## SUPRAMOLECULARLY REGULATED COPPER-BISOXAZOLINE CATALYSTS FOR THE EFFICIENT INSERTION OF CARBENOID SPECIES INTO HYDROXYL BONDS

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The catalytic insertion of copper carbenoids into O–H bonds affords synthetically useful  $\alpha$ -alkyl/aryl- $\alpha$ -alkoxy/aryloxy derivatives, which are very common in biologically active compounds [1]. We have designed supramolecularly regulated copper(I) complexes of bisoxazoline ligands [2]. The catalyst design incorporates two oxazoline units as coordinating groups at the  $\alpha$  and  $\omega$  positions of a polyethyleneoxy chain, which acts as a supramolecular regulation site. We have demonstrated that the catalytic performance of these systems can be modulated by the use of an external molecule (*i.e.* the regulation agent) [3]. This approach has been applied to an array of structurally diverse alcohols (cyclopropyl-, alkyl- and aryl-derivatives). Moreover, we have used this methodology to synthesize advanced synthetic intermediates of APIs.

$$R^{1}$$
-OH +  $R^{2}$  OEt  $R^{1}$ OEt  $R^{2}$ OEt  $R^{3}$ OEt  $R^{2}$ OEt  $R^{2}$ OEt  $R^{2}$ OEt  $R^{3}$ OEt  $R^{4}$ OEt  $R^{2}$ OEt  $R^{2}$ OEt  $R^{3}$ OEt  $R^{4}$ OEt  $R^{2}$ OEt  $R^{2}$ OEt  $R^{3}$ OEt  $R^{4}$ OEt  $R^{2}$ OEt  $R^{3}$ OEt  $R^{4}$ OEt  $R^{2}$ OEt  $R^{3}$ OEt  $R^{4}$ 

<sup>[1] (</sup>a) Chen, C.; Zhu, S.-F.; Liu, B.; Wang, L.-X.; Zhou, Q.-L. *J. Am. Chem. Soc.* **2007**, *129*, 12616-12617. (b) Bambi-Nyanguile, S.-M.; Hanson, J.; Ooms, A.; Alpan, L.; Kolh, P.; Dogne, J.-M.; Pirotte, B. *Eur. J. Med. Chem.* **2013**, *65*, 32-40.

<sup>[2]</sup> Manuscript in preparation.

<sup>[3] (</sup>a) Mon, I.; Jose, D. A.; Vidal-Ferran, A. *Chem.–Eur. J.* **2013**, *19*, 2720-2725. (b) Vidal-Ferran, A.; Mon, I.; Bauza, A.; Frontera, A.; Rovira, L. *Chem.–Eur. J.* **2015**, *21*, 11417-11426.