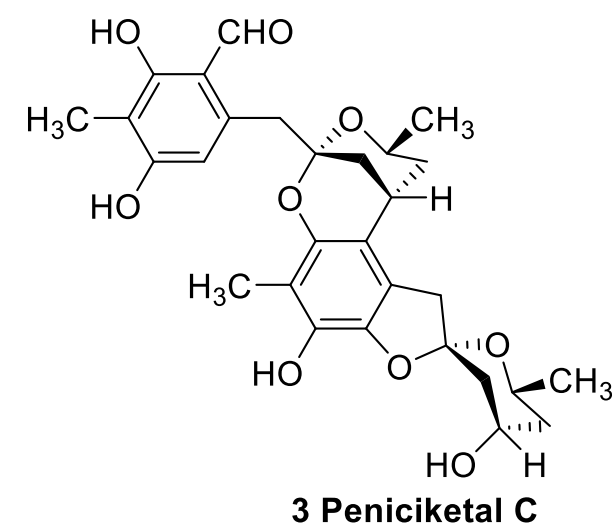
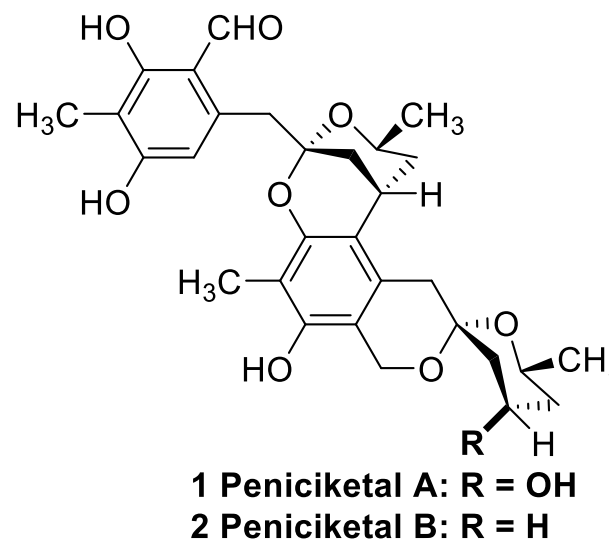


Enantioselective Total Synthesis of (+)-Peniciketals A and B: Two Architecturally Complex Spiroketal

Yifan Deng, Chia-Ping H. Yang, and Amos B. Smith III

J. Am. Chem. Soc. **2021**, 143, 4, 1740–1744

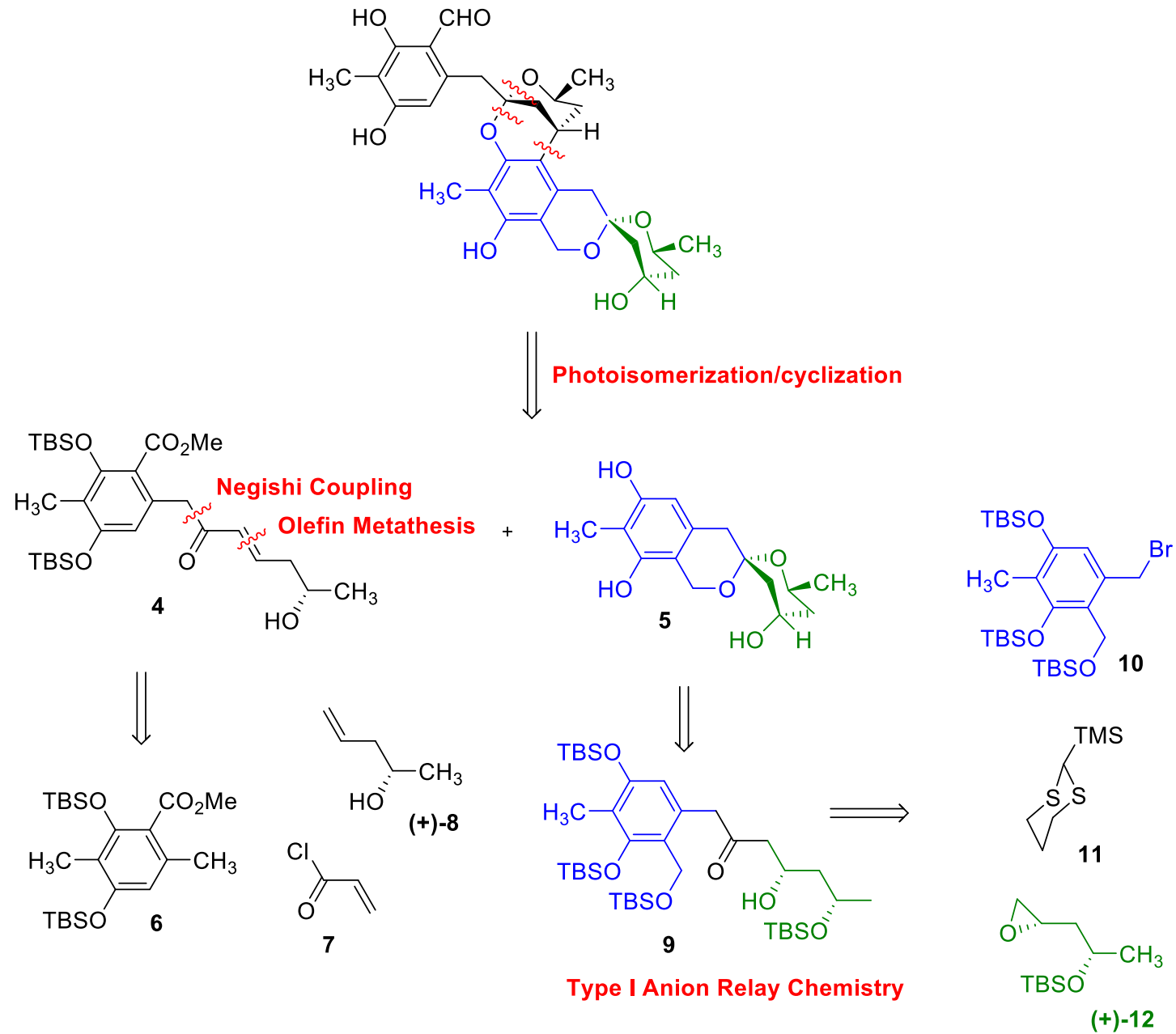
- Peniciketals A-C (**1-3**) were isolated from *Penicillium raistrickii* in 2014, and have cytotoxicity against certain cancer cells
- Peniciketal A (**1**) displays anticancer activity against three leukemia cell lines, and has high selectivity for cancer cells
- The peniciketals contain unprecedented benzannulated [5,6]- or [6,6]- spiroketal and 2,8-dioxabicyclo- [3.3.1]nonane ring systems
- This work represents the first total synthesis of Peniciketals A (**1**) and B (**2**)



