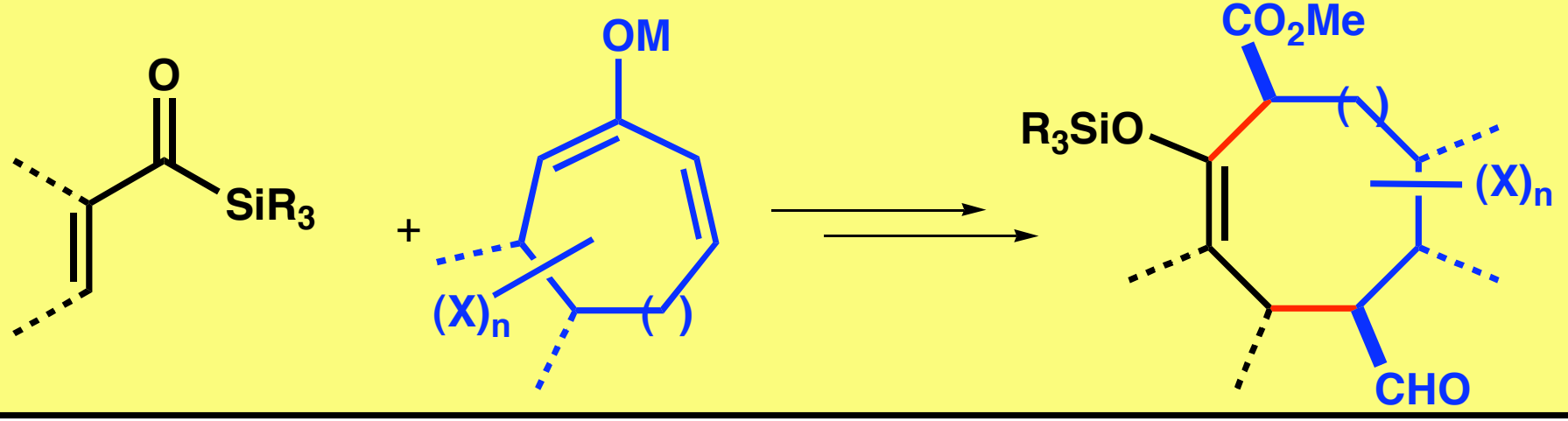
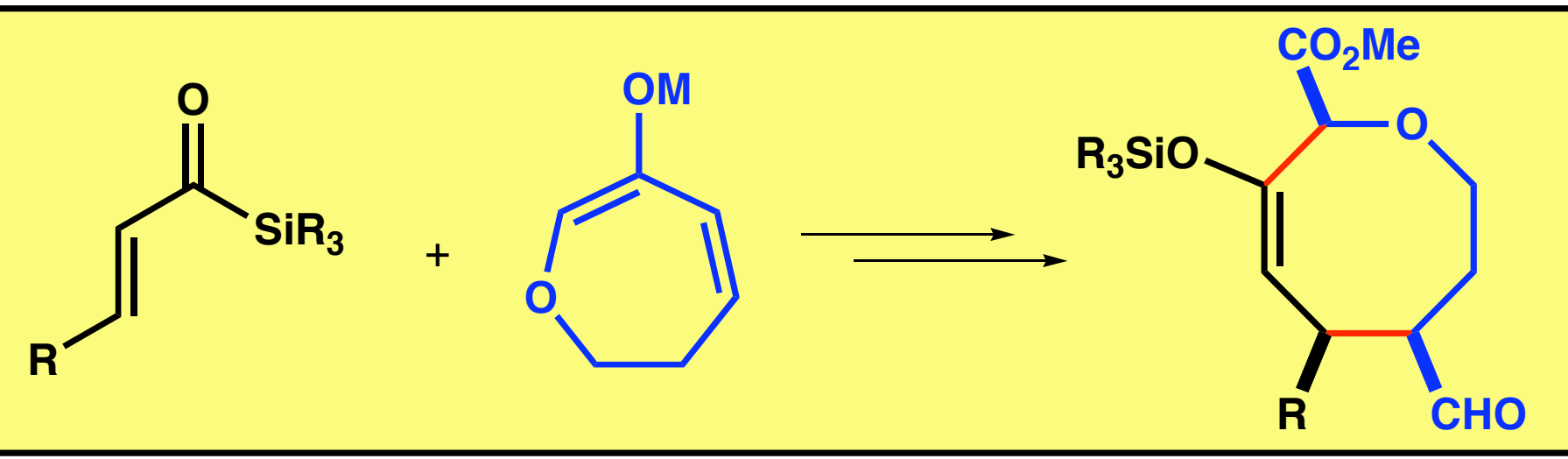
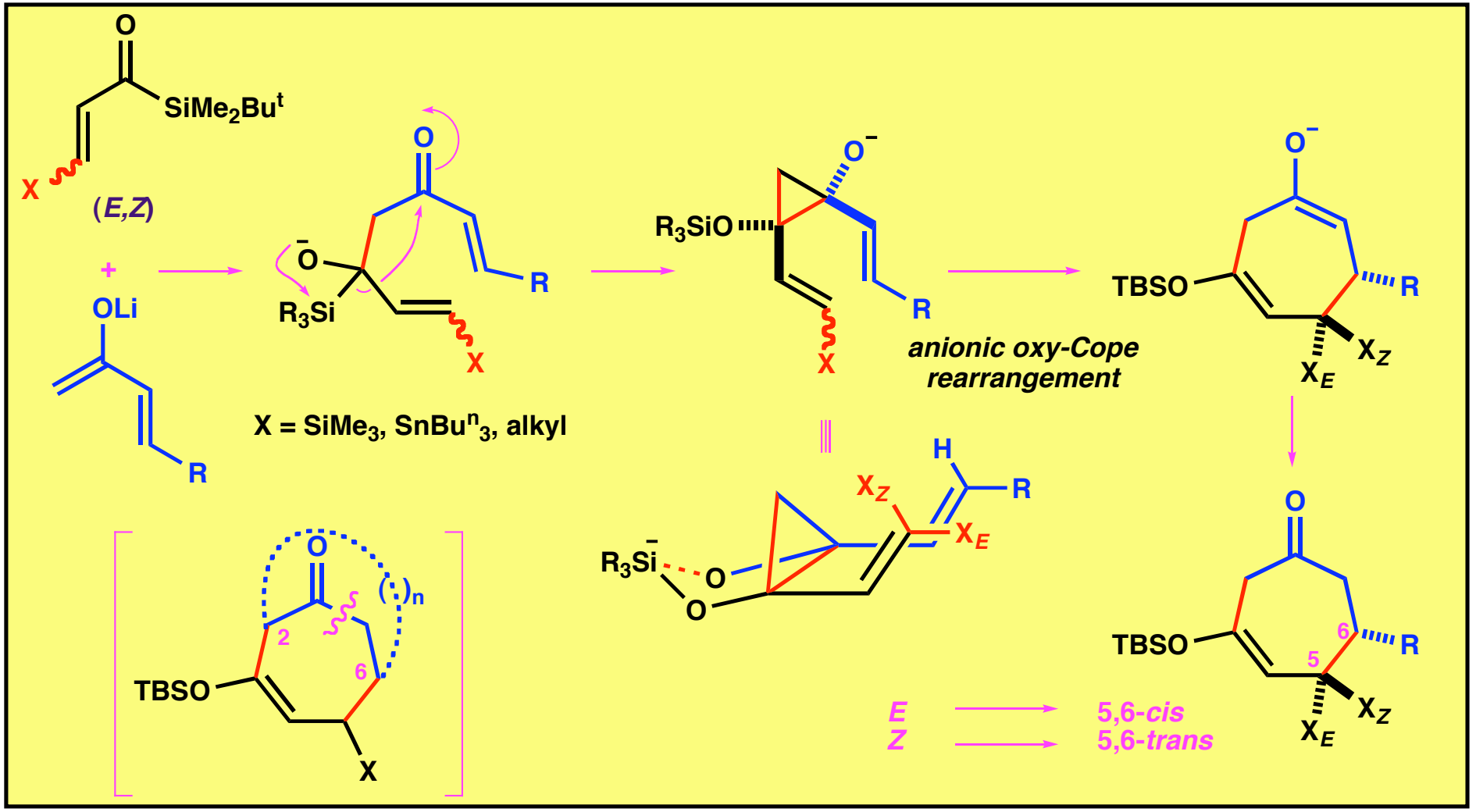
多元素含有多環縮合中員環形成反応の開発



