Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary information for

Seven-coordinate lanthanide complexes with a tripodal redox active ligand: Structural, electrochemical and spectroscopic investigations

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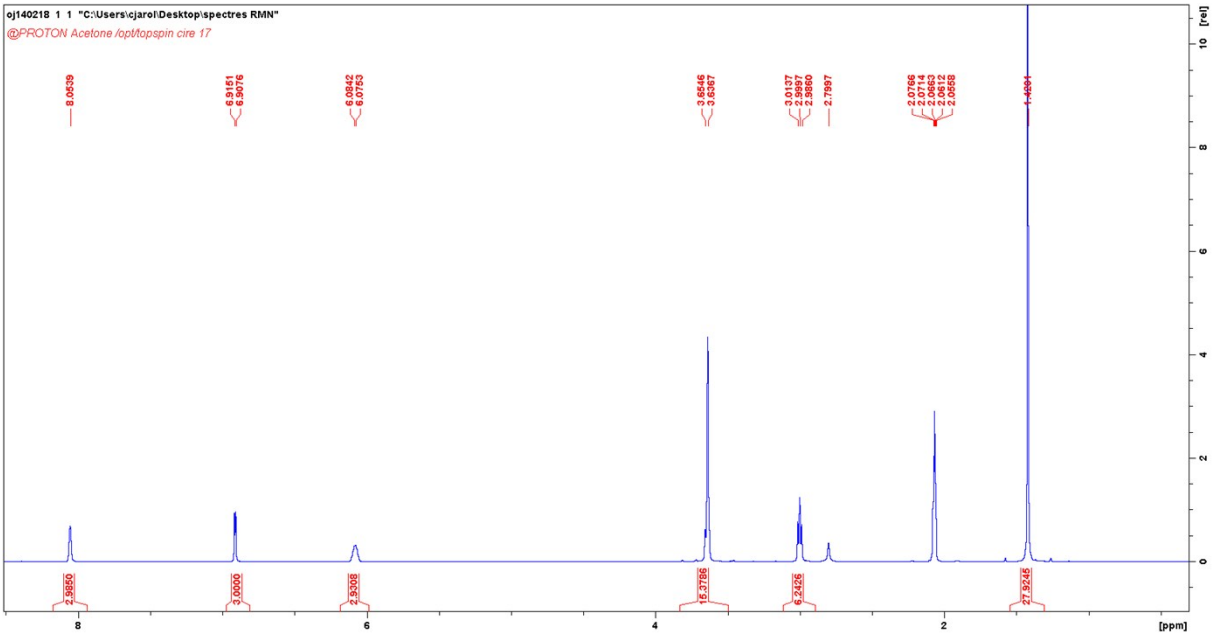

Figure S1. ^{1}H NMR spectrum (400 MHz, acetone d_6) of H_3L

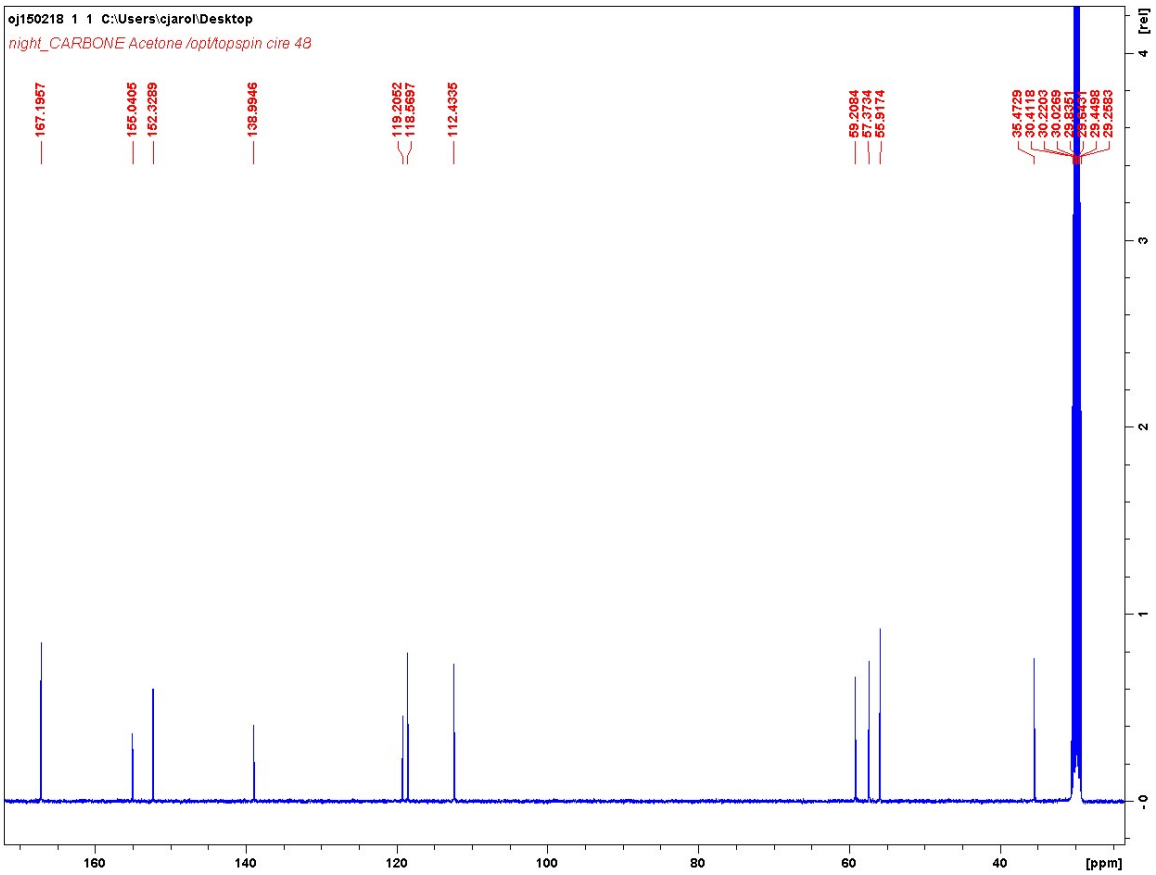

Figure S2. ^{13}C NMR spectrum (100 MHz, acetone d_6) of H_3L

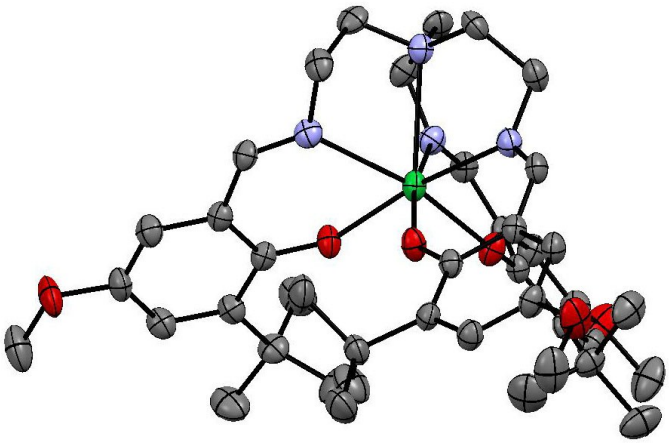

Figure S3. X-Ray crystal structure of complex **L-Yb** shown with thermal ellipsoids. Symmetry operations: -y, x-y, z, x+y, -x, z.

