Supporting Information for

Quantum Mechanics/Molecular Mechanics Study of Oxygen Binding in Hemocyanin

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Contents

Section 1: System setup by using CHARMM (ver. c29b2)

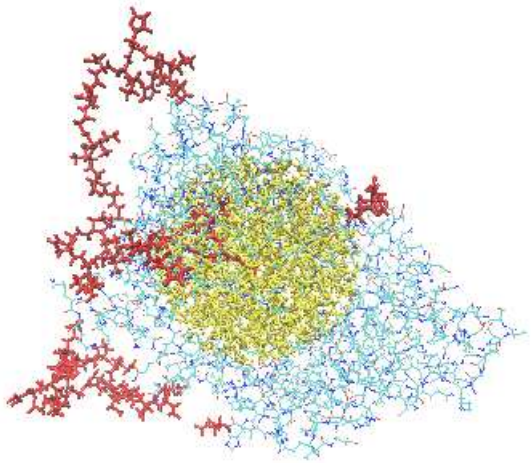

Figure S1. QM/MM model used in this study (bulk water molecules are not visualized). The added residues are shown in red, and the atoms within 20 Å from the Cu_2O_2 core are shown in yellow.

CHARMM parameters

For oxyHc, the atomic charges on the Cu_2O_2 core were evaluated at the UBH&HLYP/TZVP level by the CHELPG approach. CHARMM22 atomic charges were placed at the positions of the ligating histidine residues.

```
RESI CUO                2.00
GROUP
ATOM CU1    CU          1.565
ATOM CU2    CU          1.629
ATOM O1     O          -0.539
ATOM O2     O          -0.655
BOND CU1 O1    CU1 O2    CU2 O1    CU2 O2
ANGLE CU1 O1 O2     CU1 O2 O1     O1 CU1 O2
ANGLE CU2 O1 O2     CU2 O2 O1     O1 CU2 O2
ANGLE CU1 O1 CU2    CU1 O2 CU2
DIHE CU1 O1 O2 CU2    CU1 O2 O1 CU2
```

Protonation states of titratable residues

The following Glu and Asp amino residues were protonated:

Glu: 113, 214, 309, 528

Asp: 117

The six metal-ligating histidines (173, 177, 204, 324, 328, 364) were protonated at Nδ. The protonation states of the remaining histidines were as follows:

HSD (proton at Nδ): 30, 53, 99, 221, 239, 242, 342, 372, 383, 407, 438, 529, 605

HSE (proton at Nε): 28, 50, 172, 292, 299, 317, 335, 419, 435, 503, 513, 555

HSP (protons at both Nδ and Nε): 3, 11, 59, 133, 175, 281, 399, 456, 494, 522, 541, 588, 608, 627

System solvation

The model system was solvated in a TIP3P water ball with 45 Å radius centered at the center of oxyHc. All water molecules that overlap (within 2.8 Å of any heavy atom of the protein) were deleted. The added water molecules were optimized (500 steps with steepest descent (SD) and then 1000 step with the adopted basis Newton-Raphson (ABNR) method) and then equilibrated for 50 ps using Langevin dynamics with a stochastic boundary potential. This procedure was repeated five times.

System neutralization

After system solvation, the total charge of the initially built system was –7e. To neutralize this charge, 29 solvent water molecules that were at least 5.5 Å away from any protein atoms were replaced by 18 Na^+ and 11 Cl^- ions.

System heating and equilibration

The system was heated and equilibrated as follows: a) energy minimization for 3600 steps using the ABNR method; b) molecular dynamics (MD) for 15 ps with heating from 100 K to 300 K; c) 500 ps MD equilibration at 300 K.

Active residues during geometry optimization

The active region for oxyHc contained 990 atoms, including 12 crystal water (CW) molecules and one solvent water (SW) molecule. It comprised the following residues:

CYS48, PHE49, PHE91, ILE169, ASN170, HSE172, HSD173, TRP174, HSP175, TRP176, HSD177, LEU178, TYR180, PRO181, SER182, LEU199, PHE200, TYR201, TYR202, MET203, HSD204, GLN205, MET207, CYS208, VAL308, GLU309, SER310, LEU323, HSD324, ASN325,

TRP326, GLY327, HSD328, VAL329, MET331, VAL347, MET348, SER349, ASP350, THR351, SER352, THR353, SER354, LEU355, ASP357, ILE359, PHE360, TYR361, ASN362, TRP363, HSD364, CUO629, PHE366, ASP368, PHE371, TRP538, CW634, CW636, CW638, CW641, CW660, CW682, CW755, CW780, CW786, CW809, CW876, CW921, SW9112

The active region for deoxyHc contained 988 atoms, including 12 crystal water (CW) molecules and one solvent water (SW) molecule. It comprised the following residues:

CYS48, PHE49, PHE91, ILE169, ASN170, HSE172, HSD173, TRP174, HSP175, TRP176, HSD177, LEU178, TYR180, PRO181, SER182, LEU199, PHE200, TYR201, TYR202, MET203, HSD204, GLN205, MET207, CYS208, VAL308, GLU309, SER310, LEU323, HSD324, ASN325, TRP326, GLY327, HSD328, VAL329, MET331, VAL347, MET348, SER349, ASP350, THR351, SER352, THR353, SER354, LEU355, ASP357, ILE359, PHE360, TYR361, ASN362, TRP363, HSD364, CUI629, CUI630, PHE366, ASP368, PHE371, TRP538, CW634, CW636, CW638, CW641, CW660, CW682, CW755, CW780, CW786, CW809, CW876, CW921, SW9112

Section 2: Comparison between Gaussian09 and TURBOMOLE results

The geometry of oxyHc was optimized at the QM(BH&HLYP/TZVP)/MM level using the QM programs Gaussian 09 and TURBOMOLE for the DFT calculations. The results listed below were taken directly from the ChemShell output file.

Gaussian09

Contribution to energy from	Gaussian:	-4788.137878 (a.u.)
Contribution to energy from	dl_poly:	-210.907170 (a.u.)
Contribution to energy from additional MM energy terms:		0.000000 (a.u.)

QM/MM Energy: -4999.045047 (a.u.)

$<S^2> = 0.9803$

TURBOMOLE 6.3

Contribution to energy from	Turbomole:	-4788.138240 (a.u.)
Contribution to energy from	dl_poly:	-210.906849 (a.u.)
Contribution to energy from additional MM energy terms:		0.000000 (a.u.)

QM/MM Energy: -4999.045089 (a.u.)

