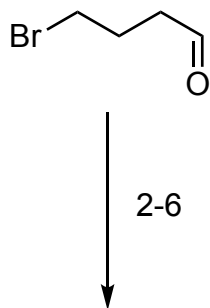
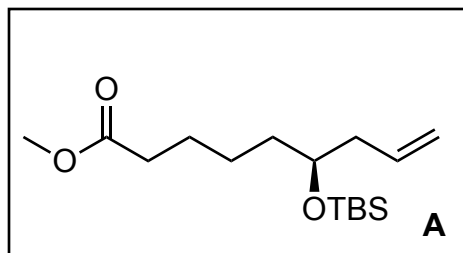
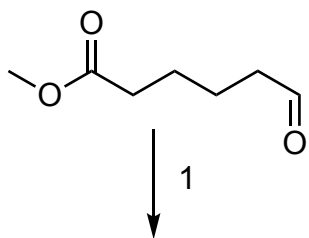


Total Synthesis of (-)-histrionicotoxin and (-)-histrionicotoxin 235A

Gilbert Stork and Kang Zhao

J. Am. Chem. Soc. **1990** 112, 5875



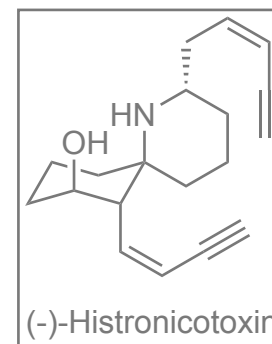
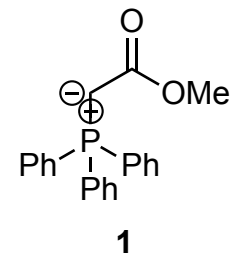
1) How? (2 steps)

- 2) **1**, THF
- 3) DIBAL
- 4) (R, R)-Diethyltartrat, (+)-DET, $\text{Ti}(\text{O}^i\text{Pr})_4$, $^t\text{BuOOH}$
- 5) $(\text{COCl})_2$, DMSO, NEt_3
- 6) $\text{Me}^+\text{PPh}_3\text{I}^-$, NaHMDS, THF

Using a borane reagent, how would you accomplish this transformation?

What model would be used to predict the stereochemistry?

Name of step 1?





7



8-9



10-15

7) LDA, -78 °C, HMPA/THF (6:11 v/v), **B**
then LDA, -78 °C, 2 h

8) O₃, then PPh₃
9) (Ph₃P⁺CH₂I)⁻, NaN(TMS)₂

10) 5% HCl, THF
11) Ph₃P, CBr₄, ether
12) NH₄Cl, AlMe₃, PhH, 40 °C
13) AcO₂, Py, DMAP
14) (CF₃CO₂)₂IPh, MeCN, H₂O
15) Et₃N, DCE, 70 °C

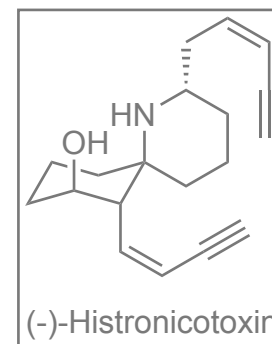
What is the mechanism of step 7?
Explain the selectivity.

What is the name of step 9 and its mechanism

hint: our colleague runs this reaction in complete darkness.

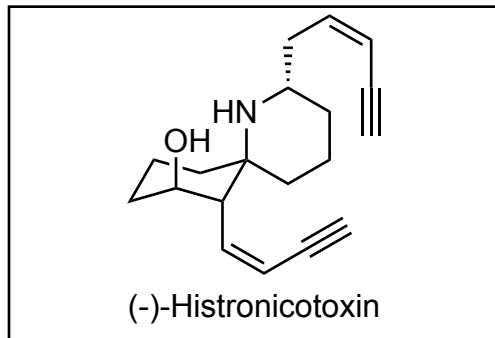
bigger hint: Look at the authors of this paper

What is the name of NaN(TMS)₂



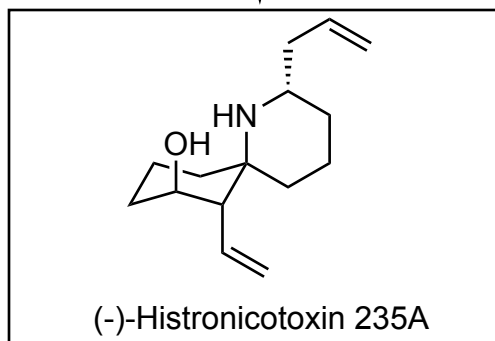


16-18



C

19-25



- 16) Pd(PPh₃)₄, CuI, PhH, TMS-acetylene
17) Bu₄N⁺F⁻
18) K₂CO₃, MeOH

- 19) 5% HCl, THF
20) Ph₃P, CBr₄, ether
21) NH₄Cl, AlMe₃, PhH, 40 °C
22) AcO₂, Py, DMAP
23) (CF₃CO₂)₂IPh, MeCN, H₂O
24) Et₃N, DCE, 70 °C
25) MeOH, Na₂CO₃ (aq)

