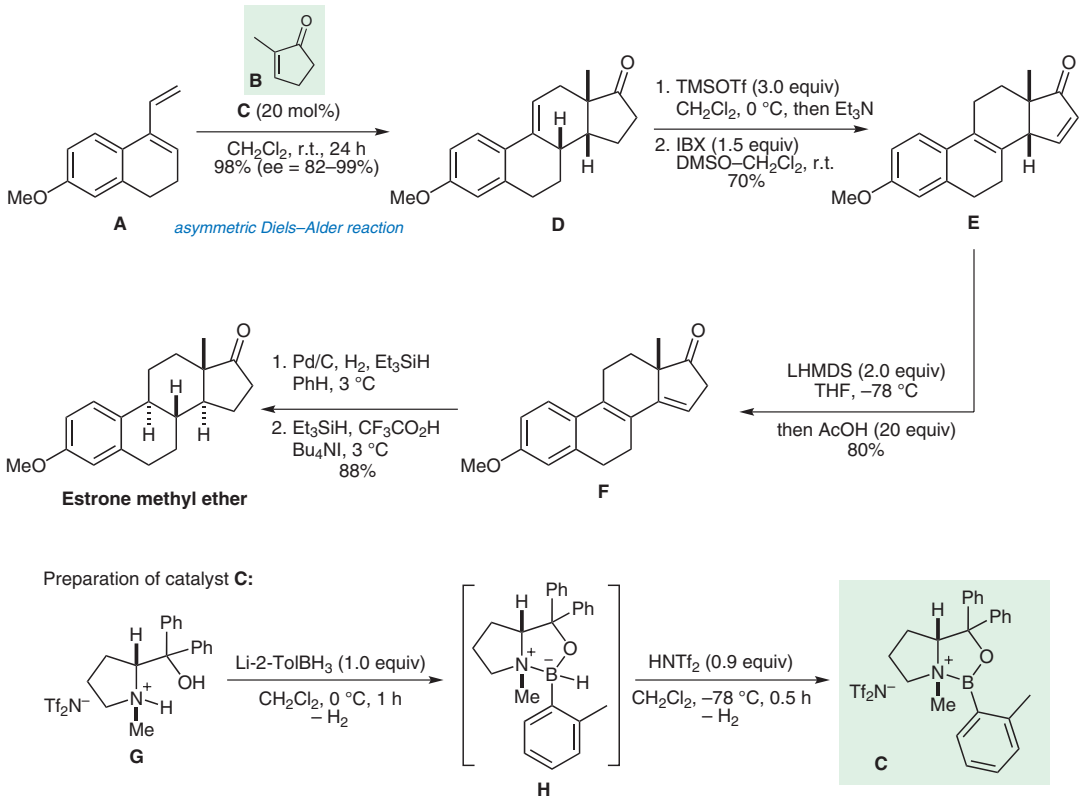
E. CANALES, E. J. COREY* (HARVARD UNIVERSITY, CAMBRIDGE, USA)

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.

SYNFACTS Contributors: Philip Kocienski
Synfacts 2009, 2, 0117-0117 Published online: 22.01.2009
DOI: 10.1055/s-0028-1087603; **Reg-No.:** K17008SF

2009 © THIEME STUTTGART • NEW YORK

Category

Synthesis of Natural Products and Potential Drugs

Key words

estrone

asymmetric Diels–Alder reaction

oxazaborolidine

SYNFACT of the month

This document was downloaded for personal use only. Unauthorized distribution is strictly prohibited.