

SUPPORTING INFORMATION

Access and unprecedented reaction pathways of Li/Cl phosphinidenoid iron(0) complexes

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Table of contents

	<u>Page</u>
1) NMR spectra	S2
a. Complex 2a	S2
b. Complex 5	S3
c. Complex 6	S4
d. Complex 7	S5
e. Complex 9	S6
f. Complex 10	S7
2) Calculated energies (hartrees) and Cartesian coordinates (Å) for all computed species	S8

1) NMR spectra

a. Complex 2a

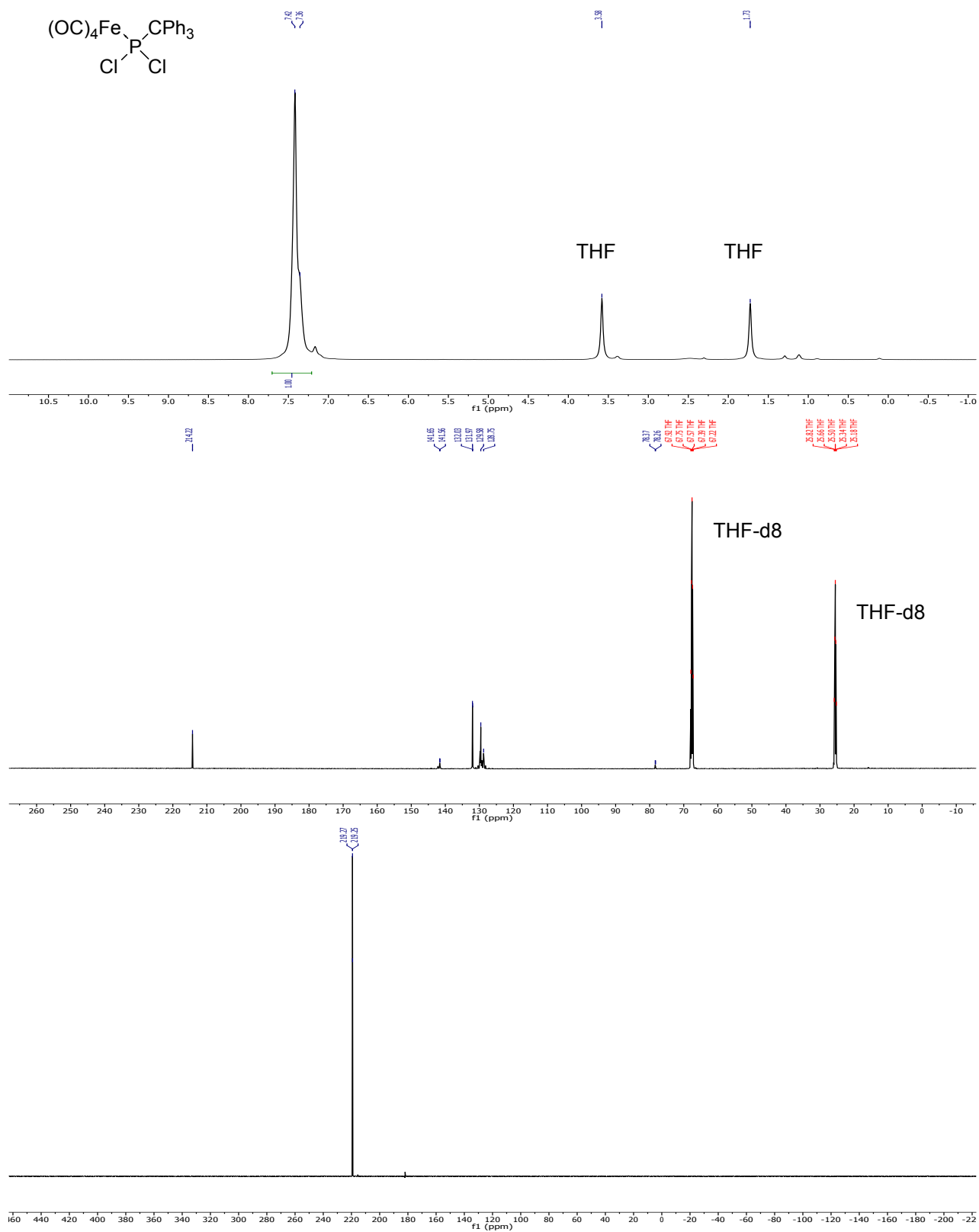


Figure 1: ^1H NMR (top), $^{13}\text{C}\{^1\text{H}\}$ NMR (mid) and ^{31}P NMR (bottom) of complex 2a in THF-d8.