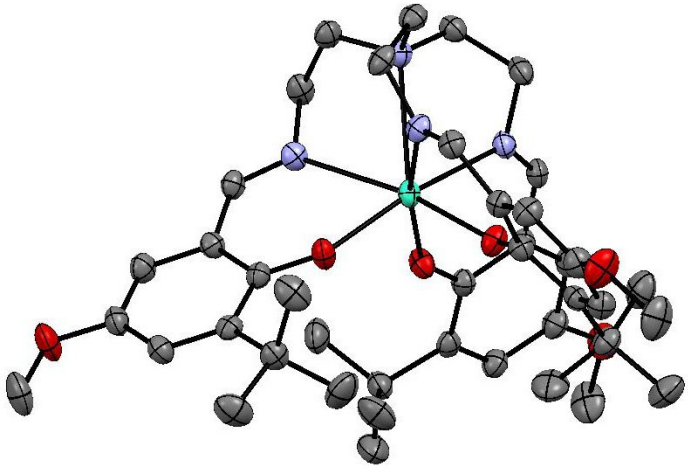

Figure S4. X-Ray crystal structure of complex **L-Tb** shown with thermal ellipsoids. Symmetry operations: -y, x-y, z, x+y, -x, z.

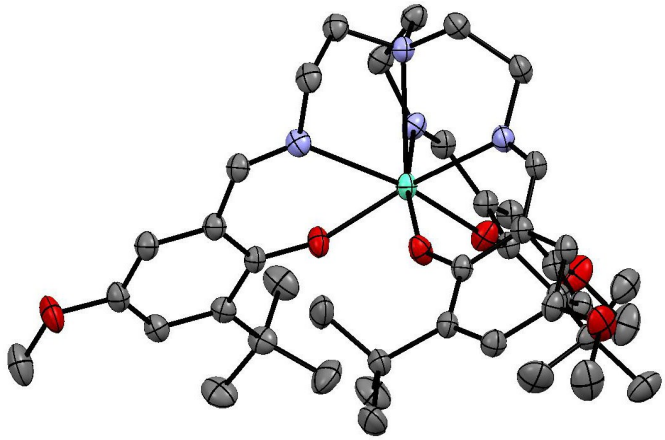

Figure S5. X-Ray crystal structure of complex **L-Eu** shown with thermal ellipsoids. Symmetry operations: -y, x-y, z, x+y, -x, z.

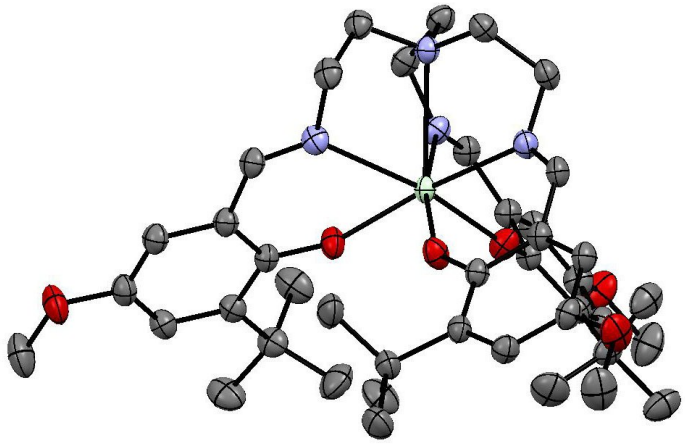

Figure S6. X-Ray crystal structure of complex **L-Nd** shown with thermal ellipsoids. Symmetry operations: -y, x-y, z, x+y, -x, z.

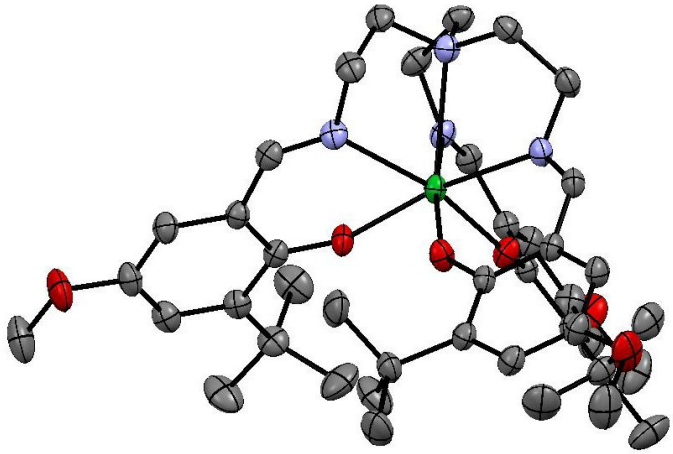

Figure S7. X-Ray crystal structure of complex **L-Lu** shown with thermal ellipsoids. Symmetry operations: -y, x-y, z, x+y, -x, z.

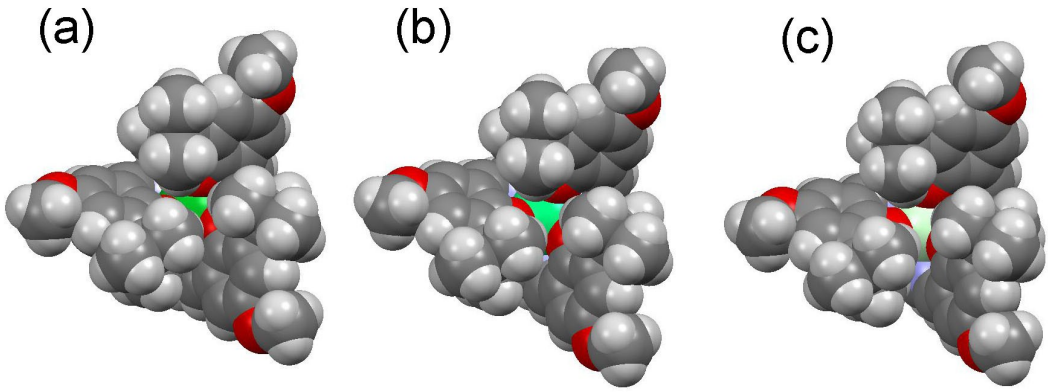

Figure S8. Spacefill views (bottom view) of (a) **L-Lu** , (b) **L-Er** and (c) **L-Nd**.

