Bisoxazoline-Fullerene Hybrid Systems for Asymmetric Catalysis

<u>Valerio CINA'</u>,^{a,b} Mariano GUAGLIARDO,^a Luca FUSARO,^b Michelangelo GRUTTADAURIA,^a Carmela APRILE,^b Francesco GIACALONE^a

^a Department of Biological, Chemical and Pharmaceutical Sciences and Technologies, University of Palermo, Italy ^b Unit of Nanomaterial Chemistry (CNano), University of Namur (UNamur), Belgium

Fullerene is the smaller member in the family of carbon nanoforms (CNFs) and it can be taken as a molecular model for other CNFs-based heterogeneous catalysts. The well-developed chemistry for C_{60} functionalization allows operating multiple additions on its cage, and this can be exploited for sensibly increasing catalyst loading or for adding different functionalities.¹ In this way, it is possible to explore synergistic or detrimental effects due to the close proximity of catalytic moieties. In addition, the peculiar solubility profile of C_{60} -derivatives may be used for recovering a homogeneous catalyst by simple precipitation.

Herein C_{60} was functionalized with a series of chiral bisoxazoline (BOX) ligands, widely used in asymmetric catalysis,² in order to form both the mono- and the hexa-adducts (Figure 1a). Monoadducts were also post-functionalized with ten 1,2-dimethylimidazolium moieties in order to get hybrid with a different solubility profile. All the C₆₀-BOX systems were employed, along with copper(II) salts as catalysts in asymmetric Henry and Diels-Alder reactions (Figure 1b). Furthermore, their ease separation from the reaction mixture can allow for a facile reuse in multiple cycles.



Figure 1 a) Fullerene and BOX based catalysts. b) Asymmetric Henry and Diels-Alder reactions.

References

- (a) Campisciano, V.; Gruttadauria, M.; Giacalone, F., *ChemCatChem* (doi:10.1002/cctc.201801414);
 (b) Su, D. S.; Perathoner, S.; Centi, G., *Chem. Rev.* 2013, *113*, 578.
- 2. (a) Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M., *JACS* **1991**, *113*,726; (b) Lowenthal, R. E.; Abiko, A.; Masamune, S., *Tetrahedron Let.* **1990**, *31*, 6005.