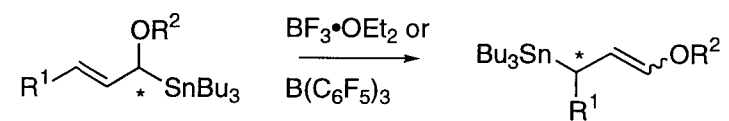


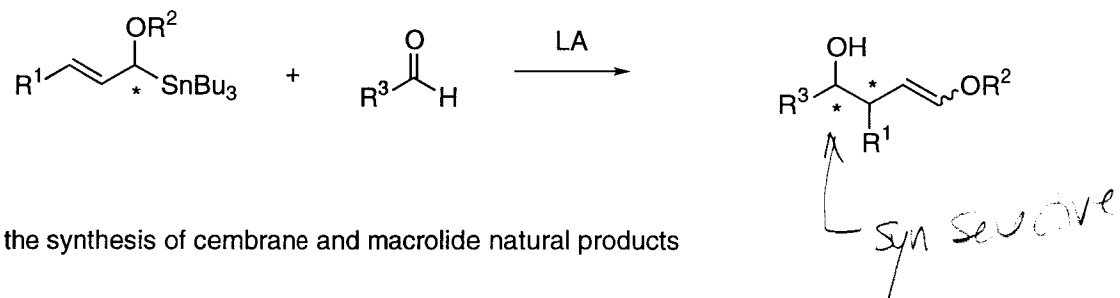
On the Isomerization of Allylic Stannanes



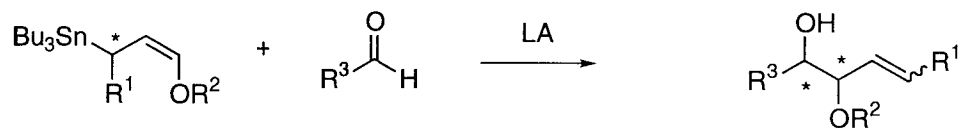
Marshall, J.A., Gill, K., *J. Organomet. Chem.* **2001**, 624, 294.

Utility of Chiral Allylic Stannanes

α -(Alkoxy) allyl stannanes

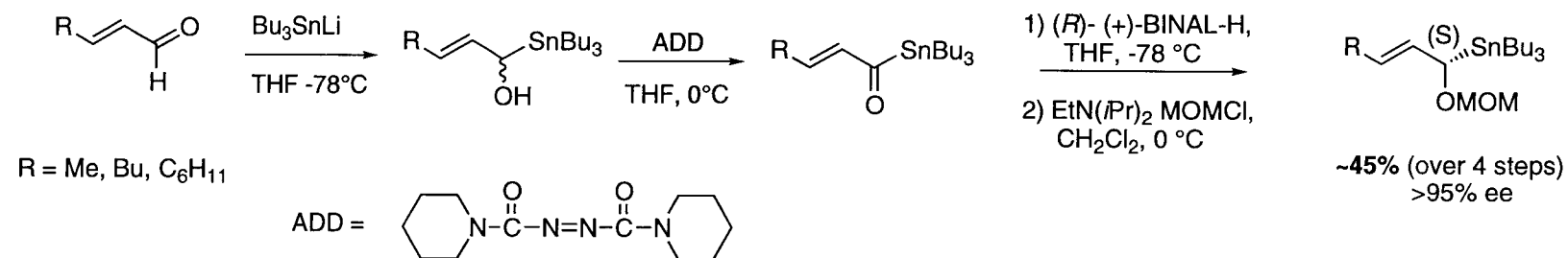


γ -(Alkoxy) allyl stannanes



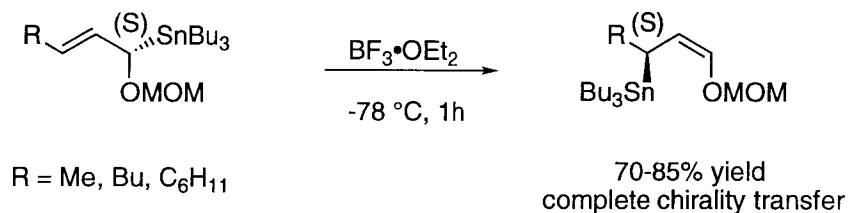
Synthesis of Chiral Allylic Stannanes

α -(Alkoxy) allyl stannanes



Chan, P. C.-M., Chong, J., M., *J. Org. Chem.* **1988**, *53*, 5584
 Marshall, J.A., Gung, W.-Y. *Tetrahedron*, **1989**, *45*, 1043

