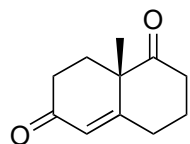
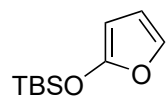
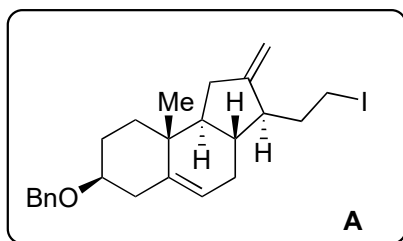


Convergent Total Synthesis of (-)-Cyclopamine

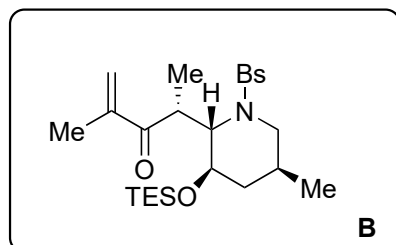
M. Sofiadis, D. Xu, A. J. Rodriguez, B. Nissl, S. Clementson, N. N. Petersen, P. S. Baran, *J. Am. Chem. Soc.* **2023**, *145*, 21760–21765.



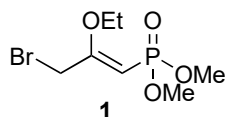
1–11



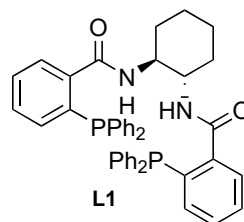
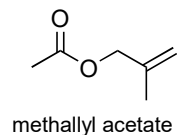
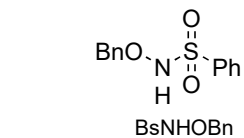
12–17



- 1) *p*TSA•H₂O, ethylene glycol
- 2) KO^tBu *then* AcOH
- 3) NaBH₄
- 4) BnBr, KHMDS *then* *p*TSA•H₂O
- 5) LDA, **1** *then* 1 M aq. HCl
- 6) Cs₂CO₃
- 7) LiHMDS, *tert*-butyl bromoacetate
- 8) Cu(OAc)₂•H₂O, dppbz, PMHS
- 9) MePPh₃Br, KO^tBu
- 10) DIBAL-H
- 11) I₂, PPh₃



- 12) Pd₂(dba)₃, L1, NH₄OAc, K₂CO₃
methallyl acetate
- 13) BsNHOBn, DBU *then* Zn, sat. aq. NH₄Cl
- 14) KO^tBu, I₂
- 15) AIBN, Bu₃SnH
- 16) LiHMDS, MeI
- 17) 2-lithiopropene *then* TESCl



6) Name of the reaction? *Horner-Wadsworth-Emmons reaction*

8) *Hint: Stryker's reagent or Sml₂ can be used.*

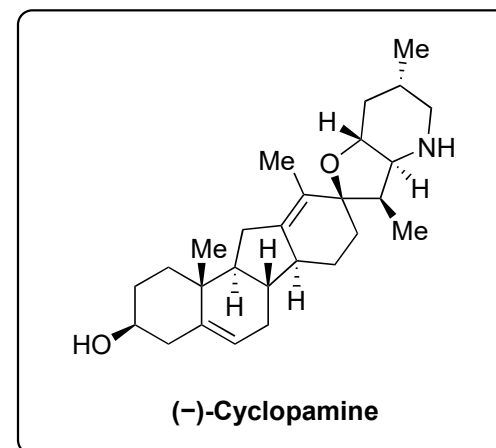
9) Name of the reaction? *Wittig olefination*

11) Name of the reaction? *Appel reaction*

12) *Hint: an Asymmetric allylic alkylation occurs*

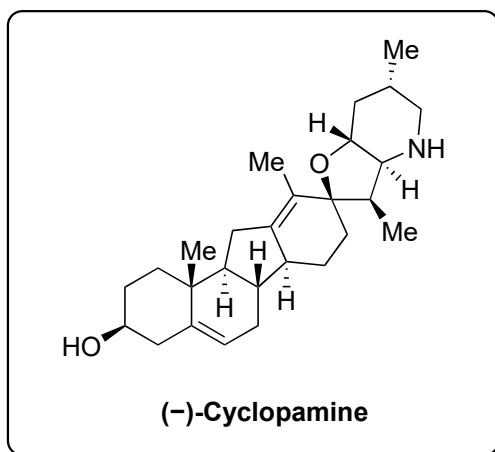
14) Name the halocyclization according to Baldwin's rules

6-endo-trig

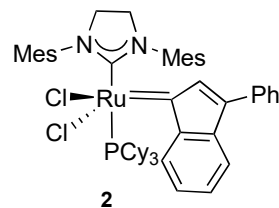


A + B

18-22



- 18) *t*BuLi, LaCl₃•2LiCl
- 19) KHMDS, Boc₂O then HF•pyr
- 20) Pd(OAc)₂, PPh₃
- 21) **2**, F₈-MePh, 70 °C
- 22) LiDBB



LiDBB = lithium 4,4'-di*tert*-butylbiphenylide

20) Name of the reaction? *Tsuji-Trost cyclization*