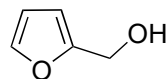


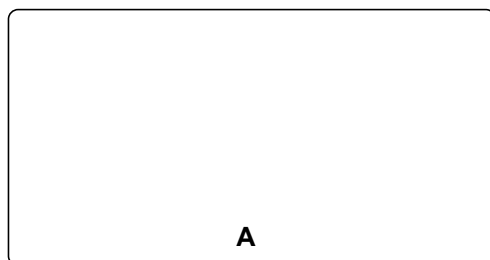
Total Synthesis of Gelsemoxonine

Jun Shimokawa, Takaaki Harada, Satoshi Yokoshima, Tohru Fukuyama

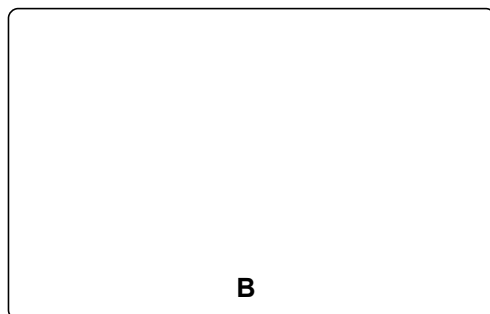
J. Am. Chem. Soc. **2011**, *133*, 17634–17637



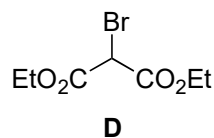
1-8



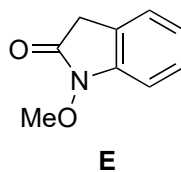
9-12



- 1) *m*-CPBA
- 2) Lipase AR, vinyl acetate
- 3) Lipase CR, *n*-BuOH/*n*-Hexane
- 4) **D**, DBU
- 5) TMSOTf, Et₃SiH
- 6) NaBH₄, MeOH
- 7) Piv₂O, pyridine, DMAP
- 8) IBX



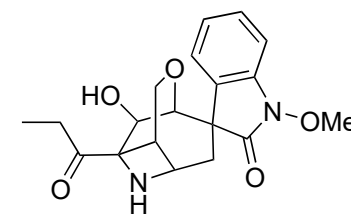
- 9) **E**, *n*-Bu₂BOTf, *i*-Pr₂NEt
- 10) MsCl, TMEDA
- 11) TMSCl, LHMDS
- 12) Toluene, 70 °C then AcOH, TBAF



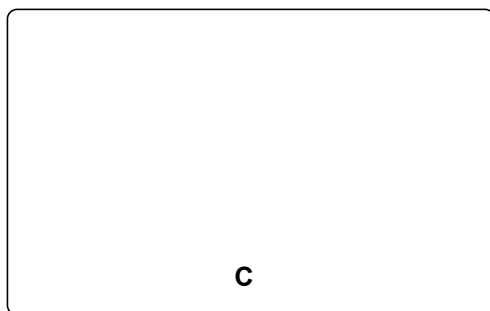
1) Name of reaction?

Hint: 74 % ee in 2), 99 % ee in 3)

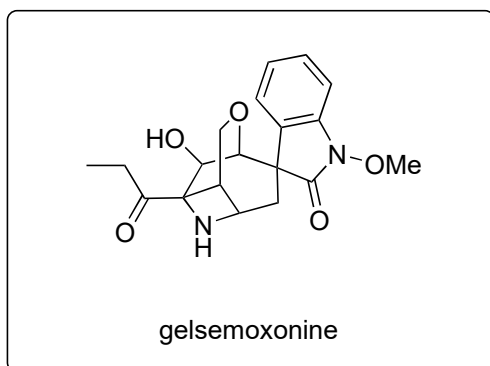
12) Name of reaction?



13-18

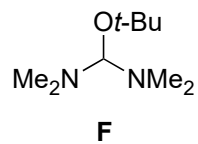


19-27



- 13) NaH, MeOH
- 14) TEMPO, PhI(OAc)₂
- 15) TMSCN, DBU *then* allyl alcohol
- 16) Pd(PPh₃)₄, pyrrolidine
- 17) (COCl)₂
- 18) NaN₃
- 19) BnOH, 80 °C

- 20) **F**, 70 °C
- 21) (COCl)₂, DMF
- 22) Pd(PPh₃)₄, Et₃SiH, NEt₃
- 23) EtMgBr
- 24) IBX
- 25) TBHP, Triton B
- 26) TMSI
- 27) EtOH, reflux



Hint: An isomerization takes place in 15)

18)+19) Name of reaction?

Triton B

