

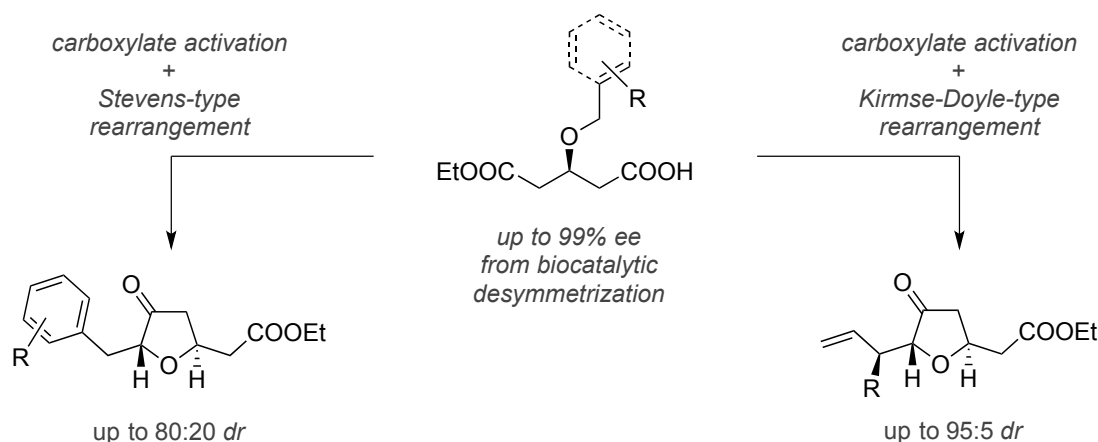
Molecular Origami: Oxonium-Ylide Rearrangements of Enzymatically Desymmetrized Glutarates

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Prochiral glutaric acid derivatives represent a popular target for investigations on enantioselective desymmetrization reactions by means of bio-, organo- or transition metal catalysts, respectively.[1] From a synthetical point of view, these transformations offer a rapid access to simple chiral building blocks which can be readily manipulated in a bidirectional manner. Due to high selectivities and facile scalability, particularly enzyme catalyzed procedures enjoy great popularity as foundation for the synthesis of complex target structures.[2] However, the direct contribution to creation of molecular complexity needs to be considered rather low.

Application of the classical glutarate desymmetrization on ether-functionalized diesters opens up new possibilities for subsequent rearrangement reaction. Thus, combination of chirality-generating biocatalytic desymmetrizations with complexity-creating oxonium-ylide rearrangements by means of transition metal catalysts allow for a quick and elegant way to synthesize complexly functionalized tetrahydrofurans in a highly enantio- and diastereoselective manner. Herein, we report on the evolution of this synthetic strategy applying both Stevens-type shifts of benzylic ethers [3] as well as [2,3]-sigmatropic rearrangements of allylic ethers according to Kirmse and Doyle [4]. The talk will cover different aspects of this novel approach, from basic method development to applications in natural product synthesis.[5]



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