b. Complex 5

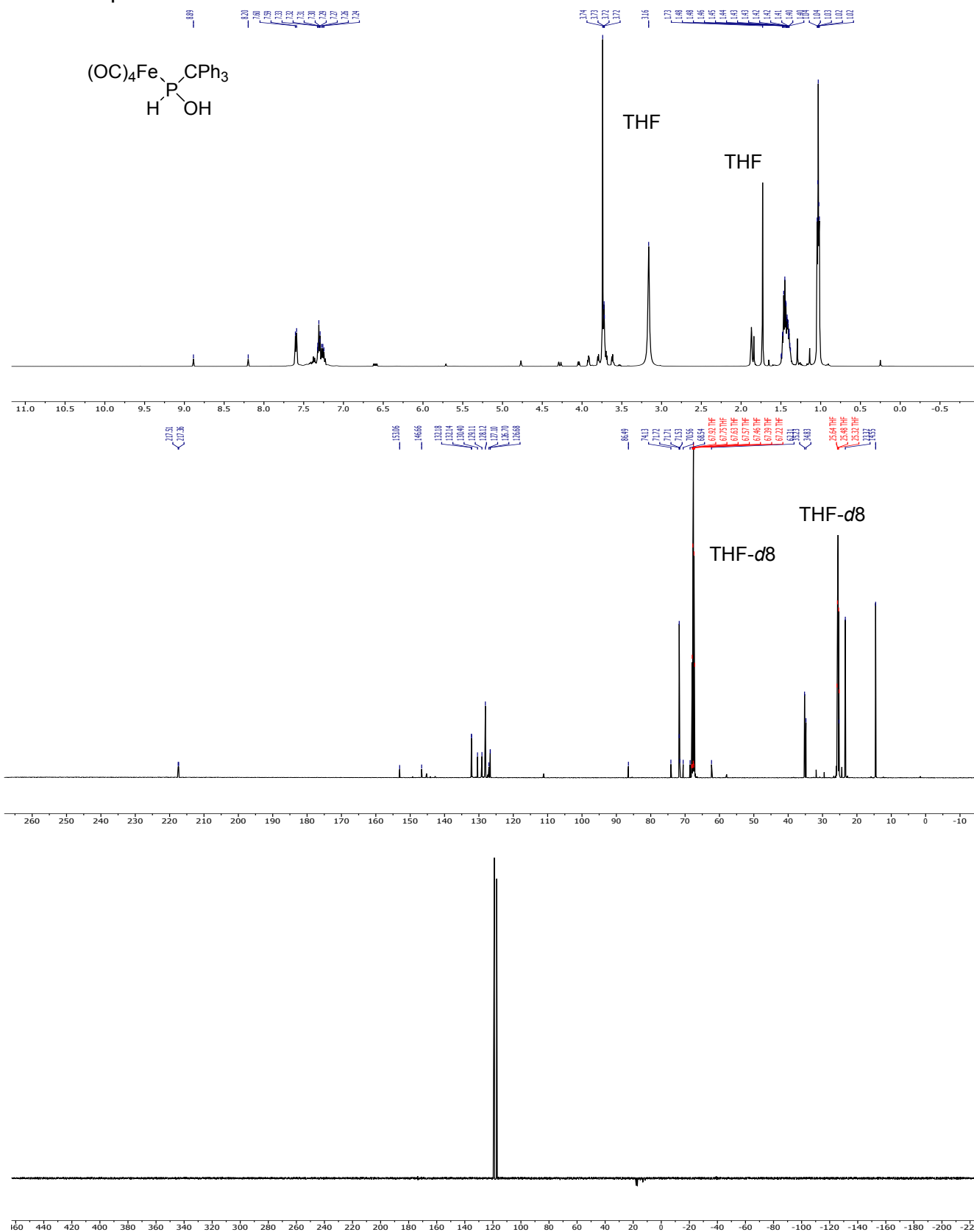
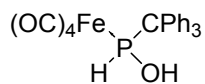


Figure 2: ¹H NMR (top), ¹³C{¹H} NMR (mid) and ³¹P NMR (bottom) of complex 5 in THF-d₈ (in solution characterization without purification).

c. Complex 6

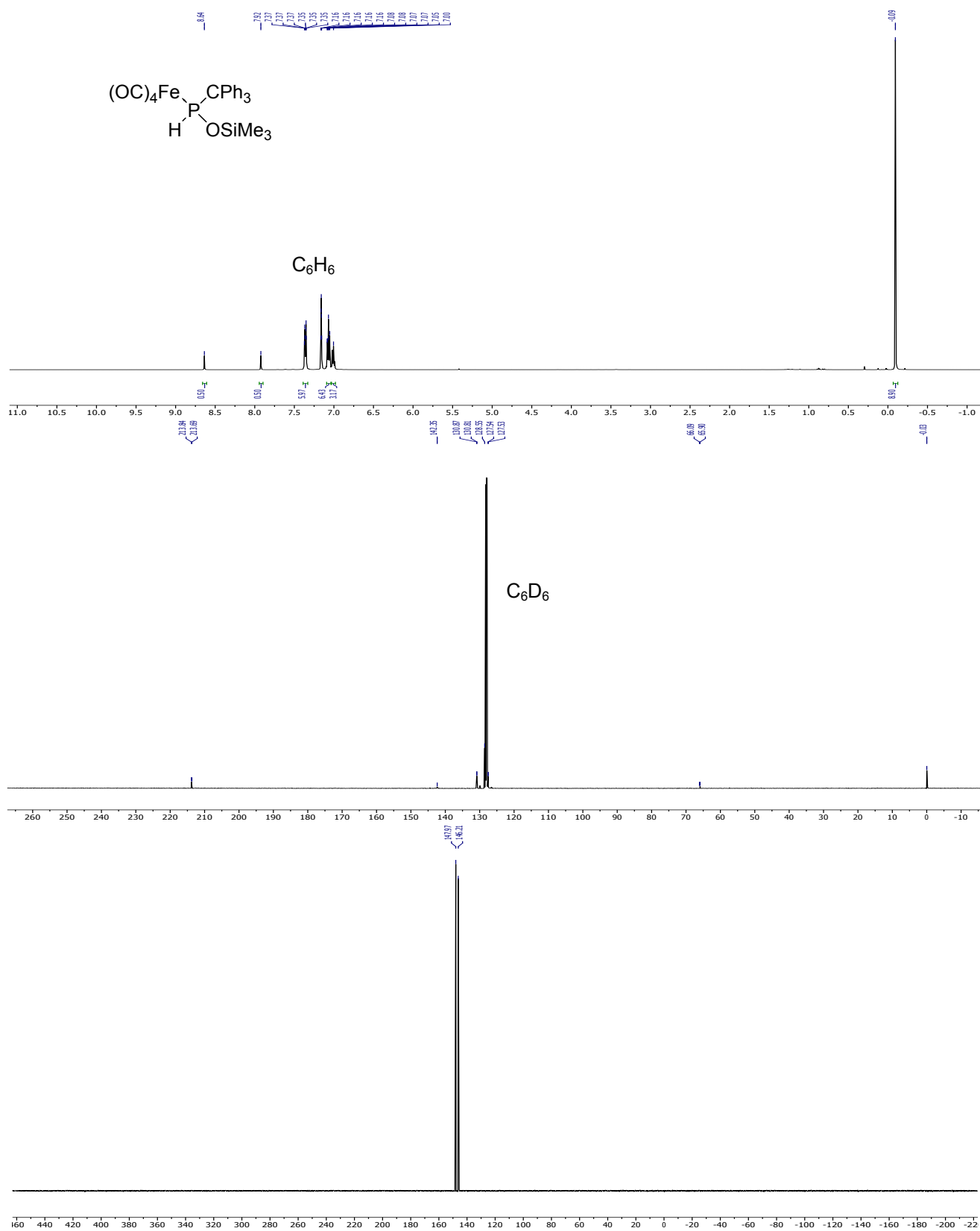


Figure 3: 1H NMR (top), $^{13}C\{^1H\}$ NMR (mid) and ^{31}P NMR (bottom) of complex 6 in C_6D_6 .

d. Complex 7

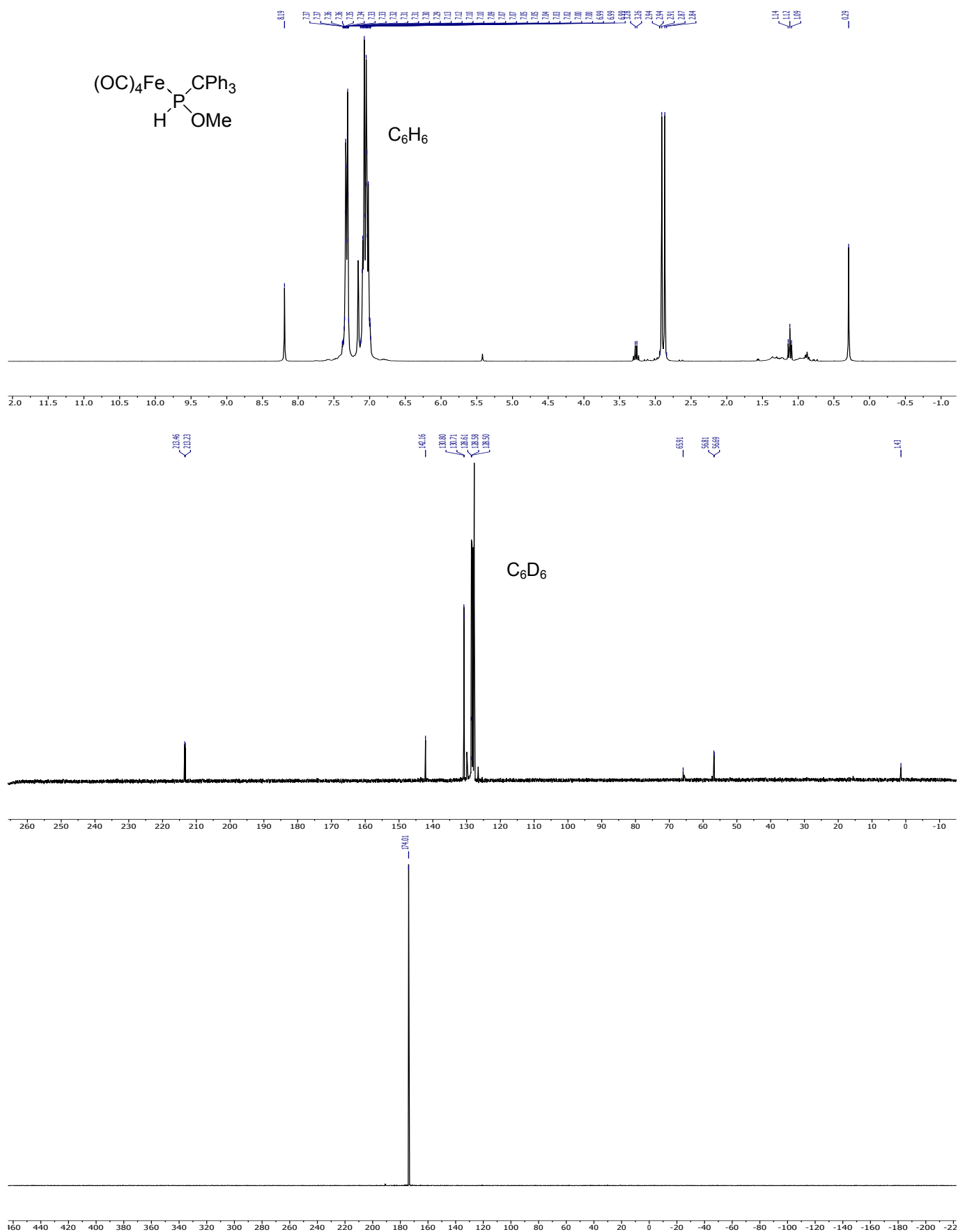


Figure 4: 1H NMR (top), $^{13}C\{^1H\}$ NMR (mid) and ^{31}P NMR (bottom) of complex 7 in C_6D_6 .

e. Complex 9

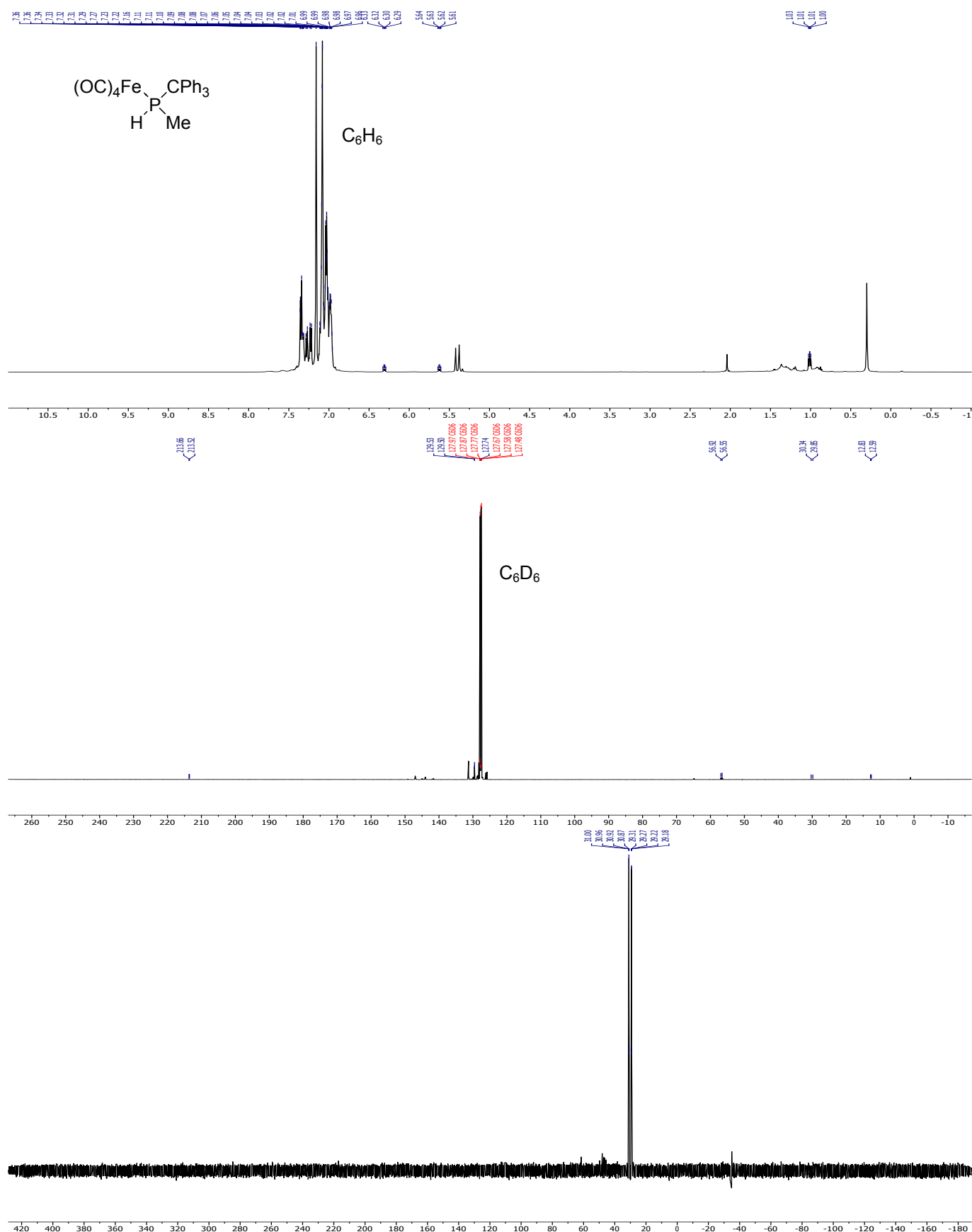


Figure 5: 1H NMR (top), $^{13}C\{^1H\}$ NMR (mid) and ^{31}P NMR (bottom) of complex 9 in C_6D_6 .

