Why Metal-Oxos React with Dihydroanthracene and Cyclohexadiene at Comparable Rates, Despite Having Different C–H Bond Strengths. A Computational Study

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1. Computational Details

1.1 BDE calculations

All density functional theory (DFT) calculations were carried out with the electronic structure code Turbomole v6.6.\(^1\) The M06-2X functional\(^2\) was chosen as benchmark calculations have shown it to be accurate for the computation of bond dissociation energies to within an average error of about 2 kcal mol\(^{-1}\).\(^3\) The def2-TZVPP basis set was employed for all atoms.\(^4\) Computations were accelerated using the multipole accelerated resolution of the identity approximation (MARI-J)\(^5\) together with the def2-TZVPP/J auxiliary basis set.\(^6\) The grid m5 was used throughout. Thermal corrections (298.15 K) were obtained from frequency calculations using analytical second derivatives and the harmonic frequencies were scaled by 0.983 as recommended by Truhlar and co-workers for the M06-2X/def2-TZVPP combination of functional and basis set.\(^7\) Frequency calculations were carried out to characterize stationary points giving no imaginary frequency for ground states and a single imaginary frequency for transition states. Small frequencies were raised to 100 cm\(^{-1}\) in order to compensate for the breakdown of the harmonic oscillator model.\(^8\) For the hydrogen atom we add 5/2*RT (1.48 kcal mol\(^{-1}\) at 298.15 K) to the electronic energy as contribution from enthalpy.

Wave function theory (WFT) calculations were carried out with the electronic structure code Molpro Version 2012.1.\(^9\) We computed energies using the jun-jun dual method of Truhlar and co-workers,\(^10\) which is based on (R)CCSD(T)-F12a\(^11\) and (R)MP2-F12\(^12\) calculations including explicit correlation in combination with the calendar basis sets jun-cc-pV(N+d)Z (N = D,T).\(^13\) The cc-pVNZ/JKFIT (N = D,T)\(^14\) (JKFIT and OPTRI) and the cc-pVNZ (N = D,T)/MP2FIT\(^15\) auxiliary basis sets were employed. For open-shell molecules, a restricted open-shell Hartree-Fock formalism was used.

The transition state for inversion of the DHA molecules was computed at the M06-2X/def2-TZVPP level of theory (\textit{vide infra}).

1.2 HAT calculations

Two individual sets of calculations were carried out: (i) using the B3LYP\(^16\) functional and (ii) using the B3LYP functional in combination with Grimme’s D3\(^17\) dispersion correction using the original zero-damping function. The details described below apply to both sets of calculations. Geometries were optimized using the def2-SVP\(^4\) basis set for all atoms except Fe and Cu where the def2-TZVP\(^4\) basis set was used. Single point energies were computed using the def2-TZVPP\(^4\) basis set for all atoms at the located stationary points. Solvation effects of MeCN (\(\varepsilon =\)
35.88 and refraction index = 1.344) and CHCl₂ (ε = 8.51 and refraction index = 1.421) were modeled using the conductor-like screening model (COSMO) in all calculations. All reported energies include the outlying charge correction. The inclusion of a solvation model aids in the reduction of self-interaction error (SIE) in the HAT calculations for the Fe⁴⁺(O) complexes as noted by Siegbahn and co-workers.

Frequency calculations were carried out to characterize stationary points giving no imaginary frequency for ground states and a single imaginary frequency for transition states. Small frequencies were raised to 100 cm⁻¹ in order to compensate for the breakdown of the harmonic oscillator model. Frequency calculations for thermal corrections were carried out using frozen charges (NumForce –cosmo option). Frequencies were used without scaling. Free energies are referenced to a 1 M standard solution state (298.15 K) and include the concentration-change term RTln(24.5) = 1.89 kcal mol⁻¹.

For the complexes [Fe⁴⁺(O)TMG₂dien(MeCN)]²⁺ and [Fe⁴⁺(O)TMG₃tren]²⁺, as well as the associated reaction paths, the S = 2 spin state, as determined experimentally, was considered. For the HAT reaction by the Cu³⁺(OH)(L) complex the reactions studied require transitioning from two closed shell fragments to two open shell fragments resembling a singlet diradical. We use a broken symmetry approach to describe the bond-breaking process. Spin-densities/populations are analyzed to ensure that the correct electronic structure was obtained. The effect of applying a spin purification procedure to remove triplet-state spin contamination was evaluated according to $E_{\text{singlet}} = \frac{2E(S_z=0) - (S_z^2)E(S_z=1)}{2 - (S_z^2)}$. The ∆∆G⁺ values discussed in the manuscript are only affected by 0.1 kcal/mol. The spin purified values are provided in brackets in Figure S4 (c) and (d) for completeness and are not further discussed.

The start and end points corresponding to the transition states are obtained from dynamic reaction coordinate calculations (DRC –t 150 -f). Start geometries for the [Fe⁴⁺(O)TMG₂dien(MeCN)]²⁺ complex were constructed from the crystal structure of the [Fe²⁺TMG₂dienCl₂] complex (CCDC# 845701) and for the [Fe⁴⁺(O)TMG₃tren]²⁺ complex from the corresponding crystal structure (CCDC# 818436). For the Cu³⁺(OH)(L) based reaction paths start geometries were based on a previously reported transition state structure for DHA oxidation.

Structural depictions and spin density plots were generated using IboView. Structural depictions and spin density plots were generated using IboView.
2. Free Energy Profiles for all HAT Pathways

2.1 [Fe^{IV}(O)TMG_2dien(MeCN)]^{2+} (σ) pathways

(a) B3LYP structures for CHD oxidation

(b) B3LYP structures for DHA oxidation

(c) B3LYP

(d) B3LYP-D3

Figure S1: B3LYP/def2-SVP(Fe:deg2-TZVP)/COSMO(ε = 35.88) structures for HAT from CHD (a) and DHA (b) by [Fe^{IV}(O)TMG_2dien(MeCN)]^{2+} via a (σ) pathway; Free Energy Profiles (298.15 K) for HAT from CHD and DHA at the B3LYP-def2-TZVPP/B3LYP-def2-SVP(Fe:deg2-TZVP) level of theory. COSMO (ε = 35.88) was used in all calculations. Data presented in section (c) was computed without Grimme’s D3 correction and data presented in section (d) with the D3 correction.
2.2 \([\text{Fe}^{IV}(O)\text{TMG}_2\text{dien(MeCN)}]^2+\) (\(\pi\)) pathways

(a) B3LYP structures for CHD oxidation

(b) B3LYP structures for DHA oxidation

(c) B3LYP

(d) B3LYP-D3

Figure S2: B3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(\(\varepsilon = 35.88\)) structures for HAT from CHD (a) and DHA (b) by \([\text{Fe}^{IV}(O)\text{TMG}_2\text{dien(MeCN)}]^2+\) via a (\(\pi\)) pathway; Free Energy Profiles (298.15 K) for HAT from CHD and DHA at the B3LYP-def2-TZVPP/B3LYP-def2-SVP(Fe:def2-TZVP) level of theory. COSMO (\(\varepsilon = 35.88\)) was used in all calculations. Data presented in section (c) was computed \textit{without} Grimme’s D3 correction and data presented in section (d) \textit{with} the D3 correction.
2.3 $[\text{Fe}^{IV}(O)\text{TMG}_3\text{tren}]^{2+}$ (σ) pathways

(a) B3LYP structures for CHD oxidation

(b) B3LYP structures for DHA oxidation

(c) B3LYP

(d) B3LYP-D3

Figure S3: B3LYP/def2-SVP(Fe: def2-TZVP)/COSMO($\varepsilon = 35.88$) structures for HAT from CHD (a) and DHA (b) by $[\text{Fe}^{IV}(O)\text{TMG}_3\text{tren}]^{2+}$ via a (σ) pathway; Free Energy Profiles (298.15 K) for HAT from CHD and DHA at the B3LYP-def2-TZVPP/B3LYP-def2-SVP(Fe: def2-TZVP) level of theory. COSMO ($\varepsilon = 35.88$) was used in all calculations. Data presented in section (c) was computed without Grimme’s D3 correction and data presented in section (d) with the D3 correction.
2.4 Cu$^{III}$(OH)(L) pathways

Cu$^{III}$(OH) pathways

(a) B3LYP structures for CHD oxidation

(b) B3LYP structures for DHA oxidation

Figure S4: B3LYP/def2-SVP(Cu:def2-TZVP)/COSMO(ε = 8.51) structures for HAT from CHD (a) and DHA (b) by Cu$^{III}$(OH)(L); Free Energy Profiles (298.15 K) for HAT from CHD and DHA at the B3LYP-def2-TZVPP/B3LYP-def2-SVP(Cu:def2-TZVP) level of theory. COSMO (ε = 8.51) was used in all calculations. Data presented in section (c) was computed without Grimme’s D3 correction and data presented in section (d) with the D3 correction. Values in brackets are spin purified.
3. Spin Density Plots of all Open-Shell Complexes

3.1 [Fe^{IV}(O)TMG_2dien(MeCN)]^{2+} (σ) pathways

(a) B3LYP structures for CHD oxidation

(b) B3LYP structures for DHA oxidation

(c) B3LYP-D3 structures for CHD oxidation

(d) B3LYP-D3 structures for DHA oxidation

Figure S5: Spin density plots for all open shell complexes at the B3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88) level of theory for HAT from CHD and DHA by [Fe^{IV}(O)TMG_2dien(MeCN)]^{2+} via (σ) pathways. Data presented in sections (a) and (b) is computed without Grimme’s D3 correction and in sections (c) and (d) with the D3 correction. Positive spin density is depicted in purple and negative spin density in green (isosurface 0.005).
3.2 [Fe^{IV}(O)TMG_{2}dien(MeCN)]^{2+} (\pi) pathways

(a) B3LYP structures for CHD oxidation

(b) B3LYP structures for DHA oxidation

(c) B3LYP-D3 structures for CHD oxidation

(d) B3LYP-D3 structures for DHA oxidation

Figure S6: Spin density plots for all open shell complexes at the B3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(\(\varepsilon = 35.88\)) level of theory for HAT from CHD and DHA by [Fe^{IV}(O)TMG_{2}dien(MeCN)]^{2+} via (\pi) pathways. Data presented in sections (a) and (b) is computed without Grimme’s D3 correction and in sections (c) and (d) with the D3 correction. Positive spin density is depicted in purple and negative spin density in green (isosurface 0.005).
3.3 $[\text{Fe}^{IV}(\text{O})\text{TMG}_3\text{tren}]^{2+}$ (σ) pathways

(a) B3LYP structures for CHD oxidation

Figure S7: Spin density plots for all open shell complexes at the B3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88) level of theory for HAT from CHD and DHA by $[\text{Fe}^{IV}(\text{O})\text{TMG}_3\text{tren}]^{2+}$ via (σ) pathways. Data presented in sections (a) and (b) is computed without Grimme’s D3 correction and in sections (c) and (d) with the D3 correction. Positive spin density is depicted in purple and negative spin density in green (isosurface 0.005).
3.4 Cu\textsuperscript{III}(OH)(L) pathways

(a) B3LYP structures for CHD oxidation

(b) B3LYP structures for DHA oxidation

(c) B3LYP-D3 structures for CHD oxidation

(d) B3LYP-D3 structures for DHA oxidation

Figure S8: Spin density plots for all open shell complexes at the B3LYP/def2-SVP(Cu:de2-TZVP)/COSMO(ε = 8.51) level of theory for HAT from CHD and DHA by Cu\textsuperscript{III}(OH)(L) via (σ) pathways. Data presented in sections (a) and (b) is computed without Grimme’s D3 correction and in sections (c) and (d) with the D3 correction. Positive spin density is depicted in purple and negative spin density in green (isosurface 0.005).
4. Experimental Determination of the Second Order Rate Constant for CHD Oxidation by Cu\textsuperscript{III}(OH)(L)

The following experiment was carried out by Mr. Debanjan Dhar in the laboratory of Professor William Tolman at the University of Minnesota and kindly provided for the comparison of CHD and DHA rates.

4.1 Materials and Methods

\([\text{Bu}_4\text{N}][\text{Cu}^{\text{II}}(\text{OH})(\text{L})] \quad (\text{L} = \text{N,N}-\text{bis}(2,6\text{-diisopropylphenyl})-2,6\text{-pyridinedicarboxamide})\)\textsuperscript{32} and \([\text{Fc}][\text{BARF}_4]^{33} \quad (\text{BARF}_4 = \text{tetrakis}(3,5\text{-bis(trifluoromethyl)}\text{-phenyl})\text{-borate})\) were synthesized using previously reported procedures. 1,2-Difluorobenzene (DFB) was dried over calcium hydride and vacuum distilled and stored over 3 Å molecular sieves in a nitrogen atmosphere dry box. 1,4-cyclohexadiene (CHD) was purchased from Sigma-Aldrich and dried over 3 Å molecular sieves and vacuum distilled. UV-vis spectra were obtained using an HP8453 (190-1100) diode array spectrophotometer. Variable temperature UV-vis experiments were performed using a Unisoku low temperature cell holder.

4.2 General Procedure for Kinetic Studies of Reaction between Cu\textsuperscript{III}(OH)(L) and 1,4-Cyclohexadiene in 1,2-Difluorobenzene.

Under an N\textsubscript{2} atmosphere, a 3.0 mL cuvette was charged with 1.8 mL of a known concentration of 1,4-cyclohexadiene solution in 1,2-difluorobenzene. The cuvette was cooled at -25 °C for approximately 10 min, after which 0.1 mL of a 2 mM stock solution of \([\text{Bu}_4\text{N}][\text{Cu}^{\text{II}}(\text{OH})(\text{L})]\) was added. After 2 min, to this was added 0.1 mL (2 mM solution) of \([\text{Fc}][\text{BARF}_4]\), which resulted in the immediate growth of an intense charge transfer band at 563 nm, consistent with the formation of the corresponding Cu\textsuperscript{III}(OH)(L) species. Decay of this feature was monitored over time by UV-vis spectroscopy. The decay traces were fit to a single exponential decay function to obtain the pseudo-first order rate constants (\(k_{\text{obs}}\)). Second order rate constants were extracted from linear fits of the plots of \(k_{\text{obs}}\) vs. substrate concentration (Figure S1).
Figure S1: Determination of the second order rate constant ($k_2$) for CHD oxidation by the Cu$^{III}$(OH)(L) complex.

\[
k = 38 \text{ M}^{-1} \text{ s}^{-1}
\]

| Equation | $y = a + b \cdot x$ |
|----------|---------------------|
| Adj. R-Square | 0.99973              |

| Parameter | Value     | Standard Error |
|-----------|-----------|----------------|
| B Intercept | 0.04572   | 0.00219        |
| B Slope   | 38.19526  | 0.31303        |
5. Coordinates and Absolute Energies

5.1 BDE calculations

Method: M06-2X/def2-TZVPP

| Element | X | Y | Z | Energy | Method |
|---------|---|---|---|--------|--------|
| C       | -1.4046313 | -0.5729506 | 0.1865345 | CHD   | E_{M06-2X/def2-TZVPP} = -233.39460833711 |
| C       | -0.0446240 | -1.2043565 | 0.1867505 |
| C       | 1.0638052 | -0.1946436 | 0.1865059 |
| C       | 0.8630094 | 1.1155965 | 0.1861086 |
| C       | -0.4969980 | 1.7470028 | 0.1858907 |
| C       | -1.6054273 | 0.7372893 | 0.1861467 |
| H       | -2.2567843 | -1.2427789 | 0.1867285 |
| H       | 2.0774017 | -0.5787197 | 0.1866752 |
| H       | 1.7151639 | 1.7854228 | 0.1859260 |
| H       | -2.6190234 | 1.1213665 | 0.1859869 |
| H       | -0.5983762 | 2.4074554 | -0.6824256 |
| H       | -0.5984238 | 2.4079425 | 1.0538316 |
| H       | 0.0567513 | -1.8648160 | 1.0550623 |
| H       | 0.0568049 | -1.8652921 | -0.6811931 |
| C       | -1.3784230 | -0.5639650 | 0.3227757 | [CHD-H]^* | E_{M06-2X/def2-TZVPP} = -232.76493438380 |
| C       | -0.0633745 | -1.0822313 | 0.3816832 |
| C       | 1.0360570 | -0.1940061 | 0.3222447 |
| C       | 0.8582968 | 1.1447504 | 0.2092943 |
| C       | -0.4997089 | 1.7648306 | 0.1394156 |
| C       | -1.6096878 | 0.7655559 | 0.2096595 |
| H       | -2.2163005 | -1.2477576 | 0.3693563 |
| H       | 2.0402414 | -0.5956586 | 0.3684931 |
| H       | 1.7151504 | 1.8044955 | 0.1663086 |
| H       | -2.6247330 | 1.1396699 | 0.1666116 |
| H       | -0.5917245 | 2.3630932 | -0.7796361 |
| H       | -0.6137877 | 2.5096723 | 0.9413216 |
| H       | 0.0998373 | -2.1456388 | 0.4721938 |
| C       | -3.5144132 | -0.7615181 | 0.1517152 | DHA   | E_{M06-2X/def2-TZVPP} = -540.69848526566 |
| C       | -3.5212029 | 0.6001798 | 0.4187428 |
| C       | -2.3641503 | -1.3615706 | -0.3406861 |
| C       | -2.3777651 | 1.3532346 | 0.1916290 |
| C       | -1.2196695 | -0.6109534 | -0.5762761 |
| C       | -1.2265792 | 0.7583302 | -0.3080883 |
| C       | 0.0448665 | -1.2270745 | -1.1196741 |
| C       | 0.0306146 | 1.5462042 | -0.5776116 |
| C       | 1.2656009 | 0.7552321 | -0.2266439 |
| C       | 1.2727226 | -0.6140972 | -0.4947006 |
| C       | 2.3833431 | 1.3472914 | 0.3469441 |
| C       | 2.3976503 | -1.3675203 | -0.1853477 |
| C       | 3.5078741 | 0.5914708 | 0.6474642 |
| C       | 3.5151780 | -0.7698266 | 0.3804091 |
| H       | -4.3993234 | -1.3556102 | 0.3337349 |
| H       | -4.4114880 | 1.0733890 | 0.8100464 |
| Element | X | Y | Z |
|---------|---|---|---|
| H       | -2.3526379 | -2.4259380 | -0.5411878 |
| H       | -2.3769647 | 2.4144880  | 0.4083343  |
| H       | 2.3708700  | 2.4084210  | 0.5638793  |
| H       | 2.3964233  | -2.4319273 | -0.3859711 |
| H       | 4.3721133  | 1.0625332  | 1.0955572  |
| H       | 4.3851218  | -1.3663582 | 0.6190811  |
| H       | 0.0658117  | 1.7941054  | 1.0955572  |
| H       | 0.0141446  | 2.4932599  | -0.0387467 |
| H       | 0.0388176  | -2.3072320 | -0.9757588 |
| H       | 0.0884982  | -1.0551186 | -2.2025836 |
| C       | -3.6689997 | -0.7121762 | 0.0220328  |
| C       | -3.6916643 | 0.6795956  | -0.0535844 |
| C       | -2.4637987 | -1.3751681 | 0.0977193  |
| C       | -2.4985507 | 1.3879125  | -0.0471438 |
| C       | -1.2439434 | -0.6697467 | 0.1015060  |
| C       | -1.2751223 | 0.7394629  | 0.0320984  |
| C       | -0.0000196 | -1.3541940 | 0.1590610  |
| C       | -0.0000127 | 1.5401553  | 0.0680441  |
| C       | 1.2750933  | 0.7394569  | 0.0320723  |
| C       | 1.2439046  | -0.6697516 | 0.1015280  |
| C       | 2.4985187  | 1.3879001  | -0.0472495 |
| C       | 2.4637645  | -1.3751711 | 0.0978011  |
| H       | 3.6916318  | 0.6795806  | -0.0536640 |
| H       | 3.6689653  | -0.7121853 | 0.0220723  |
| H       | -4.5952324 | -1.2704868 | 0.0187659  |
| H       | -4.6338210 | 1.2062145  | 0.0187659  |
| H       | -2.4380294 | -2.4563028 | 0.1520493  |
| H       | -2.5170961 | 2.4701042  | -0.1034300 |
| H       | 2.5170727  | 2.4700880  | -0.1035992 |
| H       | 2.4379953  | -2.4563029 | 0.1521866  |
| H       | 4.6337844  | 1.2062005  | -0.1169874 |
| H       | 4.5951939  | -1.2705029 | 0.0188392  |
| H       | -0.0000226 | 2.2557265  | -0.7595464 |
| H       | 0.0000002  | 2.1530098  | 0.9770107  |
| H       | -0.0000236 | -2.4350306 | 0.2170268  |

### DHA-H

| Energy | Value |
|--------|-------|
| \(\text{E}_{\text{M06-2X/def2-TZVPP}}\) | \(-540.06346911401\) |
| \(\text{H}(298.15)\text{M06-2X/def2-TZVPP}\) | \(0.212865\) |
| \(\text{E}_{\text{RCCSD(T)-F12a/jun-cc-pV(D+d)Z}}\) | \(-539.20079730\) |
| \(\text{E}_{\text{RMP2-F12/jun-cc-pV(D+d)Z}}\) | \(-539.117140429630\) |
| \(\text{E}_{\text{RMP2-F12/jun-cc-pV(T+d)Z}}\) | \(-539.17021225\) |

### H

| Energy | Value |
|--------|-------|
| \(\text{E}_{\text{M06-2X/def2-TZVPP}}\) | \(-0.49814085117\) |
| \(\text{E}_{\text{RCCSD(T)-F12a/jun-cc-pV(D+d)Z}}\) | \(-0.49933813\) |
| \(\text{E}_{\text{RMP2-F12/jun-cc-pV(D+d)Z}}\) | \(-0.49933813\) |
| \(\text{E}_{\text{RMP2-F12/jun-cc-pV(T+d)Z}}\) | \(-0.49982654\) |

### DHA-TS Inversion

| Energy | Value |
|--------|-------|
| \(\text{E}_{\text{M06-2X/def2-TZVPP}}\) | \(-540.69579592466\) |
| \(\text{H}(298.15)\text{M06-2X/def2-TZVPP}\) | \(0.225142\) |
5.2 HAT Calculations

5.2.1 [Fe⁴(0)TMG₃tren]²⁺ (σ), [Fe⁴(0)TMG₂dien(MeCN)]²⁺ (σ) and [Fe⁴(0)TMG₂dien(MeCN)]²⁺ (π) pathways (B3LYP)

Method: B3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88)

|   | CHD          | DHA          |
|---|--------------|--------------|
| C | -3.5649727   | -3.5720534   |
| C | -1.4965466   | -0.6113158   |
| C | 1.4965440    | 0.613158     |
| C | 0.6948794    | 0.613158     |
| C | -0.6948798   | -0.3720988   |
| C | 1.3751475    | 1.3651834    |
| C | -1.3751462   | -1.2318292   |
| C | 0.6957014    | 0.6211688    |
| C | -1.4111774   | -0.5812849   |
| C | -0.0432947   | -1.2131073   |
| C | 1.0725677    | -0.2006139   |
| C | 0.8695532    | 1.1239299    |
| C | -0.4983290   | 1.7557522    |
| C | -1.6141918   | 0.7432590    |
| H | -2.2712989   | -1.2609750   |
| H | 2.0967717    | -0.5915000   |
| H | 1.7296741    | 1.8036205    |
| H | -2.6383963   | 1.1341445    |
| H | -0.6019741   | 2.4319211    |
| H | -0.6021373   | 2.4331810    |
| H | 0.0604589    | -1.8899700   |
| H | 0.0604231    | -1.8898398   |
| H | -3.5649727   | -0.7620845   |
| H | -3.5720534   | 0.6113158    |
| H | -2.3968395   | -1.3720988   |
| H | -2.4109285   | 1.3651834    |
| H | -1.2318292   | -0.6211688   |

EB₃LYP/def2-SVP/COSMO(ε = 35.88): -233.0953243759
ZE₃LYP/def2-TZVP/COSMO(ε = 35.88): -233.3536128246
Chem. Pot.(298.15)/B3LYP/def2-SVP/COSMO(ε = 35.88): 0.121841
|   |   |   |   |   |
|---|---|---|---|---|
| C | -1.2389242 | 0.7618287 | -0.2901190 |   |
| C | 0.0437069  | -1.2497055 | -0.4788309 |   |
| C | 0.0292922  | 1.5542064  | 0.5358478  |   |
| C | 1.2768616  | 0.7587001  | -0.2081356 |   |
| C | 1.2839046  | -0.6243290 | -1.0849793 |   |
| C | 2.4167616  | 1.3592822  | 0.3456654  |   |
| C | 2.4306561  | -1.3781417 | -0.1899994 |   |
| C | 3.5604072  | 0.6025407  | 0.6236470  |   |
| H | -4.4661176 | -1.3599638 | 0.2854140  |   |
| H | -4.4788239 | 1.0947386  | 0.7658700  |   |
| H | -2.3880985 | 2.4475928  | 0.4063001  |   |
| H | 2.4075452  | 2.4377919  | 0.5633344  |   |
| H | 4.4422596  | 1.0838161  | 1.0557318  |   |
| H | 4.4545330  | -1.3709848 | 0.5758681  |   |
| H | 0.0645761  | 1.8375480  | -1.6078281 |   |
| H | 0.0122184  | 2.5015903  | 0.0244303  |   |
| H | 0.0370663  | -2.3385688 | -0.9235728 |   |
| H | 0.0798299  | -1.1073076 | -2.1845682 |   |

**[Fe⁴O(TMG₂dien(MeCN))]²⁺ (σ) pathway**

|   |   |   |   |   |
|---|---|---|---|---|
| Fe | 4.7688866 | 9.4501776 | 3.1777595 |   |
| N  | 4.4657054 | 11.2878440 | 2.1549187 |   |
| O  | 3.1678937 | 9.2340564 | 3.3921057 |   |
| N  | 5.1825649 | 9.8456151 | 5.0580689 |   |
| C  | 6.5890691 | 10.2129841 | 5.2979430 |   |
| H  | 6.8828455 | 9.9712978 | 6.3320619 |   |
| H  | 6.7774794 | 11.2907749 | 5.1582496 |   |
| C  | 7.4309487 | 9.4063913 | 4.3252658 |   |
| H  | 8.4971760 | 9.6820799 | 4.3854691 |   |
| H  | 7.3439721 | 8.3376971 | 4.5662835 |   |
| N  | 6.9239606 | 9.6226059 | 2.9371512 |   |
| C  | 7.3235779 | 8.5225702 | 2.0160764 |   |
| H  | 8.3959591 | 8.2715029 | 2.1696578 |   |
| H  | 7.2165095 | 8.8951927 | 0.9886868 |   |
| C  | 6.4380037 | 7.3145986 | 2.2172876 |   |
| H  | 6.6326620 | 6.5749289 | 1.4248715 |   |
| H  | 6.6702578 | 6.8204783 | 3.1755880 |   |
| N  | 5.0450921 | 7.7885302 | 2.1605444 |   |
| C  | 4.2853222 | 10.0102776 | 6.0614847 |   |
| N  | 4.3239068 | 11.1098739 | 6.8557527 |   |
| C  | 4.7336982 | 12.4162661 | 6.3486244 |   |
| H  | 4.7412909 | 12.4131775 | 5.2523414 |   |
| H  | 5.7293395 | 12.7071244 | 6.7227621 |   |

**E_{B3LYP/def2-TZVPP/COSMO(ε = 35.88)}:**  
-540.5866247568

**ZPE_{B3LYP/def2-SVP/COSMO(ε = 35.88)}:**  
0.217265

**Chem. Pot.(298.15)/B3LYP/def2-SVP/COSMO(ε = 35.88):**  
0.182819 (σ = 2)
\[
[\text{Fe}^{IV}(O)\text{TMG}_2\text{dien(MeCN)}][\text{CHD-RC (σ)}]
\]

\[
\text{E}_{\text{B3LYP/def2-SVP(Fe:df2-TZVP)/COSMO(ε = 35.88)}} = -2678.7947971799 \quad <\text{S}^2> = 6.05338439
\]
|     | x         | y         | z         |     | x         | y         | z         |
|-----|-----------|-----------|-----------|-----|-----------|-----------|-----------|
| H   | 4.2387384 | -0.2289907| 0.1424330 | C   | 3.2746535 | 1.3379649 | 1.2663394 |
| H   | 3.3408044 | -0.8033869| 1.5546201 | N   | 1.9545068 | 1.5785264 | 1.9221369 |
| C   | 4.0921359 | 1.5203807 | 1.9839165 | H   | 4.0921359 | 1.5203807 | 1.9839165 |
| H   | 3.3408044 | -0.8033869| 1.5546201 |     |           |           |           |
| C   | 1.6328590 | 3.0320899 | 2.0150576 | H   | 1.6328590 | 3.0320899 | 2.0150576 |
| H   | 3.3877973 | 2.0499345 | 0.4368873 | N   | 3.3877973 | 2.0499345 | 0.4368873 |
| C   | 1.2171688 | 3.5421515 | 0.6792848 | H   | 1.2171688 | 3.5421515 | 0.6792848 |
| H   | 0.7356718 | 2.645190  | 0.7991845 | N   | 0.7356718 | 2.645190  | 0.7991845 |
| H   | 1.9556554 | 3.603024  | -0.0462018|     |           |           |           |
| C   | 1.1271688 | 3.5421515 | 0.6792848 | H   | 1.1271688 | 3.5421515 | 0.6792848 |
| H   | 2.8764933 | -0.0462018| 0.9008118 | N   | 2.8764933 | -0.0462018| 0.9008118 |
| C   | 2.1578716 | -1.1773266| -1.1187360| H   | 2.1578716 | -1.1773266| -1.1187360|
|     | 6.2103914  | 2.6894816  | -2.4401858 |
|-----|------------|------------|------------|
| H   | -3.9919728 | 3.1236802  | -1.3832002 |
| H   | -3.4809325 | 1.4198828  | -1.5464153 |
| C   | -2.6591004 | 1.9717780  | 0.8689852  |
| H   | -2.0051241 | 2.2602255  | 1.6995647  |
| H   | -2.6831589 | 0.8737734  | 0.7908116  |
| H   | -3.791276  | 2.3311958  | 1.0786453  |
| C   | -0.9565606 | -1.1148437 | 2.7399073  |
| C   | -1.6849162 | -2.0014613 | 3.6240474  |
| H   | -2.2090886 | -1.4087569 | 4.3893369  |
| H   | -2.4187652 | -2.5753296 | 3.0357896  |
| H   | -0.9823928 | -2.6913132 | 4.1161752  |
| C   | -2.2987780 | -5.1073081 | -0.5961310 |
| C   | -3.1334050 | -5.2573805 | 0.6492129  |
| C   | -3.8673117 | -3.9950744 | 1.0212199  |
| C   | -3.7770872 | -2.8537734 | 0.3223513  |
| C   | -2.9326591 | -2.6995721 | -0.9158943 |
| C   | -2.2122460 | -3.9673423 | -1.2948519 |
| H   | -1.7444057 | -5.9916102 | -0.9308970 |
| H   | -4.5103751 | -4.0375362 | 1.9080990  |
| H   | -4.3472757 | -1.9757692 | 0.6482225  |
| H   | -1.5903710 | -3.9336808 | -2.1968783 |
| H   | -2.2028082 | -1.8756588 | -0.7794907 |
| H   | -3.5654866 | -2.3578584 | -1.7601284 |
| H   | -3.8561095 | -6.0886724 | 0.5222040  |
| H   | -2.4968681 | -5.5886604 | 1.4946425  |

|     | 9.2851410  | 3.1850415  | 3.8150415  |
|-----|------------|------------|------------|
| N   | 11.0430674 | 2.0864176  | 2.0864176  |
| O   | 8.8720609  | 3.4892696  | 3.4892696  |
| N   | 9.8042179  | 5.0408055  | 5.0408055  |
| C   | 10.5573319 | 5.0665483  | 5.0665483  |
| H   | 10.5652375 | 6.0821020  | 6.0821020  |
| H   | 11.6123994 | 4.7714585  | 4.7714585  |
| C   | 9.8764146  | 4.1126595  | 4.1126595  |
| H   | 10.4000430 | 4.0970340  | 4.0970340  |
| H   | 8.8504446  | 4.4620007  | 4.4620007  |
| N   | 9.8243897  | 2.7470834  | 2.7470834  |
| C   | 8.6798311  | 1.9594374  | 1.9594374  |
| H   | 8.5944529  | 2.0644033  | 2.0644033  |
| H   | 8.8797621  | 0.9002114  | 0.9002114  |
| C   | 7.3848552  | 2.3689885  | 2.3689885  |
| H   | 6.5791056  | 1.6918643  | 1.6918643  |
| H   | 7.0890151  | 3.3836387  | 3.3836387  |
| N   | 7.5856131  | 2.2875061  | 2.2875061  |
| C   | 9.7441535  | 6.1686478  | 6.1686478  |
| N   | 10.8052411 | 7.0194577  | 7.0194577  |
| C   | 12.1805333 | 6.5322318  | 6.5322318  |

\[
[Fe^{IV}(O)TMG_{2}dien(MeCN)]^{2+}-CHD-TS (\sigma)
\]

**EB3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(\epsilon = 35.88):**

\[
-2678.7771659493 \ (<S^{2}> 6.47328013)
\]

**EB3LYP/def2-TZVPP/COSMO(\epsilon = 35.88):**

\[
-2680.3463477638 \ (<S^{2}> 6.46761236)
\]

**ZPEB3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(\epsilon = 35.88):**

\[
0.689157
\]

**Chem. Pot. (298.15)/B3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(\epsilon = 35.88):**

\[
0.624082
\]
|  |  |  |  |  |  |
|---|---|---|---|---|---|
| H | 3.9917096 | 12.2003448 | 5.4540298 |
| H | 5.1431152 | 12.6990517 | 6.7349408 |
| H | 3.3860508 | 12.7337792 | 7.0428540 |
| C | 4.1610916 | 10.6545565 | 8.4728034 |
| H | 4.4213294 | 9.6279513 | 8.7562515 |
| H | 3.1723227 | 10.9070589 | 8.8905645 |
| H | 4.9051964 | 11.3344913 | 8.9184690 |
| N | 3.6336194 | 8.6032109 | 7.2383643 |
| H | 1.9489040 | 9.6129732 | 7.2769703 |
| H | 2.4949320 | 8.2201128 | 8.2649767 |
| C | 4.0691947 | 7.2980398 | 6.0297095 |
| C | 4.2707049 | 6.5910660 | 1.8218772 |
| N | 4.5860505 | 5.2794061 | 3.5118379 |
| C | 5.2341324 | 4.8004529 | 1.5049673 |
| H | 5.2067855 | 5.5707247 | 1.0068924 |
| C | 6.9315340 | 11.0881505 | 1.8218772 |
| C | 4.2707049 | 6.5910660 | 1.8218772 |
| N | 4.5860505 | 5.2794061 | 3.5118379 |
| C | 5.2341324 | 4.8004529 | 1.5049673 |
| H | 5.2067855 | 5.5707247 | 1.0068924 |
| C | 6.9315340 | 11.0881505 | 1.8218772 |
| C | 4.2707049 | 6.5910660 | 1.8218772 |
| N | 4.5860505 | 5.2794061 | 3.5118379 |
| C | 5.2341324 | 4.8004529 | 1.5049673 |
| H | 5.2067855 | 5.5707247 | 1.0068924 |
| C | 6.9315340 | 11.0881505 | 1.8218772 |
| C | 4.2707049 | 6.5910660 | 1.8218772 |
| N | 4.5860505 | 5.2794061 | 3.5118379 |
| C | 5.2341324 | 4.8004529 | 1.5049673 |
| H | 5.2067855 | 5.5707247 | 1.0068924 |
| C | 6.9315340 | 11.0881505 | 1.8218772 |
| C | 4.2707049 | 6.5910660 | 1.8218772 |
| N | 4.5860505 | 5.2794061 | 3.5118379 |
| C | 5.2341324 | 4.8004529 | 1.5049673 |
| H | 5.2067855 | 5.5707247 | 1.0068924 |
| C | 6.9315340 | 11.0881505 | 1.8218772 |
| C | 4.2707049 | 6.5910660 | 1.8218772 |
| N | 4.5860505 | 5.2794061 | 3.5118379 |
| C | 5.2341324 | 4.8004529 | 1.5049673 |
| H | 5.2067855 | 5.5707247 | 1.0068924 |
| C | 6.9315340 | 11.0881505 | 1.8218772 |
| C | 4.2707049 | 6.5910660 | 1.8218772 |
| N | 4.5860505 | 5.2794061 | 3.5118379 |
| C | 5.2341324 | 4.8004529 | 1.5049673 |
| H | 5.2067855 | 5.5707247 | 1.0068924 |
| C | 6.9315340 | 11.0881505 | 1.8218772 |
|   |   |   |   |   |
|---|---|---|---|---|
| C  | 0.1932010 | 9.2915236 | 3.4000411 |
| C  | -0.2492947 | 9.7871810 | 4.7229678 |
| H  | -0.9602755 | 11.3817258 | 5.9248239 |
| H  | -0.6371324 | 12.1427281 | 1.5936478 |
| H  | 0.1162464  | 9.8509516  | 1.2569806 |
| H  | -0.2234809 | 9.0868234  | 5.5631681 |
| H  | 1.3938658  | 9.1086716  | 3.4634510 |
| H  | -0.1220484 | 8.2538476  | 3.1923562 |
| H  | -1.7497681 | 12.5442795 | 3.8237375 |
| H  | -0.0633882 | 12.9149626 | 4.0202543 |

Fe 0.2946972 0.5358629 0.4576258
N -0.5586012 -0.4551866 2.1462471
O -0.9330809 -0.1875874 -0.6815360
N 1.9922772 -0.4153338 -0.0916437
C 3.1068106 -0.3020920 0.8621215
H 4.0640131 -0.5438237 0.3726425
H 3.0016339 -0.9982611 1.7119079
H 1.3938658 9.1086716 3.4634510
H -0.1220484 8.2538476 3.1923562
H -1.7497681 12.5442795 3.8237375
H -0.0633882 12.9149626 4.0202543

\[\text{Fe}^{IV}(O)\text{TMG}_2\text{dien(MeCN)}]^2+ - \text{CHD-IC (}\sigma)\]

EB3LYP/def2-SVP(Fe:2-TZVP)/COSMO(ε = 35.88):

-2678.8195904194 (<S> 7.03662745)

EB3LYP/def2-TZVPP/COSMO(ε = 35.88):

-2680.3907041418 (<S> 7.03398300)

ZPEB3LYP/def2-SVP(Fe:2-TZVP)/COSMO(ε = 35.88):

0.691013

Chem. Pot.(298.15)/B3LYP/def2-SVP(Fe:2-TZVP)/COSMO(ε = 35.88):

0.624496
|   |   |   |   |
|---|---|---|---|
| Fe | 1.7468852 | 0.4623730 | 0.2216486 |
| N  | 0.7442064 | 2.0637573 | -0.7479917 |
| O  | 0.5933707 | -0.6065980 | -0.2061384 |
| N  | 1.3165638 | 0.4765539 | 2.1386781 |
| C  | 2.0900990 | 1.4586550 | 2.9187750 |

\[\text{[Fe}^{\text{IV}}(O)\text{TMG}_2\text{dien(MeCN)}]^2^+\text{-DHA-RC (σ)}\]

\(E_{\text{B3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88)}}: -2985.7042212119 \langle S^2 \rangle 6.05358326\)
|         |         |         |         |
|---------|---------|---------|---------|
| H       | 2.1675992 | 1.1448009 | 3.9720543 |
| H       | 1.6287654 | 2.4607258 | 2.9189706 |
| C       | 3.4757217 | 1.5218912 | 2.3004483 |
| H       | 4.1005112 | 2.2929716 | 2.7815612 |
| C       | 4.5631492 | 1.3774930 | 0.0811845 |
| H       | 5.4765758 | 1.6939521 | 0.6132109 |
| C       | 5.3449098 | 1.1225163 | 0.1441731 |
| H       | 4.7413372 | 1.0654654 | 0.8004648 |
| C       | 0.2831045 | 1.0654654 | 2.7381368 |
| N       | 3.3507844 | 1.8029852 | 0.8389062 |
| C       | 4.5402173 | 1.8924178 | -0.8895209 |
| H       | 5.4765758 | 1.6939521 | 0.6132109 |
| N       | 3.3507844 | 1.8029852 | 0.8389062 |
| C       | 4.5402173 | 1.8924178 | -0.8895209 |
| H       | 5.4765758 | 1.6939521 | 0.6132109 |
| N       | 3.3507844 | 1.8029852 | 0.8389062 |

**EB3LYP/def2-TZVPP/COSMO(ε = 35.88):**

-2987.5970827314 (\(<S^2>\) 6.05599834)

**ZPEB3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88):**

0.791331

**Chem. Pot.(298.15)/B3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88):**

0.722174

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S24
| Fe  | 4.5431323 | 9.1291806 | 2.8522580 |
| N   | 4.1036280 | 10.4664865 | 1.2482468 |
| O   | 2.9048843 | 8.9064313 | 3.2657224 |
| N   | 5.1707084 | 10.2112008 | 4.4272551 |
| C   | 6.4576091 | 10.8890933 | 4.1943714 |
| H   | 6.8909234 | 11.2367717 | 5.1456273 |
| H   | 6.3506301 | 11.7792021 | 3.5505171 |
| C   | 7.4006293 | 9.8918956 | 3.5412084 |
| H   | 8.3896785 | 10.3471822 | 3.3553167 |

The table shows the coordinates for different atoms in a molecule, specifically for [FeIV(O)TMG2dien(MeCN)]2+-DHA-TS (σ).