$<S^2> = 0.9806$

After QM(BH&HLYP/TZVP)/MM geometry optimization with the QM codes Gaussian09 and TURBOMOLE, the root-mean-square deviation between the resulting Cartesian coordinates was 0.013 Å for the QM region and 0.003 Å for the complete active QM/MM region. The coord file (in Bohr) of the QM region after the optimization with TURBOMOLE is as follows:

```
$coord
-1.1837567287 -7.8116862507 -6.1431121460 N
-0.4343240936 -8.0579747184 -7.8877362147 H
-0.3353101349 -6.1759532164 -4.3369331128 C
-3.6194491945 -8.3376864021 -2.8790572218 N
-1.8716573441 -6.5080906133 -2.3210766704 C
-1.8522998576 -5.5729711316 -0.5305569048 H
-3.1503104035 -9.0682730213 -5.2042012242 C
-4.1608758751 -10.4786187999 -6.2394971701 H
-2.6876901013 -14.5316530234 4.7603297641 N
-2.8054191548 -15.9753216592 6.0313581745 H
-0.5355732720 -13.3210462220 3.9885043321 C
-3.8874061643 -11.6819479898 2.0625612997 N
-1.3103322820 -11.5451970126 2.3175283276 C
-0.2129427179 -10.2147316836 1.2695192699 H
-4.6429642083 -13.5172376150 3.5501697201 C
-6.5366759189 -14.2032229091 3.7481621067 H
-11.0349698275 -5.6330185301 4.0445549094 N
-11.7161458000 -5.0825351870 5.7530024825 H
-12.0800489297 -5.0263039283 1.7625344685 C
-8.7748392526 -7.5824308160 1.2001248646 N
-10.6536649207 -6.2429069497 0.0153424159 C
-10.8435745758 -6.2295529620 -1.9961726587 H
-9.0729209270 -7.1635091820 3.6195580062 C
-7.9163942455 -7.9145765613 5.0993418638 H
-14.3856120775 -17.9582451268 2.5846941119 N
-13.9359849118 -19.5553573713 3.5505950279 H
-16.7311177652 -17.1156844915 1.8727409160 C
-13.7545270613 -14.9396791599 -0.1110148704 N
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-16.3073747904 -15.2372196022 0.1895219104 C
-17.6272569298 -14.0986653304 -0.8290717947 H
-12.6650630401 -16.6124589709 1.3487119321 C
-10.6759508781 -16.8899541170 1.5700682566 H
-9.6115655295 -18.6798292703 -8.3909267130 N
-8.3286949168 -19.3871507712 -9.6273984962 H
-11.5366289278 -20.0353568957 -7.3262954215 C
-11.3969776864 -16.1906702994 -5.6389429429 N
-12.6396740571 -18.4623334608 -5.6378929532 C
-14.2178689750 -18.8084767346 -4.4261469390 H
-9.5788951914 -16.4064377112 -7.2955806259 C
-8.1913955770 -14.9933893536 -7.6965927967 H
-16.0085658812 -9.2531943746 -7.7141115955 N
-16.4280337001 -8.7807196295 -9.5226820646 H
-16.8059551516 -7.9454967818 -5.6444657790 C
-14.2795176826 -11.0705535870 -4.4909350482 N
-15.7298138361 -9.0982151374 -3.6375313371 C
-15.8778399581 -8.6501214007 -1.6735869633 H
-14.4893786465 -11.0963958867 -6.9545111930 C
-13.5513985604 -12.3805244445 -8.1975166533 H
-11.6561181520 -13.1201114259 -2.6907810560 Cu
-6.1571579192 -10.2521748580 -0.7035804847 Cu
-8.3461574683 -13.2822892218 -1.1470206058 O
-8.3008666685 -11.6201336051 -3.3737804810 O
1.2829472658 -4.9375298578 -4.6372918676 h
1.3315962722 -13.8936973546 4.6430372839 h
-13.6205948522 -3.6728418454 1.5688247321 h
-18.4640737843 -18.0147807833 2.5293641759 h
-11.7916382230 -22.0326028780 -7.7606265821 h
-18.0738027706 -6.3305945906 -5.8097477796 h
$end

Section 3: Cartesian coordinates of the QM region (in Å) optimized by BLYP

deoxyHc

N	-0.532086	-4.168481	-3.336490
H	-0.115743	-4.358653	-4.260588
C	-0.105141	-3.202148	-2.445331
N	-1.939405	-4.237449	-1.619342
C	-0.984894	-3.247891	-1.390109
H	-1.004208	-2.644199	-0.492140
C	-1.638774	-4.767879	-2.812600
H	-2.164579	-5.558641	-3.329710
N	-1.421354	-7.747232	2.531626
H	-1.489826	-8.509195	3.232260
C	-0.256882	-7.133268	2.091512
N	-2.053309	-6.212107	1.059305
C	-0.664839	-6.180304	1.183163
H	-0.068984	-5.481495	0.611772
C	-2.475621	-7.173388	1.891065
H	-3.497169	-7.499662	2.045325
N	-6.048773	-3.019207	2.194389
H	-6.438757	-2.727322	3.107852
C	-6.547294	-2.646314	0.956780
N	-4.745451	-3.992618	0.687319
C	-5.724655	-3.248269	0.029882
H	-5.768378	-3.192987	-1.049353
C	-4.975359	-3.826857	1.998348
H	-4.393810	-4.254507	2.804887
N	-7.598478	-9.559740	1.573631
H	-7.357140	-10.448593	2.040444
C	-8.853732	-9.082487	1.214115
N	-7.243356	-7.876538	0.175294
C	-8.618064	-8.033503	0.354801
H	-9.325687	-7.388959	-0.149924
C	-6.663461	-8.820492	0.922353
H	-5.603181	-9.002685	1.035219

N	-5.037320	-9.964490	-4.469698
H	-4.377058	-10.313584	-5.184295
C	-5.970634	-10.758911	-3.823275
N	-5.890245	-8.731092	-2.835935
C	-6.499217	-9.985053	-2.821105
H	-7.266848	-10.229994	-2.100855
C	-5.007003	-8.757606	-3.840835
H	-4.334331	-7.958967	-4.122672
N	-8.485161	-4.733727	-4.160315
H	-8.751149	-4.467743	-5.120669
C	-8.904821	-4.077769	-3.020856
N	-7.484834	-5.739926	-2.477964
C	-8.287523	-4.719439	-1.973230
H	-8.352009	-4.521868	-0.912042
C	-7.633674	-5.719484	-3.805793
H	-7.129876	-6.361652	-4.515118
CU	-6.603158	-7.292067	-1.632704
CU	-3.104402	-4.833668	-0.070128
H	0.788504	-2.595751	-2.592799
H	0.726487	-7.433351	2.453454
H	-7.343336	-1.910541	0.842660
H	-9.778069	-9.578053	1.510900
H	-6.118481	-11.801997	-4.102882
H	-9.606506	-3.245987	-3.082855

^{3}2b

N	-0.471620	-4.115209	-3.372962
H	-0.048508	-4.311555	-4.293870
C	-0.055547	-3.140120	-2.485353
N	-1.881124	-4.178198	-1.667315
C	-0.938244	-3.185294	-1.432635
H	-0.965428	-2.581285	-0.535085
C	-1.576407	-4.715347	-2.855426
H	-2.100120	-5.516080	-3.358920

N	-1.420453	-7.666143	2.559927
H	-1.501281	-8.454027	3.229575
C	-0.244587	-7.062732	2.135181
N	-2.022637	-6.054523	1.162449
C	-0.634924	-6.062141	1.271883
H	-0.026107	-5.358737	0.721186
C	-2.463613	-7.041598	1.951113
H	-3.491107	-7.358398	2.078833
N	-5.951522	-2.966253	2.189848
H	-6.329970	-2.682432	3.110621
C	-6.506873	-2.628222	0.965899
N	-4.678128	-3.925805	0.651212
C	-5.702431	-3.223264	0.018890
H	-5.787324	-3.181382	-1.058899
C	-4.862415	-3.745536	1.965889
H	-4.238809	-4.145983	2.755207
N	-7.654808	-9.540380	1.556464
H	-7.409737	-10.416060	2.045042
C	-8.911958	-9.091945	1.165594
N	-7.311303	-7.914829	0.099691
C	-8.681761	-8.081136	0.260665
H	-9.388912	-7.471139	-0.285296
C	-6.722426	-8.816273	0.888219
H	-5.658839	-8.971493	1.015113
N	-5.068777	-9.953932	-4.525344
H	-4.376312	-10.341807	-5.187874
C	-6.077741	-10.691723	-3.926792
N	-6.038800	-8.614136	-3.055541
C	-6.679875	-9.847677	-3.025713
H	-7.515173	-10.036207	-2.365224
C	-5.065020	-8.717128	-3.963304
H	-4.337772	-7.955073	-4.208502
N	-8.542870	-4.826404	-4.141188
H	-8.782355	-4.545336	-5.104614
C	-8.946720	-4.148089	-3.008504

N	-7.624370	-5.878142	-2.444682
C	-8.376973	-4.816502	-1.951082
H	-8.446132	-4.612479	-0.891079
C	-7.748786	-5.853427	-3.774650
H	-7.269178	-6.527434	-4.470428
CU	-6.379540	-7.168659	-1.551877
CU	-3.130019	-4.934574	-0.241816
O	-4.588637	-7.200977	-0.736998
O	-3.859572	-6.351859	-1.480870
H	0.843871	-2.539902	-2.622659
H	0.733463	-7.389926	2.487927
H	-7.315082	-1.903889	0.864872
H	-9.832983	-9.587542	1.472455
H	-6.209891	-11.749751	-4.153025
H	-9.619575	-3.293411	-3.078213

^{1}3

N	-0.537229	-4.150516	-3.333474
H	-0.121463	-4.299827	-4.266533
C	-0.102751	-3.237137	-2.389136
N	-1.886362	-4.362868	-1.592286
C	-0.951184	-3.373063	-1.313979
H	-0.960607	-2.836448	-0.374290
C	-1.612571	-4.807971	-2.826198
H	-2.143674	-5.577137	-3.369039
N	-1.390220	-7.711788	2.574983
H	-1.457570	-8.483656	3.265367
C	-0.228502	-7.094540	2.132344
N	-2.025358	-6.166146	1.127307
C	-0.638747	-6.131066	1.237422
H	-0.047768	-5.428845	0.666804
C	-2.447570	-7.138546	1.946543
H	-3.466842	-7.478314	2.082110
N	-5.878378	-2.940536	2.201716
H	-6.260340	-2.645330	3.116548

C	-6.441456	-2.632530	0.972705
N	-4.625898	-3.960396	0.679528
C	-5.648692	-3.266197	0.038675
H	-5.742760	-3.262693	-1.039152
C	-4.797606	-3.738638	1.986641
H	-4.172545	-4.120423	2.784657
N	-7.639685	-9.522700	1.484378
H	-7.403392	-10.390328	1.992644
C	-8.892467	-9.072561	1.080425
N	-7.279561	-7.933220	-0.003248
C	-8.652218	-8.083599	0.153114
H	-9.350222	-7.481191	-0.411843
C	-6.699000	-8.821711	0.806681
H	-5.638277	-8.978613	0.946368
N	-5.066105	-9.920516	-4.507202
H	-4.388401	-10.312997	-5.181414
C	-6.072441	-10.651426	-3.893243
N	-5.977041	-8.582133	-2.990555
C	-6.635079	-9.806569	-2.964592
H	-7.458114	-9.993012	-2.287865