f. Complex 10

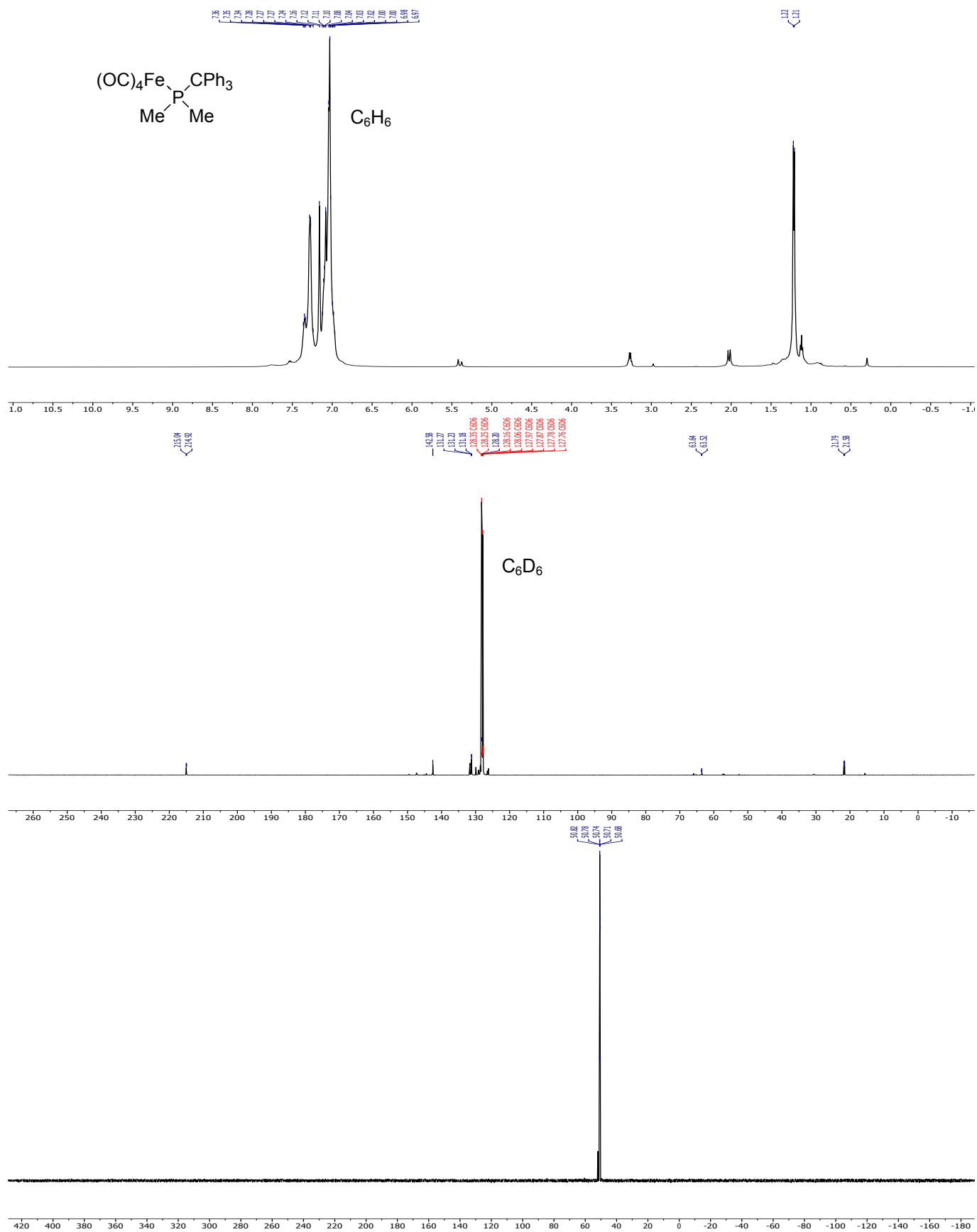


Figure 6: ¹H NMR (top), ¹³C{¹H} NMR (mid) and ³¹P NMR (bottom) of complex 10 in C₆D₆.

Calculated structures

Cartesian coordinates (in Å) and energies (in hartrees) for all computed species. Geometries and zero-point energy (ZPE) correction at the COSMO(THF)/B3LYP-D3/def2-TZVP level, whereas electronic energies are computed at the COSMO(THF)/CCSD(T)/def2-TZVPP level

2c^{ax}				E = -3133.42163610998 au			
				ZPE = 0.16087497 au			
P	0.110798	-0.277046	-0.177494	H	3.770819	-0.498563	-0.853327
C	1.931737	0.083259	0.070997	Fe	-0.766804	-2.316034	-0.101880
C	2.233637	1.577988	-0.070808	C	-1.432665	-3.985585	-0.034661
H	3.303728	1.720868	0.091252	C	-0.301443	-2.470545	1.629948
H	1.991521	1.949187	-1.065163	C	-2.395739	-1.616914	-0.420624
H	1.698261	2.173542	0.666806	C	0.192951	-2.784449	-1.551425
C	2.310785	-0.406287	1.475442	O	-1.857981	-5.042383	0.009596
H	1.746438	0.102025	2.256512	O	-0.062687	-2.602470	2.743433
H	2.174981	-1.481135	1.579317	O	-3.436290	-1.186329	-0.622830
H	3.369315	-0.189183	1.630574	O	0.752048	-3.113699	-2.496578
C	2.709372	-0.719436	-0.980721	Cl	-0.780954	1.007942	1.166768
H	2.575746	-1.791670	-0.849699	Cl	-0.291590	0.668614	-1.965921
H	2.430961	-0.446726	-1.998372				

TS(2c^{ax}→2c^{eq})				E = -3133.41692330074 au			
				ZPE = 0.16080183 au			
				ν = -35.40 cm ⁻¹			
P	0.017594	-0.335569	0.004850	H	3.539695	-0.348114	-1.180170
C	1.839269	0.086994	0.047784	Fe	-0.697011	-2.420033	-0.047788
C	2.090962	1.595627	0.074508	C	-0.293902	-2.435871	-1.806067
H	3.170034	1.760968	0.099975	C	-0.341167	-2.511455	1.718441
H	1.696076	2.087969	-0.812812	C	-0.385920	-4.187809	-0.081256
H	1.657586	2.063071	0.957442	C	-2.484406	-2.175479	-0.064273
C	2.417318	-0.578874	1.304397	O	-0.049982	-2.477454	-2.922695
H	1.983439	-0.175140	2.218874	O	-0.129280	-2.601795	2.838711
H	2.274060	-1.659033	1.289342	O	-0.191839	-5.315175	-0.102571
H	3.491263	-0.384273	1.326565	O	-3.619377	-2.046868	-0.074596
C	2.465833	-0.542872	-1.204351	Cl	-0.731220	0.740099	1.604597
H	2.322396	-1.622935	-1.225699	Cl	-0.665500	0.801910	-1.582357
H	2.066857	-0.112982	-2.122856				

2c^{eq}				E = -3133.42278273869 au			
				ZPE = 0.16148848 au			
P	0.007760	-0.274914	-0.027445	H	3.434839	-0.594006	1.368477
C	1.855181	0.011703	0.049593	C	2.447724	-0.667971	-1.193718
C	2.235682	1.491764	0.082748	H	2.195442	-1.727173	-1.237890
H	3.324723	1.565774	0.114885	H	2.115470	-0.189625	-2.114834
H	1.888309	2.018592	-0.804806	H	3.535174	-0.586996	-1.143844
H	1.837276	1.991043	0.964722	Fe	-0.783803	-2.311026	-0.055455
C	2.349275	-0.697660	1.319044	C	-0.812138	-2.339827	-1.866166
H	1.927694	-0.257146	2.222474	C	-0.750408	-2.398903	1.752809
H	2.118587	-1.762516	1.305971	C	0.413817	-3.644447	-0.100837

C	-2.581376	-2.410957	-0.025285	O	-3.722042	-2.496669	-0.005888
O	-0.826987	-2.370200	-3.004813	Cl	-0.678415	0.905061	1.540562
O	-0.727613	-2.466279	2.889976	Cl	-0.543833	0.911541	-1.641209
O	1.182440	-4.494257	-0.131077				

