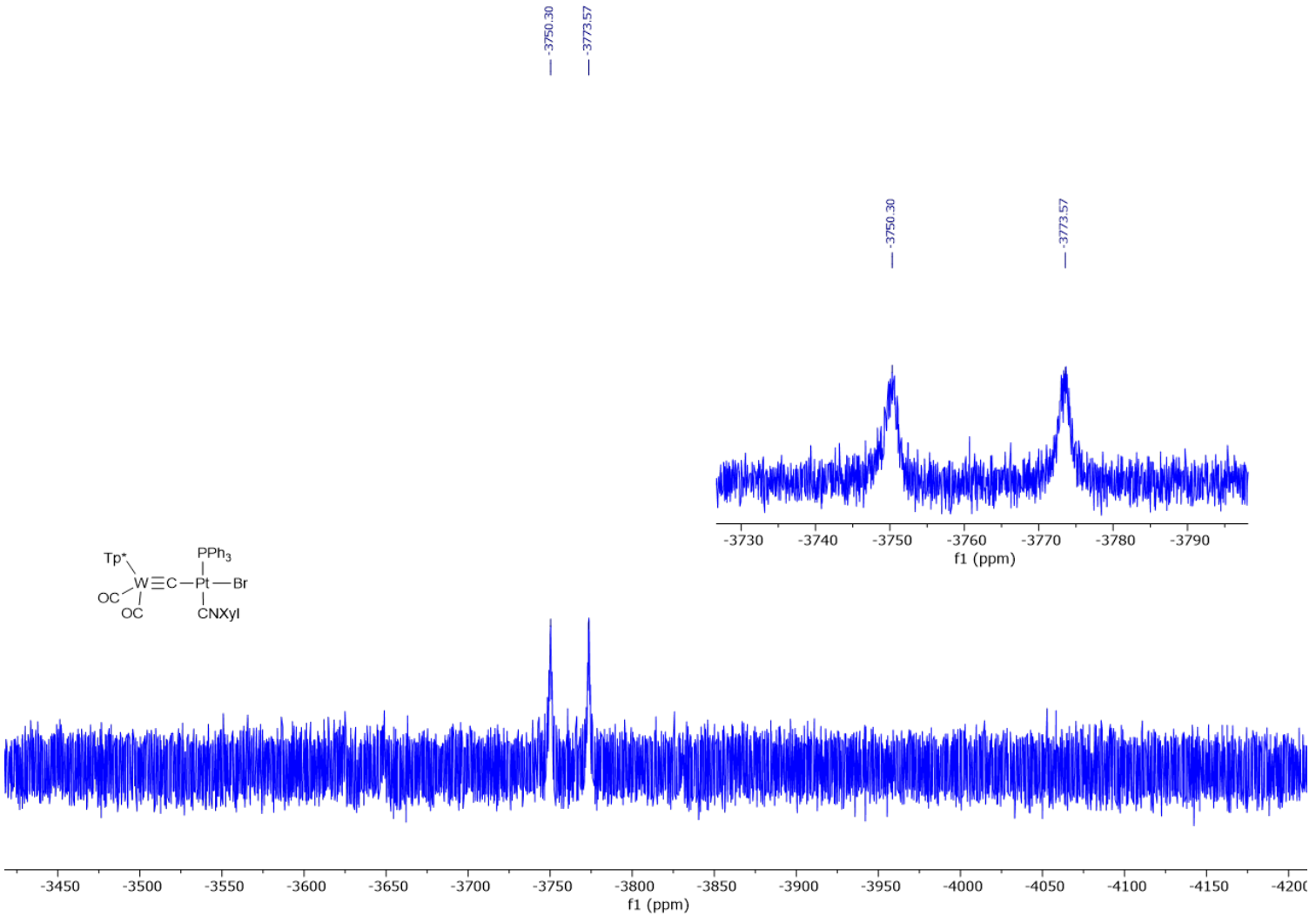

Figure S37: $^{195}Pt\{^{1}H\}$ NMR Spectrum of [WPt(μ_2-C)Br($CNC_6H_3Me_2$-2,6)$(CO)_2(PPh_3)$(Tp*)] (**4a**) (86 MHz, $CDCl_3$, 25 °C, δ)

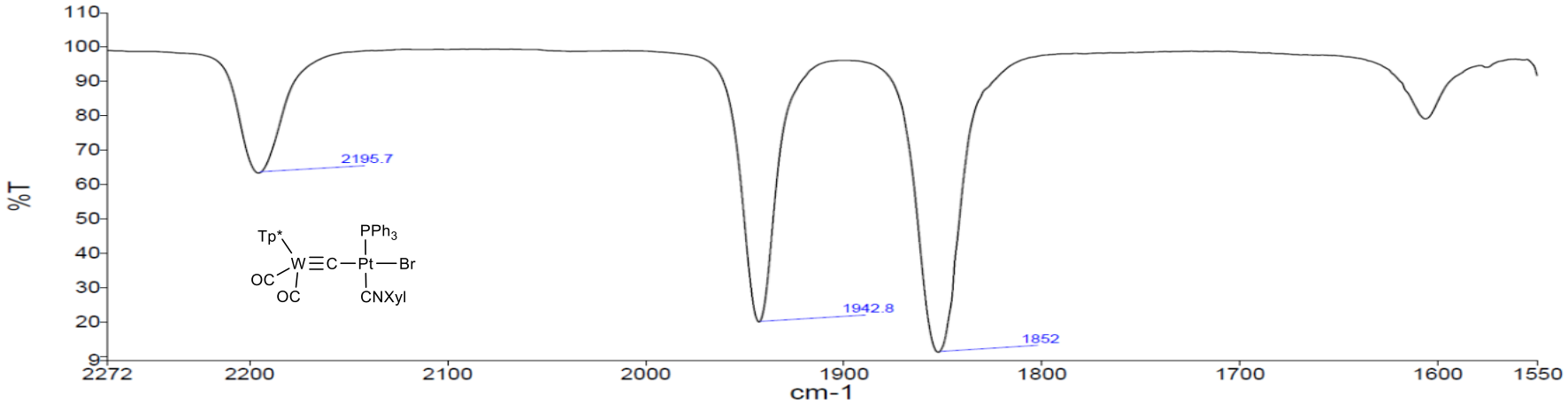

Figure S38: Infrared Spectrum of [WPt(μ_2-C)Br($CNC_6H_3Me_2$-2,6)$(CO)_2(PPh_3)$(Tp*)] (**4a**) (CH_2Cl_2, 25 °C, ν)

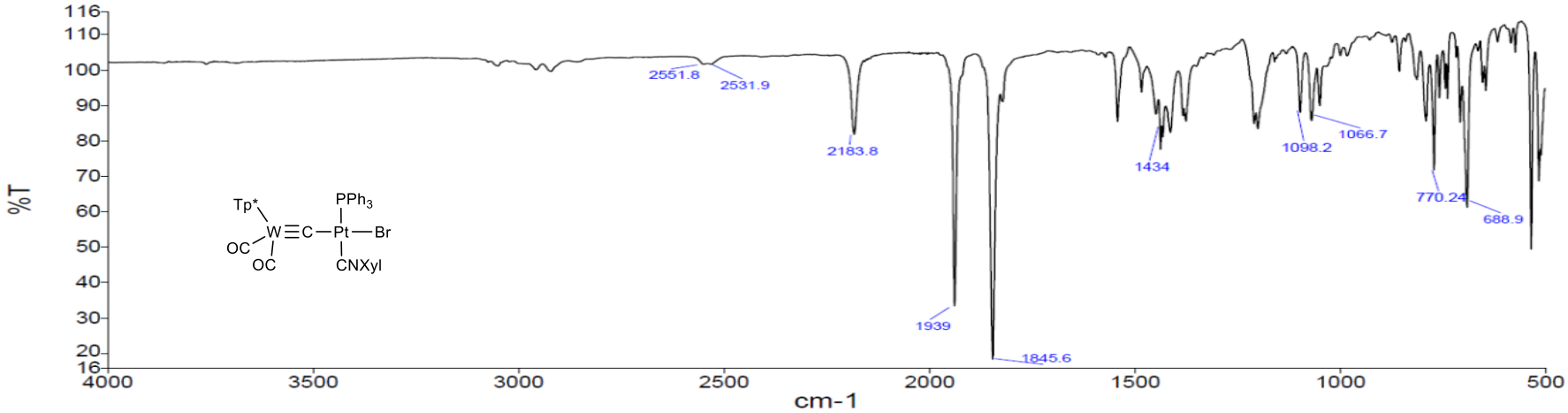

Figure S39: Infrared Spectrum of [WPt(μ_2-C)Br($CNC_6H_3Me_2$-2,6)$(CO)_2(PPh_3)$(Tp*)] (4a) (ATR, 25 °C, ν)

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 3.0 PPM / DBE: min = -1.5, max = 30.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
872 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-50 H: 0-50 11B: 1-1 N: 0-7 O: 0-2 P: 0-1 79Br: 0-1 81Br: 0-1 184W: 0-1 195Pt: 0-1

LB-5-90/AJ SYNAPTG2-Si#NotSet 11-Feb-2021
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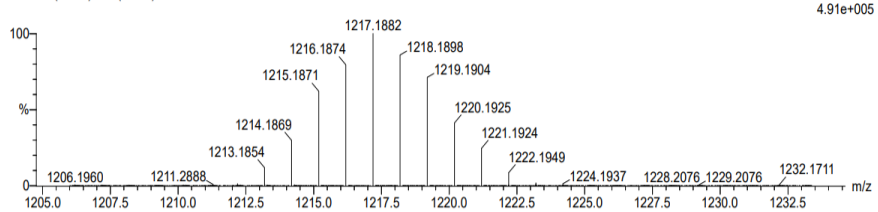
4.91e+005



Minimum:				-1.5				
Maximum:		5.0	3.0	30.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
1216.1874	1216.1884	-1.0	-0.8	29.5	1165.8	n/a	n/a	C45 H46 11B N7 O2 P 79Br 184W 195Pt

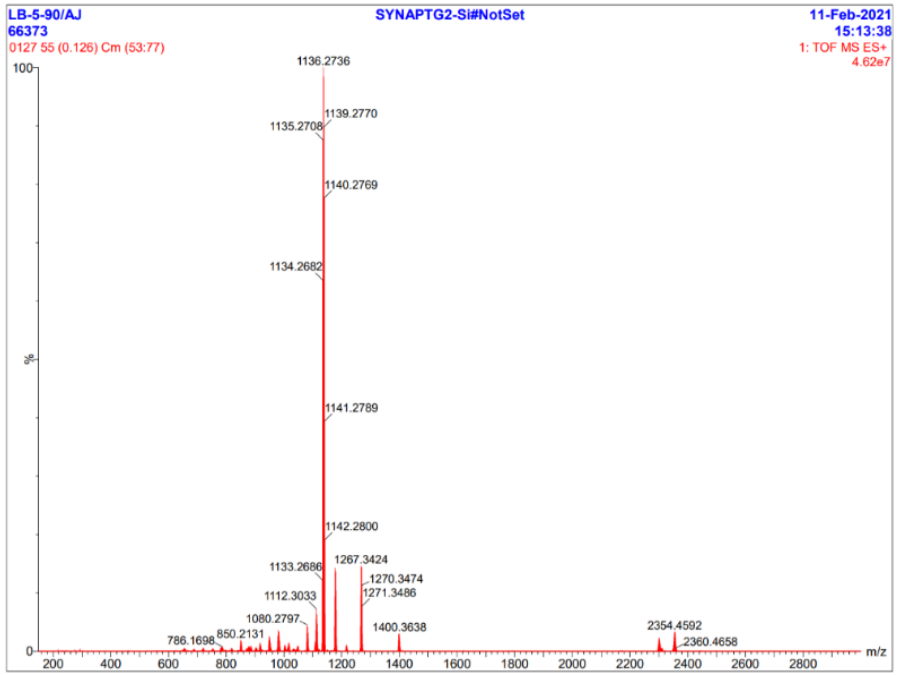


Figure S40: Mass Spectrum of [WPt(μ_2-C)Br($CNC_6H_3Me_2$-2,6)$(CO)_2(PPh_3)$(Tp*)] (**4a**)

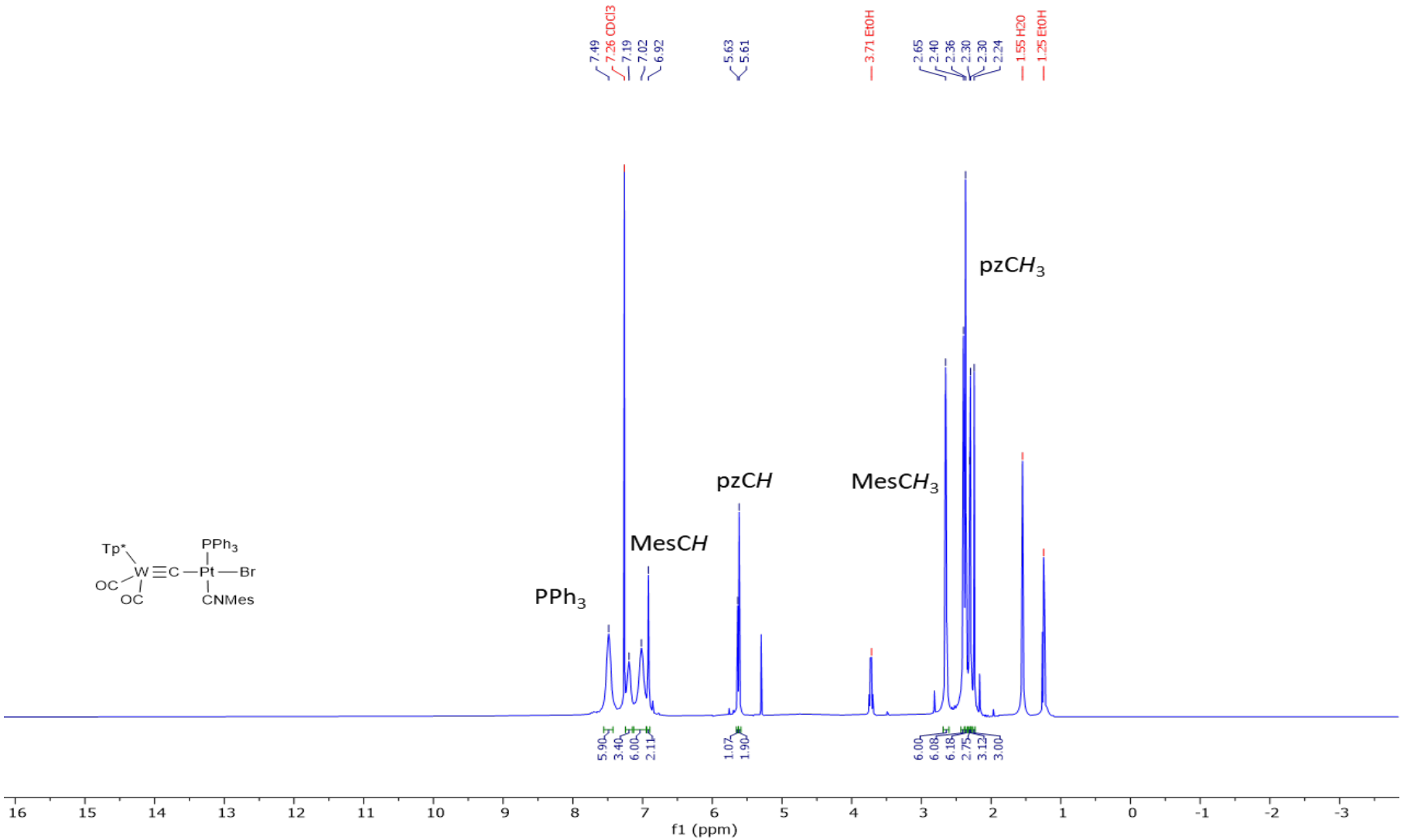


Figure S41: ^{1}H NMR Spectrum of [WPt(μ_2-C)Br($CNC_6H_2Me_3$-2,4,6)$(CO)_2(PPh_3)$(Tp*)] (**4b**) (400 MHz, $CDCl_3$, 25 °C, δ)

Please do not adjust margins

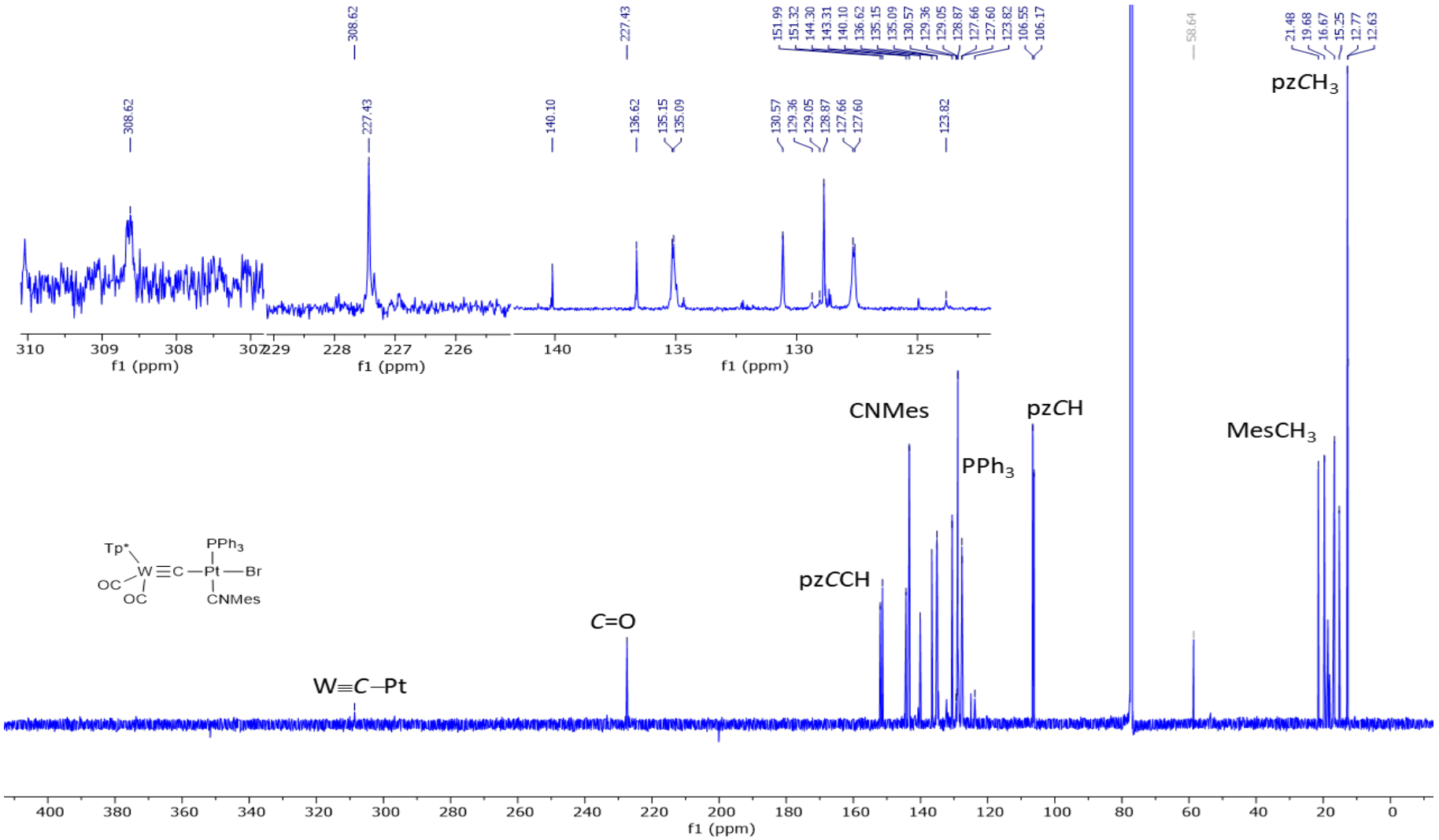


Figure S42: $^{13}C\{^{1}H\}$ NMR Spectrum of [WPt(μ_2-C)Br($CNC_6H_2Me_3$-2,4,6)$(CO)_2(PPh_3)$(Tp*)] (**4b**) (176 MHz, $CDCl_3$, 25 °C, δ)

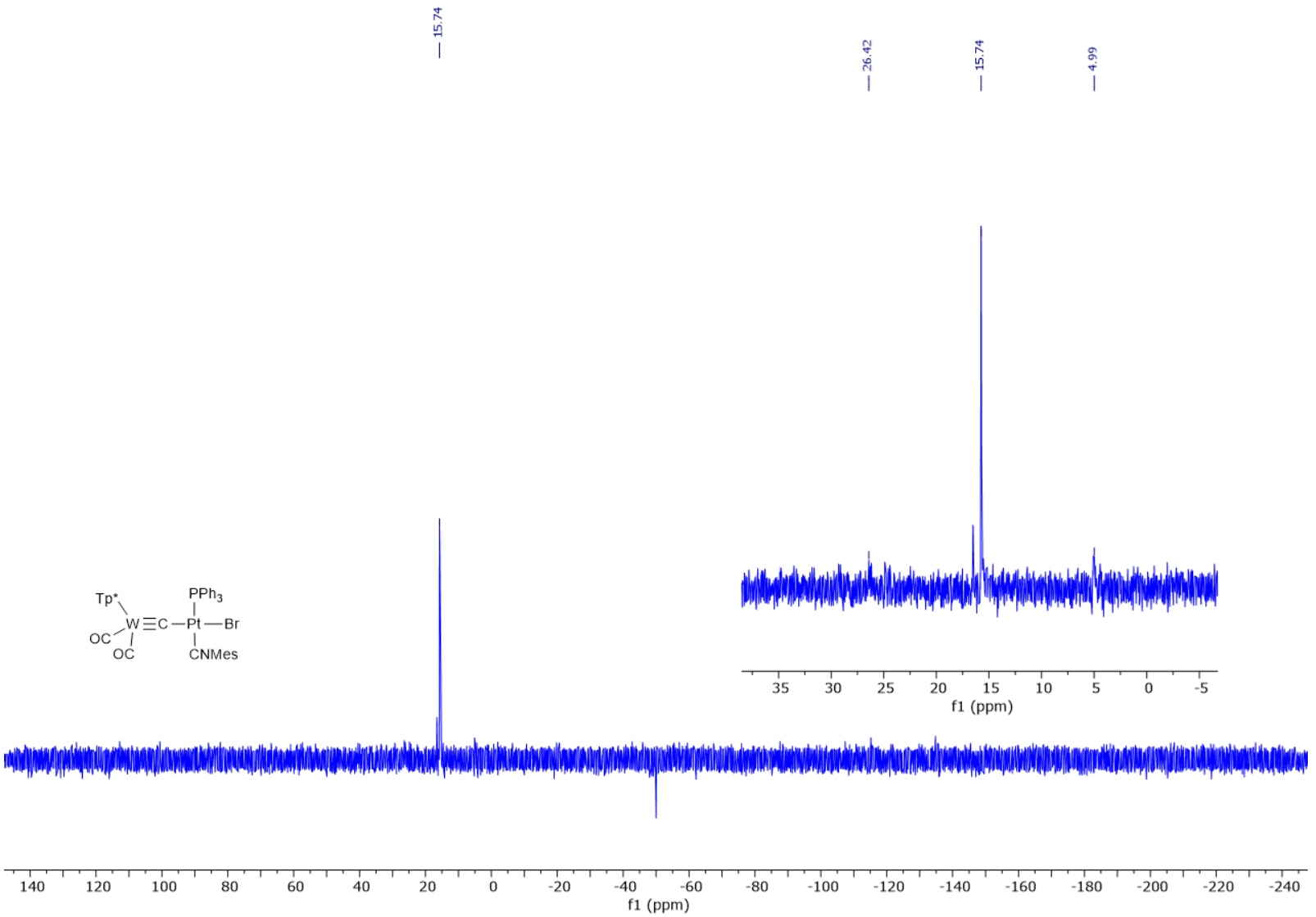


Figure S43: $^{31}P\{^{1}H\}$ NMR Spectrum of [WPt(μ_2-C)Br($CNC_6H_2Me_3$-2,4,6)$(CO)_2(PPh_3)$(Tp*)] (**4b**) (162 MHz, $CDCl_3$, 25 °C, δ)

