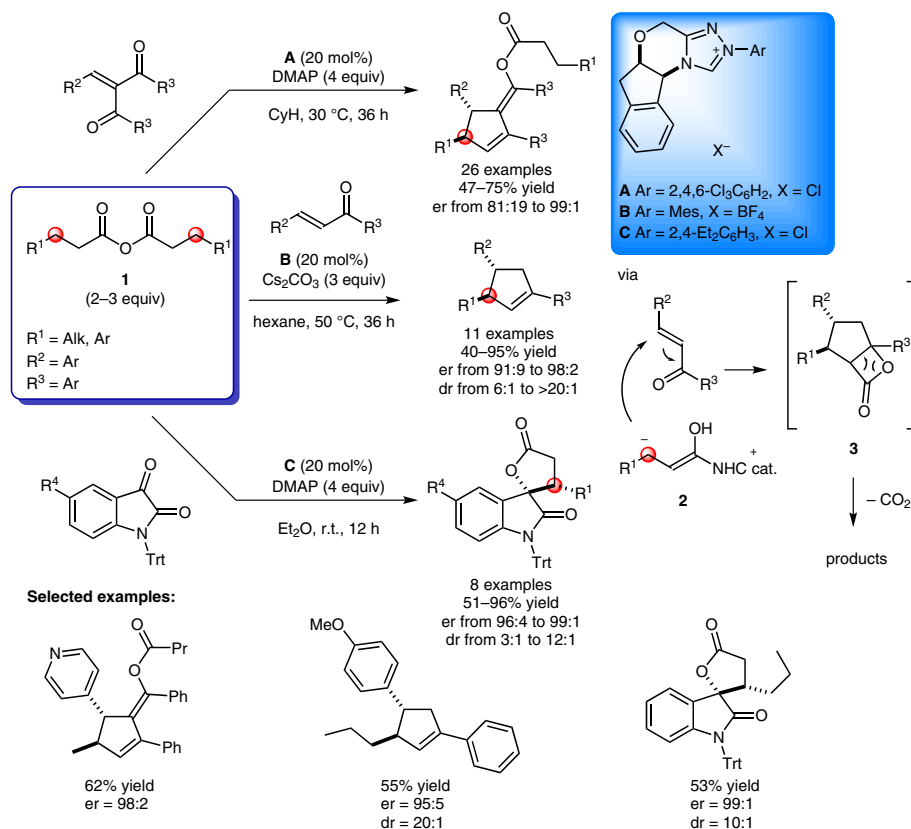


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β -Functionalization of Carboxylic Anhydrides with β -Alkyl Substituents through Carbene Organocatalysis
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β -Functionalization of Carboxylic Anhydrides with N-Heterocyclic Carbenes



Significance: Chi, Yang, and co-workers report the asymmetric β -functionalization of symmetrical aliphatic anhydrides **1**. Nucleophilic attack of the N-heterocyclic carbene catalyst to the anhydride generates the NHC-bound ester intermediate, which upon deprotonation forms nucleophile **2**. This adds to various electrophiles, such as alkylidene diketones, chalcones, and isatins, in a highly selective manner. Decarboxylation of the β -lactone intermediates **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 β -position (*Nature Chem.* **2013**, *5*, 835), overcoming the limitation of β -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.

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