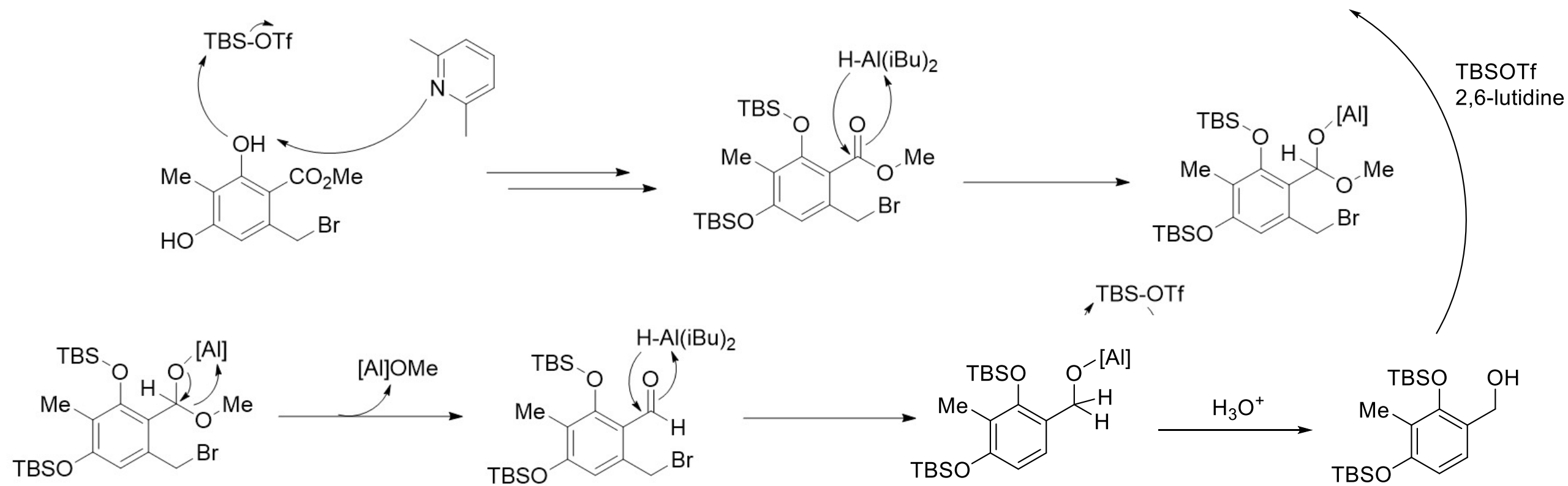
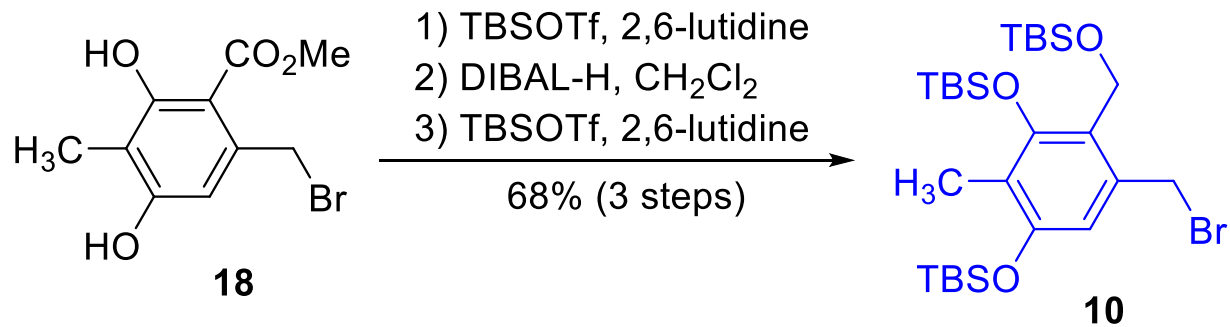
Max Eaton, Liu Group, Boston College

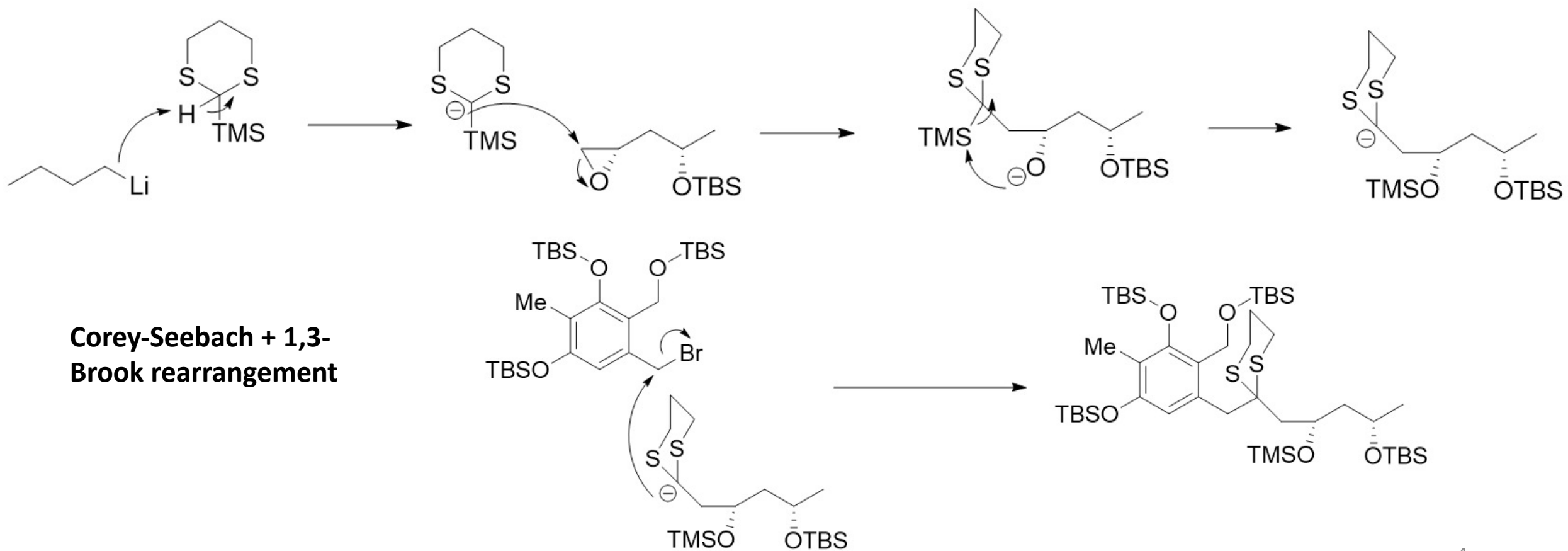
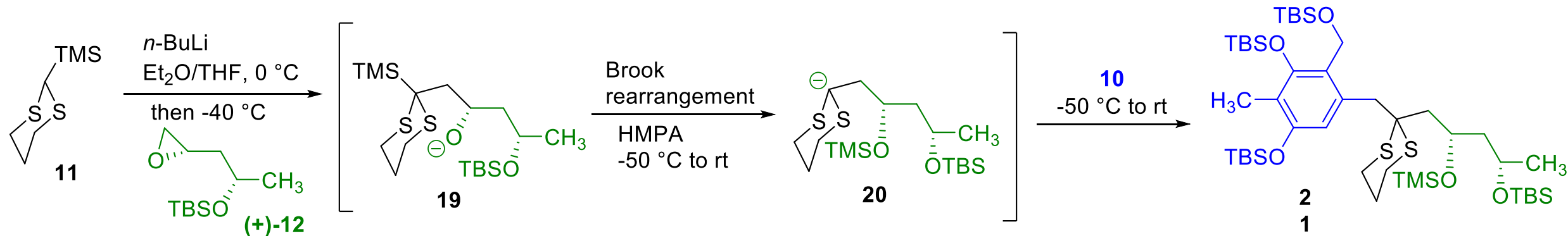
2/17/2021

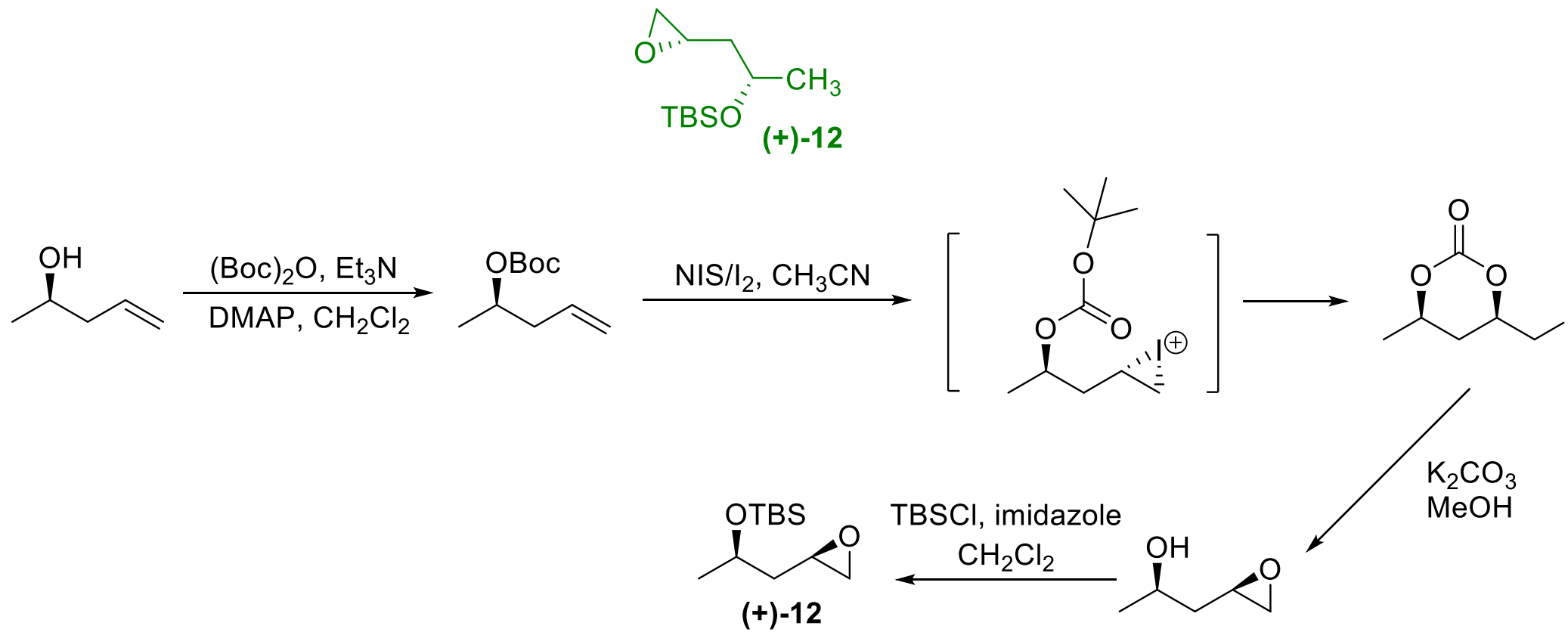
Retrosynthesis

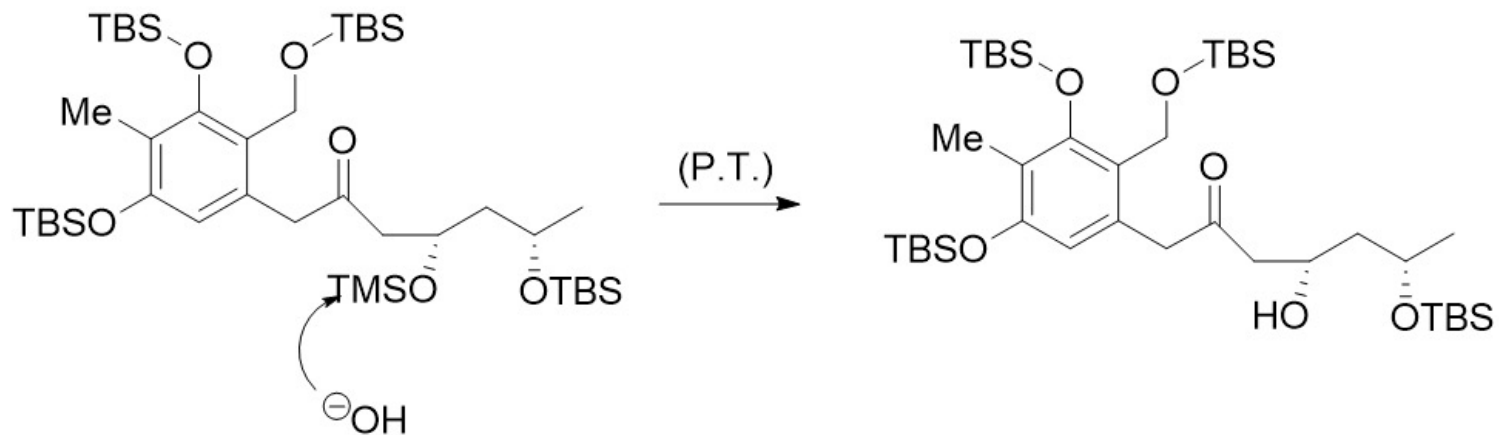
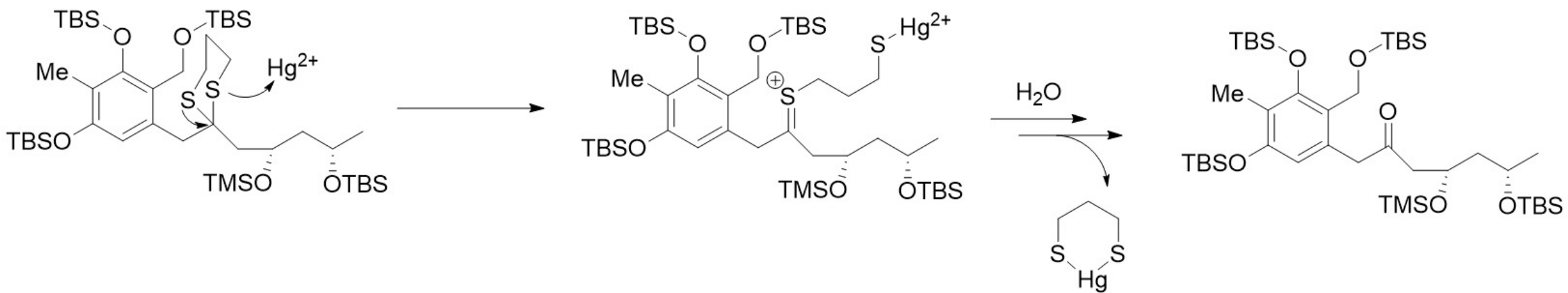
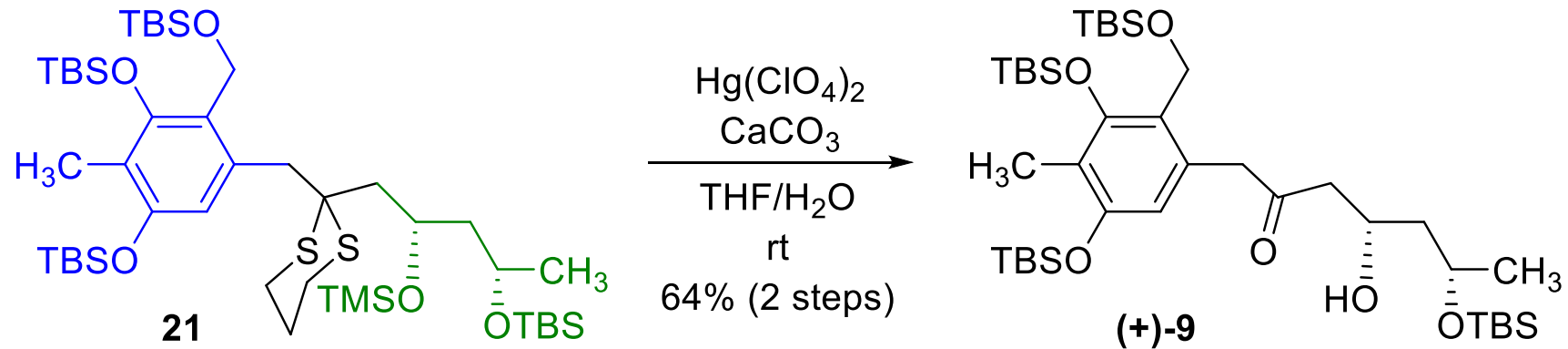


TBS protection + DIBAL-H reduction

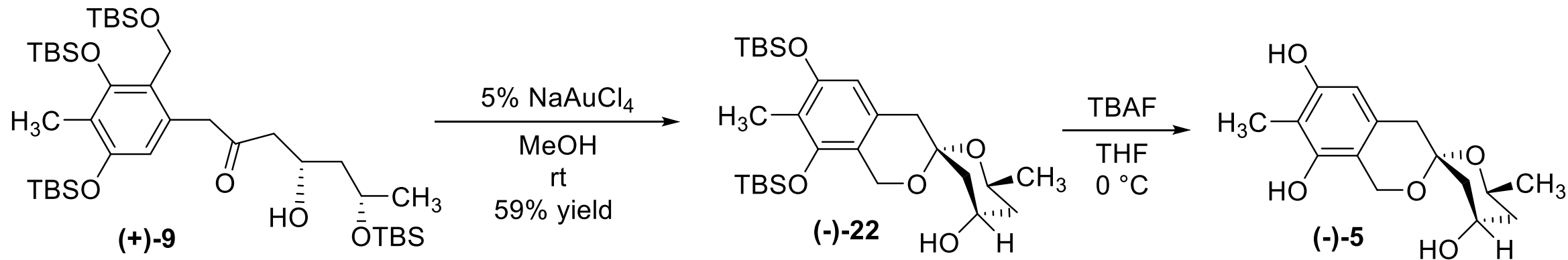




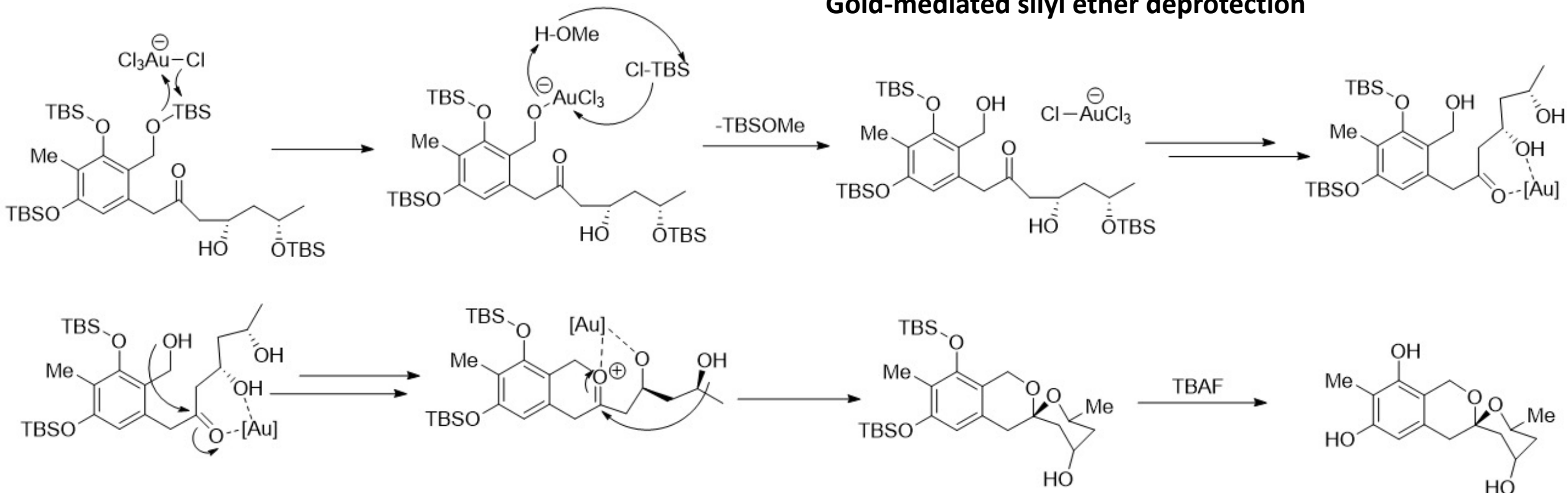


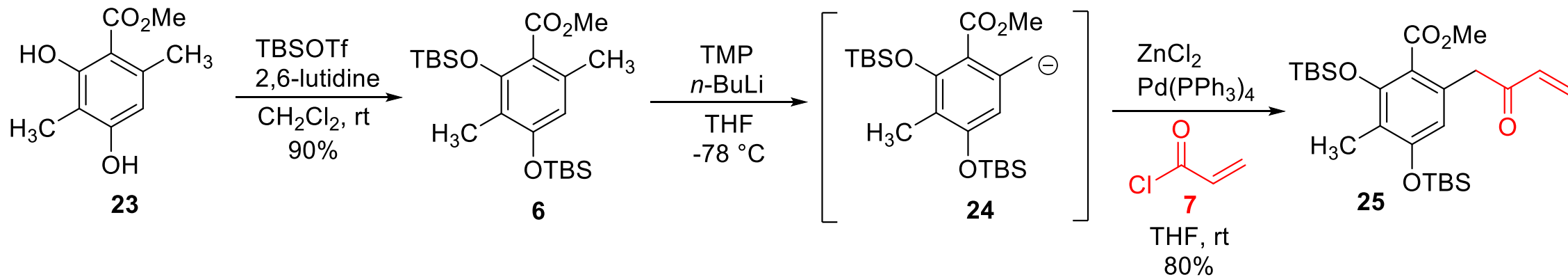


Hg-mediated dithiane deprotection

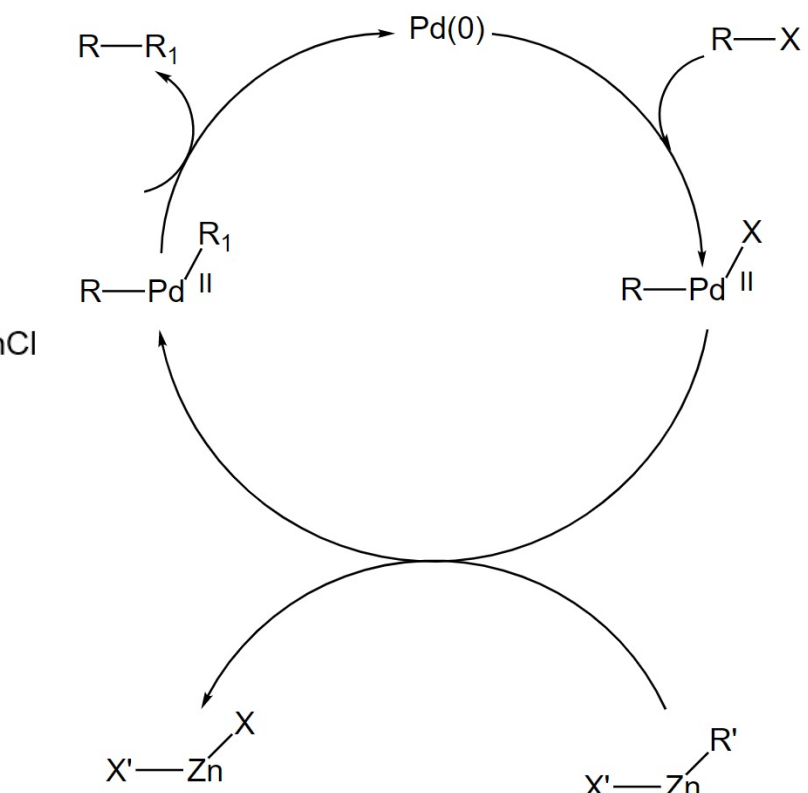
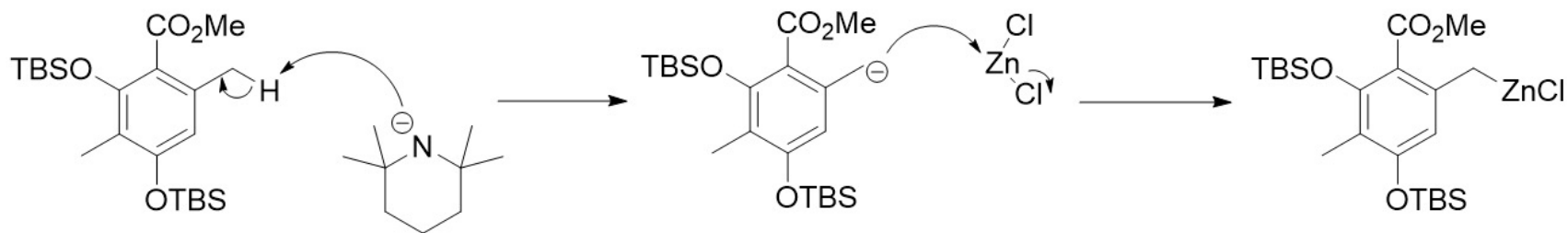


