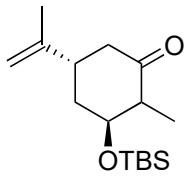
Synthesis Challenge 94

AG Wegner

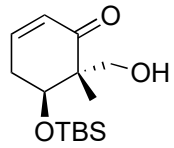
15.04.2021



A

1-3

1) DBU, HCHO (aq.), THF
2) O_3, $Cu(BF_4)_2$, $Fe(BF_4)_2$, MeOH

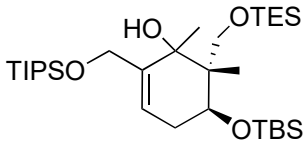


B

4-7

4) TESCl, imidazole, DMAP DMF
5) HCHO (aq.), $P(nBu)_3$, THF
6) TIPSCl, imidazole, DMAP, DCM
7) MeLi, Et_2O

Step 5) Baylis-Hillman reaction



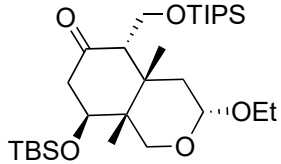
C

8-11

8) PDC, toluene, CH_3CN
9) PPTS
10) $PhNMe_2$, 1,2-dibromo-1-ethoxyethane
11) $(nBu)_3SnH$, AIBN, toluene

What is the name of the reaction in s

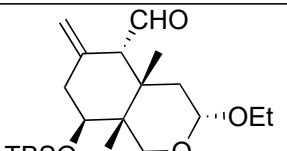
Ueno-Stork radical cyclisation



D

12-15

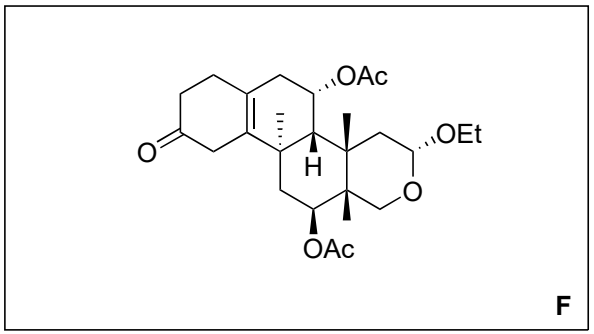
12) Ph_3PCH_3Br, tBuOK, THF
13) TBAF, THF
14) *p*-TSA, EtOH/$CHCl_3$
15) DMP, DCM



E

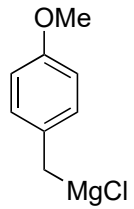
tep 11)?

16-20



F

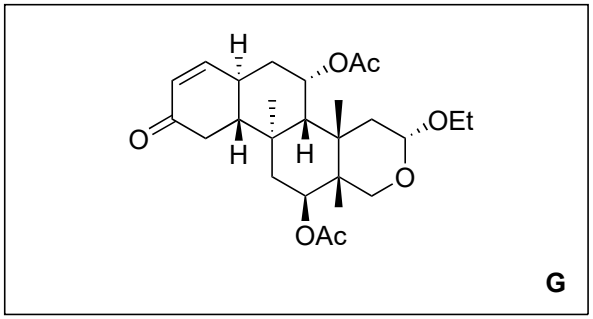
16) **I**, THF
17) Ac_2O, NEt_3
18) Co(salen^{tBu,tBu})Cl, $PhSiH_3$, acetone, then TBAF, NaOH(aq.)
19) Na, NH_3 (l)
20) Ac_2O, DMAP, then (CO_2H) (aq.)



I

TIP: Step 18 and 21 proceed via HAT

21-23

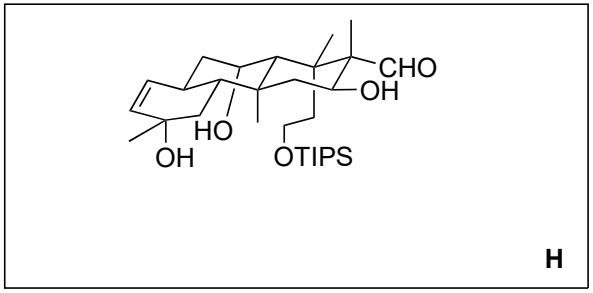


G

21) $Mn(dpm)_3$, $PhSiH_3$, TBHP, *i*PrOH, then IBX, DMSO, THF
22) NEt_3, TMSOTf
23) IBX, MPO, DMSO

IBX/4-methoxypyridine N-oxide

24-28

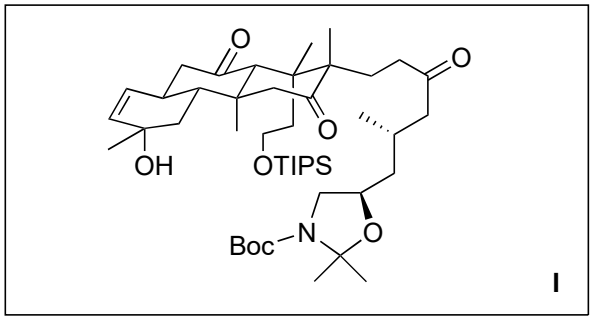


H

24) CSA, H_2O, CH_3CN
25) MeLi, Thf, then EtOH
26) $LiAlH_4$, THF
27) TIPSOTf, imidazole, THF/CH_3CN
28) $PhI(OAc)_2$, TEMPO, DCM

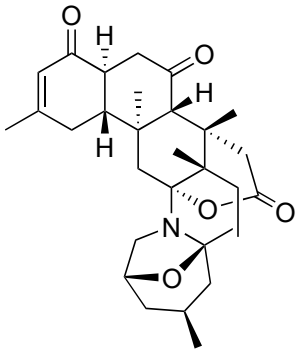
Γ (Hydrogen Atom Transfer) radical reactions

29-32



I

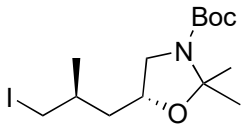
33-36



29) (*Z*)-1-bromo-2-ethoxyethene, *t*BuLi, THF, then $(CO_2H)_2$ (aq.)
30) **II**, *t*BuLi, Et_2O/THF
31) TPAP, NMO
32) $Pd(PPh_3)_4$, $(nBu)_3SnH$

33) TBAF
34) PCC. AcONa
35) 2-methyl-2-butene, $NaClO_2$, NaH_2PO_4, *t*BuOH/THF/H_2O
36) AcOH, H_2O, 100ºC, then Na_2SO_4

Steo 31) Ley-Griffith oxidation



II

Step 35) Pinnick-Lindgren-Kraus oxidation

Please, provide a beatuful 3D drawing

of the final product!