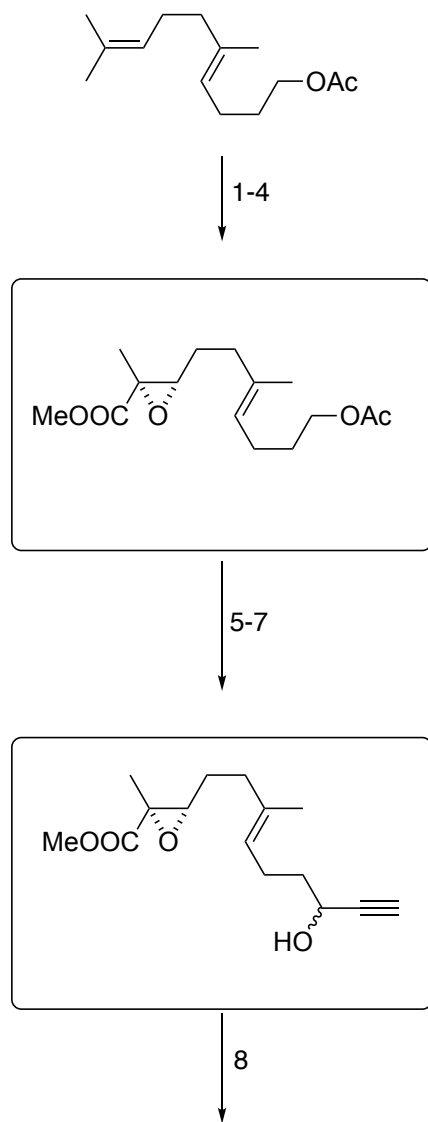
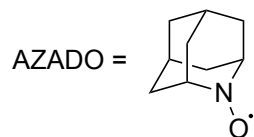


Bioinspired Total Synthesis of Sespenine

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



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

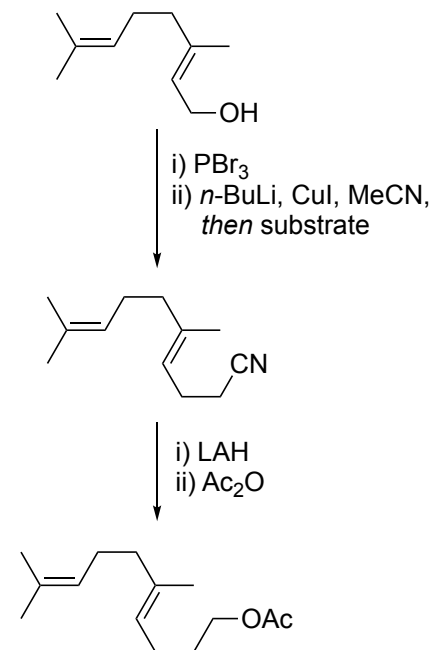


- 5) K₂CO₃, MeOH
- 6) DMP
- 7) CeCl₃, ≡—MgBr

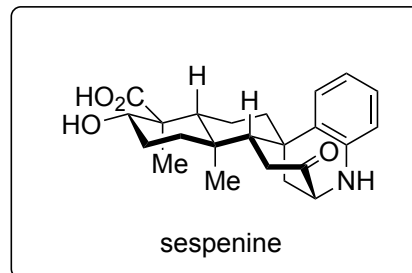
- 8) [Cp₂TiCl₂], Mn, *i*-Pr₂NEt₂

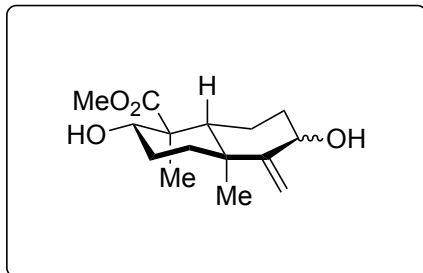
How would you synthesize the starting material?

T. Hirukawa, M. Oguchi, N. Yoshikawa, T. Kato, *Chem. Lett.* **1992**, *21*, 2343.

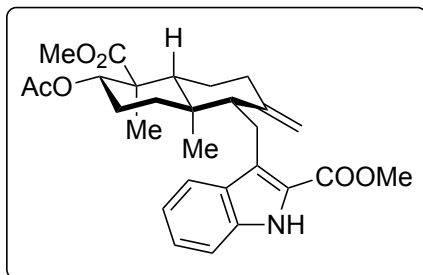


Please provide a mechanism for step 8.

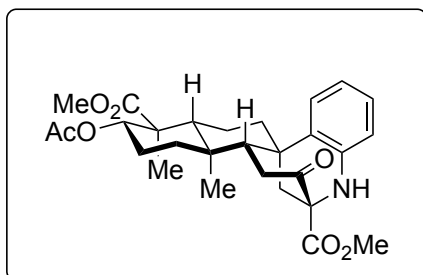




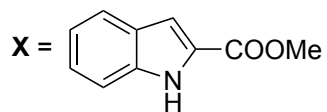
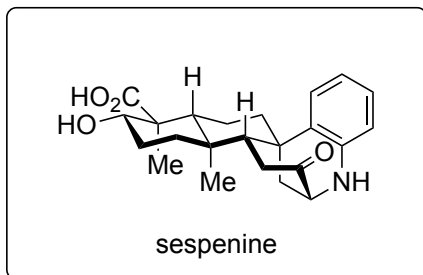
9-12



13,14

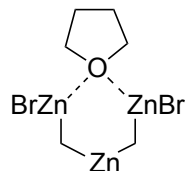


15-17



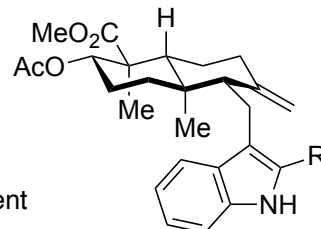
- 9) IBX
- 10) Ac_2O , NEt_3
- 11) $Bi(OTf)_3$, X
- 12) $TiCl_4$, Nysted reagent

Structure of Nysted's reagent?



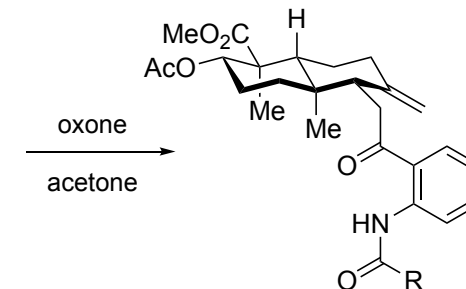
- 13) oxone, acetone
- 14) $AcOH$

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



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

Electronics reduce the overoxidized side product:



$R = H$
major product

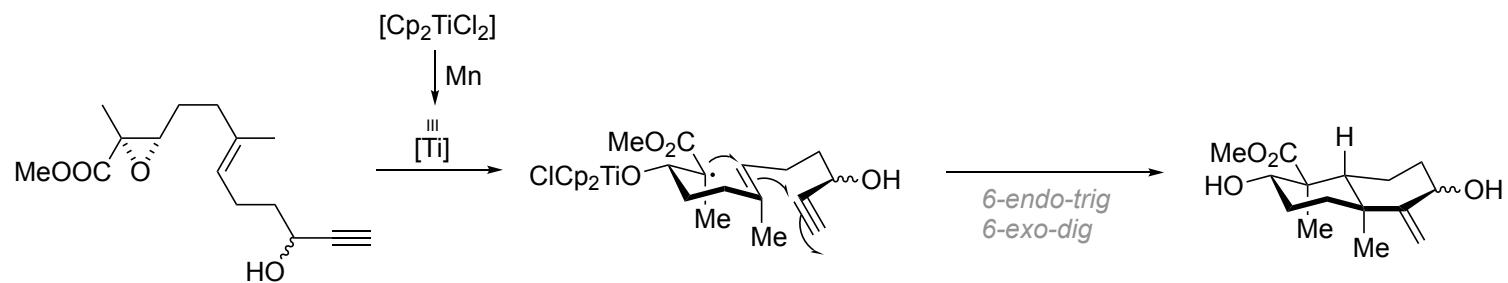
$R = COOMe$
minor side product

Please explain the transformation of step 14 with a mechanism.

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

Krapcho demethoxycarbonylation

Mechanism of step 8



Mechanism of step 14