3c E = -3336.436534978735 au (COSMO_{THF}/B3LYPD3/def2-TZVP)

P	-0.247195	0.169992	-0.255010	C	-3.297901	0.358714	2.313199
C	1.492487	0.792658	-0.166052	H	-2.650618	0.127234	1.466725
H	1.545989	1.779849	-0.628060	H	-2.907802	-0.168052	3.188747
H	1.741624	0.888754	0.893851	O	-3.298389	1.772231	2.534558
H	2.219283	0.133005	-0.638884	C	-2.003266	2.374084	2.453507
Fe	-0.278301	-2.011347	0.605965	H	-1.473264	1.967693	1.587624
C	-0.307742	-3.645430	1.318507	H	-1.416630	2.148016	3.349177
C	-0.067022	-1.175869	2.155628	C	-2.206725	3.871177	2.337398
C	-1.917461	-2.141617	-0.075977	H	-2.602830	4.266220	3.273636
C	1.144650	-2.330831	-0.418060	H	-1.253723	4.363312	2.127662
O	-0.321861	-4.699714	1.775183	O	-3.180710	4.211372	1.345384
O	0.057137	-0.603127	3.153336	C	-2.747434	4.388628	-0.007913
O	-2.986621	-2.215286	-0.509932	H	-3.460545	5.088463	-0.444850
O	2.071287	-2.512209	-1.080380	H	-1.752912	4.840793	-0.038182
Cl	-0.378225	0.028508	-2.403871	C	-2.750376	3.090485	-0.791365
Li	-4.629858	2.705630	1.348598	H	-1.940948	2.423074	-0.484046
O	-4.005991	2.447820	-0.549147	H	-2.628825	3.304830	-1.857920
C	-4.033373	1.067171	-0.925289	O	-6.184748	3.660197	1.975220
H	-3.113789	0.586615	-0.589455	C	-7.445024	3.037197	2.214710
H	-4.089658	0.965622	-2.013285	H	-7.680965	3.054855	3.282957
C	-5.261463	0.449177	-0.287521	H	-8.234916	3.554561	1.662460
H	-6.162101	0.848327	-0.755199	H	-7.365554	2.008885	1.872138
H	-5.245645	-0.634113	-0.420846	C	-6.154830	5.020575	2.402028
O	-5.378372	0.786458	1.100123	H	-6.330555	5.084316	3.480024
C	-4.731537	-0.059440	2.057863	H	-5.168233	5.410519	2.166014
H	-5.316793	0.042953	2.972363	H	-6.919358	5.600299	1.876759
H	-4.763869	-1.102791	1.736446				

3c^{an} E = -2556.06004939981 au
ZPE = 0.07315457 au

P	0.076436	-0.784213	0.330966	C	-1.380775	-0.526998	-2.075311
C	-0.041917	-0.966871	2.171188	C	-2.578771	-1.860055	0.460227
H	0.929185	-1.268008	2.567962	O	-4.812732	0.094031	-1.482543
H	-0.292147	0.018349	2.573055	O	-1.915443	2.124993	1.014915
H	-0.800844	-1.680538	2.490423	O	-0.896501	-0.603470	-3.120619
Fe	-2.115417	-0.405933	-0.451917	O	-2.863610	-2.799654	1.068712
C	-3.752261	-0.099151	-1.078456	Cl	0.525953	-2.867283	-0.090197
C	-1.994136	1.128444	0.431960				

2 H₂O E = -152.696957702446 au
ZPE = 0.04550079 au

O	-0.116705	-0.145633	-0.096569	O	-0.182809	0.426495	2.680611
H	-0.131935	0.044964	0.860645	H	-0.665261	1.247465	2.840544
H	0.813833	-0.271494	-0.313395	H	-0.660796	-0.248113	3.179243

4 H₂O

E = -305.408561072082 au

ZPE = 0.09638748 au

O	-0.134779	-0.074689	-0.018949	O	-1.527102	2.710597	2.274239
H	-0.082254	-0.020124	0.964635	H	-1.455564	2.717479	1.290377
H	0.767792	-0.220371	-0.326066	H	-1.080826	3.510159	2.577505
O	-0.150648	0.377105	2.681317	O	-1.135594	2.443327	-0.422779
H	-0.650305	1.227421	2.658644	H	-0.769786	1.527601	-0.409197
H	-0.693478	-0.235658	3.191497	H	-1.927906	2.406137	-0.971442

