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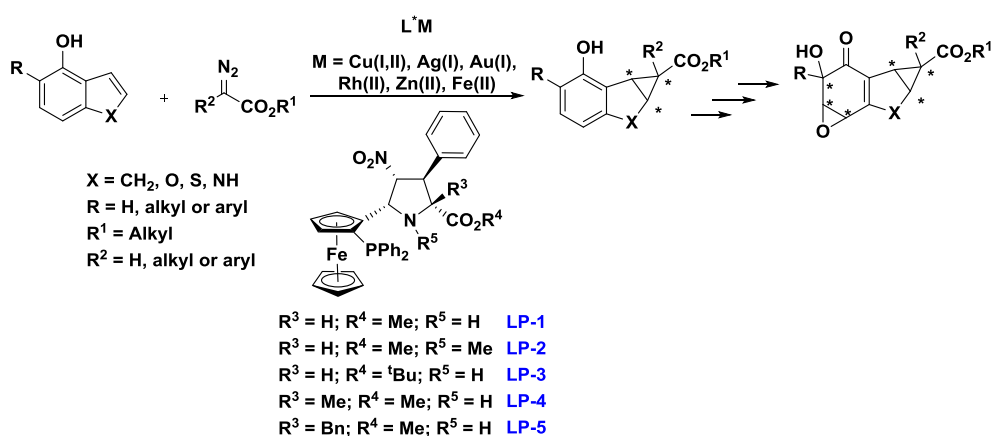
New Methods For Stereocontrolled Cycloaddition/De aromatization Reactions Under Catalytic Conditions

Aitor Lacambra, Ivan Rivilla, Fernando P. Cossío^{a*}, Stéphane Quideau^{b*}

^aDepartamento de Química Orgánica I, Universidad del País Vasco – Euskal Herriko Unibertsitatea and Donostia International Physics Center(DIPC), P^o Manuel Lardizabal 3, 20018, San Sebastián-Donostia, Spain

^bInstitut Européen de Chimie et Biologie, 2 rue Robert Escarpit, 33607, Pessac, France
aitor.lacambra@ehu.es

Our group has previously developed ferrocenyl-proline ligands that incorporate planar and central chirality. This feature makes them suitable for a particularly efficient simultaneously chiral induction. In fact, they have shown excellent diastereo- and enantioselectivity in [3+2] cycloaddition reactions between azomethine ylides and electron deficient alkenes.¹ Büchner² discovered in 1885 a route for the functionalization of benzene employing diazo compounds to provide a carbene moiety. Since then, the use of diazo compounds has been the most developed method for the metal mediated carbene transfer to C-C double bonds.³ This reaction provides a very useful method for the convergent formation of cyclopropanes. These [2+1] cycloadducts constitute attractive target molecules in natural products and bioorganic chemistry.⁴ In the present work stereoselective [2+1] reactions between fused hetero polyaromatic rings and different diazo compounds are described, in which ligands LP-1 to LP-5 constitute the source of chirality (**Scheme 1**).



Scheme 1. Asymmetric cyclopropanation reaction catalyzed by ferrocenyl-proline-metal complexes followed by oxidative dearomatization.

¹ Conde, E.; Bello, D.; de Cozár, A.; Sanchez, M.; Vazquez, M. A.; Cossío, F. P. *Chem. Sci.* **2012**, *3*, 1486-1491.

² Büchner, E.; T. Ber. *Dtsch. Chem. Ges.* **1885**, *18*, 2377.

³ Maas, G. *Chem. Soc. Rev.*, **2004**, *33*, 183-190.

⁴ (a) Kirkland, T.A.; Colucci, J.; Geraci, L. S.; Marx, M.A.; Schneider, M.; Kaelin, D.E; Martin, S.F. *J. Am. Chem. Soc.*, **2001**, *123*, 12432-12433; (b) Chen, D. Y. K.; Pouwer, R. H.; Richard, J. A. *Chem.Soc.Rev.*, **2012**, *41*, 4631-4642; (c) Özüdüru G.; Schubach, T.; Boysen M. M. K. *Org. Lett.*, **2012**, *14* (19), 4990-4993.