ELECTRONIC SUPPLEMENTARY INFORMATION

The E_3 state of FeMoco: one hydride, two hydrides or dihydrogen?

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1. Definitions of QM-regions and additional energetic results

Figure S1 shows the definitions of the three QM regions used in this study. The QM-A region was used to systematically explore all possible models in three spin states and 35 BS states (per spin state) and also used in optimizations comparing different functionals (B97-D3, r^{2}SCAN, TPSSh, B3LYP*, B3LYP, and TPSS). The QM-B region was utilized to optimize the lowest-energy state for each model (according to the results of the QM-A region). Finally, single-point calculations were carried out using the large QM-C region based on the optimized geometry of the QM-B region.

The QM-cluster model is identical to the QM-A region but instead of an MM environment, the cluster is surrounded by a continuum. The r^{2}SCAN functional was used and the same basis set as in the QM/MM calculations. The CPCM solvation model was used (relevant parameters: $\varepsilon = 4$, refrac: 1.3300; rsolv: 1.3000; surface type: Gaussian vdW; radius for H, C, N, O, S, Fe, and Mo: 1.32, 2.04, 1.86, 1.82, 2.16, 2.40, and 2.40 Å, respectively). During optimizations of the cluster model, His195, homocitrate and Cys275 were kept frozen; this is necessary as the anionic homocitrate is otherwise not well described and spontaneous proton transfer between His442 and homocitrate would occur. All other atoms were allowed to move.

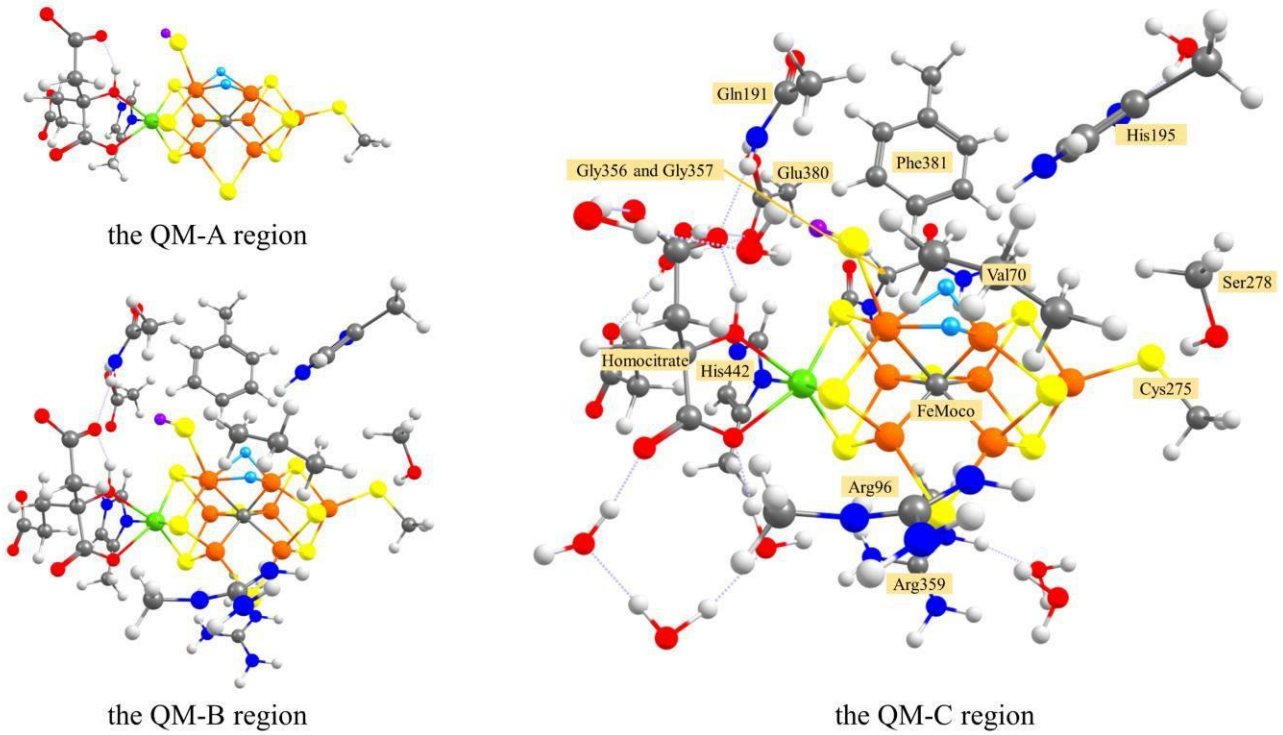


Figure S1. The definitions of QM regions. The number of atoms in the QM-A, QM-B, and QM-C regions are 59, 145, and 191 (link-atoms included), respectively.

There are 27 water molecules within 10 Å of iron ions of α-FeMoco in the crystal structure (PDB: 3U7Q[1]), and most of them located arround the negatively charged homocitrate (see Figure S2a). Figure S2c shows the positions of 10 water molecules in the QM-C region after optimization. Compared to the crystal structure(Figure S2b), two water molecules labelled ② and ④ have moved 2.21 and 3.7 Å.

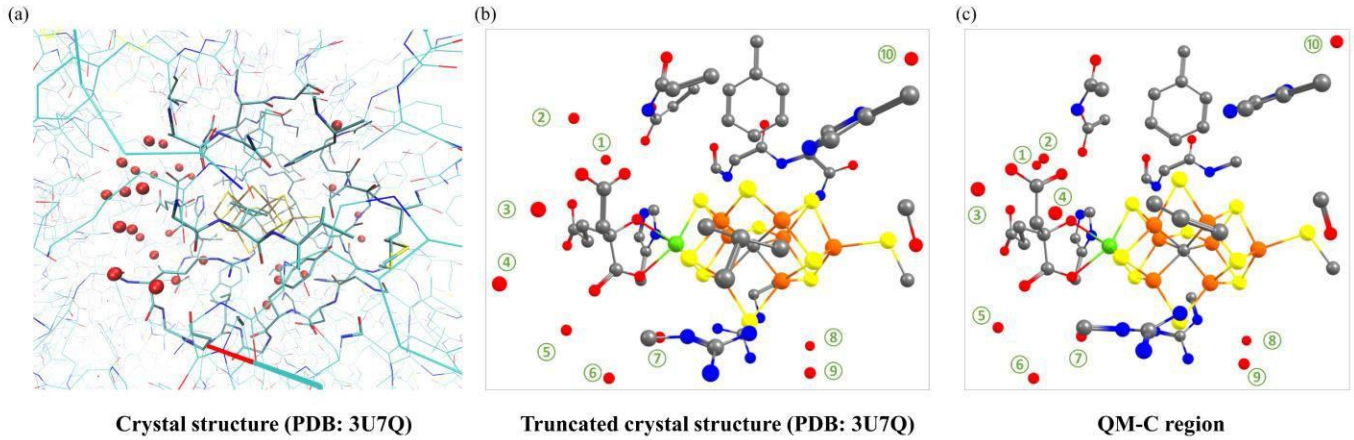


Figure S2. Comparison of the water molecules in X-ray structure (a and b) and the QM/MM optimized calculation using the QM-C region. Red balls indicate water molecules. X-ray structure PDB ID: 3U7Q[1].

Figure S3 shows the relative energies of models **e-q** (see Figure 2 in article for definitions) using different QM-region QM/MM calculations. Also shown are the results of the QM-cluster model using a model with the same size as the QM/MM-QM-A region. As shown, the QM/MM calculations, give a consistent trend towards convergence in going from QM-A, QM-B to QM-C region, with some minor deviations for QM-A. The cluster model (despite having the same QM-cluster size as the QM/MM-QM-A calculation) behaves quite different from QM/MM results, due to the lack of protein environment around FeMoco. The QM-cluster model correctly predicts the stability associated with **2hyd-OBS** models (**g-l**) but is not capable of correctly differentiating between the isomers, in particular due to the lack of residues like His195 that interact with e.g. the terminal sulfhydryl group in those isomers. A QM-cluster model that includes surrounding protein residues would be able to incorpate such effects, but this was not further explored in this work.

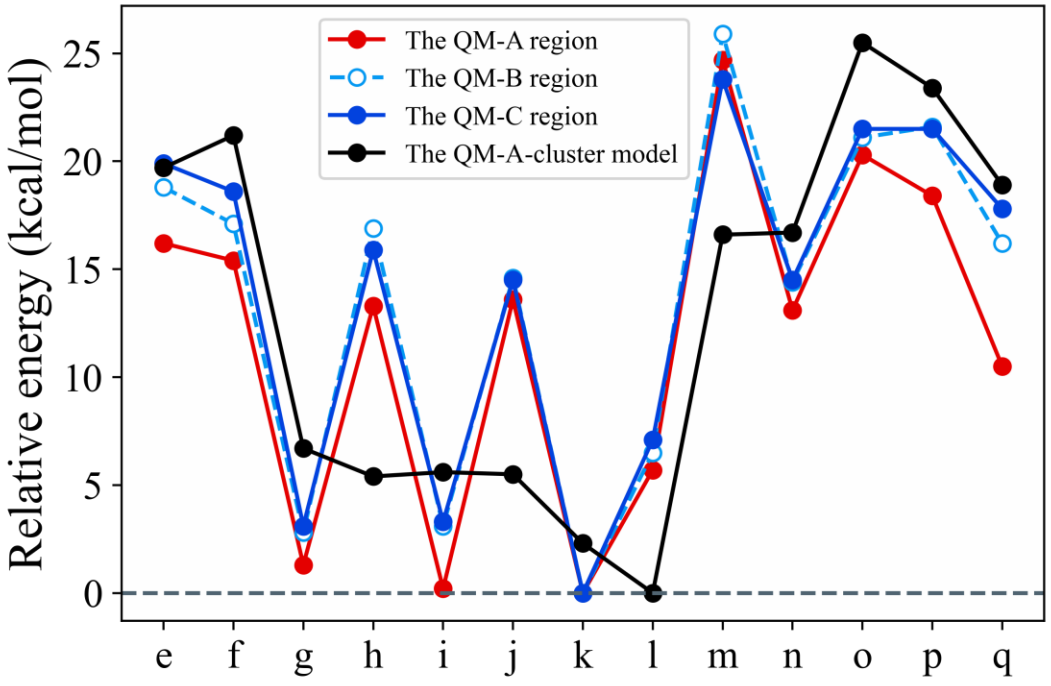


Figure S3. The relative energies of models (**e-q**) using the QM-A, QM-B, and QM-C regions from the QM/MM calculations compared to the QM-A-cluster model (r^2SCAN functional used). The spin states and BS solutions of each model are the same as used for the data in Figure 2 of the manuscript.

2. Results for a CBS_{26}-BH_{26}-TH_6 model

Figure S4 shows the results of a **CBS_{26}-BH_{26}-TH_6** model that were reported to be a little higher than the lowest-energy isomer (**3H.2x.26.2bterm**) in a study by Dance[2]. He found that there is a small energy difference between M_S = 1 and 0. We explored this model in the spin state of M_S = 0 (suggested by Dance) using all possible 35 BS solutions and our r^2SCAN-based QM/MM protocol. Our results reveal that geometry optimizations of all 35 BS solutions converged to an isomer best described as **CBS_{26}-$2TH_6$** i.e. containing two terminal hydrides at Fe6, which was found to be higher than the lowest energy isomer (**OBS_6-DH_2**, see Figure 2k in the manuscript) by 12.3 kcal/mol (r^2SCAN is used). We note in this context that a hydride in a partially bridging hydride conformation is only classified as bridging (and drawn as such) if both Fe-H distances were not longer than 2.0 Å.

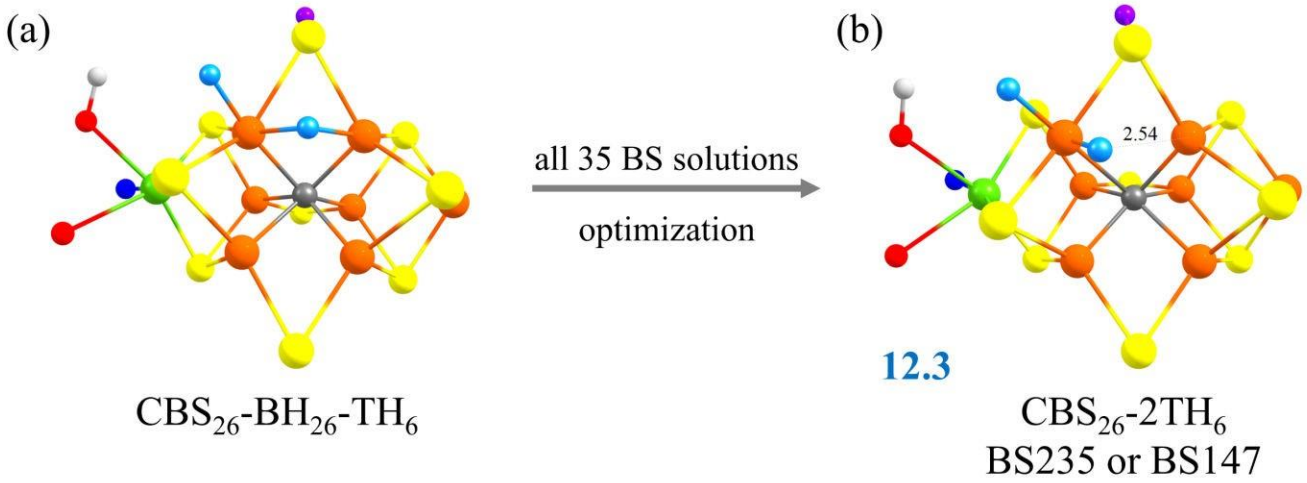


Figure S4. All states of the **CBS_{26}-BH_{26}-TH_6** (a) in M_S = 0 and 35 BS solutions were converged to **CBS_{26}-$2TH_6$** (b) using the QM-A region and r^2SCAN. The lowest-energy state of the **CBS_{26}-$2TH_6$** is 12.3 kcal/mol relative to the lowest model **OBS_6-DH_2** (see Figure 2k in the manuscript).

3. Results for CBS_{26}-DH_6 models

A H_2-bound $\mathbf{E_3}$ model with a closed belt sulfide-bridge, $\mathbf{CBS_{26}\text{-}DH_6}$ (see Figure S5) was previously found to be quite favorable in a study by Dance.[2] Such a model was investigated here in a spin state of $M_S = 0$ (as suggested by Dance) with all possible 35 BS solutions using the QM-A region and r^{2}SCAN. We found that only one BS solution (BS257) resulted in the suggested structure with a H_2 bound, which is 28.3 kcal/mol higher than the $\mathbf{OBS_6\text{-}DH_2}$ model (see Figure 2k in the manuscript). For all other BS states, H_2 dissociated (corresponds to falling back to the $\mathbf{E_1}$ redox state).

In contrast, models with an H_2 ligand and an open belt sulfide-bridge (instead of a closed belt sulfide-bridge like here) are stable and low energy structures (see Figure 2 k and l in the manuscript). Our results thus suggest that H_2-bound FeMoco structures at the $\mathbf{E_3}$ redox level are stabilized by having an open belt sulfide-bridge present.

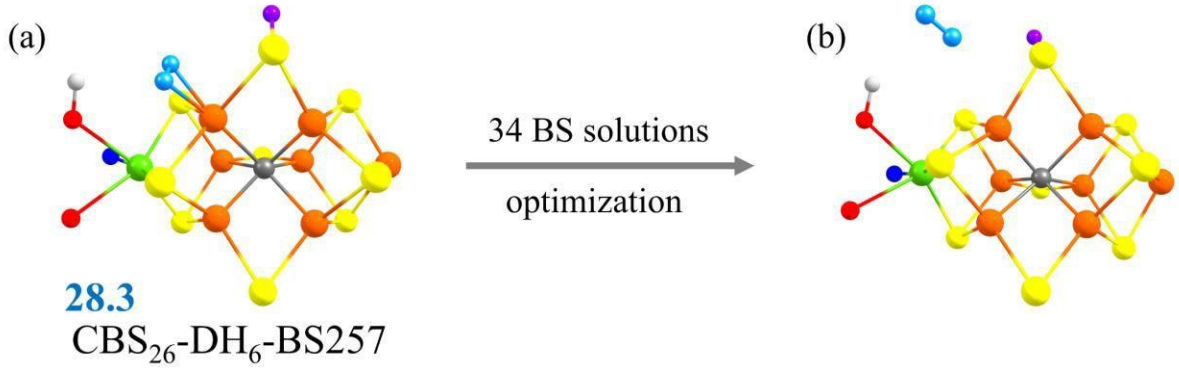


Figure S5. Results of a model containing a closed protonated belt sulfide-bridge, one H_2 at Fe6 in the spin state of $M_S = 0$ and 35 BS solutions using the QM-A region and r^{2}SCAN. The energy in blue of (a) is relative to the lowest model $\mathbf{OBS_6\text{-}DH_2}$ (see Figure 2k in the manuscript).

4. Additional results of the 2-hyd-CBS class

The optimized geometries of **CBS_{26}-$2BH_{26(5),37}$**, **CBS_{26}-$2BH_{26(3),37}$**, **CBS_{37}-$2BH_{26(5),37}$**, and **CBS_{37}-$2BH_{26(3),37}$** models are shown in Figure S6 to Figure S9. These four models contain two bridging hydrides between different pairs of iron ions (Fe2/Fe6 and Fe3/Fe7) and a protonated closed belt sulfide-bridge at S2B (between Fe2 and Fe6) or S5A (between Fe3 and Fe7), which are similar to **E_4-$2CBS_{26,37}$-$2BH_{26(3),37}$** and **E_4-$2CBS_{26,37}$-$2BH_{26(5),37}$** models (see Figure 1 in the manuscript) in the **E_4** state but with one less proton (the charge of FeMoco remains the same). A previous study[3] reported that such **E_4** models are stable, however, most BS states of four **E_3** models designed from them converged to other models with one or two terminal hydrides, shown in Figure S6 to Figure S9, which is similar to results reported by Ryde and Jiang[4] (please see models **352_** and **552_** in that paper).

We found that four converged models **CBS_{37}-BH_{37}-TH_2** (Figure S6b), **CBS_{37}-$2TH_{6,7}$** (Figure S6c), **CBS_{26}-BH_{26}-TH_3** (Figure S8c), and **CBS_{37}-BH_{37}-TH_2** (Figure S9b) are higher than the lowest-energy model (**OBS_6-DH_2**, Figure 2k in the manuscript) between 15 and 20 kcal/mol, which are similar to two models (see Figure 2 e and f in the manuscript suggested by Ryde and Cao) in energy and geometry[5].

According to results of the **CBS_{37}-$2BH_{26(3),37}$** in three spin states (M_S = 0, 1, and 2) and 35 BS solutions (Figure S6), models with a protonated closed belt-sulfide bridge and 2 bridging hydrides between different pairs of iron ions are unstable and converge to structures with 1 or 2 mostly-terminal hydrides. Energies between three spin states are small for this type of models containing two bridging hydrides between different pairs of iron ions in this study, and Dance found that M_S = 1 and 0 are also small for the **E_3** state in his study[2]. Therefore, we performed optimizations for **CBS_{26}-$2BH_{26(3),37}$**, **CBS_{26}-$2BH_{26(5),37}$**, and **CBS_{37}-$2BH_{26(5),37}$** models with M_S = 1 and 35 BS solutions.

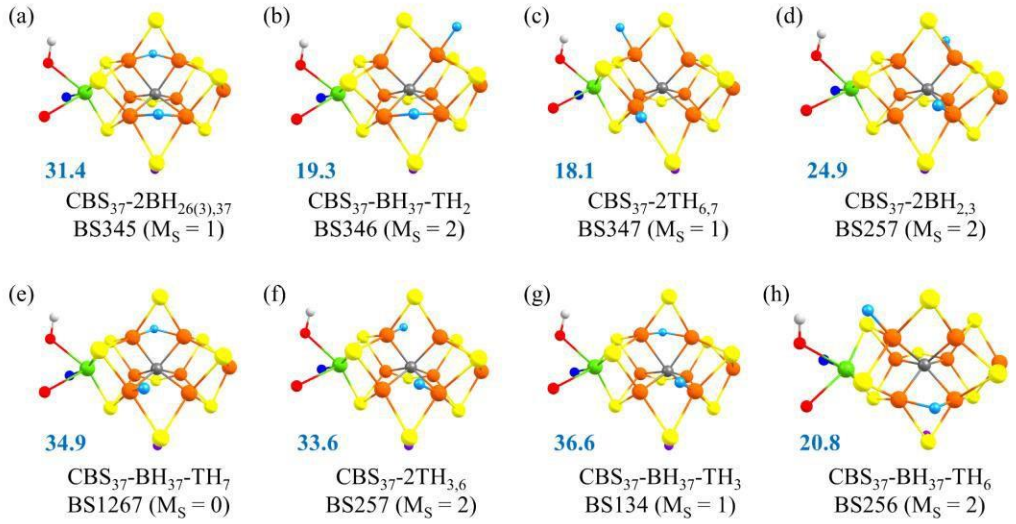


Figure S6. Models (a-h) converged from 35 BS solutions and three spin states starting from **CBS_{37}-$2BH_{26(3),37}$** (a). The energies calculated using QM-A region and r^2SCAN in blue are the lowest-energy one for each model, which are relative to the lowest model **OBS_6-DH_2** (see Figure 2k in the manuscript). A hydride is defined as bridging only if both Fe-H distances in Fe-H-Fe are not longer than 2.0 Å.

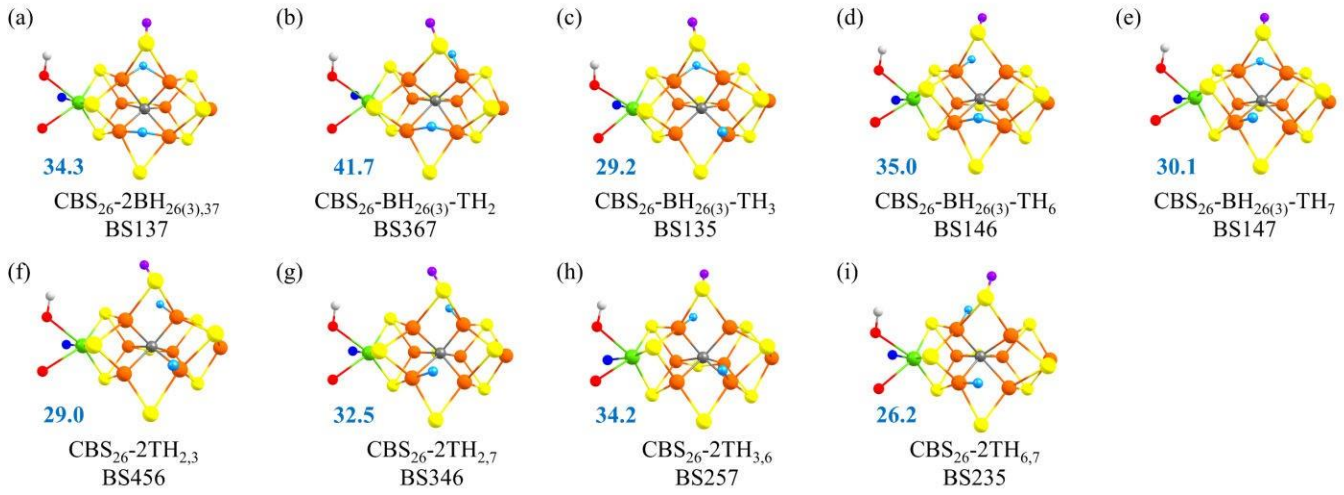


Figure S7. Models (a-i) converged from 35 BS solutions and the spin state of M_S = 1 starting from **CBS_{26}-$2BH_{26(3),37}$** (a). The energies calculated using QM-A region and r^2SCAN in blue are the lowest-energy version of each model, which are relative to the lowest model **OBS_6-DH_2** (see Figure 2k in the manuscript). A hydride is defined as bridging only if both Fe-H distances in Fe-H-Fe are not longer than 2.0 Å.

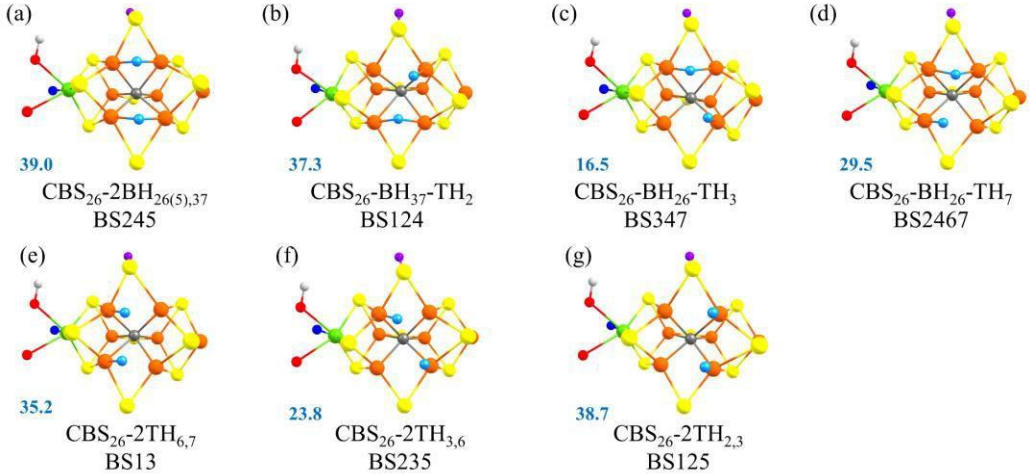


Figure S8. Models (a-g) are converged from optimizations starting from **CBS_{26}-$2BH_{26(5),37}$** (a) in the spin state of M_S = 1 and 35 BS solutions. The energies calculated using QM-A region and r^2SCAN in blue are the lowest-energy version for each model, which are relative to the lowest model **OBS_6-DH_2** (see Figure 2k in the manuscript). A hydride is defined as bridging only if both Fe-H distances in Fe-H-Fe are not longer than 2.0 Å.

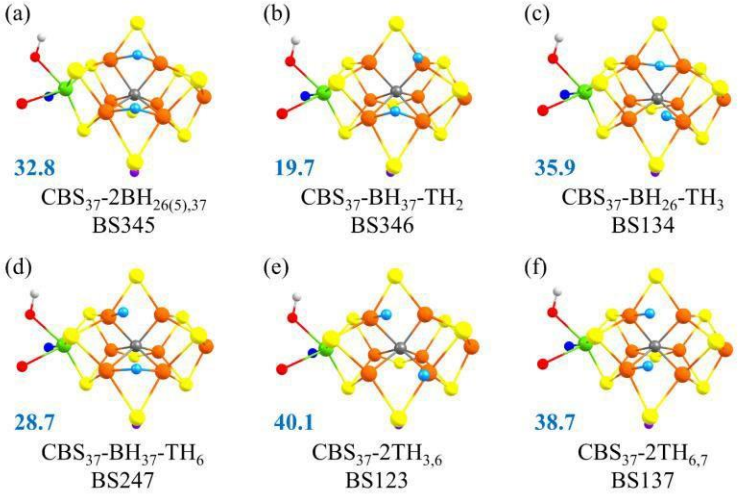


Figure S9. Models (a-f) are the lowest-energy structures found when using the structure in **CBS_{37}-$2BH_{26(5),37}$** (a) as starting structure in the spin state of M_S = 1 and 35 BS solutions. The energies calculated using QM-A region and

r^{2}SCAN in blue are the lowest-energy version for each model, and their relative energies in blue are relative to the lowest model **OBS$_6$-DH$_2$** (see Figure 2k in the manuscript). A hydride is defined as bridging only if both Fe-H distances in Fe-H-Fe are not longer than 2.0 Å.

The **CBS$_{26}$-BH$_{26}$-TH$_5$** suggested by Ryde and co-workers[5] is also investigated here. However, we obtained some other models (**CBS$_{26}$-2TH$_{5,6}$** and **CBS$_{26}$-2TH$_{2,5}$**) with a mostly terminal hydride at Fe2 or Fe6 (see Figure S10).

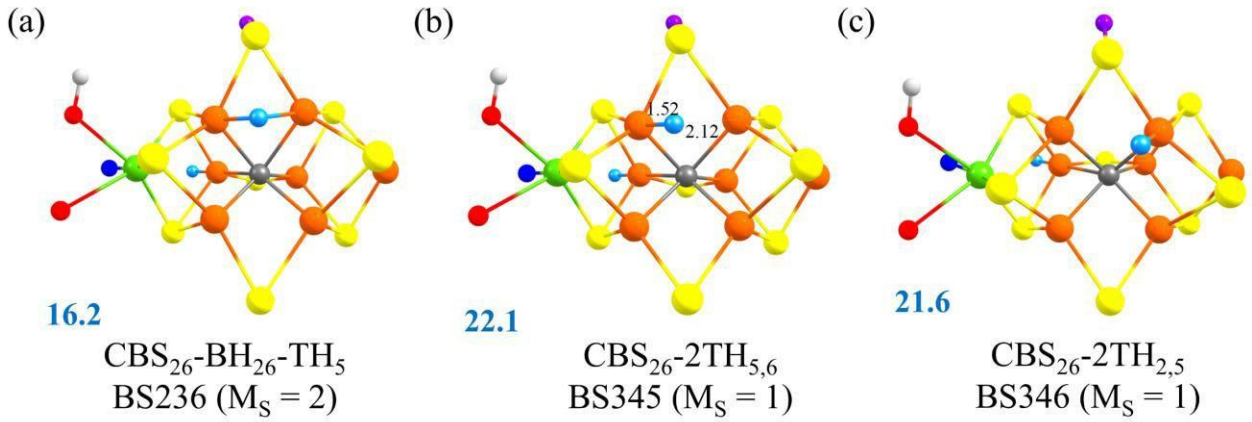
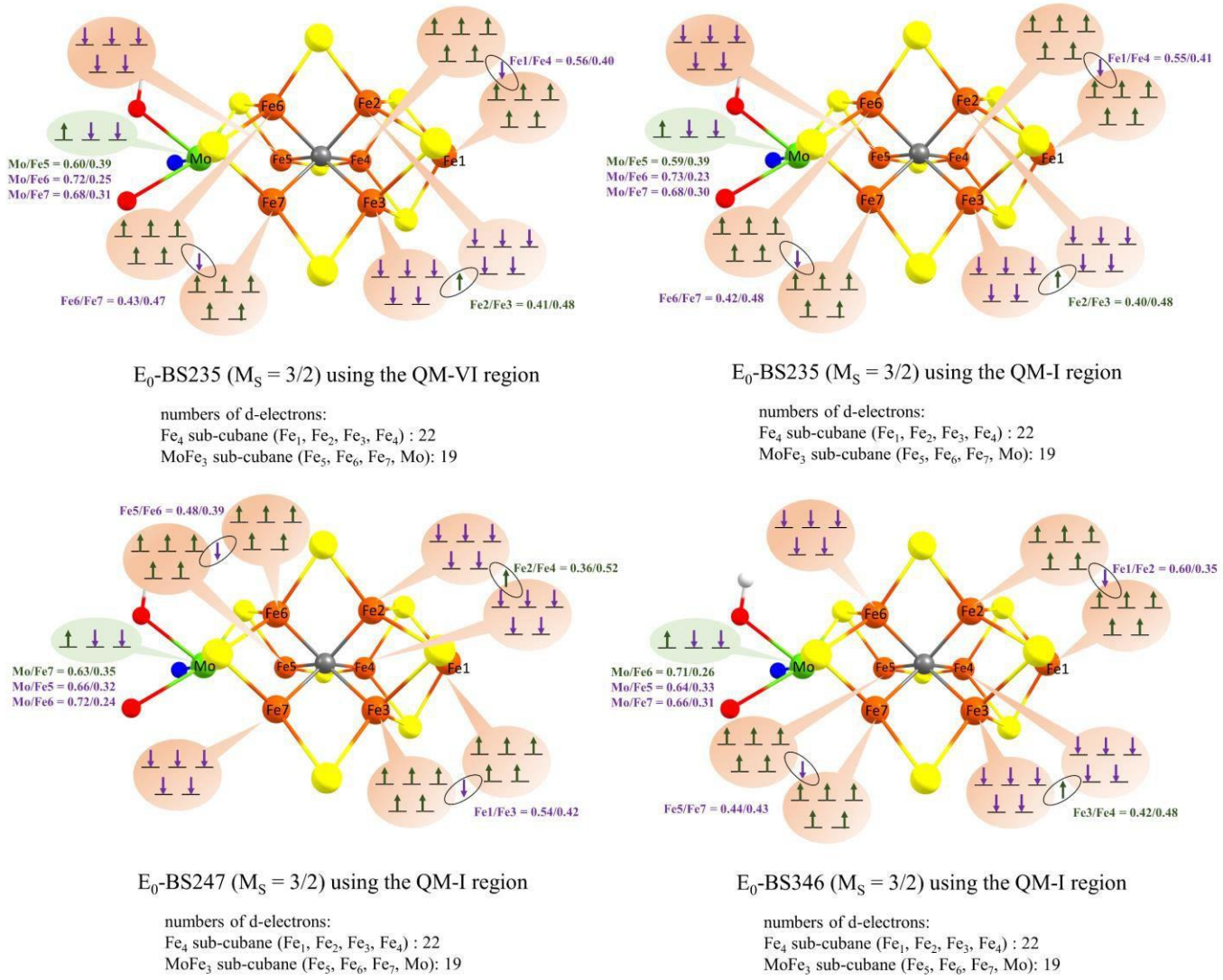


Figure S10. Models (a-c) are the lowest-energy structures found when using the structure **CBS$_{26}$-BH$_{26}$-TH$_5$** (a) suggested by Ryde and co-workers[5] as starting structure in three spin states and 35 BS solutions. The energies calculated using QM-A region and r^{2}SCAN in blue are the lowest-energy version for each model, and their relative energies in blue are relative to the lowest model **OBS$_6$-DH$_2$** (see Figure 2k in the manuscript). A hydride is defined as bridging version if both Fe-H distances in Fe-H-Fe are not longer than 2.0 Å.

