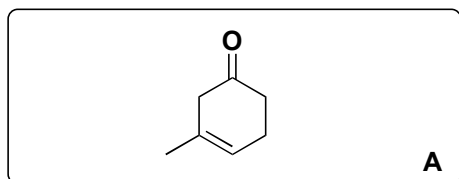


Total Synthesis of (±)-Gelsemine

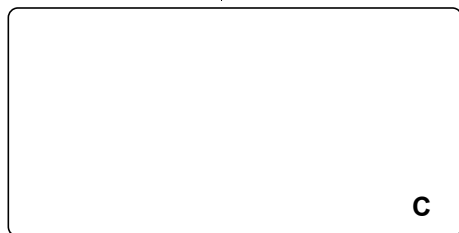
W. G. Earley, J. E. Jacobsen, A. Madin, G. P. Meier, C. J. O'Donnell, T. Oh, D. W. Old, L. E. Overman, M. J. Sharp, J. Am. Chem. Soc **2005**, 127, 18046.



↓ 1-5



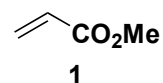
↓ 6-13



↓ 14-17



- 1) **A**, LDA, TIPSOTf
- 2) **1**, AlCl₃, -78 °C
- 3) SeO₂
- 4) Ph₃P=CH₂
- 5) KOH



- 6) DPPA, Et₃N, PMBOH, reflux
- 7) TFA, anisole
- 8) CH₂O, KCN, pH=7 buffer
- 9) TBAF
- 10) KH, 18-Crown-6, *then* ClCO₂Me
- 11) KOH
- 12) Br₂ (1.1 equiv), PMP
- 13) TFA

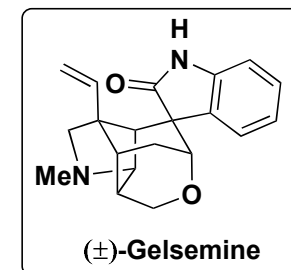
- 14) KHMDS, TESCO
- 15) PhIO, BF₃ · OEt₂, MeOH, CH₂Cl₂
- 16) KHMDS, Comin's reagent
- 17) CO, PdCl₂(dppf), MeOH, DMF, n-Bu₃N, 80 °C

- 2) Name of the reaction
- 3) Name of the reaction
- 4) Name of the reaction

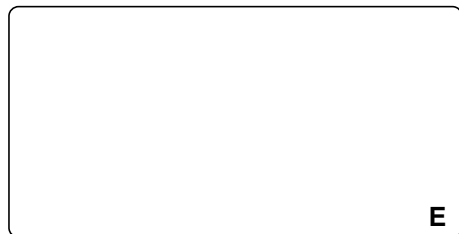
- 6) Name of the reaction
Structure of DPPA
Provide a mechanism

- 10) Name of the reaction
Provide a mechanism
- 11) *Hint*: Selective cleavage
- 13) *Hint*: 5/5/6 system is formed

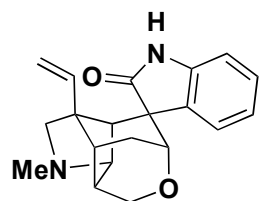
- 16) Structure of Comin's reagent



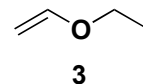
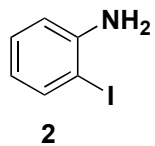
18-22



23-31



- 18) **2**, AlMe₃
- 19) NaH, MOMCl
- 20) Pd₂(dba)₃, Ag₃PO₄, Et₃N, THF
- 21) HCl, MeOH
- 22) DIBAL-H



- 23) PPTS, **3**
- 24) NaCN, DMSO, 150 °C
- 25) MeOTf, CH₂Cl₂, DTBMP
- 26) NaCN, DMSO, 90 °C
- 27) TsOH
- 28) DBU, toluene, 110 °C
- 29) HCl, *i*-Pr₂NEt
- 30) DIBAL-H
- 31) Et₃SiH, TFA, 45 °C

20) Name of reaction

21) This is not a MOM cleavage

24) *Hint*: An aziridine is formed