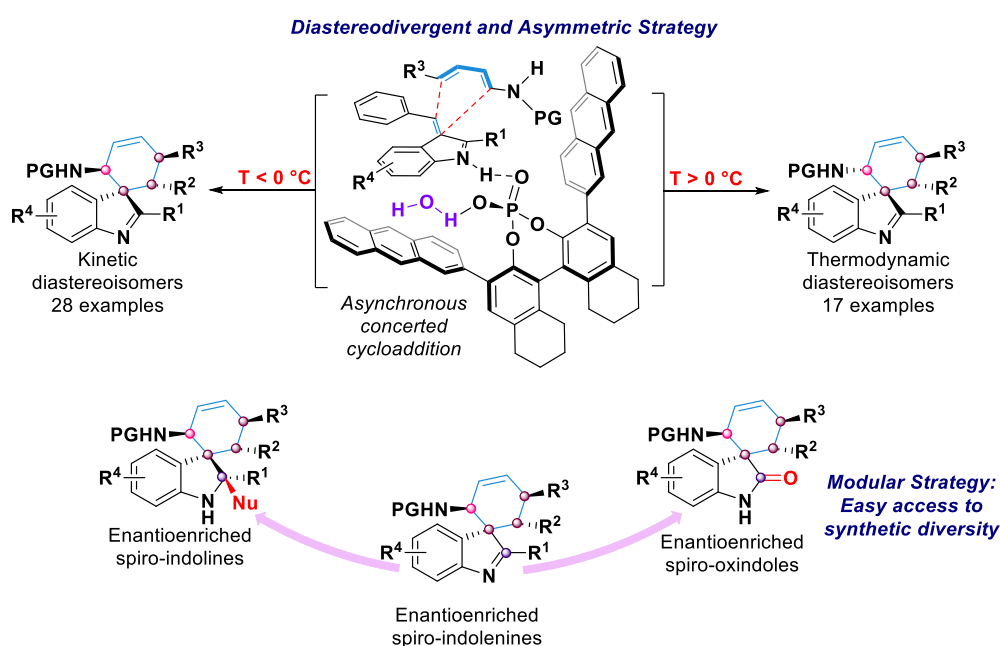


ENANTIOSELECTIVE AND DIASTEREODIVERGENT ACCESS TO SPIROCARBOCYCLIC INDOLENINES THROUGH CHIRAL PHOSPHORIC ACID-CATALYZED DEAROMATIVE CYCLOADDITION

Faced with the current environmental challenges, chemists have been actively developing new tools to access more economic and less polluting processes. Asymmetric organocatalysis, which allows for the efficient synthesis of valuable chemical compounds, is one of these solutions. In this context, we have been developing, for several years, challenging new reactivities to access enantioenriched nitrogen containing small molecules.^[1] We recently reported the asymmetric construction of spirocyclic indolenines, whose unique structural features make them attractive motifs, through intermolecular dearomatization of indoles.^[2] Due to the consequent challenges in the generation and stereocontrol of quaternary carbon centres, few such examples have been reported so far.^[3] The reaction between 2-substituted 3-indolylarylmethanols and dienecarbamates, in the presence of a chiral phosphoric acid, afforded highly substituted 6-membered carbocyclic spiroindolenines in good yields and with excellent enantioselectivities. This process proved to be highly diastereodivergent giving a selective access to two sets of diastereomers. DFT calculations revealed an unexpected mechanism at the origin of the stereocontrol. Finally, further transformations delivering attractive structures such as chiral 2,2-disubstituted spiroindolines and spirooxindoles, illustrate the large range of the synthetic possibilities offered by this methodology.



[1] Varlet, T.; Masson, G. *Chem. Commun.* **2021**, 57, 4089 – 4105.

[2] Varlet, T.; Matišić, M.; Van Elslande, E.; Neuville, L.; Gandon, V.; Masson, G. *J. Am. Chem. Soc.* **2021**, 143, 11611 – 11619.

[3] For a recent example using asymmetric rhodium catalysis, see: Becker, A.; Grugel, C. P.; Breit, B. *Org. Lett.* **2021**, 23, 3788 – 3792.