SUPPORTING INFORMATION

for

A green route to platinum *N*-heterocyclic carbene complexes: mechanism and expanded scope

Benon P. Maliszewski,[a,d] Ida Ritacco,[b] Marek Beliš,[a] Ishfaq Ibni Hashim,[a] Nikolaos V. Tzouras,[a] Lucia Caporaso,[b] Luigi Cavallo,[c] Kristof Van Hecke,[a] Fady Nahra,[*a,d] Catherine S. J. Cazin[*a] and Steven P. Nolan[*a]

[a.] *Department of Chemistry and Centre for Sustainable Chemistry, Ghent University, Krijgslaan 281 (S3), 9000 Ghent, Belgium. E-mail: steven.nolan@ugent.be*
[b.] *Dipartimento di Chimica e Biologia, Univeristy of Salerno, Via Papa Paolo Giovanni II, Fisciano, I-84084, Italy*
[c.] *KAUST Catalysis Center, Physical Sciences and Engineering Division, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia*
[d.] *VITO (Flemish Institute for Technological Research), Separation and Conversion Technology, Boeretang 200, 2400 Mol, Belgium*

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1. Computational details

1.1 General information

Values reported in the manuscript and in Figure S1 are ΔG (kcal mol^{-1}) computed in acetone as solvent. Geometries were optimized with Gaussian09 package at the PBE0-D3/TZVP-SDD level of theory. The standard triple-valence basis set with a polarization function of Ahlrichs *et al.* (TZVP) was used for H, C, N, S, O and Cl atoms while the SDD core potential was used for Pt. The reported free energies have been obtained adding thermal correction in gas-phase to the electronic energy in solvent (SMD model) calculated *via* single point energy calculations in acetone with the triple-z basis set of Ahlrichs (TZVP) for main group atoms and the SDD pseudopotential for the metal. The structure of intermediates and TS are represented in balls and sticks and C, H, O, Cl, S, N and Pt are depicted in gray, white, red, green, yellow, blue and pink, respectively.

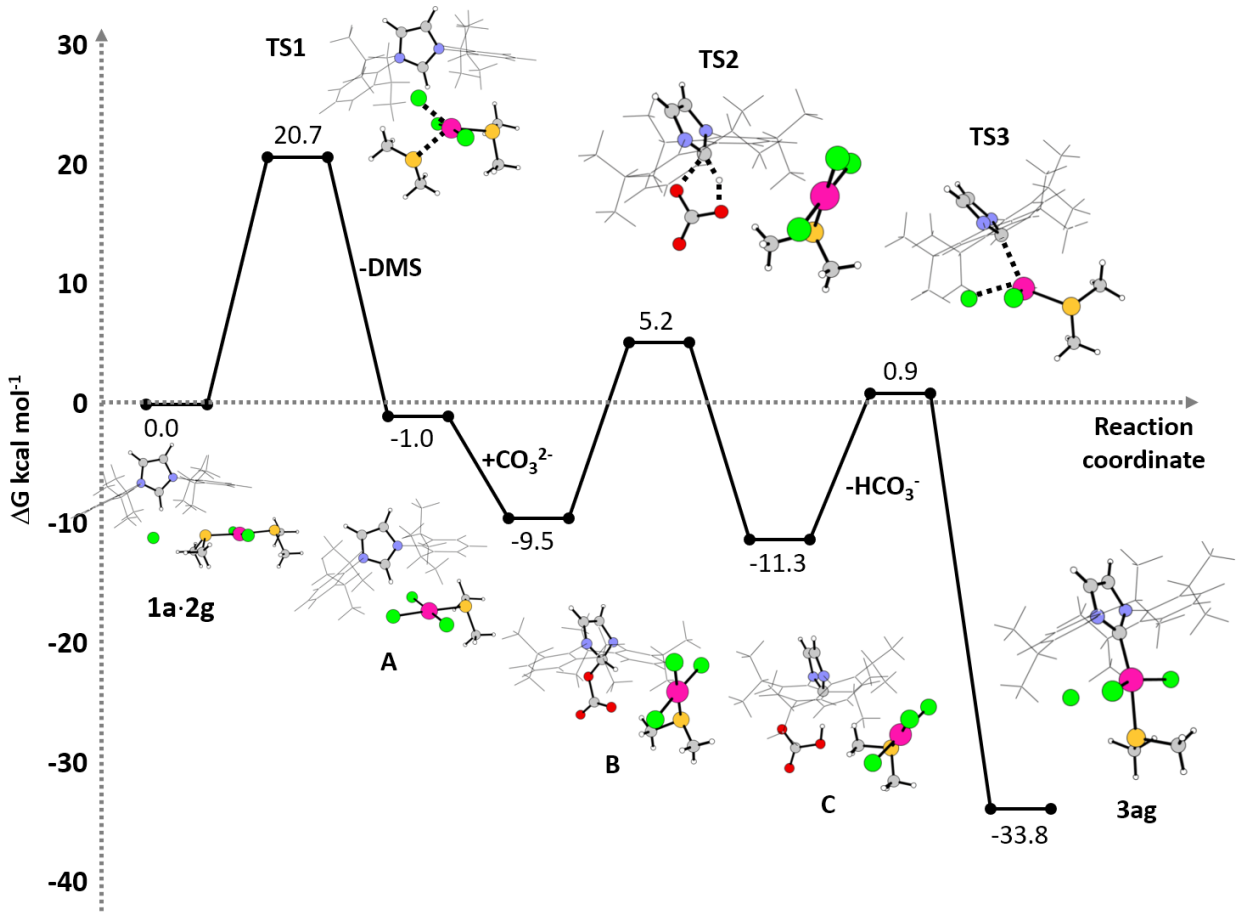


Figure S1. Computed reaction pathway.

1.2. Coordinates xyz of the intermediates and transition states (TS) involved in the reaction mechanism

PBE0-D3/SVP/SDD//PBE0-D3/TZVP/SDD

1a·2g:

Pt	3.278090	-3.175472	1.191978
C	0.123038	1.938722	-3.278812
H	-1.754572	2.788424	-4.107633
H	0.950570	2.136170	-3.937981
N	-1.791742	1.753524	-2.225870
N	0.290992	1.243534	-2.099214
C	-0.879780	1.142215	-1.471349
C	-3.187064	1.879041	-1.901506
C	-4.043391	0.835919	-2.252689
C	-3.604494	3.035846	-1.241864
C	-5.392085	1.001462	-1.954760
C	-4.962789	3.150485	-0.968409
C	-5.847447	2.148007	-1.328116
H	-6.091431	0.211901	-2.203562
H	-5.329353	4.028229	-0.449551
H	-6.902191	2.254190	-1.100420
C	1.536287	0.723577	-1.602244
C	2.215886	1.459055	-0.633530
C	1.983160	-0.501515	-2.108831
C	3.406835	0.917316	-0.154975
C	3.186769	-0.983125	-1.612862
C	3.887015	-0.284286	-0.641005
H	3.959957	1.437514	0.618240
H	3.559676	-1.941634	-1.948481
H	4.800794	-0.699399	-0.233566
C	1.697947	2.771439	-0.089371
H	0.847629	3.085158	-0.701702
C	1.144426	-1.297631	-3.084806
H	0.617289	-0.588037	-3.731640
C	-3.545666	-0.458134	-2.853600
H	-2.494442	-0.329620	-3.125173
C	-2.627076	4.077607	-0.748947
H	-1.665107	3.903653	-1.239306
Cl	-1.803207	0.040085	1.294814
H	-1.091741	0.668803	-0.482596
C	-1.190779	2.256578	-3.361064
S	1.340888	-1.894932	1.225974
S	5.296854	-4.345389	1.114156
Cl	2.258401	-4.538187	-0.420452
Cl	4.376431	-1.838227	2.770958
C	1.311267	-0.876737	2.716927
H	2.115878	-0.152113	2.630966
H	0.333908	-0.389156	2.715799
H	1.471410	-1.493169	3.599199
C	-0.019886	-3.016952	1.629176
H	-0.920624	-2.399261	1.647729
H	-0.062074	-3.762628	0.838866
H	0.166518	-3.496209	2.589080
C	5.131969	-5.822763	0.084086
H	5.000262	-5.492010	-0.943580
H	6.051357	-6.400977	0.181160
H	4.259429	-6.401366	0.379562
C	5.394487	-5.134560	2.742668
H	6.320795	-5.706668	2.801244
H	5.397893	-4.326998	3.472073
H	4.528346	-5.776124	2.897503
C	-3.057065	5.498721	-1.095764
H	-3.981258	5.775224	-0.582812
H	-2.288046	6.209171	-0.783031
H	-3.219354	5.620745	-2.169544
C	-2.416724	3.904525	0.756547
H	-1.643758	4.591000	1.112813
H	-3.340475	4.127493	1.297424
H	-2.127780	2.880978	1.010211
C	2.748743	3.874262	-0.184339
H	3.606906	3.664248	0.458359
H	3.116715	3.991388	-1.206508
H	2.322865	4.827385	0.138799
C	1.195080	2.602147	1.343131
H	0.403464	1.851137	1.409247
H	2.012342	2.297360	2.002408
H	0.798942	3.548738	1.719537
C	0.094090	-2.121093	-2.334586
H	-0.501089	-1.517338	-1.647107
H	-0.584072	-2.602725	-3.044570
H	0.585494	-2.900374	-1.748616
C	1.972359	-2.205169	-3.985396
H	2.770488	-1.657846	-4.492717
H	2.418698	-3.023236	-3.415352
H	1.329667	-2.655065	-4.745731
C	-3.618976	-1.570676	-1.806497
H	-3.095058	-1.291730	-0.888017
H	-4.659730	-1.780482	-1.544427
H	-3.178285	-2.490637	-2.198984
C	-4.298015	-0.832295	-4.126422
H	-4.240683	-0.038982	-4.875889

H	-3.874655	-1.742421	-4.558246
H	-5.354076	-1.027220	-3.924755

E(solv)= -3615.09487 A.U
Thermal correction= 0.657324

TS1:

Pt	-0.184443	-2.108935	4.177025
C	-0.482218	1.267870	-0.562755
H	-2.461330	2.238099	-0.776640
H	0.236027	1.744966	-1.205495
N	-2.234365	0.576986	0.571134
N	-0.137117	0.197922	0.243252
C	-1.207974	-0.193734	0.928646
C	-3.569868	0.426594	1.077930
C	-4.278878	-0.730130	0.725448
C	-4.087164	1.421744	1.909108
C	-5.561929	-0.865052	1.240406
C	-5.383859	1.238648	2.382800
C	-6.110937	0.109974	2.057420
H	-6.140546	-1.748260	1.003252
H	-5.818180	1.987559	3.033783
H	-7.113773	-0.018451	2.449385
C	1.121677	-0.497825	0.239118
C	2.104738	-0.121191	1.159260
C	1.279605	-1.532906	-0.684810
C	3.299728	-0.833565	1.122963
C	2.500962	-2.200969	-0.686884
C	3.498702	-1.853954	0.207356
H	4.079320	-0.589442	1.833002
H	2.664119	-3.011449	-1.388210
H	4.439923	-2.392733	0.199642
C	1.893271	1.020860	2.123818
H	0.831526	1.043498	2.385186
C	0.178970	-1.961652	-1.629349
H	-0.659474	-1.269709	-1.519162
C	-3.704520	-1.769186	-0.216205
H	-2.643278	-1.882678	0.011232
C	-3.315986	2.667424	2.282777
H	-2.262146	2.491598	2.056917
Cl	-1.154135	0.282250	3.795356
H	-1.251419	-1.041533	1.599231
C	-1.797309	1.504399	-0.356176
S	-2.343900	-2.242853	5.770659
S	1.653657	-3.401675	3.817231
Cl	-1.477226	-3.111213	2.456987
Cl	1.040900	-1.325974	5.996124
C	-2.641864	-4.028564	5.786532
H	-1.842520	-4.480268	6.373660
H	-3.602411	-4.254513	6.253051
H	-2.610126	-4.414981	4.766840
C	-3.742846	-1.738553	4.741211
H	-4.681616	-1.927956	5.263888
H	-3.618320	-0.673932	4.552904
H	-3.709831	-2.267052	3.788217
C	1.502553	-4.349731	2.285449
H	1.562797	-3.639588	1.463428
H	2.344351	-5.042224	2.237985
H	0.549477	-4.872081	2.244699
C	1.512057	-4.766943	5.006399
H	2.376399	-5.425710	4.904816
H	1.506119	-4.300996	5.990416
H	0.583454	-5.311487	4.840758
C	-3.808407	3.862996	1.465359
H	-4.851593	4.088216	1.703719
H	-3.212477	4.750386	1.692765
H	-3.754247	3.683863	0.388434
C	-3.394217	2.973685	3.775031
H	-2.753158	3.827589	4.006872
H	-4.410017	3.234574	4.084186
H	-3.042083	2.123613	4.359858
C	2.270576	2.348592	1.463633
H	3.331638	2.361728	1.197234
H	1.695189	2.541745	0.555142
H	2.084857	3.172982	2.156198
C	2.646896	0.846312	3.433735
H	2.424303	-0.113103	3.901441
H	3.729240	0.945507	3.303438
H	2.326843	1.617918	4.136055
C	-0.328859	-3.355675	-1.264263
H	-0.671033	-3.395407	-0.227290
H	-1.160062	-3.640360	-1.915204
H	0.460199	-4.102530	-1.387425
C	0.627406	-1.893854	-3.086393
H	0.977456	-0.892940	-3.349549
H	1.441204	-2.595265	-3.286438
H	-0.202096	-2.151693	-3.749582
C	-4.314794	-3.152102	-0.041088
H	-4.250721	-3.482202	0.997130
H	-5.360028	-3.183930	-0.360238
H	-3.766359	-3.871076	-0.653736
C	-3.833198	-1.301048	-1.666765
H	-3.341975	-0.339500	-1.831246
H	-3.381483	-2.030585	-2.344449
H	-4.885791	-1.190280	-1.940995

