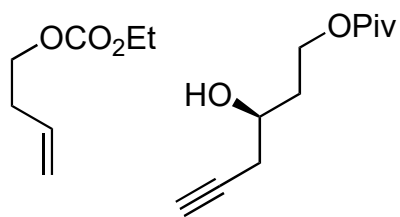
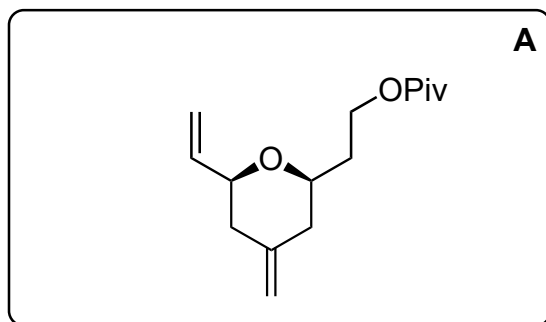


Total Synthesis of (-)-Dactylolide

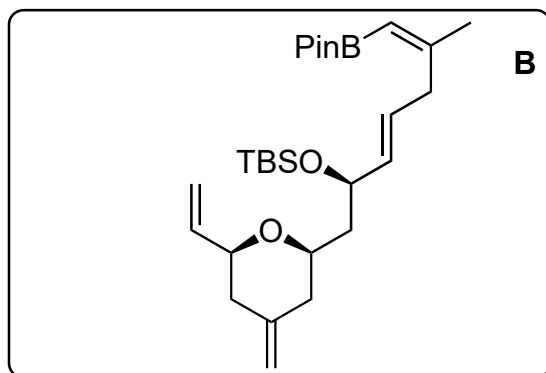
S. Y. Yun, E. C. Hansen, I. Volchkov, E. J. Cho Dr., W. Y. Lo, D. Lee, *ACIE* **2010**, *49*, 4261–4263



1–3



3–7



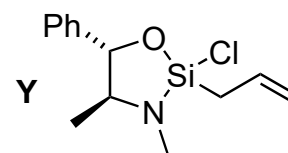
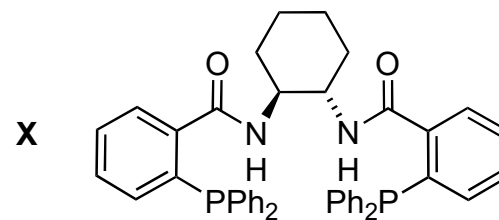
- 1) $[\text{RuCp}(\text{CH}_3\text{CN})_3]\text{PF}_6$
- 2) $\text{Pd}_2(\text{dba})_3 \bullet \text{CHCl}_3$, **X**

- 3) DIBAL
- 4) IBX
- 5) **Y**
- 6) TBSCl
- 7) $[\text{RuCp}(\text{CH}_3\text{CN})_3]\text{PF}_6$, $\text{—}\equiv\text{—BPin}$

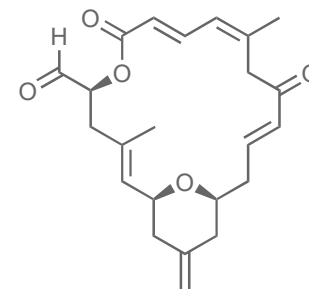
How would you prepare the starting materials?

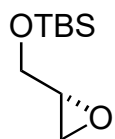
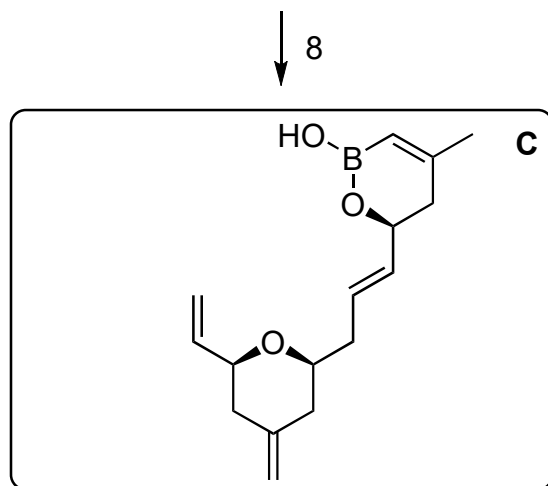
Steps 1 and 2: what kind of name reactions take place? Think of the mechanisms!

Alder-ene and Tsuji-Trost reactions

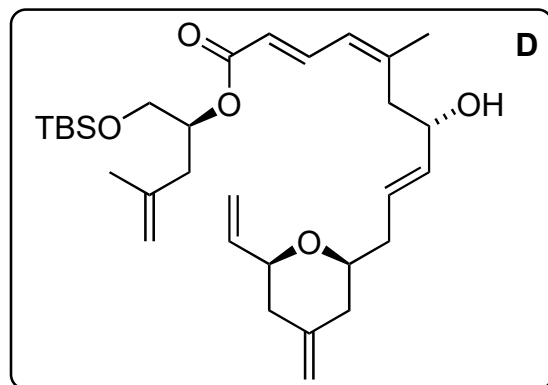


How would you prepare Y?

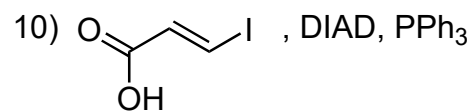
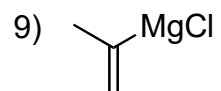




9-10



8) Re_2O_7



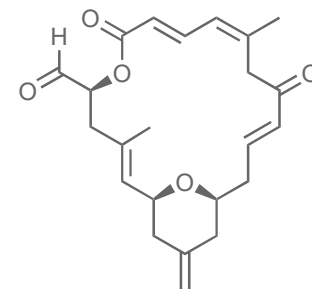
11) TIOEt, $\text{Pd}(\text{PPh}_3)_4$, **C**

Step 8: Think of a mechanism!

J. Am. Chem. Soc. **2006**, 128, 8142 and
Tetrahedron Lett. **2000**, 41, 1549

Why Thallium?

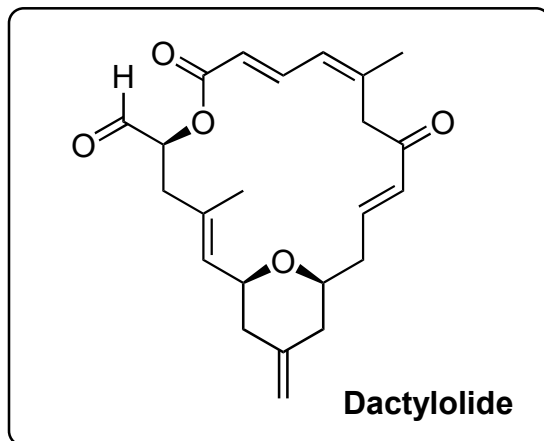
Kishi's Thallium effect - see
J. Am. Chem. Soc. **1987**, 109, 4756,
J. Am. Chem. Soc. **1989**, 111, 7525 and
Org. Lett. **2000**, 2, 2691



12–15



- 12) DMP
- 13) Grubbs II, Benzoquinone
- 14) HCl, MeOH
- 15) DMP



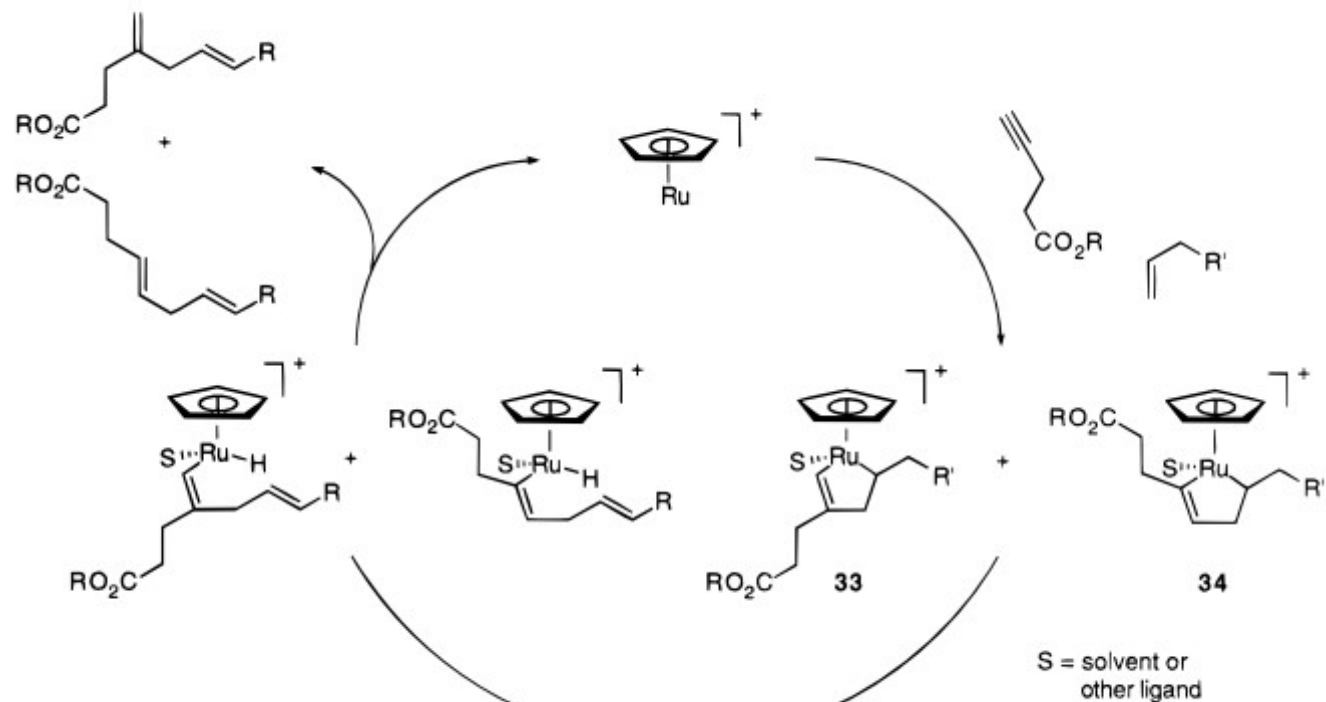
Why is Benzoquinone added?

Benzoquinone can prevent the Isomerization of double bonds what could diminish the yield significantly.

see: *J. Am. Chem. Soc.* **2005**, *127*, 17160-17161.

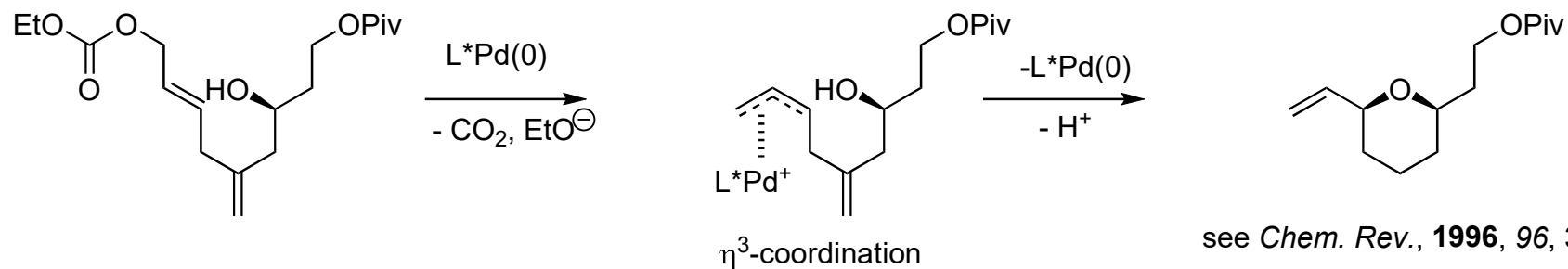
Mechanisms:

Ruthenium-catalyzed Alder-ene reaction:

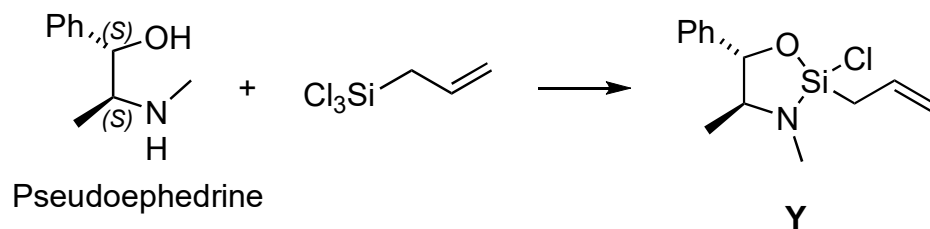


from: *J. Am. Chem. Soc.* **1998**, *120*, 9228-9236.

Tsuji-Trost reaction:



Synthesis of Leighton reagent:



from: *J. Am. Chem. Soc.* **2002**, 124, 7920-7921.

Rhenium catalyzed Isomerization of allyl silyl ethers:

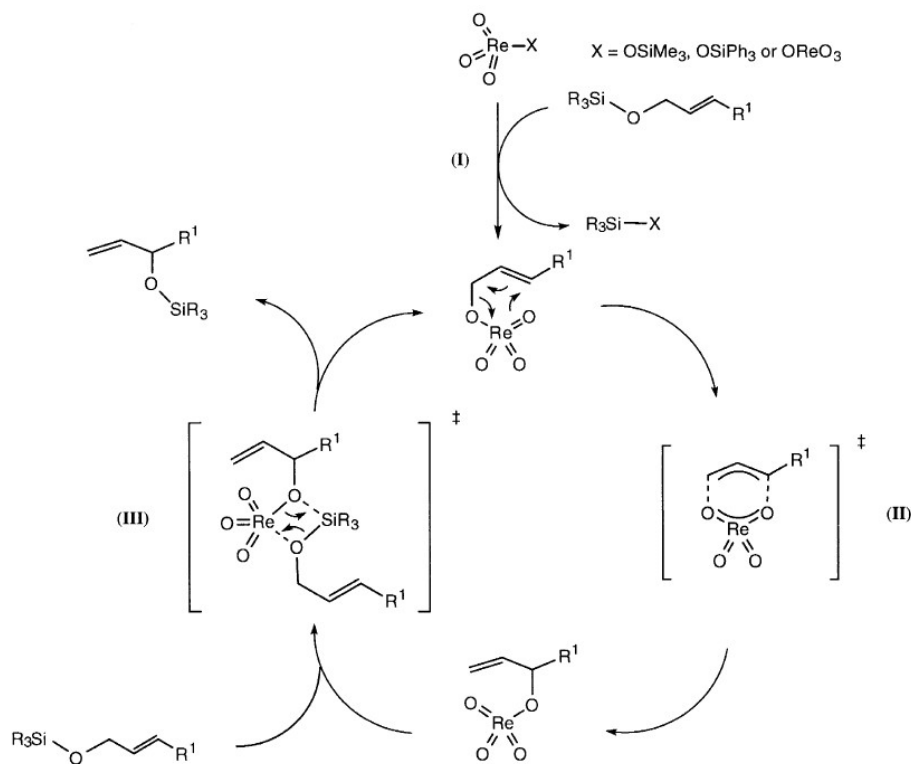


Fig. 2. Proposed mechanism of the rhenium-catalyzed isomerization of allyl silyl ethers

from: *Tet. Lett.* **2000**, 41, 1549-1552.

