Supporting Information for

Coupled electron transfer and proton hopping in the final step of CYP19-catalyzed androgen aromatization

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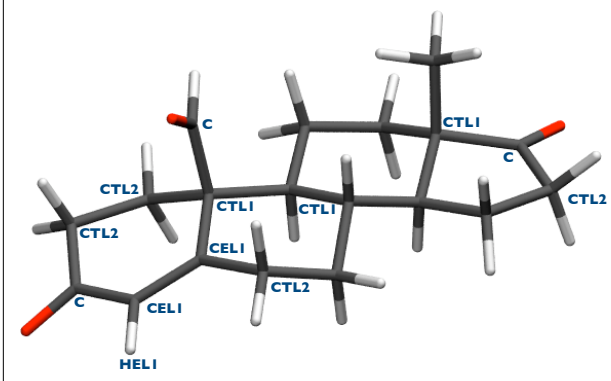
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Bonds
CTL1   C     389.502     1.533
CEL1   C     194.402     1.474

Angles
CTL2   C      CEL1     33.739    116.160
CEL1   CEL1   C        35.859    124.280
HEL1   CEL1   C        41.626    115.010
O      C      CEL1     80.353    121.675
CTL3   CTL1   C        16.335    105.083
CTL1   C      CTL2     76.646    108.128

Dihedrals
X      CEL1   C   X     3.245   2    180.00
```

Figure S1. Additional CHARMM parameters for 19-oxoandrostrenedione (19-oxoAD).

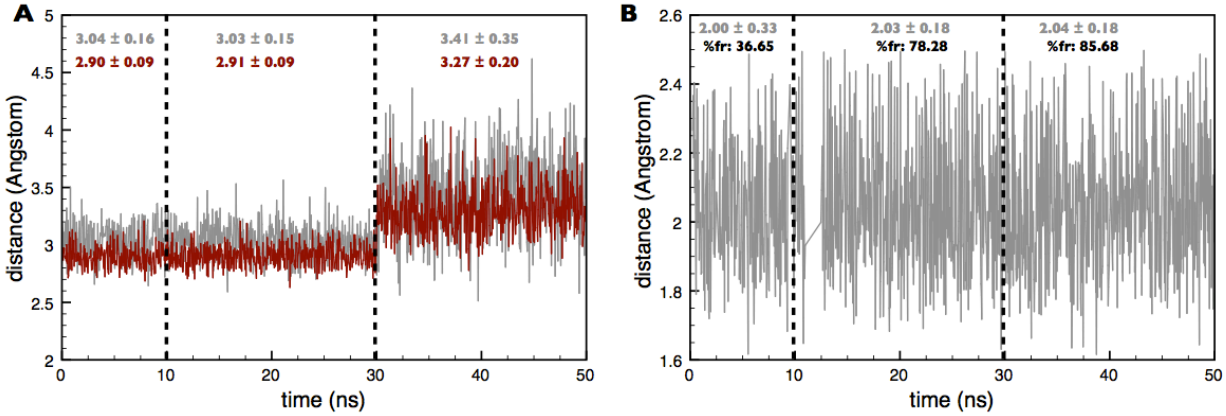


Figure S2. Time evolution of relevant active site distances in the oxyferrous CYP19/19-oxoAD MD simulation. (**A**) Distance between C19-O_d (maroon) and 1βH-O_p (gray); (**B**) Distance between H_2O and T310-O. Dotted lines specify the time points when harmonic restraints were removed. Mean distances ± standard deviation for each time window are reported in Å.

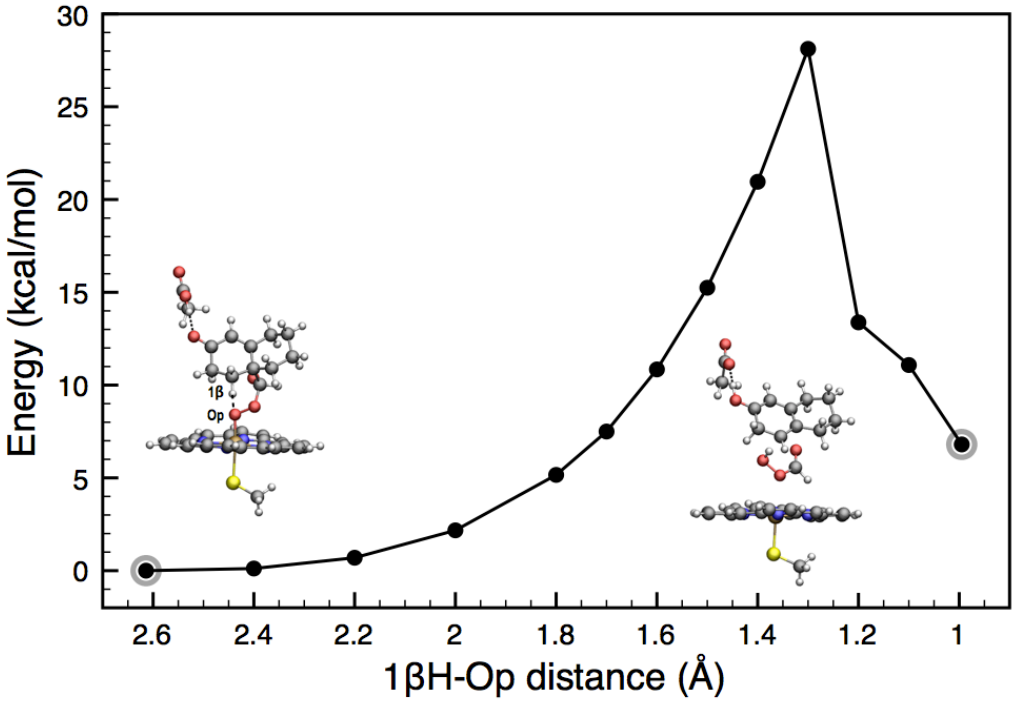


Figure S3. The transition state search for concerted deformylation. B3LYP/B1:CHARMM22 potential energy surface for 1βH abstraction from 19-oxoAD by O_p in **PH**.

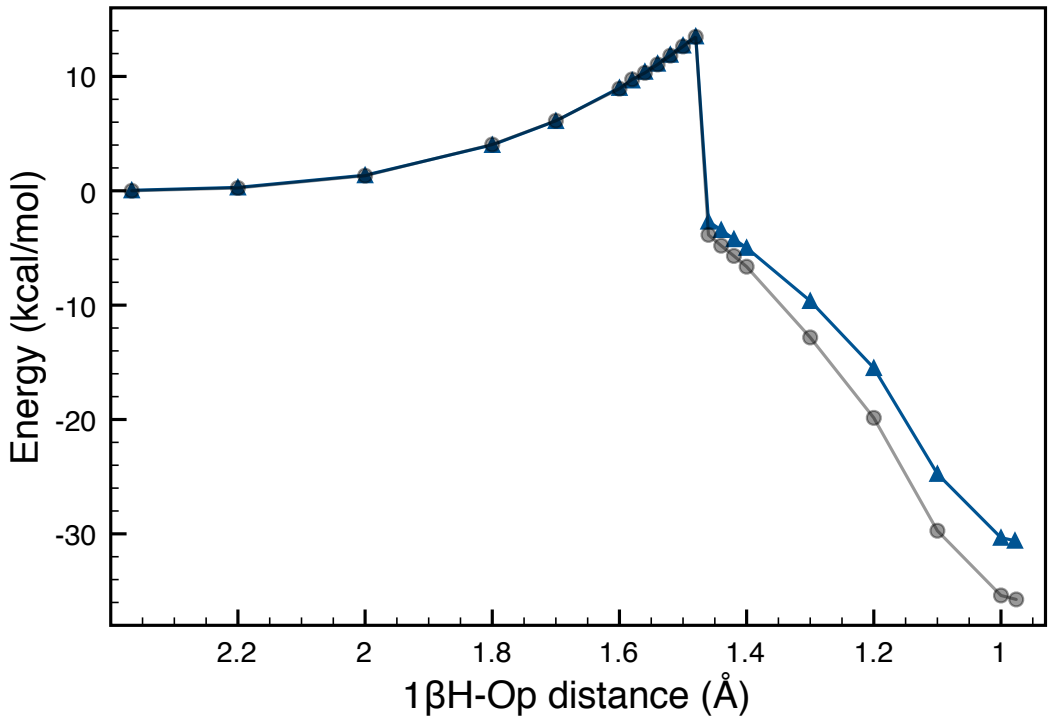


Figure S4. B3LYP/B1:CHARMM22 potential energy surface for 1β-hydrogen atom abstraction by Cpd II from ^{CC}**I2.** The quartet surface is in blue.

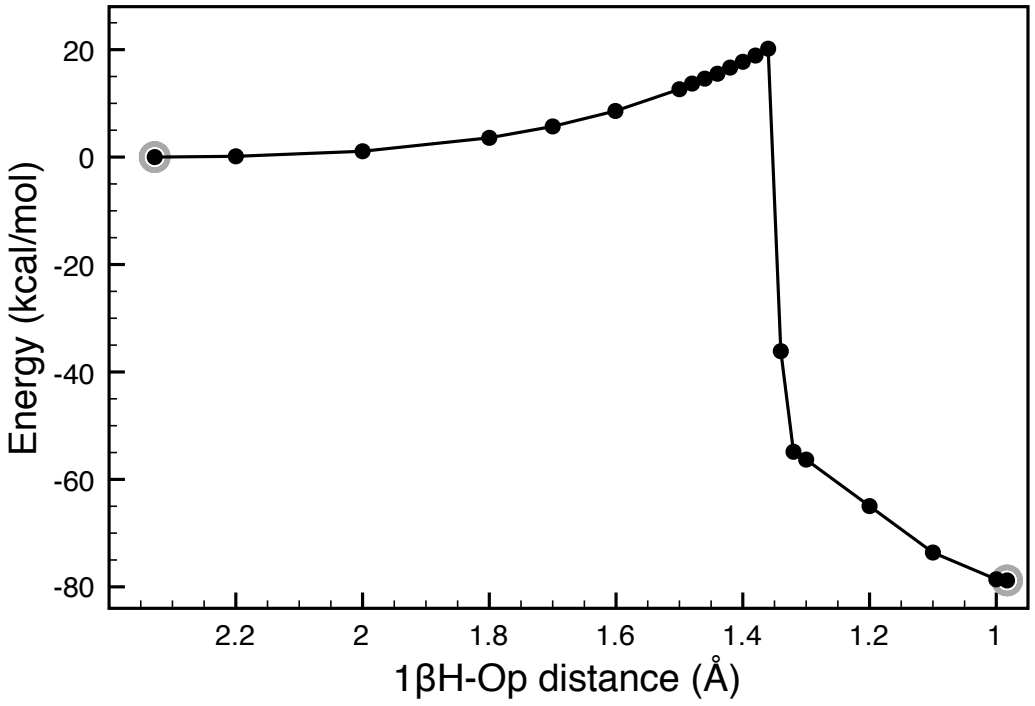


Figure S5. B3LYP/B1:CHARMM22 potential energy surface for 1βH abstraction by Cpd II from ^{OO}**I1**. The unconstrained, fully optimized data points are surrounded with gray circles

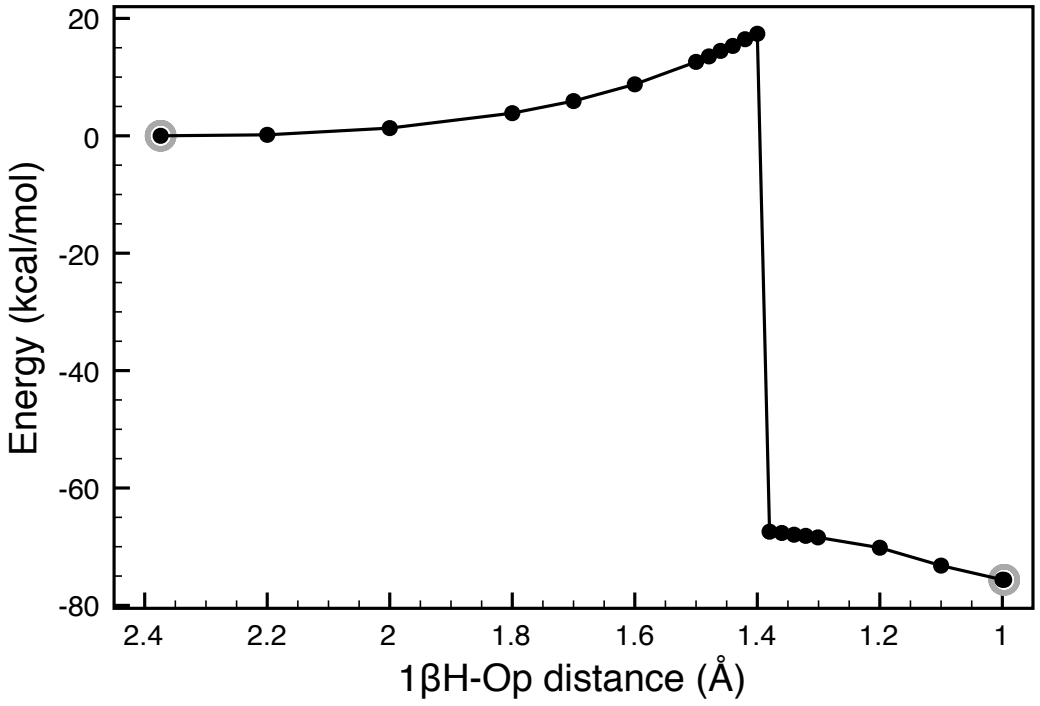


Figure S6. B3LYP/B1:CHARMM22 potential energy surface for 1βH abstraction by Cpd II from ^{OO}**HI1**. The unconstrained, fully optimized data points are surrounded with gray circles.

