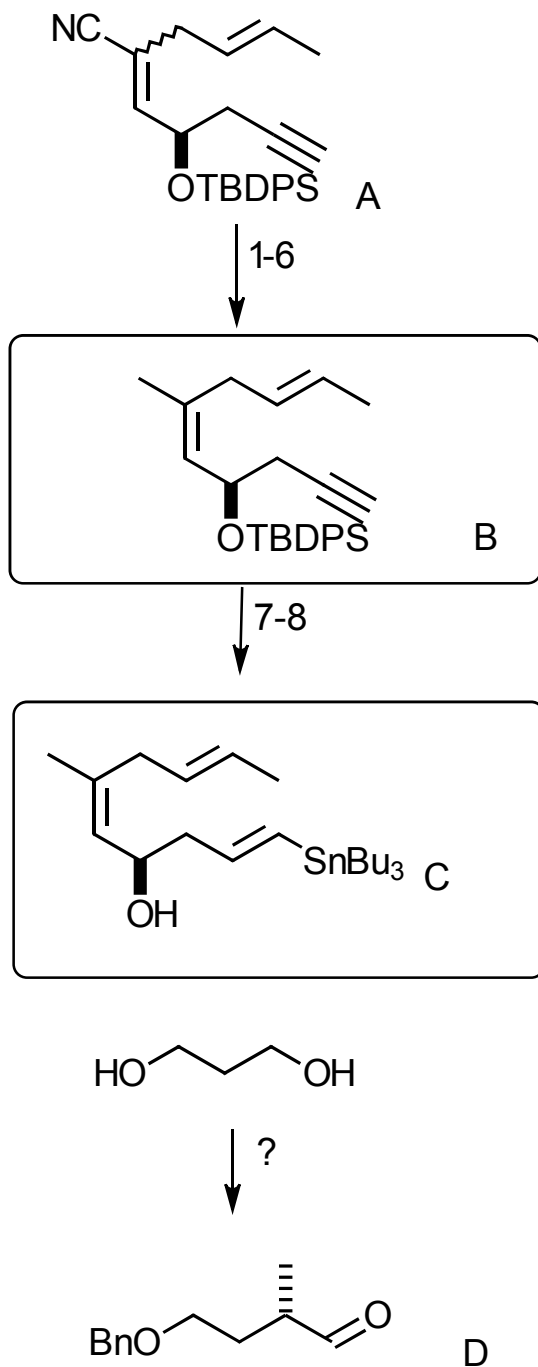


Synthesis Challenge # 46

Total Synthesis of Biselyngbyolide B,

E. Sato, Y. Tanabe, N. Nakajima, A. Ohkubo, K. Suenaga, *Org. Lett.*, **2016**, ASAP, DOI: 10.1021/acs.orglett.6b00660

28.04.2016



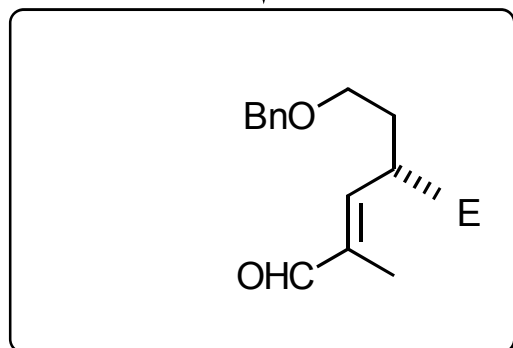
- 1) DIBAL
- 2) HCl, aq. THF
- 3) NaBH₄, MeOH
- 4) MsCl, Et₃N
- 5) LiBr, THF
- 6) LiBHEt₃, THF

- 7) TBAF, THF
- 8) Bu₃SnH, Pd(PPh₃)₄, benzene

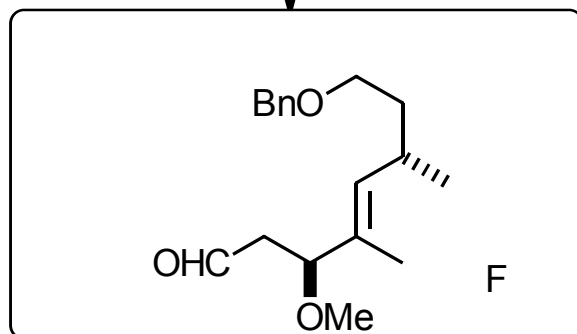
Please, design a synthesis of D from 1,3-propanediol.

