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

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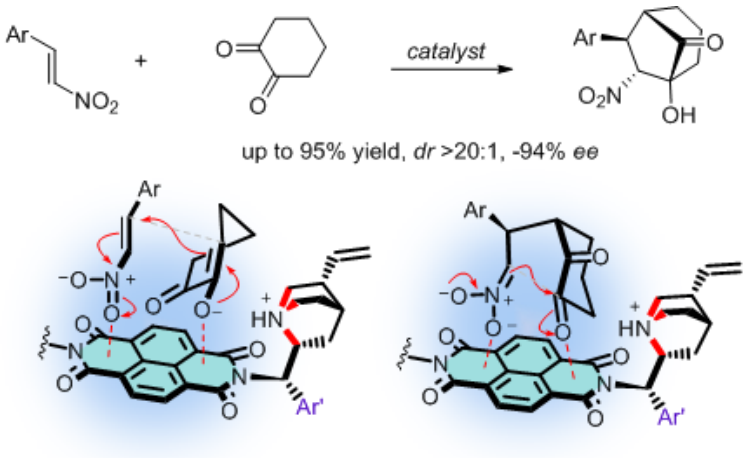
The functional relevance of anion-π interactions has been integrated into viarious systems including anion recongnition, binding, transport and catalysis.[1] The general ideal to use anion-π interactions in catalysis is to stabilize negatively charged intermediates and transition states on π-acidic surfaces. The concept has been explicitly proved validate[2] first in 2013 and later on realized also for complex reaction systems including asymmetric enamine activation,[3] iminium cascade processes[4] 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 alcaloids 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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