

Enantioenriched allylsilanes: preparation through Cu-free S_N2' catalyzed addition of Grignard reagents

Rubén PÉREZ-SEVILLANO,^a Franck FERREIRA^a and Olivier JACKOWSKI^a

^aSorbonne Université (Institut Parisien de Chimie Moléculaire, UMR CNRS 8232, 4 place Jussieu, 75252 Paris Cedex 05, France)

Allylsilanes are very useful and versatile structures extensively used in organic synthesis with a large number of applications on it.^[1] Their bench-stability and easy-handling along with their low toxicity and functional group tolerability, allow them to occupy a unique place in the armory of the organic chemist. Furthermore, because they can undergo a great variety of silicon transformations such as cross-coupling reactions, ring-closing and cross-metathesis processes, and because they are suitable to perform stereo-selective and -control C-C bond formations such as the enantioselective addition of allyl patterns to electrophiles as carbonyl groups or imines,^[1a,2] representing a complementary method to the enolate based aldol reaction, its enantioselective synthesis has been deeply investigated and several reliable reaction protocols have been developed. Since Hayashi and Kumada reported the first preparation of enantioenriched allylsilanes in 1982, many other synthetic strategies had been developed based in Pd-catalysis, Claisen rearrangement, Asymmetric Allylic Alkylation (AAA) or Asymmetric Allylic Silylation (AAS) methods among others.

However, the increasing demand for these molecules and the lack of an established method to access optically active allylsilanes with good regio- and enantioselectivity, bearing tertiary and quaternary stereogenic centres, on a wide range of substrates and a large variation of the silicon moiety, encourages us to develop a new synthetic strategy. Based on previous results published by Alexakis *et al.*^[3] we focused our method in a Cu-free alkylation of Si-substituted allylic electrophiles with Grignard reagents in the presence of a chiral *N*-Heterocyclic Carbene (NHC). The scope and limitations of this new enantioenriched allylsilane preparation by a copper-free AAA will be presented and discussed.



References :

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