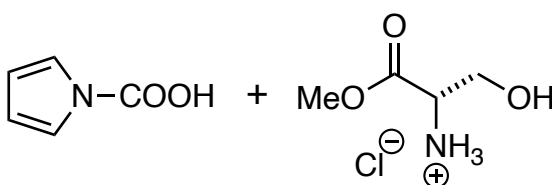


Divergent Synthesis of Natural Derivatives of (+)-Saxitoxin Including 11-Saxitoxinethanoic Acid

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

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1–4



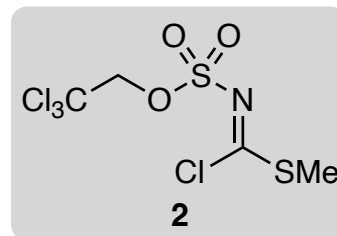
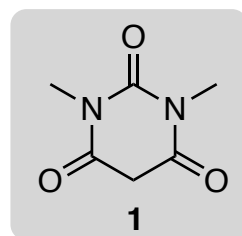
5–9



10–17



- 1) DCC, NEt_3
- 2) TBDPS-Cl, imidazole
- 3) DIBAL-H, DCM, -90°C
- 4) allylamine, *then* $\text{BF}_3 \cdot \text{OEt}_2$

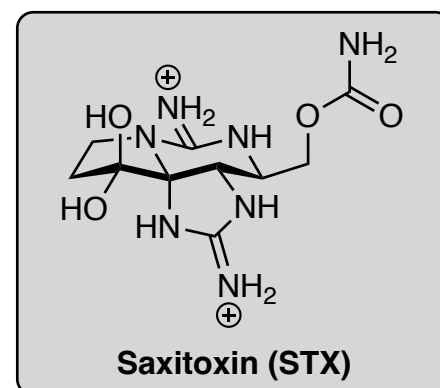


- 5) $\text{Pd}(\text{PPh}_3)_4$, **1**, *then* Na_2CO_3 , **2**,
- 6) $\text{EtOSO}_2\text{CF}_3$, 2,4,6-tri-*tert*-butylpyrimidine
- 7) NH_3 , NH_4OAc , MeOH
- 8) $\text{TrocNMI}^+ \text{OTf}^-$ (1.0 equiv.)
- 9) $\text{Rh}_2(\text{esp})_2$ (cat.), PIDA, MgO

Step 4: Which named reaction takes place?

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?