Energy calculations using B3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88):

-2985.6843261097 (<S²> 6.49026349)

Energy calculations using B3LYP/def2-TZVPP/COSMO(ε = 35.88):

-2987.5758563751 (<S²> 6.48683816)

Zero point energy calculations using B3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88):

-2985.6843261097 (<S²> 6.49026349)
|   |   |   |   |
|---|---|---|---|
| H | 7.5501237 | 9.0433360 | 4.2234183 |
| N | 6.8132034 | 9.3932337 | 2.2719853 |
| C | 7.2785998 | 8.0265709 | 1.9389830 |
| H | 8.3692313 | 7.9348547 | 2.0947519 |
| H | 7.0800298 | 7.8571483 | 0.8706531 |
| C | 6.5285692 | 6.9841756 | 2.7512170 |
| H | 6.8183554 | 5.9812552 | 2.4038341 |
| H | 6.8137020 | 7.0445612 | 3.8151975 |
| N | 5.0850381 | 7.2072496 | 2.5614029 |
| C | 4.4655898 | 10.5490176 | 5.5252269 |
| H | 4.4352358 | 11.8350909 | 5.9761469 |
| C | 4.4460850 | 12.9694276 | 5.0582017 |
| H | 4.2196778 | 12.6361822 | 4.0381196 |
| H | 5.4157254 | 13.4951669 | 5.0600434 |
| H | 3.6695350 | 13.6874909 | 5.3685997 |
| C | 4.4521449 | 12.1787079 | 7.3970699 |
| H | 4.6921607 | 11.2952301 | 8.0000755 |
| H | 3.4902916 | 12.5985216 | 7.7355040 |
| H | 5.2348348 | 12.9356664 | 7.5675588 |
| N | 3.7991867 | 9.6071538 | 6.2274718 |
| C | 2.5761002 | 9.8935968 | 6.9729093 |
| H | 2.1874957 | 10.8825971 | 6.7081530 |
| H | 2.7398931 | 9.8478955 | 8.0618668 |
| H | 1.8154904 | 9.1452150 | 6.7046725 |
| C | 4.1776132 | 8.2023111 | 6.1943326 |
| H | 5.2129898 | 8.0985916 | 5.8495677 |
| H | 3.5115396 | 7.6300185 | 5.5277546 |
| H | 4.1006024 | 7.7863111 | 7.2121303 |
| C | 7.1300232 | 10.3175602 | 1.1661374 |
| H | 8.2185687 | 10.3349596 | 0.9766205 |
| H | 6.8056181 | 11.3370883 | 1.4121530 |
| H | 6.6178094 | 9.9975976 | 0.2496533 |
| C | 4.2779869 | 6.1459487 | 2.3917240 |
| N | 5.45232552 | 4.9506297 | 2.9982469 |
| C | 5.1069179 | 4.8570683 | 4.3321349 |
| H | 5.0887451 | 5.8336945 | 4.8265301 |
| H | 6.1455100 | 4.4877237 | 4.3024705 |
| H | 4.5100507 | 4.1541498 | 4.9356487 |
| C | 4.2646256 | 3.6687788 | 2.3444292 |
| H | 4.0710871 | 3.8178486 | 1.2757888 |
| H | 3.4118550 | 3.1365439 | 2.7975554 |
| H | 5.1592391 | 3.0336793 | 2.4484881 |
| N | 3.2051336 | 6.2309320 | 1.5684279 |
| C | 1.9662778 | 5.5010430 | 1.8199389 |
| H | 1.9710042 | 5.0720891 | 2.8285622 |
| H | 1.8032205 | 4.6961285 | 1.0845682 |
| H | 1.1199181 | 6.2021738 | 1.7471451 |
| C | 3.1711197 | 7.1336666 | 0.4242080 |

**Chem. Pot.** (298.15)\text/B3LYP/def2-SVP(Fe:2SVP/def2-TZVP)/COSMO(ε = 35.88):

- **0.784392**
- **0.715142**
|       |        |        |          |
|-------|--------|--------|----------|
| H     | 4.1867952 | 7.4541830 | 0.1650045 |
| H     | 2.5544949 | 8.0228169 | 0.628767  |
| H     | 2.7397479 | 6.5999443 | -0.4375134 |
| C     | 3.7578835 | 11.2120961 | 0.4355629 |
| C     | 3.3229581 | 12.1478189 | -0.5854916 |
| C     | 2.7397479 | 6.5999443 | -0.4375134 |
| C     | 2.5544949 | 8.0228169 | 0.628767  |
| H     | 2.2402259 | 12.2724397 | -0.5404556 |
| H     | 3.8203725 | 13.1205323 | -0.4185276 |
| C     | -0.3685074 | 10.7176297 | 0.3200550 |
| C     | -0.5233787 | 12.0608046 | 0.0511364 |
| C     | -0.1232854 | 11.4764053 | -0.5404556 |
| C     | -0.9449355 | 11.0706363 | 6.0500029 |
| C     | -0.6261414 | 10.8598972 | 3.8363507 |
| C     | -1.3155285 | 10.0492987 | 6.9328857 |
| C     | -1.1546891 | 8.7082181 | 6.5577346 |
| C     | -0.4718551 | 10.4202635 | -1.3668747 |
| C     | -0.7488424 | 12.8174391 | -0.7052058 |
| C     | 0.0073467 | 8.7067482 | 0.3693986 |
| C     | -0.5311917 | 13.4793631 | 1.6832158 |
| C     | 1.1078694 | 12.1162997 | 6.3436060 |
| C     | -0.5090425 | 7.3530594 | 5.0041990 |
| C     | -1.7361164 | 10.2994729 | 7.9105385 |
| C     | -1.4483643 | 7.9069098 | 7.2490925 |
| C     | 1.1004293 | 12.0786920 | 4.0249217 |
| C     | -0.5031979 | 12.8001954 | 4.0480534 |
| C     | 0.0726594 | 8.0802558 | 2.7405350 |
| C     | 1.5288274 | 9.0430166 | 3.1873587 |

\[
[\text{Fe}^{IV}(\text{O})\text{TMG}_{2}\text{dien(\text{MeCN})}]^{2+}\text{-DHA-IC}(\sigma) \]

\[
\text{EB3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(\epsilon = 35.88)}: -2985.7220368753 \quad \text{(<S^2> 7.03807160)}
\]

\[
\text{EB3LYP/def2-TZVPP/COSMO(\epsilon = 35.88)}: -2987.6160271672 \quad \text{(<S^2> 7.03583511)}
\]

\[
\text{ZPE_{B3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(\epsilon = 35.88)}}: 0.78681
\]

\[
\text{Chem. Pot.}_{(298.15)}/\text{B3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(\epsilon = 35.88)}:
\]

S27
|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| H | 4.4330507 | 1.6459184 | -1.0660689 |   |   | 0.716232 |
| C | 4.3244894 | -0.2829282 | -0.1257160 |   |   |   |
| H | 5.119768 | -0.6762409 | -0.7874499 |   |   |   |
| H | 4.4955548 | -0.7339095 | 0.8668325 |   |   |   |
| N | 2.9904471 | -0.6036727 | -0.6499433 |   |   |   |
| C | 0.3673302 | -0.0502526 | 2.9727865 |   |   |   |
| N | -0.3620831 | 0.6306130 | 3.8993550 |   |   |   |
| C | -0.7615823 | 2.0198364 | 3.6988045 |   |   |   |
| H | -0.6322377 | 2.3063476 | 2.6480904 |   |   |   |
| H | -0.1870959 | 2.7127587 | 4.3360312 |   |   |   |
| H | -1.8278563 | 2.1247823 | 3.9568830 |   |   |   |
| C | -0.7752355 | 0.0375006 | 5.1702878 |   |   |   |
| H | -0.2398601 | -0.9036071 | 5.3422221 |   |   |   |
| H | -1.8610932 | -0.1509002 | 5.2075543 |   |   |   |
| H | -0.5206234 | 0.7352819 | 5.9842573 |   |   |   |
| N | 0.1429510 | -1.3763766 | 2.8323454 |   |   |   |
| C | -1.1856722 | -1.9660622 | 2.9730375 |   |   |   |
| H | -1.9476083 | -1.1829516 | 3.0550625 |   |   |   |
| H | -1.2509531 | -2.6280873 | 3.8518518 |   |   |   |
| H | -1.4045487 | -2.5597091 | 2.0718322 |   |   |   |
| C | 1.1711161 | -2.2945155 | 2.3583396 |   |   |   |
| H | 2.1618261 | -1.8400530 | 2.4753102 |   |   |   |
| H | 1.0060446 | -2.5570270 | 1.3012730 |   |   |   |
| H | 1.1313209 | -3.2152268 | 2.9617324 |   |   |   |
| C | 3.2215405 | 3.2662568 | 0.3897919 |   |   |   |
| H | 4.1516285 | 3.8012559 | 0.6554509 |   |   |   |
| H | 2.3917130 | 3.7190924 | 0.9484705 |   |   |   |
| H | 3.0351333 | 3.3991005 | -0.6838298 |   |   |   |
| C | 2.8545484 | -1.6273756 | -1.5135524 |   |   |   |
| N | 3.6234550 | -2.7471063 | -1.4296590 |   |   |   |
| C | 4.0876781 | -3.2824906 | -0.1539284 |   |   |   |
| H | 3.5417311 | -2.8212342 | 0.6756942 |   |   |   |
| H | 5.1686699 | -3.1211886 | -0.0085455 |   |   |   |
| H | 3.8961498 | -4.3673366 | -0.1312632 |   |   |   |
| C | 4.0647569 | -3.4885029 | -2.6100414 |   |   |   |
| H | 3.8911506 | -2.8979008 | -3.5171141 |   |   |   |
| H | 3.5512577 | -4.4596119 | -2.7048708 |   |   |   |
| H | 5.1462867 | -3.6798444 | -2.5212272 |   |   |   |
| N | 1.9527004 | -1.5516160 | -2.5227372 |   |   |   |
| C | 1.1886994 | -2.7104269 | -2.9734816 |   |   |   |
| H | 1.3685957 | -3.5694682 | -2.3175346 |   |   |   |
| H | 1.4346922 | -2.9872806 | -4.0116967 |   |   |   |
| H | 0.1151420 | -2.4642136 | -2.9268050 |   |   |   |
| C | 1.5633515 | -0.2855324 | -3.1296597 |   |   |   |
| H | 2.2867735 | 0.4972020 | -2.8736886 |   |   |   |
| H | 0.5599231 | 0.0264031 | -2.7986149 |   |   |   |
| H | 1.5469325 | -0.4052186 | -4.2249203 |   |   |   |
| C | 0.0197421 | 3.0385489 | -1.1285608 |   |   |   |
### [FeIV(O)TMG₂dien(MeCN)]²⁺ (π) pathway

| Element | X   | Y   | Z   | \( \langle S^2 \rangle \) |
|---------|-----|-----|-----|--------------------------|
| Fe      | 0.5950928 | 0.6550936 | 0.5563116 | 6.05337167 |
| N       | -0.4898703 | -0.4313406 | 2.0220278 | 6.05576575 |
| O       | -0.4168192 | 0.1828271 | -0.6306163 | 6.05576575 |
| N       | 2.1244200 | -0.4380607 | -0.0201422 | 6.05576575 |
| C       | 3.2783225 | -0.3827889 | 0.8942791 | 6.05576575 |
| H       | 4.2139457 | -0.5962543 | 0.3528600 | 6.05576575 |
| H       | 3.2095180 | -1.1198497 | 1.7120498 | 6.05576575 |
| C       | 3.3263609 | 1.0242655 | 1.4636484 | 6.05576575 |
| H       | 4.1214900 | 1.1288602 | 2.2208326 | 6.05576575 |
| H       | 3.5340484 | 1.7383134 | 0.6545349 | 6.05576575 |
| N       | 2.0004357 | 1.3593893 | 2.0637167 | 6.05576575 |
| C       | 1.7923221 | 2.8324057 | 2.1729174 | 6.05576575 |
| H       | 2.7005237 | 3.3181293 | 2.5688039 | 6.05576575 |
| H       | 0.9785649 | 2.9957555 | 2.8933698 | 6.05576575 |
| C       | 1.3943925 | 3.4055062 | 0.8262575 | 6.05576575 |

**Chem. Pot.** (298.15)/B3LYP/def2-SVP(Fe: def2-TZVP)/COSMO(\( \varepsilon = 35.88 \)):

-2678.7948298231 (<\( S^2 \)> 6.05337167)

**ZPE**

0.69563

**Chem. Pot.** (298.15)/B3LYP/def2-SVP(Fe: def2-TZVP)/COSMO(\( \varepsilon = 35.88 \)):

0.63033
| Atm | x    | y    | z    |
|-----|------|------|------|
| C   | 2.1230658 | -1.3572377 | -1.0159439 |
| N   | 2.2593819 | 3.4129132 | -0.7985122 |
| C   | 2.3926194 | -3.2917556 | 0.4869458  |
| H   | 1.6664470 | -2.7491689 | 1.1035730 |
| C   | 2.5670352 | -2.6216788 | 1.0355212 |
| H   | 3.3449814 | -3.3806814 | 1.0355212 |
| C   | 2.0052125 | -4.3076253 | 0.3087065 |
| H   | 1.0802048 | 4.4538026 | 0.9499097  |
| N   | 2.6005888 | -4.2180375 | -2.2166177 |
| H   | 4.1756406 | -3.8377650 | -1.3538775 |
| C   | 1.7052684 | -1.0198787 | -2.2530515 |
| H   | 0.7207166 | -2.8584574 | -2.5754241 |
| C   | 1.0091699 | 0.3425972 | -2.7655436 |
| H   | 2.4794782 | 0.9325865 | -2.1380962 |
| C   | 0.0933174 | 0.9515086 | -3.8302238 |
| H   | 0.8123917 | 0.8240249 | -2.7905593 |
| C   | 1.8019600 | 0.3425972 | -2.7655436 |
| H   | 2.2062183 | 0.3076387 | -3.8302238 |
| C   | 1.8884278 | 0.7489675 | 3.4105251  |
| H   | 2.6547530 | 1.1773324 | 4.0783830  |
| C   | 2.0359371 | -0.3364827 | 3.3572309 |
| H   | 0.8962075 | 0.9515086 | 3.8302238  |
| C   | -0.6555690 | 3.1540289 | -0.4705571 |
| N   | -0.3565426 | 4.1797147 | -1.3113318 |
| C   | 0.9180737 | 4.2651954 | -2.0181192 |
| H   | 1.4474970 | 3.3071942 | -1.9705356 |
| C   | 1.5643078 | 5.0587804 | -1.6080165 |
| H   | 0.7213193 | 4.4962469 | -3.0772140 |
| C   | -1.2821315 | 5.2830045 | -1.5632132 |
| H   | -2.0941681 | 5.2745592 | -0.8268356 |
| C   | -1.7102744 | 5.2413683 | -2.5782037 |
| H   | -0.7316664 | 6.2328201 | -1.4619839 |
| C   | -1.9381342 | 2.7333248 | -0.4035489 |
| C   | -2.8128805 | 2.7079147 | -1.5733209 |
| H   | -2.2405743 | 2.9089491 | -2.4858558 |
| C   | -3.6329053 | 3.4394889 | -1.4886365 |
| H   | -3.2544694 | 1.7020946 | -1.6587754 |
| C   | -2.5108972 | 2.1492923 | 0.8032130 |
| H   | -1.8773381 | 2.3706650 | 1.6694284 |
| C   | -2.6203645 | 1.0582375 | 0.7034726 |
| H   | -3.5073963 | 2.5881972 | 0.9704140 |
| C   | -1.1578802 | -1.1041905 | 2.6859130 |
| C   | -2.0000296 | -1.9430178 | 3.5110935 |
| H   | -2.5106007 | -1.3254737 | 4.2658600 |
| Element | X  | Y  | Z  | Energy | ZPE | Chem. Pot. |
|---------|----|----|----|---------|-----|------------|
| Fe      | 0.4653340 | 0.6314797 | 0.5668364 | [FeIV(O)TMG₂dien(MeCN)]²⁺-CHD-TS (π) |
| N      | -0.3773204 | -0.4196315 | 2.1898100 | E₄B3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88): -2678.7696620860 (<S²> 6.06685088) |
| O      | -0.6400653 | 0.0205103 | -0.5870524 | |
| N      | 2.0676240 | -0.4218714 | -0.0108930 | E₄B3LYP/def2-TZVPP/COSMO(ε = 35.88): -2680.3378005802 (<S²> 6.06849822) |
| C      | 3.1760447 | -0.2800300 | 0.9467549 | ZPE₄B3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88): 0.689043 |
| H      | 4.1327249 | -0.5857210 | 0.4884847 | Chem. Pot.(298.15)/B3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88): 0.624368 |
H  1.9989902  -2.1930274  -4.0196104
H  0.3345672  -1.6866455  -3.6299762
C  1.6313823   0.3598792  -2.7302300
H  2.2237768   1.0300975  -2.0969214
H  0.5781386   0.6796825  -2.7148579
H  2.0115872   0.4188250  -3.7624061
C  1.8411693   1.2221521  -3.3370782
H  2.5916505   1.8884432  -3.9147718
H  2.0370549   0.1507153  -3.4662878
H  0.8434403   1.4520686  -3.7305028
C  -1.0229189   3.0024511  -0.5303718
N  -0.9040393   3.9651460  -1.4877800
C   0.2394458   4.0340449  -2.3909689
H   0.8225378   3.1088413  -2.3403903
H   0.8973730   4.8883878  -2.1597715
H  -0.1266386   4.1533497  -3.4236625
C  -1.9000742   5.0197298  -1.6673741
H  -2.5876272   5.0431350  -0.8137841
H  -2.4798009   4.8883809  -2.5962616
H  -1.3811571   5.9905059  -1.7220808
N  -2.2687630   2.5646320  -0.2270595
C  -3.3057487   2.4030303  -1.2415863
H  -2.8638222   2.5403601  -2.2446417
H  -4.1380863   3.111869  -1.0956847
H  -3.7109094   1.3801070  -1.1765994
C  -2.6189008   2.0726012  -1.0975112
H  -1.8830468   2.4128727  -1.8352828
H  -2.6685570   0.9724815  -1.1201550
H  -3.6082703   2.4697142  -1.3753055
C  -0.8335628  -1.0316376   3.0575414
C  -1.4016754  -1.7919931   4.1526716
H  -2.4712926  -1.5529665   4.2534996
H  -1.2841430  -2.8681096   3.9556366
H  -0.8836451  -1.5352690   5.0892674
C  -1.6179141  -4.1400735  -1.1354906
C  -1.9148783  -4.6230115   0.2545827
C  -2.6471490  -3.6156921   1.0929444
C  -2.8878224  -2.3547413   0.6746549
C  -2.4244678  -1.8531423  -0.6326622
C  -1.8782506  -2.8785707  -1.5397137
H  -1.1962490  -4.8647572  -1.8400411
H  -3.0155297  -3.9485295   2.0691442
H  -3.4524088  -1.6694629   1.3158784
H  -1.6694454  -2.5843679  -2.5722625
H  -1.4890286  -0.9918185  -0.4687026
H  -3.1197386  -1.1484730  -1.1176774
H  -2.4909762  -5.5694424   0.2121721
H  -0.9728376  -4.9257511   0.7611561
### 

| Element | x Position | y Position | z Position |
|---------|------------|------------|------------|
| Fe      | 0.4285230  | 0.6192748  | 0.6001255  |
| N       | -0.7148046 | -0.4484004 | 2.0177602  |
| O       | 1.8967972  | -0.6620971 | 0.139692   |
| C       | 2.9198026  | -0.6891152 | 1.188840   |
| H       | 3.8732000  | -1.0888613 | 0.8076523  |
| H       | 2.6301955  | -1.3210774 | 2.0458300  |
| C       | 3.156218   | 0.7477568  | 2.4701952  |
| H       | 3.8405622  | 0.8213320  | 2.0458300  |
| C       | 3.4968914  | 1.3446977  | 0.8023785  |
| H       | 3.1809209  | 1.3209795  | 2.0720520  |
| C       | 1.8054802  | 2.8147951  | 1.9954689  |
| H       | 2.7751393  | 3.2087900  | 2.3428742  |
| H       | 1.0260766  | 3.1821458  | 2.6774488  |
| C       | 2.0874218  | 3.594201   | 0.5823231  |
| H       | 2.3291196  | 4.3458521  | 0.5663183  |
| N       | 0.2676099  | 2.5309918  | 0.1834576  |
| C       | 1.9770202  | -1.5495008 | -0.8734198 |
| H       | 2.3963277  | -2.8279029 | -0.6552651 |
| C       | 1.4802718  | 3.2594201  | 0.5823231  |
| H       | 3.2391196  | 3.0537008  | -0.0928350 |
| N       | 1.4080218  | 3.594201   | 0.5823231  |
| C       | 1.2978970  | -3.0126464 | 1.1334631  |
| H       | 2.9726396  | -3.6416730 | 1.2316233  |
| H       | 1.7264197  | -4.5485662 | 0.3345687  |
| C       | 3.2211869  | -3.5655839 | -1.611176  |
| H       | 3.6119593  | -2.8860453 | -2.3784278 |
| C       | 2.0874580  | -3.5369250 | 0.5819213  |
| H       | 1.2978970  | -3.0126464 | 1.1334631  |
| H       | 2.9726396  | -3.6416730 | 1.2316233  |
| H       | 1.7264197  | -4.5485662 | 0.3345687  |
| C       | 3.2211869  | -3.5655839 | -1.611176  |
| H       | 3.6119593  | -2.8860453 | -2.3784278 |
| C       | 2.0874580  | -3.5369250 | 0.5819213  |
| H       | 1.2978970  | -3.0126464 | 1.1334631  |
| H       | 2.9726396  | -3.6416730 | 1.2316233  |
| H       | 1.7264197  | -4.5485662 | 0.3345687  |
| C       | 3.2211869  | -3.5655839 | -1.611176  |
| H       | 3.6119593  | -2.8860453 | -2.3784278 |
| C       | 2.0874580  | -3.5369250 | 0.5819213  |
| H       | 1.2978970  | -3.0126464 | 1.1334631  |
| H       | 2.9726396  | -3.6416730 | 1.2316233  |
| H       | 1.7264197  | -4.5485662 | 0.3345687  |
| C       | 3.2211869  | -3.5655839 | -1.611176  |
| H       | 3.6119593  | -2.8860453 | -2.3784278 |
| C       | 2.0874580  | -3.5369250 | 0.5819213  |
| H       | 1.2978970  | -3.0126464 | 1.1334631  |
| H       | 2.9726396  | -3.6416730 | 1.2316233  |
| H       | 1.7264197  | -4.5485662 | 0.3345687  |
| C       | 3.2211869  | -3.5655839 | -1.611176  |
| H       | 3.6119593  | -2.8860453 | -2.3784278 |
| C       | 2.0874580  | -3.5369250 | 0.5819213  |
| H       | 1.2978970  | -3.0126464 | 1.1334631  |
| H       | 2.9726396  | -3.6416730 | 1.2316233  |
| H       | 1.7264197  | -4.5485662 | 0.3345687  |

$[\text{Fe}^{IV}(\text{O})\text{TMG}^{2+}\text{dien(MeCN)}\text{IC}(\pi)]^{2+}$-

**Chemical Potential (B3LYP/def2-SVP/def2-TZVP/COSMO)**

- $\text{EB3LYP/def2-SVP(Fe: def2-TZVP)/COSMO}(\varepsilon = 35.88)$:
  - $-2678.8130470238$ ($\langle S^2 \rangle = 6.08665171$)
- $\text{EB3LYP/def2-TZVP/COSMO}(\varepsilon = 35.88)$:
  - $-2680.3838297758$ ($\langle S^2 \rangle = 6.08556742$)

**ZPE**

- $\text{EB3LYP/def2-SVP(Fe: def2-TZVP)/COSMO}(\varepsilon = 35.88)$:
  - $0.693289$

- **Chemical Potential (B3LYP/def2-SVP)**

- $0.627817$
|   |   |   |   |
|---|---|---|---|
| H | -1.9544839 | 5.3511481 | -0.9507215 |
| H | -1.6830109 | 5.2069561 | -2.7164636 |
| H | -0.5625453 | 6.1662075 | -1.7112423 |
| N | -1.9791680 | 2.8517505 | -0.3905871 |
| C | -2.9187457 | 2.8101643 | -1.5069902 |
| H | -2.3906582 | 2.9331533 | -1.4591342 |
| H | -3.6947791 | 3.5881627 | -1.4186368 |
| H | -3.4148870 | 1.8258345 | -2.7164636 |
| C | -0.5625453 | 6.1662075 | -1.7112423 |
| H | -1.8159277 | 2.5942275 | 1.6912670 |
| H | -2.6894094 | 1.2793805 | 0.8420437 |
| C | -3.4691566 | 2.8662821 | 1.0749427 |
| H | -2.3906582 | 2.9331533 | -1.4591342 |
| H | -3.6947791 | 3.5881627 | -1.4186368 |
| H | -3.4148870 | 1.8258345 | 2.7164636 |
| C | -0.5625453 | 6.1662075 | -1.7112423 |
| H | -1.8159277 | 2.5942275 | 1.6912670 |
| H | -2.6894094 | 1.2793805 | 0.8420437 |
| C | -3.4691566 | 2.8662821 | 1.0749427 |
| H | -2.3906582 | 2.9331533 | -1.4591342 |
| H | -3.6947791 | 3.5881627 | -1.4186368 |
| H | -3.4148870 | 1.8258345 | 2.7164636 |
| C | -0.5625453 | 6.1662075 | -1.7112423 |
| H | -1.8159277 | 2.5942275 | 1.6912670 |
| H | -2.6894094 | 1.2793805 | 0.8420437 |
| C | -3.4691566 | 2.8662821 | 1.0749427 |
| H | -2.3906582 | 2.9331533 | -1.4591342 |
| H | -3.6947791 | 3.5881627 | -1.4186368 |
| H | -3.4148870 | 1.8258345 | 2.7164636 |
| C | -0.5625453 | 6.1662075 | -1.7112423 |
| H | -1.8159277 | 2.5942275 | 1.6912670 |
| H | -2.6894094 | 1.2793805 | 0.8420437 |
| C | -3.4691566 | 2.8662821 | 1.0749427 |
| H | -2.3906582 | 2.9331533 | -1.4591342 |
| H | -3.6947791 | 3.5881627 | -1.4186368 |
| H | -3.4148870 | 1.8258345 | 2.7164636 |

[Fe(IV)(O)TMG2dien(MeCN)]2+-DHA-RC (π)

\[ E_{B3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88)}: \]
\[ -2985.7042299745 \ \text{(<S^2> 6.05361025)} \]

\[ E_{B3LYP/def2-TZVPP/COSMO(ε = 35.88)}: \]
\[ -2987.597032176 \ \text{(<S^2> 6.05600842)} \]

\[ ZPE_{B3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88)}: \]
\[ 0.791332 \]

Chem. Pot. (298.15)/B3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88):
\[ 0.722209 \]
|     |     |     |     |
|-----|-----|-----|-----|
| H   | 4.7487666 | -0.3432311 | 0.8705500 |
| N   | 3.2538780 | -0.0472991 | -0.6407085 |
| C   | 0.2208934 | -0.5694648 | 2.6871654 |
| N   | -0.7114776 | -0.1195459 | 3.5660183 |
| C   | -1.1807110 | 1.2629161 | 3.5528623 |
| H   | -0.8856355 | 1.7570792 | 2.6195826 |
| H   | -0.7893878 | 1.8372942 | 4.4088723 |
| H   | -2.2806987 | 1.2667134 | 3.6188617 |
| C   | -1.2822779 | -0.9615111 | 4.6175359 |
| H   | -0.6925147 | -1.8780894 | 4.7330462 |
| H   | -2.3321315 | -1.2274445 | 4.4119911 |
| H   | -1.2490126 | -0.4048699 | 5.5673465 |
| N   | 0.1744761 | -1.8569509 | 2.2911682 |
| C   | -1.0797770 | -2.5875910 | 2.1189665 |
| H   | -1.9341792 | -1.9024358 | 2.1483247 |
| H   | -1.2091885 | -3.3679234 | 2.8860119 |
| H   | -1.0670691 | -3.0711717 | 1.1304216 |
| C   | 1.3686135 | -2.5920024 | 1.8882980 |
| H   | 2.2675736 | -2.0576059 | 2.2151301 |
| H   | 1.3968570 | -2.7256472 | 0.7960696 |
| H   | 1.3512278 | -3.5840981 | 2.3667834 |
| C   | 2.7797145 | 3.836920 | 1.2519125 |
| H   | 3.5852201 | 3.9623534 | 1.7346233 |
| H   | 1.8479260 | 3.5493967 | 1.8063009 |
| H   | 2.6506169 | 3.7425178 | 0.2243267 |
| C   | 3.2608773 | -0.9391924 | -1.6539325 |
| N   | 4.1607150 | -1.9573545 | -1.6995110 |
| C   | 4.6254060 | -2.6469313 | -0.4994870 |
| H   | 3.9828454 | -2.4058960 | 0.3542612 |
| H   | 5.6686560 | -2.3884358 | -0.2538501 |
| H   | 4.5728462 | -3.7337290 | -0.6723489 |
| C   | 4.7444471 | -2.4327821 | -2.9535766 |
| H   | 4.5397782 | -1.7213511 | -3.7620894 |
| H   | 4.3615655 | -3.4268482 | -3.2372813 |
| H   | 5.8360619 | -2.508814 | -2.8253686 |
| N   | 2.3843420 | -0.8136764 | -2.6752807 |
| C   | 1.8129000 | -1.9710901 | -3.3591704 |
| H   | 2.0621454 | -2.8950802 | -2.8254756 |
| H   | 2.1627909 | -2.0464144 | -4.4016292 |
| H   | 0.7162330 | -1.8651304 | -3.3701275 |
| C   | 1.8433464 | 0.4740173 | -3.0927665 |
| H   | 2.4417561 | 1.2906638 | -2.6736684 |
| H   | 0.7967222 | 0.5889687 | -2.7709342 |
| H   | 1.8806870 | 0.5342503 | -4.1921829 |
| C   | -0.1426359 | 3.0320701 | -0.8296940 |
| C   | -1.0073593 | 4.0484510 | -1.3933236 |
| H   | -0.4950676 | 4.5368491 | -2.2365007 |
| H   | -1.9427665 | 3.5890752 | -1.7487991 |
\begin{table}
\centering
\begin{tabular}{cccc}
\hline
Element & \text{X}\text{Y}\text{Z} & \text{X}\text{Y}\text{Z} & \text{X}\text{Y}\text{Z} \\
\hline
Fe  & 1.7562054 & 0.5694450 & 0.3014995 \\
N   & 0.8544378 & 2.2694508 & -0.5603767 \\
O   & 0.4406693 & -0.4877354 & -0.0126906 \\
N   & 1.4482759 & 0.7886504 & 2.2684366 \\
C   & 2.2960473 & 1.8462268 & 2.8396475 \\
H   & 2.3541807 & 1.7572761 & 3.9361077 \\
H   & 1.9131365 & 2.8586307 & 2.6232312 \\
C   & 3.6800653 & 1.6731011 & 2.2399596 \\
H   & 4.3794784 & 2.4473111 & 2.5987419 \\
H   & 4.0805106 & 0.6932613 & 2.5351680 \\
N   & 3.5872544 & 1.7211754 & 0.7517831 \\
C   & 4.7181542 & 0.9915615 & 0.1098528 \\
H   & 5.6562625 & 1.1838284 & 0.6582081 \\
H   & 4.8359169 & 1.3875732 & -0.9085341 \\
C   & 4.4028979 & -0.4899192 & 0.0301502 \\
H   & 5.1764741 & -0.9976219 & -0.5664226 \\
H   & 4.4256426 & -0.9463618 & 1.0351516 \\
N   & 3.0803951 & -0.6094704 & -0.5992725 \\
C   & 0.5046788 & 0.2352346 & 3.0532268 \\
N   & -0.1981017 & 0.9904683 & 3.9455227 \\
\hline
\end{tabular}
\end{table}

\textbf{[Fe\textsuperscript{IV}(O)TMG\textsubscript{2}dien(MeCN)]\textsuperscript{2+}-DHA-TS (π)}

\[ E_{B3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88)}: \]
\[ \text{-2985.675525812 (<S^2> 6.06687451)} \]

\[ E_{B3LYP/def2-TZVPP/COSMO(ε = 35.88)}: \]
\[ \text{-2987.5661503117 (<S^2> 6.06864081)} \]

\[ ZPE_{B3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88)}: \]
\[ 0.784396 \]

\[ \text{Chem. Pot. (298.15)/B3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88)}: \]
\[ 0.715554 \]
| C | -0.5652350 | 2.3726403 | 3.6576601 |
| H | -0.4313923 | 2.5873848 | 2.5905826 |
| H | 0.0301171  | 3.0908726 | 4.2463927 |
| H | -1.6270513 | 2.5229643 | 3.9128135 |
| C | -0.5728791 | 0.5070640 | 5.2732259 |
| H | -0.0492883 | -0.4291316 | 5.4994621 |
| H | -1.6598163 | -0.924004 | 3.0070483 |
| C | -1.0540393 | -1.6662055 | 3.2738922 |
| H | -1.8141854 | -0.8796494 | 3.3224259 |
| H | -1.0665209 | -2.2404344 | 4.2147924 |
| H | -1.3170295 | -2.3446033 | 2.4483147 |
| C | 1.2646702  | -2.0530151 | 2.5653229 |
| H | 2.2625211  | -1.6022217 | 2.6138637 |
| H | 1.0612732  | -2.3821707 | 1.5349120 |
| H | 1.2377008  | -2.9273881 | 3.2347601 |
| C | 3.5992326  | 3.131934  | 0.2972807 |
| H | 4.5748266  | 3.5914498 | 0.5292725 |
| H | 2.8148364  | 3.7060416 | 0.8045179 |
| H | 3.4339684  | 3.1778232 | -0.7862142 |
| C | 2.8633599  | -1.5771214 | -1.5046853 |
| N | 3.4883853  | -2.7850570 | -1.4279882 |
| C | 3.7865935  | -3.4286877 | -0.1530641 |
| H | 3.2406063  | -2.9369793 | 0.6585507 |
| H | 4.8653859  | -3.4126383 | 0.0750695 |
| H | 3.4614674  | -4.4807031 | -0.1986475 |
| C | 3.9493526  | -3.5086825 | -2.6116767 |
| H | 3.9175827  | -2.8574734 | -3.4929742 |
| H | 3.3477836  | -4.4122053 | -2.8055991 |
| H | 4.9938237  | -3.8206705 | -2.4496688 |
| N | 2.0397075  | -1.3526374 | -2.5562175 |
| C | 1.2236135  | -2.4078417 | -3.1494333 |
| H | 1.2208863  | -3.2965283 | -2.5078702 |
| H | 1.5764515  | -2.6876860 | -4.1555965 |
| H | 0.1872610  | -2.0468242 | -3.2438254 |
| C | 1.8260769  | -0.0183660 | -3.1010316 |
| H | 2.6391262  | 0.6501714 | -2.7951542 |
| H | 0.8672850  | 0.4094242 | -2.7679484 |
| H | 1.8143390  | -0.0799942 | -4.2005884 |
| C | 0.3780795  | 3.2451752 | -0.9571034 |
| C | -0.1917087 | 4.4856970 | -1.4432812 |
| H | -0.0296791 | 4.5646223 | -2.5287729 |
| H | -1.2714484 | 4.5064420 | -1.2346448 |
| H | 0.2972352  | 5.3339114 | -0.9398759 |
| C | -2.8023174 | 2.6325434 | -3.1562124 |
| C | -3.6818488 | 3.2709516 | -2.2704468 |
| C | -2.1936690 | 1.4338094 | -2.7839675 |
$\text{[Fe}^{\text{IV}}(\text{O})\text{TMG}_{2}\text{dien(MeCN)}_{2}\text{]}^{2+}\text{-DHA-IC (}\pi\text{)}$

$$E_{B3LYP/\text{def2-TZVPP}/\text{COSMO}(\epsilon = 35.88)}: -2985.7154660033 \left( <S^2> = 6.08206800 \right)$$

$$E_{B3LYP/\text{def2-TZVPP}/\text{COSMO}(\epsilon = 35.88)}: -2987.6096878526 \left( <S^2> = 6.08160453 \right)$$

$$ZPE_{B3LYP/\text{def2-TZVPP}/\text{COSMO}(\epsilon = 35.88)}: 0.789187$$

$$\text{Chem. Pot. (298.15)/B3LYP/def2-SVP(Fe:}\text{def2-TZVPP)/COSMO(}\epsilon = 35.88): 0.719821$$
| Element | X-Coordinate | Y-Coordinate | Z-Coordinate |
|---------|--------------|--------------|--------------|
| C       | -0.9238426   | -0.7833638   | 5.0139302    |
| H       | -0.3226152   | -1.6991777   | 5.0552218    |
| H       | -1.9919613   | -1.0523911   | 4.9620204    |
| H       | -0.7579056   | -0.2173241   | 5.9447658    |
| N       | 0.2031801    | -1.7117729   | 2.5275349    |
| C       | -1.0761717   | -2.4149811   | 2.4975492    |
| H       | -1.9042559   | -1.7154096   | 2.6588507    |
| H       | -1.1253926   | -3.2122970   | 3.2571961    |
| H       | -1.2053078   | -2.8740226   | 1.5048743    |
| C       | 1.3318645    | -2.4719442   | 2.0040538    |
| H       | 2.2703095    | -1.9569938   | 2.2406126    |
| H       | 1.2470270    | -2.5950479   | 0.9139113    |
| H       | 1.3426901    | -3.4648774   | 2.4816826    |
| C       | 2.9716102    | 3.3593495    | 0.9904292    |
| H       | 3.8453247    | 3.9187795    | 1.3640310    |
| H       | 2.0902437    | 3.6560959    | 1.5709174    |
| H       | 2.8091609    | 3.6153135    | -0.0637138   |
| C       | 3.0551114    | -0.9648613   | -1.7220810   |
| N       | 3.8595316    | -2.0580801   | -1.8346123   |
| C       | 4.2814026    | -2.8400572   | -0.6772969   |
| H       | 3.6849195    | -2.5743731   | 0.2019414    |
| H       | 5.3498601    | -2.6928921   | -0.4473386   |
| H       | 4.1211094    | -3.9092638   | -0.8907132   |
| C       | 4.3818067    | -2.5193249   | -3.1196601   |
| H       | 4.2227011    | -1.7560827   | -3.8904515   |
| H       | 3.9125306    | -3.4636012   | -3.4423595   |
| H       | 5.4655413    | -2.692234    | -3.0190264   |
| N       | 2.1911407    | -0.7073744   | -2.7314246   |
| C       | 1.4875020    | -1.7714365   | -3.4402837   |
| H       | 1.6859641    | -2.7423133   | -2.9731808   |
| H       | 1.7729026    | -1.8136746   | -4.5041123   |
| H       | 0.4037331    | -1.5794221   | -3.3799925   |
| C       | 1.7422202    | 0.6403596    | -3.0484183   |
| H       | 2.4282528    | 1.3804828    | -2.6203079   |
| H       | 0.7256764    | 0.8241065    | -2.6655848   |
| H       | 1.7298838    | 0.7633988    | -4.1431267   |
| C       | -0.2932265   | 3.1045777    | -0.4589390   |
| C       | -1.1955389   | 4.1743924    | -0.8333285   |
| H       | -0.6401750   | 4.9384674    | -1.3989086   |
| H       | -2.0081428   | 3.7766037    | -1.4610052   |
| H       | -1.6208684   | 4.6319144    | 0.0730864    |
| C       | -3.2110676   | 2.4489784    | -3.6868318   |
| C       | -4.2230598   | 3.0441323    | -2.9132661   |
| C       | -2.7626906   | 1.1707018    | -3.3743393   |
| C       | -4.7684024   | 2.3481300    | -1.8264321   |
| C       | -3.3129057   | 0.4460030    | -2.2811695   |
| C       | -4.3308179   | 1.0624284    | -1.4922405   |
| C       | -2.8941160   | -0.8888647   | -1.9899376   |
|   | C     | H     | Fe    | O     |
|---|-------|-------|-------|-------|
| C | -4.9078064 | 0.3434600 | 2.5117018 | 6.3729970 |
| C | -4.5369464 | -1.1171941 | 4.4181172 | 6.3729970 |
| C | -3.5205928 | -1.6840793 | 4.4762431 | 5.3634522 |
| C | -5.1659428 | -1.9212785 | 3.3598908 | 7.6851871 |
| C | -3.1758345 | -3.0517339 | 3.4411268 | 5.1319592 |
| C | -4.8163642 | -3.2675366 | 0.8763267 | 6.2466266 |
| C | -3.8146398 | -3.8318448 | 0.4494549 | 9.6102170 |
| H | -2.7817496 | 2.9870015 | 0.9251675 | 8.3044188 |
| H | -4.5860652 | 4.0456392 | 0.4897329 | 9.6102170 |
| H | -1.9866805 | 0.6977787 | 0.4897329 | 9.6102170 |
| H | -5.5542386 | 2.8169487 | 2.6116462 | 9.1106972 |
| H | -5.9479523 | -1.4872944 | 2.7967175 | 9.7039923 |
| H | -2.4002930 | -3.4877837 | 2.8670056 | 9.7595431 |
| H | -5.3247975 | -3.8767924 | 4.6376789 | 7.8973964 |
| H | -3.5399270 | -4.8832093 | 5.4174789 | 9.0175080 |
| H | -4.5826973 | 0.8763267 | 5.4174789 | 9.0175080 |
| H | -6.0070823 | 0.4494549 | 5.4174789 | 9.0175080 |
| H | -2.1185435 | -1.3445435 | 5.4174789 | 9.0175080 |
| H | -0.4141488 | -0.2156491 | 5.4174789 | 9.0175080 |

