Supplementary Information

On the reactivity of the photochemically derived nitrobenzene epoxide structure with hydronium

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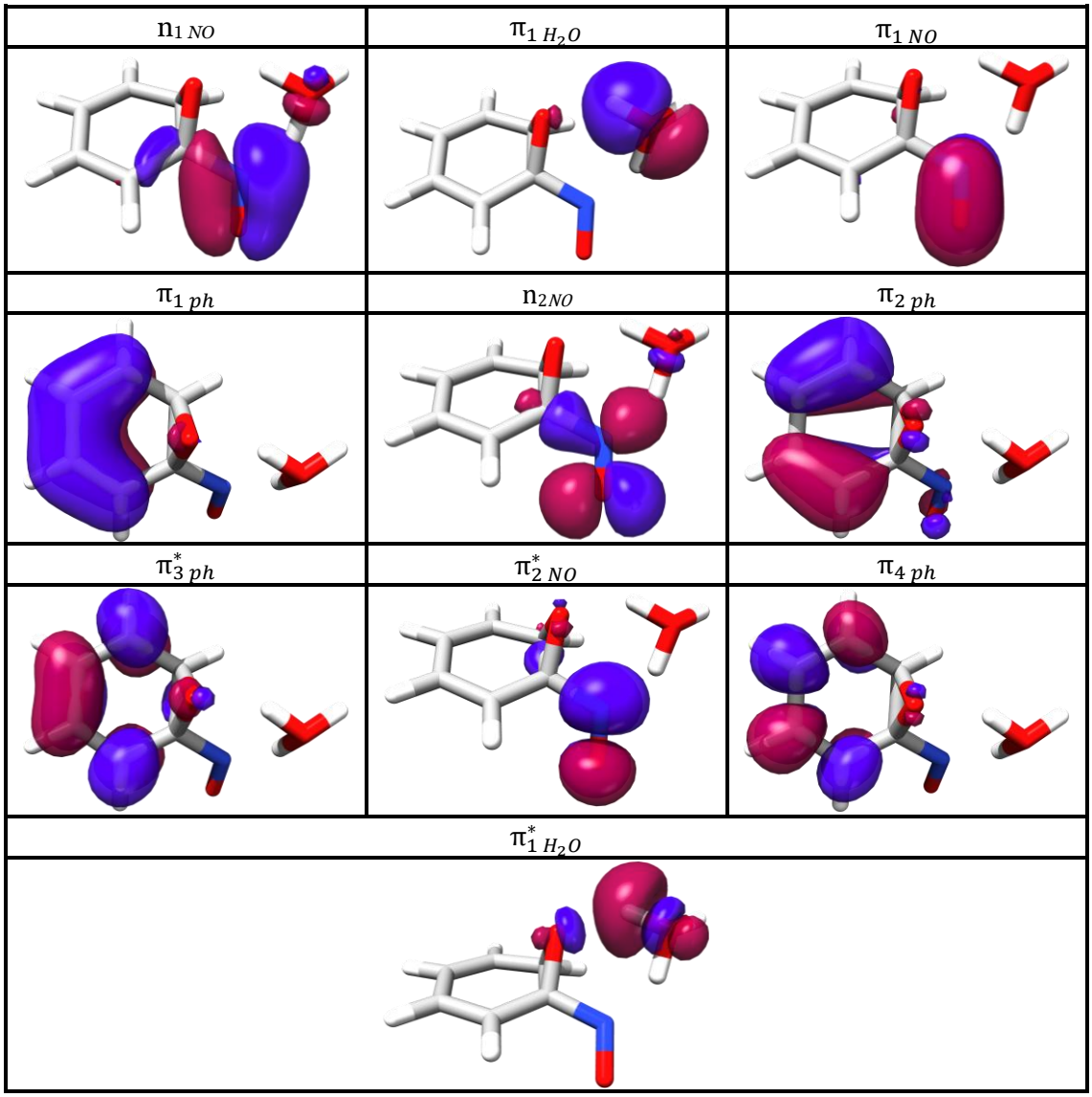

Figure S1: CAS(12,10) active space at the *[EPO—H_3O]$^+$$_{min\text{-}xpt2(12,10)}$* optimized geometry.

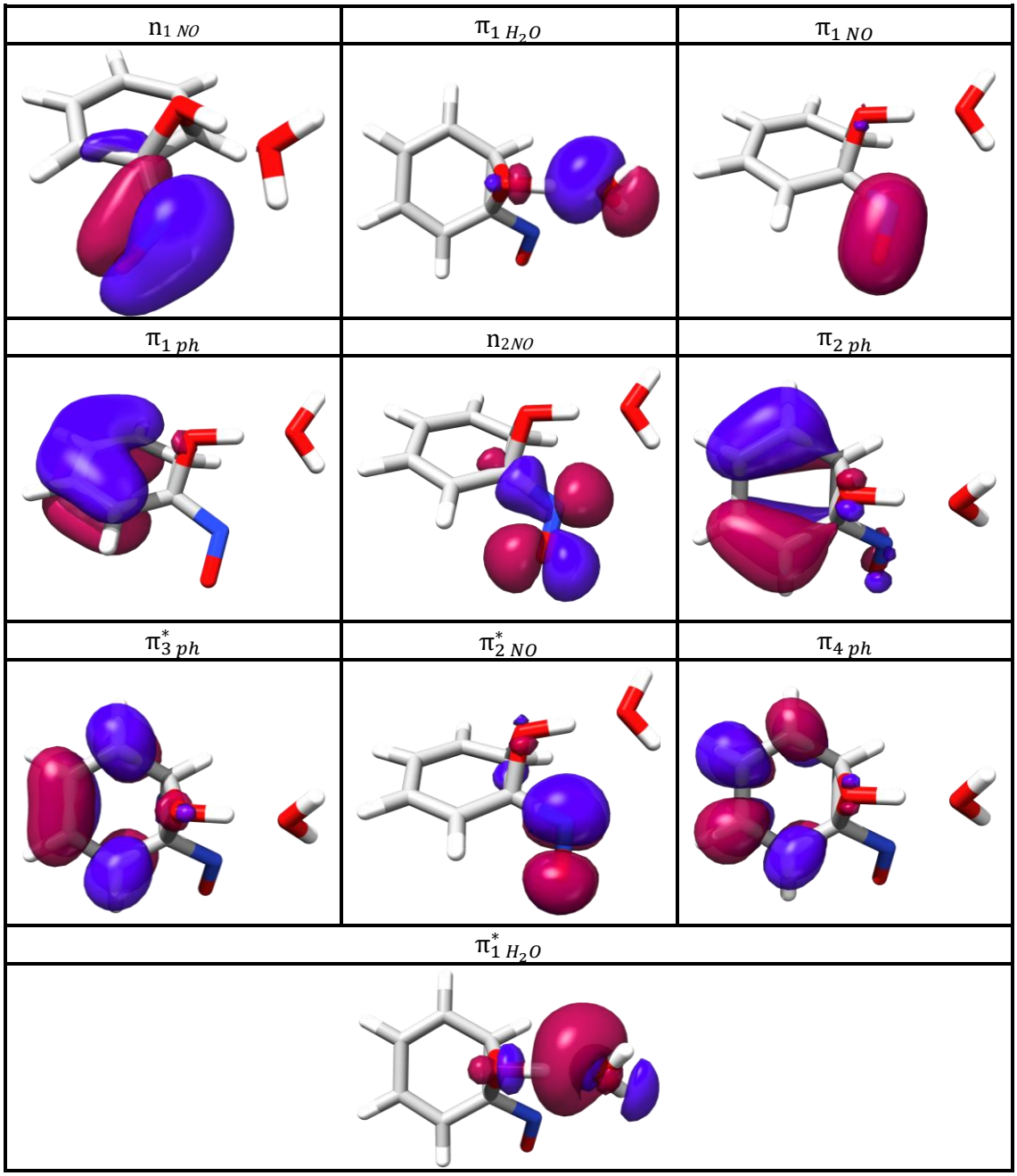

Figure S2: CAS(12,10) active space at the *[EPOH—H_2O]$^+_{min\text{-}xpt2(12,10)}$* optimized geometry.

