Supporting Information (SI)

Exploring the impact of abnormal coordination in macrocyclic *N*-heterocyclic carbene ligands on bio-inspired iron epoxidation catalysis

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1. NMR-Spectra

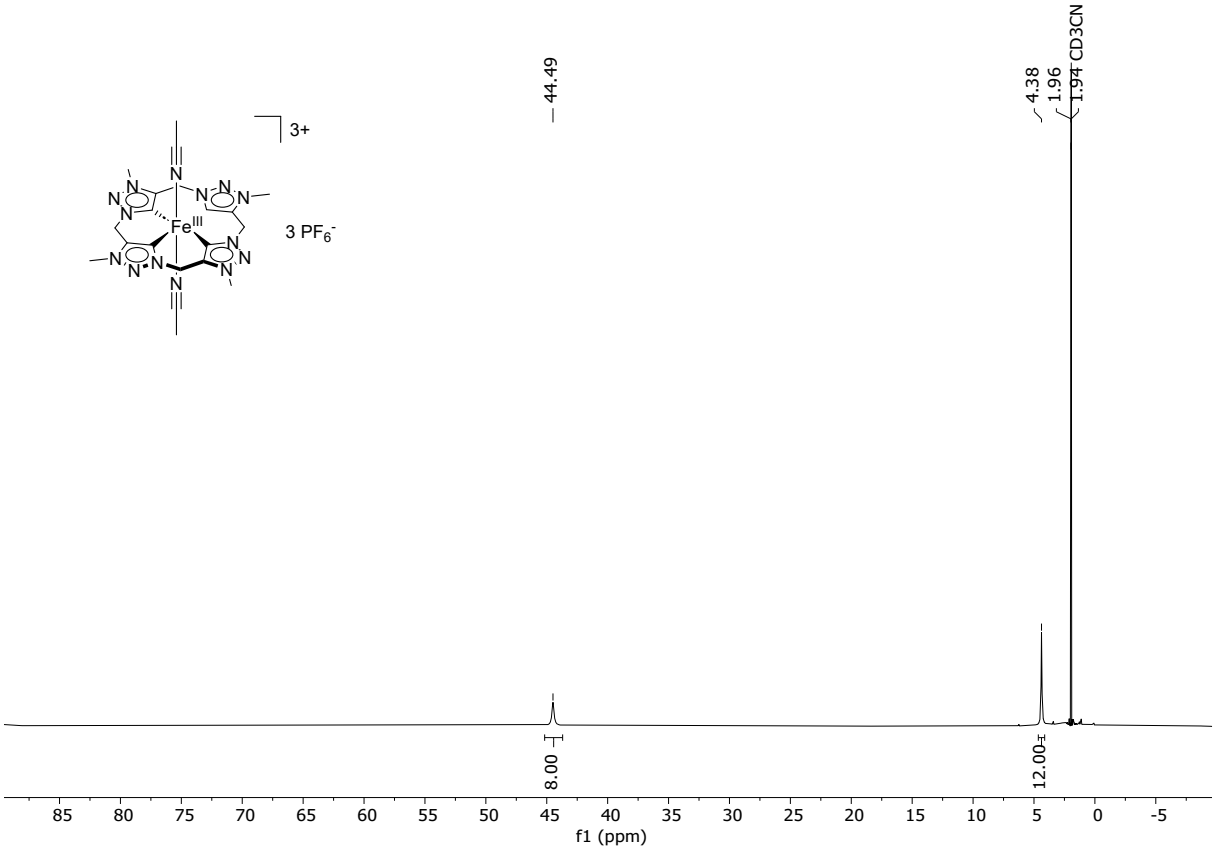


Fig. S1 ^{1}H-NMR spectrum of **2** in CD_3CN.

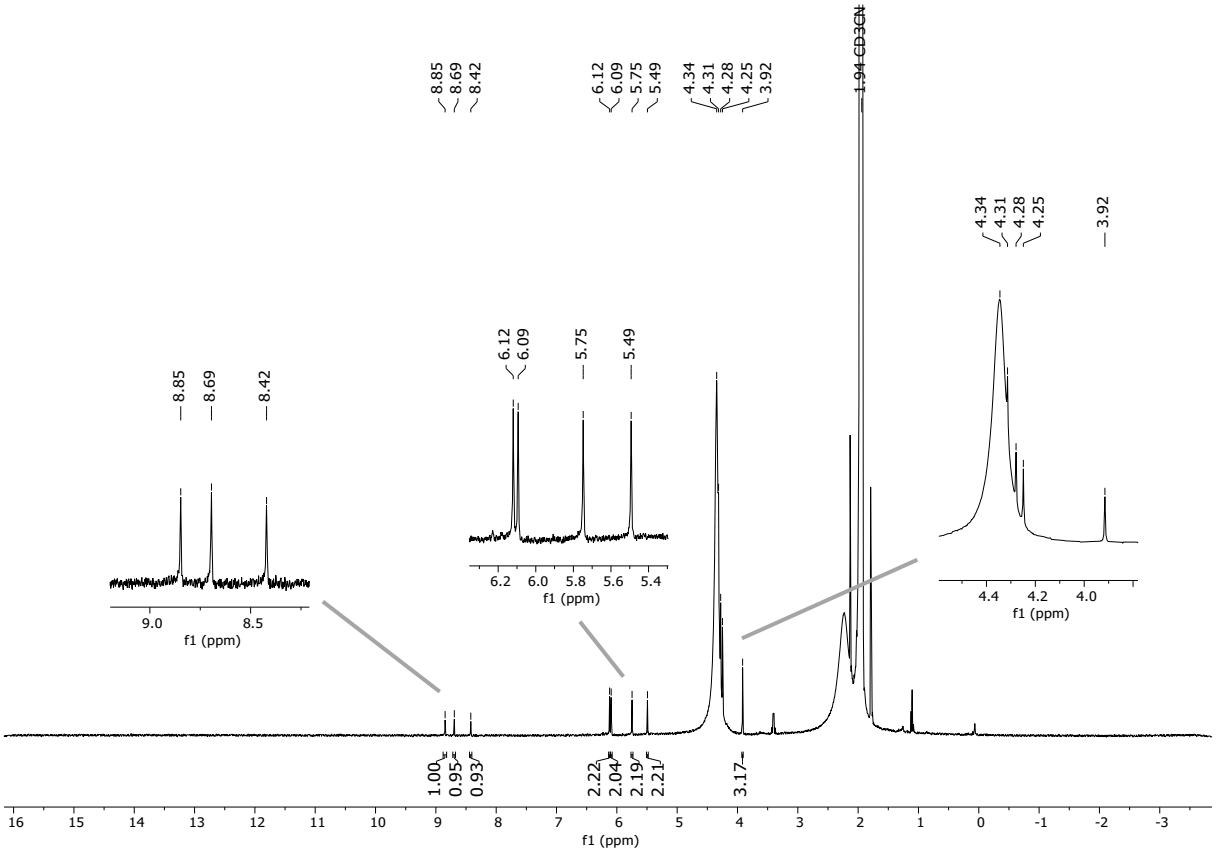


Fig. S2 ^{1}H-NMR spectrum of the reaction of **2** with 10.0 eq. H_2O_2 (50% aq.) after 21 h under argon in dry and degassed CD_3CN.

2. Single crystal X-ray diffraction

X-ray crystallographic data was collected on a Bruker D8 Venture single crystal X-ray diffractometer with the following setup: A CMOS detector (Bruker Photon-100), a Mo IMS microsource and a Helios optic using the APEX3 software package.[1] The measurement used MoK_α radiation (λ = 0.71073 Å) and was performed on a single crystal coated with perfluorinated ether. The crystal was fixed on top of a micromount sample holder and frozen under a stream of cold nitrogen at 100 K. A matrix scan was used to determine the initial lattice parameters. Reflections were corrected for Lorentz and polarisation effects, scan speed, and background using SAINT.[2] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.[3] Space group assignment was based upon systematic absences, E statistics, and successful refinement of the structure. The structure was solved by direct methods (SHELXT) with the aid of successive difference Fourier maps, and was refined against all data using SHELXL-2015 in conjunction with SHELXLE.[4-6] Hydrogen atoms were calculated in ideal positions as follows: Methyl hydrogen atoms were refined as part of rigid rotating groups, with a C–H distance of 0.98 Å and Uiso(H) = 1.5·Ueq(C). Other H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of 0.99 Å and 0.95 Å, respectively, other C–H distances of 1.00 Å and Uiso(H) = 1.2·Ueq(C). Non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing Σw(Fo2–Fc2)2 with SHELXL weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.[7] The image of the crystal structure was generated with Mercury[8] or Platon[9]. CCDC (2362784) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

A block-like specimen of complex **2**, approximate dimensions 0.034 mm x 0.144 mm x 0.163 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture system equipped with a Helios optic monochromator and a Mo TXS rotating anode (λ = 0.71073 Å).

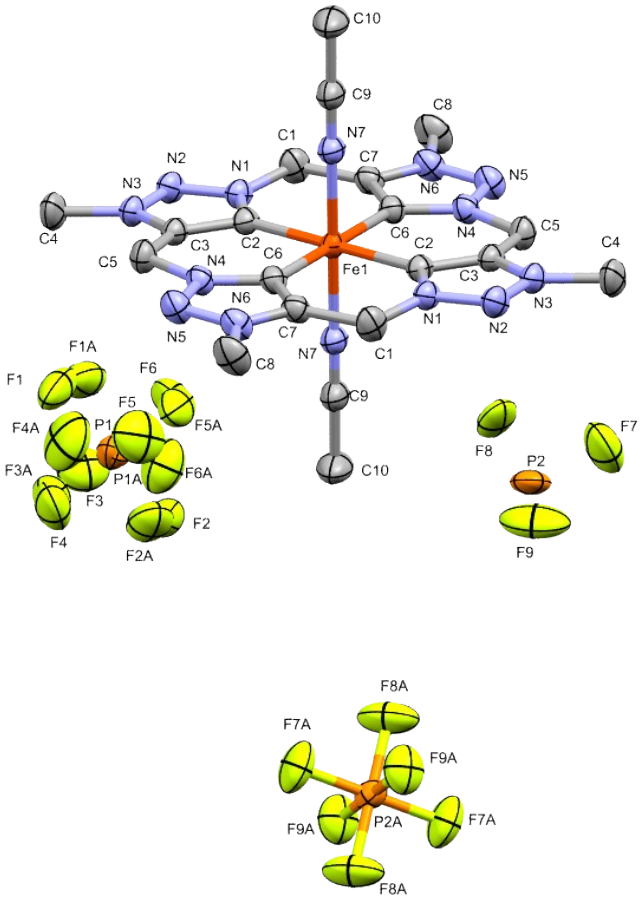


Fig. S3 ORTEP-style representation of iron(III) calix[4]3-methyl-1,2,3-triazol-5-ylidene hexafluorophosphate **2**. Hydrogen atoms are omitted for clarity and thermal ellipsoids are shown at 30% probability level.

Table S1. Crystallographic data and structure refinement parameters of complex **2**.

Sample and Crystal Data		
Identification code	ZamGr5	
CCDCnumber	2362784	
Chemical formula	$C_{20}H_{26}F_{18}FeN_{14}P_3$	
Formula weight	953.31 g/mol	
Temperature	297(2) K	
Wavelength	0.71073 Å	
Crystal size	0.034 x 0.144 x 0.163 mm	
Crystal habit	yellow block	
Crystal System	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 9.2748(2) Å b = 17.6660(5) Å c = 11.4201(3) Å	α = 90° β = 104.1930(10)° γ = 90°
Volume	1814.05(8) $Å^3$	
Z	2	
Density (calculated)	1.745g/cm^3	
Absorption coefficient	0.680 mm^{-1}	
F(000)	954	
Data Collection and Structure Refinement		
Diffractometer	Bruker D8 Venture	
Radiation Source	IMS microsource, Mo	
Theta range for data collection	2.31 to 25.72°	
Index ranges	11<=h<=11, -21<=k<=21, -13<=l<=13	
Reflections collected	67359	
Independent reflections	3447 [R(int) = 0.0691]	
Coverage of independent reflections	99.6%	
Absorption correction		
Max. and min. transmission	0.9770 and 0.8970	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Function minimised	$\Sigma w(Fo^2 - Fc^2)^2$	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Data / restraints / parameters	3447 / 393 / 357	
Goodness-of-fit on F2	1.043	
Final R indices	2868 data; I>2σ(I) all data	R1 = 0.0405, wR2 = 0.1082 R1 = 0.0499, wR2 = 0.1165
Weighting scheme	$w=1/[\sigma^2(Fo^2)+(0.0539P)^2+1.1803P]$ where $P=(Fo^2+2Fc^2)/3$	
Largest diff. max. min.	0.374 and -0.205 $eÅ^{-3}$	
R.M.S. deviation from mean	0.045 $eÅ^{-3}$	

3. Buried volume and topographic steric map calculations

The buried volume[10] and corresponding topographic maps[11] were determined for complexes **1**, **2**, **A** and **B** using *SambVca* 2.1[12]. The structure of the complexes was loaded using the respective .xyz files derived from the SC-XRD analysis. The iron atom was set as centre of the sphere (distance 0.00 Å).

a) For calculations with viewing direction on the top of the complex, *i.e.* axial MeCN ligand vertically facing towards the viewer and the complex ligand underneath: One *N*-atom of the two axial MeCN ligands was selected for the Z-negative z axis definition. One carbene *C*-atom of the ligand was selected for the xz-plane definition.

b) For calculations with viewing direction towards the complex ligand: One carbene *C*-atom of the ligand was selected for the Z-negative z axis definition. One *N*-atom of the two axial MeCN ligands was selected for the xz-plane definition.

The iron atom was selected to be deleted. The atomic radii were left on the pre-setting (bond radii scaled by 1.17). The sphere radius was left on pre-setting (3.5 Å). Distance of the coordination point from the centre of the sphere was set to 0.0 Å (pre-setting). Mesh spacing for numerical integration was set to 0.10 Å (pre-setting). H atoms were not included in the calculations (pre-setting).

Calculations regarding the percentage of buried volume $\%V_{Bur}$ of the iron centre of the respective complex show a marginal difference between compounds **1** with $88\%V_{Bur}$, **2** with $88\%V_{Bur}$, **A** with $89\%V_{Bur}$ and **B** with $89\%V_{Bur}$ (Table S2-S5). In order to gain access to the active centre of the iron catalyst, at least one of the labile MeCN ligands must be replaced.[13] Removing the labile ligands decreases the buried volume to likewise 69 – $70\%V_{Bur}$ for all complexes **1**, **2**, **A** and **B**. The topographic steric maps of the buried volume visualise again the highly symmetrical arrangement of the aNHC ligand in **1** and **2** compared to the saddle-distorted conformation of the classic NHC ligand in **A** and **B** (see ESI, Fig. S5, S7, S9 and S11).

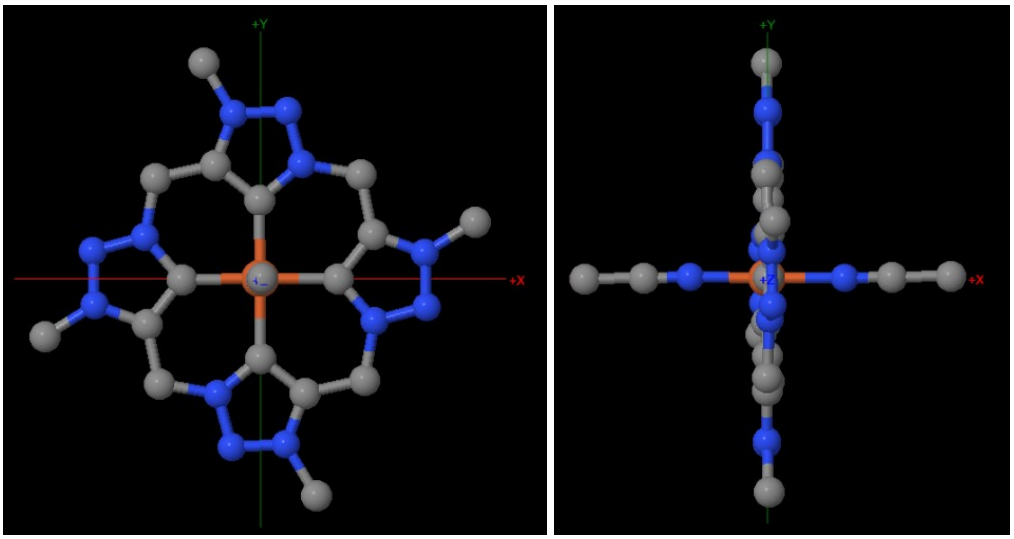


Fig. S4 Visualization of complex **1** (*JSmol* window) and assignment of the x, y, z axes with view on top (left) and towards the NHC ligand (right).

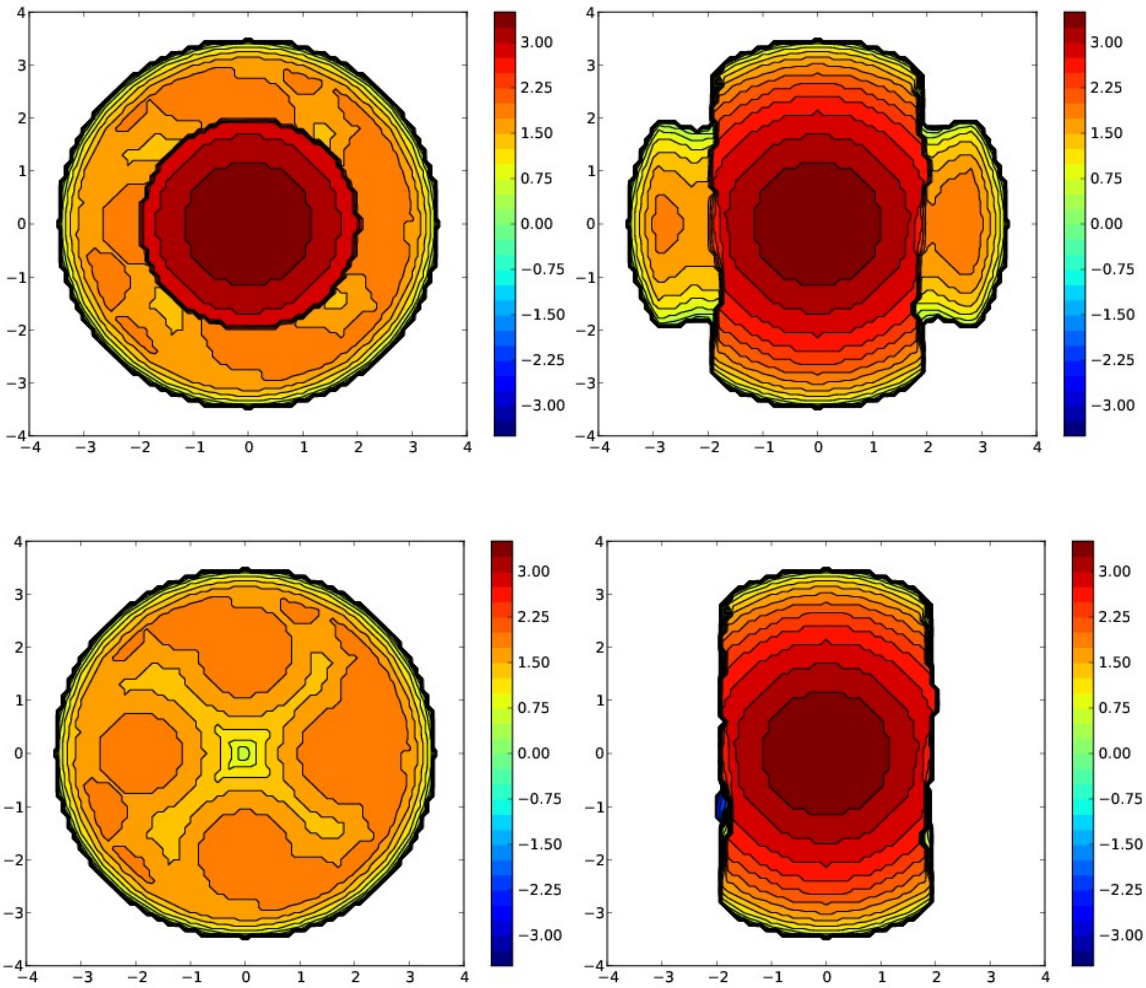


Fig. S5 Topographic steric map of the buried volume of **1** with (top) and without (bottom) labile MeCN ligands with view on top (left) and towards the NHC ligand (right). The red and blue colours show the more- and less-hindered zones in the catalytic centre, respectively.

Table S2 Calculated buried volume for **1**.

Top view, with MeCN ligands					
%V Free	**%V Buried**		**% V Tot/V Ex**		
11.9	**88.1**		99.9		
Qua-drant	**V f**	**V b**	**V t**	**%V f**	**%V b**
SW	5.3	39.5	44.9	11.9	88.1
NW	5.3	39.5	44.9	11.9	88.1
NE	5.3	39.5	44.9	11.9	88.1
SE	5.3	39.5	44.9	11.9	88.1

Side view, with MeCN ligands					
%V Free	**%V Buried**		**% V Tot/V Ex**		
12.0	**88.0**		99.9		
Qua-drant	**V f**	**V b**	**V t**	**%V f**	**%V b**
SW	5.3	39.5	44.9	11.8	88.2
NW	5.4	39.4	44.9	12.1	87.9
NE	5.3	39.5	44.9	11.8	88.2
SE	5.4	39.4	44.9	12.1	87.9

Top view, without MeCN ligands					
%V Free	**%V Buried**		**% V Tot/V Ex**		
31.2	**68.8**		99.9		
Qua-drant	**V f**	**V b**	**V t**	**%V f**	**%V b**
SW	14.0	30.9	44.9	31.2	68.8
NW	14.0	30.9	44.9	31.2	68.8
NE	14.0	30.9	44.9	31.2	68.8
SE	14.0	30.9	44.9	31.2	68.8

Side view, without MeCN ligands					
%V Free	**%V Buried**		**% V Tot/V Ex**		
31.2	**68.8**		99.9		
Qua-drant	**V f**	**V b**	**V t**	**%V f**	**%V b**
SW	14.0	30.9	44.9	31.2	68.8
NW	14.0	30.8	44.9	31.3	68.7
NE	14.0	30.9	44.9	31.2	68.8
SE	14.0	30.8	44.9	31.3	68.7

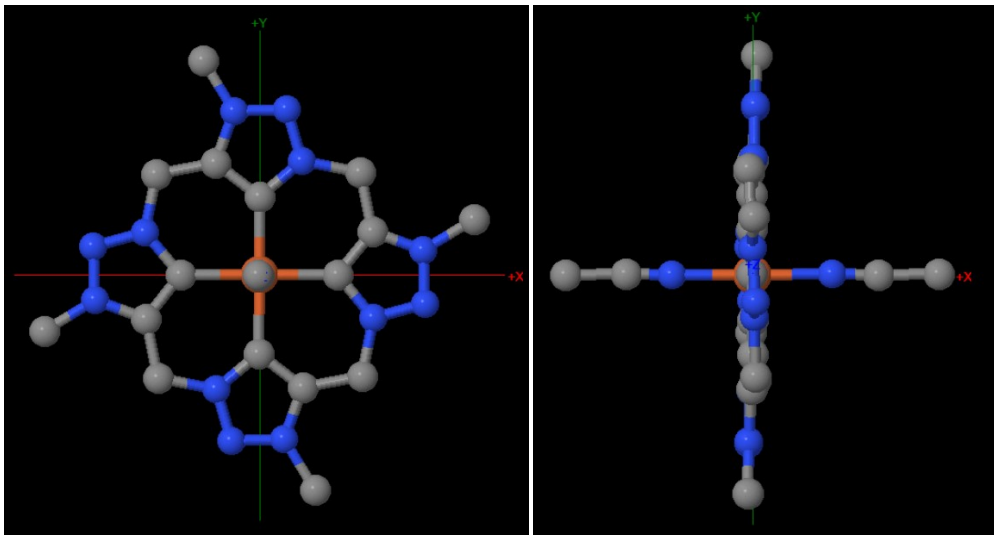


Fig. S6 Visualization of complex **2** (*JSmol* window) and assignment of the x, y, z axes with view on top (left) and towards the NHC ligand (right).

