

Design of next-generation chiral benzindenyl ligands

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Developing stereoselective catalysts is a fundamental challenge in modern organic synthesis, particularly in the pharmaceutical industry, where the chirality of molecules can significantly impact their biological activity. Transition-metal complexes featuring chiral ligands play a crucial role in catalysis, influencing both reactivity and stereoselectivity. Among various ligand classes, chiral cyclopentadienyl and indenyl derivatives have shown significant potential because of their ability to fine-tune the electronic and steric properties of complexes. However, scarce examples of chiral BINOL-based indenyl ligands effectively induce selectivity mainly because of the considerable distance from the reaction center.¹ This research proposes a new strategy for designing chiral benzindenyl ligands by integrating the indenyl unit into a chiral binaphthyl scaffold, thereby reducing the spatial distance from the metal center and potentially enhancing stereoselectivity. The ligand geometries have been optimized using computational methods to gain insights into the most favorable orientations for catalytic activity. The key step in this methodology involves the allylation of advanced intermediate **1** via Stille coupling reaction, followed by ring-closing metathesis² of compound **2** to obtain the benzindenyl ligand **3**. Finally, the chiral benzindenyl ligand will be tested in bench-mark transformations (Figure 1).

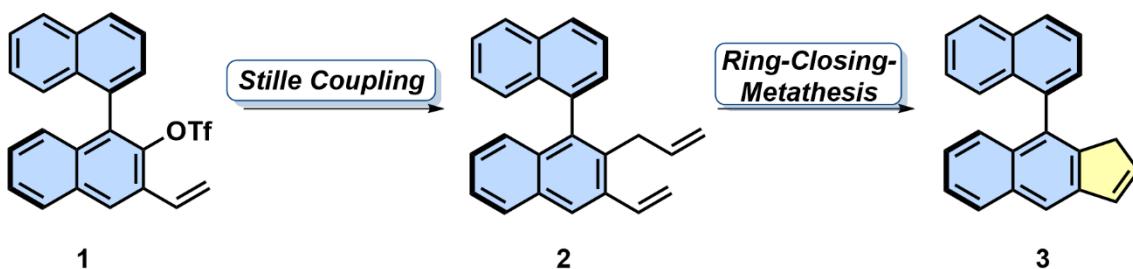


Figure 1. Proposed synthetic route towards chiral benzindenyl ligands

1) P. Jungk, T. Täufer, I. Thiel, M. Hapke, *Synthesis*, 2016, **48**, 2026

2) A. Jana, K. Misztal, A. Žak, K. Grela, *J. Org. Chem.*, 2017, **82**, 4226