[3 + 4] アニュレーションによる含酸素八員環形成反応の開発

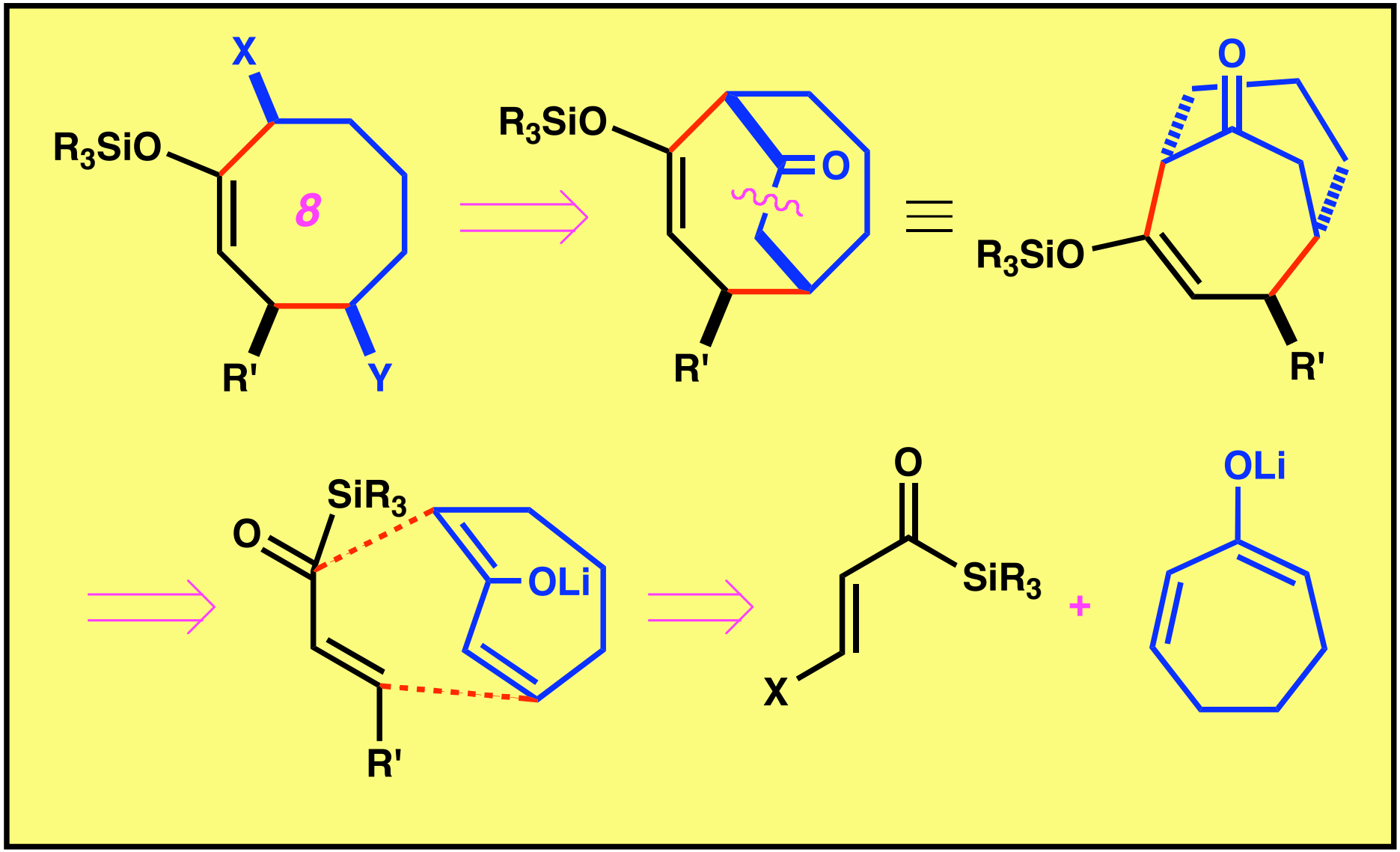


[3 + 4] Annulation Using the Reaction of Acryloylsilaneswith the Lithium Enolates of Alkenyl Methyl Ketones

