

Supporting Information

MD Simulations and QM/MM Calculations Reveal the Key Mechanistic Elements which are Responsible for the Efficient C-H Amination Reaction Performed by a Bioengineered P450 Enzyme

Surajit Kalita,¹ Sason Shaik^{2*} and Kshatresh Dutta Dubey^{1*}

¹Department of Chemistry and Center for Informatics, School of Natural Sciences, Shiv Nadar University, Dadri, Gautam Buddha Nagar, Uttar Pradesh, 201314, India.

² Institute of Chemistry, The Hebrew University of Jerusalem, Edmond J Safra Campus, Givat Ram, Jerusalem, 9140401 Israel.

Table of Content:

S.1. Impact of protonation at proximal serine in reactivity	S2-S3
Figure S2: DFT optimization of ferrous heme complex	S4
Figure S3: DFT Optimization of iron nitrenoid complex	S4
Figure S4: Results for replica simulation of variant 2	S5
Figure S5: Results for substrate upside-down simulation of variant 2	S6
Figure S6: Testing the enantioselectivity of non-selective variant 1	S7
Figure S7: Results for pro-S hydrogen abstraction and comparison with pro-R hydrogen	S8
Figure S8: QM/MM optimized transition state geometry	S8
Figure S9: Distance correlation plots between ligand and other enzyme residues	S9
Figure S10: QM/MM optimized geometry of cysteine ligated ferrous heme complex	S9
Figure S11: QM/MM PES results of cysteine ligated ferrous heme complex for iron nitrenoid formation	S10
QM coordinates of the CH amination reaction	S11-S18
QM coordinates of the Iron Nitrenoid formation reaction	S18-S22

S.1. Impact of protonation at proximal serine in reactivity: The protonation state of the serine was initially considered based on the catalytic cycle described by Arnold and coworkers in their article for intermolecular C-H amination reaction where they have considered it as protonated serine. We, however, performed QM/MM scanning and QM-only DFT study to determine the correct protonation state of proximal serine residue. Our study shows that the protonated serine is more favorable than the deprotonated one both energetically as well as structurally. In the QM/MM study, we have taken the protonated reactant complex (RC) and performed potential energy surface scanning to deprotonate the serine oxygen. During this scanning, we obtained that the energy required to break the O-H bond is high and it climbs up to ~23 kcal/mol. The exact energy barrier is uncertain as the proton starts to interact with the porphyrin nitrogen and distorts the porphyrin arrangement. This was further substantiated by DFT only study. Therefore, a use of deprotonated serine could be doubtful.

It is well known that push-pull effects along the distal and proximal axis of iron regulate the reactivity of heme complex (Denisov et. al). Therefore, protonation (or deprotonation) of the serine could play the same decisive role in the reactivity of P411. In the protonated serine most of the Fe electrons are available along the distal axis (Fe-N) making it more reactive. On the other hand, in the deprotonated serine the iron d-electrons are delocalized along Fe-O linkage making the deprotonated species less reactive. This could also be justified by comparing the Fe-N and Fe-O bond lengths in protonated and deprotonated serine complex. In the deprotonated axial serine, the Fe-O bond length becomes too short and thereby it causes elongation of the Fe-N bond (trans effect). This effect is much less significant when the axial ligand is the protonated serine.

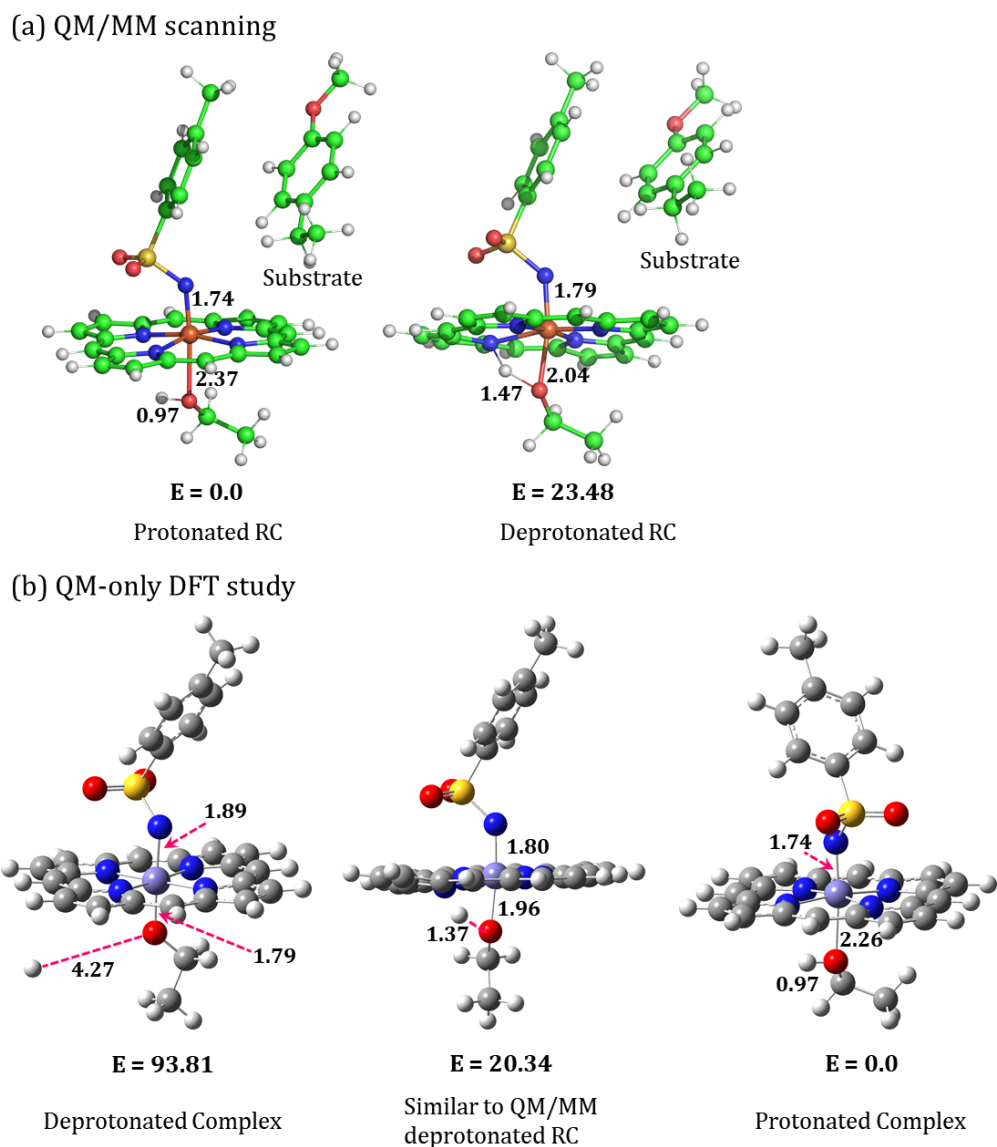


Figure S1: (a) Results of QM/MM potential energy surface scanning that shows two different protonation state of the reactant complex (RC), i.e., protonated, and deprotonated. In deprotonated RC, proton shows the probable interaction with porphyrin nitrogen atom. (b) QM-only DFT studies reveal three distinct geometries, i.e., protonated, completely deprotonated and a geometry similar to the QM/MM deprotonated RC both energetically as well as structurally. Note that distances and energies are given in Å and kcal/mol unit for both results.