5. Electron configurations of E_0 and E_3 states based on localized orbital analysis

Figure S11 shows the electron configurations as interpreted from a localized orbital analysis of the BS7 class of the **E_0** state.



E_0-BS235 (M_S = 3/2) using the QM-VI region

numbers of d-electrons:
Fe_4 sub-cubane (Fe_1, Fe_2, Fe_3, Fe_4) : 22
$MoFe_3$ sub-cubane (Fe_5, Fe_6, Fe_7, Mo): 19

E_0-BS235 (M_S = 3/2) using the QM-I region

numbers of d-electrons:
Fe_4 sub-cubane (Fe_1, Fe_2, Fe_3, Fe_4) : 22
$MoFe_3$ sub-cubane (Fe_5, Fe_6, Fe_7, Mo): 19

E_0-BS247 (M_S = 3/2) using the QM-I region

numbers of d-electrons:
Fe_4 sub-cubane (Fe_1, Fe_2, Fe_3, Fe_4) : 22
$MoFe_3$ sub-cubane (Fe_5, Fe_6, Fe_7, Mo): 19

E_0-BS346 (M_S = 3/2) using the QM-I region

numbers of d-electrons:
Fe_4 sub-cubane (Fe_1, Fe_2, Fe_3, Fe_4) : 22
$MoFe_3$ sub-cubane (Fe_5, Fe_6, Fe_7, Mo): 19

Figure S11. The localized orbital analysis of the BS7 class including BS235, BS247, and BS346 with M_S = 3/2 of the **E_0** state from our previous paper (r^2SCAN used)[3]. The QM-I and QM-VI regions defined in our previous paper are the same as the QM-A and QM-C regions in the present study, respectively.

The localized orbitals associated with hydrides or H_2 of **OBS_6-DH_2-BS147 (M_S = 1)**, **OBS_6-BH_{26}-TH_2-BS235 (M_S = 2)**, and **OBS_6-$2BH_{26}$-BS347 (M_S = 1)** models are shown in Figure S12 to Figure S14.

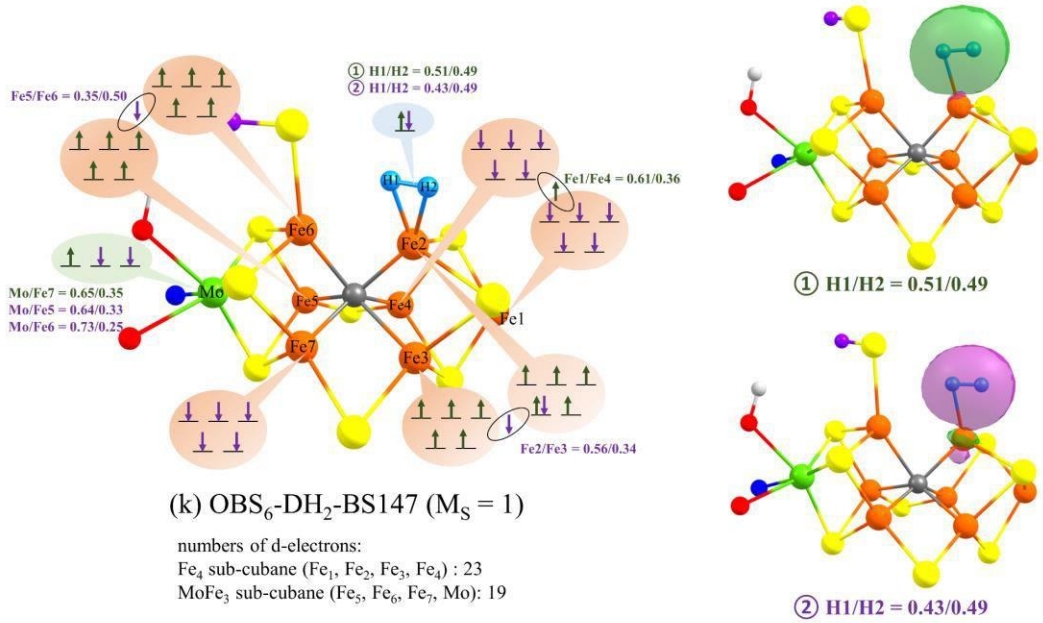


Figure S12. The localized orbital analysis of **OBS_6-DH_2-BS147 (M_S = 1)** using the QM-C region and r^2SCAN. Alpha-spin electrons are shown in green and beta-spin electrons in purple. Numbers in green and purple indicate the localized orbital populations of alpha and beta electrons, respectively.

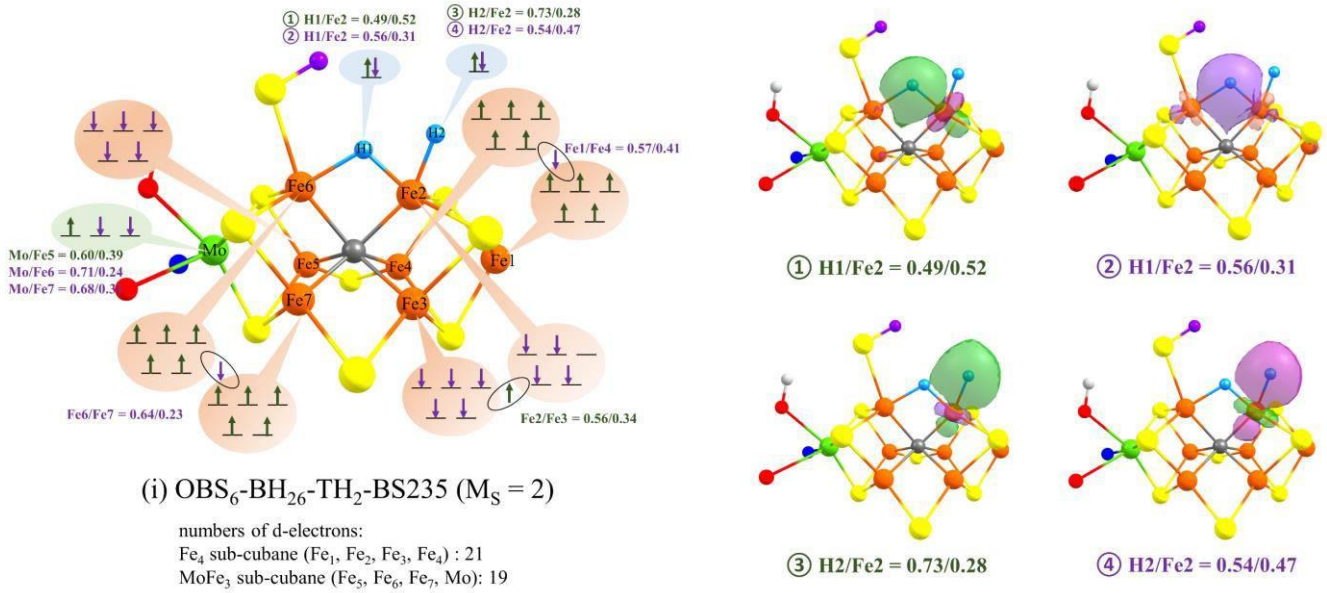


Figure S13. The localized orbital analysis of **OBS_6-BH_{26}-TH_2-BS235 (M_S = 2)** using the QM-C region and r^2SCAN. Alpha-spin electrons are shown in green and beta-spin electrons in purple. Numbers in green and purple indicate the localized orbital populations of alpha and beta electrons, respectively.

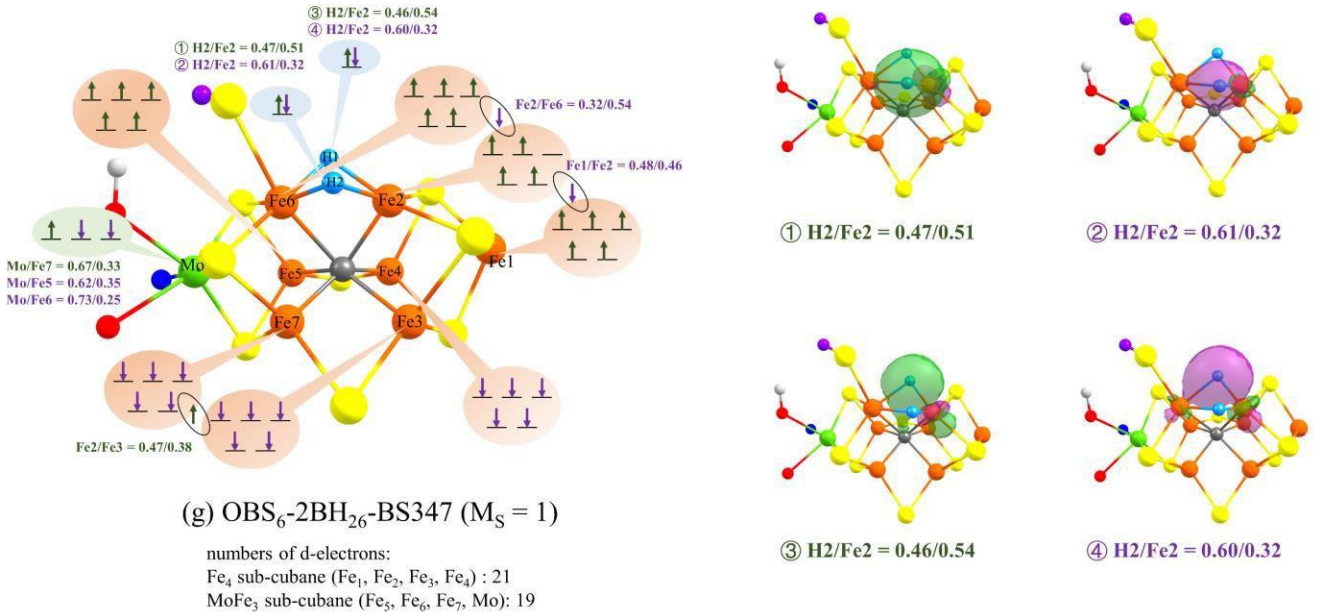


Figure S14. The localized orbital analysis of **OBS_6-$2BH_{26}$-BS347 (M_S = 1)** using the QM-C region and r^{2}SCAN. Alpha-spin electrons are shown in green and beta-spin electrons in purple. Numbers in green and purple indicate the localized orbital populations of alpha and beta electrons, respectively.

6. N_2 binding to the E_3 state models

Figure S15 shows the binding energy of N_2 to either Fe2 or Fe6 site in the **OBS-2BH$_{26}$** model of the **E$_3$** state, in three spin states and 35 BS solutions using the QM-A region.

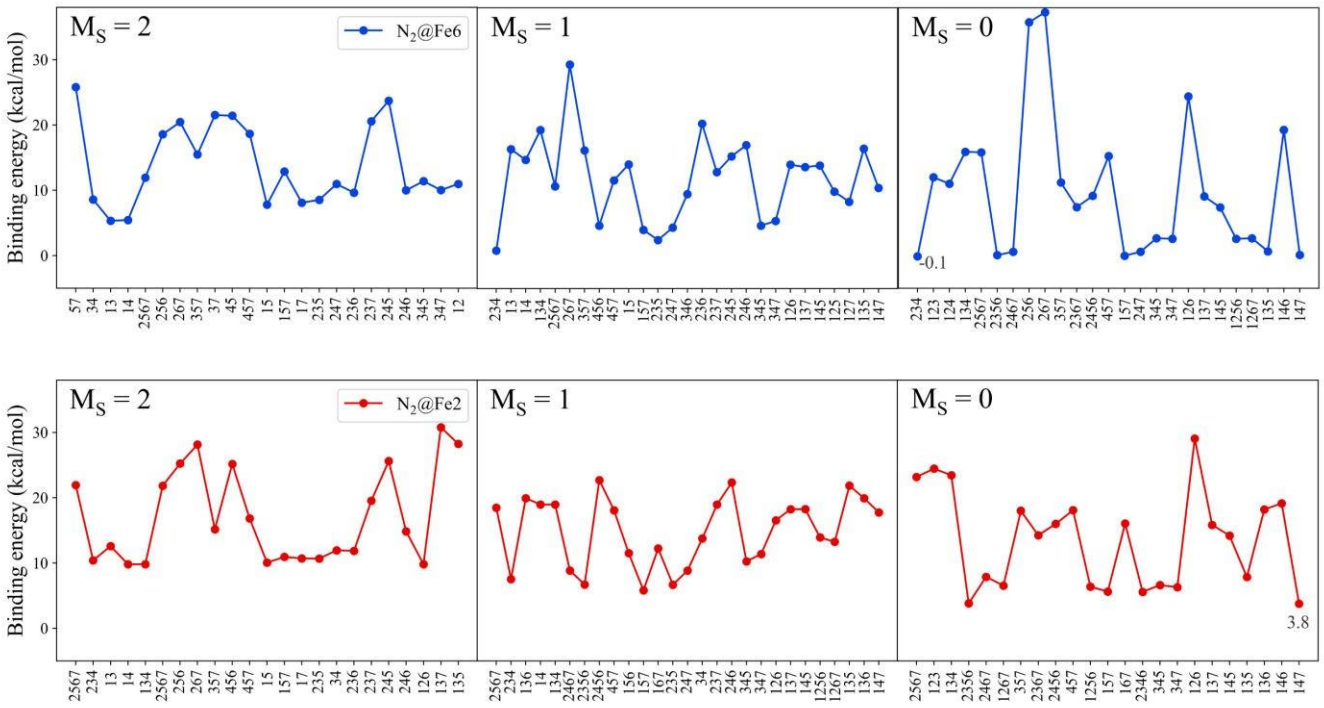


Figure S15. The binding energy of N_2 binding to the Fe2 of **OBS$_6$-2BH$_{26}$** or Fe6 of **OBS$_2$-2BH$_{26}$** in three spin states and 35 BS solutions using the QM-A region and r^{2}SCAN. Binding energies are relative to the lowest-energy model **OBS$_6$-DH$_2$** (Figure 2k in the manuscript, r^{2}SCAN used).

The ligand field diagram of N_2 bound states were derived from the combination of localized orbital analysis, diamagnetic substitution, and quasi-restricted orbital analysis.[3] The structure in Figure S16a was calculated using the QM-C region, which was analysed by using the localized orbital method indicating that the Fe2 in **OBS$_6$-2BH$_{26}$-N$_2$@Fe2** is low-spin Fe^{3+}.The Fe and Mo except Fe2 ions were then diamagnetically substituted by Ga^{3+} and In^{3+}, respectively (see Figure S16b). The single-point calculation of the diamagnetic model with an Fe^{3+} (S = 1/2) was carried out and used to obtain quasi-restricted orbitals (shown in Figure S16), which finally was used to make ligand-field diagram. The d_{xz} and d_{yz} orbitals of diamagnetically substituted FeMoco of **OBS$_6$-2BH$_{26}$-N$_2$@Fe2** overlap with π* orbitals of N_2.

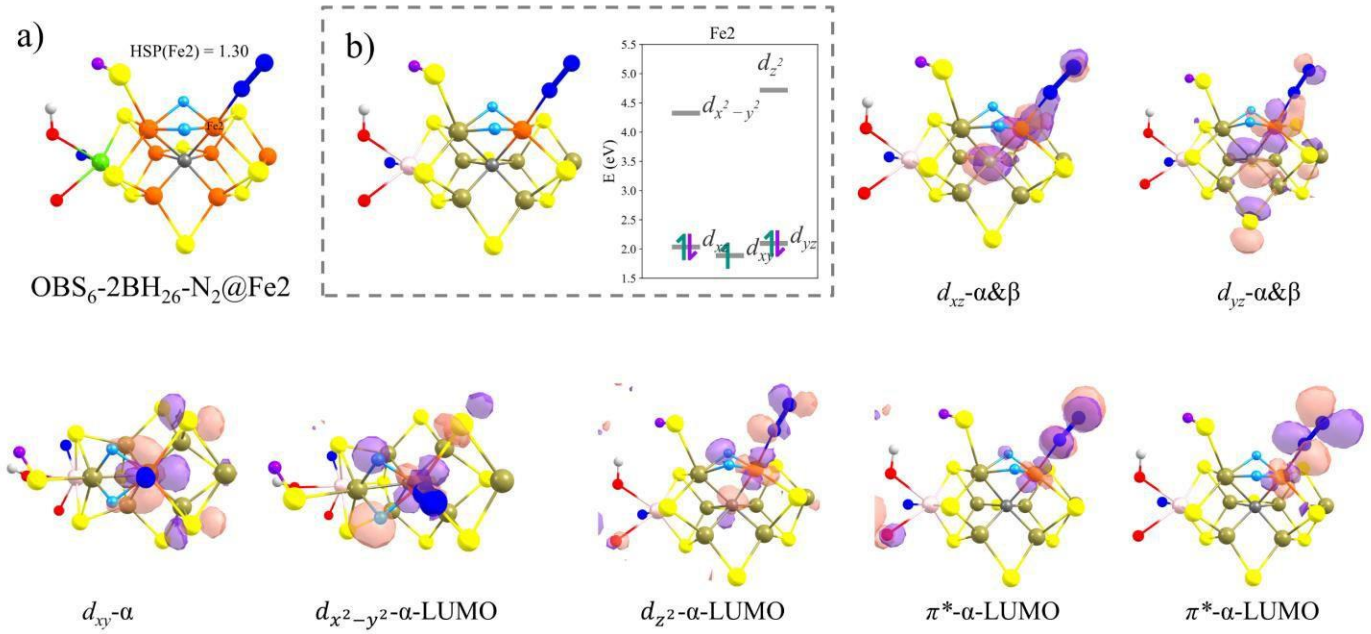


Figure S16. The structures of **OBS_6-$2BH_{26}$-N_2@Fe2-BS147 (M_S = 0)** with a full FeMoco (a) and diamagnetically substituted FeMoco (b) using the QM-C region and r^{2}SCAN. Also shown is the ligand-field diagram based on the diamagnetically substituted FeMoco and the quasi-restricted orbitals.

7. Orientations of protons of protonated S2B and S5A

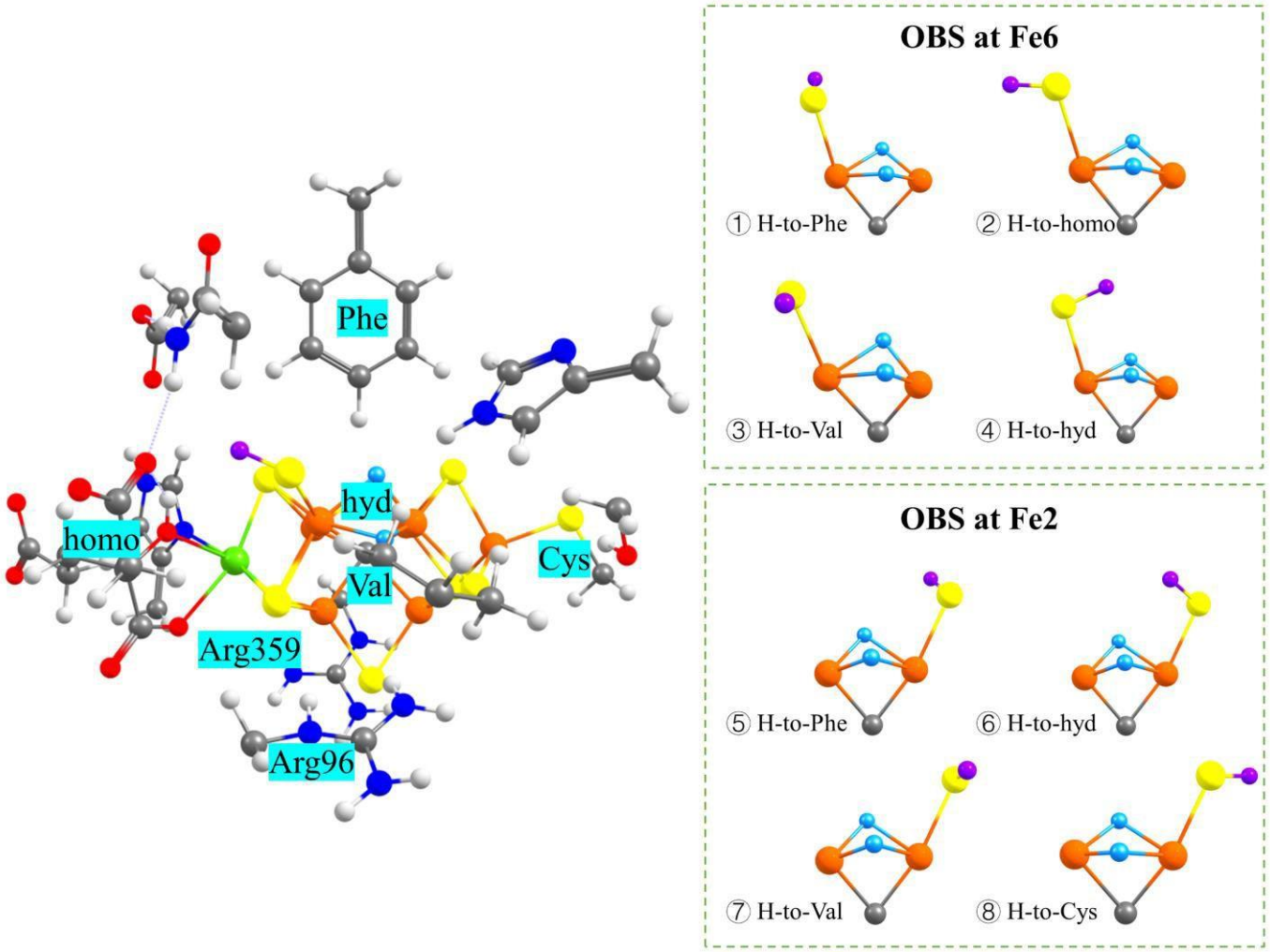


Figure S17. Different orientations of protons of either open or closed protonated belt sulfide-bridges. We use H-to-group to represent the orientation of the proton.

In this study, after optimizations of all states in spin states and 35 BS solutions for each model, the lowest-energy state was next used to explore all possible orientations of protons of either the closed or open protonated belt-sulfide bridges. The lowest-energy orientation was finally utilized in the study for obtaining results with the QM-C region (Results and Discussion section D) and was also used in the functional comparison (Results and Discussion section C).

If there is a terminal SH^- on Fe2, the proton has four orientations: H-to-Phe, H-to-hyd, H-to-Val, and H-to-Cys, shown in Figure S17. When the terminal SH^- is on Fe6, possible orientations of the proton are H-to-Phe, H-to-homo, H-to-Val, and H-to-hyd. In terms of a closed bridge at S2B (or S5A), proton orientations can be: H-to-Phe and H-to-Val (or H-to-Arg359 and H-to-Arg96).

Table S1. Relative energies of different orientations of the proton of an open bridge in **OBS_6-$2BH_{26}$** and **OBS_2-$2BH_{26}$** models (kcal/mol). All energies are relative to the lowest-energy model **OBS_6-DH_2** (see Figure 2k in the manuscript).

(g) OBS_6-$2BH_{26}$	ΔE(polarized QM energy)	ΔE(MM energy)	ΔE(QM/MM)
H-to-homo	-0.8	2.2	1.3
H-to-hyd	-0.1	1.7	1.7
H-to-Phe	converged to H-to-homo		
H-to-Val	converged to H-to-hyd		
(h) OBS_2-$2BH_{26}$	ΔE(polarized QM energy)	ΔE(MM energy)	ΔE(QM/MM)

H-to-Val	11.4	1.9	13.3
H-to-Cys	12.7	1.4	14.2
H-to-Phe	converged to H-to-Cys		
H-to-hyd	converged to H-to-Val		

Note: The spin states and BS solutions of **OBS_6-$2BH_{26}$** and **OBS_2-$2BH_{26}$** are BS347 (M_S = 1) and BS2356 (M_S = 0), respectively, which were calculated using QM-A region and r^{2}SCAN.

The lowest-energy orientation of the proton of an open belt-sulfide bridge at Fe2 in **OBS_2-$2BH_{26}$**, **OBS_2-$2BH_{26}$-TH_6** and **OBS_2-DH_6** models are H-to-Val, H-to-Cys, and H-to-Cys, respectively, shown in Table S1 to Table S3. If the proton at Fe6 in **OBS_6-$2BH_{26}$**, **OBS_6-BH_{26}-TH_2**, and **OBS_6-DH_2** models, the lowest-energy orientations are H-to-homo, H-to-hyd, and H-to-homo, respectively, shown in Table S1 to Table S3.

Table S2. Results of different orientations of the proton of an open belt sulfide-bridge in **OBS_2-$2BH_{26}$-TH_6** and **OBS_6-BH_{26}-TH_2** models (kcal/mol). All energies are relative to the lowest-energy model **OBS_6-DH_2** (see Figure 2k in the manuscript).

(j) OBS_2-BH_{26}-TH_6	ΔE(polarized QM energy)	ΔE(MM energy)	ΔE(QM/MM)
H-to-Val	converged to H-to-hyd		
H-to-Cys	9.6	4.0	13.6
H-to-Phe	14.5	2.7	17.2
H-to-hyd	10.5	3.5	14.0
(i) OBS_6-BH_{26}-TH_2			
H-to-homo	-0.9	2.1	1.2
H-to-hyd	-2.2	2.5	0.2
H-to-Phe	converged to H-to-hyd		
H-to-Val	converged to H-to-hyd		

Note: The spin states and BS solutions of **OBS_2-BH_{26}-TH_6** and **OBS_6-BH_{26}-TH_2** are BS147 (M_S = 1) and BS235 (M_S = 2), respectively, which were calculated using QM-A region and r^{2}SCAN.

Table S3. Results of different orientations of the proton of an open belt sulfide-bridge in **OBS_2-DH_6** and **OBS_6-DH_2** models (kcal/mol). All energies are relative to the lowest-energy model **OBS_6-DH_2** (see Figure 2k in the manuscript).

(l) OBS_2-DH_6	ΔE(polarized QM energy)	ΔE(MM energy)	ΔE(QM/MM)
H-to-Val	1.3	6.3	7.6
H-to-Cys	-0.7	6.4	5.7
H-to-Phe	3.8	5.3	9.1
H-to-hyd	converged to H-to-Val		
(k) OBS_6-DH_2			
H-to-homo	0.0	0.0	0.0
H-to-hyd	converged to H-to-Val		
H-to-Phe	-1.0	1.4	0.4
H-to-Val	0.4	1.3	1.7

Note: The spin states and BS solutions of **OBS_2-DH_6** and **OBS_6-DH_2** are BS346 (M_S = 2) and BS147 (M_S = 1), respectively, which were calculated using QM-A region and r^2SCAN.

Table S4 shows the relative energies of two protons on both an open belt sulfide-bridge (S2B) at Fe2 or Fe6 and a closed belt sulfide-bridge (S5A) in different orientations in **CBS_{37}-OBS_2-BH_{26}** and **CBS_{37}-OBS_6-BH_{26}** models. The lowest-energy orientation of **CBS_{37}-OBS_2-BH_{26}** and **CBS_{37}-OBS_6-BH_{26}** models are H_{S2B}-to-Cys-H_{S5A}-to-Arg359 and H_{S2B}-to-homo-H_{S5A}-to-Arg96, respectively.

Table S4. Results of different orientations of the proton of an open and a closed belt sulfide-bridge in **CBS_{37}-OBS_2-BH_{26}** and **CBS_{37}-OBS_6-BH_{26}** models (kcal/mol). All energies are relative to the lowest-energy model **OBS_6-DH_2** (see Figure 2k in the manuscript).

(m) CBS_{37}-OBS_2-BH_{26}	ΔE(polarized QM energy)	ΔE(MM energy)	ΔE(QM/MM)
H_{S2B}-to-Cys-H_{S5A}-to-Arg359	21.9	2.8	24.7
H_{S2B}-to-hyd-H_{S5A}-to-Arg359	27.1	0.0	27.1
H_{S2B}-to-Phe-H_{S5A}-to-Arg359	converged to H_{S2B}-to-hyd-H_{S5A}-to-Arg359		
H_{S2B}-to-Val-H_{S5A}-to-Arg359	converged to H_{S2B}-to-Cys-H_{S5A}-to-Arg359		
H_{S2B}-to-Cys-H_{S5A}-to-Arg96	20.5	4.4	25.0
H_{S2B}-to-hyd-H_{S5A}-to-Arg96	22.0	5.3	27.3
H_{S2B}-to-Phe-H_{S5A}-to-Arg96	converged to H_{S2B}-to-hyd-H_{S5A}-to-Arg96		
H_{S2B}-to-Val-H_{S5A}-to-Arg96	converged to H_{S2B}-to-Cys-H_{S5A}-to-Arg96		
(n) CBS_{37}-OBS_6-BH_{26}			
H_{S2B}-to-homo-H_{S5A}-to-Arg359	7.5	5.8	13.4
H_{S2B}-to-hyd-H_{S5A}-to-Arg359	7.9	5.7	13.5
H_{S2B}-to-Phe-H_{S5A}-to-Arg359	converged to H_{S2B}-to-hyd-H_{S5A}-to-Arg359		
H_{S2B}-to-Val-H_{S5A}-to-Arg359	converged to H_{S2B}-to-hyd-H_{S5A}-to-Arg359		
H_{S2B}-to-homo-H_{S5A}-to-Arg96	6.9	6.1	13.1
H_{S2B}-to-hyd-H_{S5A}-to-Arg96	7.3	6.0	13.2
H_{S2B}-to-Phe-H_{S5A}-to-Arg96	converged to H_{S2B}-to-hyd-H_{S5A}-to-Arg96		
H_{S2B}-to-Val-H_{S5A}-to-Arg96	converged to H_{S2B}-to-hyd-H_{S5A}-to-Arg96		

Note: The spin states and BS solutions of **CBS_{37}-OBS_2-BH_{26}** and **CBS_{37}-OBS_6-BH_{26}** are BS147 (M_S = 1) and BS247 (M_S = 2), respectively, which were calculated using QM-A region and r^2SCAN.

The relative energies of two protons on both closed hydrogenated S2B (between Fe2 and Fe6) and S5A (between Fe3 and Fe7) in **$2CBS_{26,37}$-$BH_{26(5)}$**, **$2CBS_{26,37}$-$BH_{26(3)}$**, and **$2CBS_{26,37}$-BH_{37}** models are shown in Table S5 to Table S7. The lowest-energy orientations of these three models are H_{S2B}-to-Phe-H_{S5A}-to-Arg359, H_{S2B}-to-Val-H_{S5A}-to-Arg359, and H_{S2B}-to-Phe-H_{S5A}-to-Arg359, respectively.

Because the energies of **CBS_{26}-$2BH_{26(5),37}$**, **CBS_{26}-$2BH_{26(3),37}$**, **CBS_{37}-$2BH_{26(5),37}$**, and **CBS_{37}-$2BH_{26(3),37}$** models are much higher than the lowest model **OBS_6-DH_2** (see Figure 2k in the manuscript), we did not investigate the orientations of protons at a closed belt sulfide-bridge (S2B or S5A). Different orientations of protons at the closed belt sulfide-bridge (S2B) of models **CBS_{26}-BH_{26}-TH_5**, **CBS_{26}-$2TH_{4,5}$** and **C3H** have been investigated in the previous paper[5].

Table S5. Results of different orientations of the proton of two closed belt sulfide-bridges in **$2CBS_{26,37}$-$BH_{26(5)}$** models (kcal/mol). All energies are relative to the lowest-energy model **OBS_6-DH_2** (see Figure 2k in the manuscript).

(o) $2CBS_{26,37}$-$BH_{26(5)}$	ΔE(polarized QM energy)	ΔE(MM energy)	ΔE(QM/MM)
H_{S2B}-to-Phe-H_{S5A}-to-Arg359	16.3	4.0	20.3

H_{S2B}-to-Phe-H_{S5A}-to-Arg96	16.4	4.6	21.0
H_{S2B}-to-Val-H_{S5A}-to-Arg359	21.6	3.2	24.8
H_{S2B}-to-Val-H_{S5A}-to-Arg96	21.7	3.8	25.5

Note: The spin state and BS solution of **$2CBS_{26,37}$-$BH_{26(5)}$** are BS14 and M_S = 2, respectively (using QM-A region and r^2SCAN).

Table S6. Results of different orientations of the proton of two closed sulfide-bridges in **$2CBS_{26,37}$-$BH_{26(3)}$** models (kcal/mol). All energies are relative to the lowest-energy model **OBS_6-DH_2** (see Figure 2k in the manuscript).

(p) $2CBS_{26,37}$-$BH_{26(3)}$	ΔE(polarized QM energy)	ΔE(MM energy)	ΔE(QM/MM)
H_{S2B}-to-Phe-H_{S5A}-to-Arg359	9.9	11.5	21.4
H_{S2B}-to-Phe-H_{S5A}-to-Arg96	11.9	10.1	22.0
H_{S2B}-to-Val-H_{S5A}-to-Arg359	8.6	9.9	18.4
H_{S2B}-to-Val-H_{S5A}-to-Arg96	9.5	9.8	19.3

Note: The spin state and BS solution of **$2CBS_{26,37}$-$BH_{26(3)}$** are BS14 and M_S = 2, respectively (using QM-A region and r^2SCAN).

Table S7. Results of different orientations of the proton of two closed sulfide-bridges in **$2CBS_{26,37}$-BH_{37}** models (kcal/mol). All energies are relative to the lowest-energy model **OBS_6-DH_2** (see Figure 2k in the manuscript).

(q) $2CBS_{26,37}$-BH_{37}	ΔE(polarized QM energy)	ΔE(MM energy)	ΔE(QM/MM)
H_{S2B}-to-Phe-H_{S5A}-to-Arg359	3.6	6.8	10.5
H_{S2B}-to-Phe-H_{S5A}-to-Arg96	6.6	8.2	14.8
H_{S2B}-to-Val-H_{S5A}-to-Arg359	8.8	6.8	15.6
H_{S2B}-to-Val-H_{S5A}-to-Arg96	5.6	5.5	11.1

Note: The spin state and BS solution of **$2CBS_{26,37}$-BH_{37}** are BS346 and M_S = 2, respectively (using QM-A region and r^2SCAN).

8. Additional information on spin-state and BS-state energies

Figure S18 shows the energy difference between the three spin states for $\mathbf{E_3}$ isomers **e** to **q** (see Figure 2), and the lowest energy BS state for each M_S state is plotted. The difference between different spin states for each isomer can be fairly large, especially for isomers **k** and **l**.

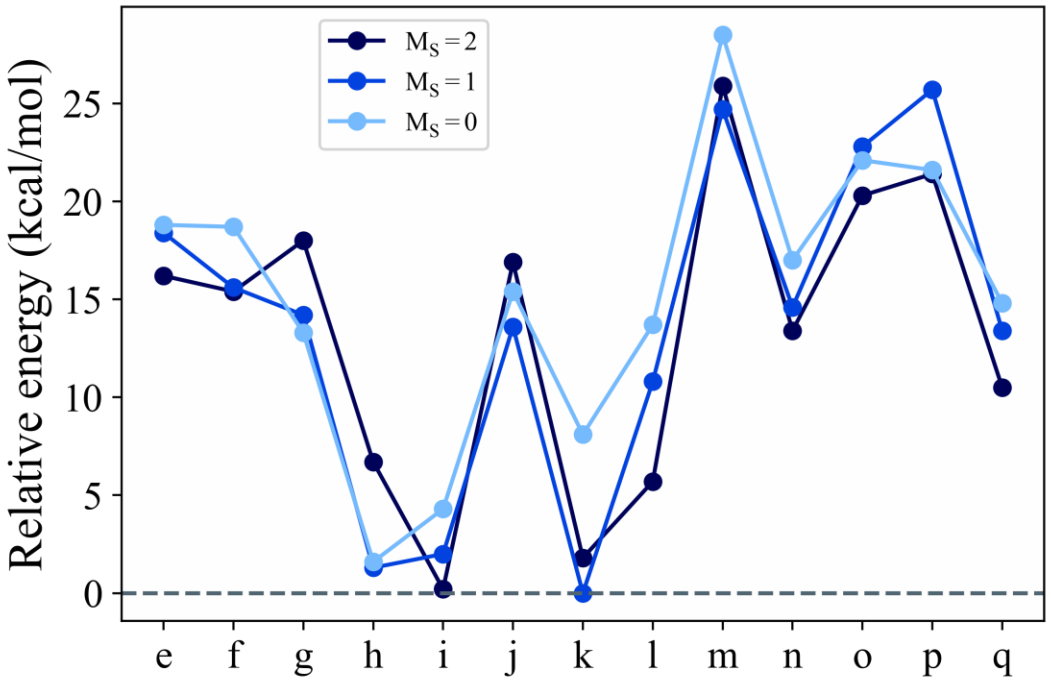


Figure S18. The spin-state energies for isomers **e-q** according to QM/MM calculations using QM-region A and r^2SCAN. The lowest-energy BS-state for each spin-state is used. The BS solutions of **e-q** models were shown in section 12.

For every spin-state of each isomer we systematically attempted spin-flipping of 3 Fe ions to find 35 different broken-symmetry states. Some calculations converged, however, to states with either 2 or 4 spin-down Fe ions. A state with only 2 spin-down Fe ions represents an alternative BS state that is typically not included in the BS-state problem of FeMoco, as such a state should generally be high in energy due to a lack of pairwise antiferromagnetic interactions (antiferromagnetic coupling is highly stabilizing). A BS-state with 4 spin-down Fe ions instead, however, should typically represent a mirror image of a BS-state with 3 spin-down Fe ions as whether a local-spin is spin-up or spin-down is arbitrary. This is complicated by the fact, however, that FeMoco is a mixed-valent system and the minority-spin electrons (typically between pairs of Fe ions) can delocalize in multiple ways or localize on different Fe ions. This means that there are actually even more SCF states and the "mirror-image states" do not have to have the same energy.

As an example: The BS2567 state was found when attempting to find BS256 for the **2CBS$_{26,37}$-BH$_{26(5)}$ (M_S = 0)** isomer. BS2567 and BS134 should be mirror-images, and as shown in Table S8, they have identical energies and Mulliken spin populations.

Table S8. The Mulliken spin populations of BS2567 and BS134 of **2CBS$_{26,37}$-BH$_{26(5)}$** with M_S = 0.

	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS2567	19.3	22.1	1.28	3.32	-3.17	3.02	3.17	-3.01	-2.14	-2.81
BS134	19.0	22.1	-1.29	-3.32	3.17	-3.01	-3.18	3.01	2.16	2.82

Note: The results in this table were calculated using QM-A region and r^2SCAN.

However, for the case of BS2567 and BS134 solutions for isomer **OBS_2-$2BH_{26}$-N_2@Fe6-M_S=1** (Figure S15), shown in Table S9, they have considerably different energies and Mulliken spin populations, suggesting that while the basic spin topology is the same, the states likely differ with respect to localization/delocalization degree of the minority-spin electrons.

Table S9. The Mulliken spin populations of BS2567 and BS134 of **OBS_2-$2BH_{26}$-N_2@Fe6** with M_S = 1.

	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS2567	20.5	19.4	-0.96	-2.83	3.24	-1.87	-2.91	3.12	0.83	3.02
BS134	10.3	10.7	0.82	3.29	-3.03	3.22	3.16	-2.77	-0.58	-2.56

Note: The results in this table were calculated using QM-A region and r^{2}SCAN.

The 35 different BS solutions can be grouped into 10 BS classes according to analysis made popular by Noodleman. In order to understand the general stability of different BS solutions of the **E_3** isomers we have grouped the 3 lowest energy BS solutions for each isomer and spin-state into which of the 10 BS classes it belongs to as shown in Table S10. We note that for the cases where the spin-flipping resulted in low-energy BS states with 4 spin-down Fe ions was, the state was grouped according to its mirror image BS if their energy difference was small, for example, if BS2356 and BS147 have a very small energy difference (< 0.5 kcal/mol) or even the same, the BS2356 was grouped into BS10 (as its mirror-image BS147). However, for the case of where BS2356 and BS147 had larger energy difference (and different electronic structure) we labelled it as BS2356 in the table.
The results in Table S8 overall reveal that the most stable BS states for **E_3** isomers belong to the BS7, BS8 and BS10 class (and to a lesser extent BS6 and BS9).

Table S10. The classification of the three lowest-energy BS states (lower than 5 kcal/mol) of each spin state and each isomer into the 10 common BS classes and selected unusual BS states.

		ΔE_{max}[a]	BS1	BS2	BS3	BS4	BS5	BS6	BS7	BS8	BS9	BS10	BS2356	BS3456	BS13	BS14
a: CBS_{26}-$2BH_{26(5),37}$	(M_S = 1)	0.8[b]								■	■					
b: CBS_{26}-$2BH_{26(3),37}$	(M_S = 1)	4.9								■	♦ ■[c]					
c: CBS_{37}-$2BH_{26(5),37}$	(M_S = 1)	3.9						■		■	■					
d: CBS_{37}-$2BH_{26(3),37}$	(M_S = 1)	2.5								■	■	■				
e: CBS_{26}-BH_{26}-TH_5	(M_S = 2)	1.6								■	■				■	
	(M_S = 1)	4.0						■		■		■				
	(M_S = 0)	3.4							■■		■					
f: CBS_{26}-$2TH_{4,5}$	(M_S = 2)	3.0							■■	■						
	(M_S = 1)	2.4		■				■		■						
	(M_S = 0)	2.1		■								■		■		
g: OBS_6-$2BH_{26}$	(M_S = 2)	1.4								■					■	■
	(M_S = 1)	3.0								■■		■				
	(M_S = 0)	3.3						■				■■				
h: OBS_2-$2BH_{26}$	(M_S = 2)	3.0							■	■	■					
	(M_S = 1)	1.3								■		■■				
	(M_S = 0)	1.3								■		■■				
i: OBS_6-BH_{26}-TH_2	(M_S = 2)	4.3							■■	■						
	(M_S = 1)	0.5						■	■			■				
	(M_S = 0)	2.8						■				■■				

j: OBS_2-BH_{26}-TH_6	(M_S = 2)	2.6														
	(M_S = 1)	1.3														
	(M_S = 0)	0.9														
k: OBS_6-DH_2	(M_S = 2)	0.5														
	(M_S = 1)	1.6														
	(M_S = 0)	0.4														
l: OBS_2-DH_6	(M_S = 2)	0[d]														
	(M_S = 1)	2.6														
	(M_S = 0)	0.6														
m: CBS_{37}-OBS_2-BH_{26}	(M_S = 2)	0.9														
	(M_S = 1)	2.0														
	(M_S = 0)	1.0														
n: CBS_{37}-OBS_6-BH_{26}	(M_S = 2)	0.6														
	(M_S = 1)	0.2														
	(M_S = 0)	0.5														
o: $2CBS_{26,37}$-$BH_{26(5)}$	(M_S = 2)	1.6														
	(M_S = 1)	0.1														
	(M_S = 0)	2.8														
p: $2CBS_{26,37}$-$BH_{26(3)}$	(M_S = 2)	3.8														
	(M_S = 1)	0.4														
	(M_S = 0)	2.2														
q: $2CBS_{26,37}$-BH_{37}	(M_S = 2)	0.5														
	(M_S = 1)	1.4														
	(M_S = 0)	2.8														
OBS_2-$2BH_{26}$-N_2@Fe6[e]	(M_S = 0)	0.1														
OBS_6-$2BH_{26}$-N_2@Fe2[e]	(M_S = 0)	2.5														

[a]The maximum energy difference between three selected BS states. [b]Only two states converged to the initial input structure (what we designed). [c]Two states belongs to the same BS class. [d]There is only one BS solution, because the second lowest-energy state is higher than the first lowest-energy state by 7.4 kcal/mol. [e]The three lowest-energy states for **OBS_2-$2BH_{26}$-N_2@Fe6** and **OBS_6-$2BH_{26}$-N_2@Fe2** are all M_S = 0, so only the M_S = 0 BS states are included. All results in this table were calculated using QM-A region and r^{2}SCAN.

9. Additional results for different functionals

Relative energies with different functionals

Figure S19 shows additional results related to the functional dependency presented in section C of the manuscript. TPSSh, B97-D3, and r^{2}SCAN give very similar trend for all isomers, and **g**, **i**, and **k** are found to be three lowest energy isomers.

B3LYP*, B3LYP, and TPSS give results quite different from the other three functionals. The **g** and **i** isomers are also lower-energy isomers when using TPSS; however, the **k** isomer is higher than **g** and **i** by about 8 kcal/mol and also less stable than **f**. B3LYP* favors **r** containing a triply protonated carbide ion, which is a little lower than **g**, **i**, and **k** isomers. The energy difference between **g**, **i**, and **k** isomers when using B3LYP* is larger than TPSSh, B97-D3, and r^{2}SCAN, and **k** with H_2 bound to Fe2 is more stable than **g** and **i**. B3LYP has a similar trend to B3LYP* but the energy difference between **r** and other isomers is much larger than B3LYP*. As dicussed in previous studies[6] from our group TPSSh, B97-D3, B3LYP* and r^{2}SCAN are known to describe Fe-Fe/Mo-Fe distances of spin-coupled sulfide-bridged Fe-Fe/Mo-Fe dimers as well as FeMoco very similarly and better than both most regular GGA/meta-GGA functionals (like TPSS) and also common hybrid functionals (like B3LYP). However, B3LYP* gives here a very different trend from TPSSh, B97-D3, and r^{2}SCAN for the energetics of the $\mathbf{E_3}$ state. TPSS was previously shown to systematically underestimate Fe-Fe/Mo-Fe distances and this was found to correlate with a tendency to overestimate covalency in the bridging Fe-S bonds[6].

The B3LYP and B3LYP* functionals favor the **C3H** $\mathbf{E_3}$ model (**r**), however, there is no experimental evidence that suggests reduced FeMoco states with a protonated carbide are ever formed. According to recent ^{13}C ENDOR measurements of multiple trapped FeMoco states, the carbide hyperfine coupling is practically unchanged, suggesting an unchanged carbide environment.

In a recent study, both TPSSh and B3LYP were found to favor the **C3H** isomer[4], but in this work we find that **C3H** is higher than isomer **k** by 25.1 kcal/mol (0.9 kcal/mol in that study[4]) when using TPSSh. The reason for this difference is most likely the basis set, we have in this work consistely used an all-electron scalar relativistic treatment with a large ZORA-def2-TZVP on the cofactor while a much smaller basis, def2-SV(P) basis set was utilized in the previous study without scalar relativistic effects included[4]. The spin state and BS solution of this model used in the previous study are M_S = 1 and BS136[4]. We explored this model in three spin states and 6 BS solutions belonging to BS10 class, and found that the lowest-energy isomer has M_S =1 and BS146 , slightly lower than BS136 by 0.6 kcal/mol.

Finally, we note that the covalency of Fe-H bonds and the ability of DFT protocols to describe such bonds is an underexplored area and few studies have been dedicated to this topic. This is likely highly relevant in this context of $\mathbf{E_3}$ isomers .

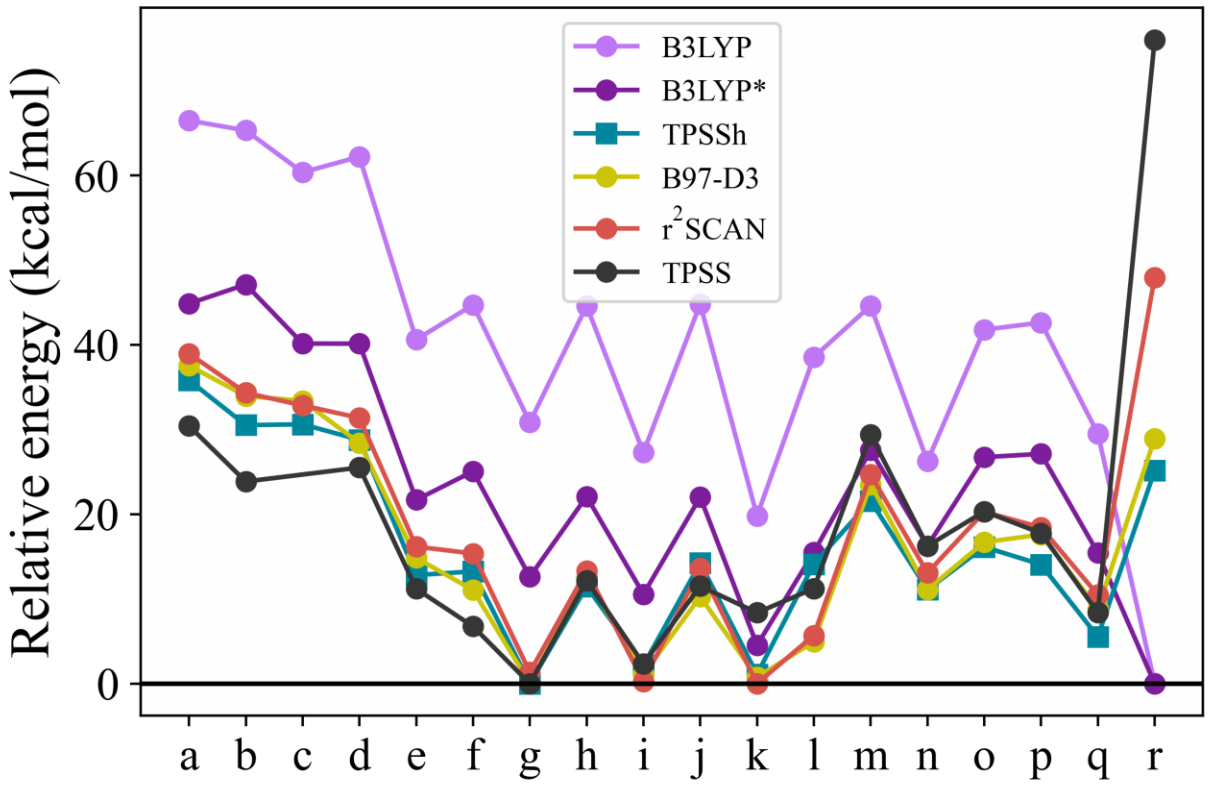


Figure S19. The comparison for isomers **a**-**r** between different functionals. The **c** isomer is missing for the TPSS functional, because three BS states of this isomer converge to other isomers with one terminal hydride on Fe2 (the distance of Fe2-hydride is longer than 2 Å), shown in Table S14 and Figure S9. The information about spin states and BS solutions of each model have been shown in Tables S12 to S28 of the SI.

Electronic structure analysis with different functionals

Figure S20 to Figure S25 shows electron configurations derived from localized orbital analysis as well as selected geometric parameters of each isomer **g**, **I** and **k** with TPSSh, B97-D3, r^{2}SCAN, B3LYP*, and TPSS used in this study.

For the **g (OBS$_6$-2BH$_{26}$)** isomer (Figure S20), the common theme is that there are four electrons associated with the two bridging hydrides, but the difference is the degree of delocalization of these electrons to either Fe2 or Fe6. The r^{2}SCAN and B3LYP* give similar electronic structures, two bridging hydrides share four electrons with Fe2, which is associated with shorter Fe2-hydride distances than Fe6-hydride (see Figure S21), and one electron has transferred from the Fe$_4$ sub-cubane to the hydrides compared to the **E$_0$** state (see Figure S11). In contrast, there are four electrons delocalized between hydrides and Fe6 for TPSSh, which is correlated with shorter Fe6-hydride distances than Fe2-hydride distances, and one electron has transferred from the MoFe$_3$-cubane to the hydrides. Interestingly, TPSS and B97-D3 give a trend in-between r^{2}SCAN, B3LYP* and TPSSh, those four electrons are shared with both Fe2 and Fe6, correlating with similar distances between hydrides and Fe2/Fe6, but one electron has transferred from MoFe$_3$ sub-cubane to hydrides and Fe2 and Fe6 share one electron. We also note that part of the trends seen may be related to different BS solutions preferred by different functionals.

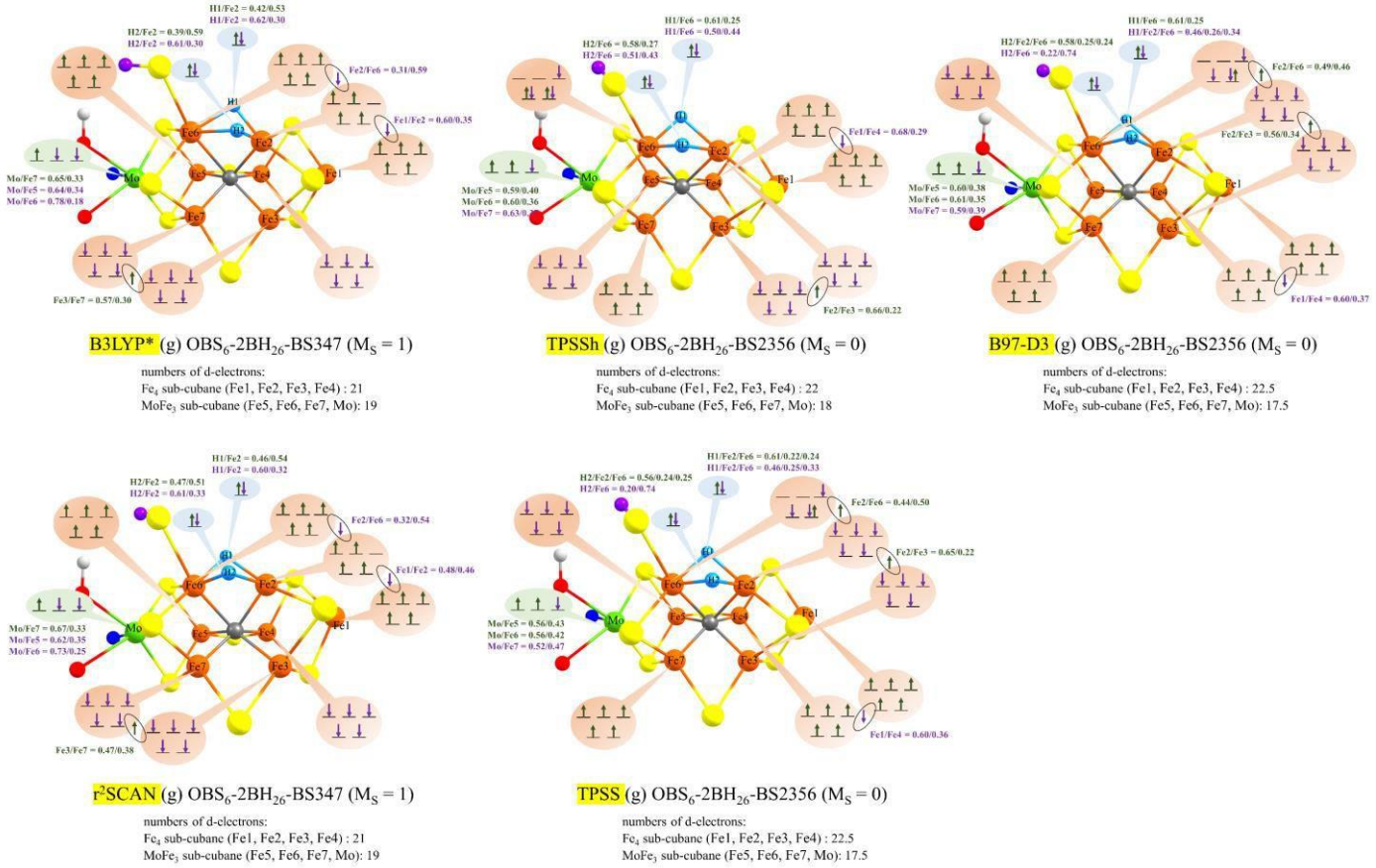


Figure S20. The comparison of electronic configurations for isomer **g** between different functionals. The green and purple numbers are localized orbital populations. The configurations of r^{2}SCAN and other functionals were calculated using the QM-C and QM-A regions, respectively. Our previous paper show that the geometric and electronic structure differences between the QM-A and QM-C region are minor[3].

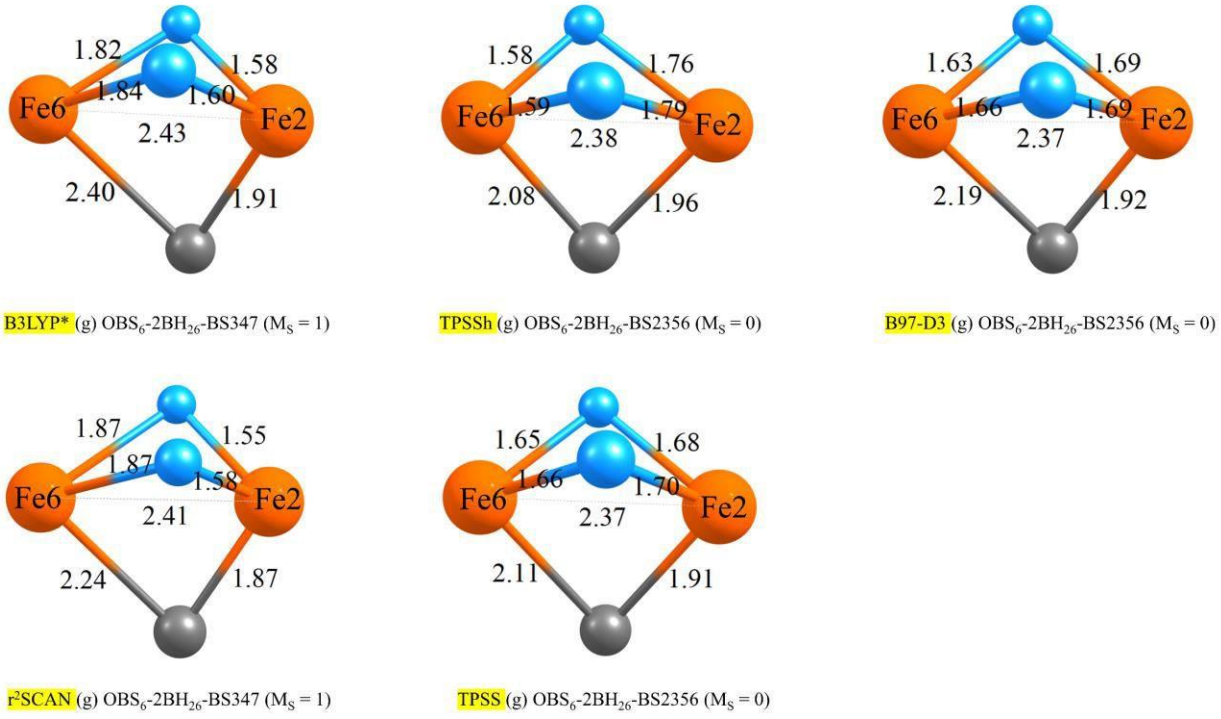


Figure S21. The comparison of key distances for isomers **g** with different functionals. The geometries of r^{2}SCAN and other functionals were calculated using the QM-C and QM-A regions, respectively. Our previous paper show that the geometric and electronic structure differences between the QM-A and QM-C region are minor[3].

For isomer **i (OBS$_6$-BH$_{26}$-TH$_2$)**, the molecular and electronic structure is overall quite similar for the five functionals in that the terminal hydride has 2 electrons associated with it (shared to different extent between H and Fe2), and the bridging hydride shares electrons with both Fe2 and Fe6, and the distances of Fe2/Fe6-hydrides are similar with differences, as shown in Figure S22 and Figure S23. There are some differences, however, associated with Fe2 vs Fe6 vs. H contribution to the bridging hydride and TPSS differs in that an electron from the MoFe$_3$ sub-cubane is donated to the hydrides while for the other functionals an Fe$_4$ sub-cubane electron has been donated. Also B3LYP* prefers localizing the minority-spin electrons while the others show more mixed-valence delocalization.

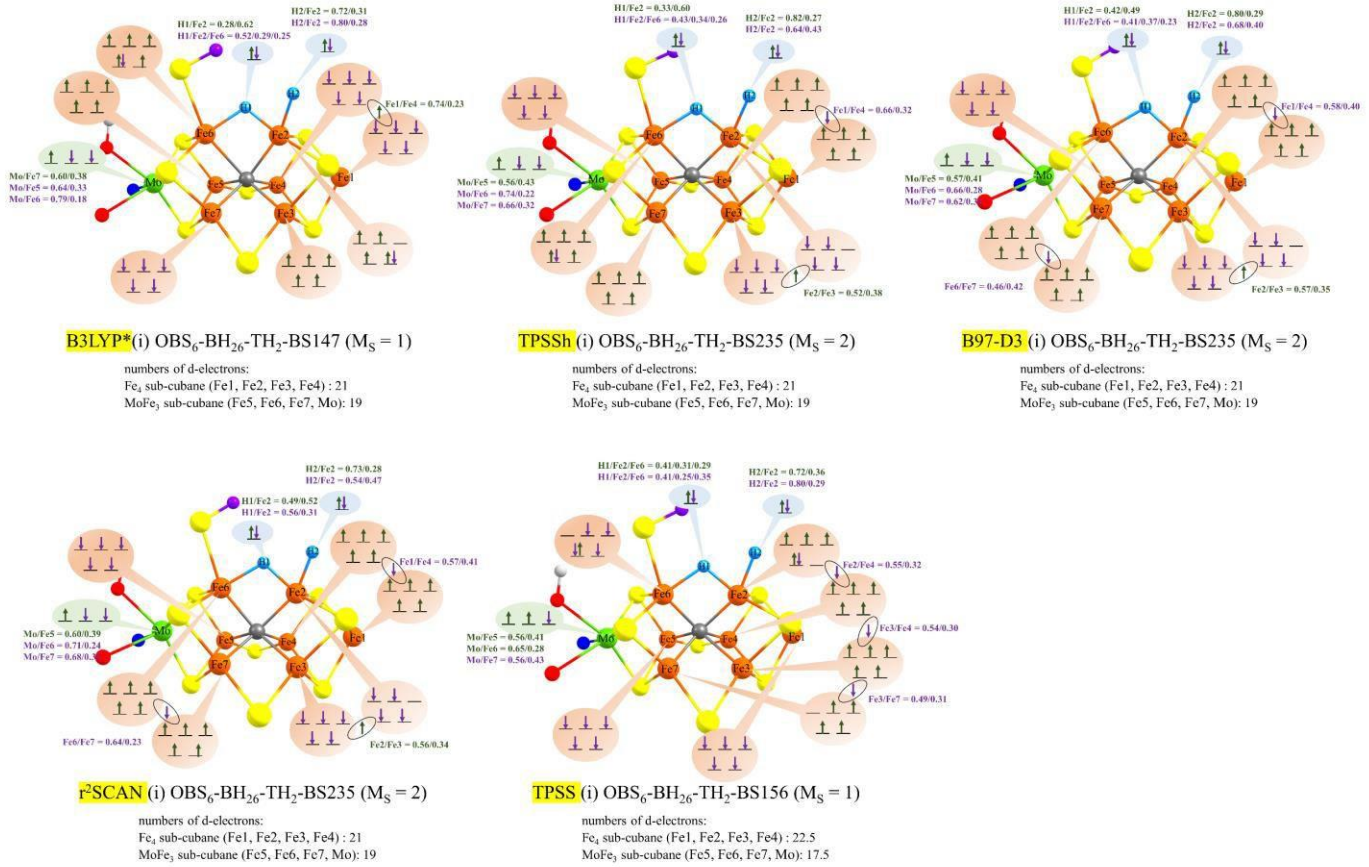


Figure S22. The comparison of electronic configurations for isomer **i** between different functionals. The green and purple numbers are localized orbital populations. The configurations of r^{2}SCAN and other functionals were calculated using the QM-C and QM-A regions, respectively. Our previous paper show that the geometric and electronic structure differences between QM-A and QM-C regions are minor[3].

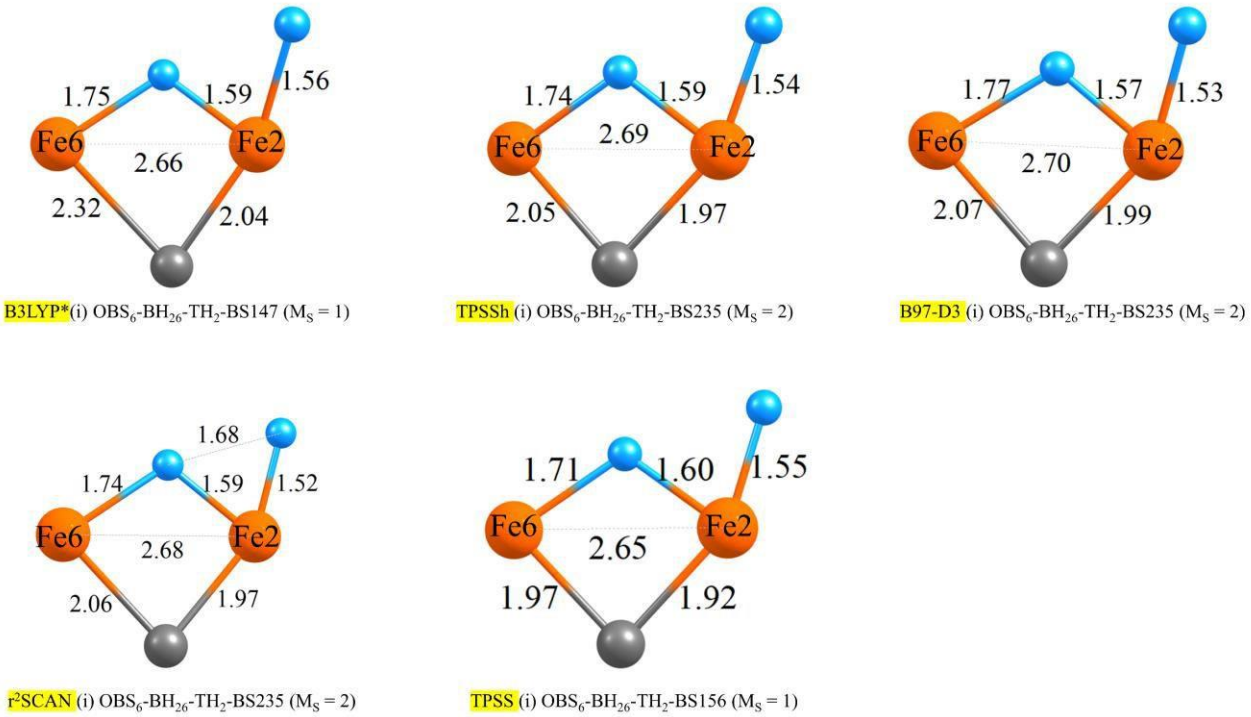


Figure S23. The comparison of key distances for isomers **i** with different functionals. The geometries of r^{2}SCAN and other functionals were calculated using the QM-C and QM-A regions, respectively. Our previous paper show that the geometric and electronic structure differences between the QM-A and QM-C region are minor[3].

The five functionals give similar electronic configurations for isomer **k (OBS$_6$-DH$_2$)** (see Figure S24) according to localized orbital analysis. Two electrons can be found in the dihydrogen ligand bound to Fe2, and 1 additional electron is located in the Fe$_4$ sub-cubane compared to the **E$_0$** state (see Figure S11). The distances of Fe2-Fe6 are overall similar (see Figure S25), but the H-H bond lengths with B97-D3 and TPSS functionals are longer than with the other functionals. This correlates with shorter Fe2-H$_2$ distances for B97-D3 and TPSS compared to the other functionals, implying that the dihydrogen ligand is more activated in B97-D3 and TPSS calculations. The H-H bond of free H$_2$ is almost the same for five functionals (see Table S11), suggesting that the differences arise from the Fe-H$_2$ interaction.

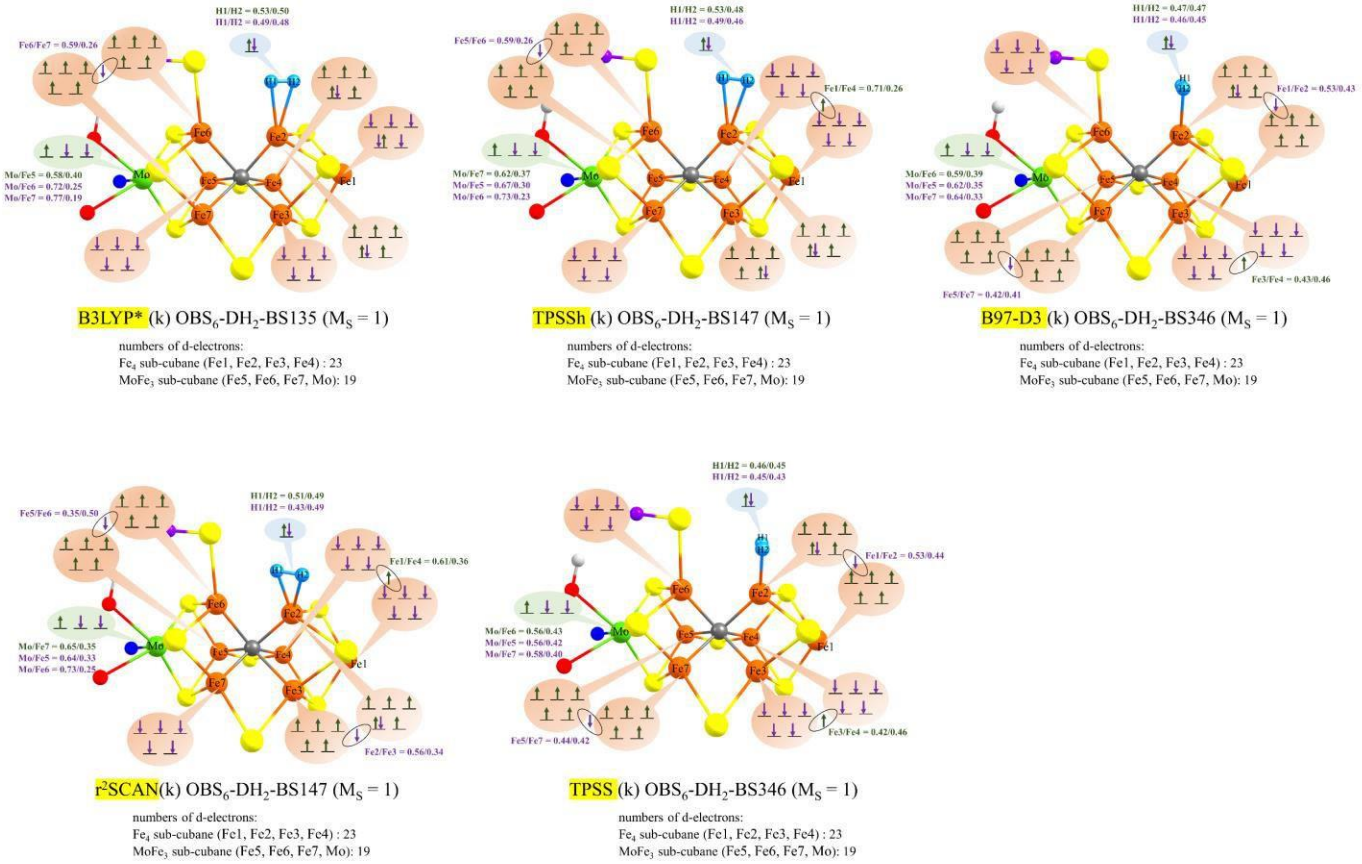


Figure S24. The comparison of electronic configurations for isomer **k** with different functionals. The green and purple numbers are localized orbital populations. The configurations of r^{2}SCAN and other functionals were calculated using the QM-C and QM-A regions, respectively. Our previous paper show that generally the geometric and electronic structure differences between the QM-A and QM-C regions are relatively minor[3].

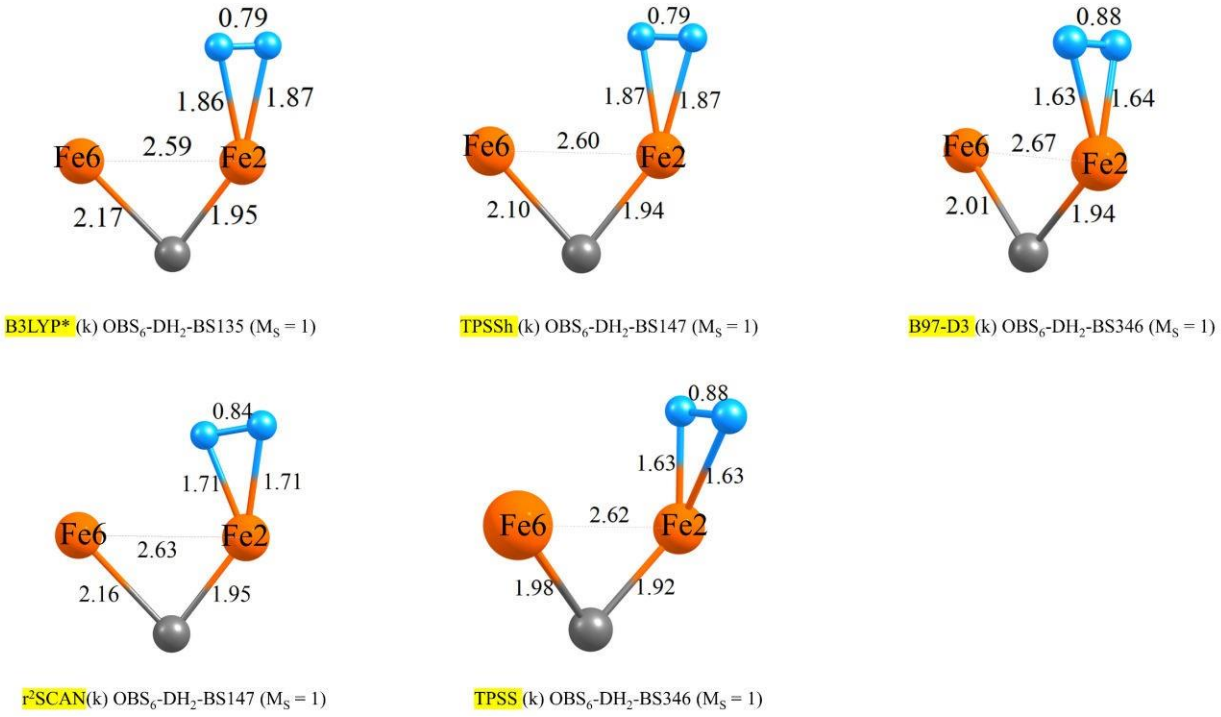


Figure S25. The comparison of key distances for isomer **k** with different functionals. The r^{2}SCAN geometry was calculated using the QM-C region while the other functionals were calculated using the QM-A region. Our previous paper show that the geometric and electronic structure differences between the QM-A and QM-C region are minor[3].

Table S11. The H-H bond of free H_2 calculated using different functionals in vacuum (same basis sets as H_2 in OBS_6-DH_2: ZORA-def2-TZVP).

	B3LYP*	TPSSh	B97-D3	r^{2}SCAN	TPSS
The H-H Bonds of free H_2	0.75 Å	0.74 Å	0.75 Å	0.74 Å	0.74 Å

Table S12 to Table S28 show relative polarized QM and QM/MM energies for all 6 functionals using QM-region A and the BS solutions calculated. All energies are relative to isomer **k** (Figure 2k) for each functional.

Table S12. The relative polarized QM and QM/MM energies between five functionals for **CBS_{26}-$2BH_{26(5),37}$** (kcal/mol).

a: CBS_{26}-$2BH_{26(5),37}$	**B3LYP***		**TPSSh**		**B97-D3**		**r^{2}SCAN**		**TPSS**		**B3LYP**	
	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM
BS245 (M_S = 1)	46.3	47.0	37.8	36.8	-	-	36.4	39.0	31.9	30.4	67.4	68.1
BS145 (M_S = 1)	46.2	44.9	37.6	35.8	38.7	37.5	37.8	39.8	34.9	34.8	68.4	66.5

Note: The '-' in the table means that this state converged to another isomer. Numbers in blue indicate the lowest one between states.

Table S13. The relative polarized QM and QM/MM energies between five functionals for **CBS_{26}-$2BH_{26(3),37}$** (kcal/mol).

b: CBS_{26}-$2BH_{26(3),37}$	**B3LYP***		**TPSSh**		**B97-D3**		**r^{2}SCAN**		**TPSS**		**B3LYP**	
	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM
BS137 (M_S = 1)	-	-	24.9	30.5	-	-	24.4	34.3	17.6	23.9	-	-
BS145 (M_S = 1)	-	-	27.1	32.1	27.8	33.9	28.3	37.8	24.0	30.2	-	-
BS245 (M_S = 1)	38.9	47.1	24.9	30.5	-	-	29.2	39.3	20.1	27.2	57.1	65.3

Note: The '-' in the table means that this state converged to another isomer. Numbers in blue indicate the lowest one between states.

Table S14. The relative polarized QM and QM/MM energies between five functionals for **CBS_{37}-$2BH_{26(5),37}$** (kcal/mol).

c: CBS_{37}-$2BH_{26(5),37}$	**B3LYP***		**TPSSh**		**B97-D3**		**r^{2}SCAN**		**TPSS**		**B3LYP**	
	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM
BS345 (M_S = 1)	43.8	40.1	36.3	30.6	-	-	35.0	32.8	-	-	64.3	60.4
BS126 (M_S = 1)	-	-	36.9	32.0	-	-	36.6	35.0	-	-	-	-
BS157 (M_S = 1)	46.1	43.1	38.3	33.1	37.1	33.4	38.1	36.7	-	-	66.2	62.9

Note: The '-' in the table means that this state converged to another isomer. Numbers in blue indicate the lowest one between states.

Table S15. The relative polarized QM and QM/MM energies between five functionals for **CBS_{37}-$2BH_{26(3),37}$** (kcal/mol).

d: CBS_{37}-$2BH_{26(3),37}$	**B3LYP***		**TPSSh**		**B97-D3**		**r^{2}SCAN**		**TPSS**		**B3LYP**	
	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM
BS345 (M_S = 1)	40.5	43.3	28.1	28.8	26.3	28.4	26.8	31.4	-	-	-	-
BS126 (M_S = 1)	44.0	47.8	28.3	30.9	-	-	28.0	33.9	-	-	-	-

BS135 (M_S = 1)	36.6	40.1	28.8	30.3	26.2	29.2	27.2	32.4	23.7	25.5[a]	58.9	62.2

[a] This state converged to BS15.
Note: The '-' in the table means that this state converged to another isomer. Numbers in blue indicate the lowest one between states.

Table S16. The relative polarized QM and QM/MM energies between five functionals for **CBS_{26}-BH_{26}-TH_5** (kcal/mol).

e: CBS_{26}-BH_{26}-TH_5	**B3LYP***		**TPSSh**		**B97-D3**		**r^2SCAN**		**TPSS**		**B3LYP**	
	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM
BS13 (M_S = 2)	32.0	31.4	17.2	14.8	16.6	14.8	16.8	17.8	13.7	11.2	56.5	55.5
BS236 (M_S = 2)	23.7	21.7	16.5	12.8	18.3	15.5	16.4	16.2	17.2	13.8	46.1	43.6
BS126 (M_S = 2)	27.4	25.9	18.4	15.6	17.5	15.7	16.9	17.8	15.9	13.1[a]	51.4	48.7
BS236 (M_S = 1)	25.7	25.7	18.8	16.8	22.2	21.1	16.6	18.4	21.1	17.5	40.7	40.6
BS2356 (M_S = 0)	32.7	29.9	21.2	16.6	22.7	18.9	19.9	18.8	21.5	17.8	51.9	49.0

[a] This state converged to BS12. Numbers in blue indicate the lowest one between states.

Table S17. The relative polarized QM and QM/MM energies between five functionals for **CBS_{26}-$2TH_{4,5}$** (kcal/mol).

f: CBS_{26}-$2TH_{4,5}$	**B3LYP***		**TPSSh**		**B97-D3**		**r^2SCAN**		**TPSS**		**B3LYP**	
	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM
BS346 (M_S = 2)	20.9	26.0	10.0	13.4	10.1	13.9	10.1	16.6	6.5	9.6	41.2	45.8
BS345 (M_S = 2)	20.2	25.2	10.8	14.0	12.5	16.3	8.9	15.4	10.9	13.6	40.6	44.7
BS234 (M_S = 1)	18.3	25.3	8.1	13.2	5.9	11.0	7.8	15.7	2.5	6.8	43.5	48.3
BS167 (M_S = 1)	18.8	25.9	8.3	13.8	7.6	13.3	7.1	15.6	4.5	7.5[a]	40.1	46.5
BS236 (M_S = 1)	19.7	25.1	13.1	16.9	13.5	17.8	11.3	18.0	10.1	12.7	43.8	48.0

[a] This state converged to BS17. Numbers in blue indicate the lowest one between states.

Table S18. The relative polarized QM and QM/MM energies between five functionals for **OBS_6-$2BH_{26}$** (kcal/mol).

g: OBS_6-$2BH_{26}$	**B3LYP***		**TPSSh**		**B97-D3**		**r^2SCAN**		**TPSS**		**B3LYP**	
	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM
BS345 (M_S = 1)	11.9	12.6[a]	5.1	4.2	2.7	1.9	1.2	1.9	5.1	5.1	-	-
BS347 (M_S = 1)	11.9	12.6	4.0	3.7	1.4	1.0	0.3	1.3	4.6	4.5	30.7	30.8
BS2356 (M_S = 0)	11.9	13.0	0.0	0.0	0.0	0.0	0.1	1.6	0.0	0.0	34.2	34.5
BS2467 (M_S = 0)	13.2	14.2	1.3	1.4	0.5	0.9	1.0	2.8	0.4	0.8	39.2	35.8
BS147 (M_S = 0)	11.9	13.0	0.0	0.0	0.0	0.0	0.0	1.6	0.0	0.0	38.7	34.3

[a] This state converged to BS347. Numbers in blue indicate the lowest one between states.

Table S19. The relative polarized QM and QM/MM energies between five functionals for **OBS_2-$2BH_{26}$** (kcal/mol).

h: OBS_2-$2BH_{26}$	**B3LYP***		**TPSSh**		**B97-D3**		**r^2SCAN**		**TPSS**		**B3LYP**	
	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM
BS147 (M_S = 1)	20.5	22.3	12.8	12.7	13.6	15.0	10.5	14.2	15.8	15.7	47.7	44.6

BS2356 (M_S = 0)	21.0	22.1	12.6	11.5	12.0	12.6	11.4	13.3	12.5	12.2	50.2	45.9
BS2467 (M_S = 0)	20.2	22.6	12.4	12.3	11.2	12.9	10.7	14.1	11.9	12.2	49.4	45.9
BS135 (M_S = 0)	20.2	22.6	12.4	12.3	11.3	13.0	10.8	14.2	11.8	12.2	49.4	45.9
BS147 (M_S = 0)	21.7	22.7	13.5	12.2	12.5	13.1	12.5	14.2	13.3	13.0	49.7	45.6

Table S20. The relative polarized QM and QM/MM energies between five functionals for **OBS_6-BH_{26}-TH_2** (kcal/mol).

i: OBS_6-BH_{26}-TH_2	**B3LYP***		**TPSSh**		**B97-D3**		**r^2SCAN**		**TPSS**		**B3LYP**	
	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM
BS235 (M_S = 2)	10.4	11.1	2.8	2.2	1.5	1.1	-2.2	0.2	3.7	3.6	28.5	29.7
BS247 (M_S = 2)	9.3	11.5	1.9	2.9	0.3	1.1	-1.9	1.7	2.8	3.5	28.7	30.1
BS156 (M_S = 1)	13.2	15.7	3.4	4.3	1.0	1.7	0.0	2.5	2.0	2.3	35.5	38.2
BS157 (M_S = 1)	13.0	15.1	3.7	4.1	1.4	1.7	0.2	2.5	3.7	4.2	39.6	41.2
BS346 (M_S = 1)	12.5	12.7	5.5	4.3	2.1	1.2	1.3	2.2	6.9	5.6	30.5	31.0
BS147 (M_S = 1)	9.6	10.6	4.1	3.9	3.0	2.5	0.5	2.0	8.5	8.2	26.8	27.3

Numbers in blue indicate the lowest one between states.

Table S21. The relative polarized QM and QM/MM energies between five functionals for **OBS_2-BH_{26}-TH_6** (kcal/mol).

j: OBS_2-BH_{26}-TH_6	**B3LYP***		**TPSSh**		**B97-D3**		**r^2SCAN**		**TPSS**		**B3LYP**	
	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM
BS235 (M_S = 1)	20.3	23.7	14.1	15.2	8.8	10.3	11.8	14.9	11.7	11.5	42.4	45.0
BS247 (M_S = 1)	20.9	23.6	15.2	15.2	11.2	12.4	12.6	14.9	13.3	13.1	45.0	47.2
BS347 (M_S = 1)	23.0	26.8	15.0	16.2	10.8	13.6	10.5	14.2	-	-	-	-
BS147 (M_S = 1)	19.0	22.0	14.5	14.7	13.2	14.7	9.6	13.6	18.3	18.3	42.3	44.8
BS2356 (M_S = 0)	23.9	25.4	14.6	14.2	14.0	15.2	12.8	15.4	-	-	44.2	45.3

Note: The '-' in the table means that this state converged to another isomer. Numbers in blue indicate the lowest one between states.

Table S22. The relative polarized QM and QM/MM energies between five functionals for **OBS_6-DH_2** (kcal/mol).

k: OBS_6-DH_2	**B3LYP***		**TPSSh**		**B97-D3**		**r^2SCAN**		**TPSS**		**B3LYP**	
	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM
BS235 (M_S = 2)	9.8	9.2	4.5	2.1	3.9	2.1	1.2	1.8	-	-	24.9	24.1
BS236 (M_S = 2)	7.8	7.0	3.6	1.8	6.2	4.8	1.1	2.0	15.5	13.6	21.4	19.8
BS346 (M_S = 1)	9.5	8.5	4.4	2.1	2.5	0.7	0.8	1.6	10.5	8.4	24.9	23.3
BS135 (M_S = 1)	5.5	4.5	5.3	2.4	4.4	2.2	1.2	1.2	14.6	12.4	23.7	21.8
BS147 (M_S = 1)	8.5	6.6	4.2	1.1	4.1	1.5	0	0.0	14.1	11.2	22.9	20.6

Note: The '-' in the table means that this state converged to another isomer; in this case, H_2 dissociates from the Fe. Numbers in blue indicate the lowest one between states.

Table S23. The relative polarized QM and QM/MM energies between five functionals for **OBS_2-DH_6** (kcal/mol).

l: OBS_2-DH_6	B3LYP*		TPSSh		B97-D3		r^2SCAN		TPSS		B3LYP	
	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM
BS346 (M_S = 2)	-	-	-	-	1.2	5.0	-0.7	5.7	8.7	11.2	-	-
BS236 (M_S = 2)	9.9	15.5	-	-	11.9	15.1	7.2	13.1	20.1	21.6	-	-
BS235 (M_S = 1)	-	-	-	-	7.5	10.3	9.3	12.1	10.7	12.0	-	-
BS347 (M_S = 1)	-	-	-	-	9.8	13.0	6.0	9.5	17.2	19.3	-	-
BS127 (M_S = 0)	21.2	24.3[a]	12.9	14.4	10.4	12.5	10.1	14.2	16.2	17.0	41.2	38.5
BS147 (M_S = 0)	20.2	23.9	12.3	14.1	12.0	14.2	8.5	13.7	16.7	17.8	-	-

[a] This state converged to BS1267.
Note: The '-' in the table means that this state converged to another minimum; in this case, H_2 dissociates from the Fe. Numbers in blue indicate the lowest one between states.

Table S24. The relative polarized QM and QM/MM energies between five functionals for **CBS_{37}-OBS_2-BH_{26}** (kcal/mol).

m: CBS_{37}-OBS_2-BH_{26}	B3LYP*		TPSSh		B97-D3		r^2SCAN		TPSS		B3LYP	
	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM
BS235 (M_S = 2)	27.6	27.5	22.3	22.8	25.7	27.4	22.7	26.7	-	-	44.1	44.6
BS247 (M_S = 2)	30.2	31.7	23.9	23.1	26.0	25.6	23.3	25.9	31.4	29.4	44.2	46.8
BS347 (M_S = 1)	28.3	30.7	24.4	25.1	22.9	23.5	22.4	25.9	27.3	25.7[a]	46.7	50.0
BS125 (M_S = 1)	35.3	34.7	24.9	26.5	26.0	27.8	21.9	26.7	34.7	35.0	50.1	50.2
BS147 (M_S = 1)	26.1	28.0	21.2	21.6	23.9	23.6	21.9	24.7	-	-	43.6	46.1

[a] This state converged to BS3467.
Note: The '-' in the table means that this state converged to another isomer. Numbers in blue indicate the lowest one between states.

Table S25. The relative polarized QM and QM/MM energies between five functionals for **CBS_{37}-OBS_6-BH_{26}** (kcal/mol).

n: CBS_{37}-OBS_6-BH_{26}	B3LYP*		TPSSh		B97-D3		r^2SCAN		TPSS		B3LYP	
	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM
BS247 (M_S = 2)	13.9	17.3	8.1	11.1	8.3	11.1	6.9	13.1	13.2	16.2	25.9	26.2
BS237 (M_S = 2)	16.6	20.1	12.1	15.0	13.5	15.1	9.0	14.0	19.6	21.5	29.4	28.4
BS347 (M_S = 1)	12.7	16.2	11.8	15.1	10.9	13.1	8.2	13.8	18.4	19.6	24.5	27.0
BS234 (M_S = 1)	20.1	21.7	10.0	13.4	9.3	11.8	9.7	14.6	15.2	17.4	24.5	28.3
BS156 (M_S = 1)	18.0	20.0	12.3	16.0	12.3	14.5	8.8	14.6	15.2	17.8	39.1	39.8

Table S26. The relative polarized QM and QM/MM energies between five functionals for **$2CBS_{26,37}$-$BH_{26(5)}$** (kcal/mol).

o: $2CBS_{26,37}$-$BH_{26(5)}$	B3LYP*		TPSSh		B97-D3		r^2SCAN		TPSS		B3LYP	
	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM
BS134 (M_S = 0)	26.4	28.4	19.2	19.2	23.9	23.4	19.0	22.1	29.6	30.0	41.8	45.3
BS2467 (M_S = 0)	22.8	27.5	12.6	16.4	17.3	20.2	15.6	22.1	18.3	21.6	39.7	43.8
BS14 (M_S = 2)	-	-	-	-	18.5	19.0	16.3	20.3	19.6	20.3	46.7	49.8

BS347 (M_S = 2)	25.7	28.2	15.0	16.1	15.5	16.7	16.7	21.0	-	-	38.2	41.8
BS126 (M_S = 2)	23.3	26.7	16.2	18.9	16.3	17.9	16.8	21.9	19.6	20.4[a]	45.0	44.8

[a] This state converged to BS12.
Note: The '-' in the table means that this state converged to another isomer. Numbers in blue indicate the lowest one between states.

Table S27. The relative polarized QM and QM/MM energies between five functionals for **2CBS$_{26,37}$-BH$_{26(3)}$** (kcal/mol).

p: 2CBS$_{26,37}$-BH$_{26(3)}$	**B3LYP***		**TPSSh**		**B97-D3**		**r^{2}SCAN**		**TPSS**		**B3LYP**	
	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM
BS134 (M_S = 0)	20.5	30.2	11.3	20.2	16.3	24.3	11.5	23.8	11.7	21.7[a]	39.7	47.4
BS2467 (M_S = 0)	22.7	30.2	4.6	15.5	8.9	19.5	7.1	21.7	9.6	20.2	47.9	64.2
BS145 (M_S = 0)	18.4	31.0	9.0	19.2	11.5	19.7	10.7	23.6	11.6	20.8	32.0	45.1
BS135 (M_S = 0)	15.4	27.1	4.5	15.5	8.9	19.5	7.2	21.6	9.6	20.2	30.4	42.6
BS14 (M_S = 2)	-	-	7.0	14.1	10.5	17.6	8.6	18.4	10.9	17.8	-	-

[a] This state converged to BS13.
Note: The '-' in the table means that this state converged to another isomer. Numbers in blue indicate the lowest one between states.

Table S28. The relative polarized QM and QM/MM energies between five functionals for **2CBS$_{26,37}$-BH$_{37}$** (kcal/mol).

q: 2CBS$_{26,37}$-BH$_{37}$	**B3LYP***		**TPSSh**		**B97-D3**		**r^{2}SCAN**		**TPSS**		**B3LYP**	
	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM
BS346 (M_S = 1)	14.9	19.5	8.2	13.0	10.6	15.2	4.4	13.4	5.23	8.4	31.6	36.0
BS135 (M_S = 1)	16.2	20.7	6.8	11.4	8.7	12.8	7.3	13.8	6.30	10.2[b]	31.2	35.3
BS167 (M_S = 2)	14.8	21.5[a]	4.7	11.2	8.5	14.1	5.3	13.4	-	-	30.0	36.7
BS235 (M_S = 2)	12.0	17.3	2.3	7.4	8.5	12.5	6.2	13.0	11.63	15.1	28.8	33.2
BS346 (M_S = 2)	9.9	15.4	0.0	5.5	4.8	8.8	3.6	10.5	6.33	10.6	23.6	29.5

[a] This state converged to BS257.
[b] This state converged to BS15.
Note: The '-' in the table means that this state converged to another isomer. Numbers in blue indicate the lowest one between states.

Table S29. The relative polarized QM and QM/MM energies between five functionals for **C3H** (kcal/mol).

r: C3H	**B3LYP***		**TPSSh**		**B97-D3**		**r^{2}SCAN**		**TPSS**		**B3LYP**	
	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM	QM	QM/MM
BS125 (M_S = 1)	13.2	14.1	-	-	31.3	28.9	47.8	47.9	73.4	76.0	10.9	12.0
BS127 (M_S = 1)	1.2	0.0	32.9	30.0	35.3	32.9	49.9	50.5	81.6	78.1	11.7	12.9
BS135 (M_S = 1)	3.3	2.7	51.7	52.0	34.7	33.0	51.3	52.3	80.3	75.9	2.7	2.0
BS136 (M_S = 1)	0.6	0.3	25.7	25.7	31.1	29.8	52.6	54.7	75.9	73.0	0.5	0.0
BS146 (M_S = 1)	0.0	0.2	25.3	25.1	34.1	31.7	47.8	49.0	105.0	105.9	0.0	0.0
BS147 (M_S = 1)	3.2	2.8	27.5	26.9	36.5	33.6	50.4	51.5	-	-	2.8	2.2

10. Additional comparisons for three lowest-energy isomers: dispersion correction and zero-point vibrational energy

Additional calculations were carried out for the 3 lowest energy isomers: **g**, **i** and **k** to see whether their relative energies might be affected much by either dispersion or zero-point vibrational effects.

Table S30 shows the effect of not including the D4 dispersion correction in r^2SCAN calculations. The effect of dispersion is found to be relatively small, not affecting much the relative energies of these 3 isomers. We note that the dispersion correction was used throughout the study.

Table S30. The relative QM/MM energies (kcal/mol) between three lowest-energy isomers with and without D4 corrections utilizing QM-region C.

	ΔE(QM/MM) with D4	ΔE(QM/MM) without D4
g: OBS_6-$2BH_{26}$	3.1	3.2
i: OBS_6-BH_{26}-TH_2	3.3	3.6
k: OBS_6-DH_2	0.0	0.0

Note: The results were calculated using r^2SCAN. The spin states and BS solutions of **OBS_6-$2BH_{26}$**, **OBS_6-BH_{26}-TH_2**, and **OBS_6-DH_2** are BS347 (M_S = 1), BS235 (M_S = 2), and BS147 (M_S = 1), respectively.

The inclusion of zero-point vibrational motion could have an effect on **E_3** isomer energies as the isomers differ in terms of Fe-H bonding. Table S31 shows the results of calculations where zero-point vibrational corrections were explicitly included via partial Hessian QM/MM calculations. Different partial Hessian approximations were tested. The ZPVE correction can change the energy differences by up to 0.7 kcal/mol as seen here but this differs with partial Hessian size and QM-region size. Overall the ZPVE effect is fairly small.

Table S31. The relative QM/MM energies between three lowest-energy isomers with and without zero-point vibrational energy (ZPVE) corrections (kcal/mol).

Including Fe2+Fe6+2hydrides/H_2 as partial Hessian using QM-A region	ΔE(QM/MM) without ZPVE	ΔE(QM/MM) with ZPVE
g: OBS_6-$2BH_{26}$	1.3	1.0
i: OBS_6-BH_{26}-TH_2	0.2	0.0
k: OBS_6-DH_2	0.0	0.3
Including FeMoco as partial Hessian using QM-A region		
g: OBS_6-$2BH_{26}$	1.3	1.1
i: OBS_6-BH_{26}-TH_2	0.2	0.0
k: OBS_6-DH_2	0.0	0.2
Including the full QM-A region as partial Hessian using QM-A region		
g: OBS_6-$2BH_{26}$	1.3	1.3
i: OBS_6-BH_{26}-TH_2	0.2	0.0
k: OBS_6-DH_2	0.0	0.5
Including the full QM-B region as partial Hessian using QM-B region		
g: OBS_6-$2BH_{26}$	2.8	2.6
i: OBS_6-BH_{26}-TH_2	3.1	2.6
k: OBS_6-DH_2	0.0	0.0

Note: The results were calculated using r^2SCAN. The spin states and BS solutions of **OBS_6-$2BH_{26}$**, **OBS_6-BH_{26}-TH_2**, and **OBS_6-DH_2** are BS347 (M_S = 1), BS235 (M_S = 2), and BS147 (M_S = 1), respectively.

11. The results of the C3H model

Functionals with at least 20% HF exchange are known to predict interstitial carbide protonation in both $\mathbf{E_3}$ and $\mathbf{E_4}$ redox states, for example, B3LYP[5,7,8]. However, according to recent ^{13}C ENDOR studies of multiple trapped FeMoco states, the carbide hyperfine coupling is practically unchanged, suggesting an unchanged carbide environment. Overall, the carbide is interpreted to as more likely having a stabilizing role during catalysis[9].

Ryde and co-workers suggested a triply protonated model **C3H** (isomer **r**) can be favorable when calculated using B3LYP and TPSSh[4]. Their previous result showed that the low-energy spin state and BS solutions of this model are $M_S = 1$ and BS136, belonging to the BS10 class[5]. We explored the **C3H** model using three spin states and 6 BS solutions (BS125, BS127, BS135, BS136, BS146, and BS147) in the BS10 class using our computational protocol at the r^{2}SCAN level. The results show that all five lowest-energy states (BS125, BS127, BS135, BS146, and BS147) are in $M_S = 1$, as shown in Table S32, and a previous study showed that BS136 with $M_S = 1$ is the lowest-ernergy state when using B3LYP, therefore, we calculated all six BS solutions in the spin state of $M_S = 1$ for other functionals (shown in Table S12 to Table S29).

The **C3H** model is higher than $\mathbf{OBS_6\text{-}DH_2}$ by 47.9 kcal/mol using r^{2}SCAN and QM-A region, shown in Table S32, which is very similar to the result reported by Ryde and co-workers[4].

Table S32. The relative polarized QM and QM/MM energies for **C3H** model using r^{2}SCAN and QM-A region (kcal/mol).

	$M_S = 0$		$M_S = 1$		$M_S = 2$	
	QM	QM/MM	QM	QM/MM	QM	QM/MM
BS125	72.4	74.5	47.8	47.9	54.3	56.3
BS127	57.9	60.5	49.9	50.5	53.9	56.1
BS135	66.1	66.9	51.3	52.3	58.4	59.6
BS136	55.8	58.5	52.6	54.7	56.2	58.1
BS146	67.1	68.2	47.8	49.0	54.9	55.4
BS147	57.8	60.9	50.4	51.5	55.6	51.6

12. The energies, spin populations of investigated models

Tables in this section shows the polarized QM energies, QM/MM energies and spin populations of metal ions of all investigated **E_3** models. The data in blue represent the lowest-energy state for each isomer.

Table S33. The relative polarized QM and QM/MM energies (kcal/mol) relative to the lowest-energy model (see Figure 2k in the manuscript) and Mulliken spin populations of Mo and 7 Fe ions for the **OBS_2-$2BH_{26}$** model.

OBS_2-$2BH_{26}$ (M_S = 2), QM-A region, H-to-val, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS567	42.1	44.3	1.08	1.48	2.54	2.80	2.97	-3.07	-1.05	-2.90
BS234	20.1	22.3	-1.12	3.34	-0.51	-3.05	-3.00	2.95	2.16	2.89
BS13	21.2	24.9	-1.20	-3.26	2.17	-3.20	2.46	2.74	2.25	2.52
BS14	21.1	21.4	-1.23	-3.27	1.96	2.41	-3.19	2.70	2.48	2.68
BS134	37.4	38.0	-1.25	-0.26	2.82	-2.82	-2.85	3.10	2.19	2.99
BS256	29.9	31.4	0.20	3.12	-3.16	1.60	3.08	-2.91	-1.15	2.71
BS267	27.8	31.7	0.23	3.19	-3.14	3.05	1.74	2.81	-1.55	-2.74
BS357	20.2	23.1	0.36	3.50	3.03	-3.00	3.35	-2.82	1.79	-2.73
BS457	19.0	24.5	0.39	3.51	3.06	3.36	-3.01	-2.84	1.80	-2.70
BS157	17.3	22.6	0.36	-3.26	3.16	3.30	3.18	-2.68	2.23	-2.44
BS235	18.4	21.0	-0.35	3.34	-1.62	-3.12	3.12	-2.99	2.34	2.79
BS247	20.7	23.5	-0.27	3.32	-1.73	3.09	-3.08	2.89	2.37	-2.91
BS245	30.2	32.7	-0.33	3.28	-2.49	3.34	-2.49	-2.66	1.83	2.93
BS246	15.1	18.0	-0.43	3.29	-3.04	2.91	-3.14	2.88	-1.65	2.72
BS345	19.6	22.2	-0.58	3.33	2.98	-2.96	-2.46	-1.55	2.17	2.83
BS347	19.1	22.5	-0.57	3.34	3.00	-2.54	-2.96	2.95	2.10	-1.38
BS126	14.0	18.3	-0.56	-3.33	-3.19	3.21	3.06	2.87	-1.16	2.84
BS137	26.9	31.7	-0.41	-3.24	3.01	-2.40	3.26	3.15	2.29	-1.85
BS145	25.2	28.2	-0.31	-3.26	3.25	3.38	-2.64	-2.28	2.27	3.05
BS127	25.8	27.9	-0.36	-3.33	-1.16	3.02	3.19	2.98	2.40	-2.76
BS135	30.9	30.6	-0.45	-2.09	2.67	-2.58	3.13	-2.35	2.47	2.85
BS147	23.1	27.6	-0.38	-3.27	3.32	3.31	-2.69	2.99	2.38	-2.05
OBS_2-$2BH_{26}$ (M_S = 1), QM-A region, H-to-val, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS567	42.2	42.9	1.18	1.76	0.79	2.93	3.12	-3.05	-2.23	-2.90
BS234	19.0	21.7	-1.11	3.34	-2.66	-2.82	-2.73	3.06	1.47	2.96
BS123	29.0	32.4	-1.24	-3.41	-1.00	-3.26	2.99	2.90	2.84	2.53
BS124	30.7	31.3	-1.24	-3.32	-0.88	2.89	-3.22	2.65	2.78	2.79
BS134	28.6	29.5	-1.25	-2.83	2.91	-2.19	-2.94	3.09	2.20	2.99
BS267	37.0	39.4	0.19	0.10	-3.06	3.08	2.89	2.84	-1.55	-2.80
BS357	24.0	25.0	0.47	3.34	2.40	-3.15	3.03	-2.96	1.65	-2.75
BS2367	26.0	27.8	0.10	3.31	-2.16	-2.69	3.29	2.80	-1.10	-2.29
BS456	39.0	40.6	0.30	3.17	1.32	2.13	-2.93	-2.87	-2.38	2.81
BS156	28.0	30.5	0.30	-3.35	2.53	2.08	2.70	-2.93	-1.64	2.39
BS157	11.6	15.7	0.27	-3.37	2.20	3.03	2.99	-2.69	2.45	-2.57
BS167	27.1	29.9	0.31	-3.35	2.38	2.67	2.22	2.62	-1.73	-2.84
BS346	24.3	27.3	-0.34	3.32	1.55	-3.03	-2.97	2.89	-2.42	2.69

BS246	21.9	26.9	-0.12	3.30	-3.02	2.70	-3.16	2.61	-2.06	1.50
BS345	9.8	14.2	-0.20	3.35	3.18	-3.11	-2.89	-2.78	1.41	2.78
BS126	18.9	23.9	-0.32	-3.34	-3.23	3.02	3.05	2.39	-1.61	1.97
BS137	20.8	24.8	-0.38	-3.27	2.62	-2.94	3.14	3.03	2.41	-2.45
BS145	20.0	23.2	-0.40	-3.27	2.48	3.23	-2.86	-2.54	2.46	2.94
BS135	13.0	15.5	-0.45	-3.29	2.76	-3.07	3.15	-2.32	2.40	2.85
BS147	10.5	14.2	-0.43	-3.32	2.99	3.19	-3.14	2.95	2.24	-2.30
OBS_2-$2BH_{26}$ (M_S = 0), QM-A region, H-to-val, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS2346	13.6	16.1	-0.63	3.35	-2.52	-2.83	-2.82	2.95	-0.96	2.84
BS123	28.0	31.3	-1.13	-3.34	-2.42	-3.09	3.12	2.95	1.22	2.77
BS134	23.8	26.1	-1.18	-3.27	2.85	-3.08	-3.09	3.03	2.18	2.90
BS2567	23.7	26.0	1.16	3.28	-2.91	3.10	3.10	-3.03	-2.12	-2.90
BS2356	11.4	13.3	0.33	3.32	-2.37	-3.11	3.13	-2.87	-1.91	2.84
BS2356 (H-to-Cys)	12.7	14.2	0.34	3.32	-2.34	-3.11	3.13	-2.87	-1.96	2.84
BS2467	10.7	14.1	0.32	3.30	-2.58	3.10	-3.09	2.94	-1.65	-2.74
BS357	29.7	30.8	0.39	3.27	-0.31	-3.24	3.18	-2.96	2.50	-2.84
BS2367	17.6	21.8	0.14	3.30	-3.12	-3.12	3.07	2.67	-0.75	-2.48
BS2456	19.9	23.7	0.13	3.29	-3.07	3.11	-3.13	-2.63	-0.50	2.47
BS457	35.1	36.2	0.65	3.21	2.52	1.89	-3.18	-2.97	1.01	-2.85
BS1256	14.9	16.6	0.16	-3.31	-2.20	3.24	3.16	-2.83	-1.56	2.85
BS157	13.4	16.0	0.63	-3.36	2.59	2.85	2.82	-2.94	0.83	-2.83
BS1267	12.4	15.3	0.17	-3.32	-2.22	3.19	3.22	2.96	-1.62	-2.70
BS345	12.4	15.5	-0.18	3.32	2.28	-3.18	-3.21	-2.92	1.50	2.70
BS126	30.6	35.1	-0.14	-3.29	-3.15	2.51	2.11	2.43	-2.12	1.79
BS137	19.6	23.6	-0.15	-3.28	3.10	-3.10	3.13	2.67	0.38	-2.47
BS145	17.4	21.8	-0.15	-3.30	3.15	3.14	-3.07	-2.64	0.59	2.50
BS135	10.8	14.2	-0.34	-3.29	2.59	-3.09	3.08	-2.93	1.64	2.72
BS136	31.2	34.4	-0.34	-3.29	1.66	-3.14	2.94	2.20	-2.43	2.66
BS147	12.5	14.2	-0.36	-3.31	2.30	3.11	-3.13	2.87	2.02	-2.83
OBS_2-$2BH_{26}$ (M_S = 0), QM-C region, r^2SCAN										
BS2356	16.7	15.9	0.32	3.30	-2.34	-3.11	3.13	-2.87	-1.95	2.87

Table S34. The relative polarized QM and QM/MM energies (kcal/mol) relative to the lowest-energy model (see Figure 2k in the manuscript) and Mulliken spin populations of Mo and 7 Fe ions for the **OBS_6-$2BH_{26}$** model.

OBS_6-$2BH_{26}$ (M_S = 2), QM-A region, H-to-homo, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS2567	18.2	21.4	0.93	3.51	-2.31	3.51	3.34	-2.68	-1.37	-2.36
BS234	8.6	11.5	-1.25	3.36	-1.66	-2.91	-2.93	2.97	2.75	2.82
BS13	5.0	8.1	-1.05	-3.24	2.47	-3.23	2.60	2.82	1.47	2.54
BS14	5.6	7.2	-1.06	-3.27	2.42	2.61	-3.23	2.74	1.56	2.70
BS134	28.9	29.3	-1.10	-0.64	3.15	-2.59	-2.84	3.14	1.45	3.02

BS356	18.1	19.2	0.07	3.19	1.04	-3.16	3.07	-3.00	-0.23	2.74
BS467	21.6	23.4	0.05	3.25	0.88	3.01	-3.14	2.90	-0.24	-2.86
BS256	13.6	15.4	0.44	3.24	-2.76	2.42	3.04	-3.00	-2.53	2.57
BS267	15.4	16.6	0.40	3.21	-2.60	2.61	3.03	2.76	-2.97	-2.83
BS357	15.3	17.1	0.20	3.38	2.82	-3.05	3.19	-2.71	1.69	-1.69
BS457	11.5	13.5	0.22	3.38	1.82	3.22	-3.02	-2.43	3.15	-2.73
BS15	8.3	11.8	0.10	-3.39	2.66	3.03	2.88	-2.93	0.02	1.97
BS157	8.5	9.4	0.27	-2.87	2.56	3.25	3.23	-2.76	2.86	-2.63
BS167	8.9	13.1	0.12	-3.39	2.64	2.86	2.95	2.24	-0.06	-2.84
BS34	15.4	17.2	-0.90	3.27	1.76	-3.13	-3.06	2.80	0.37	2.64
BS236	5.6	6.7	-0.43	3.24	-1.90	-3.11	3.09	2.75	-3.11	2.82
BS246	8.9	11.9	-0.18	3.26	-2.63	3.08	-3.06	2.85	-1.75	1.62
BS345	7.9	9.8	-0.53	3.29	2.44	-2.80	-2.36	-2.55	3.12	2.90
BS347	7.2	9.6	-0.53	3.28	2.46	-2.30	-2.84	3.00	3.04	-2.43
BS126	10.5	12.5	-0.74	-3.29	-3.03	2.77	2.73	2.98	-0.65	2.87
BS137	14.6	17.0	-0.75	-3.27	2.52	-2.58	3.22	3.15	3.28	-1.87
BS145	14.7	16.4	-0.69	-3.28	2.64	3.31	-2.70	-2.00	3.24	3.04
BS147	17.7	17.7	-0.50	-1.81	2.67	3.09	-2.66	2.99	2.82	-2.80
OBS_6-$2BH_{26}$ (M_S = 1), QM-A region, H-to-homo, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS2567	11.1	14.1	0.95	3.36	-2.99	3.32	3.29	-2.80	-1.32	-2.54
BS234	10.3	12.6	-0.99	3.34	-2.50	-2.56	-2.83	3.09	0.53	3.07
BS134	19.2	19.9	-1.11	-2.98	3.08	-1.65	-2.96	3.12	1.42	2.99
BS2356	8.1	10.2	-0.14	3.30	-2.79	-3.01	3.21	-2.03	-0.36	2.89
BS2467	6.6	10.0	-0.07	3.27	-2.72	3.22	-2.98	2.98	-0.70	-1.75
BS357	10.9	11.2	0.21	3.31	1.62	-3.18	3.00	-3.01	3.06	-2.92
BS2367	14.0	16.7	0.00	3.30	-2.65	-2.88	3.19	3.02	-0.57	-2.13
BS457	11.9	14.1	0.25	3.31	1.45	3.00	-3.08	-3.01	3.05	-2.85
BS157	3.4	7.5	0.32	-3.40	2.98	3.23	3.06	-2.67	1.45	-2.44
BS167	8.3	11.6	0.50	-3.34	2.22	2.90	3.04	2.74	-2.87	-2.72
BS235	5.2	8.0	-0.19	3.34	-2.66	-3.03	3.19	-2.81	0.69	2.83
BS236	10.4	11.3	-0.08	3.30	-2.52	-3.18	2.79	1.84	-3.08	2.64
BS245	14.0	17.3	-0.18	3.29	-2.84	3.24	-3.11	-2.69	0.98	2.78
BS246	9.6	12.5	-0.03	3.26	-2.48	2.77	-3.13	2.77	-3.09	1.67
BS345	0.1	1.9	-0.46	3.33	2.22	-3.15	-3.12	-2.85	3.10	2.82
BS347	-0.8	1.3	-0.44	3.33	2.26	-3.17	-3.13	2.94	3.01	-2.75
BS347 (H-to-hyd)	-0.1	1.7	-0.44	3.34	2.23	-3.16	-3.13	2.94	3.07	-2.76
BS126	6.6	8.7	-0.33	-3.32	-2.33	2.72	2.81	2.88	-3.11	2.64
BS137	8.8	12.0	-0.43	-3.26	2.90	-2.97	3.20	3.02	1.79	-2.12
BS145	8.5	11.1	-0.38	-3.29	2.89	3.28	-3.00	-2.37	1.98	2.90
BS136	15.8	17.9	-0.53	-3.23	2.26	-3.22	2.55	2.85	-0.99	2.59
BS146	17.5	17.8	-0.55	-3.26	2.05	2.57	-3.23	2.81	-0.82	2.70
BS147	2.8	4.3	-0.56	-3.30	2.60	3.12	-3.06	3.04	3.12	-2.76
OBS_6-$2BH_{26}$ (M_S = 0), QM-A region, H-to-homo, r^2SCAN										

	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS2567	12.2	14.6	1.08	3.41	-3.08	3.00	2.92	-3.16	-1.48	-2.88
BS2346	2.0	4.9	-0.59	3.38	-2.82	-2.88	-2.87	3.03	-1.13	2.92
BS1236	20.4	22.6	-0.70	-3.11	-2.02	-3.04	3.13	2.99	-0.42	2.83
BS134	12.2	14.6	-1.09	-3.43	3.11	-3.00	-2.89	3.15	1.43	2.88
BS2356	-1.0	1.6	0.28	3.32	-2.78	-3.02	3.18	-3.00	-1.39	2.73
BS1267	7.6	9.6	0.05	-3.32	-2.97	3.24	3.24	3.10	-0.74	-2.79
BS2367	8.5	11.1	0.19	3.31	-3.04	-3.15	3.17	2.77	-0.88	-2.78
BS2456	9.3	12.2	0.42	3.26	-2.50	3.27	-2.90	-2.96	-1.83	2.57
BS457	19.4	21.6	0.67	2.71	2.76	2.64	-3.12	-3.00	0.70	-2.89
BS1256	8.8	11.1	0.04	-3.31	-2.98	3.30	3.20	-2.92	-0.67	3.01
BS157	1.7	4.9	0.63	-3.39	2.95	2.91	2.89	-3.03	0.86	-2.92
BS2467	-0.1	2.8	0.31	3.28	-2.80	3.20	-3.00	2.80	-1.36	-2.88
BS346	9.9	11.9	-0.17	3.31	1.46	-3.23	-3.17	2.64	-3.35	2.70
BS345	7.5	9.6	-0.06	3.32	3.01	-3.24	-3.24	-3.09	0.67	2.80
BS347	8.9	11.1	-0.05	3.31	3.01	-3.29	-3.20	2.92	0.62	-3.00
BS126	15.6	17.5	0.00	-3.30	-2.57	2.69	2.51	2.12	-3.07	1.82
BS137	8.9	11.9	-0.31	-3.28	2.93	-3.26	3.06	2.99	1.08	-2.65
BS145	8.2	11.0	-0.22	-3.31	3.05	3.16	-3.18	-2.77	0.86	2.81
BS135	0.0	2.9	-0.31	-3.28	2.85	-3.19	3.00	-2.79	1.27	2.89
BS147	-1.1	1.6	-0.27	-3.32	2.86	3.02	-3.18	3.00	1.26	-2.73
OBS_6-$2BH_{26}$ (M_S = 1), QM-C region, r^2SCAN										
BS347	2.4	3.1	-0.43	3.33	2.23	-3.15	-3.11	2.94	2.98	-2.70

Table S35. The relative polarized QM and QM/MM energies (kcal/mol) relative to the lowest-energy model (see Figure 2k in the manuscript) and Mulliken spin populations of Mo and 7 Fe ions for the **OBS_6-BH_{26}-TH_2** model.

OBS_6-BH_{26}-TH_2 (M_S = 2), QM-A region, H-to-homo, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS567	26.7	30.1	1.18	3.25	1.13	3.29	3.19	-3.01	-2.65	-2.80
BS234	3.9	6.2	-1.19	3.31	-2.11	-2.80	-2.77	3.09	2.63	3.00
BS134	23.0	23.3	-1.25	-3.08	2.77	-1.10	-2.86	3.08	3.23	3.06
BS257	16.1	17.4	0.36	2.79	-2.57	2.31	3.09	-2.83	3.07	-2.68
BS356	8.5	10.3	0.34	3.35	2.37	-3.13	3.01	-2.84	-2.29	2.82
BS467	11.2	14.4	0.37	3.33	2.33	3.02	-3.11	2.92	-2.33	-2.67
BS256	16.1	17.3	0.43	3.13	-2.74	2.48	3.09	-2.98	-2.52	2.66
BS357	12.6	15.0	0.19	3.34	2.27	-3.11	3.17	-2.84	2.87	-2.21
BS367	21.1	25.1	0.45	3.43	2.60	-3.17	3.18	2.82	-2.91	-2.69
BS456	14.6	18.9	0.50	3.51	2.52	3.39	-3.12	-2.85	-3.02	2.60
BS457	15.1	17.6	0.22	3.30	2.04	3.26	-3.05	-2.39	2.94	-2.63
BS156	5.4	7.8	0.20	-3.34	2.34	3.21	2.98	-2.66	-1.76	2.99
BS157	2.9	6.1	0.22	-3.29	2.59	3.23	3.15	-2.56	3.05	-2.38
BS167	4.7	8.2	0.19	-3.34	2.31	3.03	3.16	3.08	-1.79	-2.52
BS235	-0.9	1.2	-0.39	3.30	-2.28	-3.03	3.13	-2.89	2.76	2.71
BS235 (H-to-hyd)	-2.2	0.2	-0.37	3.29	-2.24	-3.03	3.13	-2.90	2.71	2.74

BS247	-1.9	1.7	-0.33	3.27	-2.29	3.13	-3.00	2.85	2.76	-2.82
BS346	3.8	6.2	-0.30	3.32	2.89	-2.96	-2.93	2.91	-2.24	2.76
BS236	3.9	5.5	-0.38	3.25	-2.42	-3.14	3.16	2.94	-2.98	2.86
BS237	3.4	6.1	-0.48	3.27	-2.45	-3.19	3.13	2.89	2.95	-2.60
BS245	6.5	9.0	-0.45	3.24	-2.38	3.14	-3.12	-2.69	2.95	2.72
BS246	4.6	7.1	-0.38	3.22	-2.38	3.15	-3.08	2.97	-2.96	2.84
BS345	8.2	10.3	-0.42	3.27	2.87	-2.93	-2.36	-2.55	2.74	2.93
BS347	8.6	10.7	-0.43	3.27	2.90	-2.40	-2.97	3.06	2.70	-2.44
BS126	3.7	6.0	-0.29	-3.29	-2.68	3.22	3.20	3.02	-2.67	2.91
BS137	10.4	13.3	-0.53	-3.22	2.70	-2.47	3.19	3.10	3.13	-2.12
BS145	10.4	12.3	-0.47	-3.25	2.80	3.28	-2.59	-2.27	3.14	2.99
BS125	8.9	9.4	-0.46	-3.29	-2.13	3.25	3.08	-2.89	3.07	2.94
BS17	10.7	13.4	-0.36	-3.29	-0.14	2.91	3.01	2.41	2.54	-2.83
BS135	11.8	14.0	0.74	-3.22	2.68	-2.96	3.13	-2.87	3.35	2.95
BS136	14.3	15.8	-0.51	-3.22	2.82	-3.03	3.26	3.13	-1.72	2.91
BS146	22.6	23.3	-0.31	-1.96	2.45	3.22	-2.74	2.89	-2.81	2.96
BS147	15.9	17.5	-0.44	-1.90	2.56	3.05	-2.69	2.98	3.04	-2.74
OBS_6-BH_{26}-TH_2 (M_S = 1), QM-A region, H-to-homo, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS1567	36.2	37.2	1.12	-0.81	2.60	3.45	3.04	-2.89	-2.48	-2.47
BS234	1.9	5.8	-1.00	3.34	-2.31	-3.19	-2.96	2.89	2.46	2.27
BS123	14.4	16.8	-1.23	-3.35	-2.42	-3.09	3.21	3.04	2.72	2.83
BS124	13.4	15.1	-1.24	-3.31	-2.44	3.21	-3.05	3.00	2.67	2.92
BS134	22.1	23.1	-1.10	-2.86	2.75	-2.05	-2.99	3.00	2.60	2.63
BS356	10.0	12.7	0.41	3.18	0.78	-3.10	3.13	-2.85	-2.62	2.76
BS467	13.1	15.6	0.46	3.14	0.79	3.12	-3.07	2.86	-2.67	-2.70
BS256	18.2	18.9	0.40	3.17	-2.70	0.80	3.06	-3.04	-2.85	2.63
BS267	20.3	21.8	0.40	3.12	-2.71	3.02	0.86	2.70	-2.80	-2.91
BS367	17.9	18.7	0.34	3.00	1.28	-3.09	3.15	2.82	-2.99	-2.54
BS456	19.6	21.8	0.40	3.04	1.28	3.21	-3.07	-2.78	-2.96	2.70
BS156	-0.8	2.5	0.42	-3.32	2.21	3.06	2.90	-2.84	-2.73	2.57
BS157	-0.6	2.5	0.29	-3.34	2.03	3.09	2.98	-2.81	2.89	-2.70
BS167	-0.2	2.6	0.42	-3.33	2.20	2.94	3.02	2.69	-2.74	-2.72
BS235	17.0	18.5	-0.43	1.92	-2.32	-3.00	2.88	-2.86	2.73	2.73
BS247	6.7	8.4	-0.24	3.23	-2.69	3.07	-3.04	2.82	1.51	-2.89
BS346	0.5	2.2	-0.39	3.29	2.40	-3.02	-3.00	2.88	-3.09	2.77
BS236	9.7	11.2	-0.20	3.25	-2.69	-3.26	2.79	2.29	-2.98	2.58
BS237	11.9	13.3	-0.29	3.27	-3.02	-3.21	2.99	2.87	1.99	-2.82
BS245	15.8	19.1	-0.13	3.25	-2.41	2.88	-3.15	-2.73	2.71	1.31
BS246	11.2	14.2	-0.11	3.23	-2.55	2.73	-3.15	2.74	-2.98	1.89
BS347	1.5	3.9	-0.31	3.32	2.84	-3.16	-3.12	2.91	2.32	-2.69
BS126	9.8	12.4	-0.22	-3.30	-2.68	3.05	3.09	2.55	-2.78	2.13
BS137	6.9	10.0	-0.47	-3.22	2.53	-3.17	3.15	3.01	2.84	-2.54
BS145	7.4	8.7	-0.47	-3.26	2.61	3.21	-3.15	-2.67	2.87	2.89
BS125	5.9	9.1	-0.41	-3.29	-2.69	3.10	2.95	-2.85	2.54	2.41
BS127	6.0	8.4	-0.42	-3.30	-2.70	2.98	3.10	2.72	2.34	-2.78

BS135	1.3	3.6	-0.50	-3.23	2.62	-3.03	3.06	-2.82	3.06	2.86
BS136	5.2	8.5	-0.33	-3.25	2.39	-3.05	3.18	3.09	-2.85	2.82
BS146	5.1	7.1	-0.31	-3.28	2.42	3.27	-3.05	2.92	-2.87	2.97
BS147	-0.3	2.0	-0.45	-3.26	2.64	3.09	-3.03	2.97	3.03	-2.74
OBS_6-BH_{26}-TH_2 (M_S = 0), QM-A region, H-to-homo, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS1567	10.8	14.2	1.01	-3.32	2.34	3.25	3.22	-2.21	-1.94	-2.09
BS234	11.0	14.3	-0.98	3.32	-2.35	-3.24	-3.21	2.20	1.91	2.08
BS123	19.1	22.4	-1.16	-3.52	-2.56	-3.32	3.14	2.97	2.22	2.53
BS124	20.2	20.5	-1.12	-3.35	-2.51	2.99	-3.14	2.84	1.70	2.61
BS134	15.7	15.7	-1.03	-3.34	2.82	-3.20	-3.19	2.84	2.90	2.51
BS257	6.0	8.1	0.33	-3.31	-0.04	3.00	2.91	-2.89	3.05	-2.72
BS2356	2.1	4.3	0.39	3.29	-2.22	-2.91	3.13	-2.78	-2.32	2.84
BS2467	3.5	6.3	0.37	3.23	-2.36	3.14	-2.90	2.91	-1.92	-2.86
BS2357	5.3	7.4	0.11	3.28	-2.20	-2.95	3.12	-2.71	2.96	-2.06
BS2367	11.9	14.4	0.26	3.25	-2.12	-3.03	3.20	2.75	-2.50	-2.19
BS2457	6.1	9.4	0.17	3.24	-2.20	3.13	-2.91	-2.22	2.99	-2.57
BS156	7.8	10.4	0.63	-3.35	2.13	2.99	2.86	-2.97	-2.96	1.10
BS157	5.2	7.2	0.42	-3.33	2.09	2.77	2.75	-3.10	2.29	-2.98
BS167	7.6	11.0	0.52	-3.34	2.12	2.85	2.92	1.44	-3.05	-2.85
BS235	22.0	23.9	-0.25	1.73	-2.60	-3.05	2.79	-3.00	1.68	2.70
BS346	6.0	8.2	-0.38	3.31	-0.12	-2.93	-2.89	2.93	-3.04	2.74
BS2346	5.5	7.4	-0.45	3.32	-2.10	-2.75	-2.73	3.09	-2.25	2.98
BS345	7.2	10.3	-0.39	3.31	0.07	-3.07	-3.06	-2.80	2.94	2.76
BS347	9.7	12.6	-0.36	3.25	0.24	-3.04	-3.06	2.96	2.57	-2.64
BS137	13.1	16.9	-0.35	-3.19	1.95	-3.21	2.97	2.37	2.60	-2.65
BS145	12.1	14.4	-0.30	-3.25	2.06	3.06	-3.19	-2.73	2.55	2.15
BS125	11.0	13.9	-0.36	-3.27	-2.88	2.33	2.87	-3.01	2.44	2.09
BS127	11.2	13.3	-0.31	-3.27	-2.87	2.88	2.28	2.41	2.12	-2.90
BS135	3.7	6.3	-0.38	-3.23	2.40	-3.13	2.91	-2.92	1.87	2.85
BS136	6.6	9.5	-0.21	-3.24	2.17	-3.11	2.93	2.21	-3.00	2.59
BS146	5.4	7.5	-0.14	-3.28	2.19	2.98	-3.11	2.73	-2.96	2.02
BS147	2.1	4.4	-0.40	-3.29	2.22	2.92	-3.12	2.81	2.28	-2.84
OBS_6-BH_{26}-TH_2 (M_S = 2), QM-C region, r^2SCAN										
BS235	0.9	3.3	-0.37	3.30	-2.23	-3.01	3.13	-2.88	2.69	2.74

Table S36. The relative polarized QM and QM/MM energies (kcal/mol) relative to the lowest-energy model (see Figure 2k in the manuscript) and Mulliken spin populations of Mo and 7 Fe ions for the **OBS_2-BH_{26}-TH_6** model.

OBS_2-BH_{26}-TH_6 (M_S = 2), QM-A region, H-to-Cys										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS567	41.5	44.4	1.01	1.56	2.56	3.07	3.12	-3.01	-1.79	-2.79
BS234	21.5	23.7	-1.07	3.33	-2.05	-2.59	-2.59	3.15	2.19	3.07
BS13	25.3	31.0	-1.15	-3.48	2.37	-3.32	2.68	2.90	2.10	2.57
BS356	20.0	21.7	0.22	3.27	2.07	-3.15	2.94	-2.84	-1.75	2.78

BS256	27.3	30.5	0.25	2.71	-3.14	2.77	3.17	-2.99	-1.86	2.60
BS267	30.4	33.9	0.21	3.31	-3.09	2.92	2.90	2.64	-2.28	-2.87
BS367	30.1	32.2	0.11	3.29	2.24	-3.24	2.91	2.99	-1.95	-2.72
BS456	28.3	31.2	0.26	3.24	3.13	1.96	-3.02	-2.92	-1.86	2.71
BS457	21.4	29.1	0.39	3.51	3.16	3.41	-3.06	-2.95	1.80	-2.75
BS156	14.0	17.3	0.19	-3.37	2.39	3.08	2.92	-2.86	-1.16	2.75
BS167	12.7	16.9	0.07	-3.37	2.31	2.97	3.13	3.00	-1.58	-2.61
BS247	15.9	19.5	-0.24	3.32	-2.16	3.18	-2.95	2.87	2.19	-2.63
BS237	20.4	24.0	-0.33	3.30	-2.50	-3.11	3.20	3.00	2.35	-2.34
BS245	24.7	27.8	-0.29	3.30	-2.43	3.25	-3.06	-2.56	2.38	2.87
BS345	20.0	23.5	-0.30	3.30	2.95	-2.94	-2.39	-2.23	2.22	2.91
BS125	24.8	27.2	-0.40	-3.32	-2.36	3.34	3.13	-2.38	2.42	3.04
BS127	23.0	26.4	-0.47	-3.28	-2.33	3.21	3.30	3.13	2.12	-2.02
BS147	26.9	30.2	-0.41	-1.80	3.09	3.15	-2.91	2.91	2.13	-2.39
OBS_2-BH_{26}-TH_6 (M_S = 1), QM-A region, H-to-Cys, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS2567	25.3	28.6	0.92	3.52	-2.82	3.39	3.24	-2.89	-1.85	-2.58
BS234	16.4	19.2	-0.95	3.36	-2.21	-3.17	-2.91	2.97	1.72	2.82
BS123	35.1	38.4	-1.01	-3.23	-1.06	-3.19	2.89	2.88	2.43	2.60
BS356	25.9	26.6	0.24	3.13	0.26	-3.09	3.11	-2.81	-2.18	2.81
BS456	38.6	40.4	0.32	3.12	0.64	3.21	-3.10	-3.01	-2.03	2.48
BS157	13.6	17.9	0.22	-3.38	2.42	3.05	2.95	-2.69	2.21	-2.56
BS167	16.8	20.1	0.29	-3.36	2.17	2.86	2.94	2.42	-2.14	-2.82
BS235	11.0	14.9	-0.08	3.31	-2.72	-3.03	3.09	-2.99	1.43	2.72
BS247	11.7	14.9	-0.23	3.29	-2.82	3.15	-3.00	2.86	1.41	-2.81
BS346	15.3	19.3	-0.40	3.30	2.46	-3.13	-3.05	2.74	-2.65	2.62
BS237	15.6	19.5	-0.30	3.31	-3.15	-3.18	3.12	2.97	1.82	-2.70
BS245	20.6	25.1	-0.11	3.27	-3.09	3.19	-3.08	-2.97	1.89	2.77
BS347	9.6	14.2	-0.23	3.34	3.04	-3.20	-3.17	2.93	1.86	-2.55
BS137	19.7	24.5	-0.29	-3.28	2.88	-3.11	3.21	3.01	2.22	-2.53
BS125	14.2	18.6	-0.29	-3.33	-2.93	3.29	3.10	-2.79	1.94	2.92
BS127	13.1	16.9	-0.33	-3.32	-2.95	3.14	3.25	3.02	1.85	-2.65
BS135	11.6	16.0	-0.37	-3.31	3.11	-3.08	3.16	-2.49	2.07	2.82
BS147	9.6	13.6	-0.42	-3.32	3.13	3.20	-3.11	2.92	2.12	-2.40
BS147 (H-to-Phe)	14.5	17.2	-0.40	-3.32	3.20	3.19	-3.14	2.91	2.10	-2.39
BS147 (H-to-hyd)	10.5	14.0	-0.41	-3.32	3.11	3.19	-3.09	2.92	2.11	-2.39
OBS_2-BH_{26}-TH_6 (M_S = 0), QM-A region, H-to-Cys, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS1567	17.5	22.2	0.86	-3.36	2.41	3.25	3.22	-2.50	-1.47	-2.37
BS123	26.5	31.9	-1.13	-3.48	-3.09	-3.35	3.10	3.26	2.12	2.96
BS124	26.8	28.6	-1.01	-3.34	-2.32	3.06	-3.16	2.87	1.48	2.72
BS2356	12.8	15.4	0.26	3.33	-2.54	-3.06	3.13	-2.81	-1.67	2.83
BS2467	13.0	16.3	0.29	3.29	-2.83	3.14	-3.02	2.95	-1.41	-2.72

BS357	29.5	30.1	0.62	2.93	1.37	-3.14	3.09	-3.03	1.13	-2.83
BS157	15.4	17.9	0.59	-3.36	2.48	2.93	2.82	-3.02	0.97	-2.84
BS167	31.0	34.2	0.30	-3.31	1.87	2.87	1.41	2.21	-2.10	-2.89
BS247	13.0	16.3	0.29	3.29	-2.84	3.14	-3.02	2.95	-1.41	-2.72
BS126	29.3	34.4	-0.14	-3.33	-3.12	3.11	2.59	1.79	-2.41	1.67
BS135	13.0	16.3	-0.32	-3.29	2.87	-3.14	3.03	-2.94	1.36	2.72
BS136	24.6	28.1	-0.25	-3.30	2.33	-3.18	2.85	1.93	-2.60	2.48
BS146	20.4	24.9	-0.24	-3.30	2.30	2.80	-3.19	2.72	-2.38	1.52
OBS_2-BH_{26}-TH_6 (M_S = 1), QM-C region, r^2SCAN										
BS147	14.9	14.5	-0.36	-3.31	3.12	3.19	-3.09	2.91	2.13	-2.44

Table S37. The relative polarized QM and QM/MM energies (kcal/mol) relative to the lowest-energy model (see Figure 2k in the manuscript) and Mulliken spin populations of Mo and 7 Fe ions for the **OBS_6-DH_2** model.

OBS_6-DH_2 (Ms = 2), QM-A region, H-to-homo, r^2SCAN										
	ΔE(polarized QM)	Δ(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS234	2.3	4.2	-1.09	3.34	-2.11	-2.87	-2.85	3.06	2.86	2.94
BS123	23.2	23.6	-1.17	-3.00	-2.39	-2.28	3.22	3.08	3.06	3.02
BS14	19.4	18.4	-1.14	-3.24	0.93	2.70	-3.23	2.76	2.90	2.59
BS134	22.0	21.0	-1.28	-3.13	2.83	-1.29	-2.87	3.11	3.24	3.06
BS257	17.2	16.6	0.43	2.89	-2.54	2.42	3.14	-2.93	2.96	-2.79
BS256	18.9	17.7	0.42	2.96	-2.54	2.69	3.19	-3.01	-2.99	2.72
BS267	15.8	14.9	0.41	3.26	-2.87	2.99	3.14	2.79	-2.93	-2.96
BS157	3.2	5.3	0.13	-3.40	2.81	3.24	3.12	-2.59	3.03	-2.36
BS167	5.4	7.8	0.12	-3.37	2.76	3.15	3.19	3.09	-2.32	-2.61
BS235	1.2	1.8	-0.33	3.32	-2.45	-3.10	3.14	-2.88	2.95	2.74
BS247	0.0	2.3	-0.26	3.29	-2.44	3.15	-3.04	2.88	2.89	-2.82
BS236	1.1	2.0	-0.31	3.31	-2.69	-3.17	3.14	3.05	-2.87	2.90
BS237	4.2	4.9	-0.38	3.31	-2.69	-3.22	3.11	2.98	3.07	-2.62
BS245	7.3	7.7	-0.35	3.29	-2.65	3.09	-3.15	-2.71	3.09	2.85
BS246	3.3	4.0	-0.31	3.29	-2.67	3.13	-3.11	3.01	-2.86	2.95
BS345	7.1	7.5	-0.38	3.30	2.98	-3.08	-2.68	-2.70	3.00	2.94
BS347	8.1	8.4	-0.40	3.29	2.95	-2.64	-3.08	3.06	2.97	-2.58
BS126	4.4	5.7	-0.31	-3.30	-2.69	3.26	3.24	3.06	-2.71	2.95
BS137	8.9	9.4	-0.54	-3.28	2.83	-2.62	3.22	3.11	3.13	-2.15
BS145	7.9	8.0	-0.48	-3.31	2.91	3.30	-2.71	-2.31	3.16	3.01
BS125	8.4	8.4	-0.37	-3.28	-2.39	3.31	3.14	-2.82	3.04	2.96
BS127	7.9	7.7	-0.35	-3.28	-2.33	3.13	3.28	3.08	2.98	-2.75
BS135	13.1	13.2	-0.61	-3.28	2.81	-2.96	3.24	-1.87	3.22	2.97
BS147	10.7	11.0	-0.65	-3.32	2.84	3.29	-3.01	3.03	3.18	-1.64
OBS_6-DH_2 (Ms = 1), QM-A region, H-to-homo, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS234	2.2	5.3	-0.99	3.36	-2.44	-3.21	-3.04	2.78	2.84	2.32
BS123	9.8	13.4	-1.17	-3.35	-2.86	-3.17	3.20	3.06	3.14	3.00
BS124	12.4	12.2	-1.13	-3.33	-2.83	3.19	-3.16	3.10	3.17	2.90

BS134	19.3	18.2	-1.21	-3.31	2.91	-3.03	-3.01	3.23	3.16	2.97
BS356	12.4	13.4	0.29	3.20	1.08	-3.14	3.17	-2.91	-2.78	2.76
BS467	12.5	14.9	0.34	3.16	1.08	3.19	-3.10	2.84	-2.82	-2.78
BS256	29.1	27.8	0.41	0.83	-2.61	3.04	3.15	-3.00	-2.95	2.76
BS267	20.8	20.6	0.42	3.20	-2.81	3.00	1.27	2.73	-2.99	-2.94
BS357	16.2	15.8	0.28	2.71	2.62	-3.14	2.90	-3.04	2.76	-2.94
BS367	18.8	18.7	0.37	3.04	2.40	-3.21	2.99	2.56	-3.11	-2.90
BS456	18.8	19.8	0.37	3.13	2.63	2.61	-3.18	-3.01	-3.07	2.51
BS156	2.6	3.7	0.39	-3.36	2.33	3.11	2.98	-2.93	-2.86	2.59
BS167	2.9	3.8	0.38	-3.36	2.30	3.01	3.06	2.71	-2.88	-2.82
BS235	6.7	7.7	-0.36	3.28	-2.96	-3.17	3.02	-3.06	2.37	2.63
BS346	0.8	1.6	-0.39	3.30	2.43	-3.09	-3.08	2.89	-3.00	2.77
BS236	8.5	8.6	-0.17	3.29	-2.85	-3.27	2.98	2.31	-3.00	2.58
BS237	22.7	23.1	-0.38	1.89	-2.66	-3.16	2.84	2.97	3.06	-2.62
BS246	9.9	11.6	-0.09	3.26	-2.77	2.93	-3.16	2.74	-2.96	1.91
BS345	4.0	4.6	-0.43	3.30	2.57	-3.19	-3.25	-2.89	2.92	2.85
BS126	10.5	12.0	-0.40	-3.32	-2.82	3.12	2.78	2.63	-2.77	2.79
BS137	6.8	7.4	-0.47	-3.29	2.69	-3.22	3.12	3.01	2.96	-2.67
BS145	5.3	5.6	-0.47	-3.32	2.73	3.18	-3.19	-2.77	2.97	2.89
BS125	8.6	10.5	-0.34	-3.34	-2.80	3.08	3.00	-2.88	2.84	2.51
BS127	9.2	9.2	-0.33	-3.34	-2.78	3.00	3.03	2.70	2.81	-2.83
BS135	1.2	1.2	-0.47	-3.29	2.74	-3.12	3.06	-2.81	3.03	2.85
BS136	6.7	8.0	-0.53	-3.30	2.68	-3.19	3.20	3.06	-2.68	2.82
BS146	6.1	6.5	-0.46	-3.33	2.69	3.28	-3.20	2.92	-2.70	2.95
BS147	0.0	0.0	-0.43	-3.32	2.74	3.10	-3.12	2.95	3.01	-2.73
BS147 (H-to-Phe)	-1.0	0.4	-0.42	-3.31	2.73	3.09	-3.13	2.96	3.00	-2.72
BS147 (H-to-Val)	0.4	1.7	-0.40	-3.31	2.73	3.09	-3.13	2.96	2.99	-2.73
OBS_6-DH_2 (Ms = 0), QM-A region, H-to-homo, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS2567	15.6	15.8	1.01	3.33	-2.82	3.20	3.19	-2.82	-2.90	-2.49
BS134	15.6	15.7	-1.03	-3.34	2.82	-3.20	-3.20	2.84	2.90	2.52
BS257	6.0	8.1	0.33	-3.31	-0.05	3.00	2.91	-2.89	3.05	-2.72
BS2467	6.6	8.6	0.42	3.27	-1.62	3.22	-2.89	2.89	-2.89	-2.76
BS267	33.9	32.0	0.36	0.60	-2.95	2.85	2.56	2.73	-2.97	-2.98
BS2357	8.2	8.9	0.14	3.29	-2.11	-3.02	3.14	-2.72	3.05	-2.18
BS2367	13.4	14.6	0.28	3.31	-2.55	-3.09	3.22	3.00	-2.66	-1.94
BS2456	15.6	17.4	0.41	3.24	-1.18	3.27	-3.01	-2.94	-2.90	2.72
BS457	28.6	28.1	0.29	0.44	2.59	3.05	-3.11	-3.04	2.87	-2.93
BS156	11.7	12.5	0.55	-3.37	2.19	3.02	2.89	-2.92	-3.12	1.09
BS157	8.1	8.3	0.41	-3.34	1.93	2.76	2.75	-3.10	2.40	-2.99
BS167	12.7	15.3	0.26	-3.34	2.27	2.78	2.08	2.32	-2.93	-2.89
BS2345	12.8	15.3	-0.30	3.33	-2.21	-2.76	-2.14	-2.32	2.95	2.88
BS247	26.8	25.4	-0.18	2.66	-2.60	1.29	-3.16	2.85	2.56	-2.91
BS236	23.8	23.2	-0.19	1.87	-2.89	-3.26	2.68	2.37	-3.00	2.67

BS246	25.3	24.8	-0.12	2.29	-2.86	2.28	-3.29	2.82	-3.01	2.24
BS345	9.3	11.3	-0.39	3.30	0.12	-3.11	-3.10	-2.82	3.00	2.77
BS126	19.1	20.9	-0.40	-3.32	-3.02	2.70	2.57	2.83	-3.12	2.28
BS137	16.1	17.3	-0.45	-3.23	1.18	-3.27	3.00	2.97	2.94	-2.72
BS145	13.4	14.6	-0.31	-3.31	2.54	3.10	-3.22	-2.99	2.74	1.87
BS135	7.4	8.5	-0.45	-3.27	1.61	-3.21	2.88	-2.90	2.92	2.78
BS136	9.2	10.5	-0.26	-3.26	2.12	-3.14	2.97	2.33	-3.05	2.60
BS146	8.2	9.0	-0.18	-3.29	2.09	3.03	-3.13	2.74	-3.03	2.15
OBS_6-DH_2 (Ms = 1), QM-C region, r^2SCAN										
BS147	0.0	0.0	-0.40	-3.31	2.70	3.07	-3.10	2.95	3.02	-2.73

Table S38. The relative polarized QM and QM/MM energies (kcal/mol) relative to the lowest-energy model (see Figure 2k in the manuscript) and Mulliken spin populations of Mo and 7 Fe ions for the **OBS_2-DH_6** model.

OBS_2-DH_6 (Ms = 2), QM-A region, H-to-Cys, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS567	35.0	39.7	1.04	1.56	2.83	3.10	3.14	-3.00	-2.19	-2.81
BS257	11.4	17.9	0.37	3.49	-3.17	3.27	3.15	-2.91	2.06	-2.70
BS357	16.3	21.7	0.37	3.46	3.19	-3.12	3.34	-2.91	2.02	-2.90
BS456	24.4	28.4	0.37	3.20	3.17	2.41	-3.09	-2.99	-2.24	2.70
BS457	14.9	22.7	0.34	3.49	3.20	3.36	-3.11	-2.98	1.99	-2.78
BS157	8.9	17.7	0.13	-3.37	3.34	3.25	3.17	-2.55	2.30	-2.39
BS346	-0.7	5.7	-0.41	3.34	3.08	-3.08	-3.08	2.88	-2.06	2.75
BS346 (H-to-Val)	1.3	7.6	-0.36	3.36	3.12	-3.08	-3.05	2.86	-2.12	2.72
BS346 (H-to-Phe)	3.8	9.1	-0.37	3.35	3.11	-3.06	-3.08	2.87	-2.12	2.73
BS236	7.2	13.1	-0.34	3.29	-3.13	-3.28	3.14	3.03	-2.02	2.83
BS246	10.4	17.3	-0.38	3.26	-3.18	3.13	-3.21	2.94	-1.94	2.92
BS136	10.9	16.8	-0.59	-3.28	3.16	-3.13	3.26	3.10	-1.73	2.87
BS146	9.1	14.9	-0.53	-3.29	3.14	3.32	-3.15	2.97	-1.70	3.00
OBS_2-DH_6 (Ms = 1), QM-A region, H-to-Cys, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS257	17.7	22.8	0.67	3.25	-3.14	2.93	3.02	-3.09	1.54	-2.93
BS357	18.2	21.9	0.40	3.35	2.31	-3.21	3.13	-3.03	1.86	-2.90
BS457	19.8	24.1	0.36	3.33	2.23	3.20	-3.19	-3.02	1.92	-2.88
BS156	13.9	18.3	0.27	-3.37	2.33	2.99	2.86	-2.93	-2.40	2.46
BS157	8.0	15.9	0.44	-3.35	3.03	3.01	2.98	-2.90	2.03	-2.81
BS235	8.4	13.4	-0.18	3.28	-2.88	-3.04	3.17	-3.03	1.69	2.71
BS347	5.1	10.8	-0.39	3.31	2.93	-3.26	-3.22	2.96	2.40	-2.72
BS126	16.2	22.8	-0.23	-3.33	-3.17	3.10	3.09	2.20	-1.64	2.02
BS125	8.2	13.8	-0.40	-3.33	-3.03	3.28	3.14	-2.89	2.31	2.99
BS127	6.5	12.0	-0.34	-3.33	-3.03	3.14	3.25	3.09	2.27	-2.83
BS136	16.2	21.5	-0.43	-3.25	2.79	-3.20	2.67	2.77	-1.84	2.60
BS146	14.4	19.5	-0.29	-3.28	2.91	2.91	-3.21	2.67	-1.80	2.28

OBS_2-DH_6 (Ms = 0), QM-A region, H-to-Cys, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS2346	12.4	16.1	-0.42	3.37	-2.11	-2.92	-2.85	3.01	-1.60	2.89
BS257	28.4	32.5	0.89	2.91	-3.10	2.16	3.11	-3.02	0.04	-2.89
BS2356	12.6	16.1	0.33	3.30	-2.79	-3.07	3.16	-2.80	-1.45	2.85
BS357	27.4	28.9	0.39	3.01	1.30	-3.17	3.05	-3.01	1.55	-2.92
BS237	17.1	22.1	0.18	3.29	-3.18	-3.22	3.10	2.81	-0.20	-2.82
BS456	10.5	14.4	-0.01	3.33	3.02	-3.18	-3.20	-2.88	0.19	2.64
BS457	25.7	30.2	0.41	3.04	1.14	3.05	-3.13	-3.05	1.66	-2.90
BS157	12.3	16.0	0.41	-3.37	2.10	2.96	2.89	-3.02	1.56	-2.90
BS235	25.2	29.8	-0.21	1.78	-2.93	-3.02	2.94	-3.03	1.82	2.75
BS2467	11.0	16.4	0.23	3.28	-3.18	3.13	-3.05	2.93	-0.81	-2.71
BS245	19.3	25.3	0.11	3.27	-3.18	3.16	-3.14	-2.81	0.22	2.27
BS345	10.5	14.4	-0.01	3.33	3.02	-3.18	-3.20	-2.88	0.20	2.64
BS347	8.2	14.4	0.01	3.33	3.02	-3.21	-3.16	2.79	-0.06	-2.68
BS137	19.2	25.2	-0.14	-3.27	3.16	-3.15	3.15	2.84	-0.24	-2.28
BS145	16.9	22.1	-0.19	-3.29	3.17	3.24	-3.09	-2.79	0.13	2.85
BS125	8.5	14.3	-0.02	-3.33	-3.00	3.23	3.17	-2.77	-0.09	2.75
BS127	10.1	14.2	-0.03	-3.33	-3.00	3.18	3.21	2.92	-0.23	-2.64
BS135	11.0	16.4	-0.26	-3.28	3.18	-3.12	3.06	-2.93	0.79	2.72
BS147	8.5	13.7	-0.29	-3.30	3.11	3.07	-3.16	2.82	0.98	-2.84
OBS_2-DH_6 (Ms = 2), QM-C region, r^2SCAN										
BS346	6.6	7.1	-0.44	3.32	3.08	-3.06	-3.06	2.87	-2.06	2.77

Table S39. The relative polarized QM and QM/MM energies (kcal/mol) relative to the lowest-energy model (see Figure 2k in the manuscript) and Mulliken spin populations of Mo and 7 Fe ions for the **CBS_{37}-OBS_2-BH_{26}** model.

