

Electronic Supplementary Information

ONIOM investigations of heme degradation mechanism by MhuD: the critical function of heme ruffling

Chang Yuan,^a Ying Zhang,^a Hongwei Tan,^{*a} Xichen Li,^a Guangju Chen,^{*a} Zongchao Jia^b

^aCollege of Chemistry, Beijing Normal University, Beijing 100875, China

^bDepartment of Biomedical and Molecular Sciences, Queen's University, Kingston, Ontario, Canada K7N3L6

E-mail: hongwei.tan@bnu.edu.cn

Table of Contents

1 Computational Details	S2
Cluster model details of INT3 and RE4 in Scheme 1	S2
Cluster model details of RE2 in canonical HOs	S2
2 Schemes	S2
Scheme S1 The mechanism of heme degradation by HOs	S2
Scheme S2 Formation of oxoheme	S3
3 Figures	S3
Figure S1 The highest singly occupied Kohn-Sham orbital (SOMO) of ² INT1	S3
Figure S2 The optimized structures of the α -INT1, β -INT1 and γ -INT1	S3
Figure S3 The optimized structures of the Fe ^{III} -heme-MhuD _{R26S} complex	S4
Figure S4 QM/MM calculated energy profile of MhuD-catalysed heme monooxygenation with unprotonated peroxy species as an initial oxidant	S4
Figure S5 Energy profile for heme oxidation through surrogate pathway in MhuD	S5
Figure S6 The optimized structures of INT3 _{QM} and RE4 _{QM}	S6
Figure S7 The optimized structures of varying degree of ruffling Fe ^{II} -heme-O ₂ and ruffling Fe ^{II} -oxoheme-O ₂ complexes	S6
Figure S8 Optimized structures of the δ -RE2, γ -RE2 and β -RE2	S7
Figure S9 Optimized structure of RE2 in canonical HOs, in which the δ -oxoheme suffers ruffling distortion. -	S7
4 Tables	S8
Table S1 Mulliken spin population of the stationary points along the surrogate pathway of the heme oxidation in MhuD.	S8
Table S2 The porphyrin distortion degree of all stationary points in heme degradation process in MhuD	S8
Table S3 The energies of QM/MM(full system) and MM(QM-system) in heme degradation process by MhuD.	S8
5 Cartesian coordinates	S9

1 Computational Details

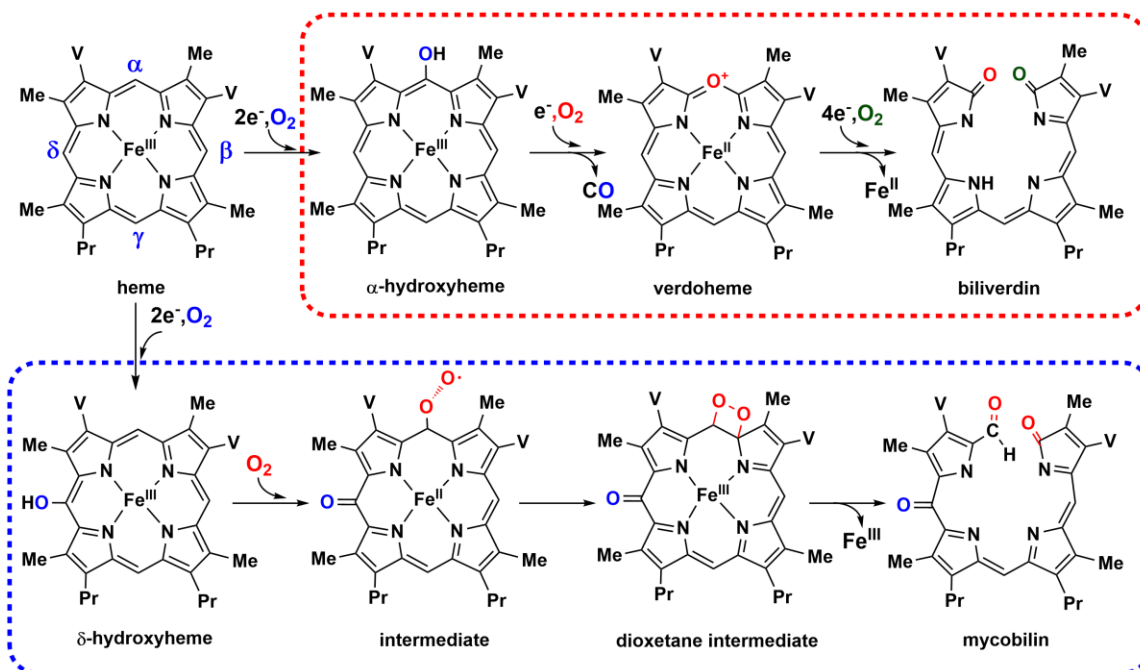
Cluster model details of INT3_{QM} and RE4_{QM} in Scheme 1

Based on the X-ray structure of MhuD, the QM models of the intermediate INT3_{QM} and RE4_{QM} are consisted of δ -oxoheme (including all side chains) with His75 as the axial ligand, the only polar residue Asn7 above the δ -meso carbon, and the dioxygen which coordinates with the iron center in INT3_{QM} or attacks on the two carbon atoms side to the keto group in RE4_{QM}.

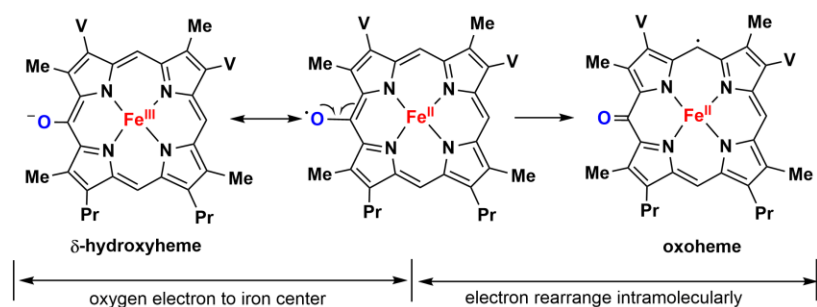
Cluster model details of RE2 in canonical HOs

The cluster model of the RE2 in canonical HOs includes planar oxoheme with His75 as the axial ligand and the dioxygen was added to α -meso carbon artificially.

2 Schemes



Scheme S1 The mechanisms of heme degradation by canonical HOs (in red box) and by MhuD (in blue box). Some less important hydrogen atoms are hidden for clarity. V = Vinyl, Me = Methyl, Pr = Propionate.



Scheme S2 Formation of the oxoheme, which means a ferrous π radical complex formed by hydroxyheme further experiencing deprotonation in the hydroxyl group and intramolecular electron transfer.

3 Figures

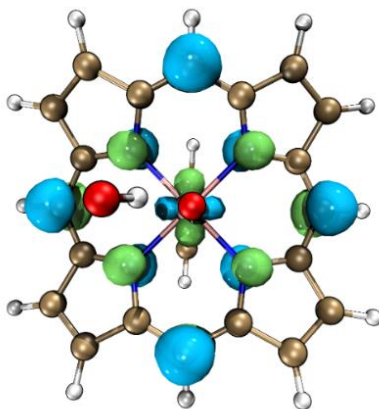


Figure S1 The highest singly occupied Kohn-Sham orbital (SOMO) of $^2\text{INT1}$, in which the orbital is composed solely of the p_z atomic orbitals from the four isolated meso-carbons.

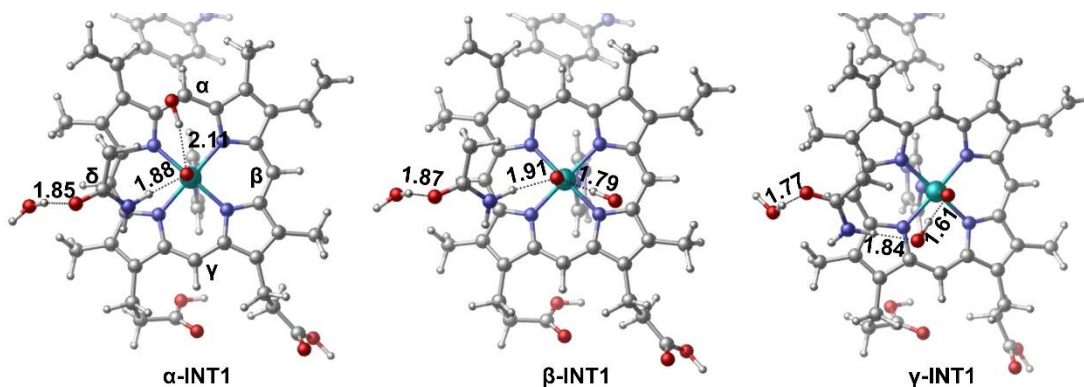


Figure S2 The optimized structures of the $\alpha\text{-INT1}$, $\beta\text{-INT1}$ and $\gamma\text{-INT1}$, which are represented as ball and stick mode, with ferric, carbon, oxygen, nitrogen and hydrogen atoms colored cyan, gray, red, blue and white, respectively (unit for distances is angstrom).

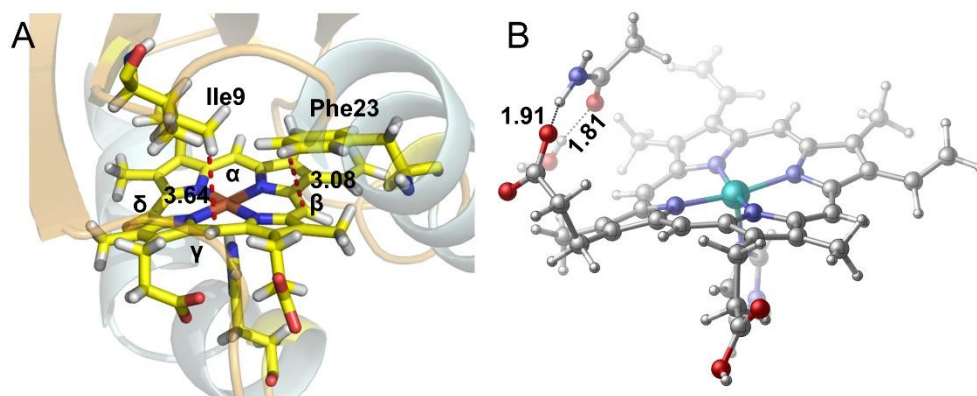


Figure S3 The hydrophobic Ile9 located on the γ -meso carbon (A) hinders the OH radical to react on it. And the optimized structures of the Fe^{III}-heme-MhuD_{R26S} complex (B), in which the propionate group (nearby δ - and γ - position) of heme turns over and forms hydrogen bond with Asn7 (unit for distances is angstrom).

