

Supporting Information of
Effect of Hydrogen Bonding on Innocent and Non-innocent Axial
Ligands Bound to Iron Porphyrins

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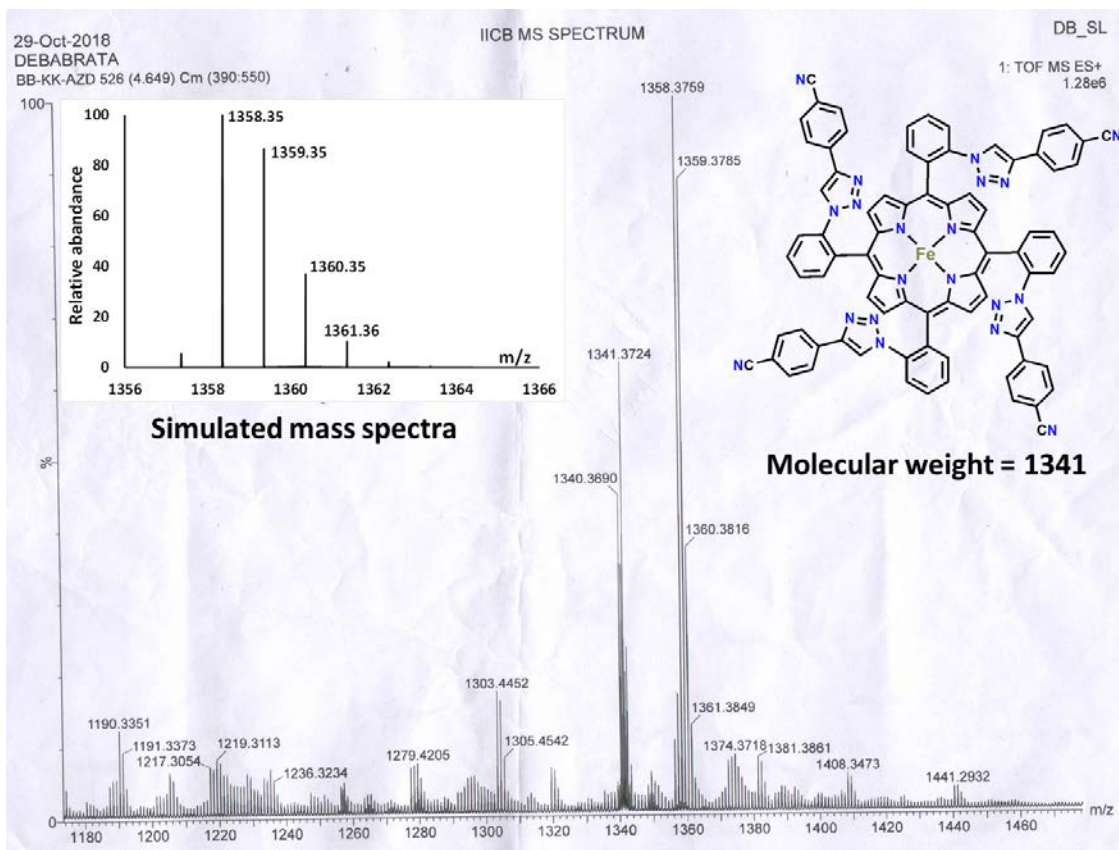


Figure S1: mass spectra of $\text{Fe}(\text{PhCN})_4$ complex. The molecule traps a water molecule, which gives the mass corresponding to molecular ion peak at m/z value=1358.37. The isotope distribution of the simulated spectra (shown in inset) matches exactly matches the isotope distribution of the molecular ion peak observed experimentally.