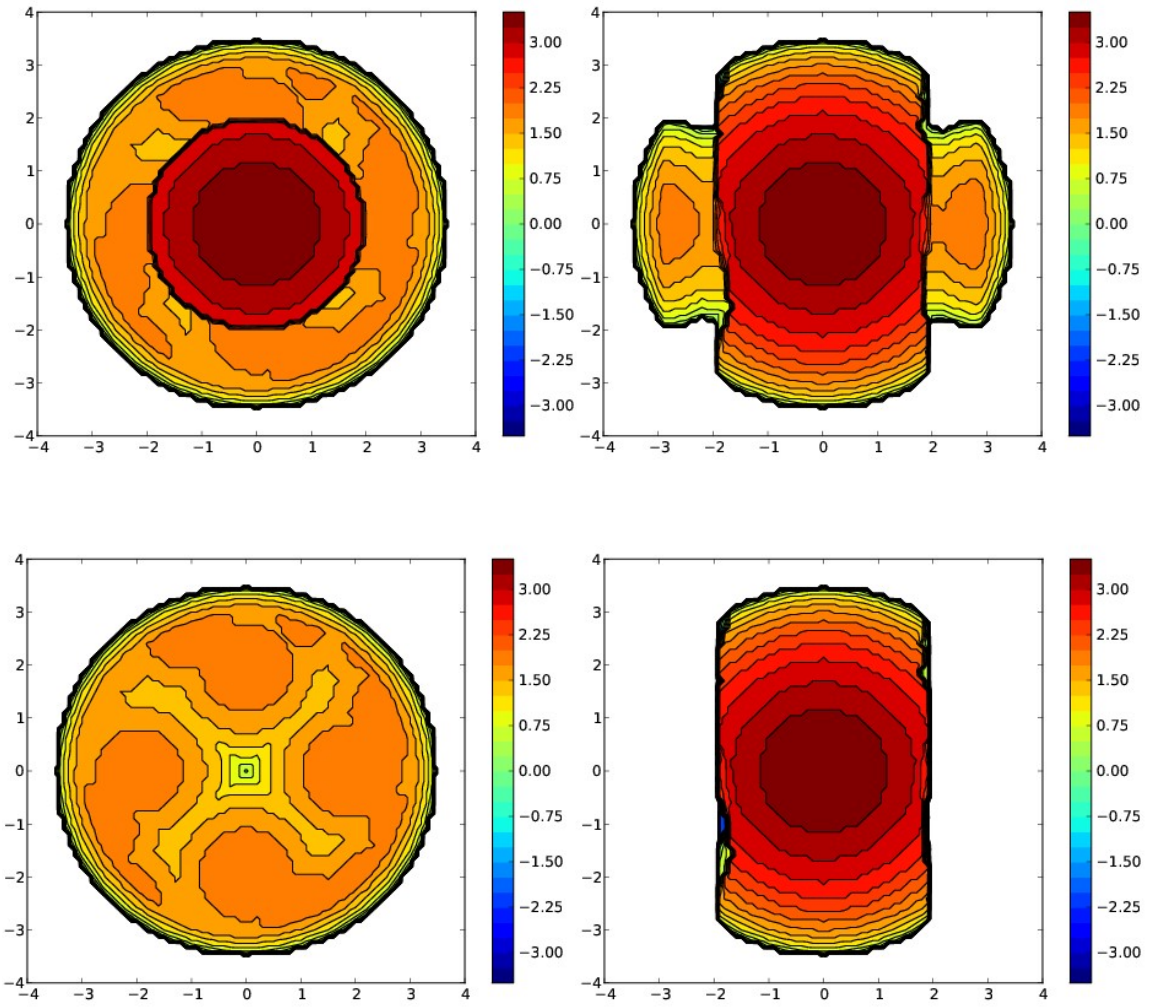


Fig. S7 Topographic steric map of the buried volume of **2** with (top) and without (bottom) labile MeCN ligands with view on top (left) and towards the NHC ligand (right). The red and blue colours show the more- and less-hindered zones in the catalytic centre, respectively.

Table S3 Calculated buried volume for **2**.

Top view, with MeCN ligands					
%V Free	**%V Buried**		**% V Tot/V Ex**		
11.9	**88.1**		99.9		
Qua-drant	**V f**	**V b**	**V t**	**%V f**	**%V b**
SW	5.3	39.6	44.9	11.8	88.2
NW	5.3	39.5	44.9	11.9	88.1
NE	5.3	39.6	44.9	11.8	88.2
SE	5.3	39.5	44.9	11.9	88.1

Side view, with MeCN ligands					
%V Free	**%V Buried**		**% V Tot/V Ex**		
11.9	**88.1**		99.9		
Qua-drant	**V f**	**V b**	**V t**	**%V f**	**%V b**
SW	5.5	39.4	44.9	12.2	87.8
NW	5.2	39.7	44.9	11.6	88.4
NE	5.5	39.4	44.9	12.2	87.8
SE	5.2	39.7	44.9	11.6	88.4

Top view, without MeCN ligands					
%V Free	**%V Buried**		**% V Tot/V Ex**		
31.3	**68.7**		99.9		
Qua-drant	**V f**	**V b**	**V t**	**%V f**	**%V b**
SW	14.0	30.8	44.9	31.3	68.7
NW	14.1	30.8	44.9	31.3	68.7
NE	14.0	30.8	44.9	31.3	68.7
SE	14.1	30.8	44.9	31.3	68.7

Side view, without MeCN ligands					
%V Free	**%V Buried**		**% V Tot/V Ex**		
31.3	**68.7**		99.9		
Qua-drant	**V f**	**V b**	**V t**	**%V f**	**%V b**
SW	14.2	30.7	44.9	31.6	68.4
NW	13.9	30.9	44.9	31.0	69.0
NE	14.2	30.7	44.9	31.6	68.4
SE	13.9	30.9	44.9	31.0	69.0

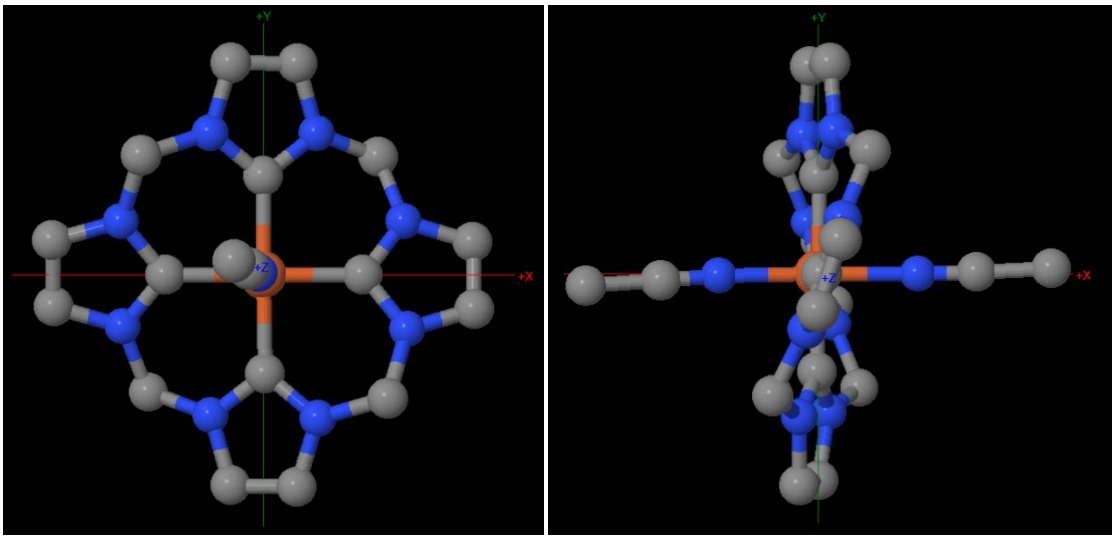


Fig. S8 Visualization of complex **A** (*JSmol* window) and assignment of the x, y, z axes with view on top (left) and towards the NHC ligand (right).

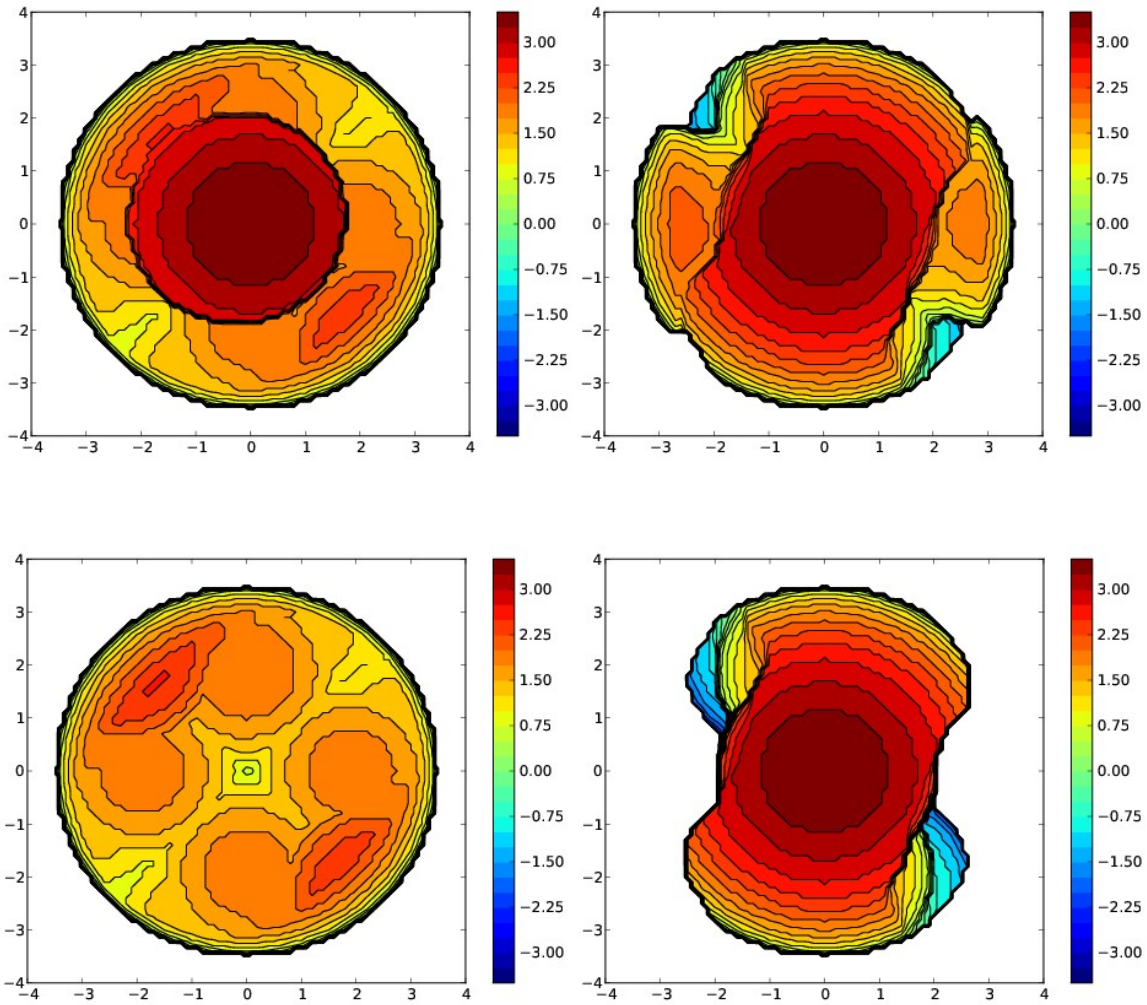


Fig. S9 Topographic steric map of the buried volume of **A** with (top) and without (bottom) labile MeCN ligands with view on top (left) and towards the NHC ligand (right). The red and blue colours show the more- and less-hindered zones in the catalytic centre, respectively.

Table S4 Calculated buried volume for **A**.

Top view, with MeCN ligands					
%V Free	**%V Buried**		**% V Tot/V Ex**		
10.9	**89.1**		99.9		
Quadrant	**V f**	**V b**	**V t**	**%V f**	**%V b**
SW	4.6	40.3	44.9	10.2	89.8
NW	4.4	40.5	44.9	9.8	90.2
NE	5.2	39.7	44.9	11.5	88.5
SE	5.5	39.4	44.9	12.2	87.8

Side view, with MeCN ligands					
%V Free	**%V Buried**		**% V Tot/V Ex**		
10.9	**89.1**		99.9		
Quadrant	**V f**	**V b**	**V t**	**%V f**	**%V b**
SW	4.6	40.2	44.9	10.3	89.7
NW	5.7	39.1	44.9	12.8	87.2
NE	4.3	40.6	44.9	9.6	90.4
SE	5.0	39.9	44.9	11.1	88.9

Top view, without MeCN ligands					
%V Free	**%V Buried**		**% V Tot/V Ex**		
29.8	**70.2**		99.9		
Quadrant	**V f**	**V b**	**V t**	**%V f**	**%V b**
SW	13.3	31.5	44.9	29.7	70.3
NW	13.3	31.5	44.9	29.7	70.3
NE	13.3	31.6	44.9	29.6	70.4
SE	13.5	31.3	44.9	30.1	69.9

Side view, without MeCN ligands					
%V Free	**%V Buried**		**% V Tot/V Ex**		
29.8	**70.2**		99.9		
Quadrant	**V f**	**V b**	**V t**	**%V f**	**%V b**
SW	13.3	31.5	44.9	29.7	70.3
NW	14.1	30.7	44.9	31.5	68.5
NE	12.7	32.1	44.9	28.4	71.6
SE	13.3	31.5	44.9	29.7	70.3

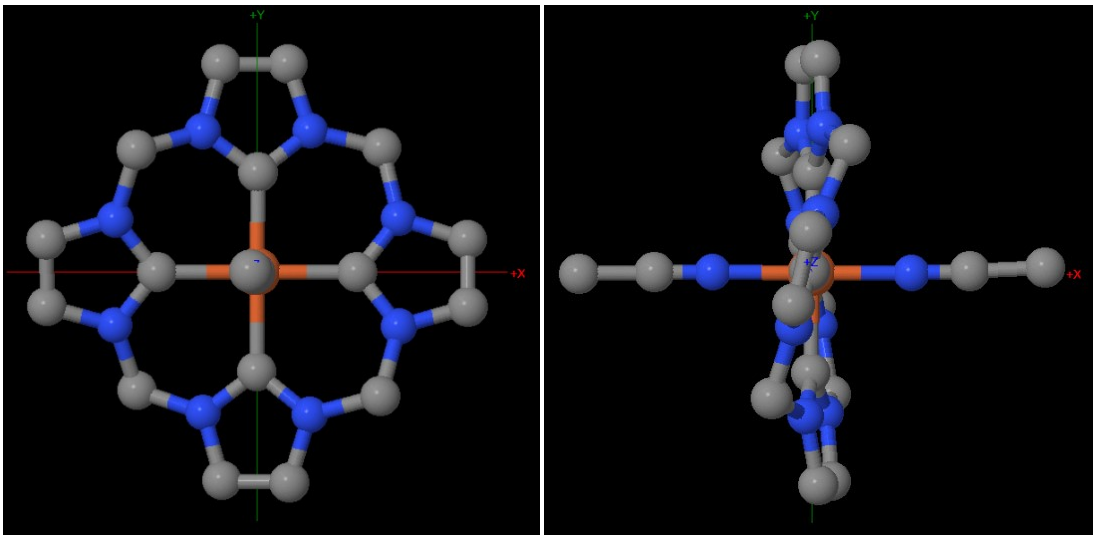


Fig. S10 Visualization of complex **B** (*JSmol* window) and assignment of the x, y, z axes with view on top (left) and towards the NHC ligand (right).

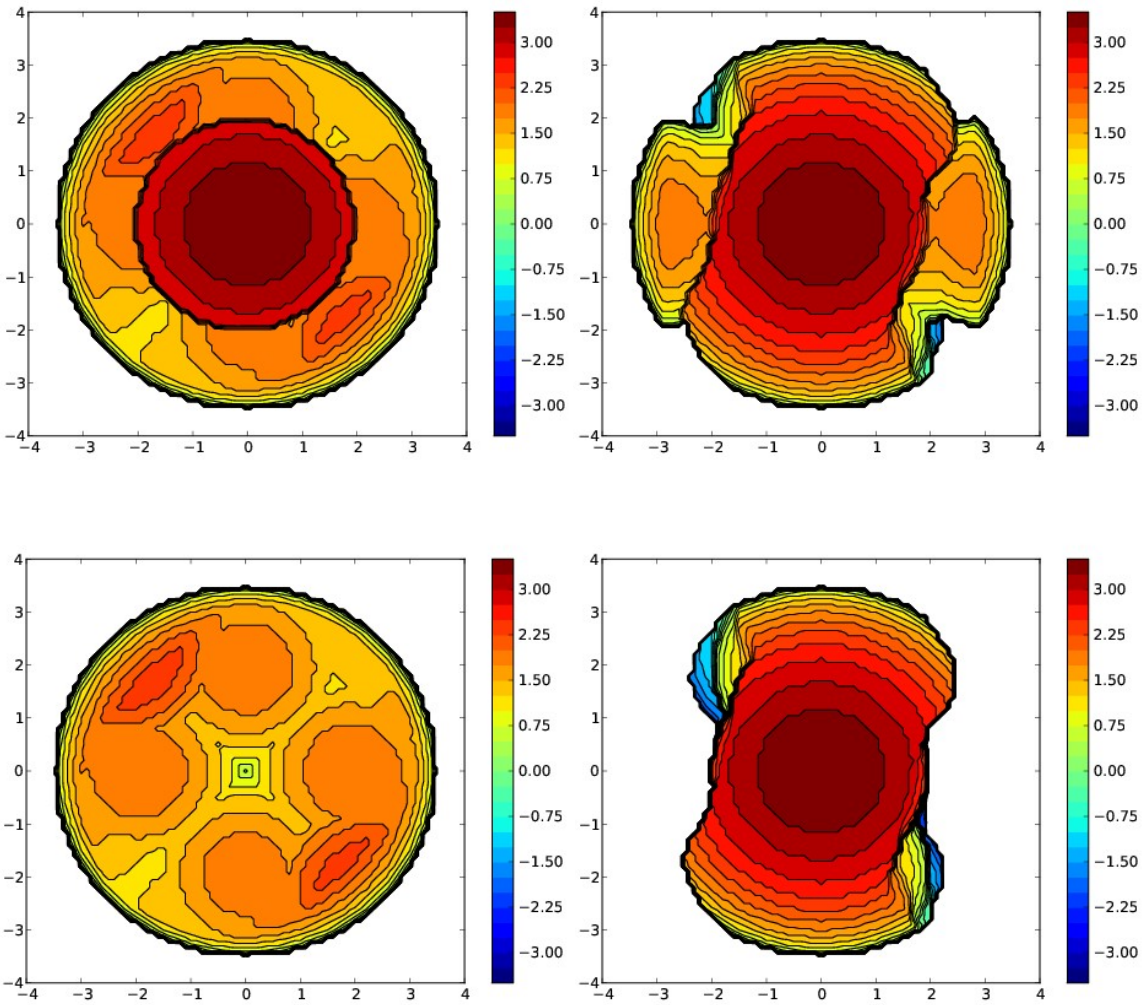


Fig. S11 Topographic steric map of the buried volume of **B** with (top) and without (bottom) labile MeCN ligands with view on top (left) and towards the NHC ligand (right). The red and blue colors show the more- and less-hindered zones in the catalytic center, respectively.

Table S5 Calculated buried volume for **B**.

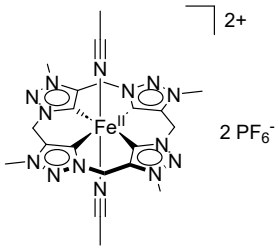
Top view, with MeCN ligands					
%V Free	**%V Buried**		**% V Tot/V Ex**		
11.4	**88.6**		99.9		
Quadrant	**V f**	**V b**	**V t**	**%V f**	**%V b**
SW	4.8	40.1	44.9	10.7	89.3
NW	5.0	39.9	44.9	11.0	89.0
NE	5.6	39.3	44.9	12.5	87.5
SE	5.2	39.7	44.9	11.6	88.4

Side view, with MeCN ligands					
%V Free	**%V Buried**		**% V Tot/V Ex**		
11.5	**88.5**		99.9		
Quadrant	**V f**	**V b**	**V t**	**%V f**	**%V b**
SW	4.9	40.0	44.9	10.9	89.1
NW	5.1	39.7	44.9	11.5	88.5
NE	4.8	40.0	44.9	10.8	89.2
SE	5.7	39.2	44.9	12.6	87.4

Top view, without MeCN ligands					
%V Free	**%V Buried**		**% V Tot/V Ex**		
30.8	**69.2**		99.9		
Quadrant	**V f**	**V b**	**V t**	**%V f**	**%V b**
SW	13.7	31.2	44.9	30.5	69.5
NW	13.7	31.2	44.9	30.5	69.5
NE	14.1	30.8	44.9	31.4	68.6
SE	13.8	31.0	44.9	30.8	69.2

Side view, without MeCN ligands					
%V Free	**%V Buried**		**% V Tot/V Ex**		
30.8	**69.2**		99.9		
Quadrant	**V f**	**V b**	**V t**	**%V f**	**%V b**
SW	13.4	31.4	44.9	30.0	70.0
NW	13.9	30.9	44.9	31.1	68.9
NE	13.6	31.3	44.9	30.2	69.8
SE	14.3	30.6	44.9	31.8	68.2

4. Thermochromism



77 K **r.t.** **400 K**

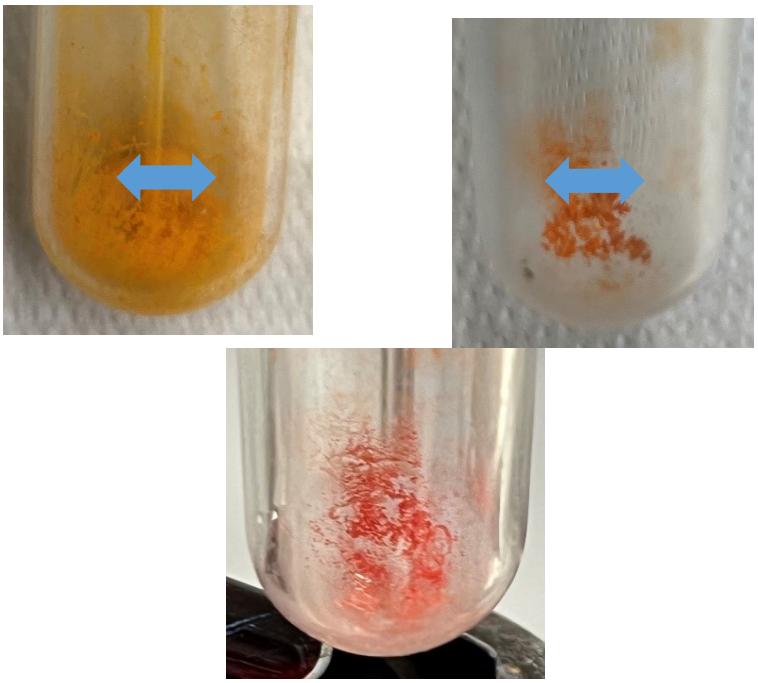
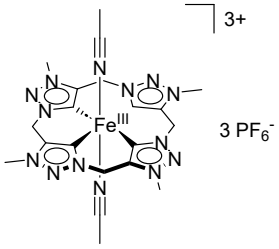


Fig. S12 Colour change of Fe^{II} complex **1** from r.t. to 77 K and to 400 K.



77 K **r.t.** **400 K**

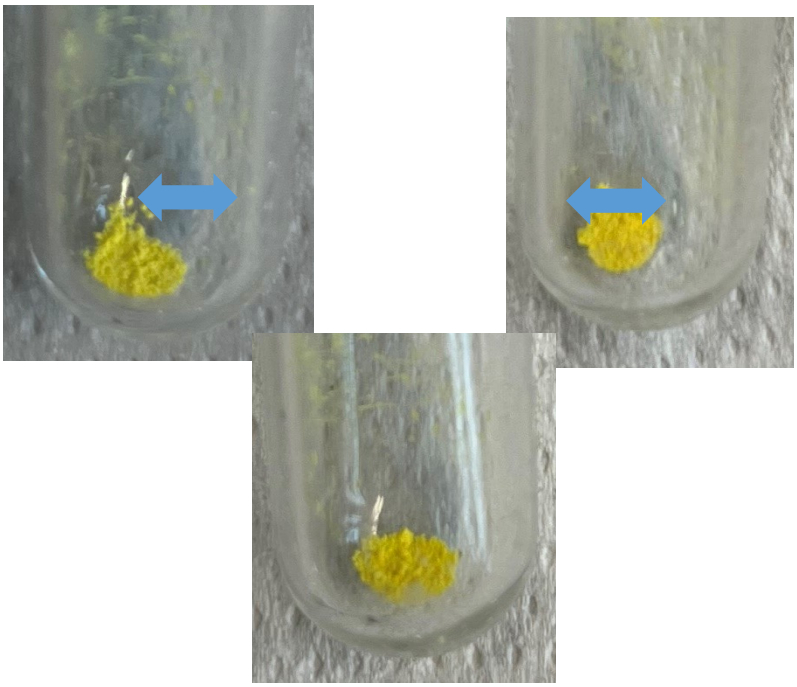


Fig. S13 Colour change of Fe^{III} complex **2** from r.t. to 77 K and to 400 K.

5. Magnetic susceptibility

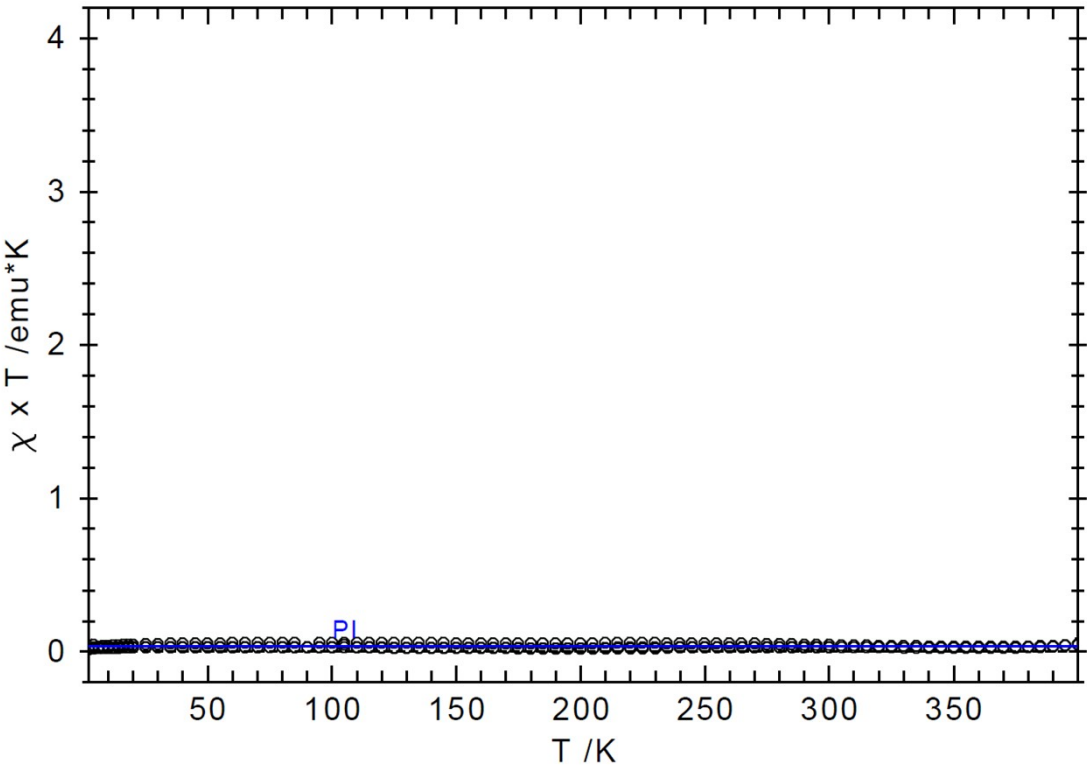


Fig. S14 Magnetic susceptibility data for **1** at 5000 Oe. Circles represent the experimental data; blue line represents the simulation.

