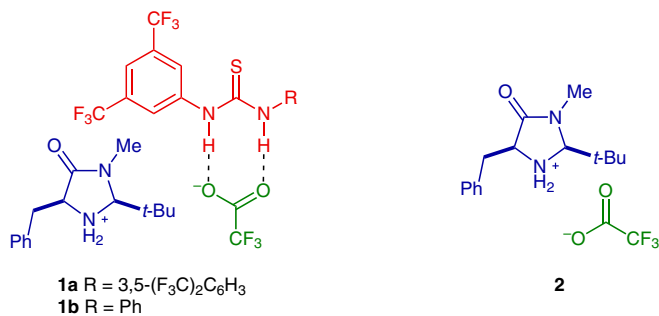
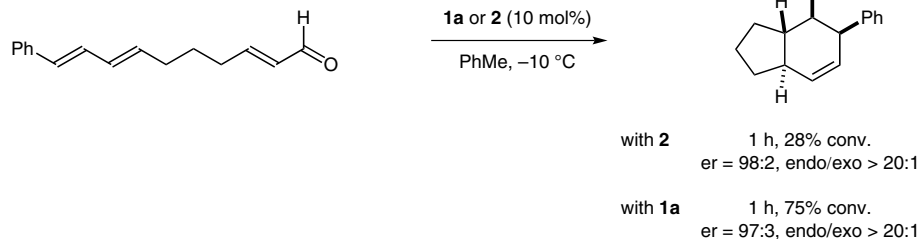


Y. WANG, T.-Y. YU, H.-B. ZHANG, Y.-C. LUO, P.-F. XU* (LANZHOU UNIVERSITY, P. R. OF CHINA)
Hydrogen-Bond-Mediated Supramolecular Iminium Ion Catalysis
Angew. Chem. Int. Ed. **2012**, *51*, 12339–12342.

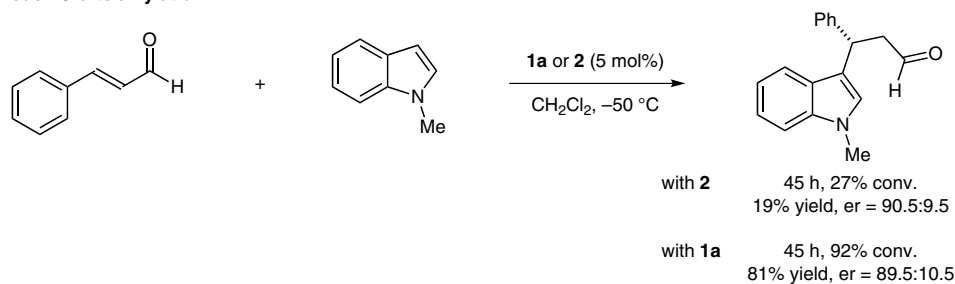
Thiourea-Assisted Iminium Catalysis



An intramolecular Diels–Alder reaction:



A Friedel–Crafts alkylation:



Significance: A thiourea-assisted iminium catalysis has been described. It was found that simple thioureas accelerate previously established reactions of α,β -unsaturated aldehydes with MacMillan's organocatalyst, presumably by binding to the counteranion of the iminium intermediate. The use of chiral thioureas did not have a significant effect on the enantioselectivity.

Comment: The profound influence of anions on reactivity and selectivity in asymmetric iminium catalysis is well established (S. Mayer, B. List *Angew. Chem. Int. Ed.* **2006**, *45*, 4193). Therefore, thioureas could be expected to influence the activity and selectivity by anion binding during the catalysis (see Review below). In the current report, a mild positive influence of thioureas on reactivity is demonstrated. Development of a chiral thiourea as the only source of asymmetric information remains as the true challenge of this approach.

Review: Z. Zhang, P. R. Schreiner *Chem. Soc. Rev.* **2009**, *38*, 1187–1198.

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