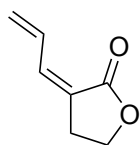


Enantioselective Total Synthesis of (+) and (-)-Nigellamine A₂

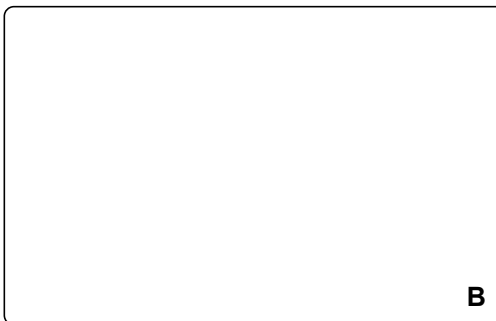
J. Bian, M. van Wingerden, J. M. Ready
J. Am. Chem. Soc. **2006**, *128*, 7428 – 7429.



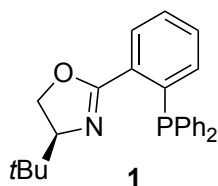
1 – 6



7 – 14



- 1) MeMgBr (3.3 eq.)
- 2) TBSCl (1.0 eq.), imidazole
- 3) *n*-BuLi, ClCOCH(CH₃)₂
- 4) HF · py
- 5) I₂, PPh₃, imidazole
- 6) NaCH(CO₂Et)₂



- 7) LiHMDS, Pd₂(dba)₃, **S-1**
- 8) I₂
- 9) (*i*-Pr)₃SiCCSO₂CF₃, λ = 300 nm, (Bu₃Sn)₂
- 10) Bu₄NF
- 11) DIBAL-H
- 12) NaBH₄
- 13) Cp₂ZrCl₂, AlMe₃, H₂O, -18 °C (36 h) to -5 °C (12 h)
then I₂ at -20 °C
- 14) 2,6-lutidine, (*t*-Bu)₂Si(OTf)₂

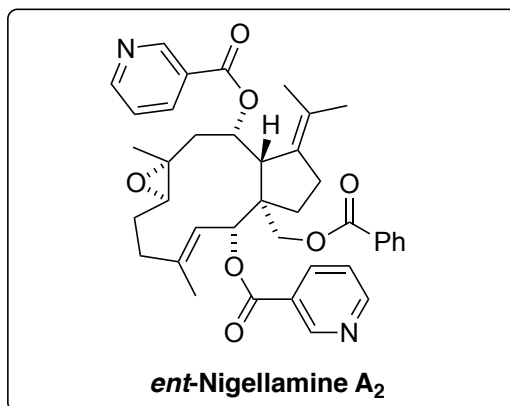
7) conceptualize the reaction, can you explain the regiochemistry? *hint: not sterics*

13) *Note: water forms a thermodynamically unstable but highly catalytically active species*

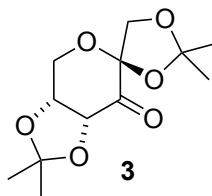
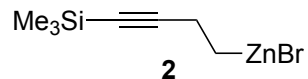
15 – 23



24 – 25



- 15) PdCl₂(dppf) cat., **2**
- 16) Bu₄NF
- 17) Cp₂ZrCl₂, Al₃Me, H₂O, then I₂
- 18) PCC, 4 Å MS
- 19) CrCl₂, Ni(acac)₂ cat., sonication
- 20) DMP
- 21) LiAlH(*i*-Bu)₂*t*-Bu
- 22) LAH
- 23) NEt₃, BzCl



- 24) **3**, oxone, K₂CO₃, Bu₄NHSO₄, MeCN/DMM
- 25) Nicotinic acid, DCC, DMAP

19) Please draw the mechanism.

24) what is the catalyst derived from? what is the mechanism?
Do you know the Name?