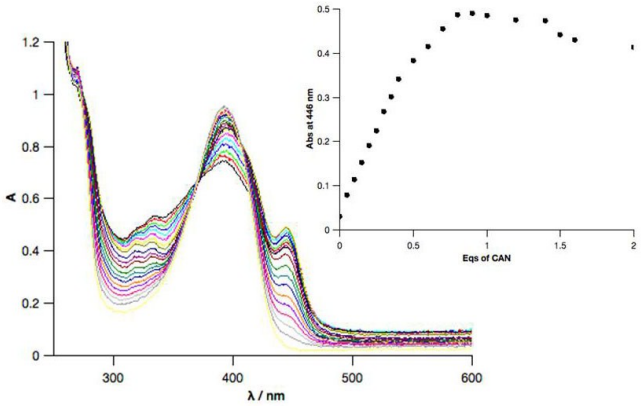

Figure S9. UV vis absorption spectra of **L-Lu** (5 x 10 $^{-5}$ M) in CH_3CN :CH_2Cl_2 8:2 upon addition of 0-2 eqs of the one electron oxidising agent CAN. Inset absorbance at 446 nm versus eqs of CAN added. *T* = 233 K, *l* = 1.000 cm.

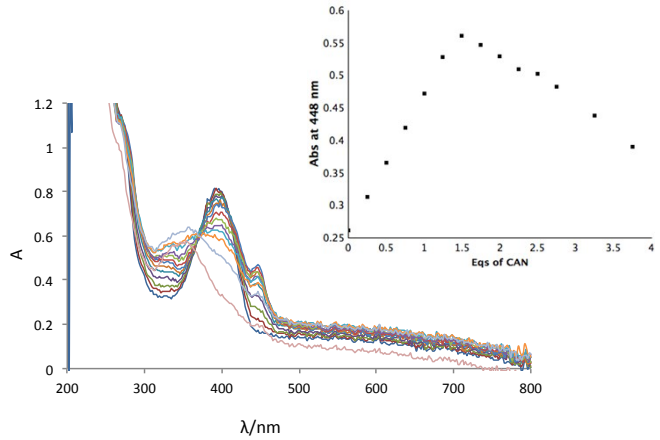

Figure S10. UV vis absorption spectra of **L-Yb** (5 x 10 $^{-5}$ M) in CH_3CN :CH_2Cl_2 8:2 upon addition of 0-2 eqs of the one electron oxidising agent CAN. Inset absorbance at 446 nm versus eqs of CAN added. *T* = 233 K, *l* = 1.000 cm.

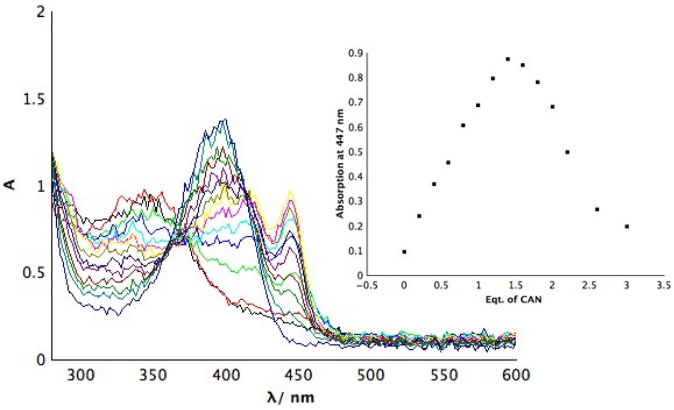

Figure S11. UV vis absorption spectra of **L-Tb** (5 x 10 $^{-5}$ M) in CH_3CN :CH_2Cl_2 8:2 upon addition of 0-2 eqs of the one electron oxidising agent CAN. Inset absorbance at 446 nm versus eqs of CAN added. *T* = 233 K, *l* = 1.000 cm.

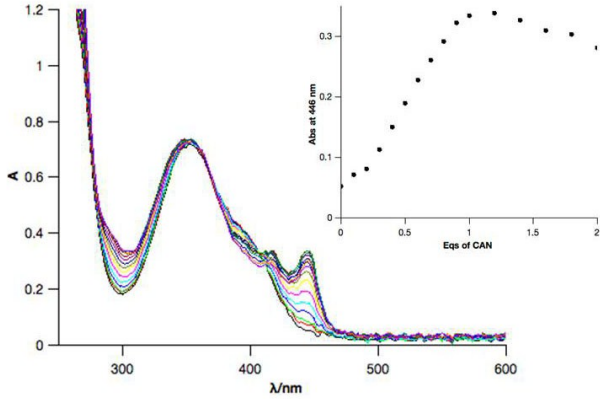

Figure S12. UV vis absorption spectra of **L-Gd** (5 x 10 $^{-5}$ M) in CH_3CN :CH_2Cl_2 8:2 upon addition of 0-2 eqs of the one electron oxidising agent CAN. Inset absorbance at 446 nm versus eqs of CAN added. *T* = 233 K, *l* = 1.000 cm.

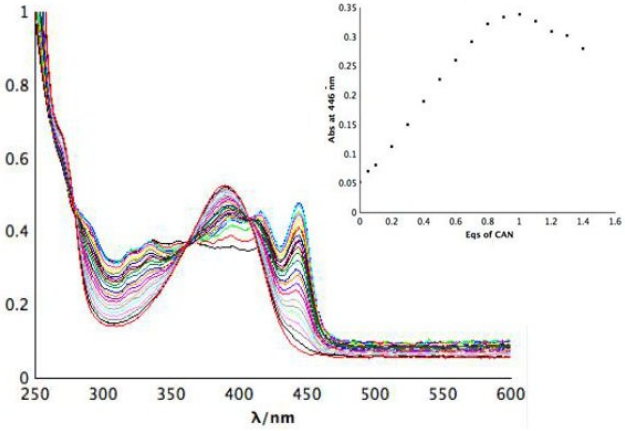

Figure S13. UV vis absorption spectra of **L-Eu** (5 x 10 $^{-5}$ M) in CH_3CN :CH_2Cl_2 8:2 upon addition of 0-2 eqs of the one-electron oxidising agent CAN. Inset absorbance at 446 nm versus eqs of CAN added. *T* = 233 K, *l* = 1.000 cm.

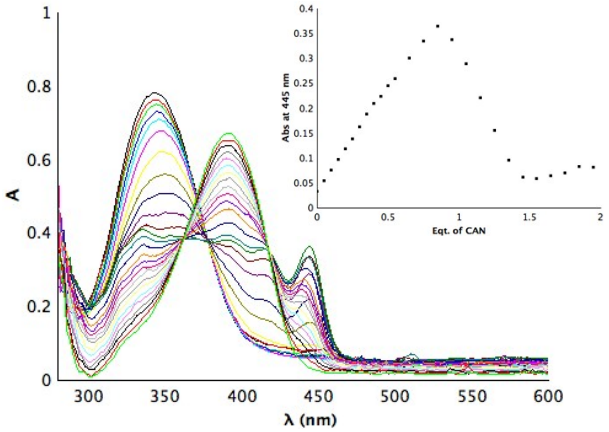

Figure S14. UV vis absorption spectra of **L-Nd** (5 x 10 $^{-5}$ M) in CH_3CN :CH_2Cl_2 8:2 upon addition of 0-2 eqs of the one electron oxidising agent CAN. Inset absorbance at 446 nm versus eqs of CAN added. *T* = 233 K, *l* = 1.000 cm.