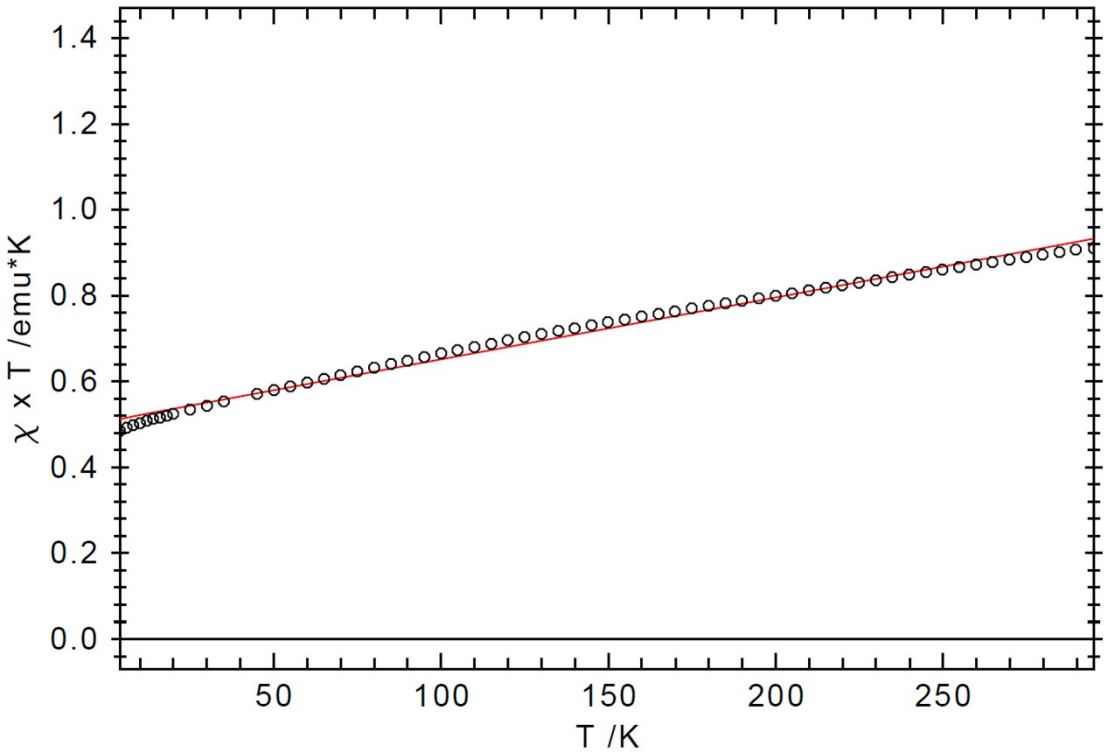


Fig. S15 Magnetic susceptibility data for **2** at 5000 Oe. Circles represent the experimental data; red line represents the simulation.

6. HR-ESI-MS

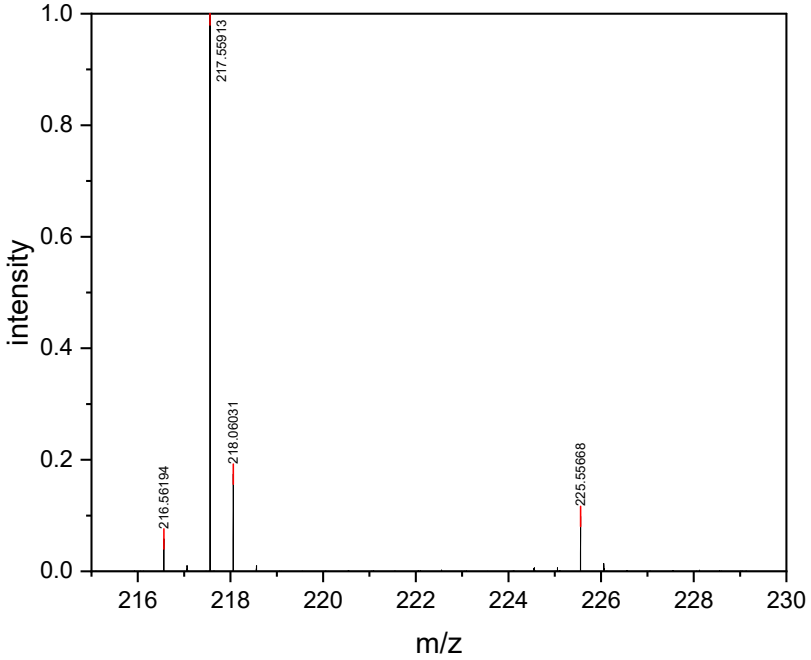


Fig. S16 HR-ESI-MS spectrum of **1** in MeCN with the addition of 10 eq. H_2O_2 (50% aq.).

HR-ESI-MS *m/z* [FeL (- H^+)]$^{2+}$ calcd.: 217.5594, found: 217.5591; [FeL]$^{2+}$ calcd.: 218.0633 found: 218.0630; [FeLO (- H^+)]$^{2+}$ calcd.: 225.5569 found: 225.5567; L = aNHC-Ligand.

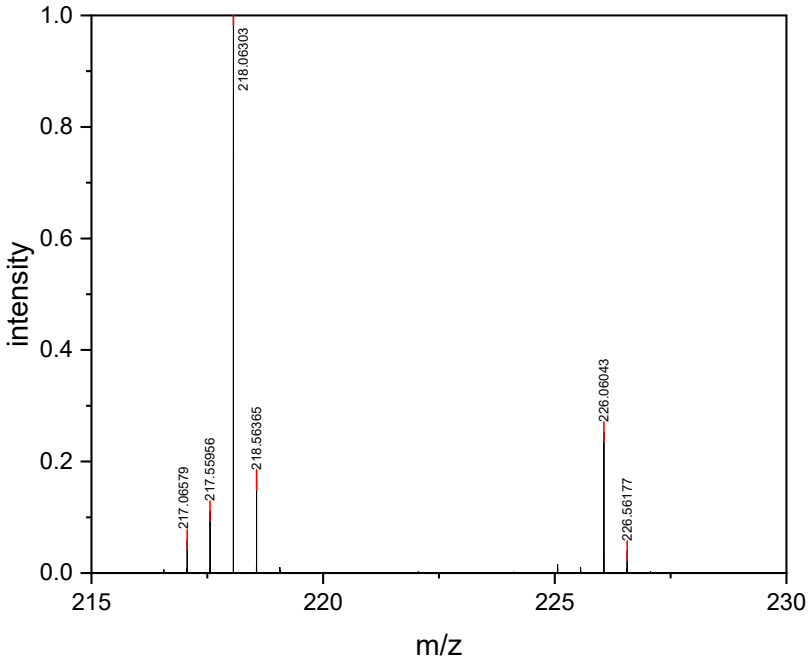


Fig. S17 HR-ESI-MS spectrum of **1** in MeCN under ambient conditions.

HR-ESI-MS *m/z* [FeL (- H^+)]$^{2+}$ calcd.: 217.5594, found: 217.5596; [FeL]$^{2+}$ calcd.: 218.0633 found: 218.0630; [FeLO]$^{2+}$ calcd.: 226.0608 found: 226.0601; L = aNHC-Ligand.

7. ^{1}H-NMR spectra of catalytic substance screening

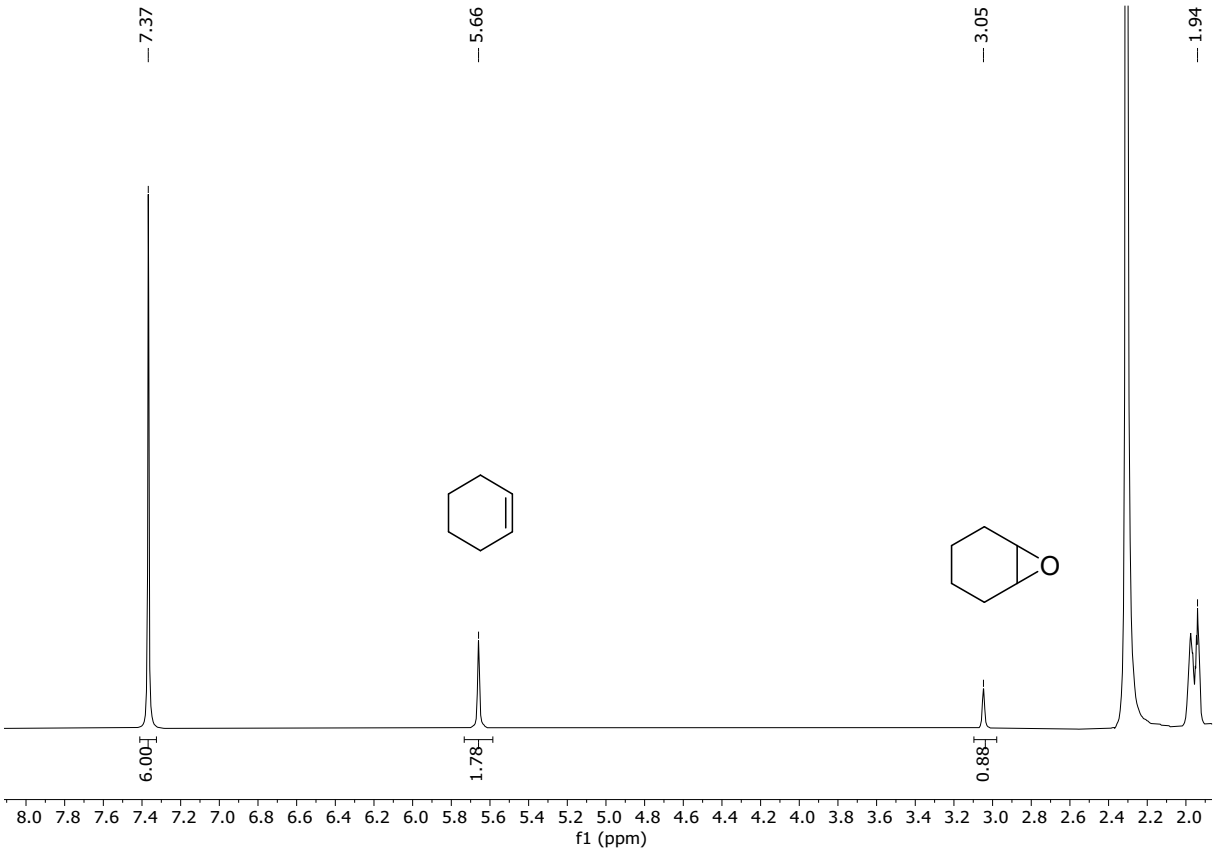


Fig. S18 Section of the ^{1}H-NMR spectrum of the epoxidation of *cis*-cyclohexene (67.3 µmol/mL, 1.00 eq.) with H_2O_2 (50% aq., 1.50 eq., 101 µmol/mL), catalyst **1** (1.35 µmol/mL, 0.005 eq.) and $Sc(OTf)_3$ as additive (8.41 µmol/mL, 0.10 eq.) at 20 °C in CD_3CN with a reaction time of 10 s.

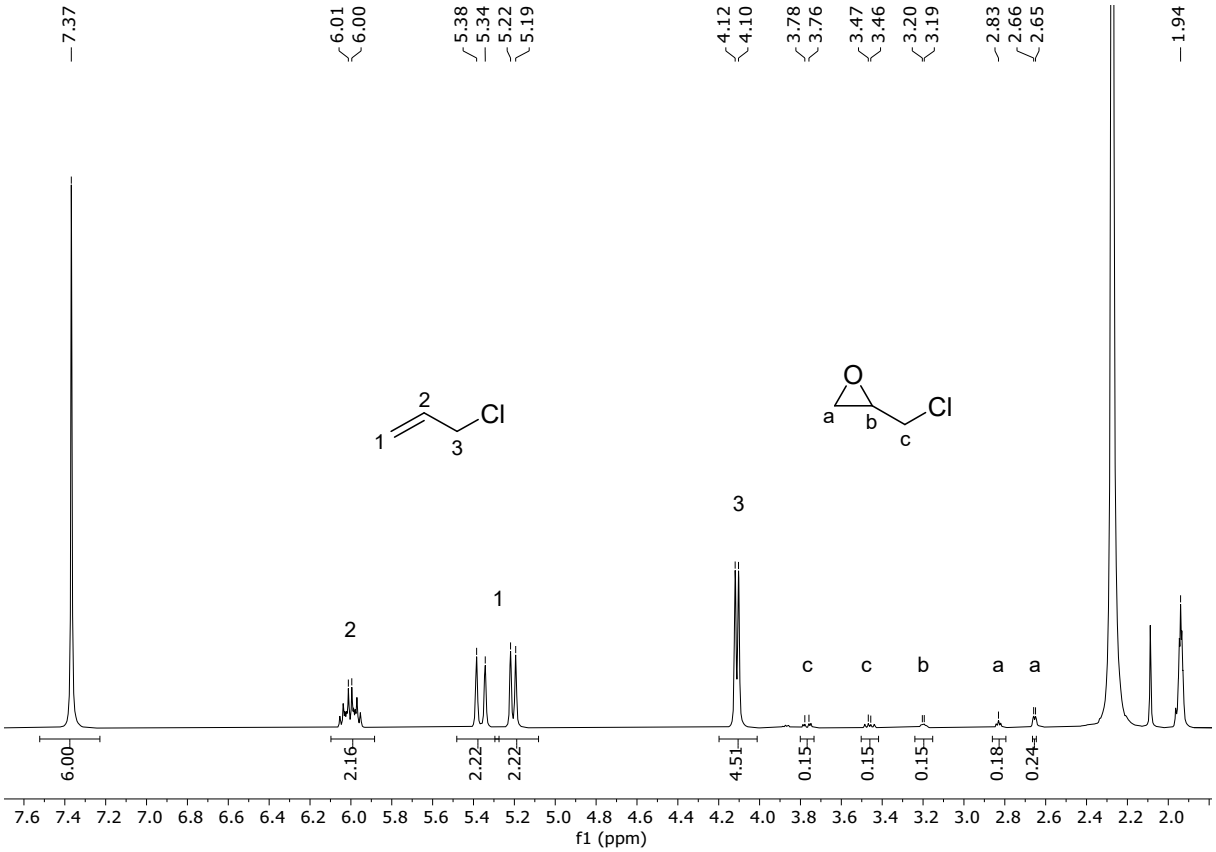


Fig. S19 Section of the ^{1}H-NMR spectrum of the epoxidation of allyl chloride (67.3 µmol/mL, 1.00 eq.) with H_2O_2 (50% aq., 1.50 eq., 101 µmol/mL), catalyst **1** (1.35 µmol/mL, 0.005 eq.) and $Sc(OTf)_3$ as additive (8.41 µmol/mL, 0.10 eq.) at 20 °C in CD_3CN with a reaction time of 1 h.

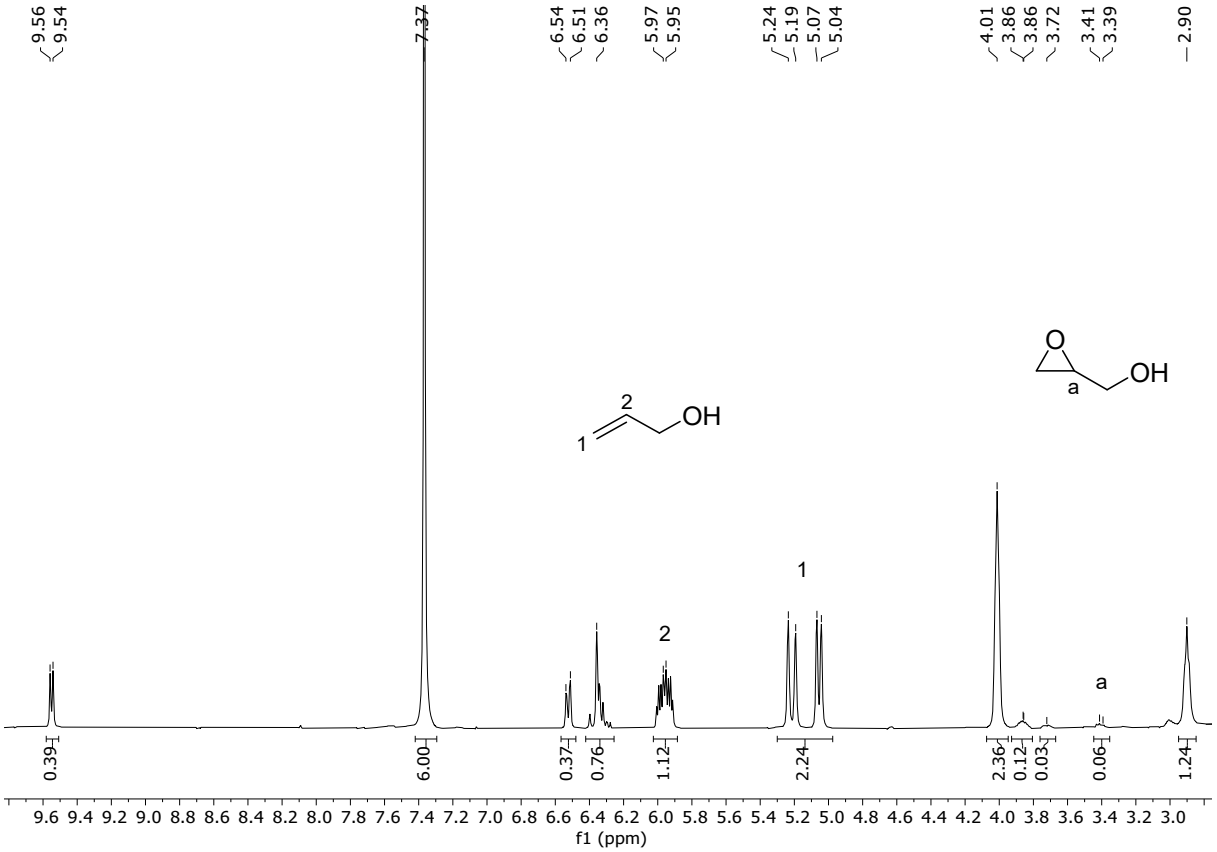


Fig. S20 Section of the ^{1}H-NMR spectrum of the epoxidation of allyl alcohol (67.3 µmol/mL, 1.00 eq.) with H_2O_2 (50% aq., 1.50 eq., 101 µmol/mL), catalyst **1** (1.35 µmol/mL, 0.005 eq.) and $Sc(OTf)_3$ as additive (8.41 µmol/mL, 0.10 eq.) at 20 °C in CD_3CN with a reaction time of 1 h. Estimation regarding the formation of diverse side products: diol (3.86 ppm), acrolein (6.22 – 6.59, 9.55 ppm).

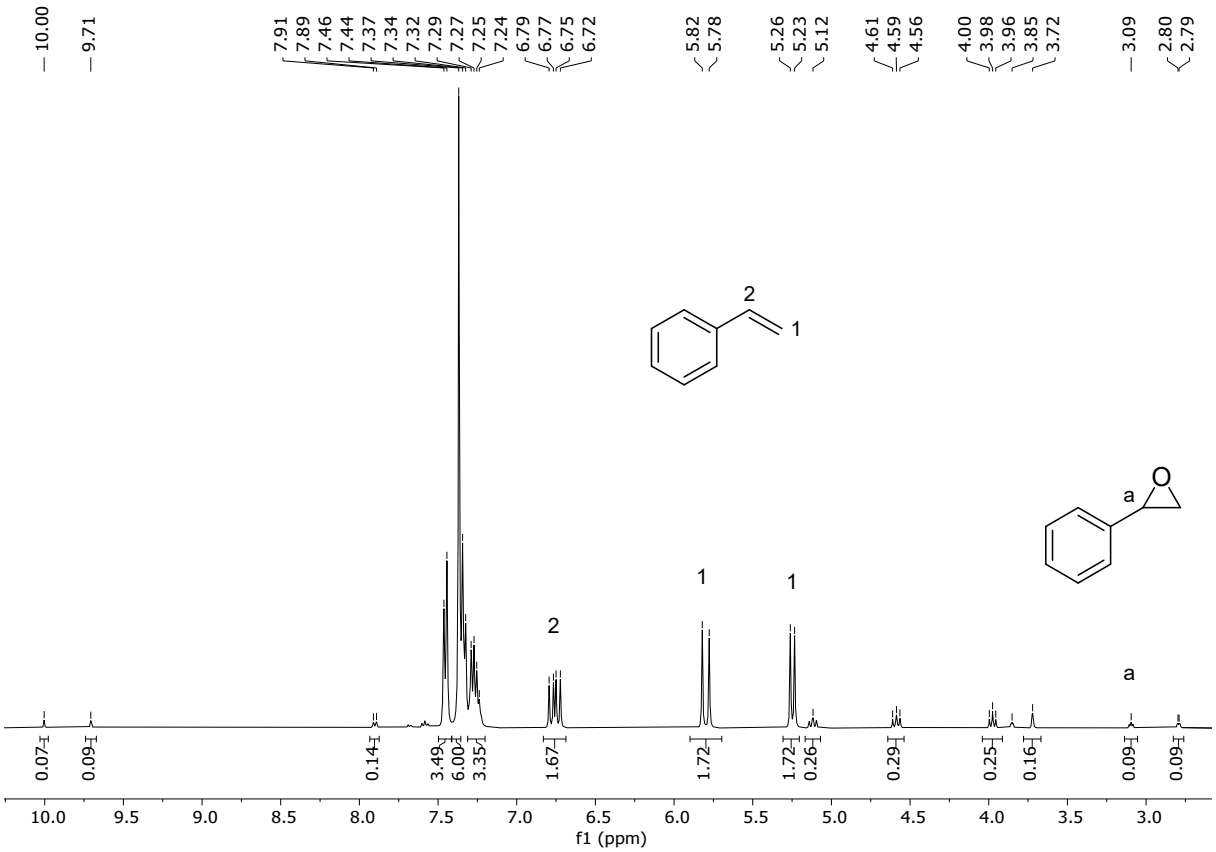


Fig. S21 Section of the ^{1}H-NMR spectrum of the epoxidation of styrene (67.3 µmol/mL, 1.00 eq.) with H_2O_2 (50% aq., 1.50 eq., 101 µmol/mL), catalyst **1** (1.35 µmol/mL, 0.005 eq.) and $Sc(OTf)_3$ as additive (8.41 µmol/mL, 0.10 eq.) at 20 °C in CD_3CN with a reaction time of 10 s. Estimation regarding the formation of diverse side products: phenethyl alcohol (3.99, 5.12 ppm), phenylacetaldehyde (9.71 ppm), benzaldehyde (10.01 ppm).

