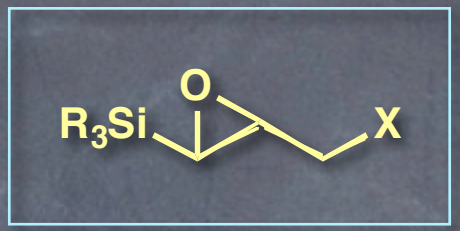
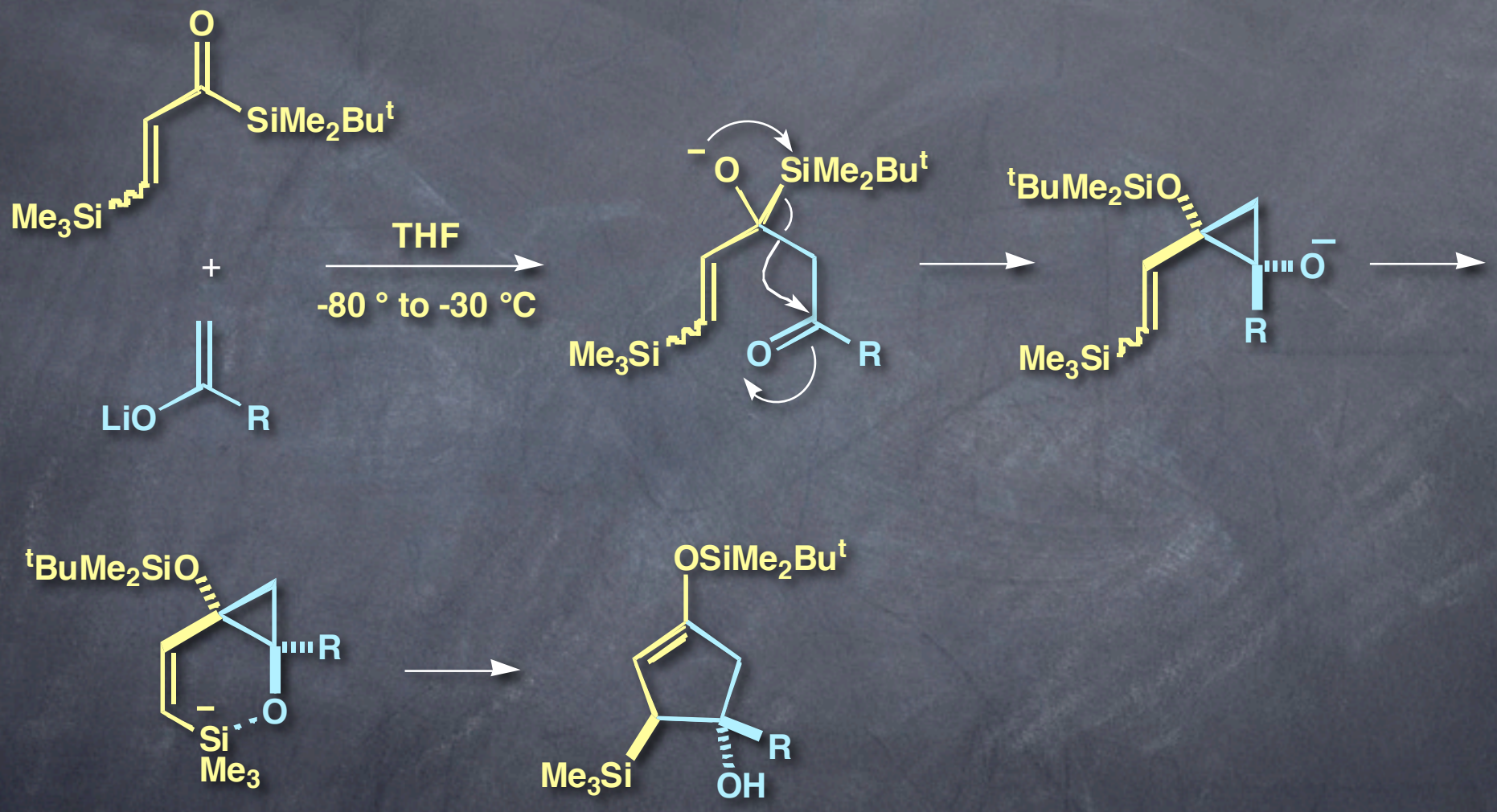
Reactions of Epoxysilanes



Use of a Trigger in Cascade-Type Reactions

Novel Use of Epoxide as a Chiral Source

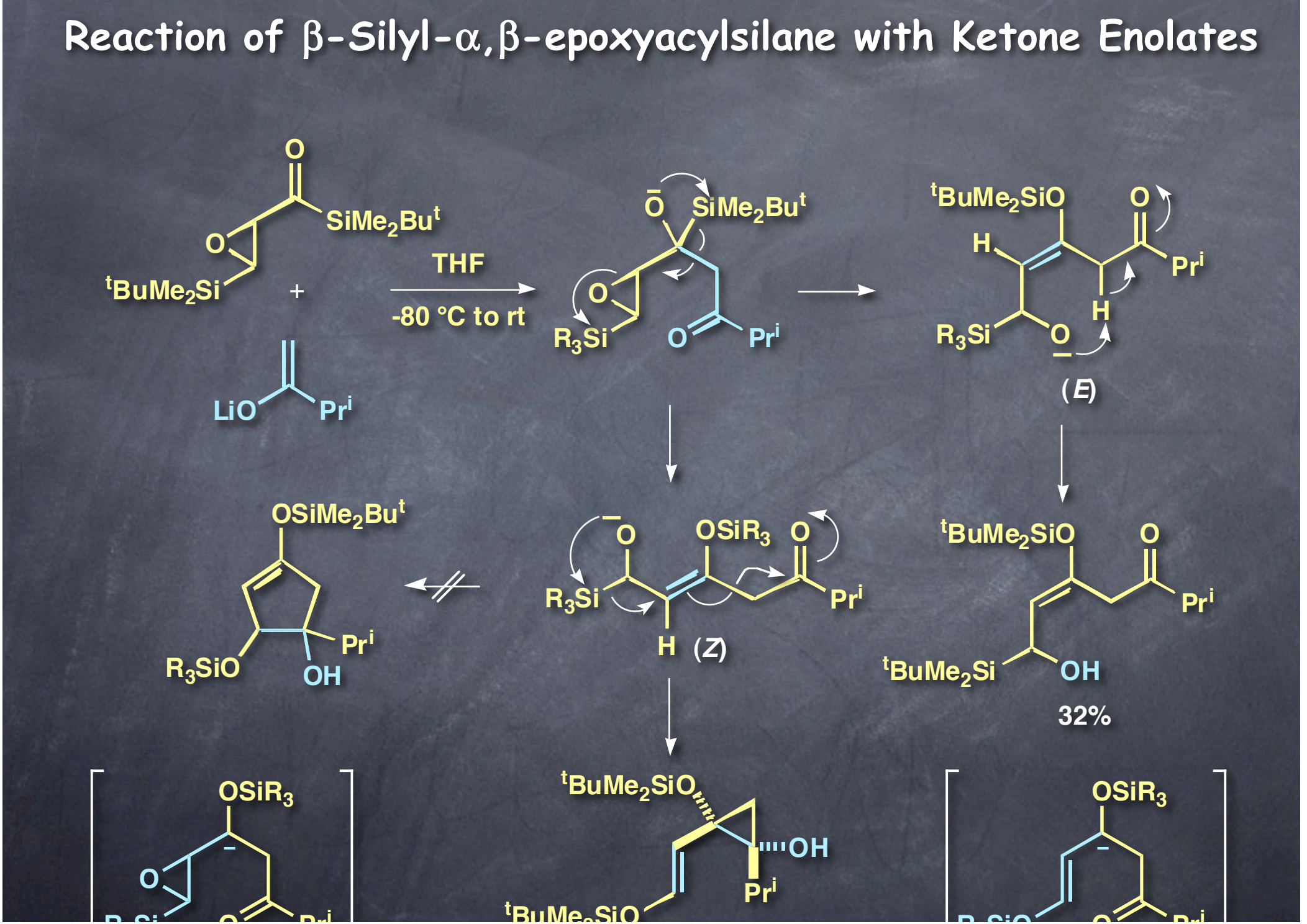
Brook Rearrangement-Mediated [3 + 2] Annulation



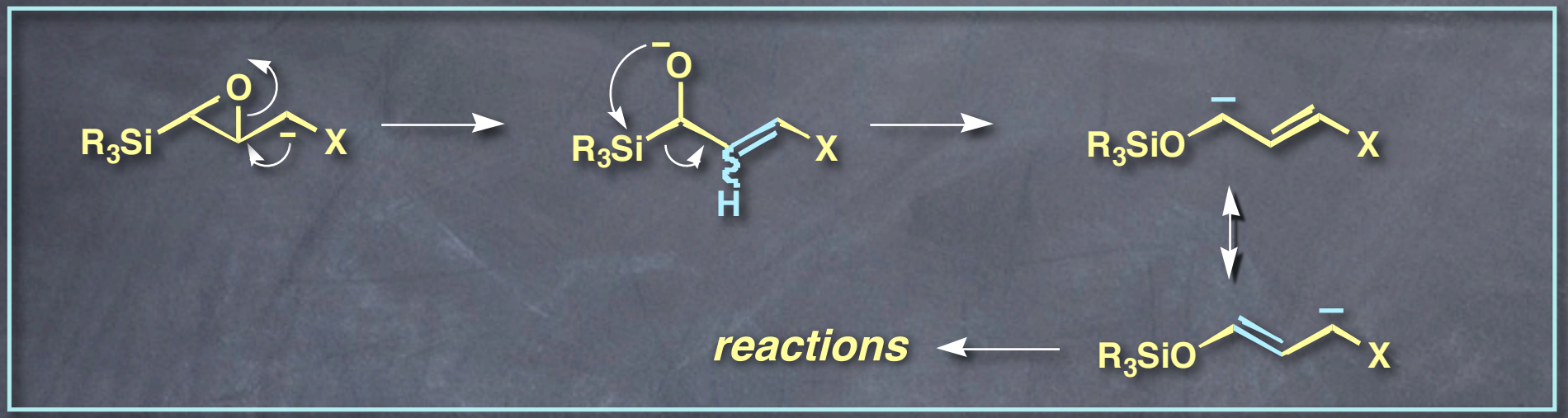
Takeda, K.; Fujisawa, M.; Makino, T.; Yoshii, E.; Yamaguchi, K. *J. Am. Chem. Soc.* **1993**, *115*, 9351-9352.

Extension of the [3 + 2] Annulation to Asymmetric Versions

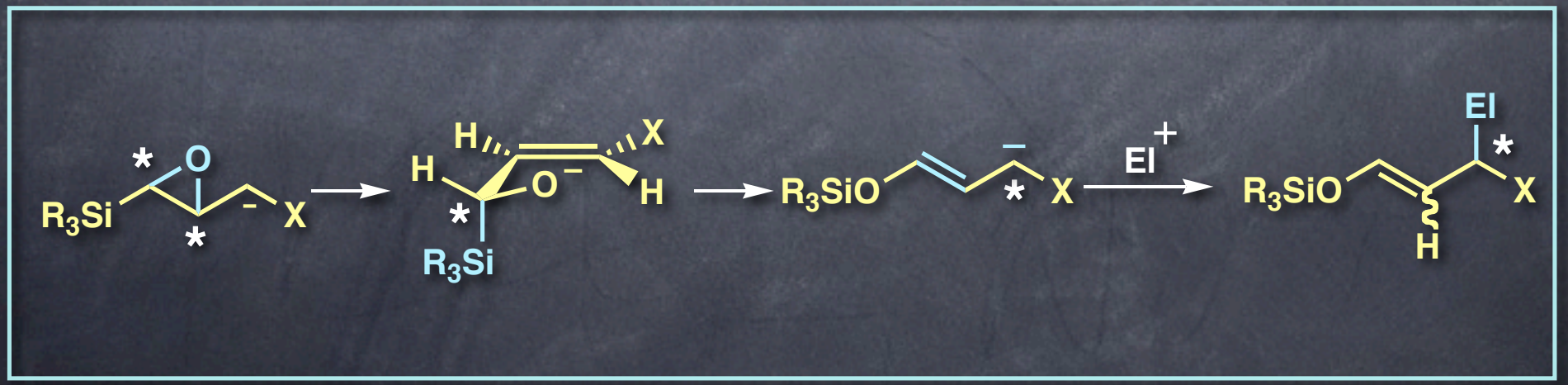
Reaction of β-Silyl-α,β-epoxyacylsilane with Ketone Enolates



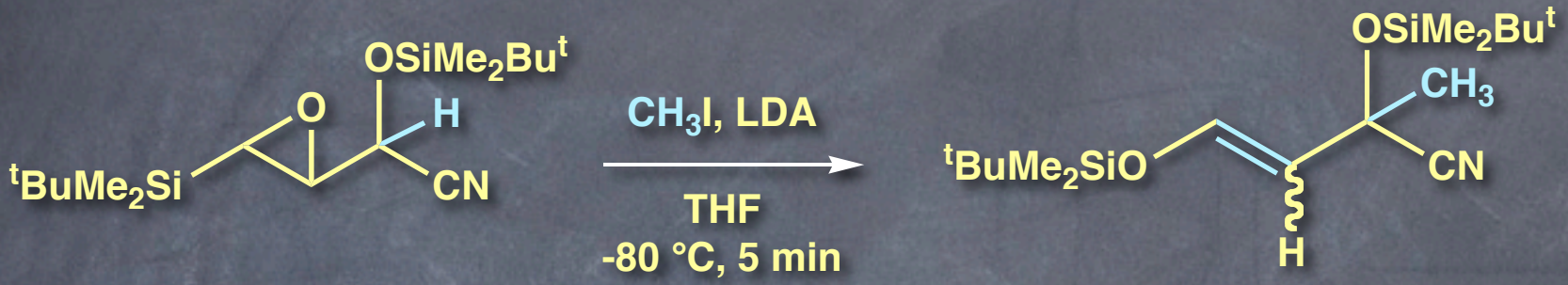
Epoxysilanes as an Efficient Trigger in Tandem Reactions

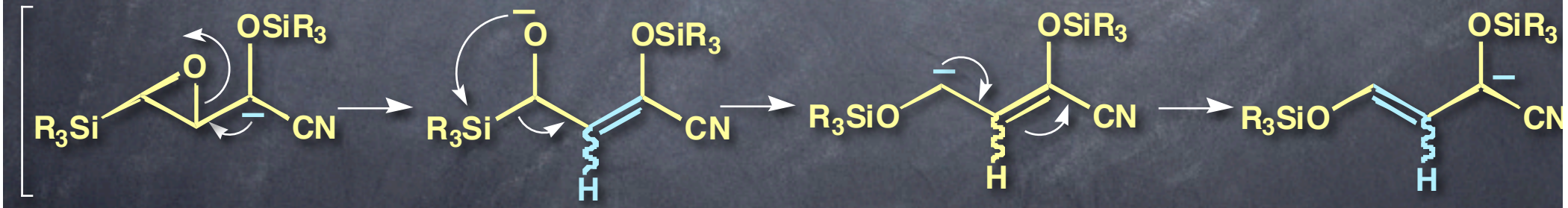


Novel Use of Epoxysilanes as a Chiral Source



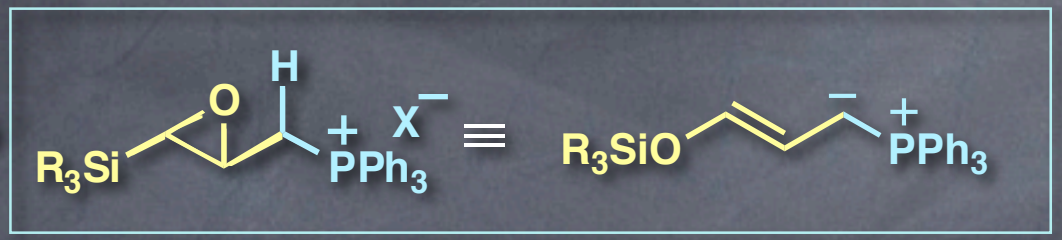
Alkylation of Metalated O-Protected Cyanohydrins of β-Silyl-α,β-epoxyaldehydes



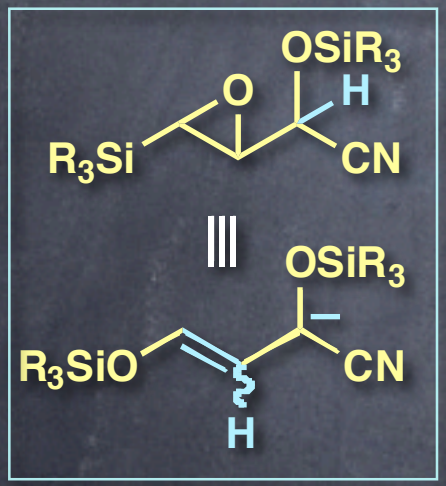


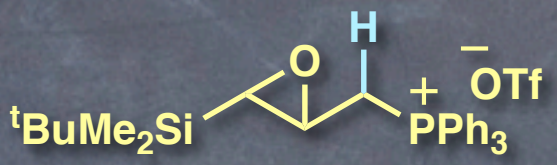
Kei Takeda, Eiji Kawanishi, Michiko Sasaki, Yuji Takahashi, Kentaro Yamaguchi *Org. Lett.* **2002**, 4, 1511-1514.
Michiko Sasaki, Eiji Kawanishi, Yoshio Nakai, Tatsuya Matsumoto, Kentaro Yamaguchi, Kei Takeda

Epoxysilanes as an Efficeint Trigger in Tandem Reactions (1)

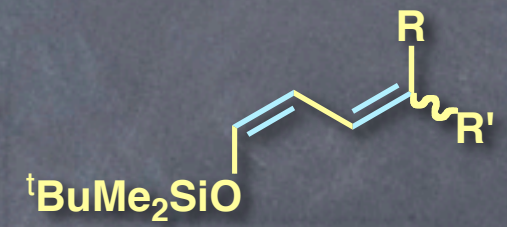


Wittig-type reactions





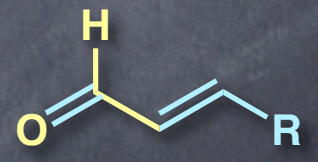
1. *n*-BuLi, THF
   -80 °C, 20 min
2. aldehyde (ketone)
   -80 ° to r.t.



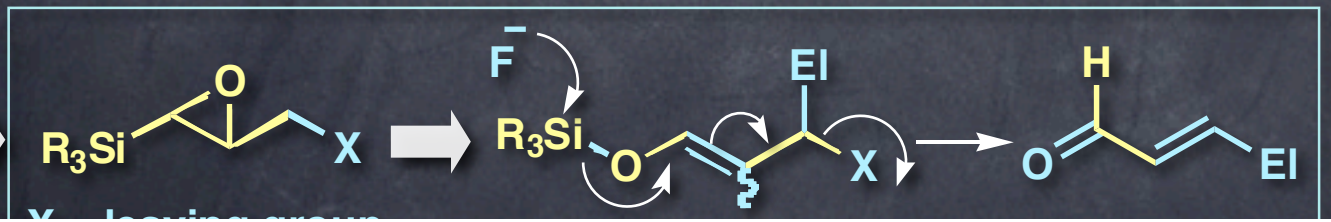
Michiko Sasaki, Mai Horai *unpublished result*

mp 76 °C

1. RX (1.0 eq)
   $NaN(SiMe_3)_2$ (1.0 eq)
   THF
2. *n*-Bu_4NF (1.0 eq)
   EtOH (3.0 eq)

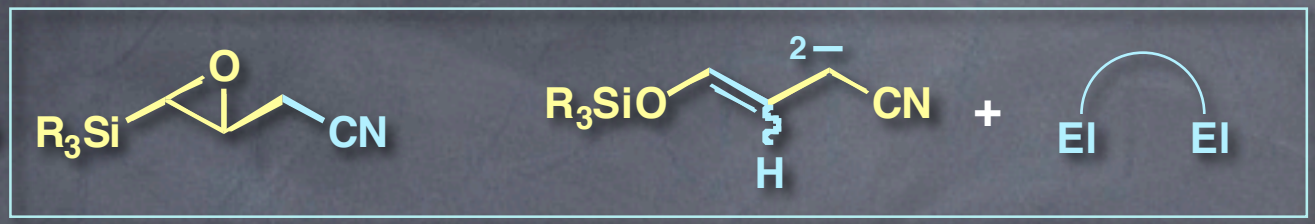


Michiko Sasaki *Org. Lett.* **2004**, *6*, 4849-485

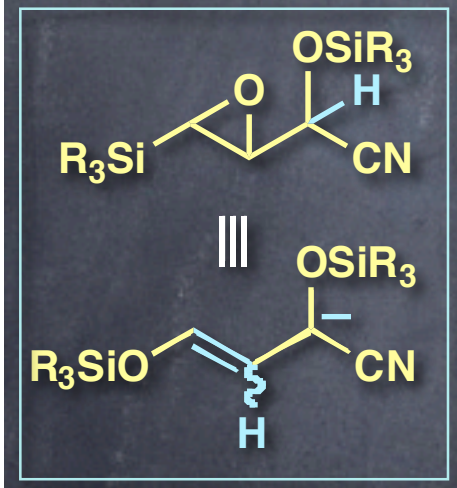


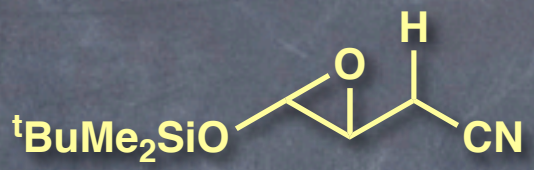
acrolein β-anion equivalent

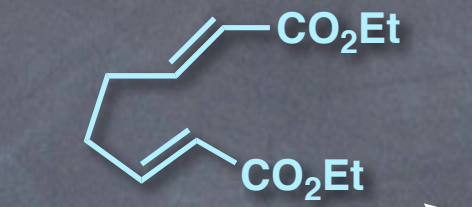
Epoxysilanes as an Efficeint Trigger in Tandem Reactions (2)



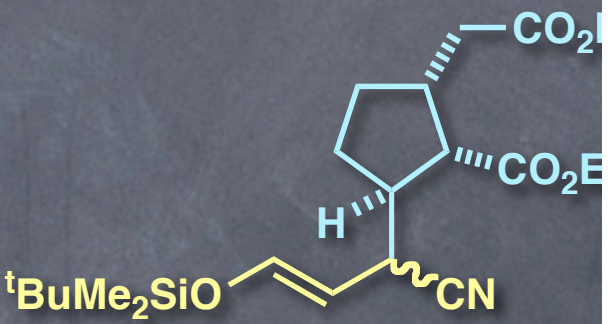
Reactions with bis-electrophiles



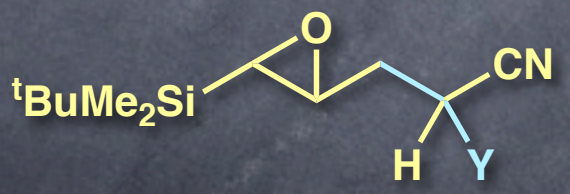




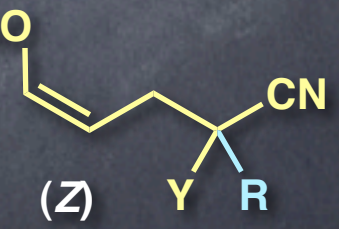
$NaN(SiMe_3)_2$ (1.0 eq)
THF, HMPA
-98 °C



Tatsuya Matsumoto *Org. Lett.* **2004**, ***6***, 4367-4369.