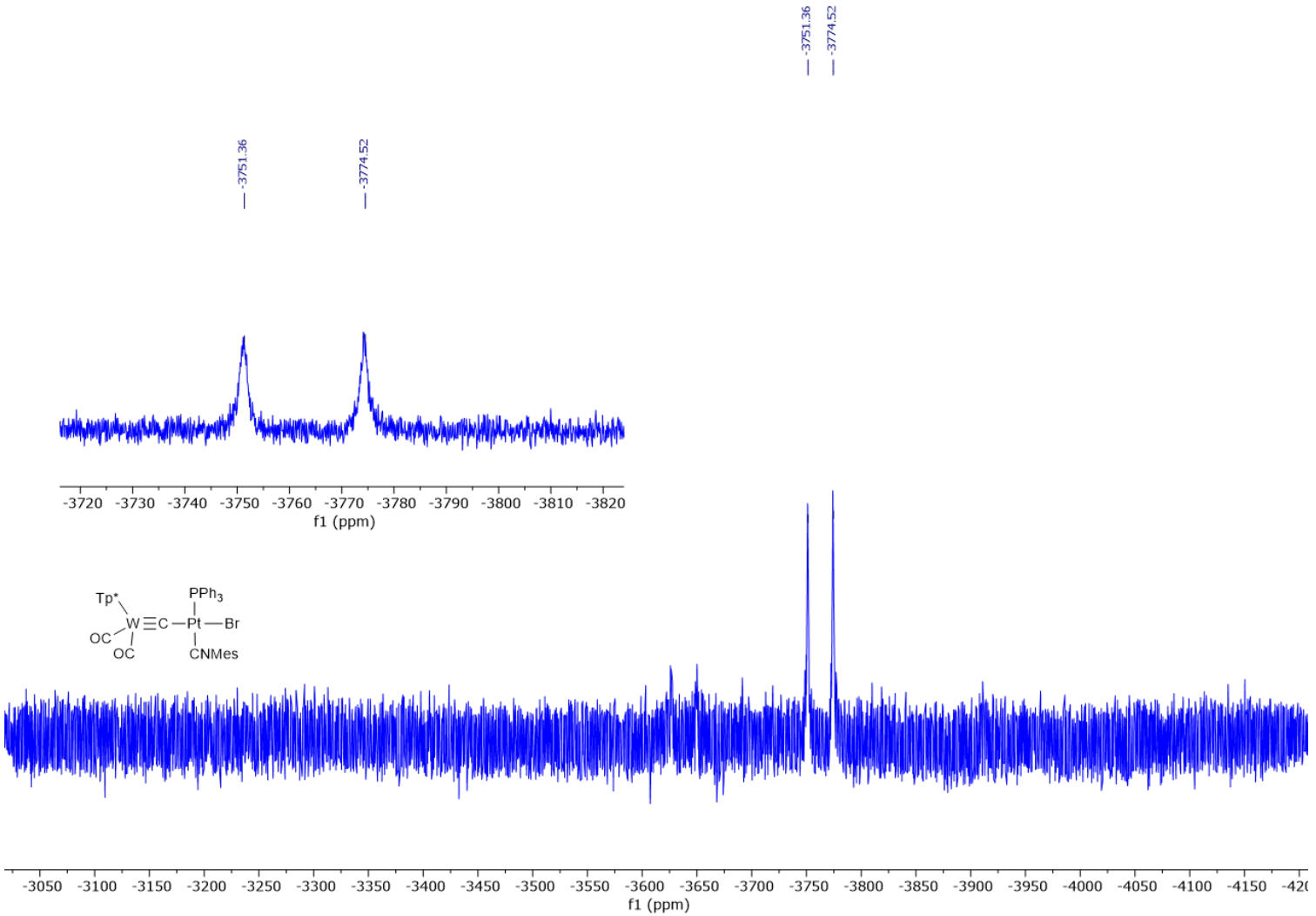


Figure S44: $^{195}Pt\{^{1}H\}$ NMR Spectrum of [WPt(μ_2-C)Br($CNC_6H_2Me_3$-2,4,6)$(CO)_2(PPh_3)$(Tp*)] (**4b**) (150 MHz, $CDCl_3$, 25 °C, δ)

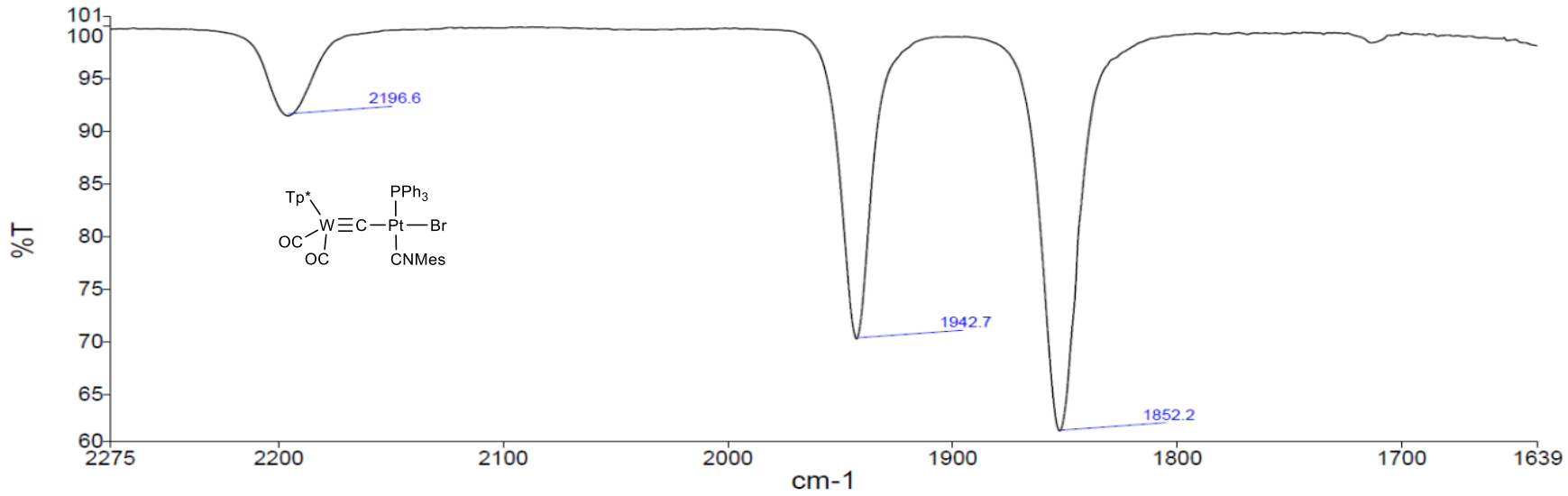


Figure S45: Infrared Spectrum of [WPt(μ_2-C)Br($CNC_6H_2Me_3$-2,4,6)$(CO)_2(PPh_3)$(Tp*)] (**4b**) (CH_2Cl_2, 25 °C, ν)

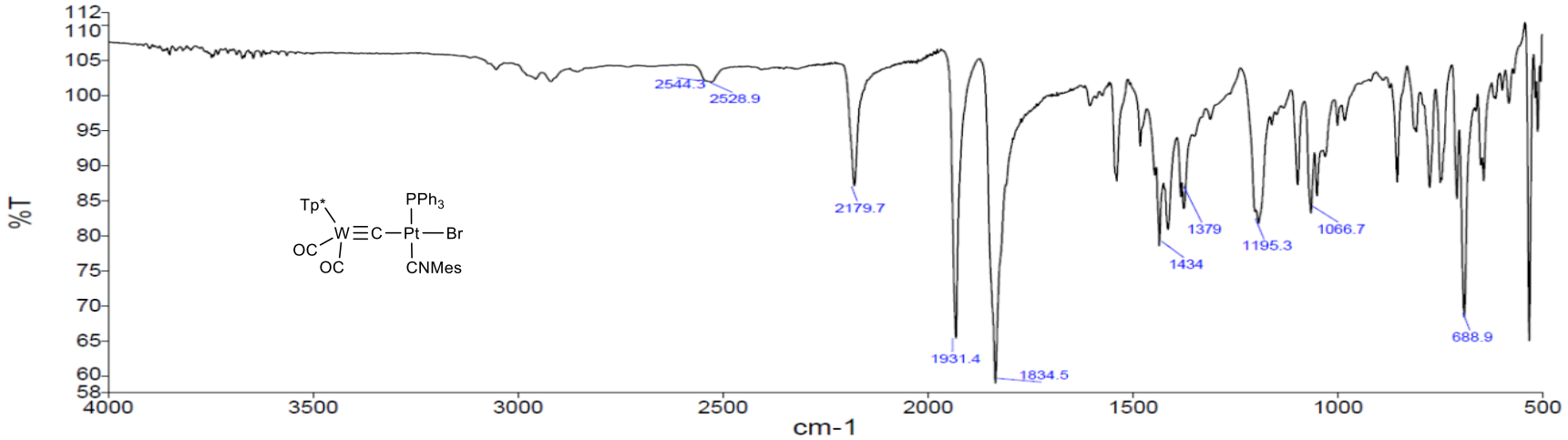
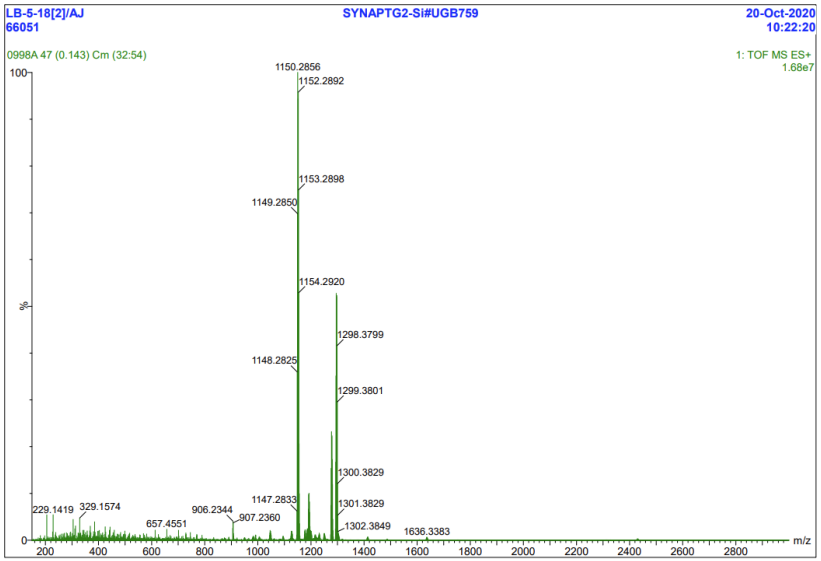


Figure S46: Infrared Spectrum of [WPt(μ_2-C)Br($CNC_6H_2Me_3$-2,4,6)$(CO)_2(PPh_3)$(Tp*)] (**4b**) (ATR, 25 °C, ν)



Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 30.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
961 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-50 H: 0-50 11B: 1-1 N: 0-8 O: 0-2 P: 0-1 79Br: 0-1 81Br: 0-1 184W: 0-1 195Pt: 0-1

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10:09:31
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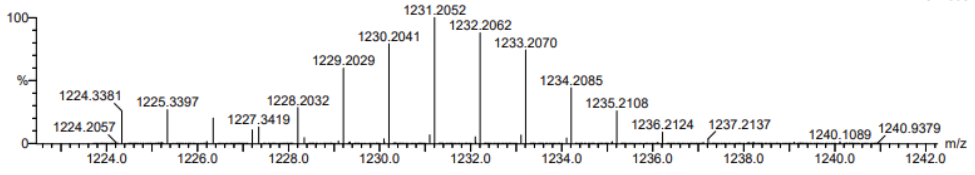
4.75e+005



Minimum:				-1.5				
Maximum:		5.0	5.0	30.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
1232.2062	1232.2020	4.2	3.4	29.5	1059.6	n/a	n/a	C46 H48 11B N7 O2 P 81Br 184W 195Pt

Figure S47: Mass Spectrum of [WPt(μ_2-C)Br($CNC_6H_2Me_3$-2,4,6)$(CO)_2(PPh_3)$(Tp*)] (**4b**)

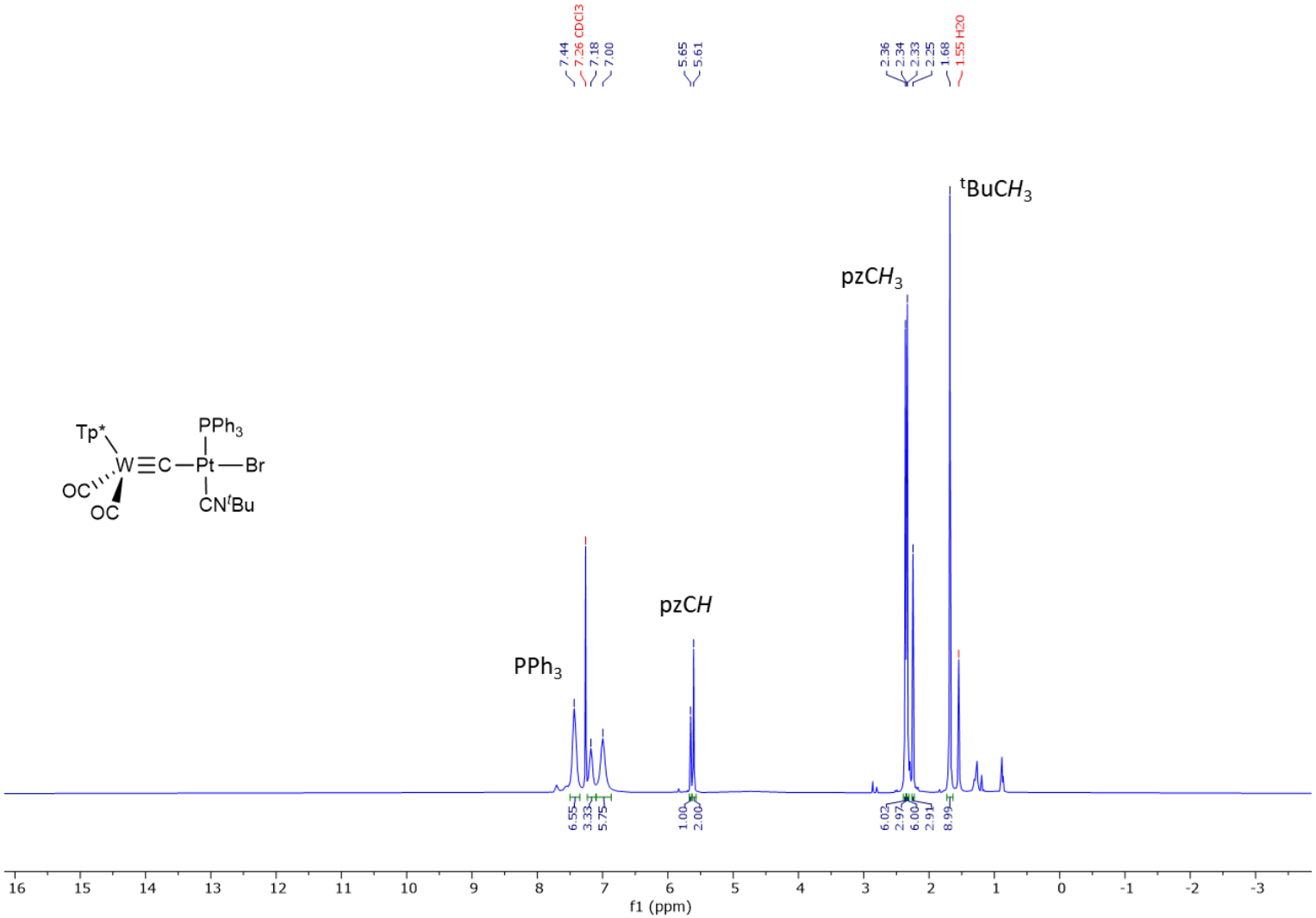


Figure S48: ^{1}H NMR Spectrum of [WPt(μ_2-C)Br(CN^{t}Bu)(CO)$_2$(PPh$_3$)(Tp*)] (**4c**) (400 MHz, $CDCl_3$, 25 °C, δ)

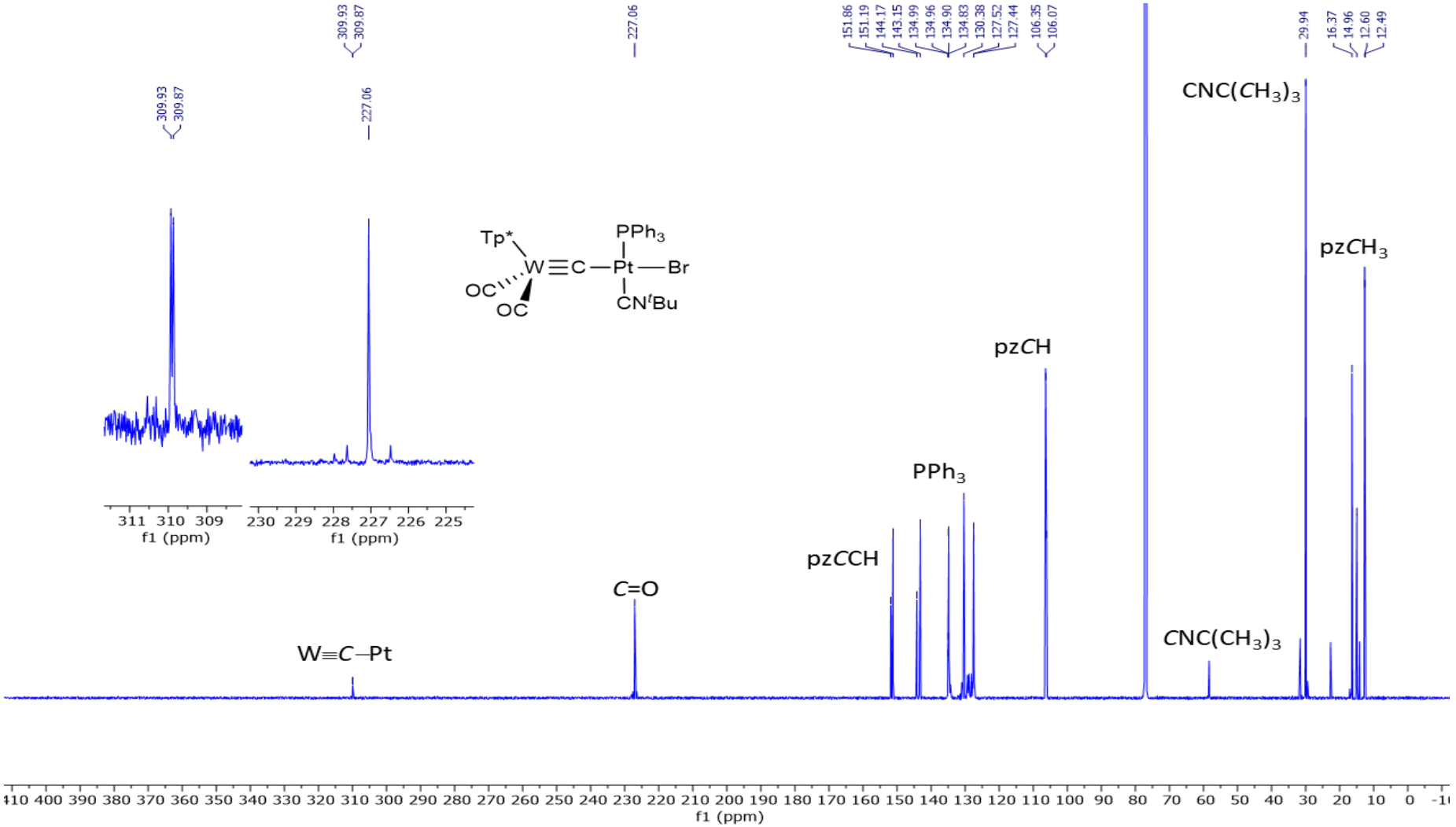


Figure S49: $^{13}C\{^{1}H\}$ NMR Spectrum of [WPt(μ_2-C)Br(CN^tBu)$(CO)_2(PPh_3)$(Tp*)] (**4c**) (151 MHz, $CDCl_3$, 25 °C, δ)

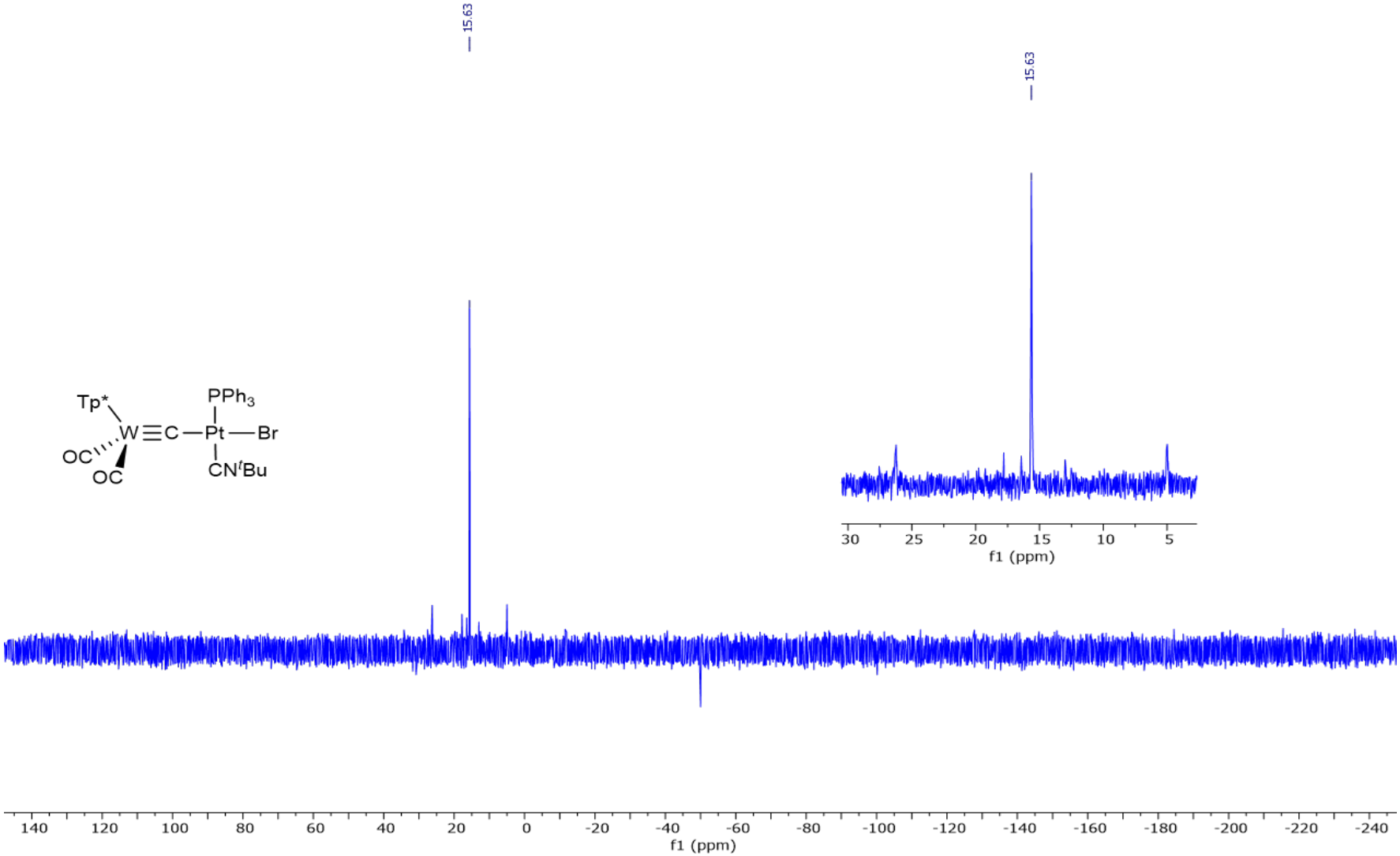


Figure S50: $^{31}P\{^{1}H\}$ NMR Spectrum of [WPt(μ_2-C)Br(CN^tBu)$(CO)_2(PPh_3)$(Tp*)] (**4c**) (162 MHz, $CDCl_3$, 25 °C, δ)

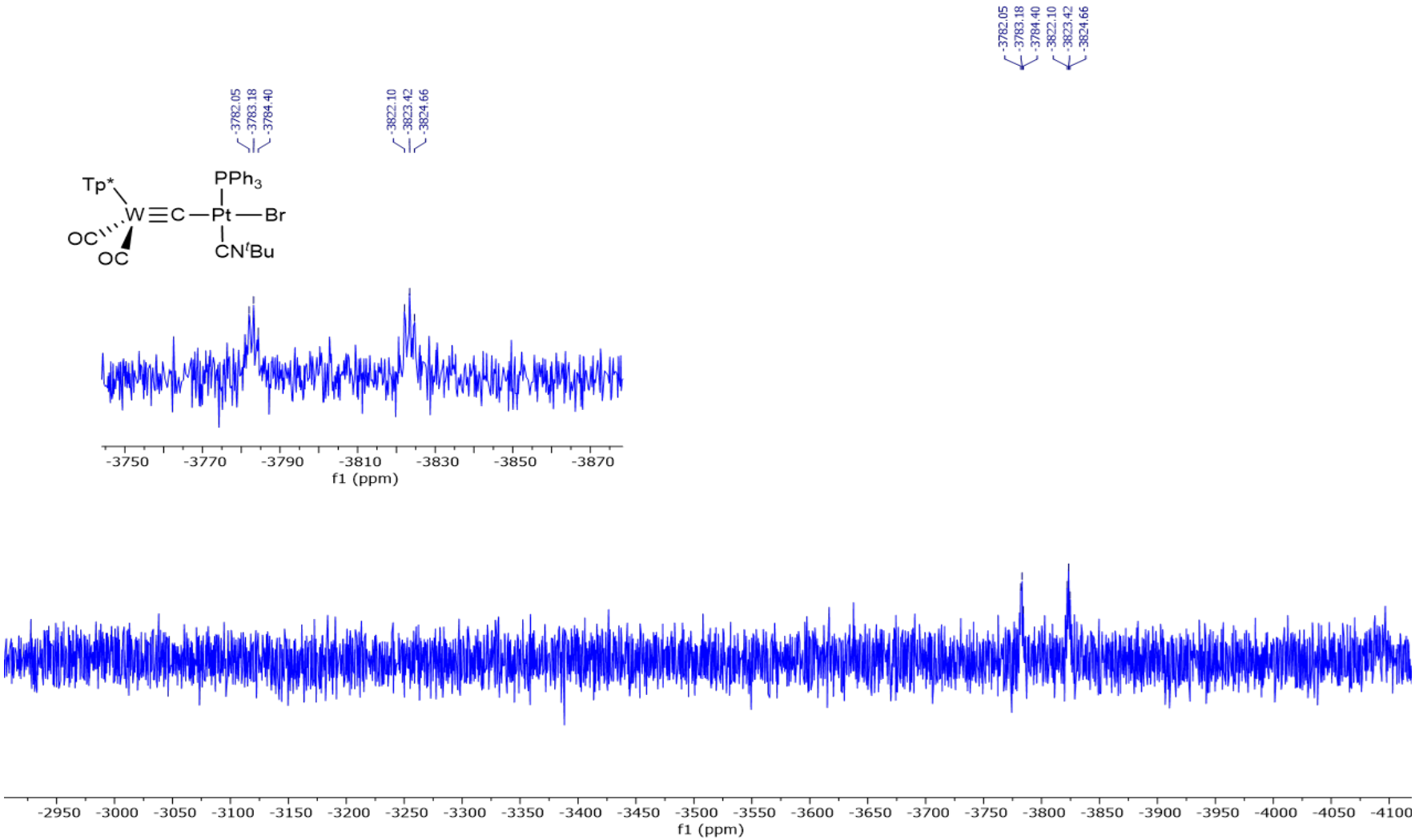


Figure S51: $^{195}Pt\{^{1}H\}$ NMR Spectrum of [WPt(μ_2-C)Br(CN^{t}Bu)(CO)$_2$(PPh$_3$)(Tp*)] (**4c**) (86 MHz, $CDCl_3$, 25 °C, δ)

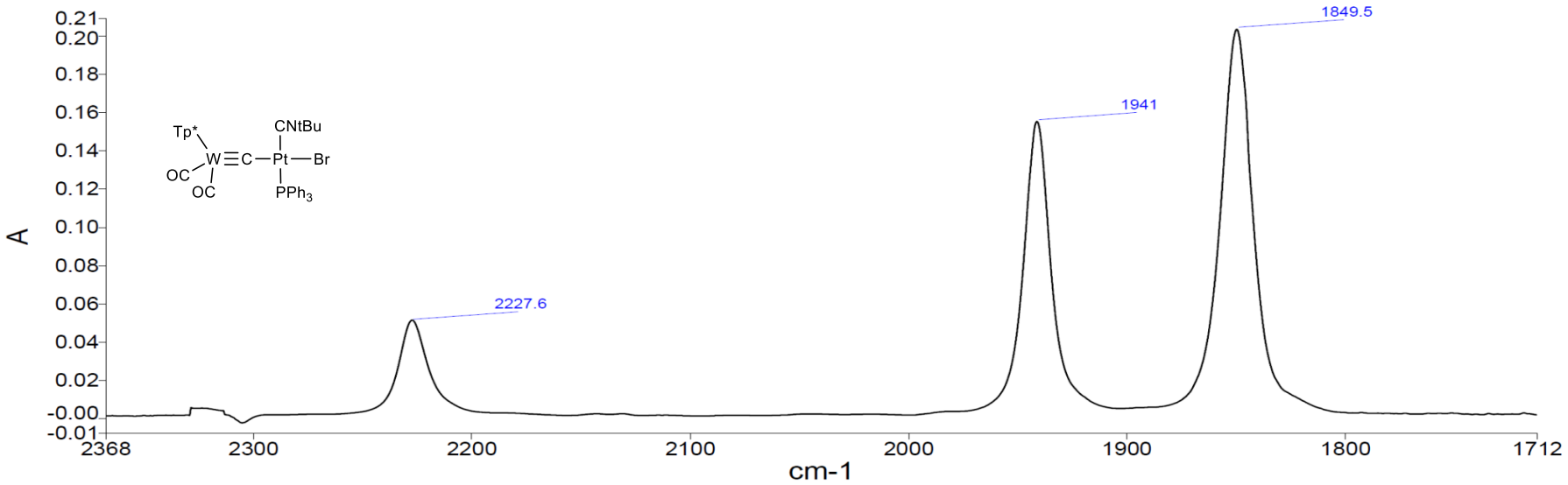


Figure S52: Infrared Spectrum of [WPt(μ_2-C)Br(CN^{t}Bu)(CO)$_2$(PPh$_3$)(Tp*)] (**4c**) (CH_2Cl_2, 25 °C, ν)

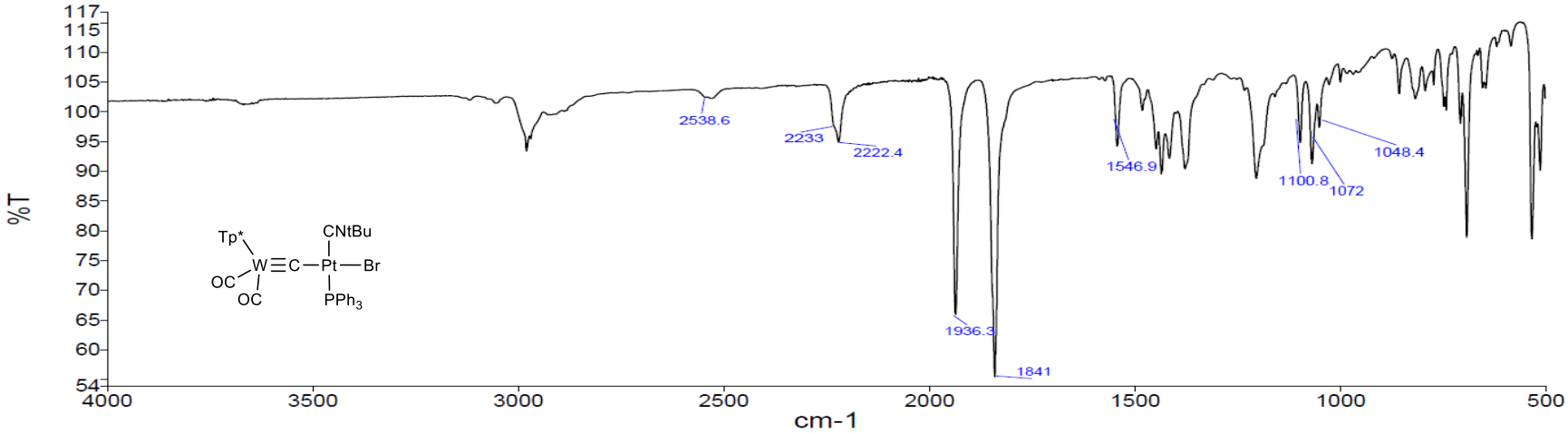


Figure S53: Infrared Spectrum of [WPt(μ_2-C)Br(CN^{t}Bu)(CO)$_2$(PPh$_3$)(Tp*)] (**4c**) (ATR, 25 °C, ν)

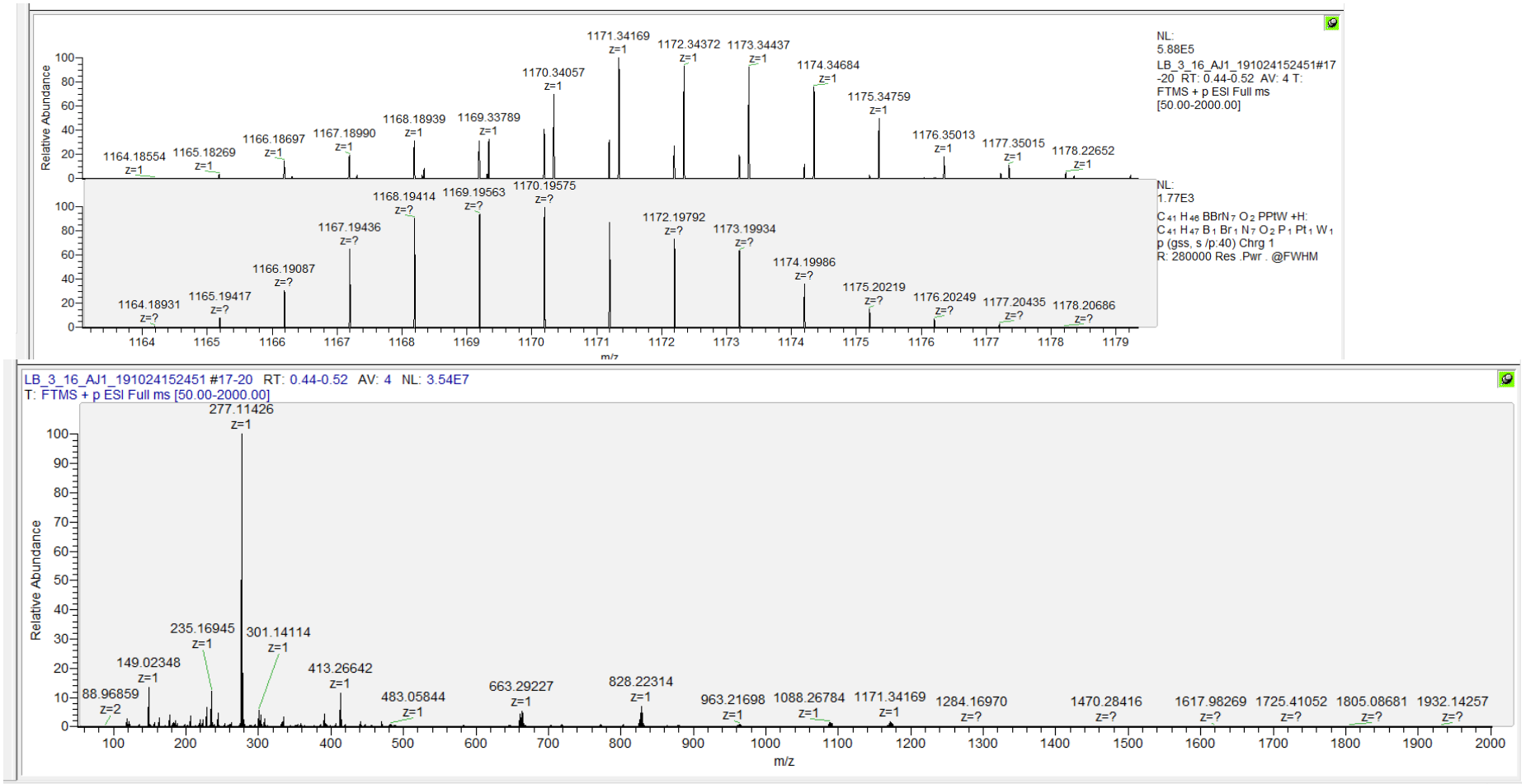


Figure S54: Mass Spectrum of [WPt(μ_2-C)Br(CN^{t}Bu)(CO)$_2$(PPh$_3$)(Tp*)] (**4c**)

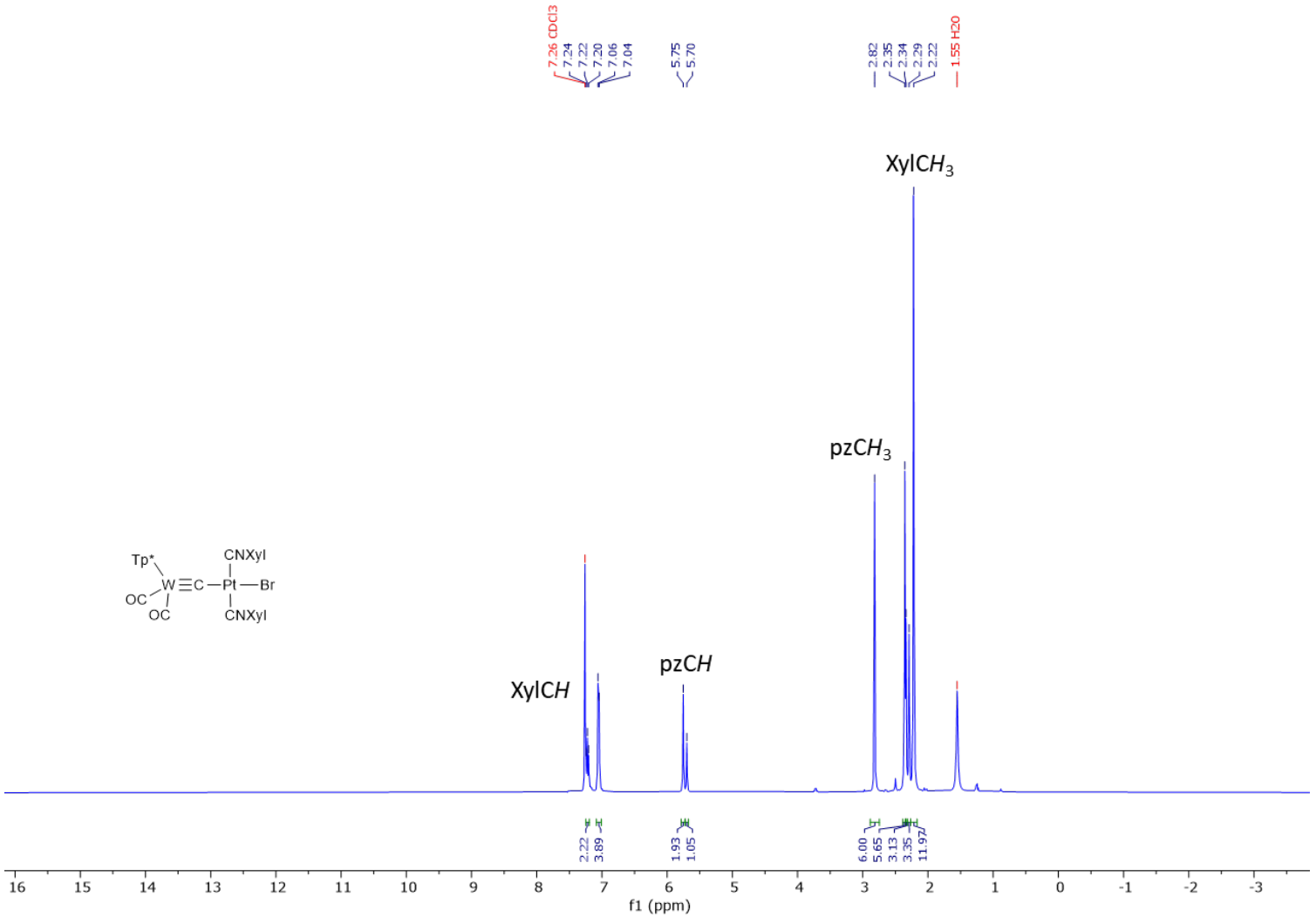


Figure S55: ^{1}H NMR Spectrum of [WPt(μ_2-C)Br($CNC_6H_3Me_2$-2,6)$_2$(CO)$_2$(Tp*)] (**5a**) (400 MHz, $CDCl_3$, 25 °C, δ)

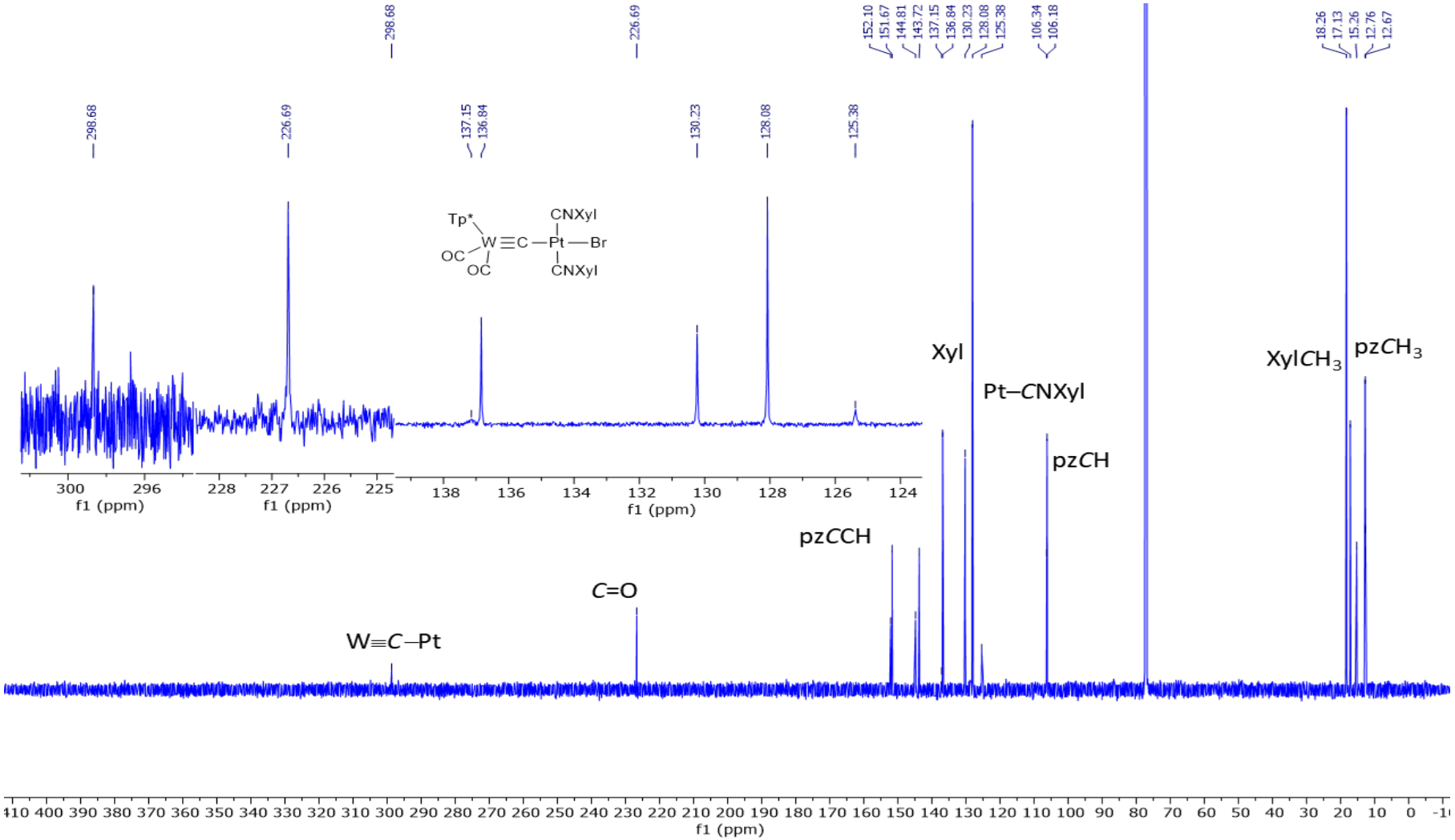


Figure S56: $^{13}C\{^{1}H\}$ NMR Spectrum of [WPt(μ_2-C)Br($CNC_6H_3Me_2$-2,6)$_2$(CO)$_2$(Tp*)] (**5a**) (151 MHz, $CDCl_3$, 25 °C, δ)

