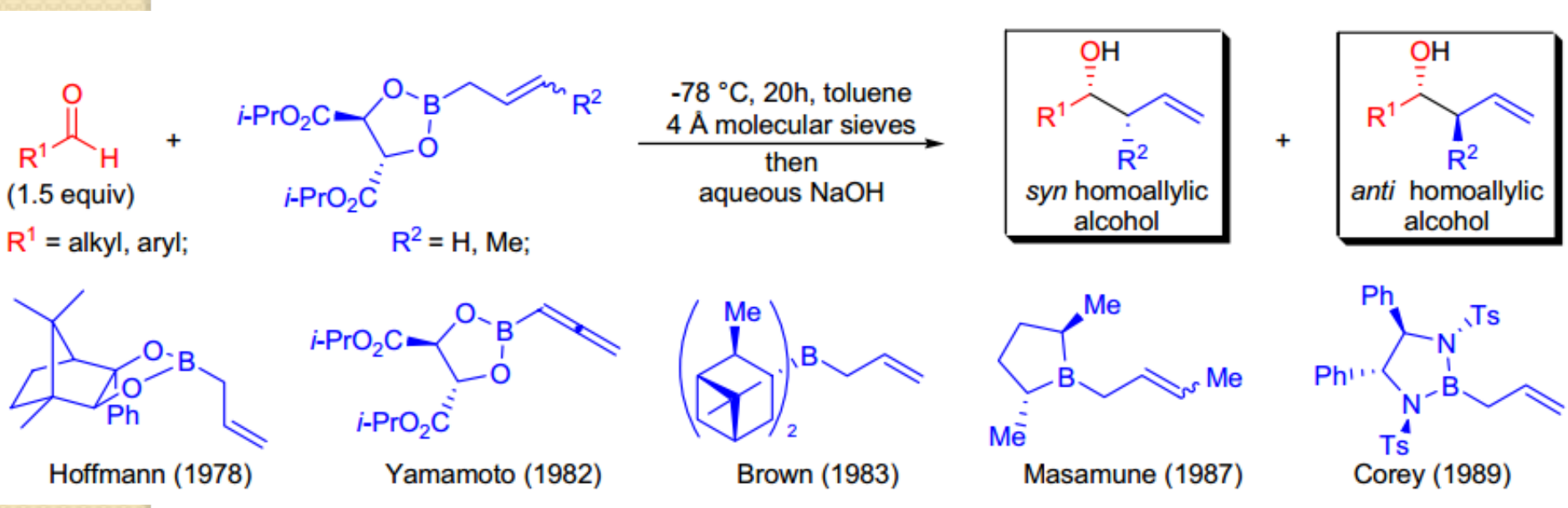
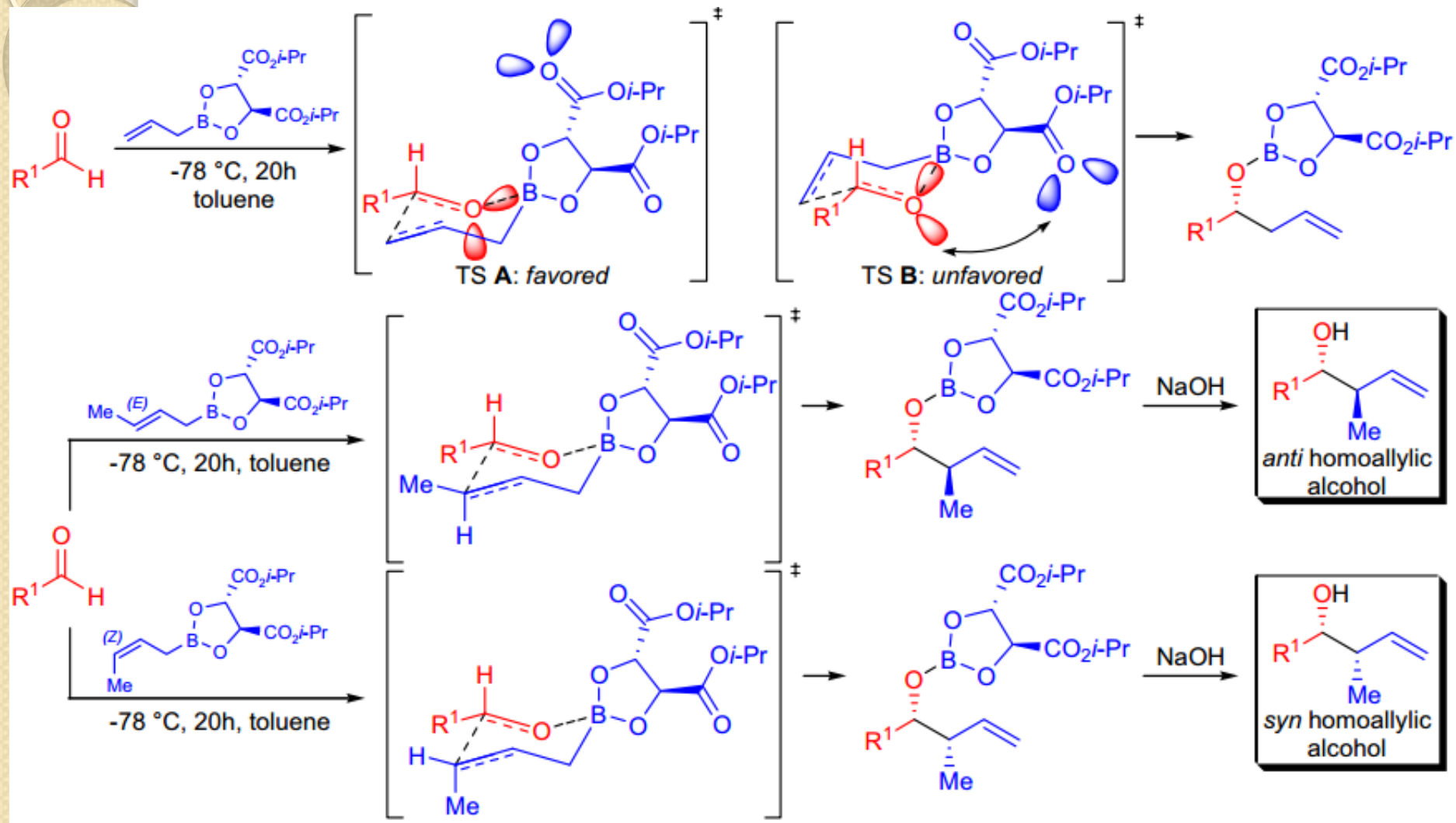
Roush Asymmetric Allylation