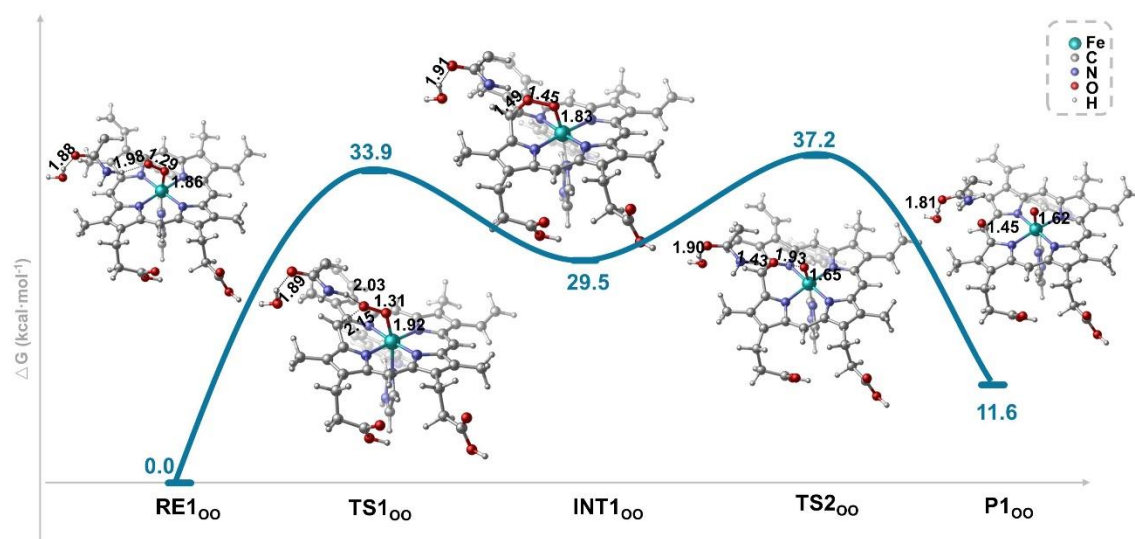


Figure S4 QM/MM calculated energy profile of MhuD-catalysed heme monoxygenation with unprotonated peroxy species as an initial oxidant in the doublet state. The key structure information of the stationary points along the reaction pathway of heme hydroxylation by MhuD are shown (Å).

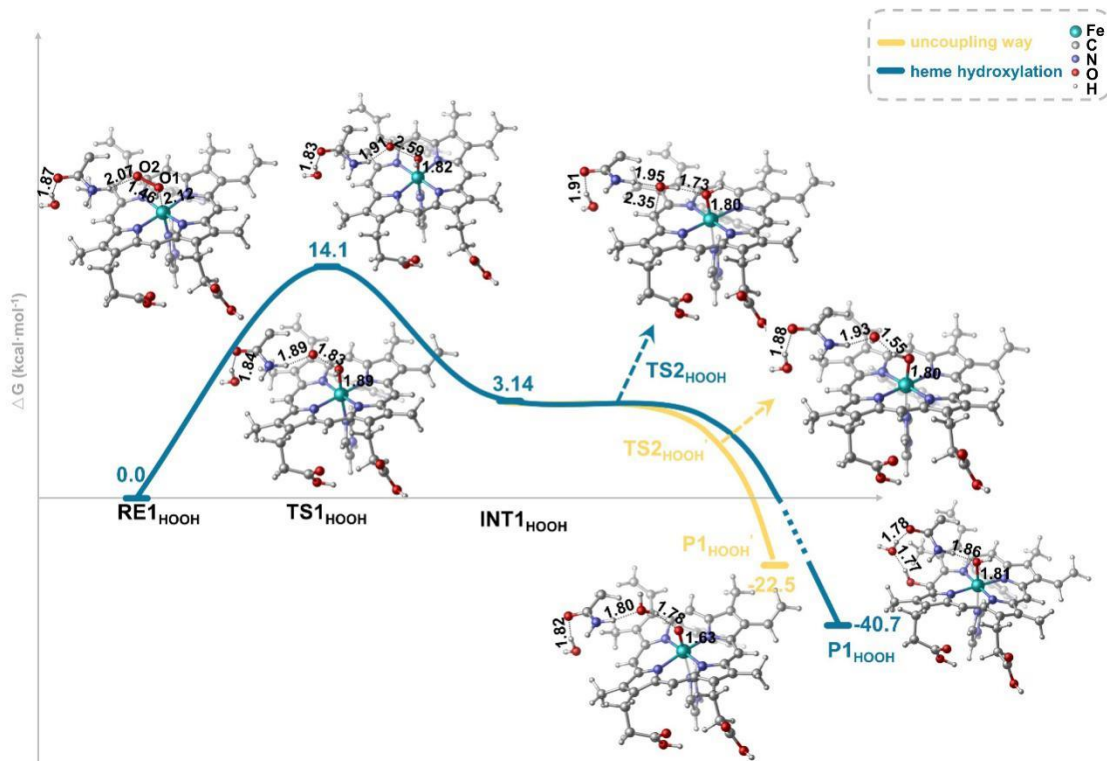


Figure S5 QM/MM calculated energy profiles of MhuD-catalysed heme oxidation through the energetically lowest spin states (doublet state) surrogate pathway. The key structure information of the stationary points along the reaction pathway of heme hydroxylation by MhuD are shown (Å). Some less important hydrogen atoms are hidden for clarity.

Surrogate heme degradation pathway with H₂O₂ as the oxidant

Experimentally, the heme surrogate oxidation reaction by hydrogen peroxide (H₂O₂) in MhuD is shown to mainly form the ferryl heme plus water whereas small amounts hydroxyheme¹. Figure S5 shows the energetically lowest spin states (doublet state) energy profile for the heme surrogate hydroxylation catalytic step, in which the rate-determining step remains O-O bond homolysis with 14.1 kcal/mol energy barrier. The subsequent hydrogen abstraction from Fe-bound hydroxyl by the floating OH radical was found to be a barrierless process. The absence of barrier is attributed to the broad and flat shoulder shape in the potential energy surface of MhuD close to the O-O bond homolysis transition state region. Therefore, the uncoupling pathway competes with the heme hydroxylation pathway after formation of the hydroxyl radical. There was experimental evidence that the ordered water network in the distal pocket of HOs plays the role of not only stabilizing and guiding the OH radical to react on the meso carbon but also suppressing the pathway that leads to ferryl heme². The disappearance of such nearby water network is correlated with the increase in the ferryl heme formation. Considering that MhuD has a hydrophobic heme binding pocket, it is therefore not strange that it mainly affords the ferryl heme in reaction with H₂O₂.

- 1 T. Matsui, S. Nambu, C. W. Goulding, S. Takahashi, H. Fujii and M. Ikeda-Saito, *Proc. Natl. Acad. Sci.*, 2016, **113**, 3779–3784.
- 2 M. Matsui, Toshitaka, Furukawa, *J. Biol. Chem.*, 2005, **280**, 2981–2989.

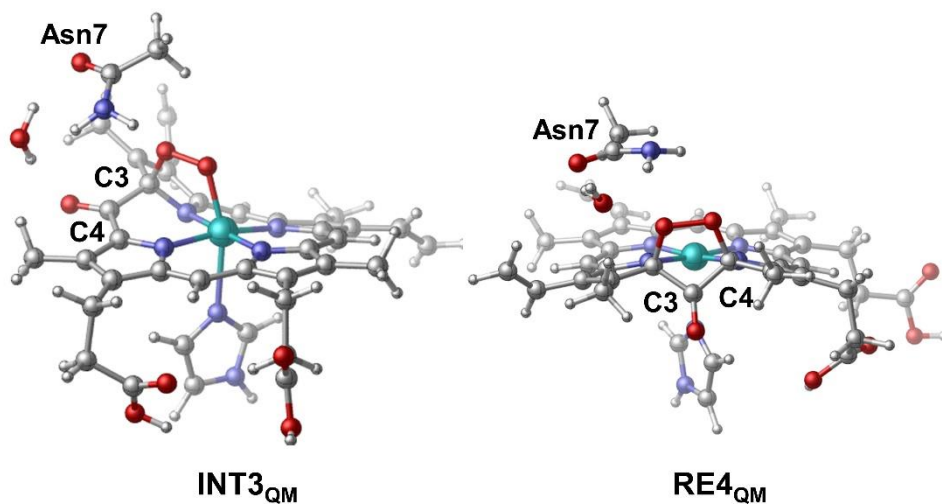


Figure S6 Optimized cluster models of INT3_{QM} and RE4_{QM}, which are represented as ball and stick mode, with ferric, carbon, oxygen, nitrogen and hydrogen atoms colored cyan, gray, red, blue and white, respectively.

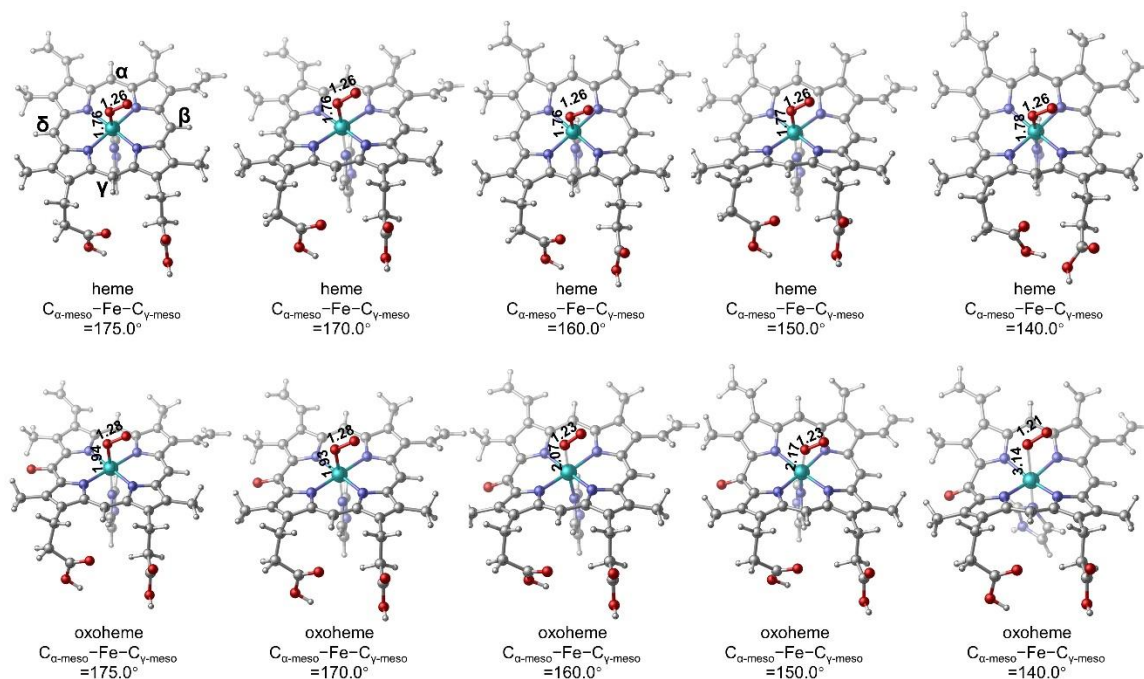


Figure S7 The optimized structures of varying degree of ruffling Fe^{II}-heme-O₂ and ruffling Fe^{II}-oxoheme-O₂ complexes by restricting the C_{α-meso}-Fe-C_{γ-meso} angle (unit for distances is angstrom).

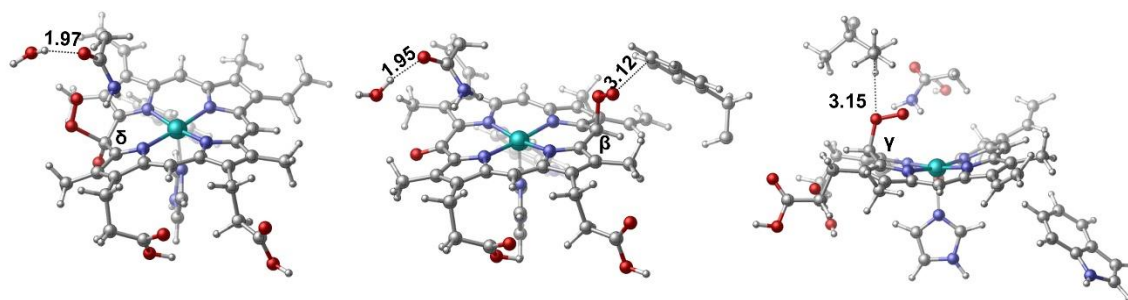


Figure S8 Optimized structures of the δ -RE2, γ -RE2 and β -RE2, which are represented as ball and stick mode, with ferric, carbon, oxygen, nitrogen and hydrogen atoms colored cyan, gray, red, blue and white, respectively (unit for distances is angstrom).

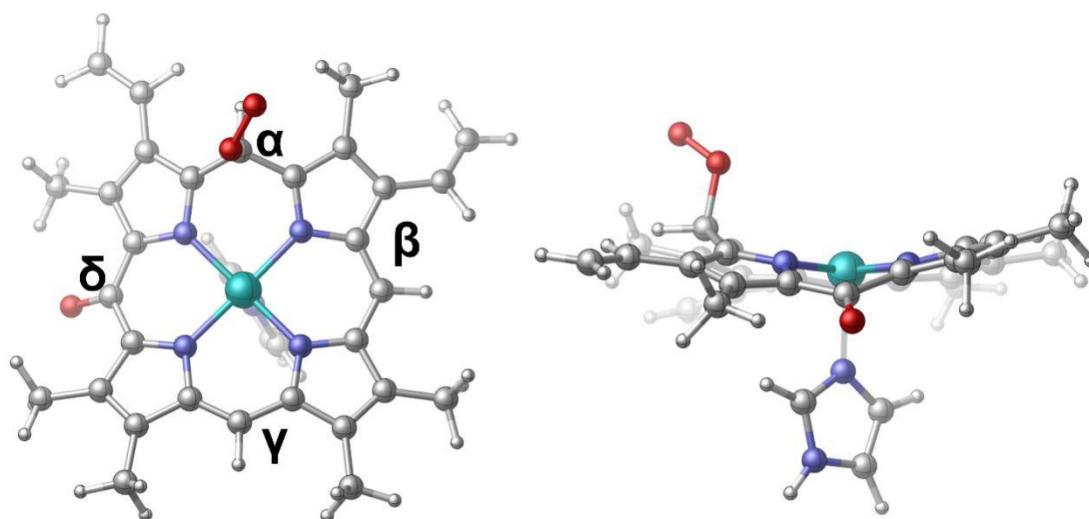


Figure S9 Optimized structure of RE2 in canonical HOs, in which the δ -oxoheme suffers ruffling distortion.

4 Tables

Table S1 Mulliken spin population of the stationary points along the surrogate pathway of the heme hydroxylation in MhuD.

	Fe	O1H	O2H	His75	porphyrin
² RE1 _{HOOH}	1.06	-0.01	0.00	-0.01	-0.04
² TS1 _{HOOH}	0.95	-0.11	-0.48	0.00	0.49
² INT1 _{HOOH}	1.00	-0.18	-0.71	0.00	0.74
² TS2 _{HOOH}	0.88	-0.41	0.01	0.00	0.51
² P1 _{HOOH}	1.01	0.08	0.00	-0.02	-0.06
uncoupling way					
² TS2 _{HOOH'}	1.01	-0.25	-0.62	-0.02	0.73
² P1 _{HOOH'}	1.32	0.77	0.01	-0.02	-0.89

Table S2 The porphyrin ruffled distortion degree of all stationary points in heme degradation process in MhuD by Normal-Coordinate Structural Decomposition analysis (Å).

	RE1	TS1	INT1	TS2	P1	oxoheme	RE2	TS3	INT2	TS4	P2
Ruffling	1.27	0.97	0.96	0.17	0.93	1.04	1.63	1.87	1.95	1.77	0.61

Table S3 The energies of QM/MM (full system) and MM (QM-system) in heme degradation process by MhuD.

		QM/MM (full system) (kcal/mol)			QM system (kcal/mol)		
		Doublet	Quartet	Sextet	Doublet	Quartet	Sextet
monooxygenation process	RE1	0.0	18.1	5.0	0.0	15.3	2.5
	TS1	22.1	23.0	35.0	21.2	22.1	33.2
	INT1	17.5	17.6	27.6	16.0	16.1	25.6
	TS2	22.0	40.5	41.2	19.2	17.9	38.5
	P1	-7.6	-7.8	1.1	-8.0	-8.3	-0.6
dioxygenation process	oxoheme +O ₂	0.0	—	—	0.0	—	—
	RE2	15.6	7.3	7.8	18.1	9.6	10.1
	TS3	31.3	19.6	28.5	32.9	20.4	29.3
	INT2	14.2	0.8	10.5	18.8	5.3	15.6
	TS4	29.7	16.1	19.1	32.5	17.9	17.9
	P2	-52.8	-71.4	-60.7	-57.0	-75.9	-63.9

5 Cartesian coordinates

The first heme hydroxylation process

²RE1

C	0.00000000	0.88141024	0.00000000	H	-3.12084400	-4.36952676	-2.57745700
H	0.71753600	0.08329024	-0.23199400	C	-2.50012200	-3.25583676	0.14269400
H	-0.25215500	0.82399324	1.06192300	C	-1.14680100	-3.37268776	-0.15448400
C	-1.21131200	0.68174524	-0.90015500	H	-0.86572200	-3.41662076	-1.20081800
O	-1.20387800	1.01707024	-2.09428600	C	-0.11650700	-3.26969876	0.77294800
N	-2.27125300	0.09562824	-0.31358300	N	-0.29310100	-3.18992976	2.13767400
H	-3.03404700	-0.21308776	-0.89927000	C	1.27989800	-3.12411976	0.42876500
H	-2.21319300	-0.24779476	0.64663200	C	1.82054600	-3.21820276	-0.96709500
H	-11.11767100	-4.61809276	5.72891200	H	1.44774500	-2.41323876	-1.61292600
C	5.97446500	-9.10211276	3.86179500	H	2.91339700	-3.19214576	-0.96840700
C	5.55337500	-9.74146276	4.99760600	H	1.51046200	-4.15985276	-1.43908500
H	6.01953500	-10.54669976	5.54851900	C	1.95125300	-2.92416676	1.61872900
N	4.34575100	-9.21743776	5.42838000	C	3.36656400	-2.64502576	1.84689400
H	3.93064500	-9.44759176	6.31791300	H	3.81251200	-3.07596976	2.74314400
C	3.98887500	-8.17522876	4.59571400	C	4.15302100	-1.89044076	1.06691600
C	2.91105700	-7.28418076	4.65162700	H	3.79158300	-1.38388276	0.17741100
H	2.17267000	-7.34269576	5.44574300	H	5.19512500	-1.74387576	1.32514600
C	2.83458600	-6.30563376	3.66555300	C	0.95666000	-3.02440176	2.67809400
H	2.03553200	-5.57328176	3.69910200	C	1.23156400	-3.00929076	4.04283900
C	3.80106900	-6.21739776	2.64065800	H	2.26462400	-2.87107276	4.32987800
H	3.70723500	-5.45076576	1.87904900	C	0.31225500	-3.22991976	5.06505900
C	4.87270300	-7.09851976	2.59487100	N	-1.03572600	-3.40962276	4.88109400
H	5.62136600	-7.03318576	1.80609700	C	0.65158100	-3.32901376	6.47313400
C	4.98380700	-8.09386676	3.58117100	C	2.02341100	-3.17323576	7.05212100
C	-3.03514200	-7.32242576	2.64106400	H	2.79259000	-3.61102276	6.40534600
N	-1.69199900	-7.40419076	2.96423000	H	2.28337300	-2.11670976	7.20033900
H	-1.15799400	-8.26915776	3.00283700	H	2.08855900	-3.65912176	8.03040200
C	-1.21319400	-6.14963576	3.15571700	C	-0.52640500	-3.59776276	7.13562400
H	-0.18389900	-5.93201376	3.39232200	C	-0.77757400	-3.84458776	8.55278800
N	-2.18185100	-5.26660176	2.98717600	H	-1.58581200	-4.54524076	8.76456700
C	-3.31583000	-5.98165876	2.66567100	C	-0.12545300	-3.31537876	9.59854700
H	-4.25416500	-5.49155976	2.46354800	H	0.67491700	-2.59168776	9.47917300
FE	-2.04782100	-3.18499476	3.14607900	H	-0.37254000	-3.59655876	10.61854200
N	-3.02368900	-3.09689776	1.39972200	C	-1.56985800	-3.60729876	6.11987400
C	-4.35829400	-2.84449276	1.23728000	C	-2.92894900	-3.60859476	6.40952500
C	-4.70131500	-2.85409676	-0.17929500	H	-3.20847400	-3.69666476	7.45270500
C	-6.06699200	-2.62613576	-0.76505700	C	-3.94143600	-3.32580276	5.49951700
H	-5.96338800	-2.13589476	-1.73993000	N	-3.76679100	-3.17938176	4.15293000
H	-6.63934600	-1.94441676	-0.13195000	C	-5.32334500	-3.06882976	5.85957300
C	-6.90226200	-3.91679776	-0.97219300	C	-5.90085000	-3.11949276	7.24327200
H	-6.32897900	-4.65515276	-1.53962000	H	-5.14908800	-2.88602276	8.00459700
H	-7.80419800	-3.66136576	-1.54004700	H	-6.70660000	-2.38690976	7.34987300
C	-7.34433500	-4.49951276	0.35579900	H	-6.32663400	-4.10376376	7.48529500
O	-6.82554300	-5.70443676	0.59930900	C	-5.97345300	-2.75660376	4.69470700
O	-8.08057900	-3.89542676	1.11922600	C	-4.98486800	-2.83683676	3.63409000
C	-3.54452100	-3.14241776	-0.85904100	C	-5.26203700	-2.66045376	2.28224100
C	-3.33854500	-3.32009176	-2.33416100	H	-6.28651200	-2.43715576	2.01700600
H	-4.23222700	-3.03795576	-2.89940800	C	-7.44008300	-2.50771976	4.54147100
H	-2.49507700	-2.72456776	-2.70638900	H	-7.65820200	-1.87166976	3.68000600
				H	-7.80166700	-1.96226876	5.41992700
				C	-8.21376900	-3.84137376	4.43140400
				H	-7.73428900	-4.62023976	5.03272500
				H	-8.20206500	-4.19476076	3.39337100
				C	-9.63974800	-3.68634976	4.87746400

O	-10.18121000	-4.82346376	5.34896900	C	-7.73599769	-4.07066881	0.57601400
O	-10.24449500	-2.62907376	4.83393300	O	-7.23119469	-5.29077281	0.76393600
O	-2.08859600	-1.41337376	3.38029300	O	-8.45061569	-3.48791781	1.37565500
O	-1.45171900	-0.63053376	2.34767900	C	-3.97299769	-2.64791981	-0.58589900
H	-0.67006600	-1.18321776	2.14380600	C	-3.77838069	-2.79483081	-2.06588200
O	-0.46509000	-1.47586776	-3.17259800	H	-4.66471769	-2.46722181	-2.61793600
H	-0.68209000	-0.53902176	-2.98115300	H	-2.91659769	-2.22394881	-2.43318600
H	-0.11927600	-1.47241276	-4.07871400	H	-3.60110969	-3.84556481	-2.33575000
H	-7.06709400	-6.03026876	1.51508200	C	-2.92467269	-2.78680881	0.40791400
H	-3.70518392	-8.12710810	2.42099549	C	-1.57657869	-2.90793681	0.09328200
H	6.85953755	-9.30928646	3.29732566	H	-1.30742169	-2.93574281	-0.95661200
				C	-0.53758969	-2.82339881	1.00977500
				N	-0.69967669	-2.74590581	2.37535200
²TS1				C	0.85627631	-2.68670681	0.65478500
C	-0.19230769	1.33012819	0.00000000	C	1.38473731	-2.79676981	-0.74394300
H	0.54913131	0.58921719	-0.32604100	H	0.99900031	-2.00419481	-1.39714300
H	-0.40215469	1.16760119	1.06160400	H	2.47727031	-2.76315881	-0.75518200
C	-1.42156269	1.15991819	-0.87788900	H	1.07671931	-3.74762981	-1.19882200
O	-1.40629669	1.45282319	-2.08487500	C	1.53807631	-2.48304981	1.83749300
N	-2.50446369	0.66159619	-0.25622700	C	2.95953531	-2.21901181	2.04914700
H	-3.30905369	0.41356019	-0.81371800	H	3.41494631	-2.66396781	2.93361900
H	-2.44089769	0.36618019	0.72484000	C	3.73930631	-1.46639881	1.26083300
H	-11.52462669	-4.22430181	5.94830400	H	3.36428331	-0.94830681	0.38373700
C	5.59759331	-8.69668281	3.97953600	H	4.78848131	-1.33165081	1.49775000
C	5.17690131	-9.34129481	5.11254500	C	0.55428631	-2.57778281	2.90504600
H	5.64229031	-10.15037081	5.65846300	C	0.84130131	-2.56800081	4.26455100
N	3.97039031	-8.81830481	5.54755000	H	1.87326931	-2.41246181	4.54572400
H	3.55275031	-9.05762681	6.43354400	C	-0.06724269	-2.81769181	5.28873700
C	3.61298031	-7.77214181	4.72033300	N	-1.41059269	-3.03155881	5.11038400
C	2.53790731	-6.87814981	4.78413800	C	0.28168331	-2.93161381	6.69231600
H	1.80264631	-6.93838281	5.58103500	C	1.65280531	-2.74346981	7.26339100
C	2.46149131	-5.89330981	3.80427400	H	2.42823631	-3.16531481	6.61345800
H	1.66580031	-5.15744281	3.84659300	H	1.88838031	-1.68037281	7.40461400
C	3.42489231	-5.80279781	2.77670000	H	1.73564331	-3.22410681	8.24268000
H	3.32969631	-5.03293181	2.01851000	C	-0.88446269	-3.24590581	7.35589200
C	4.49451931	-6.68616581	2.72367400	C	-1.12128669	-3.52873081	8.76926900
H	5.24138731	-6.61828981	1.93344200	H	-1.90189269	-4.26308181	8.97069400
C	4.60656331	-7.68688181	3.70454700	C	-0.48335669	-2.99524981	9.82116100
C	-3.41271769	-6.92827981	2.80952200	H	0.29146931	-2.24308281	9.70998700
N	-2.07630369	-7.01837481	3.16061500	H	-0.71352169	-3.30406581	10.83713500
H	-1.54358469	-7.88471881	3.18933800	C	-1.93479369	-3.26092181	6.34824300
C	-1.59933869	-5.76751281	3.38023100	C	-3.29036969	-3.28641881	6.64998600
H	-0.57428869	-5.55726581	3.64199600	H	-3.55691569	-3.38937081	7.69495500
N	-2.56057769	-4.87833381	3.20380900	C	-4.31812869	-3.00267881	5.75814100
C	-3.68855769	-5.58700381	2.84730100	N	-4.17366969	-2.86043981	4.40720300
H	-4.62211169	-5.09228181	2.63416600	C	-5.68878369	-2.73016581	6.14270700
FE	-2.45585469	-2.73325581	3.41481300	C	-6.23153569	-2.76163181	7.54032700
N	-3.44457669	-2.66297281	1.67109000	H	-5.46735369	-2.48750281	8.27500900
C	-4.78122169	-2.40962381	1.51859100	H	-7.05167369	-2.04624181	7.64586800
C	-5.12679269	-2.37880481	0.10428300	H	-6.62567369	-3.74909381	7.82002000
C	-6.49380169	-2.14224081	-0.47313300	C	-6.35821569	-2.40787981	4.99031100
H	-6.39454069	-1.60789781	-1.42525800	C	-5.39297369	-2.48817181	3.91215500
H	-7.07600169	-1.49855781	0.18944400	C	-5.68151369	-2.26662081	2.57035800
C	-7.30787969	-3.43623181	-0.73239400	H	-6.70703369	-2.03368081	2.31916400
H	-6.72441869	-4.14447681	-1.32714400	C	-7.82394469	-2.15040081	4.85319200
H	-8.21488069	-3.17527381	-1.28974800				

H	-8.04403969	-1.47943581	4.01930200	C	-8.07345576	-3.01176611	-0.00831900
H	-8.18419669	-1.64078381	5.75331800	H	-7.97186076	-2.44990211	-0.94457100
C	-8.59843269	-3.47755181	4.68878100	H	-8.65852876	-2.38901811	0.67128000
H	-8.13839869	-4.27255881	5.28384200	C	-8.88431576	-4.29955011	-0.30688700
H	-8.56118769	-3.80382181	3.64249100	H	-8.29451176	-4.99279811	-0.91286700
C	-10.03390269	-3.31650681	5.09957800	H	-9.78675576	-4.02685711	-0.86590700
O	-10.58854969	-4.44589781	5.57283100	C	-9.32196976	-4.96327311	0.98361200
O	-10.63257869	-2.25703081	5.03065100	O	-8.81553676	-6.18613911	1.14910000
O	-2.54764769	-1.12167381	3.70770500	O	-10.04414676	-4.39836511	1.78925900
O	-1.56602869	0.05118019	2.31668900	C	-5.55545476	-3.51832911	-0.12844700
H	-1.26653269	-0.87579481	2.35035400	C	-5.36294776	-3.64594211	-1.60968500
O	-0.82363269	-1.12855881	-3.00442800	H	-6.24953976	-3.31041811	-2.15616700
H	-0.99131969	-0.16990281	-2.87431200	H	-4.49977776	-3.07606011	-1.97325500
H	-0.36051269	-1.19026581	-3.85427900	H	-5.18913576	-4.69389511	-1.89236300
H	-7.46706069	-5.64333681	1.67212400	C	-4.50869676	-3.67742411	0.86228400
H	-4.08045500	-7.72741526	2.56373870	C	-3.16230176	-3.79522411	0.54984200
H	6.48229586	-8.90124180	3.41353511	H	-2.88714176	-3.79195211	-0.49913100

2INT1

C	-2.01923076	0.27243589	0.00000000	N	-2.28538376	-3.74581411	2.83923300
H	-1.30605076	-0.45916111	-0.39462400	C	-0.73689576	-3.58523311	1.11926300
H	-2.28445876	0.00463489	1.02737200	C	-0.21268076	-3.65855911	-0.28319600
C	-3.21415176	0.30829689	-0.93852200	H	-0.60118976	-2.85390711	-0.91904200
O	-3.06800976	0.49166889	-2.15540400	H	0.87954524	-3.61976011	-0.29664200
N	-4.42297176	0.16892989	-0.36201200	H	-0.51870476	-4.59917011	-0.76017900
H	-5.23592376	0.10660589	-0.95752400	C	-0.05388476	-3.41664111	2.30381900
H	-4.48774876	-0.05557911	0.63226700	C	1.36894124	-3.15628911	2.51029100
H	-13.10611276	-5.30141211	6.29203200	H	1.83878524	-3.63287411	3.37067000
C	3.97232624	-9.71787411	4.31876900	C	2.13666324	-2.38041911	1.73174100
C	3.53169424	-10.36314711	5.44412600	H	1.74371124	-1.83230911	0.88104400
H	3.98070424	-11.18111311	5.99075100	H	3.19290324	-2.25983611	1.94392000
N	2.33248424	-9.82004211	5.87442300	C	-1.03768576	-3.56580611	3.36974200
H	1.90376224	-10.05681311	6.75559100	C	-0.74330676	-3.59547111	4.72692900
C	2.00127524	-8.76030711	5.05328000	H	0.28851324	-3.44424511	5.00735700
C	0.93792724	-7.85185511	5.11108100	C	-1.64814776	-3.87569611	5.74470800
H	0.19329924	-7.90561111	5.89978600	N	-2.99043976	-4.08469211	5.55561700
C	0.88442424	-6.86227211	4.13434700	C	-1.30555276	-4.01675311	7.14612500
H	0.09613224	-6.11823711	4.16746100	C	0.06296824	-3.83825311	7.72627700
C	1.85958324	-6.77975411	3.11730500	H	0.84091024	-4.24717111	7.07126600
H	1.78429324	-6.00261411	2.36404300	H	0.29732324	-2.77775311	7.88730300
C	2.91667724	-7.67829511	3.06955600	H	0.14268224	-4.33638911	8.69723500
H	3.67136524	-7.61756111	2.28612300	C	-2.47580276	-4.34142611	7.79826000
C	3.00460524	-8.68527411	4.04654500	C	-2.71828176	-4.65393011	9.20445600
C	-5.00557576	-7.91087711	3.15499600	H	-3.49307576	-5.39928511	9.38741600
N	-3.66204576	-8.00624411	3.47557500	C	-2.08933176	-4.13576711	10.26927600
H	-3.12997276	-8.87339411	3.48368200	H	-1.32251676	-3.37312511	10.17478100
C	-3.18379976	-6.76004911	3.71664700	H	-2.31949976	-4.46649311	11.27832300
H	-2.15405876	-6.55292511	3.96210200	C	-3.52108776	-4.33325511	6.78608100
N	-4.15023576	-5.86929411	3.58174700	C	-4.87777076	-4.35443811	7.08193400
C	-5.28359776	-6.57135211	3.23081800	H	-5.14952976	-4.48815411	8.12200300
H	-6.22199476	-6.07306811	3.04862700	C	-5.89758676	-4.03409511	6.19485900
FE	-4.01540276	-3.71643511	3.86141000	N	-5.74518176	-3.83758111	4.84946500
N	-5.02734476	-3.58196111	2.12834300	C	-7.27041576	-3.78145411	6.58491000
C	-6.36341876	-3.32175911	1.97931800	C	-7.82256376	-3.86477711	7.97738600
C	-6.70823776	-3.26180611	0.56633200	H	-7.05393476	-3.66202211	8.73006100
				H	-8.61346976	-3.12236111	8.11786700