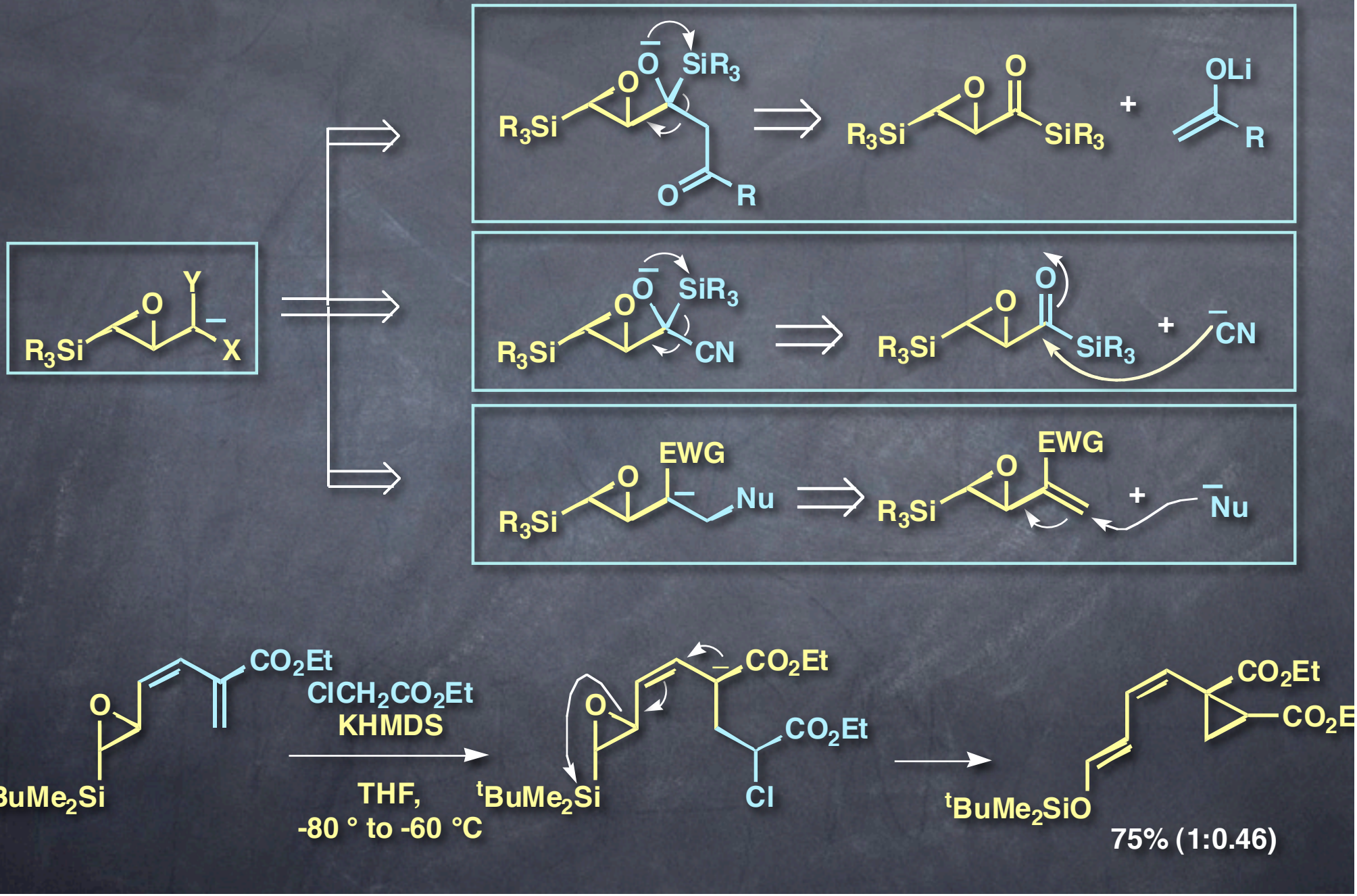


1. $NaN(SiMe_3)_2$
   THF, -30 ° to 5 °C
2. RX

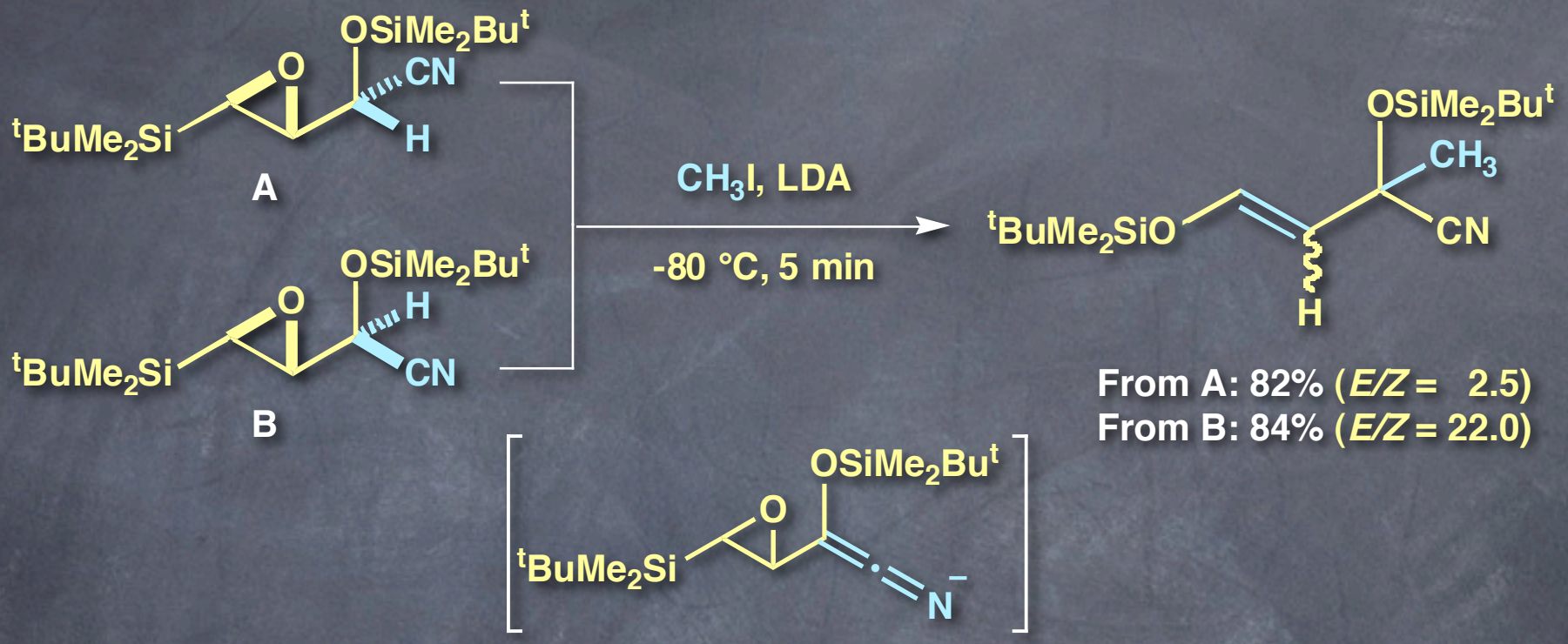


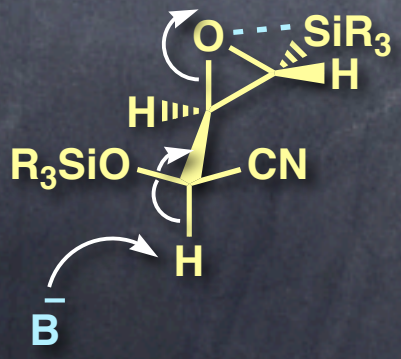
Seigo Okugawa *Org. Lett.* **2004**, *6*, 2973-2975. (31-0609).

Epoxysilanes as an Efficient Trigger in Tandem Reactions (3)

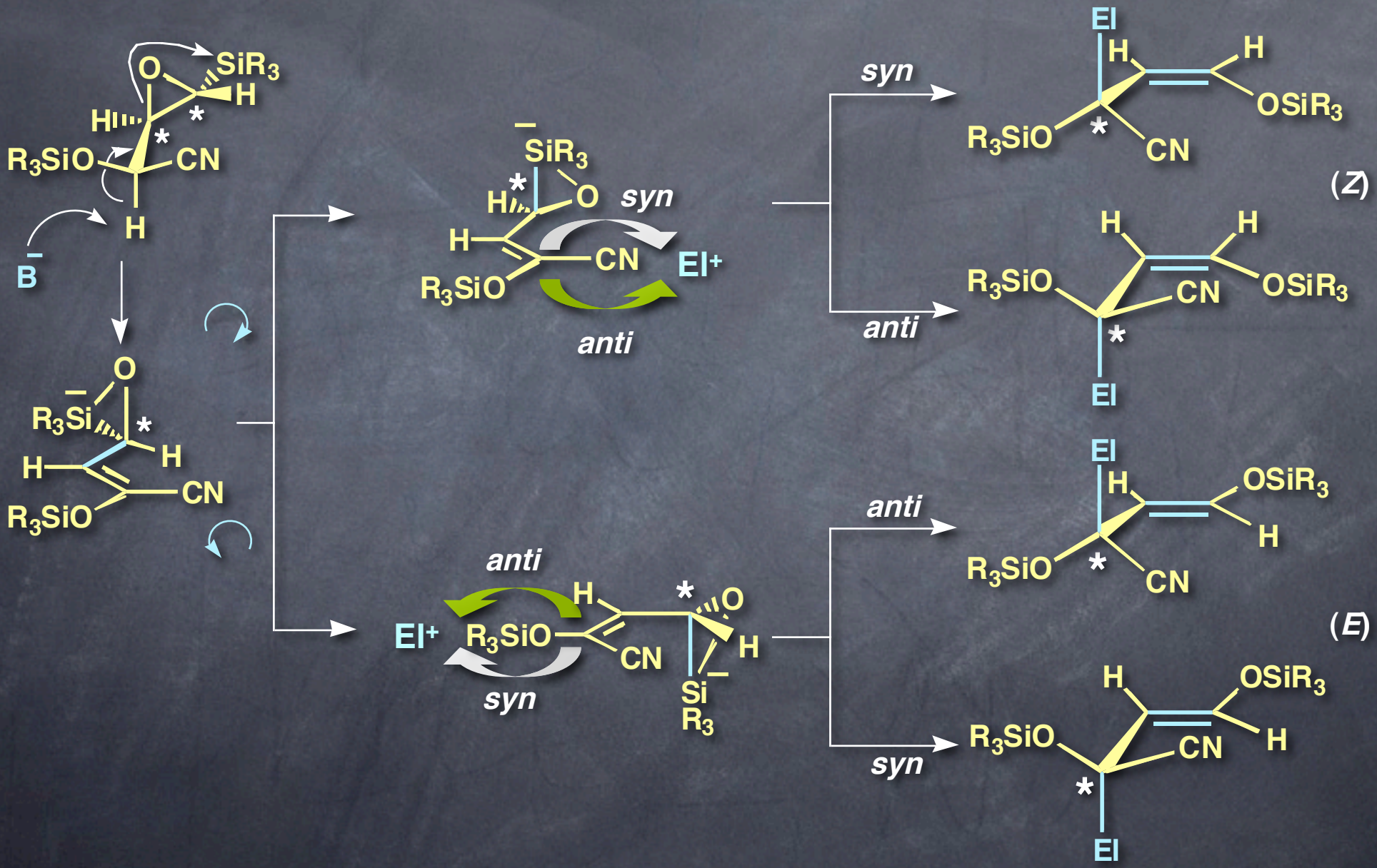


A Novel Use of Epoxysilanes as a Chiral Source (1)