C	-5.030159	-8.691248	-3.924689
H	-4.299756	-7.934701	-4.180316
N	-8.515226	-4.865977	-4.124661
H	-8.746956	-4.601154	-5.094273
C	-8.927454	-4.163360	-3.009450
N	-7.605081	-5.874317	-2.398903
C	-8.361599	-4.803726	-1.932948
H	-8.435486	-4.572526	-0.878845
C	-7.717764	-5.882033	-3.729826
H	-7.226512	-6.569648	-4.403345
CU	-6.251409	-6.991627	-1.447326
CU	-3.181463	-5.264151	-0.292001
O	-4.435155	-6.969659	-0.636125
O	-4.450996	-6.010662	-1.700053
H	0.768707	-2.599228	-2.536448

H	0.756698	-7.401133	2.483696
H	-7.254957	-1.915460	0.862733
H	-9.814375	-9.554999	1.405090
H	-6.213317	-11.708167	-4.120222
H	-9.597720	-3.307957	-3.093689

Section 4: Cartesian coordinates of the QM region (in Å) optimized by B3LYP

deoxyHc

N	-0.538106	-4.163030	-3.321362
H	-0.123575	-4.354012	-4.236920
C	-0.113374	-3.208698	-2.432667
N	-1.936388	-4.234760	-1.624003
C	-0.989651	-3.256949	-1.388542
H	-1.008728	-2.659823	-0.493259
C	-1.635847	-4.755217	-2.805002
H	-2.158844	-5.539812	-3.322981
N	-1.423731	-7.727767	2.528925
H	-1.491958	-8.486244	3.221053
C	-0.268931	-7.120948	2.088550
N	-2.052229	-6.205237	1.072661
C	-0.675494	-6.174762	1.188543
H	-0.082484	-5.481281	0.618175
C	-2.467675	-7.156018	1.896508
H	-3.484650	-7.476543	2.053958
N	-6.047497	-3.021512	2.178932
H	-6.430920	-2.733544	3.087186
C	-6.543031	-2.649487	0.952069
N	-4.760986	-3.988711	0.682759
C	-5.730772	-3.250124	0.031227
H	-5.778154	-3.195420	-1.042226
C	-4.986100	-3.823235	1.979354
H	-4.406400	-4.250217	2.780018
N	-7.593743	-9.564861	1.547106
H	-7.354958	-10.442517	2.018574

C	-8.838556	-9.087619	1.195190
N	-7.240786	-7.891253	0.170548
C	-8.603169	-8.044090	0.346484
H	-9.306995	-7.401157	-0.153313
C	-6.668547	-8.829892	0.904139
H	-5.613635	-9.013317	1.013396
N	-5.051914	-9.962906	-4.465827
H	-4.398589	-10.309646	-5.176202
C	-5.980961	-10.745069	-3.822147
N	-5.904318	-8.724747	-2.863887
C	-6.509732	-9.966120	-2.837779
H	-7.276381	-10.203508	-2.122127
C	-5.026997	-8.762268	-3.853409
H	-4.359182	-7.969135	-4.140979
N	-8.478503	-4.732009	-4.148478
H	-8.739389	-4.470845	-5.103041
C	-8.897844	-4.080948	-3.018993
N	-7.489886	-5.727866	-2.477606
C	-8.285953	-4.716309	-1.978355
H	-8.352416	-4.517721	-0.923290
C	-7.634667	-5.707396	-3.791330
H	-7.135870	-6.351053	-4.494278
CU	-6.599987	-7.281453	-1.634263
CU	-3.108883	-4.834369	-0.068655
H	0.777614	-2.598579	-2.580861
H	0.715767	-7.421608	2.446378
H	-7.340254	-1.914978	0.838054
H	-9.764058	-9.578205	1.496582
H	-6.129939	-11.789961	-4.094313
H	-9.599127	-3.248759	-3.080076

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N	-0.506772	-4.136740	-3.346628
H	-0.086083	-4.326631	-4.260325

C	-0.092646	-3.179628	-2.454239
N	-1.904000	-4.221674	-1.657000
C	-0.969959	-3.238059	-1.411423
H	-0.996276	-2.647498	-0.511902
C	-1.599024	-4.739065	-2.837794
H	-2.117618	-5.533024	-3.345770
N	-1.433553	-7.663703	2.541089
H	-1.505686	-8.444401	3.207098
C	-0.274662	-7.049587	2.120641
N	-2.051912	-6.084936	1.143195
C	-0.675613	-6.069057	1.255475
H	-0.077303	-5.365037	0.704551
C	-2.472984	-7.064515	1.928234
H	-3.490601	-7.394409	2.055170
N	-5.994484	-3.021053	2.160669
H	-6.356327	-2.735714	3.078297
C	-6.533263	-2.654896	0.950188
N	-4.762413	-3.996393	0.624924
C	-5.754386	-3.260823	0.004329
H	-5.836938	-3.203150	-1.067159
C	-4.940241	-3.824189	1.927082
H	-4.332594	-4.249967	2.707633
N	-7.615053	-9.520786	1.472876
H	-7.371087	-10.386833	1.964133
C	-8.864342	-9.071946	1.096150
N	-7.279253	-7.886520	0.056017
C	-8.638756	-8.054721	0.213129
H	-9.344488	-7.442487	-0.320470
C	-6.694588	-8.791032	0.822469
H	-5.635927	-8.946483	0.943305
N	-5.057618	-9.931189	-4.501308
H	-4.373941	-10.329159	-5.154080
C	-6.085574	-10.635565	-3.919218
N	-6.010120	-8.565720	-3.070516
C	-6.675569	-9.774195	-3.040581

H	-7.519069	-9.940330	-2.393182
C	-5.035586	-8.702303	-3.952577
H	-4.291620	-7.963090	-4.193715
N	-8.532613	-4.873209	-4.123460
H	-8.769363	-4.602374	-5.082019
C	-8.934442	-4.189866	-3.005351
N	-7.599636	-5.882446	-2.433717
C	-8.354739	-4.831818	-1.951595
H	-8.418130	-4.613451	-0.900065
C	-7.730299	-5.875722	-3.749917
H	-7.249432	-6.552622	-4.432946
CU	-6.291203	-7.076081	-1.523323
CU	-3.192722	-4.980917	-0.269958
O	-4.526468	-7.269157	-0.754556
O	-3.977349	-6.346033	-1.533797
H	0.798169	-2.567768	-2.596168
H	0.707528	-7.369817	2.468237
H	-7.332520	-1.919738	0.856392
H	-9.782768	-9.561166	1.420533
H	-6.228238	-11.695354	-4.130311
H	-9.603758	-3.332567	-3.076923

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N	-0.579412	-4.147163	-3.284902
H	-0.167128	-4.292555	-4.210282
C	-0.149305	-3.246804	-2.340836
N	-1.911947	-4.380455	-1.558868
C	-0.988988	-3.395867	-1.274300
H	-0.997375	-2.870527	-0.334999
C	-1.638716	-4.808317	-2.784571
H	-2.162398	-5.575708	-3.326742
N	-1.416113	-7.688713	2.556130
H	-1.476096	-8.458599	3.237102
C	-0.269204	-7.060854	2.122831

N	-2.061045	-6.163838	1.120110
C	-0.685985	-6.110271	1.233319
H	-0.102909	-5.407671	0.665612
C	-2.466767	-7.134252	1.927837
H	-3.476563	-7.487372	2.056879
N	-5.895158	-2.989984	2.159851
H	-6.259374	-2.693945	3.072318
C	-6.446737	-2.657044	0.944794
N	-4.686451	-4.023250	0.638647
C	-5.681648	-3.300166	0.010101
H	-5.777257	-3.280706	-1.061778
C	-4.848136	-3.808854	1.934751
H	-4.235226	-4.213335	2.723008
N	-7.603693	-9.514207	1.416271
H	-7.366731	-10.376920	1.917800
C	-8.849484	-9.059592	1.033226
N	-7.253658	-7.894726	-0.011575
C	-8.615041	-8.051174	0.141655
H	-9.313440	-7.438666	-0.400671
C	-6.676672	-8.796661	0.764031
H	-5.619983	-8.954723	0.890992
N	-5.085986	-9.898643	-4.486210
H	-4.410246	-10.286148	-5.151981
C	-6.092231	-10.620108	-3.885536
N	-6.004403	-8.562323	-3.000228
C	-6.659591	-9.775550	-2.974444
H	-7.484618	-9.957987	-2.308302
C	-5.056902	-8.678468	-3.913242
H	-4.326455	-7.927395	-4.159449
N	-8.483671	-4.866424	-4.097720
H	-8.711888	-4.612590	-5.062572
C	-8.909518	-4.172198	-2.995057
N	-7.564078	-5.839893	-2.378794
C	-8.337614	-4.791198	-1.923366
H	-8.419409	-4.556292	-0.876611

C	-7.674015	-5.854293	-3.696694
H	-7.173825	-6.535685	-4.360856
CU	-6.197245	-6.944461	-1.430483
CU	-3.240981	-5.339610	-0.333725
O	-4.371787	-7.051640	-0.699934
O	-4.351251	-6.139578	-1.790399
H	0.714185	-2.599440	-2.493713
H	0.719063	-7.366414	2.466384
H	-7.253854	-1.931577	0.843176
H	-9.769215	-9.538312	1.369363
H	-6.231476	-11.677826	-4.108943
H	-9.584703	-3.321028	-3.082820

MECP

N	-0.559432	-4.140991	-3.301430
H	-0.147642	-4.293822	-4.226193
C	-0.128405	-3.231585	-2.366982
N	-1.897786	-4.348782	-1.576413
C	-0.971296	-3.364832	-1.301311
H	-0.978682	-2.828307	-0.368279
C	-1.623366	-4.791851	-2.795665
H	-2.148355	-5.563798	-3.330005
N	-1.413993	-7.679459	2.554550
H	-1.479209	-8.454355	3.229081
C	-0.262327	-7.057807	2.125357
N	-2.048746	-6.129283	1.138377
C	-0.672611	-6.092955	1.248154
H	-0.083341	-5.390125	0.687093
C	-2.460705	-7.105311	1.935940
H	-3.473466	-7.449697	2.063769
N	-5.919499	-2.994624	2.167489
H	-6.286325	-2.699010	3.079486
C	-6.463050	-2.655679	0.950641
N	-4.700584	-4.017889	0.650347
C	-5.691602	-3.292325	0.017528

H	-5.779206	-3.266649	-1.054840
C	-4.870395	-3.810392	1.947045
H	-4.261764	-4.218262	2.736704
N	-7.611331	-9.516091	1.430731
H	-7.370832	-10.378455	1.930773
C	-8.859332	-9.065246	1.050962
N	-7.269965	-7.897448	-0.001235
C	-8.630219	-8.057906	0.156895
H	-9.332661	-7.448443	-0.383664
C	-6.688351	-8.796807	0.773509
H	-5.630674	-8.952777	0.896550
N	-5.080438	-9.905079	-4.493652
H	-4.401782	-10.297813	-5.153745
C	-6.094870	-10.618890	-3.898200
N	-6.010758	-8.554385	-3.028918
C	-6.670090	-9.765814	-3.000247
H	-7.502084	-9.941629	-2.340794
C	-5.054025	-8.680522	-3.931071
H	-4.318887	-7.934224	-4.177827
N	-8.499191	-4.864350	-4.112726
H	-8.730695	-4.604600	-5.075405
C	-8.918120	-4.174763	-3.004723
N	-7.578202	-5.852363	-2.403442
C	-8.345566	-4.803140	-1.939087
H	-8.422702	-4.575455	-0.890436
C	-7.693024	-5.858375	-3.721022
H	-7.197867	-6.537085	-4.391763
CU	-6.224220	-6.964881	-1.453526
CU	-3.230572	-5.241841	-0.303029
O	-4.427517	-7.099914	-0.709373
O	-4.259923	-6.163509	-1.730685
H	0.740678	-2.591265	-2.517817