3c-2H₂O

E = -3485.384114547907 au

ZPE = 0.45485857 au

P	0.199315	-0.636457	-0.386829	O	-4.125938	-2.583586	-4.092824
C	1.601029	-1.843090	-0.397638	C	-4.394413	-3.219841	-2.842708
H	2.461127	-1.384007	-0.887445	H	-3.866129	-2.688394	-2.048552
H	1.858323	-2.029610	0.647457	H	-4.038522	-4.254480	-2.850632
H	1.368523	-2.789786	-0.883346	C	-5.895282	-3.193789	-2.633009
Fe	-1.705494	-1.820210	0.373460	H	-6.380202	-3.857023	-3.349761
C	-3.266260	-2.571324	0.774878	H	-6.137454	-3.533047	-1.623070
C	-2.375721	-0.179501	0.405220	O	-6.452279	-1.898009	-2.879208
C	-1.344291	-2.967440	-0.936719	C	-6.531109	-0.979070	-1.784825
C	-0.816503	-2.261279	1.843306	H	-7.342796	-0.297559	-2.041134
O	-4.292423	-3.045296	0.992113	H	-6.791354	-1.500536	-0.860547
O	-2.754706	0.915090	0.471333	C	-5.244240	-0.202369	-1.598023
O	-1.079217	-3.729290	-1.761823	H	-4.444679	-0.838366	-1.213906
O	-0.258545	-2.560521	2.809275	H	-5.399327	0.613109	-0.885630
Cl	0.000796	-0.475070	-2.561796	O	-6.603497	-0.638167	-5.761015
Li	-5.311461	-0.966505	-4.368807	C	-6.332233	0.124720	-6.935721
O	-4.864291	0.308609	-2.876498	H	-6.581039	-0.454530	-7.829623
C	-3.506118	0.752909	-2.951914	H	-6.916781	1.049451	-6.930721
H	-2.851813	0.011150	-2.490877	H	-5.270912	0.357580	-6.930441
H	-3.378608	1.696301	-2.413090	C	-7.975514	-1.013101	-5.655590
C	-3.183044	0.952079	-4.419316	H	-8.267465	-1.628946	-6.511137
H	-3.730297	1.812403	-4.805855	H	-8.084386	-1.582001	-4.735831
H	-2.112845	1.131049	-4.543464	H	-8.611104	-0.123368	-5.618019
O	-3.606902	-0.156763	-5.221375	O	1.405352	0.090432	2.922671
C	-2.682933	-1.234373	-5.413621	H	0.652150	0.681602	2.733076
H	-2.974547	-1.697479	-6.356784	H	1.009664	-0.755767	3.160025
H	-1.663080	-0.854670	-5.509438	O	-0.669945	1.993945	2.483402
C	-2.747970	-2.249646	-4.292254	H	-1.321533	1.754605	1.809531
H	-2.331950	-1.844883	-3.369724	H	-0.211558	2.763127	2.122742
H	-2.170895	-3.139313	-4.560384				

TS(3c-2H₂O→Cl-replacement)

E = -3485.351818464285 au

ZPE = 0.45393353 au

v = -100.38 cm⁻¹

P	-0.382271	-0.480287	0.281137	C	-0.359385	-2.435767	-1.692900
C	1.437139	-0.448795	-0.039277	C	0.119349	-3.181000	1.110919
H	1.839856	0.520642	0.252104	O	-2.230402	-5.257203	-0.693685
H	1.946665	-1.245263	0.500666	O	-3.688165	-1.602246	0.821390
H	1.599928	-0.577136	-1.107775	O	0.096454	-2.349694	-2.749953
Fe	-1.075504	-2.624724	-0.082797	O	0.895961	-3.544435	1.879547
C	-1.771977	-4.235536	-0.441347	Cl	-0.366260	1.660289	-1.734932
C	-2.665816	-2.001981	0.463149	Li	-5.347074	-0.973704	-4.243762

O	-4.871950	0.361593	-2.839397	C	-6.982351	-0.315774	-1.998755
C	-3.454391	0.471142	-2.659177	H	-7.548481	0.457346	-2.519100
H	-3.107623	-0.327777	-1.999018	H	-7.530735	-0.603639	-1.098487
H	-3.187050	1.421370	-2.195465	C	-5.608952	0.212130	-1.628375
C	-2.820495	0.375568	-4.032791	H	-5.082135	-0.472811	-0.960541
H	-3.023643	1.285044	-4.598616	H	-5.708311	1.173079	-1.113536
H	-1.741521	0.260020	-3.929472	O	-6.317492	-0.593513	-5.869070
O	-3.387473	-0.689963	-4.813208	C	-5.696493	-0.029296	-7.022920
C	-2.753465	-1.970049	-4.758545	H	-5.951226	-0.611505	-7.913144
H	-3.039314	-2.473145	-5.683192	H	-6.023555	1.005395	-7.162146
H	-1.667250	-1.863958	-4.737964	H	-4.622908	-0.057632	-6.856606
C	-3.217615	-2.781436	-3.566123	C	-7.739739	-0.619025	-5.969354
H	-2.846541	-2.361950	-2.629758	H	-8.049078	-1.228885	-6.822975
H	-2.851754	-3.809695	-3.645111	H	-8.120297	-1.051529	-5.047719
O	-4.647604	-2.756218	-3.561987	H	-8.131353	0.395502	-6.090678
C	-5.238984	-3.083851	-2.305903	O	0.184026	-0.279450	2.423442
H	-4.736438	-2.526790	-1.512141	H	0.166559	0.707497	2.352433
H	-5.131849	-4.152040	-2.092252	H	-0.579606	-0.524733	2.964924
C	-6.709779	-2.723882	-2.392218	O	0.038030	2.351467	1.541468
H	-7.212382	-3.396431	-3.087887	H	-0.135541	2.206008	0.587446
H	-7.178080	-2.823180	-1.409994	H	0.785498	2.960756	1.578521
O	-6.912475	-1.409224	-2.919531				

3c^{an}·2H₂O

E = -2708.76476188413 au

ZPE = 0.12129779 au

P	0.436289	-0.007835	-0.293798	O	0.285821	-2.320470	2.447291
C	2.257860	-0.317218	-0.282709	O	-3.069633	-0.503413	-0.907050
H	2.787713	0.633150	-0.361527	O	1.204272	-2.818390	-2.465491
H	2.490082	-0.767369	0.685955	Cl	0.332352	0.777825	-2.329520
H	2.593506	-0.988752	-1.071985	O	-0.052727	3.032130	1.104334
Fe	-0.651658	-2.074640	-0.322079	H	0.087973	2.088184	0.896004
C	-1.487175	-3.649037	-0.322141	H	-0.417915	3.385408	0.272826
C	-0.092432	-2.218942	1.360074	O	-1.012958	3.667236	-1.535152
C	-2.128478	-1.127265	-0.671251	H	-0.626814	2.853213	-1.901729
C	0.463814	-2.534325	-1.626401	H	-1.967296	3.526086	-1.555275
O	-2.013558	-4.671206	-0.330545				

