Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Pushing the Limits of Activity and Stability: The Effects of Lewis Acids on non-heme Iron-NHC Epoxidation Catalysts

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1. Catalytic Procedure

All batch reactions were conducted in a cryostat (Julabo FP-50) with a total reaction volume of 4.0 mL. Acetonitrile (HPLC-grad) was applied as solvent for all experiments. The catalyst (0.05 mol%, 0.135 µmol; catalyst **3**: 0.025 mol%, 0.673 µmol) was added from a preformed stock solution (4.0 mg/mL in acetonitrile) according to the appropriate stoichiometry to a solution of *cis*-cyclooctene (100 mol%, 269 µmol), the respective Lewis acid (0.5 mol%, 1.345 µmol) and H_2O_2 (150 mol%, 403.5 µmol) in acetonitrile. The reaction was initiated upon addition of the catalyst. The reaction was aborted by adding electrolytically precipitated activated MnO_2 as a H_2O_2 decomposition agent. After filtration over activated neutral alumina, two GC samples were prepared for each experiment using 200 µL filtrate, 500 µL external standard (*p*-xylene, 4.0 mg/mL in *i*-PrOH) and 800 µL n-hexane, respectively. Control experiments without catalyst and additive were performed as a reference for all reactions.

Evaluation of other substrates beside *cis*-cyclooctene was performed using ^{1}H-NMR spectrocopy. Reactions were carried out at 20°C in a total volume of 1.0 mL with a catalyst concentration of 0.10 mol% in doubled absolute concentrations. A stock solution of catalyst **1** (1.53 mg mL^{-1} in CD_3CN) was added to a preformed solution of the respective substrate (100 mol%, 134.5 µmol), H_2O_2 (150 mol%, 201.8 µmol) and $Sc(OTf)_3$ (1.00 mol%, 1.35 µmol) in deuterated acetonitrile. The reaction was started upon addition of the catalyst and aborted after 5 minutes by addition of MnO_2. The suspension was filtered and C_6H_6 was added as an external standard. ^{1}H-NMR spectra were recorded for each experiment and the products were quantified by the integral ratios of the respective olefin, epoxide and *cis*-diol protons.

2. ^{1}H-NMR Spectra of Substrate Screening

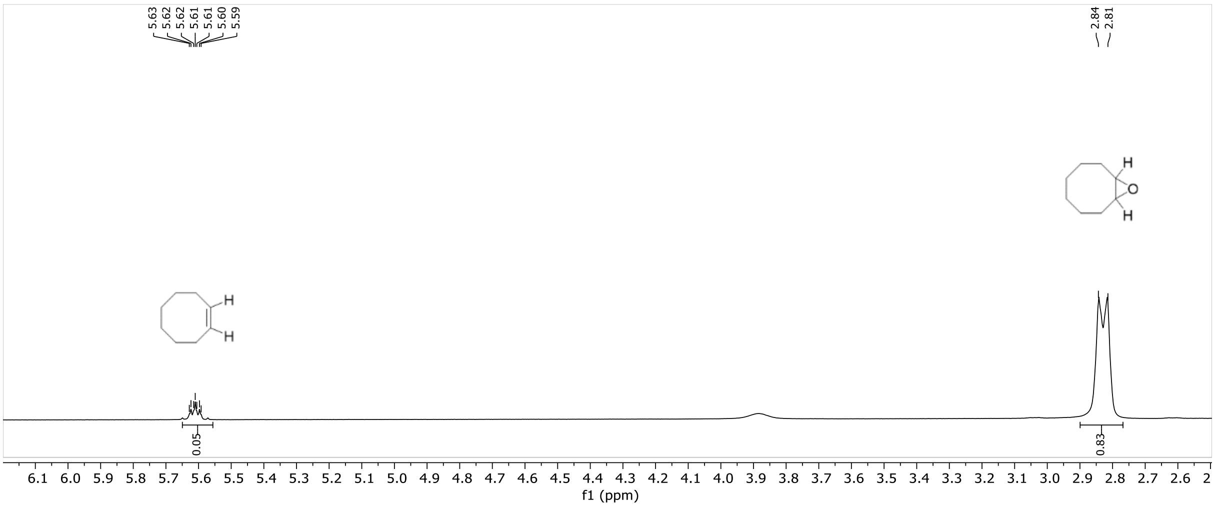

Figure 1. Section of the ^{1}H NMR spectrum of the epoxidation of *cis*-cyclooctene (100 mol%, 135 µmol) with H_2O_2 (150 mol% 202 µmol), catalyst **1** (0.10 mol%, 0.135 µmol) and $Sc(OTf)_3$ (1.00 mol%, 1.35 µmol) at 20°C in CD_3CN with a reaction time of 5 min.

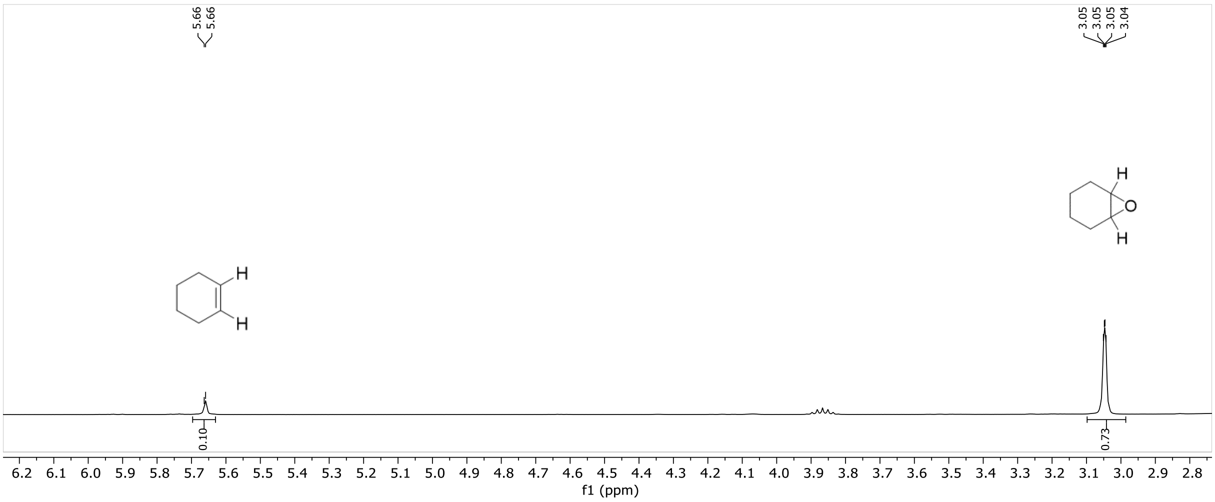

Figure 2. Section of the ^{1}H NMR spectrum of the epoxidation of cyclohexene (100 mol%, 135 µmol) with H_2O_2 (150 mol%, 202 µmol), catalyst **1** (0.10 mol%, 0.135 µmol) and $Sc(OTf)_3$ (1.00 mol%, 1.35 µmol) at 20°C in CD_3CN with a reaction time of 5 min.

