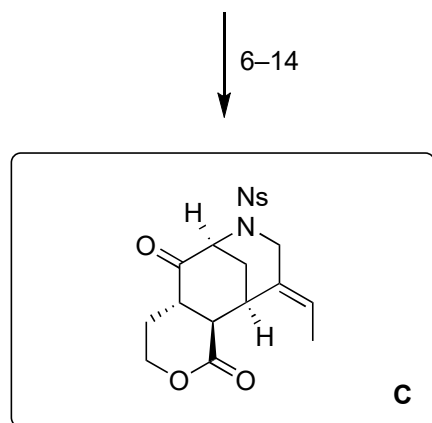
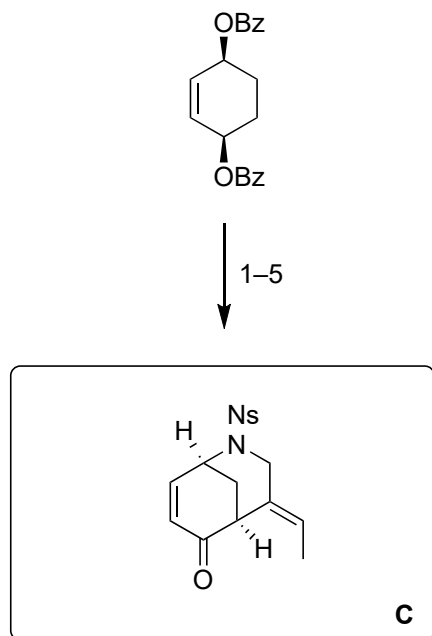


Enantioselective Total Syntheses of Akuammiline Alkaloids (+)-Strictamine, (-)-2(S)-Cathafoline, and (-)-Aspidophylline A

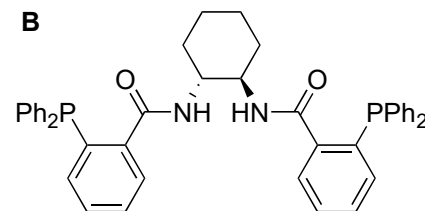
Jesus Moreno, Elias Picazo, Lucas A. Morrill, Joel M. Smith and Neil K. Garg

JACS 2016, 138, 1162–1165

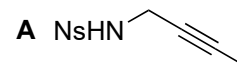
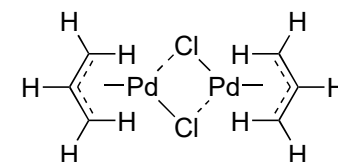


- 1) **A**, $[\text{PdCl}(\text{C}_3\text{H}_5)]_2$, **B**, Cs_2CO_3
- 2) LiOH , MeOH
- 3) PCC
- 4) TBDPSOTf , 2,6-lutidine
- 5) $\text{Au}(\text{PMe}_3)\text{Cl}$, AgOTf , PhMe/tBuOH ; then PTSA

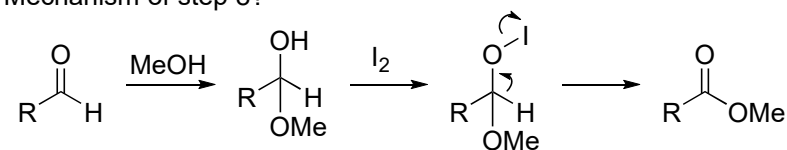
- 6) $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$, $\text{H}_2\text{O/THF}$, 65°C
- 7) $\text{Ph}_3\text{P-CH}_2\text{OMe}^+\text{Cl}^-$, KOtBu then NH_4Cl
- 8) NIS , K_2CO_3 , MeOH
- 9) NIS , $\text{H}_2\text{C=CHOEt}$
- 10) AIBN , Bu_3SnH
- 11) AcOH , $\text{H}_2\text{O/THF}$, 75°C
- 12) NaBH_4 , MeOH
- 13) PTSA , benzene, 80°C
- 14) DMP



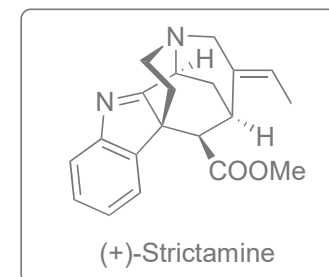
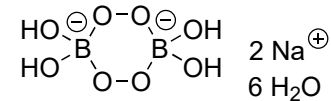
Structure of $[\text{PdCl}(\text{C}_3\text{H}_5)]_2$?

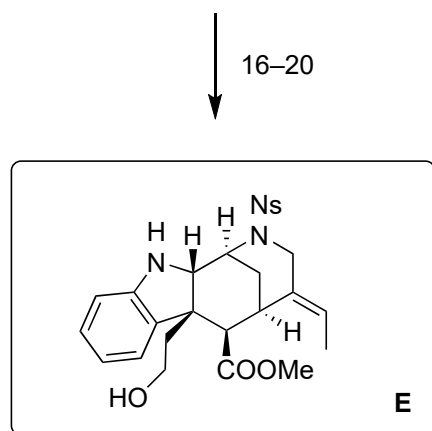
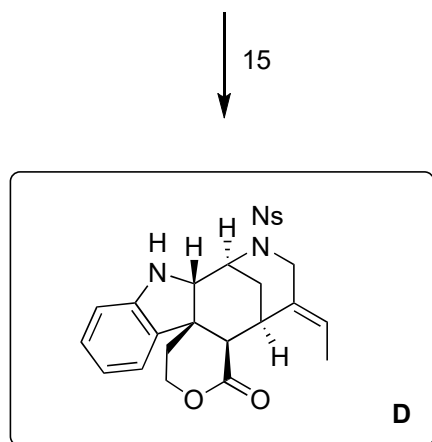


Mechanism of step 8?



Structure of $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$?





↓ 22–26

(+)-Strictamine

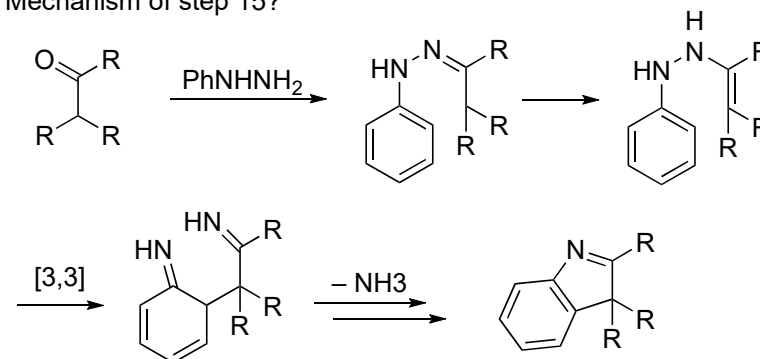
15) PhNHNH₂, TFA, DCE, 40 °C
then Et₃SiH

16) LiBH₄
17) TBSCl, imidazole, DMAP
18) DMP
19) NaClO₂, NaHPO₄,
2-methyl-2-butene,
tBuOH/H₂O/THF
20) TMSCHN₂
21) AcOH/H₂O/THF

22) MsCl, Et₃N
23) LiCl, THF, 70 °C
24) PCC
25) MetSthiol, Cs₂CO₃,
MeCN, 65 °C

MetSthiol HS—[Si]

Mechanism of step 15?



Imagine a two-step route from intermediate **D** to **E**. What could be a problem with this route?

Lactone hydrolysis followed by esterification. Treatment with NaOH/H₂O/THF followed by TMSCHN₂ only gave the undesired epimer at the position alpha to the ester functionality.

Mechanism of step 26?

