六、周环反应
（四） Sigmatropic重排反应

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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
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烯烃、羰基化合物和其他化合物的还原
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烯基化反应
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非直观Diels-Alder反应
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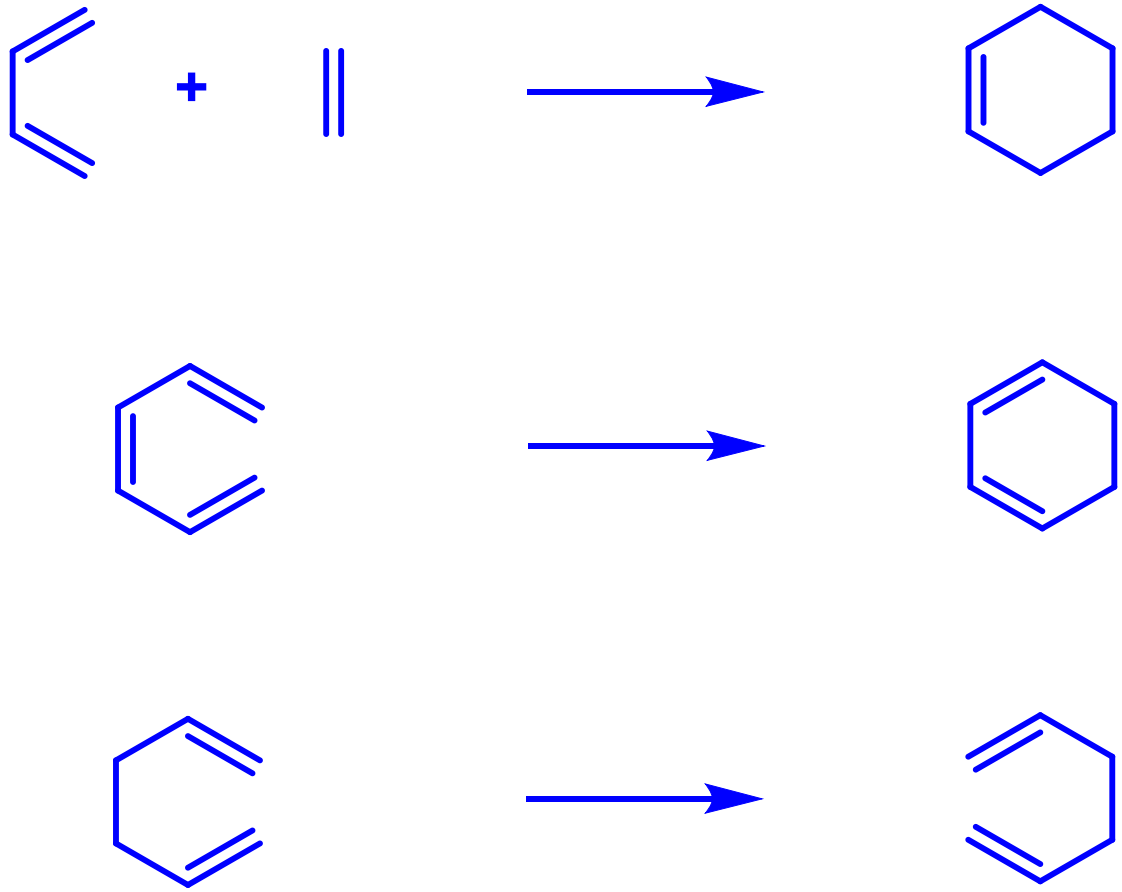
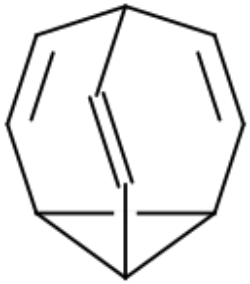
电环化反应
sigmatropic重排
七、阳离子参与的C–C键形成反应

