Supporting information

Superoxide Radical Anion Adduct of 5,5-Dimethyl-1-pyrroline *N*-Oxide (DMPO). 4. Conformational Effects on the EPR Hyperfine Splitting Constants

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Table S1. Cartesian Coodinates

DMPO-OOH I-A

C	0.986371	1.347273	0.639592
C	-0.184208	1.855693	-0.230318
C	-1.020092	0.610310	-0.511180
C	1.290575	-0.085078	0.138790
N	-0.022991	-0.469884	-0.470038
C	1.640463	-1.061419	1.264986
C	2.362197	-0.113516	-0.964977
O	-0.376234	-1.692717	-0.626445
O	-1.959589	0.437219	0.536595
H	0.673803	1.309893	1.688278
H	1.864883	1.996211	0.574854
H	0.174836	2.263740	-1.181240
H	-0.783041	2.625001	0.262888
H	-1.546809	0.588265	-1.469643
H	0.859564	-1.063823	2.032085
H	1.740258	-2.077380	0.873808
H	2.587215	-0.768827	1.731740
H	3.347060	0.120070	-0.545357
H	2.405151	-1.108492	-1.419637
H	2.144906	0.613678	-1.755307
O	-2.856586	-0.637627	0.142522
H	-2.219442	-1.383739	0.055073

DMPO-OOH II-B

C	0.484287	1.392963	0.687934
C	-0.632765	1.661124	-0.344764
C	-1.065234	0.280384	-0.849978
C	1.178885	0.093133	0.222494
N	0.093771	-0.562547	-0.566613
C	1.585280	-0.828137	1.376536
C	2.372912	0.353430	-0.712692
O	0.178686	-1.762385	-0.991209
O	-2.264748	-0.244638	-0.295560
H	0.040712	1.240549	1.675405
H	1.192430	2.224331	0.758238
H	-0.251495	2.244933	-1.190262
H	-1.482997	2.200919	0.078208
H	-1.301583	0.245625	-1.919669
H	0.729493	-1.022142	2.031750
H	1.949165	-1.784063	0.988872
H	2.378100	-0.363670	1.972555
H	3.214986	0.772516	-0.150781
H	2.693251	-0.585286	-1.175567
H	2.110396	1.056741	-1.511186
O	-2.107864	-0.333434	1.149060
H	-1.917634	-1.286350	1.233212

DMPO-OOH II-C

C	0.850041	1.420275	0.577201
C	-0.268053	1.784257	-0.424366
C	-1.030624	0.470681	-0.598787
C	1.254456	-0.030978	0.225832
N	0.015920	-0.531332	-0.447355
C	1.550408	-0.901947	1.451598
C	2.412997	-0.095460	-0.783212
O	-0.055032	-1.694406	-0.965322
O	-1.989940	0.448427	0.460060
H	0.455026	1.463139	1.597104
H	1.701238	2.105044	0.517172
H	0.146120	2.083108	-1.393349
H	-0.918679	2.587675	-0.069167
H	-1.531844	0.310803	-1.558253
H	0.715687	-0.870003	2.159137
H	1.699311	-1.941422	1.143363
H	2.456250	-0.554033	1.960834
H	3.355927	0.185542	-0.301522
H	2.504839	-1.113325	-1.173017
H	2.244054	0.580388	-1.629509
O	-2.703351	-0.815866	0.395178
H	-3.568134	-0.503801	0.069769

DMPO-OOH II-D

C	0.460469	1.504253	0.374691
C	-0.708366	1.362856	-0.623912
C	-1.023596	-0.129710	-0.591727
C	1.298551	0.216879	0.196999
N	0.271319	-0.732637	-0.334856
C	1.864990	-0.338017	1.508092
C	2.408636	0.368243	-0.856388
O	0.533151	-1.951532	-0.595732
O	-1.843672	-0.498470	0.532495
H	0.069086	1.551855	1.396506
H	1.055733	2.405651	0.202350
H	-0.400685	1.647450	-1.636876
H	-1.584914	1.959934	-0.361240
H	-1.466304	-0.545633	-1.500607
H	1.069191	-0.470869	2.248331
H	2.335268	-1.310163	1.331955

H	2.615767	0.345712	1.919561
H	3.221038	0.991735	-0.467570
H	2.812012	-0.616378	-1.110894
H	2.029459	0.830126	-1.774892
O	-3.198065	-0.055565	0.196071
H	-3.390297	0.476551	0.988175

DMPO-OOH 1-E

C	0.499057	1.495415	0.411708
C	-0.682112	1.406699	-0.578399
C	-1.027783	-0.079038	-0.579566
C	1.308474	0.195461	0.193998
N	0.255634	-0.716796	-0.353347
C	1.871472	-0.406387	1.485597
C	2.413090	0.348198	-0.864958
O	0.476867	-1.940824	-0.629739
O	-1.841880	-0.450465	0.549236
H	0.114951	1.524762	1.436457
H	1.112130	2.387972	0.256560
H	-0.377751	1.708829	-1.587505
H	-1.541333	2.013818	-0.285279
H	-1.489120	-0.461937	-1.494692
H	1.078128	-0.539146	2.228311
H	2.318343	-1.384102	1.281128
H	2.640629	0.249500	1.908147
H	3.242372	0.943433	-0.467587
H	2.792896	-0.638193	-1.147900
H	2.037064	0.842107	-1.767967
O	-3.179729	0.064451	0.275901
H	-3.652997	-0.776847	0.140299

AMPO-OOH-cis-1

C	0.395173	1.639479	-0.565670
C	-1.053673	1.916604	-0.113030
C	-1.619884	0.551762	0.265613
C	0.873812	0.435456	0.274944
N	-0.419512	-0.205170	0.657322
C	1.627966	0.843825	1.557101
C	1.804234	-0.486135	-0.563800
O	-0.528897	-1.391109	1.142180
H	1.047643	2.504671	-0.427947
H	0.428717	1.373341	-1.624157
H	-1.659640	2.386523	-0.891253
H	-1.079873	2.563026	0.770802
H	1.777554	-0.024043	2.205685
H	2.605237	1.258512	1.291435
H	1.063578	1.601996	2.111144
O	2.479547	-0.009300	-1.464955
N	1.876131	-1.777865	-0.156541
H	2.429454	-2.410131	-0.719063
H	1.161467	-2.141688	0.465977
H	-2.334580	0.538191	1.093079
O	-2.215901	-0.048675	-0.869553
O	-2.935211	-1.225614	-0.412730
H	-2.197960	-1.777514	-0.071635

AMPO-OOH-cis-2

C	-0.012090	-1.105810	-1.316795
C	1.483303	-1.283728	-0.949516
C	1.713732	-0.463974	0.320105
C	-0.736012	-0.642778	-0.020324
N	0.381968	-0.445534	0.934043
C	-1.723345	-1.675640	0.546017
C	-1.516779	0.673473	-0.284310
O	0.199438	-0.060519	2.140870
H	-0.449546	-2.037873	-1.684515
H	-0.133684	-0.355680	-2.098057
H	2.151322	-0.955758	-1.748036
H	1.706249	-2.333222	-0.728983
H	-2.065193	-1.371255	1.539831
H	-2.584771	-1.759547	-0.121460
H	-1.237622	-2.653258	0.630683
O	-2.318355	0.738448	-1.199276
N	-1.218852	1.739202	0.538561
H	-1.872863	2.511426	0.474192
H	-0.856885	1.522335	1.465208
H	2.420929	-0.897938	1.032774
O	2.239516	0.841278	0.140932
O	1.471672	1.517308	-0.893286
H	0.789235	1.973723	-0.354842

AMPO-OOH-trans-1

C	0.362154	1.611760	0.562466
C	-0.646665	1.791308	-0.592360
C	-1.384544	0.457485	-0.681768
C	0.770003	0.128663	0.522849
N	-0.391245	-0.497692	-0.162591
C	0.987546	-0.498869	1.907141
C	2.057600	-0.081801	-0.334878
O	-0.622805	-1.760816	-0.140598
H	-0.120273	1.829703	1.520259
H	1.242287	2.247731	0.456230
H	-0.125243	1.970401	-1.538598
H	-1.346951	2.613561	-0.428231
H	-1.699697	0.144502	-1.681078
H	0.108013	-0.332586	2.536983

H	1.161151	-1.574467	1.825639
H	1.857418	-0.036316	2.383694
O	2.894709	0.799997	-0.460951
N	2.179085	-1.326841	-0.861860
H	2.989856	-1.532018	-1.428552
H	1.428080	-2.002663	-0.791101
O	-2.512148	0.480710	0.174801
O	-3.288470	-0.718472	-0.093918
H	-2.656369	-1.418750	0.180541

AMPO-OOH-trans-2

C	-0.034808	1.531123	0.441526
C	-0.915002	1.493483	-0.825473
C	-1.342413	0.031528	-0.990363
C	0.638350	0.150359	0.508886
N	-0.312088	-0.705481	-0.249604
C	0.815659	-0.390944	1.934591
C	2.031878	0.170331	-0.198482
O	-0.213548	-1.978614	-0.316629
H	-0.659053	1.674660	1.326631
H	0.723410	2.314567	0.404676
H	-0.332648	1.793866	-1.703670
H	-1.789176	2.144786	-0.759089
H	-1.367376	-0.319128	-2.028135
H	-0.143886	-0.367825	2.461334
H	1.184558	-1.419645	1.917701
H	1.531604	0.232499	2.478877
O	2.696408	1.194712	-0.270760
N	2.449055	-1.038080	-0.653416
H	3.336572	-1.087632	-1.133602
H	1.823926	-1.836268	-0.651225
O	-2.650250	-0.303168	-0.559649
O	-2.789611	0.082177	0.838592
H	-2.772672	-0.801086	1.251097

CPCOMPO-OOH-cis-1

C	0.157271	-0.684025	-1.470747
C	1.544450	-1.268874	-1.100847
C	1.855824	-0.749852	0.304551
C	-0.559869	-0.417884	-0.117310
N	0.512830	-0.581578	0.876933
C	-1.796640	-1.267295	0.209586
C	-1.131994	1.017396	-0.043907
O	0.298680	-0.434977	2.124031
H	-0.426285	-1.367618	-2.094434
H	0.291915	0.250088	-2.018697
H	2.318245	-0.968157	-1.808725
H	1.506144	-2.363136	-1.070096
H	-1.795486	-2.244751	-0.279771
H	-1.829104	-1.408574	1.294438
O	-0.506040	2.048605	0.044382
C	-2.955403	-0.374576	-0.247655
H	-3.223368	-0.529733	-1.298375
H	-3.853768	-0.463375	0.365632
O	-2.475105	0.986105	-0.107109
H	2.411269	-1.444378	0.941288
O	2.638025	0.424805	0.381094
O	2.160183	1.385104	-0.598077
H	1.402859	1.804204	-0.126384

CPCOMPO-OOH-cis-2

C	0.088744	1.697101	0.739217
C	1.425341	1.868885	-0.016791
C	1.773330	0.466679	-0.508245
C	-0.656283	0.572899	0.005359
N	0.445404	-0.157125	-0.673863
C	-1.772644	0.936919	-0.990001
C	-1.394722	-0.405536	0.959303
O	0.320011	-1.371478	-1.064777
H	-0.494227	2.621216	0.777438
H	0.276929	1.363398	1.764162
H	2.221889	2.268771	0.614724
H	1.310927	2.530845	-0.881879
H	-2.335972	1.793856	-0.603916
H	-1.397335	1.184976	-1.986224
O	-1.056074	-0.720123	2.068287
C	-2.646895	-0.323775	-0.976581
H	-3.706966	-0.128718	-1.149535
H	-2.288753	-1.081979	-1.677383
O	-2.522106	-0.853625	0.363092
H	2.314568	0.405510	-1.456411
O	2.508763	-0.205727	0.493366
O	2.990896	-1.448849	-0.079858
H	2.147959	-1.938612	-0.198381

CPCOMPO-OOH-trans-1

C	0.149811	1.015637	1.300126
C	-1.008936	1.729935	0.572781
C	-1.704689	0.625540	-0.220252
C	0.625764	-0.057840	0.294201
N	-0.622181	-0.352204	-0.447779
C	1.322736	-1.302538	0.838973
C	1.685568	0.538339	-0.666187
O	-0.847196	-1.476561	-1.013760
H	-0.215574	0.514905	2.203135
H	0.948562	1.704644	1.589680

H	-0.619597	2.475246	-0.125550
H	-1.707410	2.215451	1.257879
H	1.052371	-1.530866	1.873277
H	1.041258	-2.150374	0.207203
O	1.509394	1.393313	-1.494335
C	2.812371	-0.968074	0.675248
H	3.237500	-0.490890	1.565168
H	3.428798	-1.828395	0.407479
O	2.891379	-0.024317	-0.417579
H	-2.131998	0.924395	-1.180815
O	-2.711332	0.037945	0.580877
O	-3.488555	-0.848356	-0.269910
H	-2.803912	-1.510871	-0.514697

DEPMPO-OOH-cis-1

C	1.537687	-1.686464	0.812537
C	3.023464	-1.245730	0.780412
C	2.957516	0.091912	0.049112
C	0.727999	-0.365463	0.972844
N	1.731899	0.663817	0.610430
C	0.224237	-0.128150	2.402775
P	-0.656200	-0.238138	-0.270917
O	1.478494	1.913894	0.640790
H	1.317748	-2.374478	1.632558
H	1.291639	-2.192394	-0.123069
H	3.659510	-1.963788	0.257197
H	3.423689	-1.093142	1.788332
H	1.042698	-0.292743	3.112587
H	-0.134330	0.896940	2.515263
O	-1.402718	-1.637804	-0.002211
C	-2.508265	-2.069161	-0.845159
O	-0.210485	0.024260	-1.673736
C	-3.832037	-1.892007	-0.121603
H	-4.648728	-2.278277	-0.742782
H	-3.830461	-2.441006	0.825503
H	-4.021779	-0.836048	0.089825
H	-0.590855	-0.817568	2.641041
O	2.828215	-0.259241	-1.320650
H	3.767575	0.809193	0.205853
O	-1.731377	0.835446	0.279341
C	-1.700867	2.222470	-0.176991
C	-2.944054	2.905949	0.357877
H	-2.479997	-1.518063	-1.790251
H	-2.309175	-3.122203	-1.062534
H	-0.784596	2.684342	0.198496
H	-1.673069	2.226304	-1.270230
H	-2.952146	3.954839	0.040881
H	-3.851490	2.424107	-0.020918
H	-2.966773	2.877099	1.451971
O	2.424366	0.905924	-2.077184
H	1.454204	0.722270	-2.120602

DEPMPO-OOH-cis-2

C	1.412968	-1.716792	1.073993
C	2.640902	-1.488208	0.163849
C	2.925688	0.017399	0.194862
C	0.628566	-0.380799	1.106134
N	1.687446	0.595356	0.774938
C	0.005274	-0.066963	2.470503
P	-0.654491	-0.267390	-0.248472
O	1.535209	1.852013	0.920704
H	1.731136	-1.937197	2.099425
H	0.795212	-2.553186	0.739974
H	2.425639	-1.759747	-0.870538
H	3.507778	-2.064687	0.495794
H	0.774496	-0.142005	3.246622
H	-0.407679	0.942979	2.486490
O	-1.517704	-1.593529	0.037321
C	-2.641645	-1.955226	-0.816426
O	-0.079453	-0.123046	-1.621934
C	-3.955649	-1.663020	-0.113467
H	-4.792857	-1.991911	-0.740257
H	-4.009399	-2.196755	0.840767
H	-4.061085	-0.592001	0.079985
H	-0.792561	-0.780851	2.695476
O	3.284300	0.628587	-1.026187
H	3.755372	0.313710	0.847163
O	-1.693575	0.907799	0.137176
C	-1.504840	2.265914	-0.370377
C	-2.750459	3.059060	-0.027400
H	-2.559860	-1.425428	-1.770521
H	-2.519951	-3.023912	-1.012780
H	-0.611530	2.683358	0.101140
H	-1.341531	2.210777	-1.450189
H	-2.639489	4.088901	-0.384785
H	-3.636951	2.623737	-0.500317
H	-2.911655	3.086396	1.054999
O	2.606028	0.035869	-2.162955
H	1.656883	0.271459	-2.018964

DEPMPO-OOH-trans-1

C	0.952957	-1.997807	0.181037
C	1.876708	-1.757971	-1.031665
C	2.579764	-0.437419	-0.727379
C	0.489662	-0.589834	0.626397
N	1.623229	0.256120	0.162020

C	0.270372	-0.433608	2.131724
P	-1.002259	-0.060722	-0.359756
O	1.917854	1.381481	0.700691
H	1.517568	-2.447670	1.005408
H	0.113015	-2.656845	-0.051197
H	1.286598	-1.640682	-1.943529
H	2.606445	-2.558072	-1.176033
H	1.177227	-0.735461	2.666415
H	0.045305	0.603930	2.385166
O	-2.118268	-1.041088	0.270385
C	-3.482895	-0.988730	-0.225877
O	-0.804502	-0.111147	-1.834335
C	-4.242024	-2.157855	0.371299
H	-5.281464	-2.141680	0.025191
H	-3.791330	-3.108226	0.068512
H	-4.240535	-2.104574	1.464597
H	-0.561337	-1.065608	2.453265
O	-1.462778	1.375416	0.221258
C	-1.021745	2.617515	-0.400897
C	-1.992360	3.709844	0.004987
H	-3.919310	-0.030055	0.074002
H	-3.462232	-1.039079	-1.319524
H	-0.007810	2.825012	-0.047650
H	-0.999316	2.477882	-1.485514
H	-1.675337	4.665331	-0.427949
H	-3.003231	3.487081	-0.351788
H	-2.024111	3.818833	1.093747
O	3.775842	-0.695673	-0.017431
H	2.798747	0.198285	-1.589239
O	4.518535	0.552133	0.064660
H	3.896299	1.095808	0.598734

DEPMPO-OOH-trans-2

C	1.233859	-1.773833	0.066948
C	2.086806	-1.393691	-1.161308
C	2.561552	0.040810	-0.906058
C	0.613907	-0.446254	0.562698
N	1.616911	0.547029	0.101493
C	0.425218	-0.356541	2.077522
P	-0.963643	-0.084613	-0.363007
O	1.713430	1.723271	0.584333
H	1.873126	-2.168226	0.862577
H	0.473814	-2.524348	-0.162875
H	1.473833	-1.406320	-2.065837
H	2.942900	-2.057239	-1.301105
H	1.380140	-0.562570	2.573434
H	0.087163	0.640284	2.367147
O	-1.919096	-1.233666	0.248265
C	-3.293051	-1.347479	-0.207151
O	-0.798928	-0.046255	-1.842336
C	-3.880810	-2.610115	0.393498
H	-4.923781	-2.722136	0.076926
H	-3.322789	-3.492431	0.064578
H	-3.853602	-2.569113	1.487022
H	-0.311713	-1.092840	2.408109
O	-1.607750	1.248080	0.287370
C	-1.378529	2.562886	-0.297342
C	-2.513241	3.470205	0.138401
H	-3.838913	-0.455894	0.119649
H	-3.300120	-1.382231	-1.301689
H	-0.410237	2.921632	0.062401
H	-1.337587	2.461029	-1.385689
H	-2.355689	4.477732	-0.263027
H	-3.475362	3.098460	-0.229132
H	-2.561202	3.538399	1.229957
O	3.900963	0.204068	-0.476216
H	2.538250	0.681270	-1.794415
O	4.077458	-0.525137	0.771351
H	3.995142	0.215724	1.401231

EMPO-OOH-cis-1

C	0.393590	0.986322	1.558685
C	1.570810	0.003587	1.745302
C	2.371098	0.058999	0.436262
C	0.104350	0.995771	0.037536
N	1.436417	0.691575	-0.514277
C	-0.403095	2.338618	-0.502856
O	1.739263	0.888679	-1.735414
H	0.684673	2.000184	1.855617
H	-0.487632	0.710919	2.143255
H	1.213199	-1.020576	1.871800
H	2.191161	0.259759	2.607672
H	0.296994	3.132460	-0.225016
H	-0.466811	2.306619	-1.593760
H	-1.387548	2.567040	-0.088387
O	2.872878	-1.169570	-0.046412
H	3.283578	0.665089	0.484593
C	-0.873851	-0.131237	-0.364280
O	-2.105845	0.107495	0.110664
C	-3.121335	-0.883709	-0.204914
C	-4.423862	-0.411195	0.410080
O	-0.587965	-1.110131	-1.024403
H	-3.185138	-0.977564	-1.292936
H	-2.798162	-1.849166	0.195939
H	-5.216625	-1.135260	0.193620
H	-4.333521	-0.315061	1.496741

H	-4.722490	0.558601	-0.000278
O	1.821609	-2.169221	-0.049071
H	1.247654	-1.865026	-0.786711

EMPO-OOH-cis-2

C	1.224726	-2.003671	-0.254601
C	2.115394	-0.982508	-0.994902
C	2.152457	0.247185	-0.086148
C	0.174399	-1.154517	0.480906
N	0.976646	0.060976	0.796813
C	-0.388362	-1.762321	1.766857
O	0.556942	1.007359	1.546335
H	1.808363	-2.563483	0.484621
H	0.759040	-2.711583	-0.941717
H	1.648387	-0.695188	-1.941330
H	3.118231	-1.361233	-1.204372
H	0.431605	-2.070160	2.423233
H	-1.004381	-1.029076	2.290550
H	-1.000282	-2.640803	1.536473
O	2.006653	1.413108	-0.862738
H	3.045555	0.344368	0.540504
C	-0.962907	-0.753755	-0.491716
O	-1.873842	0.016772	0.114732
C	-2.948435	0.519105	-0.721397
C	-3.829656	1.391100	0.151358
O	-1.012857	-1.085087	-1.658222
H	-2.506759	1.076084	-1.553273
H	-3.491045	-0.334091	-1.140481
H	-4.651855	1.799742	-0.446029
H	-4.257235	0.814157	0.977521
H	-3.258120	2.224427	0.571187
O	2.291931	2.553026	-0.003841
H	1.545673	2.474888	0.633156

EMPO-OOH-cis-3

C	-0.920932	0.688650	-1.509107
C	-2.410612	0.776260	-1.096029
C	-2.478501	0.225403	0.329954
C	-0.112459	0.818973	-0.185019
N	-1.137208	0.526331	0.847313
C	0.459370	2.221193	0.049969
O	-0.839252	0.468932	2.084748
H	-0.636725	1.475030	-2.213826
H	-0.734136	-0.279884	-1.975453
H	-3.057330	0.207020	-1.765858
H	-2.750318	1.817893	-1.088223
H	-0.336569	2.963873	-0.068629
H	0.858996	2.298812	1.064218
H	1.256873	2.442547	-0.663248
O	-2.824659	-1.139604	0.463482
H	-3.213453	0.713074	0.977652
C	0.944532	-0.299738	-0.082780
O	2.198734	0.153727	-0.115210
C	3.250102	-0.846807	-0.021383
C	4.576771	-0.114286	-0.053072
O	0.663300	-1.482844	0.002337
H	3.105448	-1.408300	0.905868
H	3.137942	-1.543777	-0.857340
H	5.396719	-0.837090	0.016461
H	4.693130	0.449189	-0.984296
H	4.659771	0.582193	0.787037
O	-2.082608	-1.925071	-0.507148
H	-1.193637	-1.983903	-0.086418

EMPO-OOH-trans-1

C	-0.988352	1.777999	0.579813
C	-1.756673	1.552358	-0.738955
C	-1.960609	0.041576	-0.812429
C	-0.058751	0.558379	0.718572
N	-0.811278	-0.489651	-0.046572
C	0.193894	0.096735	2.154091
O	-0.717444	-1.738266	0.214915
H	-1.684500	1.788062	1.424230
H	-0.424949	2.712373	0.573318
H	-1.152636	1.878568	-1.590435
H	-2.716704	2.072558	-0.772017
H	-0.760963	-0.057274	2.665434
H	0.752876	-0.839577	2.162955
H	0.763647	0.858322	2.697053
C	1.262208	0.795402	-0.050235
O	2.111883	-0.227687	0.114829
C	3.356160	-0.155879	-0.627431
C	4.151437	-1.404538	-0.300033
O	1.488475	1.765989	-0.743052
H	3.119222	-0.082985	-1.693484
H	3.881372	0.759971	-0.339083
H	5.099653	-1.392629	-0.848327
H	4.373204	-1.458392	0.770525
H	3.598226	-2.305023	-0.584019
O	-3.165029	-0.296094	-0.152126
H	-1.964992	-0.397424	-1.814108
O	-3.435682	-1.699486	-0.419882
H	-2.658020	-2.116845	0.016133

EMPO-OOH-trans-2

C	-1.146012	1.402861	0.872724
C	-1.851625	1.508991	-0.495127
C	-1.863716	0.087611	-1.066038
C	-0.136011	0.250573	0.722310
N	-0.775042	-0.586794	-0.342794
C	0.082581	-0.582947	1.984545
O	-0.532826	-1.826091	-0.498410
H	-1.868318	1.134871	1.647636
H	-0.650012	2.334121	1.151977
H	-1.278501	2.160214	-1.161384
H	-2.870539	1.895303	-0.420734
H	-0.884674	-0.914782	2.374595
H	0.696057	-1.457637	1.765515
H	0.579192	0.018338	2.753226
C	1.192004	0.767603	0.123445
O	2.147147	-0.173260	0.156125
C	3.407089	0.169425	-0.474080
C	4.318468	-1.035952	-0.348812
O	1.340985	1.870968	-0.361217
H	3.211627	0.434456	-1.517814
H	3.816678	1.054314	0.023188
H	5.283864	-0.820021	-0.819273
H	4.495659	-1.285813	0.702128
H	3.879963	-1.908814	-0.842234
O	-3.077756	-0.635188	-0.955324
H	-1.687241	0.038099	-2.146679
O	-3.408945	-0.775057	0.454563
H	-3.063967	-1.675059	0.609715

EMPO-OOH-trans-3

C	-0.988341	1.778962	0.578312
C	-1.756853	1.551595	-0.740069
C	-1.960058	0.040614	-0.812281
C	-0.058655	0.559605	0.718618
N	-0.811378	-0.489486	-0.044723
C	0.194471	0.100015	2.154721
O	-0.717237	-1.737790	0.218064
H	-1.684361	1.790151	1.422818
H	-0.424966	2.713340	0.570477
H	-1.153402	1.877546	-1.592057
H	-2.717248	2.071125	-0.773192
H	-0.760182	-0.052181	2.666990
H	0.752470	-0.836882	2.164624
H	0.765429	0.861828	2.696088
C	1.262157	0.795614	-0.050773
O	2.111602	-0.227552	0.114977
C	3.355741	-0.156706	-0.627609
C	4.150224	-1.405884	-0.300258
O	1.488523	1.765568	-0.744443
H	3.118603	-0.083737	-1.693609
H	3.881674	0.758799	-0.339468
H	5.098351	-1.394664	-0.848719
H	4.372138	-1.459811	0.770266
H	3.596340	-2.306009	-0.584073
O	-3.165104	-0.296950	-0.153087
H	-1.963139	-0.399280	-1.813582
O	-3.434857	-1.700699	-0.419886
H	-2.657595	-2.117324	0.017536

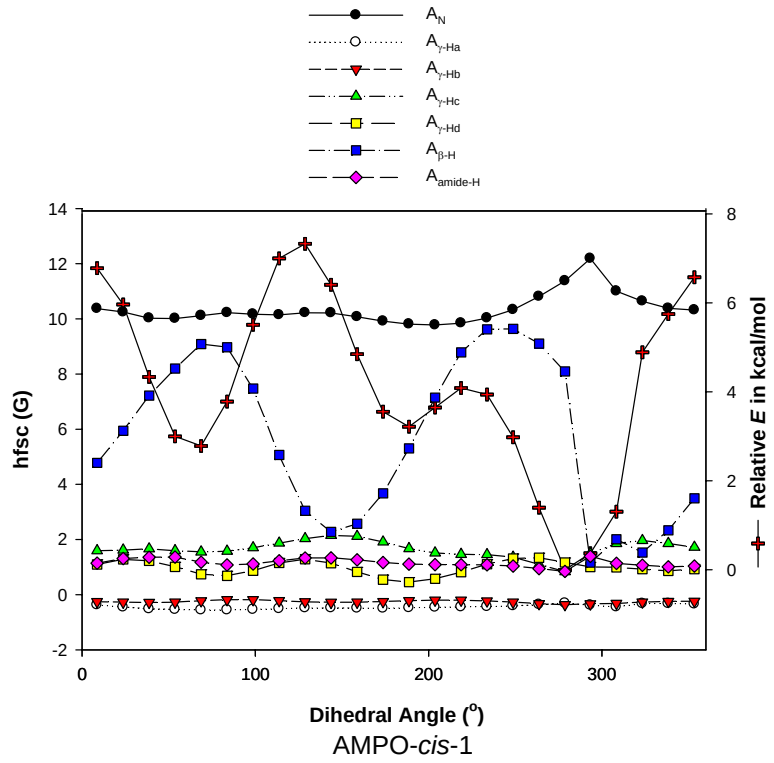
Table S2. Bottom-of-the-well reaction energies ($\Delta E_{rxn,0K}$ in kcal/mol) for the formation of DMPO-O_2H calculated with various methods and basis sets.

Level of Theory	**DMPO (Hartrees)**	**$HO_2^{\bullet}$ (Hartrees)**	**DMPO-O_2H (Hartrees)**	**$\Delta E_{rxn,0K}$ (kcal/mol)**
HF/cc-pVDZ	-362.86928	-150.18839	-513.10654	-30.7
MP2/cc-pVDZ	-364.07430	-150.53007	-514.65797	-33.6
B3LYP/cc-pVDZ	-365.19392	-150.91488	-516.15674	-30.1
B3LYP/6-311G**	-365.27652	-150.95041	-516.27241	-28.5
B3LYP/6-31G*	-365.17732	-150.89916	-516.12532	-30.7
B3LYP/aug-cc-pVDZ	-365.22501	-150.93641	-516.20386	-26.6
CBS-QB3	-364.52403	-150.74110	-515.31397	-30.6
BHandHLYP/6-311++G**	-365.04548	-150.87776	-515.97502	-32.5
BHandHLYP/6-311g**	-365.03885	-150.87163	-515.96510	-34.3
BHandHLYP/aug-cc-pVDZ	-364.99253	-150.85755	-515.90148	-32.3
BHandHLYP/cc-pVDZ	-364.96579	-150.83902	-515.86118	-35.4
mPW1K/6-31+G**	-365.12069	-150.87284	-516.04169	-30.2
BHandHLYP/6-311g**//B3LYP/6-31G*	-365.03645	-150.87046	-515.96104	-34.0
BHandHLYP/aug-cc-pVDZ//B3LYP/6-31G*	-364.99096	-150.85658	-515.89827	-31.8
BHandHLYP/cc-pVDZ//B3LYP/6-31G*	-364.96434	-150.83818	-515.85835	-35.0
CCSD(T)/cc-pVDZ//B3LYP/6-31G*	-364.18626	-150.55858	-514.79555	-31.8
CCSD/aug-cc-pVDZ //B3LYP/6-31G*	-364.21281	-150.58744	514.85083	-31.7
QCISD/cc-pVDZ//B3LYP/6-31G*	-364.14267	-150.55204	-514.74461	-31.3
QCISD/aug-cc-pVDZ //B3LYP/6-31G*	-364.21813	-150.59148	-514.85501	-28.5
ROMP2/6-311G**//B3LYP/6-31G*	-364.20257	-150.55220	-514.84697	-57.9
ROMP2/aug-cc-pVDZ//B3LYP/6-31G*	-364.15049	-150.53455	-514.78125	-60.4
ROMP2/cc-pVDZ//B3LYP/6-31G*	-364.07229	-150.49666	-514.66066	-57.5
B3LYP/6-31+G**//B3LYP/6-31G*	-365.20792	-150.91543	-516.16684	-27.3
B3LYP/cc-pVDZ//B3LYP/6-31G*	-365.19361	-150.91487	-516.15643	-30.1
B3LYP/aug-cc-pVDZ //B3LYP/6-31G*	-365.22485	-150.93638	-516.20361	-26.6

Table S3. Calculated range of hyperfine splitting constants (hfsc) (in G) for nitrogen, β-hydrogen and γ-hydrogen atoms of various adduct conformations calculated at the B3LYP/6-31G* level of theory. Values in parentheses are Δa_x's ($a_{maximum}$-$a_{minimum}$) in G.

Nitrone-O_2H Adducts	a_N	$a_{\gamma\text{-Ha}}$	$a_{\gamma\text{-Hb}}$	$a_{\gamma\text{-Hc}}$	$a_{\gamma\text{-Hd}}$	$a_{\beta\text{-H}}$	Misc.
DMPO-I	8.84-12.05 (3.21)	-0.34- -0.12 (0.22)	-0.36-0.34 (0.71)	0.52-1.69 (1.17)	0.28-2.45 (2.18)	2.96-11.0 (8.04)	
DMPO-II	8.97-12.06 (3.08)	-0.34- -0.12 (0.22)	-0.29-0.35 (0.63)	0.53-1.64 (1.11)	0.29-2.25 (1.96)	2.60-10.92 (8.32)	
							$a_{N(amide)}$
AMPO-*cis*-I	9.78-12.19 (2.41)	-0.55- -0.31 (0.25)	-0.36- -0.18 (0.18)	0.83-2.15 (1.31)	0.46-1.34 (0.88)	1.16-9.64 (8.48)	0.84-1.39 (0.55)
AMPO-*cis*-II	9.66-14.76 (5.10)	-0.54- -0.10 (0.44)	-0.35- -0.19 (0.16)	0.40-2.36 (1.96)	0.47-1.57 (1.10)	0.91-9.18 (8.27)	0.90-1.87 (0.97)
AMPO-*cis*-CO	11.14-13.96 (2.82)	-0.34-0.33 (0.67)	-0.39-0.49 (0.88)	-0.13-0.69 (0.82)	0.07-1.38 (1.31)	2.92-15.21 (12.29)	0.30-2.66 (2.37)
AMPO-*trans*-I	9.75-11.53 (1.78)	-0.39- -0.15 (0.24)	-0.19-0.25 (0.45)	0.29-1.34 (1.05)	0.66-2.23 (1.58)	3.34-9.24 (5.91)	1.39-1.97 (0.59)
AMPO-trans-II	*9.62-10.65 (1.02)*	*-0.35- -0.16 (0.19)*	*-0.19-0.13 (0.32)*	*0.50-1.40 (0.89)*	*0.89-2.26 (1.37)*	*3.51-10.19 (6.67)*	*1.43-1.96 (0.54)*
AMPO-*trans*-CO	10.49-12.64 (2.15)	-0.42- -0.26 (0.17)	-0.05-1.47 (1.52)	0.62-1.36 (0.74)	-0.07-0.78 (0.85)	4.29-9.85 (5.56)	-0.13-1.74 (1.87)
EMPO-cis-I	*8.86-11.45 (2.58)*	*-0.34- -0.04 (0.30)*	*0.18-1.28 (1.09)*	*0.04-1.40 (1.36)*	*-0.28-0.31 (0.59)*	*6.14-16.39 (10.25)*	
EMPO-*cis*-II	8.49-12.72 (4.24)	-0.27-0.07 (0.34)	0.57-1.92 (1.35)	0.31-1.05 (0.74)	-0.48-0.51 (0.98)	4.30-15.65 (11.34)	
EMPO-*cis*-CO	8.89-11.51 (2.62)	-0.52-0.11 (0.63)	-0.39-1.15 (1.54)	-0.30-2.29 (2.59)	-0.02-1.72 (1.74)	1.53-18.36 (16.83)	
EMPO-*trans*-I	8.58-11.73 (3.15)	-0.35- -0.01 (0.34)	-0.13-0.91 (1.04)	0.49-1.62 (1.13)	-0.05-2.18 (2.23)	4.00-11.06 (7.06)	
EMPO-trans-II	*8.59-10.62 (2.04)*	*-0.31- -0.01 (0.30)*	*-0.30-0.80 (1.11)*	*0.60-1.63 (1.03)*	*-0.05-2.39 (2.44)*	*3.67-11.08 (7.41)*	
EMPO-*trans*-CO	10.88-11.99 (1.11)	-0.38- -0.28 (0.01)	0.29-1.27 (0.98)	0.65-1.05 (0.40)	-0.03-0.38 (0.41)	6.46-9.21 (2.75)	
							a_P
DEPMPO-*cis*-I	8.75-11.35 (2.60)	-0.53- -0.28 (0.24)	-0.41-1.16 (1.57)	0.25-2.47 (2.21)	-0.32-1.66 (1.98)	0.72-16.83 (16.11)	37.66-54.22 (16.56)
DEPMPO-*cis*-II	9.07-11.75 (2.69)	-0.59- -0.26 (0.33)	-0.29-0.94 (1.23)	-0.03-2.67 (2.71)	-0.43-1.17 (1.60)	1.79-22.18 (20.39)	27.98-58.66 (30.68)
DEPMPO-*cis*-PO	9.48-12.02 (2.54)	-0.51- -0.40 (0.11)	-0.31-0.78 (1.10)	0.46-2.62 (2.16)	0.01-0.85 (0.84)	41.75-57.92 (16.17)	41.75-57.92 (16.17)
DEPMPO-*trans*-I	8.93-11.12 (2.18)	-0.44- -0.26 (0.17)	-0.46-0.19 (0.65)	0.44-1.41 (0.97)	0.22-2.33 (2.11)	3.89-11.54 (7.65)	39.48-49.69 (10.21)
DEPMPO-trans-II	*8.93-10.47 (1.53)*	*-0.44- -0.26 (0.18)*	*-0.47-0.19 (0.66)*	*0.49-1.40 (0.92)*	*0.22-2.32 (2.10)*	*3.83-11.61 (7.78)*	*39.51-49.65 (10.14)*
DEPMPO-*trans*-PO	10.37-12.02 (1.66)	-0.51- -0.40 (0.11)	0.19-0.78 (0.59)	0.46-1.08 (0.62)	0.01-0.59 (0.58)	6.25-10.21 (3.96)	47.10-57.92 (10.82)
CPCOMPO-cis-I	*8.45-12.05 (3.60)*	*-0.49-0.08 (0.57)*	*-0.33-0.21 (0.54)*	*0.71-2.71 (2.01)*	*0.50-1.61 (1.11)*	*1.81-8.86 (7.05)*	
CPCOMPO-*cis*-II	8.94-11.57 (2.62)	-0.41-0.43 (0.84)	-0.36- -0.01 (0.36)	0.28-2.13 (1.85)	0.41-1.50 (1.09)	1.28-8.95 (7.68)	
CPCOMPO-*trans*-I	8.58-11.38 (2.80)	-0.41- -0.08 (0.33)	-0.21-0.57 (0.78)	0.46-1.44 (0.98)	0.13-2.05 (1.92)	4.01-11.71 (7.69)	

Figure S1. Dependence of hyperfine splitting constants on ∠N-C-O-O (top) and correlation of calculated $a_{\beta\text{-H}}$ with ∠O-N-C-H dihedral angles (bottom) for AMPO-OOH-cis-I.



