

Control of axial chirality in absence of transition metals based on arynes

Frédéric R. Leroux

Université de Strasbourg (ECPM), UMR CNRS 7509
25, rue Becquerel, 67087 Strasbourg Cedex 2

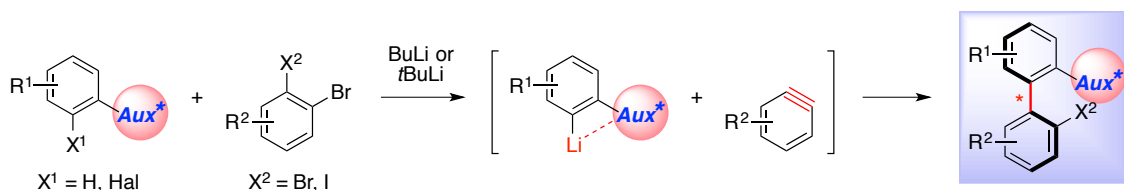
E-mail: frederic.leroux@unistra.fr

Biaryls are privileged structures due to their importance in biologically active natural products, in pharmaceutical research, in agrochemistry, or as ligands in catalysis as well as in material sciences. Their stereoselective preparation still remains a challenging goal.

The reaction of aryllithiums with in situ generated arynes has re-emerged at the beginning of the last decade as an efficient method for accessing biaryls. Our group developed this method for the synthesis of various functionalized biaryls and biaryl-based phosphorous ligands. This 'ARYNE coupling' has become a robust method for aryl-aryl coupling, and combines several advantages, as the use of cheap and/or easily accessible halogenoaromatic compounds, the access to biaryls bearing two distinct aromatic units and to poly-halogenated biaryls, which can be functionalized further, the use of lithium or magnesium reagents (i.e. in the absence of transition metals), and multi-gram reaction scales.¹

We also investigated the preparation of axially stereo-enriched biaryls, following two different strategies, based on halogen/lithium and sulfoxide/lithium exchanges or on atropo-diastereoselective couplings. The obtention of atropoenantio- or -diastereo-enriched biaryls by means of the ARYNE coupling will be discussed in the talk and compared to the Suzuki-Miyaura coupling.² Finally, the application in the synthesis of ligands and natural products will be reported.

Atropo-diastereoselective ARYNE coupling



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