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Supporting Information

Unexpected Molecular Structure of a Putative Rhenium-Dioxo-Benzocarbaporphyrin Complex. Implications for the Highest Transition Metal Valence in a Porphyrin-Type Ligand Environment

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Unexpected Molecular Structure of a Putative Rhenium-Dioxo-Benzocarbaporphyrin Complex. Implications for the Highest Transition Metal Valence in a Porphyrin-Type Ligand Environment

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A. ^{1}H NMR spectra

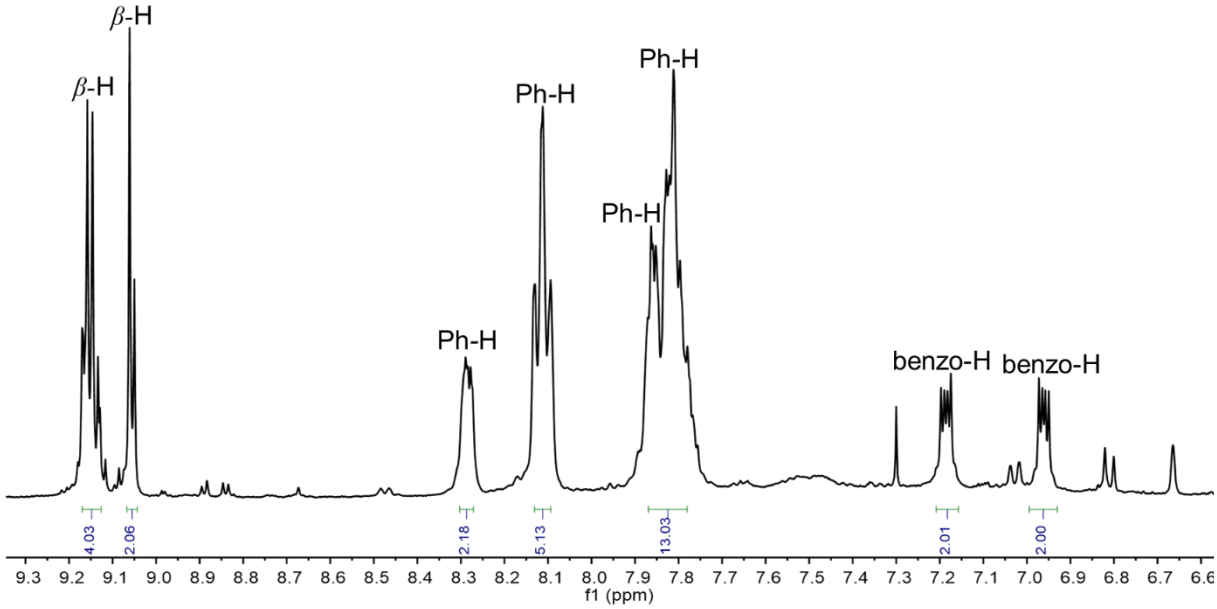

Figure S1. ^{1}H NMR spectrum of Re[TPBCP](O), in CD_2Cl_2 at 253 K.

