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

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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.

\[
\frac{<R>-<S>}{K_R} = \frac{k_R}{k_S} = \frac{A_R^e-E_a/RT}{A_S^e-E_a/RT}
\]

\[
R = 1.9858775 \times 10^{-3} \text{ kcal K}^{-1} \text{ mol}^{-1} = \frac{(E_{ae}-E_{as})}{\sigma}
\]

T = 298.15 K
E_{as} = 17.65 kcal/mol
E_{ae} = 20.47 kcal/mol

117.07

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.
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 | 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   | 44.451128  | 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 | 44.362928  | 48.7093386 |
|                                            | S    | 42.0416942 | 40.8100203 | 44.223067 |
|                                            | 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
C 44.6398658 41.8961341 48.4850057
C 44.4346560 41.0608003 49.6008103
C 44.5315519 43.0124756 51.0346225
C 44.9969055 43.8216365 49.9100924
O 45.2417447 45.1675918 49.9585978
C 45.4011459 45.7963999 51.2189150
C 44.1203360 39.5930266 49.3740736
C 43.6273998 38.7973575 50.5798978
H 45.0566069 43.8897842 47.7553203
H 44.5585241 41.4766646 47.4776490
H 44.3855720 41.0379649 51.7629302
H 44.8554790 43.4282050 52.0410749
H 44.4818283 45.7268757 51.8242636
H 46.2405855 45.3652155 51.7867675
H 45.6164287 46.8540387 51.0201094
H 45.0184778 39.1020062 48.9565357
H 43.3692688 39.5252920 48.5674546
H 42.6890585 39.2067995 50.9833890
H 44.3627955 38.7856815 51.4014866
H 43.4255842 37.7544551 50.2948192
H 49.2970231 40.5756323 44.9793047
H 48.7003672 42.0178207 42.8175102
H 44.5205603 42.1672146 39.4823080
H 42.2946101 40.7366694 39.1556885
H 40.0171910 36.6880224 41.8405034
H 40.6487471 35.2861711 44.0737019
H 44.5432626 35.4864137 47.6527464
H 46.7754980 36.9343180 47.9565432
H 48.9395582 36.9676104 42.3437505
H 47.6778256 35.6328945 42.4113009
H 40.5311502 42.2884547 48.6639537
H 40.8044275 40.6460971 46.8565333
H 42.7960339 43.6230747 44.424154
H 42.5412421 45.2639233 46.2535611

