Supporting Information for

Steric Modifications Tune the Regioselectivity of the Alkane Oxidation Catalyzed by Non-Heme Iron Complexes

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Table S1. Selected crystallographic data for bbpc and [Mn(bbpc)Cl₂].

Parameter	bbpc	[Mn(bbpc)Cl ₂]•MeCN
Formula	C ₃₂ H ₃₆ N ₄	C ₃₄ H ₃₉ Cl ₂ MnN ₅
MW	476.65	643.54
Crystal system	Monoclinic	Orthorhombic
Space group	<i>C2/c</i> (#15)	<i>P2₁2₁2₁</i> (#19)
a (Å)	17.1486(16)	10.3334(6)
b (Å)	11.4474(11)	16.4848(9)
c (Å)	14.5026(14)	18.6221(10)
α (deg)	90	90
β (deg)	109.012(2)	90
γ (deg)	90	90
V (Å ³)	2691.7(4)	3172.2(3)
Z	4	4
Cryst color	Yellow	Colorless
T (K)	193	193
Reflns collected	8963	49045
Unique reflns	2343	6673
R1 (F, I > 2σ(I))	0.08	0.0391
wR2 (F ² , all data)	0.2093	0.0700

$$R1 = \sum ||F_o| - |F_c|| / \sum ||F_o| ; wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

Figure S1. ORTEP representation of the bbpc ligand. Hydrogen atoms have been omitted for clarity. All thermal ellipsoids are drawn at 50% probability.

Figure S2. ORTEP representation of $[\text{Mn}(\text{bbpc})\text{Cl}_2]$. Hydrogen atoms have been omitted for clarity. All thermal ellipsoids are drawn at 50% probability.

Figure S3. Comparison of the UV/vis spectra of $[\text{Fe}(\text{bbpc})(\text{OTf})_2]$, $[\text{Fe}(\text{bbpc})(\text{MeCN})_2](\text{SbF}_6)_2$, and $[\text{Fe}(\text{bbpc})\text{Cl}_2]$. The above data were taken from 0.12 mM solutions of the Fe(II) compounds in MeCN. Each spectrum was acquired at 294 K.

Figure S4. UV/vis spectrum of $[\text{Mn}(\text{bbpc})\text{Cl}_2]$ in MeCN at 294 K. The sample concentration was 0.20 mM. The shoulder feature at 310 nm has $\epsilon = 390 \text{ M}^{-1} \text{ cm}^{-1}$.

Figure S5. ^1H NMR spectrum of a 0.10 M solution of $[\text{Fe}(\text{bbpc})(\text{MeCN})_2](\text{SbF}_6)_2$ in CD_3CN at 294 K. The peak at 1.94 ppm corresponds to MeCN.

Figure S6. ^1H NMR spectrum of a 0.10 M solution of $[\text{Fe}(\text{bbpc})(\text{OTf})_2]$ in CD_3CN at 294 K. The peak at 1.91 ppm corresponds to MeCN. Note that there are two diastereomers present in the crystal structure, leading to a large number of peaks in the 0-7 ppm range relative to $[\text{Fe}(\text{bbpc})(\text{MeCN})_2](\text{SbF}_6)_2$.

Table S2. Oxidation of hydrocarbon substrates catalyzed by [Fe(bbpc)(MeCN)₂](SbF₆)₂.

Substrate	Protocol ^a	[H ₂ O ₂] (mM)	TON ^b	Product Yields ^c
n-hexane	A	100	16.2	3-hexanol (6.0%) 3-hexanone (2.1%) 2-hexanol (5.8%) 2-hexanone (2.1%)
<i>tert</i> -butylcyclohexane	B	0.102→0.115	6.7	3- <i>tert</i> -butylcyclohexanone (22%) 4- <i>tert</i> -butylcyclohexanone (6%)
1,1-dimethylcyclohexane	B	0.102→0.115	8.6	2,2-dimethylcyclohexanone (8%) 3,3-dimethylcyclohexanone (10%) 4,4-dimethylcyclohexanone (18%)
adamantane	C	10	3.5	1-adamantanol (29%) 2-adamantanol/2-adamantanone (6%) ^d

All reactions were run at 298 K in MeCN. All numbers are the average of three independent reactions.

^aThree different procedures were followed:

Protocol A) The starting concentrations of the [Fe(bbpc)(MeCN)₂]²⁺ and the substrate were 1.0 mM and 1.0 M, respectively. A solution of H₂O₂ diluted in MeCN was added dropwise over the course of 1 min. The final volume of each reaction solution was 2.50 mL. After 30 min, the solution was filtered through silica gel and analyzed.

Protocol B) The general procedure was adapted from Reference 13 in order to facilitate comparison of the data. The substrate (0.50 mmol, 1 equiv) was dissolved in 1.0 mL of MeCN. The iron catalyst and the terminal oxidant, H₂O₂, were added to this solution in three portions. For each addition, the H₂O₂ was added dropwise over the course of 90 s. After the first additions, the concentrations were as follows: [Fe] = 4.26 μM, [substrate] = 85.2 μM, [H₂O₂] = 0.102 mM. 10 min after the first portion of H₂O₂ was added, further equivalents of catalyst and oxidant were added, yielding the following concentrations: [Fe] = 4.65 μM, [substrate] = 46.5 μM, [H₂O₂] = 0.112 mM. 20 min after the first portion of H₂O₂ was added, the third portions of catalyst and oxidant were added, yielding the following concentrations: [Fe] = 4.80 μM, [substrate] = 32.0 μM, [H₂O₂] = 0.115 mM. At 30 min, the reaction solution was filtered through a short plug of silica gel prior to analysis.

Protocol C) Identical to Protocol A except that the starting concentration of adamantane was 10 mM, due to the lesser solubility of this alkane in MeCN.

^bDefined as the number of moles of oxidized organic products generated per mole of Fe(II) catalyst.

^cThe products were identified by GC/MS and comparison of the retention times with those of authentic samples of the oxidized products. The concentrations of each organic product were calibrated relative to that of an internal standard (dichlorobenzene or cyclohexanone) with a known concentration. Each product yield is defined with respect to the amount of H₂O₂ added. The product yields should not be confused with product distributions; the above table accounts for all oxidized organic products.

^dInseparable mixture.

Figure S7. Oxidation of cyclohexanol to cyclohexanone in the presence and absence of acetic acid (AcOH). The data are from **Figure 3**. In order to assess the lifetime of the catalyst, the differences between the maximum observed yield and the current yield as a function of time were plotted and fit to exponential decay functions of the form: $y = a + be^{-ct}$. For the reactions run in the absence of acetic acid, $c = 0.29 (\pm 0.03) \text{ min}^{-1}$, with an $R = 0.98796$ for the overall fit. For the reactions run in the presence of acetic acid, $c = 0.20 (\pm 0.01) \text{ min}^{-1}$, with an $R = 0.99866$ for the overall fit. The results may suggest that the catalyst derived from $[\text{Fe}(\text{bbpc})(\text{MeCN})]^{2+}$ is slightly harder but less active when AcOH is present.

Figure S8. ESI Mass spectrum of the green species formed when 4 equiv of H_2O_2 reacts with 1.0 mM $[\text{Fe}(\text{bbpc})(\text{MeCN})_2](\text{SbF}_6)_2$ in MeCN at 294 K. The major m/z peak is at 564.2245.

Figure S9. Isotopic pattern predicted for [Fe(bbpc)(O₂)]⁺ (top) compared to the expanded region around the m/z peak at 564.2245 from **Figure S8** (bottom).