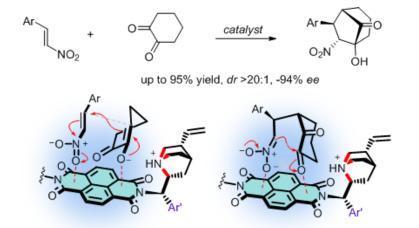
## Asymmetric Anion-π Catalysis: Diastereospecific Michael/Henry Reactions for Bicyclic Prodcuts with Quarternary Chiral Centers on NDI Surfaces

L. Liu<sup>1</sup>, Y. Cotelle<sup>1</sup>, N. Sakai<sup>1</sup>, S. Matile<sup>1</sup>\*

<sup>1</sup>University of Geneva

The functional relevance of anion- $\pi$  interactions has been integrated into viarious systems including anion recongnition, binding, transport and catalysis.<sup>1</sup> The general ideal to use anion- $\pi$  interactions in catalysis is to stabilize negatively charged intermediates and transition states on  $\pi$ -acidic surfaces. The concept has been explicitly proved validate<sup>2</sup> first in 2013 and later on realized also for complex reaction systems including asymmetric enamine activation,<sup>3</sup> iminium cascade processes<sup>4</sup> and the first anion- $\pi$  enzyme.<sup>5</sup> As a new step forward, we are now extending anion- $\pi$  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- $\pi$  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- $\pi$  enzyme in neutral water. Evidence in support of the relevance of anion- $\pi$  interactions in catalyzing the cascade process include increasing stereoselectivities and velocities in the presence of  $\pi$ -acidic surfaces and inhibition with anions in order of NO<sub>3</sub><sup>-</sup>, Br<sup>-</sup>, BF<sup>-</sup><sub>6</sub><sup>-</sup>.



Zhao, Y.; Cotelle, Y.; Sakai, N.; Matile, S. J. Am. Chem. Soc. **2016**,138, 4270. [2] Zhao,Y.; Domoto, Y.; Orentas, E.; Beuchat, C.;Emery, D.; Mareda, J.; Sakai, N.; Matile, S. Angew. Chem. Int. Ed. **2013**, 52, 9940. [3] Zhao, Y.; Cotelle, Y.; Avestro, A.-J.; Sakai, N.; Matile, S.J. Am. Chem. Soc. **2015**, 137, 11582. [4] Liu, L.; Cotelle, Y.; Avestro, A.-J.; Sakai, N.; Matile, S.J. Am. Chem. Soc. **2016**, 138, 7876. [5] Cottelle, Y.; Lebrun, V.; Sakai, N.; Ward, T. R.; Matile, S. ACS. Cent. Sci. **2016**, 2, 388.