TS1
C 48.0073426 36.5786164 42.5572041
H 47.8461587 36.7544615 43.6359923
C 47.0068011 37.4236416 41.7813205
H 47.2293212 38.4893270 41.9618626
H 47.1120065 37.2430211 40.6950291
O 45.6649286 37.1277728 42.1849438
H 45.0678139 37.7182225 41.7030708
C 47.2972641 38.5569018 46.0219834
C 46.1446734 41.2806067 42.1884813
C 42.1211333 38.6550732 41.5465055
C 43.1565776 36.0934551 45.5150339
C 47.3415039 39.5301387 45.0307296
C 48.4511506 40.4356874 44.8248013
H 48.1326585 41.2071730 43.7392468
C 46.8212638 40.7756726 43.2955259
C 44.9261831 40.8214658 41.6951202
C 44.2843476 41.3399988 40.5070935
C 43.1384855 40.6121390 40.319083
| Element | X    | Y    | Z    |
|---------|------|------|------|
| C       | 43.0921258 | 39.6390115 | 41.3944256 |
| C       | 42.0366464  | 37.7332773  | 42.584417   |
| C       | 40.9872795  | 36.7384271  | 42.7149617  |
| C       | 41.2755555  | 36.0097029  | 42.584417   |
| C       | 42.4964897  | 36.5758441  | 44.3890724  |
| C       | 44.3683333  | 36.588302   | 46.0183784  |
| C       | 45.0361977  | 36.0060771  | 44.3890724  |
| C       | 46.2167791  | 36.6865528  | 47.3143883  |
| C       | 46.2588223  | 37.6567266  | 46.238865   |
| N       | 46.3573955  | 39.7607257  | 44.1006178  |
| N       | 44.1901823  | 39.7826437  | 42.167373   |
| N       | 42.9384757  | 37.6170386  | 43.6119263  |
| N       | 45.1202520  | 37.571064   | 45.479965   |
| C       | 48.1588338  | 38.4928030  | 46.6821946  |
| C       | 46.6187702  | 42.0902636  | 46.346053   |
| C       | 41.3536664  | 38.5898206  | 40.7817484  |
| H       | 42.7005041  | 35.2609663  | 46.0495074  |
| Fe      | 44.4939425  | 38.8868154  | 44.0373497  |
| C       | 40.7897508  | 42.9286614  | 48.1639185  |
| C       | 40.9036593  | 41.8362594  | 47.2994985  |
| C       | 41.6931363  | 41.9482554  | 46.1512381  |
| C       | 42.3088671  | 43.1651415  | 45.8361778  |
| C       | 42.1791548  | 44.2510051  | 46.7021634  |
| C       | 41.4343215  | 44.1479488  | 47.8926711  |
| C       | 41.2894614  | 45.3288458  | 48.8235242  |
| S       | 41.9462354  | 40.5294979  | 45.0616033  |
| O       | 41.0963136  | 39.4309590  | 45.5555252  |
| O       | 41.7532923  | 41.0010466  | 43.6748138  |
| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| H    | 44.6652399 | 42.1571116 | 39.8944640 |
| H    | 42.4396143   | 40.7580756   | 39.4962890 |
| H    | 40.1069223   | 36.6547222   | 42.0777554 |
| H    | 40.7400016   | 35.1592538   | 44.2593459 |
| H    | 44.6381522   | 36.6547222   | 42.0777554 |
| IM   | C    | 47.9877441   | 36.5969968   | 42.5408913 |
| H    | 47.8079178   | 36.7893914   | 43.6139292 |
| C    | 46.9997719   | 37.4254625   | 41.7327962 |
| H    | 47.2255023   | 38.4944554   | 41.8834011 |
| H    | 47.1121951   | 37.2127711   | 40.6540163 |
| H    | 47.1121951   | 37.2127711   | 40.6540163 |
| C    | 45.6486603   | 37.1500184   | 42.1299176 |
| H    | 45.0585118   | 37.6830498   | 41.5771947 |
| C    | 47.1225209   | 38.7220570   | 45.9413178 |
| C    | 46.0529131   | 41.2487092   | 41.9516250 |
| C    | 41.9974489   | 38.6488017   | 41.4072158 |
| C    | 43.0806030   | 36.1100338   | 45.3778951 |
| C    | 47.2094047   | 39.6093939   | 44.8754140 |
| C    | 48.3527374   | 40.4564995   | 44.6095859 |
| C    | 48.0558791   | 41.1768125   | 43.4839676 |

| Element | X   | Y   | Z   |
|---------|-----|-----|-----|
| Fe      | 44.4018317 | 38.8980060 | 43.8439988 |
| C       | 40.8863062   | 36.7268174   | 42.5902431 |
| C       | 41.1921308   | 36.0016561   | 43.7103732 |
| C       | 42.4214572   | 36.5679846   | 44.2417435 |
| H       | 47.9627542   | 38.6988732   | 46.6312306 |
| H       | 46.5278518   | 42.0463762   | 41.3810834 |
| H       | 41.2070786   | 38.5937605   | 40.666956 |
| H       | 42.6427286   | 35.2640398   | 45.9064783 |
| C       | 40.8182996   | 42.7389023   | 48.0591958 |
| C       | 40.9956678   | 41.8542024   | 46.9945731 |
| C       | 41.7549134   | 42.2466281   | 45.8835955 |
| C       | 42.2892064   | 43.5366680   | 45.8224062 |
| C       | 42.105085    | 44.4155911   | 46.8937812 |
| C       | 41.3736093   | 44.0333265   | 48.0341489 |
C  41.1570398  44.9849073  49.1893804
S  42.0252140  41.0859348  44.5208853
O  40.8216408  40.2419654  44.4364025
O  42.4423244  41.8667215  43.3433472
N  43.3325656  40.1674557  44.9982592
H  41.6208888  45.9648420  49.0036299
H  40.0824411  45.1521976  49.3705923
H  41.5819734  44.5769911  50.1226428
C  45.5425470  43.0218519  48.2781070
C  45.0348516  41.7384207  48.2092739
C  44.5803412  41.0467080  49.3781567
C  44.6468329  41.7674654  50.6060532
C  45.1383133  43.0704686  50.6736290
C  45.6059636  43.7018874  49.5102721
O  46.1496258  44.9632096  49.4772900
C  46.1852864  45.728215  50.6784691
C  44.0977916  39.7170095  49.2751972
C  43.5641416  38.8816872  50.3926814
H  45.9067722  43.5305739  47.3833803
H  44.9675374  41.2424780  47.2369250
H  44.3027050  41.2938820  51.5275064
H  45.1617966  43.5815178  51.6368880
H  45.1690789  45.9287400  51.0571668
H  46.7646508  45.2255480  51.4675013
H  46.6718066  46.6788560  50.4269460
H  44.0693556  39.2824621  48.2708370
H  43.0507314  39.6937844  45.8631512
H  44.0587995  39.0866374  51.3573825
H  43.6727376  37.8078553  50.1739286
H  42.4796070  39.0421072  50.5512846
H  49.2897125  40.4700608  45.1663271
H  48.7077119  41.8984817  42.9916520
H  44.5439249  42.1065308  39.6704276
H  42.2993377  40.7207792  39.3289244
H  39.9975394  36.6367757  41.9657007
H  40.6530702  35.1658402  44.1563470
H  44.5423177  35.3215010  47.7306487
H  46.7759283  36.7823937  48.0739169
H  49.0038341  36.9133194  42.3051620
H  47.7844958  35.5422973  42.3555101
H  40.2152040  42.4125761  48.9064584
H  40.5081334  40.8795560  47.0155967
H  42.8314373  43.8681961  44.9368884
H  42.5300494  45.4155119  46.8290331

