Synthesis Challenge # 45

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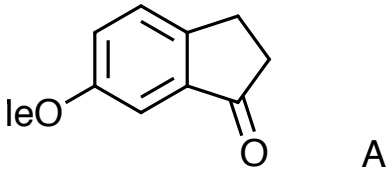
14.04.2016



A

1-4

B

5-7

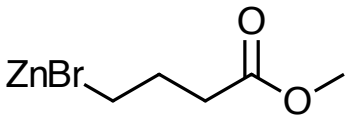
C

8-10

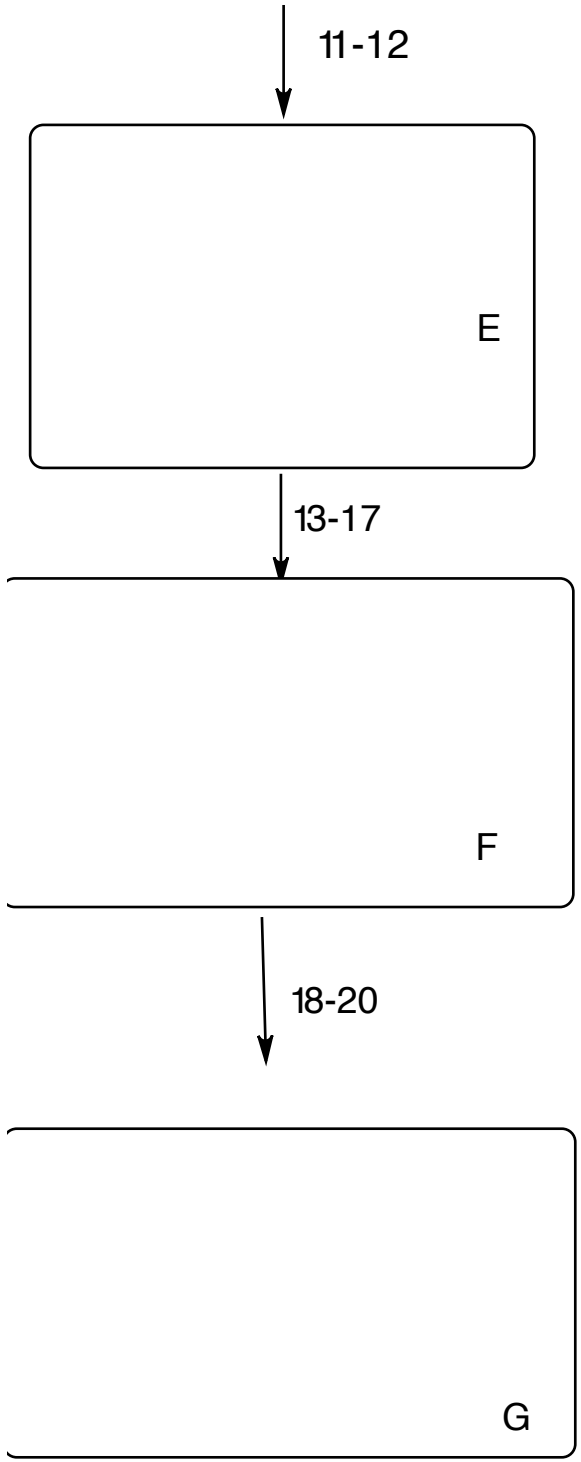
1) $NaBH_4$, CH_2Cl_2, MeOH
2) PCl_3, pyridine, CH_2Cl_2, –10°C
3) **I**, $NiBr_2$·diglyme, (*S*)-*i*Pr-Pybox, DMA
4) aq. NaOH, EtOH

5) TFAA, TFA, CH_2Cl_2, RT;
aq. Na_2CO_3, MeOH, RT
6) BBr_3, CH_2Cl_2, 0°C
7) MeMgBr, THF, 0°C;
$MgBr_2$, $TsOH·H_2O$, THF, 50°C

8) Tf_2O, pyridine, CH_2Cl_2, 0°C
9) propargyl alcohol, $PdCl_2(dppf)·CH_2Cl_2$,
pyrrolidine, TBAI, DMF, 60°C
10) H_2, Lindlar catalyst, quinoline,
EtOAc, RT



I

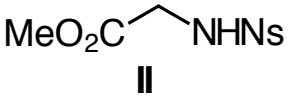


11) *n*-butyl vinyl ether, $Hg(OAc)_2$, 60°C
12) *i*Bu_3Al, hexane, 10°C

13) TBSCl, imidazole, DMF, RT
14) 9-BBN, THF, 0°C; aq. H_2O_2, aq. NaOH, 0°C to RT
15) AZADOL, $PhI(OAc)_2$, phosphate buffer (pH 6.8), MeCN, RT
16) TFA, CH_2Cl_2, RT
17) LDA, THF, –78°C; MeI, HMPA

AZADOL = 2-hydroxy-2-azaadamantane

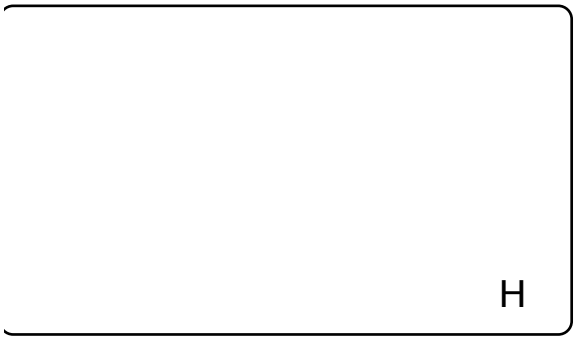
18) $LiAlH_4$, THF, 0°C
19) TIPSCl, imidazole, DMF, RT
20) **II**, DEAD, Ph_3P, toluene, 70°C



II

21-23

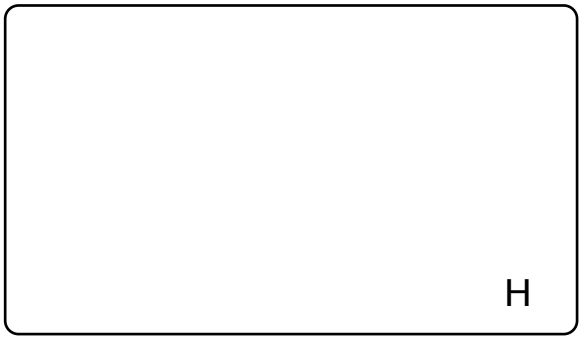
21) PhSH, K_2CO_3, DMF, 50°C
22) TBAF, THF, RT; Boc_2O, aq. $NaHCO_3$, CH_2Cl_2, RT
23) Dess–Martin periodinane, CH_2Cl_2



24

24) NaOAc, BHT, MS4Å, toluene, microwave, 200°C

BHT = 3,5-di-*tert*-butyl-4-hydroxytoluene



25-27

25) NH_3, MeOH, 70°C
26) Burgess reagent, CH_2Cl_2, RT
27) $NaBH_4$, MeOH, reflux