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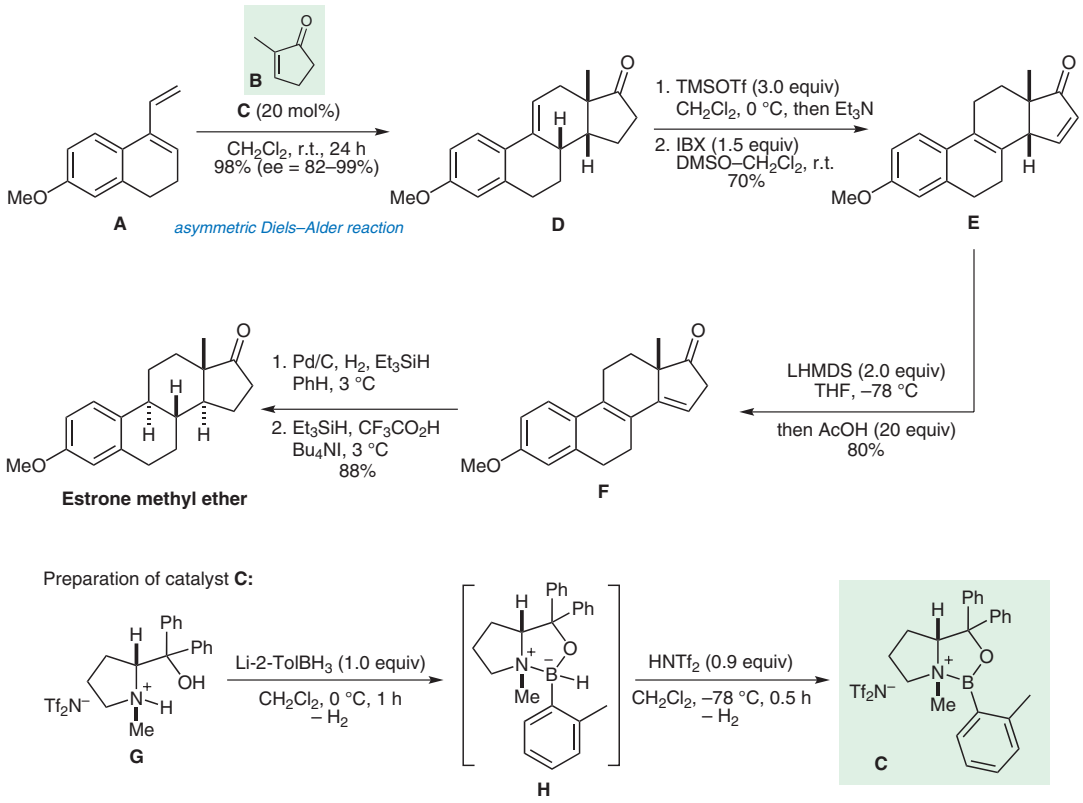
Highly Enantioselective [4+2] Cycloaddition Reactions Catalyzed by a Chiral *N*-Methyl-oxazaborolidinium Cation
Org. Lett. **2008**, *10*, 3271-3273.

Synthesis of Estrone Methyl Ether



Significance: Canales and Corey report a remarkably short and efficient synthesis of estrone methyl ether which exploits a novel *N*-methyl-oxazaborolidinium cation as a Lewis acid catalyst for an asymmetric Diels–Alder reaction. The paper cites ten further examples all proceeding with excellent yields and ee values. The reactions typically proceed in dichloromethane at –78 °C but in the estrone synthesis depicted, the cycloaddition was performed at room temperature. The ee of the adduct **D** (82%) was raised to 99% by one recrystallization.

Comment: The highly reactive catalyst **C** was generated in situ prior to use. It could not be generated by *N*-methylation of the corresponding oxazaborolidine; nor could it be generated by the reaction of *N*-methyl-1,1-diphenyl-pyrrolidinomethanol or the corresponding bistrimethylsilyl ether with $ArBBr_2$ or $ArB(OTf)_2$. For a related synthesis of estrone methyl ether see: Y.-Y. Yeung, R.-J. Chein, J. E. Corey *J. Am. Chem. Soc.* **2007**, *129*, 10346.

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Category

Synthesis of Natural Products and Potential Drugs

Key words

estrone

asymmetric Diels–Alder reaction

oxazaborolidine