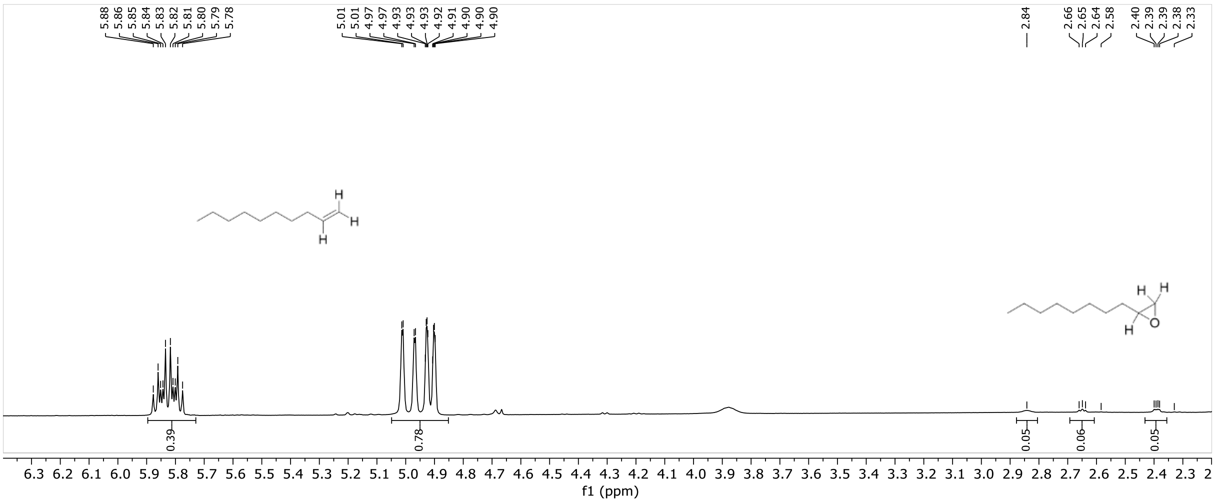

Figure 3. Section of the ^{1}H NMR spectrum of the epoxidation of 1-decene (100 mol%, 135 µmol) with H_2O_2 (150 mol%, 202 µmol), catalyst **1** (0.10 mol%, 0.135 µmol) and $Sc(OTf)_3$ (1.00 mol%, 1.35 µmol) at 20°C in CD_3CN with a reaction time of 5 min.

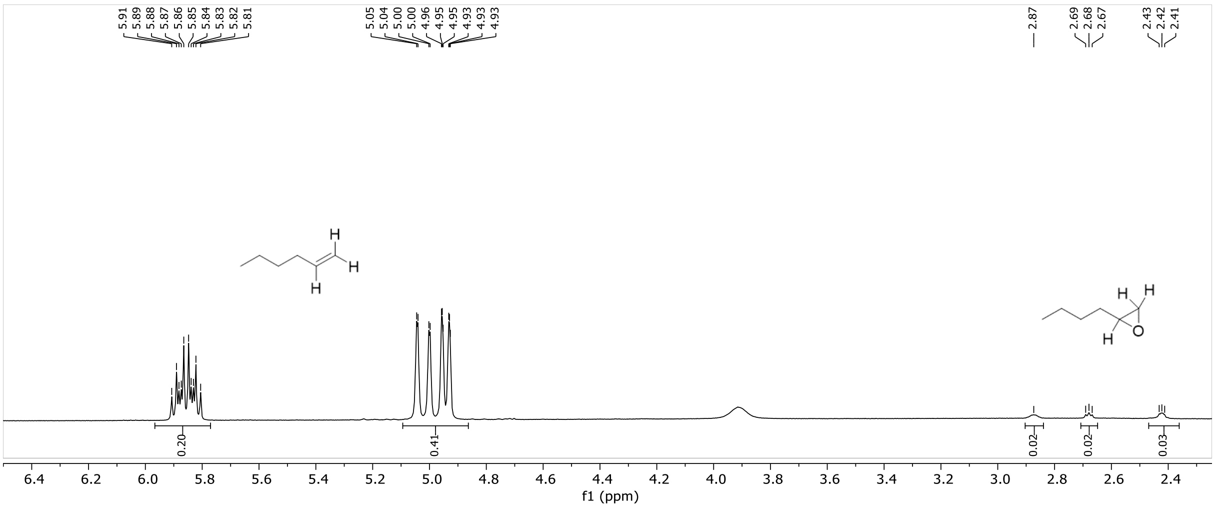

Figure 4. Section of the ^1H NMR spectrum of the epoxidation of 1-hexene (100 mol%, 135 µmol) with H_2O_2 (150 mol%, 202 µmol), catalyst **1** (0.10 mol%, 0.135 µmol) and $Sc(OTf)_3$ (1.00 mol%, 1.35 µmol) at 20°C in CD_3CN with a reaction time of 5 min.

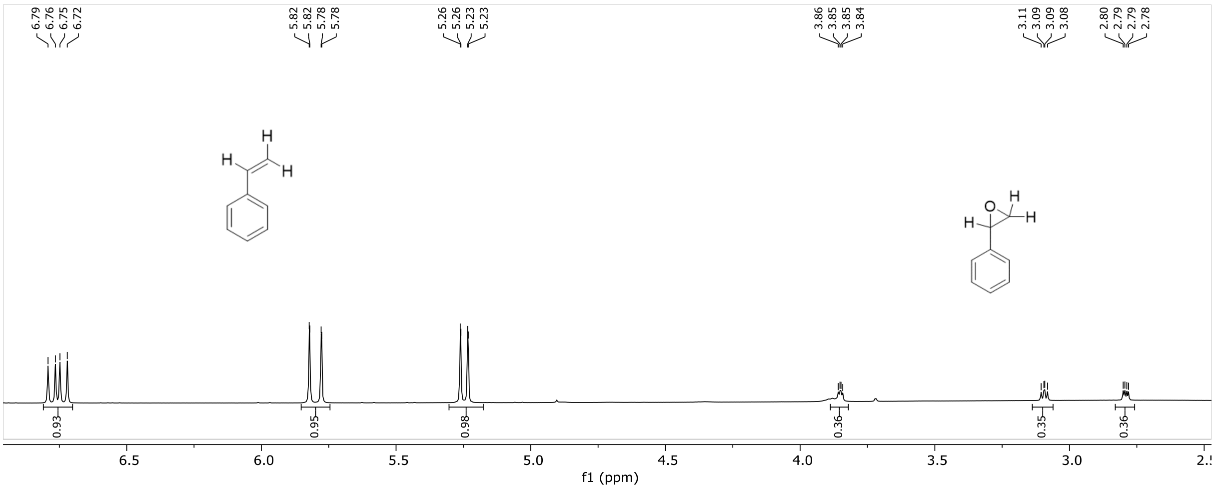

Figure 5. Section of the ^1H NMR spectrum of the epoxidation of styrene (100 mol%, 135 µmol) with H_2O_2 (150 mol%, 202 µmol), catalyst **1** (0.10 mol%, 0.135 µmol) and $Sc(OTf)_3$ (1.00 mol%, 1.35 µmol) at 20°C in CD_3CN with a reaction time of 5 min.

3. UV/Vis Spectroscopy

UV-Vis spectra were recorded on an Agilent Technologies Cary 60 UV-Vis spectrophotometer at 20°C. Solutions of 1.0 eq. **1**, **2** and **3** with an initial concentration of 1×10^{-4} M (**1** and **2**) and 0.5×10^{-4} M (**3**) in acetonitrile are treated with 10 eq. $Sc(OTf)_3$ in air and additional 1.5 eq. H_2O_2 when indicated. If not stated otherwise the solutions were not stirred or mixed.

4. Single Crystal X-Ray Diffraction

Suitable single crystals of compound Fe^{III}-cCCCC$(OTf)_3$ were obtained by slow diffusion of ether into a preformed solution of compound **1** and $Sc(OTf)_3$ (equimolar) in acetonitrile. Three OTf^- anions are displayed in the unit cell. All Fe-$C_{carbene}$ bond lengths are in accordance with the previously reported Fe^{III}-cCCCC complex proving the tricationic charge at the Fe centre.

