Electronic Supplementary Information

for

A protocol to obtain multidimensional quantum tunneling corrections derived from QM(DFT)/MM calculations for an enzyme reaction

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Table S1. RESP charges (a.u.) for the Fe coordination sphere and the substrate.

Atom	Atom Type	His545
N	N	-0.4157
H	H	0.296918
C	CT	-0.0581
H	H1	0.082154
C	CT	0.114206
H	HC	-0.018473
H	HC	-0.018473
N	NB	0.008309
C	CC	-0.025211
C	CR	-0.09944
H	H5	0.179804
N	NA	-0.084421
H	H	0.30178
C	CW	-0.194645
H	H4	0.174221
C	C	0.5973
O	O	-0.5679

Atom	Atom Type	Ile663
N	N	-0.423664
H	H	0.283954
C	CT	-0.020495
H	H1	0.144139
C	CT	0.012376
H	HC	0.061564
C	CT	-0.129463
H	HC	0.023324
H	HC	0.023324
H	HC	0.023324
C	CT	-0.047630
H	HC	0.035170
H	HC	0.035170
C	CT	-0.086106
H	HC	0.031096
H	HC	0.031096
H	HC	0.031096
C	C	0.368333
O	O2	-0.437161
O	OXT	-0.489009

Atom	Atom Type	His361	His366	His541
N	N	-0.4157	-0.4157	-0.4157
H	H	0.273195	0.353492	0.306443
C	CT	0.0188	0.0188	0.0188
H	H1	0.120538	0.077848	0.129221
C	CT	-0.093496	-0.15132	0.016624
H	HC	0.077182	0.048673	0.037324
H	HC	0.077182	0.048673	0.037324
N	NA	-0.111774	-0.168678	-0.163994
H	H	0.305275	0.313588	0.308713
C	CC	-0.035013	0.15502	0.023307
C	CR	-0.00794	-0.063105	-0.015225
H	H5	0.145093	0.196501	0.181732
N	NB	-0.020841	0.020262	-0.163891
C	CV	-0.192828	-0.295794	-0.111133
H	H4	0.181224	0.211423	0.119343
C	C	0.5973	0.5973	0.5973
O	O	-0.5679	-0.5679	-0.5679

Atom	Atom Type	Cofactor
Fe	FE	0.472681
O	OW	-0.702882
H	HW	0.419768

Atom	AtomType	Linoleic Acid	Atom	AtomType	Linoleic Acid
C1	C	0.91615	C10	CM	-0.394615
O1	O2	-0.848719	H10	HT	0.149634
O2	O2	-0.850736	C11	CT	0.412378
C2	CT	-0.314575	H11A	HT	0.039167
H2A	HT	0.045474	H11B	HT	-0.022743
H2B	HT	0.034901	C12	CM	-0.309574
C3	CT	0.020282	H12	HT	0.149156
H3A	HT	0.016183	C13	CM	-0.349471
H3B	HT	-0.000518	H13	HT	0.159179
C4	CT	0.12403	C14	CT	0.127951
H4A	HT	-0.03985	H14A	HT	-0.017336
H4B	HT	-0.00692	H14A	HT	0.006911
C5	CT	-0.056482	C15	CT	0.046761
H5A	HT	0.00154	H15A	HT	-0.000013
H5B	HT	0.003307	H15B	HT	0.017495
C6	CT	-0.056233	C16	CT	-0.095465
H6A	HT	0.016682	H16A	HT	0.005454
H6B	HT	0.005239	H16B	HT	0.011534
C7	CT	0.035731	C17	CT	0.189557
H7A	HT	0.015851	H17A	HT	-0.03203
H7B	HT	-0.010194	H17B	HT	-0.033771
C8	CT	0.033896	C18	CT	-0.252203
H8A	HT	0.033587	H18A	HT	0.051835
H8B	HT	-0.008828	H18B	HT	0.058213
C9	CM	-0.226036	H11C	HT	0.050013
H9	HT	0.14822			

Table S2. Eckart parameters and imaginary frequencies (cm^{-1}) for each structure and isotope. **A** and **B** are given in kcal/mol, and **L** is given in $bohr \cdot amu^{1/2}$.

Structure	Isotope	A	B	L	Imaginary Frequency
II-B	H	-11.0	103.5	0.79	1825
	D	-11.0	103.5	0.84	1379
IV-A	H	-13.4	100.1	0.64	1882
	D	-13.4	100.1	0.69	1418
IV-B	H	-10.9	103.0	0.74	1874
	D	-10.9	103.0	0.80	1412
VII	H	-2.2	122.5	0.65	2130
	D	-2.2	122.5	0.72	1592
X	H	-13.7	90.7	0.46	2033
	D	-13.7	90.7	0.52	1522
XI	H	-12.8	99.5	0.49	2085
	D	-12.8	99.5	0.56	1561
XIV	H	-10.8	105.1	0.76	1869
	D	-10.8	105.1	0.81	1409

Figure S1. Potential energy profiles for structure II-B obtained with two methods. The dashed line corresponds to the MEP calculated with ONIOM and the Mechanical Embedding approach, while the solid line stands for the Electrostatic Embedding MEP obtained with ONIOM. Each curve has been pictured with respect its own zero of energies. The green spot corresponds to the potential energy barrier taken from reference 32.

