Supporting Information for: First-principles study of non-heme Fe(II) halogenase SyrB2 reactivity

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S.1 Review of DFT+U methodology

The augmentation of standard exchange-correlation functionals (e.g. LDA or GGA) with a Hubbard-like U term, known as DFT+U or GGA+U, has primarily been applied to improve descriptions of correlated solid state materials. However, the fundamental underlying principles, many of which are outlined in Refs. [1,2], also serve to improve quantum chemical descriptions of transition-metal containing molecules.

The U term combats an unphysical curvature in the LDA or GGA energy with respect to occupations, which is present because of self-interaction error. In transition-metal molecules, the unphysical curvature is more commonly thought of as an overhybridization or delocalization of the $3d$ states of the metal with the associated ligands. The functional form of the U term in terms of occupations, n, from site I is:

$$E_U[n^{I\sigma}_{mm'}] = \frac{U}{2}\sum_{I,\sigma} Tr[\mathbf{n}^{I\sigma}(1-\mathbf{n}^{I\sigma})] \tag{1}$$

where the overall behavior is to penalize in energy non-integer occupations (i.e. not 0 or 1). In practice, this balances with the LDA or GGA tendency to overhybridize and instead finely tunes the relative occupancy of $3d$ levels. In the special case of electron transfer systems, the delocalization problem alone can lead to completely invalid results in which a single electron may be split between two metal sites. In a single site catalyst, the hybridization problem primarily manifests itself as overly short bond lengths, excessive bond dissociation energies, underestimated reaction exothermicities, and overestimated barrier heights. In the limit that this spurious hybridization is equal in all intermediates being compared, a cancellation of errors is possible.

However, intermediates, transition states and products almost always differ, and bond making and breaking events often produce systems which have either less or more self-interaction error, respectively. That is, in the example of O_2 binding on SyrB2 model catalyst, the bound complex in GGA overdelocalizes both the states of the Fe center and the formerly localized density of O_2. In order to obtain a dissociation energy for this complex, calculations on the isolated O_2 and SyrB2 catalyst will show that they experience markedly reduced delocalization. The result is that this self-interaction stabilizes the minimum of the binding curve more than it does the dissociated products, yielding an overestimate of the dissociation energy. Reaction step barriers and exothermicities have errors which are derived from a similar source. Interestingly, self-interaction errors in GGA can yield the incorrect spin state or symmetry for the ground state if there is a mismatch in the amount of self-interaction error between two states. For instance, a high-spin Fe state, which has density nearly exclusively in a majority spin manifold, has fewer channels for delocalization than a intermediate- or low- spin state which spreads partial $3d$ density into more majority and minority spin molecular orbitals. Furthermore, GGA can even change the essential character of the occupied molecular orbitals. While GGA errors in bond lengths and dissociation energies can be corrected for approximately, the effects on spin splittings and reaction barriers are far less systematically predictable, and, therefore, we prefer a GGA+U

approach.

A GGA+U approach for combatting self-interaction errors in standard GGA is preferred here to the more commonly applied hybrid functionals, in which a semi-empirically estimated amount of self-interaction free Hartree-Fock exchange is added to a standard LDA or GGA functional. While such hybrid functionals have been widely successful in treating organic systems, they exhibit many of the same errors as standard GGA in determining spin splittings, bond dissociation energies, and barrier heights and exothermicities. That is, it is likely that as the amount of self-interaction is not constant when comparing differing intermediates in a reaction coordinate, there is also a different amount of Hartree-Fock exchange which is appropriate for different configurations. Since the percentage of Hartree-Fock exchange is only a parameter, the appropriate amount for a given system is an unknown. We prefer here a GGA+U approach instead because the +U term we add may be calculated as an intrinsic linear response property of the system[1,2]. Specifics are not outlined here, but the GGA+U approach has been successfully applied to several small molecule systems in which standard GGA or LDA exhibit errors as large as 30 kcal/mol which have been reduced to the order of 1-2 kcal/mol by using GGA+U.

GGA+U does have its shortcomings, namely that total energies at differing values of U cannot be compared. The linear-response value of U is calculated for each intermediate and then averaged in order to obtain a global potential energy surface. In practice, common deviations of the local value of U from the global value of U by about 1-2 eV only result in energetic errors on the order of 1-2 kcal/mol. If increased accuracy is desired, the calculations may be repeated at a locally averaged U instead. Additional concerns with the method are addressed in Refs. [1,2]. Importantly, we note that GGA+U scales as favorably as standard GGA, thus making it possible to apply this method seamlessly to systems of several hundred atoms in size. Also, the GGA+U approach systematically improves upon complexes plagued by self-interaction error in a way that alternative methods, such as hybrid functionals, cannot. Where GGA+U does exhibit errors, either in over-elongation of bonds or in underestimating barrier heights, these errors are both smaller than those for GGA and can be identified systematically.

We provide here several details not included directly in the manuscript which demonstrate by example the effects of inclusion of a +U term in the calculations. Initial GGA calculations on our model SyrB2 complex without the Hubbard U correction revealed shortened iron-ligand bonds with respect to the crystal structure: the GGA Fe(II)-Cl bond length of 2.30 Å is 0.14 Å shorter than the experimental value of 2.44 Å and the calculated Fe-$O_{\alpha KG}$ distances, 1.93 Å and 2.09 Å , are shorter than experimental values by 0.10 Å. GGA+U instead recovers excellent agreement within 0.03 Å of experiment (see sections S.4 and S.6). Differences in GGA and GGA+U descriptions of electronic structure underlie these geometrical differences between GGA and GGA+U: GGA overestimates charge transfer from the iron center to surrounding ligands, predicting an Fe(III) oxidation state for the starting reactant complex, while GGA+U recovers the correct Fe(II) character (see section S.2). However, some of the superb agreement between GGA+U and experimental values from the full SyrB2 enzyme may, in part, be seen as a fortuitous cancellation of errors. That is, the absence of second

sphere ligands likely shortens iron-ligand bonds while GGA+U is known to over-elongate bonds when compared to other theoretical approaches.

S.2 Linear response value of the Hubbard U

The values of Hubbard U were calculated from linear response for several of the relevant intermediates in the reaction of SyrB2 model complex as follows:

Table S1: Values of Hubbard U calculated from linear response for several SyrB2 model complex reaction intermediates.

	Ground State		Excited State	
Configuration	$2S+1$	U (eV)	$2S+1$	U (eV)
$[Fe^{II}-OH_2]-Cl/\alpha KG$	5	5.85	3	6.46
$[Fe^{III}-O_2]-Cl/\alpha KG$	5	5.38	3	6.22
$[Fe^{IV}=O]-Cl/Succ.$	5	5.60	3	6.04
$[Fe^{III}-OH]-Cl/Succ.$	6	5.58	4	6.12
Average		5.60		6.21

The average over the lower energy spin states was obtained (U = 5.6 eV) and employed when studying reaction pathways and dissociation energies. The higher energy spin states have consistently higher values of linear-response U. However, since in these calculations we consider nearly exclusively the reactions along the ground state spin surface, we apply an average global U in our calculations consistent with the average among the lower energy spin states. Overall ,the range of values of U for these states is quite small, indicating that a global average here can appropriately capture the energetics. While in general, variation in U can be quite large, as it was in small molecule reactions in Refs. [1,2], the fact that the ligand set varies relatively slowly means that the variations in electronic structure and linear response properties are subtle.

S.3 GGA and GGA+U occupation matrices and oxidation states

The associated occupation matrices for both GGA and GGA+U=5.6 eV states of several intermediates is depicted here. The occupation matrices are obtained from projection onto $3d$ states of an isolated iron atom, and they serve as both a judge of the local iron character and as a means for calculating the +U term in the functional. Since the occupation matrices were used for determining oxidation states of intermediates, the enumeration of states which yield the associated oxidation state are also provided. The eigenvalues are the relative occupation of each state. The eigenvectors are enumerated in order of occupation, with 5 being associated with the largest occupation and 1 the smallest. The columns of the eigenvectors are ordered by the angular momentum– 1 is σ, 2 and 3 are π, 4 and 5 are δ. Occasionally, σ orbitals appear as an admixture of columns 1 and 4 or columns 1 and 5, as a result of both orbital elongation and the coordinates of the structure with respect to the definition of the canonical orbitals. The oxidation states are determined by counting the number of orbitals which are unshared, as indicated by near integer occupations (0.85-1.0 e^-).
For the $[\mathrm{Fe(II)}-\mathrm{OH_2}]-\mathrm{Cl}/\alpha\mathrm{KG}$ complex, we provide comparison to occupation matrices obtained from a larger-scale, 162 atom system that is defined by the 8 Å sphere around the iron center with hydrogen-capped unsaturated residues.

Occupation matrix for GGA $[\mathbf{Fe(II)}-\mathbf{OH_2}]-\mathbf{Cl}/\alpha\mathbf{KG}$
Quintet;Fe(III) $5e^-$;$3d_\uparrow:\delta^2\pi^2\sigma^1$; $3d_\downarrow:\delta^{0.13,0.30},\pi^{0.69,0.08}\sigma^{0.26}$

```
atom  1  spin  1
eigenvalues:  0.9940171 0.9963996 0.9972248 0.9981926 0.9989282
 eigenvectors
 1  -0.7100252 -0.1643070 -0.6199760 -0.2900251 -0.0195613
 2   0.3903634  0.2052727 -0.3548057 -0.2607593 -0.7820467
 3  -0.3482979 -0.4667985  0.6052929 -0.1414416 -0.5238344
 4  -0.4413265  0.8413014  0.2836174  0.0063204 -0.1302463
 5  -0.1655296 -0.0719545 -0.2071819  0.9098595 -0.3108919
 occupations
 0.996 -0.001 -0.001 -0.001  0.000
-0.001  0.998  0.000  0.000  0.000
-0.001  0.000  0.996 -0.001  0.000
-0.001  0.000 -0.001  0.998 -0.001
 0.000  0.000  0.000 -0.001  0.997
atom  1  spin  2
eigenvalues:  0.0812040 0.1299272 0.2553785 0.3015308 0.6870238
 eigenvectors
 1   0.2297305  0.8987210  0.1854058  0.0557720 -0.3194348
 2   0.1698841  0.0927887  0.1833572 -0.9049368  0.3316611
 3   0.7205170  0.0074821 -0.6723896  0.0581047  0.1591081
```

```
 4  -0.2247671  0.3450424 -0.0074644  0.3062226  0.8582526
 5   0.5905068 -0.2541270  0.6927058  0.2843069  0.1613983
 occupations
 0.395 -0.106  0.165  0.086  0.038
-0.106  0.147 -0.107 -0.025  0.042
 0.165 -0.107  0.452  0.104  0.051
 0.086 -0.025  0.104  0.191  0.073
 0.038  0.042  0.051  0.073  0.269
nsum =   6.4398265
```