**[FeIV(O)TMG3tren]2+ (σ) pathway**

|   | [FeIV(O)TMG3tren]2+ |
|---|-------------------|
| Fe | 2.5117018 | 6.3729970 |
| O  | 3.7856860 | 5.3634522 |
| N  | 0.8376096 | 7.6998255 |
| N  | 3.3996394 | 7.8658171 |
| N  | 1.2267776 | 5.1319592 |
| N  | 5.4174789 | 9.0175080 |
| N  | 2.2705373 | 6.6231261 |
| N  | 5.1485192 | 6.8108823 |
| N  | 0.9952763 | 3.3784508 |
| N  | 2.0330505 | 2.9786947 |
| N  | 2.4798754 | 5.6443585 |
| N  | 4.3785529 | 6.1379706 |
| C  | 1.1423972 | 8.7316161 |
| H  | 0.9251675 | 8.3044188 |
| H  | 0.4897329 | 9.6102170 |
| C  | 2.6116462 | 9.1106972 |
| H  | 2.7967175 | 9.7039923 |
| H  | 2.8670056 | 9.7595431 |
| C  | 4.6376789 | 7.8973964 |
| C  | 5.4208518 | 9.9430001 |
| H  | 4.9126374 | 9.5013807 |
| H  | 6.4641388 | 10.1521015 |
| C  | 6.3101908 | 9.3845520 |
| H  | 6.0824739 | 8.7883343 |
| H  | 6.1528416 | 10.4479815 |

**[FeIV(O)TMG3tren]2+**

|   | E_{B3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88)}: |
|---|------------------------------------------------|
|   | -2713.2952880582 (<S^2> 6.05191598) |
|   | ZPE_{B3LYP/def2-TZVP/COSMO(ε = 35.88)}: |
|   | -2714.8951214215 (<S^2> 6.05445028) |
|   | Chem. Pot.(298.15)/B3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88): |
|   | 0.662954 (σ = 3) |
| Atom | X-coordinate | Y-coordinate | Z-coordinate |
|------|--------------|--------------|--------------|
| H    | 7.3719928    | 2.0508657    | 9.2479043    |
| C    | 6.5567653    | 2.3080172    | 6.4409240    |
| H    | 7.0676207    | 3.0515976    | 7.0636676    |
| H    | 6.6254732    | 2.6328240    | 5.3897081    |
| H    | 7.079950    | 1.3397344    | 6.5369533    |
| C    | 4.3135149    | 1.4780553    | 5.8713301    |
| H    | 3.3297970    | 1.2983867    | 6.3186245    |
| C    | 4.7878904    | 0.5069090    | 5.6539949    |
| H    | 4.1878340    | 2.0326703    | 4.9288125    |
| C   | -0.3521384   | 3.9684707    | 6.8844570    |
| H   | -0.7187983   | 4.8722496    | 6.3797558    |
| H   | -1.159018    | 3.5967615    | 7.5386210    |
| C   | 0.0437652    | 2.9343300    | 5.8443610    |
| H   | 0.2361069    | 1.9663456    | 6.3370342    |
| H   | -0.7967795   | 2.7710231    | 5.1508370    |
| C   | 1.4263722    | 3.0663725    | 3.8577730    |
| C   | 1.0037607    | 0.6405771    | 4.1734577    |
| H   | 1.5989065    | 0.7757663    | 5.0819734    |
| H   | 1.4626824    | -0.1678199   | 3.5811430    |
| H   | -0.0145861   | 0.3230238    | 4.4537663    |
| C   | 0.4771906    | 1.7081148    | 2.0202830    |
| H   | 0.2805254    | 2.6895566    | 1.5732014    |
| H   | -0.4723312   | 1.1503717    | 2.0656892    |
| H   | 1.1722573    | 1.1478542    | 1.3725966    |
| C   | 2.9393355    | 3.4199663    | 1.9415056    |
| H   | 3.1499834    | 2.3531355    | 2.0799694    |
| H   | 3.8905704    | 3.9719617    | 2.0172354    |
| H   | 2.5290100    | 3.5777809    | 0.9300222    |
| C   | 1.9137422    | 5.3490736    | 3.0693708    |
| H   | 1.0839365    | 5.6091555    | 4.7363984    |
| H   | 1.7020214    | 5.7533973    | 2.0658337    |
| H   | 2.8404039    | 5.8055183    | 3.4497662    |
| C   | 0.6907691    | 5.6958125    | 8.3010630    |
| H   | 1.4134335    | 5.7867004    | 9.1229356    |
| H   | -0.3202555   | 5.8145506    | 8.7263904    |
| C   | 0.9825757    | 6.7553263    | 7.2521285    |
| H   | 0.1578596    | 6.7910685    | 6.5205881    |
| H   | 1.0187317    | 7.7465862    | 7.7319752    |
| C   | 3.0246795    | 7.4192830    | 6.1297594    |
| C   | 1.2191301    | 8.6111872    | 4.9123612    |
| H   | 0.9138067    | 7.6021915    | 4.6181122    |
| H   | 1.3556939    | 9.2080583    | 3.9958211    |
| H   | 0.4115332    | 9.0737455    | 5.5041945    |
| C   | 3.1193622    | 9.8745508    | 5.8320633    |
| H   | 3.9183922    | 9.8021671    | 6.5791324    |
| H   | 2.3648980    | 10.5896344    | 6.1983178    |
| H   | 3.5377685    | 10.2706565    | 4.8915706    |
| C   | 5.2027113    | 7.8602057    | 5.0565735    |
| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| H       | 4.5751923 | 8.1883973 | 4.2197910 |
| H       | 5.8696939 | 7.0606306 | 4.6945270 |
| H       | 5.8276762 | 8.7051161 | 5.3911093 |
| C       | 5.1053028 | 6.6048807 | 7.1685091 |
| H       | 4.4150988 | 6.4134100 | 8.0186636 |
| H       | 5.9516809 | 7.2296855 | 7.5105399 |
| H       | 5.4931964 | 5.6474729 | 6.7881964 |
| Fe      | -0.9688324 | -0.0315295 | 0.8179396 |
| O       | 0.1979603 | -0.1264185 | -0.3125066 |
| N       | -2.5090601 | 0.0904373 | 2.3006792 |
| N       | 0.1677664 | 0.7266144 | 2.3335927 |
| N       | -1.4577365 | -2.0087079 | 0.8721029 |
| N       | -2.2042811 | 1.2473725 | -0.1749975 |
| N       | 2.0178712 | 2.0722175 | 2.9544539 |
| N       | 2.3610514 | 0.0829862 | 1.8061970 |
| N       | -0.7088069 | -4.2430079 | 0.6245967 |
| N       | -0.8160128 | -2.8407245 | -1.2244556 |
| N       | -2.9912216 | -2.2749183 | -2.2749183 |
| C       | 1.8393787 | 0.3025512 | 3.6138021 |
| H       | 1.4879574 | 0.9656204 | 2.3520084 |
| H       | 3.5763631 | 0.5100734 | 1.1203772 |
| C       | -3.2552868 | -1.1979205 | 2.2679394 |
| H       | -3.9729782 | -1.1586912 | 1.4376214 |
| H       | -3.8271907 | -1.3287637 | 3.2022837 |
| C       | -2.2841616 | -2.3435534 | 2.0423354 |
| H       | -1.6773847 | -2.5023696 | 2.9497393 |

**[FeIV(O)TMG3tren]**$^{2+}$-CHD-RC ($\sigma$)

\[ \mathrm{EB3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(\epsilon = 35.88):} \]
\[ -2946.3902236849 \] (<$S^2$> 6.05271281)

\[ \mathrm{EB3LYP/def2-TZVPP/COSMO(\epsilon = 35.88):} \]
\[ -2948.2464037180 \] (<$S^2$> 6.05539672)

\[ \mathrm{ZPEB3LYP/def2-SVP(Fe:def2-TZVP)/COSMO(\epsilon = 35.88):} \]
\[ 0.847527 \]

**Chem. Pot.**(298.15)/B3LYP/def2-SVP(Fe:def2-TZVPP)/COSMO(\epsilon = 35.88):
\[ 0.777683 \]
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| H       | -2.848741 | -3.275182 | 1.875569  |
| C       | 0.987559  | 3.009051  | 0.110484  |
| C       | -0.147209 | -4.439110 | 1.956069  |
| H       | 0.219520  | -3.491385 | 2.362714  |
| H       | 0.705363  | -5.134202 | 1.885768  |
| H       | -0.882985 | -4.870376 | 2.655413  |
| C       | -0.971963 | -5.474306 | 0.118295  |
| H       | -1.601738 | -5.265895 | 0.991068  |
| H       | -1.511484 | -6.175224 | 0.539265  |
| H       | -0.041986 | -5.964861 | 0.451338  |
| C       | 0.277105  | -3.470063 | 1.957602  |
| H       | 0.988646  | -3.933866 | 1.264635  |
| H       | 0.809170  | -2.695581 | 2.533243  |
| H       | -0.086210 | -4.233751 | 2.665328  |
| C       | -1.652139 | -1.946401 | 2.016012  |
| H       | -2.549724 | -1.687426 | 1.438512  |
| H       | -1.956616 | -2.463220 | 2.935423  |
| H       | -1.113824 | -1.024028 | 2.277272  |
| C       | -3.381888 | 1.240659  | 1.935292  |
| H       | -2.899620 | 2.163059  | 2.285307  |
| H       | -4.356065 | 1.154712  | 2.445926  |
| C       | -3.545920 | 1.298202  | 0.426200  |
| H       | -4.185472 | 0.465046  | 0.088804  |
| H       | -4.095912 | 2.227237  | 0.149421  |
| C       | -1.998847 | 1.865170  | 1.348766  |
| C       | -4.010851 | 0.999999  | 2.516764  |
| H       | -3.735001 | 0.054577  | 2.039452  |
| H       | -4.090691 | 0.824845  | 3.602087  |
| H       | -5.001519 | 1.314071  | 2.147491  |
| C       | -3.120130 | 3.220434  | 3.090666  |
| H       | -2.482207 | 4.018904  | 2.694056  |
| H       | -4.167315 | 3.562071  | 3.053059  |
| H       | -2.857749 | 3.037578  | 4.146194  |
| C       | -0.238988 | 2.411326  | 2.990759  |
| H       | -0.842923 | 1.779640  | 3.653201  |
| H       | -0.782778 | 1.999138  | 2.955942  |
| H       | -0.183402 | 3.427800  | 3.415076  |
| C       | 0.084898  | 2.956451  | 0.615581  |
| H       | -0.481157 | 3.101358  | 0.310915  |
| H       | 0.468032  | 3.932857  | 0.954681  |
| H       | 0.936163  | 2.286711  | 0.419250  |
| C       | 5.463740  | -0.005873 | 2.703462  |
| C       | 5.441842  | 1.221336  | 3.576616  |
| C       | 4.163615  | 1.363432  | 4.360989  |
| C       | 3.139214  | 0.504474  | 4.267316  |
| C       | 3.143801  | -0.699378 | 3.361042  |
| C       | 4.439390  | -0.865254 | 2.609723  |
| H       | 6.377253  | -0.187528 | 2.125627  |
|     |   |   |   |   |   |   |   |   |
|-----|---|---|---|---|---|---|---|---|
| H   | 4.0914666 | 2.2200706 | -5.0410385 |
| H   | 2.2412326 | 0.6653797 | -4.8747854 |
| H   | 4.5273129 | -1.7419187 | -1.9579273 |
| H   | 2.9265057 | -1.6147206 | -3.9475355 |
| H   | 2.3010827 | -0.6307012 | -2.6427220 |
| H   | 5.6101139 | 2.1275351 | -2.9597196 |
| H   | 6.3087785 | 1.2081393 | -2.676670  |
| Fe  | 2.6250481 | 4.3115403 | 6.3260195 |
| O   | 3.9939871 | 4.1845170 | 5.3146118 |
| N   | 0.7846524 | 4.4270370 | 7.7131244 |
| N   | 3.3365789 | 3.3425791 | 8.0261986 |
| N   | 1.1981471 | 3.3070016 | 5.1778735 |
| N   | 2.3655618 | 6.3850560 | 6.4641382 |
| N   | 5.2166375 | 2.6803943 | 9.3108912 |
| N   | 4.8511197 | 1.7497729 | 7.2141463 |
| N   | 0.7135970 | 1.7614003 | 3.4449074 |
| N   | 1.7639613 | 3.7757298 | 2.9517124 |
| N   | 2.6903610 | 8.5537968 | 5.5548459 |
| C   | 1.0801394 | 3.5718307 | 8.8828083 |
| H   | 0.8365280 | 2.5313781 | 8.6258926 |
| H   | 0.4501796 | 3.8568720 | 9.7448608 |
| C   | 2.5575097 | 3.6617104 | 9.2311350 |
| H   | 2.7902623 | 4.6692035 | 9.6182558 |
| H   | 2.7793148 | 2.9547186 | 10.0458672 |
| C   | 4.4540047 | 2.6199437 | 8.1763494 |
| C   | 5.4211488 | 3.9146880 | 10.053816 |
| H   | 5.0786140 | 4.7760750 | 9.4770437 |
| H   | 6.4981762 | 4.0412915 | 10.2575451 |
| H   | 4.8935624 | 3.9045804 | 11.0271800 |
| C   | 5.8521698 | 1.4986834 | 9.8892474 |
| H   | 5.4626538 | 0.5874647 | 9.4203674 |
| H   | 5.6173853 | 1.4603757 | 10.9657889 |
| H   | 6.9496523 | 1.5205144 | 9.7799267 |
| C   | 6.2568445 | 1.4804773 | 6.9322323 |
| H   | 6.8979616 | 2.2035500 | 7.4493512 |
| H   | 6.4217537 | 1.5833378 | 5.8495353 |
| H   | 6.5499729 | 0.4598146 | 7.2304016 |
| C   | 3.9063796 | 1.0955537 | 6.3223928 |
| H   | 2.8984928 | 1.1526985 | 6.7487766 |
| H   | 4.1874130 | 0.0348907 | 6.2188232 |
| H   | 3.9044157 | 1.5625394 | 5.3256536 |
| C   | -0.3656732 | 3.9265366 | 6.9299190 |
| H   | -0.7674108 | 4.7544185 | 6.3292157 |
| H   | -1.1740583 | 3.5811889 | 7.5995076 |
| C   | 0.0817348 | 2.8118374 | 5.9963716 |
| H   | 0.3675718 | 1.9228540 | 6.5857670 |

$[\text{Fe}^{IV}(O)\text{TMG}_{3}\text{tren}]^{2+}\text{-CHD-}\text{TS (}\sigma\text{)}$

$\text{E}_{\text{B3LYP/def2-SVP(Fe:}\text{def2-TZVP)/COSMO(}\epsilon=35.88):}$

$-2946.3671746049 \ (<S^2> 6.52206113)$

$\text{E}_{\text{B3LYP/def2-TZVP/COSMO(}\epsilon=35.88):}$

$-2948.2217801537 \ (<S^2> 6.51430048)$

$\text{ZPE}_{\text{B3LYP/def2-SVP(Fe:}\text{def2-TZVP)/COSMO(}\epsilon=35.88):}$

$0.840466$

$\text{Chem. Pot.}_{\text{(298.15)/B3LYP/def2-SVP(Fe:}\text{def2-TZVP)/COSMO(}\epsilon=35.88):}$

$0.770718$
|    |     |     |     |     |     |
|----|-----|-----|-----|-----|-----|
| H  | -0.7694328 | 2.5093901 | 5.3666944 |     |     |
| C  | 1.2378739  | 2.9458504  | 3.8897312  |     |     |
| C  | 0.8007233  | 0.5248037  | 4.2112956  |     |     |
| H  | 1.5030108  | 0.6373717  | 5.0428437  |     |     |
| H  | 1.1716928  | -0.2804936 | 3.5557166  |     |     |
| H  | -0.1796151 | 0.2149894  | 4.6113236  |     |     |
| C  | -0.0281180 | 1.6565864  | 2.1902679  |     |     |
| H  | -0.2532063 | 2.6537697  | 1.7941898  |     |     |
| H  | -0.9829663 | 1.1403809  | 2.3841959  |     |     |
| H  | 0.5222076  | 1.0801643  | 1.4274879  |     |     |
| C  | 2.4238721  | 3.2869805  | 1.7462272  |     |     |
| H  | 2.6268085  | 2.2128132  | 1.8271368  |     |     |
| H  | 3.8315320  | 3.8169847  | 1.6227868  |     |     |
| H  | 1.8207234  | 3.4696745  | 0.8411570  |     |     |
| C  | 1.7654598  | 5.2210200  | 3.1113102  |     |     |
| H  | 1.0274803  | 5.5049713  | 3.8694570  |     |     |
| H  | 1.4882660  | 5.6884305  | 2.1526969  |     |     |
| H  | 2.7561045  | 5.5936066  | 3.4160783  |     |     |
| C  | 0.6338074  | 5.8492690  | 8.0877993  |     |     |
| H  | 1.3045376  | 6.0613244  | 8.9320703  |     |     |
| H  | -0.3978577 | 6.0580590  | 8.4245919  |     |     |
| C  | 1.0136024  | 6.7436585  | 6.9188748  |     |     |
| H  | 0.2683539  | 6.6369612  | 6.1112705  |     |     |
| H  | 0.9715902  | 7.7943096  | 7.2455128  |     |     |
| C  | 3.1709873  | 7.3791510  | 6.0715612  |     |     |
| C  | 1.5414766  | 8.6178497  | 4.6606259  |     |     |
| H  | 1.2636477  | 7.6171451  | 4.3176192  |     |     |
| H  | 1.8061428  | 9.2208843  | 3.7760698  |     |     |
| H  | 0.6665092  | 9.0854290  | 5.1431839  |     |     |
| C  | 3.2748363  | 9.8493385  | 5.8936986  |     |     |
| H  | 3.9741108  | 9.7464832  | 6.7317576  |     |     |
| H  | 2.4669238  | 10.5338638 | 6.2012541  |     |     |
| H  | 3.8010230  | 10.3059326 | 5.0382667  |     |     |
| C  | 5.4498556  | 7.9114756  | 5.2885347  |     |     |
| H  | 4.9238218  | 8.2573163  | 4.3913604  |     |     |
| H  | 6.2028505  | 7.1698761  | 4.9808418  |     |     |
| H  | 5.9822325  | 8.7625422  | 5.7452748  |     |     |
| C  | 5.1298934  | 6.4967065  | 7.2780414  |     |     |
| H  | 4.3885025  | 6.2999630  | 8.0607861  |     |     |
| H  | 5.9635079  | 7.0699376  | 7.7151346  |     |     |
| H  | 5.5133728  | 5.5368978  | 6.8988905  |     |     |
| C  | 7.0476580  | 1.7878396  | 3.1059738  |     |     |
| C  | 8.3349531  | 2.1938748  | 3.7601219  |     |     |
| C  | 8.3251196  | 3.6020126  | 4.2759692  |     |     |
| C  | 7.2495496  | 4.4102856  | 4.1769005  |     |     |
| C  | 5.9649956  | 3.9730633  | 3.5883996  |     |     |
| C  | 5.9803967  | 2.6087113  | 3.0158606  |     |     |
| H  | 7.0011289  | 0.7852977  | 2.6678932  |     |     |
### Table

| Element | X  | Y  | Z  |
|---------|----|----|----|
| H       | 9.2500152 | 3.9793107 | 4.7246795 |
| H       | 7.3199330 | 5.4379020 | 4.5456775 |
| H       | 5.0793315 | 2.2592650 | 2.5037111 |
| H       | 5.5128860 | 4.7265823 | 2.9183513 |
| H       | 8.5881707 | 1.4879165 | 4.5793250 |
| Fe      | -0.8533561 | 0.0043579 | 0.5570301 |
| O       | 0.3516320  | -0.341391 | -0.8223623 |
| N       | -2.3963177 | 0.0724741 | 2.3000065 |
| N       | 0.2868408  | 0.8611248 | 2.0913675 |
| N       | -1.3019818 | -2.0149712 | 0.7813779 |
| N       | -2.3492210 | 1.1914381 | -0.2635538 |
| N       | 2.1390036  | 2.2301026 | 2.6594822 |
| N       | 2.4754389  | 0.1894000 | 1.5911382 |
| N       | -0.5457068 | -4.2454063 | 0.4728242 |
| N       | -0.9064695 | -2.8709968 | -1.3636009 |
| N       | -3.3587665 | 1.9435761 | -2.2759030 |
| C       | -1.6356943 | 0.4200705 | 3.5175969 |
| H       | -1.1831663 | -0.4969935 | 3.9202931 |
| H       | -2.3041664 | 0.8285183 | 4.2972025 |
| C       | -0.5302753 | 1.4121032 | 3.1824944 |
| H       | -0.9748726 | 2.3849119 | 2.9104635 |
| H       | 0.0794956  | 1.5874327 | 4.0827190 |
| C       | 1.6042443  | 1.1009102 | 2.1085876 |
| C       | 1.4870728  | 3.5323182 | 2.5800376 |
| H       | 0.6777674  | 3.5120977 | 1.8436941 |
| H       | 2.2265793  | 4.2820861 | 2.2562806 |
| H       | 1.0789595  | 3.8513027 | 3.5536259 |
| C       | 3.3901265  | 2.2146058 | 3.4157633 |
| H       | 3.6916573  | 1.1841914 | 3.6367775 |
| H       | 3.2306138  | 2.7386584 | 4.3722842 |
| H       | 4.2065581  | 2.7249833 | 2.8780499 |
| C       | 3.7332529  | 0.5734497 | 0.9553631 |
| H       | 3.7388103  | 1.6475298 | 0.7357358 |
| H       | 3.8377576  | 0.0242927 | 0.0054450 |
| H       | 4.6066958  | 0.3300153 | 1.5831629 |
| C       | 2.2255410  | -1.2438321 | 1.6590340 |
| H       | 1.3964993  | -1.4390934 | 2.3478005 |
| H       | 3.1284207  | -1.7517403 | 2.0358225 |
| H       | 1.9775905  | -1.6633663 | 0.6706675 |
| C       | -2.9951554 | -1.2774234 | 2.3679606 |
| H       | -3.7976562 | -1.3398793 | 1.6198459 |
| H       | -3.4526847 | -1.4551422 | 3.3581382 |
| C       | -1.9482552 | -2.3392763 | 2.0603934 |
| H       | -1.2193189 | -2.3885519 | 2.8876896 |

### Reference

[Fe\textsuperscript{IV}(O)TMG\textsubscript{3}tren]\textsuperscript{2+}-CHD-IC (σ)

\[ \Delta H_{\text{ZPE}} \]s

\[ \Delta H_{\text{Chem. Pot.}} \]s

\[ \Delta H_{\text{Chem. Pot.}} \]s
|      |      |      |      |      |      |      |
|------|------|------|------|------|------|------|
|  H   | 5.4478266 | 2.3346927 | -3.1869590 |      |      |      |
|  H   | 3.0249714 | 2.0065390 | -3.4494474 |      |      |      |
|  H   | 3.4276405 | -2.2259643 | -2.5518215 |      |      |      |
|  H   | 1.9891493 | -0.2579209 | -3.1426825 |      |      |      |
|  H   | 1.3003122 | 0.1326979 | -0.8844993 |      |      |      |
|  H   | 6.5261616 | 0.4613575 | -1.7884693 |      |      |      |
|  H   | 6.7350458 | 0.1233474 | -3.4750242 |      |      |      |

|      |      |      |      |      |      |      |
|------|------|------|------|------|------|------|
|  H   | -2.0382242 | -0.2003816 | 0.0104925 |      |      |      |
|  O   | -0.4536177 | 0.1732540 | 0.0025980 |      |      |      |
|  N   | -4.1234282 | -0.6929268 | 0.0178722 |      |      |      |
|  N   | -2.2045879 | -0.6689593 | 1.9885224 |      |      |      |
|  N   | -1.9678812 | -1.7213700 | -1.3433414 |      |      |      |
|  N   | -2.7522734 | 1.6064611 | -0.6102194 |      |      |      |
|  N   | -1.4414704 | -0.2872002 | 4.1992861 |      |      |      |
|  N   | -0.0377152 | -1.2868058 | 2.6420230 |      |      |      |
|  N   | -0.6972182 | -3.4833258 | -2.2895878 |      |      |      |
|  N   | -0.0709300 | -1.2753378 | 2.6486084 |      |      |      |
|  N   | -2.3616590 | 3.5680935 | -1.8822065 |      |      |      |
|  N   | -1.0944838 | 3.1416733 | 0.0169804 |      |      |      |
|  C   | -4.4058590 | -1.3935773 | 1.3012249 |      |      |      |
|  H   | -4.1013708 | -2.4432370 | 1.1943303 |      |      |      |
|  H   | -5.4885784 | -1.3762180 | 1.5121220 |      |      |      |
|  C   | -3.6088589 | -0.7481101 | 2.4208418 |      |      |      |
|  H   | -4.0292565 | 0.2448807 | 2.6530683 |      |      |      |
|  H   | -3.7079590 | -1.3524148 | 3.3366299 |      |      |      |
|  C   | -1.2427842 | -0.7303998 | 2.927182 |      |      |      |
|  C   | -2.2432599 | 0.8895582 | 4.5165076 |      |      |      |
|  H   | -2.4532358 | 1.4677405 | 3.615432 |      |      |      |
|  H   | -1.6743342 | 1.5325709 | 5.2085751 |      |      |      |
|  H   | -3.1952667 | 0.6218630 | 5.0029646 |      |      |      |
|  C   | -0.8763981 | -0.9751314 | 5.3589535 |      |      |      |
|  H   | -0.4955941 | -1.9614415 | 5.0692810 |      |      |      |
|  H   | -1.6724599 | -1.1170313 | 6.1079101 |      |      |      |
|  H   | -0.0635776 | -0.3966904 | 5.8291502 |      |      |      |
|  C   | 1.2059064 | -0.787195 | 3.2204154 |      |      |      |
|  H   | 1.0331854 | 0.1565159 | 3.7475903 |      |      |      |
|  H   | 1.9291368 | -0.6016411 | 2.4103999 |      |      |      |
|  H   | 1.6548582 | -1.5137490 | 3.915503 |      |      |      |
|  C   | 0.1174077 | -2.3668058 | 1.6792803 |      |      |      |
|  H   | -0.8632689 | -2.8034688 | 1.4582312 |      |      |      |
|  H   | 0.7632283 | -3.1453546 | 2.1163880 |      |      |      |
|  H   | 0.5710217 | -2.0073503 | 0.7424550 |      |      |      |
|  C   | -4.3721963 | -1.5762164 | -1.1550989 |      |      |      |
|  H   | -4.4708289 | -0.9437841 | -2.0474293 |      |      |      |
|  H   | -5.3209265 | -2.1235244 | -1.0228993 |      |      |      |
|  C   | -3.2003558 | -2.5250213 | -1.3358951 |      |      |      |
|  H   | -3.2017773 | -3.2779446 | -0.5296844 |      |      |      |

|                        |      |
|------------------------|------|
| [FeIV(O)TMG3tren]2+-DHA-RC (σ) |      |
| EB3LYP/def2-SVP(Fe:1def2-TZVP)/COSMO(ε = 35.88): |      |
| -3253.2990426887 (<S2> 6.05301605) |      |
| EB3LYP/def2-TZVP/COSMO(ε = 35.88): |      |
| -3255.4782627353 (<S2> 6.05554972) |      |
| ZPEB3LYP/def2-SVP(Fe:1def2-TZVP)/COSMO(ε = 35.88): |      |
| 0.943034 |      |
| Chem. Pot.(298.15)/B3LYP/def2-SVP(Fe:1def2-TZVP)/COSMO(ε = 35.88): |      |
| 0.869432 |      |
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| H       | -3.3187383 | -3.0778168 | -2.2814514 |
| C       | -0.9232449 | -2.1552457 | -2.0664062 |
| C       | -0.9628681 | -4.5123414 | -1.2909265 |
| H       | -1.1345577 | -4.0608008 | -0.3088484 |
| H       | -0.0835113 | -5.1725897 | -1.2151574 |
| H       | -1.8342449 | -5.1330051 | -1.5590527 |
| C       | -0.1881834 | -3.9833516 | -3.5656319 |
| H       | -0.2412747 | -3.2000935 | -4.3307530 |
| H       | -0.0817319 | -4.8281263 | -3.8900974 |
| H       | 0.8516355  | -4.3421116 | -3.4857165 |
| C       | 1.3568562  | -1.5434647 | -2.7863594 |
| C       | 1.6369977  | -2.4342140 | -2.2121128 |
| H       | 1.9219829  | -0.6844487 | -2.3905422 |
| H       | 1.6500080  | -1.6888099 | -3.8394052 |
| C       | -0.4980432 | 0.0398982  | -3.1003510 |
| H       | -1.5915858 | 0.0706364  | -3.1556737 |
| H       | -0.0863350 | 0.2235978  | -4.1062420 |
| H       | -0.1482477 | 0.8314290  | -2.4200561 |
| C       | -4.8794252 | 0.5859612  | -0.0873095 |
| H       | -4.9284559 | 1.0398423  | 0.9114552  |
| H       | -5.9128810 | 0.3890738  | -0.4194178 |
| C       | -4.1585714 | 1.5284132  | -1.0351595 |
| H       | -4.2606712 | 1.1648188  | -2.0715954 |
| H       | -4.6382797 | 2.5196402  | -1.0018416 |
| C       | -2.0741588 | 2.7425220  | -0.8332596 |
| C       | -2.7771915 | 3.0764741  | -3.1908808 |
| H       | -2.6030088 | 1.9990981  | -3.2712474 |
| H       | -2.1782437 | 3.5787492  | -3.9679873 |
| H       | -3.8414290 | 3.2850326  | -3.3913972 |
| C       | -2.2909436 | 5.0240515  | -1.7686570 |
| H       | -2.2081570 | 5.3209900  | -0.7166514 |
| H       | -3.2181103 | 5.4557881  | -2.1793290 |
| H       | -1.4400614 | 5.4430370  | -2.3315590 |
| C       | 0.1114532  | 3.8194815  | -0.4450888 |
| H       | 0.1605119  | 3.8148477  | -1.5401389 |
| H       | 0.9915636  | 3.2801766  | -0.0582137 |
| H       | 0.1630428  | 4.8610653  | -0.0867362 |
| C       | -1.1255664 | 2.8374057  | 1.4392073  |
| H       | -2.1351108 | 2.5213753  | 1.7236892  |
| H       | -0.8651958 | 3.7469091  | 2.0049539  |
| H       | -0.4116976 | 2.0395978  | 1.6956708  |
| C       | 5.6064148  | -0.1890937 | 3.5335034  |
| C       | 5.0622806  | 1.1002484  | 3.5511934  |
| C       | 5.5049887  | -0.9703167 | 2.3777236  |
| C       | 4.4199887  | 1.5988387  | 2.4130380  |
| C       | 4.8551220  | -0.4801238 | 1.2355048  |
| C       | 4.3062370  | 0.8175583  | 1.2536747  |
| C       | 4.7158964  | -1.3112670 | -0.0239197 |
| Atom | X    | Y    | Z    | E    |
|------|------|------|------|------|
| C    | 3.5970613 | 1.3242928 | 0.0138887 | -3253.2719808009 (\langle S^2 \rangle = 6.51805389) |
| C    | 4.2376477 | 0.8244946 | -1.2654690 | -3255.4489572209 (\langle S^2 \rangle = 6.51339206) |
| C    | 4.7889654 | -0.4722149 | -2.4260411 | 0.936232 |
| C    | 4.2851673 | 1.6107872 | -2.4726720 |
| C    | 5.3763840 | -0.9555737 | -3.6181110 |
| C    | 4.8647609 | 1.1187580 | -3.6002015 |
| C    | 5.4123968 | -1.689062 | -3.6181110 |
| H    | 6.1166395 | -0.5837032 | 4.4165792 |
| H    | 5.1445264 | 1.7206706 | 4.4479424 |
| H    | 5.936528 | -2.974947 | 2.3598819 |
| H    | 4.0030278 | 2.6106993 | 2.4235247 |
| H    | 3.8666854 | 2.6219017 | -2.4089299 |
| H    | 5.8123543 | -2.9593487 | -2.4726720 |
| H    | 5.8743028 | -0.5584150 | 4.5295718 |
| H    | 2.5434837 | 0.9751898 | 0.040312 |
| H    | 3.5506203 | 2.4244142 | 0.0181164 |
| H    | 5.8743028 | -0.5584150 | 4.5295718 |
| H    | 2.5434837 | 0.9751898 | 0.040312 |
| H    | 3.5506203 | 2.4244142 | 0.0181164 |
| H    | 5.8743028 | -0.5584150 | 4.5295718 |
| H    | 2.5434837 | 0.9751898 | 0.040312 |
| H    | 3.5506203 | 2.4244142 | 0.0181164 |
| Fe   | 2.5858680 | 4.3344305 | 6.2945104 |
| Fe   | 3.9076802 | 4.2107058 | 5.2128329 |
| Fe   | 0.8053033 | 4.5191126 | 7.7676867 |
| Fe   | 3.3835543 | 3.4434447 | 8.0033378 |
| Fe   | 1.1200721 | 3.2211056 | 5.3048594 |
| Fe   | 2.3148657 | 6.4161873 | 6.3613351 |
| Fe   | 5.2685455 | 2.7454774 | 9.2638980 |
| Fe   | 4.8025235 | 1.7486532 | 7.2182400 |
| Fe   | 0.5288696 | 1.5645567 | 3.7103882 |
| Fe   | 1.5459624 | 3.5340203 | 3.0205756 |
| Fe   | 2.6108182 | 8.5544600 | 5.3807981 |
| Fe   | 4.4482818 | 7.3786641 | 6.1849859 |
| Fe   | 1.1798207 | 3.7545860 | 8.9765396 |
| Fe   | 0.9228590 | 2.6980971 | 8.8172867 |
| Fe   | 0.6071036 | 4.1055480 | 9.8538363 |
| Fe   | 2.6759981 | 3.8650728 | 9.2221379 |
| Fe   | 2.9342192 | 4.8999788 | 9.5083308 |
| Fe   | 2.9443074 | 3.2271926 | 10.0780300 |
| Fe   | 4.4718466 | 2.6759596 | 8.1513120 |
| Fe   | 5.5735376 | 4.0002323 | 9.9391425 |
| Fe   | 5.2540422 | 4.8516128 | 9.3310501 |
| Fe   | 6.6635719 | 4.0752939 | 10.0891963 |
| Fe   | 5.0885886 | 4.0671212 | 10.9277830 |
| Fe   | 5.8277411 | 1.5542972 | 9.8992821 |
| Fe   | 5.3716588 | 0.6484944 | 9.4829470 |
| Fe   | 5.6025939 | 1.5884212 | 10.9781817 |
| Fe   | 6.9229222 | 1.4935914 | 9.7814313 |
| Fe   | 6.1816784 | 1.3542731 | 6.9512858 |

[Fe^IV(O)TMG_3 tren]^2+ - DHA-TS (μ)

EB3LYP/def2-SVP(Fe: def2-TZVP)/COSMO(ε = 35.88):
-3253.2719808009 (\langle S^2 \rangle = 6.51805389)

EB3LYP/def2-TZVPP/COSMO(ε = 35.88):
-3255.4489572209 (\langle S^2 \rangle = 6.51339206)