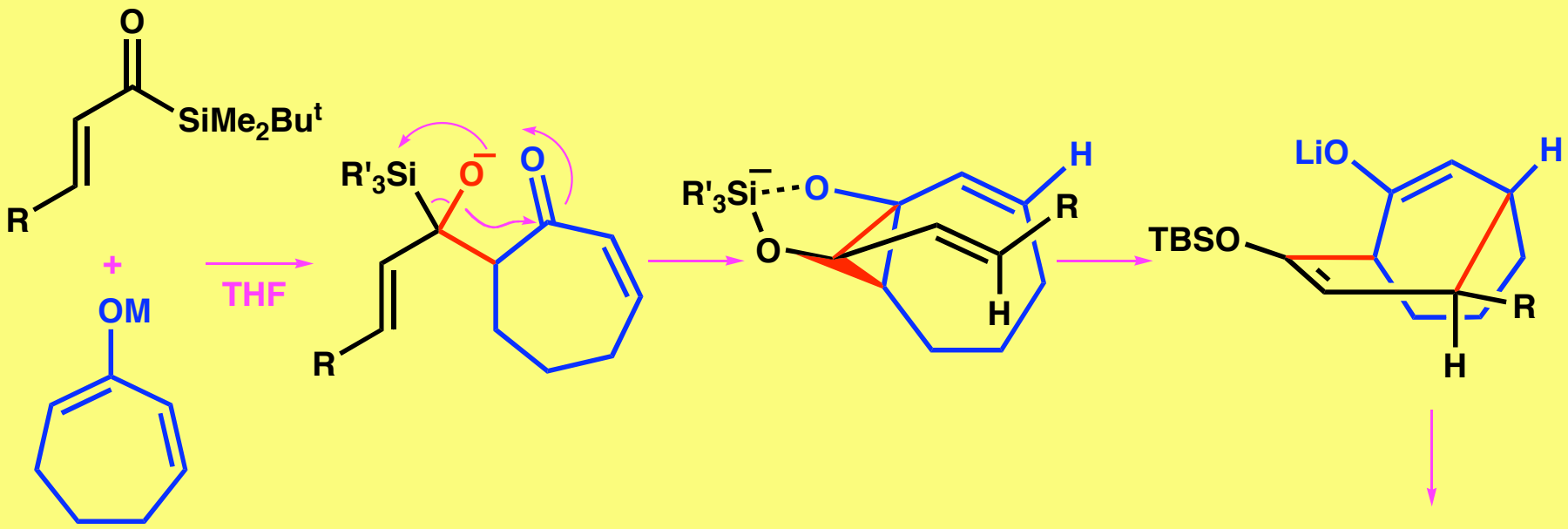


Takeda, K.; Takeda, M.; Nakajima, A.; Yoshii, E. *J. Am. Chem. Soc.***1995**, *117*, 6400-6401.
Takeda, K.; Nakajima, A.; Takeda, M.; Okamoto, Y.; Sato, T.; Yoshii, E.; Koizumi, T. *J. Am. Chem. Soc.* **1998**, *120*, 4947-4959.
Takeda, K.; Nakajima, A.; Takeda, M.; Yoshii, E. *Org. Synth.* **1999**, *76*, 199-211.