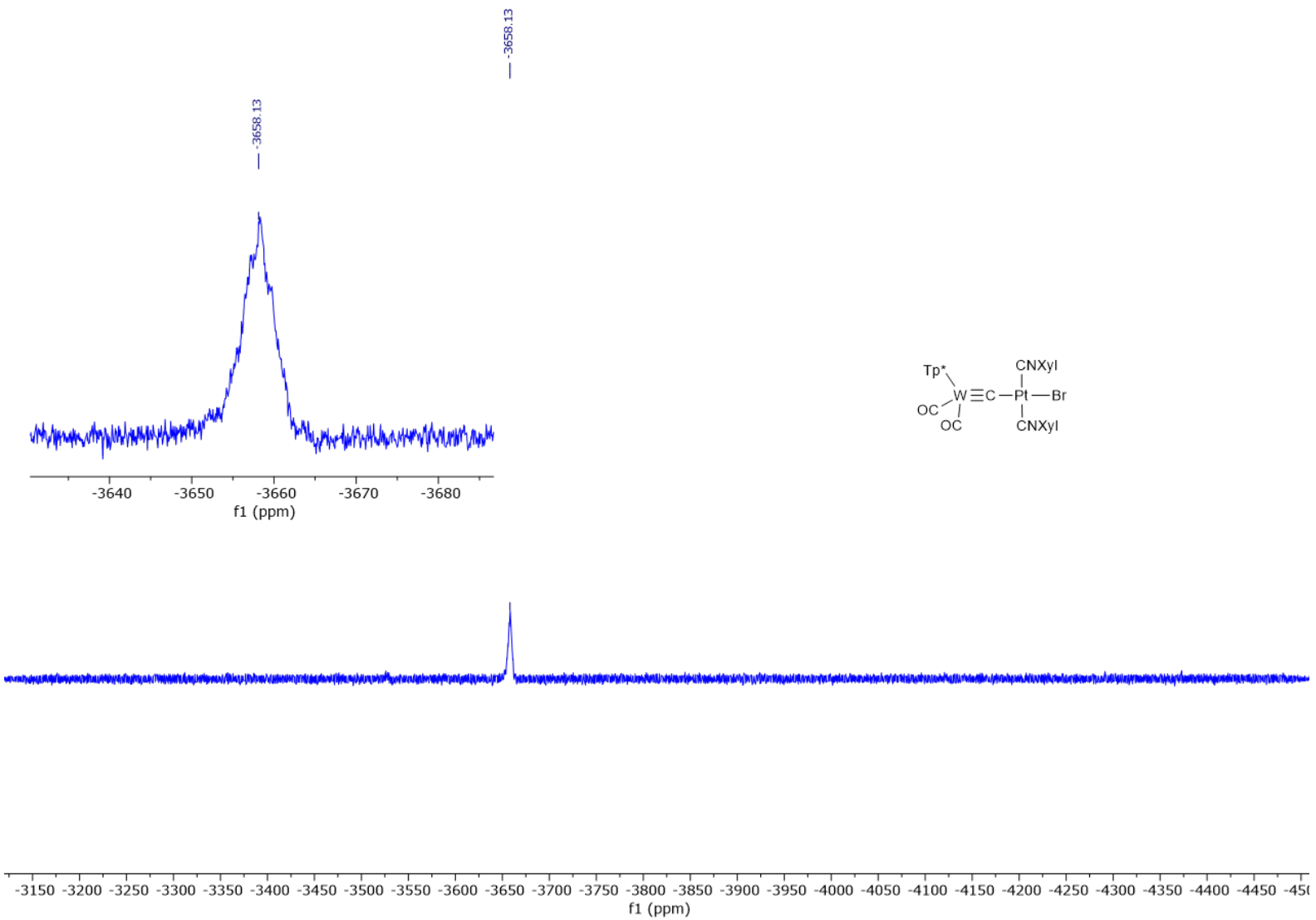


Figure S57: $^{195}Pt\{^{1}H\}$ NMR Spectrum of [WPt(μ_2-C)Br($CNC_6H_3Me_2$-2,6)$_2$(CO)$_2$(Tp*)] (**5a**) (86 MHz, $CDCl_3$, 25 °C, δ)

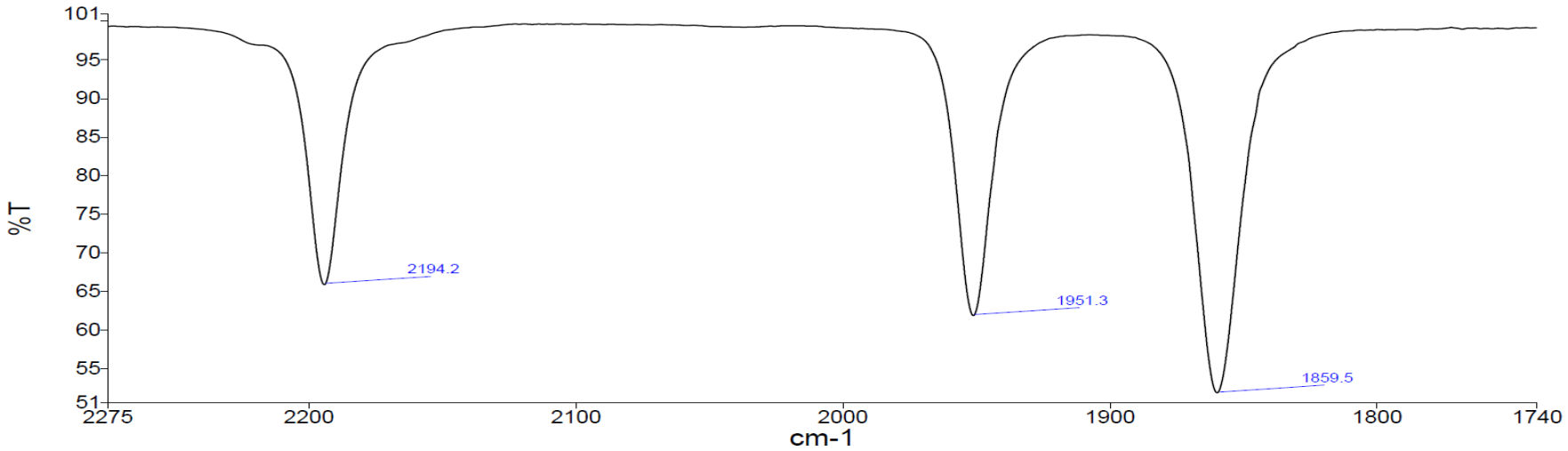


Figure S58: Infrared Spectrum of [WPt(μ$_2$-C)Br(CNC$_6$H$_3$Me$_2$-2,6)$_2$(CO)$_2$(Tp*)] (**5a**) (CH$_2$Cl$_2$, 25 °C, ν)

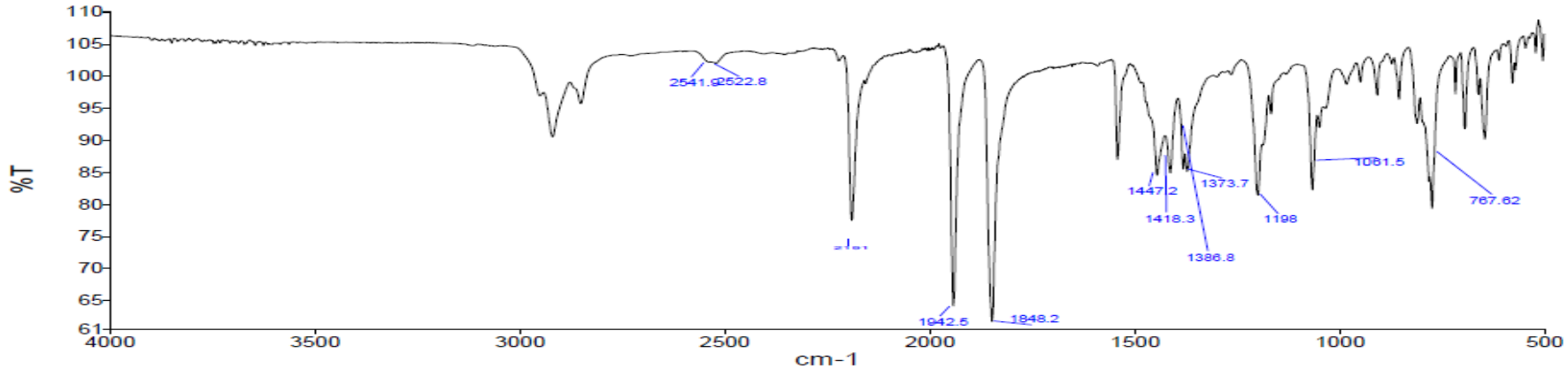


Figure S59: Infrared Spectrum of [WPt(μ$_2$-C)Br(CNC$_6$H$_3$Me$_2$-2,6)$_2$(CO)$_2$(Tp*)] (**5a**) (ATR, 25 °C, ν)

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 3.0 PPM / DBE: min = -1.5, max = 25.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
722 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-50 H: 0-50 11B: 1-1 N: 0-8 O: 0-2 79Br: 0-1 81Br: 0-1 184W: 0-1 195Pt: 0-1

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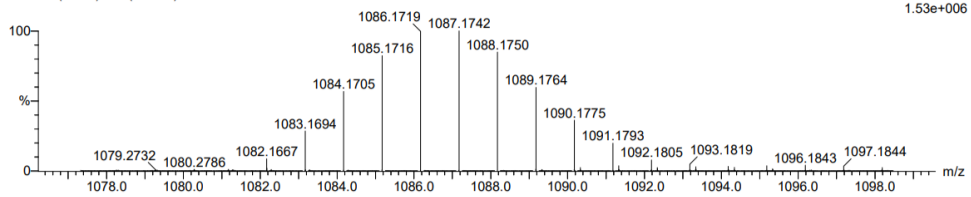
1.53e+006



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Maximum:		5.0	3.0	25.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
1085.1716	1085.1708	0.8	0.7	23.5	2975.4	n/a	n/a	C36 H40 11B N8 O2 79Br 184W 195Pt

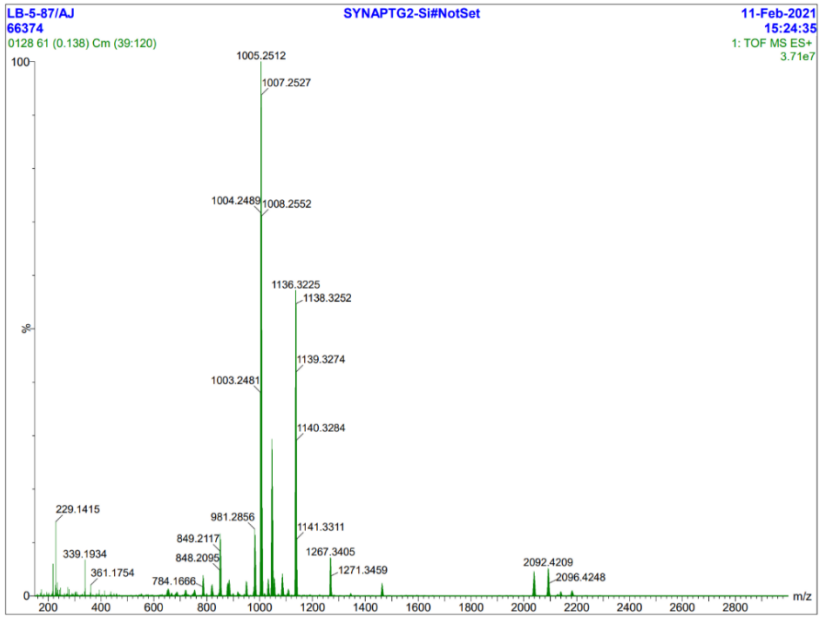


Figure S60: Mass Spectrum of [WPt(μ_2-C)Br($CNC_6H_3Me_2$-2,6)$_2$(CO)$_2$(Tp*)] (**5a**)

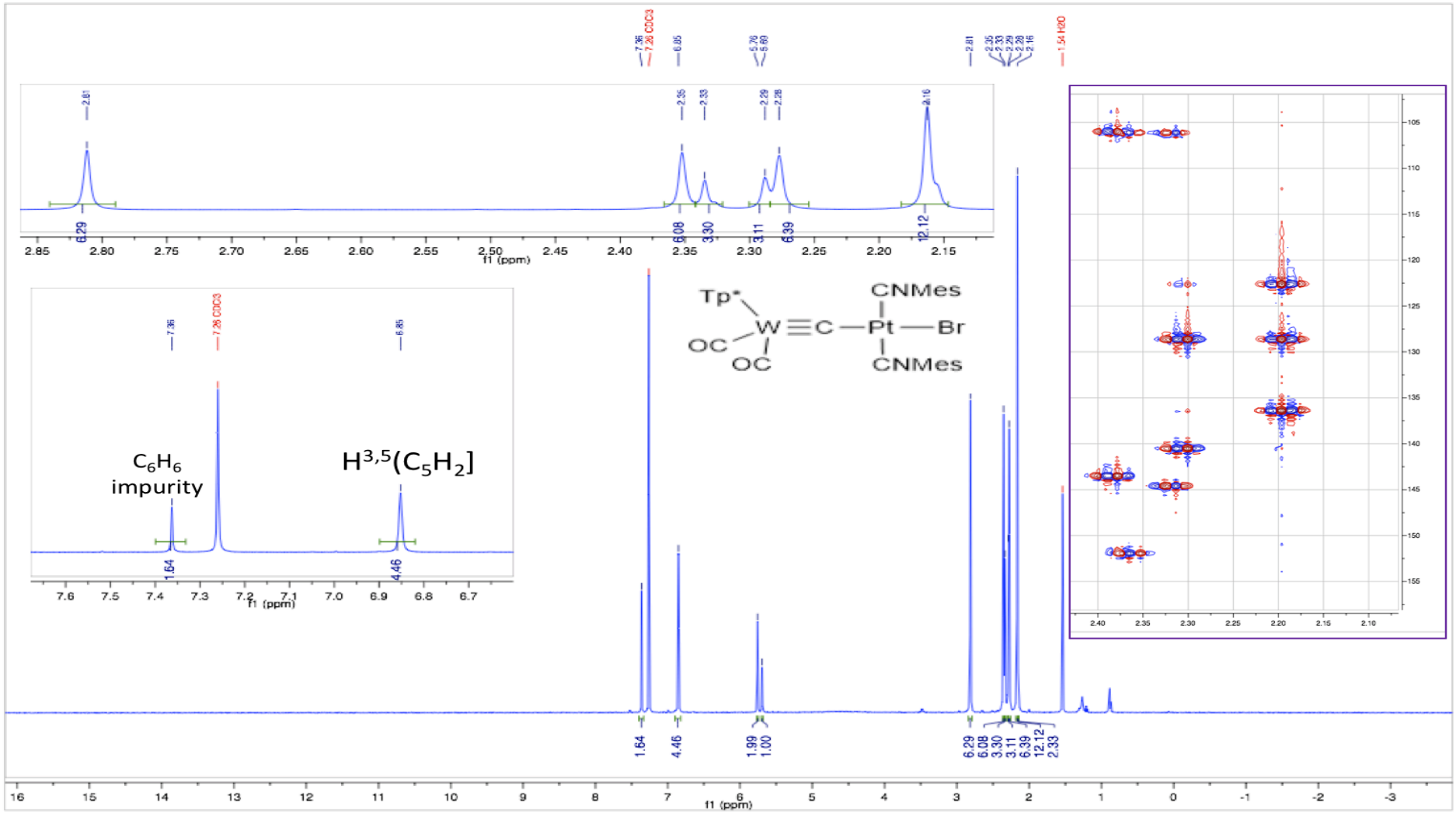


Figure S61: ^{1}H NMR Spectrum of [WPt(μ_2-C)Br($CNC_6H_2Me_3$-2,4,6)$_2$(CO)$_2$(Tp*)] (**5b**) (400 MHz, $CDCl_3$, 25 °C, δ) – Inset = ^{1}H-^{13}C HMBC spectrum indicating correlation between the 12 proton ^{1}H resonance (δ_H = 2.20) and three 13C resonances (δ_C = 122.6, 126.6 and 136.4).

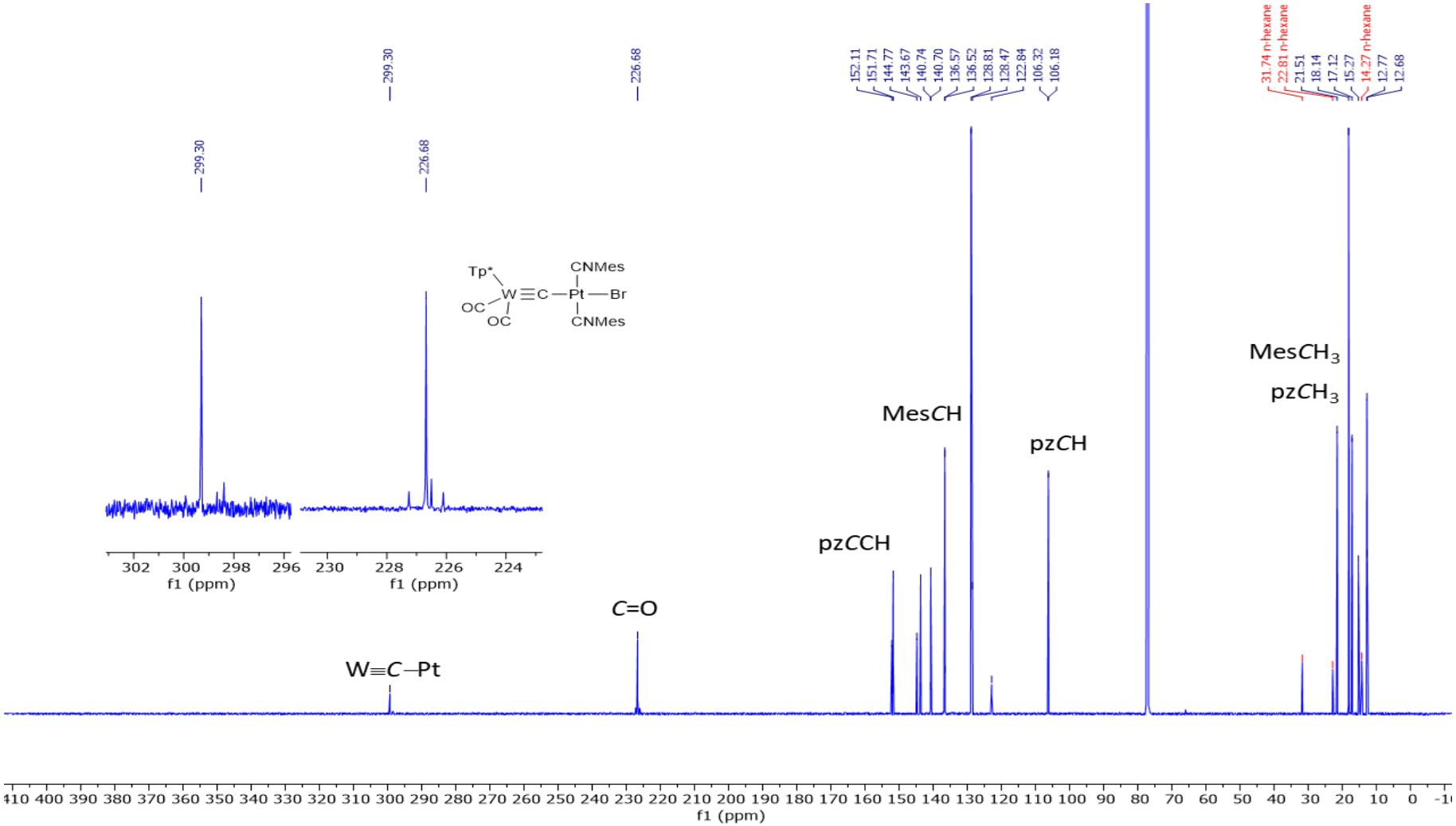


Figure S62: $^{13}C\{^1H\}$ NMR Spectrum of [WPt(μ_2-C)Br($CNC_6H_2Me_3$-2,4,6)$_2$(CO)$_2$(Tp*)] (**5b**) (151 MHz, $CDCl_3$, 25 °C, δ)

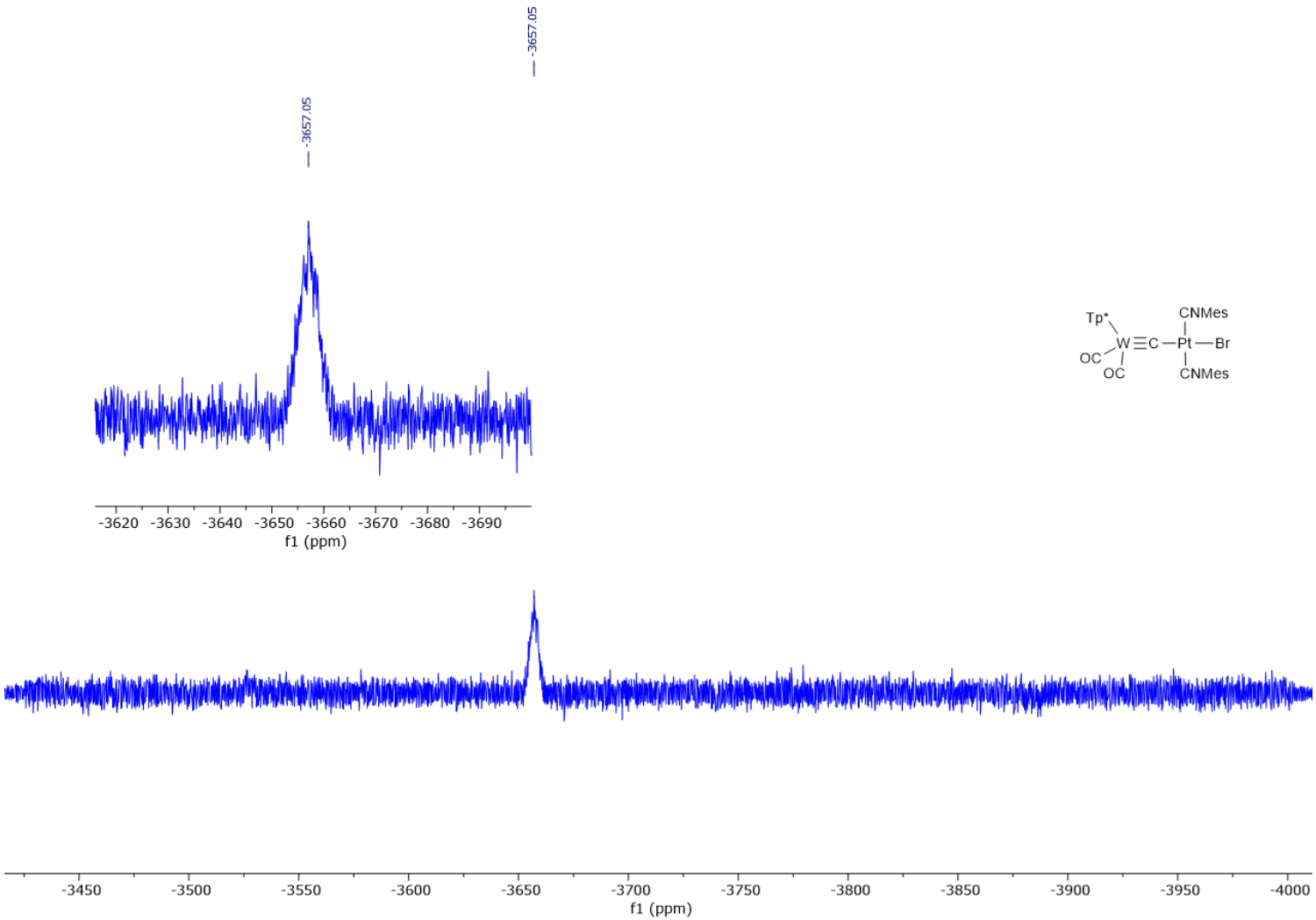


Figure S63: $^{195}Pt\{^{1}H\}$ NMR Spectrum [$WPt(\mu_2\text{-}C)Br(CNC_6H_2Me_3\text{-}2,4,6)_2(CO)_2(Tp^*)$] (**5b**) (86 MHz, $CDCl_3$, 25 °C, δ)

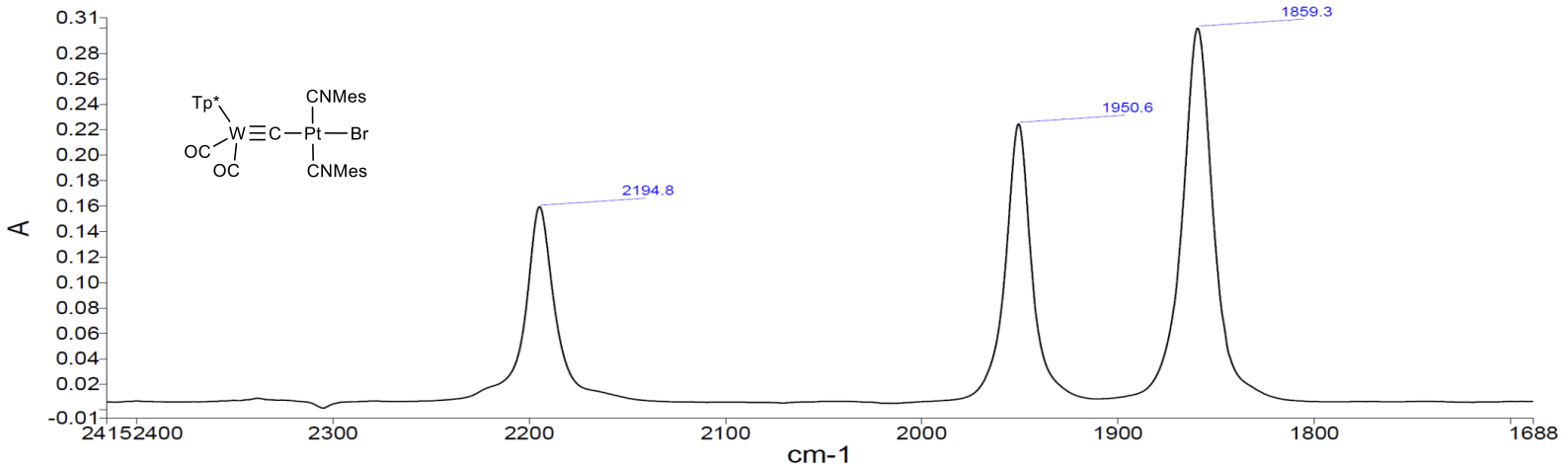


Figure S64: Infrared Spectrum of [WPt(μ2-C)Br(CNC6H2Me3-2,4,6)2(CO)2(Tp*)] (**5b**) (CH_2Cl_2, 25 °C, ν)

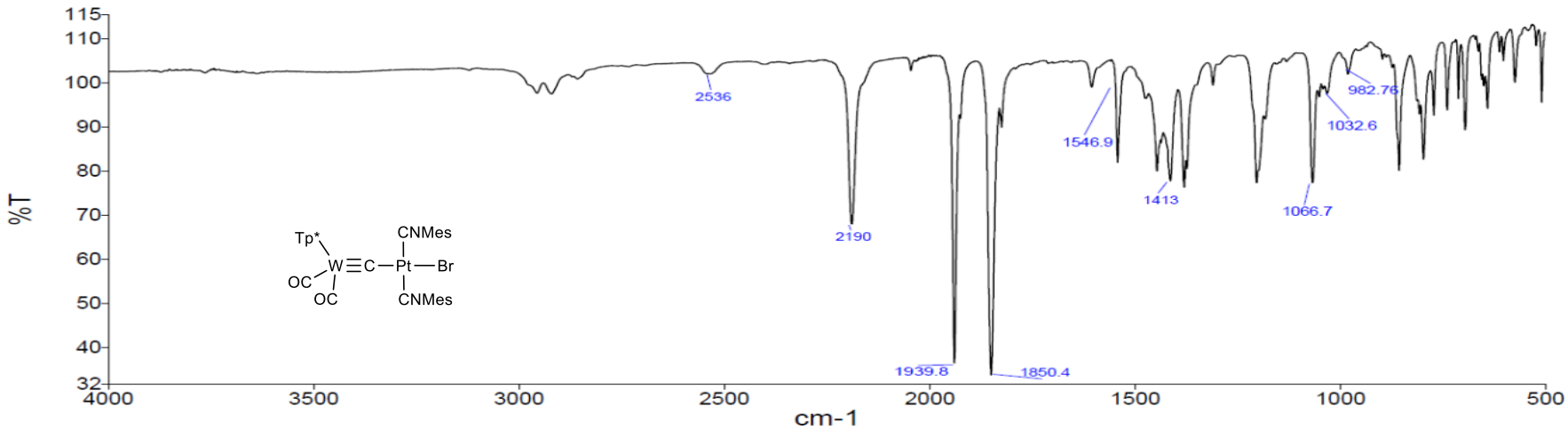


Figure S65: Infrared Spectrum of [WPt(μ2-C)Br(CNC6H2Me3-2,4,6)2(CO)2(Tp*)] (**5b**) (ATR, 25 °C, ν)

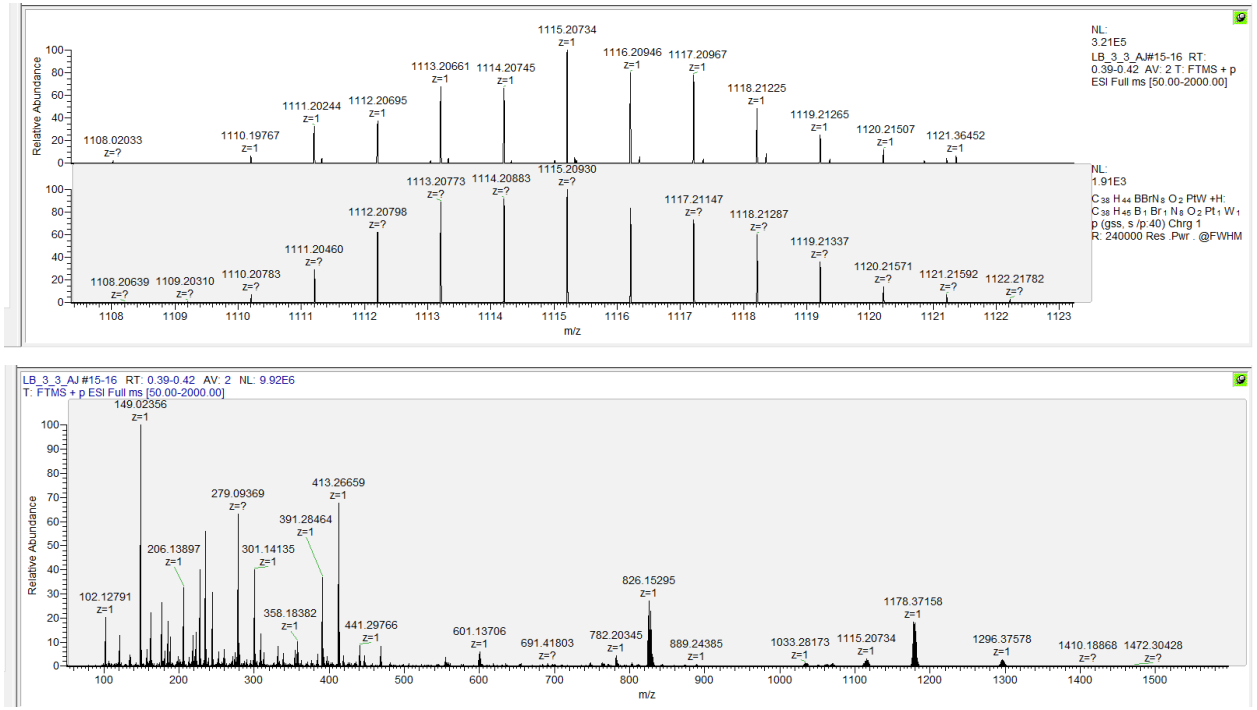


Figure S66: Mass Spectrum of [WPt(μ_2-C)Br($CNC_6H_2Me_3$-2,4,6)$_2$(CO)$_2$(Tp*)] (**5b**)

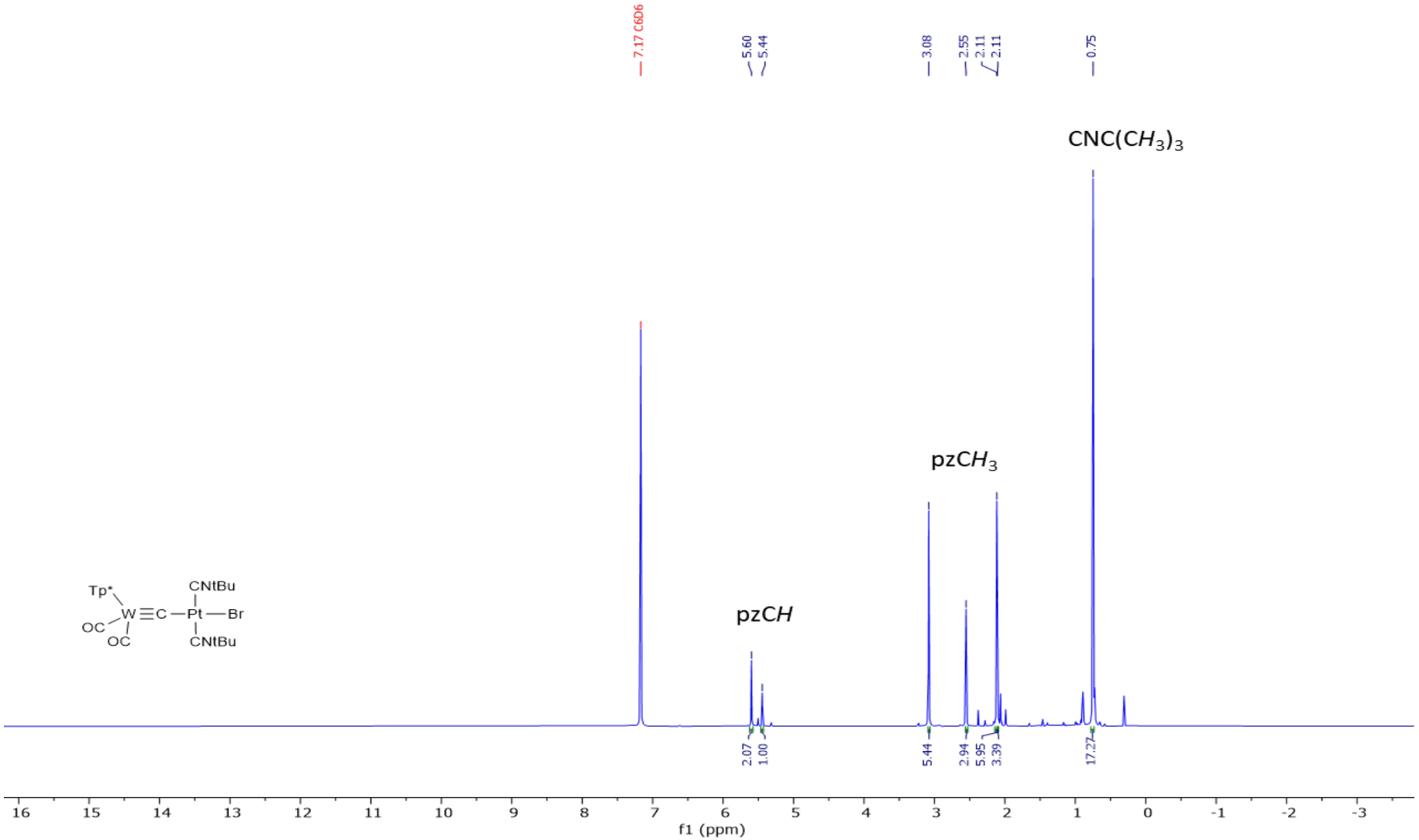


Figure S67: ^{1}H NMR Spectrum of [WPt(μ_2-C)Br(CN^{t}Bu)$_2$(CO)$_2$(Tp*)] (**5c**) (400 MHz, $CDCl_3$, 25 °C, δ)

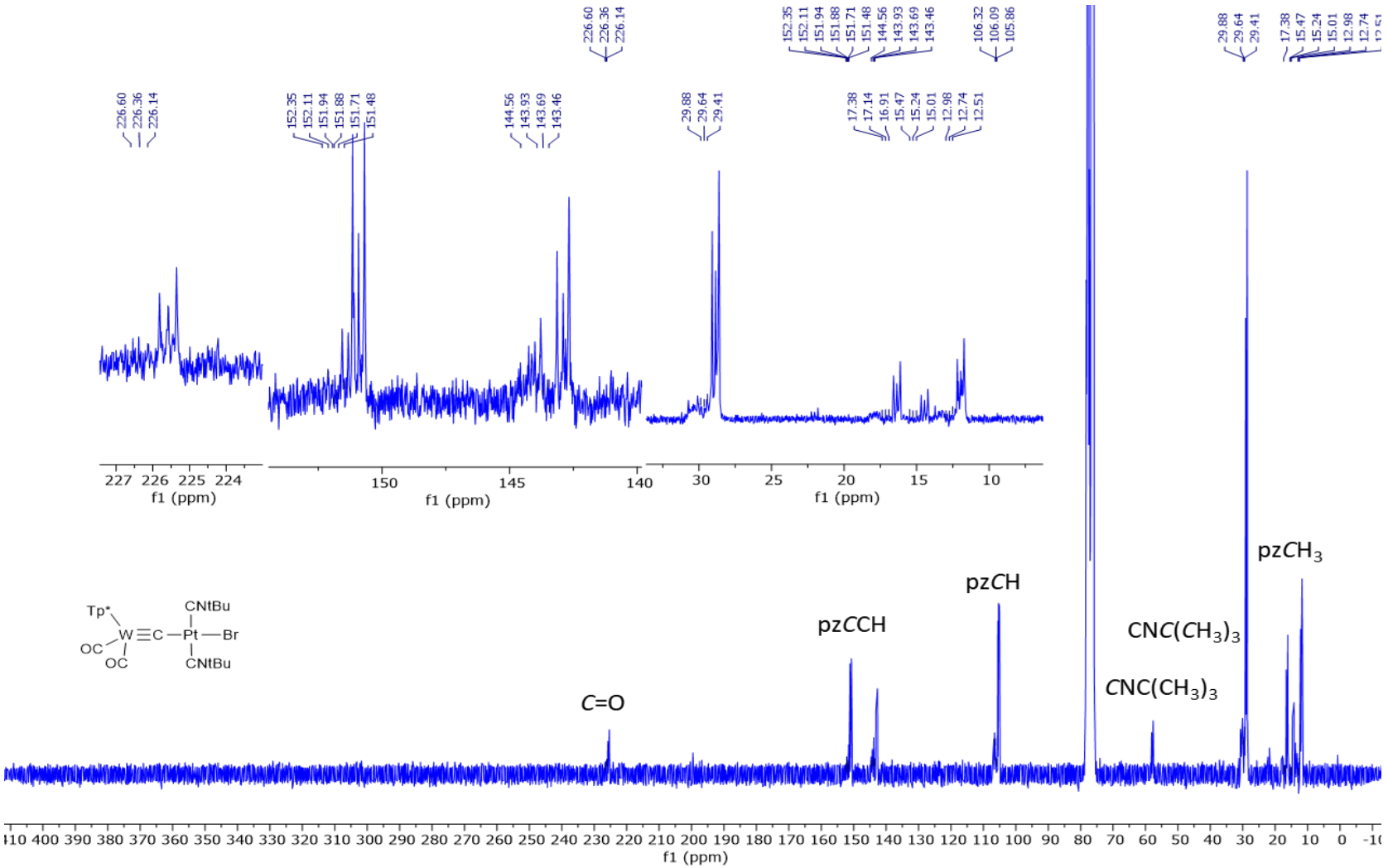


Figure S68: $^{13}C\{^{1}H\}$ NMR Spectrum of [WPt(μ_2-C)Br($CN^tBu)_2(CO)_2$(Tp*)] (**5c**) (151 MHz, $CDCl_3$, 25 °C, δ)

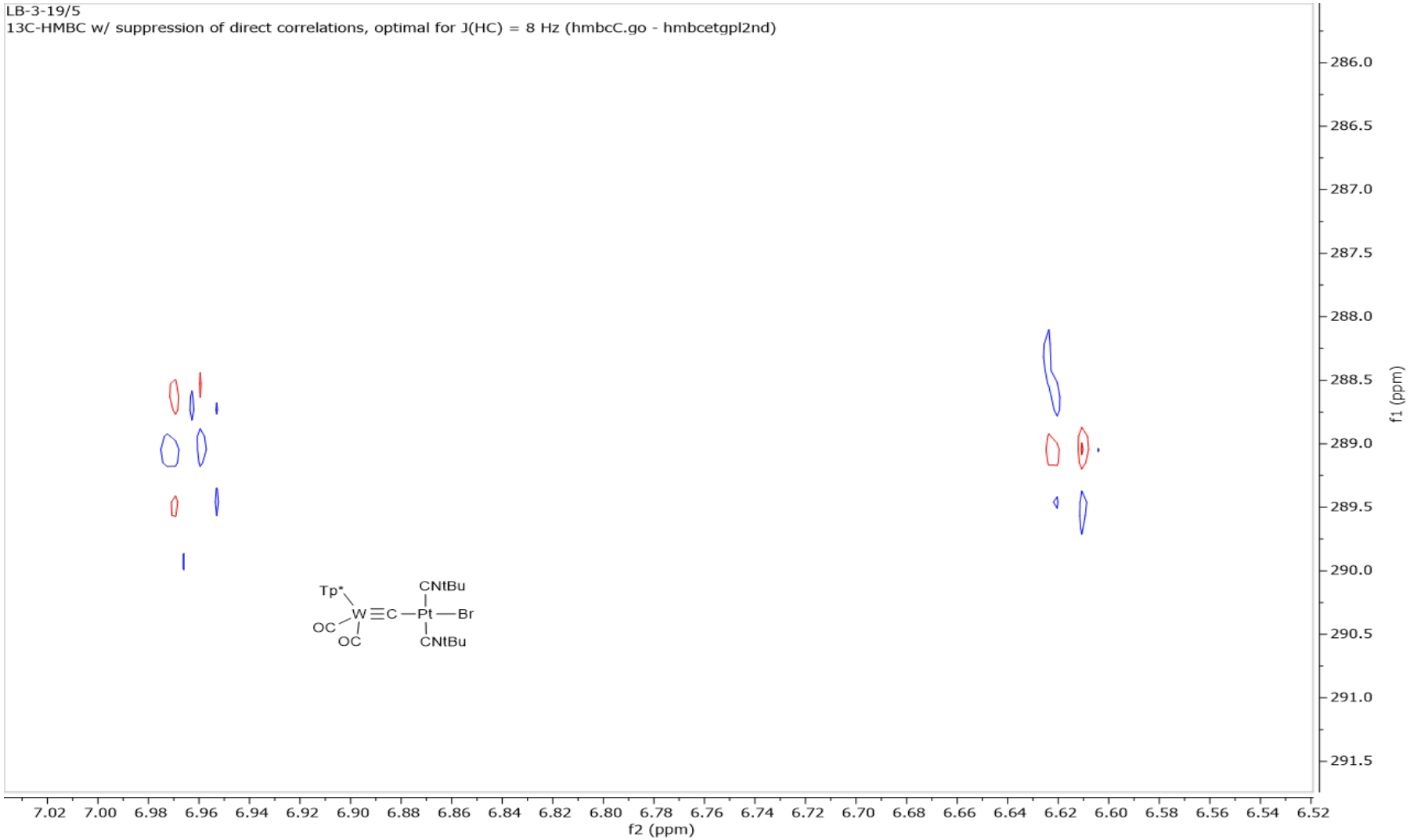


Figure S69: ^{13}C–^{1}H HMBC Spectrum of [WPt(μ_2-C)Br(CN^{t}Bu)$_2$(CO)$_2$(Tp*)] (**5c**) (151 MHz, 600 MHz, $CDCl_3$, 25 °C, δ)

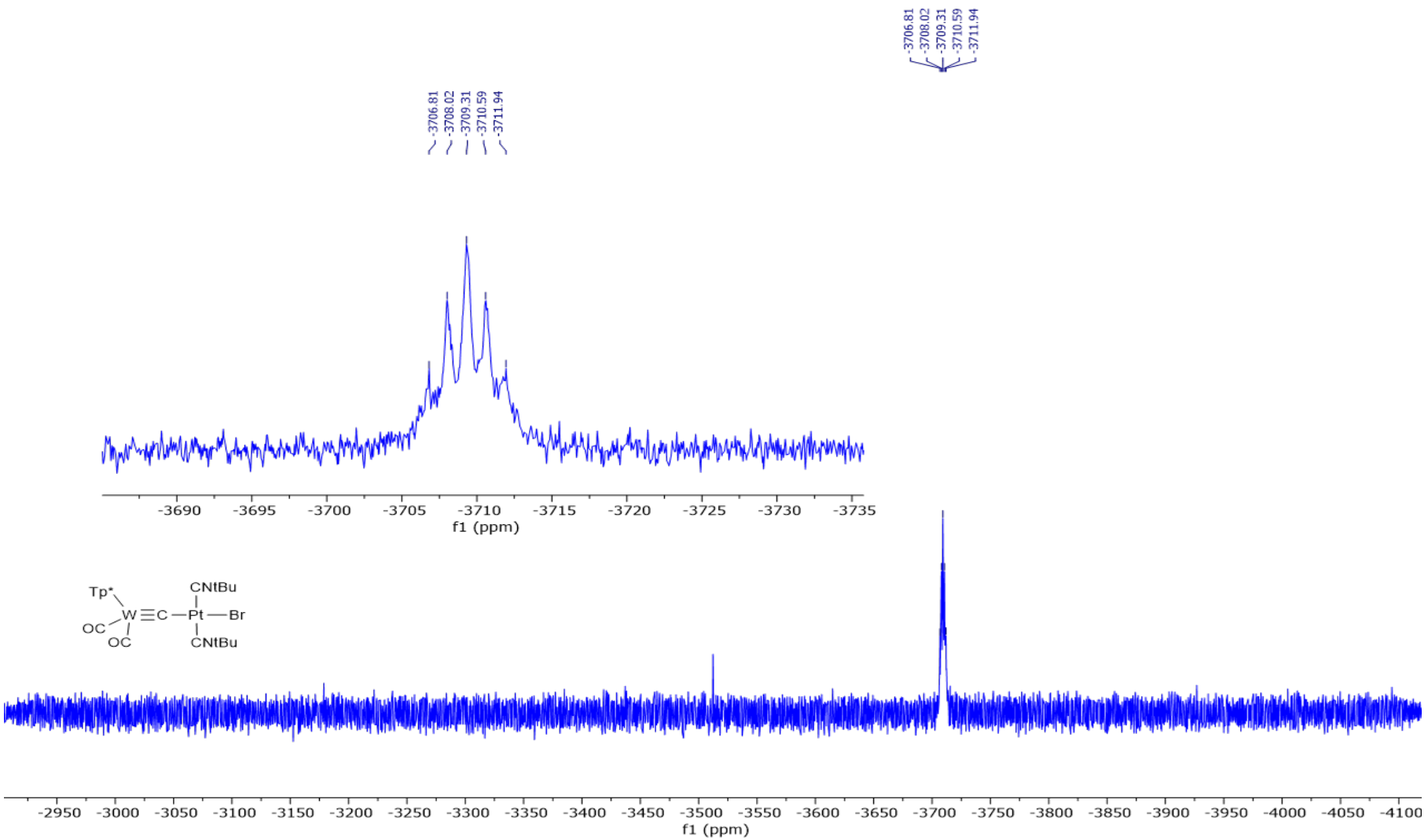


Figure S70: $^{195}Pt\{^{1}H\}$ NMR Spectrum of [WPt(μ_2-C)Br(CN^{t}Bu)$_2$(CO)$_2$(Tp*)] (**5c**) (86 MHz, $CDCl_3$, 25 °C, δ)

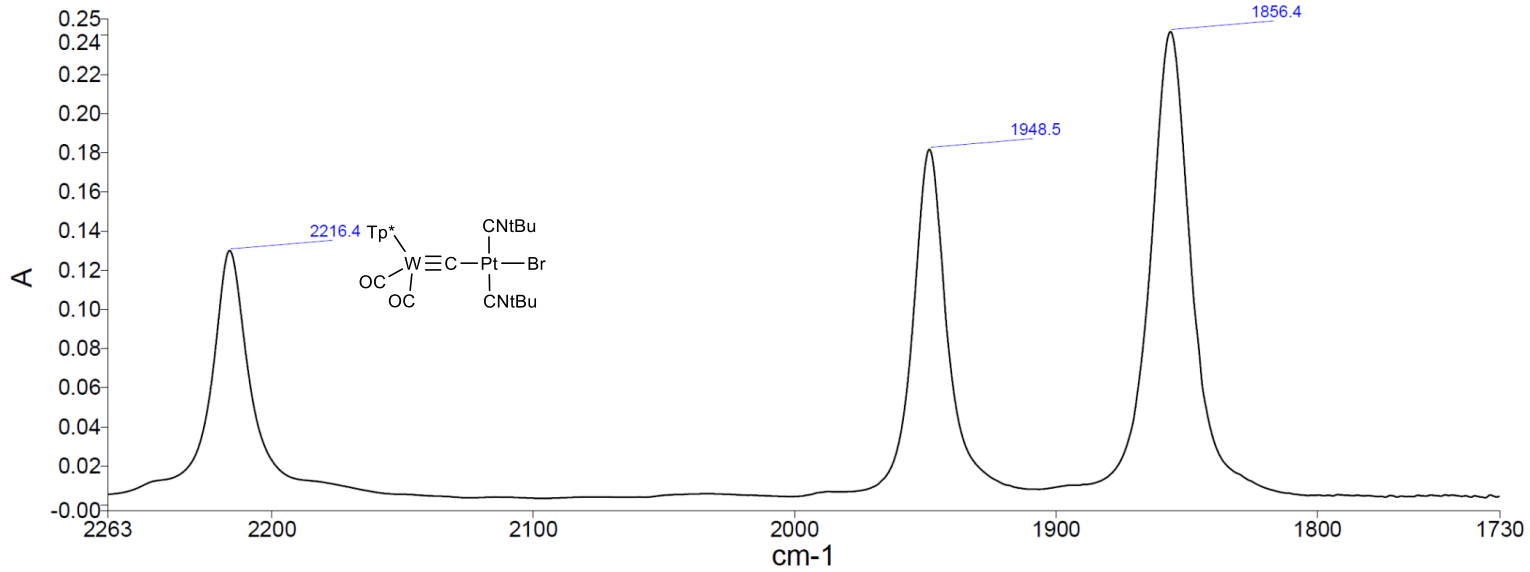


Figure S71: Infrared Spectrum of [WPt(μ_2-C)Br(CN^{t}Bu)$_2$(CO)$_2$(Tp*)] (**5c**) (CH_2Cl_2, 25 °C, ν)

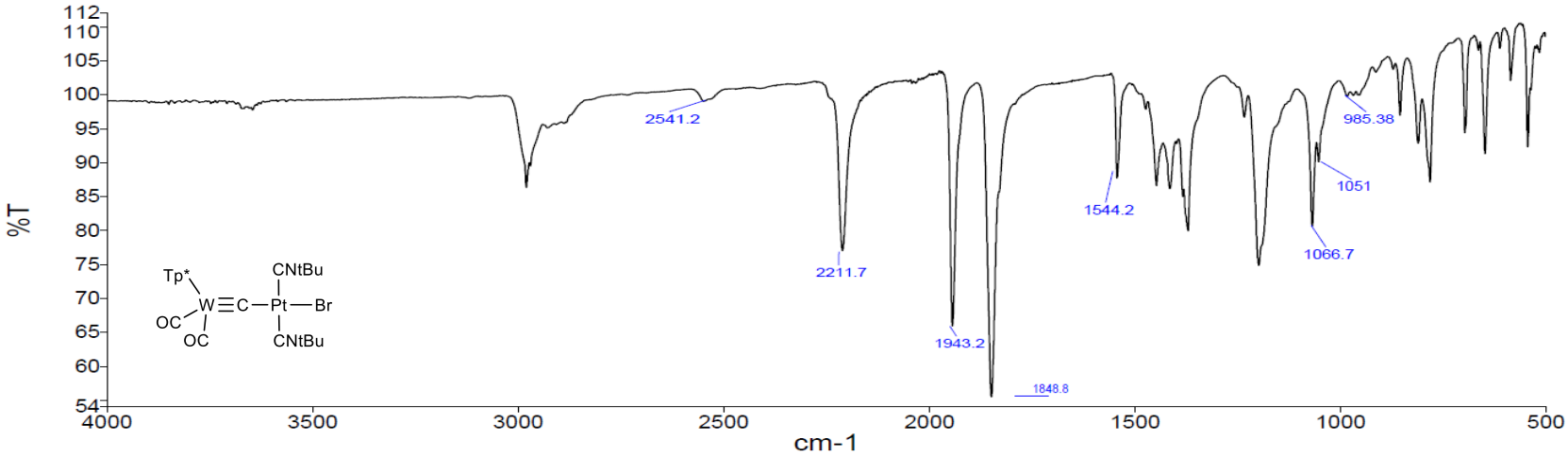


Figure S72: Infrared Spectrum of [WPt(μ_2-C)Br(CN^{t}Bu)$_2$(CO)$_2$(Tp*)] (**5c**) (ATR, 25 °C, ν)

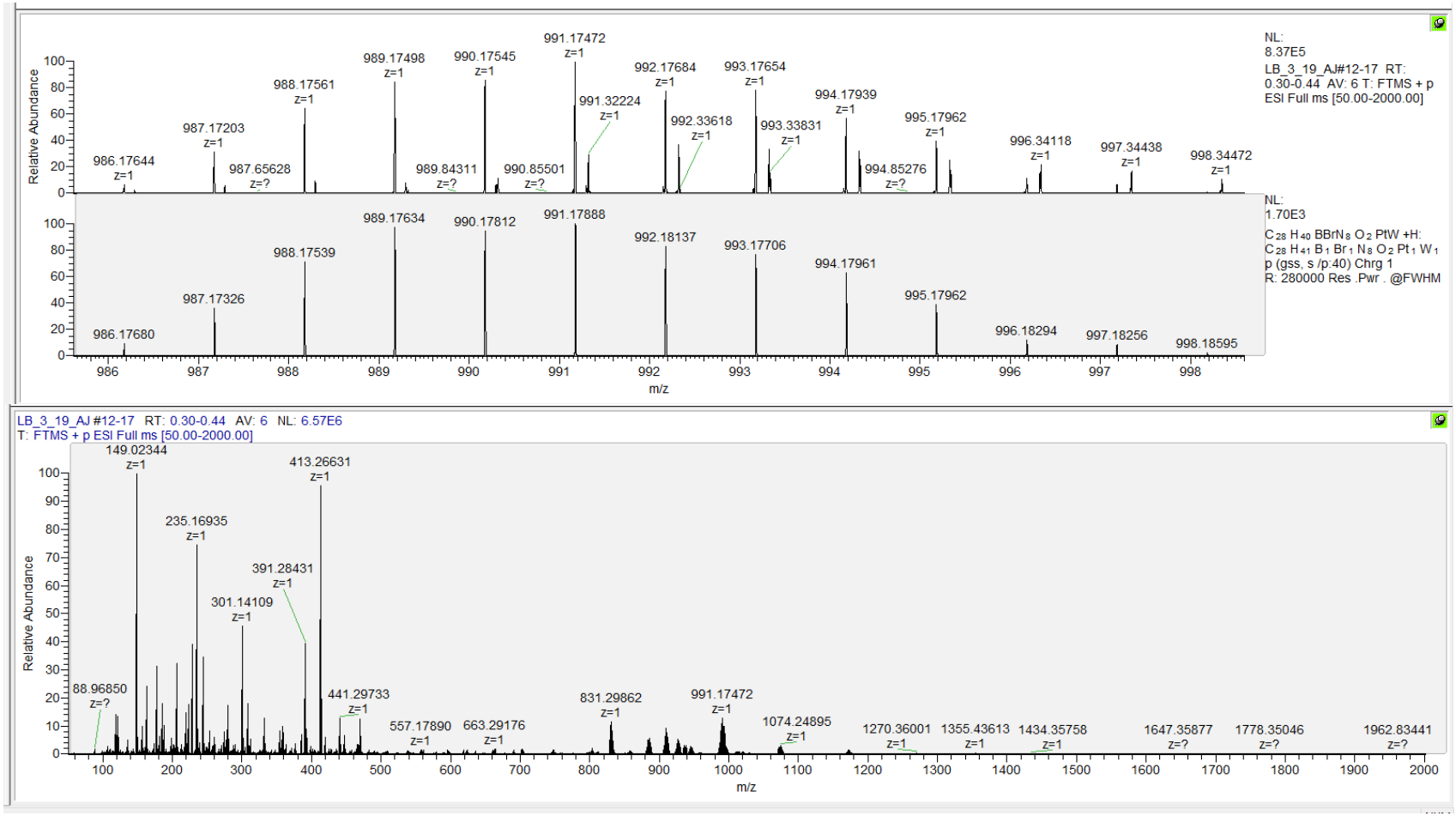


Figure S73: Mass Spectrum of [WPt(μ_2-C)Br(CN^{t}Bu)$_2$(CO)$_2$(Tp*)] (**5c**)

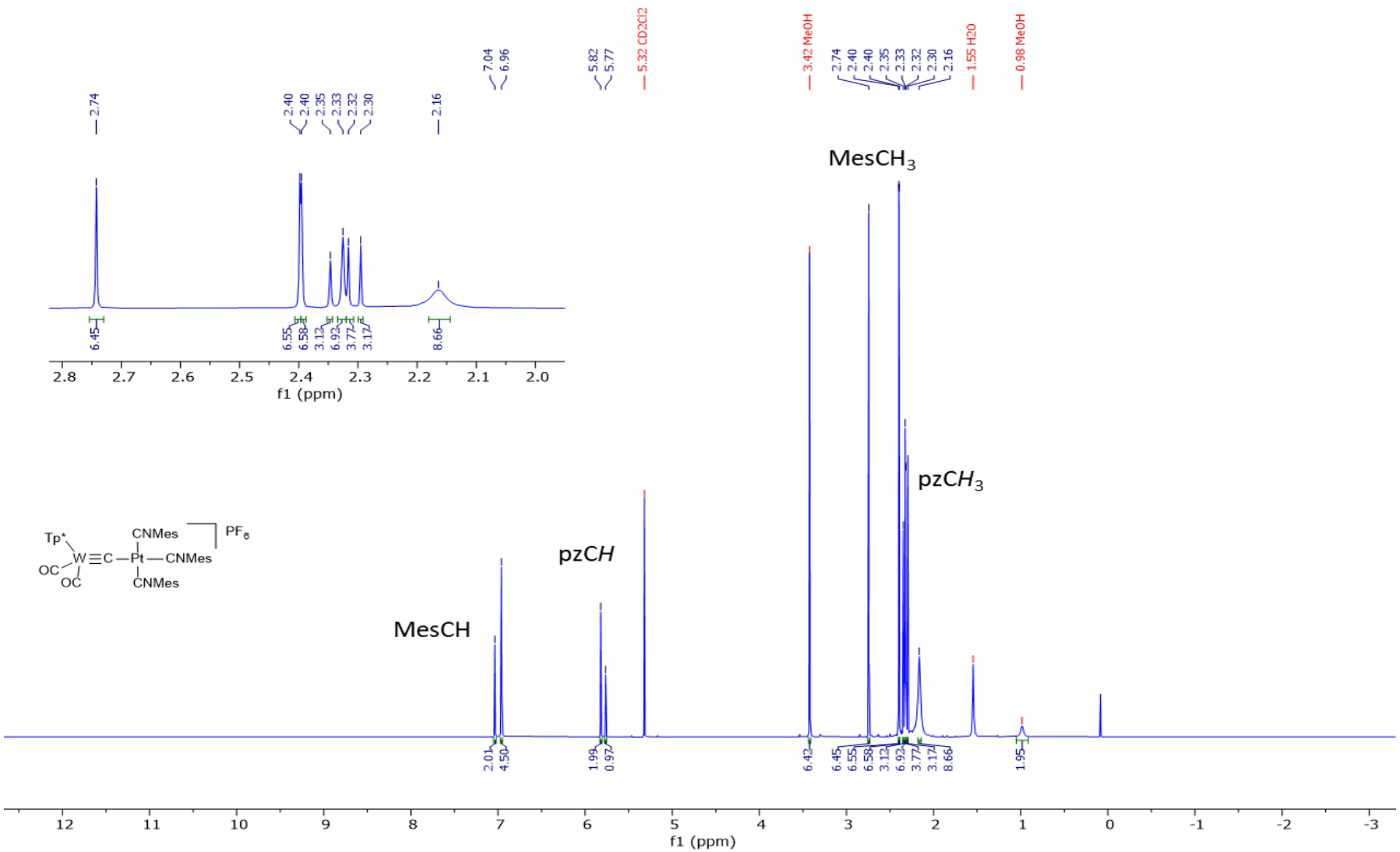


Figure S74: ^{1}H NMR Spectrum of [WPt(μ_2-C)($CNC_6H_2Me_3$-2,4,6)$_3$$(CO)_2$(Tp*)]$PF_6$ (**6**) (600 MHz, CD_2Cl_2, 25 °C, δ)

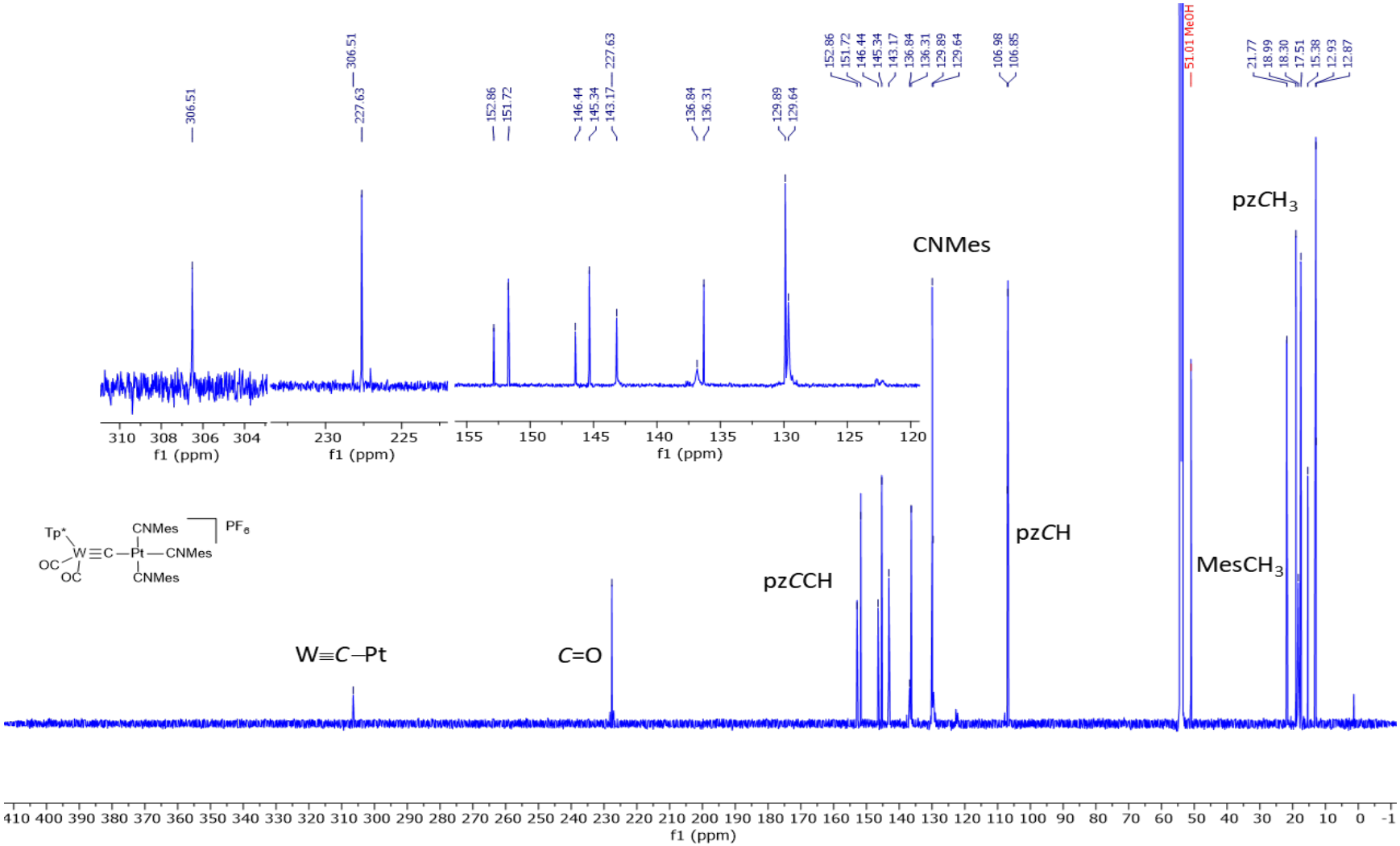


Figure S75: $^{13}C\{^{1}H\}$ NMR Spectrum of of $[WPt(\mu_2\text{-}C)(CNC_6H_2Me_3\text{-}2,4,6)_3(CO)_2(Tp^*)]PF_6$ (**6**) (151 MHz, CD_2Cl_2, 25 °C, δ)

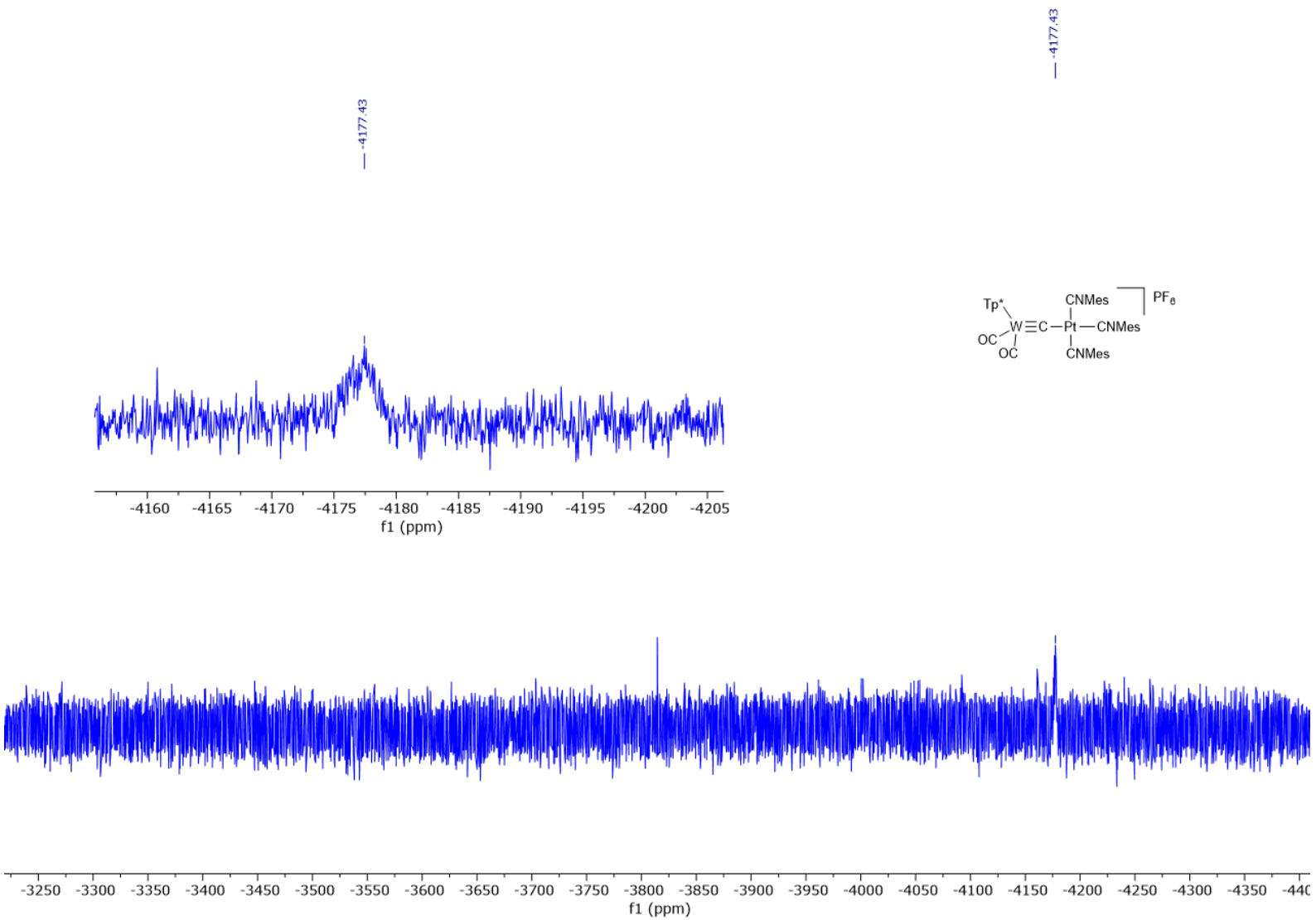


Figure S76: $^{195}Pt\{^{1}H\}$ NMR Spectrum of of $[WPt(\mu_2\text{-}C)(CNC_6H_2Me_3\text{-}2,4,6)_3(CO)_2(Tp^*)]PF_6$ (**6**) (150 MHz, CD_2Cl_2, 25 °C, δ)

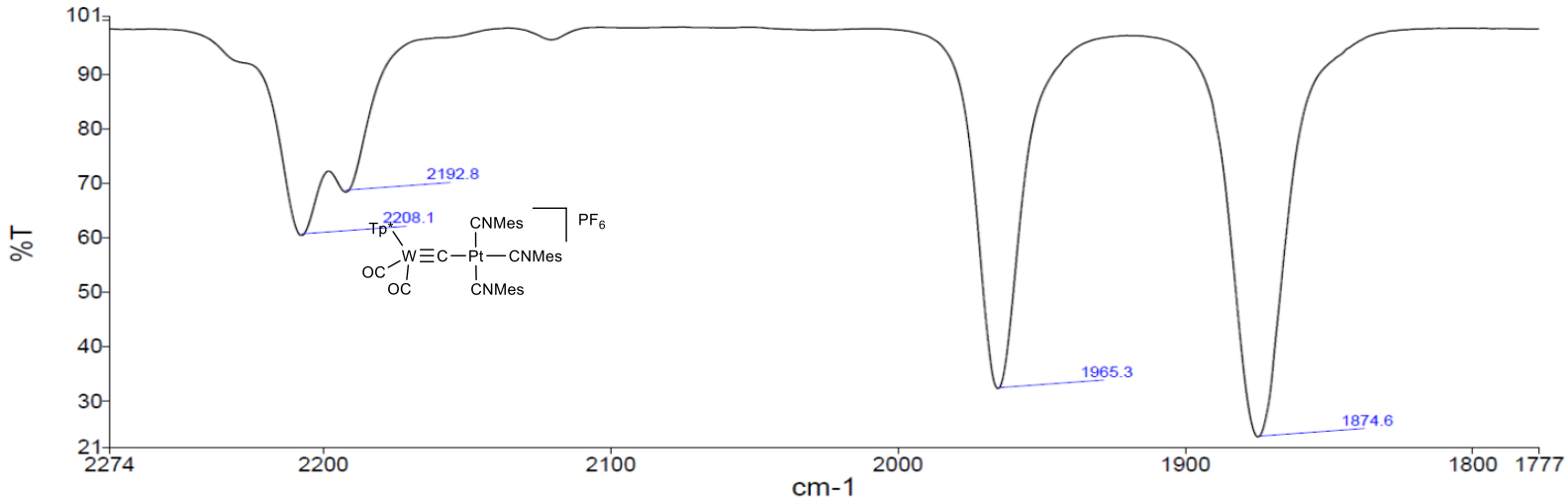


Figure S77: Infrared Spectrum of of [WPt(μ_2-C)($CNC_6H_2Me_3$-2,4,6)$_3$$(CO)_2$(Tp*)]$PF_6$ (**6**) (CH_2Cl_2, 25 °C, ν)