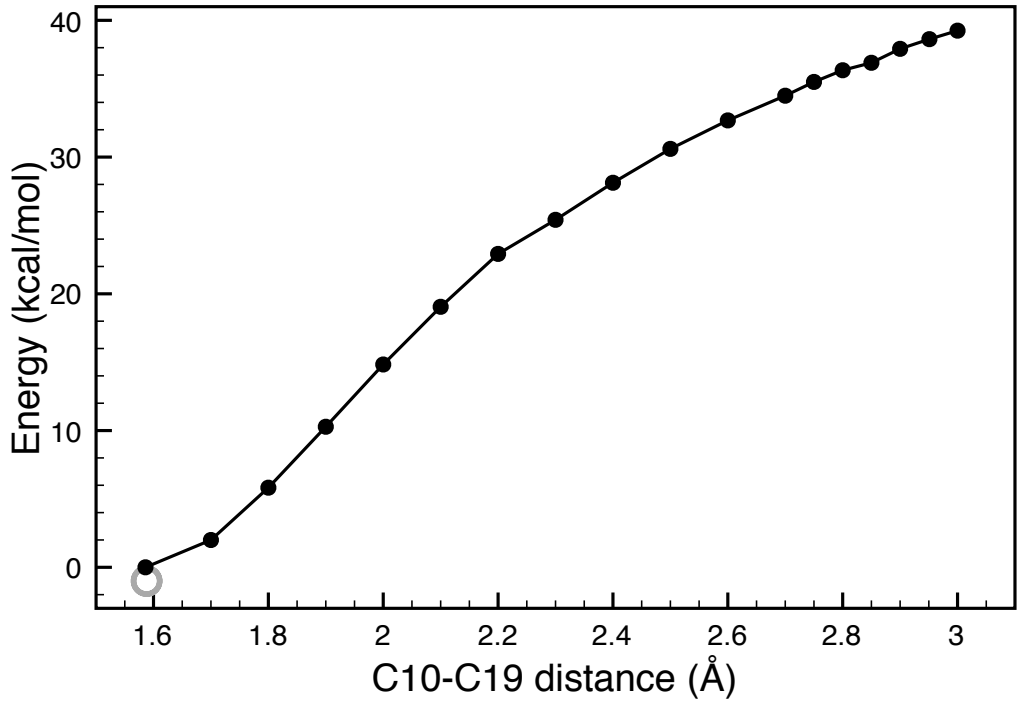


Figure S7. B3LYP/B1:CHARMM22 potential energy surface for C19-C10 cleavage from **HPH**. The unconstrained, fully optimized data points are surrounded with gray circles

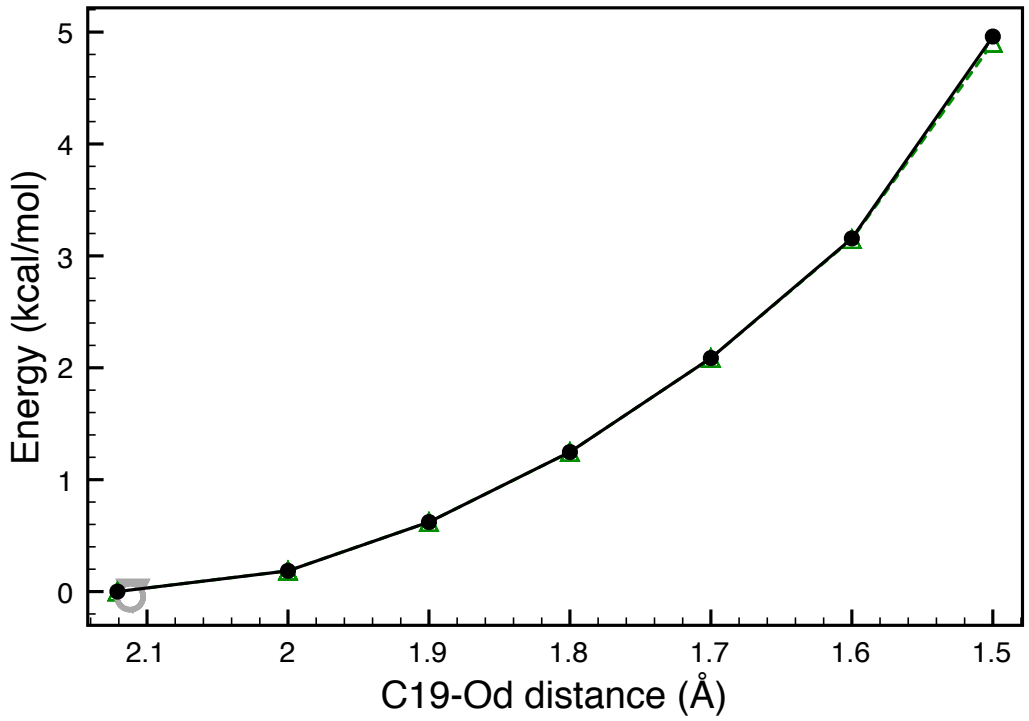


Figure S8. B3LYP/B1:CHARMM22 potential energy surface for addition of superoxo distal oxygen to 19-oxoAD under restricted (green, open triangles) and unrestricted (black, filled circles) formalism. The unconstrained, fully optimized data points are in gray.

Stepwise mechanism for C-C cleavage mediated by peroxo addition

Figure 3

Peroxohemiacetal (**PH**)

C	78.5420767	65.9644026	57.2722351
H	77.8580609	66.5111419	56.6098090
H	79.1697622	65.3346489	56.6345830
C	79.3866120	67.0288287	57.9742166
O	79.1416123	67.4991561	59.0790290
O	80.3875553	67.5274988	57.2542193
H	80.5066544	67.0871271	56.3477878
C	79.0476829	61.5656277	45.4683988
H	78.7011805	60.7207587	44.8601137
H	78.2762960	62.3397232	45.4506892
S	79.3011357	60.9920363	47.2026670
C	80.7499072	66.7339114	51.3052328
H	80.9676498	66.0970950	50.4449473
H	81.5553815	67.4842374	51.3611872
C	80.7793301	65.8763300	52.5756983
H	80.0753416	65.0401729	52.4492356
H	81.7748015	65.4546117	52.7521057
C	80.3483600	66.6618037	53.7854032
O	80.8534838	66.4457336	54.9150308
C	79.3125068	67.6397014	53.5878498
H	78.8716149	68.0779755	54.4819664
C	78.8515966	67.9913796	52.3549258
C	77.6789499	68.9291940	52.2743802
H	76.8385835	68.3490518	51.8675153
H	77.3806684	69.2618930	53.2746358
C	77.9597460	70.1253503	51.3602093
H	77.0565837	70.7492290	51.3075636
H	78.7599073	70.7404420	51.8024992
C	78.3726776	69.5934214	49.9819362
H	77.5179895	69.0491366	49.5659903
C	79.6190751	68.6619405	50.0767346
H	80.4403565	69.2708117	50.5036941
C	79.4083804	67.4592219	51.0721000
C	78.2241299	66.3746746	50.4861989
H	77.6927815	66.9848912	49.7112743
O	77.4807493	65.8257866	51.3742449
Fe	79.2814203	62.8988739	48.7860725
N	78.5911159	64.1207180	47.3064137
N	77.3833886	62.3301917	49.2475975
N	80.0082066	61.5732644	50.1859896
N	81.1870007	63.4361230	48.3265324
C	79.3168596	65.0231038	46.5752391
C	78.4377963	65.8168245	45.7223368
C	77.1613670	65.3698509	45.9661534
C	77.2822241	64.3203193	46.9756631
C	76.2398561	62.7613187	48.6401776
C	75.0607575	62.1897743	49.2931024
C	75.5188903	61.4310957	50.3461916
C	76.9882051	61.5091170	50.2665653
C	79.2686177	60.7639930	50.9980095
C	80.1269793	59.9112843	51.8190958
C	81.4278945	60.2511819	51.5204835
C	81.3179104	61.3103801	50.4983737
C	82.3184987	63.0433957	48.9979676
C	83.4652242	63.8424294	48.5937307
C	82.9929865	64.7298018	47.6587477
C	81.5690279	64.4718071	47.5089483
C	80.6984059	65.1826637	46.6781536
H	81.1409015	65.9684388	46.0697717
C	76.2064312	63.6541776	47.5681480
H	75.2241096	63.9300793	47.2019694
C	77.8772194	60.7833542	51.0604552
H	77.4393045	60.1481504	51.8248758
C	82.3803380	62.0230803	49.9462820
H	83.3738309	61.8103795	50.3329479
O	79.2244615	64.1832362	50.0811782
O	78.9382310	65.4806924	49.5384267
H	77.9816809	65.3215812	57.9510603
H	79.8914972	61.9958623	44.9290082
H	78.5943847	70.4161926	49.3022598
H	79.9783087	68.3796260	49.0871306
H	78.7550990	66.5877772	45.0201849
H	76.2260932	65.7295204	45.5372395
H	74.0484433	62.3223962	48.9113987
H	75.0096404	60.8806645	51.1372393
H	79.7410501	59.1240628	52.4667126
H	82.3834250	59.8872595	51.8980922
H	84.4575372	63.7505135	49.0352427
H	83.5469746	65.4710691	47.0828255

TURBOMOLE (QM) and ChemShell Energies (MM and QM/MM)

	B3LYP/B1	B3LYP/B2//B1	PBE0/B2/*
QM/MM	-3749.586018	-3750.264069	-3748.886301
QM	-3647.122326	-3647.800377	-3646.422609
MM	-102.463692	-102.463692	-102.463692
ZPE	0.502622	-	-

*B3LYP/B1 geometry

Figure 3

TS for C-C cleavage starting from **PH** (**^{cc}TS1**)

C	78.5381833	65.9622461	57.2622958
H	77.8572583	66.5067749	56.5948874
H	79.1713549	65.3338042	56.6287517
C	79.3779533	67.0310328	57.9653918
O	79.1234823	67.5009106	59.0699286
O	80.3777352	67.5287794	57.2495104
H	80.5025475	67.0865190	56.3351001
C	79.0598702	61.5541992	45.4808264
H	78.7152211	60.7089735	44.8720034
H	78.2844413	62.3241993	45.4668935
S	79.3212061	60.9762199	47.2125146
C	80.8262274	66.8095215	51.3265368
H	81.0466515	66.1758787	50.4634104
H	81.6355859	67.5579920	51.3786783
C	80.8588749	65.9406201	52.5909311
H	80.1954041	65.0762116	52.4374306
H	81.8658075	65.5549599	52.7849966
C	80.3646541	66.6839179	53.8075052
O	80.8589906	66.4494308	54.9459658
C	79.3044108	67.6155737	53.6020891
H	78.8134283	68.0180528	54.4862975
C	78.8950304	68.0118493	52.3501142
C	77.7057658	68.9324565	52.2660952
H	76.8715561	68.3425776	51.8575024
H	77.3992943	69.2589604	53.2657697
C	77.9690006	70.1344873	51.3557358
H	77.0585816	70.7478035	51.3008543
H	78.7612886	70.7590770	51.7986916
C	78.3900615	69.6080465	49.9784811
H	77.5422189	69.0491872	49.5664331
C	79.6523296	68.6991052	50.0726735
H	80.4770076	69.3343773	50.4577049
C	79.4926128	67.5362237	51.1047009
C	78.2356310	66.2939680	50.4438747
H	77.7679280	66.9540738	49.6765954
O	77.4866117	65.7711765	51.3153181
Fe	79.2931454	62.8663801	48.7921806
N	78.5978762	64.1101784	47.3284127
N	77.3944087	62.2959359	49.2518095
N	80.0184373	61.5374649	50.1842709
N	81.1944606	63.4189344	48.3364169
C	79.3228056	65.0125554	46.5947485
C	78.4428734	65.8068688	45.7438480
C	77.1664131	65.3612162	45.9903968
C	77.2879467	64.3100814	46.9981211
C	76.2507271	62.7328767	48.6481981
C	75.0720424	62.1564376	49.2965521
C	75.5299089	61.3905602	50.3445531
C	76.9989554	61.4680757	50.2653318
C	79.2801220	60.7290443	50.9985745
C	80.1406711	59.8909374	51.8316028
C	81.4403488	60.2404949	51.5397910
C	81.3283678	61.2895983	50.5071852
C	82.3255621	63.0289345	49.0100194
C	83.4708152	63.8316895	48.6081050
C	82.9985895	64.7174055	47.6716202
C	81.5755438	64.4564322	47.5203280
C	80.7048941	65.1690407	46.6919279
H	81.1469938	65.9536827	46.0820342
C	76.2138942	63.6368709	47.5856343
H	75.2296685	63.9123371	47.2236238
C	77.8886387	60.7416162	51.0577607
H	77.4512425	60.1060795	51.8220818
C	82.3885693	62.0083579	49.9581235
H	83.3811617	61.8033272	50.3505932
O	79.2382424	64.1278826	50.1164606
O	79.0436655	65.4511059	49.5902163
H	77.9755255	65.3197646	57.9395698
H	79.9006706	61.9893581	44.9406803
H	78.6012172	70.4293882	49.2937347
H	79.9945676	68.4009798	49.0816836
H	78.7580734	66.5782947	45.0412688
H	76.2328042	65.7232601	45.5598563
H	74.0623359	62.2878682	48.9075981
H	75.0191802	60.8366474	51.1322099
H	79.7567083	59.1078950	52.4854252
H	82.3960158	59.8905484	51.9300533
H	84.4625572	63.7438901	49.0517328
H	83.5510934	65.4604817	47.0966040

TURBOMOLE (QM) and ChemShell Energies (MM and QM/MM)

	B3LYP/B1	B3LYP/B2//B1	PBE0/B2/*
QM/MM	-3749.585787	-3750.264859	-3748.886131
QM	-3647.119840	-3647.798912	-3646.420184
MM	-102.465947	-102.465947	-102.465947
ZPE	0.502082	-	-

*B3LYP/B1 geometry

Figure 3

Peroxoformate (^{cc}**I1**)

C	78.4609376	65.8913443	57.1224763
H	77.7777597	66.3030752	56.3661743
H	79.1920017	65.2634207	56.6047277
C	79.1415096	67.1447256	57.7372933
O	78.4965490	67.8037675	58.6075194
O	80.2465378	67.4939843	57.2303529
H	80.7244898	66.8329658	55.8796634
C	79.0957561	61.5150055	45.4461327
H	78.7552263	60.6721802	44.8321214
H	78.3131363	62.2768039	45.4417231
S	79.3674117	60.9075098	47.1624037
C	81.1088190	67.0753746	51.4224047
H	81.1453845	66.4399497	50.5296614
H	82.0351444	67.6717637	51.3809853
C	81.1153822	66.1514932	52.6559480
H	80.5053008	65.2624969	52.4355842
H	82.1300209	65.7924880	52.8604456
C	80.5512969	66.8065517	53.8913745
O	81.1069112	66.3937396	55.0390158
C	79.5382752	67.6976337	53.7665595
H	79.0591234	68.1108180	54.6499257
C	79.1861167	68.2574232	52.4649826
C	78.0130456	69.2193942	52.4557452
H	77.0954374	68.6718704	52.1887499
H	77.8372206	69.5986644	53.4674964
C	78.2107560	70.3802275	51.4776566
H	77.2934167	70.9841977	51.4421027
H	79.0219621	71.0284470	51.8433730
C	78.5659666	69.8046627	50.1014308
H	77.7246336	69.1745651	49.7836405
C	79.8818795	68.9774264	50.1583571
H	80.7203772	69.6895022	50.3316043
C	79.9285615	68.0252024	51.3471550
C	78.0486404	65.8053018	50.2497809
H	77.9292325	66.8105309	49.8230573
O	77.2842329	65.3196395	51.0571034
Fe	79.3643611	62.6936693	48.7331931
N	78.6517566	64.0138716	47.3371824
N	77.4657215	62.1370613	49.2087428
N	80.0940115	61.3690272	50.1142173
N	81.2557343	63.2999580	48.3031341
C	79.3677063	64.9428773	46.6229885
C	78.4798741	65.7464069	45.7911811
C	77.2080018	65.2775770	46.0231040
C	77.3379957	64.2041970	47.0032448
C	76.3177695	62.5727551	48.6086925
C	75.1446387	61.9892408	49.2570945
C	75.6076195	61.2305303	50.3085517
C	77.0747364	61.3083893	50.2241689
C	79.3589209	60.5791188	50.9514592
C	80.2240563	59.7815224	51.8173944
C	81.5206395	60.1403375	51.5271785
C	81.4048073	61.1531825	50.4592184
C	82.3881341	62.9159243	48.9801401
C	83.5214894	63.7489776	48.6084700
C	83.0436578	64.6462117	47.6858728
C	81.6262070	64.3686642	47.5186727
C	80.7492003	65.1039434	46.7183536
H	81.1831870	65.9098574	46.1318030
C	76.2713170	63.4989641	47.5661085
H	75.2850888	63.7696533	47.2064442
C	77.9687923	60.5858642	51.0147664
H	77.5364507	59.9594778	51.7882349
C	82.4589383	61.8839230	49.9153240
H	83.4504719	61.6925989	50.3154845
O	79.3423897	63.8934114	50.1518134
O	79.1180857	65.2547025	49.6992188
H	77.9175081	65.2642542	57.8292357
H	79.9349769	61.9605216	44.9120070
H	78.7001135	70.5773812	49.3444782
H	80.1173969	68.5679464	49.1760516
H	78.7854047	66.5306792	45.0986247
H	76.2713897	65.6320510	45.5927874
H	74.1335959	62.1086694	48.8677415
H	75.0987719	60.6868849	51.1045356
H	79.8426822	59.0254714	52.5036940
H	82.4757210	59.8255744	51.9476664
H	84.5104363	63.6740169	49.0606110
H	83.5906918	65.4019587	47.1222535

TURBOMOLE (QM) and ChemShell Energies (MM and QM/MM)

	B3LYP/B1	B3LYP/B2//B1	PBE0/B2/*
QM/MM	-3749.616163	-3750.295484	-3748.912723
QM	-3647.167245	-3647.846566	-3646.463804
MM	-102.448919	-102.448919	-102.448919
ZPE	0.503503	-	-

*B3LYP/B1 geometry

Figure 3

TS for O-O cleavage starting from peroxoformate (^{cc}**TS2**)

C	78.3430873	65.8142585	57.0936953
H	77.6279842	66.2536680	56.3838490
H	79.0673249	65.2246458	56.5236398
C	79.0292193	67.0384790	57.7558295
O	78.3884247	67.6598807	58.6566759
O	80.1374018	67.4018333	57.2640862
H	80.6126322	66.7735011	55.8861973
C	79.0950049	61.5501228	45.5058333
H	78.7543349	60.7013369	44.9004103
H	78.3085812	62.3080584	45.4973027
S	79.3807692	60.9645078	47.2298960
C	81.0236462	67.0908341	51.4092851
H	80.9197428	66.4645578	50.5149694
H	82.0310807	67.5340769	51.3333410
C	80.9443921	66.1666301	52.6425533
H	80.2302746	65.3548777	52.4377940
H	81.9146746	65.6893430	52.8211295
C	80.4890098	66.8661701	53.8976814
O	80.9651464	66.3337948	55.0317371
C	79.6323516	67.9107814	53.8095940
H	79.2302184	68.3626700	54.7124014
C	79.3601287	68.5586568	52.5303268
C	78.3944328	69.7240941	52.6088398
H	77.3633363	69.3487858	52.5490533
H	78.4804199	70.1817318	53.5998404
C	78.6156051	70.7813724	51.5263753
H	77.7652570	71.4761287	51.5324334
H	79.5193600	71.3642400	51.7630602
C	78.7773423	70.0898936	50.1680742
H	77.8653289	69.5115710	49.9730566
C	80.0227244	69.1623350	50.1812238
H	80.9134603	69.8171807	50.3101546
