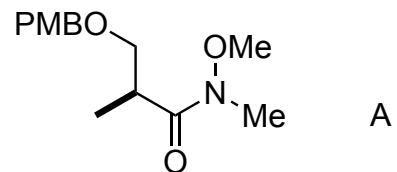


Synthesis Challenge #12 AG Wegner  
JLU Giessen  
06.02.2014



1-3



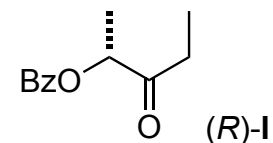
4-6



1) TBSO(CH<sub>2</sub>)<sub>4</sub>MgBr, THF, -78 °C,  
2) LiHMDS, THF ; Comins reagent, -78 - 20 °C,  
3) (MeBO)<sub>3</sub>, [Pd(PPh<sub>3</sub>)<sub>4</sub>] (10 mol %), K<sub>2</sub>CO<sub>3</sub>, dioxane, 50°C

4) DDQ, pH 7 buffer, CH<sub>2</sub>Cl<sub>2</sub>  
5) DMP, NaHCO<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>  
6) (R)-I, *c*-Hex<sub>2</sub>BCl, Et<sub>3</sub>N, Et<sub>2</sub>O, -78 - 20°C

What is Comins's reagent?



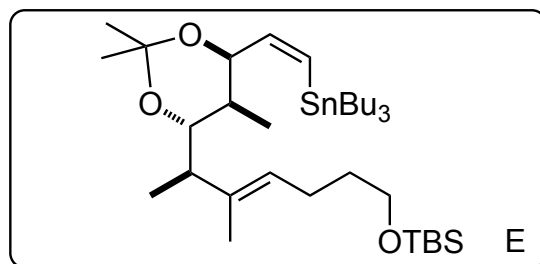
Please, provide a detailed mechanism for step 6).

↓  
7-10



- 7) TMSCl, imid, CH<sub>2</sub>Cl<sub>2</sub>
- 8) LiCCTMS, THF, -78 °C
- 9) K<sub>2</sub>CO<sub>3</sub>, MeOH
- 10) NaIO<sub>4</sub>/SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>

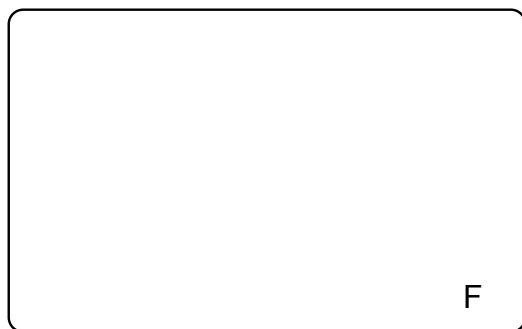
↓  
11-14



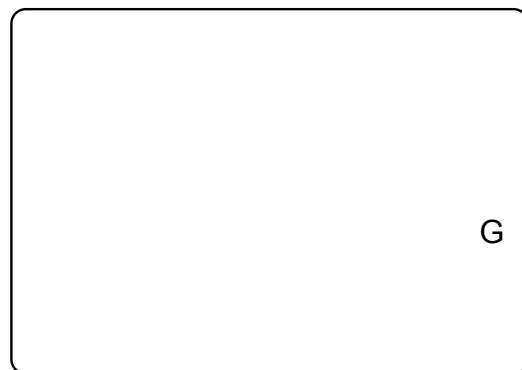
- 11) NaI, AcOH, THF
- 12) NBH(OAc)<sub>3</sub>, MeCN, AcOH (3:1), -30°C,
- 13) Me<sub>2</sub>C(OMe)<sub>2</sub>, PPTS, CH<sub>2</sub>Cl<sub>2</sub>,
- 14) *t*BuLi, Bu<sub>3</sub>SnCl, Et<sub>2</sub>O, -78°C

(R)-I

↓ 15-18

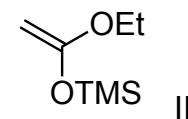


↓ 19-20

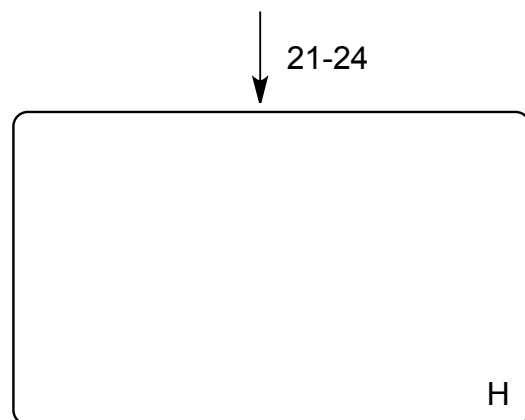


15) *c*-Hex<sub>2</sub>BCl, Et<sub>3</sub>N, Et<sub>2</sub>O; EtCHO, -78 - 20°C,  
16) TBSOTf, 2,6-lutidine, CH<sub>2</sub>Cl<sub>2</sub>, -78°C  
17) H<sub>2</sub>C=CHCH<sub>2</sub>MgBr, THF, -78°C  
18) NaIO<sub>4</sub>, MeOH, pH 7 buffer

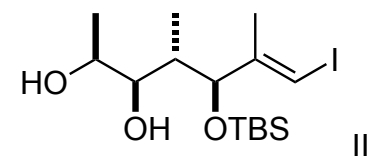
19) II, BF<sub>3</sub>·OEt<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, -78°C  
20) 3M HCl, THF, H<sub>2</sub>O



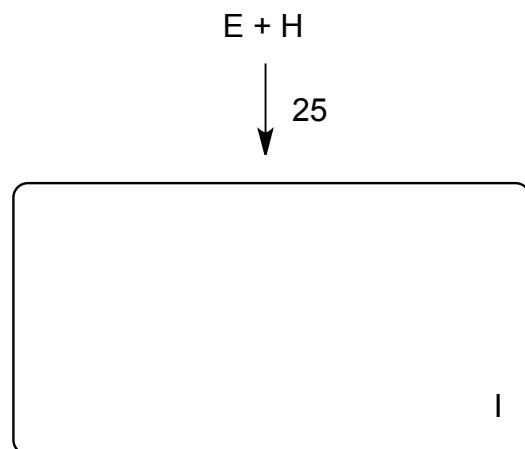
Please, provide a detailed Mechanism for step 19).



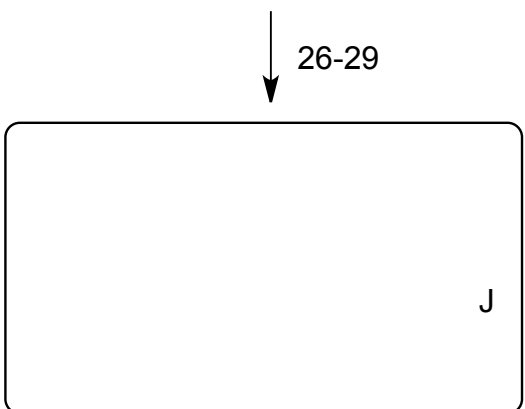
21) TMSCl, imid, CH<sub>2</sub>Cl<sub>2</sub>  
 22) **III**, Pd(OAc)<sub>2</sub> (10 mol %),  
 Ag<sub>2</sub>CO<sub>3</sub>, DMF, 80 °C  
 23) NaIO<sub>4</sub>/ SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>  
 24) [ICH<sub>2</sub>PPh<sub>3</sub>]I, NaHMDS, THF, -78 °C



Please, provide a synthesis of **III**.



25) [Pd(PPh<sub>3</sub>)<sub>4</sub>](10 mol %), CuTC,  
 Bu<sub>4</sub>NPh<sub>2</sub>PO<sub>2</sub>, DMF



26) HF·py, pyridine, THF  
 27) TEMPO, PhI(OAc)<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>  
 28) NaClO<sub>2</sub>, NaH<sub>2</sub>PO<sub>4</sub>, 2-methyl-2-butene, tBuOH, H<sub>2</sub>O, THF  
 29) TBAF, THF, 50 °C

What is the name of the reaction in step 28)?

30-32

30) TCBC, Et<sub>3</sub>N, THF; DMAP, PhMe  
31) Dowex 50WX8, MeOH  
32) TMS-imidazole, CH<sub>2</sub>Cl<sub>2</sub>; PPTS,  
MeOH; Cl<sub>3</sub>CCONCO, CH<sub>2</sub>Cl<sub>2</sub>, -78  
°C; Al<sub>2</sub>O<sub>3</sub>; PPTS, MeOH

TCBC = 2,4,6-trichlorobenzoyl chloride

