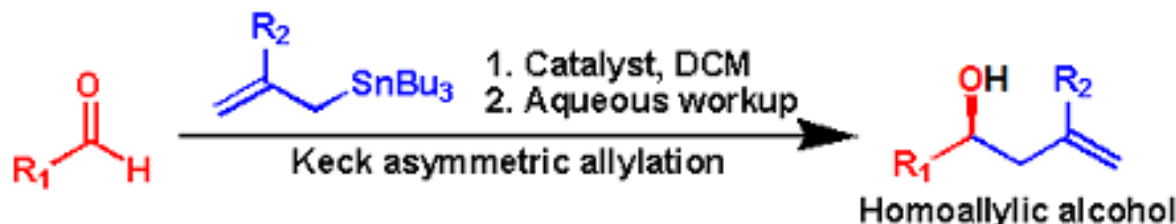


Named Allylation Reactions

- Keck asymmetric allylation
- Keck radical allylation
- Roush asymmetric allylation
- Sakurai allylation
- Tsuji-Trost reaction/allylation

Zhou Guanshen
2016-1-18

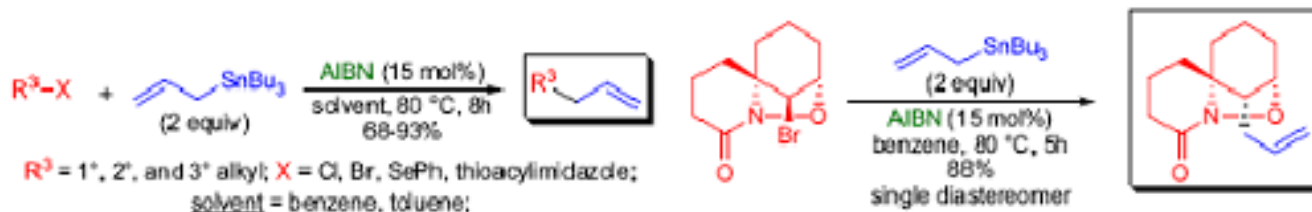
An introduction to above allylations



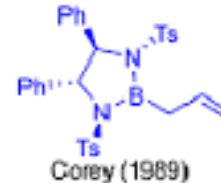
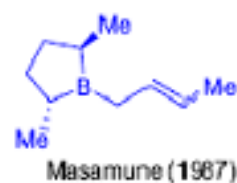
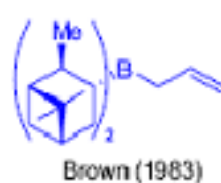
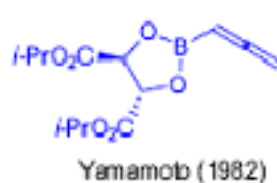
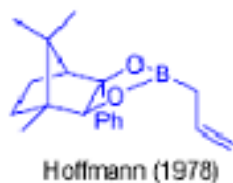
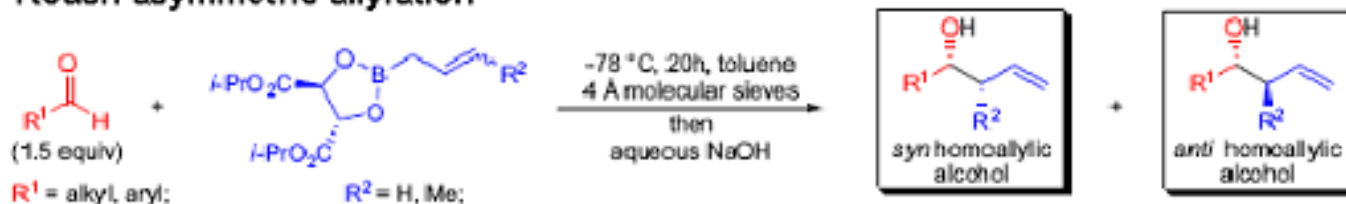
R^1 = alkyl, aryl, alkenyl; R^2 = alkyl, O-alkyl; **Mikami's catalyst**: $TiCl_2(Oi-Pr)_2$ + (*S*)-BINOL (0.3 equiv) + 4Å MS in CH_2Cl_2 , toluene, 1h, r.t.; **Keck's catalyst**: $Ti(Oi-Pr)_4$ + (*R*)-BINOL (2 equiv) + 4Å mol sieves in CH_2Cl_2 , 1h, r.t.; **Taollavini's catalyst**: $TiCl_2(Oi-Pr)_2$ + (*S*)-BINOL (slight excess) + 4Å mol. sieves in CH_2Cl_2 , 2h, r.t.;

