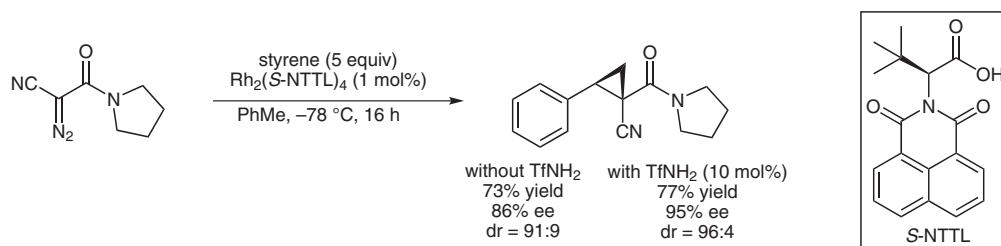


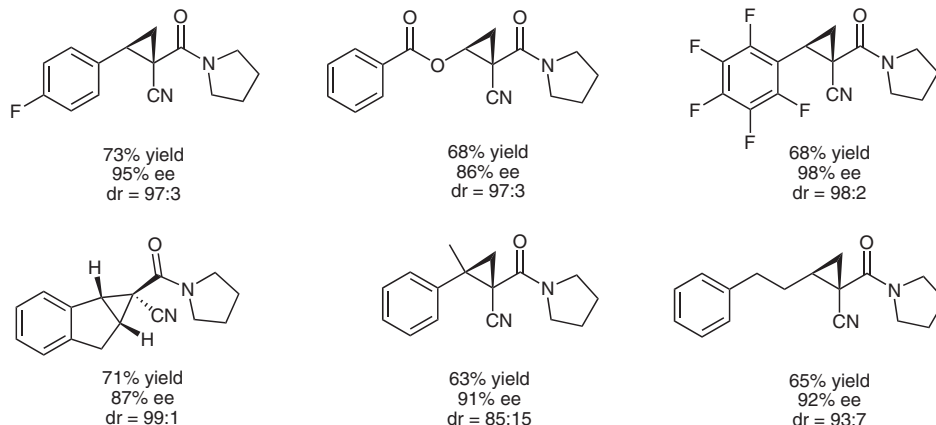
D. MARCOUX, S. AZZI, A. B. CHARETTE\* (UNIVERSITÉ DE MONTRÉAL, CANADA)

TfNH<sub>2</sub> as Achiral Hydrogen-Bond Donor Additive to Enhance the Selectivity of a Transition-Metal-Catalyzed Reaction. Highly Enantio- and Diastereoselective Rhodium-Catalyzed Cyclopropanation of Alkenes Using  $\alpha$ -Cyano Diazoacetamide*J. Am. Chem. Soc.* **2009**, *131*, 6970-6972.

## TfNH<sub>2</sub> Additive Enhances Selectivity of a Rhodium-Catalyzed Reaction



### Selected examples:



**Significance:** The present paper reports on the use of catalytic quantities of an achiral hydrogen-bond donor additive, TfNH<sub>2</sub>, to achieve enhanced enantio- and diastereoselectivities in a rhodium-catalyzed cyclopropanation.

**Comment:** It was found that increasing the amount of TfNH<sub>2</sub> did not increase the selectivity, while less than 10 mol% had a detrimental effect. Under the optimized reaction conditions a variety of olefins underwent the reaction and afforded the cyclopropanated products in good yield and with excellent enantio- and diastereoselectivity. While the TfNH<sub>2</sub> may prevent the catalyst from decomposing, the exact mode of action in increasing the selectivity of the reaction is unknown. It is proposed that the additive may interact with the cyano moiety while being on the metal carbene, thus affecting the position of the chiral ligands on rhodium. This notion is supported by the outcomes of control reactions.

**SYNFACTS Contributors:** Mark Lautens, Jacki Kitching  
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