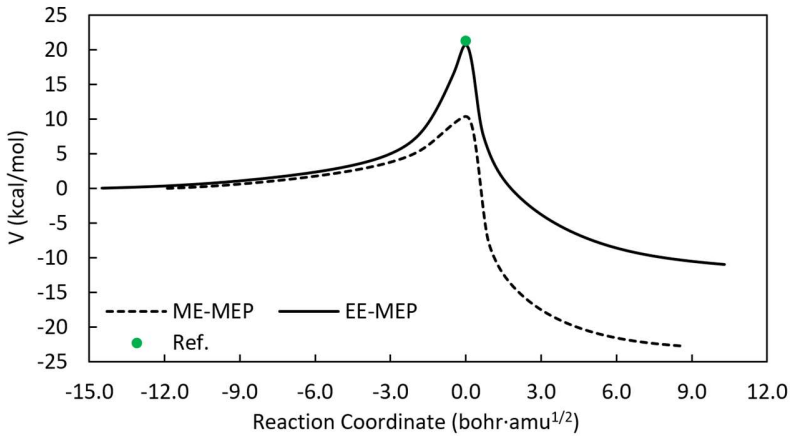

Figure S2. Potential energy profiles for structure VII obtained with two methods. The dashed line corresponds to the MEP calculated with ONIOM and the Mechanical Embedding approach, while the solid line stands for the Electrostatic Embedding MEP obtained with ONIOM. Each curve has been pictured with respect its own zero of energies. The green spot corresponds to the potential energy barrier taken from reference 32.

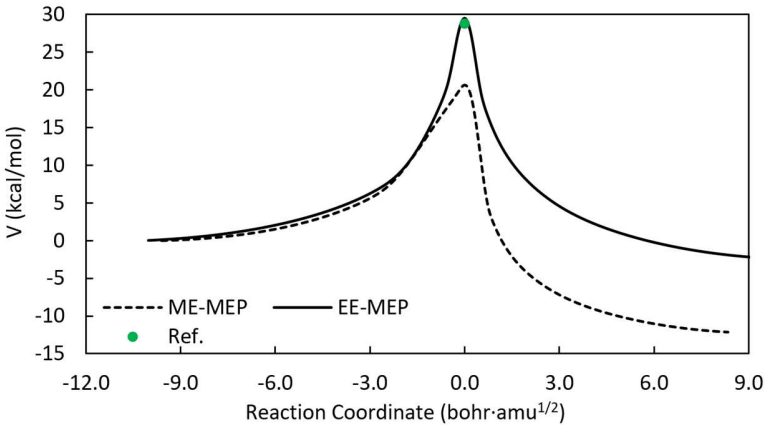

Figure S3. Adiabatic potential energy profiles (A) and zero-point energies along the reaction path (B) obtained using different interpolation levels for structure II-B.

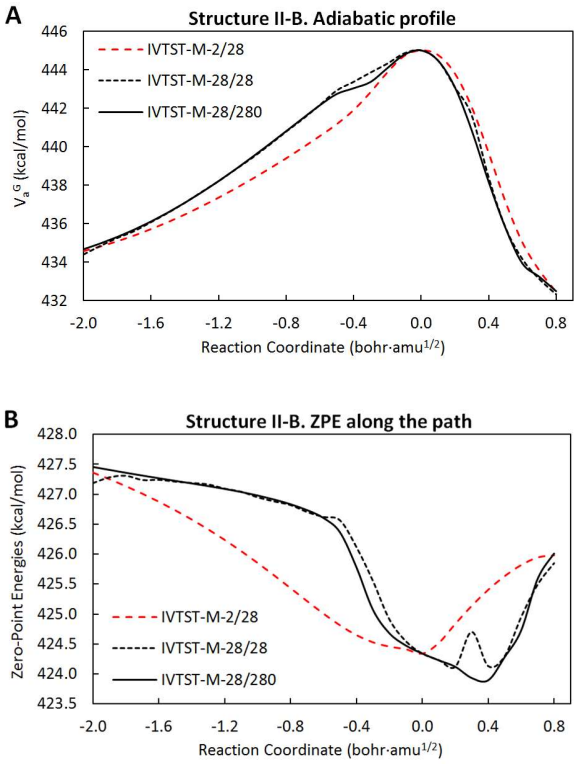

Figure S4. Adiabatic potential energy profiles (A) and zero-point energies along the reaction path (B) obtained using different interpolation levels for structure VII.

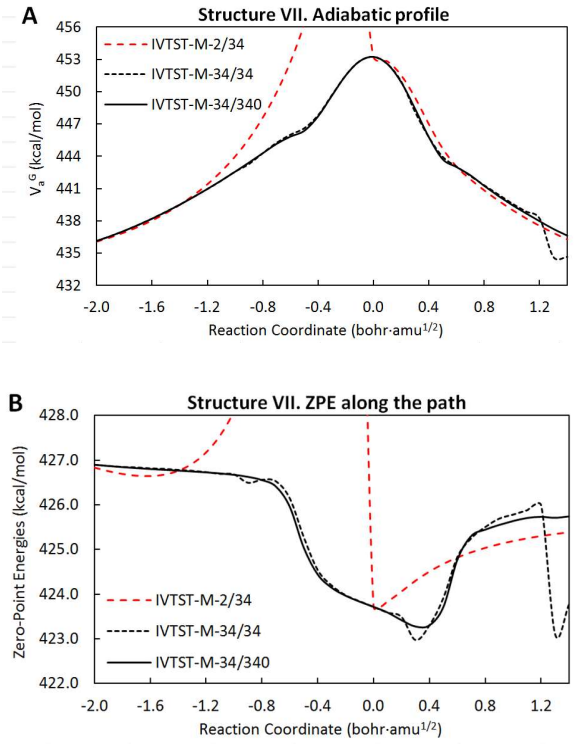

Figure S5. MEPs calculated with ONIOM and the Electronically Embedding approach with different isotopes for structure XI.

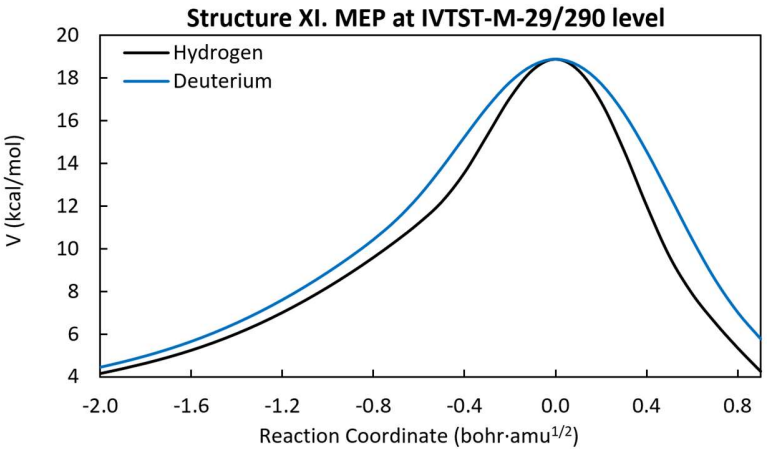

Figure S6. Adiabatic potential energy profiles (A) and zero-point energies along the reaction path (B) obtained for different isotopes in structure XI.

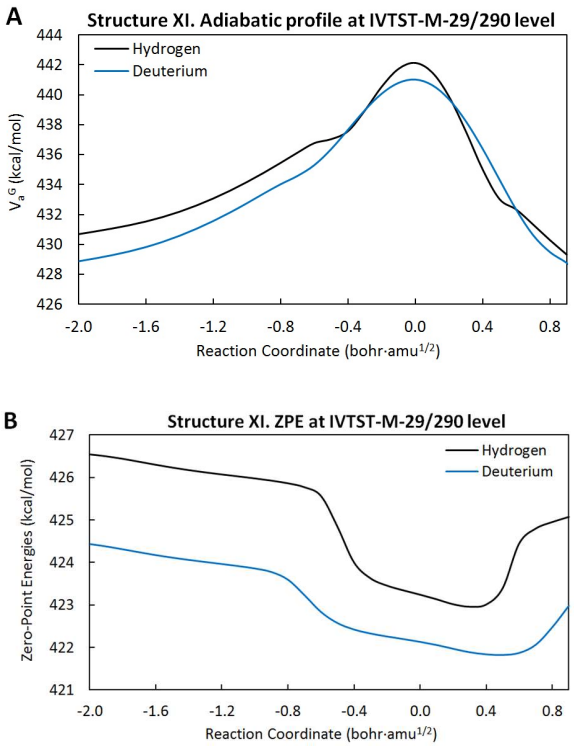

Figure S7. On the right, adiabatic potential energy profiles for Hydrogen (black) and Deuterium (blue) for structure XI calculated with the IVTST-M-29/290 highest level interpolation method only from s= -1.5 to s= 0.6 bohr amu$^{1/2}$. On the left, their corresponding functions *f(E)* calculated with the SCT method.

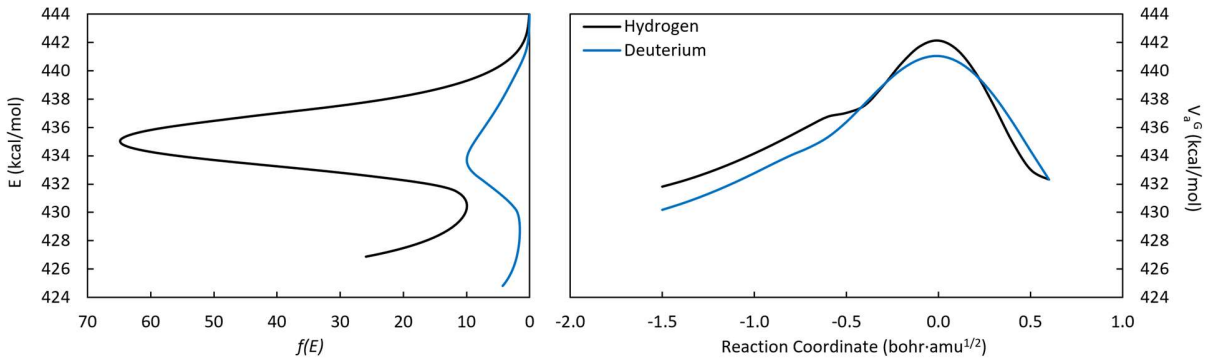

Table S3. Cartesian atomic coordinates of the QM region for the optimized Transition State geometry (ONIOM, Electrostatic Embedding) of structure II-B. **x**, **y** and **z** are given in Å.

Atom	x	y	z
C	1.084544	-10.558702	-1.327062
H	0.004031	-10.397880	-1.409612
H	1.496775	-10.470384	-2.339837
C	1.693695	-9.513298	-0.378897
H	2.759385	-9.718329	-0.201400
H	1.192721	-9.589186	0.595018
C	1.553884	-8.061131	-0.893496
H	0.523383	-7.923487	-1.252714
H	2.192643	-7.908415	-1.765862
C	1.802978	-7.029834	0.173605
H	1.034729	-7.010236	0.948357
C	2.803594	-6.133570	0.354880
H	2.673538	-5.472246	1.209117
C	4.073694	-5.876054	-0.354881
H	4.746276	-5.302258	0.289024
H	3.848761	-4.929189	-1.265501
C	4.769522	-6.968137	-1.065391
H	4.179681	-7.554580	-1.765191
C	6.059539	-7.332011	-0.921205
H	6.419828	-8.166251	-1.525275
C	7.093330	-6.769110	0.018917
H	7.241824	-7.485393	0.845703
H	6.743103	-5.840106	0.482271
C	8.448774	-6.543327	-0.672106
H	8.336995	-5.765311	-1.435551
H	8.720578	-7.459050	-1.213073
C	9.604213	-6.205603	0.276211
H	10.543776	-6.181881	-0.292548
H	9.697414	-7.005637	1.024009
C	7.443678	0.518656	-0.318117
H	8.231686	-0.198369	-0.044919
H	7.938932	1.282601	-0.927528
N	6.713414	-0.709897	-2.366627
H	7.604394	-0.577772	-2.848070
C	6.395967	-0.171182	-1.134775
C	5.627345	-1.310718	-2.881350
H	5.602381	-1.797199	-3.843017
N	4.600864	-1.206091	-2.045252
C	5.068141	-0.478445	-0.958400
H	4.417508	-0.226133	-0.137118

Atom	x	y	z
C	2.988838	-2.829496	3.539690
H	2.700529	-3.775322	4.015231
H	4.072162	-2.731105	3.661142
N	1.363870	-3.221425	1.653695
H	0.629486	-3.623098	2.245191
C	2.627930	-2.865996	2.090272
C	1.317080	-3.069449	0.312671
H	0.458477	-3.307617	-0.294524
N	2.472642	-2.619662	-0.148355
C	3.300019	-2.497380	0.953344
H	4.324278	-2.168346	0.864227
C	0.145155	2.839175	-1.493641
H	-0.880216	3.072907	-1.796775
H	0.186751	2.944416	-0.407682
N	-0.307819	0.683867	-2.737776
H	-1.227856	0.970385	-3.081377
C	0.494238	1.432790	-1.890399
C	0.289247	-0.501881	-2.975008
H	-0.129662	-1.268748	-3.601574
N	1.449411	-0.575760	-2.326961
C	1.583945	0.630604	-1.644999
H	2.443797	0.858638	-1.035254
C	3.026891	0.286067	-5.453563
H	2.133820	0.768176	-5.864885
H	3.017732	0.460811	-4.374540
N	3.212012	-2.161914	-4.730995
C	3.007054	-1.191705	-5.712312
C	3.291727	-3.321085	-5.374219
H	3.437376	-4.282732	-4.920243
N	3.123994	-3.160820	-6.703604
H	3.173177	-3.867474	-7.436877
C	2.928169	-1.818683	-6.932746
H	2.753452	-1.439720	-7.930264
C	0.816759	-4.563544	-3.385374
O	1.684172	-5.486035	-3.433975
O	0.947510	-3.415379	-2.879376
Fe	2.781281	-2.316342	-2.318524
O	3.718262	-4.143421	-2.328635
H	3.016646	-4.712994	-2.747294

Table S4. Cartesian atomic coordinates of the QM region for the optimized Transition State geometry (ONIOM, Electrostatic Embedding) of structure IV-A. **x**, **y** and **z** are given in Å.

Atom	x	y	z
C	1.226320	-10.618761	-1.230657
H	0.181305	-10.517153	-0.911277
H	1.272026	-10.379669	-2.298466
C	2.118612	-9.666496	-0.410885
H	3.179296	-9.893923	-0.583846
H	1.929104	-9.840898	0.656734
C	1.898375	-8.164027	-0.716399
H	0.824399	-7.941266	-0.620334
H	2.165340	-7.956075	-1.757465
C	2.656957	-7.277324	0.241934
H	2.303518	-7.319344	1.274509
C	3.742058	-6.502324	0.006137
H	4.160677	-5.974994	0.863392
C	4.384712	-6.254428	-1.293975
H	4.216876	-4.975090	-1.638201
H	3.806051	-6.669383	-2.121861
C	5.823983	-6.417236	-1.571846
H	6.060097	-6.197883	-2.613302
C	6.872649	-6.806934	-0.816721
H	7.838577	-6.856761	-1.325848
C	6.935526	-7.257680	0.617263
H	7.006300	-8.357973	0.627062
H	6.017600	-7.013838	1.159144
C	8.158537	-6.715066	1.384772
H	9.061021	-6.920842	0.794747
H	8.263324	-7.298913	2.307585
C	8.084131	-5.231942	1.788936
H	8.749230	-5.065803	2.644565
H	7.065094	-5.009581	2.132934
C	7.550314	0.593145	-0.187846
H	8.310430	-0.148321	0.099116
H	8.077911	1.333746	-0.798373
N	6.764878	-0.484264	-2.300109
H	7.676657	-0.396674	-2.755494
C	6.487179	-0.054688	-1.016181
C	5.661364	-1.049050	-2.822826
H	5.601206	-1.452928	-3.819445
N	4.663961	-1.027189	-1.944298
C	5.169096	-0.387138	-0.818987
H	4.550966	-0.210017	0.045994