E(solv)= -3615.065789 A.U
Thermal correction= 0.661207

A:

Pt	-0.097250	-2.543595	3.568249
C	-0.654975	0.719951	-1.008954
H	-2.643360	1.600105	-1.455453
H	0.048859	0.977515	-1.780198
N	-2.365592	0.444637	0.334672
N	-0.285528	-0.048180	0.078659
C	-1.340175	-0.205124	0.875981
C	-3.663452	0.580627	0.938380
C	-4.602379	-0.430253	0.737393
C	-3.901069	1.718676	1.712439
C	-5.857690	-0.242724	1.307805
C	-5.169981	1.851238	2.264355
C	-6.140738	0.886136	2.055843
H	-6.616907	-1.004970	1.177660
H	-5.394139	2.714156	2.880594
H	-7.123371	1.006844	2.497926
C	1.029560	-0.567691	0.334805
C	1.726805	-0.087251	1.452393
C	1.536628	-1.530981	-0.537705
C	2.992009	-0.617469	1.671899
C	2.822857	-2.000483	-0.284381
C	3.538785	-1.554603	0.810209
H	3.554792	-0.298639	2.538157
H	3.256548	-2.741353	-0.946279
H	4.530444	-1.947485	1.004986
C	1.159090	0.984852	2.363369
H	0.137155	0.696037	2.627065
C	0.761605	-2.069120	-1.720531
H	-0.271009	-1.722750	-1.638979
C	-4.295986	-1.695413	-0.029322
H	-3.235988	-1.692521	-0.293647
C	-2.824519	2.736258	2.015334
H	-1.953019	2.511773	1.395617
Cl	-2.030282	-1.248670	3.877795
H	-1.387791	-0.743208	1.820147
C	-1.963715	1.025403	-0.850886
S	1.852242	-3.735902	3.429011
Cl	-0.969473	-3.344701	1.533811
Cl	0.759631	-1.784428	5.602040
C	1.841416	-4.822517	1.983587
H	1.912882	-4.186010	1.105206
H	2.714128	-5.473660	2.050088
H	0.915827	-5.392345	1.937472
C	1.669731	-4.993890	4.723255
H	2.566801	-5.614197	4.740849
H	1.561508	-4.448962	5.659133
H	0.780820	-5.594308	4.535758
C	-3.262567	4.157003	1.673630
H	-4.102884	4.477306	2.294208
H	-2.440791	4.855580	1.849016
H	-3.567613	4.242924	0.627750
C	-2.388028	2.619743	3.476003
H	-1.563430	3.307636	3.681102
H	-3.212021	2.874865	4.147497
H	-2.066454	1.604743	3.720497
C	1.123593	2.337842	1.647322
H	2.138039	2.655402	1.390982
H	0.537903	2.320364	0.726374
H	0.690045	3.095868	2.304018
C	1.905193	1.120284	3.681580
H	1.940286	0.173855	4.222993
H	2.920956	1.499664	3.534050
H	1.378134	1.835188	4.316813
C	0.712113	-3.594470	-1.723007
H	0.291279	-3.965103	-0.787495
H	0.085624	-3.944983	-2.547139
H	1.705688	-4.029108	-1.861407
C	1.341313	-1.543891	-3.033711
H	1.372929	-0.451745	-3.063208
H	2.364806	-1.901348	-3.173928
H	0.745741	-1.891247	-3.881696
C	-4.527498	-2.926300	0.844157
H	-3.947029	-2.864832	1.765746
H	-5.584950	-3.038215	1.098696
H	-4.211715	-3.826097	0.311519
C	-5.100930	-1.761306	-1.325168
H	-4.904852	-0.897108	-1.965562
H	-4.846529	-2.665573	-1.883597
H	-6.174455	-1.786718	-1.119932

E(solv)= -3137.264934 A.U
Thermal correction= 0.588596

B:

Pt	-0.838384	-1.490258	3.249818
H	-0.288070	5.001352	-2.374599
H	2.390799	4.916089	-1.930393
N	-0.167177	2.867092	-2.081123
N	2.047254	2.794593	-1.710472
C	0.935795	1.907215	-2.063237

C	-1.441132	2.491444	-2.566064
C	-1.794421	2.700963	-3.910058
C	-2.346542	1.904625	-1.664207
C	-3.087554	2.380077	-4.313452
C	-3.619334	1.576766	-2.120106
C	-3.996233	1.823861	-3.429357
H	-3.373864	2.537059	-5.349232
H	-4.321620	1.116693	-1.433556
H	-4.995659	1.565022	-3.766233
C	3.378441	2.326985	-1.782461
C	3.906680	1.665446	-0.659888
C	4.156259	2.514213	-2.938260
C	5.231525	1.244049	-0.696897
C	5.484679	2.098236	-2.919320
C	6.023733	1.469227	-1.810114
H	5.644066	0.728767	0.164363
H	6.095021	2.238750	-3.806455
H	7.057744	1.137468	-1.820059
C	3.053508	1.374320	0.550775
H	2.120424	1.926940	0.421046
C	3.586961	3.105223	-4.209983
H	2.537546	3.331842	-4.027093
C	-0.807278	3.216176	-4.935224
H	0.142369	3.378244	-4.427202
C	-1.940200	1.574542	-0.248161
H	-1.002094	2.102022	-0.058047
H	0.789368	1.112334	-1.330940
C	1.676843	4.111961	-1.996175
C	-2.952122	2.032554	0.796908
H	-3.910553	1.518082	0.680777
H	-2.586778	1.791185	1.798175
H	-3.132802	3.110120	0.733397
C	-1.679192	0.074834	-0.120878
H	-1.300536	-0.161594	0.878195
H	-2.606246	-0.492122	-0.249424
H	-0.961621	-0.268411	-0.869588
C	3.687183	1.849599	1.854273
H	4.620203	1.317052	2.066021
H	3.908998	2.920548	1.822143
H	3.003162	1.653210	2.683643
C	2.716594	-0.114418	0.621407
H	2.241443	-0.452637	-0.302849
H	3.625197	-0.707682	0.773346
H	2.053676	-0.301797	1.469489
C	3.624712	2.096468	-5.355040
H	3.041642	1.206438	-5.107243
H	3.188453	2.541545	-6.256053
H	4.651845	1.798732	-5.593049
C	4.291298	4.406613	-4.586999
H	4.230335	5.140115	-3.778064
H	5.351314	4.238408	-4.804345
H	3.832748	4.844423	-5.479411
C	-0.549039	2.179612	-6.025644
H	-0.128131	1.266491	-5.599135
H	-1.467763	1.933221	-6.569010
H	0.173247	2.573087	-6.749368
C	-1.258822	4.549160	-5.528351
H	-1.416901	5.298978	-4.748009
H	-0.504326	4.932946	-6.222584
H	-2.197587	4.441865	-6.081877
C	1.161506	-0.143512	-3.398585
O	1.348672	-0.497912	-4.557142
O	1.123609	1.323660	-3.308078
O	1.006558	-0.751770	-2.337846
C	0.357666	4.153813	-2.214990
Cl	1.003629	-0.320611	4.112171
Cl	-2.301154	-0.105804	4.434713
Cl	-2.664038	-2.735060	2.421145
S	0.649299	-2.816411	2.111226
C	0.125695	-2.907078	0.377182
H	0.411246	-1.981939	-0.119764
H	0.655540	-3.735398	-0.095818
H	-0.954027	-3.044299	0.338831
C	0.221215	-4.509092	2.605616
H	-0.848187	-4.659822	2.456641
H	0.816992	-5.212602	2.020160
H	0.462784	-4.599596	3.663631

E(solv)= -3401.152136 A.U
Thermal correction= 0.597223

TS2:

Pt	-4.396984	-5.619912	3.178118
H	-3.417574	0.995746	-1.927127
H	-0.697112	1.121961	-1.438466
N	-3.041611	-1.121400	-1.721993
N	-0.928915	-1.023092	-1.330539
C	-1.946759	-1.902690	-1.539408
C	-4.368269	-1.630805	-1.852901
C	-4.882234	-1.880691	-3.128553
C	-5.098693	-1.870442	-0.682364
C	-6.172476	-2.398983	-3.207687
C	-6.373779	-2.410415	-0.812797
C	-6.905171	-2.671249	-2.065141
H	-6.595742	-2.614567	-4.182782

H	-6.944143	-2.649533	0.076815
H	-7.897036	-3.104479	-2.147644
C	0.429573	-1.406182	-1.165631
C	0.826672	-2.024138	0.027061
C	1.329150	-1.159698	-2.210870
C	2.177878	-2.321374	0.182646
C	2.670815	-1.461408	-1.998521
C	3.096654	-2.028762	-0.809736
H	2.505943	-2.804575	1.096462
H	3.385384	-1.278613	-2.794506
H	4.145890	-2.268574	-0.666571
C	-0.156121	-2.435560	1.097696
H	-1.126775	-2.005642	0.847316
C	0.886081	-0.630917	-3.557395
H	-0.199840	-0.543222	-3.540221
C	-4.095489	-1.569134	-4.381064
H	-3.051661	-1.436845	-4.090054
C	-4.494803	-1.619309	0.679169
H	-3.726769	-0.848515	0.558160
H	-1.919416	-3.134074	-1.468941
C	-1.366293	0.282428	-1.514588
C	-5.504601	-1.118271	1.705996
H	-6.214639	-1.900425	1.984156
H	-4.983191	-0.839265	2.624688
H	-6.060305	-0.249136	1.339943
C	-3.820928	-2.890177	1.185988
H	-3.321303	-2.721618	2.142472
H	-4.562977	-3.675111	1.355273
H	-3.091687	-3.266638	0.468710
C	0.223287	-1.922487	2.483390
H	1.172207	-2.347811	2.824527
H	0.316805	-0.832244	2.496540
H	-0.543340	-2.220524	3.203022
C	-0.312848	-3.957228	1.100813
H	-0.631779	-4.321058	0.120148
H	0.640079	-4.436329	1.350346
H	-1.041183	-4.259786	1.857316
C	1.200209	-1.633165	-4.664421
H	0.627718	-2.546517	-4.487091
H	0.887201	-1.225785	-5.631439
H	2.271196	-1.855793	-4.721257
C	1.492494	0.741593	-3.842212
H	1.243851	1.463799	-3.058637
H	2.584308	0.687930	-3.906497
H	1.121047	1.131548	-4.794928
C	-4.086213	-2.724173	-5.375390
H	-3.593922	-3.599723	-4.946796
H	-5.094515	-2.991589	-5.711615
H	-3.504991	-2.437153	-6.256841
C	-4.621531	-0.283989	-5.020457
H	-4.586995	0.555533	-4.319531
H	-4.019006	-0.020711	-5.895615
H	-5.661008	-0.400741	-5.347357
C	-1.588039	-4.047930	-3.217925
O	-1.528191	-4.876865	-4.139678
O	-1.444497	-2.756601	-3.438085
O	-1.809649	-4.389820	-1.964783
C	-2.689346	0.221387	-1.758529
Cl	-2.486545	-4.812712	4.286326
Cl	-5.780082	-4.449082	4.664569
Cl	-6.295864	-6.461978	2.063585
S	-2.986761	-6.736301	1.746301
C	-3.486594	-6.421718	0.029370
H	-3.022494	-5.501120	-0.325018
H	-3.093365	-7.234173	-0.582963
H	-4.573021	-6.373244	-0.022293
C	-3.529359	-8.463988	1.868464
H	-4.601694	-8.511653	1.678434
H	-2.964530	-9.063955	1.152029
H	-3.319929	-8.792251	2.885521

E(solv)= -3401.124764 A.U
Thermal correction= 0.593278

C:

Pt	-3.767913	-1.669730	0.846195
H	-0.487547	4.739684	-1.766567
H	2.263497	5.087011	-1.796199
N	0.105632	2.664057	-1.663431
N	2.206059	2.924531	-1.698513
C	1.257412	1.951140	-1.635327
C	-1.192595	2.061503	-1.642378
C	-1.668017	1.461980	-2.812886
C	-1.910796	2.060592	-0.440049
C	-2.934052	0.883132	-2.758113
C	-3.169093	1.467338	-0.438542
C	-3.676697	0.884982	-1.589544
H	-3.322218	0.375035	-3.632478
H	-3.739480	1.395274	0.478765
H	-4.631696	0.374572	-1.543469
C	3.604945	2.658153	-1.731214
C	4.213307	2.097783	-0.601845
C	4.326669	2.959176	-2.893223
C	5.585069	1.869188	-0.648113
C	5.698551	2.728349	-2.881097

