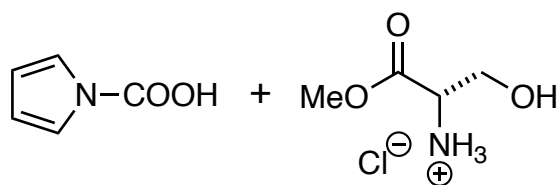


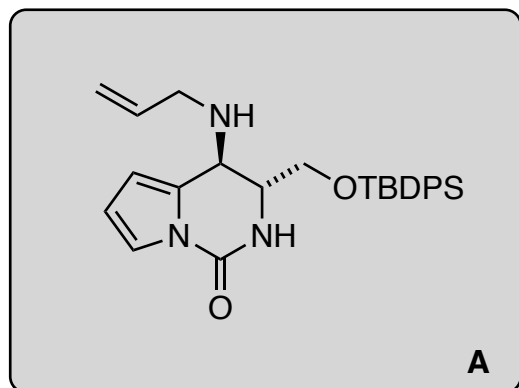
Divergent Synthesis of Natural Derivatives of (+)-Saxitoxin Including 11-Saxitoxinethanoic Acid

Walker, J. R.; Merit, J. E.; Thomas-Tran, R.; Tang, D. T. Y.; DuBois, J.

Angew. Chem. Int. Ed. **2019**, *58*, 1689–1693.

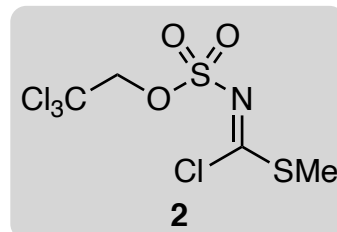
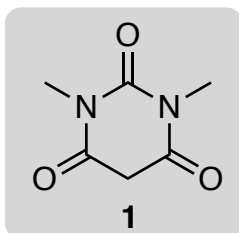


1–4



5–9

- 1) DCC, NEt₃
- 2) TBDPS-Cl, imidazole
- 3) DIBAL-H, DCM, -90°C
- 4) allylamine, *then* BF₃·OEt₂

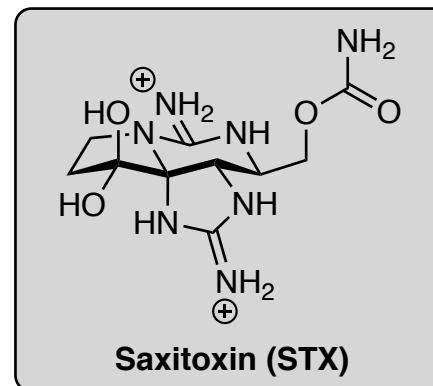


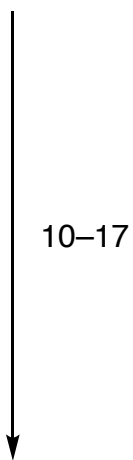
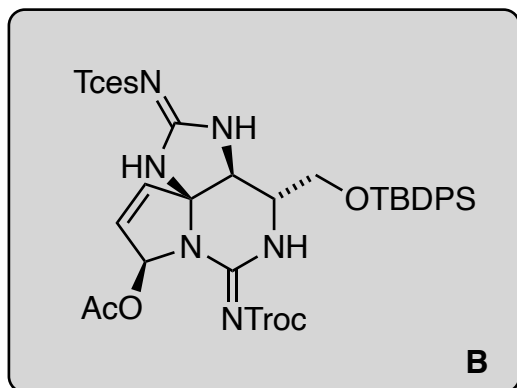
- 5) Pd(PPh₃)₄, **1**, *then* Na₂CO₃, **2**,
- 6) EtOSO₂CF₃, 2,4,6-tri-*tert*-butylpyrimidine
- 7) NH₃, NH₄OAc, MeOH
- 8) TrocNMI⁺ OTf (1.0 equiv.)
- 9) Rh₂(esp)₂ (cat.), PIDA, MgO

Step 4: Which named reaction takes place? - Pictet–Spengler reaction

Hint for step 7: Two addition/elimination reactions occur

Step 9: Please provide a mechanism for this step.





- 10) PhSH, $\text{BF}_3 \cdot \text{OEt}_2$
- 11) urea $\cdot \text{H}_2\text{O}_2$, HFIP
- 12) NaSPh, $\text{Cl}_3\text{CCH}_2\text{OH}$, 80°C
- 13) DMP
- 14) $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$, $\text{B}(\text{O}i\text{-Pr})_3$, H_2
- 15) TBAF, AcOH
- 16) CDI, then NH_3 (0.5 M in THF)
- 17) PdCl_2 , H_2 , TFA

Step 12: What is the name of this step?
Mislow–Evans rearrangement

Mechanism of step 9:

