Alkyl lithium as a source of molecular diversity in a cycloadditionfragmentation sequence

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Synthetic sequences involving cycloaddition and fragmentation reactions have been widely used in the synthesis of natural products, as they benefit from the high degree of stereocontrol in the cycloaddition step. Since 2018, our group has developed a hetero-Diels-Alder cycloaddition/fragmentation sequence from benzene oxide and nitroso- or azo-dienophile, [1] in which the alkyl lithium acts as both a base and a nucleophile. We have thus synthesized a series of highly functionalized cyclohexanes with complete control of the relative configuration of the stereocenters. We have observed a different reactivity depending on the alkyl lithium reagent. We will present our latest results in this field, including an unexpected reactivity of *tert*-butyl lithium.^[2]

References:

- [1] R. Campagne, F. Schäkel, R. Guillot, V. Alezra, C. Kouklovsky *Org. Lett.* **2018**, *20*, 1884-1896, [10.1021/acs.orglett.8b00426].
- [2] F. Rambaud, R. Guillot, V. Alezra, C. Kouklovsky *J. Org. Chem.* **2023**, 88, 7152-7161, [10.1021/acs.joc.3c00398].

