

## Supporting Information for

### A chameleon catalyst for nonheme iron-promoted olefin oxidation

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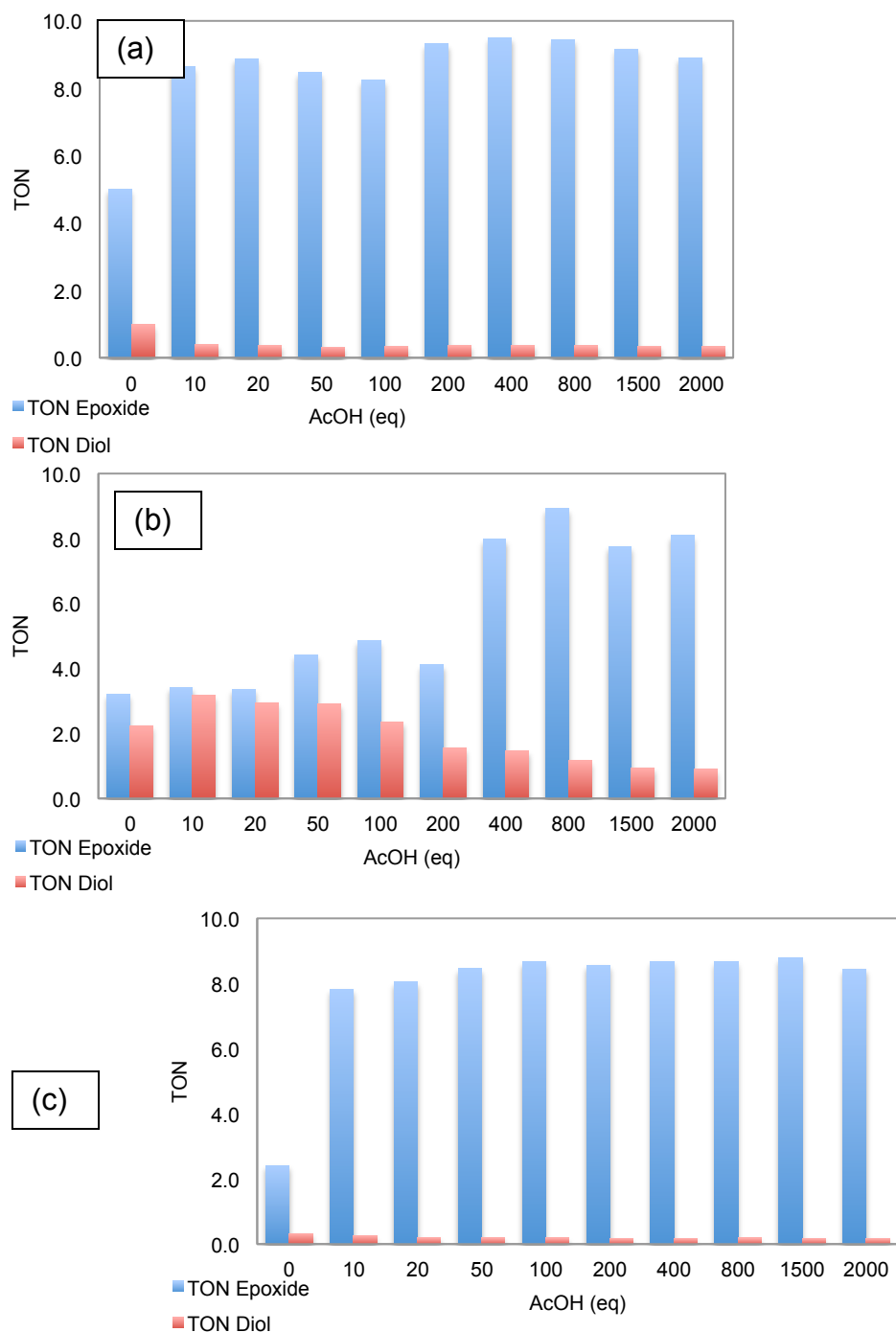
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The catalytic experiments were conducted according to published procedures.<sup>1</sup>