ZPEB3LYP/def2-SVP(Fe: def2-TZVP)/COSMO(ε = 35.88):
0.936232

Chem. Pot./B3LYP/def2-SVP(Fe: def2-TZVP)/COSMO(ε = 35.88):
0.862698
| X  | Y  | Z  |
|----|----|----|
| 6.8799748 | 2.0446224 | 7.4355814 |
| 6.3611471 | 1.3967561 | 5.8666431 |
| 6.3885471 | 0.3272258 | 7.2954391 |
| 3.8106223 | 1.1308934 | 6.3540632 |
| 2.8157258 | 1.2483304 | 6.7970719 |
| 4.0343614 | 0.0560263 | 6.2631449 |
| 3.8132532 | 1.5835929 | 5.3499533 |
| -0.3700408 | 3.9405328 | 7.0830938 |
| -0.8185112 | 4.7127817 | 6.4426606 |
| -1.1371910 | 3.6324700 | 7.8163498 |
| 0.0576462 | 2.7687445 | 6.2162113 |
| 0.3938602 | 1.9330047 | 6.8547793 |
| -0.8157646 | 2.4025145 | 5.6554237 |
| 1.0814994 | 2.7730384 | 4.0425985 |
| 0.6605742 | 0.3739571 | 4.5403887 |
| 1.3996741 | 0.5342715 | 5.3301180 |
| 1.0047627 | -0.4663632 | 3.9146810 |
| -0.2982819 | 0.0848652 | 5.0029650 |
| -0.2832343 | 1.3846567 | 2.5089025 |
| -0.5313594 | 2.3559825 | 2.0653542 |
| -1.2243818 | 0.8831884 | 2.7891356 |
| 0.2234601 | 0.7610784 | 1.7530904 |
| 2.1484321 | 2.9538861 | 1.8242311 |
| 2.3563488 | 1.8888360 | 1.9793082 |
| 3.0990860 | 3.4663582 | 1.6202755 |
| 1.4996018 | 3.0672690 | 0.9396411 |
| 1.5390883 | 4.9875963 | 3.0727344 |
| 0.8318879 | 5.3231523 | 3.8398520 |
| 1.2127470 | 5.3791117 | 2.0958559 |
| 2.5379609 | 5.3883254 | 3.3014278 |
| 0.6303495 | 5.9595129 | 8.0458874 |
| 1.3204648 | 6.2495553 | 8.8507772 |
| -0.3959978 | 6.1682481 | 8.3985664 |
| 0.9564566 | 6.7703309 | 6.8018384 |
| 0.2053233 | 6.5741337 | 6.0165768 |
| 0.8830992 | 7.8412792 | 7.0449367 |
| 3.1082386 | 7.4209252 | 5.9677355 |
| 1.4938631 | 8.5261927 | 4.4450407 |
| 1.2859785 | 7.4997709 | 4.1278735 |
| 1.7567137 | 9.1162903 | 3.5514479 |
| 0.5764201 | 8.9574851 | 4.8802926 |
| 3.0948871 | 9.8913792 | 5.7198184 |
| 3.7469661 | 9.8518447 | 6.6001338 |
| 2.2297554 | 10.5298349 | 5.9642020 |
| 3.6408899 | 10.3615867 | 4.8847555 |
| 5.4075520 | 8.0838867 | 5.3412044 |
| 4.9505506 | 8.3535714 | 4.3816821 |
| 6.2677145 | 7.4261418 | 5.1452573 |
|   |   |   |
|---|---|---|
| H | 5.7939699 | 8.9970087 | 5.8231636 |
| C | 5.0264424 | 6.6146903 | 7.2808310 |
| H | 4.2548646 | 6.4075554 | 8.0306344 |
| H | 5.8261211 | 7.2086544 | 7.7507265 |
| C | 9.3321240 | 2.1852941 | 4.9766153 |
| C | 9.0548105 | 3.3842273 | 5.6473986 |
| C | 8.5213092 | 1.7790774 | 3.9111944 |
| C | 7.9702588 | 4.1652649 | 5.2478472 |
| C | 7.4268440 | 2.5537950 | 3.5046672 |
| C | 7.1464809 | 3.7670841 | 4.1762942 |
| C | 6.5321721 | 2.1218010 | 2.3643706 |
| C | 6.0117543 | 4.6099738 | 3.7186707 |
| C | 5.6730584 | 4.4916955 | 2.2770424 |
| C | 5.9464110 | 3.2835942 | 1.5940154 |
| C | 5.1077433 | 5.5699193 | 1.5673241 |
| C | 5.6612748 | 2.1218010 | 0.2256733 |
| C | 4.8215742 | 5.4610497 | 0.2062293 |
| H | 10.1848092 | 1.5711044 | 5.2781510 |
| H | 9.6898404 | 3.7120748 | 6.4745958 |
| H | 8.7457352 | 0.8480310 | 3.3822305 |
| H | 7.7641825 | 5.1089877 | 5.7608754 |
| H | 4.9069309 | 6.5092715 | 2.0906864 |
| H | 5.8855668 | 2.2569171 | -0.3049733 |
| H | 4.3896944 | 6.3090076 | -0.3316363 |
| H | 4.8863906 | 4.1733693 | -1.5366808 |
| H | 4.9955282 | 4.3154996 | -1.5366808 |
| H | 6.1140534 | 5.6564504 | 4.0348213 |
| H | 7.0684170 | 1.4385943 | 1.6880913 |
| H | 5.6957081 | 1.5236752 | 2.7826847 |

**[FeIV(O)TMG3tren]**$^{2+}$-DHA-IC ($\sigma$)

EB3LYP/def2-SVP(Fe:def2-TZVP)/COSMO($\epsilon = 35.88$):

-3253.3137521106 ($<S^2>$ 7.04498858)

EB3LYP/def2-TZVP/COSMO($\epsilon = 35.88$):

-3255.4941296469 ($<S^2>$ 7.04338375)

ZPEB3LYP/def2-SVP(Fe:def2-TZVP)/COSMO($\epsilon = 35.88$):

0.938204

Chem. Pot. (298.15)/B3LYP/def2-SVP(Fe:def2-TZVP)/COSMO($\epsilon = 35.88$):

0.86304
|  |  |  |  |  |
|---|---|---|---|---|
| H | -3.9388696 | 0.2084876 | 2.6658769 |
| H | -3.8249996 | -1.4311858 | 3.3127956 |
| C | -1.2952130 | -1.1157119 | 3.0074726 |
| C | -2.1873941 | 0.4583277 | 4.7105893 |
| H | -2.3268162 | 1.1226761 | 3.8526113 |
| H | -1.5799377 | 0.9916166 | 5.4601244 |
| H | -3.1713947 | 0.2416101 | 5.1591034 |
| C | -1.2952130 | -1.1157119 | 3.0074726 |
| H | -2.3268162 | 1.1226761 | 3.8526113 |
| H | -1.5799377 | 0.9916166 | 5.4601244 |
| H | -3.1713947 | 0.2416101 | 5.1591034 |
| C | -1.2952130 | -1.1157119 | 3.0074726 |
| H | -2.3268162 | 1.1226761 | 3.8526113 |
| H | -1.5799377 | 0.9916166 | 5.4601244 |
| H | -3.1713947 | 0.2416101 | 5.1591034 |
5.2.2 Cu**(OH)(L) pathway (B3LYP)

Method: B3LYP/def2-SVP(Cu:def2-TZVP)/COSMO(ε = 8.51)
| Element | Coordinates | Energy | Configuration |
|---------|-------------|--------|---------------|
| C       | -1.4110746, -0.5811711, 0.1864074 | CHD | $E_{B3LYP/def2-SVP/COSMO}(\varepsilon = 8.51)$: -233.0949079571 |
| C       | -0.0433063, -1.2130284, 0.1868696 | | |
| C       | 1.0724370, -0.2005383, 0.1863025 | | |
| C       | 0.8694511, 1.1238161, 0.1860749 | | |
| C       | -0.4983187, 1.7556728, 0.1860713 | | |
| C       | -1.6140606, 0.7431835, 0.1860358 | | |
| H       | -2.2715345, -1.2603502, 0.1863915 | | |
| H       | 2.0968129, -0.5908306, 0.1862730 | | |
| H       | 1.7299106, 1.8029953, 0.1856497 | | |
| H       | -2.6384368, 1.1334754, 0.1856475 | | |
| H       | -0.6019635, 2.4320887, -0.6867080 | | |
| H       | -0.6020100, 2.4321149, 1.0588273 | | |
| H       | 0.0603226, -1.8888584, 1.0601106 | | |
| H       | 0.0604170, -1.8900523, -0.6854244 | | |
| C       | -3.5664355, -0.7614063, 0.1200915 | DHA | $E_{B3LYP/def2-SVP/COSMO}(\varepsilon = 8.51)$: -540.0041012622 |
| C       | -3.5736524, 0.6118827, 0.3884271 | | |
| C       | -2.3977057, -1.3717106, -0.3475301 | | |
| C       | -2.4120217, 1.3650768, 0.1874918 | | |
| C       | -1.2321748, -0.6213765, -0.5592466 | | |
| C       | -1.2393415, 0.7614569, -0.2886968 | | |
| C       | 0.0435691, -1.2507224, -1.0816461 | | |
| C       | 0.0291973, 1.5539064, -0.5323394 | | |
| C       | 1.2771470, 0.7582663, -0.2065563 | | |
| C       | 1.2842735, -0.6244828, -0.4775173 | | |
| C       | 2.4176903, 1.3588879, 0.3454258 | | |
| C       | 2.4318457, -1.3776383, -0.1910000 | | |
| C       | 3.5620006, 0.6028503, 0.6211548 | | |
| C       | 3.5691151, -0.7702789, 0.3519436 | | |
| H       | -4.4680029, -1.3589856, 0.2812141 | | |
| H       | -4.4809344, 1.0956988, 0.7607854 | | |
| H       | -2.3887716, -2.4473304, -0.5496337 | | |
| H       | -2.4143916, 2.4376698, 0.4052765 | | |
| H       | 2.4083347, 2.4313698, 0.5635672 | | |
| H       | 2.4336276, -2.4531365, -0.3939530 | | |
| H       | 4.4442286, 1.0843407, 1.0521171 | | |
| H       | 4.4569512, -1.3700171, 0.5709218 | | |
| H       | 0.0645358, 1.8406524, -1.6034748 | | |
| H       | 0.0120213, 2.4997593, 0.0306666 | | |
| H       | 0.0386911, -2.3392022, -0.9171856 | | |
| H       | 0.0794599, -1.1117635, -2.1817432 | | |

| Element | Coordinates | Energy | Configuration |
|---------|-------------|--------|---------------|
| C       | -4.5384713, 4.4455857, 0.1230360 | Cu$^{III}$(OH)(L) | $E_{B3LYP/def2-SVP/Cu:def2-TZVP/COSMO}(\varepsilon = 8.51)$: -3232.5271394185 |
| C       | -4.5011574, 3.3613687, 0.0047112 | | |
| C       | -4.3053119, 0.6109200, -0.2907822 | | |
| C       | -5.6595963, 2.5825155, -0.1348635 | | |
| C       | -3.2693878, 2.7098386, -0.0110868 | | |
|      | X (Å) | Y (Å) | Z (Å) |
|------|-------|-------|-------|
| N    | 5.5727999 | 1.1906173 | -0.2850837 |
| C    | 6.6396552  | 3.0652816  | -0.1264349  |
| H    | -6.456483  | 0.5598756  | -0.3954661  |
| C    | 1.8959393  | 3.287386   | 0.1200227   |
| O    | -1.7411495 | 4.5362527  | 0.2632466   |
| C    | -3.583511  | -0.8538149 | -0.4360971  |
| O    | -4.8260501 | -1.7103426 | -0.5719179  |
| N    | 7.3101321  | -1.0473585 | -0.3928425  |
| Cu   | 1.5548637  | 0.5667085  | -0.1705336  |
| H    | 0.7226318  | 0.3856141  | -0.0956722  |
| O    | 0.0250762  | -0.2822635 | -0.1947284  |
| C    | 0.4531476  | 2.7332760  | 0.1550860   |
| C    | 3.1646180  | 3.4006060  | 0.3473044   |
| C    | 1.0829180  | 2.7424222  | 1.4302739   |
| C    | 1.1840220  | 3.0388826  | -1.0262794  |
| C    | 2.5391725  | 3.3745286  | -0.9003629  |
| C    | 2.4406264  | 3.0849348  | 1.4981544   |
| H    | 3.1179791  | 3.6233459  | -1.7933155  |
| H    | 2.9426552  | 3.1084610  | 2.4686121   |
| H    | 4.2229045  | 3.6653022  | 0.4227506   |
| C    | 2.0336675  | -2.3300892 | 0.5033063   |
| C    | -0.9031739 | -4.8790225 | -0.7241638  |
| C    | -1.8016548 | -3.0962054 | 0.6718471   |
| C    | -1.6687032 | -2.8243360 | -1.7854002  |
| C    | -1.1127853 | -4.1074146 | -1.8689865  |
| C    | -1.2425458 | -4.3729260 | 0.5323538   |
| H    | -0.8374745 | -4.5145667 | -2.8450585  |
| H    | -1.0680256 | -4.9864150 | 1.4197287   |
| H    | -0.4684789 | -5.8787921 | -0.8112133  |
| C    | 0.5196601  | 3.0512578  | -2.3987991  |
| H    | -0.4678797 | 2.5790379  | -2.2893633  |
| C    | 0.2823605  | 4.4974423  | -2.8772255  |
| H    | -0.2623816 | 4.5040859  | -3.8361801  |
| H    | 1.2378491  | 5.0276045  | -3.0290503  |
| H    | -0.3078361 | 5.0645313  | -2.1407143  |
| C    | 1.2979543  | 2.2309734  | -3.4412205  |
| H    | 0.7406856  | 2.1969025  | -4.3917640  |
| H    | 1.4497057  | 1.1944874  | -3.0991318  |
| H    | 2.2875565  | 2.6664776  | -3.6565874  |
| C    | 0.3102105  | 2.4332189  | 2.7080804   |
| H    | -0.6662857 | 2.0236196  | 2.4101300   |
| C    | 0.0372772  | 3.7225731  | 3.5075815   |
| H    | -0.4939341 | 4.4642065  | 2.8906784   |
| H    | 0.9776909  | 4.1814243  | 3.8569890   |
| H    | -0.5810223 | 3.5051458  | 4.3945577   |
| C    | 1.0016068  | 1.3652267  | 3.5722813   |

**EB3LYP/def2-TZVPP/COSMO(ε = 8.51):**

\(-3234.2848324600\)

**ZPE\(_{\text{B3LYP/def2-SVP(Cu:def2-TZVP)}}\)/\(_{\text{COSMO(ε = 8.51)}}\):**

\(0.632973\)

**Chem. Pot.\(_{(298.15)}\)/\(_{\text{B3LYP/def2-SVP(Cu:def2-TZVP)}}\)/\(_{\text{COSMO(ε = 8.51)}}\):**

\(0.569457\)
Cu\textsuperscript{III}(OH)(L)-CHD-RC

\begin{align*}
\text{E}_{B3LYP/def2-SVP(Cu:def2-TZVP)/COSMO}(\epsilon = 8.51): & \quad -3465.6207230790 \\
\text{ZPE}_{B3LYP/def2-SVP(Cu:def2-TZVP)/COSMO}(\epsilon = 8.51): & \quad 0.755861 \\
\text{Chem. Pot.}(298.15)/B3LYP/def2-SVP(Cu:def2-TZVP)/COSMO(\epsilon = 8.51): & \quad 0.685164
\end{align*}
|   | 1.2634695 | -2.1193624 | -3.5989794 |
|---|-----------|------------|------------|
| H| 2.0692440 | -2.7871927 | -3.9461429 |
| H| 1.7268467 | -1.2460671 | -3.1132727 |
| H| 0.7207888 | -1.7688994 | -4.4926320 |
| C| 0.4134894 | -2.9263289 | 2.5042307  |
| H| -0.3857119| -2.1919615 | 2.3247733  |
| C| -0.2410152| -4.1680441 | 3.1420038  |
| H| -0.7434059| -3.9012675 | 3.9461429  |
| H| 0.5126227 | -4.9414699 | 3.3683806  |
| H| -0.9891089| -4.6110929 | 2.4662849  |
| C| 1.4227376 | -2.2663333 | 3.4581313  |
| H| 0.9188181 | -1.9508041 | 4.3871831  |
| H| 1.8780710 | -1.3765003 | 2.9956053  |
| H| 2.2339066 | -2.9560995 | 3.7447858  |
| H| 5.0752775 | 2.2890166 | 2.3820712  |
| H| 4.8110008 | 2.6206957 | -2.0165660 |
| H| 4.2412816 | 0.2706276 | -2.157280  |
| H| 4.5039441 | -0.0599566 | 2.2373520  |
| H| -4.4832955| 4.4323747 | 0.1393451  |
| C| -4.4480563| 3.3482342 | 0.020623   |
| C| -4.2582986| 0.5969737 | -0.2772458 |
| C| -5.6088601| 2.5721612 | -0.116453  |
| C| -3.2175157| 2.6911251 | 0.0013291  |
| N| -3.1834949| 1.3689417 | -0.1435751 |
| C| -5.5261942| 1.1801894 | -0.2682340 |
| H| -6.5878483| 3.0575931 | -0.1051239 |
| H| -6.4121943| 0.5526833 | -0.3772959 |
| C| -1.8441067| 3.3213935 | 0.1291796  |
| O| -1.7200628| 4.5385409 | 0.2697961  |
| C| -3.9298633| -0.8767962| -0.4274199 |
| O| -4.8325462| -1.7063864| -0.5630719 |
| N| -2.5947178| -1.1007617| -0.3905040 |
| N| -0.8524492| 2.3953894 | 0.0671861  |
| Cu| -1.4680191| 0.5262229 | -0.1627610 |
| H| 0.8721667 | 0.4445082 | -0.0850064 |
| O| 0.2261068 | -0.2781346| -0.1753039 |
| H| 1.1903943 | -1.3375600| -0.1939390 |
| C| 0.5082026 | 2.7886743 | 0.1651605  |
| C| 3.2190656 | 3.4865159 | 0.3499874  |
| C| 1.1437379 | 2.8113375 | 1.4377549  |
| C| 1.2375193 | 3.0977673 | -1.0169679 |
| C| 2.5900130 | 3.4477773 | -0.8955156 |
| C| 2.4984909 | 3.1677785 | 1.5023221  |
| H| 3.1636101 | 3.6984450 | -1.7912948 |
| H| 3.0008386 | 3.2074272 | 2.4721717  |
| H| 4.2738810 | 3.7658749 | 0.4228649  |
| C| -2.0836662| -2.4177947| -0.5059687 |

**Cu^{III}(OH)(L)-CHD-TS**

\[ E_{\text{B3LYP/def2-SVP}}(\text{Cu:}\text{def2-TZVP})/\text{COSMO}(\epsilon = 8.51) : -3465.6053997020 \ (\langle S^2\rangle = 0.48079694) \]

\[ E_{\text{B3LYP/def2-TZVPP}}/\text{COSMO}(\epsilon = 8.51) : -3467.6148183357 \ (S = 0; \langle S^2\rangle = 0.49509705) \]

\[ -3467.6021338349 \ (S = 1; \langle S^2\rangle = 2.01516229) \]

\[ -3467.6189914014 \ (\text{spin purified}) \]

\[ ZPE_{\text{B3LYP/def2-SVP}}(\text{Cu:}\text{def2-TZVPP})/\text{COSMO}(\epsilon = 8.51) : 0.749835 \]

\[ \text{Chem. Pot.}(298.15)/\text{B3LYP/def2-SVP}(\text{Cu:}\text{def2-TZVPP})/\text{COSMO}(\epsilon = 8.51) : 0.679808 \]
| C  | -1.0227474 | -5.0045089 | -0.7333170 |
| C  | -1.9074829 | -3.2097187 | 0.6601915  |
| C  | -1.7125028 | -2.9153311 | -1.7840236 |
| C  | -1.1876734 | -4.2127835 | -1.8715325 |
| C  | -1.3792838 | -4.5012495 | 0.5189788  |
| H  | -0.9064878 | -4.6164211 | -2.8475280 |
| H  | -1.2473549 | -5.1293977 | 1.4038457  |
| C  | 4.2034082  | -1.0941764 | -1.0955593 |
| C  | 3.0209564  | -1.7127364 | -1.3063402 |
| C  | 4.7339983  | -0.8170370 | 0.2799462  |
| H  | 4.7958653  | 0.2834305  | 0.4387561  |
| H  | 5.7921139  | -1.1401507 | 1.1482147  |
| C  | 2.1383244  | -2.1201209 | -0.1964201 |
| H  | 1.5485950  | -3.0326410 | -0.3897319 |
| C  | 3.9211215  | -1.4360177 | 1.3781809  |
| C  | 2.7406121  | -2.0521001 | 1.1482147  |
| C  | 0.5660131  | 3.0990694  | -2.3864854 |
| H  | -0.3808421 | 2.5479625  | -2.2828593 |
| H  | 0.2108961  | 4.5364923  | -2.8177517 |
| H  | -0.3421926 | 4.5313274  | -3.7721759 |
| C  | 1.1225048  | 5.1419046  | -2.9597560 |
| H  | -0.4127114 | 5.0331745  | -2.0587368 |
| C  | 1.3975456  | 2.3794566  | -3.4639263 |
| H  | 0.8197777  | 2.3128890  | -4.4027814 |
| H  | 1.6542400  | 1.3553963  | -3.1509564 |
| H  | 2.3313272  | 2.9126832  | -3.6925073 |
| C  | 0.3701701  | 2.5049986  | 2.7163536  |
| H  | -0.5551829 | 1.9890853  | 2.4183650  |
| C  | -0.0447513 | 3.8095216  | 3.4267667  |
| H  | -0.6172588 | 4.4627039  | 2.7505365  |
| H  | 0.8418292  | 4.3690395  | 3.7712667  |
| H  | -0.6691578 | 3.5908370  | 4.3094593  |
| C  | 1.1267094  | 1.5651795  | 3.6692603  |
| H  | 2.0310454  | 2.0375829  | 4.0872023  |
| H  | 1.4344227  | 0.6391423  | 3.1572482  |
| H  | 0.4823019  | 1.2872853  | 4.5194758  |
| C  | -1.9287490 | -2.0863344 | -3.0462988 |
| H  | -2.0519214 | -1.0406178 | -2.7261913 |
| C  | -3.2344401 | -2.5033097 | -3.7537261 |
| H  | -4.0928684 | -2.4418749 | -3.0672860 |
| H  | -3.1675282 | -3.5416886 | -4.1215299 |
| H  | -3.4354046 | -1.8510545 | -4.6205940 |
| C  | -0.7346149 | -2.1256807 | -4.0128912 |
| H  | -0.5787744 | -3.1289246 | -4.4428485 |
| H  | 0.1969905  | -1.8230861 | -3.5080757 |
| H  | -0.9036543 | -1.4340975 | -4.8547796 |
| C  | -2.3265391 | -2.7012959 | 2.0362657 |
### Cu\textsuperscript{III}(OH)(L)-CHD-IC

|        |        |        |        |        |        |
|--------|--------|--------|--------|--------|--------|
| H      | -2.4637703 | -1.6129081 | 1.9497906 |        |        |
| C      | -3.6852287 | -3.3021064 | 2.4500517 |        |        |
| H      | -4.0253093 | -2.8754905 | 3.4090533 |        |        |
| H      | -3.6105153 | -4.3959448 | 2.5761589 |        |        |
| H      | -4.4526644 | -3.0984162 | 1.6878669 |        |        |
| C      | -1.2601425 | -2.9369921 | 3.1183103 |        |        |
| H      | -1.5718742 | -2.4722871 | 4.0683762 |        |        |
| H      | -0.2927856 | -2.4963932 | 2.8278101 |        |        |
| H      | -1.0992499 | -4.0094117 | 3.3175717 |        |        |
| H      |  4.3224606 | -1.3811538 | 2.3953468 |        |        |
| C      |  4.8178480 | -0.7801974 | -1.9456160|        |        |
| H      |  2.6765937 | -1.8957752 | -2.3293280|        |        |
| H      |  2.1842428 | -2.4920024 |  1.9820490|        |        |

E\textsubscript{B3LYP/def2-SVP(Cu: def2-TZVP)/COSMO(\(\varepsilon = 8.51\))}:
-3465.6440302639 (\(<S^2> 1.03881585\))

E\textsubscript{B3LYP/def2-TZVPP/COSMO(\(\varepsilon = 8.51\))}:
-3467.652467610 (S = 0; \(<S^2> 1.03693909\))
-3467.6525079370 (S = 1; \(<S^2> 2.03876534\))

ZPE\textsubscript{B3LYP/def2-SVP(Cu: def2-TZVP)/COSMO(\(\varepsilon = 8.51\))}:
0.753768

Chem. Pot. (298.15)/B3LYP/def2-SVP(Cu: def2-TZVP)/COSMO(\(\varepsilon = 8.51\)):
0.682639
### Cu(III)(OH)\(_2\)DHA-RC

**E\(_{\text{B3LYP/def2-SVP(Cu:def2-TZVP)/COSMO(}\epsilon = 8.51)}\):** 
-3772.5299617668

**E\(_{\text{B3LYP/def2-TZVP/COSMO(}\epsilon = 8.51)}\):** 
-3774.8654251167

**ZPE\(_{\text{B3LYP/def2-SVP(Cu:def2-TZVP)/COSMO(}\epsilon = 8.51)}\):** 0.851331

**Chem. Pot.\(_{(298.15)}\)/B3LYP/def2-SVP(Cu:def2-TZVP)/COSMO(\epsilon = 8.51):** 0.776904

| C   | 1.4959793  | -2.5152022  | 3.5646051  |
|-----|------------|-------------|------------|
| H   | 0.9580983  | -2.2480622  | 4.4891106  |
| H   | 2.0205376  | -1.6136458  | 3.2080826  |
| H   | 2.2590607  | -3.2629516  | 3.8366414  |
| H   | 4.4066520  | 2.1600945   | 2.2477552  |
| H   | 4.9021239  | 2.0702144   | -2.1505729 |
| H   | 4.4654673  | -0.3514879  | -2.1091918 |
| H   | 3.9808838  | -0.2628446  | 2.2079519  |
| C   | -4.6826027 | 4.4246884   | 0.3184253  |
| C   | -4.6093688 | 3.3401413   | 0.2220337  |
| C   | -4.3217347 | 0.5930211   | -0.0225875 |
| C   | -5.7423697 | 2.5163338   | 0.1458920  |
| C   | -3.3555543 | 2.7340960   | 0.1698412  |
| N   | -3.2737793 | 1.4100379   | 0.0532428  |
| C   | -5.6090721 | 1.1256610   | 0.0212697  |
| H   | -6.7388239 | 2.9627906   | 0.1836285  |
| H   | -6.4717442 | 0.4602261   | -0.0408551 |
| C   | -2.0025767 | 3.4064855   | 0.2295375  |
| O   | -1.8895208 | 4.6218779   | 0.3461041  |
| C   | -3.9271638 | -0.8690320  | -0.150652  |
| O   | -4.7695914 | -1.7487858  | -0.2392066 |
| N   | -5.7254586 | -1.0074719  | -0.1507480 |
| N   | -0.9912866 | 2.4950995   | 0.1375819  |
| Cu  | -1.5678663 | 0.6520862   | -0.0178174 |
| H   | 0.7194220  | 0.5613483   | -0.0919678 |
| O   | 0.0450310  | -0.1363955  | -0.109638  |
| H   | 1.7949655  | -1.7075173  | -0.0023538 |
| C   | 0.3666944  | 2.9024086   | 0.1756557  |
| C   | 3.0558371  | 3.6734733   | 0.2484265  |
| C   | 1.0439914  | 2.9604506   | 1.4248612  |
| C   | 1.0397747  | 3.2093451   | -1.0394706 |
| C   | 2.3849196  | 3.5975275   | -0.9731682 |
| C   | 2.3890886  | 3.3549364   | 1.4329002  |
| H   | 2.9199003  | 3.8464688   | -1.8926851 |
| H   | 2.9266043  | 3.4171911   | 2.3823295  |
| H   | 4.1052118  | 3.9793506   | 0.2773355  |
| C   | -1.9601569 | -2.2743717  | -0.2527097 |
| C   | -0.7761693 | -4.7994839  | -0.4571400 |
| C   | -1.6698992 | -3.0079147  | 0.9303972  |
| C   | -1.6238880 | -2.7868081  | -1.5351608 |
| C   | -1.0404645 | -4.0578640  | -1.6102905 |
| C   | -1.0581196 | -4.2735612  | 0.7992039  |
| H   | -0.7875551 | -4.4792730  | -2.5863879 |
| H   | -0.8668083 | -4.8629528  | 1.6930536  |
| H   | -0.3222158 | -5.7913559  | -0.5374812 |
| H   | 5.9974257  | 0.4921229   | -1.7987438 |
| C   | 5.2665815  | -0.2940776  | -2.0130966 |

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**Chem. Pot. (298.15)**

(298.15)/B3LYP/def2-SVP(Cu:def2-TZVP)/COSMO(\epsilon = 8.51):

0.776904
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| C       | 3.4178578  | -2.3085713 | -2.5506520 |
| C       | 4.4774199  | -0.8021654 | -0.9712848 |
| C       | 5.1313552  | -0.7807118 | -3.3172530 |
| C       | 4.2025138  | -1.7919172 | -3.5868565 |
| C       | 3.5429021  | -1.8216877 | -1.2410596 |
| H       | 5.7543206  | -0.3756999 | -4.1198181 |
| H       | 4.0935980  | -2.1834800 | -4.6022955 |
| H       | 2.6962040  | -3.1042543 | -2.7590387 |
| C       | 4.5895618  | 0.2764473  | 0.4453642  |
| H       | 3.8229501  | 0.5124147  | 0.5902427  |
| H       | 5.8005814  | -0.5780536 | 2.9058599  |
| C       | 4.3725481  | -1.3584401 | 1.4835883  |
| C       | 3.4372212  | -2.3770562 | 1.2117421  |
| C       | 5.0677600  | -1.3651358 | 2.7014520  |
| H       | 5.8835000  | -2.3581415 | 4.5973111  |
| C       | 3.2161767  | -3.3789688 | 2.1688093  |
| H       | 2.4934142  | -4.1718495 | 1.9554979  |
| C       | 3.9071489  | -3.3748734 | 3.3848426  |
| H       | 3.7242081  | -4.1639854 | 4.1197723  |
| C       | 0.3211785  | 3.1688111  | -2.3839403 |
| H       | -0.6258513 | 2.6297038  | -2.2320653 |
| C       | -0.0357522 | 4.5936724  | -2.8533441 |
| H       | -0.6195848 | 4.5591586  | -3.7894597 |
| H       | 0.8747002  | 5.1862069  | -3.0462510 |
| H       | -0.6309507 | 5.1232510  | -2.0934526 |
| C       | 1.1095465  | 2.4026271  | -3.4590686 |
| H       | 0.5100526  | 2.3181139  | -4.3803845 |
| H       | 1.3614498  | 1.3847093  | -3.121394  |
| H       | 2.0495744  | 2.9127263  | -3.7261551 |
| C       | 0.3340294  | 2.6465682  | 2.7374029  |
| H       | -0.6343516 | 2.1897107  | 2.4851454  |
| C       | 0.0358188  | 3.9402412  | 3.5209132  |
| H       | -0.5496360 | 4.6454473  | 2.9104213  |
| H       | 0.9681943  | 4.4457555  | 3.8246058  |
| H       | -0.5385397 | 3.7160913  | 4.4353790  |
| C       | 1.1023321  | 1.6273972  | 3.5955488  |
| H       | 2.0707132  | 2.0242457  | 3.9419793  |
| H       | 1.2968467  | 0.7005764  | 3.0325661  |
| H       | 0.5155792  | 1.3653654  | 4.4913870  |
| C       | -1.9258187 | -2.0062811 | -2.8086881 |
| H       | -2.1578417 | -0.9733547 | -2.5097759 |
| C       | -3.1754602 | -2.5695739 | -3.5151260 |
| H       | -4.0431952 | -2.5802971 | -2.8371906 |
| H       | -3.0026501 | -3.6029484 | -3.8611813 |
| Element | σ (x)       | σ (y)       | σ (z)       |
|---------|-------------|-------------|-------------|
| H       | -3.4331963  | -1.9584532  | -4.3966274  |
| C       | -0.7213829  | -1.9377135  | -3.7619296  |
| H       | -0.4617037  | -2.9275851  | -4.1725715  |
| H       | 0.1664754   | -1.5381389  | -3.2471937  |
| H       | -0.9497073  | -1.2797266  | -4.6168318  |
| C       | -2.0263609  | -2.4659586  | 2.3098352   |
| H       | -2.2089222  | -1.3867037  | 2.1964825   |
| C       | -3.3337050  | -3.1008994  | 2.8263943   |
| H       | -3.6310472  | -2.6512095  | 3.7888844   |
| C       | -3.2074595  | -4.1853691  | 2.9863444   |
| H       | -4.1560608  | -2.9583743  | 2.1085965   |
| C       | -0.8871210  | -2.6255753  | 3.3296325   |
| H       | -1.1505674  | -2.1207442  | 4.2738780   |
| H       | 0.0500952   | -2.1854185  | 2.9544407   |
| H       | -0.6922575  | -3.6837639  | 3.5702604   |
| H       | -4.1902480  | 4.7419690   | -0.0685681  |
| C       | -4.2157155  | 3.6560142   | -0.1720485  |
| C       | -4.1766053  | 0.8955007   | -0.4213409  |
| C       | -5.4121869  | 2.9500565   | -0.3666348  |
| C       | -3.0286570  | 2.9254320   | -0.1116144  |
| N       | -3.0648973  | 1.6015146   | -0.2372606  |
| C       | -5.4052856  | 1.5534581   | -0.4940066  |
| H       | -6.3587170  | 3.4936762   | -0.4188390  |
| H       | -6.3196322  | 0.9774632   | -0.6448742  |
| C       | -1.6322623  | 3.4767051   | 0.0923176   |
| O       | -1.4470179  | 4.6860485   | 0.2330746   |
| C       | -3.9350734  | -0.5970693  | 0.5251618   |
| O       | -4.8815023  | -1.3707967  | -0.6928135  |
| N       | -2.6220693  | -0.9063486  | -0.4064891  |
| N       | -0.6933662  | 2.4954453   | 0.0970391   |
| Cu      | -1.3982117  | 0.6542855   | -0.1611991  |
| H       | 0.9317541   | 0.5142321   | -0.0067432  |
| O       | 0.2911303   | -0.2081232  | -0.1336511  |
| H       | 1.2174668   | -1.2266136  | -0.2180778  |
| C       | 0.6757511   | 2.8210002   | 0.2808793   |
| C       | 3.3985669   | 3.3864846   | 0.6401297   |
| C       | 1.2279034   | 2.8148767   | 1.5924216   |
| C       | 1.4920570   | 3.0968885   | -0.8515111  |
| C       | 2.8496360   | 3.3796146   | -0.6432114  |
| C       | 2.5909845   | 3.1049527   | 1.7443527   |
| H       | 3.4907748   | 3.6017478   | -1.4995949  |
| H       | 3.0315606   | 3.1152559   | 2.7442611   |
| H       | 4.4591430   | 3.6124163   | 0.7810450   |
| C       | -2.2007012  | -2.2583180  | -0.4621461  |
| C       | -1.2684741  | -4.9007102  | -0.5551253  |
| C       | -2.0757929  | -3.0010176  | 0.7435857   |
| C       | -1.8759955  | -2.8437256  | -1.7152819  |

**Cu^II(OH)(L)-DHA-TS**

\[
E_{\text{B3LYP/def2-SVP}(\text{Cu:}\text{def2-TZVP})/\text{COSMO}(\epsilon = 8.51)^\prime}:
-3772.5111701159 \ (<S^2> = 0.50062830)
\]

\[
E_{\text{B3LYP/def2-TZVP}/\text{COSMO}(\epsilon = 8.51)^{\prime}}:
-3774.8423596806 \ (S = 0; <S^2> = 0.51836229)
\]

\[
E_{\text{B3LYP/def2-TZVP}/\text{COSMO}(\epsilon = 8.51)^{\prime}}:
-3774.8300055974 \ (S = 1; <S^2> = 2.01602640)
\]

\[
E_{\text{B3LYP/def2-TZVP}/\text{COSMO}(\epsilon = 8.51)^{\prime}}:
-3774.8466818511 \ (\text{spin purified})
\]

Chem. Pot.\((298.15)/\text{B3LYP/def2-SVP}(\text{Cu:}\text{def2-TZVP})/\text{COSMO}(\epsilon = 8.51)^{\prime}:
0.845117
\]

\[
\Delta S = 1; \langle S^2 \rangle > 80\%
\]

0.771166
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| C    | -1.4088708 | -4.1662411 | -1.7342157 |
| C    | -1.6064642 | -4.3203767 | 0.6696368  |
| H    | -1.1600721 | -4.6367834 | -2.6890656 |
| H    | -1.5115815 | -4.9144481 | 1.5840294  |
| H    | -0.9038817 | -5.9312715 | -0.5912587 |
| H    | 5.9560835  | 0.2938269  | -1.5672975 |
| C    | 5.1034291  | -0.3178902 | -1.8769976 |
| C    | 2.9454448  | -1.8971253 | -2.6734163 |
| C    | 4.2006722  | -0.7768140 | -0.9092473 |
| C    | 4.9322398  | -0.6356074 | -3.2278673 |
| C    | 3.8480264  | -1.4305445 | -3.6268783 |
| C    | 3.1050643  | -1.5809400 | -1.3079347 |
| H    | 5.6480114  | -0.2703998 | -3.9692488 |
| H    | 3.7147130  | -1.6903265 | -4.6803540 |
| H    | 2.1079296  | -2.5301755 | -2.9773273 |
| C    | 4.3623199  | -0.4136126 | 0.5484752  |
| C    | 3.8628866  | 0.5646415  | 0.7193277  |
| H    | 5.4231445  | -0.2338903 | 0.7848857  |
| C    | 2.1516102  | -2.0722513 | -0.2879100 |
| H    | 1.5455100  | -2.9273720 | -0.6244670 |
| C    | 3.7724296  | -1.4241146 | 1.5046295  |
| C    | 2.6799601  | -2.2227340 | 1.0853729  |
| C    | 4.2733232  | -1.5750675 | 2.8039518  |
| H    | 5.1244202  | -0.9668359 | 3.1247615  |
| C    | 3.7050817  | -2.4954729 | 3.6904316  |
| H    | 4.1108681  | -2.6022773 | 4.7000555  |
| C    | 2.1144614  | -3.1467523 | 1.9888356  |
| H    | 1.2737534  | -3.7627839 | 1.6590682  |
| C    | 2.6216328  | -3.2854876 | 3.2791930  |
| H    | 2.1788456  | -4.0111543 | 3.9665220  |
| C    | 0.9085352  | 3.1396166  | -2.2603368 |
| H    | -0.0739738 | 2.6457404  | -2.2188755 |
| C    | 0.6668890  | 4.5973963  | -2.7020603 |
| H    | 0.1732628  | 4.6279933  | -3.6881012 |
| H    | 1.6201546  | 5.1469995  | -2.7855569 |
| H    | 0.0296844  | 5.1278491  | -1.9781682 |
| C    | 1.7574938  | 2.3752935  | -3.2891239 |
| H    | 1.2427942  | 2.3548803  | -4.2639515 |
| H    | 1.9321751  | 1.339016   | -2.9750836 |
| H    | 2.7403072  | 2.8482428  | -3.4497182 |
| C    | 0.3585417  | 2.5522046  | 2.8182285  |
| H    | -0.5723132 | 2.0868594  | 2.4604223  |
| C    | -0.0302423 | 3.8789940  | 3.5017763  |
| H    | -0.5208947 | 4.5610407  | 2.7905690  |
| H    | 0.8609199  | 4.3901882  | 3.9045884  |
| H    | -0.7220796 | 3.6962082  | 4.3412514  |
| C    | 1.0000721  | 1.5750990  | 3.8167215  |
| H    | 1.9034559  | 1.9961696  | 4.2880635  |
| Atoms | X     | Y     | Z     |
|-------|-------|-------|-------|
| H     | 1.2833545 | 0.6288416 | 3.3282594 |
| H     | 0.2900375 | 1.3403059 | 4.6266991 |
| C     | -2.1010103 | -2.0903788 | -3.0235167 |
| H     | -2.2345355 | -1.0288750 | -2.7669447 |
| C     | -3.4037269 | -2.5645870 | -3.7002750 |
| H     | -4.2595206 | -2.4656080 | -3.0154815 |
| H     | -3.3277939 | -3.6225907 | -4.0049075 |
| C     | -0.9109601 | -2.1718348 | -3.9916790 |
| H     | -0.7190987 | -3.2029687 | -4.3320373 |
| H     | 0.0090421  | -1.7893131 | -3.5235750 |
| H     | -1.1092485 | -1.5638898 | -4.8899275 |
| C     | -2.5175586 | -2.4105975 | 2.0802272 |
| H     | -2.5309377 | -1.3166366 | 1.9591372 |
| C     | -3.9591875 | -2.8513782 | 2.4112334 |
| H     | -4.3155757 | -2.3589173 | 3.3319983 |
| C     | -1.5669294 | -2.7255873 | 3.2448716 |
| H     | -1.8973658 | -2.1977518 | 4.1547447 |
| H     | -0.5368686 | -2.4070475 | 3.0226603 |
| H     | -1.5455878 | -3.8016270 | 3.4854439 |

**Cu\textsuperscript{III}(OH)(L)-DHA-IC**

\[ \text{EB3LYP/def2-SVP(Cu:def2-TZVP)/COSMO(\(\varepsilon = 8.51\))}: -3772.5449710456 (\(<S^2> 1.03125625\)) \]

\[ \text{EB3LYP/def2-TZVPP/COSMO(\(\varepsilon = 8.51\))}: -3774.8762104980 (S = 0; \(<S^2> 1.02955312\)) \]

\[ -3774.8760477380 (S = 1; \(<S^2> 2.03491663\)) \]

\[ -3774.8763831711 (\text{spin purified}) \]

\[ \text{ZPEB3LYP/def2-SVP(Cu:def2-TZVP)/COSMO(\(\varepsilon = 8.51\))}: 0.84896 \]

\[ \text{Chem. Pot.}(298.15)/B3LYP/def2-SVP(Cu:def2-TZVP)/COSMO(\(\varepsilon = 8.51\))}: 0.773707 \]
|   |   |   |   |
|---|---|---|---|
| H | 3.2243598 | 3.7507073 | -1.7006803 |
| H | 3.0911790 | 3.3342930 | 2.5719996  |
| H | 4.3510917 | 3.8603451 | 0.5036873  |
| C | -1.9008281 | -2.4424858 | -0.3063339 |
| C | -0.6938277 | -4.9686595 | -0.5137775 |
| C | -1.6214511 | -3.1878509 | 0.8713523  |
| C | -1.5892701 | -2.9701492 | -1.5892616 |
| C | -0.9851932 | -4.2345761 | -1.6650156 |
| C | -1.0159216 | -4.4469470 | 0.7405721  |
| H | -0.7448356 | -4.6590010 | 2.6430898  |
| H | -0.7998381 | -5.0366734 | 1.6349769  |
| H | -0.2234192 | -5.9526601 | -0.5947222 |
| H | 5.5461232 | 0.6660553 | -2.2094884 |
| C | 4.8186560 | -0.1445520 | -2.3158003 |
| C | 2.9686443 | -2.2161512 | -2.6115921 |
| C | 4.3020928 | -0.7513899 | -1.1663541 |
| C | 4.4244236 | -0.5541391 | -3.5946441 |
| C | 3.4926079 | -1.5958933 | -3.7388786 |
| C | 3.3583434 | -1.8130730 | -1.3050306 |
| H | 4.8430592 | -0.0648025 | -4.4778332 |
| H | 3.1838186 | -1.9215850 | -4.7357140 |
| H | 2.2521758 | -3.0352384 | -2.7169155 |
| C | 4.7182331 | -0.2702840 | 0.2060853  |
| H | 4.3317385 | 0.7602315 | 0.3498644  |
| H | 5.8160866 | -0.1524786 | 0.2392950  |
| C | 2.8466306 | -2.4733623 | -0.1424263 |
| H | 2.1451556 | -3.3033837 | -0.2735565 |
| C | 4.2650514 | -1.1216328 | 1.3715703  |
| C | 3.3249354 | -2.1769393 | 1.1740524  |
| C | 4.7433562 | -0.8676832 | 2.6612317  |
| H | 5.4673873 | -0.0609885 | 2.8121329  |
| C | 4.3156898 | -1.6248133 | 3.7578091  |
| H | 4.7046647 | -1.4077798 | 4.7560323  |
| C | 2.9022128 | -2.9365417 | 2.2986944  |
| H | 2.1876418 | -3.7495637 | 2.1448522  |
| C | 3.3892277 | -2.6645152 | 3.5710048  |
| H | 3.0548101 | -3.2609355 | 4.4240041  |
| C | 0.6179908 | 3.1464613 | -2.2651237 |
| H | -0.2979867 | 2.5449071 | -2.1578763 |
| C | 0.1804445 | 4.5715729 | -2.6618156 |
| H | -0.3883663 | 4.5554466 | -3.6068777 |
| H | 1.0589957 | 5.2233946 | -2.8082044 |
| H | -0.4525660 | 5.0224624 | -1.8827211 |
| C | 1.4635415 | 2.4994768 | -3.3736186 |
| H | 0.8719561 | 2.4169888 | -4.3001844 |
| H | 1.8004843 | 1.4880049 | -3.0950653 |
| H | 2.3592563 | 3.0957896 | -3.6136946 |
| C | 0.4593499 | 2.6485401 | 2.8469818 |
5.2.3 \([\text{Fe}^{IV}(O)\text{TMG}_3\text{tren}]^{2+} (\sigma), [\text{Fe}^{IV}(O)\text{TMG}_2\text{dien}(\text{MeCN})]^{2+} (\sigma) \) and \([\text{Fe}^{IV}(O)\text{TMG}_2\text{dien}(\text{MeCN})]^{2+} (\pi)\) pathways (B3LYP-D3)

Method: B3LYP-D3/def2-SVP(Fe: def2-TZVP)/COSMO(\(\varepsilon = 35.88\))

|   | \(\text{CHD} \) |
|---|----------------|
|   | \(E_{\text{B3LYP-D3/def2-SVP/COSMO}(\varepsilon = 35.88)}: \) |
|   | \(-233.1023616359\) |
|   | \(E_{\text{B3LYP-D3/def2-TZVP/COSMO}(\varepsilon = 35.88)}: \) |
|   | \(-233.3606579473\) |
|   | \(ZPE_{\text{B3LYP-D3/def2-SVP/COSMO}(\varepsilon = 35.88)}: \) |
|   | \(0.121825\) |
|   | \(\text{Chem. Pot.}(298.15)/\text{B3LYP-D3/def2-SVP/COSMO}(\varepsilon = 35.88): \) |
|   | \(0.121825\) |
|    |      |       |       |            | 0.094797 (σ = 4)  |
|----|------|-------|-------|------------|-------------------|
| H  | 0.0602054 | -1.8884489 | -0.6863914 |          |                  |
| C  | -3.5492648 | -0.7666814 | 0.1461993 |          |                  |
| C  | -3.5563323 | 0.6068804 | 0.4151635 |          |                  |
| C  | -2.3863934 | -1.3741389 | -0.3417281 |          |                  |
| C  | -2.4005063 | 1.3650163 | 0.1946140 |          |                  |
| C  | -1.2284241 | -0.6189383 | -0.5718221 |          |                  |
| C  | -1.2355248 | 0.7638963 | -0.3010167 |          |                  |
| C  | 0.0446237 | -1.2364957 | -1.1126839 |          |                  |
| C  | 0.0302879 | 1.5524300 | 0.3510587 |          |                  |
| C  | 1.2742013 | 0.7607970 | -0.2193002 |          |                  |
| C  | 1.2812650 | -0.6220544 | -0.4899937 |          |                  |
| C  | 2.4059580 | 1.3590973 | 0.3510587 |          |                  |
| C  | 2.4199155 | -1.3801091 | -0.1850918 |          |                  |
| C  | 3.5431270 | 0.5981354 | 0.6462273 |          |                  |
| C  | 3.5501154 | -0.7754653 | 0.3773877 |          |                  |
| H  | -4.4463858 | -1.3667970 | 0.3222208 |          |                  |
| H  | -4.4590021 | 1.0873287 | 0.8028613 |          |                  |
| H  | -2.3765914 | -2.4494525 | -0.5450393 |          |                  |
| H  | -2.4018306 | 2.4376609 | 0.4117981 |          |                  |
| H  | 2.3957653 | 2.4317408 | 0.5680144 |          |                  |
| H  | 2.4207036 | -2.4554130 | -0.3886979 |          |                  |
| H  | 4.4199033 | 1.0764022 | 1.0917333 |          |                  |
| H  | 4.4324295 | -1.3777518 | 0.6113241 |          |                  |
| H  | 0.0657789 | 1.8067672 | -1.6468147 |          |                  |
| H  | 0.0141195 | 2.5149337 | -0.0329980 |          |                  |
| H  | 0.0389850 | -2.3292727 | -0.9815508 |          |                  |
| H  | 0.0805332 | -1.0586584 | -2.2066907 |          |                  |

### [FeIV(O)TMG2dien(MeCN)]2+ (σ) pathway

|    |      |       |       |          |          |
|----|------|-------|-------|----------|----------|
| Fe | 4.7858346 | 9.4737996 | 3.1601846 |          |          |
| N  | 4.5058367 | 11.2995332 | 2.1430726 |          |          |
| O  | 3.1813417 | 9.2752017 | 3.3759226 |          |          |
| N  | 5.1974233 | 9.8797429 | 5.0214387 |          |          |
| C  | 6.5858942 | 10.3032311 | 5.2500544 |          |          |
| H  | 6.8823165 | 10.1247002 | 6.2956352 |          |          |
| H  | 6.7372338 | 11.3771086 | 5.0515443 |          |          |
| C  | 7.4442208 | 9.4719154 | 4.3130614 |          |          |
| H  | 8.5073130 | 9.7595677 | 4.3606283 |          |          |
| H  | 7.3616913 | 8.4138386 | 4.5960367 |          |          |
| N  | 6.9321335 | 9.6273521 | 2.9184544 |          |          |
| C  | 7.3384553 | 8.4898439 | 2.0443167 |          |          |
| H  | 8.4020532 | 8.2453166 | 2.2048116 |          |          |
| H  | 7.2123248 | 8.8153486 | 1.0028657 |          |          |
| C  | 6.4376160 | 7.2970625 | 2.3036750 |          |          |
| H  | 6.6279360 | 6.5115593 | 1.5562195 |          |          |
| H  | 6.6549998 | 6.8597248 | 3.2919791 |          |          |

### [FeIV(O)TMG2dien(MeCN)]2+ (σ = 2)

|    |      |       |       |          |          |
|----|------|-------|-------|----------|----------|
| Fe | 4.7858346 | 9.4737996 | 3.1601846 |          |          |
| N  | 4.5058367 | 11.2995332 | 2.1430726 |          |          |
| O  | 3.1813417 | 9.2752017 | 3.3759226 |          |          |
| N  | 5.1974233 | 9.8797429 | 5.0214387 |          |          |
| C  | 6.5858942 | 10.3032311 | 5.2500544 |          |          |
| H  | 6.8823165 | 10.1247002 | 6.2956352 |          |          |
| H  | 6.7372338 | 11.3771086 | 5.0515443 |          |          |
| C  | 7.4442208 | 9.4719154 | 4.3130614 |          |          |
| H  | 8.5073130 | 9.7595677 | 4.3606283 |          |          |
| H  | 7.3616913 | 8.4138386 | 4.5960367 |          |          |
| N  | 6.9321335 | 9.6273521 | 2.9184544 |          |          |
| C  | 7.3384553 | 8.4898439 | 2.0443167 |          |          |
| H  | 8.4020532 | 8.2453166 | 2.2048116 |          |          |
| H  | 7.2123248 | 8.8153486 | 1.0028657 |          |          |
| C  | 6.4376160 | 7.2970625 | 2.3036750 |          |          |
| H  | 6.6279360 | 6.5115593 | 1.5562195 |          |          |
| H  | 6.6549998 | 6.8597248 | 3.2919791 |          |          |
| N | 5.0545573 | 7.7845267 | 2.2160839 |
| C | 4.2918628 | 9.9813281 | 6.0203387 |
| N | 4.2734472 | 11.0654903 | 6.8312801 |
| C | 4.6405282 | 12.3952427 | 6.3397272 |
| H | 4.6384907 | 12.396548 | 5.2426977 |
| H | 5.6313476 | 12.706174 | 6.7086875 |
| H | 3.8939510 | 13.1181639 | 6.6939393 |
| C | 3.9083838 | 10.9931617 | 8.2449041 |
| H | 3.9082969 | 9.9501662 | 8.5832911 |
| H | 2.9194327 | 11.439593 | 8.4379297 |
| C | 7.4215700 | 10.8995607 | 2.3349693 |
| H | 8.5213372 | 10.770740 | 2.2581391 |
| H | 7.1233717 | 11.7461830 | 2.9631273 |
| C | 3.6155671 | 4.7014168 | 0.9244578 |
| H | 3.4660424 | 5.2142208 | -0.031886 |
| H | 2.6704449 | 4.2262061 | 1.2342067 |
| H | 4.3703162 | 3.9115302 | 0.7833112 |
| N | 3.1831250 | 8.7635994 | 0.3013197 |
| C | 1.6921480 | 6.9955157 | 1.1475916 |
| H | 1.6214127 | 6.2612623 | 1.9584585 |
| H | 1.3651984 | 6.5292466 | 0.2041425 |
| H | 1.0123031 | 7.8305486 | 1.3795664 |
| C | 3.1831250 | 8.7635994 | 0.3013197 |
| H | 4.2420306 | 8.9951149 | 0.1377217 |
| H | 2.7146024 | 9.5986770 | 0.8436585 |
| H | 2.6856079 | 8.6453204 | -0.6737902 |
| C | 4.2049469 | 12.2959388 | 1.6414617 |
| C | 3.8287404 | 13.5431651 | 1.0091718 |
| H | 4.1399946 | 13.5258513 | -0.0467248 |
| H | 2.7371206 | 13.6709684 | 1.0700966 |
| H | 4.3267878 | 14.3799541 | 1.5227180 |
|   |   |   |   |
|---|---|---|---|
| Fe | -0.3355169 | 0.4206954 | -0.6869580 |
| N | 0.8703801 | -0.5983625 | -2.0734470 |
| O | 0.5539672 | -0.0359018 | 0.5989927 |
| N | -1.873026 | 0.7338578 | -2.261132 |
| C | -3.224940 | 1.3522721 | -1.0927898 |
| H | -0.6075515 | 2.8224922 | -2.9793910 |
| C | -1.2327210 | 3.1236322 | -0.9518188 |
| H | -0.9794401 | 4.1938857 | -0.9997356 |
| C | -2.1479382 | 3.0364175 | -0.3430554 |
| C | -1.890549 | -3.5414126 | -0.5331967 |
| H | -1.1134225 | -2.9815987 | -1.0698429 |
| H | -2.7356327 | -3.7357015 | -1.121758 |
| C | -1.4659791 | -4.5093183 | -0.2208970 |
| C | -3.1163989 | -3.5544979 | 1.6131112 |
| H | -3.5914063 | -2.8710704 | 2.3268960 |
| H | -2.5185471 | -4.2992459 | 2.1633131 |
| H | -3.9079845 | -4.0859276 | 1.0614692 |
| C | -1.7721321 | -1.0112088 | 2.0549436 |
| C | -1.2186944 | -1.8099552 | 3.1443532 |
| H | -0.8605302 | -2.7716112 | 2.7671715 |
| H | -1.9588522 | -1.9724757 | 3.9437280 |
| H | -0.3570323 | -1.2700686 | 3.5667447 |
| C | -1.9098053 | 0.4098191 | 2.3507051 |
| H | -2.5068104 | 0.8997613 | 1.5732826 |
| H | -0.9190233 | 0.8868695 | 2.3979429 |
| H | -2.4142946 | 0.5256386 | 3.3219474 |
| C | -1.3149462 | 0.5523661 | -3.6571518 |
| C | -2.0197236 | 0.9647824 | -4.3982490 |
| H | -1.4055139 | -0.5403274 | -3.6484340 |
| H | -0.2921238 | 0.8190550 | -3.9464121 |
| C | 0.7561096 | 2.9079872 | 0.4594084 |
| N | 0.4139227 | 3.9396767 | 1.2741164 |
| C | -0.9098471 | 4.0555461 | 1.8771154 |
| H | -1.4552715 | 3.1100025 | 1.7872075 |
| H | -1.5024408 | 4.8609318 | 1.4132847 |
| H | -0.7933914 | 4.2829511 | 2.9485737 |
| C | 1.3455009 | 5.0177032 | 1.6005728 |

**[Fe^{IV}(O)TMG_dien(MeCN)]^{2+}-CHD-RC (σ)**

**E**

**B3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88):**

-2678.9113164419 (\(<S^2> = 6.05193047\))

**ZPE**

**B3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88):**

0.698111

**Chem. Pot.**(298.15)/**B3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88):**

0.634162
| Atom | X-coordinate | Y-coordinate | Z-coordinate |
|------|--------------|--------------|--------------|
| H    | 2.2090209    | 4.9904817    | 0.9253109    |
| H    | 1.6978379    | 4.9549275    | 2.6432544    |
| C    | 2.7978033    | 2.3912042    | 1.7289535    |
| H    | 2.1518293    | 2.5917460    | 2.5915938    |
| H    | 3.6409958    | 3.1007631    | 1.7323837    |
| C    | 2.6676103    | 1.8394453    | -1.5788436   |
| H    | 2.7068798    | 0.7464310    | -0.5473317   |
| H    | 3.1988639    | 3.6932405    | -0.7600516   |
| C    | 2.6676103    | 1.8394453    | -1.5788436   |
| H    | 2.7068798    | 0.7464310    | -0.5473317   |
| H    | 3.1988639    | 3.6932405    | -0.7600516   |

**[FeIV(O)TMG2dien(MeCN)]2+·CHD-TS (σ)**

Eb3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88):

-2678.8956380853 (<S^2> 6.42237422)

ZPEb3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88):

0.691413

Chem. Pot.(298.15)/B3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88):

0.627566
$[\text{Fe}^{IV}(\text{O})\text{TMG}_2\text{dien(MeCN)}]^2^+\cdot\text{CHD-IC (σ)}$

\begin{align*}
\text{EB3LYP-D3/def2-SVP(Fe:df2-TZVP)/COSMO}(\epsilon = 35.88): & \quad -2678.9369866803 \quad (<S^2> 7.03885069) \\
\text{EB3LYP-D3/def2-TZVP/COSMO}(\epsilon = 35.88): & \quad -2680.5065384798 \quad (<S^2> 7.03646759) \\
\text{ZPE}_{\text{B3LYP-D3/def2-SVP(Fe:df2-TZVP)/COSMO}(\epsilon = 35.88)}: & \quad 0.69354 \\
\text{Chem. Pot.} (298.15)/\text{B3LYP-D3/def2-SVP(Fe:df2-TZVP)/COSMO}(\epsilon = 35.88): & \quad 0.628654
\end{align*}

|    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| H  | 2.9203553 | 13.9407940 | 1.4191998 |
| C  | 0.2122362 | 11.5440573 | 4.7362128 |
| C  | 0.1534151 | 12.2009853 | 3.3869176 |
| C  | -0.0617447 | 11.2330270 | 2.2571700 |
| C  | -0.0195865 | 9.8968881 | 2.4271074 |
| C  | 0.2824758 | 9.2779182 | 3.7379945 |
| H  | 0.2143812 | 12.1985921 | 5.6139471 |
| C  | -0.0617447 | 11.2330270 | 2.2571700 |
| C  | -0.0195865 | 9.8968881 | 2.4271074 |
| C  | 0.2824758 | 9.2779182 | 3.7379945 |
| H  | 0.2143812 | 12.1985921 | 5.6139471 |
| H  | -0.2801311 | 9.7730316 | 5.8930187 |
| C  | 0.2824758 | 9.2779182 | 3.7379945 |
| H  | 1.4427800 | 8.9209815 | 3.6717659 |
| H  | -0.0220331 | 8.3133082 | 3.9106362 |
| H  | -0.6351289 | 12.9789788 | 3.3766529 |
| H  | 1.0848215 | 12.7841439 | 3.2196255 |
| Fe | -0.1292200 | 0.4258964 | -0.4874836 |
| N  | 1.1289945 | -0.5225680 | -1.8945332 |
| O  | 0.9208811 | -0.0203653 | 0.9350118 |
| N  | -1.7525742 | -0.6995014 | -0.1700348 |
| C  | -2.6566605 | -0.8359068 | -1.3187948 |
| H  | -3.4806222 | 0.5036520 | -2.8261095 |
| H  | -3.2442333 | 1.2211406 | -1.2162464 |
| N  | -1.4706122 | 1.0592202 | -2.3509608 |
| C  | -1.4171484 | 2.5386759 | -2.3482033 |
| H  | -2.2905476 | 2.9661651 | -2.8742359 |
| H  | -0.5132061 | 2.8373600 | -2.8999443 |
| C  | -1.3225290 | 3.0807259 | -0.9273238 |
| H  | -1.1717405 | 4.1707229 | -0.9657254 |
| H  | -2.2699955 | 2.9094528 | -0.3890394 |
| N  | -0.2000542 | 2.4147932 | -0.3467661 |
| C  | -1.9346934 | -1.4683469 | 0.9181694 |
| C  | -2.3413634 | -2.7610245 | 0.8150977 |
| C  | -1.9559529 | -3.5899771 | -0.3208571 |
| H  | -1.1103619 | -3.1340336 | -0.8494401 |
| H  | -2.7892886 | -3.7353436 | -1.0277905 |
| H  | -1.6422363 | -4.5789365 | 0.0488215 |
| C  | -3.2226934 | -3.3963321 | 1.7922474 |
| H  | -3.6570747 | -2.6419806 | 2.4590165 |
| H  | -2.6926054 | -4.1518502 | 2.3955024 |
| H  | -4.0426851 | -3.8979619 | 1.2538631 |
| N  | -1.7261756 | -0.9490976 | 2.1482540 |
| C  | -1.1846227 | -1.7329193 | 3.2534423 |
| H  | -0.8675918 | -2.7208132 | 2.9033558 |
| H  | -1.9186920 | -1.8534795 | 4.0661536 |
| H     | -0.3017301 | -1.2090540 | 3.6531200 |
| C     | -1.8210088 | 0.4826303  | 2.4023503 |
| H     | -2.4161670 | 0.9610195  | 1.6157920 |
| H     | -0.8178864 | 0.9365195  | 2.4264717 |
| H     | -2.3143074 | 0.6427351  | 3.3733365 |
| C     | -1.0771145 | 0.5323368  | -3.6686815 |
| H     | -1.7600388 | 0.8952482  | -4.4581635 |
| H     | -1.1007840 | -0.5653242 | -3.6621143 |
| H     | -0.0556509 | 0.8549347  | -3.9081033 |
| C     | 0.6065793  | 3.0971730  | 0.5659598 |
| N     | 0.1553375  | 4.1220455  | 1.3360671 |
| C     | -1.1985638 | 4.1546324  | 1.8781462 |
| H     | -1.6691597 | 3.1707287  | 1.7911428 |
| H     | -1.8273179 | 4.9005132  | 1.3649122 |
| H     | -1.1488515 | 4.4186419  | 2.9464886 |
| C     | 0.9890889  | 5.2740854  | 1.6721306 |
| H     | 1.8303292  | 5.2935815  | 1.0374041 |
| H     | 1.2968295  | 5.2637100  | 2.7308655 |
| H     | 0.4094430  | 6.1932102  | 1.4901317 |
| N     | 1.9219757  | 2.7799567  | 0.6369160 |
| C     | 2.6431406  | 2.7581805  | 1.9050725 |
| H     | 1.9625708  | 2.9674338  | 2.7383658 |
| H     | 3.4689663  | 3.4879641  | 1.9173756 |
| H     | 3.0585068  | 1.7476535  | 2.0517022 |
| C     | 2.6447293  | 2.2043797  | -0.4889816 |
| H     | 2.0842611  | 2.3616367  | -1.4184010 |
| H     | 2.8022070  | 1.1245274  | -0.3421888 |
| H     | 3.6254060  | 2.6984283  | -0.5753858 |
| C     | 1.8676089  | -1.0313175 | -2.6228059 |
| C     | 2.7850123  | -1.6465063 | -3.5577497 |
| H     | 2.7801176  | -1.0763739 | -4.4998251 |
| H     | 3.8001403  | -1.6453036 | -3.1338915 |
| H     | 2.4687010  | -2.6815006 | -3.7565233 |
| C     | 1.3492135  | -3.5287172 | -0.6749194 |
| C     | 3.0753238  | -3.5287172 | -0.6749194 |
| C     | 3.6848391  | -2.5847144 | 0.1085151 |
| C     | 3.1715207  | -2.5847144 | 0.1085151 |
| C     | 3.0103589  | -2.5847144 | 0.1085151 |
| C     | 2.0103589  | -2.9134819 | 1.8825352 |
| H     | 0.4600624  | -4.3473442 | 1.5182077 |
| H     | 3.5012605  | -3.7987139 | -1.6452587 |
| H     | 4.5922655  | -2.0871793 | -0.2474028 |
| H     | 1.6405483  | -2.6669580 | 2.8813072 |
| H     | 1.4760831  | -0.8063732 | 1.0647913 |
| H     | 3.6857590  | -1.5128630 | 2.0174280 |
| H     | 1.9750622  | -5.3397811 | -0.2928729 |
| H     | 1.0195418  | -4.0776877 | -0.9945039 |
| Element | x       | y       | z         |
|---------|---------|---------|-----------|
| Fe      | 1.3092622 | 0.7546715 | 0.3784955 |
| N       | 0.4968548 | 2.2172917 | -0.904615 |
| O       | 0.6218800 | 0.9296301 | 2.180856  |
| C       | 1.198932  | 2.0432533 | 2.946602  |
| H       | 1.0983848 | 1.8684039 | 4.029242  |
| H       | 0.7067453 | 3.0057006 | 2.727767  |
| C       | 2.6677225 | 2.0988090 | 2.560178  |
| H       | 3.1923602 | 2.9403934 | 3.041399  |
| H       | 3.1548827 | 1.1657676 | 2.874146  |
| N       | 2.7726369 | 2.2095645 | 1.074057  |
| C       | 4.0919440 | 1.7402023 | 0.560360  |
| H       | 4.9090217 | 2.1371707 | 1.185842  |
| H       | 4.2076296 | 2.1439533 | -0.454819 |
| C       | 5.0260016 | -0.1111034 | 0.495556  |
| H       | 4.1559363 | -0.1995222 | 1.512128  |
| N       | 2.9076198 | -0.1987986 | -0.222065 |
| C       | -0.4100749 | 0.2206323 | 2.703025  |
| N       | -1.4624801 | 0.8607787 | 3.263063  |
| C       | -1.8750131 | 2.1817230 | 2.796893  |
| H       | -1.4330023 | 2.3926959 | 1.815712  |
| H       | -1.5841476 | 2.9724498 | 3.507707  |
| C       | -2.2255907 | 0.3262987 | 4.390056  |
| H       | -1.6837074 | -0.5036880 | 4.858057  |
| H       | -3.2257520 | -0.0167059 | 4.079218  |
| H       | -2.3479789 | 1.1257410 | 5.137202  |
| N       | -0.3689576 | -1.1230275 | 2.680877  |
| C       | -1.5623214 | -1.9606771 | 2.592395  |
| H       | -2.4441283 | -1.3549198 | 2.369705  |
| H       | -1.7266912 | -2.5305325 | 3.520276  |
| H       | -1.4239721 | -2.6716178 | 1.764802  |
| C       | 0.8900569  | -1.8492971 | 2.559892  |
| H       | 1.7290252  | -1.2011982 | 2.836180  |
| H       | 1.0295390  | -2.1981831 | 1.525366  |
| H       | 0.8663642  | -2.7181796 | 3.234727  |
| C       | 2.5580771  | 3.6171839 | 0.663186  |
| C       | 3.3373481  | 4.2593963 | 1.105900  |
| H       | 1.5740562  | 3.9673247 | 0.996808  |
| H       | 2.6103227  | 3.6951188 | -0.428213 |
| C       | 2.9206180  | -1.3014919 | -0.994190 |
| N       | 3.7458694  | -2.3481504 | -0.728632 |
| C       | 4.0702253  | -2.7635176 | 0.632105  |
| H       | 3.3890779  | -2.2932594 | 1.348408  |
| H       | 5.1090152  | -2.5118296 | 0.901412  |
| H       | 3.9464808  | -3.8554164 | 0.708968  |
| C       | 4.3759408  | -3.1329901 | -1.788706 |

$$[\text{Fe}^4(\text{O})\text{TMG}_2\text{dien(MeCN)}]^2^+\text{-DHA-RC (σ)}$$

$$E_{B3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88)}: -2985.8471857051 (<S^2> 6.05269199)$$

$$E_{B3LYP-D3/def2-TZVP/COSMO(ε = 35.88)}: -2987.7376222869 (<S^2> 6.05486530)$$

$$ZPE_{B3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88)}: 0.794496$$

Chem. Pot. (298.15)/B3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88): 0.727192
\[ \text{Fe}^{IV}(\text{O})\text{TMG}_2\text{dien(MeCN)}\text{]}^2^+\text{-DHA-TS} (\sigma) \]

\[ \text{E}_{\text{B3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO}(\epsilon = 35.88)^{\text{2}}} = -2985.8279795301 \ 
\text{ (<S^2> 6.48039190)} \]
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| C       | 6.2233615  | 10.7838150 | 4.8050529  |
| H       | 6.6410591  | 10.8983291 | 5.8178030  |
| H       | 6.0732900  | 11.7997888 | 4.4023256  |
| C       | 7.1968298  | 10.0133290 | 3.9245572  |
| H       | 8.1720611  | 10.5263360 | 3.8575337  |
| H       | 7.3675445  | 9.0249946  | 4.3728266  |
| N       | 6.6108747  | 9.8313056  | 2.5713036  |
| C       | 7.1112000  | 8.6123970  | 1.8918799  |
| H       | 8.2079132  | 8.5273741  | 1.9965843  |
| H       | 6.8812390  | 8.7136502  | 0.8215031  |
| C       | 6.4140870  | 7.3687562  | 2.4227773  |
| H       | 7.3675445  | 6.4979264  | 1.8239371  |
| H       | 6.7268171  | 7.1687499  | 3.4616010  |
| N       | 4.9670296  | 7.5876397  | 2.333637   |
| C       | 4.2486979  | 9.9627154  | 5.9738294  |
| H       | 4.9847462  | 12.9596064 | 6.3971437  |
| H       | 3.2103870  | 12.9590436 | 6.6114104  |
| C       | 4.2086444  | 7.5143740  | 5.8980565  |
| H       | 5.2499076  | 7.6222870  | 5.5734108  |
| H       | 3.6050936  | 7.1416009  | 5.0560511  |
| C       | 4.1629467  | 6.7910996  | 6.7263621  |
| C       | 6.8748381  | 11.0191568 | 1.7379760  |
| H       | 7.9591531  | 11.1398919 | 1.5654568  |
| H       | 4.954530  | 11.9232549 | 2.2315138  |
| H       | 6.3728735  | 10.9122151 | 0.7682500  |
| C       | 4.1461945  | 6.5959084  | 1.9593315  |
| N       | 4.4202773  | 5.2887459  | 2.2166277  |
| C       | 5.1158908  | 4.8543794  | 3.4229366  |
| H       | 5.1689189  | 5.6695253  | 4.1500948  |
| H       | 6.1372666  | 4.5035316  | 3.2019396  |
| H       | 4.5546534  | 4.0233327  | 3.8793634  |
| C       | 4.0514096  | 4.2178718  | 1.2931534  |
| H       | 3.7697857  | 4.6358426  | 0.3193497  |
| H       | 3.2181274  | 3.6088755  | 1.6810263  |
| H       | 4.9233744  | 3.5593913  | 1.1515483  |
| N       | 3.0119299  | 6.8839780  | 1.2770271  |
|   |  1.7676531 |  6.1566571 |  1.5022069 |
|---|-------------|-------------|-------------|
| C |  1.8645139 |  5.4856480 |  2.3636537 |
| H |  1.4660405 |  5.5725093 |  0.6175428 |
| H |  1.8645139 |  5.4856480 |  2.3636537 |
| H |  0.9711654 |  6.8837809 |  1.7258146 |
| C |  3.8919592 |  8.4417623 |  0.1719725 |
| C |  1.8645139 |  5.4856480 |  2.3636537 |
| C |  2.8956810 |  8.0595072 |  0.4239609 |
| C |  3.4431009 | 12.9116668 |  0.1419095 |
| C |  3.4431009 | 12.9116668 |  0.1419095 |
| Fe |  1.1965026 |  6.8231208 |  0.2364298 |
| N |  0.4947346 |  2.2484576 | -0.9887124 |
| O | -0.0131880 | -0.5394677 | -0.3489013 |
| N |  0.5995574 |  0.9062624 |  2.119618 |
| C |  1.127522 |  2.0833877 |  2.8232547 |
| H |  0.9721820 |  1.9812047 |  3.9112802 |
| H |  0.5939054 |  3.0049953 |  2.5155617 |
| C |  2.5963770 |  2.1914647 |  2.4990198 |

$[\text{Fe}^{IV}(\text{O})\text{TMG}_2\text{dien(MeCN)}]^2-\text{DHA-IC (}\sigma\text{)}$

$\text{E}^\text{B3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(}\varepsilon=35.88\text{)}$:

-2985.8627953930 ($\langle S^2\rangle$ 7.04023782)

$\text{E}^\text{B3LYP-D3/def2-TZVPP/COSMO(}\varepsilon=35.88\text{)}$:

-2987.7538662395 ($\langle S^2\rangle$ 7.03845116)
|   |   |   |   |   |
|---|---|---|---|---|
| H | 3.0518454 | 3.0597020 | 3.0073168 |   |
| H | 3.1012997 | 1.2876974 | 2.8644343 |   |
| N | 2.7892891 | 2.2854304 | 1.0307762 |   |
| C | 4.0943507 | 1.7417791 | 0.5976222 |   |
| H | 4.9154132 | 2.1298608 | 1.2241297 |   |
| H | 4.2680653 | 2.0887560 | -0.4356304 |   |
| C | 4.0850337 | 0.2183931 | 0.5976222 |   |
| H | 5.0288984 | -0.1481054 | 0.1651274 |   |
| H | 4.0413086 | -0.1603073 | 1.6327433 |   |
| N | 2.9324611 | -0.2341510 | -0.1858794 |   |
| C | -0.3959133 | 0.1690884 | 2.6568521 |   |
| N | -1.440345 | 0.7560746 | 3.2950604 |   |
| C | -1.9161467 | 2.0797370 | 2.9088122 |   |
| H | -1.5587117 | 2.3326720 | 1.9027786 |   |
| H | -1.5886225 | 2.8592887 | 3.6162784 |   |
| H | -3.0163434 | 2.0693042 | 2.8930918 |   |
| C | -2.1368567 | 0.1373076 | 4.4205718 |   |
| H | -1.5626257 | -0.7165120 | 4.7994138 |   |
| H | -3.1477294 | -0.2006783 | 4.1383739 |   |
| H | -2.2315901 | 0.8805673 | 5.2280631 |   |
| N | -0.3541417 | -1.1770243 | 2.5671240 |   |
| C | -1.5516743 | -1.9866868 | 2.3697571 |   |
| H | -2.4307148 | -1.3486053 | 2.2509385 |   |
| H | -1.7138545 | -2.6825022 | 3.2080989 |   |
| H | -1.4304650 | -2.5662069 | 1.4418139 |   |
| C | 0.8998157 | -1.8897341 | 2.3648649 |   |
| H | 1.7417111 | -1.2745353 | 2.7030761 |   |
| H | 1.0321135 | -2.136058 | 1.2993646 |   |
| H | 0.8789157 | -2.8228224 | 2.9483685 |   |
| C | 2.6358836 | 3.6784978 | 0.5789466 |   |
| H | 3.4209520 | 4.3226708 | 1.0149442 |   |
| H | 1.6548811 | 4.0704139 | 0.8785242 |   |
| H | 2.7098593 | 3.7254185 | -0.0150269 |   |
| C | 3.0365438 | -1.2995842 | -0.9942220 |   |
| N | 3.8528496 | -2.3491335 | -0.7126106 |   |
| C | 4.1244725 | -2.7847276 | 0.6529532 |   |
| H | 3.4147599 | -2.3274338 | 1.3486137 |   |
| H | 5.1500859 | -2.5308437 | 0.9670746 |   |
| H | 4.0047571 | -3.8784011 | 0.7089199 |   |
| C | 4.5341997 | -3.1119809 | -1.7564464 |   |
| H | 4.4869080 | -2.5753768 | -2.7114895 |   |
| H | 4.0982047 | -4.1167178 | -1.8828291 |   |
| H | 5.5924905 | -3.2278802 | -1.4729883 |   |
| N | 2.3210578 | -1.3423567 | -2.1453153 |   |
| C | 1.7103374 | -2.5748623 | -2.6318702 |   |
| H | 1.8049496 | -3.3714316 | -1.8848218 |   |
| H | 2.1597851 | -2.9105446 | -3.5807995 |   |
| H | 0.6376689 | -2.3896931 | -2.8012358 |   |

ZPE \text{B3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO}(\varepsilon = 35.88): 0.789606

Chem. Pot. \text{(298.15)/B3LYP-D3/def2-SVP(Fe:def2-
TZVP)/COSMO}(\varepsilon = 35.88): 0.720699
[FeIV(O)TMG2dien(MeCN)]2+ (π) pathway

| Element | X (Å) | Y (Å) | Z (Å) |
|---------|-------|-------|-------|
| C       | 1.9542856 | -0.1387651 | -2.8795680 |
| H       | 2.5559027 | 0.7109489 | -2.5361600 |
| H       | 0.8879347 | 0.1008712 | -2.7511856 |
| H       | 2.1438926 | -0.3007085 | -3.9526212 |
| C       | 0.1428601 | 3.0898859 | -1.6977100 |
| C       | -0.2784657 | 4.1508851 | -2.5867207 |
| H       | -0.3409242 | 3.7642723 | -3.6153376 |
| H       | -1.2629737 | 4.5290440 | -2.2719304 |
| H       | 0.4552100 | 4.9711498 | -2.5500118 |
| C       | -1.4575658 | -0.5769421 | -4.4928002 |
| H       | -1.6369244 | 0.7938808 | -4.2398823 |
| H       | -2.1438926 | -1.5161584 | -3.5674297 |
| C       | 0.1428601 | 3.0898859 | -1.6977100 |
| C       | -0.2784657 | 4.1508851 | -2.5867207 |
| H       | -0.3409242 | 3.7642723 | -3.6153376 |
| H       | -1.2629737 | 4.5290440 | -2.2719304 |
| H       | 0.4552100 | 4.9711498 | -2.5500118 |
| C       | -1.4575658 | -0.5769421 | -4.4928002 |
| H       | -1.6369244 | 0.7938808 | -4.2398823 |
| H       | -2.1438926 | -1.5161584 | -3.5674297 |
| C       | 0.1428601 | 3.0898859 | -1.6977100 |
| C       | -0.2784657 | 4.1508851 | -2.5867207 |
| H       | -0.3409242 | 3.7642723 | -3.6153376 |
| H       | -1.2629737 | 4.5290440 | -2.2719304 |
| H       | 0.4552100 | 4.9711498 | -2.5500118 |
| C       | -1.4575658 | -0.5769421 | -4.4928002 |
| H       | -1.6369244 | 0.7938808 | -4.2398823 |
| H       | -2.1438926 | -1.5161584 | -3.5674297 |