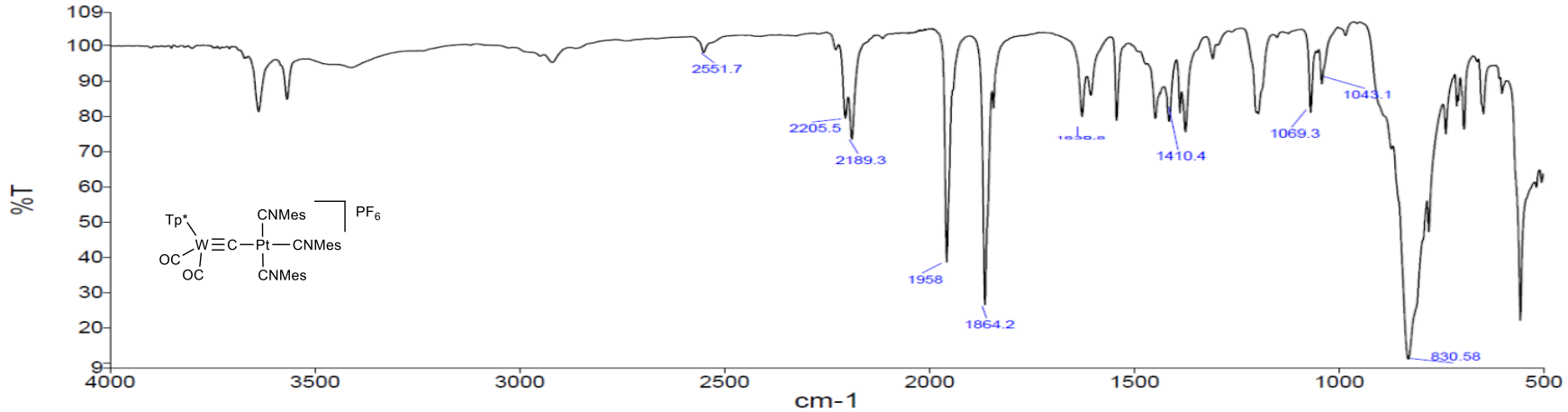
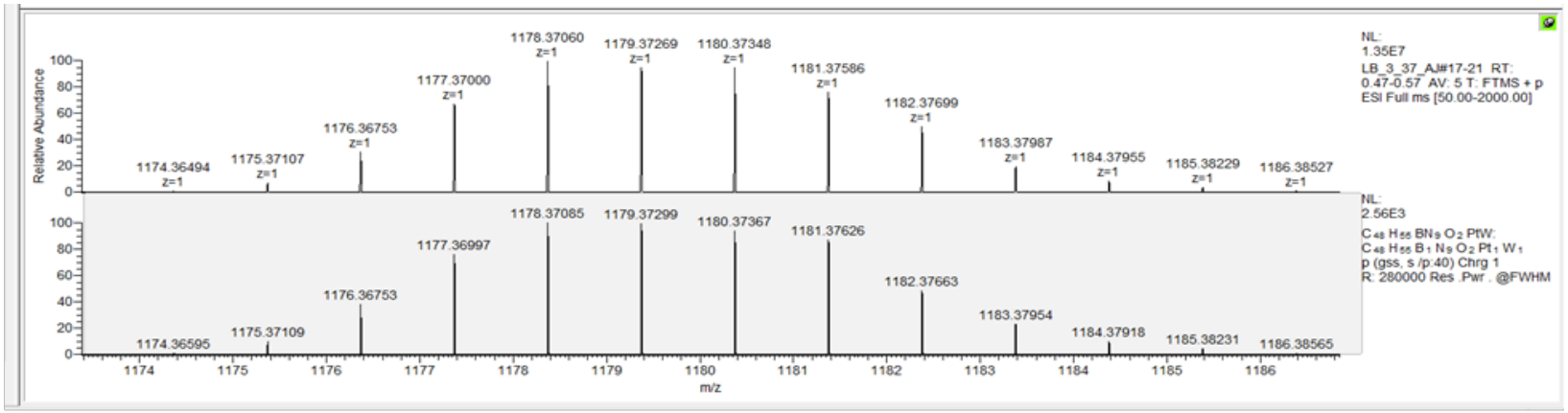


Figure S78: Infrared Spectrum of of [WPt(μ_2-C)($CNC_6H_2Me_3$-2,4,6)$_3$$(CO)_2$(Tp*)]$PF_6$ (**6**) (ATR, 25 °C, ν)



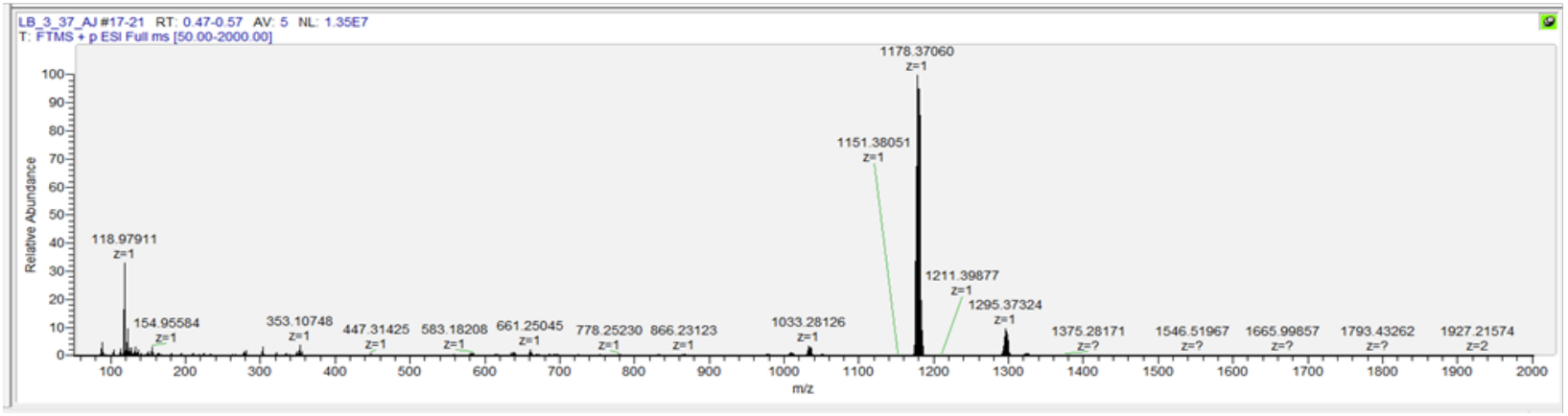


Figure S79: Mass Spectrum of of [WPt(μ_2-C)($CNC_6H_2Me_3$-2,4,6)$_3$$(CO)_2$(Tp*)]$PF_6$ (**6**)

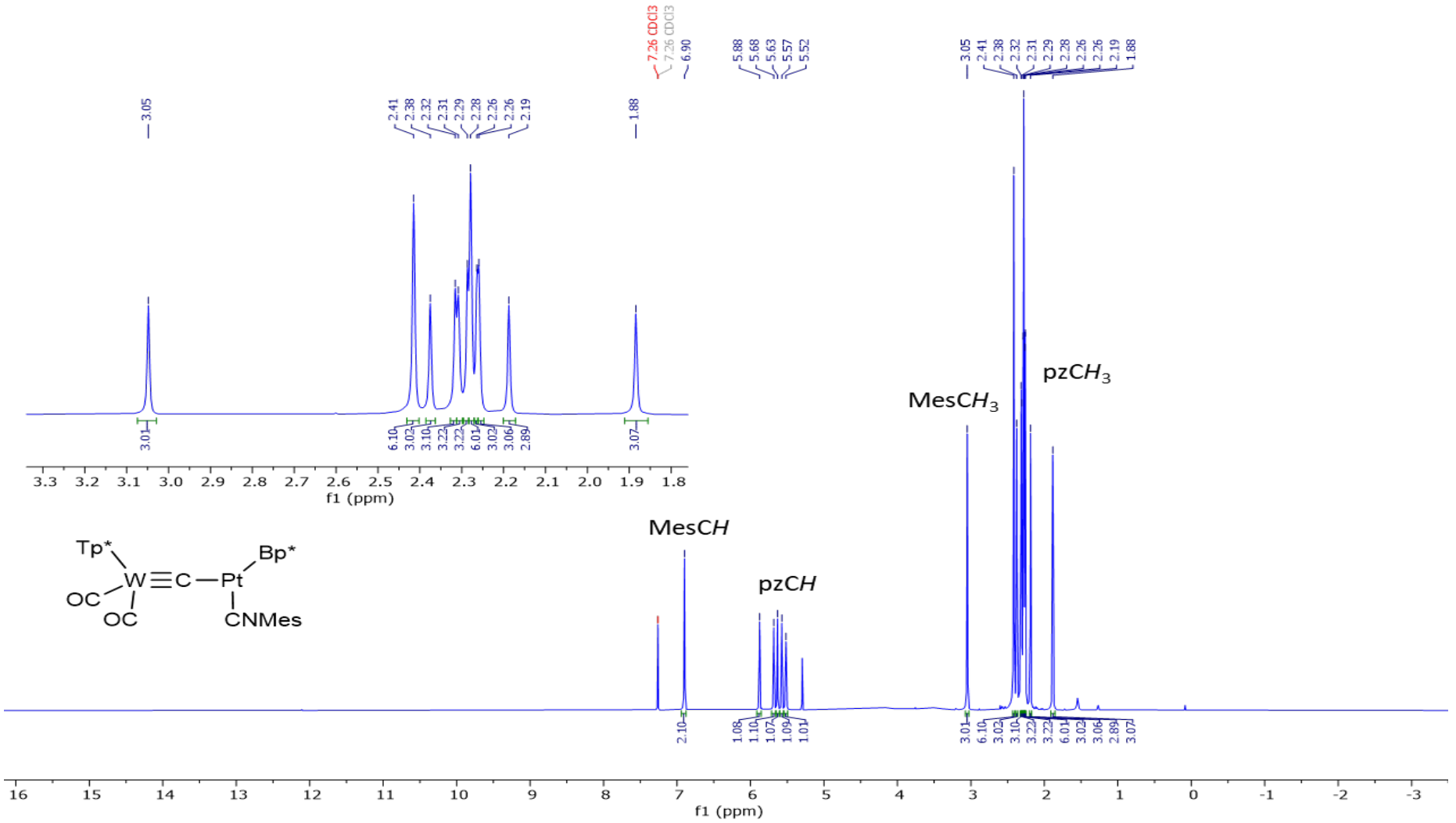


Figure S80: ^{1}H NMR Spectrum of [WPt(μ_2-C)($CNC_6H_2Me_3$-2,4,6)$(CO)_2$(Bp*)(Tp*)] (**8a**) (400 MHz, $CDCl_3$, 25 °C, δ)

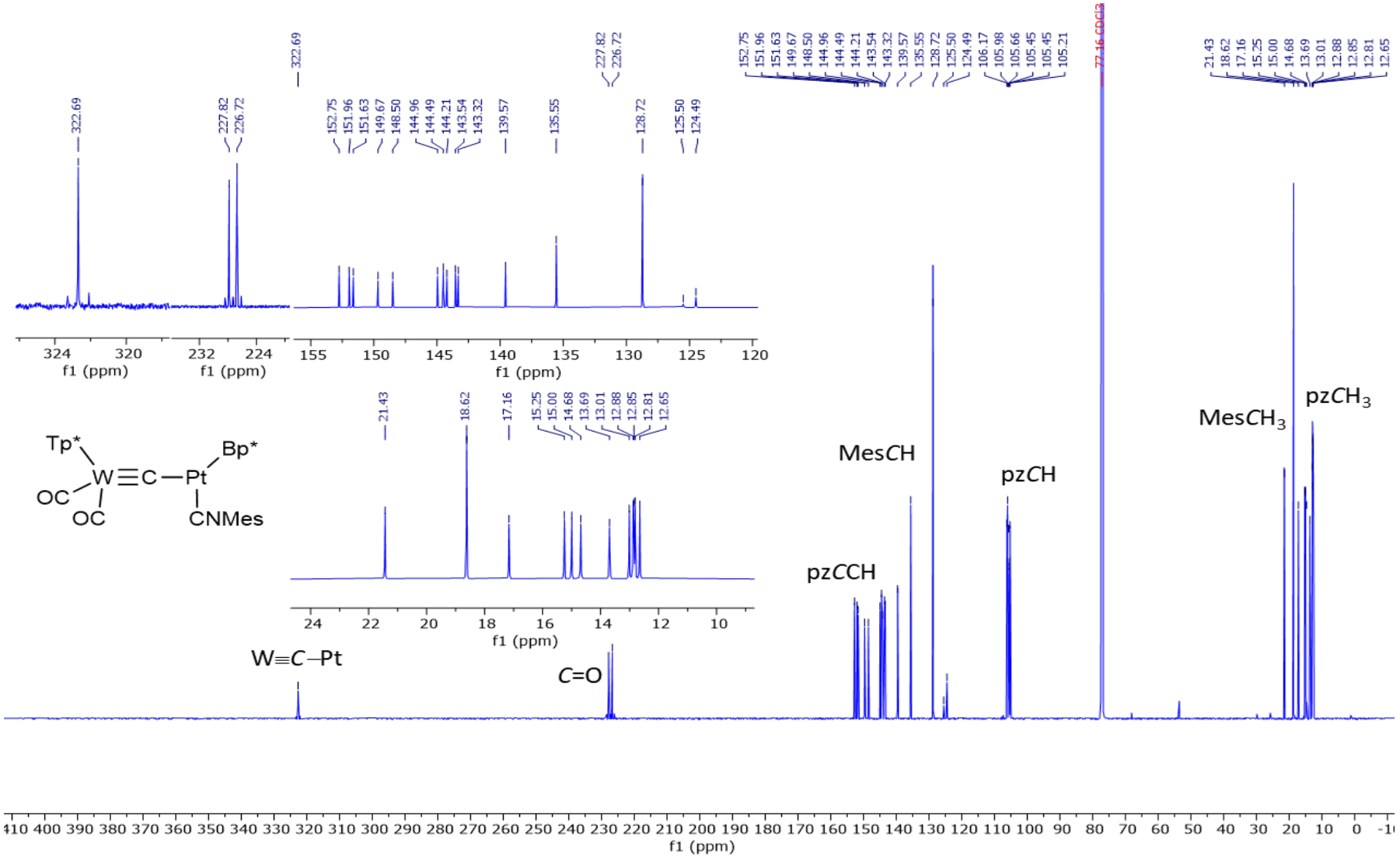


Figure S81: $^{13}C\{^{1}H\}$ NMR Spectrum of [WPt(μ_2-C)($CNC_6H_2Me_3$-2,4,6)$(CO)_2$(Bp*)(Tp*)] (**8a**) (151 MHz, $CDCl_3$, 25 °C, δ)

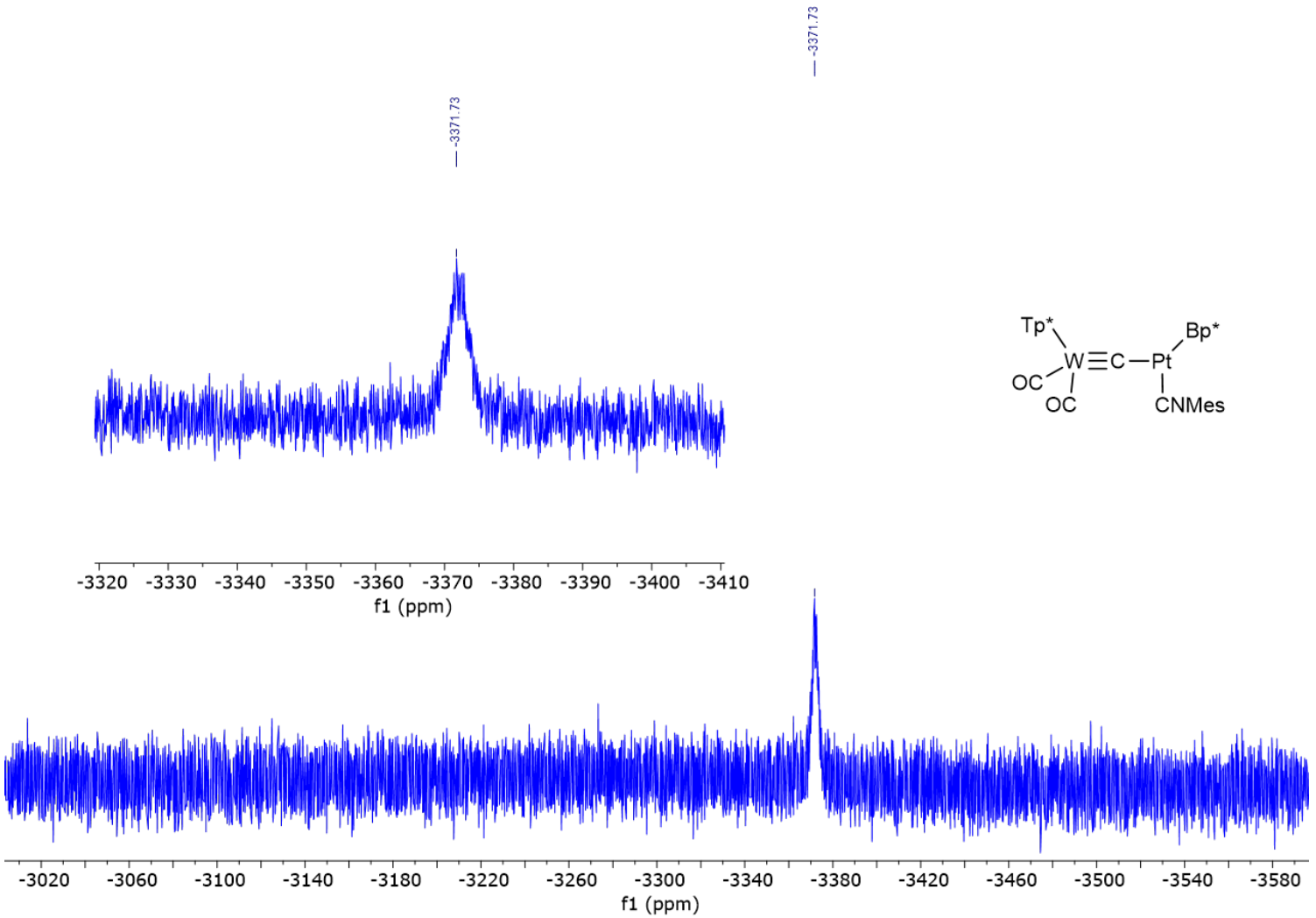


Figure S82: $^{195}Pt\{^{1}H\}$ NMR Spectrum of [WPt(μ_2-C)($CNC_6H_2Me_3$-2,4,6)$(CO)_2$(Bp*)(Tp*)] (**8a**) (150 MHz, $CDCl_3$, 25 °C, δ)

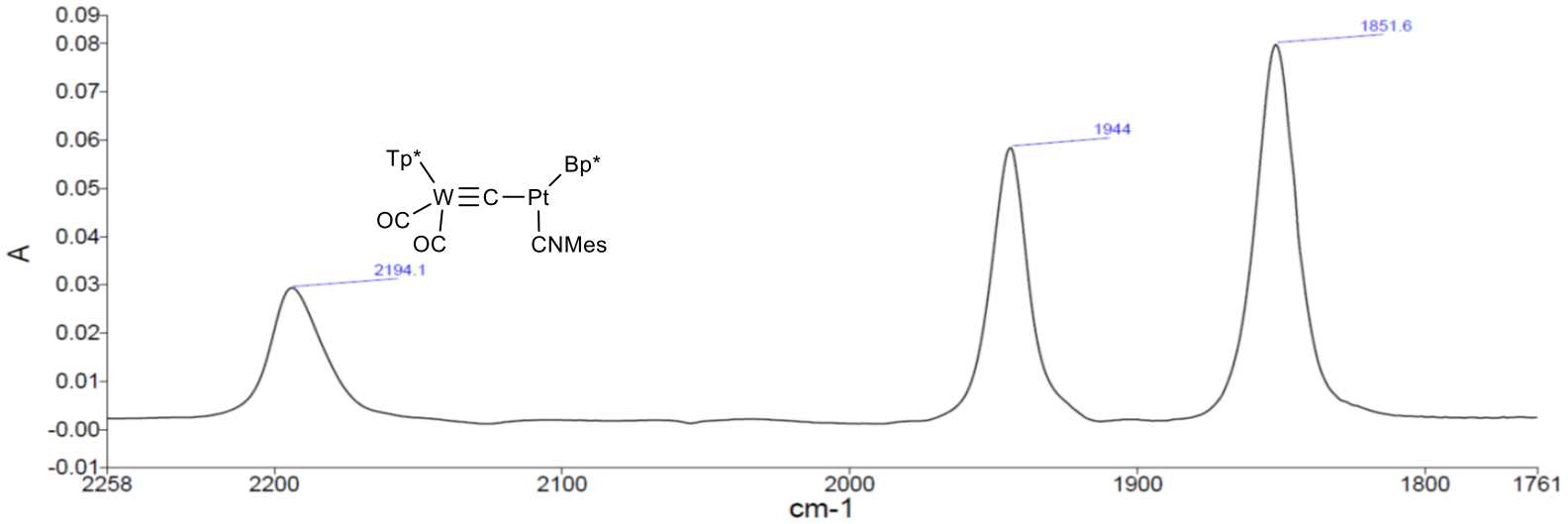


Figure S83: Infrared Spectrum of [WPt(μ_2-C)($CNC_6H_2Me_3$-2,4,6)$(CO)_2$(Bp*)(Tp*)] (**8a**) (CH_2Cl_2, 25 °C, ν)

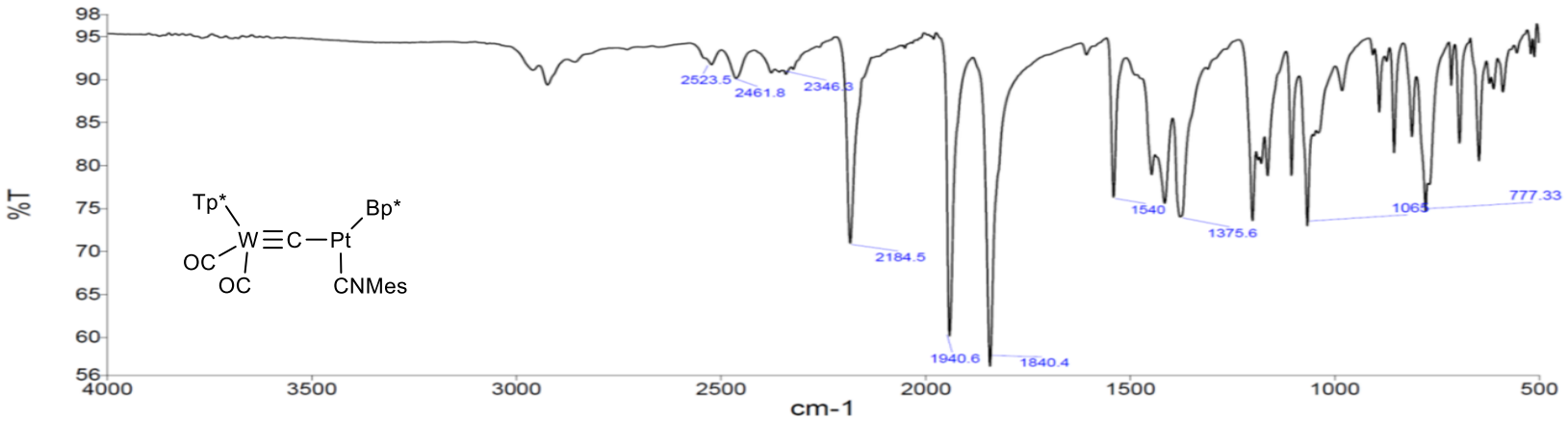


Figure S84: Infrared Spectrum of [WPt(μ_2-C)($CNC_6H_2Me_3$-2,4,6)$(CO)_2$(Bp*)(Tp*)] (**8a**) (ATR, 25 °C, ν)

