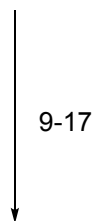
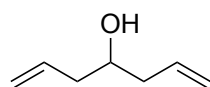
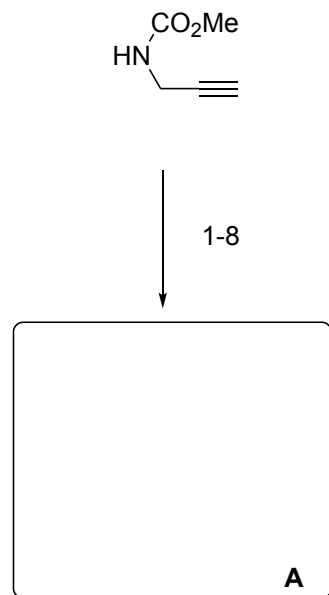


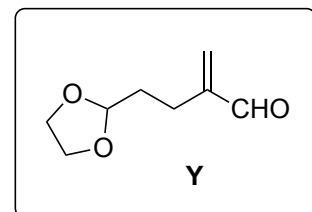
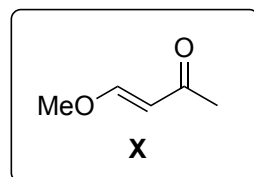
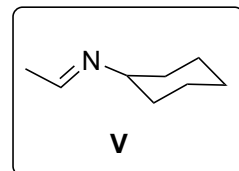
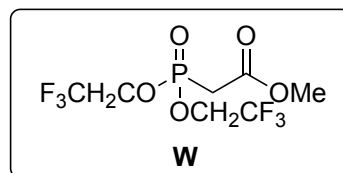
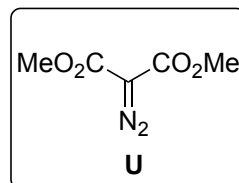
Total Synthesis of Leucascandrolide A

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.



- 1) *n*-BuLi, TIPSOTf, then *n*-BuLi, TsCN
- 2) **U**, Rh₂(OAc)₄, then HF
- 3) H₂, Pd/CaSO₄
- 4) LiEt₃BH
- 5) PPh₃, CBr₄
- 6) **V**, Et₂NLi, HMPA
then substrate
- 7) **W**, KHMDS
- 8) LiOH



- 9) **X**, PPTS
- 10) TFA, then LiOH
- 11) benzyl 2,2,2-trichloroacetimidate, TfOH
- 12) **Y**, Cy₂BCl, TEA
- 13) MeCHO, Sml₂
- 14) MeOTf, 2,6-di-*t*-Bu-pyridine
- 15) LAH
- 16) (Me₂HSi)₂NH, H₂PtCl₆
- 17) TBAF

Hint: a cyclization happens in step 2

Step 3: name of catalyst?

Hint: a methoxy is eliminated in step 4

Name of step 5?

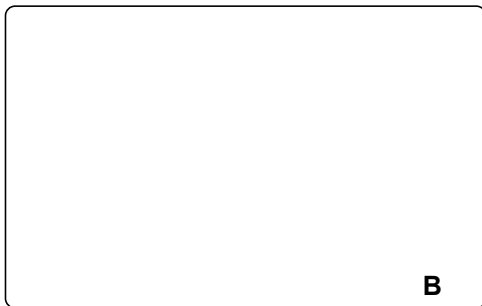
Name of step 7?

Step 10: A cyclization happens. Name the reaction?

Step 11: Name of the reagent?

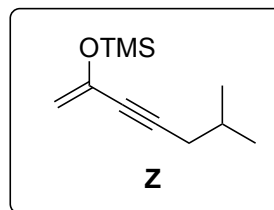
Name of step 13? Explain the selectivity by providing a transition state.

Which conditions lead to the opposite selectivity?



18-26

- 18) cat. H_2SO_4 , then Ac_2O , pyridine
- 19) ZnCl_2 , **Z**
- 20) L-Selectride
- 21) OsO_4 , NMO
- 22) Red-Al
- 23) $\text{Pb}(\text{OAc})_4$
- 24) PCC
- 25) DDQ
- 26) DIAD, 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