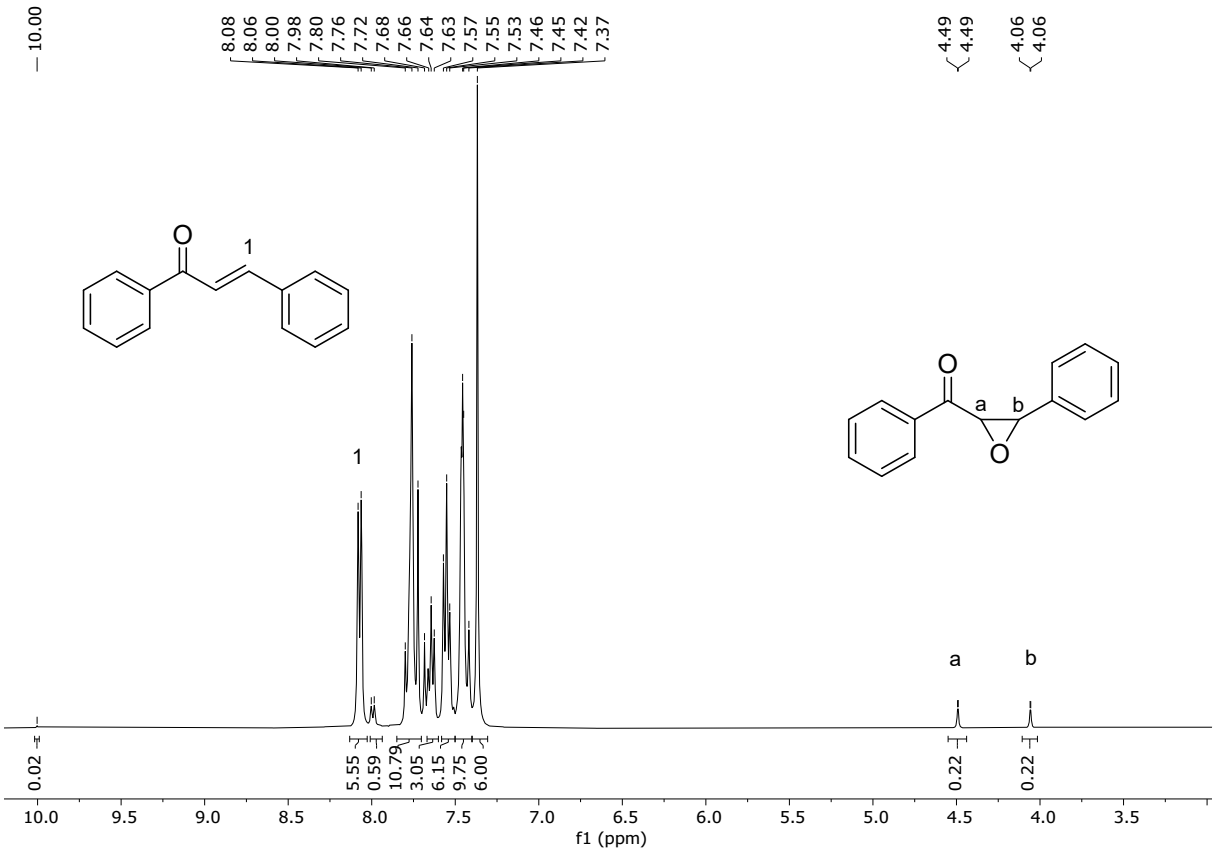


Fig. S22 Section of the ^{1}H-NMR spectrum of the epoxidation of chalcone (67.3 µmol/mL, 1.00 eq.) with H_2O_2 (50% aq., 1.50 eq., 101 µmol/mL), catalyst **1** (1.35 µmol/mL, 0.005 eq.) and $Sc(OTf)_3$ as additive (8.41 µmol/mL, 0.10 eq.) at 20 °C in CD_3CN with a reaction time of 10 s. Estimation regarding the formation of the side product: benzaldehyde (10.00 ppm).

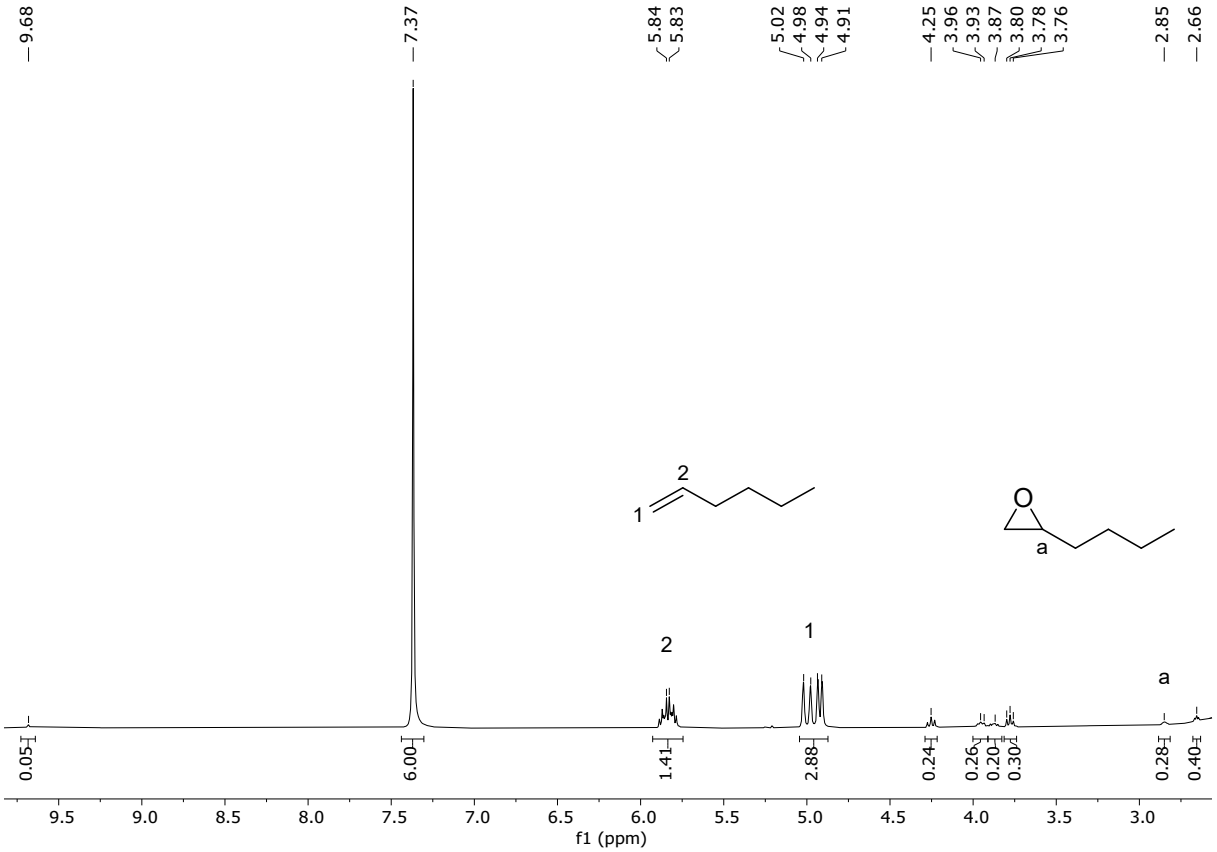


Fig. S23 Section of the ^{1}H-NMR spectrum of the epoxidation of 1-hexene (67.3 µmol/mL, 1.00 eq.) with H_2O_2 (50% aq., 1.50 eq., 101 µmol/mL), catalyst **1** (1.35 µmol/mL, 0.005 eq.) and $Sc(OTf)_3$ as additive (8.41 µmol/mL, 0.10 eq.) at 20 °C in CD_3CN with a reaction time of 1 h. Estimation regarding the formation of the side product: diol (3.70 – 4.30 ppm), aldehyde (9.68 ppm).

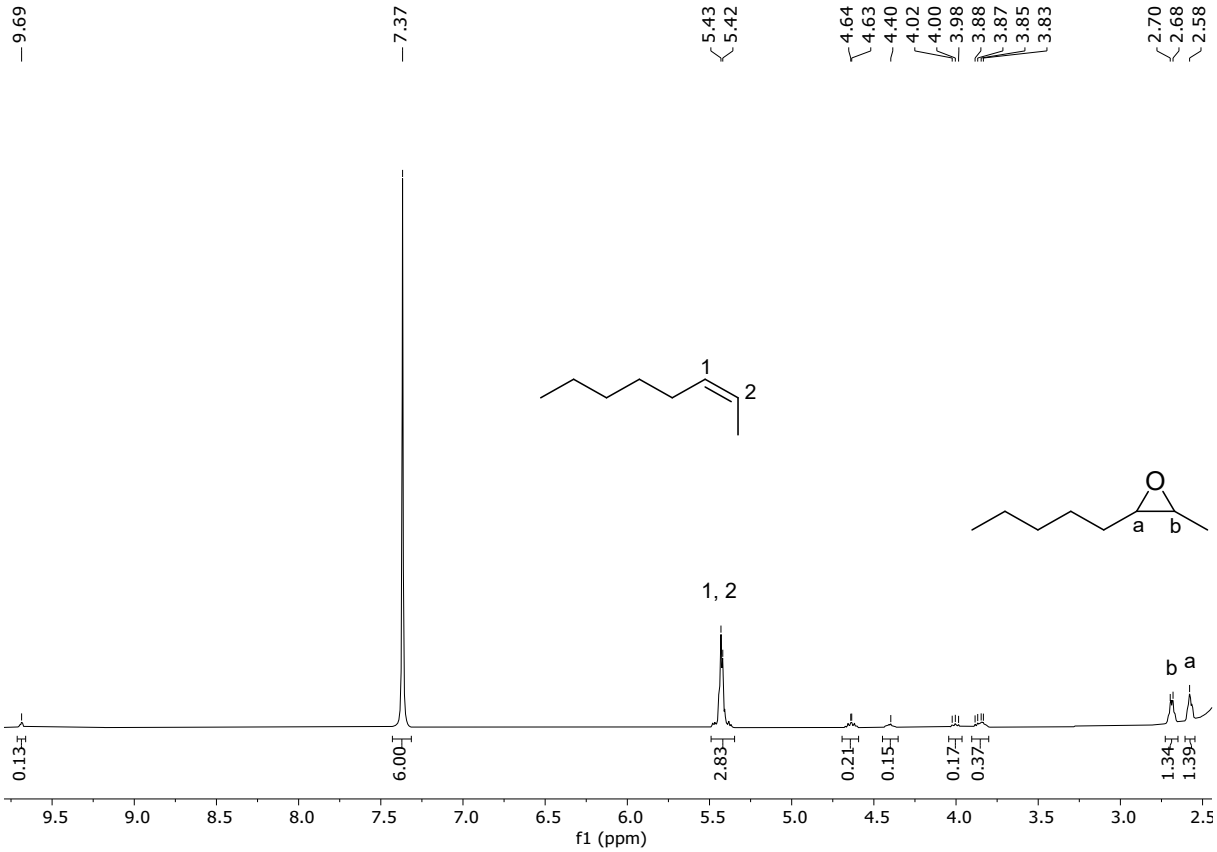


Fig. S24 Section of the ^{1}H-NMR spectrum of the epoxidation of *cis*-2-octene (67.3 µmol/mL, 1.00 eq.) with H_2O_2 (50% aq., 1.50 eq., 101 µmol/mL), catalyst **1** (1.35 µmol/mL, 0.005 eq.) and $Sc(OTf)_3$ as additive (8.41 µmol/mL, 0.10 eq.) at 20 °C in CD_3CN with a reaction time of 1 h. Full conversion, estimation regarding the formation of diverse side products: diols (3.70 – 4.10 ppm), aldehyde (9.69 ppm).

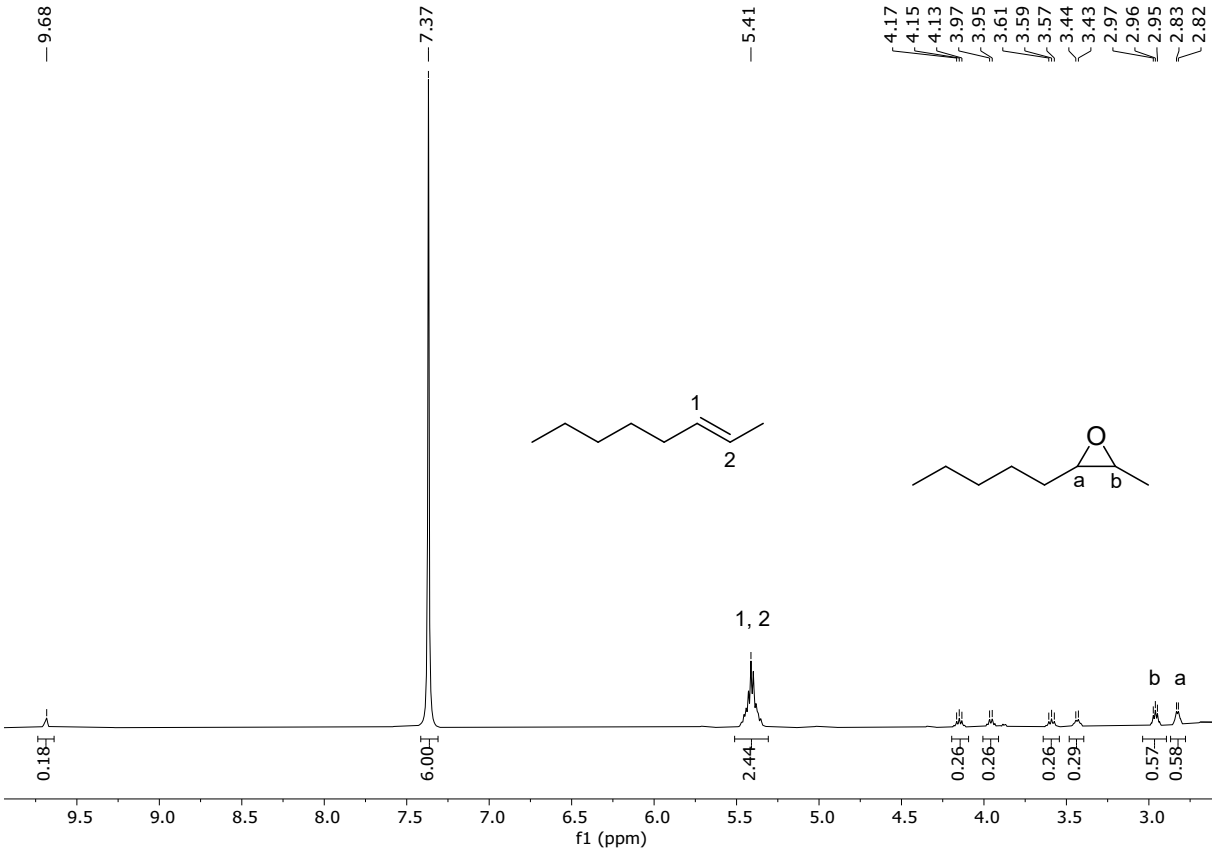


Fig. S25 Section of the ^{1}H-NMR spectrum of the epoxidation of *trans*-2-octene (67.3 µmol/mL, 1.00 eq.) with H_2O_2 (50% aq., 1.50 eq., 101 µmol/mL), catalyst **1** (1.35 µmol/mL, 0.005 eq.) and $Sc(OTf)_3$ as additive (8.41 µmol/mL, 0.10 eq.) at 20 °C in CD_3CN with a reaction time of 1 h. Full conversion, estimation regarding the formation of diverse side products: diols (3.40 – 4.20 ppm), aldehyde (9.68 ppm).

8. DFT calculations

Optimisation and single point calculations were performed using Gaussian 16[14] and processed with GaussView 6.0[15]. Initial parameters for the gas phase calculations were imported from the respective crystal structures or modified accordingly. Geometry optimizations were carried out without applying constraint coordinates. The hybrid functional including dispersion B97D3/gen was used and the def2-SVP basis set was applied for small atoms. For Fe the Stuttgart/Dresden 1997 SDD relativistic effective core potential (ECP) and its respective basis was utilized. The obtained structures are true ground states, as shown by the absence of significant imaginary frequencies (< 8 cm^{-1}) found by vibrational analysis. Solvation calculations were performed using the SCRF = Acetonitrile (ε = 35.688) option with both the universal solvation model (SMD) and the polarizable continuum model (PCM).[16,17] CD Löwdin charges were calculated for gas phase molecules applying the IOp (6/80 = 1) keyword in Gaussian. In accordance to previous investigations, backbone modified complexes are calculated in the catalytically active oxidation state +III in doublet state[18-22].

The dissociation of the labile acetonitrile ligand was calculated *via* DFT. As dative bond dissociation energies (BDE) in the gas phase are expectedly higher due to the lacking stabilisation of the released free acetonitrile molecule, solvent model calculations (SMD, PCM) were employed (Table S6a).[16-18] Comparing complex **2** to **1**, the dative bond dissociation energies are raised by 18 – 25% in solution, attributed to the lower electron density at the Fe^{III} centre. Regarding the reaction free energy of the dissociation step, the difference amounts to 12 – 22 kJ mol^{-1} between **1** and **2**. The comparison to the Gibbs free energy of the overall epoxidation of *cis*-cyclooctene with hydrogen peroxide as oxidant of -49 kJ mol^{-1}, suggests that the a five coordinate iron species is a rather short lived intermediate and the empty coordination site will be occupied rapidly with an oxidant molecule or another MeCN molecule in an equilibrium.

Table S6 BDEs and ΔG of the dative bond toward one labile acetonitrile ligand of **1** and **2**.

	BDE [kJ mol^{-1}]			**ΔG [kJ mol^{-1}]**		
	gas phase	**SMD (MeCN)**	**PCM (MeCN)**	**gas phase**	**SMD (MeCN)**	**PCM (MeCN)**
1	130.25	79.84	90.40	78.70	42.69	52.65
2	174.56	94.32	112.97	139.68	50.67	74.94

Bond dissociation energy (BDE). Solvation model based on density (SMD). Polarisable continuum model PCM.

Table S7 Comparison of DFT calculated selected structural parameters of **1** and **2**.

		Bond lengths [Å]		Bond angles [°]		
		Fe–C_{NHC}[a]	**Fe–NCMe[b]**	**MeCN–Fe–NCMe**	**C_{NHC}–Fe–C_{NHC}[c]**	**C_{NHC}–Fe–C_{NHC}[d]**
1	gas phase	1.9298(1)	1.8835(0)	179.990	179.922(3)	90.000(1)
	SMD(MeCN)	1.9294(1)	1.8780(0)	179.994	179.979(1)	90.000(1)
	PCM(MeCN)	1.9258(0)	1.8760(0)	179.980	179.889(1)	90.000(1)
2	gas phase	1.9703(0)	1.9114(0)	180.000	180.000(0)	90.000(2)
	SMD(MeCN)	1.9664(4)	1.8932(0)	180.000	180.000(0)	90.000(1)
	PCM(MeCN)	1.9568(1)	1.8930(1)	179.974	179.875(6)	90.000(1)

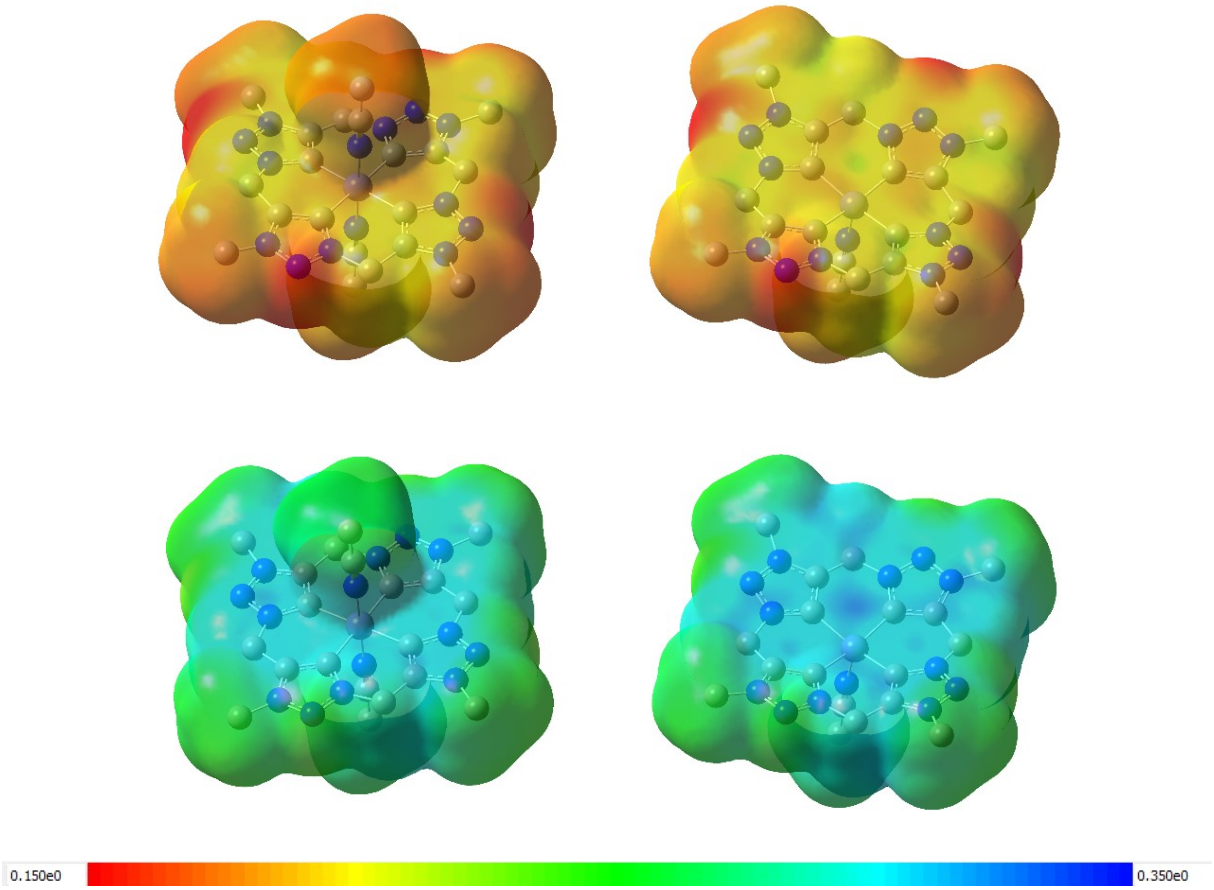


Fig. S26 Electrostatic potential (ESP) mapped total density plots of Fe^{II} complexes **1** and **1**-MeCN with the removal of one labile MeCN ligand (top), and Fe^{III} complexes **2** and **2**-MeCN with the removal of one labile MeCN ligand (bottom). The red and blue colours show more- and less-negative charges, respectively.

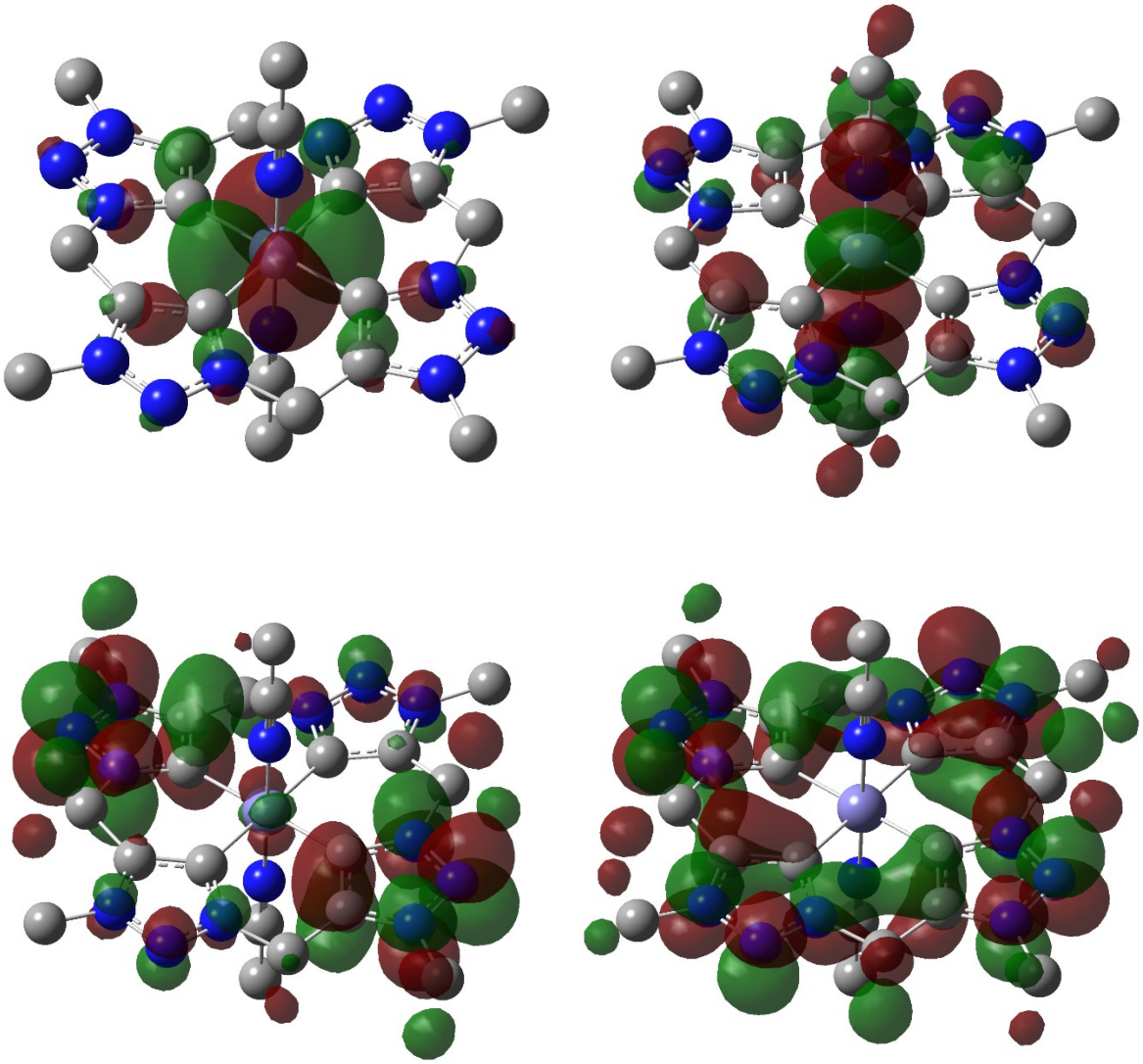


Fig. S27 Isodensity plots of the HOMO (top, left), HOMO-1 (top, right). LUMO (bottom, left) and LUMO+1 (bottom, right) of **1**. Hydrogen atoms are omitted for clarity. All Isovalues MO = 0.02, Density = 0.0004 and Laplacian = 0.00.