Occupation matrix for GGA 162 atom complex $[\mathbf{Fe(II)-OH_2}]-\mathbf{Cl}/\alpha\mathbf{KG}$
Quintet;Fe(III) $5e^{-}$;$3d_{\uparrow}:\delta^{2}\pi^{2}\sigma^{1}$; $3d_{\downarrow}:\delta^{0.05,0.29}$, $\pi^{0.66,0.12}\sigma^{0.26}$

```
spin 1
eigenvalues:  0.9830817 0.9848731 0.9940010 0.9965156 0.9974190
 eigenvectors
 1  -0.3521413  0.3113858 -0.5813260  0.4110226  0.5216856
 2   0.1752463 -0.8677907 -0.1733921  0.4157150  0.1155170
 3  -0.4615966 -0.3590385  0.0164626 -0.6735547  0.4517444
 4   0.6228385  0.0444865 -0.6408095 -0.4455400  0.0308278
 5  -0.4942530 -0.1381683 -0.4701992 -0.0778436 -0.7137763
 occupations
 0.994  0.003 -0.002  0.000  0.003
 0.003  0.986  0.001  0.002 -0.001
-0.002  0.001  0.992  0.004  0.005
 0.000  0.002  0.004  0.991 -0.003
 0.003 -0.001  0.005 -0.003  0.993
spin  2
eigenvalues:  0.0533567 0.1259889 0.2590165 0.2874076 0.6629233
 eigenvectors
 1   0.2589510 -0.1071250 -0.5680427 -0.0974633  0.7676569
 2   0.3977195  0.2108521  0.7431563  0.1662949  0.4662889
 3  -0.7868107  0.3172830  0.0147436  0.3795282  0.3687837
 4   0.3569176  0.1125962 -0.2851648  0.8578180 -0.2067880
 5  -0.1682333 -0.9114380  0.2085902  0.2880166  0.1204778
 occupations
 0.269  0.024 -0.012  0.018 -0.019
 0.024  0.646 -0.033 -0.030 -0.016
-0.012 -0.033  0.133 -0.015  0.019
 0.018 -0.030 -0.015  0.290 -0.008
-0.019 -0.016  0.019 -0.008  0.071
nsum =   6.4650380
```

Occupation matrix for GGA + U $[\mathbf{Fe(II)-OH_2}]-\mathbf{Cl}/\alpha\mathbf{KG}$
Quintet; Fe(II) $6e^{-}$;$3d_{\uparrow}:\delta^{2}\pi^{2}\sigma^{1}$; $3d_{\downarrow}:\delta^{0.21,0.05}$, $\pi^{0.95,0.03}\sigma^{0.15}$

```
spin  1
eigenvalues:  0.9947801 0.9970040 0.9981402 0.9988598 0.9996248
 eigenvectors
 1   0.2325788 -0.1547226  0.9097099  0.2884229  0.1058685
 2  -0.8714961 -0.1095498  0.1305989  0.0649826  0.4552082
 3  -0.3842698 -0.1252868  0.2810556 -0.3515287 -0.7962885
 4  -0.1357891  0.9605929  0.1605971  0.1538054 -0.0968246
 5  -0.1424769 -0.1600756 -0.2249181  0.8748491 -0.3716544
 occupations
 0.997  0.000 -0.001  0.000  0.000
 0.000  0.999  0.001  0.000  0.000
-0.001  0.001  0.995 -0.001  0.000
 0.000  0.000 -0.001  0.999 -0.001
 0.000  0.000  0.000 -0.001  0.998
spin  2
eigenvalues:  0.0354089 0.0547922 0.1468947 0.2102464 0.9455464
 eigenvectors
 1  -0.3063173 -0.8712169 -0.3236580  0.0762745  0.1912549
 2   0.1122186 -0.0679928  0.1082992 -0.8958281  0.4105451
 3  -0.8008639  0.0269540  0.5672828 -0.1060182 -0.1576095
 4   0.2076970 -0.2941280  0.0016577 -0.3481221 -0.8655397
 5   0.4572260 -0.3861609  0.7494693  0.2434038  0.1444802
 occupations
 0.305 -0.174  0.262  0.096  0.044
-0.174  0.186 -0.262 -0.067 -0.007
 0.262 -0.262  0.583  0.157  0.089
 0.096 -0.067  0.157  0.127  0.079
 0.044 -0.007  0.089  0.079  0.191
nsum =   6.3812973
```

Occupation matrix for GGA + U 162 atom complex $[\mathbf{Fe(II)-OH_2}]-\mathbf{Cl}/\alpha\mathbf{KG}$
Quintet;Fe(II) $6e^{-}$;$3d_{\uparrow}:\delta^{2}\pi^{2}\sigma^{1}$; $3d_{\downarrow}:\delta^{0.14,0.21}, \pi^{0.97,0.03}\sigma^{0.03}$

```
spin 1
eigenvalues:  0.9880317 0.9896347 0.9951735 0.9968503 0.9977820
 eigenvectors
 1   0.2972893 -0.6394276  0.4597451 -0.1861821 -0.5066774
 2  -0.0087606  0.6909286  0.3481074 -0.5120272 -0.3730821
 3  -0.4635251 -0.3148430  0.0758482 -0.6921637  0.4485251
 4  -0.7678835 -0.0142211  0.4240141  0.4330372 -0.2069867
 5   0.3271724  0.1200900  0.6942007  0.1911871  0.6000579
 occupations
 0.996  0.002 -0.001  0.000  0.002
 0.002  0.990  0.001  0.001 -0.001
-0.001  0.001  0.995  0.002  0.003
 0.000  0.001  0.002  0.994 -0.002
 0.002 -0.001  0.003 -0.002  0.994
spin  2
eigenvalues:  0.0298501 0.0337537 0.1369979 0.2160290 0.9756527
 eigenvectors
 1   0.4975879  0.1432586  0.7308657  0.0292870  0.4436901
 2   0.6951653 -0.2652842 -0.3088904 -0.5738206 -0.1472621
 3  -0.5052214 -0.0046780  0.2289401 -0.7956273  0.2435016
 4   0.0228085  0.0218944 -0.5335991  0.0890626  0.8404405
 5  -0.1156831 -0.9532051  0.1824295  0.1700506  0.1257763
 occupations
 0.048  0.009 -0.021  0.022  0.009
 0.009  0.209 -0.026 -0.011  0.007
-0.021 -0.026  0.305 -0.052 -0.419
 0.022 -0.011 -0.052  0.127  0.062
 0.009  0.007 -0.419  0.062  0.703
nsum =   6.3619755
```

Occupation matrix for GGA $[\mathbf{Fe(II)-OH_2}]-\mathbf{Cl}/\alpha\mathbf{KG}$
Triplet; Fe(II)/Fe(III)? $5/6e^{-}$;$3d_{\uparrow}:\delta^{1,0.54}\pi^{2}\sigma^{1}$; $3d_{\downarrow}:\delta^{1,0.39},\pi^{0.53,0.11}\sigma^{0.26}$

```
spin  1
eigenvalues:  0.5379138 0.9834689 0.9901938 0.9942188 0.9960839
 eigenvectors
 1  -0.1095411  0.3150781 -0.1893538  0.3405038  0.8584456
 2   0.5361921  0.1618218  0.7974077  0.1977821  0.1064659
 3   0.5079127  0.6977809 -0.3947432 -0.2625929 -0.1742107
 4   0.5934588 -0.4920487 -0.4152629  0.4822310 -0.0265494
 5   0.3005498 -0.3814832 -0.0045560 -0.7371822  0.4697680
 occupations
 0.985  0.013 -0.013  0.016  0.043
 0.013  0.947  0.027 -0.048 -0.123
-0.013  0.027  0.970  0.027  0.073
 0.016 -0.048  0.027  0.942 -0.134
 0.043 -0.123  0.073 -0.134  0.658
spin  2
eigenvalues:  0.1176820 0.2561953 0.3892595 0.5260497 0.9807751
 eigenvectors
 1   0.0260482  0.8353803  0.0500409  0.3395905 -0.4285271
 2   0.8208375 -0.0051485 -0.5694459  0.0432674  0.0076494
 3  -0.2083449  0.3324041 -0.2703671  0.2868658  0.8310894
 4  -0.4935877  0.0671921 -0.7428613 -0.3573329 -0.2689362
 5   0.1962417  0.4325575  0.2197408 -0.8202606  0.2308025
 occupations
 0.356  0.040  0.138 -0.078  0.047
 0.040  0.311  0.038 -0.290  0.154
 0.138  0.038  0.449 -0.072  0.064
-0.078 -0.290 -0.072  0.773 -0.059
 0.047  0.154  0.064 -0.059  0.381
nsum =   6.7718407
```

Occupation matrix for GGA + U $[\mathbf{Fe(II)-OH_2}]-\mathbf{Cl}/\alpha\mathbf{KG}$
Triplet; Fe(II) $6e^{-}$;$3d_{\uparrow}:\delta^{2}\pi^{2}\sigma^{0.25}$; $3d_{\downarrow}:\delta^{0.21,0.05}$, $\pi^{0.99,0.98}\sigma^{0.16}$

```
spin  1
eigenvalues:  0.2549145 0.9909813 0.9955894 0.9976750 0.9990405
 eigenvectors
 1   0.8345574 -0.1393383 -0.4959135 -0.0942720 -0.1711180
 2  -0.4971194  0.1066314 -0.8100142 -0.2921830 -0.0028688
 3  -0.0832449 -0.8435486 -0.0989926  0.1032010  0.5109266
 4   0.1825027  0.5046003 -0.1585859  0.3057242  0.7703600
 5   0.1270798  0.0549440  0.2509938 -0.8953347  0.3408956
 occupations
 0.479  0.087  0.305  0.057  0.106
 0.087  0.982 -0.051 -0.009 -0.017
 0.305 -0.051  0.811 -0.037 -0.063
 0.057 -0.009 -0.037  0.992 -0.013
 0.106 -0.017 -0.063 -0.013  0.976
spin  2
eigenvalues:  0.0533123 0.1608565 0.2139967 0.9709367 0.9891774
 eigenvectors
 1   0.2237922  0.0277836  0.1888841 -0.8719208  0.3914360
 2  -0.7990528  0.0274599  0.5673597 -0.1424752 -0.1362507
 3   0.1958162 -0.3165663 -0.0027461 -0.3468976 -0.8608695
 4  -0.4938776  0.1653876 -0.7928850 -0.3131963 -0.0444214
 5   0.1707996  0.9332238  0.1172672 -0.0320179 -0.2917945
 occupations
 0.379  0.062  0.329  0.138 -0.042
 0.062  0.910 -0.016 -0.058 -0.218
 0.329 -0.016  0.678  0.216 -0.008
 0.138 -0.058  0.216  0.166  0.072
-0.042 -0.218 -0.008  0.072  0.256
nsum =   6.6264804
```

Occupation matrix for GGA $[\mathbf{Fe(III)-O_2}]-\mathbf{Cl}/\alpha\mathbf{KG}$
Quintet; Fe(III) $5e^{-}$;$3d_{\uparrow}:\delta^{2}\pi^{2}\sigma^{0.9}$; $3d_{\downarrow}:\delta^{0.55,0.30}$, $\pi^{0.2,0.1}\sigma^{0.16}$

```
spin  1
eigenvalues:  0.8721801 0.9867729 0.9911968 0.9954858 0.9961101
 eigenvectors
 1  -0.4448137  0.3730540  0.3030109  0.3568501  0.6661936
 2   0.4805632  0.6309604 -0.5746392  0.0913815  0.1799645
 3  -0.1212308 -0.5822825 -0.5805922 -0.0773329  0.5506202
 4   0.7242817 -0.2191587  0.4863882 -0.0820503  0.4290452
 5   0.1786587 -0.2750205 -0.0656777  0.9228189 -0.1911452
 occupations
 0.969  0.017  0.019  0.019  0.036
 0.017  0.973 -0.012 -0.017 -0.030
 0.019 -0.012  0.980 -0.013 -0.023
 0.019 -0.017 -0.013  0.980 -0.029
 0.036 -0.030 -0.023 -0.029  0.939
spin  2
eigenvalues:  0.1094334 0.1603893 0.2115913 0.2944935 0.5526740
 eigenvectors
 1  -0.3612209 -0.6594669 -0.4900383  0.2904149  0.3318804
 2  -0.7139672  0.1084943 -0.2065935 -0.3522108 -0.5583427
 3  -0.3148819 -0.4331218  0.8371332  0.0981561 -0.0531821
 4  -0.5105076  0.5816116  0.1194406  0.2243564  0.5800932
 5   0.0013092 -0.1657285  0.0460826 -0.8553574  0.4886434
 occupations
 0.194 -0.045 -0.031 -0.012 -0.032
-0.045  0.204 -0.029  0.081  0.026
-0.031 -0.029  0.187  0.000  0.024
-0.012  0.081  0.000  0.450 -0.152
-0.032  0.026  0.024 -0.152  0.294
nsum =   6.1703273
```

Occupation matrix for GGA + U [Fe(III)−O_2]−Cl/αKG
Quintet; Fe(III) $5e^{-}$;$3d_{\uparrow}:\delta^{2}\pi^{2}\sigma^{0.9}$; $3d_{\downarrow}:\delta^{0.77,0.15}\pi^{0.18,0.03}\sigma^{0.03}$

```
spin  1
eigenvalues:  0.9336635 0.9940004 0.9952243 0.9973008 0.9977537
 eigenvectors
 1   0.4115769 -0.3264249 -0.2904279 -0.3884926 -0.6991255
 2  -0.4797716 -0.5514964  0.6340586 -0.1130887 -0.2255030
 3   0.2049921  0.6771308  0.5900588 -0.1393658 -0.3631527
 4   0.2679102 -0.1608589  0.1119007  0.8912843 -0.3089323
 5   0.6975859 -0.3239086  0.3910629 -0.1499133  0.4827556
 occupations
 0.986  0.007  0.008  0.010  0.018
 0.007  0.989 -0.006 -0.008 -0.014
 0.008 -0.006  0.990 -0.007 -0.012
 0.010 -0.008 -0.007  0.988 -0.018
 0.018 -0.014 -0.012 -0.018  0.966
spin  2
eigenvalues:  0.0302761 0.0337464 0.1492976 0.1798544 0.7732524
 eigenvectors
 1   0.0316368 -0.7681715 -0.2847228  0.4624826  0.3375714
 2   0.7723873  0.1188064  0.5038175  0.2821684  0.2363297
 3   0.0998545  0.5627073 -0.6215938  0.1757306  0.5060924
 4  -0.6219794  0.1720480  0.5213621  0.3106838  0.4638946
 5   0.0747504 -0.2226154  0.0830877 -0.7609764  0.5990543
 occupations
 0.096 -0.021 -0.050 -0.068 -0.003
-0.021  0.109 -0.042  0.146 -0.053
-0.050 -0.042  0.123 -0.035  0.036
-0.068  0.146 -0.035  0.479 -0.306
-0.003 -0.053  0.036 -0.306  0.360
nsum =   6.0843697
```

Occupation matrix for GGA $[\mathbf{Fe(III)-O_2}]-\mathbf{Cl}/\alpha\mathbf{KG}$
Triplet; Fe(III) $5e^{-}$;$3d_{\uparrow}:\delta^{2}\pi^{2}\sigma^{0.65}$; $3d_{\downarrow}:\delta^{0.28,0.15}\pi^{0.92,0.22}\sigma^{0.16}$

```
spin  1
eigenvalues:  0.6483649 0.9552740 0.9803846 0.9880854 0.9946903
 eigenvectors
 1   0.5516776 -0.3067685 -0.4052295 -0.3732946 -0.5458802
 2  -0.0542755 -0.0548974  0.2686202  0.6737011 -0.6841129
 3  -0.4402149 -0.8937790  0.0186132 -0.0421824  0.0724159
 4  -0.0643697  0.0532374  0.7659262 -0.5783996 -0.2680173
 5  -0.7034013  0.3181261 -0.4202889 -0.2654289 -0.3961403
 occupations
 0.886  0.053  0.078  0.072  0.103
 0.053  0.951 -0.043 -0.039 -0.058
 0.078 -0.043  0.931 -0.057 -0.068
 0.072 -0.039 -0.057  0.926 -0.053
 0.103 -0.058 -0.068 -0.053  0.872
spin  2
eigenvalues:  0.1480337 0.1637471 0.2190462 0.2797313 0.9243509
 eigenvectors
 1   0.3195297 -0.1115964 -0.3430172  0.8715310 -0.0906640
 2   0.6617549 -0.3375234  0.3835038 -0.0784028  0.5430803
 3   0.3653398  0.3546395 -0.7433852 -0.3552229  0.2489030
 4   0.4004257 -0.4366236 -0.1038450 -0.3197486 -0.7321176
 5  -0.4076362 -0.7464682 -0.4145584 -0.0765782  0.3144757
 occupations
 0.315  0.219  0.110 -0.003 -0.126
 0.219  0.616  0.225  0.054 -0.137
 0.110  0.225  0.324  0.047 -0.101
-0.003  0.054  0.047  0.175  0.005
-0.126 -0.137 -0.101  0.005  0.304
nsum =   6.3017084
```

Occupation matrix for GGA + U [Fe(III)−O_2]−Cl/αKG
Triplet; Fe(III) $5e^{-}$;$3d_{\uparrow}:\delta^{2}\pi^{2}\sigma^{0.83}$; $3d_{\downarrow}:\delta^{0.15,0.04}\pi^{1,0.1}\sigma^{0.06}$

```
spin  1
eigenvalues:  0.8266948 0.9838528 0.9926953 0.9936001 0.9974970
 eigenvectors
 1  -0.4818400  0.4535775  0.2175168  0.2959860  0.6535873
 2   0.0907868 -0.0571099 -0.1430183 -0.8291596  0.5296568
 3   0.5120296  0.8319773 -0.1687325 -0.0496065 -0.1212766
 4  -0.0919838  0.1650500  0.8600127 -0.3638428 -0.3037992
 5  -0.6992515  0.2675411 -0.4051415 -0.3000737 -0.4304478
 occupations
 0.966  0.027  0.015  0.020  0.041
 0.027  0.967 -0.013 -0.018 -0.038
 0.015 -0.013  0.988 -0.009 -0.017
 0.020 -0.018 -0.009  0.976 -0.020
 0.041 -0.038 -0.017 -0.020  0.937
spin  2
eigenvalues:  0.0416380 0.0585601 0.1047299 0.1544404 0.9827662
 eigenvectors
 1  -0.4325619 -0.4078559 -0.1005612 -0.7420906  0.2928017
 2  -0.6508505  0.4464453 -0.1087062 -0.0872245 -0.5980427
 3   0.1111197  0.5123640 -0.7422172 -0.0844966  0.4087902
 4  -0.5145152  0.2506959  0.3988606  0.3538808  0.6229802
 5   0.3349782  0.5558551  0.5177781 -0.5561674  0.0373951
 occupations
 0.185  0.159  0.136 -0.196 -0.015
 0.159  0.359  0.257 -0.284  0.046
 0.136  0.257  0.347 -0.251  0.028
-0.196 -0.284 -0.251  0.347  0.004
-0.015  0.046  0.028  0.004  0.103
nsum =   6.1164746
```

Occupation matrix for GGA [Fe(IV)=O]−Cl/succ.
Quintet; Fe(IV) $4e^{-}$;$3d_{\uparrow}:\delta^{2}\pi^{2}\sigma^{0.6}$; $3d_{\downarrow}:\delta^{0.43,0.40}\pi^{0.43,0.16}\sigma^{0.20}$

```
spin  1
eigenvalues:  0.5878639 0.9907740 0.9921490 0.9955053 0.9957470
 eigenvectors
 1  -0.4449712 -0.0523276 -0.0712107  0.8902435  0.0407176
 2   0.2555587 -0.1053267  0.1898703  0.0938581  0.9374092
 3   0.7504923 -0.4173541 -0.3187828  0.3351726 -0.2204850
 4   0.1930868  0.7805662 -0.5703045  0.0902993  0.1415369
 5  -0.3690109 -0.4502222 -0.7293892 -0.2795756  0.2257428
 occupations
 0.913 -0.008 -0.012  0.161  0.007
-0.008  0.994 -0.002  0.020  0.001
-0.012 -0.002  0.993  0.026  0.000
 0.161  0.020  0.026  0.672 -0.015
 0.007  0.001  0.000 -0.015  0.991
spin  2
eigenvalues:  0.1621507 0.2048540 0.3988132 0.4258616 0.4267829
 eigenvectors
 1   0.2238140 -0.0481875  0.9324840  0.2208438  0.1711342
 2   0.8093379 -0.2112868 -0.3147818  0.4482051  0.0188335
 3  -0.4762953  0.1451724 -0.1065190  0.8473536  0.1507092
 4   0.1334016  0.4240329 -0.1298285 -0.1687377  0.8700990
 5  -0.2241121 -0.8672698 -0.0564301 -0.0621256  0.4365465
 occupations
 0.262  0.043  0.000 -0.082 -0.012
 0.043  0.416 -0.002  0.020  0.002
 0.000 -0.002  0.174 -0.021 -0.040
-0.082  0.020 -0.021  0.349 -0.015
-0.012  0.002 -0.040 -0.015  0.418
nsum =   6.1805016
```

Occupation matrix for GGA + U [Fe(IV)=O]−Cl/succ.
Quintet; Fe(IV) $4e^{-}$;$3d_{\uparrow}:\delta^{2}\pi^{2}\sigma^{0.7}$; $3d_{\downarrow}:\delta^{0.35,0.37}\pi^{0.40,0.08}\sigma^{0.12}$

```
spin  1
eigenvalues:  0.7331506 0.9944138 0.9948621 0.9965893 0.9969035
 eigenvectors
 1  -0.4592029 -0.0551156 -0.0681506  0.8831809  0.0379733
 2  -0.5684949  0.2761612 -0.0611487 -0.2516648 -0.7303932
 3   0.5612066 -0.3081992 -0.3719459  0.2703176 -0.6153414
 4   0.3352429  0.9086861 -0.1118046  0.2217158  0.0156062
 5  -0.1964831 -0.0001010 -0.9169364 -0.1855447  0.2935902
 occupations
 0.940 -0.006 -0.008  0.106  0.004
-0.006  0.995 -0.001  0.013  0.001
-0.008 -0.001  0.995  0.016  0.000
 0.106  0.013  0.016  0.791 -0.009
 0.004  0.001  0.000 -0.009  0.994
spin  2
eigenvalues:  0.0804569 0.1232691 0.3522261 0.3721384 0.3983441
 eigenvectors
 1   0.0347894  0.0093427  0.9750796  0.1041210  0.1925642
 2   0.8354100 -0.2800647 -0.0871559  0.4616280  0.0543816
 3   0.4250528 -0.2030109  0.1228183 -0.8416579 -0.2337613
 4  -0.1371311 -0.2091801  0.1605976  0.2598154 -0.9187726
 5  -0.3184416 -0.9146074 -0.0273430 -0.0128967  0.2473342
 occupations
 0.197  0.067  0.007 -0.090 -0.013
 0.067  0.374 -0.008  0.029 -0.004
 0.007 -0.008  0.093 -0.018 -0.053
-0.090  0.029 -0.018  0.302 -0.016
-0.013 -0.004 -0.053 -0.016  0.361
nsum =   6.0423541
```

