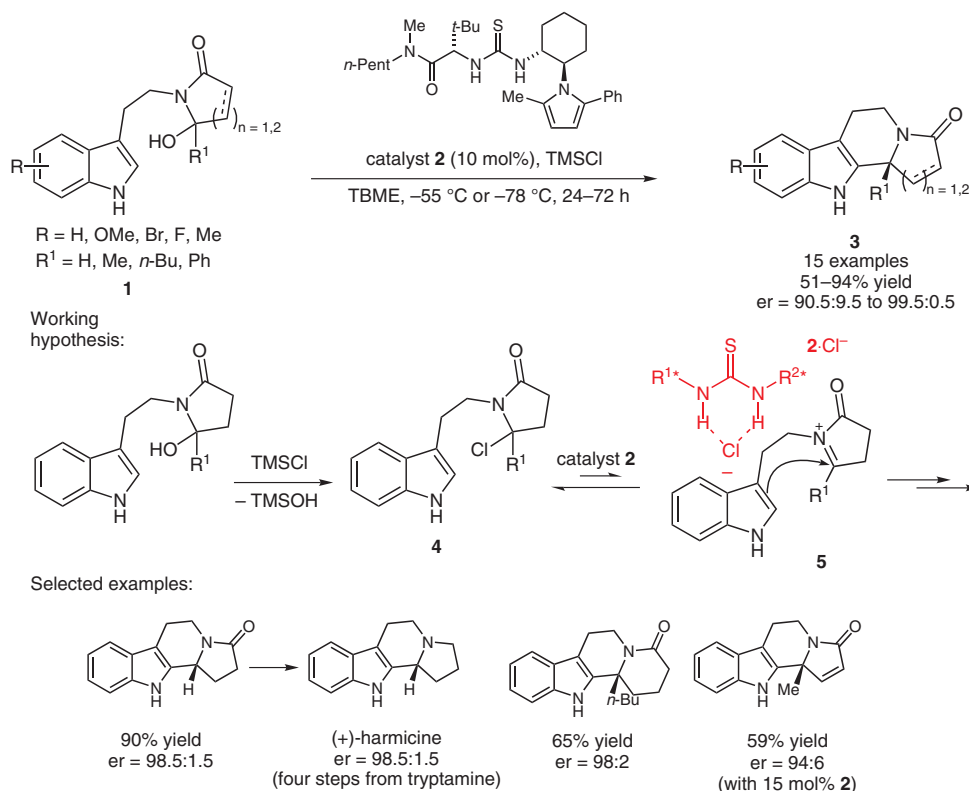


Thiourea Catalysis via Anion Binding



Significance: Asymmetric Pictet–Spengler-type cyclizations of β -indolyl ethyl hydroxylactams **1** have been achieved in the presence of thiourea derivative **2** as chiral catalyst. Both indolizidinones (**3**, $n = 1$) and quinolizidinones (**3**, $n = 2$) are obtained in good to excellent yields and optical purities. TMSCl is required for the generation of chlorolactams **4**. Plausibly thiourea catalyst **2** abstracts the chloride from **4** generating a chiral *N*-acyl iminium chloride–thiourea complex **5** as reactive intermediate. Subsequent cyclization in the chiral environment provided by the chiral thiourea–chloride anion complex (**2**·Cl[–]) leads to enantio-merically enriched products.

Comment: In 2004, Taylor and Jacobsen have discovered Pictet–Spengler-type reactions, which proceed through initial acylation of imines and are promoted by thiourea catalysts of type **2** (*J. Am. Chem. Soc.* **2004**, 126, 10558). In the present study, the Jacobsen group describes a new reaction variant and elucidates the unprecedented reaction mechanism supported by their experimental observations and the well-known anion-binding properties of (thio)ureas. Since the chiral information is exclusively provided by the chiral counteranion (**2**·Cl[–]) during the enantiodetermining step, this study may be considered a new example of asymmetric counteranion-directed catalysis (S. Mayer, B. List *Angew. Chem. Int. Ed.* **2006**, 45, 4193).