The asymmetric Claisen-Cope rearrangement

Johanna Breinsperger,^a Maximilian Kaiser,^a Peter Gärtner,^a Institute of Applied Synthetic Chemistry, TU Wien, 1060 Vienna, Austria johanna.breinsperger@tuwien.ac.at

The Claisen rearrangement has become a valuable tool in organic synthesis for carbon-carbon bond formation since its discovery in 1912. Therefore, an asymmetric version of this [3,3] sigmatropic rearrangement proceeding enantioselectively during bond formation is of significant interest. Although the catalytic asymmetric aromatic ortho-Claisen rearrangement has been reported successfully, the rearrangement into the para position has been largely disregarded and underdeveloped. This study aimed to establish a working protocol for the asymmetric aromatic *para* Claisen rearrangement, using an Europium catalyst.

The enantioenriched ethers 1 and 1' were obtained by Palladium-catalysed Tsuji-Trost alkylation, employing both cyclic and acyclic allylic carbonates, achieving high yields and high enantiomeric ratios. The reaction conditions of the Claisen-Cope rearrangement to their corresponding C-alkylated isomers 2 and 2' were extensively screened for solvent, temperature, and catalyst. The conditions were optimised to enable the reaction to be performed at lower temperatures, including ambient, and without the need for an inert atmosphere. This resulted in exceptional yields and excellent enantiomeric ratios of the products.