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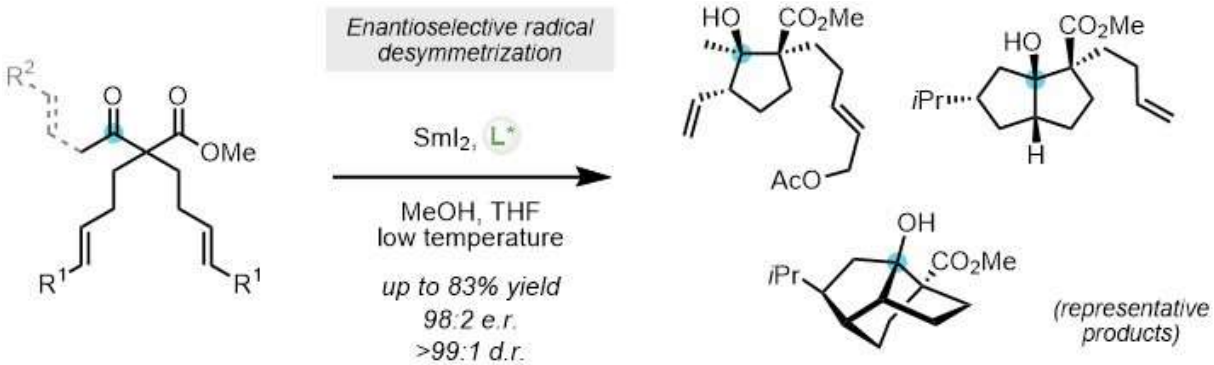
ENANTIOSELECTIVE CYCLIZATIONS AND CASCADES OF SAMARIUM KETYL RADICALS

Nicolas Kern [1], Mateusz Plesniak [2], Joseph J. W. Mcdouall [2], David J. Procter [2]

[1]*Laboratoire d'Innovation Moléculaire et Applications, UMR 7042 CNRS/Université de Strasbourg, équipe SYBIO - Strasbourg (France),*
[2]*School of Chemistry, University of Manchester - Manchester (Royaume-Uni)*
nicolas.kern@unistra.fr (Nicolas Kern)

Radical cyclization cascades have the potential to deliver complex, densely packed, polycyclic architectures, with control of three-dimensional shape, in one step. In 1977, Kagan[1] described the first convenient preparation of samarium diiodide (SmI_2), a powerful single electron transfer reagent which has found many applications in organic synthesis, from selective reductions to radical cascades building multiple C-C bonds.[2,3] Since this initial breakthrough, asymmetric induction in Sm(II) radical chemistry has remained elusive in spite of the reagent's versatility. Here, we demonstrate that enantioselective Sm(II)-mediated radical cyclizations and cascades that exploit a simple, recyclable chiral ligand can convert symmetrical ketoesters into complex carbocyclic products bearing multiple stereocentres with high enantio- and diastereocontrol.[4] A preliminary computational study has been used to probe the origin of the enantioselectivity.



References
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