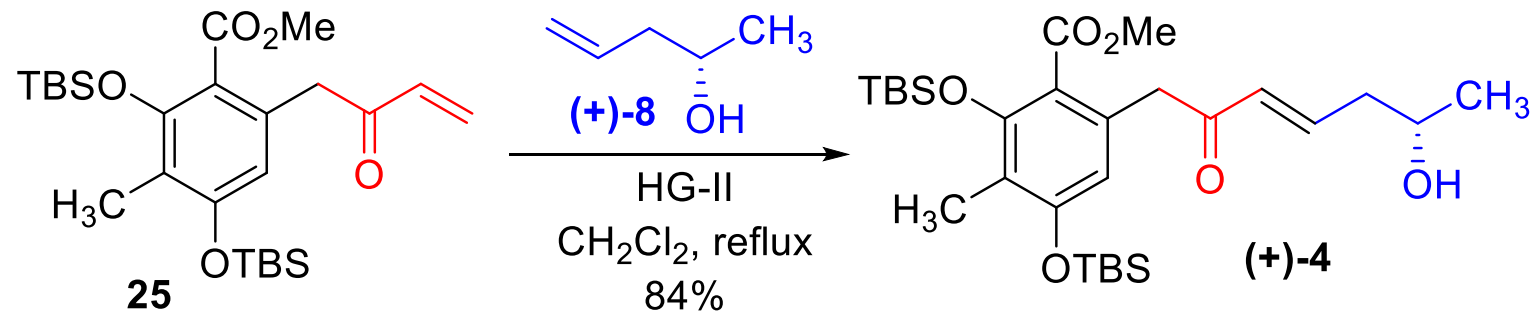
Gold-mediated silyl ether deprotection



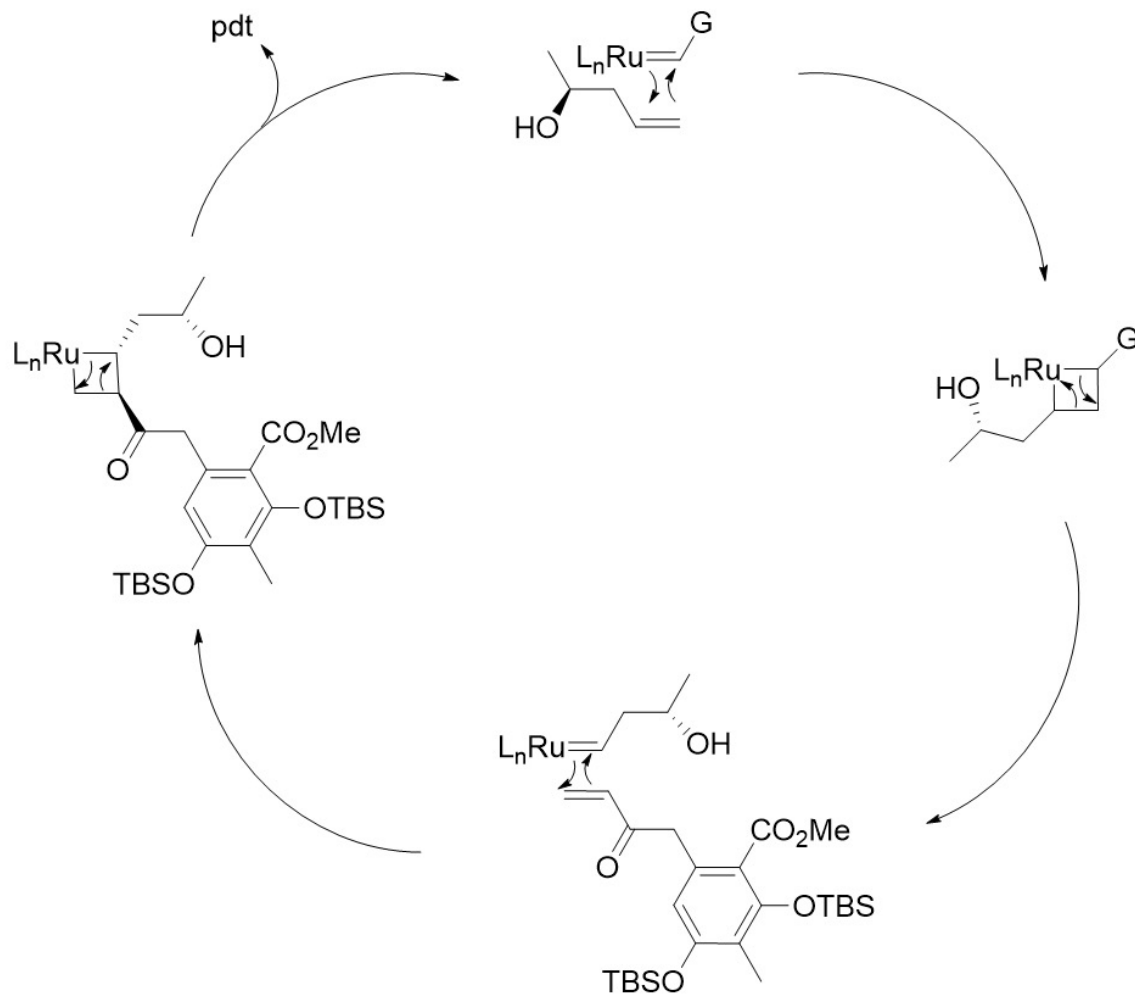


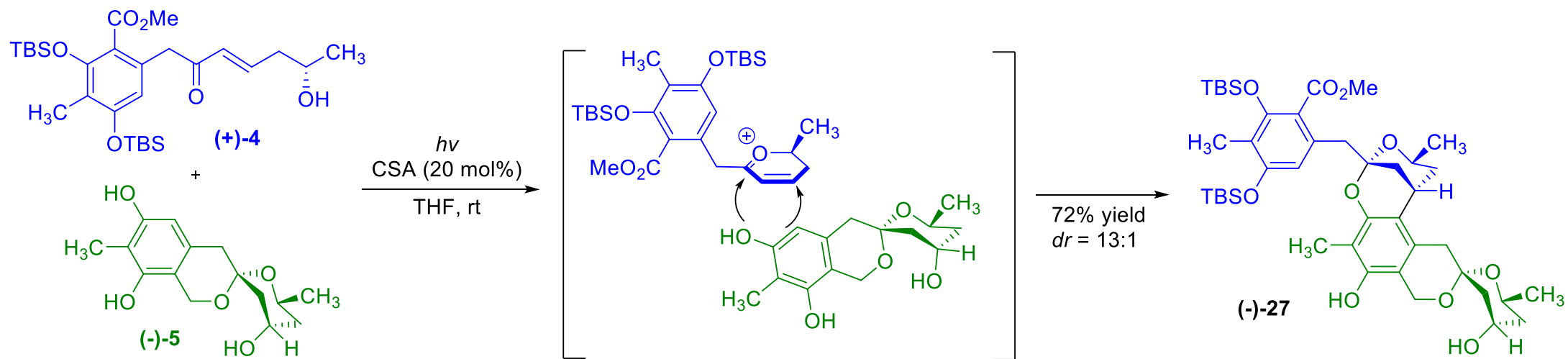
Benzylic metalation, Negishi coupling



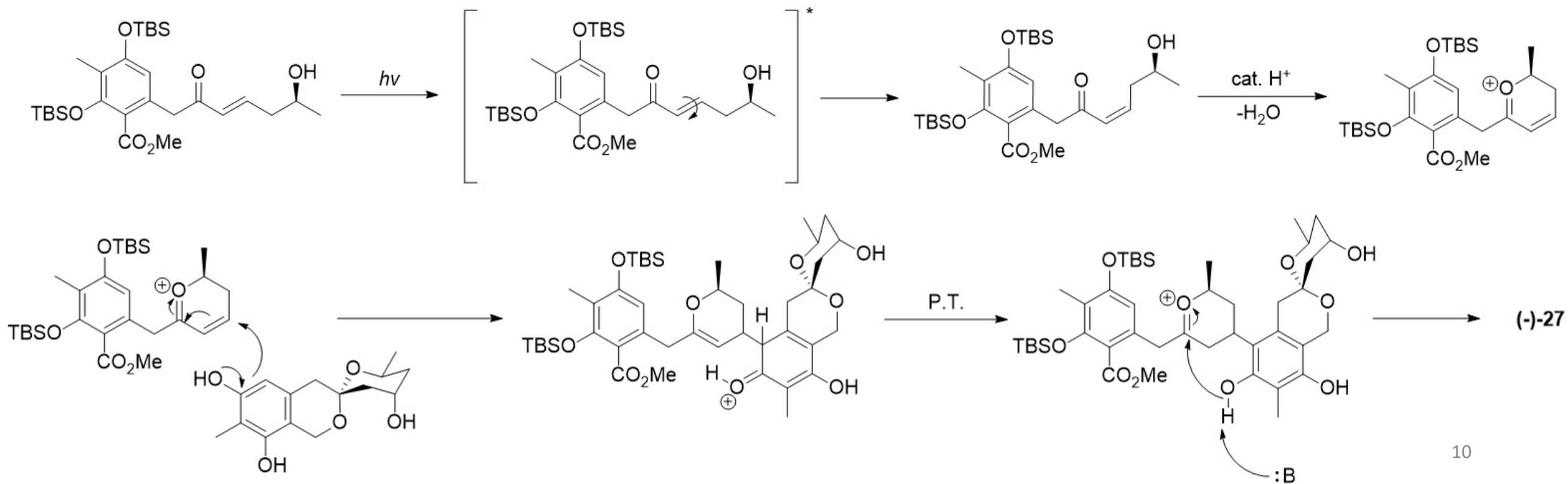


