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Supporting Information

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**Enhanced Catalytic Activity and Unexpected Products from the Oxidation of  
Cyclohexene by Organic Nanoparticles of 5,10,15,20-tetrakis-(2,3,4,5,6-  
pentafluorophenyl)porphyrinato iron(III) in Water Using O<sub>2</sub>**

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Table ESI-1. Control reactions

Solution <sup>A</sup> / nanoparticle <sup>B</sup>	Conditions	%Oxide	% ene-1-ol	% ene-1-one	TON#	comment
Solution	CH <sub>3</sub> CN/CH <sub>3</sub> OH without H <sub>2</sub> O <sub>2</sub>	-	-	-	-	No reaction
Solution	CH <sub>3</sub> CN/CH <sub>3</sub> OH H <sub>2</sub> O <sub>2</sub> with 5% H <sub>2</sub> O and PEG	95 ±5	5±1	<1		
Solution	CH <sub>3</sub> CN no CH <sub>3</sub> OH H <sub>2</sub> O <sub>2</sub>	Trace	-	-	-	References <sup>[1-4]</sup>
Cyclohexene	H <sub>2</sub> O <sub>2</sub>	-	-	-	-	No reaction
No porphyrin	H <sub>2</sub> O/PEG164/H <sub>2</sub> O <sub>2</sub>	-	-	-	-	No reaction
No porphyrin	H <sub>2</sub> O/PEG164/O <sub>2</sub>	-	-	-	-	No reaction
10±5 nm ONP	Argon atmosphere	-	-	-	-	No reaction
10±5 nm ONP	pH 7.5	-	-	-	-	No reaction
	pH 7.0	-	-	-	-	No reaction
10 nm ONP	6.5 mL air	<1	23	77	80-100	O <sub>2</sub> limited
10 nm ONP	6.5 mL O <sub>2</sub>	<1	24	76	525-550	O <sub>2</sub> limited
10±5 nm ONP	23 °C, H <sub>2</sub> O <sub>2</sub>	-	30	70	150-200	
10±5 nm ONP	29-30 °C, H <sub>2</sub> O <sub>2</sub>	-	34	66	135-160	

ONP = organic nanoparticles.

<sup>A</sup>Solution reactions: 0.1 mM catalyst in 3:1 acetonitrile:methanol, 50 µL cyclohexene, and 80 µL 30% H<sub>2</sub>O<sub>2</sub> (added slowly, 1µl/min, to the reaction with a syringe pump) in 9.5 mL vial (porphyrin: substrate: H<sub>2</sub>O<sub>2</sub> = 1:2000:3000) was reacted for 4 h. This is similar to the cyclooctene oxidations reported previously.<sup>1-4</sup>

<sup>B</sup> ONP reactions: 2.5 mL porphyrin ONP (70 µM, 1.75 x 10<sup>-7</sup> moles in porphyrin content) were mixed with 25 µL or 200 µL of cyclohexene and 40 µL 30% H<sub>2</sub>O<sub>2</sub> (porphyrin: substrate: H<sub>2</sub>O<sub>2</sub> = 1:2000:3000, H<sub>2</sub>O<sub>2</sub> slowly added to the reaction with a syringe pump) and reacted for 24 h. Alternatively, the 2.5 mL porphyrin ONP suspension was mixed with 200 µL of cyclohexene and 125 mL O<sub>2</sub> (added by opening the reaction to a separatory funnel at 1 atm; porphyrin:substrate:O<sub>2</sub> 1:16,000:40,000) and reacted for 24h.

All ONP reactions were run exhaustively. The TON = (moles products)/(moles porphyrin) has an error of ± 5%. The ONP solution had a pH = 6.5-7.0 Products were extracted into CH<sub>2</sub>Cl<sub>2</sub> and analyzed using an Agilent 5975 series GC-MS with a HP-5 column (HP-5HS 5% phenylmethylsiloxane, 30m x 0.250mm, 0.25 micron nominal). Control reactions: neither H<sub>2</sub>O<sub>2</sub> nor O<sub>2</sub> react directly with cyclohexene under these conditions, and both an oxygen source and Fe<sup>III</sup>TPPF<sub>20</sub>, as either the nanoparticle or the solvated molecule, are needed for product formation.

*Homogeneous reactions.* For the homogeneous protic solvent reactions, a 1.0 mM stock solution of the iron porphyrin complex in 3:1 acetonitrile:methanol was used. The reaction was initiated in a 9 mL screw capped vial by mixing 250 µL of the 1.0 mM porphyrin stock solution in 2.5 mL solvent (3:1 acetonitrile:methanol, 0.1 mM) and 50 µL cyclohexene. Whereupon 80 µL of 30% H<sub>2</sub>O<sub>2</sub> was slowly added to the reaction via a teflon cannula securely fitted through a hole in the cap using a syringe pump over the course of 80 min (1 µL/min). The reaction was stirred for four hours (UV-visible spectra

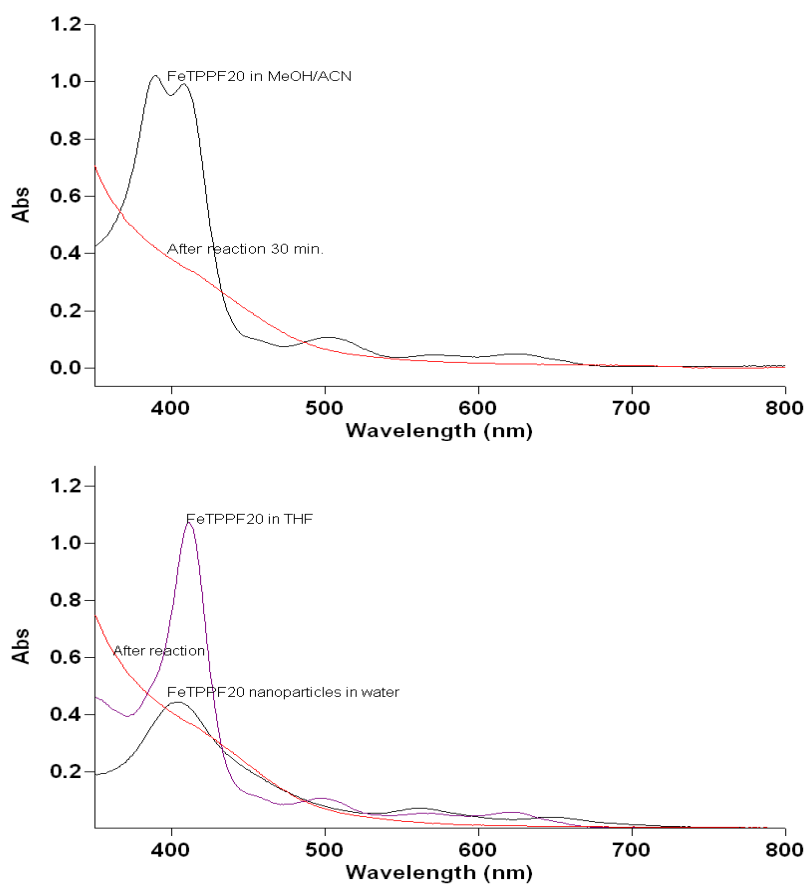
indicate that most of the porphyrin has decomposed by ca. 30 min). The ratio of porphyrin: substrate: H<sub>2</sub>O<sub>2</sub> = 1:2000:3000 equivalents. An aliquot of the reaction was analyzed by GC-MS and product yields were determined relative to an added toluene internal standard. Of the three possible products, cyclohexene oxide was obtained in greater than 99% (see supporting information).

*Other substrates and controls.* When 2-cyclohexene-1-one is placed in the 10% H<sub>2</sub>O<sup>18</sup> water and stirred for 16 h, GC-MS indicates  $8.3 \pm 1$  % O<sup>18</sup> incorporated into the ketone, thus comes from the exchange of water from the acetal hydrate. To examine the role of the ONP and possibly the Lewis acid metal ion center, the ketone was mixed with ZnTPP nanoparticles in the 10% H<sub>2</sub>O<sup>18</sup> water. The incorporation of the O<sup>18</sup> is  $5.3 \pm 0.5$  %; thus the partition of cyclohexene one into the NP “protects” the compound from exchange with the labeled water. The Fe<sup>III</sup>TPPF<sub>20</sub> porphyrin in solution may merely catalyze the hydrate formation of the ketone.

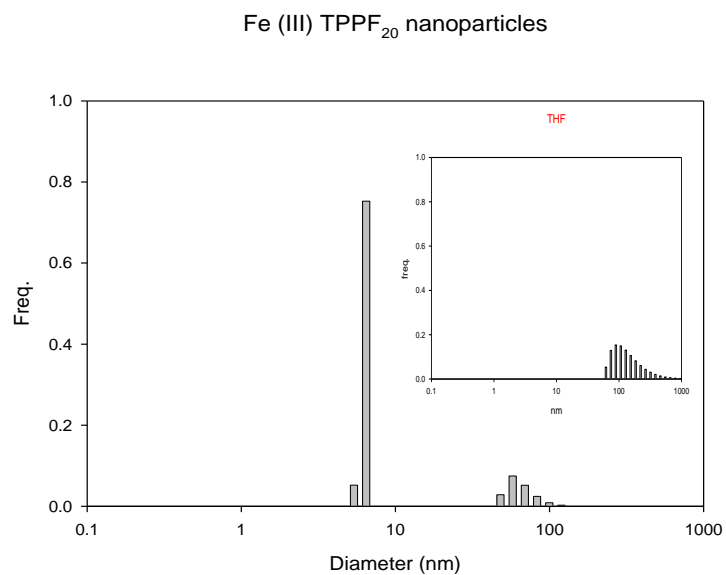
Using the standard conditions used in the studies, the epoxide is a substrate that forms only the gem diol with a TON of ca. 2300. The octanol/water partition coefficient for cyclohexene is ca. 724, while that of cyclohexanol is ca. 18. When 0.2 mL of 2-cyclohexene-1-ol is added to the mostly aqueous solution containing the ONP, it partitions 40-fold less into the ONP, so reacts proportionally less (so is not detected in this experiment). This is strong evidence that the cyclohexene partitions into the ONP, reacts to form the alcohol, and the alcohol is further oxidized before it can escape from the ONP. The epoxide is not an intermediate in the formation of the alcohol or ketone.

The addition of ca. 3% water and PEG to the solution phase reaction in acetonitrile/methanol has no effect on the product ratio or the TON (only the epoxide is formed).

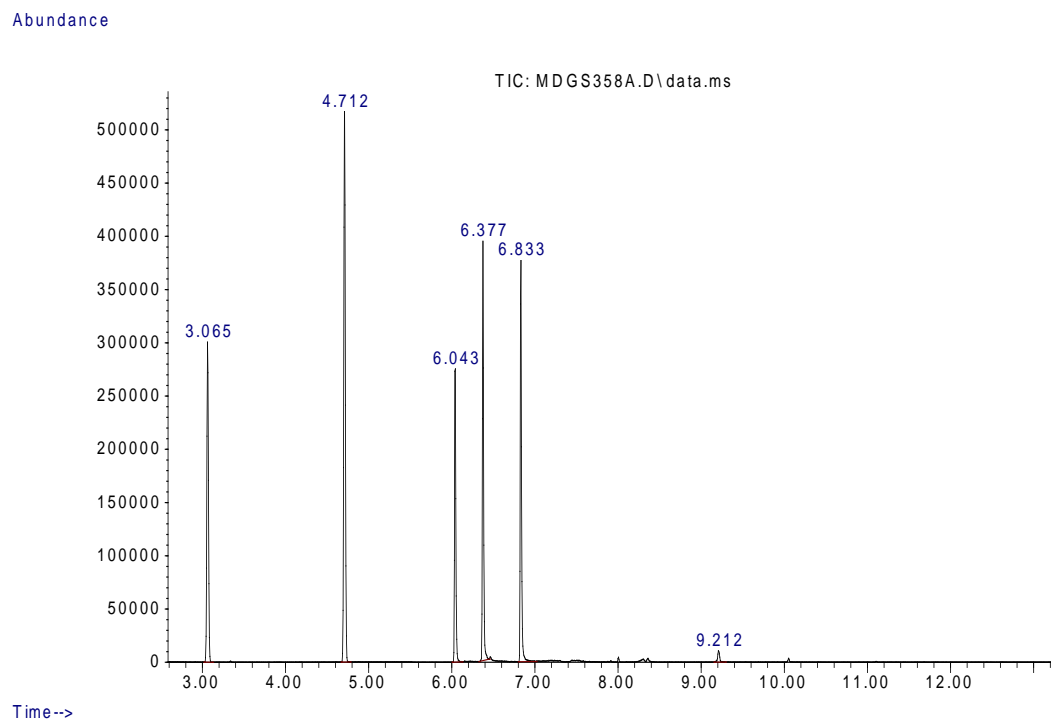
Note that using the ONP the oxidation of d-limonene yields the cyclic allyl ketone at about half the rate with a TON of 640 at 1 atm O<sub>2</sub>, but the rate increases by a ca. 2-fold and the TON is ca. 1260 using 1.7 atm O<sub>2</sub>; thus the competition between the rates of substrate versus self-oxidation is exquisitely balanced.



**Figure ESI-1.** Top: typical UV-visible spectra of the solvated Fe<sup>III</sup>TPPF<sub>20</sub> in CH<sub>3</sub>CN/CH<sub>3</sub>OH (black) and after ca. 30 min reaction (red). Bottom: Fe<sup>III</sup>TPPF<sub>20</sub> in THF (purple), the 10±3 nm ONP catalysts in water (black), and the solution after 24 h reaction (red).

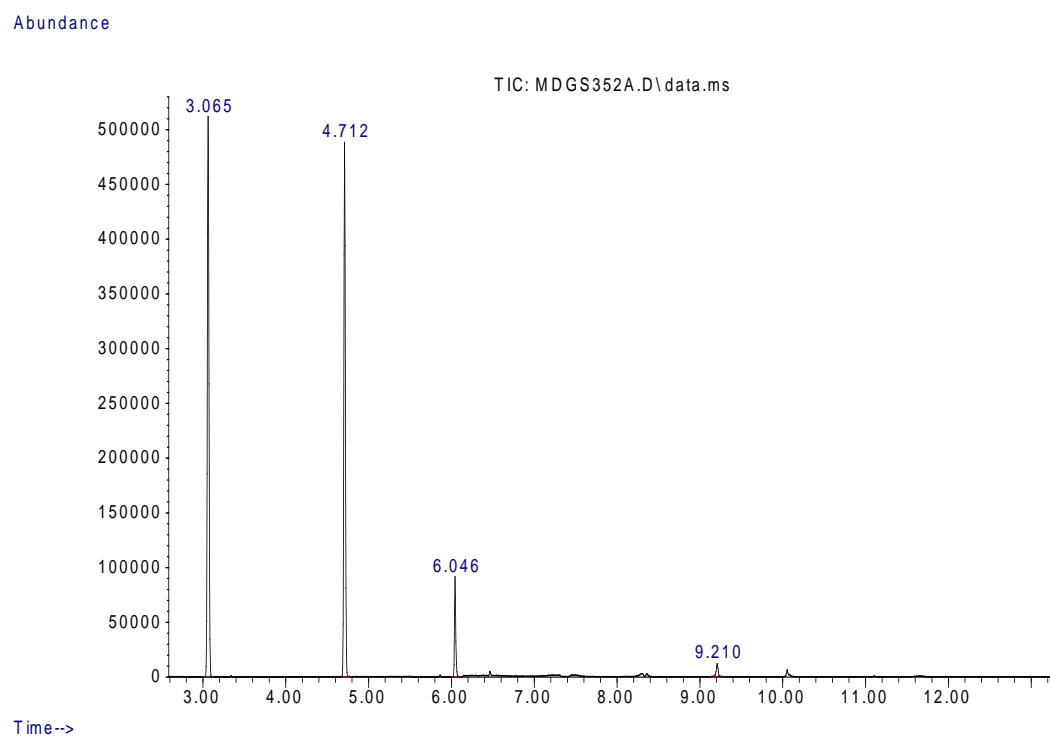


**Figure ESI-2.** Typical dynamic light scattering data indicating the diameter of the catalytic organic nanoparticles ( $10 \pm 5$  nm). The peaks at 70-100 nm are due to transient solvent micelles composed of the mixture of solvents; see the DLS of the water/THF blank in the inset.

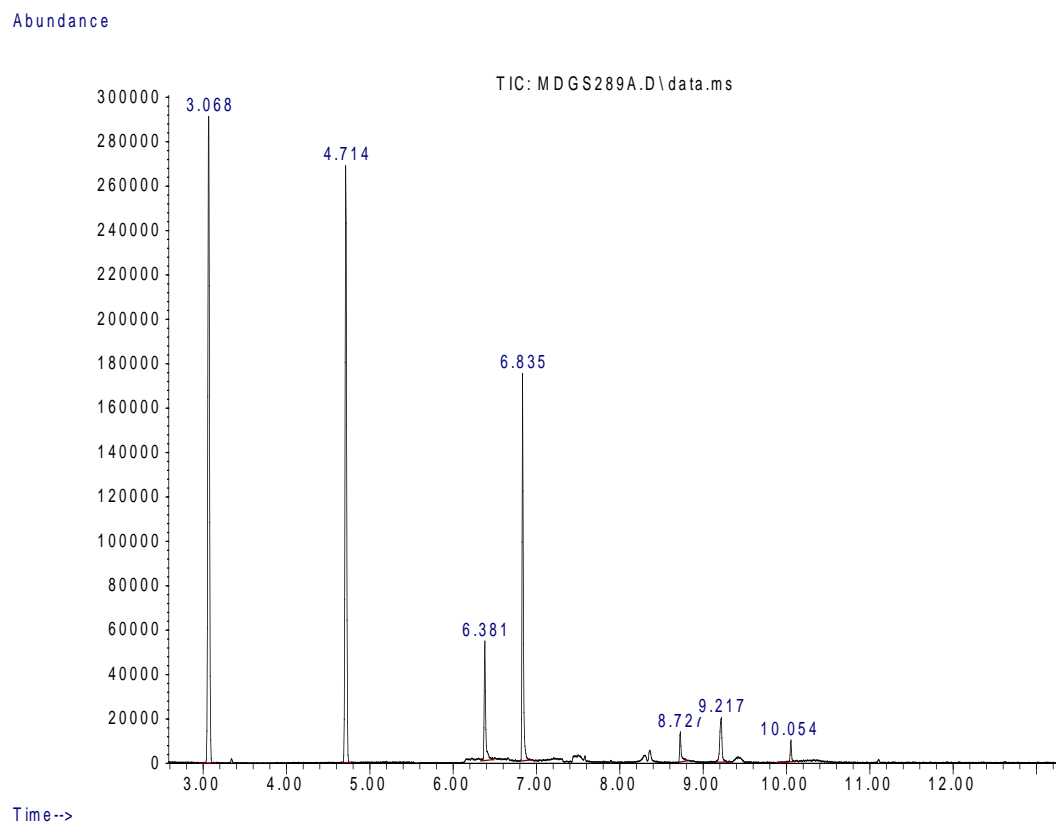


**Figure ESI-3.** GC of standards 3.06 min = cyclohexene, 4.71 min = toluene, 6.04 min = cyclohexene oxide, 6.37 min = 2-cyclohexene-1-ol, and 6.83 min = 2-cyclohexene-1-one. Mass spectrometry confirms the identity of each compound. The peaks at 9.21 min are polysiloxanes from the column.



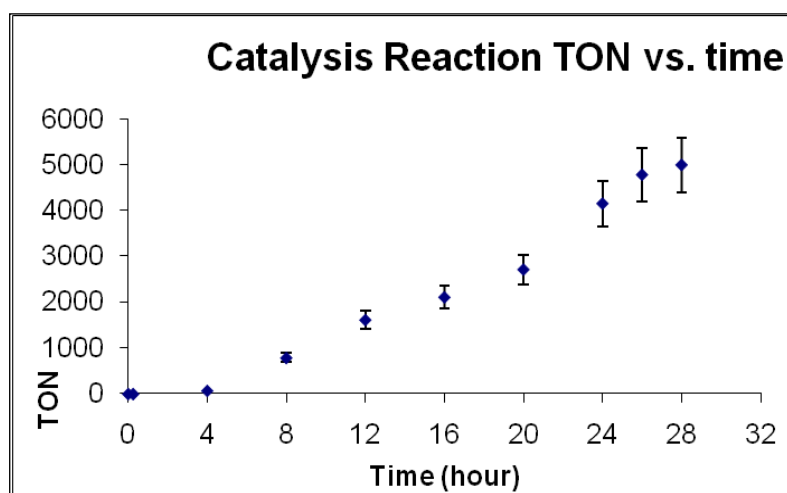
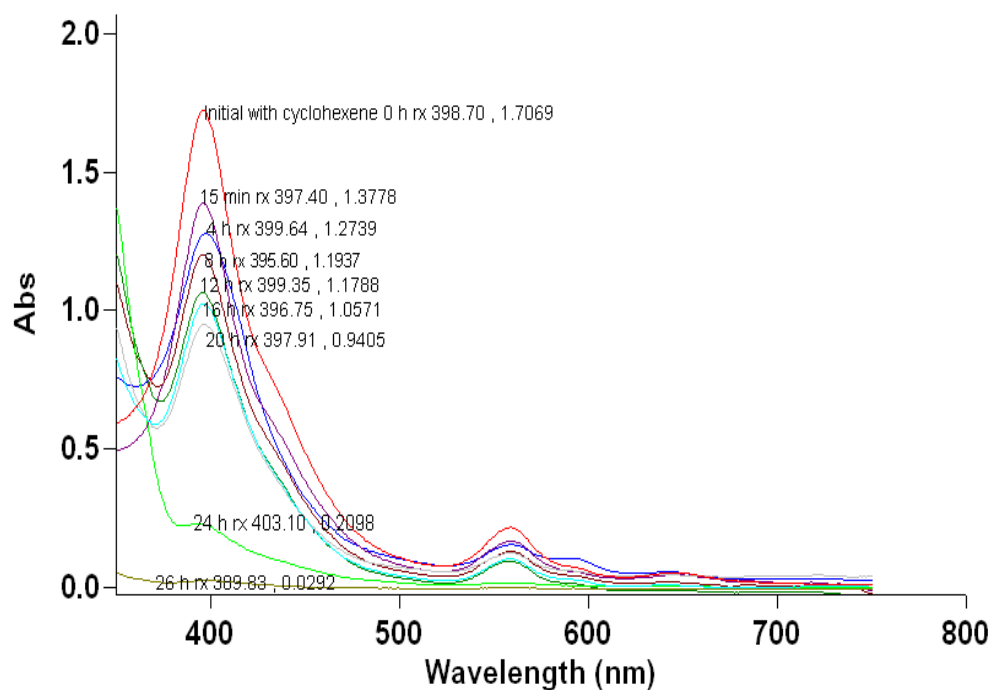


**Figure ESI-4.** GC of a standard, solution phase reaction run similarly as reported previously.<sup>1-4</sup> 3.06 min = cyclohexene, 4.71 min = toluene, 6.04 min = cyclohexene oxide. Mass spectrometry confirms the identity of each compound. The peaks at 9.21 min are polysiloxanes from the column.



**Figure ESI-5.** GC-MS of a typical ONP catalyst reaction using 125 mL O<sub>2</sub>. 3.06 min = cyclohexene, 4.71 min = toluene, 6.38 min = 2-cyclohexene-1-ol, 6.84 min = 2-cyclohexene-1-one. Mass spectrometry confirms the identity of each compound. The peaks at 9.27 min and 10.05 min are polysiloxane from the column. The peak at 8.72 min is the PEG from the ONP preparation.

The Fe<sup>III</sup>TPPF<sub>20</sub> stock solution in THF Soret maximum is at 414 nm, whereas in the ONP the Soret is at 401 nm, and after addition of cyclohexene the further blue shifts to 398 nm. The blue shift is consistent with both H-aggregation and with  $\mu$ -oxo dimers.



**Fig. ESI-6.** Top: UV-visible of the ONP solution taken during the course of a catalytic reaction. Bottom: TON (for both products) versus time. The error bars represent the average of three different experiments.

The standardized response of the GC (area) for each component in CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL total volume) is reported in **Table ESI-2**:

**Table ESI-2.** The standard response of GC area for each component

Compounds	Response factor	Ratio to toluene	Volume used	Corrected area	Moles injected
Cyclohexene	1.30	1.76	20 $\mu$ L	4040215	$7.52 \times 10^{-10}$
Toluene	2.29	1	20 $\mu$ L	6782091	$7.17 \times 10^{-10}$
Cyclohexene oxide	1.00	2.29	20 $\mu$ L	3109662	$7.54 \times 10^{-10}$
2-cyclohexene 1-ol	1.21	1.90	20 $\mu$ L	3877485	$7.77 \times 10^{-10}$
2-cyclohexene 1-one	1.86	1.86	20 $\mu$ L	4014942	$7.88 \times 10^{-10}$

A response factor of 1.90 for the combined products was used to calculate the TON for all reactions. The TON for each reaction was calculated based on the corrected area for each peak using the internal standard (toluene) and the response factor obtained in GC-MS.

***For O<sub>2</sub> reactions:***

The 2.7 mL reaction mixture volume was extracted once with 8.0 mL CH<sub>2</sub>Cl<sub>2</sub> and the layers were allowed to separate. The water fraction and some of the organic fraction was removed to leave a total volume of 6.0 mL of CH<sub>2</sub>Cl<sub>2</sub> (this assures the same volume for every reaction assay). To this volume was added 20  $\mu$ L toluene. 4.0  $\mu$ L of the extract was diluted into 1.0 mL dichloromethane and then 2.0  $\mu$ L of this solution is injected into the GC-MS.

**TON** = moles products/moles porphyrin =  $5.31 \times 10^{-4} / 1.75 \times 10^{-7} = 3037$ , since the porphyrin slowly decomposes in the reaction mixture, TON is for reactions run until [porphyrin] < 0.2  $\mu$ M, ca. 24 h.

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