

Supporting Information

Use of Broken-Symmetry Density Functional Theory to Characterize the IspH Oxidized State: Implications for IspH Mechanism and Inhibition

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Table S1. Relative energies (kcal mol⁻¹) of the four valence isomers considered in this study, computed using DFT/COSMO and DFT/SCRF methods. The net spins on the different Fe atoms are given, relative to the Fe atom numbering in Figure 2B (e.g. βααβ indicates that Fe2 and Fe3 are each net spin α, while Fe1 and Fe4 are each net spin β). The energies of the lowest-energy states are set to zero and are indicated with bold-type font. The energy values of the lowest-energy valence isomers correspond to the relative energies given in Table 4A and 4C ($\Delta E_{\text{Tot,COSMO,pH=7}}$ and $\Delta E_{\text{Tot,SCRF,pH=7}}$).

	Relative energies (kcal mol ⁻¹)	
	DFT/COSMO	DFT/SCRF
RO⁻P⁻E^H		
βαβα	11.8	5.7
βααβ	7.9	0.0
αββα	7.9	0.0
ααββ	12.6	5.2
RO⁻P^HE^H		
βαβα	3.8	7.1
βααβ	0.3	2.2
αββα	0.0	2.4
ααββ	3.9	8.1
RO^HP⁻E⁻		
βαβα	15.4	7.7
βααβ	8.4	0.0
αββα	10.5	0.6
ααββ	13.3	4.6
RO^HP^HE⁻		
βαβα	10.4	11.7
βααβ	5.3	6.1
αββα	9.5	10.2
ααββ	12.2	13.4
RO^HP⁻E^H		
βαβα	6.3	9.2
βααβ	2.9	5.5
αββα	2.9	5.5
ααββ	8.0	10.3
RO^HP^HE^H		
βαβα	2.1	17.1
βααβ	0.0	13.3
αββα	0.0	13.3
ααββ	4.9	18.8

Table S2. Tabulation of isomer shifts (given in mm s^{-1}) for different protonation state conformers computed using the DFT/COSMO method and compared with experiment.¹ The error with respect to the experimental values is given as mean absolute error (MAE).

	Exp	$\text{RO}^- \text{P}^- \text{E}^{\text{H}}$	$\text{RO}^- \text{P}^{\text{H}} \text{E}^{\text{H}}$	$\text{RO}^{\text{H}} \text{P}^- \text{E}^-$	$\text{RO}^{\text{H}} \text{P}^{\text{H}} \text{E}^-$	$\text{RO}^{\text{H}} \text{P}^- \text{E}^{\text{H}}$	$\text{RO}^{\text{H}} \text{P}^{\text{H}} \text{E}^{\text{H}}$
Fe1	0.64	0.44	0.44	0.54	0.53	0.53	0.54
Fe2	0.38	0.42	0.42	0.39	0.38	0.38	0.38
Fe3	0.42	0.43	0.42	0.41	0.40	0.40	0.40
Fe4	0.42	0.43	0.42	0.41	0.40	0.40	0.39
AVG	0.47	0.43	0.43	0.44	0.43	0.43	0.43
MAE	-	0.07	0.06	0.03	0.04	0.04	0.04

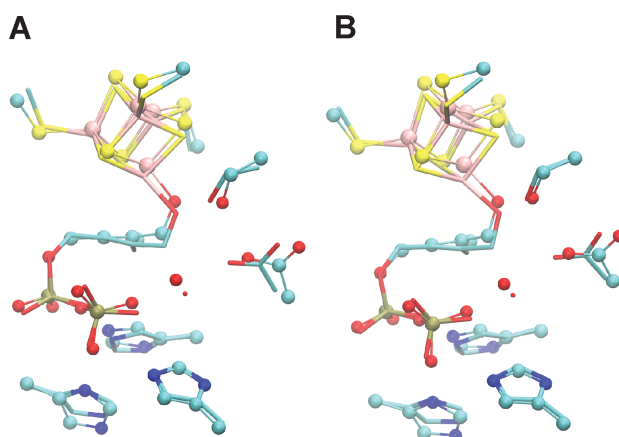
¹ Ahrens-Botzong, A.; Janthawornpong, K.; Wolny, J. A.; Tambou, E. N.; Rohmer, M.; Krasutsky, S.; Poulter, C. D.; Schunemann, V.; Seemann, M. *Angew Chem Int Edit* **2011**, *50*, 11976.

Table S3. Tabulation of quadrupole splittings (given in mm s^{-1}) for different protonation state conformers computed using the DFT/COSMO method and compared with experiment.² The error with respect to the experimental values is given as mean absolute error (MAE).

	Exp	$\text{RO}^- \text{P}^- \text{E}^{\text{H}}$	$\text{RO}^- \text{P}^{\text{H}} \text{E}^{\text{H}}$	$\text{RO}^{\text{H}} \text{P}^- \text{E}^-$	$\text{RO}^{\text{H}} \text{P}^{\text{H}} \text{E}^-$	$\text{RO}^{\text{H}} \text{P}^- \text{E}^{\text{H}}$	$\text{RO}^{\text{H}} \text{P}^{\text{H}} \text{E}^{\text{H}}$
Fe1	1.22	-0.64	-0.66	0.93	0.97	1.04	1.12
Fe2	0.92	1.03	1.03	1.11	1.08	1.18	1.17
Fe3	1.33	1.10	1.10	1.16	1.17	1.26	1.26
Fe4	1.33	0.88	0.83	0.65	0.61	0.53	0.52
AVG	1.21	0.91	0.91	0.96	0.96	1.00	1.02
MAE	-	0.34	0.35	0.33	0.32	0.33	0.31

² Ahrens-Botzong, A.; Janthawornpong, K.; Wolny, J. A.; Tambou, E. N.; Rohmer, M.; Krasutsky, S.; Poulter, C. D.; Schunemann, V.; Seemann, M. *Angew Chem Int Edit* **2011**, *50*, 11976.

Figure S1. Superposition of the geometry optimized (A) RO-P-E^H and (B) RO^HP-E⁻ states (each represented by the ball and stick format) onto the [4Fe-4S] IspH:HMBPP crystal structure (licorice).³



³ Grawert, T.; Span, I.; Eisenreich, W.; Rohdich, F.; Eppinger, J.; Bacher, A.; Groll, M. *P Natl Acad Sci USA* **2010**, *107*, 1077.

Text S1. Coordinate file (xyz format) for the lowest-energy RO-P-E^H state as computed from a DFT/SCRF single point energy calculation following geometry optimization of the active site quantum cluster at the OLYP/TZP level of theory. This low-energy state corresponds to a broken symmetry (BS) state where Fe1, Fe2, Fe3 and Fe4 (as numbered in Fig. 2B) have net spins of β , α , α and β , respectively.

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0.0000

Fe	-36.890346779	-0.094277390	10.800501781
Fe	-38.004529562	-2.354695182	9.545363495
Fe	-37.976574231	0.100055981	8.274356649
Fe	-35.620000053	-1.265912134	8.658972766
S	-39.078830368	-0.402777995	10.261798826
S	-36.103905272	-2.305868371	10.676770511
S	-36.021446848	1.008317599	8.881313436
S	-37.309952082	-1.962015724	7.297888211
S	-39.145960012	-4.322316737	9.918952819
C	-40.429904238	-4.528045674	8.618514918
H	-40.087000000	-5.237000000	7.860000000
H	-41.341989733	-4.917731385	9.079386572
H	-40.659447462	-3.574008167	8.139245632
S	-33.343383840	-1.636816294	8.397979105
C	-32.776576579	-1.182705617	10.093567307
H	-31.801000000	-1.623000000	10.285000000
H	-32.718907165	-0.096720934	10.201624859
H	-33.475368014	-1.573872340	10.832237040
S	-39.415661605	1.465562070	7.083054780
C	-38.296298618	2.757487013	6.397401599
H	-38.869000000	3.673000000	6.263000000
H	-37.478249584	2.953684345	7.091088317
H	-37.886447579	2.440735610	5.434806556
O	-36.175911803	0.985022465	12.179295933
C	-36.502932475	0.738726979	13.544816750
H	-37.402740895	1.296972831	13.822472906
H	-35.674212428	1.130386096	14.158522581
C	-36.724690938	-0.730086154	13.867283452
C	-37.994079151	-1.166009346	13.940850778
H	-38.791117490	-0.439625280	13.791769542
C	-35.492206482	-1.583904355	14.065440572
H	-34.675531103	-1.238479735	13.423589822

H	-35.137586209	-1.510246561	15.100638251
H	-35.658329092	-2.640651730	13.844819315
C	-38.491822871	-2.561303608	14.159814946
H	-37.752980221	-3.215477117	14.627719131
H	-38.788716925	-3.008757607	13.204552414
O	-39.719905684	-2.590517646	14.946710338
P	-39.672005775	-2.440374868	16.562830455
O	-38.494952636	-3.264093742	17.109711946
O	-41.061021879	-2.800329624	17.044179385
O	-39.252979276	-0.925959750	16.900872946
P	-39.922742151	0.644227086	16.863498629
O	-38.774164651	1.509883242	16.391607584
O	-41.190068106	0.611432937	16.031893685
O	-40.209041487	0.868443809	18.403346034
C	-35.064000000	-5.724000000	10.267000000
O	-33.945281477	-6.167444290	10.596103317
H	-35.163629796	-4.792852621	9.693090509
N	-36.233686682	-6.313417521	10.540989496
H	-37.109354138	-5.865555393	10.279273468
H	-36.262767851	-7.165289241	11.087441216
C	-37.835138038	-5.656484371	19.807042503
H	-37.109080514	-5.833268038	18.993092340
O	-37.797569395	-6.337881899	20.854069454
N	-38.691948239	-4.671428864	19.518654473
H	-38.632488974	-4.236839392	18.583894611
C	-39.795000000	-4.261000000	20.371000000
H	-39.563808828	-4.559809310	21.396053892
H	-40.697495286	-4.816851656	20.086139569
C	-40.148588840	-2.775516054	20.300755453
H	-40.430066405	-2.517284862	19.279685264
H	-41.052358013	-2.654926478	20.910692093
C	-39.112843014	-1.819414334	20.802537219
N	-38.980552662	-0.528348721	20.310737740
H	-39.507811098	-0.053033954	19.495646720
C	-38.028927396	0.104835563	20.996649158
H	-37.708310050	1.123076282	20.845459797
N	-37.541522023	-0.735996526	21.911675616
H	-36.814926946	-0.512271738	22.579025367
C	-38.195543239	-1.940483902	21.816790900
H	-37.957240848	-2.763382397	22.472747928
C	-32.924000000	0.447000000	16.553000000
H	-32.181741103	1.248494863	16.460383929
H	-32.395982529	-0.507787896	16.459626007
H	-33.625665788	0.534909625	15.720450161
C	-33.646976172	0.554918022	17.905732081
H	-32.917228268	0.546144356	18.723261672

H	-34.179915226	1.507917585	17.968700628
C	-34.624823239	-0.555956924	18.097196150
N	-34.263509013	-1.792442136	18.599536468
H	-33.363170785	-2.034470905	18.995484262
C	-35.289966012	-2.644521491	18.497701610
H	-35.271655778	-3.675596057	18.811301094
N	-36.310437402	-1.991805573	17.948437652
H	-37.226806190	-2.444530805	17.640528666
C	-35.929129924	-0.693459033	17.696006056
H	-36.603478563	0.007555581	17.224718705
C	-30.321000000	1.083000000	7.036000000
H	-29.973534570	0.124120794	7.459547932
O	-29.515388347	1.910344780	6.568113901
N	-31.649067233	1.233407065	7.089839597
H	-32.236978732	0.472451283	7.430183402
H	-32.085056075	2.059779244	6.699759557
C	-36.911000000	6.089000000	22.221000000
H	-36.799252287	7.026997719	22.778269629
H	-37.263465076	5.321641180	22.920701935
H	-35.919780331	5.790694514	21.866229475
C	-37.891991028	6.267918743	21.055923494
H	-38.865257223	6.593123748	21.440841964
H	-37.529106680	7.077305101	20.407055634
C	-38.087490655	5.029218687	20.233082755
N	-37.063146621	4.474263023	19.485542033
C	-37.589880774	3.412265020	18.889851195
H	-37.090180666	2.755759762	18.193128440
N	-38.888905208	3.243612727	19.215202738
H	-39.471156601	2.458600501	18.875369271
C	-39.227274585	4.266190308	20.073342478
H	-40.222253559	4.365279227	20.487123713
C	-33.593000000	4.997000000	17.938000000
H	-32.696013016	4.421901016	17.684449718
H	-33.245844701	6.015475473	18.165568740
N	-34.176504052	4.418106409	19.142336234
H	-35.198513824	4.509693628	19.295120538
C	-33.448957773	3.934983238	20.155217232
H	-34.073486116	3.586764052	20.996677859
O	-32.203265032	3.847585412	20.205520148
C	-34.543614252	5.037845144	16.749137356
H	-34.797877020	4.021031800	16.434695652
H	-35.481088279	5.529234860	17.030100219
C	-33.889332314	5.802732051	15.595946395
H	-32.901913631	5.372650046	15.368527303
H	-33.702985785	6.845973480	15.869582085
C	-34.621050439	5.808742608	14.272328582

O	-34.432823042	6.669553461	13.412064887
O	-35.442501455	4.767463228	14.116443729
C	-37.942000000	5.930000000	10.930000000
H	-38.249120974	6.444557547	10.012901587
H	-38.837111006	5.537544939	11.423435025
H	-37.472966767	6.667111090	11.592492953
C	-36.977505749	4.793542318	10.602047945
H	-37.503239615	4.052605354	9.987757039
C	-35.726056541	5.255334210	9.855390380
H	-35.064673496	4.407127874	9.647797894
H	-36.001320049	5.709616240	8.895295177
H	-35.170513026	5.998349007	10.437906441
O	-36.629969203	4.139407243	11.857189878
C	-43.719576163	0.874951229	6.195371253
H	-43.018174792	0.333106303	5.536443520
O	-44.953494143	0.803247420	6.031654492
N	-43.088757584	1.584336418	7.141727583
H	-42.073548402	1.518245166	7.151086818
C	-43.747000000	2.383000000	8.174000000
H	-44.534930335	2.975976024	7.698005289
H	-44.231033166	1.722164237	8.904207856
C	-42.766782056	3.313641468	8.892801542
H	-42.242765510	3.920914223	8.141334376
C	-43.501125801	4.244843767	9.850167366
H	-42.785843878	4.906032201	10.348051812
H	-44.226063830	4.861543312	9.308302454
H	-44.037334478	3.676258023	10.618742598
O	-41.800188248	2.549825032	9.644229980
H	-41.013846702	2.407147089	9.086214185
C	-43.148000000	-0.495000000	19.676000000
H	-42.125068717	-0.584445101	19.313157750
H	-43.107551835	-0.476579009	20.775015785
C	-43.958916296	-1.727022205	19.274632890
H	-43.571162518	-2.595574487	19.827145333
H	-45.006317519	-1.597558979	19.562534107
O	-43.959405292	-1.988290517	17.868608313
H	-43.035857708	-2.128355973	17.588582806
C	-43.745833721	0.842098410	19.244848098
O	-44.946184069	1.130160537	19.448891738
N	-42.860022489	1.685847592	18.679215623
H	-41.899167197	1.340772103	18.528355387
C	-43.209000000	2.973000000	18.111000000
H	-43.762897276	3.579032661	18.831398966
H	-42.279823805	3.500769563	17.877240781
C	-44.069116660	2.914753242	16.842143065
O	-45.038379987	3.697248716	16.702195247

N	-43.698443066	2.013674748	15.927918704
H	-42.822657059	1.486841330	16.064242653
C	-44.412000000	1.890000000	14.669000000
H	-44.493788990	2.884060284	14.212277869
H	-45.440747066	1.557188634	14.856418284
C	-43.741797022	0.956366022	13.659657964
H	-44.193772460	1.160063664	12.685973529
H	-42.674640162	1.179929654	13.580451544
C	-43.973956854	-0.529205935	13.920104805
O	-45.069673190	-1.066740548	13.636586397
N	-42.936685419	-1.210069206	14.424446300
H	-43.068304761	-2.178451334	14.678962885
H	-42.142544635	-0.720758250	14.834088609
C	-41.764000000	-6.382000000	14.826000000
H	-41.147153170	-7.090209016	14.256638697
H	-42.797607751	-6.747453072	14.817466022
H	-41.728465549	-5.414684870	14.311979012
C	-41.238810168	-6.265180460	16.251005948
H	-41.246536698	-7.250938848	16.732836054
H	-40.199893421	-5.912483500	16.242368921
O	-42.036902813	-5.395001520	17.069777024
H	-41.662211181	-4.481177441	17.016521633
O	-38.810131866	3.927269146	15.138945267
H	-37.968668470	3.905928060	14.660599864
H	-38.854791685	3.033994151	15.575680020
O	-42.557333804	-0.281398203	10.548321200
H	-42.350250787	0.632296635	10.279038806
H	-41.670752347	-0.653089442	10.686370531
O	-43.574331065	-6.355914702	19.191071176
H	-43.035664177	-5.978065070	18.456060080
H	-44.472288145	-6.042161801	19.001447395
H	-36.455377770	3.191020331	11.705884649
H	-35.813878986	4.726243117	13.183208453

Text S2. Coordinate file (xyz format) for the lowest-energy RO-P^{HE}H state as computed from a DFT/SCRF single point energy calculation following geometry optimization of the active site quantum cluster at the OLYP/TZP level of theory. This low-energy state corresponds to a BS state where Fe1, Fe2, Fe3 and Fe4 (as numbered in Fig. 2B) have net spins of β , α , α and β , respectively.

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0.0000

Fe	-36.839941231	-0.080007814	10.802147033
Fe	-38.006022049	-2.330152903	9.561121462
Fe	-37.965767553	0.129626958	8.304961166
Fe	-35.613430820	-1.256732687	8.668214198
S	-39.048613261	-0.364985482	10.308135392
S	-36.097615303	-2.307498637	10.681354263
S	-35.996089309	1.024316933	8.882339254
S	-37.322698834	-1.928558929	7.316905134
S	-39.159357636	-4.292927131	9.910410126
C	-40.420933445	-4.489246743	8.584699666
H	-40.087000000	-5.237000000	7.860000000
H	-41.359678685	-4.825090247	9.034025890
H	-40.598821405	-3.545713670	8.064711438
S	-33.346711378	-1.639587415	8.404752888
C	-32.786484121	-1.202039545	10.106249665
H	-31.801000000	-1.623000000	10.285000000
H	-32.753464789	-0.117572270	10.236079930
H	-33.472506949	-1.624359104	10.839642071
S	-39.420925656	1.511750581	7.168974397
C	-38.293772886	2.768398783	6.438899881
H	-38.869000000	3.673000000	6.263000000
H	-37.481967161	2.996921760	7.130423643
H	-37.875698502	2.411212930	5.494329912
O	-36.077265409	1.008529947	12.158003006
C	-36.394037764	0.774246479	13.521053362
H	-37.279336657	1.354126053	13.809440231
H	-35.555373489	1.144188856	14.137139702
C	-36.648577846	-0.692809324	13.842463098
C	-37.925319557	-1.112489317	13.860943778
H	-38.702798158	-0.374296061	13.667524198
C	-35.438188240	-1.566274090	14.073678740
H	-34.599008826	-1.232181529	13.456141991

H	-35.112347853	-1.497700647	15.118135662
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H	-37.727951636	-3.193494418	14.466526616
H	-38.810166610	-2.901211619	13.092337655
O	-39.662190973	-2.510005920	14.884708301
P	-39.553828480	-2.438880582	16.494280786
O	-38.433793051	-3.324049561	17.017197904
O	-40.956197791	-2.615435890	17.013853441
O	-38.976643226	-0.924151758	16.815038599
P	-39.419271509	0.628164948	16.978440587
O	-38.235802391	1.483883559	16.639358179
O	-40.608940488	0.836327641	15.874677502
O	-40.049405568	0.773285164	18.366228944
C	-35.064000000	-5.724000000	10.267000000
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N	-36.245556702	-6.297301551	10.526058427
H	-37.111076784	-5.847919636	10.234241586
H	-36.295839669	-7.125038355	11.107081751
C	-37.840185032	-5.689637667	19.854872481
H	-37.112931824	-5.891664901	19.048066872
O	-37.822886464	-6.345086545	20.914800681
N	-38.682319735	-4.693475938	19.541163213
H	-38.616021686	-4.298850121	18.597058427
C	-39.795000000	-4.261000000	20.371000000
H	-39.608586788	-4.603458979	21.390675815
H	-40.711411676	-4.766174490	20.040787943
C	-40.074370501	-2.760857426	20.342623828
H	-40.299142248	-2.448937740	19.321378554
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C	-39.010918522	-1.882548338	20.919061840
N	-38.823390087	-0.577680379	20.491954100
H	-39.314061374	-0.108383638	19.701222227
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H	-37.524128852	1.021781011	21.127549740
N	-37.430527070	-0.893701158	22.102144980
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H	-37.917950122	-2.929354028	22.567670445
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H	-32.403154885	-0.503630204	16.399260107
H	-33.678652618	0.557522267	15.771794790
C	-33.557669381	0.515232954	17.953040223
H	-32.780379162	0.490310515	18.724653824

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C	-34.517186296	-0.607257237	18.168398934
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C	-35.172080369	-2.691798914	18.616916499
H	-35.157411123	-3.712093305	18.964080274
N	-36.177167680	-2.066278646	18.007266057
H	-37.062800426	-2.517479226	17.687869188
C	-35.802713806	-0.771839207	17.725514216
H	-36.460028498	-0.085823802	17.212104570
C	-30.321000000	1.083000000	7.036000000
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H	-36.726798259	6.994650552	22.812517328
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H	-35.944233214	5.713641046	21.875028325
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H	-38.800189502	6.780467381	21.411074131
H	-37.401599491	7.169406501	20.414761435
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C	-37.592189189	3.434424861	19.032686706
H	-37.086657301	2.714918523	18.407688185
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C	-39.251648609	4.428132531	20.083657061
H	-40.256857033	4.583990017	20.451094015
C	-33.593000000	4.997000000	17.938000000
H	-32.719548897	4.393929188	17.667866231
H	-33.211336922	6.004995344	18.155411836
N	-34.172506093	4.437945985	19.154943363
H	-35.187895902	4.550947986	19.321768958
C	-33.447097200	3.945953357	20.166333031
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C	-34.570127419	5.059954481	16.770567896
H	-34.860490390	4.048952610	16.468057192
H	-35.486390634	5.579943640	17.071141879
C	-33.921646941	5.801357136	15.599329997
H	-32.951807816	5.342136671	15.354132247
H	-33.701762760	6.840406678	15.863067507
C	-34.675262066	5.821990550	14.288207198

O	-34.491744196	6.685770527	13.430315179
O	-35.507787057	4.787830340	14.136829872
C	-37.942000000	5.930000000	10.930000000
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H	-38.852134591	5.539480221	11.397875352
H	-37.483490628	6.656157816	11.611592049
C	-36.979769016	4.793194774	10.607575734
H	-37.495288303	4.063699584	9.971691123
C	-35.709799451	5.258576638	9.896184237
H	-35.046485108	4.411552888	9.690280349
H	-35.965184022	5.725255326	8.936601016
H	-35.164405110	5.992340497	10.499649598
O	-36.673265008	4.120806420	11.864563618
C	-43.626032000	0.722629363	6.325508669
H	-42.894409360	0.214735019	5.672958962
O	-44.846160893	0.485989651	6.238827918
N	-43.044930558	1.581351356	7.173681005
H	-42.028716809	1.624377028	7.136651251
C	-43.747000000	2.383000000	8.174000000
H	-44.537244652	2.953057289	7.672369171
H	-44.234909165	1.722893238	8.901633383
C	-42.805145316	3.349288350	8.898495890
H	-42.280485475	3.956354117	8.147207966
C	-43.582076744	4.278903277	9.822672269
H	-42.892484098	4.962060502	10.327056576
H	-44.305576919	4.872446500	9.254217438
H	-44.125954835	3.711299510	10.586711597
O	-41.831398569	2.632166966	9.687841187
H	-41.044331696	2.469709934	9.134037201
C	-43.148000000	-0.495000000	19.676000000
H	-42.111275272	-0.582229750	19.352871031
H	-43.158849741	-0.520372389	20.774047956
C	-43.953219566	-1.694843911	19.172153691
H	-43.576343648	-2.604526986	19.659259977
H	-45.004595445	-1.583092943	19.450595778
O	-43.925854487	-1.832618040	17.747009185
H	-43.011580760	-2.045774893	17.489080387
C	-43.731313758	0.847353767	19.268349476
O	-44.894050004	1.182426730	19.557564894
N	-42.880494086	1.642521342	18.569104096
H	-41.927385209	1.309076830	18.428439402
C	-43.209000000	2.973000000	18.111000000
H	-43.907289404	3.443334273	18.807000231
H	-42.302873511	3.586291142	18.106955782
C	-43.828720370	3.094589246	16.723100522
O	-44.245499779	4.203089856	16.335922674

N	-43.850990278	1.968182762	15.997358324
H	-43.536778316	1.122522118	16.455609302
C	-44.412000000	1.890000000	14.669000000
H	-44.363932827	2.893247492	14.240289152
H	-45.474947784	1.620942144	14.719124770
C	-43.696947487	0.916853001	13.729193457
H	-44.058254373	1.129260144	12.719035139
H	-42.619053763	1.095520434	13.725059487
C	-44.030387664	-0.551534168	13.974602654
O	-45.199981513	-0.967985863	13.873920284
N	-43.001436261	-1.366437889	14.275734800
H	-43.182892665	-2.344442596	14.452846603
H	-42.060430826	-1.030607286	14.415083544
C	-41.764000000	-6.382000000	14.826000000
H	-41.121359768	-7.113468791	14.318827803
H	-42.787900521	-6.774063623	14.830068399
H	-41.747443987	-5.454506825	14.241218100
C	-41.264255678	-6.151157256	16.243869883
H	-41.259072129	-7.098276601	16.797002841
H	-40.234313583	-5.776606690	16.227035789
O	-42.100359922	-5.237962324	16.981986270
H	-41.691117954	-4.346961716	16.946749118
O	-38.984711177	3.739704649	15.051561904
H	-38.266600527	3.979825612	14.445084124
H	-38.583185811	3.063669573	15.636635993
O	-42.510416552	-0.223981778	10.626800380
H	-42.349902324	0.691137123	10.331196617
H	-41.611334514	-0.592613660	10.625300666
O	-43.707232830	-6.190103907	19.092194741
H	-43.157723257	-5.813595153	18.367939373
H	-44.613982591	-5.960765184	18.834667751
H	-36.424462871	3.190846404	11.696700119
H	-40.309258669	1.523611938	15.255100166
H	-35.873754700	4.743337212	13.202856035

Text S3. Coordinate file (xyz format) for the lowest-energy RO^HP-E⁻ state as computed from a DFT/SCRF single point energy calculation following geometry optimization of the active site quantum cluster at the OLYP/TZP level of theory. This low-energy state corresponds to a BS state where Fe1, Fe2, Fe3 and Fe4 (as numbered in Fig. 2B) have net spins of β , α , α and β , respectively.

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0.0000

Fe	-36.963073988	-0.058123418	10.596341215
Fe	-38.008872932	-2.264446202	9.463449651
Fe	-37.888552871	0.118432979	8.091362382
Fe	-35.609979328	-1.263559750	8.633165546
S	-39.093792519	-0.288729209	10.023526640
S	-36.165134792	-2.215287278	10.667910106
S	-35.967628366	1.023668526	8.791081723
S	-37.227639581	-1.982836121	7.252325095
S	-39.221355403	-4.139771388	9.827374448
C	-40.337138289	-4.309633918	8.376087865
H	-40.087000000	-5.237000000	7.860000000
H	-41.376138202	-4.344886503	8.714496879
H	-40.212239924	-3.477238021	7.681858368
S	-33.365724308	-1.697606420	8.430941419
C	-32.804242895	-1.238864145	10.124051839
H	-31.801000000	-1.623000000	10.285000000
H	-32.805792659	-0.153366141	10.251728566
H	-33.463393559	-1.687625839	10.866881935
S	-39.251271980	1.345299467	6.731699071
C	-38.222507609	2.798533103	6.263005325
H	-38.869000000	3.673000000	6.263000000
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H	-37.792203088	2.656294098	5.268366850
O	-36.280193235	1.176916268	12.161584606
C	-36.695999844	0.923961443	13.557531570
H	-37.631600568	1.451765970	13.739770302
H	-35.915004445	1.359901895	14.192629616
C	-36.852509079	-0.548578689	13.824275001
C	-38.108008055	-1.028966031	13.897996560
H	-38.938150024	-0.338660703	13.756053254
C	-35.606925889	-1.386097675	14.039048645
H	-34.700217027	-0.780651673	13.961177439

H	-35.608674825	-1.856089778	15.028750872
H	-35.518391922	-2.190677652	13.304265906
C	-38.525864872	-2.443659712	14.155362693
H	-37.731682780	-3.047979682	14.600339108
H	-38.824196041	-2.919808930	13.213346486
O	-39.717319907	-2.518756705	14.982166865
P	-39.602922879	-2.387300161	16.603874075
O	-38.443185228	-3.266054182	17.097741994
O	-40.990595917	-2.701411521	17.121880687
O	-39.117009395	-0.900070721	16.935348238
P	-39.816038418	0.669781174	16.929415671
O	-40.142133220	0.858340607	18.461677544
O	-41.057054045	0.623815921	16.061740262
O	-38.645800553	1.536033713	16.504243487
C	-35.064000000	-5.724000000	10.267000000
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H	-37.118923497	-5.878233615	19.027752944
O	-37.865737273	-6.386553264	20.865961500
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H	-38.606893971	-4.249156683	18.599494901
C	-39.795000000	-4.261000000	20.371000000
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H	-40.709014696	-4.783404935	20.059456004
C	-40.101256547	-2.763820565	20.334231044
H	-40.374238464	-2.475183524	19.319067941
H	-41.000611463	-2.627225573	20.947627818
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H	-36.678693581	-0.649838785	22.624693324
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H	-32.418459681	-0.516493239	16.430950507
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H	-32.850756610	0.530310629	18.723970027

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N	-36.266576413	-1.991976027	17.994982453
H	-37.174478861	-2.447633067	17.681826465
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H	-36.559976124	-0.001796445	17.245015124
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H	-38.799761733	6.733593160	21.376610200
H	-37.396821328	7.115737737	20.386063772
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H	-33.187029555	6.008126027	18.085069451
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C	-33.418286229	4.110778161	20.236297722
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H	-33.171000064	4.834004098	15.180159296
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O	-35.889891674	4.998074448	14.174548911
C	-37.942000000	5.930000000	10.930000000
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O	-36.805902828	3.918356833	11.793707487
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O	-44.786175815	0.388422627	6.337107915
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C	-43.662322190	4.295322838	9.803999594
H	-43.000004854	4.976754335	10.345654465
H	-44.329321931	4.888882099	9.170266134
H	-44.273231725	3.752758696	10.534592507
O	-41.960248467	2.586907465	9.840292737
H	-41.108249227	2.471774892	9.392778650
C	-43.148000000	-0.495000000	19.676000000
H	-42.116753014	-0.583039060	19.335995065
H	-43.134404308	-0.484842985	20.775608682
C	-43.951323222	-1.720531313	19.241897899
H	-43.565809824	-2.598453566	19.782723580
H	-45.002466271	-1.601005330	19.520332473
O	-43.933454061	-1.950573221	17.831931443
H	-43.003513489	-2.061396108	17.561417933
C	-43.734338967	0.844910629	19.241998699
O	-44.926038369	1.151698581	19.467119395
N	-42.855251442	1.673113871	18.641616379
H	-41.890601282	1.337750149	18.506892615
C	-43.209000000	2.973000000	18.111000000
H	-43.794442018	3.538633906	18.839855440
H	-42.285141667	3.531325181	17.929933035
C	-44.025057123	2.973214679	16.816837597
O	-44.872646920	3.873001941	16.612024636

N	-43.750429375	1.987646363	15.956745437
H	-42.932530792	1.401542822	16.141168756
C	-44.412000000	1.890000000	14.669000000
H	-44.485996051	2.894942958	14.239101781
H	-45.441213468	1.533145659	14.800698253
C	-43.670369116	0.990777691	13.678984920
H	-44.077143621	1.194975150	12.685384545
H	-42.607638274	1.248176840	13.661954535
C	-43.872133331	-0.503556162	13.912102439
O	-44.960894010	-1.056544666	13.635706675
N	-42.811888196	-1.175101970	14.383553394
H	-42.918124562	-2.154359066	14.607463439
H	-42.019494952	-0.685294756	14.796815360
C	-41.764000000	-6.382000000	14.826000000
H	-41.055827961	-7.102281930	14.394911382
H	-42.757840388	-6.845357175	14.828775637
H	-41.792209743	-5.500643728	14.174648401
C	-41.337610410	-6.003425951	16.232689451
H	-41.270554158	-6.904940937	16.858833482
H	-40.342861876	-5.545166643	16.214667275
O	-42.276062526	-5.093180360	16.834966894
H	-41.808301570	-4.228262528	16.947921814
O	-38.658269654	3.954680421	15.204541057
H	-37.729679068	4.108340299	14.967750870
H	-38.666770935	3.076728503	15.662472036
O	-42.643325028	-0.444640204	10.452986032
H	-42.474381836	0.498387297	10.283186311
H	-41.745956876	-0.805194493	10.515684946
O	-44.036688816	-6.324011692	18.633773350
H	-43.410624133	-5.830108268	18.052291644
H	-44.682577525	-5.652470604	18.903321170
H	-36.461095433	4.437009423	12.565679880
H	-36.422298478	2.145232902	11.982036849

Text S4. Coordinate file (xyz format) for the lowest-energy RO^HP^HE⁻ state as computed from a DFT/SCRF single point energy calculation following geometry optimization of the active site quantum cluster at the OLYP/TZP level of theory. This low-energy state corresponds to a BS state where Fe1, Fe2, Fe3 and Fe4 (as numbered in Fig. 2B) have net spins of β , α , α and β , respectively.

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0.0000

Fe	-36.934190017	-0.076342543	10.636255829
Fe	-38.005746838	-2.249165195	9.503662312
Fe	-37.895597428	0.139531651	8.169773073
Fe	-35.614432230	-1.260424340	8.655513801
S	-39.077769059	-0.280897901	10.117130223
S	-36.151028803	-2.236367269	10.689534812
S	-35.959075866	1.029622721	8.849166338
S	-37.254668266	-1.942893969	7.288498247
S	-39.228356653	-4.122320526	9.808581389
C	-40.284093464	-4.265377620	8.311133705
H	-40.087000000	-5.237000000	7.860000000
H	-41.338133798	-4.193545930	8.590470918
H	-40.045747019	-3.487835843	7.584638121
S	-33.378534938	-1.707863893	8.441200198
C	-32.825350646	-1.290490183	10.147611573
H	-31.801000000	-1.623000000	10.285000000
H	-32.885785587	-0.213406809	10.320668128
H	-33.451182135	-1.806556983	10.875450026
S	-39.289210490	1.399418421	6.888500678
C	-38.224743234	2.806097569	6.373757992
H	-38.869000000	3.673000000	6.263000000
H	-37.475305700	3.021188983	7.134644614
H	-37.731824834	2.588228907	5.423605452
O	-36.155985974	1.106345549	12.232253869
C	-36.604164575	0.848734691	13.611239996
H	-37.521489106	1.412067555	13.778303222
H	-35.827806026	1.244567844	14.276417207
C	-36.826598295	-0.624012931	13.854579874
C	-38.099801401	-1.060428107	13.842626454
H	-38.890238628	-0.341801704	13.629753744
C	-35.633645060	-1.515724191	14.129980610
H	-34.701876273	-0.947581970	14.156973036

H	-35.736907175	-2.033740915	15.088822540
H	-35.517296993	-2.288791292	13.365905242
C	-38.591667347	-2.453177828	14.079146009
H	-37.828337390	-3.115222069	14.490885532
H	-38.958519927	-2.890227284	13.144018257
O	-39.766564087	-2.463702281	14.950984887
P	-39.604419221	-2.397777927	16.564601771
O	-38.480742936	-3.294804711	17.047498628
O	-40.994852650	-2.549207216	17.118716784
O	-38.993809179	-0.895808906	16.860072283
P	-39.398581721	0.669306617	17.030360831
O	-40.016559882	0.823499480	18.419234081
O	-40.600481351	0.894704530	15.930992529
O	-38.203920750	1.488180825	16.656045085
C	-35.064000000	-5.724000000	10.267000000
O	-34.002175697	-6.271808613	10.620694885
H	-35.060026703	-4.812984805	9.650460099
N	-36.292324571	-6.162201131	10.566709599
H	-37.114052914	-5.654387896	10.252029058
H	-36.417284357	-6.994018100	11.129930043
C	-37.842317024	-5.682015943	19.823751479
H	-37.123768899	-5.871988576	19.006031956
O	-37.811592818	-6.348997192	20.875780568
N	-38.688906147	-4.683240343	19.529070116
H	-38.631925500	-4.281540702	18.586987177
C	-39.795000000	-4.261000000	20.371000000
H	-39.613598030	-4.640354356	21.378897933
H	-40.719386928	-4.741340547	20.024869071
C	-40.055968906	-2.757194881	20.402892793
H	-40.315598832	-2.407834794	19.402561813
H	-40.951346683	-2.618351064	21.022304986
C	-38.963024555	-1.907694049	20.965314030
N	-38.794867366	-0.585472271	20.583739172
H	-39.301532596	-0.095925548	19.822527671
C	-37.802600856	-0.033487227	21.285901180
H	-37.458217133	0.985602772	21.214530589
N	-37.323422878	-0.967033769	22.106235055
H	-36.571409813	-0.822145127	22.767652931
C	-38.019430474	-2.140227795	21.933050428
H	-37.786605428	-3.022429860	22.508796411
C	-32.924000000	0.447000000	16.553000000
H	-32.169029717	1.228652762	16.411871712
H	-32.431775604	-0.522435352	16.426739312
H	-33.675897773	0.558517300	15.769139346
C	-33.557578150	0.574262633	17.949031217
H	-32.781533473	0.567253981	18.722062475

H	-34.081568891	1.530821715	18.036492168
C	-34.528374878	-0.531452537	18.197599863
N	-34.178498330	-1.742872685	18.765010150
H	-33.283303844	-1.969495471	19.182344029
C	-35.196675133	-2.603441995	18.681474297
H	-35.188003826	-3.619333973	19.041539782
N	-36.205104650	-1.974844626	18.078850744
H	-37.086782116	-2.428077918	17.769609683
C	-35.821640522	-0.686804452	17.774925750
H	-36.479890372	0.000280347	17.264051088
C	-30.321000000	1.083000000	7.036000000
H	-29.942689416	0.091666030	7.341646346
O	-29.555517380	1.962626164	6.599402019
N	-31.644661343	1.215934392	7.184969939
H	-32.211437849	0.429631850	7.494436913
H	-32.102644330	2.076722096	6.911403101
C	-36.911000000	6.089000000	22.221000000
H	-36.696774487	6.981120555	22.823322440
H	-37.404565198	5.357330089	22.871500833
H	-35.956300019	5.665454308	21.900557822
C	-37.794727214	6.439387619	21.020660923
H	-38.739784543	6.878589022	21.358327795
H	-37.293815094	7.196777748	20.402906920
C	-38.069865626	5.213230464	20.213032192
N	-37.036878240	4.514482583	19.614994160
C	-37.587583099	3.429617448	19.099985357
H	-37.083832421	2.670952641	18.522650776
N	-38.918657647	3.384760154	19.339277228
H	-39.521946281	2.620253026	19.042912852
C	-39.248430058	4.518337998	20.049219193
H	-40.259023119	4.720019714	20.377447974
C	-33.593000000	4.997000000	17.938000000
H	-32.738327983	4.358754269	17.685310958
H	-33.191338464	6.013455446	18.054460864
N	-34.133607491	4.549900548	19.219866795
H	-35.155366767	4.604017114	19.374178754
C	-33.381163462	4.201066996	20.268172120
H	-33.985197977	3.925267405	21.150441647
O	-32.132521064	4.161658087	20.313734135
C	-34.625481290	4.985646816	16.812127276
H	-35.016052388	3.973417750	16.660150748
H	-35.480095220	5.609765662	17.097020329
C	-34.013218132	5.513528823	15.512751405
H	-33.257745184	4.803403189	15.144147204
H	-33.480233581	6.451380952	15.702047884
C	-34.985693741	5.759744713	14.340691693

O	-34.691020109	6.714825058	13.558642933
O	-35.986743771	4.984027092	14.214251471
C	-37.942000000	5.930000000	10.930000000
H	-38.101672425	6.530538905	10.026483782
H	-38.904406320	5.505649098	11.238340631
H	-37.585087905	6.594394740	11.725336339
C	-36.928065635	4.805440009	10.650763052
H	-37.341284778	4.164584913	9.863055475
C	-35.571616093	5.335862071	10.178765575
H	-34.901711743	4.501461634	9.942584647
H	-35.684369064	5.949841029	9.275964086
H	-35.104435198	5.947267094	10.958811433
O	-36.774418284	3.918091902	11.781315057
C	-43.515215083	0.585866695	6.482552276
H	-42.758694897	0.060499087	5.873556521
O	-44.723259779	0.285048424	6.424893071
N	-42.982786869	1.545428113	7.251842142
H	-41.975155370	1.662339704	7.186503578
C	-43.747000000	2.383000000	8.174000000
H	-44.491570338	2.949664336	7.602371232
H	-44.297324817	1.743734859	8.874428658
C	-42.865771940	3.362872545	8.950015975
H	-42.271268176	3.948683913	8.235319379
C	-43.714514657	4.317108706	9.780479410
H	-43.071490106	5.026184591	10.309609058
H	-44.398283622	4.881782242	9.138482668
H	-44.310005220	3.769773386	10.520262379
O	-41.967388203	2.655689847	9.842403114
H	-41.121621408	2.535905010	9.382716131
C	-43.148000000	-0.495000000	19.676000000
H	-42.112762333	-0.594078885	19.350409511
H	-43.150547290	-0.495246611	20.774838386
C	-43.960876111	-1.703728519	19.209380476
H	-43.577568969	-2.601455735	19.716082311
H	-45.008770060	-1.585084730	19.497329625
O	-43.951818755	-1.877514623	17.789611574
H	-43.032053963	-2.050150227	17.522933250
C	-43.727817694	0.842430970	19.245974881
O	-44.902117543	1.169804646	19.491873805
N	-42.860095162	1.652429931	18.586581496
H	-41.896935708	1.336940212	18.481651262
C	-43.209000000	2.973000000	18.111000000
H	-43.817479354	3.497151633	18.850631399
H	-42.290096102	3.552792702	17.980037014
C	-43.969215118	3.040215606	16.788158030
O	-44.637516229	4.052604815	16.505876172

N	-43.802759374	1.984119768	15.976669105
H	-43.272763200	1.201880855	16.338203360
C	-44.412000000	1.890000000	14.669000000
H	-44.456953963	2.901629309	14.255363888
H	-45.451011510	1.547114749	14.754172554
C	-43.666792714	0.984067056	13.686253794
H	-44.051147300	1.215431899	12.688963151
H	-42.597188255	1.213408081	13.675821188
C	-43.931695949	-0.506190208	13.885594909
O	-45.071920093	-0.978143415	13.728949479
N	-42.875949124	-1.274955825	14.216897814
H	-43.012095720	-2.264910031	14.364530912
H	-41.958286875	-0.899101890	14.397223908
C	-41.764000000	-6.382000000	14.826000000
H	-41.038411061	-7.060668909	14.358903444
H	-42.727661375	-6.901576407	14.878812614
H	-41.878036859	-5.505781954	14.176998426
C	-41.286981805	-5.978413546	16.208769744
H	-41.167445548	-6.869338105	16.840496043
H	-40.307858492	-5.491787940	16.145344724
O	-42.227295547	-5.090726991	16.849183863
H	-41.793649617	-4.217515048	16.947707587
O	-38.574766715	4.081324893	15.182150769
H	-37.690840095	4.357600715	14.869087707
H	-38.378940704	3.336680097	15.774834775
O	-42.591398724	-0.333218182	10.532027101
H	-42.454495411	0.604743848	10.310196876
H	-41.691883743	-0.690767447	10.477545074
O	-44.203415366	-6.248964899	18.526059818
H	-43.517439616	-5.791243699	17.989821956
H	-44.688304349	-5.527596517	18.953867095
H	-36.475677220	4.443570223	12.566154683
H	-40.284607425	1.579475427	15.319808690
H	-36.288733490	2.071264930	12.050728959

Text S5. Coordinate file (xyz format) for the lowest-energy RO^{HP}-E^H state as computed from a DFT/SCRF single point energy calculation following geometry optimization of the active site quantum cluster at the OLYP/TZP level of theory. This low-energy state corresponds to a BS state where Fe1, Fe2, Fe3 and Fe4 (as numbered in Fig. 2B) have net spins of α , β , β and α , respectively.

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0.0000

Fe	-36.980822900	-0.236467879	10.706553391
Fe	-37.996690611	-2.401698913	9.495425988
Fe	-37.940497617	0.110933481	8.268496578
Fe	-35.641904357	-1.287093905	8.682488557
S	-39.102379519	-0.468616026	10.172590943
S	-36.140359744	-2.358037792	10.686101335
S	-36.009121327	0.984446053	8.991696241
S	-37.279928868	-1.937939171	7.297999360
S	-39.135325861	-4.309858617	9.885273543
C	-40.433916276	-4.518589601	8.604783267
H	-40.087000000	-5.237000000	7.860000000
H	-41.336541126	-4.904765673	9.085404530
H	-40.667003728	-3.570290565	8.117137292
S	-33.390186799	-1.655756893	8.438403585
C	-32.787682964	-1.196123089	10.118544514
H	-31.801000000	-1.623000000	10.285000000
H	-32.733258429	-0.109404664	10.224236916
H	-33.455772346	-1.604694856	10.876304468
S	-39.354292203	1.478895243	7.126496821
C	-38.266344028	2.778012451	6.409438865
H	-38.869000000	3.673000000	6.263000000
H	-37.448928533	3.011372332	7.091680634
H	-37.859602845	2.448454025	5.450872822
O	-36.109658225	1.033347104	12.297648419
C	-36.493542504	0.727460129	13.706554440
H	-37.409821617	1.290093911	13.869288311
H	-35.705553478	1.146355940	14.340440991
C	-36.704907822	-0.742443458	13.927435948
C	-37.981442588	-1.169154341	13.961922453
H	-38.771797009	-0.429582370	13.844771098
C	-35.477401995	-1.604698350	14.115752657
H	-34.640666245	-1.264651189	13.495576616

H	-35.131937747	-1.560208522	15.154321937
H	-35.650433794	-2.651859232	13.865214440
C	-38.490481999	-2.564096436	14.157546274
H	-37.754061334	-3.225027791	14.619082660
H	-38.772444373	-2.992604369	13.188837892
O	-39.715326560	-2.584779023	14.930818761
P	-39.663026475	-2.440562727	16.557927147
O	-38.491087190	-3.275512311	17.090180525
O	-41.056751097	-2.784418924	17.029447046
O	-39.223093014	-0.930138373	16.882664380
P	-39.893752115	0.644945810	16.854028163
O	-38.724240330	1.493245430	16.385992726
O	-41.145559168	0.615143848	16.000404694
O	-40.190124234	0.867436963	18.385395789
C	-35.064000000	-5.724000000	10.267000000
O	-33.942682732	-6.131501879	10.626198296
H	-35.172741802	-4.820326424	9.652245387
N	-36.226171731	-6.323326015	10.552823439
H	-37.104510002	-5.913824486	10.249820690
H	-36.246249658	-7.166755051	11.112301564
C	-37.829965361	-5.656497462	19.815240798
H	-37.105190174	-5.836716280	19.000587657
O	-37.790401041	-6.330823746	20.865521549
N	-38.689482728	-4.673713426	19.522311197
H	-38.631907361	-4.249619856	18.585189642
C	-39.795000000	-4.261000000	20.371000000
H	-39.566977328	-4.561164423	21.396125941
H	-40.697964560	-4.814434693	20.082988173
C	-40.143996433	-2.774405127	20.301873211
H	-40.423007751	-2.513772230	19.280736541
H	-41.048583558	-2.651176532	20.909913615
C	-39.106183101	-1.821840438	20.806586085
N	-38.973162763	-0.529080039	20.319352520
H	-39.494922386	-0.059149570	19.506811791
C	-38.020903353	0.102835702	21.005546248
H	-37.701541761	1.121835643	20.857150128
N	-37.533103814	-0.741490171	21.916244925
H	-36.804525679	-0.520333986	22.582520189
C	-38.187091308	-1.945727602	21.818580383
H	-37.948673756	-2.769992780	22.472623474
C	-32.924000000	0.447000000	16.553000000
H	-32.180370301	1.246089934	16.456132267
H	-32.400750620	-0.509493653	16.454751588
H	-33.629065353	0.537881475	15.723805400
C	-33.639511174	0.556798367	17.910230372
H	-32.903452460	0.544646761	18.721431271

H	-34.168301507	1.511868526	17.979407866
C	-34.617793060	-0.552905471	18.108227606
N	-34.252385059	-1.791089152	18.602812652
H	-33.349120135	-2.033448185	18.992607378
C	-35.277213139	-2.644854068	18.503430998
H	-35.256275515	-3.676982678	18.813276080
N	-36.301807238	-1.991579805	17.961731823
H	-37.213641315	-2.442174221	17.655782847
C	-35.924347453	-0.690556142	17.714010748
H	-36.606981940	0.013688596	17.260143851
C	-30.321000000	1.083000000	7.036000000
H	-29.976749999	0.119938881	7.452744655
O	-29.515712342	1.910325865	6.570589810
N	-31.649184048	1.241511196	7.097533722
H	-32.240178166	0.477579741	7.416775056
H	-32.081799786	2.067520955	6.702847657
C	-36.911000000	6.089000000	22.221000000
H	-36.794612083	7.025603612	22.779547026
H	-37.270333154	5.323373794	22.918952015
H	-35.920765497	5.784890699	21.868547436
C	-37.887556830	6.276147956	21.053648752
H	-38.859980798	6.606827547	21.435469710
H	-37.517702985	7.082754270	20.405634464
C	-38.087186055	5.038424224	20.231250527
N	-37.062869185	4.479102982	19.486814406
C	-37.589913222	3.414926057	18.896234277
H	-37.088891718	2.753107070	18.205422120
N	-38.889627282	3.249337088	19.221269248
H	-39.472189662	2.466182707	18.881896206
C	-39.228000714	4.276664997	20.073421594
H	-40.223297790	4.379073925	20.485252418
C	-33.593000000	4.997000000	17.938000000
H	-32.697247779	4.421033790	17.681694110
H	-33.244064440	6.014239230	18.167166297
N	-34.175910620	4.415684576	19.140993201
H	-35.196969862	4.510551151	19.296520818
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O	-32.200143304	3.858138779	20.205470030
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H	-34.801288717	4.028381972	16.434722367
H	-35.478136466	5.541121610	17.029504145
C	-33.881043129	5.806746750	15.598636392
H	-32.895937215	5.370691736	15.373066015
H	-33.689276458	6.848000004	15.874676197
C	-34.607303972	5.822673578	14.273848707

O	-34.426504024	6.688314186	13.419715112
O	-35.424904088	4.773481299	14.103479190
C	-37.942000000	5.930000000	10.930000000
H	-38.261055754	6.461975131	10.027077675
H	-38.829915738	5.520331380	11.422077055
H	-37.473561955	6.657866615	11.602906451
C	-36.974323641	4.814814764	10.571030881
H	-37.496949297	4.082693347	9.942522081
C	-35.716364505	5.286007508	9.845639616
H	-35.048235078	4.442289272	9.638488711
H	-35.981729460	5.746019602	8.886167946
H	-35.169421508	6.023643892	10.442269461
O	-36.639371086	4.142134275	11.821427804
C	-43.705995794	0.853017254	6.210402210
H	-42.999378886	0.315951583	5.553061256
O	-44.938916666	0.762654574	6.054386207
N	-43.081689272	1.583990092	7.146115462
H	-42.067076045	1.532017723	7.151140676
C	-43.747000000	2.383000000	8.174000000
H	-44.532889896	2.975498980	7.694102325
H	-44.234748401	1.722338664	8.901463920
C	-42.774057690	3.319215124	8.894963082
H	-42.246746241	3.924832886	8.144841782
C	-43.513325720	4.251674422	9.846217093
H	-42.800803758	4.914405135	10.345857925
H	-44.234824679	4.866785182	9.298279153
H	-44.054184079	3.685030856	10.612835130
O	-41.804579788	2.560244027	9.654216565
H	-41.010492093	2.440026877	9.104339230
C	-43.148000000	-0.495000000	19.676000000
H	-42.124279838	-0.586501115	19.315726593
H	-43.109994329	-0.476576897	20.774925806
C	-43.959539580	-1.724978863	19.269928677
H	-43.569148100	-2.596683816	19.815475128
H	-45.005725895	-1.598188868	19.562692441
O	-43.965453564	-1.976210827	17.861607983
H	-43.043546284	-2.120999919	17.580204370
C	-43.744238350	0.841428276	19.242418941
O	-44.943662197	1.131553396	19.445154991
N	-42.858060432	1.684857877	18.674846754
H	-41.898747030	1.341498010	18.522636940
C	-43.209000000	2.973000000	18.111000000
H	-43.764330843	3.575186321	18.833253562
H	-42.281596594	3.504840177	17.879110612
C	-44.068925287	2.915891416	16.842093920
O	-45.036953084	3.698118232	16.700277044

N	-43.699206630	2.012801719	15.928047809
H	-42.825223919	1.487005145	16.063680837
C	-44.412000000	1.890000000	14.669000000
H	-44.493945761	2.884665269	14.213682238
H	-45.440433169	1.556307728	14.855300749
C	-43.740833635	0.959098218	13.658767903
H	-44.193681548	1.163486080	12.685861088
H	-42.674162762	1.185471615	13.580591208
C	-43.971780170	-0.526457921	13.919275800
O	-45.068074121	-1.063386388	13.642660968
N	-42.930335377	-1.208794324	14.418039087
H	-43.067879528	-2.174228641	14.681116005
H	-42.139981261	-0.718727549	14.834070725
C	-41.764000000	-6.382000000	14.826000000
H	-41.142438742	-7.088692670	14.259998830
H	-42.794412887	-6.755869952	14.821591937
H	-41.738516576	-5.417894881	14.305451327
C	-41.238166933	-6.252486325	16.248504481
H	-41.236112413	-7.234675817	16.736641412
H	-40.202769220	-5.890463533	16.236812602
O	-42.045117008	-5.383569460	17.059433231
H	-41.670184945	-4.470870539	17.008931019
O	-38.865631213	3.904744885	15.105405762
H	-37.962828211	4.005624548	14.778728390
H	-38.862372170	3.020591876	15.560698602
O	-42.626748874	-0.264098081	10.547507849
H	-42.366408539	0.636084334	10.279612252
H	-41.770377226	-0.688823223	10.704464149
O	-43.600912394	-6.339280872	19.170516991
H	-43.057147615	-5.959814558	18.440183162
H	-44.495844584	-6.019958950	18.978131127
H	-36.371259373	3.232125307	11.623593019
H	-35.148447038	0.922159551	12.223796480
H	-35.796985332	4.758588663	13.175535258

Text S6. Coordinate file (xyz format) for the RO^HP^HE^H state as computed from a DFT/SCRF single point energy calculation following geometry optimization of the active site quantum cluster at the OLYP/TZP level of theory. This low-energy state corresponds to a BS state where Fe1, Fe2, Fe3 and Fe4 (as numbered in Fig. 2B) have net spins of β , α , α and β , respectively.

205

0.0000

Fe	-36.925580246	-0.230899110	10.726973829
Fe	-37.987005153	-2.385942414	9.512923533
Fe	-37.936031400	0.140850107	8.314890573
Fe	-35.635608977	-1.273005193	8.684626680
S	-39.067834723	-0.448595821	10.234454084
S	-36.112597185	-2.360909872	10.683091169
S	-35.989881616	1.002609178	9.007959788
S	-37.297666581	-1.899791912	7.316253906
S	-39.152403506	-4.283911807	9.876759289
C	-40.424879138	-4.477754802	8.567598825
H	-40.087000000	-5.237000000	7.860000000
H	-41.357449410	-4.806589839	9.033312637
H	-40.600008251	-3.538798547	8.039621699
S	-33.388873528	-1.642204737	8.434608751
C	-32.796653020	-1.214599279	10.127288222
H	-31.801000000	-1.623000000	10.285000000
H	-32.766479595	-0.130009379	10.261978148
H	-33.458256915	-1.657747210	10.871500253
S	-39.363384138	1.528842747	7.221851389
C	-38.266472984	2.788107451	6.455038408
H	-38.869000000	3.673000000	6.263000000
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H	-37.852815277	2.412681305	5.516646413
O	-35.956902675	1.063766574	12.296897157
C	-36.364967232	0.771258122	13.689500257
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H	-35.586815922	1.166742205	14.348253925
C	-36.619693274	-0.696868130	13.898789291
C	-37.903363962	-1.101058339	13.864348419
H	-38.672842952	-0.346339476	13.707933127
C	-35.420555301	-1.585888021	14.121755973
H	-34.559853654	-1.259144374	13.528244727

H	-35.105119059	-1.550704181	15.169651131
H	-35.608959824	-2.627733464	13.862447159
C	-38.450661890	-2.483998581	14.028324766
H	-37.729975089	-3.186773699	14.447810989
H	-38.791953995	-2.871067227	13.062960001
O	-39.655291865	-2.476147336	14.852223680
P	-39.545158611	-2.407336472	16.472227715
O	-38.425474351	-3.295104708	16.982079525
O	-40.950330676	-2.573202819	16.981411381
O	-38.963373640	-0.891407531	16.777113398
P	-39.414714810	0.659922870	16.951873689
O	-38.232160088	1.508813080	16.584594164
O	-40.614133864	0.853730048	15.854398046
O	-40.022952328	0.802542171	18.344924272
C	-35.064000000	-5.724000000	10.267000000
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H	-37.114165941	-5.895773911	19.044304755
O	-37.809626355	-6.333195932	20.920297860
N	-38.683633633	-4.696635323	19.539627450
H	-38.624504254	-4.315709009	18.593006269
C	-39.795000000	-4.261000000	20.371000000
H	-39.606113324	-4.602553053	21.390205980
H	-40.712278321	-4.766040902	20.043743475
C	-40.070823250	-2.760695064	20.342402978
H	-40.291918858	-2.446510049	19.320858518
H	-40.991516893	-2.609365767	20.919246298
C	-39.006457985	-1.886578799	20.922780401
N	-38.818134847	-0.579497771	20.502601783
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H	-36.711987874	-0.734834532	22.807808915
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H	-37.915225974	-2.940519848	22.568014971
C	-32.924000000	0.447000000	16.553000000
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H	-32.404813857	-0.503630330	16.396550256
H	-33.682495940	0.555921185	15.775434665
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H	-32.769480724	0.493297295	18.722539844

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N	-36.174772773	-2.062011314	18.033918794
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C	-30.321000000	1.083000000	7.036000000
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H	-38.793548661	6.790954110	21.404036969
H	-37.388977701	7.173870745	20.413474198
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H	-34.061904180	3.636337004	21.024010915
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H	-35.486688715	5.584032671	17.074418297
C	-33.922376620	5.794865759	15.600510465
H	-32.955710902	5.330278395	15.353187549
H	-33.694768866	6.832561954	15.862860109
C	-34.678650241	5.823814584	14.293646016

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C	-37.942000000	5.930000000	10.930000000
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O	-36.674301143	4.126324933	11.834394215
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O	-41.835675462	2.620266697	9.690626139
H	-41.038721668	2.488381931	9.146186207
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H	-43.575567926	-2.605455028	19.662277056
H	-45.004667556	-1.584309554	19.458896802
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C	-43.837006557	3.092841181	16.726247151
O	-44.264743648	4.198258333	16.343282945

N	-43.847610862	1.968431097	15.995822697
H	-43.529562992	1.123687543	16.452943479
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H	-45.475256983	1.621954246	14.720285874
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H	-42.621469824	1.092346910	13.722105923
C	-44.034691651	-0.552921477	13.966769542
O	-45.201089073	-0.971349735	13.852996491
N	-43.005457078	-1.367744509	14.272602637
H	-43.187981044	-2.344859290	14.453480338
H	-42.071095067	-1.026253077	14.437543933
C	-41.764000000	-6.382000000	14.826000000
H	-41.116246776	-7.111048621	14.321670806
H	-42.782829668	-6.785570119	14.840378484
H	-41.762792255	-5.460121913	14.232343450
C	-41.258399618	-6.132171399	16.237595004
H	-41.239203501	-7.072786243	16.800836426
H	-40.233041654	-5.746409833	16.211582183
O	-42.101573801	-5.220157581	16.970767287
H	-41.697480892	-4.329070316	16.930795439
O	-38.994192178	3.774808361	15.059867249
H	-38.240434668	4.148836625	14.580296839
H	-38.589831148	3.111115683	15.658874780
O	-42.561945034	-0.207072282	10.619352696
H	-42.366073715	0.699479537	10.318094655
H	-41.685428386	-0.620753566	10.608506550
O	-43.722808842	-6.183389457	19.071824691
H	-43.171567687	-5.805415982	18.350392560
H	-44.628482206	-5.951278256	18.814033453
H	-36.301670911	3.255964359	11.624987658
H	-40.358042464	1.588619793	15.272017540
H	-34.998314953	0.931043991	12.231025742
H	-35.897564106	4.780746503	13.216629730