AMPO-*cis*-1

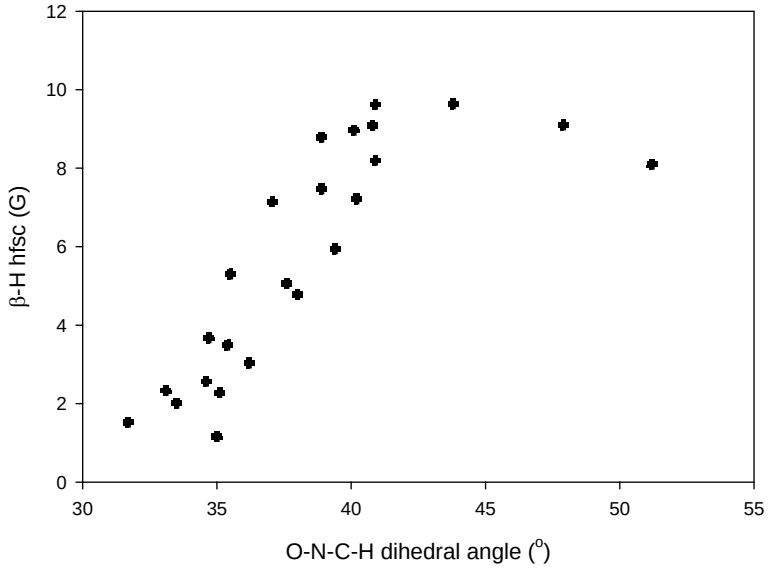
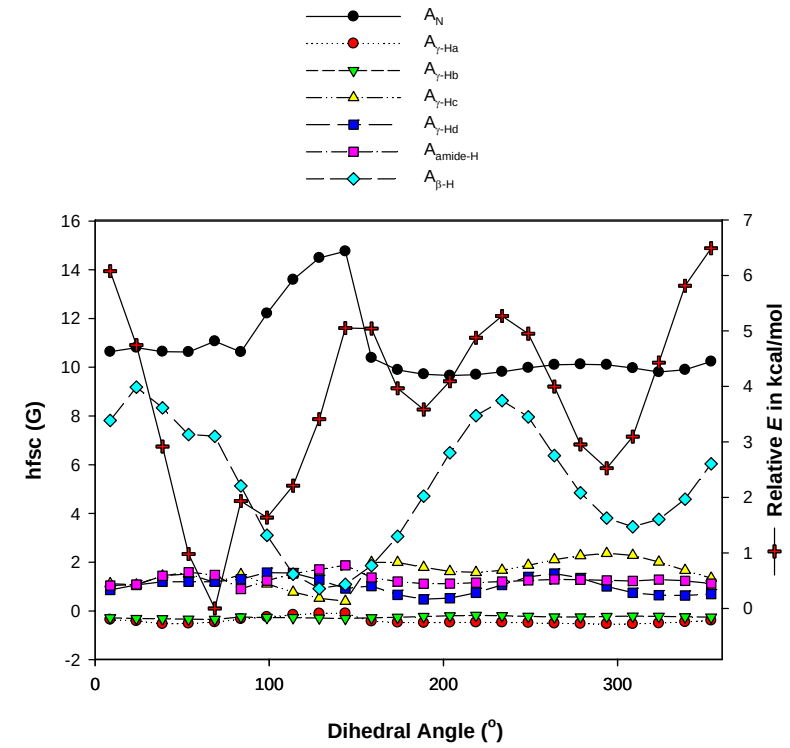


Figure S2. Dependence of hyperfine splitting constants on ∠N-C-O-O (top) and correlation of calculated $a_{\beta\text{-H}}$ with ∠O-N-C-H dihedral angles (bottom) for AMPO-OOH-cis-II.



AMPO-*cis*-2

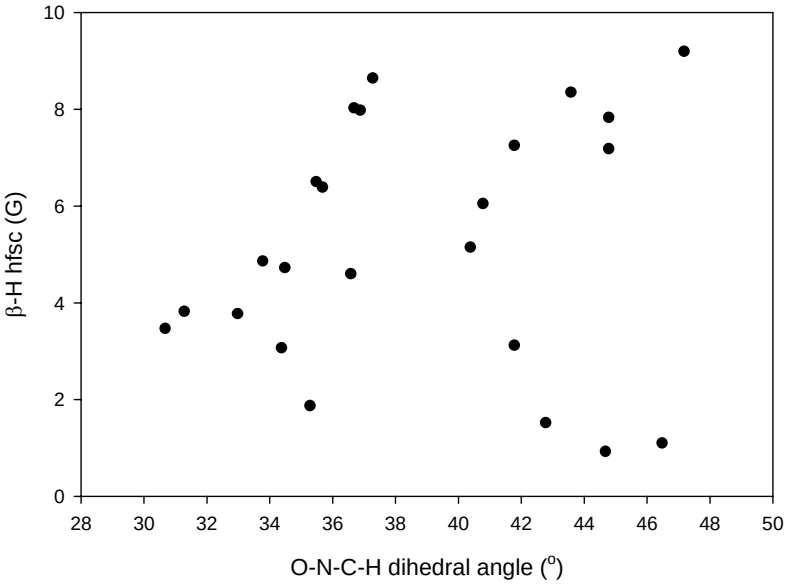
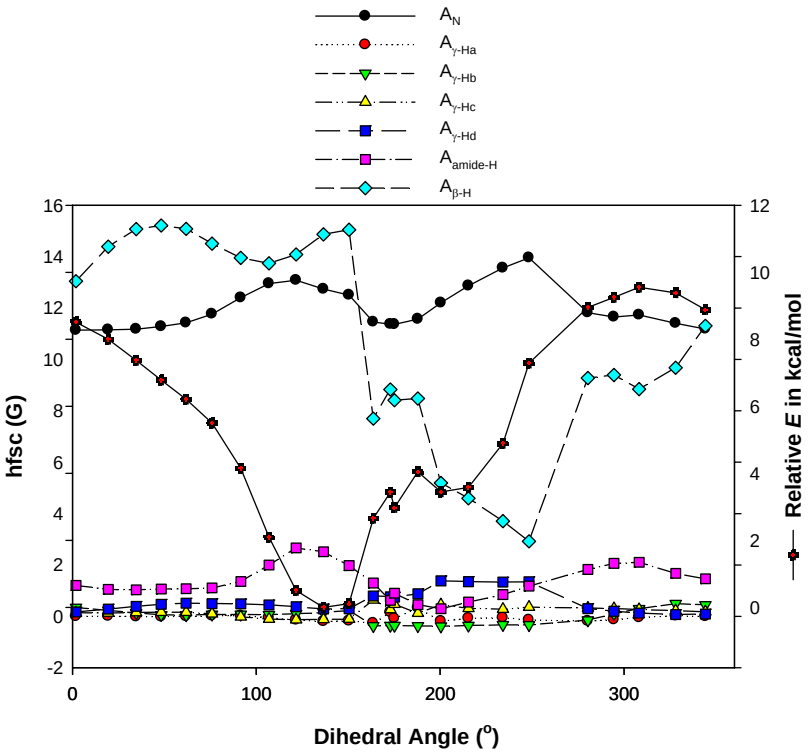


Figure S3. Dependence of hyperfine splitting constants on ∠N-C-C-O (top) and correlation of calculated $a_{\beta\text{-H}}$ with ∠O-N-C-H dihedral angles (bottom) for AMPO-OOH-cis-CO.



AMPO-*cis*-3

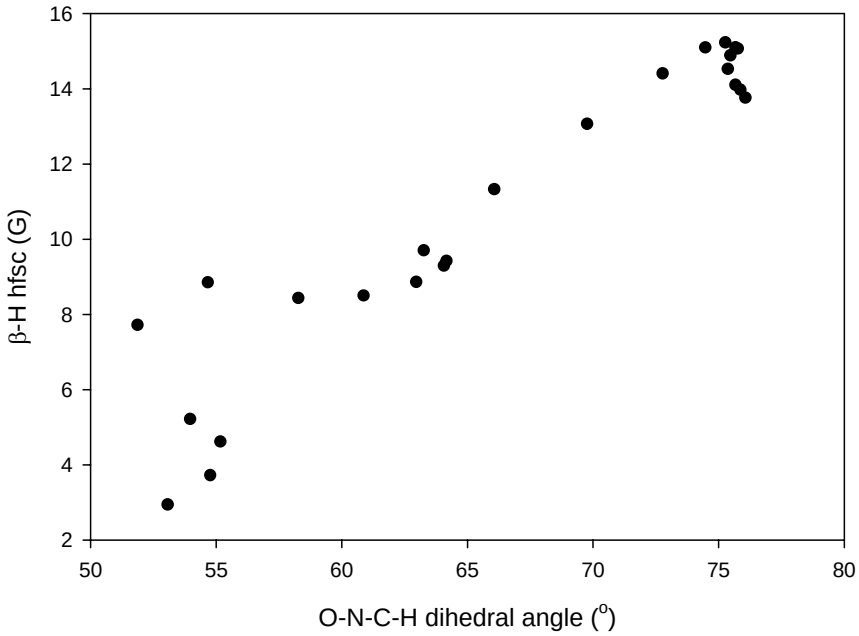


Figure S4. Dependence of hyperfine splitting constants on ∠N-C-O-O (top) and correlation of calculated $a_{\beta\text{-}H}$ with ∠O-N-C-H dihedral angles (bottom) for AMPO-OOH-trans-I.

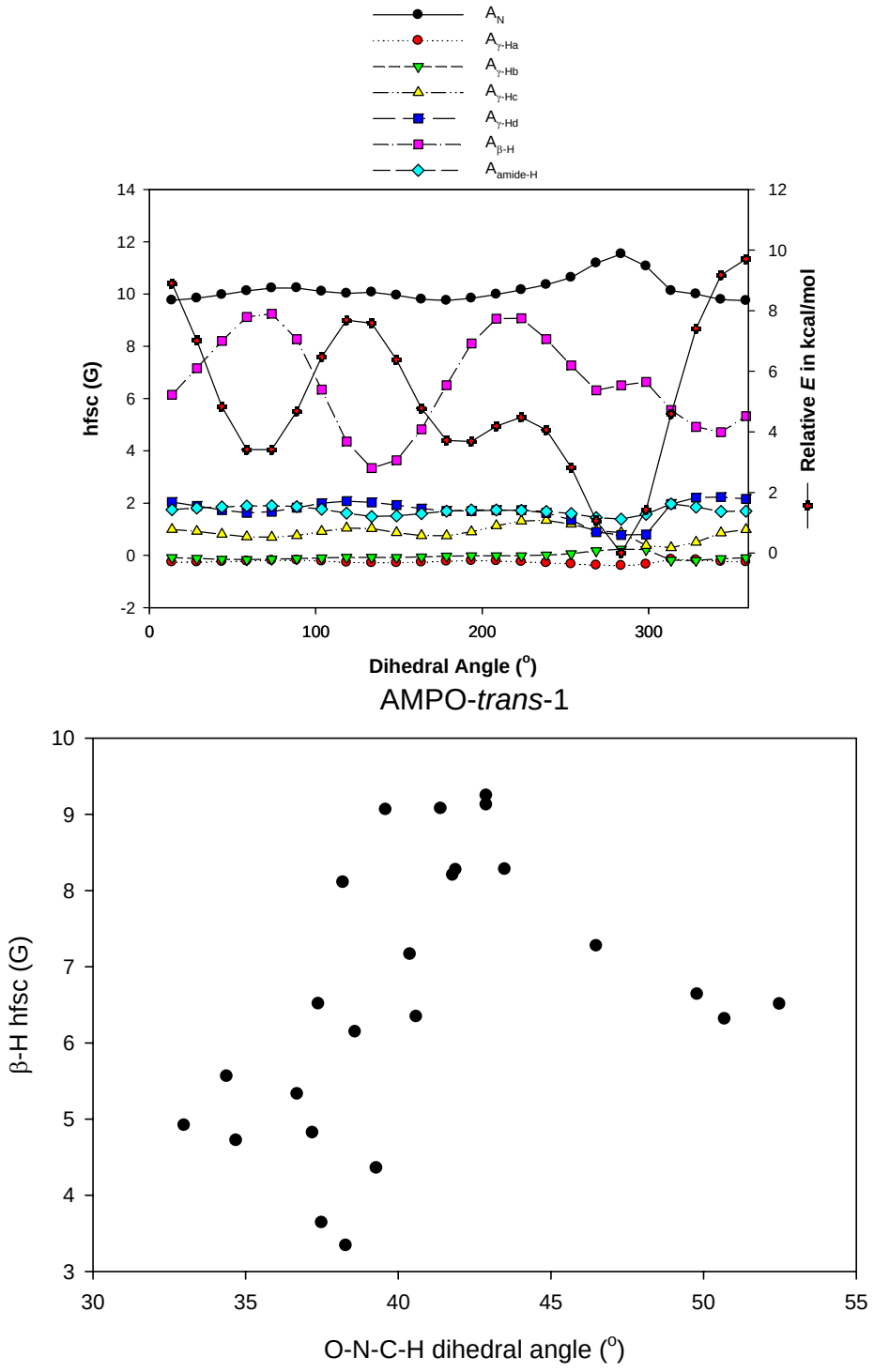
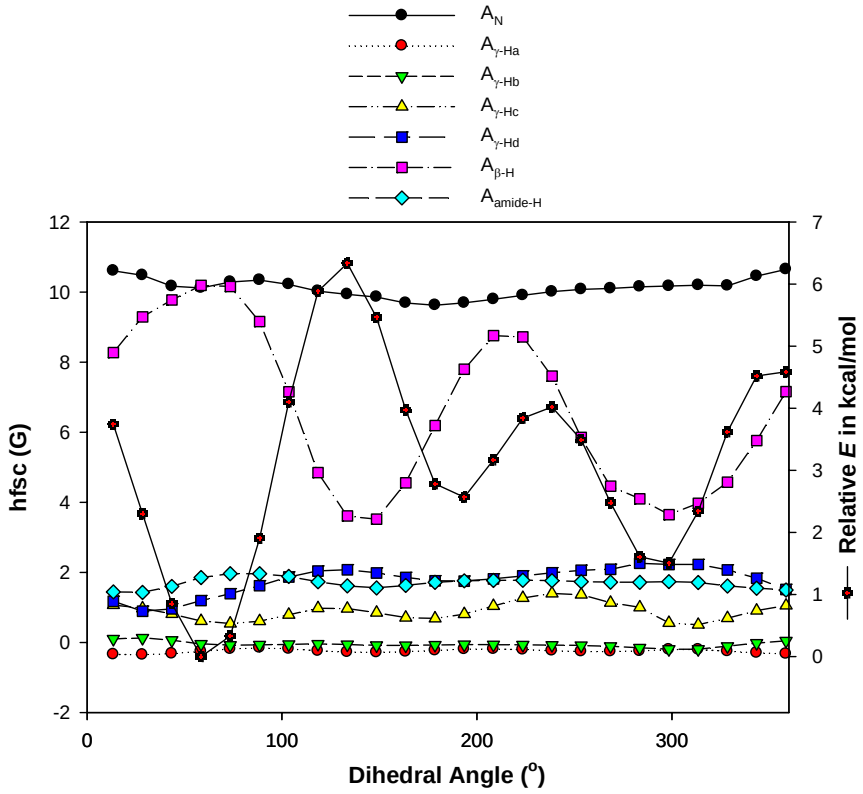


Figure S5. Dependence of hyperfine splitting constants on ∠N-C-O-O (top) and correlation of calculated $a_{\beta\text{-H}}$ with ∠O-N-C-H dihedral angles (bottom) for AMPO-OOH-trans-II.



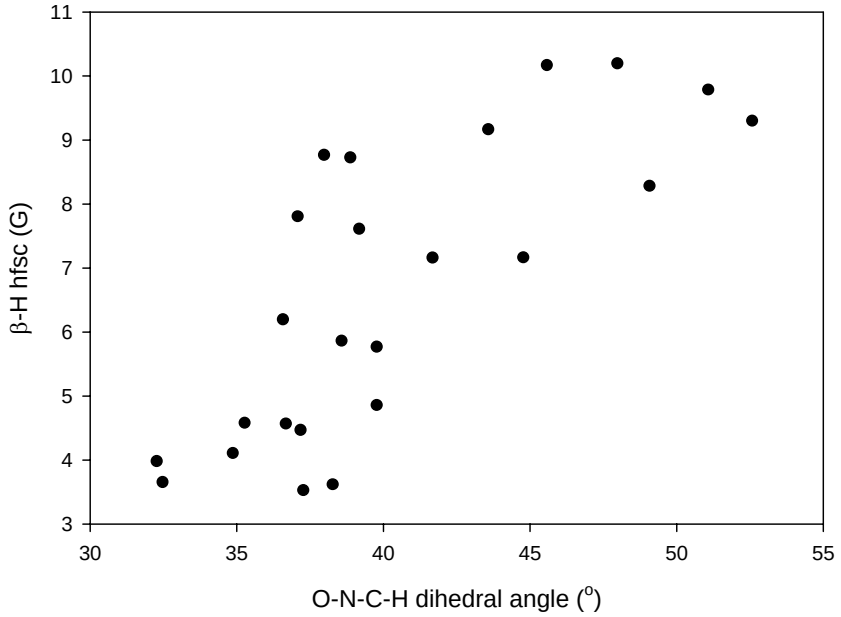


Figure S6. Dependence of hyperfine splitting constants on ∠N-C-C-O (top) and correlation of calculated $a_{\beta\text{-H}}$ with ∠O-N-C-H dihedral angles (bottom) for AMPO-OOH-trans-CO.

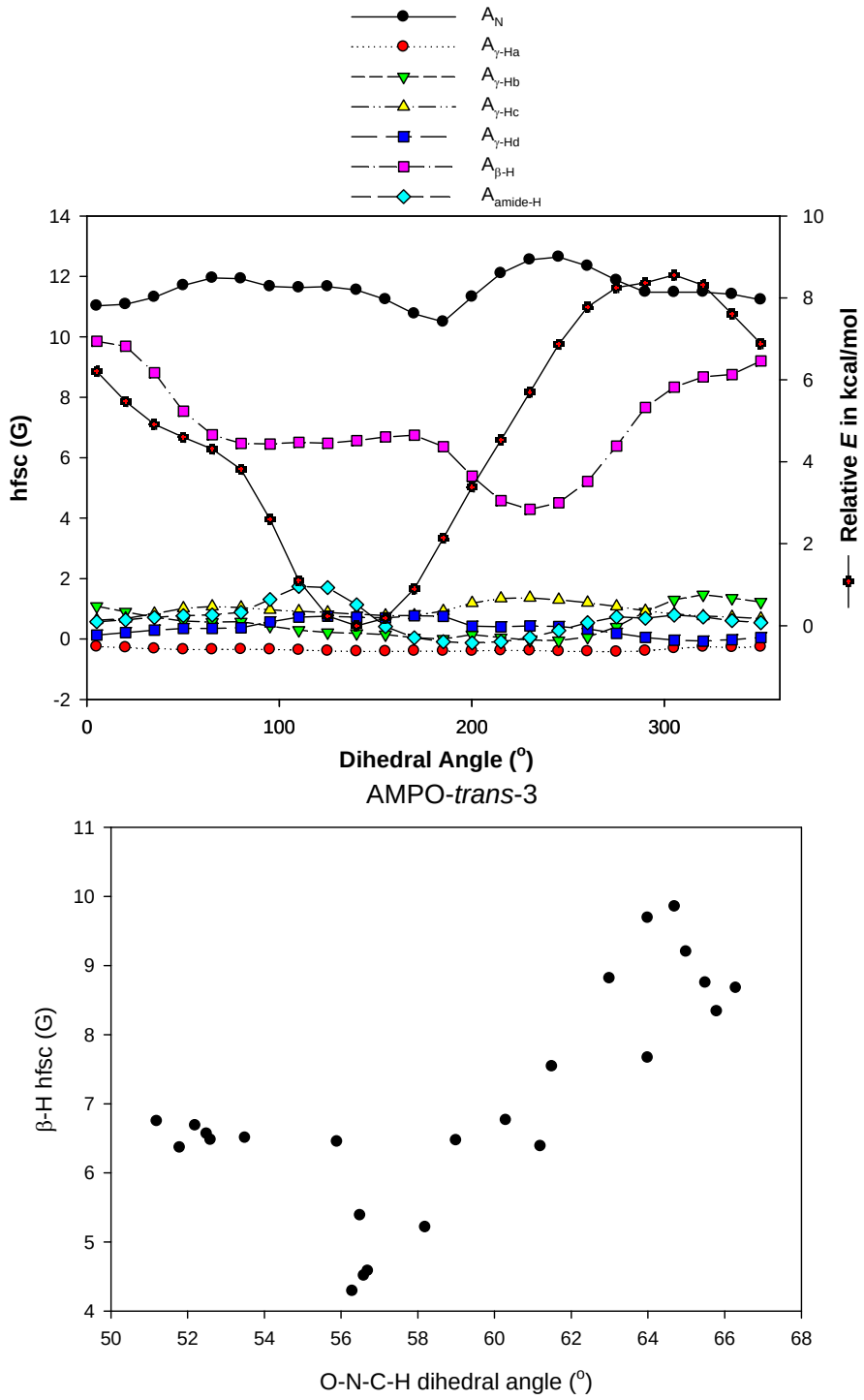


Figure S7. Dependence of hyperfine splitting constants on ∠N-C-O-O (top) and correlation of calculated $a_{\beta\text{-H}}$ with ∠O-N-C-H dihedral angles (bottom) for DMPO-OOH-I.

