Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

Key words

copper catalysis

Friedel–Crafts reaction

nitroalkenes

conjugate addition

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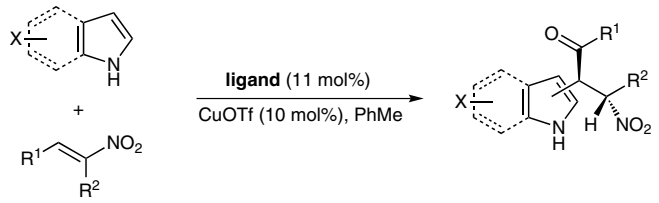
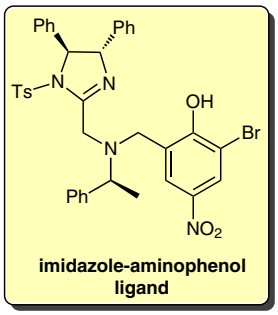
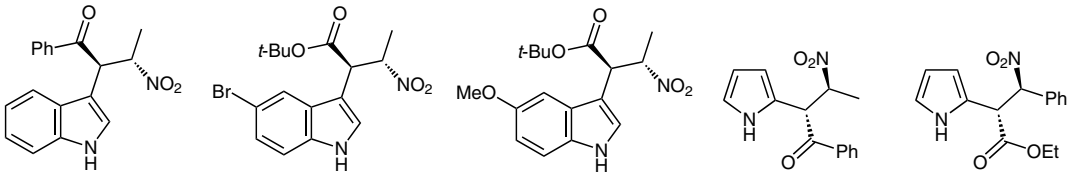
Copper(I)-Catalyzed Asymmetric Conjugate Addition–Protonation of Nitroalkenes





Selected examples:



92% yield
dr (*anti*/*syn*) = 90:10
93% ee (*anti*)
83% ee (*syn*)

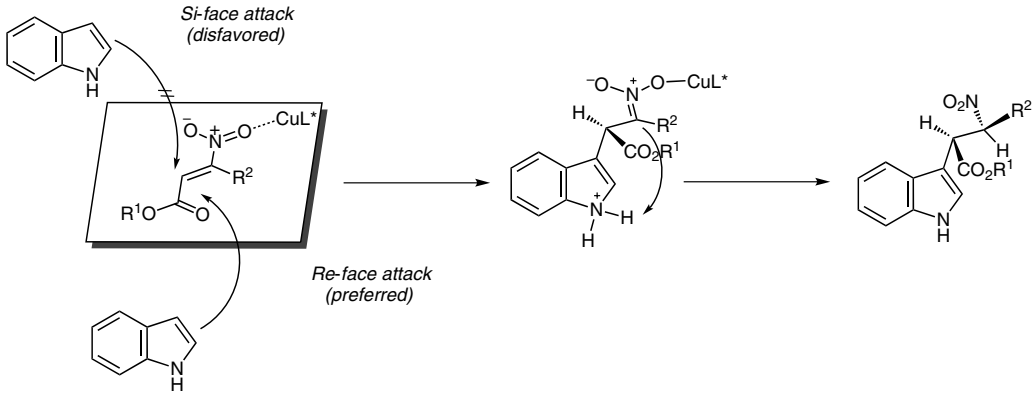
84% yield
dr (*anti*/*syn*) = 91:9
90% ee (*anti*)
70% ee (*syn*)

96% yield
dr (*anti*/*syn*) = 90:10
87% ee (*anti*)
65% ee (*syn*)

80% yield
dr (*anti*/*syn*) = 93:7
80% ee (*anti*)
15% ee (*syn*)

98% yield
dr (*anti*/*syn*) = 53:47
91% ee (*anti*)
68% ee (*syn*)

Proposed mechanism:



Significance: An asymmetric conjugate addition–protonation sequence of indoles and pyrrole to trisubstituted nitroalkenes is described. The process is catalyzed by a copper(I)/imidazole-aminophenol complex.

Comment: The reaction is believed to take place by initial enantio-determining conjugate addition followed by a diastereoselective intramolecular protonation of the nitronate. Epimerization of the product, which could lead to decreased diastereoselectivity, was not found to be significant.

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