Mechanism

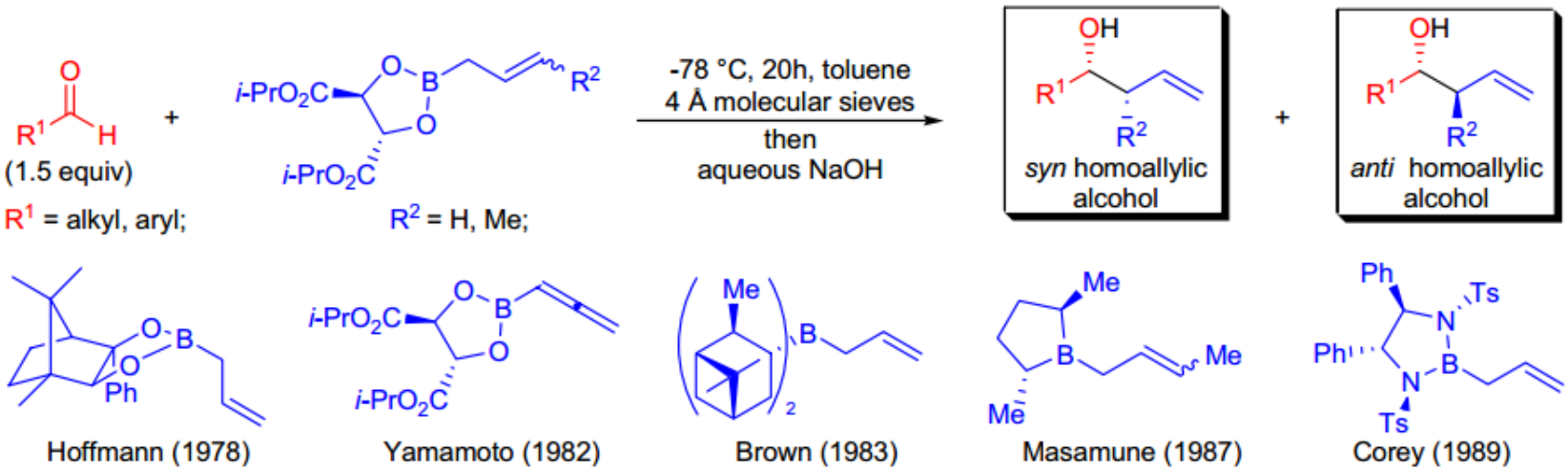

-78 °C, 20h
toluene
TS A: favored
TS B: unfavored
(E)
-78 °C, 20h, toluene
(Z)
-78 °C, 20h, toluene
NaOH
NaOH
anti homoallylic alcohol
syn homoallylic alcohol

