Rh(III)-Catalyzed Asymmetric Synthesis of P-Stereogenic Phosphinamides

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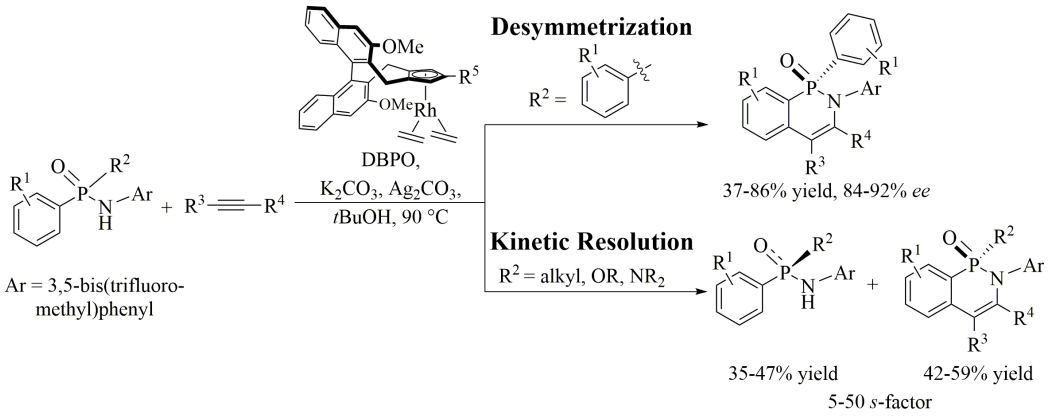
Chiral phosphorus compounds are widely employed as organocatalysts or ligands for enantioselective transition-metal catalyzed transformations.[1] Most commonly, the chirality comes from a stereogenic carbon, an axis of chirality, or a chiral plane. One might expect a better relay of chirality during catalysis with *P*-stereogenic phosphorus ligands due to a closer proximity to the transition metal. However, this area of research remains under explored due to challenges associated with *P*-stereogenic ligand synthesis.

Herein we report the first example of a chiral cyclopentadienyl[2] Rh(III)-catalyzed asymmetric synthesis of *P*-stereogenic phosphinamides. For prochiral phosphinamide substrates, enantioriched heterocycles were accessed *via* annulation with internal alkynes.[3] In contrast, with chiral phosphinamide substrates, kinetic resolution yielded both the cyclic phosphamides and unreacted starting materials, with selectivity-factors up to 50. Kinetic studies reveal that a concerted-metalation-deprotonation is the stereo-determining step when an inorganic base is employed, in contrast to previous reports from our group.[4]



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