Total Synthesis of (±)-Ginkgolide B

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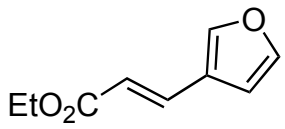


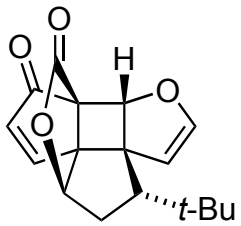
1–5

1) *t*-$Bu_2CuCNLi_2$
2) *i*-Bu_2AlH
3) MgBr—≡
4) TESCl
5) *n*-BuLi, $ClCO_2Et$

B

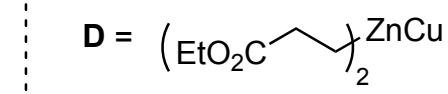
6–11

6) **D**, THF/HMPA
7) hv, 366 nm
8) aq. HF, then MsCl, NEt_3,
9) EtOH, reflux,
then benzene PPTS
10) PhSeCl, HCl, then $NaIO_4$



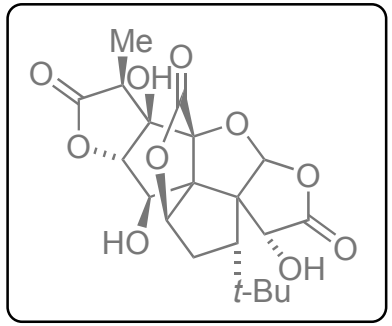
C

Step 3: Only the syn alcohol is used. How would you recycle the *anti*-diasteromer?

D = 

How can **D** be prepared?

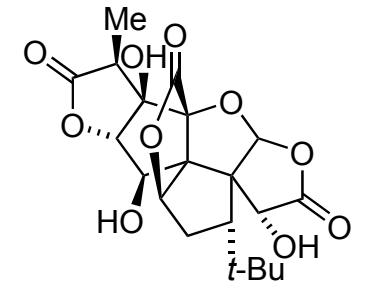
Step 8: Hint: the benzene, PPTS step is needed to complete conversion

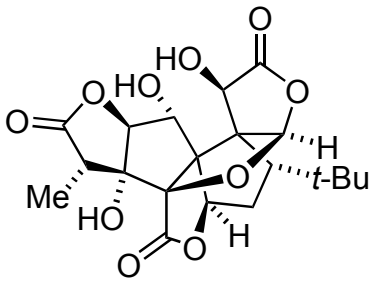


11–16

E

17–22





ginkgolide B

11) DMDO, then H_2O, *p*-TsOH
12) MeOH, *p*-TsOH, $CH(OMe)_3$
13) CS_2, DBU, then MeI
14) AIBN, Bu_3SnH, 60 °C
15) $HNEt_2$, *t*-BuLi, Davis oxaziridine
16) $(EtCO)_2O$, Et_3N

17) LDA, –78 °C
18) CSA, MeOH
19) PPTS, pyridine, C_6H_5Cl, reflux
20) $VO(acac)_2$, t-BuOOH,
then *p*-TsOH
21) DMDO
22) HOAc, NaOAc, Br_2

Step 17: Diastereomeric mixture obtained. Only the syn is used in the further steps