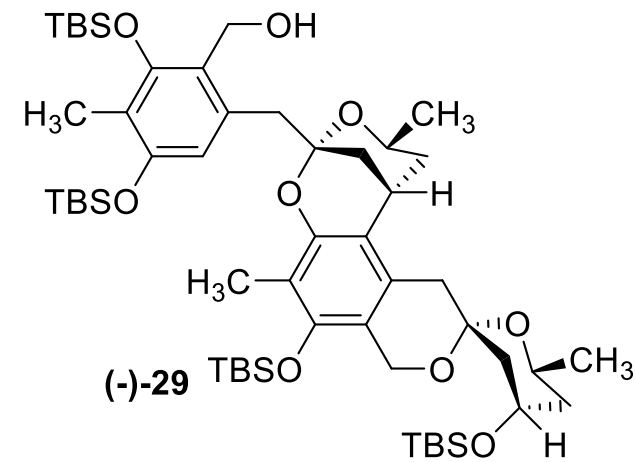
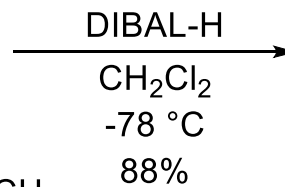
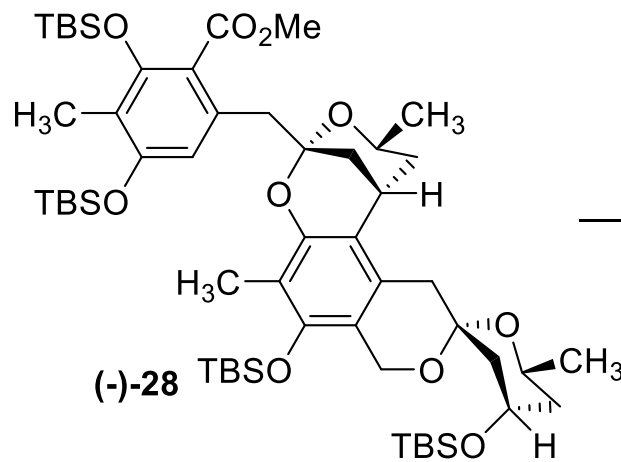
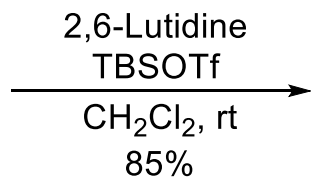
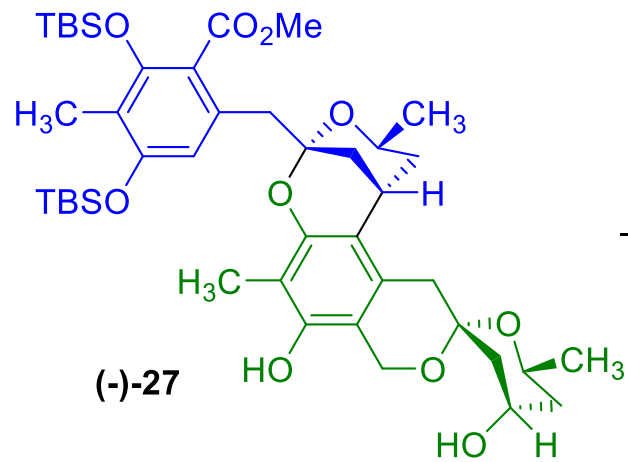
Olefin metathesis



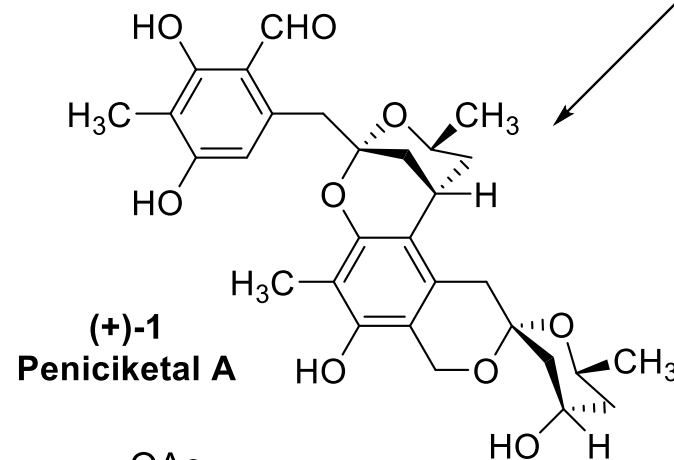


Photoisomerization/cyclization

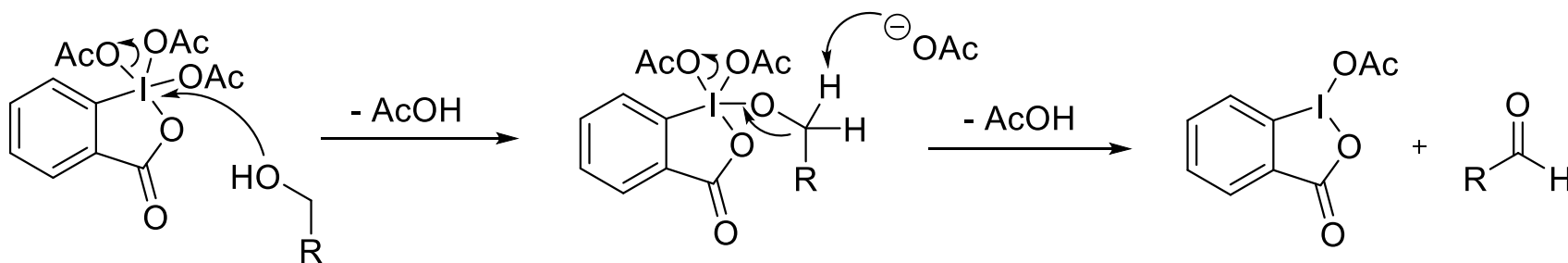


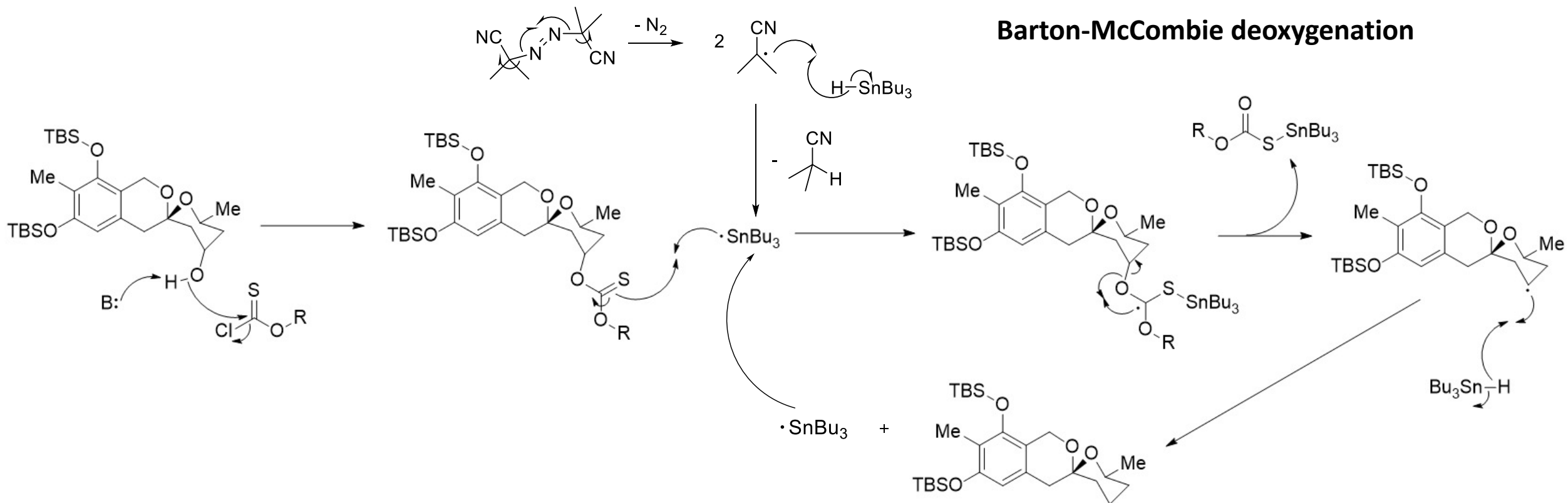
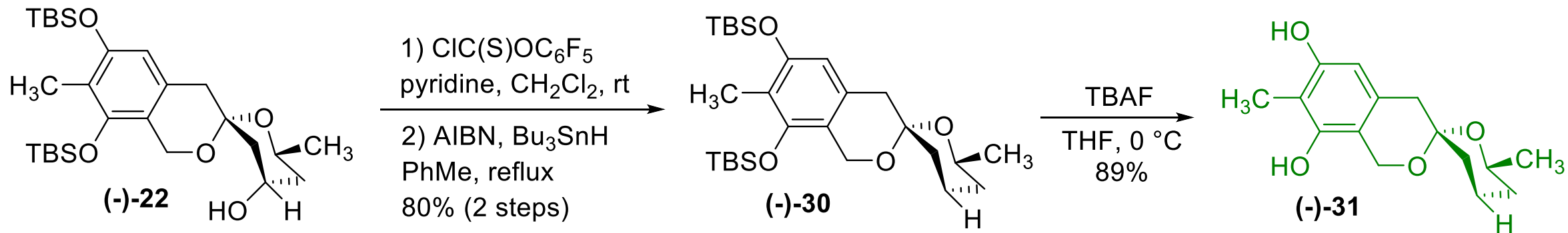


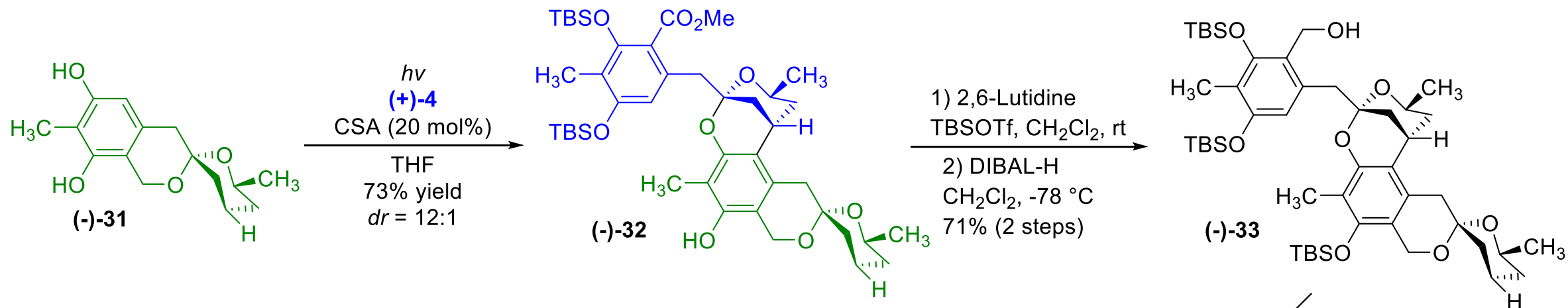
1) DMP, NaHCO₃
CH₂Cl₂, rt
2) TBAF, THF
rt, 62% (2 steps)



Dess-Martin Oxidation







1) PCC, NaHCO_3
 mol. sieves, CH_2Cl_2 , rt
 2) TBAF, THF, rt
 61% (2 steps)

PCC oxidation

