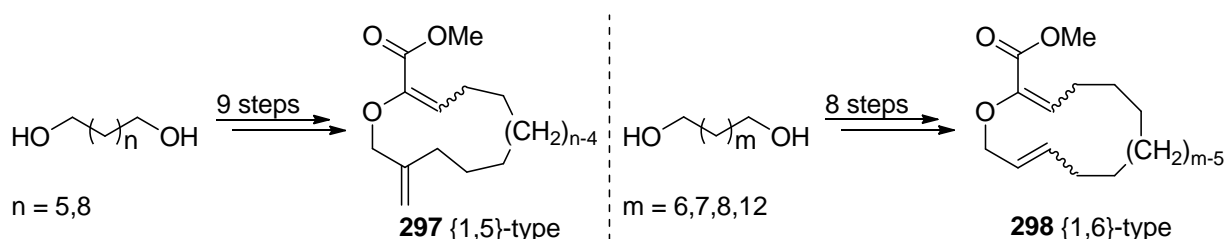


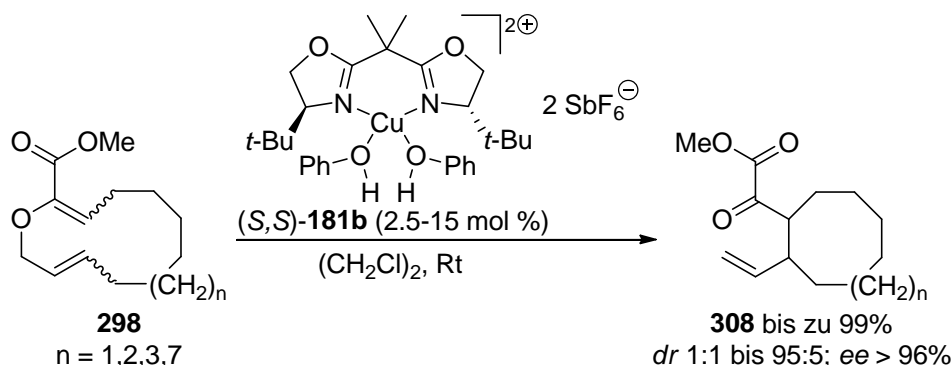
# Abstract

## Copper(II)-catalyzed {1,5}-/{1,6}-transannular catalytic asymmetric Gosteli–Claisen-rearrangement for the construction of medium- and large-sized Carbacycles

The present dissertation presents experimental studies concerning the first uncatalyzed and Copper(II)-catalyzed {1,5}- and {1,6}-transannular Gosteli–Claisen rearrangement (TGC). In the first instance a reliable and scalable 9- respectively 8-step synthesis for cyclic 2-alkoxycarbonyl-substituted allyl vinyl ethers **297** and **298** starting from commercially available diols was developed. Key feature was an intramolecular HWE reaction.



The {1,5}-TGC was investigated with 5 allyl vinyl ethers. The Ring size had a significant influence on the efficiency of this type of rearrangement. As a matter of principle the synthesis of highly strained cyclononanes was possible. Full conversion was only achieved with a catalyst. Besides an isomerization of the exocyclic double bond of the product, decomposition was observed under all tested conditions. The study concerning the uncatalyzed and catalyzed {1,6}-TGC for the construction of the medium- and large-sized Carbacycles **308** included 12 different allyl vinyl ethers. Ring size and double bond configuration were varied. The substrate as well as the catalyst structure were determinants for the efficiency of the {1,6}-TCAGC. In some cases excellent yields, high diastereoselectivities and an excellent enantiomeric excess was achieved with *t*-Bu-BOX-based catalysts e.g. (*S,S*)-**181b**. A *trans*-substituted highly strained cyclononane unit, the characteristic structural element of the Xenicane diterpenoids, was part of the synthesized Carbacycles.



**Key words:** allyl vinyl ether,  $\alpha$ -keto ester, Gosteli–Claisen rearrangement, transannular reactions, copper, asymmetric catalysis, medium-sized carbacycles