

Jiangpeng Liu  
 Liu Research Group  
 4/5/2023

# Enantioselective Total Synthesis of (+)-Alterbrassicene C

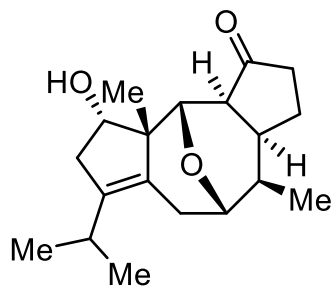
Noah J. Sims, Weston C. Bonnet, Danielle M. Lawson, and John L. Wood\*



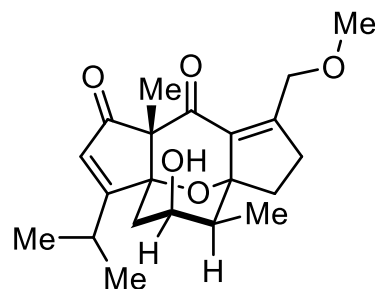
Cite This: *J. Am. Chem. Soc.* 2023, 145, 37–40



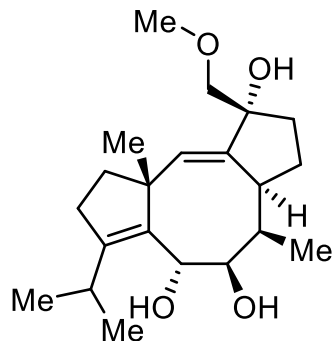
Read Online



**(-)-Alterbrassicene B**  
 No syntheses to date



**(+)-Alterbrassicene C**  
 This work, first synthesis

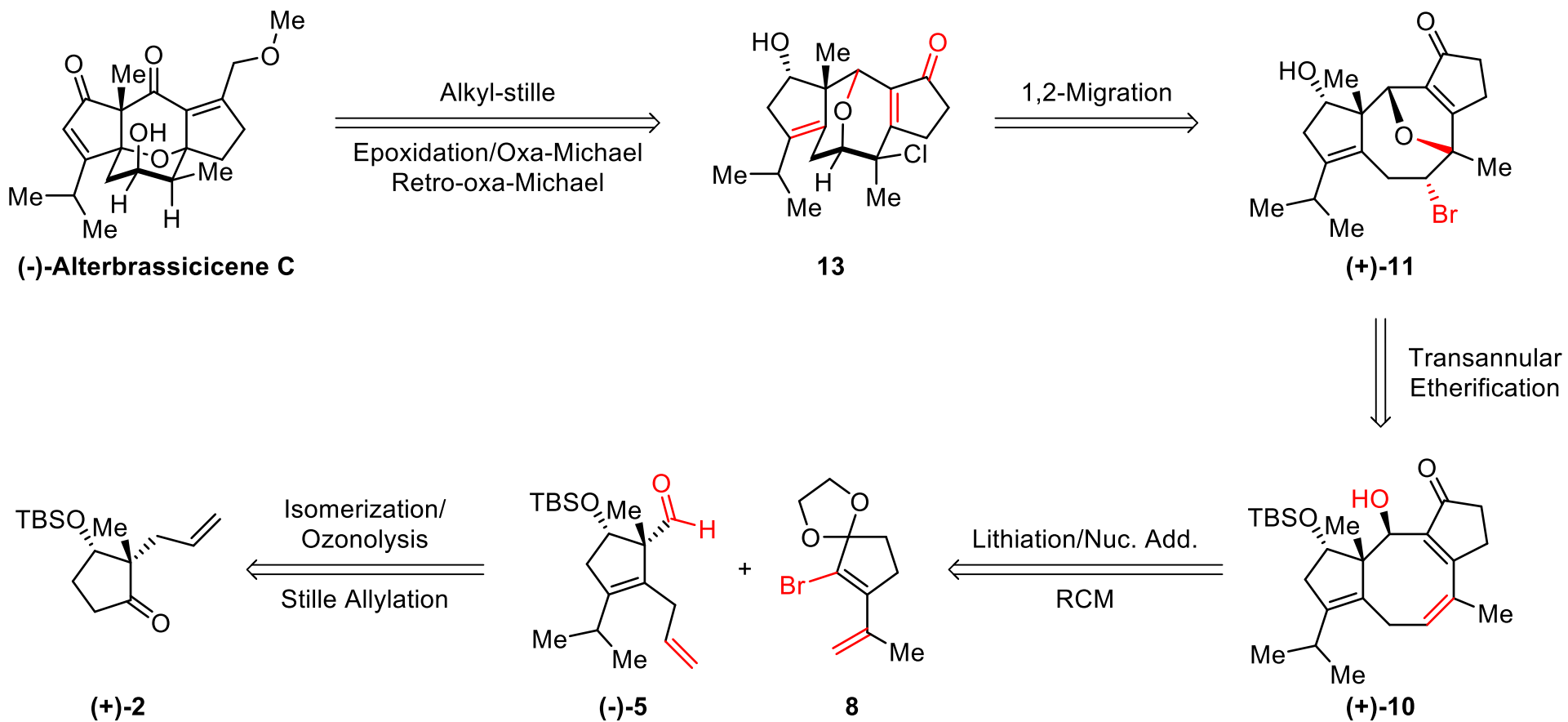


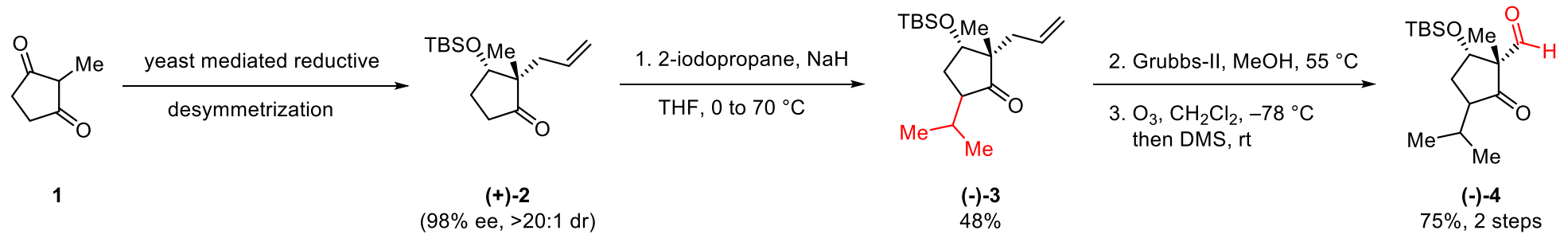
