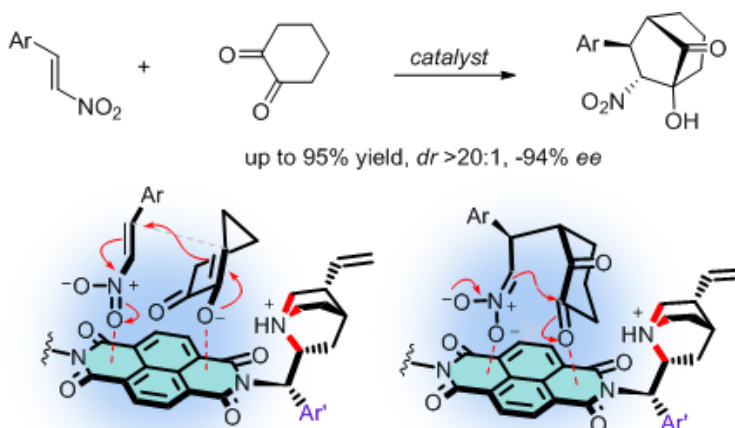


Asymmetric Anion- π Catalysis: Diastereospecific Michael/Henry Reactions for Bicyclic Products with Quarternary Chiral Centers on NDI Surfaces

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The functional relevance of anion- π interactions has been integrated into various systems including anion recognition, binding, transport and catalysis.¹ The general idea to use anion- π interactions in catalysis is to stabilize negatively charged intermediates and transition states on π -acidic surfaces. The concept has been explicitly proved validate² first in 2013 and later on realized also for complex reaction systems including asymmetric enamine activation,³ iminium cascade processes⁴ and the first anion- π enzyme.⁵ As a new step forward, we are now extending anion- π catalysis to a more complicated cascade system to prepare bicyclic compounds with four stereogenic centers including one quaternary carbon center from achiral substrates. Hybridization of cinchona alkaloids with naphthalenediimides (NDI) affords a new anion- π cinchona fusion catalyst which results in much improved diastereoselectivity and enantioselectivity compared to previous catalysts and controls. Moreover, the cascade transformation was also realized by artificial anion- π enzyme in neutral water. Evidence in support of the relevance of anion- π interactions in catalyzing the cascade process include increasing stereoselectivities and velocities in the presence of π -acidic surfaces and inhibition with anions in order of NO_3^- , Br^- , BF_4^- , PF_6^- .



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