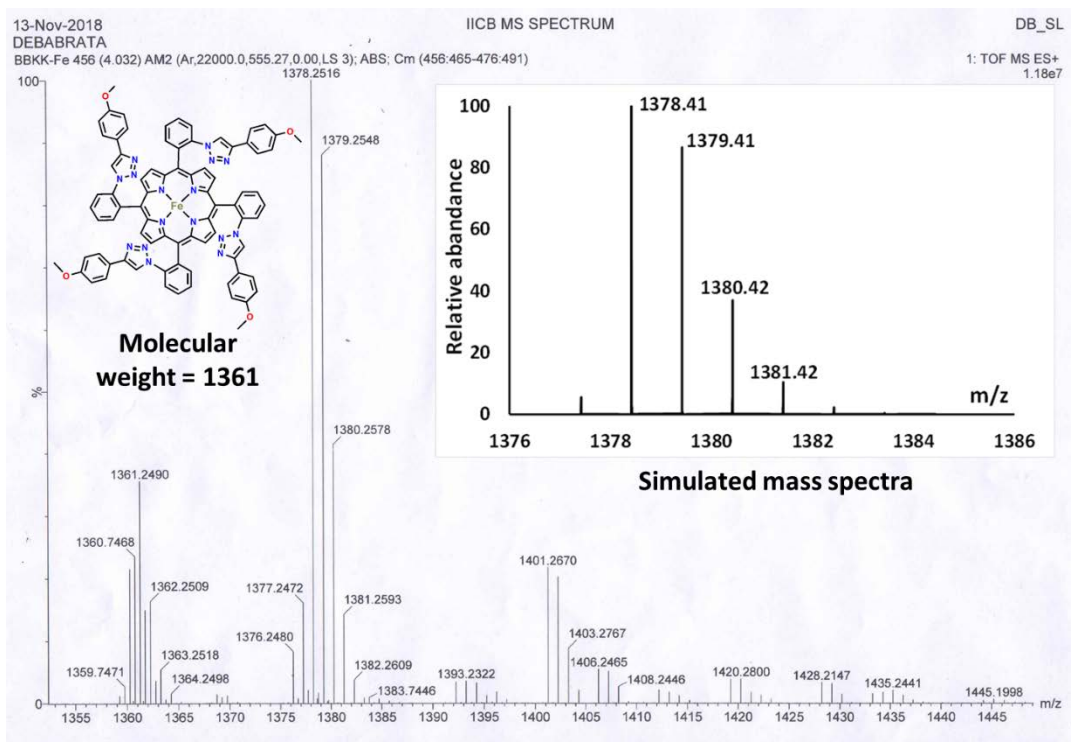


Figure S2: mass spectra of $\text{Fe}(\text{PhOMe})_4$ complex. The molecule traps a water molecule which gives the mass corresponding to molecular ion peak at m/z value= 1378.25. The isotope distribution of the simulated spectra (shown in inset) matches exactly matches the isotope distribution of the molecular ion peak observed experimentally.

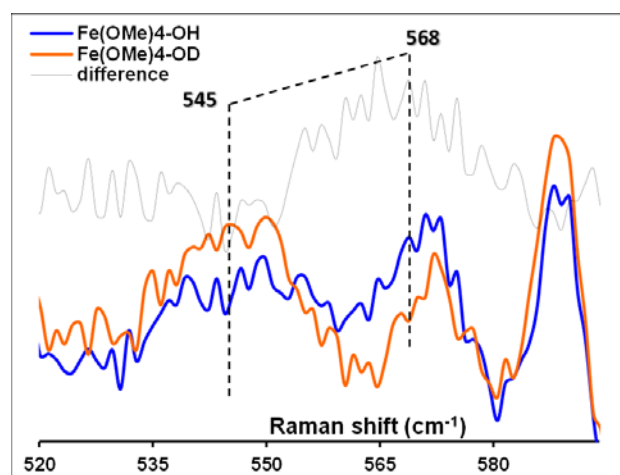


Figure S3: Stretching frequency of Fe-O in hydroxide complex of $\text{Fe}(\text{PhOMe})_4$. Blue spectra represents stretching frequency of Fe-O^{16} , red spectra represents stretching frequency of Fe-O^{18} , black dotted spectra represents the difference between stretching frequency of $^{16}\text{O}_2$ and $^{18}\text{O}_2$ in all the three spectra.

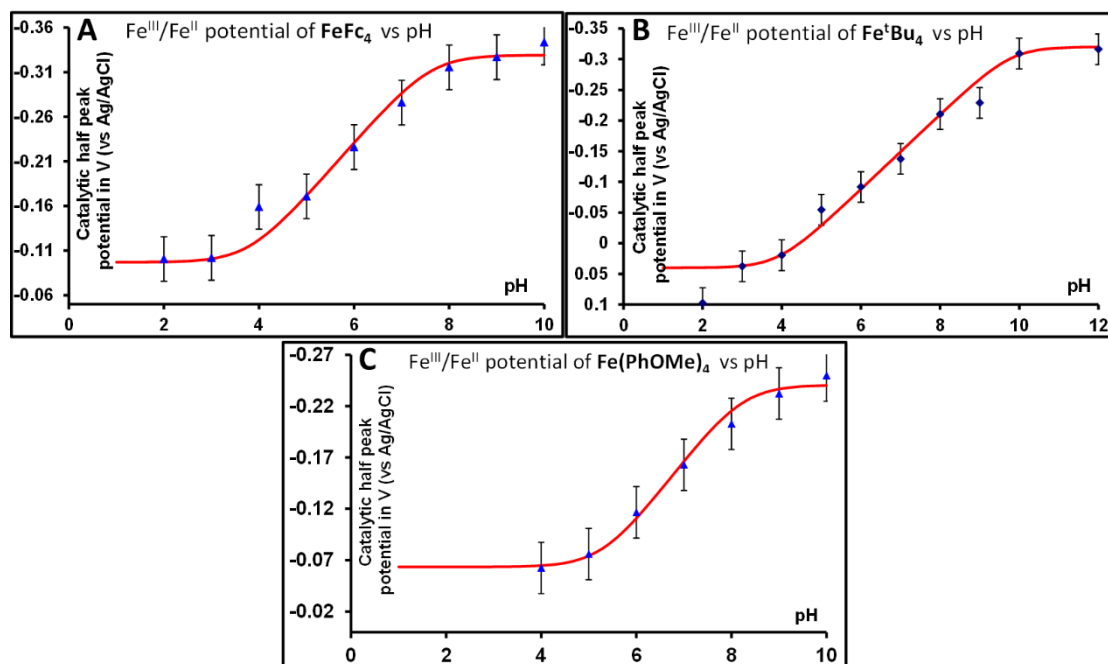


Figure S4: Plot of $\text{Fe}^{\text{III/II}}$ reduction potential of (A) FeFc_4 , (B) Fe^tBu_4 , (C) $\text{Fe}(\text{PhOMe})_4$ physisorbed on edge plane graphite (EPG) Vs pH of the buffer solution using Ag/AgCl as reference electrode and Pt as counter electrode.

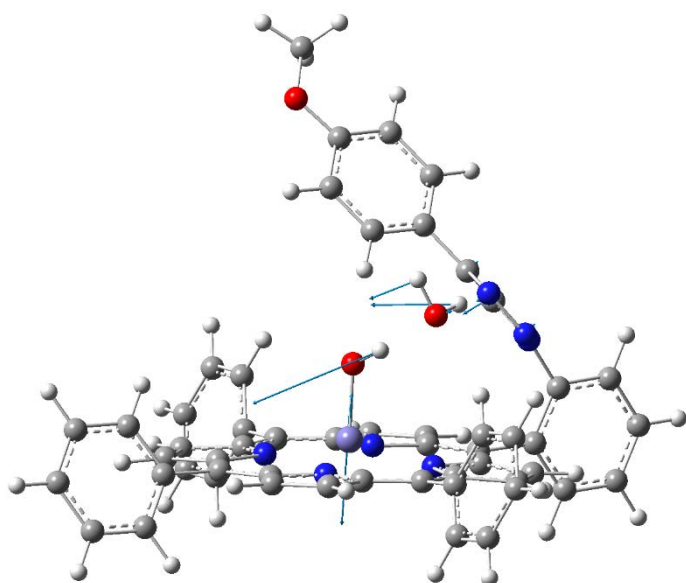


Figure S5: Representation of displacement vectors in Fe-OH stretching frequency of hydroxide complex of FePhOMe.

