



# 六、周环反应

## (一) 非直观Diels-Alder反应

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2018年12月3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

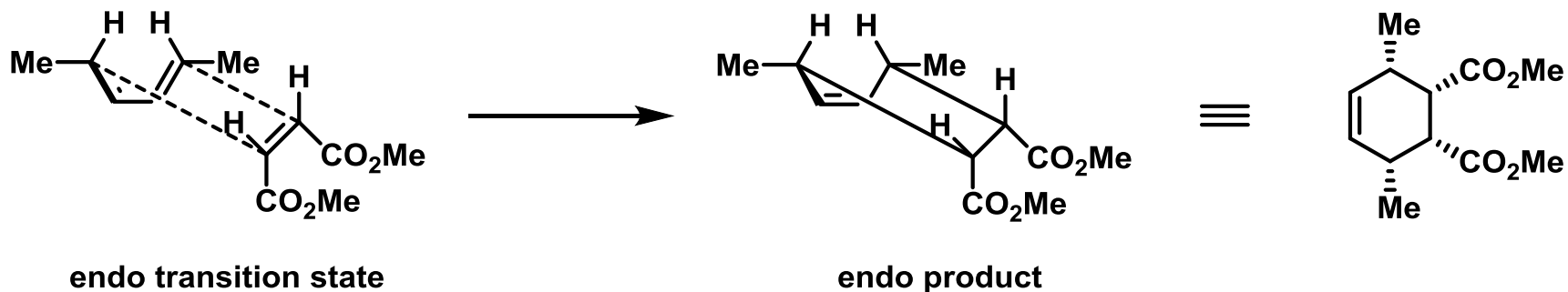
### 电环化反应

### sigmatropic重排

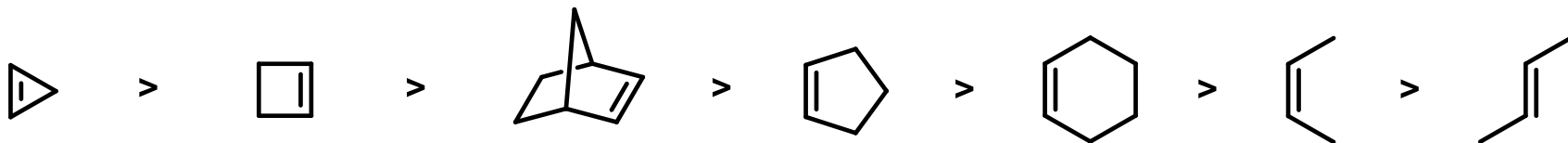
## 七、阳离子参与的C-C键形成反应

# Diels-Alder反应的一些常识

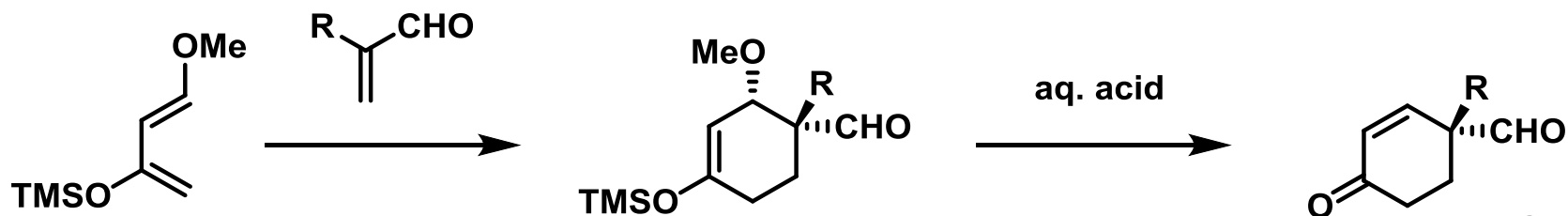
## Alder endo rule



## Dienophile reactivity



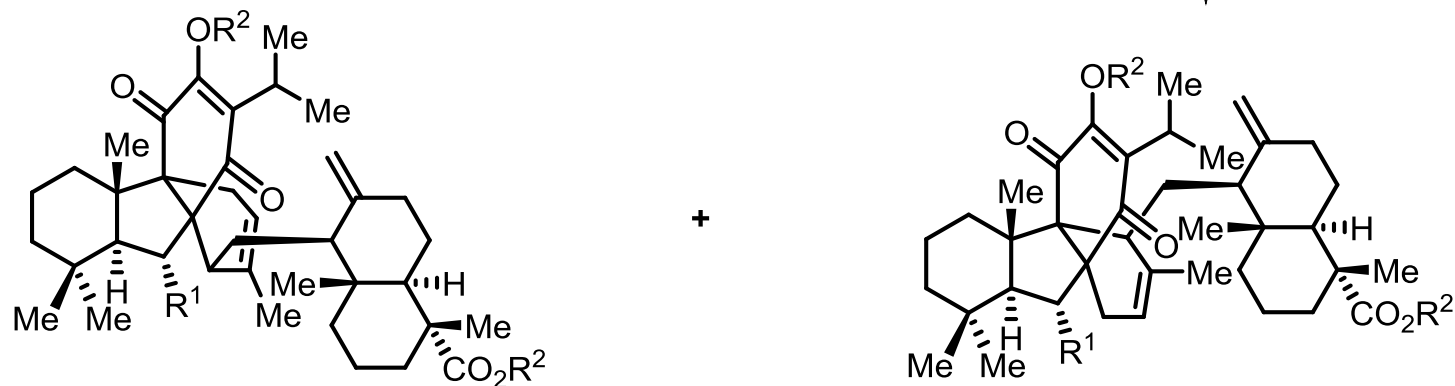
## Danishefsky Diene



# 直观Diels-Alder反应



d)  $\text{Er}(\text{fod})_3$ ,  
neat, 120 °C



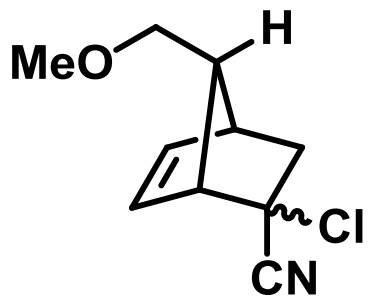
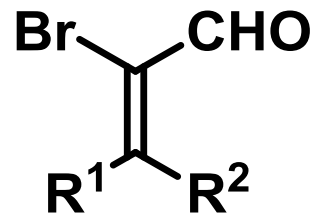
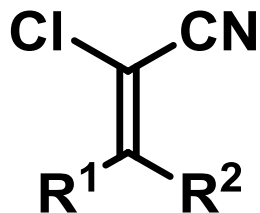
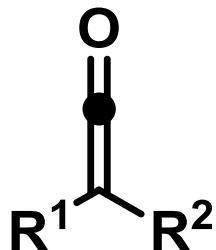
37:  $\text{R}^1 = \text{CH}_2\text{OH}$ ,  $\text{R}^2 = \text{Me}$ ; 21%  
 39:  $\text{R}^1 = \text{CHO}$ ,  $\text{R}^2 = \text{Me}$ ; 95%  
 6:  $\text{R}^1 = \text{CHO}$ ,  $\text{R}^2 = \text{H}$ ,  
 taiwaniadduct C; 83%

e) DMP  
 f)  $\text{LiI}$ , 80 °C;  
 $t\text{-BuOK/DMSO}$

36:  $\text{R}^1 = \text{CH}_2\text{OH}$ ,  $\text{R}^2 = \text{Me}$ ; 52%  
 38:  $\text{R}^1 = \text{CHO}$ ,  $\text{R}^2 = \text{Me}$ ; 93%  
 2:  $\text{R}^1 = \text{CHO}$ ,  $\text{R}^2 = \text{H}$ ,  
 taiwaniadduct B; 77%