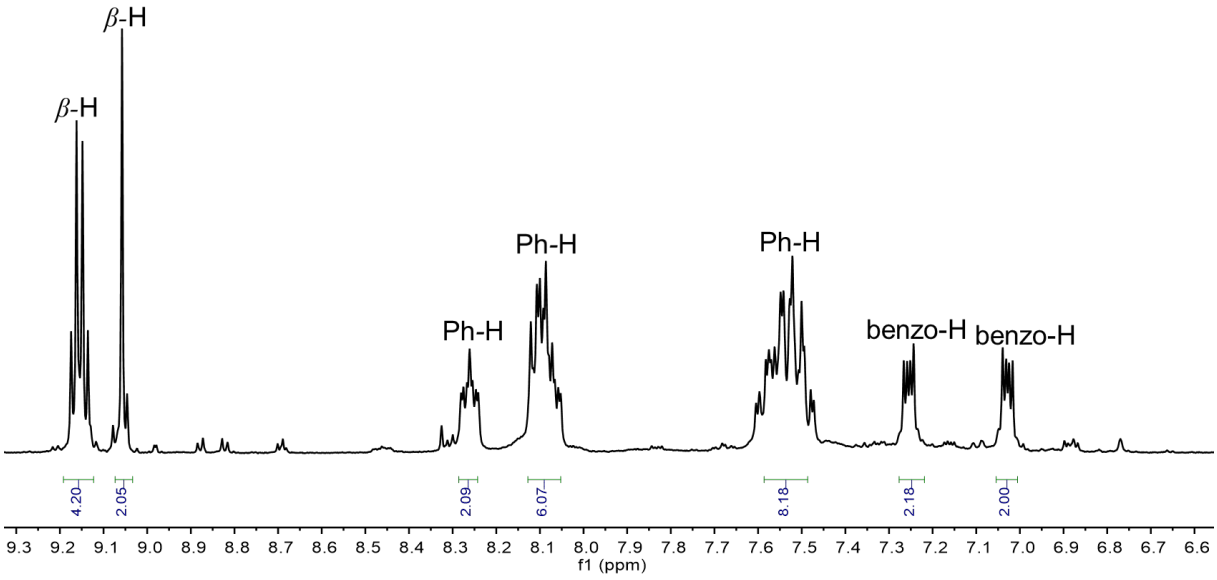

Figure S2. ^{1}H NMR spectrum of Re[T*p*FPBCP](O), in CD_2Cl_2 at 253 K.

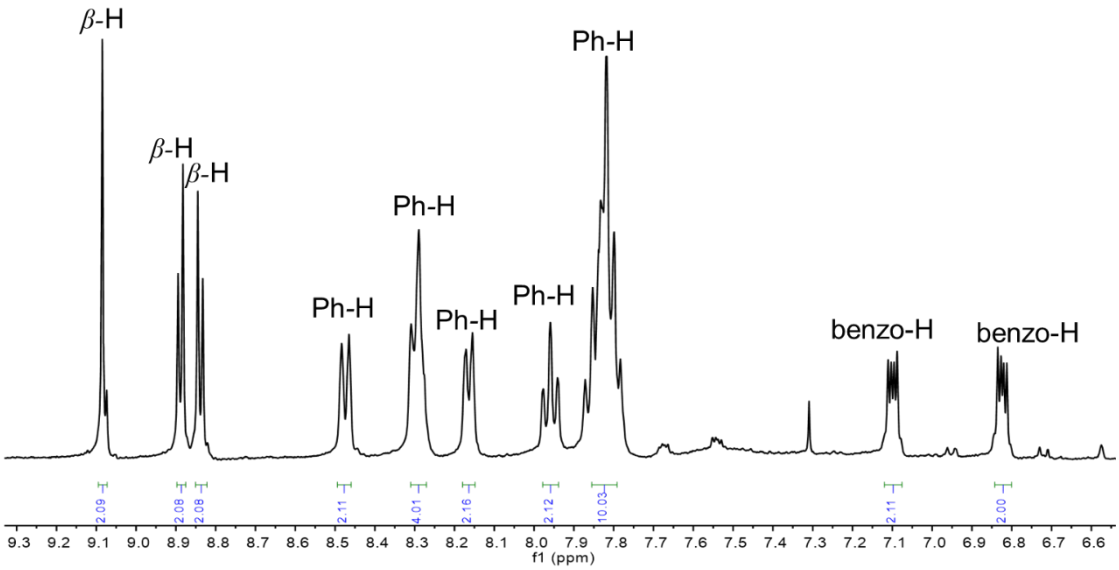

Figure S3. ^{1}H NMR spectrum of Re[TPBCP](O)$_2$, in CD_2Cl_2 at 253 K.

