Pd Asymmetric Allylic Alkylation (AAA). A Powerful Synthetic Tool

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抄録

Palladium catalyzed asymmetric allylic alkylations represent a challenging problem because the mechanism of the reaction places the chiral environment distal to the bond breaking or making events responsible for the asymmetric induction. Furthermore, unlike virtually every other asymmetric process, many strategies can be employed for introduction of asymmetry and many different types of bonds can be formed. While over 100 different ligands have been designed, a family of ligands derived from 2-diphenylphosphinobenzoic or 1-naphthoic acid and chiral scalemic diamines have been successful in inducing excellent enantioselectivity by five different enantiodiscriminating events. These methods have already provided practical strategies towards numerous biological targets—some of which are adenosine and its enantiomer, aflatoxin B, aristeromycin, calanolide A and B, carbovir, cyclophellitol, ethambutol, galanthamine, mannostatin, neplanocin, phyllanthocin, sphingofungins E and F, tetraponaines, vigabatrin, and valienamine.
Allylic alkylation is a valuable tool for organic synthesis. The most fundamental and important problem in the reaction between allylic electrophiles and organometallic reagents is the regio- and stereocontrol (Scheme 12). The asymmetric allylic alkylation (AAA) has emerged as one of the most powerful and commonly used catalytic asymmetric transformations in total synthesis (see Chapter 4.5). Rama and coworkers initially uncovered that Ni, Pd, and Rh catalysts are able to catalyze the asymmetric decarboxylative alkylation of crotyl phenyl carbonates.196 Interestingly, the branched product was formed as the major product using these metals. Palladium-catalyzed asymmetric allylic alkylation (AAA) has proven to be an exceptionally powerful method for the efficient construction of stereogenic centers. Palladium-catalyzed Asymmetric Allylic Alkylation: Nitrogen Nucleophiles. A formidable challenge in asymmetric synthesis is the stereocontrolled construction of carbon-nitrogen bonds. Nitrogen nucleophiles such as alkylamines, azides, amides, imides, and N-heterocycles have all been employed in asymmetric allylic alkylation reactions. Alkylamines Nucleophiles: References Tools. Request permission. Export citation. Bo-Wen Pan, Yang Shi, You-Ping Tian, Ying Zhou, Jian Zhou, Jin-Sheng Yu, Synthesis of Multifunctional α,α-Difluoroketones through Allylic Alkylation of Difluoroenoxysilanes with MBH Carbonates, Chemistry – An Asian Journal, 10.1002/asia.202001145, 0, 0, (2020). Wiley Online Library. Xingfeng Bai, Caizhi Wu, Shaozhong Ge, Yixin Lu, Pd/Cu-Catalyzed Enantioselective Sequential Heck/Sonogashira Coupling: Asymmetric Synthesis of Oxindoles Containing Trifluoromethylated Quaternary Stereogenic Centers, Angewandte Chemie, 10.1002/ange.201913148, 132, 7, (2786-2790), (2019). Wiley Online Library.