Y.-Q. WANG, S.-M. LU, Y.-G. ZHOU* (DALIAN INSTITUTE OF CHEMICAL PHYSICS AND SHANGHAI INSTITUTE OF ORGANIC CHEMISTRY, P. R. OF CHINA)

Highly Enantioselective Pd-Catalyzed Asymmetric Hydrogenation of Activated Imines *J. Org. Chem.* **2007**, *72*, 3729-3734.

Asymmetric Imine Hydrogenation with Palladium Complexes

$$\begin{array}{c} {\sf EWG} \\ {\sf N} \\ {\sf PP-ligand} \end{array} \underbrace{ \begin{array}{c} {\sf Pd}({\sf CF_3CO_2})_2 \; (2\; {\sf mol\%}) \\ {\sf PP-ligand} \; (2.4\; {\sf mol\%}) \\ {\sf 600-1000} \; {\sf psi} \; {\sf H_2}, \; {\sf TFE}, \; {\sf r.t.} \end{array} }_{\sf R^1} \\ {\sf R^1} = {\sf Ar}, \; {\sf R^2} = {\sf Me}, \; {\sf Et} \\ {\sf EWG} = {\sf P(O)Ph_2}, \; {\sf Ts} \\ \end{array} }_{\sf 80\% \; yield} \\ {\sf 85-99\% \; ee} \\ {\sf PP-ligand} = \underbrace{ \begin{array}{c} {\sf O} \\ {\sf PPh_2} \\ {\sf OPPh_2} \\ {\sf PPh_2} \\ {\sf OPPh_2} \\ {\sf OPPh_2} \\ {\sf OPPh_2} \\ {\sf OPPh_3} \\ {\sf OPPh_2} \\ {\sf OPPh_3} \\ {\sf OPPh_4} \\ {\sf OPPh_2} \\ {\sf OPPh_3} \\ {\sf OPPh_4} \\ {\sf OPPh_5} \\ {\sf OPPh_6} \\ {\sf OPPh$$

Selected examples:

Significance: The asymmetric hydrogenation of imines represents a potentially powerful method for generating chiral amines for possible use in preparing biologically active compounds. This substrate class remains a challenging target for many transition-metal catalysts developed so far.

Review: For a review on asymmetric imine hydrogenation: S. Kobayashi, H. Ishitani *Chem. Rev.* **1999**, *99*, 1069-1094.

Comment: The presented method relies on a strongly electron-withdrawing group on the nitrogen which is crucial to obtain high reactivity. TFE as solvent in combination with an electron-rich PP-ligand and a weakly coordinating anion is also important for high conversion. The catalytic system tolerates a large variety of substituted aromatic rings for R¹ as well as bulky substituents or rings in the *ortho* position. For R² it is limited to methyl groups to obtain high enantiomeric excess. For R^2 = Et the selectivity drops but the chiral amines can still be isolated in good ee values. Cyclic sulfatams can also be hydrogenated with high selectivity, yielding important chiral structural units for agricultural and pharmaceutical agents.

 SYNFACTS Contributors: Mark Lautens, Michael Langer

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Category

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Key words

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