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**CATALYSIS &  
CHEMICAL ENGINEERING**

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**Theme:** Contemporary Innovations and Emerging Novel  
Research in Catalysis and Chemical Engineering

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### New rhodium-sp<sup>3</sup> diphosphine catalytic systems for the asymmetric addition of aryl boronic acids to azaarenes

Catalytic asymmetric conjugate reaction stands out as one of the most useful synthetic tools for the preparation of chiral compounds although its application to the synthesis of chiral azaarenes has been scarcely investigated till now (*Ad. Synth. Catal.* 2020, 362, 3142). Starting from the established expertise gained in my research group in the synthesis of chiral phosphine ligands and their application in homogeneous catalysis (*Inorg. Chem.* 2021, 60(5), 976; *Catalysts* 2020, 10(8), 914) we prepared a novel chiral phosphorus ligand, called (*R,R*)-EPHOS, designed and synthesized starting from the optically active 1,4-(*E*)-2-butene. Its *cis* analogue, called (*R,R*)-ZEDPHOS had been already successfully employed in the enantioselective reduction of carbonyl groups affording satisfactory enantioselectivity. This new diphosphine features a stereogenic sp<sup>3</sup> carbon atom combined to the presence of a C<sub>2</sub> axial chirality, the one featuring the atropisomeric diphosphines. A combined 31P-NMR and computational approach shed light on the different coordination mode to the rhodium

centre respect to (*R,R*)-ZEDPHOS, suggesting the ability of (*R,R*)-EPHOS to form complexes with phosphorus atoms in *cis* configuration and revealing the asymmetric disposition of the aryl groups responsible for the chiral recognition of the substrate enantiofaces. Thus, (*R,R*)-EPHOS was applied to the asymmetric rhodium catalyzed 1,4-addition of different substituted arylboronic acids to azaarenes in comparison with other. When applied to (*E*)-1-phenyl-3-(pyridin-2-yl)prop-2-en-1-one (1), (*R,R*)-EPHOS-Rh( catalytic system afforded the product 1a in a remarkable 94% e.e.



#### BIOGRAPHY

Dr. Giorgio Facchetti is actually a researcher fellow and Adjunct Professor of Organometallic Chemistry at the Department of Pharmaceutical Sciences, University of Milan. In 2015 he was awarded of the prestigious fellowship "Fondazione Confalonieri" soon after receiving his PhD in Chemical Sciences in 2014 at the University of Milan with a thesis entitled "New antiproliferative transition metal complexes: development and synthesis". His research interests deal with the synthesis of hybrid catalysts ("artificial metallo-enzymes"), the design and synthesis of new chiral ligands for homogeneous catalysis and with theranostic metal-based complexes.