

Iron-Catalyzed Aerobic Oxidative Kinetic Resolution of Secondary Alcohols

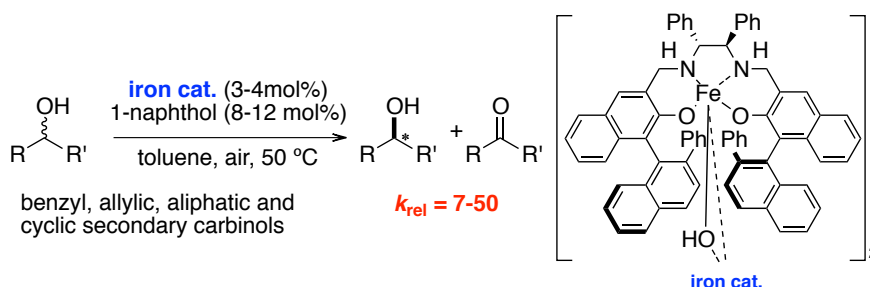
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Asymmetric oxidation reactions are essential methods for material transformations. To realize sustainable society, it is important to develop oxidation reactions using a highly atom-efficient oxidant and a complex bearing an abundant transition metal as the reaction site. Hence, asymmetric oxidation using ubiquitous molecular oxygen as the oxidant and the complex of abundant iron as the complex has attracted a growing interest.

In this context, we have recently investigated iron-catalyzed asymmetric aerobic oxidation, and we could report the first example of iron-catalyzed asymmetric oxidative coupling of 2-naphthols using iron(salan) complex as the catalyst.^[1] Based on the mechanistic study of this coupling reaction, we could further discover highly cross- and enantio-selective coupling between two different 2-naphthols.^[2] We could also propose that these coupling reactions proceed via a radical anion pathway including a naphthoxide-bound iron-salan intermediate. We were intrigued by the catalysis of this intermediate and examined the iron(salan) catalyzed oxidative kinetic resolution of racemic secondary alcohols in the presence of catalytic amount of naphthol as an additive. Intensive investigation clarified that 1-naphthol was the most effective additive for the system. This oxidative kinetic resolution could be applied for various secondary alcohols such as benzylic, allylic and non-activated aliphatic alcohols with high enantiomer differentiation.^[3]

We will discuss about our recent studies on asymmetric catalysis of aerobic oxidation by iron-salan complexes.



[1] Egami, H.; Katsuki, T. *J. Am. Chem. Soc.* **2009**, *131*, 6082-6083.

[2] Egami, H.; Matsumoto, K.; Oguma, T.; Kunisu, T.; Katsuki, T. *J. Am. Chem. Soc.* **2010**, *131*, 13633-13635.

[3] Kunisu, T.; Oguma, T.; Katsuki, T. *J. Am. Chem. Soc.* **2011**, *133*, 12937-12939.