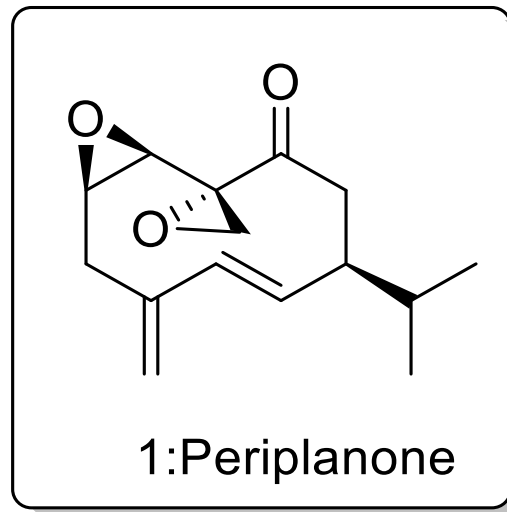


Total Synthesis of Periplanone B



Sonam Shivtarkar

CEM 852

1/24/2022

- 1) Nicolaou, K. C., & Sorensen, E. J. (1996). *Classics in total synthesis: targets, strategies, methods*. John Wiley & Sons.
- 2) Still, W. C. (1979). (+-)-Periplanone-B. Total synthesis and structure of the sex excitant pheromone of the American cockroach. *Journal of the American Chemical Society*, 101(9), 2493-2495.

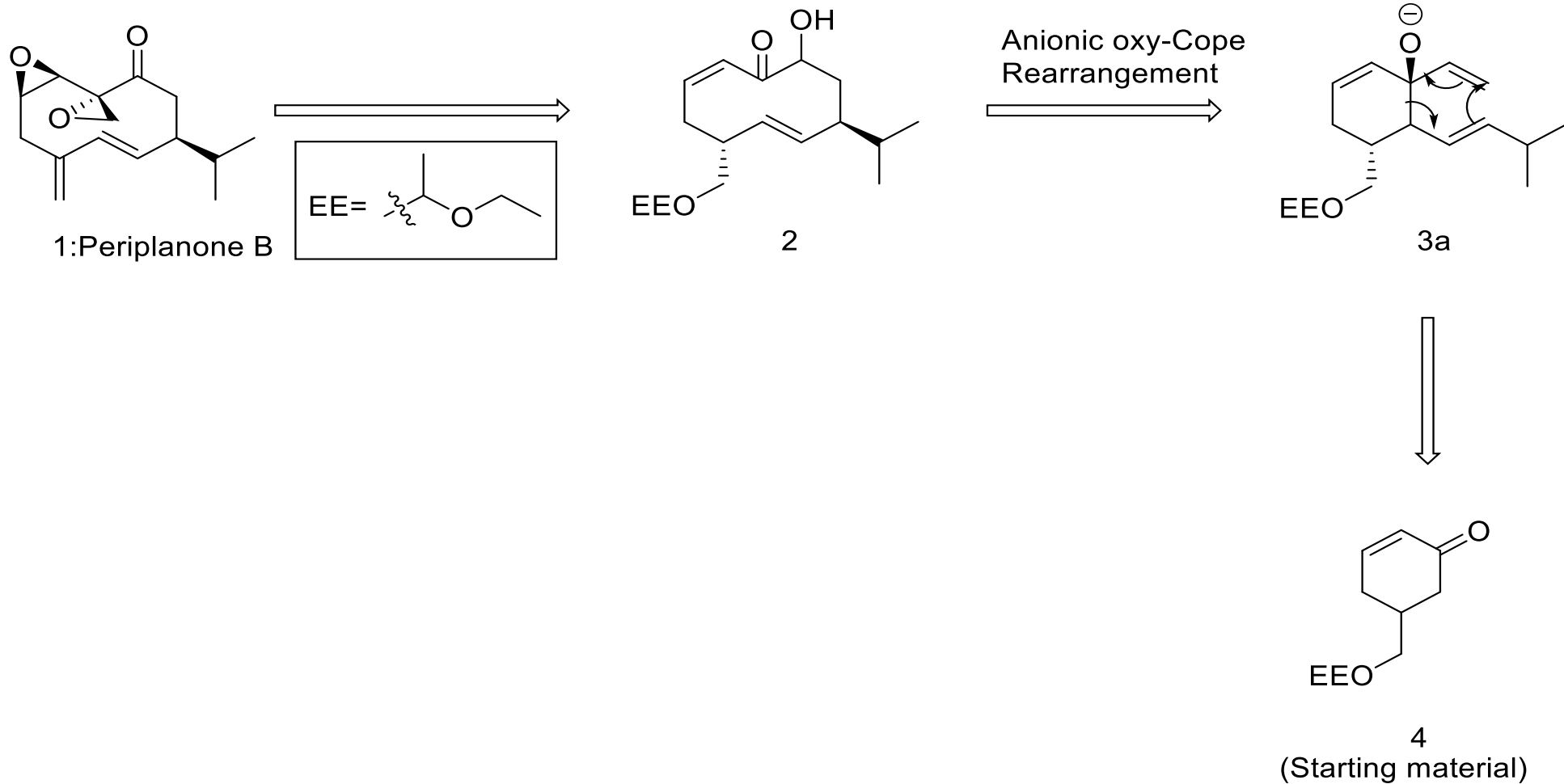
Introduction:

- 1952: first reported as constituent of excretion from female American cockroaches of species *Periplaneta americana*
- Potent sex pheromone stored in only minute amounts ($\ll 1 \mu\text{g}$)
- 1976: Persoons *et al.* reported isolation of two active compounds, periplanones A & B
- Periplanone B present in larger amount
- Constitution known but stereochemistry undetermined
- 1979: W. C. Still reported gross structure and its first total synthesis

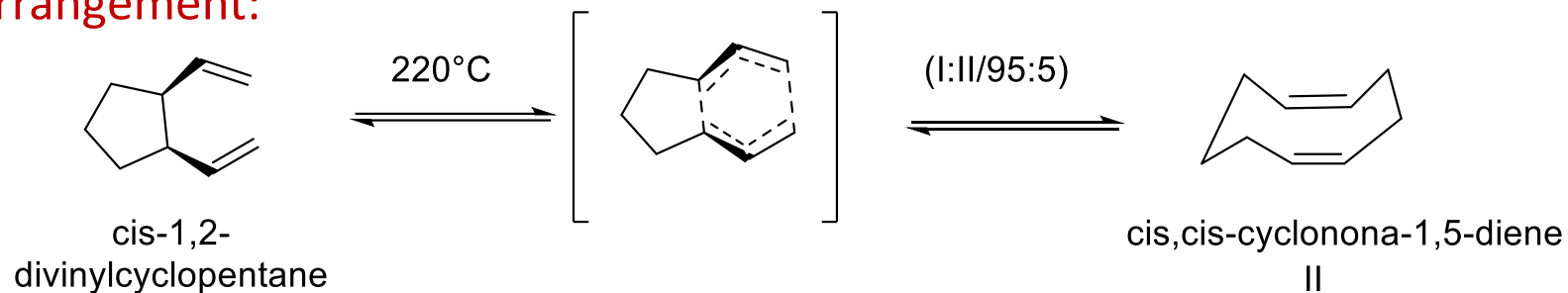
1) Roth, L. M., & Willis, E. R. (1952). A study of cockroach behavior. *The American Midland Naturalist*, 47(1), 66-129.

2) Persoons, C. J., et al. "Sex pheromones of the American cockroach, *Periplaneta americana*: A tentative structure of periplanone-B." *Tetrahedron Letters* 17.24 (1976): 2055-2058.

