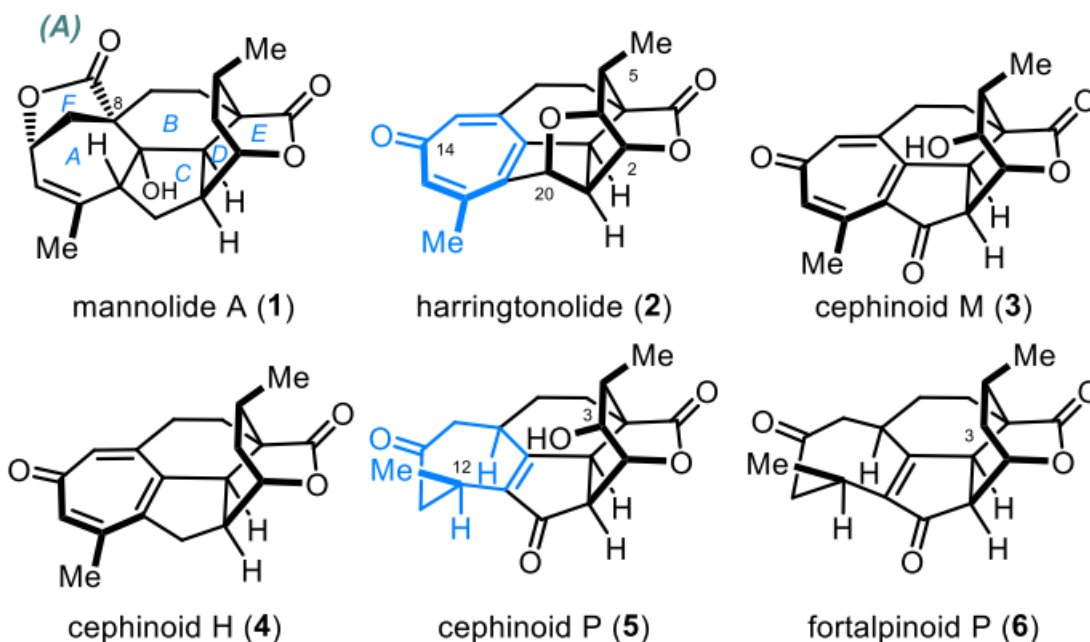


Asymmetric Total Synthesis of *Cephalotaxus* Diterpenoids: Cephinoid P, Cephafortoid A, 14-*epi*-Cephafortoid A and Fortalpinoids M-N, P

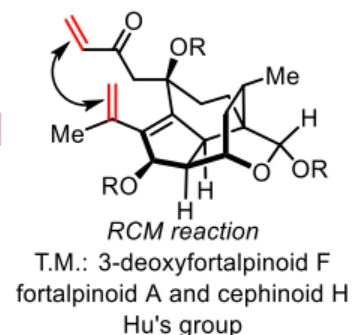
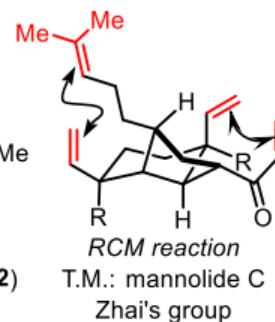
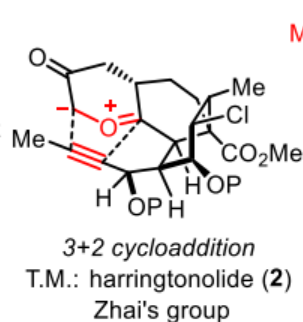
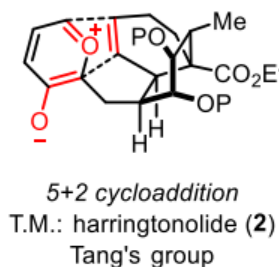
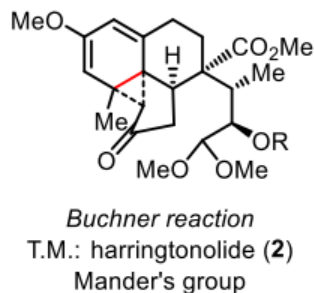
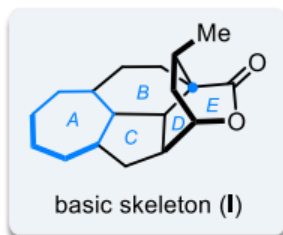
Hui Wang, Yi Liu, Hongyuan Zhang, Baochao Yang, Haibing He, and Shuanhu Gao*

 Cite This: <https://doi.org/10.1021/jacs.3c05455>

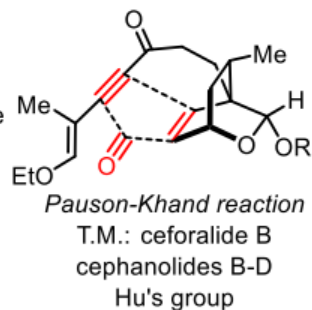
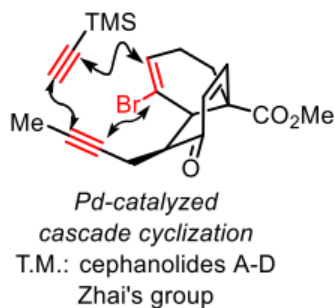
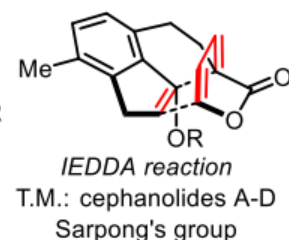
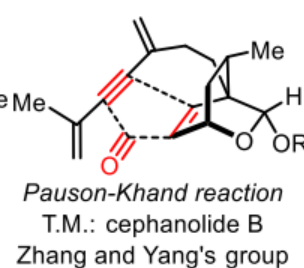
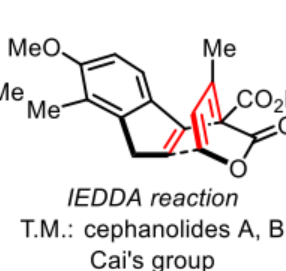
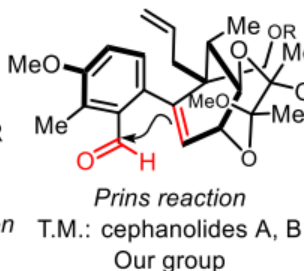
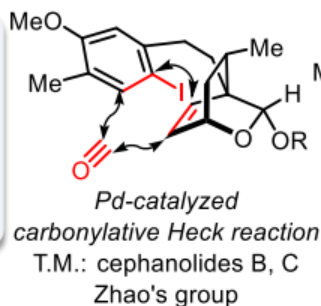
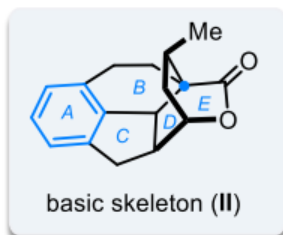
 Read Online



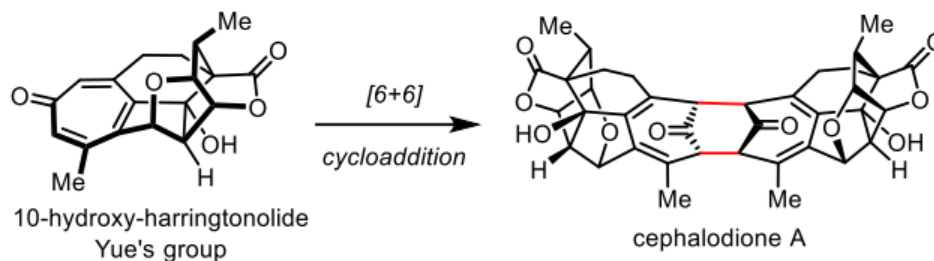
(A)



(B)



(C)

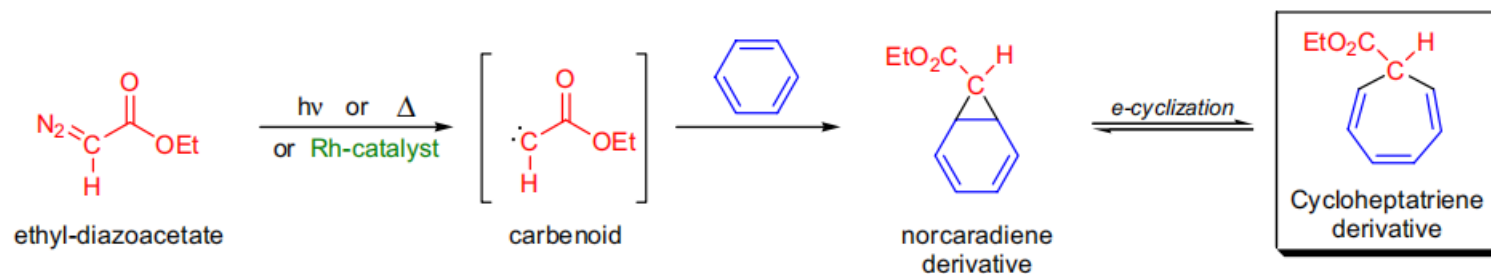


BUCHNER METHOD OF RING EXPANSION

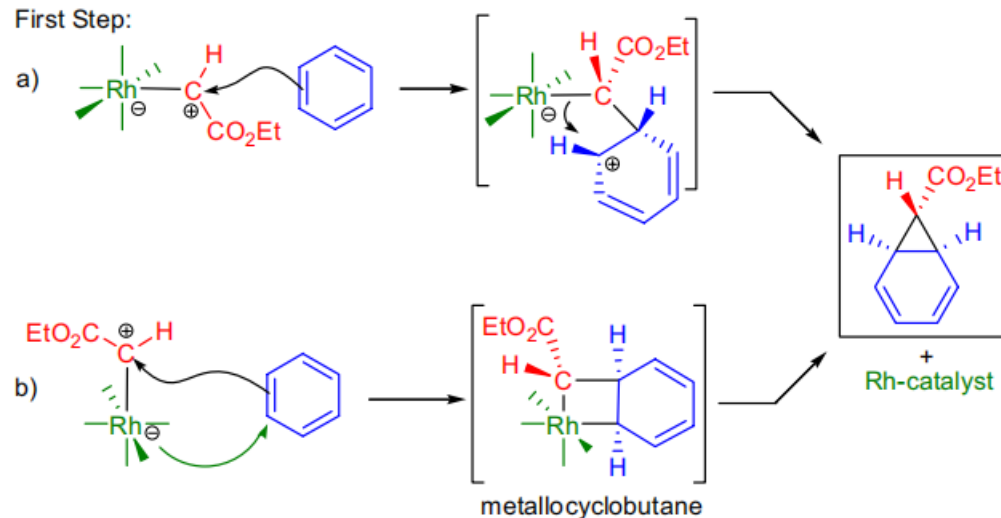
(References are on page 555)

Importance:

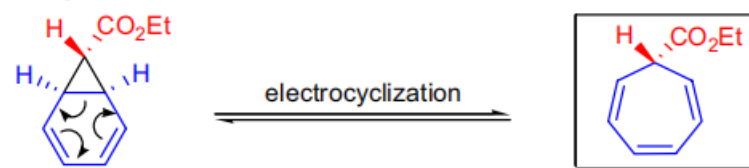
[Seminal Publications¹⁻³; Reviews⁴⁻⁹; Modifications & Improvements¹⁰⁻²⁰]

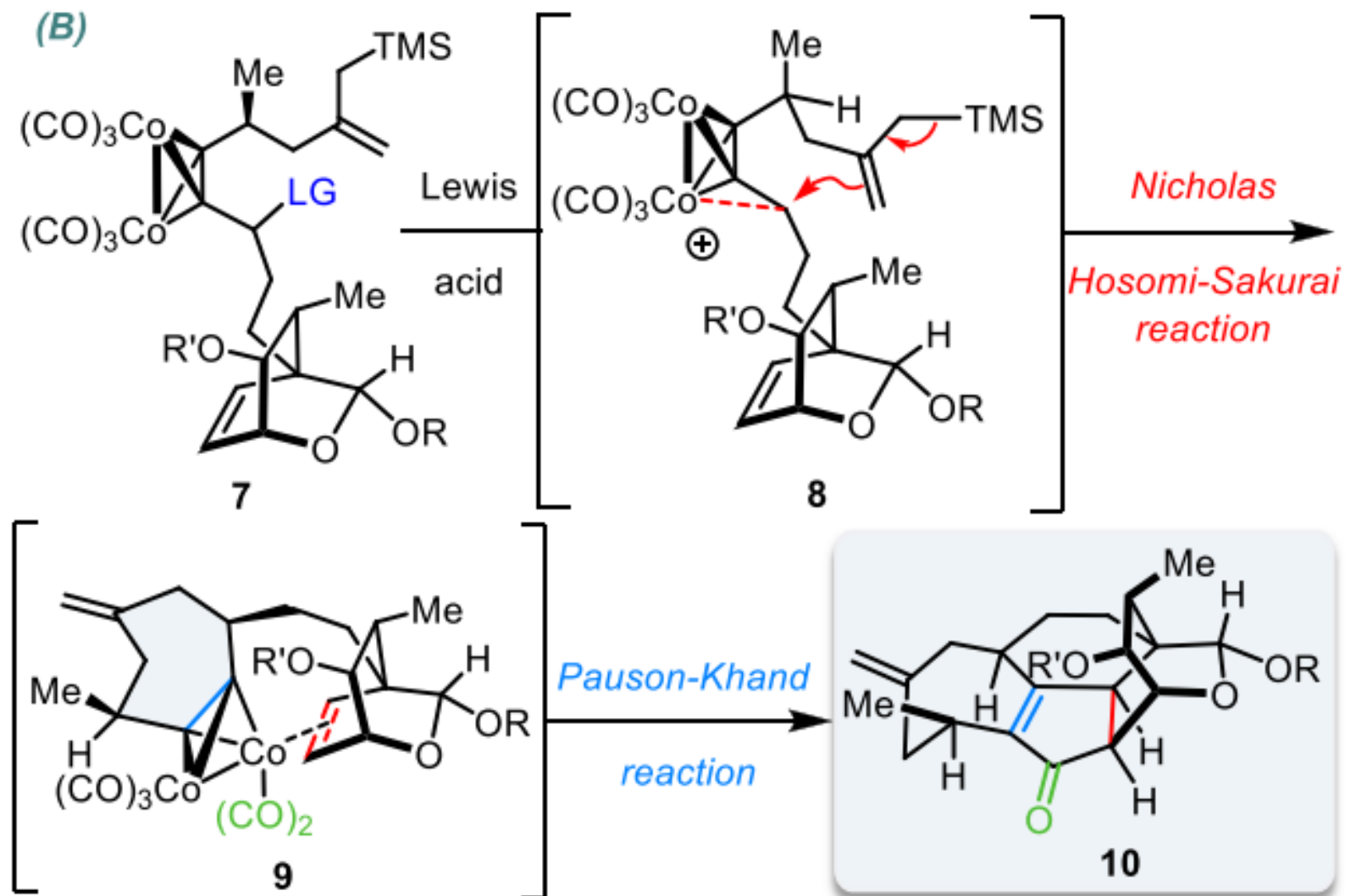


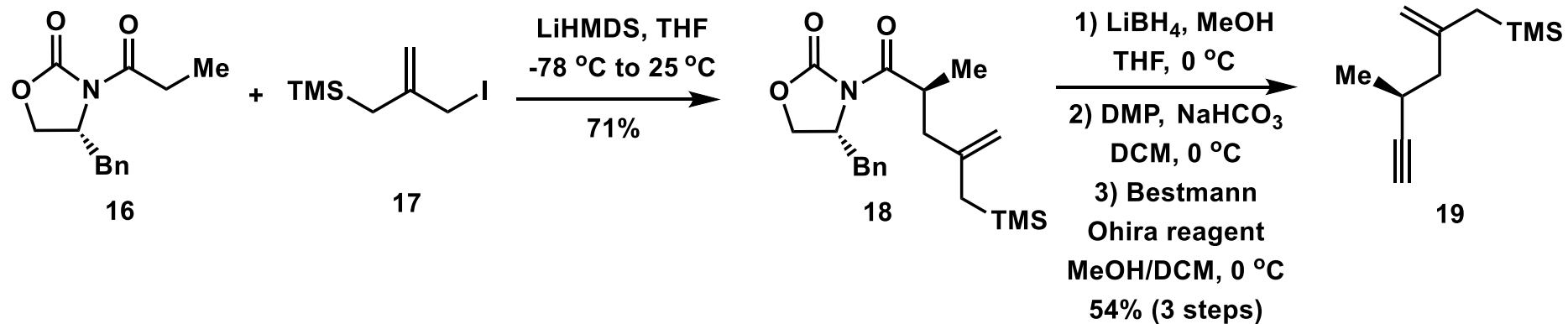
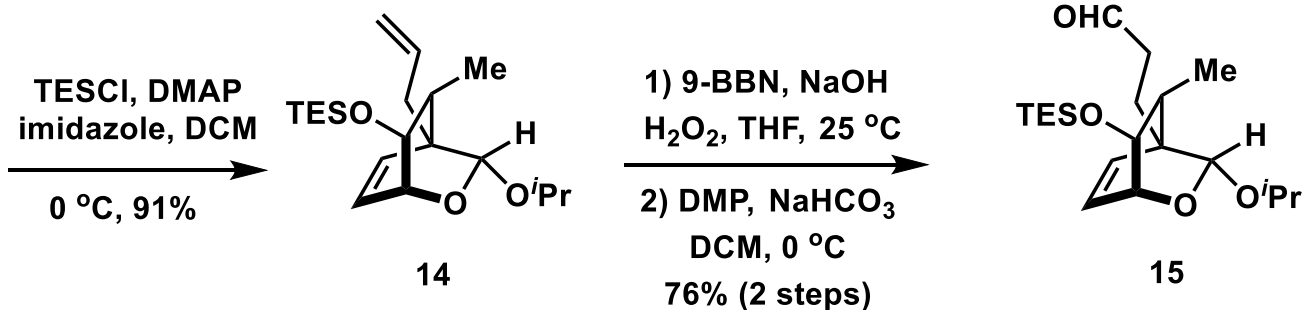
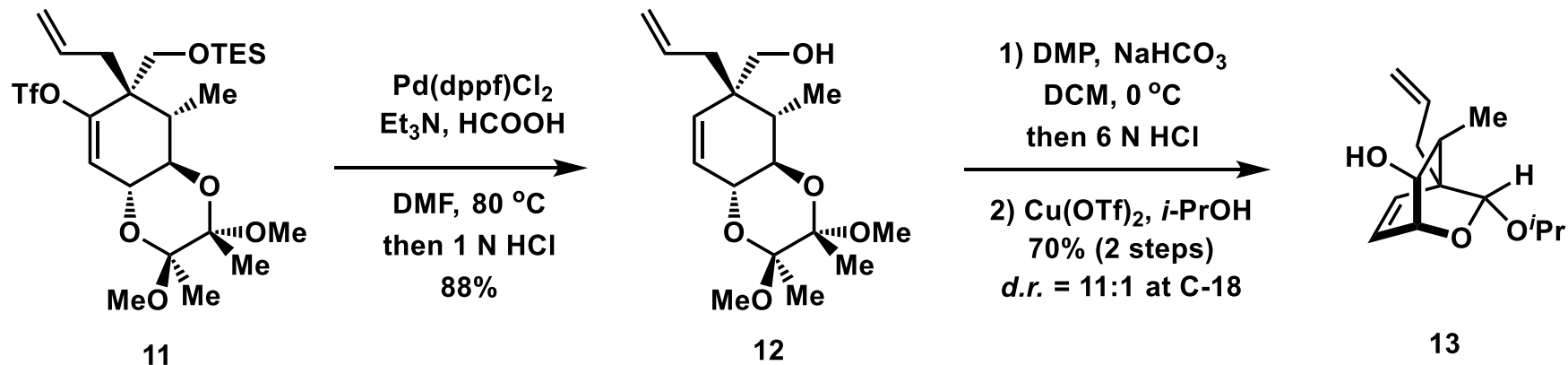
First Step:

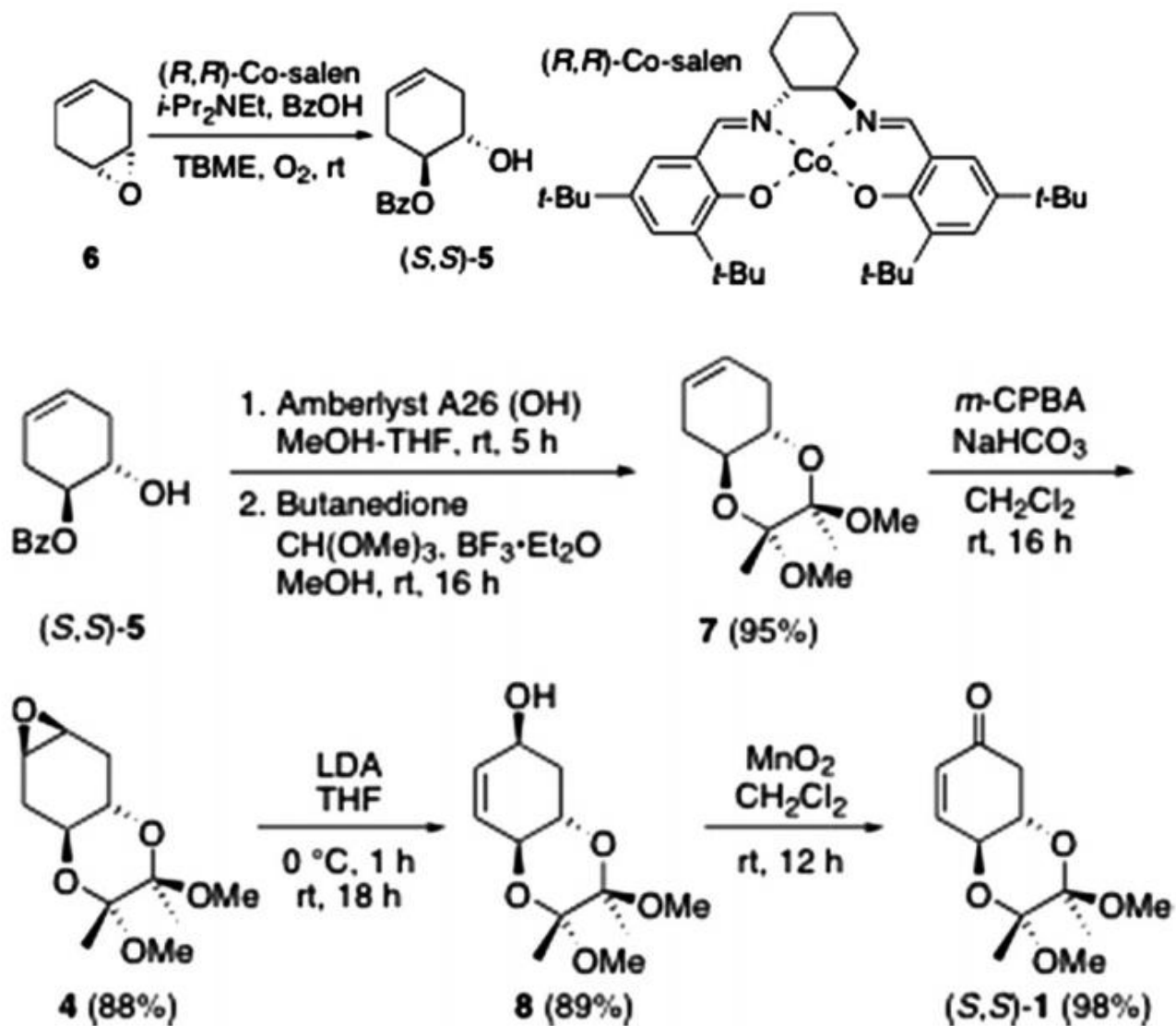


Second Step:



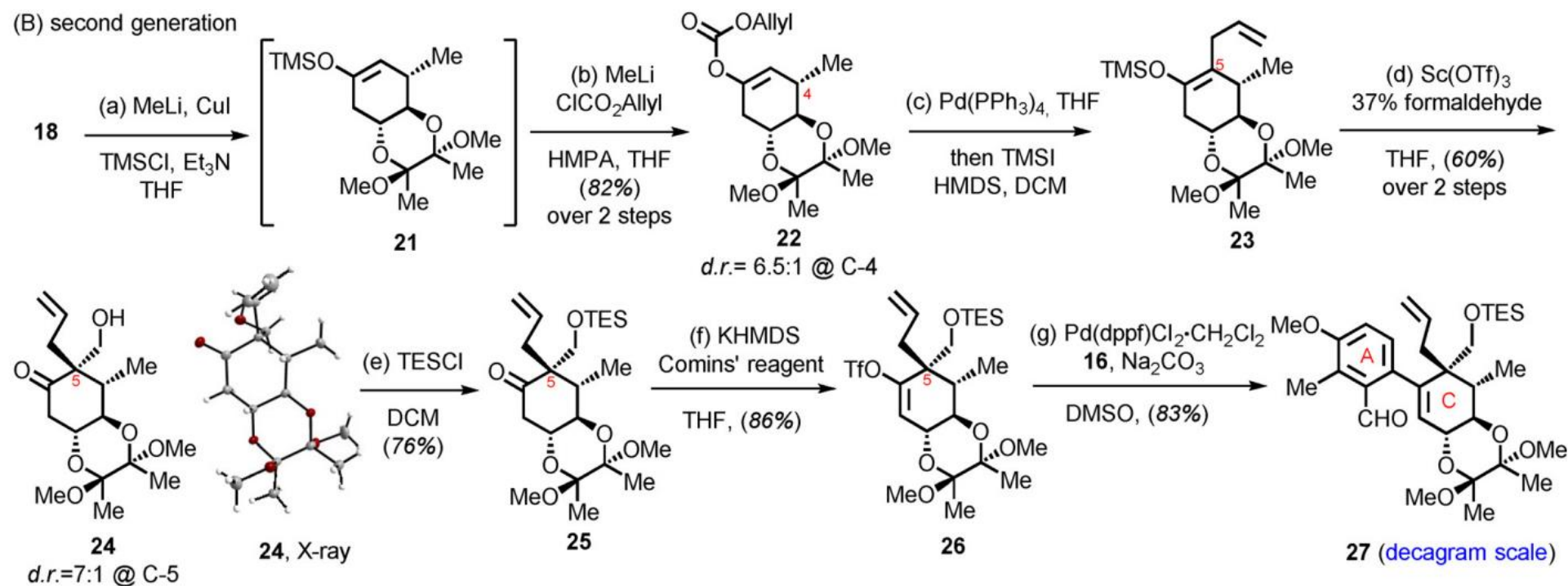




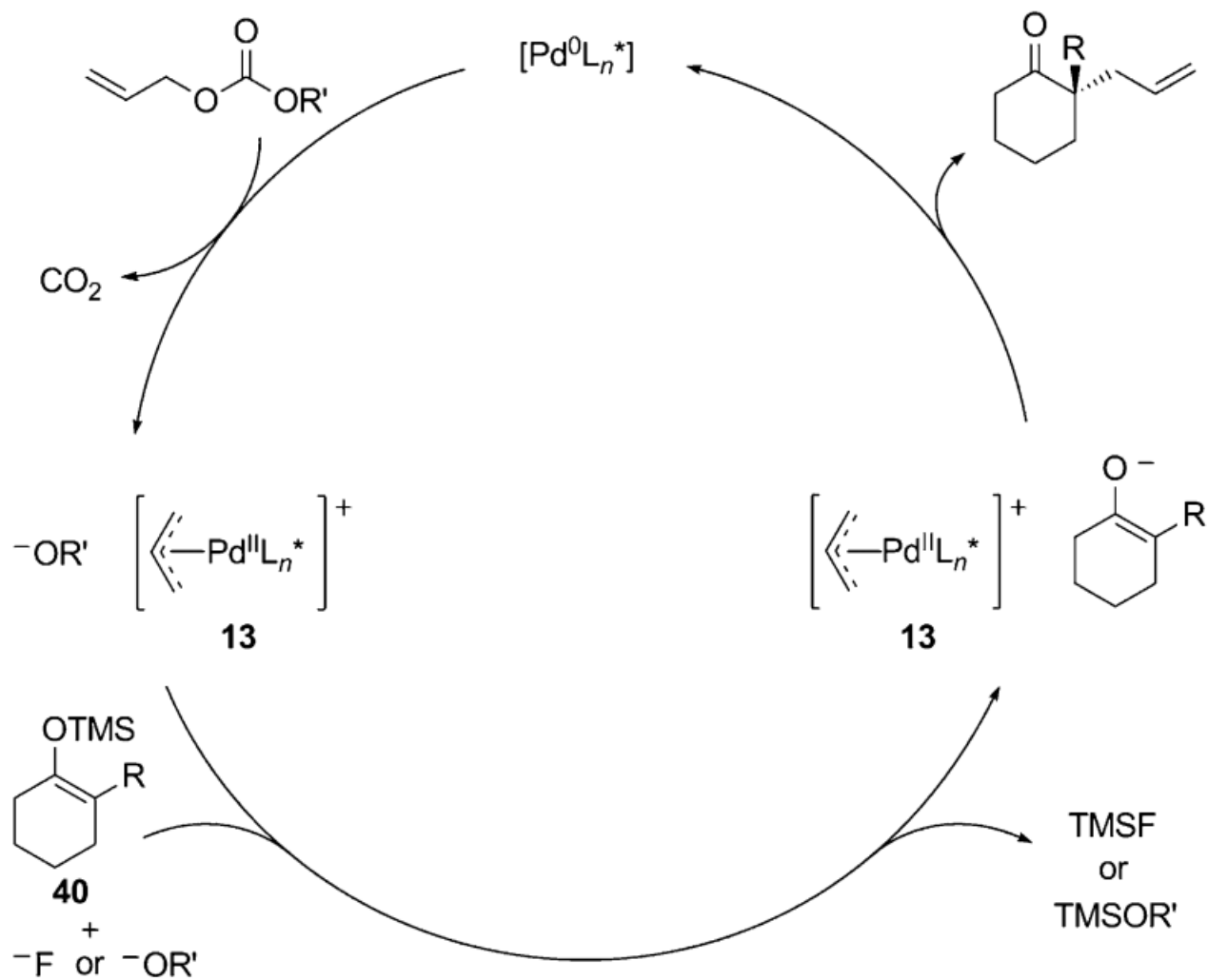


Scheme 3

(B) second generation

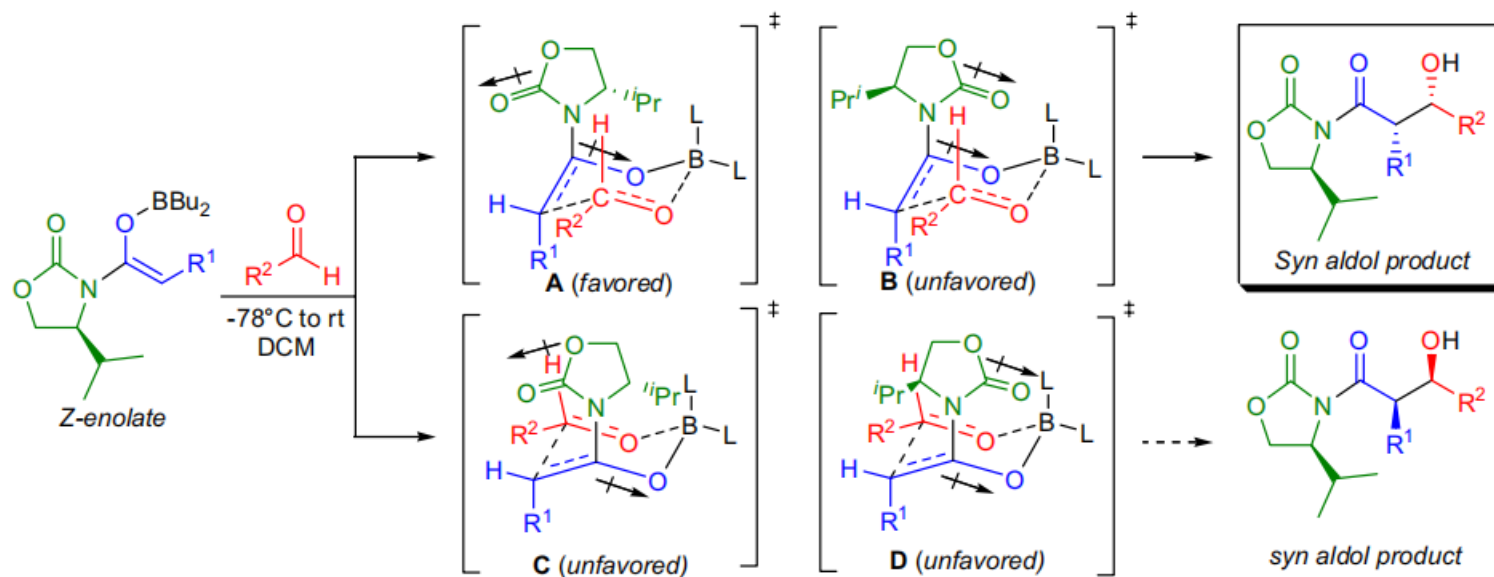
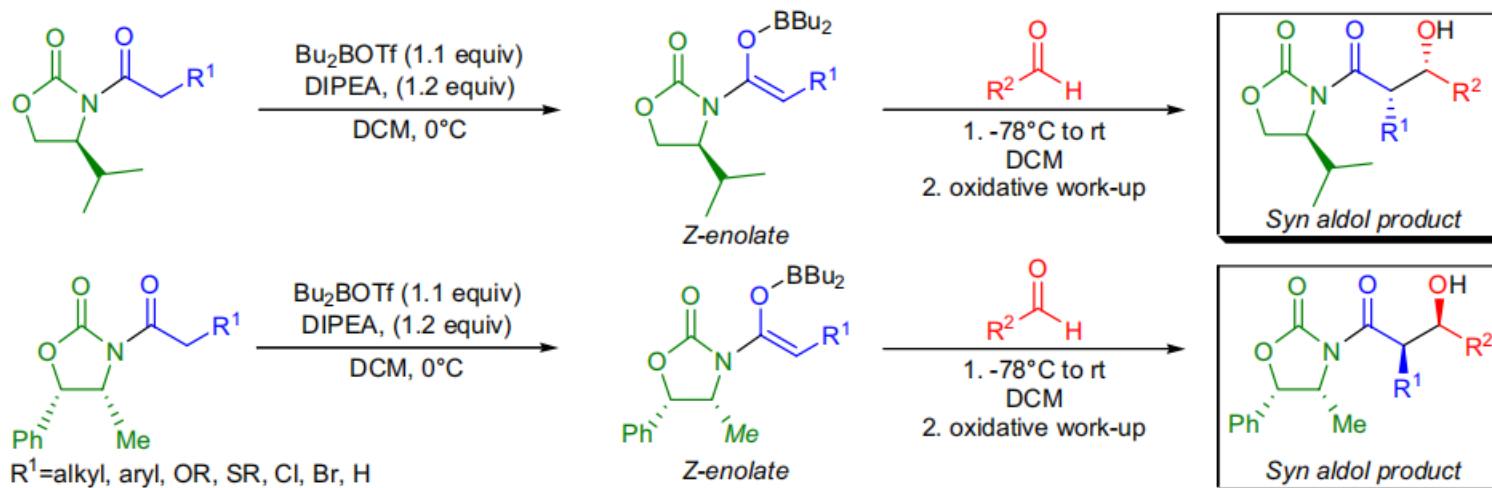


Angew. Chem. Int. Ed., 2020, 59, 20417.



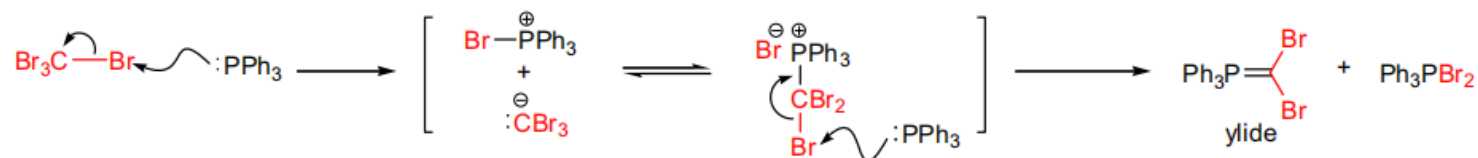
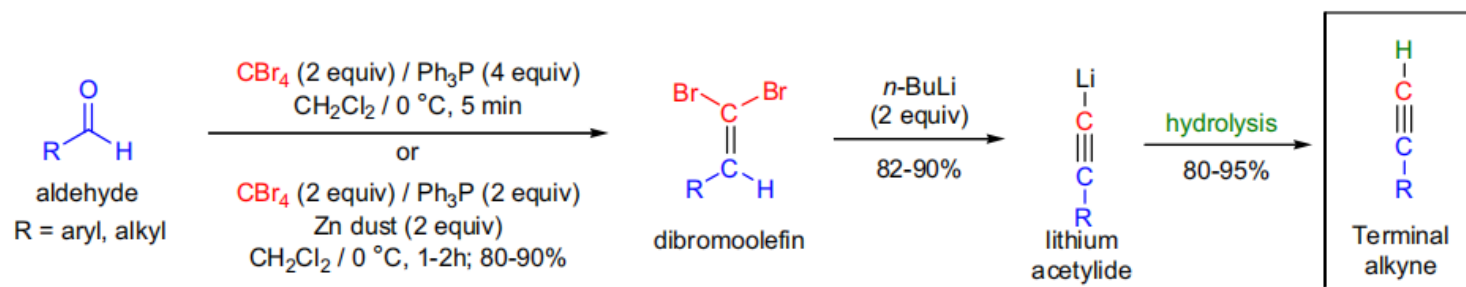
EVANS ALDOL REACTION

(References are on page 583)

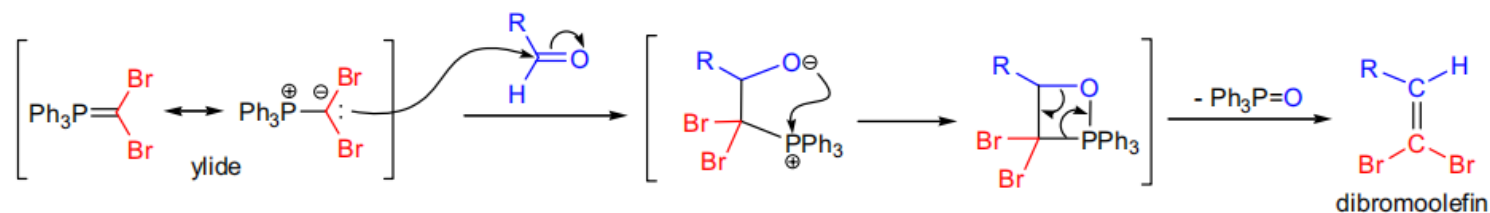


COREY-FUCHS ALKYNE SYNTHESIS

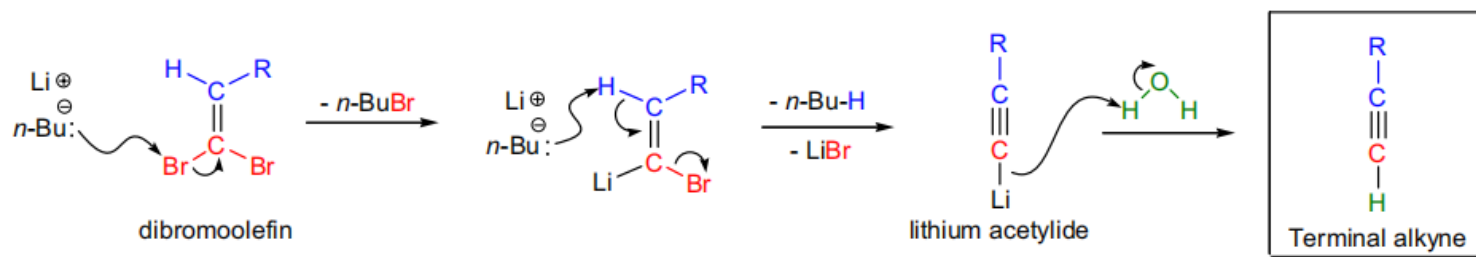
(References are on page 566)



Reaction of the phosphorous ylide with the aldehyde:



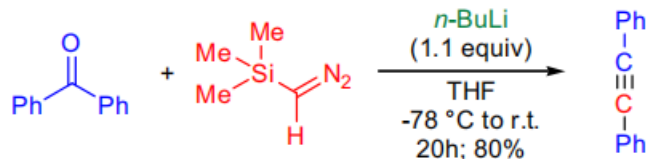
Conversion of dibromoolefin to terminal alkyne:



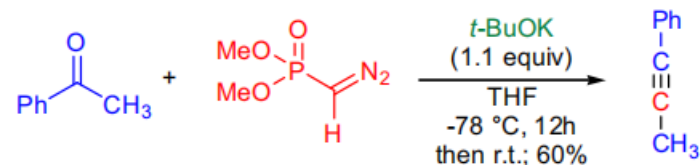
SEYFERTH-GILBERT HOMOLOGATION

(References are on page 672)

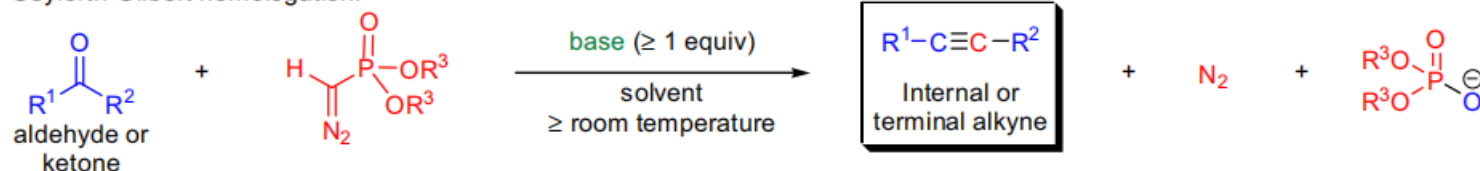
Colvin & Hamill (1973):



