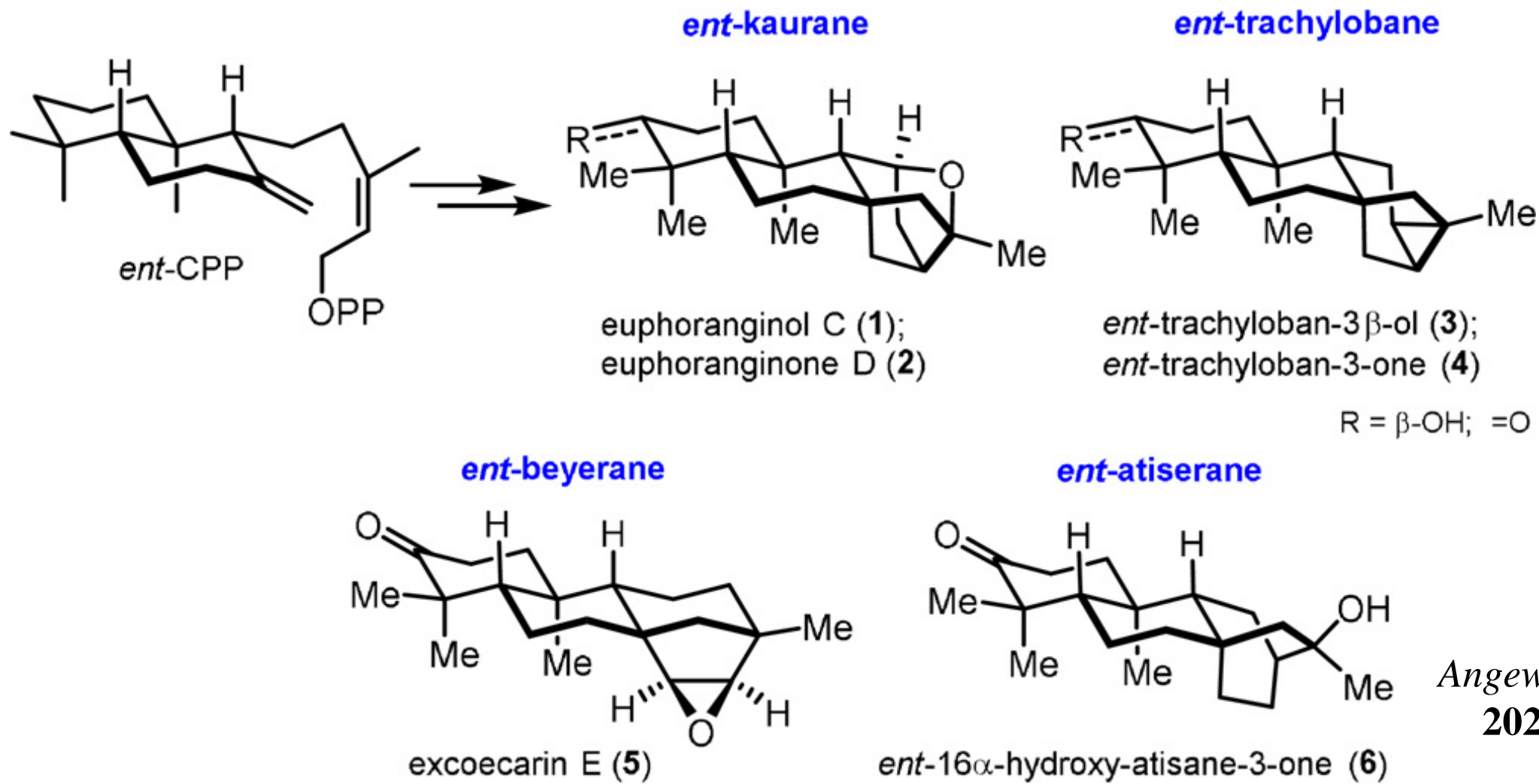


Divergent Total Synthesis of Euphoranginol C, Euphoranginone D, *ent*-Trachyloban-3 β -ol, *ent*-Trachyloban-3-one, Excoecarin E, and *ent*-16 α -Hydroxy-atisane-3-one

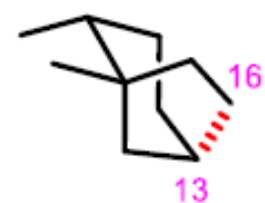
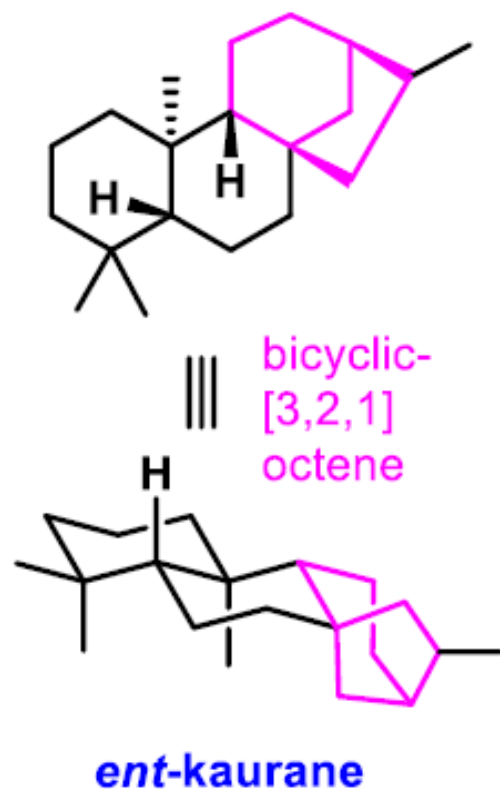
Ze-Jun Xu⁺, *Yan Zong*⁺, *Ya-Nan Qiao*, *Jiao-Zhen Zhang*, *Xuyuan Liu*, *Ming-Zhu Zhu*, *Yuliang Xu*, *Hongbo Zheng*, *Liyuan Fang*, *Xiao-ning Wang*, and *Hong-Xiang Lou*^{*}



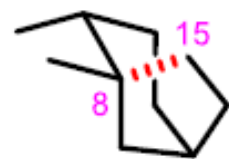
Angew. Chem. Int. Ed.
2020, 59, 19919.

(A): selected approaches to bicyclic-[3,2,1]octene skeleton of *ent*-kaurane

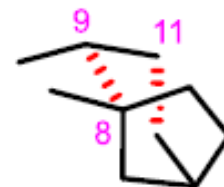
(1) bond-forming cyclization approaches:



Ireland, 1962;
Mori, 1966;
Corey, 1997;
Ihara, 1998;
Hong, 2014; Ma, 2017; 2019
Lee, 2018; Jia, 2020 etc.



Reisman, 2013;
Lei, 2019;
Luo, 2018; 2019.



Ding, 2017;
Lei, 2020.



Paquette, 1997.

(2) fragmentation of "overbred" intermediate:

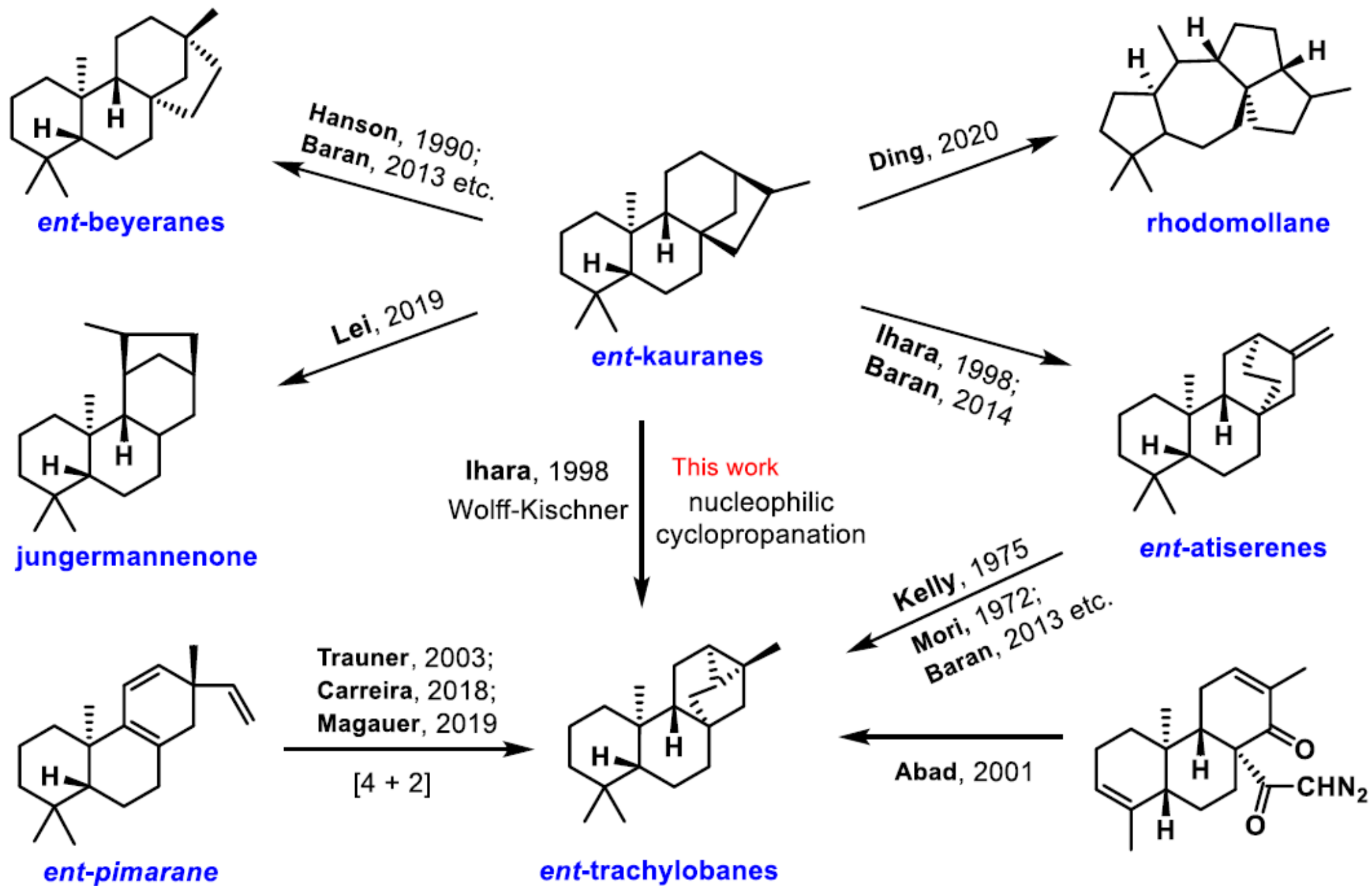


Mori, 1972;
Corey, 1987;
Abad, 2006;
Baran, 2013. etc.

