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Dimers Derived From Densely Substituted Unnatural Prolines As Precursors Of γ-Peptides And Their Use In Organocatalysis

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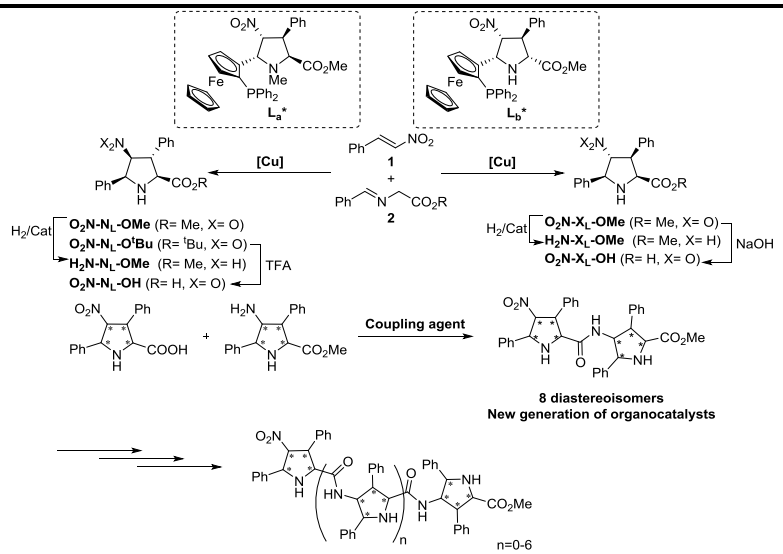
The synthesis of novel hybrid ferrocenylpyrrolidine ligands $\mathbf{L_a}^*$ and $\mathbf{L_b}^*$ via [3+2] cycloadditions has been described by our group.[1] Both ligands in turn provided densely substituted unnatural L- and D-proline derivatives in a stereodivergent manner. The powerful feature of having nitro and ester groups gives the opportunity to orthogonally synthesize different γ-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.[1,2] 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 γ-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.