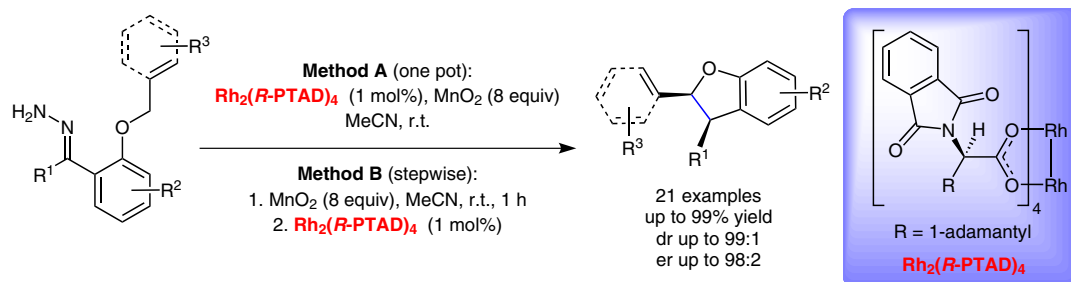
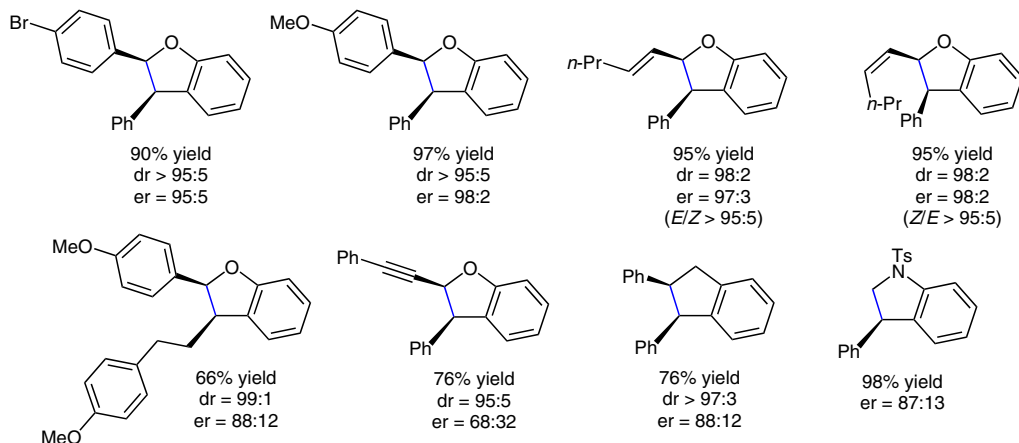


Enantioselective C–H Insertion Reactions of Donor–Donor Carbenoids



Selected examples:



Significance: Transition-metal carbenoids, which can be generated in situ from a variety of different precursors, demonstrate a diverse range of reactivity, such as the ability to perform allylic and benzylic C–H functionalizations (see Review below). While the use of acceptor–acceptor and donor–acceptor metal carbenoids is commonplace, the application of donor–donor metal carbenoids in a diastereo- and enantioselective C–H functionalization has not been previously demonstrated. Herein, Shaw and co-workers report the first Rh-catalyzed asymmetric insertion reactions of donor–donor carbenoids, which provide access to substituted dihydrobenzofurans.

Comment: The donor–donor rhodium carbenoid is generated in situ from the corresponding hydrazine in the presence of MnO_2 . The methodology demonstrates a broad substrate scope, with a variety of functional groups tolerated on the benzylic or allylic ether as well as on the hydrazine motif. Allylic ethers containing a 1,2-disubstituted olefin do not undergo *E/Z*-isomerization under the reaction conditions. To demonstrate the utility of the method, an enantioselective total synthesis of *E*- δ -viniferin was achieved.

Review: M. P. Doyle, R. Duffy, M. Ratnikov, L. Zhou *Chem. Rev.* **2010**, *110*, 704–724.