DFT optimised coordinate

(A) FePhOMe-OH complex

Fe	3.31298100	8.86799200	5.90199100
N	5.19735600	9.46218300	5.20937300
N	2.52243500	9.83634800	4.21289100
N	1.47228700	9.23571600	6.83107000
N	4.14521100	8.84203400	7.82763000
C	6.54470000	8.89072600	7.21377300
C	4.60055500	10.15359800	2.90423300
C	3.20541100	10.15717600	3.06165300
C	1.18756000	10.00784400	3.93582900
C	6.95097700	9.88932700	3.77200100
C	7.49098800	9.54503800	4.97281000
C	6.39168000	9.26951700	5.86768500
C	5.51618500	9.84465900	3.92603800
C	1.02314300	10.44680000	2.56885800
C	2.26979800	10.54620800	2.03142600
C	2.06394800	8.52891800	9.13064100
C	3.46117000	8.51203700	8.97416900
C	1.15655700	8.91350000	8.13195300
C	0.13049500	9.82913100	4.84328900
C	4.39452300	8.13039500	10.00825900

C	5.48295500	8.68534500	8.11148800
C	5.64260200	8.24296700	9.47788700
C	-0.81041700	9.39117900	7.13794500
C	-0.27045400	9.02671800	8.33092000
C	0.28144100	9.50804100	6.20001700
H	7.47212500	10.15780700	2.86481700
H	8.53706800	9.48895300	5.23559700
H	0.07916800	10.68183900	2.09709800
H	2.53920200	10.86888700	1.03622000
H	4.12438900	7.81479900	11.00534900
H	6.58682800	8.03467300	9.95923700
H	-1.85210200	9.56031600	6.90620700
H	-0.78287000	8.85009900	9.26514500
C	7.93865900	8.69107100	7.72586600
C	8.49471500	9.57799100	8.66128700
C	8.71772100	7.61130300	7.28067300
C	9.79328000	9.39119400	9.13805800
H	7.90370000	10.42085300	9.00875400
C	10.01574000	7.42326300	7.75815500
H	8.29517400	6.91478800	6.56194000
C	10.55791400	8.31289000	8.68810000
H	10.20814000	10.09130600	9.85860200
H	10.60162900	6.57837700	7.40560500
H	11.56873800	8.16676200	9.05950600
C	-1.26435000	9.93835700	4.29908500
C	-1.98009400	11.14194100	4.33335200
C	-1.89346300	8.82613100	3.70509300
C	-3.26282400	11.23761200	3.78853100
H	-1.51426000	12.01171600	4.78711200
C	-3.17272000	8.91081500	3.15677300
C	-3.85957900	10.12451800	3.19493800
H	-3.79412700	12.18449700	3.82651400
H	-3.62323700	8.02540400	2.71861600
H	-4.85714100	10.19516400	2.77147400
C	1.49501400	8.05162900	10.43136000
C	0.84965500	6.80497800	10.48486500
C	1.59246700	8.81666800	11.60284800

C	0.31540500	6.33821200	11.68693800
H	0.78382100	6.20684800	9.57911200
C	1.05590500	8.34791100	12.80382900
H	2.08508000	9.78472300	11.56700200
C	0.41622300	7.10745800	12.84874400
H	-0.17783200	5.37000300	11.71576400
H	1.13506900	8.95411300	13.70264700
H	-0.00109900	6.74247200	13.78362900
C	5.14965600	10.52402000	1.55899700
C	5.05524200	9.63263500	0.47901700
C	5.76425000	11.76862800	1.35096200
C	5.56368500	9.97615300	-0.77504900
H	4.58679200	8.66417300	0.63114000
C	6.27262800	12.11263900	0.09718400
H	5.83719300	12.46857900	2.17883400
C	6.17409100	11.21695700	-0.96963800
H	5.48625400	9.27125600	-1.59881600
H	6.74257800	13.08222300	-0.04602400
H	6.57035700	11.48408300	-1.94573500
O	3.20067600	7.11061800	5.53429000
C	-0.50683000	7.02156300	2.62749700
C	0.19155400	5.96870400	3.18262100
N	-1.19117300	7.57753100	3.66555800
N	-0.93857500	6.90845200	4.81258100
N	-0.11457000	5.94292300	4.52104400
O	1.45920900	5.35992300	6.85491000
H	0.81471400	5.45023100	6.11311500
H	1.86812800	4.49256900	6.71136800
H	-0.52462900	7.43786300	1.63299900
C	1.14143900	5.03490400	2.55601500
C	2.42516300	4.85614700	3.10775300
C	0.80162900	4.32572400	1.39967400
C	3.32476400	3.97893900	2.51794100
H	2.72674900	5.44721100	3.97057700
C	1.70305600	3.44433500	0.79735300
H	-0.18876000	4.44673200	0.96776700
C	2.97103000	3.26384200	1.36248300

H	4.32102100	3.84119000	2.92686700
H	1.40426700	2.90561600	-0.09467400
O	3.92925000	2.42775700	0.86579000
C	3.63228800	1.68621800	-0.30482800
H	3.41925000	2.34441500	-1.15808400
H	4.52451400	1.09527200	-0.52056200
H	2.77960100	1.01110400	-0.15124600
H	2.64623200	6.53656800	6.11324100

(B) FePhCN-OH complex

Fe	3.31785300	8.85113100	5.96869300
N	5.20428000	9.44712000	5.29008200
N	2.54395100	9.75035700	4.23483000
N	1.45398500	9.21446100	6.85088500
N	4.11322000	8.89525700	7.90684700
C	6.52317700	8.95056700	7.33327100
C	4.64136700	10.06714200	2.95601900
C	3.24374100	10.05227500	3.08796000
C	1.21179200	9.89083700	3.92766800
C	6.97817000	9.85842100	3.87269700
C	7.50072900	9.55338300	5.09162400
C	6.38926000	9.28830700	5.97430100
C	5.54168400	9.79908500	4.00236300
C	1.06658200	10.28983000	2.54660600
C	2.32190500	10.39690000	2.03041000
C	2.01315600	8.59845300	9.18475400
C	3.41302900	8.59610500	9.05262300
C	1.11879800	8.93121900	8.15632800
C	0.14060000	9.71682600	4.81936100
C	4.33252700	8.25905400	10.11393900
C	5.44789700	8.76179700	8.21835400
C	5.58822000	8.36593700	9.60075100
C	-0.83729700	9.33107600	7.10774300
C	-0.31375400	9.02106100	8.32331600
C	0.27052800	9.44049800	6.18800100

H	7.51189000	10.10924700	2.96784000
H	8.54244900	9.51787200	5.37433400
H	0.12825700	10.49821600	2.05136600
H	2.60537700	10.69843400	1.03247600
H	4.04866200	7.97366600	11.11625100
H	6.52606500	8.18274400	10.10413300
H	-1.87752600	9.47055400	6.85096200
H	-0.84114400	8.86659800	9.25309400
C	7.91006000	8.77995400	7.87408100
C	8.44078800	9.69658600	8.79543100
C	8.70752800	7.69748100	7.46974300
C	9.73282100	9.53560600	9.29858900
H	7.83580500	10.54215300	9.11084500
C	9.99895200	7.53541200	7.97372000
H	8.30498900	6.97811400	6.76209900
C	10.51587100	8.45419800	8.88951700
H	10.12828000	10.25838200	10.00749700
H	10.59934100	6.68818300	7.65281000
H	11.52160800	8.32839000	9.28144100
C	-1.24521500	9.77311900	4.24521300
C	-2.00124700	10.95214500	4.23853200
C	-1.82718100	8.62783900	3.66663600
C	-3.27723300	10.99043600	3.67096500
H	-1.57311000	11.84751100	4.67931600
C	-3.09903500	8.65365000	3.09676800
C	-3.82693000	9.84394200	3.09571500
H	-3.84069900	11.91922300	3.67743400
H	-3.51217000	7.74361200	2.67251800
H	-4.81925300	9.87073400	2.65548900
C	1.42851500	8.16123100	10.49252800
C	0.79515000	6.91046400	10.58094700
C	1.50092300	8.96826100	11.63739800
C	0.24774300	6.48078200	11.79089300
H	0.74900100	6.27996700	9.69622800
C	0.95110600	8.53659000	12.84622500
H	1.98427800	9.93958800	11.57454900
C	0.32334600	7.29178400	12.92585600

H	-0.23577300	5.50890600	11.84713200
H	1.01074600	9.17495400	13.72397100
H	-0.10407600	6.95569100	13.86692700
C	5.21027800	10.41097100	1.61181200
C	5.15715200	9.48745600	0.55644300
C	5.80410400	11.66163700	1.38136800
C	5.68586000	9.80522200	-0.69600100
H	4.70580600	8.51384600	0.72635000
C	6.33228200	11.98014100	0.12903200
H	5.84558900	12.38614300	2.19007300
C	6.27507800	11.05245600	-0.91319500
H	5.64146100	9.07538000	-1.50013300
H	6.78585300	12.95462200	-0.03220100
H	6.68740700	11.29956500	-1.88782100
O	3.23789800	7.07622100	5.65454100
C	-0.33220300	6.87155200	2.66151000
C	0.39375900	5.86045500	3.25654300
N	-1.07786300	7.40443100	3.66670000
N	-0.83969300	6.75646100	4.82954100
N	0.04124200	5.83064600	4.58257400
O	1.50350600	5.36397100	7.03620700
H	0.89667900	5.40318500	6.26126500
H	1.91344200	4.48728400	6.97879800
H	-0.33058800	7.27806900	1.66276100
C	1.41969900	4.97777300	2.67627400
C	2.68259900	4.88211600	3.28652300
C	1.15809800	4.24792500	1.50604400
C	3.65796400	4.05527100	2.73798200
H	2.91089600	5.49947500	4.15494700
C	2.13171000	3.42344100	0.95262300
H	0.17947700	4.31427600	1.03889600
C	3.38922900	3.31845800	1.57092100
H	4.63743600	3.98752700	3.20076800
H	1.92590400	2.85425100	0.05183000
C	4.39592600	2.46787300	1.00568500
N	5.21119600	1.77745100	0.54461400
H	2.69942600	6.52232800	6.26658700

(C) Fe^tBu-OH complex

Fe	3.37141800	8.92105200	5.91090900
N	5.24978200	9.56712800	5.25082300
N	2.58709700	9.84419100	4.19361400
N	1.50105900	9.22151200	6.79770400
N	4.16370100	8.93469500	7.85376500
C	6.57220400	9.03188200	7.28196900
C	4.68042700	10.24580300	2.93405100
C	3.28238100	10.19116300	3.05772600
C	1.25315900	9.94674700	3.88263000
C	7.01921800	10.04850600	3.85053500
C	7.54453900	9.71141500	5.05991100
C	6.43555600	9.40435700	5.93207400
C	5.58327700	9.96412900	3.97526800
C	1.10064100	10.36763700	2.50887700
C	2.35432700	10.52859300	2.00233700
C	2.06654500	8.58998800	9.12492100
C	3.46670100	8.60851800	8.99374900
C	1.16773900	8.91568500	8.09742000
C	0.18522400	9.72017600	4.76610600
C	4.39052400	8.26284900	10.04935700
C	5.49942900	8.81099500	8.16267800
C	5.64473200	8.39108300	9.53779000
C	-0.79378400	9.27134800	7.04232500
C	-0.26776000	8.96702700	8.25812600
C	0.31582300	9.42001200	6.12958600
H	7.55118300	10.33478000	2.95518100
H	8.58641200	9.68084200	5.34287100
H	0.15804000	10.55082400	2.01194700
H	2.63133400	10.85975700	1.01201700
H	4.11047000	7.95631600	11.04647200
H	6.58456500	8.20838800	10.03773800
H	-1.83605900	9.38479300	6.78163700
H	-0.79621900	8.79104200	9.18335900
C	7.96109300	8.86180200	7.81801300

C	8.48584600	9.76273500	8.75808800
C	8.76710200	7.79505600	7.38957200
C	9.77990000	9.60179900	9.25613700
H	7.87414900	10.59609100	9.09248100
C	10.06062200	7.63296900	7.88824100
H	8.36900600	7.08795700	6.66719200
C	10.57140700	8.53606800	8.82292300
H	10.17029800	10.31239400	9.98006800
H	10.66758600	6.79778800	7.54844600
H	11.57873300	8.41021700	9.21086500
C	-1.20267900	9.76526500	4.19857600
C	-1.94477300	10.95295600	4.15496600
C	-1.80543700	8.60191800	3.68472500
C	-3.23449600	10.98056100	3.62000500
H	-1.49724400	11.86113000	4.54787800
C	-3.09383300	8.61844100	3.15030900
C	-3.81166300	9.81388200	3.11628900
H	-3.78831100	11.91502400	3.59895200
H	-3.52383400	7.69520600	2.77437000
H	-4.81583900	9.83076300	2.70299800
C	1.48707700	8.13230500	10.42762500
C	0.84298300	6.88555900	10.49759600
C	1.57412000	8.91673000	11.58731300
C	0.30055600	6.43802500	11.70326100
H	0.78340300	6.27403600	9.60043500
C	1.02956000	8.46707700	12.79190200
H	2.06463700	9.88528000	11.53908200
C	0.39171000	7.22637800	12.85298700
H	-0.19177600	5.46975500	11.74464000
H	1.10067300	9.08859500	13.68086000
H	-0.03197200	6.87628600	13.79068600
C	5.24640000	10.64736800	1.60505300
C	5.19313100	9.77179800	0.50941200
C	5.83701600	11.90834800	1.42742500
C	5.71703700	10.14586100	-0.72937100
H	4.74376500	8.79081200	0.63724300
C	6.36138200	12.28307200	0.18920500

H	5.87840200	12.59692500	2.26688200
C	6.30319700	11.40264700	-0.89315000
H	5.67094400	9.45248100	-1.56517000
H	6.81190100	13.26503800	0.07011800
H	6.71168200	11.69384800	-1.85719700
O	3.29646800	7.16212200	5.54512700
C	-0.26727700	6.84797700	2.74507600
C	0.29579200	5.72492100	3.31357500
N	-1.07731100	7.36636400	3.70912200
N	-1.02495000	6.61418800	4.82924500
N	-0.20294500	5.62776000	4.58703700
O	1.47016400	5.50791400	6.97631800
H	0.79978700	5.44242700	6.25873300
H	1.88454400	4.63232800	7.00249800
H	-0.14704200	7.32527400	1.78640100
H	2.70427500	6.60017500	6.09517800
C	1.25407400	4.70909200	2.72544600
C	0.48173100	3.39945100	2.44087300
H	-0.32134200	3.56174700	1.71200300
H	1.15950800	2.63732300	2.03723200
H	0.03074800	3.00689200	3.35840600
C	2.40113600	4.42756400	3.71955300
H	2.92128700	5.34719600	4.00850200
H	2.01605900	3.95959300	4.63162800
H	3.12189600	3.73485500	3.26821800
C	1.84461100	5.25345100	1.41061200
H	2.53597700	4.52105200	0.97897700
H	1.06366400	5.44782600	0.66485900
H	2.39978000	6.18300300	1.58039900

(D) FePf-OH

Fe	3.28370900	8.93095500	5.71050300
N	5.19287000	9.52462200	5.10681200
N	2.55673600	10.01765600	4.08816800
N	1.42313000	9.23732900	6.63353000

N	4.06571400	8.73043600	7.64107500
C	6.47981700	8.73264700	7.07193600
C	4.66613300	10.48406200	2.88138700
C	3.26653700	10.46883300	2.99896900
C	1.22546800	10.13665000	3.76376100
C	6.98828200	10.02701600	3.74687300
C	7.49212000	9.52307200	4.90569100
C	6.36629600	9.21299900	5.75573800
C	5.54966300	10.03285400	3.87802700
C	1.09165400	10.68878100	2.43575000
C	2.35121300	10.91317300	1.97202500
C	1.96271200	8.52739200	8.94427000
C	3.36098400	8.47190000	8.79674000
C	1.06932100	8.87601400	7.91444600
C	0.13943200	9.80500300	4.59280900
C	4.27384800	8.11765200	9.85681900
C	5.39716300	8.54351400	7.94763500
C	5.52778100	8.14551100	9.32911500
C	-0.87738500	9.16317200	6.80717700
C	-0.37259000	8.83848100	8.02929400
C	0.24938500	9.41626100	5.93911200
H	7.53494500	10.36923300	2.88055600
H	8.52949400	9.38420600	5.17227700
H	0.15308800	10.89990200	1.94378100
H	2.64115200	11.34043000	1.02330300
H	3.98672100	7.87766500	10.86998800
H	6.46041100	7.92892100	9.82872400
H	-1.91463600	9.23940400	6.51449600
H	-0.91859000	8.59185700	8.92841600
C	7.85804800	8.44078300	7.58568600
C	8.47487600	9.28945500	8.51794400
C	8.56041700	7.31265700	7.13462600
C	9.75994800	9.01558200	8.98931000
H	7.94326300	10.17034900	8.86721000
C	9.84534700	7.03847500	7.60630100
H	8.09047900	6.64777700	6.41524500
C	10.44865300	7.88892200	8.53511600

H	10.22388900	9.68559000	9.70838500
H	10.37303100	6.15793900	7.24947900
H	11.44901200	7.67553600	8.90201200
C	-1.23257800	9.83284600	3.98569300
C	-2.04291000	10.96681500	4.10001800
C	-1.72342700	8.69746100	3.29250000
C	-3.32262700	11.00136300	3.54541400
H	-1.65329300	11.82953500	4.63384000
C	-3.01279200	8.73312900	2.73541800
C	-3.79645200	9.87892100	2.86633800
H	-3.93714600	11.89164400	3.64346900
H	-3.37886800	7.86198900	2.21177800
H	-4.79101500	9.88681600	2.42797300
C	1.38247000	8.15465500	10.27617200
C	1.36772000	6.81498200	10.69731500
C	0.83974000	9.13454100	11.12107000
C	0.82508200	6.46655100	11.93541900
H	1.77526300	6.04842100	10.04288500
C	0.29865700	8.78502300	12.35959600
H	0.85006200	10.17393200	10.80448300
C	0.29068500	7.45030400	12.77023900
H	0.81792900	5.42495900	12.24558900
H	-0.11364600	9.55661900	13.00440200
H	-0.13036500	7.17846900	13.73444000
C	5.25569400	11.00447500	1.60539100
C	5.15568000	10.26551100	0.41626800
C	5.91815300	12.24153200	1.57469400
C	5.70333800	10.75111900	-0.77228900
H	4.65133400	9.30332500	0.43039100
C	6.46540400	12.72744200	0.38602900
H	5.99655300	12.82459900	2.48821100
C	6.35940100	11.98366500	-0.79106000
H	5.61975100	10.16354000	-1.68272200
H	6.97098400	13.68949200	0.37999100
H	6.78518600	12.36188800	-1.71652400
O	3.03251500	7.23310600	5.14428100
O	2.00642200	5.61774000	7.29174000

H	1.61047500	6.44607000	7.61250400
H	1.26452100	5.12448700	6.90769700
H	2.86180000	6.53226000	5.80641100
N	-0.88030900	7.57079100	3.20057700
H	0.03470000	7.69223700	3.61544900
C	-1.12655500	6.34470800	2.61559700
C	0.03319100	5.32309200	2.73867400
C	-0.34110400	4.08204100	1.91169300
H	-0.45832900	4.33483300	0.85338500
H	0.44764600	3.32638500	2.00233600
H	-1.28569500	3.64858400	2.25084100
C	1.36197100	5.91732500	2.21530000
H	1.78221600	6.67934600	2.88086000
H	2.11259000	5.12101100	2.14899900
H	1.23851300	6.34498800	1.21360600
C	0.19491600	4.92306400	4.22537400
H	0.94568800	4.12787100	4.31046400
H	0.53946200	5.76665300	4.83356100
H	-0.74928100	4.54756100	4.63773900
O	-2.18157800	6.06707600	2.05864900