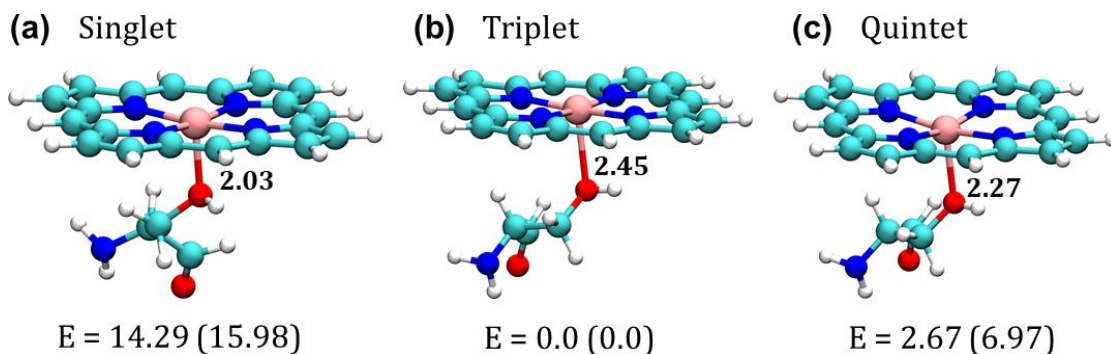


Figure S2: DFT optimization of ferrous heme complex at ground state for three different spin multiplicities. Optimized bond parameters are in Å unit. The relative energies are shown in kcal/mol. The values in parentheses are single-point energies at an extensive basis set (def2-TZVP).

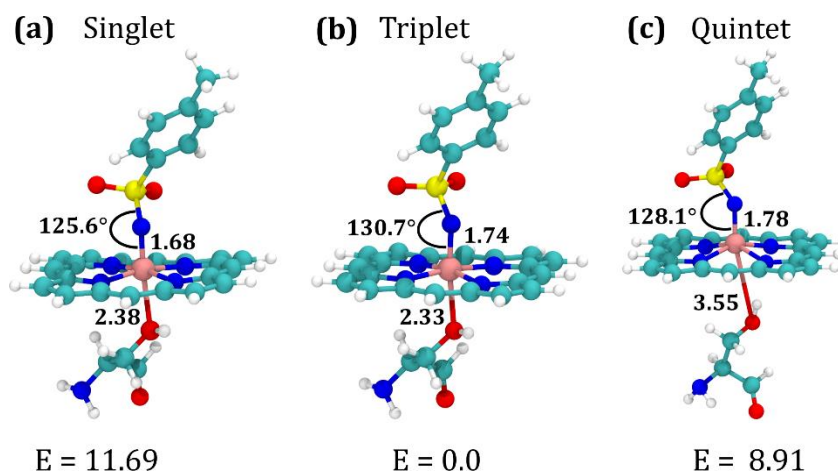


Figure S3: The optimized geometry of iron nitrenoid at different multiplicities. The energy values are evaluated using single-point calculation on optimized geometry using the larger basis set def2-TZVP. All the energies are reported in kcal/mol.

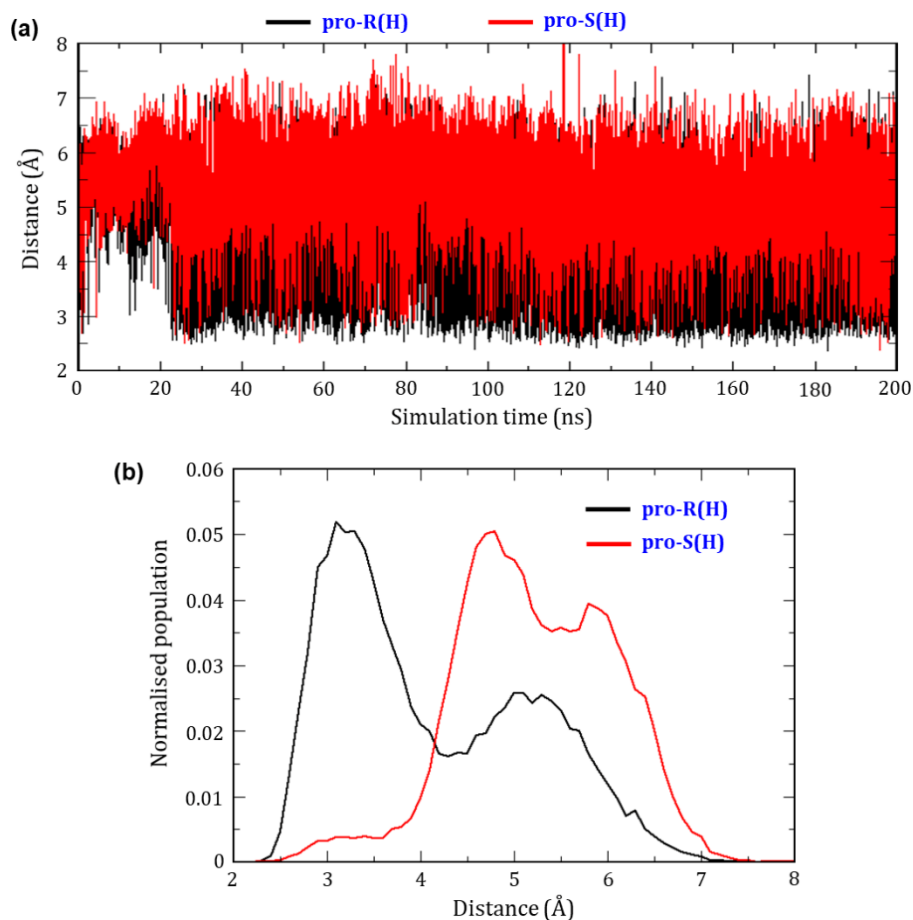


Figure S4: (a) Evolution of distance with time between the pro-R and pro-S hydrogens with the reactive nitrogen (N1) for entire 200 ns replica **variant 2** simulation. (b) The Boltzmann population distribution plot corresponds to distance plots between the pro-R and pro-S hydrogens with the reactive nitrogen (N1) over the entire 200 ns simulation. Note that black and red represent pro-R and pro-S hydrogens for both distance and population distribution plots respectively.

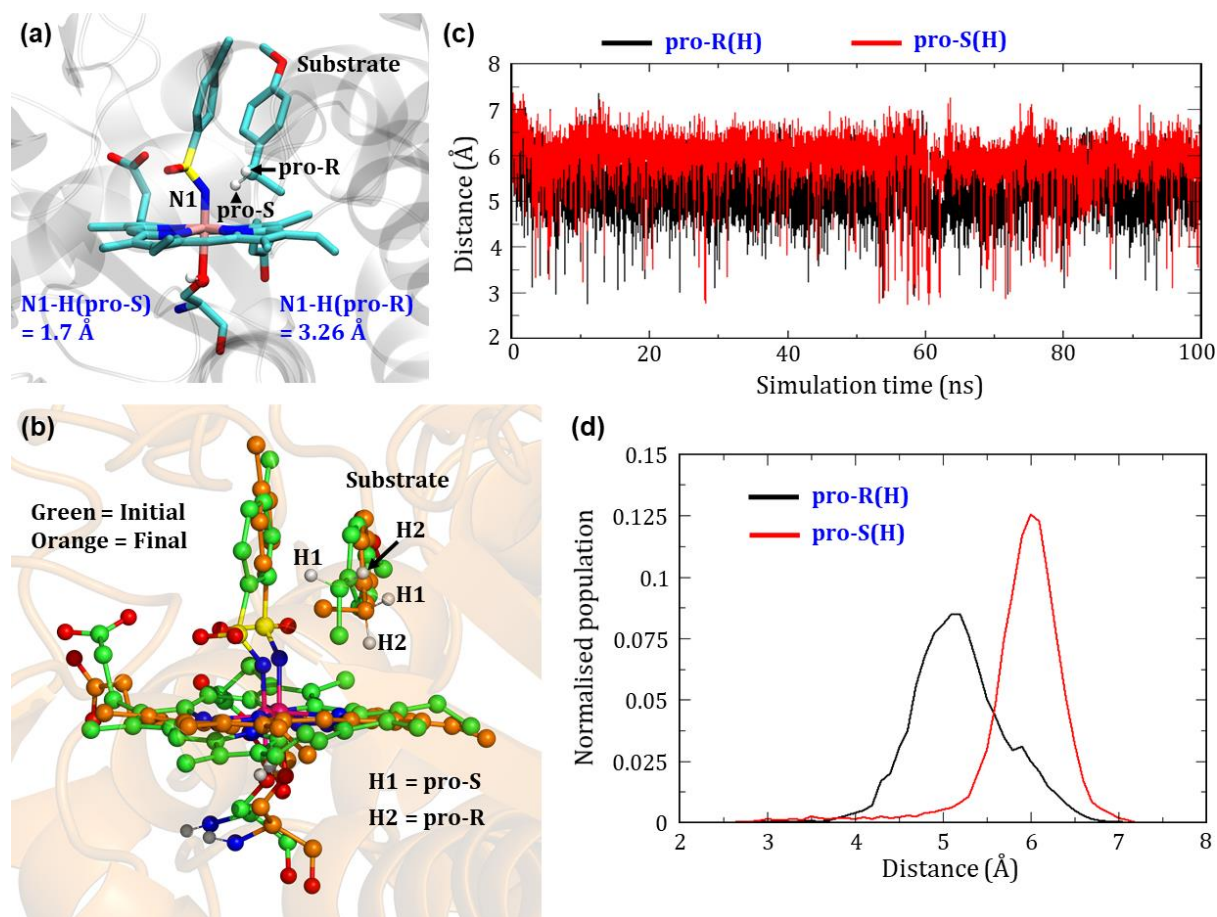


Figure S5: (a) Substrate docked geometry at which the pro-S hydrogen is facing the reactive nitrogen (N1) in **variant 2**. (b) Superimposed image of the snapshots considered from before and after production MD run. Here, green and orange represent the initial and final snapshots. The H1 and H2 hydrogens describe the pro(S) and pro(R) respectively. (c) Distance plots between reactive nitrogen (N1) and pro-R (black) as well as pro-S (red) hydrogens. (d) Boltzmann distribution plot corresponding to the above distance plots with identical color classification.

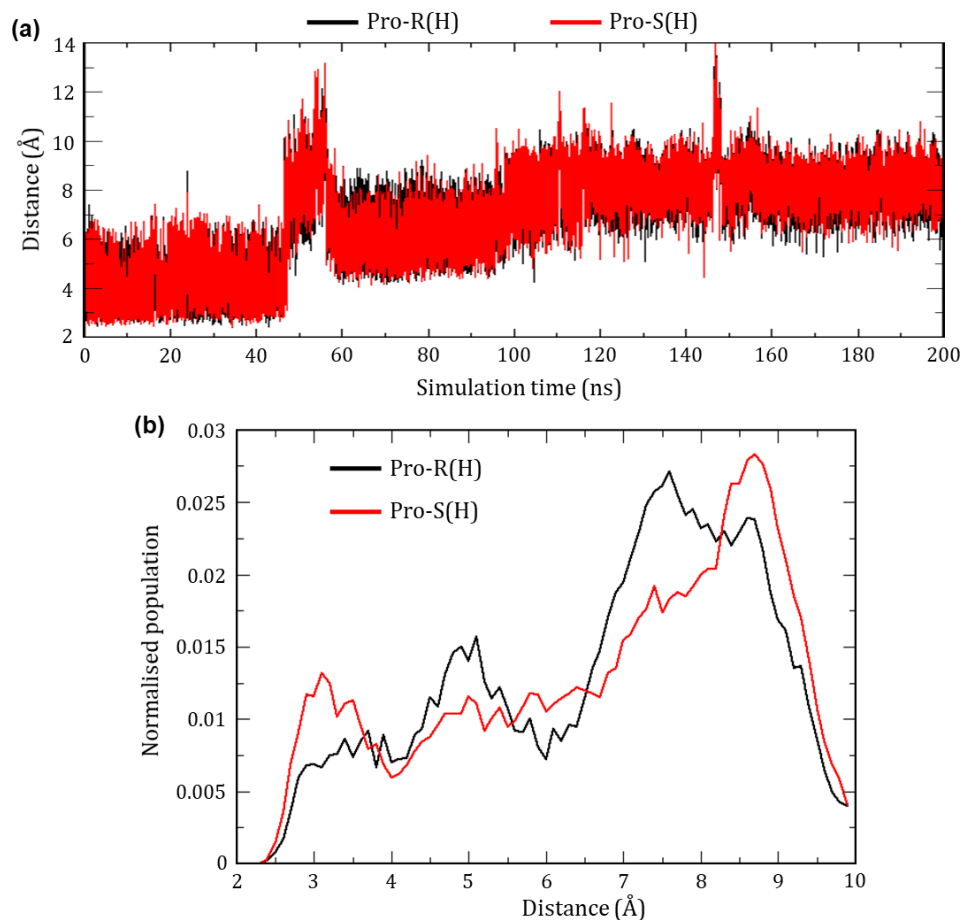


Figure S6: (a) Evolution of distance with time between the pro-R and pro-S hydrogens with the reactive nitrogen (N1) for entire 200 ns replica **variant 1** simulation. (b) The Boltzmann population distribution plot corresponds to distance plots between the pro-R and pro-S hydrogens with the reactive nitrogen (N1) over the entire 200 ns simulation. Note that black and red represent pro-R and pro-S hydrogens for both distance and population distribution plots respectively.

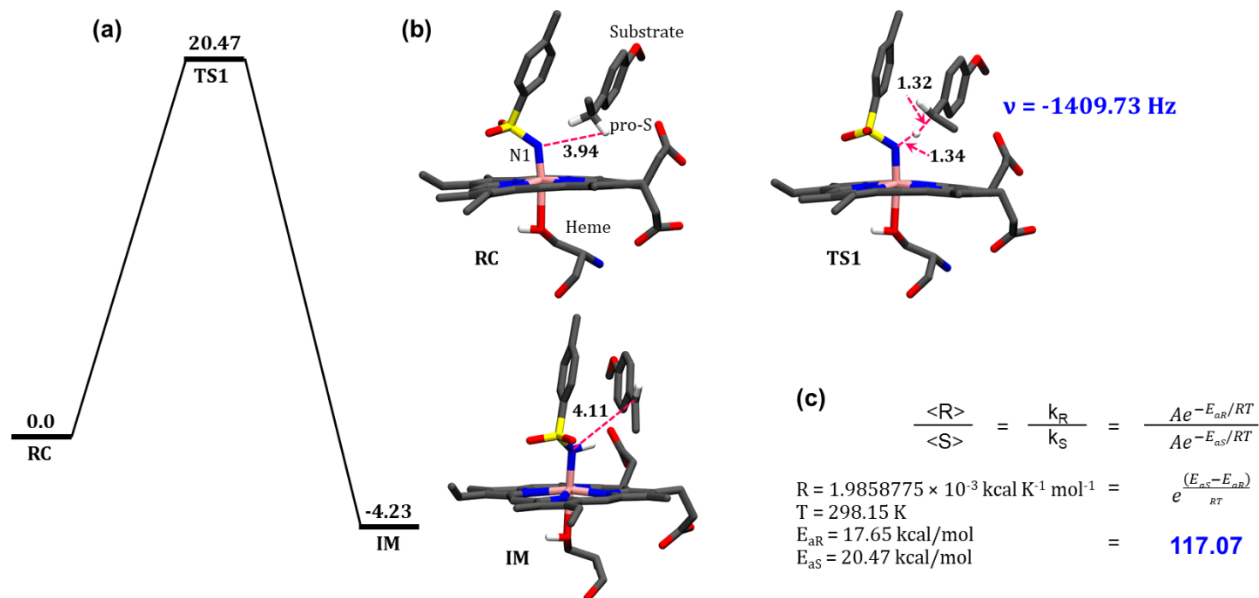


Figure S7: (a) Energy profile diagram for the abstraction of pro-S hydrogen obtained from the PES scanning. Energies are relative to RC and reported in kcal/mol unit. All the energies are Grimme dispersion (GD-3) and ZPE corrected in the same level of theory (ub3lyp/def2-SVP). (b) The key geometries RC, TS, and IM obtained from the PES scanning. All the distances are in Å unit. (c) Arrhenius equation shows the comparative rate constant data.