H	0.723633	-7.369386	2.470131
H	-7.268441	-1.928610	0.846804
H	-9.777803	-9.548094	1.384631

H	-6.234960	-11.677897	-4.114869
H	-9.591155	-3.321213	-3.085616

Section 5: Cartesian coordinates of the QM region (in Å) optimized by BH&HLYP

deoxyHc

N	-0.535957	-4.160220	-3.319295
H	-0.123415	-4.351682	-4.224837
C	-0.116155	-3.214304	-2.433055
N	-1.930171	-4.230643	-1.644649
C	-0.990103	-3.262141	-1.403281
H	-1.011171	-2.670432	-0.512975
C	-1.626251	-4.742958	-2.811112
H	-2.144981	-5.521676	-3.328271
N	-1.420401	-7.721031	2.530022
H	-1.488369	-8.473978	3.213524
C	-0.274757	-7.118863	2.089435
N	-2.046799	-6.210517	1.090448
C	-0.679409	-6.180309	1.199348
H	-0.090395	-5.491812	0.631641
C	-2.453583	-7.151457	1.905289
H	-3.464565	-7.466485	2.065628
N	-6.050615	-3.022542	2.169243
H	-6.426682	-2.738639	3.070794
C	-6.544182	-2.652784	0.951336
N	-4.778248	-3.981881	0.684522
C	-5.742215	-3.250244	0.037785
H	-5.792308	-3.196745	-1.028570
C	-4.999496	-3.815880	1.965672
H	-4.421383	-4.239999	2.759807
N	-7.591386	-9.570444	1.537374
H	-7.356951	-10.437708	2.009021
C	-8.826335	-9.092633	1.188672
N	-7.237308	-7.905728	0.182429
C	-8.590146	-8.055527	0.352431

H	-9.288489	-7.415244	-0.143355
C	-6.675494	-8.839108	0.903725
H	-5.627416	-9.023862	1.009804
N	-5.057702	-9.962886	-4.467966
H	-4.411643	-10.306751	-5.172469
C	-5.982597	-10.733672	-3.824612
N	-5.903261	-8.722148	-2.891820
C	-6.507271	-9.952797	-2.855872
H	-7.270069	-10.182922	-2.143794
C	-5.034904	-8.770663	-3.867741
H	-4.372162	-7.984273	-4.160059
N	-8.473574	-4.730740	-4.136322
H	-8.728647	-4.476139	-5.083977
C	-8.892610	-4.082702	-3.015887
N	-7.495980	-5.714686	-2.475595
C	-8.286653	-4.709451	-1.982586
H	-8.354553	-4.509215	-0.935203
C	-7.637419	-5.694980	-3.774382
H	-7.144376	-6.340207	-4.469486
CU	-6.580394	-7.268946	-1.624832
CU	-3.108799	-4.841116	-0.072008
H	0.773642	-2.602039	-2.579549
H	0.711210	-7.418447	2.444660
H	-7.342506	-1.919429	0.837603
H	-9.753710	-9.578874	1.491348
H	-6.134754	-11.779895	-4.089815
H	-9.593875	-3.250493	-3.076909

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N	-0.497761	-4.085477	-3.315499
H	-0.094082	-4.295633	-4.220554
C	-0.063562	-3.130893	-2.447744
N	-1.877919	-4.117377	-1.628818
C	-0.928340	-3.154407	-1.410339

H	-0.936454	-2.549628	-0.528867
C	-1.589492	-4.649260	-2.791131
H	-2.118356	-5.428174	-3.295442
N	-1.406753	-7.657120	2.537247
H	-1.495188	-8.424796	3.201701
C	-0.243293	-7.083462	2.106159
N	-1.984507	-6.091759	1.135665
C	-0.617761	-6.111162	1.239753
H	-0.008257	-5.430521	0.685283
C	-2.421216	-7.037322	1.928657
H	-3.442463	-7.320832	2.080989
N	-6.040793	-2.979142	2.192416
H	-6.432780	-2.704357	3.090312
C	-6.530849	-2.622528	0.969576
N	-4.721100	-3.893576	0.722900
C	-5.700301	-3.193329	0.065006
H	-5.739532	-3.139429	-1.001932
C	-4.962710	-3.737966	2.001173
H	-4.380514	-4.144531	2.801621
N	-7.621875	-9.582922	1.537441
H	-7.375586	-10.444836	2.011456
C	-8.864904	-9.114008	1.205885
N	-7.301669	-7.928343	0.163719
C	-8.649347	-8.083216	0.357588
H	-9.358994	-7.451105	-0.132241
C	-6.720500	-8.851938	0.882283
H	-5.668685	-9.029615	0.969304
N	-5.110791	-9.982938	-4.495345
H	-4.446083	-10.317885	-5.186221
C	-6.025839	-10.768532	-3.857570
N	-6.028873	-8.741795	-2.961547
C	-6.595812	-9.987900	-2.915549
H	-7.366787	-10.228087	-2.216320
C	-5.138829	-8.780175	-3.917901
H	-4.494975	-7.978676	-4.210197

N	-8.488355	-4.703921	-4.149213
H	-8.743318	-4.446165	-5.096118
C	-8.903987	-4.059549	-3.025877
N	-7.531723	-5.712965	-2.493395
C	-8.309665	-4.700943	-1.994934
H	-8.379361	-4.508634	-0.946048
C	-7.666849	-5.681757	-3.792339
H	-7.180361	-6.328857	-4.490221
CU	-6.678608	-7.297849	-1.647018
CU	-3.018422	-4.686527	-0.020717
O	-4.250570	-7.105260	-0.936322
O	-3.618045	-6.844430	-1.902339
H	0.840281	-2.540010	-2.596039
H	0.733618	-7.407757	2.464692
H	-7.338381	-1.900863	0.846462
H	-9.787841	-9.607483	1.510414
H	-6.160505	-11.817580	-4.121067
H	-9.605589	-3.227422	-3.084066

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N	-0.495760	-4.082807	-3.316342
H	-0.091990	-4.293583	-4.221197
C	-0.061958	-3.127518	-2.449262
N	-1.875271	-4.114833	-1.629052
C	-0.926308	-3.151067	-1.411507
H	-0.934418	-2.545831	-0.530365
C	-1.586924	-4.647008	-2.791323
H	-2.115452	-5.426296	-3.295313
N	-1.405630	-7.654619	2.537926
H	-1.494265	-8.422674	3.201896
C	-0.241936	-7.081120	2.107389
N	-1.982503	-6.088032	1.137248
C	-0.615823	-6.108060	1.241583
H	-0.006013	-5.427409	0.687494
C	-2.419731	-7.033968	1.929549

H	-3.441131	-7.317223	2.081345
N	-6.039522	-2.977808	2.192415
H	-6.431266	-2.702671	3.090319
C	-6.529810	-2.621406	0.969599
N	-4.721393	-3.894335	0.722794
C	-5.700248	-3.193468	0.064969
H	-5.740101	-3.140263	-1.001978
C	-4.962330	-3.737819	2.001115
H	-4.380309	-4.144659	2.801553
N	-7.624150	-9.583509	1.535244
H	-7.377336	-10.445221	2.009268
C	-8.867551	-9.114251	1.205735
N	-7.305610	-7.928782	0.161132
C	-8.652962	-8.083283	0.357417
H	-9.363103	-7.450646	-0.130990
C	-6.723586	-8.852585	0.878694
H	-5.671677	-9.030410	0.964360
N	-5.111812	-9.985761	-4.493942
H	-4.447126	-10.320211	-5.185097
C	-6.026212	-10.771901	-3.856012
N	-6.030188	-8.745269	-2.959678
C	-6.596248	-9.991766	-2.913640
H	-7.366792	-10.232197	-2.214049
C	-5.140420	-8.783037	-3.916407
H	-4.497130	-7.981236	-4.209004
N	-8.491809	-4.698178	-4.151576
H	-8.747297	-4.440177	-5.098285
C	-8.906699	-4.054261	-3.027792
N	-7.536003	-5.709240	-2.496700
C	-8.312908	-4.696914	-1.997355
H	-8.382423	-4.505173	-0.948349
C	-7.671258	-5.676985	-3.795631
H	-7.185407	-6.323798	-4.494228
CU	-6.695999	-7.300883	-1.655972
CU	-3.015893	-4.681408	-0.020079

O	-4.221371	-7.120032	-0.929245
O	-3.592023	-6.854001	-1.894948
H	0.842161	-2.537024	-2.597432
H	0.734696	-7.406406	2.465784
H	-7.337331	-1.899731	0.846465
H	-9.790124	-9.608145	1.510688
H	-6.160711	-11.820650	-4.120785
H	-9.608786	-3.222518	-3.085641

^{1}TS1

N	-0.497362	-4.099550	-3.318832
H	-0.093281	-4.312510	-4.222793
C	-0.064316	-3.140070	-2.455210
N	-1.881836	-4.119163	-1.636226
C	-0.932262	-3.156462	-1.420255
H	-0.942786	-2.547271	-0.541894
C	-1.591330	-4.659412	-2.793664
H	-2.120948	-5.442658	-3.291400
N	-1.409853	-7.659895	2.532023
H	-1.496344	-8.427099	3.196927
C	-0.248419	-7.077666	2.106464
N	-1.992810	-6.097971	1.128542
C	-0.626417	-6.107739	1.238649
H	-0.019117	-5.423027	0.686697
C	-2.426005	-7.047126	1.918602
H	-3.446017	-7.338473	2.064305
N	-6.039378	-2.988595	2.184328
H	-6.424805	-2.712595	3.084561
C	-6.536563	-2.630048	0.964906
N	-4.734232	-3.909860	0.705203
C	-5.714659	-3.204765	0.054462
H	-5.760348	-3.149339	-1.012131
C	-4.966061	-3.752693	1.984928
H	-4.380219	-4.163032	2.780692
N	-7.633191	-9.564875	1.514401

H	-7.394018	-10.425878	1.994207
C	-8.871992	-9.100757	1.159520
N	-7.295162	-7.926585	0.128677
C	-8.645838	-8.080619	0.300632
H	-9.347704	-7.457072	-0.211035
C	-6.723090	-8.840784	0.865671
H	-5.671989	-9.015021	0.967022
N	-5.091684	-9.977161	-4.502635
H	-4.423718	-10.331138	-5.181468
C	-6.042898	-10.733577	-3.882176
N	-6.019096	-8.697326	-3.009813
C	-6.619290	-9.927788	-2.964837
H	-7.413474	-10.140624	-2.282357
C	-5.102937	-8.768775	-3.938901
H	-4.427195	-7.987851	-4.215388
N	-8.501616	-4.761487	-4.141928
H	-8.752708	-4.501142	-5.089181
C	-8.909893	-4.108015	-3.020551
N	-7.541584	-5.762084	-2.483658
C	-8.313650	-4.744527	-1.988072
H	-8.378781	-4.546185	-0.939942
C	-7.681456	-5.739521	-3.782453
H	-7.199680	-6.394745	-4.476087
CU	-6.529692	-7.256118	-1.614400
CU	-3.029384	-4.707252	-0.046854
O	-4.452807	-7.160134	-0.909902
O	-3.746866	-6.752371	-1.784883
H	0.839650	-2.549149	-2.602603
H	0.729260	-7.400195	2.464496
H	-7.342086	-1.905187	0.847531
H	-9.794859	-9.589562	1.471697
H	-6.181417	-11.786626	-4.127055
H	-9.601163	-3.267289	-3.078804

^{3}TS1

N	-0.496894	-4.104364	-3.318883
H	-0.092056	-4.317612	-4.222383
C	-0.065528	-3.143011	-2.456220
N	-1.883720	-4.121399	-1.638310
C	-0.934993	-3.157993	-1.422593
H	-0.947071	-2.547295	-0.545265
C	-1.591597	-4.663925	-2.794059
H	-2.120308	-5.449311	-3.289627
N	-1.410277	-7.663194	2.529504