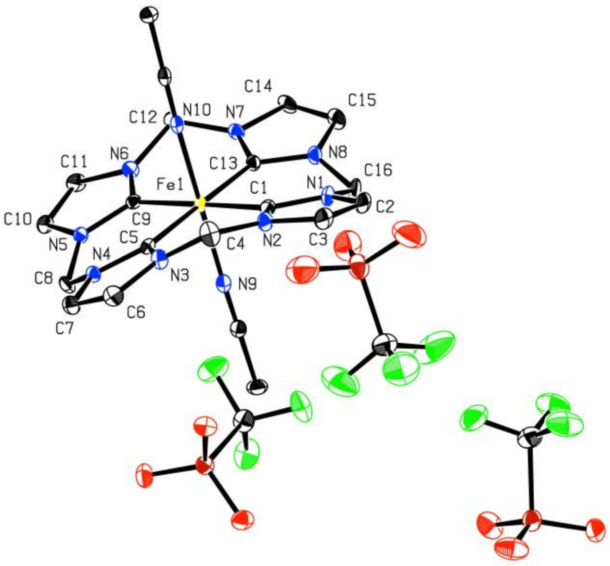

Figure 6. ORTEP style representation of Fe^{III}-cCCCC$(OTf)_3$. Thermal ellipsoids are shown at a 50% probability level. Hydrogen atoms are omitted for clarity. Element colors: yellow –iron, black – carbon, blue – nitrogen, dark red – sulfur, red – oxygen, green – fluorine. Selected bond lengths (Å) and angles (°): Fe1-C1 = 1.942(4), Fe1-C5 = 1.938(4), Fe1-C9 = 1.935(4), Fe1-C13 = 1.945(4); N9-Fe1-N10 = 179.19(14), N10-Fe1-C9 = 90.97(14), C9-Fe1-C5 = 90.77(16).

The data were collected on a X-Ray single crystal diffractometer (Bruker, rotating-anode TXS) equipped with a CMOS detector (Bruker Photon), a fine-focused sealed tube with MoK_α radiation ($\lambda = 0.71073$ Å), and Helios optic monochromator. The crystals were mounted on a microsampler with perfluorinated ether. The X-Ray measurements were conducted using the APEX software package. The crystal was frozen under a stream of cold nitrogen (OXFORD CRYOSYSTEMS cooling device). A matrix scan was used to determine the initial lattice parameters. Intensities were integrated and the raw data were corrected for Lorentz, polarization effects, scan speed, background, and arising from the scaling procedure, for latent decay and absorption effects using SAINT and SADABS. Space group assignment was based upon systematic absences, E statistics, and successful refinement of the structure. The structure was solved by a combination of direct methods and difference Fourier syntheses and were refined against all data using SHELXL-2014. Hydrogen atoms were assigned to ideal positions and refined using a riding model with isotropic thermal parameters 1.2 times that of the attached carbon atom (1.5 times for methyl hydrogen atoms). If not mentioned otherwise, non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma_w(F_o^2-F_c^2)^2$ with SHELXL-2014 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. Images of the crystal structure were generated by PLATON.

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication (CCDC 1977385). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223-336-033; e-mail, deposit@ccdc.cam.ac.uk.

Table 1. Crystallographic data and structure refinement parameters.

Compound name	**Fe^{III}-cCCCC(OTf)$_3$**
CCDC	1977385
Chemical formula	$C_{23}H_{22}F_9FeN_{10}O_9S_3$
Fw [g mol^{-1}]	905.53
T [K]	100(2)
Crystal system	triclinic
Space group	*P* -1
a [Å]	9.1084(6)
b [Å]	11.7267(7)
c [Å]	16.3308(9)
α [deg]	85.341(2)
β [deg]	89.880(2)
γ [deg]	70.285(2)
V [Å^3]	1636.05(17)
Z	2
Density (calcd) [g cm^{-3}]	1.838
μ [mm^{-1}]	0.772
F (000)	914
Crystal size (mm^3)	0.028 × 0.085 × 0.182
ϑ range for data collection [deg]	2.14 to 25.68
Reflections collected	60492
Independent reflections	6192 [R(int) = 0.0219]
Data/restrains/parameters	6192 / 0 / 498
GOF on F^2	1.046
Final R1	R1 = 0.0635
wR2 [I > 2σ(I)]	wR2 = 0.1688
Largest diff. peak and hole [eÅ^{-3}]	2.793 and -0.915

5. References

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