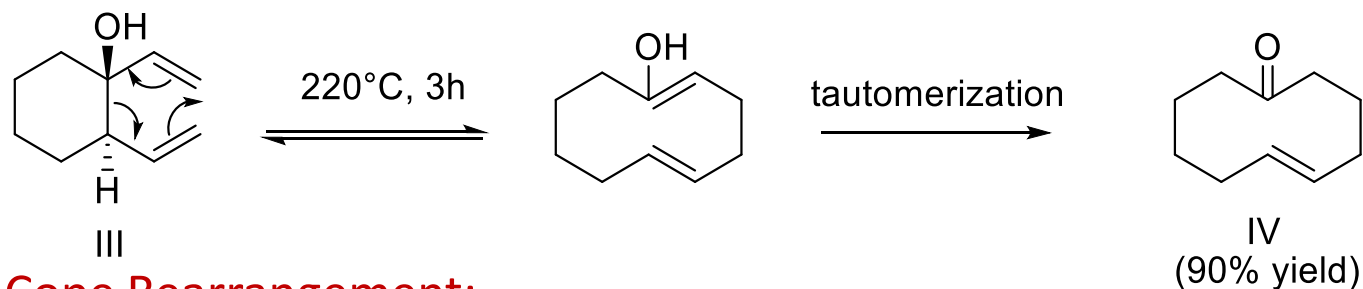
Retrosynthetic Analysis



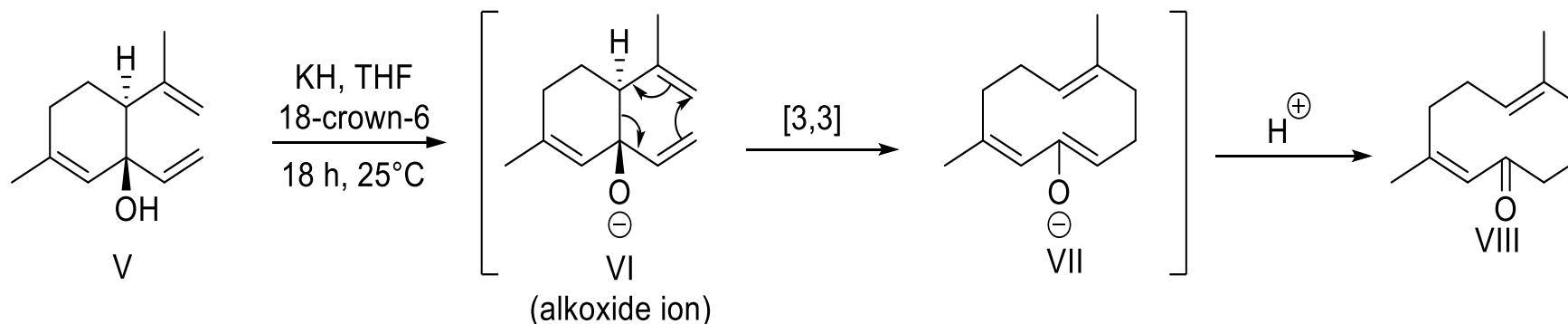
Cope Rearrangement:



oxy-cope Rearrangement:



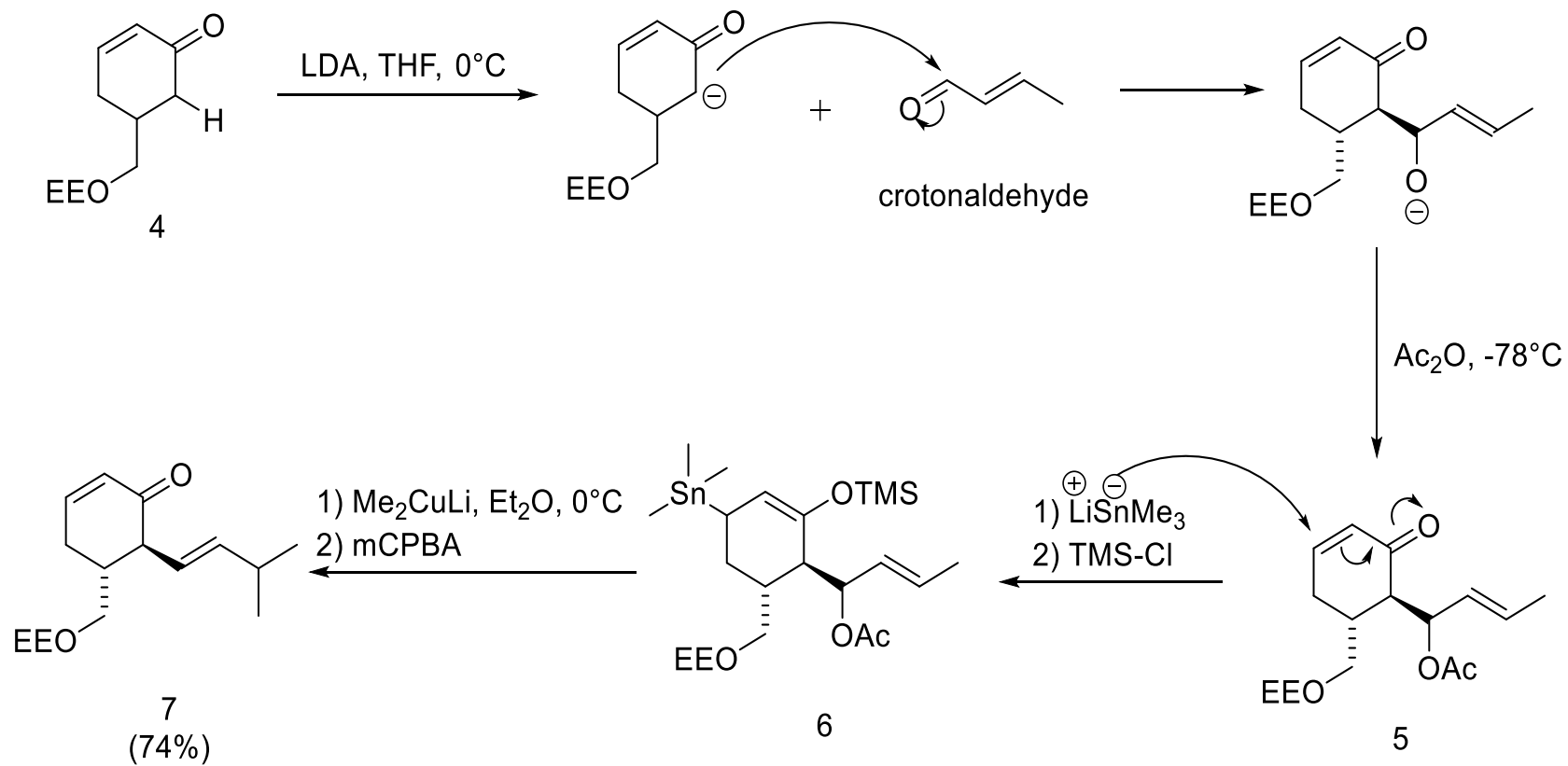
Anionic oxy-Cope Rearrangement:



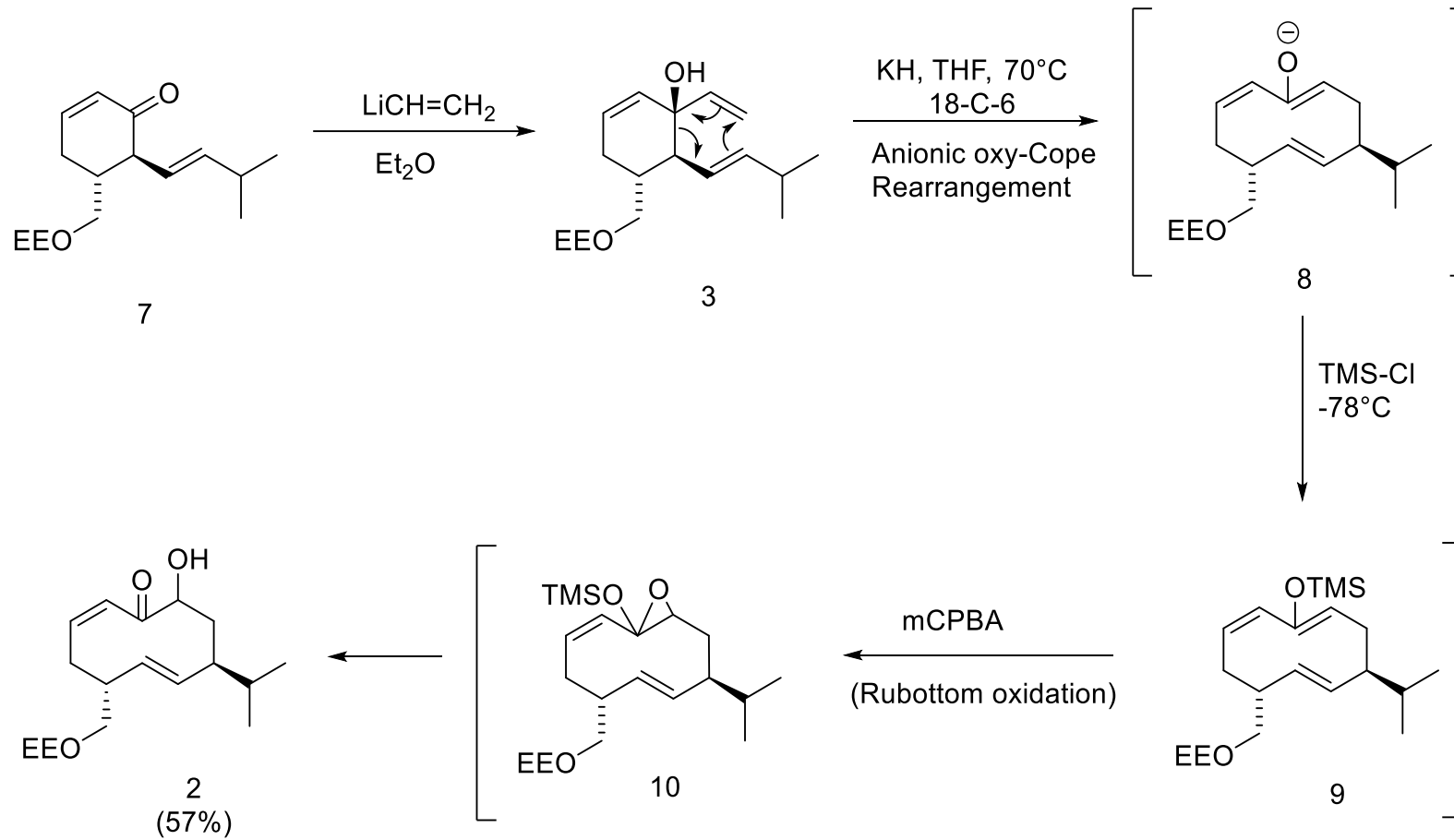
1) Vogel, E.; Grimme, W.; Dinné, E. Thermal Equilibrium between Cis-1, 2-Divinylcyclo-pentane and Cis, Cis-1, 5-Cyclononadiene. *Angewandte Chemie International Edition in English* **1963**, 2 (12), 739–740.

