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Enantioselective Polyene Cyclization via Organo-SOMO Catalysis

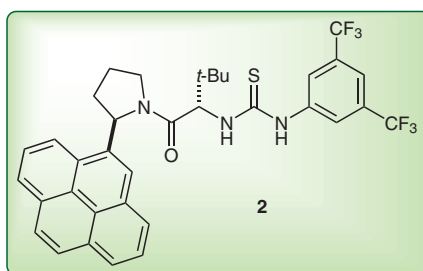
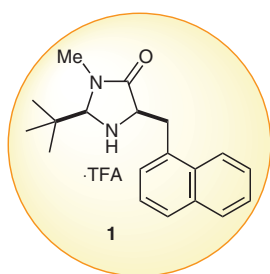
J. Am. Chem. Soc. **2010**, *132*, 5027-5029.

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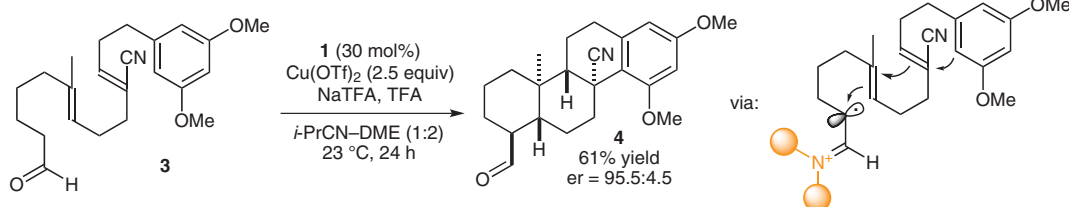
Enantioselective Thiourea-Catalyzed Cationic Polycyclizations

J. Am. Chem. Soc. **2010**, *132*, 5030-5032.

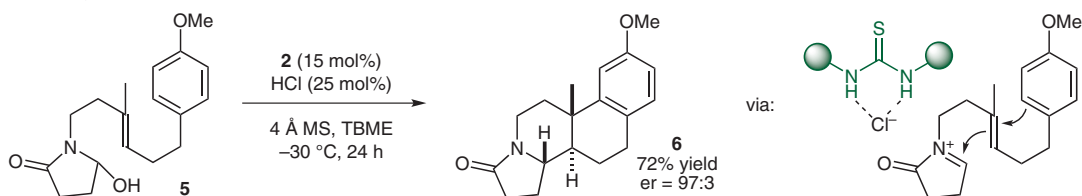
Organocatalytic Carbocyclizations



Rendler and MacMillan:



Knowles, Lin and Jacobsen:



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 Brønsted 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.

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Synfacts 2010, 6, 0709-0709 Published online: 20.05.2010
DOI: 10.1055/s-0029-1220005; Reg-No.: B04710SF

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Category

Organo- and Biocatalysis

Key words

polyene cyclization

cationic polycyclization

organo-SOMO catalysis

thiourea catalysis

SYNFACTS
of the month