Occupation matrix for GGA [Fe(IV)=O]−Cl/succ.
Triplet; Fe(IV) $4e^{-}$;$3d_{\uparrow}:\delta^{1,0.5}\pi^{2}\sigma^{0.4}$; $3d_{\downarrow}:\delta^{0.43,0.42}\pi^{1,0.44}\sigma^{0.29}$

```
spin  1
eigenvalues:  0.3977059 0.4859566 0.9804376 0.9900988 0.9926662
 eigenvectors
 1   0.7191649  0.1611846  0.1845864  0.6499442 -0.0179369
 2   0.6183479  0.1924253  0.0733470 -0.7548038 -0.0742275
 3   0.0612937  0.0295838 -0.0194222 -0.0421385  0.9966017
 4   0.2766441 -0.4046164 -0.8704437  0.0408870 -0.0202382
 5   0.1419818 -0.8788643  0.4499984 -0.0663043  0.0233228
 occupations
 0.491 -0.129 -0.101 -0.042  0.030
-0.129  0.958 -0.026  0.011  0.009
-0.101 -0.026  0.968 -0.043  0.005
-0.042  0.011 -0.043  0.453 -0.021
 0.030  0.009  0.005 -0.021  0.978
 spin  2
eigenvalues:  0.2886359 0.4223852 0.4342424 0.4447746 0.9853264
 eigenvectors
 1  -0.8197485  0.1538919 -0.1539434 -0.4884283 -0.2051069
 2   0.4639118 -0.2669898  0.0451625 -0.8384945 -0.0915944
 3  -0.2515431 -0.6405436 -0.1716810 -0.0214294  0.7046250
 4  -0.1258738 -0.7033733  0.1028863  0.2311138 -0.6522443
 5  -0.1835212 -0.0019172  0.9665412 -0.0670217  0.1662004
 occupations
 0.353  0.021 -0.117 -0.047 -0.040
 0.021  0.435  0.002  0.007  0.009
-0.117  0.002  0.946 -0.046  0.083
-0.047  0.007 -0.046  0.394 -0.023
-0.040  0.009  0.083 -0.023  0.448
nsum =   6.4222295
```

Occupation matrix for GGA + U [Fe(IV)=O]−Cl/succ.
Triplet; Fe(IV) $4e^{-}$;$3d_{\uparrow}:\delta^{2}\pi^{1,0.76}\sigma^{0.74}$;$3d_{\downarrow}:\delta^{0.07,0.21}\pi^{1,0.06}\sigma^{0.11}$

```
spin  1
eigenvalues:  0.7369983 0.7617539 0.9943715 0.9959887 0.9967513
 eigenvectors
 1  -0.5118424 -0.0446654 -0.0338603  0.8567220  0.0300534
 2  -0.2226218 -0.9018190 -0.0193790 -0.1918777  0.3161795
 3  -0.8014064  0.1820693  0.1546688 -0.4523154 -0.3099788
 4   0.0932580 -0.2870000 -0.5727521  0.0448066 -0.7608425
 5  -0.1936686  0.2630766 -0.8040588 -0.1503778  0.4734545
 occupations
 0.925 -0.013 -0.004  0.112  0.006
-0.013  0.768 -0.001  0.004  0.010
-0.004 -0.001  0.996  0.008  0.000
 0.112  0.004  0.008  0.804 -0.005
 0.006  0.010  0.000 -0.005  0.992
spin  2
eigenvalues:  0.0589228 0.0731207 0.1118726 0.2075111 0.9929478
 eigenvectors
 1   0.1319240 -0.1973329 -0.7041829 -0.0513390 -0.6671930
 2   0.0751882 -0.2773827  0.6783013  0.2282544 -0.6365634
 3   0.9121285  0.1668088 -0.0264878  0.3493512  0.1320932
 4  -0.3534364 -0.0717620 -0.2038306  0.9049913  0.0968340
 5   0.1415880 -0.9225744 -0.0422532 -0.0648750  0.3504499
 occupations
 0.140 -0.110  0.005 -0.039  0.047
-0.110  0.857  0.036  0.048 -0.299
 0.005  0.036  0.073 -0.023 -0.023
-0.039  0.048 -0.023  0.192 -0.008
 0.047 -0.299 -0.023 -0.008  0.182
nsum =   6.1302386
```

Occupation matrix for GGA [Fe(III)−OH]−Cl/succ.
Sextet; Fe(III) $5e^{-}$;$3d_{\uparrow}:\delta^{2}\pi^{2}\sigma^{1}$; $3d_{\downarrow}:\delta^{0.33,0.45}\pi^{0.12,0.25}\sigma^{0.20}$

```
spin  1
eigenvalues:  1.0029409 1.0039065 1.0049503 1.0052189 1.0056664
 eigenvectors
 1  -0.2548907 -0.1852217  0.0171874 -0.7017150 -0.6387678
 2   0.9117159 -0.1628953 -0.2929404 -0.2243819 -0.0779609
 3   0.2020650  0.9080449  0.2447543 -0.0655103 -0.2653826
 4  -0.2509328  0.3283893 -0.8817310 -0.1622544  0.1594277
 5  -0.0027033 -0.0822982 -0.2766520  0.6531697 -0.7000376
 occupations
 1.004  0.000  0.000  0.000  0.000
 0.000  1.005  0.000  0.000  0.000
 0.000  0.000  1.005  0.000  0.000
 0.000  0.000  0.000  1.004 -0.001
 0.000  0.000  0.000 -0.001  1.004
spin  2
eigenvalues:  0.1215822 0.2045589 0.2544606 0.3341755 0.4113519
 eigenvectors
 1   0.1631923  0.8171442  0.2597340  0.3995768 -0.2802147
 2   0.5325841 -0.4191321 -0.1688578  0.7138659 -0.0506454
 3  -0.1080792 -0.3036096  0.9321928  0.1300556  0.1012040
 4  -0.5700379 -0.2241781 -0.0878193  0.2193721 -0.7542975
 5  -0.5942206  0.1190339 -0.1653169  0.5154564  0.5828446
 occupations
 0.318 -0.007  0.018 -0.086 -0.013
-0.007  0.163 -0.033 -0.023  0.054
 0.018 -0.033  0.249 -0.023 -0.001
-0.086 -0.023 -0.023  0.253  0.051
-0.013  0.054 -0.001  0.051  0.343
nsum =   6.3488121
```

Occupation matrix for GGA + U [Fe(III)−OH]−Cl/succ.
Sextet; Fe(III) $5e^{-}$;$3d_{\uparrow}:\delta^{2}\pi^{2}\sigma^{1}$; $3d_{\downarrow}:\delta^{0.45,0.08}\pi^{0.15,0.22}\sigma^{0.29}$

```
spin  1
eigenvalues:  1.0040725 1.0047993 1.0054974 1.0056492 1.0060692
 eigenvectors
 1   0.3730316 -0.1845787 -0.2567958 -0.5679481 -0.6620189
 2  -0.9004791 -0.1543698  0.1210916 -0.2482081 -0.2983907
 3  -0.2007877  0.6854644 -0.6994265 -0.0163131 -0.0189533
 4   0.0966738  0.6680557  0.6372373 -0.0083927 -0.3717714
 5  -0.0179824 -0.1610616 -0.1553186  0.7845325 -0.5780318
 occupations
 1.005  0.000  0.000  0.000  0.000
 0.000  1.006  0.000  0.000  0.000
 0.000  0.000  1.005  0.000  0.000
 0.000  0.000  0.000  1.005 -0.001
 0.000  0.000  0.000 -0.001  1.005
spin  2
eigenvalues:  0.0815562 0.1450419 0.2244013 0.2934211 0.4461270
 eigenvectors
 1  -0.1830327 -0.6012169 -0.1373255 -0.6440666  0.4139532
 2   0.5260300 -0.6076506 -0.2733224  0.5233720  0.0736875
 3  -0.3282061 -0.4364157  0.7890381  0.2527047 -0.1240217
 4   0.6138766  0.2285157  0.5153379 -0.1571439  0.5297818
 5  -0.4530208  0.1631594 -0.1352121  0.4719175  0.7260597
 occupations
 0.269  0.003  0.043 -0.093 -0.043
 0.003  0.153 -0.022 -0.015  0.074
 0.043 -0.022  0.238 -0.021  0.007
-0.093 -0.015 -0.021  0.194  0.105
-0.043  0.074  0.007  0.105  0.336
nsum =   6.2166351
```

Occupation matrix for GGA [Fe(III)−OH]−Cl/succ.
Quartet; Fe(III) $5e^{-}$;$3d_{\uparrow}:\delta^{2}\pi^{2}\sigma^{0.6}$; $3d_{\downarrow}:\delta^{0.4,0.32}\pi^{1,0.24}\sigma^{0.22}$

```
spin  1
eigenvalues:  0.5947124 0.9931136 0.9961313 1.0037765 1.0047542
 eigenvectors
 1  -0.7082431  0.0819544  0.1125481  0.4469128  0.5284667
 2  -0.2478117 -0.8381902 -0.3383577 -0.3192998  0.1399580
 3   0.6178789 -0.1605377 -0.3115603  0.4924579  0.5028606
 4   0.1804148 -0.4646164  0.8492634  0.1736143 -0.0138486
 5  -0.1505231 -0.2215397 -0.2335140  0.6524262 -0.6693834
 occupations
 0.795  0.022  0.033  0.126  0.151
 0.022  0.993 -0.007 -0.017 -0.016
 0.033 -0.007  0.997 -0.021 -0.022
 0.126 -0.017 -0.021  0.920 -0.098
 0.151 -0.016 -0.022 -0.098  0.888
spin  2
eigenvalues:  0.2178908 0.2395764 0.3173604 0.4031960 0.9989536
 eigenvectors
 1   0.4722305 -0.4513257  0.1562959  0.7398318  0.0390389
 2  -0.0961035 -0.1734764  0.9030456 -0.2504147  0.2871780
 3  -0.6447089 -0.2952562  0.1460446  0.2347700 -0.6486357
 4  -0.5740612  0.1986445 -0.0921823  0.4737846  0.6308920
 5  -0.1502222 -0.7997344 -0.3609068 -0.3321936  0.3118523
 occupations
 0.350  0.083  0.041 -0.039 -0.075
 0.083  0.710  0.202  0.212 -0.139
 0.041  0.202  0.336  0.078 -0.100
-0.039  0.212  0.078  0.357 -0.026
-0.075 -0.139 -0.100 -0.026  0.423
nsum =   6.7694651
```

Occupation matrix for GGA + U [Fe(III)−OH]−Cl/succ.
Quartet; Fe(III) $5e^{-}$;$3d_{\uparrow}:\delta^{2}\pi^{2}\sigma^{0.76}$; $3d_{\downarrow}:\delta^{0.36,0.10}\pi^{1,0.11}\sigma^{0.19}$

```
spin  1
eigenvalues:  0.7628402 1.0022128 1.0033051 1.0060297 1.0063318
 eigenvectors
 1  -0.6800114  0.0774541  0.0954180  0.4615860  0.5562545
 2   0.6346829  0.4609406 -0.0291970  0.5693984  0.2442218
 3   0.2651629 -0.7099636 -0.4663421  0.0613383  0.4521095
 4  -0.1808220  0.4859268 -0.8108496 -0.2627251  0.0683892
 5  -0.1781968 -0.2033752 -0.3392506  0.6244493 -0.6495048
 occupations
 0.892  0.012  0.016  0.075  0.091
 0.012  1.002 -0.003 -0.010 -0.010
 0.016 -0.003  1.003 -0.011 -0.012
 0.075 -0.010 -0.011  0.953 -0.063
 0.091 -0.010 -0.012 -0.063  0.930
spin  2
eigenvalues:  0.1002973 0.1151654 0.1914284 0.3617344 0.9934838
 eigenvectors
 1   0.4131672 -0.5766790  0.1113129  0.6942163  0.0490655
 2   0.0746220 -0.0418018  0.8772206 -0.2482015  0.4019506
 3  -0.6685406 -0.3352775  0.3302945  0.1064091 -0.5658845
 4  -0.5868732  0.1909770 -0.0888938  0.4784795  0.6182741
 5  -0.1798827 -0.7188955 -0.3179574 -0.4649669  0.3654316
 occupations
 0.260  0.107  0.046 -0.005 -0.119
 0.107  0.582  0.189  0.319 -0.187
 0.046  0.189  0.214  0.121 -0.130
-0.005  0.319  0.121  0.355 -0.081
-0.119 -0.187 -0.130 -0.081  0.351
nsum =   6.5428289
```

S.4 Dependence on U of spin splittings, bond lengths, bond energies

The splittings of the two lowest spin states of several intermediates are provided for GGA and GGA+U=5.6 eV:

Table S2: Splittings of several SyrB2 model complex intermediates in kcal/mol. The splittings have been calculated using both GGA and GGA+U with an average U of 5.6 eV. The splitting increases for the oxo and hydroxyl intermediates, while it stays the same or decreases for dioxygen and water, respectively.