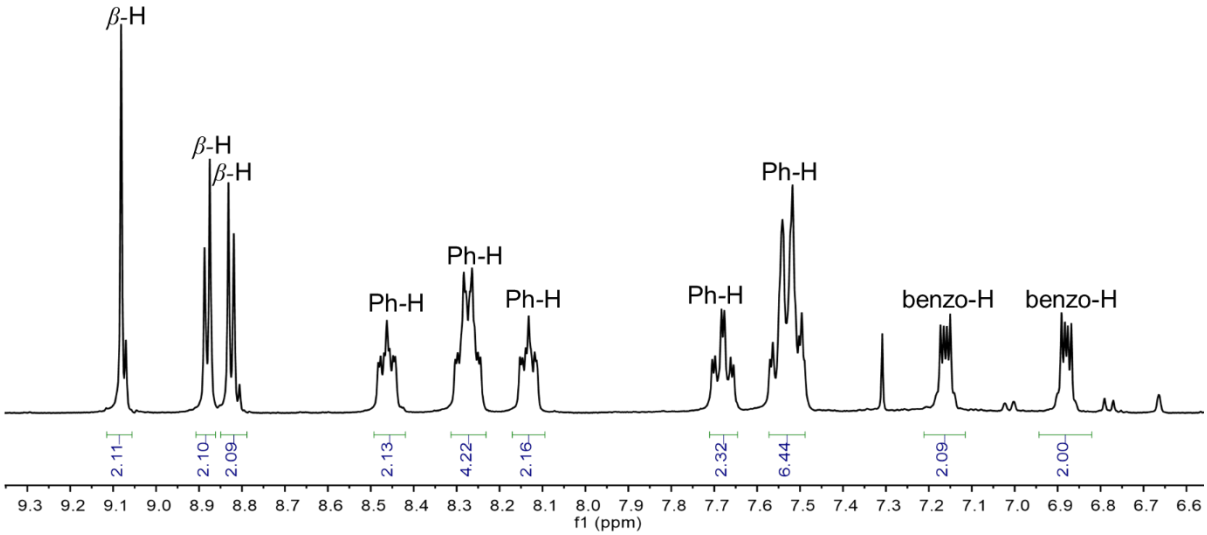

Figure S4. ^{1}H NMR spectrum of Re[T*p*FPBCP](O)$_2$, in CD_2Cl_2 at 253 K.

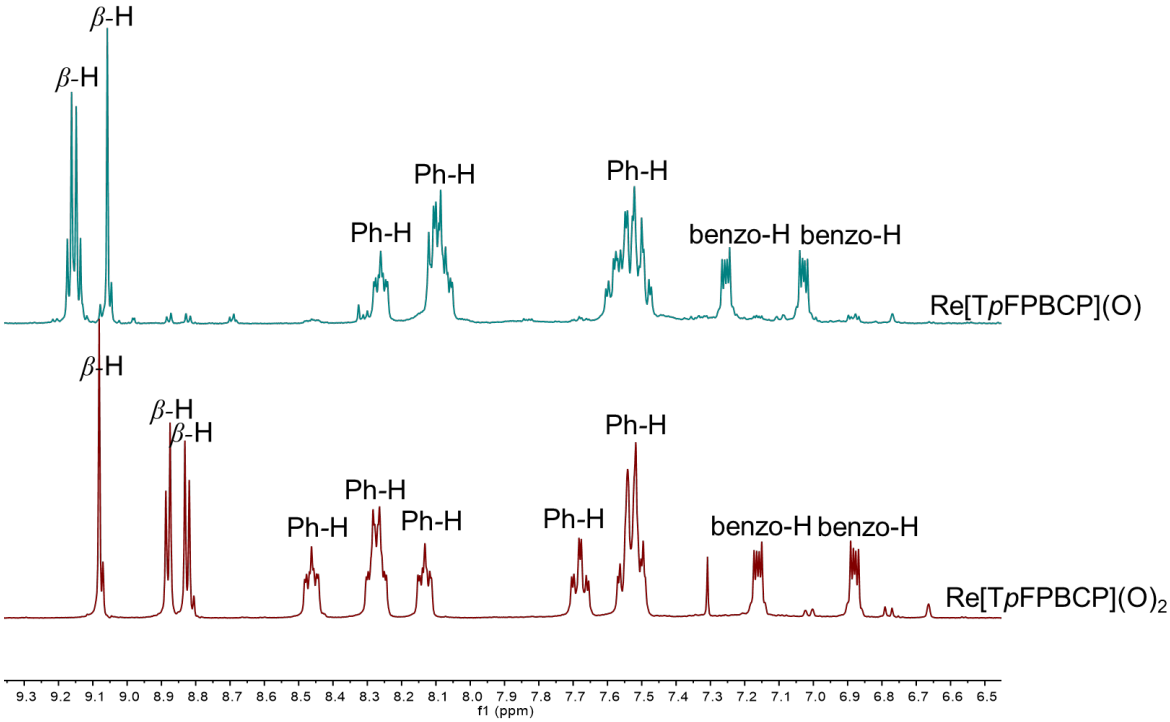

Figure S5. Comparison of the ^{1}H NMR spectra of Re[T*p*FPBCP](O) (top) and Re[T*p*FPBCP](O)$_2$ (bottom) in CD_2Cl_2 at 253 K.