2) Still, W. C. An Expeditious Route to the Germacrane. Total Synthesis of (.+-.)-Acoragermacrone and (.+-.)-Preisocalamendiol. *Journal of the American Chemical Society* **1977**, 99 (12), 4186–4187.

Total Synthesis of Periplanone B

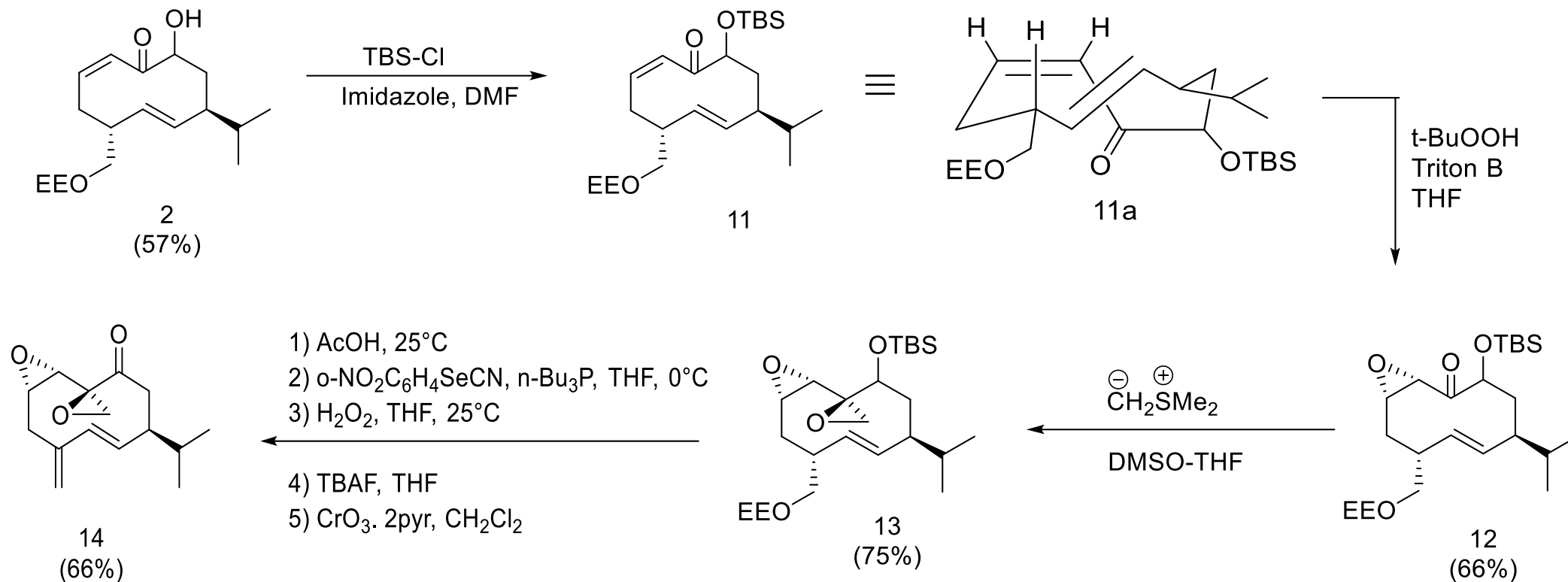


Contd..



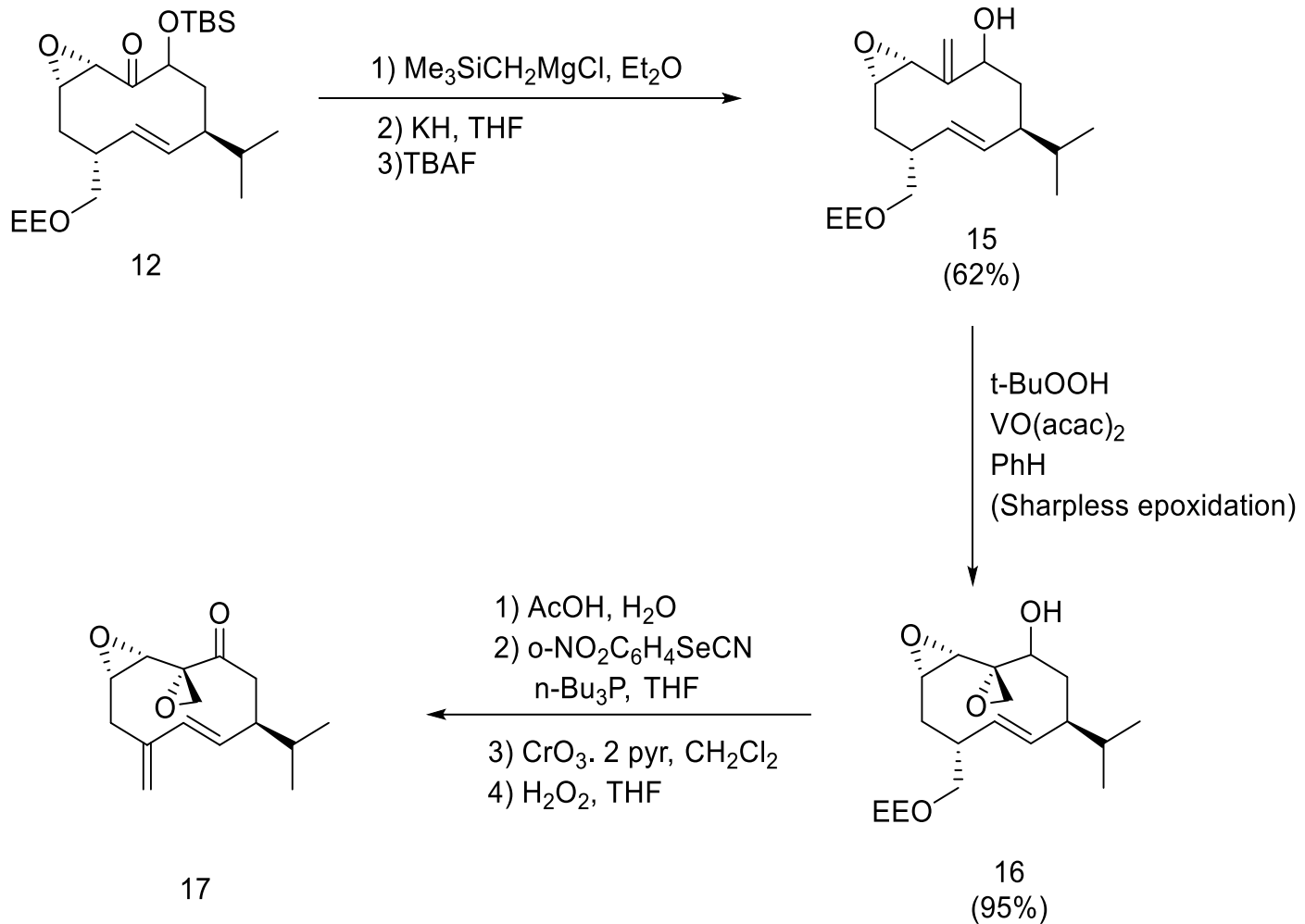
- Planes of olefinic groups and plane of ring are perpendicular
- Peripheral attack by reagents on more accessible double bond

Synthesis of 1st diastereomer



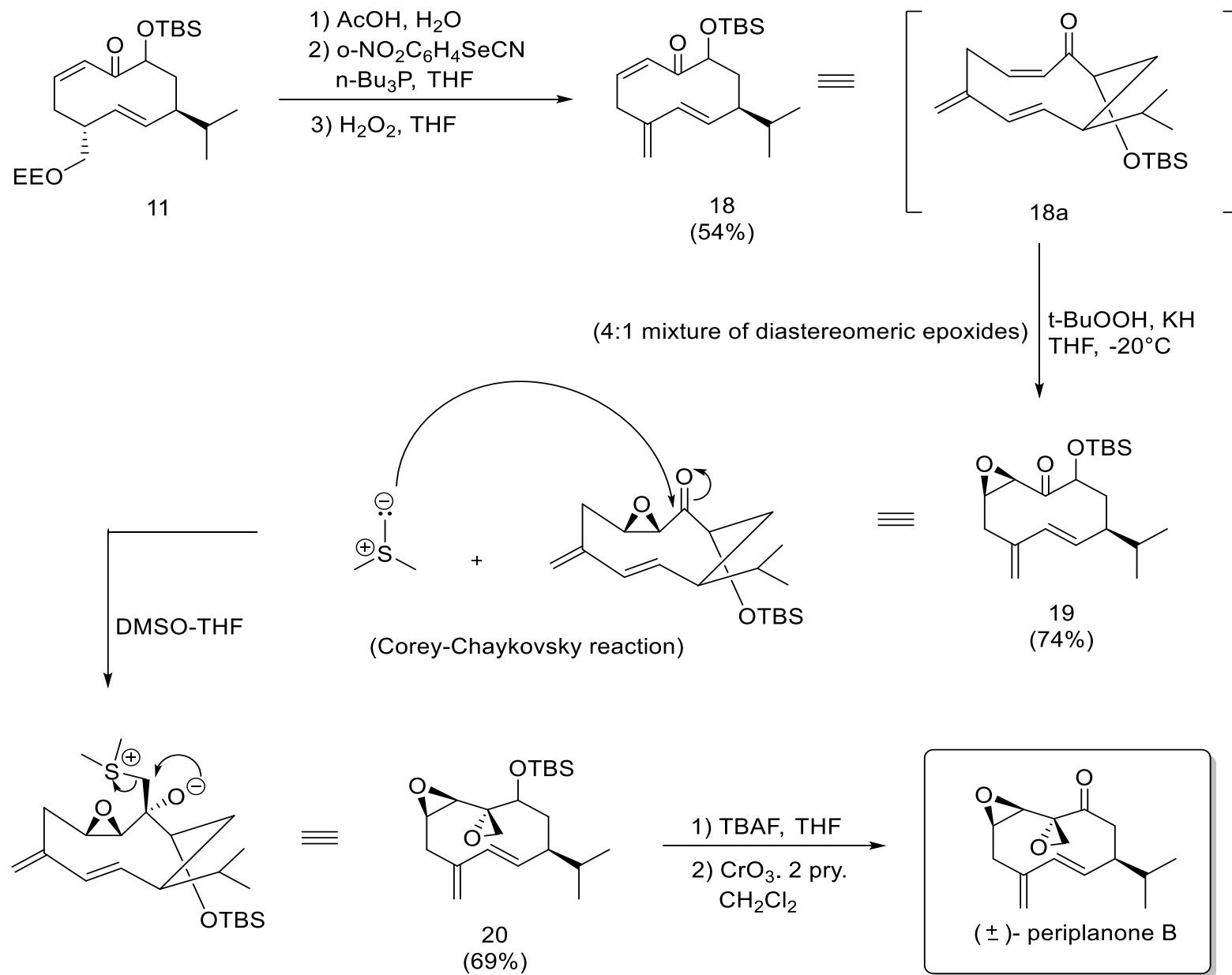
Spectroscopic data of 14 not identical to natural periplanone

Synthesis of 2nd diastereomer



Spectroscopic properties of 17 not identical to natural periplanone B

Synthesis of 3rd diastereomer



Conclusion:

- Demonstrates significance of anionic-oxy cope rearrangement
- Conformational preferences of ten-membered ring helps achieve stereochemical control
- Key intermediate 2 leads to synthesis of three diastereomers
- Still demonstrated beautiful synthesis with the constitution and relative stereochemistry of the American cockroach sex pheromone periplanone B

THANK YOU!