[FeIV(O)TMG2dien(MeCN)]2+ (π) pathway

$[\text{Fe}^{IV}(\text{O})\text{TMG}_2\text{dien(MeCN)}]^2+ (\pi)$

$E_{\text{B3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(}\epsilon = 35.88\text{)}}:\ -2678.9124553028 \ (<S^2> 6.05188503)$

$E_{\text{B3LYP-D3/def2-TZVP/COSMO(}\epsilon = 35.88\text{)}}:\ -2680.4812635465 \ (<S^2> 6.05421978)$

$Z_{\text{PEB3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(}\epsilon = 35.88\text{)}}:$
|   |  N   |  C   |  H   |  H   |  C   |  H   |  H   |  C   |  H   |  H   |  C   |  H   |
|---|------|------|------|------|------|------|------|------|------|------|------|------|
| 1 | 1.2464404 | 1.2053385 | 0.2596459 | 1.9996823 | 1.6836601 | 0.8060679 | 2.4036372 | 1.3546790 | 3.2339063 | 3.2339063 | 0.8060679 |
| 2 | 1.0602929 | 2.5493285 | 3.0089333 | -1.4959963 | -3.5597313 | -3.0267022 | -3.7299032 | -4.5398166 | -3.5477239 | -3.5477239 | -3.8554373 |
| 3 | 2.3946654 | 2.4767512 | 0.6256222 | -2.014835 | -0.9863318 | 0.9473821 | -1.972850 | 0.1848567 | -1.3633953 | -1.3633953 | -1.9727850 |
| 4 | 2.3946654 | 2.4767512 | 0.6256222 | -2.014835 | -0.9863318 | 0.9473821 | -1.972850 | 0.1848567 | -1.3633953 | -1.3633953 | -1.9727850 |
| 5 | 2.3946654 | 2.4767512 | 0.6256222 | -2.014835 | -0.9863318 | 0.9473821 | -1.972850 | 0.1848567 | -1.3633953 | -1.3633953 | -1.9727850 |
| 6 | 2.9633907 | 2.9633907 | 0.3127937 | 0.3127937 | 0.3127937 | 0.3127937 | 0.3127937 | 0.3127937 | 0.3127937 | 0.3127937 | 0.3127937 |
| 7 | 0.698061 | 0.698061 | 0.698061 | 0.698061 | 0.698061 | 0.698061 | 0.698061 | 0.698061 | 0.698061 | 0.698061 | 0.698061 |

Chem. Pot. (298.15)/B3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(\(\varepsilon = 35.88\)):

|   |  N   |  C   |  H   |  H   |  C   |  H   |  H   |  C   |  H   |  H   |  C   |  H   |
|---|------|------|------|------|------|------|------|------|------|------|------|------|
| 8 | 1.0602929 | 1.2053385 | 0.2596459 | 1.9996823 | 1.6836601 | 0.8060679 | 2.4036372 | 1.3546790 | 3.2339063 | 3.2339063 | 0.8060679 |
| 9 | 2.3946654 | 2.4767512 | 0.6256222 | -2.014835 | -0.9863318 | 0.9473821 | -1.972850 | 0.1848567 | -1.3633953 | -1.3633953 | -1.9727850 |
| 10 | 2.9633907 | 2.9633907 | 0.3127937 | 0.3127937 | 0.3127937 | 0.3127937 | 0.3127937 | 0.3127937 | 0.3127937 | 0.3127937 | 0.3127937 |
| 11 | 0.698061 | 0.698061 | 0.698061 | 0.698061 | 0.698061 | 0.698061 | 0.698061 | 0.698061 | 0.698061 | 0.698061 | 0.698061 |

0.698061

0.634122
$[\text{Fe}^{\text{IV}}(\text{O})\text{TMG}_2\text{dien(MeCN)}]^{2+}$-CHD-TS ($\pi$)

$E_{\text{B3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO($\epsilon = 35.88$)}}$:

$-2678.8928803855$ ($<S^2> = 6.06219379$)

$E_{\text{B3LYP-D3/def2-TZVPP/COSMO($\epsilon = 35.88$)}}$:

$-2680.4600743158$ ($<S^2> = 6.06368298$)

ZPE$_{\text{B3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO($\epsilon = 35.88$)}}$:

$0.691699$

Chem. Pot. (298.15)/B3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO($\epsilon = 35.88$):

$0.62848$

| Element | $x$-coordinate | $y$-coordinate | $z$-coordinate |
|---------|----------------|----------------|----------------|
| H       | -0.456101      | -0.650079      | 0.5594121      |
| N       | -0.465145      | -0.392044      | 2.1430184      |
| O       | -0.718654      | 0.1106939      | 0.6065010      |
| C       | 1.9240976      | -0.4688210     | -0.0031066     |
| C       | 3.0094800      | -0.4336800     | 0.9836119      |
| H       | 3.9516697      | -0.8108847     | 0.558522       |
| C       | 2.7870424      | -1.0525576     | 1.8694601      |
| C       | 3.1689458      | 1.0240828      | 1.3872765      |
| H       | 3.9568620      | 1.1601226      | 2.1466943      |
| H       | 3.4433633      | 1.6095184      | 0.4991779      |
| N       | 1.8655101      | 1.5356433      | 1.9056099      |
| C       | 1.7472306      | 3.0161171      | 1.7600966      |
| H       | 2.7058590      | 3.5023316      | 2.0073264      |
| H       | 0.9940098      | 3.3583314      | 2.4831006      |
| C       | 1.2736549      | 3.3637050      | 0.3610308      |
| H       | 1.0419656      | 4.4383333      | 0.3030127      |
| H       | 2.0702436      | 3.1646790      | -0.3761904     |
| N       | 0.0871241      | 2.5421373      | 0.1052712      |
| C       | 2.0135075      | -1.3058991     | -1.0503448     |
| N       | 2.5253893      | -2.5571376     | -0.8942390     |
| C       | 2.2998103      | -3.3066397     | 0.3356313      |
| H       | 1.4849638      | -2.8477900     | 0.9090994      |
| H       | 3.2049176      | -3.3518528     | 0.9643040      |
| H       | 2.0078933      | -4.3731413     | 0.0774285      |
| C       | 3.3821842      | -3.2033535     | -1.8845987     |
| H       | 3.6993060      | -2.4794396     | -2.6446782     |
$[\text{Fe}^{IV}(O)\text{TMG}_2\text{dien(MeCN)}]^2-\text{CHD-IC (}\pi)$

$E_{\text{B3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(}\epsilon = 35.88)}$: -2678.9331937799 ($<S^2> 6.08368116$)

$E_{\text{B3LYP-D3/def2-TZVP/COSMO(}\epsilon = 35.88)}$: -2680.5021632039 ($<S^2> 6.08275989$)

$ZPE_{\text{B3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(}\epsilon = 35.88)}$: 0.695919

$\text{Chem. Pot.} (298.15)/\text{B3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(}\epsilon = 35.88)$: 0.631999
|   |   |   |   |
|---|---|---|---|
| N | -0.0863667 | 4.0513836 | -1.3578054 |
| C | 1.2899120 | 4.0836459 | -1.8390223 |
| H | 1.7666976 | 3.1087244 | -1.6989437 |
| H | 1.8871781 | 4.8540023 | -1.3238660 |
| H | 1.2866385 | 4.3114387 | -2.9170445 |
| C | -0.9151914 | 5.1852342 | -1.7592712 |
| H | -1.8431177 | 5.2018083 | -1.1750421 |
| H | -1.1653088 | 5.1517240 | -2.8328250 |
| H | -0.3598337 | 6.1167320 | -1.5635869 |
| N | -1.8677513 | 2.6975486 | -0.7217597 |
| C | -2.5080211 | 2.6230508 | -2.0309200 |
| H | -1.7873142 | 2.8459247 | -2.8257200 |
| H | -3.600351 | 3.3180662 | -2.1060367 |
| C | -2.8725436 | 1.5939113 | -2.1837018 |
| C | -2.6215039 | 2.0824134 | 0.3600525 |
| H | -2.140022 | 2.2905243 | 1.3233199 |
| H | -2.6883973 | 0.9922711 | 0.2200436 |
| H | -3.639842 | 2.5035433 | 0.3712357 |
| C | -1.8983473 | -1.2692715 | 2.3239431 |
| C | -2.8440567 | -1.9970365 | 3.1451795 |
| H | -3.8662653 | -1.8208912 | 2.7804134 |
| H | -2.6191309 | -3.0730556 | 3.1029380 |
| C | -2.7594142 | -1.6493295 | 4.1867012 |
| C | -1.3027690 | -3.5360613 | -1.3057700 |
| C | -2.0402208 | -4.0580134 | -0.1071632 |
| C | -3.3528009 | -3.3709412 | 0.1380746 |
| C | -3.7949188 | -2.3390115 | -0.6494766 |
| C | -3.0396415 | -1.8855390 | -1.7663569 |
| C | -1.8030487 | -2.5195849 | -2.0794453 |
| H | -0.3526936 | -4.0118673 | -1.5647912 |
| H | -3.9643484 | -3.7275411 | 0.9713402 |
| H | -4.7541332 | -1.8618020 | -0.4267850 |
| H | -1.2442583 | -2.1821676 | -2.9561482 |
| H | -0.9067859 | -0.7537071 | -0.9615449 |
| H | -3.4075348 | -1.0654829 | -2.3862694 |
| H | -2.1943320 | -5.1551301 | -2.046380 |
| H | -1.3959347 | -3.9926924 | 0.7995783 |

**[FeIV(O)TMG2dien(MeCN)]²⁺-DHA-RC (π)**

\[ \text{EB3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88):} \]

\[-2985.8471964201 \langle S^2 \rangle \ 6.05268463 \]

\[ \text{EB3LYP-D3/def2-TZVP/COSMO(ε = 35.88):} \]

\[-2987.7376292103 \langle S^2 \rangle \ 6.05485736 \]

\[ \text{ZPE B3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88):} \]

\[ 0.79455 \]
| Element | X      | Y      | Z      |
|---------|--------|--------|--------|
| N       | 2.6609756 | 2.2845744 | 1.1661873 |
| C       | 3.9362432 | 2.0660697 | 0.4240622 |
| H       | 4.7912064 | 2.4317678 | 1.0171167 |
| H       | 3.8797041 | 2.6573810 | -0.5001279 |
| C       | 4.0860824 | 0.6002752 | 0.0645950 |
| H       | 4.9426912 | 0.4677277 | -0.6139656 |
| H       | 4.2975770 | 0.1041490 | 3.3711623 |
| H       | 1.6958124 | 1.4344648 | 0.4240622 |
| C       | -0.0932464 | -0.3044019 | 2.7314751 |
| H       | -0.3817145 | 2.1099761 | 4.1836494 |
| H       | 2.7922116 | 1.3444076 | 0.4240622 |
| H       | 1.591156 | -0.0730091 | 5.5011316 |
| C       | 1.6693997 | -0.7058325 | 2.3354751 |
| H       | 1.0451375 | -3.2859460 | 3.1486843 |
| H       | 0.9696128 | -3.0738688 | 1.3760104 |
| C       | 1.3502778 | -2.1587377 | 2.0432898 |
| H       | 2.1591397 | -1.4817139 | 2.3393122 |
| H       | 1.3795974 | -2.2998669 | 0.9521106 |
| H       | 1.4929665 | -3.1313103 | 2.5379785 |
| C       | 2.2712144 | 3.7106960 | 1.0637213 |
| H       | 3.0423485 | 4.3423955 | 1.5324114 |
| H       | 1.3125763 | 3.8824801 | 1.5673953 |
| H       | 2.1725568 | 3.9913774 | 0.0095138 |
| C       | 2.8397041 | -0.7570464 | -1.5437492 |
| N       | 3.7803599 | -1.7372325 | -1.5794297 |
| C       | 4.3169932 | -2.3514424 | -0.3694005 |
| H       | 3.6983421 | -2.0951329 | 0.4964806 |
| H       | 5.3564136 | -2.0391675 | -0.1769418 |
| H       | 4.3000103 | -3.4462978 | -0.4895959 |
| C       | 4.3297153 | -2.2456839 | -2.8349830 |
| H       | 4.0659219 | -1.5769267 | -3.6629915 |
| H       | 3.9692810 | -3.2627902 | -3.0603696 |
| H       | 5.4275509 | -2.2785631 | -2.7493211 |
| H       | 1.9096327 | -0.7259892 | -2.5221113 |
| C       | 1.3634488 | -1.9477684 | -3.1063524 |
| H       | 1.6643739 | -2.8229082 | -2.5190189 |
| H       | 1.6840177 | -2.0820831 | -4.1521304 |
| H       | 0.2657866 | -1.8782225 | -3.0857892 |
| C       | 1.2572358 | 0.5054733 | -2.9530716 |
| H       | 1.8244125 | 1.3735733 | -2.5987358 |

Chem. Pot. (298.15)/B3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88): 0.727264
|   | X   | Y   | Z   |
|---|-----|-----|-----|
| H | 0.2294297 | 0.5596811 | -2.5656272 |
| H | 1.2234183 | 0.5217979 | -4.0534833 |
| C | -0.3671640 | 3.2624655 | -1.0627316 |
| C | -0.9822954 | 4.3687590 | -1.7655031 |
| H | -1.1874064 | 4.0727692 | -2.8050866 |
| H | -1.9238857 | 4.6470853 | -1.2689196 |
| H | -0.2968116 | 5.2304434 | -1.7559668 |
| C | -2.3858366 | 0.3658038 | -4.4617920 |
| C | -2.7173596 | 1.5823625 | -3.8554566 |
| C | -2.2583067 | -0.7870599 | 3.6788827 |
| C | -2.9072953 | 1.6361811 | -2.4698514 |
| C | -2.4287547 | -0.7347721 | 2.2883633 |
| C | -2.7453461 | 0.4935743 | -1.6758551 |
| C | -2.2707911 | -1.9596109 | 1.4152455 |
| C | -2.8779247 | 0.5416986 | -0.1707571 |
| C | -3.4931913 | -0.7178188 | 0.3964819 |
| C | -3.2076084 | -1.9482176 | 0.2956399 |
| C | -4.3084332 | -0.6937951 | 1.5369248 |
| C | -3.7539424 | -3.1284679 | 2.2270471 |
| C | -4.8321535 | -1.8783909 | 2.0672460 |
| C | -4.5566139 | -3.0999876 | 1.4412228 |
| H | -2.420512 | 0.3103020 | -5.5441313 |
| H | -2.8425517 | 2.4845008 | -4.4608420 |
| H | -2.0254581 | -1.7438747 | 4.1560103 |
| H | -3.1975858 | 2.5781346 | -1.9964499 |
| H | -4.5364570 | 0.2635690 | 2.0150053 |
| H | -3.5355115 | -4.0831243 | -0.1924146 |
| H | -5.4610128 | -1.8460153 | 2.9610112 |
| H | -4.9680193 | -4.0295929 | 1.8435994 |
| H | -1.8565479 | 0.6384497 | 0.2423758 |
| H | -3.4372227 | 1.4336124 | 0.1502340 |
| H | -2.3930397 | -2.8812919 | -2.0043990 |
| H | -1.2334752 | -1.9637288 | -1.0268089 |

**[Fe IV(O)TMG2dien(MeCN)] 2+-DHA-TS (π)**

\[
\text{EB3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88)} = -2985.8205751957 \, (<S^2> 6.06140423) \\
\text{EB3LYP-D3/def2-TZVPP/COSMO(ε = 35.88)} = -2987.7100429454 \, (<S^2> 6.06299607) \\
\text{ZPEB3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88)} = 0.787135
\]

Chem. Pot.(298.15)/B3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88):
|  C     | 4.4048884 | -0.4626168 | 0.0471124 | 0.719866 |
|  H     | 5.1911313 | -0.9676559 | -0.5344713 |
|  H     | 4.4288929 | -0.8898413 | 1.0641408  |
|  N     | 3.0872774 | -0.6256788 | -0.5740001 |
|  C     | 0.4491411 | 0.1990726  | 2.9410350  |
|  N     | -0.3495915| 0.9356091  | 3.7605602  |
|  C     | -0.7254715| 2.3024412  | 3.4177363  |
|  H     | -0.5344951| 2.4890382  | 2.3536610  |
|  H     | -0.1755345| 3.0458735  | 4.0186219  |
|  H     | -1.8022072| 2.4361076  | 3.6080980  |
|  C     | -0.8188490| 0.4575123  | 5.0588996  |
|  H     | -0.2869656| -0.4587302 | 5.3414172  |
|  H     | -1.9037671| 0.2613043  | 5.0580123  |
|  H     | -0.6081903| 1.2288175  | 5.8171287  |
|  N     | 0.2873219 | -1.1382166 | 2.8970244  |
|  C     | -1.0089488| -1.7854408 | 3.0660135  |
|  H     | -1.8105799| -1.0423736 | 3.0927193  |
|  H     | -1.0433099| -2.3919409 | 3.9852671  |
|  H     | -1.1905357| -2.4408870 | 2.2015602  |
|  C     | 1.3612653 | -2.0300037 | 2.4788074  |
|  H     | 2.3270632 | -1.5175175 | 2.5579632  |
|  H     | 1.2068578 | -2.3456868 | 1.4361773  |
|  H     | 1.3667125 | -2.9149689 | 3.1336993  |
|  C     | 3.4701284 | 3.1291368  | 0.2041274  |
|  H     | 4.4307705 | 3.6320082  | 0.4047847  |
|  H     | 2.6704585 | 3.6882480  | 0.7037432  |
|  H     | 3.2818101 | 3.1277310  | -0.8764400 |
|  C     | 2.8559679 | -1.6115739 | -1.4505053 |
|  N     | 3.5018308 | -2.8057755 | -1.3755653 |
|  C     | 3.8616649 | -3.4132226 | -0.0991199 |
|  H     | 3.3377049 | -2.9129278 | 0.7213824  |
|  H     | 4.9476085 | -3.3686175 | 0.0858202  |
|  H     | 3.5547196 | -4.4713136 | -0.1081742 |
|  C     | 3.9116298 | -3.5511270 | -2.5635869 |
|  H     | 3.838920  | -2.9158210 | -3.4544756 |
|  H     | 3.3013349 | -4.4571045 | -2.7130243 |
|  H     | 4.9626200 | -3.8586147 | -2.4413980 |
|  N     | 1.9801109 | -1.4174102 | -2.4631254 |
|  C     | 1.1399650 | -2.4944821 | -2.9771530 |
|  H     | 1.1751346 | -3.3604029 | -2.3056032 |
|  H     | 1.4416855 | -2.8063897 | -3.9900773 |
|  H     | 0.0990626 | -2.1403741 | -3.0251414 |
|  C     | 1.6797912 | -0.0871863 | -2.9744029 |
|  H     | 2.4930685 | 0.6053322  | -2.7260715 |
|  H     | 0.7436554 | 0.3041435  | -2.5477423 |
|  H     | 1.5755257 | -0.1382617 | -4.0687737 |
|  C     | 0.2835764 | 3.1788543  | -0.8921997 |
|  C     | -0.2644237| 4.4543945  | -1.3019256 |
[FeIV(O)TMG2dien(MeCN)]2+-DHA-IC (π)

EB3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88):
-2985.8538807335 (<S^2> 6.07905533)

EB3LYP-D3/def2-TZVPP/COSMO(ε = 35.88):
-2987.7452109988 (<S^2> 6.07861123)

ZPEB3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88):
0.791536

Chem. Pot.(298.15)/B3LYP-D3/def2-SVP(Fe:def2-
TZVP)/COSMO(ε = 35.88):
0.723438
|    |    |    |    |
|----|----|----|----|
| C  | -0.0157465 | 0.0459360 | 2.7376556 |
| N  | -1.0671420 | 0.6110744 | 3.3888220 |
| C  | -1.6805349 | 1.8402588 | 2.8993167 |
| H  | -1.3926651 | 2.0110971 | 1.8543592 |
| H  | -1.3918989 | 2.7181361 | 3.5009679 |
| H  | -2.7764838 | 1.7382405 | 2.9485181 |
| C  | -1.6227568 | 0.0687794 | 4.6262614 |
| H  | -0.9413076 | -0.6776224 | 5.0516712 |
| H  | -2.6114981 | -0.3927652 | 4.4670961 |
| H  | -1.7370789 | 0.8893925 | 5.3521972 |
| N  | 0.1231294 | -1.2947255 | 2.7600132 |
| C  | -1.0215066 | -2.1995854 | 2.7497169 |
| H  | -1.9432351 | -1.6514477 | 2.5262105 |
| H  | -1.1366048 | -2.7334783 | 3.7065807 |
| C  | 1.4144664 | -1.9325043 | 2.5365605 |
| H  | 2.2255110 | -1.2277271 | 2.7546336 |
| H  | 1.4936583 | -2.2604230 | 1.4893098 |
| H  | 1.5036650 | -2.8031645 | 3.2038529 |
| C  | 2.5974754 | 3.4300140 | 0.1119018 |
| H  | 3.4216295 | 4.1250662 | 0.3409634 |
| H  | 1.6670228 | 3.8419302 | 0.5180060 |
| H  | 2.4982815 | 3.3298116 | -0.9759981 |
| C  | 3.0811489 | -1.3555167 | -1.3119891 |
| N  | 3.9274710 | -2.4056891 | -1.1436257 |
| C  | 4.3178495 | -2.8869010 | 0.1769311 |
| H  | 3.6692152 | -2.4577397 | 0.9470158 |
| H  | 5.3666563 | -2.6398060 | 0.4100326 |
| H  | 4.2052394 | -3.9825157 | 0.2056670 |
| C  | 4.5187681 | -3.1219863 | -2.2713064 |
| H  | 4.3736625 | -2.5548917 | -3.1986334 |
| H  | 4.0854270 | -4.1287853 | -2.3914354 |
| H  | 5.6006125 | -3.2307657 | -2.0927082 |
| N  | 2.2647524 | -1.3579933 | -2.3917750 |
| C  | 1.6083573 | -2.5760813 | -2.8547061 |
| H  | 1.8027293 | -3.4039844 | -2.1634088 |
| H  | 1.9392161 | -2.8600534 | -3.8667277 |
| H  | 0.5204719 | -2.4029091 | -2.8784855 |
| C  | 1.7562804 | -0.1243800 | -2.9729603 |
| H  | 2.4149847 | 0.7148668 | -2.7177052 |
| H  | 0.7404031 | 0.0965192 | -2.6088071 |
| H  | 1.7251059 | -0.2311417 | -4.0680723 |
| C  | -0.5645143 | 2.7779888 | -1.0104828 |
| C  | -1.4465266 | 3.8556918 | -1.4013532 |
| H  | -1.3207139 | 4.0629109 | -2.4738698 |
| H  | -2.4915220 | 3.5677784 | -1.2140016 |
| H  | -1.1987855 | 4.7566992 | -0.8190733 |
| C  | -3.4567860 | 2.3635630 | -3.7401564 |
\[\text{[Fe}^{IV}(O)\text{TMG}_3\text{tren}]^{2+} (\sigma) \text{ pathway}\]

| C | -4.4842067 | 2.8066678 | -2.8906248 |
| C | -2.7083626 | 1.2419865 | -3.3987498 |
| C | -4.7366973 | 2.1301789 | -1.6883912 |
| C | -2.9754891 | 0.5235634 | -2.2023831 |
| C | -3.9952819 | 1.0023369 | -1.3254425 |
| C | -2.3026765 | -0.7019333 | -1.9047648 |
| C | -4.2199107 | 0.3067797 | -0.0020999 |

\[
\text{ZPE}_{\text{B3LYP-D3/def2-SVP(Fe:edef2-TZVP)/COSMO(}\epsilon = 35.88\text{)}}: \quad 0.726585
\]

\[
\text{Chem. Pot.}_{(298.15)/\text{B3LYP-D3/def2-SVP(Fe:edef2-TZVP)/COSMO(}\epsilon = 35.88\text{)}}: \quad 0.666116 (\sigma = 3)
\]
| Element | X  | Y  | Z  |
|---------|----|----|----|
| H       | 0.4616585 | 9.0832956 | 5.4569889 |
| C       | 3.2063028 | 9.7936291 | 5.7422168 |
| H       | 3.9949763 | 9.7150477 | 6.4999558 |
| H       | 2.4820024 | 10.5569216 | 6.0666336 |
| H       | 3.6517135 | 10.1262407 | 4.7898058 |
| C       | 5.210863 | 7.6508296 | 5.0666336 |
| H       | 4.6058512 | 7.9760438 | 4.2118133 |
| H       | 5.8262911 | 6.7946865 | 4.7450232 |
| H       | 5.8818805 | 8.4726970 | 5.3669380 |
| C       | 5.0192543 | 6.4806052 | 7.2236609 |
| H       | 4.3173389 | 6.3202296 | 8.0489947 |
| H       | 5.8790611 | 7.0655155 | 7.5839464 |
| H       | 5.3710155 | 5.5019923 | 6.8637199 |

**Fe**
-0.9133655 -0.0077933 0.7188512
O 0.1830448 -0.0062660 -0.4843244
N -2.3449025 -0.0309893 2.3012602
N 0.3312123 0.5019202 2.2080771
N -1.4771641 -1.9279584 0.7188512
N -2.1598778 1.3952061 -0.0291854
N 2.3330557 1.6052280 2.8096722
N 2.4010030 -0.3028267 1.4840447
N -0.8459804 -4.0893136 -0.1968571
N -1.0518557 -2.3487038 -1.7210590
N -3.0023495 2.4813976 -1.9570207
N -0.7470982 2.6275372 -1.4237537
C -1.5818271 0.0181242 3.5790207
H -1.2254411 -0.9956663 3.8038158
H -2.2407985 0.3404920 4.4022554
C -0.3849383 0.9391901 3.4126525
H -0.7229781 1.9858104 3.3329528
H 0.2582823 0.8794109 4.3045115
C 1.6667455 0.6106001 2.1595103
C 1.7905601 2.9507771 2.9520876
H 0.9373783 3.0934750 2.2823580
H 2.5683778 3.6811756 2.6768514
H 1.4723875 3.1573985 3.9874708
C 3.6290470 1.3880079 3.4487964
H 3.8341431 0.3145988 3.5387344
H 3.5986333 1.8204990 4.4617477
H 4.4504771 1.8689296 2.8922650
C 3.6364591 0.0432336 0.7894339
H 3.7200247 1.1295440 0.6704311
H 3.6096338 -0.4082261 -0.2114224
H 4.5277177 -0.3354161 1.3166458
C 1.9566542 -1.6763652 1.3112437
H 1.1362378 -1.8818240 2.0081450
H 2.7938959 -2.3581109 1.5260795

**[Fe IV(O)TMG3tren]2+-CHD-RC (σ)**

\[
\begin{align*}
\text{E}_{\text{B3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88)}} & : -2946.5429520195 \quad (<S^2> \ 6.05142420) \\
\text{ZPE}_{\text{B3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88)}} & : 0.850417 \\
\text{Chem. Pot. (298.15)/B3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88)}} & : 0.781968
\end{align*}
\]
|   | X    | Y    | Z    | X    | Y    | Z    |
|---|------|------|------|------|------|------|
| H | 1.5981370 | -1.8496465 | 0.2853121 | H | -3.1241699 | -1.2936177 | 2.1673350 |
| C | -3.8976648 | -1.1381312 | 1.4041346 | H | -3.6260616 | -1.5321918 | 3.1196317 |
| C | -2.2007170 | -2.4134111 | 1.7153193 | H | -1.5136404 | -2.6860413 | 2.5337335 |
| H | -2.7916199 | -3.3129966 | 1.4817502 | C | -1.1194237 | -2.7768738 | -0.4360014 |
| C | -0.2182123 | -4.5575396 | 1.0330257 | H | 0.2020532 | -3.7194285 | 1.5953184 |
| C | 0.0204877 | -3.8080618 | -2.6427903 | H | 0.7473960 | -3.3785641 | -2.1059096 |
| C | -2.3318678 | -1.5995557 | -3.1977935 | H | -0.4353988 | -3.4337152 | -3.4506186 |
| C | -1.9102654 | -1.2907706 | -2.2277440 | H | -2.7264256 | -1.1169777 | -1.5188896 |
| C | -2.3318678 | -1.5995557 | -3.1977935 | H | -0.2869106 | -5.5448544 | -1.6544557 |
| H | -1.3485816 | -0.3534773 | -2.3567255 | C | 0.2340028 | 1.1730397 | 2.1293471 |
| C | 2.6662577 | 2.0371908 | 2.5402340 | H | -4.142609 | 1.0534494 | 2.6955279 |
| C | 3.4604628 | 1.4060124 | 0.6508757 | H | -4.1316644 | 0.6230138 | 0.2610541 |
| C | -3.9779925 | 2.3679232 | 0.5101433 | H | 2.2414948 | 4.4746283 | -2.1633349 |
| C | -1.9778118 | 2.1428507 | -1.1230351 | H | -0.776909 | 4.2023006 | -2.4707752 |
| C | -4.1140644 | 1.5872961 | -2.2572724 | H | -3.8959371 | 0.5707106 | -1.9185770 |
| C | -4.2635364 | 1.5577975 | -3.3487226 | H | 5.05226 | 1.9277545 | -1.786846 |
| C | 3.0673027 | 3.7859894 | -2.6125837 | H | 2.3419498 | 4.4746283 | -2.1633349 |
| H | -4.0776909 | 4.2023006 | -2.4707752 | H | -2.8735957 | 3.7129191 | -3.6958185 |
| C | -0.2698684 | 2.7222535 | -2.7976459 | H | -0.9783913 | 2.2460124 | -3.4852797 |
| H | 0.6881406 | 2.1866250 | -2.8756399 | H | -0.1125264 | 3.7684584 | -3.1079153 |
| C | 0.2254229 | 2.9697214 | -0.3979390 | H | -0.2727919 | 2.9926479 | 0.5771910 |
| H | 0.6436127 | 3.9663165 | -0.6140171 | H | 1.0406357 | 2.2318886 | -0.3581371 |
| C | 4.7648208 | -1.2127639 | -2.5561386 |
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | 5.5887033 | 0.0189556 | -2.2846540 |
| C    | 4.7921859 | 1.2939838 | -2.3812571 |
| C    | 3.4768371 | 1.3244624 | -2.6333278 |
| C    | 2.6386930 | 0.0901098 | -2.8437781 |
| C    | 3.4488206 | -1.1796094 | -2.8082879 |
| H    | 5.2894317 | -2.1746454 | -2.5359709 |
| H    | 5.3376527 | 2.2319659 | -2.2279147 |
| H    | 2.9635946 | 2.2912669 | -2.6832898 |
| H    | 2.9125575 | -2.1168060 | -2.9919837 |
| H    | 6.0566796 | -0.0563298 | -1.2814788 |
| H    | 6.4523725 | 0.0573998 | -2.9779840 |
| Fe   | 2.6034545 | 4.4018110 | 6.2897386 |
| O    | 3.9355685 | 4.3882740 | 5.2258933 |
| N    | 0.8329856 | 4.3412420 | 7.7514161 |
| N    | 3.4485246 | 3.4455948 | 7.8869959 |
| N    | 1.2398864 | 3.3491648 | 5.1818485 |
| N    | 2.2009444 | 6.4181251 | 6.4853617 |
| N    | 5.4736552 | 2.8274200 | 8.9451081 |
| N    | 4.9269087 | 1.9657793 | 6.8570663 |
| N    | 0.8689160 | 1.8924682 | 3.3475614 |
| N    | 1.7947713 | 3.9964401 | 3.0108092 |
| N    | 2.3983660 | 8.6160477 | 5.6178658 |
| N    | 4.2971041 | 7.3900693 | 6.1564474 |
| C    | 1.2511029 | 3.4805659 | 8.8791782 |
| H    | 1.0785076 | 2.4322161 | 8.5990977 |
| H    | 0.6460953 | 3.6922540 | 9.7784787 |
| C    | 2.7373736 | 3.6737813 | 9.1484997 |
| H    | 2.9213809 | 4.6889395 | 9.5408596 |
| H    | 3.0634945 | 2.9672269 | 9.9275500 |
| C    | 4.6024123 | 2.7708142 | 7.8968294 |
| C    | 5.6608924 | 4.0342312 | 9.7399340 |
| H    | 5.2101434 | 4.8952571 | 9.2384912 |
| H    | 6.7400851 | 4.2273595 | 9.8524288 |
| H    | 5.2204395 | 3.9367391 | 10.7463381 |
| C    | 6.2489624 | 1.6688846 | 9.3808206 |
| H    | 5.8588712 | 0.7540621 | 8.9188551 |
| H    | 6.1554736 | 1.5713480 | 10.4746067 |
| H    | 7.3189922 | 1.7705133 | 9.1338596 |
| C    | 6.2975479 | 1.7905921 | 6.3947065 |
| H    | 6.9559351 | 2.5421841 | 6.8046106 |
| H    | 6.3091880 | 1.9347643 | 5.3056466 |
| H    | 6.6848657 | 0.7828068 | 6.6183661 |
| C    | 3.9131365 | 1.3495173 | 6.0179579 |
| H    | 2.9526250 | 1.3505332 | 6.5450011 |
| H    | 4.2047293 | 0.3090897 | 5.8039654 |

[FeIV(O)TMGtren]2+-CHD-TS (σ)

| Term | Value |
|------|-------|
| $\Delta H$ | -2946.5236426768 (<S^2> 6.50946640) |
| $\Delta E$ | -2948.3775944569 (<S^2> 6.50015134) |
| ZPE | 0.843587 |
| Chem. Pot. | 0.775481 |
| H  | 3.7992050 | 1.8984162 | 5.0708812 |
|----|-----------|-----------|-----------|
| C  | -0.3063874 | 3.7780464 | 6.9946180 |
| H  | -0.7891018 | 4.5918884 | 6.4368228 |
| H  | -1.0591603 | 3.3503584 | 7.6803280 |
| C  | 0.1893588  | 2.7363176 | 6.0011132 |
| H  | 0.5657558  | 1.8519167 | 6.5437337 |
| H  | -0.6547057 | 2.3944981 | 5.3822741 |
| C  | 1.3082601  | 3.0717266 | 3.8773288 |
| C  | 0.9914411  | 0.6163535 | 4.0407867 |
| H  | 1.6459412  | 0.7107478 | 4.9104660 |
| H  | 1.4368947  | -0.1236847| 3.3599985 |
| H  | 0.0114485  | 0.2344695 | 4.3722634 |
| C  | 0.2046701  | 1.8253890 | 2.0481782 |
| H  | -0.0822080 | 2.8294954 | 1.7136520 |
| H  | -0.7106745 | 1.2200231 | 2.1501689 |
| H  | 0.8430815  | 1.3567331 | 1.2805092 |
| C  | 2.5711267  | 3.6338514 | 1.8323828 |
| H  | 2.8836936  | 2.5838776 | 1.8859797 |
| H  | 3.4722686  | 4.2655867 | 1.7989744 |
| H  | 2.0087114  | 3.7951965 | 0.8977894 |
| C  | 1.6925228  | 5.4220114 | 3.2717968 |
| H  | 0.9298599  | 5.952491 | 4.0385372 |
| H  | 1.3970248  | 5.9401322 | 2.3456810 |
| H  | 2.6505327  | 5.8301202 | 3.6290238 |
| C  | 0.5975884  | 5.7388076 | 8.1707129 |
| H  | 1.2995849  | 5.9814450 | 8.9801666 |
| H  | -0.4261439 | 5.8626065 | 8.5668309 |
| C  | 0.8544365  | 6.6814597 | 7.0055933 |
| H  | 0.0861774  | 6.5324506 | 6.2274423 |
| H  | 0.7558441  | 7.7210661 | 7.3539037 |
| C  | 2.9433060  | 7.4502526 | 6.0801622 |
| C  | 1.1965833  | 8.6603157 | 4.7953145 |
| H  | 0.9305243  | 7.6597247 | 4.4450902 |
| H  | 1.3886846  | 9.2910205 | 3.9116916 |
| H  | 0.3386761  | 9.0854760 | 5.3427367 |
| C  | 2.9647039  | 9.9205538 | 5.9511844 |
| H  | 3.7068451  | 9.8216509 | 6.7524096 |
| H  | 2.1548575  | 10.5768629| 6.3099385 |
| H  | 3.4369959  | 10.4028432| 5.0788090 |
| C  | 5.1573892  | 8.0546841 | 5.1849058 |
| H  | 4.5700523  | 8.3945554 | 4.3238284 |
| H  | 5.9103788  | 7.3415823 | 4.8207094 |
| H  | 5.6873572  | 8.9167041 | 5.6230071 |
| C  | 4.9721714  | 6.5974903 | 7.1728519 |
| H  | 4.2688752  | 6.3793804 | 7.9852083 |
| H  | 5.8201010  | 7.1731273 | 7.5765367 |
| H  | 5.3360348  | 5.6434846 | 6.7649295 |
| C  | 7.2741475  | 2.5730138 | 2.9168805 |
|        |        |        |        |        |
|--------|--------|--------|--------|--------|
|        |        |        |        |        |
| C      | 8.4455687 | 2.8011654 | 3.8270367 |        |
| C      | 8.3265904 | 4.0480566 | 4.6523472 |        |
| C      | 7.2532123 | 4.8624243 | 4.5975103 |        |
| C      | 6.0745226 | 4.5831137 | 3.7488023 |        |
| C      | 6.2076365 | 3.3984540 | 2.8742991 |        |
| H      | 7.3166048 | 1.7031559 | 2.2533043 |        |
| H      | 9.1670152 | 4.2974507 | 5.3083284 |        |
| H      | 7.2424968 | 5.7657773 | 5.2134637 |        |
| H      | 5.3955658 | 3.1880479 | 2.1735951 |        |
| H      | 5.6765691 | 5.4730746 | 3.2297695 |        |
| H      | 5.0841989 | 4.4153898 | 4.4879629 |        |
| H      | 8.5928961 | 1.9208870 | 4.4879629 |        |
| H      | 9.3835987 | 2.8285436 | 3.2353089 |        |

