

## Development of method for the synthesis of chiral multisubstituted cyclopentadienyl ligands

Marko Purić<sup>1</sup>, Nikola Topolovčan<sup>2</sup>

<sup>1</sup>University of Zagreb Faculty of Science, Zagreb, Croatia

<sup>2</sup>Ruđer Bošković Institute, Zagreb, Croatia

Email: [marko.puric98@gmail.com](mailto:marko.puric98@gmail.com)

Efficient chiral cyclopentadienyl ligands, whose chirality originates from the 1,2-substitution of a fixed chiral backbone such as mannitol or BINOL, have been known since 2012 and 2013, respectively. Transition metal complexes of these cyclopentadienyl ligands have been successfully used in numerous stereoselective transformations.[1] Recent research suggests that additional substitution of the cyclopentadiene ring positively influences the modulation of the stereoelectronic properties of the catalytic pockets of these complexes.[2] Such a dependence of multisubstitution and the stereoelectronic properties of catalysts indicates the need for parameterization of this relationship, as well as the need for newer and more efficient methods for the synthesis of these cyclopentadienyl ligands. This study approached the development of a methodology with the basic hypothesis that such multisubstituted cyclopentadienyl ligands can be prepared by the reaction of non-terminal diyne with low-valent organozirconium(II) species (Negishi's reagent), generating corresponding zirconabicyclic intermediates.[3] The planned synthetic route begins with the synthesis of the diynes with already decorated sidewalls at the 3,3'-positions, which have been found to be a fundamental prerequisite for the efficiency of chiral cyclopentadienyl ligands. The synthesis concludes with a *one pot* cyclization of the diynes with the Negishi's reagent, followed by cross coupling with an alkyl-diiodide (diiodomethane) catalyzed by copper(I) chloride in the presence of DMPU as shown in Figure 1. The product is a chiral multisubstituted cyclopentadienyl ligand with an extended sidewall and an added frontwall.

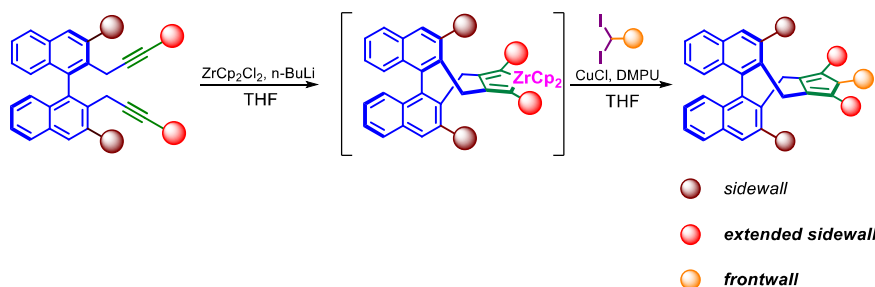


Fig. 1: Planned route for chiral multisubstituted cyclopentadiene ligand synthesis.

### References

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