Supplementary Information

A new understanding on how heme metabolism occurs in heme oxygenase: water-assisted oxo mechansim

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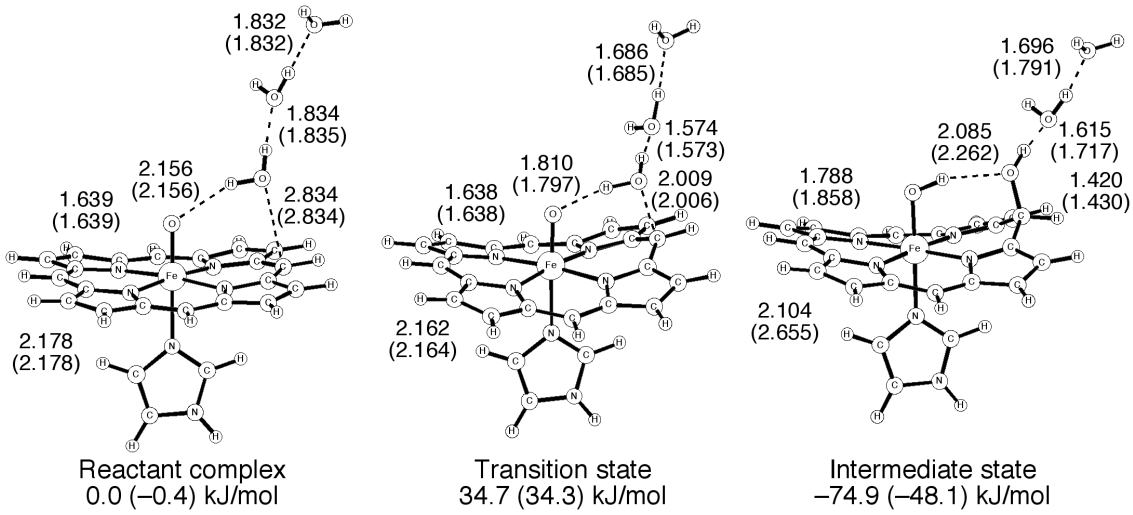

Figure S1. Computed geometrical and energetical changes in heme oxidation by the iron–oxo species with the aid of three water molecules in the doublet (quartet) state. Unit in Å.

Table S1. Calculated energy changes (kJ/mol) on the small model calculations. RC, TS, and I stands for reactant complex, transition state, and intermediate, respectively.

	B3LYP/ 6-311G(d,p)	B3LYP/ cc-pVTZ	M06/ cc-pVTZ	CAM-B3LYP/ cc-pVTZ
Doublet state with the bridging water molecule				
RC	0.0	0.0	0.0	0.0
TS	54.0	64.9	59.0	54.8
I	–64.0	–60.7	–78.7	–97.9
Quartet state with the bridging water molecule				
RC	–0.4	–0.4	0.0	–0.4
TS	53.6	64.4	57.7	54.8
I	–13.4	–17.6	–66.9	–48.1
Doublet state with the bridging and additional water molecules				
RC	0.0	0.0	0.0	0.0
TS	23.8	35.6	26.8	25.1
I	–86.2	–82.4	–102.1	–123.0
Quartet state with the bridging and additional water molecules				
RC	–0.4	–0.4	–0.4	–0.4
TS	23.0	34.7	25.9	25.1
I	–36.0	–39.7	–92.0	–74.1

Table S2. Important Coulomb interactions (kJ/mol) between the QM and MM point charges.

	Doublet		Quartet	
	TS	I	TS	I
ARG136	31.9	14.2	32.3	16.9
ASP140	–26.7	–8.0	–27.0	–8.2
SER142	–0.4	–3.9	–0.4	–9.8
GLY143	7.4	0.6	7.7	–11.0
LYS179	–10.4	–6.1	–10.3	–3.1
ARG183	–13.8	–5.5	–13.8	–3.1
HEM 300	40.7	17.8	41.0	11.2

Table S3. The QM/MM energy differences (kJ/mol) between the larger and smaller QM models.

	Smaller QM	Larger QM
	Doublet	
RC	0.0	0.0
TS	76.1	83.7
I	–77.7	–69.0
	Quartet	
RC	–1.2	–1.2
TS	76.3	83.7
I	–39.4	–36.0

Table S4. Amino acids in the distal heme pocket of P450s.

PDB Code	P450 family	Residue Name	Residue Sequence	Distance [Å]
1akd	P450cam		α-meso	
		THR	252	3.318
		GLY	248	4.655
		VAL	253	4.662
			β-meso	
		VAL	295	4.063
			γ-meso	
		CAM (substrate)	420	3.981
		THR	101	4.914
			δ-meso	
		GLY	248	4.761
		CAM (substrate)	420	4.883
		LEU	245	4.996
1t2b[a]	P450cin		α-meso	
		GLY	238	3.515

		THR	243	3.764
		ASN	242	3.946
			β-meso	
		ASN	242	3.990
		CNL (substrate)	500	4.087
		ALA	285	4.280
		HOH	504	4.794
			γ-meso	
		CNL (substrate)	500	4.071
			δ-meso	
		LEU	235	4.723
		ILE	234	4.831
		GLY	238	4.839
		CNL	500	4.937
2bmh	P450BM3		α-meso	
		THR	268	3.469
		THR	269	3.747
		GLY	265	4.226
		ALA	264	4.243
			β-meso	
		ALA	328	3.831
		THR	268	4.928
			γ-meso	
		PHE	87	3.847
			δ-meso	
		ALA	264	4.003
		GLY	265	4.824
3c6g	P450 2R1		α-meso	
		THR	314	3.179
		ALA	310	3.944

		THR	315	4.239
		GLY	311	4.590
			β-meso	
		VAL	375	3.842
		THR	314	4.818
			γ-meso	
		ILE	379	3.760
			δ-meso	
		ALA	310	3.298
		LEU	307	4.721
		GLY	311	4.786
1cl6[b]	P450nor		α-meso	
		NO (substrate)	502	3.877
		GLY	240	3.959
		MET	244	4.277
			β-meso	
		NO (substrate)	502	3.590
		SER	286	4.104
			γ-meso	
		NO (substrate)	502	3.837
			δ-meso	
		ALA	239	3.655
		GLY	240	4.279
		LEU	236	4.947
1cpt	P450terp		α-meso	
		THR	271	3.543
		ALA	267	3.954
		THR	272	4.097
		GLY	268	4.591
			β-meso	

		VAL	314	3.618
		THR	271	4.719
			γ-meso	
		PHE	317	4.729
		THR	103	4.953
			δ-meso	
		ALA	267	3.508
		GLY	268	4.669
		ILE	264	4.850
3el3	P450 170A1		α-meso	
		ILE	279	3.806
		GLY	275	4.181
		THR	278	4.460
			β-meso	
		VAL	338	4.145
		THR	278	4.720
			γ-meso	
		EL (substrate)		3.870
			δ-meso	
		ILE	271	4.143
		GLY	275	4.394
2d09[c]	P450 158A2		α-meso	
		GLY	242	3.755
		ALA	245	3.939
		VAL	246	4.900
			β-meso	
		FLV (substrate)	431	3.946
		HOH	529	4.053
		HIS	287	4.372
		HOH	525	4.651

			γ-meso	
		FLV (substrate)	431	3.245
		HOH	680	4.464
		HOH	664	4.673
		HOH	545	4.728
			δ-meso	
		GLY	242	4.170
		HOH	664	4.226
		LEU	239	4.230
		LEU	238	4.232
1dt6	P450 2C5		α-meso	
		THR	298	3.470
		THR	299	3.885
		ALA	294	4.465
		GLY	295	4.666
			β-meso	
		LEU	359	4.452
		THR	298	4.723
			γ-meso	
		LEU	363	4.245
			δ-meso	
		ALA	294	3.744
		GLY	295	4.056
		LEU	291	4.424
		ASP	290	4.676
3e4e	P450 2E1		α-meso	
		THR	303	3.042
		4PZ (inhibitor)	501	3.443
		ALA	299	3.647
		THR	304	4.281

			β-meso	
		4PZ (inhibitor)	501	3.761
		VAL	364	3.924
		THR	303	4.982
			γ-meso	
		4PZ (inhibitor)	501	3.364
		LEU	368	4.042
			δ-meso	
		ALA	299	3.380
		4PZ (inhibitor)	501	3.773
		LEU	296	4.893
3e5k	P450 105P1		α-meso	
		THR	242	3.921
		ALA	237	4.924
		THR	241	4.632
			β-meso	
		PHE	286	3.617
			γ-meso	
		PIM (ligand)		3.885
		LEU	88	4.298
			δ-meso	
		ALA	237	3.880
		LEU	234	4.597
1e9x	CYP51		α-meso	
		THR	260	3.386
		PIM (inhibitor)	470	4.271
		ALA	256	4.340
		GLY	257	4.436
			β-meso	
		LEU	321	4.046

		PIM (inhibitor)	470	4.202
		THR	260	4.863
			γ-meso	
		PIM (inhibitor)	470	3.662
			δ-meso	
		ALA	256	3.833
		VAL	395	4.089
		HIS	101	4.755
1egy [d]	P450eryF		α-meso	
		9AP (substrate)	800	3.879
		ALA	241	4.114
		ALA	245	4.212
		SER	246	4.785
		GLY	242	4.886
			β-meso	
		9AP (substrate)	800	3.278
		PRO	288	4.419
			γ-meso	
		9AP (substrate)	800	3.321
			δ-meso	
		9AP (substrate)	800	3.845
		LEU	238	4.278
3eqm	P450 19A1		α-meso	
		THR	310	3.699
		MET	311	4.628
			β-meso	
		VAL	370	4.078
			γ-meso	
		ASD (ligand)		3.644
		ARG	115	3.962
			δ-meso	

		ALA	306	4.167
1f4t	CYP119		α-meso	
		THR	213	3.328
		THR	214	3.872
		PIM (inhibitor)	411	4.157
		GLY	210	4.245
			β-meso	
		PIM (inhibitor)	411	3.835
		VAL	254	3.970
			γ-meso	
		PIM (inhibitor)	411	4.121
		LEU	69	4.200
			δ-meso	
		PIM (inhibitor)	411	4.041
2f9q	P450 2D6		α-meso	
		THR	309	3.221
		THR	310	3.997
		ALA	305	4.172
		GLY	306	4.325
			β-meso	
		VAL	370	4.351
		THR	309	4.574
			γ-meso	
		PHE	120	4.099
			δ-meso	
		ALA	305	3.728
		LEU	302	4.649
		GLY	306	4.685
2fdu	P450 2A6		α-meso	

		THR	305	3.318
		D1G (inhibitor)	501	3.813
		GLY	301	4.046
		VAL	306	4.589
			β-meso	
		D1G (inhibitor)	501	3.798
		ILE	366	4.220
			γ-meso	
		D1G (inhibitor)	501	3.574
		LEU	370	4.500
		ARG	101	4.894
			δ-meso	
		D1G (inhibitor)	501	3.389
		GLY	301	4.967
2fr7	CYP199A2		α-meso	
		THR	255	3.321
		THR	256	4.014
		ALA	251	4.184
		GLY	252	4.403
			β-meso	
		VAL	298	3.611
		THR	255	4.781
			γ-meso	
		LEU	100	4.416
			δ-meso	
		ALA	251	3.548
		LEU	248	4.423
		GLY	252	4.561
2hi4	P450 1A		α-meso	
		THR	321	3.090

		VAL	322	4.716
		ALA	317	4.741
			β-meso	
		LEU	382	3.900
		THR	321	4.618
		BHF (inhibitor)	800	4.624
			γ-meso	
		BHF (inhibitor)	800	4.250
			δ-meso	
		ALA	317	3.516
		GLY	318	4.705
		ASP	313	4.911
1izo[e]	P450 152A1		α-meso	
		PRO	243	4.012
		PAM (substrate)	601	4.926
		ILE	247	4.931
			β-meso	
		PAM (substrate)	601	4.143
			γ-meso	
			δ-meso	
		ASN	239	3.722
		PRO	243	4.102
2j0d	P450 3A4		α-meso	
		THR	309	3.999
		ALA	305	4.075
		GLY	306	4.260
		THR	310	4.571
			β-meso	
		ERY (substrate)	1498	4.011
			γ-meso	

		ARG	105	4.001
		ERY (substrate)	1498	4.227
			δ-meso	
		ALA	305	3.646
		PHE	302	4.800
2jjp	P450 113A1		α-meso	
		THR	245	3.663
		KLN (inhibitor)	413	4.019
			β-meso	
		KLN (inhibitor)	413	3.569
		PHE	288	3.938
			γ-meso	
		KLN (inhibitor)	413	3.843
			δ-meso	
		KLN	413	3.496
		ALA	241	4.241
		LEU	238	4.572
1lfk[f]	P450 Monooxygenase		α-meso	
		ALA	236	3.961
		ASN	240	4.318
		GLY	237	4.322
		ILE	241	4.529
			β-meso	
		ASN	240	3.936
		PRO	283	4.174
			γ-meso	
		MET	89	4.580
			δ-meso	
		ALA	236	3.567

		GLY	237	4.929
2ij7	CYP121		α-meso	
		SER	237	3.819
		THR	238	4.227
		GLY	234	4.897
		ALA	233	4.852
			β-meso	
		PHE	280	3.521
		SER	237	4.916
			γ-meso	
		TPF (ligand)		3.852
			δ-meso	
		ALA	233	4.199
		GLY	234	4.832
		PHE	230	4.849
1n97	CYP175A1		α-meso	
		THR	225	3.581
		ALA	221	3.707
		VAL	226	4.300
		GLY	222	4.437
			β-meso	
		ALA	268	4.247
			γ-meso	
		LEU	80	3.902
			δ-meso	
		ALA	221	3.395
		LEU	218	4.850
		GLY	222	4.975
3na0	CYP11A1		α-meso	

		THR	330	3.292
		GLY	326	4.327
		THR	331	4.900
		2DC (substrate)	602	4.963
			β-meso	
		2DC (substrate)	602	3.997
		ILE	390	4.500
		SER	391	4.967
			γ-meso	
		2DC (substrate)	602	4.046
		ARG	120	4.067
			δ-meso	
		2DC (substrate)	602	3.592
		GLY	326	4.547
1odo	CYP154A1		α-meso	
		THR	246	3.428
		PIM(inhibitor)	1408	3.960
		THR	247	4.002
		ALA	242	4.393
			β-meso	
		PIM(inhibitor)	1408	4.074
		VAL	289	4.273
		THR	246	4.678
			γ-meso	
		PIM (inhibitor)	1408	3.774
		PHE	88	4.547
			δ-meso	
		ALA	242	3.749
		PIM (inhibitor)	1408	4.083
		MET	239	4.717

1og2	P450 2C9		α-meso	
		THR	302	3.629
		ALA	297	3.869
		THR	301	4.680
		GLY	298	4.887
			β-meso	
		LEU	362	3.483
		THR	301	4.649
			γ-meso	
		LEU	366	4.786
			δ-meso	
		ALA	297	3.559
		GLY	298	4.621
2p85	P450 2A13		α-meso	
		THR	305	3.198
		ALA	301	4.085
		VAL	306	4.944
			β-meso	
		MET	365	4.675
		LEU	366	4.735
			γ-meso	
		IND (substrate)	507	3.588
		IND (substrate)	501	4.212
		LEU	370	4.947
			δ-meso	
		ALA	301	3.694
		IND (substrate)	507	4.881
		LEU	298	4.947
1n6b	P450 2C5		α-meso	
		THR	298	3.361

		ALA	294	3.878
		GLY	295	4.187
		THR	299	4.124
			β-meso	
		LEU	359	4.329
			γ-meso	
		DMZ (ligand)		3.969
		ARG	97	4.996
			δ-meso	
		ALA	294	3.595
1pkf	P450epok		α-meso	
		THR	258	3.483
		ALA	254	4.218
		THR	259	4.380
			β-meso	
		EPD (ligand)		3.447
			γ-meso	
		EPD (ligand)		4.653
		PHE	96	4.810
			δ-meso	
		ALA	254	3.818
2q9f	P450 46A1		α-meso	
		THR	306	3.572
		ALA	302	3.834
		SER	307	4.169
			β-meso	
		ALA	367	3.973
		THR	306	4.769
			γ-meso	
		VAL	126	4.794