H	-1.495941	-8.430153	3.194477
C	-0.249703	-7.077408	2.106373
N	-1.995135	-6.101130	1.127021
C	-0.628949	-6.107342	1.239218
H	-0.022411	-5.420996	0.688306
C	-2.427190	-7.052181	1.914935
H	-3.446418	-7.347344	2.057365
N	-6.038771	-2.991361	2.180991
H	-6.421491	-2.714521	3.081936
C	-6.538141	-2.631788	0.962808
N	-4.741018	-3.918468	0.698478
C	-5.720648	-3.209700	0.050359
H	-5.768134	-3.153034	-1.016265
C	-4.968605	-3.759643	1.978572
H	-4.381879	-4.171640	2.772938
N	-7.630759	-9.554805	1.503551
H	-7.391220	-10.412467	1.990447
C	-8.869930	-9.095072	1.143409
N	-7.293404	-7.928192	0.103569
C	-8.644382	-8.082863	0.275107
H	-9.347438	-7.465302	-0.241703
C	-6.720855	-8.835878	0.850413
H	-5.669963	-9.006947	0.955729
N	-5.082636	-9.972604	-4.502469
H	-4.412023	-10.334194	-5.175341

C	-6.047971	-10.718239	-3.890276
N	-6.019416	-8.675973	-3.029667
C	-6.630198	-9.901977	-2.985532
H	-7.434584	-10.106365	-2.312232
C	-5.091552	-8.761319	-3.946460
H	-4.405769	-7.987876	-4.217741
N	-8.504792	-4.784953	-4.137890
H	-8.751904	-4.520791	-5.085484
C	-8.911298	-4.127800	-3.017722
N	-7.557204	-5.791917	-2.477122
C	-8.322121	-4.767483	-1.983541
H	-8.386236	-4.563540	-0.936585
C	-7.693308	-5.768800	-3.776860
H	-7.213383	-6.426552	-4.468882
CU	-6.456224	-7.217357	-1.592606
CU	-3.035923	-4.721139	-0.057317
O	-4.479868	-7.214458	-0.856539
O	-3.865653	-6.695081	-1.757854
H	0.838316	-2.551884	-2.603538
H	0.728182	-7.399433	2.464293
H	-7.342931	-1.905836	0.847161
H	-9.791704	-9.583086	1.460018
H	-6.185850	-11.772831	-4.128797
H	-9.597268	-3.282812	-3.076948

^{1}2a

N	-0.490610	-4.133093	-3.329849
H	-0.081200	-4.346748	-4.230462
C	-0.066384	-3.167583	-2.466610
N	-1.896045	-4.137330	-1.664734
C	-0.947744	-3.176928	-1.442136
H	-0.968018	-2.563543	-0.566808
C	-1.593515	-4.686532	-2.812840
H	-2.122175	-5.476330	-3.301935
N	-1.414193	-7.676424	2.513948

H	-1.496144	-8.442939	3.178147
C	-0.258140	-7.069443	2.106205
N	-2.009897	-6.113331	1.116815
C	-0.645465	-6.098725	1.242746
H	-0.044665	-5.400362	0.700500
C	-2.434182	-7.077071	1.890596
H	-3.449474	-7.393848	2.010411
N	-6.033402	-3.011655	2.164721
H	-6.399492	-2.732866	3.071269
C	-6.551932	-2.648187	0.956074
N	-4.773283	-3.956413	0.657759
C	-5.756544	-3.236195	0.029169
H	-5.816571	-3.170224	-1.036463
C	-4.974374	-3.792937	1.940247
H	-4.377447	-4.211628	2.723451
N	-7.641678	-9.483348	1.420547
H	-7.394556	-10.322564	1.937467
C	-8.887241	-9.052277	1.044087
N	-7.327019	-7.899420	-0.024813
C	-8.676740	-8.066348	0.142936
H	-9.384166	-7.477681	-0.399793
C	-6.738802	-8.772804	0.756816
H	-5.684794	-8.916519	0.874915
N	-5.061367	-9.933350	-4.496032
H	-4.380978	-10.325214	-5.142056
C	-6.089027	-10.630966	-3.927490
N	-6.022812	-8.573846	-3.100604
C	-6.686260	-9.774622	-3.069859
H	-7.530259	-9.938380	-2.434242
C	-5.045787	-8.715536	-3.960094
H	-4.305157	-7.980923	-4.194629
N	-8.513060	-4.923759	-4.109515
H	-8.740421	-4.635389	-5.055881
C	-8.916946	-4.267547	-2.985469
N	-7.602213	-5.963571	-2.453507

C	-8.348887	-4.924754	-1.951925
H	-8.408252	-4.724143	-0.903821
C	-7.723344	-5.924498	-3.758354
H	-7.244877	-6.584655	-4.448390
CU	-6.287301	-7.120020	-1.561253
CU	-3.097756	-4.842397	-0.155123
O	-4.563537	-7.344886	-0.767192
O	-4.182883	-6.419839	-1.599892
H	0.837234	-2.575328	-2.610749
H	0.721584	-7.387403	2.462729
H	-7.352603	-1.915634	0.854295
H	-9.800943	-9.539753	1.384064
H	-6.232742	-11.691274	-4.135238
H	-9.574132	-3.399966	-3.044440

^{3}2b

N	-0.494829	-4.130584	-3.327335
H	-0.087440	-4.346056	-4.228395
C	-0.067710	-3.164192	-2.466775
N	-1.894880	-4.132674	-1.657779
C	-0.945585	-3.171989	-1.439473
H	-0.963126	-2.556901	-0.565309
C	-1.596102	-4.683408	-2.806455
H	-2.126632	-5.472977	-3.293880
N	-1.414775	-7.669069	2.518574
H	-1.497445	-8.435868	3.182668
C	-0.257860	-7.066638	2.106902
N	-2.008732	-6.107531	1.118960
C	-0.643905	-6.096752	1.242049
H	-0.042179	-5.401124	0.697429
C	-2.434200	-7.068129	1.896372
H	-3.450166	-7.380886	2.020991
N	-6.038018	-3.006252	2.169952
H	-6.407658	-2.727405	3.075207
C	-6.551853	-2.643231	0.959163

N	-4.769061	-3.946898	0.668731
C	-5.751098	-3.228803	0.035613
H	-5.807026	-3.163385	-1.030237
C	-4.976335	-3.784533	1.950602
H	-4.382031	-4.201860	2.736534
N	-7.645282	-9.499158	1.412236
H	-7.404073	-10.337684	1.932642
C	-8.887084	-9.058484	1.034924
N	-7.317035	-7.923141	-0.038585
C	-8.667973	-8.077128	0.130433
H	-9.370211	-7.483625	-0.413849
C	-6.736674	-8.799164	0.745008
H	-5.684359	-8.952651	0.864609
N	-5.069458	-9.936897	-4.494218
H	-4.391802	-10.325139	-5.144839
C	-6.088249	-10.640213	-3.917185
N	-6.021766	-8.585790	-3.081942
C	-6.679241	-9.788976	-3.049614
H	-7.516666	-9.958314	-2.407003
C	-5.054324	-8.720595	-3.952689
H	-4.320702	-7.981301	-4.194804
N	-8.507419	-4.915399	-4.104075
H	-8.737792	-4.638357	-5.052854
C	-8.909825	-4.247645	-2.986543
N	-7.582807	-5.929413	-2.438604
C	-8.333191	-4.889020	-1.947541
H	-8.390127	-4.675628	-0.901869
C	-7.710386	-5.907685	-3.742558
H	-7.231778	-6.574230	-4.426404
CU	-6.271349	-7.094454	-1.539572
CU	-3.087517	-4.814272	-0.135432
O	-4.529379	-7.326310	-0.763106
O	-4.241951	-6.400138	-1.618526
H	0.836569	-2.573400	-2.612760
H	0.721642	-7.385535	2.463200

H	-7.353435	-1.912107	0.854324
H	-9.803899	-9.540172	1.374770
H	-6.231746	-11.699676	-4.129351
H	-9.572425	-3.384627	-3.051566

^{1}TS2

N	-0.528954	-4.133188	-3.323236
H	-0.113161	-4.317343	-4.227784
C	-0.104712	-3.206647	-2.416934
N	-1.917085	-4.233996	-1.649565
C	-0.976928	-3.275444	-1.385804
H	-0.994860	-2.708572	-0.479427
C	-1.618485	-4.724531	-2.824865
H	-2.141571	-5.500489	-3.341296
N	-1.412844	-7.694934	2.533750
H	-1.478348	-8.459140	3.202700
C	-0.271261	-7.067939	2.115291
N	-2.048419	-6.154398	1.130735
C	-0.683099	-6.111128	1.247384
H	-0.098752	-5.405736	0.696078
C	-2.448292	-7.123289	1.912571
H	-3.455271	-7.464582	2.037108
N	-5.975473	-3.000397	2.157502
H	-6.326824	-2.710221	3.066194
C	-6.517534	-2.651925	0.954425
N	-4.775170	-4.004707	0.639923
C	-5.757982	-3.275693	0.021112
H	-5.841455	-3.228652	-1.043895
C	-4.939210	-3.809733	1.923507
H	-4.331248	-4.224713	2.700254
N	-7.623250	-9.491181	1.397964
H	-7.377556	-10.334072	1.910248
C	-8.868256	-9.055991	1.023347
N	-7.305224	-7.893277	-0.031093
C	-8.655034	-8.062498	0.130872

H	-9.361231	-7.468877	-0.408132
C	-6.719050	-8.773953	0.742303
H	-5.664770	-8.916378	0.859260
N	-5.070411	-9.908290	-4.479332
H	-4.394511	-10.301073	-5.128616
C	-6.093499	-10.606017	-3.901240
N	-6.009953	-8.550346	-3.063674
C	-6.676006	-9.750521	-3.030799
H	-7.511325	-9.915050	-2.384110
C	-5.044083	-8.693095	-3.935144
H	-4.302073	-7.960313	-4.171349
N	-8.495996	-4.909120	-4.101817
H	-8.724474	-4.635781	-5.052407
C	-8.906963	-4.241002	-2.987300
N	-7.575172	-5.915927	-2.429887
C	-8.333652	-4.877945	-1.944245
H	-8.398574	-4.664216	-0.899056
C	-7.696770	-5.897054	-3.735024
H	-7.211028	-6.563206	-4.414071
CU	-6.242110	-7.047142	-1.521461
CU	-3.208900	-5.057586	-0.267913
O	-4.532606	-7.258824	-0.739455
O	-4.112174	-6.338376	-1.605770
H	0.782049	-2.589212	-2.560095
H	0.715540	-7.374426	2.462216
H	-7.317784	-1.918680	0.854337
H	-9.783335	-9.539198	1.365703
H	-6.236611	-11.665622	-4.112956
H	-9.571433	-3.379733	-3.056316

^{3}TS2

N	-0.547876	-4.134649	-3.314250
H	-0.129093	-4.308497	-4.219595
C	-0.124152	-3.221767	-2.393285
N	-1.932670	-4.266985	-1.640137

C	-0.994073	-3.310205	-1.361534
H	-1.013282	-2.758180	-0.446296
C	-1.633809	-4.738459	-2.823851
H	-2.154047	-5.508154	-3.351670
N	-1.420598	-7.697542	2.542369
H	-1.477824	-8.461575	3.212336
C	-0.285551	-7.062704	2.117075
N	-2.074466	-6.165071	1.139438
C	-0.708720	-6.110513	1.249704
H	-0.132105	-5.403281	0.692949
C	-2.463474	-7.135765	1.925400
H	-3.466026	-7.487391	2.054709
N	-5.980331	-3.018624	2.141717
H	-6.322649	-2.726005	3.053097
C	-6.524890	-2.659480	0.942559
N	-4.810706	-4.044442	0.614785
C	-5.782954	-3.294763	0.003050
H	-5.875769	-3.247707	-1.060983
C	-4.961657	-3.846817	1.900087
H	-4.355713	-4.275378	2.670756
N	-7.605368	-9.497718	1.377369
H	-7.362496	-10.344938	1.883919
C	-8.848230	-9.051977	1.007647
