β-Functionalization of Carboxylic Anhydrides with N-Heterocyclic Carbenes

**Significance:** Chi, Yang, and co-workers report the asymmetric β-functionalization of symmetrical aliphatic anhydrides \( \mathbf{1} \). Nucleophilic attack of the N-heterocyclic carbene catalyst to the anhydride generates the NHC-bound ester intermediate, which upon deprotonation forms nucleophile \( \mathbf{2} \). This adds to various electrophiles, such as alkylidene diketones, chalcones, and isatins, in a highly selective manner. Decarboxylation of the \( \beta \)-lactone intermediates \( \mathbf{3} \) yields the final products. For almost all substrates tested, consistently very high enantioselectivities accompanied with good diastereoselectivities were achieved.

**Comment:** In continuation of the work by the Chi group on the activation of esters with NHC catalysts for the functionalization of the \( \beta \)-position (Nature Chem. 2013, 5, 835), overcoming the limitation of \( \beta \)-aryl substrates is the main objective of the current work. Under the previous reaction conditions, only low yields (8−40%) were obtained. The presented solution for these challenging substrates utilizes anhydride substrates instead, affording the desired products in moderate to very good yields under the optimized conditions.