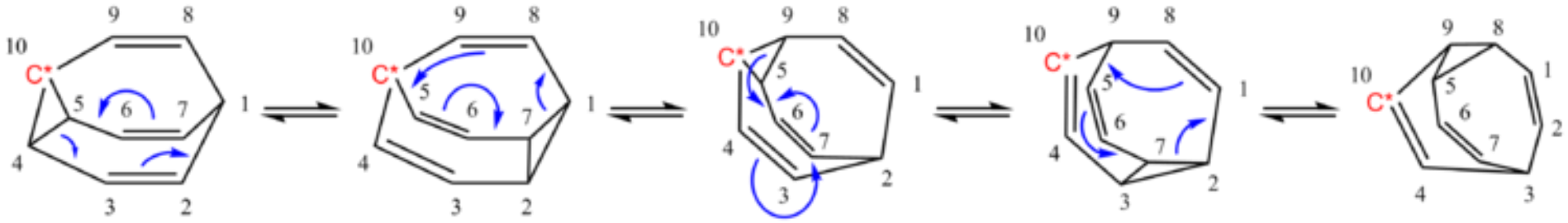
三类周环反应的对比



- 反应的难易
- 反应的产出
- 底物易得与否

Bullvalene的氢谱信号

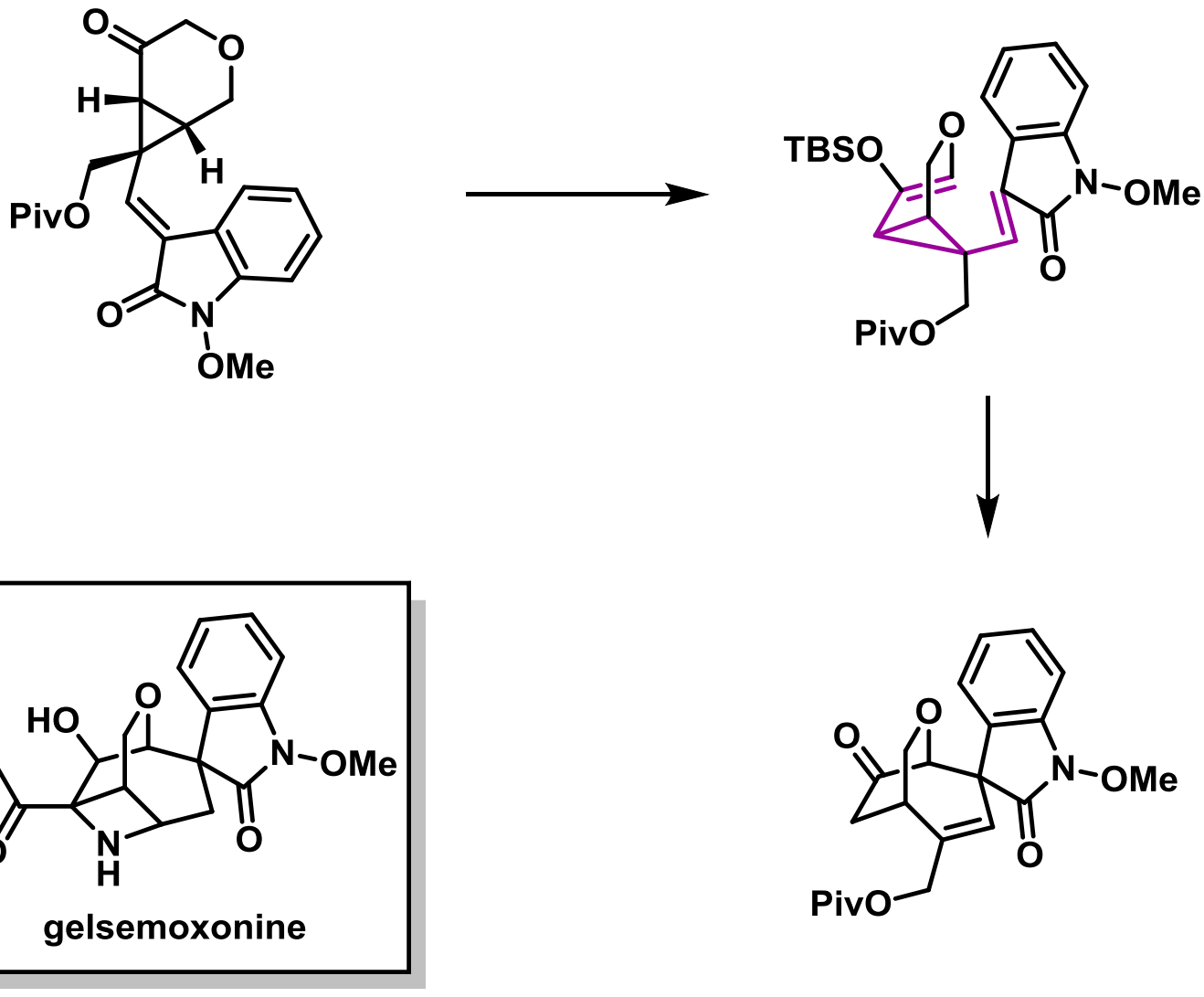




A sharp singlet at 4.2 ppm.

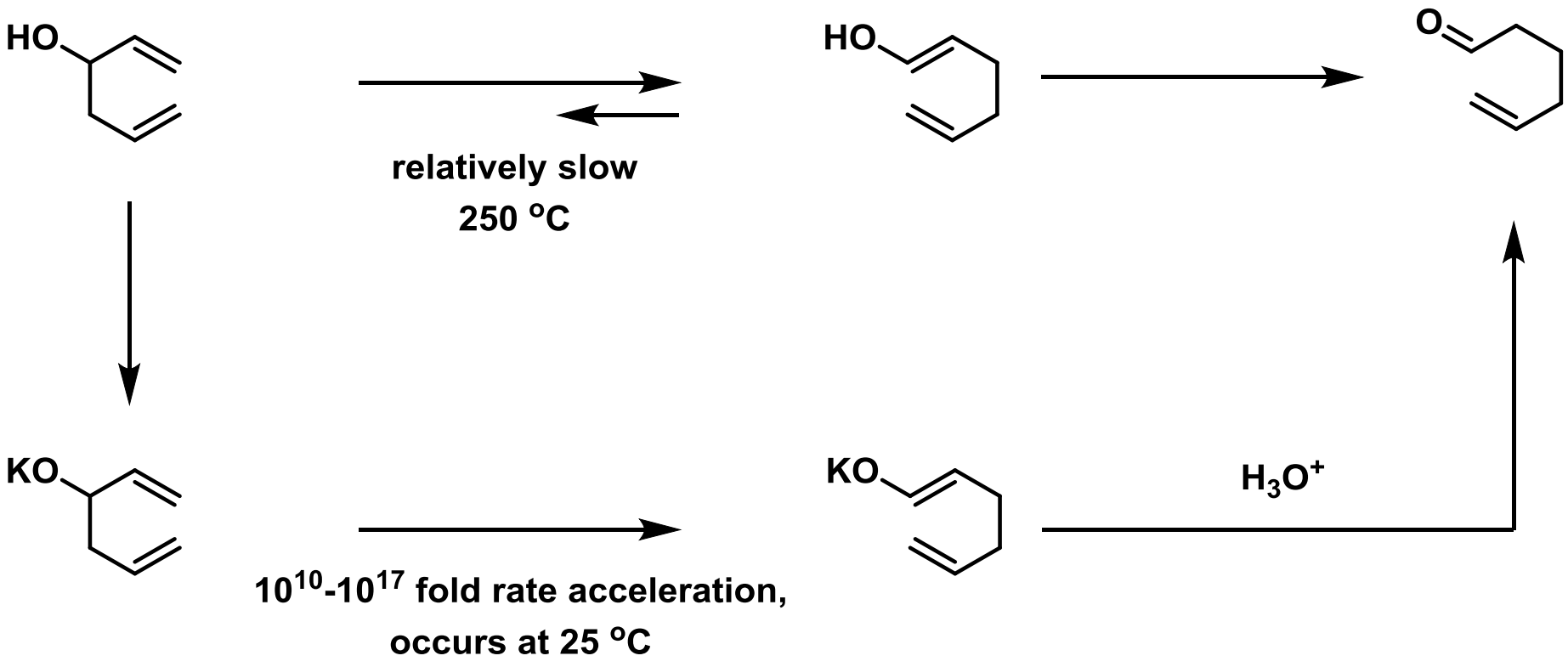
Doering and Roth, *Tetrahedron* **1963**, *19*, 715.

环张力驱动的Cope重排

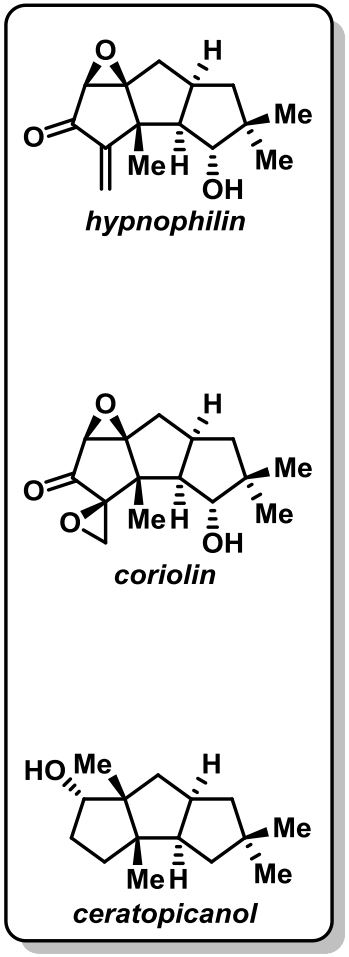


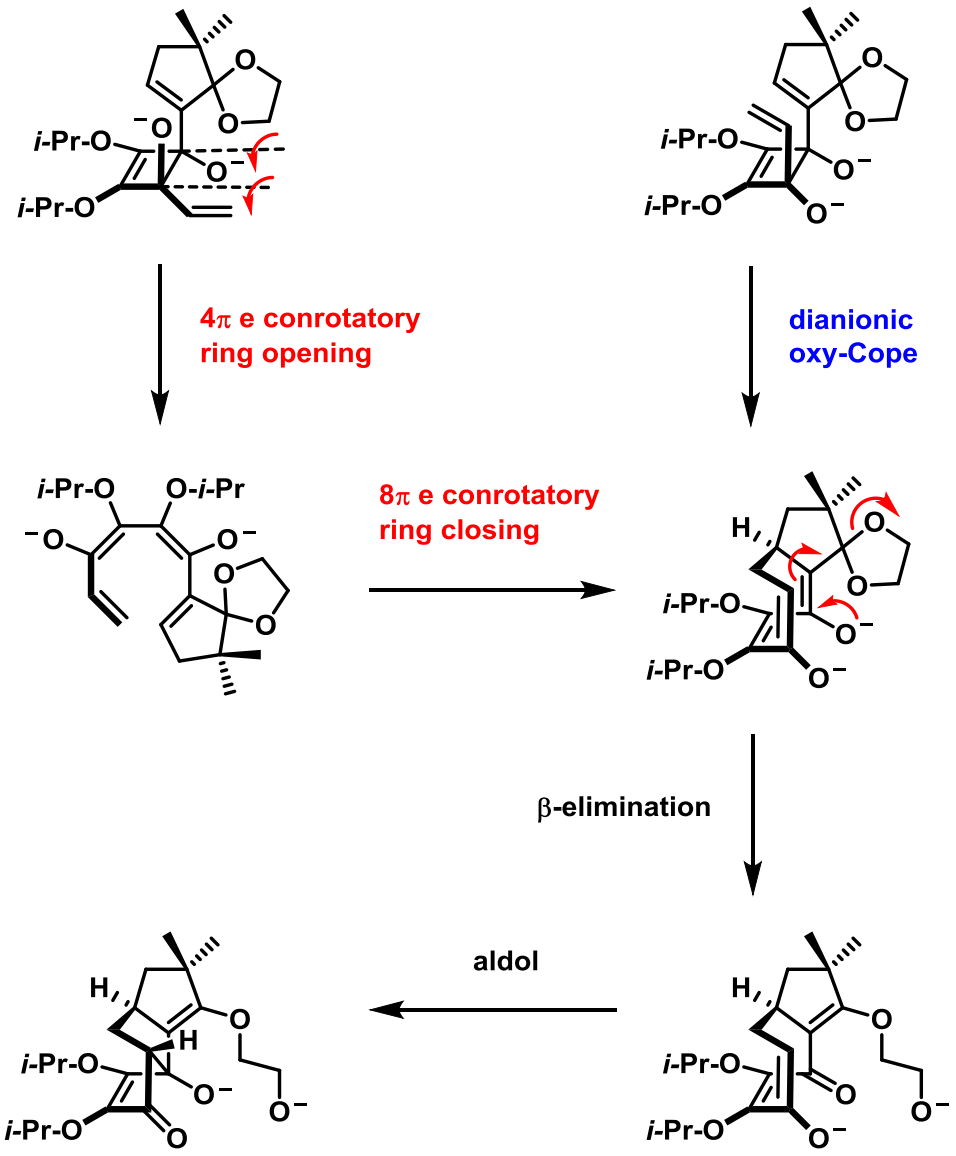
Fukuyama, et al. *J. Am. Chem. Soc*. **2011**, *133*, 17634.

Oxy-Cope重排


HO
relatively slow
250 °C
HO
O
KO
10^10-10^17 fold rate acceleration,
occurs at 25 °C
KO
H3O+

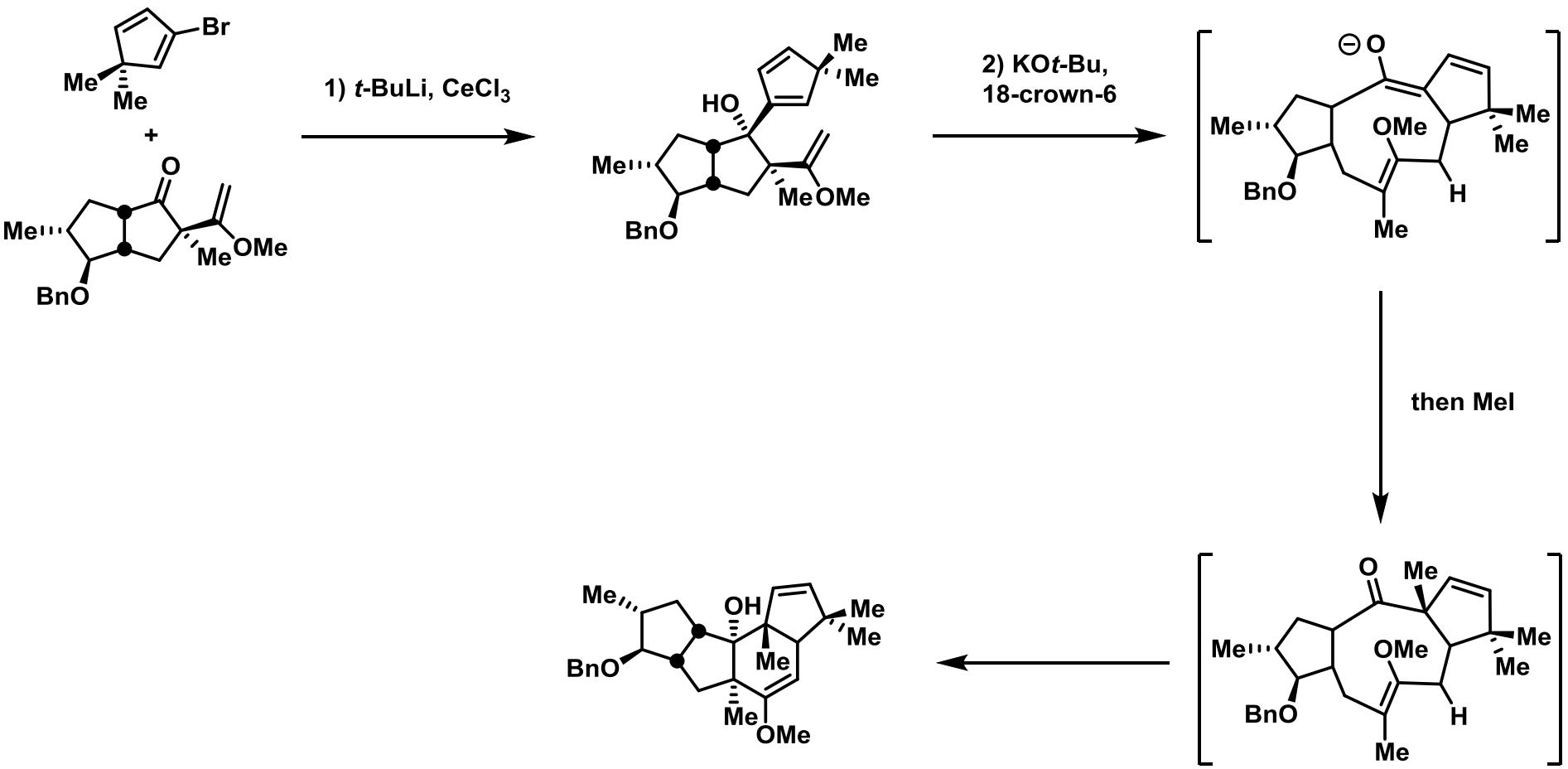
Oxy-Cope重排





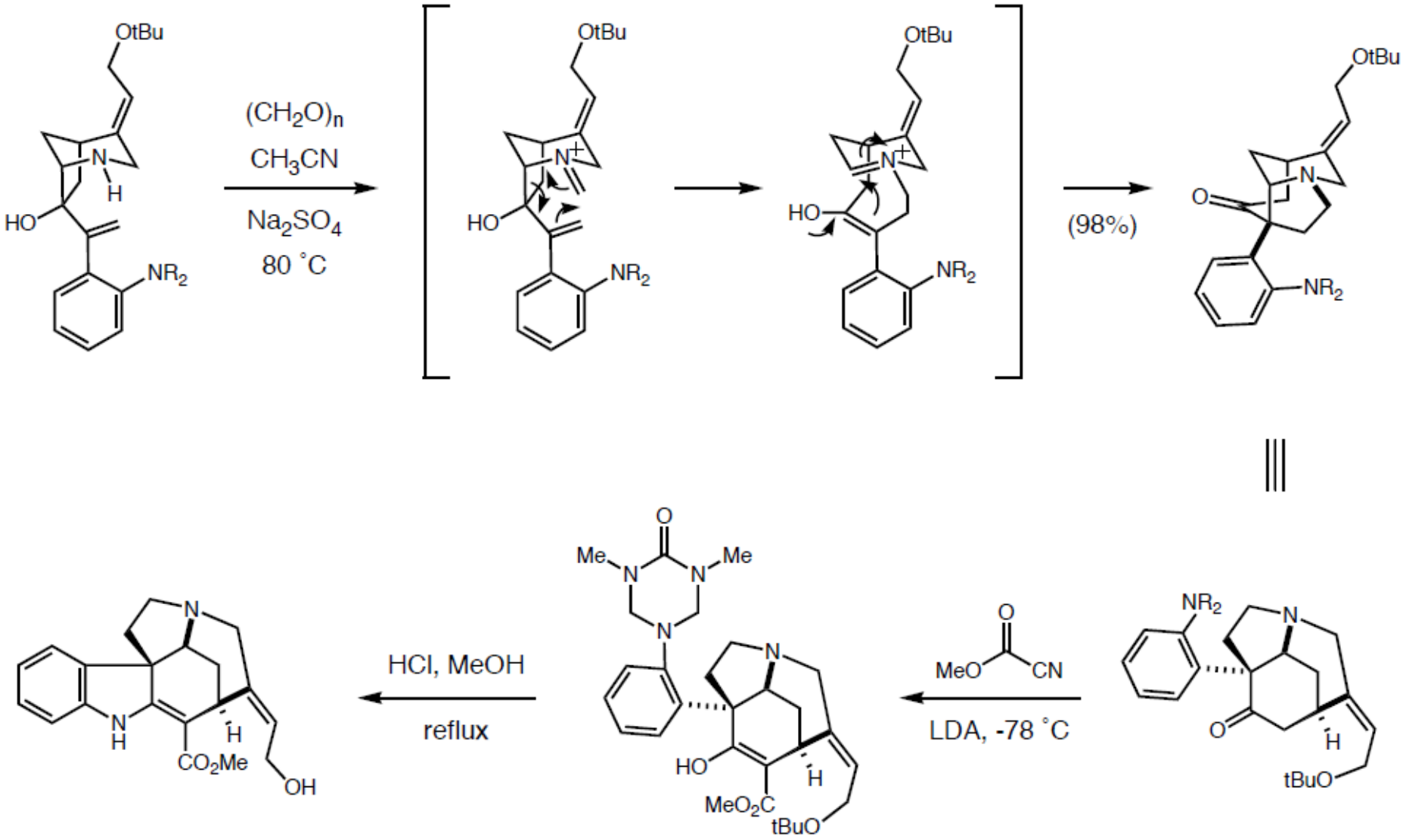
Paquette, et al. *J. Am. Chem. Soc*. **2002**, *124*, 9199.

Oxy-Cope重排



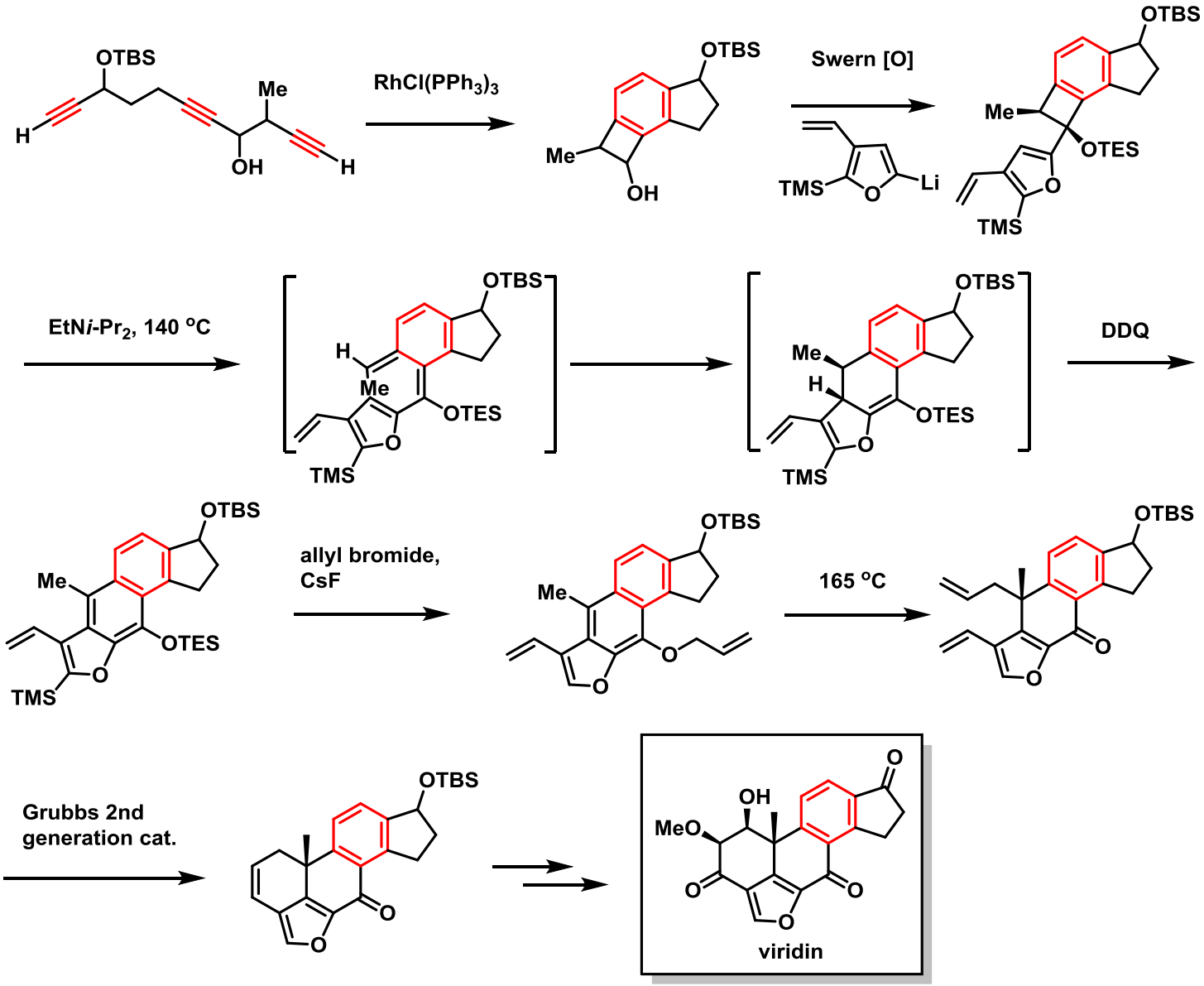
Paquette, et al. *J. Am. Chem. Soc.* **2002**, *124*, 6542.

Aza-Cope重排



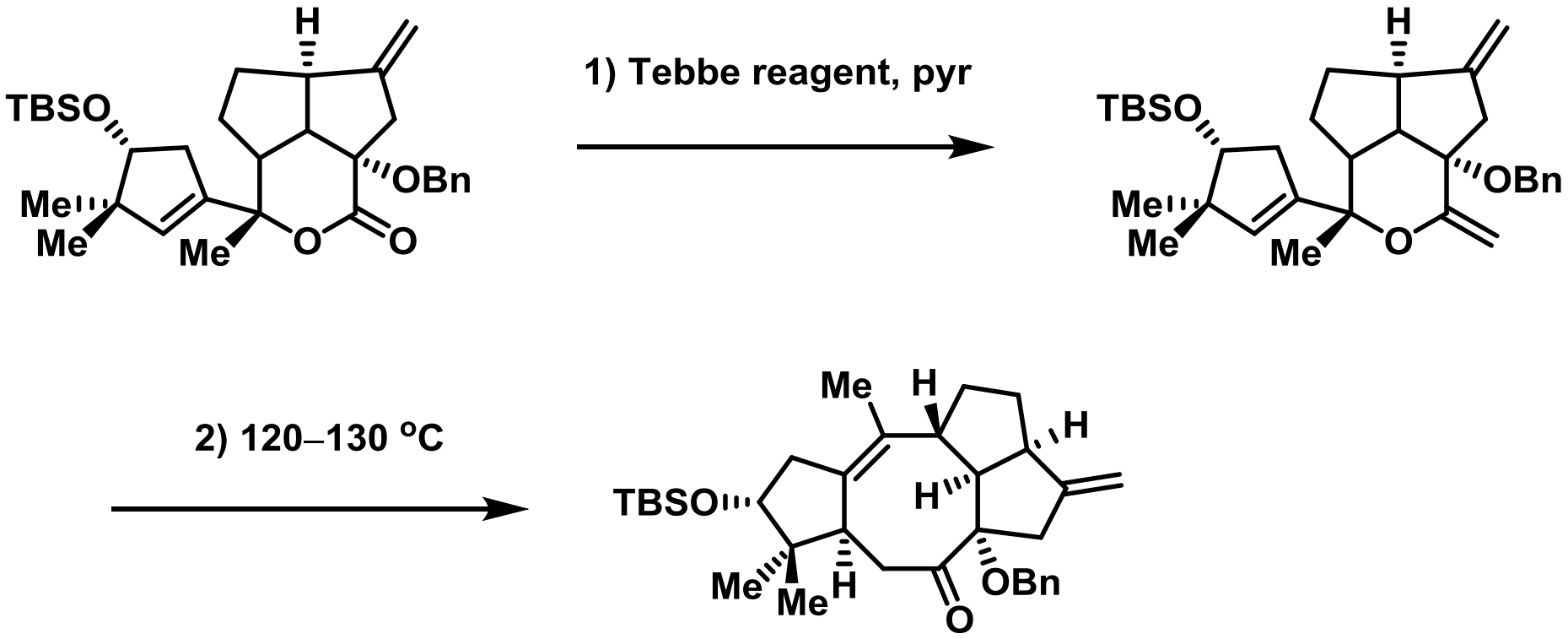
Overman, et al. *J. Am. Chem. Soc.* **1993**, *115*, 9293.

Claisen重排



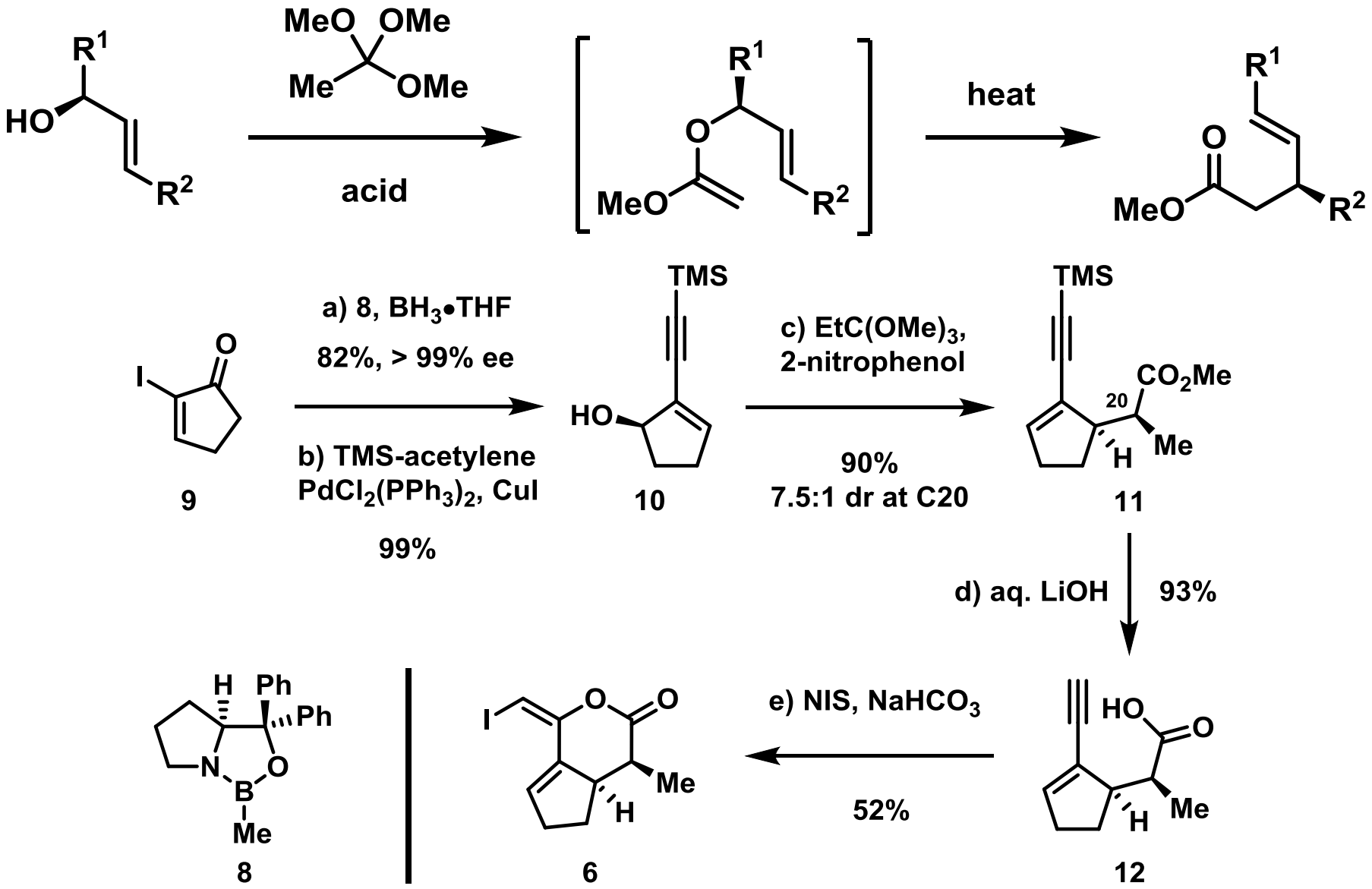
Sorensen, et al. *Angew. Chem. Int. Ed.* **2004**, *43*, 1998.

Claisen重排



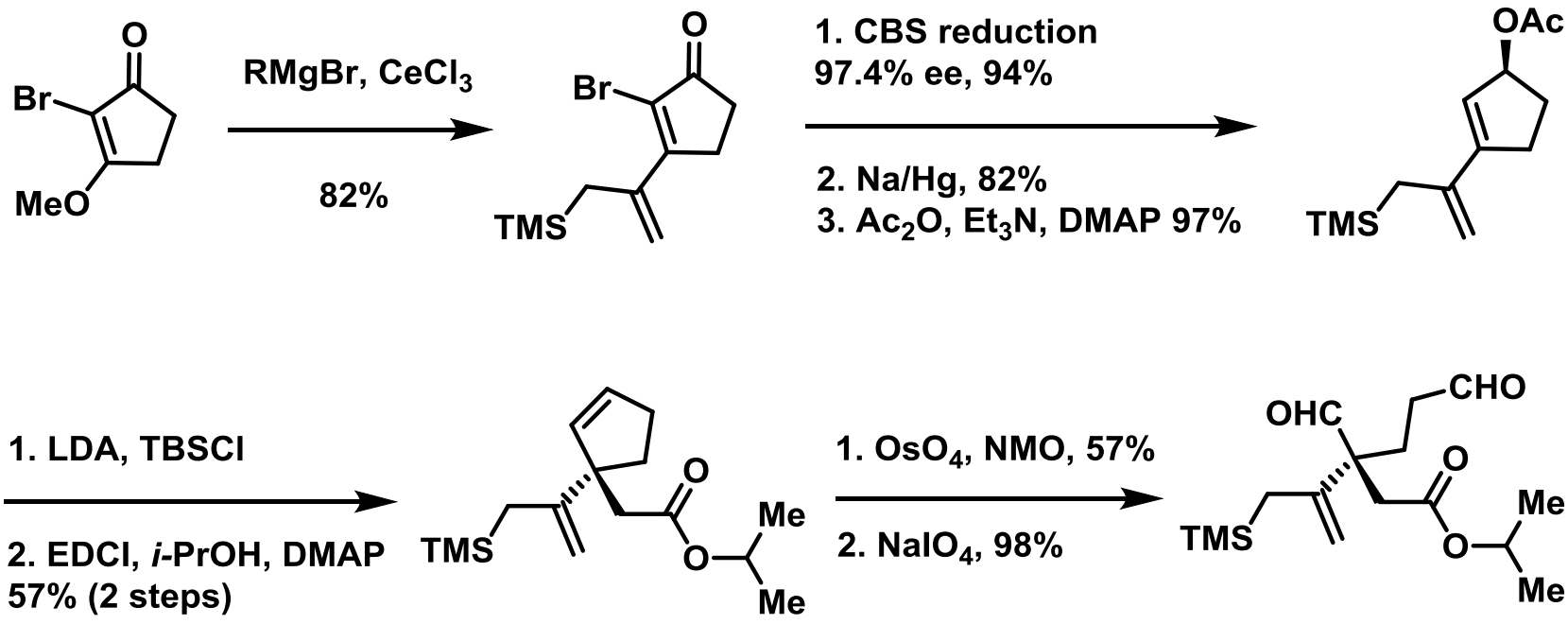
Paquette, et al. *J. Am. Chem. Soc*. **1996**, *118*, 727.

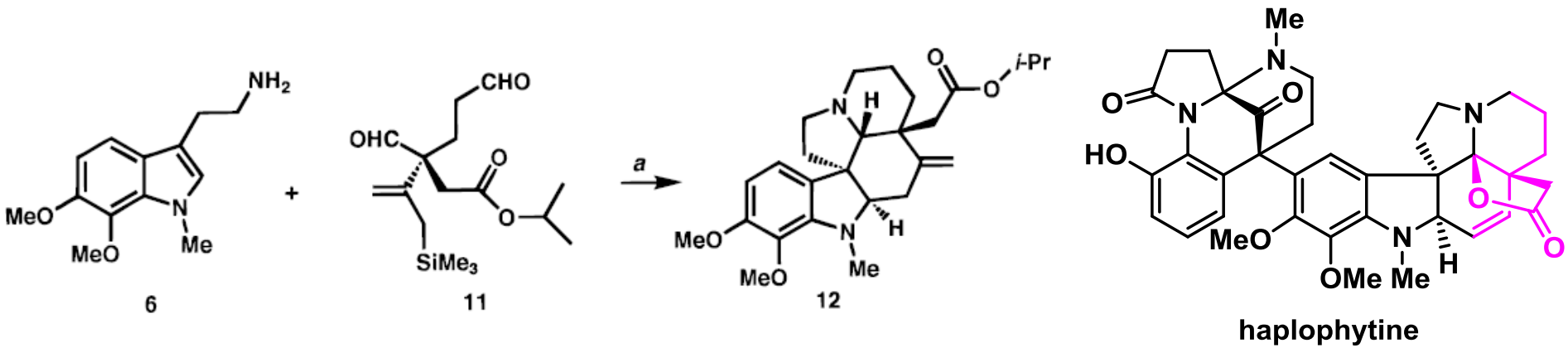
Johnson–Claisen重排



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

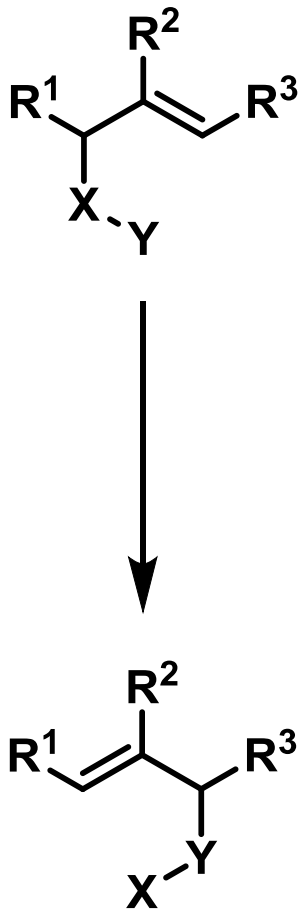
Ireland–Claisen重排





He, Bo, Altom, Corey, *J. Am. Chem. Soc*. **1999**, *121*, 6771.

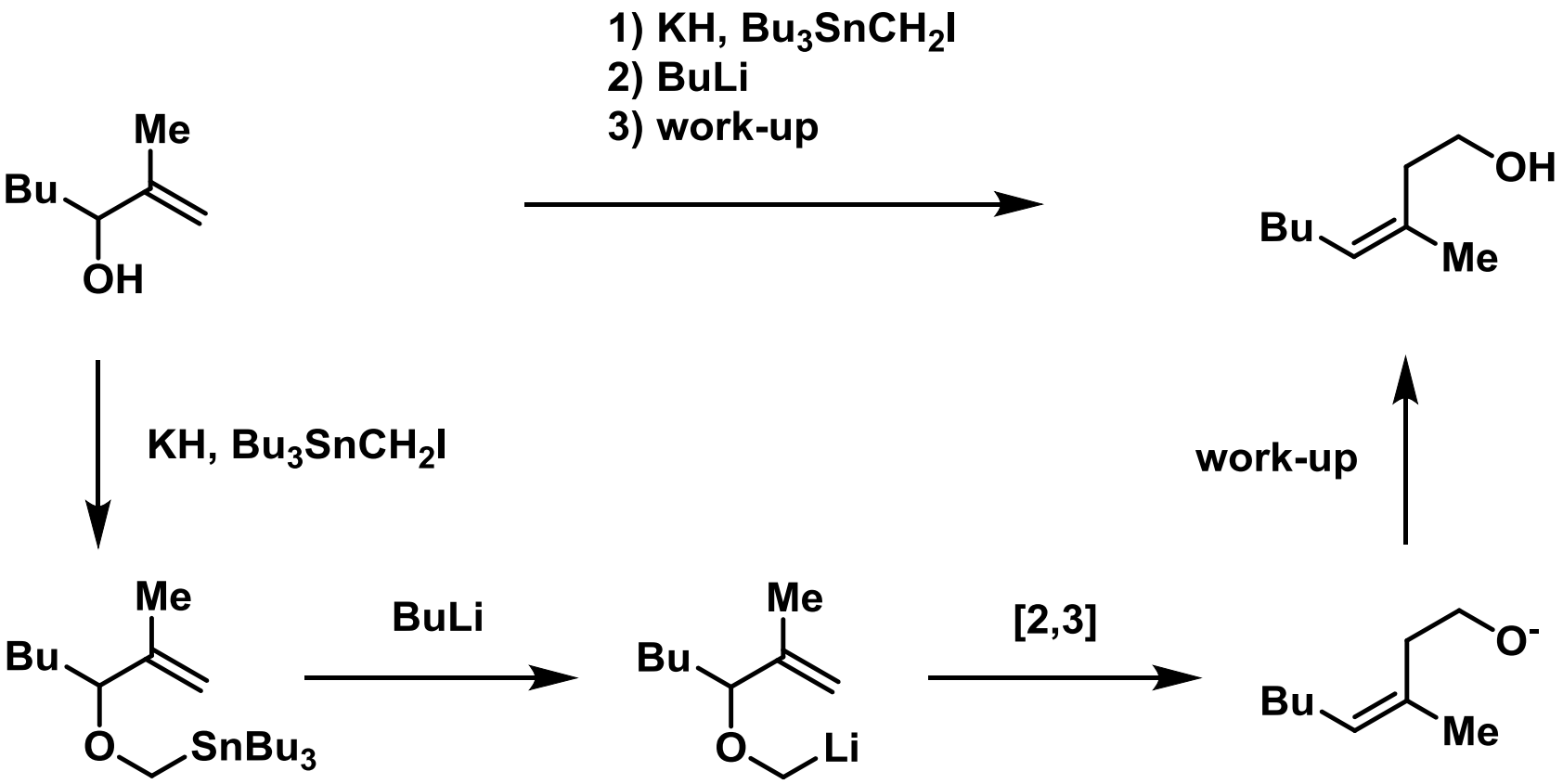
[2,3]-Sigmatropic重排



Representative X-Y pairs

O-C
N-C
N-O
S-C
S-O
O-P
C-C
S-N
S-S

[2,3]-Sigmatropic重排



Still and Mitra, *J. Am. Chem. Soc.* **1978**, *100*, 1927.

谢　谢！

2018年12月24日