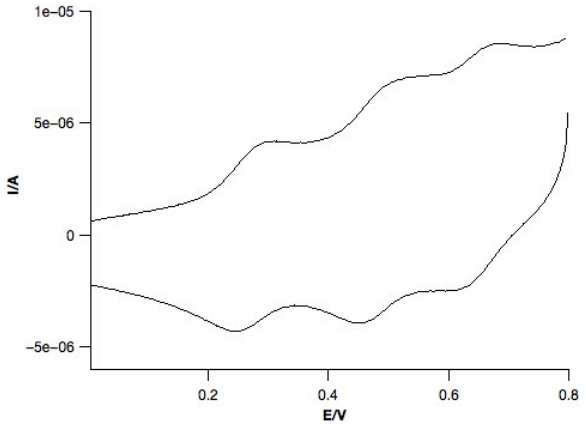

Figure S15. Cyclic voltammogram of a 0.5 mM solution of **L-Lu** in CH_3CN:CH_2Cl_2 8:2 containing TBAP (0.1 M) at a carbon working electrode. *T* = 298 K, v = 0.1 Vs^{-1}. Ref: $AgNO_3$/Ag (remove 0.09 V to convert to Fc^+/Fc).

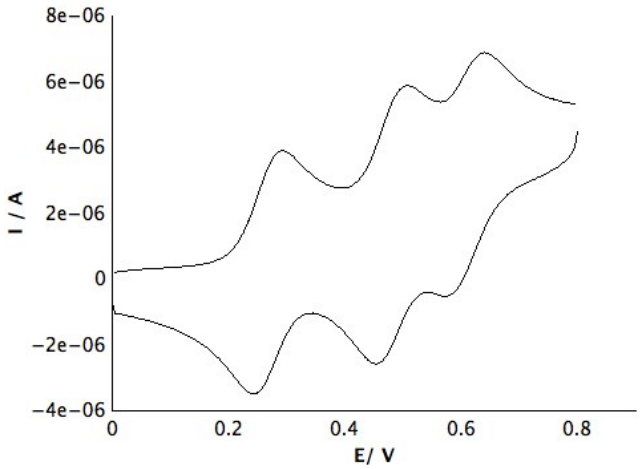

Figure S16. Cyclic voltammogram of a 0.5 mM solution of **L-Yb** in CH_3CN:CH_2Cl_2 8:2 containing TBAP (0.1 M) at a carbon working electrode. *T* = 298 K, v = 0.1 Vs^{-1}. Ref: $AgNO_3$/Ag (remove 0.09 V to convert to Fc^+/Fc).

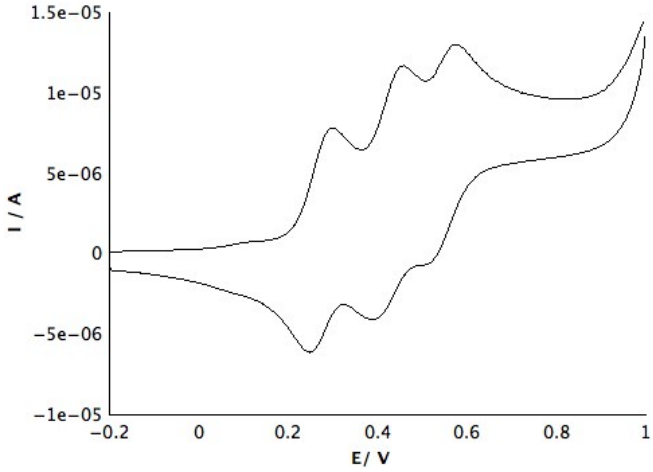

Figure S17. Cyclic voltammogram of a 0.5 mM solution of **L-Er** in CH_3CN:CH_2Cl_2 8:2 containing TBAP (0.1 M) at a carbon working electrode. *T* = 298 K, v = 0.1 Vs^{-1}. Ref: $AgNO_3$/Ag (remove 0.09 V to convert to Fc^+/Fc).

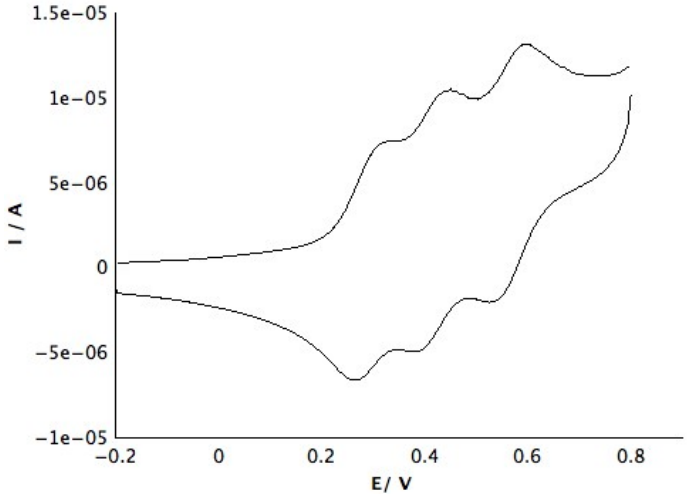

Figure S18. Cyclic voltammogram of a 0.5 mM solution of **L-Gd** in CH_3CN:CH_2Cl_2 8:2 containing TBAP (0.1 M) at a carbon working electrode. *T* = 298 K, v = 0.1 Vs^{-1}. Ref: $AgNO_3$/Ag (remove 0.09 V to convert to Fc^+/Fc).

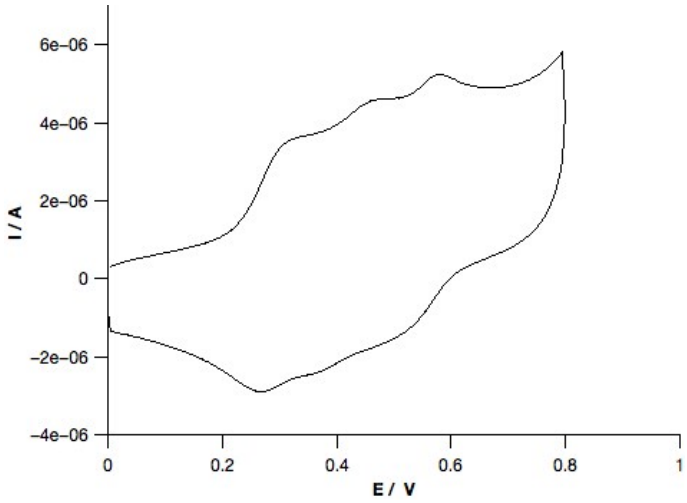

Figure S19. Cyclic voltammogram of a 0.5 mM solution of **L-Eu** in CH_3CN:CH_2Cl_2 8:2 containing TBAP (0.1 M) at a carbon working electrode. *T* = 298 K, v = 0.1 Vs^{-1}. Ref: $AgNO_3$/Ag (remove 0.09 V to convert to Fc^+/Fc).

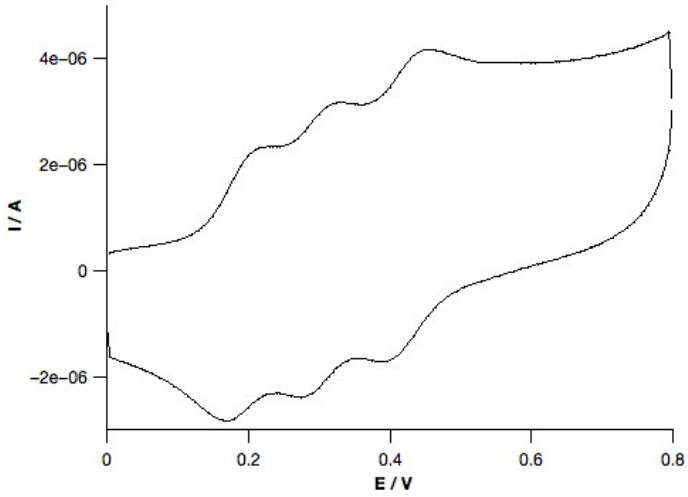

Figure S20. Cyclic voltammogram of a 0.5 mM solution of **L-Nd** in CH_3CN:CH_2Cl_2 8:2 containing TBAP (0.1 M) at a carbon working electrode. *T* = 298 K, v = 0.1 Vs^{-1}. Ref: $AgNO_3$/Ag (remove 0.09 V to convert to Fc^+/Fc).

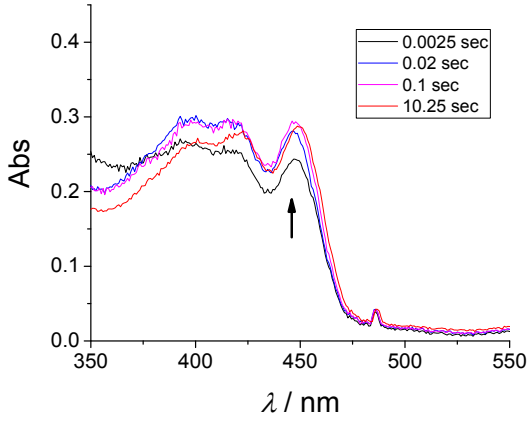

Figure S21. Representative stopped-flow kinetic trace for the oxidation of **L-Ln** complexes by 1 eq. of CAN in a CH_3CN:CH_2Cl_2 9:1 mixture. Ln = Er; Final concentrations are 5 x 10^{-5} M. *T* = 233 K; Dead time of the apparatus: 4 msec; The times at which the spectra were recorded are indicated in the figure.

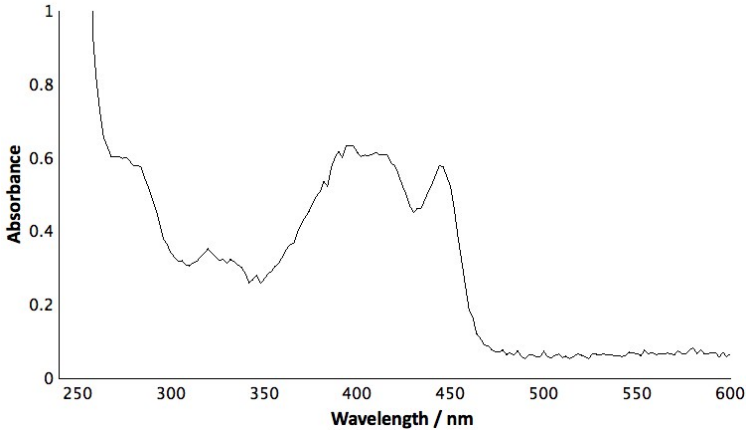

Figure S22. Representative UV-vis absorption spectrum of **L-Ln** complexes (1 x 10^{-4}M) in CH_3CN:CH_2Cl_2 8:2 mixture (0.1 M TBAP) after electrolysis at 0.6 V. Ln = Gd; T = 233 K.

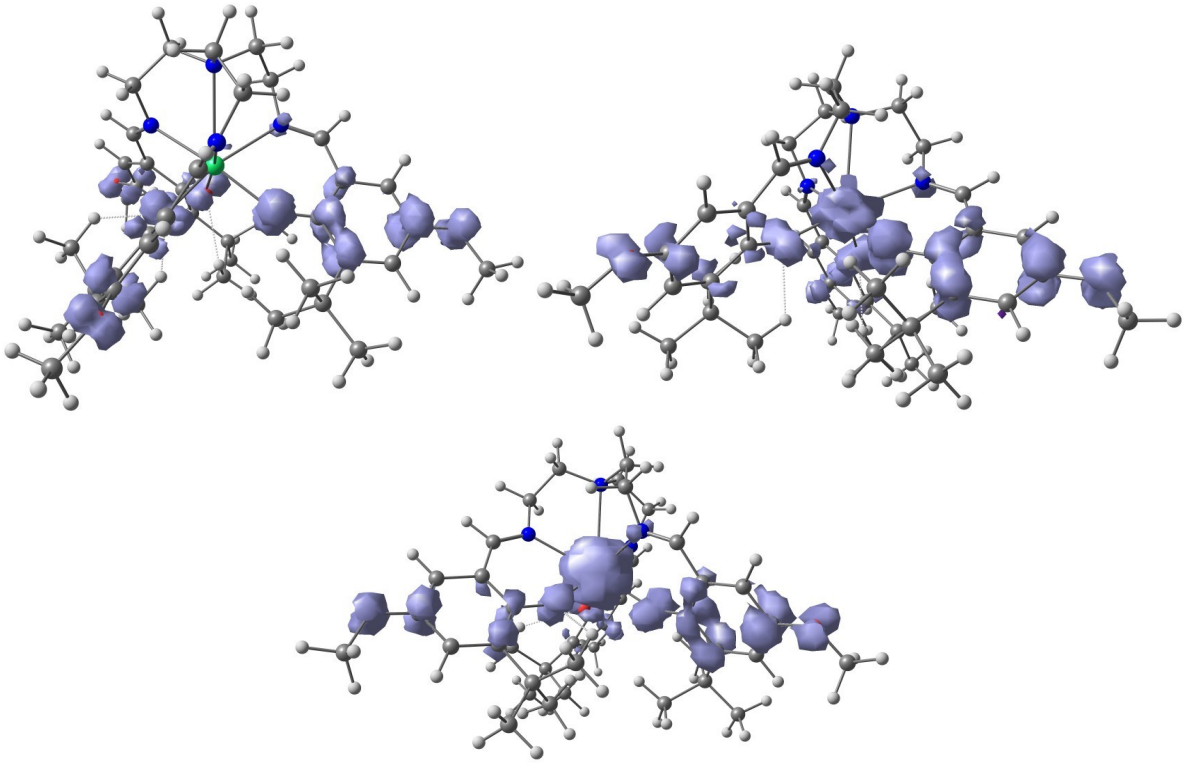

Figure S23. Spin density plots (side view) for the **L-Ln**$^{+}$ complexes (B3LYP/TZVP-SARC(ZORA): (left, top) **L-Lu**$^{+}$; (right, top) **L-Yb**$^{+}$; (bottom) **L-Nd**$^{+}$.

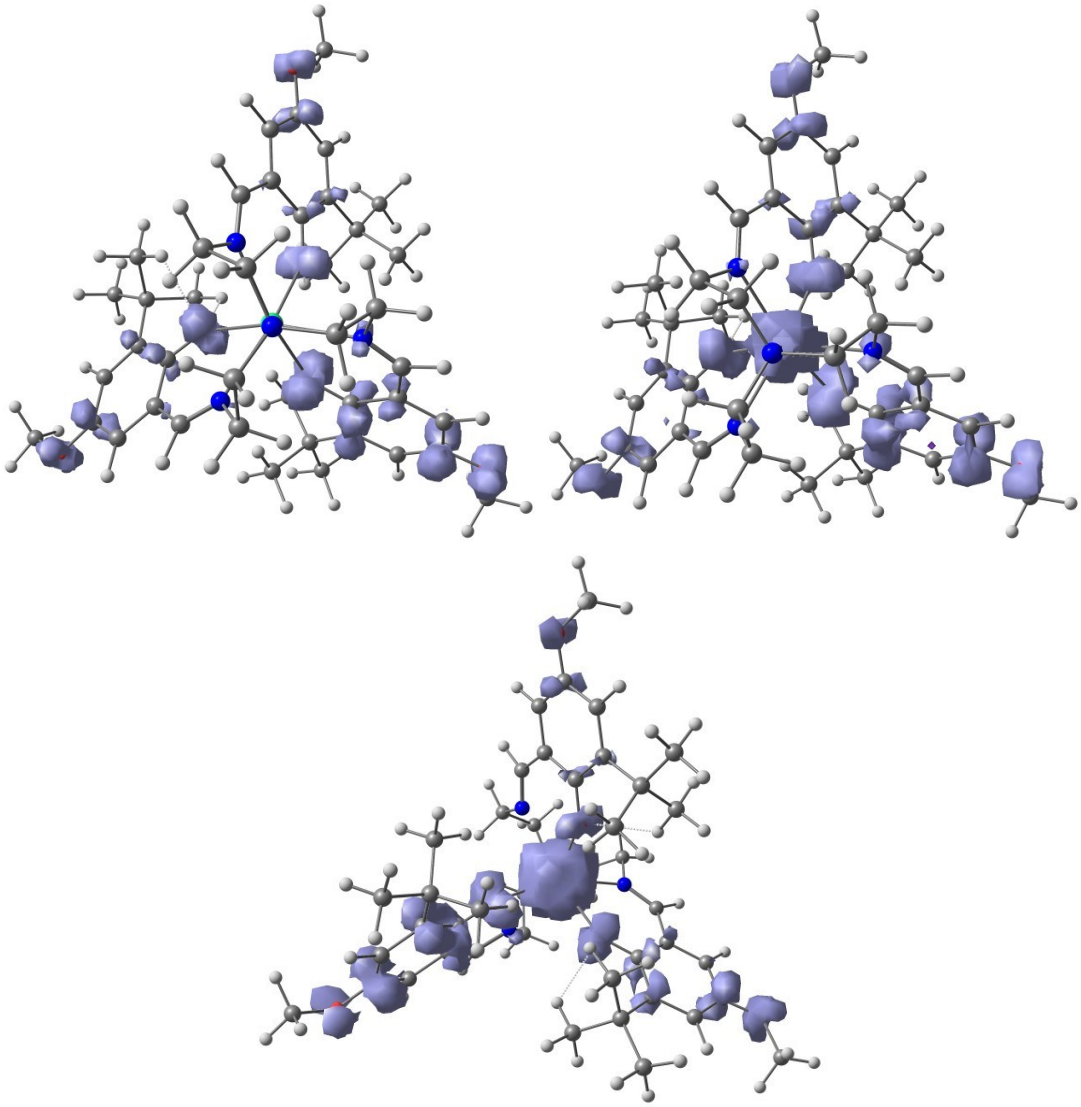

Figure S24. Spin density plots (top view) for the **L-Ln**$^{+}$ complexes (B3LYP/TZVP-SARC(ZORA): (left, top) **L-Lu**$^{+}$; (right, top) **L-Yb**$^{+}$; (bottom) **L-Nd**$^{+}$.

Cartesian coordinates for the L-Ln$^+$ complexes (B3LYP/TZVP-SARC(ZORA):

(a) **L-Lu$^+$**

Lu	0.098027969	9.042193473	2.712345087
O	-3.555837217	15.094600578	4.645853977
N	0.140163178	9.054864093	-0.155851167
O	-1.381586545	10.133889842	3.930015804
N	-0.082991397	11.252169430	1.699585029
C	-1.611141519	12.389324241	3.252077305
C	-2.897361857	11.491317858	5.172404920
C	0.671225356	11.400471354	0.457373717
H	1.722378281	11.158713553	0.642123783
H	0.630695671	12.429276595	0.083232173
C	-0.731999776	12.281862630	2.113629184
H	-0.643083181	13.207893182	1.536018459
C	0.082166939	10.463142339	-0.591097866
H	-0.961566921	10.741897568	-0.737242335
H	0.589364282	10.605066619	-1.554154421
C	-1.934748753	11.276340659	4.113658830
C	-3.355340424	10.332686918	6.066490628
C	-2.181332122	13.640854894	3.464273148
H	-1.956418032	14.474161421	2.810531279
C	-3.072892597	13.842737073	4.508855808
C	-4.340568447	10.789353654	7.157435566
H	-3.911806815	11.539399432	7.827715811
H	-4.608629533	9.923578399	7.764205016
H	-5.262572489	11.190855250	6.734994955
C	-2.158678044	9.664564657	6.779051078
H	-1.518574660	9.126563906	6.086551209
H	-2.547401067	8.952784214	7.511141343
H	-1.547352906	10.394652515	7.312980868
C	-3.421806674	12.760135673	5.335476181
H	-4.133567537	12.928508761	6.125315559
C	-4.098292581	9.288881619	5.199030473
H	-4.968080588	9.735600352	4.712377378
H	-4.453474234	8.469493512	5.827865027
H	-3.453700716	8.869762125	4.429357510
C	-4.516646356	15.385309921	5.659394042
H	-5.453191131	14.850900167	5.478864694
H	-4.691298132	16.454732690	5.590088226
H	-4.135197403	15.145317455	6.655529466
O	-3.952235427	3.349789355	4.872207429
O	-0.238908182	7.230321265	3.818085820
N	-1.808274332	7.907297720	1.640078519
C	-2.251756617	6.125326672	3.281478922
C	-0.818547244	5.316767119	5.122492392
C	-2.214083431	8.432562761	0.338515745
H	-2.505115042	9.481238078	0.446927758
H	-3.073612807	7.885786135	-0.060887134
C	-2.497525053	6.923736076	2.107872794
H	-3.376430254	6.604113546	1.536760365
C	-1.038122993	8.297107144	-0.623953953
H	-0.773190404	7.240771986	-0.681758629
H	-1.321858838	8.606587462	-1.637990914
C	-1.065819601	6.268850125	4.074266876
C	0.489191029	5.353851331	5.929784565
C	-3.192214129	5.134858735	3.575889330
H	-4.086338467	5.032521676	2.973344302