		ΔE (kcal/mol)	
Configuration	States	GGA	GGA+U
$[Fe^{II}-OH_2]-Cl/\alpha KG$	5→3	46	37
$[Fe^{III}-O_2]-Cl/\alpha KG$	5→3	1	3
$[Fe^{IV}=O]-Cl/Succ.$	5→3	11	19
$[Fe^{III}-OH]-Cl/Succ.$	6→4	6	9

Table S3: Bond lengths and dissociation energies for key ligands in the model SyrB2 complex. The structural parameters at the GGA level for both the lowest energy and first excited spin are considered here and compared against the GGA+U values which are presented in the papaer as well. GGA tends to overestimate dissociation energies and underestimate bond lengths.

		r_e (Å)		D_e (kcal/mol)	
Ligand	$2S+1$	GGA	GGA+U	GGA	GGA+U
H_2O	5	2.35	2.40	7	6
	3	2.04	2.10	8	7
O_2	5	1.80	1.84	18	16
	3	1.85	1.88	12	26
O	5	1.63	1.65	50	42
	3	1.69	1.74	28	23
OH	6	1.85	1.88	57	52
	4	1.80	1.84	51	43
Cl	6	2.30	2.34	19	13
	4	2.26	2.29	12	5

While the ground state for GGA and GGA+U are primarily in agreement here, in many similar systems (see Refs. [1,2]), incorrect spin ordering and splitting can yield mechanistically incorrect predictions. Importantly, the high-spin, quintet ferryl-oxo intermediate which is observed experimentally and known to participate in radical abstraction is further stabilized by GGA+U. Also, the increased separation of the quintet and triplet for bound dioxygen is also likely to be mechanistically relevant.

As mentioned before, GGA can overestimate bond dissociation energies. We compare here the GGA and GGA+U dissociation energies and equilibrium bond lengths of those bonds discussed in more detail in the manuscript. These overestimates in bond dissociation energies can be mechanistically relevant (e.g. when determining why SyrB2 halogenates but does not hydroxylate).

Overall, GGA dissociation energies tend to be significantly higher, on the order of 5-10 kcal/mol at least, than the GGA+U dissociation energies. The bond lengths are also markedly shorter, indicating stronger bonding that has been experimentally measured. Overestimates of both hydroxyl and chlorine binding are relevant because they suggest that GGA would find both functionalizations to be more prohibitive than they are calculated to be using GGA+U.

S.5 GGA and GGA+U reaction step energetics

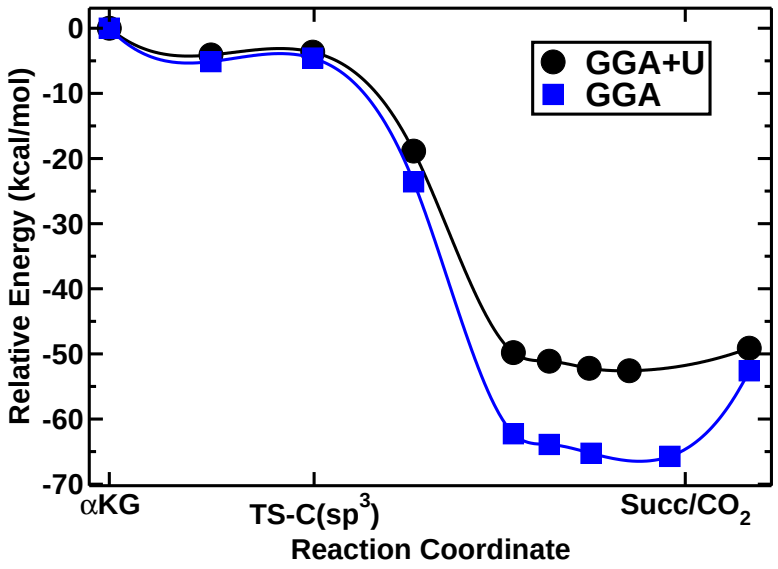

Figure S1: Comparison of minimum energy paths for oxidative decarboxylation of αKG. The GGA+U path (black circles) does not have unphysical stabilization of a partially bound CO_2 intermediate, but the GGA path (blue squares) stabilizes such structures by around 13 kcal/mol.

As an example of the effect of the +U term on reaction energetics, we provide here a comparison of the minimum energy path of GGA and GGA+U for the oxidative decarboxylation step in particular. Here, standard GGA shows a local minimum by nearly 13 kcal/mol associated with partially bound CO_2 and partial cleavage of the O-O bond between the forming iron-oxo intermediate and the succinate molecule. GGA+U instead shows that there is no stabilization of this state, simply a small energetic cost of 2 kcal/mol for torsion of the succinate back to the equatorial plane. The other changes in reaction step energetics with a +U term are comparable to that observed for the oxidative decarboxylation step. That is, GGA barriers are likely overestimates, while self-interaaction errors tend to promote the underestimation of reaction step exothermicities.

Table S4: Comparison of GGA and GGA+U activation energies, E_a, and reaction energetics, ΔE_r, in kcal/mol. Self-interaction errors result in the overestimate of activation energies and less favorable reaction energetics for GGA results when compared against GGA+U results.

		CH_4 (kcal/mol)			L-Thr (kcal/mol)		
GGA							
SyrB2	E_a	22	0		16	0	6
	ΔE_r	10	-16		3	-18	-23
Coupled	E_a	-	-	-	10	0	-
	ΔE_r	-	-	-	-	-15	-
GGA+U							
SyrB2	E_a	9	0		7	0	4
	ΔE_r	-3	-14		-4	-20	-29
Coupled	E_a	-	-	-	3	0	-
	ΔE_r	-	-	-	-	-24	-

S.6 Additional structural parameters and Cartesian coordinates

The use of a +U term has some effect on bond lengths, as was mentioned earlier. In fact, GGA+U has a tendency to overelongate bonds. However, it appears that the critical bond lengths of the isolated gas phase complex of first shell residues are systematically shorter than they would be in the protein environment. The result is that the GGA+U values for bond lengths thus far give a description in good agreement with experimental values. Several GGA and GGA+U bond lengths between the iron center and ligands which were not discussed in detail in the manuscript (namely Fe-His and Fe-αKG/succinate distances and angles) are summarized in the table below:

Table S5: Bond lengths and angles of several ligands as a function of oxidation state and configuration. The O_a and O_b oxygens refer to the atoms of αKG or succinate which ligate iron, where a is the oxygen in line with the equatorial His and b is in line with Cl. The Fe-His distances measured are for His_{eq}, the His in the plane with Cl and αKG, while His_{ax} is out of the plane in the distal axial position. The His-Fe-His angle is larger compared to crystal structure values since there is no protein backbone constraining the movement of the imidazole rings.

Configuration	H-Fe-H $\angle\ ^o$	Fe-His_{eq} Å	Fe-His_{ax} Å	Fe-O_a Å	Fe-O_b Å	Fe-Cl Å
Crystal structure	69	2.18	2.22	2.03	2.19	2.44
$[Fe^{II}-OH_2]-Cl/\alpha KG$	80	2.17	2.25	2.03	2.22	2.41
$[Fe^{II}]-Cl/\alpha KG$	86	2.23	2.22	2.05	2.30	2.38
$[Fe^{III}-O_2]-Cl/\alpha KG$	86	2.23	2.18	2.03	2.50	2.31
$[Fe^{IV}=O]-Cl/Succ.$	85	2.17	2.15	2.12	2.70	2.30
$[Fe^{III}-OH]-Cl/Succ.$	85	2.22	2.27	2.22	2.37	2.32
$[Fe^{III}-OH]/Succ.$	86	2.17	2.14	2.12	2.17	N/A

All of the bond lengths measured are for GGA+U with the lowest energy spin state. The change in oxidation state upon O_2 binding results in a shortening of the Fe-Cl bond length. Upon decarboxylation of αKG, bidentate succinate coordination is preferred only in some configurations. The Fe-His bond length fluctuation is small and the distances are comparable to that of the crystal structure. Thus, despite the lack of tethering of the imidazoles to the backbone and the large fluctuation in His-Fe-His angles, the bond lengths and therefore the likely underlying influence on electronic structure of the His residues is comparable to the full protein.

Cartesian coordinates for GGA $[Fe^{II}-OH_2]-Cl/\alpha KG$

```
  38
-694.97271477 Ry
 C     2.941960     0.646327     0.346890
 N     1.755324     1.018719    -0.130221
 C     1.882015     2.340787    -0.525097
 C     3.157428     2.767271    -0.269908
 N     3.814348     1.685438     0.278798
Fe     0.090604    -0.051252     0.117214
 O    -1.382620    -1.254599     0.410406
 C    -1.101646    -2.530446     0.657324
 O    -1.933866    -3.418093     0.861005
 N     0.132252     0.667671     2.179912
 C     0.850716     0.127354     3.229630
 C     0.941414     1.042830     4.246385
 N     0.257290     2.153718     3.802756
 C    -0.219759     1.889233     2.556558
 O     1.198496    -1.778947     0.497435
 C     0.505189    -2.853707     0.698899
 C     1.098757    -4.193376     0.951998
 C     2.595961    -4.279393     0.708156
 C     3.149170    -5.654912     0.967032
 O     2.501066    -6.650433     1.228084
Cl    -1.280673     1.560295    -0.815739
 O     4.516157    -5.674609     0.873314
 O     0.027696    -0.660724    -2.156166
 H     1.035441     2.867129    -0.949401
 H     4.782943     1.662642     0.580422
 H     3.160843    -0.334863     0.749366
 H     1.246922    -0.881220     3.192596
 H     0.132953     3.019716     4.315334
 H    -0.795649     2.593122     1.964981
 H     1.425036     1.015019     5.214430
 H     3.640288     3.722254    -0.434349
 H    -0.583439     0.090559    -1.962200
 H     0.819720    -0.239915    -2.538525
 H     4.786773    -6.602327     1.051002
 H     2.838191    -4.012407    -0.333498
 H     3.153184    -3.565834     1.334635
 H     0.550823    -4.922588     0.330582
 H     0.856335    -4.489644     1.990371
```

Cartesian coordinates for $\mathbf{GGA + U\,[Fe^{II}{-}OH_2]{-}Cl/\alpha KG}$

```
   38
 -694.873846311 Ry
 C     0.744786     0.217455     3.148805
 N     0.095436     0.722312     2.044030
 C    -0.512106     1.829987     2.431111
 N    -0.272503     2.058815     3.749181
 C     0.528445     1.036802     4.223944
Fe    -0.003532    -0.026736    -0.075658
 O     1.132920    -1.862089     0.442801
 C     0.407695    -2.857718     0.632316
 C     0.990209    -4.214033     0.838075
 C     2.495094    -4.197617     0.634064
 C     3.137775    -5.532919     0.845530
 O     4.493886    -5.466841     0.672116
 N     1.945864     0.857546    -0.452163
 C     2.161749     2.186462    -0.748082
 C     3.509488     2.435778    -0.740106
 N     4.109584     1.226065    -0.440676
 C     3.127581     0.303693    -0.275014
 O    -0.069784    -0.939450    -2.294343
Cl    -1.193080     1.902937    -0.893849
 O    -1.402291    -1.401653     0.447769
 C    -1.017673    -2.606775     0.645920
 O    -1.666037    -3.644531     0.867767
 O     2.557337    -6.560256     1.132315
 H     1.311433     2.834081    -0.943962
 H     5.101915     1.055704    -0.340431
 H     3.299129    -0.743546    -0.031209
 H     1.330522    -0.694048     3.093439
 H    -0.627042     2.838729     4.291444
 H    -1.106683     2.454181     1.764786
 H     0.866891     0.988906     5.250219
 H     4.086830     3.338993    -0.897721
 H     4.830555    -6.378399     0.824553
 H     2.764282    -3.841115    -0.372479
 H     2.984322    -3.463409     1.291207
 H     0.471276    -4.945248     0.188154
 H     0.691628    -4.538552     1.854715
 H     0.076625    -1.848704    -2.598338
 H    -0.443180    -0.403124    -3.019317
```

Cartesian coordinates for GGA $[Fe^{II}]-Cl/\alpha KG$

```
  35
-660.6897585607 Ry
 C    -0.535607     1.722404     2.418156
 N     0.122985     0.624207     2.071333
 C     0.769666     0.174916     3.206310
 C     0.493703     1.016427     4.252072
 N    -0.333120     1.992067     3.731898
Fe     0.000000     0.000000     0.000000
Cl    -1.112084     1.773071    -1.002216
 N     2.021552     0.788021    -0.472635
 C     3.229087     0.269496    -0.275649
 N     4.183790     1.219291    -0.458142
 C     3.554675     2.403724    -0.785672
 C     2.214799     2.120055    -0.792327
 O    -1.276738    -1.524369     0.137919
 C    -0.950525    -2.710695     0.529511
 C     0.576681    -2.920757     0.653669
 C     1.104870    -4.304323     0.877677
 C     2.615283    -4.364706     0.728698
 C     3.227210    -5.715592     0.976174
 O     4.577954    -5.677258     0.746055
 O     1.268160    -1.859867     0.528581
 O    -1.683997    -3.663251     0.808063
 O     2.650767    -6.721504     1.341736
 H     1.360694     2.758800    -0.990598
 H     5.185716     1.082129    -0.368952
 H     3.441565    -0.753350     0.013326
 H     1.386199    -0.716782     3.197881
 H    -0.723181     2.778720     4.240085
 H    -1.133458     2.319108     1.734337
 H     0.801222     1.013121     5.290322
 H     4.103371     3.318270    -0.973788
 H     4.922904    -6.575562     0.943910
 H     2.921941    -4.031486    -0.274412
 H     3.104281    -3.656625     1.416055
 H     0.574003    -4.974963     0.182863
 H     0.769650    -4.649997     1.871156
```

Cartesian coordinates for $\mathbf{GGA+U\,[Fe^{II}]-Cl}/\alpha\mathbf{KG}$

```
   35
 -660.5925000334 Ry
 C    -0.495314     1.791730     2.472918
 N     0.135405     0.681446     2.111029
 C     0.779443     0.211311     3.239130
 C     0.532107     1.050595     4.294305
 N    -0.276523     2.047805     3.787852
Fe     0.000000     0.000000     0.000000
Cl    -1.150825     1.806197    -1.033791
 N     2.007826     0.840273    -0.472848
 C     3.206819     0.309796    -0.267243
 N     4.168067     1.260404    -0.394138
 C     3.550525     2.457763    -0.697967
 C     2.209982     2.180103    -0.748115
 O    -1.393406    -1.488478     0.167537
 C    -1.061436    -2.659888     0.588833
 C     0.474116    -2.876273     0.616643
 C     1.034947    -4.232303     0.892047
 C     2.544244    -4.261425     0.720899
 C     3.182942    -5.604413     0.943250
 O     4.536758    -5.522283     0.751667
 O     1.215784    -1.898810     0.432903
 O    -1.779624    -3.588382     0.973261
 O     2.623770    -6.640108     1.248303
 H     1.364086     2.823796    -0.966644
 H     5.166476     1.113621    -0.284709
 H     3.405150    -0.728936    -0.030294
 H     1.371045    -0.696486     3.222000
 H    -0.647933     2.836630     4.306926
 H    -1.095040     2.407250     1.808250
 H     0.843782     1.029220     5.331405
 H     4.107685     3.374774    -0.842758
 H     4.898076    -6.421932     0.906485
 H     2.827125    -3.920288    -0.287938
 H     3.029934    -3.542529     1.399569
 H     0.512451    -4.964178     0.255355
 H     0.718069    -4.516384     1.910801
```

Cartesian coordinates for GGA $[Fe^{III}-O_2]-Cl/\alpha KG$

```
  37
-724.2060822990 Ry
 C     0.618871     0.266288     3.373361
 N     0.081456     0.722761     2.184863
 C    -0.337257     1.962246     2.402627
 N    -0.079130     2.320850     3.686774
 C     0.529382     1.253210     4.318527
Fe     0.131227    -0.406928     0.329257
 O    -1.479802    -1.113901     0.721419
 O    -1.917238    -1.428097     1.908703
 N     1.862419     0.830267    -0.080021
 C     3.098727     0.529153     0.293855
 N     3.905814     1.607759     0.131268
 C     3.148233     2.646682    -0.371922
 C     1.880201     2.145383    -0.499598
Cl     1.421235    -2.107530     1.101644
 O    -0.153570    -0.683242    -1.592175
 C    -0.979358    -0.030196    -2.347881
 O    -1.288201    -0.258193    -3.517281
 C    -1.602080     1.198521    -1.638408
 O    -1.206932     1.489013    -0.505176
 C    -2.631615     1.995521    -2.371233
 C    -3.309961     3.030731    -1.491649
 C    -4.250565     3.942421    -2.232176
 O    -4.494707     3.922598    -3.423386
 O    -4.819807     4.844543    -1.374477
 H     1.022325    -0.737732     3.445106
 H    -0.303405     3.215815     4.110600
 H    -0.822312     2.596902     1.670219
 H     0.983600     2.635419    -0.859867
 H     4.895030     1.642217     0.355767
 H     3.407541    -0.436007     0.684690
 H     3.564348     3.624460    -0.579852
 H     0.836308     1.288080     5.357072
 H    -5.408545     5.412018    -1.918403
 H    -3.870438     2.550865    -0.673179
 H    -2.564740     3.661496    -0.982273
 H    -3.336433     1.293226    -2.844307
 H    -2.130223     2.454497    -3.242843
```

Cartesian coordinates for $\mathbf{GGA + U\,[Fe^{III}{-}O_2]{-}Cl/\alpha KG}$

```
  37
-724.0304652296 Ry
 C     2.129275     2.031443    -0.556548
 N     2.167279     0.743193    -0.063068
 C     3.439852     0.459267     0.171635
 N     4.217534     1.520281    -0.154058
 C     3.403509     2.532884    -0.618158
Fe     0.575444    -0.664577     0.443500
 O     0.538992    -1.751121    -1.268058
 C     0.031805    -1.332704    -2.375495
 C    -0.858605    -0.062424    -2.233197
 C    -1.676931     0.283261    -3.440232
 C    -2.582373     1.495994    -3.321730
 C    -3.214154     1.865976    -4.642491
 O    -4.206643     2.789703    -4.478987
 N    -0.008108     0.632369     2.164503
 C     0.430490     0.292121     3.431809
 C     0.158081     1.314558     4.296654
 N    -0.460959     2.288763     3.541731
 C    -0.546235     1.841480     2.262489
 O    -0.990692    -1.577560     0.777310
 O    -1.786866    -1.395859     1.815680
Cl     1.884124    -2.077595     1.727430
 O     0.176492    -1.805202    -3.504807
 O    -0.841153     0.592685    -1.186163
 O    -2.905306     1.433631    -5.737849
 H     0.922517    -0.660457     3.598001
 H    -0.787484     3.185482     3.880492
 H    -1.003310     2.409506     1.461172
 H     1.195732     2.502246    -0.835750
 H     5.227906     1.556351    -0.072954
 H     3.794276    -0.479599     0.586294
 H     3.791329     3.490060    -0.940749
 H     0.351548     1.433504     5.355621
 H    -4.550155     2.985553    -5.380082
 H    -3.381610     1.345932    -2.582495
 H    -2.024764     2.377471    -2.967094
 H    -2.242450    -0.624476    -3.708352
 H    -0.980471     0.376898    -4.288708
```

Cartesian coordinates for GGA [Fe^{IV}=O]−Cl/Succ.

```
  34
-649.3875390892 Ry
 C     2.789603     0.941568     0.798163
 N     2.961421     1.059208    -0.568498
 C     4.268440     1.092701    -0.796438
 N     4.937931     0.999072     0.377235
 C     4.016846     0.902294     1.401457
Fe     1.434884     1.184300    -2.021496
 O     0.144716     1.246693    -3.017702
 N     1.052759    -0.861959    -1.663392
 C     0.110696    -1.317930    -0.850203
 N     0.014801    -2.664399    -0.978871
 C     0.931343    -3.079367    -1.924758
 C     1.570240    -1.942632    -2.345288
 O     1.004245     3.007655    -1.220735
 C     0.125440     2.715546    -0.321752
 O    -0.146358     1.524557    -0.012844
Cl     3.011916     1.072754    -3.662107
 C    -0.546632     3.888570     0.367479
 C    -1.875710     3.517768     1.009411
 C    -2.352354     4.522971     2.021267
 O    -1.721143     5.467305     2.461000
 O    -3.626822     4.242960     2.439534
 H     1.798919     0.904464     1.234256
 H     4.309919     0.818830     2.440399
 H     5.947531     1.004588     0.477677
 H     4.718812     1.176085    -1.780269
 H    -0.499155    -0.700538    -0.199976
 H    -0.633082    -3.259519    -0.474084
 H     1.039888    -4.118247    -2.208993
 H     2.344505    -1.812704    -3.092834
 H    -0.655649     4.704928    -0.358843
 H     0.147600     4.265229     1.136351
 H    -2.666101     3.371524     0.257987
 H    -1.785802     2.544613     1.520002
 H    -3.846414     4.924042     3.112906
```

Cartesian coordinates for $\mathbf{GGA+U\,[Fe^{IV}{=}O]-Cl/Succ}$.

```
  34
-649.0722751638 Ry
 C     2.789603     0.941568     0.798163
 N     2.961421     1.059208    -0.568498
 C     4.268440     1.092701    -0.796438
 N     4.937931     0.999072     0.377235
 C     4.016846     0.902294     1.401457
Fe     1.408383     1.186471    -2.046719
 O     0.101464     1.249674    -3.055861
 N     1.015853    -0.915511    -1.678864
 C     0.073790    -1.371482    -0.865675
 N    -0.022106    -2.717952    -0.994343
 C     0.894437    -3.132920    -1.940229
 C     1.533334    -1.996185    -2.360760
 O     0.861363     2.996610    -1.078219
 C    -0.018905     2.588964    -0.194133
 O    -0.231311     1.365318     0.025411
Cl     3.002056     1.073749    -3.704642
 C    -0.762922     3.673352     0.563000
 C    -2.071832     3.184676     1.166299
 C    -2.612881     4.092190     2.236421
 O    -2.040930     5.040926     2.742713
 O    -3.871239     3.711745     2.622966
 H     1.798919     0.904464     1.234256
 H     4.309919     0.818830     2.440399
 H     5.947531     1.004588     0.477677
 H     4.718812     1.176085    -1.780269
 H    -0.536061    -0.754090    -0.215448
 H    -0.669988    -3.313071    -0.489555
 H     1.002982    -4.171799    -2.224465
 H     2.307599    -1.866256    -3.108306
 H    -0.915250     4.527672    -0.109906
 H    -0.096734     4.038760     1.361537
 H    -2.847653     3.042061     0.399158
 H    -1.928049     2.187138     1.613581
 H    -4.134575     4.333452     3.336870
```

Cartesian coordinates for GGA [Fe^{III}–OH]–Cl/Succ.

```
   35
 -650.6415379287 Ry
 C     4.274593     0.926108    -0.694685
 N     2.981065     1.086611    -0.456333
 C     2.830493     1.066737     0.916243
 C     4.052691     0.893086     1.511980
 N     4.958404     0.804799     0.473693
Fe     1.328217     1.278927    -2.066150
 O     0.023371     1.665440    -0.255513
 C     0.254111     2.906411    -0.457346
 C    -0.469302     3.965731     0.343440
 C    -1.778598     3.466874     0.939232
 C    -2.385969     4.419536     1.930053
 O    -1.928288     5.492566     2.279474
 N     0.991852    -0.816700    -1.622401
 C     1.527493    -1.908063    -2.274024
 C     0.958628    -3.052314    -1.779865
 N     0.063895    -2.634346    -0.814134
 C     0.109052    -1.279179    -0.749176
 O     1.111326     3.259406    -1.336067
Cl     2.946541     1.089312    -3.687147
 O    -0.143302     1.381360    -3.190672
 O    -3.562396     3.932288     2.436579
 H     1.853683     1.179080     1.371668
 H     4.352770     0.827796     2.550580
 H     5.960702     0.674025     0.561113
 H     4.724151     0.895215    -1.681458
 H    -0.493163    -0.667033    -0.087752
 H    -0.536700    -3.233041    -0.257486
 H     1.099261    -4.097933    -2.023212
 H     2.274784    -1.781458    -3.049014
 H    -0.621459     4.843046    -0.298940
 H     0.208248     4.301059     1.146531
 H    -2.525135     3.258896     0.156369
 H    -1.627313     2.498689     1.441068
 H    -3.881558     4.608688     3.073481
 H     0.080700     1.481113    -4.135394
```

Cartesian coordinates for $\mathbf{GGA+U\,[Fe^{III}{-}OH]-Cl/Succ}$.

```
   35
 -650.4770990741 Ry
 C     4.249368     0.919518    -0.700336
 N     2.957744     1.088418    -0.454677
 C     2.810646     1.074035     0.918209
 C     4.034465     0.895100     1.508192
 N     4.933873     0.798395     0.466473
Fe     1.350748     1.276293    -2.043869
 O    -0.053383     1.719710    -0.192336
 C     0.198208     2.966799    -0.356385
 C    -0.523539     4.002834     0.474677
 C    -1.826294     3.489269     1.072629
 C    -2.442917     4.435482     2.065518
 O    -1.997894     5.513533     2.416270
 N     1.014548    -0.878380    -1.621869
 C     1.549659    -1.976098    -2.262327
 C     0.980571    -3.115261    -1.755943
 N     0.084336    -2.687731    -0.796261
 C     0.129666    -1.332022    -0.745815
 O     1.149211     3.361604    -1.305869
Cl     2.985147     1.084795    -3.680969
 O    -0.120785     1.381557    -3.212197
 O    -3.614070     3.931898     2.568938
 H     1.838577     1.190691     1.380889
 H     4.342022     0.830455     2.544527
 H     5.935194     0.663189     0.556331
 H     4.691028     0.882327    -1.690981
 H    -0.475411    -0.714679    -0.091336
 H    -0.511859    -3.281624    -0.229679
 H     1.125796    -4.163686    -1.983660
 H     2.294333    -1.859609    -3.041445
 H    -0.694493     4.891261    -0.147382
 H     0.161696     4.331439     1.273203
 H    -2.570746     3.282844     0.287764
 H    -1.673580     2.520702     1.573810
 H    -3.946061     4.596342     3.212137
 H     0.174202     1.470510    -4.138269
```

Cartesian coordinates for GGA TS from αKG decarboxylation step

```
  37
-724.2249987480 Ry
 C     1.651132    -1.924107    -2.495709
 N     0.967303    -0.882520    -1.901492
 C     0.148538    -1.419864    -1.008153
 N     0.285243    -2.770259    -1.007164
 C     1.236678    -3.108755    -1.947897
Fe     1.313714     1.280615    -2.214631
 O     1.426245     3.298415    -2.104798
 C     0.360329     3.843214    -1.634866
 O     0.089201     5.021448    -1.434223
Cl     2.803450     0.919810    -3.857640
 N     2.717531     1.082309    -0.599397
 C     2.428727     1.069399     0.750429
 C     3.563037     0.756478     1.449373
 N     4.549558     0.583097     0.499053
 C     4.004609     0.788049    -0.723817
 O    -0.324860     1.475172    -3.241729
 O    -1.160465     2.443288    -2.713731
 C    -0.712333     2.728906    -1.263967
 C    -1.908791     3.290975    -0.518854
 C    -2.850098     2.211888    -0.003529
 C    -3.932999     2.764902     0.883930
 O    -4.769449     1.771387     1.327080
 O    -0.105247     1.670295    -0.763904
 O    -4.084222     3.928065     1.206720
 H     1.429327     1.293072     1.104527
 H     3.753564     0.645703     2.509792
 H     5.519447     0.342489     0.680739
 H     4.539388     0.713634    -1.665940
 H    -0.530840    -0.867179    -0.369617
 H    -0.228270    -3.419678    -0.419196
 H     1.521777    -4.135560    -2.140617
 H     2.380950    -1.733944    -3.274296
 H    -2.426963     4.003554    -1.174721
 H    -1.518253     3.889842     0.314614
 H    -3.326370     1.653509    -0.824569
 H    -2.294943     1.460633     0.580594
 H    -5.432402     2.216848     1.899652
```

Cartesian coordinates for GGA+U TS from αKG decarboxylation step

```
  37
-724.0540396796 Ry
 C     4.004609     0.788049    -0.723817
 N     2.717531     1.082309    -0.599397
 C     2.428727     1.069399     0.750429
 C     3.563037     0.756478     1.449373
 N     4.549558     0.583097     0.499053
Fe     1.313714     1.280615    -2.214631
 O    -0.136819     1.678966    -0.731625
 C    -0.743904     2.737577    -1.231688
 C    -1.940362     3.299646    -0.486575
 C    -2.881669     2.220559     0.028750
 C    -3.964570     2.773573     0.916209
 O    -4.115793     3.936736     1.238999
 N     0.967303    -0.882520    -1.901492
 C     1.651132    -1.924107    -2.495709
 C     1.236677    -3.108755    -1.947897
 N     0.285242    -2.770259    -1.007164
 C     0.148538    -1.419864    -1.008153
 O     1.428659     3.341691    -2.102442
 C     0.362743     3.886491    -1.632510
 O     0.091615     5.064725    -1.431867
Cl     2.845224     0.909693    -3.903712
 O    -0.324860     1.475172    -3.241729
 O    -1.160465     2.443289    -2.713731
 O    -4.801020     1.780058     1.359359
 H     1.429327     1.293072     1.104527
 H     3.753564     0.645703     2.509792
 H     5.519447     0.342489     0.680739
 H     4.539388     0.713634    -1.665940
 H    -0.530840    -0.867179    -0.369617
 H    -0.228271    -3.419678    -0.419196
 H     1.521776    -4.135560    -2.140617
 H     2.380950    -1.733944    -3.274296
 H    -2.464669     4.004192    -1.146234
 H    -1.549707     3.907291     0.340460
 H    -3.357942     1.662180    -0.792290
 H    -2.326514     1.469304     0.612873
 H    -5.463973     2.225519     1.931931
```

Cartesian coordinates for GGA TS from methane hydrogen abstraction step

```
   39
  -665.3422354525 Ry
 C     2.867509     0.898940     0.953375
 N     3.024309     1.032883    -0.412093
 C     4.327855     1.106323    -0.643163
 N     5.010798     1.024711     0.525242
 C     4.098366     0.892992     1.553649
Fe     1.466516     1.185021    -2.013553
 O     0.117601     1.602136    -0.170000
 C     0.304675     2.832361    -0.437486
 C    -0.396095     3.914533     0.352390
 C    -1.704713     3.450175     0.974770
 C    -2.277095     4.437985     1.953813
 O    -1.714543     5.419079     2.405906
 N     1.085104    -0.931206    -1.715458
 C     0.125225    -1.385175    -0.922505
 N     0.031308    -2.732637    -1.041956
 C     0.971719    -3.153617    -1.962411
 C     1.617053    -2.018008    -2.376238
 O     1.113651     3.148321    -1.382409
Cl     3.129329     1.199259    -3.609976
 O     0.001787     1.247213    -3.134524
 O    -3.553359     4.099378     2.318072
 C    -0.040926     4.295923    -4.421670
 H     1.881787     0.830770     1.397426
 H     4.400766     0.812820     2.589873
 H     6.020106     1.062735     0.620360
 H     4.771773     1.215905    -1.628105
 H    -0.500401    -0.769183    -0.286148
 H    -0.627852    -3.324805    -0.548476
 H     1.086673    -4.194874    -2.235148
 H     2.410280    -1.896783    -3.105225
 H    -0.546870     4.784143    -0.301520
 H     0.296382     4.253753     1.140289
 H    -2.463178     3.231166     0.208220
 H    -1.554670     2.495965     1.505945
 H    -3.838897     4.778581     2.968106
 H    -0.950797     4.111131    -4.987824
 H    -0.091043     4.694865    -3.411756
 H     0.929461     4.105199    -4.874332
 H     0.098934     2.176222    -3.448435
```

Cartesian coordinates for GGA+U TS from methane hydrogen abstraction step

```
  39
-665.1702445024 Ry
 C     2.867509     0.898940     0.953375
 N     3.024309     1.032883    -0.412093
 C     4.327855     1.106323    -0.643163
 N     5.010798     1.024711     0.525242
 C     4.098366     0.892992     1.553649
Fe     1.466516     1.185021    -2.013553
 O     0.082747     1.612914    -0.122366
 C     0.269822     2.843139    -0.389853
 C    -0.430949     3.925310     0.400024
 C    -1.739566     3.460952     1.022404
 C    -2.311948     4.448762     2.001446
 O    -1.749397     5.429857     2.453540
 N     1.085104    -0.931206    -1.715458
 C     0.125225    -1.385175    -0.922505
 N     0.031308    -2.732637    -1.041956
 C     0.971719    -3.153617    -1.962411
 C     1.617053    -2.018008    -2.376238
 O     1.107553     3.182249    -1.371501
Cl     3.146948     1.199410    -3.626891
 O    -0.022023     1.248224    -3.152746
 O    -3.588212     4.110156     2.365706
 C    -0.064736     4.296934    -4.439892
 H     1.881787     0.830770     1.397426
 H     4.400766     0.812820     2.589873
 H     6.020106     1.062735     0.620360
 H     4.771773     1.215905    -1.628105
 H    -0.500401    -0.769183    -0.286148
 H    -0.627852    -3.324805    -0.548476
 H     1.086673    -4.194874    -2.235148
 H     2.410280    -1.896783    -3.105225
 H    -0.583221     4.794299    -0.254365
 H     0.262156     4.265711     1.186862
 H    -2.498031     3.241943     0.255853
 H    -1.589524     2.506742     1.553579
 H    -3.873751     4.789359     3.015739
 H    -0.974607     4.112142    -5.006046
 H    -0.114853     4.695876    -3.429979
 H     0.905651     4.106210    -4.892554
 H     0.075124     2.177233    -3.466657
```

Cartesian coordinates for GGA TS_{-H} from L-Thr coupled mechanism

```
  51
-820.8761470380 Ry
 C    -1.169527    -0.256946     3.010519
 N    -0.092344    -0.108663     2.155467
 C     0.992089    -0.019578     2.918896
 N     0.647240    -0.107763     4.223106
 C    -0.722038    -0.258746     4.305484
Fe    -0.098608     0.000000     0.000000
 O    -2.449298     0.370046     0.261769
 C    -2.094585     1.587443     0.266088
 C    -3.112635     2.706249     0.333149
 C    -4.483938     2.303674    -0.191406
 C    -5.556861     3.305748     0.138625
 O    -5.450895     4.255439     0.894259
 N    -0.566286    -2.093413    -0.005629
 C    -1.792239    -2.579278    -0.145505
 N    -1.731990    -3.924916    -0.306459
 C    -0.405976    -4.308782    -0.275189
 C     0.309258    -3.155243    -0.088689
 O    -0.853444     1.914482     0.233770
Cl     2.258187    -0.039419     0.224081
 O    -0.213197     0.068968    -1.840490
 O    -6.725665     3.017937    -0.512318
 C     2.854761    -0.509580    -2.749977
 C     2.469730    -1.166871    -4.043599
 O     1.592256    -0.275562    -4.736272
 C     3.635766    -1.486384    -4.992770
 C     4.614182    -2.533641    -4.492548
 O     5.909584    -2.171086    -4.758293
 N     3.037028    -1.965101    -6.252648
 O     4.325279    -3.616979    -4.012044
 H    -2.180188    -0.339888     2.630557
 H    -1.239079    -0.347813     5.252495
 H     1.296929    -0.062449     5.000088
 H     2.000943     0.096699     2.537505
 H    -2.701127    -1.987953    -0.151519
 H    -2.528066    -4.539344    -0.439617
 H    -0.099262    -5.340718    -0.389452
 H     1.380526    -3.003573    -0.021837
 H    -2.710548     3.574162    -0.205991
 H    -3.193650     3.021999     1.386176
```

H	-4.473532	2.142677	-1.279873
H	-4.785875	1.333839	0.236879
H	-7.375525	3.696290	-0.223936
H	0.870425	-0.202731	-2.310609
H	1.948065	-2.122531	-3.821992
H	4.178291	-0.552715	-5.199136
H	1.583508	-0.599754	-5.664718
H	3.396232	-1.189984	-2.081693
H	3.454448	0.397435	-2.910434
H	3.721487	-2.007183	-7.010207
H	2.652485	-2.905310	-6.114613
H	6.472767	-2.927715	-4.482014

Cartesian coordinates for GGA+U TS_{-H} from L-Thr coupled mechanism

```
  51
-820.7449516990 Ry
 C    -1.148750    -0.264192     3.042864
 N    -0.069057    -0.118620     2.199838
 C     1.014151    -0.029923     2.957590
 N     0.665353    -0.116011     4.260839
 C    -0.705652    -0.265412     4.337708
Fe    -0.073939     0.009897     0.048563
 O    -2.396107     0.367927     0.256419
 C    -2.065766     1.600488     0.272226
 C    -3.098642     2.701577     0.335533
 C    -4.471362     2.296294    -0.178095
 C    -5.545910     3.297346     0.152121
 O    -5.442480     4.252130     0.901890
 N    -0.557936    -2.107380     0.013431
 C    -1.783586    -2.586799    -0.134127
 N    -1.731561    -3.931587    -0.310367
 C    -0.407748    -4.321694    -0.282511
 C     0.311381    -3.172882    -0.083456
 O    -0.833034     1.945180     0.267936
Cl     2.351780    -0.025301     0.231553
 O    -0.035673     0.042653    -1.786620
 O    -6.717167     3.003629    -0.493339
 C     3.045273    -0.484434    -2.408952
 C     2.553325    -1.107597    -3.649860
 O     1.669028    -0.216952    -4.327054
 C     3.718103    -1.429746    -4.626500
 C     4.696464    -2.471608    -4.112606
 O     5.989020    -2.114826    -4.387804
 N     3.109822    -1.901796    -5.878554
 O     4.400632    -3.543832    -3.613546
 H    -2.155471    -0.344503     2.651013
 H    -1.223066    -0.352155     5.284514
 H     1.313442    -0.071546     5.039610
 H     2.021941     0.086209     2.570692
 H    -2.688795    -1.989767    -0.137176
 H    -2.530220    -4.541195    -0.451595
 H    -0.102893    -5.352936    -0.406307
 H     1.383847    -3.028920    -0.015084
 H    -2.699893     3.570645    -0.205185
 H    -3.169240     3.021564     1.388850
```

H	-4.463464	2.132099	-1.265727
H	-4.768002	1.327166	0.255429
H	-7.362624	3.687855	-0.208349
H	1.073854	-0.063564	-2.048714
H	2.047110	-2.069645	-3.420116
H	4.256933	-0.493976	-4.830550
H	1.648545	-0.539653	-5.257315
H	3.472608	-1.115845	-1.635767
H	3.335705	0.565123	-2.425607
H	3.783168	-1.912939	-6.645984
H	2.745719	-2.851548	-5.752869
H	6.558026	-2.865425	-4.104756

Cartesian coordinates for GGA TS_{+Cl} from L-Thr coupled mechanism

```
  51
-820.9206637513 Ry
 C    -1.773593    -2.609837    -0.120612
 N    -0.544604    -2.135759     0.021122
 C     0.319597    -3.204346    -0.081198
 C    -0.404751    -4.349835    -0.286016
 N    -1.728105    -3.953998    -0.306307
Fe    -0.086822     0.000000     0.000000
 O    -0.799744     1.971133     0.295039
 C    -2.030612     1.629998     0.302483
 C    -3.075465     2.720516     0.371164
 C    -4.445363     2.294065    -0.131793
 C    -5.525547     3.290861     0.187753
 O    -6.695102     2.981842    -0.453885
 N    -0.039475    -0.131172     2.216555
 C     1.047216    -0.043400     2.971256
 N     0.707147    -0.127822     4.281369
 C    -0.663442    -0.274496     4.367087
 C    -1.112661    -0.274296     3.073088
Cl     2.420162    -0.041198     0.125305
 O    -0.232074     0.051363    -1.853260
 O    -2.357161     0.395964     0.276043
 O    -5.428678     4.253912     0.927602
 H    -2.124219    -0.352591     2.693839
 H    -1.178549    -0.357659     5.314955
 H     1.354744    -0.081000     5.059540
 H     2.054464     0.073007     2.584774
 H    -2.678246    -2.011979    -0.115287
 H    -2.528479    -4.558115    -0.446761
 H    -0.108474    -5.381966    -0.417662
 H     1.392283    -3.065188    -0.011976
 H    -2.695165     3.590785    -0.180613
 H    -3.146797     3.046828     1.421526
 H    -4.442788     2.111790    -1.216858
 H    -4.734463     1.329465     0.316678
 H    -7.346383     3.660253    -0.174650
 H     0.538906    -0.025639    -2.449538
 C     4.114143    -1.410650    -4.464499
 C     2.967680    -1.098518    -3.469784
 H     2.473389    -2.058659    -3.208631
 H     4.642144    -0.468443    -4.662494
```

O	2.042870	-0.230337	-4.132719
H	2.016800	-0.559286	-5.061149
C	3.552208	-0.458493	-2.281381
H	4.152264	-1.074000	-1.618535
H	3.717540	0.615447	-2.289577
N	3.525542	-1.882981	-5.723113
H	4.194614	-1.840644	-6.493542
H	3.202349	-2.849234	-5.626095
C	5.100349	-2.438743	-3.931293
O	4.808835	-3.494011	-3.394695
O	6.390621	-2.095609	-4.230213
H	6.956756	-2.842804	-3.930771

Cartesian coordinates for GGA+U TS_{+Cl} from L-Thr coupled mechanism

```
  51
-820.7643902438 Ry
 C     0.318240    -3.190383    -0.079658
 N    -0.545411    -2.119392     0.023851
 C    -1.772537    -2.596567    -0.121578
 N    -1.727630    -3.940384    -0.307555
 C    -0.405297    -4.336648    -0.285606
Fe    -0.052822     0.040427     0.044893
 O    -0.077794     0.045215    -1.819988
 N    -0.044593    -0.127416     2.218383
 C    -1.122470    -0.272666     3.065584
 C    -0.680089    -0.274302     4.360305
 N     0.690737    -0.126790     4.282987
 C     1.038538    -0.040796     2.977607
 O    -2.356608     0.379341     0.261761
 C    -2.034740     1.611981     0.288434
 O    -0.800398     1.957787     0.285490
Cl     2.388241    -0.017458     0.228072
 C    -3.076572     2.705890     0.357388
 C    -4.451221     2.290501    -0.146543
 C    -5.530395     3.290462     0.177067
 O    -6.699805     2.984892    -0.465917
 O    -5.432305     4.251520     0.919417
 C     3.319872    -0.435371    -2.124935
 C     2.762373    -1.069412    -3.328597
 C     3.907197    -1.383719    -4.321617
 N     3.310255    -1.857966    -5.576794
 O     1.841817    -0.194027    -3.985985
 C     4.888283    -2.415156    -3.785577
 O     4.592661    -3.472840    -3.256699
 O     6.180596    -2.068914    -4.071580
 H    -2.132184    -0.354880     2.675095
 H    -1.196599    -0.362166     5.308428
 H     1.340087    -0.083911     5.059268
 H     2.045536     0.072640     2.593242
 H    -2.680060    -1.998223    -0.119352
 H    -2.527962    -4.549711    -0.452214
 H    -0.103889    -5.366977    -0.418456
 H     1.390115    -3.055516    -0.013073
 H    -2.689249     3.574817    -0.190152
 H    -3.142953     3.028482     1.409758
```

```
H    -4.446000     2.113102    -1.232486
H    -4.741850     1.323246     0.295898
H    -7.351295     3.669184    -0.184969
H     0.735999    -0.001500    -2.394367
H     2.269130    -2.033081    -3.074735
H     4.442740    -0.447007    -4.523944
H     1.808657    -0.518679    -4.915585
H     3.828124    -1.054378    -1.393705
H     3.493085     0.638659    -2.117781
H     3.981506    -1.837746    -6.343936
H     2.976733    -2.821814    -5.468097
H     6.747765    -2.811294    -3.772231
```

1. Kulik, H.J.; Marzari, N. Journal of Chemical Physics **2008**, *129*, 134314.
2. Kulik, H.J.; Cococcioni, M.; Scherlis, D.A.; Marzari, N. Physical Review Letters **2006**, *97*, 103001.