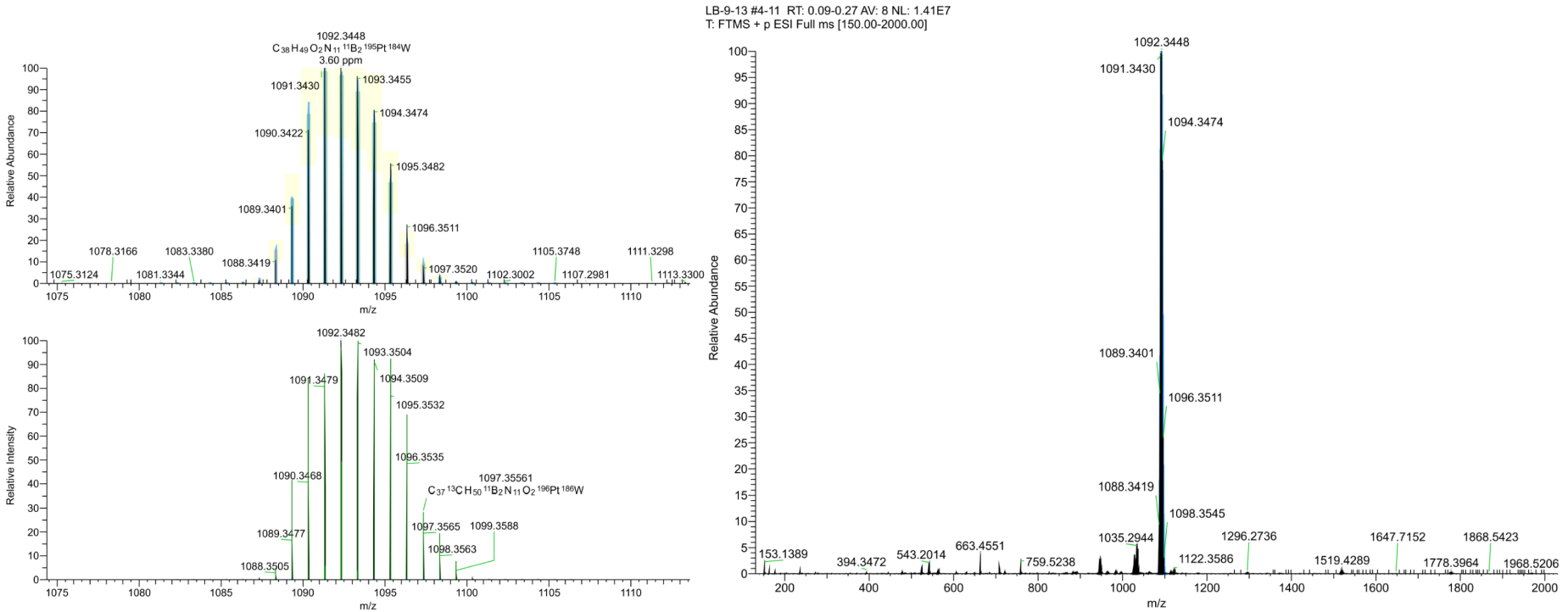


Figure S85: Mass Spectrum of of [WPt(μ_2-C)($CNC_6H_2Me_3$-2,4,6)$(CO)_2$(Bp*)(Tp*)] (**8a**)

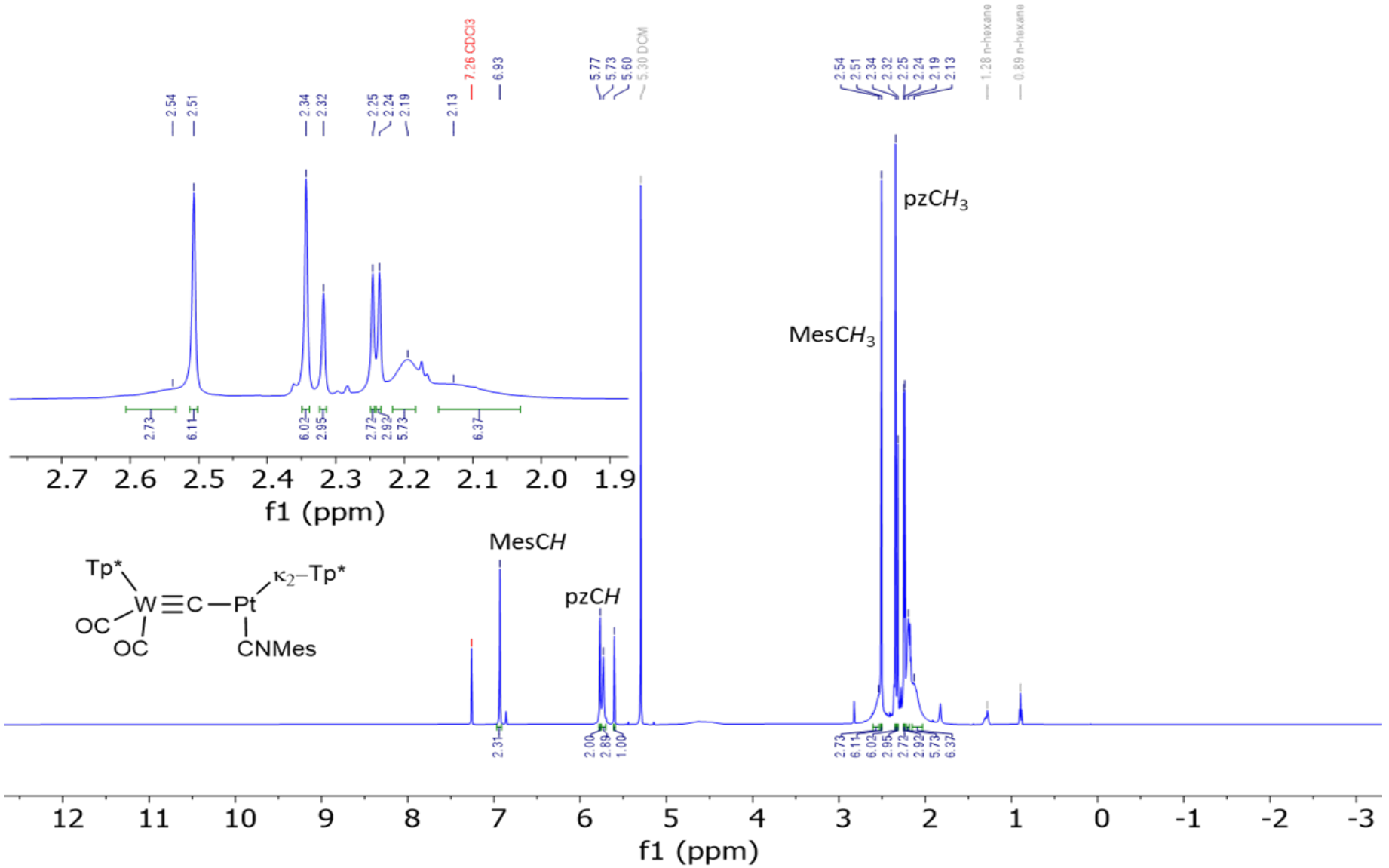


Figure S86: ^{1}H NMR Spectrum of [WPt(μ_2-C)($CNC_6H_2Me_3$-2,3,6)$(CO)_2(Tp^*)_2$] (**8b**) (600 MHz, $CDCl_3$, 25 °C, δ)

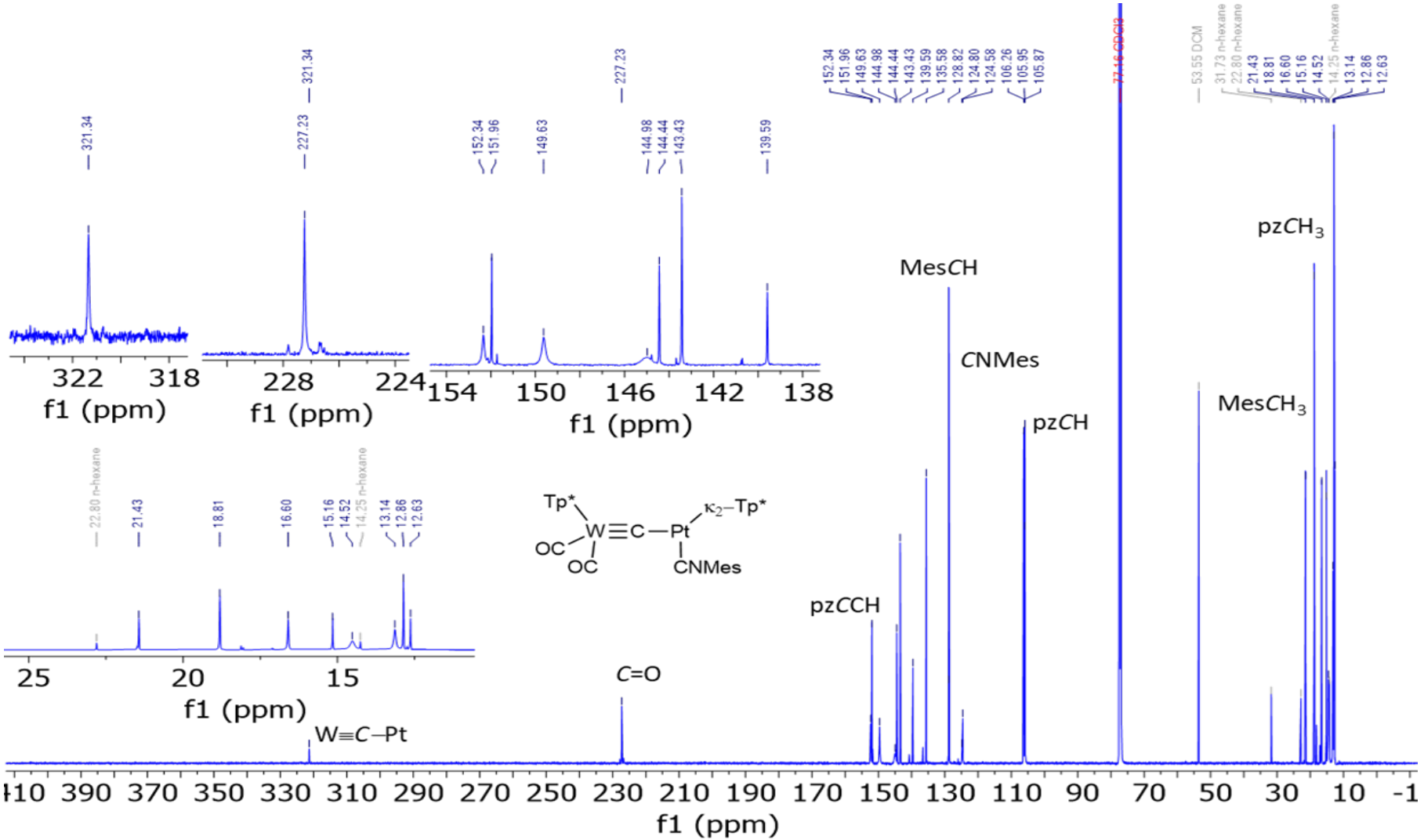


Figure S87: $^{13}C\{^{1}H\}$ NMR Spectrum of [WPt(μ_2-C)($CNC_6H_2Me_3$-2,3,6)$(CO)_2(Tp^*)_2$] (**8b**) (151 MHz, $CDCl_3$, 25 °C, δ)

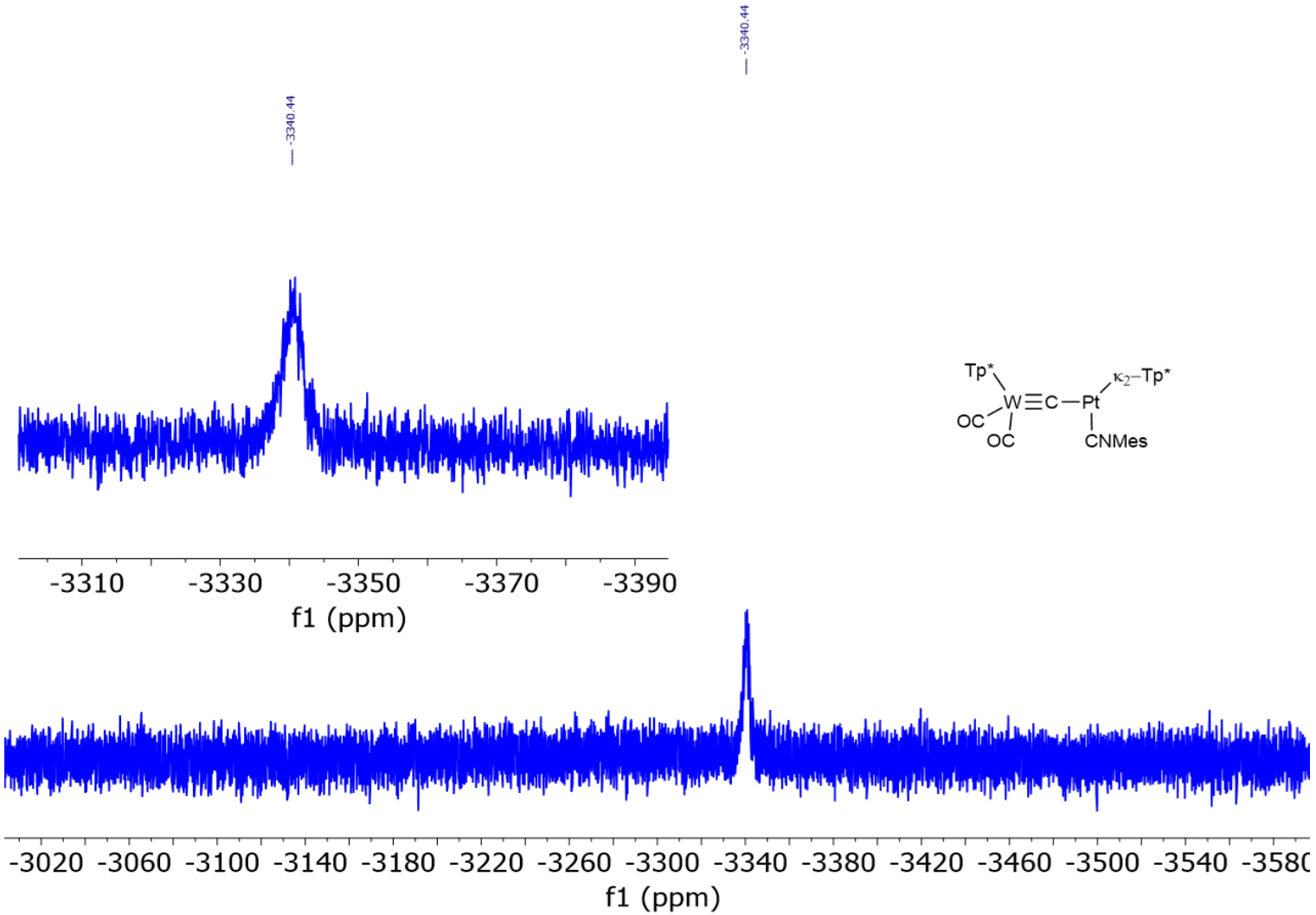


Figure S88: $^{195}Pt\{^{1}H\}$ NMR Spectrum of $[WPt(\mu_2\text{-}C)(CNC_6H_2Me_3\text{-}2,3,6)(CO)_2(Tp^*)_2]$ (**8b**) (150 MHz, $CDCl_3$, 25 °C, δ)

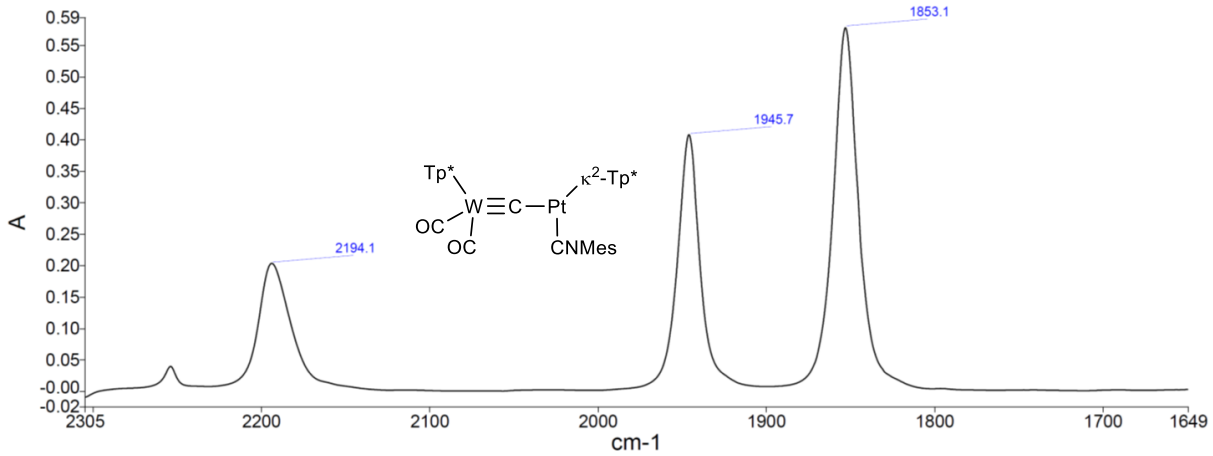


Figure S89: Infrared Spectrum of [WPt(μ_2-C)($CNC_6H_2Me_3$-2,3,6)$(CO)_2(Tp^*)_2$] (**8b**) (CH_2Cl_2, 25 °C, ν)

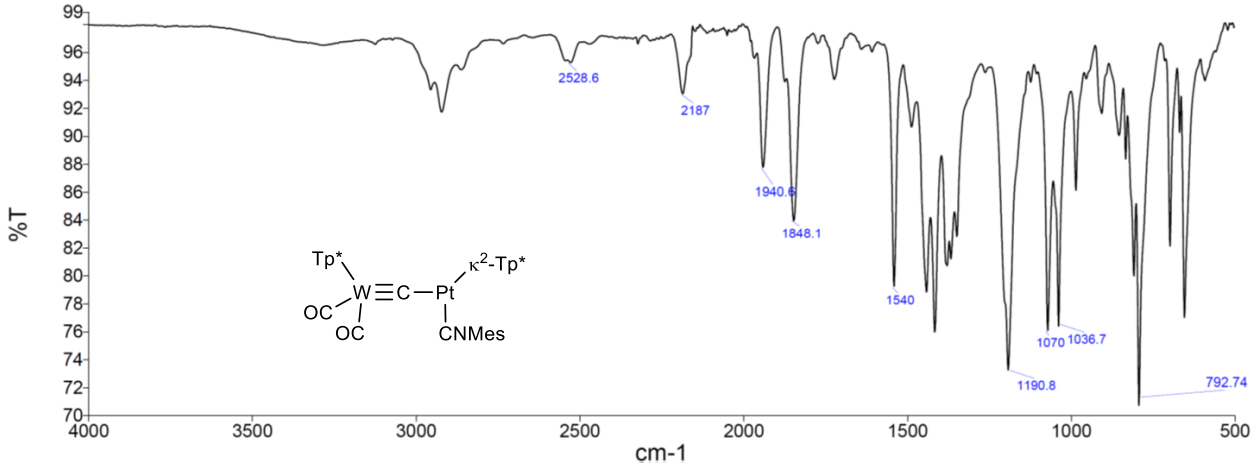


Figure S90: Infrared Spectrum of [WPt(μ_2-C)($CNC_6H_2Me_3$-2,3,6)$(CO)_2(Tp^*)_2$] (**8b**) (ATR, 25 °C, ν)

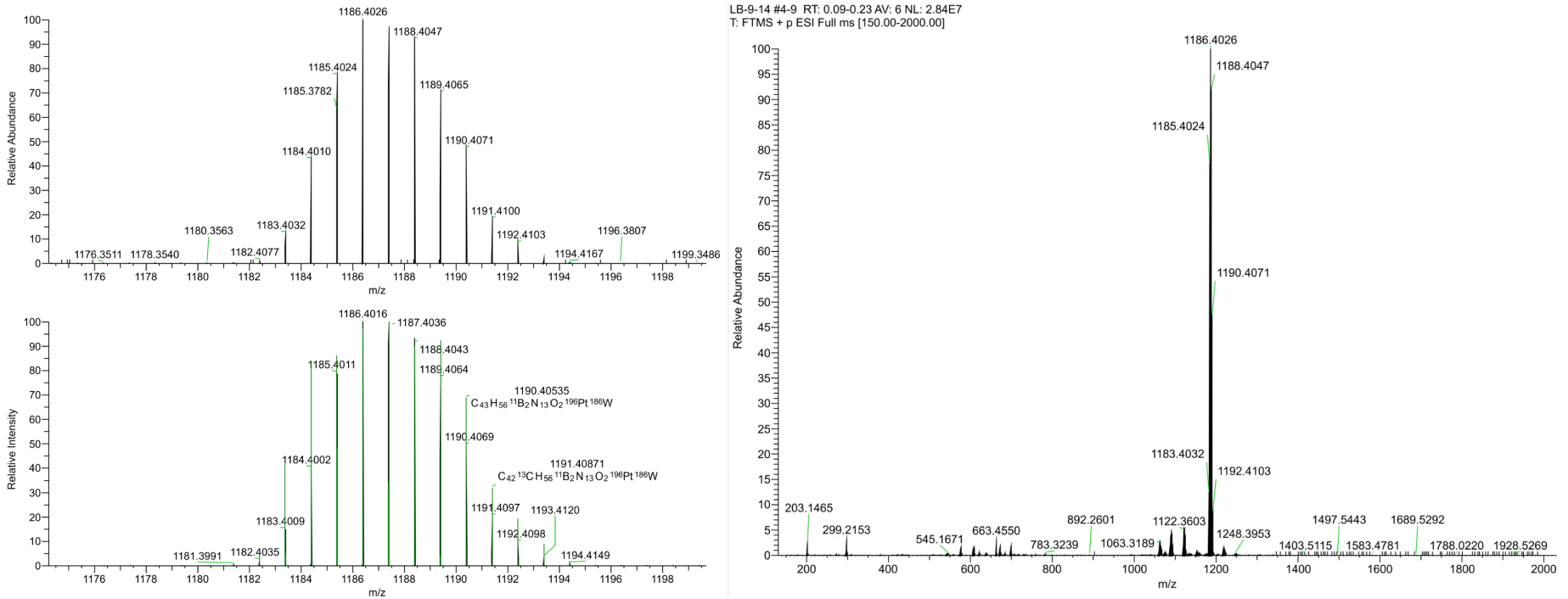


Figure S91: Mass Spectrum of [WPt(μ_2-C)($CNC_6H_2Me_3$-2,3,6)$(CO)_2(Tp^*)_2$] (**8b**)