

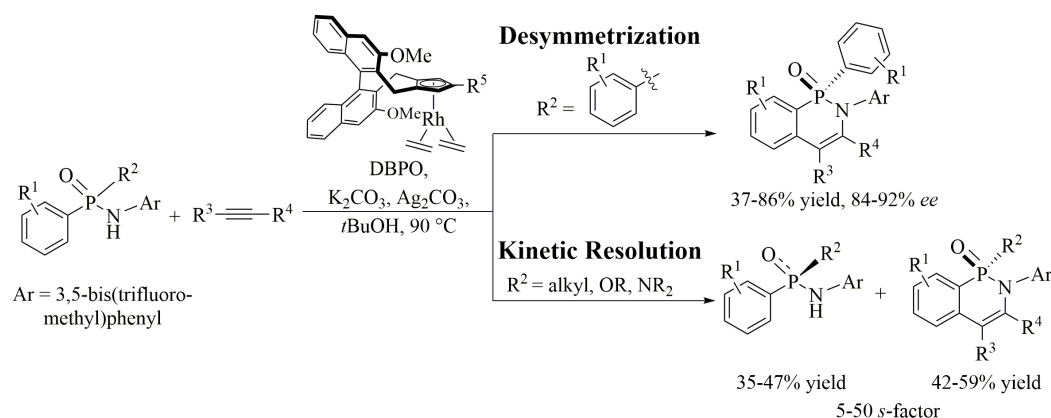
Rh(III)-Catalyzed Asymmetric Synthesis of *P*-Stereogenic Phosphinamides

Y. Sun¹, N. Cramer^{1*}

¹LCSA EPF Lausanne

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]



[1] *Phosphorus Ligands in Asymmetric Catalysis: Synthesis and Applications*, Vols. 1-3 (Eds. : A. Börner), Wiley-VCH, Weinheim, **2008**.

[2] C. G. Newton, D. Kossler, and N. Cramer, *J. Am. Chem. Soc.* **2016**, *138*, 3935.

[3] Y. Sun, N. Cramer, *Angew. Chem. Int. Ed.* **2017**, *56*, 364.

[4] B. Ye, N. Cramer, *Acc. Chem. Res.* **2015**, *48*, 1308.