Formation of Eight-Membered Carbocycles by [3 + 4] Annulation

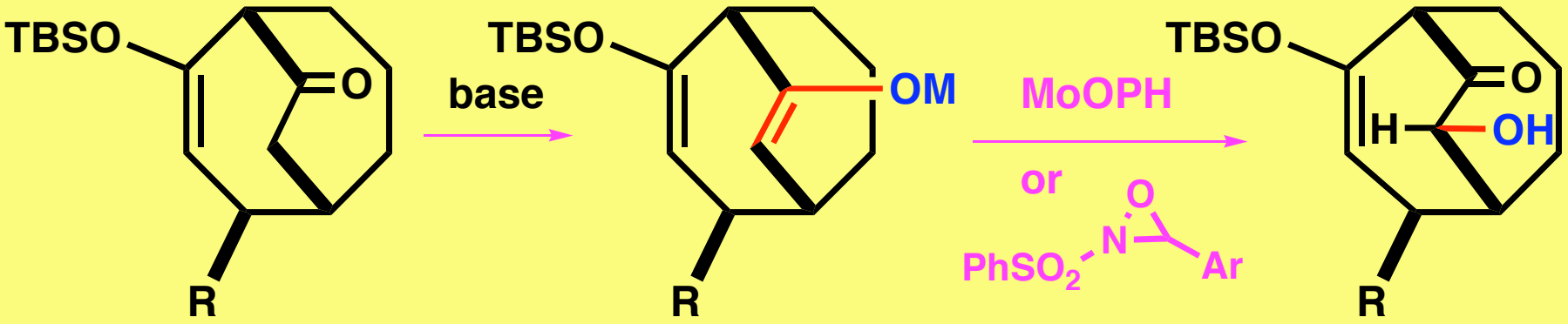


Synthesis of Eight-Membered Carbocycles by [3 + 4] Annulation



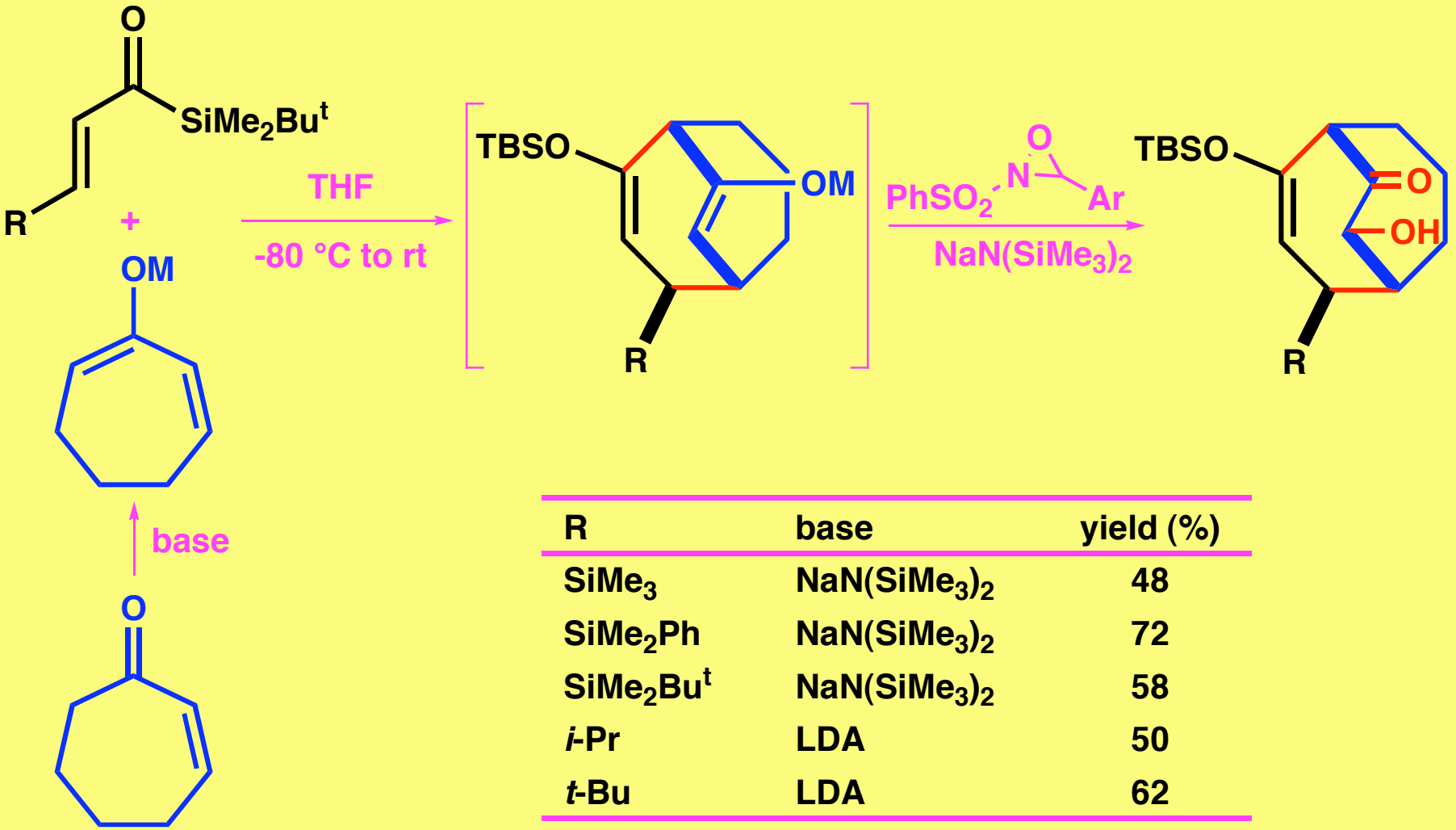
R	conditions	yield (%)
$SiMe_3$	-80 °C, 30 min	66
$SiMe_2Bu^t$	-80 ° to 0 °C	65
i-Pr	-80 °C, 30 min	45
t-Bu	-80 ° to 0 °C	84
c-C_6H_{11}	-80 ° to 0 °C	45

α-Hydroxylation of Bicyclo[2.2.2]decenones



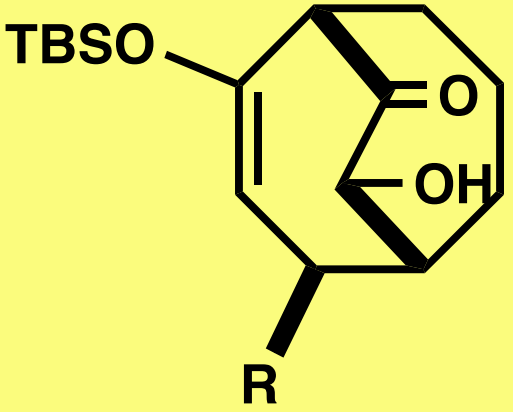
		yield (%)	
R	base	Vedejs 法	Davis 法
$SiMe_3$	LDA	52	
$SiMe_3$	$NaN(SiMe_3)_2$		76
t-Bu	LDA	66	
t-Bu	$NaN(SiMe_3)_2$		71

Tandem [3 + 4] Annulation /α-Hydroxylation



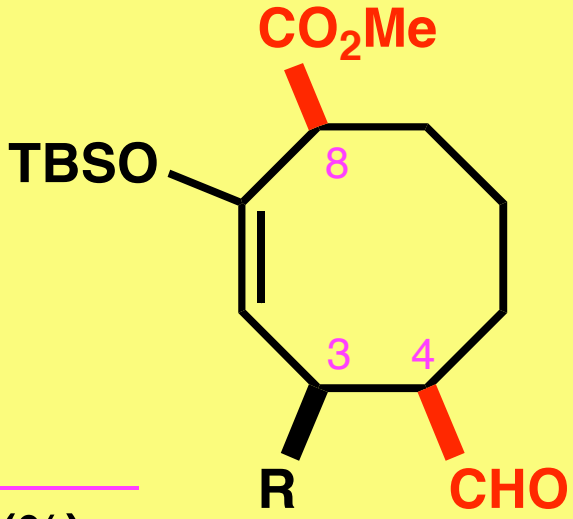
R	base	yield (%)
$SiMe_3$	$NaN(SiMe_3)_2$	48
$SiMe_2Ph$	$NaN(SiMe_3)_2$	72
$SiMe_2Bu^t$	$NaN(SiMe_3)_2$	58
i-Pr	LDA	50
t-Bu	LDA	62

Oxidative Cleavage of α-Hydroxyketones



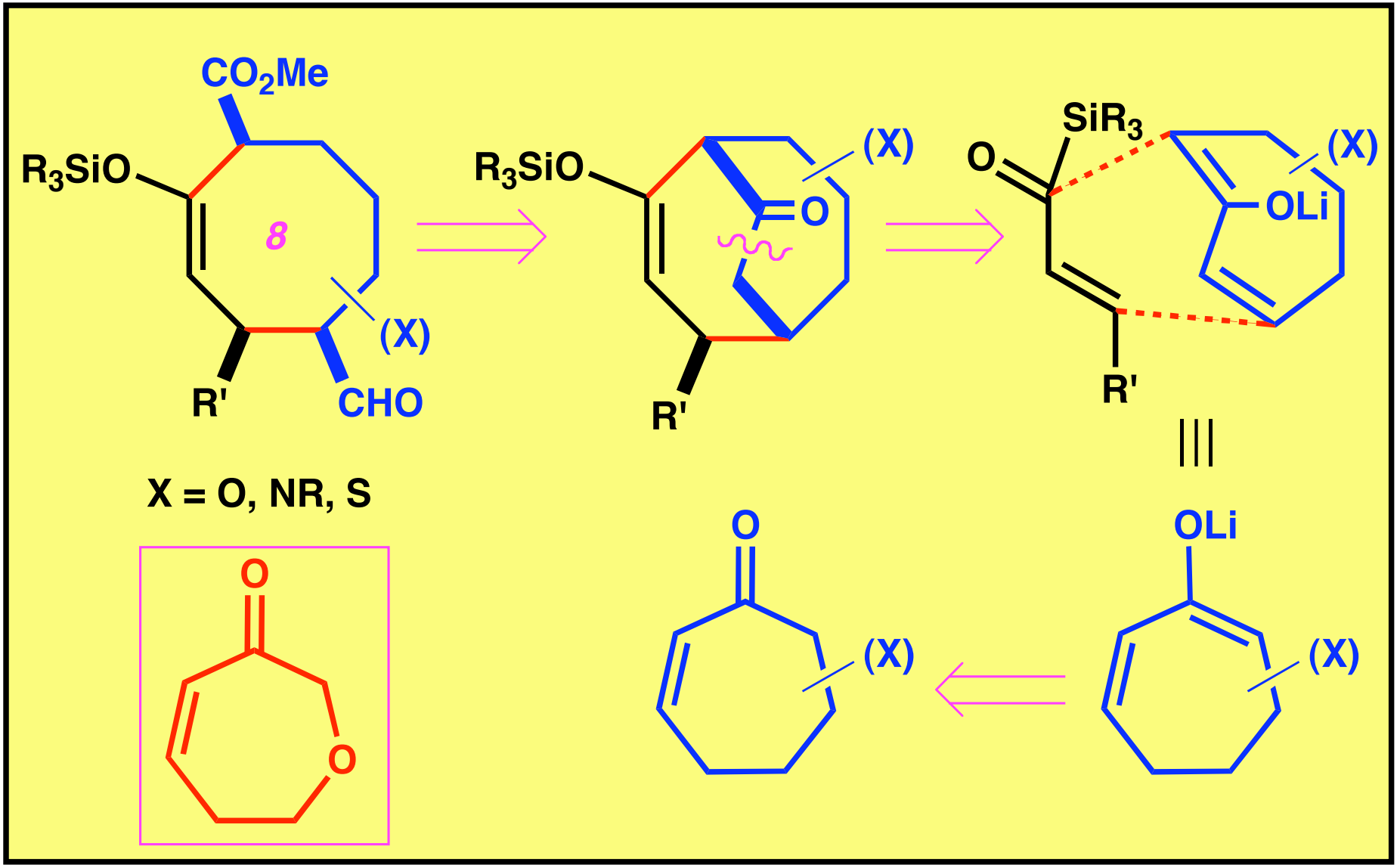
$Pb(OAc)_4$

Benzene-MeOH
0 °C

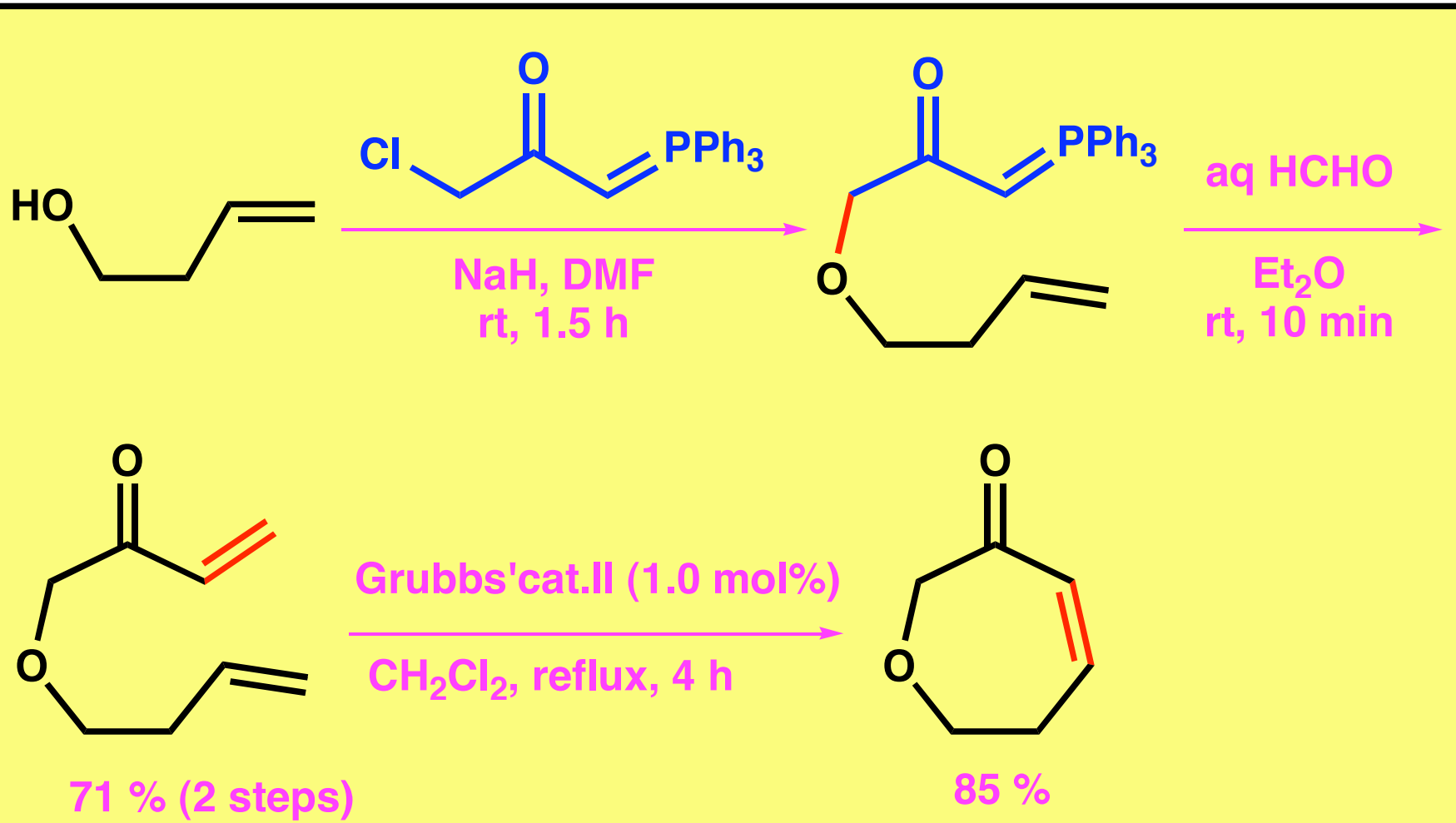


R	yield (%)
$SiMe_3$	95
$SiMe_2Ph$	96
$SiMe_2Bu^t$	95
i-Pr	97
t-Bu	93

