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N-aryl effects on the catalyst reactivity of imidazolylidene in $a^3 \rightarrow d^3$ -umpolung addition: Structural study and mechanistic investigation

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N-Heterocyclic carbenes (NHCs) have become widely utilized as organocatalysts in the formation of challenging C-C bonds. Conjugated Breslow intermediates, derived from the reaction of $\alpha\beta$ -enal and NHCs, have emerged as a powerful tool for a variety of transformations. Since the concept of conjugated umpolung through the intermediacy of catalytically generated homoenolates and activated carboxylates, many investigations have revealed their utility to synthesize various heterocycles such as γ -butyrolactones, γ -lactams and cyclopentenes. However, there are few methods for tuning the catalytic reactivity of NHCs by either rational design of NHC catalysts or appropriate additives for cooperative catalysis. This is particularly true of imidazolylidene catalysts, only a few members of which are utilized effectively for NHC catalysis. In this study, structural and kinetic investigation of a series of imidazolylidene catalysts with various N-aryl groups for homoenolate-mediated γ -butyrolactone formation. Our study revealed that the reaction rate and catalytic reactivity can be clearly increased by the combination of 2,6-diethylphenyl groups as N-aromatic rings and a small excess amount of DBU as base compared to the originally reported conditions. Details of the structural studies, mechanistic investigations including parallel KIE experiments, and applications to the design of novel imidazolylidene catalysts will be discussed.

Biography

Tetsuo Narumi has completed his PhD from Kyoto University with Prof. Nobutaka Fujii. He spent a year in US as a JSPS Postdoctoral Fellow with Prof. Jeffrey W Bode at the University of Pennsylvania. In 2009, he began his academic career in Japan, at Tokyo Medical and Dental University with Prof. Hirokazu Tamamura. In 2013, he began his independent career at Shizuoka University, in Japan, as an Associate Professor in the Bioorganic Chemistry. He has published more than 50 papers in reputed journals and serves as a Leading Researcher in the field of Peptidomimetic Science.

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