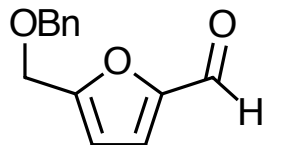


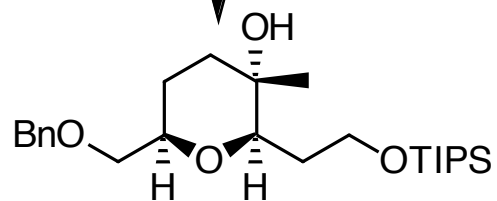
# Synthesis Challenge # 31

AG Wegner

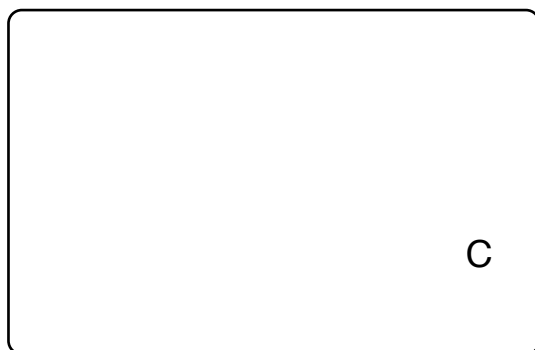
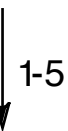
09.04.2015



A



B

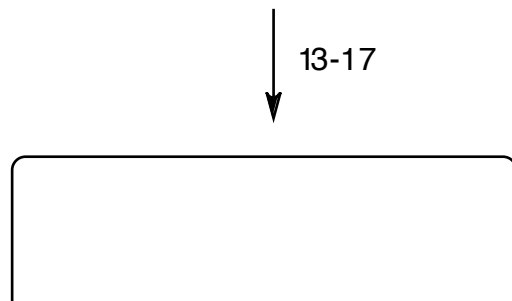
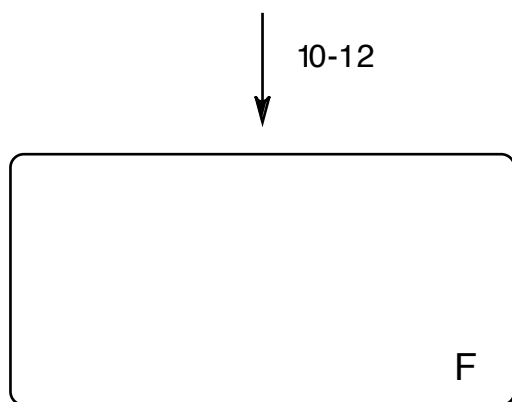
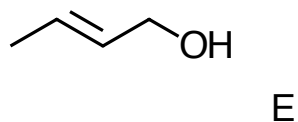
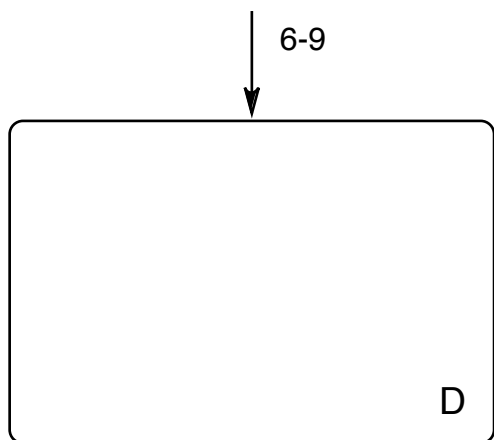


C

Please design an asymmetric synthesis of B starting from A.

- 1)  $\text{Ac}_2\text{O}$ ,  $i\text{Pr}_2\text{NEt}$ , DMAP
- 2)  $\text{Pd}(\text{OH})_2/\text{C}$  (10 mol %),  $\text{H}_2$  (1.0 atm)
- 3) DMP,  $\text{NaHCO}_3$
- 4)  $\text{CeCl}_3$ , MeLi, THF,  $-78^\circ\text{C}$
- 5) DMP,  $\text{NaHCO}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,

Please, provide a detailed mechanism for step 3 and 5).



- 6)  $\text{CeCl}_3$ , vinylMgBr
- 7)  $\text{Bu}_4\text{NF}$
- 8) TESOTf, 2,6-lutidine
- 9)  $\text{O}_3$ , pyridine

- 10)  $\text{Ti}(\text{OiPr})_4$  (cat), (+)-diisopropyl L-tartrate (cat), tBuOOH
- 11) TsCl,  $\text{Et}_3\text{N}$ , DMAP (cat)
- 12) NaH, PMBOH, DMF,

- 13) CuI, vinylMgBr
- 14) TBSCl, imidazole, DMF
- 15) 9-BBN, THF, then 3 N NaOH, 30 wt %  $\text{H}_2\text{O}_2$
- 16)  $\text{PPh}_3$ , PTSH, DIAD
- 17) Ammonium molybdate tetrahydrate (cat), 30 wt %  $\text{H}_2\text{O}_2$

Please, provide a detailed mechanism for step 9).

Please, provide a detailed mechanism for step 15). What is the name of the reaction in 16)?

D + G

↓ 18-21



↓ 22-25



- 18) LiHMDS
- 19) AcOH/THF/H<sub>2</sub>O = 1/4/1
- 20) Pd/C (10 mol %), H<sub>2</sub>
- 21) DMP (1.2 equiv), NaHCO<sub>3</sub>

- 22) methyl acrylate, PBu<sub>3</sub> (cat)
- 23) CBr<sub>4</sub>, PPh<sub>3</sub>, iPr<sub>2</sub>NEt
- 24) DDQ, pH = 7.0 buffer
- 25) DMP, NaHCO<sub>3</sub>

Please, provide a detailed mechanism for step 18)?

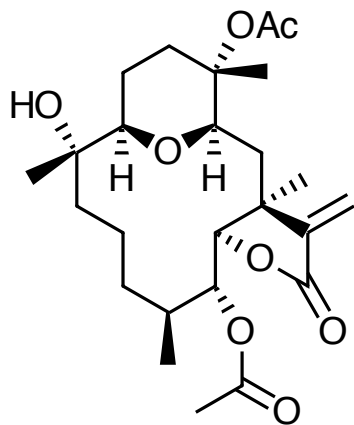
Please, provide a detailed mechanism for sequence 22).

26



J

27-30



26)  $\text{CrCl}_2$ , 4 Å molecular sieves

- 27) MeOH,  $\text{CF}_3\text{COOH}/\text{CH}_2\text{Cl}_2 = 1/4$
- 28)  $\text{Bu}_4\text{NF}$
- 29) NaH
- 30)  $\text{Ac}_2\text{O}$ ,  $\text{iPr}_2\text{NEt}$ , DMAP

Please provide a mechanism for step 26.