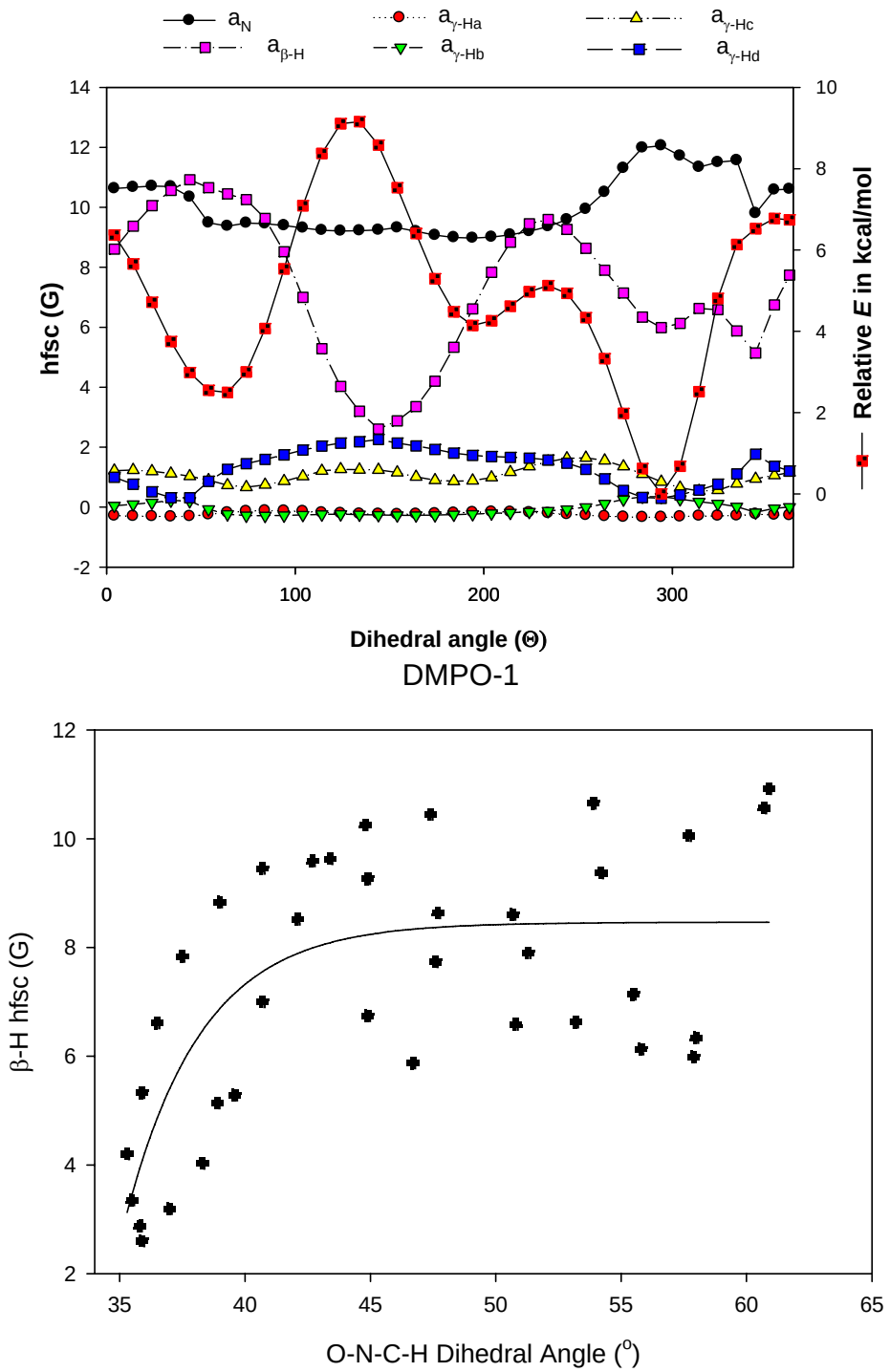
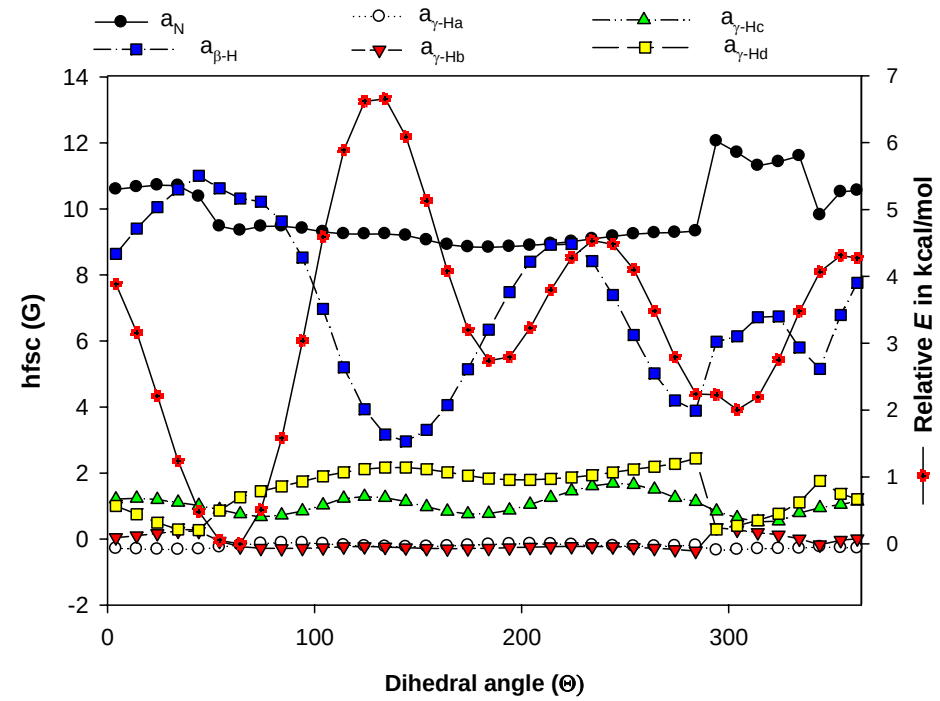


Figure S8. Dependence of hyperfine splitting constants on ∠N-C-O-O (top) and correlation of calculated $a_{\beta\text{-H}}$ with ∠O-N-C-H dihedral angles (bottom) for DMPO-OOH-II.



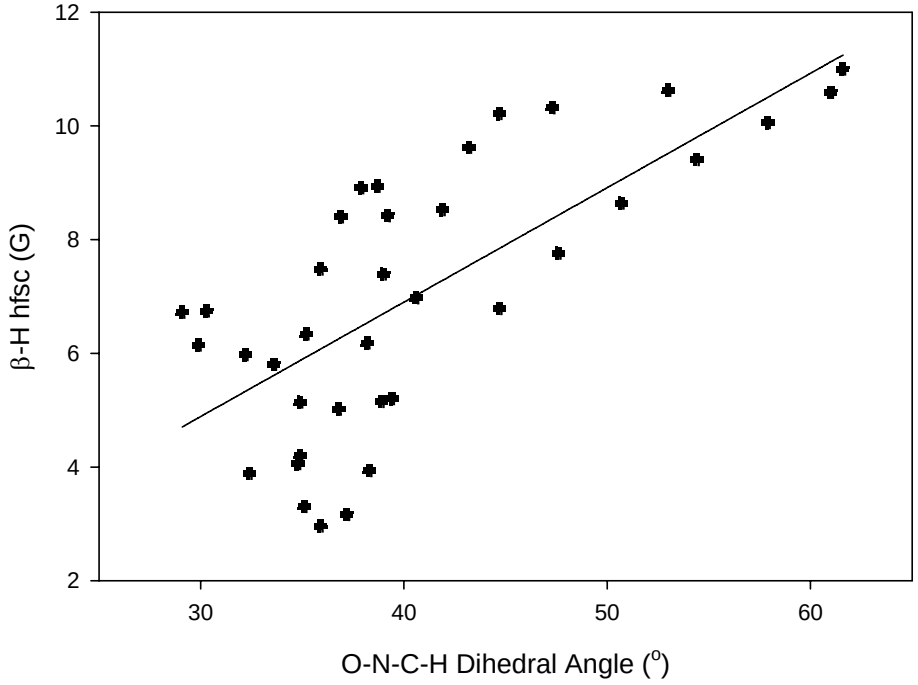
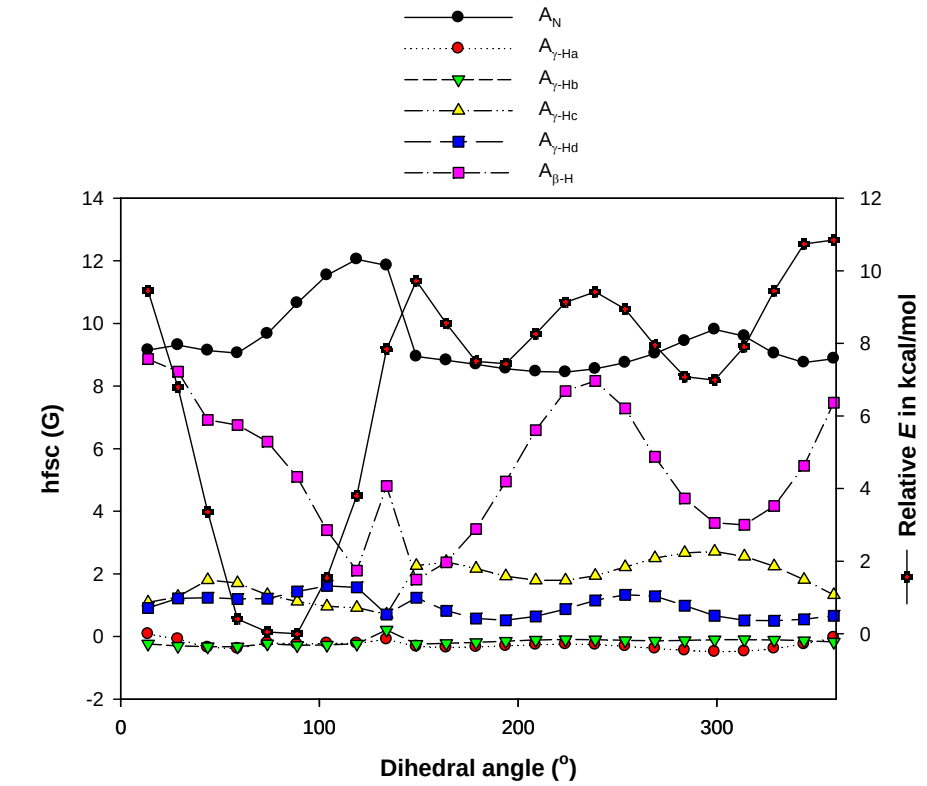


Figure S9. Dependence of hyperfine splitting constants on ∠N-C-O-O (top) and correlation of calculated $a_{\beta\text{-H}}$ with ∠O-N-C-H dihedral angles (bottom) for CPCOMPO-OOH-cis-I.



CPCOMPO-*cis*-1

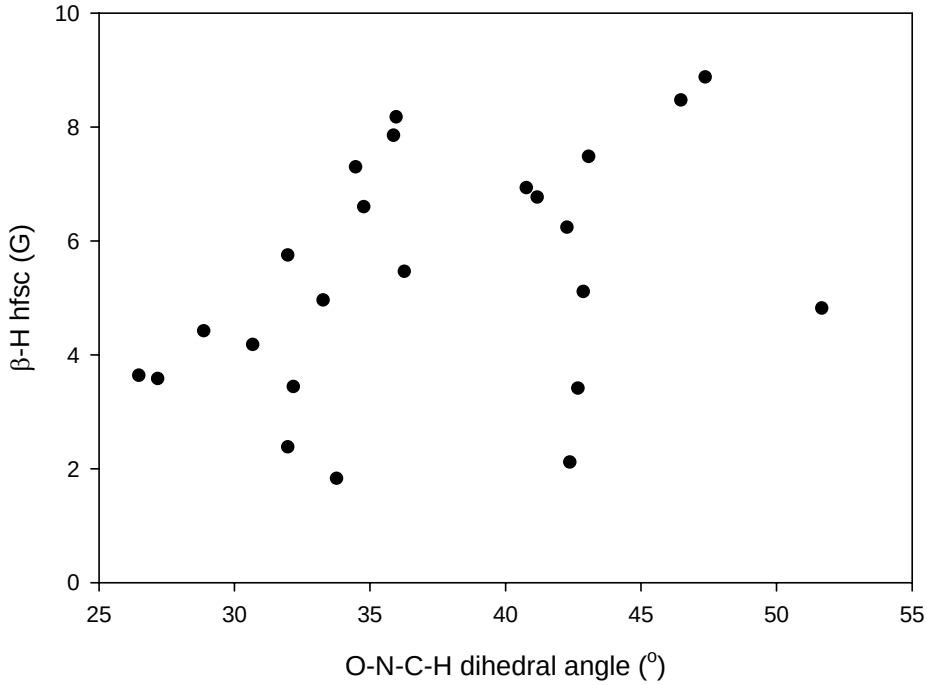


Figure S10. Dependence of hyperfine splitting constants on ∠N-C-O-O (top) and correlation of calculated $a_{\beta\text{-H}}$ with ∠O-N-C-H dihedral angles (bottom) for CPCOMPO-OOH-cis-II.

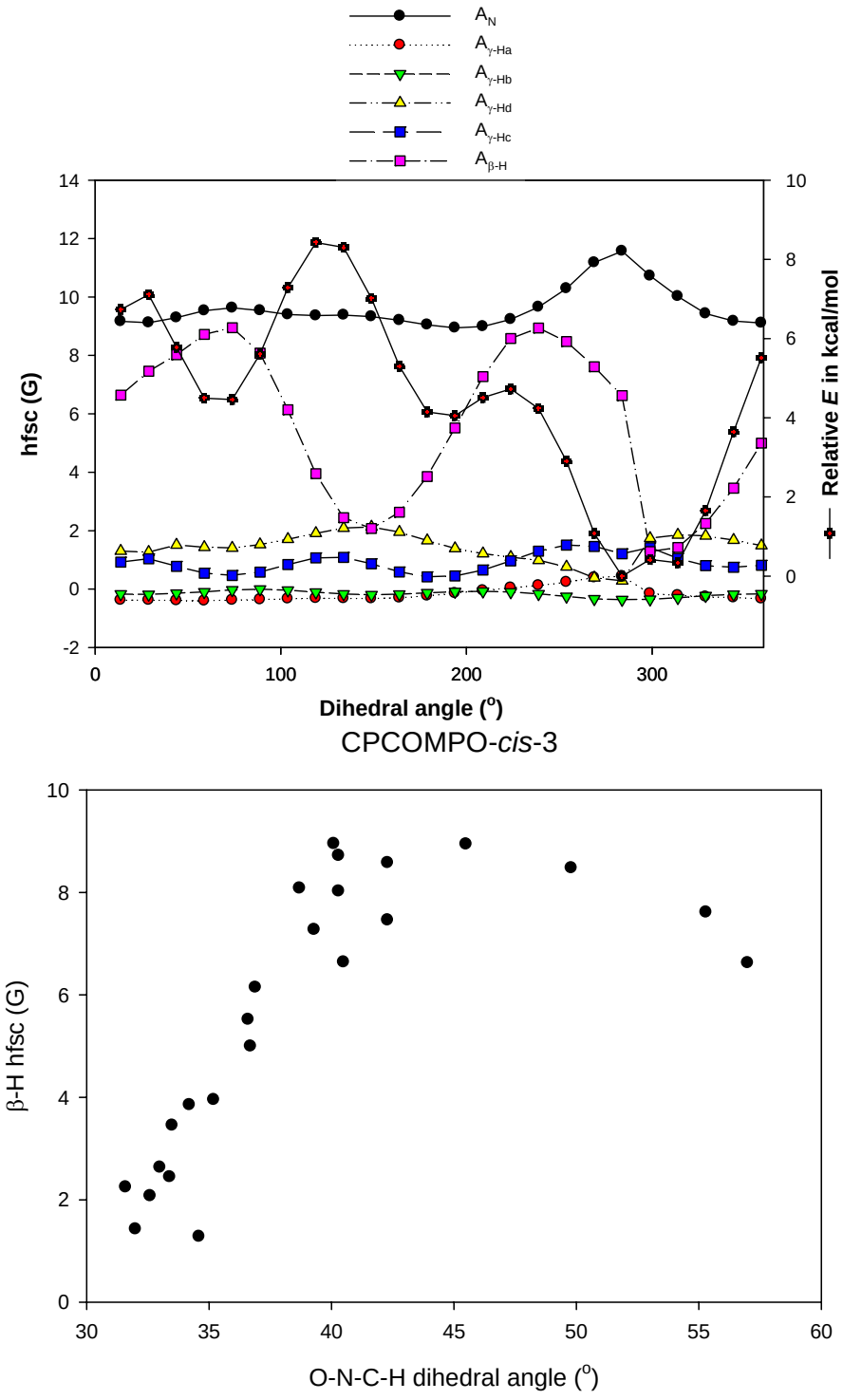


Figure S11. Dependence of hyperfine splitting constants on ∠N-C-O-O (top) and correlation of calculated $a_{\beta\text{-H}}$ with ∠O-N-C-H dihedral angles (bottom) for CPCOMPO-OOH-trans-I.

