Total Synthesis of Gelsemoxonine

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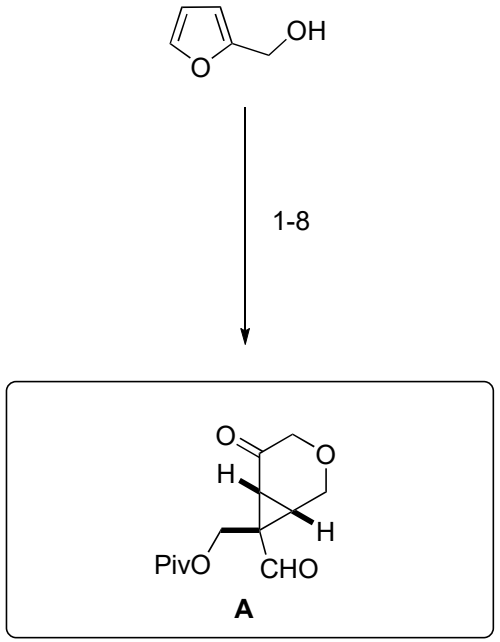
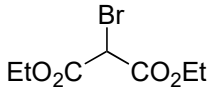
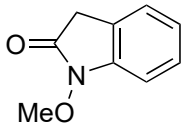


1) *m*-CPBA
2) Lipase AR, vinyl acetate
3) Lipase CR, *n*-BuOH/*n*-Hexane
4) **D**, DBU
5) TMSOTf, Et_3SiH
6) $NaBH_4$, MeOH
7) Piv_2O, pyridine, DMAP
8) IBX



D

9) **E**, *n*-Bu_2BOTf, *i*-Pr_2NEt
10) MsCl, TMEDA
11) TMSCl, LHMDS
12) Toluene, 70 °C *then* AcOH, TBAF

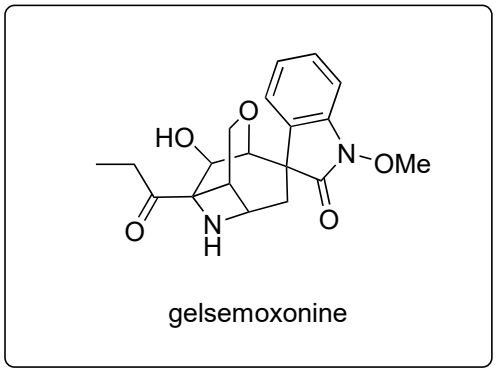


E

1) Name of reaction? Achmatowicz

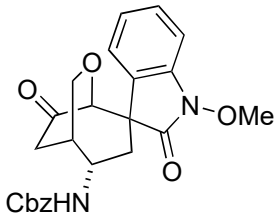
Hint: 74 % ee in 2), 99 % ee in 3):
Step 3) to get rid of unwanted stereoisomer

12) Name of reaction?
Cope rearrangement



gelsemoxonine

13-19



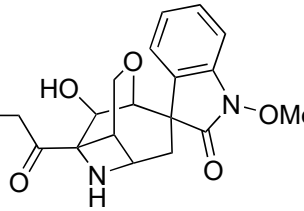
C

13) NaH, MeOH
14) TEMPO, $PhI(OAc)_2$
15) TMSCN, DBU *then* allyl alcohol
16) $Pd(PPh_3)_4$, pyrrolidine
17) $(COCl)_2$
18) NaN_3
19) BnOH, 80 °C

Hint: An isomerization takes place in 15)

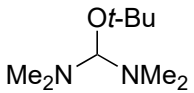
18)+19) Name of reaction? Curtius rearrangement

20-27



gelsemoxonine

20) **F**, 70 °C
21) $(COCl)_2$, DMF
22) $Pd(PPh_3)_4$, Et_3SiH, NEt_3
23) EtMgBr
24) IBX
25) TBHP, Triton B
26) TMSI
27) EtOH, reflux



F

Triton B