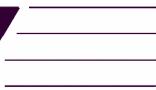


**CHEMISTRY**   
**A EUROPEAN JOURNAL**

Supporting Information

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**A Novel Platform for Modeling Oxidative Catalysis in Non-Heme Iron  
Oxygenases with Unprecedented Efficiency**

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## 1) Experimental section

### *Materials*

Reagents and solvents used were of commercially available reagent quality unless otherwise stated. H<sub>2</sub><sup>18</sup>O<sub>2</sub> (90% <sup>18</sup>O-enriched, 2% solution in H<sub>2</sub>O) and H<sub>2</sub><sup>18</sup>O (95% <sup>18</sup>O-enriched) were received from ICON Isotopes. Solvents were purchased from SDS. CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN were distilled over CaH<sub>2</sub> under nitrogen. THF and diethyl ether were distilled over Na/benzophenone under nitrogen.

### *Instrumentation*

IR spectra were taken in a Mattson-Galaxy Satellite FT-IR spectrophotometer using a MKII Golden Gate single reflection ATR system. UV-vis spectroscopy was performed on a Cary 50 Scan (Varian) UV-vis spectrophotometer with 1 cm or 0.2 cm quartz cells. NMR spectra were taken on Bruker DPX200 spectrometer using standard conditions. Elemental analyses were performed using a CHNS-O EA-1108 elemental analyzer from Fisons. The ESI-MS experiments were performed on a Navigator LC/MS chromatograph from Thermo Quest Finigan, using acetonitrile as a mobile phase. Product analyses were performed on a Perkin-Elmer Sigma 3 gas chromatography (AT-1701 column, 30 m) and a flame-ionization detector. GC mass spectral analyses were performed on a HP5898 GC (DB-5 column, 60 m) with a Finnigan MAT 95 mass detector or a HP6890 GC (HP-5 column, 30 m) with an Agilent 5973 mass detector. A 4% NH<sub>3</sub>/CH<sub>4</sub> mix was used as the ionization gas for chemical ionization analyses. The products were identified by comparison of their GC retention times and GC/MS with those of authentic compounds.

### *Synthesis of ligands*

1,4-dimethyl-1,4,7-triazacyclononane trihydrobromide,<sup>[1]</sup> 2-chloromethyl-6-methylpyridine hydrochloride,<sup>3</sup> 1,4-diisopropyl-7-(2-pyridylmethyl)-1,4,7-triazacyclononane (<sup>iPr,H</sup>PyTACN),<sup>[2]</sup> and 1,4-diisopropyl-7-(6-methyl-2-pyridylmethyl)-1,4,7-triazacyclononane (<sup>iPr,Me</sup>PyTACN)<sup>[3]</sup> were synthesized as previously described.

**1-(2-pyridylmethyl)-4,7-dimethyl-1,4,7-triazacyclononane (<sup>Me,H</sup>PyTACN).** 2-Picolyl chloride hydrochloride (0.43 g, 2.6 mmols), 1,4-dimethyl-1,4,7-triazacyclononane trihydrobromide (1.02 g, 2.6 mmols) and anhydrous acetonitrile (35 mL) were mixed in a 50 mL flask. Na<sub>2</sub>CO<sub>3</sub> (1.90 g) and tetrabutylammonium bromide, TBABr (0.04 g) were added directly as solids and the resulting mixture was heated at reflux under N<sub>2</sub> for 20 hours. After cooling to room temperature, the resulting yellow mixture was filtered and the filter cake was washed with CH<sub>2</sub>Cl<sub>2</sub>. The