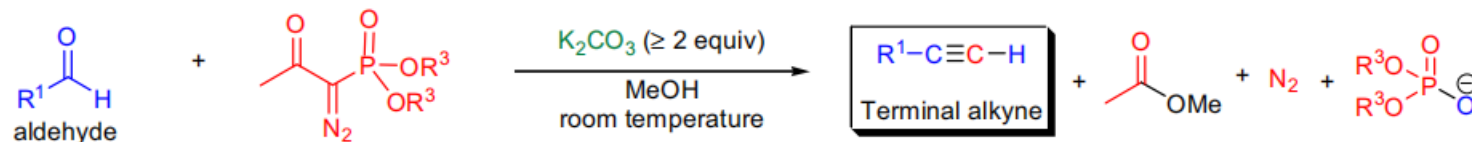
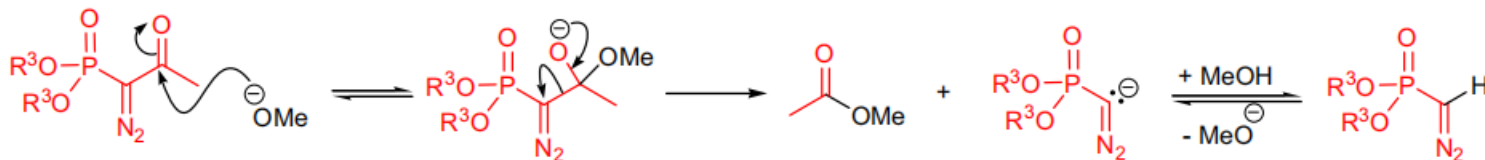
Gilbert & Weerasooriya (1979):



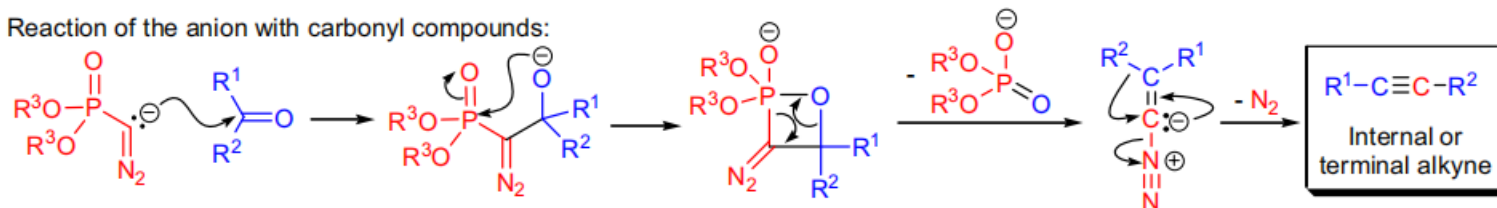
Seyferth-Gilbert homologation:

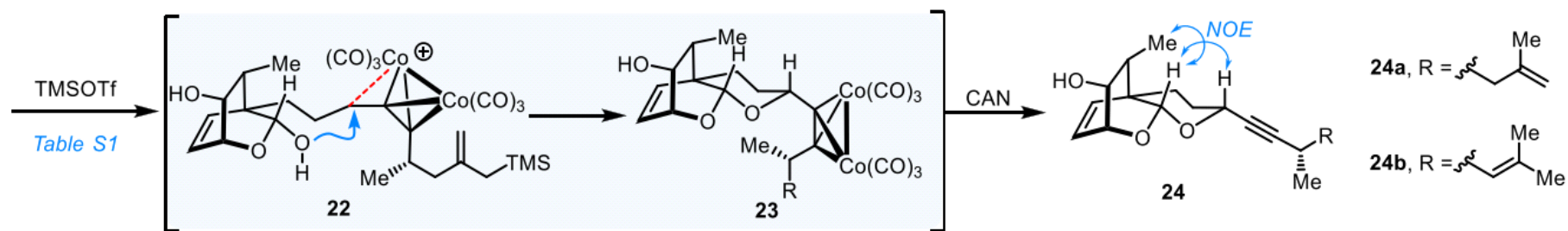
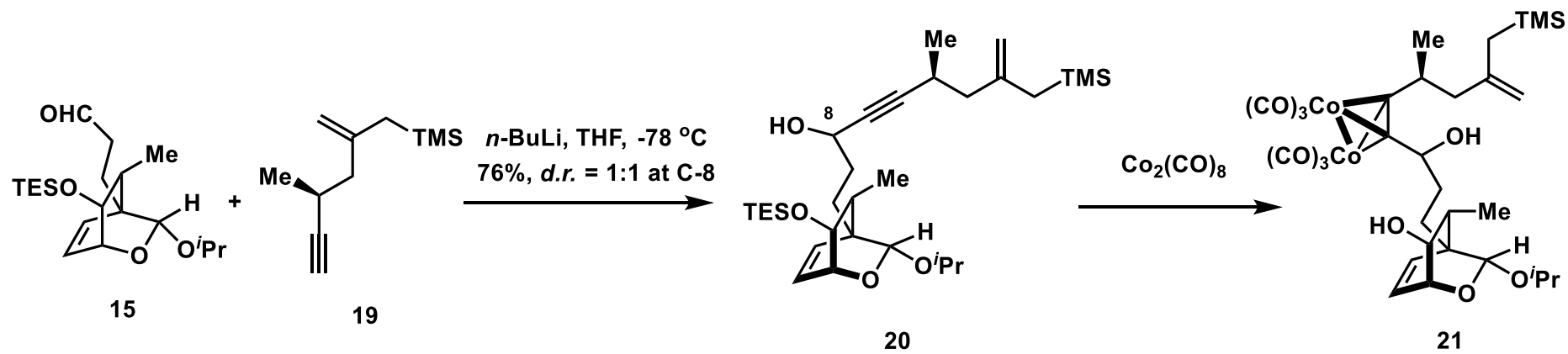


Modification for the synthesis of terminal alkynes (Ohira & Bestmann):

 R^1 = alkyl, aryl, heteroaryl; R^2 = H, aryl, heteroaryl; R^3 = Me, Et; base: *n*-BuLi, KO-*t*Bu

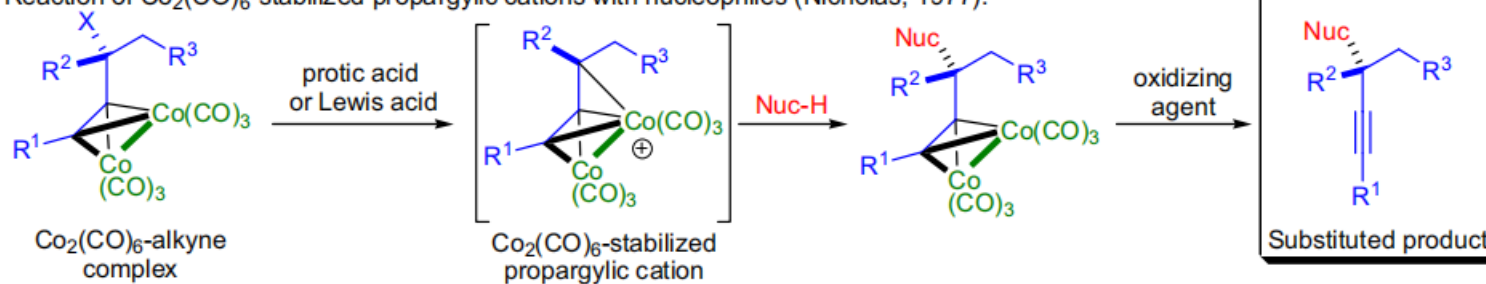
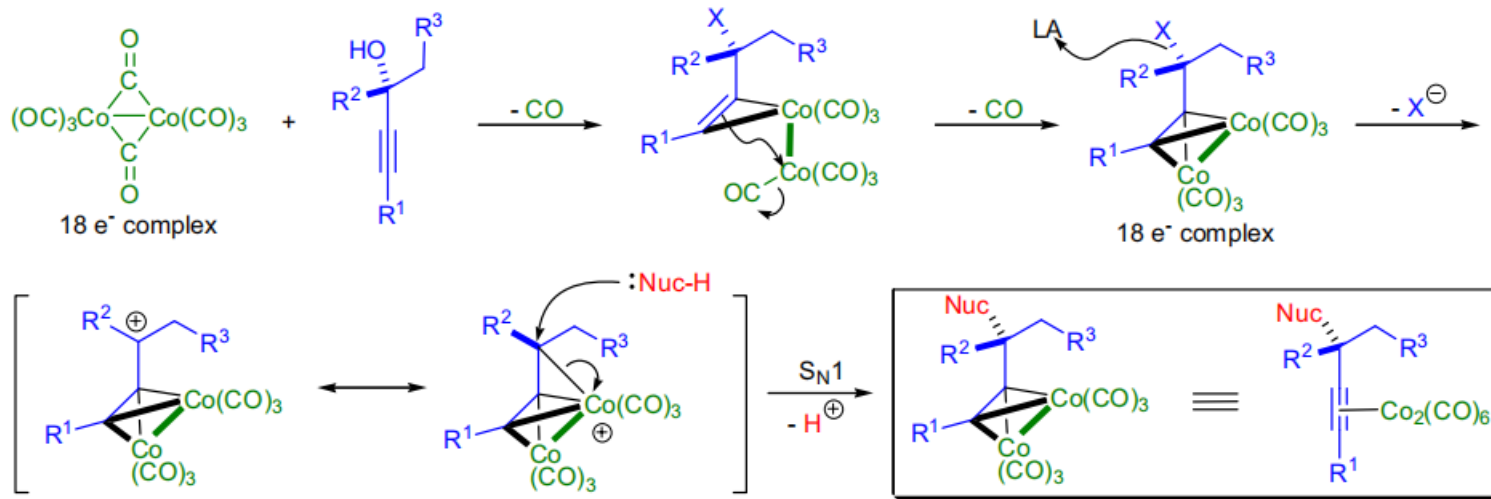
Reaction of the anion with carbonyl compounds:





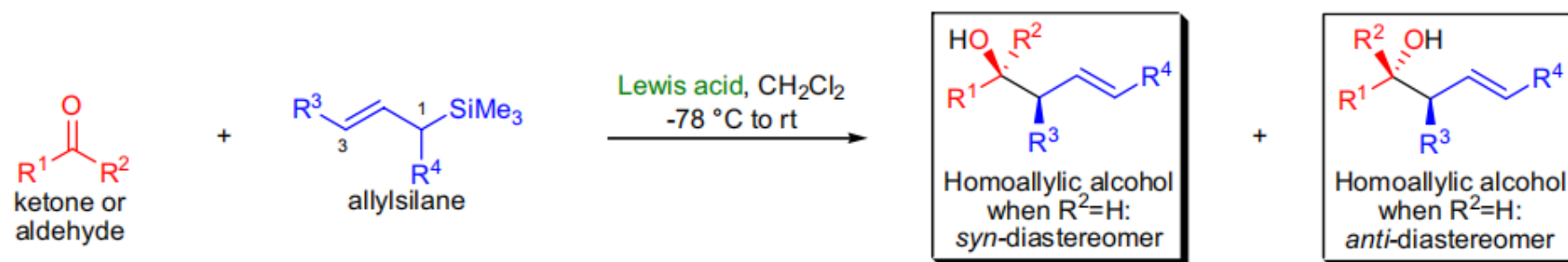
NICHOLAS REACTION

(References are on page 639)

