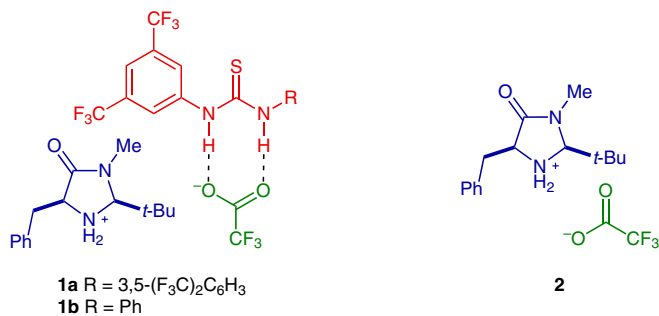
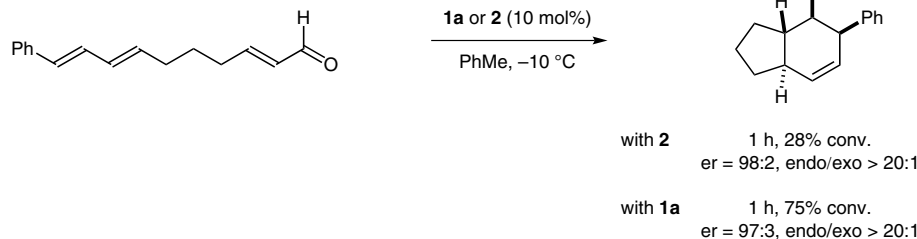


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Hydrogen-Bond-Mediated Supramolecular Iminium Ion Catalysis  
*Angew. Chem. Int. Ed.* **2012**, *51*, 12339–12342.

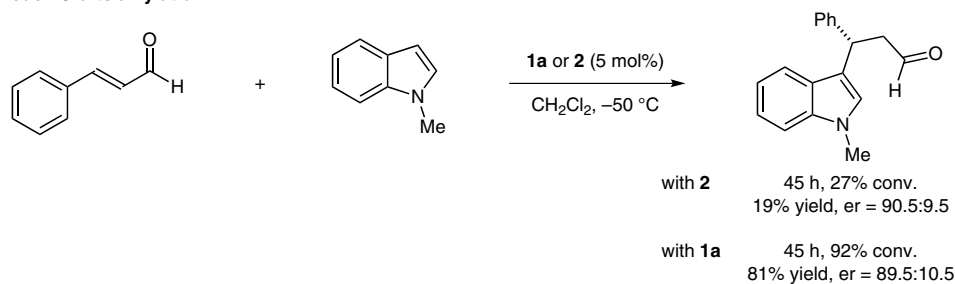
## Thiourea-Assisted Iminium Catalysis



### 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  $\alpha,\beta$ -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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