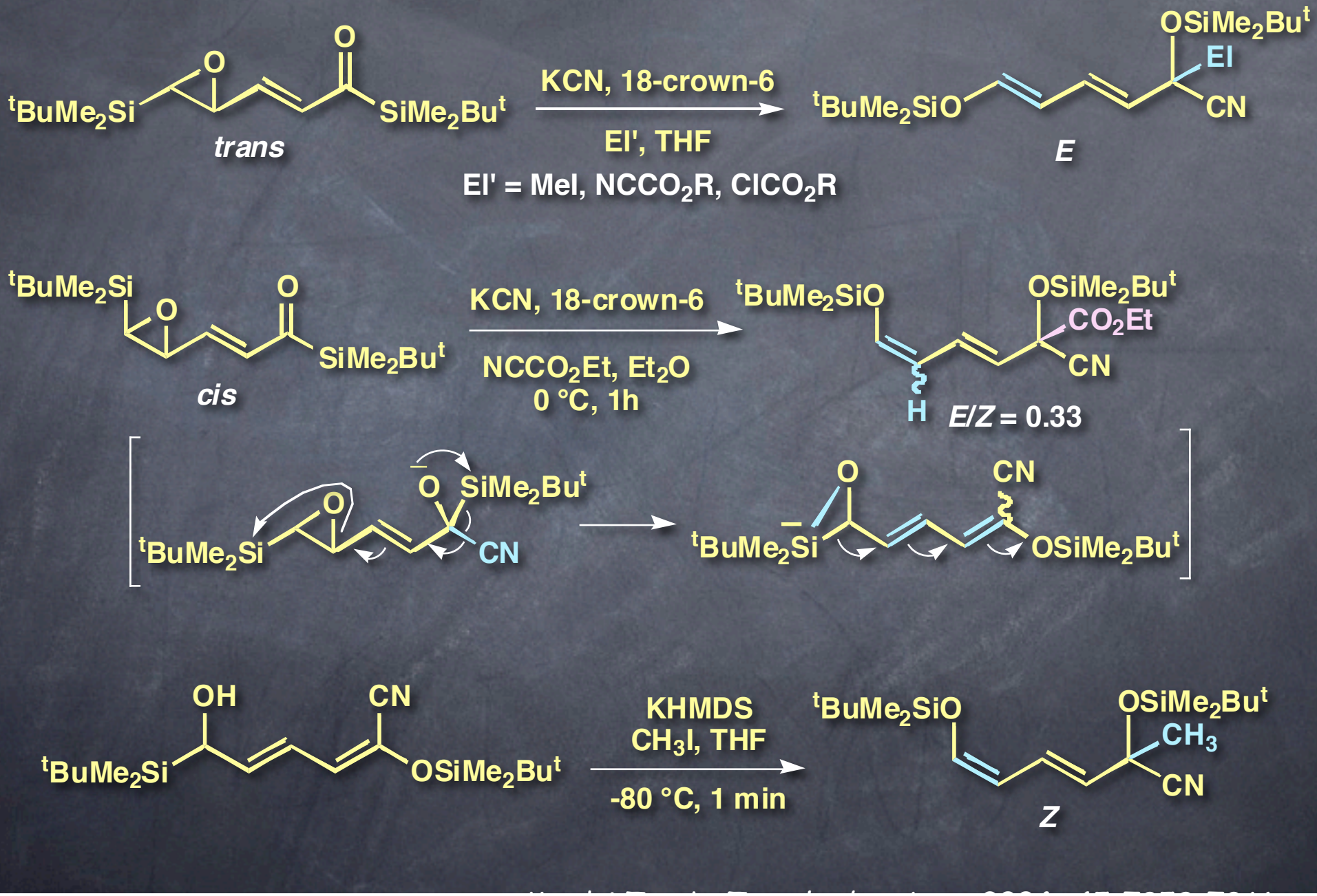




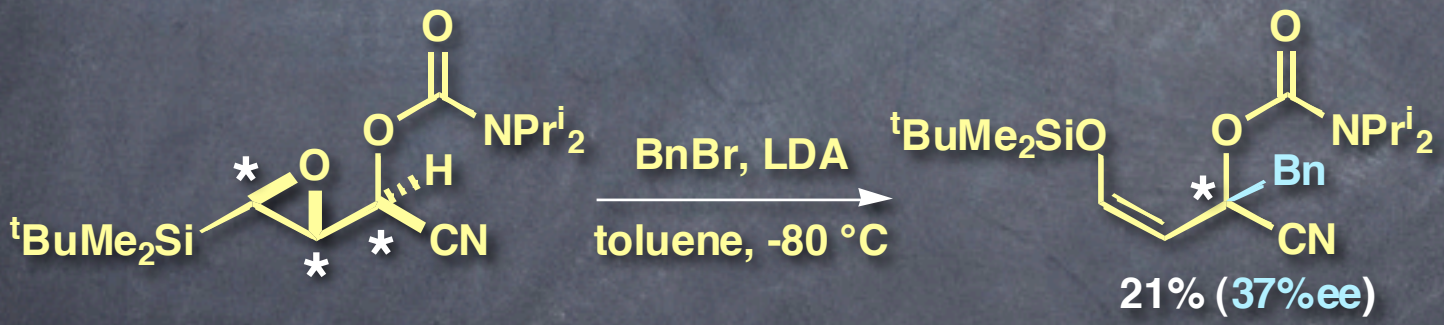
A Novel Use of Epoxysilanes as a Chiral Source (2)

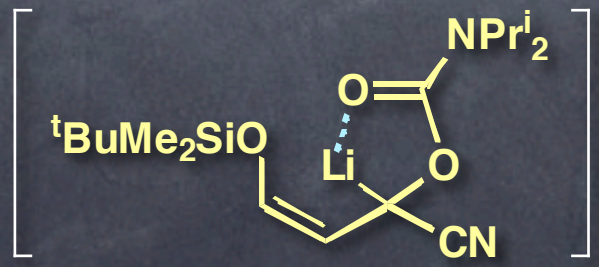


A Novel Use of Epoxysilanes as a Chiral Source (3)

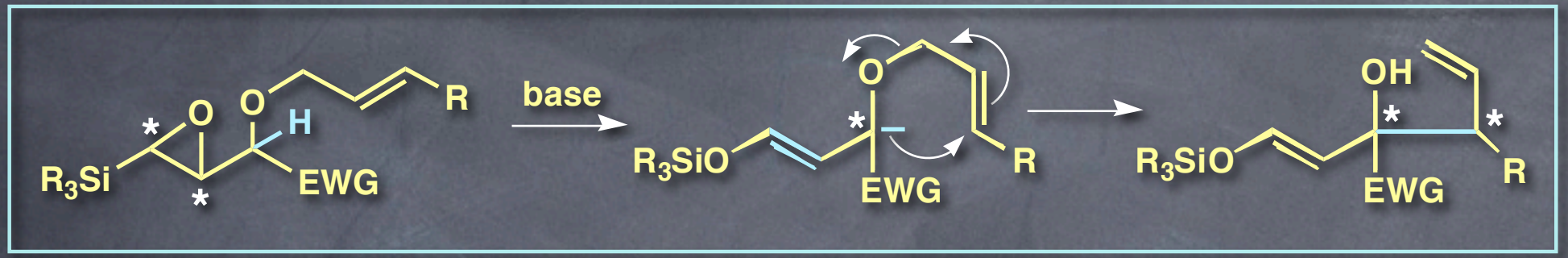


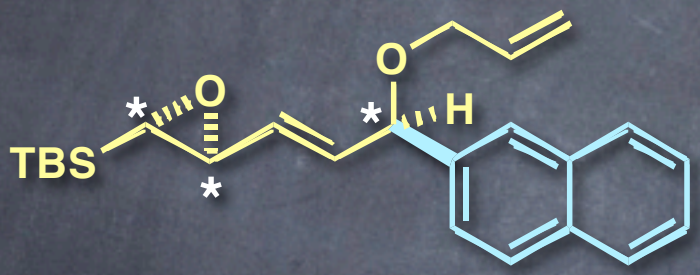
Chirality Transfer of Epoxides to Carbanions





Intramolecular Trapping of Chiral Cabanions by an Electrophile (1)



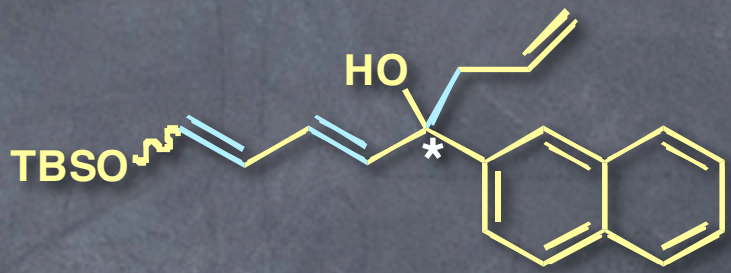


A (90%ee)

n-BuLi (1.5 eq)

Et_2O (0.076M)

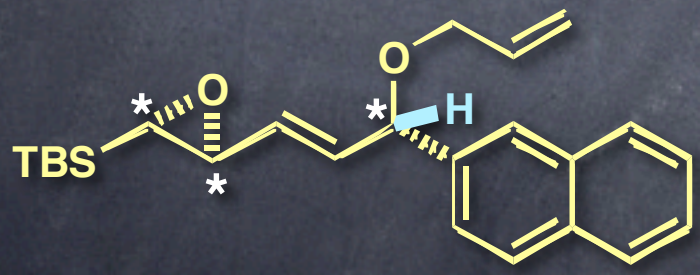
27 ° to 30 °C, 7 min



B (70% (*E*/*Z* = 0.19))

(*E*) 81%ee (90%ee)

(*Z*) 73%ee (81%ee)

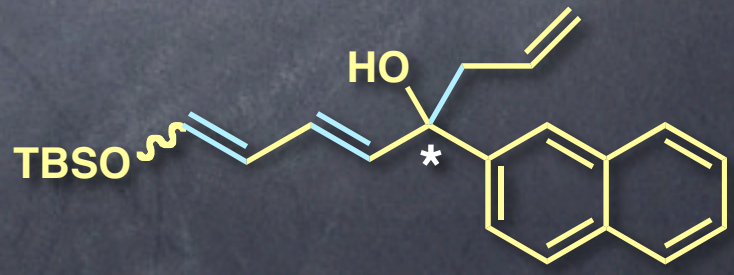


A' (90%ee)

n-BuLi (1.5 eq)

Et_2O (0.076M)

27 ° to 30 °C, 7 min

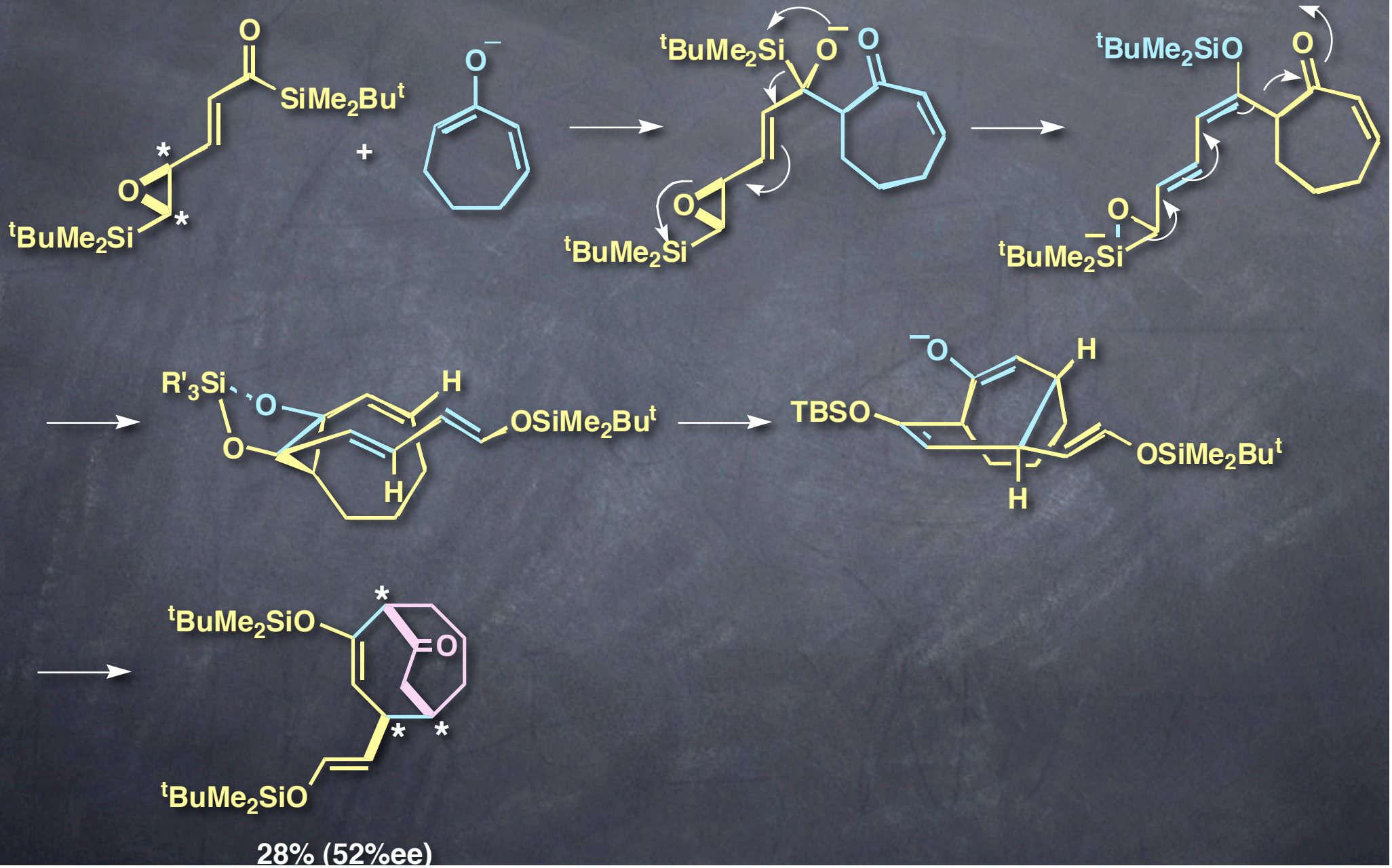


ent-B (77% (*E*/*Z* = 2.2))

(*E*) 81%ee (90%ee)

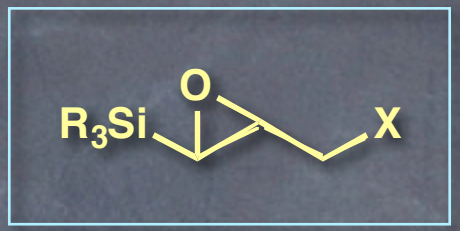
(*Z*) 56%ee (62%ee)

Intramolecular Trapping of Chiral Carbanions by an Electrophile (2)



28% (52%ee)

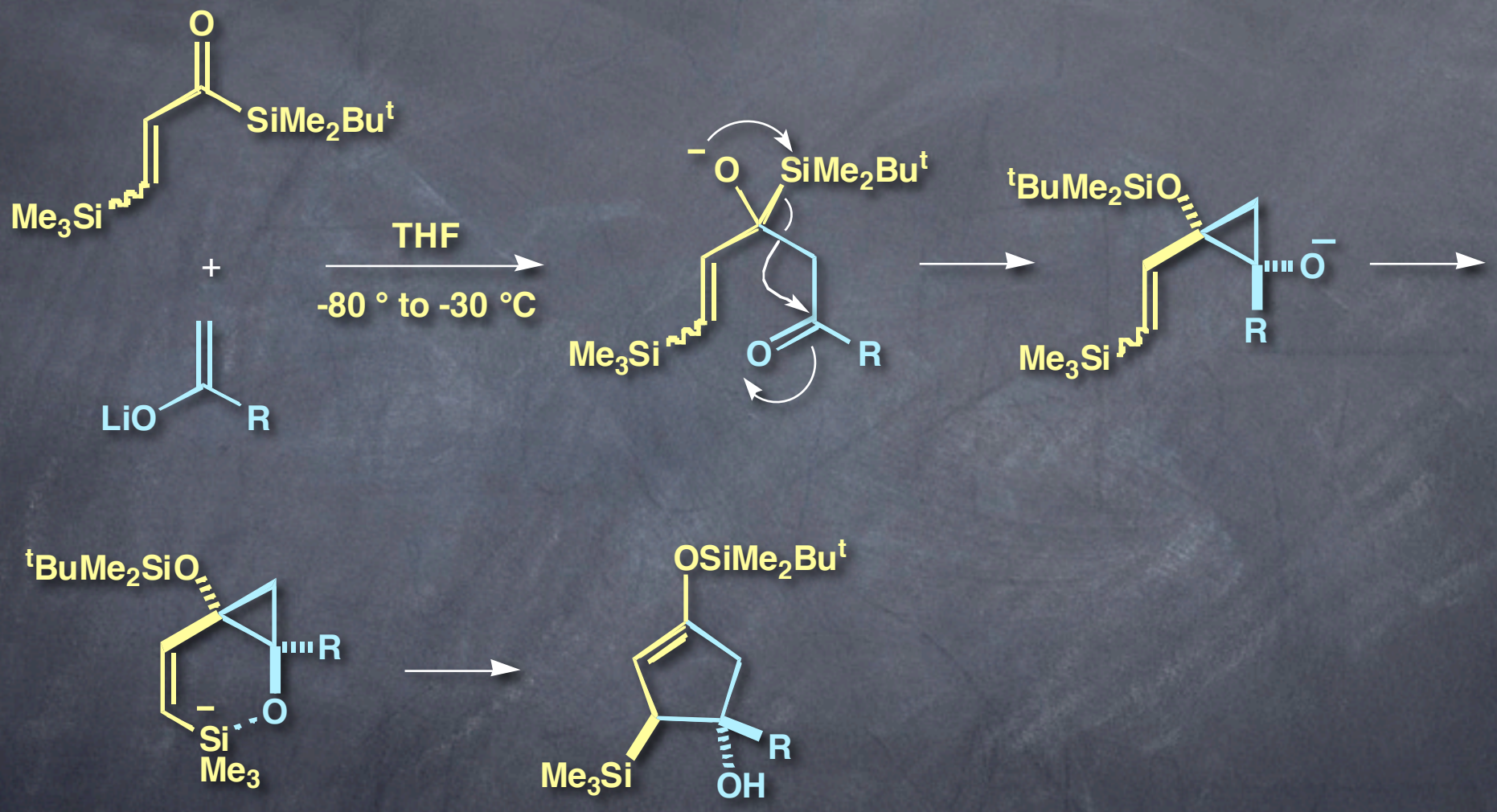
Reactions of Epoxysilanes



Use of a Trigger in Cascade-Type Reactions

Novel Use of Epoxide as a Chiral Source

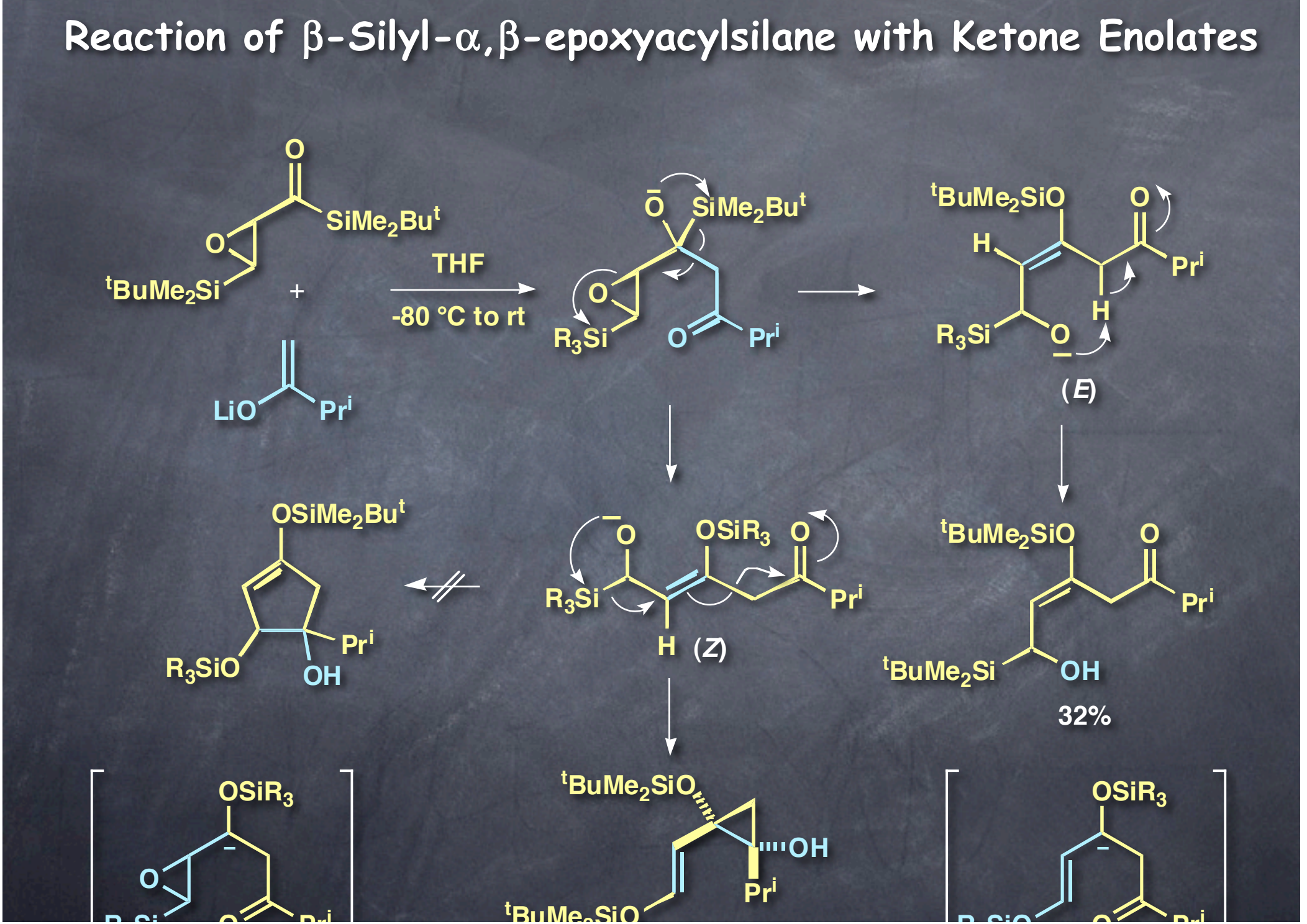
Brook Rearrangement-Mediated [3 + 2] Annulation



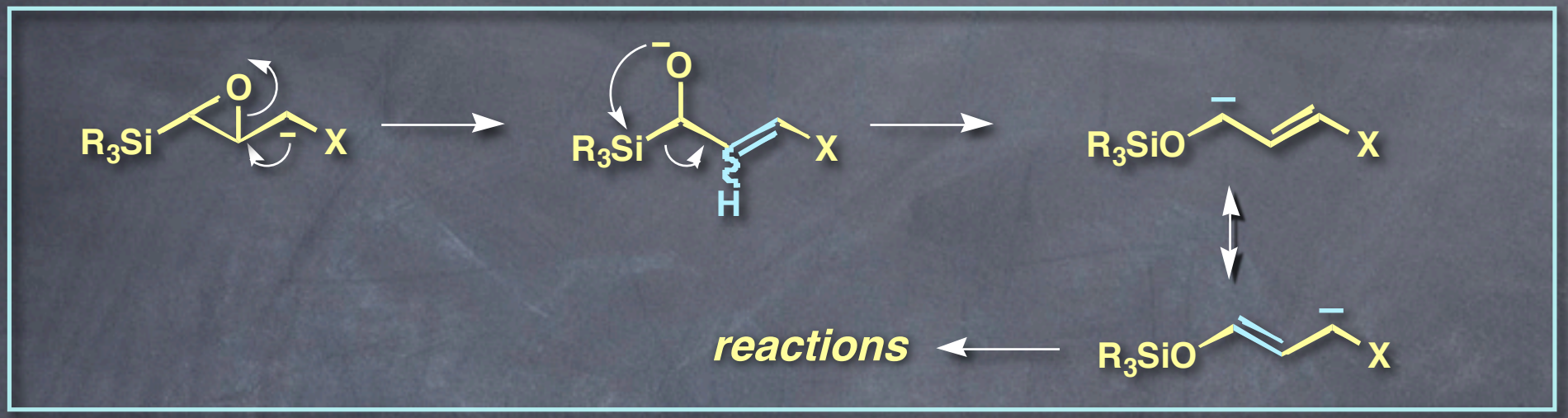
Takeda, K.; Fujisawa, M.; Makino, T.; Yoshii, E.; Yamaguchi, K. *J. Am. Chem. Soc.* **1993**, *115*, 9351-9352.

Extension of the [3 + 2] Annulation to Asymmetric Versions

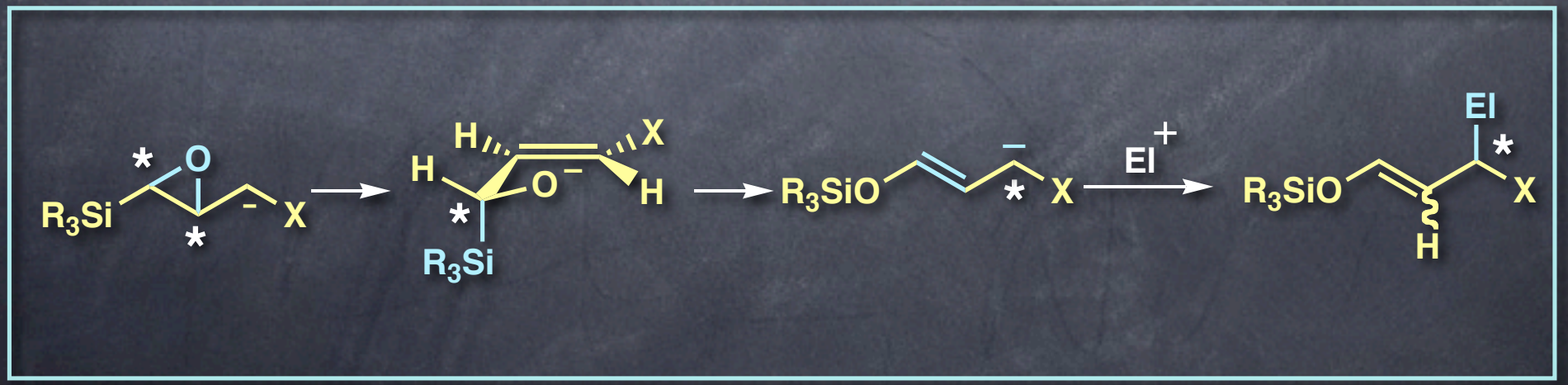
Reaction of β-Silyl-α,β-epoxyacylsilane with Ketone Enolates



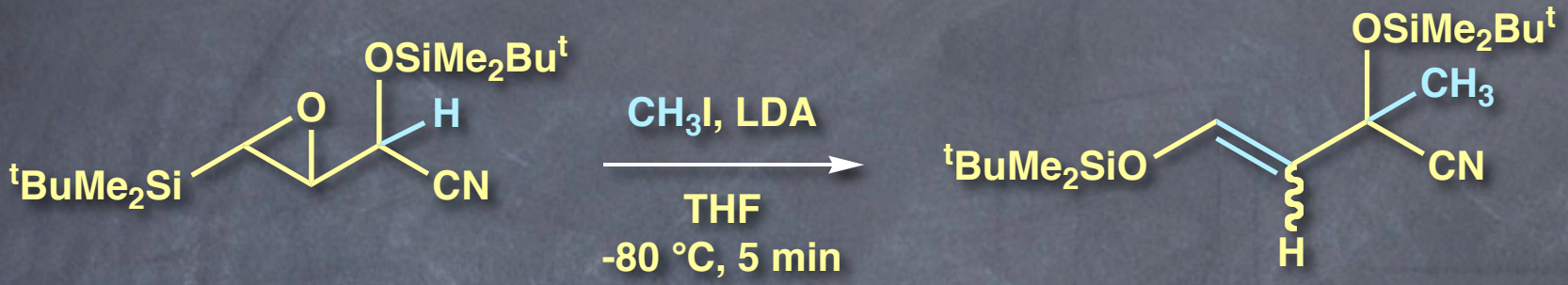
Epoxysilanes as an Efficient Trigger in Tandem Reactions

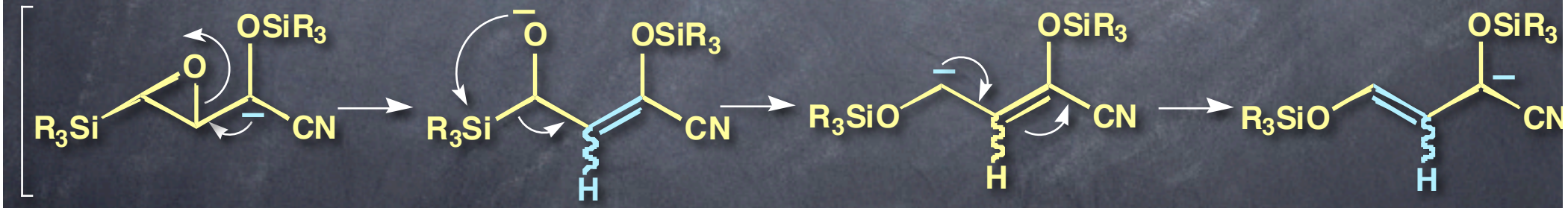


Novel Use of Epoxysilanes as a Chiral Source



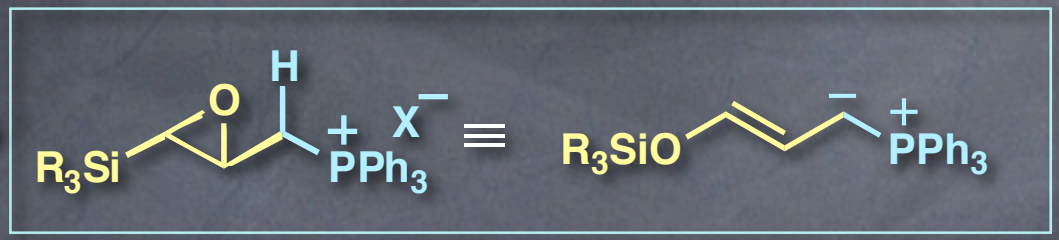
Alkylation of Metalated O-Protected Cyanohydrins of β-Silyl-α,β-epoxyaldehydes



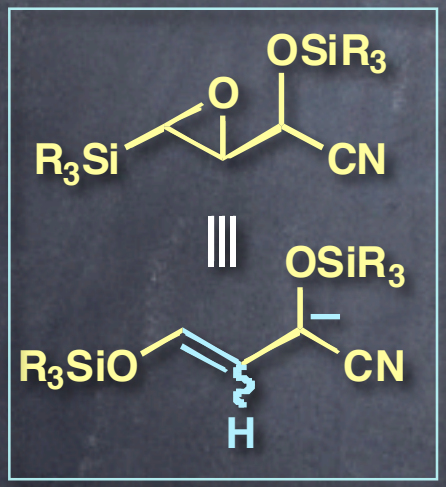


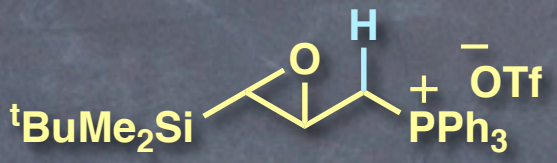
Kei Takeda, Eiji Kawanishi, Michiko Sasaki, Yuji Takahashi, Kentaro Yamaguchi *Org. Lett.* **2002**, 4, 1511-1514.
Michiko Sasaki, Eiji Kawanishi, Yoshio Nakai, Tatsuya Matsumoto, Kentaro Yamaguchi, Kei Takeda

Epoxysilanes as an Efficeint Trigger in Tandem Reactions (1)

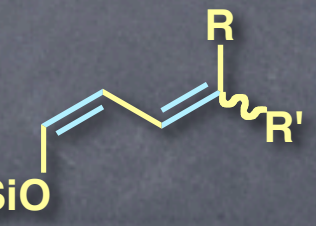


Wittig-type reactions





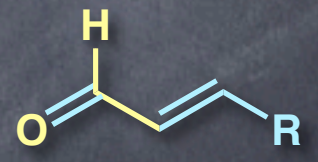
1. *n*-BuLi, THF
   -80 °C, 20 min
2. aldehyde (ketone)
   -80 ° to r.t.



Michiko Sasaki, Mai Horai *unpublished result*

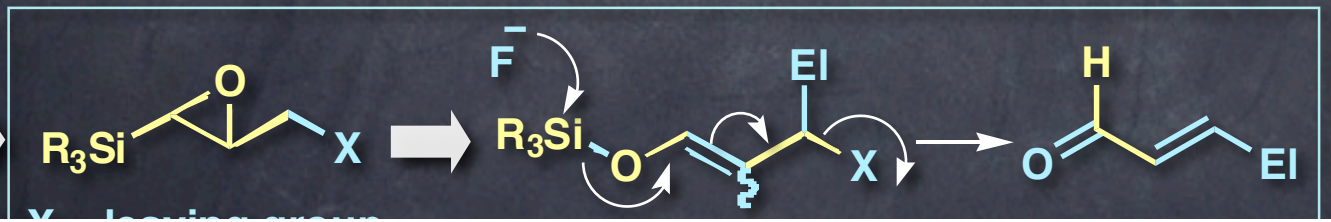
mp 76 °C

1. RX (1.0 eq)
   $NaN(SiMe_3)_2$ (1.0 eq)
   THF
2. *n*-Bu_4NF (1.0 eq)
   EtOH (3.0 eq)



68-85%

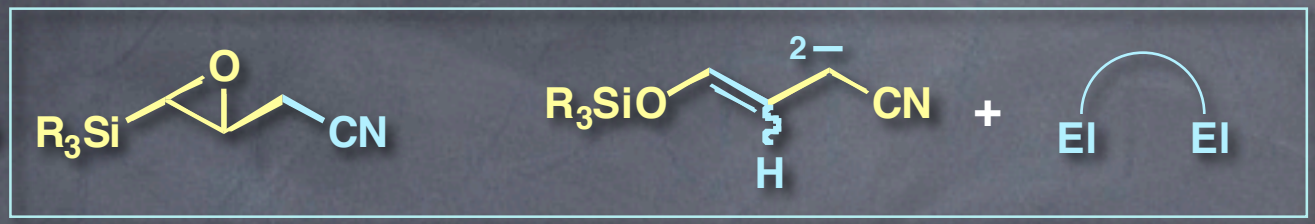
Michiko Sasaki *Org. Lett.* **2004**, *6*, 4849-485



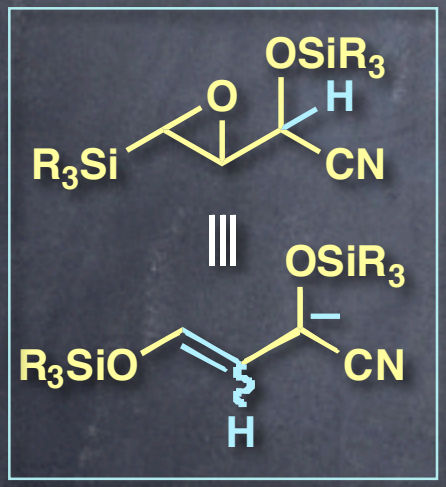
X = leaving group

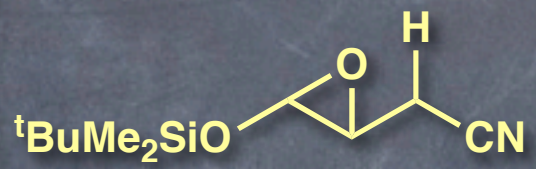
acrolein β-anion equivalent

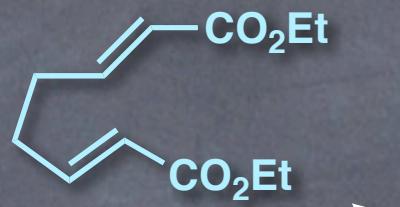
Epoxysilanes as an Efficeint Trigger in Tandem Reactions (2)



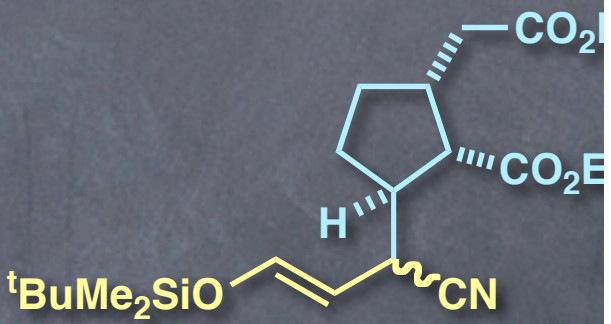
Reactions with bis-electrophiles



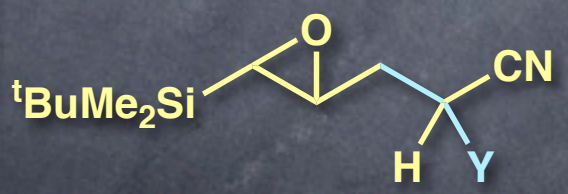




$NaN(SiMe_3)_2$ (1.0 eq)
THF, HMPA
-98 °C

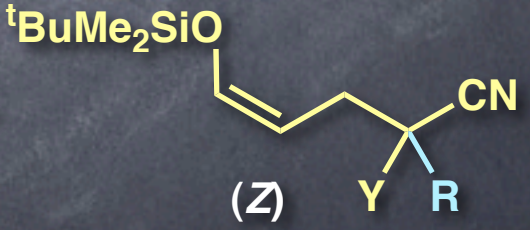


Tatsuya Matsumoto *Org. Lett.* **2004**, ***6***, 4367-4369.

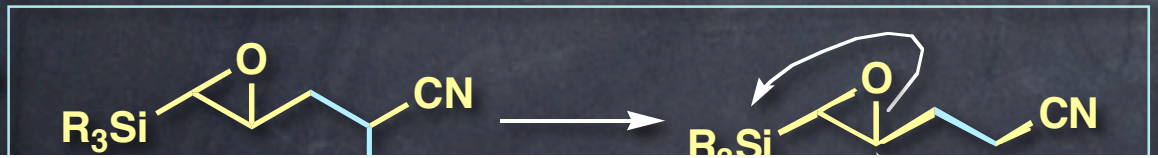


1. $NaN(SiMe_3)_2$
THF, -30 ° to 5 °C

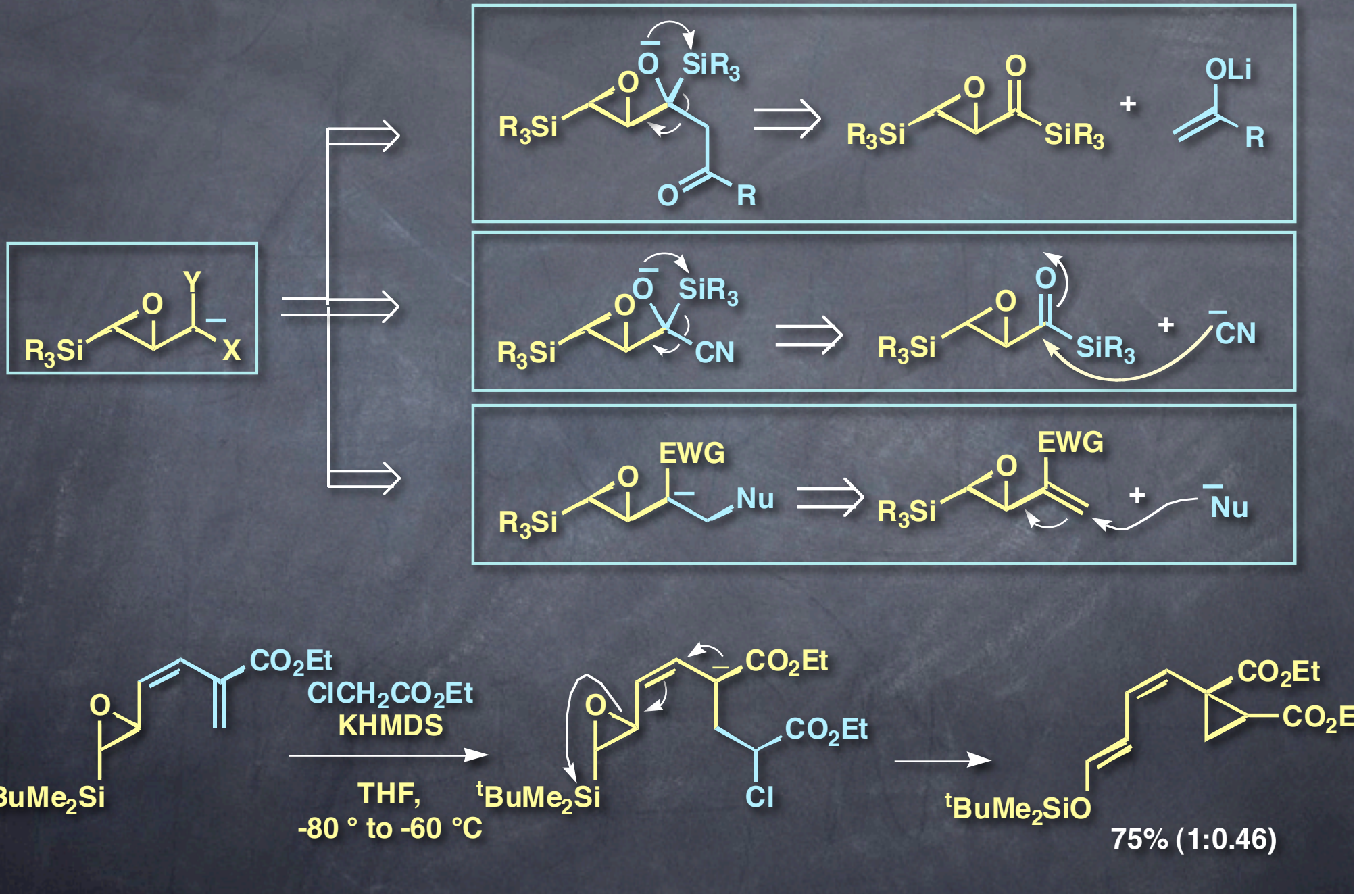
2. RX



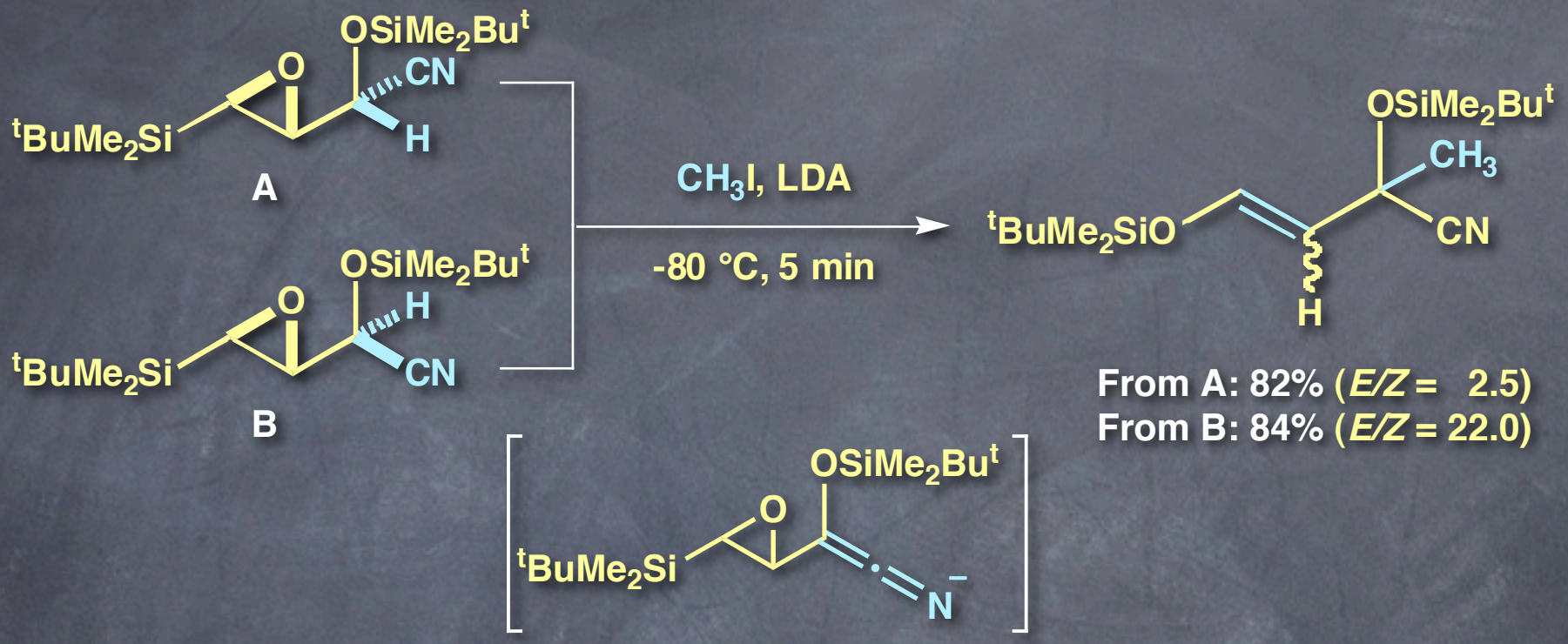
Seigo Okugawa *Org. Lett.* **2004**, *6*, 2973-2975. (31-0609).

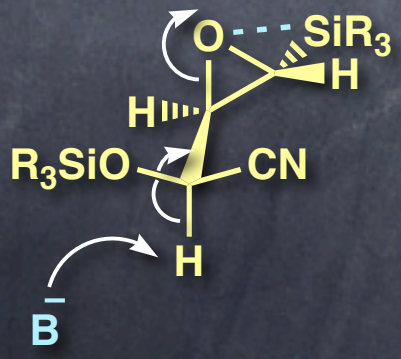


Epoxysilanes as an Efficient Trigger in Tandem Reactions (3)

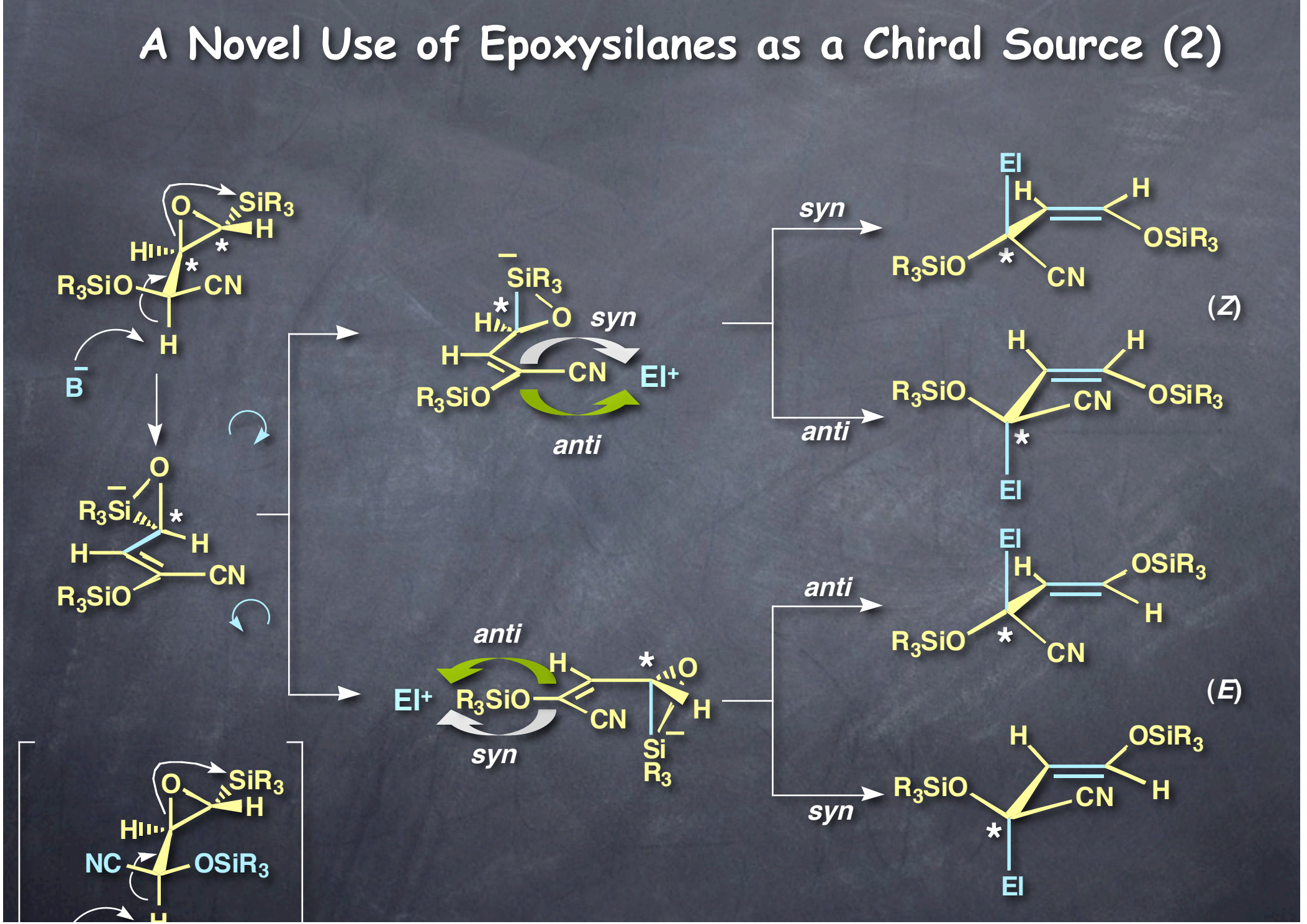


A Novel Use of Epoxysilanes as a Chiral Source (1)

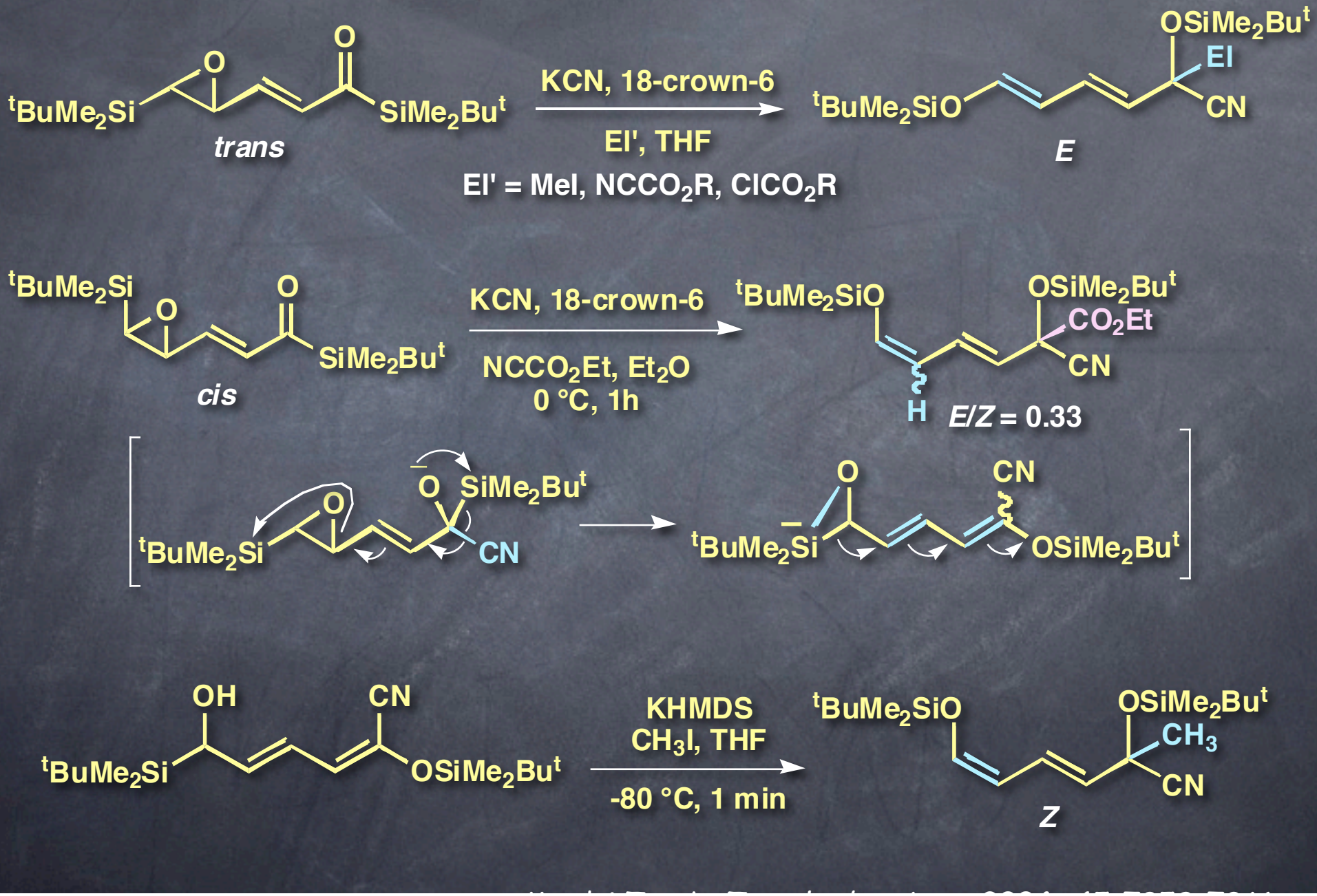




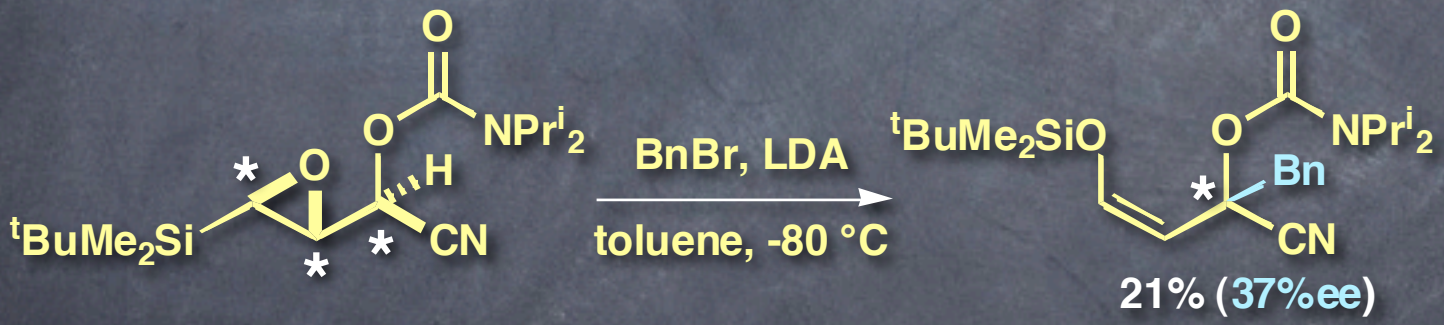
A Novel Use of Epoxysilanes as a Chiral Source (2)

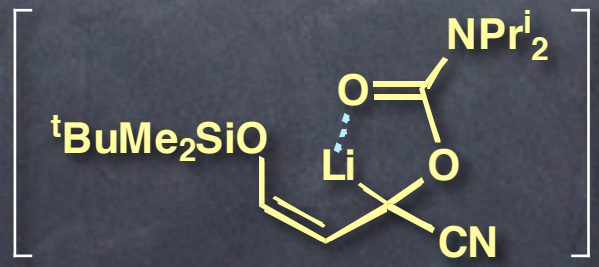


A Novel Use of Epoxysilanes as a Chiral Source (3)

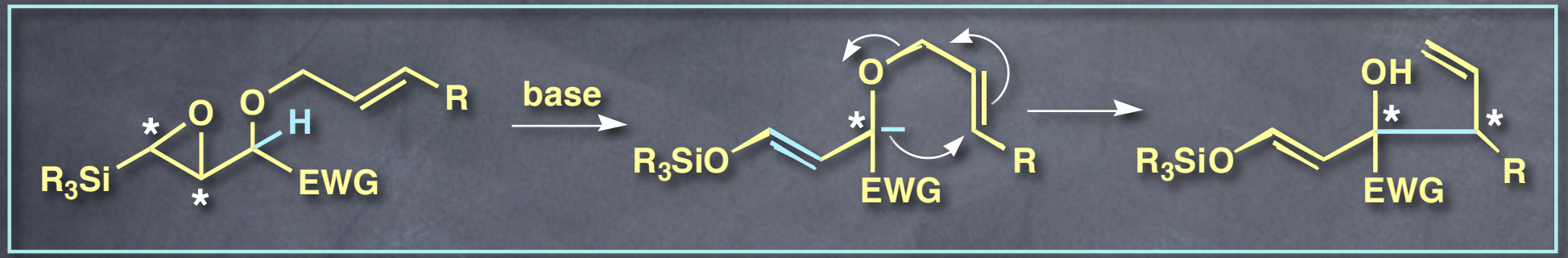


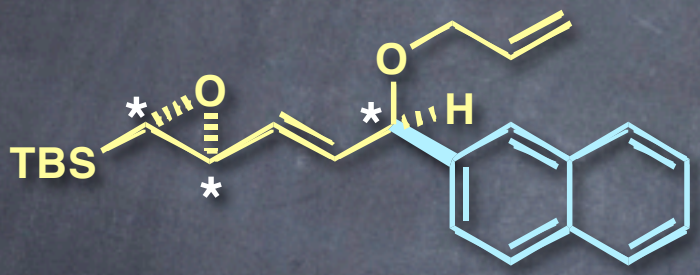
Chirality Transfer of Epoxides to Carbanions





Intramolecular Trapping of Chiral Cabanions by an Electrophile (1)



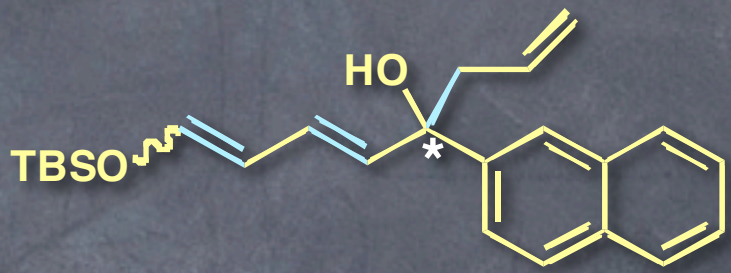


A (90%ee)

n-BuLi (1.5 eq)

Et_2O (0.076M)

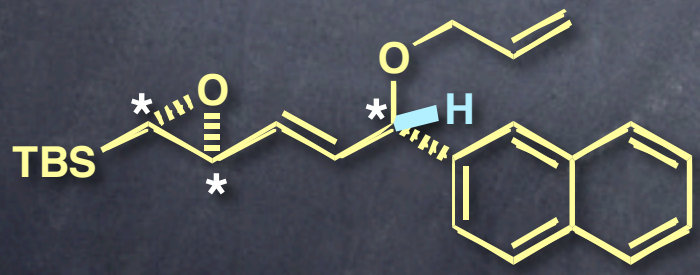
27 ° to 30 °C, 7 min



B (70% (*E*/*Z* = 0.19))

(*E*) 81%ee (90%ee)

(*Z*) 73%ee (81%ee)

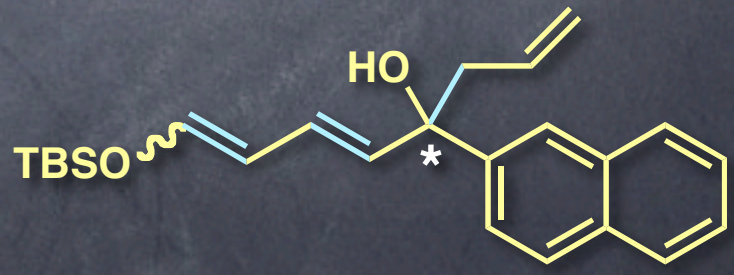


A' (90%ee)

n-BuLi (1.5 eq)

Et_2O (0.076M)

27 ° to 30 °C, 7 min



ent-B (77% (*E*/*Z* = 2.2))

(*E*) 81%ee (90%ee)

(*Z*) 56%ee (62%ee)

Intramolecular Trapping of Chiral Carbanions by an Electrophile (2)