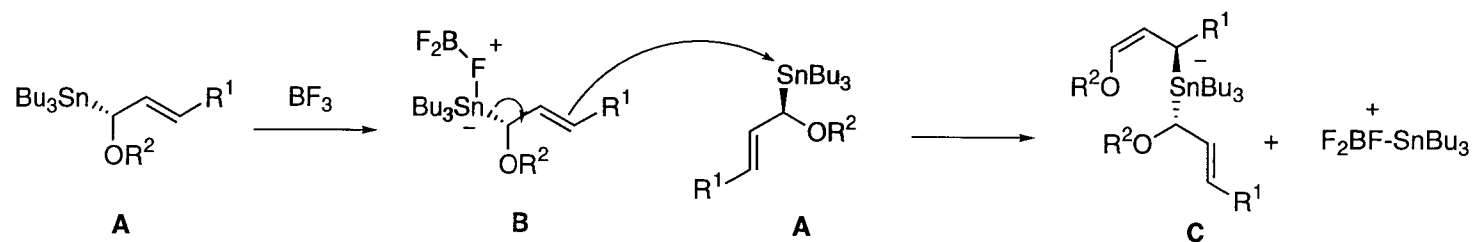
γ -(Alkoxy) allyl stannanes



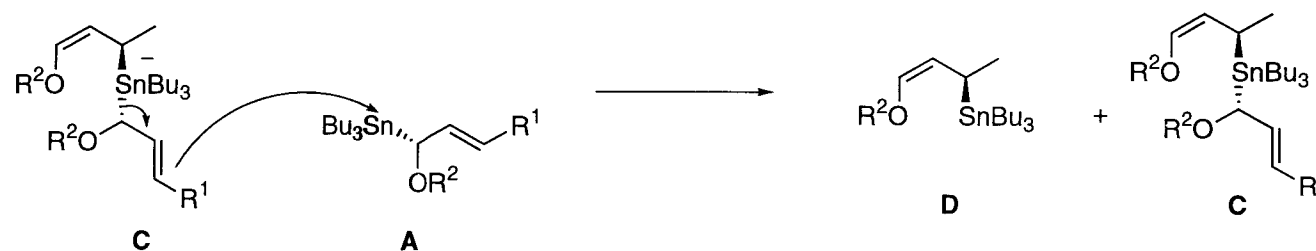
Marshall, J.A., Welmaker, G.S., Gung, B.W. *J. Am. Chem. Soc.* **1991**, *113*, 647.

