Universität Zürich[UZH]

Total Synthesis of Guanacastepenes N and O

C. M. Gampe, E. M. Carreira, *Angew. Chem. Int. Ed.* **2011**, *50*, 2962-2965

Gademann Group
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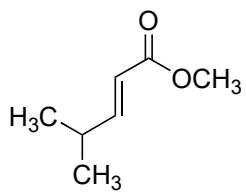


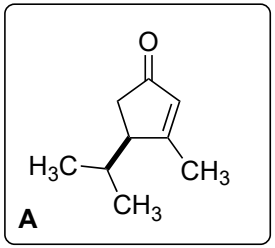
1) **1**, $CuBr \cdot SMe_2$, HMPA, TMSCl, THF, -40 °C

96%

2) CsF, DMSO, RT

60%

Related to which named reaction?



A

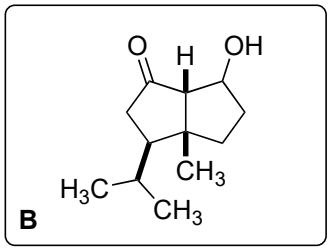
3) But-3-enyllithium, lithium 2-thienyl-CuCN, $BF_3 \cdot OEt_2$, THF, -78 °C

51%, 2x recycling: **70%**, d.r. >95:5

Name of 4)?

4) OsO_4 (5 mol%), NMO, aq. THF; $NaIO_4/SiO_2$

5) KOH, MeOH, RT



B

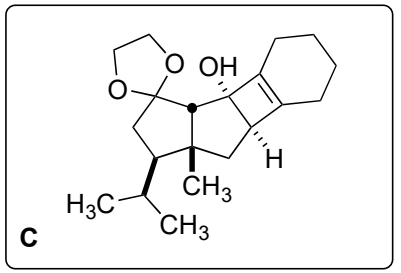
6) $(CH_2OH)_2$, $(EtO)_3CH$, *p*TsOH, RT

7) DMSO, $(COCl)_2$, NEt_3, DCM

53% over 4 steps

8) **2**, $KOCEt_3$, THF, -78 °C to RT

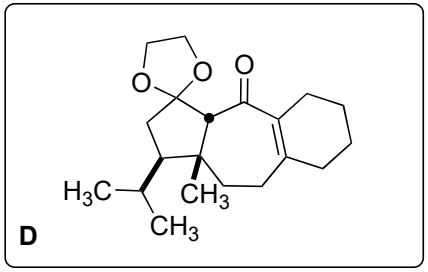
74%



C

9) $[Fe_2(CO)_9]$, benzene, 90 °C, *then* DBU

51%



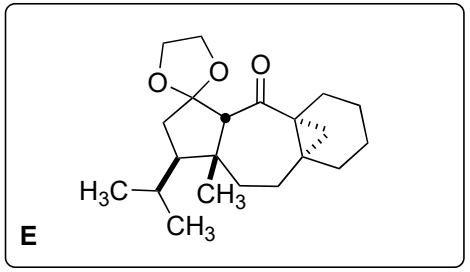
D

10) DIBAL-H, *n*BuLi, -78 °C, 30 min, d.r. >95:5

11) $ZnEt_2$, TFA, CH_2I_2, DCM, 0 °C, 15 min, **61%**

12) PDC, Ac_2O, DCM, RT, **99%**

Name and mechanism of 11)?

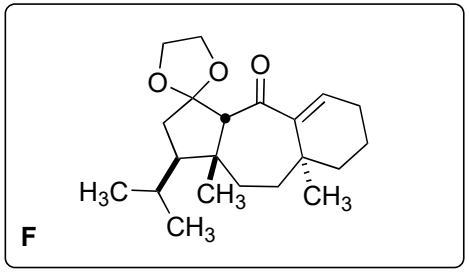


E

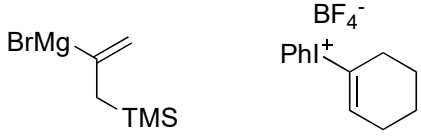
13) Li/NH_3, THF, then SiO_2, DCM, O_2

14) Me_2S, acetone, RT, **79%** over 2 steps

15) $SOCl_2$, py, RT, **95%**

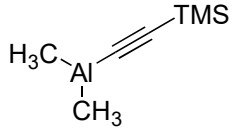


F

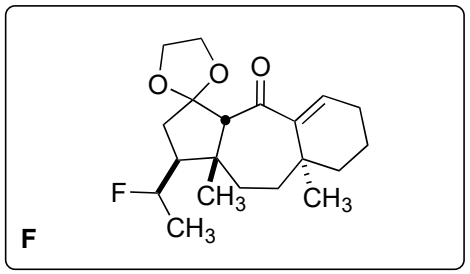


1

2

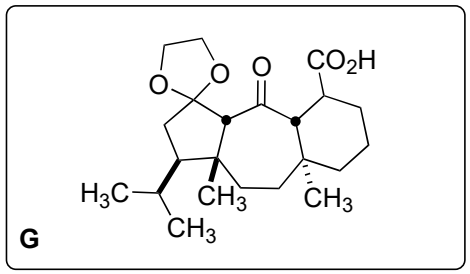


3



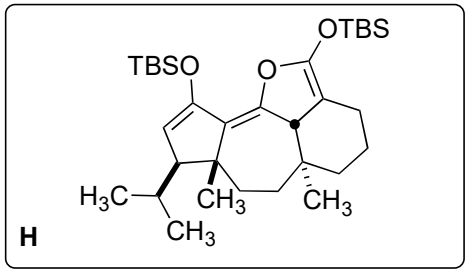
18) **3**, Et_2O, RT, *then* NaOMe, MeOH, **81%**

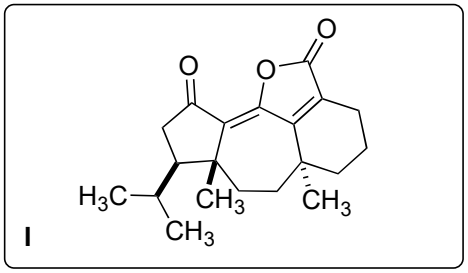
19) $RuCl_3$, oxone (excess), $NaHCO_3$, H_2O, MeCN, EtOAc, RT, **55%** (1x recycling)



20) HCl (0.1 M), THF, 57 °C *then* $(COCl)_2$, py, DCM, 0 °C, 15 min, **79%**

21) TBSOTf (4.0 eq.), NEt_3, DCM

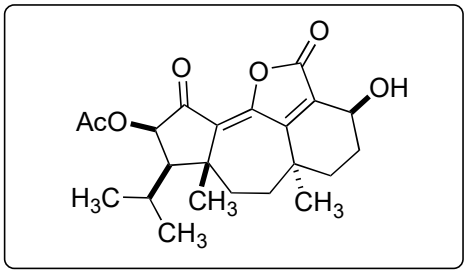




23) $Mn(OAc)_3$, benzene, MS 3 A, 80 °C, **68%**, d.r. (α/β)=1:4

24) NBS, $(PhCOO)_2$, CCl_4, 80 °C, 1 h, **58%**

25) nBu_3SnH, air, toluene, RT, 16 h, then PPh_3, **47%**

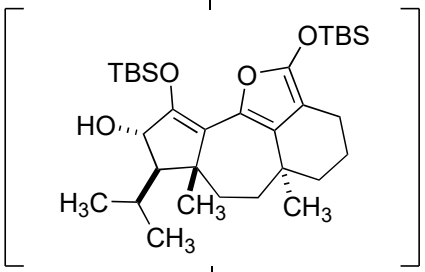


Guanacastepene N

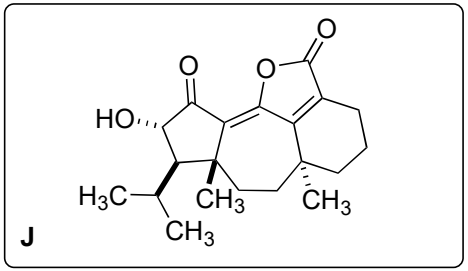
22) OsO_4, NMO, $MeSO_2NH_2$, acetone, *t*BuOH, H_2O, 0 °C

over 2 steps: **I**: **40%, J**: **29%**, d.r. (α/β) = 9:1

Elimination



Oxidation and elimination



26) Ac_2O, NEt_3, DMAP, DCM, RT, **87%**

27) NBS, $(PhCOO)_2$, CCl_4, 80 °C, **76%**

28) nBu_3SnH, air, toluene, RT, 16 h, then PPh_3, **72%**

Guanacastepene O