B. ESI mass spectra

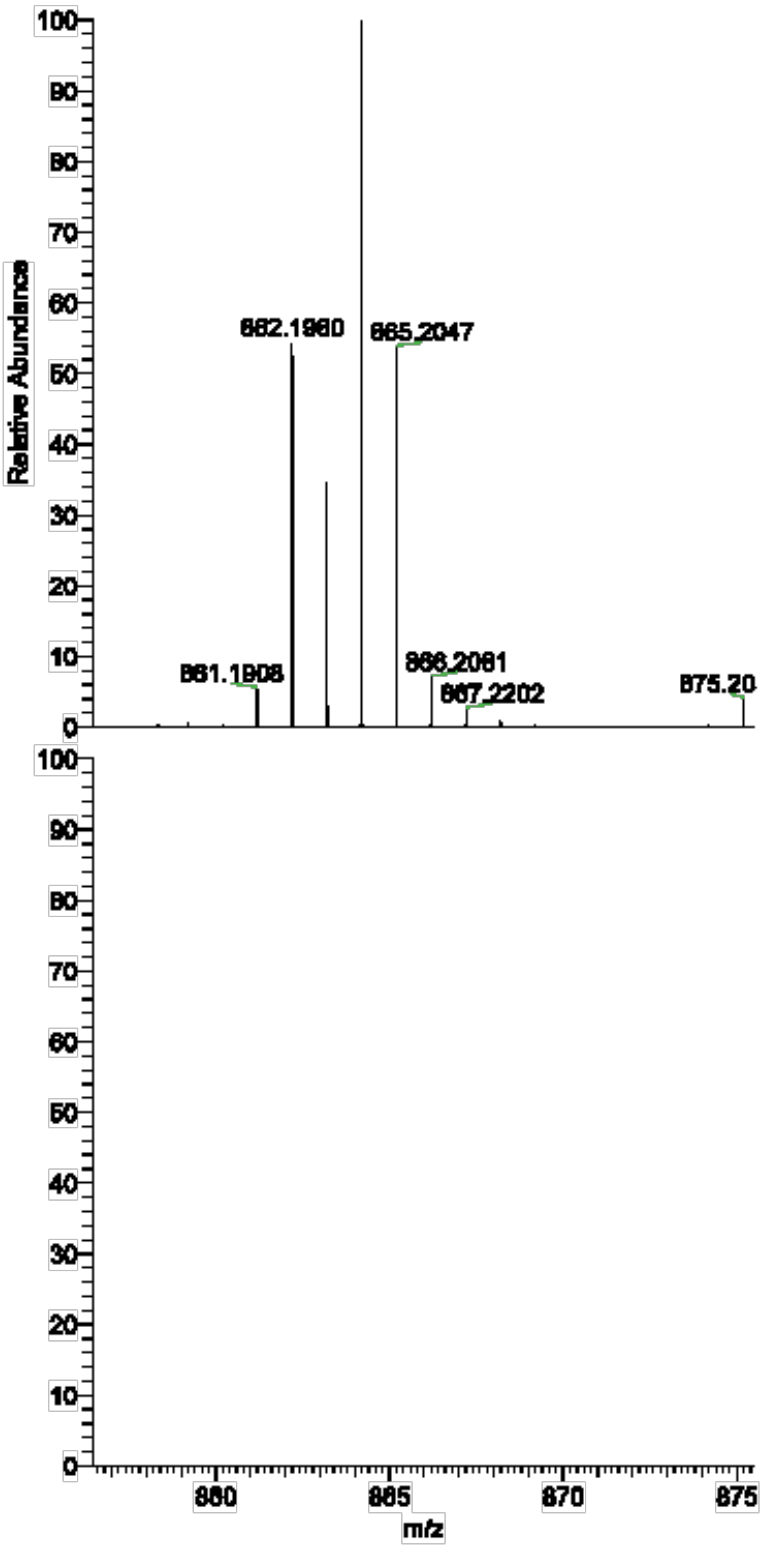

Figure S6. ESI (positive mode) MS of Re[TPBCP](O): experimental (top) and simulation (bottom).

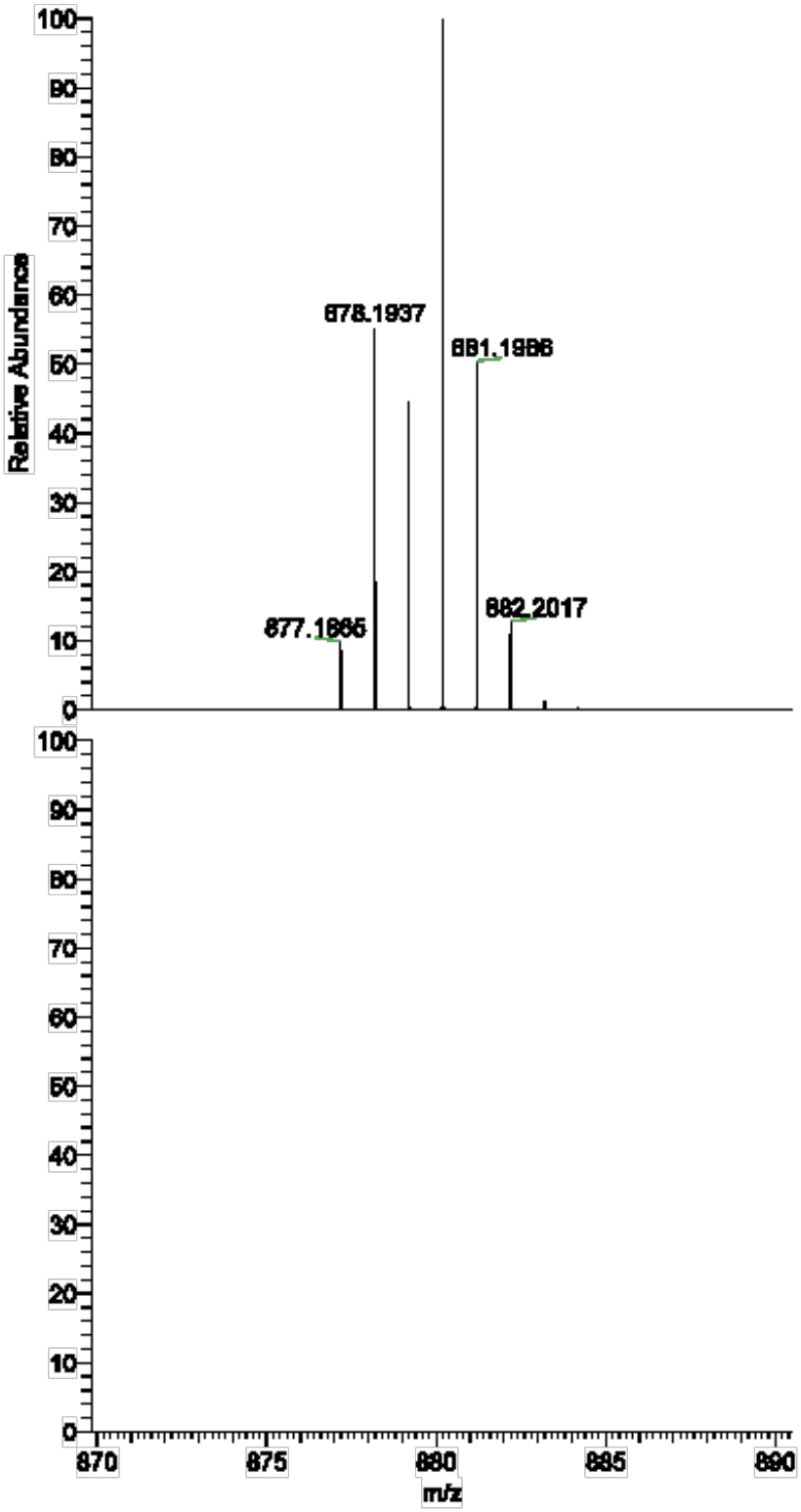

Figure S7. ESI (positive mode) MS of Re[TPBCP](O)$_2$: experimental (top) and simulation (bottom).

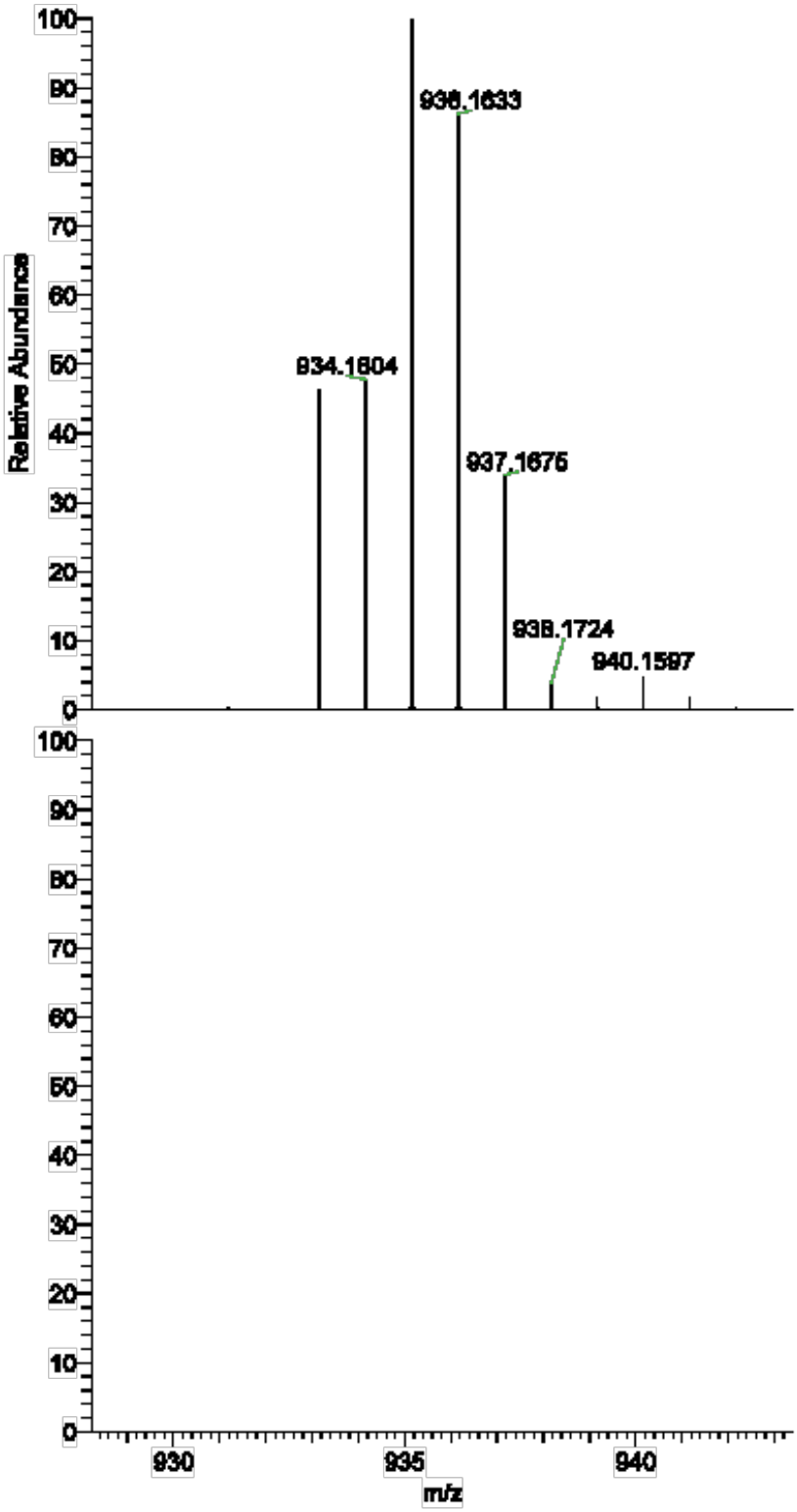

Figure S8. ESI (positive mode) MS of Re[T*p*FPBCP](O): experimental (top) and simulation (bottom).

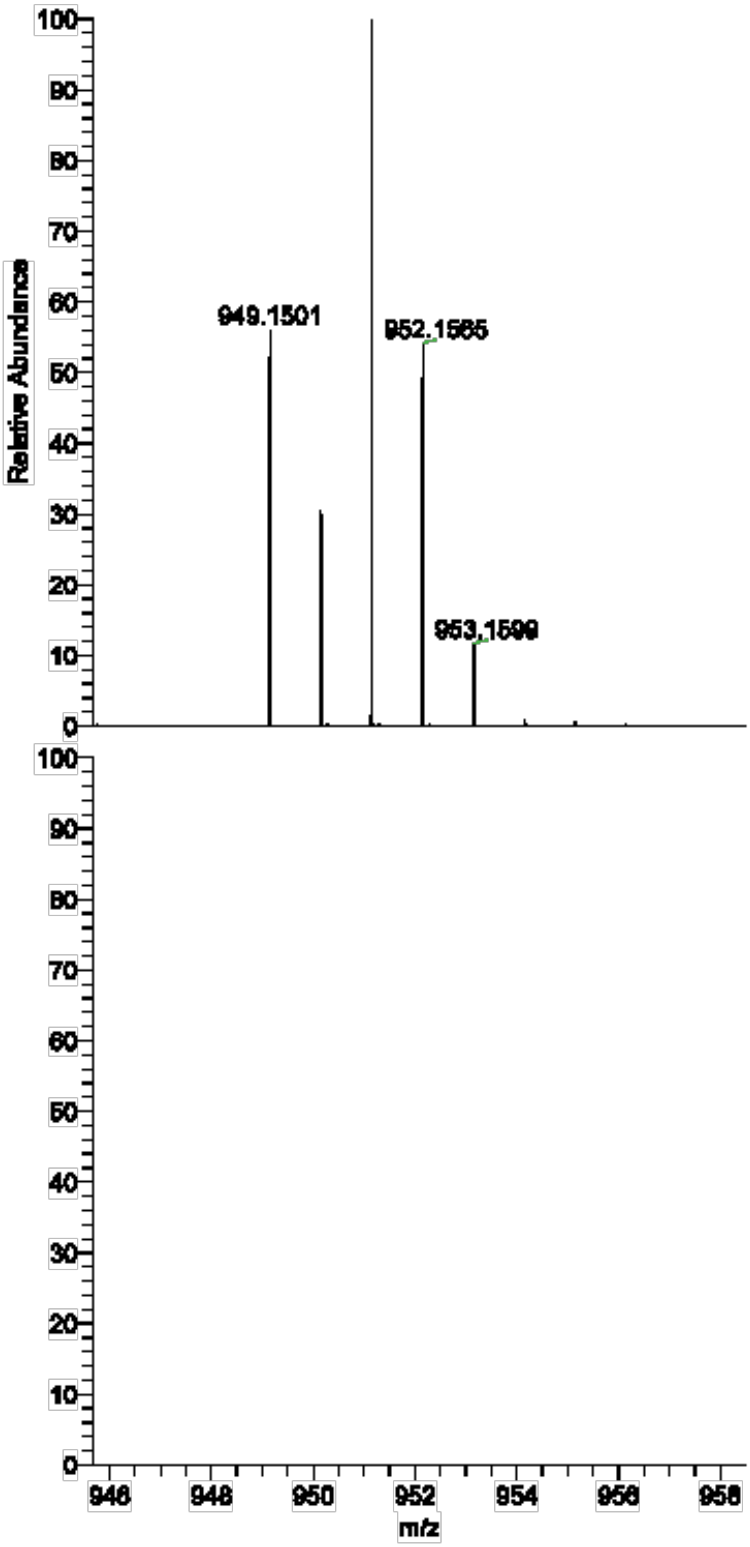

Figure S9. ESI (positive mode) MS of Re[T*p*FPBCP](O)$_2$: experimental (top) and simulation (bottom).

C. Optimized B3LYP-D3(ZORA-STO-TZ2P Cartesian coordinates (Å)

(a) Re[BCPO](O) (C_s)

Re	0.600845	-0.192344	0.000014
O	0.248422	-1.841074	0.000204
O	-0.403531	1.518931	-0.000324
N	0.603669	0.181353	2.059257
N	0.603707	0.181195	-2.059300
N	2.610951	-0.029478	-0.000030
C	1.295430	0.286239	4.235895
C	1.296099	0.287042	-4.235719
C	1.704955	0.113960	2.877360
C	1.704993	0.113044	-2.877254
C	3.011871	-0.059614	-2.436374
C	3.011976	-0.057270	2.436405
C	3.434204	-0.127184	-1.121445
C	3.434216	-0.124995	1.121373
C	4.779271	-0.284531	-0.681952
C	4.779424	-0.282980	0.682187
C	-0.053069	0.475897	-4.226892
C	-0.053905	0.473972	4.226839
C	-0.495014	0.423287	-2.867403
C	-0.495336	0.422408	2.867214
C	-1.554697	0.800953	-0.000418
C	-1.831677	0.492069	-2.469464
C	-1.831729	0.491431	2.468750
C	-2.305861	0.493575	1.168665
C	-2.306318	0.494178	-1.169649
C	-3.634139	0.087248	0.707625
C	-3.634513	0.087220	-0.708159
C	-4.755283	-0.331316	1.409102
C	-4.756136	-0.332114	-1.408499
C	-5.889882	-0.712757	0.697798
C	-5.890283	-0.712890	-0.696168
H	1.957786	0.271511	5.086175
H	1.958771	0.272793	-5.085769
H	3.779133	-0.123742	-3.195689
H	3.779291	-0.120973	3.195697
H	5.626933	-0.390809	-1.339582
H	5.626993	-0.388190	1.340006
H	-0.700666	0.643496	-5.072463
H	-0.701946	0.640048	5.072390
H	-2.554785	0.446450	-3.275032
H	-2.555246	0.445061	3.273916
H	-4.754798	-0.361951	2.490835
H	-4.756424	-0.363685	-2.490278
H	-6.778481	-1.021101	1.232628
H	-6.779141	-1.021847	-1.230380

(b) Re[BCPO](O) (symmetry-unconstrained)

Re	0.207476	-0.191020	1.516523
O	0.280393	1.555408	1.241539
O	0.431212	-1.939536	1.572085
N	0.081197	-0.079173	3.589990
N	0.381524	-0.307287	-0.552835
N	2.364595	-0.106904	1.709866

C	0.622126	0.001568	5.797920
C	1.131980	0.116091	4.462034
C	1.269274	-0.332373	-2.645129
C	1.565812	-0.463690	-1.239535
C	2.479033	0.217548	4.110912
C	2.827964	-0.516752	-0.661055
C	3.073310	0.084057	2.847024
C	3.214591	-0.361391	0.689711
C	4.476563	-0.031978	2.534361
C	4.562664	-0.321633	1.204010
C	-0.056371	-0.040127	-2.755212
C	-0.604430	-0.016379	-1.420953
C	-0.704253	-0.309430	5.704368
C	-1.036319	-0.355842	4.310971
C	-1.802733	-0.191262	1.397015
C	-1.973223	0.171603	-1.061495
C	-2.342814	-0.534655	3.775121
C	-2.535407	0.119009	0.195935
C	-2.723695	-0.468954	2.451291
C	-3.962550	0.023280	0.532954
C	-4.077003	-0.350533	1.895133
C	-5.102400	0.216119	-0.237528
C	-5.328344	-0.516722	2.475148
C	-6.349288	0.047242	0.352119
C	-6.461519	-0.317392	1.695714
H	1.207497	0.122990	6.694796
H	1.989837	-0.428218	-3.441151
H	3.163689	0.319421	4.943654
H	3.647933	-0.616785	-1.361605
H	5.286176	0.074547	3.237981
H	5.456458	-0.485939	0.624189
H	-0.617060	0.136464	-3.658803
H	-1.397573	-0.482560	6.511286
H	-2.644084	0.284961	-1.905469
H	-3.121833	-0.633826	4.522582
H	-5.027825	0.504913	-1.277829
H	-5.425326	-0.807321	3.513150
H	-7.244879	0.202607	-0.234913
H	-7.442805	-0.448821	2.132189