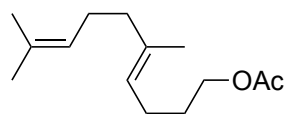
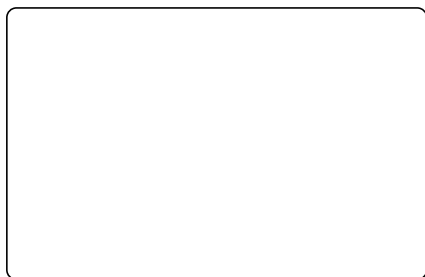


Bioinspired Total Synthesis of Sespenine

Yu Sun, Pengxi Chen, Deliang Zhang, Martin Baunach, Christian Hertweck, Ang Li, *Angew. Chem. Int. Ed.* **2014**, 53, 9012-9016.



1-4



5-7



8

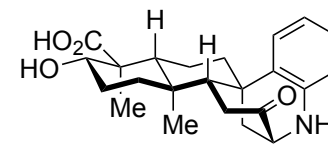
- 1) *t*-BuOOH, SeO₂
- 2) Ti(O*i*-Pr)₄, (+)-DET, *t*-BuOOH, -40°C
- 3) AZADO, PhI(OAc)₂, H₂O
- 4) MeI, K₂CO₃

- 5) K₂CO₃, MeOH
- 6) DMP
- 7) CeCl₃, ≡—MgBr

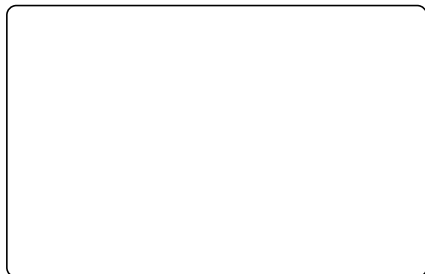
- 8) [Cp₂TiCl₂], Mn, *i*-Pr₂NEt₂, TMS-Cl
then aq. HCl workup

How would you synthesize the starting material?

Please provide a mechanism for step 8.



sespenine



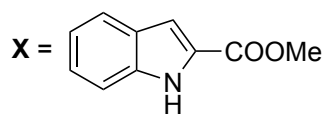
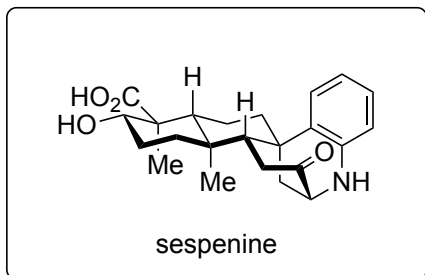
9-12



13,14



15,16



- 9) IBX (1eq)
- 10) Ac_2O , NEt_3
- 11) $Bi(OTf)_3$, X
- 12) $TiCl_4$, Nysted reagent

- 13) oxone, acetone
- 14) $AcOH$

- 15) $NaCl$, Δ
- 16) K_2CO_3 , $MeOH$

What could be the reason for using the C2-substituted indol, while in the end that position is not functionalized?

Structure of Nysted's reagent?

Please explain the transformation of step 14 with a mechanism.

What is the name associated with the reaction in step 15?