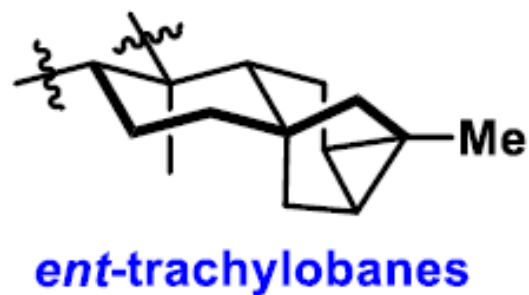


This work
De Mayo reaction

(B) selected interconversions of these tetracyclic diterpenoids

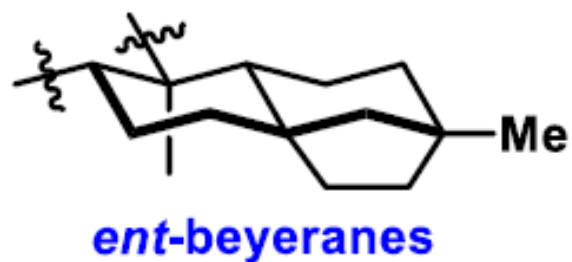


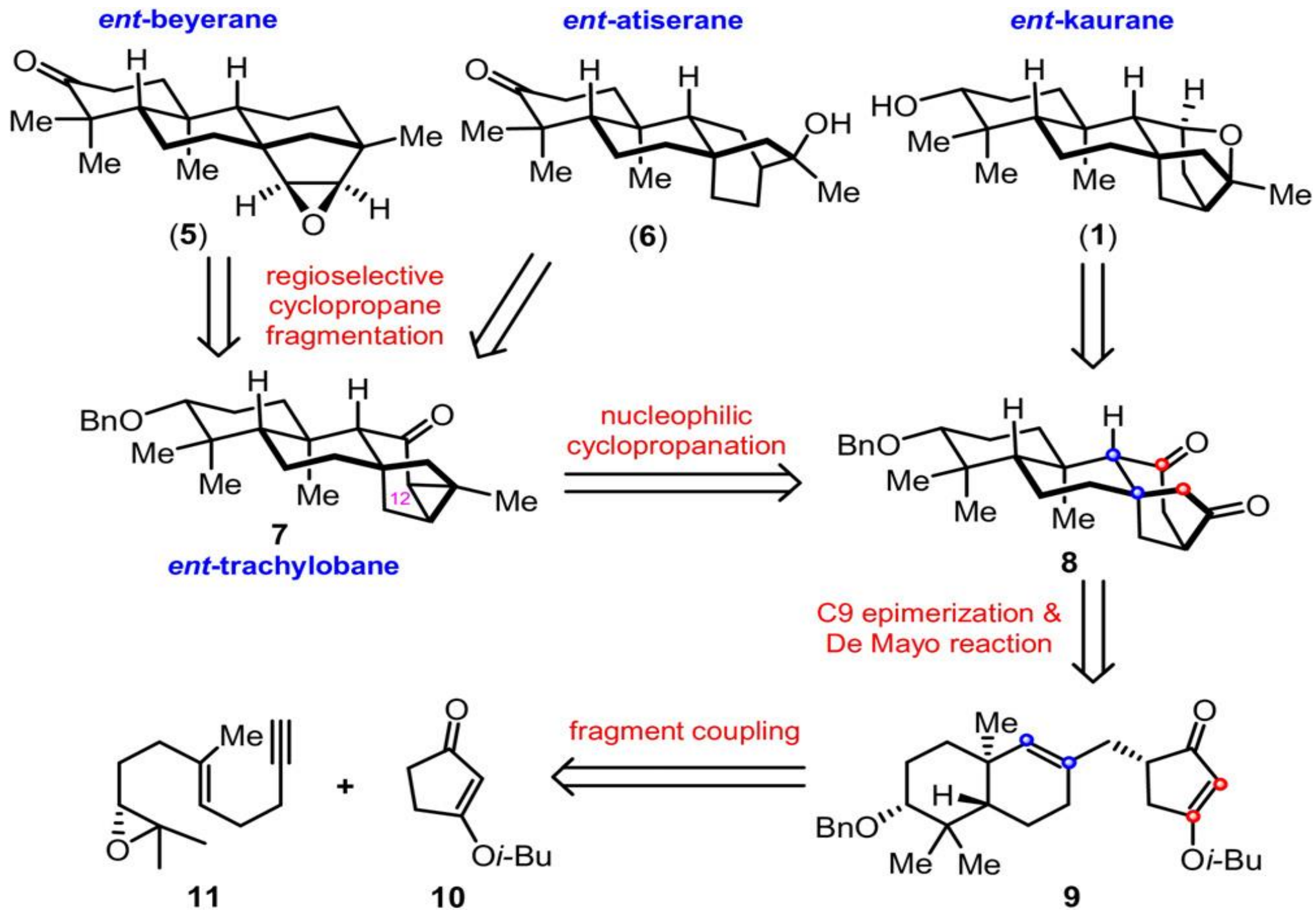
Regioselective fragmentation
of the cyclopropane ring



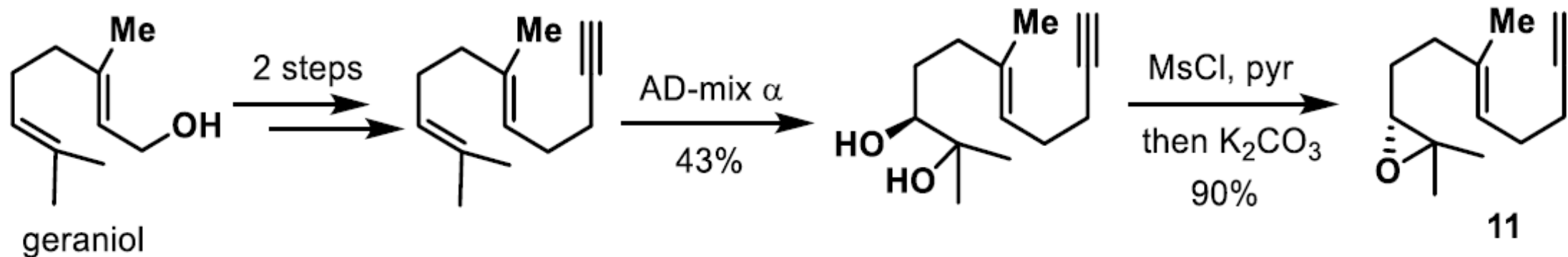
Abad, 2006
reductive cleavage

This work
nucleophilic attack
and protonation

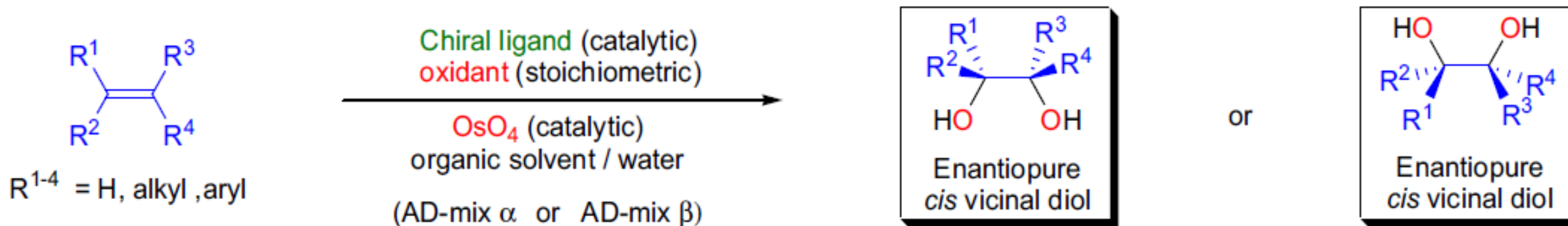


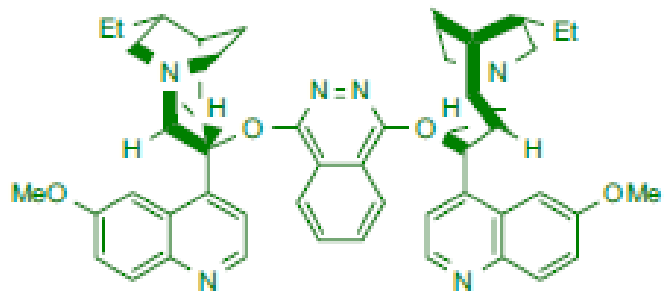
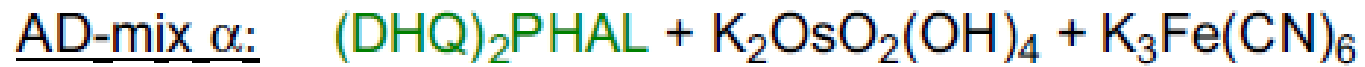
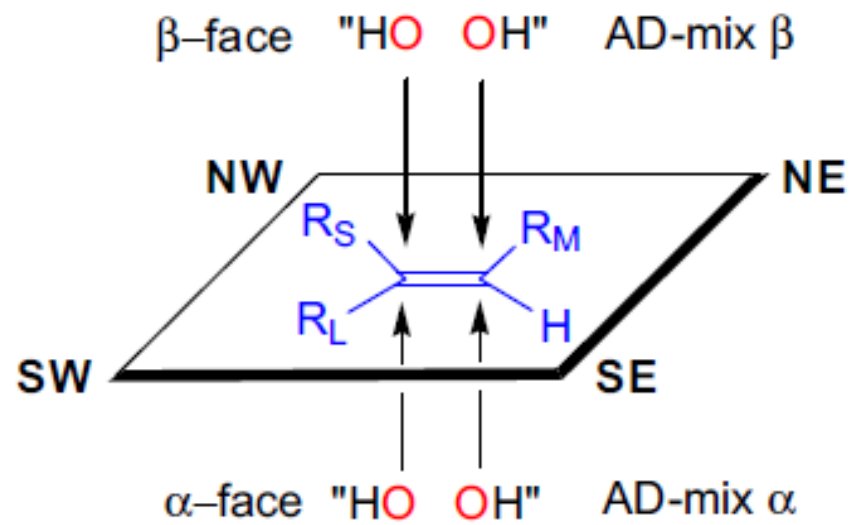


