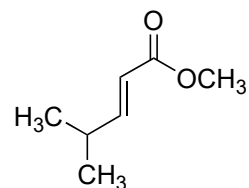




Total Synthesis of Guanacastepenes N and O

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



1) **1**, CuBr·SMe₂, 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,
BF₃·OEt₂, THF, -78 °C

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

Name of 4)?

4) OsO₄ (5 mol%), NMO,
aq. THF; NaIO₄/SiO₂

5) KOH, MeOH, RT

B

6) (CH₂OH)₂, (EtO)₃CH,
pTsOH, RT

7) DMSO, (COCl)₂,
NEt₃, DCM

53% over 4 steps

8) **2**, KOEt₃, THF,
-78 °C to RT

74%

C

9) [Fe₂(CO)₉], benzene,
90 °C, then DBU

51%

D

10) DIBAL-H, *n*BuLi,
-78 °C, 30 min, d.r. >95:5
11) ZnEt₂, TFA, CH₂I₂, DCM,
0 °C, 15 min, 61%

12) PDC, Ac₂O, DCM,
RT, 99%

Name and mechanism of 11)?

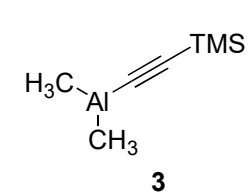
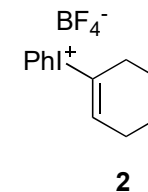
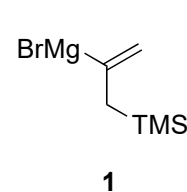
E

13) Li/NH₃, THF,
then SiO₂, DCM, O₂

14) Me₂S, acetone, RT,
79% over 2 steps

15) SOCl₂, py, RT, 95%

F





18) **3**, Et₂O, RT, *then* NaOMe, MeOH, **81%**

19) RuCl₃, oxone (excess), NaHCO₃, H₂O,
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.), NEt₃, DCM



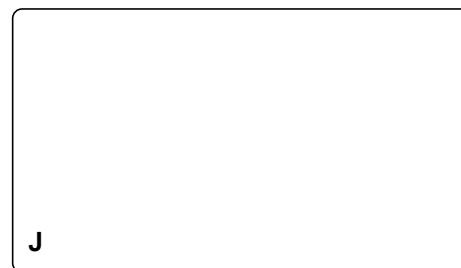
22) OsO₄, NMO, MeSO₂NH₂,
acetone, *t*BuOH, H₂O, 0 °C

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



Elimination ↑

Oxidation and elimination ↓



23) Mn(OAc)₃, benzene, MS 3 A, 80 °C,

68%, d.r. (α/β)=1:4

24) NBS, (PhCOO)₂, CCl₄, 80 °C, 1 h, **58%**

25) *n*Bu₃SnH, air, toluene, RT, 16 h,
then PPh₃, **47%**



Guanacastepene N

26) Ac₂O, NEt₃, DMAP, DCM, RT, **87%**

27) NBS, (PhCOO)₂, CCl₄, 80 °C, **76%**

28) *n*Bu₃SnH, air, toluene, RT, 16 h,
then PPh₃, **72%**



Guanacastepene O