Atom	x	y	z
C	3.165207	-2.657662	3.619727
H	2.941773	-3.600831	4.136836
H	4.243475	-2.494646	3.707896
N	1.492579	-3.145352	1.803881
H	0.752830	-3.417771	2.459144
C	2.771935	-2.781939	2.186729
C	1.415290	-3.060331	0.456095
H	0.534827	-3.294961	-0.119676
N	2.572900	-2.668723	-0.056833
C	3.427879	-2.504267	1.017314
H	4.459286	-2.213673	0.887140
C	0.226266	2.840550	-1.196556
H	-0.818032	3.073115	-1.434181
H	0.339814	2.923017	-0.111913
N	-0.274986	0.718426	-2.482218
H	-1.203801	1.027965	-2.779609
C	0.559590	1.448942	-1.650766
C	0.322654	-0.458601	-2.779692
H	-0.117323	-1.220425	-3.402189
N	1.510873	-0.535252	-2.188354
C	1.666202	0.650686	-1.483588
H	2.561813	0.867486	-0.923341
C	2.990851	0.382030	-5.384891
H	2.093971	0.862225	-5.796177
H	2.981423	0.549869	-4.304669
N	3.271044	-2.055501	-4.677438
C	2.990036	-1.097097	-5.649955
C	3.377291	-3.211296	-5.323585
H	3.613699	-4.164218	-4.886866
N	3.153678	-3.059809	-6.645670
H	3.158420	-3.783045	-7.363949
C	2.885881	-1.727597	-6.867141
H	2.685269	-1.352666	-7.861246
C	0.976101	-4.515909	-3.167530
O	1.896821	-5.360346	-3.294799
O	1.050115	-3.351923	-2.667068
Fe	2.893477	-2.262849	-2.210539
O	3.965433	-3.974429	-2.459852
H	3.259534	-4.537096	-2.891583

Table S5. Cartesian atomic coordinates of the QM region for the optimized Transition State geometry (ONIOM, Electrostatic Embedding) of structure IV-B. **x**, **y** and **z** are given in Å.

Atom	x	y	z
C	1.207495	-10.542516	-1.296135
H	0.123275	-10.436239	-1.159135
H	1.418467	-10.363500	-2.356474
C	1.936981	-9.508017	-0.414795
H	3.016018	-9.712085	-0.383828
H	1.572383	-9.594789	0.617767
C	1.733062	-8.051238	-0.906652
H	0.671342	-7.934394	-1.179982
H	2.296769	-7.880990	-1.827035
C	2.015592	-7.004882	0.142961
H	1.273089	-6.987245	0.942193
C	3.005756	-6.091314	0.292537
H	2.884000	-5.440240	1.157585
C	4.261887	-5.806489	-0.430723
H	4.963868	-5.313078	0.248158
H	4.058379	-4.778769	-1.260190
C	4.911522	-6.835885	-1.269721
H	4.324864	-7.244261	-2.088465
C	6.167681	-7.302934	-1.126022
H	6.513279	-8.053732	-1.840485
C	7.174572	-6.940008	-0.063338
H	7.262189	-7.777317	0.651090
H	6.824412	-6.083760	0.522883
C	8.573134	-6.651012	-0.636695
H	8.505637	-5.819934	-1.347574
H	8.894998	-7.522037	-1.224046
C	9.652304	-6.379546	0.422218
H	10.636476	-6.351816	-0.062852
H	9.672644	-7.213948	1.138416
C	7.482124	0.683053	-0.172883
H	8.240850	-0.053084	0.129665
H	8.015882	1.406407	-0.797970
N	6.701497	-0.438494	-2.259958
H	7.605917	-0.329068	-2.724476
C	6.418486	0.017350	-0.987697
C	5.602247	-1.006644	-2.782091
H	5.550298	-1.430236	-3.770737
N	4.601169	-0.971751	-1.909495
C	5.099142	-0.311151	-0.791743
H	4.475494	-0.114792	0.064981

Atom	x	y	z
C	3.122983	-2.609734	3.614024
H	2.910695	-3.559907	4.122638
H	4.198877	-2.434961	3.703337
N	1.459053	-3.102723	1.790774
H	0.718309	-3.390152	2.438547
C	2.731101	-2.722920	2.181236
C	1.382276	-2.998987	0.444574
H	0.510122	-3.249912	-0.137093
N	2.531643	-2.577778	-0.058229
C	3.382914	-2.414646	1.017480
H	4.408515	-2.103494	0.892959
C	0.204741	2.883177	-1.231870
H	-0.845369	3.105997	-1.450102
H	0.334183	2.961246	-0.148827
N	-0.262791	0.778389	-2.564661
H	-1.175588	1.093982	-2.903493
C	0.544224	1.494470	-1.694040
C	0.333228	-0.401207	-2.847464
H	-0.093576	-1.151745	-3.492300
N	1.496184	-0.495347	-2.210729
C	1.634898	0.683137	-1.489892
H	2.508887	0.885533	-0.891939
C	2.976154	0.383461	-5.380986
H	2.070165	0.847036	-5.791405
H	2.967406	0.560937	-4.302333
N	3.260250	-2.045773	-4.640194
C	2.999543	-1.098322	-5.630079
C	3.395977	-3.207046	-5.269589
H	3.621189	-4.151953	-4.809751
N	3.211448	-3.070190	-6.600632
H	3.245551	-3.792491	-7.318098
C	2.940258	-1.742002	-6.842865
H	2.765177	-1.379746	-7.846726
C	1.001941	-4.502897	-3.174174
O	1.909255	-5.369255	-3.222450
O	1.066755	-3.324333	-2.706127
Fe	2.864374	-2.230540	-2.212867
O	3.932872	-3.957380	-2.275007
H	3.288372	-4.576013	-2.724396

Table S6. Cartesian atomic coordinates of the QM region for the optimized Transition State geometry (ONIOM, Electrostatic Embedding) of structure VII. **x**, **y** and **z** are given in Å.

Atom	x	y	z
C	5.658023	-6.527227	-6.442696
H	4.965094	-6.147842	-7.201758
H	6.629105	-6.686838	-6.932648
C	5.778768	-5.558176	-5.266485
H	6.332825	-6.039935	-4.449324
H	4.782583	-5.325071	-4.877172
C	6.511278	-4.249945	-5.593698
H	7.500636	-4.504102	-6.011675
H	6.716031	-3.728975	-4.655298
C	5.792527	-3.311647	-6.529324
H	5.330869	-3.747329	-7.415126
C	5.682023	-1.976958	-6.347012
H	5.099927	-1.412226	-7.074700
C	6.285260	-1.217053	-5.224953
H	5.422788	-1.453680	-4.150131
H	6.085984	-0.142069	-5.280562
C	7.730711	-1.522449	-5.048416
H	8.108579	-2.170641	-5.839504
C	8.690889	-1.134301	-4.184366
H	9.693003	-1.495736	-4.431613
C	8.681125	-0.317561	-2.927962
H	7.666655	-0.079976	-2.596177
H	9.178603	0.642346	-3.138881
C	9.481897	-1.047643	-1.821748
H	10.318537	-1.566085	-2.307308
H	8.853438	-1.821228	-1.364209
C	10.022895	-0.097584	-0.750088
H	9.197355	0.375083	-0.202772
H	10.575868	0.710384	-1.241175
C	6.425657	3.003814	-0.262993
H	7.414030	2.520146	-0.206191
H	6.606716	3.990626	-0.704339
N	5.763413	2.126232	-2.517890
H	6.538723	2.572208	-3.018614
C	5.511934	2.222845	-1.159745
C	4.795838	1.384076	-3.089273
H	4.762908	1.142075	-4.139354
N	3.921814	0.967768	-2.182993
C	4.350275	1.505998	-0.974236
H	3.774883	1.379630	-0.070873
C	3.495213	-2.505119	2.912805
H	3.514084	-3.566838	3.192176
H	4.511617	-2.124306	3.069909
N	2.283043	-3.305268	0.847074
H	1.937199	-4.172679	1.267373
C	3.111926	-2.394163	1.473399
C	2.082736	-2.897641	-0.425005
H	1.464239	-3.427447	-1.126396
N	2.741748	-1.766139	-0.667940
C	3.373902	-1.445607	0.521029
H	4.013911	-0.583709	0.621032
C	-1.720589	2.474548	-0.545012
H	-2.770106	2.384799	-0.847260
H	-1.680994	2.297122	0.532878
N	-1.392938	0.600039	-2.216951
H	-2.360460	0.582975	-2.536557
C	-0.875177	1.464523	-1.267822
C	-0.389677	-0.166288	-2.706177
H	-0.521573	-0.919328	-3.466618
N	0.761162	0.154051	-2.125171
C	0.470870	1.173859	-1.229829
H	1.232199	1.633135	-0.616874
C	1.332554	2.226750	-4.950442
H	0.338897	2.555351	-5.278471
H	1.302630	2.122839	-3.862789
N	2.431872	-0.058645	-4.918515
C	1.696659	0.920695	-5.576109
C	2.713372	-0.981381	-5.830363
H	3.253626	-1.893941	-5.647614
N	2.204666	-0.649884	-7.035366
H	2.230478	-1.197088	-7.900116
C	1.542216	0.548504	-6.888290
H	1.034659	1.022568	-7.716617
C	1.921829	-3.522949	-3.831418
O	3.098730	-3.921621	-3.983556
O	1.543256	-2.425306	-3.306056
Fe	2.694197	-0.788598	-2.709845
O	4.506549	-1.668473	-3.266220
H	4.202113	-2.581616	-3.509881

Table S7. Cartesian atomic coordinates of the QM region for the optimized Transition State geometry (ONIOM, Electrostatic Embedding) of structure X. **x**, **y** and **z** are given in Å.

Atom	x	y	z
C	6.243460	-7.426489	-4.910312
H	7.071994	-7.647085	-5.598962
H	6.697898	-7.177681	-3.940717
C	5.443127	-6.222235	-5.419359
H	4.584692	-6.014988	-4.771690
H	5.042718	-6.430577	-6.421893
C	6.329277	-4.965247	-5.485592
H	7.288133	-5.254462	-5.945988
H	6.583219	-4.644027	-4.470032
C	5.736846	-3.832435	-6.278365
H	5.260218	-4.120419	-7.218171
C	5.784491	-2.515495	-5.987857
H	5.337802	-1.836787	-6.715986
C	6.347919	-1.859773	-4.793442
H	6.914457	-2.531679	-4.146203
H	5.268187	-1.703628	-3.968213
C	7.036730	-0.583168	-5.050781
H	6.713942	-0.066315	-5.956392
C	8.025507	0.009171	-4.342127
H	8.456030	0.923561	-4.749253
C	8.559822	-0.424634	-3.004342
H	7.882906	-1.152268	-2.552539
H	8.537177	0.445977	-2.332031
C	9.995085	-0.990050	-2.990777
H	10.685687	-0.278553	-3.463197
H	10.032055	-1.908932	-3.600275
C	10.451391	-1.302642	-1.556989
H	9.744268	-1.991661	-1.075044
H	10.442059	-0.385362	-0.955481
C	6.530406	2.848997	-0.797468
H	7.462996	2.269573	-0.709771
H	6.801276	3.760366	-1.342215
N	5.654334	1.910500	-2.950762
H	6.359315	2.362753	-3.542467
C	5.510979	2.083641	-1.584926
C	4.633028	1.162254	-3.403705
H	4.529057	0.846613	-4.429275
N	3.818734	0.821647	-2.411577
C	4.352259	1.411744	-1.273552
H	3.866665	1.312792	-0.316568

Atom	x	y	z
C	3.722391	-2.228630	2.969626
H	3.771682	-3.268350	3.325093
H	4.736922	-1.825280	3.050062
N	2.314425	-3.103223	1.060548
H	1.899510	-3.894601	1.547956
C	3.262187	-2.222597	1.547964
C	2.034298	-2.769699	-0.216380
H	1.316161	-3.294640	-0.818364
N	2.752485	-1.718524	-0.598263
C	3.522727	-1.373365	0.502437
H	4.237926	-0.565483	0.472650
C	-1.653860	2.521049	-0.827155
H	-2.692916	2.567385	-1.162711
H	-1.687289	2.330829	0.246950
N	-1.508891	0.495532	-2.366557
H	-2.504045	0.495528	-2.609013
C	-0.909177	1.418327	-1.524267
C	-0.564078	-0.376312	-2.799392
H	-0.756449	-1.186746	-3.485895
N	0.624096	-0.062212	-2.286901
C	0.417374	1.056726	-1.498122
H	1.228134	1.520880	-0.958112
C	1.441296	1.919858	-5.170399
H	0.428618	2.243840	-5.440779
H	1.489418	1.905552	-4.078574
N	2.304624	-0.473344	-4.958966
C	1.703081	0.539991	-5.699315
C	2.457646	-1.501642	-5.785459
H	2.909616	-2.448557	-5.536946
N	1.973423	-1.215502	-7.009975
H	2.024251	-1.810173	-7.836228
C	1.493327	0.076704	-6.974580
H	1.046718	0.535557	-7.845683
C	1.967735	-3.913055	-3.424535
O	3.175298	-4.243270	-3.563719
O	1.514210	-2.763877	-3.129763
Fe	2.595051	-0.972641	-2.721254
O	4.329486	-1.896837	-3.106998
H	4.057018	-2.836550	-3.315972

Table S8. Cartesian atomic coordinates of the QM region for the optimized Transition State geometry (ONIOM, Electrostatic Embedding) of structure XI. **x**, **y** and **z** are given in Å.

Atom	x	y	z
C	6.260183	-6.930579	-5.449451
H	7.185551	-7.211983	-5.973311
H	6.548275	-6.672806	-4.421274
C	5.630802	-5.700661	-6.115948
H	4.681369	-5.437564	-5.637111
H	5.416197	-5.900074	-7.175108
C	6.595860	-4.507716	-5.997557
H	7.577962	-4.813705	-6.397858
H	6.753782	-4.309452	-4.934225
C	6.171755	-3.229453	-6.662991
H	5.863933	-3.305503	-7.707265
C	6.213434	-1.999903	-6.103790
H	5.939633	-1.154721	-6.738195
C	6.585034	-1.654319	-4.719924
H	6.977964	-2.487652	-4.133860
H	5.373732	-1.560435	-4.069578
C	7.363783	-0.418372	-4.545077
H	7.197380	0.342422	-5.311898
C	8.262485	-0.106241	-3.577564
H	8.736209	0.875081	-3.641275
C	8.669575	-0.926378	-2.378096
H	8.096808	-1.858175	-2.318323
H	8.421535	-0.347444	-1.471773
C	10.172126	-1.271235	-2.287822
H	10.767920	-0.379119	-2.523895
H	10.415592	-2.016535	-3.055636
C	10.524520	-1.804548	-0.891234
H	9.809660	-2.584567	-0.606184
H	10.430190	-1.001833	-0.147591
C	6.197892	2.897001	-0.539899
H	7.161028	2.368683	-0.462185
H	6.436050	3.874285	-0.973726
N	5.540852	2.049559	-2.804650
H	6.281661	2.556675	-3.299087
C	5.273197	2.149734	-1.451010
C	4.598801	1.281004	-3.379962
H	4.589147	1.011553	-4.424337
N	3.720283	0.858773	-2.478414
C	4.124915	1.414637	-1.273128
H	3.581798	1.222458	-0.362327
C	3.287976	-2.705052	2.619209
H	3.329205	-3.769825	2.883674
H	4.289977	-2.300309	2.802302
N	2.180355	-3.526691	0.504868
H	1.876603	-4.418656	0.896407
C	2.927321	-2.575604	1.173890
C	1.967270	-3.099491	-0.757546
H	1.400314	-3.656180	-1.480801
N	2.547559	-1.918096	-0.954951
C	3.139961	-1.584662	0.251500
H	3.741443	-0.698053	0.368227
C	-1.660384	2.395839	-0.731083
H	-2.715912	2.408824	-1.019076
H	-1.643232	2.202731	0.346830
N	-1.533073	0.453836	-2.381959
H	-2.524148	0.438762	-2.614111
C	-0.923015	1.329938	-1.495018
C	-0.586536	-0.340039	-2.941059
H	-0.799504	-1.104519	-3.672636
N	0.614255	-0.023975	-2.467266
C	0.412892	1.014036	-1.571619
H	1.238662	1.472909	-1.052411
C	1.538734	2.213871	-5.268941
H	0.576608	2.625043	-5.597451
H	1.478192	2.082442	-4.184793
N	2.454950	-0.156320	-5.284971
C	1.771623	0.883479	-5.911797
C	2.552460	-1.127501	-6.184595
H	3.038001	-2.077810	-6.025630
N	1.953508	-0.779267	-7.346102
H	1.777440	-1.379104	-8.150168
C	1.443530	0.491999	-7.185507
H	0.886787	0.983078	-7.970609
C	1.899265	-3.692896	-4.110123
O	3.098760	-4.031575	-4.243912
O	1.462063	-2.584602	-3.651009
Fe	2.548609	-0.931866	-2.993310
O	4.335199	-1.792203	-3.352704
H	4.075810	-2.704731	-3.658706