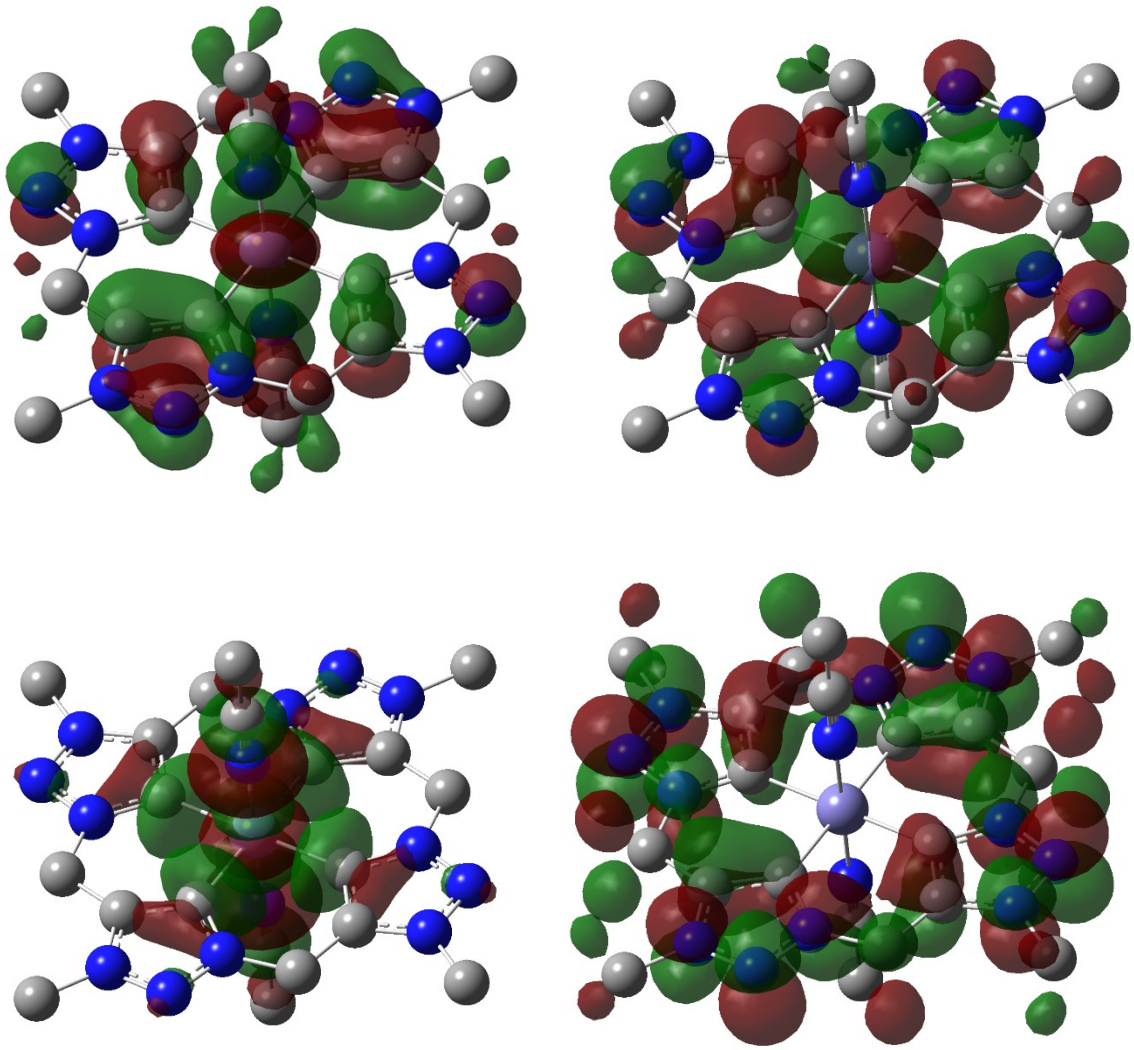


Fig. S28 Isodensity plots of the α-HOMO (SOMO) (top, left), HOMO-1 (top, right), LUMO (bottom, left) and LUMO+1 (bottom, right) of **2**. Hydrogen atoms are omitted for clarity. All Isovalues MO = 0.02, Density = 0.0004 and Laplacian = 0.00.

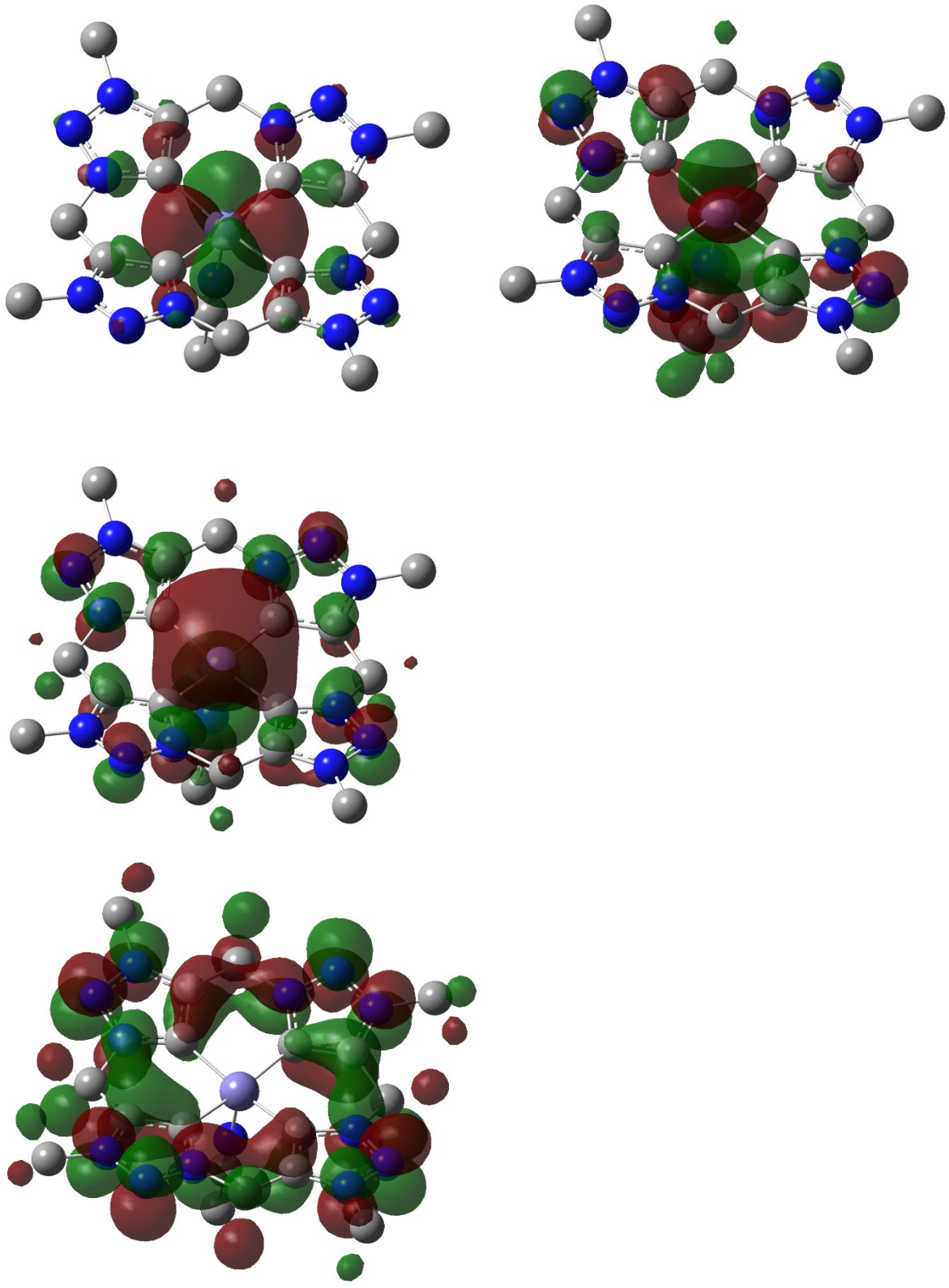


Fig. S29 Isodensity plots of the HOMO (top, left), HOMO-1 (top, right), LUMO (bottom, left) and LUMO+1 (bottom, right) of **1**-MeCN. Hydrogen atoms are omitted for clarity. All Isovalues MO = 0.02, Density = 0.0004 and Laplacian = 0.00.

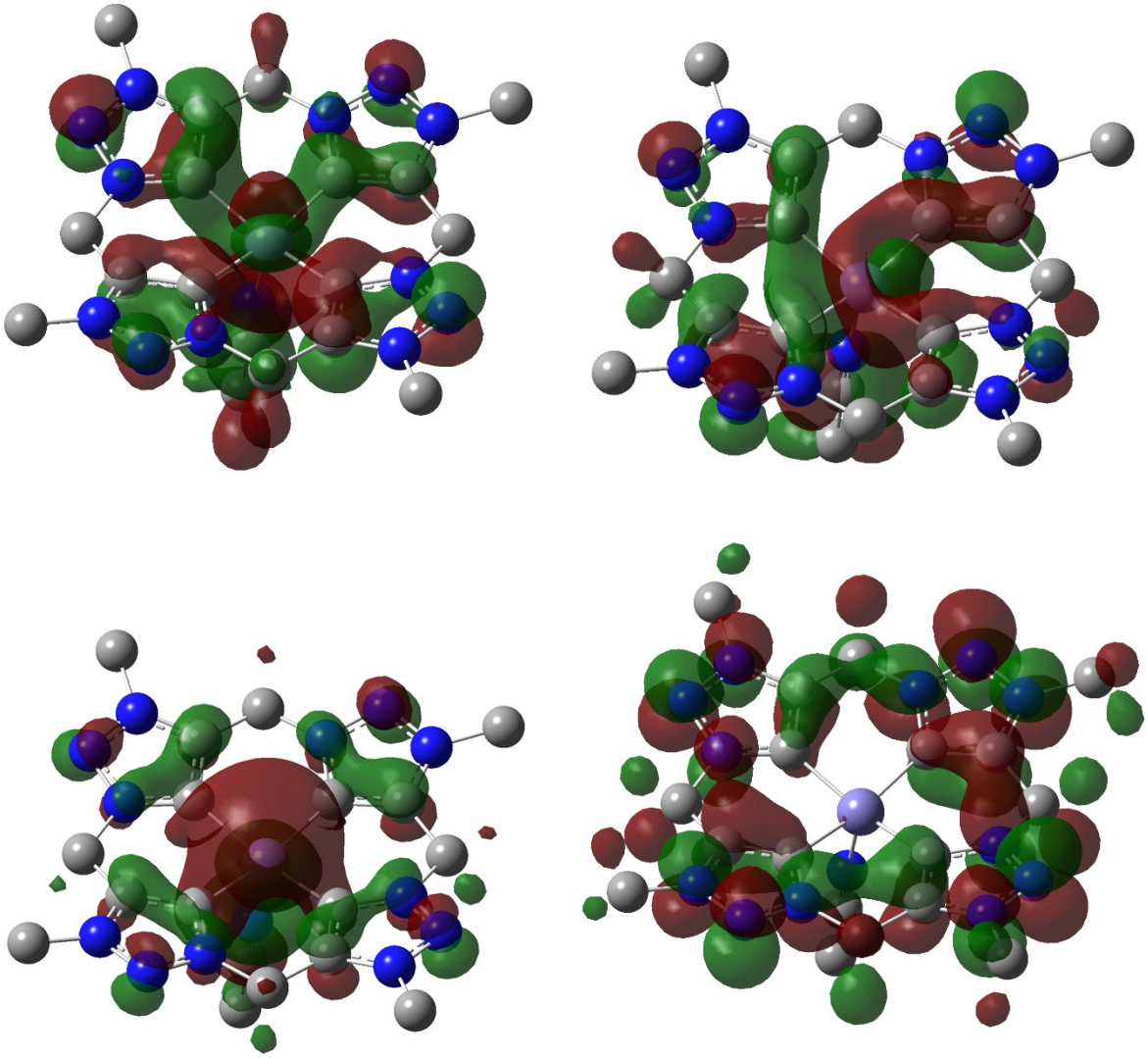


Fig. S30 Isodensity plots of the α-HOMO (SOMO) (top, left), HOMO-1 (top, right), LUMO (bottom, left) and LUMO+1 (bottom, right) of **2**-MeCN. Hydrogen atoms are omitted for clarity. All Isovalues MO = 0.02, Density = 0.0004 and Laplacian = 0.00.

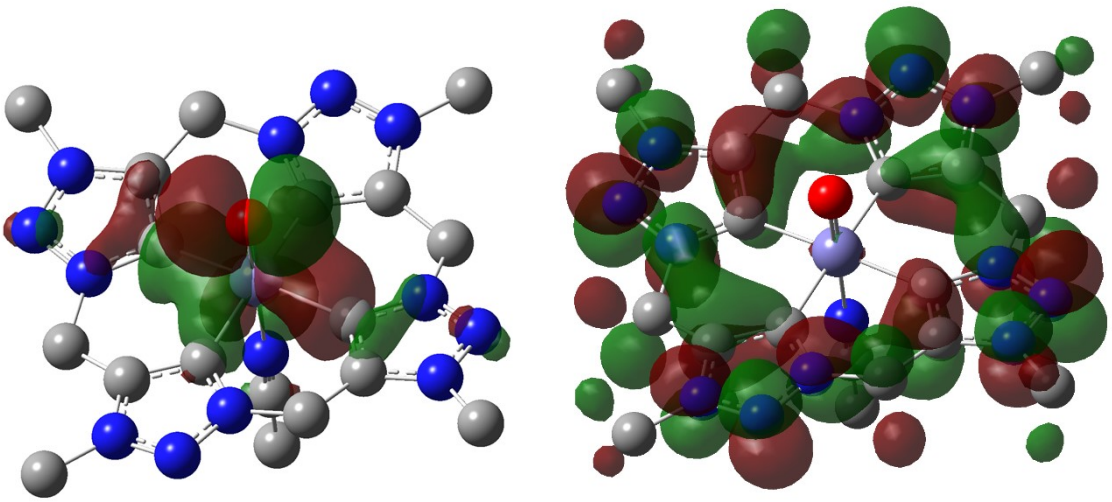


Fig. S31 Isodensity plots of the α-HOMO (SOMO) (left) and LUMO (right) of the proposed structure of oxioiron(IV) aNHC species $Fe^{IV}[cCCCC]_{trz}O(MeCN)$. Hydrogen atoms are omitted for clarity. All Isovalues MO = 0.02, Density = 0.0004 and Laplacian = 0.00.

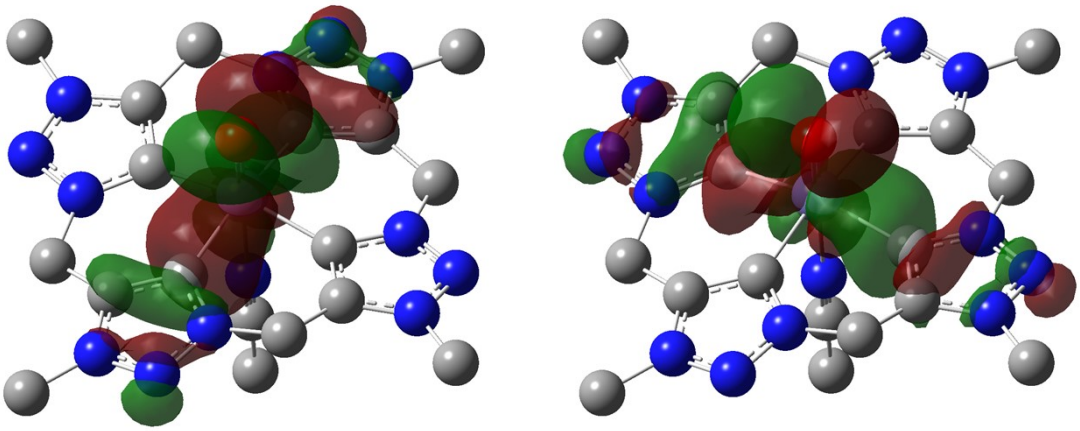


Fig. S32 Isodensity plots of the α-HOMO (SOMO) (left) and LUMO (right) of the proposed structure of oxioiron(V) aNHC species $Fe^{V}[cCCCC]_{trz}O(MeCN)$. Hydrogen atoms are omitted for clarity. All Isovalues MO = 0.02, Density = 0.0004 and Laplacian = 0.00.

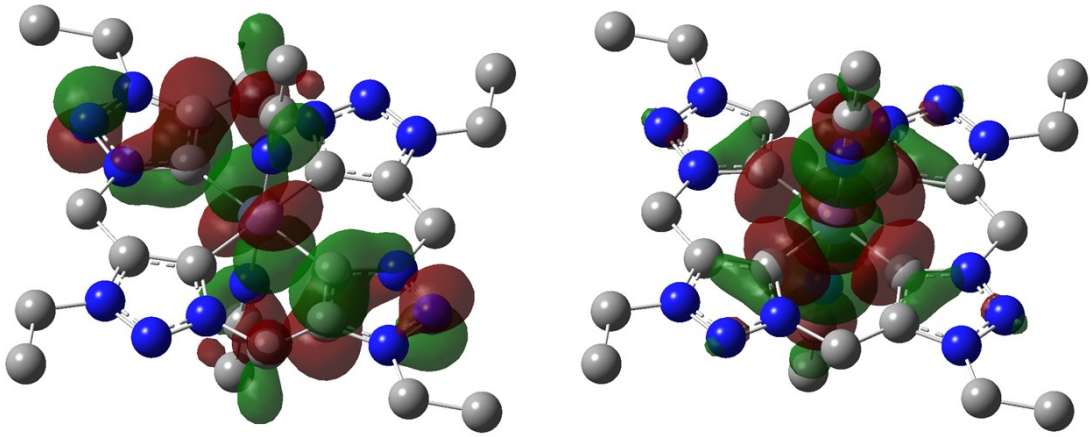


Fig. S33 Isodensity plots of the α-HOMO (SOMO) (left) and LUMO (right) of **2a**. Hydrogen atoms are omitted for clarity. All Isovalues MO = 0.02, Density = 0.0004 and Laplacian = 0.00.

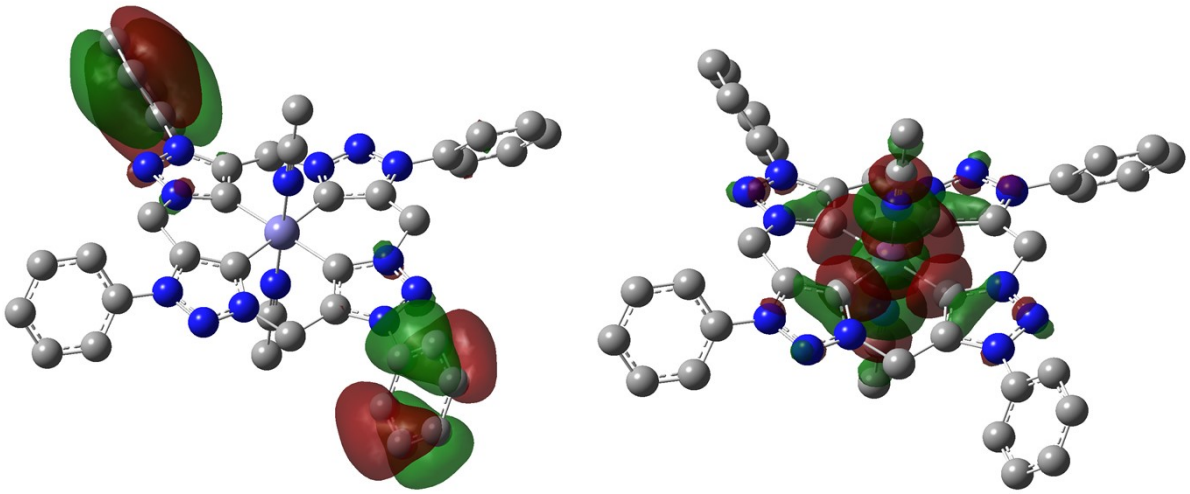


Fig. S34 Isodensity plots of the α-HOMO (SOMO) (left) and LUMO (right) of **2b**. Hydrogen atoms are omitted for clarity. All Isovalues MO = 0.02, Density = 0.0004 and Laplacian = 0.00.

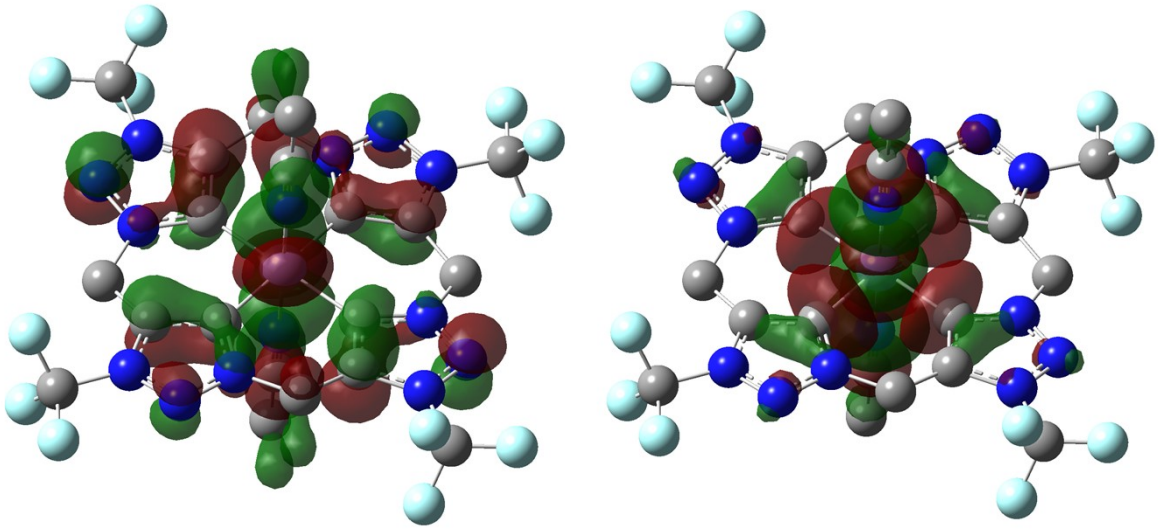


Fig. S35 Isodensity plots of the α-HOMO (SOMO) (left) and LUMO (right) of **2c**. Hydrogen atoms are omitted for clarity. All Isovalues MO = 0.02, Density = 0.0004 and Laplacian = 0.00.

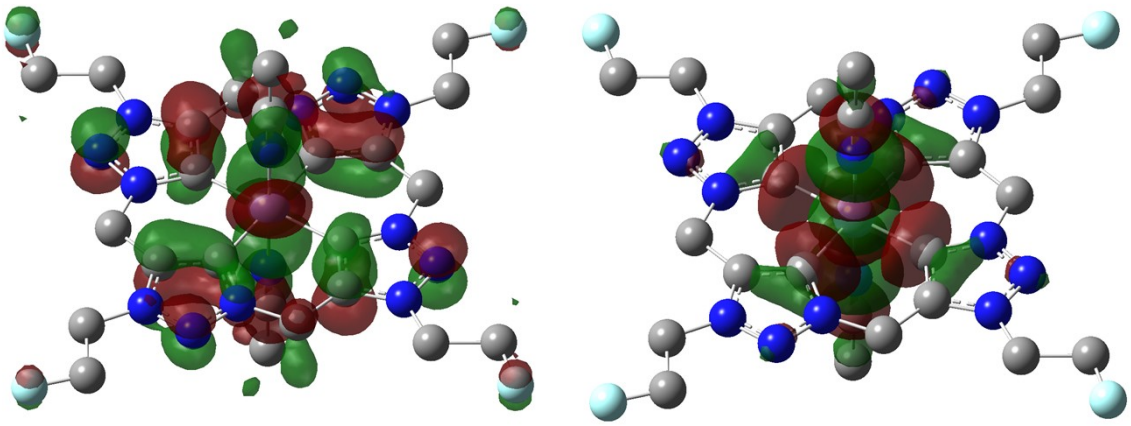


Fig. S36 Isodensity plots of the α-HOMO (SOMO) (left) and LUMO (right) of **2d**. Hydrogen atoms are omitted for clarity. All Isovalues MO = 0.02, Density = 0.0004 and Laplacian = 0.00.

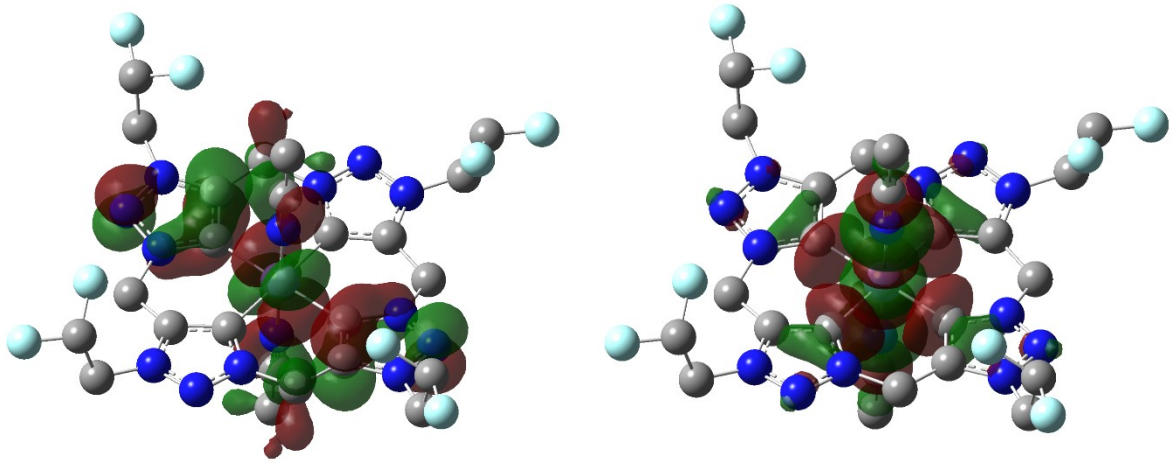


Fig. S37 Isodensity plots of the α-HOMO (SOMO) (left) and LUMO (right) of **2e**. Hydrogen atoms are omitted for clarity. All Isovalues MO = 0.02, Density = 0.0004 and Laplacian = 0.00.

Table S8 Coordinates of **1** calculated by Gaussian (charge 2, multiplicity 1, SCF: E(gas phase) = -1665.863124 h, E(SMD) = -1666.082486 h, E(PCM) = -1666.051313 h).

Atom	gas phase			SMD			PCM		
	Coordinate [Å]			Coordinate [Å]			Coordinate [Å]		
	X	Y	Z	X	Y	Z	X	Y	Z
Fe	0.00000827	0.00012856	-0.00016860	-0.00041092	0.00014538	-0.00004514	-0.00008195	-0.00023426	-0.00003870
N	-2.75611032	1.21482730	-0.13780873	2.67575511	1.37308858	-0.16250127	-2.71372729	1.28885977	-0.17650213
N	-3.44047293	2.35961498	-0.08475030	3.99710629	1.17853511	-0.11086128	-3.36662549	2.45325980	-0.11077859
N	-2.50681075	3.27334837	0.09481499	4.11345369	-0.12152351	0.09387009	-2.40801642	3.33369897	0.11547156
N	1.21482630	2.75610716	0.14018992	1.37243688	-2.67556022	0.17123846	1.28892709	2.71347158	0.17542278
N	2.35969068	3.44042902	0.08817802	1.17810054	-3.99703432	0.12182171	2.45338842	3.36632581	0.11019711
N	3.27339681	2.50690121	-0.09225435	-0.12178249	-4.11391694	-0.08374581	3.33395097	2.40759489	-0.11505197
N	0.00153300	-0.00148067	1.88328881	-0.00578398	0.00369053	1.87797078	-0.00151048	0.00032757	1.87595918
C	-3.53516353	-0.00653652	-0.39143726	2.21262663	2.74059907	-0.44075495	-3.50614139	0.09118204	-0.49210601
C	-1.38613527	1.34266893	0.00261603	1.91466612	0.23461018	0.00324492	-1.34825343	1.37494814	0.00078955
C	-1.24732478	2.72724785	0.15488903	2.89809334	-0.74777268	0.17324753	-1.16976368	2.75009003	0.19203252
C	-2.89384791	4.68043665	0.20835317	5.44077187	-0.71710714	0.21385554	-2.74912487	4.74691621	0.26219980
C	-0.00656078	3.53512635	0.39382478	2.73964162	-2.21162394	0.44958620	0.09110120	3.50596084	0.49026744
C	1.34258355	1.38628997	-0.00171115	0.23401330	-1.91493131	0.00311181	1.37510439	1.34792475	-0.00127179
C	2.72719955	1.24753698	-0.15388843	-0.74808199	-2.89878839	-0.16606044	2.75037876	1.16931249	-0.19142139
C	4.68057592	2.89393586	-0.20464612	-0.71719181	-5.44147769	-0.20170730	4.74728017	2.74857374	-0.26098176
C	0.00283444	-0.00341851	3.05168333	-0.01079300	0.00677561	3.04649423	-0.00295845	0.00110644	3.04399742
C	0.00457270	-0.00684417	4.50855733	-0.02004518	0.00845131	4.49960104	-0.00660111	0.00264890	4.49954440
H	-3.89720285	0.03296255	-1.43772378	2.43531149	2.97019548	-1.50030369	-3.77944078	0.13525345	-1.56401343
H	-4.42872788	0.02905549	0.25652115	2.80997490	3.43286530	0.17635602	-4.44375604	0.14819412	0.08592500
H	-2.56773847	5.07673022	1.18376822	5.53867665	-1.19236429	1.20322632	-2.44610776	5.09775048	1.26144577
H	-3.98786721	4.73959338	0.12690395	6.18542639	0.08247139	0.09928558	-3.83552527	4.84902268	0.14021961
H	-2.42617413	5.25931086	-0.60496248	5.57043130	-1.47514151	-0.57537739	-2.22699611	5.33252295	-0.51107206
H	0.02896368	4.42865798	-0.25418937	3.43255874	-2.81086696	-0.16493604	0.14843849	4.44352284	-0.08780676
H	0.03305251	3.89728369	1.44006625	2.96813394	-2.43103324	1.51007090	0.13460094	3.77934933	1.56218861
H	5.25890744	2.42567399	0.60872235	-1.47609377	-5.56958060	0.58694105	5.33233964	2.22668078	0.51286392
H	4.73975638	3.98788786	-0.12234863	0.08227035	-6.18589201	-0.08480054	4.84937700	3.83501082	-0.13932842
H	5.07748746	2.56849152	-1.18003347	-1.19139035	-5.54137402	-1.19139099	5.09875878	2.44516765	-1.25988471
H	-0.87332646	-0.55433736	4.89611951	0.12098339	1.03544458	4.88219365	-0.90146509	-0.51957536	4.88178536
H	-0.02986320	1.02605162	4.89922783	0.79458759	-0.62878056	4.88864025	-0.01342219	1.03863567	4.88207737
H	0.91831524	-0.49367923	4.89418657	-0.98339011	-0.38004585	4.87660971	0.89198674	-0.50960849	4.88645219
N	2.75603573	-1.21459405	-0.14173069	-2.67590816	-1.37315809	-0.17014659	2.71375329	-1.28938451	-0.17320969
N	3.44043907	-2.35940558	-0.08985686	-3.99743594	-1.17868210	-0.12257945	3.36654344	-2.45382476	-0.10701753
N	2.50692746	-3.27323663	0.09003211	-4.11450877	0.12173855	0.07949260	2.40768647	-3.33424347	0.11824779
N	-1.21461045	-2.75600595	0.13931200	-1.37378495	2.67608591	0.16132857	-1.28931854	-2.71399003	0.17428763

N	-2.35940153	-3.44040898	0.08696310	-1.17909318	3.99749678	0.11167370	-2.45370587	-3.36682310	0.10770924
N	-3.27326725	-2.50678026	-0.09208356	0.12150159	4.11406205	-0.08952938	-3.33400813	-2.40809801	-0.11857660
C	3.53493184	0.00701216	-0.39467500	-2.21168297	-2.74115339	-0.44418542	3.50652631	-0.09174717	-0.48811459
C	1.38619870	-1.34248923	-0.00020877	-1.91545028	-0.23432812	-0.00400839	1.34811484	-1.37543007	0.00288380
C	1.24750245	-2.72715707	0.15145814	-2.89945984	0.74824126	0.16141347	1.16938693	-2.75059790	0.19372541
C	2.89403500	-4.68041295	0.20224450	-5.44219208	0.71741821	0.19473635	2.74853887	-4.74751596	0.26499535
C	0.00699162	-3.53497971	0.39202494	-2.74205526	2.21264777	0.43534476	-0.09182483	-3.50666750	0.48997999
C	-1.34256781	-1.38605310	-0.00115561	-0.23489854	1.91518775	-0.00248822	-1.37527478	-1.34843934	-0.00251369
C	-2.72724417	-1.24728218	-0.15251652	0.74795136	2.89879129	-0.16867162	-2.75032292	-1.16983703	-0.19437164
C	-4.68041009	-2.89386518	-0.20484915	0.71735695	5.44152002	-0.20659791	-4.74717830	-2.74908007	-0.26602263
H	4.42891421	-0.02923938	0.25266568	-2.81140445	-3.43231122	0.17186199	4.44351641	-0.14864936	0.09093840
H	3.89626214	-0.03151906	-1.44123384	-2.43017581	-2.97276064	-1.50416571	3.78099652	-0.13599850	-1.55971039
H	2.42627767	-5.25856996	-0.61153666	-5.56949593	1.47449473	-0.59579328	2.22701208	-5.33290634	-0.50884838
H	3.98803553	-4.73946807	0.12054363	-6.18649697	-0.08230367	0.07892907	3.83503267	-4.84971405	0.14393743
H	2.56807799	-5.07760025	1.17734678	-5.54307808	1.19391615	1.18321628	2.44460826	-5.09852852	1.26390267
H	-0.03143263	-3.89648769	1.43852533	-2.97466313	2.43433083	1.49442948	-0.13661852	-3.78096019	1.56158743
H	-0.02930310	-4.42882028	-0.25550715	-3.43261583	2.81051719	-0.18317989	-0.14842023	-4.44375704	-0.08895106
H	-5.07737296	-2.56723601	-1.17981394	1.19490500	5.54057115	-1.19475245	-5.09758912	-2.44564750	-1.26529101
H	-4.73942475	-3.98793005	-0.12395648	-0.08247524	6.18604870	-0.09300224	-4.84939505	-3.83552226	-0.14451234
H	-5.25876826	-2.42669218	0.60912278	1.47357202	5.57025768	0.58452847	-5.33307721	-2.22722154	0.50721160
N	-0.00161426	0.00147827	-1.88362853	0.00498592	-0.00320904	-1.87804854	0.00115185	-0.00016773	-1.87603476
C	-0.00315487	0.00296272	-3.05202278	0.01044318	-0.00604755	-3.04657311	0.00245609	0.00046010	-3.04407396
C	-0.00546432	0.00474875	-4.50889814	0.02909405	-0.01168512	-4.49958556	0.00933858	0.00256599	-4.49961045
H	0.87119876	0.55340194	-4.89761364	-0.10922930	-1.03977199	-4.88029091	0.90439805	0.52686642	-4.87855181
H	0.02909292	-1.02862347	-4.89819755	-0.78283216	0.62446604	-4.89579809	0.01780503	-1.03219361	-4.88527411
H	-0.91859954	0.49263455	-4.89473492	0.99505076	0.37561167	-4.87122664	-0.88904586	0.51510119	-4.88671949

Table S9 Coordinates of **2** calculated by Gaussian (charge 3, multiplicity 2, SCF: E(gas phase) = -1665.458341 h, E(SMD) = -1665.919714 h, E(PCM) = -1665.875881 h).

Atom	**gas phase**			**SMD**			**PCM**		
	Coordinate [Å]			**Coordinate [Å]**			**Coordinate [Å]**		
	X	**Y**	**Z**	**X**	**Y**	**Z**	**X**	**Y**	**Z**
Fe	0.00000000	0.00000000	0.00000000	0.00000000	0.00000000	0.00000000	-0.00049448	0.00009153	0.00003395
C	-1.67298132	2.35144905	-2.14175802	-1.67832598	2.35386316	-2.12112066	1.31245405	-3.27407833	0.44633413
H	-2.74528566	2.61990178	-2.11508002	-2.74626191	2.63108342	-2.07688338	1.62055326	-4.13515172	-0.16840348
H	-1.23021358	2.88798771	-3.00128619	-1.22967868	2.89531272	-2.97281820	1.39251476	-3.57393455	1.50756967
C	-0.98254973	-0.09519144	-1.70516570	-0.97713589	-0.08177577	-1.70480979	-0.74214263	-1.81071431	-0.00085846
C	-1.23253627	-1.22878268	-2.47528337	-1.23561731	-1.21821157	-2.46756556	-2.07501378	-2.16904111	-0.17358959
C	-2.46581940	-1.60590272	-4.69070030	-2.51130370	-1.61765583	-4.62972607	-3.27877133	-4.41557486	-0.23470885
H	-2.98707824	-0.92778501	-5.38065374	-3.03194180	-0.95158173	-5.33092621	-2.93359888	-5.45184840	-0.12675494
H	-3.16717228	-2.36342992	-4.30477650	-3.20979530	-2.36014873	-4.21218563	-3.73536970	-4.26741126	-1.22513654
H	-1.62372826	-2.09480619	-5.20690529	-1.67687671	-2.13095883	-5.13304785	-4.00583740	-4.17285536	0.55588793
C	-0.85174332	-2.66277674	-2.25816148	-0.84263695	-2.64626907	-2.26931614	-3.27373237	-1.31214961	-0.44769768
H	-1.74754313	-3.30871865	-2.20340966	-1.73705841	-3.29292181	-2.23302865	-3.56880884	-1.39017686	-1.51040276
H	-0.23445939	-3.04214039	-3.09342474	-0.21519370	-2.99541425	-3.10875951	-4.13741271	-1.62124880	0.16280732
C	0.30568805	-1.94530948	-0.06747191	0.30424711	-1.94057604	-0.08267304	-1.81134149	0.74191232	0.00410253
C	0.98995947	-2.72684197	0.86074564	0.99029709	-2.71908369	0.84624823	-2.16991373	2.07461677	0.17763009
C	1.51795323	-5.23180450	0.99324265	1.51262362	-5.19956443	1.00120414	-4.41773566	3.27689732	0.24037042
H	1.28369981	-6.08075307	0.33597161	1.32680979	-6.05232540	0.33460306	-5.45386673	2.92980057	0.13737413
H	1.06998159	-5.39001017	1.98768632	1.02680178	-5.35960793	1.97697552	-4.17980657	4.00299665	-0.55254047
H	2.61014614	-5.11400189	1.08221360	2.59444694	-5.04837457	1.14319942	-4.26651230	3.73510481	1.22955651
C	2.62413200	0.46455327	-1.53677851	2.63033837	0.46618629	-1.48434023	0.00606638	0.00304888	3.05548782
C	3.86466710	0.68463863	-2.26210716	3.88302015	0.68609508	-2.17777022	0.01240553	0.00259241	4.50634674
H	3.99501634	-0.08942936	-3.03965431	4.00884966	-0.07144656	-2.97135001	-0.99260921	-0.25033257	4.88545940
H	4.72466067	0.64009239	-1.56985571	4.72263725	0.60801532	-1.46460862	0.29821605	1.00110870	4.87925505
H	3.85194680	1.67677971	-2.74816095	3.88679125	1.69217472	-2.63286001	0.73730334	-0.74208823	4.87745822
N	-1.58474351	0.90668133	-2.42801963	-1.59974722	0.91407648	-2.41068532	-0.10967463	-3.01449848	0.15984879
N	-2.16817868	0.49203508	-3.54886554	-2.20592827	0.49611598	-3.51871121	-0.92252794	-4.06566463	0.09686681
N	-1.95107765	-0.80359464	-3.57129651	-1.97881928	-0.80086372	-3.54114030	-2.11355571	-3.54003410	-0.10363871
N	-0.08452945	-2.86253135	-1.01373819	-0.08568218	-2.85451178	-1.02606453	-3.01497334	0.10927187	-0.15728917
N	0.29413649	-4.10969283	-0.74947911	0.29392570	-4.10221431	-0.76217162	-4.06629362	0.92169033	-0.09379188

N	0.94518407	-4.02034306	0.38824082	0.94561176	-4.00611168	0.37798320	-3.54106079	2.11273392	0.10754943
N	1.63022441	0.28837795	-0.95523353	1.62648298	0.28899747	-0.92482966	0.00260012	0.00234149	1.89298690
C	1.67298132	-2.35144905	2.14175802	1.67832598	-2.35386316	2.12112066	-1.31258784	3.27396196	0.44853051
H	2.74528566	-2.61990178	2.11508002	2.74626191	-2.63108342	2.07688338	-1.38896289	3.57181861	1.51055025
H	1.23021358	-2.88798771	3.00128619	1.22967868	-2.89531272	2.97281820	-1.62217903	4.13640483	-0.16349413
C	0.98254973	0.09519144	1.70516570	0.97713589	0.08177577	1.70480979	0.74124621	1.81091390	-0.00316852
C	1.23253627	1.22878268	2.47528337	1.23561731	1.21821157	2.46756556	2.07386431	2.16928879	-0.17730946
C	2.46581940	1.60590272	4.69070030	2.51130370	1.61765583	4.62972607	3.27711385	4.41610202	-0.24182493
H	2.98707824	0.92778501	5.38065374	3.03194180	0.95158173	5.33092621	2.93247085	5.45222369	-0.13086639
H	3.16717228	2.36342992	4.30477650	3.20979530	2.36014873	4.21218563	4.00681665	4.17162228	0.54580420
H	1.62372826	2.09480619	5.20690529	1.67687671	2.13095883	5.13304785	3.73055356	4.26976008	-1.23395799
C	0.85174332	2.66277674	2.25816148	0.84263695	2.64626907	2.26931614	3.27222573	1.31217394	-0.45212631
H	1.74754313	3.30871865	2.20340966	1.73705841	3.29292181	2.23302865	4.13652544	1.62172403	0.15726052
H	0.23445939	3.04214039	3.09342474	0.21519370	2.99541425	3.10875951	3.56624325	1.38959770	-1.51518098
C	-0.30568805	1.94530948	0.06747191	-0.30424711	1.94057604	0.08267304	1.81007630	-0.74191067	0.00041833
C	-0.98995947	2.72684197	-0.86074564	-0.99029709	2.71908369	-0.84624823	2.16885527	-2.07438917	0.17480296
C	-1.51795323	5.23180450	-0.99324265	-1.51262362	5.19956443	-1.00120414	4.41656144	-3.27647533	0.23962530
H	-1.28369981	6.08075307	-0.33597161	-1.32680979	6.05232540	-0.33460306	5.45261099	-2.93015918	0.13303306
H	-1.06998159	5.39001017	-1.98768632	-1.02680178	5.35960793	-1.97697552	4.26760043	-3.73203350	1.23039470
H	-2.61014614	5.11400189	-1.08221360	-2.59444694	5.04837457	-1.14319942	4.17614674	-4.00485018	-0.55043912
N	1.58474351	-0.90668133	2.42801963	1.59974722	-0.91407648	2.41068532	0.10863885	3.01471587	0.15700996
N	2.16817868	-0.49203508	3.54886554	2.20592827	-0.49611598	3.51871121	0.92130724	4.06596716	0.09274842
N	1.95107765	0.80359464	3.57129651	1.97881928	0.80086372	3.54114030	2.11224305	3.54039679	-0.10861507
N	0.08452945	2.86253135	1.01373819	0.08568218	2.85451178	1.02606453	3.01369698	-0.10902641	-0.16024318
N	-0.29413649	4.10969283	0.74947911	-0.29392570	4.10221431	0.76217162	4.06516174	-0.92126537	-0.09582640
N	-0.94518407	4.02034306	-0.38824082	-0.94561176	4.00611168	-0.37798320	3.54003529	-2.11232078	0.10574850
C	-2.62413200	-0.46455327	1.53677851	-2.63033837	-0.46618629	1.48434023	-0.00390084	-0.00343901	-3.05542254
C	-3.86466710	-0.68463863	2.26210716	-3.88302015	-0.68609508	2.17777022	0.00019893	-0.00584400	-4.50626861
H	-3.99501634	0.08942936	3.03965431	-4.00884966	0.07144656	2.97135001	1.03212479	0.11655494	-4.87755750
H	-4.72466067	-0.64009239	1.56985571	-4.72263725	-0.60801532	1.46460862	-0.40739630	-0.96068742	-4.88024401
H	-3.85194680	-1.67677971	2.74816095	-3.88679125	-1.69217472	2.63286001	-0.62086087	0.82410928	-4.88452737
N	-1.63022441	-0.28837795	0.95523353	-1.62648298	-0.28899747	0.92482966	-0.00405042	-0.00141898	-1.89304460

Table S10 Coordinates of **1**-MeCN calculated by Gaussian (charge 2, multiplicity 1, SCF: E(gas phase) = -1533.242747 h, E(SMD) = -1533.471750 h, E(PCM) = -1533.438315 h).

Atom	**gas phase**			**SMD**			**PCM**		
	Coordinate [Å]			**Coordinate [Å]**			**Coordinate [Å]**		
	X	**Y**	**Z**	**X**	**Y**	**Z**	**X**	**Y**	**Z**
Fe	-0.00019963	0.00007354	0.01717425	-0.00042861	0.00049508	-0.06509939	0.00017580	0.00006028	-0.08211227
N	1.41721203	-2.65346985	-0.37391476	1.50680896	-2.60657026	-0.38556067	1.44494319	-2.63267020	-0.43088924
N	2.61043686	-3.22656972	-0.50862084	2.72442585	-3.14245592	-0.46148661	2.64954604	-3.20048349	-0.47286269
N	3.45957247	-2.22768626	-0.37417630	3.53401495	-2.10874012	-0.32121834	3.47987703	-2.19399758	-0.27017444
N	2.66477806	1.40992822	-0.18151084	2.61595914	1.50181137	-0.18710634	2.64288101	1.43746272	-0.13766932
N	3.25725068	2.57887491	-0.40134175	3.16514529	2.70248393	-0.35755842	3.23019979	2.61791086	-0.31658970
N	2.25274149	3.42351184	-0.52559895	2.12679038	3.50818581	-0.48747396	2.21925283	3.44452798	-0.51369072
C	0.25861216	-3.54923221	-0.47021705	0.37810051	-3.53342223	-0.51714871	0.29499996	-3.51508759	-0.66541452
C	1.44096447	-1.28320650	-0.14968044	1.48145496	-1.23453503	-0.19637997	1.44916606	-1.26659961	-0.20520155
C	2.82146577	-1.03292171	-0.15895683	2.85182027	-0.93504372	-0.16028906	2.82256424	-1.00478372	-0.10448728
C	4.89753170	-2.49147647	-0.47314992	4.97950524	-2.31086325	-0.34893163	4.91930287	-2.44690901	-0.23405005
C	3.54034119	0.25942436	0.06958494	3.52852332	0.37984941	0.05832592	3.50533258	0.29490329	0.18802975
C	1.27661431	1.44269479	-0.15275482	1.23057270	1.48192827	-0.19994985	1.26002350	1.45074416	-0.21081947
C	1.03509354	2.80426977	-0.38590015	0.93684889	2.83831877	-0.40038208	1.00736812	2.80618665	-0.46011549
C	2.52881857	4.83604321	-0.79665865	2.33427350	4.93614015	-0.70700396	2.48356649	4.85821829	-0.77374832
H	0.33910836	-4.29553472	0.34318545	0.47724949	-4.30839251	0.26471908	0.38853802	-4.37906259	0.01573764
H	0.34134338	-4.10557241	-1.42228575	0.46518776	-4.04495204	-1.49319895	0.37122487	-3.90634776	-1.69702248
H	5.31514620	-1.94295150	-1.33337712	5.40809359	-1.75265062	-1.19692105	5.41828057	-1.83152191	-0.99898031
H	5.03356626	-3.57188186	-0.61867815	5.17207238	-3.38610344	-0.46494957	5.08003418	-3.51212975	-0.44565666
H	5.39619144	-2.17132467	0.45581520	5.41479990	-1.94377182	0.59408198	5.31269896	-2.19523872	0.76330822
H	3.90264379	0.32603156	1.11467491	3.89606962	0.45474097	1.09975405	3.76854773	0.35845582	1.26139593
H	4.42123686	0.36382609	-0.58588936	4.39886402	0.49910281	-0.60783473	4.43902675	0.40617501	-0.38623669
H	2.09967134	5.11592960	-1.77276412	1.87886112	5.22513402	-1.66785328	2.15175748	5.11397240	-1.79265165

H	3.61895490	4.97123458	-0.81491945	3.41602350	5.12633434	-0.72492515	3.56446309	5.02409755	-0.67609065
H	2.08654135	5.45691961	-0.00072542	1.86026801	5.50111146	0.11168397	1.93965531	5.47196824	-0.03891618
N	-1.41764339	2.65370021	-0.37314165	-1.50800228	2.60783752	-0.38164530	-1.44438550	2.63278136	-0.43150672
N	-2.61086063	3.22683581	-0.50760600	-2.72567126	3.14362300	-0.45736815	-2.64895936	3.20065470	-0.47343966
N	-3.46000392	2.22795708	-0.37328804	-3.53517080	2.10980335	-0.31737915	-3.47935020	2.19418345	-0.27092701
N	-2.66520205	-1.40971277	-0.18136057	-2.61696475	-1.50068304	-0.18599288	-2.64240550	-1.43730465	-0.13841414
N	-3.25770125	-2.57869305	-0.40092952	-3.16628699	-2.70123764	-0.35676062	-3.22966646	-2.61783921	-0.31695676
N	-2.25321025	-3.42330061	-0.52543357	-2.12805700	-3.50679944	-0.48847916	-2.21867483	-3.44448065	-0.51372960
C	-0.25908160	3.54950700	-0.46944763	-0.37942935	3.53490738	-0.51301310	-0.29437769	3.51516132	-0.66581862
C	-1.44138167	1.28338120	-0.14919566	-1.48251374	1.23571117	-0.19297433	-1.44868811	1.26666621	-0.20609976
C	-2.82188572	1.03313479	-0.15839331	-2.85285617	0.93612081	-0.15683431	-2.82209381	1.00491509	-0.10538542
C	-4.89796686	2.49184095	-0.47190170	-4.98067890	2.31180240	-0.34540046	-4.91875960	2.44717221	-0.23472411
C	-3.54075309	-0.25924959	0.06987796	-3.52931941	-0.37895717	0.06133369	-3.50484920	-0.29474072	0.18724414
C	-1.27702860	-1.44243186	-0.15301057	-1.23158498	-1.48071183	-0.20045079	-1.25955237	-1.45054763	-0.21157492
C	-1.03554228	-2.80400621	-0.38618151	-0.93804497	-2.83694344	-0.40227797	-1.00681666	-2.80606644	-0.46032869
C	-2.52932807	-4.83590419	-0.79606509	-2.33574783	-4.93459899	-0.70882584	-2.48292322	-4.85828850	-0.77321869
H	-0.34202752	4.10611659	-1.42133709	-0.46751252	4.04779751	-1.48825119	-0.37020389	3.90617815	-1.69754978
H	-0.33944421	4.29556920	0.34419059	-0.47783035	4.30879009	0.27003532	-0.38819885	4.37929154	0.01509476
H	-5.39634284	2.17227820	0.45742154	-5.41621815	1.94435295	0.59735571	-5.31210057	2.19560533	0.76268449
H	-5.03392768	3.57218112	-0.61797573	-5.17330517	3.38706261	-0.46113361	-5.07945378	3.51238391	-0.44640547
H	-5.31594150	1.94288410	-1.33167485	-5.40895879	1.75384013	-1.19371522	-5.41781859	1.83174595	-0.99956880
H	-4.42164363	-0.36352722	-0.58562836	-4.40035071	-0.49767741	-0.60400679	-4.43861147	-0.40606296	-0.38690415
H	-3.90316705	-0.32606787	1.11493062	-3.89575645	-0.45476707	1.10310341	-3.76796240	-0.35822065	1.26066634
H	-2.08723480	-5.45652601	0.00017144	-1.86109043	-5.50015148	0.10908662	-1.93908295	-5.47170482	-0.03805550
H	-3.61946931	-4.97103283	-0.81445411	-3.41751562	-5.12476084	-0.72598456	-3.56382635	-5.02415234	-0.67560611
H	-2.10003418	-5.11614315	-1.77200221	-1.88113584	-5.22293898	-1.67024767	-2.15098865	-5.11447677	-1.79197080
N	0.00052810	-0.00040507	1.83060489	0.00165289	-0.00159808	1.74271074	-0.00083529	-0.00004683	1.72508336
C	0.00164061	-0.00089152	3.00052143	0.00406158	-0.00399484	2.91370461	-0.00198286	-0.00029348	2.89495761
C	0.00388379	-0.00179154	4.45700392	0.00959337	-0.01034384	4.36699560	-0.00432653	-0.00119134	4.34983835
H	0.48001871	0.91677679	4.84511127	0.48055589	0.91149623	4.75455441	0.49079839	0.90735690	4.73656972
H	-1.02887779	-0.04918748	4.84723102	-1.02353836	-0.06770342	4.75577981	-1.03997779	-0.02624957	4.73334964
H	0.56160156	-0.87381072	4.84382498	0.57632617	-0.88057278	4.74569727	0.53394692	-0.88527456	4.73559624

Table S11 Coordinates of **2**-MeCN calculated by Gaussian (charge 3, multiplicity 2, SCF: E(gas phase) = -1532.819601 h, E(SMD) = -1533.302759 h, E(PCM) = -1533.253453 h).

