



六、周环反应

(二) 电环化反应

李昂

中国科学院上海有机化学研究所
生命有机化学国家重点实验室

2018年12月10日



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

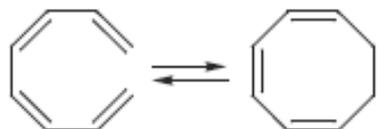
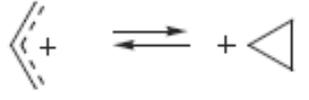
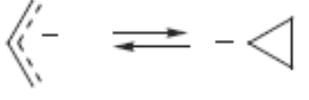
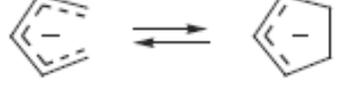
1,3-偶极环加成反应

电环化反应

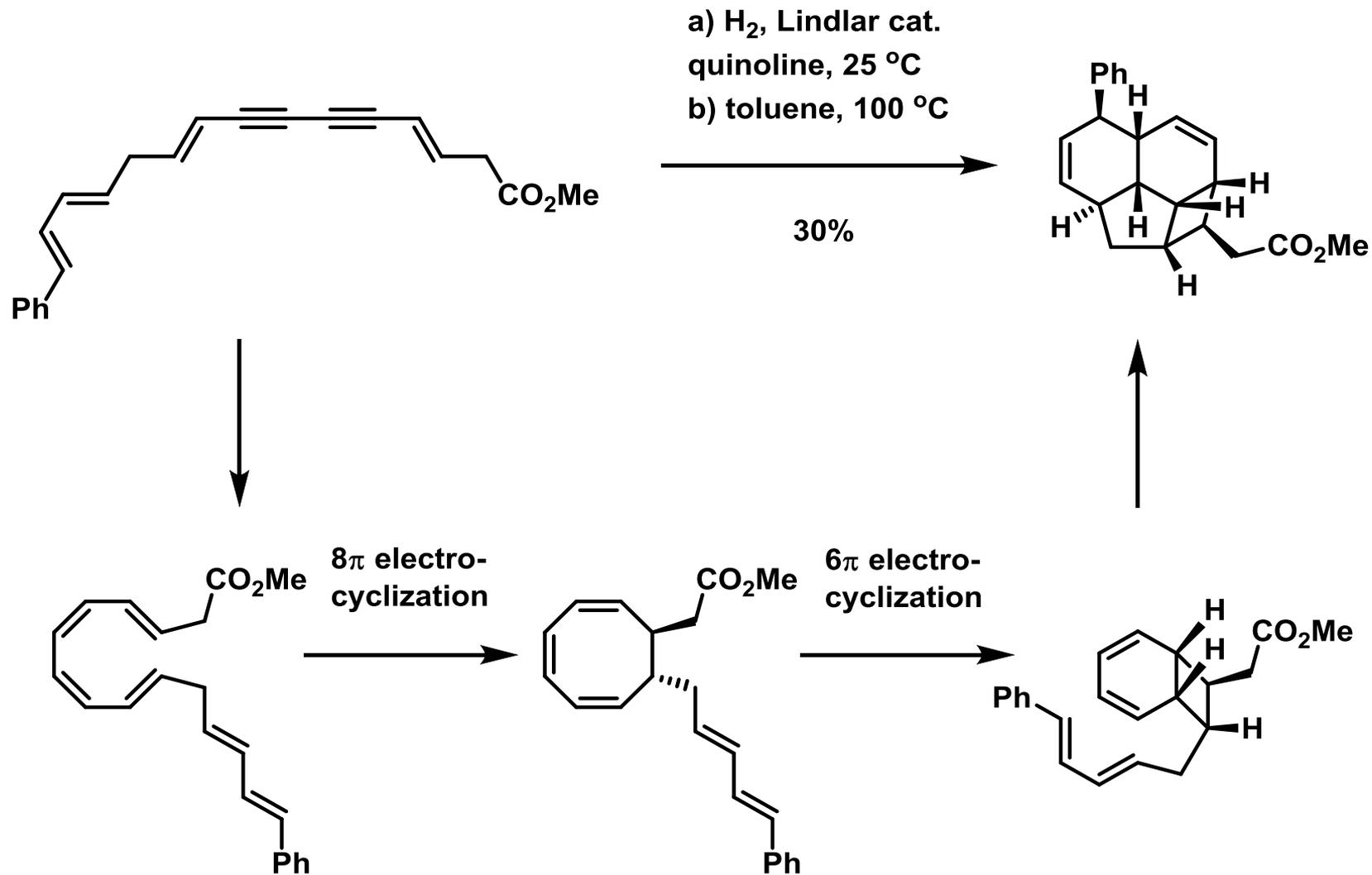
sigmatropic重排

七、阳离子参与的C-C键形成反应

电环化反应的类型

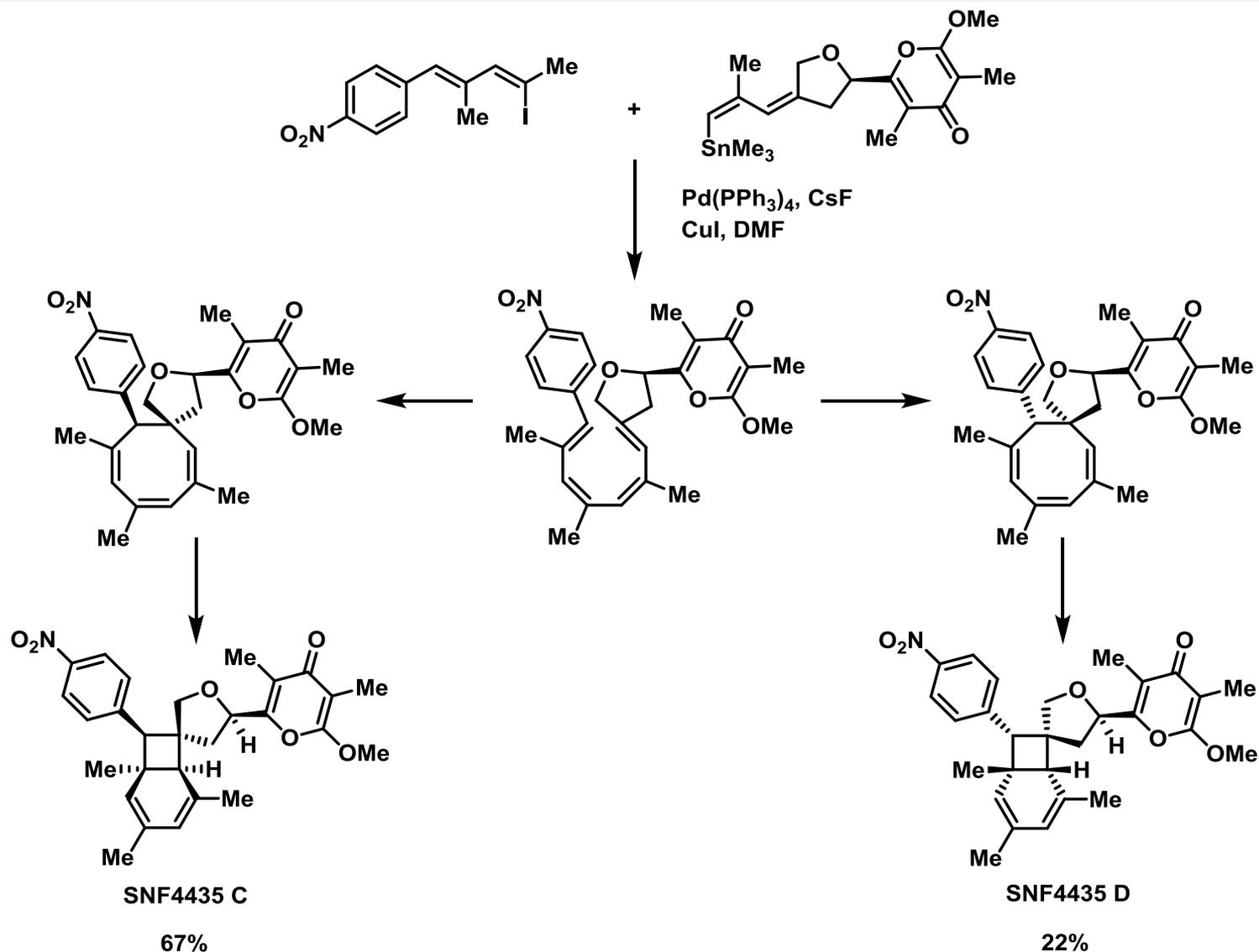
System	π electrons	Thermal Reaction Ground State (HOMO)	$h\nu$ Reaction Excited State (LUMO)
	$4 \pi e^-$	conrotatory	disrotatory
	$6 \pi e^-$	disrotatory	conrotatory
	$8 \pi e^-$	conrotatory	disrotatory
	$2 \pi e^-$	disrotatory	conrotatory
	$4 \pi e^-$	conrotatory	disrotatory
	$4 \pi e^-$	conrotatory	disrotatory
	$6 \pi e^-$	disrotatory	conrotatory

串联电环化反应



Nicolaou, et al. *J. Am. Chem. Soc.* **1982**, *104*, 5555, 5557, 5557, 5560.

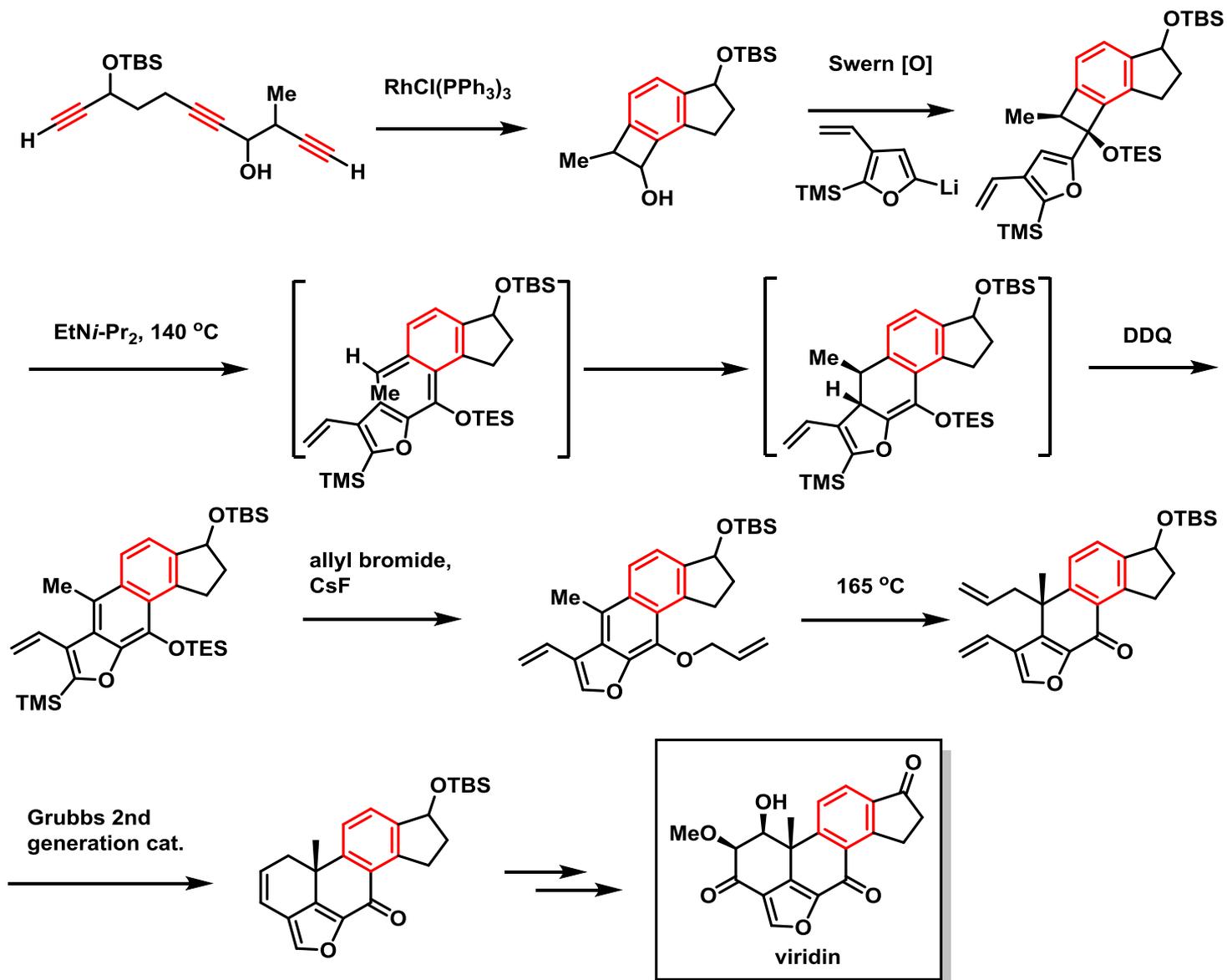
串联电环化反应



Parker and Lim, *J. Am. Chem. Soc.* **2004**, 126, 15968.

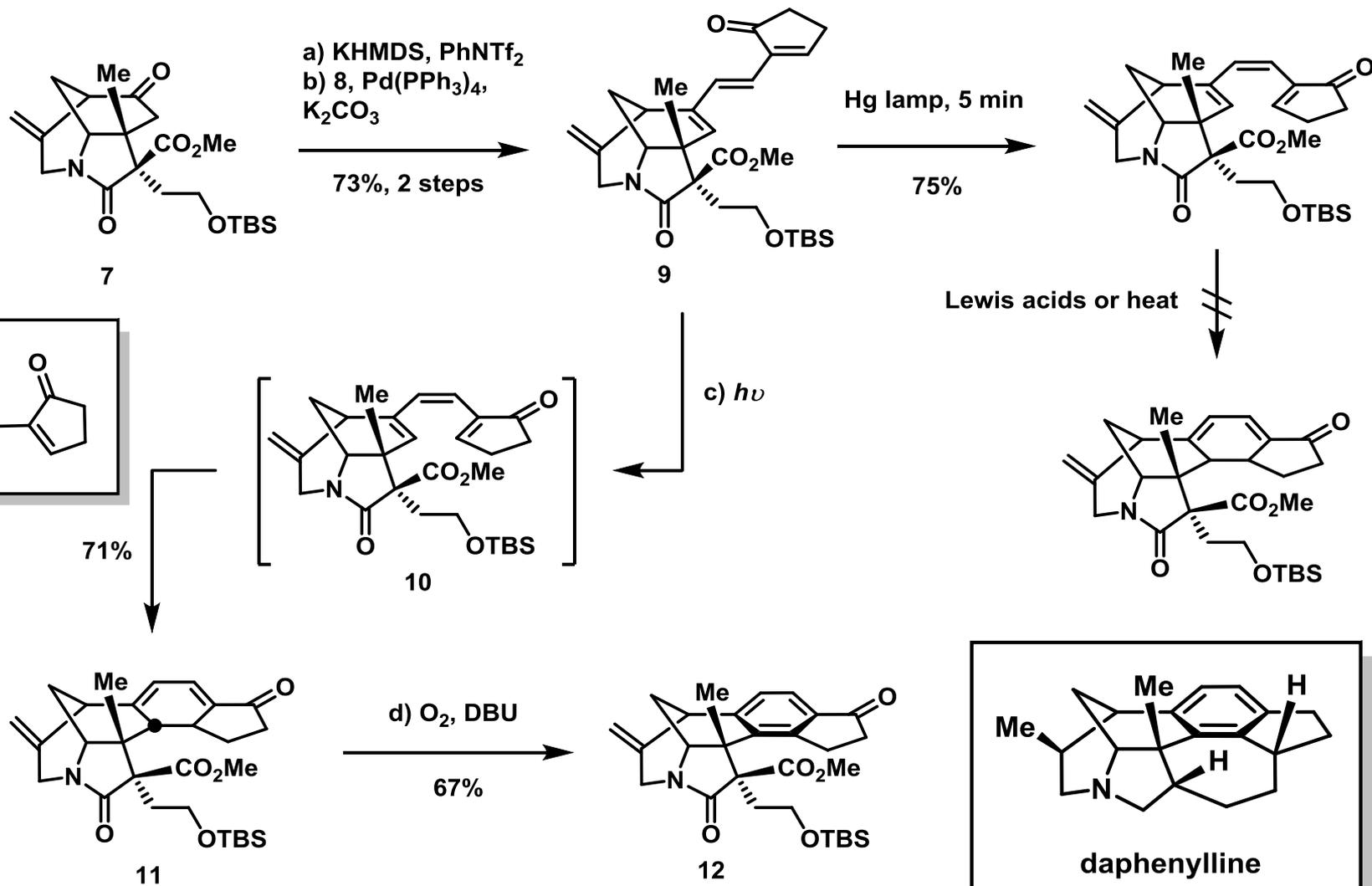
Beaudry and Trauner, *Org. Lett.* **2005**, 15, 4475.

电环化/芳构化

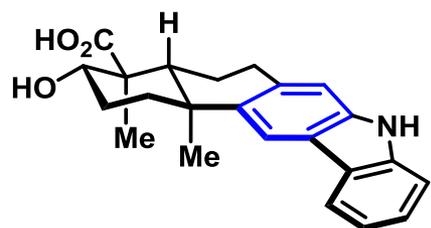
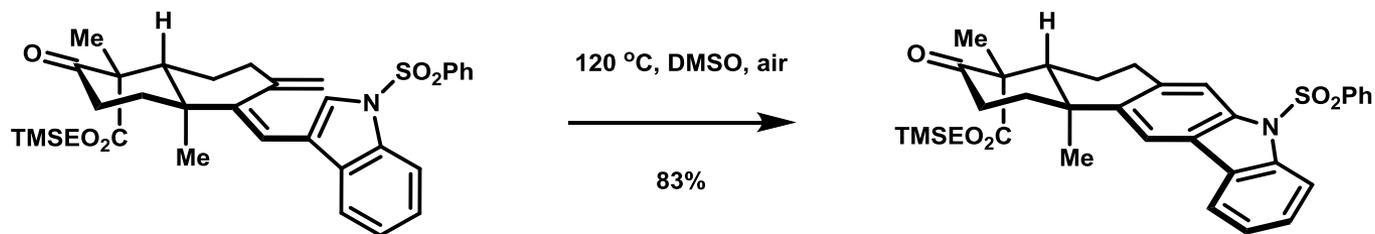
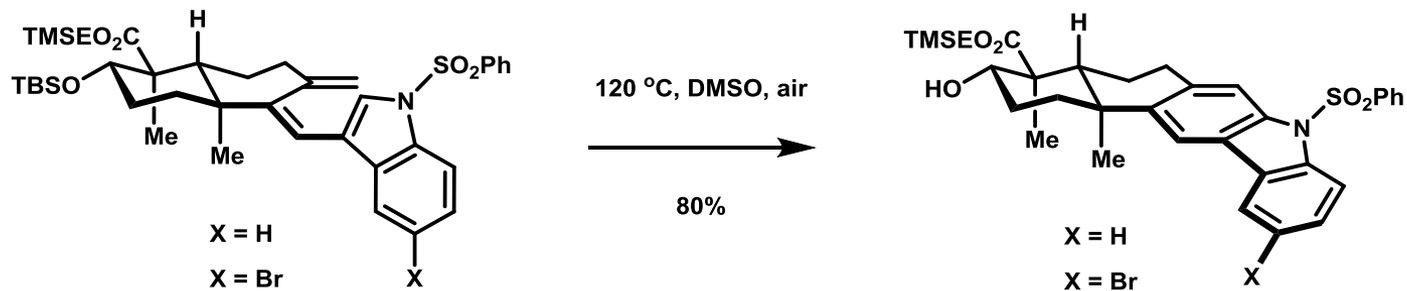


Sorensen, et al. *Angew. Chem. Int. Ed.* **2004**, 43, 1998.

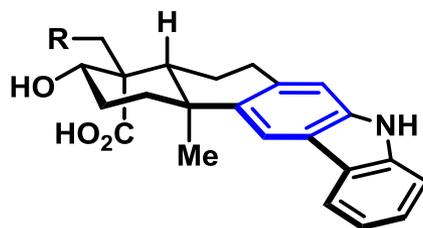
电环化/芳构化



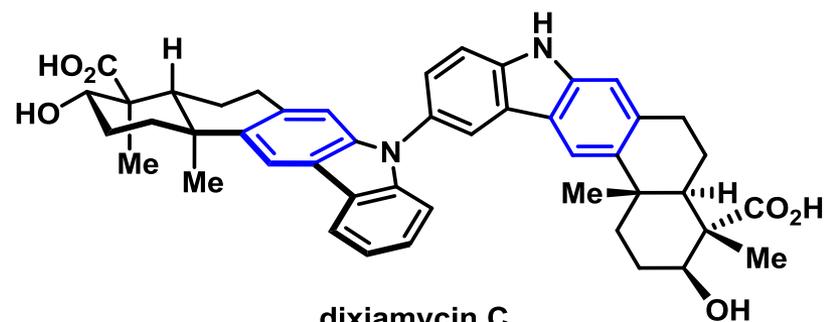
电环化/芳构化



xiamycin A

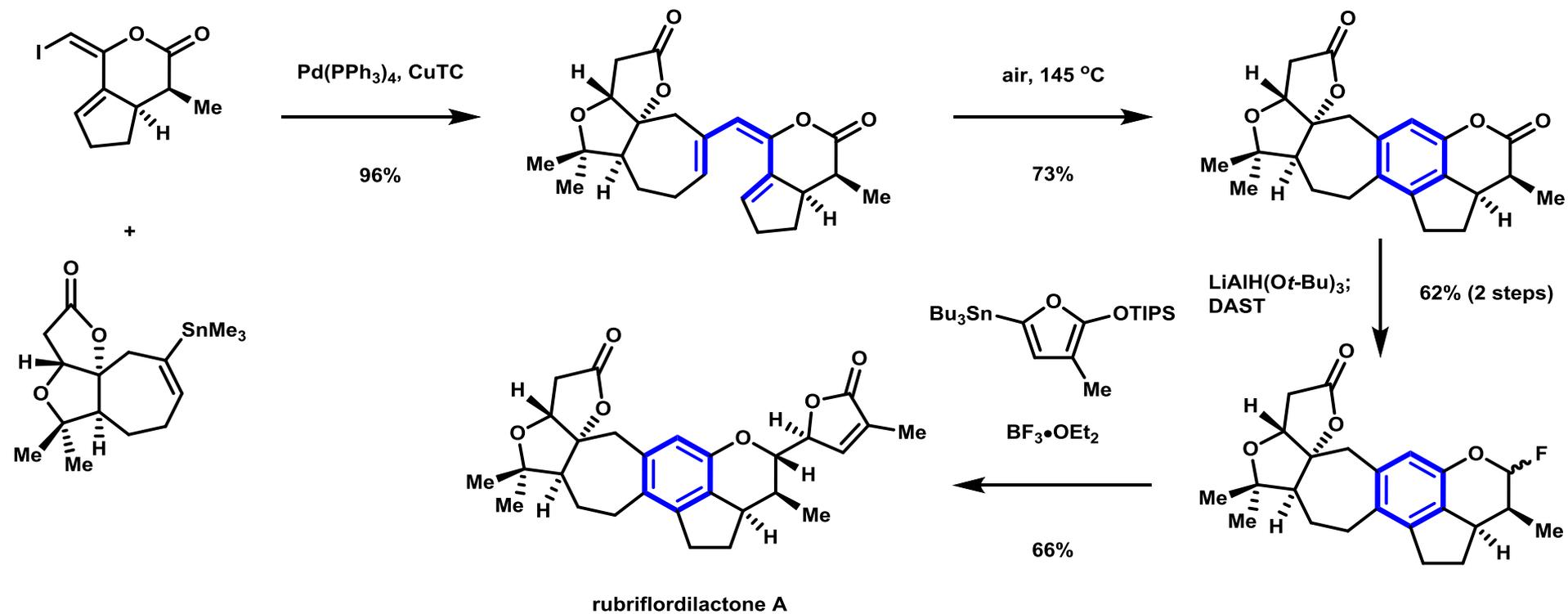


R = H; oridamycin A
R = OH; oridamycin B



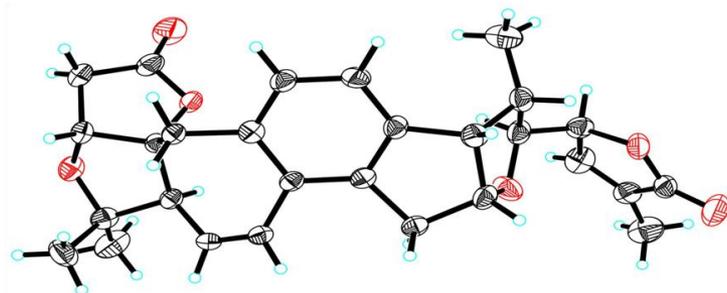
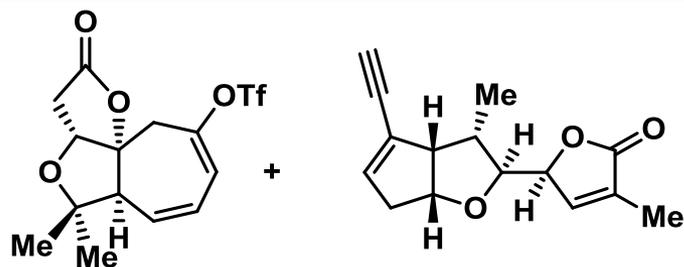
dixiamycin C

电环化/芳构化



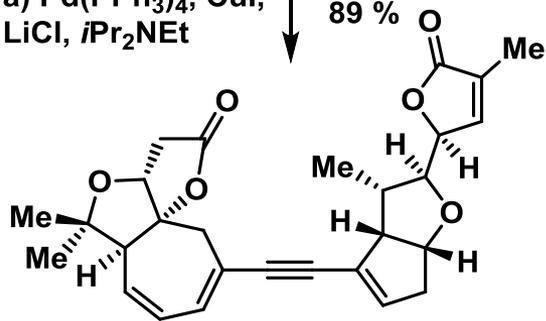
Li, et al. *J. Am. Chem. Soc.* **2014**, *136*, 16477.

电环化/芳构化



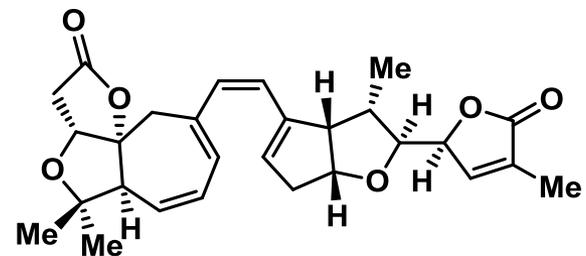
a) Pd(PPh₃)₄, Cul,
LiCl, *i*Pr₂NEt

89 %

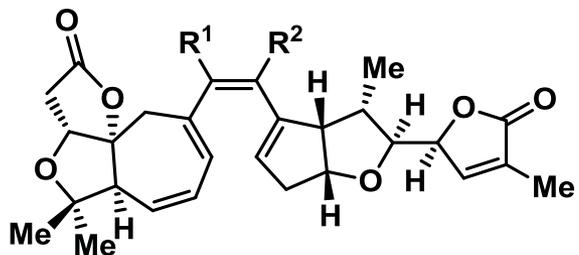


b) H₂, Lindlar cat.

