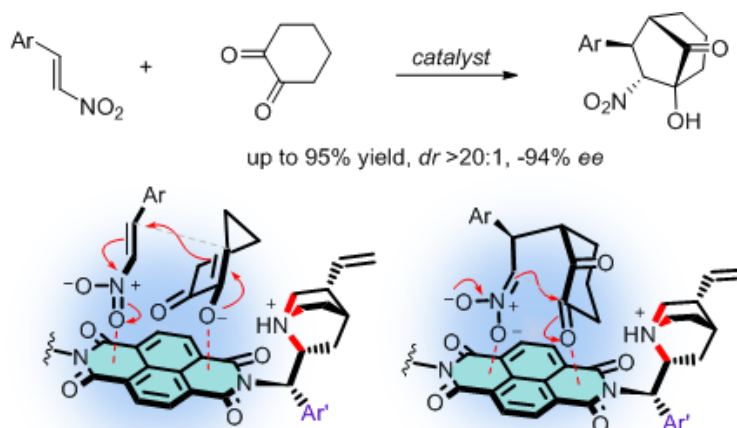


**Asymmetric Anion- $\pi$  Catalysis: Diastereospecific Michael/Henry Reactions for Bicyclic Products with Quarternary Chiral Centers on NDI Surfaces**L. Liu<sup>1</sup>, Y. Cotellet<sup>1</sup>, N. Sakai<sup>1</sup>, S. Matile<sup>1\*</sup><sup>1</sup>University of Geneva

The functional relevance of anion- $\pi$  interactions has been integrated into various systems including anion recognition, binding, transport and catalysis.<sup>1</sup> The general idea 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 and validated<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 alkaloids 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  $\text{NO}_3^-$ ,  $\text{Br}^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ .



[1] Zhao, Y.; Cotellet, 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.; Cotellet, Y.; Avestro, A.-J.; Sakai, N.; Matile, S. *J. Am. Chem. Soc.* **2015**, *137*, 11582. [4] Liu, L.; Cotellet, Y.; Avestro, A.-J.; Sakai, N.; Matile, S. *J. Am. Chem. Soc.* **2016**, *138*, 7876. [5] Cotellet, Y.; Lebrun, V.; Sakai, N.; Ward, T. R.; Matile, S. *ACS. Cent. Sci.* **2016**, *2*, 388.