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

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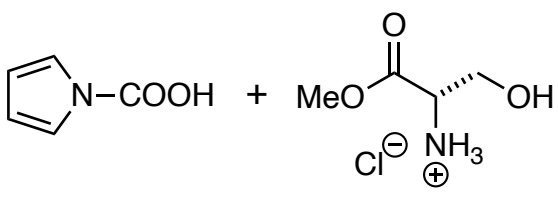
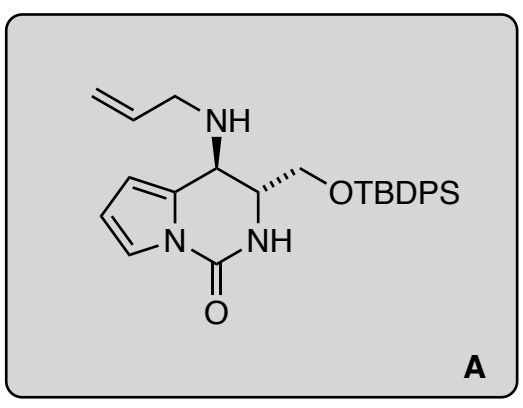
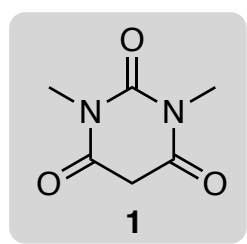


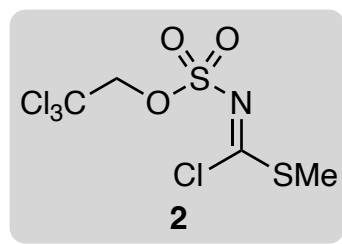
1–4

1) DCC, NEt_3
2) TBDPS-Cl, imidazole
3) DIBAL-H, DCM, -90°C
4) allylamine, *then* BF_3•OEt_2

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



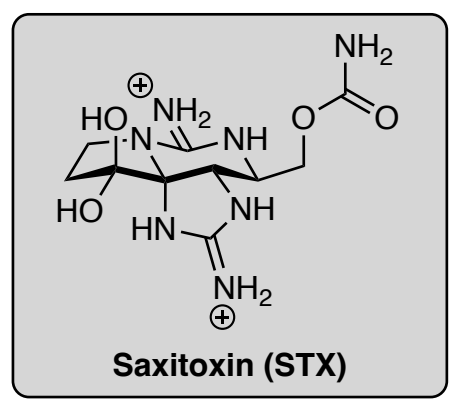


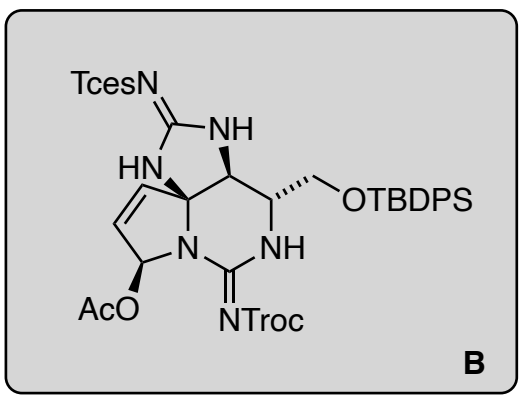


Hint for step 7: Two addition/elimination reactions occur
Step 9: Please provide a mechanism for this step.

5–9

5) $Pd(PPh_3)_4$, **1**, *then* Na_2CO_3, **2**,
6) $EtOSO_2CF_3$, 2,4,6-tri-*tert*-butylpyrimidine
7) NH_3, NH_4OAc, MeOH
8) TrocNMI$^+$ $^-$OTf (1.0 equiv.)
9) $Rh_2(esp)_2$ (cat.), PIDA, MgO

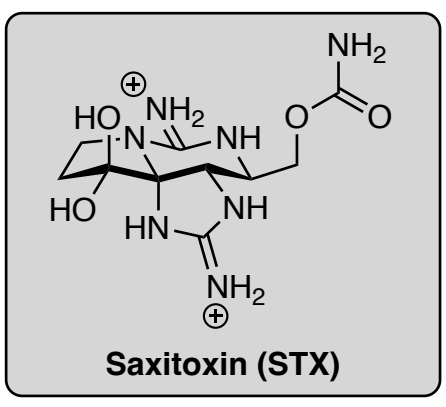




10–17

10) PhSH, BF_3 • OEt_2
11) urea • H_2O_2, HFIP
12) NaSPh, Cl_3CCH_2OH, 80°C
13) DMP
14) $[Ir(cod)(PCy_3)(py)]PF_6$, $B(Oi\text{-}Pr)_3$, 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: