Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Hydrogen Atom Abstraction by a synthetic heme Ferric Superoxide and Hydroperoxide Species

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1.1 Experimental details:

1.1.1 Synthesis of Fe porphyrin complex:

The iron porphyrin complex ($FeQH_2$ in Figure 1E) is synthesized as reported previously.[1] First o-amino tetraphenyl porphyrin was synthesized following reported procedure. The hydroxyl groups of 2,5-dihydroxy benzoic acid were blocked by performing acetylation of hydroxyl groups using acetic anhydride and pyridine. It is now reacted with thionyl chloride under argon atmosphere in THF followed by addition of o-amino tetraphenyl porphyrin, which leads to formation of porphyrin macrocycle with a tethered acetylated hydroquinone ring through an amide linkage. Hydrolysis of acetyl group by stirring the porphyrin with 4% HCl-MeOH mixture for 3-4 hours generates porphyrin ring with a hydroquinone moiety attached to it. It was characterised by recording mass spectra (Figure S1, S.I). It was then metalated with $FeBr_2$ in dry degassed THF under argon atmosphere. An acidic work-up with HCl-H_2O followed by column chromatography in 60-120 silica gel were performed to obtain pure $Fe^{III}QH_2$ (Scheme S1, S.I). The final product was then characterised using mass spectroscopy (Figure S2, S.I). Anal Calcd for $C_{63}H_{61}ClFeN_5O_3$: C, 73.64; H, 6.98; N, 6.82. Found C, 74.34; H, 5.54; N, 6.47.

1.1.2 Preparation and spectroscopic investigation of intermediates:

All solvent used in this investigation was dried and degassed (three cycles of freeze-pump-thaw) before use. All the preparation and reactions were performed inside a N_2 glove box or in air tight sample holders. To prepare 1mM solutions of the metallo-porphyrin, 0.819 mg portion of $FeQH_2$ complex was dissolved in 1 mL of dry degassed dichloromethane (DCM) or THF solvent. A 2.4 mg portion of Na_2S was dissolved in methanol, so that the final strength of the solution was 10 mM. To this 0.5 equivalent (generally ~10 µl solution) of Na_2S was added at room temperature to reduce ferric porphyrin to its ferrous state. 200 µl of this 1 mM $Fe^{II}QH_2$ solution was taken in 3 EPR tubes. O_2 gas was bubbled to this sample tubes at -80 °C and kept at low temperature and was frozen in liq. N_2 at different times (3 mins, 13 mins, 20 mins etc.). These samples are then characterized with Resonance Raman at 77 K and EPR at 77 K and 4 K. Both in DCM and THF the complex show similar reactivity towards O_2, though in THF the kinetics is slower than that in DCM. The ferric superoxide species is characterised in THF by recording resonace Raman spectroscopy, while for other two intermediates ferric heme hydroperoxide and ferryl species, resonance Raman data

were collected in DCM at -80 °C. This is because, in THF there is a huge background from solvent in the range 700-900 cm^{-1} region (S1, S.I). Thus, samples were prepared in DCM for characterisation of ferric heme hydroperoxide and ferryl species using resonance Raman spectroscopy. In THF the ferric superoxide is formed after an incubation time of 1-2 minutes at -80ºC in presence of oxygen. When the sample is kept for 3-4 minutes at -80ºC Fe^{III}-OOH[SQ] species started forming and the population of the species gets maximised at 13 minutes in THF. In DCM the kinetics of the reaction is faster. When the sample is kept for 2-3 min in DCM at -80ºC both ferric hydroperoxo and ferryl species along with some amount of ferric superoxide species have been observed.

1.1.3 Kinetic Measurements

The time traces for kinetic measurements are performed by following the EPR signal intensity with time. For kinetic study in EPR solvent THF was used. The EPR signal is quantified against a 1mM $CuSO_4$ standard. The H/D isotope KIE is obtained by replacing the source of proton MeOH with CH_3OD.

1.2 Resonance Raman

The resonance Raman data are collected at 77 K in a finger Dewar unless otherwise indicated. The data are generally collected over 10-20 mins with ~10 mW power at the sample at 413.1 nm. Generally, 3 scans are obtained, and the signals are averaged.

1.3 Computational details:

All calculations were performed at the IACS Inorganic HPC cluster using Gaussian 03 software. B3LYP functionals[2, 3] were used to obtain the optimized geometries and frequencies. A mixed basis set with 6-311 g* on the Fe, N and S atoms and 6-31g* on the C and H atoms were used for optimization and frequency calculations. Negative frequencies were found for the structures of transition state reported. Final energies were calculated using 6-311+g* basis set on all atoms. PCM model was used for solvent correction of energies.

2. Results:

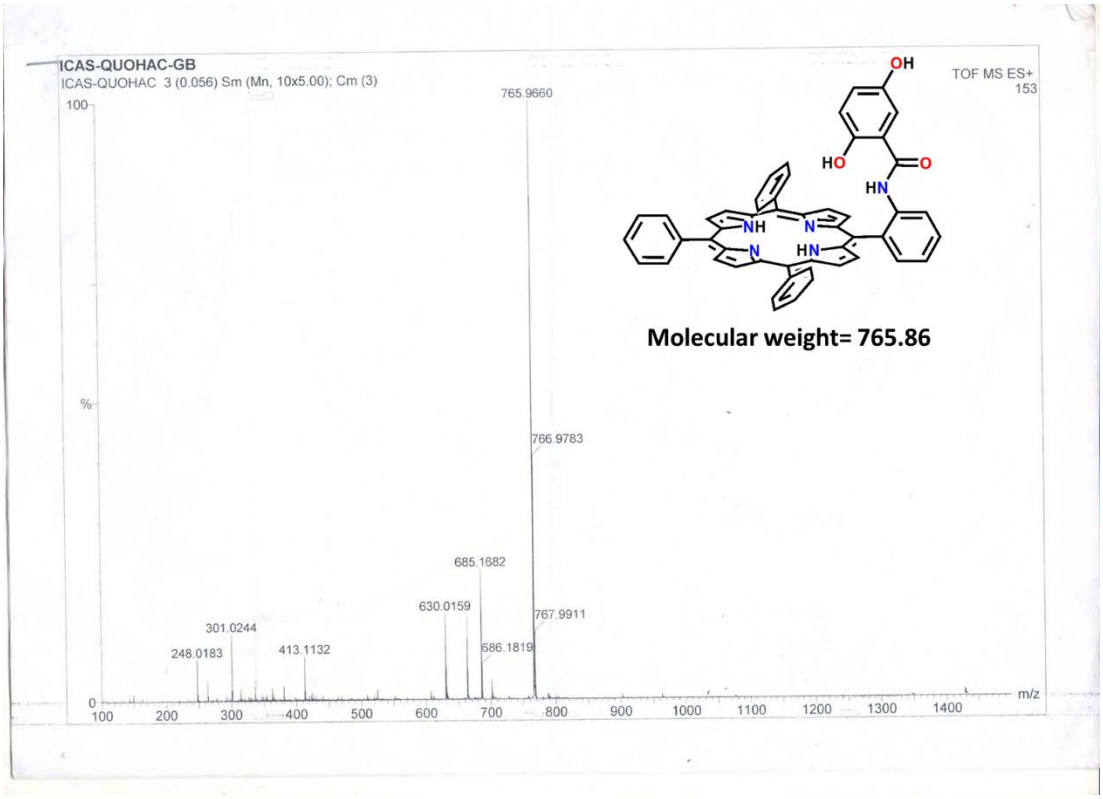


Figure S1: Mass spectra of metal free porphyrin macrocycle with a hydroquinone ring attached to it.

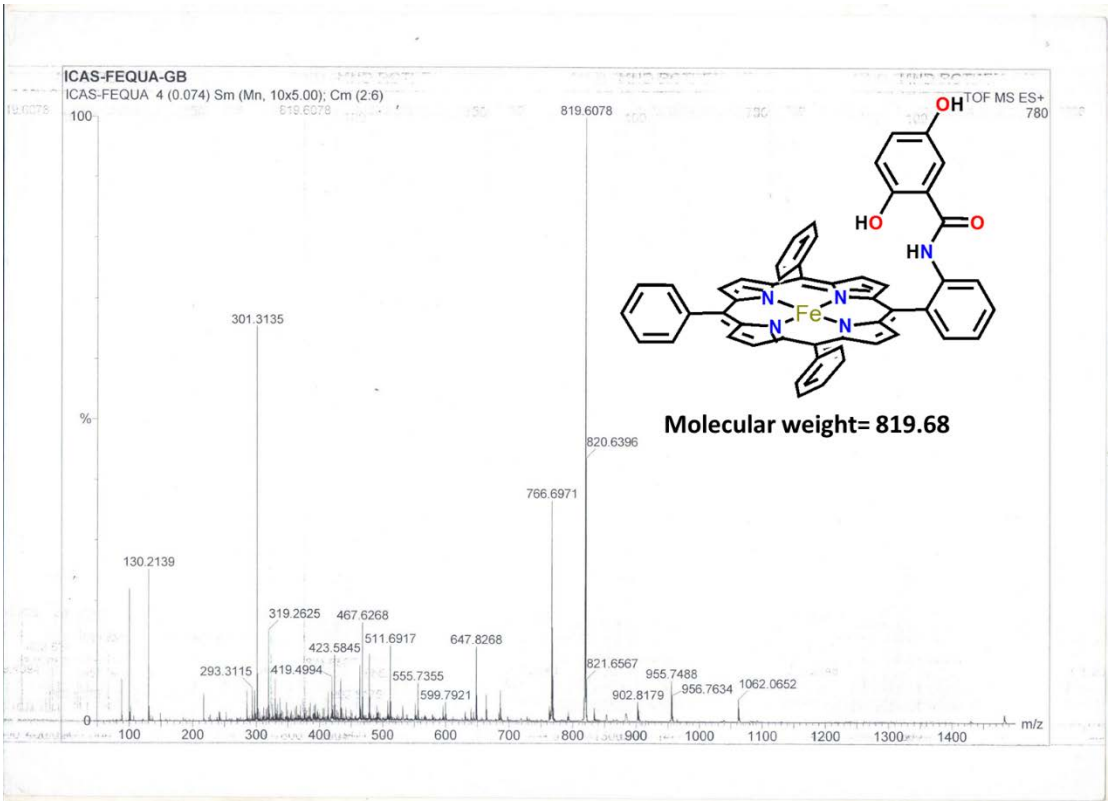
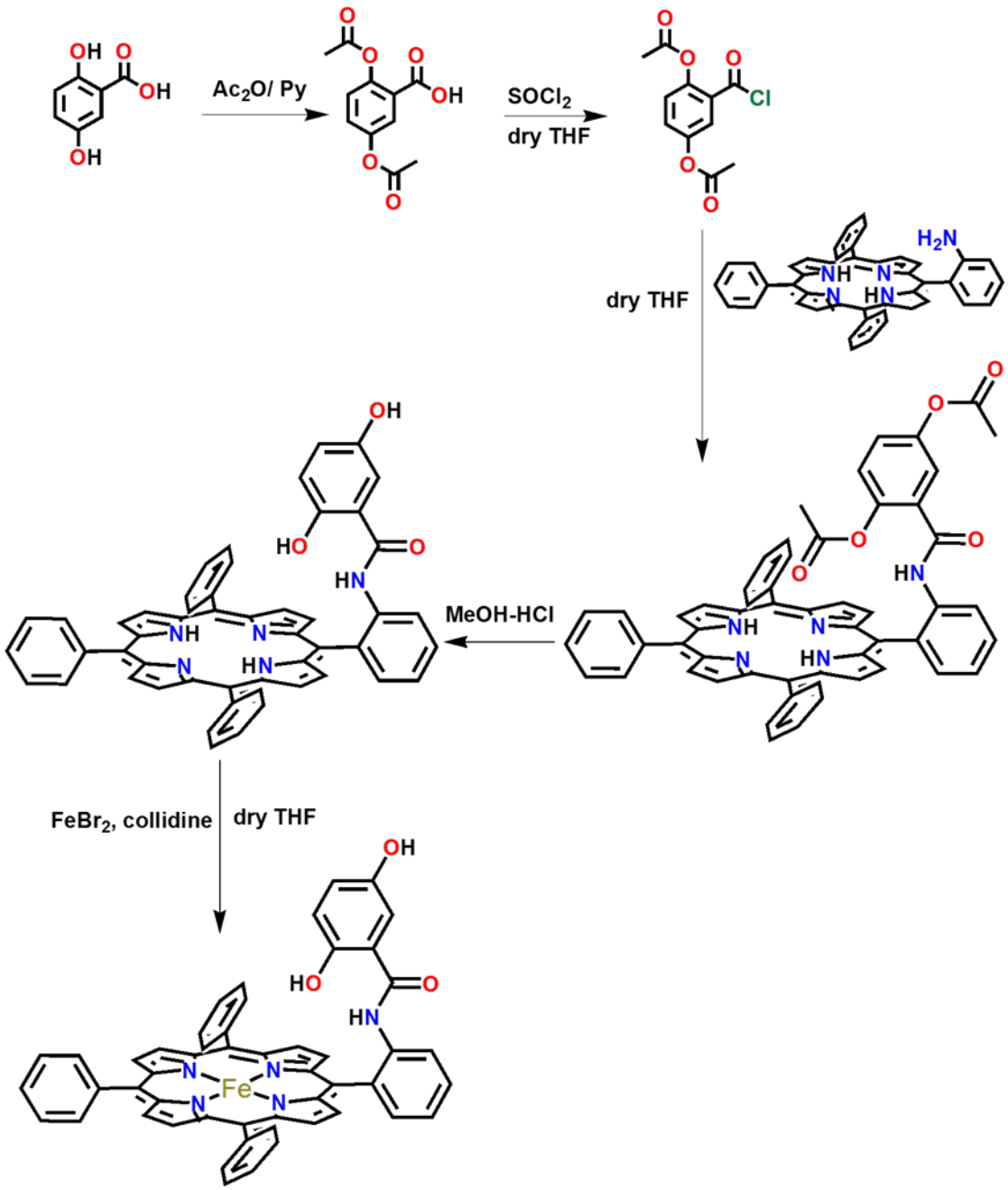


Figure S2: mass spectra of metallated porphyrin $FeQH_2$.



Scheme S1: schematic representation of synthesis of $FeQH_2$ complex.

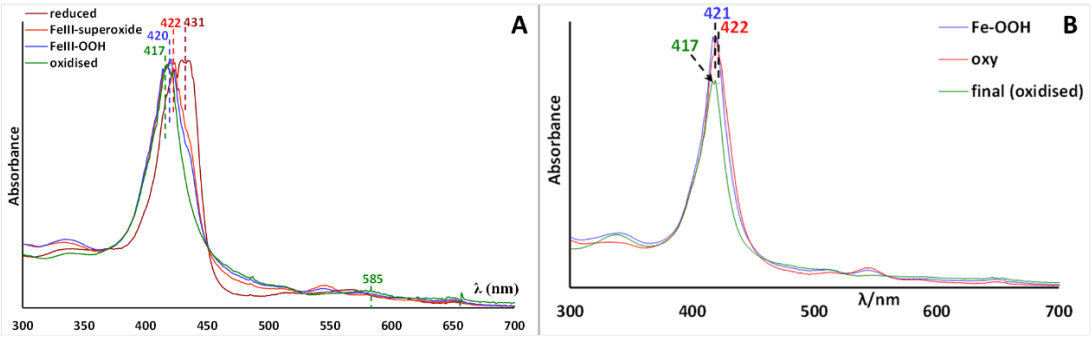


Figure S3: UV-Vis absorption spectra of (A) concentrated solution and (B) dilute

solution of reduce FeQH2 (in red), ferric superoxide intermediate (in orange), ferric hydroperoxide intermediate (in blue) and oxidised ferric porphyrin (in green).

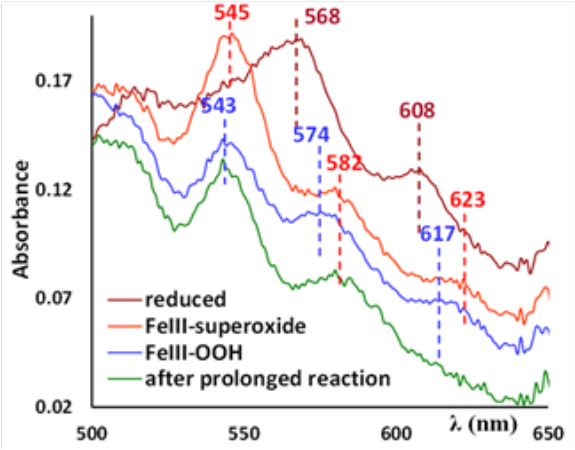


Figure S4: Absorption spectral change of Q band of Fe porphyrin upon addition of O_2 to ferrous porphyrin. Absorption spectra of Fe^{II}-QH_2 (in red), Fe^{III}-$OO^{\cdot-}$-QH_2 (in orange), and Fe^{III}-OOH-SQ (in blue). The green trace represents the absorption spectra after prolonged reaction.

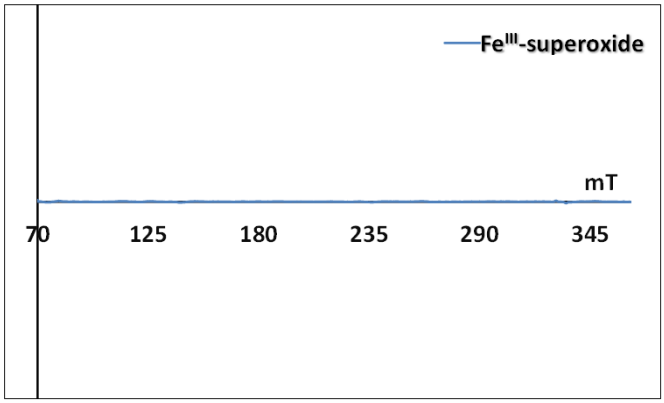


Figure S5: EPR spectra of 6C ferric superoxide complex of $FeQH_2$ recorded at 77K.

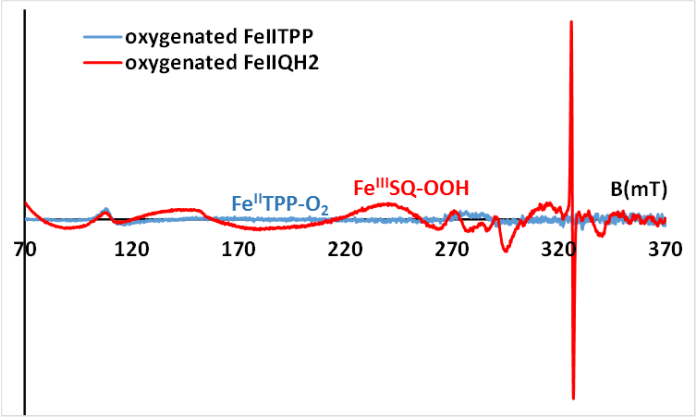


Figure S6: EPR spectra of Fe^{III}-OOH-SQ species (in red) and solution of Fe^{II}TPP after addition of hydroquinone and O_2 at -80ºC (in blue) recorded at 77K.

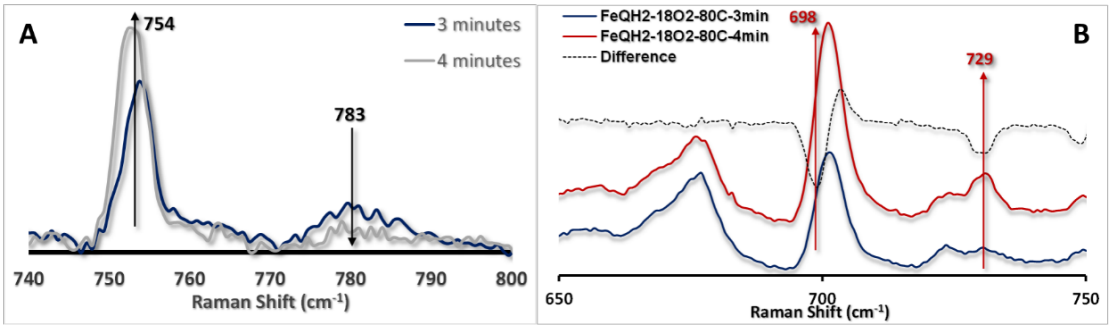


Figure S7: (A) Resonance Raman data of $FeQH_2$ after addition of $^{16}O_2$ at -80℃. The band at 783 cm^{-1} decays with time and a band at 754 cm^{-1} grows in simultaneously. (B) Resonance Raman data of $FeQH_2$ after addition of $^{18}O_2$ at -80ºC. The intensity of the peaks at 729 and 698 cm^{-1} increases with time.

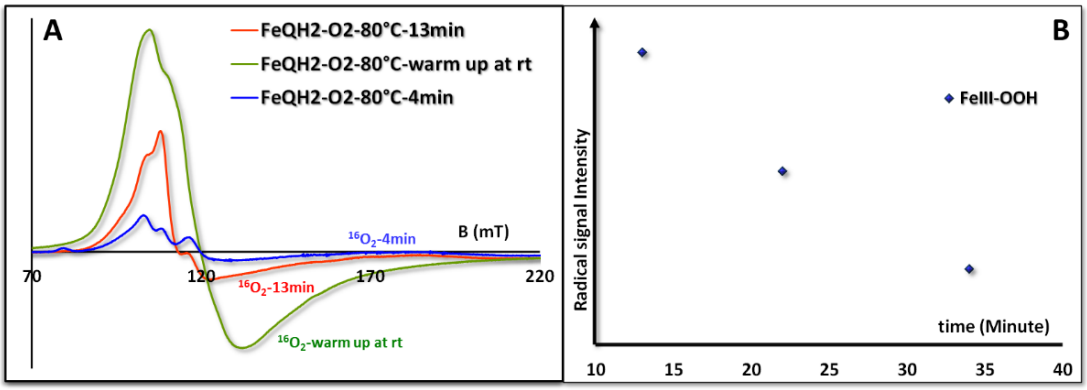


Figure S8: (A) Growth of Fe^{III} high spin signal with time when the oxygenated $FeQH_2$ is kept at -80°C for 4min (in blue), 13 min (in orange) and finally the sample is warmed up at room temperature (in green). (B) Decay of radical signal of Fe^{III}-OOH[SQ] species with time

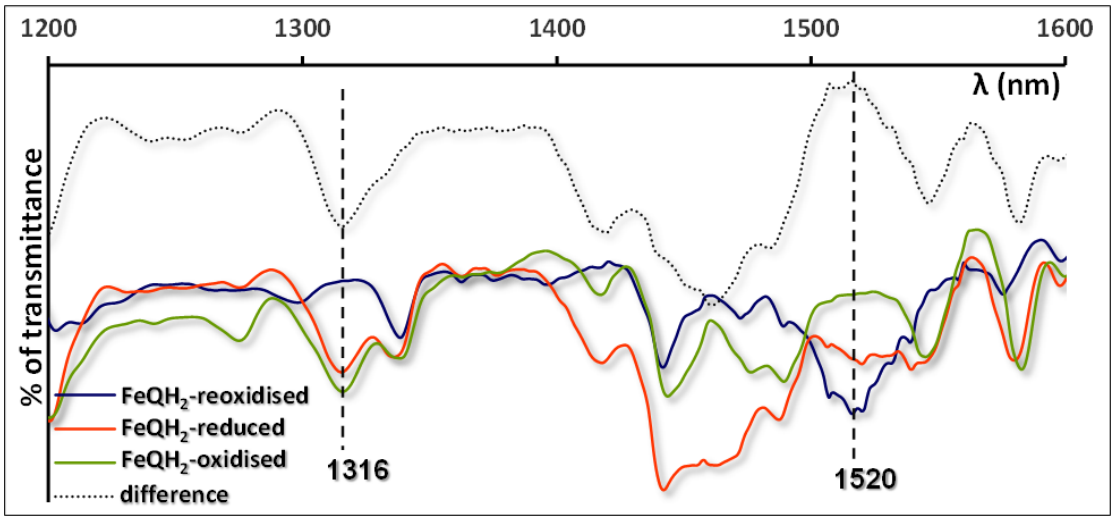


Figure S9: IR spectra of resting state of oxidised $FeQH_2$ (in green), reduced form of

$FeQH_2$ (in red) and final product after reduction of oxygen by $FeQH_2$ (in blue) recorded at room temperature.

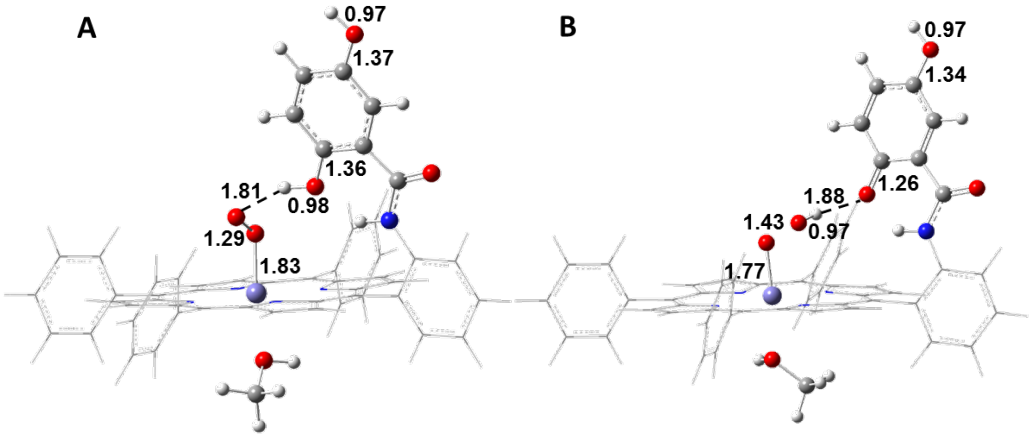


Figure S10: DFT optimised structure of ^{1}I (A) and ^{3}II (B)

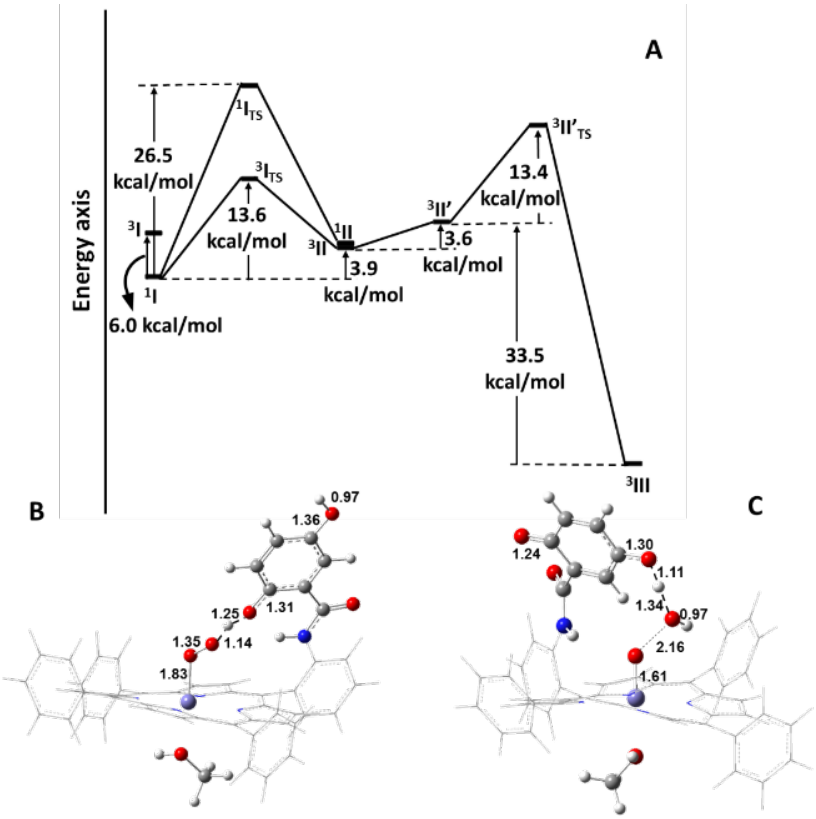


Figure S11: (A) Energy profile diagram of formation of Fe^{III}-hydroperoxide (intermediate II) and Fe^{IV}-oxo (intermediate III) from Fe^{III}-superoxide (intermediate I) complex via 2 consecutive HAT's from hydroquinone group. DFT optimised structure of $^3I_{TS}$ (B) and $^3II_{TS}$' (C).

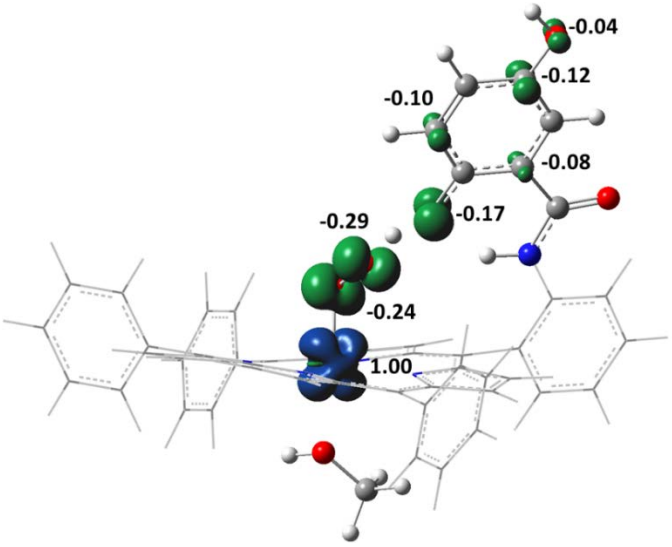


Figure S12: spin density plot of $^{1}I_{TS}$

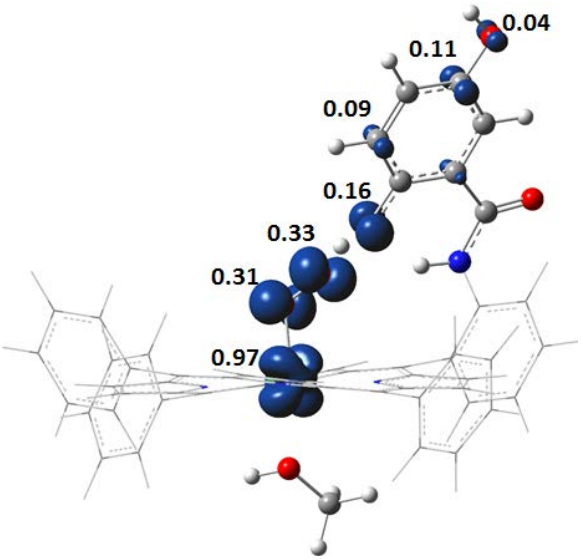


Figure S13: DFT calculated spin density plot of $^{3}I_{TS}$

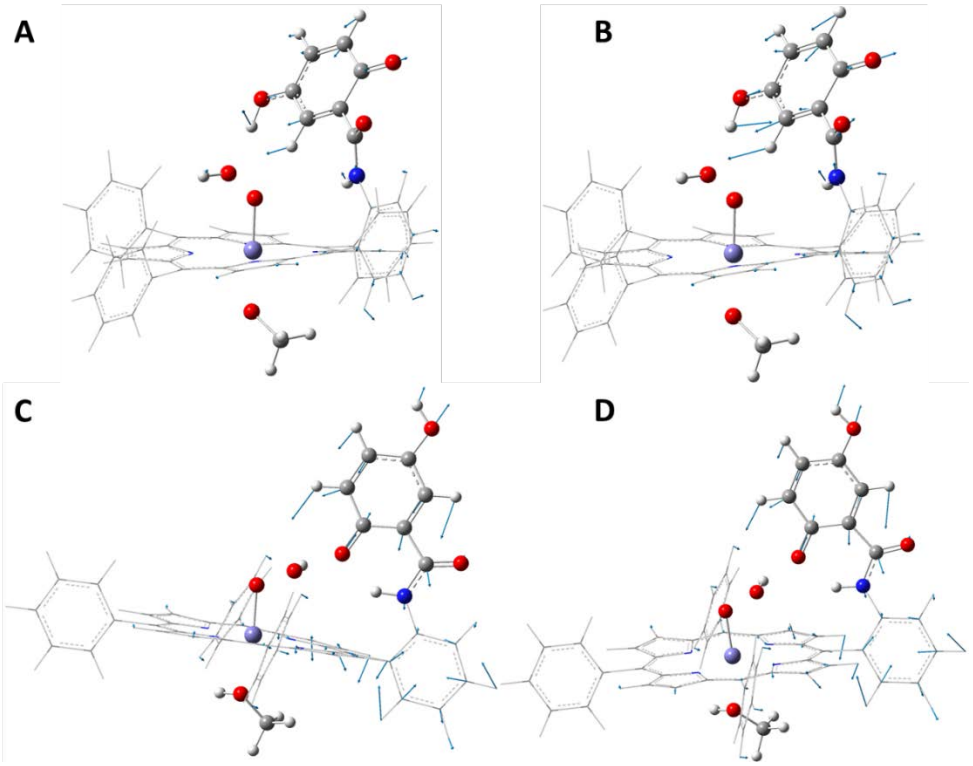


Figure S14: Representation of displacement vector of the frequency involving asymmetric stretching frequency of C-O bonds of semiquinone ring in (A) ^{3}II', (B) deuterated ^{3}II', (C) ^{3}II, and (D) deuterated ^{3}II intermediates.

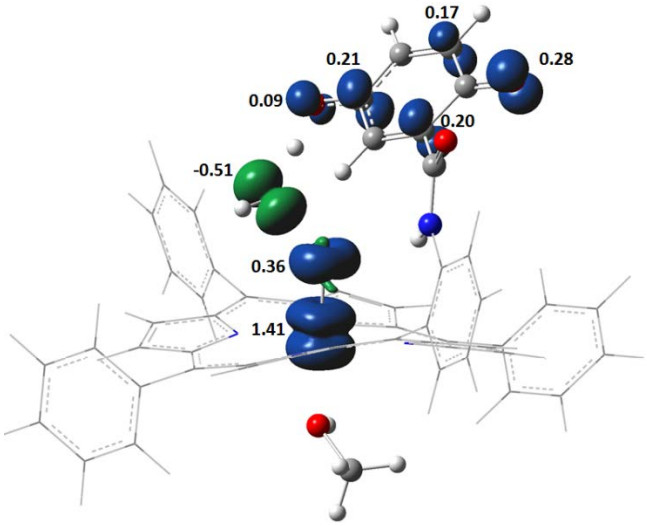


Figure S15: DFT calculated spin density plot of $^{3}II_{TS}$'

3. Optimised coordinates:

1) B3LYP optimised structures of ^{1}I:

Fe	3.47737700	9.43330400	5.94534500
N	5.32321100	9.80382400	5.23867900
N	2.71998700	9.99835200	4.15167100
N	1.61747600	9.18467200	6.65976100

N	4.21670900	9.02858500	7.75458800
C	6.63556600	9.29514700	7.27719600
C	4.80933900	10.42400500	2.89467700
C	3.42033800	10.30901300	3.00104100
C	1.38697100	9.99409200	3.78692300
C	7.11194800	10.34171800	3.87427800
C	7.61864600	10.04273600	5.09814000
C	6.50216600	9.69175900	5.94200200
C	5.68031400	10.19820000	3.96687500
C	1.25302700	10.33153800	2.39248900
C	2.50741400	10.53086300	1.90878800
C	2.13157300	8.46796800	8.97182300
C	3.52243800	8.57952800	8.86048500
C	1.25511700	8.77341100	7.92573500
C	0.30038800	9.71426800	4.62219200
C	4.44067500	8.22431900	9.91190700
C	5.55037800	8.96526800	8.09763500
C	5.69264000	8.46593800	9.44246100
C	-0.68690500	9.07616700	6.82894400
C	-0.18124000	8.71994000	8.03865600
C	0.43632600	9.35061900	5.96785400
H	7.64785900	10.63667900	2.98448700
H	8.65218300	10.05142700	5.41059700
H	0.31346800	10.40355000	1.86455700
H	2.79868200	10.80349200	0.90526700
H	4.15589600	7.82873900	10.87539600
H	6.63425900	8.30503300	9.94600800
H	-1.72274600	9.14992800	6.53124600
H	-0.72254800	8.44952100	8.93299000
O	3.36939100	11.47711900	6.40977300
C	2.64759300	12.03604900	7.51942800
H	2.85682000	13.10878400	7.58790300
H	3.02010600	11.53259100	8.41044900
H	1.57138200	11.86225100	7.42598100
H	3.05546200	11.86733900	5.57662700
C	8.01402800	9.20016600	7.85595100
C	8.44531600	10.11131800	8.83271500
C	8.90140000	8.19654600	7.43601100
C	9.72922900	10.02361900	9.37330700
H	7.76831900	10.89454400	9.16265500
C	10.18503100	8.10786800	7.97691500
H	8.57545700	7.48034400	6.68693300
C	10.60318200	9.02155400	8.94665600
H	10.04720100	10.74104500	10.12528300
H	10.85655900	7.32130600	7.64295000
H	11.60270900	8.95266900	9.36745300
C	-1.08376700	9.81973400	4.04507300
C	-1.68818700	11.07966500	3.96385700
C	-1.79198600	8.68226300	3.57478600
C	-2.96841300	11.24423800	3.43688100
H	-1.13404400	11.94176800	4.32628600
C	-3.08362200	8.85271400	3.04184700
C	-3.65670900	10.12100600	2.97867800
H	-3.41750500	12.23205800	3.38648900
H	-3.61407300	7.98217600	2.68528800
H	-4.65560500	10.22517100	2.56284900

C	1.55503700	7.98276200	10.26561400
C	0.93990500	6.72307700	10.34400400
C	1.61840700	8.77168800	11.42497300
C	0.40279000	6.26623300	11.54846600
H	0.89251200	6.10061500	9.45499600
C	1.08097900	8.31535600	12.62958200
H	2.08826200	9.75037000	11.37657100
C	0.47129600	7.06084000	12.69481400
H	-0.06577900	5.28661000	11.59090800
H	1.13564800	8.94233700	13.51568800
H	0.05275000	6.70487800	13.63232000
C	5.39178600	10.80033200	1.56561100
C	5.42411100	9.87337600	0.51236200
C	5.91340700	12.08470300	1.34713000
C	5.96320900	10.22250800	-0.72708300
H	5.02746400	8.87466600	0.67233100
C	6.45397700	12.43379000	0.10826200
H	5.89060700	12.81201900	2.15426800
C	6.47993900	11.50340500	-0.93262800
H	5.98193800	9.49123300	-1.53078800
H	6.85091400	13.43407900	-0.04379700
H	6.89968100	11.77479000	-1.89751300
O	3.57062900	7.71125700	5.33155000
O	3.17236000	6.76212300	6.12354300
N	-1.16072200	7.43094100	3.66582500
H	-0.22277500	7.42656000	4.05711700
C	-1.65682600	6.19461100	3.30837300
C	-0.76416300	5.00471500	3.57775800
C	0.53794700	5.03637200	4.12828100
C	-1.32418100	3.75972400	3.26031900
C	1.22531600	3.84016600	4.35637900
C	-0.63604300	2.57068700	3.48455300
H	-2.32178300	3.73901100	2.83769000
C	0.64562500	2.61369000	4.04197100
H	2.22564100	3.87925900	4.78036800
H	1.19681500	1.69342900	4.22830500
O	1.11519100	6.23798500	4.41359500
H	1.92974400	6.14581000	4.95620300
O	-1.26212400	1.39642100	3.14684700
H	-0.67085200	0.65671600	3.35397500
O	-2.76915600	6.03105700	2.81001200

2) B3LYP optimised structure of ^{3}I:

Fe	3.46151600	9.45693900	5.93129900
N	5.31578100	9.87805700	5.26783400
N	2.72199000	10.05421200	4.16378900
N	1.60088500	9.17057900	6.62080300
N	4.19900000	8.94478300	7.71008500
C	6.62385500	9.07971400	7.21316900
C	4.80581100	10.71572700	2.99270600
C	3.42402000	10.50940700	3.06245800
C	1.40278800	9.97561300	3.75867800
C	7.11285500	10.49554700	3.94611600
C	7.61919600	10.01343900	5.11212000
C	6.49936700	9.61912400	5.92876400

C	5.67908500	10.39628600	4.03860200
C	1.28112600	10.39022900	2.38525900
C	2.52486800	10.74152400	1.96288900
C	2.09705200	8.52857600	8.95604000
C	3.49069700	8.55671400	8.82653300
C	1.22778100	8.81541300	7.90031500
C	0.30891900	9.60995600	4.55218200
C	4.39390400	8.12769300	9.86301200
C	5.52874700	8.77645700	8.03000700
C	5.65301700	8.25229500	9.36697700
C	-0.70354200	9.00909400	6.76047600
C	-0.21059200	8.74232600	7.99712600
C	0.42841700	9.27054300	5.90498700
H	7.65278000	10.87303300	3.09039500
H	8.65593700	9.92933800	5.40279400
H	0.35501300	10.41693200	1.83041800
H	2.81731600	11.11314300	0.99214100
H	4.09302500	7.75991800	10.83265300
H	6.58664200	8.01006200	9.85255500
H	-1.73552100	9.04098600	6.44277100
H	-0.75985400	8.50978500	8.89716900
O	3.45448600	11.45282900	6.58865600
C	2.29812200	12.30759600	6.61496700
H	2.57593700	13.28408700	7.02496200
H	1.57387500	11.82779300	7.27110200
H	1.86720700	12.42297100	5.61537000
H	4.15167700	11.85865700	6.04727800
C	8.00278800	8.82734700	7.74271500
C	8.54899500	9.63944500	8.74878300
C	8.77715700	7.77201800	7.23610200
C	9.83530500	9.40228100	9.23651500
H	7.96021300	10.46248400	9.14460600
C	10.06298100	7.53384800	7.72443600
H	8.36142500	7.13474500	6.46065200
C	10.59585500	8.34846000	8.72570900
H	10.24361200	10.04324100	10.01351000
H	10.64659500	6.70912900	7.32400100
H	11.59697500	8.16312000	9.10556300
C	-1.06448700	9.65434500	3.94329800
C	-1.68830500	10.89831100	3.78234700
C	-1.75198600	8.48096000	3.53424400
C	-2.96614900	11.01290000	3.23787300
H	-1.15128500	11.78838100	4.10003000
C	-3.04297700	8.60158700	2.98533600
C	-3.63524700	9.85417500	2.84400100
H	-3.42921600	11.98933900	3.12755600
H	-3.55908700	7.70340800	2.68027900
H	-4.63285100	9.91790500	2.41706100
C	1.51485400	8.12351600	10.27500000
C	0.86667600	6.88701100	10.42335100
C	1.61215500	8.96960300	11.39068100
C	0.32775800	6.50875600	11.65400100
H	0.79489000	6.22017000	9.56880700
C	1.07183800	8.59205400	12.62115900
H	2.11046400	9.92968700	11.28709100
C	0.42775100	7.36045800	12.75617500

H	-0.16701800	5.54608400	11.75137300
H	1.15217600	9.26206000	13.47316200
H	0.00740900	7.06598100	13.71401600
C	5.38918800	11.25266900	1.72081800
C	5.46830300	10.44954400	0.57221600
C	5.87536500	12.56744300	1.65553700
C	6.01506900	10.95006500	-0.61050300
H	5.10249200	9.42741700	0.61364900
C	6.42347500	13.06823800	0.47334900
H	5.81885300	13.19979700	2.53766600
C	6.49405300	12.26077800	-0.66349700
H	6.07027800	10.31317800	-1.48932600
H	6.79176300	14.09025100	0.44054200
H	6.91997200	12.65001300	-1.58429800
O	3.61741200	7.71686400	5.23298500
O	3.21885800	6.74248600	6.00694400
N	-1.10497000	7.24465100	3.69067300
H	-0.14270400	7.27099500	4.01886400
C	-1.61580700	5.98113500	3.47425500
C	-0.70677000	4.82157200	3.80847800
C	0.64186000	4.90602900	4.22401700
C	-1.30038100	3.55529700	3.71416300
C	1.34094200	3.73948500	4.55132400
C	-0.60030400	2.39632000	4.03634800
H	-2.33251200	3.49497200	3.38970300
C	0.72739200	2.49259100	4.46510600
H	2.37661000	3.81857400	4.87142300
H	1.28803800	1.59654000	4.72656200
O	1.25490700	6.12274000	4.27414800
H	2.06980400	6.10566900	4.83037500
O	-1.26038000	1.19771200	3.92153800
H	-0.65420800	0.48304100	4.16946200
O	-2.75536100	5.77345800	3.06106500

3) B3LYP optimised structure of $^{1}I_{TS}$:

Fe	3.42756700	9.43592500	5.88645200
N	5.28770900	9.87142000	5.24825800
N	2.70416600	10.11245800	4.13198000
N	1.56854700	9.20167900	6.56974000
N	4.15037700	8.90394300	7.66400300
C	6.57224500	8.92630200	7.14253900
C	4.79285200	10.85637900	3.02929500
C	3.41241800	10.62833700	3.06653800
C	1.40019100	9.99406300	3.69743400
C	7.09608900	10.53440700	3.96843800
C	7.59189900	9.94981100	5.09187000
C	6.46356500	9.53319600	5.88589200
C	5.65975500	10.46413500	4.05700800
C	1.29209700	10.44479900	2.33162100
C	2.52726500	10.86690700	1.95342000
C	2.03972400	8.60060200	8.92109700
C	3.43318000	8.56043500	8.78694700
C	1.18119500	8.88659800	7.85560500
C	0.30703000	9.58322200	4.46999300
C	4.32193900	8.07983500	9.81453300

C	5.47155500	8.65776700	7.96580900
C	5.57929600	8.12074800	9.30033300
C	-0.73402200	9.03971000	6.68247900
C	-0.25814400	8.82401000	7.93641400
C	0.40869400	9.27326200	5.83338300
H	7.64457300	10.96006100	3.14106000
H	8.62693400	9.81599300	5.36991900
H	0.37950600	10.44997500	1.75429700
H	2.82564900	11.28379000	1.00295100
H	4.01113200	7.73247800	10.78866300
H	6.50138100	7.81808800	9.77386000
H	-1.76216100	9.06004500	6.35187400
H	-0.82092600	8.62826700	8.83688500
O	3.44870600	11.43825600	6.58634600
C	2.33179300	12.34017600	6.51410600
H	2.61536900	13.30846800	6.93987200
H	1.53722800	11.89738600	7.11277300
H	1.98679000	12.46410600	5.48285100
H	4.20291600	11.81081600	6.10006600
C	7.94233900	8.57819300	7.63811500
C	8.54003500	9.29484000	8.68671500
C	8.66050400	7.52516500	7.04965800
C	9.81984800	8.96590600	9.13679400
H	7.99713200	10.11708400	9.14477700
C	9.93989500	7.19559400	7.49987800
H	8.20543200	6.96153900	6.24001300
C	10.52348400	7.91492900	8.54476900
H	10.26819600	9.53427400	9.94751500
H	10.47884500	6.37397200	7.03547300
H	11.51972200	7.65871500	8.89518400
C	-1.05571900	9.56360300	3.84151200
C	-1.70067000	10.78146000	3.58597600
C	-1.72398000	8.35202000	3.52342500
C	-2.98091500	10.83257800	3.03815700
H	-1.18003900	11.70163300	3.83770800
C	-3.01953200	8.40905100	2.97498400
C	-3.63373600	9.63647600	2.73993000
H	-3.46075900	11.78998500	2.85589200
H	-3.52597400	7.48270200	2.74731400
H	-4.63417200	9.65106200	2.31515000
C	1.44767600	8.25541100	10.25234400
C	0.74106500	7.05667300	10.43950500
C	1.59847000	9.12394600	11.34481400
C	0.19615400	6.73816400	11.68436700
H	0.62922800	6.37154600	9.60400900
C	1.05216300	8.80631200	12.58941900
H	2.14331500	10.05453400	11.21120900
C	0.34900300	7.61241400	12.76260400
H	-0.34443800	5.80402900	11.81185300
H	1.17431700	9.49334700	13.42270600
H	-0.07599800	7.36434700	13.73150800
C	5.38793600	11.48036600	1.80333300
C	5.50246100	10.75443500	0.60733300
C	5.85290400	12.80404900	1.83181300
C	6.06165800	11.33920600	-0.53008400
H	5.15463100	9.72568300	0.57640700

C	6.41325700	13.38936900	0.69505400
H	5.77051600	13.37662100	2.75195300
C	6.51816900	12.65844500	-0.48983800
H	6.14428100	10.76125300	-1.44673600
H	6.76473400	14.41704000	0.73534100
H	6.95371800	13.11312400	-1.37550300
O	3.53958700	7.78566200	5.18025600
O	2.93183800	6.79186100	5.88420900
N	-1.05458500	7.13751500	3.74928300
H	-0.05490100	7.17152100	3.96223400
C	-1.58407400	5.86759200	3.72503400
C	-0.62036600	4.74663200	4.03278000
C	0.78551000	4.90250200	4.28221500
C	-1.18020700	3.47155800	4.05934400
C	1.54810900	3.73477000	4.56761900
C	-0.40820000	2.34242200	4.34823300
H	-2.23939300	3.36488000	3.85468400
C	0.96628100	2.48133400	4.60873700
H	2.61125400	3.85905800	4.75126500
H	1.57116800	1.60383000	4.83245100
O	1.37241600	6.07260600	4.22903100
H	2.30671800	6.32641000	5.09419100
O	-1.03955700	1.13272300	4.36189900
H	-0.39358700	0.43924400	4.56955600
O	-2.76556700	5.61863700	3.48650100

4) B3LYP optimised structure of $^{3}I_{TS}$:

Fe	3.42601000	9.45473600	5.88695700
N	5.28591900	9.87940200	5.25071400
N	2.70434900	10.11482600	4.13282800
N	1.56290100	9.20337800	6.56556800
N	4.14659700	8.89933900	7.65464000
C	6.56932200	8.91956800	7.13700700
C	4.79353200	10.86413900	3.03166600
C	3.41373900	10.62869700	3.06576800
C	1.40015200	9.99433100	3.69589300
C	7.09563800	10.55091700	3.97517800
C	7.59068500	9.96096600	5.09596500
C	6.46154500	9.53797200	5.88606800
C	5.65927900	10.47718800	4.06141400
C	1.29509200	10.43743500	2.32888700
C	2.53126700	10.86059800	1.95122000
C	2.03507800	8.59719900	8.91373300
C	3.42783200	8.55120300	8.77653400
C	1.17529600	8.88943300	7.85036000
C	0.30393300	9.58812400	4.46714500
C	4.31464900	8.05804900	9.79942200
C	5.46711900	8.64476800	7.95557400
C	5.57223700	8.09627400	9.28512000
C	-0.74109900	9.05071100	6.68017700
C	-0.26492000	8.83276300	7.93338800
C	0.40277300	9.27987200	5.83071500
H	7.64454400	10.98098400	3.15035200
H	8.62550500	9.82653100	5.37458600
H	0.38402100	10.43817600	1.74909000

H	2.83033400	11.27393500	0.99941700
H	4.00266200	7.70463800	10.77099400
H	6.49287500	7.78566700	9.75630800
H	-1.76934100	9.07518700	6.35006700
H	-0.82745100	8.63883700	8.83441400
O	3.43546000	11.43875700	6.59349900
C	2.31359200	12.33567200	6.52455000
H	2.59159800	13.30147500	6.95924600
H	1.51934700	11.88368100	7.11649400
H	1.97255700	12.46574900	5.49279600
H	4.19101800	11.82074400	6.11661500
C	7.93850500	8.56520300	7.63045200
C	8.53601200	9.27041900	8.68689100
C	8.65622800	7.51754700	7.03191200
C	9.81509100	8.93562300	9.13474700
H	7.99354700	10.08846000	9.15295800
C	9.93487700	7.18209400	7.47988200
H	8.20128600	6.96266000	6.21617500
C	10.51824100	7.89006400	8.53263700
H	10.26324800	9.49522800	9.95165400
H	10.47342500	6.36473500	7.00754600
H	11.51390300	7.62927300	8.88131400
C	-1.05686500	9.56680900	3.83446700
C	-1.70548700	10.78283800	3.57998400
C	-1.71950000	8.35360100	3.51083300
C	-2.98465800	10.83014700	3.02918800
H	-1.18901900	11.70441900	3.83517900
C	-3.01374800	8.40656400	2.95922300
C	-3.63219000	9.63228400	2.72625400
H	-3.46785200	11.78608500	2.84807500
H	-3.51569700	7.47873000	2.72750200
H	-4.63163100	9.64427400	2.29906900
C	1.44433700	8.25124900	10.24527400
C	0.72659500	7.05863400	10.42959400
C	1.60735300	9.11316900	11.34130400
C	0.18296100	6.73976900	11.67491900
H	0.60523500	6.37834700	9.59148300
C	1.06234800	8.79521700	12.58637300
H	2.16076100	10.03901600	11.21001000
C	0.34816000	7.60746600	12.75663600
H	-0.36624000	5.81034800	11.80006000
H	1.19413400	9.47721100	13.42233500
H	-0.07582800	7.35908000	13.72590500
C	5.38806700	11.48961400	1.80622200
C	5.51070300	10.76221300	0.61191400
C	5.84466200	12.81621700	1.83365500
C	6.06950800	11.34845300	-0.52493900
H	5.16964700	9.73116300	0.58192200
C	6.40471900	13.40297000	0.69748000
H	5.75603800	13.38989700	2.75252900
C	6.51762700	12.67060300	-0.48577700
H	6.15849200	10.76935100	-1.44026900
H	6.74973200	14.43286300	0.73694400
H	6.95293600	13.12639400	-1.37098800
O	3.57143400	7.77566900	5.15521600
O	2.94455500	6.78748900	5.84347800

N	-1.04486400	7.14183900	3.73504200
H	-0.04573700	7.18206000	3.94688200
C	-1.56915000	5.86977100	3.71516200
C	-0.60383400	4.75423200	4.03878200
C	0.80032500	4.91289700	4.28435400
C	-1.16448000	3.47984200	4.09259700
C	1.56255400	3.75484400	4.59889100
C	-0.39339700	2.35727400	4.40708100
H	-2.22372900	3.36968800	3.89030600
C	0.98007100	2.50223600	4.66737400
H	2.62557500	3.88229000	4.78079200
H	1.58494700	1.63032700	4.91184800
O	1.38844700	6.08543500	4.19866300
H	2.29897500	6.32258600	5.02206800
O	-1.02503700	1.14797100	4.44625200
H	-0.37962700	0.45955400	4.67161000
O	-2.74865600	5.61548400	3.47318200

5) B3LYP optimised structure of ^{1}II:

Fe	3.39197600	9.27415400	6.26419400
N	5.25143400	9.60477600	5.51262200
N	2.59004900	9.66287100	4.46081900
N	1.54960500	9.16710700	7.04693300
N	4.20434400	9.09332000	8.10147900
C	6.61022200	9.29864200	7.55842600
C	4.66594800	9.93094300	3.12706000
C	3.27345800	9.90977900	3.28975100
C	1.25253500	9.75788500	4.14310000
C	7.00896000	9.79243200	4.02016700
C	7.55068600	9.64399500	5.25808900
C	6.45361600	9.50605600	6.18289500
C	5.57547200	9.77604500	4.18187400
C	1.09324000	10.11111900	2.75487800
C	2.34165300	10.19995600	2.22565700
C	2.13965200	8.66528200	9.39668700
C	3.52695600	8.79803600	9.25963100
C	1.23391800	8.84057100	8.34435900
C	0.18184800	9.54413800	5.01927000
C	4.45809600	8.61668900	10.34999000
C	5.53809900	9.10042600	8.43628900
C	5.70173600	8.80915100	9.84198400
C	-0.74585800	8.97308400	7.27870500
C	-0.19930800	8.72824100	8.49644200
C	0.34964700	9.24314000	6.37677200
H	7.52688200	9.90516300	3.07930800
H	8.59629500	9.61904400	5.52734800
H	0.14589500	10.27401500	2.26100700
H	2.61640200	10.45193100	1.21213800
H	4.18436800	8.36304000	11.36339100
H	6.64944200	8.74295900	10.35566300
H	-1.79029700	8.97501800	7.00359200
H	-0.70832400	8.49454800	9.41977800
O	3.44246800	11.38913200	6.63026200
C	2.46198100	12.34381200	6.20556200
H	2.72134200	13.33880100	6.58505400

H	1.51528200	12.02606200	6.64193300
H	2.36711400	12.36934700	5.11494900
H	4.31032500	11.61432100	6.25537000
C	8.00073700	9.25896500	8.11702000
C	8.49056000	10.32106900	8.89268000
C	8.84024400	8.15944100	7.87928100
C	9.78469400	10.28672600	9.41521500
H	7.84986600	11.17794500	9.08289000
C	10.13470800	8.12460900	8.40068200
H	8.46814700	7.32795100	7.28724100
C	10.61113900	9.18831400	9.16998200
H	10.14733200	11.11999300	10.01160500
H	10.76918100	7.26309800	8.20914400
H	11.61872500	9.16087100	9.57633100
C	-1.21840200	9.68680600	4.49514600
C	-1.94601400	10.83577400	4.83098100
C	-1.84569500	8.69779800	3.69390500
C	-3.25944900	11.02649300	4.40446200
H	-1.46022000	11.58818100	5.44600300
C	-3.17275900	8.88901800	3.26785200
C	-3.86593400	10.04372200	3.62328600
H	-3.79855000	11.92800600	4.68149900
H	-3.64438100	8.12206500	2.67138300
H	-4.89008500	10.16957100	3.28204300
C	1.59338800	8.30924900	10.74660700
C	1.08765400	7.02355000	10.99448200
C	1.57558800	9.24992100	11.78790600
C	0.57817200	6.68783800	12.25007000
H	1.10217900	6.28682500	10.19618600
C	1.06666200	8.91456900	13.04393100
H	1.96046000	10.24963900	11.60575000
C	0.56617700	7.63227100	13.27871000
H	0.19413500	5.68612300	12.42474800
H	1.05834600	9.65717300	13.83768900
H	0.16991800	7.37084900	14.25636500
C	5.20559700	10.12704000	1.74410400
C	5.01207300	9.14278700	0.76108600
C	5.90856600	11.29091700	1.39403500
C	5.50889500	9.31597000	-0.53150300
H	4.47040500	8.23781000	1.02170000
C	6.40583500	11.46524400	0.10145200
H	6.05876500	12.06493600	2.14170400
C	6.20801900	10.47775000	-0.86577100
H	5.35202900	8.54067900	-1.27704500
H	6.94341400	12.37573300	-0.15056400
H	6.59462700	10.61319900	-1.87236100
O	3.59499400	7.54084000	5.96801400
O	2.38920500	6.84058000	5.63730700
N	-1.10342300	7.55098900	3.34569800
H	-0.10118200	7.56721400	3.53850800
C	-1.55427300	6.41236500	2.73538400
C	-0.51250400	5.33723800	2.50463100
C	0.92798700	5.50778500	2.69853500
C	-0.99556100	4.12082500	2.07166600
C	1.77783800	4.35802800	2.44752400
C	-0.13179200	3.03181300	1.83371600

H	-2.06235900	4.00323400	1.91573900
C	1.26512300	3.15812200	2.02843600
H	2.84174200	4.49799400	2.60934400
H	1.91742100	2.30596000	1.84608600
O	1.44549900	6.60187500	3.05815200
H	2.40162200	6.86003400	4.65772800
O	-0.70059400	1.88024200	1.41974000
H	-0.01961700	1.19821300	1.29579900
O	-2.71835100	6.20484300	2.39512700

6) B3LYP optimised structure of ^{3}II:

Fe	3.39452800	9.27305000	6.26525100
N	5.25394800	9.60600600	5.51407800
N	2.59310100	9.65852000	4.46099900
N	1.55246800	9.16418200	7.04716200
N	4.20646100	9.09375000	8.10261100
C	6.61197800	9.30936100	7.56179800
C	4.66933500	9.92180200	3.12686100
C	3.27676500	9.90078000	3.28916700
C	1.25565500	9.75534000	4.14324200
C	7.01203400	9.79294100	4.02222700
C	7.55324000	9.65165200	5.26124300
C	6.45588200	9.51346900	6.18564600
C	5.57850100	9.77291700	4.18286000
C	1.09681100	10.10466200	2.75406500
C	2.34534500	10.18866500	2.22415200
C	2.14241900	8.65727900	9.39586000
C	3.52944700	8.79392500	9.25981300
C	1.23672900	8.83447000	8.34376500
C	0.18471800	9.54517200	5.02007800
C	4.46053100	8.61470100	10.35062700
C	5.53989500	9.10649800	8.43860900
C	5.70365100	8.81414400	9.84410200
C	-0.74311900	8.97173300	7.27880200
C	-0.19654700	8.72265600	8.49567800
C	0.35245300	9.24287200	6.37729700
H	7.53043200	9.90332400	3.08135100
H	8.59872100	9.63120100	5.53136200
H	0.14977700	10.26803000	2.25976100
H	2.62037300	10.43671300	1.20973800
H	4.18717100	8.35804700	11.36336800
H	6.65120500	8.75159300	10.35851900
H	-1.78760500	8.97528800	7.00386200
H	-0.70563100	8.48679000	9.41842600
O	3.44273800	11.38875000	6.63006100
C	2.46132500	12.34233500	6.20518500
H	2.72077300	13.33808400	6.58264300
H	1.51534700	12.02496800	6.64341400
H	2.36487000	12.36607100	5.11466000
H	4.30998600	11.61384800	6.25366500
C	8.00197700	9.27731000	8.12212400
C	8.48486000	10.34248900	8.89793900
C	8.84790100	8.18233500	7.88609000
C	9.77850300	10.31567000	9.42211400
H	7.83913500	11.19585400	9.08692600

C	10.14188500	8.15503100	8.40912600
H	8.48117100	7.34843500	7.29408900
C	10.61140500	9.22179600	9.17844500
H	10.13570700	11.15124400	10.01855900
H	10.78138900	7.29696200	8.21886500
H	11.61862500	9.20019700	9.58605800
C	-1.21556400	9.69228600	4.49709200
C	-1.93958800	10.84280700	4.83541100
C	-1.84659900	8.70641600	3.69490400
C	-3.25289400	11.03800400	4.41050500
H	-1.45107700	11.59283500	5.45118000
C	-3.17348400	8.90216600	3.27037200
C	-3.86299900	10.05828300	3.62833000
H	-3.78910100	11.94062000	4.68956200
H	-3.64782900	8.13753900	2.67306300
H	-4.88710600	10.18765900	3.28827500
C	1.59610600	8.29626900	10.74439900
C	1.09049600	7.00955600	10.98728600
C	1.57775900	9.23301500	11.78924200
C	0.58071500	6.66901100	12.24144600
H	1.10539000	6.27585000	10.18622100
C	1.06854300	8.89281800	13.04384300
H	1.96238800	10.23352400	11.61095800
C	0.56824100	7.60954400	13.27364600
H	0.19682700	5.66656500	12.41222300
H	1.05980600	9.63244400	13.84037500
H	0.17174100	7.34436400	14.25019300
C	5.20917100	10.11243500	1.74322600
C	5.01624800	9.12393000	0.76436600
C	5.91135700	11.27530100	1.38822700
C	5.51301200	9.29194400	-0.52892900
H	4.47503600	8.21977500	1.02876700
C	6.40857600	11.44444800	0.09493600
H	6.06095000	12.05261700	2.13258800
C	6.21144800	10.45272000	-0.86808800
H	5.35663400	8.51341700	-1.27119700
H	6.94554500	12.35422300	-0.16093500
H	6.59801200	10.58413600	-1.87523100
O	3.60037500	7.53945900	5.97063700
O	2.39527800	6.83812200	5.63620500
N	-1.10808000	7.55795900	3.34429300
H	-0.10576000	7.57079800	3.53699300
C	-1.56242700	6.42181500	2.73200300
C	-0.52383900	5.34393300	2.49986300
C	0.91717100	5.50998500	2.69518300
C	-1.01020400	4.12954100	2.06516700
C	1.76375800	4.35770100	2.44377100
C	-0.14944300	3.03823800	1.82642900
H	-2.07725700	4.01520700	1.90851200
C	1.24772900	3.16000900	2.02257900
H	2.82791200	4.49420400	2.60689000
H	1.89751400	2.30602900	1.83973800
O	1.43745600	6.60188600	3.05644300
H	2.40826500	6.86303100	4.65724900
O	-0.72135400	1.88897500	1.41046800
H	-0.04237400	1.20498900	1.28629100

O	-2.72706400	6.21839600	2.39116400

7) B3LYP optimised structure of ^{3}II':

Fe	0.74320800	0.09691600	-0.66436500
N	1.71826700	-1.65835000	-0.54943800
N	-0.88733900	-0.84188900	-1.36650400
N	-0.16406500	1.85929700	-0.97540100
N	2.42796400	1.03374700	-0.10469200
C	3.84699700	-0.91098700	0.47271000
C	-0.04447200	-3.17016300	-1.42831900
C	-1.02617200	-2.18856200	-1.62120700
C	-2.12379000	-0.28305400	-1.60059500
C	2.17649300	-3.92497800	-0.54608800
C	3.24524600	-3.30076400	0.01604200
C	2.95706900	-1.88956400	0.01579300
C	1.22012300	-2.90162500	-0.88811800
C	-3.05334600	-1.29449700	-2.03868100
C	-2.36758600	-2.46789000	-2.07806000
C	1.70545600	3.38562600	-0.42205200
C	2.63424600	2.39639300	-0.07297400
C	0.38683800	3.10939800	-0.80246900
C	-2.45305500	1.07197600	-1.47928400
C	3.94688400	2.68355700	0.45156300
C	3.58981100	0.46197900	0.37385400
C	4.53010700	1.49050700	0.74324500
C	-1.79522500	3.48041400	-1.22658900
C	-0.62100300	4.12497800	-1.00242500
C	-1.50328500	2.06742000	-1.22245400
H	2.03275900	-4.98335400	-0.70534500
H	4.15315200	-3.74721000	0.39374500
H	-4.08400600	-1.11019900	-2.30674900
H	-2.73120700	-3.43999100	-2.37604700
H	4.35161800	3.67448600	0.59505300
H	5.50804300	1.31351800	1.16573900
H	-2.77112500	3.90945200	-1.39794800
H	-0.44666400	5.18941400	-0.95189200
O	1.51444500	0.16139100	-2.61035400
C	0.73298500	0.30417400	-3.80839500
H	1.40183900	0.42061800	-4.66745300
H	0.14046400	1.20910600	-3.68118600
H	0.06665100	-0.55097000	-3.95611400
H	2.06208700	-0.63988600	-2.66010100
C	5.14533800	-1.35691400	1.07238200
C	6.35766500	-1.18716100	0.38588200
C	5.16886200	-1.96062300	2.33946100
C	7.56245400	-1.60713400	0.95220900
H	6.35129900	-0.72769600	-0.59885200
C	6.37347600	-2.38069300	2.90589400
H	4.23586000	-2.09570100	2.87973700
C	7.57374000	-2.20481500	2.21418100
H	8.49137100	-1.47076800	0.40476800
H	6.37320500	-2.84278200	3.88948900
H	8.51138200	-2.53200000	2.65520100
C	-3.89039000	1.48289100	-1.58701100
C	-4.38204700	2.07318600	-2.75763100

C	-4.75413900	1.33741400	-0.47364700
C	-5.69294300	2.54182600	-2.83629100
H	-3.71337200	2.17440300	-3.60853300
C	-6.06931800	1.82476700	-0.54952400
C	-6.52542100	2.42300200	-1.72205200
H	-6.05503300	3.00043800	-3.75200900
H	-6.71045900	1.73845700	0.31684300
H	-7.54694500	2.79151600	-1.76292100
C	2.13693700	4.81839600	-0.32509200
C	1.68487300	5.64086400	0.71858100
C	3.01281800	5.36172800	-1.27749400
C	2.09490500	6.97239300	0.80517000
H	1.01176400	5.22997300	1.46601800
C	3.42339500	6.69315800	-1.19107200
H	3.36815700	4.73463000	-2.09068200
C	2.96514800	7.50253200	-0.14962800
H	1.73637500	7.59359800	1.62158200
H	4.09909700	7.09802800	-1.93988200
H	3.28430700	8.53901300	-0.08211000
C	-0.38284600	-4.59225300	-1.75766100
C	-1.30599900	-5.31094700	-0.98152500
C	0.22296400	-5.23675700	-2.84748900
C	-1.61737100	-6.63603900	-1.29004700
H	-1.77321100	-4.82666500	-0.12872400
C	-0.08805800	-6.56195300	-3.15656200
H	0.93837600	-4.69134600	-3.45725200
C	-1.01013100	-7.26520800	-2.37892500
H	-2.33159600	-7.17746100	-0.67556900
H	0.38795900	-7.04293200	-4.00699500
H	-1.25298700	-8.29676000	-2.61892300
O	0.03676000	0.07987300	0.97862400
O	0.93636400	-0.37743400	2.02514200
N	-4.27389700	0.67248500	0.67271900
H	-3.49378100	0.04629900	0.52682800
C	-4.74800200	0.77531500	1.97268200
C	-4.05486700	-0.13555200	2.94969200
C	-4.89376400	-0.86753600	3.91069700
C	-2.67724800	-0.26599000	2.97631600
C	-4.18427500	-1.64750700	4.91415600
C	-2.04339800	-1.07628500	3.95214100
H	-2.04754800	0.26278500	2.26338800
C	-2.81995000	-1.74873900	4.93180900
H	-4.80296200	-2.17107700	5.63666200
H	-2.29642500	-2.34726700	5.67164200
O	-6.14299600	-0.87032300	3.86119900
H	1.43004400	0.44066700	2.22258300
O	-0.71704100	-1.24486300	4.02182500
H	-0.22786900	-0.84153500	3.26052200
O	-5.64606500	1.53157000	2.30591900

8) B3LYP optimised structure of $^{3}II_{TS}$':

Fe	0.65887800	0.14014900	-0.65256400
N	1.62224100	-1.61298600	-0.58926600
N	-0.90465100	-0.77214100	-1.49590400
N	-0.16206200	1.90300100	-1.07786500

N	2.34177400	1.05758500	-0.13149100
C	3.59946500	-0.90236900	0.70284300
C	-0.05326900	-3.08401200	-1.68222000
C	-1.02523600	-2.09270900	-1.86950300
C	-2.14688200	-0.20720800	-1.66561500
C	2.01452600	-3.88671200	-0.51302200
C	2.98328200	-3.28769300	0.23192500
C	2.75018800	-1.87005000	0.16525800
C	1.14648000	-2.84423100	-0.99797000
C	-3.06279700	-1.18322400	-2.19848000
C	-2.35832100	-2.33512100	-2.36799800
C	1.76734700	3.40085600	-0.68101100
C	2.64553900	2.39775000	-0.25164300
C	0.42171900	3.14524200	-0.97541500
C	-2.48061300	1.13164800	-1.42383300
C	3.98202200	2.63676800	0.23410400
C	3.43168300	0.46580200	0.46207100
C	4.45070000	1.45164000	0.71119200
C	-1.79083800	3.53561300	-1.17273900
C	-0.59024600	4.16843800	-1.07466000
C	-1.51732900	2.12142200	-1.20114200
H	1.86903000	-4.94191700	-0.69143000
H	3.79402700	-3.75502600	0.77137400
H	-4.09747800	-0.98765200	-2.44165400
H	-2.70889800	-3.27482800	-2.76808300
H	4.48349800	3.59296900	0.22131400
H	5.41275000	1.24333900	1.15633000
H	-2.77498900	3.97484500	-1.24284400
H	-0.39956300	5.23066800	-1.03125000
O	1.54835400	0.21350800	-2.70635200
C	0.81870900	0.37964200	-3.92897800
H	1.51428000	0.49144500	-4.76850100
H	0.23682500	1.29442000	-3.81720300
H	0.13911000	-0.45910200	-4.11341600
H	2.05392700	-0.61519700	-2.73283000
C	4.74236500	-1.33176000	1.56723100
C	5.90852700	-1.89931400	1.03427400
C	4.63916100	-1.15725900	2.95640200
C	6.95585000	-2.28291800	1.87468800
H	5.99607200	-2.03187000	-0.04094500
C	5.68591400	-1.54491500	3.79391200
H	3.72365200	-0.73506400	3.36191700
C	6.84642800	-2.10626000	3.25557800
H	7.85698300	-2.71719200	1.44970700
H	5.59277800	-1.41175900	4.86845500
H	7.66124700	-2.40615700	3.90915000
C	-3.92610900	1.51679400	-1.38425200
C	-4.53146300	2.16113300	-2.46913600
C	-4.68702100	1.26471400	-0.21391400
C	-5.86339800	2.57051800	-2.41705000
H	-3.93734200	2.34335100	-3.36087600
C	-6.02561700	1.69037400	-0.16002100
C	-6.59818500	2.33538000	-1.25440800
H	-6.31628300	3.06906900	-3.26918500
H	-6.59256600	1.51540600	0.74314200
H	-7.63569400	2.65281200	-1.19201300

C	2.24224900	4.81817600	-0.73587700
C	2.61089100	5.51359900	0.42714700
C	2.30710800	5.48930300	-1.96753000
C	3.03916300	6.84006300	0.35855700
H	2.54773800	5.01280500	1.38903300
C	2.73797600	6.81486500	-2.03658300
H	2.02376300	4.96143600	-2.87386300
C	3.10593900	7.49409900	-0.87347100
H	3.31424200	7.36415200	1.26992900
H	2.78730400	7.31562000	-2.99980500
H	3.43965300	8.52681400	-0.92603200
C	-0.34701600	-4.48395800	-2.12269200
C	-1.35662200	-5.24186400	-1.50741800
C	0.39947200	-5.07263200	-3.15558600
C	-1.61725500	-6.54901800	-1.92087800
H	-1.92887600	-4.80454200	-0.69439700
C	0.13774900	-6.37933000	-3.57036300
H	1.18548800	-4.49759600	-3.63781500
C	-0.87260500	-7.12079100	-2.95469600
H	-2.39907600	-7.12202400	-1.42981600
H	0.72214100	-6.81632900	-4.37569300
H	-1.07649900	-8.13843500	-3.27633600
O	-0.00653700	0.07415800	0.81389300
O	1.14099700	-0.07100100	2.63959800
N	-4.07373600	0.57224200	0.84928300
H	-3.18397600	0.13721500	0.64053700
C	-4.56006600	0.36875300	2.13000900
C	-3.70143600	-0.51720900	2.99320200
C	-4.39083400	-1.61185500	3.70741200
C	-2.36034500	-0.28368900	3.18979700
C	-3.59506400	-2.33292400	4.69928100
C	-1.61051400	-1.03879500	4.15404700
H	-1.84219100	0.50739800	2.65471000
C	-2.27810400	-2.05842400	4.91028400
H	-4.11131000	-3.11845500	5.24327600
H	-1.68339700	-2.60236800	5.63835600
O	-5.56553900	-1.93790000	3.46416500
H	1.17899000	0.90061900	2.57901200
O	-0.35366900	-0.80820700	4.42030800
H	0.24387300	-0.39736000	3.58167200
O	-5.59559600	0.85665600	2.55543500

9) B3LYP optimised structure of ^{3}III:

Fe	0.52490500	-0.18846800	-0.71190600
N	1.58799500	-1.89904600	-0.79587400
N	-0.97627900	-1.08999500	-1.69845700
N	-0.37752700	1.56906300	-0.98360000
N	2.14422400	0.74474100	-0.00125700
C	3.52338600	-1.22248600	0.58646500
C	-0.01594800	-3.34950500	-2.01207500
C	-1.03594500	-2.39888000	-2.12695800
C	-2.23793600	-0.57173500	-1.88422200
C	2.12508200	-4.13898200	-0.97882200
C	3.07223000	-3.56402600	-0.18989800
C	2.74510900	-2.16576700	-0.08893600

C	1.18302200	-3.10625600	-1.32908000
C	-3.10830500	-1.57318400	-2.44946300
C	-2.35386100	-2.68698000	-2.64227800
C	1.39490700	3.09452500	-0.17573700
C	2.31679300	2.09990900	0.16325100
C	0.12355700	2.81763500	-0.68366300
C	-2.62011400	0.75151900	-1.63858800
C	3.58002100	2.36182000	0.80895500
C	3.24777000	0.14921200	0.56153400
C	4.14666300	1.15517600	1.07245300
C	-2.04167400	3.15512500	-1.20984500
C	-0.90469200	3.81430000	-0.85798700
C	-1.70645900	1.75476000	-1.28678400
H	2.04210700	-5.17521800	-1.27172700
H	3.92270600	-4.03403800	0.28145500
H	-4.14967700	-1.42081600	-2.69287300
H	-2.65856100	-3.63101400	-3.06904100
H	3.96417800	3.34546300	1.03539700
H	5.09372300	0.94999100	1.54930500
H	-3.01778000	3.56804100	-1.42080900
H	-0.76562400	4.87542700	-0.71081700
O	1.49479400	0.14985400	-2.69177800
C	0.80871200	0.33552400	-3.93589100
H	1.52700600	0.57138500	-4.72953600
H	0.13708000	1.18238400	-3.79475000
H	0.22135200	-0.54695400	-4.21117000
H	2.07616800	-0.62604900	-2.74984300
C	4.69602800	-1.69142300	1.38989100
C	5.88435100	-2.12045500	0.78106100
C	4.60008500	-1.69970200	2.79117800
C	6.96193800	-2.55059700	1.55804000
H	5.96512200	-2.10880800	-0.30288700
C	5.67926600	-2.13369000	3.56312700
H	3.66948300	-1.37669800	3.25290000
C	6.86100100	-2.55831500	2.95083100
H	7.87963200	-2.87605100	1.07495600
H	5.59455700	-2.14236000	4.64672800
H	7.69948000	-2.89389100	3.55555900
C	-4.07632100	1.10721000	-1.66483700
C	-4.77677200	1.30585800	-2.85843700
C	-4.76772200	1.25303100	-0.43498500
C	-6.13074400	1.64614300	-2.85318700
H	-4.24312300	1.19936400	-3.79907000
C	-6.12701000	1.59625400	-0.42675600
C	-6.79548700	1.79149300	-1.63510400
H	-6.65674500	1.80058400	-3.79087900
H	-6.63512700	1.70814700	0.52149200
H	-7.84884600	2.05772400	-1.61767100
C	1.73589000	4.52007700	0.14051900
C	1.56116800	5.00756000	1.44529900
C	2.22290500	5.38270900	-0.85113500
C	1.87243900	6.33427100	1.74837000
H	1.17442700	4.34076700	2.21179400
C	2.53418000	6.70942100	-0.54482000
H	2.36030200	5.00945000	-1.86255000
C	2.36014700	7.18741500	0.75543500

H	1.73162500	6.70140400	2.76157000
H	2.91350800	7.36766200	-1.32208500
H	2.60244400	8.21974800	0.99354200
C	-0.24686600	-4.72599500	-2.55777200
C	-1.14134500	-5.61142500	-1.93598500
C	0.44355400	-5.16049400	-3.69957300
C	-1.34424500	-6.89428100	-2.44737800
H	-1.67105700	-5.29085900	-1.04331700
C	0.24061100	-6.44310500	-4.21182400
H	1.14047100	-4.48497100	-4.18856200
C	-0.65501700	-7.31334600	-3.58741400
H	-2.03774700	-7.56767900	-1.95083800
H	0.78110300	-6.76072200	-5.09960300
H	-0.81331500	-8.31213900	-3.98502500
O	-0.10856100	-0.45093000	0.75381400
O	1.39024200	-0.46856600	3.24343700
N	-4.03176600	1.03923000	0.74806900
H	-3.09664900	0.67344000	0.61231400
C	-4.36007700	1.34435400	2.04750800
C	-3.19156900	1.13585600	2.98500200
C	-3.35122700	0.17601500	4.12539000
C	-2.03694800	1.81090300	2.81852600
C	-2.18845600	0.01038000	5.03384900
C	-0.88243100	1.63355700	3.73097600
H	-1.88578200	2.50848300	1.99861800
C	-1.03091500	0.66417800	4.84152200
H	-2.32946500	-0.70164600	5.84187000
H	-0.16115600	0.51908600	5.47259900
O	-4.37368200	-0.47556000	4.28168400
H	0.91863200	-0.61269100	2.39696800
O	0.15749400	2.26804800	3.56237800
H	1.52880400	0.49180600	3.25589000
O	-5.43487100	1.77124600	2.43812200

Reference:

1. I. Tabushi, N. Koga and M. Yanagita, *Tetrahedron Letters*, 1979, **20**, 257-260.
2. A. D. Becke, *Physical Review A*, 1988, **38**, 3098-3100.
3. A. D. Becke, *The Journal of Chemical Physics*, 1993, **98**, 5648-5652.
4. A. W. Schaefer, M. T. Kieber-Emmons, S. M. Adam, K. D. Karlin and E. I. Solomon, *Journal of the American Chemical Society*, 2017, **139**, 7958-7973.