SYDNONE-BASED APPROACH TO HETEROHELICENES THROUGH 1,3-DIPOLAR-CYCLOADDITIONS

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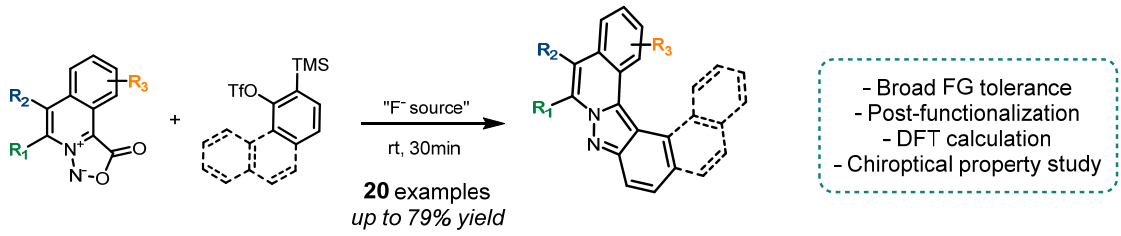
Despite their fascinating structure and unique properties, the synthetic access to (hetero)helicenes remains challenging and requires multistep convergent procedures. We reasoned that a late-stage formation of this helicoidal structure through sydnone/aryne 1,3-dipolar cycloadditions could allow a fast access to new Polycyclic Heteroaromatic Hydrocarbon (PHH).



Scheme 1. General scheme of heterohelicene synthesis

This strategy involved the design and synthesis of *ortho*-substituted polyaromatic sydnones. Over the process, an unprecedented regioselectivity in the cycloaddition step towards the more sterically constrained product was observed.[1] The origins of this phenomena were studied by DFT calculations in collaboration with the group of Prof. K. N. Houk (UCLA). The study of the chiroptical properties of the [7]-azahelicenes separated enantiomers have been realized and revealed similar property to carbohelicene's. This method allows the divergent access up to [8]-heterohelicenes and has been extended to substituted sydnones (EWG and EDG) and arynes with always the same observed regioselectivity (20 examples, *30-79%* yield) (Scheme 1). [2]

[1] a) Nakazawa, S et al. *J. Chem. Soc., Perkin Trans. 1* **1974**, 621-621; b) Cheong, P. H.-Y. et al. *J. Am. Chem. Soc.* **2010**, *132*, 1267–1269

[2] Yen-Pon, E. et al. *J. Am. Chem. Soc*, **2019**, 141 (*4*), 1435–1440