Keck's general process (1982):

Keck's specific example (1982):

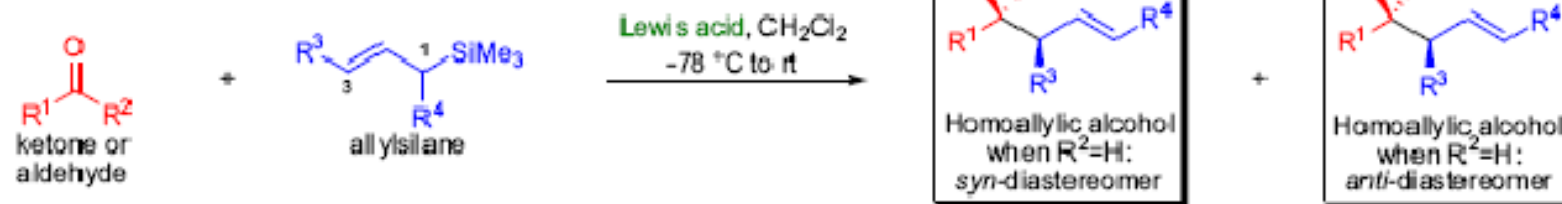


Roush asymmetric allylation



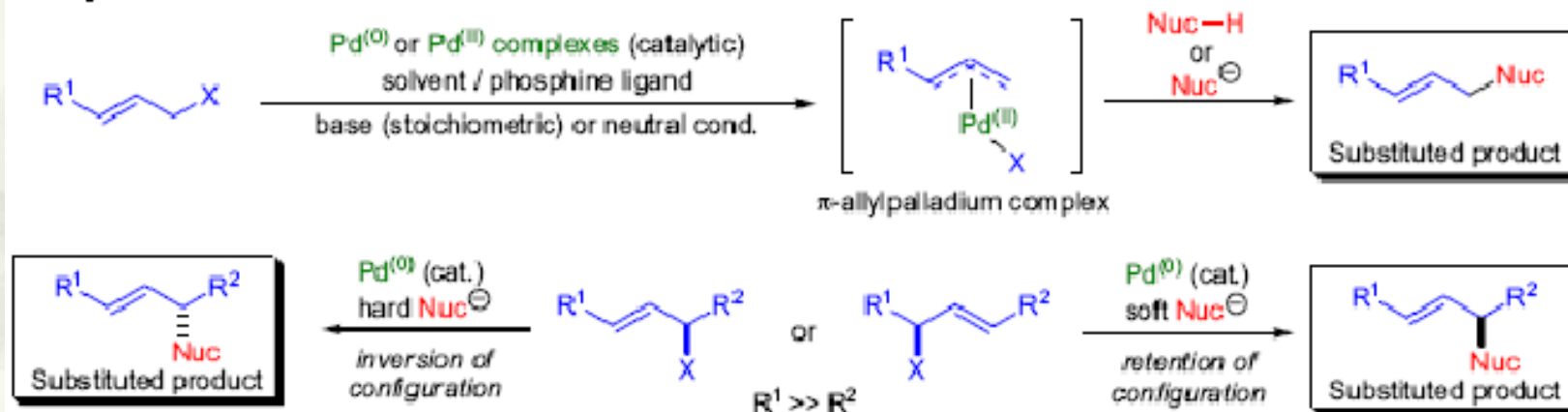
An introduction to above allylations

Sakurai allylation



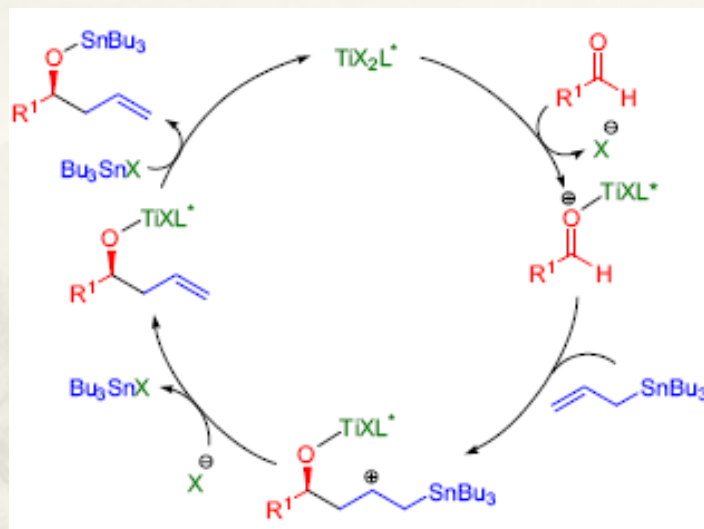
R^1 = alkyl, aryl; R^2 = H, alkyl, aryl; R^3 and R^4 = H, alkyl, aryl; Lewis acid = $TiCl_4$, $BF_3 \cdot OEt_2$, $SnCl_4$, $EtAlCl_2$

Tsuji-Trost reaction

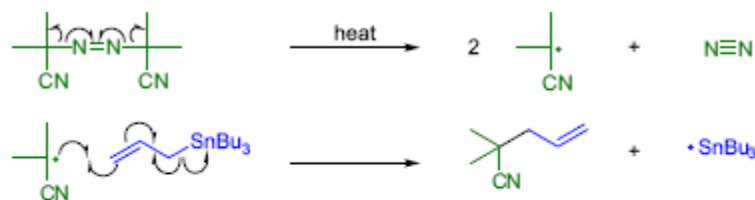


$R^{1,2}$ = H, alkyl, aryl; X = OH, OPh, OCOR, OCONHR, OCO₂R, OP(O)(OR)₂, Cl, NO₂, SO₂Ph, NR₂, NR₃X, SR₂X
soft Nuc-H = $R^3R^4CH_2$, enamines, enolates; $R^{3,4}$ = CO₂R, CN, NO₂, SO₂Ph, COR, NC, N=(CMe₂), SPh, alkenyl
Pd-complexes: Pd(PPh₃)₄, Pd₂(dba)₃, [Pd(allyl)Cl]₂; ligands: PPh₃, dba

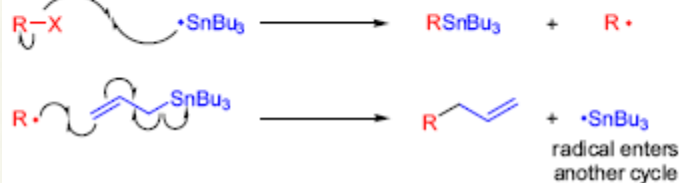
Mechanism—Keck allylation



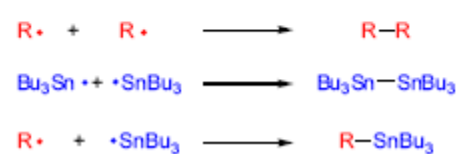
Initiation step:



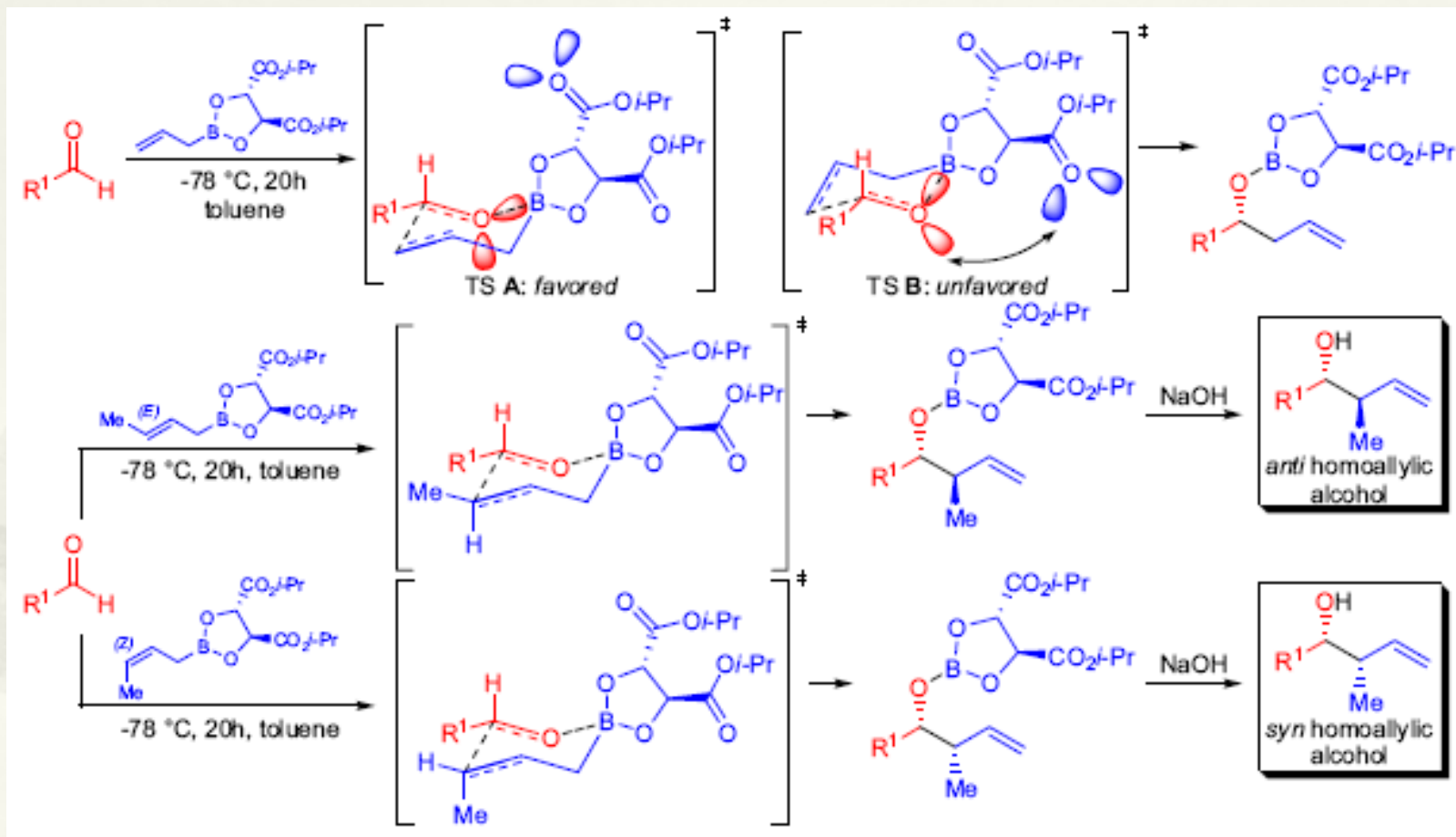
Propagation step:



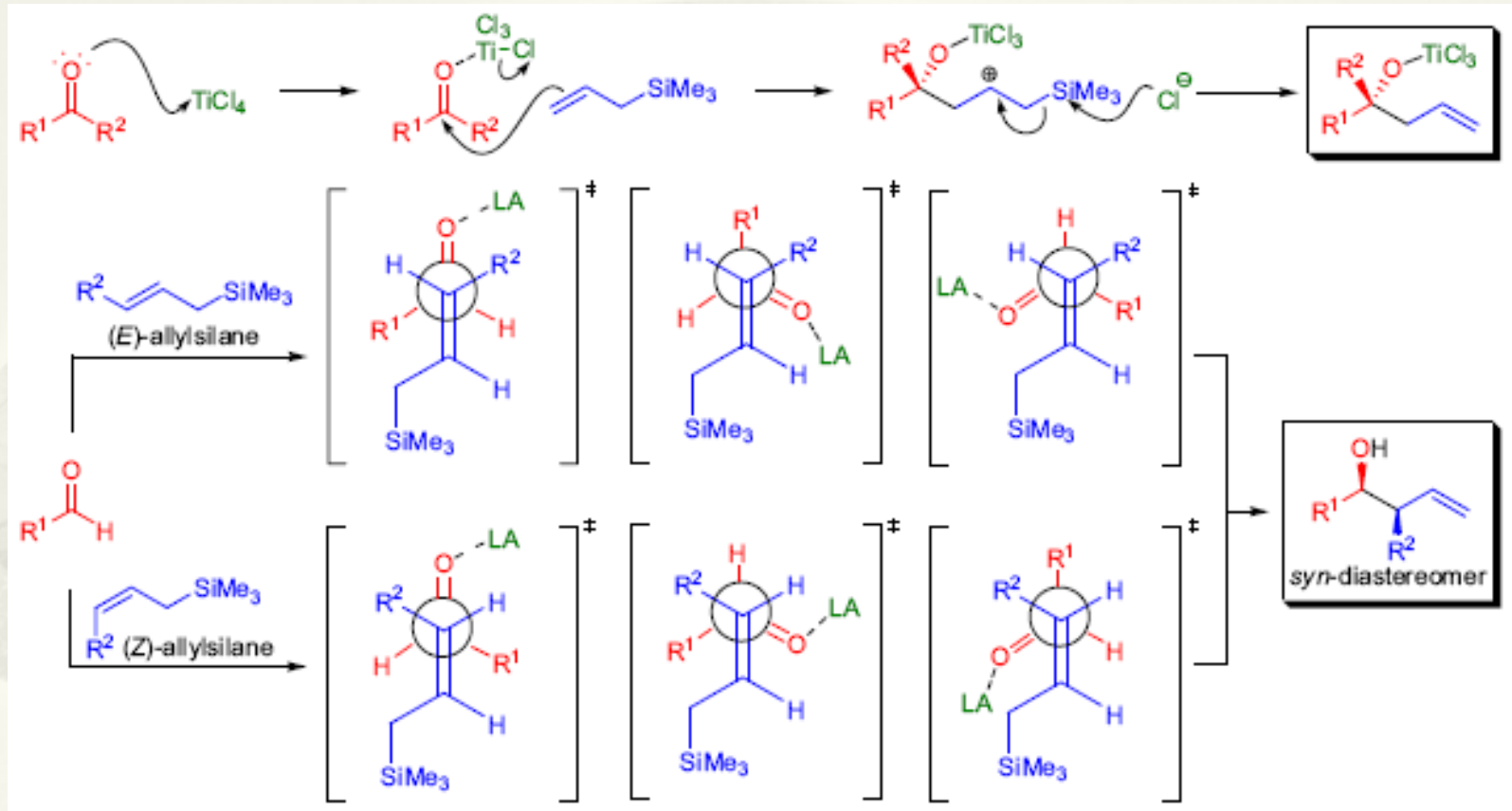
Termination steps



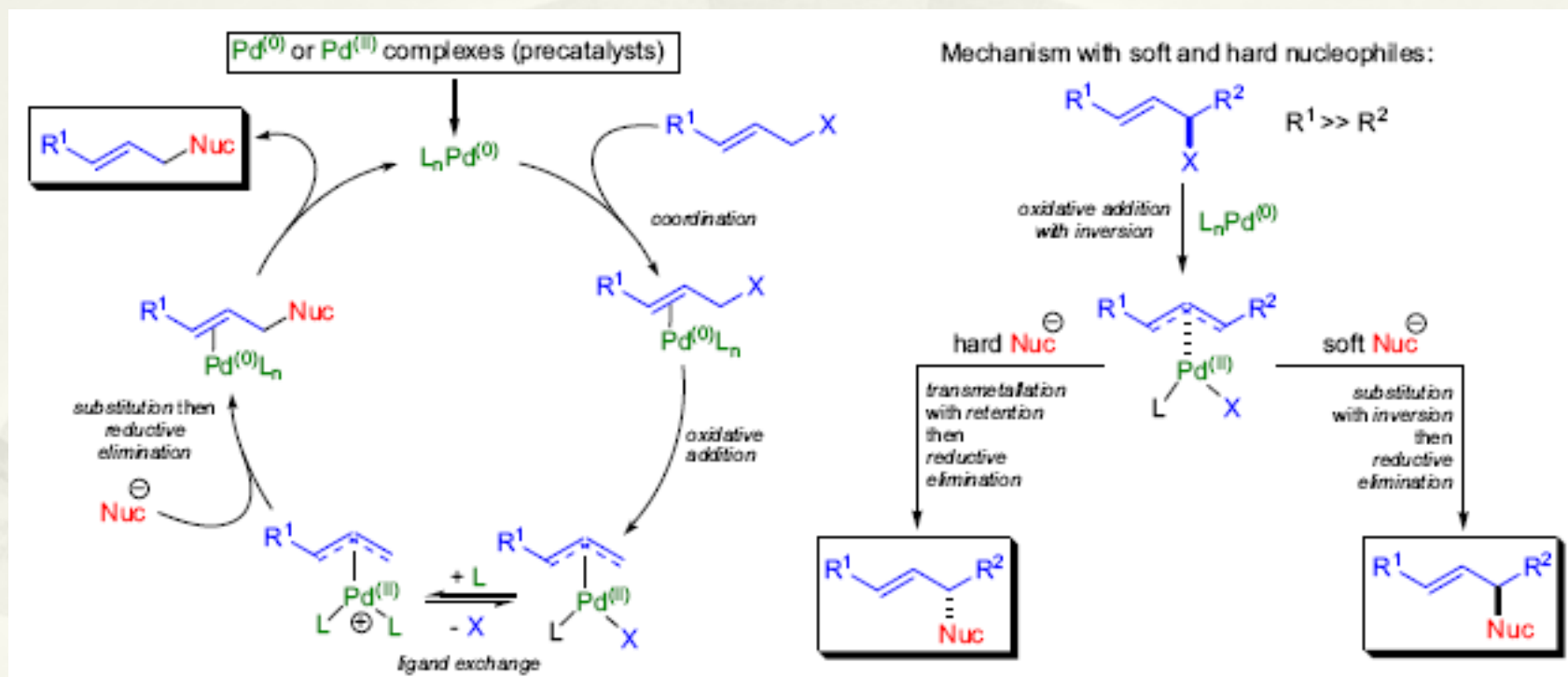
Mechanism—Roush allylation



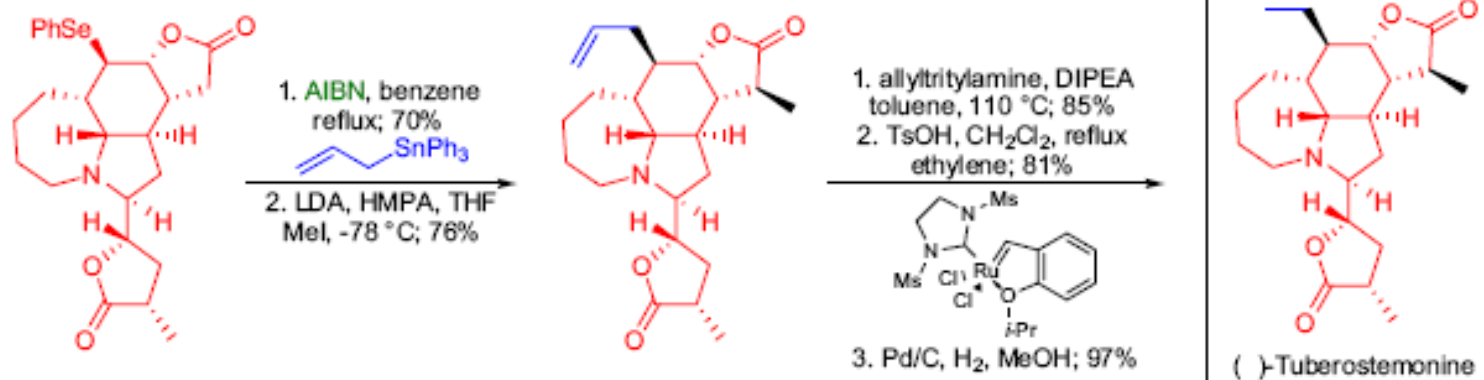
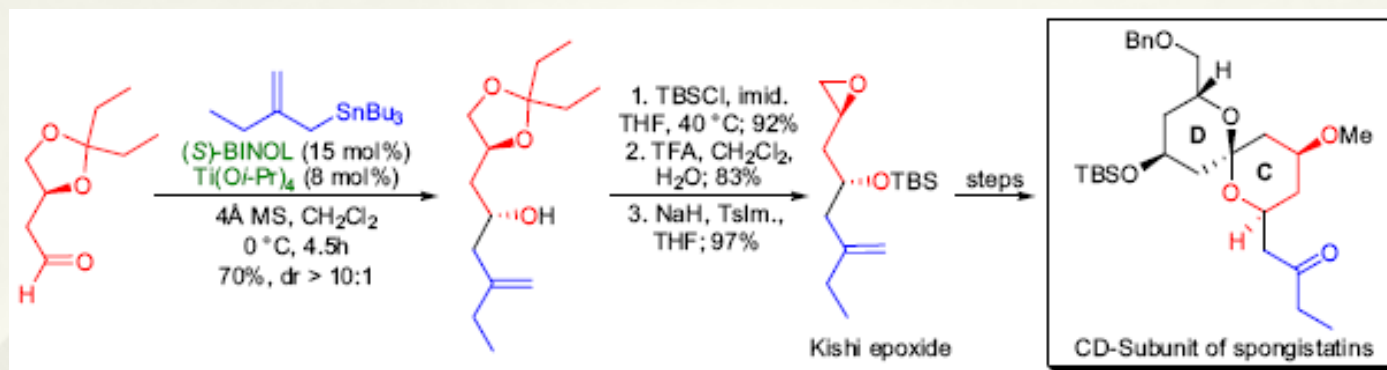
Mechanism—Sakurai allylation



Mechanism—Tsuji-Trost reaction



Synthetic applications



Synthetic applications