Initial Mechanistic Proposal: Nucleophilic BF_3

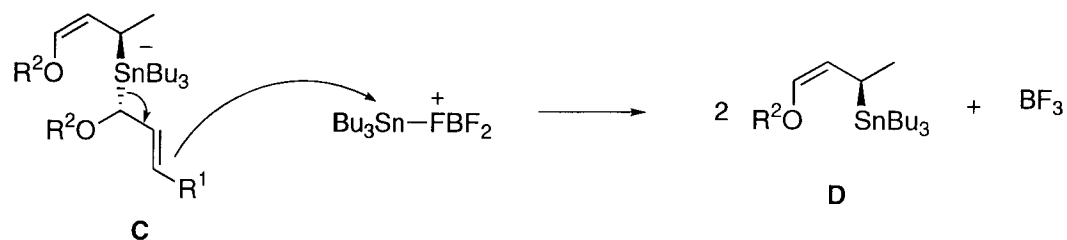
Initiation



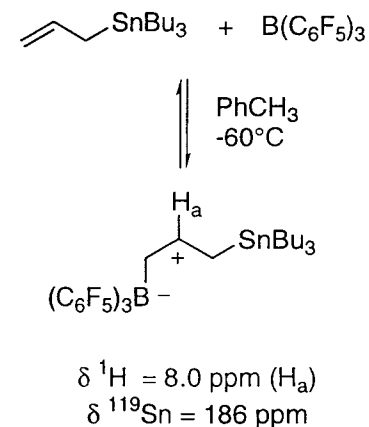
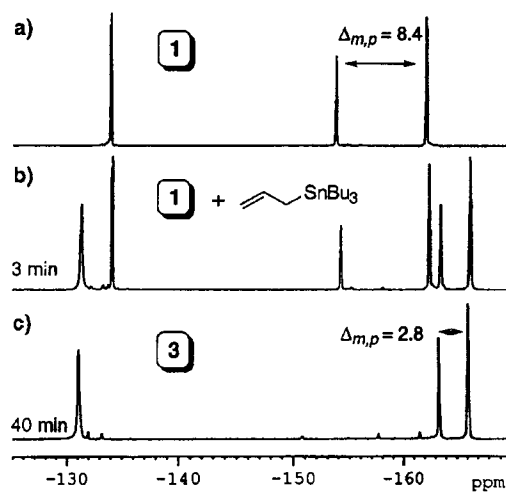
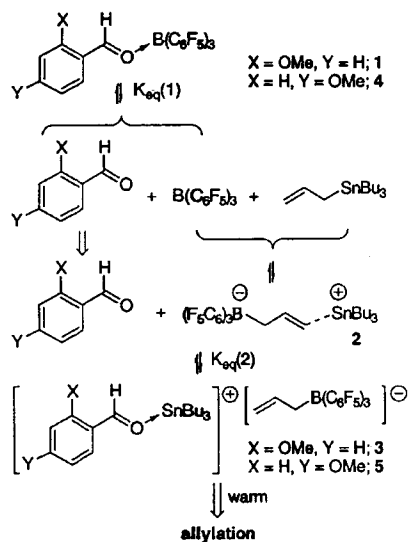
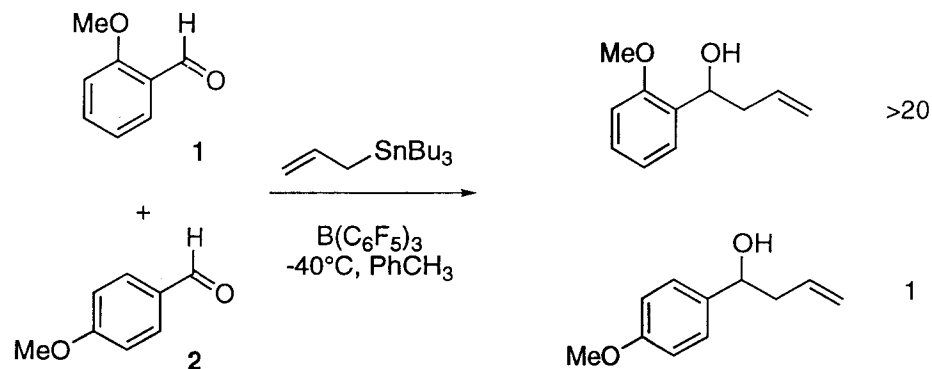
Propagation



Termination

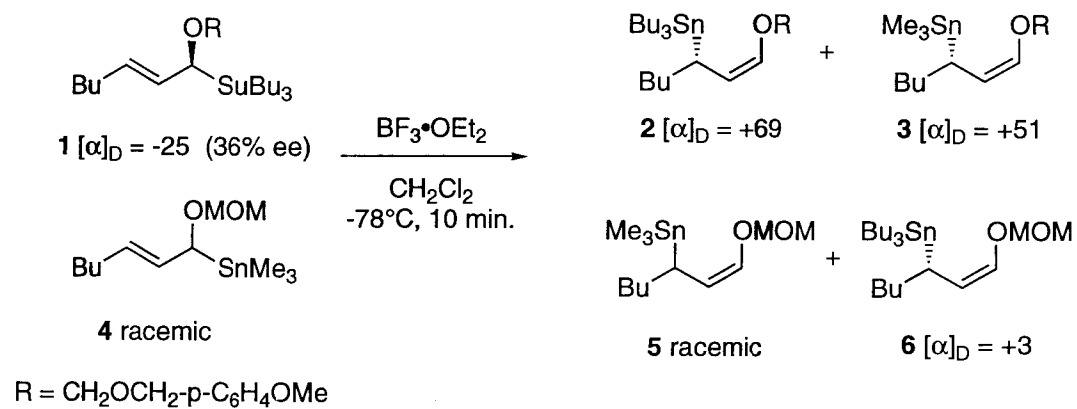


Piers NMR Study of B(C₆F₅)₃ Catalyzed Allylstannation



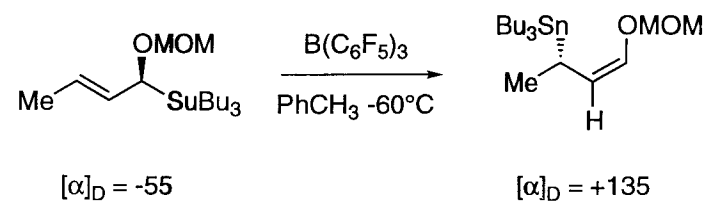
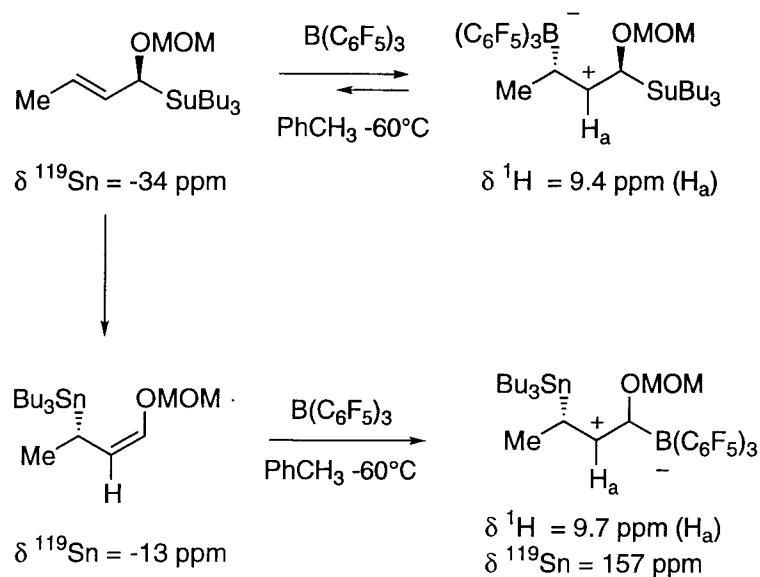
- The chemical shifts for H_a and Sn are consistent with both the Sn and C2 assuming considerable positive character