**(-)-Cotylenol**  
 Several syntheses

## Introduction:

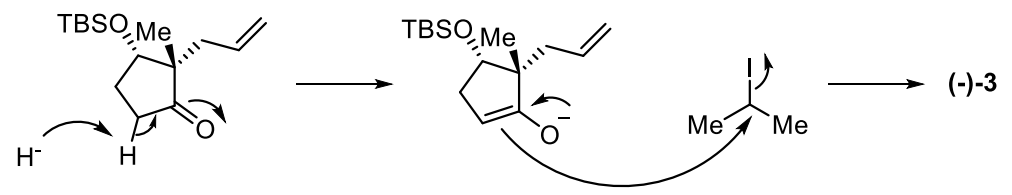
- A novel fusicoccane diterpenoid recently isolated from the fungal plant pathogen *Alternaria brassicicola*.
- It features a unprecedented 5,6,6,5- tetracyclic oxa-bridged ring system.
- The first total synthesis of **(+)-Alterbrassicene C** was accomplished

# Retro-synthetic route

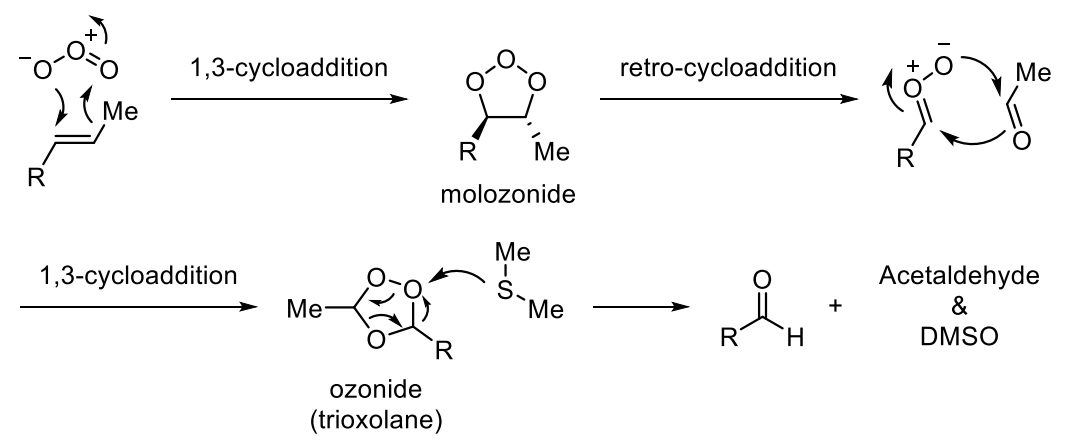




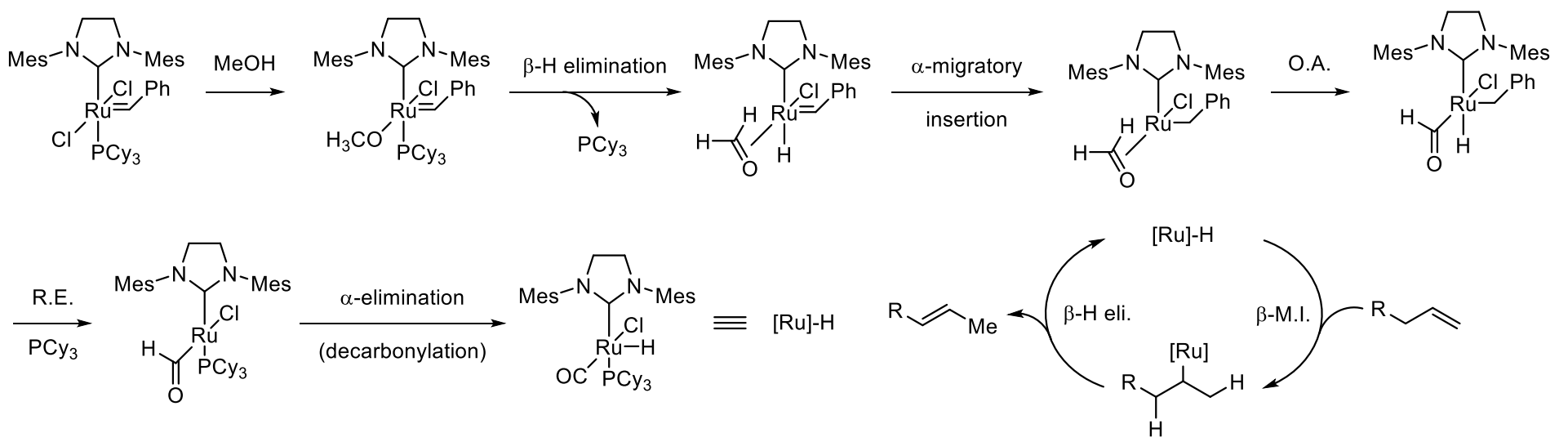
Alkylation:

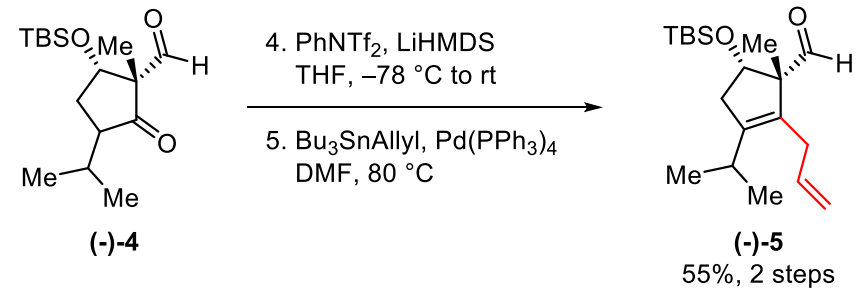


Ozonolysis:

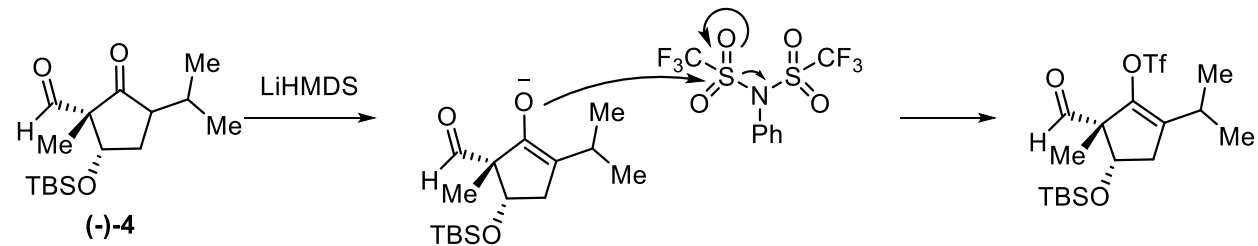


Isomerization of terminal alkene:

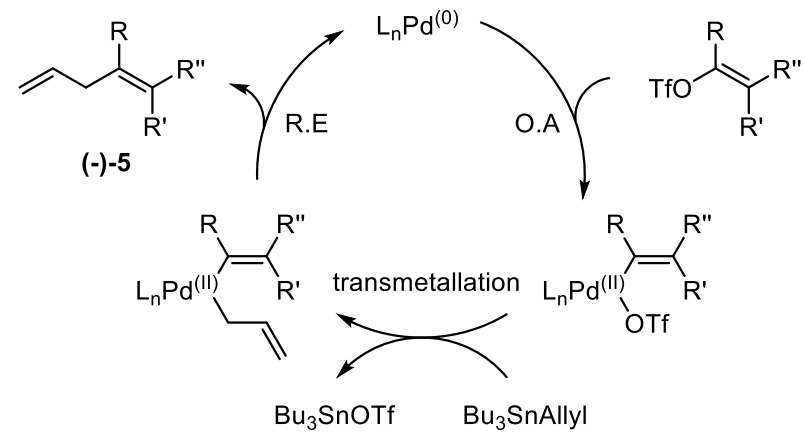


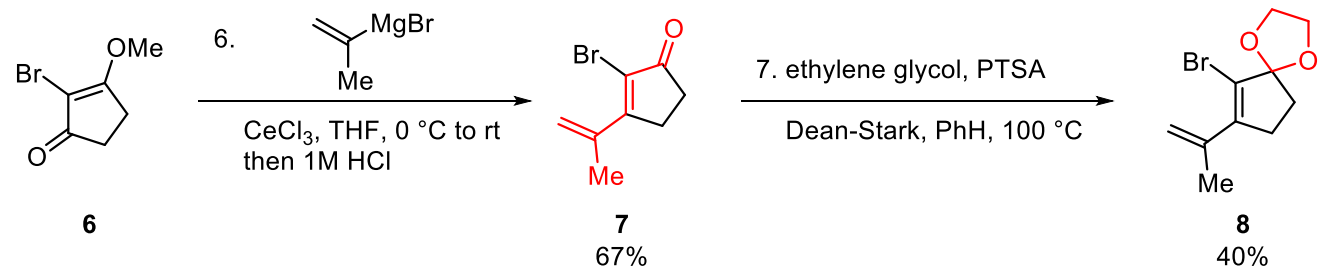


Formation of vinyl triflate:

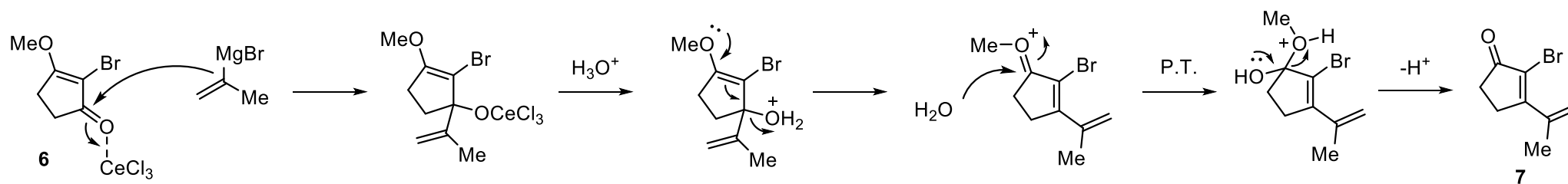


Stille Cross-coupling:

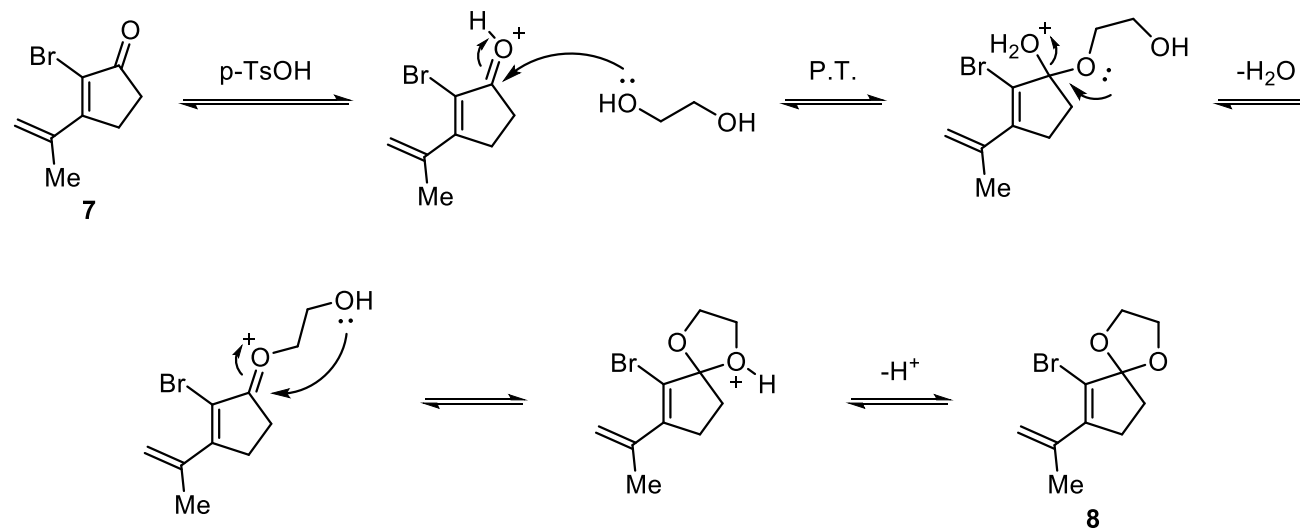


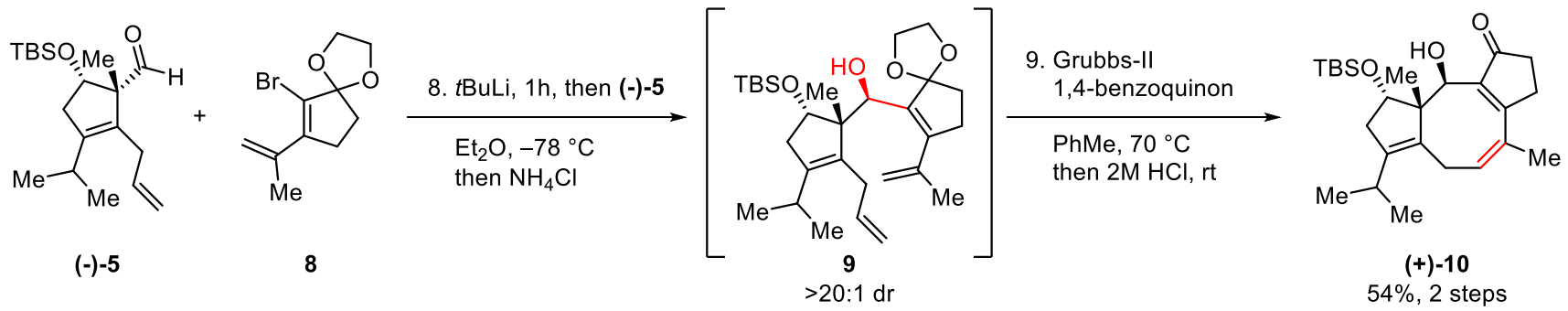


Stork-Danheiser reaction: Install a nucleophile while ultimately "switching" the position of the carbonyl

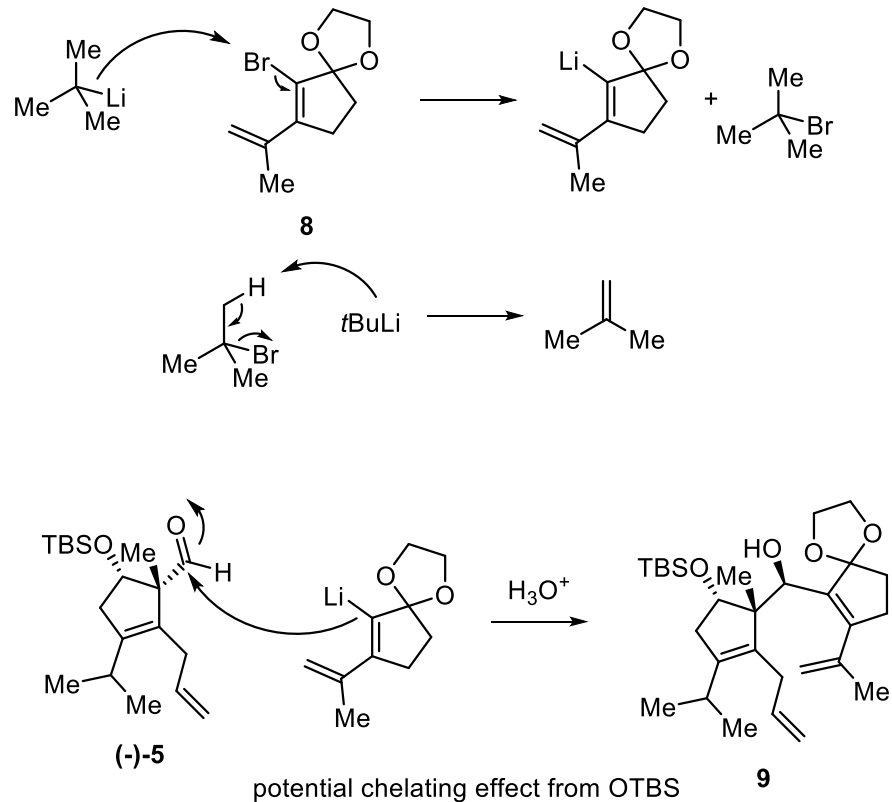


Protection of ketone with ethylene glycol

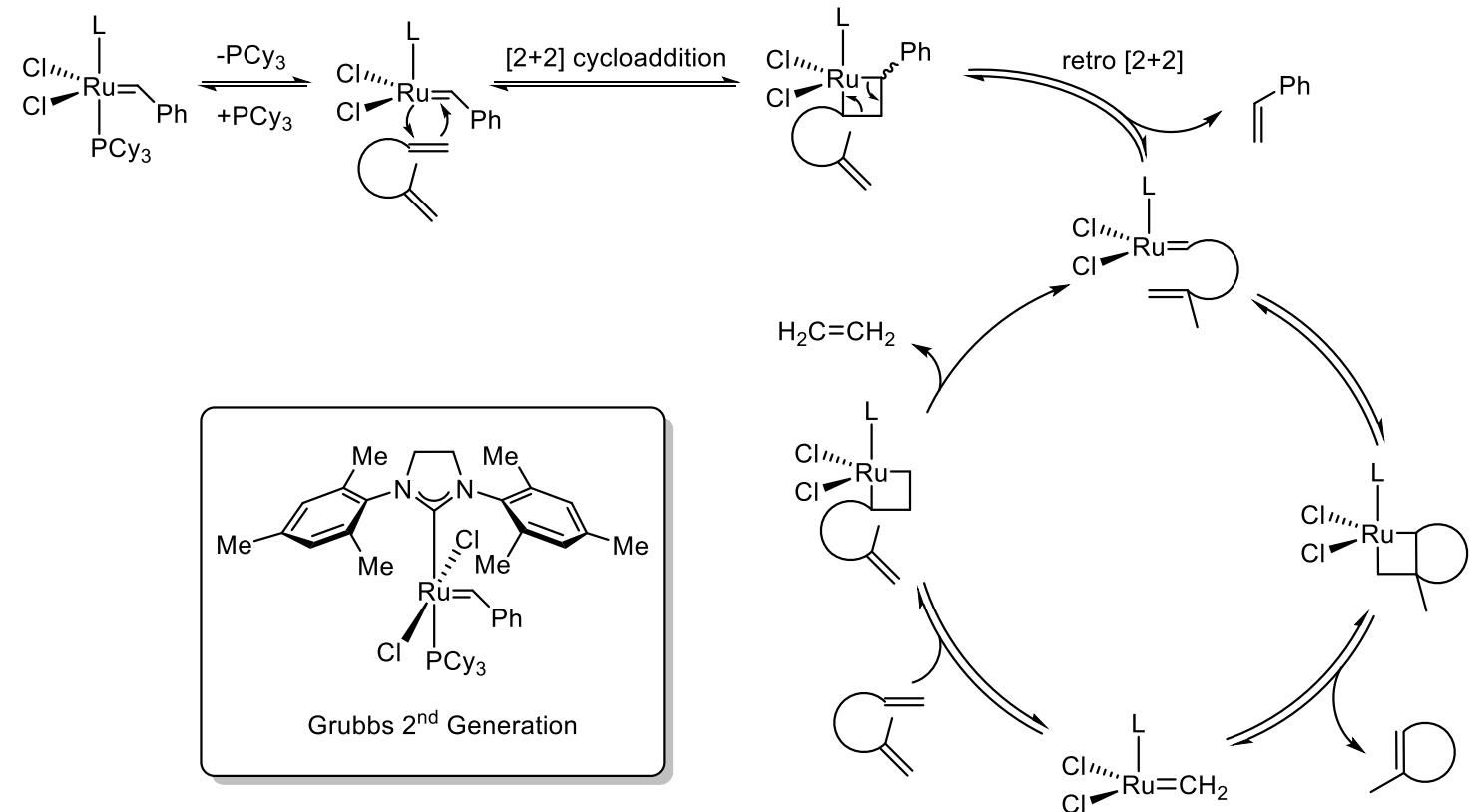


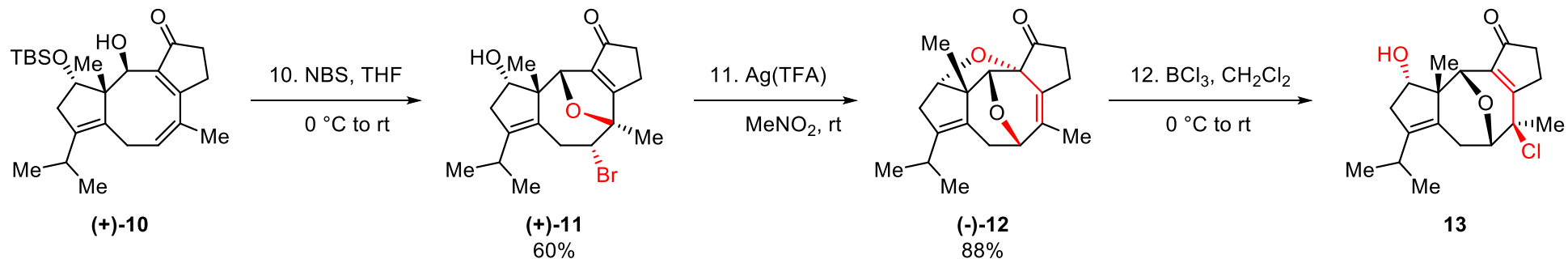


Lithium-halogen exchange and nucleophilic attack:

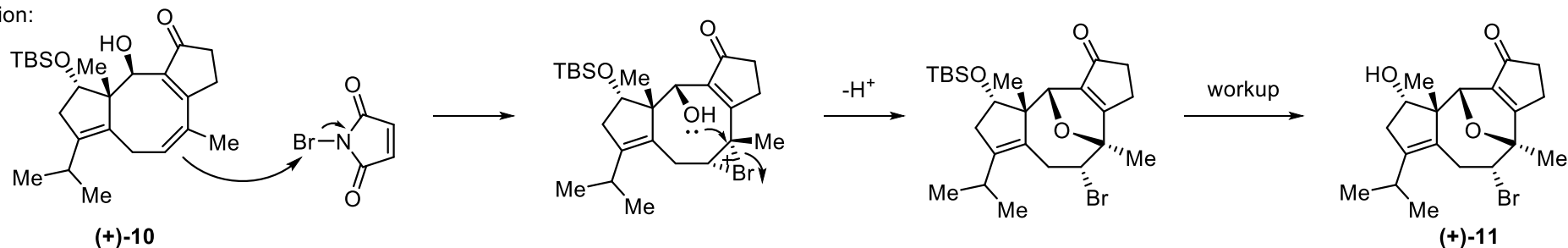


Ring-closing metathesis reaction (RCM):

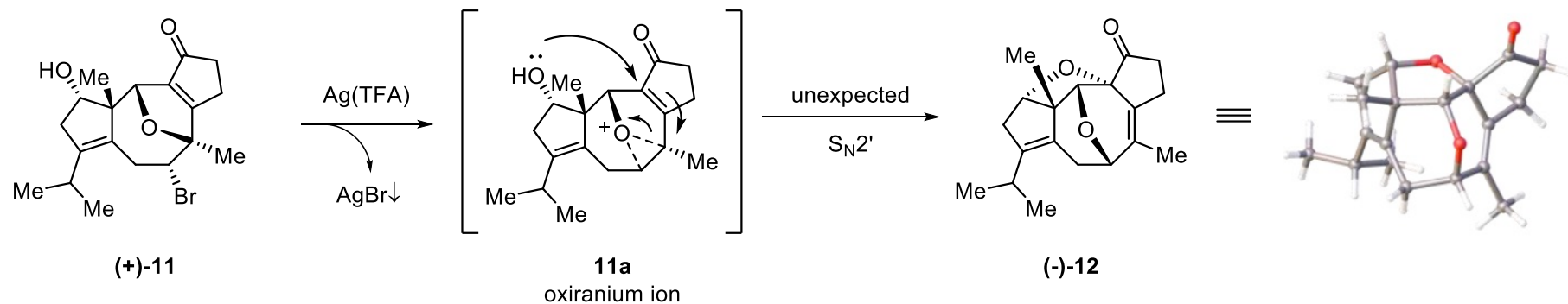




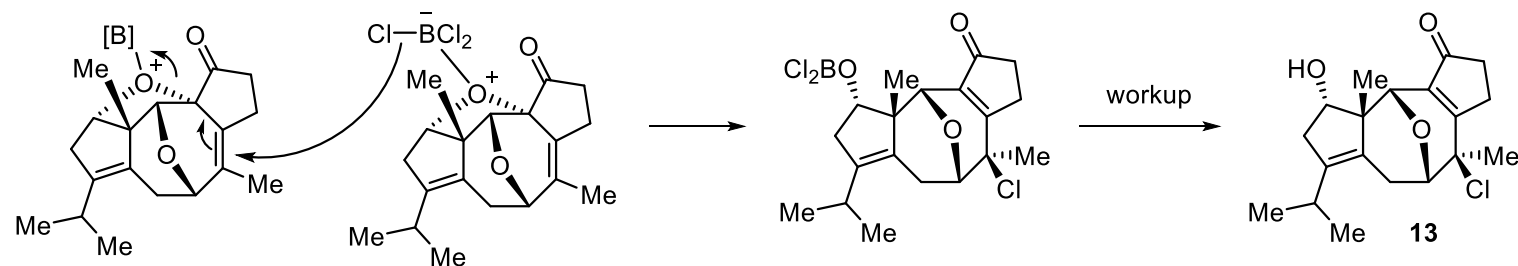
Transannular haloetherification:

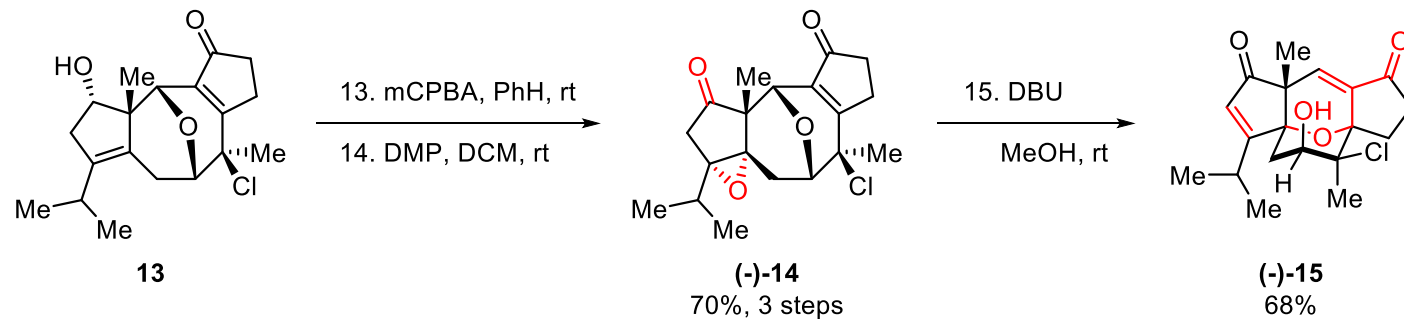


1,2-Migration:

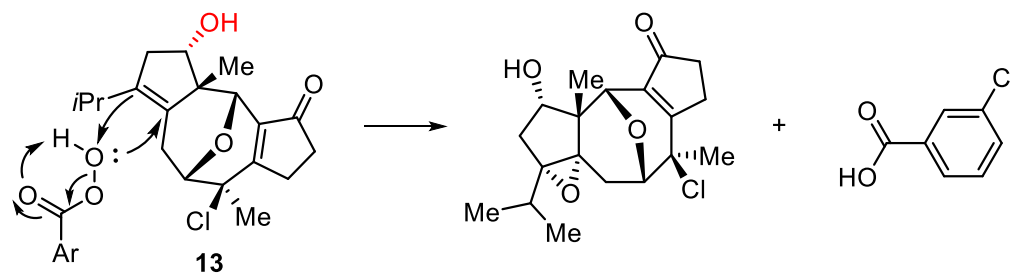


Reverse S<sub>N</sub>2' with BCl<sub>3</sub>:

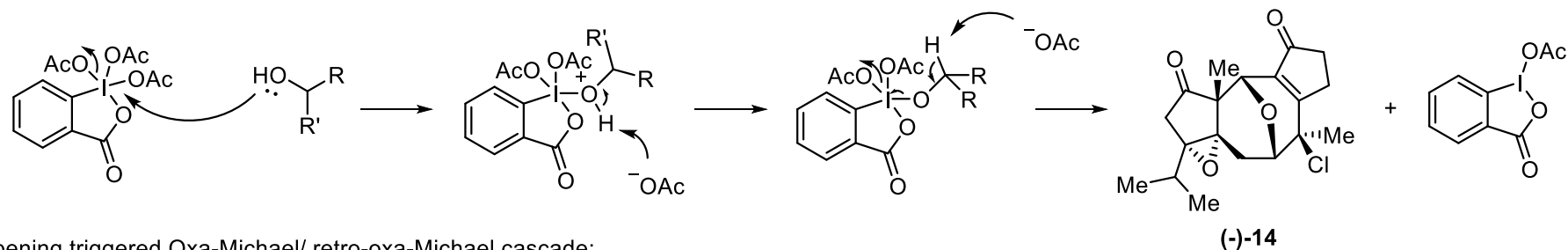




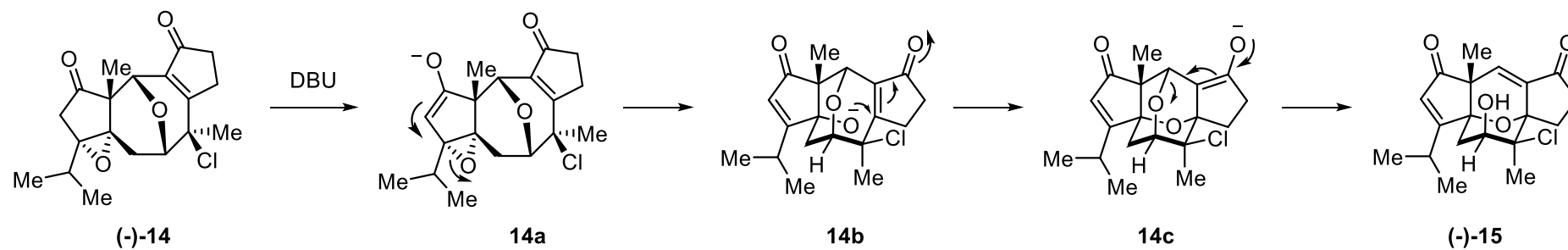
Prilezhaev epoxidation:



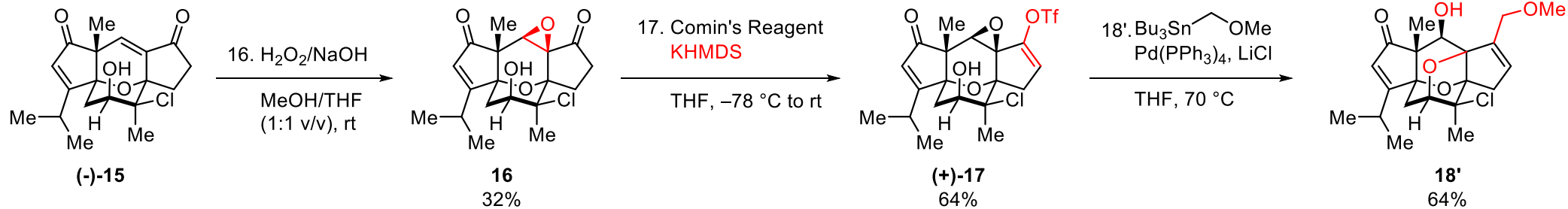
Dess-Martin oxidation:



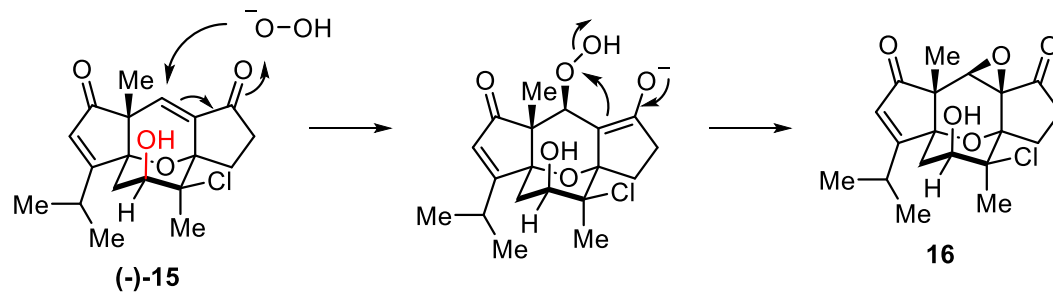
Ring-opening triggered Oxa-Michael/ retro-oxa-Michael cascade:



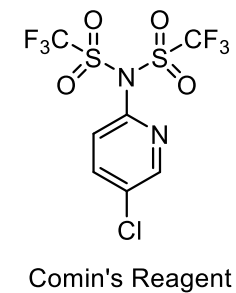




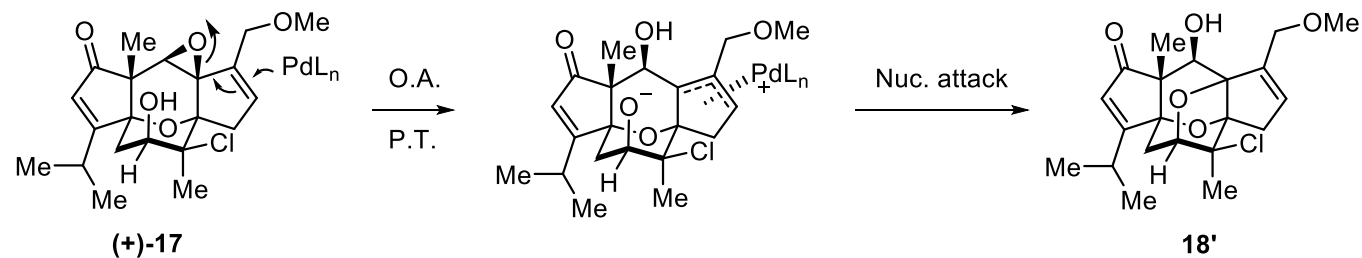
Weitz-Scheffer epoxidation (nucleophilic epoxidation):

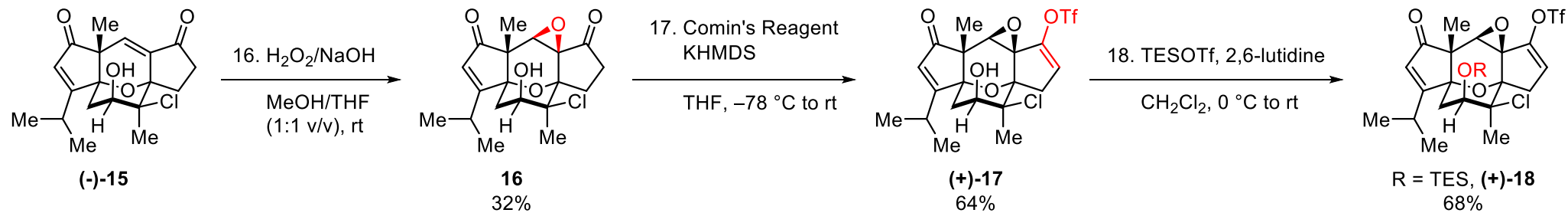


Formation of vinyl triflate:

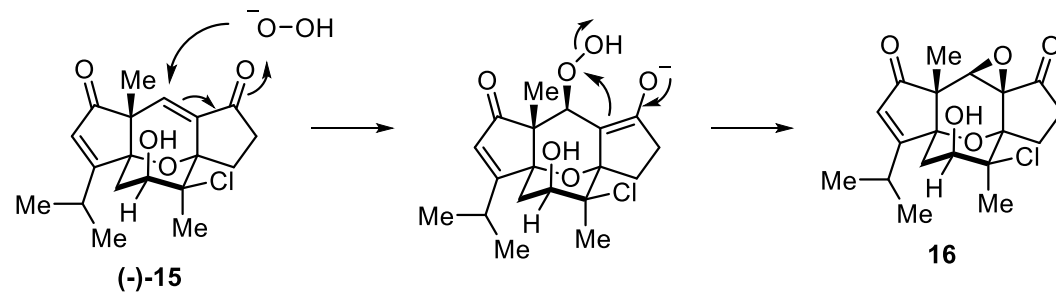


First attempt of Stille Cross-coupling with unexpected ring-opening of epoxide:

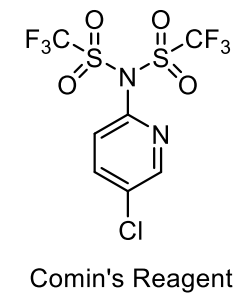




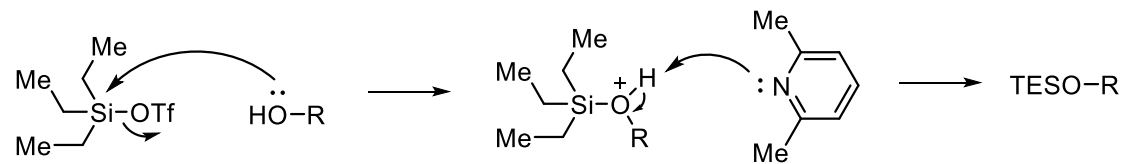
Weitz-Scheffer epoxidation (nucleophilic epoxidation):

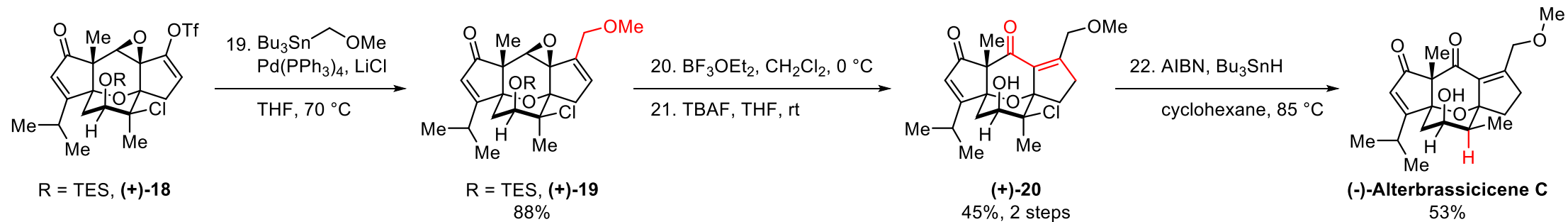


Formation of vinyl triflate:

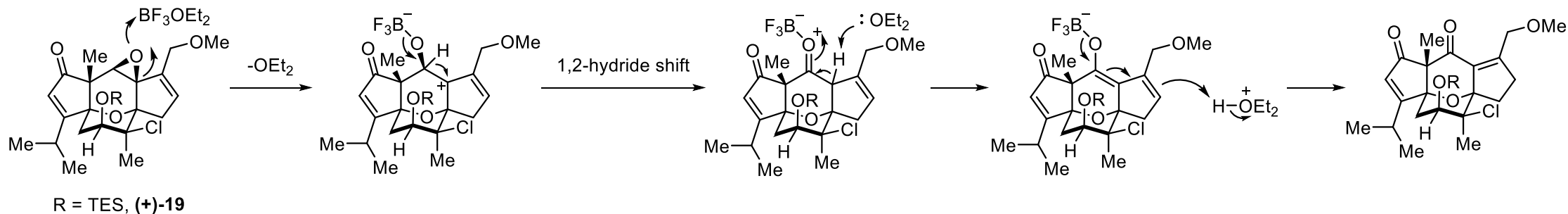


TES protection:

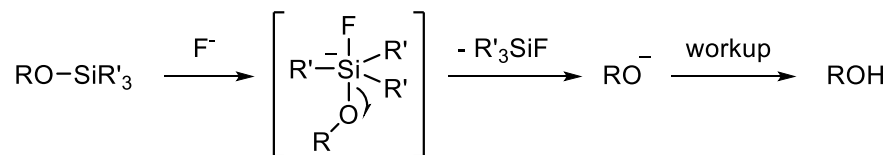




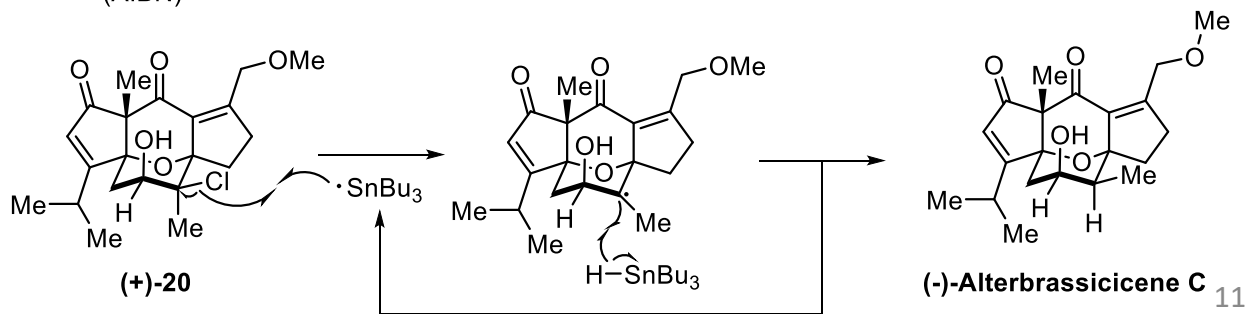
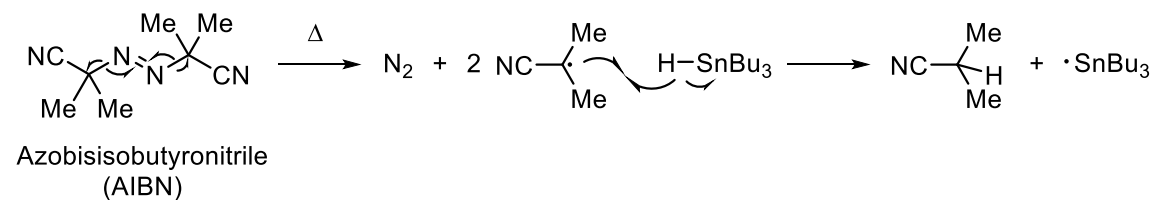
Meinwald rearrangement and alkene isomerization:



Desilylation with TBAF:



Radical dehalogenation:



Thanks for your attention