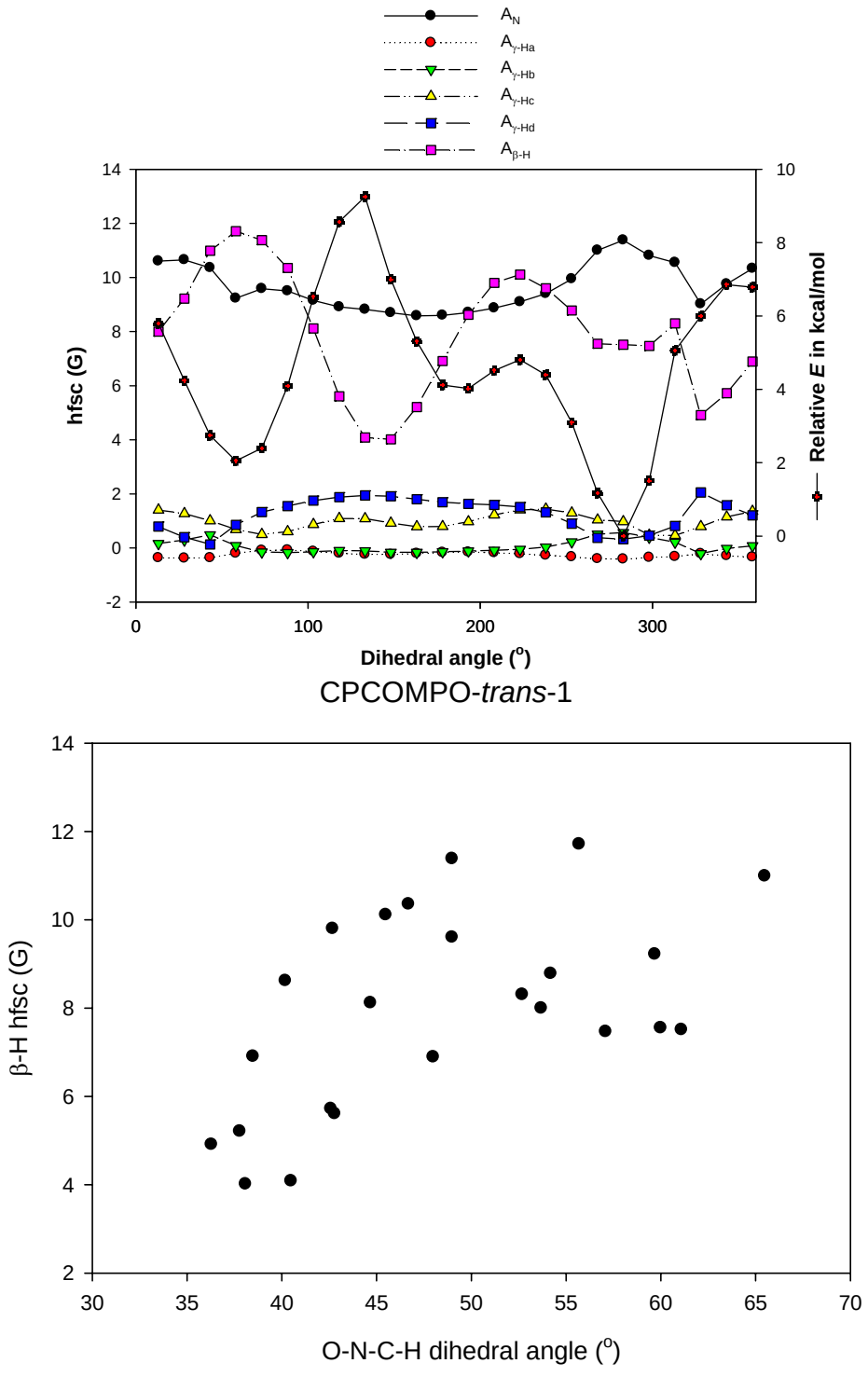
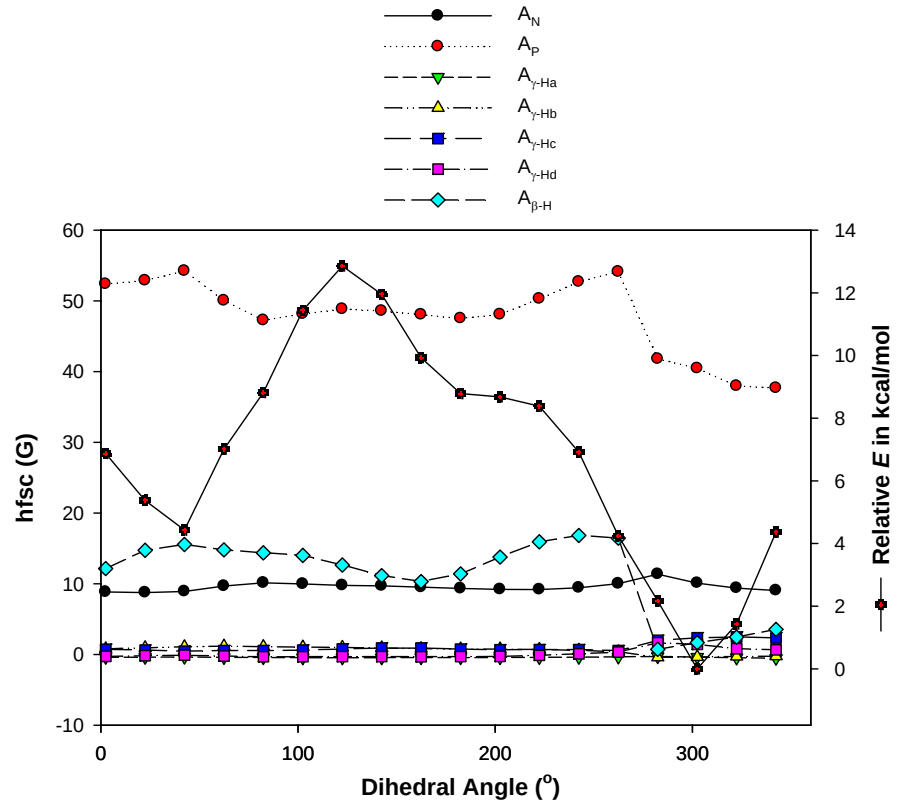


Figure S12. Dependence of hyperfine splitting constants on ∠N-C-O-O (top) and correlation of calculated $a_{\beta\text{-H}}$ with ∠O-N-C-H dihedral angles (bottom) for DEPMPO-OOH-cis-I.



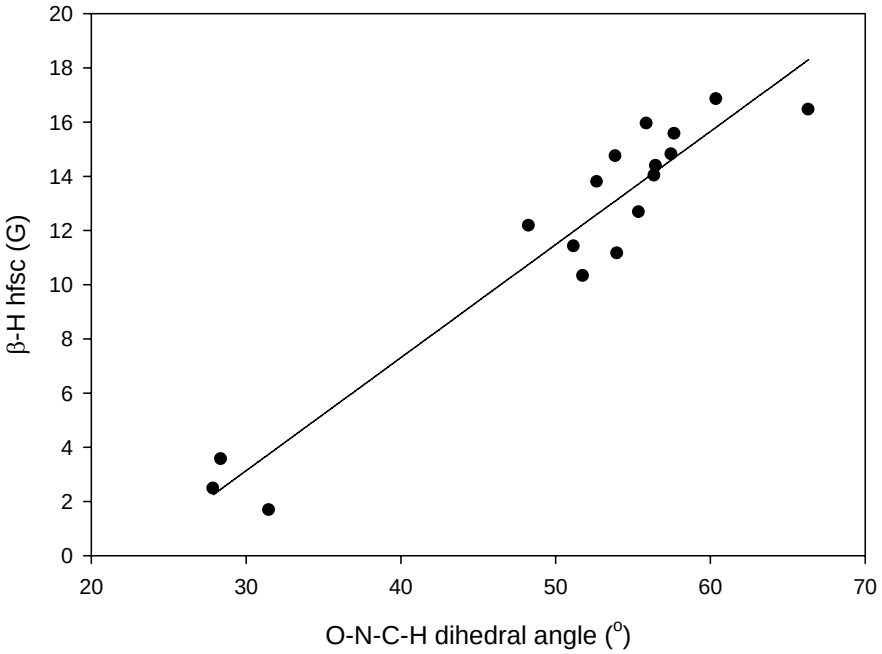


Figure S13. Dependence of hyperfine splitting constants on ∠N-C-O-O (top) and correlation of calculated $a_{\beta\text{-H}}$ with ∠O-N-C-H dihedral angles (bottom) for DEPMPO-OOH-cis-II.

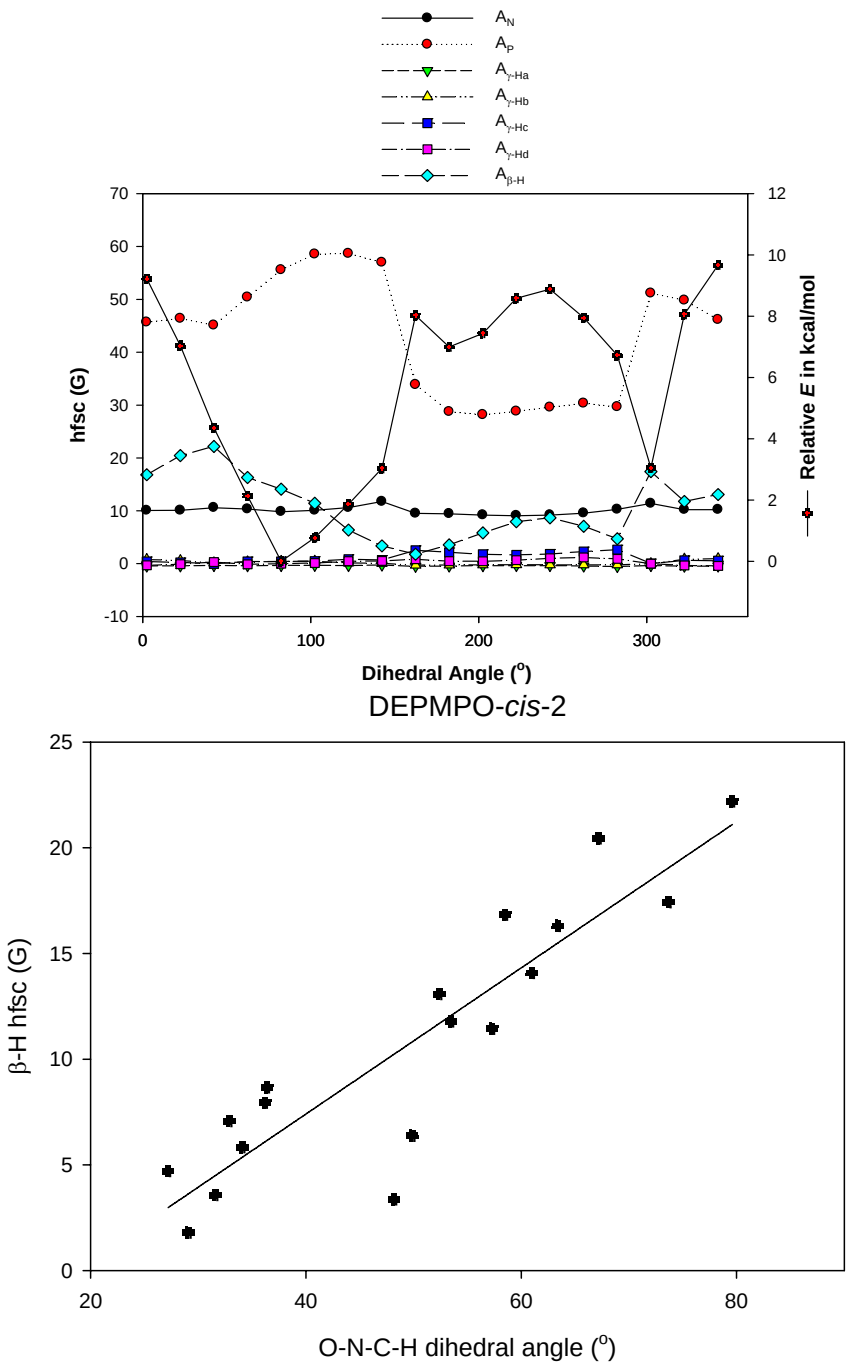


Figure S14. Dependence of hyperfine splitting constants on ∠N-C-P-O (top) and correlation of calculated $a_{\beta\text{-H}}$ with ∠O-N-C-H dihedral angles (bottom) for DEPMPO-OOH-cis-PO.

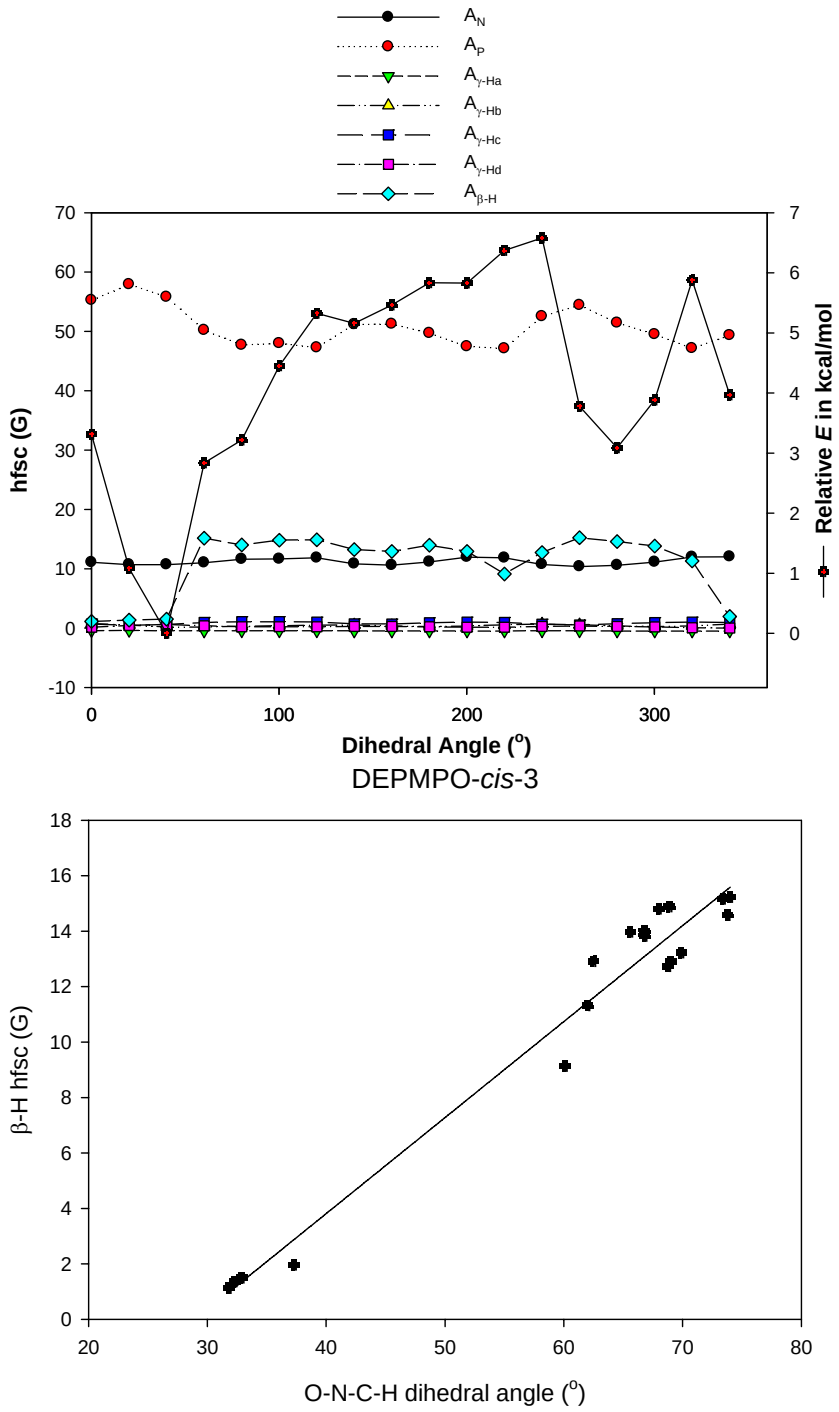
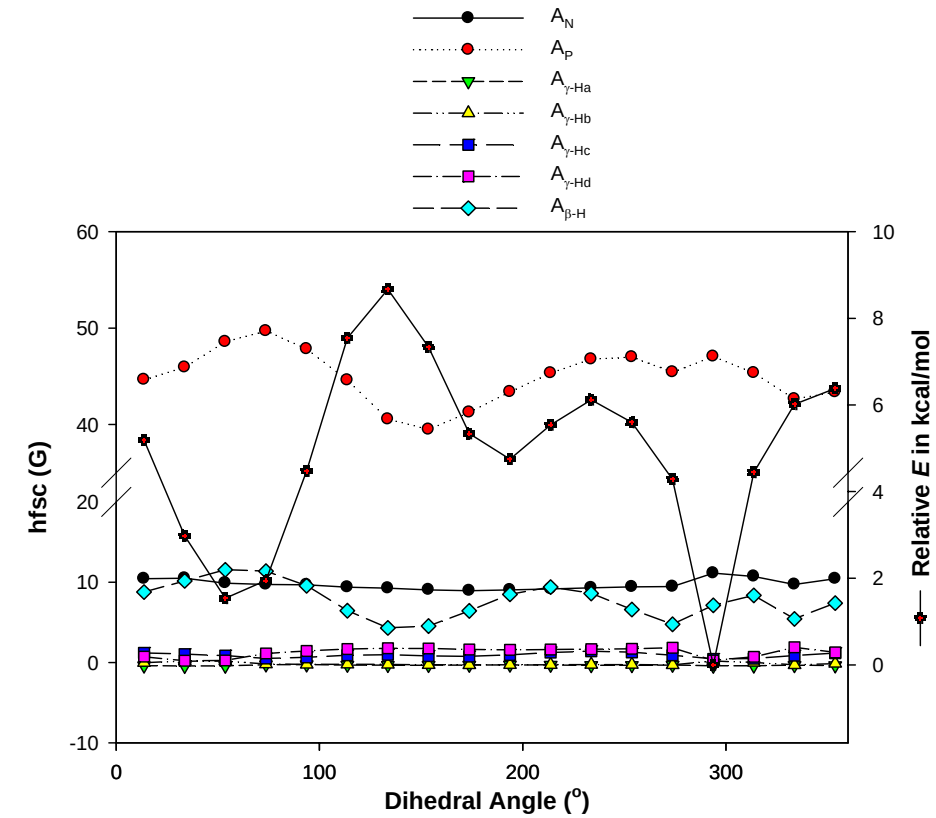


Figure S15. Dependence of hyperfine splitting constants on ∠N-C-O-O (top) and correlation of calculated $a_{\beta\text{-H}}$ with ∠O-N-C-H dihedral angles (bottom) for DEPMPO-OOH-trans-I.



DEPMPO-*trans*-1

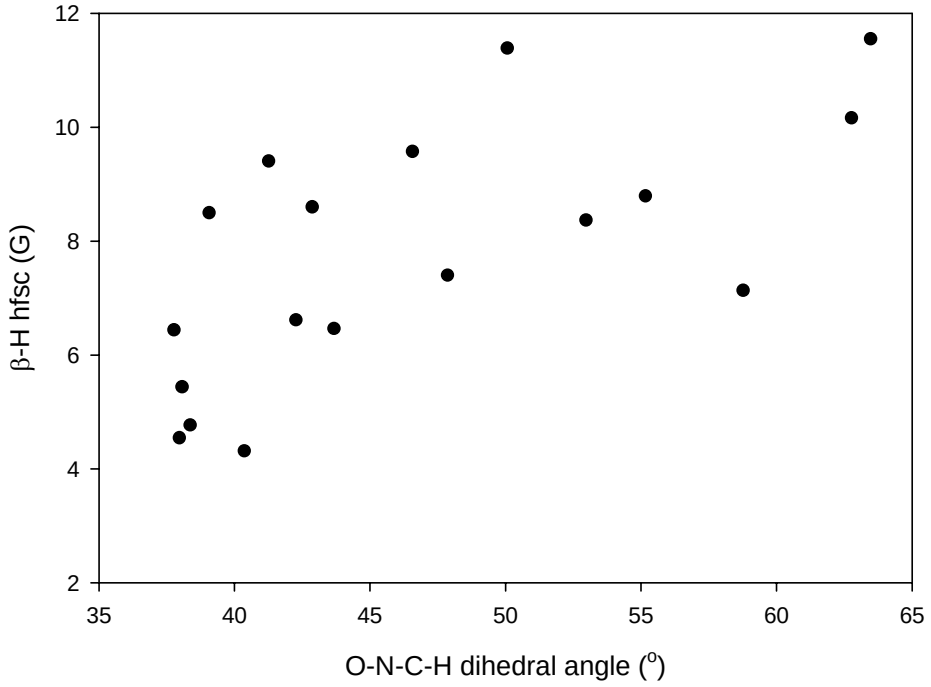


Figure S16. Dependence of hyperfine splitting constants on ∠N-C-O-O (top) and correlation of calculated $a_{\beta\text{-H}}$ with ∠O-N-C-H dihedral angles (bottom) for DEPMPO-OOH-trans-II.