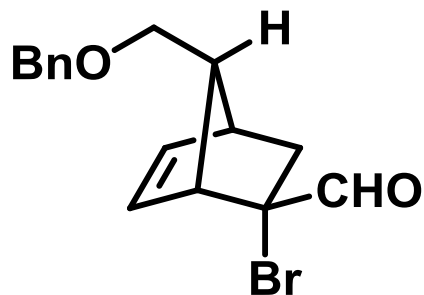
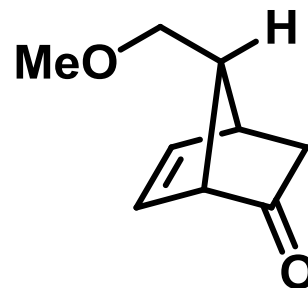
e)  
 f)

# 非直观Diels-Alder反应：Ketene等价物



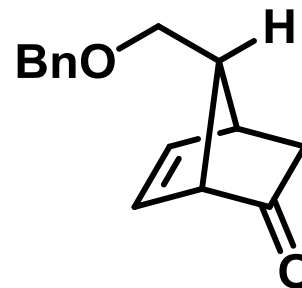
aq. KOH

*Mechanism?*

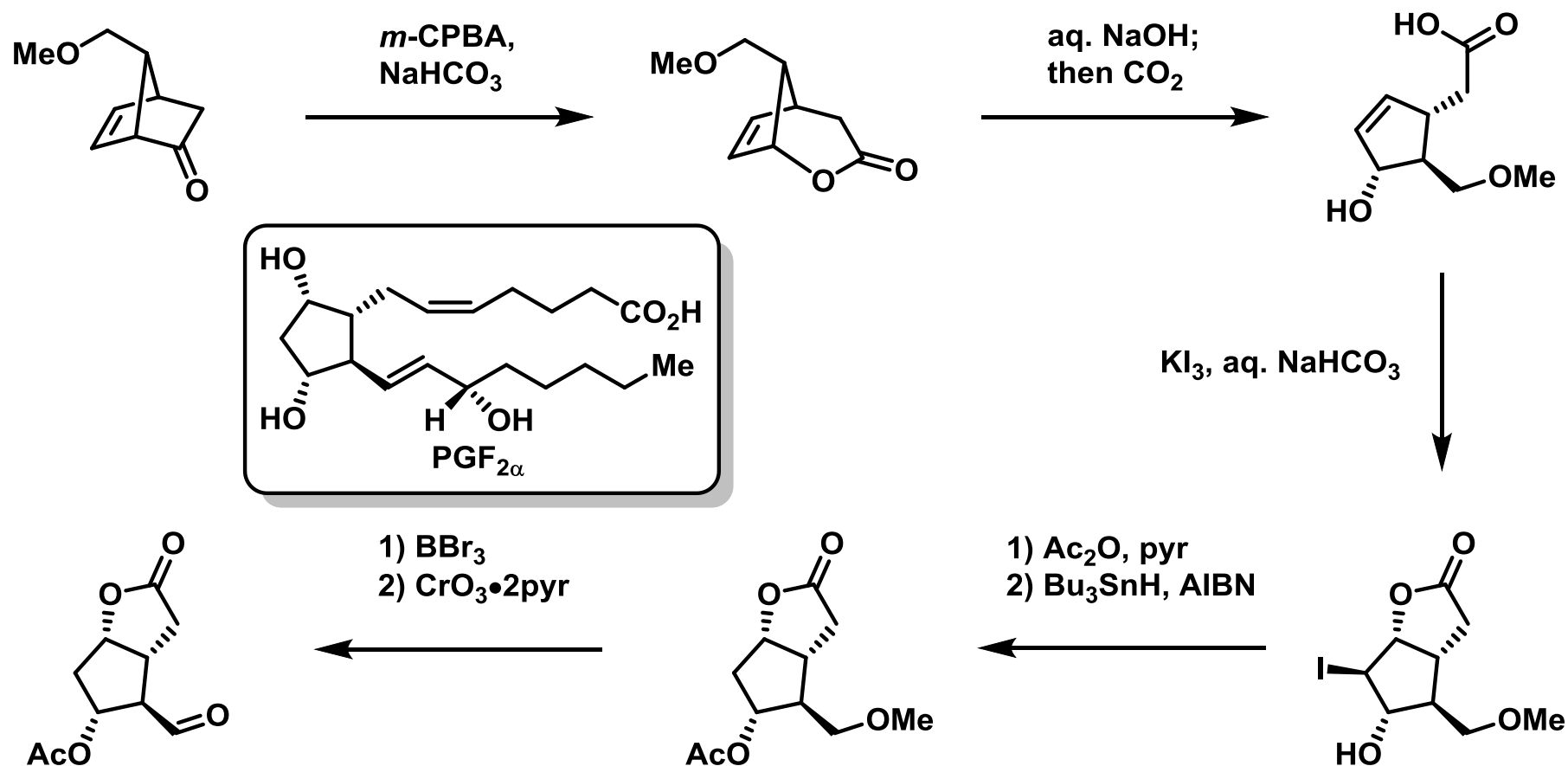


