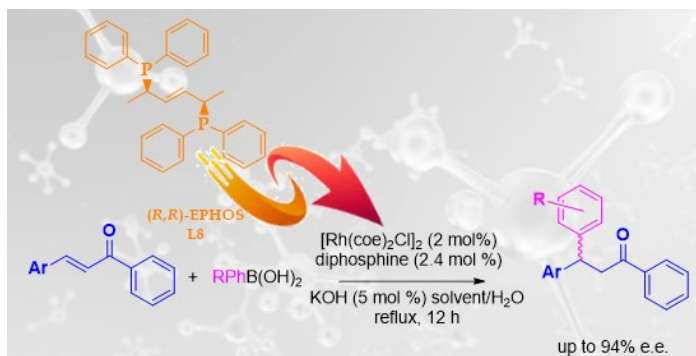


## New $sp^3$ diphosphine-based rhodium catalysts for the asymmetric addition of aryl boronic acids to azaarenes

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Enantioselective catalysis using metal complexes provides one of the most general and flexible methods for the synthesis of chiral compounds [1,2]. In these regards, the proper combination of the selected metal with the correctly designed enantiopure ligand is the determining step for obtaining synthetic processes with high efficiency. Catalytic asymmetric conjugate reaction [3] stands out as one of the most useful method for the preparation of chiral compounds but although routinely employed, its application to the synthesis of chiral azaarenes has been scarcely investigated. Starting from our established expertise in the synthesis of chiral phosphine ligands [4,5] and in the field of asymmetric homogeneous catalysis, we prepared a novel chiral phosphorus ligand, hereafter called  $(R,R)$ -EPHOS, designed and synthesized starting from the optically active 1,4- $(E)$ -2-butene taking inspiration from the *cis* analogue  $(R,R)$ -ZEDPHOS ligand. This new diphosphine features a stereogenic  $sp^3$  carbon atom combined to the presence of a  $C_2$  axial chirality, the one typically present in atropisomeric diphosphines. Computational studies, supported by  $^{31}P$ -NMR analyses 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 disposed in *trans* configuration with respect to each other, with the  $C=C$  bond of the ligand in the metal centre coordination sphere.  $(R,R)$ -EPHOS together with other chiral diphosphines, was applied to the asymmetric rhodium catalyzed 1,4-addition of different substituted arylboronic acids to azaarenes. When applied to  $(E)$ -1-phenyl-3-(pyridin-2-yl)prop-2-en-1-one (**1**),  $(R,R)$ -EPHOS-based catalytic system afforded the product **1a** in a remarkable 94% e.e. [6].

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