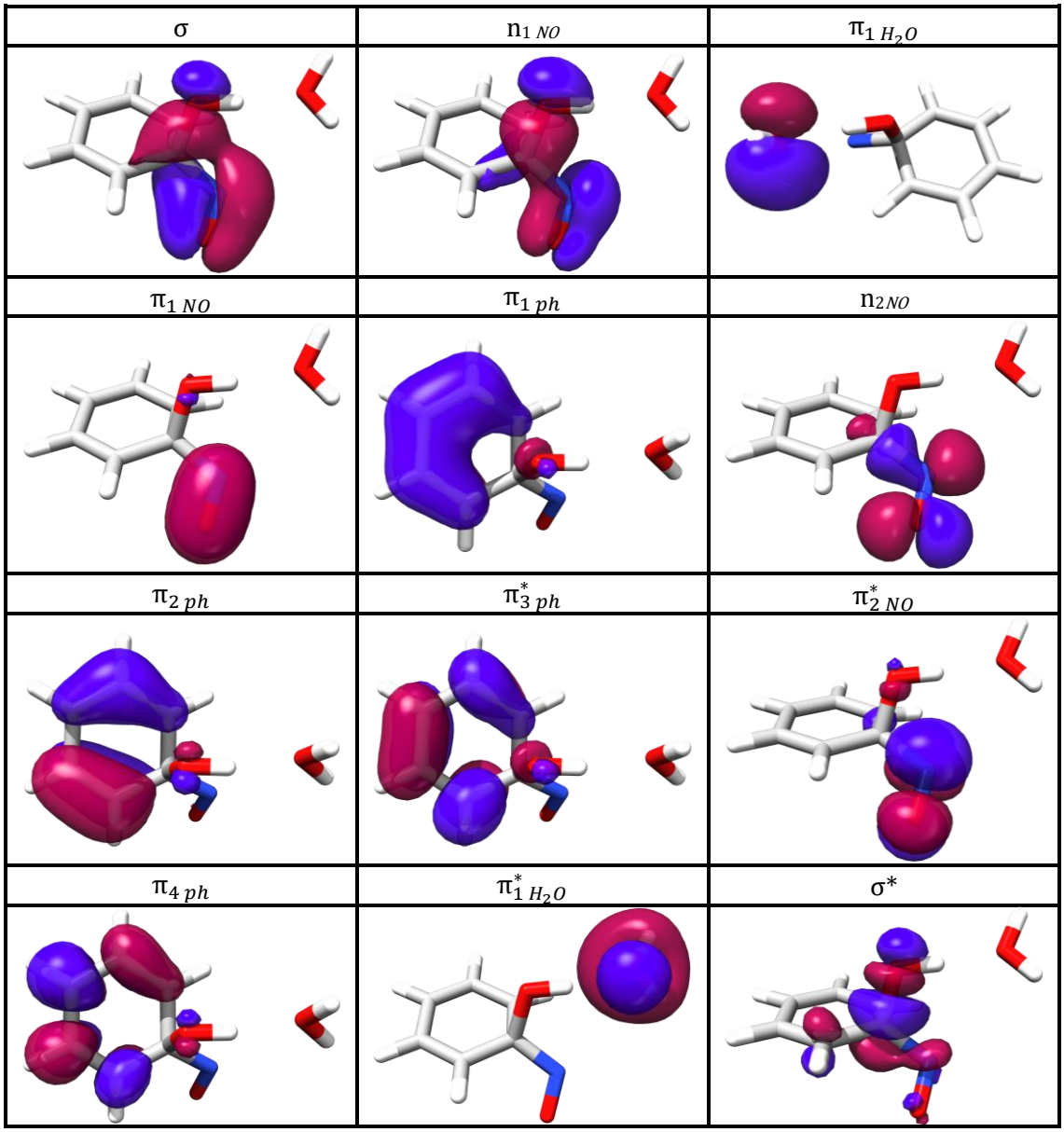

Figure S3: CAS(14,12)-R1 active space at the *[C_1OHNO—H_20]$^+_{TS\text{-}cas}$* optimized geometry.

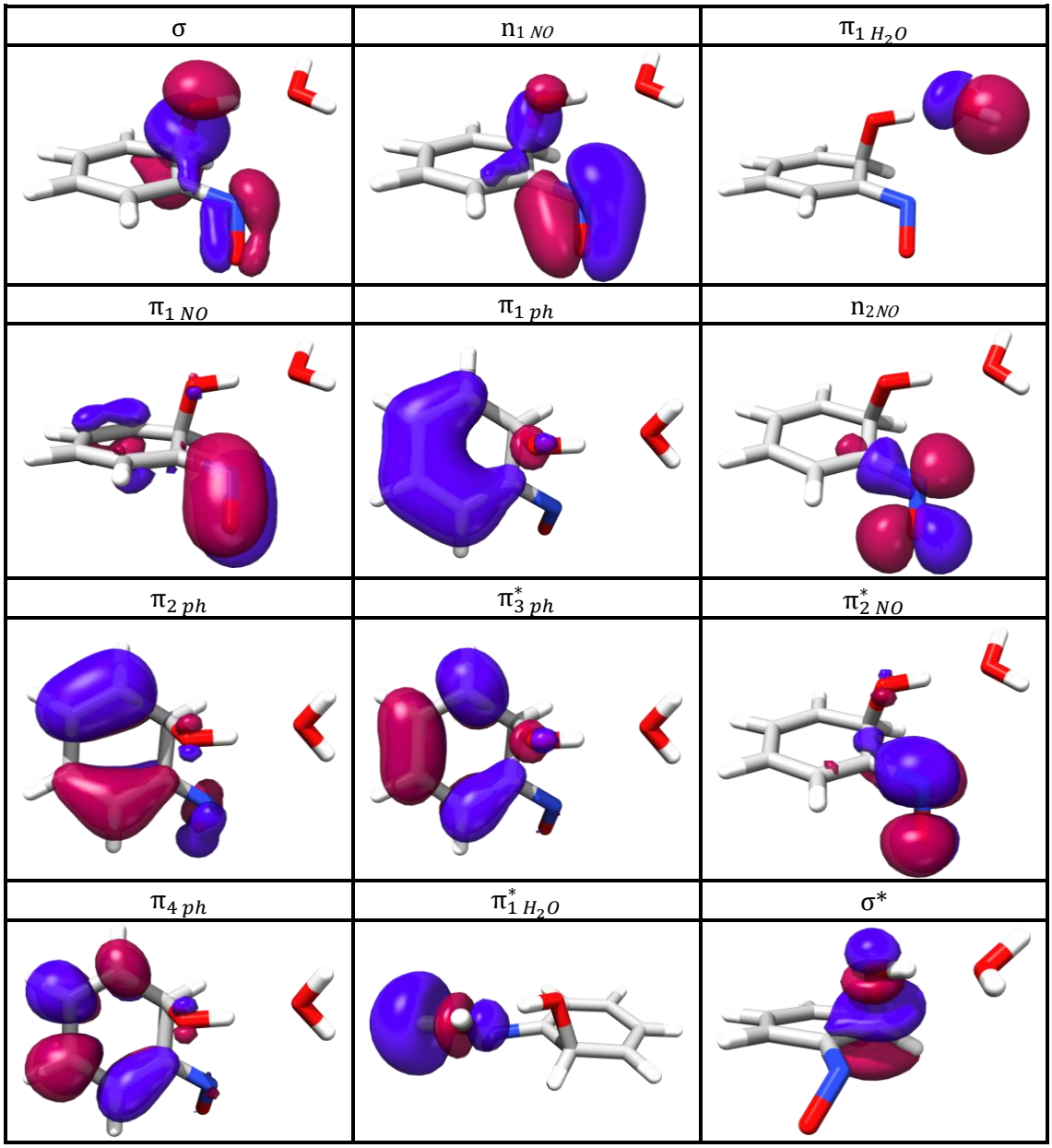

Figure S4. CAS(14,12)-R2 active space at the *[C_1NOC_2OH—H_20]$^+_{TS\text{-}cas}$* optimized geometry.

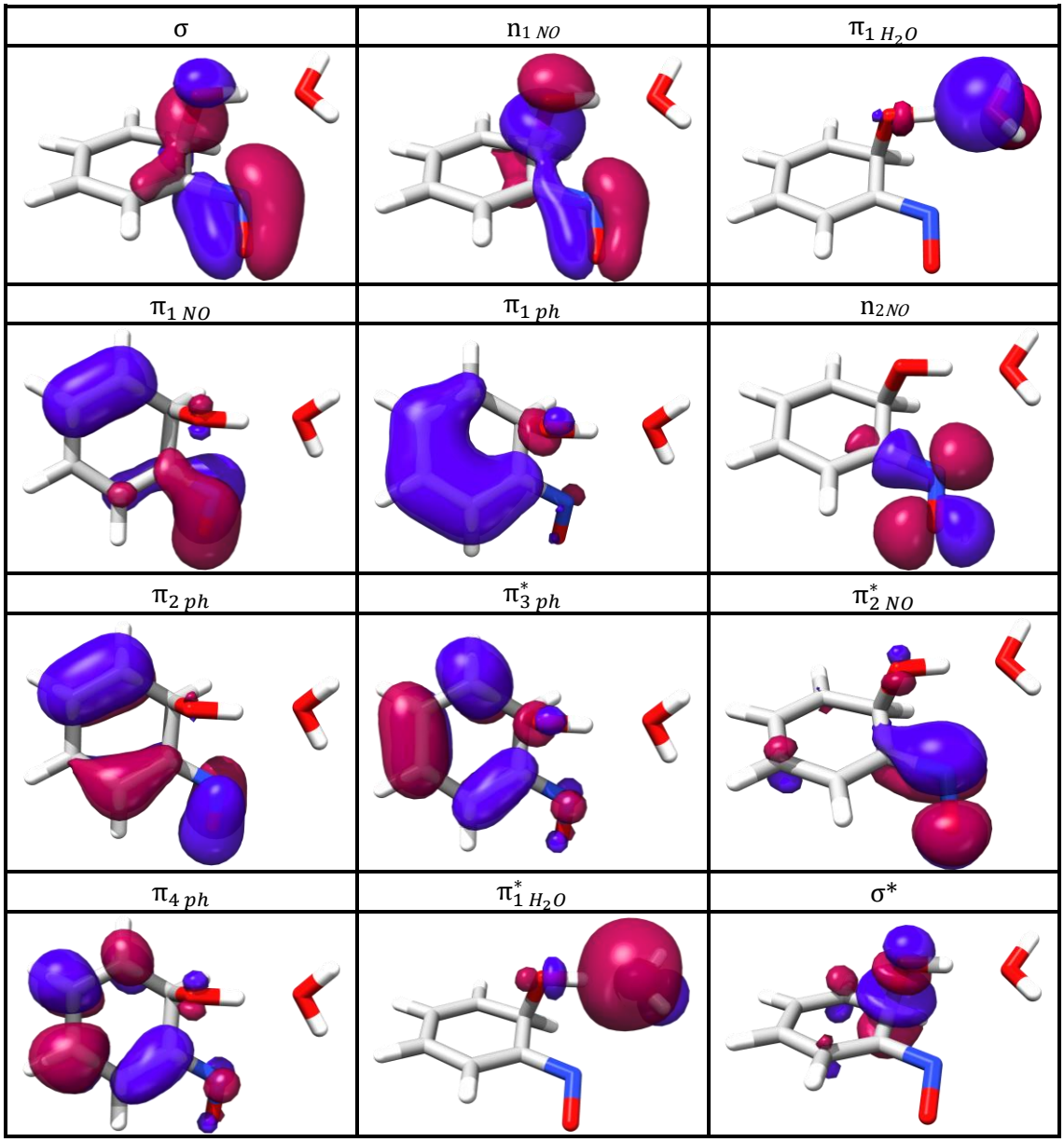

Figure S5. CAS(14,12)-R2 active space at the $[C_1NOC_2OH—H_20]^+_{TS\text{-}xpt2}$ optimized geometry.

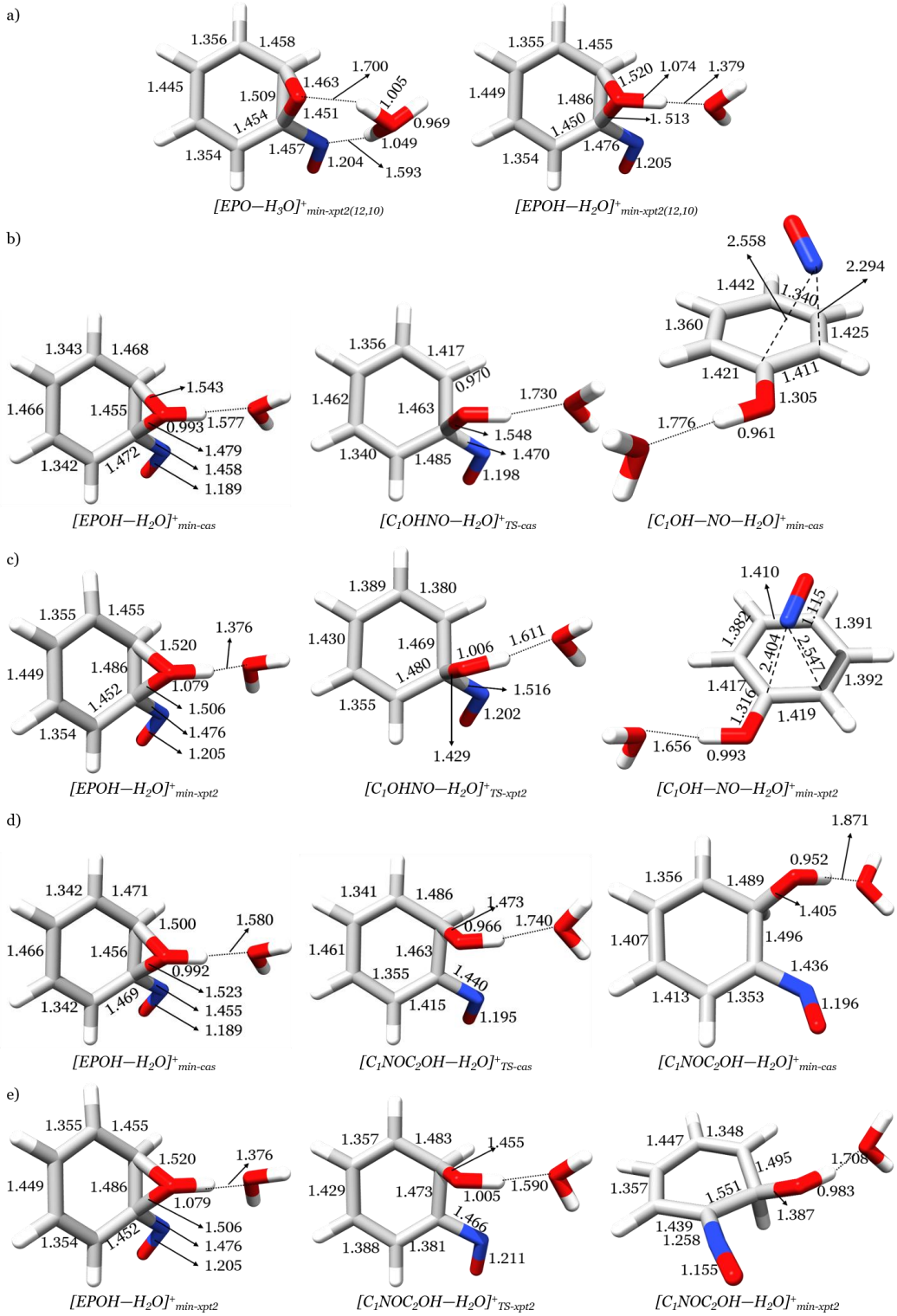

Figure S6. Optimized structures discussed in the main text: XMS-CASPT2(12,10) optimized geometries characterizing the epoxide protonation process (a); CASSCF(14,12) optimized geometries characterizing Reaction 1 (b); XMS-CASPT2(14,12) optimized geometries characterizing Reaction 1 (c); CASSCF(14,12) optimized geometries characterizing Reaction 2 (d); XMS-CASPT2(14,12) optimized geometries characterizing Reaction 2 (e). Bond lengths are reported in Å.

