

Catalytic α -Oxidation of Carboxylic Acids via Radical Process

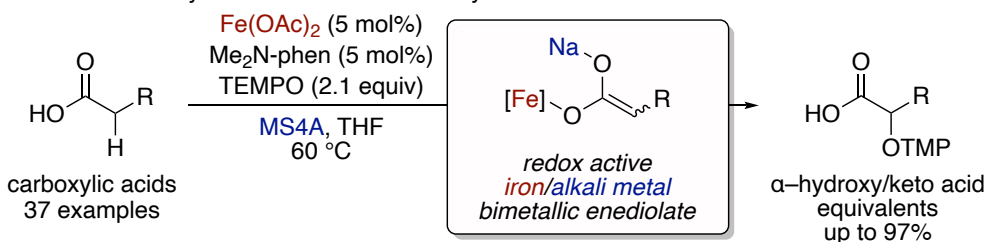
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Ubiquitous carboxylic acids are ideal carbonyl donors for the synthesis of functionalized carboxylic acid derivatives. Also, carboxylic acids get attention as a radical precursor in redox active catalysis recently. The innate Brønsted acidic carboxylic acid functionality disrupts the deprotonation of α -protons. Therefore, stoichiometric amount of base is required for conventional enolization methods.¹ Furthermore, recent enolization methods were only applied to redox neutral coupling using $2e^-$ electrophiles and catalytic α -functionalization of carboxylic acids through a $1e^-$ radical process, which could complement the chemoselectivity, and functional group tolerance restricted in the classical $2e^-$ ion reaction, has never been achieved.

Herein, we developed direct α -oxidation of carboxylic acids via radical process through redox active Lewis acid activation strategy (Scheme 1).² The present catalysis required no external Brønsted base and exhibited wide functional group tolerance. In this reaction, the addition of molecular sieves dramatically improved the product yield. Extensive mechanistic studies revealed that alkali metal in molecular sieves substantially increased the catalytic activity. It was clarified that this catalytic system is an iron and alkali metal bimetallic cooperative catalytic system in which the efficient enolization of carboxylic acids. This mechanism enables the chemoselective functionalization of carboxylic acids in the presence of carbonyl compounds such as ketones, esters, and amides.

Scheme 1. Catalytic α -Oxidation of Carboxylic Acids via Radical Process



- Direct α -Functionalization of Carboxylic Acids via Radical Process
- Enolization without Stoichiometric Brønsted Base Reagent
- Heterobimetallic Catalysis with Alkali Metal in Molecular Sieves

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