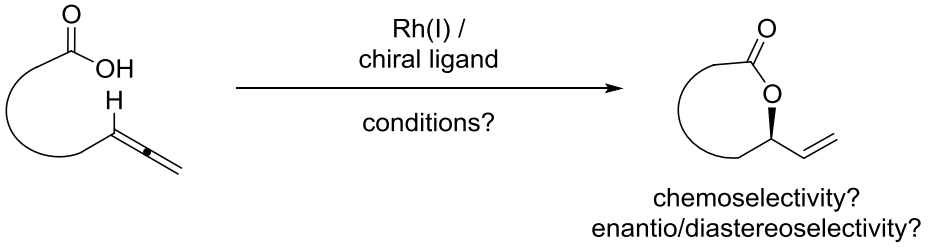
Enantioselective Macrolactonization *via* Intramolecular Rhodium-Catalyzed Coupling of Allenes with Carboxylic Acids

Stephanie Ganss (Freiburg, Germany)
Prof. Dr. Bernhard Breit, Albert-Ludwigs University Freiburg, Germany.

Macrocyclic natural products are captivating due to their often complex molecular architecture of large ring sizes combined with a broad diversity of functional groups and high stereochemical complexity. A frequently occurring motive is the macrolactone scaffold present in innumerable diverse natural compounds.[1] Though their syntheses starting from *ω*-seco acids has been well explored, these procedures are rather unattractive in terms of the modern demands for resource saving organic syntheses. Great efforts have been made to overcome these limitations and to further improve the synthetic routes. However, an asymmetric variant of the cyclization is so far unprecedented.

Our group is interested in the atom-economic Rh-catalyzed addition of pronucleophiles to alkynes and allenes. In this context, a very efficient enantioselective hydro-carboxylation toward branched allylic esters was developed.[2] Based on these findings we were encouraged to investigate the potential of the first enantioselective and atom-economic macrolactonization from intramolecular addition of carboxylic acids to terminal allenes.[3]



Literature:
[1] For a review see: Parenty, A.;Moreau, X.; Campagne, J.-M., *Chem. Rev.* **2006**, *106*, 911-939 and references therein.
[2] a) Koschker, P.; Lumbroso, A.; Breit, B. *J. Am. Chem. Soc.* **2011**, *133*, 20746-20749; b) Koschker, P.; Kähny, M.; Breit, B. *J. Am. Chem. Soc.* **2015,** *137*, 3131-3137; c) Lumbroso, A.; Abermil, N.; Breit, B. *Chem. Sci.* **2012**, *3*, 789-793.
[3] Ganss, S.; Breit, B. *Angew. Chem. Int. Ed.* **2016**, *55*, 9738-9742.