**Fe**

|        |        |        |        |        |
|--------|--------|--------|--------|--------|
|        | -0.7990526 | -0.0044602 | 0.5325437 |        |
| O      | 0.3974778  | 0.0141229 | -0.8413424 |        |
| N      | -2.3462975 | -0.0382943 | 2.2882572 |        |
| N      | 0.3709819  | 0.5481969 | 2.1339950 |        |
| N      | -1.4139584 | -1.9622216 | 0.5010343 |        |
| N      | -2.1785248 | 1.3734919 | -0.1083423 |        |
| N      | 2.3922544  | 1.5955055 | 2.7927576 |        |
| N      | 2.4322012  | -0.3394482 | 1.5029401 |        |
| N      | -0.8249427 | -4.1460702 | -2.198070 |        |
| N      | -1.1187806 | -2.4365285 | -1.7627350 |        |
| N      | -3.0308013 | 2.5125041 | -2.0062463 |        |
| N      | -0.8123998 | 2.7782291 | -1.3743866 |        |
| C      | -1.5599527 | 0.1113781 | 3.5282681 |        |
| H      | -1.1700180 | -0.8752836 | 3.8144158 |        |
| H      | -2.1933693 | 0.4739911 | 4.3578373 |        |
| C      | -0.3820058 | 1.0481508 | 3.2883883 |        |
| H      | -0.7489153 | 2.0747509 | 3.1174455 |        |
| H      | 0.2466019  | 1.080890 | 4.1918522 |        |
| C      | 1.7054679  | 0.6143680 | 2.1428618 |        |
| C      | 1.8950904  | 2.9614887 | 2.9037767 |        |
| H      | 1.0603195  | 3.1231522 | 2.2163315 |        |
| H      | 2.7034583  | 3.6596445 | 2.6327167 |        |
| H      | 1.5638792  | 3.1953246 | 3.9291176 |        |
| C      | 3.6646752  | 1.3423964 | 3.4650816 |        |
| H      | 3.8321655  | 0.2639619 | 3.5713254 |        |
| H      | 3.6251968  | 1.7898747 | 4.4725345 |        |
| H      | 4.5146187  | 1.7898747 | 2.9234823 |        |
| C      | 3.6904750  | -0.0487080 | 0.8262137 |        |
| H      | 3.8201596  | 1.0324839 | 0.6999914 |        |
| H      | 3.6634382  | -0.5099225 | -0.1718145 |        |
| H      | 4.5594472  | -0.4577193 | 1.3678530 |        |
| C      | 1.9553146  | -1.7070682 | 1.3709213 |        |
| H      | 1.1287535  | -1.8724373 | 2.0704423 |        |
| H      | 2.7748023  | -2.4035305 | 1.6093014 |        |

**[Fe^{IV}(O)TMG^3tren]^2+ - CHD-IC (σ)**

\[ E\text{B3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88):} -2946.5636030582 \ (<S^2> 7.04129636) \]

\[ E\text{B3LYP-D3/def2-TZVPP/COSMO(ε = 35.88):} -2948.4186051997 \ (<S^2> 7.03867054) \]

\[ Z\text{PEB3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88): 0.845622} \]

\[ \text{Chem. Pot. (298.15)/B3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88): 0.776052} \]
| Atom | x      | y      | z      |
|------|--------|--------|--------|
| C    | 1.5983941 | -1.9112099 | 0.3492400 |
| C    | -3.0332891 | -1.3426245 | 2.1937245 |
| H    | -3.8369588 | -1.2578163 | 1.4494015 |
| H    | -3.4990134 | -1.6146851 | 3.1579606 |
| C    | -2.0574908 | -2.4196830 | 1.7351774 |
| H    | -1.3167563 | -2.6108825 | 2.5306234 |
| H    | -2.6022661 | -3.3634888 | 1.5758921 |
| C    | -1.1143886 | -2.8363701 | -0.4640761 |
| C    | -0.1374008 | -4.5991925 | 0.9830467 |
| H    | 0.2884353  | -3.7531271 | 1.5275348 |
| H    | 0.6879470  | -5.2697721 | 0.6936625 |
| H    | -0.8133029 | -5.1521611 | 1.6561388 |
| C    | -1.1928641 | -5.2083998 | -1.1530615 |
| H    | -1.9152866 | -4.8355981 | -1.8889314 |
| H    | -1.6621410 | -6.0291079 | -0.5869382 |
| H    | -0.3145130 | -5.6139519 | -1.6827028 |
| C    | -0.1051788 | -2.8750655 | -2.7128996 |
| H    | 0.6747645  | -3.4536988 | -2.2032831 |
| H    | 0.3638230  | -1.9832288 | -3.1593940 |
| H    | -0.5355795 | -3.4861039 | -3.5236170 |
| C    | -1.9973880 | -1.3807497 | -2.2376199 |
| H    | -2.8022987 | -1.2238916 | -1.5106741 |
| H    | -2.4381899 | -1.6820794 | -3.2014737 |
| H    | -1.4450104 | -0.4378582 | -2.3718075 |
| C    | -3.2521570 | 1.1026600  | 2.0464260  |
| H    | -2.7765398 | 2.0122433  | 2.4382957  |
| H    | -4.2086588 | 0.9685844  | 2.5829578  |
| C    | -3.4840258 | 1.2811466  | 0.5512620  |
| H    | -4.0737623 | 0.4336040  | 0.1623602  |
| H    | -4.0825898 | 2.1896113  | 0.3805388  |
| C    | -2.0188270 | 2.1942873  | -1.1500963 |
| C    | -4.0868148 | 1.5755886  | -2.3694149 |
| H    | -3.8297254 | 0.5620308  | -2.0511577 |
| H    | -4.2003136 | 1.5715002  | -3.4656165 |
| H    | -5.0548002 | 1.8560726  | -1.9221157 |
| C    | -3.1404181 | 3.8327542  | -2.6225928 |
| H    | -2.4706937 | 4.5431699  | -2.1235276 |
| H    | -4.1765417 | 4.1907435  | -2.5095655 |
| H    | -2.9011342 | 3.8060103  | -3.6989037 |
| C    | -0.2683705 | 2.9398285  | -2.7158190 |
| H    | -0.9169324 | 2.4562916  | -3.4556124 |
| H    | 0.7163838  | 2.4485136  | -2.7569255 |
| H    | -0.1411378 | 4.0016249  | -2.9840350 |
| C    | 0.0958562  | 3.1054357  | -0.2889774 |
| H    | -0.4506518 | 3.0913575  | 0.6609612  |
| H    | 0.5093592  | 4.1137614  | -0.4514204 |
| H    | 0.9254220  | 2.3840462  | -0.2297242 |
| C    | 4.6960928  | -1.2059539 | -2.5163037 |
\[
\text{Table 1. Geometric parameters of } [\text{Fe}^{IV}(\text{O})\text{TMG}_{3}\text{tren}]^{2+}-\text{DHA-RC } (\sigma) \\
\]

| At.  | X     | Y     | Z     |
|------|-------|-------|-------|
| C    | 5.5360931 | -0.0073289 | -2.1809186 |
| C    | 4.7924062 | 1.2941769 | -2.2627926 |
| C    | 3.4783815 | 1.3565986 | -2.6492580 |
| C    | 2.7445292 | 0.1812128 | -2.9778083 |
| C    | 3.3834565 | -1.0896844 | -2.8947437 |
| H    | 5.1670915 | -2.1916702 | -2.4574962 |
| H    | 5.3365079 | 2.2093041 | -2.0110636 |
| H    | 2.9842239 | 2.3312201 | -2.7076322 |
| H    | 2.8121088 | -1.9901714 | -3.1376846 |
| H    | 1.7077376 | 0.2522956 | -3.3129288 |
| H    | 1.3379334 | 0.0820455 | -1.0500092 |
| H    | 5.9922349 | -0.1271225 | -1.1729964 |
| H    | 6.4313409 | 0.0252218 | -2.8424235 |
| Fe   | 0.1565893 | -0.1381174 | 1.8265869 |
| O    | 0.1418367 | -0.0613245 | 0.2268001 |
| N    | 0.7386348 | -0.2267944 | 3.9373856 |
| N    | 0.6234681 | -2.1028349 | 1.9416610 |
| N    | 1.6762080 | 1.2000614 | 1.8972868 |
| N    | 1.6753600 | 0.4127600 | 1.8972868 |
| N    | 0.4462782 | -4.2771957 | 1.0203246 |
| N    | 1.4401318 | -2.5696810 | 0.1974666 |
| N    | 3.4101584 | 2.3211415 | 0.7666022 |
| N    | 1.1998052 | 2.6675083 | 0.1385724 |
| N    | 3.7130170 | 1.5077645 | 1.951704 |
| N    | 3.0831398 | -0.3854900 | 0.7665612 |
| C    | -1.1813700 | -1.5370584 | 4.2138069 |
| H    | -2.2502241 | -1.4453741 | 3.9813466 |
| H    | -1.0846367 | -1.7901587 | 5.2826335 |
| C    | -0.5716320 | -2.6020259 | 3.3208402 |
| C    | 0.4636451 | -2.8110782 | 3.6387721 |
| H    | -1.1345222 | -3.5419785 | 3.4294839 |
| C    | -0.8184618 | -2.9667127 | 0.9380958 |
| C    | 0.7646366 | -4.7225754 | 1.6986080 |
| H    | 1.4109137 | -3.8739547 | 1.9369405 |
| H    | 1.3223560 | -5.3976240 | 1.0291901 |
| H    | 0.5356278 | -5.2691074 | 2.6284874 |
| C    | -1.2529915 | -5.3475647 | 0.4385062 |
| H    | -2.2469206 | -4.9720810 | 0.1676260 |
| H    | -1.3723315 | -6.1447355 | 1.1895529 |
| H    | -0.7764184 | -5.7855083 | -0.4544101 |
| C    | -1.0715176 | -3.0940750 | -1.5074433 |
| H    | -0.1438753 | -3.6735037 | -1.4442757 |
| H    | -0.8921531 | -2.2500943 | -2.1872932 |
| H    | -1.8654848 | -3.7265347 | -1.9371541 |
| C    | -2.4421224 | -1.5169131 | -0.2093933 |
| H    | -2.7628128 | -1.3111670 | 0.8174198 |
| H    | -3.3105662 | -1.8506241 | -0.7999428 |

\[
\text{[Fe}^{IV}(\text{O})\text{TMG}_{3}\text{tren}]^{2+}-\text{DHA-RC } (\sigma) \\
\]

\[
\text{E}_{\text{B3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO}(\varepsilon = 35.88)}: \\
-3253.4702932659 \text{ (<S}^2> 6.05235696) \\
\text{E}_{\text{B3LYP-D3/def2-TZVP/COSMO}(\varepsilon = 35.88)}: \\
-3255.6479784981 \text{ (<S}^2> 6.05471527) \\
\text{ZPE}_{\text{B3LYP-D3/def2-SVP(Fe:def2-TZVP/COSMO}(\varepsilon = 35.88)}: \\
0.946335 \\
\text{Chem. Pot. (298.15)/B3LYP-D3/def2-SVP(Fe:def2-TZVP/COSMO}(\varepsilon = 35.88): \\
0.87412 \text{ kcal/mol} 
\]
|   | X    | Y    | Z    |
|---|------|------|------|
| H | -2.0386441 | -0.5885994 | -0.6418501 |
| C | -1.4324860 | 0.9094879 | 4.2711631 |
| H | -0.8214380 | 1.8167213 | 4.3655709 |
| H | -1.9288698 | 0.7285070 | 5.2390653 |
| C | -2.4315177 | 1.1013609 | 3.1445336 |
| H | -3.1427302 | 0.2587473 | 3.1205896 |
| H | -3.0222829 | 2.0126328 | 3.3247149 |
| C | -2.0873879 | 2.0375400 | 1.0214503 |
| C | -4.4594306 | 1.3274975 | 0.9578624 |
| H | -4.0311466 | 0.3231300 | 1.0214503 |
| H | -5.1411808 | 1.3552556 | 0.9024239 |
| H | -5.0490811 | 1.5232066 | 1.8689245 |
| C | -3.8818423 | 3.6620246 | 0.4274579 |
| H | -3.0801707 | 4.3962271 | 0.5709356 |
| H | -4.7132392 | 3.9230764 | 1.1019192 |
| C | -4.2476680 | 3.722512 | -0.6109680 |
| C | -1.5091563 | 3.0241416 | -1.2417664 |
| H | -2.3848340 | 2.4667072 | -1.5952959 |
| H | -0.6519832 | 2.7565054 | -1.8715127 |
| H | -1.6971060 | 4.1033183 | -1.3618242 |
| C | 0.1573567 | 2.9647058 | 0.5686912 |
| H | 0.2211309 | 2.8710082 | 1.6582414 |
| C | 0.4105824 | 3.9966120 | 0.2787529 |
| H | 0.8782766 | 2.2688339 | 0.1141284 |
| C | 0.7846728 | -0.1055606 | 4.6219545 |
| H | 1.2607048 | -1.0947992 | 4.6293319 |
| H | 0.6404416 | 0.2125096 | 5.6678231 |
| C | 1.6664634 | 0.8603713 | 3.8490279 |
| H | 1.2779043 | 1.883276 | 3.9451122 |
| H | 2.6803856 | 0.8601460 | 4.2779187 |
| C | 2.7993576 | 0.5220101 | 1.7310347 |
| C | 3.3324859 | 2.8562028 | 2.3623746 |
| H | 2.2591089 | 3.0108155 | 2.229501 |
| H | 3.8685283 | 3.5831775 | 1.7311269 |
| C | 3.5889603 | 3.0571093 | 3.4157633 |
| H | 5.1526667 | 1.2731840 | 1.8715382 |
| H | 5.3616564 | 0.1954005 | 1.8409890 |
| H | 5.6328847 | 1.6904802 | 2.7703616 |
| H | 5.5980969 | 1.7536864 | 0.9857121 |
| C | 3.8205572 | -0.0412347 | -0.4427788 |
| H | 3.8417256 | 1.0461869 | -0.5854479 |
| H | 3.3055332 | -0.4929542 | -1.3022096 |
| H | 4.8541167 | -0.4237317 | -0.4243355 |
| C | 2.6016414 | -1.7561490 | 0.8282129 |
| H | 2.2466852 | -1.9688807 | 1.8416985 |
| H | 3.4280521 | -2.4418594 | 0.5827635 |
| H | 1.7710844 | -1.9149663 | 0.1240563 |
| C | -0.0978718 | -3.1667485 | -4.9766905 |
| C  | 1.1731809 | -3.1267792 | -4.3914114 |
| C  | -0.9123937 | -2.0299779 | -4.9470606 |
| C  | 1.6228292 | -1.9482713 | -3.7871218 |
| C  | -0.4745187 | -0.8518686 | -4.3256680 |
| C  | 0.8083297 | -0.8079441 | -3.7453788 |
| C  | -1.3617396 | 0.3692294  | -4.2177748 |
| C  | 1.2558389 | 0.4641010  | -3.0609718 |
| C  | 0.7026468 | 1.7097361  | -3.7150733 |
| C  | -0.5840762 | 1.6649625  | -4.2851804 |
| C  | 1.4181003 | 2.9158518  | -3.7179290 |
| C  | -1.1317593 | 2.8270323  | -4.8456767 |
| C  | 0.8613524 | 4.0750746  | -4.2679953 |
| C  | -0.4182367 | 4.0303292  | -4.8339449 |
| H  | -0.4540688 | -4.0818503 | -5.4574257 |
| H  | 1.8167178  | -4.0104388 | -4.4111596 |
| H  | -1.9072887 | -2.0597997 | -5.4014827 |
| H  | 2.6209148  | -1.9139621 | -3.3396776 |
| H  | 2.4187354  | 2.9482763  | -3.2760075 |
| H  | -2.1319826 | 2.7903533  | -5.2878872 |
| H  | 1.4267232  | 5.0108899  | -4.2581976 |
| H  | -0.8593496 | 4.9311669  | -5.2691694 |
| H  | 0.9084531  | 0.4305475  | -2.0070546 |
| H  | 2.3537825  | 0.5139504  | -3.0203986 |
| H  | -2.1570204 | 0.3469902  | -4.9782188 |
| H  | -1.8820770 | 0.3315978  | -3.2376354 |

| Fe | -0.3796608 | 0.0235024 | 1.7190311 |
| O  | -0.0226506 | -0.0187595 | 0.0529880 |
| N  | -0.8343958 | 0.0459205  | 3.9630135 |
| N  | 0.1980091  | -1.8707445 | 2.2318231 |
| N  | -2.4063868 | 0.3555470  | 1.6890283 |
| N  | 0.8269976  | 1.5865924  | 2.3591795 |
| N  | 1.4122343  | -3.8227552 | 1.6560787 |
| N  | -0.3651072 | -3.1155416 | 0.3380448 |
| N  | -4.4491429 | 0.3191213  | 0.4842329 |
| N  | -2.6821414 | 1.6362075  | -0.2435044 |
| N  | 2.0939944  | 3.5211689  | 1.8377364 |
| N  | 2.7629720  | 1.4411107  | 1.0324567 |
| C  | -0.6295343 | -1.3395045 | 4.4408592 |
| H  | -1.5529873 | -1.9077471 | 4.2642436 |
| H  | -0.4304274 | -1.3525819 | 5.5269123 |
| C  | 0.5007534  | -1.9975428 | 3.6617379 |
| H  | 1.4620303  | -1.5176722 | 3.9155551 |
| H  | 0.5828022  | -3.0528680 | 3.9638972 |
| C  | 0.4236141  | -2.9096077 | 1.4193792 |
| C  | 2.7016853  | -3.4582163 | 2.2274489 |
| H  | 2.8208782  | -2.3723329 | 2.2477067 |
| H  | 3.5066299  | -3.8806593 | 1.6034966 |

**[FeIV(O)TMG<sub>3</sub>tren]<sup>2+</sup>-DHA-TS (σ)**

EB3LYP-D3/def2-SVP(Fe:def2-TZVP)/COSMO(ε = 35.88):

-3253.4513279768 (<S²> 6.48938568)

EB3LYP-D3/def2-TZVP/P/COSMO(ε = 35.88):

-3255.6272794767 (<S²> 6.48416285)

ZPEB3LYP-D3/def2-SVP(Fe:tmg2-TZVP)/COSMO(ε = 35.88):

0.939819

Chem. Pot. (298.15)/B3LYP-D3/def2-SVP(Fe:tmg2-

TZVP)/COSMO(ε = 35.88):

0.868057
|   |   |   |   |
|---|---|---|---|
| H | 2.8210028 | -3.8467383 | 3.2526430 |
| C | 1.2318406 | -5.2496312 | 1.4008733 |
| H | 0.1728906 | -5.4762299 | 1.2290101 |
| H | 1.5657682 | -5.8122844 | 2.2878148 |
| C | 0.1258797 | -3.7186003 | -0.8947074 |
| H | 1.2204642 | -3.7339782 | -0.9092532 |
| H | -0.2089934 | -3.1043967 | -1.7416545 |
| C | -1.7364447 | -2.6404214 | 0.2840530 |
| H | -2.0893932 | -2.4341922 | 1.2998569 |
| H | -2.3712230 | -3.4188560 | -0.1673988 |
| H | -1.8113751 | -1.7165458 | -0.3099443 |
| C | -2.2387098 | 0.4896009 | 4.0999555 |
| H | -2.2606257 | 1.5874729 | 4.0739689 |
| H | -2.6569095 | 0.1693391 | 5.0705338 |
| C | -3.0648084 | -0.0397735 | 2.9395498 |
| H | -3.1590069 | -1.1368341 | 3.0156305 |
| H | -4.0834667 | 0.3719584 | 3.0036100 |
| C | -3.1628599 | 0.7471514 | 0.6586246 |
| C | -4.8886167 | -1.0358712 | 0.7907248 |
| H | -4.0334802 | -1.6844562 | 0.9940950 |
| H | -5.4279196 | -1.4451422 | -0.0794644 |
| H | -5.5671278 | -1.0594851 | 1.6597874 |
| C | -5.4996248 | 1.2085579 | -0.0047975 |
| H | -5.1604171 | 2.2509680 | 0.0212399 |
| H | -6.3778490 | 1.1136786 | 0.6545357 |
| H | -5.0117939 | 0.9558570 | -1.0320373 |
| C | -3.0510711 | 1.5874425 | -1.6541032 |
| H | -3.5518376 | 0.6397703 | -1.8855442 |
| H | -2.1379953 | 1.6502028 | -2.2577680 |
| H | -3.7117632 | 2.4231720 | -1.9378626 |
| C | -1.6835183 | 2.6309876 | 0.1124927 |
| H | -1.6650017 | 2.7523850 | 1.2017588 |
| H | -1.9504117 | 3.5929362 | -0.3528603 |
| H | -0.6823223 | 2.3296831 | -0.2267563 |
| C | 0.1113879 | 1.0059717 | 4.5697366 |
| H | 1.0640401 | 0.4902785 | 4.7536086 |
| H | -0.2680745 | 1.3677419 | 5.5418530 |
| C | 0.3605120 | 2.1573464 | 3.6064508 |
| H | -0.5625735 | 2.7467246 | 3.4694683 |
| H | 1.1091207 | 2.8348352 | 4.0440076 |
| C | 1.8656808 | 2.1759233 | 1.7348657 |
| C | 1.0064033 | 4.4906423 | 1.8430951 |
| H | 0.0741709 | 4.0194300 | 1.5184539 |
| H | 1.2456122 | 5.3041958 | 1.1387659 |
| H | 0.8509092 | 4.9342576 | 2.8410934 |
| C | 3.4226909 | 4.0760704 | 2.0861015 |
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| H       | 4.1274710 | 3.2794844 | 2.3529175 |
| H       | 3.3602491 | 4.7727377 | 2.9382369 |
| H       | 3.8121698 | 4.6303195 | 1.2159432 |
| C       | 3.6017407 | 2.9136932 | -0.4333098|
| H       | 3.119931  | -0.0180265| -0.224269 |
| H       | 3.7171833 | 1.2753633 | -0.825759 |
| H       | 4.6115991 | 2.2617930 | 0.343974  |
| C       | 2.9507215 | 0.0223875 | 1.2976907 |
| H       | 2.6065558 | -0.2043156| 2.3130636 |
| H       | 4.0199893 | -0.224269 | 1.2186544 |
| H       | 2.3742371 | -0.5951995| 0.5930133 |
| C       | 2.3019571 | -3.5164464| -3.7723572|
| C       | 3.1119931 | -2.9033422| -2.8061588|
| C       | 1.1398148 | -3.287859 | -2.4163859|
| C       | 2.735641  | -1.356914 | -1.586103 |
| C       | 0.7658944 | -4.0442183| -0.5213752|
| C       | 1.5850188 | -1.004551 | -0.129607 |
| C       | -0.5213752| -0.9549184| -4.1190693|
| C       | 1.1929910 | -0.318473 | -2.196047 |
| C       | 0.3671874 | 2.5681511 | -2.960557 |
| C       | -1.259413 | 1.3569714 | -4.8787578|
| C       | -0.4295540| 3.358691  | -3.7887483|
| C       | -1.2446283| 2.7506767 | -4.754059 |
| H       | 2.5779356 | -4.491648 | -4.181817 |
| H       | 0.5093178 | -3.3560685| -4.970799 |
| H       | 3.3901797 | -1.172497 | -1.548729 |
| H       | 1.0112263 | 3.0381361 | -2.211491 |
| H       | -1.8970785| 0.8850572 | -5.632026 |
| H       | -0.4147140| 4.4467594 | -3.686542 |
| H       | -1.8687978| 3.3631727 | -5.409919 |
| H       | 0.5352610 | 0.1101342 | -1.151877 |
| H       | 2.0306912 | 0.8690154 | -1.755737 |
| H       | -0.8279081| -1.2866344| -5.123034 |
| H       | -1.3251627| -1.302019 | -3.435844 |

Fe     -0.1551138 -0.0868732  1.5385494
O      0.0154277 -0.0160009 -0.2588974
N      -0.4131187 -0.2463606  3.8723823
N      -0.6182836 -2.0736601  1.7827963
N      -1.7206047  1.2127330  1.8898245
N      1.7088470  0.5132768  2.2117708
N     -0.5646674 -4.2074008  0.7439212
N     -1.7881188 -2.4731804 -0.1949378
N     -3.5615222  2.3775064  0.9451452
N     -1.4150805  2.7212408  0.1359269

\[ \text{[Fe}^{4+}(O)\text{TMG}_3\text{tren}]^{2+} - \text{DHA-IC (}\sigma\text{)} \]

\( \begin{align*}
\mathbf{E}_{\text{B3LYP-D3/def2-SVP(Fe:}\text{def2-TZVP)/COSMO}(\varepsilon = 35.88)} & : -3253.4855233643 \quad (<S^2> 7.03286810) \\
\mathbf{E}_{\text{B3LYP-D3/def2-TZVPP/COSMO}(\varepsilon = 35.88)} & : -3255.6626558995 \quad (<S^2> 7.03084143) \\
\mathbf{ZPE}_{\text{B3LYP-D3/def2-SVP(Fe:}\text{def2-TZVP)/COSMO}(\varepsilon = 35.88)} & : 0.941853
\end{align*} \)
|   |    |    |    |    |
|---|---|---|---|---|
|N  | 3.7588499 | 1.6113297 | 1.7769765 |
|N  | 3.1993812 | -0.3301192 | 0.6195447 |
|C  | -0.9455831 | -1.5989224 | 4.1332681 |
|H  | -2.0372406 | -1.5713570 | 4.0117634 |
|H  | -0.7335328 | -1.9138551 | 5.1708513 |
|C  | -0.3732827 | -2.5931390 | 3.1301073 |
|H  | 0.7062152 | -2.7258247 | 5.3195497 |
|H  | -0.3301192 | 0.6195447 |
|C  | -0.9455831 | -1.5989224 | 4.1332681 |
|H  | -2.0372406 | -1.5713570 | 4.0117634 |
|H  | -0.7335328 | -1.9138551 | 5.1708513 |
|C  | -0.3732827 | -2.5931390 | 3.1301073 |
|H  | 0.7062152 | -2.7258247 | 5.3195497 |
|H  | -0.3301192 | 0.6195447 |

Chem. Pot.(298.15)/B3LYP-D3/def2-SVP(Fe:deff-TZVP)/COSMO(ε = 35.88):

0.868414
| C   | 0.9307288 | -0.0337062 | 4.4405191 |
| H   | 1.4785704 | -0.9860182 | 4.4124818 |
| H   | 0.8694221 | 0.2854846  | 5.4968110 |
| C   | 1.6888728 | 0.9867630  | 3.6020585 |
| H   | 1.2077630 | 1.976802   | 3.6821509 |
| H   | 2.7074256 | 1.094160   | 4.0043785 |
| C   | 2.8628268 | 0.6056372  | 1.5424036 |
| H   | 2.2692890 | 3.0977765  | 1.8447170 |
| H   | 3.9073364 | 3.6757353  | 1.4568119 |
| H   | 3.4948308 | 3.2326834  | 3.1374041 |
| C   | 5.1982820 | -0.0589110 | -0.4776030 |
| H   | 4.1220529 | -0.6949543 | -1.3746187 |
| H   | 3.7726424 | -0.5872829 | -2.7999944 |
| H   | 5.5707258 | 1.8362175  | 2.7999944 |
| H   | 5.4098075 | 0.3021645  | 1.9156042 |
| C   | 4.1574921 | 1.0158879  | -0.6949543 |
| H   | 2.6575170 | -1.8783495 | 1.6730094 |
| H   | 3.4564223 | -2.4025548 | 0.4416350 |
| C   | 1.2537234 | -3.3856055 | -3.7635896 |
| C   | -0.5876156 | -2.2585659 | -4.8759508 |
| C   | 1.6933720 | -2.1658333 | -3.2637270 |
| C   | -0.1679881 | -1.0222681 | -4.3750692 |
| C   | 1.0029620 | -0.9600637 | -3.5627610 |
| C   | -0.9763756 | 0.2273029  | -4.6380242 |
| C   | 1.4762659 | 0.3060223  | -3.0969852 |
| C   | -0.1679881 | -1.0222681 | -4.3750692 |
| C   | 1.4489445 | 2.7879996  | -3.1204957 |
| C   | -0.8460890 | 2.7516815  | -4.7162348 |
| C   | 0.8830453 | 3.9861853  | -3.5386334 |
| C   | -0.2671704 | 3.9718916  | -4.3461337 |
| H   | -0.2369832 | -4.3918507 | -4.9795081 |
| H   | 1.7992965 | -4.3024972 | -3.5259204 |
| H   | -1.4820993 | -2.3036029 | -5.5031788 |
| H   | 2.5914029 | -2.1246615 | -2.6420709 |
| H   | 2.3495182 | 2.7924973  | -2.4994749 |
| H   | -1.7479326 | 2.7463585  | -5.3357747 |
| H   | 1.3323634 | 4.9369479  | -3.2406421 |
| H   | -0.7145516 | 4.9113004  | -4.6804850 |
| H   | 0.4644855 | 0.0947860  | -1.1075480 |
| H   | 2.396006 | 0.3444327  | -2.5128604 |
| H   | -1.3242127 | 0.2404863  | -5.6850261 |
### 5.2.4 Cu\textsuperscript{III}(OH) pathway (B3LYP-D3)

**Method:** B3LYP-D3/def2-SVP(Fe: def2-TZVP)/COSMO(\(\varepsilon = 8.51\))

|          | CHD                                                                 | DHA                                                                  |
|----------|----------------------------------------------------------------------|----------------------------------------------------------------------|
| C        | -1.4118919 -0.5812107 0.1864666                                      |                                                                       |
| C        | -0.0434186 -1.2122965 0.1868101                                      |                                                                       |
| C        | 1.0732293 -0.2003316 0.1863369                                      |                                                                       |
| C        | 0.8702683 1.1238559 0.1861765                                       |                                                                       |
| C        | -0.4982046 1.7549418 0.1859693                                      |                                                                       |
| C        | -1.6148530 0.7429767 0.1861132                                      |                                                                       |
| H        | -2.2710917 -1.2618718 0.1865000                                      |                                                                       |
| H        | 2.0968466 -0.5924153 0.1862660                                      |                                                                       |
| H        | 2.0968466 0.5239473 -0.1863657                                      |                                                                       |
| H        | 2.0968466 1.8045174 0.1859217                                      |                                                                       |
|          |                                                                     |                                                                       |
| C        | 3.5497633 -0.7663013 0.1449849                                      |                                                                       |
| C        | 3.5567773 0.6070146 0.4140184                                       |                                                                       |
| C        | -2.3868223 -1.3737445 -0.3421200                                    |                                                                       |
| C        | -2.4008192 1.3647660 0.1943482                                       |                                                                       |
| C        | -1.2286556 -0.6189297 -0.5713775                                    |                                                                       |
| C        | -1.2357311 0.7636913 -0.3005658                                     |                                                                       |
| C        | 0.0445716 -1.2368234 -1.1114020                                    |                                                                       |
| C        | 0.0302477 1.5522147 -0.5652714                                      |                                                                       |
| H        | 1.2744365 0.7606115 -0.2189928                                      |                                                                       |
| H        | 1.2815052 -0.6220344 -0.4896593                                    |                                                                       |
| H        | 2.4063801 1.3588709 0.3505875                                       |                                                                       |
| H        | 2.4203645 -1.3797285 -0.1854719                                    |                                                                       |
| C        | 3.5436581 0.5982478 0.6450835                                       |                                                                       |
| C        | 3.5506576 -0.7751246 0.3762814                                      |                                                                       |
| H        | -4.4469757 -1.3663159 0.3205997                                     |                                                                       |
| H        | -4.4595339 1.0875520 0.8012734                                      |                                                                       |
| H        | -2.3769879 -2.4490740 -0.5452558                                    |                                                                       |
| H        | -2.4020015 2.4373138 0.4119243                                      |                                                                       |
| H        | 2.3960999 2.4314566 0.5677378                                       |                                                                       |
| H        | 2.4210664 -2.4550667 -0.3887981                                    |                                                                       |
| H        | 4.4205132 1.0765845 1.0902460                                       |                                                                       |
| H        | 4.4330148 -1.3773518 0.6099908                                      |                                                                       |
| H        | 0.0656300 1.8023954 -1.6451127                                      |                                                                       |
| H        | 0.0140610 2.5139343 -0.0301347                                      |                                                                       |
| H        | 0.0388879 -2.3294541 -0.9785348                                     |                                                                       |
| H        | 0.0804298 -1.0609377 -2.2057912                                    |                                                                       |
|   |   |   |   |
|---|---|---|---|
| H | -4.5914508 | 4.4682746 | 0.2429564 |
| C | -4.5581195 | 3.3890409 | 0.0851513 |
| C | -4.3662518 | 0.6501713 | -0.3108641 |
| C | -5.7173026 | 2.6171264 | -0.0899855 |
| C | -3.3281719 | 2.7365423 | 0.0513946 |
| N | -3.2938140 | 1.4197824 | -0.1414757 |
| C | -5.6322476 | 1.2308514 | -0.2914234 |
| H | -6.6965836 | 3.1009054 | -0.0689424 |
| H | -6.5145150 | 0.6036505 | -0.4290559 |
| C | -1.9516227 | 3.3429931 | 0.2045465 |
| O | -1.7838337 | 4.5402012 | 0.4017165 |
| C | -4.0152393 | -0.8087789 | -0.4963697 |
| O | -4.8728425 | -1.6664626 | -0.6719352 |
| N | -2.6674297 | -0.9940607 | -0.4351969 |
| N | -0.9843573 | 2.3888821 | 0.0891948 |
| Cu | -1.6215001 | 0.6003844 | -0.1780624 |
| H | 0.6721552 | 0.3861681 | -0.0965633 |
| O | -0.405143 | -0.2586881 | -0.2355506 |
| C | 0.3909803 | 2.7024101 | 0.1739082 |
| C | 3.1194402 | 3.2436886 | 0.3364864 |
| C | 1.0556346 | 2.5391942 | 1.4166303 |
| C | 1.0870836 | 3.0976284 | -0.9979980 |
| C | 2.4564370 | 3.3721116 | -0.8871686 |
| C | 2.4264497 | 2.8246563 | 1.4746113 |
| H | 3.0204027 | 3.6828425 | -1.7691043 |
| H | 2.9635035 | 2.7184764 | 2.4195280 |
| H | 4.1889976 | 3.4619111 | 0.4005928 |
| C | -2.0644009 | -2.2601409 | -0.5324236 |
| C | -0.8354024 | -4.7514183 | -0.7305059 |
| C | -1.9437727 | -3.0646455 | 0.6306780 |
| C | -1.5322088 | -2.6712047 | -1.7809318 |
| C | -0.9282154 | -3.9319097 | -1.8585125 |
| C | -1.3328299 | -4.3177168 | 0.5022249 |
| H | -0.5201042 | -4.2825443 | -2.8088083 |
| H | -1.2319138 | -4.9657575 | 1.3752792 |
| H | -0.3611057 | -5.7337053 | -0.8095369 |
| C | 0.3734658 | 3.1450718 | -2.3430791 |
| H | -0.6957686 | 3.3088856 | -2.1426101 |
| C | 0.8440411 | 4.2904071 | -3.2494858 |
| H | 0.2140580 | 4.3390503 | -4.1523873 |
| H | 1.8841485 | 4.1493974 | -3.5862968 |
| H | 0.7810405 | 5.2620788 | -2.7337295 |
| C | 0.5006751 | 1.7813151 | -3.0527414 |
| H | -0.1026087 | 1.7621602 | -3.9753663 |
| H | 0.1713858 | 0.9556340 | -2.4039756 |
| H | 1.5513411 | 1.5869687 | -3.3274455 |

\[ \text{\textit{Cu}^{III}(OH)(L)} \]

\[ E_{\text{B3LYP-D3-def2-SVP}}(\text{Cu:def2-TZVP})/\text{COSMO}(\epsilon = 8.51) : -3232.6379302794 \]

\[ E_{\text{B3LYP-D3-def2-TZVP}}/\text{COSMO}(\epsilon = 8.51) : -3234.3954435859 \]

\[ \text{ZPE}_{\text{B3LYP-D3-def2-SVP}}(\text{Cu:def2-TZVP})/\text{COSMO}(\epsilon = 8.51) : 0.635055 \]

\[ \text{Chem. Pot.}(298.15)/\text{B3LYP-D3-def2-SVP(Cu:def2-TZVP)/COSMO(\epsilon = 8.51)} : 0.572492 \]
| C  | 0.2798924 | 2.1009260 | 2.6511548 |
| H  | -0.6109085 | 1.5593712 | 2.2963247 |
| C  | -0.2169240 | 3.3326637 | 3.4326384 |
| H  | -0.7985010 | 4.0061723 | 2.7845030 |
| H  | 0.6368493 | 3.9039550 | 3.8350562 |
| H  | -0.8526470 | 3.0261983 | 4.2800274 |
| C  | 1.0606598 | 1.1351232 | 3.5519104 |
| H  | 1.9236974 | 1.6228458 | 4.0338986 |
| H  | 1.4302220 | 0.2694522 | 2.9793539 |
| H  | 0.4069098 | 0.7574201 | 4.3544211 |
| C  | -1.6614556 | -1.7702508 | -2.9997942 |
| H  | -1.7296640 | -0.7370125 | -2.6268178 |
| C  | -2.9710355 | -2.0742426 | -3.7534197 |
| H  | -3.8416994 | -3.0928462 | -4.1767686 |
| H  | -3.1178449 | -1.3633650 | -4.5838925 |
| C  | -0.4467585 | -1.8256602 | -3.9343416 |
| H  | -0.3542652 | -2.8016763 | -4.4366186 |
| H  | 0.4856053 | -1.6334128 | -3.3804633 |
| H  | -0.5412170 | -1.0590580 | -4.7204253 |
| C  | -2.4018099 | -2.5379158 | 1.9844609 |
| H  | -3.2071825 | -1.8111545 | 1.8002221 |
| C  | -2.9757067 | -3.6191162 | 2.9095309 |
| H  | -3.3968044 | -3.1553805 | 3.8196286 |
| H  | -2.2043266 | -4.3370187 | 3.2333532 |
| H  | -3.7818047 | -4.1847469 | 2.4150344 |
| C  | -1.2462756 | -1.7753649 | 2.6647697 |
| H  | -1.5926638 | -1.2773194 | 3.5855903 |
| H  | 0.8149187 | -1.0200316 | 1.9910059 |
| H  | -0.4352141 | -2.4720281 | 2.9369674 |

| H  | -5.6005232 | 0.6614407 | 0.2148683 |
| C  | -4.8489282 | -0.1264355 | 0.1436797 |
| C  | -2.8623194 | -2.0551515 | -0.0356155 |
| C  | -5.1883214 | -1.4860209 | 0.0608206 |
| C  | -3.4974280 | 0.2103917 | 0.1315114 |
| N  | -2.5860223 | -0.7556419 | 0.0436161 |
| C  | -4.1920219 | -2.4704215 | -0.0304670 |
| H  | -6.2401345 | -1.7812832 | 0.0675964 |
| H  | -4.4243659 | -3.5346193 | -0.0952409 |
| C  | -2.8829185 | 1.5905829 | 0.2004972 |
| O  | -3.5671122 | 2.6032761 | 0.2880538 |
| C  | -1.6192813 | -2.9132927 | -0.1174323 |
| O  | -1.6786894 | -4.1346263 | -0.2072969 |
| N  | -0.4973678 | -2.1437184 | -0.0774817 |
| N  | -1.5215597 | 1.5233419 | 0.1476124 |
| Cu | -0.7945695 | -0.2439196 | 0.0387739 |
| H  | 1.1307696 | 1.0722061 | 0.2067431 |

**Cu^{III}(OH)(L)-CHD-RC**

\[ \text{EB3LYP-D3/def2-SVP(Cu:df2-TZVP)/COSMO}(\varepsilon = 8.51): -3465.7587837766 \]

\[ \text{EB3LYP-D3/def2-TZVPP/COSMO}(\varepsilon = 8.51): -3467.7693930849 \]

\[ \text{ZPEB3LYP-D3/def2-SVP(Cu:df2-TZVP)/COSMO}(\varepsilon = 8.51): 0.758544 \]

\[ \text{Chem. Pot.}(298.15)/B3LYP-D3/def2-SVP(Cu:df2-TZVPP)/COSMO}(\varepsilon = 8.51): 0.689108 \]
| O  | 0.9556485 | 0.1361354 | 0.0202690 |
|---|---|---|---|
| H | 3.1936322 | -0.9129435 | 0.5173071 |
| C | -0.7267257 | 2.6930260 | 0.1683935 |
| C | 0.8412114 | 4.9955490 | 0.2193820 |
| C | -0.2059165 | 3.1468405 | 1.4056055 |
| C | -0.4262975 | 3.3501397 | -1.0524983 |
| C | 0.3542616 | 4.5120854 | -0.9980263 |
| C | 0.152 | 5.0433925 | -1.9197405 |
| C | 0.9785789 | 4.6918646 | 2.3467320 |
| C | 1.4517035 | 5.9023670 | 0.2394281 |
| C | 0.8011765 | -2.6816459 | -0.1177931 |
| C | 3.7776113 | -3.7368357 | -0.2110623 |
| C | 1.4198975 | -3.1018905 | 1.0882904 |
| C | 1.4851544 | -2.7282865 | -1.3591252 |
| C | 2.7747593 | -3.2724520 | -1.3824460 |
| C | 2.7087972 | -3.6429038 | 1.0127590 |
| H | 3.3224945 | -3.3312527 | -2.3251656 |
| H | 3.2101382 | -3.9814034 | 1.9219182 |
| H | 4.3865044 | -4.1571150 | -0.2482168 |
| C | 3.9621855 | 1.3190852 | 1.6142119 |
| C | 4.1791510 | 0.1138851 | 1.0725277 |
| C | 3.5319794 | 2.5200527 | -0.8133457 |
| H | 2.5358850 | 2.8618097 | -1.1565427 |
| H | 4.1967232 | 3.3819331 | -1.0230074 |
| C | 4.0122305 | -0.1819012 | 0.3923445 |
| H | 4.9148225 | -0.6878062 | 0.7886821 |
| C | 3.4837299 | 2.2533309 | 0.6689928 |
| C | 3.7003799 | 1.0444127 | 1.2053455 |
| C | -0.8712302 | 2.7553911 | -2.3822411 |
| H | -1.7491327 | 2.1232287 | -2.1820056 |
| C | -1.2954685 | 3.8068160 | 3.4161029 |
| H | -1.7073159 | 3.3116890 | -4.3104754 |
| H | -0.4446960 | 4.4236627 | -3.7492998 |
| H | -2.0671190 | 4.4806193 | -3.0101424 |
| C | 0.2342094 | 1.8335172 | 2.9379697 |
| H | -0.1168514 | 1.3024452 | -3.8381858 |
| H | 0.5525981 | 1.0878138 | 2.1939624 |
| H | 1.1242743 | 2.4224441 | -3.2167223 |
| C | -0.5168760 | 2.3960423 | 2.6933208 |
| H | -0.7689150 | 1.3621848 | 2.4088177 |
| C | -1.7586774 | 2.9975152 | 3.3786935 |
| H | -2.6167197 | 3.0292376 | 2.6898268 |
| H | -1.5532609 | 4.0295792 | 3.7104557 |
| H | -2.0412881 | 2.4043766 | 4.2644993 |
| C | 0.6782445 | 2.3167675 | 3.6525213 |
| H | 0.9440499 | 3.3031879 | 4.0665457 |
| H | 1.5641813 | 1.9066397 | 3.1437754 |
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| H    | 0.4362519 | 1.6583734 | 4.5023565 |
| C    | 0.8047694 | -2.2327707 | -2.6265627 |
| H    | 0.0583780 | -1.4857471 | -2.3159161 |
| C    | 0.0459078 | -3.3858467 | -3.3118802 |
| H    | -0.6518417 | -3.8761130 | -2.6155588 |
| H    | 0.7535603 | -4.1515212 | -3.6733047 |
| H    | -0.5270036 | -3.0155547 | -4.1787102 |
| C    | 1.7590211 | -1.5265648 | -3.5974564 |
| H    | 2.4956514 | -2.2212518 | -4.0341902 |
| H    | 2.3026328 | -0.7162835 | -3.0890509 |
| H    | 1.1880136 | -1.0890960 | -4.4325366 |
| C    | 0.7298217 | -2.8858578 | 2.4283124 |
| H    | -0.3532419 | -2.8429072 | 2.2387393 |
| C    | 0.9680368 | -4.0176498 | 3.4366701 |
| H    | 0.3570337 | -3.8542197 | 4.3393720 |
| H    | 2.0204434 | -4.0656144 | 3.7614914 |
| H    | 0.6976590 | -4.9977573 | 3.0115945 |
| C    | 1.1442131 | -1.5175974 | 3.0084660 |
| H    | 0.5716753 | -1.2898910 | 3.9231998 |
| H    | 0.9866487 | -0.7132251 | 2.2749186 |
| H    | 2.2167638 | -1.5196299 | 3.2673384 |
| H    | 3.2312435 | 3.1000798 | 1.3153772 |
| H    | 4.0755677 | 1.4584822 | -2.6954852 |
| H    | 4.4657886 | -0.7269278 | -1.7127782 |
| H    | 3.6277427 | 0.9129575 | 2.2910086 |
| H    | -4.5541131 | 4.2849085 | 0.2774878 |
| C    | -4.4939981 | 3.2048436 | 0.1344291 |
| C    | -4.2434479 | 0.4614889 | -0.2264294 |
| C    | -5.6361690 | 2.4022472 | -0.0188835 |
| C    | -3.2490776 | 2.5778272 | 0.0977112 |
| N    | -3.1911410 | 1.2607997 | -0.0749088 |
| C    | -5.5235564 | 1.0148506 | -0.2029209 |
| H    | -6.6261676 | 2.8641844 | 0.0046877 |
| H    | -6.3947608 | 0.3694422 | -0.3258161 |
| C    | -1.8813646 | 3.2247618 | 0.2334747 |
| O    | -1.7625064 | 4.4347713 | 0.4150628 |
| C    | -3.8648500 | -0.997946 | -0.4127346 |
| O    | -4.7276992 | -1.8610856 | -0.5865600 |
| N    | -2.5230059 | -1.1647042 | -0.3624197 |
| N    | -0.8847735 | 2.3070777 | 0.1301551 |
| Cu   | -1.4684010 | 0.4654045 | -0.1186066 |
| H    | 0.8897979 | 0.3446085 | -0.0388912 |
| O    | 0.2105170 | -0.3424093 | -0.1587056 |
| H    | 1.1184765 | -1.4230456 | -0.1712464 |
| C    | 0.4790496 | 2.6608034 | 0.2241937 |
| C    | 3.2079509 | 3.2346487 | 0.4009475 |
| C    | 1.1480276 | 2.4940109 | 1.4663929 |

Cu(II)(OH)(L)-CHD-TS

EB3LYP-D3/def2-SVP(Cu:deff-TZVP)/COSMO(ε = 8.51):
-3465.7410374778 (<S^2> = 0.43940638)

EB3LYP-D3/def2-TZVPP/COSMO(ε = 8.51):
-3467.7497649775 (S = 0; <S^2> = 0.45695148)
-3467.7361455118 (S = 1; <S^2> = 2.01530241)
-3467.7537981851 (spin purified)

ZPEB3LYP-D3/def2-SVP(Cu:deff-TZVP)/COSMO(ε = 8.51):
0.75227

Chem. Pot.(298.15)/B3LYP-D3/def2-SVP(Cu:deff-
TZVP)/COSMO(ε = 8.51):
0.683264
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| C | 1.1811552 | 3.0660101 | -0.9417729 |
| C | 2.5463169 | 3.3573109 | -0.8247179 |
| C | 2.5146104 | 2.7963539 | 1.5320598 |
| H | 3.1097518 | 3.6772378 | -1.7036365 |
| H | 3.0500277 | 2.6846584 | 2.4769820 |
| H | 4.2721551 | 3.4747139 | 0.4723679 |
| C | -1.8976127 | -2.4204931 | -0.5240804 |
| C | -0.5184284 | -4.8304938 | -0.8315628 |
| C | -1.6908182 | -3.2504120 | 0.6054380 |
| C | -1.3834659 | -2.7701502 | -1.7977267 |
| C | -0.7011348 | -3.9867598 | -1.9301743 |
| C | -1.0030901 | -4.4588166 | 0.4249888 |
| C | -0.3012646 | -4.2823056 | -2.9026409 |
| H | -0.8317730 | -5.1180356 | 1.2788883 |
| H | 0.0178074 | -5.7760209 | -0.9522149 |
| C | 3.9046477 | -0.8295338 | -1.2914355 |
| C | 2.8887211 | -1.7189776 | -1.3364154 |
| C | 4.3759009 | -0.2148280 | -0.0062814 |
| C | 4.1320325 | 0.8731416 | -0.0099595 |
| C | 5.4824135 | -0.2270727 | 0.0497969 |
| C | 2.1393062 | -2.1048591 | -0.1274066 |
| C | 1.6763987 | -3.1030909 | -0.1558318 |
| C | 3.7771308 | -0.8396076 | 1.2194376 |
| C | 2.7627838 | -1.7290395 | 1.1547580 |
| C | 0.4762533 | 3.1001787 | -2.2922811 |
| H | -0.5926844 | 3.2756450 | -2.1001090 |
| C | 0.9618066 | 4.2265832 | -3.2143180 |
| H | 0.3338969 | 4.2702848 | -4.1189438 |
| H | 2.0006354 | 4.0682675 | -3.5478264 |
| H | 0.9103648 | 5.2063824 | -2.7128274 |
| C | 0.5992008 | 1.7262057 | -2.9822357 |
| H | 0.0216970 | 1.7044223 | -3.9211141 |
| H | 0.2385570 | 0.9122106 | -2.3362815 |
| H | 1.6536442 | 1.5079172 | -3.2218893 |
| C | 0.3755118 | 2.0252260 | 2.6919969 |
| H | -0.4734614 | 1.4272934 | 2.3238857 |
| C | -0.2137772 | 3.2325654 | 3.4469305 |
| H | -0.8136361 | 3.8674903 | 2.7772379 |
| H | 0.5951254 | 3.8545071 | 3.8669336 |
| H | -0.8542004 | 2.8974479 | 4.2799173 |
| C | 1.1913421 | 1.1195309 | 3.6232279 |
| H | 2.0025527 | 1.6684309 | 4.1293647 |
| H | 1.6400249 | 0.2820494 | 3.0665460 |
| H | 0.5398872 | 0.7016562 | 4.4075613 |
| C | -1.5997358 | -1.8440067 | -2.9866112 |
| H | -1.7055899 | -0.8257792 | -2.5802982 |
| C | -2.9212492 | -2.1877392 | -3.7008986 |
| H | -3.7658284 | -2.1859834 | -2.9948392 |
Cu\textsuperscript{III}(OH)(L)-CHD-IC

\begin{align*}
\text{E}_{\text{B3LYP-D3/def2-TZVP}}\text{(Cu:def2-TZVP)/COSMO(}\varepsilon = 8.51\text{)}: & \quad -3465.7828945679 \quad (\langle S^2 \rangle = 1.04071524) \\
\text{E}_{\text{B3LYP-D3/def2-TZVP}/\text{COSMO}(}\varepsilon = 8.51\text{)}: & \quad -3467.7910857678 \quad (S = 0, \langle S^2 \rangle = 1.03901619) \\
& \quad -3467.7911092310 \quad (S = 1; \langle S^2 \rangle = 2.03915370) \\
& \quad -3467.7910603994 \quad (\text{spin purified}) \\
\text{ZPE}_{\text{B3LYP-D3/def2-TZVP/COSMO}(}\varepsilon = 8.51\text{)}: & \quad 0.756091 \\
\text{Chem. Pot.}(298.15)/\text{B3LYP-D3/def2-TZVP/COSMO(}\varepsilon = 8.51\text{)}: & \quad 0.686013
\end{align*}
|  |  |  |  |  |  |
|---|---|---|---|---|---|
| H | 1.6381916 | 5.7981312 | 0.2002059 |  |
| C | 0.8189780 | -2.7213181 | -0.0781296 |  |
| C | 3.4462317 | -3.6798236 | -0.1900442 |  |
| C | 1.4646362 | -3.1279323 | 1.1180256 |  |
| C | 1.4988630 | -2.7542876 | -1.3225686 |  |
| C | 2.8119630 | -3.2467655 | -1.3555036 |  |
| C | 2.7780722 | -3.6150999 | 1.0354141 |  |
| C | 3.4460848 | -4.0591400 | -0.2334089 |  |
| H | 2.6660503 | 2.8370654 | -1.1111942 |  |
| H | 4.3430664 | 3.2563071 | -1.0097701 |  |
| C | 4.2120292 | -0.1128215 | 0.5403641 |  |
| C | 3.6017745 | 2.2419689 | 0.7381035 |  |
| C | 3.8842402 | 1.0326888 | 1.3236043 |  |
| C | -1.0528976 | 2.9503446 | -2.4205177 |  |
| H | -2.0233507 | 2.4776199 | -2.2074101 |  |
| C | -1.3096918 | 4.0666702 | -3.4415785 |  |
| H | -1.8321928 | 3.6593979 | -4.3222654 |  |
| H | -0.3717783 | 4.5205834 | -3.8020505 |  |
| H | -1.9327289 | 4.8680477 | -3.0129688 |  |
| C | -0.1298793 | 1.8673427 | -3.0142204 |  |
| H | -0.5595015 | 1.4448585 | -3.9374661 |  |
| H | 0.0384252 | 1.0429091 | -2.3063165 |  |
| H | 0.8581831 | 2.2925489 | -3.2593044 |  |
| C | -0.5154492 | 2.3670149 | 2.6131197 |  |
| H | -0.7527012 | 1.3322559 | 2.3154390 |  |
| C | -1.7880679 | 2.9449353 | 3.2620266 |  |
| H | -2.6206129 | 2.9780970 | 2.5428975 |  |
| H | -1.6040891 | 3.9745149 | 3.6137023 |  |
| H | -2.0965372 | 2.3375000 | 4.1294226 |  |
| C | 0.6426793 | 2.2929445 | 3.6160682 |  |
| H | 0.8758251 | 3.2769172 | 4.0546485 |  |
| H | 1.5599477 | 1.9069131 | 3.1430053 |  |
| H | 0.3802898 | 1.6182336 | 4.4466082 |  |
| C | 0.7912366 | -2.2944587 | -2.5910062 |  |
| H | 0.0159126 | -1.5754693 | -2.2813235 |  |
| C | 0.0624465 | -3.4785423 | -3.2544151 |  |
| H | -0.6134936 | -3.9749797 | -2.5410629 |  |
| H | 0.7904220 | -4.2278882 | -3.6097378 |  |
| H | -0.5292608 | -3.1394906 | -4.1213773 |  |
| C | 1.7094751 | -1.5637118 | -3.5791713 |  |
| H | 2.4647967 | -2.2349611 | -4.0199253 |  |
| H | 2.2365610 | -0.7301462 | -3.0880692 |  |
|     | H     | C     | H     | C     |
|-----|-------|-------|-------|-------|
| H   | 1.1157735 | -1.1489922 | -4.4098237 |       |
| C   | 0.7596175  | -2.9631073  | 2.4599307 |       |
| H   | 0.3191445  | -4.0095132  | 3.5073605 |       |
| C   | 0.5261672  | -3.9117375  | 4.4021568 |       |
| H   | 2.2068187  | -3.8842205  | 3.8362220 |       |
| H   | 0.104901 | -5.0331778  | 3.1159412 |       |
| C   | 0.9816089  | -1.5366490  | 3.0012402 |       |
| H   | 0.4188942  | -1.3732510  | 3.9348769 |       |
| H   | 0.6592041  | -0.7741826  | 2.2766138 |       |
| C   | 0.9816089  | -1.5366490  | 3.0012402 |       |
| H   | -4.5464764 | 4.1601746   | 0.4858432 |       |
| C   | -4.4415490 | 3.0858214   | 0.5988648 |       |
| C   | -4.0679394 | 0.3690299   | 0.1734432 |       |
| C   | -5.5429190 | 2.2157674   | 0.5705728 |       |
| C   | -3.1750766 | 2.5997222   | 0.395705  |       |
| N   | -3.0520745 | 1.2277236   | 0.2068730 |       |
| C   | -5.3658864 | 0.8399240   | 0.3585056 |       |
| H   | -6.5490532 | 2.6145147   | 0.7194862 |       |
| H   | -6.2015569 | 0.1386964   | 0.3331436 |       |
| C   | -1.8467382 | 3.2600583   | 0.3809792 |       |
| O   | -1.7589486 | 4.4683799   | 0.5693154 |       |
| C   | -3.6222695 | -1.0532647  | -0.0789864 |       |
| O   | -4.4185185 | -1.9812769  | -0.1488699 |       |
| N   | -2.2666396 | -1.1209924  | -0.2050834 |       |
| N   | -0.8235390 | 2.3906748   | 0.1468223 |       |
| Cu  | -1.3385886 | 0.5615692   | -0.1617983 |       |
| H   | 0.195291 | 0.5606700   | 0.6555938 |       |
| O   | 0.2678481 | -0.141951   | -0.5025869 |       |
| H   | 1.2664654 | -2.732157   | -0.5511717 |       |
| C   | 0.5269902 | 2.8011906   | 0.1953676 |       |
| C   | 3.1844199 | 3.6269011   | 0.2844596 |       |
| C   | 1.1940017 | 2.8427182   | 1.4459793 |       |
| C   | 1.2002163 | 3.0938063   | 1.0181529 |       |
| C   | 2.5324816 | 3.5186861   | 0.9461696 |       |
| C   | 2.5246003 | 3.2791013   | 1.4653716 |       |
| H   | 3.0748639 | 3.7591864   | 1.8623849 |       |
| H   | 3.0594674 | 3.3396638   | 2.4159711 |       |
| H   | 4.2243861 | 3.9625233   | 0.3211905 |       |
| C   | -1.6019392 | -2.3387459  | -0.4366067 |       |
| C   | -0.3444976 | -4.7793637  | -0.9067792 |       |
| C   | -1.2476261 | -3.1580556  | 0.6699511 |       |
| C   | -1.2775472 | -2.7050916  | 1.7656093 |       |

**Cu^{II}(OH)(L)-DHA-RC**

\[ \text{EB3LYP-D3/def2-SVP(Cu:def2-TZVP)/COSMO(\epsilon = 8.51):} \]
\[ -3772.6905852519 \]

\[ \text{EB3LYP-D3/def2-TZVP/COSMO(\epsilon = 8.51):} \]
\[ -3775.0223000453 \]

\[ \text{ZPEB3LYP-D3/def2-SVP(Cu:def2-TZVP)/COSMO(\epsilon = 8.51):} \]
\[ 0.854417 \]

\[ \text{Chem. Pot.(298.15)/B3LYP-D3/def2-SVP(Cu:def2-TZVP)/COSMO(\epsilon = 8.51):} \]
\[ 0.781454 \]
|   |   |   |   |   |
|---|---|---|---|---|
| C | -0.6541352 | -3.9414808 | -1.9782999 |   |
| C | -0.6302060 | -4.3846160 | 0.4045153 |   |
| H | -0.3988277 | -4.2496556 | -2.9954129 |   |
| H | -0.3538488 | -5.0428544 | 1.2290998 |   |
| H | 0.1436081 | -5.7407197 | -1.0895835 |   |
| H | 4.6859693 | 1.4498864 | -0.8672130 |   |
| C | 4.2969817 | 0.5722047 | -1.3886505 |   |
| C | 3.2936027 | -1.6634311 | -2.7091318 |   |
| C | 3.5951042 | -0.3996016 | -0.6607491 |   |
| C | 4.4873874 | 0.4396345 | -2.7667638 |   |
| C | 3.9773611 | -0.6816676 | -3.4317125 |   |
| C | 3.0957629 | -1.5354812 | -1.3263613 |   |
| H | 5.0281321 | 1.2117830 | -3.3208600 |   |
| H | 4.1174300 | -0.7937578 | -4.5105984 |   |
| H | 2.8988859 | -2.5440653 | -3.2245228 |   |
| C | 3.3254596 | -0.2322284 | 0.8186576 |   |
| H | 2.3563560 | 0.2866314 | 0.9316357 |   |
| H | 4.0720589 | 0.4326372 | 1.2793945 |   |
| C | 2.3290021 | -2.5748543 | -0.5452103 |   |
| H | 2.3761038 | -3.5530072 | -1.0459778 |   |
| C | 3.2381257 | -1.5434534 | 1.5660122 |   |
| C | 2.7660680 | -2.6879182 | 0.8957219 |   |
| C | 3.5769610 | -1.6297058 | 2.9245960 |   |
| H | 3.9430074 | -0.7376735 | 3.4421684 |   |
| C | 3.4486807 | -2.8349819 | 3.6218386 |   |
| H | 3.7116884 | -2.8848933 | 4.6821704 |   |
| C | 2.6596421 | -3.8980438 | 1.5966976 |   |
| C | 2.2962653 | -4.7859625 | 1.0725610 |   |
| C | 2.9911214 | -3.9763152 | 2.9526602 |   |
| H | 2.8939283 | -4.9263055 | 3.4856989 |   |
| C | 0.4664402 | 2.9789145 | -2.3474937 |   |
| H | -0.3617858 | 2.2687138 | -2.1954734 |   |
| C | -0.1601599 | 4.3340414 | -2.7276762 |   |
| H | -0.7703104 | 4.2398180 | -3.6414945 |   |
| C | 0.6277346 | 5.0825049 | -2.9184978 |   |
| H | -0.7995342 | 4.7174225 | -1.9172605 |   |
| C | 1.3396245 | 2.4159850 | -3.4766575 |   |
| H | 0.7246073 | 2.2381347 | -4.3737527 |   |
| H | 1.8076290 | 1.4626210 | -3.1864272 |   |
| H | 2.1445858 | 3.1123702 | -3.7636404 |   |
| C | 0.4763260 | 2.4523494 | 2.7315031 |   |
| C | -0.4296767 | 1.8973748 | 2.4416359 |   |
| C | 0.0243064 | 3.7093597 | 3.4989612 |   |
| H | -0.5946622 | 4.3581404 | 2.8608429 |   |
| H | 0.8985028 | 4.2925016 | 3.8352582 |   |
| H | -0.5622186 | 3.4314698 | 4.3905914 |   |
| C | 1.3060135 | 1.5147400 | 3.6221541 |   |
| H | 2.2220781 | 2.0014818 | 3.9947888 |   |
|  |  |  |  |
|---|---|---|---|
| H   | 1.5994057 | 0.6011451 | 3.0838029 |
| H   | 0.7147725 | 1.2104404 | 4.5010658 |
| C   | -1.5814483 | -1.7825133 | -2.9360256 |
| H   | -2.0384764 | -0.8708217 | -2.5240173 |
| C   | -2.6026665 | -2.4118982 | -3.8985588 |
| H   | -3.5317424 | -2.6767366 | -3.3680092 |
| H   | -2.2041509 | -3.3290580 | -4.3639471 |
| H   | -2.8564428 | -1.7081478 | -4.7088364 |
| C   | -0.2914186 | -1.3515072 | -3.6541852 |
| H   | 0.2195616  | -2.2108177 | -4.4524135 |
| H   | 0.4020805  | -0.8829606 | -2.9408323 |
| H   | 0.5745732  | -2.3081925 | -2.6833516 |
| C   | -1.4999174 | -2.6768153 | 2.0938905 |
| H   | -2.4274763 | -2.0832784 | 2.0748979 |
| C   | -1.7097027 | -3.8122699 | 3.1050605 |
| H   | -2.0113026 | -3.9457644 | 4.0796754 |
| H   | -0.7832411 | -4.3852608 | 3.2710338 |
| H   | -2.4925052 | -4.5126210 | 2.7740343 |
| C   | -0.3616693 | -1.7435134 | 2.5570955 |
| H   | -0.1566232 | -0.9524069 | 1.8222657 |
| H   | 0.5745732  | -2.3081925 | 2.6833516 |

|  |  |  |  |
|---|---|---|---|
| Cu  | 1.4024211 | 0.5727944 | -0.2317894 |
| H   | 0.9630622 | 0.4262429 | -0.2232260 |
| O   | 0.2786995  | -0.2657232 | -0.2465541 |
| H   | 1.1085046 | -1.3457375 | -0.2381851 |
| C   | 0.5916628 | 2.7557385 | 0.0288514 |
| C   | 3.3197325 | 3.3579891 | 0.1709745 |
| C   | 1.2145185 | 2.8702342 | 1.2983607 |
| C   | 1.3392494 | 2.8946390 | -1.1686916 |
| C   | 2.7064147 | 3.1932184 | -1.0712686 |
| C   | 2.5771422 | 3.1909457 | 1.3438947 |

**CuII(OH)(L)-DHA-TS**

\[ \text{EB3LYP-D3/def2-SVP(Cu:def2-TZVP)/COSMO(\varepsilon = 8.51)}: \]

-3772.6706428579 (<S^2> 0.47252884)

\[ \text{EB3LYP-D3/def2-TZVP/COOMO(\varepsilon = 8.51)}: \]

-3775.009736851 (S = 0; <S^2> 0.49819223)

-3774.9891593620 (S = 1; <S^2> 2.01620343)

-3775.004892311 (spin purified)

\[ \text{ZPE}_{\text{B3LYP-D3/def2-SVP(Cu:def2-TZVP)/COSMO(\varepsilon = 8.51)}}: \]

0.84792

\[ \text{Chem. Pot.(298.15)/B3LYP-D3/def2-SVP(Cu:def2-TZVP)/COSMO(\varepsilon = 8.51)}: \]

0.775156
| Atoms | X    | Y    | Z    |
|-------|------|------|------|
| H     | 3.3019439 | 3.2902012 | -1.9822314 |
| H     | 3.0762396 | 3.2847765 | 2.3117835  |
| H     | 4.3860725 | 3.5922905 | 0.2280792  |
| C     | -1.9472513 | -2.3157400 | -0.6129496 |
| C     | -0.6670144 | -4.7740402 | 0.2919062  |
| C     | -1.8455493 | -3.2000167 | -0.9514674 |
| C     | -1.4098002 | -2.6519099 | 1.1178494  |
| C     | -0.7687214 | -4.4314522 | 2.3117835  |
| H     | 0.3450672  | -4.1735168 | 2.9930191  |
| H     | -1.1172263 | -5.1393880 | 1.1178494  |
| C     | 5.4782808  | 0.8938576  | -1.0772452 |
| C     | 3.0911677  | 1.4798665  | 0.2280792  |
| C     | 3.9221763  | -0.5281009 | -0.6170322 |
| C     | 4.8360099  | -2.8453935 | 2.3117835  |
| C     | 3.9760392  | -3.3622337 | 2.3117835  |
| H     | 5.5271227  | 0.3550124  | -3.5064170 |
| C     | 3.0493363  | -1.1381068 | 2.3117835  |
| H     | 3.1643232  | 0.6905501  | 0.9598909  |
| H     | 4.8192091  | 1.2128590  | 2.3117835  |
| C     | 2.0715245  | -0.2343413 | 2.3117835  |
| H     | 1.5815444  | -0.6436449 | 2.3117835  |
| C     | 3.3296589  | 1.7342622  | 2.3117835  |
| C     | 2.4428079  | 1.1896450  | 2.3117835  |
| C     | 3.6656693  | 3.0909689  | 2.3117835  |
| H     | 4.3548973  | 3.5120224  | 2.3117835  |
| C     | 3.1278233  | 3.9120077  | 2.3117835  |
| C     | 3.988129   | 4.4273604  | 2.3117835  |
| C     | 2.4230557  | -2.9062237 | 2.3117835  |
| C     | 3.8457932  | 0.8505654  | 2.3117835  |
| H     | 3.1643232  | 0.9598909  | 2.3117835  |
| H     | 4.8192091  | 1.2128590  | 2.3117835  |
| C     | 2.0715245  | -0.2343413 | 2.3117835  |
| H     | 1.5815444  | -0.6436449 | 2.3117835  |
| C     | 3.3296589  | 1.7342622  | 2.3117835  |
| C     | 2.4428079  | 1.1896450  | 2.3117835  |
| C     | 3.6656693  | 3.0909689  | 2.3117835  |
| H     | 4.3548973  | 3.5120224  | 2.3117835  |
| C     | 3.1278233  | 3.9120077  | 2.3117835  |
| C     | 3.988129   | 4.4273604  | 2.3117835  |
| C     | 2.4230557  | -2.9062237 | 2.3117835  |
| C     | 3.8457932  | 0.8505654  | 2.3117835  |
| H     | 3.1643232  | 0.9598909  | 2.3117835  |
| H     | 4.8192091  | 1.2128590  | 2.3117835  |
| C     | 2.0715245  | -0.2343413 | 2.3117835  |
| H     | 1.5815444  | -0.6436449 | 2.3117835  |
| C     | 3.3296589  | 1.7342622  | 2.3117835  |
| C     | 2.4428079  | 1.1896450  | 2.3117835  |
| C     | 3.6656693  | 3.0909689  | 2.3117835  |
| H     | 4.3548973  | 3.5120224  | 2.3117835  |
| C     | 3.1278233  | 3.9120077  | 2.3117835  |
| C     | 3.988129   | 4.4273604  | 2.3117835  |
| C     | 2.4230557  | -2.9062237 | 2.3117835  |
| C     | 3.8457932  | 0.8505654  | 2.3117835  |
| H     | 3.1643232  | 0.9598909  | 2.3117835  |
| H     | 4.8192091  | 1.2128590  | 2.3117835  |
| C     | 2.0715245  | -0.2343413 | 2.3117835  |
| H     | 1.5815444  | -0.6436449 | 2.3117835  |
| C     | 3.3296589  | 1.7342622  | 2.3117835  |
| C     | 2.4428079  | 1.1896450  | 2.3117835  |
| C     | 3.6656693  | 3.0909689  | 2.3117835  |
| H     | 4.3548973  | 3.5120224  | 2.3117835  |
| C     | 3.1278233  | 3.9120077  | 2.3117835  |
| C     | 3.988129   | 4.4273604  | 2.3117835  |
| C     | 2.4230557  | -2.9062237 | 2.3117835  |
| C     | 3.8457932  | 0.8505654  | 2.3117835  |
| H     | 3.1643232  | 0.9598909  | 2.3117835  |
| H     | 4.8192091  | 1.2128590  | 2.3117835  |
| C     | 2.0715245  | -0.2343413 | 2.3117835  |
| H     | 1.5815444  | -0.6436449 | 2.3117835  |
| C     | 3.3296589  | 1.7342622  | 2.3117835  |
| C     | 2.4428079  | 1.1896450  | 2.3117835  |
| C     | 3.6656693  | 3.0909689  | 2.3117835  |
|   |   |   |                           |                           |                       |
|---|---|---|---------------------------|---------------------------|-----------------------|
| H | -0.6063092 | 2.4408627 | 2.3184644               |                           |                       |
| C | 0.5534047  | 3.6733751 | 3.6231110               |                           |                       |
| H | 0.1916201  | 4.6265908 | 3.2056938               |                           |                       |
| H | 1.5895307  | 3.8219308 | 3.9698538               |                           |                       |
| H | -0.0590372 | 3.4299270 | 4.5069383               |                           |                       |
| C | 0.9240983  | 1.1943702 | 3.1387363               |                           |                       |
| H | 1.9820172  | 1.2321859 | 3.4464990               |                           |                       |
| H | 0.8268792  | 0.3995188 | 2.3829522               |                           |                       |
| H | 0.3254262  | 0.9036978 | 4.0177239               |                           |                       |
| H | -1.5921123 | -1.6992917 | -3.0572062             |                           |                       |
| H | -1.5436308 | -0.6757534 | -2.6508112             |                           |                       |
| C | -2.9938900 | -1.8810294 | -3.6743214             |                           |                       |
| H | -3.7858657 | -1.8125032 | -2.9141181             |                           |                       |
| H | -3.0739338 | -2.8735312 | -4.1498927             |                           |                       |
| H | -3.1826369 | -1.1169621 | -4.4470593             |                           |                       |
| C | -0.5060986 | -1.8055115 | -4.1329061             |                           |                       |
| H | -0.5385631 | -2.7728270 | -4.6607672             |                           |                       |
| H | 0.4979971  | -1.6800347 | -3.7027381             |                           |                       |
| H | -2.4094107 | -2.7969637 | -1.8515980             |                           |                       |
| H | -3.3632389 | -2.2820513 | 1.6562425              |                           |                       |
| C | -2.7288065 | -3.9868625 | 2.7663865              |                           |                       |
| H | -3.2533885 | -3.6354466 | 3.6694203              |                           |                       |
| H | -1.8140754 | -4.5028548 | 3.1029061              |                           |                       |
| H | -3.3717689 | -4.7269965 | 2.2635762              |                           |                       |
| C | -1.4779878 | -1.8057778 | 2.5761186              |                           |                       |
| H | -1.9415331 | -1.4506468 | 3.5113813              |                           |                       |
| H | -1.2491281 | -0.9289364 | 1.9559796              |                           |                       |
| H | -0.5179396 | -2.2824931 | 2.8265151              |                           |                       |

**Cu^{III}(OH)(L)-DHA-IC**

\[ E_{B3LYP-D3/def2 TZVP/COSMO(\epsilon = 8.51)}: -3772.7083616292 \ (<S^2> 1.03681583) \]

\[ E_{B3LYP-D3/def2-TZVPP/COSMO(\epsilon = 8.51)}: -3775.0388727157 \ (S = 0; <S^2> 1.03541793) \]

\[ -3775.0388596882 \ (S = 1; <S^2> 2.03599411) \]

\[ -3775.038866999 \ (\text{spin purified}) \]

**ZPE**

\[ E_{B3LYP-D3/def2 TZVP/COSMO(\epsilon = 8.51)}: 0.852027 \]

**Chem. Pot.**

\[ E_{B3LYP-D3/def2 TZVP/COSMO(\epsilon = 8.51)}: 0.778106 \]
| H  | 0.8830765 | -0.9371731 | -0.6832474 |
| C  | 0.4569529 | 3.0608384  | -0.0399043 |
| C  | 3.0961804 | 3.9874720  | -0.0468659 |
| C  | 1.2326561 | 2.9661319  | 1.1418901  |
| C  | 1.0062118 | 3.5883485  | -1.2372085 |
| C  | 2.3299005 | 4.0490910  | -1.2148863 |
| C  | 2.5517512 | 3.4435553  | 1.1172716  |
| H  | 2.7757266 | 4.4661248  | -2.1200091 |
| H  | 3.1609778 | 3.3922548  | 2.0235894  |
| C  | 4.1256092 | 4.3562952  | -0.0497952 |
| C  | -1.4237614 | -2.3370140 | -0.5898623 |
| C  | 0.0828548 | -4.6191952 | -1.1747057 |
| C  | -1.0148275 | -3.2152635 | 0.4624393  |
| C  | -0.3152990 | -3.601540  | 0.1391281  |
| H  | 0.0674978 | -3.9416477 | -3.2177145 |
| H  | -0.0315342 | -5.0602040 | 0.9255036  |
| H  | 0.6672986 | -5.515323  | -1.4010732 |
| H  | 4.1942935 | 1.5044484  | -0.3112321 |
| C  | 3.8654907 | 0.5983675  | -0.8244352 |
| C  | 2.9835951 | -1.6991534 | -2.1534294 |
| C  | 3.7548061 | -0.5942101 | -0.1046343 |
| C  | 3.5440153 | 0.6566985  | -2.1888155 |
| C  | 3.140894 | -0.5034404 | -2.8536352 |
| C  | 3.2871173 | -1.7718999 | -0.7654518 |
| H  | 3.6246357 | 1.6054536  | -2.7234278 |
| H  | 2.8654059 | -0.4631039 | -3.9169232 |
| H  | 2.6169694 | -2.5960820 | -2.6591719 |
| C  | 4.1565565 | -0.6658566 | 1.3479373  |
| H  | 3.9540973 | 0.2927788  | 1.8499898  |
| H  | 5.2604569 | -0.7805513 | 1.3839516  |
| C  | 3.0551065 | -2.9625768 | -0.0116484 |
| H  | 2.7052148 | -3.8548656 | -0.5340635 |
| C  | 3.5522042 | -1.8149993 | 2.1196575  |
| C  | 3.1066470 | -2.9735670 | 1.4153530  |
| C  | 3.4806824 | -1.7913106 | 3.5140917  |
| H  | 3.8027346 | -0.8936543 | 4.0500649  |
| C  | 3.0080040 | -2.8970030 | 4.2331835  |
| H  | 2.9540915 | -2.8557895 | 5.3241100  |
| C  | 2.6585514 | -4.0960784 | 2.1609521  |
| H  | 2.3284948 | -4.9876994 | 1.6226760  |
| C  | 2.6096252 | -4.0578112 | 3.5495972  |
| H  | 2.2489528 | -4.9258896 | 4.1076831  |
| C  | 0.1667352 | 3.6079409  | -2.5109818 |
| H  | -0.8744961 | 3.7921120  | -2.2034969 |
| C  | 0.5544552 | 4.7199664  | -3.4940696 |
| H  | -0.1707621 | 4.7605223  | -4.3227600 |
|      | X      | Y      | Z     |
|------|--------|--------|-------|
|      | H      | 1.5479374 | 4.5471170 | -3.9402482 |
|      | H      | 0.5696571 | 5.7059328 | -3.0026412 |
| C    | 0.2038157 | 2.2342354 | -3.2090742 |
| H    | -0.4706985 | 2.2158571 | -4.0807104 |
| H    | -0.1027530 | 1.4241711 | -2.5310206 |
| H    | 1.2225607 | 2.0008802 | -3.5581085 |
| H    | 0.5696571 | 5.7059328 | -3.0026412 |
| C    | 0.2038157 | 2.2342354 | -3.2090742 |
| H    | -0.4706985 | 2.2158571 | -4.0807104 |
| H    | -0.1027530 | 1.4241711 | -2.5310206 |
| H    | 1.2225607 | 2.0008802 | -3.5581085 |
| C    | 1.4998267 | 1.3051493 | 3.0565702 |
| H    | 2.4824084 | 1.686457 | 3.3802814 |
| H    | 1.6666122 | 0.4805150 | 2.3481559 |
| H    | 1.0009052 | 0.8831555 | 3.948920 |
| C    | -1.4641355 | -1.6443318 | -3.0419587 |
| H    | -1.5574567 | -0.6380795 | -2.6016077 |
| C    | -2.8680392 | -2.045764 | -3.5360314 |
| H    | -3.5817969 | -2.116451 | -2.7015014 |
| H    | -2.8305973 | -3.0313403 | -4.0304561 |
| H    | -3.2513321 | -1.312152 | -4.2651786 |
| C    | -0.7442238 | -1.5341002 | -4.2072837 |
| H    | -0.4091114 | -2.4730755 | -4.7800315 |
| H    | 0.5336570 | -1.2715944 | -3.8514689 |
| H    | -0.8022425 | -0.7489546 | -4.9073536 |
| C    | -1.4311861 | -2.8827303 | 1.9039575 |
| H    | -2.4472175 | -2.4579277 | 1.8803392 |
| C    | -1.4742459 | -4.1048337 | 2.8309381 |
| H    | -1.8796553 | -3.8156014 | 3.8138831 |
| H    | -0.4676886 | -4.5194376 | 3.0042083 |
| H    | -2.1102321 | -4.9056428 | 2.4207217 |
| C    | -0.4834481 | -1.8126785 | 2.4822828 |
| H    | -0.7841531 | -1.5383396 | 3.5068133 |
| H    | -0.4849416 | -0.8956191 | 1.8776503 |
| H    | 0.5518896 | -2.1841424 | 2.5186830 |

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