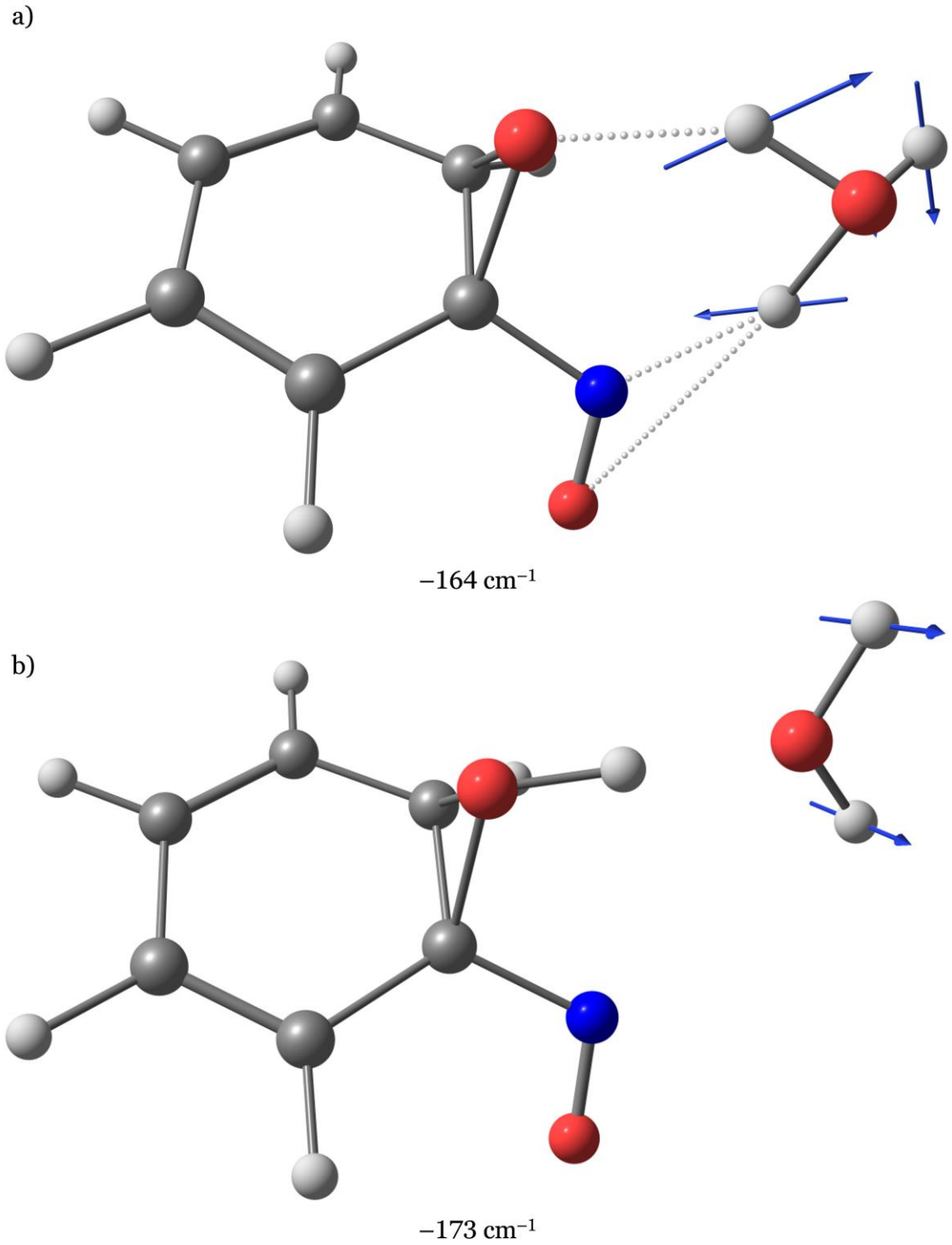

Figure S7. Vibrational modes associated to the imaginary frequency calculated for the *[EPO-H_3O]$^+_{min\text{-}xpt2(12,10)}$* (a) and *[EPOH-$H_2O$]$^+_{min\text{-}xpt2(12,10)}$* (b) optimized geometries.

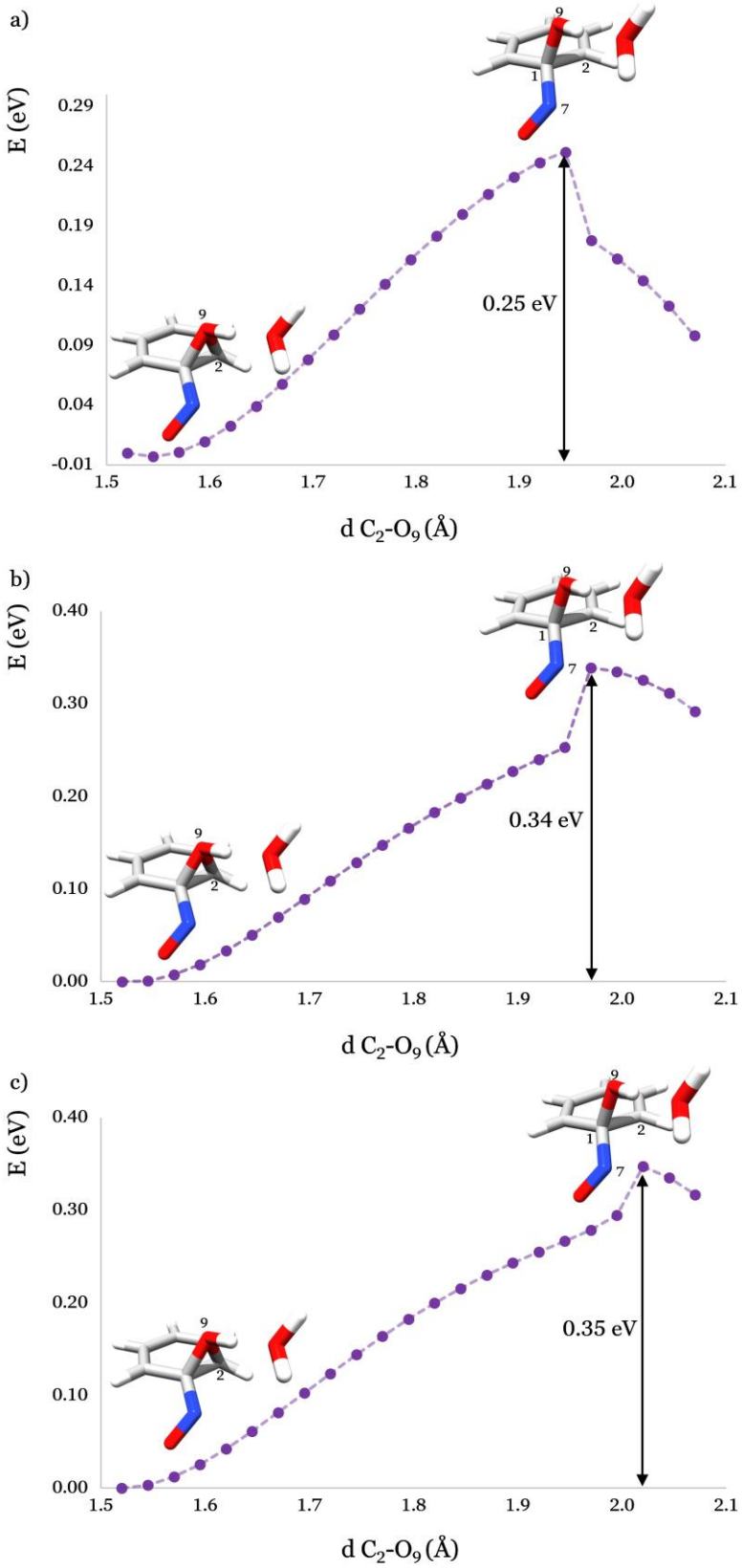

Figure S8. Relaxed scan from the *[EPOH—H_2O]$^+_{min\text{-}xpt2(12,10)}$* geometry along the C_2O_9 bond distance computed at the CASSCF(14,12) (a); XMS-CASPT2(14,12)//CASSCF(14,12) (b), and XMS-CASPT2(14,12) (c) levels.

