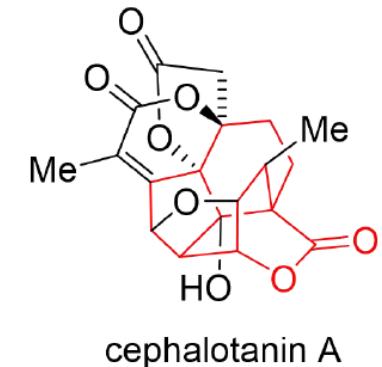
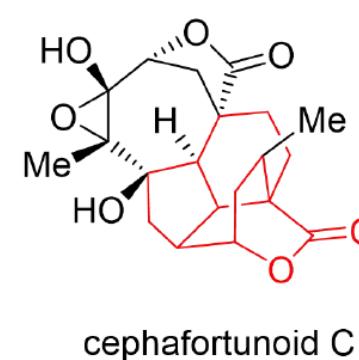
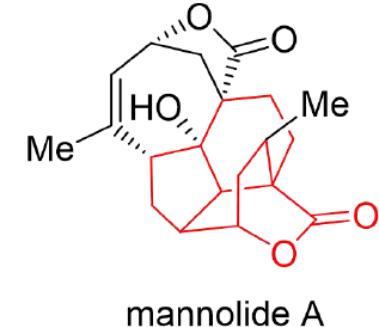
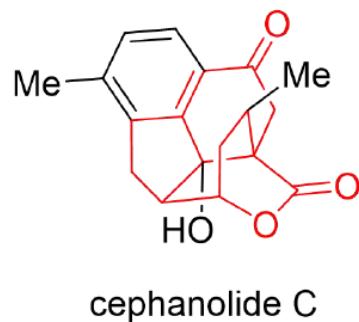
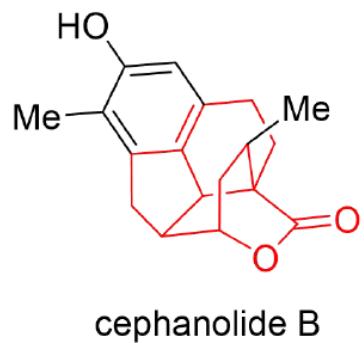
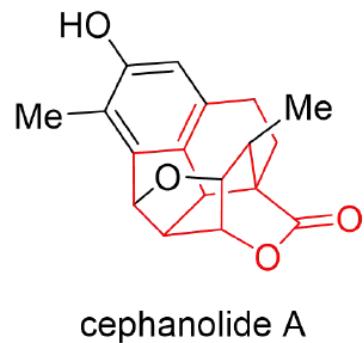
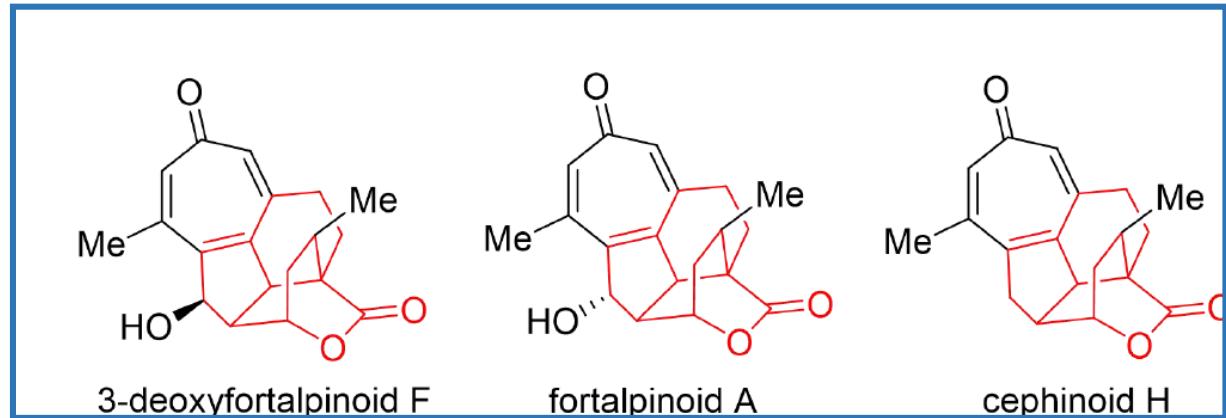
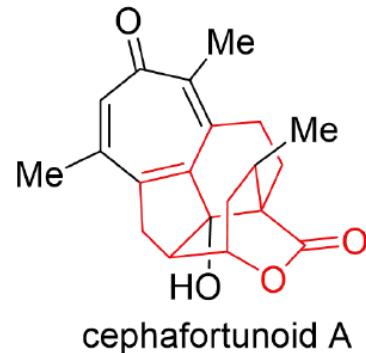
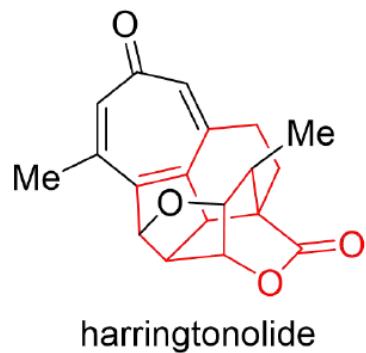
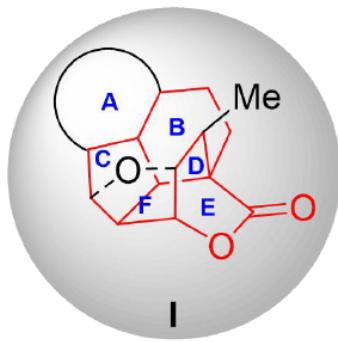


Total Synthesis of (+)-3-Deoxyfortalpinoid F, (+)-Fortalpinoid A, and (+)-Cephinoid H



