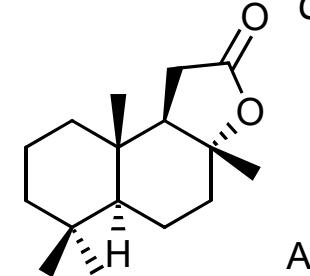


# Synthesis Challenge # 61

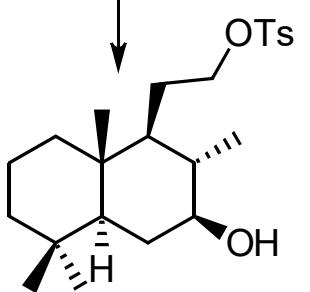
Total Synthesis and Stereochemical Assignment of Actinoranone, Y. Guo, M. Zhao, Z. Xu, T. Ye,

Chem. Eur. J. 2017, 23, ASAP, DOI: 10.1002/chem.201700476

02.03.2017

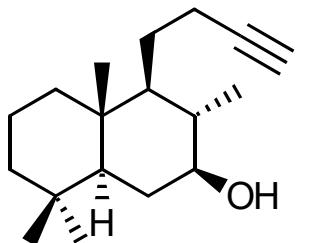


A



B

↓ 3-5

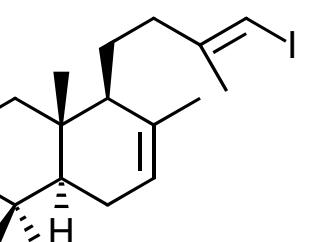


C

multiple steps, then:  
1) TBAF, THF  
2) TsCl, NEt<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>

3) TESOTf, 2,6-lutidine, CH<sub>2</sub>Cl<sub>2</sub>,  
-78 to -50 °C  
4) NaI, acetone, reflux  
5) TMS acetylene, nBuLi, THF, HMPA;  
TBAF, THF

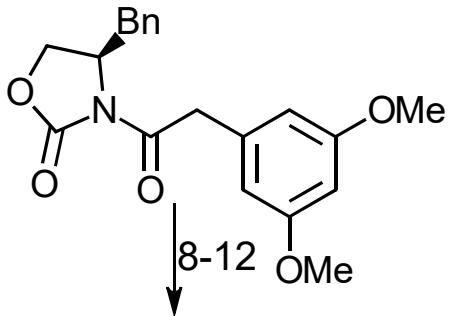
6) AlMe<sub>3</sub>, ZrCp<sub>2</sub>Cl<sub>2</sub>, then I<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>  
7) MsCl, NEt<sub>3</sub>, DMAP;  
LiBr, Li<sub>2</sub>CO<sub>3</sub>, DMF, 150°C



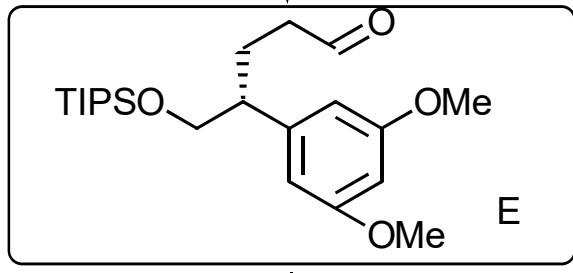
D

Please provide a synthesis strategy from A to B.

S. Poigny, S. Nouri, A. Chiaroni,  
M. Guyot, M. Samadi, *J. Org. Chem.*  
**2001**, 66, 7263.

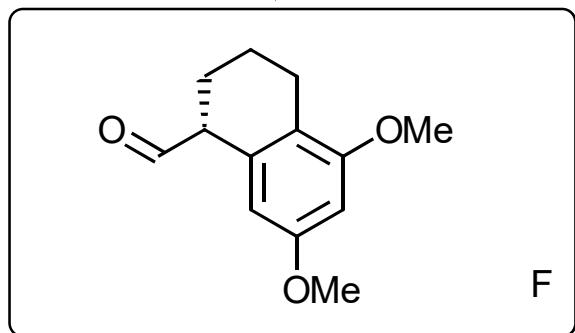


- 8) LiHMDS, allyl bromide, THF,  
-78 to -30°C
- 9) LiBH<sub>4</sub>, THF/MeOH, 0°C-RT
- 10) TIPSCl, imidazole, CH<sub>2</sub>Cl<sub>2</sub>
- 11) 9-BBN, THF ; then H<sub>2</sub>O<sub>2</sub>,  
Na<sub>2</sub>CO<sub>3</sub> (aq.)
- 12) SO<sub>3</sub>·Py, DMSO, NEt<sub>3</sub>



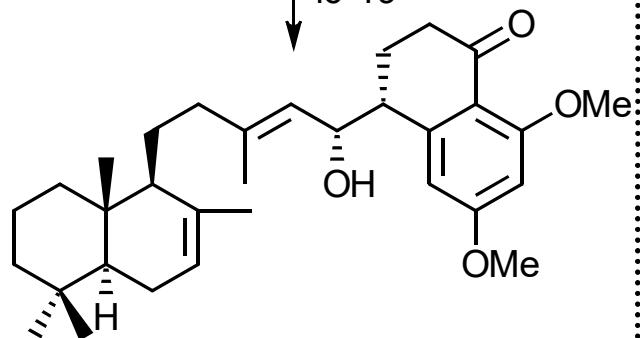
13-15

- 13) *p*-TSA, toluene
- 14) Pd/C, H<sub>2</sub>, EtOH ;
- 15) TBAF, THF; Dess-Martin  
periodinane, CH<sub>2</sub>Cl<sub>2</sub>, NaHCO<sub>3</sub>



16-19

- 16) D, *n*BuLi, Et<sub>2</sub>O, then F,  
-78°C to -60°C, d.r.=5:1
- 17) PNB-Cl, DMAP, NEt<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>
- 18) DDQ, dioxane, buffer pH 7.0
- 19) LiOH, THF/H<sub>2</sub>O



TMCDA = *trans*-N,N,N',N'-tetramethyl  
1,2-diamino-cyclohexane

PNB = *p*-nitrobenzoyl chloride