



六、周环反应

(一) 非直观Diels-Alder反应

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一、概论

二、基础知识

构象分析

有机反应的热力学和动力学

构象对反应活性的影响

立体电子效应

三、氧化态的调整

烯烃、醇和其他化合物的氧化

烯烃、羰基化合物和其他化合物的还原

四、C-X键形成反应

五、一些形成C-C键的基本反应

烯醇和烯醇负离子化学

有机锂、镁和铜试剂的制备和反应

自由基反应

烯基化反应

六、周环反应

非直观Diels-Alder反应

1,3-偶极环加成反应

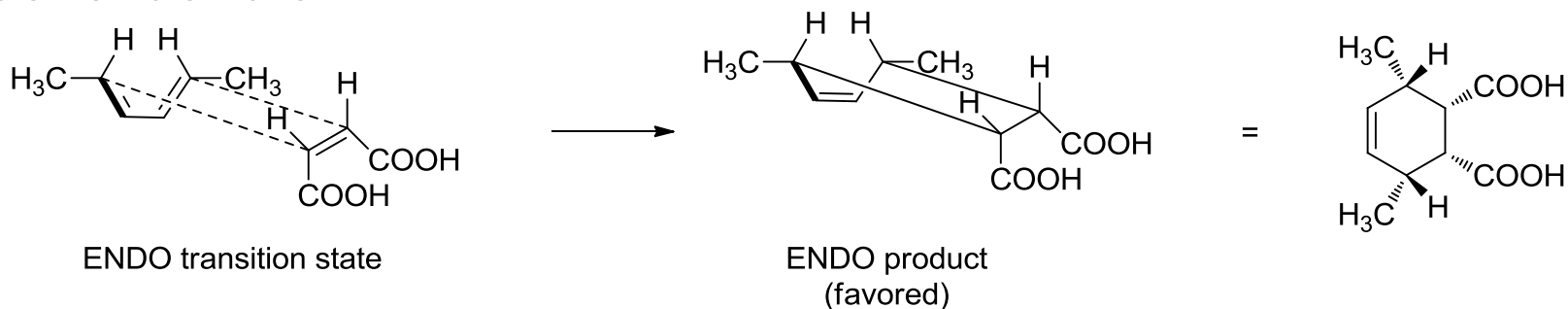
电环化反应

sigmatropic重排

七、阳离子参与的C-C键形成反应

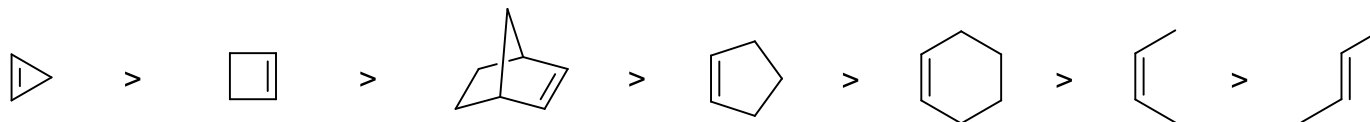
Diels-Alder反应的一些常识

Alder endo rule



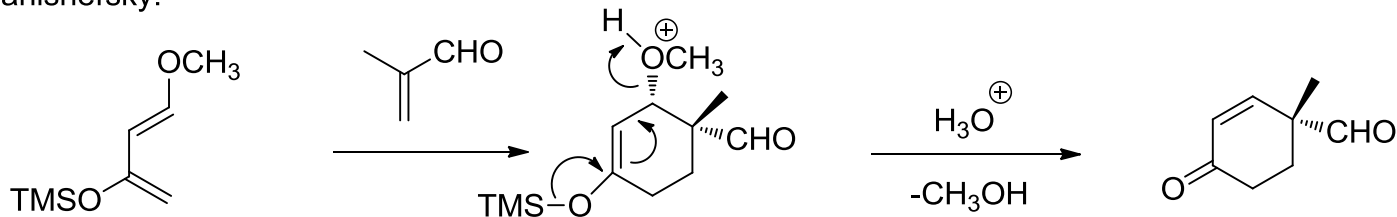
Dienophile reactivity

Strain in dienophile

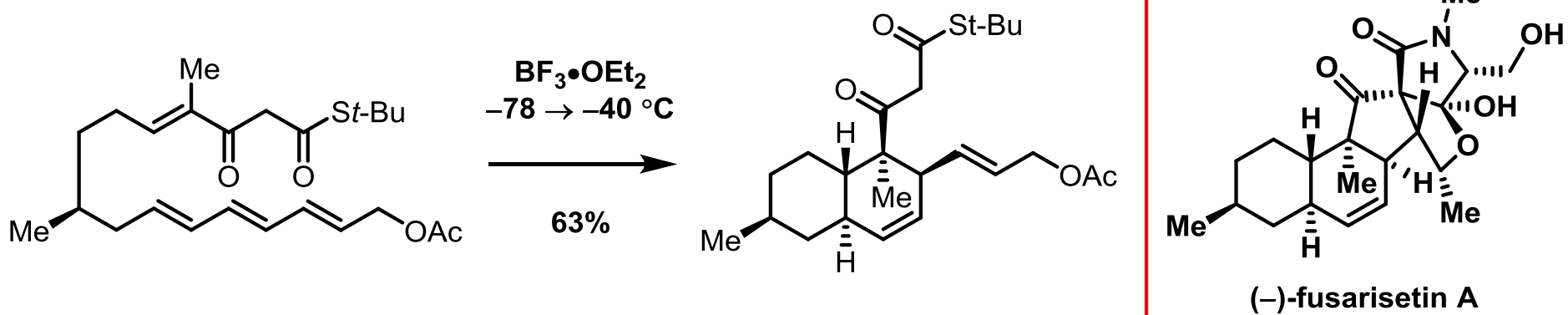


Danishefsky Diene

Danishefsky:

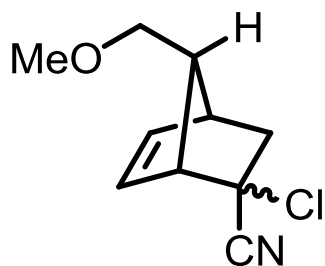
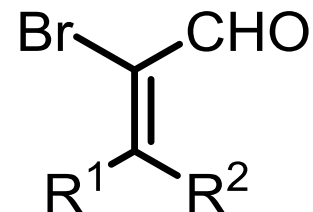
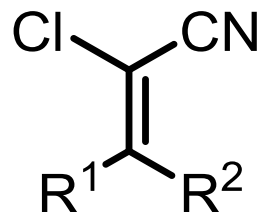
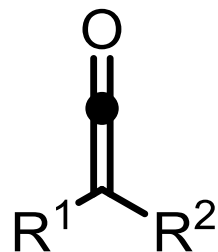


直观Diels-Alder反应：Fusarisetin A的全合成



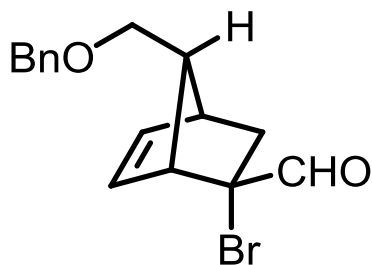
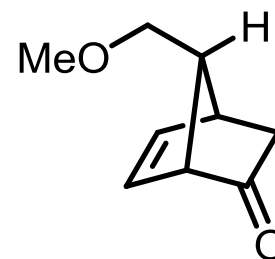
J. Deng, B. Zhu, Z. Lu, H. Yu, A. Li, *J. Am. Chem. Soc.* **2012**, 134, 920.

非直观Diels-Alder反应：Ketene等价物



KOH, H₂O
(80%)

Mechanism?

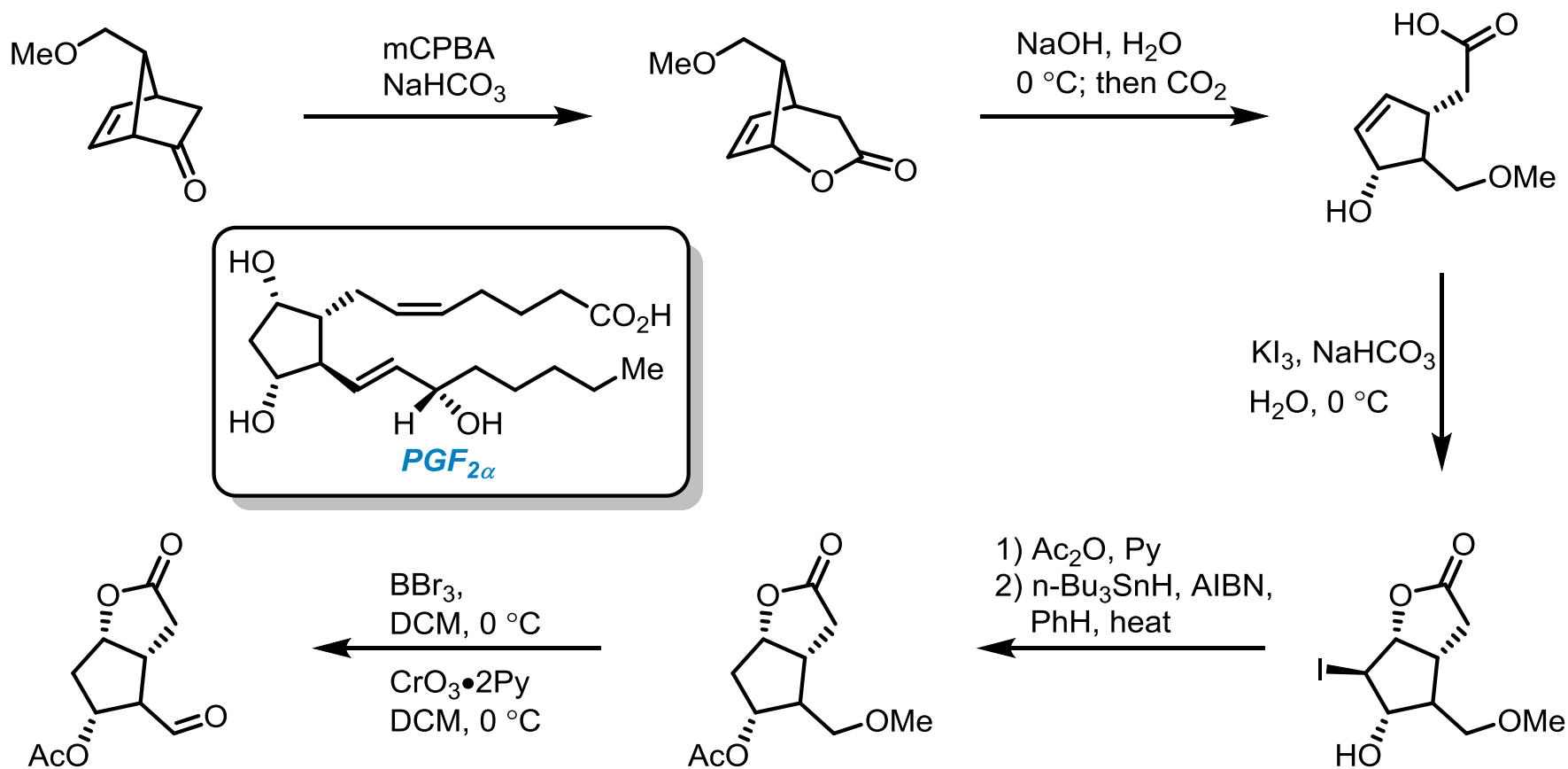


1) NaBH₄
2) K₂CO₃, H₂O

Mechanism and structure?

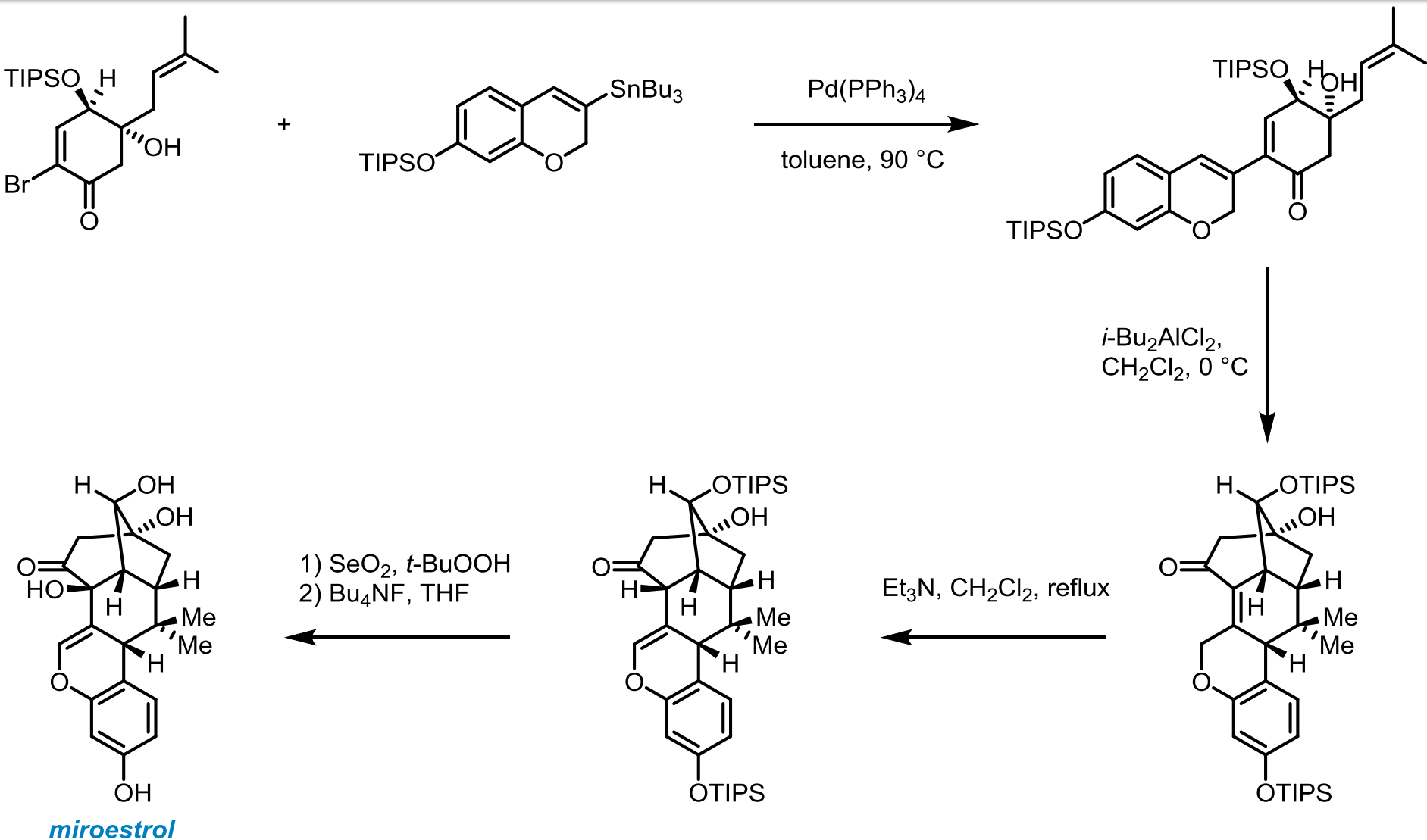
Mass spec: SM-Br+H₃O
treatment with Pb(OAc)₄
gives IR = 1740 cm⁻¹

非直观Diels-Alder反应的应用：PGF₂α的合成



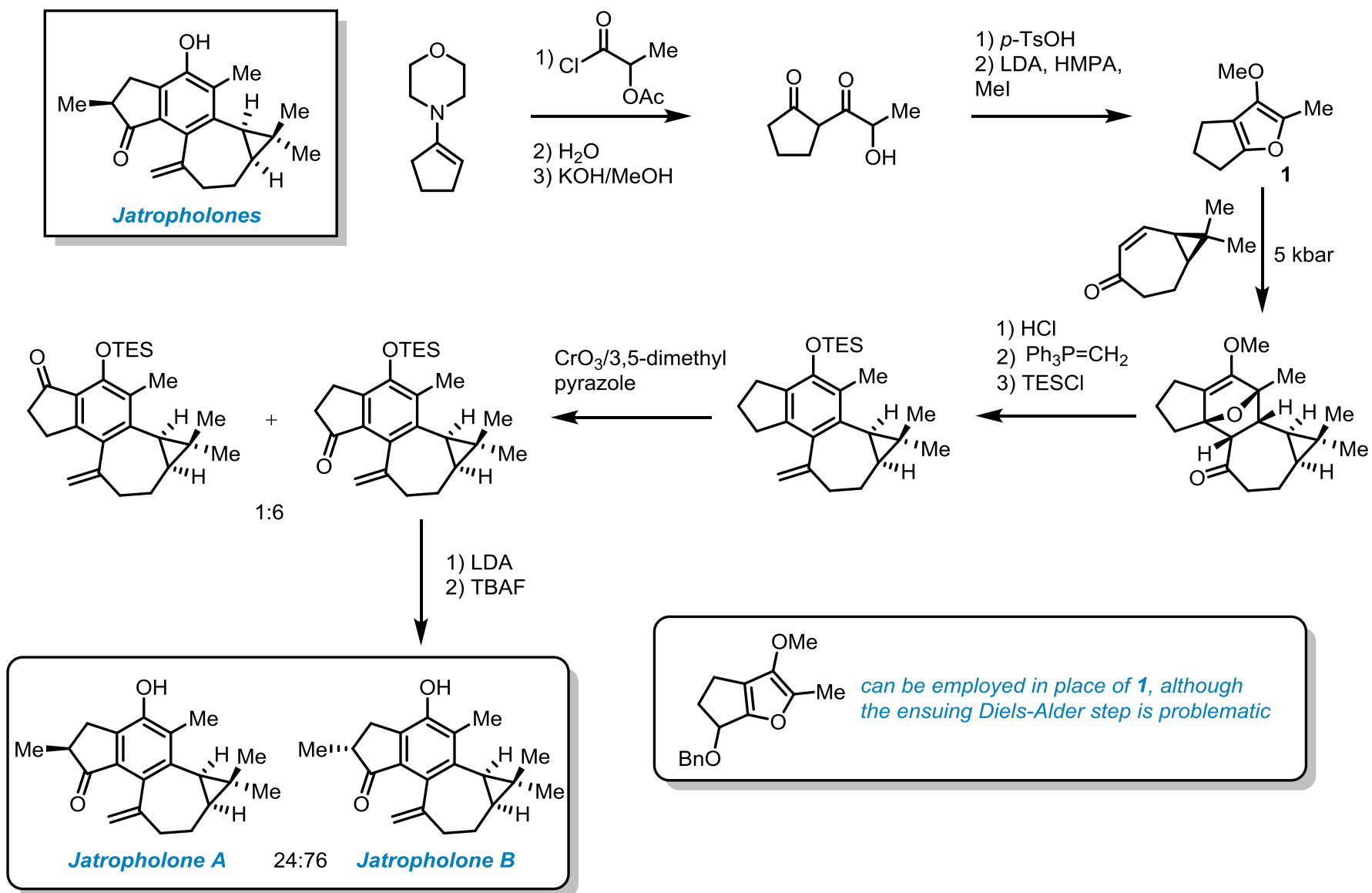
E. J. Corey, et al. *J. Am. Chem. Soc.* **1969**, *91*, 5675.

非直观Diels–Alder反应的应用：Miroestrol的合成

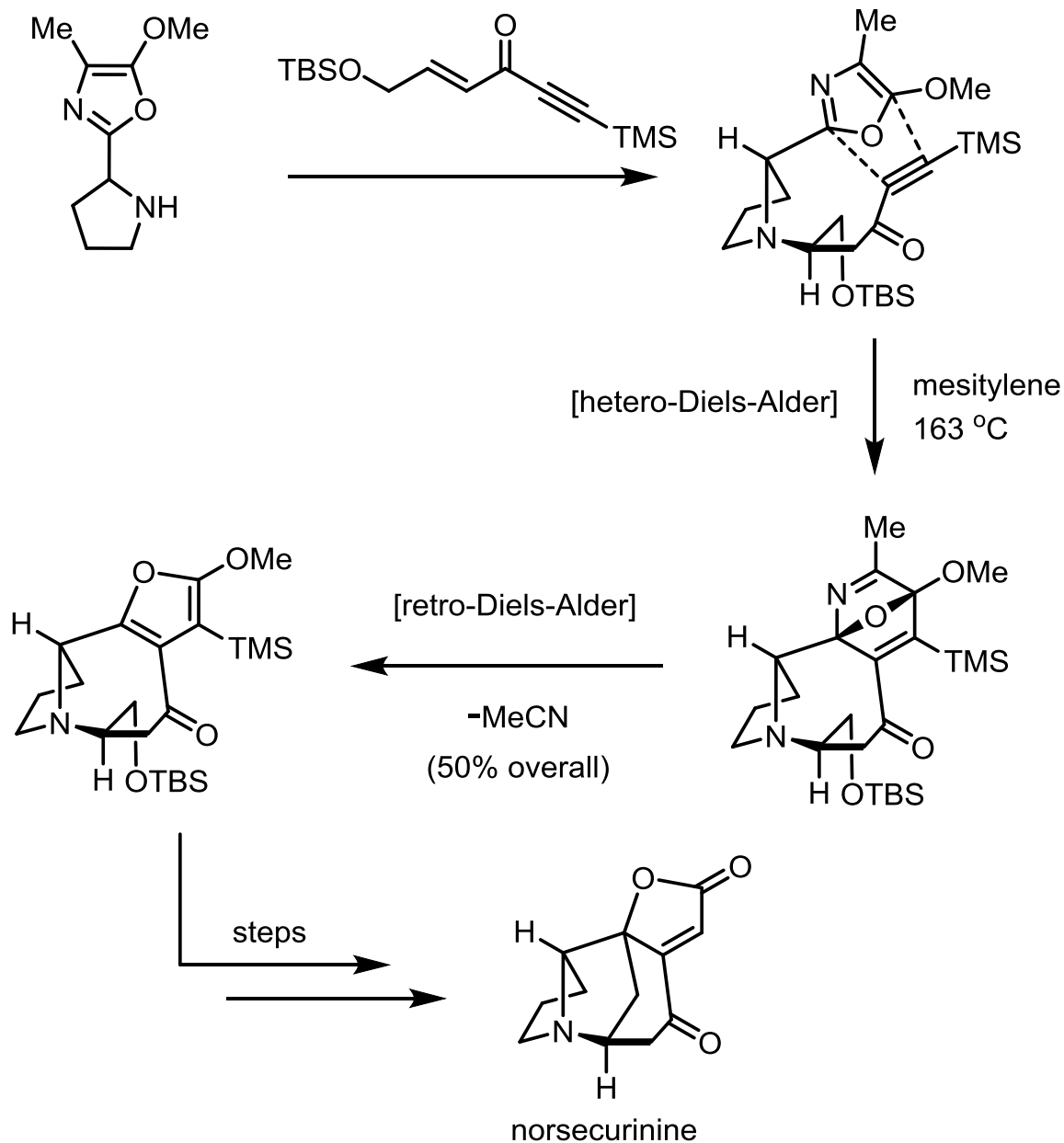


E. J. Corey, et al. *J. Am. Chem. Soc.* **1993**, *115*, 9327.

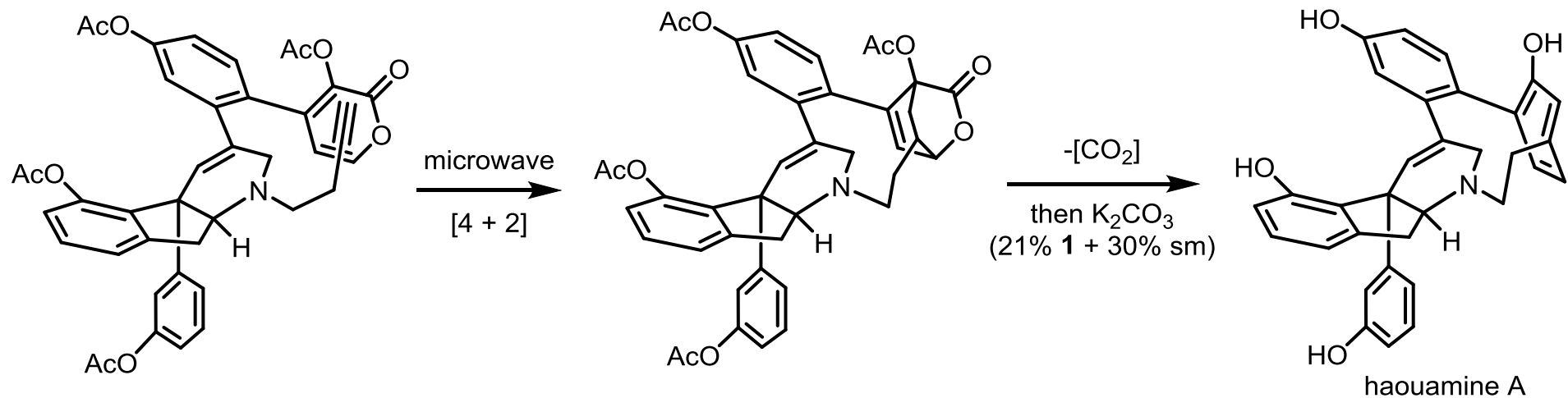
非直观Diels-Alder反应的应用：Jatropholones A和B的合成



非直观Diels-Alder反应：Jacobi Diene

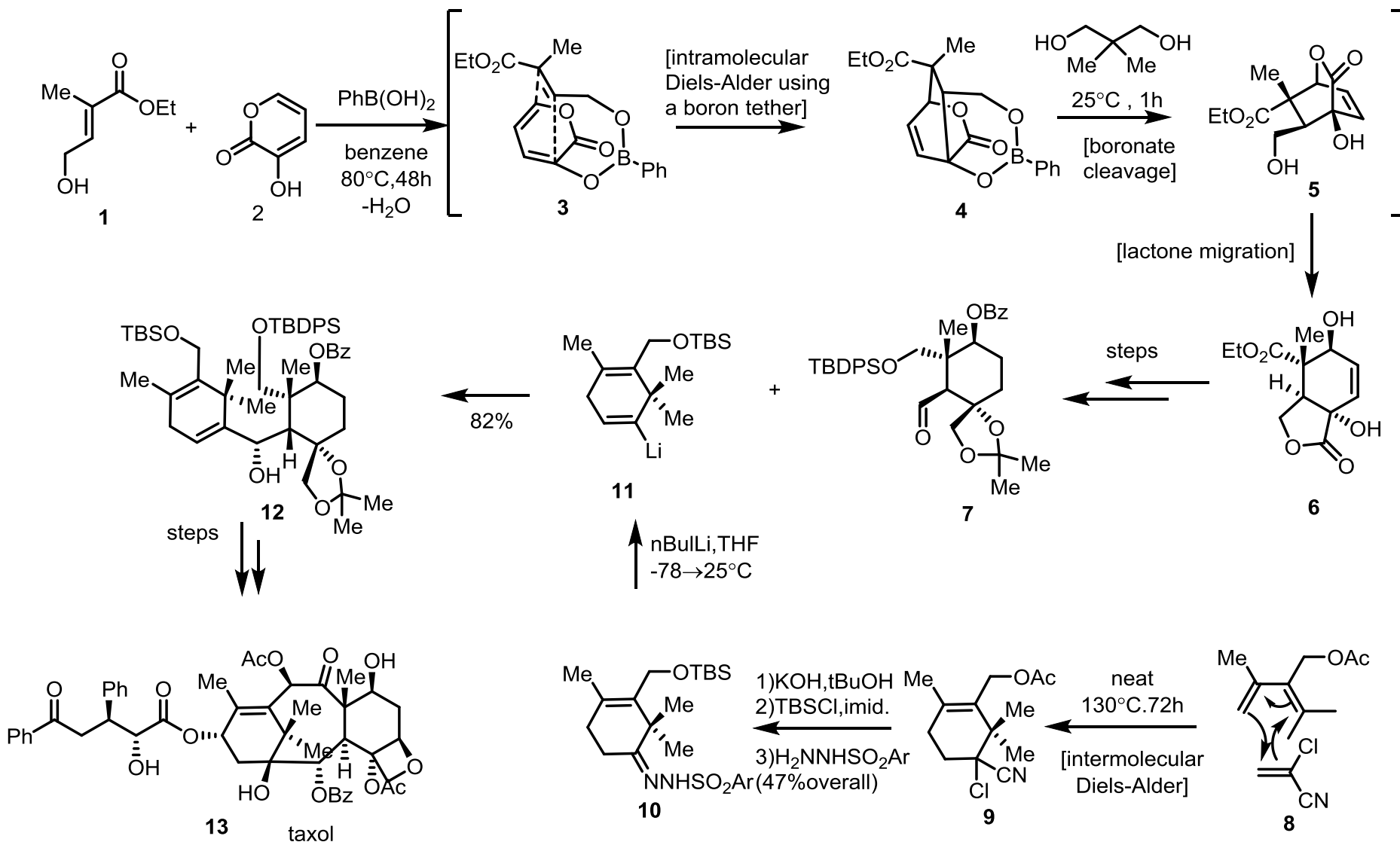


非直观Diels-Alder反应：Pyrone Based Diels-Alder



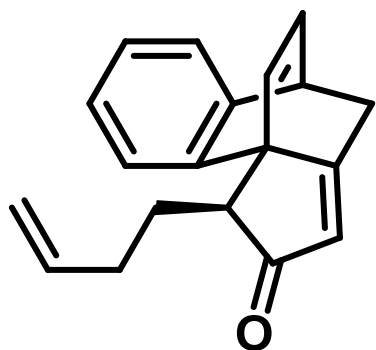
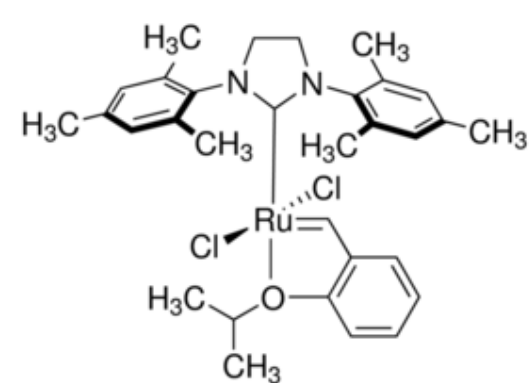
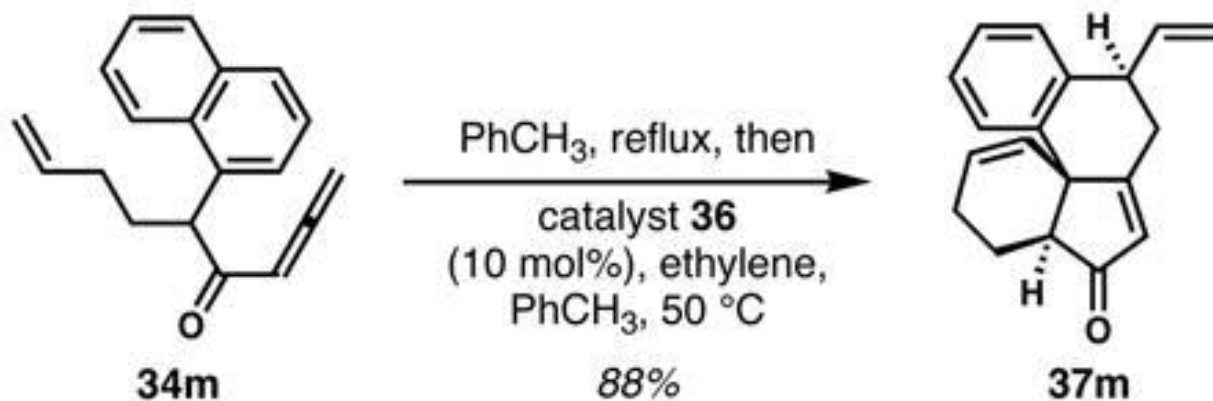
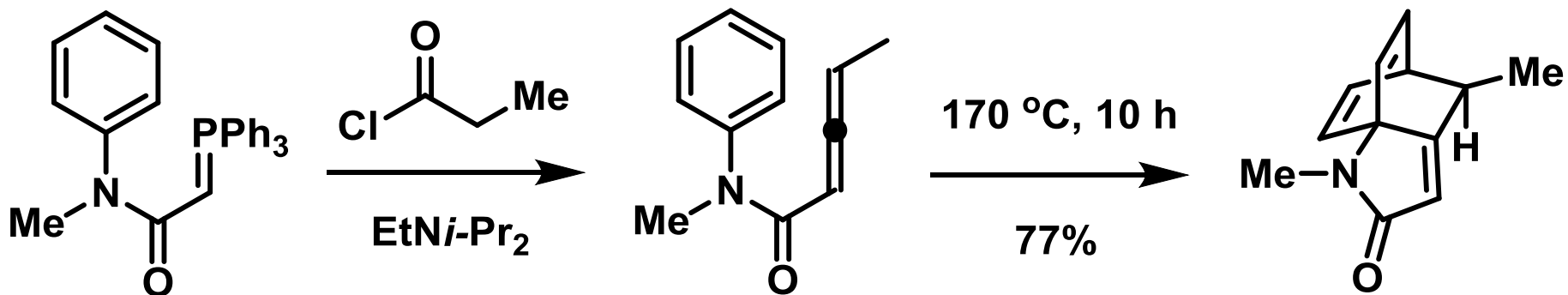
P. S. Baran, N. Z. Burns, *J. Am. Chem. Soc.* **2006**, 128, 3908.

非直观Diels-Alder反应：Pyrone Based Diels-Alder



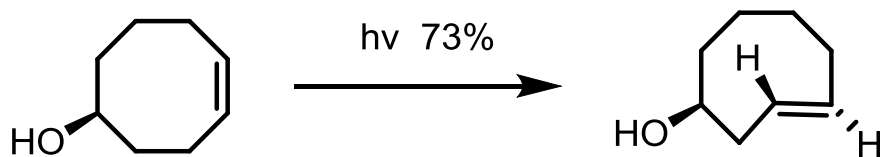
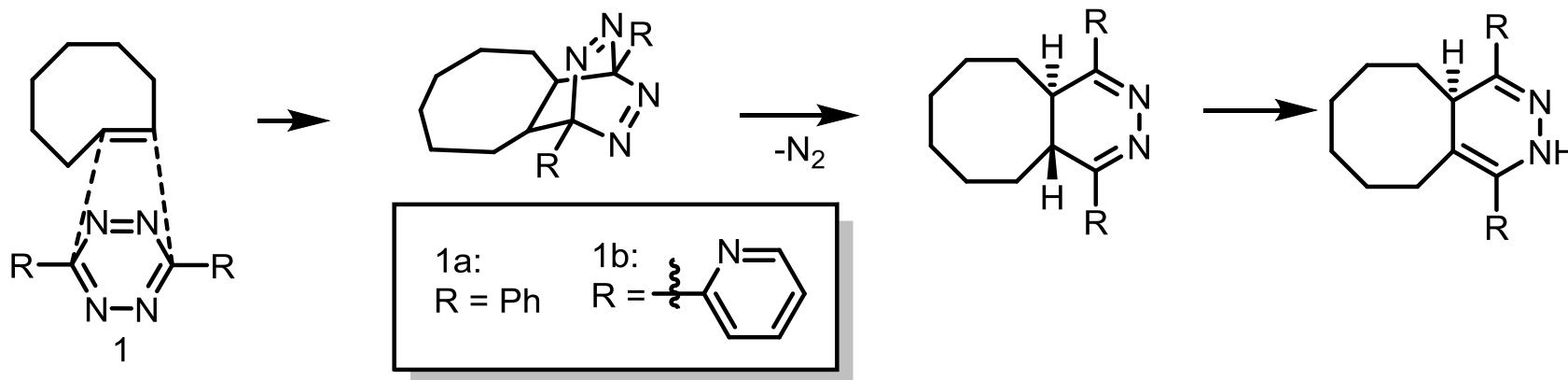
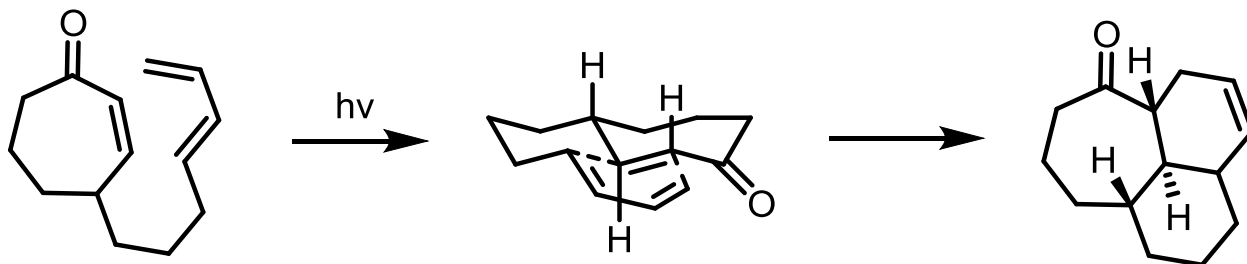
K. C. Nicolaou, Z. Yang, et al. *Nature* **1994**, 367, 630.

非直观Diels-Alder反应：苯环直接作为亲双烯体



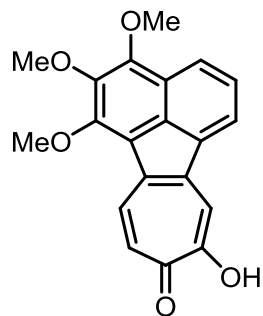
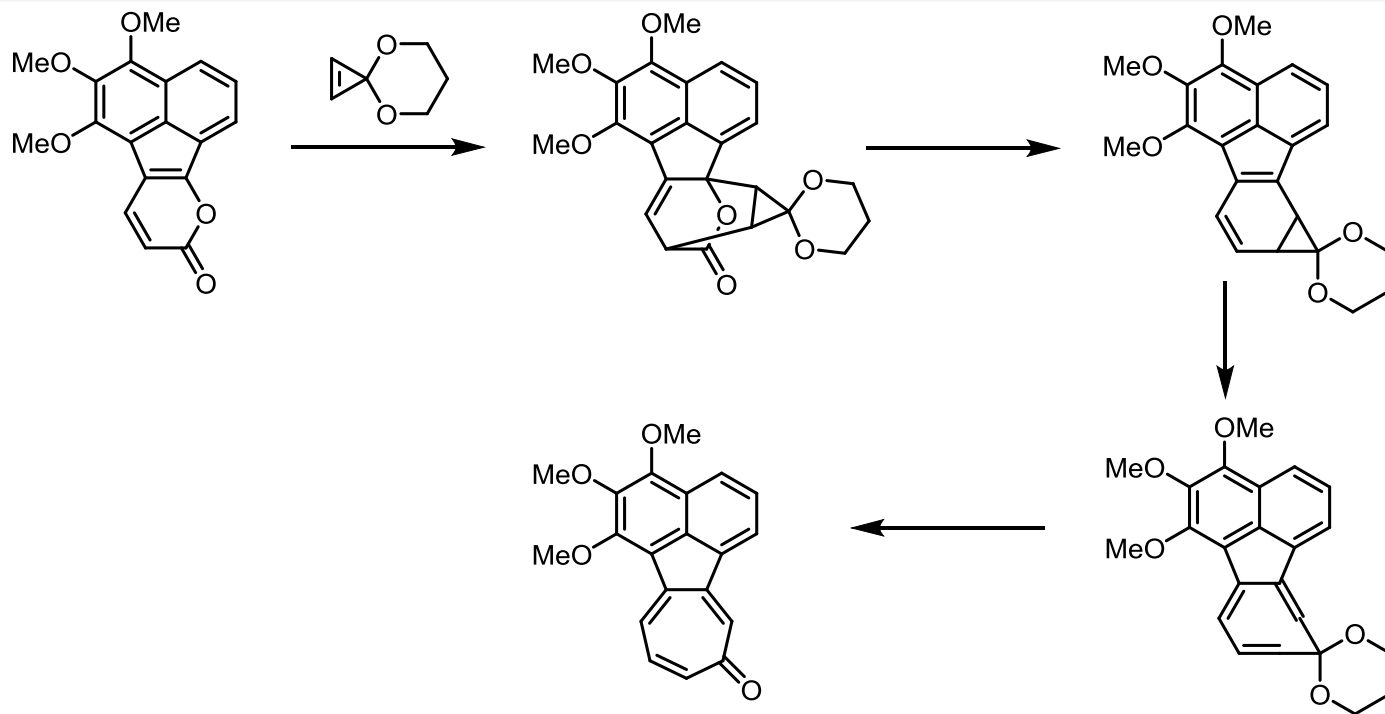
G. Himbert, L. Henn, *Angew. Chem. Int. Ed.* **1982**, 21, 620.
C. D. Vanderwal, et al. *J. Am. Chem. Soc.* **2013**, 135, 7339

