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Linear Free Energy Relationships of Organocatalyzed Asymmetric Michael Additions

Natan de Moura Uchiyama, Álvaro Tobias Gonçalves de Almeida e Silva, Bruno Matos Paz
Institute of Chemistry, University of São Paulo, USP Butantã.
***e-mail:** natan.uchiyama@usp.br*

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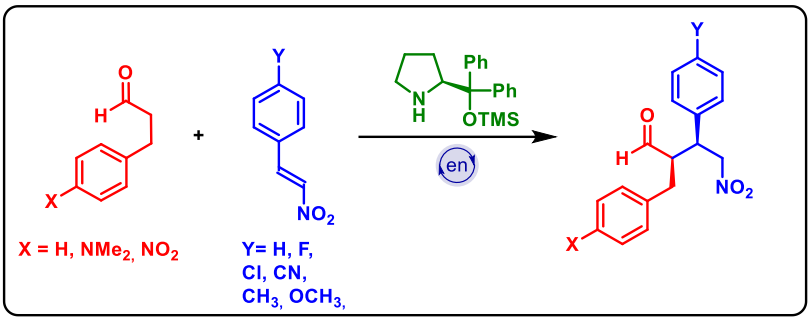
ABSTRACT

The enantioselective Michael addition between aldehydes and nitroolefins mediated by *in situ* generated enamines was the first asymmetric C–C bond formation using diarylprolinil silyl ether catalysts. Originally described by Hayashi and co-workers in 2005,[1] studies of the mechanism of this reaction were performed by several groups[2-6]

This transformation was shown to be a multistep process that involves intermediates such as aminocyclobutanes[2] and dihydrooxazine *N*-oxides.[3] These could either be productive reactive intermediates (on-cycle species) that lead to the observed product or resting states (off-cycle species).[7]

For this reaction, the rate determining step and the stereodetermining step seem to not coincide.[2] This leaves an open question about the influence of Linear Free Energy Relationships (LFER)[8] on the selectivity and the reactivity of the system. In order to answer this fundamental question, we undertook kinetic experiments to obtain the appropriate Hammett plots for *para*-substituted nitrostyrenes and hydrocinnamaldehydes.



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