Table S9. Cartesian atomic coordinates of the QM region for the optimized Transition State geometry (ONIOM, Electrostatic Embedding) of structure XIV. **x**, **y** and **z** are given in Å.

Atom	x	y	z
C	0.778573	-10.327837	-0.365365
H	-0.311371	-10.265776	-0.463491
H	1.202129	-10.157075	-1.361033
C	1.302550	-9.254444	0.600581
H	2.401837	-9.277601	0.619326
H	0.970041	-9.457897	1.628617
C	0.852373	-7.834666	0.179943
H	-0.236640	-7.758097	0.285340
H	1.047440	-7.698527	-0.886257
C	1.518745	-6.742523	0.977291
H	1.078557	-6.513842	1.950062
C	2.635753	-6.066518	0.625884
H	3.016647	-5.315232	1.317523
C	3.383451	-6.264736	-0.634321
H	3.185024	-5.211798	-1.419796
H	2.876399	-6.999717	-1.257910
C	4.835813	-6.559351	-0.625846
H	5.105273	-7.414340	-1.245609
C	5.871377	-5.953521	-0.010684
H	6.844381	-6.422057	-0.157003
C	5.873206	-4.684180	0.788227
H	6.308640	-4.869140	1.782963
H	4.847366	-4.344306	0.954153
C	6.639670	-3.521846	0.110662
H	6.337808	-2.598476	0.623767
H	6.285265	-3.411321	-0.920750
C	8.175048	-3.568355	0.142452
H	8.521858	-3.787400	1.162122
H	8.544904	-2.569291	-0.122296
C	6.764599	0.606640	-1.546629
H	7.630661	-0.038224	-1.331023
H	7.104517	1.293731	-2.328335
N	5.819827	-0.968106	-3.244112
H	6.638028	-0.896457	-3.849997
C	5.637578	-0.229363	-2.086495
C	4.699221	-1.672302	-3.501042
H	4.577468	-2.323895	-4.351125
N	3.778983	-1.447093	-2.572256
C	4.354360	-0.528063	-1.695112
H	3.812840	-0.143277	-0.847329

Atom	x	y	z
C	2.982095	-2.193532	3.200740
H	2.816401	-3.040303	3.882650
H	4.066307	-2.048038	3.142559
N	1.167799	-3.061027	1.675497
H	0.553677	-3.407293	2.417775
C	2.430477	-2.526077	1.855960
C	0.929908	-3.151494	0.348970
H	0.029382	-3.559258	-0.082379
N	1.959109	-2.689579	-0.340653
C	2.903534	-2.305805	0.589739
H	3.867778	-1.919194	0.302040
C	-0.502462	2.495018	-1.708748
H	-1.563766	2.755056	-1.786654
H	-0.191805	2.703903	-0.682054
N	-1.208323	0.286507	-2.759254
H	-2.138403	0.602222	-3.040033
C	-0.292447	1.041759	-2.036854
C	-0.671320	-0.924445	-3.027545
H	-1.187059	-1.700909	-3.569414
N	0.553926	-1.003125	-2.517854
C	0.794630	0.216117	-1.899178
H	1.736266	0.438339	-1.425381
C	1.864504	-0.509261	-5.906347
H	0.941836	-0.035790	-6.264550
H	1.986374	-0.212839	-4.860780
N	1.956726	-2.867352	-4.914007
C	1.745729	-1.998344	-5.984013
C	1.815415	-4.094571	-5.407527
H	1.867953	-5.010965	-4.845038
N	1.510945	-4.059823	-6.721788
H	1.347762	-4.834300	-7.359854
C	1.459944	-2.740041	-7.100706
H	1.216338	-2.453969	-8.113464
C	-0.244880	-5.034773	-2.878854
O	0.612421	-5.965599	-2.860523
O	-0.055336	-3.817863	-2.594129
Fe	1.926505	-2.696880	-2.539733
O	2.761668	-4.535387	-2.472081
H	1.968044	-5.144242	-2.608122