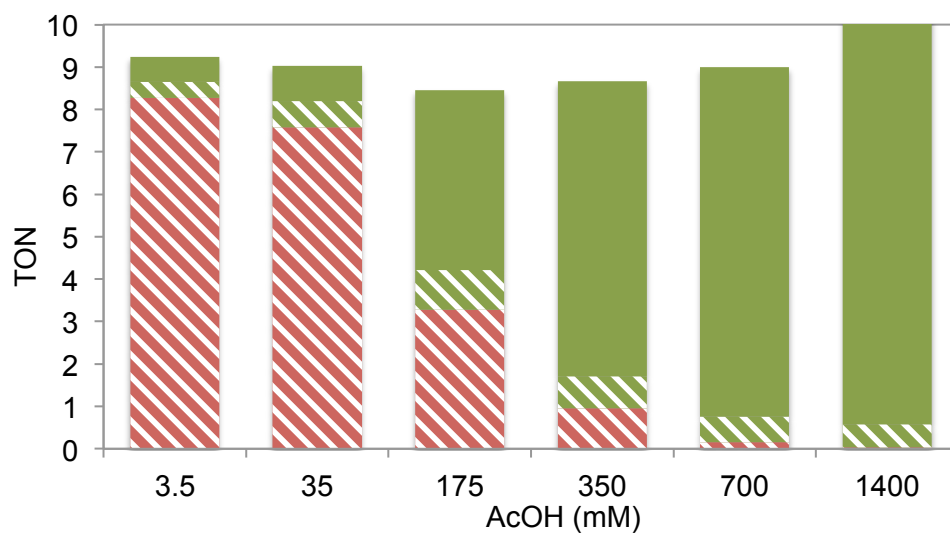
**Table S1:** Competition experiments for the oxidation of olefin pairs by **2 $\alpha$** , **2 $\beta$** , **3 $\alpha$**  and **3 $\beta$**  with 10 eq of H<sub>2</sub>O<sub>2</sub> in the absence and in the presence of 2000 eq. AcOH.

| Competition experiments (D/E) |           |         |         |         |         |
|-------------------------------|-----------|---------|---------|---------|---------|
| Catalyst                      | Acid (eq) | A vs C  |         | F vs C  |         |
|                               |           | A       | C       | F       | C       |
| <b>2<math>\alpha</math></b>   | 0         | 0.5/0.0 | 0.8/4.8 | 0.3/0.0 | 0.2/5.4 |
|                               | 2000      | 0.0/0.0 | 0.3/7.3 | 0.0/0.0 | 0.2/7.6 |
| <b>2<math>\beta</math></b>    | 0         | 8.0/0.0 | 1.0/0.5 | 8.9/0.0 | 0.0/1.0 |
|                               | 2000      | 0.0/0.0 | 0.4/9.6 | 0.0/0.0 | 0.4/8.9 |
| <b>3<math>\alpha</math></b>   | 0         | 0.7/0.0 | 0.3/1.9 | 0.6/0.0 | 0.1/2.0 |
|                               | 2000      | 0.0/0.0 | 0.2/8.0 | 0.0/0.0 | 0.2/7.5 |
| <b>3<math>\beta</math></b>    | 0         | 5.6/0.0 | 0.6/1.2 | 6.1/0.0 | 1.0/1.9 |
|                               | 2000      | 0.0/0.0 | 0.8/7.2 | 0.0/0.0 | 0.6/6.9 |

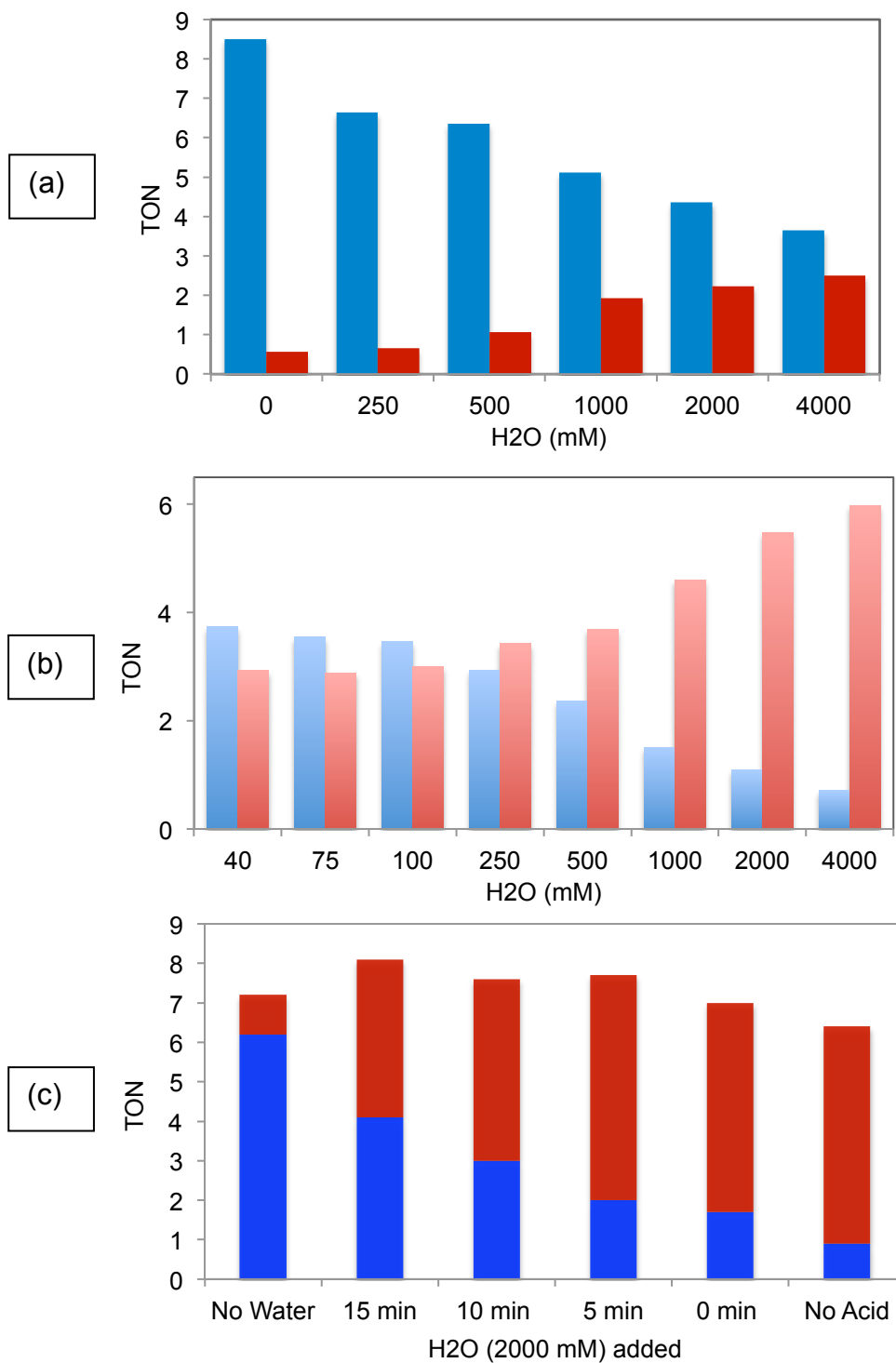
A = derived from tert-butyl acrylate, C = derived from cyclooctene, and F = derived from dimethyl fumarate. All experiments were carried out at ambient temperature with 0.7 mM catalyst, 10 eq. H<sub>2</sub>O<sub>2</sub> and 1000 eq. olefin. In experiments conducted in the presence of AcOH, this additive was added prior to addition of H<sub>2</sub>O<sub>2</sub>.



**Figure S1.** AcOH concentration dependence of product yields in the (a) **2 $\alpha$** -catalyzed oxidation of cyclooctene; (b) **3 $\beta$** -catalyzed oxidation of cyclooctene; (c) **3 $\alpha$** -catalyzed oxidation of cyclooctene. All experiments were carried out at ambient temperature with 0.7 mM catalyst, 10 eq. H<sub>2</sub>O<sub>2</sub> and 1000 eq. olefin. Maximum epoxide selectivity occurred at >10 eq. AcOH for the **2 $\alpha$**  and **3 $\alpha$**  catalysts and at much higher AcOH equivalents for the **3 $\beta$**  catalyst.



**Figure S2.** TON diol (stripes) and TON epoxide (solid) as a function of AcOH concentration in the competitive oxidation of cyclooctene (green) and *tert*-butyl acrylate (red). All experiments were carried out at ambient temperature with 0.7 mM catalyst, 10 eq. H<sub>2</sub>O<sub>2</sub> and 1000 eq. olefin in MeCN.



**Figure S3.** (a) cyclooctene oxidation by **2β** and 10 eq. H<sub>2</sub>O<sub>2</sub> in the presence of 500 eq. AcOH and 0-4000 eq. H<sub>2</sub>O; (b) 1-octene oxidation by **2β** and 10 eq. H<sub>2</sub>O<sub>2</sub> in the presence of 500 eq. AcOH and 0-4000 eq. H<sub>2</sub>O. (c) Addition of 2000 eq. H<sub>2</sub>O at particular time-points in the catalytic oxidation of 1-octene by **2β**/10 eq. H<sub>2</sub>O<sub>2</sub>/100 eq. AcOH. Red bars = TON *cis*-diol; blue bars = TON epoxide. Reaction conditions: 0.7 mM **2β** and 1000 eq. olefin substrate in MeCN at ambient temperature.

The results in Figure S3C indicate that the electrophilic epoxide-selective oxidant formed in the presence of AcOH can revert upon addition of H<sub>2</sub>O to the nucleophilic diol-selective oxidant. As an Fe<sup>III</sup>(OOH)(AcOH) adduct is the likely precursor to the electrophilic Fe<sup>V</sup>(O)(OAc) oxidant in cyclooctene epoxidation by **2β** in the presence of AcOH (Figure 2), the corresponding nucleophilic oxidant in the absence of AcOH itself must derive from an Fe<sup>III</sup>-OOH species as well for the two transformations to be connected by a rapid equilibrium.

References:

1. (a) K. Chen, M. Costas, J. H. Kim, A. K. Tipton and L. Que, *J. Am. Chem. Soc.*, 2002, 124, 3026; (b) R. Mas-Balleste and L. Que, *J. Am. Chem. Soc.*, 2007, 129, 15964.