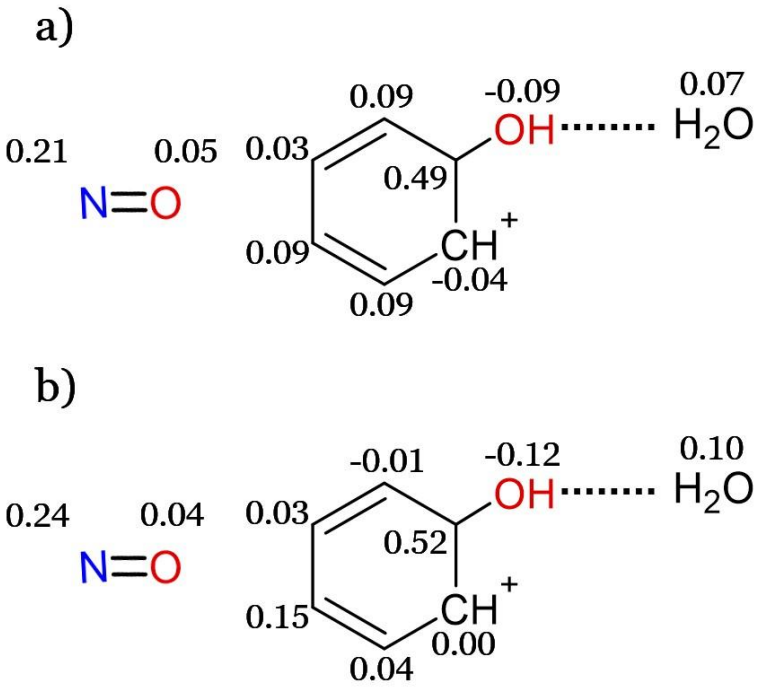

Figure S9. Mulliken charges calculated for the $[C_1OH—NO—H_20]^+_{min\text{-}cas}$ (a) and $[C_1OH—NO—H_20]^+_{min\text{-}xpt2}$ (b) structures.

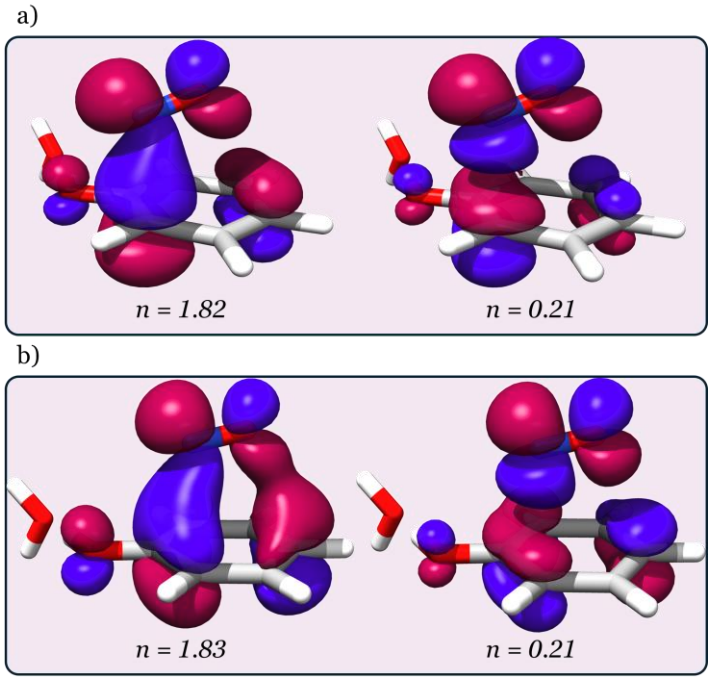

Figure S10. Key active orbitals describing the π–π interaction between the NO fragment and the phenyl ring obtained in the CASSCF(14,12) wave functions of the $[C_1OH—NO—H_20]^+_{min\text{-}cas}$ (a) and $[C_1OH—NO—H_20]^+_{min\text{-}xpt2}$ (b) structures. The natural occupation number of each orbital is also reported.

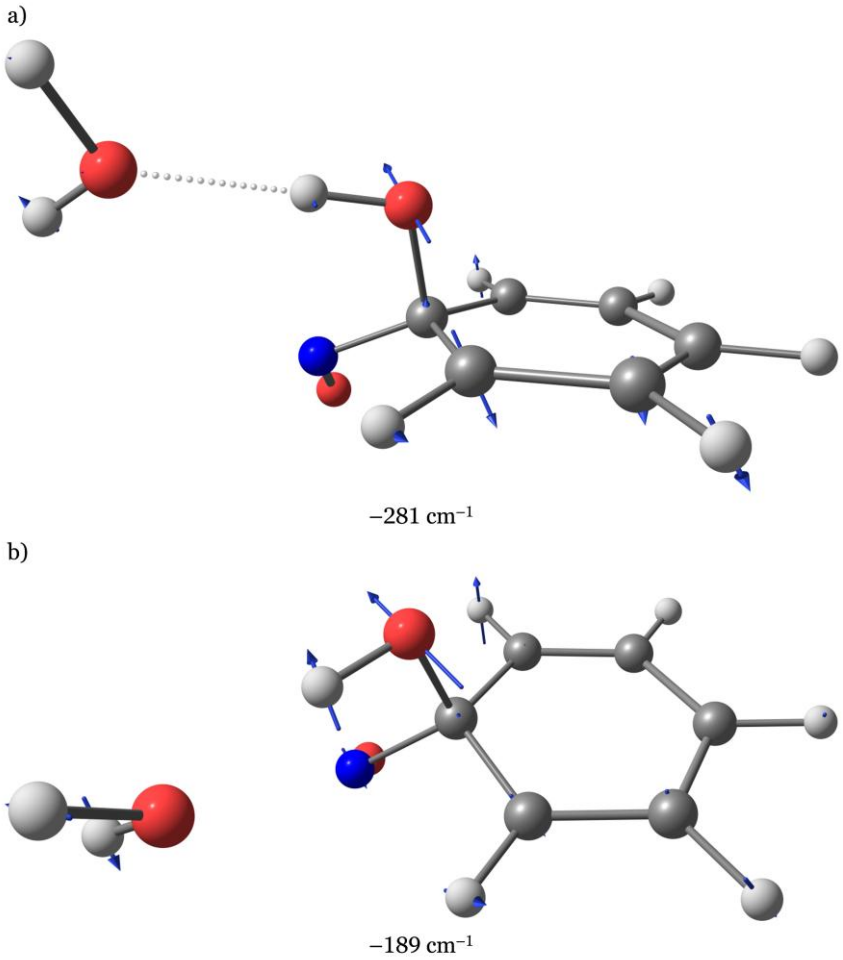

Figure S11. Vibrational modes associated to the imaginary frequency calculated for the $[C_1OHNO—H_20]^+_{TS\text{-}cas}$ (a) and $[C_1OHNO—H_20]^+_{TS\text{-}xpt2}$ (b) optimized geometries.

