

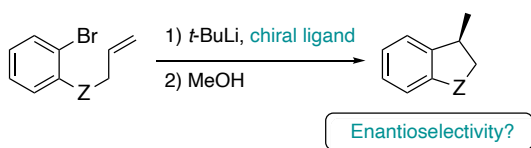
Stereoselectivity Control in Intramolecular Carbolithiation Reactions

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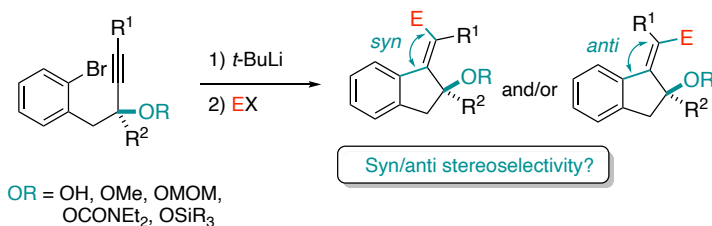
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The intramolecular carbolithiation of alkenes and alkynes, followed by electrophile trapping, offers an attractive strategy for building functionalized carbocyclic and heterocyclic systems.¹ It is well established that the structure and reactivity of organolithium can be tuned by chelation effects.² In this communication, we will describe how we had used chelation to control the stereoselectivity of the intramolecular carbolithiation reaction. Our results on chiral ligand-mediated carbolithiation of alkenes will be first presented (scheme, a)^{3,4} then we will focus on intramolecular *anti*-carbolithiation of alkynes guided by propargylic oxygen-based substituents (scheme, b).⁵

a) Enantioselective intramolecular carbolithiation of alkenes



b) Intramolecular *anti*-carbolithiation of alkynes : Stereo-directing effect of Li-coordinating substituents



Scheme. Stereo-controlled intramolecular carbolithiation reactions

References :

- [1] Y. Minko, I. Marek, in *Lithium Compounds in Organic Synthesis* (Eds.: R. Luisi, V. Capriati), Wiley-VCH, Weinheim, 2014, 329-350. [2] H. J. Reich *Chem. Rev.* **2013**, *113*, 7130-7178, [10.1021/cr400187u]. [3] H. Guyon, A. Boussonnière, A.-S. Castanet *J. Org. Chem.* **2017**, *82*, 4949-4957, [10.1021/acs.joc.7b0042]. [4] H. Guyon, A. Boussonnière, A.-S. Castanet *J. Org. Chem.* **2020**, *85*, 8933-8943, [10.1021/acs.joc.0c00832] [5] K. U. Ly, A. Boussonnière, A.-S. Castanet *Eur. J. Org. Chem.* **2022**, e202101409, [10.1002/ejoc.202101409].