C	80.0078956	68.2199210	51.3817421
C	77.7879878	66.3223612	50.2284090
H	77.6359363	67.3454561	49.8263308
O	77.1135297	65.9551408	51.1935251
Fe	79.2614247	62.8631842	48.8369263
N	78.5790872	64.0547531	47.3652691
N	77.3810136	62.1915608	49.2281403
N	80.0131260	61.4730203	50.1642282
N	81.1637567	63.4320825	48.3972042
C	79.2922156	64.9982303	46.6622463
C	78.4034727	65.7800498	45.8173605
C	77.1357909	65.2921274	46.0324323
C	77.2634232	64.2247410	47.0143745
C	76.2363227	62.5924391	48.6052126
C	75.0675823	61.9889289	49.2410443
C	75.5301706	61.2590466	50.3130238
C	76.9954973	61.3703559	50.2528624
C	79.2794001	60.6748192	50.9968524
C	80.1476846	59.8556605	51.8346977
C	81.4443303	60.2038854	51.5307922
C	81.3269698	61.2410629	50.4915036
C	82.3040179	63.0258857	49.0480374
C	83.4451731	63.8314950	48.6439810
C	82.9663453	64.7297407	47.7238636
C	81.5412862	64.4776044	47.5889123
C	80.6666572	65.1897256	46.7708355
H	81.0957509	65.9894779	46.1734673
C	76.1959021	63.5075124	47.5545709
H	75.2134230	63.7634351	47.1770958
C	77.8905793	60.6754124	51.0632022
H	77.4622193	60.0546719	51.8427181
C	82.3805354	61.9811429	49.9633945
H	83.3725780	61.7789414	50.3555566
O	79.1254966	63.9627302	50.0880978
O	78.6612045	65.7100467	49.5194505
H	77.8264106	65.1467532	57.7832954
H	79.9300665	61.9959299	44.9654679
H	78.8881174	70.8062587	49.3540617
H	80.1978084	68.7144922	49.2030372
H	78.7088259	66.5630187	45.1232527
H	76.1990068	65.6337833	45.5922354
H	74.0641329	62.0654401	48.8223537
H	75.0200711	60.7212741	51.1121895
H	79.7694904	59.0880930	52.5098834
H	82.4017713	59.8640129	51.9255831
H	84.4417089	63.7367855	49.0752731
H	83.5190071	65.4694776	47.1447084

TURBOMOLE (QM) and ChemShell Energies (MM and QM/MM)

	B3LYP/B1	B3LYP/B2//B1	PBE0/B2/*
QM/MM	-3749.592556	-3750.270899	-3748.878938
QM	-3647.168009	-3647.846353	-3646.454392
MM	-102.424546	-102.424546	-102.424546
ZPE	0.500966	-	-

*B3LYP/B1 geometry

Figure 3

Cpd II/deformylated substrate and formate (^{cc}**I2**)

C	78.3600345	65.8492934	57.1665465
H	77.6365650	66.4217059	56.5681641
H	79.0093453	65.2920426	56.4866148
C	79.1543378	66.8910307	57.9549090
O	78.7226383	67.4447816	58.9666211
O	80.3115369	67.2750674	57.4398459
H	80.5201199	66.8285699	56.5564310
C	79.0866266	61.5152926	45.4561672
H	78.7307260	60.6925543	44.8235957
H	78.3120052	62.2874118	45.4687183
S	79.3693838	60.8900041	47.1669279
C	80.6316978	66.7422167	51.4395458
H	80.2590459	66.1267511	50.6079852
H	81.6779949	66.9810230	51.1804256
C	80.5799347	65.8727888	52.7086908
H	79.7299866	65.1807204	52.6158168
H	81.4804216	65.2585446	52.7990237
C	80.3549843	66.6397820	53.9842136
O	80.8352837	66.2403689	55.0753112
C	79.5362693	67.8076281	53.9017977
H	79.1885439	68.2502403	54.8317507
C	79.2724925	68.4608910	52.6919924
C	78.4043044	69.6984134	52.7697222
H	77.3542684	69.3823717	52.7188205
H	78.5311404	70.1495456	53.7572496
C	78.6796292	70.7263414	51.6699403
H	77.8785464	71.4750199	51.6928750
H	79.6266746	71.2500361	51.8745797
C	78.7434399	70.0044307	50.3185877
H	77.7906571	69.4917887	50.1621320
C	79.9092521	68.9764373	50.3036531
H	80.8520613	69.5489209	50.4339472
C	79.8528171	68.0296878	51.4926886
C	76.2287470	67.4647225	51.2380169
H	76.3414434	68.1389641	50.3560425
O	75.2488263	67.7508080	52.0004572
Fe	79.4203837	62.8315698	48.9222187
N	78.7170071	64.0643552	47.4603130
N	77.5291527	62.2043344	49.3269824
N	80.1573159	61.4129424	50.1962283
N	81.3235523	63.3436696	48.4130776
C	79.4308672	64.9961209	46.7483178
C	78.5473726	65.7445832	45.8614990
C	77.2882136	65.2249377	46.0474385
C	77.4134363	64.1852024	47.0627520
C	76.3906565	62.5538832	48.6604351
C	75.2184113	61.9391210	49.2875675
C	75.6712362	61.2661067	50.3992700
C	77.1368376	61.3999657	50.3583529
C	79.4185105	60.6378845	51.0445681
C	80.2784696	59.7813811	51.8527920
C	81.5789452	60.0947773	51.5253755
C	81.4711814	61.1436807	50.4949478
C	82.4660683	62.9185449	49.0434682
C	83.6098778	63.7231867	48.6391214
C	83.1260224	64.6390333	47.7386427
C	81.6939995	64.4057916	47.6234029
C	80.8121172	65.1582203	46.8440431
H	81.2456976	65.9566744	46.2462434
C	76.3558035	63.4313848	47.5774684
H	75.3807448	63.6314179	47.1479925
C	78.0319035	60.6915335	51.1576508
H	77.6032939	60.0784592	51.9444812
C	82.5338201	61.8609021	49.9490207
H	83.5294253	61.6243306	50.3145708
O	79.3827476	63.9930629	50.0774741
O	77.0502888	66.5353871	51.3278102
H	77.8297343	65.1420311	57.8042205
H	79.9250687	61.9613940	44.9213075
H	78.8788102	70.6978212	49.4885570
H	80.0284763	68.5085143	49.3264631
H	78.8431514	66.5195177	45.1543513
H	76.3614217	65.5230267	45.5572688
H	74.2198695	61.9639951	48.8512624
H	75.1579271	60.7549563	51.2137056
H	79.8843888	59.0029797	52.5061357
H	82.5310480	59.7209670	51.9019821
H	84.6127277	63.6170148	49.0527472
H	83.6740165	65.3782393	47.1543966

TURBOMOLE (QM) and ChemShell Energies (MM and QM/MM)

	B3LYP/B1	B3LYP/B2//B1	PBE0/B2/*
QM/MM	-3749.667156	-3750.345498	-3748.953127
QM	-3647.259749	-3647.938091	-3646.545720
MM	-102.407407	-102.407407	-102.407407
ZPE	0.501974		

*B3LYP/B1 geometry

Figure 3

TS for 1βH abstraction by Cpd II from the deformylated substrate (^{CC}**TS3**)

C	78.3957289	65.8213121	57.1231083
H	77.6733961	66.3999311	56.5293271
H	79.0295988	65.2488567	56.4410137
C	79.2164272	66.8578124	57.8919479
O	78.8011305	67.4301477	58.9013456
O	80.3748438	67.2132452	57.3639013
H	80.5831560	66.7481623	56.4844105
C	79.0958699	61.6217118	45.5447535
H	78.7179000	60.7851537	44.9440458
H	78.3327359	62.4052026	45.5434798
S	79.3923648	61.0465673	47.2749385
C	80.4491763	66.3915925	51.3372362
H	79.8740910	65.6043188	50.6780268
H	81.4061751	66.5099529	50.8028616
C	80.6876583	65.6666406	52.6879990
H	80.0033135	64.8052480	52.7403113
H	81.6998433	65.2513421	52.7450981
C	80.4139221	66.4613041	53.9404639
O	80.9462140	66.1377847	55.0377778
C	79.5154082	67.5566249	53.8450741
H	79.1708220	68.0118904	54.7697426
C	79.2161229	68.1753385	52.6313339
C	78.3633213	69.4246660	52.7301908
H	77.3093407	69.1302407	52.6527836
H	78.4783196	69.8481348	53.7321490
C	78.6740360	70.4760059	51.6659602
H	77.8960988	71.2497577	51.7057873
H	79.6344336	70.9653751	51.8909469
C	78.7262914	69.7829209	50.2988383
H	77.7551031	69.3106844	50.1303682
C	79.8619903	68.7167194	50.2639842
H	80.8125699	69.2618060	50.4428905
C	79.7663883	67.7185192	51.4171107
C	76.1008673	67.3931084	51.2086909
H	76.2070550	68.0641786	50.3239474
O	75.1632214	67.7141597	52.0106552
Fe	79.4271452	63.0862252	49.0197933
N	78.7279873	64.2334188	47.5025807
N	77.5382947	62.4310570	49.4186394
N	80.1537053	61.6593332	50.2953013
N	81.3184984	63.5393624	48.4792013
C	79.4403923	65.1458511	46.7636291
C	78.5569948	65.8453052	45.8389493
C	77.3037776	65.3110567	46.0250058
C	77.4293275	64.3120781	47.0778152
C	76.4116970	62.7002357	48.6956234
C	75.2473545	62.0388970	49.2881326
C	75.6860536	61.4163825	50.4343275
C	77.1421057	61.6336273	50.4540615
C	79.4177822	60.8908017	51.1522517
C	80.2688147	59.9681165	51.8933225
C	81.5658055	60.2198718	51.5036564
C	81.4646438	61.3119610	50.5213316
C	82.4665285	63.0758117	49.0713386
C	83.6213826	63.8369890	48.6244745
C	83.1386894	64.7582300	47.7289793
C	81.6984600	64.5715299	47.6558858
C	80.8208882	65.3120978	46.8596578
H	81.2587821	66.0867233	46.2347215
C	76.3804757	63.5409304	47.5848963
H	75.4130915	63.6916701	47.1191218
C	78.0351048	60.9660819	51.2889026
H	77.6098851	60.3706434	52.0906774
C	82.5334091	62.0020491	49.9567643
H	83.5322311	61.7215352	50.2797776
O	79.3848188	64.3202762	50.1285441
O	76.8866506	66.4316652	51.2622764
H	77.8621367	65.1278101	57.7730320
H	79.9333807	62.0384614	44.9853235
H	78.8767203	70.5042235	49.4956196
H	79.9974064	68.2955148	49.2678338
H	78.8452592	66.5955391	45.1026618
H	76.3813740	65.5747425	45.5076010
H	74.2707314	61.9943204	48.8061712
H	75.1675172	60.8778027	51.2274972
H	79.8634452	59.1860253	52.5352535
H	82.5133488	59.7719513	51.8029814
H	84.6290871	63.7055985	49.0185996
H	83.6936153	65.4702241	47.1180880

TURBOMOLE (QM) and ChemShell Energies (MM and QM/MM)

	B3LYP/B1	B3LYP/B2//B1	PBE0/B2/*
QM/MM	-3749.645708	-3750.324242	-3748.932738
QM	-3647.237043	-3647.915577	-3646.524072
MM	-102.408665	-102.408665	-102.408665

*B3LYP/B1 geometry

Figure 3

1(10),4-diene-3-one/
Fe(III)OH(^{cc}**I3**)

C	78.3596195	65.8139481	57.1350070
H	77.6352005	66.3650313	56.5177468
H	79.0127945	65.2417781	56.4712556
C	79.1426221	66.8841470	57.8954642
O	78.7017717	67.4643227	58.8885997
O	80.2988311	67.2593191	57.3721295
H	80.4992107	66.7988159	56.4940069
C	79.0809530	61.5933013	45.5306791
H	78.7084137	60.7672161	44.9122149
H	78.3145707	62.3730615	45.5482028
S	79.3876379	60.9766320	47.2413894
C	80.5379255	66.8524364	51.4107517
H	78.5384703	64.6465279	50.2375371
H	80.9231870	66.4087565	50.4968139
C	80.6289072	65.9824131	52.6185951
H	79.8614581	65.1926558	52.4812104
H	81.5809767	65.4405600	52.6619181
C	80.3474591	66.6681437	53.9252234
O	80.7868870	66.2085265	55.0055938
C	79.5479547	67.8580927	53.8624415
H	79.1546880	68.2624445	54.7912847
C	79.3536626	68.5291137	52.6881518
C	78.4706848	69.7517268	52.7275148
H	77.4375721	69.3913091	52.6240586
H	78.5440049	70.2052159	53.7191619
C	78.7381464	70.7795259	51.6264875
H	77.9321614	71.5224296	51.6585103
H	79.6841091	71.3094503	51.8208262
C	78.7915807	70.0554295	50.2749684
H	77.8424810	69.5312637	50.1304810
C	79.9871870	69.0588009	50.2487489
H	80.8966669	69.6726837	50.3935186
C	79.9535421	68.0746004	51.4233828
C	76.6527808	67.1806701	50.9807683
H	76.8757415	67.6739457	50.0081155
O	75.8958453	67.8366894	51.7632305
Fe	79.3806000	62.8684195	48.9210871
N	78.6620184	64.1499081	47.5127448
N	77.4807028	62.2943415	49.3496979
N	80.1278354	61.4847300	50.2306850
N	81.2874175	63.4078649	48.4644101
C	79.3881743	65.0688467	46.7944413
C	78.5147831	65.8175070	45.8959890
C	77.2493950	65.3098609	46.0786395
C	77.3623234	64.2739656	47.0984748
C	76.3381652	62.6307346	48.6808813
C	75.1727670	61.9926854	49.2941177
C	75.6320013	61.3073170	50.3969748
C	77.0958037	61.4679094	50.3686345
C	79.3837140	60.7062232	51.0676483
C	80.2359443	59.8235150	51.8608971
C	81.5384985	60.1201499	51.5274595
C	81.4372226	61.1885970	50.5141366
C	82.4352424	62.9655572	49.0693534
C	83.5842269	63.7552701	48.6453526
C	83.0969108	64.6736928	47.7490930
C	81.6576029	64.4584916	47.6621893
C	80.7730553	65.2167241	46.8879779
H	81.2122547	66.0040760	46.2791105
C	76.3011274	63.5174628	47.6036209
H	75.3263211	63.7191306	47.1733580
C	77.9949024	60.7632222	51.1701921
H	77.5622276	60.1428715	51.9493961
C	82.5042801	61.8984247	49.9648602
H	83.5019730	61.6453787	50.3147579
O	79.3748679	64.1403597	50.2338415
O	77.1585793	66.0504411	51.1432838
H	77.8340773	65.1215552	57.7926269
H	79.9187679	62.0239505	44.9823416
H	78.9055201	70.7557652	49.4475542
H	80.1174483	68.6037581	49.2668963
H	78.8197350	66.5822487	45.1816775
H	76.3262476	65.6120500	45.5841226
H	74.1776610	62.0112214	48.8497229
H	75.1208018	60.7699149	51.1956866
H	79.8371891	59.0413326	52.5068472
H	82.4894751	59.7228081	51.8821841
H	84.5902191	63.6394241	49.0486215
H	83.6467485	65.4039852	47.1554448

TURBOMOLE (QM) and ChemShell Energies (MM and QM/MM)

	B3LYP/B1	B3LYP/B2//B1	PBE0/B2/*
