

Linear Free Energy Relationships of Organocatalysed Asymmetric Michael Additions

Álvaro Tobias G.A. Silva (IC),¹ Natan M. Uchiyama (PG),² Bruno Matos Paz (PQ),³

a_pharm@usp.br; natan.uchiyama@usp.br, brunompaz@iq.usp.br

Institute of Chemistry, University of São Paulo, USP Butantã.

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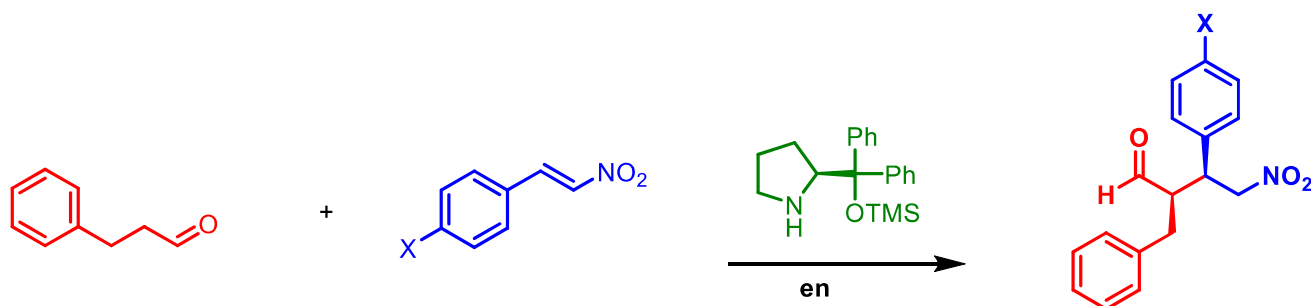
Highlights

This work aims to investigate the Mechanism of Aminocatalyzed Michael Additions to Nitroolefins via Linear Free Energy Relationships.

Abstract

The enantioselective Michael addition between aldehydes and nitroolefins mediated by enamines generated *in situ* was the first asymmetric C–C bond formation using diarylprolinol silyl ether catalysts. Originally described by Hayashi and collaborators in 2005,¹ studies on the mechanism of this reaction have been conducted by several groups^{2–4}. This transformation was shown to be a multistep process involving intermediates such as aminocyclobutanes² and N-oxides of dihydrooxazine.³ These could be reactive productive intermediates (species in the cycle) that lead to the observed product or resting states (species outside the cycle).⁵

X = H, F, Cl, CH₃, OCH₃



For this reaction, the rate determining step the stereodetermining step do not seem to coincide.² This raises an open question regarding the influence of Linear Free Energy Relationships (LFER)⁶ on the selectivity and reactivity of the system. To address this fundamental question, we conducted kinetic experiments to obtain the appropriate Hammett plots for para-substituted nitrostyrenes and hydrocinamaldehydes.

The products of the organocatalyzed reactions will be characterized for use in mass spectrometry experiments to monitor the rate of consumption of the nitrostyrenes and formation of the products. This way, we can determine the kinetic constants and obtain the linear free energy relationships using two complementary physical methods.

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