

# 螺缩酮的不对称催化合成

报告： 时磊      检查：

# 目 录



简介

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不对称螺缩酮化反应

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$\gamma$ -Rubromycin的全合成

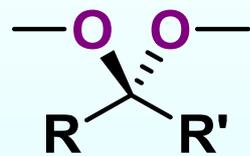
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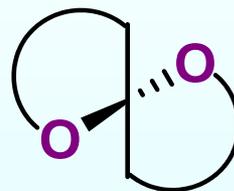
总结与展望

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# 1. 简介



缩酮



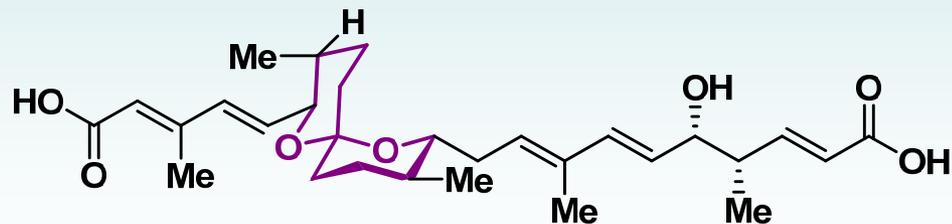
螺缩酮

# 1. 简介

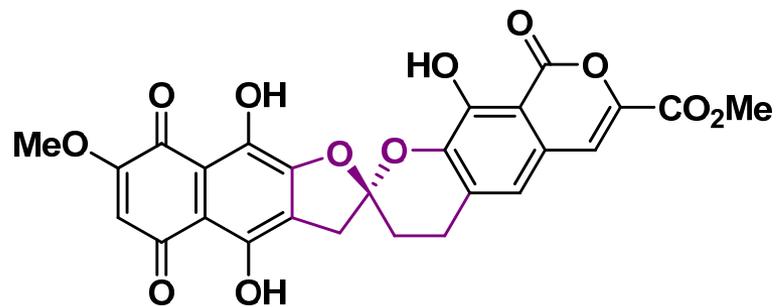


(*R*)-Olean

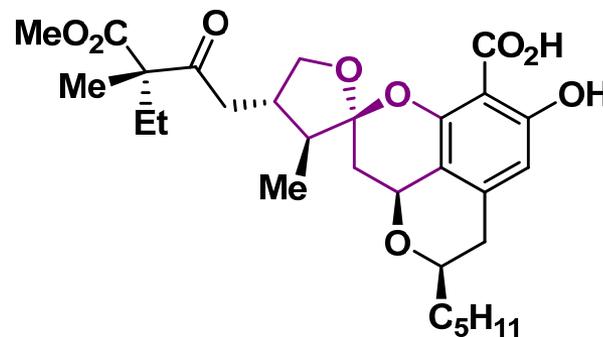
(*S*)-Olean



Spirfungin B

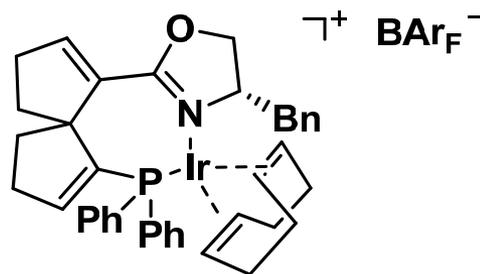
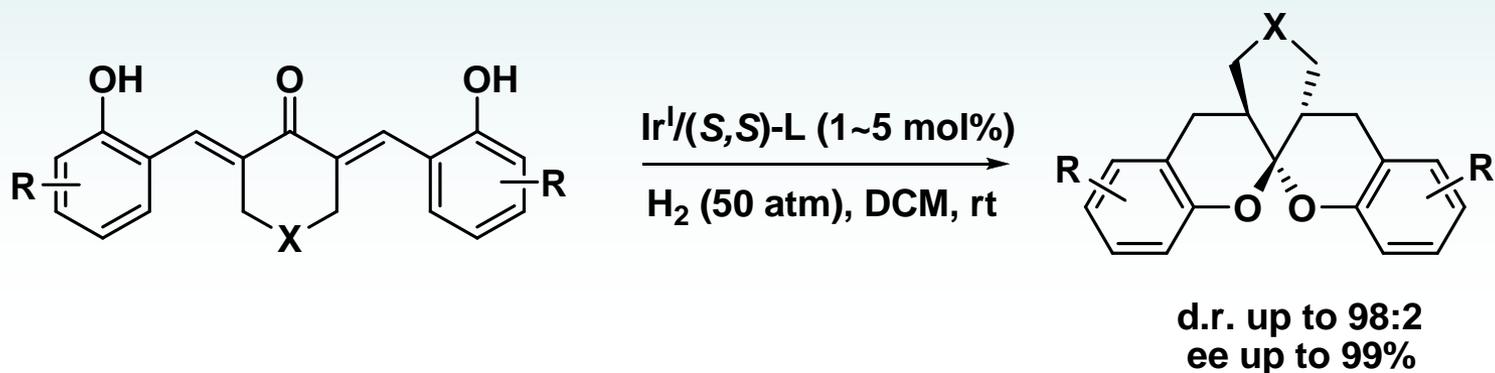


$\gamma$ -Rubromycin 玉红霉素

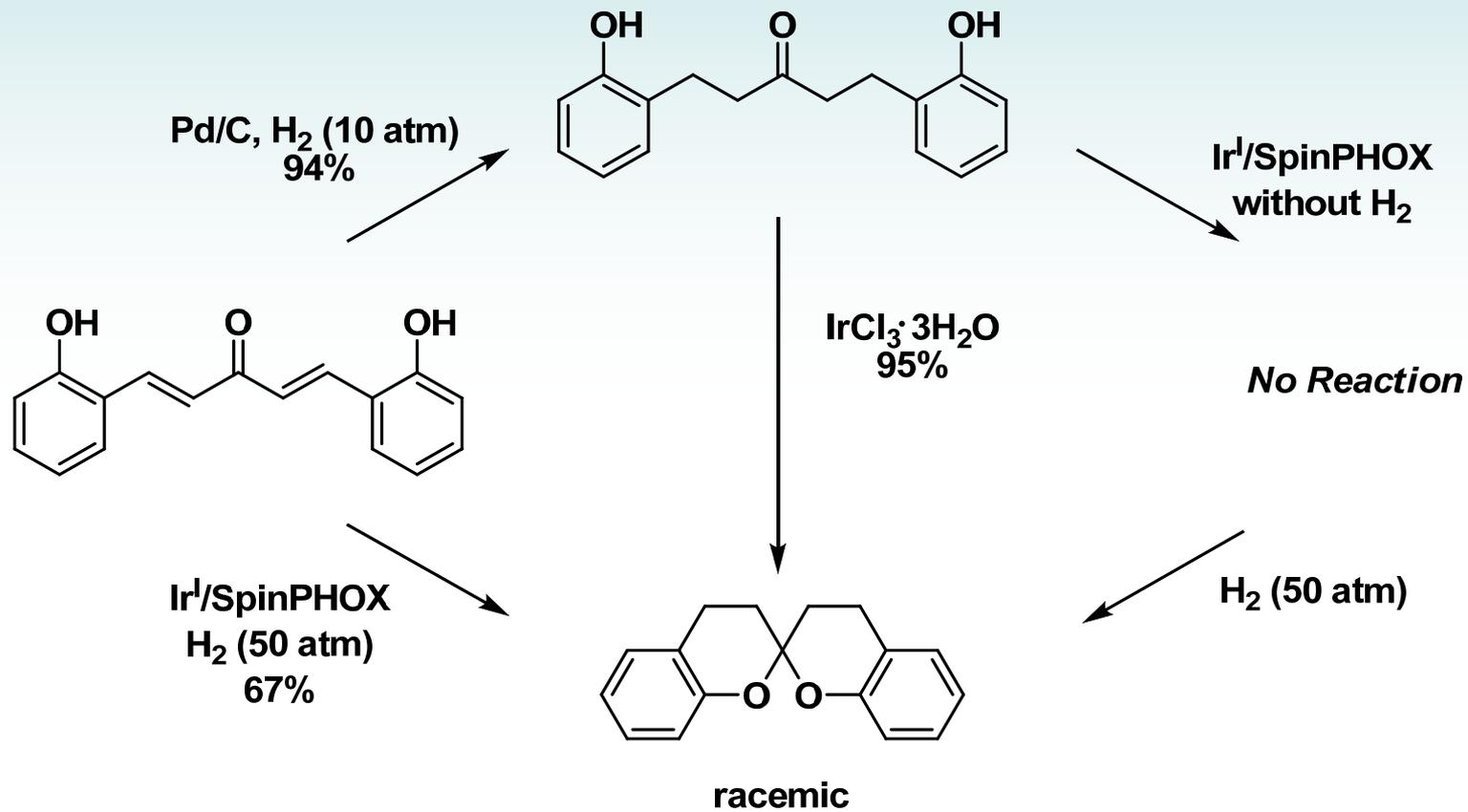


Berkelic acid

## 2.1 金属催化的不对称螺缩酮化



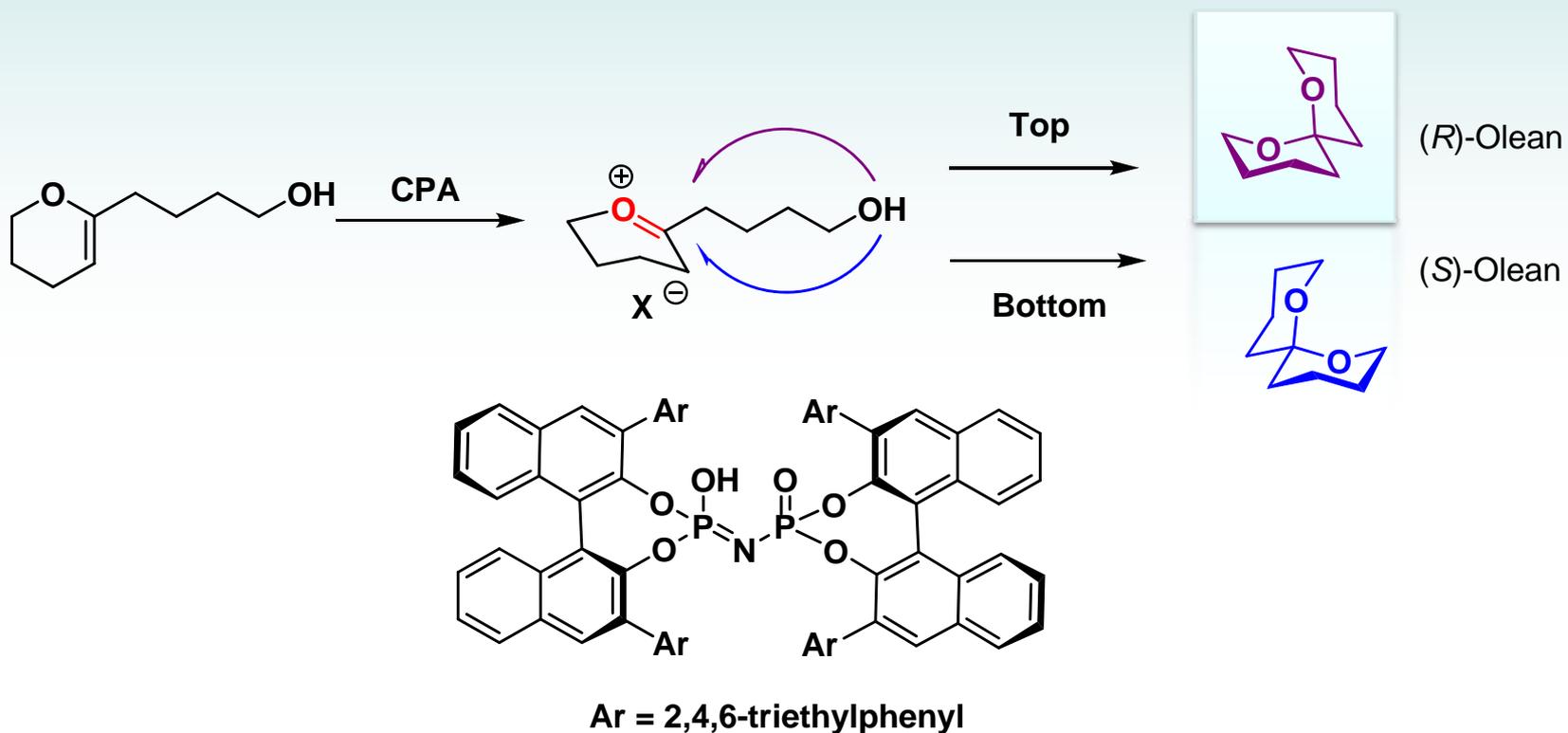
Ding, K. *Angew. Chem. Int. Ed.* **2012**, *51*, 936.



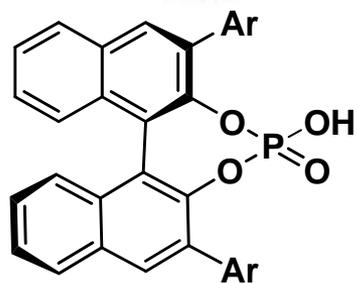
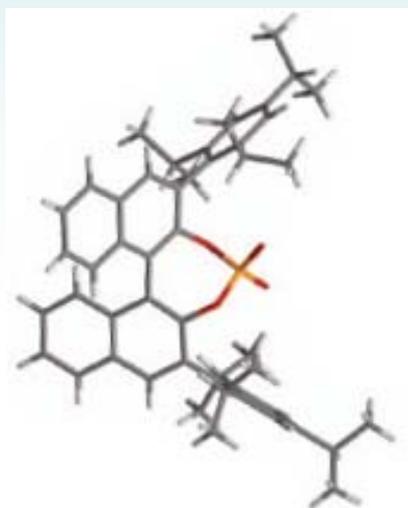
反应的要素：三价铱



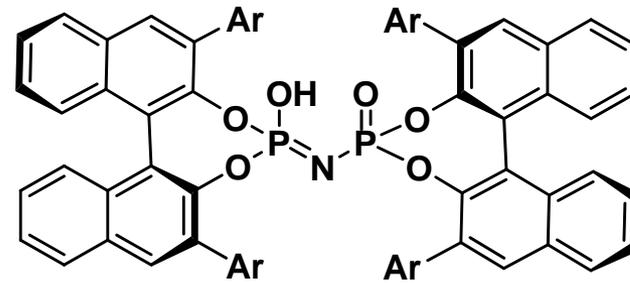
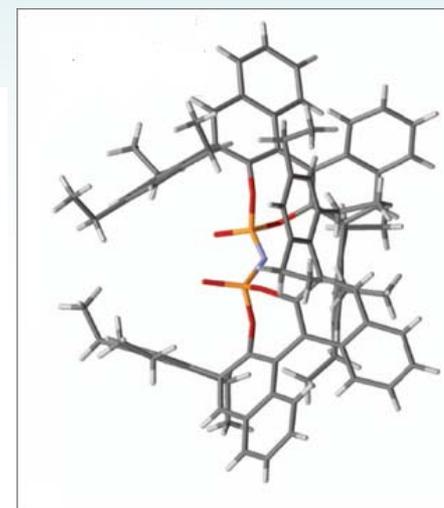
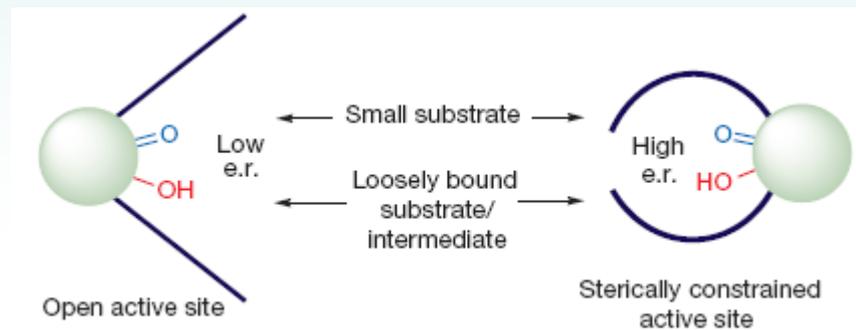
## 2.2 有机催化的不对称螺缩酮化



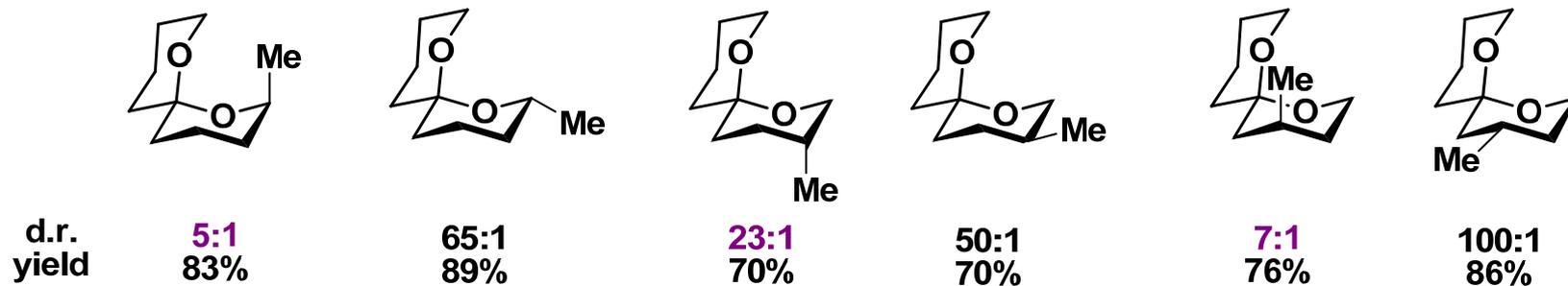
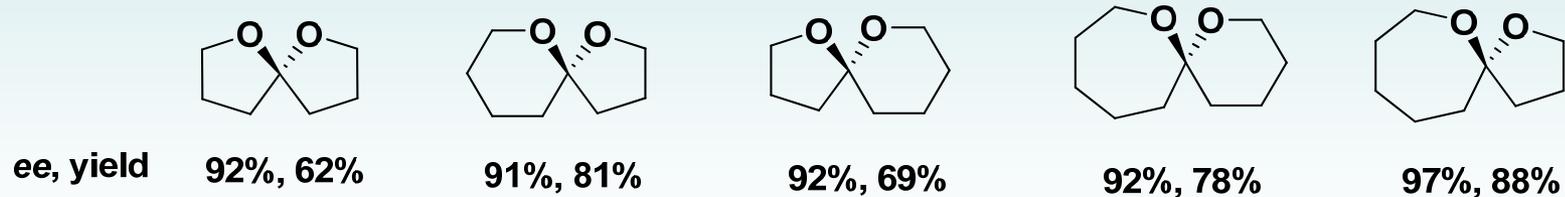
List, B. et al. *Nature* **2012**, 483, 315.

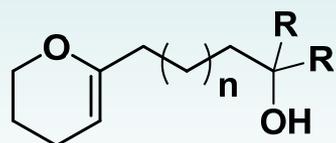


Ar = 2,4,6-triisopropylphenyl

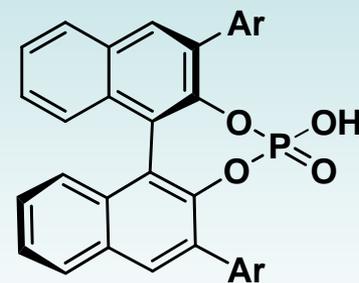
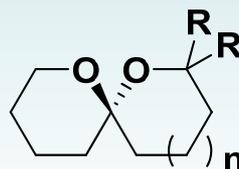


Ar = 2,4,6-triethylphenyl

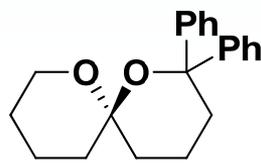




*(R)*-TRIP (5 mol%)

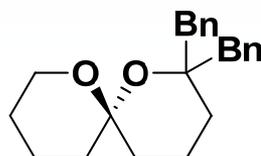


Ar = 2,4,6-triisopropylphenyl

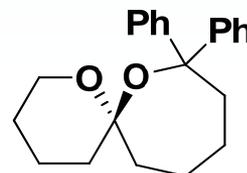


ee, yield

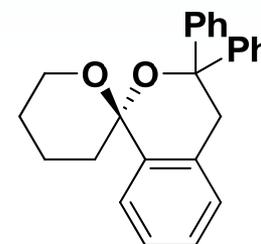
92%, 96%



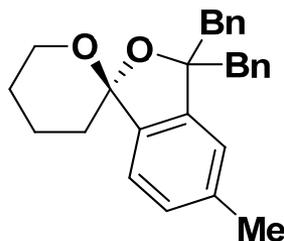
75%, 82%



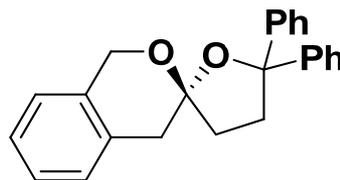
94%, 96%



96%, 93%

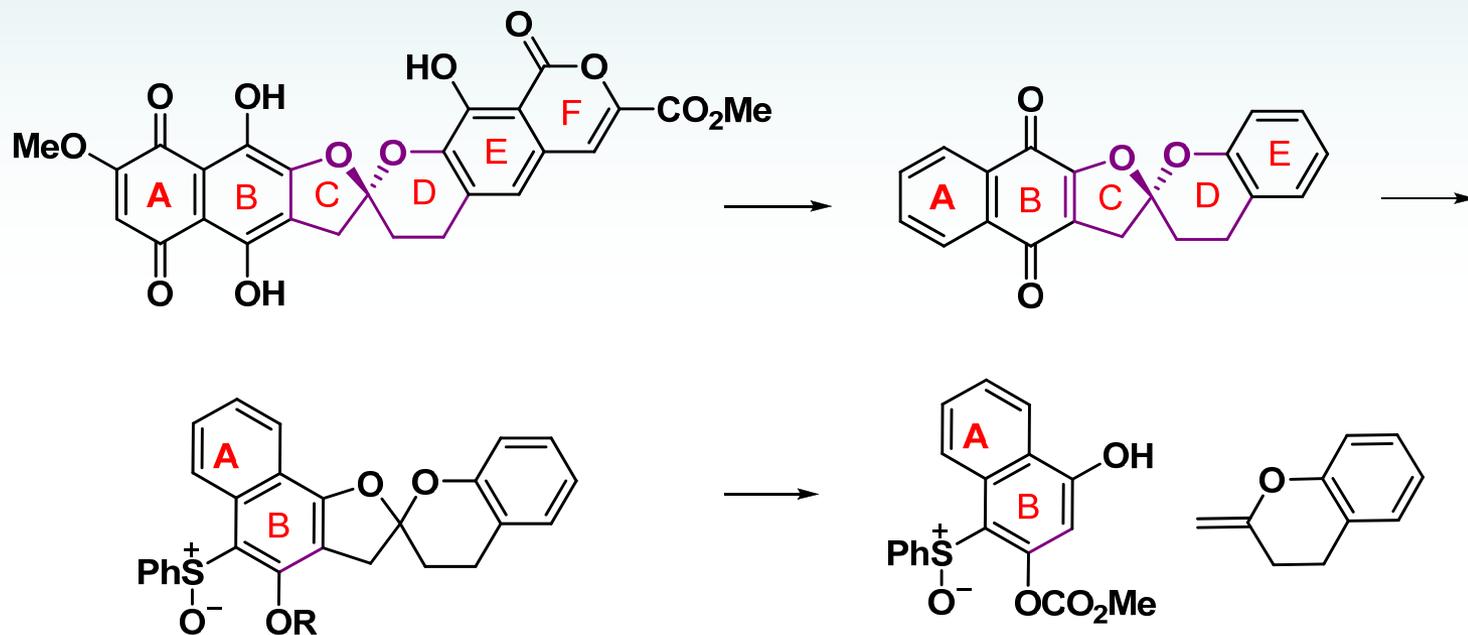


74%, 88%

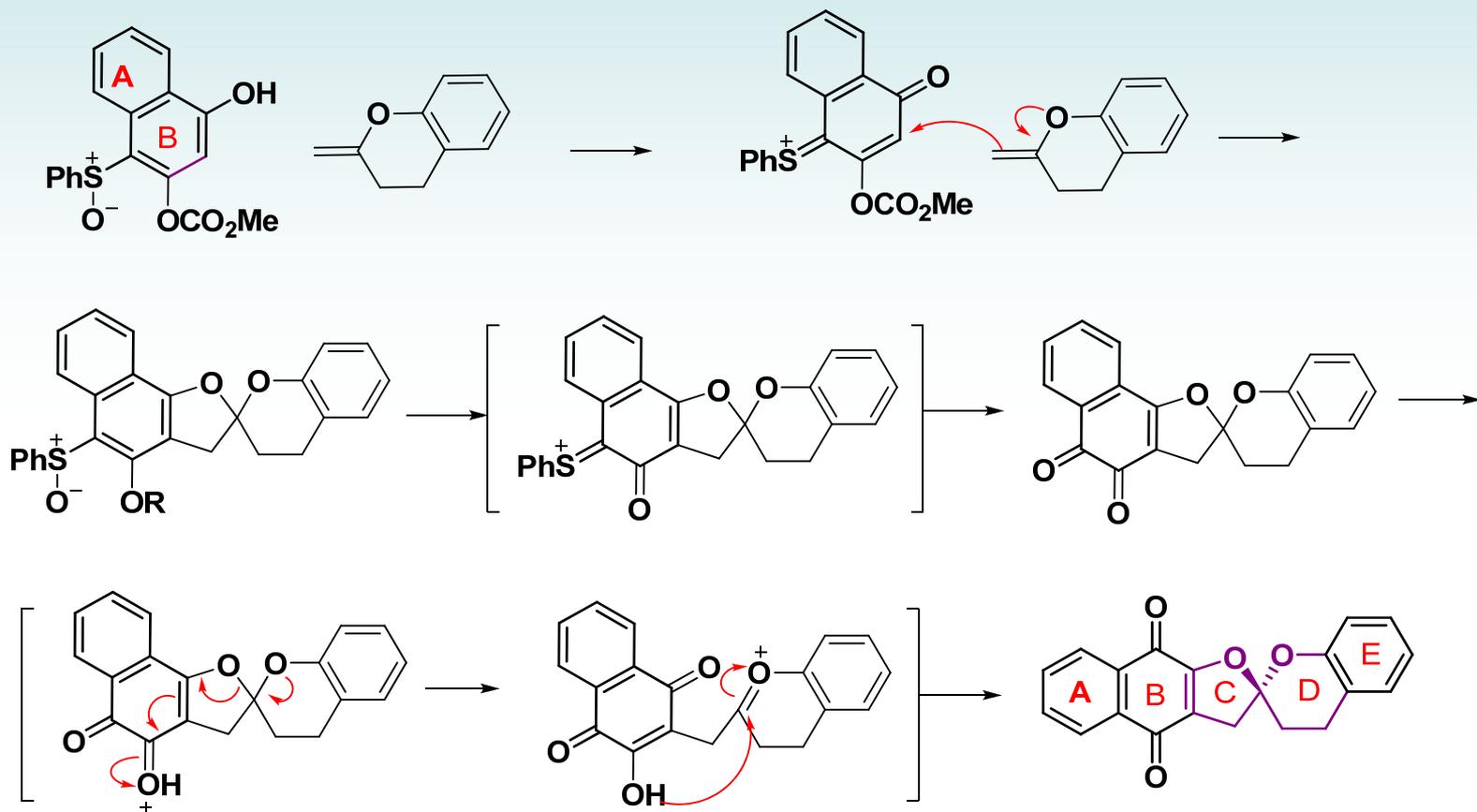


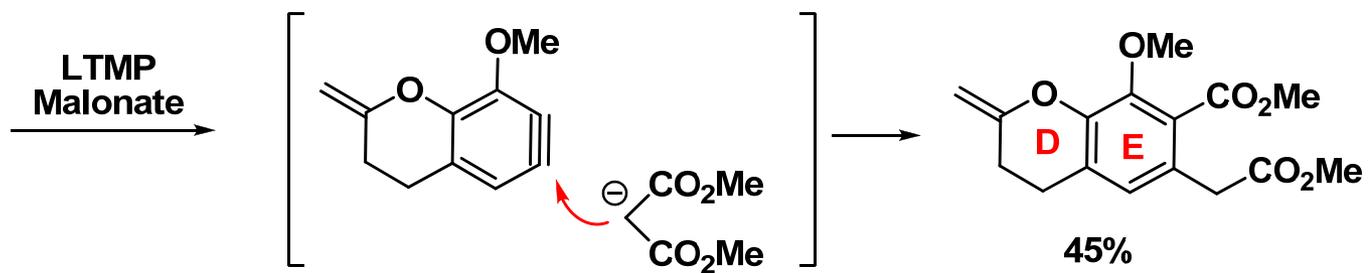
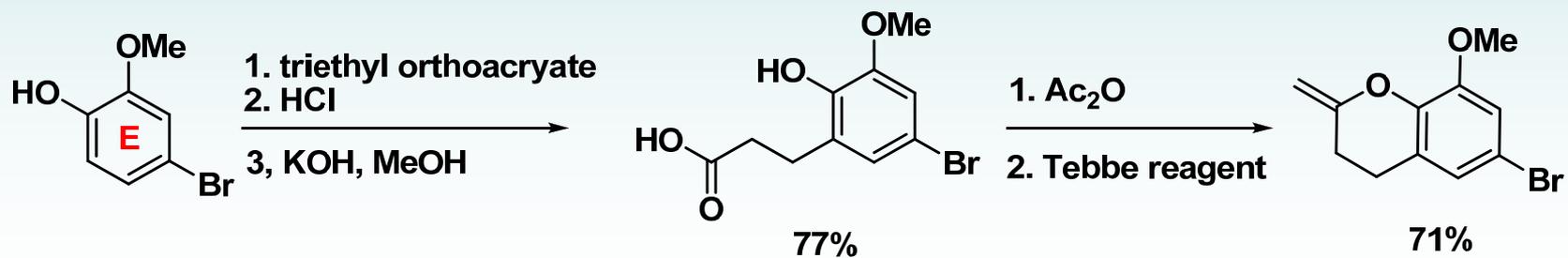
90%, 89%

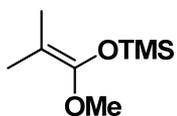
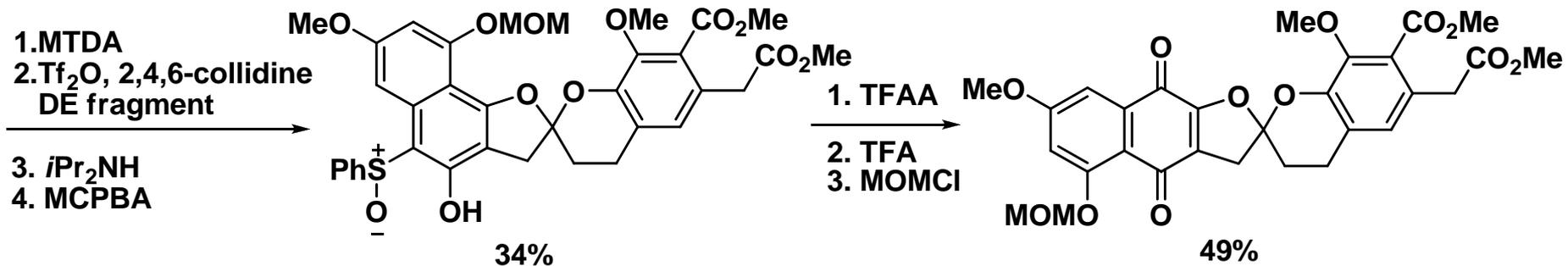
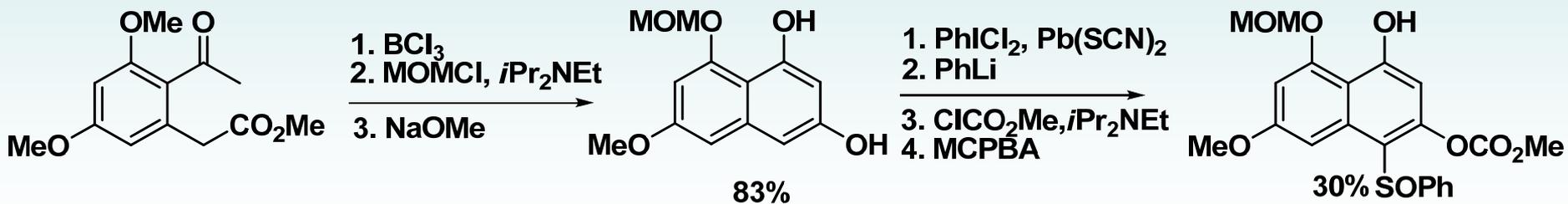
### 3. (+/-)- $\gamma$ -Rubromycin的全合成



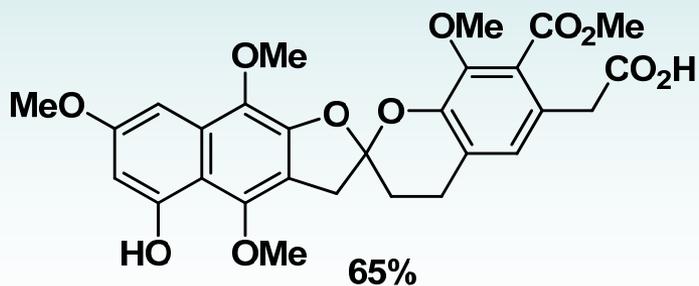
Forsyth, C. J. et al. *Angew. Chem. Int. Ed.* **2007**, 46, 279.



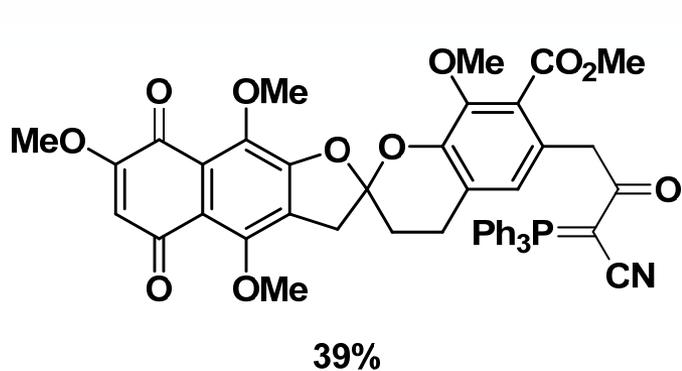




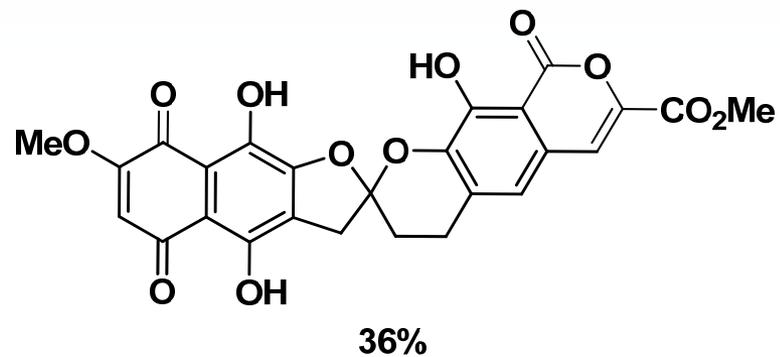
1.  $\text{Na}_2\text{S}_2\text{O}_4$ ,  $\text{Me}_2\text{SO}$   
2. TFA  
3. KOH, MeOH



1.  $[\text{Co}(\text{Salen})_2]$ ,  $\text{O}_2$   
2.  $\text{Ph}_3\text{P}=\text{CHCN}$ , EDCI



1. DMSO  
2.  $\text{BBr}_3$



## 4. 总结与展望

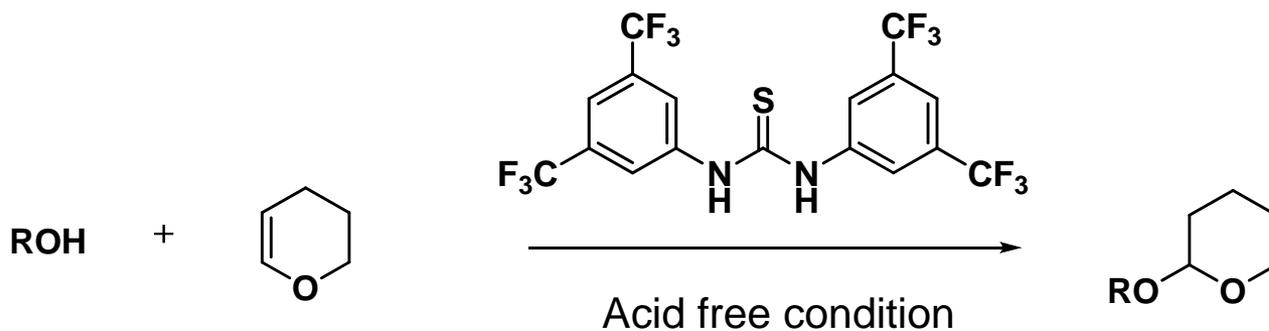
### *Simple, but challenging*

- 酸性条件不稳定，导致消旋化
- 分子体积小，立体化学不易控制

### ■ 新催化剂体系

路易斯酸催化剂：手性Ir<sup>III</sup> ?

中性硫脲催化剂：



Schreiner, P. R. et al. *Synthesis* **2007**, 779

## 参考文献

- 1) Ding, K. *Angew. Chem. Int. Ed.* **2012**, 51, 936.
- 2) Ding, K. *Angew. Chem. Int. Ed.* **2012**, 51, 9276.
- 3) List, B. et al. *Nature* **2012**, 483, 315
- 4) Nagorny, P. et al. *J. Am. Chem. Soc.* **2012**, 134, 8074.
- 5) Forsyth, C. J. et al. *Angew. Chem. Int. Ed.* **2007**, 46, 279.

水平有限，欢迎批评指正！