The Synthesis of Chiral Epoxy Intermediate **11**

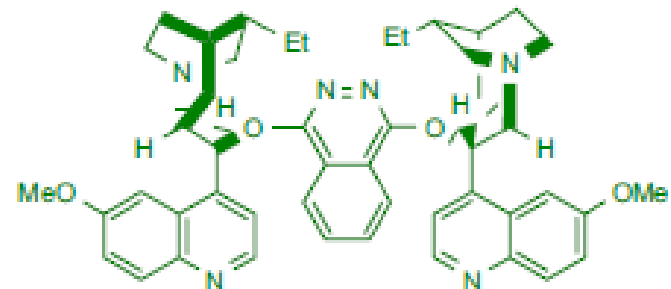


The Second Process: Sharpless asymmetric dihydroxylation



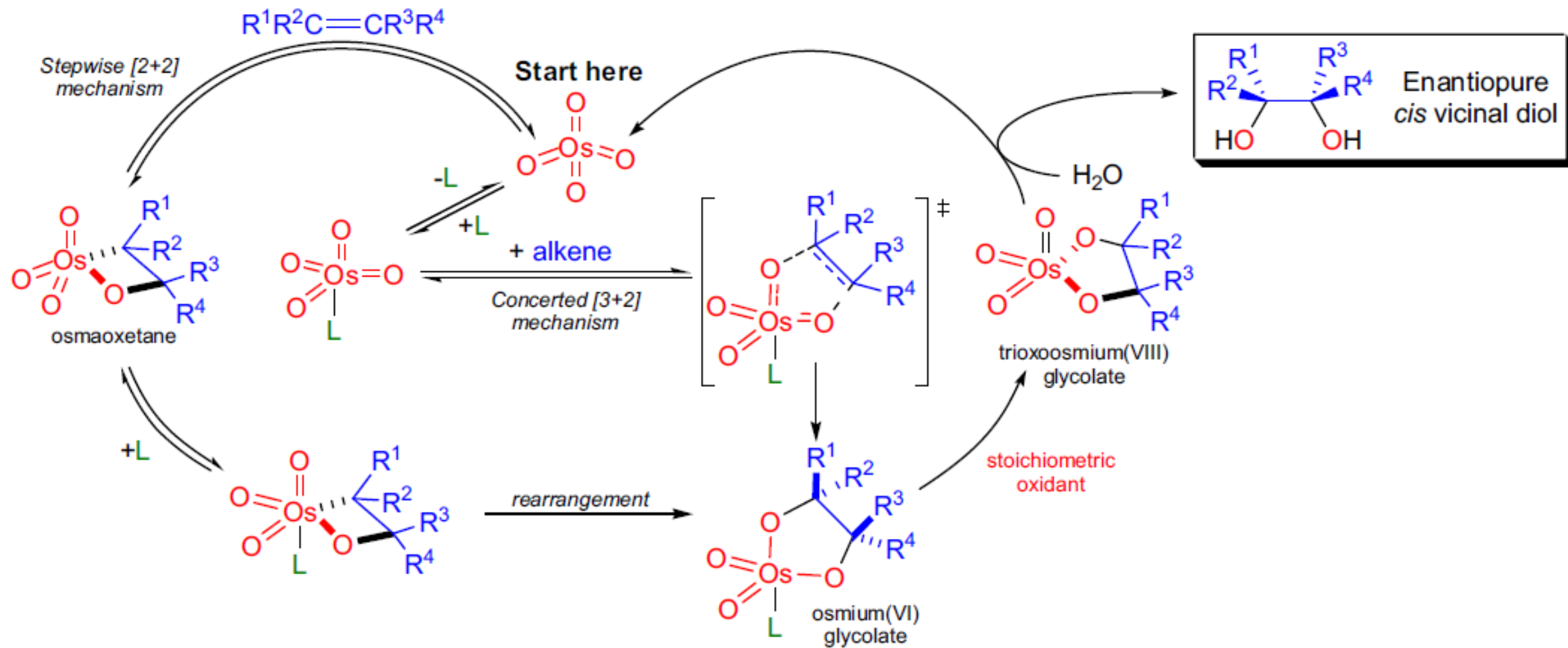


$(DHQ)_2PHAL$

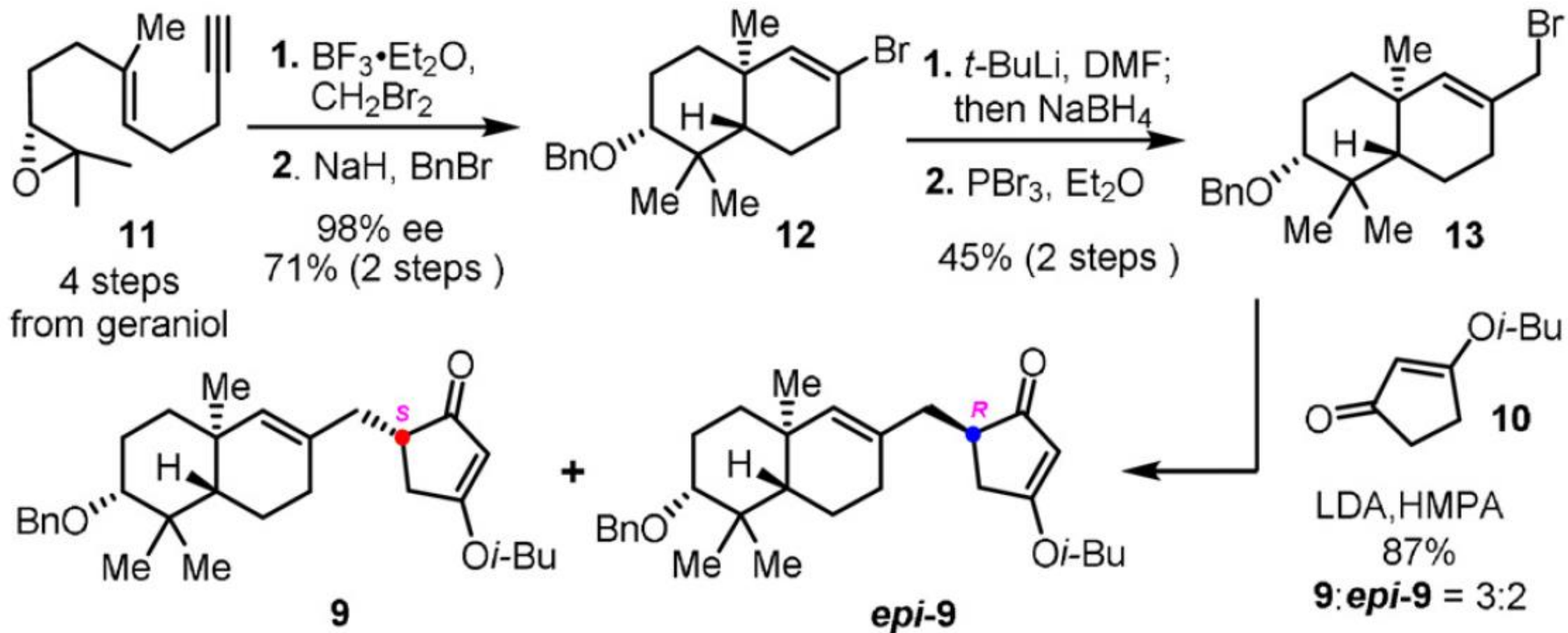


$(DHQD)_2PHAL$

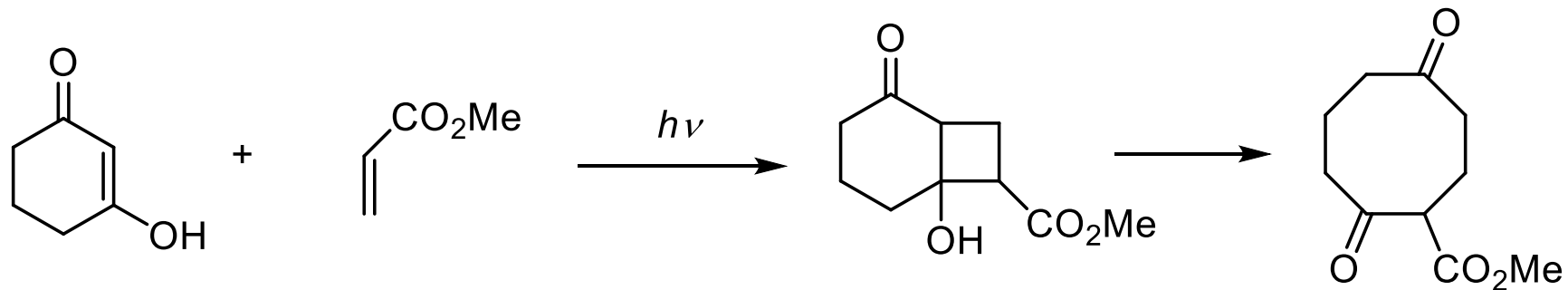
Mechanism:



Divergent Total Synthesis of Natural Products 1–6

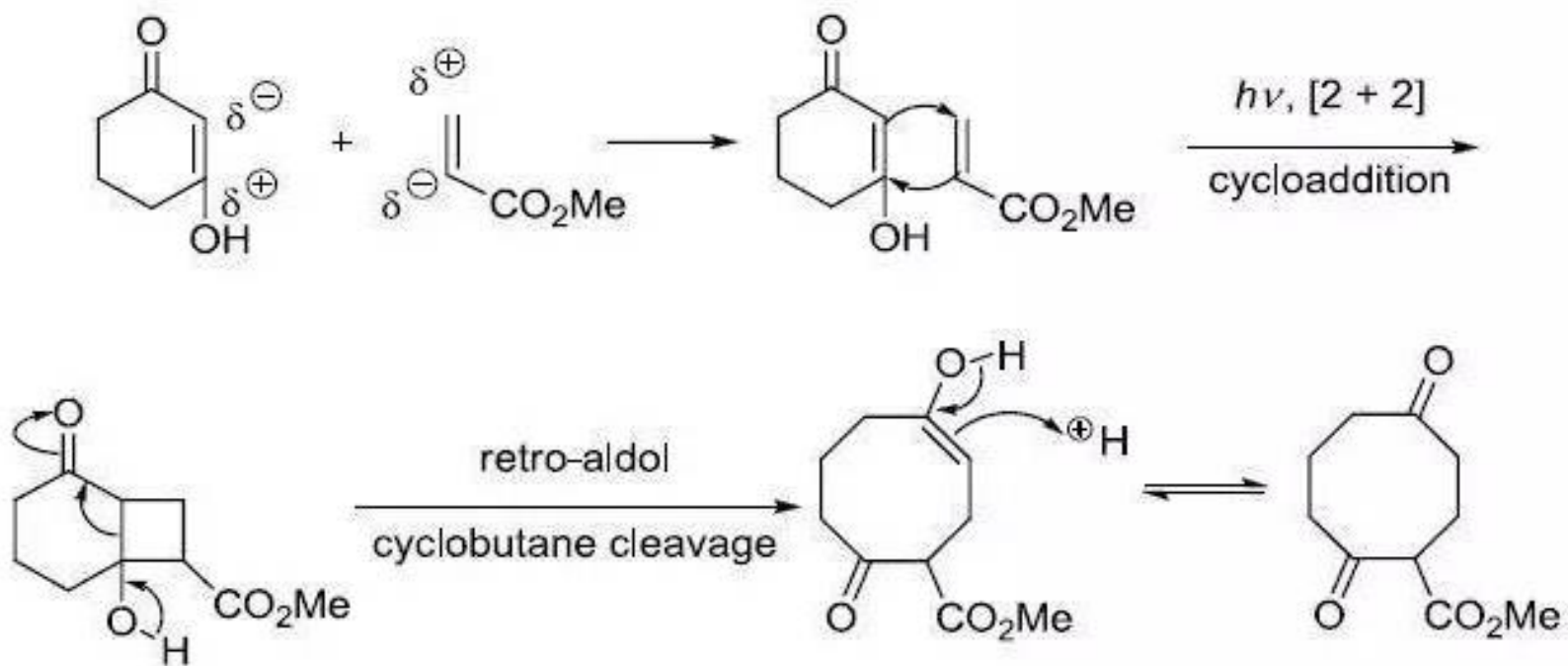


De Mayo Reaction



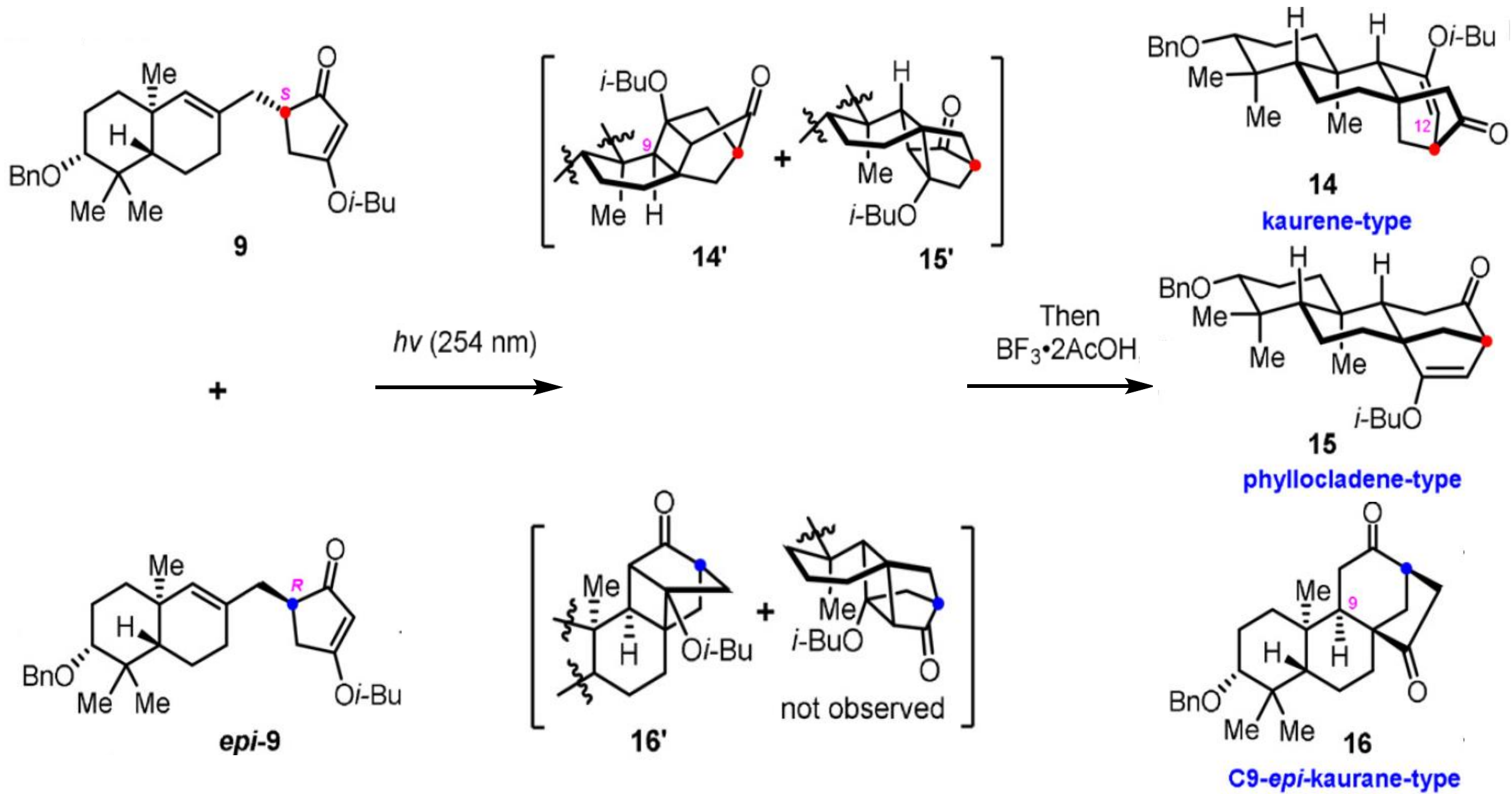
Mechanism:

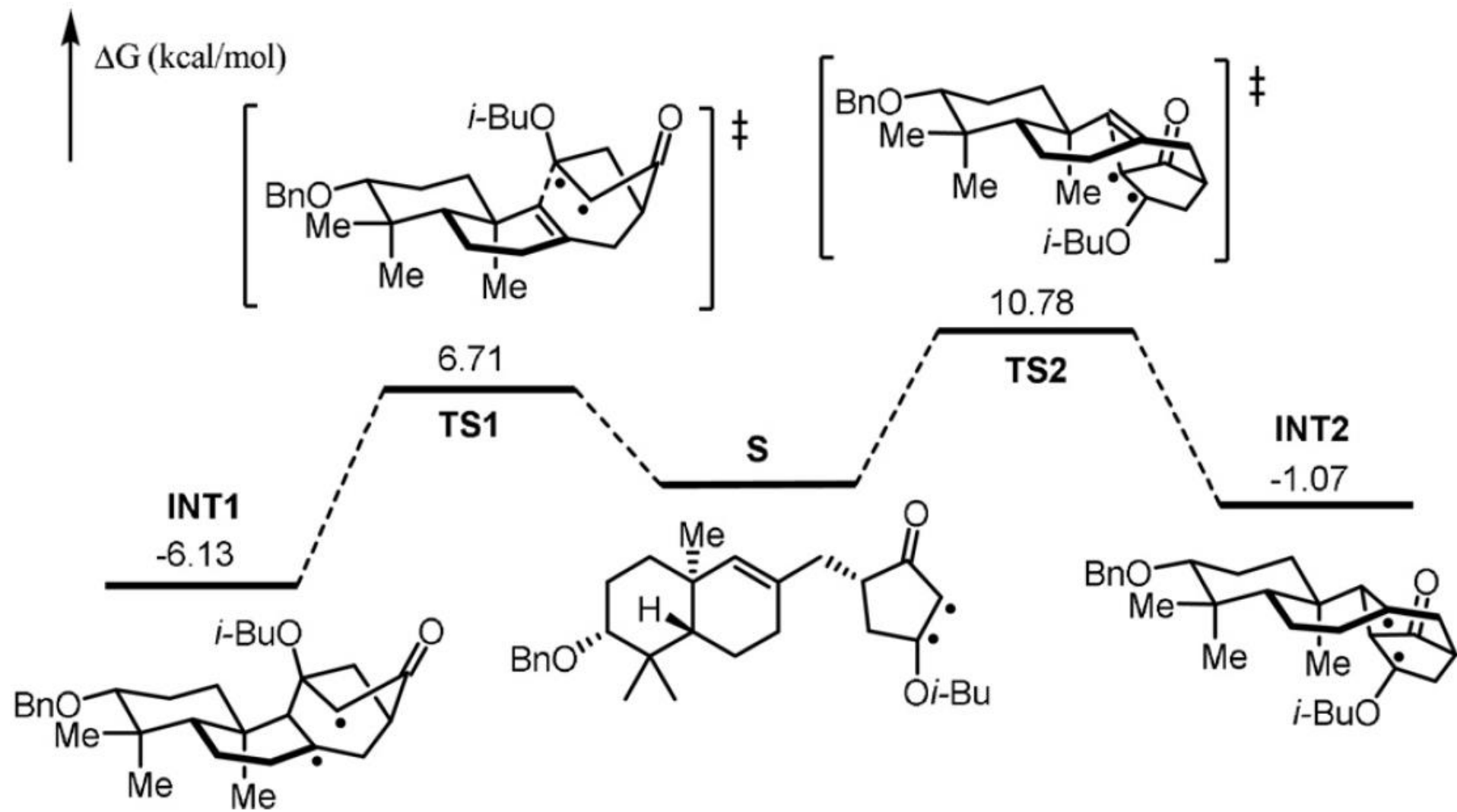
Head to tail alignment gives the major product:



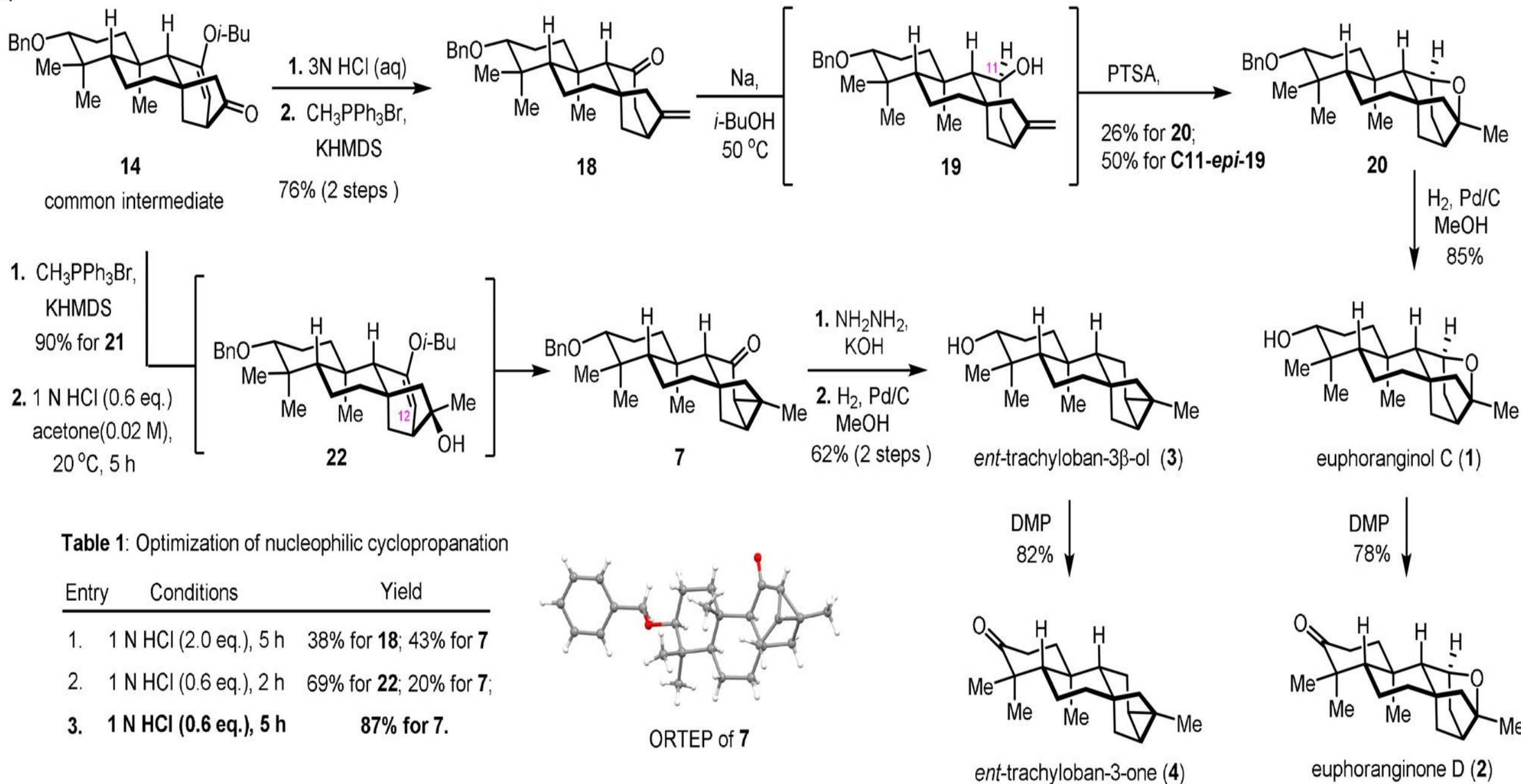
J. Org. Chem. **1969**, 34, 794-806.

Acc. Chem. Res. **1971**, 4, 41-48. (Review).





(A)

**Table 1:** Optimization of nucleophilic cyclopropanation

Entry	Conditions	Yield
1.	1 N HCl (2.0 eq.), 5 h	38% for 18 ; 43% for 7
2.	1 N HCl (0.6 eq.), 2 h	69% for 22 ; 20% for 7 ;
3.	1 N HCl (0.6 eq.), 5 h	87% for 7 .

(B)

