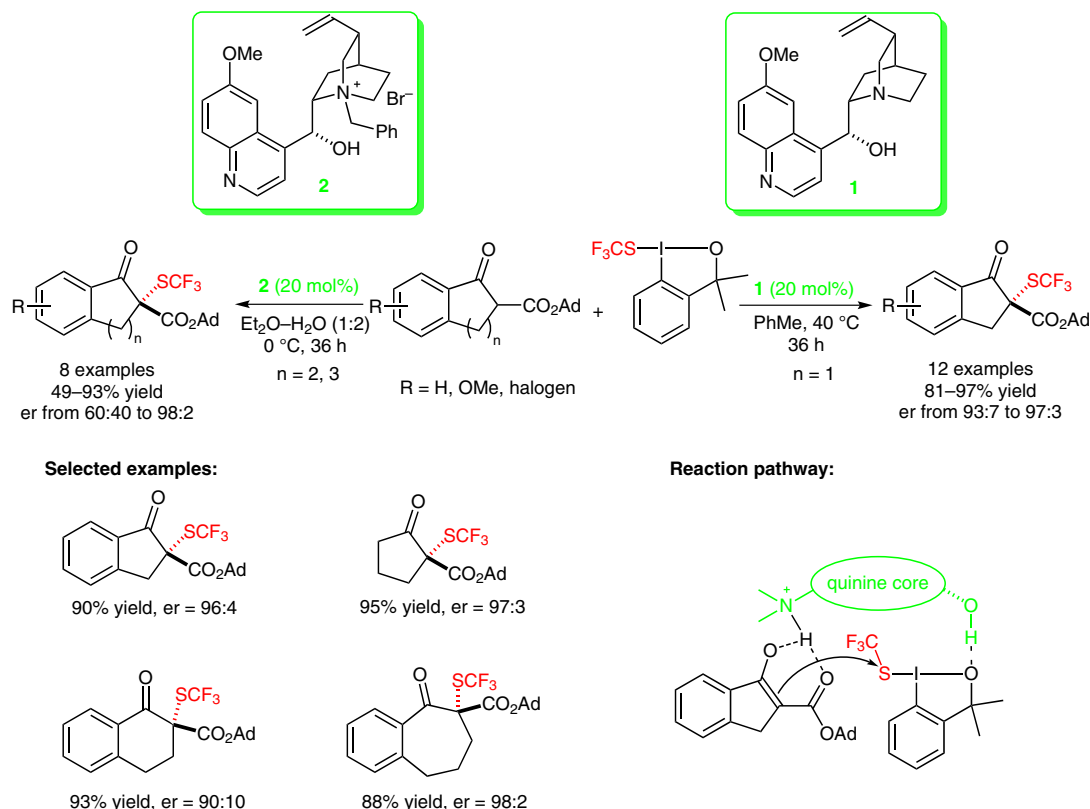


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Enantioselective Electrophilic Trifluoromethylthiolation of  $\beta$ -Ketoesters: A Case of Reactivity and Selectivity Bias for Organocatalysis  
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## Organocatalytic Trifluoromethylthiolation of $\beta$ -Keto Esters



**Significance:** A highly enantioselective trifluoromethylthiolation of  $\beta$ -keto esters is reported by Shen and co-workers. The reaction is catalyzed by quinine **1** or the quinine-derived phase-transfer catalyst **2**. Good to excellent yields and enantioselectivities are obtained by utilizing different catalysts for different ring sizes of the  $\beta$ -keto esters. The free hydroxyl group of the catalyst is crucial for reactivity, and the  $\text{SCF}_3$ -substituted quaternary ammonium pathway was ruled out by control experiments. The proposed reaction pathway involves a dual activation, in which the catalyst activates both the  $\beta$ -keto ester and the  $\text{SCF}_3$  reagent via a double hydrogen bonding.

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**Comment:** The introduction of fluorine functional groups into different molecules is of great importance for the pharmaceutical and agrochemical industries. Here, the authors report a practical procedure for highly enantioselective trifluoromethylthiolation of  $\beta$ -keto esters. This methodology provides a straightforward way to build quaternary carbon centers with a  $\text{SCF}_3$  group, which potentially could lead to useful drug candidates. At the same time, Rueping and co-workers report a very similar study, but utilizing different  $\text{SCF}_3$  sources (T. Bootwicha, X. Liu, R. Pluta, I. Atodiresei, M. Rueping *Angew. Chem. Int. Ed.* **2013**, 52, 12856).