

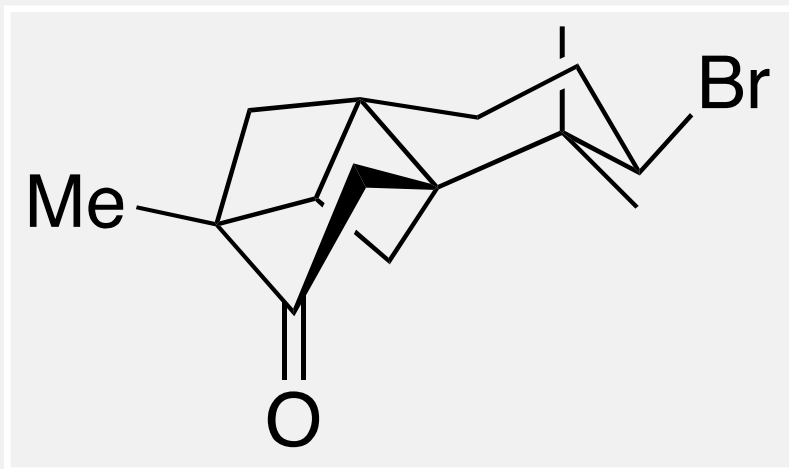
TOTAL SYNTHESIS OF APLYDACTONE



Chenguang Liu, Rwnzhi Chen, Yang Shen, Zhanhao Liang, Yuhui
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Presenter: Arzoo Chhabra

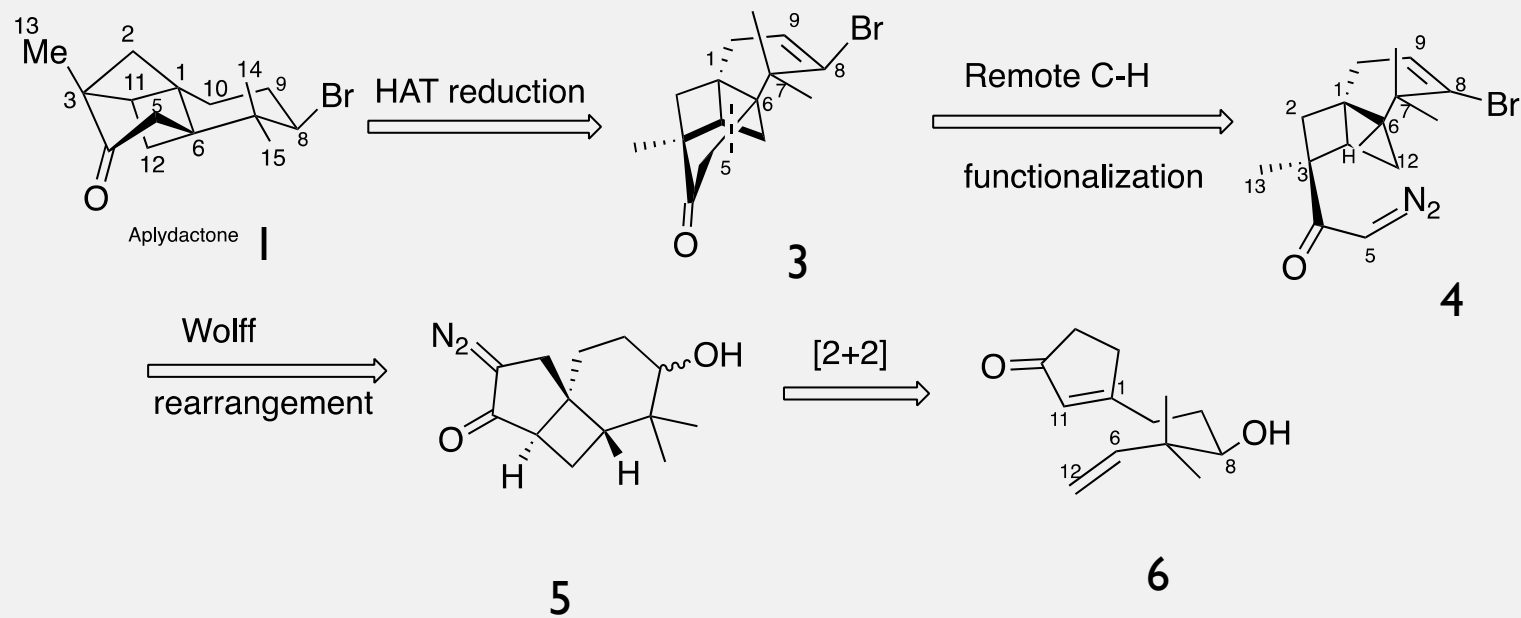


APLYDACTONE

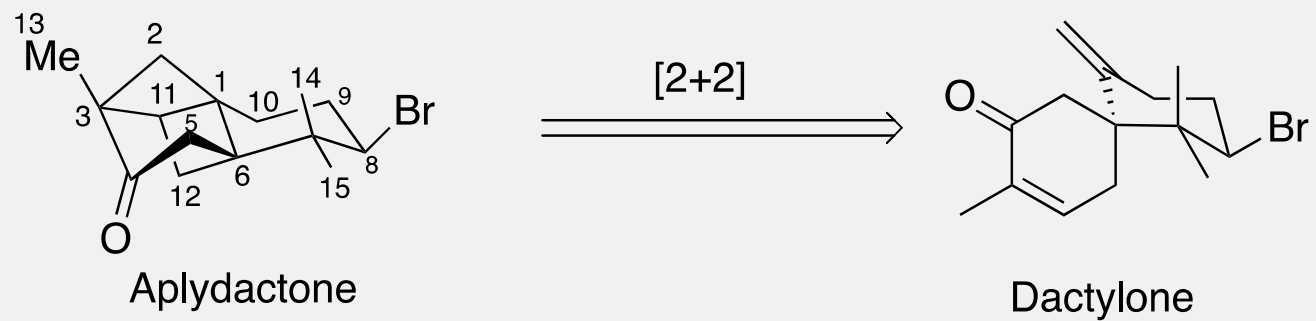
- Halogenated **ladderane sesquiterpenoid** natural product
- First disclosed by **Stonik** and coworkers in **2001**
- possess an unprecedented **tetracyclic** skeleton
- Paper dedicated to **Samuel Danishefsky**

- “Spotted sea hare” *Aplysia Dactylomela* dwells in tropical seas and feast on algae that produces halogenated terpenoids.

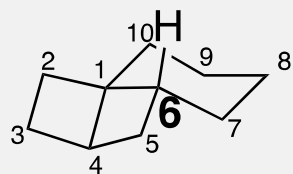
RETROSYNTHETIC ANALYSIS



THE BIOSYNTHETIC RELATIONSHIP



CONFORMATIONAL ANALYSIS OF 6/4/4 RINGS

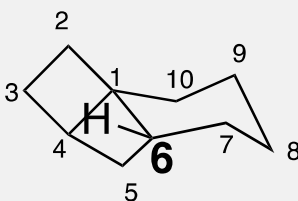


A

chair

ΔG_{gas}

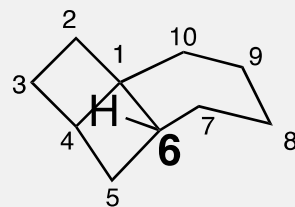
(kCal/mol) 0.0



B

chair

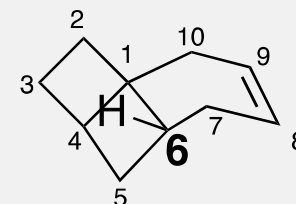
2.0



C

Twist boat

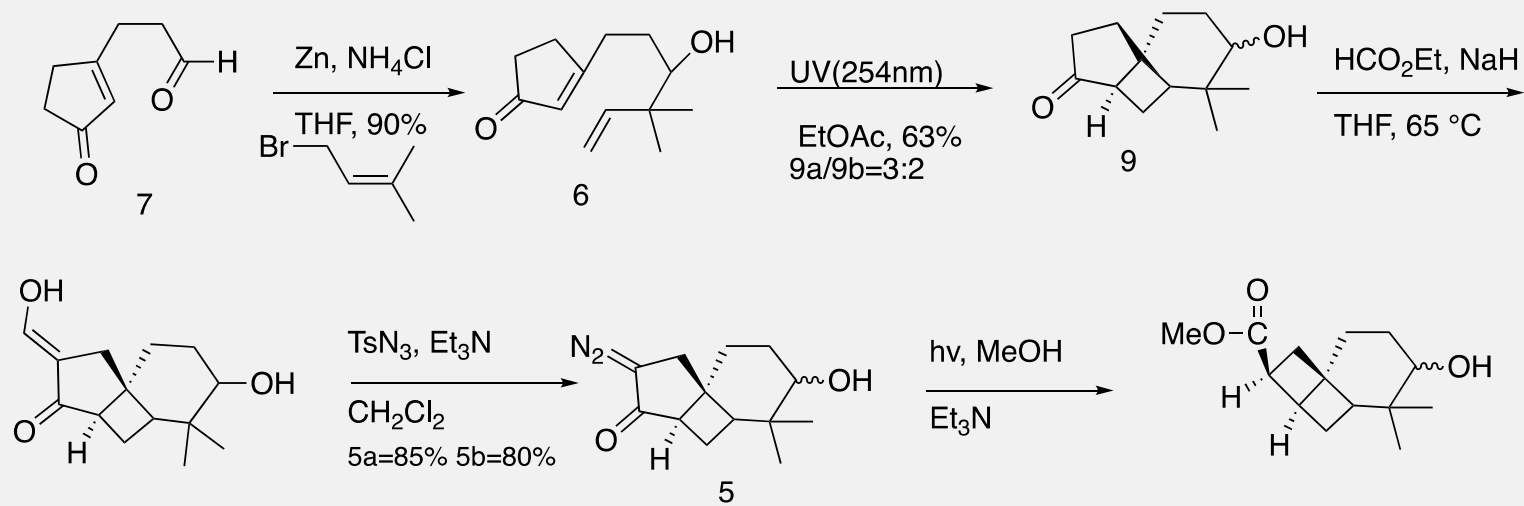
1.5

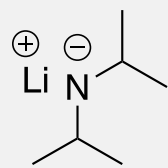


D

boat

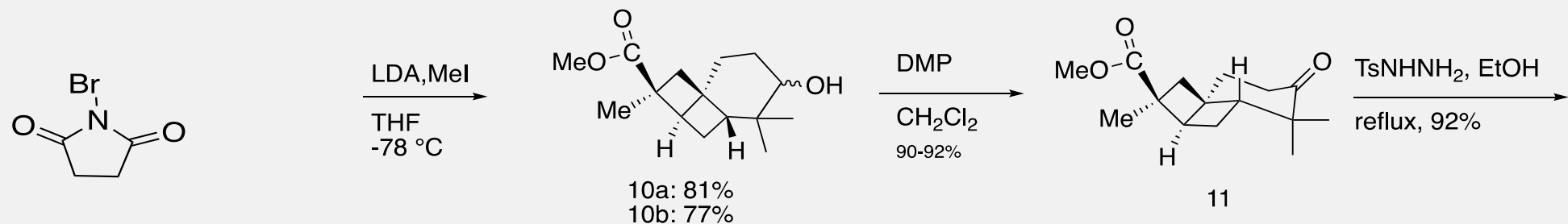
SYNTHESIS



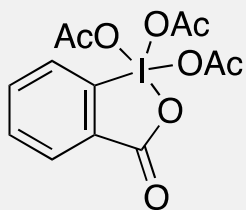
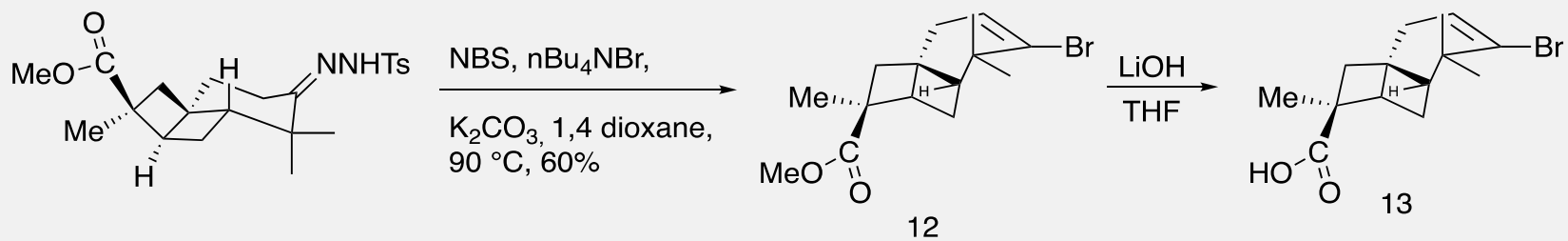


LDA

CONT..

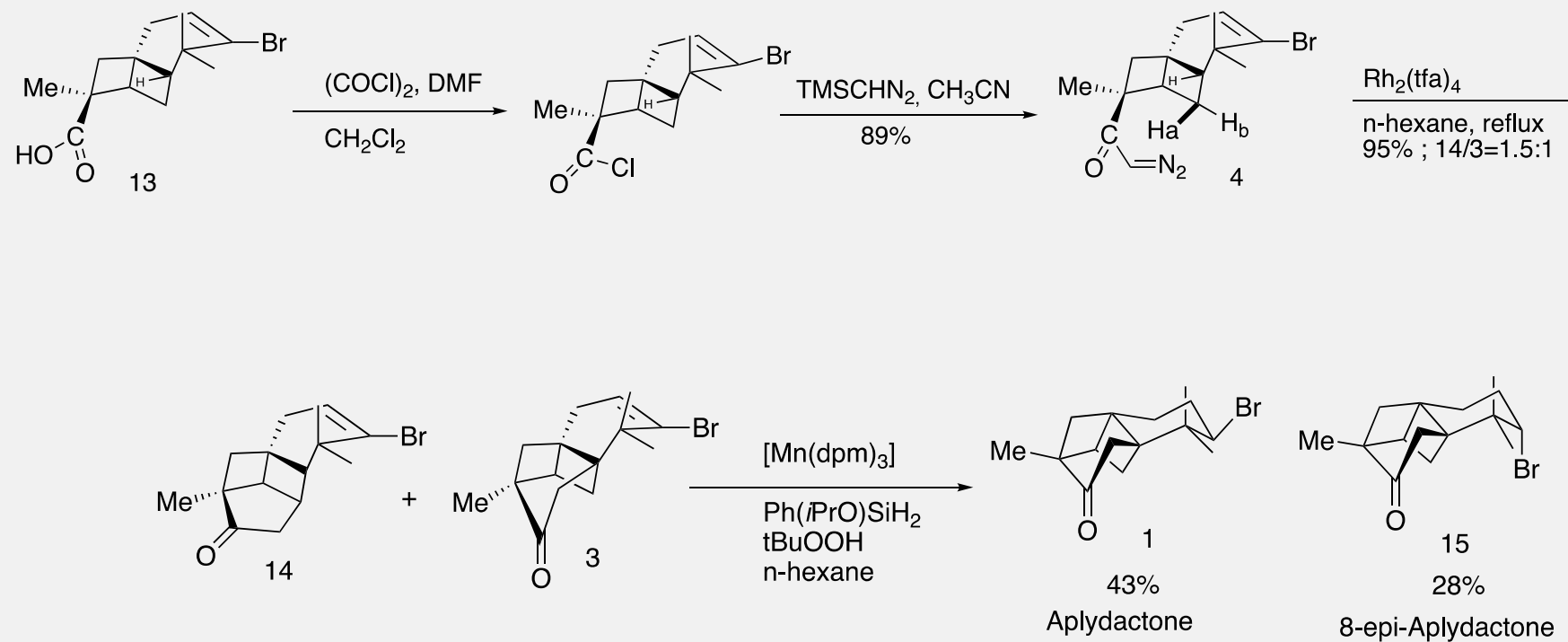


NBS

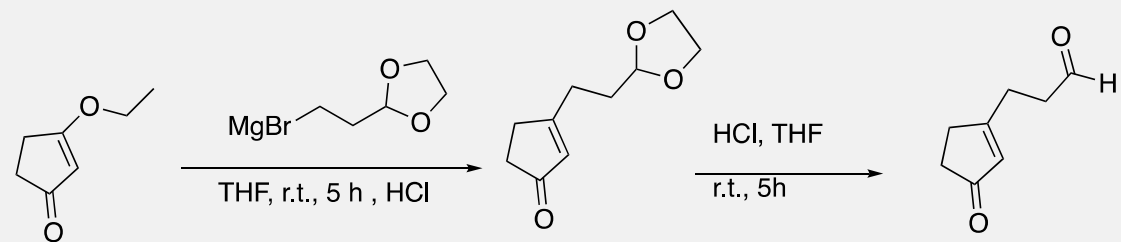


DMP

CONT..

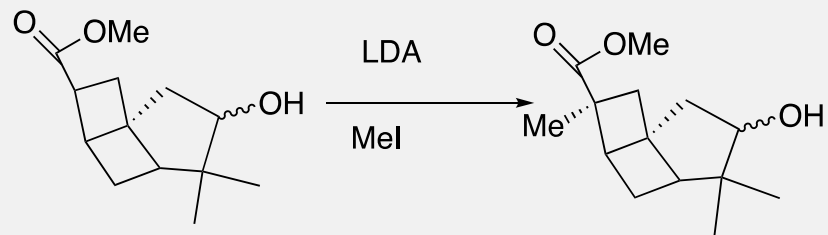
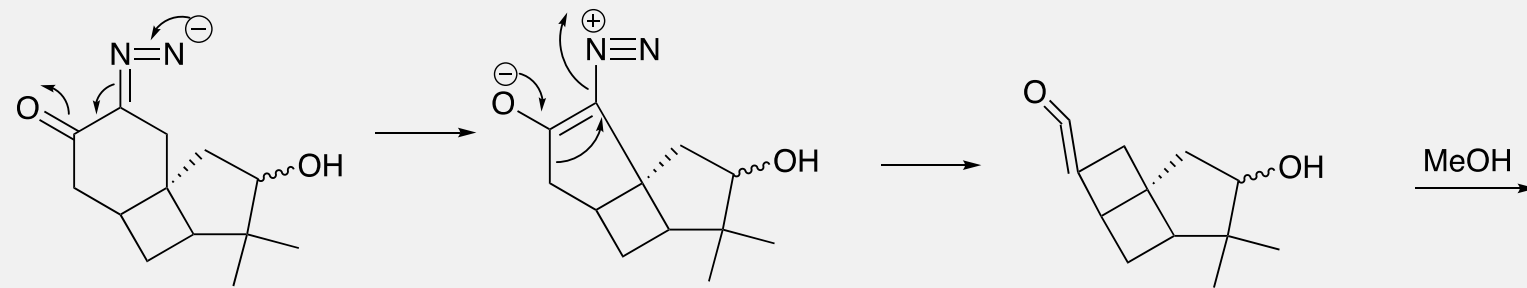


SYNTHESIS OF STARTING MATERIAL

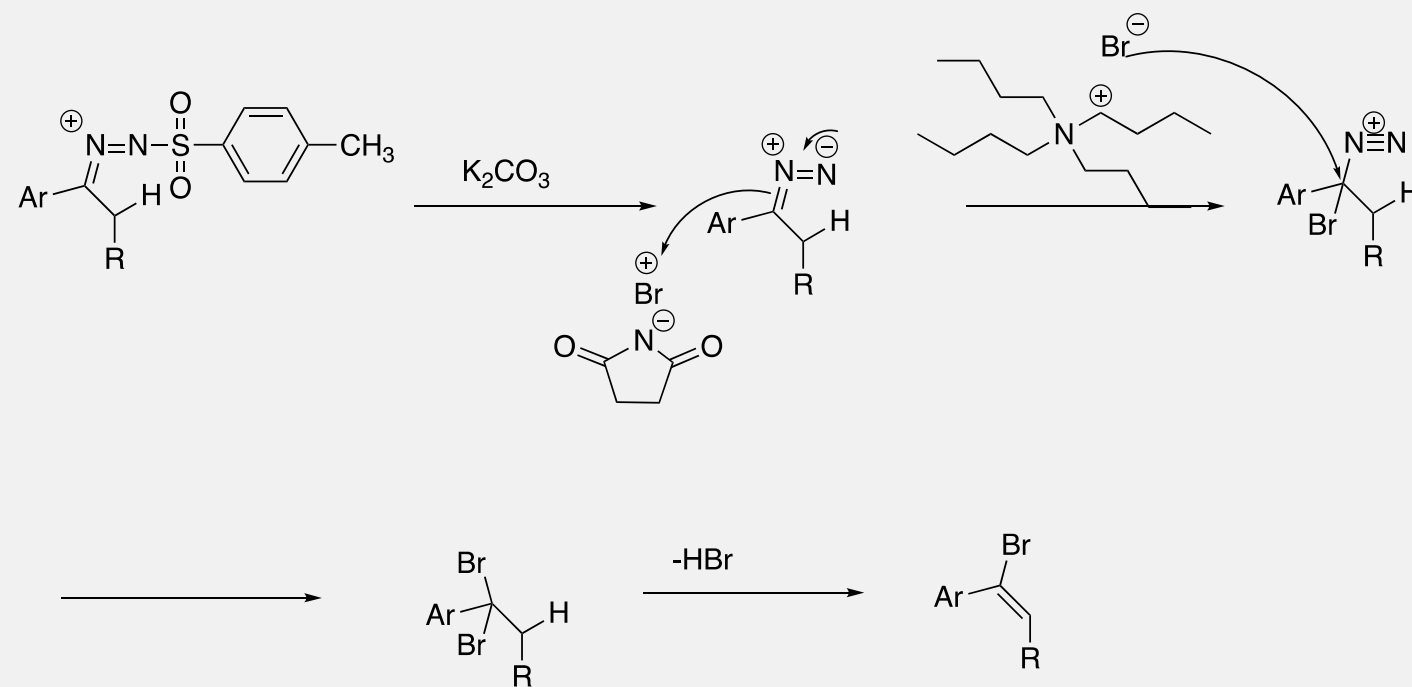


Reference: Day-Shin Hsu, Chih-Hao Chen and Chi-Wei Hsu, Synthesis of Spiranes by Thiol-Mediated Acyl Radical Cyclization, *Eur J. Org. Chem.* **2016**,589

MECHANISM (WOLFF CONTRACTION)



FORMATION OF VINYL BROMIDE



Reference: D. P. Ojha, K. R. Prabhu, *Org Lett.* **2015**, 17, 18

C-H CARBENOID INSERTION MECHANISM