General features

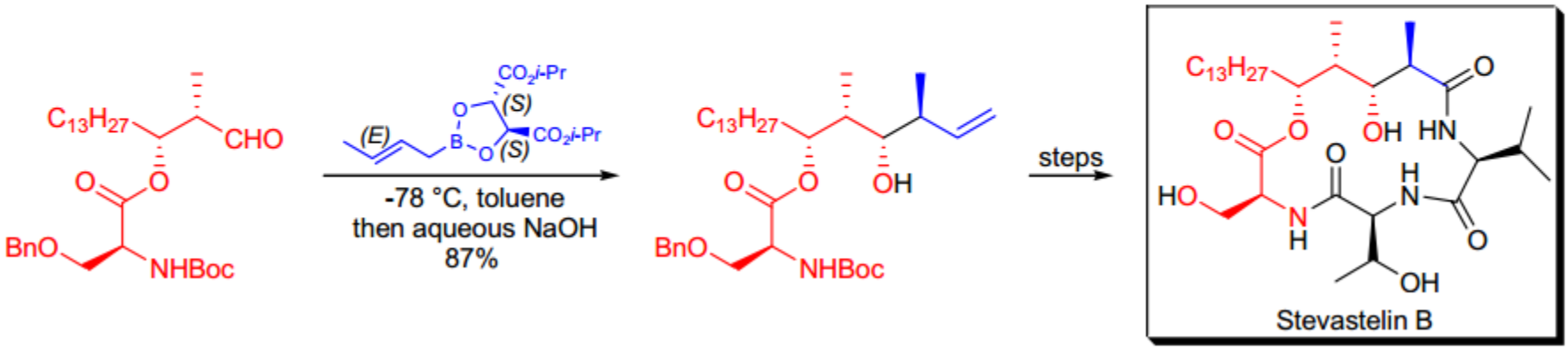
1) This method provides access to both enantiomers of the homoallylic alcohol product by selecting the proper enantiomer of the diisopropyltartrate ester for the preparation of the reagent;

2) Both aliphatic and aromatic aldehydes are suitable substrates;

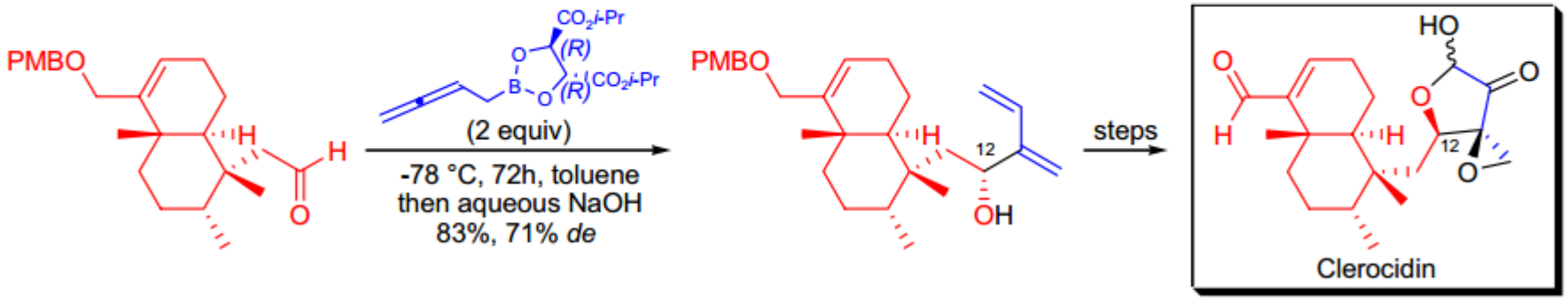
3) (E)-crotylboronate derivatives lead to the formation of the *anti* diastereomer as the major product, while (Z)-crotylboronates give the *syn* product.



Stevastelins are depsipeptides exhibiting immunosuppressant activity. The first total synthesis of *stevastelin B* was described by Y. Yamamoto and co-workers.[30] To construct four consecutive stereocenters, the *Evans aldol reaction* and the *Roush asymmetric allylation* were utilized. In the allylation step, the authors used (*S*,*S*)-diisopropyltartrate-derived (*E*)-crotyl boronate. The *anti* homoallylic alcohol product formed as the only diastereomer.



