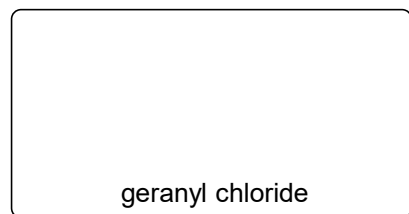

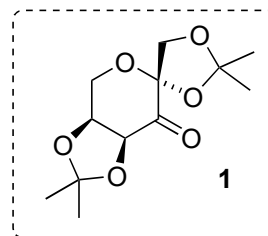


Total Synthesis of the Protein Phosphatase 2A Inhibitor Lactodehydrothyriferol

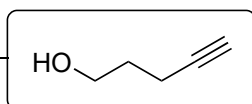
D. J. Clausen, S. Wan and P. E. Floreancig
Angew. Chem. Int. Ed. **2011**, *50*, 5178–5181



- 1) n -BuLi, TMS ; then TBAF
- 2) AD-mix- β , $\text{CH}_3\text{SO}_2\text{NH}_2$
- 3) **1**, Oxone, K_2CO_3 , Bu_4NHSO_4 ; then py-CSA
- 4) TESCl, DMAP, imidazole
- 5) Et_3SiH , $[\text{CpRu}(\text{NCCH}_3)_3]\text{PF}_6$; then I_2 , 2,6-lutidine



How would you synthesize **1**? name?



- 6) Me_3Al , Cp_2ZrCl_2 ; then I_2
- 7) $\text{H}_2\text{C}=\text{CHMgBr}$, $\text{Pd}(\text{PPh}_3)_4$
- 8) $(\text{COCl})_2$, DMSO, Et_3N
- 9) Ph_2CH_2 , n -BuLi
- 10) NaH ; then MeI



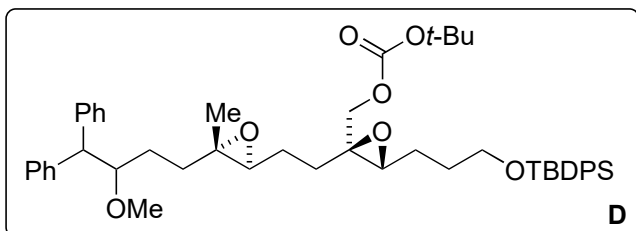
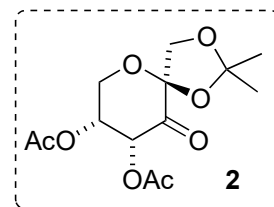
- 11) TBDPSCl, imidazole
- 12) n -BuLi; then $(\text{CH}_2\text{O})_n$
- 13) Bu_3SnH , $\text{Pd}(\text{PPh}_3)_4$; then I_2
- 14) Boc_2O , N -methylimidazole



6) Regioselectivity?

B

- 15) 9-BBN; then **C**, Pd(Pt-Bu₃)₂, K₃PO₄
16) Oxone, **1**, K₂CO₃, Bu₄NHSO₄; then **2**

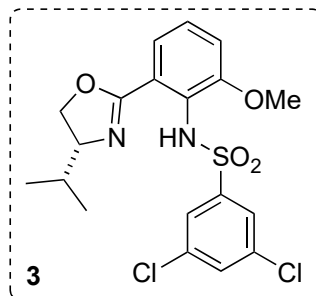


- 17) hν, *N*-methylquinolinium hexafluorophosphate,
O₂, Na₂S₂O₃, NaOAc
18) *m*-CPBA, Sc(OTf)₃
19) IBX, DMSO

- 17) Mechanism?
18) Mechanism?



- 20) CrCl₂, NiCl₂·DMP, **3**, **A**, proton sponge
Mn, Cp₂ZrCl₂, LiCl
21) K₂CO₃, MeOH
22) TsCl, Et₃N, Bu₂SnO
23) NaBH₄, HMPA, 50 °C
24) Me₃P=CHCN
25) TBAF



- 22) Role of Bu₂SnO?