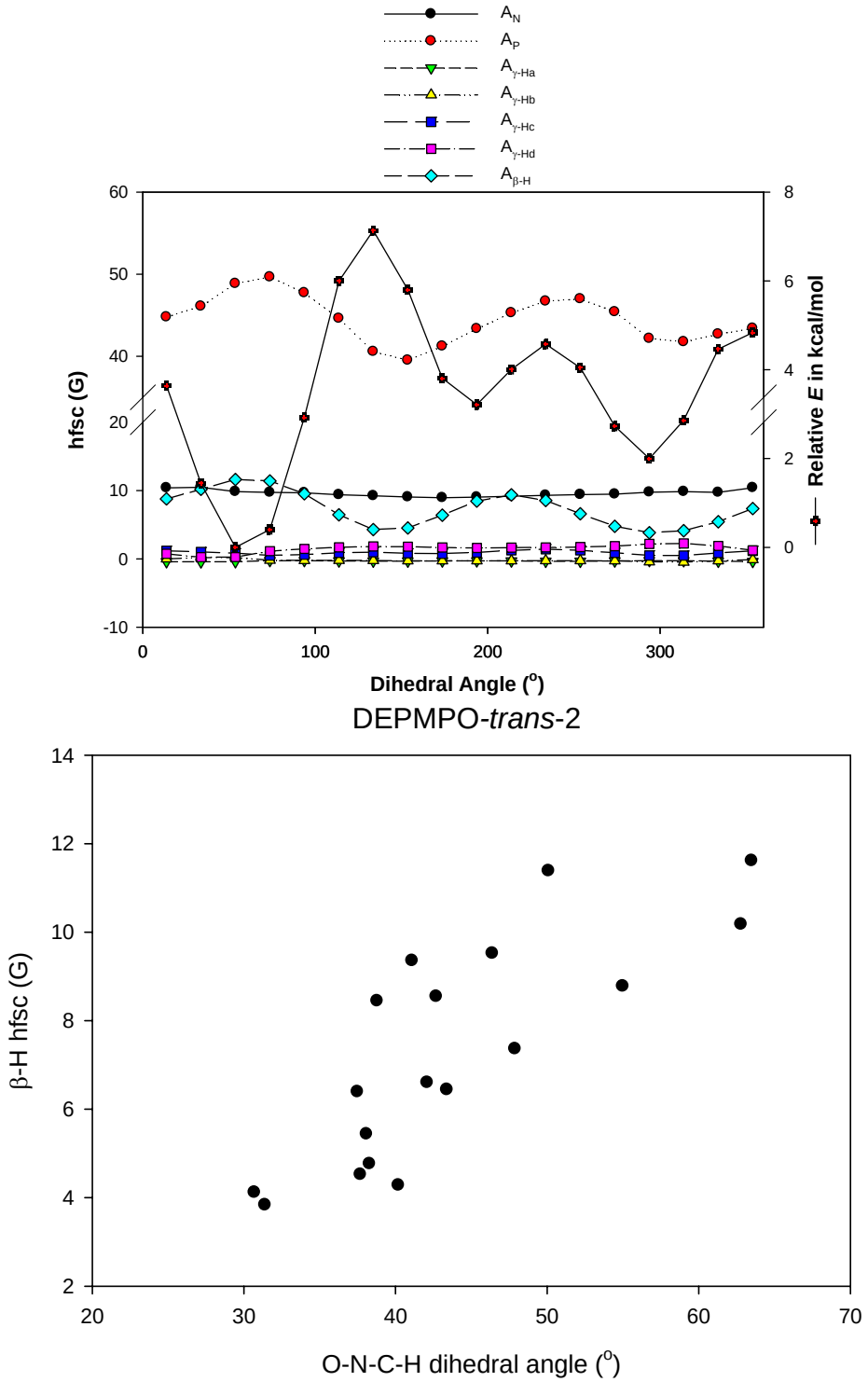


Figure S17. Dependence of hyperfine splitting constants on ∠N-C-P-O (top) and correlation of calculated $a_{\beta\text{-H}}$ with ∠O-N-C-H dihedral angles (bottom) for DEPMPO-OOH-trans-PO.

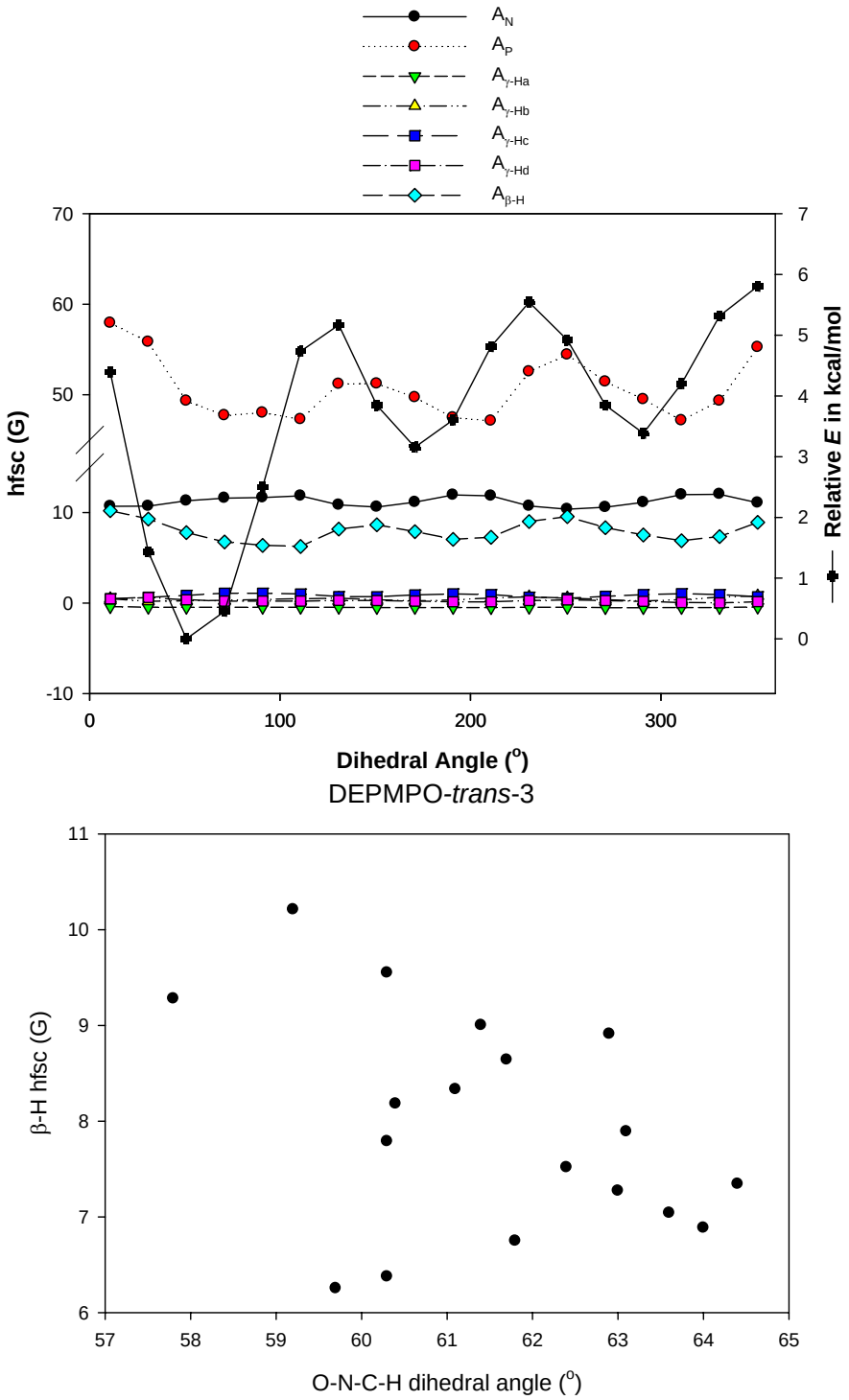


Figure S18. Dependence of hyperfine splitting constants on ∠N-C-O-O (top) and correlation of calculated $a_{\beta\text{-H}}$ with ∠O-N-C-H dihedral angles (bottom) for EMPO-OOH-cis-I.

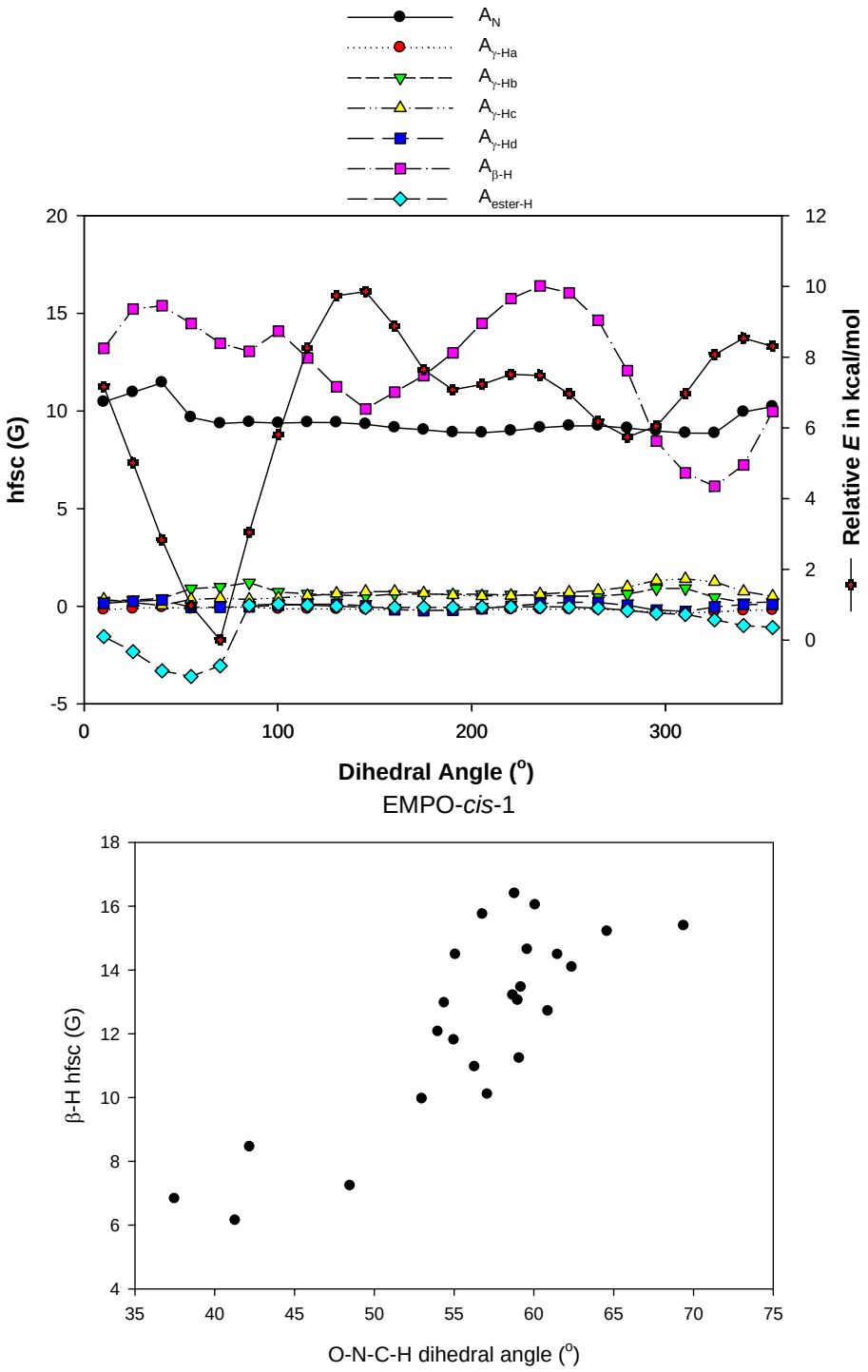
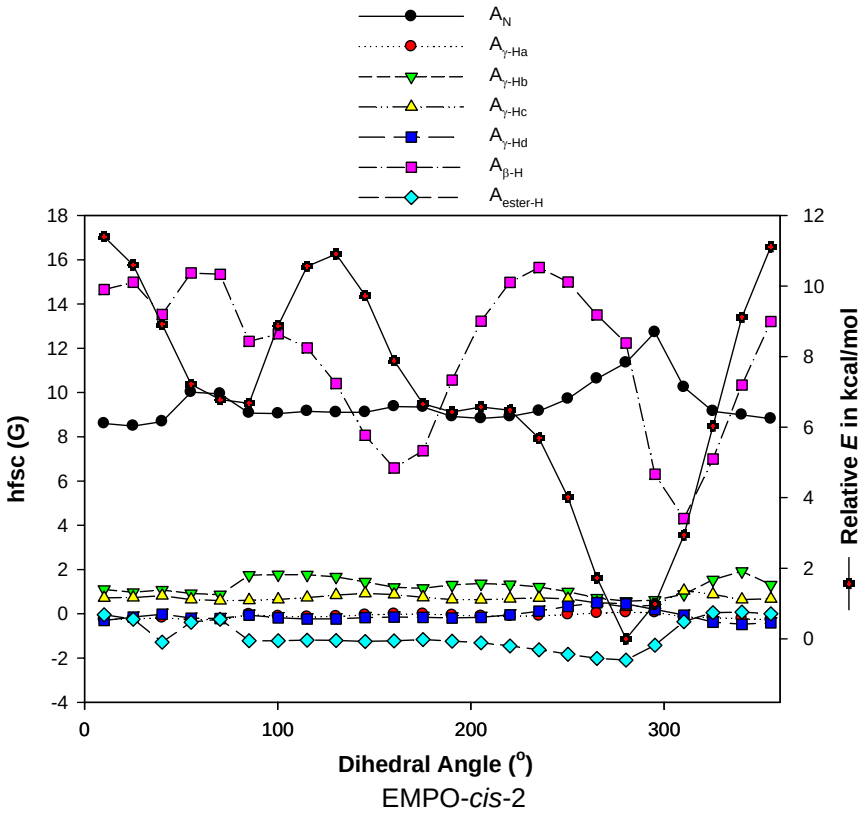


Figure S19. Dependence of hyperfine splitting constants on ∠N-C-O-O (top) and correlation of calculated $a_{\beta\text{-H}}$ with ∠O-N-C-H dihedral angles (bottom) for EMPO-OOH-cis-II.



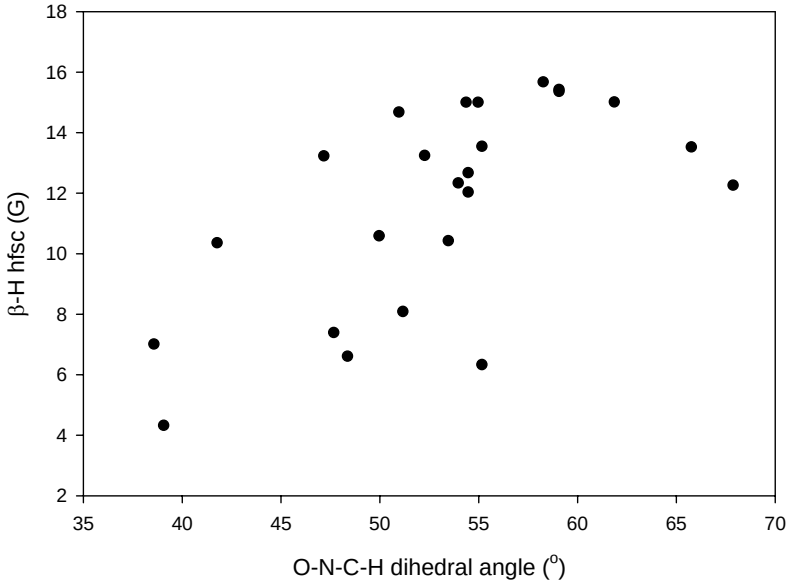


Figure S20. Dependence of hyperfine splitting constants on ∠N-C-C-O (top) and correlation of calculated $a_{\beta\text{-H}}$ with ∠O-N-C-H dihedral angles (bottom) for EMPO-OOH-cis-CO.

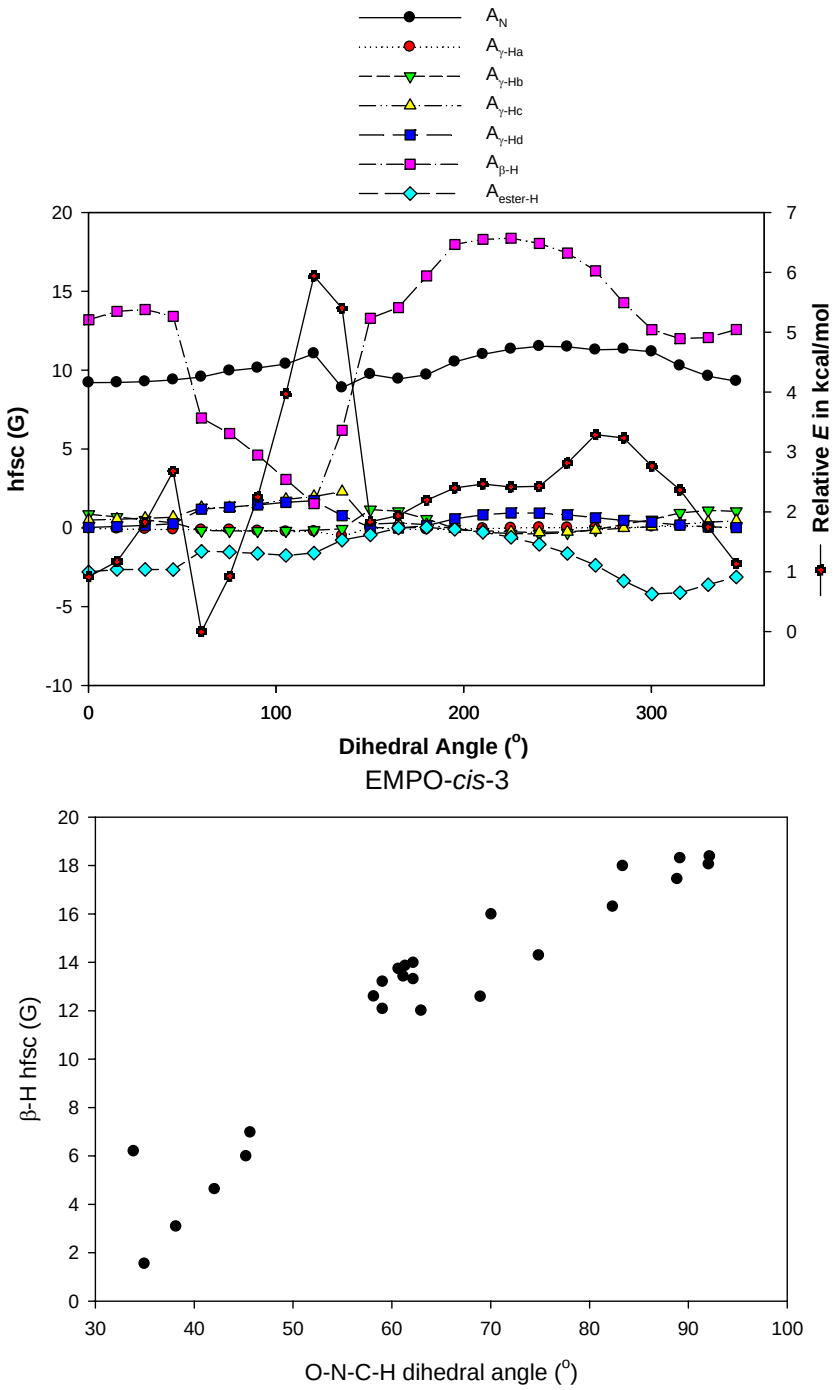
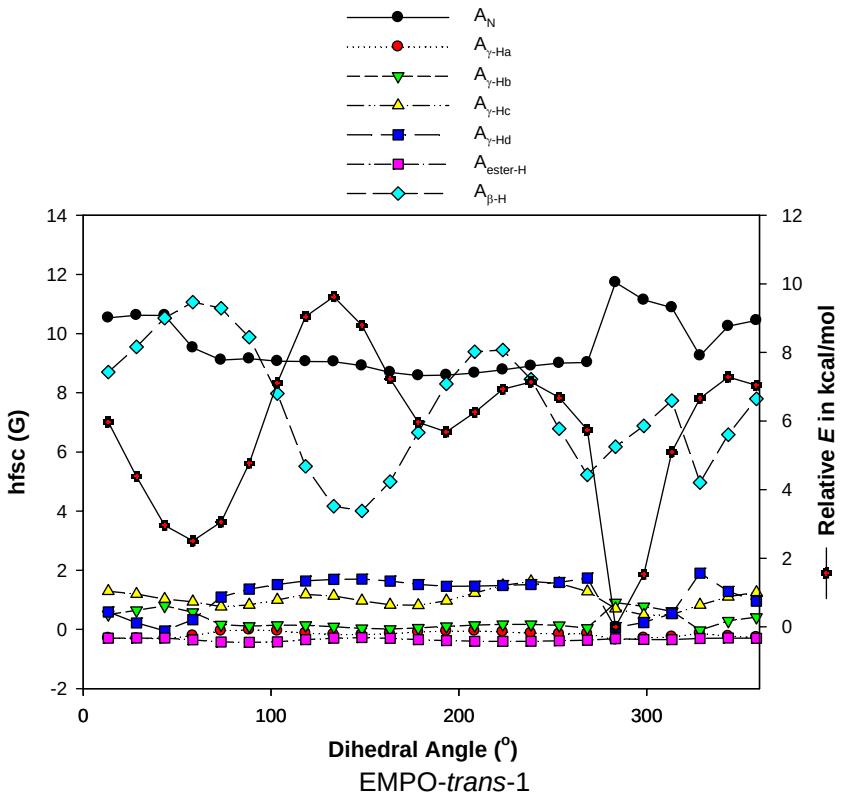


Figure S21. Dependence of hyperfine splitting constants on ∠N-C-O-O (top) and correlation of calculated $a_{\beta\text{-H}}$ with ∠O-N-C-H dihedral angles (bottom) for EMPO-OOH-trans-I.



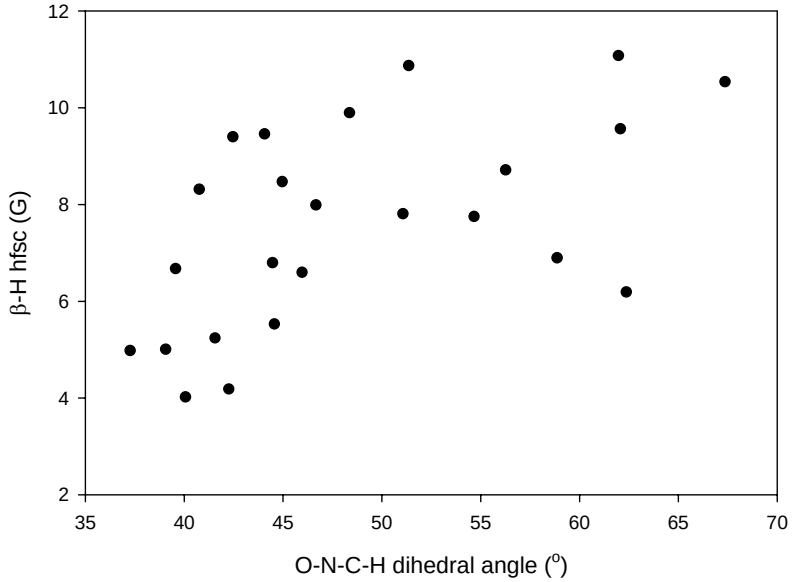
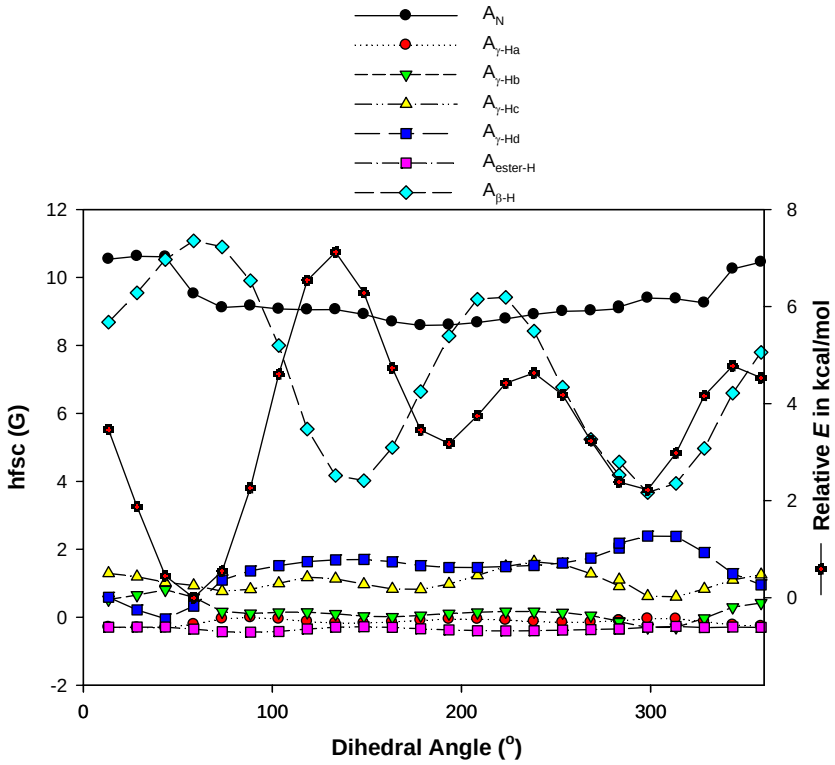


Figure S22. Dependence of hyperfine splitting constants on ∠N-C-O-O (top) and correlation of calculated $a_{\beta\text{-H}}$ with ∠O-N-C-H dihedral angles (bottom) for EMPO-OOH-trans-II.



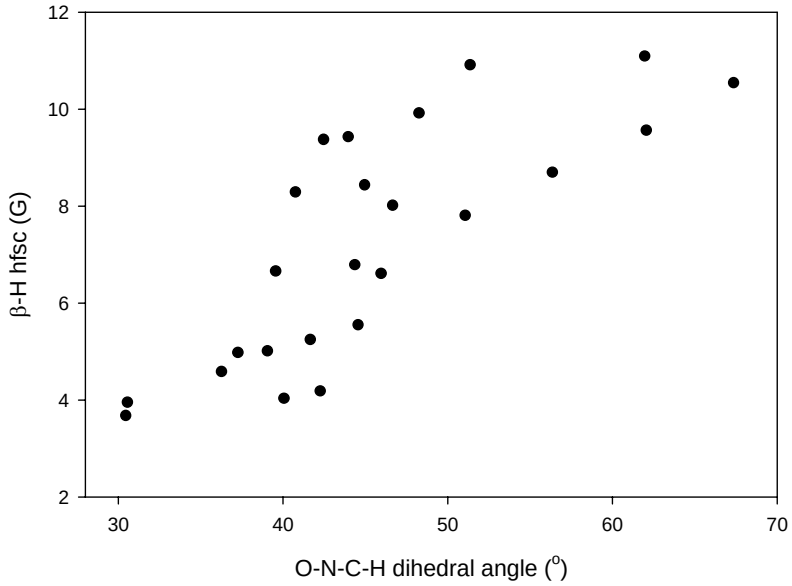


Figure S23. Dependence of hyperfine splitting constants on ∠N-C-C-O (top) and correlation of calculated $a_{\beta\text{-H}}$ with ∠O-N-C-H dihedral angles (bottom) for EMPO-OOH-trans-CO.

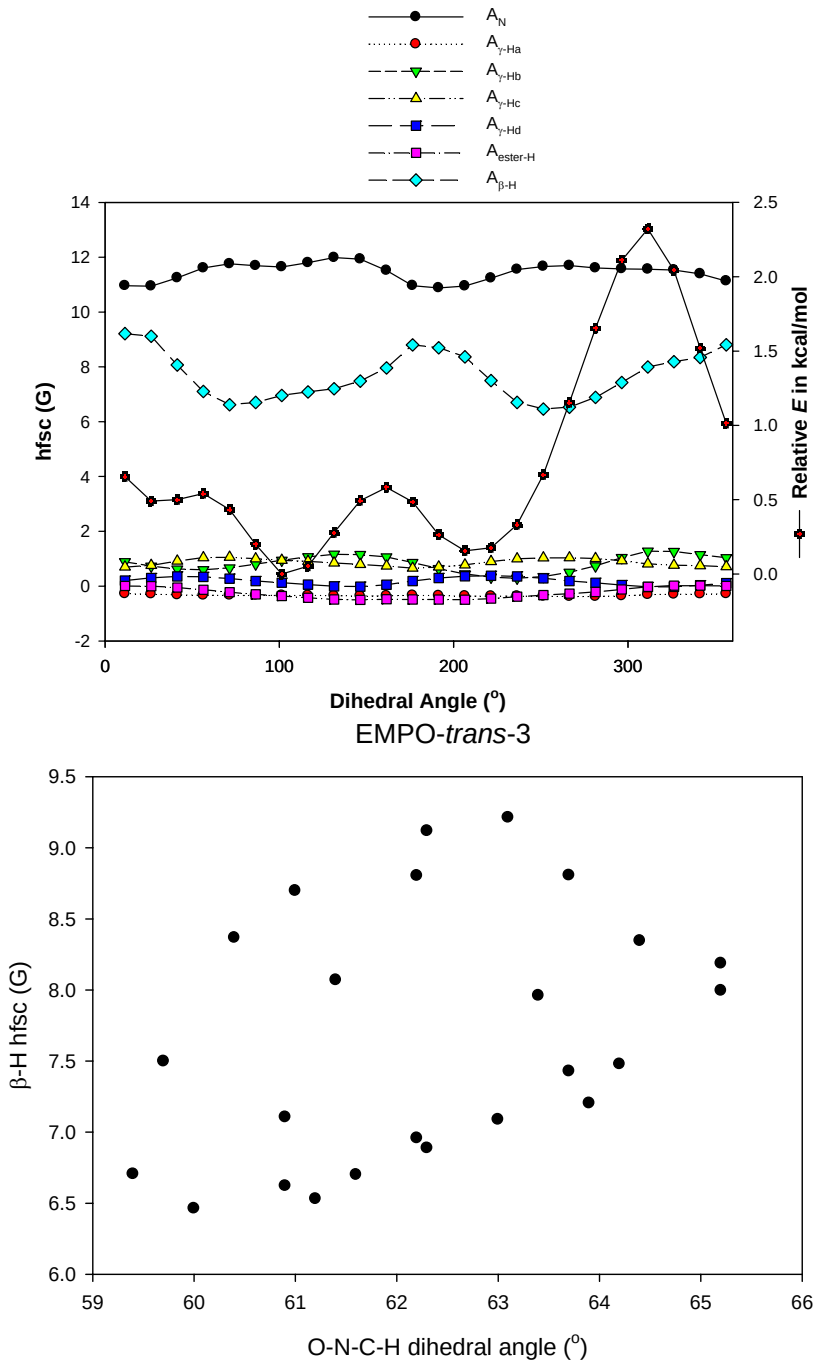
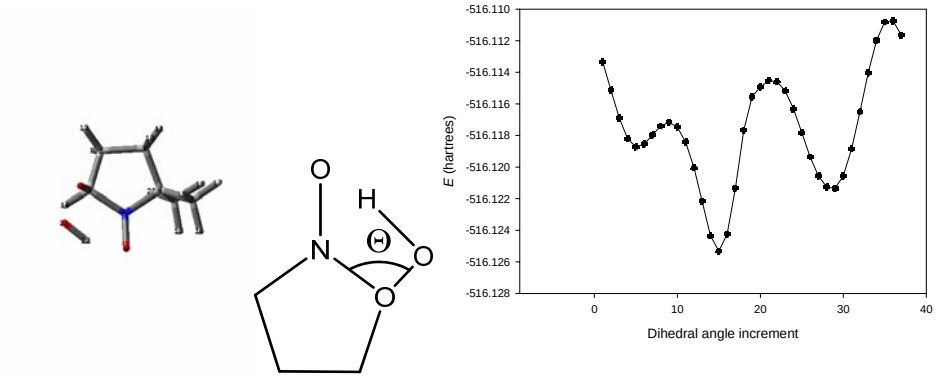


Figure S24. Potential energy surface as a function of ∠N-C-O-O dihedral angles for DMPO-OOH showing the most preferred conformations.

DMPO-OOH-I (NCOO) 75.92°



DMPO-OOH-II (NCOO) 54.08°

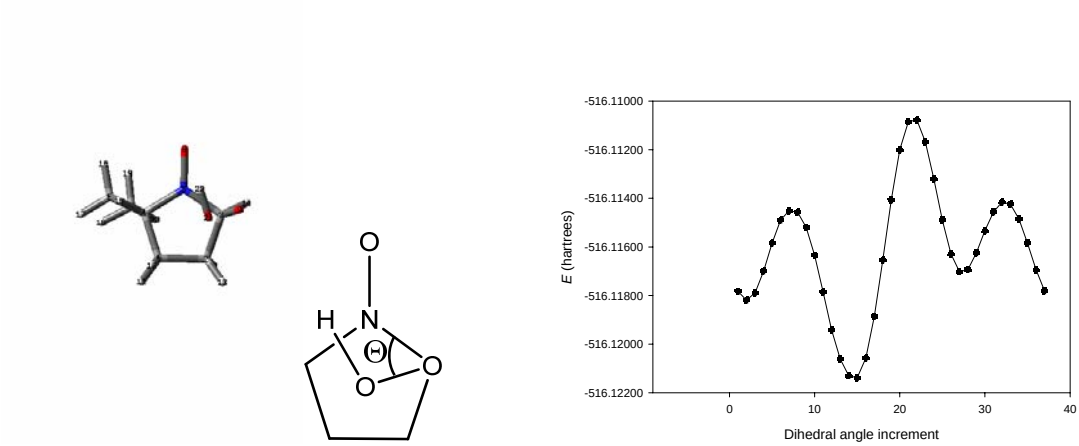
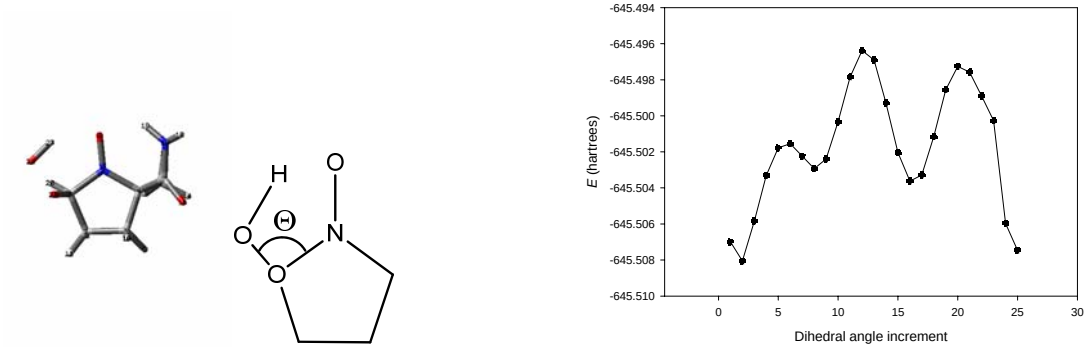
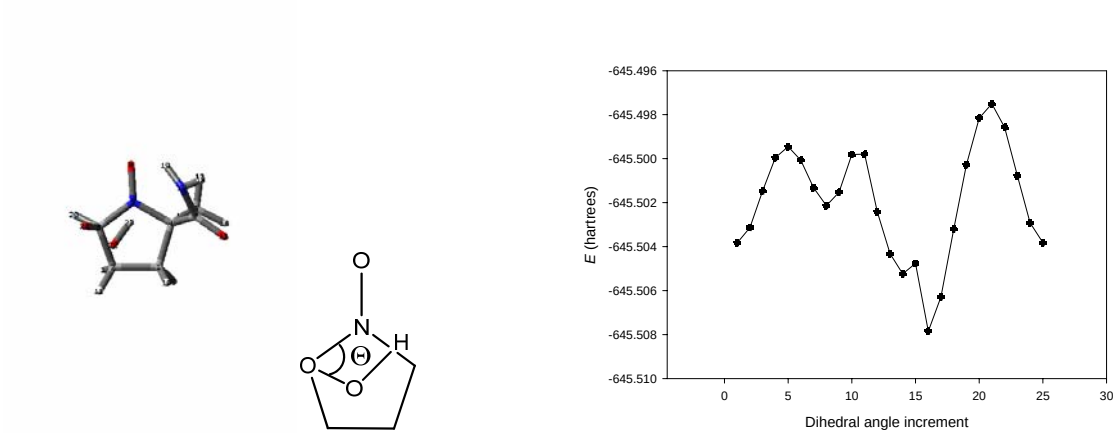


Figure S25. Potential energy surface as a function of ∠N-C-O-O dihedral angles for AMPO-OOH showing the most preferred conformations.