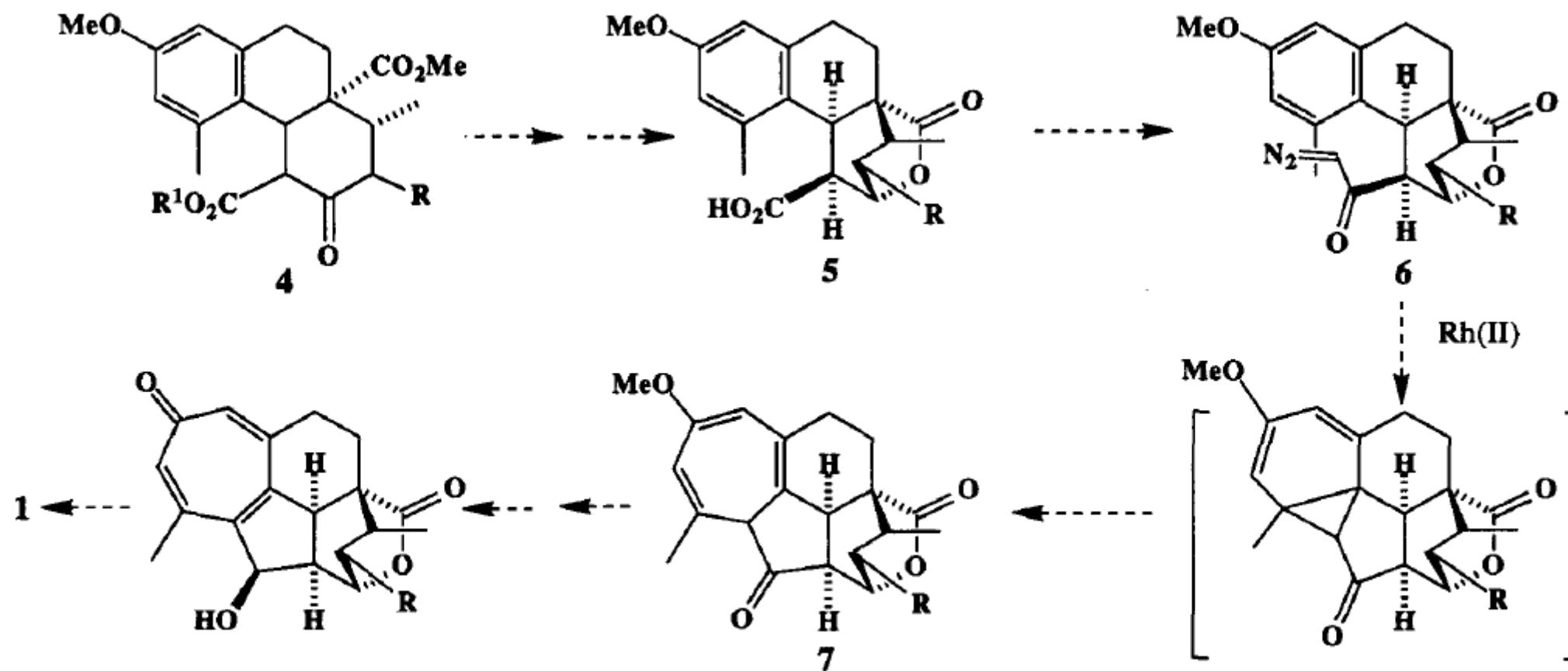
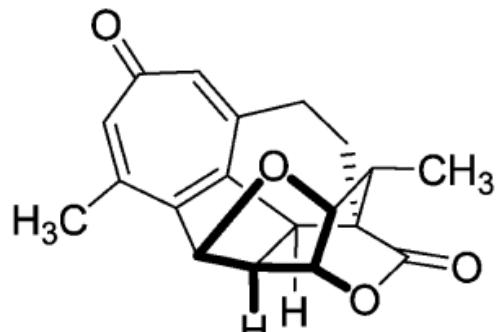
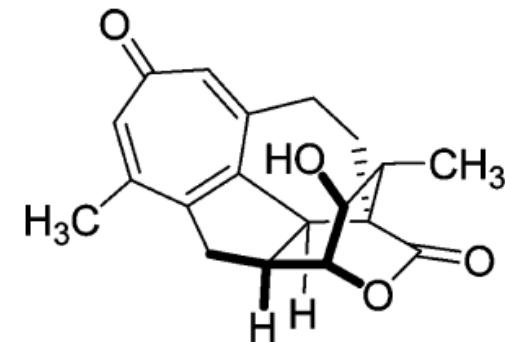


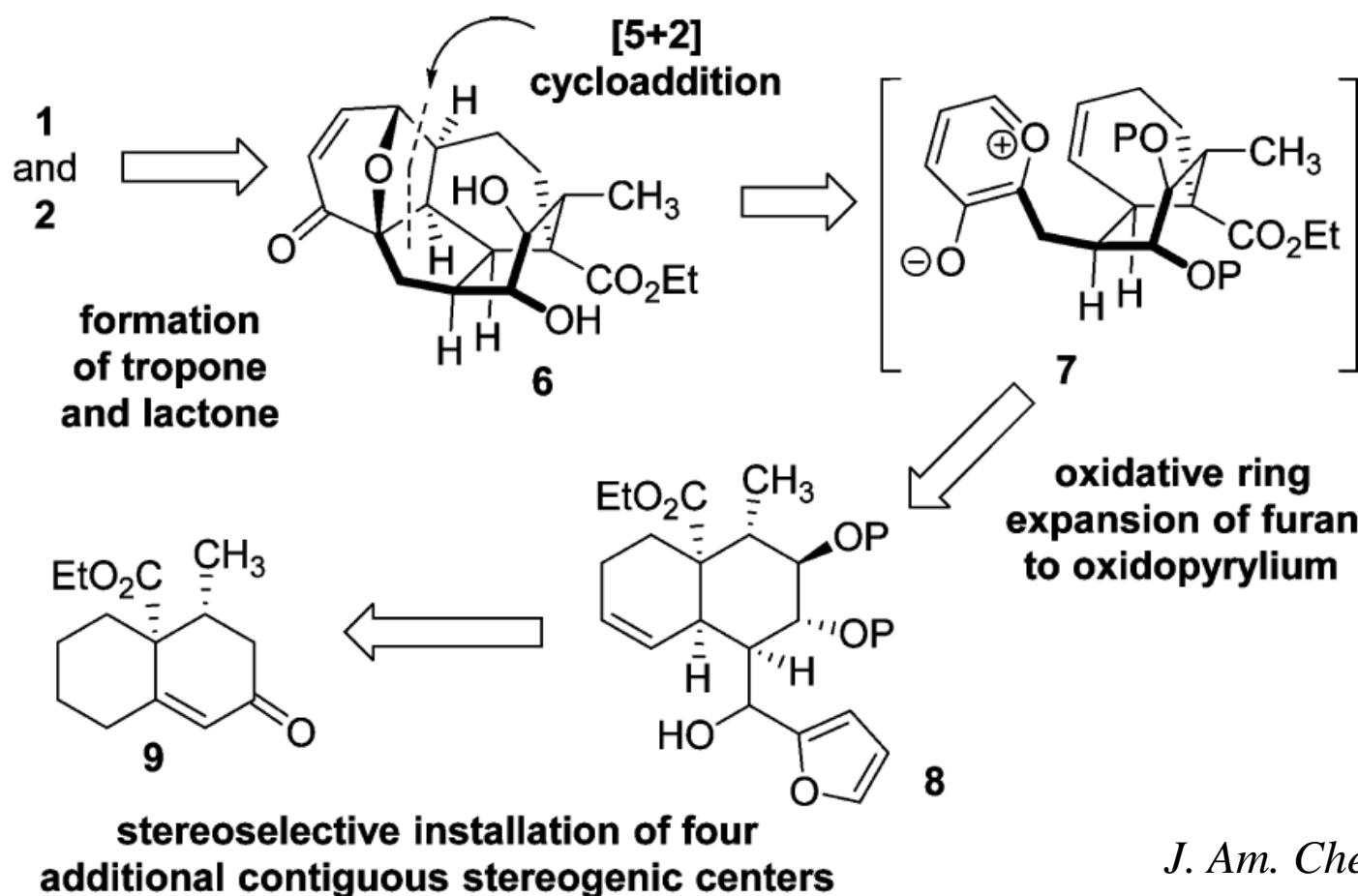
Fig. 1. Synthetic strategy for the total synthesis of harringtonolide 3

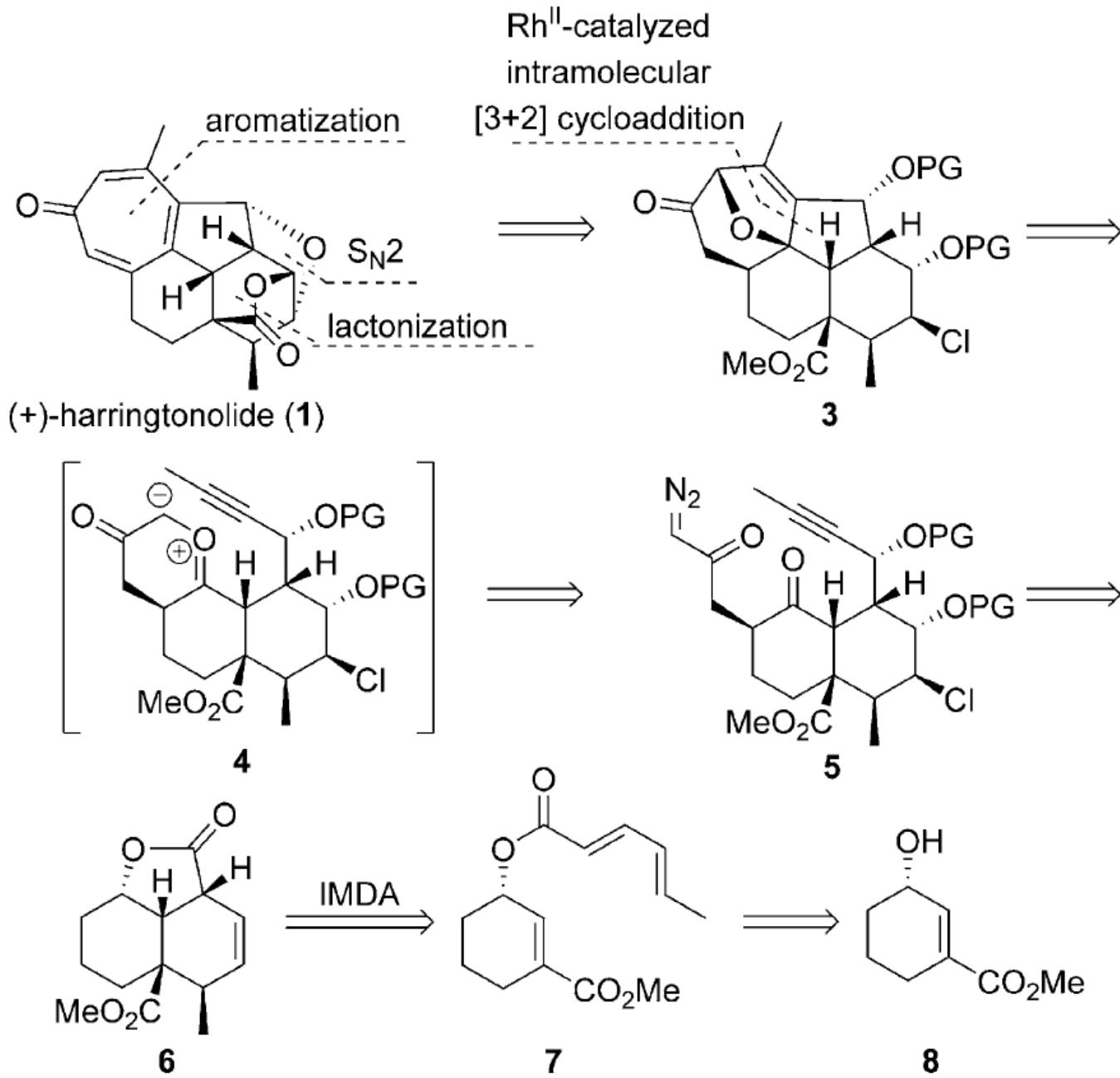


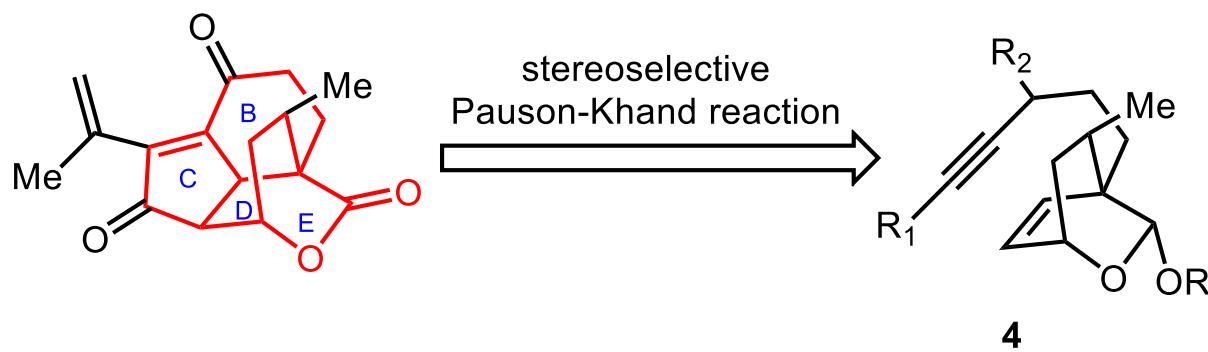
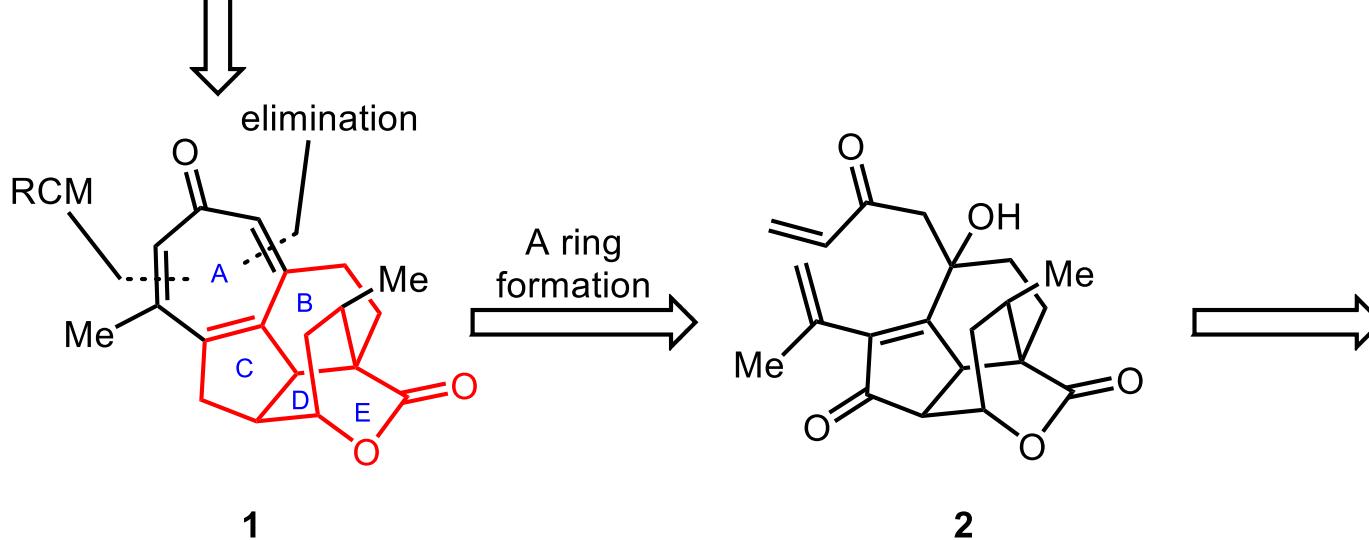
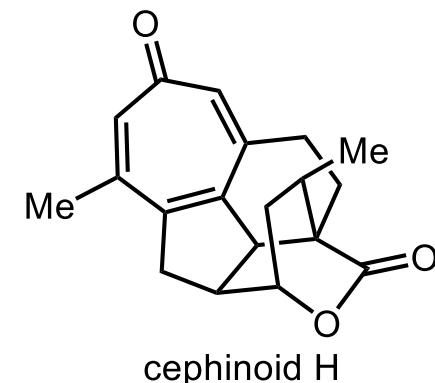
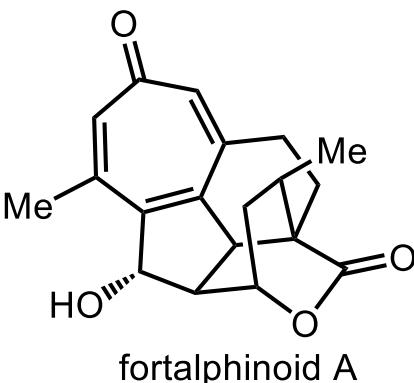
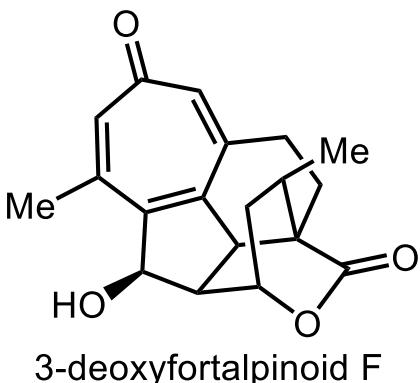
1 harringtonolide

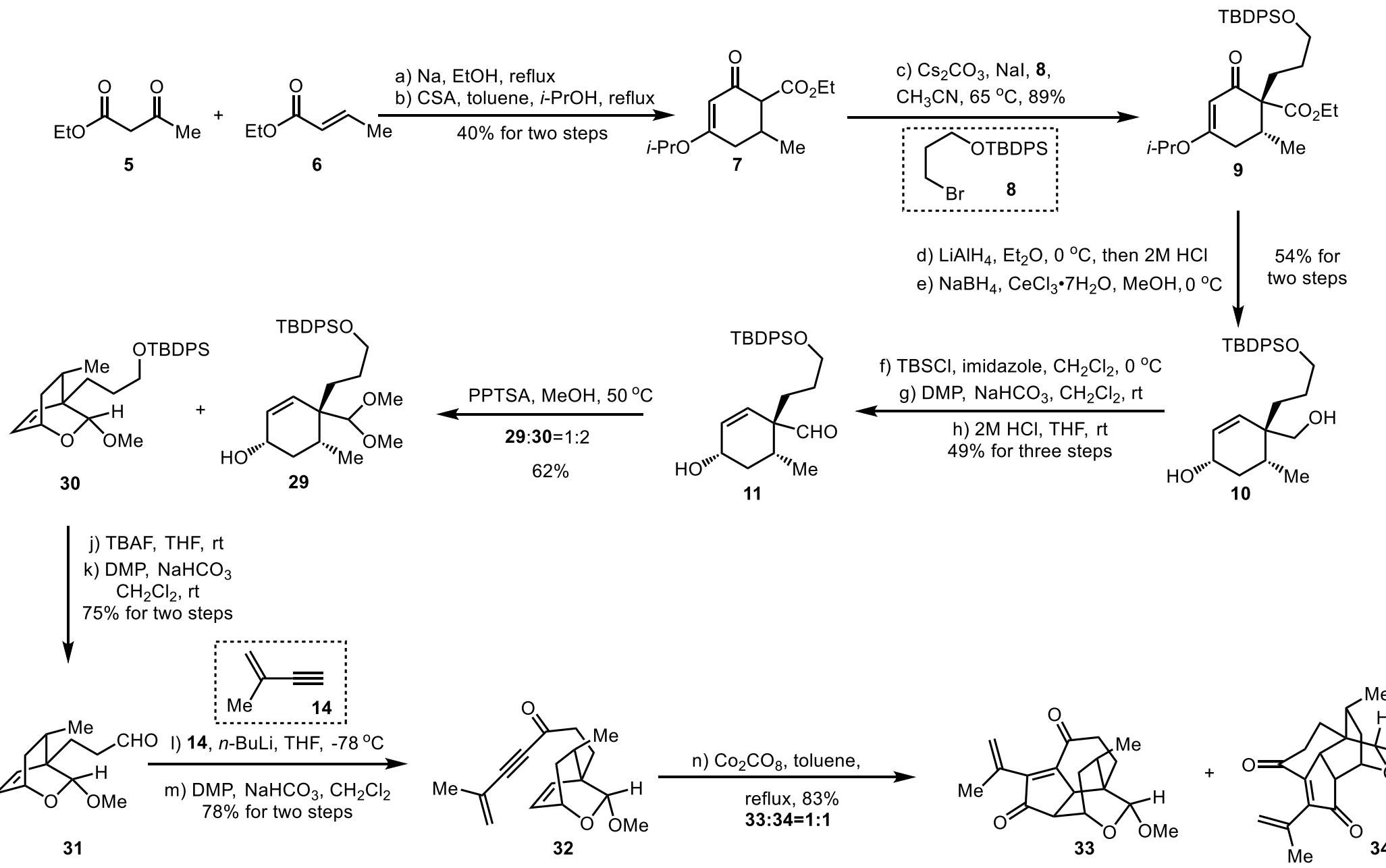


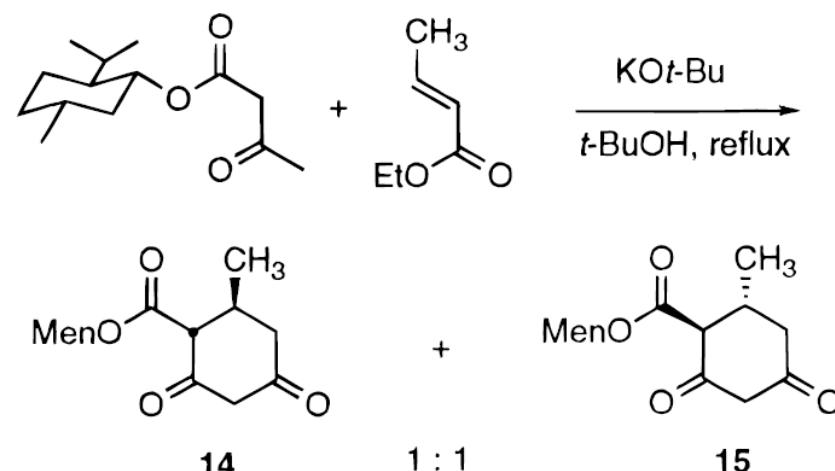
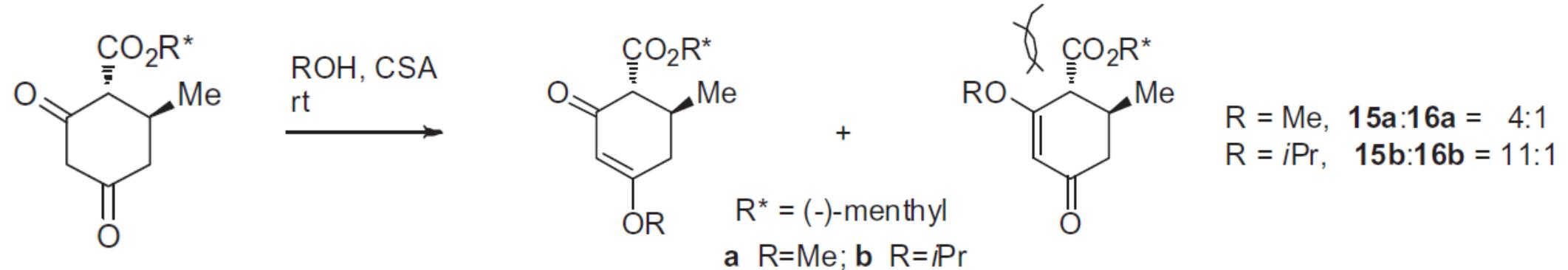
2 hainanolidol











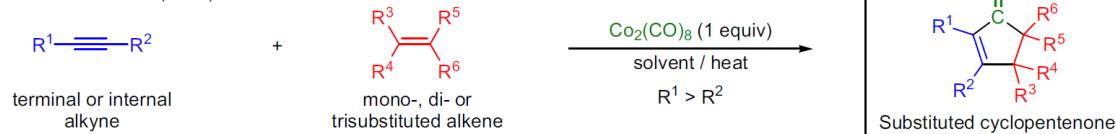
36% yield after
recrystallization

Men = menthyl

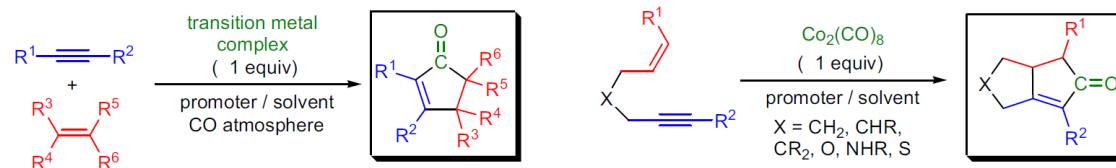
PAUSON-KHAND REACTION

(References are on page 647)

Pauson & Khand (1973):



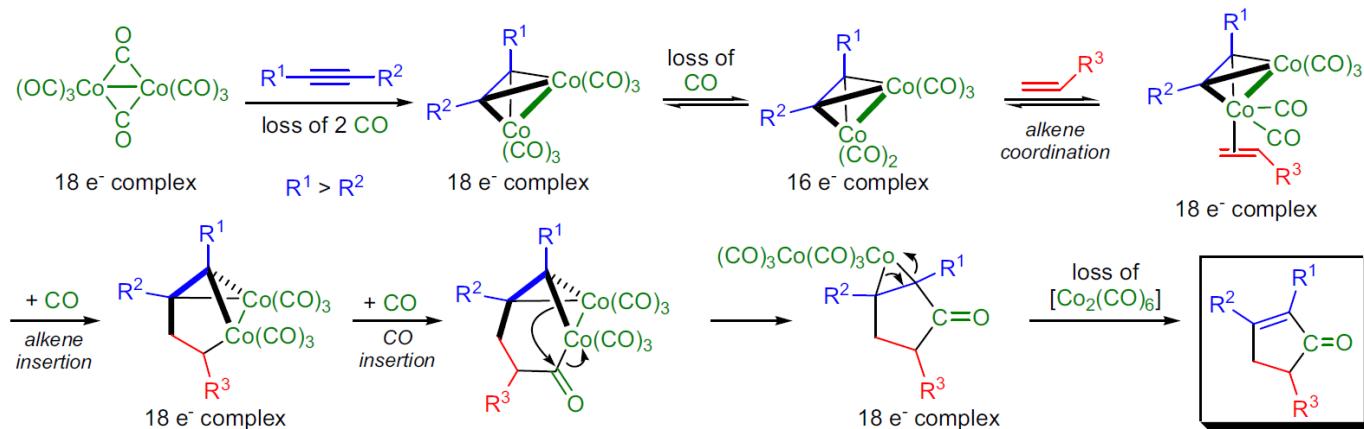
Modified P-K reaction:

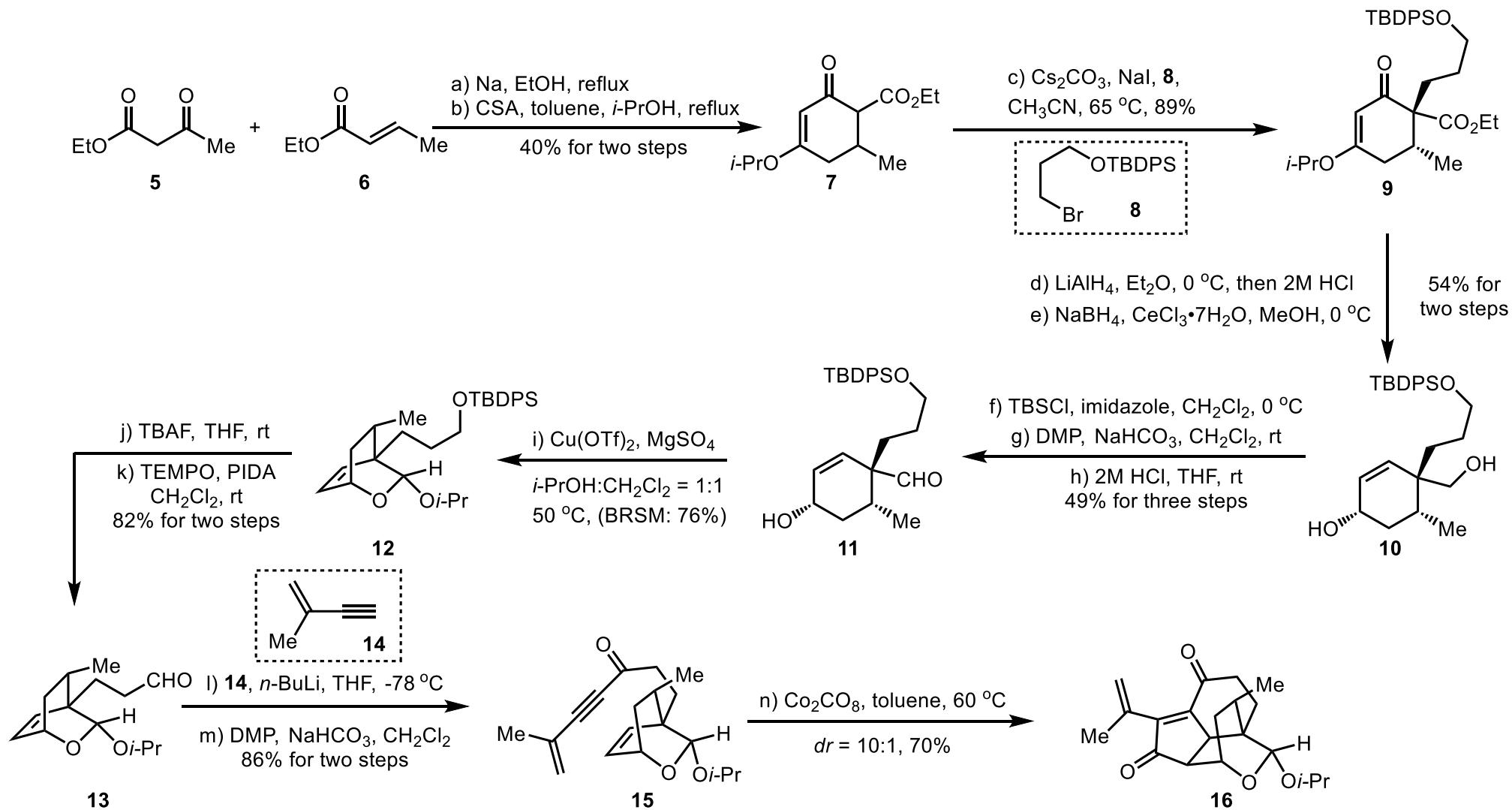


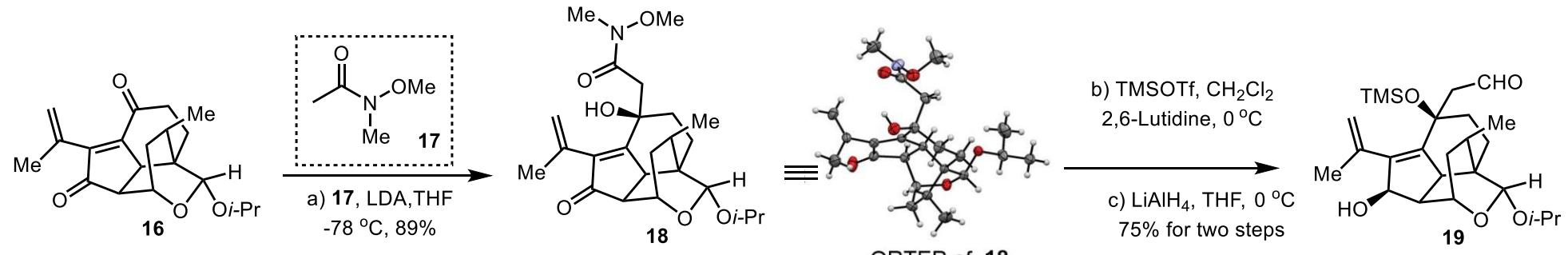
R^{1-6} = H, alkyl, aryl, substituted alkyl and aryl; transition metal complex: $\text{Co}_2(\text{CO})_8$, $\text{Fe}(\text{CO})_5$, $\text{Ru}_2(\text{CO})_{12}$, Cp_2TiR_2 , $\text{Ni}(\text{COD})_2$, $\text{W}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, $[\text{RhCl}(\text{CO})_2]_2$; promoter: NMO, TMAO, RSCH_3 , high-intensity light/photolysis, "hard" Lewis base

Mechanism:

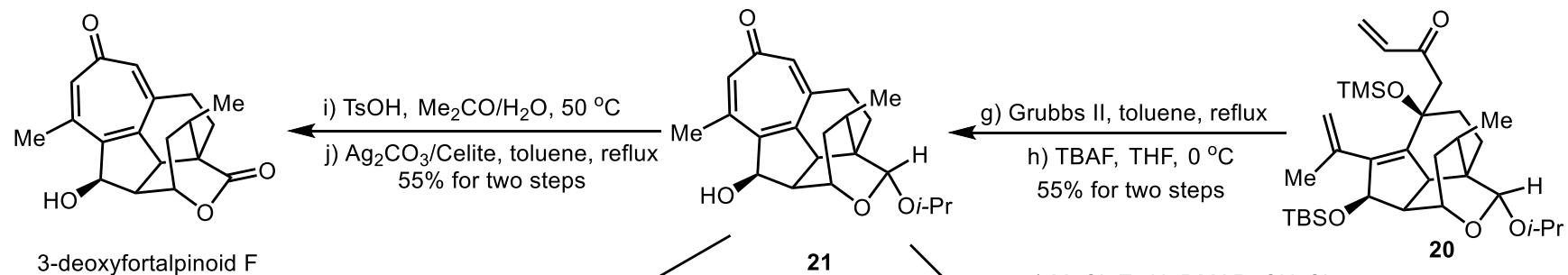
The mechanism of the *Pauson-Khand reaction* has not been fully elucidated. However, based on the regio- and stereochemical outcome in a large number of examples, a reasonable hypothesis has been inferred.



