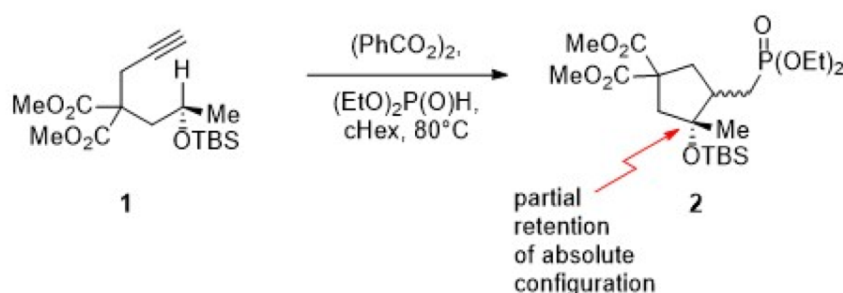


Retention of Absolute Configuration in Hydrogen Atom Transfer/Cyclisation CascadeC. Gloor¹, I. Kovalova¹, V. Soulard¹, P. Locher¹, Y. Kavanagh¹, M. Pichowicz¹, P. Renaud^{1*}¹University of Bern

Due to the nature of radicals, few stereoselective reactions are known in which a radical is generated at a chiral center with retention of the absolute configuration. In an early report by Heiba and Dessau, the formation of an optically active lactone was observed although the reaction proceeds through a radical at the chiral center *via* a 1,5-H shift.^[1] The level of retention was however unknown. Recently, Curran and coworkers published a related cyclisation process of α -amide radicals involving retention of chirality.^[2, 3]

Meanwhile, our group reported a radical cyclisation involving phosphonyl and thiyl radicals to access cyclopentane derivatives.^[4] We decided to use this reaction as the starting point to study whether retention of chirality is possible and the factors influencing the stereochemical outcome.

The alkynyl malonate **1** was readily synthesized in a five-step procedure starting from (*S*)-(-)-ethyl lactate. Treatment of **1** with diethylphosphite afforded the cyclic product **2** with partial retention of configuration (Scheme 1)



[1] El-Ahmadi I. Heiba, Ralph M. Dessau, *J. Am. Chem. Soc.*, **1967**, 89, 2238-2239

[2] Aniruddha Sasmal, Tsuyoshi Taniguchi, Peter Wipf, Dennis P. Curran, *Can. J. Chem.*, **2013**, 91, 1-5

[3] For a review on memory of chirality see: Hongwu Zhao, Danny C. Hsu, Paul R. Carlier, *Synthesis*, **2005**, 1-16

[4] a) Florent Beaufils, Fabrice Dénès, Phillippe Renaud, *Angew. Chem. Int. Ed.*, **2005**, 44, 5273-5275

b) Florent Beaufils, Fabrice Dénès, Phillippe Renaud, *Org. Lett.*, **2004**, 6, 2563-2566