60 %



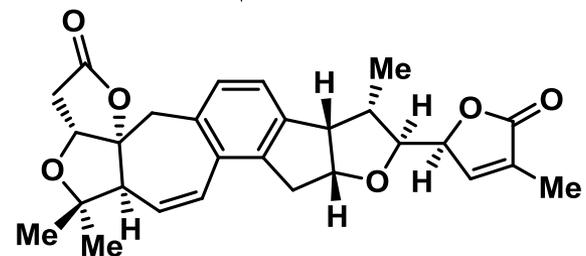
d) 1, 3-AmOSiMe₂H, 87 %



e) 135 °C; DDQ

f) AgF

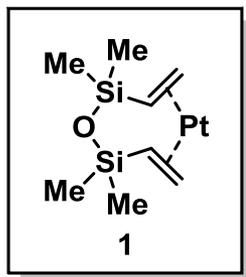
73 % (2 steps)



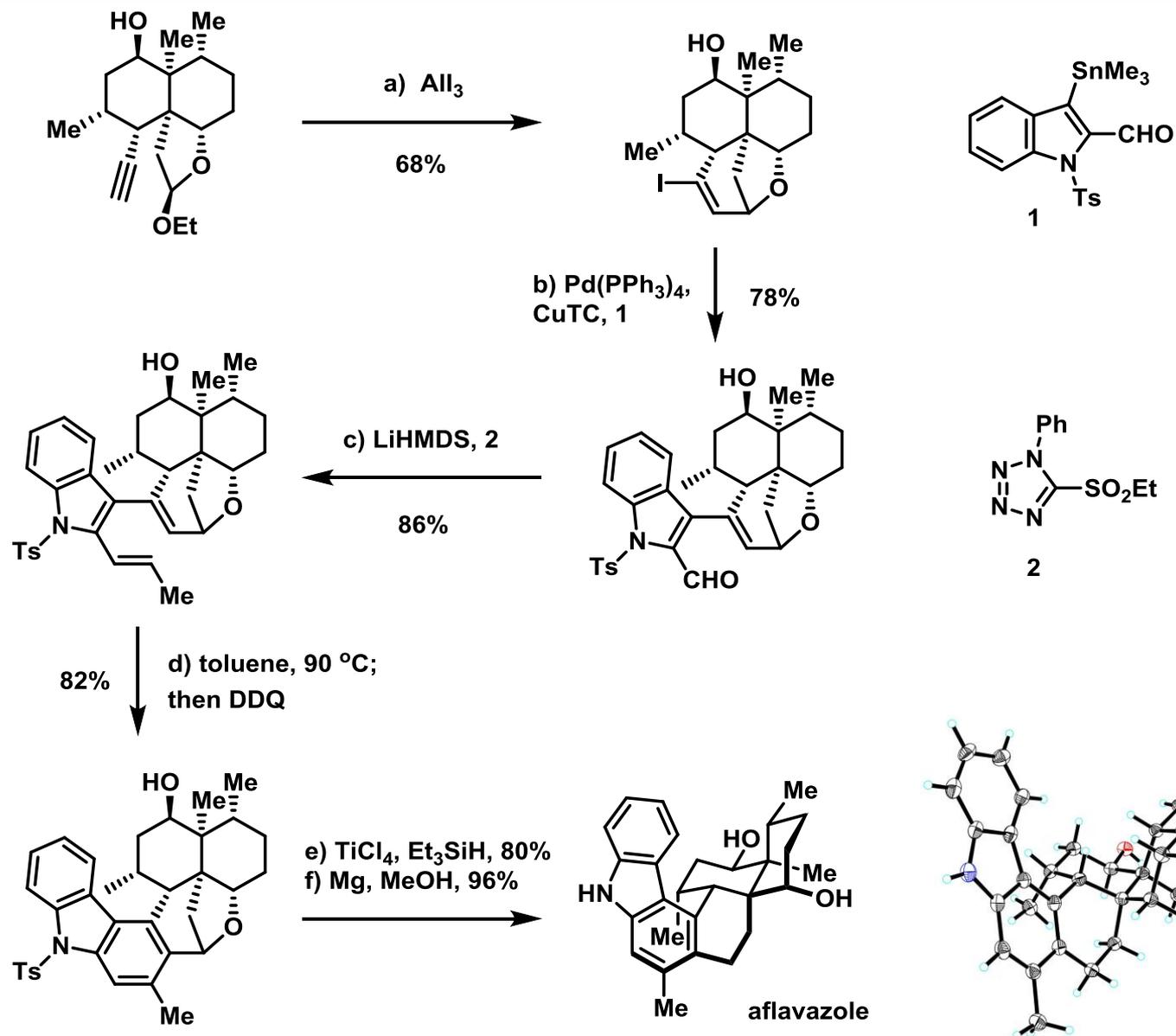
rubriflordilactone B

2: R¹ = (3-AmO)Me₂Si, R² = H

3: R¹ = H, R² = (3-AmO)Me₂Si

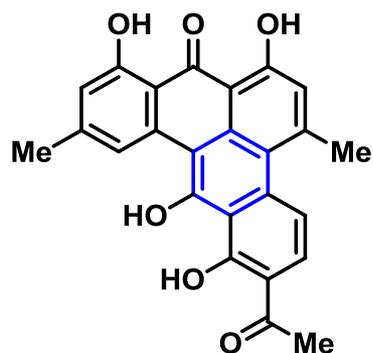


电环化/芳构化

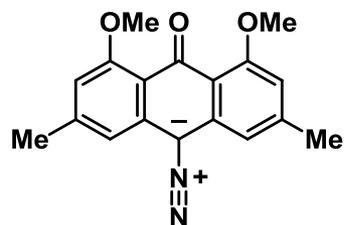


Li, et al. *J. Am. Chem. Soc.* **2016**, *138*, 15555.

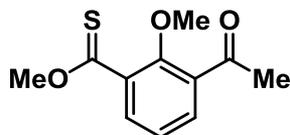
电环化/芳构化



clostrubin



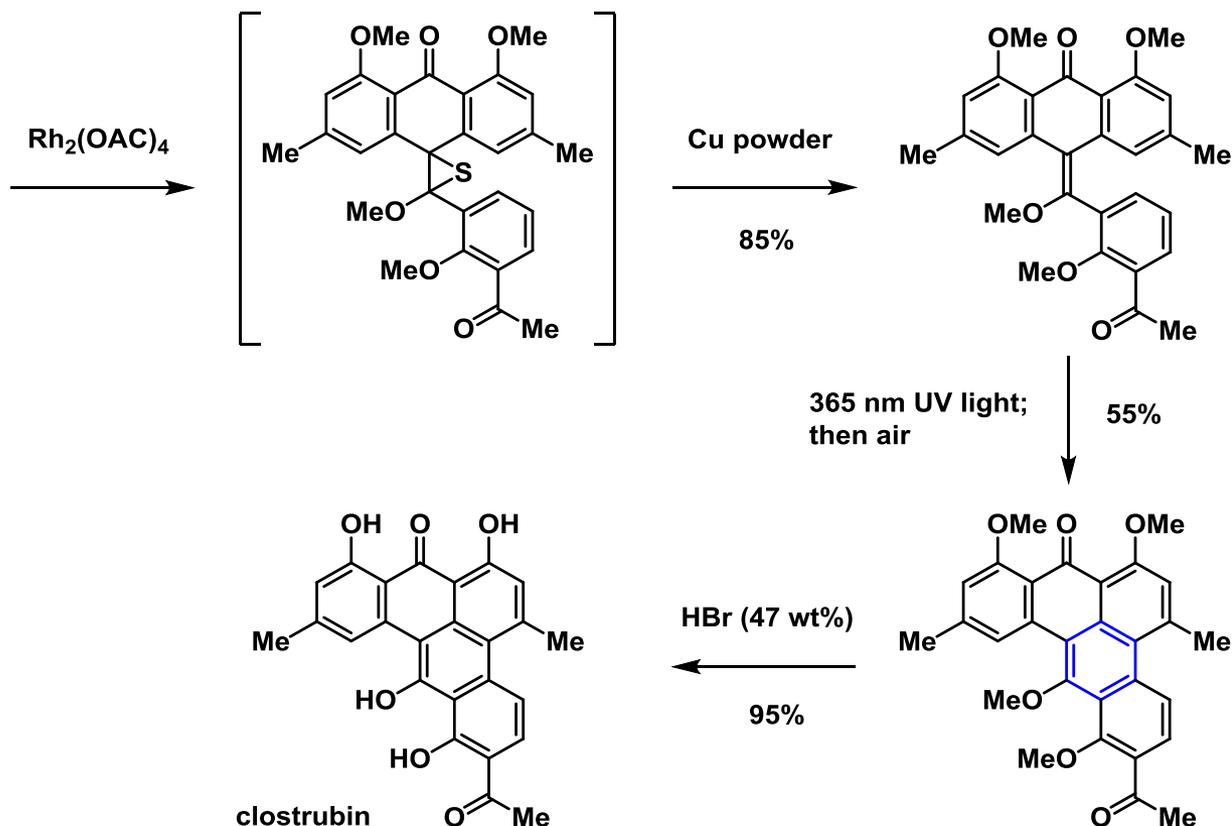
+



- Isolated from the bacterium *Clostridium beijerinckii*.
- Antibiotic activity.

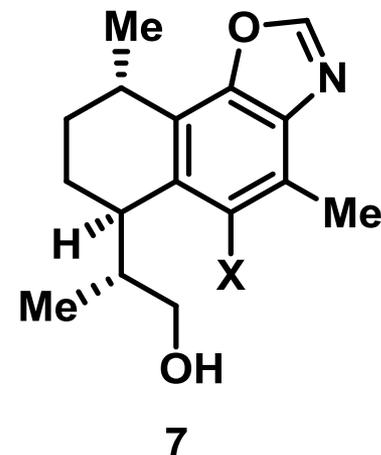
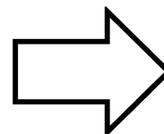
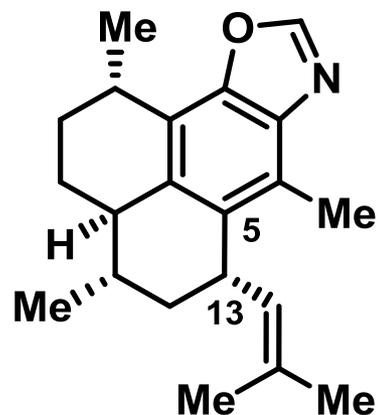
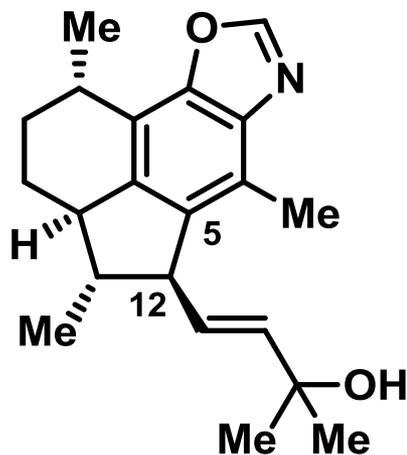
MRSA: MIC = 0.12 μM ; VRE: MIC = 0.97 μM

Hertweck, C. et al. *Angew. Chem. Int. Ed.* **2014**, 53, 7856.