H	-8.25996476	-4.84815711	8.20117500	C	-4.16830358	-7.18684885	3.68400329
C	-7.93848976	-3.42168611	5.44297700	H	-5.11872858	-6.70272385	3.52962829
C	-6.96909276	-3.45824111	4.36681100	FE	-2.94322458	-4.29739985	4.35269029
C	-7.26310576	-3.20142811	3.03286500	N	-4.00771158	-4.13305385	2.64505329
H	-8.28985976	-2.96546311	2.78939000	C	-5.37360258	-4.02354085	2.51280329
C	-9.40769676	-3.17234611	5.31308100	C	-5.72831158	-3.82812385	1.11176129
H	-9.63405476	-2.47002211	4.50703100	C	-7.11235058	-3.72631185	0.53750729
H	-9.77319576	-2.70450011	6.23405100	H	-7.07358258	-3.11045685	-0.36788071
C	-10.17017176	-4.49879611	5.09086900	H	-7.78150358	-3.22199885	1.23864229
H	-9.71903076	-5.30817111	5.67260600	C	-7.74690158	-5.09114185	0.17234929
H	-10.10610276	-4.78988011	4.03583900	H	-7.05537258	-5.70201185	-0.41471171
C	-11.61829176	-4.36226711	5.46692100	H	-8.64654258	-4.91458685	-0.42946671
O	-12.16242776	-5.50259111	5.92785500	C	-8.17106258	-5.82586785	1.42734429
O	-12.23615476	-3.31528411	5.38238500	O	-7.66040958	-7.05148685	1.53576029
O	-3.94702276	-2.11271511	4.12798500	O	-8.89789358	-5.30951985	2.26104529
O	-3.76629676	-0.21752711	2.35128300	C	-4.54962558	-3.76565485	0.42116229
H	-3.72569676	-1.02178311	2.95065700	C	-4.33067358	-3.62791885	-1.05328171
O	-2.37617776	-2.16128811	-2.71716200	H	-5.25643358	-3.35510785	-1.56800771
H	-2.50212976	-1.18863511	-2.72173400	H	-3.56737258	-2.88348285	-1.29761071
H	-1.75131776	-2.34143411	-3.43639700	H	-3.98241658	-4.57266185	-1.49240671
H	-9.05018876	-6.55995111	2.04814900	C	-3.49700958	-3.89903785	1.40997629
H	-5.67671838	-8.70556622	2.90412394	C	-2.14433158	-3.64689685	1.13178529
H	4.85582206	-9.93629783	3.75607352	H	-1.90127958	-3.38360285	0.10969729

²TS2

C	-0.72109758	-0.06415885	0.00860029	N	-1.19771558	-4.22316085	3.31060529
H	0.01958942	-0.71903785	-0.45942671	C	0.31716942	-3.72740285	1.62471429
H	-0.99707258	-0.46623185	0.98451329	C	0.84117242	-3.41907385	0.25568429
C	-1.90320558	0.02088215	-0.93907571	H	1.29345442	-2.42027885	0.22109129
O	-1.75528358	0.20320515	-2.15443871	H	1.63035842	-4.13043985	-0.02462171
N	-3.12365458	-0.07450185	-0.36105171	H	0.06861942	-3.44095685	-0.51621471
H	-3.91836558	-0.14787385	-0.98161471	C	1.04645242	-3.92829285	2.78083029
H	-3.18766258	-0.50611185	0.56575529	C	2.48783542	-3.89224285	2.97983729
H	-12.09594458	-5.99973885	6.60399229	H	2.85612242	-4.36762685	3.88679229
C	5.12458342	-10.36935785	4.55426929	C	3.41589442	-3.35650485	2.16796329
C	4.69150142	-11.03527485	5.66976829	H	3.18268042	-2.84160385	1.24431329
H	5.14997442	-11.85525285	6.20523829	H	4.46602642	-3.40611585	2.43718429
N	3.48206442	-10.51692885	6.10300329	C	0.07441642	-4.21342185	3.82762029
H	3.06834442	-10.75656485	6.99054029	C	0.38511142	-4.38408385	5.16645229
C	3.13998742	-9.44912885	5.29665929	H	1.43013642	-4.33672985	5.43856129
C	2.06562542	-8.55491185	5.36373729	C	-0.52249058	-4.59428885	6.20032029
H	1.31925942	-8.62892285	6.14924929	N	-1.88037958	-4.69397285	6.03906129
C	2.00211042	-7.55470785	4.39851929	C	-0.15370058	-4.75739285	7.58947529
H	1.20288042	-6.82336985	4.43881629	C	1.23595442	-4.65360485	8.13734329
C	2.97791542	-7.44543785	3.38477729	H	1.98270742	-5.06216885	7.44712129
H	2.89766942	-6.65618585	2.64508829	H	1.51431842	-3.60928185	8.33176429
C	4.04597542	-8.32996785	3.32852629	H	1.32284742	-5.19093185	9.08697529
H	4.80185942	-8.25104885	2.54798729	C	-1.32874258	-5.00010685	8.27059629
C	4.14328842	-9.34777785	4.29277529	C	-1.55563658	-5.29594385	9.68246929
C	-3.87259758	-8.52083585	3.57346629	H	-2.37961058	-5.97937885	9.88892829
N	-2.52102558	-8.60132385	3.86352129	C	-0.85649358	-4.83152385	10.72807129
H	-1.97403158	-9.45898585	3.83498229	H	-0.03682358	-4.12973085	10.61017929
C	-2.05798558	-7.35144485	4.12077929	H	-1.08248658	-5.14354485	11.74384829
H	-1.02690858	-7.13503585	4.35175129	C	-2.38990258	-4.92899485	7.28142629
N	-3.03933458	-6.47085885	4.02624229	C	-3.74184658	-4.92947585	7.60348829
				H	-3.99325258	-5.05986285	8.64868929

C	-4.78288358	-4.65797585	6.73129629	C	-4.40176356	-7.40796021	2.31013200
N	-4.66013958	-4.48973685	5.37529029	N	-3.06840056	-7.48109121	2.67585800
C	-6.15925458	-4.46802885	7.14017229	H	-2.53428256	-8.34456621	2.74380300
C	-6.67846858	-4.52435485	8.54570829	C	-2.59516456	-6.22159021	2.84628300
H	-5.87861658	-4.38215285	9.27767129	H	-1.57089656	-5.99615921	3.09997300
H	-7.40944058	-3.72804785	8.71315329	N	-3.55794356	-5.34325521	2.62542700
H	-7.17675358	-5.47676385	8.77371629	C	-4.68234556	-6.06742621	2.29198200
C	-6.86489058	-4.18700785	5.99904629	H	-5.61435156	-5.58204421	2.05088700
C	-5.91314458	-4.21348985	4.91036529	FE	-3.40023056	-3.18534321	2.64173200
C	-6.25936358	-4.02146185	3.57232529	N	-4.38903456	-3.29210121	0.88176100
H	-7.30608158	-3.871115785	3.34842229	C	-5.70881856	-2.89111321	0.70083300
C	-8.33857058	-3.96723985	5.87872629	C	-6.04481156	-2.97982621	-0.69351500
H	-8.57491258	-3.21510085	5.12130929	C	-7.39578056	-2.70283521	-1.29211000
H	-8.71350658	-3.56739985	6.82828129	H	-7.27486056	-2.27856521	-2.29415000
C	-9.08517658	-5.28036485	5.55750529	H	-7.92125956	-1.95184621	-0.69874300
H	-8.68982558	-6.10798285	6.15277029	C	-8.30628156	-3.95413521	-1.42267100
H	-8.94205758	-5.54661085	4.50353929	H	-7.79285556	-4.73734821	-1.98676600
C	-10.55652258	-5.12241785	5.81596629	H	-9.21475056	-3.66816521	-1.96479800
O	-11.14395358	-6.23873185	6.28109829	C	-8.72500456	-4.47985821	-0.06354800
O	-11.15341258	-4.07306985	5.64817829	O	-8.22068756	-5.68714521	0.20379800
O	-2.92935758	-2.68879785	4.58015629	O	-9.43078456	-3.83936121	0.69944600
O	-2.51378158	-1.59322985	1.88951129	C	-4.92176256	-3.46687221	-1.34826400
H	-2.62781158	-1.86126585	2.82845429	C	-4.83347856	-3.78935221	-2.81587000
O	-1.34049058	-2.58910985	-2.52069071	H	-4.14431356	-3.12103521	-3.34244100
H	-1.34844758	-1.61338885	-2.61156371	H	-4.46891556	-4.80706921	-2.98401300
H	-0.55439658	-2.87837585	-3.00973371	H	-5.81783156	-3.69743521	-3.28601300
H	-7.91363658	-7.44741485	2.42348329	C	-3.91812356	-3.63007821	-0.33036600
H	-4.53699892	-9.32034360	3.31997423	C	-2.53433556	-4.20718521	-0.53550400
H	6.01234151	-10.56776343	3.99086819	H	-2.58817956	-5.26316421	-0.21392900
				C	-1.46341556	-3.57188621	0.32706600
				N	-1.65854456	-3.38401421	1.64685300
				C	-0.12113856	-3.25025421	-0.05780900
				C	0.52805344	-3.41017821	-1.40475300
				H	0.21615444	-4.33768521	-1.88877400
				H	1.61739144	-3.41543121	-1.29874400
				H	0.26216644	-2.59485121	-2.08924400
				C	0.51626744	-2.83756421	1.11626000
				C	1.88599144	-2.38915821	1.32033700
				H	2.33003844	-2.62297321	2.28846800
				C	2.64786644	-1.69623821	0.46030400
				H	2.30092544	-1.37143121	-0.51464300
				H	3.65556544	-1.41702121	0.74231400
				C	-0.44708756	-2.97001821	2.17673700
				C	-0.18242356	-2.87303321	3.53543400
				H	0.83463544	-2.63244421	3.81642900
				C	-1.07387856	-3.15066821	4.57057300
				N	-2.41953656	-3.35506821	4.38229900
				C	-0.73547056	-3.27446321	5.96991200
				C	0.63368644	-3.14270221	6.56110500
				H	1.40403444	-3.56568321	5.90651800
				H	0.68828944	-3.66382421	7.52144700
				H	0.89670344	-2.09403221	6.75191400
				C	-1.91392656	-3.57196221	6.62855400
				C	-2.16497956	-3.85276521	8.03860700
				H	-2.97937956	-4.55243421	8.23121200

2P1

C	-1.51016956	-3.35891721	9.10077000	H	0.96973031	-8.14127136	5.12955800
H	-0.70141256	-2.64064521	9.00593600	C	1.68723931	-7.21531736	3.30840400
H	-1.76006156	-3.67013121	10.11139900	H	0.86254631	-6.51207236	3.24900400
C	-2.95452256	-3.57267621	5.61558400	C	2.69639131	-7.17223936	2.32325000
C	-4.31813956	-3.57292721	5.89819100	H	2.61697631	-6.46288336	1.50582800
H	-4.60930556	-3.66457021	6.93780700	C	3.78709231	-8.03026336	2.38604200
C	-5.31814656	-3.26810121	4.97552800	H	4.56725831	-8.00021736	1.62643900
N	-5.12790956	-3.14025421	3.62861000	C	3.87774331	-8.95411036	3.44321200
C	-6.69271856	-2.98862921	5.31717600	C	-4.21479369	-8.43546336	2.40396800
C	-7.28740856	-3.03136421	6.69416800	N	-2.84781569	-8.52637236	2.58175100
H	-7.66584956	-4.02933821	6.95906500	H	-2.33315969	-9.39463036	2.70356900
H	-8.13170856	-2.33883421	6.77028300	C	-2.32975869	-7.27224436	2.60764400
H	-6.55931956	-2.73925621	7.45938100	H	-1.27293269	-7.07086736	2.70037400
C	-7.33185556	-2.68319321	4.13778500	N	-3.29112369	-6.37952336	2.46273700
C	-6.33793656	-2.77658621	3.09597900	C	-4.46436469	-7.08903636	2.33553100
C	-6.58741956	-2.60736921	1.73537700	H	-5.41301069	-6.59520736	2.19392400
H	-7.59553856	-2.32814821	1.45883700	FE	-3.07129869	-4.14921636	2.35513100
C	-8.80464356	-2.47951921	3.97060800	N	-4.29400569	-4.10704036	0.76616200
H	-9.04186556	-1.93040321	3.05650700	C	-5.63681869	-3.72432036	0.74862700
H	-9.18452656	-1.87220721	4.79764900	C	-6.15364369	-3.84196936	-0.60570200
C	-9.54021056	-3.83979621	3.98373900	C	-7.56862969	-3.57868236	-1.02578100
H	-8.99689756	-4.57472021	4.58710400	H	-7.57954569	-3.15464936	-2.03599800
H	-9.58565456	-4.24699721	2.96750300	H	-8.01517069	-2.83642736	-0.36370500
C	-10.93490456	-3.71253121	4.52755100	C	-8.46732169	-4.84708336	-1.02590700
O	-11.43579556	-4.86594921	5.00260900	H	-8.01955769	-5.62763736	-1.64655200
O	-11.55186156	-2.66168721	4.55106300	H	-9.44440269	-4.58004036	-1.44280800
O	-3.29291656	-1.55900221	2.59146100	C	-8.68571269	-5.35470236	0.38679200
O	-2.18043156	-4.27575321	-1.89621500	O	-8.13062869	-6.55462336	0.60269700
H	-2.09137756	-3.36982421	-2.27103900	O	-9.27705569	-4.70843636	1.23462700
O	-2.04919856	-1.82248821	-3.23092300	C	-5.12631369	-4.32344936	-1.38131200
H	-2.25646156	-0.91520921	-2.90486700	C	-5.12282669	-4.58328336	-2.85803900
H	-1.42260456	-1.71768521	-3.96249800	H	-6.03991469	-4.20598336	-3.32228000
H	-8.43352856	-5.98833421	1.13218100	H	-4.26622269	-4.09278636	-3.33578200
H	-5.06524754	-8.21819636	2.09057248	H	-5.02805369	-5.65048936	-3.07949300
H	5.48597697	-9.37770102	2.97776879	C	-4.00361069	-4.48670236	-0.47757400

Hydroxyheme to mycobilin in MhuD

⁴RE2

C	-0.81730769	0.01602564	0.00000000	C	0.20932531	-4.93088436	-2.13866200
H	-0.01376769	-0.72542036	-0.10098800	H	0.27532231	-4.04056036	-2.77977900
H	-1.12941169	-0.00098136	1.04806800	H	1.19487431	-5.41279636	-2.14527300
C	-1.94556169	-0.38380836	-0.93260700	H	-0.51694369	-5.60680136	-2.58806900
O	-2.21224969	0.21884964	-1.97707000	C	0.62267231	-4.02711836	0.28127700
N	-2.64908169	-1.48424836	-0.54012000	C	2.01527931	-3.60009236	0.22245300
H	-3.18070669	-1.94318436	-1.27066900	H	2.48237931	-3.36563636	1.17792600
H	-2.23356869	-2.11336036	0.13921800	C	2.76088531	-3.38570636	-0.87387500
H	-12.04363869	-5.37439136	5.12893100	H	2.39610831	-3.53937436	-1.88162400
C	4.87225231	-9.92410936	3.83553500	H	3.77369931	-3.00979536	-0.77679500
C	4.41260531	-10.48917536	4.99643600	C	-0.21507469	-3.87956836	1.41455500
H	4.86450631	-11.25159036	5.61606200	C	0.22409531	-3.41038336	2.74681000
N	3.18311431	-9.95330936	5.34184600	H	1.29829131	-3.53625036	2.87019800
H	2.71299631	-10.14932136	6.21127200	C	-0.51068069	-3.92424936	3.93511500
C	2.84236931	-8.98307936	4.42053200	N	-1.84745969	-4.02592036	3.93412600
C	1.74326931	-8.11743836	4.36714000	C	0.05258731	-4.23985836	5.21737700

C	1.50454631	-4.35394836	5.56653200	H	6.99786063	-11.10104311	5.09028100
H	2.14253631	-4.38984436	4.67946800	N	5.34404563	-9.75435511	4.89874700
H	1.85055031	-3.52989436	6.20201800	H	4.89806463	-9.96657811	5.77718400
H	1.68717831	-5.28155136	6.11922200	C	5.03795863	-8.70255011	4.05690000
C	-1.02909969	-4.51416836	6.05145800	C	3.97216163	-7.79463211	4.07465900
C	-1.05771569	-4.90772636	7.45227600	H	3.20524463	-7.84198111	4.84210900
H	-1.97845469	-5.39036136	7.77975700	C	3.94793763	-6.81311211	3.08754600
C	-0.09190069	-4.74999036	8.37347000	H	3.15248663	-6.07407211	3.08113300
H	0.85500331	-4.26575836	8.16118300	C	4.95177663	-6.73864911	2.09845600
H	-0.23449369	-5.09603136	9.39337700	H	4.90072763	-5.96289911	1.34226400
C	-2.21049669	-4.34663036	5.23647500	C	6.00812863	-7.63965111	2.09003300
C	-3.51458269	-4.30508936	5.68922000	H	6.78607563	-7.58424311	1.32960900
H	-3.66665369	-4.46266736	6.75245400	C	6.07098663	-8.63681211	3.08013800
C	-4.65098569	-3.99078636	4.93527500	C	-1.95855137	-8.19054311	2.42114900
N	-4.63435569	-3.82941536	3.57066900	N	-0.58925937	-8.29211211	2.58339000
C	-5.97062569	-3.75952836	5.45881300	H	-0.07333637	-9.16717511	2.62869300
C	-6.40237369	-3.83503536	6.89476500	C	-0.06342337	-7.04720611	2.66555600
H	-5.55472169	-3.75301436	7.58416100	H	0.99472863	-6.85167511	2.75613900
H	-7.09289569	-3.02117936	7.13953300	N	-1.02829537	-6.14759711	2.57861900
H	-6.92588269	-4.77487436	7.11212800	C	-2.20781037	-6.84327411	2.42485800
C	-6.76474269	-3.44654036	4.37241300	H	-3.15404637	-6.33817911	2.31402000
C	-5.91105069	-3.52050936	3.21605500	FE	-0.82842937	-3.97644511	2.58582500
C	-6.35651769	-3.41306736	1.87538700	N	-1.95743337	-3.77633811	0.94784100
H	-7.40084269	-3.16038236	1.73893400	C	-3.28285437	-3.37407611	0.87263600
C	-8.24998869	-3.25282536	4.38397000	C	-3.72465037	-3.41797411	-0.49216900
H	-8.59709869	-2.66355036	3.53224100	C	-5.11112737	-3.12363711	-0.98528700
H	-8.54016069	-2.69506236	5.28375100	H	-5.05889737	-2.60405211	-1.94831900
C	-8.95664169	-4.62062536	4.37652300	H	-5.62394737	-2.45725111	-0.29028000
H	-8.62643069	-5.24121036	5.21515800	C	-5.97721837	-4.39941411	-1.17144800
H	-8.68858169	-5.15652736	3.46247400	H	-5.47459737	-5.10987611	-1.83279300
C	-10.45753169	-4.49326536	4.38657400	H	-6.93326537	-4.11330511	-1.62358700
O	-11.06295769	-5.56887336	4.91737700	C	-6.26505637	-5.04029011	0.17180600
O	-11.04633169	-3.51726036	3.96347500	O	-5.74286037	-6.26484011	0.29651200
O	1.13183631	-1.25436236	2.40642500	O	-6.88327737	-4.46432011	1.05173800
O	0.05217331	-1.88298136	2.80917600	C	-2.65803837	-3.89692111	-1.24576400
O	-2.08803969	-1.97304036	-3.86946500	C	-2.60007237	-4.09109311	-2.73394300
H	-2.00658069	-1.17003736	-3.31960200	H	-3.51269037	-3.71777311	-3.21004700
H	-2.45761369	-1.60126236	-4.69527600	H	-1.74548537	-3.55690011	-3.16795500
H	-8.18019469	-6.80735036	1.56074900	H	-2.47292837	-5.14496511	-2.99779300
O	-2.69454069	-5.77398136	-1.90365800	C	-1.59999537	-4.11538111	-0.31436400
H	-4.92079004	-9.23654100	2.33509296	C	-0.27546737	-4.64221011	-0.69702400
H	5.78320101	-10.15501593	3.32391539	C	0.87388463	-4.26866711	0.11304500
				N	0.77544263	-3.90479211	1.45409300
				C	2.18838163	-4.12336411	-0.34935800
				C	2.69445963	-4.39550411	-1.73538900
				H	2.83828663	-3.46382011	-2.30022800
				H	3.66670263	-4.90333211	-1.69939800
				H	1.99171363	-5.01488911	-2.29034200
				C	2.93818563	-3.63279411	0.75633800
				C	4.32171063	-3.17912011	0.81171900
				H	4.72397863	-3.00897011	1.81026800
				C	5.13908363	-2.89086911	-0.21331400
				H	4.85369363	-2.98537811	-1.25356900
				H	6.13541263	-2.51492011	-0.01199200
				C	2.04577063	-3.57166211	1.84000000
4TS3							
C	1.26602563	0.27243589	0.00000000				
H	2.00392163	-0.51730811	-0.19800800				
H	1.09970963	0.28546989	1.08328200				
C	-0.00289637	-0.06261211	-0.76338500				
O	-0.31638137	0.47146789	-1.83111100				
N	-0.77483437	-1.01672411	-0.17615000				
H	-1.49051137	-1.45171711	-0.74338100				
H	-0.37617737	-1.59643711	0.55171000				
H	-9.88261637	-5.12328311	4.94882200				
C	7.03668263	-9.66019411	3.39920000				
C	6.56221163	-10.29320011	4.51802400				

