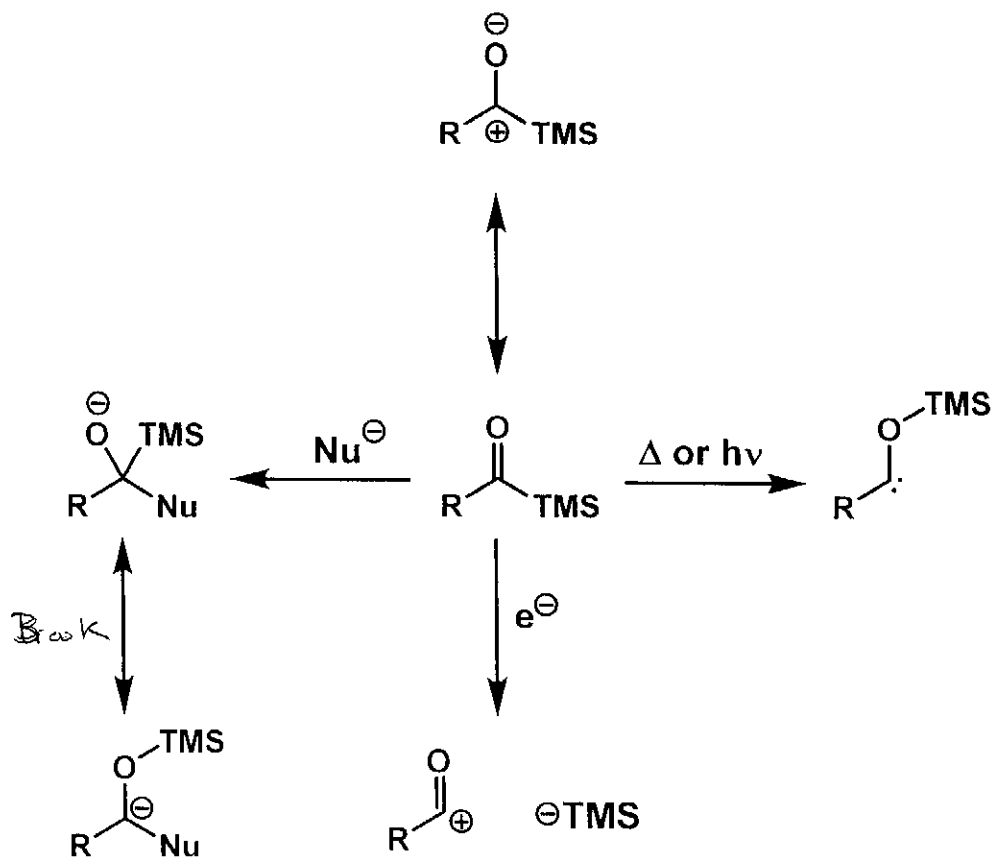


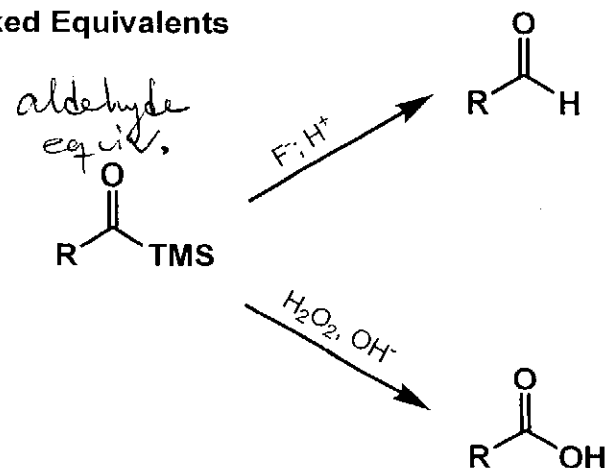
Brook  
JACS 1957, 49, 4373

- first reported acylsilane by Brook in 1957
- lemon yellow in color
- <sup>13</sup>C resonance for C=O 220-260 ppm
- UV absorption 399
- n-π\* 380-420 nm vs. 273 nm for acetone
- extinction coefficient ε = 100-300 M<sup>-1</sup>cm<sup>-1</sup>

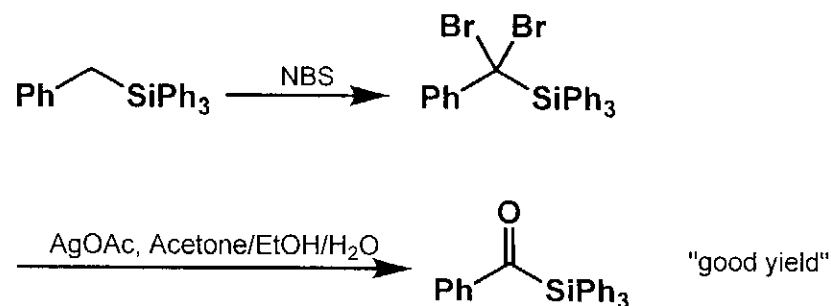
### General Reactivity of Acylsilanes



### Masked Equivalents



### Brook's First Synthesis

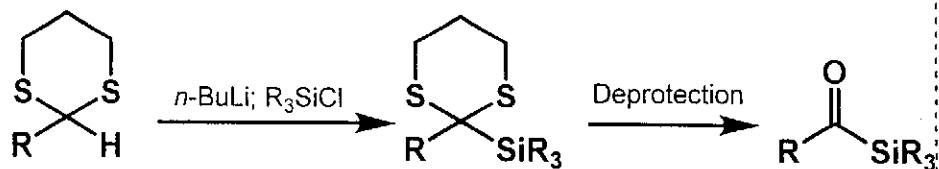


- direct oxidation with KMnO<sub>4</sub> or chromic acid failed to give the desired product. Only Ph<sub>3</sub>SiOH was isolated.  
-noted that the acylsilane is extremely labile in basic media resulting in Ph<sub>3</sub>SiOH and PhCHO

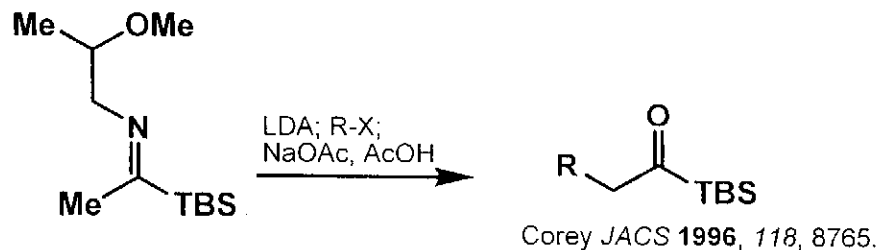
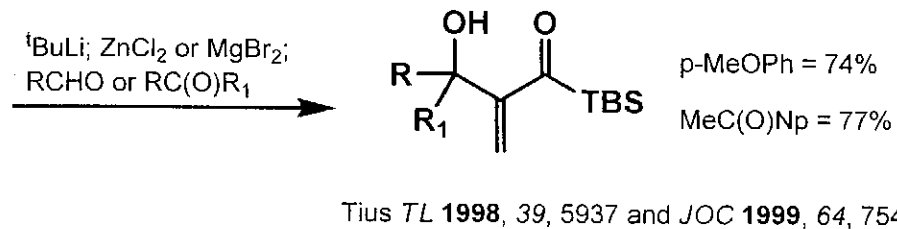
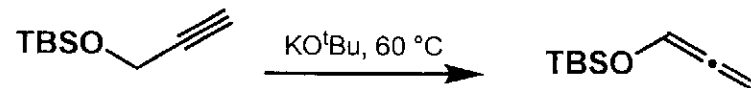
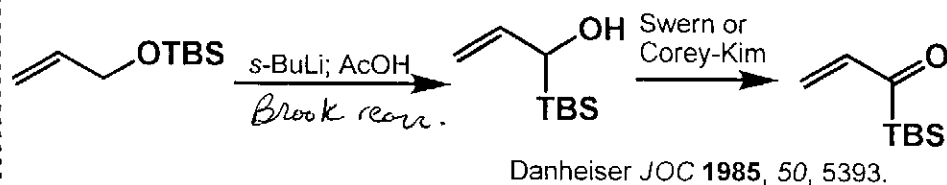
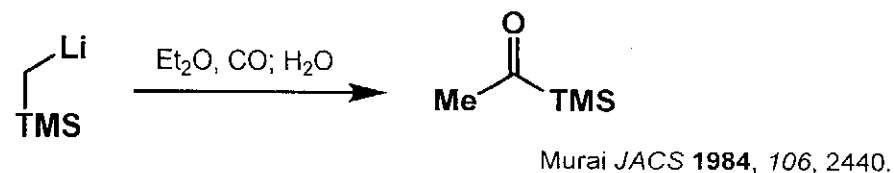
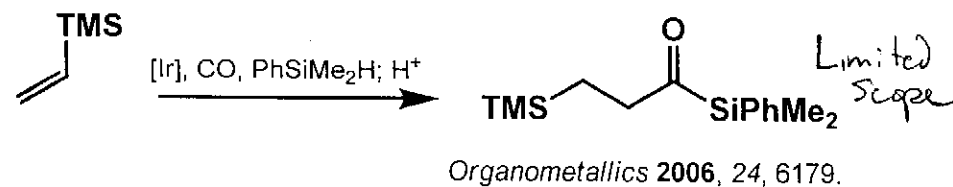
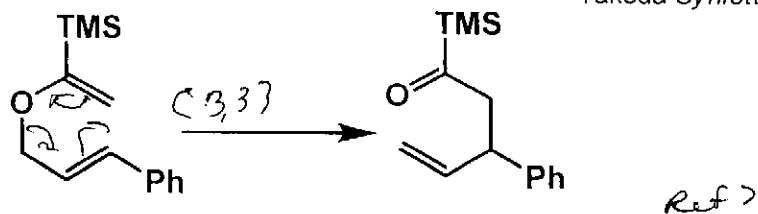
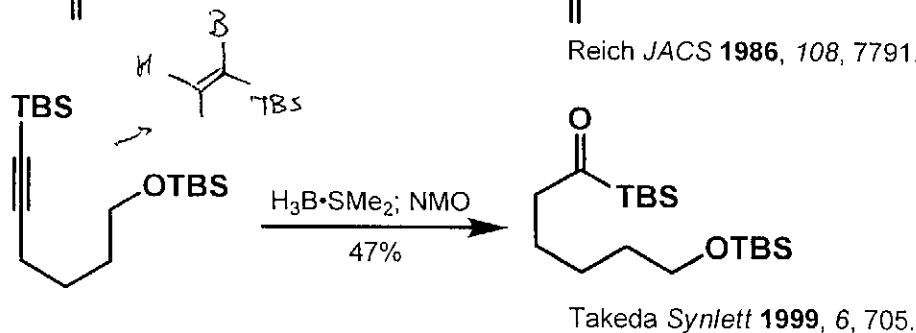
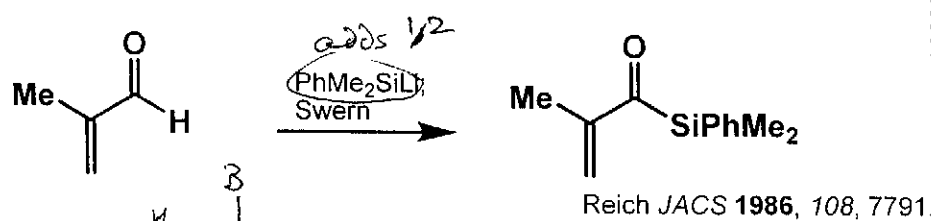
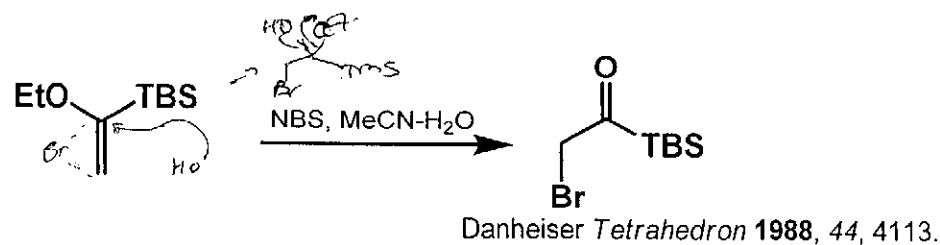
-Reacted abnormally with PhMgBr and PhLi yielding Ph<sub>4</sub>Si in 5% and 10% yield respectively

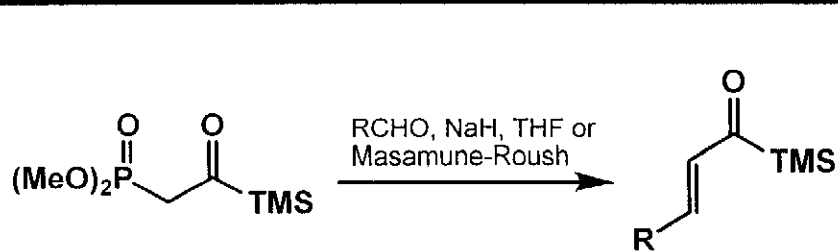
gets Ph<sub>4</sub>Si

## Alternative Preparations



Conditions:  $\text{Hg}^{+2}$ , Chloramine-T/MeOH,  $\text{Fe}(\text{NO}_3)_2$ , PIFA, CAN

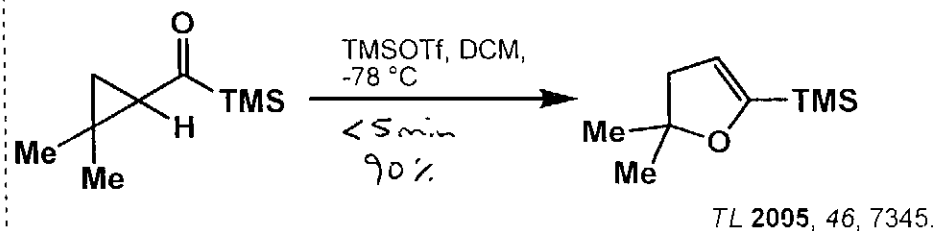
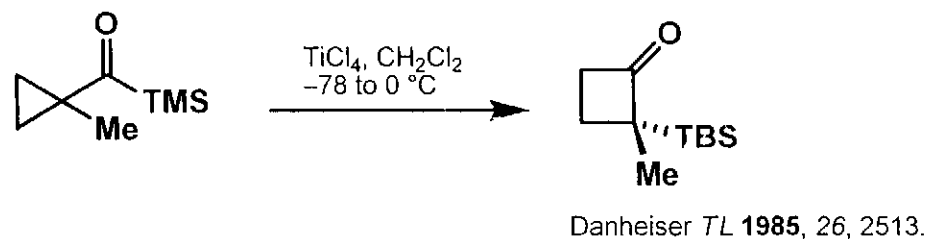
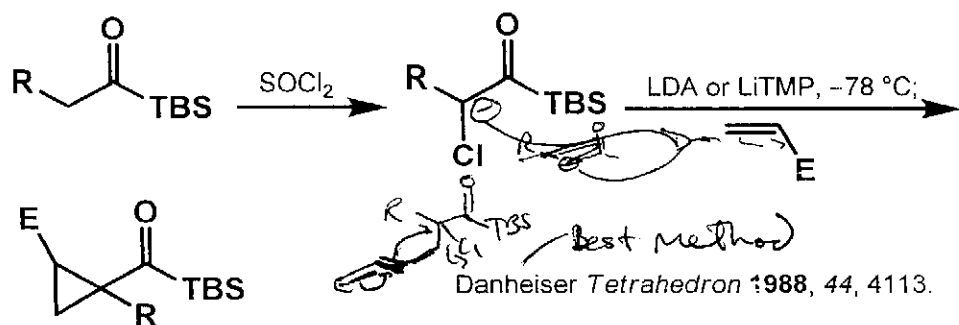
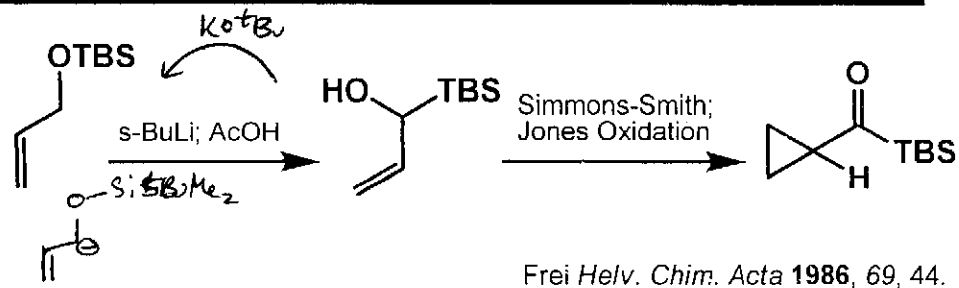
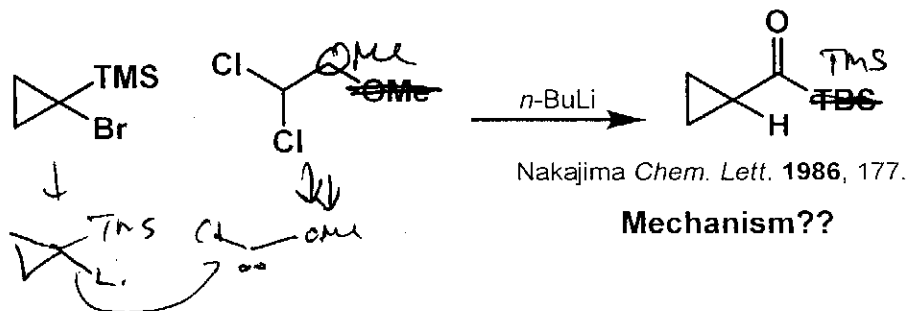
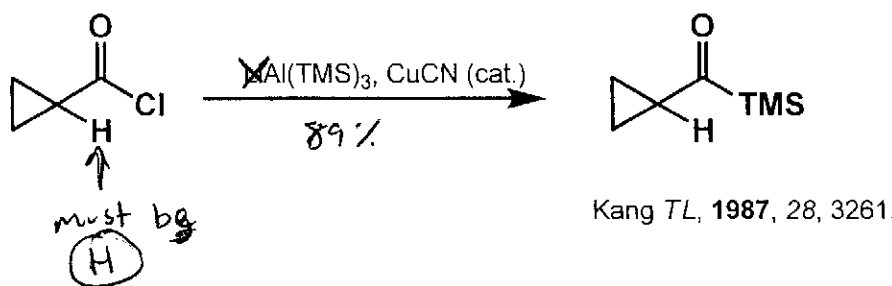
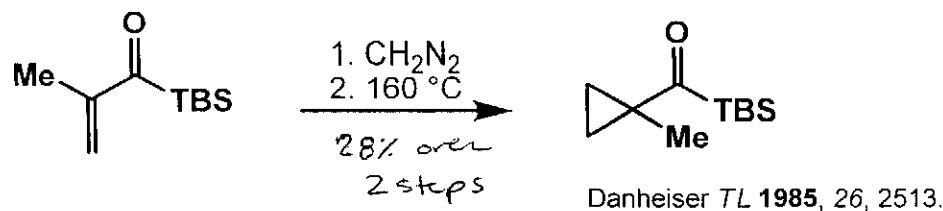




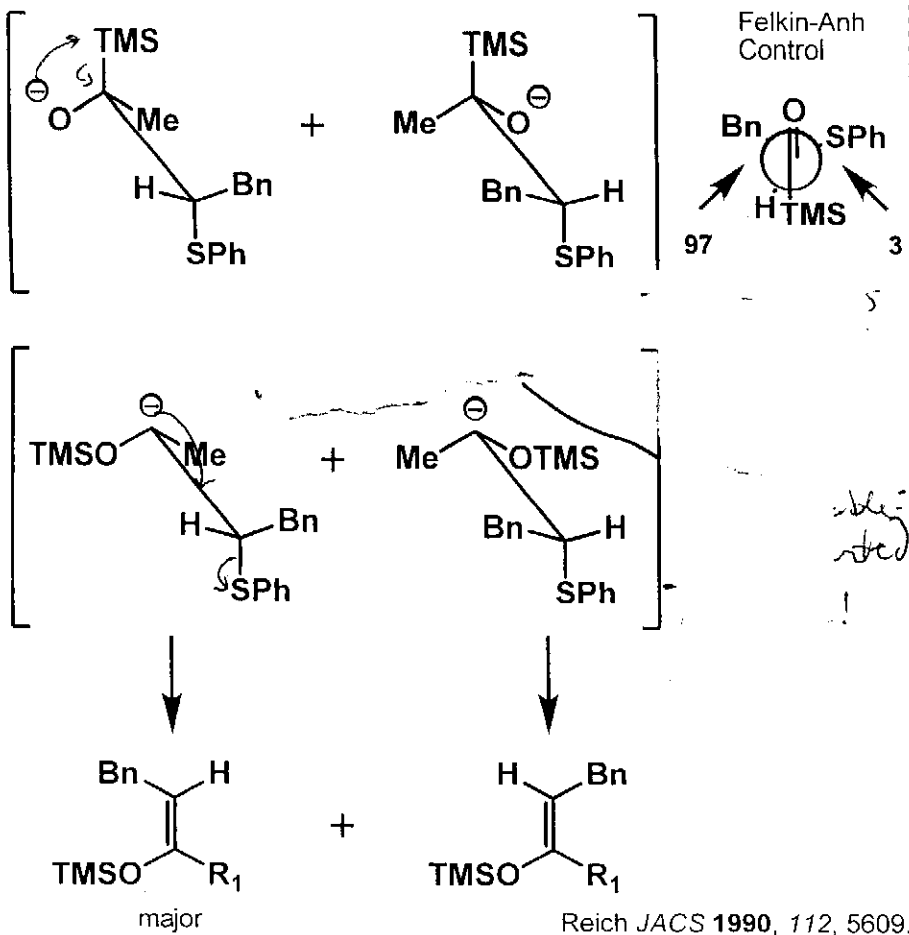
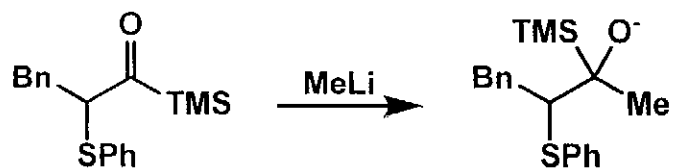
Danheiser

### Cyclopropylacylsilanes & Their Chemistry

(b/c of interesting reactivity...)



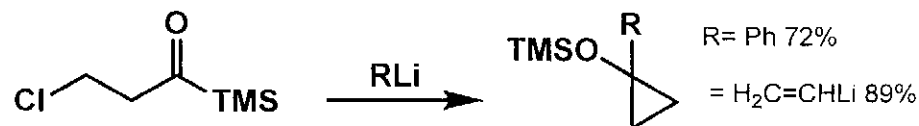
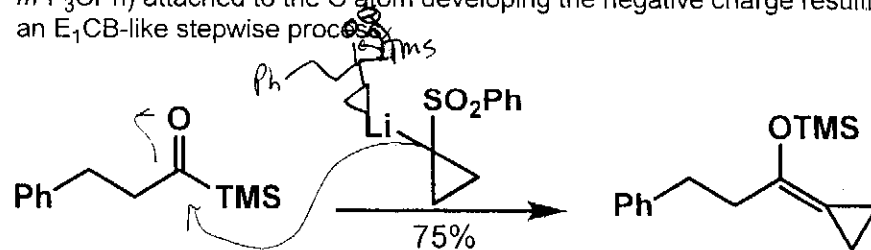
## Silyl Enol &amp; Allenol Ether Formation



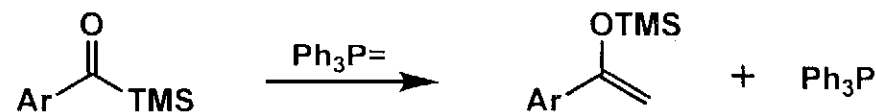
-formation of the *E*-enol ether is 1500x faster than the *Z*-enol ether due to the  $A_{1,2}$  strain between the Me and Bn groups

-C to O migration is a concerted process with development of negative charge at the C-Si carbon atom with simultaneous cleavage of the C-S bond

-selectivity decreases dramatically if there is a stabilizing group (ie: alkynyl or *m*-F<sub>3</sub>CPh) attached to the C atom developing the negative charge resulting in an E<sub>1</sub>CB-like stepwise process



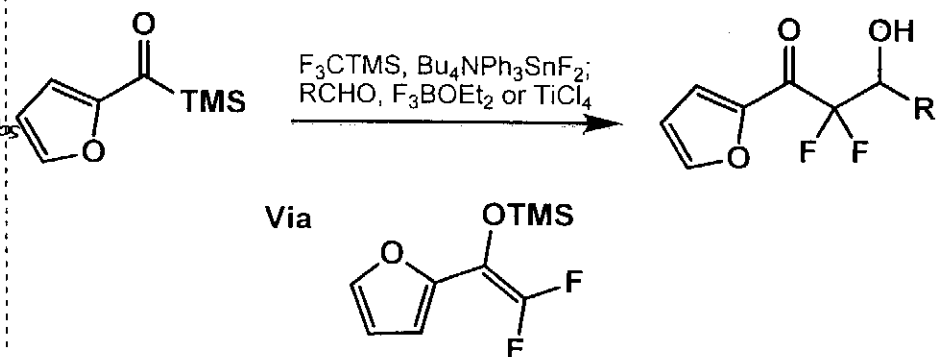
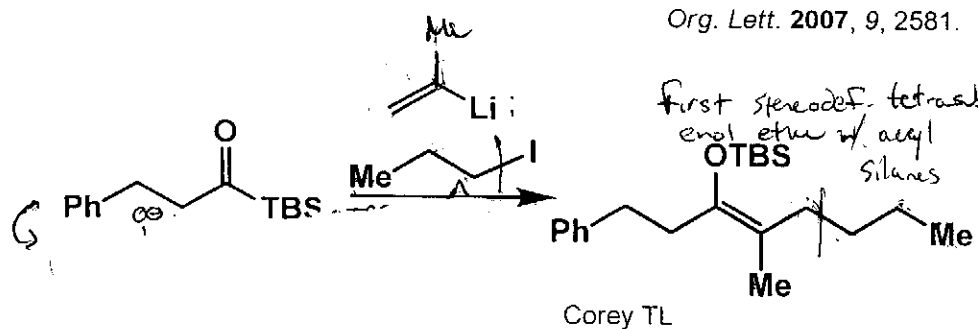
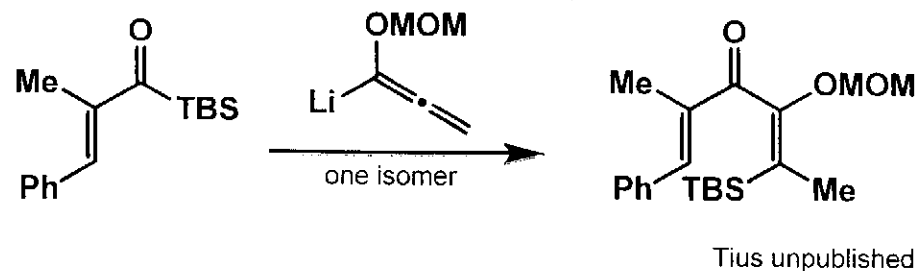
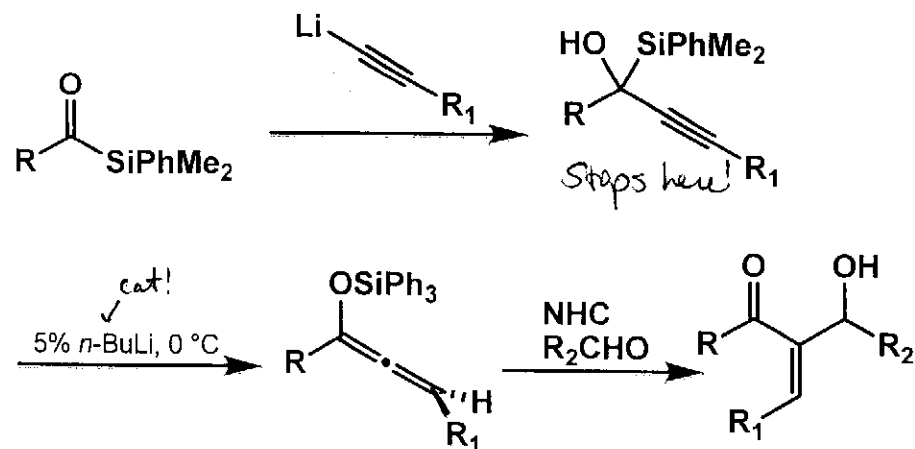
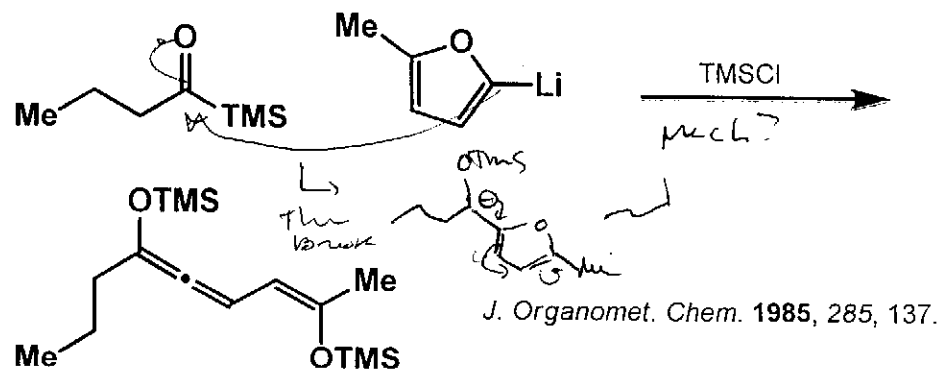
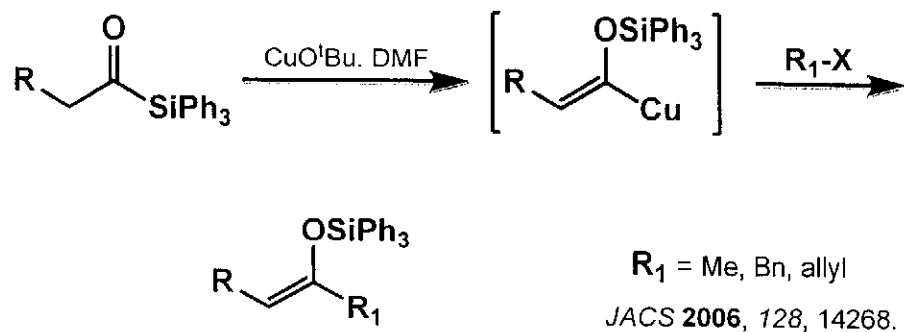
-R group must be able to stabilize the carbanion intermediate for this process to occur



But

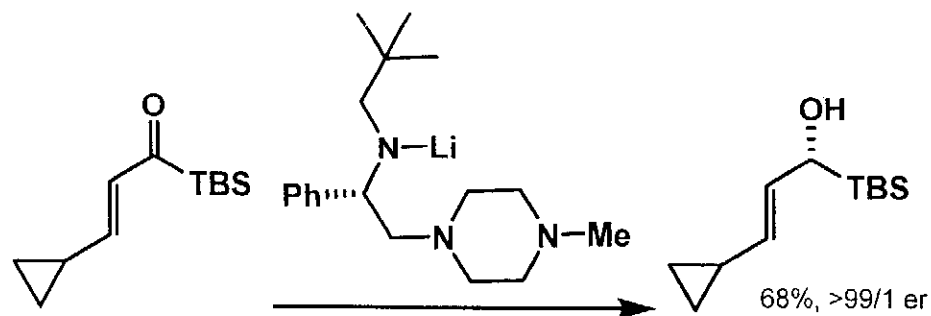
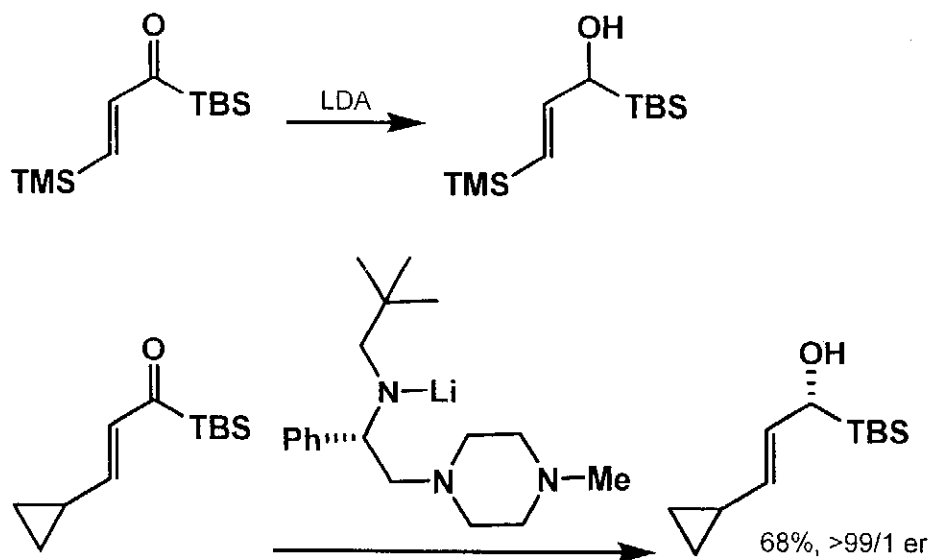


# Acylsilanes

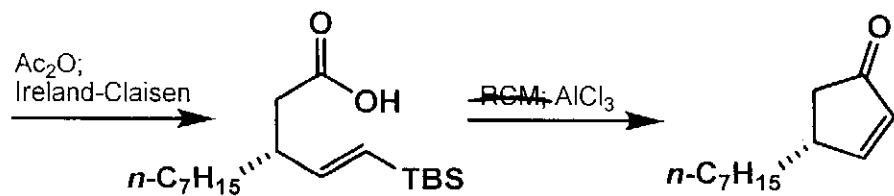
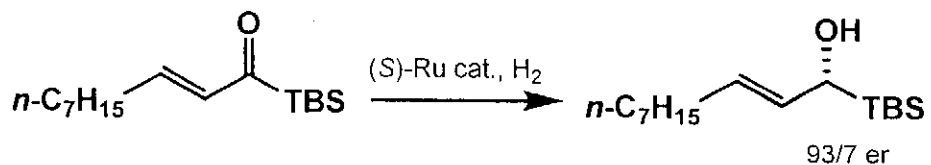


## Hydride Addition

-Brook observed that acylsilanes are susceptible to hydride transfer from RLi and RMgX. 8% for EtLi, 17% *n*-BuLi, 85% *s*-BuLi and 75% *t*-BuLi.

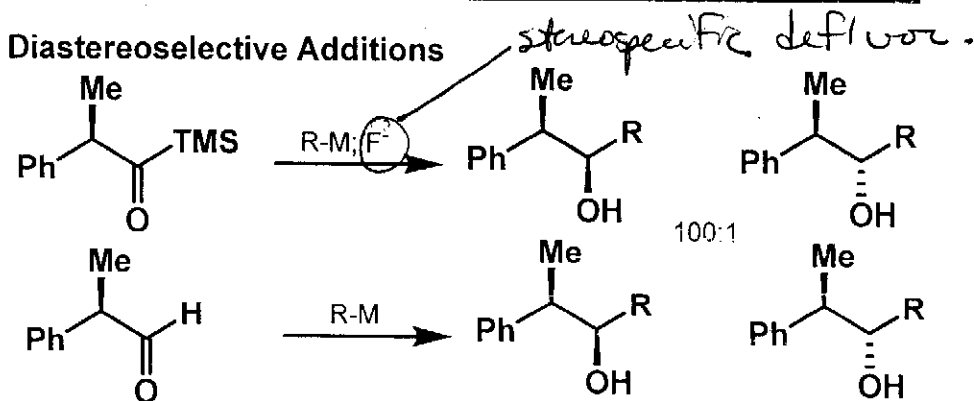


Takeda *Org. Lett.* 1999, 1, 237.

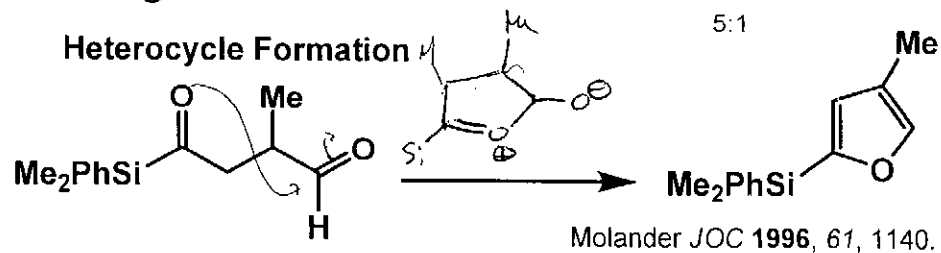


ACIE 2008, 47, 1770.

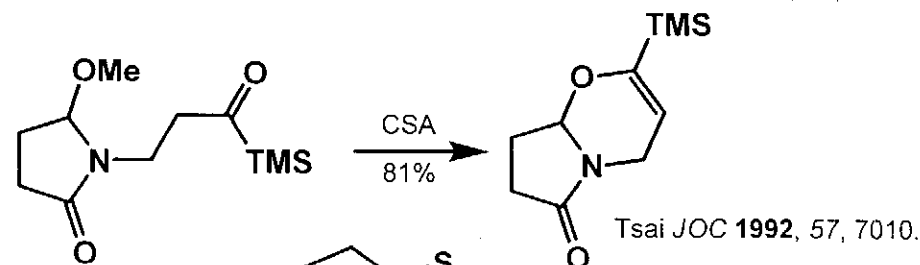
## Diastereoselective Additions



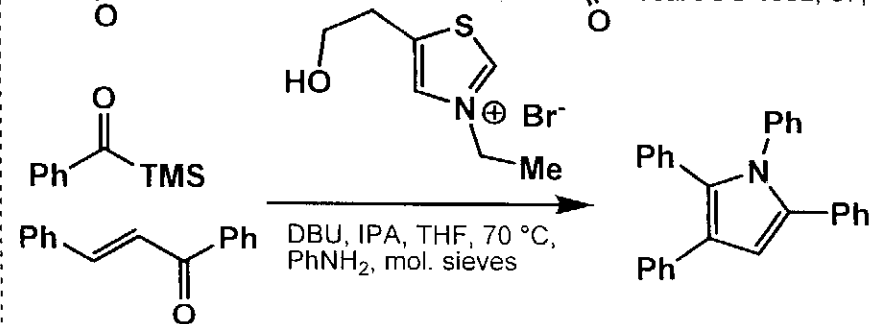
## Heterocycle Formation



Molander *JOC* 1996, 61, 1140.

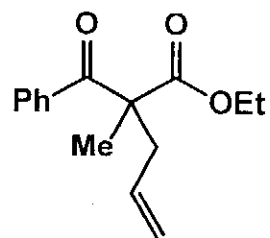
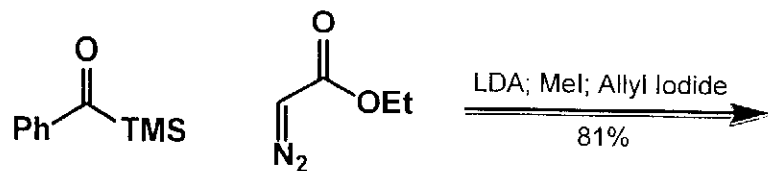
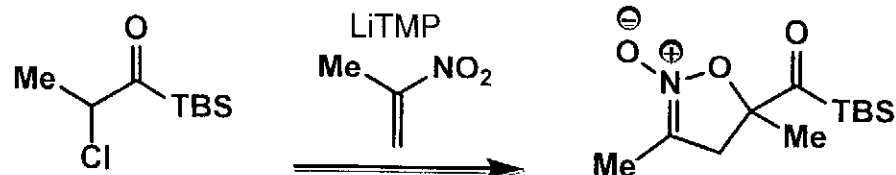
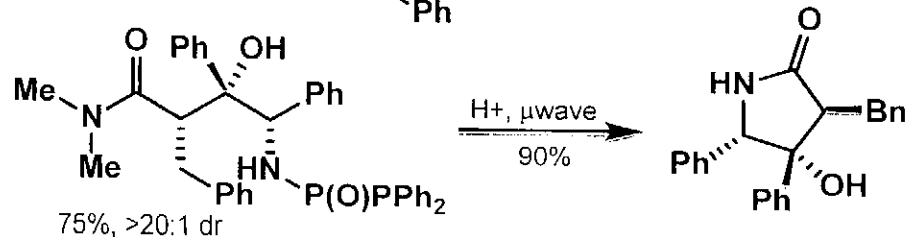
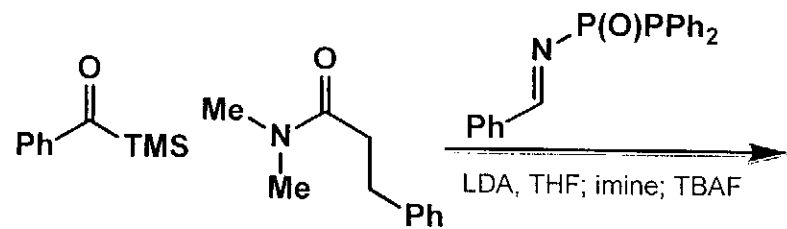


Tsai *JOC* 1992, 57, 7010.

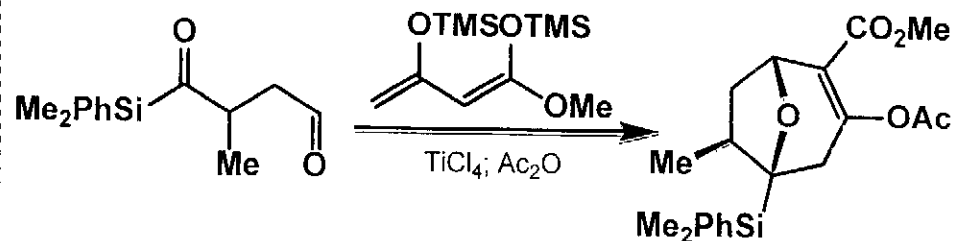
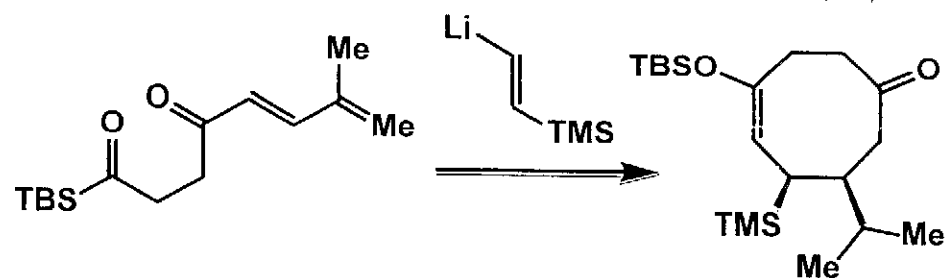
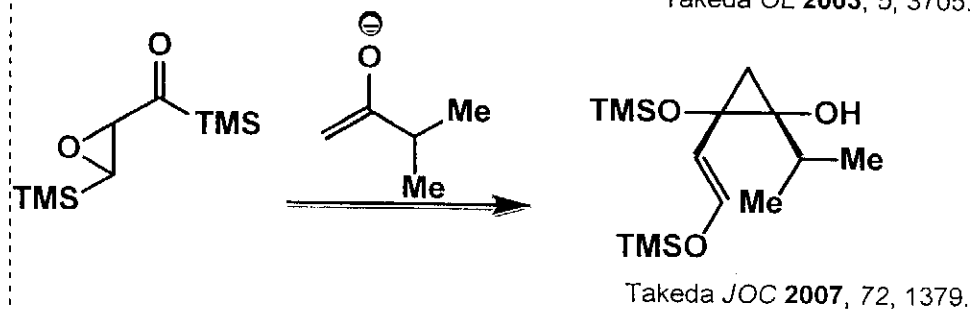
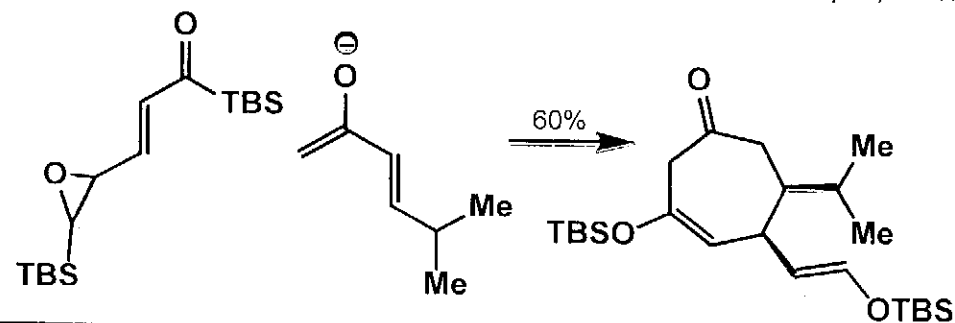


Johnson *OL* 2004, 6, 2465.

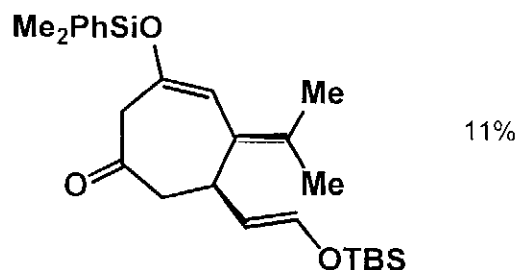
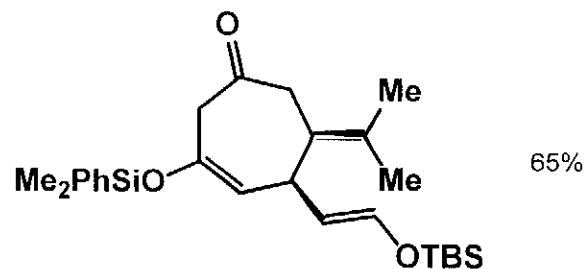
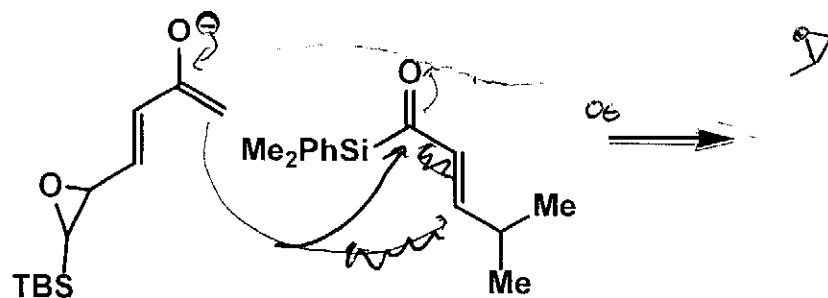
## Tandem Processes &amp; Cycloadditions

Scheidt *Chem. Commun.* 2008, 1926.Danheiser *Tetrahedron* 1988, 44, 4113.

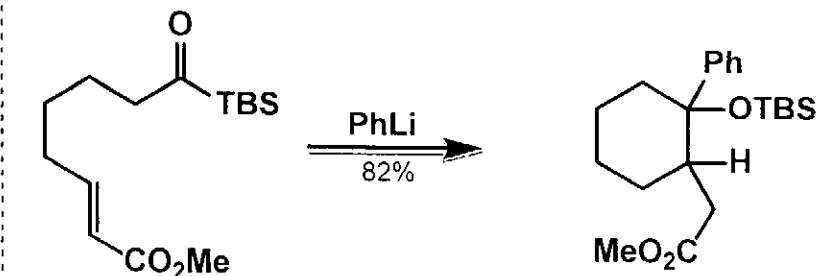
75%, &gt;20:1 dr

Scheidt *ACIE* 2008, 120, 2326.Molander *JOC* 1995, 60, 130.Takeda *OL* 2003, 5, 3705.Takeda *JOC* 2007, 72, 1379.

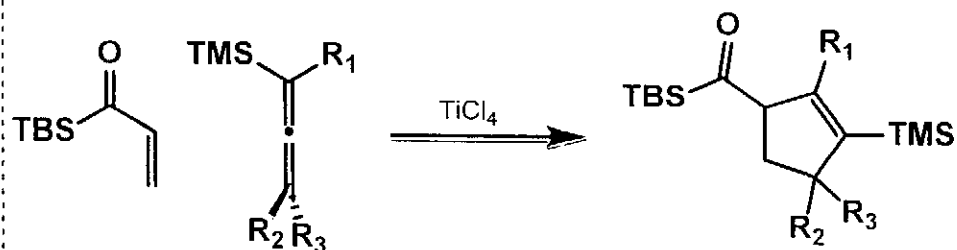
# Acylsilanes



Mechanism??

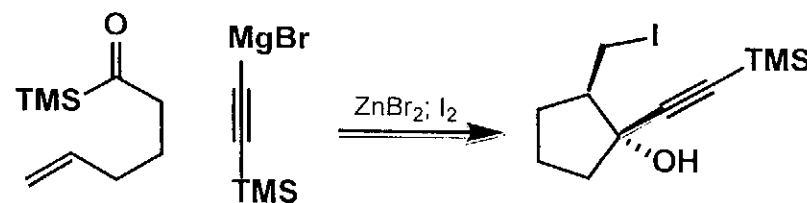
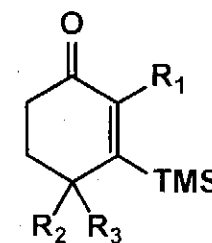


Takeda *Synlett* 1999, 6, 705.



-cyclopentenone products are formed at  $-78\text{ }^{\circ}\text{C}$   
while cyclohexenone products are formed above  $-78\text{ }^{\circ}\text{C}$

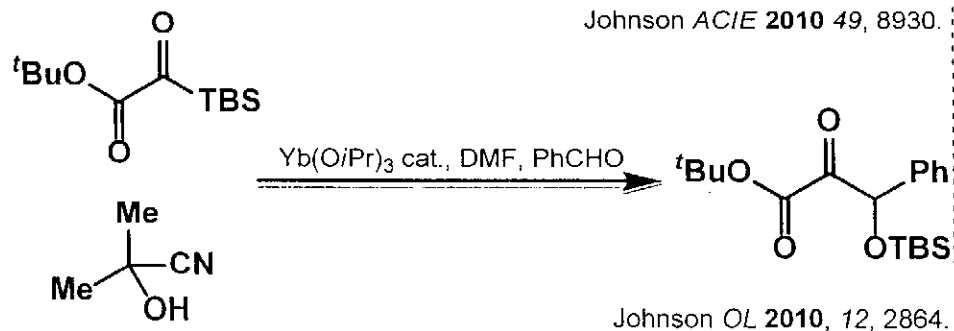
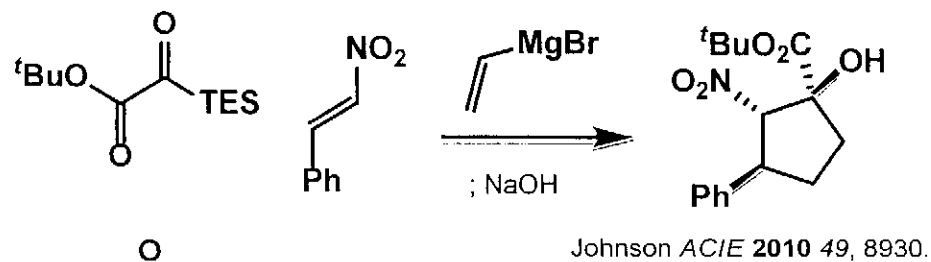
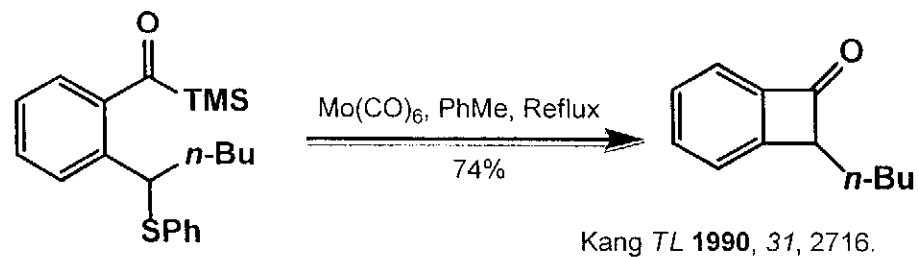
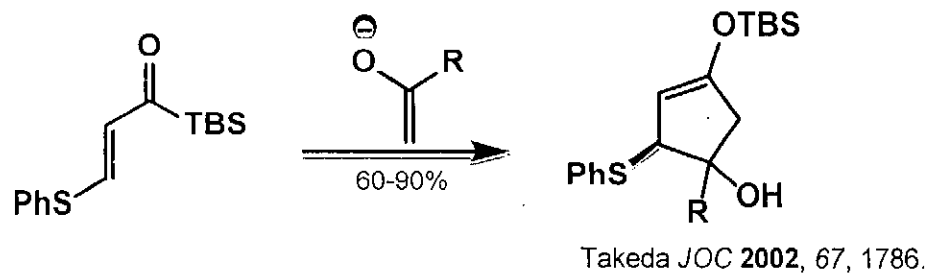
Danheiser *TL* 1986, 26, 2513.



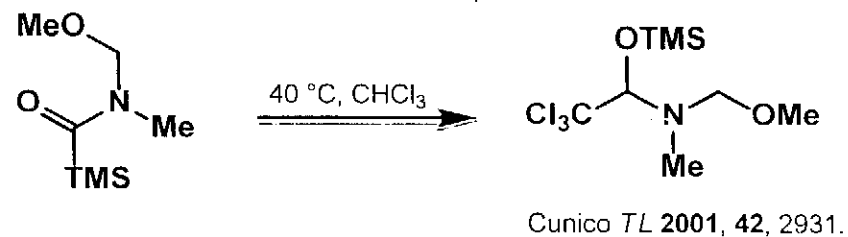
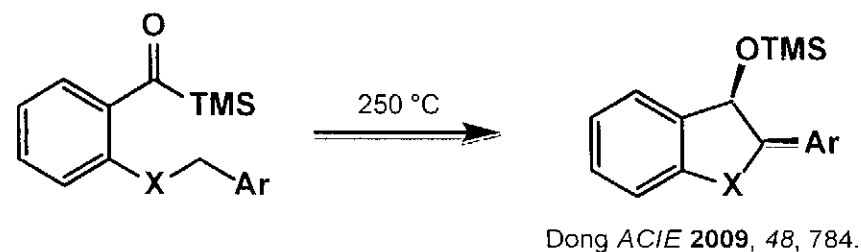
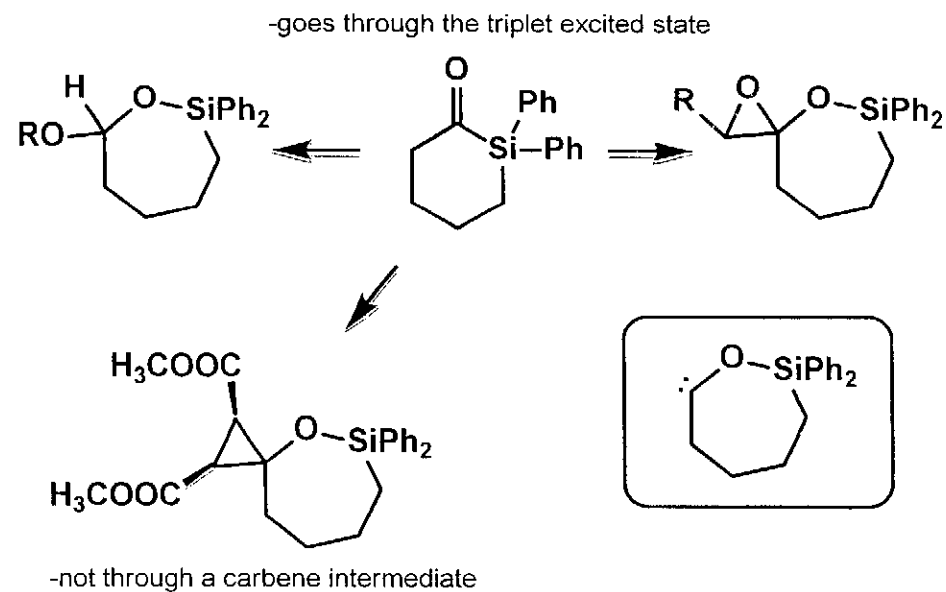
Mechanism??

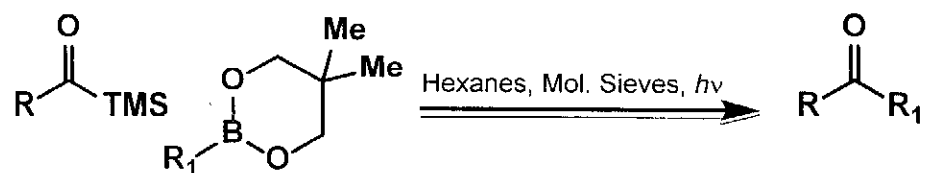
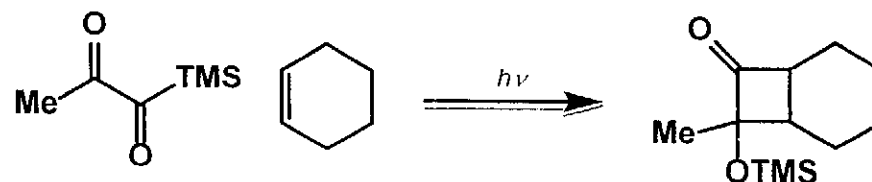
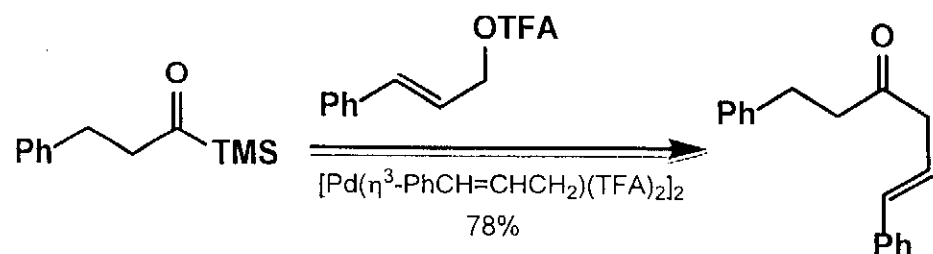
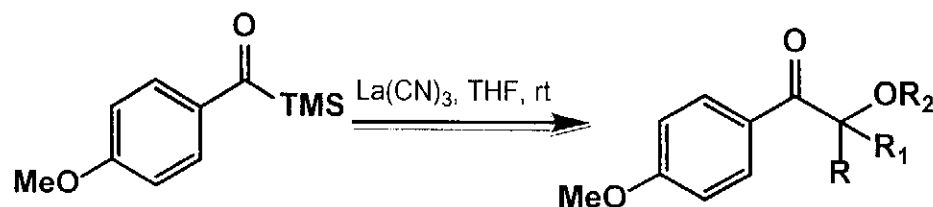
Marek *Eur. JOC* 2009, 1749.



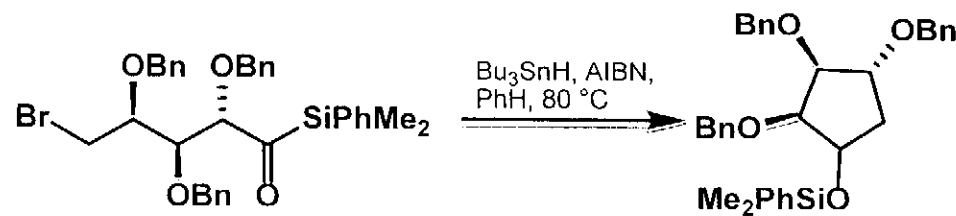


## Photochemistry &amp; Miscellaneous Rxns

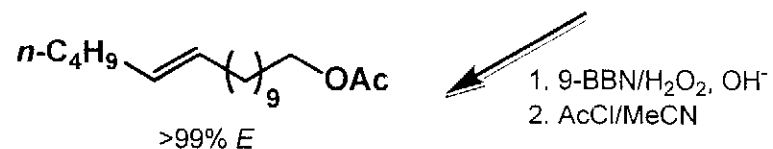
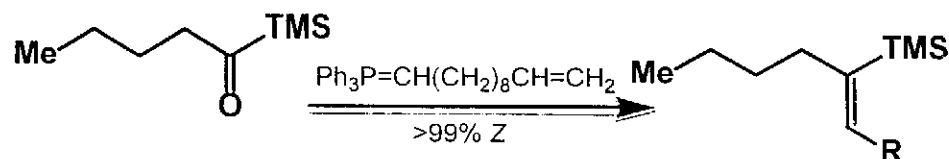
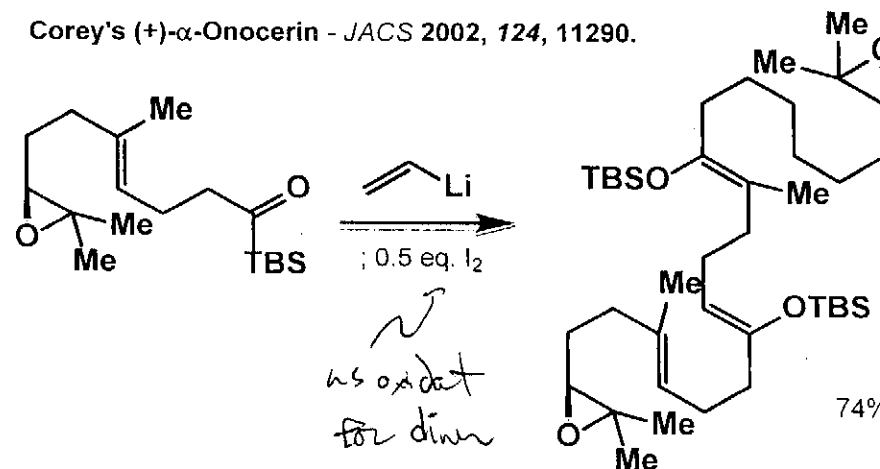


Kusama *JACS* 2011, 133, 3716.Wright *JACS* 1988, 110, 4457.Tsuji *JACS* 2001, 123, 10489.

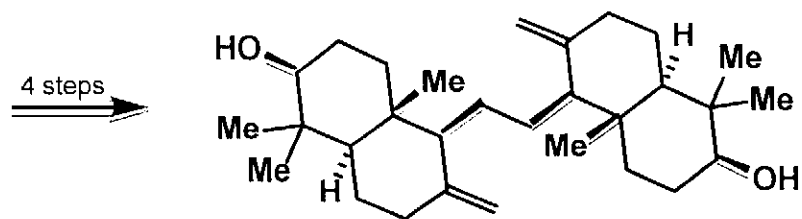
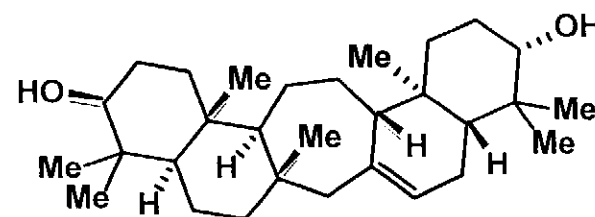
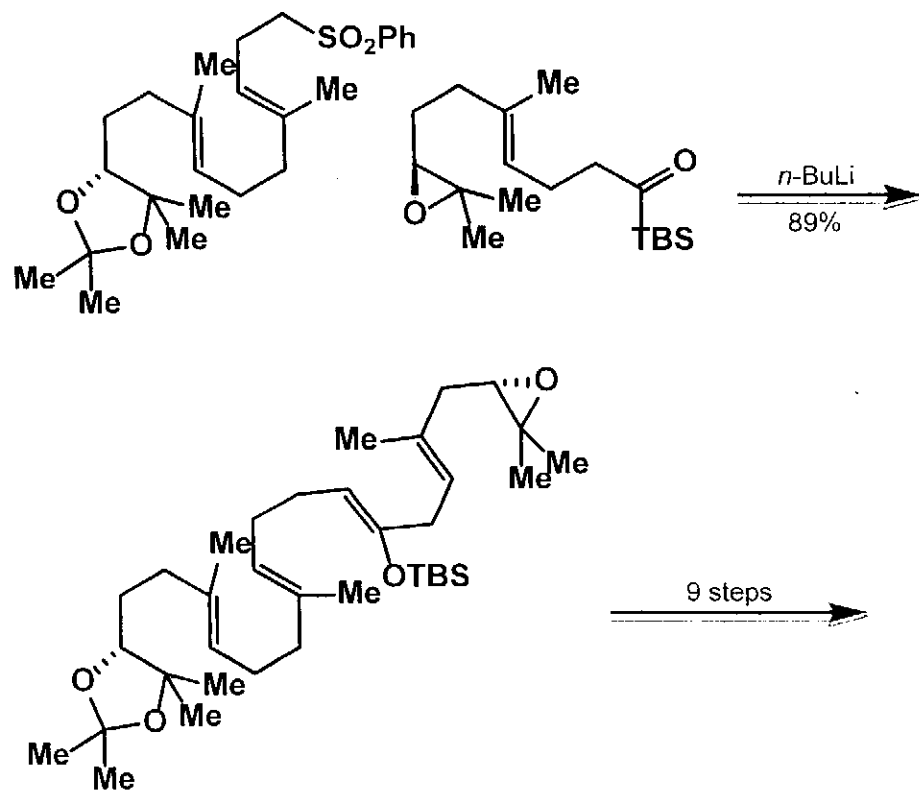
-works well with aldehydes and ketones

Johnson *JOC* 2010, 75, 3317.Tsai *TL* 2009, 50, 3805.

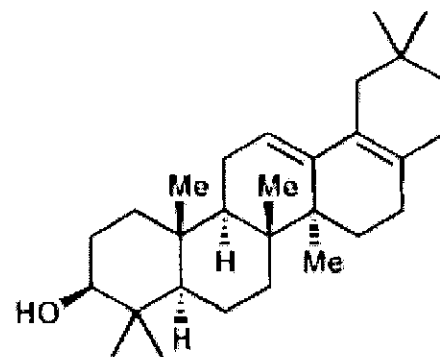
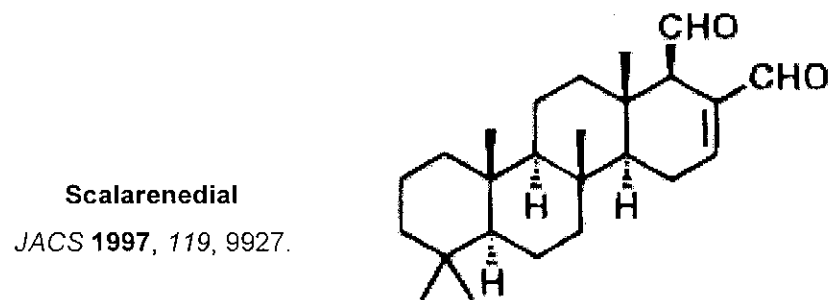
## Acylsilanes In Total Synthesis

Soderquist's Moth Pheromone Synthesis - *TL* 1988 29, 2777.1. 9-BBN/ $\text{H}_2\text{O}_2$ ,  $\text{OH}^-$   
2.  $\text{AcCl}/\text{MeCN}$ Corey's (+)- $\alpha$ -Onocerin - *JACS* 2002, 124, 11290.as oxidant  
for dimer

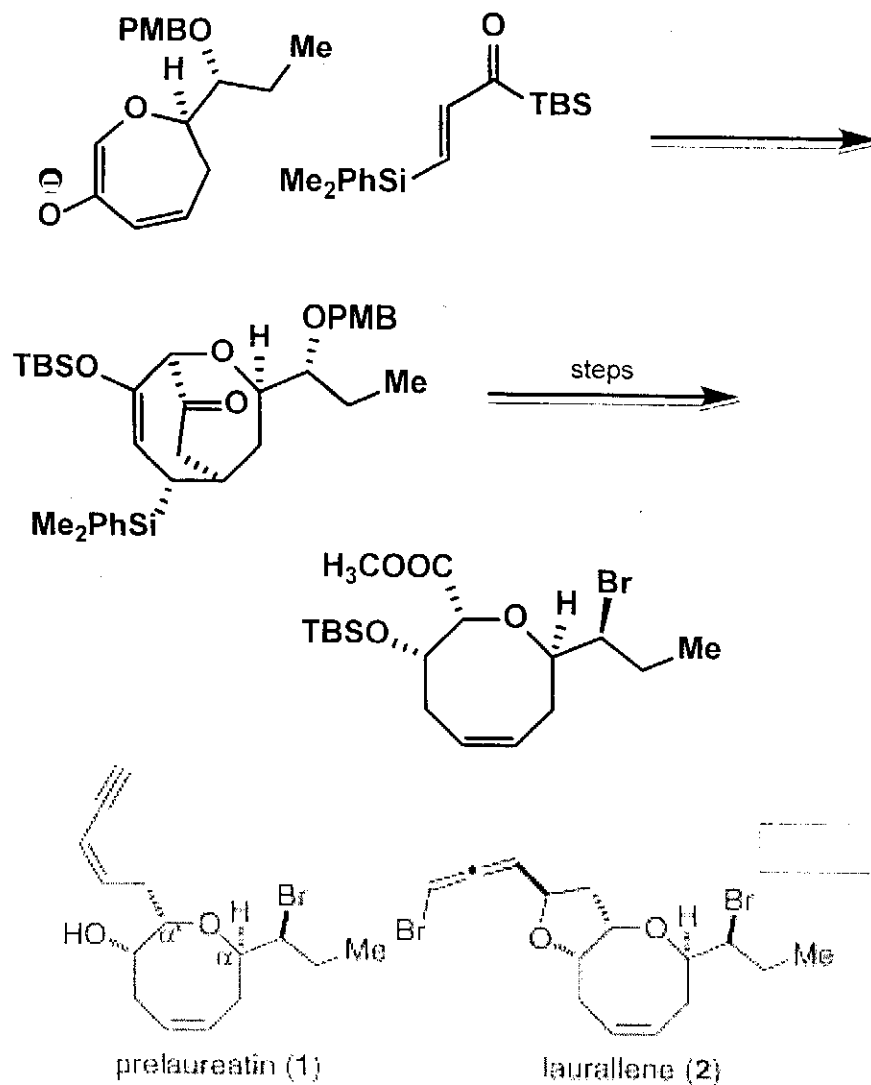
74%

Corey's Serratenediol *OL* 2001, 3, 3215.

Corey has also prepared the following NPs following a similar approach to those outlined above

Aegiceradienol  
*JACS* 1999, 121, 9999.Scalarenedial  
*JACS* 1997, 119, 9927.

Takeda's Formal Synthesis Of Prelaureatin & Laurallene -  
*JOC* 2010, 75, 3941.



Tsai's *ent*-Swainsonine - *Tetrahedron* 2011, 67, 1564.

