X. WANG, T. YANG, X. CHENG, Q. SHEN* (SHANGHAI INSTITUTE OF ORGANIC CHEMISTRY, P. R. OF CHINA AND OAK RIDGE NATIONAL LABORATORY, USA)
Enantioselective Electrophilic Trifluoromethylthiolation of β -Ketoesters: A Case of Reactivity and Selectivity Bias for Organocatalysis
Angew. Chem. Int. Ed. **2013**, 52, 12860–12864.

Organocatalytic Trifluoromethylthiolation of β -Keto Esters

Significance: A highly enantioselective trifluoromethylthiolation of β -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 β -keto esters. The free hydroxyl group of the catalyst is crucial for reactivity, and the 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 β -keto ester and the SCF_3 reagent via a double hydrogen bonding.

SYNFACTS Contributors: Benjamin List, Qinggang Wang
Synfacts 2014, 10(1), 0094 Published online: 13.12.2013
DOI: 10.1055/s-0033-1340412; **Reg-No.:** B12513SF

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 β -keto esters. This methodology provides a straightforward way to build quaternary carbon centers with a 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 SCF_3 sources (T. Bootwicha, X. Liu, R. Pluta, I. Atodiresei, M. Rueping *Angew. Chem. Int. Ed.* **2013**, 52, 12856).