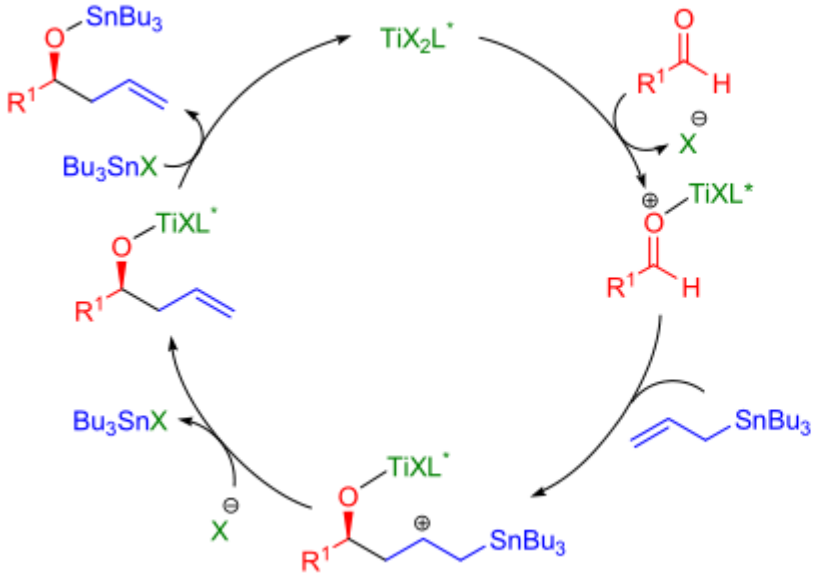
E.A. Theodorakis and co-workers reported the total synthesis of *clerocidin*, a diterpenoid antibiotic.[31] To form the C12 stereocenter and the diene moiety, they applied an asymmetric homoallenylboration method.[32] The reaction of the aldehyde and (*S*,*S*)-diisopropyltartrate-derived homoallenyl boronate provided the alcohol with a 6:1 diastereoselectivity and 83% yield.



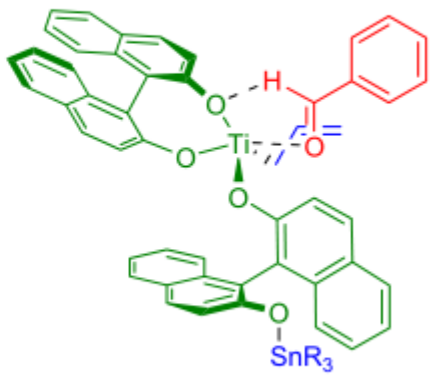
Keck asymmetric allylation

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

Mechanism:

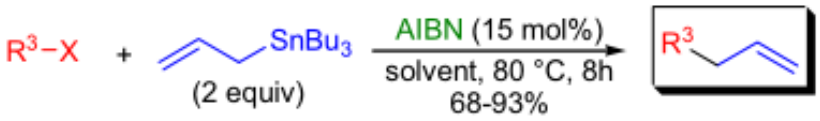


Corey's stereochemical model:



Keck radical allylation

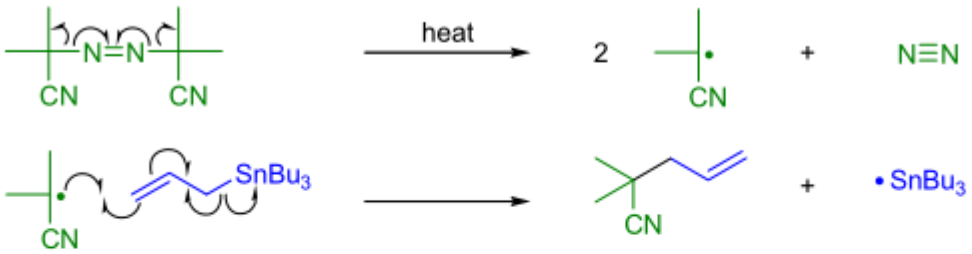
Keck's general process (1982):



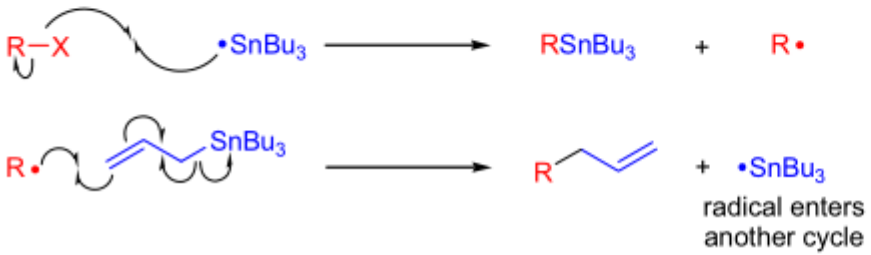
R^3 = 1°, 2°, and 3° alkyl; X = Cl, Br, SePh, thioacylimidazole;
solvent = benzene, toluene;