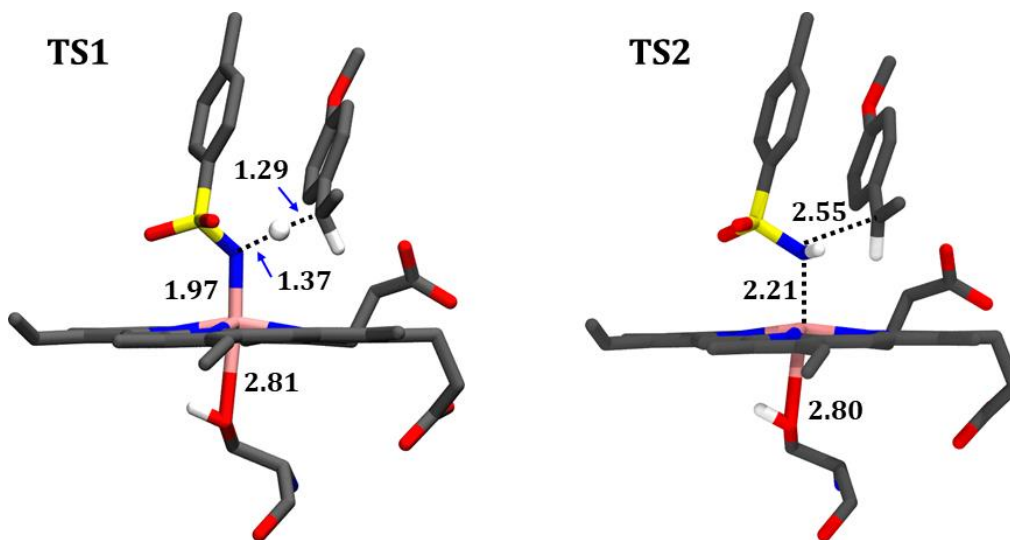


Figure S8: QM/MM optimized transition state geometry for C-H amination reaction; where TS1 and TS2 denote hydrogen abstraction and rebound process, respectively. Bond parameters are in Å unit.

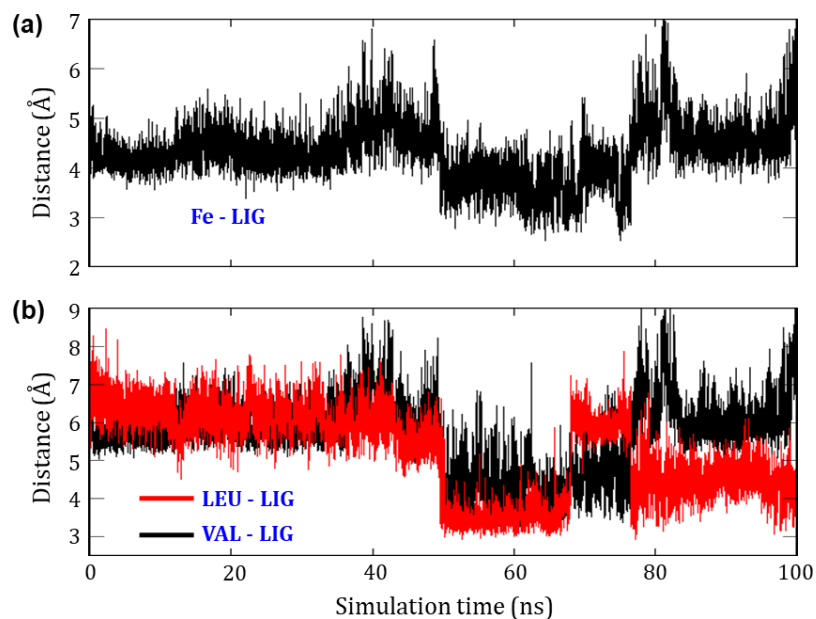


Figure S9: a) The distance between N1 of tosyl azide (TAZ) and Fe of heme porphyrin. (b) Black and red plots show the distance between V328 and L263 with TAZ, respectively.

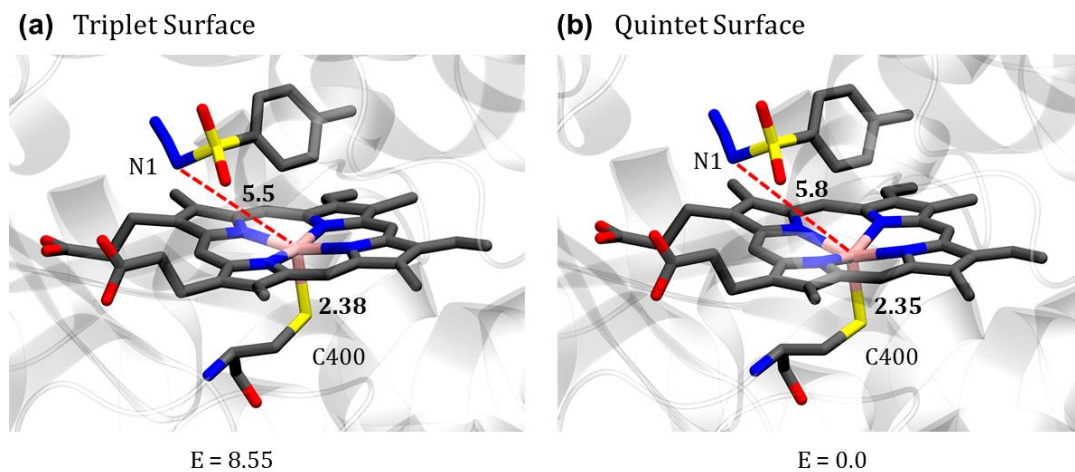
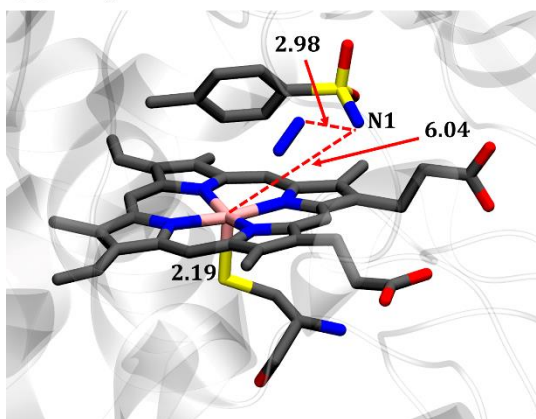


Figure S10: QM/MM optimized geometry of a representative MD snapshot and their relative energy in kcal/mol at (a) Triplet and (b) Quintet surface. The bond parameters are in Å unit.

(a) Triplet Surface



(b) Quintet Surface

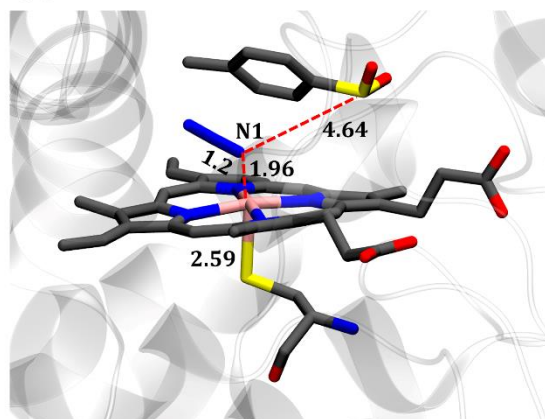


Figure S11: Results for the potential energy surface scanning for the formation of iron nitrenoid in the axial serine to cysteine mutated P411 system. It has been performed in both triplet and quintet surface. Substrate molecule is tosyl azide. All the bond parameters are shown in Å unit.