Marshall's Crossover Experiments



- The reaction is inter molecular. A 1:1 mixture of **1** and **4** gave rise to all four possible isomers in roughly equal amounts
- The reaction is bimolecular. This was demonstrated by dilution studies and that there is a slight enantioenrichment in **6**.

Marshall $B(C_6F_5)_3$ Catalyzed Isomerization Studies

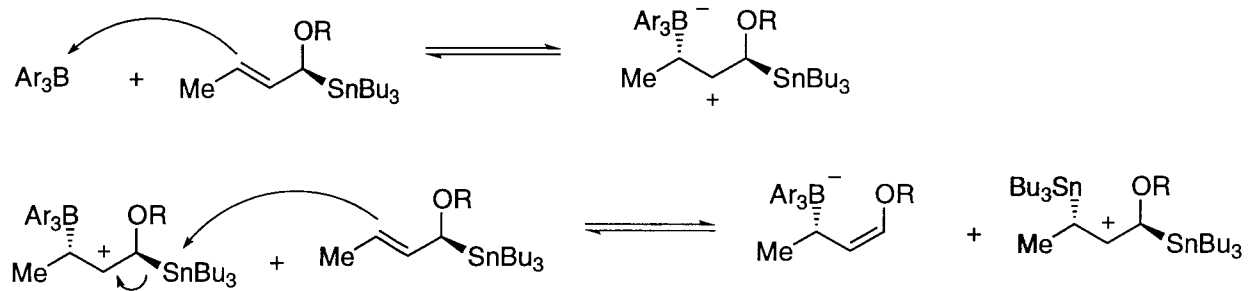


- Down field shift of Sn resonance indicative of cationic character to the Sn center
- A slight merging of the *meta* and *para* ^{19}F resonances of the C_6F_5 groups was observed indicating ate character at boron

