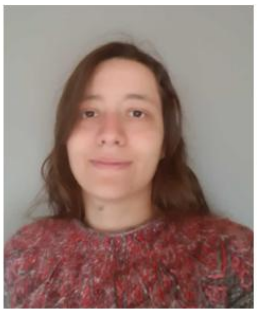
TUNABLE REGIOSELECTIVE NITROSO DIELS-ALDER REACTION ON CONJUGATED TRIENE CARBAMATES CATALYSED BY CHIRAL PHOSPHORIC ACIDS



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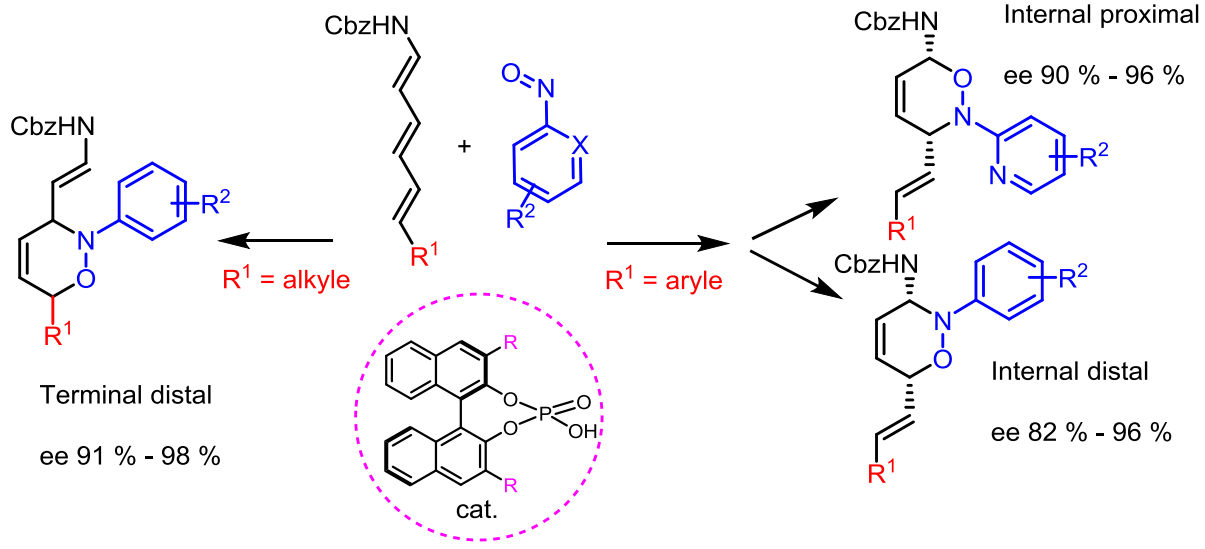
The nitroso Diels−Alder[1] reaction has attracted considerable attention among synthetic chemists because of the utility of the resulting 3,6-dihydro-1,2-oxazines for the synthesis of natural products and biologically active molecules.[2] Among others, we contributed to the field by providing enantioselective entry to the transformation. As such, we demonstrate that chiral phosphoric acids[3] were highly efficient catalysts to drive a regio-, stereo- and enantioselective cycloaddition between nitrosoarenes and diene carbamates.[4]

In this new work, we explored the reactivity of conjugates triene carbamates within the catalytic enantioselective nitroso Diels−Alder context. Regioselectivity is a particularly challenging task: not only can the nitroso dienophile form two regioisomeric adducts on a single diene (proximal or distal regioisomers),[5] but there are two diene with which the cycloaddition reaction can occur. In this communication, we will discuss how catalyst's choice and electronic properties of reacting partners allow tuning selectivity. Overall, we will describe conditions allowing a selective synthesis of three individual regioisomers among four possible, each with high enantioselectivity.



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