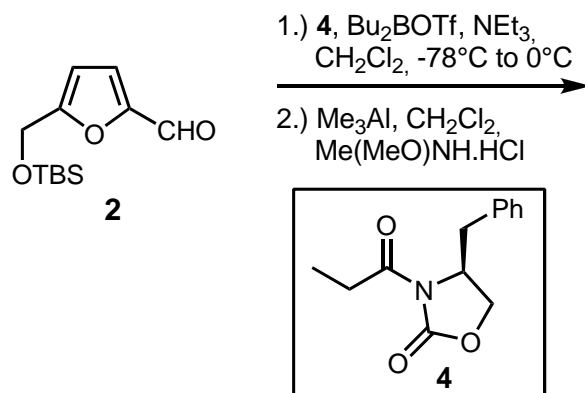
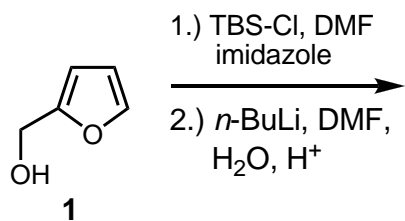
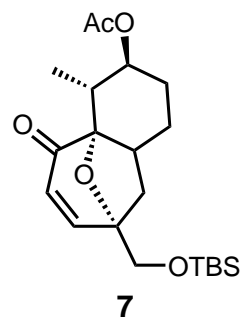
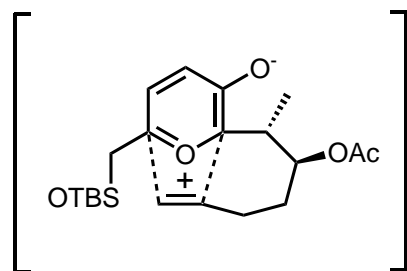
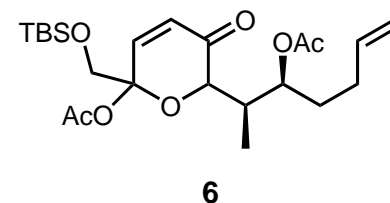
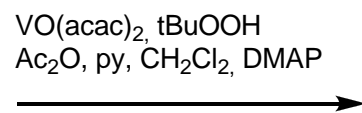
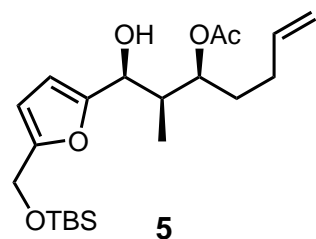


Total Synthesis of Phorbol

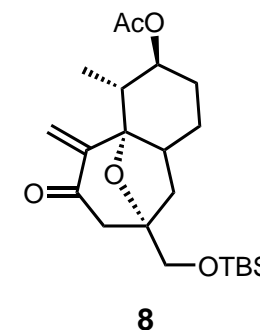
Denksport Rita Fürst
28.05.2009



- 1.) 3-butenyl-MgBr, THF, 60°C
- 2.) DIBAL-H, THF, -78°C
- 3.) TMS-imidazole, THF, AcCl, py, DMAP; then citric acid, MeOH

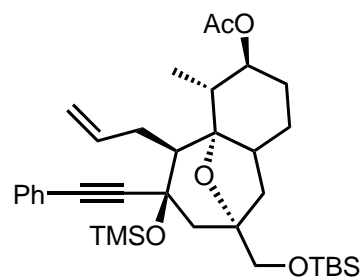


- 1.) H₂, Pd(C), EtOAc
- 2.) tBuOK, Ph₃PCH₃Br, toluene
- 3.) SeO₂, tBuO₂H, CH₂Cl₂; MnO₂, CH₂Cl₂



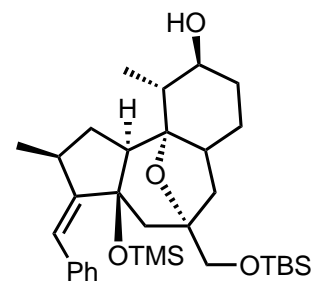
1.) $(\text{CH}_2\text{CH})_2\text{Cu}(\text{CN})\text{Li}_2$,
 Et_2O , then HCl
(axial protonation)

2.) PhCCLi , LiBr , THF
3.) HMPA , TMSCl



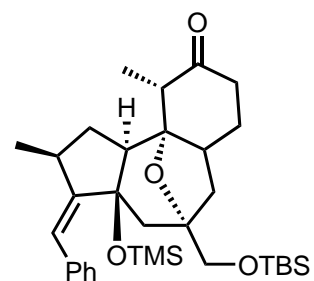
9

1.) Cp_2ZrCl_2 , $n\text{BuLi}$,
 THF ; HOAc



10

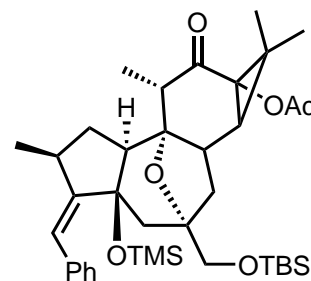
PCC , CH_2Cl_2 ,
 NaOAc



11

1.) LDA , THF , -78°C , TMS-Cl
2.) PhSCl , CH_2Cl_2 , -78°C
3.) $\text{Pb}(\text{OAc})_4$, PhH
4.) $m\text{-CPBA}$, CH_2Cl_2

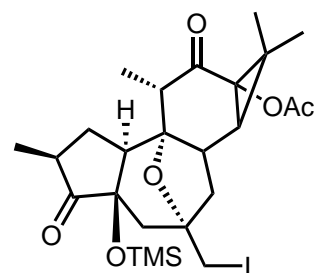
5.) $\text{P}(\text{OEt})_3$, PhH
6.) $\text{Ph}_2\text{S}=\text{C}(\text{CH}_3)_2$, CH_2Cl_2



12

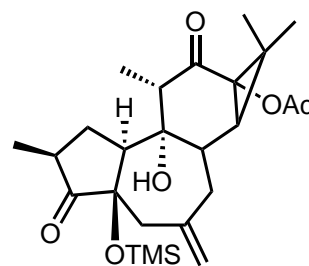
1.) HF (49%), MeCN , 0°C
2.) O_3 , CH_2Cl_2 , MeOH , -78°C
 $(\text{NH}_2)_2\text{C}=\text{S}$

3.) Tf_2O , py , CH_2Cl_2 , 0°C
4.) $n\text{Bu}_4\text{NI}$, MeCN



13

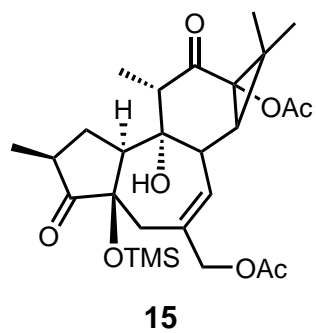
Zn , EtOH , 80°C



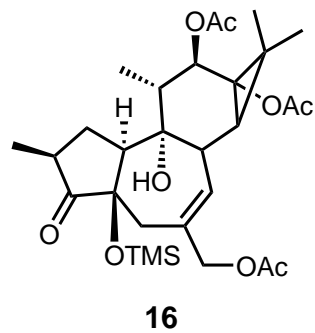
14

1.) SeO_2 , $t\text{BuOOH}$, CH_2Cl_2
2.) SOCl_2 , py , Et_2O , 0°C

3.) KOAc , 18-crown-6, AgOAc
 MeCN



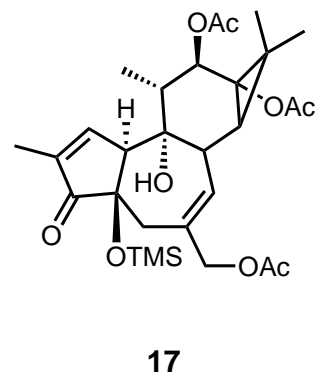
1.) NaBH(OAc)₃, THF
2.) Ac₂O, DMAP, py
CH₂Cl₂



1.) MSTFA, DMAP, DABCO
MeCN, 100°C
2.) NBS, THF
3.) Li₂CO₃, LiBr, DMF, 130°C



MSTFA=N-Methyl-N-trimethylsilyl trifluoroacetamid



1.) TBAF, THF, -20°C
2.) Ba(OH)₂, MeOH