combined filtrates were evaporated under reduced pressure. To the resulting residue, 1M NaOH (30 mL) was added and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 20 mL). The combined organic layers were dried over anhydrous MgSO<sub>4</sub> and the solvent was removed under reduced pressure. The resulting residue was treated with n-pentane (50 mL) and stirred for 12 hours. The mixture was filtered and the solvent from the yellow filtrates was removed under reduced pressure to yield 0.55 g of a pale yellow oil (2.2 mmols, 86 %). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 27°C): *d* = 8.52 (d, <sup>3</sup>*J*(H,H) = 4.8 Hz, 1 H; pyH<sub>α</sub>), 7.66 (t, <sup>3</sup>*J*(H,H) = 7.8 Hz, 1 H; pyH<sub>γ</sub>), 7.48 (d, <sup>3</sup>*J*(H,H) = 7.8 Hz, 1 H; pyH<sub>β</sub>), 7.15 (m, 1 H; pyH<sub>β</sub>), 3.85 (s, 2 H; py-CH<sub>2</sub>), 2.86 – 2.80 (m, 8 H; N-CH<sub>2</sub>-CH<sub>2</sub>), 2.71 – 2.65 (m, 4 H; N-CH<sub>2</sub>-CH<sub>2</sub>), 2.37 ppm (s, 6 H; N-CH<sub>3</sub>); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 27°C): *d* = 160.37 (pyC<sub>q</sub>), 148.87 (pyC<sub>α</sub>), 136.18 (pyC<sub>γ</sub>), 123.22, 121.75 (pyC<sub>β</sub>), 64.61 (py-CH<sub>2</sub>-N), 57.06, 56.86, 55.94 (N-CH<sub>2</sub>-C), 46.54 ppm (N-CH<sub>3</sub>); FT-IR (ATR): ? = 2922 – 2759 (C-H)<sub>sp3</sub>, 1589, 1453 cm<sup>-1</sup> (py); ESI-MS: *m/z*: 249.2 [M+H]<sup>+</sup>.

**1-(6-methyl-2-pyridylmethyl)-4,7-dimethyl-1,4,7-triazacyclononane** (<sup>Me,Me</sup>PyTACN). 2-Chloromethyl-6-methylpyridine hydrochloride (0.44 g, 2.5 mmols), 1,4-dimethyl-1,4,7-triazacyclononane trihydrobromide (1.00 g, 2.5 mmols) and anhydrous acetonitrile (30 mL) were mixed in a 50 mL flask. Na<sub>2</sub>CO<sub>3</sub> (1.85 g) and tetrabutylammonium bromide, TBABr (0.04 g) were added directly as solids and the resulting mixture was heated at reflux under N<sub>2</sub> for 15 hours. After cooling to room temperature, the resulting yellow mixture was filtered and the filter cake was washed with CH<sub>2</sub>Cl<sub>2</sub>. The combined filtrates were evaporated under reduced pressure. To the resulting residue, 1M NaOH (30 mL) was added and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 20 mL). The combined organic layers were dried over anhydrous MgSO<sub>4</sub> and the solvent was removed under reduced pressure to yield 0.60 g of a pale yellow oil (2.3 mmols, 92 %). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 27°C): *d* = 7.54 (t, <sup>3</sup>*J*(H,H) = 7.6 Hz, 1H; pyH<sub>γ</sub>), 7.29 (d, <sup>3</sup>*J*(H,H) = 7.4 Hz, 1 H; pyH<sub>β</sub>), 7.00 (d, <sup>3</sup>*J*(H,H) = 7.4 Hz, 1 H; pyH<sub>β</sub>), 3.82 (s, 2 H; py-CH<sub>2</sub>), 2.84 – 2.79 (m, 8 H; N-CH<sub>2</sub>-CH<sub>2</sub>), 2.68 – 2.66 (m, 4 H; N-CH<sub>2</sub>-CH<sub>2</sub>), 2.53 (s, 3 H; py-CH<sub>3</sub>), 2.36 ppm (s, 6 H; N-CH<sub>3</sub>); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 27°C): *d* = 159.85, 157.41 (pyC<sub>q</sub>), 136.38 (pyC<sub>γ</sub>), 121.16, 119.93 (pyC<sub>β</sub>), 64.83 (py-CH<sub>2</sub>-N), 57.20, 57.06, 56.28 (N-CH<sub>2</sub>-C), 46.65 (N-CH<sub>3</sub>), 24.38 ppm (py-CH<sub>3</sub>); FT-IR (ATR): ? = 2960 – 2802(C-H)<sub>sp3</sub>, 1578, 1456, 1358 cm<sup>-1</sup> (py); ESI-MS: *m/z*: 263.1 [M+H]<sup>+</sup>.

### *Synthesis of complexes*

[Fe(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>(<sup>iPr,H</sup>PyTACN)] (1CF<sub>3</sub>SO<sub>3</sub>). A solution of Fe(CH<sub>3</sub>CN)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> (292 mg, 0.67 mmols) in anhydrous THF (2 mL) was added dropwise to a vigorously stirred solution of <sup>iPr,H</sup>PyTACN (205 mg, 0.67 mmols) in THF (1.5 mL). After a few seconds the solution became cloudy and a pale yellow precipitate appeared. After stirring for 1 hour the solution was filtered

off and the resultant pale yellow solid dried under vacuum. The solid was dissolved in  $\text{CH}_2\text{Cl}_2$  and filtered through Celite. Slow diethyl ether diffusion over the resultant solution afforded, in a few days, 300 mg of pale brown crystals (0.46 mmols, 68 %).  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , 200 MHz,  $27^\circ\text{C}$ ):  $d = 97.81, 90.82, 55.84, 53.97, 45.02, 41.18, 18.6, -3.76$  ppm; FT-IR (ATR):  $\nu = 2988 - 2948$  ( $\text{C-H}$ )<sub>sp3</sub>, 1299 (py), 1236, 1212, 1154, 1020, 628  $\text{cm}^{-1}$  ( $\text{CF}_3\text{SO}_3$ ); UV/Vis ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 256 (4600), 335 nm ( $260 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$ ); ESI-MS:  $m/z$ : 200.5  $[\text{M}+\text{CH}_3\text{CN}-2\text{CF}_3\text{SO}_3]^{2+}$ , 221.1  $[\text{M}+2\text{CH}_3\text{CN}-2\text{CF}_3\text{SO}_3]^{2+}$ , 509.0  $[\text{M}-\text{CF}_3\text{SO}_3]^+$ ; elemental analysis calcd (%) for  $\text{C}_{20}\text{H}_{32}\text{F}_6\text{FeN}_4\text{O}_6\text{S}_2$ : C 36.48, H 4.90, N 8.51, S 9.74; found: C 36.46, H 5.16, N 8.73, S 9.08.

**$[\text{Fe}(\text{CF}_3\text{SO}_3)_2(\textit{iPr,Me}\text{PyTACN})](2\text{CF}_3\text{SO}_3)$** . A solution of  $\text{Fe}(\text{CF}_3\text{SO}_3)_2(\text{CH}_3\text{CN})_2$  (77 mg, 0.18 mmols) in anhydrous  $\text{CH}_2\text{Cl}_2$  (1 mL) was added dropwise to a vigorously stirred solution of  $\textit{iPr,Me}\text{PyTACN}$  (56 mg, 0.18 mmols) in  $\text{CH}_2\text{Cl}_2$  (1 mL). The resulting pale yellow solution was stirred for further 2 hours and then it was filtered through Celite. Slow diethyl ether diffusion over this solution afforded 99 mg of white crystals (0.15 mmols, 83 %).  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{CN}$ ,  $27^\circ\text{C}$ ):  $d = 89.00, 74.34, 53.52, 46.05, -18.24, -23.06$  ppm; FT-IR (ATR):  $\nu = 2922 - 2853$  ( $\text{C-H}$ )<sub>sp3</sub>, 1289 (py), 1248, 1225, 1184, 1025, 633  $\text{cm}^{-1}$  ( $\text{CF}_3\text{SO}_3$ ); UV/Vis ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 267 (4200), 330 nm ( $180 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$ ); ESI-MS:  $m/z$ : 207.8  $[\text{M}+\text{CH}_3\text{CN}-2\text{CF}_3\text{SO}_3]^{2+}$ , 228.2  $[\text{M}+2\text{CH}_3\text{CN}-2\text{CF}_3\text{SO}_3]^{2+}$ , 523.3  $[\text{M}-\text{CF}_3\text{SO}_3]^+$ ; elemental analysis calcd (%) for  $\text{C}_{21}\text{H}_{34}\text{F}_6\text{FeN}_4\text{O}_6\text{S}_2$ : C 37.51, H 5.10, N 8.33, S 9.54; found: C 37.37, H 5.30, N 8.61, S 8.87.

