

Impact of electronic properties and additives in asymmetric epoxidation reactions using iron complexes and H₂O₂

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Inspired by oxidations taking place at oxygenases, the combination of iron-based catalysts and hydrogen peroxide is an attractive approach for developing oxidation methods because of availability, low cost and low toxicity considerations.¹ Cytochromes P450 (Cyt-P450) constitute a paradigmatic example where the powerful electron-donating properties of the apical thiolate and the H-accepting character of a nearby threonine residue assist the O–O cleavage step of ferric hydroperoxide species via the so-called “push–pull” effect.² In 2013, our group reported the electron-rich groups on the pyridine of PdP-Fe-(OTf)₂ facilitates the heterolytic O-O cleavage and stabilizes the high valent iron-oxo, leading to highly stereoselective oxygen atom transfer. Most recently, We demonstrated that amino acids as suitable ligands in epoxidation reactions with aqueous H₂O₂ using electron-rich bioinspired non-heme iron catalysts, extending the substrate scope of these systems to the challenging terminal olefins. The present approach is appealing as it provides proof of concept that the versatility of these systems can be extended straightforwardly towards novel classes of substrates without requiring an elaborate development of novel chiral catalysts.

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