TS2
C  48.0007614  36.5657669  42.5661899
H  47.8293087  36.7295909  43.6455308
C  46.9867100  37.3981659  41.7932537
H  47.1844197  38.4653030  41.9915259
H  47.1058911  37.2350596  40.7050592
O  45.6477345  37.0664772  42.1797496
H  45.0445385  37.6937837  41.7526167
C  47.2208690  38.5468830  46.1137710
C  46.0603291  41.1778247  42.2153017
C  42.0207300  38.5708085  41.6382646
|  C  |  X      |  Y      |  Z      |  C  |  X      |  Y      |  Z      |
|-----|---------|---------|---------|----|---------|---------|---------|
| 43.1504433 | 35.9739454 | 45.5639323 | 41.7626141 | 42.2809027 | 46.1861488 |
| 47.2615970 | 39.5012038 | 45.1023260 | 42.3404585 | 43.5529534 | 46.2590511 |
| 48.3821830 | 40.3884938 | 44.8592722 | 42.0029390 | 44.4108254 | 47.3100027 |
| 48.060690 | 41.1307949 | 43.7551773 | 41.0936961 | 44.0209301 | 48.3083150 |
| 46.7363634 | 40.7015833 | 43.3666898 | 40.7476452 | 44.9470346 | 49.452243 |
| 44.8418583 | 40.7135904 | 41.7225541 | 42.1876520 | 41.1702587 | 44.8156993 |
| 44.194276 | 41.2273281 | 40.5348392 | 40.9419390 | 40.4861803 | 44.4270809 |
| 43.0362857 | 40.5132904 | 40.3680687 | 42.9167371 | 41.9806864 | 43.8278255 |
| 42.9937040 | 39.5515038 | 41.4562362 | N  | 43.2491039 | 40.0178923 | 45.427016 |
| 41.9633679 | 37.6372573 | 42.6700783 | H  | 40.8575448 | 46.0036774 | 49.1667816 |
| 40.9371296 | 36.6129037 | 42.7899063 | H  | 39.7137783 | 44.8000858 | 49.7998116 |
| 41.2523563 | 35.8711717 | 43.8959318 | H  | 41.4115543 | 44.7720087 | 50.3188971 |
| 42.4694976 | 36.4554462 | 44.4471654 | C  | 46.2089038 | 43.4356564 | 47.7247998 |
| 44.3463504 | 36.4710924 | 46.0882706 | C  | 45.7006125 | 42.2068607 | 47.3519911 |
| 45.0235697 | 35.9246735 | 47.2460754 | C  | 44.6970057 | 41.5536065 | 48.1208686 |
| 46.1803103 | 36.6443175 | 47.4011459 | C  | 44.2235268 | 42.2255003 | 49.2765245 |
| 46.1982046 | 37.6267369 | 46.3368895 | C  | 44.7509749 | 43.4504777 | 49.6761001 |
| 45.2676912 | 39.7172498 | 44.1769693 | C  | 45.7482065 | 44.0642436 | 48.8992689 |
| 44.1047774 | 39.6885764 | 42.2599786 | O  | 46.3261078 | 45.2619252 | 49.2056465 |
| 42.8742614 | 37.5271046 | 43.6899071 | C  | 46.0139860 | 45.8952306 | 50.4488002 |
| 45.0651351 | 37.5177068 | 45.5669773 | C  | 44.2658567 | 40.2444306 | 47.7485436 |
| 48.0837189 | 38.5003223 | 46.7748768 | C  | 43.2603010 | 39.4671996 | 48.5295770 |
| 46.5367651 | 41.9749200 | 41.6453027 | H  | 46.9790959 | 43.9287070 | 47.1298614 |
| 41.2362305 | 38.5056916 | 40.8907198 | H  | 46.0678496 | 41.7174094 | 46.4482660 |
| 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 |
| Element | X coordinates | Y coordinates | Z coordinates |
|---------|---------------|---------------|---------------|
| H       | 46.6293161    | 46.8012311    | 50.4956179    |
| H       | 44.9106689    | 39.6990059    | 47.0686202    |
| H       | 42.6278863    | 39.3341464    | 45.8736658    |
| H       | 43.6576255    | 39.2156630    | 49.5324896    |
| H       | 43.0192455    | 38.5137377    | 48.0384012    |
| H       | 42.3304925    | 40.0356471    | 48.6927319    |
| C       | 48.0292580    | 36.5758022    | 42.5108492    |
| C       | 47.0434476    | 37.4054540    | 41.7017730    |
| O       | 46.6293161    | 36.5758022    | 42.5108492    |

