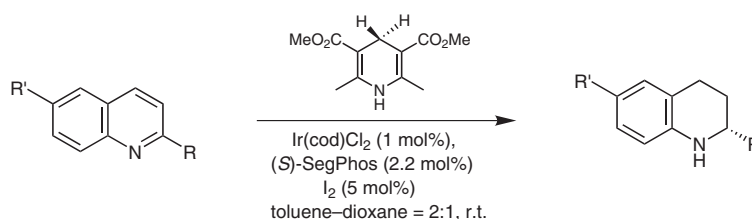


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Iridium-Catalyzed Asymmetric Transfer Hydrogenation of Quinolines with Hantzsch Esters

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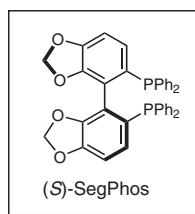
## Highly Enantioselective Hydrogenation of Quinolines



R = Me, Et, *n*-Bu, *n*-Pent, phenethyl  
3,4-methylenedioxyphenethyl, Ph  
3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>,  
Ph<sub>2</sub>CH(OH)CH<sub>2</sub>

R' = H, F, Me, MeO

43–98% yield  
10–88% ee



**Significance:** 1,4-Dihydropyridines have been recognized as a potential source of hydrogen when undergoing dehydroaromatization. Such strategy has been exploited here for highly enantioselective hydrogenation of quinolines. Reduction proceeds smoothly under mild conditions and minimal investment of the catalyst to give a variety of amine products. The reaction is sensitive to the electron-withdrawing substituents in the 6-position which cause decreased reactivity.

**Comment:** Organocatalytic transformations using Hantzsch esters as hydrogen source reported so far are important from the safety point of view. For this reason, the methodology described here is a valuable alternative. Hydrogen produced in situ (from 1,4-dihydropyridine and Ir salt) enables reduction of quinolines without the use of external hydrogen gas. It would be even more beneficial to improve the methodology to a truly organocatalytic transformation (List and co-workers reported organocatalytic transfer hydrogenation of  $\alpha,\beta$ -unsaturated carbonyl compounds and imines using Hantzsch esters: *J. Am. Chem. Soc.* **2006**, *128*, 13368; *Angew. Chem. Int. Ed.* **2005**, *44*, 7427).

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