1) NaBH<sub>4</sub>  
2) aq. K<sub>2</sub>CO<sub>3</sub>

*Mechanism?*

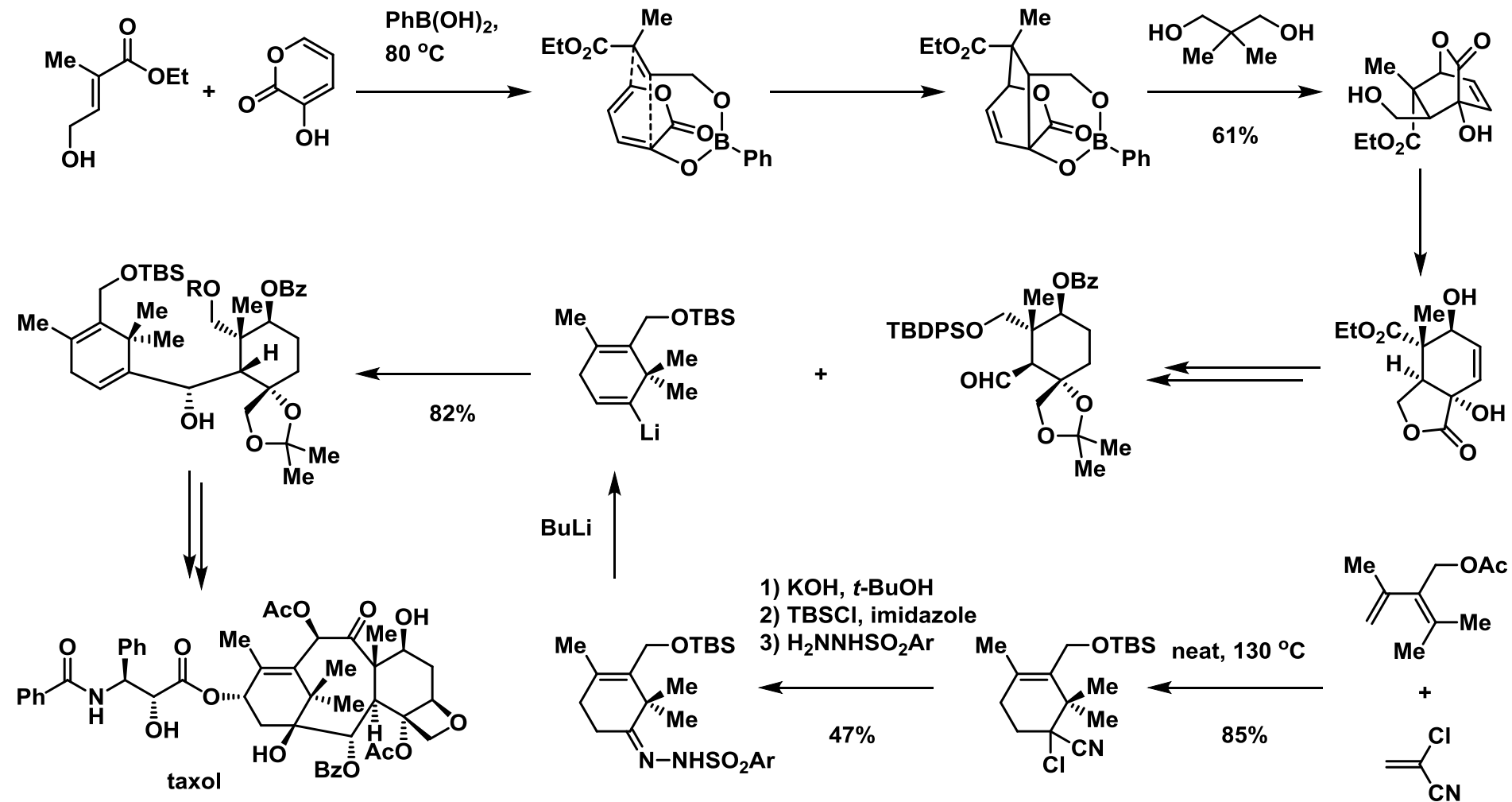


# 非直观Diels-Alder反应：Ketene等价物

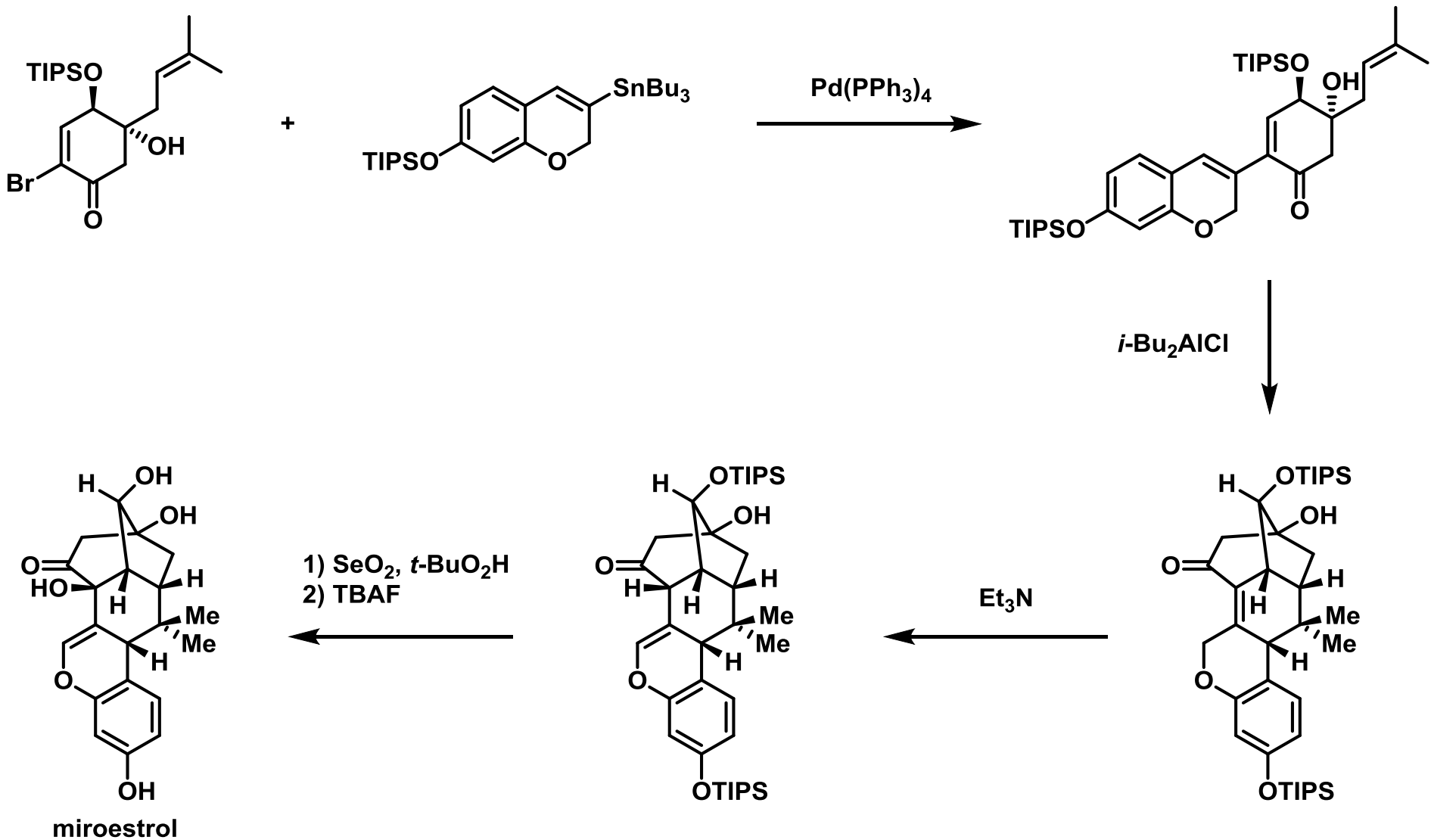


Corey, et al. *J. Am. Chem. Soc.* **1969**, *91*, 5675.

# 非直观Diels-Alder反应：Ketene等价物



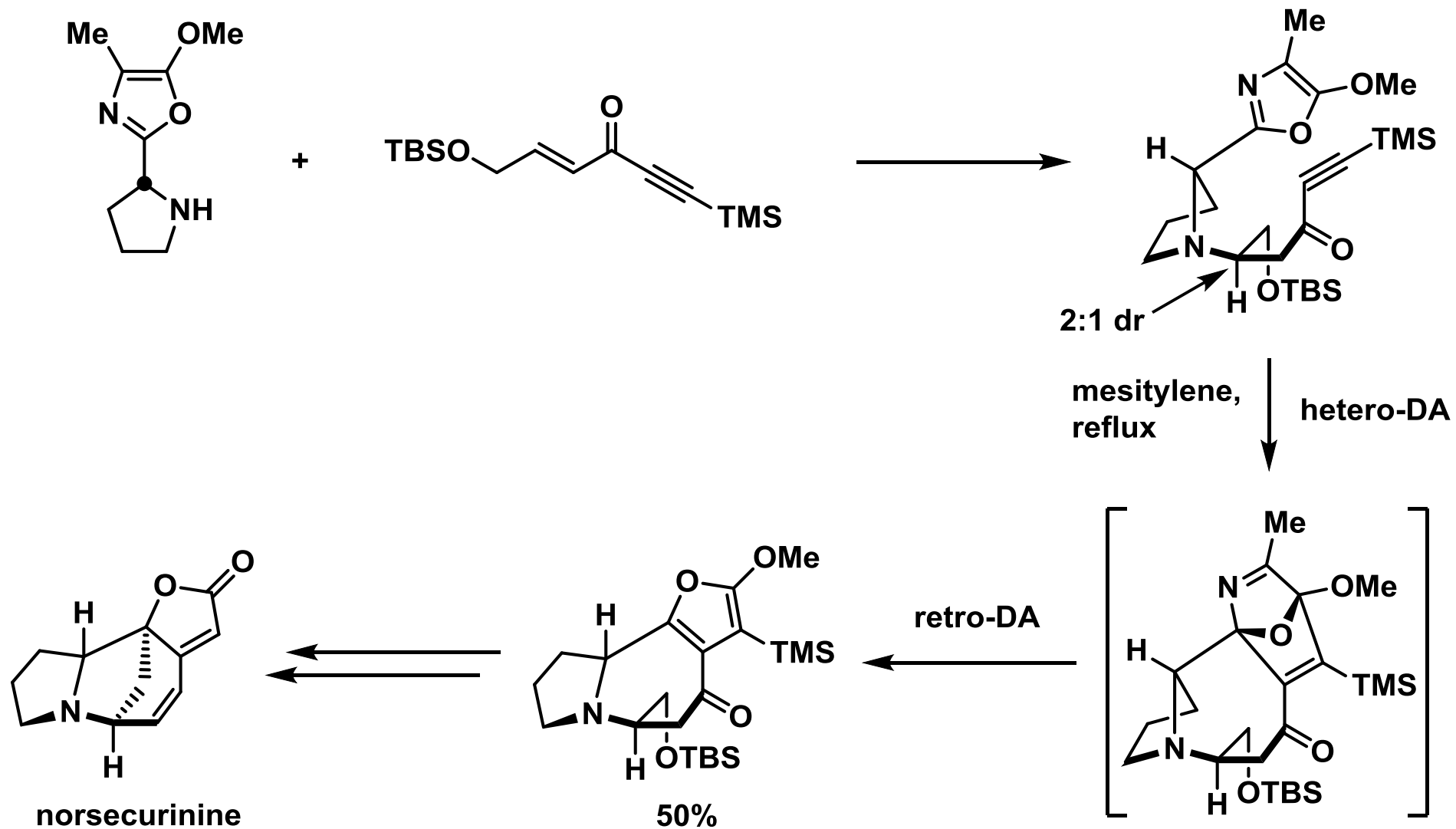
# 非直观Diels-Alder反应：多取代六元环的构建



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

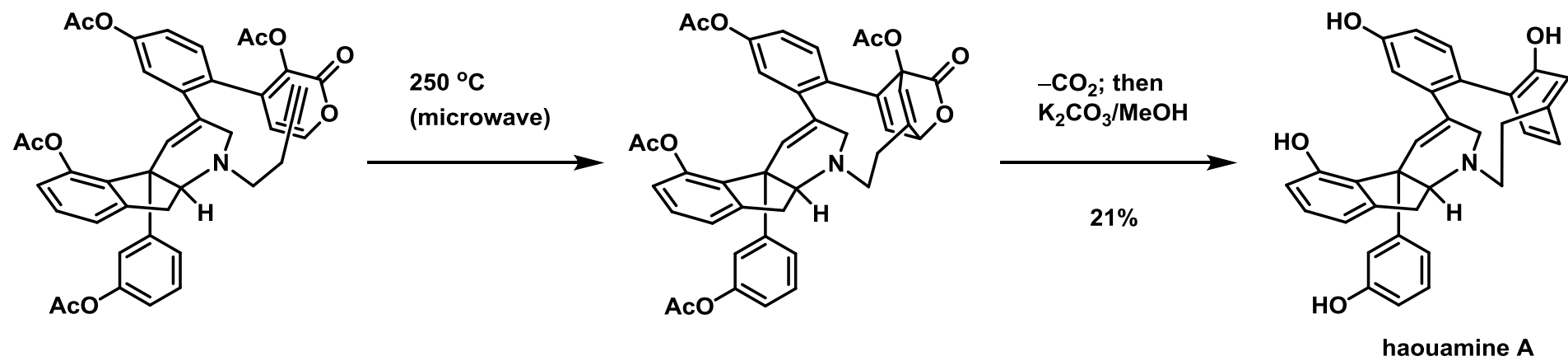


# 非直观Diels-Alder反应：DA/retro-DA



Jacobi, et al. *J. Am. Chem. Soc.* **1991**, *113*, 5384.

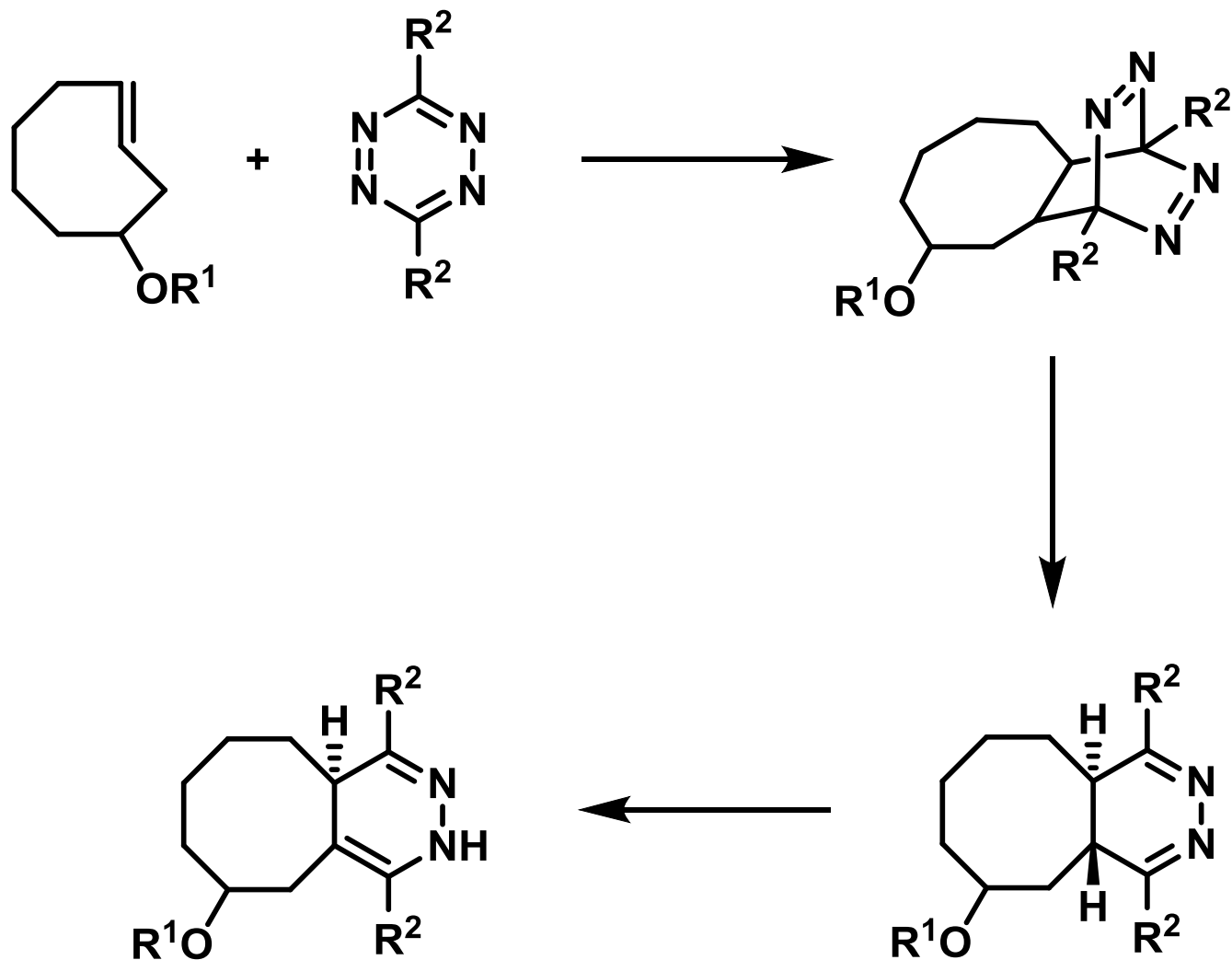
# 非直观Diels-Alder反应：DA/retro-DA



Baran, and Burns, *J. Am. Chem. Soc.* **2006**, 128, 3908.