N	-7.278810	-7.882035	-0.029776
C	-8.629333	-8.046035	0.130084
H	-9.332431	-7.439780	-0.399032
C	-6.697541	-8.775257	0.732494
H	-5.644391	-8.924000	0.849962
N	-5.071052	-9.900027	-4.473424
H	-4.396098	-10.294902	-5.121706
C	-6.094450	-10.594949	-3.892320
N	-6.006233	-8.537687	-3.057496
C	-6.674010	-9.735683	-3.022860
H	-7.507451	-9.898377	-2.373429
C	-5.043266	-8.683183	-3.930653

H	-4.299642	-7.952979	-4.168956
N	-8.480954	-4.894384	-4.095209
H	-8.714666	-4.632968	-5.047339
C	-8.894992	-4.218452	-2.986459
N	-7.537104	-5.868869	-2.415536
C	-8.308796	-4.836664	-1.939157
H	-8.372636	-4.611851	-0.896395
C	-7.666359	-5.867421	-3.719508
H	-7.176714	-6.535698	-4.393544
CU	-6.209651	-7.008998	-1.494798
CU	-3.241391	-5.105883	-0.283634
O	-4.497549	-7.286264	-0.731189
O	-4.106136	-6.387179	-1.631611
H	0.755297	-2.593444	-2.534166
H	0.706034	-7.362654	2.455979
H	-7.318657	-1.918181	0.850488
H	-9.765014	-9.531095	1.351187
H	-6.239025	-11.654779	-4.101905
H	-9.567094	-3.363614	-3.061284

^{1}3

N	-0.625273	-4.140562	-3.253785
H	-0.228850	-4.275296	-4.175958
C	-0.176582	-3.271610	-2.300878
N	-1.914911	-4.412802	-1.526249
C	-0.989929	-3.444054	-1.233974
H	-0.979470	-2.946532	-0.287893
C	-1.666407	-4.803670	-2.755123
H	-2.200561	-5.551842	-3.301046
N	-1.427412	-7.675002	2.527364
H	-1.490537	-8.439544	3.199349
C	-0.287005	-7.040365	2.113759
N	-2.059891	-6.170468	1.095163
C	-0.695609	-6.102493	1.226913
H	-0.113573	-5.402245	0.668992

C	-2.461485	-7.136850	1.887229
H	-3.464356	-7.496449	1.995121
N	-5.834526	-2.978147	2.143411
H	-6.191476	-2.683434	3.047802
C	-6.395185	-2.665661	0.937112
N	-4.645742	-4.017709	0.638549
C	-5.645037	-3.314838	0.012554
H	-5.751762	-3.314642	-1.051301
C	-4.796119	-3.787456	1.918219
H	-4.179321	-4.178417	2.700873
N	-7.606536	-9.503508	1.365053
H	-7.368682	-10.348090	1.877231
C	-8.847645	-9.059728	0.985867
N	-7.272245	-7.907730	-0.063230
C	-8.623483	-8.066828	0.093942
H	-9.322222	-7.466768	-0.447540
C	-6.695931	-8.791013	0.711530
H	-5.643459	-8.936265	0.831666
N	-5.093203	-9.884598	-4.454906
H	-4.419281	-10.260553	-5.113567
C	-6.100180	-10.603746	-3.873610
N	-6.020487	-8.566082	-2.988499
C	-6.673385	-9.770724	-2.974215
H	-7.498878	-9.955461	-2.320816
C	-5.071525	-8.679617	-3.879389
H	-4.343411	-7.930575	-4.107213
N	-8.468405	-4.892878	-4.082739
H	-8.688275	-4.638979	-5.039322
C	-8.894724	-4.207064	-2.985509
N	-7.559538	-5.864072	-2.379075
C	-8.329063	-4.822818	-1.924652
H	-8.411994	-4.591172	-0.884509
C	-7.666178	-5.870535	-3.683106
H	-7.168154	-6.546251	-4.343522
CU	-6.164876	-6.943541	-1.430116

CU	-3.259479	-5.419487	-0.370138
O	-4.410951	-7.029726	-0.621311
O	-4.397525	-6.128529	-1.783103
H	0.679390	-2.615845	-2.460098
H	0.700817	-7.345443	2.459014
H	-7.209704	-1.948609	0.834832
H	-9.764762	-9.534584	1.334399
H	-6.238147	-11.660874	-4.100573
H	-9.565203	-3.351999	-3.071474

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N	-0.628927	-4.140301	-3.243234
H	-0.229091	-4.275014	-4.164283
C	-0.188142	-3.264281	-2.293000
N	-1.925624	-4.408449	-1.520298
C	-1.005742	-3.434121	-1.228871
H	-1.000922	-2.931542	-0.285406
C	-1.669294	-4.805375	-2.745866
H	-2.197888	-5.560083	-3.288266
N	-1.436627	-7.670689	2.522027
H	-1.495916	-8.438145	3.190950
C	-0.298941	-7.030231	2.109697
N	-2.077063	-6.161089	1.098072
C	-0.712423	-6.089595	1.227705
H	-0.133351	-5.385864	0.671133
C	-2.473475	-7.133052	1.886066
H	-3.474220	-7.498632	1.993444
N	-5.861708	-3.002965	2.132207
H	-6.214280	-2.708852	3.038620
C	-6.414299	-2.670174	0.927818
N	-4.684651	-4.044691	0.619721
C	-5.670982	-3.319448	-0.001911
H	-5.773880	-3.303477	-1.066077
C	-4.835021	-3.825126	1.901810
H	-4.225448	-4.232523	2.681579

N	-7.590427	-9.500962	1.349982
H	-7.352496	-10.350964	1.853685
C	-8.832176	-9.048621	0.982575
N	-7.256858	-7.881467	-0.051897
C	-8.608239	-8.040795	0.107001
H	-9.307652	-7.430024	-0.421604
C	-6.680389	-8.780004	0.705361
H	-5.627769	-8.931356	0.816828
N	-5.092492	-9.874665	-4.446719
H	-4.413376	-10.251708	-5.098914
C	-6.110960	-10.590216	-3.880521
N	-6.034054	-8.553456	-2.991558
C	-6.692600	-9.755043	-2.988051
H	-7.527247	-9.936854	-2.345690
C	-5.073017	-8.670650	-3.868894
H	-4.336989	-7.924891	-4.081249
N	-8.455808	-4.880063	-4.074619
H	-8.678377	-4.632404	-5.032193
C	-8.889766	-4.195012	-2.979727
N	-7.534809	-5.833788	-2.367467
C	-8.317205	-4.800381	-1.916790
H	-8.403522	-4.566314	-0.877529
C	-7.641988	-5.846616	-3.671751
H	-7.137007	-6.519866	-4.329328
CU	-6.144446	-6.920007	-1.421623
CU	-3.280344	-5.419840	-0.376946
O	-4.371210	-7.086291	-0.662647
O	-4.335714	-6.195662	-1.830912
H	0.667551	-2.608200	-2.452415
H	0.689934	-7.335666	2.451606
H	-7.223684	-1.946646	0.830497
H	-9.748306	-9.524795	1.331906
H	-6.246095	-11.647735	-4.107371
H	-9.565851	-3.344652	-3.068404

MECP

N	-0.570025	-4.136444	-3.297128
H	-0.157587	-4.299032	-4.207499
C	-0.139133	-3.235921	-2.367011
N	-1.927148	-4.308830	-1.607127
C	-0.992743	-3.348307	-1.324825
H	-1.003563	-2.811758	-0.400633
C	-1.642879	-4.757441	-2.804351
H	-2.167328	-5.520999	-3.337280
N	-1.422857	-7.690640	2.537657
H	-1.481664	-8.455215	3.208415
C	-0.285992	-7.056112	2.115996
N	-2.070146	-6.165221	1.126060
C	-0.704544	-6.107935	1.243169
H	-0.126524	-5.402808	0.686144
C	-2.463400	-7.135819	1.914302
H	-3.465818	-7.490007	2.037609
N	-5.938380	-3.007333	2.142113
H	-6.285140	-2.713920	3.051569
C	-6.487606	-2.661465	0.940835
N	-4.762993	-4.037325	0.621740
C	-5.743439	-3.300650	0.005430
H	-5.840459	-3.266831	-1.058505
C	-4.914251	-3.829975	1.905686
H	-4.305288	-4.247763	2.679717
N	-7.605841	-9.499552	1.374037
H	-7.364357	-10.345889	1.882055
C	-8.848168	-9.054317	1.001595
N	-7.277185	-7.889736	-0.038955
C	-8.627610	-8.052100	0.119906
H	-9.329447	-7.447514	-0.412868
C	-6.697295	-8.779708	0.726443
H	-5.644256	-8.927459	0.844550
N	-5.077283	-9.895833	-4.468300
H	-4.402666	-10.285179	-5.119422

C	-6.096028	-10.597581	-3.887089
N	-6.010424	-8.546011	-3.038019
C	-6.673789	-9.745684	-3.009097
H	-7.505046	-9.914633	-2.358468
C	-5.051530	-8.682210	-3.915950
H	-4.312253	-7.946547	-4.151308
N	-8.477619	-4.893712	-4.091880
H	-8.707207	-4.634580	-5.045132
C	-8.895063	-4.215083	-2.986372
N	-7.543993	-5.867292	-2.405706
C	-8.314655	-4.832808	-1.935290
H	-8.383938	-4.606084	-0.893102
C	-7.666483	-5.868219	-3.709029
H	-7.174310	-6.538733	-4.379157
CU	-6.197632	-6.987169	-1.471464
CU	-3.250562	-5.193991	-0.301043
O	-4.474034	-7.216214	-0.697242
O	-4.183159	-6.314416	-1.686748
H	0.733737	-2.599679	-2.513166
H	0.704473	-7.357650	2.456762
H	-7.287430	-1.927066	0.845921
H	-9.765081	-9.532203	1.346502
H	-6.238756	-11.656677	-4.101590
H	-9.566682	-3.360142	-3.064284

Section 6: Cartesian coordinates of the QM region (in Å) optimized by M06-2X

deoxyHc

N	-0.522716	-4.182608	-3.357014
H	-0.091793	-4.355161	-4.271291
C	-0.113544	-3.249449	-2.444043
N	-1.945073	-4.289100	-1.692422
C	-1.006120	-3.320933	-1.417622
H	-1.041069	-2.744130	-0.508876
C	-1.623803	-4.782995	-2.872103

H	-2.138355	-5.558639	-3.412356
N	-1.413899	-7.733830	2.540819
H	-1.464528	-8.487548	3.241366
C	-0.277458	-7.117358	2.079612
N	-2.082832	-6.247189	1.078585
C	-0.710098	-6.190821	1.173747
H	-0.137492	-5.493925	0.583827
C	-2.470525	-7.188899	1.916057
H	-3.480791	-7.523050	2.092109
N	-6.125440	-3.080765	2.139189
H	-6.484728	-2.783483	3.055134
C	-6.625709	-2.690334	0.924359
N	-4.896920	-4.079702	0.625275
C	-5.848745	-3.313973	-0.009063
H	-5.909755	-3.256130	-1.082833
C	-5.095347	-3.911013	1.919396
H	-4.514811	-4.359594	2.708669
N	-7.574180	-9.574594	1.542041
H	-7.347074	-10.465286	1.997830
C	-8.803444	-9.080071	1.176616
N	-7.176807	-7.856962	0.247886
C	-8.539689	-8.009940	0.372842
H	-9.224416	-7.343528	-0.124942
C	-6.632142	-8.823702	0.954083
H	-5.580865	-9.019233	1.082638
N	-5.056555	-9.942934	-4.479352
H	-4.420489	-10.313905	-5.194661
C	-5.989812	-10.691347	-3.809997
N	-5.857137	-8.657058	-2.899405
C	-6.487412	-9.880013	-2.836053
H	-7.249005	-10.083305	-2.101661
C	-4.999758	-8.734973	-3.895088
H	-4.320574	-7.961808	-4.211209
N	-8.465730	-4.715438	-4.106651