C	-2.979575893	4.265375006	4.631583125
C	0.566504883	4.226935042	6.973034757
H	-0.213117141	4.299550331	7.735451112
H	1.526406483	4.292345054	7.485985844
H	0.501380626	3.238782785	6.512346274
C	0.611853256	6.698060500	6.677811003
H	0.659519956	7.534346295	5.988323211
H	1.514185664	6.707331156	7.292445086
H	-0.243672365	6.849614747	7.337850082
C	-1.787905242	4.360144301	5.373698653
H	-1.624245535	3.643361546	6.160211623
C	1.684601905	5.161585891	4.970793679
H	1.618669066	4.192443798	4.472979708
H	2.622078031	5.203551763	5.529401650
H	1.710458034	5.934234417	4.208187350
C	-3.739120932	2.352465398	5.866448399
H	-2.841642668	1.767202769	5.648864473
H	-4.610993368	1.704785783	5.829352545
H	-3.653141800	2.794003486	6.862438829
O	7.159526345	9.251673050	4.594821182
O	1.746234650	9.768274401	3.891048779
N	2.063169488	8.049572844	1.724203413
C	3.817924950	8.811535165	3.270445576
C	3.675612254	10.410860156	5.143564230
C	1.822628265	7.357728625	0.461999785
H	1.024884037	6.620097874	0.592192734
H	2.712200621	6.820177675	0.115631579
C	3.279133608	8.080550351	2.153702719
H	4.024303019	7.499721169	1.599886448
C	1.399996093	8.399252641	-0.571302933
H	2.182134884	9.154719840	-0.631367197
H	1.294554351	7.938941461	-1.560996154
C	3.022229167	9.672577988	4.098322745
C	2.872909106	11.333417717	6.076659828
C	5.194946283	8.692813191	3.481129031
H	5.798032131	8.050456570	2.852823654
C	5.817642381	9.416010103	4.481539150
C	3.758656040	12.048520334	7.112759776
H	4.291426402	11.349341719	7.759669967
H	3.119278158	12.657235570	7.751144393
H	4.491064340	12.717781385	6.652463942
C	1.837135659	10.499306312	6.859779713
H	1.205056190	9.919147598	6.195700366
H	1.199072254	11.160113227	7.448474586
H	2.332926057	9.805450691	7.544130253
C	5.045135674	10.261203538	5.296545669
H	5.534170596	10.815212429	6.080682633
C	2.160457667	12.440087157	5.267063617
H	2.884418182	13.045496622	4.717338944
H	1.622955401	13.095738297	5.955170786
H	1.442975340	12.042483480	4.552823559
C	7.897939220	10.073077322	5.490484368
H	7.721917933	11.133755966	5.294453831
H	8.945313819	9.843998607	5.311418195
H	7.656187240	9.853766161	6.534092813

(b) **L-Yb^{+}**

Yb	0.091765156	9.042157489	2.729898954

O	-3.582785039	15.118796150	4.604152164
N	0.130445896	9.065693706	-0.127502083
O	-1.405501123	10.153889038	3.924284285
N	-0.059619755	11.272948633	1.725689343
C	-1.612572944	12.413218182	3.248702212
C	-2.918083380	11.520770806	5.158675416
C	0.693883139	11.407407810	0.481932833
H	1.742182210	11.152980976	0.664112156
H	0.664483109	12.435150991	0.103627193
C	-0.718917985	12.302222725	2.121833019
H	-0.630576077	13.222984788	1.535573950
C	0.085464242	10.475915619	-0.561013081
H	-0.956279911	10.767549964	-0.697359304
H	0.584783194	10.611295035	-1.529170905
C	-1.948613197	11.301153781	4.107103383
C	-3.379379359	10.369457857	6.060089700
C	-2.187100154	13.664267812	3.448627494
H	-1.953657315	14.495853984	2.795683095
C	-3.094207327	13.868016929	4.479689146
C	-4.372044439	10.837127776	7.140950636
H	-3.961848461	11.614467988	7.790935347
H	-4.619520530	9.981824939	7.770492700
H	-5.303332367	11.203026856	6.705200689
C	-2.184861205	9.706446919	6.780481444
H	-1.544628172	9.169101819	6.087239668
H	-2.573413304	8.993049840	7.510937610
H	-1.575608325	10.437225883	7.316041629
C	-3.448865094	12.788734000	5.307911338
H	-4.169273243	12.959884210	6.088830375
C	-4.120646087	9.310316473	5.206537381
H	-4.877532539	9.773795837	4.567998245
H	-4.634785177	8.611285498	5.868552408
H	-3.439469023	8.745083732	4.576297332
C	-4.560189177	15.411300991	5.601266567
H	-5.493965296	14.877359030	5.404848672
H	-4.732788274	16.480791495	5.528000389
H	-4.196680391	15.171866278	6.604016707
O	-3.927910208	3.302994211	4.855647356
O	-0.237867819	7.217197669	3.829015447
N	-1.816770273	7.903403504	1.662327247
C	-2.244691043	6.102441343	3.285502257
C	-0.808456892	5.292398507	5.121661584
C	-2.226655095	8.445924487	0.369644067
H	-2.512180088	9.494616737	0.492311058
H	-3.090451227	7.908087781	-0.032774064
C	-2.498710410	6.910481773	2.120650308
H	-3.376751465	6.591227551	1.547921242
C	-1.055804922	8.320195677	-0.600982897
H	-0.796336087	7.263947304	-0.679236041
H	-1.342225283	8.650438793	-1.607286992
C	-1.060100254	6.248136540	4.079044288
C	0.498157937	5.331918522	5.931034482
C	-3.178971997	5.102840337	3.572623248
H	-4.072214197	4.998879233	2.969020394
C	-2.961373254	4.228158499	4.621921407
C	0.582319874	4.196554446	6.965016664
H	-0.198354154	4.257189163	7.727448365
H	1.541411304	4.264363219	7.479282756
H	0.524363853	3.212246133	6.495499387