Coordinates of atoms in the QM region of the QM/MM calculations for different complex

QM coordinates of the CH amination reaction

RC

C 47.9180151 36.6804658 42.5928787
H 47.7605838 36.8832230 43.6664481
C 46.9561756 37.5411168 41.7875737
H 47.2384423 38.5994843 41.8880274
H 47.0069340 37.2849050 40.7159602
O 45.5875116 37.3700569 42.2246072
H 45.0104861 37.6695138 41.5066237
C 47.1403343 38.8166584 45.7588590
C 46.0482756 41.3366137 41.7711375
C 42.0560091 38.6480394 41.2112355
C 43.0861298 36.2279880 45.2667291
C 47.2216116 39.7038638 44.6896144
C 48.3611728 40.5583190 44.4207784
C 48.0552690 41.2860814 43.3037952
C 46.7286681 40.8642134 42.8916291
C 44.8333971 40.8538520 41.2936895
C 44.1645439 41.3503750 40.1100759
C 43.0278897 40.6056838 39.9514340
C 43.0164968 39.6373145 41.0298880
C 41.9780570 37.7536705 42.2724859
C 40.9140244 36.7812392 42.4529311
C 41.2027588 36.0974987 43.6015942
C 42.4375153 36.6651992 44.1183360
C 44.2715939 36.7441650 45.7834412

C 44.9181259 36.2662995 46.9899320
C 46.0617392 37.0042041 47.1357317
C 46.1028539 37.9264830 46.0153913
N 46.2522097 39.8911316 43.7371352
N 44.1248505 39.8022163 41.8311342
N 42.8918330 37.6646170 43.2915598
N 45.0021977 37.7542363 45.2146943
H 47.9778891 38.8053738 46.4539726
H 46.5139474 42.1412442 41.2015431
H 41.2754202 38.5715315 40.4626669
H 42.6284224 35.4089175 45.8201137
Fe 44.4541128 38.9195428 43.6230639
C 41.0565230 42.5923412 47.7585789
C 41.2203906 41.6470690 46.7420903
C 41.8775036 42.0061450 45.5613680
C 42.3349137 43.3184509 45.3819044
C 42.1701956 44.2505148 46.4065142
C 41.5387315 43.9060205 47.6177840
C 41.3587220 44.9362928 48.7093386
S 42.0416942 40.8100203 44.2230367
O 40.9979973 39.7893769 44.3948763
O 42.1006381 41.5894322 42.9746062
N 43.5386719 40.0985808 44.5231089
H 42.2728977 45.5357578 48.8459289
H 40.5443579 45.6375188 48.4591870
H 41.1036507 44.4675950 49.6711199

C	44.9227451	43.2490162	48.6301557	H	44.5432626	35.4864137	47.6527464
C	44.6398658	41.8961341	48.4850057	H	46.7754980	36.9343180	47.9565432
C	44.4346560	41.0608003	49.6008103	H	48.9395582	36.9676104	42.3437505
C	44.5315519	41.6458969	50.8676362	H	47.6778256	35.6328945	42.4113009
C	44.8049633	43.0124756	51.0346225	H	40.5311502	42.2884547	48.6639537
C	44.9969055	43.8216365	49.9100924	H	40.8044275	40.6460971	46.8565333
O	45.2417447	45.1675918	49.9585978	H	42.7960339	43.6230747	44.4424154
C	45.4011459	45.7963999	51.2189150	H	42.5412421	45.2639233	46.2535611
C	44.1203360	39.5930266	49.3740736				
C	43.6273998	38.7973575	50.5798978	TS1			
H	45.0566069	43.8897842	47.7553203	C	48.0073426	36.5786164	42.5572041
H	44.5585241	41.4766646	47.4776490	H	47.8461587	36.7544615	43.6359923
H	44.3855720	41.0379649	51.7629302	C	47.0068011	37.4236416	41.7813205
H	44.8554790	43.4282050	52.0410749	H	47.2293212	38.4893270	41.9618626
H	44.4818283	45.7268757	51.8242636	H	47.1120065	37.2430211	40.6950291
H	46.2405855	45.3652155	51.7867675	O	45.6649286	37.1277728	42.1849438
H	45.6164287	46.8540387	51.0201094	H	45.0678139	37.7182225	41.7030708
H	45.0184778	39.1020062	48.9565357	C	47.2972641	38.5569018	46.0219834
H	43.3692688	39.5252920	48.5674546	C	46.1446734	41.2806067	42.1884813
H	42.6890585	39.2067995	50.9833890	C	42.1211333	38.6550732	41.5465055
H	44.3627955	38.7856815	51.4014866	C	43.1565776	36.0934551	45.5150339
H	43.4255842	37.7544551	50.2948192	C	47.3415039	39.5301387	45.0307296
H	49.2970231	40.5756323	44.9793047	C	48.4511506	40.4356874	44.8248013
H	48.7003672	42.0178207	42.8175102	C	48.1326585	41.2071730	43.7392468
H	44.5205603	42.1672146	39.4823080	C	46.8212638	40.7756726	43.2955259
H	42.2946101	40.7366694	39.1556885	C	44.9261831	40.8214658	41.6951202
H	40.0171910	36.6880224	41.8405034	C	44.2843476	41.3399988	40.5070935
H	40.6487471	35.2861711	44.0737019	C	43.1384855	40.6121390	40.3199083

C	43.0921258	39.6390115	41.3944256	N	43.5606222	40.1610862	45.2079977
C	42.0366464	37.7332773	42.5844417	H	42.1566711	46.0032525	48.7591528
C	40.9872795	36.7384271	42.7149617	H	40.3952207	45.9191128	48.5645646
C	41.2755555	36.0097029	43.8374625	H	41.1679886	45.0098399	49.8704045
C	42.4964897	36.5758441	44.3890724	C	46.1293378	43.3428403	47.7306040
C	44.3688333	36.5588302	46.0183784	C	45.6262686	42.1011529	47.3751201
C	45.0361697	36.0060771	47.1785899	C	44.6916925	41.4182218	48.1868683
C	46.2167791	36.6865528	47.3143883	C	44.2760464	42.0594115	49.3664923
C	46.2588223	37.6567266	46.2388865	C	44.7915376	43.3041942	49.7507001
N	46.3573955	39.7607257	44.1006178	C	45.7223559	43.9518062	48.9297578
N	44.1901823	39.7826437	42.2167373	O	46.2914361	45.1704576	49.2132819
N	42.9384757	37.6170386	43.6119263	C	46.0175188	45.7889015	50.4689070
N	45.1202520	37.5711064	45.4749965	C	44.2302051	40.0667538	47.7814769
H	48.1588338	38.4928030	46.6821946	C	43.1950111	39.3438937	48.6137965
H	46.6187702	42.0902636	41.6346053	H	46.8528282	43.8560706	47.0953000
H	41.3536664	38.5898206	40.7817484	H	45.9535959	41.6354854	46.4435731
H	42.7005041	35.2609663	46.0495074	H	43.5464984	41.5757588	50.0189909
Fe	44.4939425	38.8868154	44.0373497	H	44.4554604	43.7538925	50.6853274
C	40.7897508	42.9286614	48.1639185	H	44.9492804	46.0467462	50.5640492
C	40.9036593	41.8362594	47.2994985	H	46.3119822	45.1468438	51.3126978
C	41.6931363	41.9482554	46.1512381	H	46.6143377	46.7087082	50.4997627
C	42.3088671	43.1651415	45.8361778	H	45.0875167	39.4226911	47.5396301
C	42.1791548	44.2510051	46.7021634	H	43.8322275	40.1422724	46.5539713
C	41.4343215	44.1479488	47.8926711	H	42.3099292	39.9660983	48.8098393
C	41.2894614	45.3288458	48.8235242	H	43.6082563	39.0336725	49.5914466
S	41.9462354	40.5294979	45.0616033	H	42.8580429	38.4357513	48.0953863
O	41.0963136	39.4309590	45.5555252	H	49.3696795	40.4841525	45.4096286
O	41.7532923	41.0010466	43.6748138	H	48.7696761	41.9698767	43.2914089

H	44.6652399	42.1571116	39.8944640	C	46.7279206	40.7652548	43.0689396
H	42.4396143	40.7580756	39.4962890	C	44.8273654	40.7882992	41.4784140
H	40.1069223	36.6547222	42.0777554	C	44.1686085	41.2983679	40.2981835
H	40.7400016	35.1592538	44.2593459	C	43.0112158	40.5821834	40.1426123
H	44.6381522	35.2110562	47.8091380	C	42.9754506	39.6206522	41.2257908
H	46.9617566	36.5631171	48.1004159	C	41.9337588	37.7213720	42.4418519
H	49.0193024	36.8992950	42.3098787	C	40.8863062	36.7268174	42.5902431
H	47.7948936	35.5276255	42.3613707	C	41.1921308	36.0016561	43.7103732
H	40.1723674	42.8152188	49.0550052	C	42.4214572	36.5679846	44.2417435
H	40.3608180	40.9182325	47.5244812	C	44.2534477	36.6367488	45.9141543
H	42.8904550	43.2595703	44.9191687	C	44.9086469	36.1322859	47.1009678
H	42.6758090	45.1874657	46.4483068	C	46.0464867	36.8777359	47.2696210

IM

C	47.9877441	36.5969968	42.5408913	C	46.0816730	37.8314899	46.1825110
H	47.8079178	36.7893914	43.6139292	N	46.2412763	39.8011914	43.9204045
C	46.9997719	37.4254625	41.7327962	N	44.0960106	39.7566940	42.0208273
H	47.2255023	38.4944554	41.8834011	N	42.8536843	37.6045280	43.4519122
H	47.1121951	37.2127711	40.6540163	N	44.9714763	37.6827650	45.3833203
O	45.6486603	37.1500184	42.1299176	H	47.9627542	38.6988732	46.6312306
H	45.0585118	37.6830498	41.5771947	H	46.5278518	42.0463762	41.3810834
C	47.1225209	38.7220570	45.9413178	H	41.2070786	38.5937605	40.6666956
C	46.0529131	41.2487092	41.9516250	H	42.6427286	35.2640398	45.9064783
C	41.9974489	38.6488017	41.4072158	Fe	44.4018317	38.8980060	43.8439988
C	43.0806030	36.1100338	45.3778951	C	40.8182996	42.7389023	48.0591958
C	47.2094047	39.6093939	44.8754140	C	40.9956678	41.8542024	46.9945731
C	48.3527374	40.4564995	44.6095859	C	41.7549134	42.2466281	45.8835955
C	48.0558791	41.1768125	43.4839676	C	42.2892064	43.5366680	45.8224062
				C	42.1010585	44.4155911	46.8937812
				C	41.3736093	44.0333265	48.0341489

C	41.1570398	44.9849073	49.1893804	H	43.6727376	37.8078553	50.1739286
S	42.0252140	41.0859348	44.5208853	H	42.4796070	39.0421072	50.5512846
O	40.8216408	40.2419654	44.4364025	H	49.2897125	40.4700608	45.1663271
O	42.4423244	41.8667215	43.3433472	H	48.7077119	41.8984817	42.9916520
N	43.3325656	40.1674557	44.9982592	H	44.5439249	42.1065308	39.6704276
H	41.6208888	45.9648420	49.0036299	H	42.2993377	40.7207792	39.3289244
H	40.0824411	45.1521976	49.3705923	H	39.9975394	36.6367757	41.9657007
H	41.5819734	44.5769911	50.1226428	H	40.6530702	35.1658402	44.1563470
C	45.5425470	43.0218519	48.2781070	H	44.5423177	35.3215010	47.7306487
C	45.0348516	41.7384207	48.2092739	H	46.7759283	36.7823937	48.0739169
C	44.5803412	41.0467080	49.3781567	H	49.0038341	36.9133194	42.3051620
C	44.6468329	41.7674654	50.6060532	H	47.7844958	35.5422973	42.3555101
C	45.1383133	43.0704686	50.6736290	H	40.2152040	42.4125761	48.9064584
C	45.6059636	43.7018874	49.5102721	H	40.5081334	40.8795560	47.0155967
O	46.1496258	44.9632096	49.4772900	H	42.8314373	43.8681961	44.9368884
C	46.1852864	45.7278215	50.6784691	H	42.5300494	45.4155119	46.8290331
C	44.0977916	39.7170095	49.2751972				
C	43.5641416	38.8816872	50.3926814	TS2			
H	45.9067722	43.5305739	47.3833803	C	48.0007614	36.5657669	42.5661899
H	44.9675374	41.2424780	47.2369250	H	47.8293087	36.7295909	43.6455308
H	44.3027050	41.2938820	51.5275064	C	46.9867100	37.3981659	41.7932537
H	45.1617966	43.5815178	51.6368880	H	47.1844197	38.4653030	41.9915259
H	45.1690789	45.9287400	51.0571668	H	47.1058911	37.2350596	40.7050592
H	46.7646508	45.2255480	51.4675013	O	45.6477345	37.0664772	42.1797496
H	46.6718066	46.6788560	50.4269460	H	45.0445385	37.6937837	41.7526167
H	44.0693556	39.2824621	48.2708370	C	47.2208690	38.5468830	46.1137710
H	43.0507314	39.6937844	45.8631512	C	46.0603291	41.1778247	42.2153017
H	44.0587995	39.0866374	51.3573825	C	42.0207300	38.5708085	41.6382646

C	43.1504433	35.9739454	45.5639323	C	41.7626141	42.2809027	46.1861488
C	47.2615970	39.5012038	45.1023260	C	42.3404585	43.5529534	46.2590511
C	48.3821830	40.3884938	44.8592722	C	42.0029390	44.4108254	47.3100027
C	48.0600690	41.1307949	43.7551773	C	41.0936961	44.0209301	48.3083150
C	46.7363634	40.7015833	43.3366898	C	40.7476452	44.9470346	49.4522243
C	44.8418583	40.7135904	41.7225541	S	42.1876520	41.1702587	44.8156993
C	44.1942736	41.2273281	40.5348392	O	40.9419390	40.4861803	44.4270809
C	43.0362857	40.5132904	40.3680687	O	42.9167371	41.9806864	43.8278255
C	42.9937040	39.5515038	41.4562362	N	43.2491039	40.0178923	45.4270716
C	41.9633679	37.6372573	42.6700783	H	40.8575448	46.0036774	49.1667816
C	40.9371296	36.6129037	42.7899063	H	39.7137783	44.8000858	49.7998116
C	41.2523563	35.8711717	43.8959318	H	41.4115543	44.7720087	50.3188971
C	42.4694976	36.4554462	44.4471654	C	46.2089038	43.4356564	47.7247998
C	44.3463504	36.4710924	46.0882706	C	45.7006125	42.2068607	47.3519911
C	45.0235697	35.9246735	47.2460754	C	44.6970057	41.5536065	48.1208686
C	46.1803103	36.6443175	47.4011459	C	44.2235268	42.2255003	49.2765245
C	46.1982046	37.6267369	46.3368895	C	44.7509749	43.4504777	49.6761001
N	46.2676912	39.7172498	44.1769693	C	45.7482065	44.0642436	48.8992689
N	44.1047774	39.6885764	42.2599786	O	46.3261078	45.2619252	49.2056465
N	42.8742614	37.5271046	43.6899071	C	46.0139860	45.8952306	50.4488002
N	45.0651351	37.5177068	45.5669773	C	44.2658567	40.2444306	47.7485436
H	48.0837189	38.5003223	46.7748768	C	43.2603010	39.4671996	48.5295770
H	46.5367651	41.9749200	41.6453027	H	46.9790959	43.9287070	47.1298614
H	41.2362305	38.5056916	40.8907198	H	46.0678496	41.7174094	46.4482660
H	42.7246365	35.1110202	46.0764798	H	43.4431547	41.7690804	49.8876904
Fe	44.4611324	38.7672957	44.0612517	H	44.3771069	43.9221771	50.5847198
C	40.5107895	42.7437559	48.2054745	H	44.9492264	46.1750310	50.4953643
C	40.8252221	41.8833761	47.1493953	H	46.2629784	45.2499041	51.3038066

H	46.6293161	46.8012311	50.4956179	H	45.0928453	37.6356245	41.5315828
H	44.9106689	39.6999059	47.0686202	C	47.3500469	38.5607138	45.9651092
H	42.6278863	39.3341464	45.8736658	C	46.2041208	41.2354242	42.0941146
H	43.6576255	39.2156630	49.5324896	C	42.1282846	38.6733276	41.5268068
H	43.0192455	38.5153737	48.0384012	C	43.2121209	36.0855439	45.4690466
H	42.3304925	40.0356471	48.6927319	C	47.4084885	39.5143948	44.9521934
H	49.3141288	40.4329118	45.4228068	C	48.5155093	40.4282828	44.7469300
H	48.7038893	41.8697064	43.2781319	C	48.1965191	41.1866915	43.6531610
H	44.5762678	42.0407089	39.9179444	C	46.8898797	40.7349875	43.2017744
H	42.3345755	40.6561868	39.5463323	C	44.9678854	40.7983211	41.6137316
H	40.0628814	36.5163274	42.1461437	C	44.3066668	41.3372433	40.4401750
H	40.7377569	35.0062836	44.3145284	C	43.1419370	40.6333068	40.2764497
H	44.6511595	35.1048173	47.8602524	C	43.1054292	39.6536856	41.3520730
H	46.9388385	36.5200644	48.1739740	C	42.0578127	37.7367927	42.5572467
H	49.0105216	36.9003101	42.3284244	C	40.9954631	36.7517457	42.7024526
H	47.8101566	35.5128068	42.3587967	C	41.2994067	36.0140017	43.8142885
H	39.7700081	42.4165195	48.9350130	C	42.5429564	36.5629961	44.3425480
H	40.3065750	40.9284224	47.0649223	C	44.4240286	36.5587776	45.9792476
H	43.0365584	43.8867894	45.4895931	C	45.0815770	36.0271593	47.1585742
H	42.4583227	45.4006608	47.3403124	C	46.2589633	36.7142685	47.2949226
				C	46.3074726	37.6667530	46.2007580
PC				N	46.4344926	39.7188071	44.0070626
C	48.0292580	36.5758022	42.5108492	N	44.2212334	39.7782430	42.1511586
H	47.8458310	36.7646489	43.5834729	N	42.9831929	37.6010610	43.5610679
C	47.0434476	37.4054540	41.7017730	N	45.1767555	37.5633432	45.4259114
H	47.2613034	38.4752435	41.8566645	H	48.2069378	38.5088176	46.6335730
H	47.1538704	37.1936972	40.6230509	H	46.6817131	42.0380497	41.5317302
O	45.6902101	37.1250293	42.0975964	H	41.3430366	38.6189363	40.7784263

H 42.7576364 35.2530872 46.0070128
Fe 44.6876332 38.6886023 43.8132890
C 40.6045902 43.1279541 48.6406973
C 40.9129317 41.9608443 47.9459827
C 41.9309229 41.9865630 46.9863338
C 42.5667691 43.1834588 46.6524566
C 42.2340746 44.3500972 47.3465614
C 41.2831096 44.3340942 48.3830528
C 41.0302888 45.5599348 49.2251128
S 42.4531455 40.4199943 46.2820455
O 41.3064424 39.7015609 45.7216738
O 43.6448793 40.6361763 45.4298855
N 42.8239397 39.5525224 47.6845222
H 40.9791467 46.4756491 48.6185252
H 40.0979338 45.4780641 49.8007691
H 41.8543603 45.7021875 49.9474101
C 45.9989153 42.9204440 47.9963638
C 45.4752778 41.6478112 47.7944997
C 44.5787998 41.0665960 48.7107190
C 44.2328952 41.8164658 49.8412258
C 44.7578237 43.0961635 50.0669625
C 45.6457118 43.6540575 49.1384127
O 46.2185673 44.8965798 49.2685652
C 46.0161235 45.6302703 50.4753282
C 44.0827386 39.6418119 48.4683811
C 43.8157438 38.8540505 49.7573390
H 46.6971041 43.3545212 47.2781118
H 45.7599199 41.0934974 46.8982165

H 43.5394814 41.4063166 50.5774142
H 44.4650963 43.6415820 50.9645655
H 44.9570741 45.9143563 50.5995272
H 46.3446872 45.0640120 51.3598783
H 46.6230769 46.5408509 50.3933161
H 44.8869724 39.1319470 47.9128416
H 42.5714439 38.5848267 47.4782388
H 44.6840463 38.8973224 50.4297313
H 43.6091084 37.7961886 49.5311992
H 42.9382067 39.2496298 50.2898638
H 49.4329927 40.4777319 45.3333139
H 48.8259028 41.9564156 43.2065425
H 44.6892872 42.1479701 39.8201824
H 42.4311655 40.7874951 39.4646018
H 40.1026459 36.6807637 42.0812393
H 40.7609211 35.1712487 44.2477257
H 44.6800195 35.2416275 47.7986981
H 47.0023470 36.5995736 48.0837781
H 49.0442050 36.8988106 42.2792992
H 47.8260889 35.5220881 42.3198620
H 39.8202120 43.0848144 49.3963142
H 40.3764529 41.0405908 48.1770480
H 43.3366994 43.1980228 45.8810537
H 42.7498149 45.2769076 47.0953613

QM coordinates of the Iron Nitrenoid
formation reaction

RC

C	39.3718339	43.7272379	49.2393556	N	40.8789203	42.7466867	44.5650792
H	40.3203274	43.1852408	49.3669217	N	42.9118052	44.3825257	45.7509014
C	39.0026083	43.7369775	47.7600058	N	42.7861003	42.7970153	48.1585177
H	38.8055997	42.7029680	47.4272252	Fe	41.8606855	42.7501788	46.3544034
H	38.0849777	44.3279889	47.5930194	C	47.8389465	38.8168449	43.5256864
O	40.0700264	44.2998340	46.9865661	C	47.2870144	39.6879126	44.4638149
H	39.8333886	44.2742708	46.0468709	C	46.1146349	39.3104129	45.1306778
C	41.7578391	40.8212319	49.1576726	C	45.4856231	38.0847474	44.8691850
C	39.3752944	40.8594978	44.9598255	C	46.0577244	37.2296371	43.9255845
C	42.0559165	44.5822089	43.4656203	C	47.2421109	37.5750093	43.2402192
C	44.1592821	44.7970469	47.8119763	C	47.8679648	36.6353113	42.2438108
C	40.9082516	40.4382119	48.1209076	S	45.3810469	40.4489396	46.2832055
C	39.9823177	39.3135314	48.1539667	O	44.6227036	39.7580278	47.3157229
C	39.3205505	39.3073980	46.9563649	O	46.3565275	41.4944970	46.6154330
C	39.8401998	40.4488772	46.2112403	N	44.1180785	41.2446300	45.3257397
C	39.8454683	41.9218109	44.1866571	N	44.5398637	41.8518370	44.3268860
C	39.3570752	42.2780473	42.8616073	N	44.8337730	42.4246930	43.3964664
C	40.1338968	43.3154774	42.4186427	H	45.5730610	36.2736740	43.7053290
C	41.0857139	43.5824166	43.4883201	H	44.5701538	37.8093279	45.3985767
C	42.8867328	44.9795082	44.5151414	H	47.7670260	40.6426984	44.6769529
C	43.7697776	46.1329762	44.4849963	H	48.7500591	39.1179391	43.0025026
C	44.2920627	46.2629975	45.7442451	H	48.6938721	36.0705120	42.7111487
C	43.7767509	45.1338458	46.5124103	H	47.1444991	35.8999990	41.8677749
C	43.7198650	43.7127065	48.5773844	H	48.3018320	37.1703702	41.3864205
C	44.1507985	43.4135422	49.9345659	H	41.7570380	40.1848369	50.0425839
C	43.4406623	42.3113612	50.3355455	H	38.5689867	40.2693599	44.5243117
C	42.6151306	41.9232067	49.2020738	H	42.1574251	45.1423609	42.5361081
N	40.8076282	41.1109916	46.9271138	H	44.9105792	45.4423446	48.2671803

H	39.8055583	38.6752109	49.0196284	C	39.5088353	42.2562170	42.8245958
H	38.5857987	38.5920351	46.5869561	C	40.2400297	43.3338783	42.3970525
H	38.5464771	41.7627690	42.3463538	C	41.1884393	43.6156580	43.4589859
H	40.0819742	43.8835677	41.4898560	C	42.9378853	45.0473597	44.5115621
H	43.9244236	46.7843963	43.6248779	C	43.8003916	46.2121250	44.4977579
H	44.9254723	47.0744384	46.1026067	C	44.3692104	46.2976502	45.7414407
H	44.9371895	43.9345119	50.4806858	C	43.8955860	45.1366655	46.4822145
H	43.4547488	41.8269759	51.3118854	C	43.8497391	43.7091546	48.5359881
H	38.6201914	43.1903037	49.8179767	C	44.2589172	43.4333253	49.9021637
H	39.5258869	44.7552962	49.5671223	C	43.4982036	42.3762882	50.3326072
				C	42.6725006	41.9826565	49.2040998
TS				N	40.9731567	41.0913635	46.8894443
C	39.4836579	43.6646877	49.1781055	N	41.0420450	42.7337113	44.5139362
H	40.4179256	43.1312452	49.4026752	N	43.0094238	44.4065828	45.7248448
C	39.2206073	43.5974593	47.6793999	N	42.8886534	42.8134884	48.1343198
H	38.9761492	42.5623919	47.3890036	Fe	42.1208182	42.6414754	46.2675948
H	38.3663403	44.2403026	47.4019998	C	47.4066574	38.9939598	43.9775142
O	40.3772189	44.0408928	46.9416445	C	46.8088644	39.9069465	44.8456869
H	40.1328928	44.1362522	46.0070937	C	45.5543270	39.6120471	45.3896565
C	41.7975805	40.8990873	49.1777310	C	44.9020370	38.4107994	45.0904100
C	39.5845156	40.8075113	44.8952429	C	45.5204821	37.5044694	44.2237342
C	42.0943489	44.6691949	43.4690155	C	46.7785244	37.7776829	43.6496827
C	44.3113793	44.7719508	47.7620147	C	47.4491030	36.7876412	42.7313570
C	41.0109908	40.4708587	48.1132097	S	44.7885717	40.7721814	46.5262259
C	40.0782540	39.3560496	48.1462865	O	44.0786317	40.0083688	47.5612534
C	39.4667031	39.3070244	46.9227178	O	45.8163576	41.7488012	46.9344309
C	40.0253542	40.4131032	46.1567499	N	43.5620964	41.5690638	45.6001993
C	40.0307707	41.8811620	44.1270983	N	44.3000276	41.8351238	44.2051843

N	43.8777305	42.2358394	43.2290339	H	38.2264879	44.3341491	47.5217976
H	45.0153619	36.5647492	43.9810368	O	40.2467462	44.2830815	47.0297264
H	43.9319718	38.1845118	45.5377540	H	40.0917775	44.1819186	46.0783751
H	47.3132121	40.8370284	45.1060828	C	41.8546793	40.8956643	49.2765967
H	48.3805010	39.2381648	43.5434636	C	39.5703278	40.8554081	45.0268252
H	46.7571557	35.9954705	42.4141940	C	42.3435837	44.5019270	43.5257561
H	47.8620224	37.2729031	41.8330044	C	44.2989078	44.8358397	47.9308969
H	48.2997310	36.3014276	43.2398025	C	41.0367136	40.4945687	48.2255485
H	41.7563488	40.2966688	50.0851774	C	40.0996220	39.3856351	48.2622112
H	38.7746292	40.2188760	44.4643605	C	39.4622511	39.3538440	47.0500499
H	42.1537878	45.2739520	42.5641382	C	40.0076027	40.4633817	46.2881642
H	45.1134032	45.3717761	48.1921710	C	40.0731953	41.8924653	44.2469162
H	39.8749154	38.7362179	49.0195157	C	39.6289327	42.2246284	42.9074065
H	38.7296371	38.5858134	46.5696519	C	40.4460584	43.2292210	42.4563212
H	38.7053187	41.7332005	42.3060575	C	41.3716042	43.5090821	43.5390560
H	40.1671462	43.8864010	41.4603168	C	43.1084824	44.9429447	44.6025049
H	43.8976695	46.9138688	43.6694103	C	43.9302756	46.1353213	44.5959401
H	44.9912620	47.1142751	46.1078323	C	44.4007574	46.3015018	45.8730204
H	45.0653172	43.9506651	50.4219191	C	43.9205687	45.1582197	46.6303602
H	43.4990457	41.8919954	51.3090943	C	43.8499318	43.7596946	48.6900941
H	38.7032793	43.1540449	49.7423043	C	44.2629513	43.4674398	50.0496205
H	39.6184150	44.7069448	49.4672554	C	43.5308047	42.3808873	50.4529290
				C	42.7142268	41.9906376	49.3172467
IM				N	40.9717427	41.1321842	47.0109272
C	39.4228362	43.7532046	49.2442348	N	41.1103736	42.7130847	44.6358097
H	40.3699919	43.2233310	49.4246534	N	43.1049005	44.3695323	45.8501443
C	39.1326619	43.7417482	47.7469898	N	42.9071582	42.8527072	48.2690955
H	38.9428905	42.7032410	47.4240683	Fe	42.2394517	42.5898429	46.3568665

C	47.5024977	39.0313511	43.8730008	H	44.0639702	46.8024405	43.7443858
C	46.9055393	39.9118843	44.7781509	H	44.9789886	47.1483620	46.2425387
C	45.6910023	39.5644074	45.3765131	H	45.0566308	43.9935523	50.5800407
C	45.0710551	38.3437569	45.0765753	H	43.5269124	41.8867847	51.4244816
C	45.6858757	37.4714091	44.1754472	H	38.6577694	43.2192609	49.8078340
C	46.9126564	37.7938110	43.5598544	H	39.5571850	44.7871190	49.5621004
C	47.5888430	36.8257057	42.6209271				
S	44.9060219	40.6899320	46.5322249				
O	44.3398554	39.8694939	47.6288923				
O	45.8972030	41.7400324	46.8650045				
N	43.6435654	41.3726595	45.7623537				
N	43.4846278	41.8079770	40.9702545				
N	43.4854045	40.9406433	40.2931952				
H	45.2053835	36.5167798	43.9396895				
H	44.1225752	38.0779320	45.5495856				
H	47.3866337	40.8565535	45.0305237				
H	48.4481570	39.3185441	43.4044882				
H	46.8879556	36.0651806	42.2483973				
H	48.0471463	37.3316673	41.7575350				
H	48.4041367	36.2901170	43.1385379				
H	41.8395720	40.2688301	50.1681783				
H	38.7521831	40.2803689	44.5931936				
H	42.4954692	45.0337864	42.5865418				
H	45.0663585	45.4650365	48.3816717				
H	39.9056398	38.7567822	49.1311082				
H	38.7322350	38.6278011	46.6922715				
H	38.8258062	41.7143225	42.3757648				
H	40.4226878	43.7554152	41.5020463				