Abstract

Optically active allenes are versatile synthetically useful building blocks not only in the synthesis of natural products but also as intermediates in the preparation of biologically active molecules. The development of novel and flexible methodologies for the generation of these kinds of substrates are therefore of highest interest. This thesis deals with the chemoenzymatic synthesis of optically active, axially chiral allenes. The reaction of a propargylic acetate and arylzinc bromides in the presence of $Pd(PPh_3)_4$ delivered different prochiral allenic diols, whose desymmetrization catalysed by porcine pancreatic lipase gave rise to a wide range of allene derivatives in good to excellent yield and enantiomeric excesses up to 99%. The value and applicability of the thus obtained enantiomerically enriched allenic monoesters was demonstrated in the first total synthesis of the norlignans hyperione A and the unnatural enantiomer of hyperione B. Moreover, during the studies towards the synthesis of the sesquiterpene taylofuran based on allenic building blocks, an unexpected rearrangement was identified that consequently served as the foundation for the development of a migratory dynamic kinetic resolution. The combination of a lipase-catalysed acylation (Novozym 435) and an acid-catalysed reversible 1,3-hydroxy shift (Dowex 50WX4-100) in a biphasic system allowed for the preparation of a broad range of carbocyclic decanoates from racemic tertiary alcohols in high yield and excellent enantioselectivity.