H	-8.724013	-4.478946	-5.068882

C	-8.898267	-4.044260	-2.998435
N	-7.465293	-5.642733	-2.410934
C	-8.279583	-4.639875	-1.941340
H	-8.354413	-4.418686	-0.890520
C	-7.606974	-5.662193	-3.719278
H	-7.096264	-6.322329	-4.399952
CU	-6.466906	-7.189738	-1.559334
CU	-3.179454	-4.911072	-0.134151
H	0.769257	-2.624972	-2.581005
H	0.713675	-7.406562	2.429018
H	-7.404548	-1.934396	0.824182
H	-9.736197	-9.561237	1.470755
H	-6.151535	-11.740324	-4.058111
H	-9.609100	-3.221989	-3.080008

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N	-0.622011	-4.061138	-3.275440
H	-0.212641	-4.165292	-4.212530
C	-0.192549	-3.186321	-2.312635
N	-1.918721	-4.367117	-1.543685
C	-1.009949	-3.381372	-1.239975
H	-1.011693	-2.890527	-0.281860
C	-1.658418	-4.752535	-2.783187
H	-2.182109	-5.515446	-3.334941
N	-1.430212	-7.664256	2.522715
H	-1.492181	-8.444015	3.194198
C	-0.284111	-7.030168	2.106509
N	-2.066728	-6.127496	1.108890
C	-0.696780	-6.071225	1.227753
H	-0.115147	-5.362430	0.665163
C	-2.474309	-7.108191	1.895561
H	-3.485737	-7.469088	2.001799
N	-5.915325	-3.056388	2.104627
H	-6.268073	-2.754729	3.020226
C	-6.463274	-2.709866	0.895642

N	-4.734546	-4.104474	0.581532
C	-5.718136	-3.368383	-0.042955
H	-5.815095	-3.348459	-1.116425
C	-4.887901	-3.891399	1.873699
H	-4.277583	-4.310558	2.657060
N	-7.576901	-9.516154	1.334362
H	-7.332214	-10.381817	1.831294
C	-8.824099	-9.052850	0.980877
N	-7.244895	-7.857994	-0.039113
C	-8.600128	-8.019653	0.118152
H	-9.301118	-7.390473	-0.402682
C	-6.659851	-8.779546	0.699684
H	-5.598463	-8.933862	0.806267
N	-5.097859	-9.861313	-4.436063
H	-4.416649	-10.246719	-5.096870
C	-6.117843	-10.579608	-3.861880
N	-6.039807	-8.530863	-2.972577
C	-6.700095	-9.736801	-2.961073
H	-7.536230	-9.914304	-2.305940
C	-5.074268	-8.647283	-3.859788
H	-4.333332	-7.894395	-4.070193
N	-8.443841	-4.844329	-4.071789
H	-8.673933	-4.596801	-5.038550
C	-8.887326	-4.159277	-2.974521
N	-7.523335	-5.800421	-2.353166
C	-8.312120	-4.767567	-1.901206
H	-8.398039	-4.535755	-0.852990
C	-7.622823	-5.815831	-3.667148
H	-7.106444	-6.492249	-4.326558
CU	-6.121223	-6.909136	-1.426033
CU	-3.259046	-5.417293	-0.406294
O	-4.327826	-7.090072	-0.684269
O	-4.313653	-6.202520	-1.867613
H	0.660920	-2.525046	-2.462217
H	0.703018	-7.348382	2.441747

H	-7.260932	-1.972650	0.804421
H	-9.738586	-9.531563	1.331042
H	-6.249790	-11.637367	-4.089487
H	-9.570577	-3.315245	-3.068571

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N	-0.628248	-4.068058	-3.268181
H	-0.218321	-4.173415	-4.204920
C	-0.200746	-3.190374	-2.306974
N	-1.927093	-4.370834	-1.537583
C	-1.019864	-3.383074	-1.235178
H	-1.022741	-2.890296	-0.278060
C	-1.664343	-4.759681	-2.775524
H	-2.186081	-5.526193	-3.324292
N	-1.435779	-7.660257	2.523211
H	-1.494573	-8.440025	3.194980
C	-0.292092	-7.022897	2.105444
N	-2.079174	-6.124642	1.110674
C	-0.708963	-6.065076	1.227122
H	-0.129987	-5.354891	0.663462
C	-2.482355	-7.106977	1.897751
H	-3.492115	-7.471645	2.006529
N	-5.926195	-3.064018	2.099399
H	-6.274213	-2.762120	3.016890
C	-6.475763	-2.710536	0.893310
N	-4.758921	-4.117214	0.569642
C	-5.738739	-3.371464	-0.049846
H	-5.838834	-3.347029	-1.123010
C	-4.905840	-3.905666	1.863285
H	-4.295446	-4.331195	2.643082
N	-7.562065	-9.514761	1.327840
H	-7.319302	-10.381974	1.823393
C	-8.808495	-9.049149	0.974290
N	-7.226166	-7.851431	-0.038233
C	-8.581973	-8.012407	0.116251

H	-9.281371	-7.380960	-0.404096
C	-6.643171	-8.777152	0.697088
H	-5.581985	-8.935243	0.801317
N	-5.097900	-9.860810	-4.431739
H	-4.416757	-10.246404	-5.092039
C	-6.118891	-10.578297	-3.858190
N	-6.040906	-8.528600	-2.969916
C	-6.701327	-9.734402	-2.958192
H	-7.538463	-9.911340	-2.304261
C	-5.074439	-8.646294	-3.855925
H	-4.331978	-7.894370	-4.064329
N	-8.433818	-4.847331	-4.068713
H	-8.664878	-4.602927	-5.036051
C	-8.880954	-4.161673	-2.973134
N	-7.504972	-5.791374	-2.347568
C	-8.300806	-4.762633	-1.898560
H	-8.388739	-4.529187	-0.850905
C	-7.606014	-5.812184	-3.661635
H	-7.086558	-6.488650	-4.318612
CU	-6.099257	-6.895590	-1.418839
CU	-3.276801	-5.419511	-0.407628
O	-4.294439	-7.129714	-0.709823
O	-4.272572	-6.250298	-1.897734
H	0.651028	-2.527152	-2.457588
H	0.695741	-7.341161	2.438553
H	-7.269698	-1.968676	0.807413
H	-9.723039	-9.526704	1.325883
H	-6.250003	-11.636165	-4.085767
H	-9.565946	-3.319169	-3.068216

MECP

N	-0.558110	-4.094895	-3.313236
H	-0.141613	-4.245683	-4.237447
C	-0.134196	-3.180782	-2.387682
N	-1.917944	-4.268435	-1.612702

C	-0.989243	-3.294979	-1.336344
H	-1.003373	-2.750700	-0.409153
C	-1.631392	-4.727447	-2.816015
H	-2.156895	-5.502922	-3.346647
N	-1.423605	-7.670375	2.524371
H	-1.489353	-8.446391	3.198307
C	-0.274683	-7.045277	2.104315
N	-2.054635	-6.125468	1.111241
C	-0.684431	-6.082315	1.227378
H	-0.098584	-5.374996	0.666015
C	-2.465153	-7.099924	1.899744
H	-3.479725	-7.446326	2.018252
N	-6.003533	-3.057152	2.120466
H	-6.352089	-2.756218	3.038409
C	-6.545712	-2.698387	0.913731
N	-4.815613	-4.086770	0.591649
C	-5.794765	-3.342890	-0.029021
H	-5.882556	-3.302856	-1.102492
C	-4.974185	-3.887564	1.885351
H	-4.365332	-4.313562	2.665969
N	-7.590296	-9.511894	1.361161
H	-7.346909	-10.375352	1.862729
C	-8.835570	-9.052212	0.998048
N	-7.252363	-7.865684	-0.024696
C	-8.608706	-8.026058	0.128436
H	-9.308001	-7.402045	-0.400871
C	-6.670235	-8.781555	0.724886
H	-5.609892	-8.939177	0.839594
N	-5.088592	-9.885687	-4.452910
H	-4.412003	-10.277154	-5.116454
C	-6.105995	-10.596609	-3.867031
N	-6.021831	-8.539688	-3.000306
C	-6.683822	-9.745176	-2.972373
H	-7.516988	-9.915566	-2.311419
C	-5.060674	-8.666434	-3.891909

H	-4.320200	-7.919233	-4.122573
N	-8.463123	-4.867478	-4.075876
H	-8.696957	-4.613099	-5.040376
C	-8.892625	-4.182117	-2.973088
N	-7.528492	-5.829083	-2.369149
C	-8.309297	-4.794033	-1.906623
H	-8.381937	-4.563220	-0.857308
C	-7.642449	-5.842441	-3.682725
H	-7.136656	-6.520127	-4.348832
CU	-6.152337	-6.957449	-1.449743
CU	-3.208239	-5.162515	-0.302571
O	-4.359072	-7.198031	-0.715777
O	-4.243679	-6.310666	-1.788197
H	0.741764	-2.548344	-2.531846
H	0.710356	-7.361658	2.447343
H	-7.333968	-1.950845	0.824840
H	-9.751488	-9.531471	1.343697
H	-6.243903	-11.654916	-4.088470
H	-9.571286	-3.333703	-3.060716

Section 7: Cartesian coordinates of the QM region (in Å) optimized by CAM-B3LYP

deoxyHc

N	-0.550713	-4.167067	-3.302750
H	-0.138739	-4.357522	-4.218727
C	-0.124547	-3.218828	-2.414969
N	-1.935917	-4.245824	-1.607911
C	-0.993032	-3.271041	-1.372884
H	-1.009759	-2.677518	-0.475401
C	-1.640114	-4.759344	-2.784958
H	-2.163271	-5.544181	-3.302783
N	-1.435734	-7.708676	2.521261
H	-1.505050	-8.469302	3.210346
C	-0.284022	-7.104863	2.082581
N	-2.059539	-6.190744	1.073356

C	-0.687367	-6.162150	1.187130
H	-0.094183	-5.469604	0.615667
C	-2.473458	-7.136789	1.891758
H	-3.491679	-7.454123	2.048908
N	-6.036528	-3.030335	2.167127
H	-6.418913	-2.743491	3.075518
C	-6.530029	-2.658211	0.944191
N	-4.756466	-3.992743	0.676184
C	-5.723624	-3.257485	0.026938
H	-5.772065	-3.203585	-1.046476
C	-4.980315	-3.828559	1.965705
H	-4.398403	-4.255990	2.764662
N	-7.586594	-9.564570	1.525005
H	-7.346160	-10.437885	2.002806
C	-8.827762	-9.088563	1.176757
N	-7.238176	-7.904569	0.147609
C	-8.595178	-8.053161	0.327706
H	-9.298989	-7.412039	-0.174328
C	-6.667619	-8.835575	0.879346
H	-5.612299	-9.019942	0.984427
N	-5.059003	-9.953417	-4.457596
H	-4.406682	-10.298136	-5.168978
C	-5.985774	-10.732598	-3.816558
N	-5.912626	-8.718330	-2.867464
C	-6.514736	-9.955802	-2.839043
H	-7.281223	-10.192034	-2.122668
C	-5.038569	-8.757105	-3.849958
H	-4.372459	-7.962624	-4.137668
N	-8.467249	-4.738924	-4.140007
H	-8.726277	-4.476592	-5.094188
C	-8.885711	-4.092027	-3.012837
N	-7.484835	-5.733844	-2.476976
C	-8.276731	-4.725536	-1.977666
H	-8.341971	-4.528461	-0.922227
C	-7.627882	-5.710773	-3.783702

H	-7.131095	-6.357231	-4.485655
CU	-6.606496	-7.283297	-1.642493
CU	-3.108879	-4.834523	-0.062427
H	0.763155	-2.604821	-2.566787
H	0.700674	-7.408158	2.438182
H	-7.328941	-1.925472	0.830616
H	-9.753146	-9.575589	1.484225
H	-6.134608	-11.778035	-4.086702