8

Marshall's Revised Mechanism

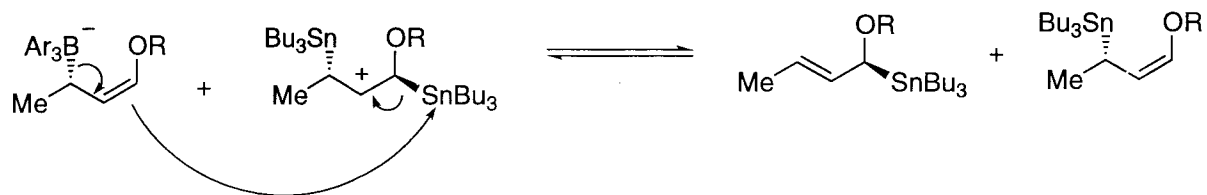
Initiation



Propagation

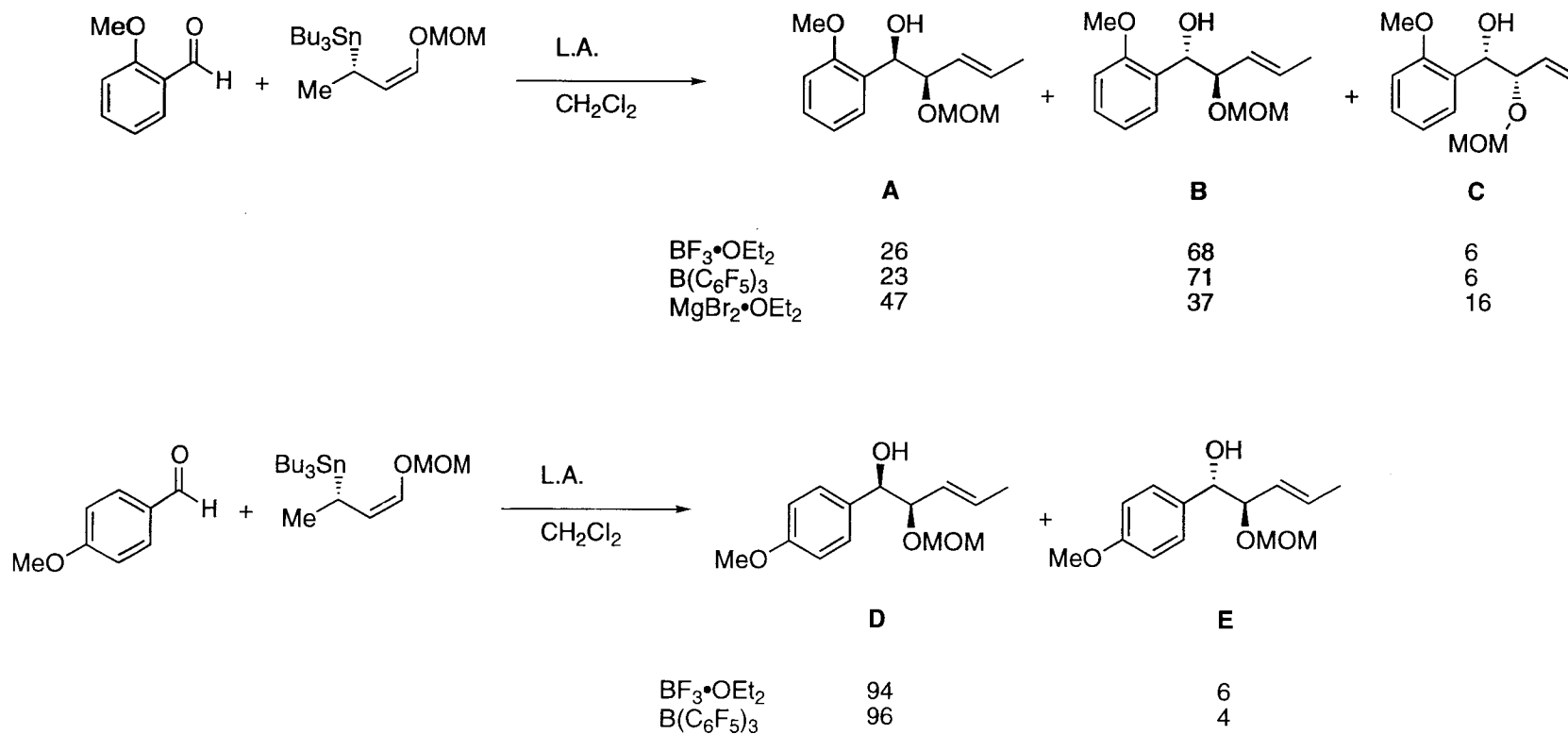


Termination



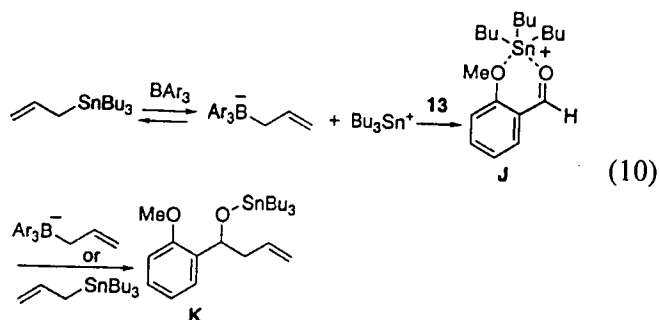
Comparison of $\text{BF}_3 \cdot \text{OEt}_2$ and $\text{B}(\text{C}_6\text{F}_5)_3$

- Attempts to detect the intermediates in the $\text{BF}_3 \cdot \text{OEt}_2$ catalyzed isomerizations by NMR were unsuccessful thus an analogy between the two Lewis Acids was drawn based on a product analysis of the allylation of *o*- and *p*-methoxybenzaldehyde