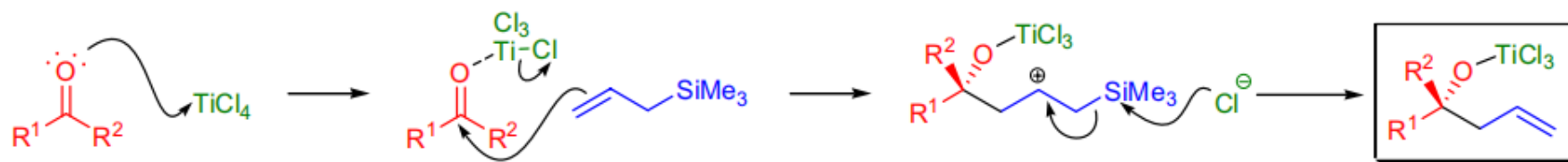
Reaction of $\text{Co}_2(\text{CO})_6$ -stabilized propargylic cations with nucleophiles (Nicholas, 1977):**Mechanism:** 2,22,20,23

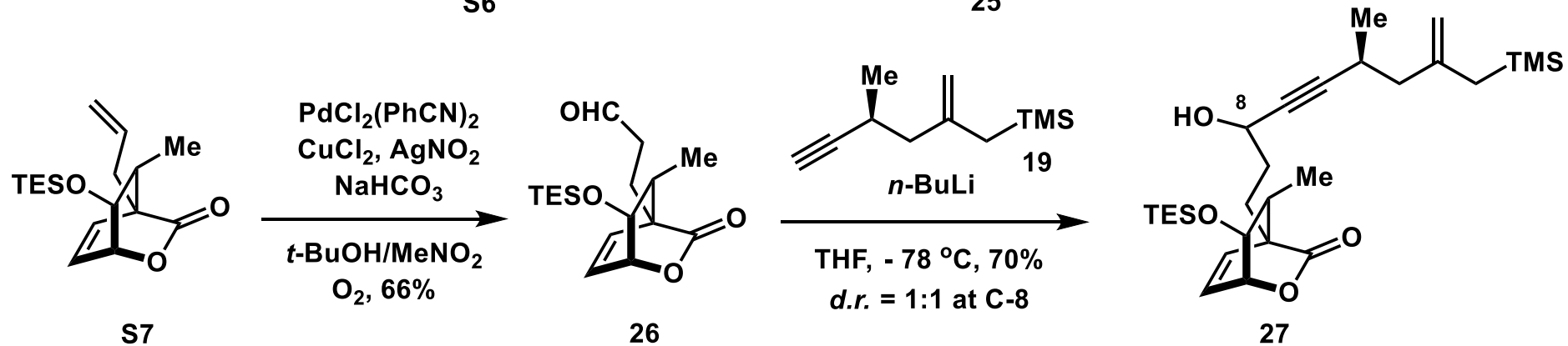
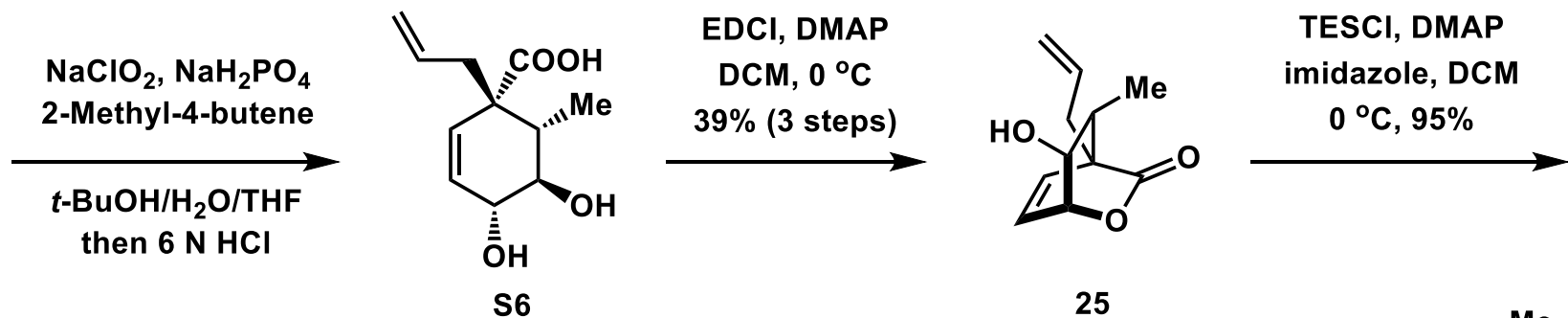
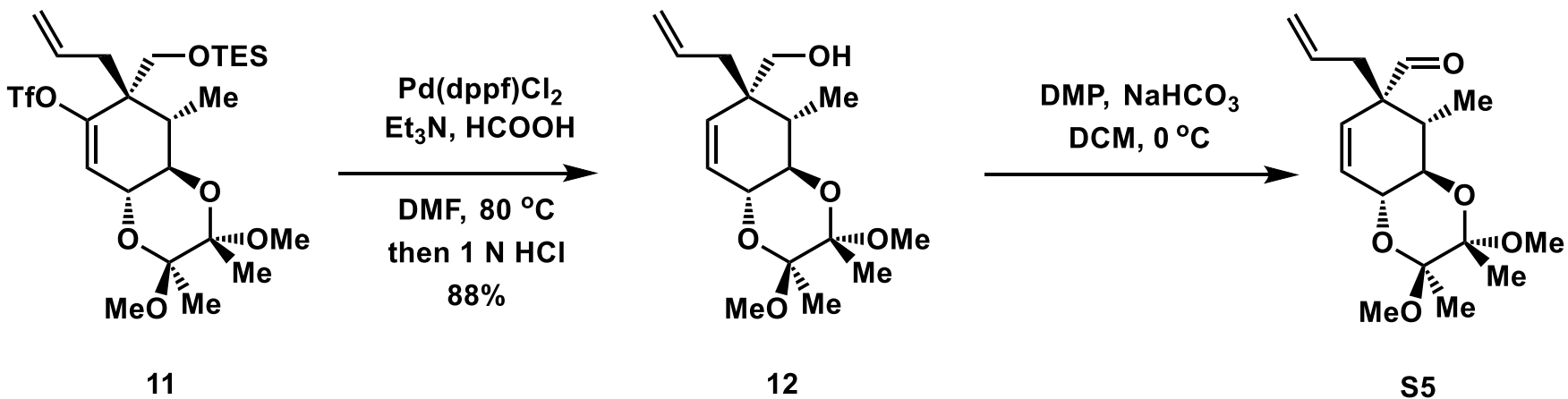
SAKURAI ALLYLATION

(References are on page 668)

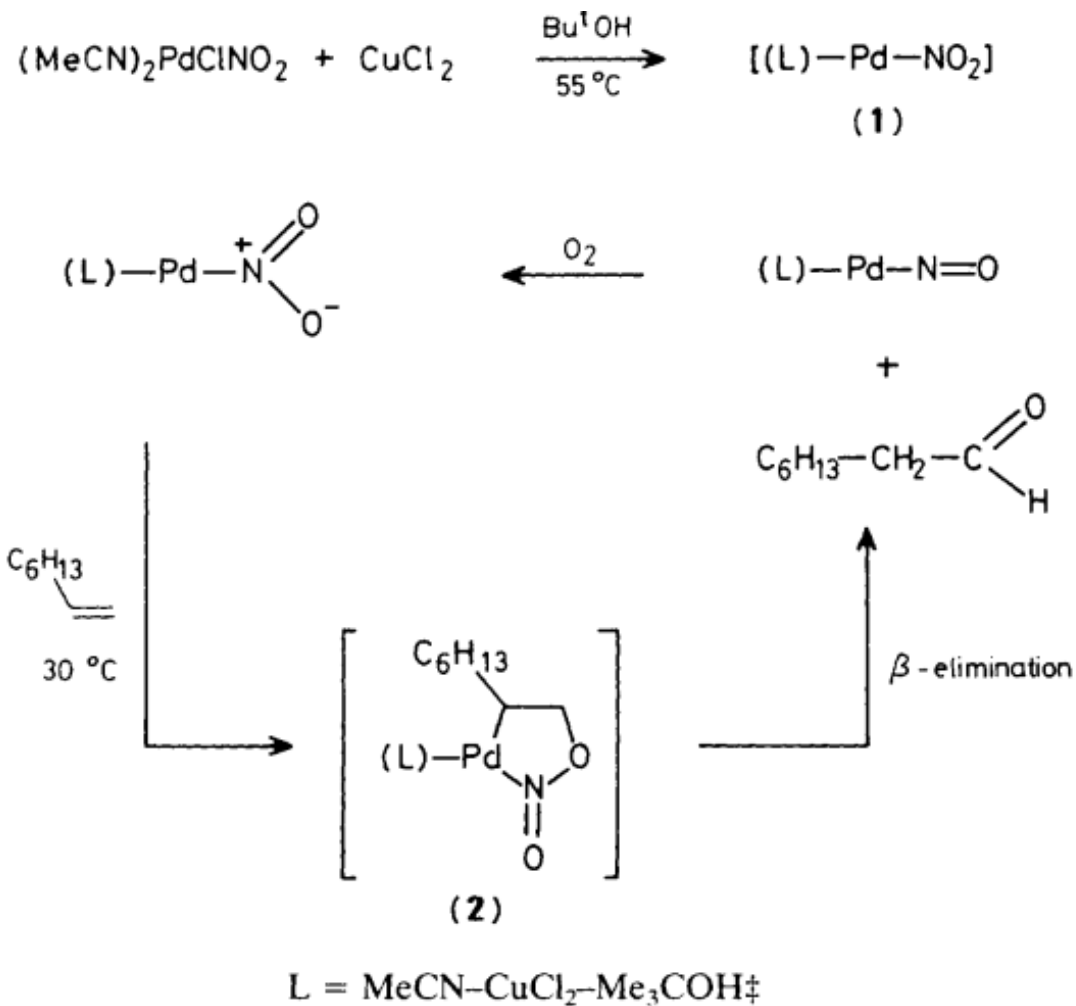


R^1 = alkyl, aryl; R^2 = H, alkyl, aryl; R^3 and R^4 = H, alkyl, aryl; Lewis acid = TiCl_4 , $\text{BF}_3 \cdot \text{OEt}_2$, SnCl_4 , EtAlCl_2