			δ-meso	
		ALA	302	3.764
		PHE	299	4.487
		GLY	303	4.736
2rfb	CYP231A2		α-meso	
		THR	201	3.183
		GLY	197	3.462
		GLY	198	4.188
		THR	202	4.492
			β-meso	
		ILE	241	3.644
		THR	201	4.880
		HOH	925	4.964
			γ-meso	
		ILE	57	4.340
			δ-meso	
		GLY	197	4.061
		GLY	198	4.362
		LEU	194	4.819
		LEU	193	4.902
1ue8	P450		α-meso	
		THR	215	3.514
		THR	214	3.594
		ALA	210	3.967
		GLY	211	4.152
			β-meso	
		VAL	254	3.580
			γ-meso	
		LEU	69	4.115
			δ-meso	

		ALA	210	4.290
1ued	P450 Oxyc		α-meso	
		THR	249	3.302
		GLY	245	3.749
		GLY	246	4.500
		VAL	250	4.741
			β-meso	
		VAL	292	3.607
		THR	249	4.905
		PG4 (substrate)	4502	4.928
			γ-meso	
		PG4 (substrate)	4502	3.718
			δ-meso	
		GLY	245	3.913
		LEU	242	4.405
		GLY	246	4.413
		ALA	241	4.949
2ve3	P450 120A1		α-meso	
		THR	258	2.960
		ALA	254	4.134
			β-meso	
		VAL	318	3.498
			γ-meso	
		REA (ligand)		3.827
			δ-meso	
		ALA	254	3.491
2wgy	P450 130		α-meso	
		THR	247	3.549
		ALA	243	3.827

		VAL	248	4.231
		GLY	244	4.280
			β-meso	
		VAL	290	3.618
		THR	247	4.749
			γ-meso	
		VAL	90	4.744
			δ-meso	
		ALA	243	3.624
		MET	240	4.144
		GLY	244	4.856
2z36	P450 MoxA		α-meso	
		THR	249	3.528
		ALA	245	3.607
		GLY	246	4.089
		THR	250	4.280
			β-meso	
		ALA	348	3.780
		MES (substrate)	4574	4.424
		ALA	292	4.612
			γ-meso	
		MES (substrate)	4574	3.822
		LEU	96	3.998
			δ-meso	
		ALA	245	4.064
2z3u	P450StaP		α-meso	
		THR	258	3.145
		ALA	254	3.773
		THR	259	4.095
		PHE	357	4.986

			β-meso	
		VAL	301	4.024
		THR	258	4.474
		CRR (substrate)	501	4.552
			γ-meso	
		CRR (substrate)	501	3.900
		VAL	99	4.932
			δ-meso	
		ALA	254	4.167
		GLY	255	4.814
2zbz	P450 105A1		α-meso	
		THR	248	2.980
		ALA	244	4.561
		THR	249	4.917
			β-meso	
		ALA	291	3.793
			γ-meso	
		ILE	96	4.366
			δ-meso	
		ALA	244	3.501

[a]ASN242 is not essential for the enzymatic reaction, which is demonstrated by the N242A mutational study.

[b]Nitric oxide reductase. Amino acids to activate O_2 are not required.

[c]Bound dioxygen will be protonated by His287 in vicinity of the *β-meso* carbon atom.

[d]SER246 participates in the proton transfer.

[e]PAM is involved in the proton delivery.

[f]Inactive protein. See J.Biol.Chem. 2002, 277, 47476-47485.

Coordinates

The optimized structure of the small model including the bridging water molecule of RC in the doublet state.

	X	Y	Z
H	3.291069	–12.863004	1.944748
C	2.507863	–12.203592	1.576561
C	2.421456	–11.420539	0.452894
H	3.154295	–11.292242	–0.340033
N	1.320504	–12.011408	2.250075
H	1.053069	–12.445571	3.128383
C	0.567284	–11.14247	1.537531
H	–0.424323	–10.815193	1.844885
N	1.20781	–10.765539	0.442017
O	–2.578996	–7.114547	–1.721482
O	–0.073527	–8.364193	–2.18905
H	–3.117418	–7.188933	–2.527872
H	–1.675658	–7.389109	–1.992467
Fe	0.482363	–9.397918	–1.057265
C	3.16939	–10.006926	–3.07685
C	–1.146884	–12.096364	–2.392025
C	–2.309589	–8.577221	0.723149
C	2.259679	–6.988001	0.598108
N	0.947572	–10.8167	–2.428848
C	2.08256	–10.86291	–3.204977
C	1.997542	–11.953971	–4.148793
C	0.797591	–12.566769	–3.925508
C	0.154275	–11.830987	–2.861306
N	–1.35207	–10.226812	–0.817466
C	–1.850878	–11.330878	–1.475173
C	–3.240734	–11.528682	–1.131172
C	–3.57962	–10.50811	–0.288956
C	–2.387777	–9.712219	–0.110539

N	0.075099	–8.096276	0.443626
C	–1.155878	–7.857891	1.007148
C	–1.074219	–6.761593	1.943654
C	0.225983	–6.343834	1.938779
C	0.918862	–7.173253	0.979291
N	2.371459	–8.669466	–1.181987
C	2.916933	–7.658852	–0.427524
C	4.251543	–7.351851	–0.891073
C	4.491575	–8.176688	–1.953058
C	3.308665	–8.991023	–2.113938
H	4.003475	–10.150633	–3.769239
H	–1.669992	–12.946804	–2.83785
H	–3.232978	–8.255167	1.210145
H	2.816091	–6.202159	1.115866
H	0.369464	–13.428406	–4.437917
H	2.764857	–12.210845	–4.879243
H	5.38389	–8.239244	–2.576492
H	4.904662	–6.591175	–0.462508
H	0.680688	–5.533808	2.509275
H	–1.911421	–6.369914	2.521395
H	–4.543513	–10.30094	0.175744
H	–3.869107	–12.335315	–1.51005

The optimized structure of the small model including the bridging water molecule of RC in the quartet state.

	X	Y	Z
H	3.291072	–12.862989	1.944745
C	2.507898	–12.203589	1.576556
C	2.421448	–11.420505	0.452887
H	3.154302	–11.292243	–0.340001
N	1.320495	–12.011414	2.250078
H	1.053095	–12.445573	3.128337

C	0.5673	–11.142491	1.537468
H	–0.424319	–10.815237	1.844877
N	1.207798	–10.765491	0.441954
O	–2.57891	–7.114719	–1.721575
O	–0.07338	–8.364327	–2.188998
H	–3.117408	–7.188957	–2.527961
H	–1.675591	–7.389136	–1.992514
Fe	0.482149	–9.397868	–1.057274
C	3.169527	–10.006691	–3.076657
C	–1.146679	–12.096443	–2.392192
C	–2.309771	–8.577471	0.722999
C	2.259381	–6.987949	0.598301
N	0.94768	–10.81653	–2.428669
C	2.082385	–10.863021	–3.204994
C	1.997577	–11.953894	–4.148737
C	0.797514	–12.566724	–3.925474
C	0.15399	–11.831096	–2.861228
N	–1.351804	–10.226784	–0.817661
C	–1.851056	–11.330814	–1.47506
C	–3.240702	–11.528725	–1.13125
C	–3.579566	–10.508069	–0.288998
C	–2.387891	–9.711912	–0.110407
N	0.074959	–8.096539	0.443572
C	–1.15574	–7.857767	1.007231
C	–1.074239	–6.761622	1.943656
C	0.225995	–6.343851	1.93878
C	0.919248	–7.173173	0.979316
N	2.37128	–8.669325	–1.181829
C	2.917113	–7.658908	–0.427704
C	4.251537	–7.351856	–0.891089
C	4.491547	–8.176702	–1.953044
C	3.308761	–8.99114	–2.114192

H	4.003448	–10.150605	–3.769213
H	–1.67008	–12.946793	–2.837787
H	–3.233006	–8.255161	1.210183
H	2.816074	–6.202186	1.11582
H	0.369448	–13.428351	–4.437861
H	2.764787	–12.210825	–4.879195
H	5.383887	–8.239277	–2.57655
H	4.904725	–6.591158	–0.462563
H	0.680685	–5.533841	2.509244
H	–1.911399	–6.369922	2.521355
H	–4.543403	–10.300925	0.175778
H	–3.869077	–12.335327	–1.510114

The optimized structure of the small model including the bridging water molecule of TS in the doublet state.