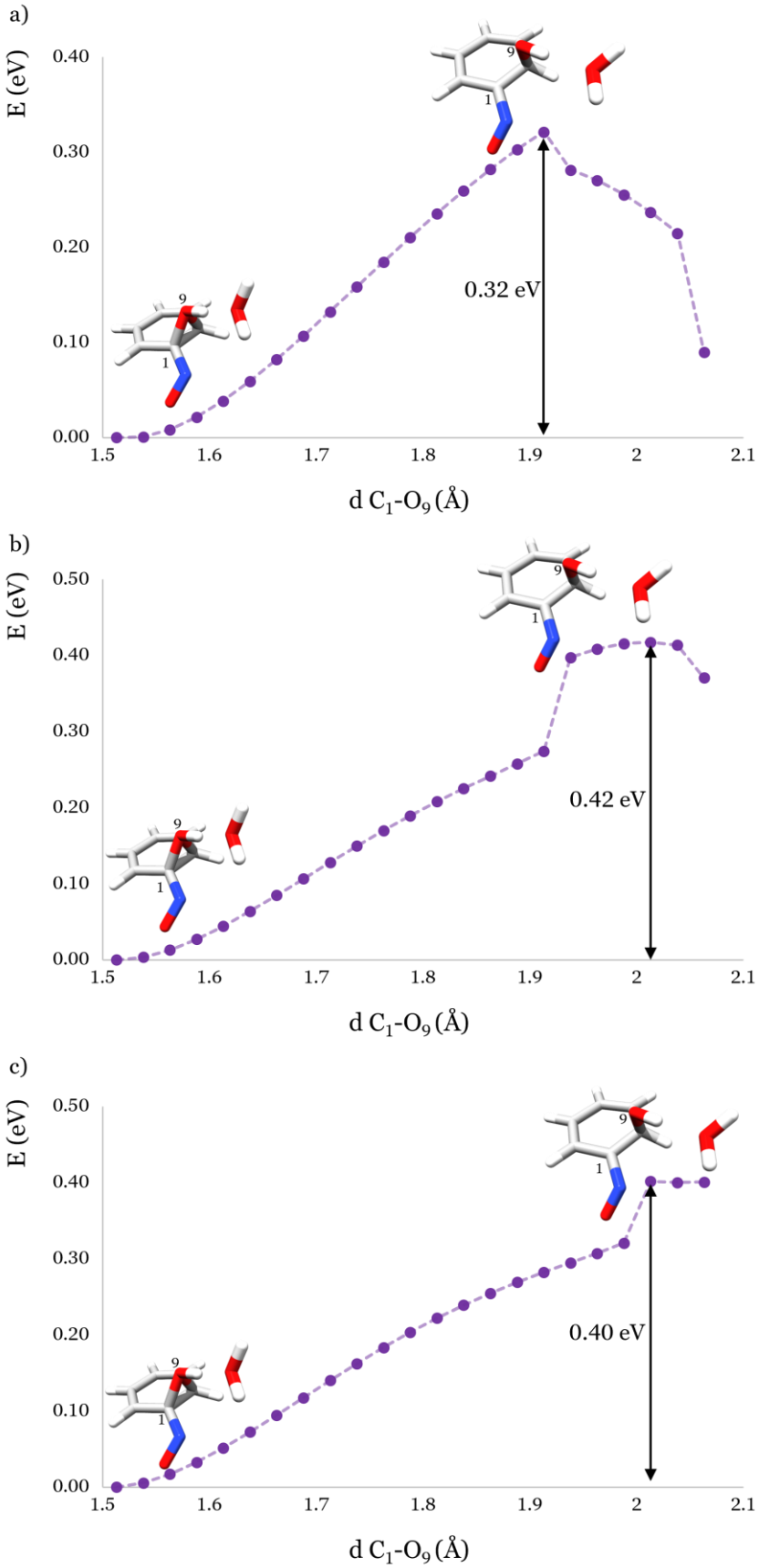

Figure S12. Relaxed scan from the *[EPOH—H_2O]$^+_{min\text{-}xpt2(12,10)}$* geometry along the C_1O_9 bond distance computed at the CASSCF(14,12) (a), XMS-CASPT2(14,12)//CASSCF(14,12) (b) and XMS-CASPT2(14,12) (c) levels.

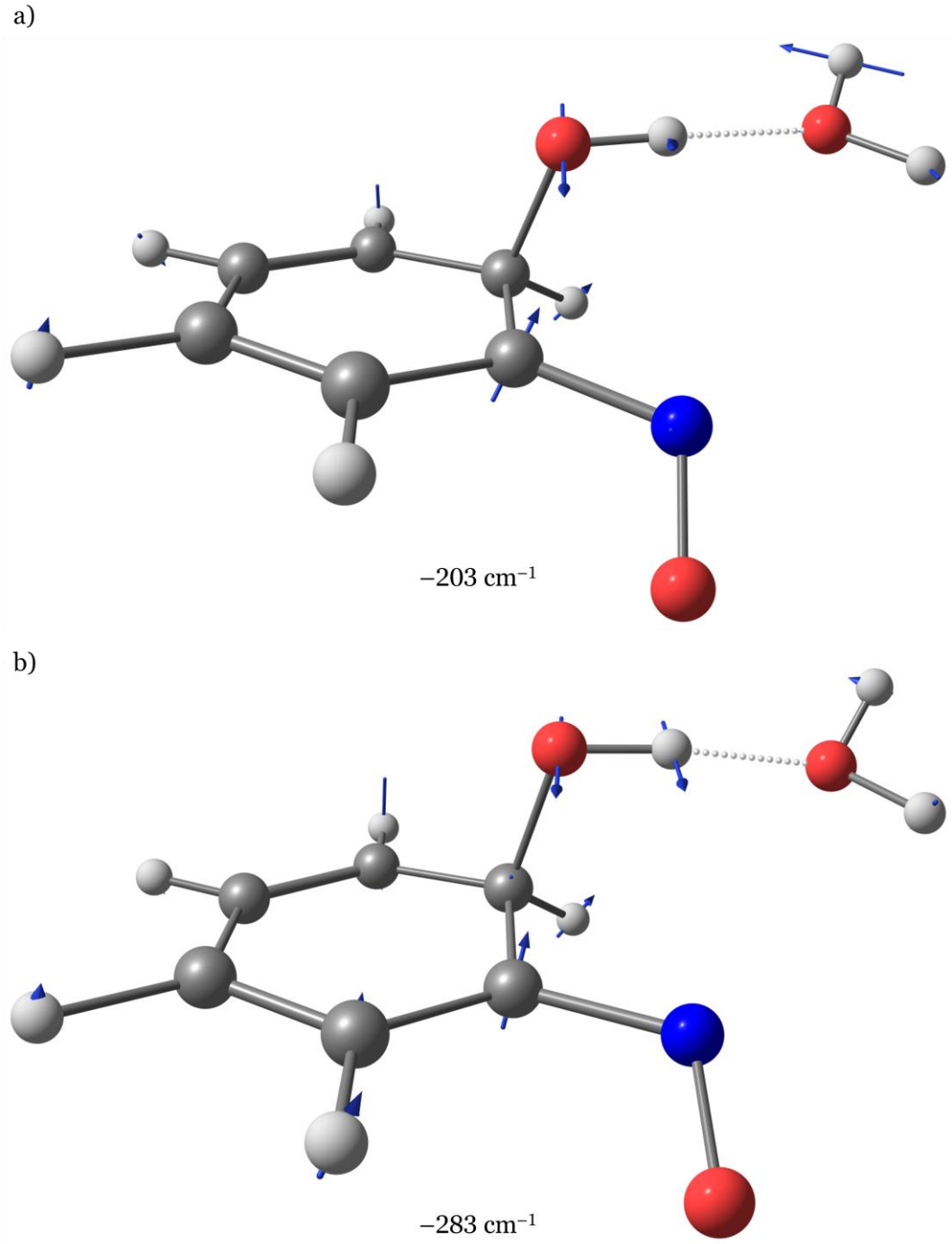

Figure S13. Vibrational modes associated to the imaginary frequency calculated for the $[C_1NOC_2OH—H_20]^+_{TS\text{-}cas}$ (a) and $[C_1NOC_2OH—H_20]^+_{TS\text{-}xpt2}$ (b) optimized geometries.