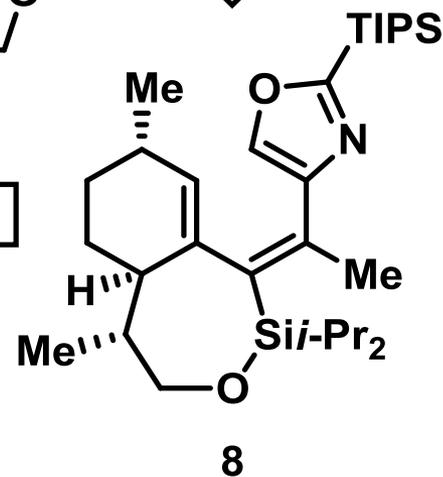
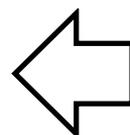
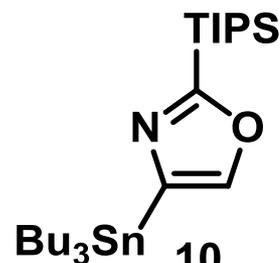
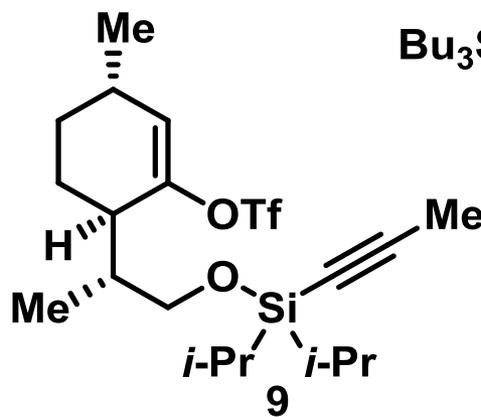
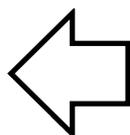
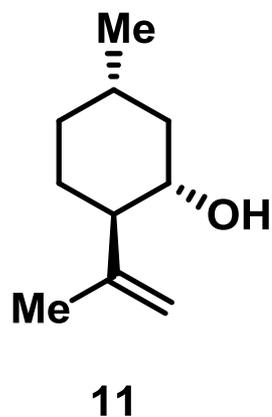
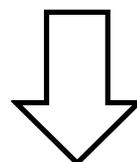
Li, et al. *Nature Commun.* **2015**, 6, 6445.

