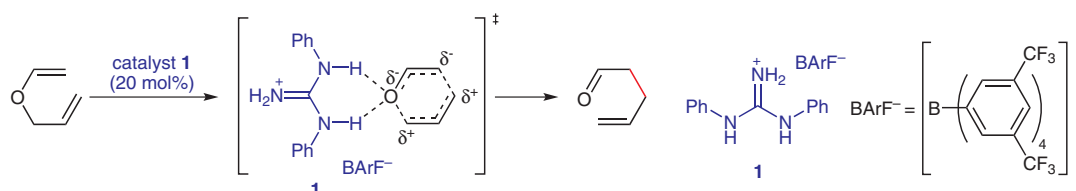
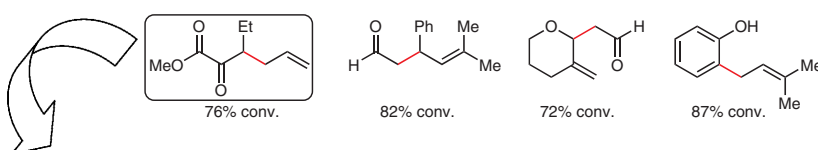


Organocatalytic Asymmetric Claisen Rearrangement

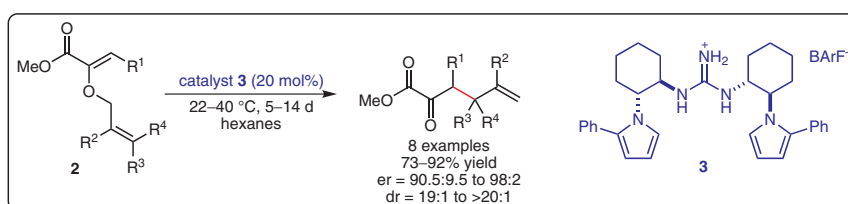
General strategy of the guanidinium salt-catalyzed Claisen rearrangement:



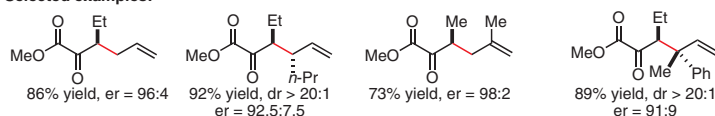
Selected examples:



Asymmetric variant with ester-substituted allyl vinyl ethers **2**:



Selected examples:



Significance: Catalysis of the Claisen rearrangement by simple guanidinium salts such as *N,N'*-diphenylguanidinium salt **1** is reported. A broad variety of substituted allyl vinyl ethers (see selected examples) were suitable substrates for this interesting transformation. Moreover, highly enantioselective Claisen rearrangements of ester-substituted allyl vinyl ethers **2** have been achieved using *C*₂-symmetric guanidinium salt **3** as the catalyst. Other types of substrates failed to give satisfying results in the asymmetric variant. The weakly coordinating counterion BArF⁻ was found to be crucial for catalytic activity of the respective guanidinium salt.

Comment: (Thio)ureas constitute a privileged class of H-bonding catalysts (see Review below). However, in catalytic Claisen rearrangements only modest rate accelerations have been realized by means of this catalyst class (see, for example: M. Hiersemann, T. Strassner and co-workers *J. Org. Chem.* **2007**, *72*, 4001). Although guanidinium BArF species exhibit similar *pK*_a values as *N,N'*-diarylthioureas, they possess superior catalytic activity in this transformation. This work complements the metal-catalyzed asymmetric Claisen rearrangement developed by the Hiersemann group (*Angew. Chem. Int. Ed.* **2001**, *40*, 4700).

Review: M. S. Taylor, E. N. Jacobsen *Angew. Chem. Int. Ed.* **2006**, *45*, 1520-1543.