	X	Y	Z
H	3.306641	–12.953592	1.600803
C	2.525884	–12.267369	1.279589
C	2.383043	–11.508693	0.145286
H	3.051936	–11.430256	–0.708612
N	1.406817	–12.004575	2.041999
H	1.193957	–12.403764	2.951285
C	0.636231	–11.119459	1.370594
H	–0.311508	–10.736818	1.745594
N	1.201974	–10.800056	0.216881
O	–2.416112	–7.44826	–1.485466
O	–0.237841	–8.364493	–2.315026
H	–3.133945	–7.768956	–2.07106
H	–1.478527	–7.758261	–1.926093
Fe	0.429599	–9.436412	–1.244444
C	3.021358	–9.75716	–3.384722
C	–0.950873	–12.350445	–2.364006

C	–2.434636	–8.433361	0.046705
C	2.208183	–7.276327	0.704989
N	0.937435	–10.795788	–2.617626
C	2.001112	–10.713688	–3.471859
C	1.982857	–11.828502	–4.390483
C	0.909283	–12.60326	–4.046026
C	0.249683	–11.936417	–2.947885
N	–1.340161	–10.351783	–1.004809
C	–1.722753	–11.586433	–1.480477
C	–3.087707	–11.834865	–1.119922
C	–3.544946	–10.694496	–0.486257
C	–2.436549	–9.797273	–0.435064
N	–0.011255	–8.220205	0.287352
C	–1.258252	–7.908777	0.70792
C	–1.216388	–6.963114	1.775445
C	0.119304	–6.694717	1.9985
C	0.859531	–7.448259	1.02695
N	2.268024	–8.66154	–1.325392
C	2.834675	–7.782249	–0.440093
C	4.144326	–7.392616	–0.907548
C	4.340508	–8.02664	–2.103955
C	3.167798	–8.836311	–2.340763
H	3.812945	–9.79517	–4.137824
H	–1.374209	–13.296816	–2.711361
H	–3.384493	–8.080958	0.457084
H	2.793205	–6.601847	1.336071
H	0.574154	–13.534896	–4.502911
H	2.714699	–12.000292	–5.180212
H	–3.647211	–12.74083	–1.355046
H	–4.54298	–10.499869	–0.091951
H	–2.081589	–6.544226	2.289723
H	0.552762	–6.007574	2.725698

H	4.813081	–6.703441	–0.391064
H	5.207505	–7.97347	–2.76296

The optimized structure of the small model including the bridging water molecule of TS in the quartet state.

	X	Y	Z
H	3.307087	–12.953827	1.601984
C	2.525973	–12.268196	1.280381
C	2.383037	–11.509483	0.146048
H	3.051412	–11.430787	–0.708219
N	1.40686	–12.005488	2.04281
H	1.193752	–12.404834	2.951987
C	0.636392	–11.120221	1.371302
H	–0.311275	–10.73707	1.745978
N	1.202166	–10.800875	0.217691
O	–2.412449	–7.450729	–1.487185
O	–0.234568	–8.364891	–2.318015
H	–3.132688	–7.767508	–2.072241
H	–1.475134	–7.760989	–1.93037
Fe	0.427661	–9.435544	–1.244065
C	3.021642	–9.757399	–3.384385
C	–0.949858	–12.350855	–2.362922
C	–2.433934	–8.433299	0.046211
C	2.208279	–7.27727	0.705433
N	0.937944	–10.796229	–2.616739
C	2.000986	–10.713032	–3.472133
C	1.982881	–11.827833	–4.390805
C	0.90987	–12.603181	–4.045852
C	0.25065	–11.936824	–2.947027
N	–1.339393	–10.351915	–1.003222
C	–1.721851	–11.586754	–1.479705
C	–3.087161	–11.834709	–1.120116

C	–3.544757	–10.69428	–0.486943
C	–2.436328	–9.797217	–0.434907
N	–0.011116	–8.222141	0.288226
C	–1.257891	–7.908719	0.707268
C	–1.216036	–6.962909	1.774577
C	0.119581	–6.695356	1.998324
C	0.859993	–7.449868	1.027804
N	2.267893	–8.662102	–1.32488
C	2.834522	–7.782832	–0.439893
C	4.144003	–7.392675	–0.907423
C	4.340068	–8.026335	–2.104047
C	3.167331	–8.835938	–2.341081
H	3.813969	–9.796648	–4.136613
H	–1.373775	–13.296584	–2.711297
H	–3.383525	–8.079941	0.456384
H	2.792633	–6.600907	1.335166
H	0.575382	–13.534867	–4.50302
H	2.71429	–11.999733	–5.180859
H	–3.646563	–12.740864	–1.35467
H	–4.542759	–10.499859	–0.092414
H	–2.0813	–6.544964	2.289543
H	0.552927	–6.007617	2.72506
H	4.813363	–6.704685	–0.390168
H	5.207185	–7.97302	–2.762803

The optimized structure of the small model including the bridging water molecule of I in the doublet state.

	X	Y	Z
H	3.127667	–12.845712	1.923389
C	2.373067	–12.160407	1.54348
C	2.312169	–11.406352	0.398742
H	3.038991	–11.331841	–0.406394

N	1.20306	–11.891988	2.223277
H	0.924058	–12.288868	3.115613
C	0.485164	–11.007813	1.494394
H	–0.486848	–10.624515	1.799698
N	1.131212	–10.693548	0.38174
O	–2.596943	–7.302992	–1.047522
O	–0.013477	–8.270221	–2.430829
H	–3.431658	–7.52007	–1.501639
H	–0.823919	–7.789612	–2.165891
Fe	0.48861	–9.378139	–1.121052
C	3.117615	–9.87612	–3.210756
C	–1.03842	–12.182409	–2.256676
C	–2.443302	–8.15636	0.096916
C	2.275665	–7.161846	0.718465
N	0.964697	–10.779001	–2.480851
C	2.052997	–10.778822	–3.312919
C	1.986411	–11.895522	–4.223554
C	0.845792	–12.585894	–3.904119
C	0.219633	–11.857617	–2.827441
N	–1.367864	–10.140711	–0.938259
C	–1.777206	–11.396426	–1.399915
C	–3.145153	–11.624411	–0.99798
C	–3.556601	–10.484978	–0.351309
C	–2.423461	–9.595492	–0.346403
N	0.019247	–8.02911	0.305634
C	–1.17711	–7.691843	0.760528
C	–1.096118	–6.742759	1.843579
C	0.237455	–6.495932	2.033401
C	0.945664	–7.274277	1.040171
N	2.363716	–8.665661	–1.222528
C	2.928976	–7.753292	–0.399816
C	4.255237	–7.407153	–0.850488

C	4.468399	–8.120698	–2.001393
C	3.283019	–8.915449	–2.21237
H	3.924628	–9.974773	–3.943448
H	–1.50079	–13.113932	–2.597581
H	–3.284581	–8.006286	0.79724
H	2.879445	–6.484311	1.32984
H	0.453837	–13.492261	–4.366204
H	2.724441	–12.128356	–4.991636
H	5.351344	–8.124641	–2.640993
H	4.924013	–6.698483	–0.361268
H	0.703209	–5.818689	2.749915
H	–1.945239	–6.308861	2.37165
H	–4.538217	–10.268961	0.072237
H	–3.723843	–12.523499	–1.213204

The optimized structure of the small model including the bridging water molecule of I in the quartet state.