Coppi, A.; Ricci, A.; Taddei, M. *J. Org. Chem.* **1988**, *53*, 911–913.
Heapy, A. M.; Wagner, T. W.; Brimble, M. M. *Synlett* **2007**, 2359–2362.

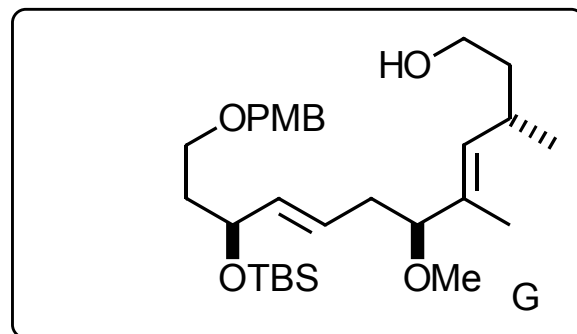
9-11



12-16



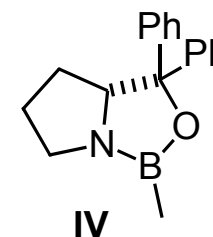
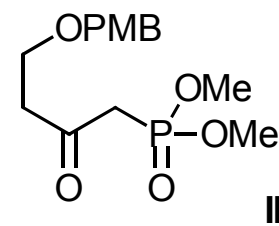
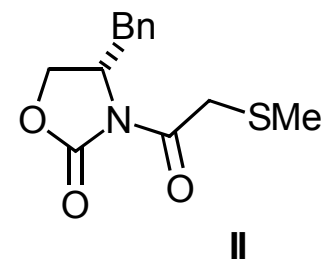
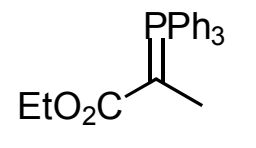
17-20



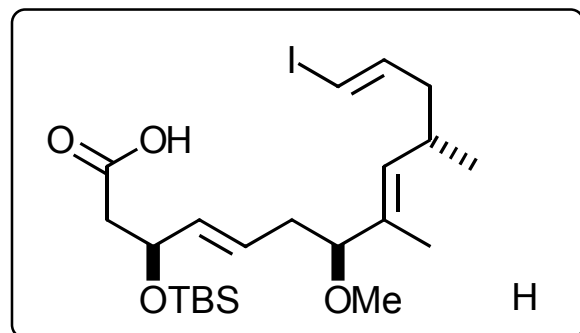
9) **I**, benzene reflux
10) DIBAL
11) DMP

12) **II**, TiCl₄, *i*Pr₂NEt, *N*-Me-pyrrolidone
13) Bu₃SnH, AIBN, benzene reflux
14) Me₃OBf₄, proton sponge
15) LiBH₄, Et₂O, H₂O
16) DMP

17) **III**, NaH
18) BH₃*SMe₂, (*R*)-Me-CBS (**IV**), toluene
19) TBSCl, imidazole, DMF
20) LiDBB, THF, -78°C

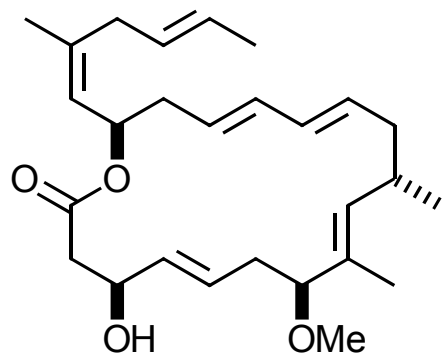


21-25



C + **H**

26-29



- 21) TMPO, BAIB, CH₂Cl₂
- 22) CHI₃, CrCl₂, THF/dioxane
- 23) DDQ, ph 7 buffer
- 24) DMP
- 25) NaClO₂, NaH₂PO₄, 2-Me-2-butene
t-BuOH

- 26) MNBA, DMAP, Et₃N, CH₂Cl₂
- 27) Pd₂(dba)₃, LiCl, DMF
- 28) TBAF, AcOH, THF

MNBA = 2-Methyl-6-nitrobenzoic anhydride