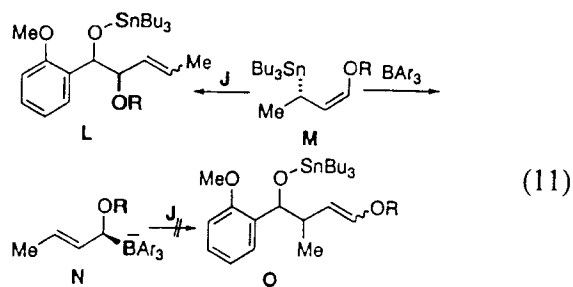


Rationale for rate enhancement with *o*-methoxy groups

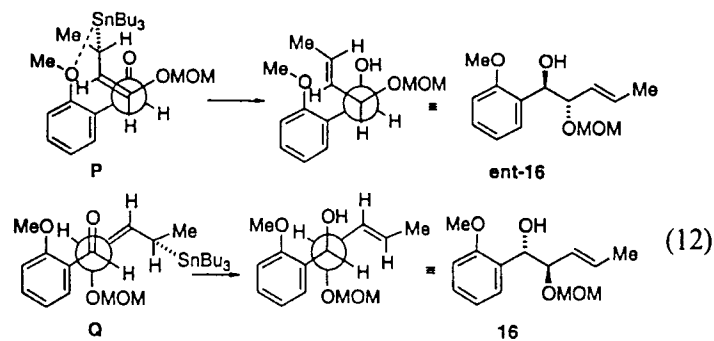
Rationale by Peirs



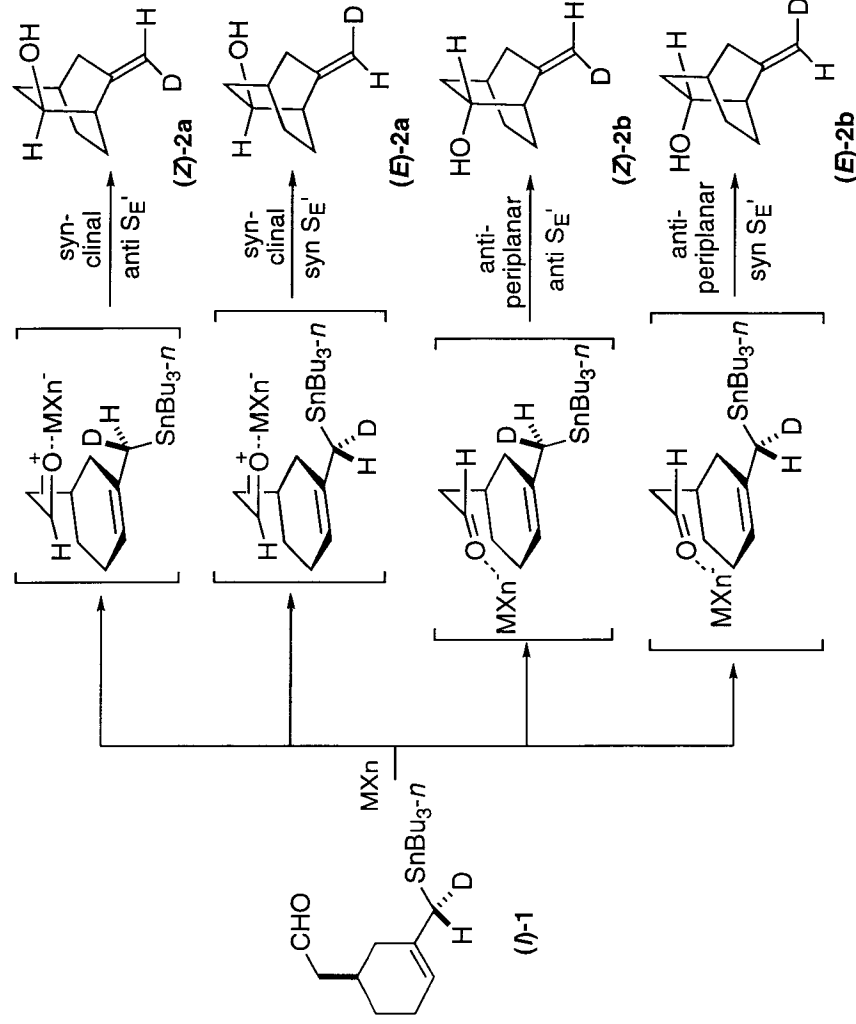
Marshall's rebuttal:



Marshall's rationale:



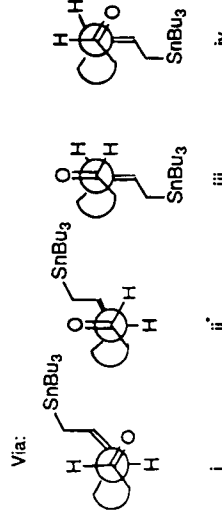
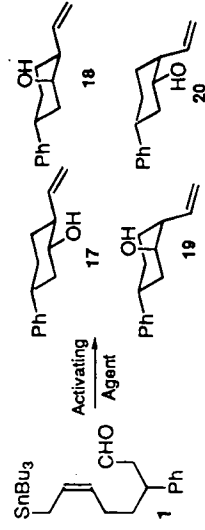
Denmark's Demonstration of the synclinal anti SE' addition of allylstannanes to aldehydes



entry	reagent	temp, °C (time, min)	proximal/ distal (2a/2b)	(2a) Z/E	(2b) Z/E	proximal anti/syn SE'	distal anti/syn SE'
1	TiCl ₄	-85 (10)	88/12	89/11	95/5	94/6	>99/1
2	SnCl ₄	-70 (5)	94/6	86/14	95/5	91/9	>99/1
3	SnCl ₄	-70 (5)	94/6	88/12	95/5	93/7	>99/1
4	BF ₃ ·OEt ₂	-70 (15)	86/14	92/8	95/5	97/3	>99/1
5	CF ₃ SO ₃ H	-70 (10)	97/3	93/7	-	98/2	-
6	CF ₃ CO ₂ H	-70 (10)	>99/1	93/7	-	98/2	-
7	CCl ₃ CO ₂ H	-70 (30)	99/1	93/7	-	98/2	-
8g	-	90	>99/1	5/95	-	<1/99	-

