

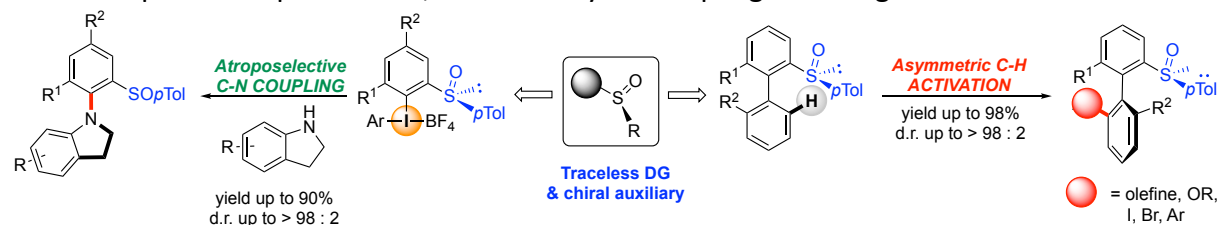
Sulfoxide as efficient tool for axial C-C and C-N chirality

Joanna Wencel-Delord, CR2

UMR 7509, Laboratoire de Chimie Moléculaire, Université de Strasbourg, 67087, Strasbourg

Axial chirality is a fascinating feature of many natural compounds, biologically active scaffolds and advanced materials. Besides, atropisomeric ligands such as BINAP, BINOL, phosphoric acid and phosphoramidites for example are recognized as privileged scaffolds in asymmetric catalysis. Accordingly, although synthesis of the axially chiral compounds has been attracting great attention of the scientific community,¹ general strategies allowing access to a large panel of such stereogenic molecules are still missing. Following this objective we have recently developed an asymmetric C-H activation pathway to build up very efficiently an unlimited panel of the atropisomerically pure biaryls. This concept involves direct, Pd-catalyzed functionalization of the biaryl precursors bearing a sulfoxide moiety. The stereogenic sulfoxide plays a role of both, directing group and chiral auxiliary, hence allowing the atroposelective C-H activation and subsequent functionalization with an array of coupling partners (C-C, C-O, C-X bond formation).² Furthermore, traceless character of the sulfoxide moiety permits various post-modifications of the newly generated axially chiral compounds. This powerful asymmetric C-H activation strategy can thus be used to conceive expedient synthetic routes towards chiral biaryls of interest (precursor of Steganone³), and also paves the way towards unique tridimensional structures.⁴

Recently we have also discovered that sulfoxide may be efficiently applied in a context of unprecedented atroposelective C-N couplings. This unmet goal could now be reached by developing highly active stereogenic reagents such as iodanes bearing the sulfoxide moiety in *ortho*-position. Accordingly, a Cu-catalyzed sterically demanding coupling between the sulfoxide iodanes and amines could be achieved under remarkably mild conditions, warranting excellent stereoselectivity and high yields. This coupling is therefore a first example of atroposelective, metal-catalyzed coupling affording C-N chiral scaffolds.⁵



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² a) Q. Dherbassy, G. Schwertz, M. Chessé, C. K. Hazra, J. Wencel-Delord, F. Colobert, *Chem. Eur. J.* **2016**, *22*, 1735 ; b) C. K. Hazra, Q. Dherbassy, J. Wencel-Delord, F. Colobert, *Angew. Chem. Int. Ed.* **2014**, *53*, 13871.

³ Q. Dherbassy, J. Wencel-Delord, F. Colobert, *Tetrahedron* **2016**, *72*, 5238–5245.

⁴ Q. Dherbassy, J.-P. Djukic, J. Wencel-Delord, F. Colobert, Publication submitted

⁵ J. Rae, J. Frey, S. Jerhaoui, S. Choppin, J. Wencel-Delord, F. Colobert, Publication submitted