电环化/芳构化

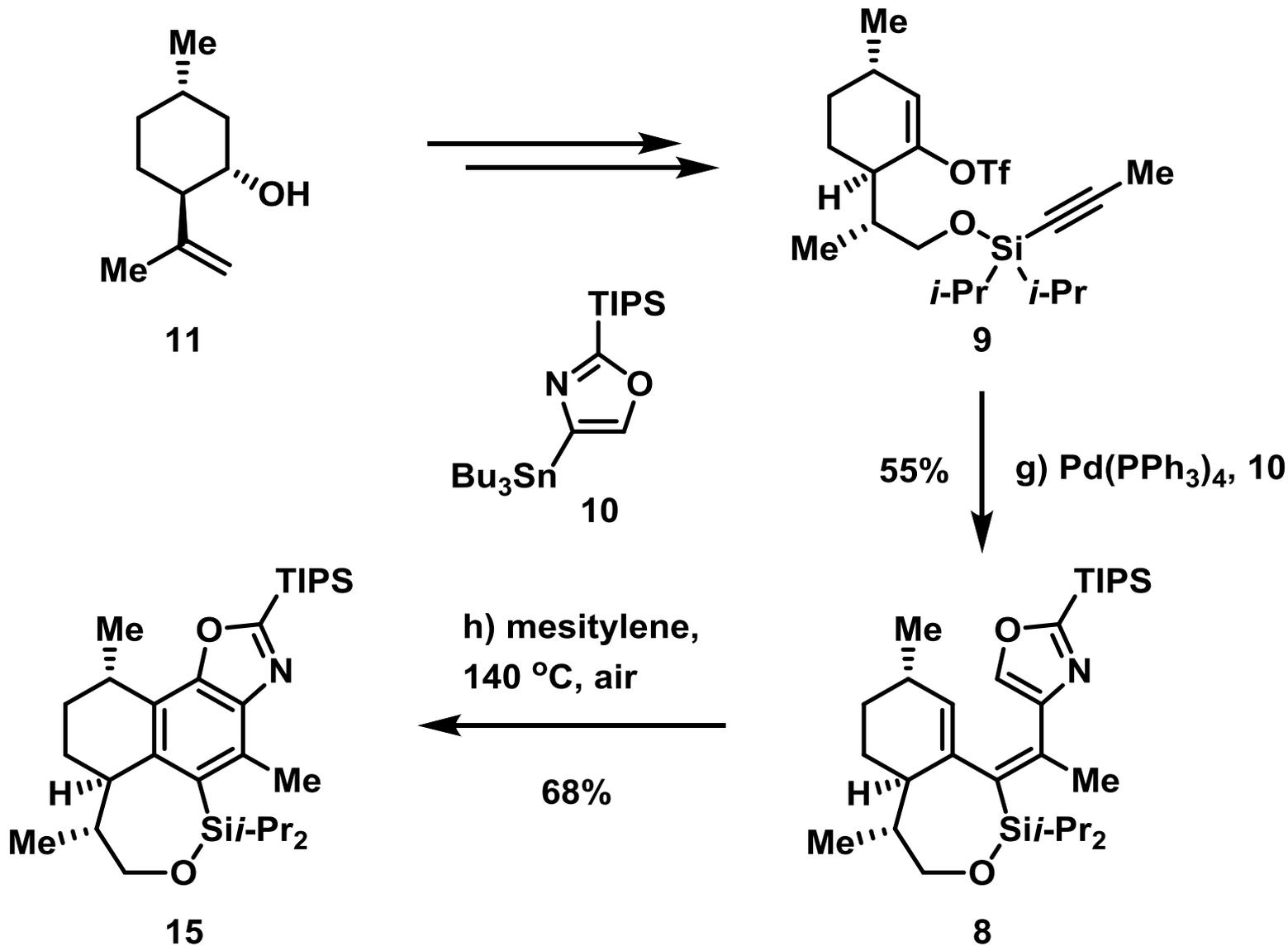


1: ileabethoxazole

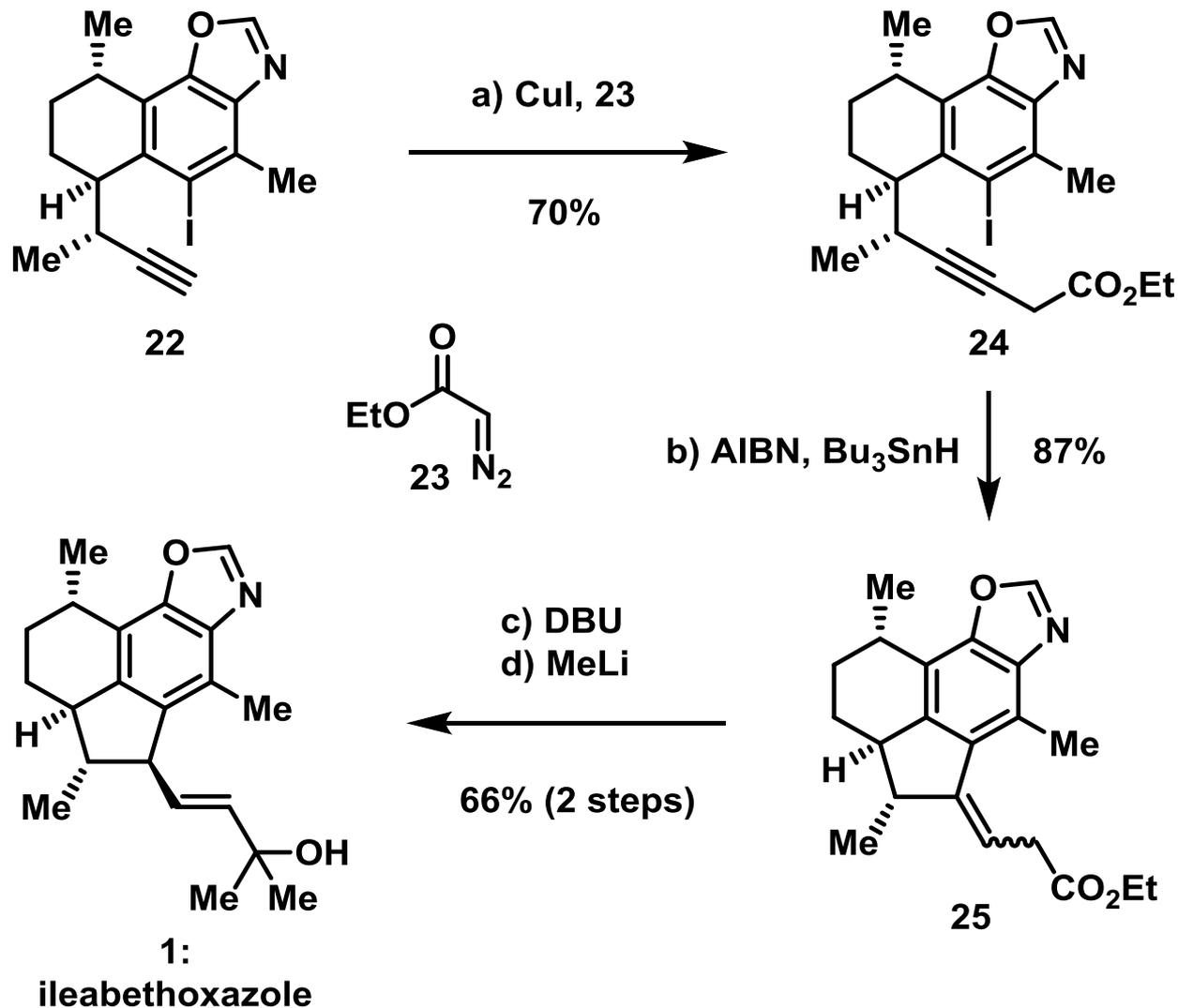
2: pseudopteroxazole



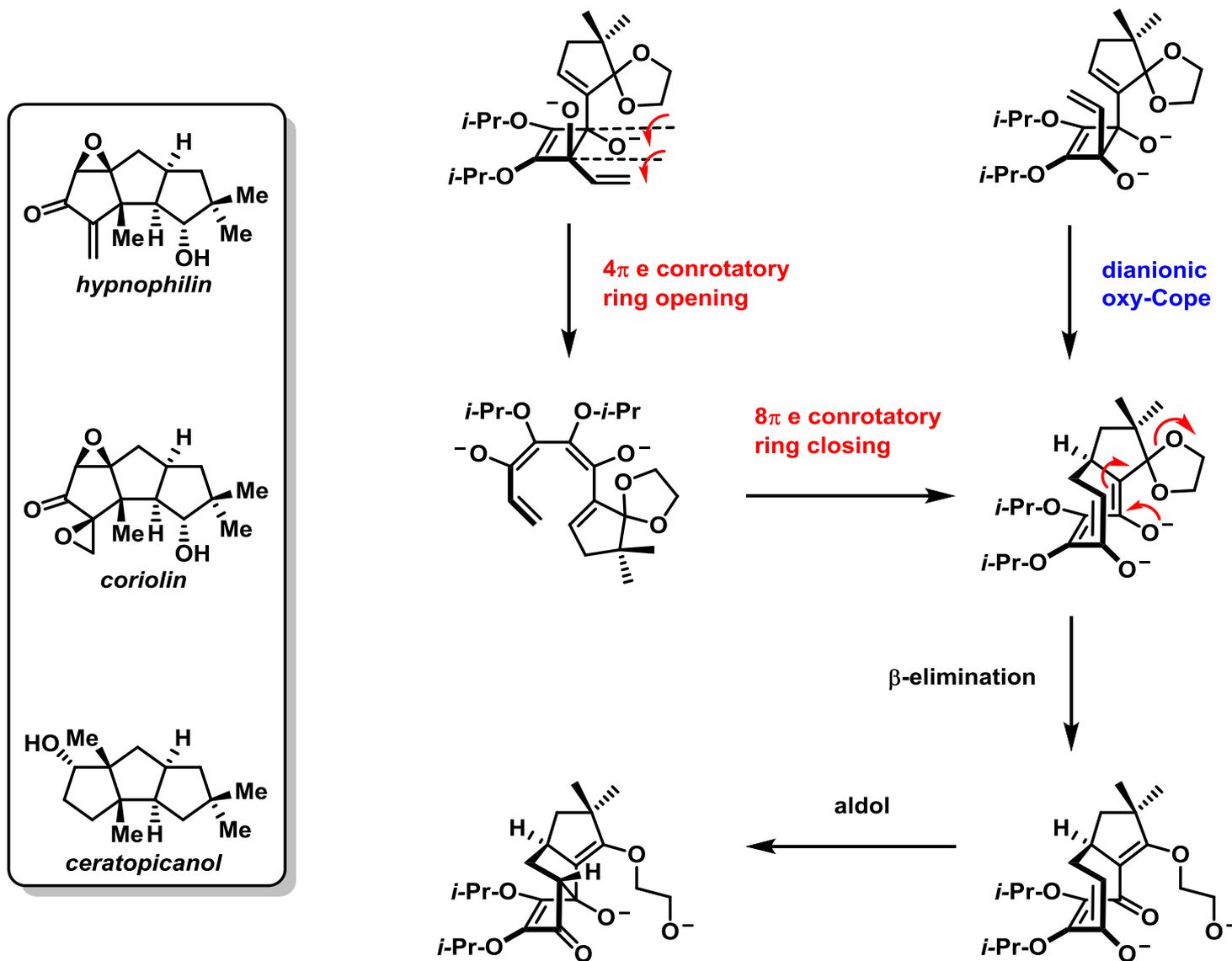
电环化/芳构化



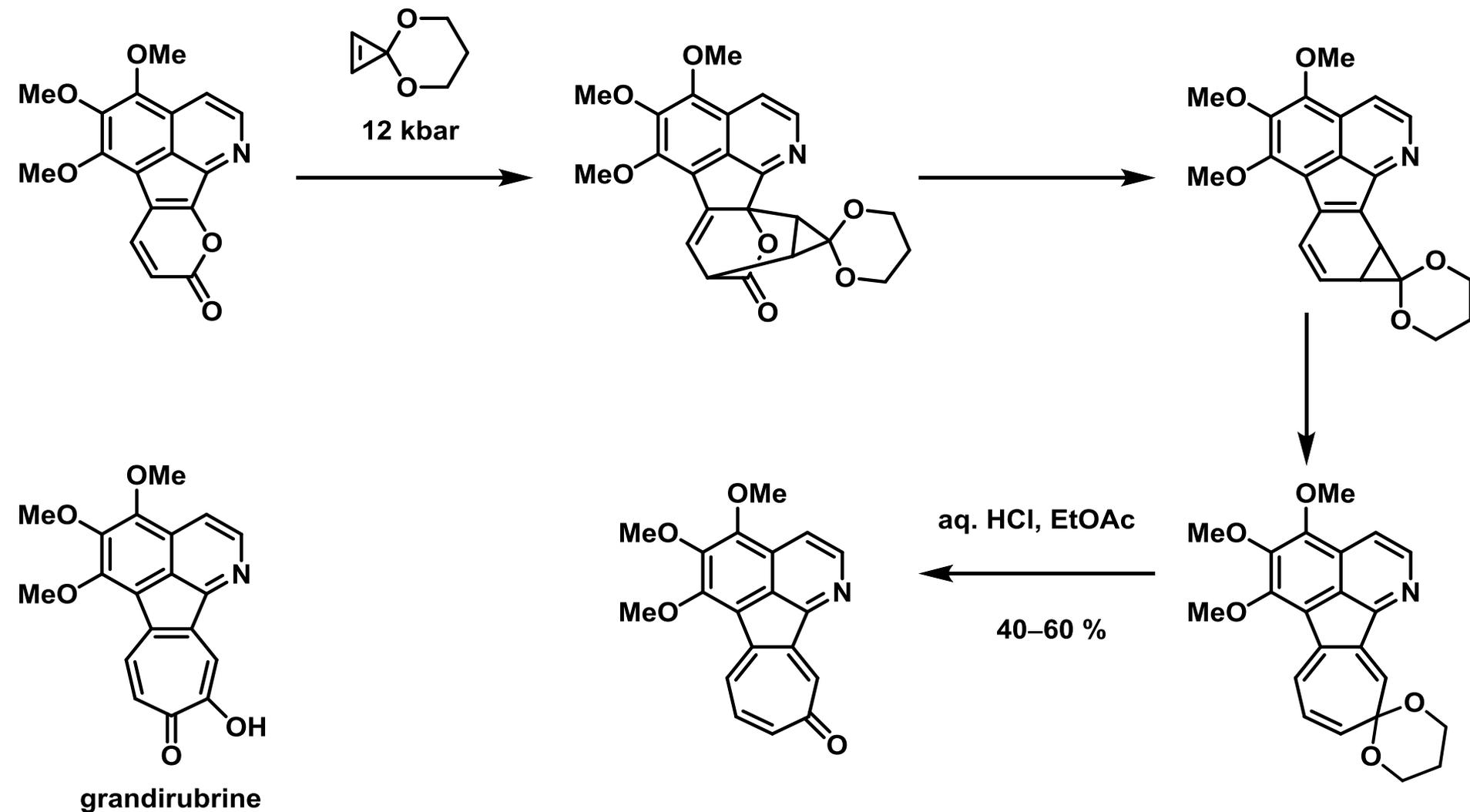
电环化/芳构化



电开环反应

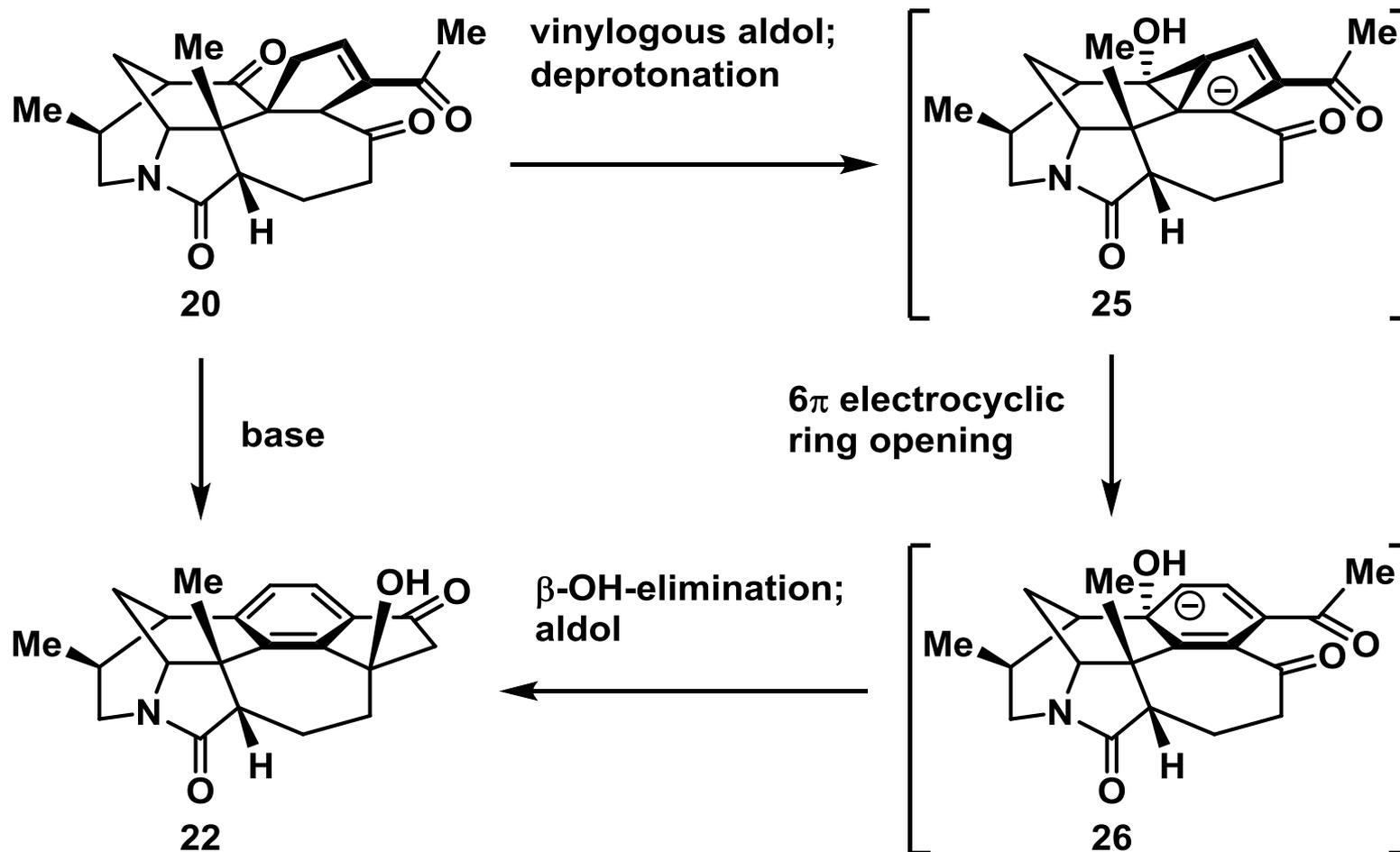


电开环反应

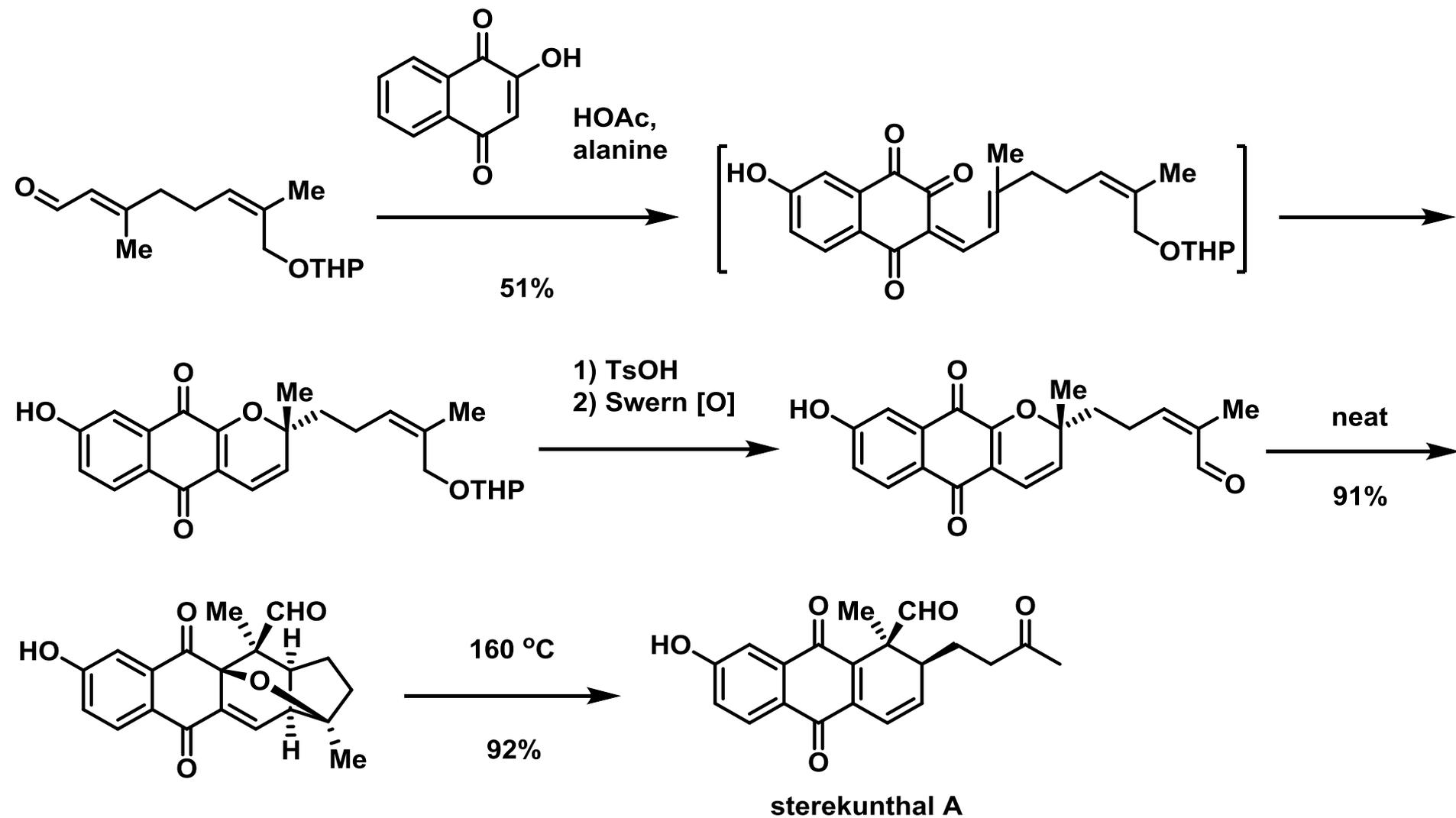


Boger, et al. *J. Am. Chem. Soc.* **1995**, *117*, 12452.

电开环反应

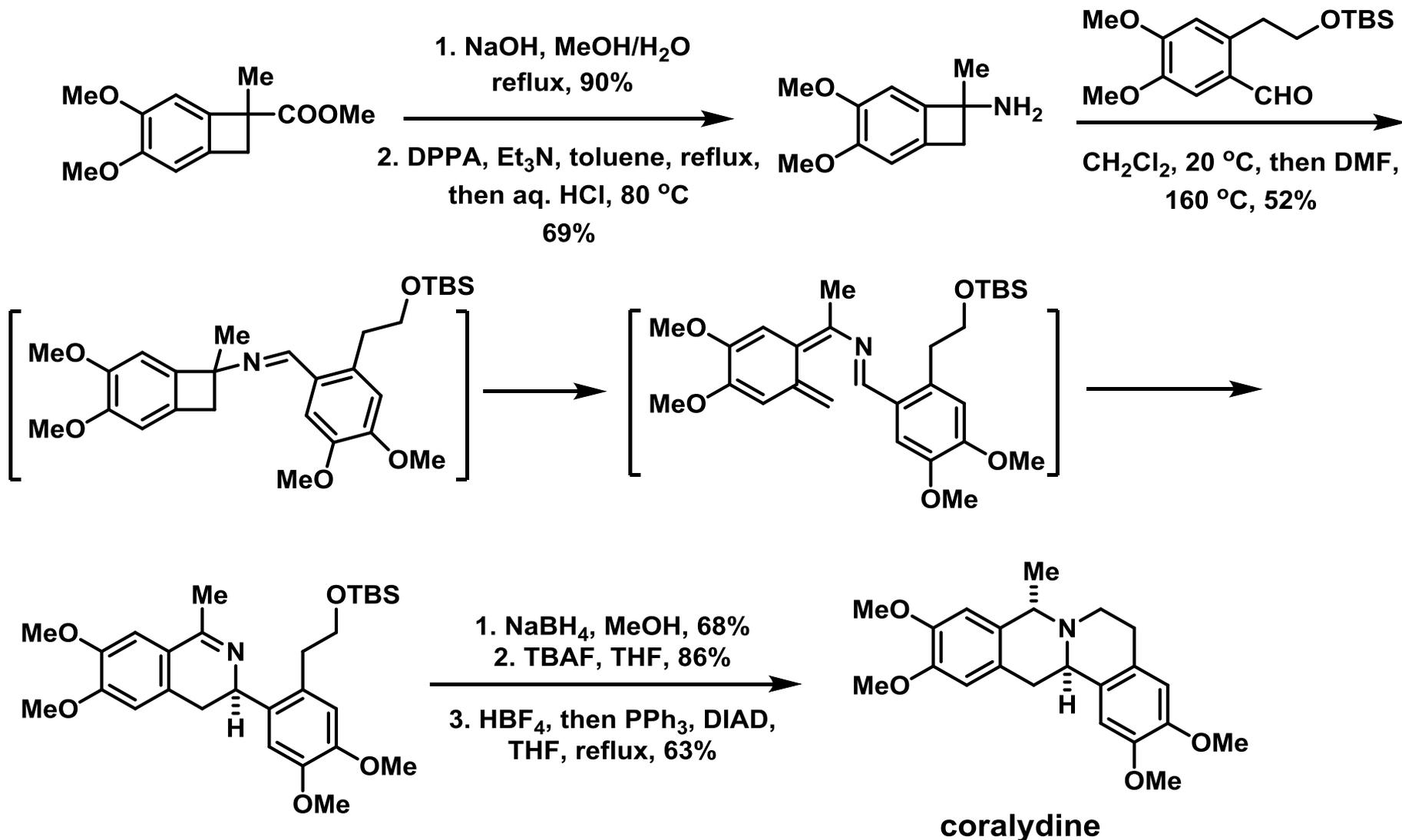


氧杂电环化



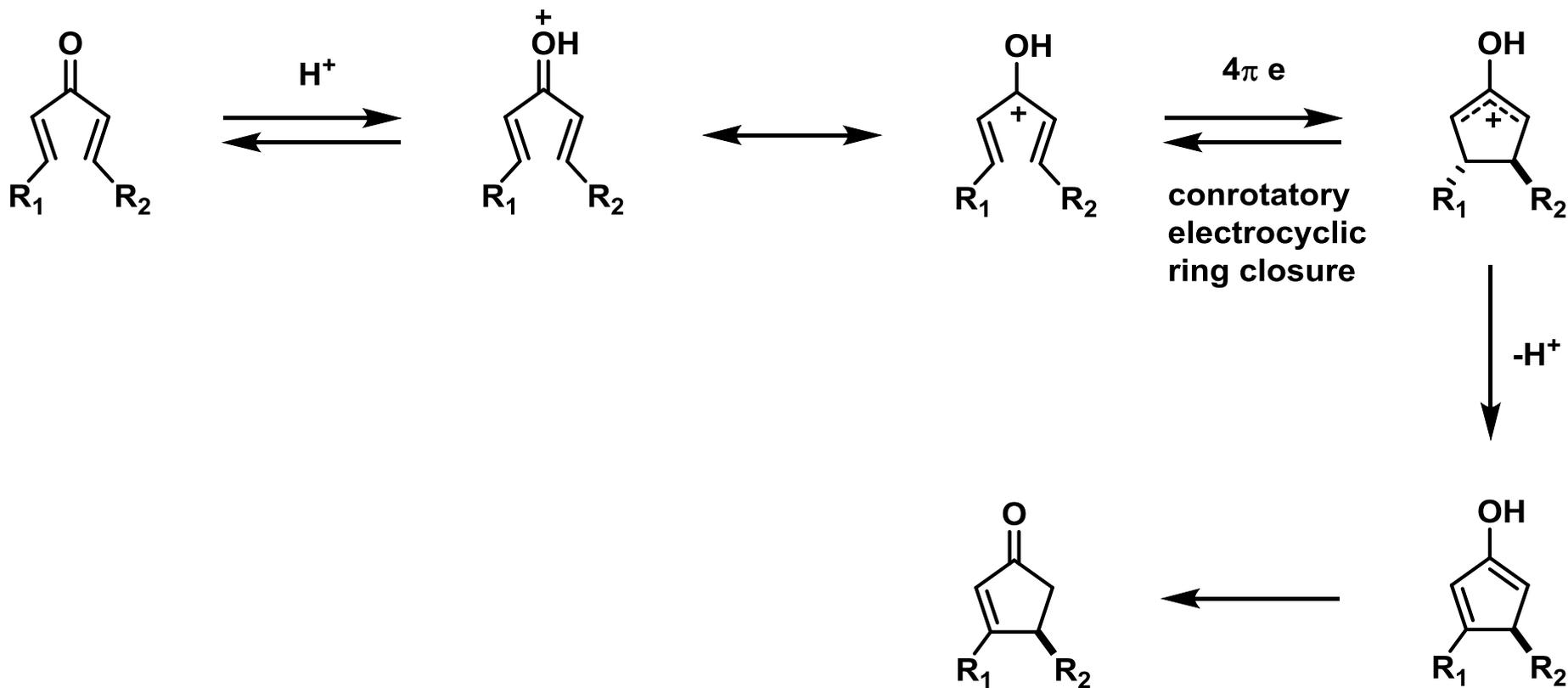
Malerich and Trauner, *J. Am. Chem. Soc.* **2003**, 125, 9554.

氮杂电环化



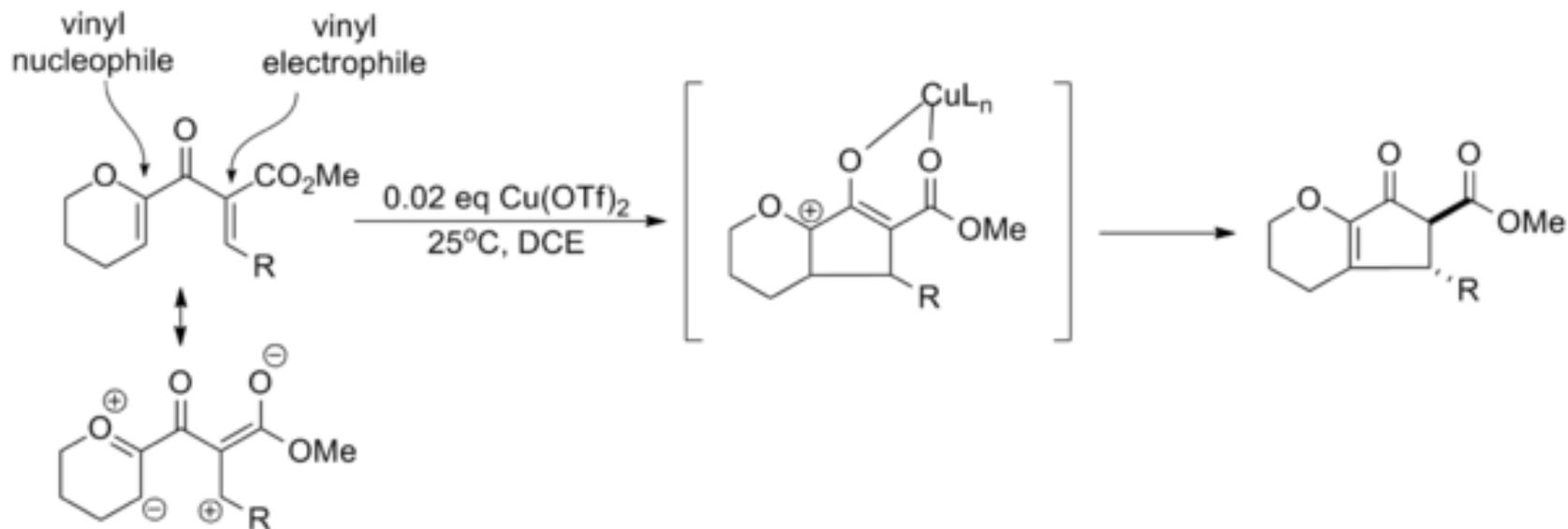
O. Baudoin. et al. *Angew. Chem. Int. Ed.* **2009**, *48*, 179.

Nazarov反应

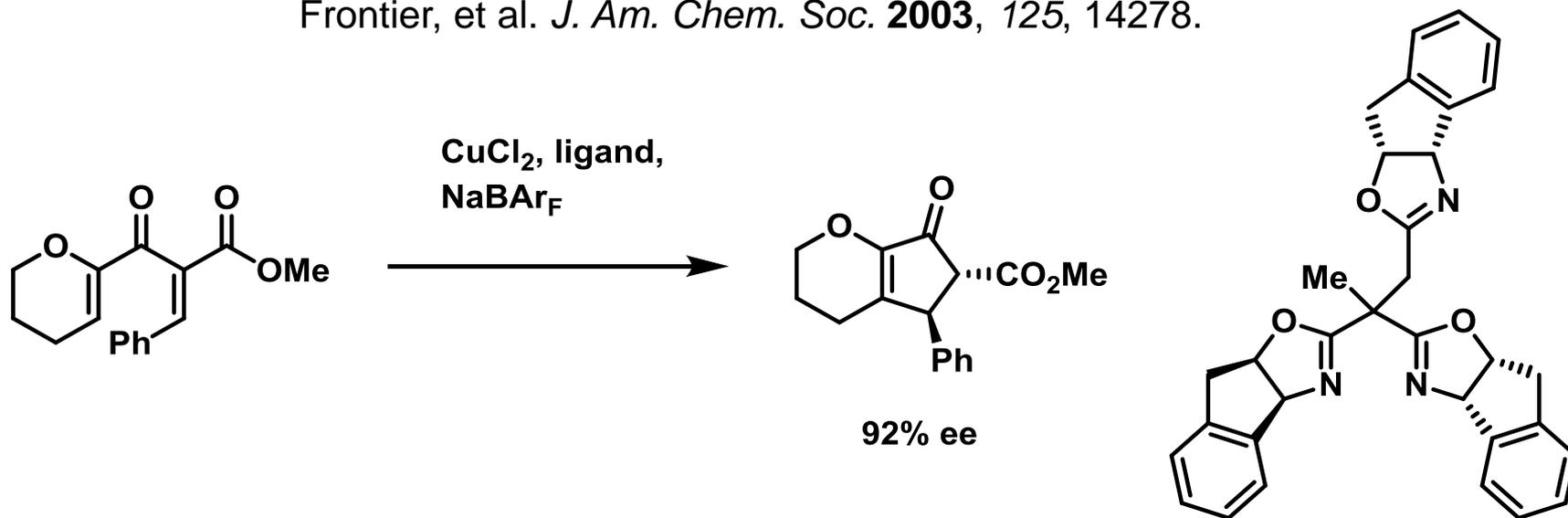


Nazarov, et al. *Bull. Acad. Sci. USSR* **1946**, 633.

Nazarov反应



Frontier, et al. *J. Am. Chem. Soc.* **2003**, *125*, 14278.



Tang, et al. *Angew. Chem. Int. Ed.* **2010**, *49*, 4463.



谢 谢!