Mechanism:

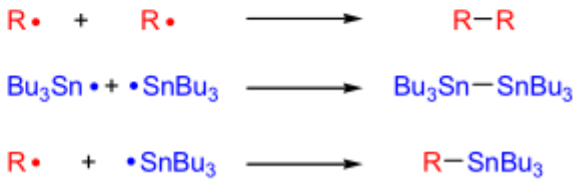
Initiation step:



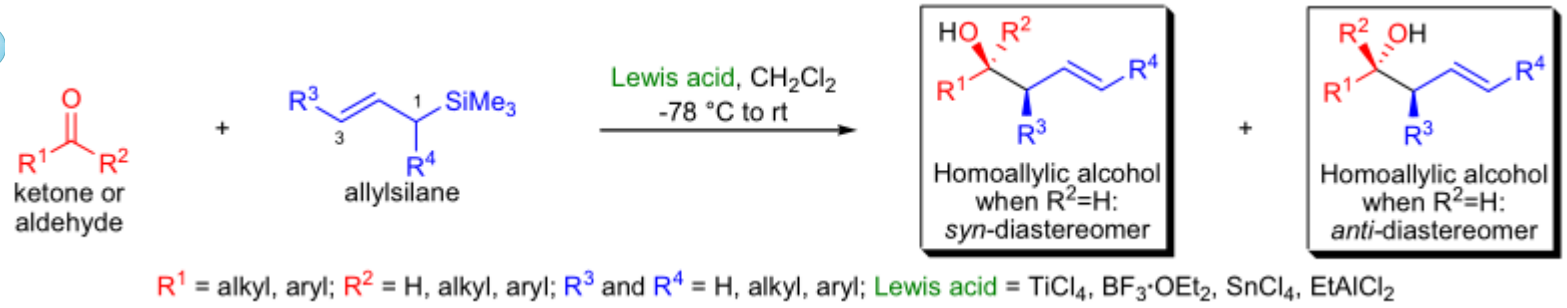
Propagation step:



Termination steps

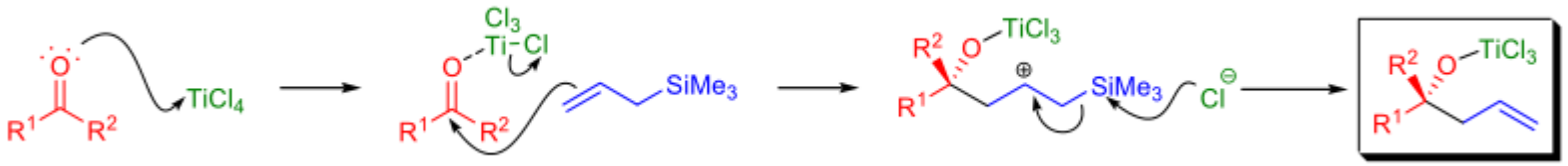


Sakurai allylation

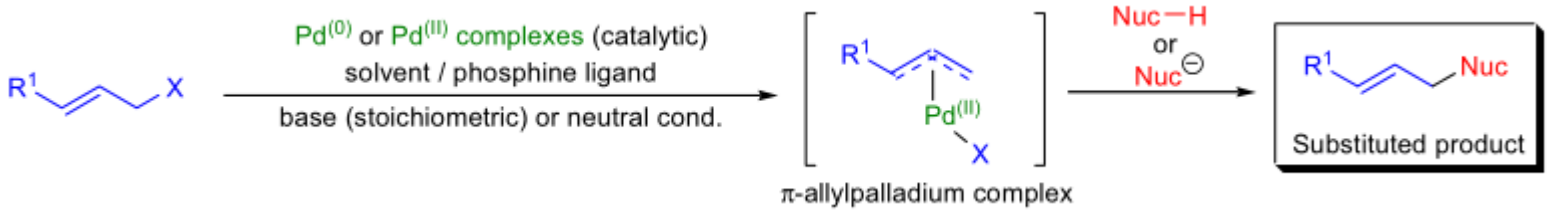


R^1 = alkyl, aryl; R^2 = H, alkyl, aryl; R^3 and R^4 = H, alkyl, aryl; Lewis acid = $TiCl_4$, $BF_3{\cdot}OEt_2$, $SnCl_4$, $EtAlCl_2$

Mechanism:



Tsuji-Trost reaction/allylation



Mechanism: