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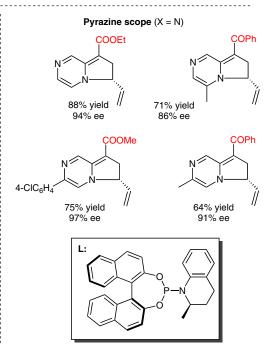
Direct Asymmetric Dearomatization of Pyridines and Pyrazines by Iridium-Catalyzed Allylic Amination Reactions *Angew. Chem. Int. Ed.* **2014**, *53*, 6986–6989.

Iridium-Catalyzed Asymmetric Dearomatization of Pyridines and Pyrazines

General reaction:

$$\begin{array}{c|c} \textbf{GWE} & \textbf{H}_{\alpha} & & & & & & & & & & & & & & & & & \\ \textbf{(2 mol\%)} & & & & & & & & & & & & & & & \\ \textbf{(2 mol\%)} & & & & & & & & & & & & & & \\ \textbf{L (4 mol\%)} & & & & & & & & & & & & & \\ \textbf{THF, r.t.} & & & & & & & & & & & & \\ \textbf{2-40 h} & & & & & & & & & & & & \\ \textbf{electron-rich (nucleophilic)} & & & & & & & & & & \\ \textbf{key intermediate} & & & & & & & & & & \\ \textbf{key intermediate} & & & & & & & & & \\ \end{array}$$

Ar = 2-OMeC₆H₄



Significance: The authors report an Ir-catalyzed enantioselective allylic dearomatization of pyridines and pyrazines. The respective products are obtained in high yields (up to 99%) and with excellent enantioselectivity (up to 99% ee) under very mild reaction conditions. Due to the prevalence of pyridine and pyrazine motifs within biologically active compounds, the derived products could potentially serve as useful intermediates for target-oriented synthesis.

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 Synfacts 2014, 10(8), 0819
 Published online: 18.07.2014

 DOI: 10.1055/s-0034-1378409; Reg-No.: L08514SF

Comment: The presence of an electron-with-drawing group (EWG) acidifies the α -position, enabling a deprotonation which provides electron density to the heteroaromatic ring. The increased electron density of the heterocycle enables the direct nucleophilic attack of the pendant Ir–allyl species.

Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

Key words

pyridines

pyrazines

dearomatization

iridium

asymmetric catalysis