H	-9.586318	-3.259151	-3.072290

^{1}3

N	-0.639354	-4.071641	-3.268033
H	-0.228695	-4.173871	-4.202847
C	-0.217520	-3.196206	-2.302945
N	-1.942123	-4.383865	-1.542972
C	-1.037875	-3.393806	-1.237598
H	-1.043826	-2.901405	-0.280833
C	-1.674454	-4.765353	-2.778992
H	-2.189861	-5.527401	-3.337077
N	-1.437422	-7.678751	2.529596
H	-1.493370	-8.451256	3.207339
C	-0.297481	-7.042320	2.102668
N	-2.087683	-6.164688	1.098554
C	-0.717796	-6.099263	1.216406
H	-0.139779	-5.393035	0.648620
C	-2.484954	-7.134974	1.899556
H	-3.492824	-7.497016	2.022505
N	-5.892313	-3.030170	2.126734
H	-6.251971	-2.736499	3.040757
C	-6.430796	-2.676116	0.916592
N	-4.699982	-4.063266	0.604965
C	-5.677745	-3.320145	-0.018085
H	-5.769760	-3.290071	-1.090196
C	-4.862966	-3.860639	1.895674

H	-4.259138	-4.284736	2.680621
N	-7.569999	-9.516223	1.345854
H	-7.331430	-10.378567	1.847731
C	-8.813457	-9.051226	0.983757
N	-7.227088	-7.882033	-0.051520
C	-8.583479	-8.033772	0.110629
H	-9.283202	-7.409244	-0.416039
C	-6.650631	-8.793985	0.701451
H	-5.592739	-8.956112	0.814876
N	-5.079380	-9.881179	-4.461887
H	-4.403301	-10.271233	-5.124389
C	-6.096477	-10.591326	-3.875424
N	-5.997428	-8.542862	-2.991649
C	-6.663329	-9.745526	-2.974126
H	-7.495536	-9.920728	-2.314845
C	-5.045665	-8.667329	-3.889063
H	-4.305864	-7.920858	-4.121973
N	-8.443127	-4.860634	-4.083125
H	-8.675614	-4.608997	-5.046932
C	-8.882320	-4.181898	-2.981005
N	-7.507637	-5.817170	-2.374873
C	-8.299829	-4.789520	-1.916613
H	-8.383522	-4.558774	-0.869142
C	-7.616679	-5.828239	-3.685880
H	-7.103754	-6.499339	-4.351078
CU	-6.157676	-6.927611	-1.437490
CU	-3.262052	-5.379340	-0.365822
O	-4.360053	-7.059437	-0.702736
O	-4.332279	-6.175628	-1.816346
H	0.632950	-2.530670	-2.450692
H	0.693433	-7.351469	2.435207
H	-7.236182	-1.947982	0.820461
H	-9.731354	-9.524918	1.331823
H	-6.238796	-11.649167	-4.096296
H	-9.563128	-3.335034	-3.066967

^{3}**3**

N	-0.639799	-4.076448	-3.265410
H	-0.226796	-4.182718	-4.198607
C	-0.219965	-3.196936	-2.303208
N	-1.955539	-4.372106	-1.546735
C	-1.048337	-3.384355	-1.242083
H	-1.057762	-2.885650	-0.288580
C	-1.681072	-4.762608	-2.778096
H	-2.194521	-5.527668	-3.333964
N	-1.446115	-7.670845	2.528727
H	-1.498217	-8.445126	3.204578
C	-0.309132	-7.030257	2.100267
N	-2.105586	-6.154324	1.102727
C	-0.735205	-6.086205	1.217129
H	-0.160153	-5.377872	0.648714
C	-2.496812	-7.127679	1.902777
H	-3.502664	-7.493964	2.029326
N	-5.918384	-3.047532	2.117506
H	-6.268462	-2.751778	3.034763
C	-6.460461	-2.683720	0.912096
N	-4.747529	-4.088421	0.585027
C	-5.720070	-3.331165	-0.029775
H	-5.816700	-3.292012	-1.101139
C	-4.899788	-3.887833	1.878141
H	-4.294906	-4.320510	2.657419
N	-7.554089	-9.516255	1.342541
H	-7.317882	-10.382799	1.838597
C	-8.796121	-9.046414	0.981367
N	-7.204054	-7.866693	-0.035763
C	-8.561573	-8.019422	0.120279
H	-9.259302	-7.388363	-0.401459
C	-6.631818	-8.788348	0.708414
H	-5.574548	-8.955895	0.821122
N	-5.086683	-9.877161	-4.465539

H	-4.410606	-10.268514	-5.127101
C	-6.101917	-10.586559	-3.875108
N	-6.003667	-8.534848	-2.997196
C	-6.667848	-9.738394	-2.975085
H	-7.498592	-9.912749	-2.313781
C	-5.053660	-8.661541	-3.896092
H	-4.314502	-7.915662	-4.132489
N	-8.431784	-4.851218	-4.078586
H	-8.666773	-4.606422	-5.043505
C	-8.875448	-4.170023	-2.979682
N	-7.483336	-5.788524	-2.365908
C	-8.286064	-4.766494	-1.912882
H	-8.371891	-4.531432	-0.866694
C	-7.595651	-5.808687	-3.676808
H	-7.079156	-6.480252	-4.338685
CU	-6.136883	-6.906676	-1.427274
CU	-3.290218	-5.357351	-0.364043
O	-4.311623	-7.125790	-0.759998
O	-4.251434	-6.256472	-1.858914
H	0.632853	-2.534474	-2.451241
H	0.682900	-7.339674	2.429206
H	-7.259869	-1.948214	0.822398
H	-9.714887	-9.519082	1.328527
H	-6.243877	-11.644914	-4.093739
H	-9.561760	-3.327951	-3.068885

MECP

N	-0.588254	-4.069268	-3.323431
H	-0.191771	-4.200946	-4.262077
C	-0.138000	-3.172682	-2.391074
N	-1.875910	-4.294438	-1.583824
C	-0.948956	-3.318523	-1.315968
H	-0.923231	-2.790834	-0.376745
C	-1.633327	-4.720895	-2.801904
H	-2.172703	-5.488685	-3.328964

N	-1.433673	-7.649185	2.546085
H	-1.513074	-8.436069	3.204752
C	-0.272550	-7.044807	2.128145
N	-2.033220	-6.060093	1.168988
C	-0.660977	-6.060414	1.276189
H	-0.052933	-5.362103	0.729049
C	-2.462251	-7.038578	1.942908
H	-3.482578	-7.358299	2.063499
N	-5.905615	-2.989853	2.186818
H	-6.274268	-2.687770	3.094428
C	-6.454275	-2.676888	0.970604
N	-4.684294	-4.021616	0.688857
C	-5.684089	-3.320271	0.047684
H	-5.770220	-3.322224	-1.024619
C	-4.851125	-3.793347	1.978096
H	-4.231719	-4.180267	2.771303
N	-7.611882	-9.489300	1.441727
H	-7.357657	-10.343497	1.951452
C	-8.864185	-9.068090	1.060944
N	-7.304637	-7.895599	-0.009286
C	-8.656213	-8.078421	0.155079
H	-9.377007	-7.495736	-0.393679
C	-6.710090	-8.763299	0.773083
H	-5.647491	-8.895614	0.895295
N	-5.064344	-9.906285	-4.494558
H	-4.380831	-10.300836	-5.149361
C	-6.083650	-10.614627	-3.910628
N	-6.011266	-8.554215	-3.061326
C	-6.670104	-9.761538	-3.032704
H	-7.509674	-9.939618	-2.381784
C	-5.047004	-8.684899	-3.942118
H	-4.308024	-7.940832	-4.183092
N	-8.521923	-4.886307	-4.133843
H	-8.747614	-4.592386	-5.090944
C	-8.942275	-4.231465	-3.010603

N	-7.660092	-5.955797	-2.465939
C	-8.405224	-4.912160	-1.969545
H	-8.493522	-4.722243	-0.913876
C	-7.753582	-5.907822	-3.771565
H	-7.268271	-6.571217	-4.467742
CU	-6.255071	-7.007036	-1.526122
CU	-3.219946	-5.132403	-0.290607
O	-4.580613	-7.120708	-0.752426
O	-4.189563	-6.071380	-1.595105
H	0.734385	-2.537802	-2.545797
H	0.708148	-7.378705	2.466982
H	-7.262286	-1.954068	0.857842
H	-9.776051	-9.559457	1.400245
H	-6.223400	-11.674107	-4.125198
H	-9.599162	-3.363875	-3.072683

Section 8: The magnetic orbitals for the non-bridged superoxo intermediate ^{3}2a

The two singly occupied molecular orbitals (MOs) in spin-restricted open-shell Kohn-Sham calculations correspond to the two lowest unoccupied ß-spin MOs, i.e., LUMO and LUMO+1, obtained in UDFT calculations, as previously described for mononuclear CuO_2 model complexes. These magnetic orbitals consist of the superoxide π^*_v orbital (LUMO) and the Cu d_{xy} orbital, with the latter showing some antibonding interaction with the superoxide π^*_σ orbital (LUMO+1), as depicted in Figure S2.

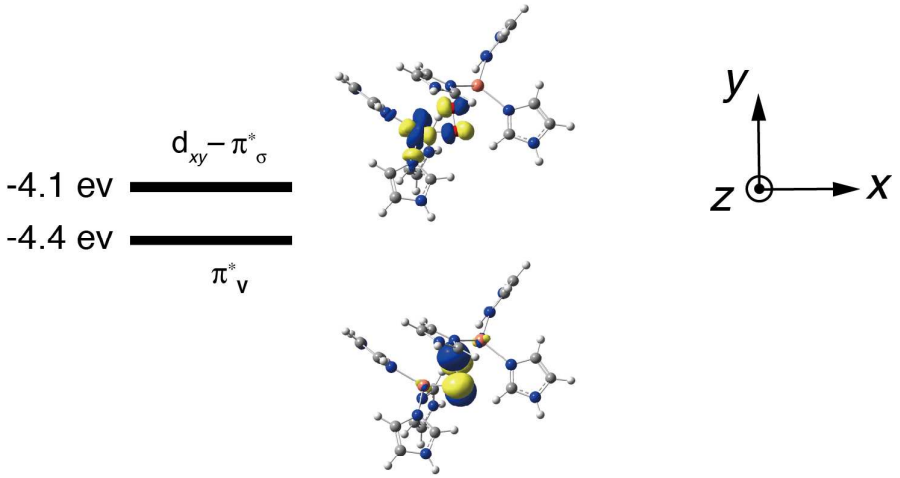

Figure S2 The magnetic orbitals of non-bridged superoxo intermediate (^{3}**2a**).

Section 9: Total energies at the minimum-energy crossing point (MECP)

Method	$E^{S\,a}$	$E^{T\,a}$	$\lvert\Delta E\rvert^{\,b}$
UB3LYP	-5000.163566	-5000.163539	0.027
UBH&HLYP	-4999.028225	-4999.028189	0.032
UM06-2X	-4999.384765	-4999.384740	0.025
UCAM-B3LYP	-4999.559635	-4999.559675	0.040

[a] In E_h.

[b] In mE_h.

Section 10: Full citations for references 14, 59, 61, and 82.

[14] Funahashi, Y.; Nishikawa, T.; Wasada-Tsutsui, Y.; Kajita, Y.; Yamaguchi, S.; Arii, H.; Ozawa, T.; Jitsukawa, K. Tosha, T.; Hirota, S.; Kitagawa, T.; Masuda, H. Formation of a Bridged Butterfly-Type $\mu{:}\eta^2{-}\eta^2$-Peroxo Dicopper Core Structure with a Carboxylate Group. *J. Am. Chem. Soc*. **2008**, *130*, 16444-16445.

[59] Sherwood, P.; de Vries, A. H.; Guest, M. F.; Schreckenbach, G.; Catlow, C. R. C.; French, S. A.; Sokol, A. A.; Bromley, S. T.; Thiel, W.; Turner, A. J.; Billeter, S.; Terstegen, F.; Thiel, S.; Kendrck, J.; Rogers, S. C.; Casci, J.; Watson, M.; King, F.; Karlsen, E.; Sjøvoll, M.; Fahmi, A.; Schäfer, A.; Lennartz, C. QUASI: A General Purpose Implementation of the QM/MM Approach and its Application to Problems in Catalysis. *J. Mol. Struct. (THEOCHEM)* **2003**, *632*, 1-28.

[61] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision B.01; Gaussian, Inc.: Wallingford CT, 2009.

[82] Woertink, J. S.; Tian, L.; Maiti, D.; Lucas, H. R.; Himes, R. A.; Karlin, K. D.; Neese, F.; Würtele, C.; Holthausen, M. C.; Bill, E.; Sundermeyer, J. Schindler, S.; Solomon, E. I. Spectroscopic and Computational Studies of an End-on Bound Superoxo-Cu(II) Complex: Geometric and Electronic Factors That Determine the Ground State. *Inorg. Chem*. **2010**, *49*, 9450-9459.