非直观Diels-Alder反应：反式环烯作为亲双烯体

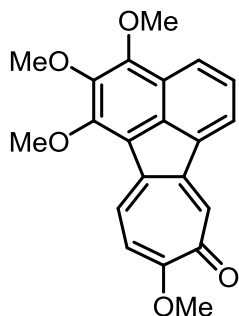


J. M. Fox, et al. *J. Am. Chem. Soc.*, 2008, **130**, 3760.

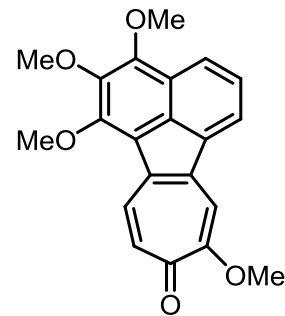
非直观Diels-Alder反应：环丙烯作为亲双烯体



Grandirubrine

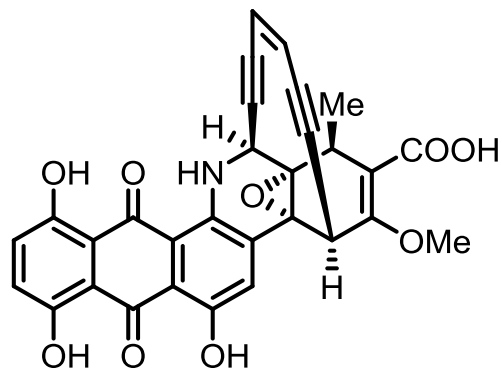


Imerubrine

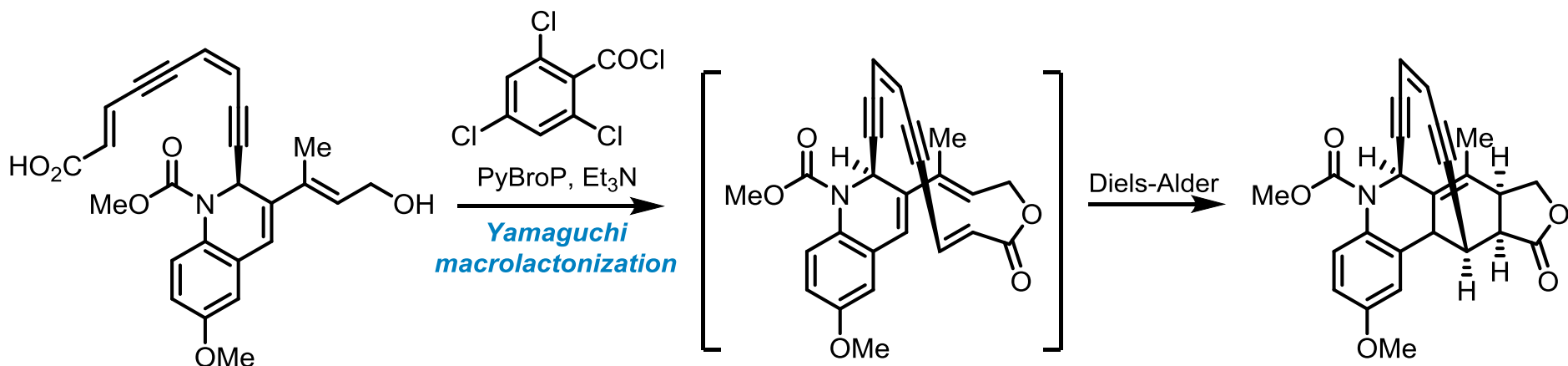
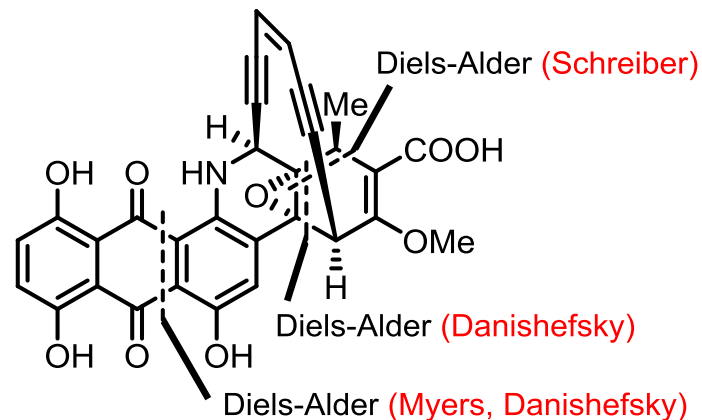
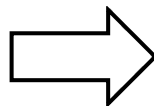


Isoimerubrine

Diels-Alder反应的一些有趣应用：Dyngemicin A合成

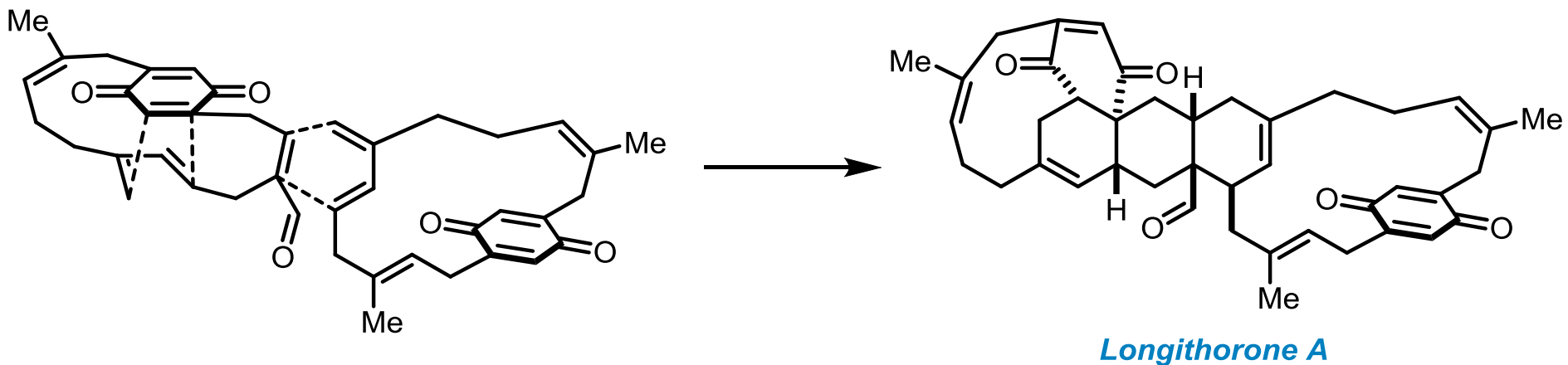


Dyngemicin A



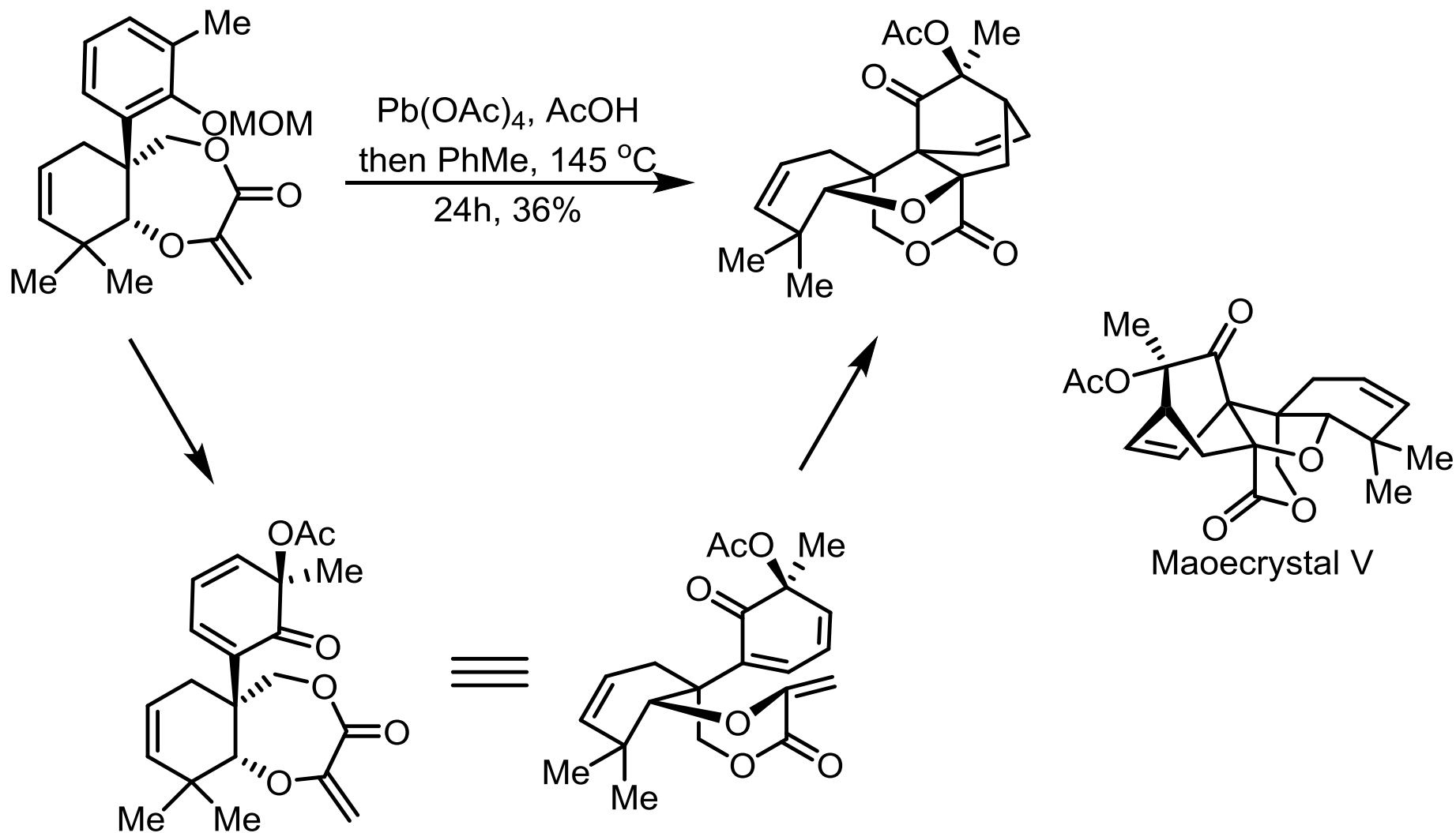
J. L. Wood, J. A. Porco, J. Taunton, A. Y. Lee, J. Clardy, S. L. Schreiber,
J. Am. Chem. Soc. **1992**, *114*, 5898.

Diels-Alder反应的一些有趣应用：Longithorone A合成



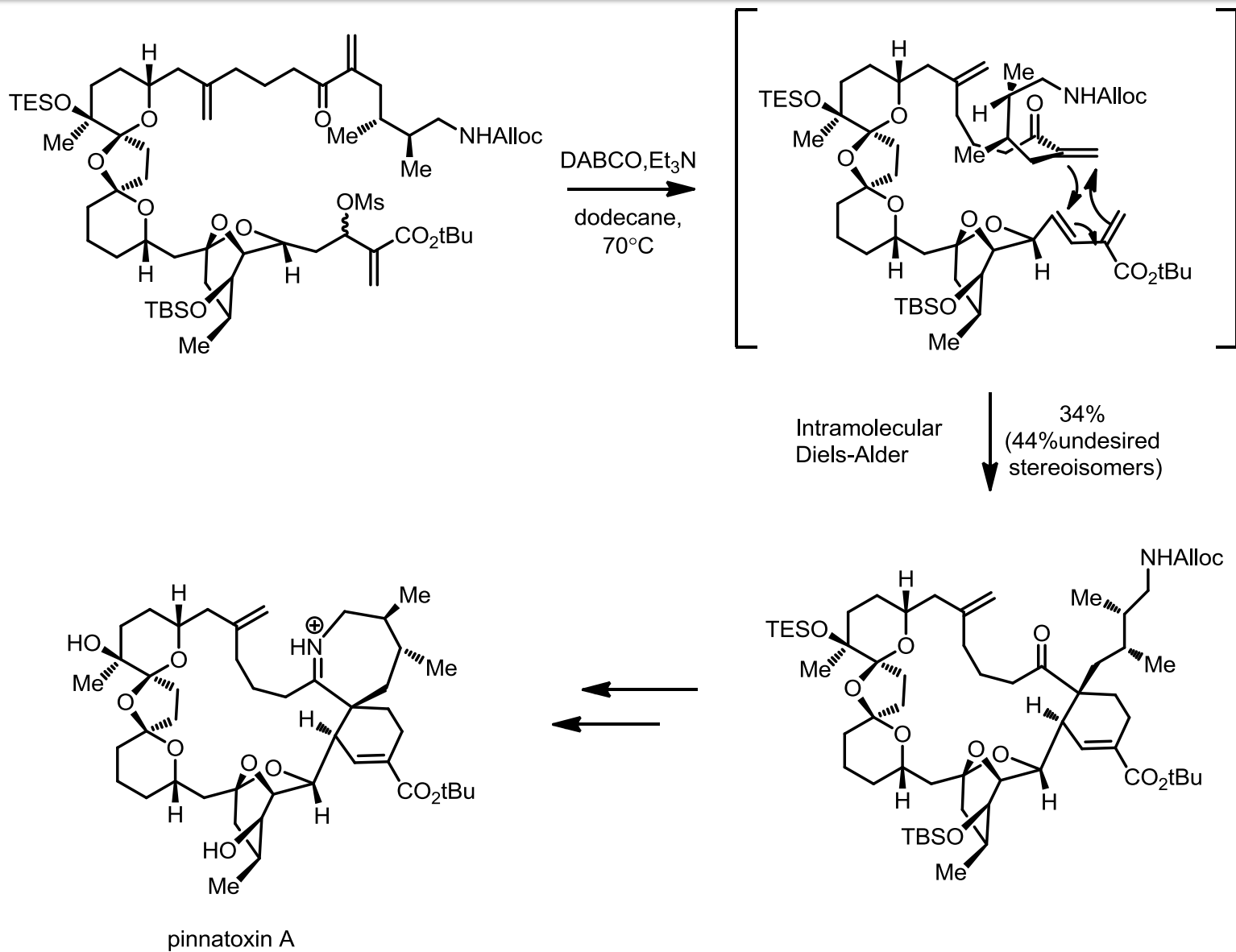
M. E. Layton, C. M. Morales, M. D. Shair, *J. Am. Chem. Soc.* **2002**, 124, 773.

Diels-Alder反应的一些有趣应用：Maoecrystal V合成



J. Gong, G. Lin, W. Sun, C. Li, Z. Yang, *J. Am. Chem. Soc.* **2010**, *132*, 16745.

Diels-Alder反应的一些有趣应用：Pinnatoxin A合成



Y. Kishi et al. *J. Am. Chem. Soc.* **1998**, *120*, 7647.