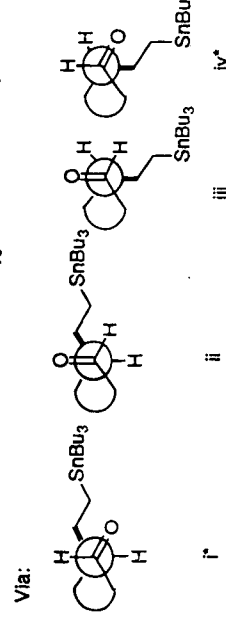
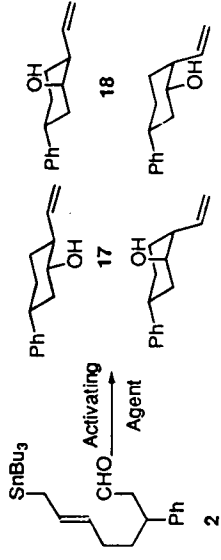
Keck's Demonstration of the synclinal anti SE' addition of allylstannanes to aldehydes

Table 1. Products Resulting from the Cyclization of 1

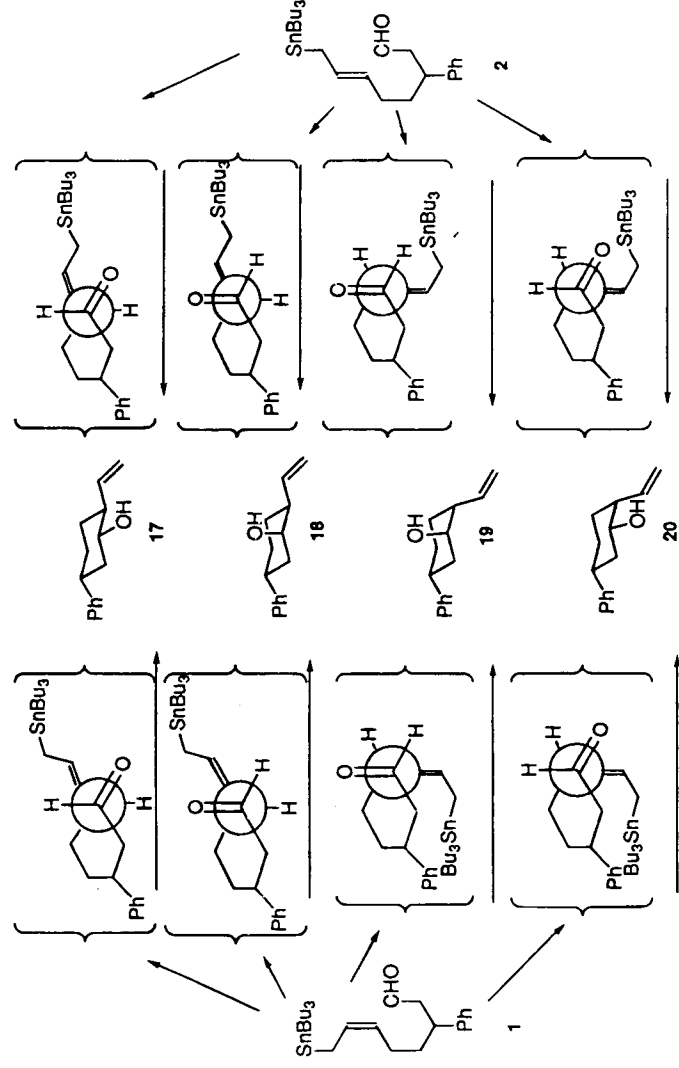


reagent	17	18*	19	20	time	temp (°C)
CF ₃ CO ₂ H	4	96	0	0	<20 min	-78 to +25
BF ₃ ·OEt ₂	15	85	<1	<1	<30 min	-78
MgBr ₂ ·OEt ₂	15	85	0	0	1 h	-23
TiCl ₄	5	91	≈1	<1	<10 min	-90
SnCl ₄	10	90	<1	<1	<10 min	-90
thermal	5	95	0	0	<12 h	25