H	3.27500174	-3.67054672	2.11082000	H	1.47614766	-0.19622501	-0.58243500
C	3.67746774	-3.06523772	0.17097500	H	1.43560566	0.54205999	1.01665400
H	3.36829474	-2.88581172	-0.85268900	C	-0.46518634	0.46815899	-0.00314800
H	4.69024374	-2.77945972	0.43485000	O	-1.17359834	0.68901399	-0.99457900
C	0.49885474	-3.82417772	1.96353300	N	-0.98716734	0.05412099	1.17975400
C	0.80399874	-3.28696572	3.30031700	H	-1.99176534	-0.01405801	1.24954300
H	1.78559874	-3.63009772	3.63656200	H	-0.41442134	-0.12375501	2.00941900
C	-0.28346026	-3.32883972	4.37462200	H	-10.24225634	-4.28044301	4.93584600
N	-1.50379526	-4.04159072	4.16720900	C	6.71472466	-8.95883901	3.41446700
C	0.12783974	-3.61434472	5.80720800	C	6.26662166	-9.54592501	4.56909300
C	1.30793374	-2.95338172	6.42990500	H	6.72465266	-10.31886301	5.17100400
H	1.45768974	-1.97249672	5.97010000	N	5.04150366	-9.01557401	4.93942700
H	1.16065274	-2.82216272	7.50582600	H	4.57935966	-9.23021401	5.80965800
H	2.23130374	-3.53626072	6.29775400	C	4.69444666	-8.02382901	4.04372300
C	-0.83779626	-4.36947272	6.38543000	C	3.60288966	-7.14715401	4.02693900
C	-0.95085926	-4.86284372	7.75502400	H	2.83850266	-7.18885401	4.79767600
H	-1.95602826	-5.12051272	8.08107400	C	3.54918566	-6.20619801	3.00299000
C	0.04684374	-5.05785272	8.63080700	H	2.73759466	-5.48440701	2.98222100
H	1.08848874	-4.87083672	8.39085200	C	4.55062566	-6.14119201	2.01027300
H	-0.15250626	-5.42994172	9.63182200	H	4.48169166	-5.39386601	1.22697400
C	-1.92478226	-4.48972272	5.38978100	C	5.62871866	-7.01682301	2.03110200
C	-3.23456826	-4.73433872	5.70814600	H	6.40265166	-6.97149901	1.26610000
H	-3.49155826	-5.02034772	6.71926200	C	5.71968266	-7.97504201	3.05700000
C	-4.27292726	-4.29476672	4.85835500	C	-2.36422634	-7.30330001	1.63930800
N	-4.11695026	-4.03558972	3.52766900	N	-1.01446034	-7.38811001	1.93332500
C	-5.60741426	-3.98832472	5.28554700	H	-0.50771634	-8.25374101	2.10319400
C	-6.12534326	-4.09012072	6.69002500	C	-0.49585534	-6.13850801	1.97198500
H	-5.35098826	-3.82967672	7.42103400	H	0.54625266	-5.92663501	2.15829000
H	-6.95784226	-3.39769072	6.84288100	N	-1.44561634	-5.25304001	1.72489000
H	-6.49417326	-5.09558872	6.93477200	C	-2.60816934	-5.96166401	1.51245600
C	-6.28581626	-3.55157972	4.16626900	H	-3.53740834	-5.46838701	1.27687700
C	-5.35929326	-3.59707372	3.07000000	FE	-1.32392434	-3.07833401	1.82868500
C	-5.66473126	-3.38130072	1.74596300	N	-2.34439634	-2.91240101	0.12665900
H	-6.68067826	-3.09080172	1.51244600	C	-3.69504734	-2.64853301	-0.03054000
C	-7.75396326	-3.28850472	4.07915200	C	-4.07242034	-2.85314701	-1.39961100
H	-8.00973226	-2.62886972	3.24717000	C	-5.46218034	-2.75779901	-1.95774600
H	-8.08946526	-2.77938272	4.98981300	H	-5.41344534	-2.45055401	-3.00794000
C	-8.50562326	-4.63130972	3.94437200	H	-6.03080534	-1.98799101	-1.43416200
H	-8.08016726	-5.38221772	4.61716600	C	-6.25934034	-4.09209501	-1.89516200
H	-8.39390126	-5.01296272	2.92342900	H	-5.68546934	-4.89519401	-2.36512200
C	-9.96989026	-4.46933772	4.23392400	H	-7.19732434	-3.95916601	-2.44540100
O	-10.55542926	-5.59195472	4.68593000	C	-6.61386134	-4.46412201	-0.46883400
O	-10.56021926	-3.41396472	4.09224900	O	-5.98995234	-5.57189901	-0.04336000
O	-0.47995226	-1.88707672	4.16598800	O	-7.37026134	-3.79941701	0.21909400
O	0.76605574	-1.81774572	3.34884400	C	-2.93092434	-3.26479401	-2.07263700
O	-1.22624926	-1.60496372	-3.97788100	C	-2.80761334	-3.61189601	-3.52598800
H	-1.36741726	-0.92759972	-3.29212500	H	-3.71712934	-3.34071701	-4.07232800
H	-1.59148026	-1.16857672	-4.77515400	H	-1.95736134	-3.09549801	-3.98225600
H	-7.36260426	-6.80973272	1.03826000	H	-2.61990734	-4.68072201	-3.67049200
O	-1.47892926	-5.32900372	-1.84471000	C	-1.88766834	-3.27357301	-1.09603200
H	-4.17935613	-9.23481034	2.16910078	C	-0.50064334	-3.65507901	-1.39998700
H	6.39338747	-10.13515675	2.87267875	C	0.57528166	-3.28665001	-0.48800200
				N	0.38459366	-2.96973001	0.86167400
				C	1.93829266	-3.23147301	-0.83081800
				C	2.54291566	-3.47634201	-2.18205700
⁴TS4							
C	1.04166666	0.62499999	0.00000000				

H	2.56325566	-2.54813201	-2.76960000	H	-3.06223301	-8.10746406	1.53439439
H	3.57244366	-3.83613301	-2.08509600	H	7.61747985	-9.18353924	2.88584344
H	1.95779866	-4.20183601	-2.74467800				
C	2.62096466	-2.86860701	0.35223200	4P2			
C	4.03449766	-2.60271201	0.57549200	C	-0.03996004	1.20379619	0.00000000
H	4.35608266	-2.63101701	1.61373200	H	0.36890696	0.39368819	-0.61243900
C	4.95458566	-2.24805101	-0.33452400	H	0.42462796	1.14170719	0.99004700
H	4.74027066	-2.11308801	-1.38720300	C	-1.53803304	0.99714319	0.12225900
H	5.96482266	-2.02910701	-0.00814100	O	-2.32703404	1.13454219	-0.81687000
C	1.63200066	-2.77731201	1.37090900	N	-1.94147404	0.62036719	1.36391300
C	2.00124866	-2.37031601	2.77413700	H	-2.91869404	0.41431519	1.50619800
H	2.71130566	-3.11598701	3.18764700	H	-1.26933804	0.39292519	2.09513600
C	0.82234566	-2.19446301	3.75569300	H	-11.49286904	-3.85047081	4.77885700
N	-0.37736034	-3.03177001	3.50384600	C	5.39418996	-8.95498581	3.35593800
C	1.21653166	-2.57901201	5.20045100	C	5.29882396	-9.75479981	4.45979300
C	2.48012666	-2.12355401	5.84053500	H	6.02458096	-10.43790581	4.87719700
H	3.34808866	-2.54758401	5.32068900	N	4.04876296	-9.63166881	5.05253500
H	2.56889466	-1.03383601	5.78457600	H	3.91751196	-9.84260181	6.03495700
H	2.54644866	-2.42991101	6.88612900	C	3.33925796	-8.66568681	4.36659400
C	0.23688166	-3.34523501	5.73150700	C	2.06847696	-8.14584581	4.61836700
C	0.09493966	-3.95758001	7.05762100	H	1.48933396	-8.50347181	5.46632000
H	-0.35791934	-4.95230301	7.05056700	C	1.59863496	-7.16120581	3.75929600
C	0.45185666	-3.44219701	8.24194100	H	0.62954896	-6.71201181	3.94452500
H	0.88745466	-2.45281201	8.34360600	C	2.36818596	-6.72991081	2.65831100
H	0.33354666	-4.01511401	9.15763500	H	1.98064196	-5.96278181	1.99664900
C	-0.83426234	-3.43249901	4.72317300	C	3.62615896	-7.26364181	2.40510300
C	-2.16520634	-3.57300401	5.03885800	H	4.21403496	-6.93639181	1.54947400
H	-2.42231934	-3.80869501	6.06552200	C	4.13952496	-8.24335581	3.27069000
C	-3.18207034	-3.11988201	4.18092100	C	-3.87528804	-6.71974981	1.61518000
N	-3.00913534	-2.88216701	2.84025500	N	-2.50588804	-6.89418581	1.56234800
C	-4.51781434	-2.80588301	4.58551500	H	-2.04024104	-7.79269281	1.45120700
C	-5.06507534	-2.86688501	5.98185700	C	-1.90416604	-5.71179281	1.82195900
H	-4.28026534	-2.69670701	6.72798300	H	-0.83578404	-5.57027081	1.80074400
H	-5.82356434	-2.09176501	6.13259000	N	-2.81842404	-4.77826881	2.04691100
H	-5.53822634	-3.83250501	6.20027800	C	-4.04605204	-5.39449781	1.92080800
C	-5.18931634	-2.40785301	3.44478300	H	-4.96615204	-4.84695781	2.03641400
C	-4.24944434	-2.47942501	2.36423000	FE	-2.47944704	-2.60093981	2.20128100
C	-4.55755634	-2.35292001	1.01919800	N	-3.25966404	-2.24172381	0.41601800
H	-5.58244734	-2.11043901	0.76938100	C	-4.60766104	-2.12916781	0.10517600
C	-6.66047634	-2.15365501	3.36917400	C	-4.79016704	-2.15392181	-1.31033700
H	-6.94494134	-1.61960701	2.45995400	C	-6.11893404	-2.09582081	-2.01740700
H	-6.95839234	-1.51411501	4.20682700	H	-5.95365704	-1.78369181	-3.05321100
C	-7.42016134	-3.49496401	3.47325700	H	-6.75650004	-1.32800381	-1.56711800
H	-6.87691434	-4.19896801	4.11214700	C	-6.91564504	-3.43245481	-2.06380100
H	-7.48840334	-3.96304901	2.48605600	H	-6.27490804	-4.23804481	-2.43257400
C	-8.80340134	-3.32425401	4.03630700	H	-7.74583004	-3.30168881	-2.76779700
O	-9.31705934	-4.46022201	4.52200000	C	-7.52705904	-3.83066981	-0.73003400
O	-9.38521134	-2.25313101	4.05287700	O	-7.02428004	-4.98107881	-0.25972400
O	0.21452666	-0.98021001	3.63890900	O	-8.37510404	-3.17160381	-0.14901500
O	2.58002766	-1.15301801	2.52542000	C	-3.51715204	-2.24018081	-1.87269000
O	0.38535466	-0.03709401	-3.27454400	C	-3.15322804	-2.27346481	-3.32664500
H	-0.21555834	0.27905699	-2.57259600	H	-4.04417304	-2.35267081	-3.95736300
H	-0.08555034	0.13161399	-4.11286000	H	-2.59304204	-1.37749481	-3.61127200
H	-6.16116034	-5.73617701	0.92142300	H	-2.49990204	-3.12386381	-3.55322600
O	-0.28245434	-4.23854201	-2.47023500	C	-2.60503604	-2.26719081	-0.77421000

C -1.14545704 -2.17125881 -0.90677000
 C -0.26030004 -2.46762581 0.21905700
 N -0.69525504 -2.89328181 1.45795800
 C 1.14864296 -2.49353281 0.14917700
 C 2.01043596 -2.17581081 -1.03494000
 H 2.26214396 -1.10747081 -1.06708800
 H 2.95252696 -2.72640381 -0.97698400
 H 1.50416296 -2.40912481 -1.97065800
 C 1.60045796 -2.95481481 1.40919500
 C 2.97579896 -3.15083181 1.85778500
 H 3.12366696 -3.91516181 2.61447500
 C 4.03655596 -2.43591581 1.45257300
 H 3.96442196 -1.59983281 0.76492400
 H 5.02452396 -2.64742781 1.84925800
 C 0.44189696 -3.23306281 2.17168600
 C 0.40706296 -3.86104381 3.48247700
 H -0.58284104 -4.24277981 3.80113900
 C -0.55816504 -1.28055481 4.17683300
 N -1.76547304 -1.94163081 3.91035900
 C -0.15384304 -1.60307281 5.58030100
 C 1.12703396 -1.12641381 6.14989900
 H 1.45146196 -0.23547981 5.61040300
 H 1.03612696 -0.89999781 7.21473100
 H 1.90281496 -1.89599481 6.02978100
 C -1.15781904 -2.32837881 6.14341500
 C -1.31040004 -2.85911481 7.49190100
 H -2.31502104 -3.18521781 7.75391000
 C -0.35139104 -3.01823481 8.41789800
 H 0.68927796 -2.77039981 8.24008600
 H -0.58421004 -3.43511381 9.39330200
 C -2.21486104 -2.43839281 5.11806600
 C -3.52405804 -2.74839481 5.34494200
 H -3.84669304 -3.01727881 6.34268400
 C -4.51605704 -2.48458281 4.36623500
 N -4.24531304 -2.36017781 3.03290400
 C -5.89569104 -2.22227881 4.63060100
 C -6.55167904 -2.21472681 5.97973100
 H -5.85321404 -1.90467081 6.76571000
 H -7.39196704 -1.51360081 5.99706600
 H -6.95053204 -3.20156081 6.25222400
 C -6.48280804 -1.93871281 3.40808000
 C -5.45042104 -2.04107681 2.42127200
 C -5.61375004 -1.95987581 1.05237200
 H -6.61400604 -1.77513681 0.68350500
 C -7.94078104 -1.71814981 3.16393600
 H -8.11948004 -1.24481581 2.19604600
 H -8.34319004 -1.03490881 3.91795300
 C -8.69874604 -3.06169981 3.26008600
 H -8.14432104 -3.77741981 3.87534600
 H -8.79049204 -3.51465081 2.26762900
 C -10.06518304 -2.89786381 3.86787500
 O -10.57214404 -4.03743381 4.34923500
 O -10.63716404 -1.82271281 3.92768800
 O 0.01695696 -0.51289681 3.41070100
 O 1.38217196 -4.03352881 4.20923300

O -0.92866804 0.76341819 -3.27387000
 H -1.50317604 0.91831119 -2.49962900
 H -0.62764104 -0.14993481 -3.13235300
 H -7.36868204 -5.18489081 0.64817500
 O -0.67307204 -1.84792081 -2.00898500
 H 6.22795887 -8.87249806 2.69041176
 H -4.63454009 -7.45612446 1.45335073

INT3_{QM}

C 35.44383700 32.69501800 38.17611300
 H 35.59688300 31.61035700 38.21031300
 H 36.22176000 33.12931400 37.53842500
 C 35.51480400 33.25694600 39.58351600
 O 34.51265500 33.69652100 40.16290500
 N 36.74850300 33.27779200 40.15725300
 H 36.75753300 33.47415500 41.16028600
 H 37.45335400 32.64540200 39.80221000
 C 39.24410100 25.60172600 46.18733300
 H 38.46725100 25.26596400 46.88679800
 H 40.06163000 24.86956800 46.22866500
 C 38.71694200 25.77588800 44.79957600
 N 38.28816100 24.71884000 44.01009300
 H 38.28922000 23.74358100 44.27267300
 C 37.86122700 25.22500300 42.81983700
 H 37.47647800 24.61224400 42.01812900
 N 37.98643800 26.53598700 42.79419100
 C 38.51815900 26.88819400 44.01888300
 H 38.72631100 27.91856900 44.26512600
 FE 37.34147400 27.98531400 40.87549500
 N 38.12264400 29.47282200 42.04417700
 C 39.45161300 29.77780900 42.20247500
 C 39.60843600 30.79526300 43.20659700
 C 40.90772300 31.38185000 43.68888500
 H 40.75728000 32.42967200 43.96934300
 H 41.65845000 31.38139700 42.89152800
 C 41.50735200 30.64978900 44.91557200
 H 40.78064500 30.58443800 45.72898600
 H 42.37507300 31.21446400 45.28174400
 C 42.00697300 29.26787700 44.55874000
 O 41.55587800 28.30698000 45.40000900
 O 42.74258700 29.01266900 43.62628300
 C 38.32986400 31.12958900 43.63556000
 C 37.94899600 32.17438400 44.64361000
 H 37.41165500 33.00498500 44.17241100
 H 37.28539300 31.76885800 45.41381100
 H 38.83669800 32.58388800 45.13698000
 C 37.43847200 30.31183000 42.86450300
 C 35.99093200 30.42200100 42.83738800
 C 35.24710100 29.66764400 41.71343500
 N 35.58590800 28.26897000 41.65490400
 C 33.72560600 29.71639900 41.79894600
 C 32.95690500 30.98977500 41.86514400
 H 33.17230100 31.61940800 40.99147400
 H 31.88176500 30.80542500 41.91679800
 H 33.26988200 31.56383300 42.74234200

C	33.28082200	28.43388400	41.75676300
C	31.91068200	27.90647200	41.80049700
H	31.76683300	27.02757500	42.43129600
C	30.85382700	28.39433900	41.13949800
H	30.93472300	29.23894200	40.46166300
H	29.86981000	27.94702100	41.24926400
C	34.46322200	27.56776900	41.55617400
C	34.40395500	26.23974800	41.09547400
H	33.46069900	25.71247500	41.15434400
C	35.41392300	25.71661500	40.30126300
N	36.61893100	26.32193800	40.03855000
C	35.28720300	24.48596800	39.51412300
C	34.08320600	23.59622300	39.51970100
H	33.15873500	24.17984700	39.59020200
H	34.08770700	22.89708900	40.36755000
H	34.03738900	23.00075700	38.60317400
C	36.41925200	24.39208700	38.74822800
C	36.78511400	23.39695100	37.74325900
H	37.37003500	23.76987800	36.90293000
C	36.47803400	22.09131700	37.76489700
H	35.93815900	21.63261700	38.58776100
H	36.78355000	21.43315600	36.95672700
C	37.25851600	25.54826100	39.09171400
C	38.51708600	25.78322600	38.60152800
H	38.90766200	25.10177000	37.85490200
C	39.40621700	26.77433400	39.08641400
N	39.11079900	27.66830200	40.06387700
C	40.79226600	26.87756900	38.69886800
C	41.44978700	26.05382300	37.63111800
H	41.50615700	24.99221000	37.90793900
H	42.47159200	26.39434900	37.43955900
H	40.90255700	26.11018700	36.68182700
C	41.35586800	27.83746000	39.51282700
C	40.29874200	28.32319800	40.36790600
C	40.45673000	29.25077800	41.37959300
H	41.46184600	29.62135600	41.54458600
C	42.79354400	28.27331600	39.56051300
H	42.87002600	29.34303000	39.78126300
H	43.25520400	28.14452800	38.57569000
C	43.61784200	27.49284000	40.60121800
H	43.55482700	26.41175300	40.42561300
H	43.23474600	27.66066300	41.61527100
C	45.07638400	27.89259600	40.59277100
O	45.81112100	27.11336900	41.42704600
O	45.56830100	28.78880500	39.94219700
O	36.65038000	29.50404200	39.76548300
O	35.66184100	30.28328000	40.45446200
O	35.60058400	33.97583000	42.75693700
H	35.36345400	33.12627600	43.16790100
H	35.01386500	34.03844400	41.96963000
H	41.92893600	27.46562000	45.07240200
O	35.37565200	31.15930200	43.61306400
H	39.63152200	26.55633200	46.55396900
H	34.46112300	32.91052000	37.75373200
H	46.72478400	27.45222100	41.37152900

RE4_{QM}

C	35.11618100	31.83050400	37.57718500
H	34.81270500	30.92883600	38.11423000
H	36.19820700	31.80638500	37.42557900
C	34.65294300	33.04660200	38.35436800
O	33.49727700	33.11881700	38.79630400
N	35.53874900	34.07201400	38.47734200
H	35.26190300	34.80554100	39.13214000
H	36.52737700	33.86641000	38.41391700
C	39.10614600	27.80179600	45.26660200
N	38.70846400	26.59006400	44.72085500
H	38.62459200	25.71411000	45.21639800
C	38.43853900	26.78908300	43.40009800
H	38.10709900	26.00730200	42.73235400
N	38.63814100	28.04586400	43.06345300
C	39.05217700	28.68531000	44.21583900
H	39.27831200	29.74106100	44.22561000
FE	38.38493100	28.84763800	40.84481900
N	39.34902200	30.54644400	41.18397600
C	40.67108700	30.73724300	41.40438300
C	40.93367700	32.13184600	41.83491200
C	42.27672200	32.66654900	42.25348900
H	42.31531000	33.74329100	42.05638200
H	43.07957800	32.21196900	41.66360600
C	42.58934800	32.45743800	43.76105200
H	41.78336700	32.86326100	44.37713900
H	43.51813100	32.98669600	44.00075800
C	42.81264700	30.99718300	44.09123100
O	41.83468600	30.48191600	44.87015000
O	43.74595200	30.33345000	43.68830900
C	39.76478200	32.80407600	41.81045500
C	39.43842500	34.22432700	42.13205200
H	40.33769700	34.84097500	42.22322100
H	38.79866000	34.65642400	41.35369600
H	38.88441900	34.29160200	43.07820600
C	38.69142700	31.82823700	41.40106800
C	37.57217400	31.59469400	42.43395700
C	36.42049600	31.11020800	41.55525800
N	36.62780100	29.70733600	41.21762500
C	35.00680200	31.24953700	42.07104900
C	34.47867900	32.53651000	42.61133000
H	34.43442800	33.32211300	41.84738900
H	33.47288300	32.39899400	43.01604500
H	35.13042500	32.90427000	43.41433200
C	34.42505700	30.03774900	41.93211300
C	33.03907000	29.65732300	42.23620400
H	32.90224800	28.76803100	42.85278400
C	31.96387700	30.31569300	41.78711500
H	32.05529000	31.16914400	41.12025700
H	30.95844100	29.99711700	42.04921500
C	35.43687200	29.09129500	41.40751400
C	35.15831100	27.77598100	41.07869100
H	34.14047500	27.42956400	41.20944900
C	36.07781900	26.90768600	40.47008900
N	37.41046400	27.18888400	40.28676600

C	35.74879600	25.61963700	39.91145700
C	34.39715400	24.97537200	39.97421300
H	33.85969000	25.25520300	40.88716700
H	33.75766400	25.25804900	39.12587500
H	34.48760700	23.88407700	39.96093800
C	36.91323500	25.12785800	39.34562100
C	37.14424700	23.86613400	38.65155100
H	38.16165300	23.47861200	38.70139600
C	36.24746700	23.14717300	37.95673300
H	35.22294100	23.47245200	37.80847600
H	36.53211200	22.21034300	37.48632500
C	37.94645400	26.11165200	39.61311000
C	39.29872000	25.96485800	39.31796200
H	39.59529900	25.06363000	38.79270000
C	40.31722700	26.83470200	39.68012200
N	40.13177800	28.03994100	40.32811900
C	41.73150900	26.56888300	39.51999700
C	42.30191100	25.35432300	38.84968200
H	41.90476000	25.22901500	37.83439800
H	43.39115900	25.41726000	38.77039800
H	42.06708700	24.43465800	39.40221400
C	42.39910800	27.61512900	40.10842400
C	41.38130200	28.53193000	40.59051700
C	41.64668000	29.78275600	41.16740500
H	42.67965600	30.04093800	41.35641400
C	43.88183700	27.82511800	40.23584300
H	44.14976400	28.85886500	39.98946000
H	44.41200000	27.20551000	39.50468100
C	44.42154900	27.50138400	41.64112200
H	44.16824300	26.47541900	41.93518500
H	43.97218200	28.15582800	42.39863900
C	45.92052500	27.67309100	41.73839100
O	46.40010600	27.21529000	42.92395600
O	46.64320500	28.15200500	40.89137300
O	36.53234100	31.97952400	40.43639500
O	38.00230600	32.28022700	40.24203500
O	33.75401700	35.34161700	40.37416800
H	33.41629400	34.55299100	39.88262100
H	33.19537500	36.07557100	40.07725500
H	42.01967800	29.52634400	44.95427000
O	37.61744500	31.75057100	43.62725300
H	47.36039300	27.38860800	42.90539300
H	34.61853400	31.82470200	36.60071500
H	39.39084561	28.00307275	46.27820162