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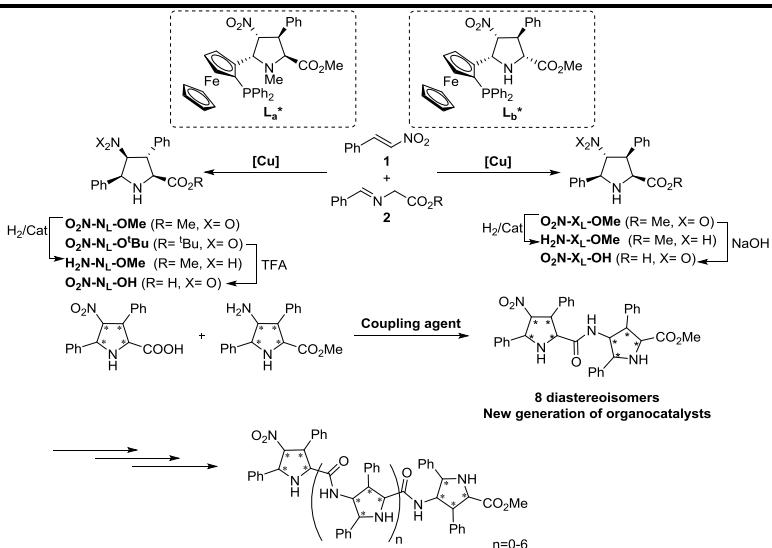
**Dimers derived from densely substituted unnatural prolines as precursors of  $\gamma$ -peptides and their use in organocatalysis**

Maddalen Agirre, M<sup>a</sup> de Gracia Retamosa, Andrea Ruiz-Olalla and Fernando P. Cossío \*

*Departamento de Química Orgánica I, Universidad del País Vasco-Euskal Herriko Unibertsitatea and Donostia International Physics Center (DIPC), Pº Manuel de Lardizabal 3, 20018 San Sebastián-Donostia, Spain*

[maddalen.agirre@ehu.es](mailto:maddalen.agirre@ehu.es)

The synthesis of novel hybrid ferrocenylpyrrolidine ligands **L<sub>a</sub>\*** and **L<sub>b</sub>\*** via [3+2] cycloadditions has been described by our group.<sup>1</sup> Both ligands in turn provided densely substituted unnatural L- and D- proline derivatives in a stereodivergent manner. The powerful feature of having nitro and ester groups gives the opportunity to orthogonally synthesize different  $\gamma$ -proline oligopeptides with different substitution patterns and chiral centers. Supported by the efficiency of Proline-based organocatalysts in numerous chemical transformations, our densely substituted pyrrolidine derivatives have been used in aldol reactions with good results.<sup>1,2</sup> In this communication, we present our results on the structure/activity relationship of the new generation of oligomeric catalysts. The main conclusion is that in the case of the  $\gamma$ -dipeptides, the stereochemistry of the aldol adducts depends on both monomeric units in a nearly additive manner.



1. Conde, E., Bello, D., de Cózar, A., Sánchez, M., Vázquez, M. A., Cossío, F. P., *Chem. Sci.* **2012**, *3*, 1486-1491.
2. Retamosa, M.G., de Cózar, A., Sánchez, M., Miranda, J.I., Sansano, J.M., Castelló, L.M., Nájera, C., Jiménez, A.I., Sayago, F.J., Cativiela, C., Cossío, F.P., *Chem. Sci.*, Submitted.