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## **ACCEPTED MANUSCRIPT**

## Kinetics and enantioselectivity of the Baeyer-Villiger oxidation of cyclohexanones by chiral tetrapyridyl oxoiron(IV) complex

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## Abstract

The previously reported oxoiron(IV) complex,  $[Fe^{IV}(asN4Py)(O)]^{2+}$  with chiral pentadentate ligand, asN4Py (asN4Py = *N*,*N*-bis(2-pyridylmethyl)-1,2-di(2-pyridyl)ethylamine), is effective for the Baeyer-Villiger oxidation of cyclohexanone derivatives. The reaction is shown to be first order in both cyclohexanone and the oxoiron(IV) species. The second order rate constant is smaller by one order of magnitude than that obtained for the related achiral  $[Fe^{IV}(N4Py)(O)]^{2+}$  complex. Oxidation of 4-substituted cyclohexanone derivatives by the chiral oxoiron(IV) complex attains moderate enantioselectivities up to 45% enantiomeric excess (ee).

*Keywords:* Biomimetics; Baeyer-Villiger oxidation; Iron(IV)-oxo complex; Enantioselectivity, Kinetics

Baeyer-Villiger (B.-V.) oxidation of ketones into esters or lactones by organic peroxyacids as stoichiometric oxidants has a wide range of application, from the synthesis of steroids, antibiotics, pheromones, and herbicides to the synthesis of intermediates for polymerization [1-8]. Since the classical B.-V. reaction lacks of the chemo-, regio-, and enantioselectivity, that are expected for organic synthesis, and the oxidants which are used are hazardous and expensive, these limitations led to the application of biocatalytic processes [9-15]. Baeyer-Villiger monooxygenases (BVMO) are considered highly valuable catalysts for the synthesis of fine chemicals [16-19]. BVMOs can be classified into three groups: Type I BVMOs contain a flavin adenine dinucleotide (FAD) as cofactor and use nicotinamide adenine dinucleotide phosphate (NADPH) as electrons source. Type II BVMOs use flavin mononucleotide (FMN) as flavin cofactor and nicotinamide adenine dinucleotide (NADH) as electron donor. Type III BVMOs are specific cytochrome P450s, which are involved in the synthesis of brassinosteroids, steroidal hormones essential for the growth and development of plants [20,21]. These heme-containing Download English Version:

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