Thiourea-Assisted Iminium Catalysis

**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.