Organocatalytic Carbocyclizations

**Significance:** The research groups of MacMillan and Jacobsen have developed examples of organocatalytic carbocyclizations. Rendler and MacMillan employed organo-SOMO catalysis for cyclizations of polyene aldehydes (e.g., 3). Polycycles (e.g., 4) were obtained in good yields and enantioselectivity with 30 mol% of secondary amine catalyst 1. Jacobsen and co-workers developed thiourea catalyst 2 which effects polycyclization of hydroxylactams (e.g., 5). Polycycles (e.g., 6) were obtained in moderate to good yields and enantiomeric ratios up to 97:3.

**Comment:** The biosynthesis of complex cyclic terpenes from polyene precursors has inspired the development of biomimetic polyene cyclizations (R. A. Yoder, J. N. Johnston *Chem. Rev.* **2005**, 105, 4730). An enantioselective polyene cyclization induced by Lewis acid assisted chiral Bronsted acid has been developed recently (H. Ishibashi, K. Ishihara, H. Yamamoto *J. Am. Chem. Soc.* **2004**, 126, 11122). The cationic polycyclization reported by Jacobsen is initiated by the formation of a catalyst-bound iminium–chloride ion pair. As the enantioselectivity of the reaction is highly dependent on the size of the arene substituent in 2, stabilizing cation–π-interactions were proposed. Rendler and MacMillan have accomplished radical polycyclization of polyenals using the previously established organo-SOMO catalysis concept.