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Favouring Trienamine Activation through Unconjugated Dienals

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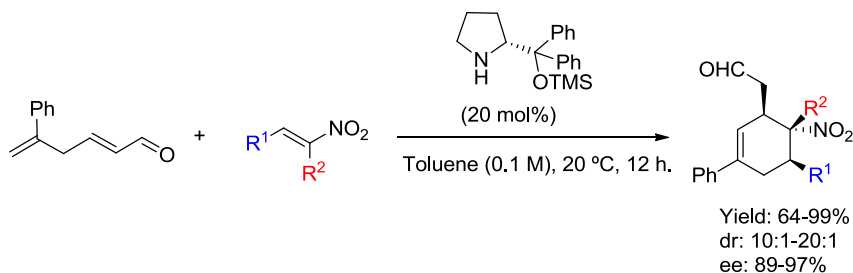
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The possibility for primary or secondary amines to activate enolizable aldehydes or ketones towards a variety of reactions opened the way for their α -functionalization in a catalytic and enantioselective fashion. In the same line, the β -functionalization of enones and enals is possible through the catalytic formation of an α,β -unsaturated iminium ion. More recently, the combination of these two activation manifolds along with the principle of vinylogy has opened the possibility for the remote functionalization of unsaturated aldehydes and ketones, allowing the γ - and δ -functionalization through dienamine catalysis and vinylogous iminium ion activation respectively. Much more recently, it has also been shown that even a more remote ε -functionalization is also possible by the formation of trienamine intermediates¹ which, if conformationally locked, also allow the selective installation of ε -stereocenters with high level of stereochemical control.

The implementation of a reaction through dienamine or trienamine intermediates entails that the conjugation level of the starting material has to increase from a simple aldehyde or ketone to an α,β -unsaturated or $\alpha,\beta,\gamma,\delta$ -polyunsaturated aldehyde or ketone respectively and this involves a progressive depletion of its reactivity towards condensation with the aminocatalyst.

In this work, unconjugated 2,5-dienals are proposed to constitute more reactive substrates than the corresponding fully conjugated $\alpha,\beta,\gamma,\delta$ -unsaturated aldehydes towards organocatalytic activation through trienamine intermediates. This has been demonstrated in the Diels-Alder reaction with nitroalkenes,² which proceeds with clean β,ε -selectivity to afford the final products in high yields and stereoselectivities, while the related polyconjugated 2,4-dienals were found to be completely unreactive.



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