QM/MM	-3749.724322	-3750.410970	-3749.020571
QM	-3647.311474	-3647.998122	-3646.607723
MM	-102.412848	-102.412848	-102.412848
ZPE	0.501389	-	-

*B3LYP/B1 geometry

Figure 3

TS for 2βH deprotonationn by Fe(III)OH from the deformylated substrate (^{cc}**TS4**)

C	78.3778142	65.6522052	56.9005836
H	77.6473339	66.2050718	56.2914956
H	78.9604002	65.0154173	56.2284572
C	79.2708235	66.7286223	57.5094206
O	78.9884492	67.3533653	58.5362595
O	80.3337668	67.0535685	56.7968404
H	80.4003108	66.5340255	55.9113577
C	79.1239799	61.7328138	45.6992899
H	78.7154956	60.8920622	45.1253953
H	78.3701905	62.5231309	45.7185739
S	79.4763303	61.1517135	47.4176778
C	80.7517280	66.9059512	51.0512556
H	78.4268707	64.7919659	50.4634419
H	81.2904134	66.6240517	50.1484179
C	80.7222630	65.9023958	52.1009420
H	79.9501929	65.0208630	51.4174171
H	81.6034325	65.2565253	52.1683363
C	80.2224797	66.3578426	53.4038615
O	80.5361342	65.8107860	54.5065892
C	79.4126777	67.5415595	53.4039460
H	78.9268610	67.8170491	54.3364427
C	79.3556683	68.3936249	52.3351441
C	78.5385402	69.6591005	52.5102468
H	77.4779324	69.3843575	52.4482572
H	78.6980179	70.0361722	53.5256770
C	78.8215056	70.7500064	51.4763711
H	78.0287158	71.5050243	51.5507159
H	79.7750008	71.2549359	51.6966683
C	78.8706137	70.1001391	50.0892236
H	77.9319789	69.5578413	49.9364950
C	80.0882286	69.1351227	49.9924187
H	80.9886884	69.7633002	50.1364054
C	80.0611809	68.0901147	51.1063325
C	76.6141055	67.1504546	50.9464964
H	76.9828925	67.7062503	50.0559053
O	75.8024957	67.7783826	51.6906154
Fe	79.3863351	62.9839805	49.0872468
N	78.6665773	64.2577885	47.6715845
N	77.4901164	62.3735997	49.4758417
N	80.1319133	61.5850156	50.3671145
N	81.2804692	63.5445523	48.6535854
C	79.3926701	65.1641161	46.9359818
C	78.5256415	65.8700098	45.9983726
C	77.2661244	65.3452883	46.1691113
C	77.3747968	64.3404125	47.2186718
C	76.3554322	62.6756616	48.7761484
C	75.1952894	62.0030760	49.3582585
C	75.6456106	61.3296343	50.4725911
C	77.1033739	61.5325369	50.4827582
C	79.3888621	60.7814076	51.1821777
C	80.2385477	59.8447559	51.9108989
C	81.5392841	60.1194739	51.5500162
C	81.4417053	61.2428689	50.6007839
C	82.4374009	63.0616543	49.2128482
C	83.5918272	63.8129848	48.7440412
C	83.1038708	64.7345903	47.8499173
C	81.6571955	64.5653022	47.8146215
C	80.7761883	65.3161020	47.0301219
H	81.2201738	66.0790536	46.3949701
C	76.3222390	63.5549093	47.6937752
H	75.3562052	63.7219091	47.2294590
C	78.0012053	60.8387335	51.2933660
H	77.5705221	60.2097935	52.0659646
C	82.5098253	61.9632041	50.0688069
H	83.5098546	61.6786539	50.3848293
O	79.2728716	64.2904508	50.4911687
O	77.0266356	65.9726063	51.0616534
H	77.8582610	65.0287710	57.6282241
H	79.9532220	62.1296322	45.1136627
H	78.9545284	70.8400241	49.2932367
H	80.1981022	68.7186887	48.9911310
H	78.8287564	66.6239624	45.2719132
H	76.3500680	65.6165463	45.6443960
H	74.2088955	62.0025901	48.8944768
H	75.1304997	60.7733502	51.2557100
H	79.8362483	59.0491362	52.5379642
H	82.4877076	59.6714547	51.8463910
H	84.6046436	63.6744740	49.1223059
H	83.6579825	65.4406316	47.2314252

TURBOMOLE (QM) and ChemShell Energies (MM and QM/MM)

	B3LYP/B1	B3LYP/B2//B1	PBE0/B2/*
QM/MM	-3749.706912	-3750.393497	-3749.006941
QM	-3647.298271	-3647.984856	-3646.598300
MM	-102.408641	-102.408641	-102.408641
ZPE	0.496840	-	-

*B3LYP/B1 geometry

Figure 3

Estrone, formate and $Fe(III)OH_2$ (^{CC}**ES**)

C	78.2991127	65.8293870	57.0801238
H	77.5726912	66.3101557	56.4095900
H	79.0047768	65.2537866	56.4727042
C	79.0202937	67.0106481	57.7833688
O	78.3961350	67.6164582	58.7058454
O	80.1389252	67.3557810	57.3044718
H	80.6465193	66.7003794	55.9361217
C	79.1326833	61.5914853	45.5524421
H	78.7728808	60.7373081	44.9662651
H	78.3494673	62.3514291	45.5594583
S	79.4630019	60.9959585	47.2645396
C	80.9661654	67.0490695	51.5495713
H	78.5464586	64.6908226	50.4103058
H	81.4961387	66.7157669	50.6585000
C	81.2373227	66.3919647	52.7471489
H	79.7887343	63.8620906	51.0310935
H	81.9660419	65.5865164	52.7855571
C	80.6410672	66.8296669	53.9426679
O	81.0393758	66.2686389	55.1009629
C	79.6887389	67.8530500	53.8705001
H	79.1991063	68.1833579	54.7829411
C	79.4172299	68.5104364	52.6666694
C	78.3992855	69.6304020	52.6980217
H	77.4013434	69.2006200	52.5488841
H	78.3964126	70.0851720	53.6929565
C	78.6309868	70.6904585	51.6186473
H	77.7810360	71.3860022	51.6280909
H	79.5377907	71.2724650	51.8506517
C	78.7733369	69.9847710	50.2618674
H	77.8658553	69.3939242	50.0989134
C	80.0360268	69.0741934	50.2583486
H	80.9110384	69.7481939	50.3629456
C	80.0859741	68.1443343	51.4763646
C	77.2030888	66.6325769	50.4415724
H	77.7323613	66.8406933	49.4911305
O	76.4693919	67.5309246	50.8979920
Fe	79.4192369	62.7189869	48.7944731
N	78.6922716	64.0770526	47.4588817
N	77.5325940	62.1899057	49.2823086
N	80.1642140	61.4049329	50.1774384
N	81.3066498	63.3290360	48.3960882
C	79.4094275	65.0123289	46.7512086
C	78.5287302	65.7804042	45.8784982
C	77.2654650	65.2728758	46.0648250
C	77.3873250	64.2188558	47.0651188
C	76.3828719	62.5545003	48.6321974
C	75.2217255	61.9273301	49.2535923
C	75.6822579	61.2301287	50.3496462
C	77.1441986	61.3640942	50.3064954
C	79.4260682	60.6252913	51.0261377
C	80.2857772	59.7878474	51.8541608
C	81.5856311	60.1017187	51.5291843
C	81.4793871	61.1289810	50.4780984
C	82.4574460	62.9037193	49.0198301
C	83.5923087	63.7174558	48.6207392
C	83.1012935	64.6385599	47.7270780
C	81.6728917	64.4012517	47.6115615
C	80.7910536	65.1648895	46.8432802
H	81.2262262	65.9695651	46.2566986
C	76.3309868	63.4630229	47.5757513
H	75.3481638	63.6815721	47.1741423
C	78.0381623	60.6631833	51.1156549
H	77.6071872	60.0528629	51.9017622
C	82.5381491	61.8432573	49.9225661
H	83.5363035	61.6159305	50.2852238
O	79.3935563	64.1218894	50.1831727
O	77.3958554	65.4641874	50.9169894
H	77.7884839	65.1421415	57.7546743
H	79.9642664	62.0231762	44.9955049
H	78.8711188	70.6971719	49.4427275
H	80.1886461	68.6119202	49.2831167
H	78.8292291	66.5589326	45.1773131
H	76.3411007	65.5911666	45.5828414
H	74.2234372	61.9650892	48.8176322
H	75.1679145	60.7015345	51.1522080
H	79.8928875	59.0329288	52.5351910
H	82.5382555	59.7535140	51.9283417
H	84.5911806	63.6260691	49.0473186
H	83.6473840	65.3829894	47.1477021

TURBOMOLE (QM) and ChemShell Energies (MM and QM/MM)

	B3LYP/B1	B3LYP/B2//B1	PBE0/B2/*
QM/MM	-3749.760697	-3750.449887	-3749.064206
QM	-3647.329023	-3648.018213	-3646.632532
MM	-102.431674	-102.431674	-102.431674
ZPE	0.501984	-	-

*B3LYP/B1 geometry

Figure 5

TS for O-O cleavage starting from **PH** (**^{OO}TS1**)

C	78.4611376	65.9483245	57.2621454
H	77.7561187	66.5069078	56.6316025
H	79.0855497	65.3457077	56.5957059
C	79.3060939	67.0013922	57.9787395
O	79.0787417	67.4448453	59.0972625
O	80.2965615	67.5264827	57.2566526
H	80.4078836	67.1056119	56.3463458
C	79.0612059	61.5840198	45.5080911
H	78.7053773	60.7466638	44.8949203
H	78.2909474	62.3599834	45.5031680
S	79.3376958	61.0023811	47.2369389
C	80.4972553	66.6967126	51.2607239
H	80.5911610	66.0171645	50.4104155
H	81.3922069	67.3401108	51.2712928
C	80.4758969	65.8699589	52.5508542
H	79.6712833	65.1231021	52.4863334
H	81.4168701	65.3275817	52.6895265
C	80.2078173	66.7244268	53.7594824
O	80.7244440	66.4660383	54.8704266
C	79.3000019	67.8349723	53.5854933
H	78.9685843	68.3444175	54.4890079
C	78.8171349	68.2087824	52.3740702
C	77.7890202	69.3027080	52.3084793
H	76.8806753	68.8610969	51.8872641
H	77.5293555	69.6588689	53.3090298
C	78.2110036	70.4426491	51.3793916
H	77.4012704	71.1835008	51.3562773
H	79.1104554	70.9421156	51.7721182
C	78.4727208	69.8315558	49.9976873
H	77.5358019	69.3766926	49.6583658
C	79.6057784	68.7650355	50.0679032
H	80.4863873	69.2769557	50.5001665
C	79.2514032	67.5893401	51.0601367
C	77.9457323	66.7076942	50.5504707
H	77.4197770	67.4080140	49.8271487
O	77.1524241	66.3348925	51.5366924
Fe	79.2637410	62.9826776	48.8822955
N	78.5891950	64.1616710	47.3801145
N	77.3761641	62.3502596	49.2796738
N	80.0033712	61.6084478	50.2354623
N	81.1812530	63.4915796	48.4106352
C	79.3159869	65.0704568	46.6561676
C	78.4403933	65.8440183	45.7822651
C	77.1670050	65.3793217	46.0054377
C	77.2823831	64.3365418	47.0196918
C	76.2370946	62.7484394	48.6451614
C	75.0601846	62.1475950	49.2719641
C	75.5135715	61.4107757	50.3428022
C	76.9807434	61.5268231	50.2969419
C	79.2598457	60.8066281	51.0521697
C	80.1154359	59.9508937	51.8706055
C	81.4175948	60.2794424	51.5654423
C	81.3129881	61.3377552	50.5437716
C	82.3174601	63.0787993	49.0609692
C	83.4708804	63.8573187	48.6356728
C	82.9992315	64.7469306	47.7027099
C	81.5676626	64.5156951	47.5816868
C	80.6971227	65.2313376	46.7568136
H	81.1394520	66.0103662	46.1401096
C	76.2071991	63.6423409	47.5750916
H	75.2270262	63.8953952	47.1872333
C	77.8690159	60.8248011	51.1118246
H	77.4303140	60.1980898	51.8824134
C	82.3788064	62.0482037	49.9961621
H	83.3727196	61.8213378	50.3728038
O	79.1922222	64.1744726	50.0849288
O	78.2709088	65.8015914	49.5469618
H	77.9175592	65.2806605	57.9305868
H	79.9014433	62.0162776	44.9647490
H	78.7184412	70.6045871	49.2696004
H	79.9403832	68.4414281	49.0823148
H	78.7552665	66.6093108	45.0728649
H	76.2351907	65.7226510	45.5560896
H	74.0597586	62.2347803	48.8481566
H	74.9982549	60.8557914	51.1267076
H	79.7252936	59.1651634	52.5175084
H	82.3710620	59.9099001	51.9428083
H	84.4680920	63.7510454	49.0626873
H	83.5568202	65.4749253	47.1134858

TURBOMOLE (QM) and ChemShell Energies (MM and QM/MM)

	B3LYP/B1	B3LYP/B2//B1	PBE0/B2/*
QM/MM	-3749.569174	-3750.245784	-3748.862622
QM	-3647.130255	-3647.806866	-3646.423704
MM	-102.438919	-102.438919	-102.438919
ZPE	0.501109	-	-

*B3LYP/B1 geometry

Figure 5

Cpd II / oxyradical substrate (^{oo}**I1**)

C	78.4317831	65.9507600	57.2534767
H	77.7241565	66.5091192	56.6255491
H	79.0572746	65.3522922	56.5843871
C	79.2756129	67.0051932	57.9691499
O	79.0584154	67.4405630	59.0924711
O	80.2549688	67.5410616	57.2385458
H	80.3489393	67.1298448	56.3231664
C	79.0725479	61.5057035	45.4357550
H	78.7194875	60.6928879	44.7883952
H	78.3025589	62.2826163	45.4527263
S	79.3379934	60.8595621	47.1392900
C	80.2633562	66.7398366	51.2228827
H	80.2563249	66.0496961	50.3752825
H	81.2152330	67.2960274	51.1906476
C	80.2319000	65.9220509	52.5178321
H	79.3787541	65.2309378	52.4899684
H	81.1347818	65.3114805	52.6186055
C	80.0735541	66.7918592	53.7339507
O	80.5991362	66.4881041	54.8280876
C	79.2484765	67.9739130	53.5935887
H	78.9823612	68.4995024	54.5093844
C	78.7563660	68.3897961	52.4006184
C	77.7867885	69.5354378	52.3559325
H	76.8411415	69.1321084	51.9803394
H	77.5812114	69.9140689	53.3597537
C	78.2286769	70.6477733	51.3972131
H	77.4392641	71.4082328	51.3736350
H	79.1455483	71.1271432	51.7733519
C	78.4588436	70.0229374	50.0151916
H	77.5034458	69.6033762	49.6842634
C	79.5476259	68.9156398	50.0930563
H	80.4331001	69.3871833	50.5600475
C	79.1117346	67.7611235	51.0706479
C	77.7053277	67.0109622	50.5791842
H	77.1250179	67.8754154	50.1064422
O	77.0164507	66.5275336	51.5975222
Fe	79.4000058	62.7866934	48.8961041
N	78.6999848	64.0370073	47.4435031
N	77.5023449	62.1806470	49.3104299
N	80.1372491	61.3658733	50.1747696
N	81.3097566	63.3026119	48.3888035
C	79.4187916	64.9614553	46.7286857
C	78.5362332	65.7474686	45.8723697
C	77.2674406	65.2701372	46.0920764
C	77.3907833	64.2144053	47.0918184
C	76.3590803	62.6007442	48.6964063
C	75.1827489	62.0160873	49.3402682
C	75.6414402	61.2759536	50.4060587
C	77.1101187	61.3562978	50.3266367
C	79.3939911	60.5873931	51.0166374
C	80.2537753	59.7758565	51.8707759
C	81.5544077	60.1263669	51.5808220
C	81.4484514	61.1424891	50.5183628
C	82.4473869	62.8992867	49.0432023
C	83.5895828	63.7092287	48.6426995
C	83.1101914	64.6079130	47.7227755
C	81.6820839	64.3592634	47.5927967
C	80.8018642	65.1071788	46.8077838
H	81.2365281	65.9055590	46.2108987
C	76.3203960	63.5072840	47.6383642
H	75.3378091	63.7627501	47.2568334
C	78.0040746	60.6207967	51.1036958
H	77.5718859	59.9953563	51.8793360
C	82.5099668	61.8654269	49.9753556
H	83.5018698	61.6543329	50.3658514
O	79.3808881	63.9129586	50.0830800
O	77.8820272	66.3103417	49.4525327
H	77.8917247	65.2794270	57.9210959
H	79.9150884	61.9560202	44.9109628
H	78.7173216	70.7745425	49.2693061
H	79.9094635	68.5824530	49.1203659
H	78.8400354	66.5309808	45.1781944
H	76.3317535	65.6073021	45.6461213
H	74.1769400	62.1173747	48.9326461
H	75.1302594	60.7479209	51.2110073
H	79.8653918	59.0050982	52.5364758
H	82.5049970	59.8026142	52.0046508
H	84.5870097	63.6205198	49.0732070
H	83.6556827	65.3539603	47.1449180

TURBOMOLE (QM) and ChemShell Energies (MM and QM/MM)

	B3LYP/B1	B3LYP/B2//B1	PBE0/B2/*
QM/MM	-3749.579025	-3750.256006	-3748.872663
QM	-3647.144703	-3647.821684	-3646.438342
MM	-102.434322	-102.434322	-102.434322
ZPE	0.500884	-	-

*B3LYP/B1 geometry

Figure 5

TS for 1βH abstraction by Cpd II from the oxyradical substrate (^{oo}**TS2**)

C	78.4788271	65.9420065	57.2291805
H	77.7728806	66.4977985	56.5968845
H	79.0941047	65.3255441	56.5667864
C	79.3369117	66.9986116	57.9243921
O	79.1223553	67.4562712	59.0399099
O	80.3246925	67.5110730	57.1888090
H	80.4272484	67.0927364	56.2766494
C	79.0787429	61.5506875	45.4777845
H	78.7213409	60.7234084	44.8516972
H	78.3094606	62.3283645	45.4806049
S	79.3500023	60.9461781	47.1987278
C	80.0094147	66.3652207	51.1461527
H	79.7208444	65.4389257	50.4747221
H	80.9969175	66.7241227	50.8166254
C	80.1756711	65.7386730	52.5435178
H	79.3618445	65.0186661	52.7156886
H	81.1078843	65.1660762	52.5952760
C	80.1166235	66.6911053	53.7028411
O	80.7193349	66.4622418	54.7779448
C	79.2679079	67.8484877	53.5530738
H	79.0584166	68.4253495	54.4529099
C	78.7073265	68.2045960	52.3724456
C	77.7810413	69.3887227	52.3525451
H	76.8114820	69.0501297	51.9772389
H	77.6088256	69.7617905	53.3650513
C	78.2895130	70.4893284	51.4140468
H	77.5494006	71.2997335	51.4035363
H	79.2326102	70.9050653	51.8004705
C	78.4868590	69.8669986	50.0255523
H	77.5095309	69.5019388	49.6958612
C	79.5110692	68.6905904	50.0813669
H	80.4179797	69.0924039	50.5701223
C	78.9890854	67.5356640	51.0359144
C	77.5228821	66.9470182	50.5570366
H	76.9743974	67.8772001	50.1851577
O	76.8467376	66.4288728	51.5710334
Fe	79.4064589	62.9707313	48.9264312
N	78.7121113	64.1366378	47.4205352
N	77.5116914	62.3508782	49.3464752
N	80.1339663	61.5598261	50.2300284
N	81.3115327	63.4307592	48.3937920
C	79.4303345	65.0529493	46.6937335
C	78.5458480	65.8097771	45.8155725
C	77.2805135	65.3214993	46.0308370
C	77.4046666	64.2881884	47.0510962
C	76.3744083	62.7007932	48.6785889
C	75.2003000	62.0833472	49.2958402
C	75.6492680	61.3954768	50.3999905
C	77.1141530	61.5399800	50.3726202
C	79.3916216	60.7934972	51.0841921
C	80.2463184	59.9400242	51.9000030
C	81.5490868	60.2424966	51.5672788
C	81.4466545	61.2789725	50.5264340
C	82.4516764	63.0088540	49.0322230
C	83.6007225	63.7930625	48.6087778
C	83.1217063	64.6937563	47.6905199
C	81.6897941	64.4696927	47.5787519
C	80.8119854	65.2072195	46.7803964
H	81.2485960	65.9941710	46.1698532
C	76.3383499	63.5711748	47.5920230
H	75.3587475	63.7917931	47.1826391
C	78.0044148	60.8423151	51.1855097
H	77.5731840	60.2369605	51.9769139
C	82.5137550	61.9730521	49.9617028
H	83.5088655	61.7344558	50.3272426
O	79.3892674	64.1917517	50.0463499
O	77.5994943	66.3253092	49.3738408
H	77.9352197	65.2878103	57.9107850
H	79.9196548	61.9878424	44.9394267
H	78.7645687	70.6216419	49.2897144
H	79.8599341	68.3727379	49.0988550
H	78.8462353	66.5792306	45.1043937
H	76.3443001	65.6457700	45.5765028
H	74.2092085	62.1186341	48.8435582
H	75.1318177	60.8550216	51.1925938
H	79.8490233	59.1691817	52.5603249
H	82.5001206	59.8700769	51.9479424
H	84.6013045	63.6889132	49.0283670
H	83.6729796	65.4237961	47.0978934

TURBOMOLE (QM) and ChemShell Energies (MM and QM/MM)

	B3LYP/B1	B3LYP/B2//B1	PBE0/B2/*
QM/MM	-3749.546873	-3750.224504	-3748.842455
QM	-3647.113563	-3647.791193	-3646.409144
MM	-102.433311	-102.433311	-102.433311

*B3LYP/B1 geometry

Figure 5

1(10),4-diene-3-one/Fe(III)OH (^{oo}**I2**)

C	78.4518054	65.8073878	57.1287997
H	77.7477701	66.3308692	56.4666545
H	79.1193497	65.2095143	56.5030845
C	79.2117754	66.9151141	57.8570543
O	78.7607971	67.5118250	58.8363909
O	80.3532863	67.3052969	57.3146909
H	80.5560484	66.8352517	56.4390252
C	79.0871077	61.5579343	45.5131908
H	78.7230780	60.7275070	44.8951623
H	78.3159386	62.3327037	45.5278403
S	79.3923370	60.9495481	47.2279935
C	80.6272761	66.8459501	51.3647402
H	78.6728175	64.8088195	49.9780486
H	81.0499845	66.4208383	50.4588288
C	80.7311106	65.9837808	52.5792418
H	79.9922023	65.1683689	52.4327789
H	81.7021475	65.4783143	52.6389315
C	80.4077928	66.6663856	53.8786499
O	80.8567390	66.2345101	54.9675096
C	79.5498310	67.8130661	53.7962780
H	79.1120493	68.1969226	54.7139388
C	79.3303751	68.4557053	52.6102807
C	78.3494444	69.5997134	52.6046497
H	77.3693714	69.1527220	52.3880144
H	78.2774665	70.0228697	53.6101061
C	78.6346105	70.6746264	51.5548687
H	77.8009587	71.3879717	51.5636108
H	79.5469883	71.2317511	51.8214421
C	78.7935308	69.9891546	50.1923828
H	77.8851386	69.4216199	49.9797261
C	80.0244498	69.0382371	50.1978318
H	80.9087899	69.6786519	50.3812949
C	79.9898230	68.0410392	51.3620339
C	76.8801070	67.0822726	50.4347888
H	76.4244544	68.0511335	50.1038165
O	76.6279485	66.7859253	51.6432956
Fe	79.3927470	62.8552210	48.8875190
N	78.6902078	64.1272958	47.4655988
N	77.4913953	62.2848591	49.3070968
N	80.1287667	61.4901044	50.2289298
N	81.3078679	63.3762285	48.4292189
C	79.4218006	65.0457806	46.7555062
C	78.5575986	65.7983908	45.8512470
C	77.2918504	65.2944041	46.0220572
C	77.3940152	64.2608258	47.0480662
C	76.3542037	62.6347337	48.6384180
C	75.1813943	62.0164247	49.2577102
C	75.6322044	61.3364851	50.3680615
C	77.0975584	61.4770482	50.3378599
C	79.3778153	60.7147789	51.0621663
C	80.2224720	59.8276738	51.8597313
C	81.5279609	60.1172396	51.5305202
C	81.4350857	61.1853658	50.5153768
C	82.4488859	62.9416348	49.0546008
C	83.5990642	63.7365196	48.6464818
C	83.1197752	64.6540552	47.7439526
C	81.6843247	64.4315316	47.6355652
C	80.8051707	65.1912137	46.8561111
H	81.2480191	65.9836096	46.2562163
C	76.3257472	63.5194784	47.5577040
H	75.3506197	63.7336114	47.1341311
C	77.9881869	60.7764408	51.1529183
H	77.5473777	60.1643687	51.9346819
C	82.5080892	61.8835541	49.9621445
H	83.5030903	61.6314872	50.3213203
O	79.3623924	64.1397539	50.1817740
O	77.5351665	66.4469792	49.5919545
H	77.9082042	65.1414662	57.7989585
H	79.9229708	61.9947671	44.9667692
H	78.9130181	70.7123431	49.3856687
H	80.1927319	68.6017707	49.2133295
H	78.8682063	66.5718981	45.1489111
H	76.3797328	65.6111172	45.5162896
H	74.1896548	62.0343635	48.8058283
H	75.1139249	60.8133613	51.1716749
H	79.8181176	59.0458196	52.5025906
H	82.4758378	59.7132062	51.8859818
H	84.6016527	63.6245910	49.0592225
H	83.6729881	65.3878616	47.1578211

TURBOMOLE (QM) and ChemShell Energies (MM and QM/MM)

	B3LYP/B1	B3LYP/B2//B1	PBE0/B2/*
QM/MM	-3749.705094	-3750.392577	-3749.002514
QM	-3647.280523	-3647.968007	-3646.577943
MM	-102.424570	-102.424570	-102.424570
ZPE	0.501590	-	-

*B3LYP/B1 geometry

Figure 5

TS for 2βH abstraction by Fe(III)OH from the deformylated substrate (^{oo}**TS3**)

C	78.4676833	65.6262818	56.8765231
H	77.7567366	66.1487442	56.2200803
H	79.0658301	64.9599098	56.2480676
C	79.3414121	66.7356369	57.4519024
O	79.0471811	67.3869477	58.4597538
O	80.3947708	67.0589169	56.7271218
H	80.4645397	66.5243000	55.8463258
C	79.1335506	61.6694801	45.6707380
H	78.7404472	60.8221623	45.0952724
H	78.3701327	62.4502437	45.6857501
S	79.4828753	61.0976670	47.3935249
C	80.8209830	66.8850223	51.0118504
H	78.6138847	64.9642288	50.1275766
H	81.3746043	66.6157619	50.1146665
C	80.7805048	65.8672626	52.0509953
H	79.9972658	65.0143444	51.3619340
H	81.6613075	65.2214227	52.1193943
C	80.2776458	66.3198109	53.3543639
O	80.6104214	65.7924934	54.4621078
C	79.4313308	67.4760800	53.3461433
H	78.9201588	67.7328728	54.2703560
C	79.3550561	68.3195518	52.2723056
C	78.4596606	69.5334692	52.4140153
H	77.4249894	69.2036215	52.2488185
H	78.5010993	69.8860511	53.4495540
C	78.7718142	70.6616912	51.4311508
H	77.9669486	71.4062189	51.4920773
H	79.7074805	71.1698806	51.7116118
C	78.8893089	70.0426392	50.0345087
H	77.9757125	69.4753367	49.8392576
C	80.1279839	69.1049079	49.9552129
H	81.0161753	69.7465591	50.1165128
C	80.1048164	68.0525443	51.0620068
C	76.8636820	67.0655552	50.3807781
H	76.5379537	68.0867271	50.0616392
O	76.4202816	66.7032961	51.5095651
Fe	79.4204630	62.9567236	49.0390719
N	78.7152414	64.2077066	47.6007133
N	77.5202179	62.3628302	49.4328406
N	80.1536834	61.5793287	50.3554051
N	81.3208308	63.4921896	48.6002407
C	79.4449992	65.1187478	46.8790406
C	78.5857933	65.8319357	45.9395881
C	77.3263587	65.3097422	46.0985390
C	77.4256156	64.3043970	47.1507147
C	76.3897054	62.6711450	48.7308067
C	75.2226104	62.0183627	49.3218817
C	75.6656680	61.3543139	50.4454342
C	77.1252557	61.5424536	50.4538560
C	79.4034590	60.7845030	51.1721470
C	80.2441709	59.8426941	51.9050515
C	81.5475445	60.1028840	51.5417840
C	81.4601148	61.2237789	50.5883876
C	82.4719750	63.0187995	49.1811397
C	83.6271026	63.7793839	48.7315185
C	83.1454107	64.7031595	47.8352028
C	81.7023735	64.5222299	47.7750413
C	80.8258509	65.2745245	46.9861781
H	81.2721458	66.0475816	46.3649413
C	76.3647431	63.5396502	47.6380575
H	75.3968588	63.7173725	47.1813412
C	78.0154099	60.8530087	51.2769954
H	77.5770954	60.2354529	52.0549604
C	82.5350080	61.9289934	50.0490539
H	83.5325116	61.6423732	50.3718971
O	79.3052688	64.3049018	50.3905102
O	77.5826653	66.4328695	49.5828896
H	77.9306931	65.0338490	57.6172872
H	79.9598064	62.0786667	45.0894170
H	78.9744347	70.7960945	49.2514856
H	80.2507665	68.6956534	48.9524659
H	78.8927919	66.5980635	45.2276424
H	76.4209379	65.5956258	45.5632351
H	74.2393178	62.0138090	48.8515824
H	75.1443606	60.8099313	51.2328050
H	79.8342563	59.0518071	52.5331710
H	82.4917833	59.6448200	51.8361595
H	84.6363878	63.6469549	49.1212264
H	83.7012003	65.4149463	47.2248554

TURBOMOLE (QM) and ChemShell Energies (MM and QM/MM)

	B3LYP/B1	B3LYP/B2//B1	PBE0/B2/*
QM/MM	-3749.689358	-3750.376453	-3748.990341
QM	-3647.270545	-3647.957640	-3646.571528
MM	-102.418813	-102.418813	-102.418813
ZPE	0.496776	-	-

*B3LYP/B1 geometry

Figure 5

Estrone, formate and $Fe(III)OH_2$(**^{oo}ES**)

C	78.3354562	65.8103574	57.0991169
H	77.6094677	66.2730604	56.4152948
H	79.0404070	65.2247466	56.5008120
C	79.0544227	67.0109962	57.7680118
O	78.4462333	67.6272150	58.6937883
O	80.1551328	67.3653217	57.2533950
H	80.6600327	66.7050488	55.8936925
C	79.1253504	61.5745327	45.5580004
H	78.7699794	60.7122573	44.9813388
H	78.3371590	62.3286088	45.5636953
S	79.4765606	61.0026025	47.2763704
C	81.0286862	67.0715925	51.5115498
H	78.5441342	64.9850417	49.9662436
H	81.5899334	66.7667568	50.6284557
C	81.2872305	66.4042673	52.7081190
H	79.8575374	64.4318700	50.7591295
H	82.0275155	65.6096781	52.7547618
C	80.6704577	66.8291303	53.8996432
O	81.0683175	66.2791667	55.0609921
C	79.7041313	67.8384912	53.8189355
H	79.1988507	68.1571604	54.7269978
C	79.4401216	68.4978775	52.6150668
C	78.4060274	69.6040407	52.6377611
H	77.4157780	69.1695499	52.4439058
H	78.3568846	70.0304127	53.6437237
C	78.6710365	70.6938161	51.5959177
H	77.8266391	71.3962107	51.6011327
H	79.5748544	71.2620402	51.8668258
C	78.8458841	70.0183267	50.2299412
H	77.9433121	69.4354711	50.0291110
C	80.0989027	69.0969572	50.2237284
H	80.9783744	69.7630046	50.3344277
C	80.1347325	68.1559042	51.4336602
C	77.0671027	66.8701262	50.3419390
H	76.7051233	67.8533973	49.9743553
O	76.7010893	66.5486293	51.4959055
Fe	79.3584082	62.7690318	48.8022892
N	78.6499923	64.0711955	47.4162295
N	77.4647551	62.2077761	49.2364442
N	80.1007808	61.4583768	50.1897501
N	81.2486151	63.4001732	48.4614920
C	79.3742972	65.0149756	46.7292204
C	78.5047505	65.7815498	45.8458285
C	77.2400574	65.2757083	46.0150620
C	77.3481477	64.2195861	47.0139938
C	76.3201930	62.5732549	48.5839555
C	75.1534414	61.9630867	49.2140618
C	75.6102145	61.2761230	50.3179705
C	77.0740232	61.3999508	50.2722341
C	79.3522350	60.6726286	51.0216478
C	80.2022403	59.8244894	51.8492288
C	81.5067735	60.1332076	51.5348844
C	81.4114672	61.1760917	50.5004774
C	82.4034152	62.9601949	49.0722981
C	83.5438546	63.7559391	48.6569307
C	83.0572864	64.6734162	47.7565661
C	81.6258152	64.4500623	47.6510344
C	80.7504062	65.1893857	46.8527250
H	81.1889863	65.9897152	46.2625917
C	76.2825877	63.4756906	47.5202484
H	75.3026293	63.7062254	47.1195305
C	77.9630438	60.7092387	51.0944267
H	77.5246798	60.1048476	51.8811045
C	82.4781119	61.8929233	49.9637361
H	83.4738724	61.6527377	50.3245065
O	79.1149085	64.1500533	50.1998383
O	77.7647076	66.2095476	49.5249692
H	77.8222322	65.1348855	57.7835184
H	79.9529356	62.0088850	44.9971909
H	78.9428821	70.7358479	49.4151890
H	80.2390307	68.6374076	49.2453395
H	78.8144854	66.5646225	45.1537823
H	76.3228482	65.6069734	45.5281768
H	74.1560806	61.9958715	48.7755837
H	75.0932219	60.7629099	51.1287709
H	79.8065432	59.0630650	52.5213324
H	82.4565341	59.7644840	51.9222656
H	84.5469986	63.6491756	49.0696898
H	83.6115637	65.4064539	47.1704783

TURBOMOLE (QM) and ChemShell Energies (MM and QM/MM)

	B3LYP/B1	B3LYP/B2//B1	PBE0/B2/*
QM/MM	-3749.748281	-3750.437656	-3749.051446
QM	-3647.323609	-3648.012984	-3646.626775
MM	-102.424671	-102.424671	-102.424671
ZPE	0.501980	-	-

*B3LYP/B1 geometry

Stepwise mechanism for protonated peroxohemiacetal

Figure 6

Protonated Peroxohemiacetal (**HPH**)

C	78.5979611	66.0227317	57.3459208
H	77.9177868	66.5787898	56.6877586
H	79.2239535	65.3867630	56.7128904
C	79.4380030	67.0814670	58.0620092
O	79.1741816	67.5641166	59.1511122
O	80.4655938	67.5718272	57.3603635
H	80.6099780	67.1156975	56.4857525
C	79.1261147	61.5812083	45.5329211
H	78.7899769	60.7072952	44.9621473
H	78.3341716	62.3311303	45.5033295
S	79.4225012	61.0452987	47.2733056
C	80.7955804	66.6756824	51.3155487
H	80.9989635	66.0080761	50.4754919
H	81.5537284	67.4689568	51.2819171
C	80.9634912	65.8993805	52.6260575
H	80.3697394	64.9761060	52.5929591
H	82.0062275	65.6013394	52.7781710
C	80.5004977	66.6847975	53.8257093
O	81.0080195	66.5087501	54.9469806
C	79.4047126	67.6199303	53.6312701
H	78.9945713	68.0748217	54.5310209
C	78.8627536	67.8958270	52.4232847
C	77.6541281	68.7901553	52.3513146
H	76.7990790	68.2057775	51.9784545
H	77.3776704	69.1297205	53.3540913
C	77.8806279	69.9861892	51.4171108
H	76.9538167	70.5712630	51.3705922
H	78.6574726	70.6335515	51.8524880
C	78.3035387	69.4766213	50.0311021
H	77.4546421	68.9413319	49.5907391
C	79.5700292	68.5698088	50.1178262
H	80.3641125	69.1846554	50.5758236
C	79.4086318	67.3417101	51.1115598
C	78.3478374	66.2920841	50.5737290
H	77.4966068	66.8380046	50.1481948
O	77.8830973	65.4229684	51.5695814
H	78.2834701	64.5538210	51.2821714
Fe	79.3593444	62.8761986	48.7217691
N	78.6657662	64.1299397	47.2794027
N	77.4528127	62.3776386	49.2347233
N	80.0701929	61.5819204	50.1607041
N	81.2587902	63.4239212	48.3031876
C	79.3964922	65.0496171	46.5725005
C	78.5213756	65.8598844	45.7338728
C	77.2436032	65.4068495	45.9568106
C	77.3558524	64.3418787	46.9481030
C	76.3085219	62.7869069	48.6053522
C	75.1314117	62.2061865	49.2455711
C	75.5831569	61.4634706	50.3146020
C	77.0495943	61.5544180	50.2555170
C	79.3214105	60.7932865	50.9879438
C	80.1683733	59.9325111	51.8100740
C	81.4724874	60.2421833	51.4977375
C	81.3779463	61.2891388	50.4629964
C	82.3901904	63.0117832	48.9655782
C	83.5389156	63.8106378	48.5719816
C	83.0694963	64.7129624	47.6494970
C	81.6446975	64.4699492	47.4985443
C	80.7777419	65.2032438	46.6836136
H	81.2233972	65.9958051	46.0884915
C	76.2759511	63.6767442	47.5313586
H	75.2925808	63.9432664	47.1609879
C	77.9324951	60.8373456	51.0634651
H	77.4892217	60.2174059	51.8357768
C	82.4482304	61.9793564	49.9008120
H	83.4416808	61.7456020	50.2725680
O	79.3671775	64.2565559	50.0358475
O	78.8406815	65.5243354	49.4963473
H	78.0297733	65.3823278	58.0205407
H	79.9577121	62.0155156	44.9780432
H	78.5244425	70.3176340	49.3738612
H	79.9535412	68.3230532	49.1278279
H	78.8395975	66.6345266	45.0362119
H	76.3185253	65.7717449	45.5105498
H	74.1297664	62.3024912	48.8266457
H	75.0637183	60.9091570	51.0962582
H	79.7700349	59.1573173	52.4646484
H	82.4220528	59.8691850	51.8814877
H	84.5320067	63.7132567	49.0105629
H	83.6276403	65.4494669	47.0714807

TURBOMOLE (QM) and ChemShell Energies (MM and QM/MM)

	B3LYP/B1	B3LYP/B2//B1	PBE0/B2/*
QM/MM	-3750.018374	-3750.695595	-3749.323546
QM	-3647.524769	-3648.201990	-3646.829942
MM	-102.493604	-102.493604	-102.493604
ZPE	0.518391	-	-

*B3LYP/B1 geometry

Figure 6

TS for O-O cleavage starting from **HPH** (**^{OO}HTS1**)

C	78.5994451	66.0190510	57.3293194
H	77.9186607	66.5753030	56.6717945
H	79.2211308	65.3801443	56.6948532
C	79.4463636	67.0769691	58.0383977
O	79.1918187	67.5596567	59.1299362
O	80.4689181	67.5654638	57.3285268
H	80.6053660	67.1120663	56.4501714
C	79.1299605	61.5711678	45.5255648
H	78.7895773	60.7052574	44.9451812
H	78.3396779	62.3239730	45.5027179
S	79.4289162	61.0202095	47.2601614
C	80.7107985	66.6648114	51.2764764
H	80.8556718	65.9806088	50.4363208
H	81.5087648	67.4178609	51.2177225
C	80.8779538	65.8918397	52.5907644
H	80.2490829	64.9921866	52.5797762
H	81.9123234	65.5572938	52.7239528
C	80.4659062	66.6964863	53.7966577
O	80.9879911	66.5036726	54.9095153
C	79.3981119	67.6653816	53.6216487
H	79.0149728	68.1303080	54.5282168
C	78.8478792	67.9597270	52.4212853
C	77.6614258	68.8851878	52.3674119
H	76.7873251	68.3182677	52.0147793
H	77.4084720	69.2355097	53.3726278
C	77.8930572	70.0705007	51.4197093
H	76.9732301	70.6670819	51.3791376
H	78.6831645	70.7098966	51.8428993
C	78.2995416	69.5489287	50.0322396
H	77.4455014	69.0179470	49.5980855
C	79.5546888	68.6287459	50.1211938
H	80.3490494	69.2307044	50.5974723
C	79.3545110	67.3962246	51.0985500
C	78.2293334	66.4056861	50.5670035
H	77.3327901	67.0096388	50.3472424
O	77.8697383	65.4639027	51.5720012
H	78.2270595	64.6167284	51.2099109
Fe	79.3525345	62.9180860	48.7721407
N	78.6698342	64.1073843	47.3034139
N	77.4472744	62.3517496	49.2358782
N	80.0728791	61.5439034	50.1448342
N	81.2656014	63.4147671	48.3170090
C	79.4027254	65.0328811	46.6007836
C	78.5278151	65.8375629	45.7615507
C	77.2497926	65.3825767	45.9816544
C	77.3571274	64.3186049	46.9695985
C	76.3032478	62.7661713	48.6149747
C	75.1275198	62.1874319	49.2586779
C	75.5824317	61.4411436	50.3230377
C	77.0493191	61.5277037	50.2569579
C	79.3217545	60.7606796	50.9755730
C	80.1696693	59.9080065	51.8017519
C	81.4744854	60.2227760	51.4942576
C	81.3818108	61.2644296	50.4568242
C	82.3958500	63.0001597	48.9797827
C	83.5450649	63.7995285	48.5870004
C	83.0768280	64.7032329	47.6663245
C	81.6510342	64.4626351	47.5181726
C	80.7819059	65.1942028	46.7074777
H	81.2215029	65.9907517	46.1137183
C	76.2733717	63.6573600	47.5444245
H	75.2922991	63.9271593	47.1716544
C	77.9336943	60.8057626	51.0562143
H	77.4938669	60.1885198	51.8321642
C	82.4527393	61.9638807	49.9075492
H	83.4442349	61.7322673	50.2851668
O	79.3547716	64.1374961	49.9645497
O	78.5150701	65.7496974	49.4050992
H	78.0319684	65.3819898	58.0076922
H	79.9611433	62.0080699	44.9721045
H	78.5218271	70.3845746	49.3686497
H	79.9539806	68.3852257	49.1366480
H	78.8433827	66.6165045	45.0674805
H	76.3263534	65.7494581	45.5336314
H	74.1248572	62.2890398	48.8434551
H	75.0651551	60.8871354	51.1063423
H	79.7730393	59.1355942	52.4606377
H	82.4233724	59.8547230	51.8844077
H	84.5389168	63.6993475	49.0232214
H	83.6331747	65.4392343	47.0859396

TURBOMOLE (QM) and ChemShell Energies (MM and QM/MM)

	B3LYP/B1	B3LYP/B2//B1	PBE0/B2/*
QM/MM	-3749.998093	-3750.674700	-3749.295220
QM	-3647.505642	-3648.182248	-3646.802769
MM	-102.492451	-102.492451	-102.492451
ZPE	0.516025	-	-

*B3LYP/B1 geometry

Figure 6

Cpd II / oxyradical substrate (^{oo}**HI1**)

C	78.5883188	66.0162756	57.2614583
H	77.9143623	66.5812665	56.6044470
H	79.2125487	65.3813211	56.6255107
C	79.4385191	67.0639518	57.9812813
O	79.1995622	67.5269727	59.0837584
O	80.4503508	67.5660843	57.2625976
H	80.5648920	67.1257974	56.3759961
C	79.1216011	61.6018989	45.5106669
H	78.7508393	60.7751654	44.8934024
H	78.3542754	62.3800959	45.5212144
S	79.4058622	60.9675126	47.2140192
C	80.4664344	66.6894031	51.1846259
H	80.5201508	65.9869993	50.3476629
H	81.3334704	67.3599034	51.0966188
C	80.6180162	65.9031011	52.4948005
H	79.9316289	65.0472064	52.5039905
H	81.6304684	65.4961955	52.5856635
C	80.3093681	66.7298890	53.7121219
O	80.8601507	66.5097624	54.8048047
C	79.2985085	67.7684907	53.5754820
H	78.9735442	68.2478968	54.4971695
C	78.7454016	68.1250370	52.3939428
C	77.6250027	69.1309163	52.3782047
H	76.7026532	68.6160819	52.0753849
H	77.4295870	69.5005241	53.3884934
C	77.8714970	70.2928413	51.4044817
H	76.9608349	70.9026742	51.3646948
H	78.6769540	70.9248073	51.8089189
C	78.2579038	69.7505459	50.0168942
H	77.4028359	69.2236963	49.5825395
C	79.4914991	68.8104815	50.1245574
H	80.2690789	69.3795393	50.6668437
C	79.1935889	67.5700508	51.0471620
C	77.9244858	66.6902923	50.4928087
H	77.0326035	67.3137148	50.7035990
O	77.7671510	65.5293956	51.2728527
H	78.3078631	64.7942789	50.8374645
Fe	79.4229389	62.7943567	48.9125255
N	78.7195960	64.0850436	47.5000017
N	77.5180312	62.2022815	49.3273369
N	80.1513032	61.3494428	50.1638748
N	81.3262611	63.3239819	48.4261988
C	79.4492786	65.0092345	46.7805467
C	78.5722138	65.7908997	45.9187225
C	77.3013913	65.3179890	46.1337458
C	77.4156926	64.2668260	47.1385070
C	76.3720069	62.6391475	48.7199765
C	75.1965587	62.0436058	49.3512550
C	75.6546698	61.2748603	50.3969149
C	77.1226874	61.3522694	50.3198308
C	79.4021794	60.5579033	50.9928268
C	80.2594159	59.7350045	51.8385736
C	81.5601155	60.0917667	51.5606658
C	81.4586471	61.1233237	50.5121372
C	82.4642759	62.9032253	49.0729264
C	83.6119758	63.7050265	48.6699593
C	83.1377014	64.6094953	47.7543014
C	81.7055788	64.3767723	47.6323179
C	80.8307813	65.1388107	46.8524290
H	81.2717906	65.9283632	46.2503469
C	76.3370235	63.5637448	47.6815529
H	75.3569199	63.8216274	47.2964162
C	78.0156129	60.5951515	51.0808739
H	77.5799937	59.9542144	51.8400103
C	82.5240232	61.8585174	49.9887075
H	83.5134517	61.6426555	50.3804760
O	79.4114819	63.8963409	50.1537214
O	77.9325056	66.4863240	49.1863262
H	78.0135920	65.3744525	57.9291549
H	79.9623709	62.0312686	44.9658602
H	78.4905341	70.5766245	49.3449242
H	79.9552764	68.5813178	49.1651508
H	78.8773826	66.5708688	45.2211648
H	76.3749057	65.6522333	45.6668714
H	74.1906252	62.1570846	48.9471676
H	75.1411317	60.7231251	51.1842733
H	79.8713978	58.9552045	52.4938754
H	82.5089091	59.7603670	51.9826036
H	84.6091943	63.6079726	49.0991473
H	83.6853372	65.3479886	47.1688195

TURBOMOLE (QM) and ChemShell Energies (MM and QM/MM)

	B3LYP/B1	B3LYP/B2//B1	PBE0/B2/*
QM/MM	-3750.007683	-3750.684396	-3749.305126
QM	-3647.517893	-3648.194606	-3646.815337
MM	-102.489790	-102.489790	-102.489790
ZPE	0.514438	-	-

*B3LYP/B1 geometry

Figure 6

TS for 1βH abstraction by Cpd II from the oxyradical substrate (^{oo}**HTS2**)

C	78.6197959	66.0072738	57.2351455
H	77.9471905	66.5699910	56.5746404
H	79.2366503	65.3591561	56.6051275
C	79.4804478	67.0570721	57.9398526
O	79.2484250	67.5317709	59.0390765
O	80.4930580	67.5474620	57.2139020
H	80.6117133	67.1029555	56.3298348
C	79.1406505	61.6303520	45.5581551
H	78.7693322	60.7858498	44.9655944
H	78.3695178	62.4040997	45.5556154
S	79.4371206	61.0388820	47.2778786
C	80.2187407	66.3309425	51.1239879
H	79.9599582	65.3823319	50.4741151
H	81.1544048	66.7534559	50.7372662
C	80.4906033	65.7226128	52.5127725
H	79.7913940	64.8894952	52.6885130
H	81.4943196	65.2867140	52.5487591
C	80.3041889	66.6405361	53.6854911
O	80.9286510	66.4898229	54.7512373
C	79.2919915	67.6732968	53.5517816
H	79.0186105	68.2053676	54.4611671
C	78.6993983	67.9914962	52.3788255
C	77.6271936	69.0491659	52.3843340
H	76.6706814	68.5961458	52.0941004
H	77.4736291	69.4236888	53.3998989
C	77.9342440	70.1975174	51.4146384
H	77.0575575	70.8564020	51.3803681
H	78.7741799	70.7839947	51.8181317
C	78.2853265	69.6333891	50.0268770
H	77.4048675	69.1427220	49.6023196
C	79.4744378	68.6290988	50.1167327
H	80.2855735	69.1481680	50.6601762
C	79.1104819	67.4006587	51.0356593
C	77.6793178	66.6207796	50.4699544
H	76.8722585	67.2939046	50.8051645
O	77.5132917	65.4274066	51.1900352
H	78.1019889	64.7342394	50.7599560
Fe	79.4600730	62.9276893	48.9194326
N	78.7576829	64.1510504	47.4632371
N	77.5496705	62.3442677	49.3554100
N	80.1734657	61.5002076	50.2056290
N	81.3567571	63.4119477	48.4182867
C	79.4853089	65.0708946	46.7426856
C	78.6088797	65.8342902	45.8663223
C	77.3402458	65.3477139	46.0682382
C	77.4518907	64.3124172	47.0861794
C	76.4091310	62.7192025	48.6989179
C	75.2356863	62.1011315	49.3108498
C	75.6846647	61.3802837	50.3944735
C	77.1495928	61.5064778	50.3610658
C	79.4235927	60.7226346	51.0460866
C	80.2742667	59.8657080	51.8614984
C	81.5785452	60.1818908	51.5502885
C	81.4837793	61.2252735	50.5156530
C	82.4950456	62.9785782	49.0557899
C	83.6462652	63.7629651	48.6386418
C	83.1727564	64.6705778	47.7247429
C	81.7395147	64.4567489	47.6137904
C	80.8663756	65.2135560	46.8285248
H	81.3077327	66.0000913	46.2228958
C	76.3765122	63.6081434	47.6281611
H	75.3988718	63.8353455	47.2181838
C	78.0380740	60.7785242	51.1499214
H	77.6035747	60.1539707	51.9232770
C	82.5537324	61.9330042	49.9721165
H	83.5460225	61.6939538	50.3425107
O	79.4640725	64.1246289	50.1105172
O	77.6933962	66.5199729	49.1750509
H	78.0430251	65.3779240	57.9128775
H	79.9761320	62.0519610	44.9993324
H	78.5357955	70.4543885	49.3550944
H	79.9169779	68.3950050	49.1485257
H	78.9121821	66.6092408	45.1623865
H	76.4169048	65.6766205	45.5914486
H	74.2419592	62.1597141	48.8668441
H	75.1656419	60.8227525	51.1741150
H	79.8760026	59.0858340	52.5105352
H	82.5262831	59.8143661	51.9437156
H	84.6463076	63.6550789	49.0585730
H	83.7253004	65.3964796	47.1282296

TURBOMOLE (QM) and ChemShell Energies (MM and QM/MM)

	B3LYP/B1	B3LYP/B2//B1	PBE0/B2/*
QM/MM	-3749.979978	-3750.658167	-3749.280644
QM	-3647.489053	-3648.167242	-3646.789718
MM	-102.490926	-102.490926	-102.490926

*B3LYP/B1 geometry

Figure 6

1(10),4-diene-3-one/Fe(III)OH_2 (^{oo}**HI2**)

C	78.6305856	65.9989421	57.3887881
H	77.9726341	66.5432015	56.7013324
H	79.2721707	65.3526774	56.7834671
C	79.4512108	67.0690234	58.1124700
O	79.1658718	67.5615452	59.1934641
O	80.4926752	67.5458824	57.4273520
H	80.6257345	67.0774281	56.5528881
C	79.1745506	61.4999563	45.5013044
H	78.8582641	60.6297497	44.9129092
H	78.3685020	62.2357023	45.4733198
S	79.4402607	60.9191439	47.2285091
C	80.7752178	66.9895344	51.4546324
H	79.0500535	65.0053943	49.5008744
H	81.3342322	66.6647077	50.5810383
C	80.9517883	66.1534773	52.6801590
H	80.3437559	65.2395139	52.5455692
H	81.9849239	65.8064036	52.7987329
C	80.4690433	66.7865531	53.9588951
O	80.9256682	66.4170155	55.0588389
C	79.4459618	67.7919920	53.8264710
H	78.9166203	68.1036511	54.7231522
C	79.1723365	68.3749411	52.6236076
C	78.0189168	69.3437355	52.5459644
H	77.1284771	68.7589145	52.2696515
H	77.8019416	69.7410043	53.5412865
C	78.2034786	70.4631939	51.5198701
H	77.2693350	71.0364504	51.4742099
H	78.9975254	71.1479271	51.8559642
C	78.5569368	69.8389186	50.1637304
H	77.7428179	69.1730042	49.8590945
C	79.8984794	69.0521664	50.2411920
H	80.6909120	69.7916178	50.4664286
C	79.9510873	68.0605339	51.4070934
C	77.3656352	66.2248174	50.6639591
H	76.6072250	66.9758677	50.9792364
O	77.6846614	65.3525214	51.5302020
H	78.8225637	64.2035375	50.7390174
Fe	79.4417908	62.6792565	48.6713802
N	78.7390026	64.0221292	47.3128736
N	77.5467731	62.2048730	49.2222121
N	80.1519382	61.3887053	50.0958990
N	81.3308082	63.2870637	48.2698694
C	79.4558430	64.9717059	46.6210340
C	78.5700435	65.7755553	45.7915907
C	77.3016160	65.2896394	45.9959216
C	77.4257582	64.2097946	46.9660551
C	76.4033280	62.5900663	48.5735958
C	75.2282796	61.9912703	49.2008609
C	75.6766038	61.2868146	50.2959663
C	77.1407747	61.3873707	50.2461015
C	79.4116270	60.6131467	50.9469570
C	80.2669785	59.7722159	51.7753266
C	81.5676688	60.0829956	51.4499817
C	81.4643905	61.1081443	50.3953136
C	82.4657625	62.8663017	48.9239360
C	83.6058406	63.6932245	48.5624010
C	83.1309467	64.6205130	47.6669122
C	81.7101701	64.3688611	47.5057714
C	80.8354395	65.1317999	46.7278290
H	81.2712183	65.9488077	46.1592897
C	76.3598062	63.4964425	47.5147975
H	75.3728435	63.7434144	47.1404772
C	78.0252604	60.6688401	51.0483961
H	77.5863164	60.0590521	51.8308195
C	82.5288911	61.8095577	49.8330949
H	83.5239448	61.5779054	50.2022987
O	79.4435408	64.2166562	49.9666452
O	77.8069054	66.3251246	49.4971219
H	78.0461579	65.3705760	58.0608497
H	80.0039189	61.9583727	44.9627238
H	78.6768097	70.6013291	49.3940374
H	80.1601119	68.6474496	49.2635319
H	78.8736460	66.5674354	45.1068879
H	76.3727355	65.6558861	45.5587593
H	74.2379094	62.0296800	48.7472554
H	75.1527836	60.7643521	51.0964111
H	79.8736084	59.0137631	52.4521395
H	82.5189532	59.7329944	51.8507605
H	84.5977279	63.6044963	49.0055188
H	83.6832451	65.3704932	47.1007296

TURBOMOLE (QM) and ChemShell Energies (MM and QM/MM)

	B3LYP/B1	B3LYP/B2//B1	PBE0/B2/*
QM/MM	-3750.128222	-3750.815393	-3749.430623
QM	-3647.630953	-3648.318123	-3646.933353
MM	-102.497270	-102.497270	-102.497270

*B3LYP/B1 geometry

Table S1: NPA spin densities (charges) for species illustrated in Figure 3 initiated via C-C cleavage from PH

	PH	^{CC}TS1	^{CC}I1	^{CC}TS2	^{CC}I2	^{CC}TS3	^{CC}I3	^{CC}TS4	^{CC}ES
B3LYP/B1:CHARMM									
Fe	0.85 (1.26)	0.89 (1.27)	0.99 (1.28)	1.29 (1.29)	1.19 (1.26)	1.30 (1.32)	0.97 (1.32)	1.06 (1.36)	1.04 (1.29)
Op	0.18 (-0.38)	0.15 (-0.38)	0.06 (-0.42)	0.16 (-0.36)	0.86 (-0.50)	0.73 (-0.56)	0.10 (-0.46)[b]	0.04 (-0.45)[b]	0.01 (0.09)[b,c]
Porphyrin	-0.05 (-1.14)	-0.05 (-1.12)	-0.06 (-1.05)	-0.07 (-0.84)	-0.04 (-0.96)	-0.04 (-0.92)	-0.05 (-1.10)	-0.05 (-1.04)	-0.05 (-0.99)
SCH_3	0.00 (-0.73)	0.00 (-0.72)	0.00 (-0.63)	-0.02 (-0.67)	-0.01 (-0.80)	-0.02 (-0.79)	-0.02 (-0.76)	-0.04 (-0.68)	0.00 (-0.52)
substrate[a]	0.00 (-0.21)	0.00 (-0.34)	0.00 (-0.08)	-0.01 (-0.07)	-0.99 (0.06)	-0.96 (0.02)	0.00 (0.06)[b]	-0.01 (-0.12)[b]	0.00 (-0.10)[b,c]
Formate	0.03 (-0.71)	0.02 (-0.60)	0.00 (-0.19)	-0.34 (-0.45)	-0.01 (-0.98)	-0.01 (-0.98)	0.00 (-0.97)	0.00 (-0.96)	0.00 (-0.87)
D309	0.00 (-0.09)	0.00 (-0.10)	0.00 (-0.91)[d]	0.00 (-0.91)[d]	0.00 (-0.08)	0.00 (-0.09)	0.00 (-0.08)	0.00 (-0.10)	0.00 (-0.91)[d]
B3LYP/B2//B1:CHARMM									
Fe	0.70 (0.94)	0.74 (0.94)	0.83 (0.93)	1.08 (0.98)	0.98 (0.97)	1.08 (1.02)	0.83 (1.02)	0.91 (1.03)	0.88 (0.94)
Op	0.23 (-0.36)	0.20 (-0.37)	0.10 (-0.40)	0.25 (-0.32)	0.97 (-0.44)	0.83 (-0.49)	0.14 (-0.43)[b]	0.08 (-0.41)[b]	0.04 (0.12)[b,c]
Porphyrin	0.00 (-0.97)	0.00 (-0.95)	0.01 (-0.87)	0.01 (-0.70)	0.03 (-0.83)	0.04 (-0.79)	0.01 (-0.94)	0.01 (-0.87)	0.02 (-0.81)
SCH_3	0.04 (-0.61)	0.04 (-0.59)	0.06 (-0.50)	0.03 (-0.55)	0.02 (-0.70)	0.01 (-0.70)	0.02 (-0.65)	0.00 (-0.55)	0.07 (-0.37)
substrate[a]	0.00 (-0.22)	0.00 (-0.35)	0.00 (-0.08)	-0.01 (-0.08)	-0.98 (0.04)	-0.95 (0.01)	0.00 (0.04)[b]	-0.01 (-0.13)[b]	0.00 (-0.10)[b,c]
Formate	0.02 (-0.71)	0.01 (-0.59)	-0.01 (-0.17)	-0.36 (-0.43)	-0.01 (-0.98)	-0.01 (-0.98)	0.00 (-0.97)	0.00 (-0.97)	0.00 (-0.86)
D309	0.00 (-0.08)	0.00 (-0.09)	0.00 (-0.91)[d]	0.00 (-0.91)[d]	0.00 (-0.08)	0.00 (-0.08)	0.00 (-0.07)	0.00 (-0.09)	0.00 (-0.91)[d]
PBE0/B2//B3LYP/B1:CHARMM									
Fe	0.75 (0.97)	0.79 (0.98)	0.86 (0.96)	1.16 (1.02)	1.00 (0.99)	1.12 (1.05)	0.86 (1.05)	0.95 (1.06)	0.90 (0.97)
Op	0.20 (-0.37)	0.17 (-0.38)	0.09 (-0.41)	0.23 (-0.34)	0.96 (-0.44)	0.81 (-0.50)	0.12 (-0.45)[b]	0.06 (-0.43)[b]	0.03 (0.12)[b,c]
Porphyrin	-0.01 (-0.97)	0.00 (-0.96)	0.00 (-0.88)	0.00 (-0.71)	0.02 (-0.85)	0.02 (-0.80)	0.00 (-0.95)	0.00 (-0.88)	0.01 (-0.83)
SCH_3	0.04 (-0.62)	0.04 (-0.60)	0.06 (-0.51)	0.02 (-0.56)	0.02 (-0.70)	0.01 (-0.70)	0.01 (-0.65)	-0.01 (-0.56)	0.06 (-0.38)
substrate[a]	0.00 (-0.22)	0.00 (-0.36)	0.00 (-0.08)	0.00 (-0.08)	-0.99 (0.05)	-0.96 (0.01)	0.00 (0.05)[b]	-0.01 (-0.13)[b]	0.00 (-0.10)[b,c]
Formate	0.01 (-0.71)	0.00 (-0.60)	-0.01 (-0.17)	-0.41 (-0.42)	-0.01 (-0.98)	-0.01 (-0.98)	0.00 (-0.98)	0.00 (-0.97)	0.00 (-0.87)
D309	0.00 (-0.08)	0.00 (-0.09)	0.00 (-0.91)[d]	0.00 (-0.91)[d]	0.00 (-0.07)	0.00 (-0.08)	0.00 (-0.07)	0.00 (-0.09)	0.00 (-0.91)[d]

[a] Consists of all the atoms of the 19-oxoAD intermediate except for the aldehyde unit (C19, O and H) which are included with the distal oxygen atom in the formate unit. [b]The 1β-hydrogen of 19-oxoAD is not included in the substrate but added to O_p. [c] The 2β-hydrogen of 19-oxoAD is not included in the substrate but added to O_p. [d] D309H hops to the 19-oxoAD intermediate, D309H spin and charges are considered with the substrate.

Table S2: NPA spin densities (charges) for species illustrated in Figure 5 initiated via O-O cleavage from PH

	PH	^{OO}TS1	^{OO}I1	^{OO}TS2	^{OO}I2	^{OO}TS3	^{OO}ES
B3LYP/B1:CHARMM							
Fe	0.85 (1.26)	0.99 (1.25)	1.16 (1.26)	1.36 (1.32)	0.95 (1.32)	1.04 (1.35)	1.08 (1.32)
Op	0.18 (-0.38)	0.70 (-0.42)	0.87 (-0.48)	0.68 (-0.56)	0.11 (-0.45)[b]	0.04 (-0.45)[b]	0.01 (0.09)[b,c]
Porphyrin	-0.05 (-1.14)	-0.04 (-1.01)	-0.04 (-0.97)	-0.05 (-0.93)	-0.05 (-1.11)	-0.05 (-1.04)	-0.05 (-0.98)
SCH_3	0.00 (-0.73)	-0.02 (-0.77)	-0.01 (-0.80)	-0.02 (-0.80)	-0.01 (-0.76)	-0.03 (-0.69)	-0.03 (-0.55)
substrate[a]	0.00 (-0.21)	-0.03 (-0.14)	-0.11 (-0.09)	-0.10 (-0.09)	0.00 (0.06)[b]	-0.01 (-0.12)[b]	0.00 (-0.10)[b,c]
Formate	0.03 (-0.71)	-0.61 (-0.84)	-0.87 (-0.84)	-0.86 (-0.87)	0.00 (-0.96)	0.00 (-0.94)	0.00 (-0.87)
D309	0.00 (-0.09)	0.00 (-0.08)	0.00 (-0.08)	0.00 (-0.08)	0.00 (-0.08)	0.00 (-0.10)	0.00 (-0.91)[d]
B3LYP/B2//B1:CHARMM							
Fe	0.70 (0.94)	0.81 (0.96)	0.96 (0.97)	1.14 (1.03)	0.81 (1.01)	0.89 (1.02)	0.92 (0.98)
Op	0.23 (-0.36)	0.78 (-0.38)	0.97 (-0.42)	0.77 (-0.49)	0.16 (-0.42)[b]	0.08 (-0.42)[b]	0.04 (0.12)[b,c]
Porphyrin	0.00 (-0.97)	0.02 (-0.87)	0.03 (-0.84)	0.03 (-0.80)	0.01 (-0.95)	0.01 (-0.88)	0.02 (-0.80)
SCH_3	0.04 (-0.61)	0.02 (-0.66)	0.02 (-0.70)	0.02 (-0.70)	0.03 (-0.65)	0.02 (-0.56)	0.03 (-0.42)
substrate[a]	0.00 (-0.22)	-0.03 (-0.14)	-0.12 (-0.10)	-0.11 (-0.10)	0.00 (0.04)[b]	-0.01 (-0.13)[b]	0.00 (-0.10)[b,c]
Formate	0.02 (-0.71)	-0.60 (-0.83)	-0.86 (-0.84)	-0.86 (-0.87)	0.00 (-0.96)	0.00 (-0.94)	0.00 (-0.87)
D309	0.00 (-0.08)	0.00 (-0.07)	0.00 (-0.07)	0.00 (-0.07)	0.00 (-0.08)	0.00 (-0.10)	0.00 (-0.91)[d]
PBE0/B2//B3LYP/B1:CHARMM							
Fe	0.75 (0.97)	0.82 (0.98)	0.98 (0.99)	1.19 (1.06)	0.84 (1.04)	0.93 (1.05)	0.96 (1.01)
Op	0.20 (-0.37)	0.83 (-0.38)	0.97 (-0.42)	0.74 (-0.51)	0.13 (-0.44)[b]	0.07 (-0.43)[b]	0.03 (0.12)[b,c]
Porphyrin	-0.01 (-0.97)	0.02 (-0.89)	0.02 (-0.86)	0.02 (-0.81)	0.00 (-0.96)	0.00 (-0.89)	0.00 (-0.82)
SCH_3	0.04 (-0.62)	0.02 (-0.67)	0.02 (-0.71)	0.02 (-0.70)	0.02 (-0.65)	0.01 (-0.57)	0.00 (-0.43)
substrate[a]	0.00 (-0.22)	-0.03 (-0.14)	-0.11 (-0.10)	-0.11 (-0.11)	0.00 (0.04)[b]	-0.01 (-0.13)[b]	0.00 (-0.10)[b,c]
Formate	0.01 (-0.71)	-0.66 (-0.82)	-0.87 (-0.84)	-0.87 (-0.86)	0.00 (-0.96)	0.00 (-0.95)	0.00 (-0.87)
D309	0.00 (-0.08)	0.00 (-0.07)	0.00 (-0.07)	0.00 (-0.07)	0.00 (-0.08)	0.00 (-0.10)	0.00 (-0.91)[d]

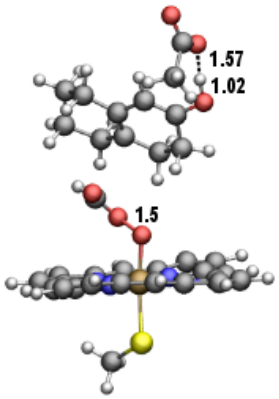
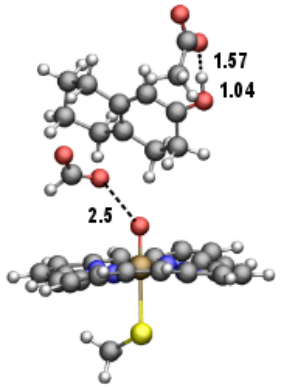
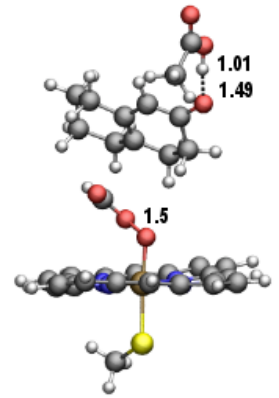
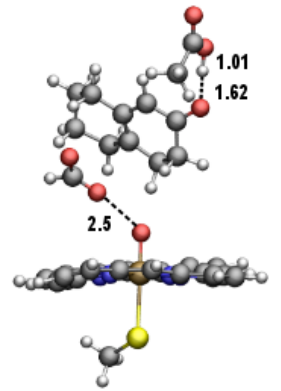
[a] Consists of all the atoms of the 19-oxoAD intermediate except for the aldehyde unit (C19, O and H) which are included with the distal oxygen atom in the formate unit. [b] The 1β-hydrogen of 19-oxoAD is not included in the substrate but added to O_p. [c] The 2β-hydrogen of 19-oxoAD is not included in the substrate but added to O_p. [d] D309H hops to the 19-oxoAD intermediate, D309H spin and charges are considered with the substrate.

Table S3: NPA spin densities (charges) for species illustrated in Figure 6 initiated via O-O cleavage from HPH

	HPH	^{OO}HTS1	^{OO}HI1	^{OO}HTS2	^{OO}HI2
B3LYP/B1:CHARMM					
Fe	1.00 (1.27)	1.30 (1.30)	1.40 (1.32)	1.56 (1.36)	1.05 (1.27)
Op	0.04 (-0.52)	0.26 (-0.52)	0.67 (-0.66)	0.49 (-0.73)	0.00 (0.08)[b,c]
Porphyrin	-0.06 (-1.03)	-0.07 (-0.86)	-0.21 (-0.75)	-0.13 (-0.79)	-0.05 (-1.00)
SCH_3	0.01 (-0.55)	-0.03 (-0.60)	-0.04 (-0.66)	-0.06 (-0.64)	0.00 (-0.46)
substrate[a]	0.00 (-0.05)	0.00 (-0.06)	-0.11 (0.01)	-0.22 (0.06)	0.00 (0.06)[b]
Formic Acid	0.00 (-0.07)	-0.46 (-0.20)	-0.70 (-0.20)	-0.64 (-0.20)	0.00 (-0.88)[c]
D309	0.00 (-0.06)	0.00 (-0.06)	0.00 (-0.06)	0.00 (-0.06)	0.00 (-0.07)
B3LYP/B2//B1:CHARMM					
Fe	0.84 (0.92)	1.08 (0.96)	1.17 (0.99)	1.31 (1.03)	0.87 (0.92)
Op	0.08 (-0.50)	0.35 (-0.48)	0.75 (-0.60)	0.58 (-0.67)	0.02 (0.12)[b,c]
Porphyrin	0.01 (-0.86)	0.01 (-0.71)	-0.07 (-0.65)	-0.02 (-0.66)	0.02 (-0.83)
SCH_3	0.07 (-0.41)	0.04 (-0.47)	0.02 (-0.55)	0.01 (-0.52)	0.08 (-0.31)
substrate[a]	0.00 (-0.03)	0.00 (-0.04)	-0.12 (0.03)	-0.23 (0.07)	0.00 (0.05)[b]
Formic Acid	0.00 (-0.07)	-0.47 (-0.20)	-0.74 (-0.17)	-0.65 (-0.20)	0.00 (-0.89)[c]
D309	0.00 (-0.05)	0.00 (-0.05)	0.00 (-0.05)	0.00 (-0.05)	0.00 (-0.06)
PBE0/B2//B3LYP/B1:CHARMM					
Fe	0.87 (0.95)	1.11 (0.99)	1.23 (1.02)	1.39 (1.07)	0.92 (0.95)
Op	0.07 (-0.51)	0.40 (-0.50)	0.72 (-0.63)	0.54 (-0.70)	0.02 (0.12)[b,c]
Porphyrin	0.00 (-0.87)	0.00 (-0.74)	-0.04 (-0.71)	-0.02 (-0.69)	0.00 (-0.84)
SCH_3	0.06 (-0.42)	0.02 (-0.48)	0.02 (-0.56)	0.02 (-0.53)	0.05 (-0.32)
substrate[a]	0.00 (-0.04)	0.00 (-0.05)	-0.13 (0.04)	-0.24 (0.06)	0.00 (0.05)[b]
Formic Acid	0.00 (-0.06)	-0.53 (-0.18)	-0.81 (-0.11)	-0.69 (-0.16)	0.00 (-0.89)[c]
D309	0.00 (-0.05)	0.00 (-0.05)	0.00 (-0.05)	0.00 (-0.05)	0.00 (-0.06)

[a] Consists of all the atoms of the 19-oxoAD intermediate except for the aldehyde unit (C19, O and H) which are included with the distal oxygen atom in the formic acid unit. [b] The 1β-hydrogen of 19-oxoAD is not included in the substrate but added to O_p. [c] The formic acid transfers the proton to hydroxy ferric species. Hydrogen atom of formic acid is added to O_p.

Table S4: NPA spin densities (charges) for species illustrated in Figure 4

B3LYP/B1:CHARMM					STRUCTURES	
	I (O-O :1.5 Å)	**I' (O-O :2.5 Å)**	**II (O-O :1.5 Å)**	**II' (O-O :2.5 Å)**	**I**	**I'**
Fe	0.99 (1.27)	1.15 (1.25)	0.98 (1.27)	1.11 (1.24)		
Op	0.06 (-0.41)	0.90 (-0.46)	0.07 (-0.41)	0.93 (-0.43)		
Porphyrin	-0.06 (-1.04)	-0.04 (-0.98)	-0.06 (-1.05)	-0.04 (-1.00)		
SCH_3	0.00 (-0.63)	-0.01 (-0.81)	0.00 (-0.65)	-0.01 (-0.82)		
substrate[a]	0.00 (-0.08)	-0.90 (0.74)	0.00 (-0.85)	-0.98 (0.04)		
Formate	0.00 (-0.20)	-0.10 (-0.86)	0.00 (-0.20)	-0.01 (-0.95)		
D309	0.00 (-0.90)[b]	0.00 (-0.88)[b]	0.00 (-0.13)	0.00 (-0.08)		
B3LYP/B2//B1:CHARMM						
Fe	0.83 (0.93)	0.94 (0.97)	0.82 (0.94)	0.91 (0.96)		
Op	0.11 (-0.39)	1.00 (-0.40)	0.12 (-0.39)	1.03 (-0.37)		
Porphyrin	0.01 (-0.86)	0.03 (-0.86)	0.01 (-0.87)	0.03 (-0.87)		
SCH_3	0.06 (-0.50)	0.02 (-0.72)	0.06 (-0.51)	0.02 (-0.73)	**II**	**II'**
substrate[a]	0.00 (-0.08)	-0.89 (0.73)	0.00 (-0.85)	-0.97 (0.02)		
Formate	-0.01 (-0.18)	-0.10 (-0.84)	-0.01 (-0.19)	-0.02 (-0.94)		
D309	0.00 (-0.91)[b]	0.00 (-0.88)[b]	0.00 (-0.12)	0.00 (-0.08)		
PBE0/B2//B3LYP/B1:CHARMM						
Fe	0.86 (0.96)	0.96 (0.99)	0.85 (0.96)	0.92 (0.98)		
Op	0.09 (-0.40)	0.99 (-0.40)	0.10 (-0.40)	1.03 (-0.37)		
Porphyrin	0.00 (-0.88)	0.02 (-0.87)	0.00 (-0.89)	0.02 (-0.89)		
SCH_3	0.06 (-0.51)	0.02 (-0.72)	0.06 (-0.52)	0.02 (-0.73)		
substrate[a]	0.00 (-0.08)	-0.90 (0.74)	0.00 (-0.86)	-0.98 (0.02)		
Formate	-0.01 (-0.18)	-0.09 (-0.85)	-0.01 (-0.18)	-0.01 (-0.94)		
D309	0.00 (-0.91)[b]	0.00 (-0.88)[b]	0.00 (-0.12)	0.00 (-0.08)		

[a] Consists of all the atoms of the 19-oxoAD intermediate except for the aldehyde unit (C19, O and H) which are included with the distal oxygen atom in the formate unit.

[b] D309H is restrained on the 19-oxoAD intermediate, D309H spin and charges are considered with the substrate.