TS(3c^{an}·2H₂O→5c+H₂O·Cl)

E = -2708.72756443543 au

ZPE = 0.11751566 au

v = -137.64 cm⁻¹

P	0.149276	0.129189	-0.814388	O	-0.823329	-1.313759	2.387915
C	1.761180	0.264608	0.006311	O	-3.025325	-0.752337	-2.346414
H	2.225832	1.219695	-0.233158	O	1.281378	-3.240819	-1.726315
H	1.584744	0.207141	1.080267	Cl	0.671726	0.474071	-2.809251
H	2.405147	-0.558012	-0.300980	O	-0.918553	1.909976	1.375577
Fe	-0.967769	-1.788928	-0.512270	H	-0.493401	1.316828	-0.415672
C	-1.913150	-3.281077	-0.212378	H	-0.570301	1.378931	2.100019
C	-0.890160	-1.461601	1.251011	O	-3.270563	1.057934	0.876333
C	-2.232568	-1.146023	-1.615455	H	-3.124543	0.159934	0.560102
C	0.402486	-2.674651	-1.248703	H	-2.314882	1.401349	1.107143
O	-2.519420	-4.230310	-0.012882				

5c E = -2172.55766031867 au
ZPE = 0.09674147 au

P	-0.023053	-0.048016	0.023980	C	-2.660746	-1.076277	-0.098496
C	-0.005220	0.175989	1.815268	O	-4.422369	0.758482	-2.549622
H	1.013086	0.076641	2.192214	O	-1.984118	2.973290	0.031148
H	-0.395539	1.162671	2.063209	O	-0.572495	-0.563211	-3.545581
H	-0.639005	-0.584739	2.272626	O	-3.127193	-1.923541	0.520209
Fe	-1.936763	0.244625	-1.066301	O	1.187831	0.930773	-0.448936
C	-3.459523	0.552889	-1.971527	H	0.985484	1.397574	-1.270539
C	-1.960605	1.910010	-0.403376	H	0.552429	-1.324398	-0.113136
C	-1.094159	-0.239046	-2.574993				

H₂O·Cl⁻ E = -536.232081606334 au
ZPE = 0.02277805 au

Cl	-0.059867	0.078827	1.597736	H	1.737170	0.793680	-1.289979
O	1.785459	1.412159	-0.552466	H	1.198151	1.017235	0.133500

3c^{an}·4H₂O E = -2861.47432376892 au
ZPE = 0.170505759 au

P	0.050114	-0.796091	0.356459	Cl	0.539979	-2.872939	-0.085826
C	-0.046397	-0.983595	2.190214	O	-0.538625	4.026464	-1.316486
H	0.930726	-1.274343	2.578396	H	-0.875398	3.537491	-0.556430
H	-0.303916	-0.000334	2.592062	H	-0.050370	3.369853	-1.855784
H	-0.797469	-1.703154	2.514083	O	0.842335	2.213997	-2.947622
Fe	-2.110589	-0.419098	-0.450233	H	1.451439	1.633605	-2.432812
C	-3.761211	-0.122325	-1.063461	H	0.195814	1.612154	-3.336953
C	-1.977122	1.138334	0.384001	O	2.455376	0.504567	-1.511843
C	-1.389507	-0.492868	-2.070184	H	1.869415	0.265390	-0.762217
C	-2.586010	-1.875959	0.467291	H	2.434701	-0.299632	-2.068928
O	-4.824758	0.062402	-1.453882	O	1.860982	-1.881791	-2.951842
O	-1.866165	2.167796	0.900592	H	1.544993	-2.382264	-2.180978
O	-0.900887	-0.508950	-3.121036	H	1.051739	-1.597221	-3.398038
O	-2.869769	-2.815234	1.071885				

TS(3c^{an}·4H₂O→5c+(H₂O)₃·Cl⁻) E = -2861.44757632792 au
ZPE = 0.1630587 au
ν = -462.70 cm⁻¹

P	-0.209129	-0.887606	0.196110	Cl	0.184570	-2.768436	1.043168
C	0.219556	0.196944	1.582812	O	0.559689	3.546714	0.330226
H	1.215664	-0.044175	1.951010	H	-0.384865	3.672307	0.472198
H	0.198861	1.226554	1.227788	H	0.614726	2.813455	-0.343911
H	-0.514771	0.062140	2.376251	O	0.646342	1.514420	-1.374030
Fe	-2.278504	-0.783589	-0.671051	H	1.485936	0.785332	-1.711740
C	-3.891316	-0.724418	-1.448659	H	0.044651	1.620513	-2.117809
C	-2.261620	1.001459	-0.476732	O	2.315422	-0.116297	-2.016946
C	-1.576522	-1.611146	-2.095837	H	0.906831	-0.852257	-0.654104
C	-2.921081	-1.695602	0.734026	H	3.211839	0.221353	-1.918585
O	-4.918839	-0.688215	-1.949640	O	1.681173	-1.241231	-4.328357
O	-2.317689	2.138666	-0.331301	H	1.953752	-0.809902	-3.464709
O	-1.109420	-2.145632	-3.000933	H	0.826477	-1.644550	-4.141580
O	-3.352311	-2.280547	1.622765				

(H₂O)₃·Cl⁻

E = -688.944156270946 au

ZPE = 0.07284086 au

Cl	-0.077414	-0.043228	1.552727	H	3.044143	-0.095891	0.445183
O	1.870685	1.398855	-0.596154	H	2.084916	-0.818544	1.366417
H	1.628434	0.682592	-1.205164	O	0.899149	-1.375288	-1.217130
H	1.239209	1.263682	0.137382	H	1.724070	-1.593256	-0.753963
O	2.949178	-0.934996	0.923967	H	0.332975	-1.060542	-0.484937