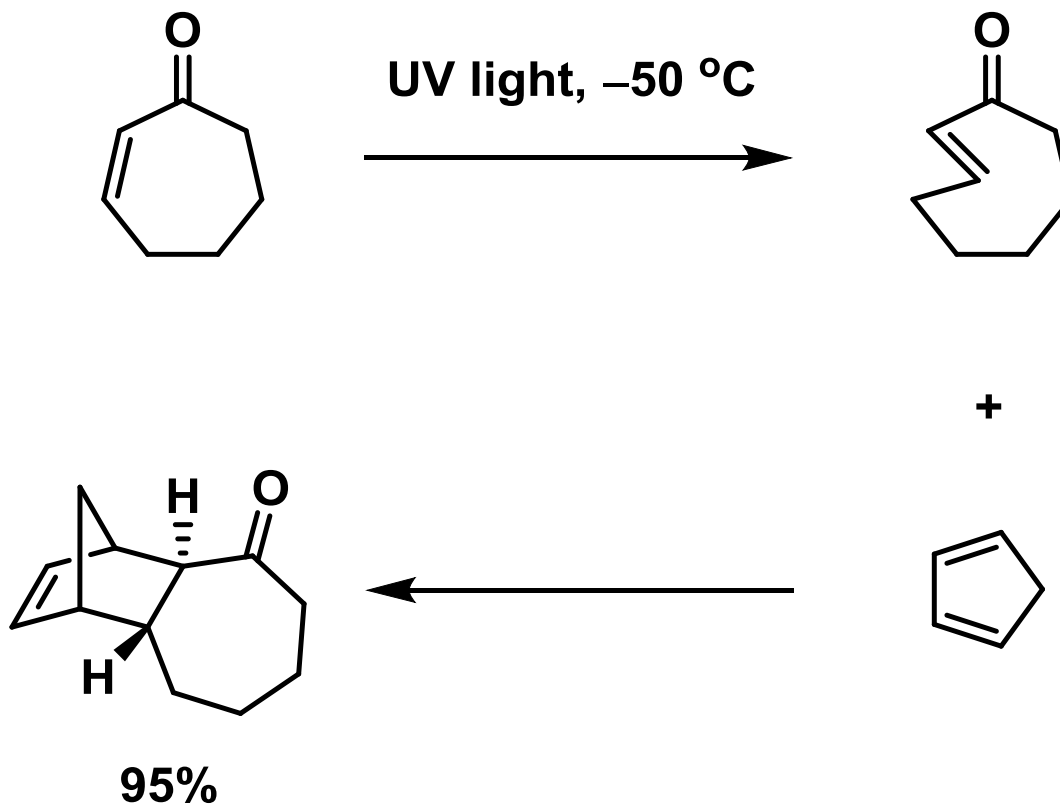
# 非直观Diels-Alder反应：tetrazine ligation



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

Wu and Devaraj, *Acc. Chem. Res.* **2018**, *51*, 1249.

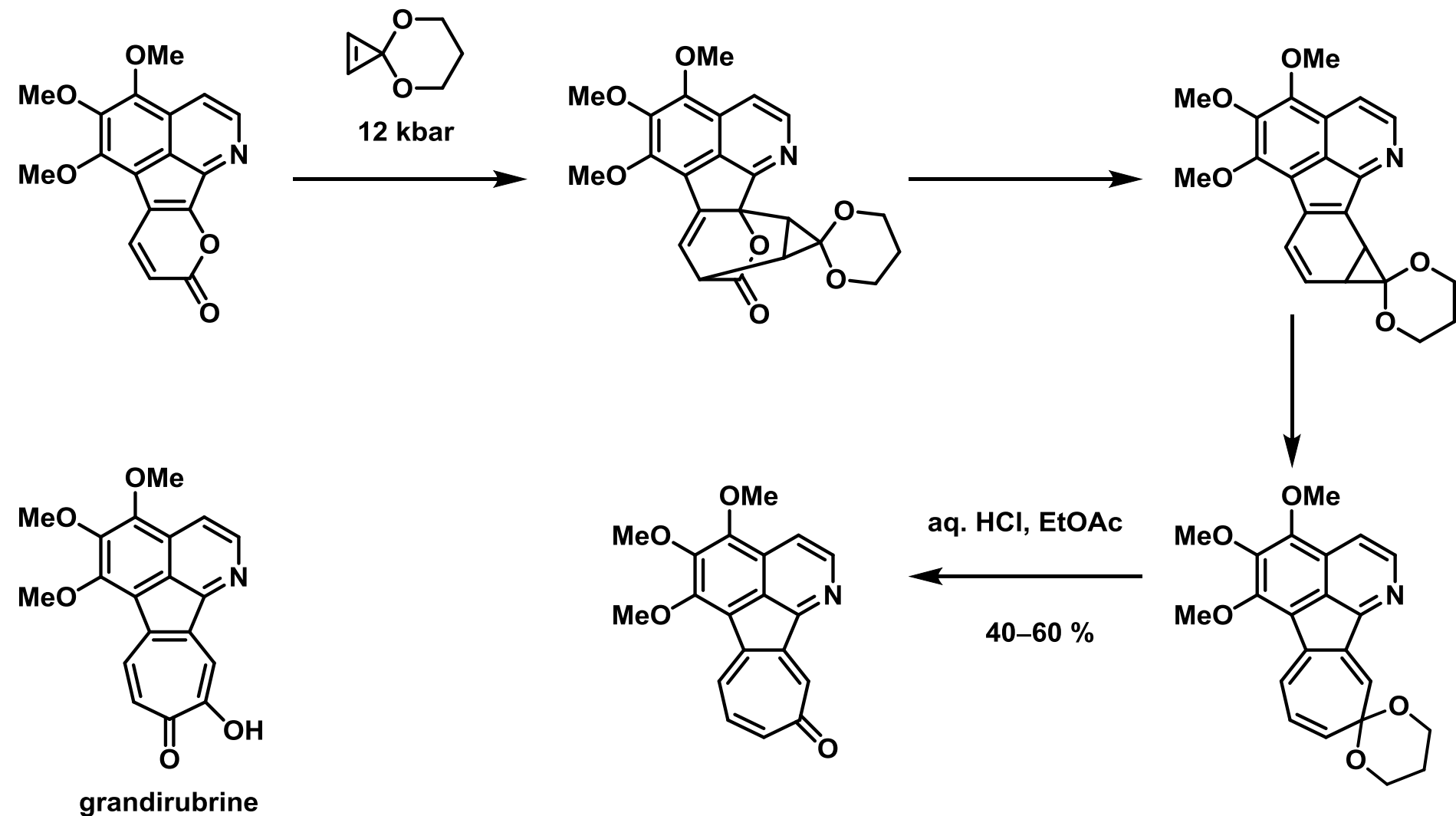
# 非直观Diels-Alder反应：反式环庚烯酮



Corey, et al. *J. Am. Chem. Soc.* **1965**, 87, 2051.

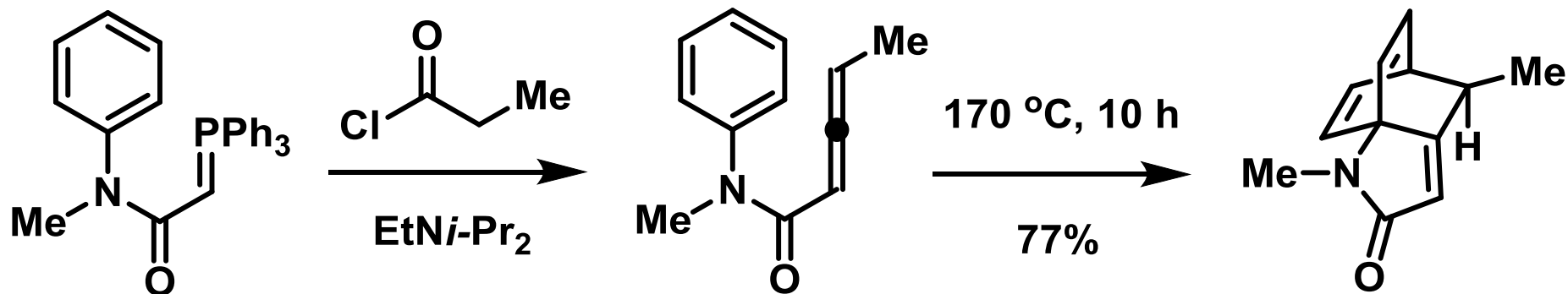
Eaton, et al. *J. Am. Chem. Soc.* **1965**, 87, 2051.

# 非直观Diels-Alder反应：环丙烯



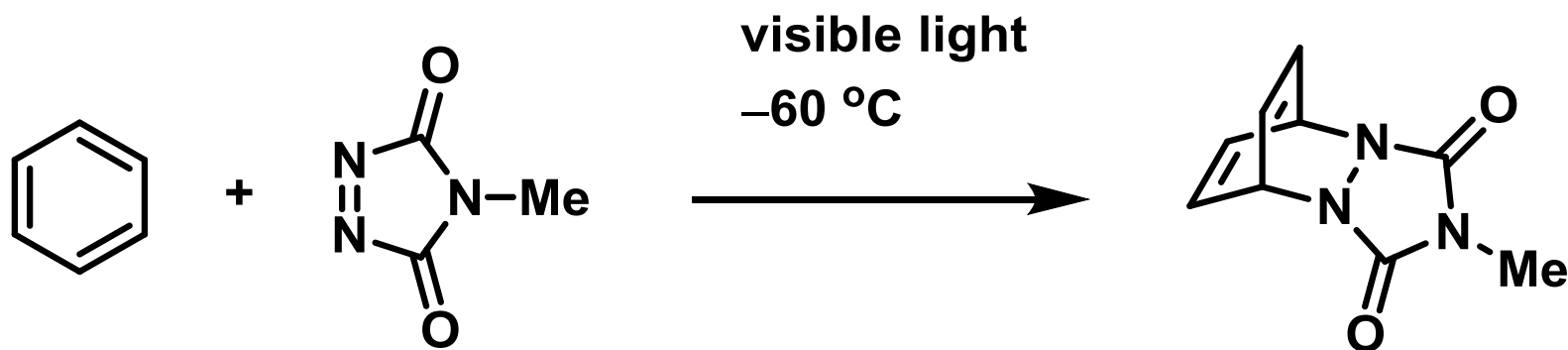
Boger, et al. *J. Am. Chem. Soc.* **1995**, *117*, 12452.

# 非直观Diels-Alder反应：苯环作为二烯



Himbert, et al. *Angew. Chem. Int. Ed.* **1982**, 21, 620.

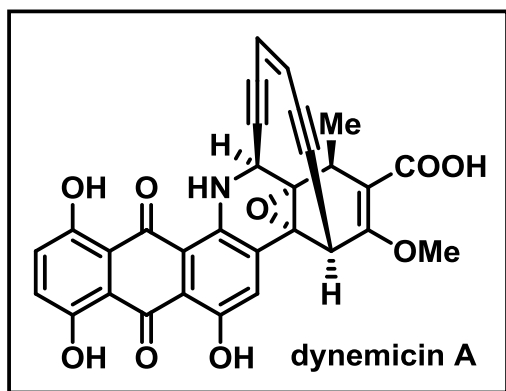
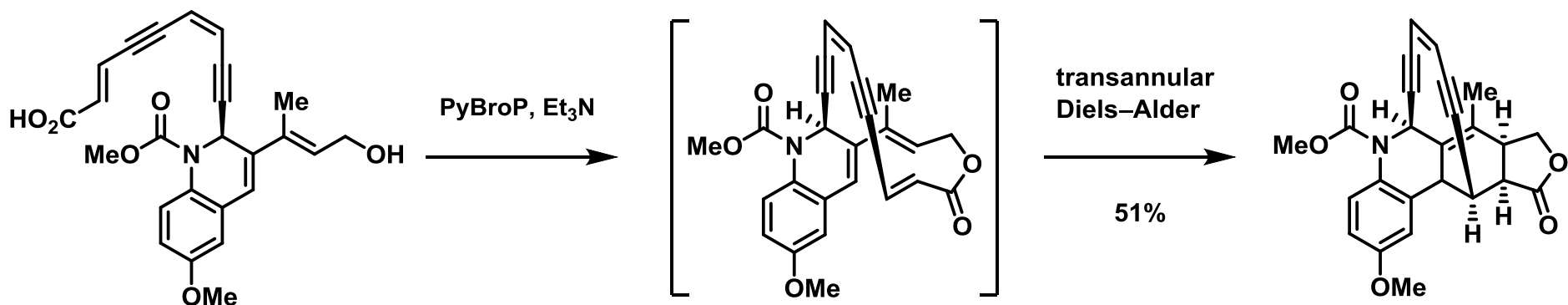
Vanderwal, Houk, et al. *J. Am. Chem. Soc.* **2013**, 135, 7339.



Sheridan, et al. *J. Am. Chem. Soc.* **1989**, 111, 9247.

Sarlah, et al. *Nature Chem.* **2016**, 8, 922.

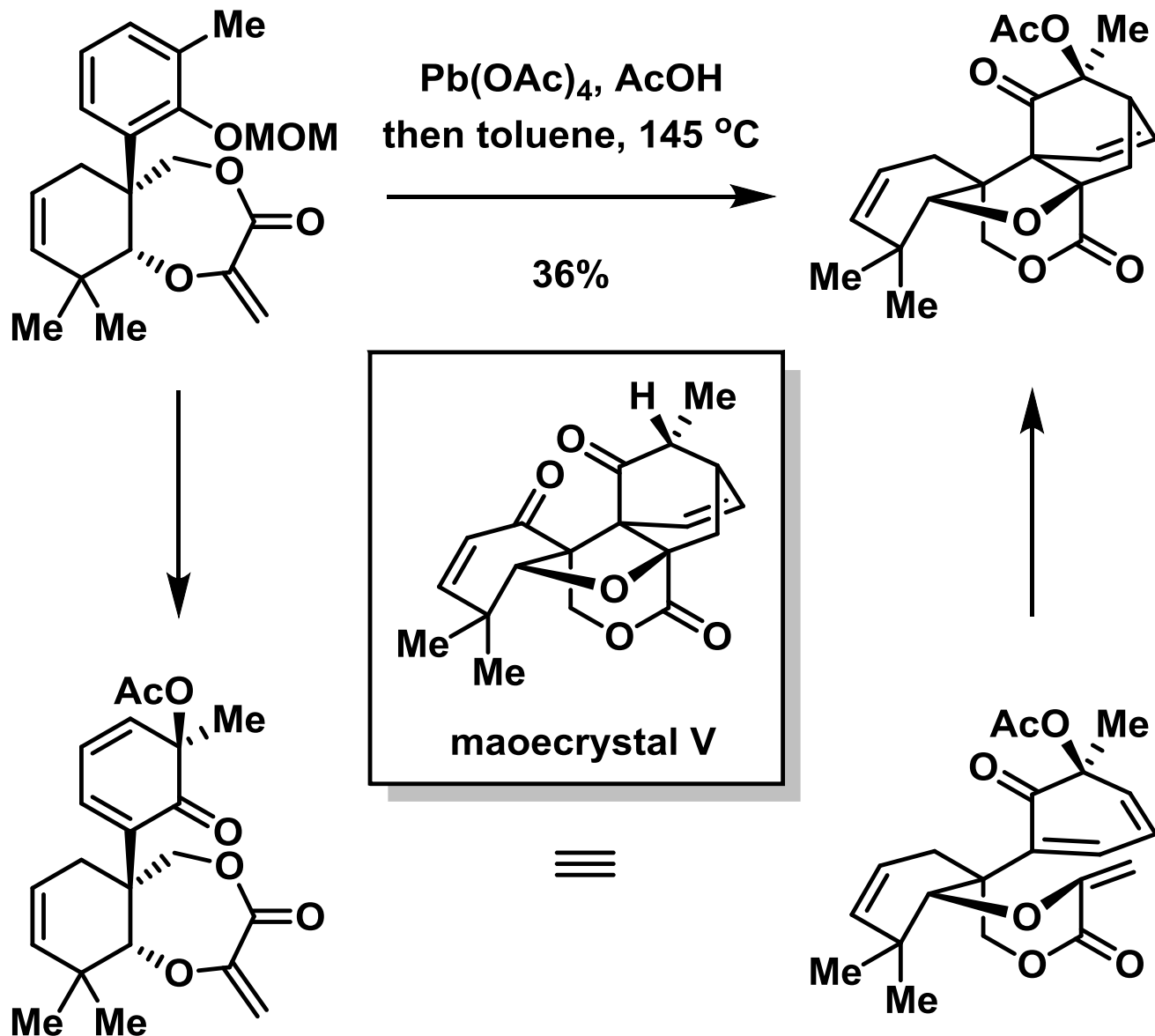
# 非直观Diels-Alder反应：串联反应



Schreiber, et al. *J. Am. Chem. Soc.* **1992**, *114*, 5898.

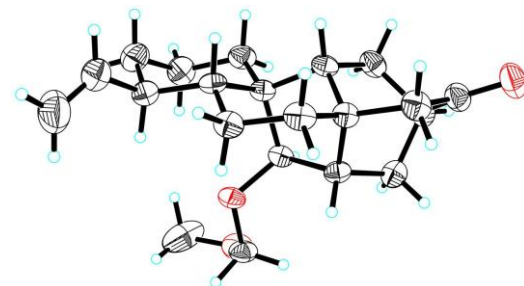
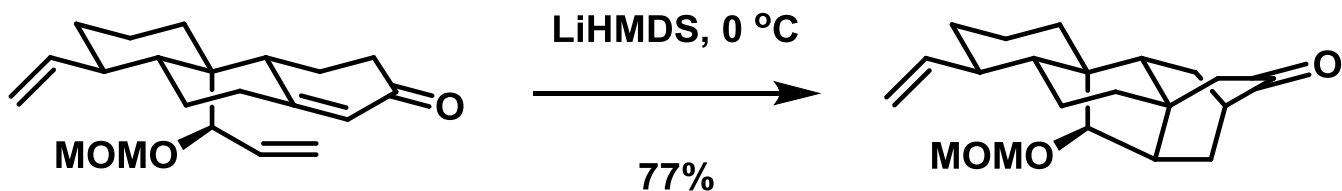
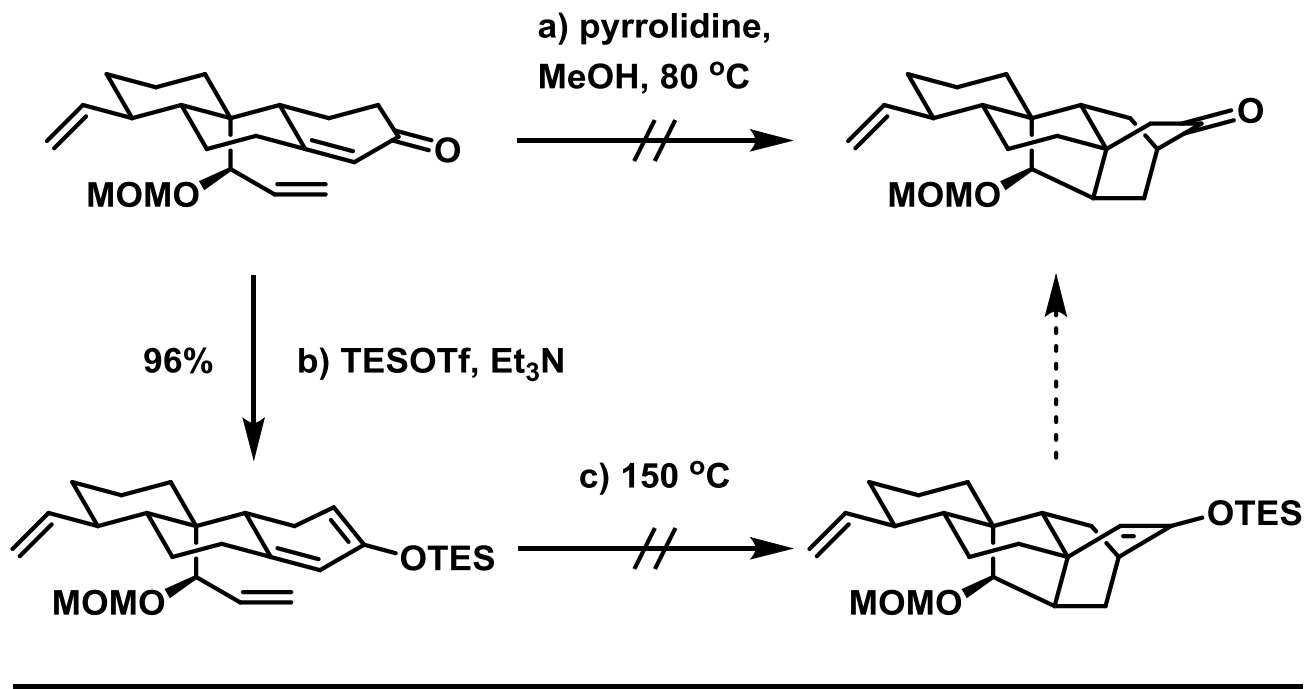


# 非直观Diels-Alder反应：高度拥挤并环体系的构建



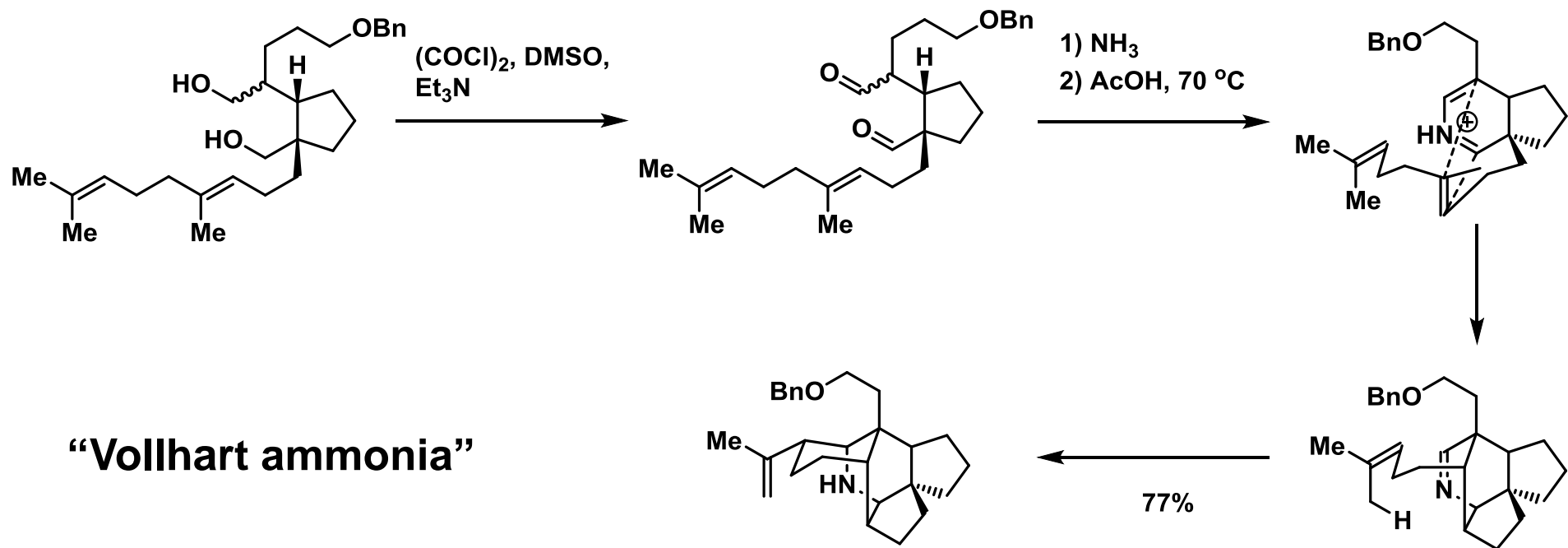
Yang, et al. *J. Am. Chem. Soc.* **2010**, *132*, 16745.

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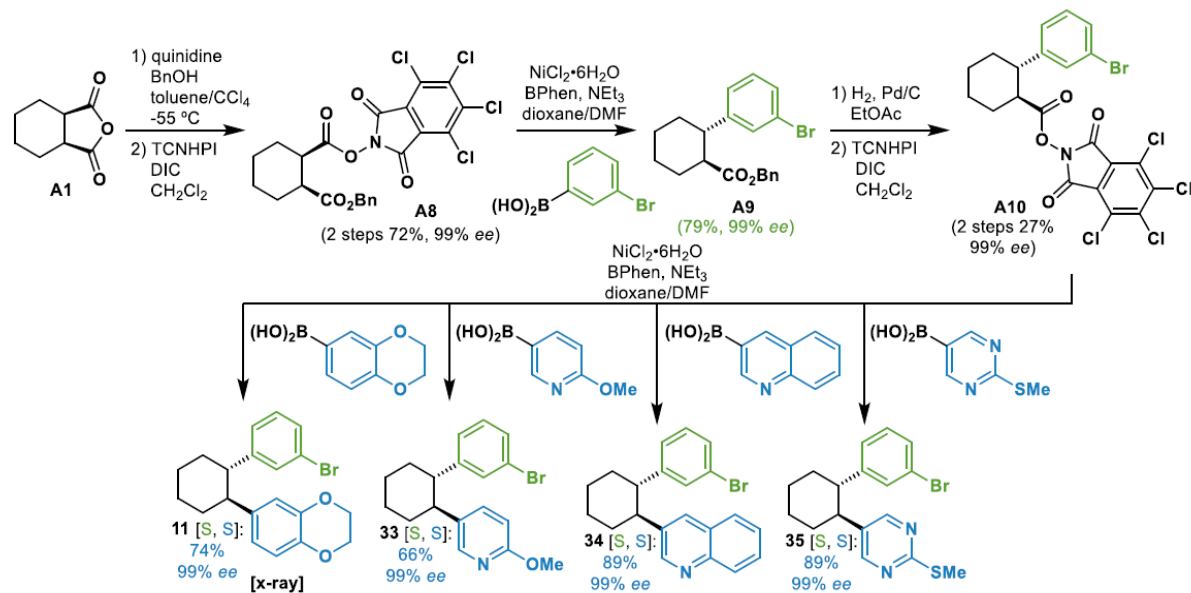
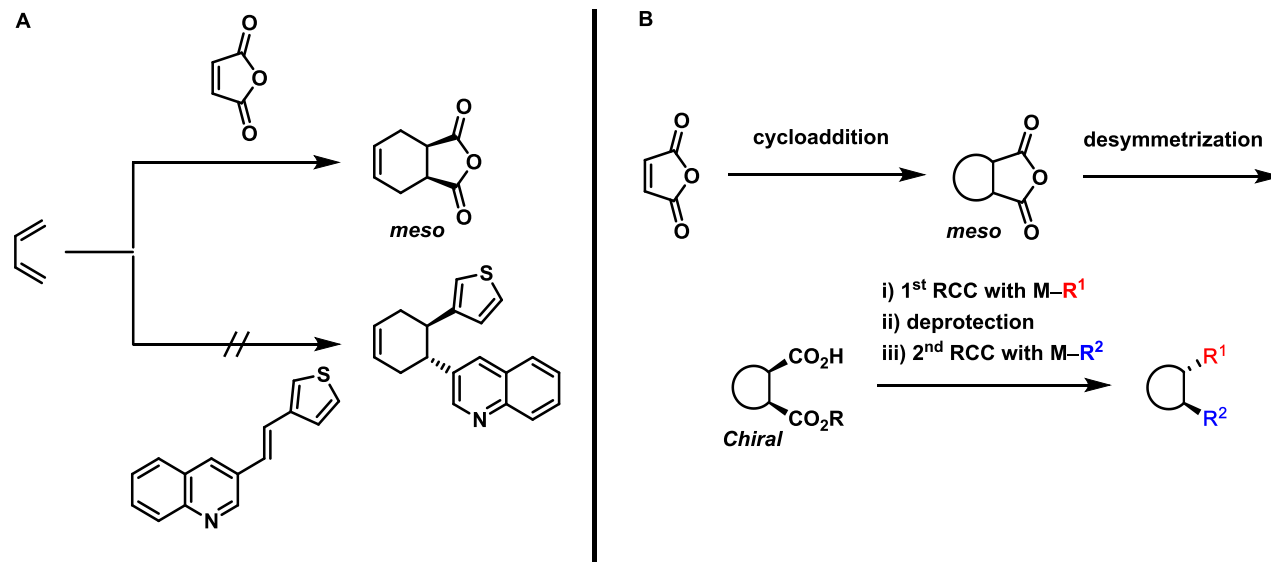
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# 非直观Diels-Alder反应：高度拥挤并环体系的构建



Heathcock, et al. *J. Am. Chem. Soc.* **1988**, *110*, 8734.

# 直观的非直观Diels-Alder反应



Baran, et al. *Nature* **2018**, 560, 350; Ye and Li, *Nature* **2018**, 560, 314.



谢 谢!