Atom	**gas phase**			**SMD**			**PCM**		
	Coordinate [Å]			**Coordinate [Å]**			**Coordinate [Å]**		
	X	**Y**	**Z**	**X**	**Y**	**Z**	**X**	**Y**	**Z**
Fe	0.03817481	-0.00795896	0.14085880	-0.03700280	0.00308035	-0.09184646	0.04108500	0.00736900	-0.05968500
N	-2.93537692	-0.52839403	-0.30141730	2.95581771	0.44715172	-0.23044064	-2.68384900	-1.29429500	-0.22893900
N	-3.83807823	-1.46062952	-0.55852588	3.90206048	1.36409437	-0.37666199	-3.32083500	-2.44050000	-0.41155800
N	-3.15593832	-2.58474959	-0.58751133	3.23956034	2.49836931	-0.49616364	-2.35714200	-3.32751300	-0.56036400
N	0.55275937	-2.99152405	-0.29506819	-0.47106862	3.00031973	-0.38934905	1.33985500	-2.72234100	-0.38977000
N	1.51127426	-3.88084877	-0.48587477	-1.41323639	3.93166473	-0.42718451	2.51241600	-3.33644200	-0.42373500
N	2.62927287	-3.19115501	-0.40542259	-2.54003959	3.26478393	-0.26744955	3.39231000	-2.37472500	-0.22792000
C	-3.43495881	0.84689519	-0.16438541	3.39220865	-0.93866641	-0.01606615	-3.50083500	-0.10424900	0.04495900
C	-1.64272329	-1.00190531	-0.16703264	1.67468813	0.94634719	-0.26392040	-1.31157300	-1.39415000	-0.26956200
C	-1.81710164	-2.37674972	-0.36078624	1.88443007	2.31503471	-0.43987417	-1.11275000	-2.75799400	-0.48501700
C	-3.85464627	-3.85044668	-0.86364587	3.96368977	3.75512454	-0.67285312	-2.69192600	-4.73254400	-0.79767900
C	-0.82757201	-3.49561569	-0.31338408	0.91758834	3.44621040	-0.56124850	0.14717000	-3.54934300	-0.62181100
C	1.00125718	-1.69995514	-0.09061459	-0.94821204	1.72309105	-0.22006140	1.41829100	-1.36478800	-0.18411000
C	2.39054392	-1.85787993	-0.17426286	-2.32958720	1.91783658	-0.14254832	2.79467800	-1.15007300	-0.08202100
C	3.91894813	-3.87952160	-0.58155601	-3.81512639	3.98046113	-0.25187595	4.82029100	-2.69743900	-0.19007700
H	-3.93746352	0.93145141	0.81918072	3.78127133	-1.01692903	1.01631057	-3.83457300	-0.15904200	1.09814600
H	-4.20864289	0.99670585	-0.93657557	4.22861805	-1.13955539	-0.70479031	-4.39643500	-0.16182700	-0.59294900
H	-3.48219428	-4.27352455	-1.81109473	3.65329361	4.21689191	-1.62353256	-2.34400500	-5.02547100	-1.80062900
H	-4.92803471	-3.62998434	-0.94805844	5.03809791	3.52859742	-0.68750723	-3.78261000	-4.83391900	-0.72842600
H	-3.67715027	-4.55255987	-0.03328413	3.72217607	4.42753072	0.16553541	-2.20268600	-5.35296300	-0.03124800
H	-0.97750115	-4.12004665	0.58879561	1.12532569	4.22035222	0.19780123	0.16939500	-4.38457900	0.09923100
H	-0.92638098	-4.16271403	-1.18803504	1.00305123	3.92307735	-1.55425988	0.23053600	-3.98262100	-1.63463500

H	4.42058393	-3.48904385	-1.48229169	-4.42179553	3.65103214	-1.11051990	5.34012800	-2.13619300	-0.98177000
H	3.71234417	-4.95204311	-0.70367094	-3.60027978	5.05506955	-0.32239762	4.92294600	-3.77658800	-0.36201600
H	4.54422587	-3.71407598	0.31032720	-4.34031766	3.75203666	0.68870392	5.22736600	-2.42784200	0.79634800
N	2.99680332	0.52424650	-0.17726136	-3.00920773	-0.44597949	-0.14135294	2.74650100	1.30646700	-0.09874100
N	3.90736711	1.45013240	-0.42435623	-3.96141234	-1.35927251	-0.26847195	3.39316300	2.44710200	-0.28049200
N	3.23120519	2.57829481	-0.47779132	-3.30631646	-2.49705945	-0.39927611	2.43802700	3.33998300	-0.44992400
N	-0.48558611	2.97061561	-0.32536897	0.41111830	-2.99032055	-0.39679201	-1.26631300	2.73006000	-0.41169900
N	-1.43172781	3.86422708	-0.56228536	1.34968148	-3.92327658	-0.47679996	-2.43599700	3.34700300	-0.48846800
N	-2.55358242	3.17858512	-0.53996284	2.48380498	-3.25864106	-0.37104032	-3.32561900	2.38354000	-0.35702800
C	3.48530473	-0.85239365	-0.01246294	-3.43286459	0.93997412	0.09731523	3.54940100	0.11123300	0.19456800
C	1.70438174	1.01001617	-0.05423050	-1.73032734	-0.95537382	-0.18097430	1.37324900	1.42091600	-0.13939700
C	1.89003307	2.37967551	-0.26170242	-1.94992509	-2.32143021	-0.35276480	1.18846100	2.78267100	-0.37130900
C	3.94093094	3.83670139	-0.76077170	-4.03913487	-3.75078477	-0.56219604	2.78624600	4.73837000	-0.70615200
C	0.88970936	3.48801369	-0.25216129	-0.98230821	-3.44972216	-0.48036789	-0.06784100	3.57314900	-0.53627100
C	-0.95201893	1.68102598	-0.13343262	0.89931932	-1.71415612	-0.23324256	-1.35811600	1.36889600	-0.22324700
C	-2.33253384	1.84793301	-0.28061033	2.28050713	-1.91443290	-0.21547618	-2.73664400	1.15873000	-0.18680600
C	-3.82938692	3.86889410	-0.79141123	3.75689785	-3.97573076	-0.42456627	-4.75356900	2.70606700	-0.39997900
H	4.29125144	-1.00501261	-0.75023715	-4.29557726	1.14447607	-0.55694203	4.46703000	0.17557100	-0.41040300
H	3.94589392	-0.93601887	0.99181560	-3.78235214	1.01561540	1.14412287	3.84744600	0.15354200	1.25899600
H	3.74928611	4.55274912	0.05430767	-3.78884786	-4.42096702	0.27548105	2.28606500	5.37600700	0.03853500
H	5.01487107	3.61079706	-0.81962623	-5.11257763	-3.51942018	-0.56210801	3.87601400	4.83474800	-0.61787000
H	3.58937331	4.24494281	-1.72266182	-3.74377992	-4.21740233	-1.51525014	2.45985000	5.01415900	-1.72109900
H	1.03204898	4.17342971	-1.10591649	-1.11375969	-3.96791200	-1.44692280	-0.10002100	4.05955600	-1.52719800
H	0.97973020	4.09532152	0.66959054	-1.14483616	-4.19330839	0.31979281	-0.13561600	4.36865600	0.22632600
H	-4.50759780	3.70243943	0.06061475	4.32471026	-3.76424940	0.49499615	-5.22221400	2.40861200	0.55021600
H	-3.61455835	4.94141708	-0.89854837	3.53704103	-5.04873834	-0.50407334	-4.84642400	3.78978400	-0.54707600
H	-4.27652242	3.48110266	-1.72157148	4.32438872	-3.63242234	-1.30432461	-5.22093800	2.16752200	-1.23906500
N	-0.22943904	0.03602881	1.95223421	0.16598405	-0.01694761	1.71605035	-0.20107800	-0.03126400	1.74159500
C	-0.33643783	0.04974893	3.11472229	0.27975017	-0.01576455	2.87488524	-0.33617600	-0.05572500	2.89734900
C	-0.46557062	0.06570018	4.55947737	0.42963238	-0.01362040	4.31327532	-0.50559600	-0.08647500	4.33532500
H	0.24259467	-0.65542440	5.00815399	0.38562809	1.02248455	4.69287159	0.37279000	-0.56557900	4.80168700
H	-0.24807620	1.07471852	4.95448257	-0.37755241	-0.60940730	4.77484822	-0.60962400	0.94099900	4.72402400
H	-1.49225211	-0.22231808	4.85176441	1.40556674	-0.45753268	4.58006013	-1.40927100	-0.66716700	4.58941100

Table S12 Löwdin charges of **1** in atomic units.

Atom	Type	H separate	H summed into heavy atoms
		Charge	Charge
1	Fe	-1.793295	-1.793295
2	N	0.123565	0.123565
3	N	-0.036279	-0.036279
4	N	0.126541	0.126541
5	N	0.123585	0.123585
6	N	-0.036262	-0.036262
7	N	0.126534	0.126534
8	N	0.226816	0.226816
9	C	0.078775	0.195637
10	C	0.093227	0.093227
11	C	-0.009595	-0.009595
12	C	0.056278	0.215411
13	C	0.078777	0.195611
14	C	0.093236	0.093236
15	C	-0.009633	-0.009633
16	C	0.056274	0.215403
17	C	0.075804	0.075804
18	C	-0.041695	0.177017
19	H	0.059929	0.000000
20	H	0.056933	0.000000
21	H	0.049399	0.000000
22	H	0.059632	0.000000
23	H	0.050102	0.000000
24	H	0.056953	0.000000

25	H	0.059881	0.000000
26	H	0.050122	0.000000
27	H	0.059635	0.000000
28	H	0.049372	0.000000
29	H	0.073099	0.000000
30	H	0.072627	0.000000
31	H	0.072987	0.000000
32	N	0.123592	0.123592
33	N	-0.036267	-0.036267
34	N	0.126516	0.126516
35	N	0.123571	0.123571
36	N	-0.036284	-0.036284
37	N	0.126527	0.126527
38	C	0.078780	0.195666
39	C	0.093218	0.093218
40	C	-0.009625	-0.009625
41	C	0.056272	0.215403
42	C	0.078773	0.195684
43	C	0.093216	0.093216
44	C	-0.009595	-0.009595
45	C	0.056276	0.215413
46	H	0.056910	0.000000
47	H	0.059976	0.000000
48	H	0.050104	0.000000
49	H	0.059631	0.000000
50	H	0.049396	0.000000
51	H	0.060013	0.000000
52	H	0.056897	0.000000
53	H	0.049422	0.000000
54	H	0.059628	0.000000
55	H	0.050087	0.000000
56	N	0.226815	0.226815
57	C	0.075811	0.075811
58	C	-0.041694	0.177018
59	H	0.072712	0.000000
60	H	0.073185	0.000000
61	H	0.072815	0.000000

Table S13 Löwdin charges of **2** in atomic units.

Atom	Type	H separate Charge	H summed into heavy atoms Charge
1	Fe	-1.474885	-1.474885
2	C	0.851140	0.229429
3	H	0.072137	0.000000
4	H	0.072178	0.000000
5	C	0.063561	0.063561
6	C	0.005483	0.005483
7	C	0.066359	0.254888
8	H	0.070644	0.000000
9	H	0.058980	0.000000
10	H	0.058905	0.000000
11	C	0.085121	0.229434
12	H	0.072210	0.000000
13	H	0.072103	0.000000
14	C	0.063562	0.063562
15	C	0.005474	0.005474
16	C	0.066358	0.254890
17	H	0.070646	0.000000
18	H	0.058910	0.000000
19	H	0.058977	0.000000
20	C	0.145518	0.145518

21	C	-0.033094	0.233573
22	H	0.088895	0.000000
23	H	0.088880	0.000000
24	H	0.088893	0.000000
25	N	0.135990	0.135990
26	N	0.002944	0.002944
27	N	0.139136	0.139136
28	N	0.135977	0.135977
29	N	0.002953	0.002953
30	N	0.139131	0.139131
31	N	0.195500	0.195500
32	C	0.085114	0.229429
33	H	0.072137	0.000000
34	H	0.072178	0.000000
35	C	0.063561	0.063561
36	C	0.005483	0.005483
37	C	0.066359	0.254888
38	H	0.070644	0.000000
39	H	0.058980	0.000000
40	H	0.058905	0.000000
41	C	0.085121	0.229434
42	H	0.072210	0.000000
43	H	0.072103	0.000000
44	C	0.063562	0.063562
45	C	0.005474	0.005474
46	C	0.066358	0.254890
47	H	0.070646	0.000000
48	H	0.058910	0.000000
49	H	0.058977	0.000000
50	N	0.135990	0.135990
51	N	0.002944	0.002944
52	N	0.139136	0.139136
53	N	0.135977	0.135977
54	N	0.002953	0.002953
55	N	0.139131	0.139131
56	C	0.145518	0.145518
57	C	-0.033094	0.233573
58	H	0.088895	0.000000
59	H	0.088880	0.000000
60	H	0.088893	0.000000
61	N	0.195500	0.195500

Table S14 Löwdin charges of **1**-MeCN in atomic units.

Atom	Type	H separate Charge	H summed into heavy atoms Charge
1	Fe	-1.399131	-1.399131
2	N	0.126714	0.126714
3	N	-0.025866	-0.025866
4	N	0.129393	0.129393
5	N	0.127429	0.127429
6	N	-0.024001	-0.024001
7	N	0.127010	0.127010
8	C	0.076503	0.202138
9	C	0.068201	0.068201
10	C	-0.002088	-0.002088
11	C	0.058050	0.222960
12	C	0.079748	0.204533
13	C	0.066206	0.066206
14	C	0.000091	0.000091
15	C	0.058084	0.222780
16	H	0.063449	0.000000

17	H	0.062186	0.000000
18	H	0.052547	0.000000
19	H	0.061376	0.000000
20	H	0.050987	0.000000
21	H	0.065843	0.000000
22	H	0.058942	0.000000
23	H	0.052271	0.000000
24	H	0.061450	0.000000
25	H	0.050976	0.000000
26	N	0.126746	0.126746
27	N	-0.025803	-0.025803
28	N	0.129405	0.129405
29	N	0.127429	0.127429
30	N	-0.023985	-0.023985
31	N	0.127042	0.127042
32	C	0.076505	0.202157
33	C	0.068186	0.068186
34	C	-0.002106	-0.002106
35	C	0.058055	0.222957
36	C	0.079737	0.204417
37	C	0.066204	0.066204
38	C	0.000129	0.000129
39	C	0.058090	0.222797
40	H	0.062184	0.000000
41	H	0.063468	0.000000
42	H	0.050987	0.000000
43	H	0.061384	0.000000
44	H	0.052531	0.000000
45	H	0.058951	0.000000
46	H	0.065729	0.000000
47	H	0.050999	0.000000
48	H	0.061451	0.000000
49	H	0.052257	0.000000
50	N	0.249057	0.249057
51	C	0.078458	0.078458
52	C	-0.039665	0.180537
53	H	0.073526	0.000000
54	H	0.073198	0.000000
55	H	0.073478	0.000000

Table S15 Löwdin charges of **2**-MeCN in atomic units.

Atom	Type	H separate Charge	H summed into heavy atoms Charge
1	Fe	-1.141500	-1.141500
2	N	0.139310	0.139310
3	N	0.016516	0.016516
4	N	0.140212	0.140212
5	N	0.142180	0.142180
6	N	0.021967	0.021967
7	N	0.140676	0.140676
8	C	0.085344	0.238548
9	C	0.053971	0.053971
10	C	0.018358	0.018358
11	C	0.068283	0.263308
12	C	0.084637	0.238617
13	C	0.040022	0.040022
14	C	0.025164	0.025164
15	C	0.068546	0.264709
16	H	0.079205	0.000000
17	H	0.074000	0.000000
18	H	0.062512	0.000000

19	H	0.072463	0.000000
20	H	0.060050	0.000000
21	H	0.078204	0.000000
22	H	0.075776	0.000000
23	H	0.062686	0.000000
24	H	0.072902	0.000000
25	H	0.060575	0.000000
26	N	0.141715	0.141715
27	N	0.019314	0.019314
28	N	0.140768	0.140768
29	N	0.139459	0.139459
30	N	0.018617	0.018617
31	N	0.140766	0.140766
32	C	0.086225	0.243101
33	C	0.038534	0.038534
34	C	0.022416	0.022416
35	C	0.068632	0.264498
36	C	0.085168	0.239430
37	C	0.054716	0.054716
38	C	0.018895	0.018895
39	C	0.068274	0.263555
40	H	0.075469	0.000000
41	H	0.081408	0.000000
42	H	0.060593	0.000000
43	H	0.072600	0.000000
44	H	0.062673	0.000000
45	H	0.075160	0.000000
46	H	0.079102	0.000000
47	H	0.059840	0.000000
48	H	0.072625	0.000000
49	H	0.062816	0.000000
50	N	0.217117	0.217117
51	C	0.178110	0.178110
52	C	-0.027468	0.256930
53	H	0.096237	0.000000
54	H	0.093415	0.000000
55	H	0.094746	0.000000

Table S16 Coordinates of the oxoiron(IV) aNHC species $Fe^{IV}[cCCCC]_{trz}O(MeCN)$ calculated by Gaussian (charge 2, multiplicity 3, SCF: E(gas phase) = -1608.58386 h, E(SMD) = -1608.396220 h, E(PCM) = -1608.551107 h).

Atom	**gas phase**			**SMD**			**PCM**		
	Coordinate [Å]			**Coordinate [Å]**			**Coordinate [Å]**		
	X	**Y**	**Z**	**X**	**Y**	**Z**	**X**	**Y**	**Z**
Fe	-0.00056190	0.00011965	-0.21709907	-0.00121005	0.00546244	-0.51602674	-0.00057896	0.00025533	-0.51676418
N	1.33851350	-2.69513318	-0.36414707	-2.64605445	-1.46128151	-0.35104068	-2.74415746	-1.25479573	-0.40832777
N	2.51325896	-3.32180831	-0.38294677	-3.21344453	-2.65156459	-0.16951198	-3.41110768	-2.38934299	-0.21522549
N	3.39130453	-2.35858940	-0.18423514	-2.19005921	-3.47437508	-0.03745171	-2.46197869	-3.28391743	-0.01483481
N	2.70946862	1.33748220	-0.05871020	1.47150193	-2.62735690	-0.14933112	1.26269705	-2.72492804	-0.08631607
N	3.34367228	2.50019082	-0.19913130	2.68009554	-3.18154409	-0.06639465	2.42529838	-3.37057247	-0.00856353
N	2.37153853	3.37009220	-0.39376979	3.50796559	-2.16420265	-0.20905432	3.32620999	-2.42959465	-0.21611139
C	0.14595608	-3.50804934	-0.66459260	-3.54192151	-0.31932527	-0.59123925	-3.52523310	-0.04807553	-0.72700863
C	1.41753036	-1.33860752	-0.15609329	-1.27252706	-1.47804721	-0.34791000	-1.37765026	-1.37733650	-0.34615484
C	2.79003488	-1.12961706	-0.03825719	-0.98664738	-2.82526932	-0.13411726	-1.20574679	-2.73307684	-0.07957671
C	4.81958890	-2.68403806	-0.15615746	-2.42197115	-4.89654187	0.19824716	-2.82285669	-4.67416194	0.25797352
C	3.54071747	0.14828016	0.20310148	0.32300536	-3.53356268	0.00312452	0.04725159	-3.52126061	0.15274252
C	1.34077649	1.41686726	-0.15565433	1.48211817	-1.26920002	-0.35204171	1.37492742	-1.38166288	-0.34710040
C	1.13088278	2.77667390	-0.37454471	2.84570091	-0.97760731	-0.38153176	2.75434322	-1.20089307	-0.42476943
C	2.70269643	4.77913079	-0.62062746	4.95020119	-2.39130381	-0.17718864	4.74761977	-2.77380046	-0.20208751
H	0.22676259	-4.44242536	-0.08240519	-4.40998179	-0.42929111	0.07880689	-4.46306025	-0.10071510	-0.15245075
H	0.19455527	-3.78293375	-1.73593436	-3.91191407	-0.38746308	-1.63150263	-3.78921671	-0.08657525	-1.80058325
H	5.32927216	-2.17113159	-0.98837357	-1.95750751	-5.47710560	-0.61476040	-2.32613442	-5.32888565	-0.47483631

H	4.92147014	-3.77182518	-0.27166270	-3.50681300	-5.06728518	0.21854159	-3.91312795	-4.76483708	0.16713843
H	5.25257386	-2.36451819	0.80541620	-1.97042485	-5.18029311	1.16237880	-2.50305462	-4.94239042	1.27736419
H	3.89734817	0.20749047	1.24981594	0.40024416	-4.01331960	0.99546427	0.08774680	-3.88854648	1.19454844
H	4.42982020	0.22295984	-0.44606722	0.41701091	-4.33111362	-0.75530275	0.09094812	-4.40382348	-0.50833880
H	2.35101095	5.08251228	-1.62023285	5.38986057	-2.05349479	-1.12898894	5.19423557	-2.52048666	-1.17576335
H	3.79451812	4.88502479	-0.56003773	5.12251441	-3.46692072	-0.03610397	4.83189930	-3.85217317	-0.01475898
H	2.22114408	5.39978243	0.15242136	5.38699593	-1.82092356	0.65811462	5.25002677	-2.21008954	0.59982623
N	-1.33966535	2.69541527	-0.36193896	2.64372875	1.47107131	-0.34616154	2.74307419	1.25526532	-0.40992452
N	-2.51438280	3.32215004	-0.37969314	3.21156571	2.66028696	-0.15910628	3.41019298	2.38966820	-0.21654933
N	-3.39235540	2.35887416	-0.18105497	2.18853447	3.48215549	-0.01874431	2.46122448	3.28422472	-0.01535625
N	-2.71051227	-1.33733261	-0.05784603	-1.47314930	2.63579948	-0.12831416	-1.26353355	2.72533283	-0.08472623
N	-3.34473201	-2.50004994	-0.19812916	-2.68161438	3.19001874	-0.04395696	-2.42608797	3.37097925	-0.00618212
N	-2.37268755	-3.36983662	-0.39361344	-3.50965581	2.17356566	-0.19182212	-3.32712154	2.43003483	-0.21334690
C	-0.14733395	3.50848537	-0.66282865	3.53901348	0.33091094	-0.59728649	3.52396889	0.04864351	-0.72943750
C	-1.41861993	1.33876724	-0.15458039	1.27018837	1.48764130	-0.33847955	1.37660174	1.37787888	-0.34709772
C	-2.79106244	1.12977902	-0.03615820	0.98488354	2.83350479	-0.11555978	1.20491724	2.73350719	-0.07981938
C	-4.82059022	2.68440518	-0.15182732	2.42102440	4.90292210	0.22471394	2.82235182	4.67429940	0.25798778
C	-3.54179469	-0.14824657	0.20433561	-0.32446309	3.54095319	0.02876176	-0.04792747	3.52173069	0.15328161
C	-1.34187560	-1.41661733	-0.15565575	-1.48398378	1.27853731	-0.33699136	-1.37592236	1.38209891	-0.34556274
C	-1.13206282	-2.77634864	-0.37510335	-2.84764531	0.98754329	-0.36877073	-2.75538585	1.20135864	-0.42247641
C	-2.70389957	-4.77889558	-0.62025925	-4.95185091	2.40075597	-0.16124752	-4.74852446	2.77423291	-0.19846750
H	-0.19666172	3.78385640	-1.73401183	3.90524491	0.40636926	-1.63837737	3.78730574	0.08745902	-1.80315853
H	-0.22777000	4.44259116	-0.08015592	4.40936649	0.43651838	0.07044173	4.46213963	0.10114700	-0.15542911
H	-5.25288476	2.36461366	0.80996669	1.97154579	5.18107583	1.19143427	2.50275721	4.94212776	1.27754688
H	-4.92247892	3.77223909	-0.26687955	3.50590642	5.07356344	0.24358402	3.91262538	4.76483909	0.16704431
H	-5.33092298	2.17181053	-0.98383711	1.95481500	5.48818567	-0.58393279	2.32563596	5.32942927	-0.47446203
H	-4.43067317	-0.22253761	-0.44520197	-0.41967930	4.34362837	-0.72406191	-0.09213285	4.40413252	-0.50798901
H	-3.89891228	-0.20804908	1.25084413	-0.40008808	4.01389315	1.02450403	-0.08767503	3.88931166	1.19501043
H	-2.22231590	-5.39944381	0.15285560	-5.39000081	1.82774157	0.67153616	-5.25045238	2.21051175	0.60373984
H	-3.79571806	-4.88474546	-0.55954860	-5.12427357	3.47593755	-0.01699702	-4.83270244	3.85260481	-0.01108927
H	-2.35231532	-5.08241368	-1.61985574	-5.39009929	2.06604598	-1.11480084	-5.19570711	2.52091406	-1.17188226
N	0.00130826	-0.00058179	1.88532071	0.00331852	-0.01119686	1.58783149	0.00121850	-0.00059665	1.58240889
C	0.00487740	-0.00130851	3.04978185	0.00907171	-0.04120466	2.75087133	0.00421176	-0.00207706	2.74534592
C	0.01043370	-0.00218061	4.50539411	0.01742741	-0.08590602	4.20010089	0.00860564	-0.00378218	4.19756628
H	0.51168047	0.90550688	4.88528450	0.92081286	-0.61496269	4.55127732	0.89609428	-0.54409975	4.56884439
H	-1.02417235	-0.02284386	4.89084543	0.01737986	0.94075235	4.60626819	0.03434922	1.03336643	4.57321027
H	0.54673764	-0.89016148	4.88397517	-0.87923973	-0.61921418	4.56185203	-0.90109776	-0.50151983	4.57455691
O	-0.00101196	0.00056783	-1.87437707	-0.00363625	0.01340199	-2.17650064	-0.00139537	0.00045275	-2.17660809

Table S17 Coordinates of the oxoiron(V) aNHC species $Fe^{V}[cCCCC]_{trz}O(MeCN)$ calculated by Gaussian (charge 3, multiplicity 2, SCF: E(gas phase) = -1607.912749 h, E(SMD) = -1608.396220 h, E(PCM) = -1608.349534 h).

Atom	gas phase			SMD			PCM		
	Coordinate [Å]			Coordinate [Å]			Coordinate [Å]		
	X	Y	Z	X	Y	Z	X	Y	Z
Fe	-0.00050655	-0.00042714	-0.53584822	-0.00067736	-0.00725898	-0.68017305	0.00216487	0.00056457	-0.69759563
N	3.02748152	0.00288857	-0.40311787	2.90196038	0.83258741	-0.46918957	2.86810272	0.92475135	-0.51448440
N	4.10423969	0.75657601	-0.22979886	3.72091746	1.83144949	-0.17225500	3.66603601	1.92826619	-0.18182439
N	3.62986508	1.96696160	-0.02833004	2.91671403	2.84637930	0.07399654	2.84045054	2.90743295	0.12937883
N	0.00054427	2.98338704	-0.03406333	-0.82810198	2.82944637	-0.02136649	-0.91199167	2.78836117	0.02493388
N	-0.77939773	4.05390583	-0.05231293	-1.88246614	3.62746742	0.04774890	-1.98881509	3.55677508	0.08891181
N	-1.99317358	3.58909263	-0.25902824	-2.91420333	2.84738514	-0.20505297	-2.99060706	2.75988033	-0.22422250
C	3.23171536	-1.42207911	-0.70329679	3.48350847	-0.47175987	-0.79949844	3.46516052	-0.35603489	-0.91332984
C	1.84231140	0.69120557	-0.32523985	1.57446156	1.16694440	-0.43300708	1.53320209	1.22000956	-0.43817136
C	2.25348024	1.99284263	-0.06901684	1.59734862	2.50490659	-0.06245571	1.52521158	2.53725189	-0.00263884
C	4.56137017	3.08599985	0.18605562	3.46697805	4.14510248	0.45639602	3.37671057	4.19778570	0.56676443
C	1.44163065	3.22603160	0.17346447	0.48100747	3.44239812	0.24379842	0.37442420	3.40868568	0.38100500
C	-0.68673867	1.80765327	-0.22466124	-1.15249082	1.53221416	-0.32254620	-1.19267337	1.49526417	-0.33054288
C	-2.00874069	2.21981766	-0.37153530	-2.53967227	1.55345925	-0.43708396	-2.57411262	1.48359520	-0.48967661
C	-3.12087987	4.53095036	-0.36276498	-4.26533698	3.40858901	-0.22090023	-4.35657012	3.28985976	-0.24846213
H	4.11288160	-1.75920129	-0.13201606	4.43768696	-0.56202022	-0.25878271	4.46205825	-0.41697099	-0.45328593

H	3.47628589	-1.51972900	-1.77934803	3.69615947	-0.50344652	-1.88428605	3.59178331	-0.36180785	-2.01148763
H	4.45548789	3.80896724	-0.63952086	3.16510906	4.89503795	-0.29146319	3.08258324	4.97721256	-0.15275797
H	5.58160673	2.67727247	0.19683730	4.56072301	4.05273956	0.49101348	4.47001102	4.10880368	0.60450846
H	4.33654049	3.56871725	1.15072840	3.07078031	4.42179388	1.44631694	2.97958292	4.43383983	1.56564897
H	1.57569698	3.59561078	1.20786415	0.50851914	3.73529072	1.30909636	0.36963500	3.58283320	1.47274381
H	1.73304692	4.04703647	-0.50571252	0.54911833	4.36150535	-0.36191852	0.41523470	4.39034172	-0.11839417
H	-3.58478940	4.43178009	-1.35752780	-4.70573974	3.24700747	-1.21710952	-4.78080353	3.15223199	-1.25411928
H	-2.72057575	5.54650820	-0.23352852	-4.18527164	4.48184914	-0.00180924	-4.30143474	4.35746434	0.00039794
H	-3.85436356	4.30940255	0.42939219	-4.86991668	2.90071267	0.54709196	-4.96154914	2.75503470	0.49977305
N	-3.02835068	-0.00362668	-0.40096423	-2.90313676	-0.84476282	-0.45902102	-2.86431180	-0.92380453	-0.52177728
N	-4.10500830	-0.75716047	-0.22650304	-3.72211540	-1.84168324	-0.15577641	-3.66299027	-1.92715875	-0.19040279
N	-3.63058936	-1.96753174	-0.02520207	-2.91785047	-2.85457743	0.09856247	-2.83811586	-2.90661557	0.12174305
N	-0.00127372	-2.98413958	-0.03303554	0.82678289	-2.83851814	0.00159376	0.91455585	-2.78772402	0.02534872
N	0.77882429	-4.05457323	-0.05070329	1.88094839	-3.63651785	0.07314195	1.99117228	-3.55632361	0.09067307
N	1.99245146	-3.58974795	-0.25812482	2.91249182	-2.85832179	-0.18621822	2.99366241	-2.75921300	-0.21967324
C	-3.23280117	1.42111386	-0.70199144	-3.48470850	0.45623404	-0.80258894	-3.46057378	0.35726921	-0.92087626
C	-1.84315134	-0.69198867	-0.32372883	-1.57553715	-1.17842042	-0.41887720	-1.52958736	-1.21942365	-0.44365490
C	-2.25422873	-1.99352715	-0.06693035	-1.59844612	-2.51362342	-0.03877923	-1.52259197	-2.53677433	-0.00838828
C	-4.56203242	-3.08636848	0.19043916	-3.46800415	-4.15126511	0.48783727	-3.37537666	-4.19671866	0.55864337
C	-1.44239503	-3.22702578	0.17400098	-0.48218375	-3.44987327	0.27143612	-0.37273269	-3.40850565	0.37745596
C	0.68578944	-1.80847355	-0.22463939	1.15107079	-1.54307669	-0.30747369	1.19607053	-1.49428770	-0.32822169
C	2.00779463	-2.22055485	-0.37171360	2.53802949	-1.56554782	-0.42468089	2.57781834	-1.48262725	-0.48465892
C	3.12029856	-4.53151186	-0.36108795	4.26324410	-3.42036023	-0.20245645	4.35961744	-3.28930787	-0.24195498
H	-3.47784730	1.51803163	-1.77800284	-3.69581017	0.47713280	-1.88791827	-3.58518617	0.36381980	-2.01925326
H	-4.11373049	1.75856731	-0.13054155	-4.43961338	0.55158748	-0.26409312	-4.45831263	0.41785419	-0.46261869
H	-4.33702267	-3.56812307	1.15555146	-3.07053900	-4.42347102	1.47847152	-2.98087549	-4.43202873	1.55876021
H	-5.58226244	-2.67762189	0.20107652	-4.56166840	-4.05845221	0.52344491	-4.46878004	-4.10782203	0.59346183
H	-4.45632937	-3.81013415	-0.63445596	-3.16734289	-4.90476131	-0.25697234	-3.07928932	-4.97664195	-0.15952160
H	-1.73379109	-4.04696818	-0.50649827	-0.55121894	-4.37181544	-0.32986706	-0.41210842	-4.38969389	-0.12298995
H	-1.57661246	-3.59833358	1.20773206	-0.50857820	-3.73769937	1.33811728	-0.37088885	-3.58376649	1.46904066
H	3.85337123	-4.30967365	0.43137344	4.86953723	-2.91033368	0.56276069	4.96313886	-2.75578699	0.50838383
H	2.72004020	-5.54706987	-0.23171798	4.18291202	-4.49284797	0.02027446	4.30386516	-4.35732241	0.00499624
H	3.58464274	-4.43258893	-1.35566827	4.70192477	-3.26235082	-1.19999481	4.78588823	-3.15003683	-1.24652599
N	0.00103308	0.00064924	1.66393362	0.00164390	0.01082946	1.45734092	-0.00293032	-0.00024011	1.44527618
C	0.00350656	0.00308633	2.82949395	0.00589460	0.04827777	2.61903606	-0.01352848	-0.00286421	2.60745343
C	0.00756616	0.00702741	4.28297929	0.01227476	0.10361355	4.06470836	-0.02952688	-0.00856049	4.05628748
H	-0.58872650	0.85607208	4.66313675	-0.88841729	0.63587034	4.41787382	-0.86877083	0.60828973	4.42028040
H	-0.42784028	-0.93280482	4.66768052	0.01697492	-0.92132683	4.47506877	-0.15198961	-1.04286729	4.42045818
H	1.04207249	0.09886097	4.66025829	0.91406089	0.64000576	4.40879123	0.91966700	0.40317964	4.43948106
O	-0.00101316	-0.00067955	-2.09665571	-0.00143761	-0.01603658	-2.25016587	0.00438527	0.00134376	-2.26485728

Table S18 Coordinates of the oxoiron(IV) aNHC species $Fe^{IV}[cCCCC]_{trz}O(MeCN)$ calculated by Gaussian (charge 2, multiplicity 3, SCF: E = -1475.744736 h).

Atom	Coordinate [Å]		
	X	Y	Z
Fe	0.00000265	-0.00000407	0.32833349
N	-2.63085020	1.46669079	0.06752492
N	-3.20176707	2.64474866	-0.13788308
N	-2.18674418	3.46944258	-0.30400506
N	1.47685711	2.62105094	-0.18328453
N	2.68303273	3.16869497	-0.27057259
N	3.51075317	2.15767640	-0.09749111
C	-3.51289684	0.33326443	0.38383867
C	-1.25097301	1.47999671	0.04778750
C	-0.97657995	2.82416057	-0.20445074
C	-2.44352759	4.89009225	-0.55951574
C	0.33412700	3.53684736	-0.32173525
C	1.47763558	1.26110146	0.04831721
C	2.84287648	0.97391202	0.09395855
C	4.95736620	2.40059140	-0.11984996

H	-4.44171110	0.46518012	-0.19485105
H	-3.77443762	0.39951685	1.45806351
H	-1.98413288	5.49417379	0.23975147
H	-3.53166523	5.04173458	-0.56439566
H	-2.01953315	5.17077633	-1.53738423
H	0.42875465	4.04921693	-1.29696784
H	0.43123315	4.31091952	0.46210906
H	5.39364932	2.10179082	0.84687664
H	5.11605223	3.47474575	-0.28713301
H	5.41441122	1.82163159	-0.93879061
N	2.63085102	-1.46668792	0.06751375
N	3.20176750	-2.64474592	-0.13789594
N	2.18674514	-3.46944140	-0.30401209
N	-1.47685679	-2.62104663	-0.18327423
N	-2.68303354	-3.16868804	-0.27058099
N	-3.51075302	-2.15766922	-0.09750112
C	3.51290039	-0.33326134	0.38381579
C	1.25097203	-1.47999963	0.04779705
C	0.97658066	-2.82416456	-0.20443627
C	2.44352797	-4.89009104	-0.55952446
C	-0.33412875	-3.53684958	-0.32170517
C	-1.47763645	-1.26109951	0.04833866
C	-2.84287669	-0.97390724	0.09396660
C	-4.95736646	-2.40058006	-0.11988471
H	3.77446258	-0.39951697	1.45803526
H	4.44170453	-0.46517409	-0.19489136
H	2.01950313	-5.17078225	-1.53737767
H	3.53166627	-5.04172752	-0.56443956
H	1.98416244	-5.49417067	0.23976100
H	-0.43123785	-4.31090488	0.46215566
H	-0.42875889	-4.04923919	-1.29692676
H	-5.41439381	-1.82163132	-0.93884314
H	-5.11605220	-3.47473654	-0.28715447
H	-5.39366716	-2.10176387	0.84682897
O	-0.00001190	-0.00002363	1.95360387

Table S19 Coordinates of the oxoiron(V) aNHC species $Fe^{V}[cCCCC]_{trz}O(MeCN)$ calculated by Gaussian (charge 3, multiplicity 2, SCF: E(gas phase) = -1475.298415 h).

Atom	**Coordinate [Å]**		
	X	**Y**	**Z**
Fe	-0.00000300	-0.00000900	0.51003100
N	-2.93016500	0.67975800	0.19369200
N	-3.80648200	1.61231400	-0.12821900
N	-3.07674800	2.66770400	-0.42121800
N	0.66282000	2.85512800	-0.30553900
N	1.66728100	3.70840900	-0.34052700
N	2.73866800	2.99996900	-0.04900100
C	-3.42479400	-0.64340400	0.58272500
C	-1.61468700	1.08620100	0.12866800
C	-1.73294400	2.40959700	-0.28816900
C	-3.73557700	3.92128000	-0.82835000
C	-0.67000200	3.40670100	-0.59753000
C	1.05015600	1.56184800	-0.00229100
C	2.43413100	1.68272300	0.16587500
C	4.05294000	3.66747300	0.01447100
H	-4.41037900	-0.78708300	0.11095000
H	-3.56896500	-0.66284600	1.68148500
H	-3.49329000	4.71073400	-0.09807100
H	-4.81989000	3.74109700	-0.84067100
H	-3.38739100	4.20409200	-1.83508200

H	-0.69266500	3.70148400	-1.66441500
H	-0.78286100	4.32907600	0.00054700
H	4.47884400	3.53086400	1.02149000
H	3.89166100	4.73629100	-0.18623900
H	4.71602000	3.23492900	-0.75252900
N	2.93018100	-0.67975800	0.19370100
N	3.80648700	-1.61231900	-0.12823800
N	3.07673600	-2.66770300	-0.42121800
N	-0.66282400	-2.85512700	-0.30554600
N	-1.66727900	-3.70841200	-0.34051400
N	-2.73867100	-2.99996600	-0.04900400
C	3.42480600	0.64341200	0.58271800
C	1.61470800	-1.08617900	0.12868100
C	1.73293200	-2.40957600	-0.28817000
C	3.73555500	-3.92128400	-0.82835200
C	0.66999900	-3.40668200	-0.59754500
C	-1.05015800	-1.56184500	-0.00229400
C	-2.43413400	-1.68272600	0.16588100
C	-4.05294200	-3.66747100	0.01446600
H	3.56899100	0.66286600	1.68147500
H	4.41038200	0.78709800	0.11092700
H	3.38738000	-4.20408100	-1.83509200
H	4.81986900	-3.74111400	-0.84065600
H	3.49324800	-4.71074400	-0.09808600
H	0.78287100	-4.32906500	0.00051800
H	0.69267000	-3.70144800	-1.66443500
H	-4.71602300	-3.23492700	-0.75253400
H	-3.89166300	-4.73628800	-0.18624200
H	-4.47884700	-3.53085900	1.02148500
O	0.00001800	-0.00002900	2.05888500

Table S20 Calculation of different ΔH° [Hartree] and [kJ mol^{-1}].

Compound	ΔH° [Hartree]			ΔH° [kJ mol^{-1}]		
	gas phase	SMD	PCM	gas phase	SMD	PCM
1	-1665.355501	-1665.573219	-1665.541399	-4372390.87	-4372962.49	-4372878.94
2	-1664.94828	-1665.408009	-1665.363861	-4371321.70	-4372528.73	-4372412.82
1-MeCN	-1532.785339	-1533.013274	-1532.979076	-4024327.91	-4024926.35	-4024836.56
2-MeCN	-1532.361236	-1532.842549	-1532.792943	-4023214.43	-4024478.11	-4024347.87
$Fe^{IV}[cCCCC]_{trz}O(MeCN)$	-1607.885221	-1608.120014	-1608.087002	-4221502.65	-4222119.10	-4222032.42
$Fe^{V}[cCCCC]_{trz}O(MeCN)$	-1475.332510	-	-	-3873485.51	-	-
$Fe^{IV}[cCCCC]_{trz}O$	-1607.449151	-1607.930996	-1607.883184	-4220357.75	-4221622.83	-4221497.30
$Fe^{V}[cCCCC]_{trz}O$	-1474.886003	-	-	-3872313.20	-	-
MeCN	-132.520553	-132.529534	-132.527891	-347932.71	-347956.29	-347951.98
cis-cyclooctene	-312.667748	-312.675301	-312.668998	-820909.17	-820929.00	-820912.45
cyclooctene oxide	-387.770767	-387.780812	-387.774625	-1018092.15	-1018118.52	-1018102.28
H_2O_2	-151.342281	-151.352587	-151.348983	-397349.16	-397376.22	-397366.75
H_2O	-76.316585	-76.323810	-76.322826	-200369.19	-200388.16	-200385.58

Table S21 Calculation of different ΔH° [kcal mol^{-1}] and [eV].

Compound	ΔH° [kcal mol^{-1}]			ΔH° [eV]		
	gas phase	SMD	PCM	gas phase	SMD	PCM
1	-1045015.57	-1045152.19	-1045132.22	-45315.49	-45321.41	-45320.55
2	-1044760.04	-1045048.52	-1045020.82	-45304.41	-45316.92	-45315.72
1-MeCN	-961827.40	-961970.43	-961948.97	-41708.16	-41714.36	-41713.43
2-MeCN	-961561.27	-961863.30	-961832.17	-41696.62	-41709.72	-41708.37
$Fe^{IV}[cCCCC]_{trz}O(MeCN)$	-1008952.80	-1009100.13	-1009079.42	-43751.68	-43758.07	-43757.17
$Fe^{V}[cCCCC]_{trz}O(MeCN)$	-925775.58	-	-	-40144.83	-	-
$Fe^{IV}[cCCCC]_{trz}O$	-1008679.16	-1008981.52	-1008951.52	-43739.82	-43752.93	-43751.63
$Fe^{V}[cCCCC]_{trz}O$	-925495.39	-	-	-40132.68	-	-
MeCN	-83157.04	-83162.68	-83161.65	-3605.98	-3606.22	-3606.18
cis-cyclooctene	-196199.95	-196204.69	-196200.73	-8507.91	-8508.11	-8507.94
cyclooctene oxide	-243327.32	-243333.62	-243329.74	-10551.51	-10551.79	-10551.62
H_2O_2	-94967.74	-94974.20	-94971.94	-4118.13	-4118.41	-4118.31
H_2O	-47888.89	-47893.42	-47892.80	-2076.63	-2076.82	-2076.80

Table S22 Calculation of different ΔG° [Hartree] and [kJ mol^{-1}].

Compound	ΔG° [Hartree]		ΔG° [kJ mol^{-1}]			
	gas phase	SMD	gas phase	SMD	gas phase	SMD
1	-1665.453792	-1665.681118	-1665.453792	-1665.681118	-1665.453792	-1665.681118
2	-1665.057415	-1665.512037	-1665.057415	-1665.512037	-1665.057415	-1665.512037
1-MeCN	-1532.875633	-1533.107743	-1532.875633	-1533.107743	-1532.875633	-1533.107743
2-MeCN	-1532.456032	-1532.935623	-1532.456032	-1532.935623	-1532.456032	-1532.935623
$Fe^{IV}[cCCCC]_{trz}O(MeCN)$	-1607.979198	-1608.216089	-1607.979198	-1608.216089	-1607.979198	-1608.216089
$Fe^{V}[cCCCC]_{trz}O(MeCN)$	-1475.417876	-	-1475.417876	-	-1475.417876	-
$Fe^{IV}[cCCCC]_{trz}O$	-1607.546972	-1608.025116	-1607.546972	-1608.025116	-1607.546972	-1608.025116
$Fe^{V}[cCCCC]_{trz}O$	-1474.969790	-	-1474.969790	-	-1474.969790	-
MeCN	-132.548182	-132.557116	-132.548182	-132.557116	-132.548182	-132.557116
cis-cyclooctene	-312.667748	-312.675301	-312.667748	-312.675301	-312.667748	-312.675301
cyclooctene oxide	-387.770767	-387.780812	-387.770767	-387.780812	-387.770767	-387.780812
H_2O_2	-151.342281	-151.352587	-151.342281	-151.352587	-151.342281	-151.352587
H_2O	-76.316585	-76.323810	-76.316585	-76.323810	-76.316585	-76.323810

Table S23 Calculation of different ΔG° [kcal mol^{-1}] and [eV].

Compound	ΔG° [kcal mol^{-1}]			ΔG° [eV]		
	gas phase	SMD	gas phase	SMD	gas phase	SMD
1	-1045077.25	-1045219.90	-1045077.25	-1045219.90	-1045077.25	-1045219.90
2	-1044828.52	-1045113.80	-1044828.52	-1045113.80	-1044828.52	-1045113.80
1-MeCN	-961884.06	-962029.71	-961884.06	-962029.71	-961884.06	-962029.71
2-MeCN	-961620.76	-961921.70	-961620.76	-961921.70	-961620.76	-961921.70
$Fe^{IV}[cCCCC]_{trz}O(MeCN)$	-1009011.77	-1009160.42	-1009011.77	-1009160.42	-1009011.77	-1009160.42
$Fe^{V}[cCCCC]_{trz}O(MeCN)$	-925829.14	-	-925829.14	-	-925829.14	-
$Fe^{IV}[cCCCC]_{trz}O$	-1008740.55	-1009040.58	-1008740.55	-1009040.58	-1008740.55	-1009040.58
$Fe^{V}[cCCCC]_{trz}O$	-925547.97	-	-925547.97	-	-925547.97	-
MeCN	-83174.38	-83179.99	-83174.38	-83179.99	-83174.38	-83179.99
cis-cyclooctene	-196199.95	-196204.69	-196199.95	-196204.69	-196199.95	-196204.69
cyclooctene oxide	-243327.32	-243333.62	-243327.32	-243333.62	-243327.32	-243333.62
H_2O_2	-94967.74	-94974.20	-94967.74	-94974.20	-94967.74	-94974.20
H_2O	-47888.89	-47893.42	-47888.89	-47893.42	-47888.89	-47893.42

Table S24 BDEs and ΔG of dative bonds toward one labile acetonitrile ligand.

Compound	BDE [kJ mol^{-1}]			ΔG [kJ mol^{-1}]		
	gas phase	SMD	PCM	gas phase	SMD	PCM
1	130.25	79.84	90.40	78.70	42.69	52.65
2	174.56	94.32	112.97	139.68	50.67	74.94
$Fe^{IV}[cCCCC]_{trz}O(MeCN)$	20.18	-	-	8.25	-	-
$Fe^{V}[cCCCC]_{trz}O(MeCN)$	26.73	-	-	18.20	-	-

Table S25 ΔH and ΔG of overall epoxidation reaction: products (epoxide + H_2O), reactants (*cis*-cyclooctene + H_2O_2).

ΔH [kJ mol^{-1}]			ΔG [kJ mol^{-1}]		
gas phase	SMD	PCM	gas phase	SMD	PCM
-51.18	-50.73	-52.46	-48.52	-48.15	-49.87

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