Table S1. CASSCF(14,12), XMS-CASPT2//CASSCF(14,12), and XMS-CASPT2(14,12) absolute energies (in a.u.) calculated for all the different critical points characterized on the S_0 potential energy surface. All energies are reported with respect to the S_0 energy of the $[EPOH—H_2O]^+_{min}$ geometry for each methodology.

Reaction	Structure[a]	E (eV)		
		CASSCF(14,12)	XMS-CASPT2// CASSCF(14,12)	XMS-CASPT2(14,12)
1	$[EPOH—H_2O]^+_{min}$	−511.1247395	−512.8682102	−512.8682092
	$[C_1OHNO—H_20]^+_{TS}$	−511.1170855	−512.8487545	−512.8554544
	$[C_1OH—NO—H_20]^+_{min}$	−511.2045358	−512.9464597	−512.9591092
2	$[EPOH—H_2O]^+_{min}$	−511.1311113	−512.8617291	−512.8676271
	$[C_1NOC_2OH—H_20]^+_{min}$	−511.120349	−512.8486239	−512.8521172
	$[C_1NOC_2OH—H_20]^+_{TS}$	−511.1424805	−512.8620363	−512.8750685

[a] The energy for the $[EPOH—H_2O]^+_{min}$ has two different values due to the distinct active space used for Reaction 1 and 2.

Table S2. Cartesian coordinates x, y, z (in Å) of the characterized critical-point geometries.

$[EPO—H_3O]^+$ XMS-CASPT2(12,10)

O	-0.044182067	3.138037491	0.502807288
C	-1.282098047	-1.243581881	-0.983472213
C	-0.644030937	0.055858892	-0.812137320
H	-0.679952018	0.775904025	-1.621287964
C	-0.927937177	-2.288619105	-0.195755894
C	0.193056032	-2.222074007	0.713426184
C	0.952846080	-1.107761132	0.833529840
C	0.515283171	0.100901930	0.153500032
N	1.461913006	1.181977183	-0.085371107
O	-0.766999030	0.683917143	0.502905186
O	2.620160293	0.867501961	-0.187181106
H	1.870121394	-1.080537079	1.401678347
H	0.477580880	-3.116399433	1.247190341
H	-1.434115325	-3.234818189	-0.313906886
H	-2.010063376	-1.350706936	-1.773089337
H	-0.700406836	2.380631386	0.575734793
H	0.762548120	2.600872311	0.102467237
H	-0.363725220	3.858896498	-0.061037950

$[EPOH—H_2O]^+$ XMS-CASPT2(12,10)

O	-0.276194021	3.164866233	0.312464020
C	-1.272026095	-1.162986085	-0.958005071
C	-0.461701032	0.040277003	-0.846238063

H	-0.453881031	0.776335055	-1.639671121
C	-1.009138072	-2.219926161	-0.151386011
C	0.124139008	-2.240565164	0.751086056
C	0.989211071	-1.202566088	0.840134062
C	0.694462048	0.001347000	0.086908007
N	1.718748125	1.028126073	-0.185508011
O	-0.560703042	0.737688056	0.500753038
O	2.836331205	0.578129044	-0.156016011
H	1.895864137	-1.235283091	1.423994101
H	0.311636022	-3.139139228	1.319644094
H	-1.618630118	-3.107899227	-0.226475014
H	-2.043309148	-1.194562087	-1.711366124
H	-0.423916031	1.795146133	0.376234028
H	0.520763040	3.550889256	-0.065756004
H	-0.971656071	3.830126280	0.329207025

[EPOH—H_2O]$^+$ CASSCF(14,12)

O	0.251382200	4.131935600	0.527850000
C	-0.628522100	-0.333107800	-0.603239200
C	0.244008100	0.844193300	-0.510533300
H	0.262164000	1.559182000	-1.308826200
C	-0.374091500	-1.399213200	0.172419600
C	0.767362500	-1.433492400	1.091877000
C	1.616549800	-0.401880700	1.211700800
C	1.365018100	0.811910400	0.417035300
N	2.435004900	1.763188500	0.143584500
O	0.177336600	1.584628000	0.841627600
O	3.506015700	1.248592300	0.092272700
H	2.475545200	-0.423210300	1.848763600
H	0.929394800	-2.324297900	1.664249200
H	-0.997362300	-2.267951900	0.108359100
H	-1.432658900	-0.311420000	-1.308822900
H	0.255772800	2.567458000	0.722920100
H	1.022928500	4.645968900	0.348386000
H	-0.443128400	4.721316200	0.776685800

[C_1OHNO—H_2O]$^+{}_{TS}$ CASSCF(14,12)

O	0.291726927	4.241928668	0.444252329
C	-0.614541583	-0.375985756	-0.651450629
C	0.234702539	0.754305750	-0.561909896
H	0.136771743	1.587920356	-1.230144123
C	-0.325161833	-1.455970217	0.115221318
C	0.795322184	-1.475525598	1.053896211
C	1.576209378	-0.399991450	1.222840631
C	1.270556798	0.841891231	0.467368722
N	2.381918606	1.733724194	0.106910771
O	0.215910731	1.630069138	1.093505101
O	3.441799364	1.195220231	0.112293444
H	2.406998803	-0.391533125	1.896779050
H	0.980352756	-2.377108526	1.600758570
H	-0.932331073	-2.335853104	0.033681895

H	-1.436288870	-0.361484741	-1.336319004
H	0.328908741	2.574501781	0.904435079
H	1.068845472	4.749922411	0.273660745
H	-0.388979861	4.847768867	0.690530230

$[C_1OH—NO—H_2O]^+_{min}$ CASSCF(14,12)

O	0.046075560	4.429310620	0.402333260
C	-0.344197930	-0.225717790	-0.785088320
C	-0.060930370	0.989465850	-0.243566920
H	-0.407987130	1.902026270	-0.683854900
C	0.090579370	-1.454305490	-0.167388300
C	0.813686210	-1.419532880	0.960033220
C	1.214873040	-0.162839880	1.497802120
C	0.720564270	1.037002700	0.942587670
N	3.010391200	0.239500600	0.128148990
O	1.046997800	2.150682820	1.540147950
O	2.940559250	-0.331055180	-0.821918760
H	1.761612010	-0.097182850	2.416547020
H	1.135757000	-2.317317950	1.447448360
H	-0.195884360	-2.385681010	-0.612052390
H	-0.926563670	-0.279116180	-1.683414220
H	0.698993760	2.941188600	1.118959880
H	0.585095270	5.092668070	0.001750870
H	-0.696901300	4.874702690	0.777834480

$[EPOH—H_2O]^+$ XMS-CASPT2(14,12)

O	0.27345782	3.98627192	0.40172849
C	-0.63126683	-0.32721533	-0.61451496
C	0.18079194	0.87545354	-0.50476115
H	0.18936664	1.61019572	-1.29909221
C	-0.37369108	-1.38082356	0.19773825
C	0.75534998	-1.39853775	1.10551904
C	1.62020969	-0.36079129	1.19503577
C	1.32975231	0.84293623	0.43766871
N	2.36164154	1.86367434	0.17189471
O	0.07979946	1.58079732	0.83808517
O	3.47436766	1.40089180	0.17452294
H	2.52448891	-0.39324117	1.78264501
H	0.94044812	-2.29552341	1.67737591
H	-0.98396881	-2.26831341	0.12371431
H	-1.39761695	-0.36088400	-1.37272291
H	0.20481928	2.64133057	0.68487823
H	1.16676385	4.35024744	0.36252985
H	-0.28198880	4.61733565	0.87406585

$[C_1OHNO—H_2O]^+_{TS}$ XMS-CASPT2(14,12)

O	0.26420587	4.02447053	0.21472242
C	-0.60281117	-0.27546917	-0.64508107
C	0.18222140	0.84585379	-0.47186386
H	0.01221744	1.76702839	-1.01608524
C	-0.28295319	-1.42403753	0.06786274