Table 2. Products Resulting from the Cyclization of 2

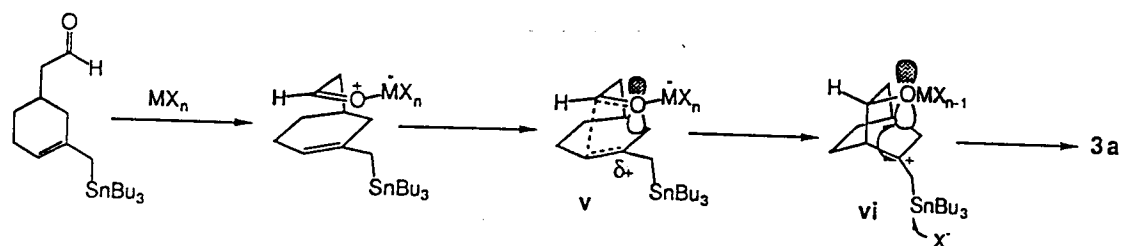


reagent	17*	18	19	20*	time	temp (°C)
CF ₃ CO ₂ H	81	6	1	8	3 h	-78 to +25
BF ₃ ·OEt ₂	60	24	6	6	30 min	-78
MgBr ₂ ·OEt ₂	55	32	2	11	1 h	-23
TiCl ₄	35	39	18	8	<5 min	-90
SnCl ₄	29	6	51	14	<10 min	-90
thermal	9	80	2	9	≈250 h	110



Rationale for synclinal attack of Stannanes

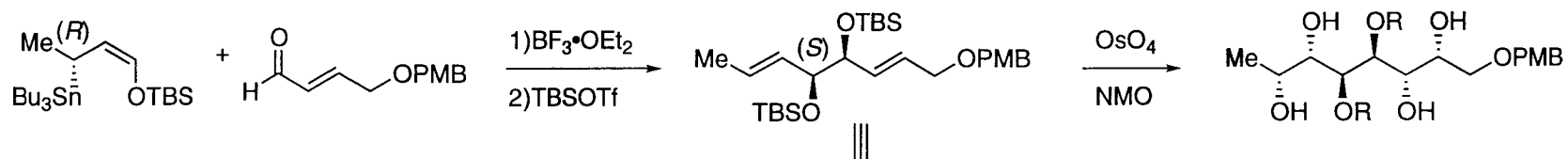
- Coulombic attraction: unsymmetrical transition state **v** would be favored in non-polar solvents due to smaller charge separation



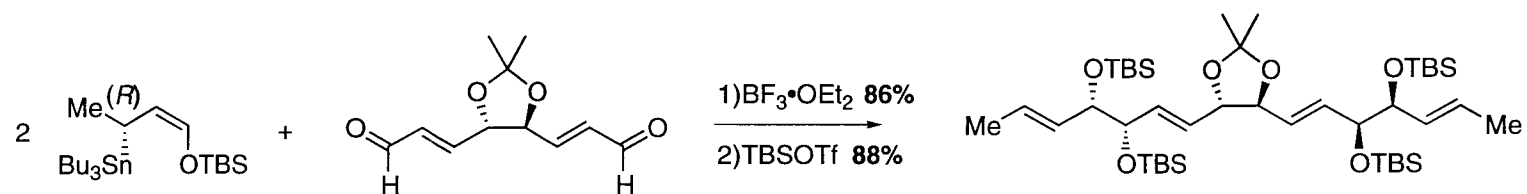
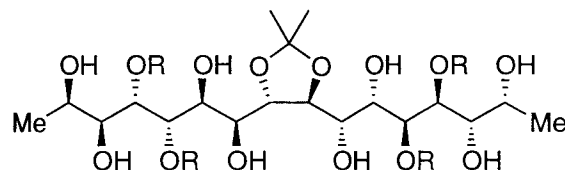
- Secondary orbital overlap: In-phase overlap between oxygen and the metal bearing carbon is present only in the synclinal transition **vii**



Polyol Synthesis via γ (Silyloxy) Allylic Stannanes



R = TBS

OsO₄, NMO 55%

R = TBS

Marshall, J.A., *Chem Rev.* **1996**, *96*, 31.Gung, B.W., Melnick, J.P., Wolf, M.A., Marshall, J.A., Beaudoin, S., *J. Org. Chem.* **1994**, *59*, 5609.

Conclusions

- $\text{BF}_3 \cdot \text{OEt}_2$ acting as a nucleophile was discarded
- Electrophilic activation of the olefin by the Lewis acid followed by attack at the Sn is now believed to be the operative mechanism
- This isomerization mechanism can be used to explain the Lewis acid catalyzed isomerization of other allylic stannanes (*E-Z* crotyl stannane isomerization).
- Alkyl tin centers are subject to nucleophilic attack and can form hypercoordinate ate complexes