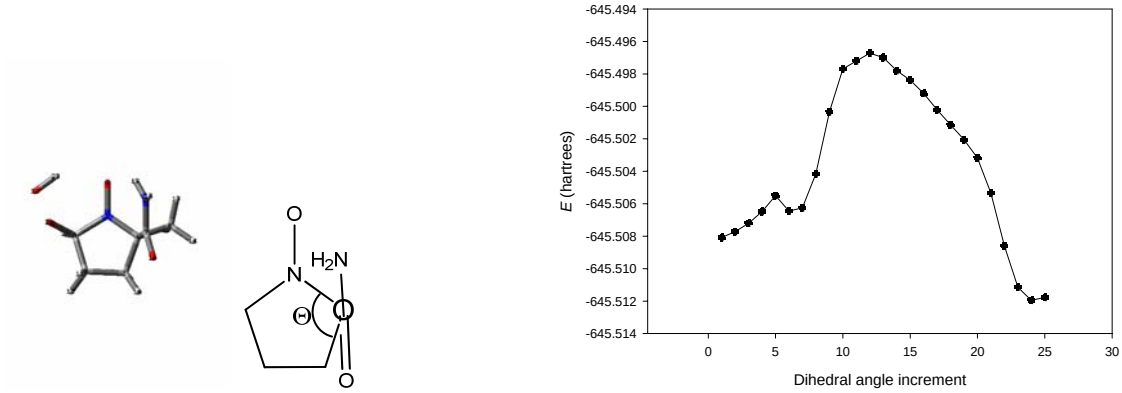
AMPO-OOH-cis-I (CNOO) 81.29°



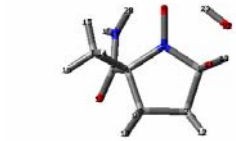
AMPO-OOH-cis-II (CNOO) 68.71°

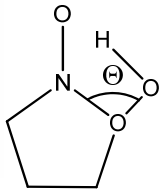


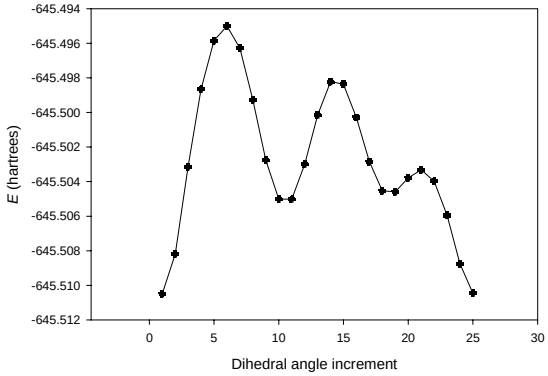
AMPO-OOH-cis-CO (NCCO) 136.54°



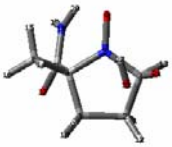
AMPO-OOH-trans-I (CNOO) 76.49°

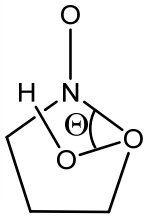


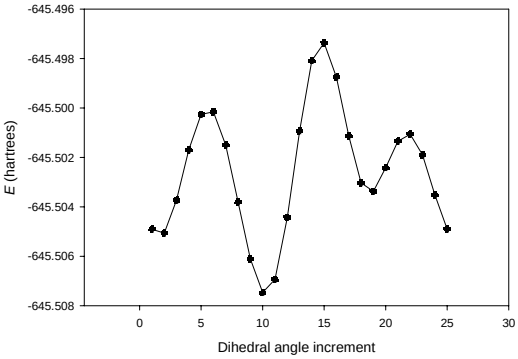




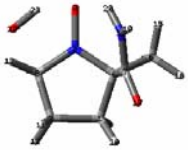
AMPO-OOH-trans-II (CNOO) 58.51°

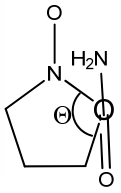






AMPO-OOH-trans-CO (NCCO) 140.13°





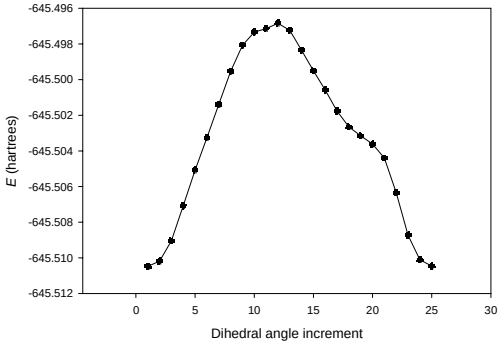
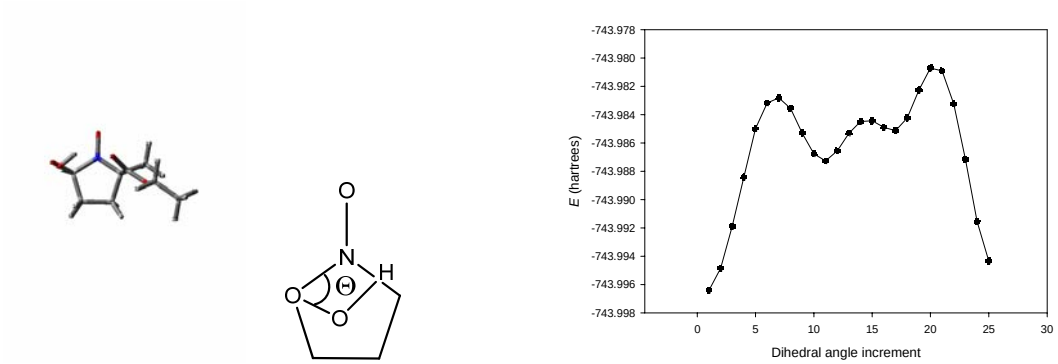
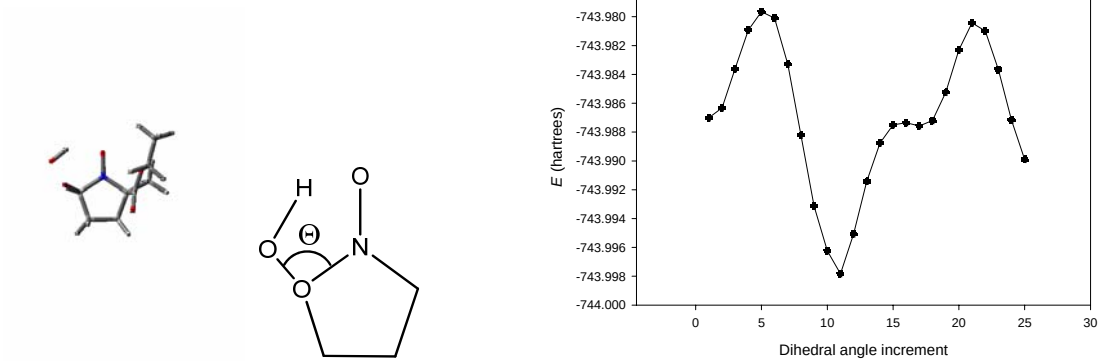


Figure S26. Potential energy surface as a function of ∠N-C-O-O dihedral angles for EMPO-OOH showing the most preferred conformations.

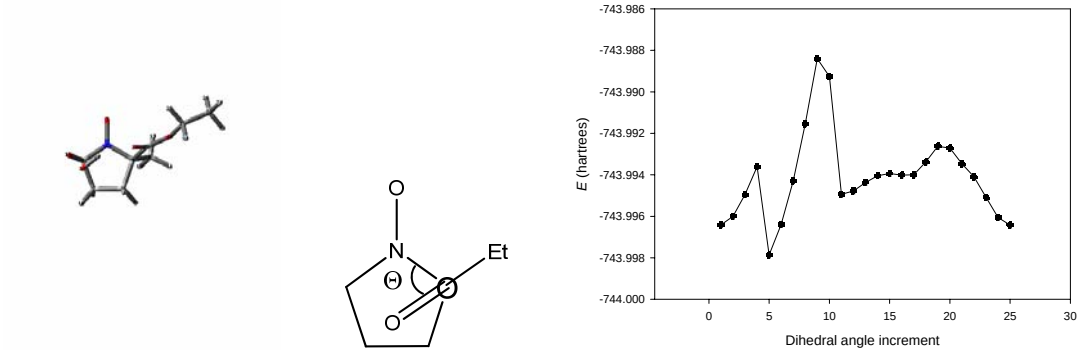
EMPO-OOH-cis-I (CNOO) 70.22°



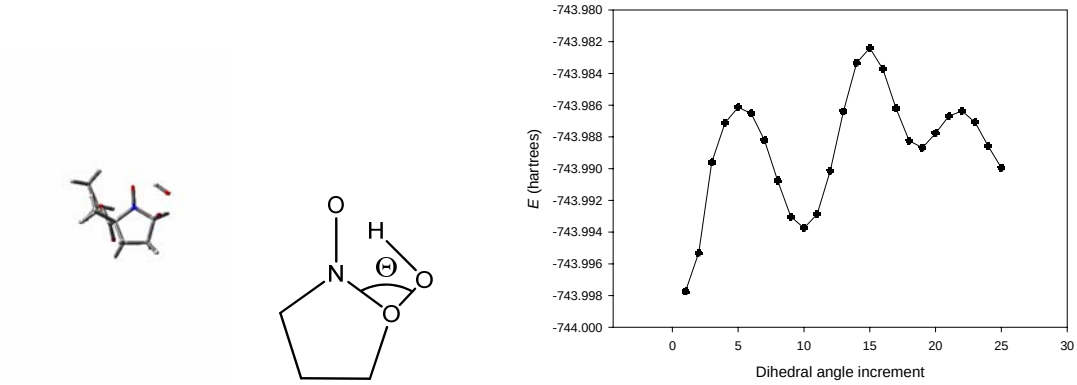
EMPO-OOH-cis-II (CNOO) 79.77°



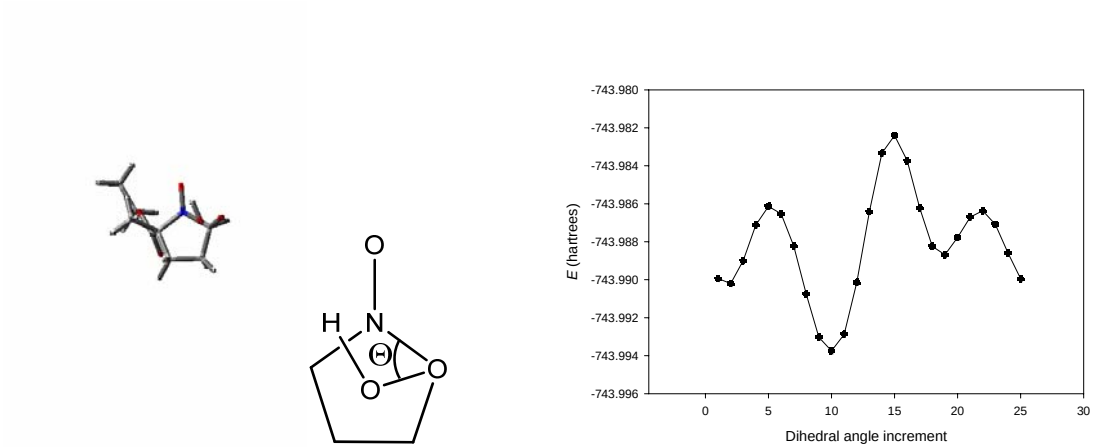
EMPO-OOH-cis-CO (NCCO) 60.2°



EMPO-OOH-trans-I (CNOO) 76.62°



EMPO-OOH-trans-II (CNOO) 58.38°



EMPO-OOH-trans-CO (NCCO) 101.42°

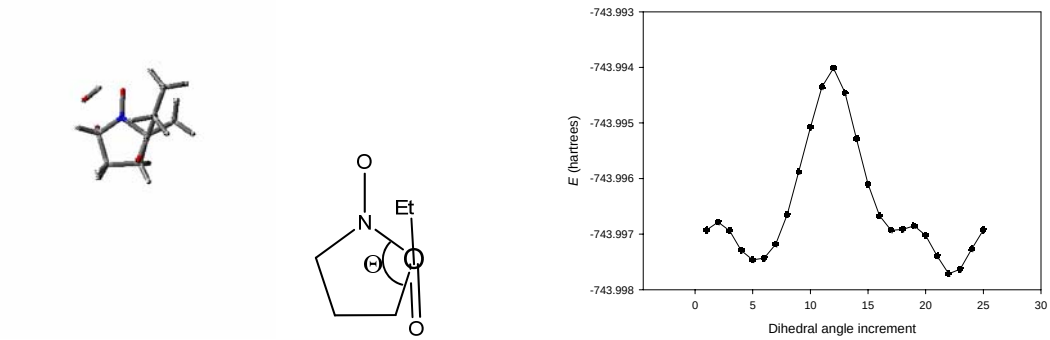
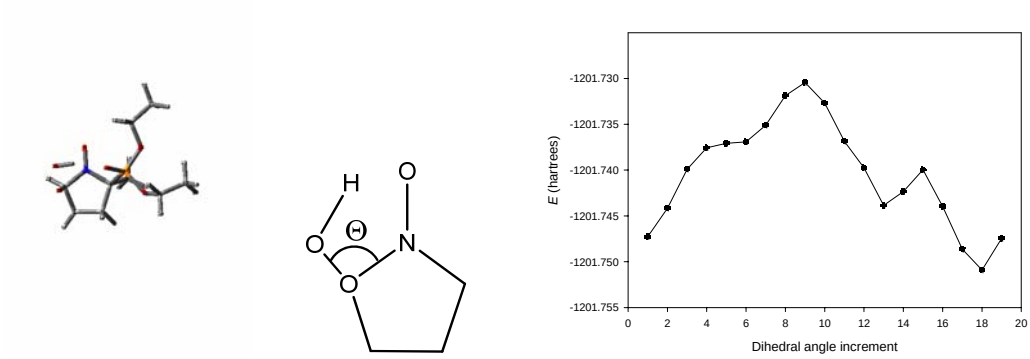
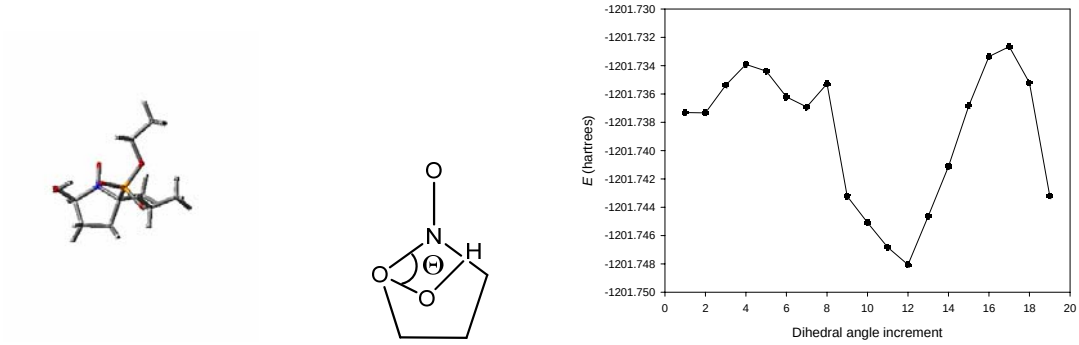


Figure S27. Potential energy surface as a function of ∠N-C-O-O dihedral angles for DEPMPO-OOH showing the most preferred conformations.

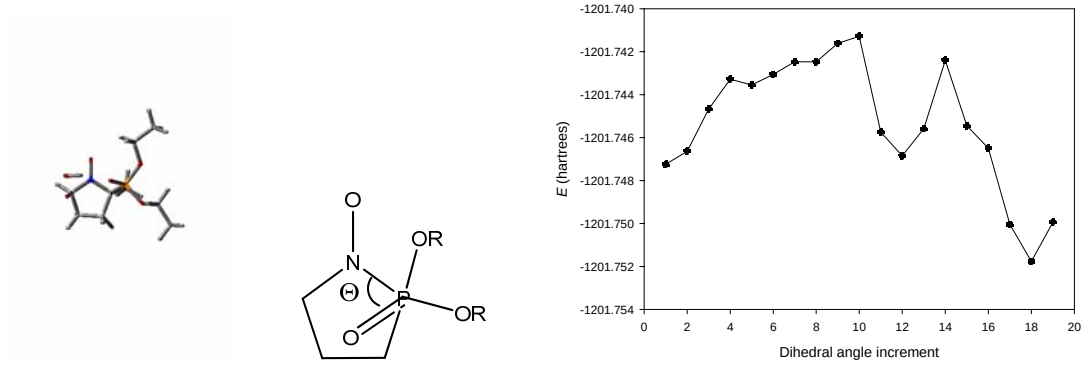
DEPMPO-OOH-cis-I (CNOO) 57.60°



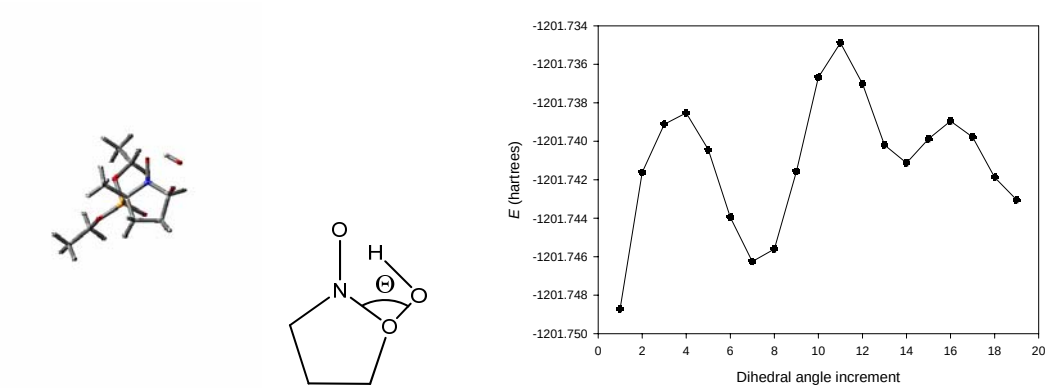
DEPMPO-OOH-cis-II (CNOO) 82.40°



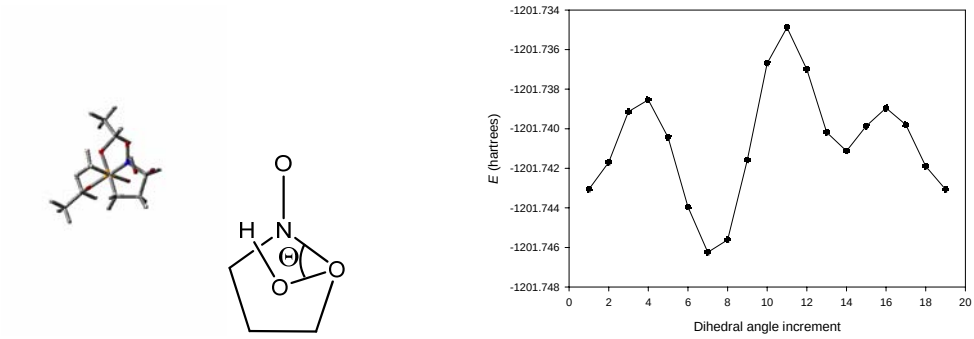
DEPMPO-OOH-cis-PO (NCPO) 40.07°



DEPMPO-OOH-trans-I (CNOO) 66.30°



DEPMPO-OOH-trans-II (CNOO) 53.70°



DEPMPO-OOH-trans-PO (NCPO) 50.84°

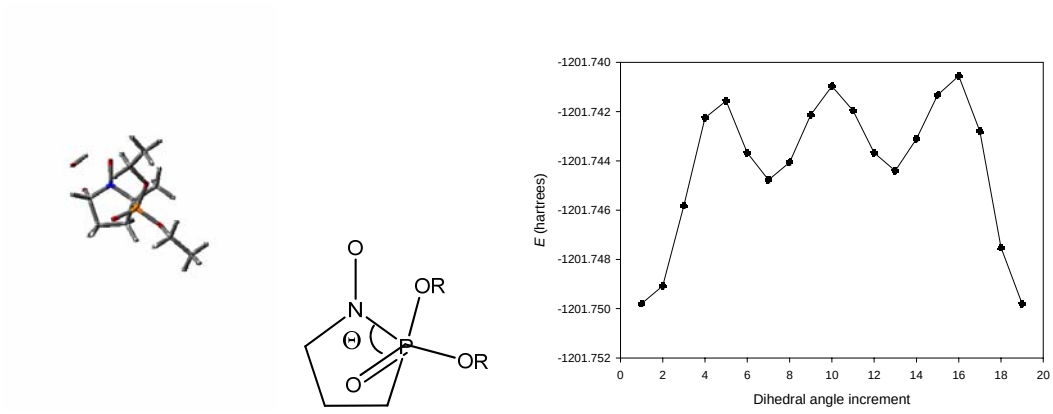
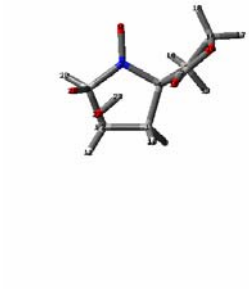
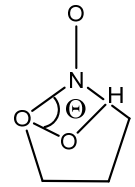
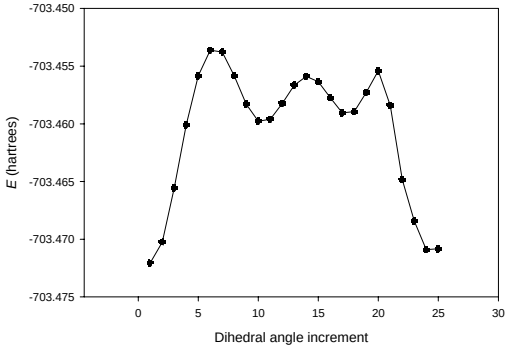


Figure S28. Potential energy surface as a function of ∠N-C-O-O dihedral angles for CPCOMPO-OOH showing the most preferred conformations.

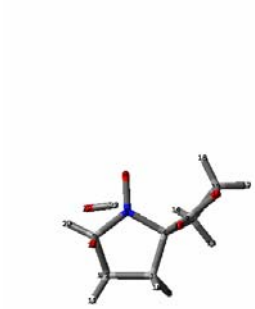
CPCOMPO-OOH-cis-I (CNOO) 73.78°

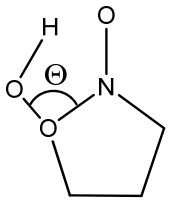


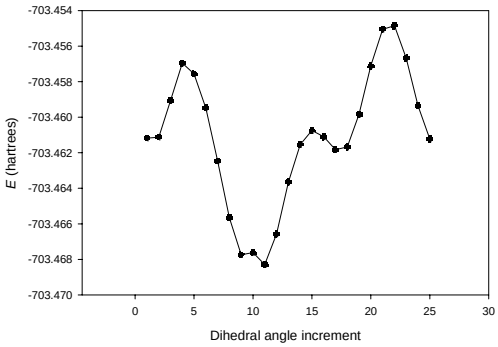




CPCOMPO-OOH-cis-II (CNOO) 76.21°







CPCOMPO-OOH-trans-I (CNOO) 76.95°