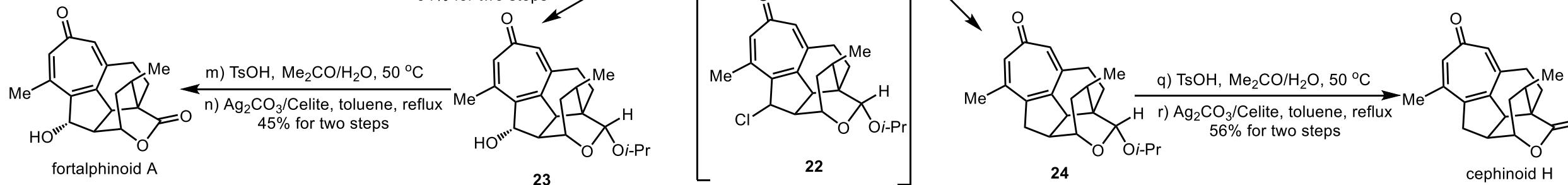




d) TBSOTf, 2,6-Lutidine, CH₂Cl₂, 0 °C
e) CH₂CHMgBr, THF, 0 °C
f) DMP, NaHCO₃, CH₂Cl₂, rt
44% for three steps

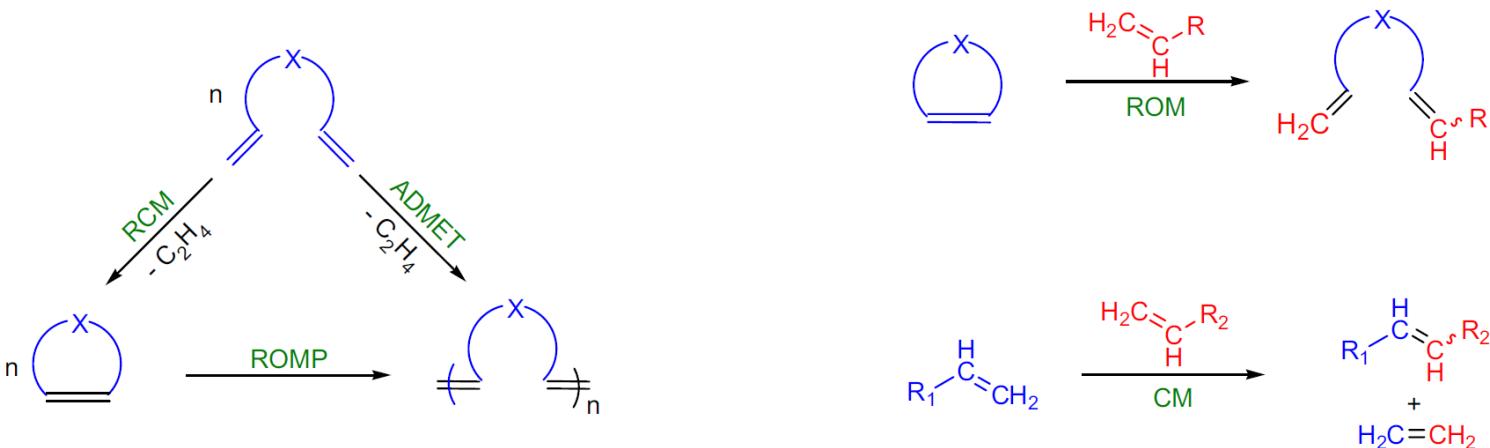


k) MsCl, Et₃N, DMAP, CH₂Cl₂, rt
l) AgBF₄, Me₂CO/H₂O
54% for two steps

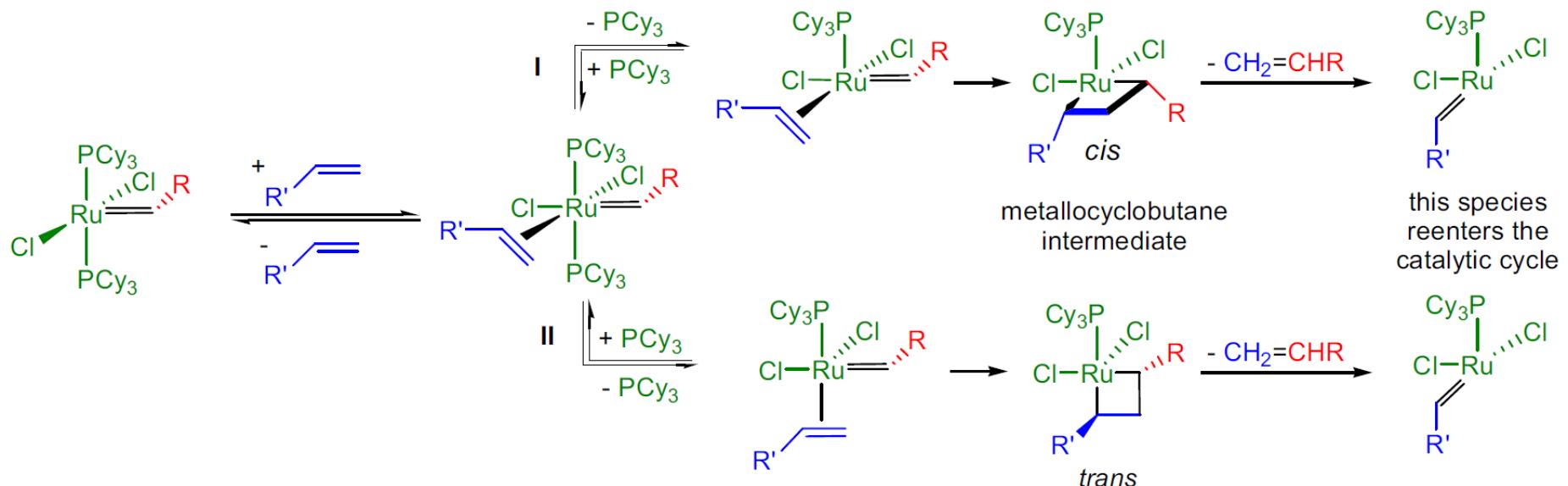


ALKENE (OLEFIN) METATHESIS

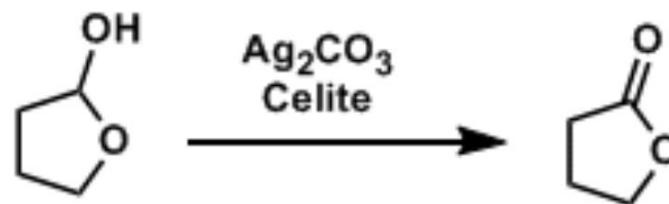
(References are on page 534)



Mechanism:



Fetizon试剂



反应机理