Formation of Eight-Membered Heterocycles by [3 + 4] Annulation

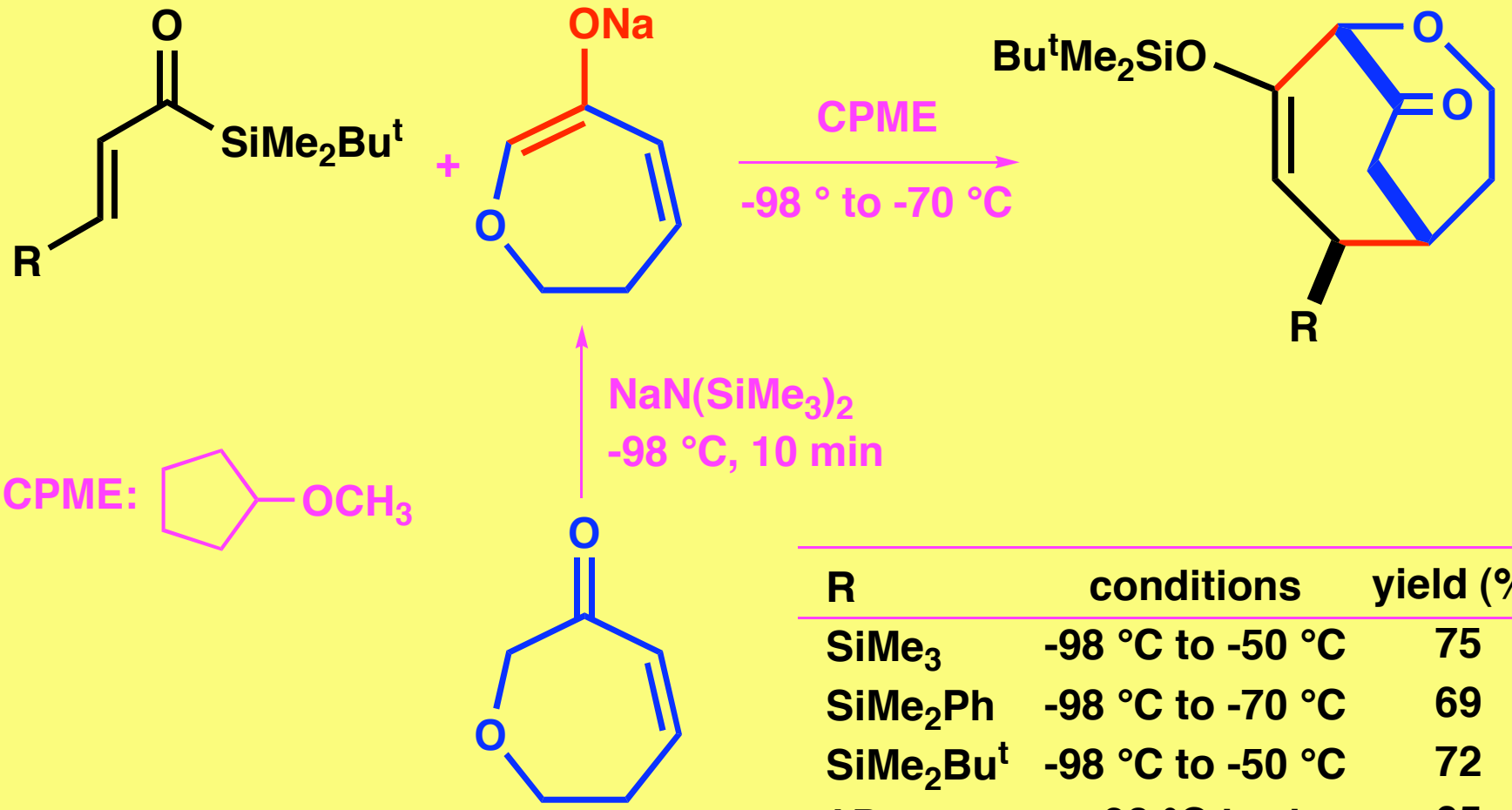


Preparation of 6-Oxa-2-cycloheptenone



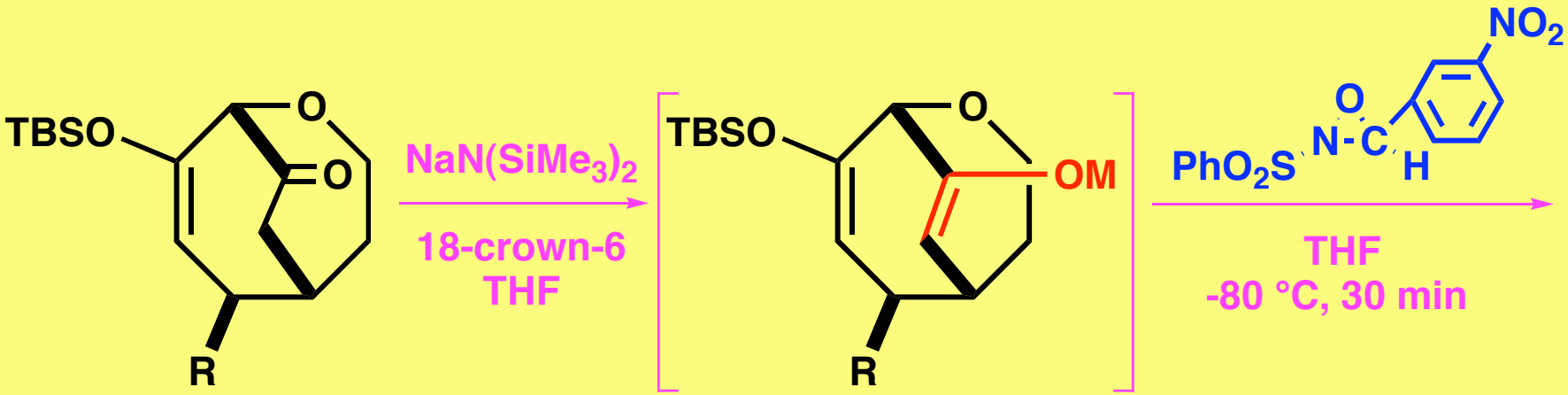
Cossy, J.; Taillier, C.; Bellosta, V. *Tetrahedron Lett.* **2002**, *43*, 7263-7266.

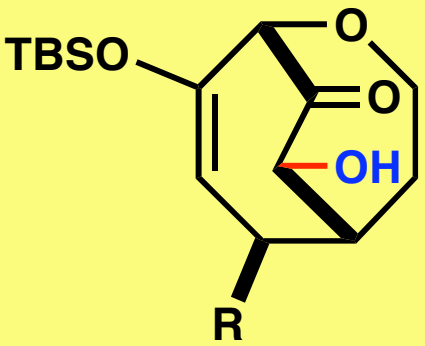
Formation of Eight-Membered Heterocycles by [3 + 4] Annulation (I)



R	conditions	yield (%)
$SiMe_3$	-98 °C to -50 °C	75
$SiMe_2Ph$	-98 °C to -70 °C	69
$SiMe_2Bu^t$	-98 °C to -50 °C	72
i-Pr	-98 °C to rt	65
t-Bu	-98 °C to rt	57

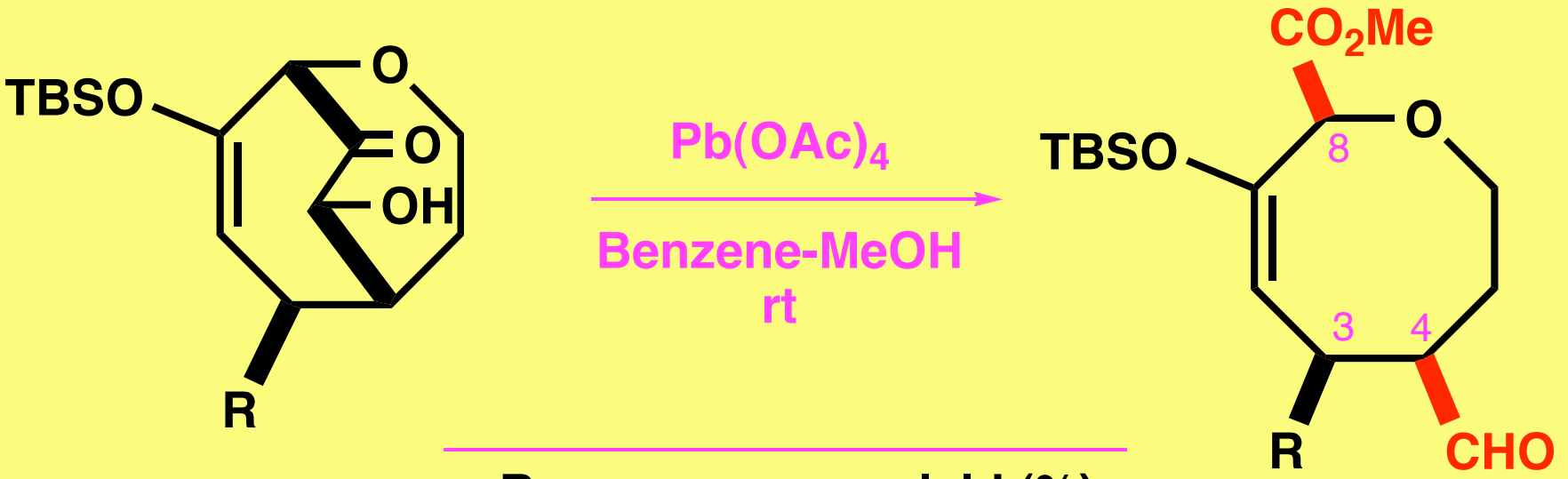
α-Hydroxylation of 2-Oxabicyclo[2.2.2]decene Derivatives





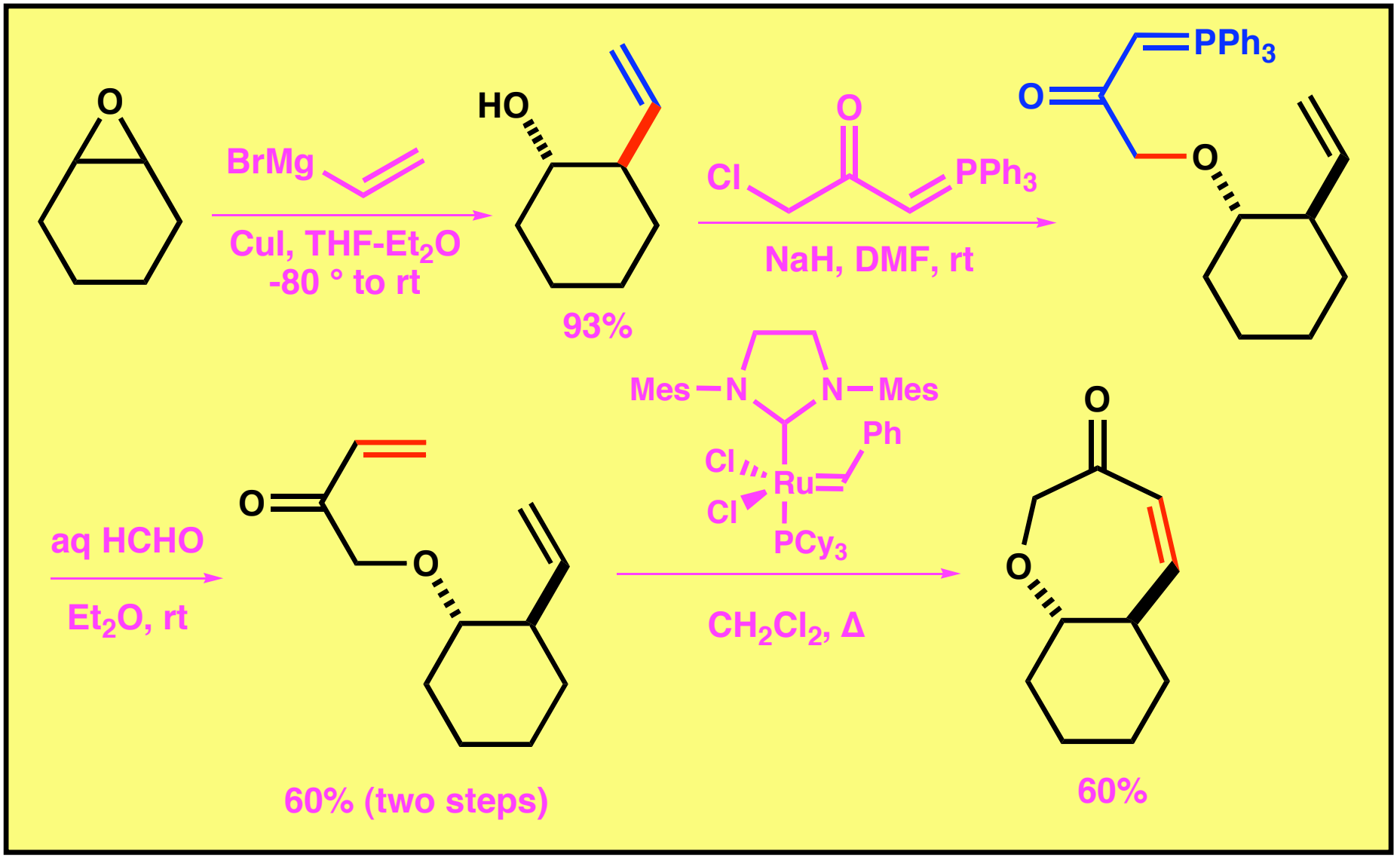
R	yield (%)
$SiMe_3$	56
$SiMe_2Ph$	86
$SiMe_2Bu^t$	76
i-Pr	66
t-Bu	86

Oxidative Cleavage of α-Hydroxyketones



R	yield (%)
$SiMe_3$	93
$SiMe_2Ph$	99
$SiMe_2Bu^t$	100
i-Pr	100
t-Bu	97

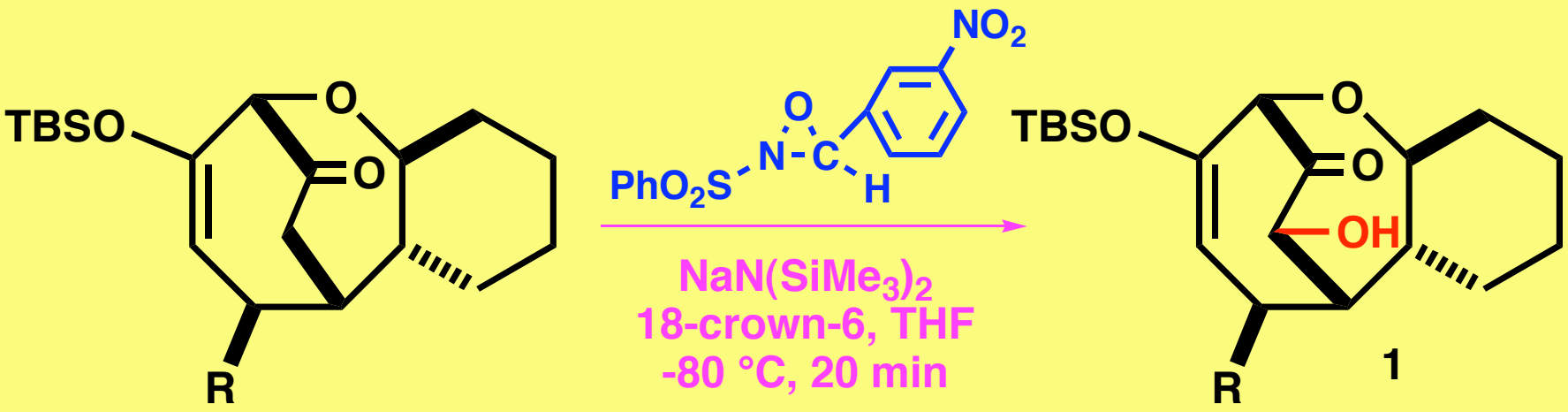
Synthesis of 2-Oxabicyclo[5.4.0]undec-5-en-4-one

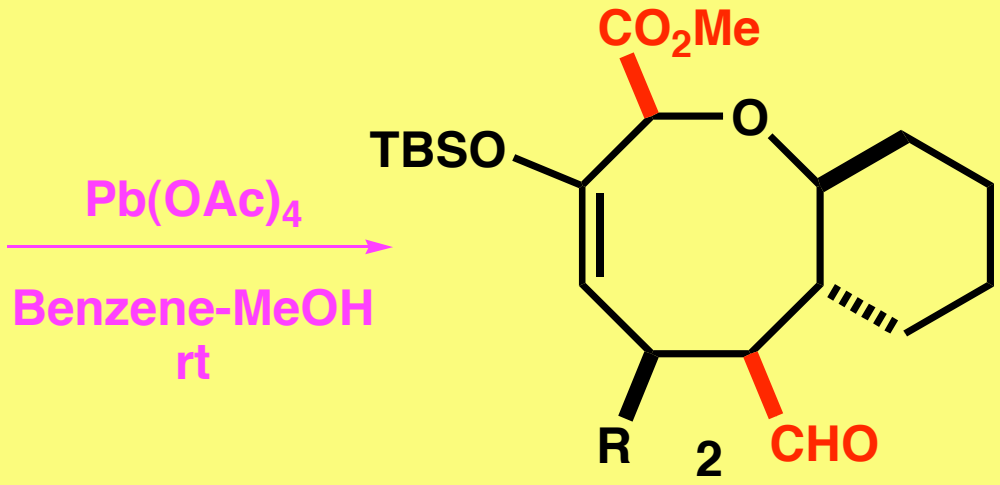


[3 + 4] Annulation Using 2-Oxabicyclo[5.4.0]undec-5-en-4-one

R	yield (%)
$SiMe_3$	89
$SiMe_2Ph$	85
$SiMe_2Bu^t$	82
i-Pr	70
t-Bu	83

α-Hydroxylation and Oxidative Cleavage of 2-Oxatricyclo-[7.3.2.0^{3,8}]tetradec-4-en-13-one derivative





	yield (%)	
R	1	2
$SiMe_3$	52	93
$SiMe_2Ph$	59	100
$SiMe_2Bu^t$	49	83
i-Pr	39	80
t-Bu	40	99