C	0.610620274	6.669371685	6.691866480
H	0.631017940	7.515213362	6.012653723
H	1.524636914	6.687370590	7.288839802
H	-0.233236989	6.793157356	7.372549822
C	-1.771832012	4.327463373	5.366239371
H	-1.603692291	3.608432144	6.149788419
C	1.696658150	5.153482600	4.973433216
H	1.636293314	4.187083232	4.469621549
H	2.632581141	5.195307182	5.534820425
H	1.721599332	5.930367719	4.215050250
C	-3.707308384	2.300660004	5.842469261
H	-2.804061029	1.724786038	5.622986647
H	-4.572941290	1.645000925	5.799227542
H	-3.627292021	2.734535076	6.842395711
O	7.173034653	9.246389744	4.581367379
O	1.760910323	9.765976714	3.898336079
N	2.062097375	8.041614547	1.737021145
C	3.827467074	8.805055918	3.269780401
C	3.692194023	10.402338815	5.147615611
C	1.808129338	7.354206421	0.475459937
H	1.007360862	6.620609589	0.610191111
H	2.692052197	6.812881380	0.120081960
C	3.280991021	8.073408575	2.156027924
H	4.022767346	7.493957370	1.596181149
C	1.384491199	8.401899585	-0.551128050
H	2.170949135	9.152652874	-0.613168262
H	1.270709095	7.946087470	-1.541938364
C	3.035614176	9.666225744	4.101811081
C	2.890627018	11.323976666	6.082421510
C	5.204528624	8.686450892	3.475695439
H	5.806060279	8.044522376	2.845460153
C	5.831020511	9.409392741	4.475066254
C	3.777078287	12.036565691	7.119609447
H	4.310025395	11.336154093	7.765043762
H	3.138262391	12.644519970	7.759305364
H	4.509402449	12.706541131	6.660213743
C	1.853264982	10.490086986	6.864058640
H	1.220855306	9.910805648	6.199401432
H	1.215297887	11.151182831	7.452501625
H	2.347640360	9.795427544	7.548600742
C	5.061916414	10.253194970	5.295106307
H	5.554143333	10.806073009	6.077982242
C	2.179520219	12.432715188	5.274194280
H	2.904326359	13.039301014	4.726848259
H	1.641051146	13.086868228	5.962995200
H	1.463257116	12.036655122	4.558017433
C	7.915070804	10.064552806	5.477549159
H	7.738960616	11.125751102	5.284747662
H	8.961597661	9.835017940	5.294391388
H	7.676022390	9.842214751	6.521068702

(c) **L-Nd^{+}**

Nd	7.868608512	4.465244195	7.692874569
O	0.587854010	4.702665388	6.000191598
N	7.863893543	4.484936468	10.652615840
O	5.990686517	3.919513223	6.573895409
N	5.772717349	5.521197286	8.853707416
C	3.972216102	4.927369394	7.276612632

C	4.006223149	3.410031422	5.334917369
C	6.039394637	6.103652630	10.164286842
H	5.144762288	6.560188660	10.603515071
H	6.794031557	6.890056590	10.070891820
C	4.553858100	5.557806298	8.438390590
H	3.827516287	6.110154631	9.044784854
C	6.555546717	5.009978196	11.099322932
H	6.625376417	5.390851405	12.127047063
H	5.831024215	4.195566473	11.107447919
C	4.709767476	4.077285303	6.391912411
C	4.751172421	2.493695397	4.350217465
C	2.597214109	5.114908224	7.101171324
H	2.038006051	5.745329252	7.780696825
C	1.923597401	4.468905572	6.081011252
C	3.817605327	1.826940001	3.325283156
H	3.288283083	2.548958965	2.700483049
H	3.078425145	1.172110144	3.795223246
H	4.417963266	1.205375284	2.660238061
C	5.779527331	3.330831051	3.560752215
H	6.411712636	3.913814513	4.222443385
H	5.275000217	4.023391246	2.882024184
H	6.419815398	2.677012980	2.966822192
C	2.640207115	3.624734507	5.217887175
H	2.107027169	3.128876375	4.424020229
C	5.456507484	1.347973206	5.110137162
H	4.728551152	0.737404792	5.648947554
H	6.183341432	1.717946951	5.827998380
H	5.977739666	0.705545147	4.397095161
C	-0.208476786	3.922817406	5.117174161
H	-0.062358776	2.854032295	5.292811265
H	0.007204748	4.148907327	4.069090464
H	-1.241297952	4.185724305	5.332696413
O	11.842893168	-1.645169204	6.018111657
O	9.440816874	3.251777261	6.542508319
N	8.259848832	2.187470049	8.861403770
C	9.818561586	1.052869047	7.331131648
C	10.924546799	1.868358175	5.276591453
C	7.536528622	2.069298948	10.123238562
H	7.635565731	1.067452113	10.557438550
H	6.470655573	2.242511362	9.940244836
C	8.971173653	1.181023076	8.492629671
H	8.954869702	0.289922985	9.129635780
C	8.071962862	3.096050981	11.116333864
H	7.611259562	2.940104033	12.100940104
H	9.142751967	2.929863395	11.234472685
C	10.036412747	2.113624422	6.383223321
C	11.187498679	2.944391427	4.210655433
C	10.447342694	-0.182941867	7.173737400
H	10.300222952	-0.981069219	7.890265621
C	11.292698057	-0.410990273	6.100226207
C	12.177831675	2.481977296	3.127765102
H	11.827288790	1.615156387	2.561715312
H	13.160812811	2.252748296	3.545179058
H	12.313051808	3.295772000	2.415327422
C	9.854528706	3.307843062	3.518500058
H	9.194600754	3.836273113	4.201882203
H	9.337967571	2.417068944	3.156173454
H	10.043851921	3.957839414	2.662284390
C	11.525708029	0.623405196	5.180984470

H	12.197033929	0.439099110	4.359849550
C	11.789921996	4.216386422	4.848881296
H	12.786465946	4.028322120	5.255739224
H	11.157219686	4.600824168	5.644066423
H	11.874105101	4.990765358	4.083908485
C	12.729674114	-1.952307383	4.945954629
H	13.646666848	-1.361700064	5.009393456
H	12.250956033	-1.791764002	3.975360473
H	12.968494982	-3.006172342	5.059177393
O	11.356092963	10.925625792	6.071010331
O	8.323033654	6.408149686	6.495380322
N	9.735483933	5.916632394	8.877789744
C	10.034406636	7.805021516	7.320514764
C	8.771237788	8.405289495	5.270049235
C	10.152316852	5.383914420	10.172144595
H	10.941660921	5.999278238	10.617343002
H	10.555797571	4.376162497	10.035946013
C	10.307089027	6.999404718	8.490539421
H	11.094080902	7.416551439	9.130061768
C	8.952254508	5.371314181	11.113743012
H	9.264022459	5.104680286	12.132417154
H	8.567446867	6.390505329	11.164343999
C	9.007853574	7.485507468	6.361188380
C	7.666345326	8.134078746	4.243685089
C	10.799150842	8.957326672	7.180438371
H	11.571867632	9.201448837	7.898315465
C	10.569660957	9.829319760	6.122519386
C	7.550993682	9.248622872	3.187699188
H	8.464063624	9.376182636	2.600518292
H	7.295228559	10.211936607	3.634278219
H	6.751971491	8.979933653	2.497734078
C	7.945002657	6.812111427	3.492923334
H	8.000263579	5.970185661	4.174961369
H	8.881240509	6.870841634	2.934610115
H	7.135444547	6.625843681	2.787406233
C	9.558147641	9.539514781	5.189364521
H	9.403172792	10.239199819	4.385584497
C	6.291287241	8.054614845	4.947841145
H	6.069346598	8.986858467	5.473924295
H	6.239270704	7.241330798	5.665208641
H	5.511108522	7.906199677	4.199528423
C	11.126128935	11.917922035	5.072971456
H	10.134791560	12.364913824	5.183558388
H	11.235792982	11.506776713	4.066200098
H	11.886550820	12.676378028	5.233958288