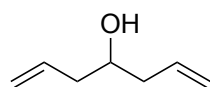
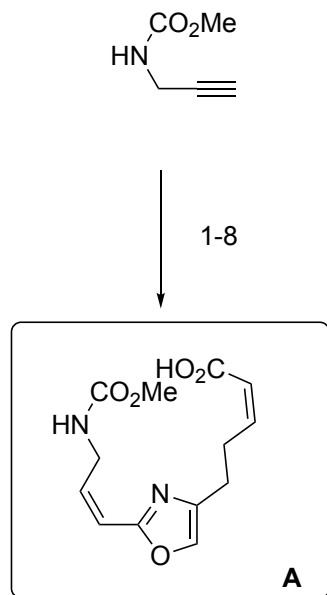


## Toatal Synthesis of Leucascandrolide A

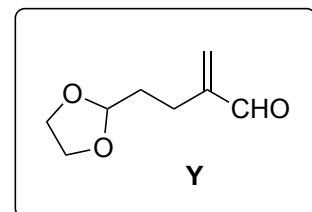
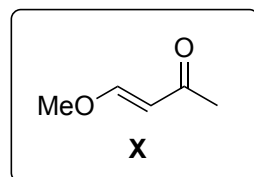
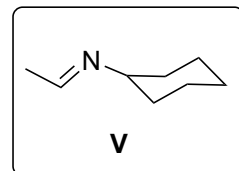
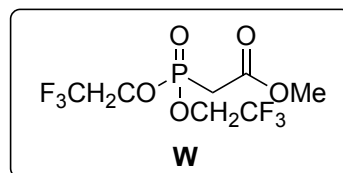
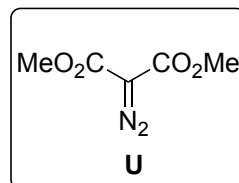
Ying Wang, Jelena Janjic, and Sergey A. Kozmin *J. Am. Chem. Soc.* **2002**, *124*, 13670–13671.

Sergey A. Kozmin *Org. Lett.* **2001**, *3*, 755–758.



9-17

- 1) *n*-BuLi, TIPSOTf, then *n*-BuLi, TsCN
- 2) **U**, Rh<sub>2</sub>(OAc)<sub>4</sub>, then HF
- 3) H<sub>2</sub>, Pd/CaSO<sub>4</sub>
- 4) LiEt<sub>3</sub>BH
- 5) PPh<sub>3</sub>, CBr<sub>4</sub>
- 6) **V**, Et<sub>2</sub>NLi, HMPA  
then substrate
- 7) **W**, KHMDS
- 8) LiOH



- 9) **X**, PPTS
- 10) TFA, then LiOH
- 11) benzyl 2,2,2-trichloroacetimidate, TfOH
- 12) **Y**, Cy<sub>2</sub>BCl, TEA
- 13) MeCHO, Sml<sub>2</sub>
- 14) MeOTf, 2,6-di-*t*-Bu-pyridine
- 15) LAH
- 16) (Me<sub>2</sub>HSi)<sub>2</sub>NH, H<sub>2</sub>PtCl<sub>6</sub>
- 17) TBAF

Hint: a cyclization happens in step 2

Step 3: name of catalyst?

Lindlar catalyst

Hint: a methoxy is eliminated in step 4

Name of step 5?

Appel reaction

Name of step 7?

HWE Still-Genari modification

Step 10: A cyclization happens. Name the reaction?

Prins reaction.

Step 11: Name of the reagent?

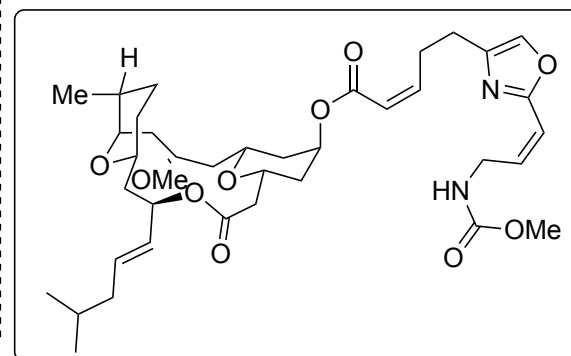
Bundles reagent

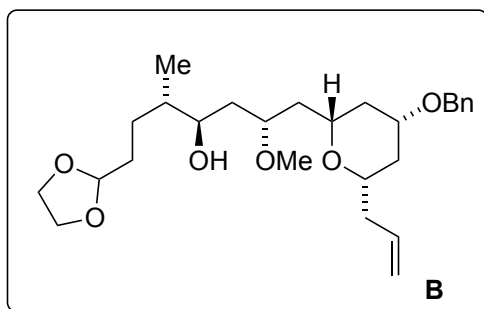
Name of step 13? Explain the selectivity by providing a transition state.

See below.

Which conditions lead to the opposite selectivity?

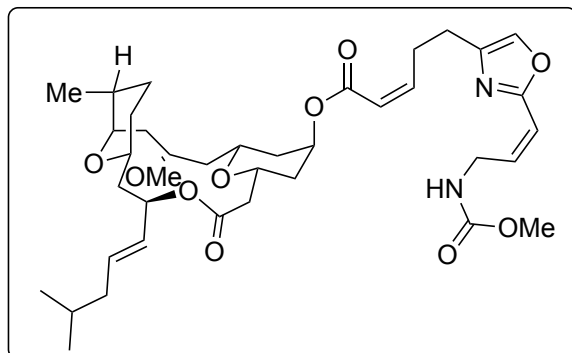
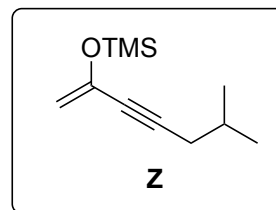
Narasaka–Prasad reduction: Bu<sub>2</sub>BOMe, NaBH<sub>4</sub>





18-26

- 18) cat.  $\text{H}_2\text{SO}_4$ , then  $\text{Ac}_2\text{O}$ , pyridine
- 19)  $\text{ZnCl}_2$ , **Z**
- 20) L-Selectride
- 21)  $\text{OsO}_4$ , NMO
- 22) Red-Al
- 23)  $\text{Pb}(\text{OAc})_4$
- 24) PCC
- 25) DDQ
- 26) DIAD,  $\text{PPh}_3$ , **A**



Hint: a lactol is formed in step 18.

Structure of Red-Al?

Hint: a spontaneous cyclization happens in this step.

Step 26: Name reaction

Mitsunobu reaction

Step 13: Evans Tishchenko reduction