**$[\text{Fe}(\text{CF}_3\text{SO}_3)_2(\textit{Me,H}\text{PyTACN})](3\text{CF}_3\text{SO}_3)$** . In an anaerobic glove box, a solution of  $\text{Fe}(\text{CH}_3\text{CN})_2(\text{CF}_3\text{SO}_3)_2$  (90 mg, 0.21 mmols) in anhydrous THF (2 mL) was added dropwise to a vigorously stirred solution of  $\textit{Me,H}\text{PyTACN}$  (51 mg, 0.21 mmols) in THF (1.5 mL). After a few seconds the solution became cloudy and a yellow precipitate appeared. After stirring for 1 hour the solution was filtered off and the resultant yellow solid was dried under vacuum. This solid was dissolved in  $\text{CH}_2\text{Cl}_2$  and filtered through Celite. Slow diethyl ether diffusion over the resultant solution afforded, in a few days, 109 mg of yellow crystals (0.18 mmols, 86 %).  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{CN}$ ,  $27^\circ\text{C}$ ):  $d = 13.69, 10.32, 8.40, 6.25, 4.33, 1.97$  ppm;  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $27^\circ\text{C}$ ):  $d = 118.53, 92.45, 49.92, 36.52, 32.30, 17.73$  ppm; FT-IR (ATR):  $\nu = 2862$  ( $\text{C-H}$ )<sub>sp3</sub>, 1285 (py), 1224, 1158, 1026, 634  $\text{cm}^{-1}$  ( $\text{CF}_3\text{SO}_3$ ); UV/Vis ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 239 (13900), 385 (3200), 550 nm ( $65 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$ ); ESI-MS:  $m/z$ : 192.8  $[\text{M}+2\text{CH}_3\text{CN}-2\text{CF}_3\text{SO}_3]^{2+}$ , 453.1  $[\text{M}-\text{CF}_3\text{SO}_3]^+$ , 494.1  $[\text{M}+\text{CH}_3\text{CN}-\text{CF}_3\text{SO}_3]^+$ ; elemental analysis calcd (%) for  $\text{C}_{16}\text{H}_{24}\text{F}_6\text{FeN}_4\text{O}_6\text{S}_2 \cdot 1/4\text{CH}_3\text{CN}$ : C 32.35, H 4.07, N 9.76, S 10.47; found: C 32.49, H 4.04, N 9.66, S 10.30.

**[Fe(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>(<sup>Me,Me</sup>PyTACN)] (4CF<sub>3</sub>SO<sub>3</sub>)**. A solution of Fe(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> (293 mg, 0.67 mmols) in anhydrous THF (2 mL) was added dropwise to a vigorously stirred solution of <sup>Me,Me</sup>PyTACN (176 mg, 0.67 mmols) in THF (1 mL). After a few seconds the solution became cloudy and a pale yellow precipitate appeared. After stirring for 1 hour the solution was filtered off and the resultant pale yellow solid was dried under vacuum. This solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and filtered through Celite. Slow diethyl ether diffusion over the resultant solution afforded 299 mg of pale yellow needles (0.48 mmols, 72 %). <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN, 27°C): *d* = 84.33, 54.18, 48.03, -2.98 ppm; FT-IR (ATR):  $\nu$  = 2928 – 2872 (C-H)<sub>sp3</sub>, 1285 (py), 1222, 1157, 1023, 635 cm<sup>-1</sup> (CF<sub>3</sub>SO<sub>3</sub>); UV/Vis (CH<sub>3</sub>CN):  $\lambda_{\text{max}}$  (*e*) = 267 (5100), 340 nm (255 mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup>); ESI-MS *m/z*: 199.8 [M+2CH<sub>3</sub>CN-2CF<sub>3</sub>SO<sub>3</sub>]<sup>2+</sup>, 467.1 [M-CF<sub>3</sub>SO<sub>3</sub>]<sup>+</sup>, 509.0 [M-CF<sub>3</sub>SO<sub>3</sub>+CH<sub>3</sub>CN]<sup>+</sup>; elemental analysis calcd (%) for C<sub>17</sub>H<sub>26</sub>F<sub>6</sub>FeN<sub>4</sub>O<sub>6</sub>S<sub>2</sub>·1/2H<sub>2</sub>O: C 32.65, H 4.35, N 8.96, S 10.25; found: C 32.60, H 4.18, N 9.04, S 9.29.

