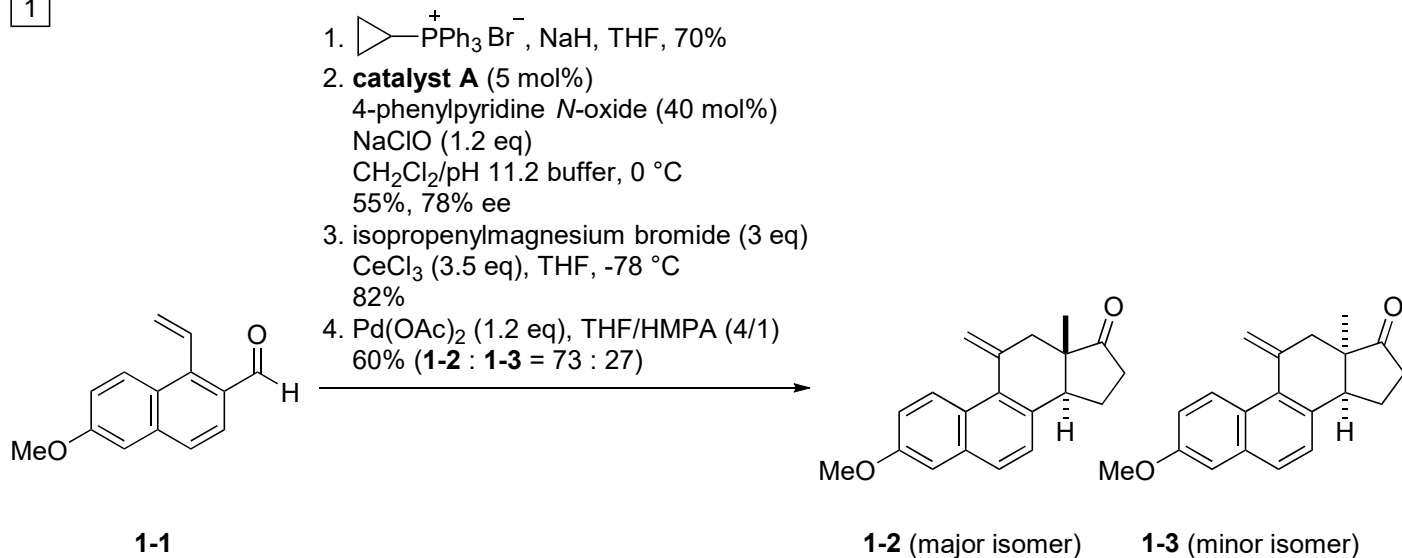


Problem Session (5) -Revised-

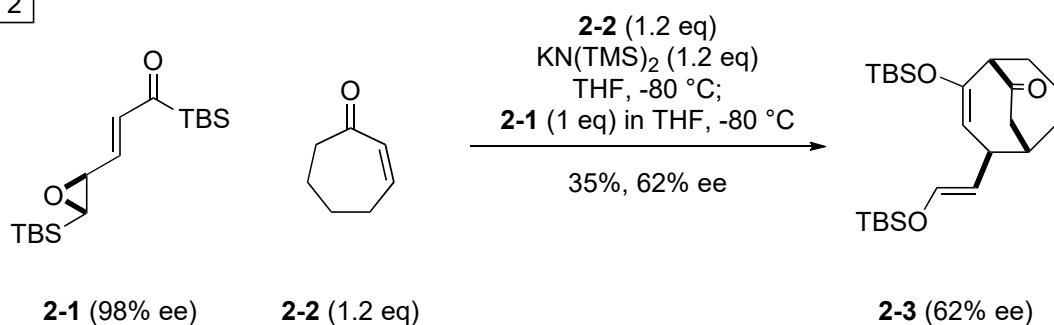
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Please provide the reaction mechanisms.

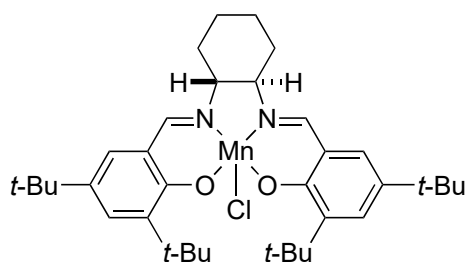
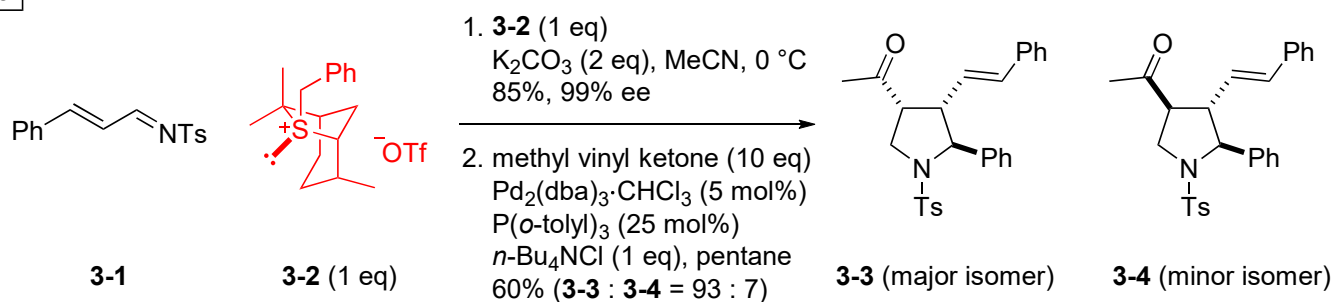
1



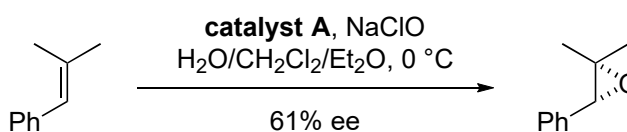
2



3



Hint:



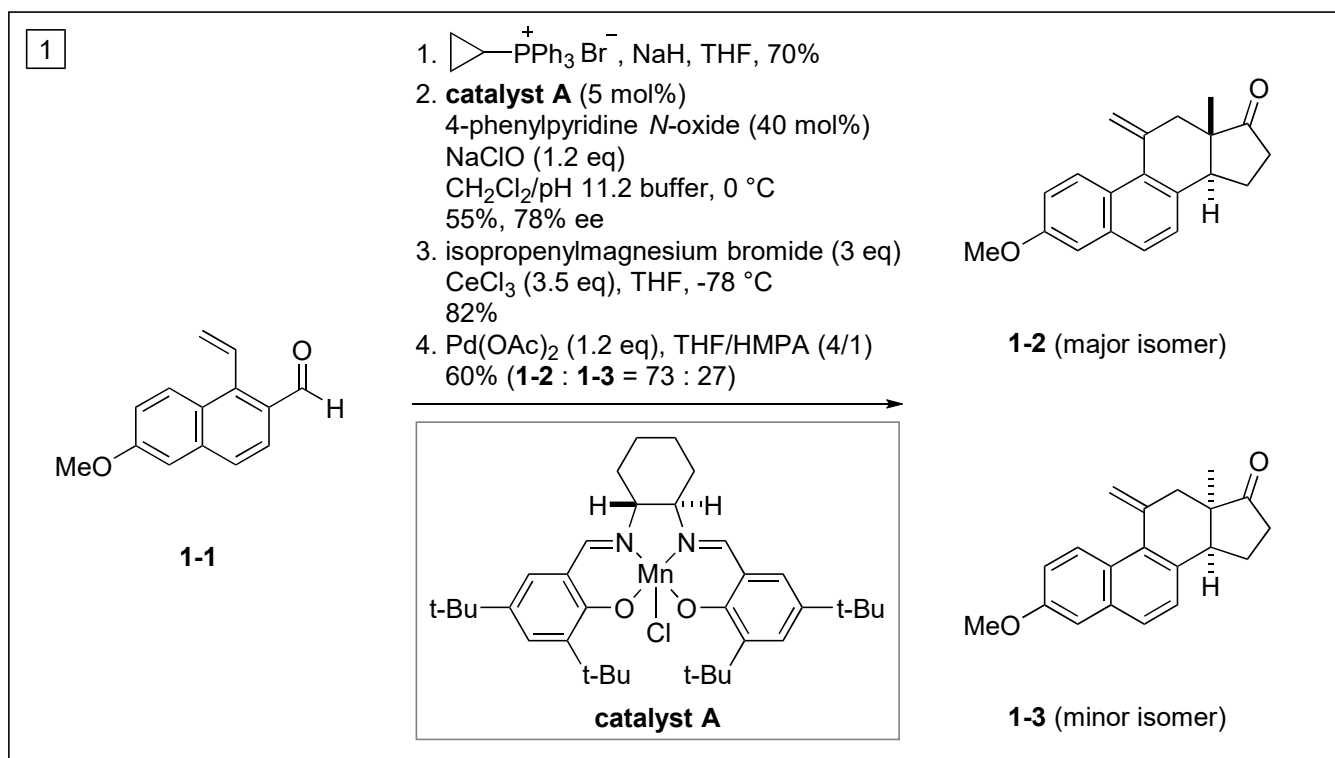
* The yield was not described in the paper.
J. Am. Chem. Soc. **2005**, *127*, 13672.

Problem Session (5) -Answer-

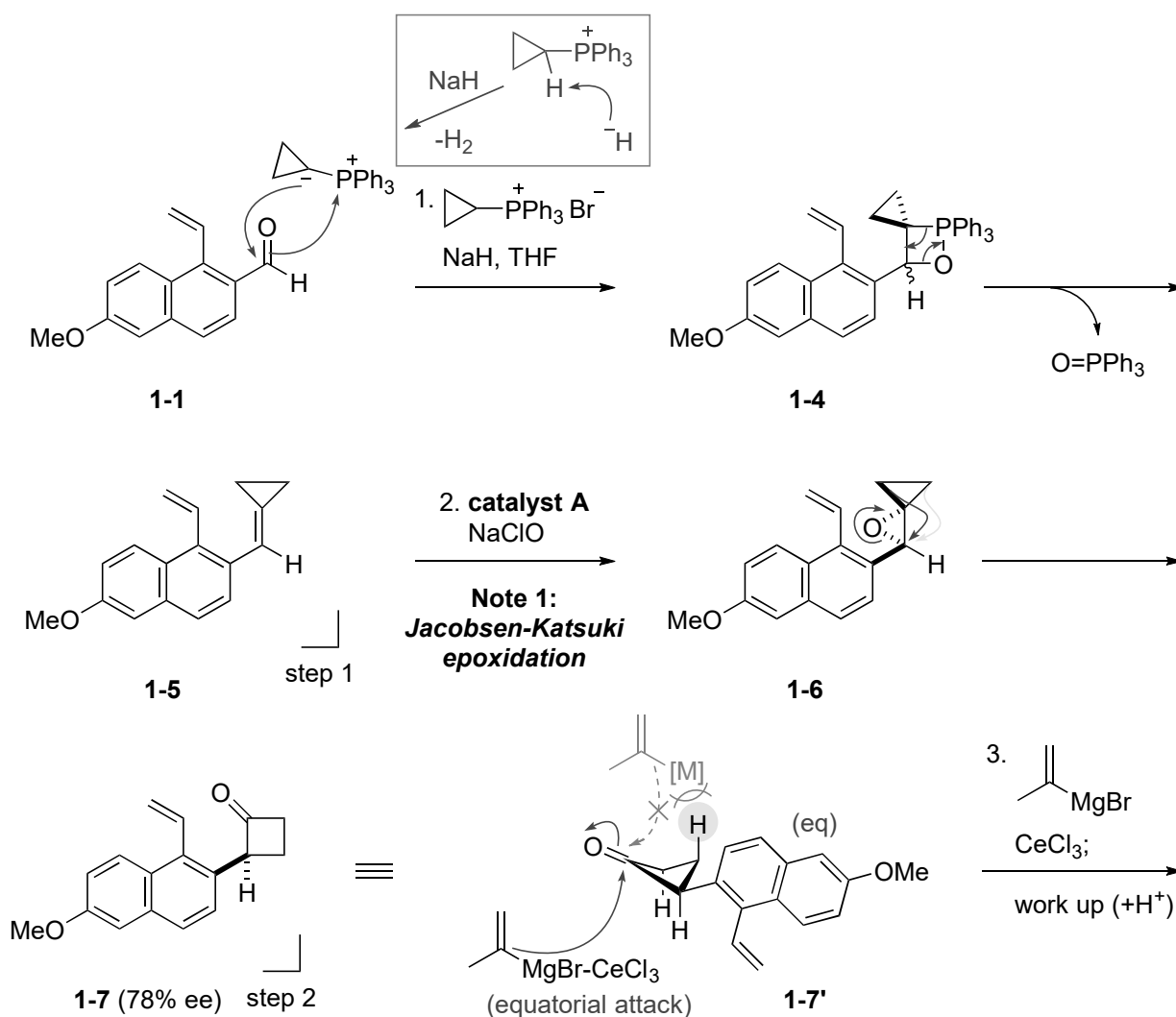
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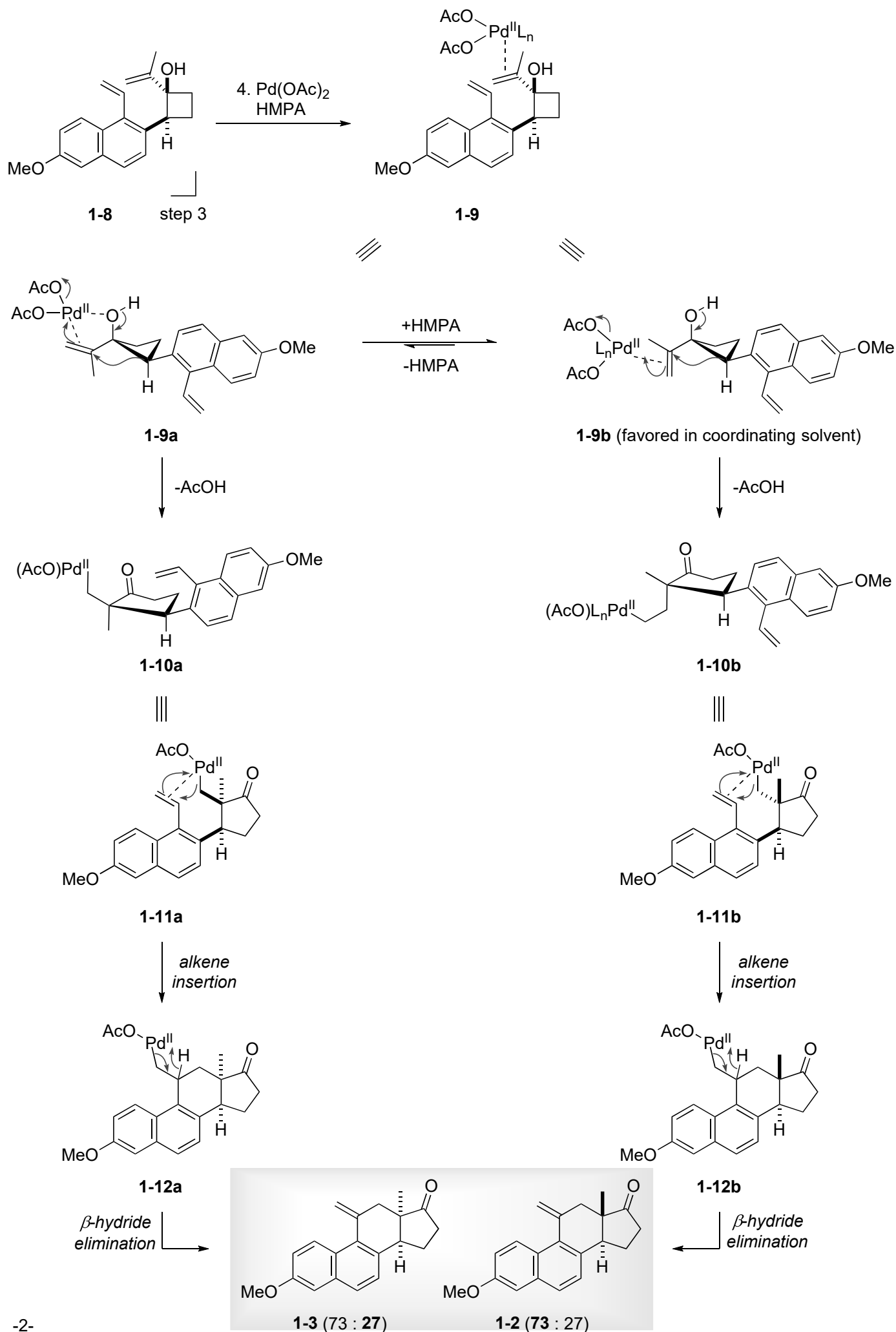
Topic: Chirality transfer from asymmetric epoxide/aziridine

Problem 1: Total synthesis of (+)-equilenin



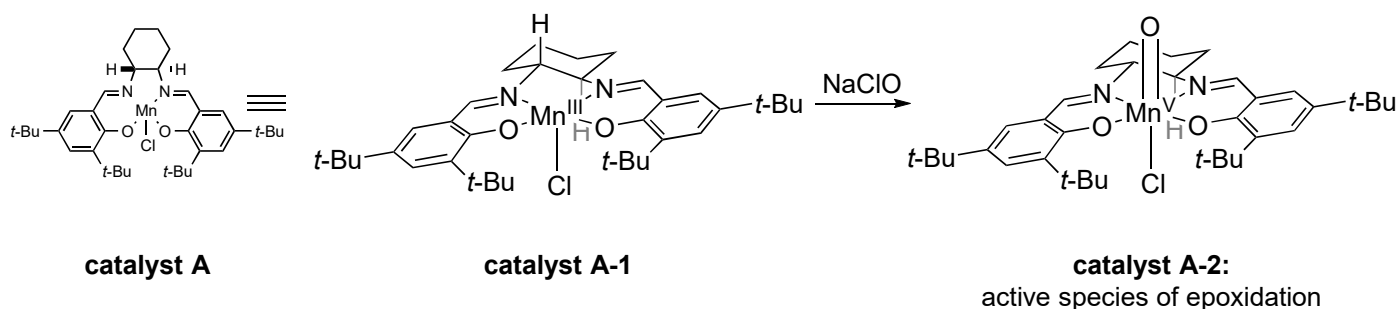
Nemoto, H.; Yoshida, M.; Fukumoto, K.; Ihara, M. *Tetrahedron. Lett.* **1999**, *40*, 907.
Yoshida, M.; Ismail, M. A.-H.; Nemoto, H.; Ihara, M. *J. Chem. Soc., Perkin Trans. 1*, **2000**, 2629.



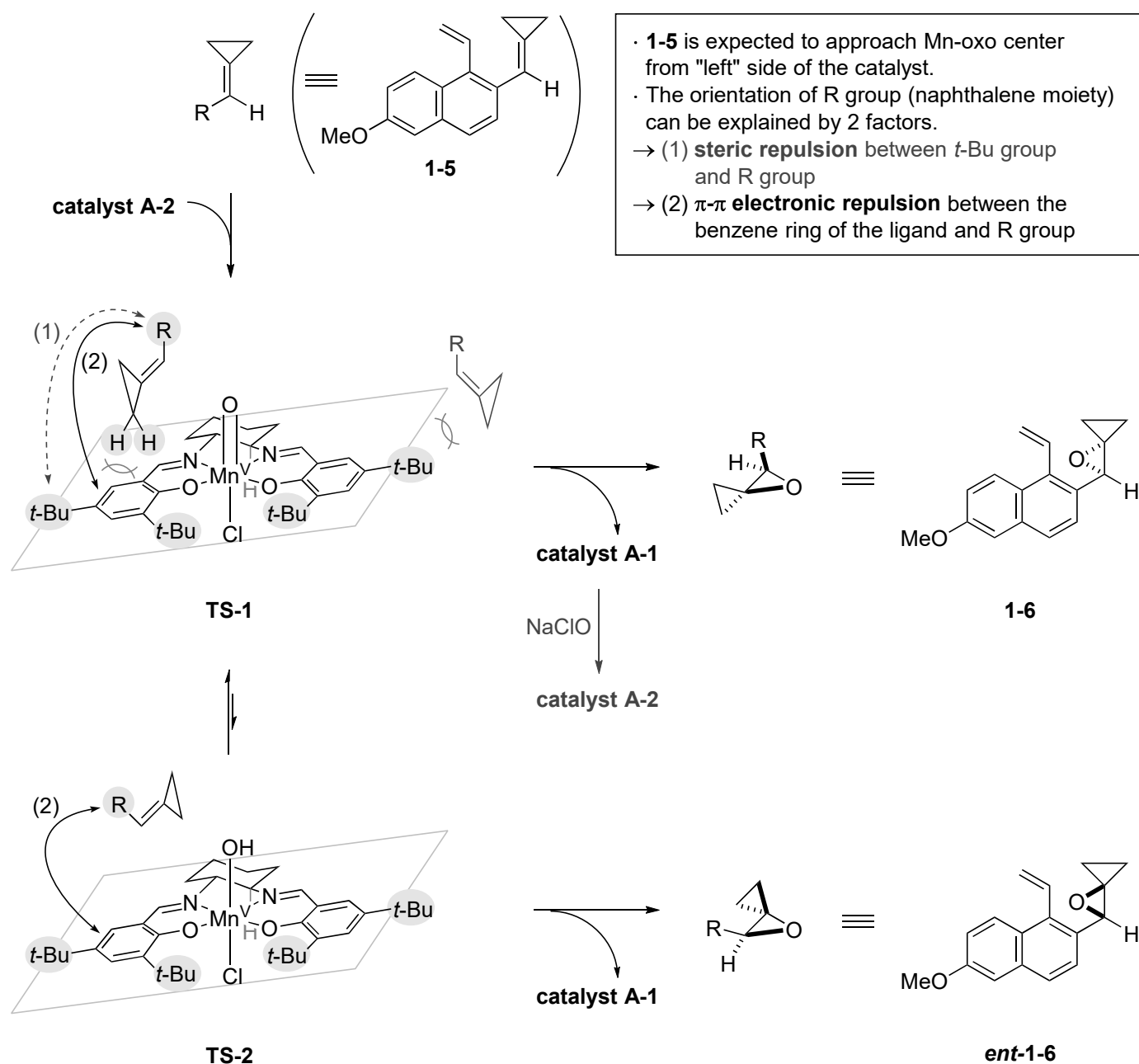


Note 1: Jacobsen-Katsuki epoxidation

1-1. The 3D-structure of catalyst A

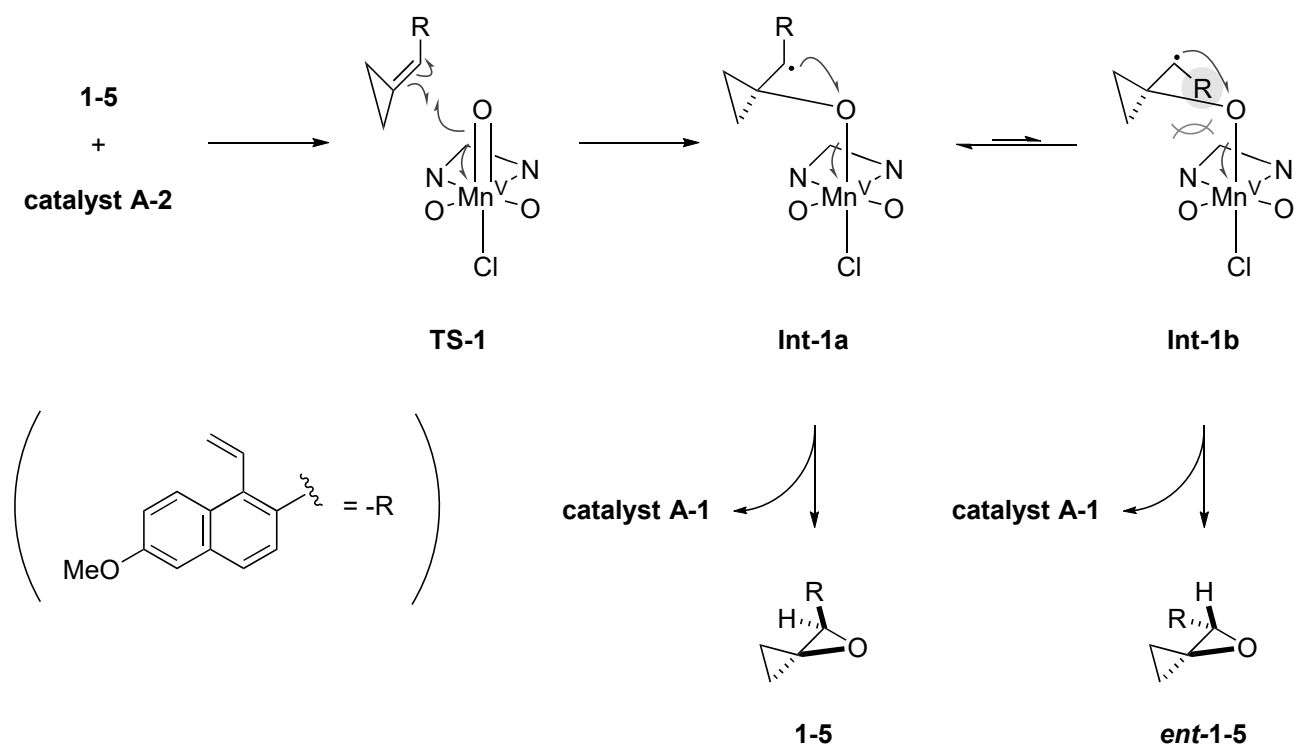


1-2. Facial selectivity of epoxidation of trisubstituted olefin **1-5**



Trisubstituted olefin **1-X** seems to suffer from steric repulsion between cyclopropyl group and *t*-Bu group.
→ **ent-1-5** was also produced via **TS-2** (78% ee, **1-6** : **ent-1-6** = 89 : 11).

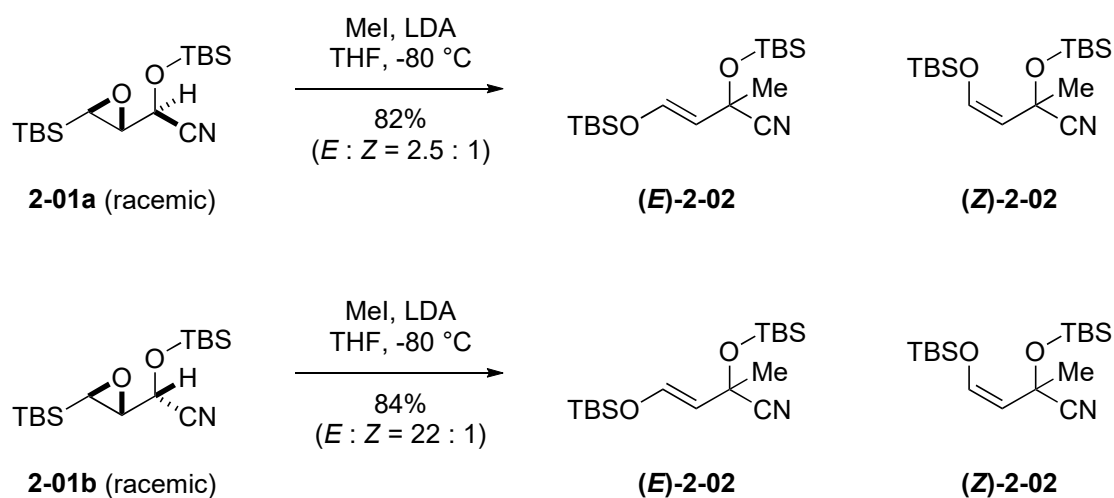
1-3. The mechanism of the oxygen transfer: radical pathway



The radical pathway is considered based on experimental results of isomerization. In **Int-1a** and **Int-1b**, the radical is generated at benzylic position and stabilized by R group, naphthalene moiety. * Aryl, alkenyl and alkynyl group are more suitable for R than alkyl group.

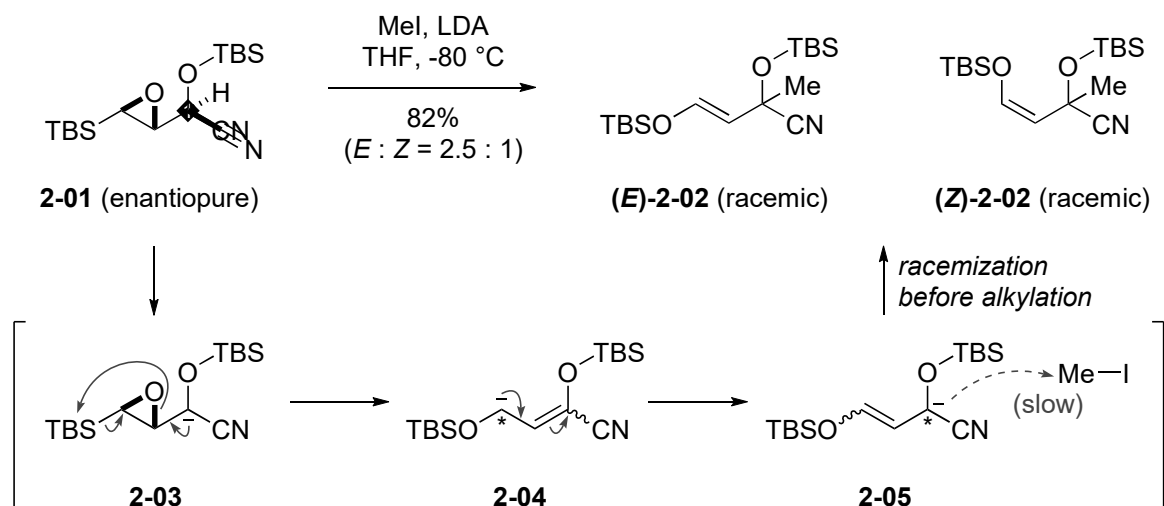
Problem 2: Asymmetric epoxysilane rearrangement investigated by Takeda

Research background of problem 2:

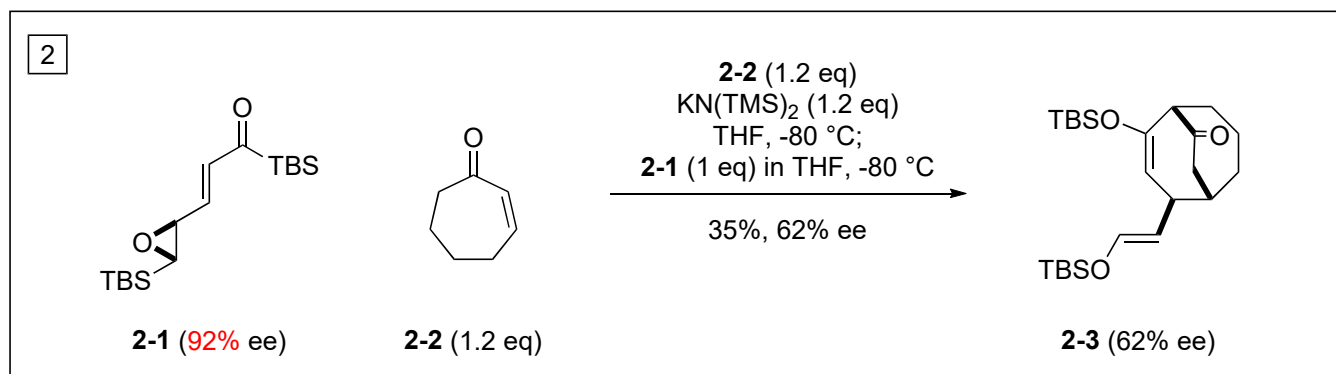
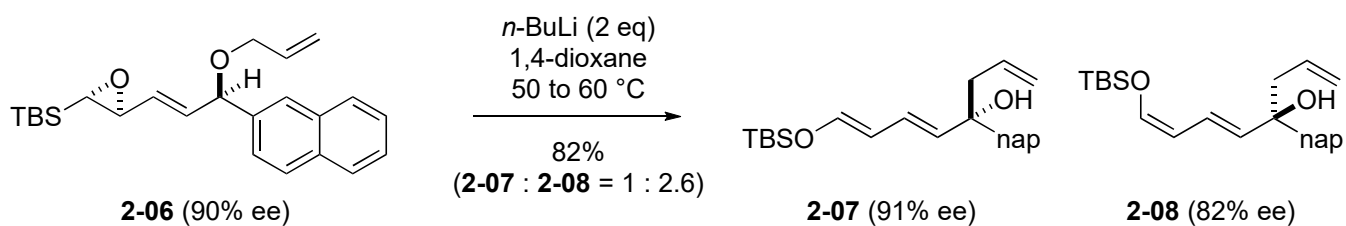


· E/Z ratio was changed between the reaction from **2-01a** and **2-01b**.
 · No methylated compound was obtained other than **2-02**.
 → All process (deprotonation ~ epoxide opening ~ alkylation) would occur in a concerted manner?

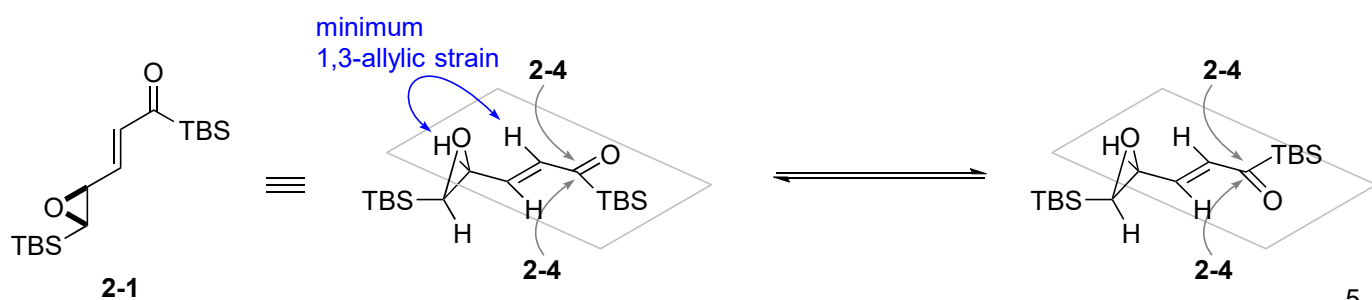
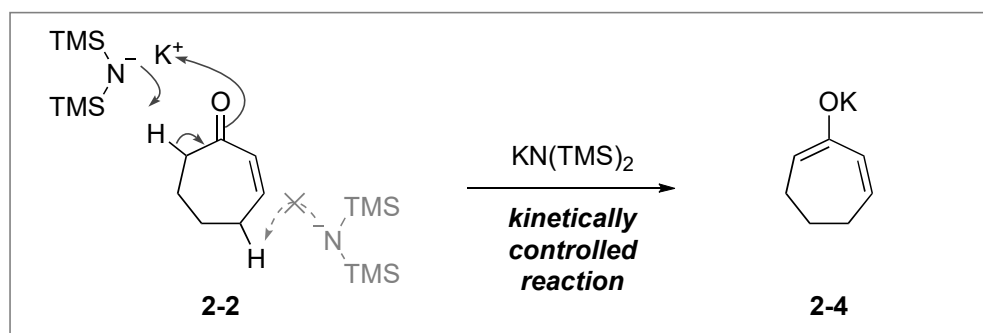
· Attempted trapping of chiral carboanion derived from enantiopure **2-01**

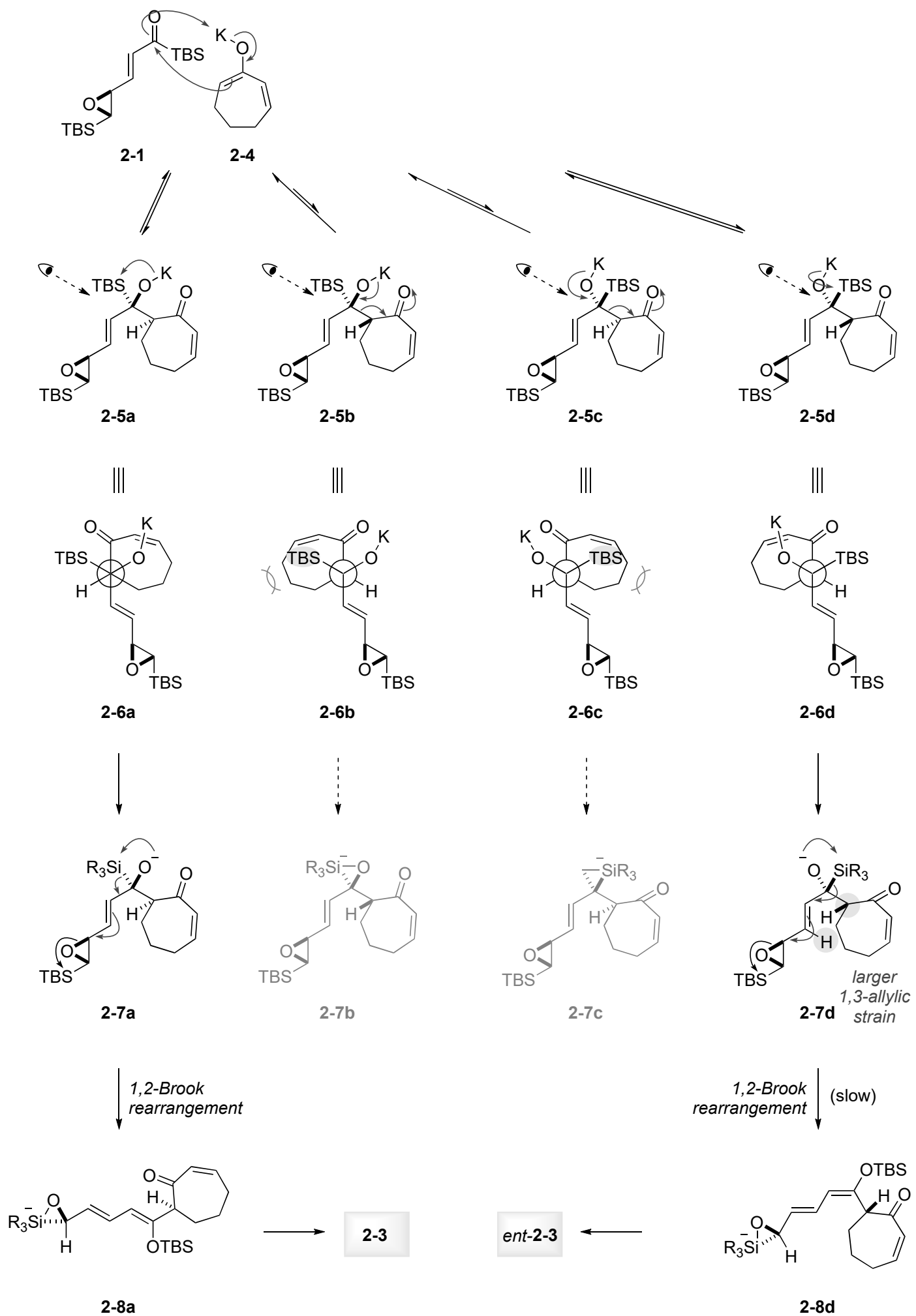


→ Trapping of chiral carboanion by intramolecular alkylation (2,3-Wittig rearrangement)

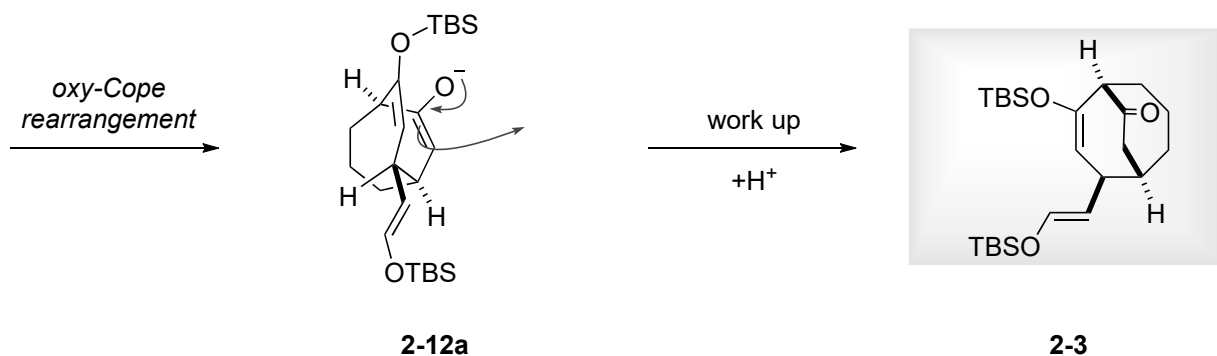
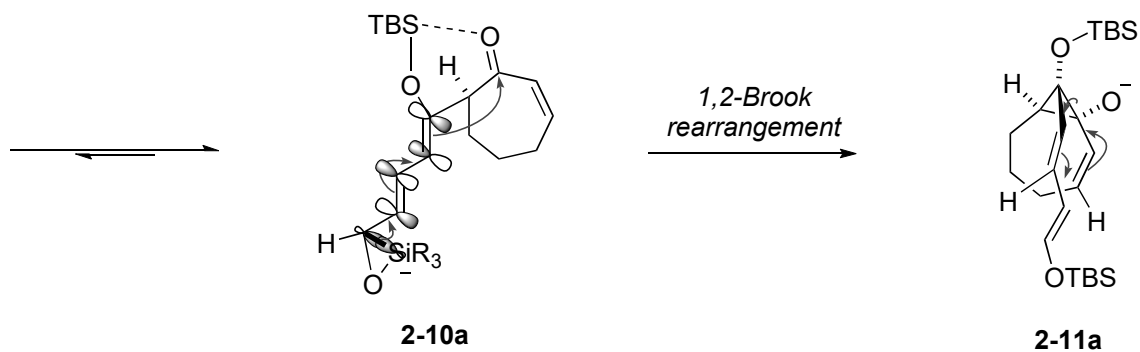
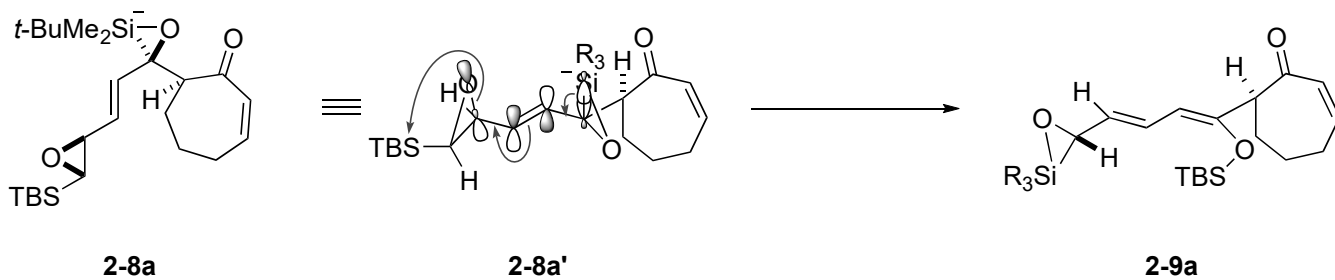


Nakai, Y.; Kawahata, M.; Yamaguchi, K.; Takeda, K. *J. Org. Chem.* **2007**, *72*, 1379.

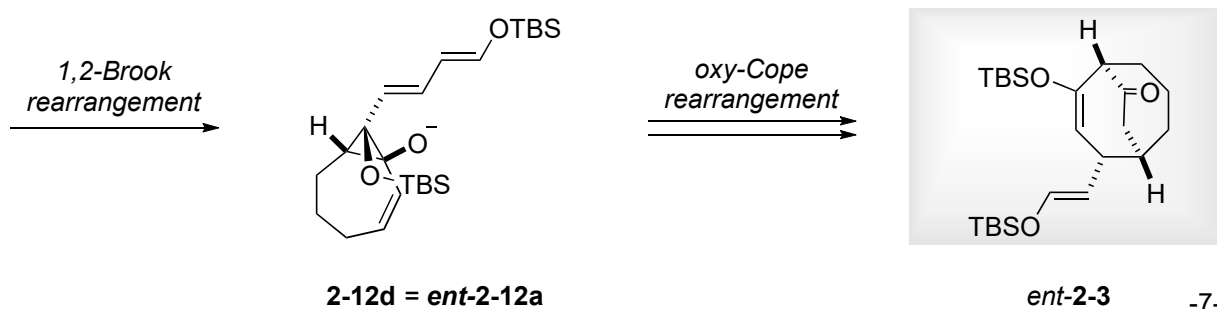
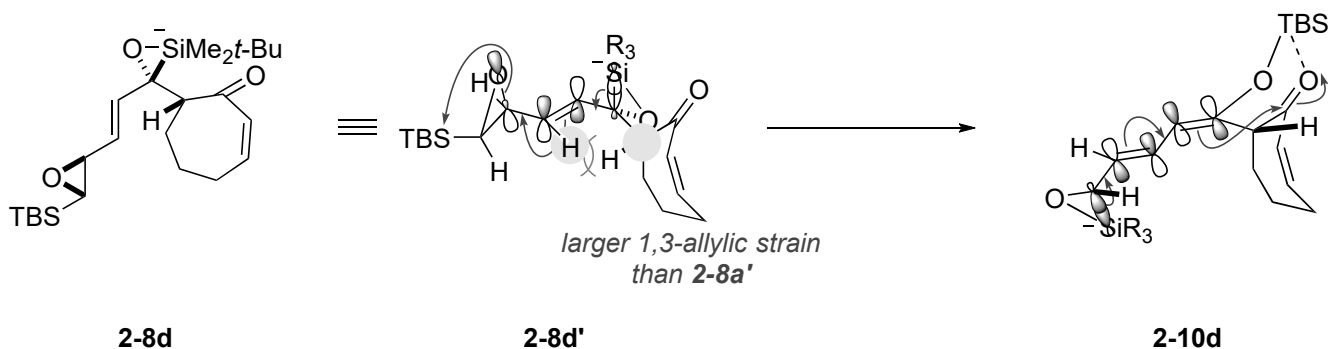




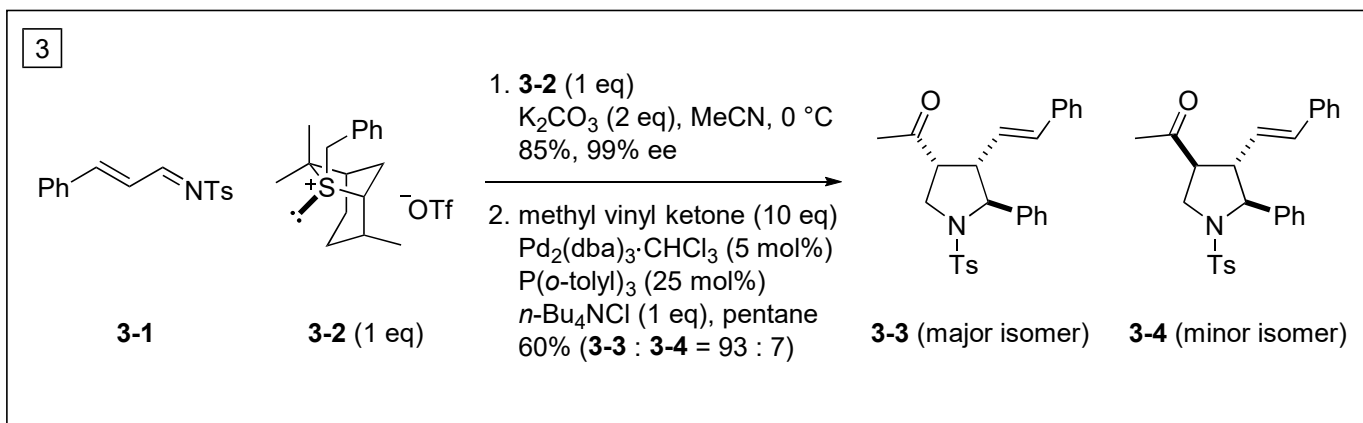
· From **2-8a**



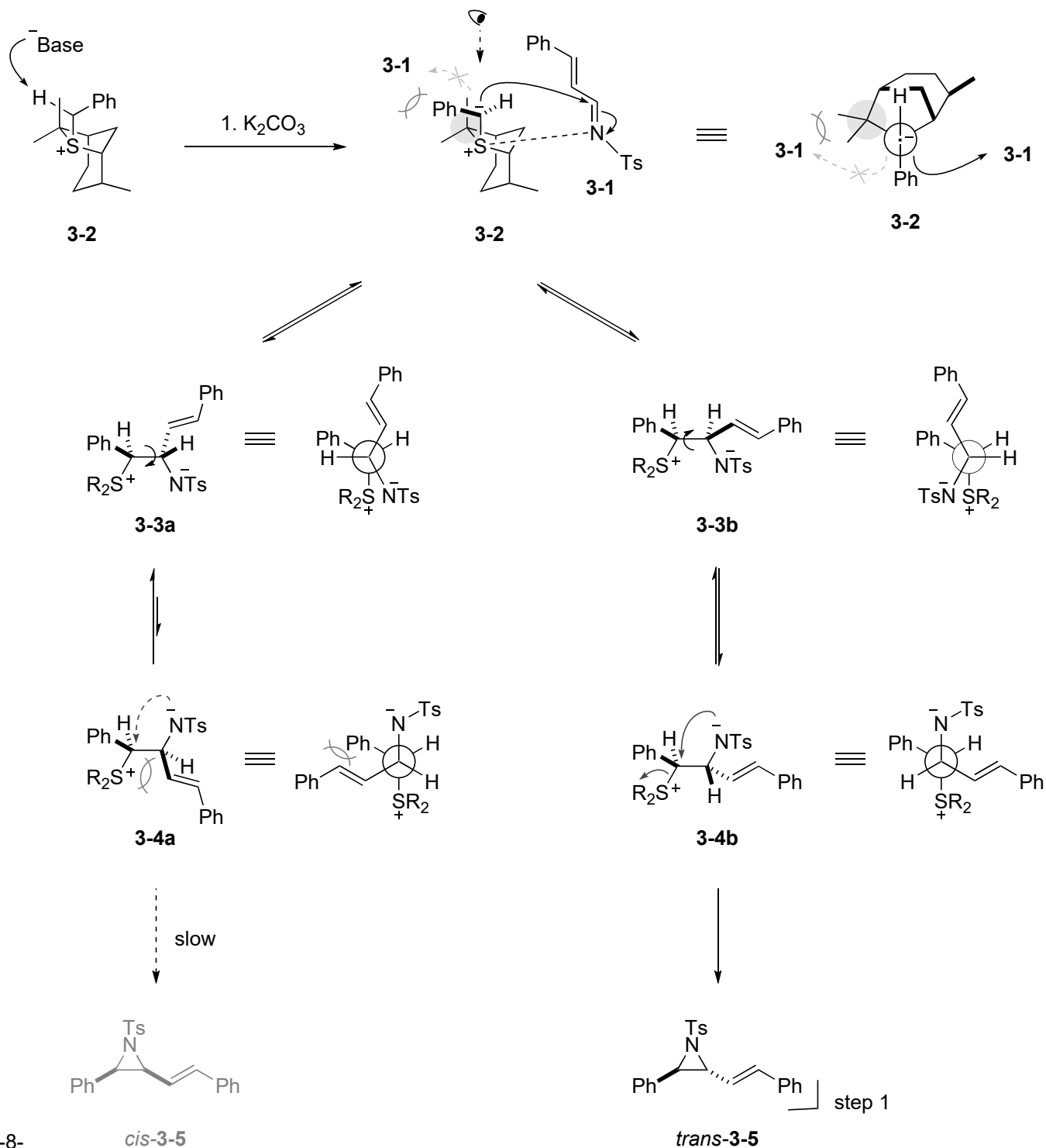
· From **2-8d**

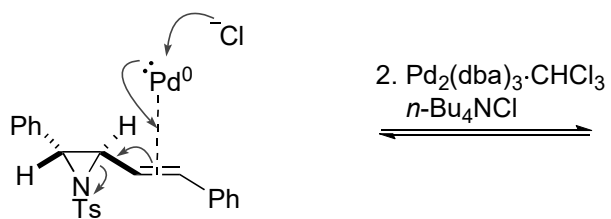


Problem 3: Total synthesis of (-)- α -kainic acid

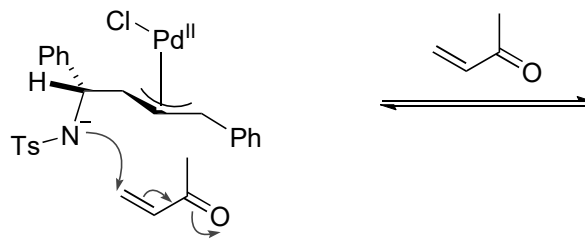


Lowe, A. M.; Ostovar, M.; Ferrini, S.; Chen, C. C.; Lawrence, P. G.; Fontana, F.; Calabrese, A. A.; Aggarwal, V. A. *Angew. Chem. Int. Ed.* **2011**, *50*, 6370.



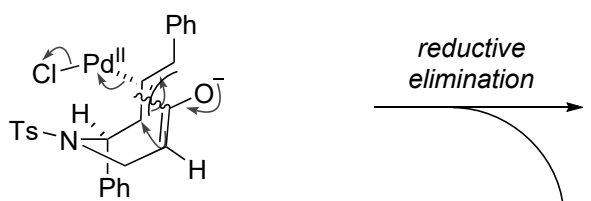


trans-3-5

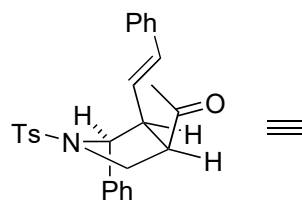


3-6

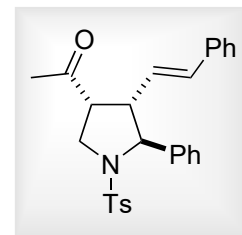
elolate: electron-rich
 π -allyl Pd complex: electron-poor



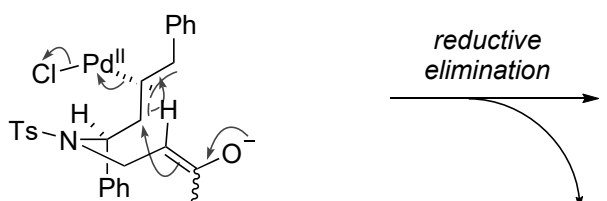
3-7



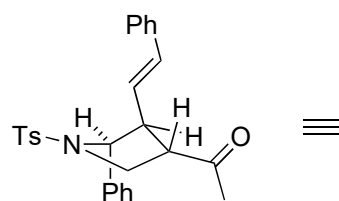
3-3



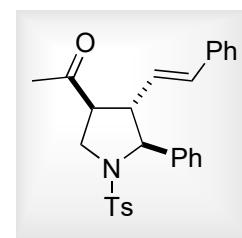
3-3 (93 : 7)



3-8



3-4



3-4 (93 : 7)