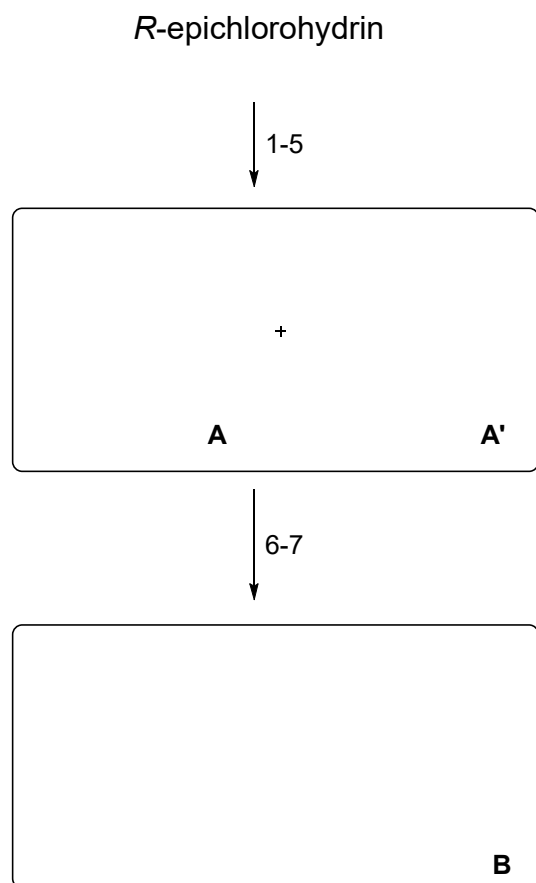


Development, Mechanistic Elucidation, and Rational Optimization of a Tandem Ireland Claisen/Cope Rearrangement Reaction for Rapid Access to the (Iso)Cyclocitrinol Core
C. W. Plummer, C. S. Wei, C. E. Yozwiak, A. Soheili, S. O. S., James L. Leighton *J. Am. Chem. Soc.*, **2014**, *136*, 9878–9881



- 1) vinylmagnesium bromide, CuBr
- 2) ethynyltrimethylsilane, BuLi, BF₃
- 3) TIPSOTf, 2,6-Lutidine
- 4) K₂CO₃, MeOH
- 5) Co₂(CO)₈, TMTU, CO (1 atm)

Note: continue with the *R* isomer on the new stereocenter

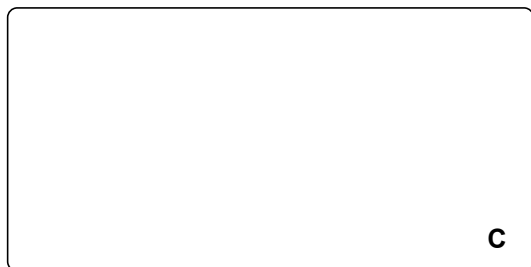
- 6) H₂O₂, NaOH
- 7) CH₃PPh₃Br, LiHMDS

TMTU = tetramethylthiourea

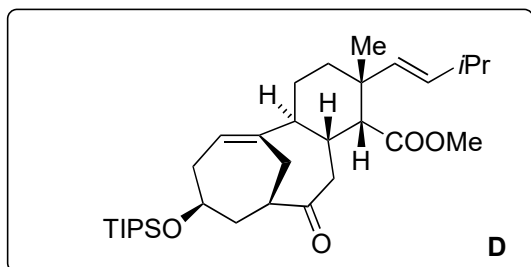
5: Hint two Diastereomers are formed, Name the reaction

geranial

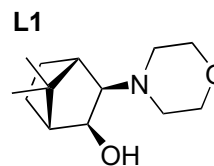
8-11



12-17

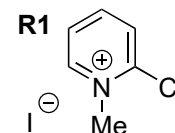


- 8) $i\text{Pr}_2\text{Zn}$, **L1** then Ac_2O
- 9) $m\text{-CPBA}$
- 10) $\text{HIO}_4 \cdot \text{H}_2\text{O}$
- 11) $\text{CH}_3\text{PPh}_3\text{Br}$, LiHMDS



8) Hint S Isomer

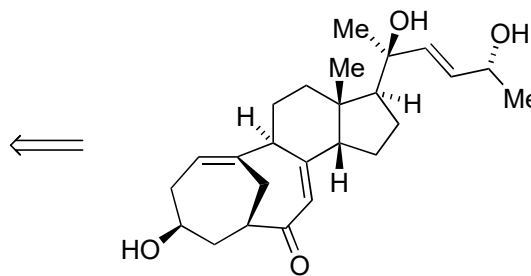
- 12) HG-II, **B**
- 13) AllylMgBr
- 14) Acrylic Acid, NEt_3 , **R1**
- 15) HG-II
- 16) Me_2PhSiCl , DBU then 1 M HCl
- 17) TMSCHN_2



12) provide a Mechanism

14) Name the reagent **R1**

16) provide a Mechanism



Cyclocitrinol