C	0.79597863	-1.48378971	1.00416520
C	1.54761248	-0.38303584	1.24723082
C	1.21996013	0.88913076	0.56662801
N	2.39769744	1.76146933	0.17769406
O	0.33373258	1.67880240	1.36215930
O	3.44698614	1.17619259	0.18891091
H	2.38670090	-0.39709205	1.92724066
H	1.00314194	-2.41727652	1.50412230
H	-0.87593974	-2.31529729	-0.09168245
H	-1.43562366	-0.26432100	-1.33139637
H	0.31872410	2.61293226	0.99023818
H	1.10492788	4.48465650	0.11238873
H	-0.38405446	4.70358718	0.42905669

$[C_1OH—NO—H_2O]^+_{min}$ XMS-CASPT2(14,12)

O	0.07235062	4.27768631	0.35296055
C	-0.24226655	-0.21339144	-0.79591495
C	0.04031705	1.01207418	-0.22306525
H	-0.26437864	1.93844563	-0.69133243
C	0.17205571	-1.41177007	-0.18026671
C	0.81837505	-1.38077917	1.05142555
C	1.13368390	-0.15721813	1.63491831
C	0.74241994	1.05362378	1.00712433
N	2.67280848	0.46211991	-0.29825494
O	1.05947209	2.17294775	1.62162926
O	2.62220131	-0.44497625	-0.94523100
H	1.65898547	-0.09343638	2.57941046
H	1.11060817	-2.29838634	1.54177259
H	-0.05298928	-2.35956269	-0.65046494
H	-0.77295924	-0.25149263	-1.73664374
H	0.70756635	2.97257280	1.14946636
H	0.65218378	4.99737291	0.07985368
H	-0.69771423	4.70796884	0.73892287

$[EPOH—H_2O]^+$ CASSCF(14,12)

O	0.244821800	4.132232900	0.497379800
C	-0.634873200	-0.338342300	-0.596821800
C	0.231563700	0.847278300	-0.502796300
H	0.248539200	1.546574400	-1.315431600
C	-0.370960300	-1.403993700	0.175766600
C	0.770303100	-1.431951300	1.095804500
C	1.622766900	-0.401307300	1.203554100
C	1.373114900	0.802925900	0.399436200
N	2.425565400	1.768576800	0.122488400
O	0.128655100	1.584111500	0.799952800
O	3.510369600	1.281366200	0.129221800
H	2.480287800	-0.417692900	1.842601500
H	0.930187500	-2.317505500	1.676816100
H	-0.988072500	-2.277046500	0.110128400
H	-1.437634900	-0.321733500	-1.304096200
H	0.237987600	2.565996800	0.705199400

H	1.056403500	4.627153300	0.360906700
H	-0.396299900	4.737162700	0.836200500

[$C_1NOC_2OH—H_2O$]+$_{TS}$ CASSCF(14,12)

O	0.183903373	4.252562881	0.312120780
C	-0.629182927	-0.261472214	-0.501699257
C	0.264510781	0.910288246	-0.312834892
H	0.333033444	1.580403614	-1.151538198
C	-0.368440079	-1.405617000	0.146471402
C	0.800520246	-1.525416140	1.014759221
C	1.705674673	-0.528213520	1.166331910
C	1.508873396	0.652968741	0.412360880
N	2.506551174	1.689498213	0.345084872
O	-0.008093580	1.633165973	0.940721608
O	3.577631106	1.238632816	0.066061976
H	2.564055230	-0.613406598	1.799530968
H	0.946488866	-2.446320591	1.544255395
H	-1.004299575	-2.259695133	0.035981227
H	-1.473138662	-0.151719329	-1.151051912
H	0.098097907	2.581218941	0.788203212
H	0.972712443	4.787878753	0.425428844
H	-0.546171746	4.849049123	0.356123416

[$C_1NOC_2OH—H_2O$]+$_{min}$ CASSCF(14,12)

O	0.170258700	4.286121500	-0.400258000
C	-0.792784700	-0.092188800	0.421613200
C	0.207232000	1.007691600	0.338962600
H	0.151230000	1.361245100	-0.697106300
C	-0.437727300	-1.400723300	0.415628400
C	0.928979300	-1.731234300	0.452948200
C	1.963409000	-0.769401200	0.488004400
C	1.618285300	0.538591200	0.499512400
N	2.598955000	1.587514400	0.489576200
O	-0.118678200	2.032152300	1.243794000
O	3.474083900	1.431828200	1.290380600
H	2.985633500	-1.083612000	0.542032600
H	1.203555200	-2.770260200	0.483871500
H	-1.168018600	-2.183360300	0.431396200
H	-1.822040700	0.206260900	0.459129000
H	-0.031752600	2.877465800	0.814329000
H	1.003647400	4.755157600	-0.484517400
H	-0.501542100	4.930557200	-0.552985500

[$EPOH—H_2O$]$^+$ XMS-CASPT2(14,12)

O	0.271603980	3.982958460	0.388919610
C	-0.633231700	-0.323120080	-0.608814730
C	0.176237650	0.880860240	-0.494829380
H	0.183549260	1.617350540	-1.288091940
C	-0.372323520	-1.380208400	0.197521400
C	0.758946430	-1.400449620	1.102601510
C	1.623335660	-0.362707800	1.194079330

C	1.331026240	0.843042040	0.439983050
N	2.361173560	1.863649570	0.177386680
O	0.081917440	1.579385460	0.848563650
O	3.474131740	1.399226140	0.175733190
H	2.528957250	-0.396279680	1.779387200
H	0.945525190	-2.298814460	1.671768710
H	-0.980727780	-2.268714530	0.120401310
H	-1.402410720	-0.353669500	-1.364312160
H	0.197865400	2.638123840	0.689493170
H	1.168111510	4.338177110	0.356627430
H	-0.280962250	4.624995010	0.849893310

[$C_1NOC_2OH—H_2O$]+$_{TS}$ XMS-CASPT2(14,12)

O	0.304562925	4.109850526	0.208864505
C	-0.673167291	-0.271799571	-0.461216490
C	0.183221438	0.927186259	-0.290300390
H	0.230905178	1.564908578	-1.170365355
C	-0.351179170	-1.435093332	0.158669084
C	0.836745569	-1.530137266	0.946967935
C	1.738390096	-0.484032299	1.081605705
C	1.464522906	0.681818576	0.393576331
N	2.365780432	1.837461845	0.412959101
O	-0.216663384	1.670183553	0.894662293
O	3.524105268	1.491581307	0.485480185
H	2.627282039	-0.565289402	1.689660560
H	1.043044965	-2.460553301	1.460171389
H	-0.982419470	-2.304772575	0.062556689
H	-1.554094053	-0.185813536	-1.080068602
H	0.016219182	2.632925721	0.721857245
H	1.184189721	4.468051677	0.365661917
H	-0.308720178	4.837328717	0.355569706

[$C_1NOC_2OH—H_2O$]+$_{min}$ XMS-CASPT2(14,12)

O	-0.717119900	3.980981100	-0.187991600
C	-0.424907300	0.593207200	0.350795400
C	0.943242300	1.110636600	0.040135200
H	1.087342700	1.064643600	-1.052181200
C	-0.662575800	-0.719520900	0.545013100
C	0.420030500	-1.677477600	0.605184600
C	1.724370500	-1.305880400	0.655677600
C	1.999898600	0.103224700	0.563902000
N	3.098077300	0.647473900	0.846577600
O	1.278206700	2.351146500	0.562662300
O	4.071151800	1.239214900	1.038958100
H	2.535146200	-2.003898800	0.794870100
H	0.188206900	-2.730731700	0.684494200
H	-1.671036400	-1.075483900	0.689248100
H	-1.215099300	1.331308300	0.328174800
H	0.615609900	3.016748900	0.271802800
H	-0.723479800	4.516835600	-0.987733100
H	-1.114339400	4.541376300	0.486721400