	X	Y	Z
H	3.141575	–13.004458	2.001445
C	2.398457	–12.294349	1.644097
C	2.309202	–11.550991	0.490723
H	3.002377	–11.518472	–0.34841
N	1.273682	–11.97118	2.372242
H	1.023485	–12.344416	3.282736
C	0.559842	–11.066238	1.653758
H	–0.381451	–10.640549	2.002576
N	1.160545	–10.792562	0.510793
O	–2.674175	–7.265327	–0.98194
O	–0.192479	–8.059499	–2.540997
H	–3.534124	–7.467228	–1.39416
H	–0.979252	–7.540073	–2.281905
Fe	0.434952	–9.254286	–1.295017

C	3.151031	–9.897981	–3.218169
C	–1.052657	–12.150758	–2.352746
C	–2.452049	–8.164901	0.114955
C	2.25592	–7.100838	0.660207
N	0.964884	–10.765461	–2.545338
C	2.082982	–10.793193	–3.339692
C	2.030068	–11.920337	–4.234273
C	0.864067	–12.586204	–3.949783
C	0.213264	–11.837223	–2.906917
N	–1.370862	–10.110871	–1.019287
C	–1.782522	–11.363062	–1.491549
C	–3.134333	–11.60858	–1.056037
C	–3.533583	–10.488348	–0.369114
C	–2.412758	–9.586075	–0.381894
N	0.012602	–7.999686	0.289634
C	–1.182094	–7.687128	0.761401
C	–1.100554	–6.743261	1.849711
C	0.231385	–6.471035	2.019085
C	0.935959	–7.229435	1.009257
N	2.335981	–8.618392	–1.287072
C	2.897171	–7.700713	–0.459765
C	4.238496	–7.391344	–0.879044
C	4.475651	–8.135637	–2.006731
C	3.285807	–8.91149	–2.240649
H	3.986108	–10.023417	–3.913747
H	–1.519173	–13.079566	–2.694509
H	–3.27484	–8.071612	0.846618
H	2.868647	–6.418682	1.257258
H	0.476315	–13.494559	–4.411653
H	2.790377	–12.177049	–4.972425
H	5.380086	–8.173444	–2.614413
H	4.907945	–6.690161	–0.3802

H	0.696163	–5.785703	2.728532
H	–1.948516	–6.331322	2.39706
H	–4.500975	–10.293463	0.095407
H	–3.710109	–12.5083	–1.274327

The optimized structure of the small model including the bridging and additional water molecules of RC in the doublet state.

	X	Y	Z
H	3.268652	–12.865089	1.934588
C	2.49076	–12.198607	1.568031
C	2.40736	–11.417802	0.442462
H	3.137163	–11.298003	–0.354721
N	1.308495	–11.991889	2.24675
H	1.040235	–12.421301	3.127075
C	0.561448	–11.116641	1.534856
H	–0.425747	–10.778141	1.844687
N	1.200982	–10.750181	0.435586
O	–2.244225	–4.489873	–2.249388
H	–2.020101	–4.516659	–3.196797
H	–3.030313	–3.918642	–2.187402
O	–2.675258	–7.159449	–1.603693
O	–0.089262	–8.348492	–2.192488
H	–2.531862	–6.186927	–1.701332
H	–1.857494	–7.568761	–1.959488
Fe	0.478753	–9.381975	–1.066142
C	3.168604	–9.9844	–3.085834
C	–1.128701	–12.103822	–2.376841
C	–2.329751	–8.521714	0.645105
C	2.264164	–7.005202	0.627579
N	0.948651	–10.800023	–2.439629
C	2.0735	–10.847364	–3.213539
C	1.999239	–11.946245	–4.147996

C	0.805831	–12.570703	–3.916638
C	0.156092	–11.833091	–2.857907
N	–1.350114	–10.220648	–0.819911
C	–1.840605	–11.329789	–1.456285
C	–3.230497	–11.528252	–1.119595
C	–3.584141	–10.488636	–0.304767
C	–2.398805	–9.687337	–0.127746
N	0.068686	–8.07952	0.430287
C	–1.153889	–7.817229	0.960776
C	–1.077022	–6.735882	1.913914
C	0.231933	–6.344113	1.948781
C	0.932743	–7.17183	0.994443
N	2.369641	–8.661311	–1.18095
C	2.920564	–7.676033	–0.416764
C	4.257522	–7.370088	–0.868595
C	4.497024	–8.17813	–1.944967
C	3.311701	–8.983218	–2.124121
H	4.000493	–10.131792	–3.78018
H	–1.649388	–12.961767	–2.811128
H	–3.256253	–8.175076	1.106861
H	2.833185	–6.235699	1.156191
H	0.387299	–13.442352	–4.42027
H	2.769233	–12.201096	–4.876656
H	5.393212	–8.236363	–2.563273
H	4.913135	–6.6216	–0.422823
H	0.688132	–5.553002	2.544278
H	–1.920247	–6.336803	2.477861
H	–4.556858	–10.272089	0.136696
H	–3.853813	–12.34336	–1.488233

The optimized structure of the small model including the bridging and additional water molecules of RC in the quartet state.

	X	Y	Z
H	3.268669	–12.865073	1.934587
C	2.490751	–12.198577	1.568017
C	2.407331	–11.417791	0.442463
H	3.137172	–11.297968	–0.354733
N	1.30849	–11.991903	2.246731
H	1.040245	–12.421341	3.127092
C	0.561447	–11.116628	1.534812
H	–0.425765	–10.778176	1.844698
N	1.200945	–10.750125	0.435435
O	–2.244184	–4.489872	–2.249439
H	–2.020125	–4.516706	–3.196866
H	–3.030287	–3.918641	–2.187446
O	–2.675171	–7.159483	–1.6036
O	–0.089248	–8.348474	–2.192699
H	–2.5318	–6.186965	–1.701324
H	–1.857509	–7.568786	–1.959526
Fe	0.478724	–9.381915	–1.06576
C	3.168501	–9.984508	–3.085828
C	–1.128833	–12.103734	–2.376741
C	–2.329571	–8.521623	0.645207
C	2.264192	–7.005226	0.627434
N	0.948548	–10.799947	–2.439659
C	2.073677	–10.847317	–3.213666
C	1.999243	–11.946276	–4.148031
C	0.805839	–12.570723	–3.916651
C	0.156183	–11.833096	–2.857934
N	–1.349968	–10.22052	–0.819764
C	–1.840536	–11.329985	–1.45644
C	–3.230535	–11.528211	–1.11956
C	–3.584136	–10.488671	–0.30478
C	–2.398835	–9.687321	–0.127717

N	0.068772	–8.0796	0.430051
C	–1.154176	–7.817321	0.960844
C	–1.076947	–6.735859	1.913972
C	0.231855	–6.344091	1.948786
C	0.93273	–7.171779	0.994526
N	2.369529	–8.661423	–1.180987
C	2.920536	–7.67594	–0.416635
C	4.257538	–7.370136	–0.868633
C	4.497017	–8.178163	–1.94495
C	3.311748	–8.98323	–2.124159
H	4.000461	–10.131822	–3.780182
H	–1.649406	–12.961764	–2.811187
H	–3.256236	–8.175036	1.106879
H	2.833122	–6.235677	1.156201
H	0.387298	–13.442341	–4.420254
H	2.769277	–12.20105	–4.876629
H	5.393224	–8.23635	–2.563286
H	4.913114	–6.621575	–0.422821
H	0.688161	–5.553039	2.544305
H	–1.920252	–6.336803	2.477864
H	–4.556864	–10.272068	0.136671
H	–3.853813	–12.343371	–1.488229

The optimized structure of the small model including the bridging and additional water molecules of TS in the doublet state.

	X	Y	Z
H	3.249345	–12.610164	2.152872
C	2.490085	–11.966459	1.713529
C	2.449501	–11.269487	0.531853
H	3.204454	–11.21187	–0.249123
N	1.288552	–11.702507	2.337469
H	0.988447	–12.063975	3.237735

C	0.572028	–10.876913	1.540321
H	–0.420907	–10.507573	1.791326
N	1.24944	–10.597055	0.438464
O	–2.376459	–4.980184	–1.059567
H	–2.590316	–4.206125	–1.609807
H	–1.622475	–4.739829	–0.491969
O	–2.47863	–7.502873	–1.823368
O	0.002519	–8.368343	–2.373824
H	–2.441266	–6.518918	–1.606669
H	–1.576037	–7.772803	–2.192137
Fe	0.579477	–9.342503	–1.185021
C	3.398756	–9.752209	–3.02215
C	–0.630366	–12.344851	–2.274425
C	–2.430514	–8.405542	–0.130866
C	2.112053	–6.968667	0.734319
N	1.252842	–10.773016	–2.419916
C	2.40535	–10.726957	–3.156366
C	2.502266	–11.896892	–3.999197
C	1.40366	–12.664666	–3.728872
C	0.622016	–11.940006	–2.753592
N	–1.18405	–10.299965	–1.045981
C	–1.492624	–11.561626	–1.507494
C	–2.879206	–11.84244	–1.250545
C	–3.41576	–10.70213	–0.696591
C	–2.338034	–9.767371	–0.584471
N	–0.03316	–8.039286	0.221174
C	–1.324109	–7.765877	0.527477
C	–1.403889	–6.71843	1.49882
C	–0.102123	–6.354654	1.78128
C	0.740679	–7.160788	0.94299
N	2.410737	–8.517992	–1.14859
C	2.865469	–7.553782	–0.286616

C	4.214017	–7.172906	–0.640852
C	4.548778	–7.900471	–1.748934
C	3.417848	–8.751982	–2.040913
H	4.270843	–9.830547	–3.676908
H	–1.002023	–13.315706	–2.613233
H	–3.423161	–8.086647	0.193418
H	2.613295	–6.221574	1.356063
H	1.129353	–13.628845	–4.15802
H	3.320929	–12.105336	–4.68852
H	5.482114	–7.884017	–2.312507
H	4.813351	–6.429282	–0.114582
H	0.247587	–5.593146	2.479411
H	–2.324632	–6.31578	1.922171
H	–4.448805	–10.517894	–0.400688
H	–3.389207	–12.772694	–1.502624

The optimized structure of the small model including the bridging and additional water molecules of TS in the quartet state.

	X	Y	Z
H	3.260508	–12.606413	2.153468
C	2.497585	–11.96576	1.716171
C	2.452461	–11.266333	0.536176
H	3.205885	–11.203887	–0.245874
N	1.294814	–11.710007	2.341156
H	0.997254	–12.075809	3.240532
C	0.573283	–10.886627	1.545891
H	–0.422463	–10.525167	1.797295
N	1.24898	–10.599962	0.444735
O	–2.38311	–4.975455	–1.069577
H	–2.586423	–4.198088	–1.619053
H	–1.640634	–4.738265	–0.485522
O	–2.480167	–7.500896	–1.827437

O	0.010404	–8.370923	–2.373521
H	–2.445371	–6.515674	–1.615911
H	–1.578618	–7.770438	–2.19514
Fe	0.578526	–9.340883	–1.178343
C	3.395119	–9.743788	–3.020434
C	–0.627834	–12.34372	–2.266001
C	–2.431272	–8.401703	–0.131445
C	2.110899	–6.971429	0.744992
N	1.254044	–10.770838	–2.413297
C	2.401949	–10.71852	–3.156902
C	2.493599	–11.882401	–4.009019
C	1.397207	–12.652759	–3.736846
C	0.621794	–11.93589	–2.750363
N	–1.182875	–10.298373	–1.038836
C	–1.489787	–11.561723	–1.496926
C	–2.876666	–11.842399	–1.240468
C	–3.414941	–10.700019	–0.692239
C	–2.337962	–9.764253	–0.5821
N	–0.034436	–8.038679	0.22602
C	–1.325893	–7.762469	0.528
C	–1.406071	–6.716818	1.501474
C	–0.104406	–6.356743	1.789064
C	0.739087	–7.16302	0.951715
N	2.409989	–8.517779	–1.139836
C	2.864357	–7.554185	–0.277162
C	4.211028	–7.168796	–0.634331
C	4.544655	–7.892896	–1.744962
C	3.415172	–8.746816	–2.036008
H	4.265628	–9.817349	–3.677801
H	–0.999676	–13.314248	–2.605535
H	–3.424246	–8.081349	0.189788
H	2.611173	–6.224583	1.367664

H	1.120396	–13.61309	–4.172813
H	3.306664	–12.085587	–4.706513
H	5.476083	–7.87208	–2.311487
H	4.809173	–6.423813	–0.108648
H	0.244754	–5.597595	2.490178
H	–2.327304	–6.314675	1.924438
H	–4.448419	–10.514862	–0.398735
H	–3.386516	–12.773438	–1.489839

The optimized structure of the small model including the bridging and additional water molecules of I in the doublet state.

	X	Y	Z
H	3.113543	–12.741758	2.095263
C	2.371397	–12.085826	1.64511
C	2.361117	–11.383815	0.46637
H	3.129718	–11.332525	–0.301301
N	1.161634	–11.809403	2.248157
H	0.840996	–12.171252	3.141129
C	0.470795	–10.971339	1.441978
H	–0.522215	–10.592054	1.676173
N	1.171664	–10.694427	0.353415
O	–3.714237	–5.266003	–0.668395
H	–4.629481	–5.073798	–0.94118
H	–3.21396	–4.440254	–0.795948
O	–2.640169	–7.593805	–1.510248
O	0.125308	–8.422754	–2.622627
H	–3.008929	–6.696536	–1.296709
H	–0.771699	–8.055129	–2.479994
Fe	0.582704	–9.461297	–1.24227
C	3.369019	–9.95508	–3.122412
C	–0.766491	–12.368808	–2.353901
C	–2.473502	–8.307862	–0.290035

C	2.160633	–7.088135	0.598211
N	1.199673	–10.902078	–2.503341
C	2.344894	–10.89395	–3.260759
C	2.375057	–12.045209	–4.128767
C	1.237763	–12.761928	–3.858851
C	0.518046	–12.016491	–2.855533
N	–1.255904	–10.28628	–1.153005
C	–1.585681	–11.579645	–1.585222
C	–2.972928	–11.842152	–1.267779
C	–3.46959	–10.692725	–0.714342
C	–2.370179	–9.758264	–0.672202
N	–0.027098	–8.078177	0.091058
C	–1.268001	–7.770631	0.43975
C	–1.298007	–6.748823	1.460072
C	0.009049	–6.430458	1.721443
C	0.814956	–7.238219	0.832704
N	2.436301	–8.680023	–1.253193
C	2.912468	–7.711506	–0.435267
C	4.257188	–7.344058	–0.805383
C	4.575911	–8.104309	–1.901244
C	3.43255	–8.944526	–2.158616
H	4.230431	–10.058978	–3.789439
H	–1.170003	–13.330636	–2.685148
H	–3.360755	–8.176903	0.355722
H	2.693245	–6.353408	1.209852
H	0.906712	–13.698244	–4.308728
H	3.170349	–12.281459	–4.836325
H	5.504529	–8.110353	–2.472782
H	4.867032	–6.59136	–0.304823
H	0.399038	–5.691136	2.422138
H	–2.200579	–6.320812	1.896382
H	–4.487603	–10.486405	–0.383129

H	–3.500286	–12.772142	–1.483119

The optimized structure of the small model including the bridging and additional water molecules of I in the quartet state.

	X	Y	Z
H	3.161201	–12.830213	2.205232
C	2.411609	–12.17461	1.767071
C	2.381927	–11.459332	0.593214
H	3.145137	–11.398818	–0.181714
N	1.207507	–11.909215	2.384107
H	0.897471	–12.279726	3.276901
C	0.508373	–11.064201	1.582074
H	–0.485937	–10.692958	1.832367
N	1.192656	–10.774516	0.492229
O	–3.718732	–5.241902	–0.643484
H	–4.633973	–5.009499	–0.883299
H	–3.186485	–4.440528	–0.79487
O	–2.704501	–7.577769	–1.526369
O	–0.068507	–8.248967	–2.791704
H	–3.071998	–6.684025	–1.294377
H	–0.979073	–7.909153	–2.670245
Fe	0.537059	–9.325516	–1.429401
C	3.392253	–9.949401	–3.140716
C	–0.772455	–12.343819	–2.400009
C	–2.485058	–8.296872	–0.317303
C	2.163094	–7.053836	0.551455
N	1.185352	–10.852273	–2.562156
C	2.353713	–10.870092	–3.289396
C	2.39622	–12.039685	–4.126491
C	1.247249	–12.744398	–3.86784
C	0.506981	–11.977139	–2.901848
N	–1.270972	–10.267792	–1.204978

C	–1.594883	–11.564643	–1.627294
C	–2.971359	–11.840901	–1.280721
C	–3.467728	–10.693833	–0.720621
C	–2.378613	–9.746052	–0.705754
N	–0.025652	–8.028646	0.016607
C	–1.268171	–7.750559	0.388174
C	–1.295094	–6.761007	1.437442
C	0.011226	–6.431694	1.692607
C	0.816005	–7.202995	0.77463
N	2.438465	–8.638474	–1.306713
C	2.916044	–7.67454	–0.479802
C	4.272916	–7.338138	–0.821193
C	4.603103	–8.112369	–1.906058
C	3.452369	–8.929946	–2.186568
H	4.26896	–10.083441	–3.781089
H	–1.159553	–13.314146	–2.724102
H	–3.352855	–8.181233	0.356578
H	2.697284	–6.336008	1.180517
H	0.925066	–13.692653	–4.298282
H	3.209129	–12.297378	–4.805691
H	5.544453	–8.139377	–2.455581
H	4.887919	–6.598696	–0.307747
H	0.399362	–5.709027	2.411616
H	–2.197391	–6.363481	1.901821
H	–4.478604	–10.501434	–0.360712
H	–3.495442	–12.775787	–1.482929

The coordinates for the atoms in the QM region of the QM/MM optimized structure of RC in the doublet state.

	X	Y	Z
C	3.299052	–11.197858	3.563927
H	3.808674	–12.165021	3.695943

H	4.066115	–10.409288	3.506077
C	2.464463	–11.197095	2.320706
C	2.298455	–10.257513	1.334727
H	2.857132	–9.336387	1.205347
N	1.545241	–12.184485	2.017565
H	1.434060	–13.065156	2.519076
C	0.856653	–11.822021	0.916165
H	0.075337	–12.439002	0.472482
N	1.290015	–10.648502	0.473872
O	–4.353662	–3.863312	–2.24877
H	–3.682175	–3.308762	–2.694556
H	–3.849765	–4.447867	–1.620739
O	–4.753969	–3.586972	1.609692
H	–5.336191	–3.276989	0.837180
H	–5.325339	–4.128512	2.179565
O	–3.200047	–5.065351	–0.127278
H	–3.686842	–4.625129	0.616759
H	–2.258666	–4.806308	–0.072048
O	–5.842186	–2.720259	–0.550641
H	–5.356182	–3.153544	–1.348884
H	–6.748306	–2.489276	–0.805845
O	–3.053034	–7.596977	–1.309816
O	–0.242619	–8.374271	–2.090012
H	–3.128096	–6.738495	–0.844354
H	–2.116769	–7.686037	–1.583553
Fe	0.424528	–9.409815	–1.007399
C	3.229063	–10.057365	–2.853989
C	–1.1925	–11.987174	–2.560886
C	–2.255591	–8.97895	1.063168
C	1.989436	–6.7442	0.433811
N	0.913489	–10.748937	–2.440379
C	2.106814	–10.834404	–3.106071

C	2.034832	–11.827703	–4.148254
C	0.760908	–12.320361	–4.125249
C	0.087224	–11.65704	–3.030019
N	–1.327332	–10.389492	–0.705403
C	–1.826567	–11.424443	–1.457382
C	–3.154629	–11.770288	–1.008023
C	–3.467419	–10.904625	–0.001875
C	–2.315891	–10.052001	0.166898
N	–0.023866	–8.143187	0.516171
C	–1.197733	–8.08466	1.212037
C	–1.206387	–6.934158	2.082897
C	–0.007892	–6.298323	1.898998
C	0.712125	–7.069965	0.914402
N	2.268176	–8.577869	–1.161003
C	2.718134	–7.456236	–0.51328
C	4.069224	–7.146534	–0.923495
C	4.433250	–8.114284	–1.814751
C	3.290581	–8.983243	–1.958382
H	4.125353	–10.269436	–3.438874
H	–1.737432	–12.759408	–3.101245
H	–3.139828	–8.813164	1.681185
H	2.462536	–5.860099	0.857050

The coordinates for the atoms in the QM region of the QM/MM optimized structure of RC in the quartet state.

	X	Y	Z
C	3.301613	–11.199909	3.565412
H	3.807797	–12.169241	3.695543
H	4.070088	–10.412837	3.507022
C	2.466975	–11.197535	2.322260
C	2.299605	–10.258706	1.335952
H	2.856302	–9.336959	1.208135

N	1.547987	–12.1849	2.019846
H	1.439921	–13.066815	2.519621
C	0.858472	–11.823059	0.919002
H	0.073547	–12.437747	0.480346
N	1.291312	–10.649837	0.475167
O	–4.349671	–3.859594	–2.240482
H	–3.683954	–3.297051	–2.68467
H	–3.841545	–4.436683	–1.607592
O	–4.75757	–3.581726	1.613641
H	–5.342687	–3.277284	0.840699
H	–5.328567	–4.106363	2.199518
O	–3.207024	–5.060671	–0.127001
H	–3.695551	–4.62237	0.617358
H	–2.263297	–4.811359	–0.065859
O	–5.838772	–2.719673	–0.54694
H	–5.351801	–3.156708	–1.344069
H	–6.733231	–2.455651	–0.810766
O	–3.045874	–7.590376	–1.331967
O	–0.241695	–8.378919	–2.08836
H	–3.126447	–6.732599	–0.867062
H	–2.111046	–7.672655	–1.612225
Fe	0.425536	–9.410496	–1.001841
C	3.231985	–10.05834	–2.851912
C	–1.189514	–11.988183	–2.559678
C	–2.253131	–8.984015	1.069368
C	1.989445	–6.74271	0.433821
N	0.915608	–10.748356	–2.440874
C	2.109022	–10.83555	–3.105085
C	2.038729	–11.830661	–4.146297
C	0.764596	–12.323115	–4.123572
C	0.089220	–11.657805	–3.030109
N	–1.324698	–10.392617	–0.700769

C	–1.824513	–11.424665	–1.455329
C	–3.154099	–11.770023	–1.008389
C	–3.466583	–10.905783	–0.00013
C	–2.314148	–10.055253	0.172247
N	–0.021053	–8.146946	0.521123
C	–1.194957	–8.088069	1.216261
C	–1.206041	–6.933856	2.082409
C	–0.00873	–6.295896	1.896618
C	0.713455	–7.069901	0.915603
N	2.269106	–8.57667	–1.160393
C	2.719147	–7.455237	–0.513843
C	4.069936	–7.145392	–0.925167
C	4.434178	–8.112795	–1.81675
C	3.291849	–8.982306	–1.959194
H	4.130508	–10.274929	–3.432356
H	–1.733404	–12.761995	–3.09916
H	–3.137707	–8.816499	1.686551
H	2.461013	–5.856345	0.854054

The coordinates for the atoms in the QM region of the QM/MM optimized structure of TS in the doublet state.

	X	Y	Z
C	3.294173	–11.198717	3.526384
H	3.788636	–12.17657	3.644656
H	4.074838	–10.422531	3.480627
C	2.460415	–11.165425	2.280853
C	2.304732	–10.211823	1.305016
H	2.874482	–9.297434	1.184347
N	1.528408	–12.136932	1.965952
H	1.409959	–13.025117	2.452379
C	0.843286	–11.752312	0.870980
H	0.054938	–12.35635	0.425054

N	1.288797	–10.57764	0.440550
O	–4.402139	–3.639499	–2.472663
H	–3.746459	–3.052295	–2.900199
H	–3.871805	–4.278299	–1.932235
O	–4.713794	–3.808003	1.361814
H	–5.32867	–3.411396	0.659043
H	–5.275152	–4.356553	1.936207
O	–3.177857	–5.12137	–0.514192
H	–3.71309	–4.786038	0.258727
H	–2.287261	–4.721564	–0.430585
O	–5.876564	–2.687969	–0.637741
H	–5.415541	–3.025415	–1.488631
H	–6.770639	–2.3767	–0.846869
O	–2.64227	–7.661618	–1.104031
O	–0.324124	–8.292944	–2.117129
H	–2.815128	–6.687797	–0.904058
H	–1.725405	–7.808274	–1.593566
Fe	0.438540	–9.330701	–1.063062
C	3.212049	–9.939823	–2.961667
C	–1.042772	–12.144758	–2.364203
C	–2.400494	–8.506911	0.434625
C	2.093876	–6.771452	0.519794
N	0.930713	–10.696223	–2.463281
C	2.097813	–10.748077	–3.170485
C	2.039853	–11.787886	–4.166013
C	0.804297	–12.362532	–4.058148
C	0.140970	–11.705309	–2.955792
N	–1.299231	–10.318497	–0.751247
C	–1.692786	–11.522365	–1.300171
C	–2.988881	–11.871392	–0.806896
C	–3.423261	–10.816366	–0.031519
C	–2.355194	–9.873441	–0.033573

N	0.001725	–8.053766	0.443313
C	–1.223706	–7.873301	0.983872
C	–1.213107	–6.813496	1.935439
C	0.076420	–6.312939	1.938322
C	0.806687	–7.076346	0.976702
N	2.282536	–8.509601	–1.202375
C	2.769447	–7.434307	–0.498422
C	4.115581	–7.13013	–0.923805
C	4.446818	–8.056919	–1.867887
C	3.288067	–8.897793	–2.039509
H	4.096938	–10.140112	–3.567389
H	–1.515763	–13.032983	–2.778331
H	–3.330426	–8.232634	0.937982
H	2.595478	–5.922829	0.983427

The coordinates for the atoms in the QM region of the QM/MM optimized structure of TS in the quartet state.

	X	Y	Z
C	3.294729	–11.199161	3.527326
H	3.789338	–12.176861	3.645969
H	4.075152	–10.422737	3.481350
C	2.461430	–11.166621	2.281670
C	2.306273	–10.213719	1.305068
H	2.875883	–9.299181	1.184423
N	1.529311	–12.138099	1.967318
H	1.410334	–13.025708	2.454431
C	0.844773	–11.753641	0.871624
H	0.055997	–12.357355	0.426109
N	1.290642	–10.579631	0.440461
O	–4.402398	–3.639521	–2.472797
H	–3.746595	–3.052434	–2.900277
H	–3.872289	–4.277741	–1.931449

O	–4.714299	–3.80794	1.362240
H	–5.32902	–3.411345	0.659285
H	–5.275774	–4.356277	1.936714
O	–3.178258	–5.120648	–0.514029
H	–3.713421	–4.785242	0.259043
H	–2.287545	–4.721027	–0.430567
O	–5.876415	–2.688399	–0.637778
H	–5.41561	–3.025489	–1.488993
H	–6.77059	–2.377136	–0.84641
O	–2.64126	–7.660785	–1.105574
O	–0.31791	–8.293951	–2.123943
H	–2.81564	–6.68682	–0.906567
H	–1.726536	–7.805764	–1.595002
Fe	0.435755	–9.328475	–1.062715
C	3.211923	–9.940743	–2.959408
C	–1.042169	–12.145464	–2.363495
C	–2.400698	–8.505952	0.433764
C	2.094325	–6.771539	0.520392
N	0.931151	–10.69865	–2.461454
C	2.097745	–10.748969	–3.169157
C	2.039673	–11.787423	–4.166408
C	0.803891	–12.361869	–4.059516
C	0.141272	–11.70616	–2.955752
N	–1.299116	–10.317312	–0.751627
C	–1.692076	–11.521832	–1.300212
C	–2.988426	–11.870749	–0.80746
C	–3.423565	–10.815343	–0.033158
C	–2.355651	–9.872208	–0.03497
N	0.001589	–8.054346	0.442778
C	–1.224003	–7.873159	0.983236
C	–1.212942	–6.813304	1.934655
C	0.076683	–6.313311	1.937776

C	0.806792	–7.076914	0.976172
N	2.283140	–8.509552	–1.2003
C	2.770074	–7.433664	–0.498032
C	4.115855	–7.128939	–0.924487
C	4.446686	–8.056332	–1.868251
C	3.287845	–8.89787	–2.038268
H	4.096487	–10.140366	–3.565594
H	–1.515785	–13.033499	–2.777193
H	–3.330609	–8.2319	0.937366
H	2.595014	–5.922822	0.984654

The coordinates for the atoms in the QM region of the QM/MM optimized structure of I in the doublet state.

	X	Y	Z
C	3.276241	–11.18985	3.521917
H	3.771361	–12.168988	3.632304
H	4.057547	–10.414181	3.474040
C	2.428210	–11.146602	2.284326
C	2.263356	–10.185409	1.315830
H	2.836367	–9.272767	1.195741
N	1.491725	–12.112967	1.971318
H	1.379765	–13.006991	2.448492
C	0.797660	–11.718432	0.883325
H	0.012604	–12.325424	0.435417
N	1.239342	–10.541262	0.456536
O	–4.406438	–3.695435	–2.383294
H	–3.737687	–3.128106	–2.817472
H	–3.898447	–4.31577	–1.798748
O	–4.783995	–3.666652	1.493970
H	–5.383267	–3.312192	0.755490
H	–5.342624	–4.227285	2.059048
O	–3.276934	–5.08106	–0.329747

H	–3.755937	–4.65192	0.430154
H	–2.337515	–4.805876	–0.281837
O	–5.889912	–2.674915	–0.599768
H	–5.417002	–3.048498	–1.431667
H	–6.771649	–2.350684	–0.837996
O	–2.955836	–7.709415	–0.849787
O	–0.160625	–8.328834	–2.45894
H	–3.148145	–6.76542	–0.613269
H	–1.029564	–7.966644	–2.196099
Fe	0.464005	–9.35887	–1.100133
C	3.255572	–9.996674	–2.963545
C	–1.029248	–12.144664	–2.362657
C	–2.526072	–8.418857	0.313376
C	2.053349	–6.766042	0.430329
N	0.981904	–10.750578	–2.459162
C	2.149896	–10.80439	–3.178057
C	2.076727	–11.834493	–4.179258
C	0.832748	–12.395115	–4.066872
C	0.192117	–11.726194	–2.959035
N	–1.343321	–10.250987	–0.836968
C	–1.698469	–11.506913	–1.353113
C	–2.996108	–11.877245	–0.840822
C	–3.447437	–10.820652	–0.099041
C	–2.394216	–9.836956	–0.14338
N	–0.079821	–7.978564	0.278935
C	–1.265974	–7.802863	0.847413
C	–1.229936	–6.775069	1.853608
C	0.051124	–6.277057	1.844462
C	0.766871	–7.025436	0.846399
N	2.308469	–8.541219	–1.243535
C	2.776843	–7.461984	–0.561301
C	4.127193	–7.152194	–0.952361

C	4.479046	–8.088734	–1.887122
C	3.330479	–8.935443	–2.058459
H	4.144031	–10.197711	–3.566164
H	–1.477189	–13.0589	–2.750731
H	–3.296805	–8.372052	1.104845
H	2.565651	–5.932751	0.911568

The coordinates for the atoms in the QM region of the QM/MM optimized structure of I in the quartet state.

	X	Y	Z
C	3.290112	–11.177842	3.566312
H	3.791618	–12.152086	3.684706
H	4.065882	–10.396937	3.521013
C	2.450527	–11.149561	2.325098
C	2.278356	–10.199958	1.344426
H	2.849918	–9.285727	1.211771
N	1.519142	–12.124548	2.023640
H	1.409583	–13.011682	2.513174
C	0.825213	–11.738312	0.929032
H	0.037025	–12.349235	0.489486
N	1.259838	–10.567564	0.489439
O	–4.408168	–3.686138	–2.377396
H	–3.733113	–3.1264	–2.811367
H	–3.908388	–4.314293	–1.79436
O	–4.793508	–3.666614	1.490791
H	–5.388976	–3.300785	0.754521
H	–5.361117	–4.219705	2.054311
O	–3.3036	–5.095443	–0.330584
H	–3.782171	–4.664276	0.429198
H	–2.360589	–4.835174	–0.273185
O	–5.891161	–2.654901	–0.59755
H	–5.420416	–3.029269	–1.429564

H	–6.766477	–2.314055	–0.837099
O	–3.032072	–7.72278	–0.911716
O	–0.36335	–8.356984	–2.755522
H	–3.214586	–6.778669	–0.67016
H	–1.171452	–7.879327	–2.490962
Fe	0.395763	–9.261543	–1.28087
C	3.246309	–9.981139	–2.99975
C	–1.057176	–12.150532	–2.390781
C	–2.561959	–8.417108	0.242790
C	2.055040	–6.736511	0.362793
N	0.947379	–10.719612	–2.507452
C	2.130110	–10.778039	–3.210594
C	2.063505	–11.826972	–4.189074
C	0.819471	–12.39208	–4.076402
C	0.163396	–11.713242	–2.987969
N	–1.395354	–10.272519	–0.870873
C	–1.741534	–11.529217	–1.38222
C	–3.040758	–11.9008	–0.866217
C	–3.495847	–10.837616	–0.135861
C	–2.442271	–9.847094	–0.190723
N	–0.108798	–7.913008	0.125659
C	–1.288986	–7.784254	0.734761
C	–1.236591	–6.800431	1.776964
C	0.040818	–6.285128	1.760389
C	0.747490	–6.984779	0.727923
N	2.322645	–8.498439	–1.302301
C	2.798176	–7.430341	–0.610528
C	4.159157	–7.145955	–0.978987
C	4.505832	–8.087507	–1.912437
C	3.343289	–8.91193	–2.102329
H	4.133253	–10.205616	–3.595653
H	–1.483791	–13.072464	–2.783272

H	–3.306429	–8.359926	1.059002
H	2.567908	–5.927759	0.883096