C	6.325855	2.189308	-1.771850
H	6.075094	1.420336	0.209234
H	6.276038	2.943697	-3.773191
H	7.394024	1.997347	-1.791543
C	3.428511	1.701219	0.627118
H	2.418519	2.097279	0.520042
C	3.670964	3.511721	-4.139993
H	2.591376	3.420215	-4.011745
C	-0.824206	1.416451	-4.066911
H	0.229197	1.329917	-3.782073
C	-1.279696	2.575222	0.836344
H	-0.626052	3.412828	0.571781
H	1.676149	0.097719	-2.219770
C	1.659397	4.197359	-1.751976
C	-2.297846	3.075012	1.854029
H	-2.894246	2.249873	2.250619
H	-1.778094	3.537861	2.698634
H	-2.973443	3.816382	1.417566
C	-0.406975	1.479669	1.455319
H	0.151529	1.874800	2.311088
H	-1.033230	0.658332	1.813211
H	0.307220	1.087713	0.728203
C	4.019203	2.288718	1.905737
H	5.014272	1.884854	2.115731
H	4.104038	3.377250	1.842652
H	3.378286	2.043736	2.757427
C	3.309824	0.180490	0.714359
H	2.891853	-0.234694	-0.205072
H	4.293155	-0.274574	0.874540
H	2.662684	-0.101677	1.550016
C	4.028260	2.701476	-5.382299
H	3.684442	1.669658	-5.250539
H	3.515216	3.126171	-6.251900
H	5.103620	2.727720	-5.589381
C	4.023314	4.988374	-4.326112
H	3.760641	5.590306	-3.451590
H	5.097809	5.110234	-4.498683
H	3.495551	5.398177	-5.192596
C	-1.098540	0.197627	-4.935983
H	-1.052181	-0.719835	-4.345960
H	-2.075189	0.244510	-5.431349
H	-0.319567	0.129724	-5.697993
C	-0.975334	2.703010	-4.878170
H	-0.712000	3.583422	-4.286032
H	-0.312567	2.672651	-5.747884
H	-2.006178	2.826140	-5.229604
C	2.419364	-0.658660	-3.825159
O	2.906035	-1.669537	-4.331324
O	2.256512	0.489767	-4.320446
O	1.974356	-0.793723	-2.503828
C	0.321282	4.029170	-1.735846
Cl	-3.244269	-0.628105	2.889827
Cl	-6.010454	-1.016837	1.075777
Cl	-4.285416	-2.758042	-1.175819
S	-1.544355	-2.190638	0.625731
C	-1.024172	-1.569737	-0.994120
H	-1.059535	-0.484726	-0.938752
H	0.000049	-1.879758	-1.207656
H	-1.726702	-1.919107	-1.748570
C	-1.463313	-3.967932	0.278332
H	-2.163518	-4.203032	-0.522925
H	-0.437922	-4.222205	0.005196
H	-1.753654	-4.485991	1.191353

E(solv)= -3401.150262 A.U
Thermal correction= 0.592422

TS3:

Pt	1.096799	-0.685246	-2.017332
H	-0.380483	4.622944	-2.821905
H	2.388163	4.744088	-2.700930
N	0.006960	2.596123	-2.189661
N	2.125160	2.688281	-2.098750
C	1.090088	1.823311	-1.896067
C	-1.372601	2.250424	-2.049597
C	-2.169427	2.213283	-3.197347
C	-1.901016	2.053509	-0.770883
C	-3.539957	2.046148	-3.029199
C	-3.275639	1.882518	-0.655661
C	-4.094223	1.895670	-1.771011
H	-4.177531	2.005488	-3.905564
H	-3.708267	1.722006	0.326243
H	-5.165108	1.758469	-1.660965
C	3.501450	2.484724	-1.766469
C	3.879302	2.610325	-0.426495
C	4.428753	2.267696	-2.787447
C	5.228484	2.483110	-0.116014
C	5.770052	2.170636	-2.430221
C	6.168675	2.270492	-1.109711
H	5.548245	2.555297	0.917518
H	6.508642	1.987523	-3.202258
H	7.218293	2.174987	-0.850597
C	2.856981	2.818035	0.666957
H	1.956089	3.228842	0.203663
C	4.008144	2.125387	-4.230035

H	2.932682	1.937392	-4.245822
C	-1.586222	2.277505	-4.591215
H	-0.498770	2.238713	-4.505446
C	-1.032860	1.980773	0.463063
H	0.005103	1.980412	0.131369
C	1.698201	3.941110	-2.507211
C	-1.244706	3.185141	1.375198
H	-2.275773	3.230325	1.740041
H	-0.582398	3.128661	2.244984
H	-1.034874	4.119815	0.848261
C	-1.248518	0.661646	1.198211
H	-0.535453	0.567942	2.023035
H	-2.255591	0.593175	1.620914
H	-1.110250	-0.174467	0.509288
C	3.310658	3.810998	1.731073
H	4.154053	3.427892	2.312287
H	3.612137	4.763279	1.287171
H	2.493755	4.003695	2.432377
C	2.485822	1.472159	1.282917
H	2.101781	0.802111	0.511410
H	3.365337	1.002261	1.733532
H	1.724332	1.597980	2.059300
C	4.651151	0.913410	-4.894022
H	4.450525	0.017420	-4.306069
H	4.211195	0.765954	-5.883182
H	5.733167	1.036972	-5.016170
C	4.303785	3.401472	-5.016635
H	3.797587	4.270665	-4.588490
H	5.378208	3.614180	-5.032029
H	3.965279	3.292067	-6.050947
C	-1.988822	1.048307	-5.401811
H	-1.699796	0.140746	-4.871330
H	-3.066607	1.029318	-5.596652
H	-1.467683	1.054902	-6.362790
C	-1.984259	3.563216	-5.312942
H	-1.667020	4.455691	-4.766661
H	-1.527493	3.595744	-6.306218
H	-3.070045	3.621786	-5.440756
C	0.356729	3.883188	-2.562502
Cl	-1.229158	-0.962425	-2.278465
Cl	1.261033	-0.025625	-4.442944
Cl	3.455336	-0.790319	-1.794083
S	0.898994	-2.356493	-0.490152
C	1.974118	-2.056884	0.942567
H	1.518356	-1.254217	1.519419
H	2.020139	-2.966348	1.545251
H	2.962146	-1.753034	0.596329
C	1.830537	-3.749594	-1.192026
H	2.826589	-3.401321	-1.465155
H	1.869091	-4.567553	-0.468173
H	1.291007	-4.057371	-2.085841

E(solv)= -3136.738002 A.U
Thermal correction= 0.577141

3ag:

Pt	-0.044171	-1.049847	0.417800
H	-1.458006	3.770457	-0.572440
H	1.310574	3.881623	-0.328237
N	-1.101220	1.727876	-0.029736
N	1.032548	1.805426	0.125350
C	-0.016817	0.945772	0.246435
C	-2.501334	1.420856	0.050889
C	-3.116521	0.739617	-0.999884
C	-3.198023	1.912178	1.156909
C	-4.493466	0.559381	-0.912018
C	-4.573113	1.712900	1.191864
C	-5.216087	1.044246	0.164646
H	-5.000905	0.019624	-1.702170
H	-5.142022	2.068461	2.044479
H	-6.288950	0.887057	0.210179
C	2.422679	1.601985	0.409201
C	2.828636	1.630792	1.742446
C	3.311097	1.494705	-0.666471
C	4.195476	1.554823	1.996679
C	4.665627	1.451118	-0.357497
C	5.104934	1.481923	0.956717
H	4.547763	1.555881	3.022341
H	5.383054	1.349786	-1.163158
H	6.167479	1.429946	1.171729
C	1.837836	1.685683	2.883417
H	0.861533	1.945416	2.468391
C	2.830542	1.343780	-2.093783
H	1.819494	0.926912	-2.073564
C	-2.332559	0.232788	-2.182281
H	-1.307137	0.021070	-1.866805
C	-2.503721	2.589684	2.318701
H	-1.431247	2.593889	2.115278
C	0.609816	3.075268	-0.210294
C	-2.949900	4.042108	2.467875
H	-4.020458	4.103295	2.683535
H	-2.413688	4.526165	3.289438
H	-2.762881	4.613471	1.555190
C	-2.706358	1.812657	3.617227
H	-2.129026	2.272176	4.425712

H	-3.758399	1.810131	3.917284
H	-2.383597	0.777772	3.493109
C	2.190427	2.757375	3.910282
H	3.128352	2.531201	4.425073
H	2.293624	3.739476	3.441648
H	1.406543	2.820494	4.670285
C	1.695460	0.311956	3.535562
H	1.382999	-0.431434	2.798565
H	2.646645	-0.011010	3.969589
H	0.943438	0.342196	4.329318
C	3.668852	0.347172	-2.888175
H	3.841125	-0.560817	-2.309784
H	3.102742	0.059252	-3.776948
H	4.633578	0.772744	-3.189251
C	2.783973	2.676445	-2.840804
H	2.117630	3.400043	-2.367184
H	3.782431	3.122603	-2.903856
H	2.416888	2.502026	-3.854938
C	-2.868179	-1.075891	-2.744745
H	-2.984226	-1.823200	-1.954605
H	-3.833976	-0.947087	-3.245957
H	-2.140601	-1.438982	-3.475066
C	-2.241451	1.291923	-3.279916
H	-1.836802	2.233178	-2.896439
H	-1.562632	0.919295	-4.051810
H	-3.229493	1.495070	-3.708689
C	-0.727181	3.023351	-0.318748
Cl	-2.062588	-1.177470	1.612388
Cl	0.450971	-0.883652	-3.975973
Cl	2.190453	-1.376261	-0.192944
S	-0.368822	-3.367996	0.014668
C	0.842423	-4.277320	1.007617
H	0.522327	-4.205726	2.046562
H	0.853732	-5.321645	0.692776
H	1.820433	-3.812553	0.880867
C	0.330829	-3.597741	-1.645352
H	1.414694	-3.521439	-1.591865
H	0.007102	-4.568603	-2.022615
H	-0.011519	-2.783155	-2.295120

E(solv)= -3136.792382 A.U
Thermal correction= 0.576187

CO_3^{2-}:

C	0.217200	2.960247	-4.233909
O	1.518249	2.960247	-4.234021
O	-0.433204	4.087006	-4.233996
O	-0.433204	1.833488	-4.233950

E(solv)= -263.853444 A.U
Thermal correction= -0.01163

HCO_3^-:

C	0.249746	2.898551	-4.234016
O	1.484174	3.072559	-4.233980
O	-0.498146	4.125542	-4.233966
O	-0.445414	1.884055	-4.233911
H	0.202882	4.783598	-4.233984

E(solv)= -264.378299 A.U
Thermal correction= 0.000814

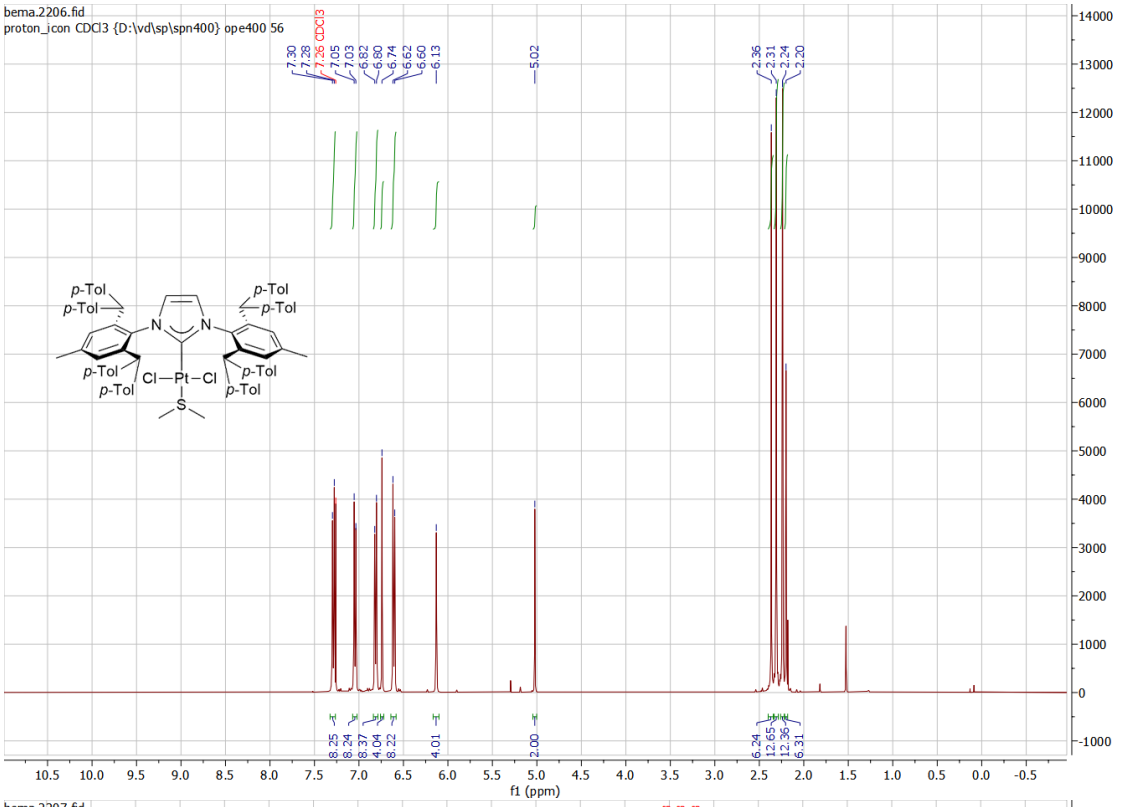
DMS:

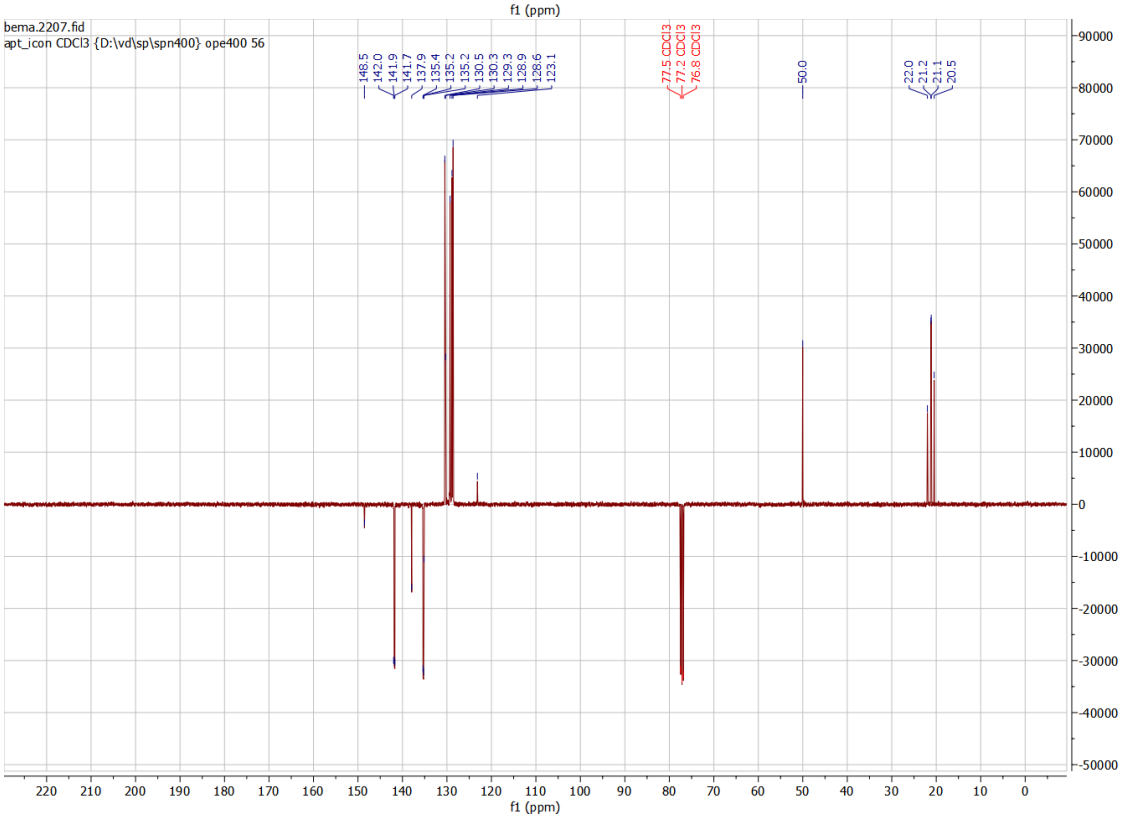
S	-2.150359	-5.173827	5.123292
C	-3.562489	-4.660805	4.113087
H	-3.544874	-5.262547	3.204373
H	-4.504993	-4.839668	4.633791
H	-3.487524	-3.607305	3.837432
C	-2.389945	-4.063074	6.532283
H	-3.348801	-4.246870	7.020321
H	-1.590057	-4.267882	7.243938
H	-2.326587	-3.017688	6.224873

E(solv)= -477.811713 A.U
Thermal correction= 0.048868

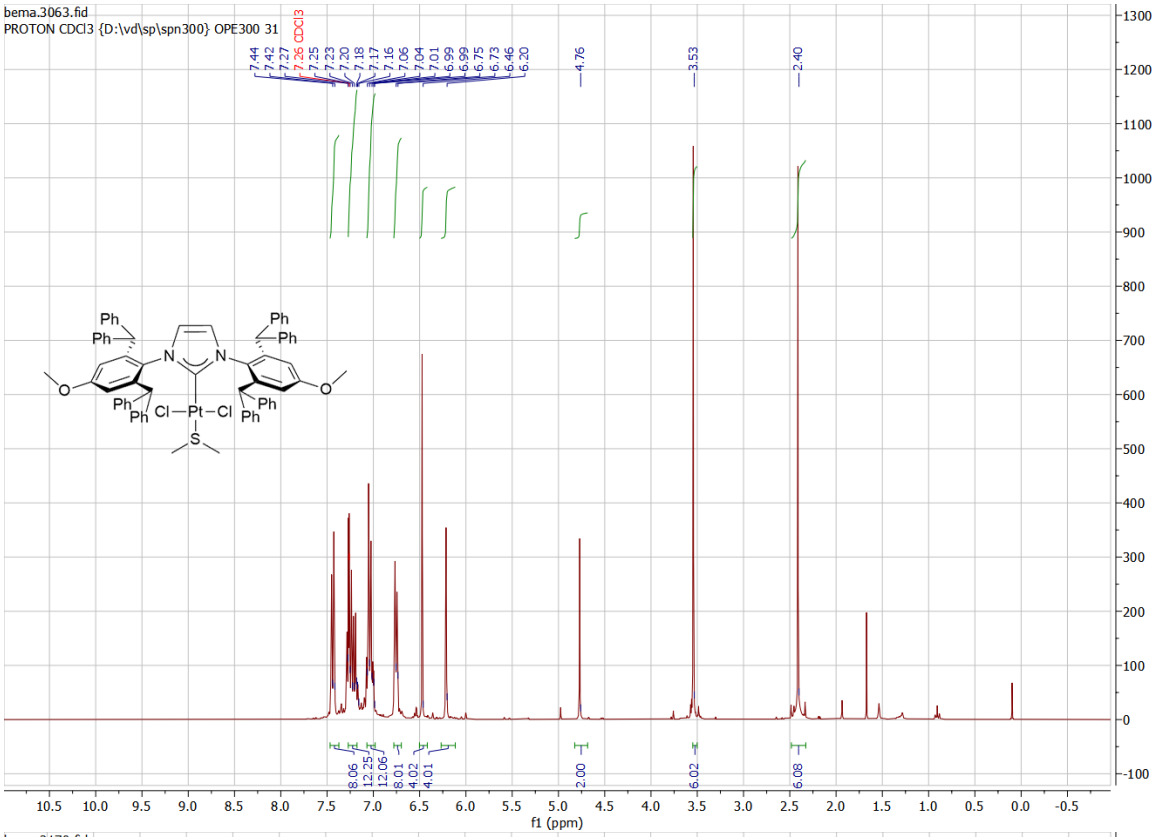
2. NMR spectra

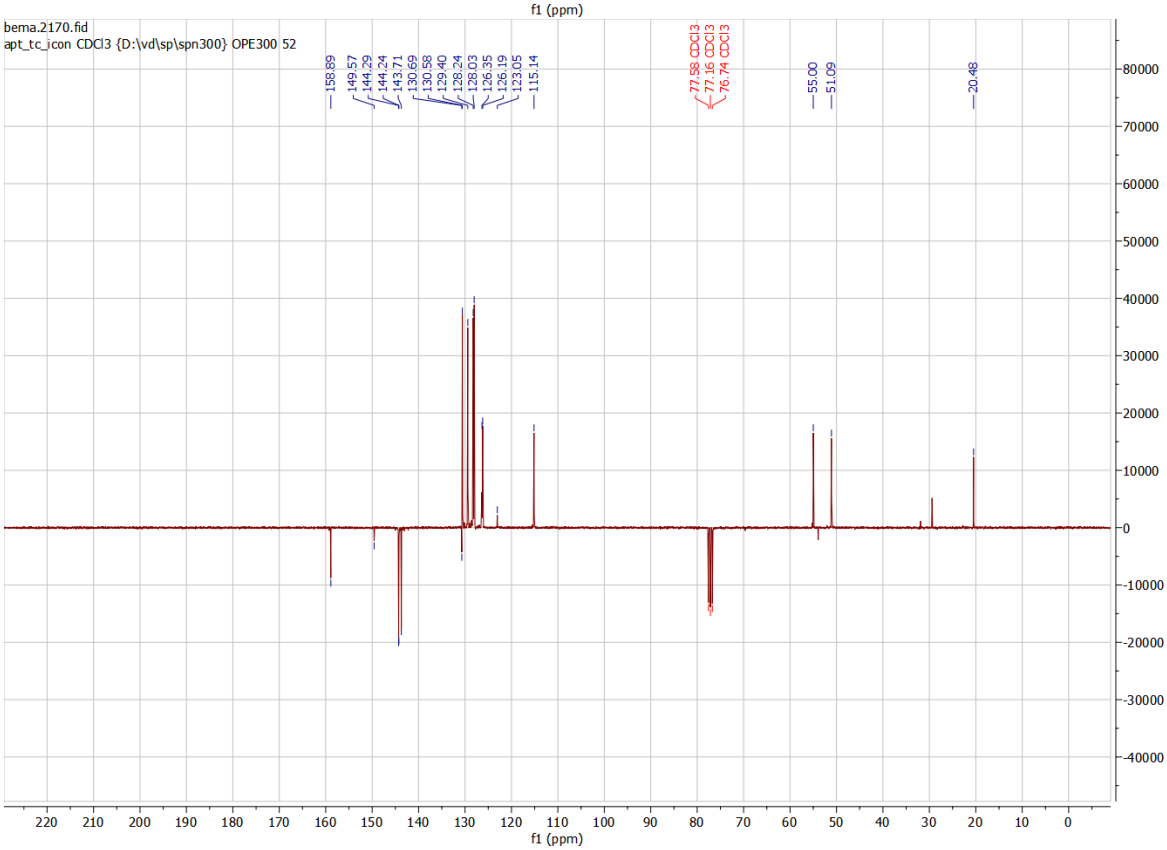
2.1. ^{1}H and $^{13}C\{^{1}H\}$ apt NMR of $[Pt(IPr^{*Tol})(DMS)Cl_2]$ (3aa)



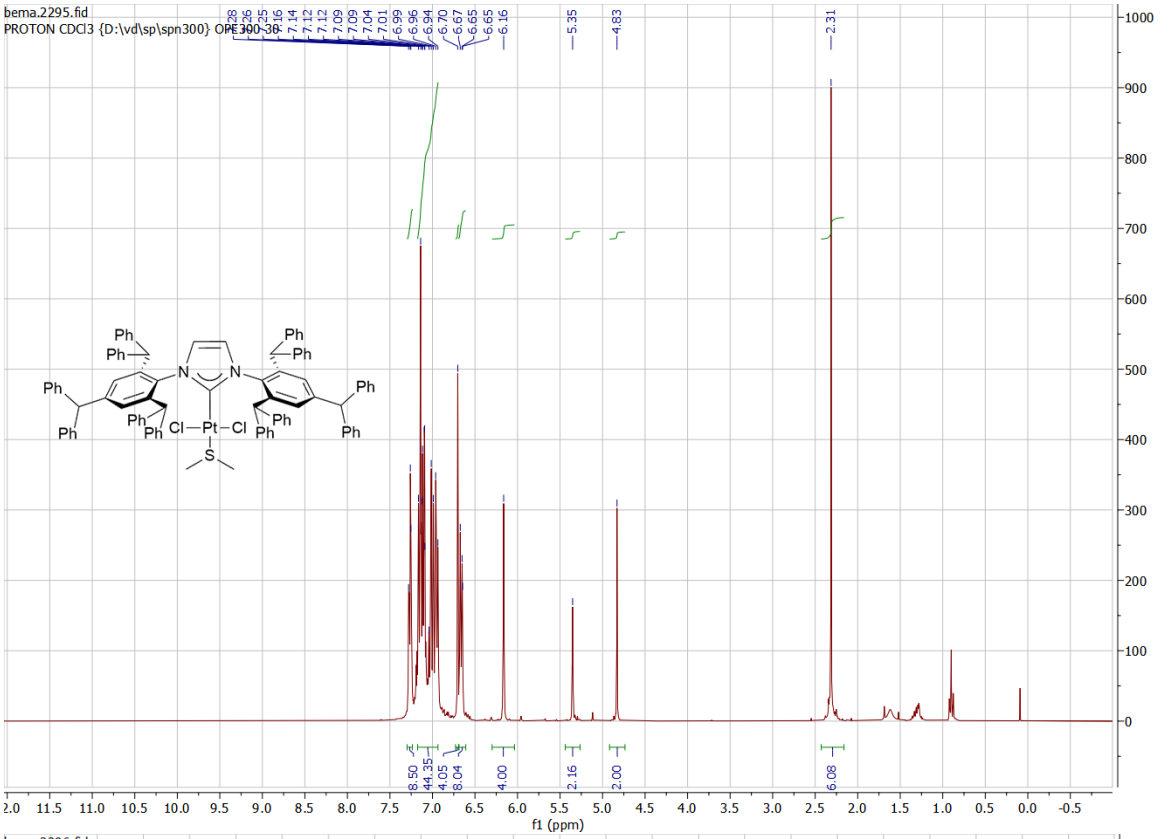


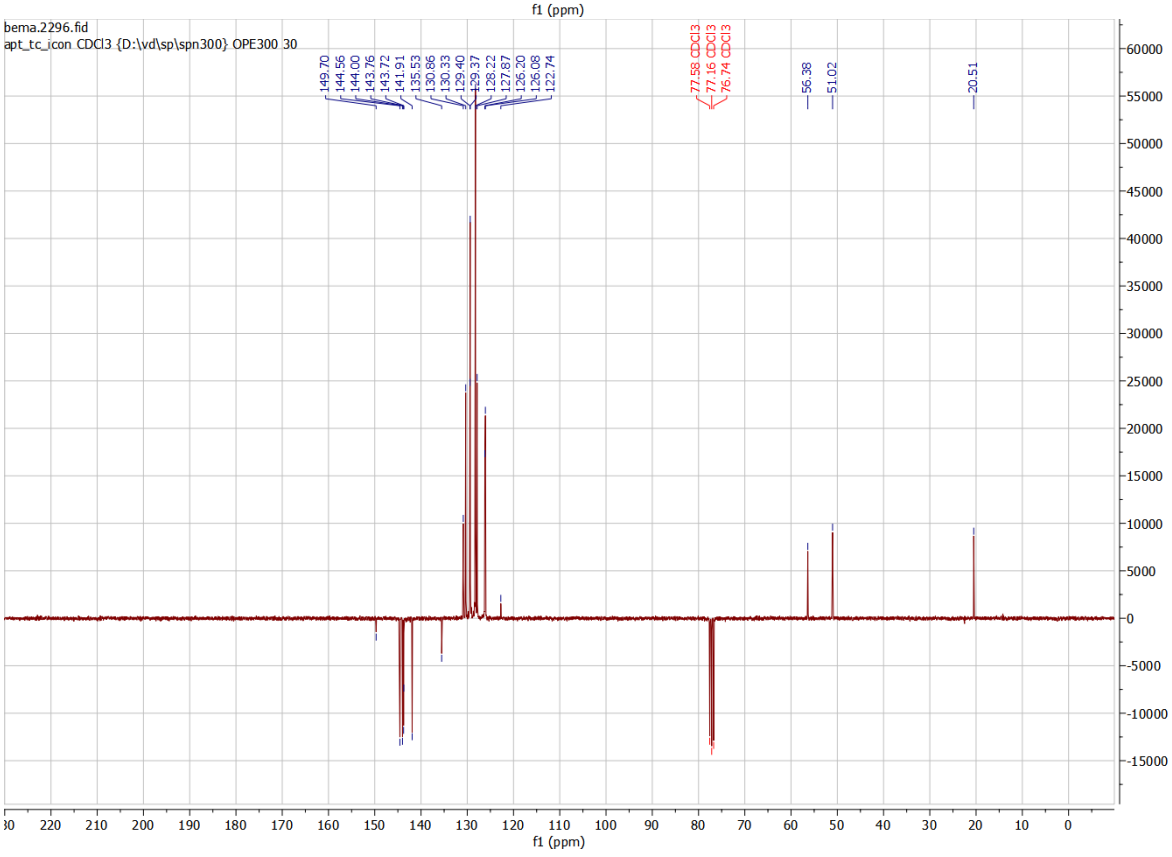
2.2. ^{1}H and $^{13}C\{^{1}H\}$ apt NMR of [Pt(IPr*^{OMe})(DMS)Cl_2] (3ab)



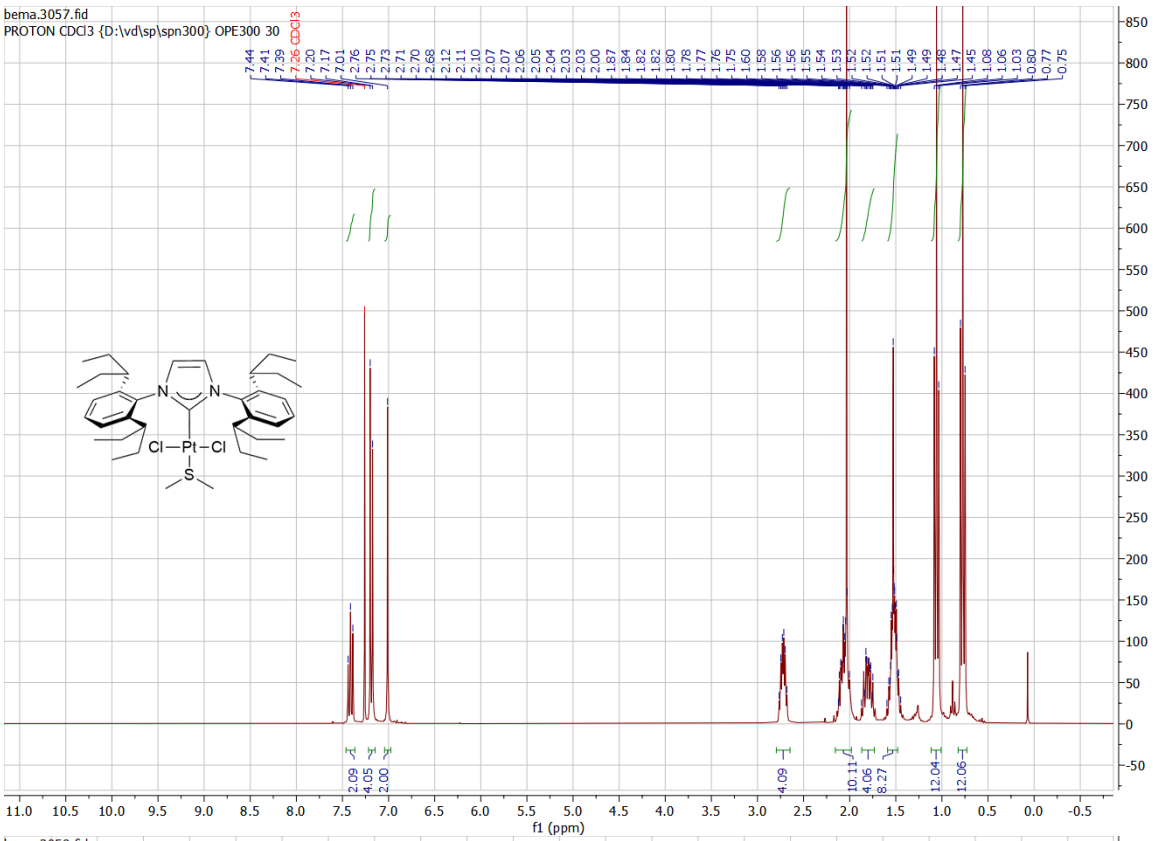


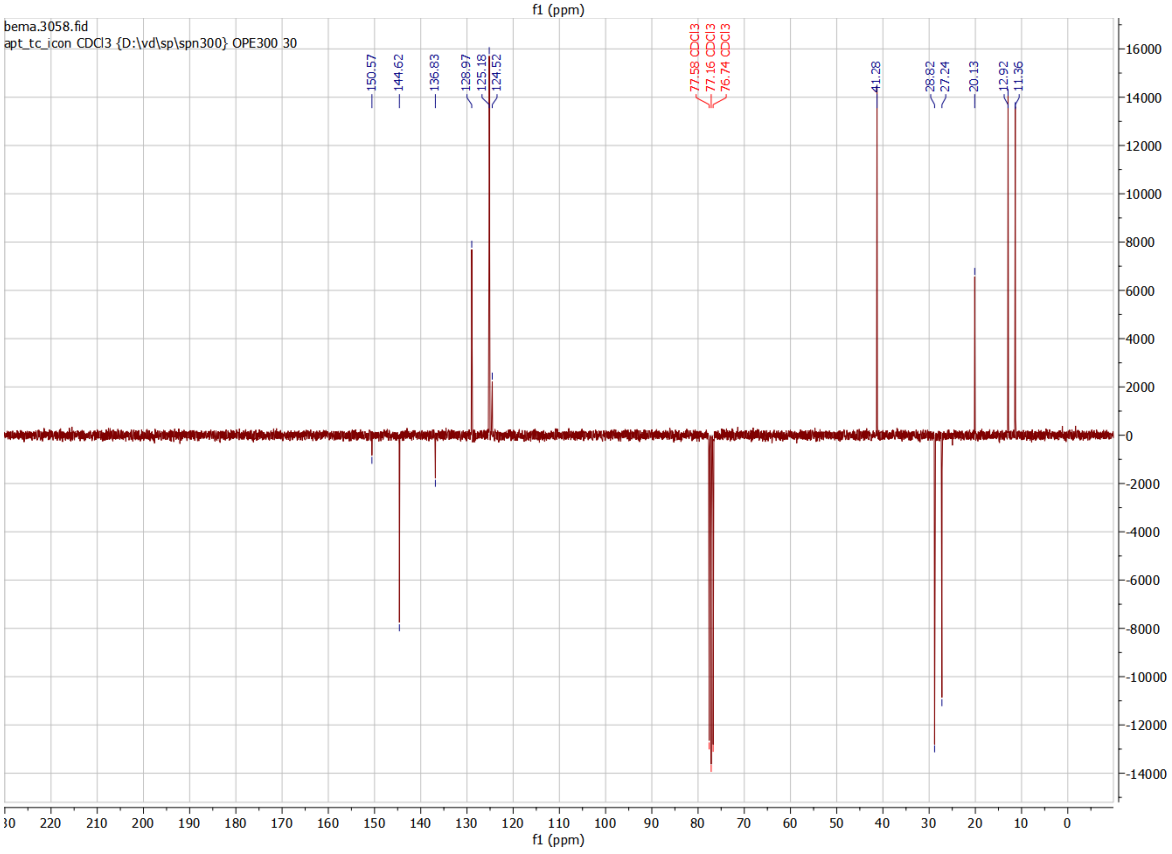
2.3. ^{1}H and $^{13}C\{^{1}H\}$ apt NMR of [Pt(IPr#)(DMS)Cl_2] (3ac)



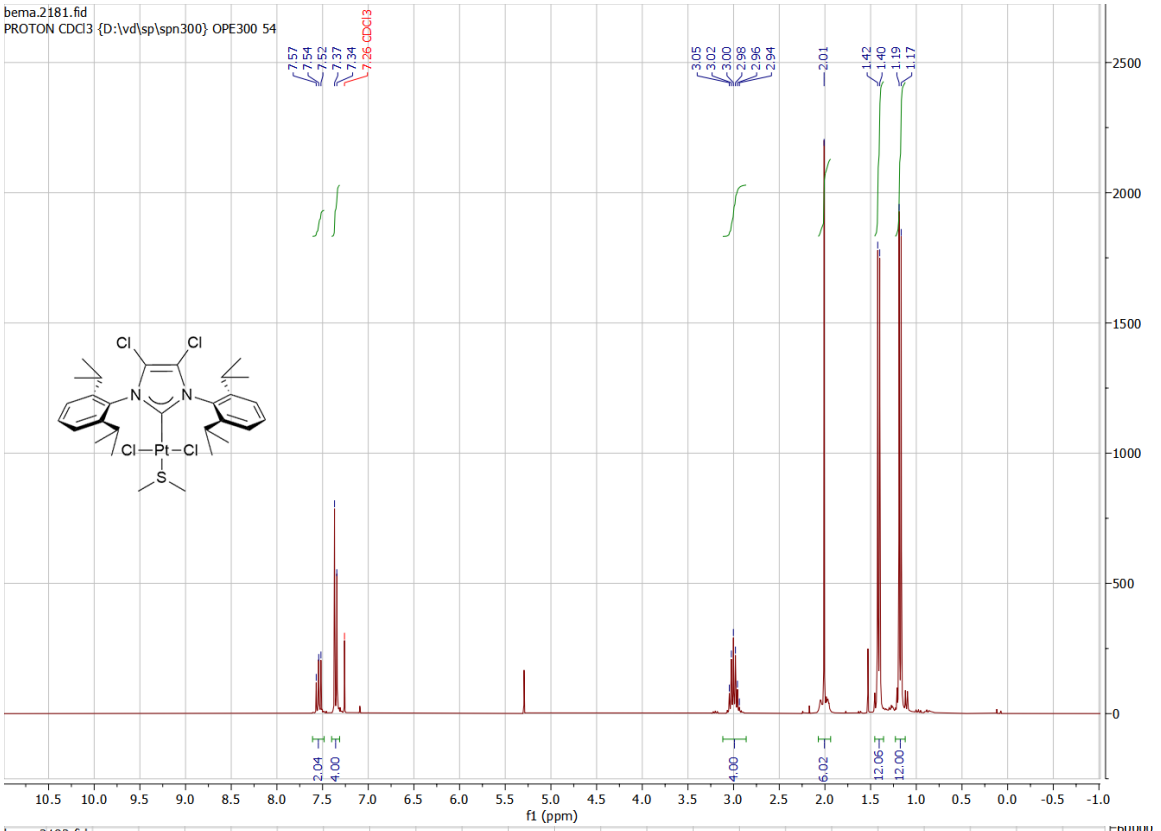


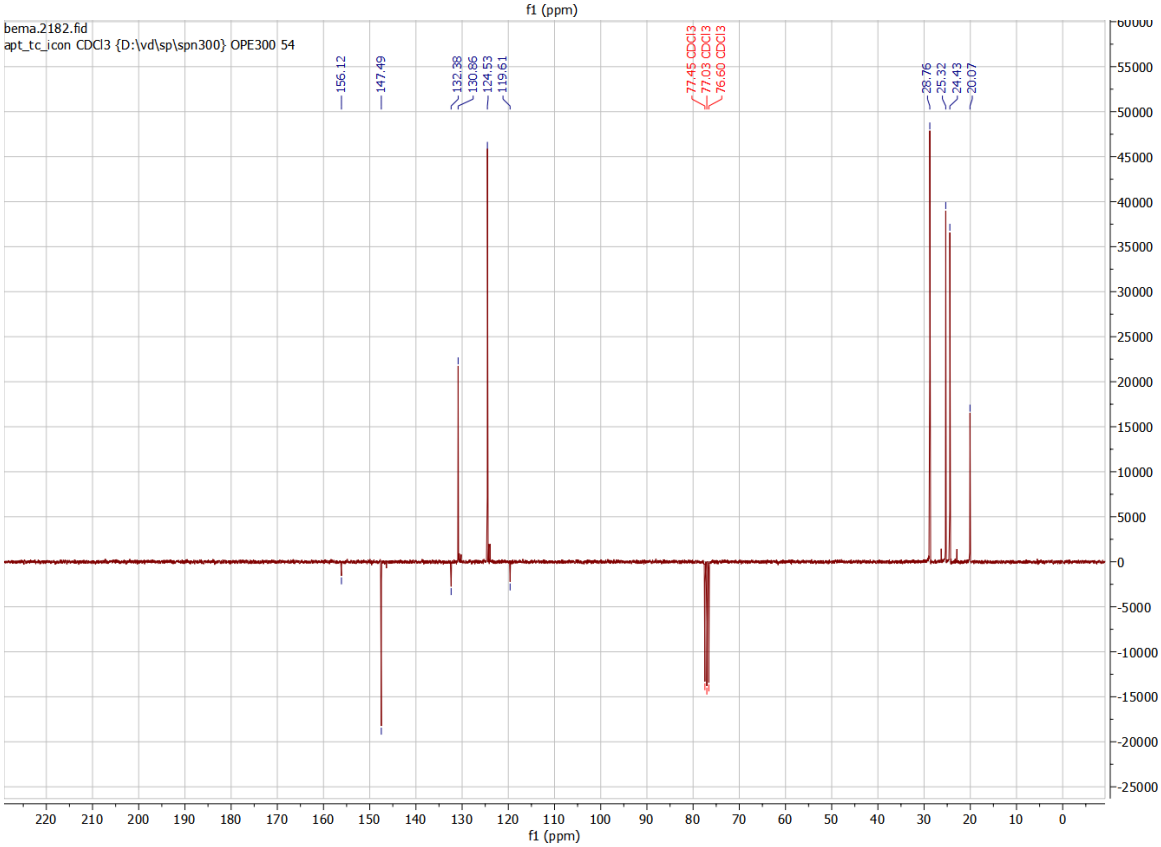
2.4. ^{1}H and $^{13}C\{^{1}H\}$ apt NMR of $[Pt(IPent)(DMS)Cl_2]$ (3ad)



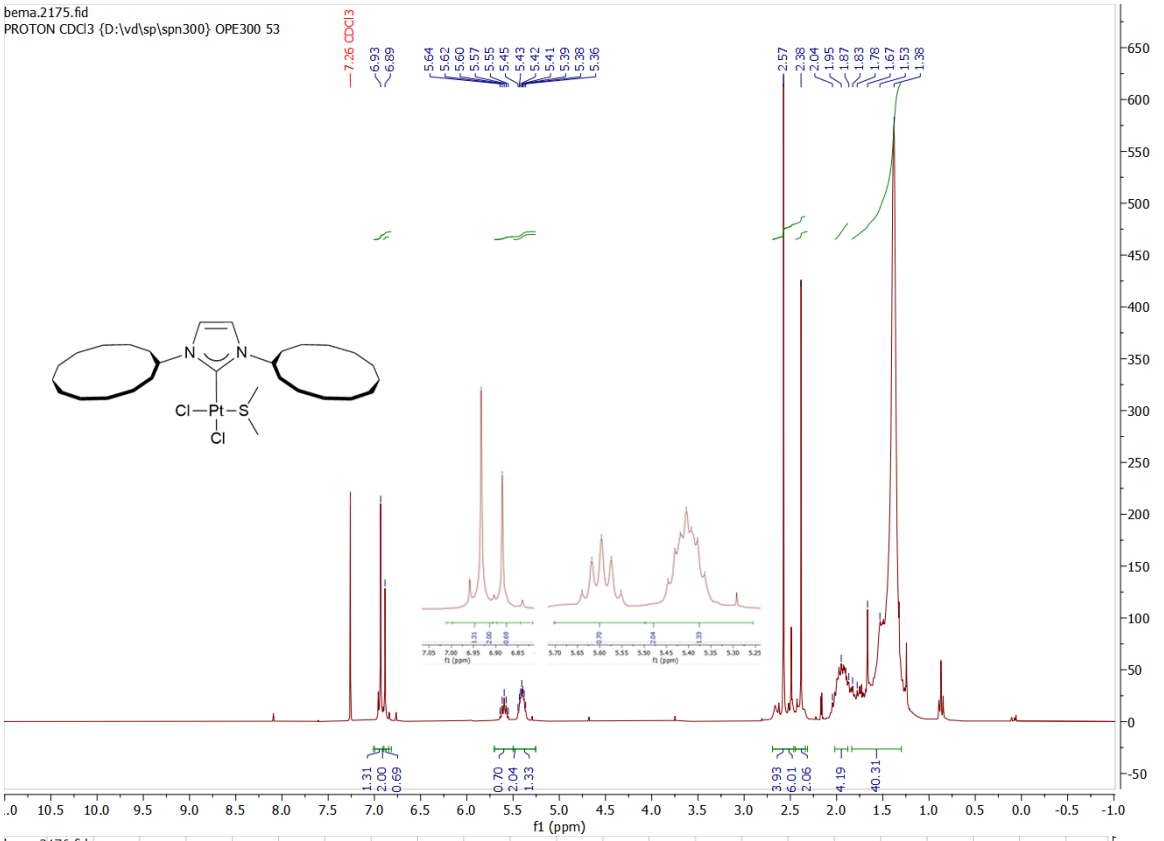


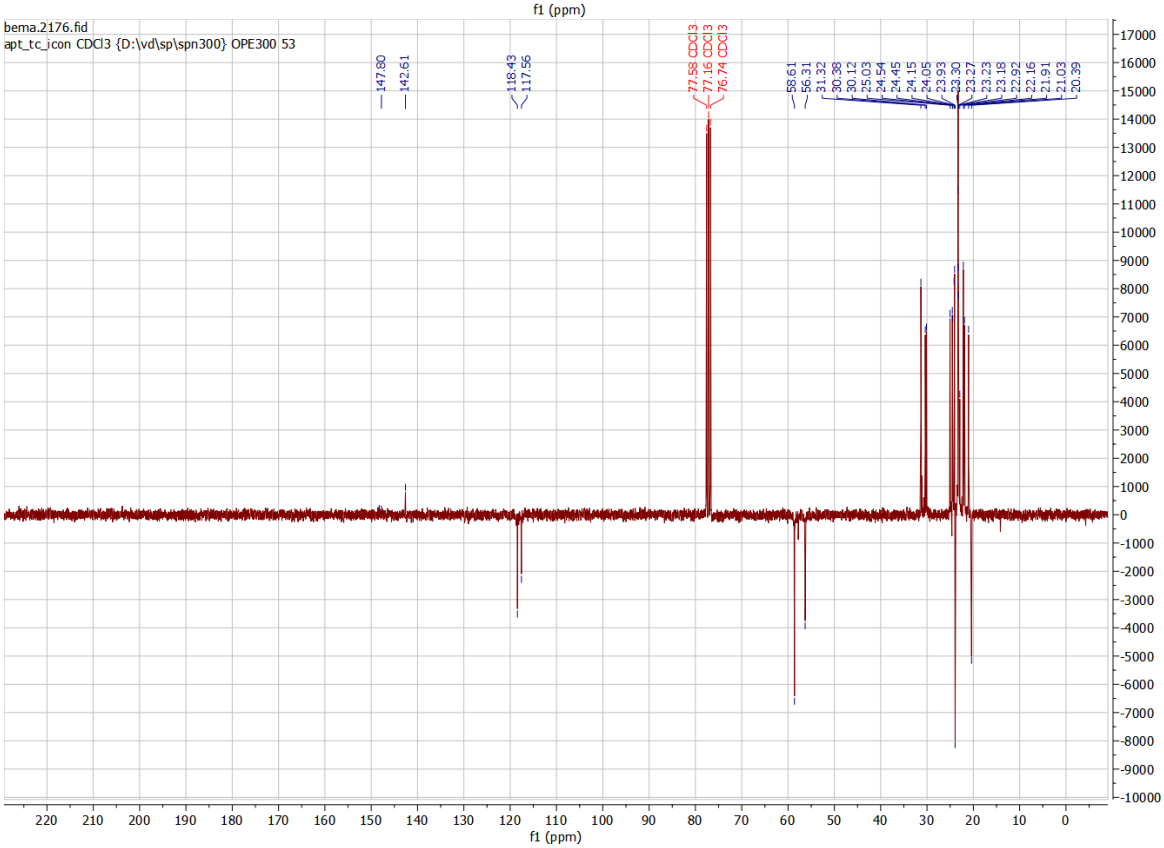
2.5. ^{1}H and $^{13}C\{^{1}H\}$ apt NMR of $[Pt(IPr^{Cl})(DMS)Cl_2]$ (3ae)



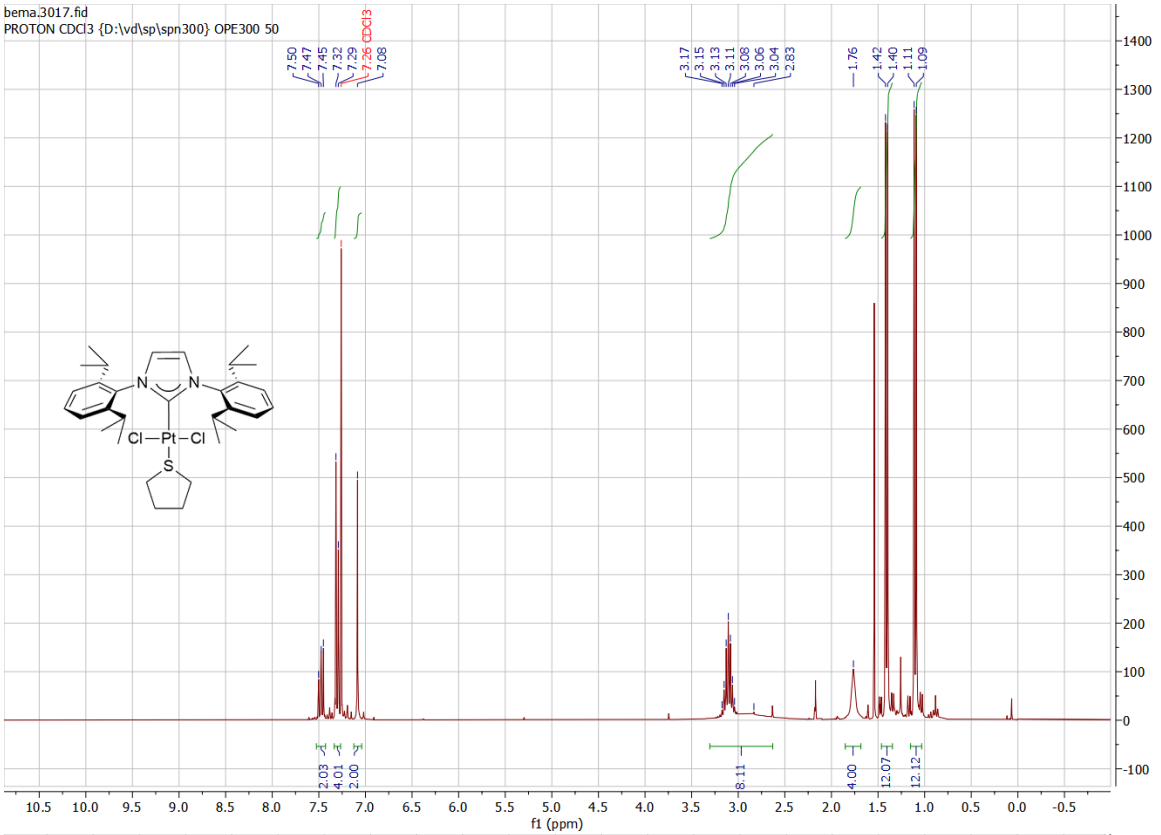


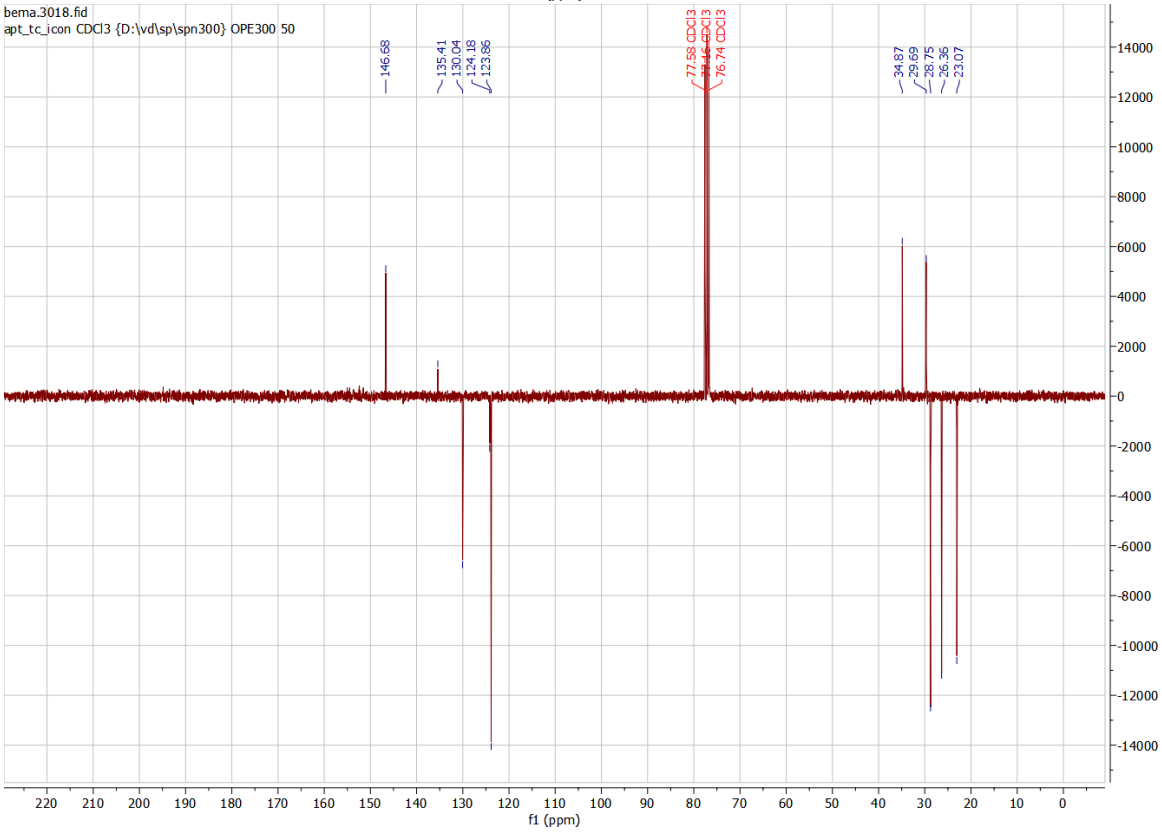
2.6. ^{1}H and $^{13}C\{^{1}H\}$ apt NMR of $[Pt(IDD)(DMS)Cl_2]$ (3af)



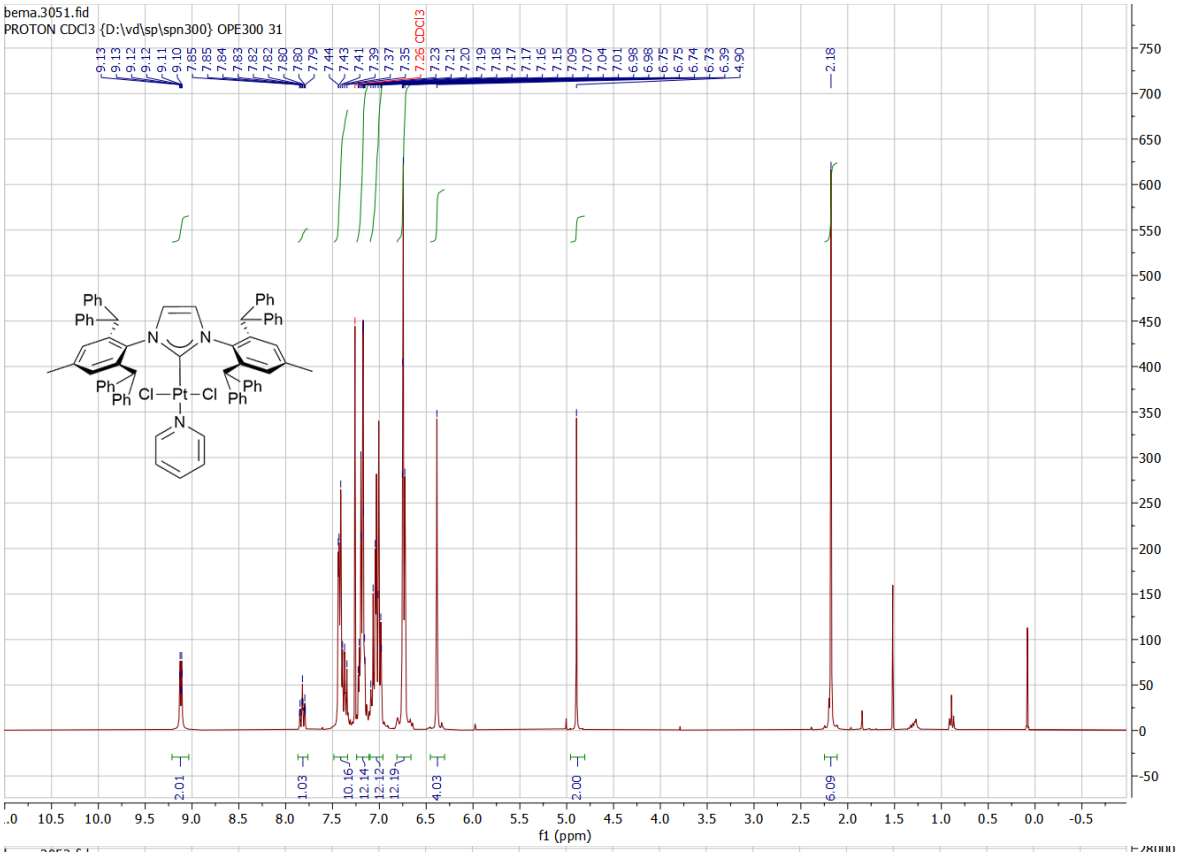


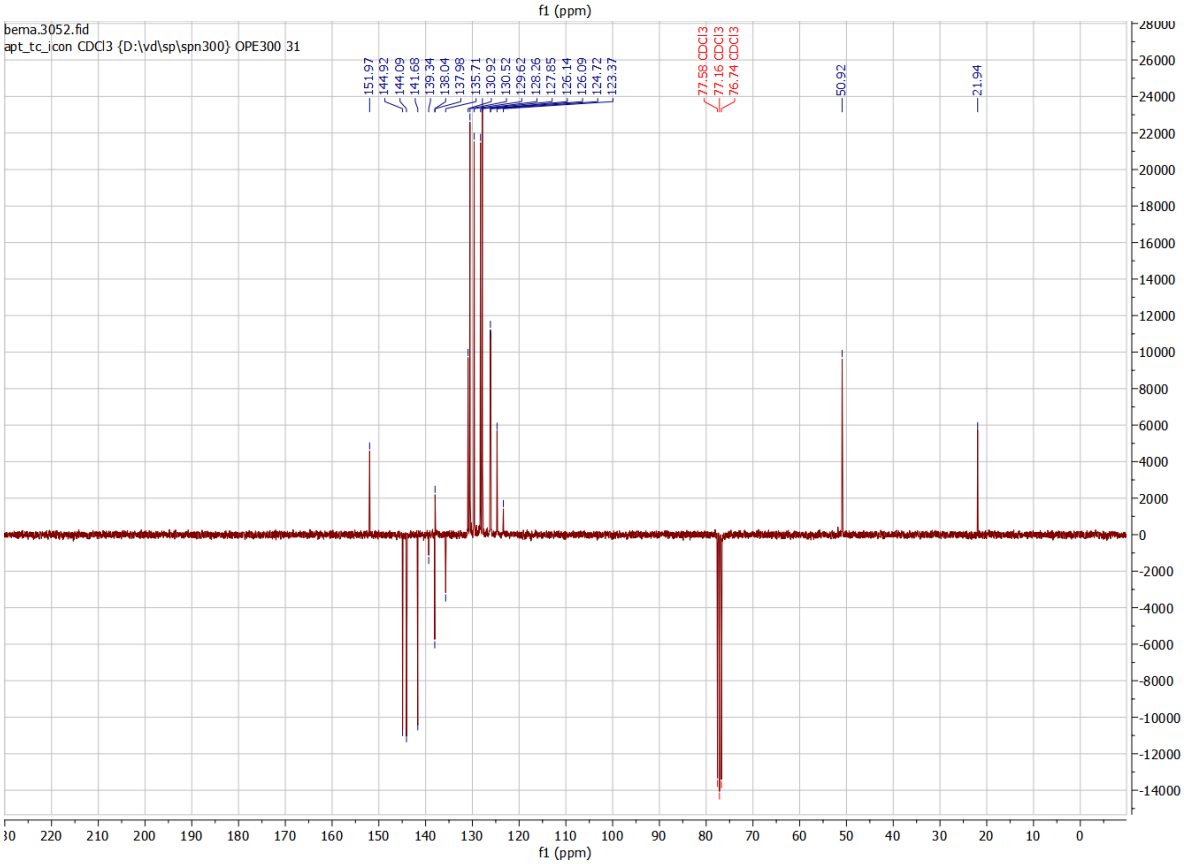
2.7. ^{1}H and $^{13}C\{^{1}H\}$ apt NMR of [Pt(IPr)(THT)Cl_2] (3bg)



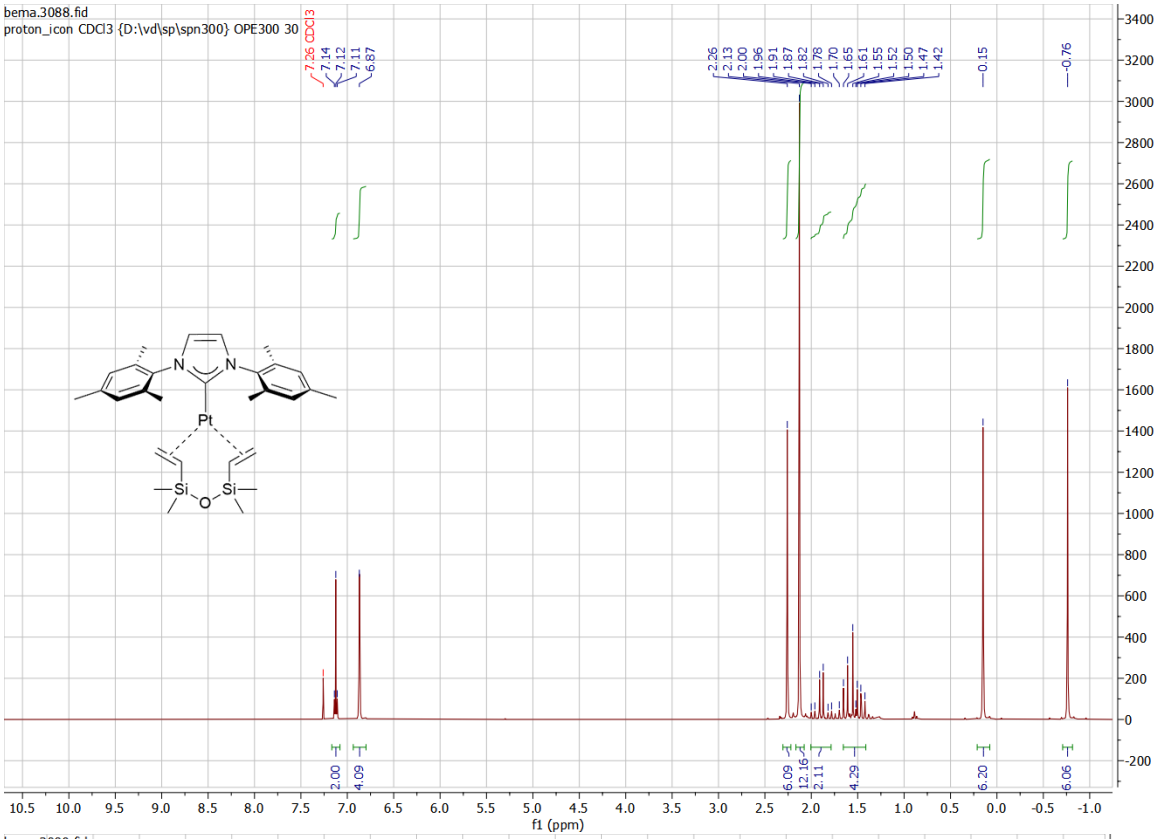


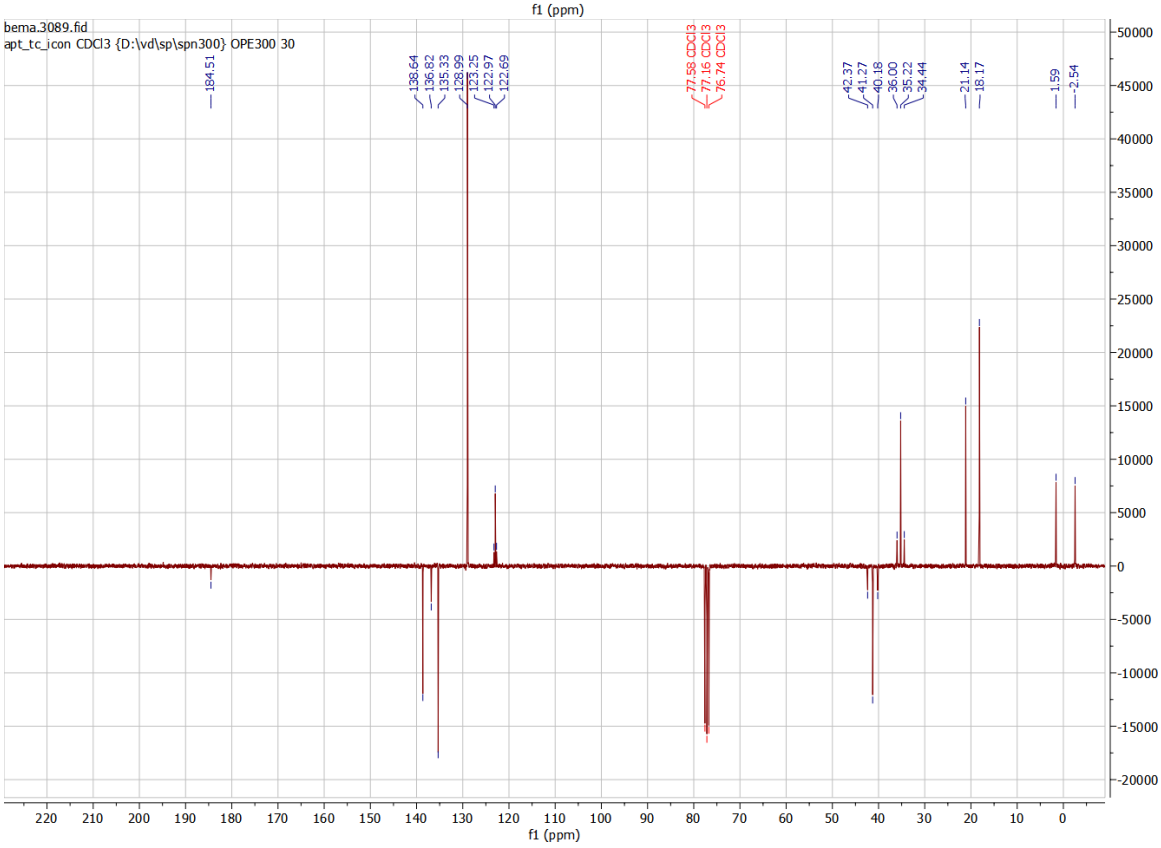
2.8. ^{1}H and $^{13}C\{^{1}H\}$ apt NMR of $[Pt(IPr^*)(Py)Cl_2]$ (3ch)



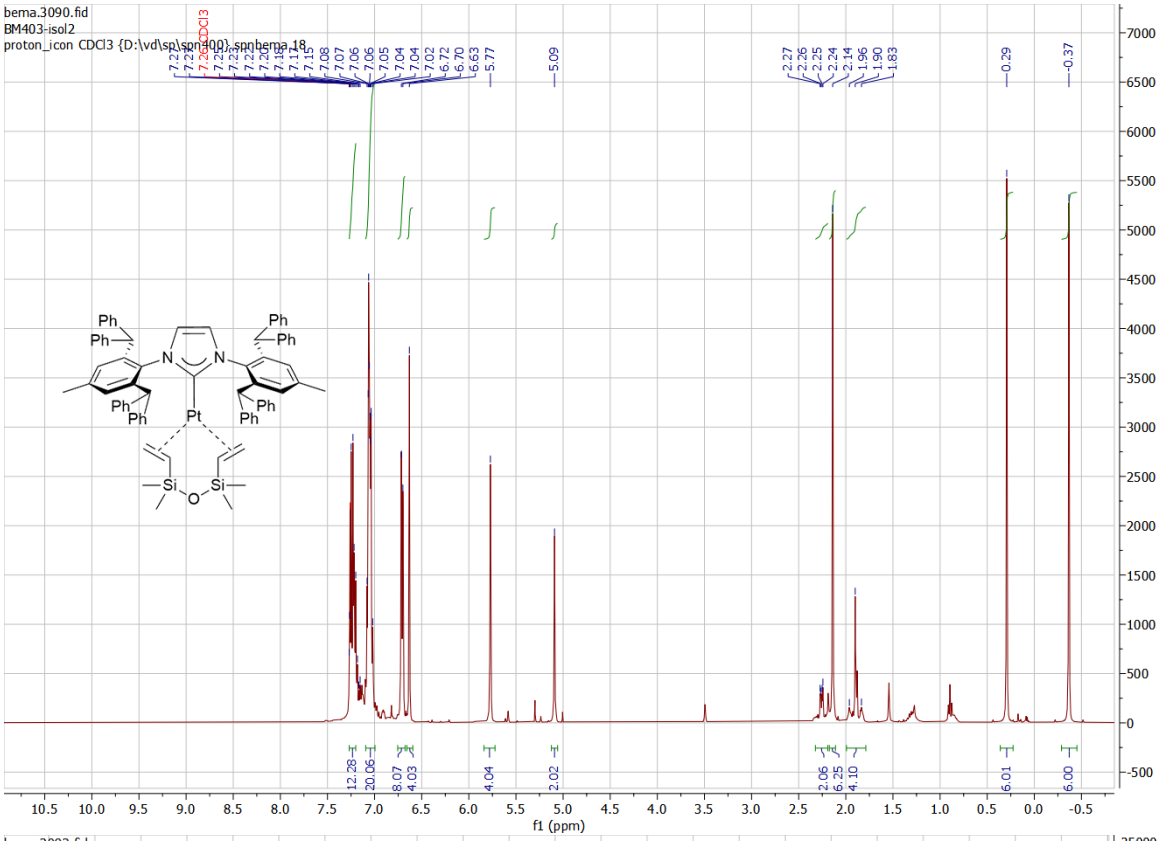


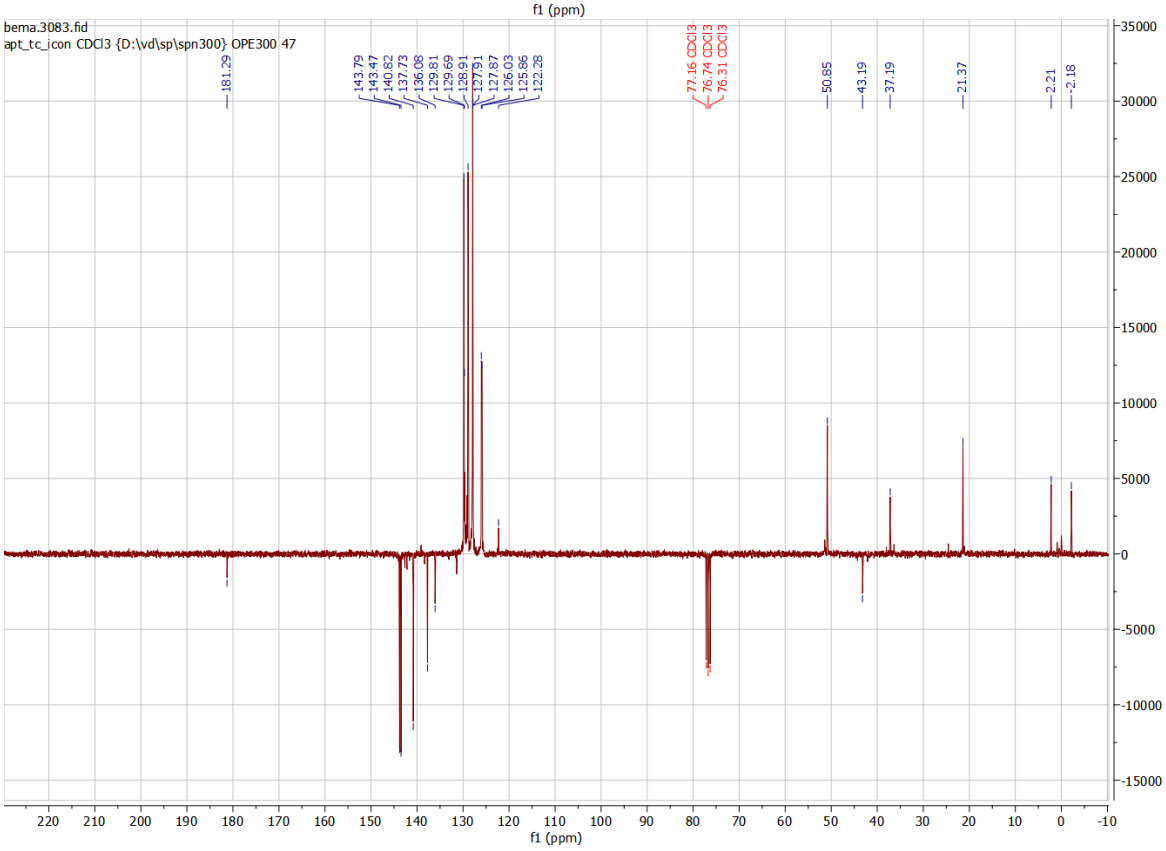
2.9. ^{1}H and $^{13}C\{^{1}H\}$ apt NMR of [Pt(IMes)(dvtms)] (5a)



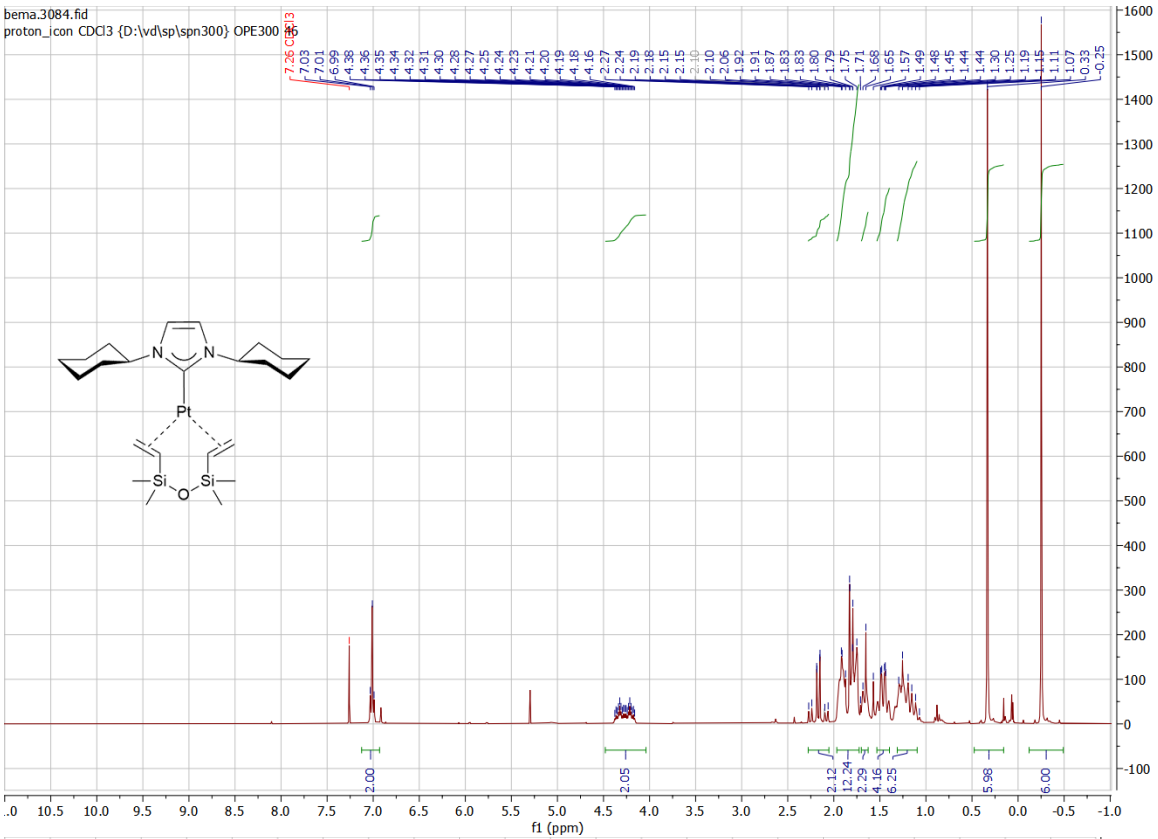


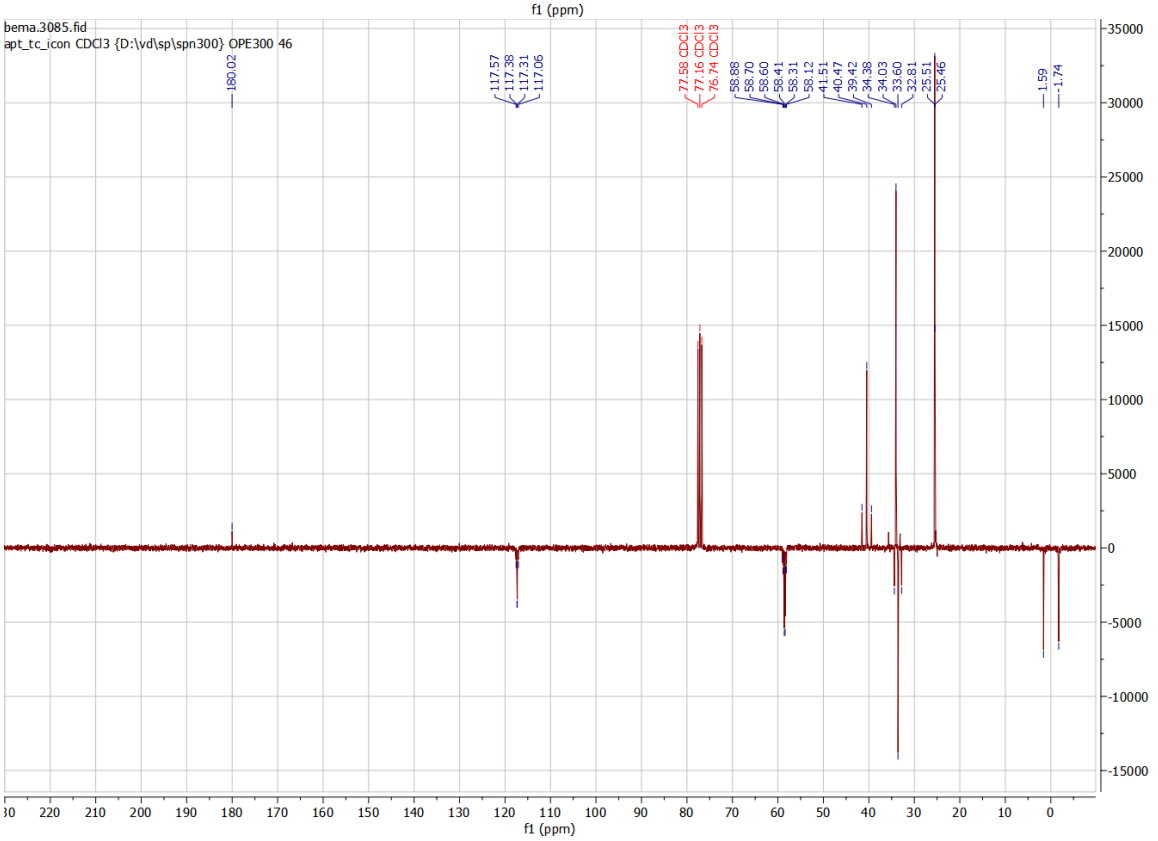
2.10. ^{1}H and $^{13}C\{^{1}H\}$ apt NMR of [Pt(IPr*)(dvtms)] (5b)





2.11. ^{1}H and $^{13}C\{^{1}H\}$ apt NMR of [Pt(ICy)(dvtms)] (5c)





3. Author Contributions

Benon P. Maliszewski: conducted the experimental work; writing/editing of manuscript.
Ida Ritacco: conducted/validated the computational work; writing/editing of manuscript.
Marek Beliš: carried out the single X-ray study.
Ishfaq Ibni Hashim: carried out the ligand and complex syntheses.
Nikolaos V. Tzouras: carried out the syntheses and assisted in manuscript assembly.
Lucia Caporaso: conducted/validated the computational work.
Luigi Cavallo: conducted and supervised/validated the computational work.
Kristof Van Hecke: supervised/validated the XRD results.
Fady Nahra: supervised the experimental work; writing/editing of manuscript
Catherine S. J. Cazin: supervised the ligand and complex syntheses work, edited manuscript, secured funding.
Steven P. Nolan: concept originator, supervised project, secured funding.