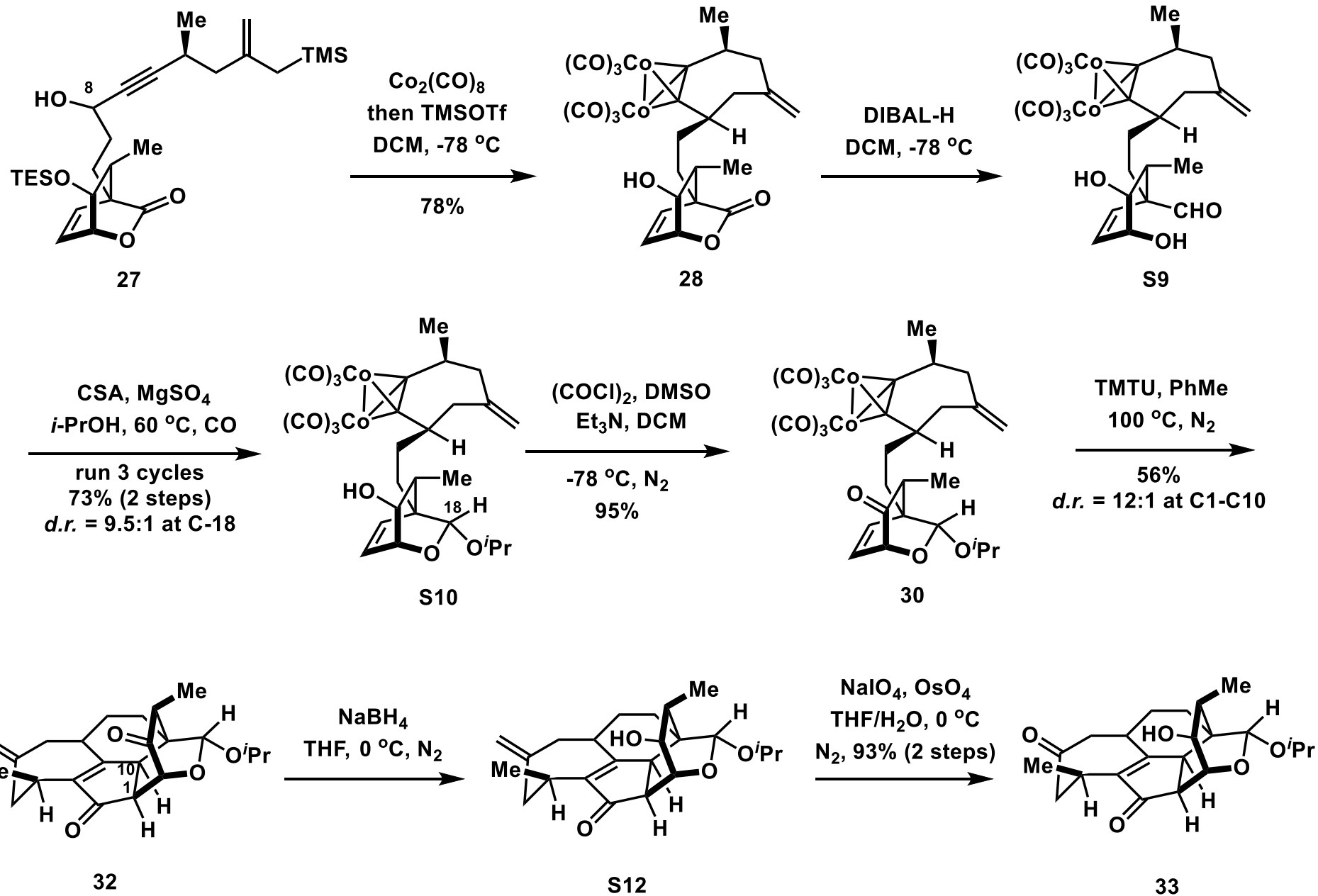


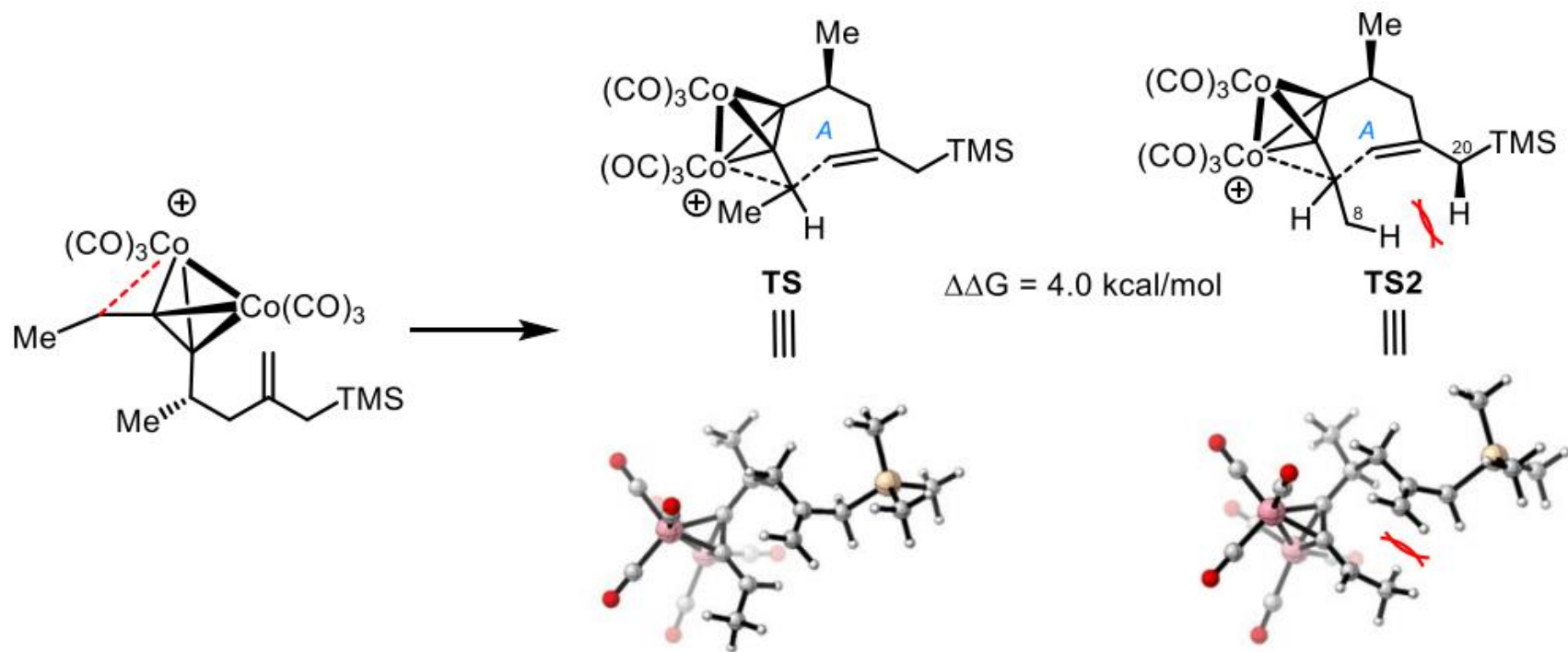


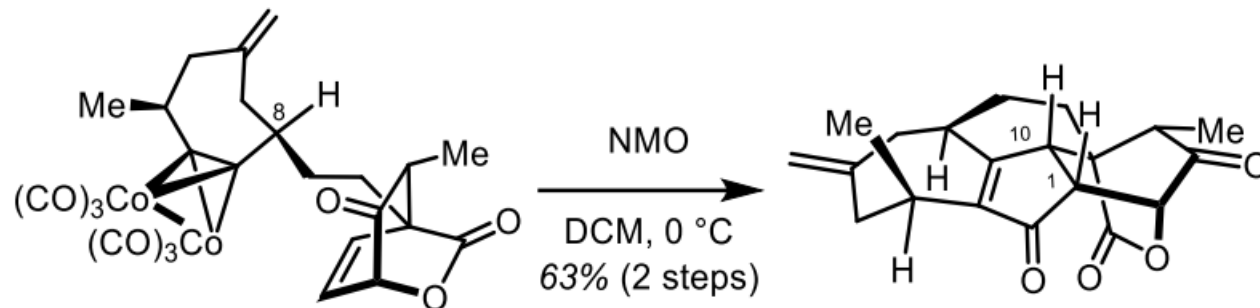
aza-Wacker reaction



Scheme 1



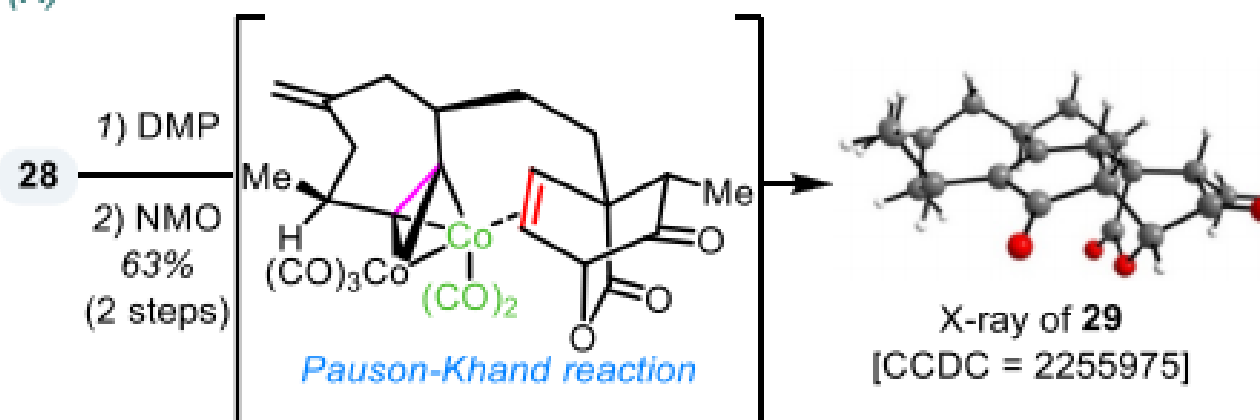




S8

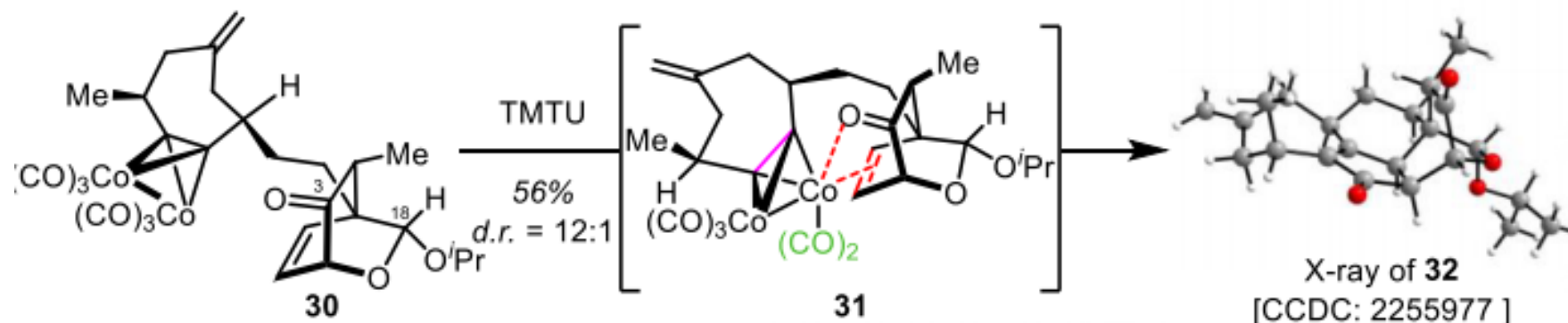
29

(A)