CBS_{37}-OBS_2-BH_{26} (Ms = 2), QM-A region, H_{S2B}-to-Cys-H_{S5A}-to-Arg359, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS567	47.1	45.7	1.25	2.77	2.78	2.62	3.10	-3.13	-2.73	-3.01
BS234	31.0	30.5	-1.14	3.35	-2.20	-2.65	-2.85	3.11	2.77	2.98
BS356	36.4	35.3	0.31	3.23	2.77	-3.05	3.02	-2.93	-2.48	2.74
BS467	33.0	32.4	0.25	3.34	2.80	2.94	-3.14	2.90	-2.63	-2.80
BS256	35.6	36.9	0.20	3.31	-3.19	3.15	3.16	-2.97	-2.70	2.64
BS267	33.3	34.1	0.07	3.31	-3.21	3.03	3.16	2.81	-2.68	-2.91
BS357	30.5	30.5	0.48	3.28	2.88	-2.93	3.25	-2.97	2.42	-2.87
BS367	35.4	33.9	0.39	3.27	2.78	-3.01	3.01	2.81	-2.80	-2.84
BS456	33.7	34.2	0.27	3.36	3.08	2.99	-3.10	-3.00	-2.75	2.77
BS457	33.4	33.6	0.38	3.36	2.94	3.18	-3.03	-3.01	2.50	-2.71
BS156	33.8	32.8	0.34	-3.15	2.62	3.13	3.05	-2.84	-2.50	2.98
BS157	30.4	33.4	0.40	-3.18	2.83	3.10	3.10	-2.86	2.91	-2.58
BS167	30.7	29.7	0.17	-3.23	2.68	3.01	3.20	3.01	-2.38	-2.71
BS235	22.7	26.7	-0.31	3.29	-2.86	-2.94	3.15	-2.50	2.82	2.76
BS247	23.3	25.9	-0.38	3.33	-2.91	3.04	-3.03	2.93	2.69	-2.16
BS236	28.7	30.8	-0.44	3.28	-2.68	-3.10	3.05	3.00	-2.39	2.79
BS237	23.7	26.8	-0.21	3.32	-3.08	-3.04	3.18	3.05	2.69	-2.49

BS245	31.2	31.5	-0.41	3.31	-2.77	3.05	-2.70	-2.66	2.82	2.88
BS246	28.5	30.4	-0.48	3.36	-2.68	2.98	-3.15	2.93	-2.34	2.91
BS345	29.5	31.4	-0.23	3.30	3.06	-3.00	-2.86	-2.33	2.75	2.91
BS347	24.2	27.2	-0.21	3.34	2.97	-2.56	-3.07	2.99	2.66	-2.52
BS126	32.6	32.4	-0.67	-3.30	-2.84	3.01	3.20	3.07	-1.73	2.89
BS145	35.3	35.6	-0.32	-3.29	3.19	3.24	-2.71	-2.35	2.82	3.02
BS125	28.7	32.4	-0.47	-3.29	-2.70	3.24	3.13	-2.21	2.85	2.97
BS136	33.1	35.7	-0.71	-3.35	3.07	-2.88	3.26	3.16	-1.66	2.83
BS146	32.3	33.6	-0.88	-3.33	3.07	3.22	-3.10	3.08	-1.28	3.04
CBS_{37}-OBS_2-BH_{26} (Ms = 1), QM-A region, H_{S2B}-to-Cys-H_{S5A}-to-Arg359, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS124	35.4	35.0	-1.41	-3.26	-2.34	3.10	-3.05	3.09	2.83	3.03
BS134	37.1	37.1	-1.29	-3.31	2.88	-2.49	-2.93	3.18	2.89	3.00
BS257	37.0	36.6	0.72	3.32	-3.22	2.87	3.06	-3.09	1.22	-2.94
BS356	36.6	35.9	0.44	3.22	2.25	-3.11	2.90	-2.93	-2.83	2.00
BS3467	28.2	31.1	0.05	3.32	3.16	-2.44	-3.02	3.02	-1.35	-1.55
BS2356	36.9	37.8	0.31	3.28	-2.63	-0.52	3.22	-2.91	-2.27	2.81
BS357	37.5	35.5	0.53	3.28	2.28	-3.10	3.03	-3.09	2.05	-2.97
BS367	40.3	40.2	0.42	3.18	2.80	-2.96	1.38	2.70	-2.86	-2.87
BS456	36.6	40.8	0.28	3.24	3.14	0.57	-2.89	-2.87	-2.65	2.73
BS156	25.3	27.5	0.11	-3.38	2.32	2.98	2.98	-2.86	-2.52	2.58
BS157	31.3	31.0	0.20	-3.36	2.11	2.90	2.99	-2.83	2.78	-2.55
BS167	33.7	33.5	0.27	-3.34	2.37	2.91	2.55	2.87	-2.66	-2.75
BS235	24.1	27.2	-0.35	3.30	-2.84	-2.99	3.12	-3.00	2.42	2.17
BS247	25.5	30.1	-1.40	3.33	-2.88	3.09	-3.04	3.01	2.71	-3.11
BS346	27.6	27.9	-0.43	3.27	2.72	-3.02	-3.12	2.92	-2.84	2.56
BS236	30.0	31.9	-1.04	3.27	-3.00	-3.16	2.99	2.98	-3.12	2.81
BS237	32.7	33.6	-0.20	3.28	-3.17	-3.17	3.03	2.40	2.51	-2.79
BS245	26.8	30.6	-0.48	3.32	-3.06	2.97	-3.15	-2.93	2.70	2.60
BS246	27.0	30.6	-0.35	3.32	-3.11	2.96	-3.19	2.86	-2.80	2.19
BS345	28.8	28.7	-0.31	3.28	3.05	-3.11	-3.01	-2.88	2.24	2.78
BS347	22.4	25.9	-0.10	3.35	2.89	-3.06	-3.19	2.81	1.76	-2.58
BS126	25.3	30.8	-0.57	-3.33	-3.03	2.91	3.12	2.89	-2.59	2.57
BS145	30.9	31.1	-0.59	-3.32	2.80	3.13	-2.94	-2.64	2.82	2.84
BS125	21.9	26.7	-0.48	-3.32	-3.08	2.86	3.06	-2.72	2.84	2.87
BS127	27.9	31.0	-0.54	-3.27	-3.17	2.68	2.64	2.98	2.68	-1.80
BS135	27.5	27.5	-0.47	-3.36	2.69	-3.02	3.15	-2.48	2.76	2.82
BS136	32.8	33.6	-0.55	-3.34	2.86	-3.10	2.95	2.98	-2.39	2.71
BS146	28.2	28.9	-0.62	-3.30	2.87	2.94	-3.18	2.98	-2.38	2.83
BS147	21.9	24.7	-0.62	-3.30	2.49	3.02	-3.16	2.96	2.79	-2.01
BS147 (H_{S2B}-to-hyd-H_{S5A}-to-Arg359)	27.1	27.1	-0.61	-3.30	2.57	3.05	-3.16	2.93	2.76	-2.04
BS147 (H_{S2B}-to-Cys-H_{S5A}-to-Arg96)	20.5	25.0	-0.63	-3.30	2.48	3.02	-3.16	2.96	2.81	-2.00
BS147 (H_{S2B}-to-hyd-H_{S5A}-to-Arg96)	22.0	27.3	-0.62	-3.30	2.58	3.03	-3.17	2.92	2.77	-2.00
CBS_{37}-OBS_2-BH_{26} (Ms = 0), QM-A region, H_{S2B}-to-Cys-H_{S5A}-to-Arg359, r^2SCAN										

	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS1567	28.8	28.8	1.27	-2.90	2.79	3.16	3.28	-2.83	-2.57	-2.64
BS234	23.4	28.5	-1.29	2.91	-2.85	-3.15	-3.28	2.86	2.58	2.66
BS123	29.2	31.4	-1.30	-3.36	-3.03	-3.18	2.92	2.96	2.61	2.74
BS124	28.5	29.5	-1.31	-3.25	-3.00	2.90	-3.24	2.91	2.55	2.91
BS134	33.2	34.0	-1.24	-3.32	2.75	-3.11	-3.17	3.04	2.86	2.72
BS356	35.1	39.5	0.46	3.14	0.12	-3.01	3.13	-2.91	-3.02	1.89
BS467	48.2	50.8	0.32	0.84	2.74	2.66	-3.18	2.48	-2.85	-2.76
BS2356	29.6	29.1	0.47	3.30	-2.55	-2.46	3.24	-2.93	-2.49	2.82
BS2367	34.4	34.4	0.39	3.34	-2.65	-3.05	3.12	3.05	-2.10	-2.71
BS2357	28.9	32.1	0.46	3.29	-2.68	-2.36	3.19	-2.82	2.63	-2.25
BS3467	28.1	30.1	0.40	3.32	3.15	-2.46	-2.94	2.72	-2.67	-2.05
BS456	34.7	35.2	0.30	3.28	3.18	-2.14	-2.66	-2.51	-2.60	2.60
BS2457	35.2	37.5	0.28	3.29	-2.85	3.10	-2.75	-2.43	2.75	-1.80
BS157	30.7	35.6	0.52	-3.36	1.98	2.74	2.81	-3.04	1.85	-2.86
BS167	34.3	39.4	0.53	-3.34	2.37	2.64	2.30	1.53	-2.83	-2.80
BS2347	33.8	35.0	-0.25	3.35	-2.40	-1.85	-2.71	2.96	2.67	-2.27
BS2345	40.6	39.8	-0.34	3.36	-2.44	-1.49	-2.94	-2.28	2.83	2.78
BS345	32.6	31.0	-0.21	3.24	2.34	-3.12	-3.27	-2.98	1.87	2.61
BS347	34.1	33.6	-0.07	3.26	2.59	-3.19	-3.16	2.75	1.22	-2.93
BS1267	32.8	31.0	0.16	-3.24	-2.34	3.11	3.27	3.01	-1.84	-2.62
BS137	38.4	39.4	-0.37	-3.34	2.34	-3.12	3.07	2.53	2.27	-2.86
BS145	34.1	33.7	-0.57	-3.33	2.79	3.06	-3.14	-2.92	2.51	2.25
BS125	28.1	30.0	-0.44	-3.32	-3.10	2.40	2.94	-2.84	2.44	2.45
BS127	34.9	35.1	-0.33	-3.29	-3.17	2.15	2.69	2.52	2.58	-2.60
BS135	32.3	32.1	-0.28	-3.35	2.51	-3.03	3.04	-2.98	1.85	2.71
BS136	34.4	37.5	-0.32	-3.30	2.89	-3.11	2.83	2.46	-2.71	1.66
BS146	29.2	32.1	-0.49	-3.30	2.67	2.32	-3.20	2.82	-2.63	2.33
BS147	29.4	29.1	-0.51	-3.30	2.53	2.51	-3.24	2.93	2.51	-2.83
CBS_{37}-OBS_2-BH_{26} (Ms = 1), QM-C region, r^2SCAN										
BS147	22.1	23.8	-0.61	-3.30	2.50	3.02	-3.15	2.97	2.79	-2.00

Table S40. The relative polarized QM and QM/MM energies (kcal/mol) relative to the lowest-energy model (see Figure 2k in the manuscript) and Mulliken spin populations of Mo and 7 Fe ions for the **CBS_{37}-OBS_6-BH_{26}** model.

CBS_{37}-OBS_6-BH_{26} (Ms = 2), QM-A region, H_{S2B}-to-homo-H_{S5A}-to-Arg359, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS567	32.0	36.5	1.35	2.90	2.36	3.05	3.20	-3.07	-3.18	-2.76
BS234	16.6	20.7	-1.36	3.34	-2.66	-2.79	-2.91	3.16	3.28	2.94
BS123	22.1	26.1	-1.18	-3.30	2.06	-3.20	2.70	2.83	2.18	2.32
BS14	16.6	20.4	-1.26	-3.30	2.64	2.42	-3.24	2.68	2.40	2.26
BS257	16.1	18.2	0.28	3.34	-3.17	2.83	3.04	-2.97	3.01	-2.68
BS356	20.3	23.6	0.45	3.24	3.04	-3.10	3.06	-2.96	-1.80	1.91
BS467	14.5	19.9	0.49	3.32	2.90	2.93	-3.18	2.90	-2.98	-2.58
BS256	16.7	19.0	0.51	3.32	-3.07	3.10	3.10	-2.99	-3.00	2.61
BS267	17.1	19.7	0.44	3.31	-3.07	2.97	3.13	2.72	-3.13	-2.79

BS357	18.5	21.1	0.32	3.28	2.85	-3.11	3.10	-3.00	3.01	-2.67
BS367	17.8	20.7	0.53	3.21	2.96	-3.06	3.16	2.73	-3.20	-2.58
BS456	16.5	22.1	0.54	3.37	3.07	3.15	-3.14	-2.82	-3.09	2.66
BS457	20.2	23.3	0.26	3.35	2.86	3.00	-3.16	-2.79	3.02	-2.79
BS156	12.3	17.0	0.42	-3.36	2.98	3.14	3.11	-2.54	-2.68	2.85
BS157	10.0	17.5	0.38	-3.37	2.77	3.06	3.08	-2.84	2.95	-1.92
BS167	9.5	14.8	0.42	-3.37	2.98	3.04	3.18	2.90	-2.80	-2.31
BS235	11.5	15.9	-0.36	3.29	-2.95	-2.95	3.18	-2.50	2.96	2.63
BS247	7.5	13.4	-0.45	3.32	-2.93	3.07	-3.05	2.87	2.78	-2.15
BS247 (H_{S2B}-to-hyd-H_{S5A}-to-Arg359)	7.9	13.5	-0.44	3.32	-2.93	3.08	-3.06	2.89	2.78	-2.15
BS247 (H_{S2B}-to-homo-H_{S5A}-to-Arg96)	6.9	13.1	-0.45	3.32	-2.93	3.09	-3.06	2.87	2.77	-2.14
BS247 (H_{S2B}-to-hyd-H_{S5A}-to-Arg96)	7.3	13.2	-0.43	3.32	-2.93	3.09	-3.07	2.88	2.77	-2.16
BS346	11.3	14.8	-0.26	3.27	3.17	-2.85	-3.06	3.02	-2.60	2.71
BS236	14.8	18.3	-0.26	3.27	-2.67	-2.99	3.14	2.88	-2.95	2.83
BS237	9.0	14.0	-0.41	3.33	-3.09	-3.12	3.12	2.89	2.98	-2.33
BS245	14.6	19.8	-0.54	3.29	-2.98	3.08	-2.76	-2.51	3.15	2.68
BS246	13.5	17.4	-0.28	3.27	-2.52	3.12	-3.01	3.02	-3.05	2.75
BS345	18.5	21.7	-0.49	3.33	3.10	-2.57	-3.11	-2.71	3.16	2.78
BS347	8.2	13.8	-0.34	3.31	3.09	-3.01	-3.15	2.96	2.97	-2.21
BS126	21.0	25.9	-0.39	-3.19	-1.13	3.00	3.14	2.93	-3.08	2.56
BS137	13.3	18.2	-0.56	-3.27	2.94	-2.89	3.22	3.06	3.15	-1.95
BS145	17.9	22.3	-0.68	-3.26	3.16	3.21	-2.77	-2.23	3.28	2.92
BS125	24.9	28.9	-0.65	-3.20	-1.00	2.96	2.97	-2.89	3.10	2.73
BS127	12.5	17.8	-0.60	-3.28	-3.01	3.07	3.27	3.14	3.03	-2.02
BS135	20.1	23.8	-0.54	-3.31	3.24	-2.70	3.15	-2.36	3.30	2.83
BS136	19.4	23.0	-0.29	-3.32	3.10	-2.45	3.28	3.14	-2.70	2.84
BS146	20.3	23.8	-0.33	-3.27	3.14	3.27	-2.75	3.05	-2.55	3.00
BS147	14.5	19.0	-0.73	-3.27	3.24	3.04	-3.00	3.03	3.28	-1.82
CBS_{37}-OBS_6-BH_{26} (Ms = 1), QM-A region, H_{S2B}-to-homo-H_{S5A}-to-Arg359, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS567	38.2	39.9	1.36	1.10	2.81	2.77	3.05	-3.12	-3.03	-2.84
BS234	9.7	14.6	-1.15	3.36	-2.85	-2.86	-2.98	2.93	2.39	2.63
BS123	17.4	22.6	-1.38	-3.35	-2.96	-3.02	3.22	3.08	3.18	2.93
BS124	19.3	21.7	-1.45	-3.18	-2.84	3.13	-3.13	3.14	3.10	2.94
BS134	22.5	24.7	-1.36	-3.33	3.15	-2.54	-2.84	3.15	2.72	2.91
BS257	24.5	27.8	0.27	2.99	-3.11	2.84	2.31	-3.05	2.57	-2.75
BS356	18.4	22.1	0.76	3.19	2.83	-3.05	2.99	-3.07	-3.18	1.72
BS2467	19.3	23.8	0.10	3.32	-2.38	3.13	-3.00	3.02	-1.98	-0.96
BS256	18.6	22.3	0.63	3.34	-3.05	2.94	2.99	-3.05	-3.06	1.20
BS267	27.6	28.9	0.58	3.34	-3.14	2.61	2.90	1.83	-3.22	-2.94
BS2357	15.9	20.0	0.10	3.26	-2.20	-2.46	3.27	-2.82	3.06	-1.10
BS367	29.1	31.5	0.50	3.12	0.86	-2.98	3.21	2.73	-3.14	-2.53
BS456	18.3	26.0	0.58	3.35	2.88	3.05	-3.19	-2.99	-3.03	1.36
BS457	22.7	26.0	0.30	3.25	1.51	2.94	-3.13	-2.96	3.05	-2.85
BS156	8.8	14.6	0.34	-3.38	2.92	3.00	3.03	-2.76	-2.93	2.18

BS157	11.7	16.1	0.23	-3.37	2.69	2.84	2.98	-2.92	2.79	-2.69
BS167	16.1	20.5	0.34	-3.35	2.91	2.87	3.07	2.26	-3.08	-2.64
BS235	8.3	15.3	-0.47	3.31	-3.00	-3.01	3.14	-2.99	2.81	1.90
BS247	16.8	20.0	-0.48	3.29	-3.02	2.34	-3.08	2.80	2.84	-2.78
BS346	8.2	15.4	-0.38	3.28	3.15	-2.92	-3.05	2.89	-3.17	2.08
BS236	16.0	21.9	-0.45	3.27	-2.92	-3.11	3.09	2.80	-3.08	2.12
BS237	14.8	18.8	-0.39	3.29	-3.15	-3.19	2.99	2.34	2.77	-2.79
BS245	10.6	16.5	-0.41	3.29	-3.02	3.01	-3.14	-2.69	3.05	1.67
BS246	10.8	17.0	-0.40	3.28	-2.90	2.97	-3.14	2.93	-3.02	2.12
BS345	11.4	17.3	-0.48	3.28	3.07	-3.06	-3.16	-2.87	3.02	2.15
BS2457	20.4	25.4	0.03	3.26	-2.16	3.22	-2.66	-2.27	3.26	-1.58
BS126	12.4	17.5	-0.36	-3.29	-3.08	2.95	3.17	2.95	-2.98	2.57
BS137	22.2	27.3	-0.42	-3.34	2.64	-3.21	3.00	2.56	2.01	-2.66
BS145	15.1	19.8	-0.63	-3.32	2.94	3.11	-3.10	-2.53	3.01	2.68
BS125	11.2	15.7	-0.65	-3.29	-3.08	2.95	3.09	-2.89	3.08	2.79
BS127	17.3	22.1	-0.45	-3.26	-3.15	2.87	3.07	2.44	2.66	-2.13
BS135	14.9	21.2	-0.58	-3.31	3.18	-2.85	3.07	-2.92	3.19	2.32
BS136	16.0	19.1	-0.51	-3.33	3.00	-2.92	3.07	2.95	-2.96	2.73
BS146	9.3	14.8	-0.43	-3.33	3.08	3.17	-3.05	2.98	-2.99	2.65
BS147	11.9	17.1	-0.55	-3.30	2.81	2.91	-3.15	2.97	2.46	-1.90
CBS_{37}-OBS_6-BH_{26} (Ms = 0), QM-A region, H_{S2B}-to-homo-H_{S5A}-to-Arg359, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS1567	16.1	18.8	1.08	-2.99	3.08	3.04	3.29	-2.61	-2.59	-2.47
BS234	10.9	17.0	-0.67	3.38	-2.84	-2.88	-2.90	2.92	2.87	-0.47
BS123	16.9	22.8	-1.27	-3.37	-3.19	-3.11	3.18	3.02	2.33	2.59
BS124	17.8	22.8	-1.41	-3.41	-2.98	3.03	-3.24	2.91	2.88	2.58
BS134	17.3	21.0	-1.29	-3.36	3.02	-3.03	-3.17	2.85	2.90	2.44
BS2357	13.1	17.5	0.27	3.31	-2.85	-2.42	3.18	-2.74	2.89	-2.25
BS2356	17.7	21.1	0.46	3.28	-2.17	-2.90	3.23	-2.84	-2.10	2.45
BS2467	11.4	17.6	0.53	3.30	-2.57	3.11	-2.94	2.93	-2.83	-2.08
BS2367	17.6	22.8	0.37	3.32	-2.71	-3.00	3.19	2.65	-2.62	-1.73
BS3456	22.5	25.1	0.44	3.24	3.23	-1.98	-2.77	-2.42	-2.89	2.74
BS2457	15.9	22.0	0.06	3.31	-3.01	2.99	-3.05	-2.64	2.93	-0.92
BS156	17.4	21.6	0.39	-3.36	2.81	1.62	2.91	-2.90	-2.90	2.11
BS157	18.0	20.8	0.51	-3.39	2.52	2.81	2.91	-3.08	1.36	-2.83
BS167	23.2	27.8	0.75	-3.37	2.86	2.80	2.57	0.66	-3.08	-2.74
BS247	17.5	21.7	-0.42	3.35	-2.78	-1.72	-2.87	2.91	2.92	-2.08
BS237	29.9	34.9	-0.22	3.28	-3.13	-3.19	2.35	1.54	2.26	-2.77
BS345	23.9	28.7	-0.48	3.16	0.99	-3.05	-3.11	-2.91	3.22	2.18
BS126	18.0	23.7	-0.27	-3.31	-3.12	2.91	3.07	2.63	-2.84	1.24
BS137	22.2	27.3	-0.42	-3.34	2.64	-3.21	3.00	2.56	2.01	-2.66
BS145	17.3	22.8	-0.40	-3.32	2.69	3.03	-3.17	-2.64	2.66	1.66
BS125	10.6	17.1	-0.44	-3.29	-3.14	2.89	3.03	-2.94	2.89	1.37
BS127	22.5	25.1	-0.49	-3.24	-3.23	1.92	2.80	2.44	2.93	-2.74
BS135	11.5	17.5	-0.59	-3.30	2.60	-3.11	2.93	-2.92	2.83	2.13
BS136	15.9	22.1	-0.09	-3.31	3.02	-2.96	3.09	2.72	-2.90	0.73

BS146	13.4	17.7	-0.32	-3.33	2.91	2.73	-3.19	2.82	-2.90	1.87
BS147	17.6	21.3	-0.49	-3.28	2.13	2.88	-3.24	2.85	2.10	-2.38
CBS_{37}-OBS_6-BH_{26} (Ms = 2), QM-C region, r^2SCAN										
BS247	11.6	14.5	-0.41	3.31	-2.90	3.10	-3.03	2.85	2.75	-2.20

Table S41. The relative polarized QM and QM/MM energies (kcal/mol) relative to the lowest-energy model (see Figure 2k in the manuscript) and Mulliken spin populations of Mo and 7 Fe ions for the **$2CBS_{26,37}$-$BH_{26(5)}$** model.

$2CBS_{26,37}$-$BH_{26(5)}$ (Ms = 2), QM-A region, H_{S2B}-to-Phe-H_{S5A}-to-Arg359, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS13	18.1	24.4	-1.17	-3.31	2.85	-3.07	2.89	3.04	2.04	1.01
BS14	16.3	20.3	-1.35	-3.32	2.63	2.42	-3.20	2.72	2.17	2.60
BS14 (H_{S2B}-to-Phe-H_{S5A}-to-Arg96)	16.4	21.0	-1.37	-3.32	2.64	2.47	-3.19	2.72	2.15	2.59
BS14 (H_{S2B}-to-Val-H_{S5A}-to-Arg359)	21.6	24.8	-1.39	-3.31	2.60	2.41	-3.20	2.71	2.23	2.61
BS14 (H_{S2B}-to-Val-H_{S5A}-to-Arg96)	21.7	25.5	-1.41	-3.30	2.60	2.45	-3.19	2.72	2.22	2.61
BS257	27.1	29.9	0.30	3.34	-2.92	2.95	3.08	-2.93	2.31	-2.70
BS256	22.3	26.2	0.24	3.32	-3.20	2.93	3.09	-3.07	-1.57	1.98
BS267	30.7	31.4	0.41	3.34	-3.19	2.82	2.70	2.54	-2.03	-3.00
BS357	19.7	23.5	0.33	3.28	3.08	-3.02	3.23	-2.97	1.89	-2.20
BS457	22.1	26.5	0.28	3.33	3.16	3.23	-3.03	-2.55	1.85	-2.66
BS157	23.6	25.8	0.29	-2.94	3.26	3.19	3.18	-2.81	1.81	-2.28
BS167	22.3	27.3	0.38	-3.37	2.84	3.07	3.20	2.98	-2.49	-2.55
BS235	21.3	25.6	-0.43	3.31	-2.86	-2.97	3.18	-2.46	2.66	2.80
BS247	16.0	23.4	-0.38	3.31	-2.74	3.12	-3.03	2.87	2.43	-2.28
BS236	19.7	25.0	-0.53	3.31	-3.02	-3.16	3.15	3.00	-1.54	2.13
BS245	23.1	29.3	-0.56	3.30	-2.75	3.10	-2.72	-2.63	2.78	2.87
BS246	15.8	22.2	-0.41	3.27	-2.89	3.08	-3.15	2.92	-1.60	2.25
BS345	27.2	28.9	-0.53	3.26	3.13	-2.23	-2.60	-2.55	2.13	2.93
BS347	16.7	21.0	-0.31	3.30	3.13	-2.57	-3.08	3.05	1.95	-1.99
BS126	16.8	21.9	-0.57	-3.29	-3.00	2.95	3.19	3.04	-1.18	2.61
BS145	26.3	31.3	0.73	-3.27	3.11	3.24	-2.83	-2.70	2.73	2.94
BS135	28.5	32.6	0.56	-3.28	3.08	-2.53	3.14	-2.86	2.85	2.91
BS147	27.5	31.9	-0.43	-2.74	3.30	3.22	-3.06	3.02	2.17	-1.87
$2CBS_{26,37}$-$BH_{26(5)}$ (Ms = 1), QM-A region, H_{S2B}-to-Phe-H_{S5A}-to-Arg359, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS2567	22.6	25.9	1.23	3.32	-2.07	3.17	3.26	-2.83	-2.38	-2.61
BS134	26.7	29.0	-1.40	-3.34	3.17	-2.19	-2.78	3.13	2.35	3.03
BS256	27.4	30.6	0.36	3.28	-3.12	1.26	3.09	-3.08	-1.92	1.90
BS267	38.0	39.4	0.80	3.32	-3.08	2.79	2.54	0.68	-2.42	-2.98
BS357	22.5	24.4								
BS457	21.4	25.1	0.51	3.35	3.03	3.12	-3.17	-3.05	1.06	-2.83
BS157	17.8	22.8	0.33	-3.40	3.12	2.98	3.03	-2.82	1.63	-2.49
BS346	17.3	25.3	-0.28	3.27	2.87	-2.97	-3.07	2.81	-2.66	2.02
BS237	23.3	26.4	-0.09	3.33	-3.20	-3.14	3.10	2.62	1.19	-2.25

BS245	20.9	27.6	-0.58	3.30	-3.01	3.01	-3.16	-2.93	2.63	2.57
BS246	19.8	25.9	-0.07	3.31	-2.93	2.96	-3.12	2.86	-1.71	0.25
BS345	23.4	28.8	-0.55	3.29	3.18	-2.73	-3.12	-2.77	2.10	2.42
BS137	17.1	22.9	-0.47	-3.32	3.01	-3.09	3.07	2.99	1.93	-2.03
BS125	20.7	25.8	-0.66	-3.29	-2.90	2.88	3.05	-2.75	2.74	2.89
BS135	23.0	26.1	-0.50	-3.33	2.86	-2.87	3.13	-2.50	2.30	2.99
BS136	17.1	22.9	-0.47	-3.32	3.00	-3.09	3.07	2.99	1.94	-2.03
2CBS$_{26,37}$-BH$_{26(5)}$ (Ms = 0), QM-A region, H$_{S2B}$-to-Phe-H$_{S5A}$-to-Arg359, r^{2}SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS2567	19.3	22.1	1.28	3.32	-3.17	3.02	3.17	-3.01	-2.14	-2.81
BS134	19.0	22.1	-1.29	-3.32	3.17	-3.01	-3.18	3.01	2.16	2.82
BS2367	21.7	25.0	0.66	3.36	-2.82	-2.93	3.20	2.75	-2.21	-2.71
BS357	35.4	37.4	0.57	2.42	2.67	-3.14	2.83	-3.09	1.03	-2.88
BS167	31.9	36.9	0.49	-3.33	2.49	2.80	2.09	1.81	-2.80	-2.89
BS246	15.6	22.1	0.53	3.32	-2.82	3.08	-3.07	2.88	-2.07	-2.38
BS137	25.7	29.9	-0.27	-3.31	2.72	-3.14	2.92	2.36	1.61	-2.43
BS145	21.2	24.9	-0.69	-3.36	2.86	2.95	-3.20	-2.76	2.21	2.69
BS125	23.4	29.1	-0.50	-3.28	-2.95	2.72	2.97	-2.82	2.47	1.77
BS136	26.7	33.3	-0.23	-3.30	2.80	-3.11	2.88	2.44	-2.55	1.61
2CBS$_{26,37}$-BH$_{26(5)}$ (Ms = 2), QM-C region, r^{2}SCAN										
BS14	24.0	21.5	-1.36	-3.32	2.62	2.35	-3.20	2.71	2.25	2.64

Table S42. The relative polarized QM and QM/MM energies (kcal/mol) relative to the lowest-energy model (see Figure 2k in the manuscript) and Mulliken spin populations of Mo and 7 Fe ions for the **2CBS$_{26,37}$-BH$_{26(3)}$** model.

2CBS$_{26,37}$-BH$_{26(3)}$ (Ms = 2), QM-A region, H$_{S2B}$-to-Phe-H$_{S5A}$-to-Arg359, r^{2}SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS13	10.3	25.7	-1.20	-3.32	2.70	-3.08	2.92	3.06	2.30	0.95
BS14	9.9	21.4	-1.42	-3.30	2.21	2.47	-3.20	2.75	2.58	2.56
BS14 (H$_{S2B}$-to-Phe-H$_{S5A}$-to-Arg96)	11.9	22.0	-1.46	-3.28	1.53	2.70	-3.15	2.73	2.90	2.62
BS14 (H$_{S2B}$-to-Val-H$_{S5A}$-to-Arg359)	8.6	18.4	-1.46	-3.29	1.86	2.54	-3.18	2.74	2.81	2.59
BS14 (H$_{S2B}$-to-Val-H$_{S5A}$-to-Arg96)	9.5	19.3	-1.48	-3.28	1.69	2.65	-3.16	2.74	2.85	2.60
BS134	32.2	42.3	-1.41	-0.73	3.17	-2.47	-3.06	3.10	2.35	2.77
BS257	20.6	33.0	0.37	3.31	-3.05	2.97	3.09	-2.93	2.40	-2.62
BS267	21.8	30.1	0.27	3.34	-3.22	2.85	2.77	2.55	-1.89	-2.98
BS357	12.2	25.2	0.40	3.29	3.14	-3.00	3.27	-2.95	1.75	-2.30
BS157	12.9	25.3	0.45	-3.00	2.58	3.02	3.14	-2.91	3.01	-2.54
BS235	15.4	28.7	-0.34	3.28	-2.61	-2.94	3.20	-2.54	2.59	2.69
BS247	11.9	26.5	-0.52	3.34	-2.87	3.06	-3.07	2.97	2.58	-2.11
BS236	14.9	28.6	-0.33	3.33	-2.19	-3.10	3.20	3.01	-2.74	2.22
BS237	13.8	26.7	-0.32	3.33	-3.04	-3.02	3.21	3.07	2.55	-2.39
BS245	18.8	33.1	-0.45	3.32	-2.84	3.13	-2.77	-2.63	2.75	2.78
BS345	18.1	29.4	-0.39	3.27	3.19	-2.22	-2.73	-2.51	1.85	2.91
BS347	12.4	24.2	-0.45	3.31	2.87	-2.39	-3.08	3.08	2.35	-2.11

BS127	15.4	31.0	-0.61	-3.29	-2.87	3.03	3.29	3.19	2.70	-1.71
BS147	15.3	30.8	0.41	-3.28	2.51	3.15	-3.06	3.10	3.23	-2.14
2CBS$_{26,37}$-BH$_{26(3)}$ (Ms = 1), QM-A region, H$_{S2B}$-to-Phe-H$_{S5A}$-to-Arg359, r^{2}SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS2567	15.5	27.2	1.30	3.31	-1.86	3.20	3.23	-2.86	-2.62	-2.55
BS134	17.5	30.3	-1.43	-3.34	3.17	-2.45	-2.62	3.26	2.38	2.94
BS256	24.4	33.6	0.40	3.26	-2.81	0.21	3.17	-3.05	-2.04	2.34
BS267	23.5	39.2	-0.66	3.28	-3.13	2.97	1.63	2.85	-2.37	-2.89
BS457	10.7	25.7	0.45	3.35	2.91	3.12	-3.19	-3.02	1.21	-2.86
BS236	18.5	32.1	-0.20	3.27	-2.37	-3.20	3.04	2.29	-2.82	1.76
BS237	22.2	34.5	-0.30	3.29	-3.04	-3.17	3.03	2.43	2.34	-2.72
BS245	16.3	30.5	-0.49	3.33	-2.97	3.04	-3.19	-2.96	2.53	2.43
BS345	11.7	26.2	-0.41	3.28	3.11	-3.01	-2.69	-2.72	1.79	2.45
BS126	16.3	28.4	-0.66	-3.32	-2.95	2.56	2.71	2.98	-1.80	2.49
BS137	12.1	26.1	-0.56	-3.32	2.80	-3.11	3.08	3.04	2.26	-1.99
BS145	12.7	25.9	-0.55	-3.29	3.10	3.17	-2.93	-2.45	2.13	2.82
BS127	18.5	32.6	-0.73	-3.27	-3.11	2.70	2.74	3.06	2.56	-1.82
BS146	14.5	28.1	-0.46	-3.36	2.92	3.14	-3.19	2.95	-2.29	2.59
2CBS$_{26,37}$-BH$_{26(3)}$ (Ms = 0), QM-A region, H$_{S2B}$-to-Phe-H$_{S5A}$-to-Arg359, r^{2}SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS134	11.5	23.8	-1.33	-3.32	3.12	-3.02	-3.19	3.06	2.24	2.78
BS2356	17.9	25.6	0.58	3.31	-2.44	-2.53	3.25	-3.01	-2.30	2.48
BS1267	10.1	24.3	0.31	-3.30	-2.99	3.13	3.26	3.03	-1.52	-2.16
BS2367	11.2	23.8	0.55	3.34	-3.05	-3.02	3.17	2.78	-1.77	-2.51
BS3457	20.7	34.2	0.19	3.29	3.12	-2.56	-2.69	-2.83	1.75	-0.48
BS2467	7.1	21.7	0.40	3.33	-2.93	3.07	-3.09	2.91	-1.91	-2.29
BS345	9.9	24.2	-0.36	3.30	3.00	-3.14	-3.25	-3.02	1.50	2.20
BS137	19.2	32.8	-0.30	-3.32	2.75	-3.10	2.95	2.44	1.66	-2.52
BS145	10.7	23.6	-0.57	-3.35	3.07	3.02	-3.18	-2.80	1.77	2.55
BS127	25.5	37.4	-0.44	-3.27	-3.13	2.15	2.74	2.59	2.49	-2.62
BS135	7.2	21.6	-0.45	-3.34	2.94	-3.08	3.08	-2.90	1.92	2.31
2CBS$_{26,37}$-BH$_{26(3)}$ (Ms = 2), QM-C region, r^{2}SCAN										
BS14	21.4	21.5	-1.44	-3.29	1.69	2.52	-3.17	2.74	2.89	2.66

Table S43. The relative polarized QM and QM/MM energies (kcal/mol) relative to the lowest-energy model (see Figure 2k in the manuscript) and Mulliken spin populations of Mo and 7 Fe ions for the **2CBS$_{26,37}$-BH$_{37}$** model.

2CBS$_{26,37}$-BH$_{37}$ (Ms = 2), QM-A region, H$_{S2B}$-to-Phe-H$_{S5A}$-to-Arg359, r^{2}SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS234	11.0	18.4	-1.39	3.35	-2.64	-2.72	-2.82	3.19	3.02	3.04
BS124	26.5	31.0	-1.37	-2.64	-2.69	3.31	-2.78	3.22	2.98	3.26
BS14	9.6	15.9	-1.35	-3.29	2.40	2.51	-3.18	2.75	2.56	2.33
BS257	13.5	19.7	0.44	3.38	-3.09	3.08	3.22	-2.90	2.13	-2.58
BS356	12.9	18.0	0.32	3.30	2.96	-3.07	3.06	-2.92	-2.70	2.54

BS467	10.1	17.9	0.48	3.30	2.98	2.93	-3.18	2.85	-2.73	-2.77
BS256	10.4	14.9	0.30	3.36	-3.02	2.06	3.25	-2.99	-2.20	2.76
BS267	16.1	21.3	0.52	3.32	-3.04	2.06	3.20	2.96	-2.73	-2.75
BS357	14.8	20.2	0.37	3.27	3.14	-3.09	3.15	-3.09	1.72	-1.92
BS456	12.7	20.6	0.34	3.35	3.21	3.08	-3.03	-2.53	-2.65	1.90
BS457	15.0	22.0	0.41	3.33	3.16	3.12	-3.15	-2.95	2.72	-2.81
BS156	8.1	15.4	0.21	-3.36	3.00	3.23	3.06	-2.83	-2.48	3.03
BS157	5.7	14.9	0.44	-3.40	3.15	3.04	3.07	-2.78	3.02	-2.54
BS167	5.3	13.4	0.34	-3.40	3.04	3.04	3.20	3.00	-2.52	-2.64
BS235	6.2	13.0	-0.40	3.31	-2.95	-3.01	3.18	-2.47	2.76	2.80
BS247	7.5	14.0	-0.32	3.26	-2.86	3.08	-3.03	2.95	2.64	-2.21
BS346	3.6	10.5	-0.45	3.33	3.11	-2.96	-3.05	2.87	-2.16	2.67
BS346 (H_{S2B}-to-Phe-H_{S5A}-to-Arg96)	6.6	14.8	-0.46	3.33	3.11	-2.97	-3.05	2.88	-2.17	2.72
BS346 (H_{S2B}-to-Val-H_{S5A}-to-Arg359)	8.8	15.6	-0.42	3.33	3.11	-2.96	-3.05	2.88	-2.24	2.75
BS346 (H_{S2B}-to-Val-H_{S5A}-to-Arg96)	5.6	11.1	-0.41	3.34	3.11	-2.95	-3.05	2.87	-2.23	2.69
BS236	10.1	15.9	-0.36	3.33	-3.18	-3.17	3.14	2.99	-2.16	2.73
BS237	12.6	20.2	-0.32	3.31	-3.14	-3.02	3.10	2.44	2.54	-1.52
BS245	15.0	22.4	-0.52	3.28	-2.27	2.92	-2.58	-2.51	2.92	2.33
BS246	11.6	16.5	-0.50	3.33	-2.55	2.08	-3.08	3.03	-1.60	2.84
BS345	9.0	15.7	-0.51	3.31	3.12	-2.93	-2.74	-2.65	2.85	2.89
BS347	9.3	16.8	-0.43	3.30	3.13	-3.00	-3.16	2.93	1.93	-1.19
BS126	13.1	19.4	-0.41	-3.28	-2.93	3.28	3.24	3.04	-2.51	3.05
BS137	10.4	18.2	-0.69	-3.30	2.88	-2.93	3.05	3.03	2.76	-1.05
BS145	16.5	22.9	-0.41	-3.27	3.21	3.35	-2.89	-2.48	2.93	3.08
BS125	13.1	19.3	-0.41	-3.33	-2.80	3.34	3.19	-2.51	2.89	3.12
BS127	14.0	20.0	-0.39	-3.35	-2.75	3.11	3.30	3.12	2.83	-2.11
BS135	13.3	20.8	-0.49	-3.27	3.25	-2.51	3.14	-2.43	3.00	2.85
BS136	12.2	18.2	-0.62	-3.27	3.06	-2.90	3.26	3.13	-1.77	2.77
BS146	13.2	18.9	-0.57	-3.31	3.09	3.37	-3.14	2.99	-1.78	3.10
BS147	24.5	29.1	-0.45	-1.98	3.16	3.09	-3.05	2.92	2.64	-2.50
$2CBS_{26,37}$-BH_{37} (Ms = 1), QM-A region, H_{S2B}-to-Phe-H_{S5A}-to-Arg359, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS3567	12.7	18.8	1.23	3.28	3.17	-2.04	3.25	-2.84	-2.57	-2.45
BS234	10.2	17.9	-1.18	3.35	-2.86	-2.89	-2.93	2.77	2.64	2.63
BS256	11.7	17.6	0.44	3.35	-3.05	1.59	3.15	-3.09	-2.85	2.29
BS367	24.0	30.3	0.46	3.31	2.85	-3.24	2.46	2.17	-2.97	-3.03
BS456	11.4	19.3	0.55	3.37	3.10	2.97	-3.17	-3.04	-2.84	1.09
BS156	6.1	15.4	0.37	-3.40	2.96	3.11	3.03	-2.84	-2.48	1.60
BS157	10.1	16.9	0.40	-3.39	3.09	2.98	3.02	-2.94	2.05	-2.73
BS167	13.3	21.4	0.42	-3.36	2.95	2.88	2.21	2.78	-2.67	-2.78
BS235	8.7	14.6	-0.42	3.33	-2.99	-3.04	3.15	-3.01	1.97	2.65
BS247	9.0	14.4	-0.23	3.28	-2.91	3.02	-3.03	2.80	1.83	-2.84
BS346	4.4	13.4	-1.41	3.33	3.12	-2.98	-3.08	2.96	-3.12	2.76
BS236	11.6	18.1	-0.37	3.31	-3.21	-3.19	3.04	2.45	-2.87	2.57
BS237	16.6	22.5	-0.20	3.31	-3.18	-2.79	3.07	2.31	1.75	-2.68

BS245	12.2	20.5	-0.49	3.32	-3.01	2.00	-2.80	-2.70	2.90	2.58
BS246	10.1	17.4	-0.27	3.35	-3.13	1.77	-3.21	2.90	-2.15	2.48
BS345	9.1	14.8	-0.42	3.32	3.05	-3.13	-3.22	-2.88	2.30	2.79
BS126	9.5	16.7	-0.45	-3.31	-2.94	3.10	3.18	2.99	-2.35	1.71
BS145	10.8	18.5	-0.61	-3.31	3.17	2.84	-2.96	-2.45	2.87	2.62
BS125	11.4	18.5	-0.51	-3.33	-3.13	3.15	3.07	-2.87	2.67	2.97
BS127	12.6	18.4	-0.37	-3.35	-3.10	2.98	3.05	2.95	2.67	-2.58
BS135	7.3	13.8	-0.57	-3.29	2.87	-3.02	3.02	-2.76	2.87	2.85
BS136	12.2	18.5	-0.60	-3.27	2.88	-3.07	2.77	2.90	-2.27	2.68
BS146	8.1	14.8	-0.53	-3.33	3.02	2.67	-3.20	2.92	-1.63	2.47
BS147	9.1	15.0	-0.45	-3.34	3.16	3.09	-3.17	2.91	2.64	-2.51
$2CBS_{26,37}$-BH_{37} (Ms = 0), QM-A region, H_{S2B}-to-Phe-H_{S5A}-to-Arg359, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS1567	15.6	20.5	1.16	-2.88	3.17	3.17	3.22	-2.86	-2.53	-2.67
BS234	15.2	20.5	-1.18	2.89	-3.16	-3.19	-3.22	2.87	2.58	2.65
BS123	12.8	20.7	-1.33	-3.34	-3.20	-3.14	3.00	2.93	2.66	2.61
BS124	7.9	14.8	-1.29	-3.25	-3.02	3.11	-3.16	3.04	2.79	2.17
BS257	25.9	30.6	0.44	1.80	-3.10	1.60	2.99	-2.93	2.11	-2.69
BS2356	15.9	20.2	0.29	3.31	-2.51	-2.93	3.18	-2.73	-2.00	2.66
BS256	27.1	32.2	0.41	1.96	-3.09	1.58	3.03	-3.08	-2.84	2.32
BS2357	11.1	17.6	0.43	3.32	-2.47	-2.72	3.23	-2.95	2.47	-2.00
BS2367	13.8	20.8	0.53	3.34	-3.15	-2.90	3.14	2.75	-2.35	-2.07
BS3456	14.3	19.5	0.12	3.32	3.12	-2.96	-2.96	-2.52	-1.36	2.76
BS157	14.7	20.3	0.72	-3.39	2.93	2.88	2.91	-2.94	0.19	-2.76
BS167	18.8	26.4	0.54	-3.35	2.73	2.77	2.02	1.63	-2.84	-2.88
BS2346	18.8	24.1	-0.37	3.33	-1.40	-2.70	-2.84	2.92	-2.38	2.71
BS236	27.0	32.4	-0.33	1.88	-3.18	-3.18	2.81	2.42	-2.83	2.55
BS245	13.2	20.5	-0.36	3.34	-3.13	1.91	-3.15	-2.98	2.18	2.40
BS3467	7.5	15.6	0.42	3.33	3.07	-2.79	-3.11	2.93	-2.25	-2.13
BS1367	13.3	20.5	0.28	-3.34	3.13	-1.96	3.15	3.00	-2.12	-2.36
BS145	13.6	20.5	-0.64	-3.35	3.03	2.76	-3.17	-2.78	2.61	2.30
BS125	7.5	15.5	-0.46	-3.33	-3.07	2.83	3.10	-2.92	2.27	2.11
BS127	15.1	19.8	-0.07	-3.32	-3.08	3.02	3.08	2.68	0.77	-2.71
BS135	14.5	19.8	-0.39	-3.28	2.72	-3.03	2.93	-2.82	1.51	2.70
BS136	16.8	22.5	-0.39	-3.25	2.13	-3.14	2.62	2.36	-2.61	2.62
BS146	11.0	17.6	-0.45	-3.32	2.52	2.72	-3.24	2.94	-2.47	2.00
BS147	15.6	20.2	-0.32	-3.32	2.52	2.94	-3.18	2.73	2.02	-2.65
$2CBS_{26,37}$-BH_{37} (Ms = 2), QM-C region, r^2SCAN										
BS346	16.5	17.8	-0.39	3.32	3.12	-2.85	-3.04	2.86	-2.21	2.57

Table S44. The relative polarized QM and QM/MM energies (kcal/mol) relative to the lowest-energy model (see Figure 2k in the manuscript) and Mulliken spin populations of Mo and 7 Fe ions for the **CBS_{26}-BH_{26}-TH_5** model.

CBS_{26}-BH_{26}-TH_5 (Ms = 2), QM-A region, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7

BS13	16.8	17.8	-1.10	-3.23	2.58	-3.19	2.61	2.18	1.99	2.59
BS14	24.2	24.6	-1.18	-3.27	2.49	2.55	-3.16	2.07	2.17	2.83
BS256	36.8	35.5	0.28	3.23	-3.04	1.42	3.04	-2.49	-1.92	2.71
BS357	28.0	27.0	0.20	3.31	3.12	-3.10	3.25	-2.41	2.03	-2.83
BS457	22.3	23.3	0.25	3.32	3.05	3.28	-3.04	-2.24	1.97	-2.84
BS157	27.7	27.7	0.23	-2.89	2.93	2.97	3.12	-2.08	2.21	-2.70
BS236	16.4	16.2	-0.33	3.32	-3.07	-3.24	3.13	2.31	-1.44	2.78
BS246	22.3	23.1	-0.30	3.25	-2.96	3.18	-3.11	2.24	-1.54	2.75
BS345	20.4	21.4	-0.59	3.30	2.91	-2.99	-2.69	-2.01	2.50	3.00
BS126	16.9	17.8	-0.46	-3.30	-2.96	3.21	3.06	2.32	-0.96	2.84
BS145	26.8	27.8	-0.40	-3.30	3.13	3.34	-2.56	-1.94	2.31	3.09
BS135	28.4	29.2	-0.57	-3.25	3.21	-2.86	3.19	-1.71	2.43	3.03
BS17	25.9	27.2	-0.07	-3.37	2.98	2.77	2.34	1.66	1.20	-2.88
CBS_{26}-BH_{26}-TH_5 (Ms = 1), QM-A region, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS2567	28.2	28.3	1.07	3.39	-2.98	3.33	3.23	-2.33	-1.99	-2.63
BS134	31.9	32.5	-1.21	-2.60	3.13	-2.76	-2.26	2.34	2.26	3.02
BS2356	25.8	24.8	0.03	3.31	-2.68	-2.92	3.12	-1.75	-1.08	2.97
BS267	34.2	34.1	0.58	3.20	-3.01	2.95	1.65	1.87	-2.28	-3.02
BS357	28.5	28.4	0.36	3.35	2.80	-3.23	2.72	-2.41	1.18	-2.77
BS457	31.2	31.3	0.26	3.04	2.82	2.37	-3.05	-2.24	1.74	-2.86
BS157	20.2	21.6	0.42	-3.37	3.07	2.90	2.92	-2.24	1.32	-2.68
BS236	16.6	18.4	-1.43	3.32	-3.19	-3.28	3.02	2.41	-2.28	2.98
BS246	26.4	27.5	-0.21	3.25	-3.13	2.72	-3.21	2.26	-1.84	2.10
BS347	23.2	23.2	-0.30	3.30	3.02	-3.12	-2.93	3.00	1.61	-2.61
BS126	22.7	23.5	-0.39	-3.29	-2.94	2.68	2.75	2.18	-1.94	2.86
BS137	23.3	23.3	-0.41	-3.26	3.18	-2.82	3.13	2.35	1.97	-2.03
BS145	22.9	22.9	-0.63	-3.32	2.76	3.09	-2.97	-2.11	2.27	2.98
BS135	21.9	22.4	-0.60	-3.26	2.69	-3.13	3.05	-1.89	2.16	2.91
BS147	23.7	23.9	-0.31	-3.33	3.18	3.21	-2.82	2.42	2.24	-2.37
CBS_{26}-BH_{26}-TH_5 (Ms = 0), QM-A region, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS2567	26.9	27.3	1.13	3.35	-3.14	3.15	2.54	-2.34	-2.13	-2.87
BS134	26.7	27.2	-1.14	-3.37	3.15	-3.14	-2.54	2.32	2.16	2.89
BS2456	22.0	22.1	0.34	3.26	-2.84	3.27	-2.98	-2.38	-1.91	2.68
BS1256	22.5	22.1	0.16	-3.30	-3.02	3.19	3.15	-2.02	-1.42	2.91
BS2356	19.9	18.8	0.32	3.33	-2.79	-3.06	3.16	-2.53	-2.07	2.84
BS347	22.4	22.2	-0.18	3.30	3.03	-3.18	-3.15	1.98	1.44	-2.89
BS126	36.2	37.2	-0.11	-3.28	-3.15	2.45	2.56	2.17	-2.01	1.56
BS137	22.0	22.0	-0.36	-3.27	2.90	-3.27	3.00	2.35	1.91	-2.68
BS145	30.1	29.4	-0.35	-3.32	2.80	3.06	-2.99	-2.44	1.38	2.17
CBS_{26}-BH_{26}-TH_5 (Ms = 2), QM-C region, r^2SCAN										
BS236	23.0	19.9	-0.26	3.31	-2.94	-3.21	3.11	2.25	-1.60	2.76

Table S45. The relative polarized QM and QM/MM energies (kcal/mol) relative to the lowest-energy model (see Figure 2k in the manuscript) and Mulliken spin populations of Mo and 7 Fe ions for the **CBS_{26}-$2TH_{4,5}$** model.

CBS_{26}-$2TH_{4,5}$ (Ms = 2), QM-A region, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS567	34.2	38.2	1.05	3.07	3.05	1.83	2.56	-2.28	-2.62	-3.01
BS13	15.2	22.5	-1.07	-3.21	2.38	-3.15	2.20	2.02	2.83	2.37
BS14	23.7	28.7	-1.16	-3.28	1.93	2.49	-2.85	1.97	2.47	2.75
BS257	19.0	26.5	0.33	3.27	-2.97	3.06	2.59	-2.21	2.40	-2.68
BS356	14.9	21.1	0.30	3.31	2.95	-3.11	2.53	-2.41	-2.63	2.65
BS467	21.6	29.0	0.43	3.28	3.14	3.18	-2.79	1.77	-2.64	-2.76
BS256	22.7	30.2	0.36	3.32	-3.02	3.07	2.62	-2.53	-2.76	2.58
BS267	16.6	24.0	0.44	3.46	-2.95	3.26	2.66	2.32	-2.68	-2.76
BS357	20.0	26.2	0.22	3.35	3.17	-3.08	2.71	-2.46	2.64	-2.85
BS367	19.7	26.5	0.40	3.40	3.21	-2.93	2.64	2.17	-2.71	-2.45
BS456	25.0	31.6	0.23	3.21	2.91	2.21	-2.68	-2.25	-2.71	2.56
BS457	24.8	32.1	0.14	3.28	2.89	2.80	-2.65	-2.14	2.15	-2.73
BS156	17.4	23.8	0.24	-2.93	2.90	3.18	2.45	-2.28	-2.62	2.66
BS157	16.3	22.9	0.17	-2.91	3.19	2.95	2.50	-2.10	2.61	-2.67
BS167	15.1	21.5	0.35	-2.86	3.17	3.27	2.51	2.43	-2.48	-2.61
BS235	11.0	18.3	-0.41	3.31	-2.84	-2.98	2.83	-1.88	2.65	2.81
BS247	14.3	22.5	-0.31	3.24	-2.92	3.10	-2.55	2.40	2.62	-2.07
BS346	10.1	16.6	-0.37	3.31	3.00	-3.13	-2.62	2.24	-1.76	2.73
BS236	18.5	24.0	-0.18	3.30	-2.04	-2.88	2.69	2.15	-2.27	2.73
BS237	24.6	29.7	-0.27	3.26	-1.81	-2.60	2.71	2.18	2.67	-2.45
BS245	13.7	21.5	-0.48	3.23	-3.01	2.81	-2.48	-2.08	2.81	2.59
BS246	17.9	24.4	-0.25	3.24	-2.78	3.00	-2.54	2.39	-2.47	2.86
BS345	8.9	15.4	-0.54	3.30	2.94	-3.09	-2.58	-2.27	2.72	2.86
BS347	17.2	25.2	-0.31	3.32	3.13	-3.20	-2.44	2.46	2.86	-2.34
BS126	15.1	20.4	-0.53	-3.29	-2.78	3.25	2.57	2.27	-0.55	2.93
BS137	23.5	31.9	-0.58	-3.23	3.21	-2.45	2.57	2.29	2.96	-0.77
BS145	21.4	28.0	-0.54	-3.30	2.85	3.23	-2.48	-1.97	2.67	2.98
BS125	17.7	24.2	-0.48	-3.32	-2.60	3.34	2.65	-1.88	2.80	3.06
BS17	15.8	22.1	-0.14	-3.33	2.08	2.82	2.35	2.31	1.43	-2.80
BS135	19.8	27.6	-0.59	-3.23	3.23	-2.75	2.62	-1.69	3.06	2.87
BS136	30.5	35.0	-0.35	-2.20	3.06	-2.56	2.60	2.29	-1.90	2.75
BS146	20.1	26.1	-0.46	-3.31	3.01	3.25	-2.60	2.33	-1.65	2.99
CBS_{26}-$2TH_{4,5}$ (Ms = 1), QM-A region, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS567	37.6	42.1	1.14	1.44	2.59	2.41	2.49	-2.33	-2.68	-3.02
BS234	7.8	15.7	-1.05	3.32	-2.77	-2.90	-2.41	2.17	2.53	2.68
BS123	25.9	33.0	-1.11	-3.12	-1.36	-2.95	2.68	2.28	2.88	2.76
BS124	21.6	27.5	-1.10	-3.32	-2.76	3.31	-2.36	2.26	2.70	3.00
BS257	23.3	29.7	0.48	3.27	-3.07	2.94	2.25	-2.45	1.50	-2.79
BS356	22.5	30.0	0.33	3.30	2.73	-3.19	1.98	-2.43	-2.78	2.02
BS256	25.7	32.9	0.40	3.23	-3.00	1.57	2.56	-2.54	-2.85	2.46

BS267	23.5	30.5	0.48	3.11	-2.96	3.08	1.60	2.31	-2.70	-2.83
BS357	27.5	32.9	0.21	3.24	1.28	-2.94	2.63	-2.44	2.64	-2.74
BS367	20.6	26.2	0.45	3.30	2.97	-3.23	2.53	2.09	-2.88	-2.94
BS456	31.8	38.7	0.30	3.24	2.79	1.10	-2.62	-2.40	-2.82	2.10
BS157	12.6	19.8	0.11	-3.35	2.92	2.91	2.40	-2.15	2.25	-2.67
BS167	7.1	15.6	0.40	-3.33	2.89	3.09	2.39	2.39	-2.66	-2.66
BS235	15.3	22.8	-0.45	3.27	-2.83	-3.08	2.31	-2.65	2.49	2.72
BS247	13.8	20.4	-0.20	3.25	-2.97	3.09	-2.55	2.12	1.95	-2.80
BS346	17.2	23.3	-0.29	3.28	2.20	-3.13	-2.59	2.27	-2.56	2.72
BS236	11.3	18.0	-0.08	3.36	-3.13	-3.21	2.62	2.19	-2.50	2.66
BS237	16.2	22.9	-0.21	3.32	-3.01	-2.93	2.67	2.28	2.64	-2.70
BS245	20.0	26.5	-0.26	3.24	-2.93	2.80	-2.42	-2.46	1.37	2.33
BS246	18.3	27.0	-0.11	3.24	-3.18	2.70	-2.67	2.26	-2.66	2.23
BS345	15.4	21.0	-0.22	3.31	2.98	-3.07	-2.45	-1.75	-0.36	2.85
BS347	14.1	21.3	-0.21	3.29	2.93	-3.20	-2.73	2.35	2.22	-2.66
BS126	13.0	19.6	-0.20	-3.27	-2.84	3.09	2.57	2.25	-2.46	2.84
BS137	15.9	23.2	-0.40	-3.24	2.96	-2.66	2.46	2.36	2.89	-2.20
BS145	19.1	25.3	-0.61	-3.32	2.76	2.53	-2.73	-2.00	2.68	2.68
BS125	17.0	24.3	-0.46	-3.32	-3.01	2.90	2.61	-2.08	2.69	2.69
BS127	12.1	19.5	-0.30	-3.31	-2.86	3.15	2.58	2.34	2.72	-2.14
BS135	15.0	21.7	-0.53	-3.26	2.87	-3.07	2.57	-2.15	2.77	2.80
BS136	11.6	18.4	-0.38	-3.23	2.95	-3.06	2.55	2.28	-1.79	2.80
BS146	22.1	28.0	-0.45	-3.31	2.64	2.71	-2.83	2.19	-1.85	2.90
BS147	15.2	21.7	-0.45	-3.36	3.14	3.15	-2.72	2.38	2.59	-2.65
CBS_{26}-$2TH_{4,5}$ (Ms = 0), QM-A region, r^2SCAN										
	ΔE(polarized QM)	ΔE(QM/MM)	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
BS1567	14.0	20.4	0.99	-2.86	3.13	3.21	2.49	-2.16	-2.48	-2.57
BS234	14.0	20.3	-1.01	2.87	-3.15	-3.20	-2.50	2.15	2.49	2.59
BS123	22.9	28.4	-1.06	-3.30	-3.01	-2.99	2.65	2.31	2.76	2.95
BS124	17.5	22.8	-1.04	-3.33	-3.08	2.89	-2.67	2.25	2.47	2.77
BS134	15.7	23.8	-1.11	-3.42	2.98	-3.21	-2.70	2.23	2.87	2.59
BS2457	13.3	20.9	0.26	3.25	-2.82	3.19	-2.29	-1.91	2.49	-2.64
BS2467	19.9	25.6	0.25	3.25	-2.81	3.14	-2.57	1.92	-0.77	-2.70
BS2356	19.6	25.3	0.20	3.31	-2.49	-2.85	2.62	-2.39	-1.65	2.75
BS267	29.4	36.7	0.63	3.18	-3.05	3.02	1.08	1.32	-2.98	-2.92
BS3567	17.6	22.9	1.02	3.33	3.09	-2.88	2.64	-2.28	-2.45	-2.75
BS367	26.0	32.5	0.56	3.21	2.93	-3.25	1.23	1.54	-2.89	-3.03
BS156	24.8	31.0	0.35	-3.30	1.18	3.02	2.36	-2.46	-2.64	1.90
BS157	16.6	23.1	0.54	-3.33	2.34	3.11	2.37	-2.29	0.41	-2.70
BS167	13.8	21.6	0.60	-3.32	2.73	2.73	2.21	1.12	-2.65	-2.77
BS3456	12.8	18.7	0.20	3.30	2.99	-3.11	-2.60	-2.28	-1.89	2.81
BS236	19.8	27.4	-0.18	3.21	-3.22	-3.21	2.00	1.97	-2.78	2.61
BS237	18.8	24.4	-0.17	3.32	-3.09	-3.25	2.57	2.24	1.72	-2.87
BS3467	19.7	26.5	0.18	3.30	2.97	-3.13	-2.65	2.41	-0.82	-2.43
BS126	19.4	26.9	-0.19	-3.29	-3.06	2.87	2.51	2.07	-2.69	2.23
BS137	18.8	25.6	-0.33	-3.24	2.88	-3.22	2.47	2.21	2.62	-2.80

BS145	24.1	30.0	-0.28	-3.34	3.03	2.81	-2.73	-2.33	0.39	2.57
BS125	19.8	26.5	-0.18	-3.30	-2.93	3.17	2.66	-2.42	0.61	2.50
BS135	20.0	25.6	-0.25	-3.25	2.85	-3.13	2.56	-1.89	0.64	2.72
BS136	13.6	20.8	-0.30	-3.25	2.85	-3.19	2.31	1.88	-2.49	2.64
BS146	24.3	30.2	-0.26	-3.27	1.71	2.64	-2.79	2.38	-2.54	2.43
BS147	19.4	25.3	-0.23	-3.31	2.50	2.85	-2.64	2.36	1.70	-2.74
CBS_{26}-$2TH_{4,5}$ (Ms = 2), QM-C region, r^2SCAN										
BS345	20.0	18.6	-0.55	3.29	2.93	-3.07	-2.57	-2.25	2.74	2.86

Cartesian coordinates of structures

As additional supplementary material, we provide a compressed archive containing XYZ-files with optimized Cartesian coordinates (in Å) of the QM-regions and QM-cluster calculations of all calculated isomers.

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