**PC**

| Element | X coordinates | Y coordinates | Z coordinates |
|---------|---------------|---------------|---------------|
| C       | 48.0292580    | 36.5758022    | 42.5108492    |
| H       | 47.8458310    | 36.7646489    | 43.5834729    |
| C       | 47.0434476    | 37.4054540    | 41.7017730    |
| H       | 47.2613034    | 38.4752435    | 41.8566645    |
| H       | 47.1538704    | 37.1936972    | 40.6230509    |
| O       | 45.6902101    | 37.1250293    | 42.0975964    |
QM coordinates of the Iron Nitrenoid formation reaction

RC
| Atom | X             | Y             | Z             |
|------|---------------|---------------|---------------|
| C    | 39.3718339    | 43.7272379    | 49.2393556    |
| H    | 40.3203274    | 43.1852408    | 49.3669217    |
| C    | 39.0026083    | 43.7369775    | 47.7600058    |
| H    | 38.8055997    | 43.209680     | 47.4272252    |
| H    | 38.0849777    | 43.1852408    | 46.9865661    |
| O    | 40.0700264    | 44.2998340    | 47.608709     |
| H    | 39.833386     | 44.2742708    | 46.048709     |
| C    | 41.7578391    | 40.8212319    | 49.157626    |
| C    | 42.0559165    | 44.5822089    | 43.4656203    |
| C    | 44.1592821    | 47.970469     | 47.8119763    |
| C    | 40.9082516    | 40.4382119    | 48.1209076    |
| C    | 39.9823177    | 39.3135314    | 48.1539667    |
| O    | 43.72870144   | 39.6879126    | 44.4638149    |
| C    | 43.7767509    | 45.1304129    | 45.1306778    |
| C    | 43.7198650    | 41.2181098    | 44.1866571    |
| C    | 43.9570752    | 42.270473     | 42.8616073    |
| C    | 40.1338968    | 43.154774     | 42.4186427    |
| C    | 41.0857139    | 43.5824166    | 43.4883201    |
| C    | 42.867328     | 44.9795082    | 44.5151414    |
| C    | 43.7697776    | 46.1329762    | 44.4849963    |
| C    | 44.2920627    | 46.2629975    | 45.7442451    |
| C    | 43.7767509    | 45.1338458    | 46.5124103    |
| C    | 43.7198650    | 43.7127065    | 48.5773844    |
| C    | 44.1507985    | 43.4135422    | 49.9345659    |
| C    | 43.4406623    | 42.313612     | 50.3355455    |
| C    | 42.6151306    | 41.9232067    | 49.2020738    |
| N    | 40.8076282    | 41.1109916    | 46.9271138    |
| N    | 40.8378920    | 42.7466867    | 44.5650792    |
| N    | 42.9118052    | 44.3825257    | 45.7509014    |
| N    | 42.7861003    | 42.7970153    | 48.158177    |
| Fe   | 41.8606855    | 42.7501788    | 46.3544034    |
| C    | 47.8389465    | 38.8168449    | 43.5256864    |
| C    | 47.2870144    | 39.6879126    | 44.4638149    |
| C    | 46.1146349    | 39.3104129    | 45.1306778    |
| C    | 45.4856231    | 38.0847474    | 44.8691850    |
| C    | 46.0577244    | 37.2296371    | 43.9255845    |
| C    | 47.2421109    | 37.5750093    | 43.2402192    |
| C    | 47.8679648    | 36.6353113    | 42.2438108    |
| S    | 45.3810469    | 40.4489396    | 46.2832055    |
| O    | 44.6227036    | 39.7580278    | 47.3157229    |
| O    | 46.3565275    | 41.4944970    | 46.6154330    |
| C    | 44.1180785    | 41.2446300    | 45.3257397    |
| C    | 44.5398637    | 41.8518370    | 44.3268860    |
| C    | 44.8337730    | 42.4246930    | 43.3964664    |
| H    | 45.5730610    | 36.2736740    | 43.7053290    |
| C    | 44.5701538    | 37.8093279    | 45.3985767    |
| C    | 47.7670260    | 40.6426984    | 44.6769529    |
| C    | 48.7500591    | 39.1179391    | 43.0025026    |
| C    | 48.6938721    | 36.0705120    | 42.7111487    |
| C    | 47.1444991    | 35.8999990    | 41.8677749    |
| C    | 48.3018320    | 37.1703702    | 41.3864205    |
| C    | 41.7570380    | 40.1848369    | 50.0425839    |
| C    | 38.5689867    | 40.2693599    | 44.5243117    |
| C    | 42.1574251    | 45.1423609    | 42.5361811    |
| 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  43.433253  49.9021637
H  39.5258869  44.7552962  49.5671223  C  43.4982036  42.3762882  50.3326072
       C  42.6725006  41.9826565  49.2040998
TS
C  39.4836579  43.6646877  49.1781055  N  40.9731567  41.0913635  46.8894443
H  40.4179256  43.1312452  49.4026752  N  41.0420450  42.7337113  44.5139362
C  39.2206073  43.5974593  47.6793999  N  43.0094238  44.4065828  45.7248448
H  38.9761492  42.5623919  47.3890036  N  42.8886534  42.8134884  48.1343198
H  38.3663403  44.2403026  47.4019998  Fe  42.1208182  42.6414754  46.2675948
O  40.3772189  44.0408928  46.9416445  C  47.4066574  38.9939598  43.9775142
H  40.1328928  44.1362522  46.007937  C  46.8088644  39.9069465  44.8456869
C  41.7975805  40.8990873  49.1777310  C  45.5543270  39.6120471  45.3896565
C  39.5845156  40.8075113  44.8952429  C  44.9020370  38.4107994  45.0904100
C  42.0943489  44.6691949  43.4690155  C  45.5204821  37.5044694  44.2237342
C  44.3113793  44.7719508  47.7620147  C  46.7785244  37.7776829  43.6496827
C  41.0109908  40.4708587  48.1132097  C  47.4491030  36.7876412  42.7313570
C  40.0782540  39.3560496  48.1462865  S  44.7885717  40.7721814  46.5262259
C  39.4667031  39.3070244  46.9227178  O  44.0786317  40.0083688  47.5612534
C  40.0253542  40.4131032  46.1567499  O  45.8163576  41.7488012  46.9344309
C  40.0307707  41.8811620  44.1270983  N  43.5620964  41.5690638  45.6001993
       N  44.3000276  41.8351238  44.2051843
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| N       | 43.8777305 | 42.2358394 | 43.2290339 |
| H       | 45.0153619 | 36.5647492 | 43.9810368 |
| H       | 43.9319718 | 38.1845118 | 45.5377540 |
| H       | 47.3132121 | 40.8370284 | 45.1060828 |
| H       | 48.3805010 | 39.2381648 | 43.5434636 |
| H       | 46.7571557 | 35.9954705 | 42.4141940 |
| H       | 47.8620224 | 37.2729031 | 41.8330044 |
| H       | 48.2997310 | 36.3014276 | 43.2398025 |
| H       | 41.7563488 | 40.2966688 | 50.0851774 |
| H       | 38.7746292 | 40.2188760 | 44.4643605 |
| H       | 42.1537878 | 45.2739520 | 42.5641382 |
| H       | 45.1134032 | 45.3717761 | 48.1921710 |
| H       | 39.8749154 | 38.7362179 | 49.0195157 |
| H       | 38.7296371 | 38.5858134 | 46.5696519 |
| H       | 38.7053187 | 41.7332005 | 42.3060575 |
| H       | 40.1671462 | 43.8864010 | 41.4603168 |
| H       | 43.8976695 | 46.9138688 | 43.6694103 |
| H       | 44.9912620 | 47.1142751 | 46.1078323 |
| H       | 45.0653172 | 43.9506651 | 50.4219191 |
| H       | 43.4990457 | 41.8919954 | 51.3090943 |
| H       | 38.7032793 | 43.1540449 | 49.7423043 |
| H       | 39.6184150 | 44.7069448 | 49.4672554 |

**IM**

| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| C       | 39.4228362 | 43.7532046 | 49.2442348 |
| H       | 40.3699919 | 43.2233310 | 49.4246534 |
| C       | 39.1326619 | 43.7417482 | 47.7469898 |
| H       | 38.9428905 | 42.7032410 | 47.4240683 |

| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| H       | 38.2264879 | 44.3341491 | 47.5217976 |
| O       | 40.2467462 | 44.2830815 | 47.0297264 |
| H       | 40.0917775 | 44.1819186 | 46.0783751 |
| C       | 41.8546793 | 40.8956643 | 49.2765967 |
| C       | 39.5703278 | 40.8554081 | 45.0268252 |
| C       | 42.3435837 | 44.5019270 | 43.5257616 |
| C       | 44.2989078 | 44.8358397 | 47.9308969 |
| C       | 41.0367136 | 40.4945687 | 48.2255485 |
| C       | 40.0996220 | 39.3856351 | 48.2622112 |
| C       | 39.4622511 | 39.3538440 | 47.0500499 |
| C       | 40.0076027 | 40.4633817 | 46.2881642 |
| C       | 40.0731953 | 41.8924653 | 44.2469162 |
| C       | 39.6289327 | 42.2246284 | 42.9074065 |
| C       | 40.4460584 | 43.2292210 | 42.4563212 |
| C       | 41.3716042 | 43.5090821 | 43.5390560 |
| C       | 43.1084824 | 44.9429447 | 44.6025049 |
| C       | 43.9302756 | 46.1353213 | 44.5959401 |
| C       | 44.4007574 | 46.3015018 | 45.8730204 |
| C       | 43.9205687 | 45.1582197 | 46.6303620 |
| C       | 43.8499318 | 43.7596946 | 48.6900941 |
| C       | 44.2629513 | 43.4674398 | 50.0496205 |
| C       | 43.5308047 | 42.3808873 | 50.4529290 |
| C       | 42.7142268 | 41.9906376 | 49.3172467 |
| N       | 40.9717427 | 41.1321842 | 47.0109272 |
| N       | 41.1103736 | 42.7130847 | 44.6358097 |
| N       | 43.1049005 | 44.3695323 | 45.8501443 |
| N       | 42.9071582 | 42.8527072 | 48.2690955 |
| Fe      | 42.2394517 | 42.5898429 | 46.3568665 |
| C   | 47.5024977 | 39.0313511 | 43.8730008 |
|-----|------------|------------|------------|
| C   | 46.9055393 | 39.9118843 | 44.7781509 |
| C   | 45.6910023 | 39.5644074 | 45.3765131 |
| C   | 45.0710551 | 38.3437569 | 45.0715973 |
| C   | 45.6858757 | 37.4714091 | 44.1754472 |
| C   | 46.9126564 | 37.7938110 | 45.598544  |
| S   | 47.5888430 | 36.8257057 | 42.6209271 |
| 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 | 43.404882  |
| 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 |