Pauson-Khand reaction

X-ray of **29**
[CCDC = 2255975]

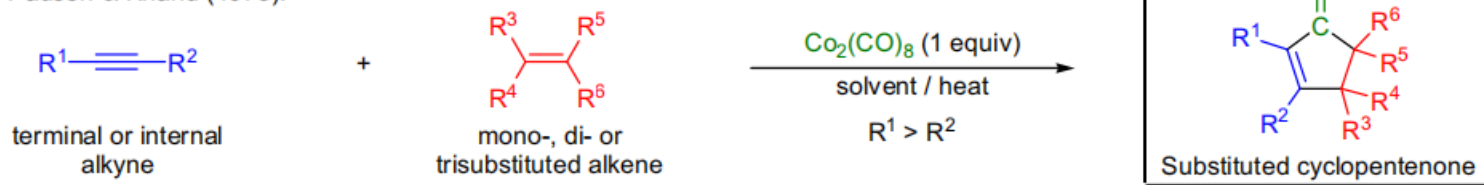


X-ray of **32**
[CCDC: 2255977]

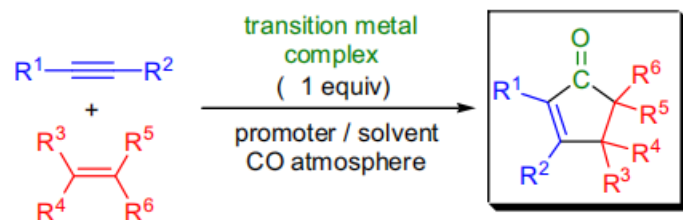
PAUSON-KHAND REACTION

(References are on page 647)

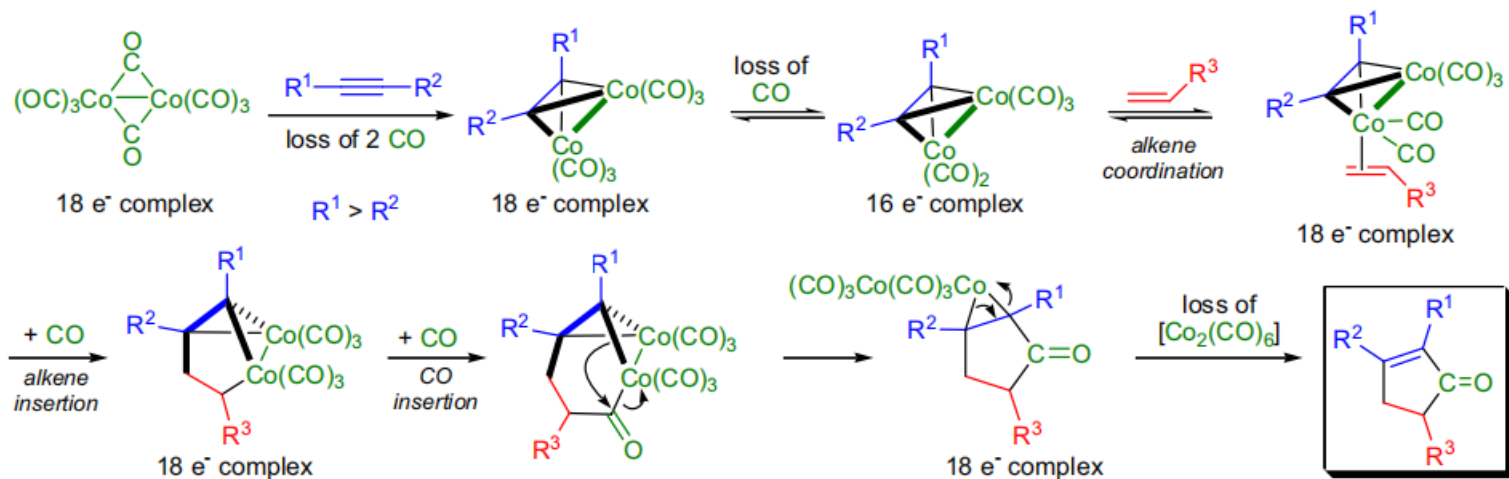
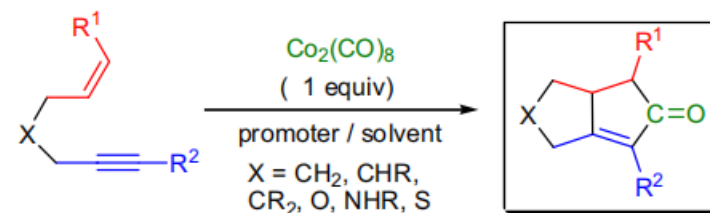
Pauson & Khand (1973):

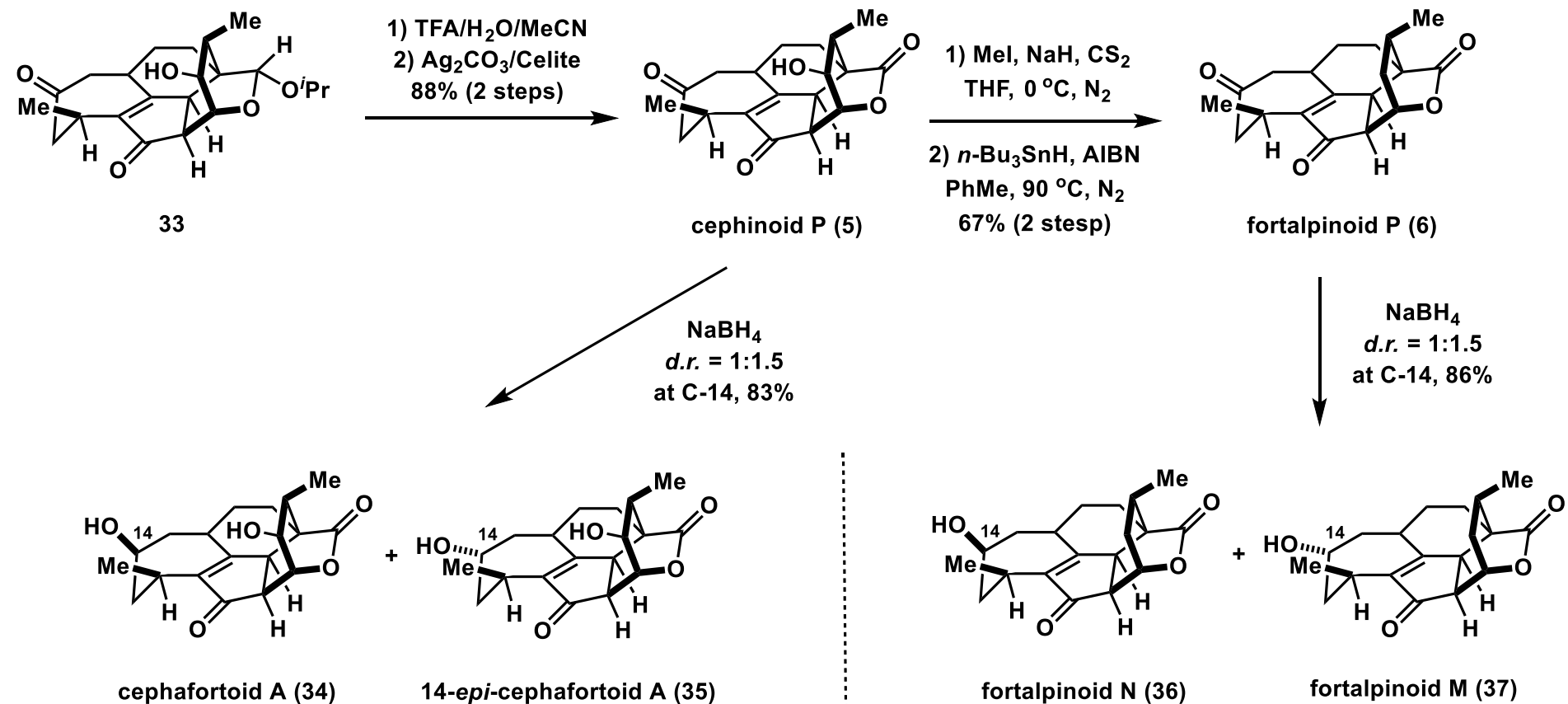


Modified P-K reaction:



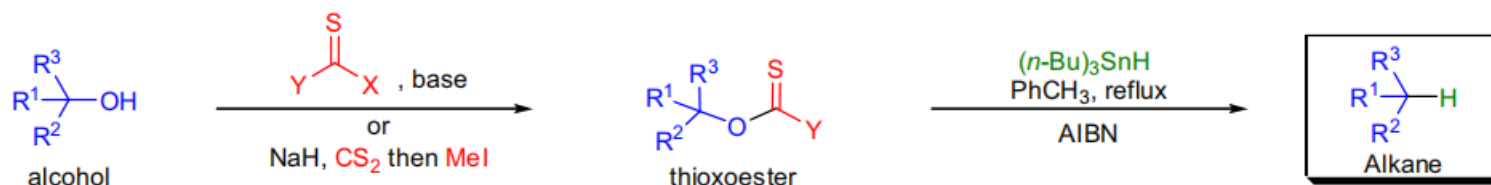
Intramolecular variant:



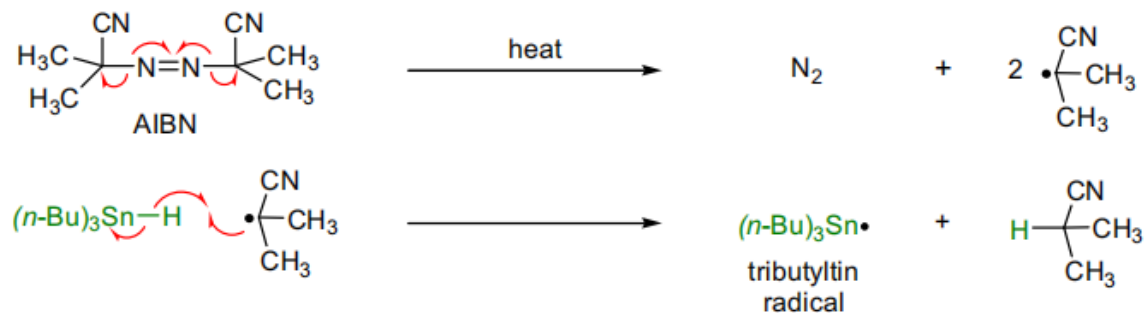


BARTON-McCOMBIE RADICAL DEOXYGENATION REACTION

(References are on page 546)

Y = SMe, imidazolyl, OPh, OMe; X = Cl, imidazolyl; base: NaH

Initiation step:



Propagation step:

