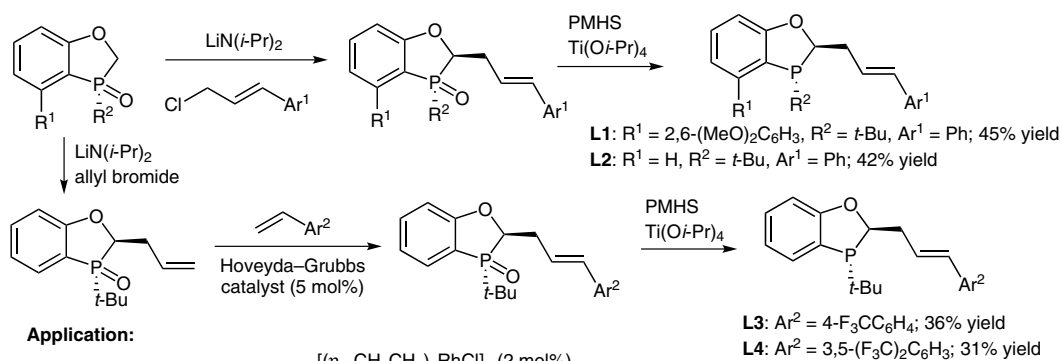
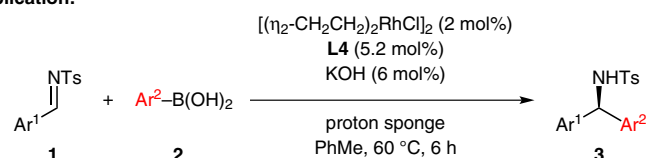


J. D. SIEBER,* D. CHENNAMADHAVUNI, K. R. FANDRICK, B. QU, Z. S. HAN, J. SAVOIE, S. MA, L. P. SAMANKUMARA, N. GRINBERG, H. LEE, J. J. SONG, C. H. SENANAYAKE (BOEHRINGER INGELHEIM PHARMACEUTICALS, RIDGEFIELD, USA)
Development of New P-Chiral P, π -Dihydrobenzooxaphosphole Hybrid Ligands for Asymmetric Catalysis
Org. Lett. **2014**, *16*, 5494–5497.

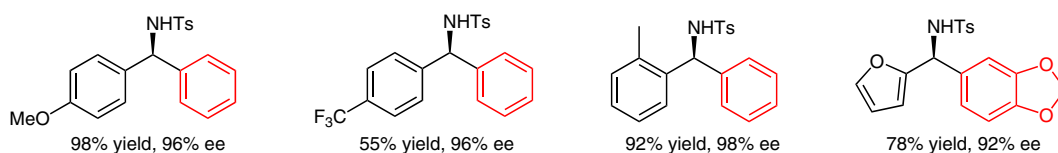
P-Chiral P, π -Dihydrobenzooxaphosphole Ligands in Asymmetric Catalysis



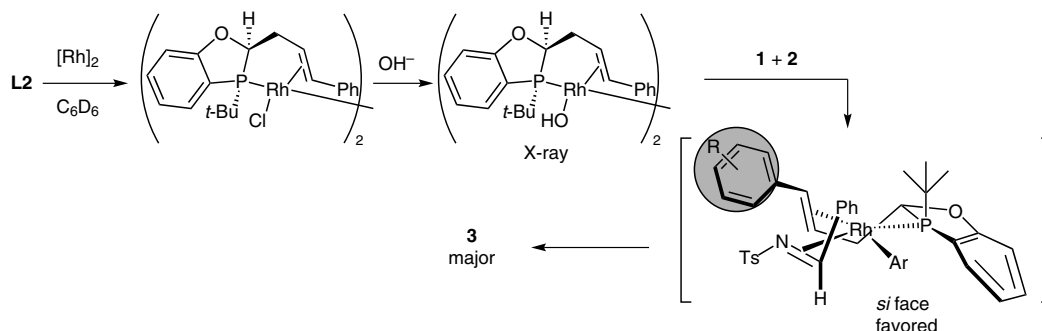
Application:



Selected examples:



Stereochemical model:



Significance: A new family of P-chiral P, π -hybrid ligands has been synthesized from a chiral dihydrobenzooxaphosphole core (Z. S. Han et al. *J. Am. Chem. Soc.* **2013**, *135*, 2474). These newly developed ligands show a very high level of enantiocontrol in the rhodium-catalyzed addition of aryl boronic acids to tosyl imines.

Comment: The synthesis of the ligands with strong electron-withdrawing substituents (like CF₃) failed by the alkylation with cinnamyl derivatives, alternatively an allylation and subsequent metathesis strategy was employed. Steric and electronic properties were controlled easily by varying the substituents on the phosphorus atom and on the π -system.

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