**[Fe(CH<sub>3</sub>CN)<sub>2</sub>(<sup>Me,H</sup>PyTACN)] ([3CH<sub>3</sub>CN]PF<sub>6</sub>)**. FeCl<sub>2</sub> (11 mg, 0.09 mols) was added directly as a solid to a vigorously stirred solution of <sup>Me,H</sup>PyTACN (21 mg, 0.09 mmols) in CH<sub>3</sub>CN. The initially pale yellow solution became gradually bright orange as the FeCl<sub>2</sub> got dissolved. After stirring for 30 minutes, AgPF<sub>6</sub> (44 mg, 0.17 mmols) was added which caused the immediate precipitation of AgCl and an evident color change of the solution from bright orange to red. After stirring for 30 minutes (to ensure the complete precipitation of AgCl), the solution was filtered through Celite. Slow diethyl ether diffusion over the resultant solution afforded, in a few days, 39 mg of red crystals (0.06 mmols, 67 %). <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN, 27°C): *d* = 13.92, 12.07, 10.85, 10.44, 10.24, 9.69, 8.77, 7.73, 6.41, 4.32, 2.18, 1.97 ppm; FT-IR (ATR):  $\nu$  = 2953 – 2827 (C-H)<sub>sp3</sub>, 820, 555 cm<sup>-1</sup> (PF<sub>6</sub>); ESI-MS: *m/z*: 152.0 [M-2CH<sub>3</sub>CN-2PF<sub>6</sub>]<sup>2+</sup>; elemental analysis calcd (%) for C<sub>18</sub>H<sub>30</sub>F<sub>12</sub>FeN<sub>6</sub>P<sub>2</sub>·1/3 CH<sub>3</sub>CN: C 32.50, H 4.53, N 12.86; found: C 31.97, H 4.47, N 12.43.

***Crystallographic data for  $1CF_3SO_3$  and  $[3CH_3CN]PF_6$***

**Crystal-Structure Determination.** Crystals of  $1CF_3SO_3$  (CCDC 662658) were grown by slow diffusion of diethyl ether into a  $CH_2Cl_2$  solution of the corresponding compound. Crystals of  $[3CH_3CN]PF_6$  (CCDC 662659) were grown by slow diffusion of diethyl ether into a  $CH_3CN$  solution of the compound. The crystals were used for low temperature (100(2) K) X-ray structure determination. The measurements were carried out on a *BRUKER SMART APEX CCD* diffractometer using graphite-monochromated Mo *K* $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) from an X-ray tube. For compound  $1CF_3SO_3$ , the measurements were made in the range 1.99 to 28.15 ° for  $\theta$ . Full-sphere data collection was carried out with  $\theta$  and  $\phi$  scans. A total of 38135 reflections were collected of which 6626 [R(int) = 0.0785] were unique. For compound  $[3CH_3CN]PF_6$ , the measurements were made in the range 2.41 to 28.33° for  $\theta$ . Full-sphere data collection was carried out with  $\theta$  and  $\phi$  scans. A total of 20265 reflections were collected of which 3386 [R(int) = 0.0288] were unique. The asymmetric unit contains half of the molecule. Programs used: data collection, Smart version 5.631 (Bruker AXS 1997-02); data reduction, Saint + version 6.36A (Bruker AXS 2001); absorption correction, SADABS version 2.10 (Bruker AXS 2001). Structure solution and refinement were done using SHELXTL Version 6.14 (Bruker AXS 2000-2003). The structures were solved by direct methods and refined by full-matrix least-squares methods on  $F^2$ . The non-hydrogen atoms were refined anisotropically. The H-atoms were placed in geometrically optimized positions and forced to ride on the atom to which they are attached.

**Table S1.** Crystal data for 1CF<sub>3</sub>SO<sub>3</sub> and [3CH<sub>3</sub>CN]PF<sub>6</sub>.

Compound	1CF <sub>3</sub> SO <sub>3</sub>	[3CH <sub>3</sub> CN]PF <sub>6</sub>
Empirical formula	C <sub>20</sub> H <sub>32</sub> F <sub>6</sub> FeN <sub>4</sub> O <sub>6</sub> S <sub>2</sub>	C <sub>18</sub> H <sub>30</sub> F <sub>12</sub> FeN <sub>6</sub> P <sub>2</sub>
Formula weight	658.47	676.27
Temperature	100(2) K	100 (2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	P21/c	P21/m
Unit cell dimensions	a = 8.994(3) Å a = 90° b = 20.446(6) Å β = 91.735(5)° c = 15.012(5) Å γ = 90°	a = 7.9099(4) Å a = 90° b = 9.8035(5) Å β = 90.9770(10)° c = 16.6584(9) Å γ = 90°
Volume	2759.4(14) Å <sup>3</sup>	1291.58(12) Å <sup>3</sup>
Density (calculated)	1.585 g·cm <sup>-3</sup>	1.739 g·cm <sup>-3</sup>
Absorption coefficient	0.781 mm <sup>-1</sup>	0.816 mm <sup>-1</sup>
F(000)	1360	688
Cell formula units_Z	4	2
Crystal size	0.1 x 0.05 x 0.01 mm	0.4 x 0.2 x 0.1 mm
Theta range for data collection	1.99 to 28.15°	2.41 to 28.33°
Limiting indices	-11 ≤ h ≤ 11 -27 ≤ k ≤ 26 -19 ≤ l ≤ 19	-10 ≤ h ≤ 10 -12 ≤ k ≤ 13 -21 ≤ l ≤ 21
Reflections collected	38135	20265
Independent reflections	6626	3386
Completeness to theta	[R(int) = 0.0785] 98.1 % (theta = 28.15°)	[R(int) = 0.0288] 99.4 % (theta = 28.33°)
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	6626 / 0 / 356	3386 / 0 / 235
Goodness-of-fit on F <sup>2</sup>	1.120	1.242
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0650 wR <sub>2</sub> = 0.1302	R <sub>1</sub> = 0.0930 wR <sub>2</sub> = 0.2102
R indices (all data)	R <sub>1</sub> = 0.1002 wR <sub>2</sub> = 0.1408	R <sub>1</sub> = 0.0960 wR <sub>2</sub> = 0.2113
Largest diff. peak and hole	0.542 and -0.733 e. Å <sup>-3</sup>	1.300 and -1.103 e. Å <sup>-3</sup>

**Table S2.** Selected bond lengths (Å) and angles (°) for 1CF<sub>3</sub>SO<sub>3</sub> and [3CH<sub>3</sub>CN]PF<sub>6</sub>.

1CF <sub>3</sub> SO <sub>3</sub>		[3CH <sub>3</sub> CN]PF <sub>6</sub>	
Fe-N1	2.207(4)	Fe-N1	1.971(6)
Fe-N2	2.253(3)	Fe-N2	2.015(5)
Fe-N3	2.288(3)	Fe-N2A	2.015(5)
Fe-N4	2.259(3)	Fe-N4	2.021(6)
Fe-O1	2.119(3)	Fe-N5	1.926(4)
Fe-O4	2.179(3)	Fe-N5A	1.926(4)
N1-Fe-N2	75.50(12)	N1-Fe-N2	88.31(19)
N1-Fe-N4	112.86(13)	N1-Fe-N2A	88.31(19)
N2-Fe-N3	78.29(12)	N1-Fe-N5	92.33(17)
N2-Fe-N4	79.25(12)	N1-Fe-N5A	92.33(17)
N3-Fe-N4	82.49(12)	N2-Fe-N2A	85.9(3)
N1-Fe-O1	95.63(12)	N2-Fe-N5	93.11(19)
N1-Fe-O4	83.19(12)	N2-Fe-N4	96.02(19)
N2-Fe-O4	114.53(12)	N2A-Fe-N4	96.29(14)
N3-Fe-O1	115.95(12)	N2A-Fe-N5A	93.11(19)
N3-Fe-O4	88.56(11)	N4-Fe-N5	93.25(18)
N4-Fe-O1	86.68(11)	N4-Fe-N5A	93.25(18)
O1-Fe-O4	82.98(11)	N5-Fe-N5A	87.9(3)

### ***Reaction conditions for catalysis***

In a typical reaction, 0.36 mL of a 70 mM (25  $\mu$ mol), 700 mM (250  $\mu$ mol) or 2100 mM (750  $\mu$ mol)  $\text{H}_2\text{O}_2$  solution (diluted from a 35%  $\text{H}_2\text{O}_2$  aqueous solution) in  $\text{CH}_3\text{CN}$  was delivered by syringe pump over 30 min at 25  $^\circ\text{C}$  under air (for alkanes) or  $\text{N}_2$  (for olefins) to a vigorously stirred  $\text{CH}_3\text{CN}$  solution (2.14 mL) containing the iron catalyst (2.5  $\mu$ mol) and the substrate (2500  $\mu$ mol). The final concentrations of reagents were 1 mM iron catalyst, 10 mM, 100 mM or 300 mM  $\text{H}_2\text{O}_2$  and 1 M substrate (for adamantane, due to low solubility, only 25  $\mu$ mol of substrate were added and so the final concentration was 10 mM for this substrate). Catalytic reactions in the presence of water were carried out in the same way but 45  $\mu\text{L}$  of  $\text{H}_2\text{O}$  (2500  $\mu$ mol) were added together with the oxidant (final  $\text{H}_2\text{O}$  concentration was 1 M). The solution was stirred for an additional 10 min after syringe pump addition. The rest of the work-up was different depending on the substrates:

- *Alkanes*: biphenyl (internal standard) was added at this point and the iron complex was removed by passing the solution through a short path of basic alumina followed by elution with 2 mL of AcOEt. The resulting solution was subjected to GC analysis.

- *Olefins*: the organic products were esterified by 1 mL acetic anhydride together with 0.1 mL 1-methylimidazole and extracted with  $\text{CHCl}_3$ . Biphenyl (internal standard) was added and the solution was washed with 1 M  $\text{H}_2\text{SO}_4$ , sat.  $\text{NaHCO}_3$  and  $\text{H}_2\text{O}$ . The organic layer was dried with  $\text{MgSO}_4$  and subjected to GC analysis

For the measurement of kinetic isotope effects, a substrate mixture of cyclohexane- $d_{12}$ -cyclohexane 1:3 was used in order to improve the accuracy of the KIE values obtained.

In isotopic labeling experiments involving  $\text{H}_2^{18}\text{O}$ , 1000 equivalents of  $\text{H}_2^{18}\text{O}$  were added to the  $\text{H}_2\text{O}_2$  solution and delivered by syringe pump to the catalyst solution. In experiments involving  $\text{H}_2^{18}\text{O}_2$ , 70 mM  $\text{H}_2^{18}\text{O}_2$  (diluted by  $\text{CH}_3\text{CN}$  from the commercially available 2%  $\text{H}_2^{18}\text{O}_2/\text{H}_2\text{O}$  solution) was used instead of  $\text{H}_2\text{O}_2$ . Samples were concentrated by removing part of the solvent under vacuum before injecting into the GC-MS instrument. The incorporation of  $^{18}\text{O}$  into the alcohols products was measured by the relative intensity in the GC-MS of the peaks corresponding to the labeled and non-labeled alcohols. All reactions were run at least in duplicate, and the data reported was the average of these reactions.

## 2) Catalysis results

**Table S3.** Oxidation of *cis*-1,2-dimethylcyclohexane by complexes **1-4CF<sub>3</sub>SO<sub>3</sub>**.

complex	1R,2R + 1S,2S (TN) <sup>[a]</sup>	1R,2S + 1S,2R (TN) <sup>[a]</sup>	RC <sup>[b]</sup> (%)	yield <sup>[c]</sup> (%)
<b>1CF<sub>3</sub>SO<sub>3</sub></b>	0.8	0.06	86	9
<b>2CF<sub>3</sub>SO<sub>3</sub></b>	0.3	0.04	76	3
<b>3CF<sub>3</sub>SO<sub>3</sub></b>	2.8	0.10	93	29
<b>4CF<sub>3</sub>SO<sub>3</sub></b>	2.8	0.08	94	29

1R,2R; 1S,2S; 1R,2S; 1S,2R: different isomers of 1,2-dimethylcyclohexanol depending on the specific configuration of carbons 1 and 2.

[a] TN = (mol of product)/(mol of catalyst). [b] RC = retention of configuration in the oxidation of the tertiary C-H bonds of *cis*-1,2-dimethylcyclohexane, expressed as the ratio of the tertiary alcohols: [(1R,2R + 1S,2S) - (1R,2S + 1S,2R)]/[(1R,2R + 1S,2S) + (1R,2S + 1S,2R)]. [c] Yield based on the oxidant.

**Table S4.** Oxidation of adamantane by complexes **1-4CF<sub>3</sub>SO<sub>3</sub>**.

complex	1-ol (TN) <sup>[a]</sup>	2-ol (TN) <sup>[a]</sup>	2-one (TN) <sup>[a]</sup>	3 <sup>o</sup> /2 <sup>o</sup> <sup>[b]</sup>	yield <sup>[c]</sup> (%)
<b>1CF<sub>3</sub>SO<sub>3</sub></b>	1.0	0.1	0.1	15	11
<b>2CF<sub>3</sub>SO<sub>3</sub></b>	0.7	0.08	0.02	21	8
<b>3CF<sub>3</sub>SO<sub>3</sub></b>	1.7	0.13	0.04	30	19
<b>4CF<sub>3</sub>SO<sub>3</sub></b>	3.4	0.3	0.3	17	40

1-ol: 1-adamantanol; 2-ol: 2-adamantanol; 2-one: 2-adamantanone

[a] TN = (mol of product)/(mol of catalyst). [b] 3<sup>o</sup>/2<sup>o</sup> = 3 x (1-ol)/(2-ol+2-one). [c] Yield based on the oxidant.

**Table S5.** Oxidation of *cis*-2-heptene by complexes **1-4CF<sub>3</sub>SO<sub>3</sub>**.

complex	diol (TN) <sup>[a]</sup>	RC diol (%) <sup>[b]</sup>	epoxide (TN) <sup>[a]</sup>	RC epoxide (%) <sup>[b]</sup>	yield <sup>[c]</sup> (%)	diol/epoxide <sup>[d]</sup>
<b>1CF<sub>3</sub>SO<sub>3</sub></b>	7.1	> 99	0.6	88	77	10.5
<b>2CF<sub>3</sub>SO<sub>3</sub></b>	2.7	97	0.1	64	28	17.0
<b>3CF<sub>3</sub>SO<sub>3</sub></b>	3.7	90	1.6	93	53	2.3
<b>4CF<sub>3</sub>SO<sub>3</sub></b>	4.7	90	1.2	91	59	4.0

[a] TN = (mol of product)/(mol of catalyst). [b] RC = percentage of retention of configuration in the dihydroxylation and in the epoxidation expressed as the ratio of the diols or epoxides: 100(cis - trans)/(cis + trans). [c] Yield based on the oxidant. [d] diol/epoxide = (mol of diol)/(mol of epoxide)

**Table S6.** Oxidation of cyclooctene by complexes **1-4CF<sub>3</sub>SO<sub>3</sub>** under air.

complex	eq. H <sub>2</sub> O <sub>2</sub>	diol (TN) <sup>[a]</sup>	epoxide (TN) <sup>[a]</sup>	yield <sup>[b]</sup> (%)	diol/epoxide <sup>[c]</sup>
<b>1CF<sub>3</sub>SO<sub>3</sub></b>	10	6.6	1.9	85	3.5
<b>1CF<sub>3</sub>SO<sub>3</sub></b>	100	58.0	12.4	70	4.7
<b>2CF<sub>3</sub>SO<sub>3</sub></b>	10	6.2	1.4	76	4.4
<b>2CF<sub>3</sub>SO<sub>3</sub></b>	100	14.8	6.4	21	2.3
<b>3CF<sub>3</sub>SO<sub>3</sub></b>	10	3.9	5.1	90	0.8
<b>3CF<sub>3</sub>SO<sub>3</sub></b>	100	38.0	59.6	98	0.6
<b>4CF<sub>3</sub>SO<sub>3</sub></b>	10	4.7	3.7	84	1.3
<b>4CF<sub>3</sub>SO<sub>3</sub></b>	100	66.3	19.9	86	3.3

[a] TN = (mol of product)/(mol of catalyst). [b] Yield based on the oxidant. [c] diol/epoxide = (mol of diol)/(mol of epoxide)

### 3) References

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