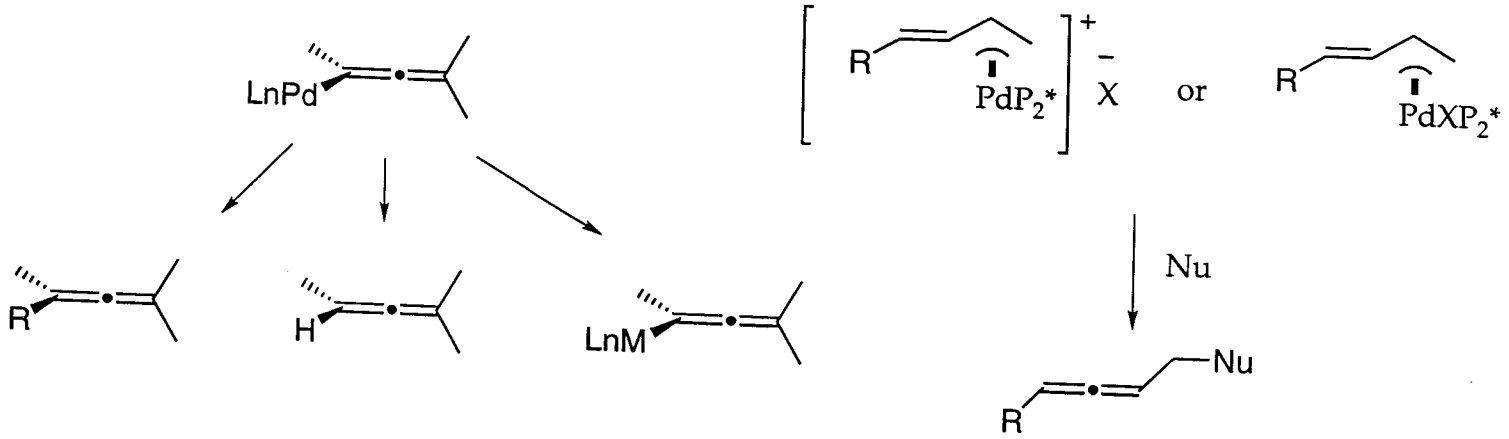
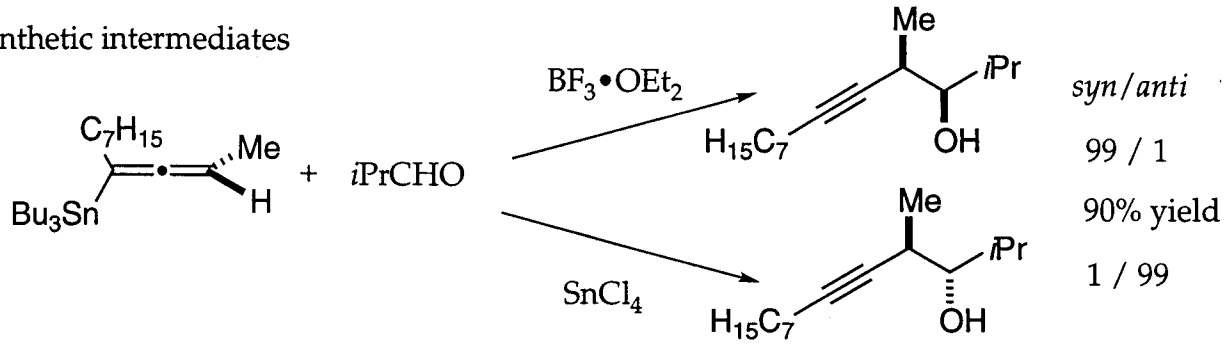
Yu Fan May-8-2001

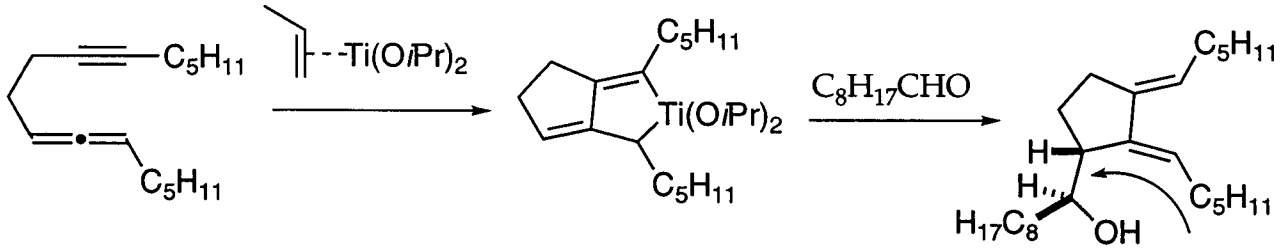
Palladium Catalyzed Asymmetric Synthese Of Chiral Allenes



Allenes as useful synthetic intermediates

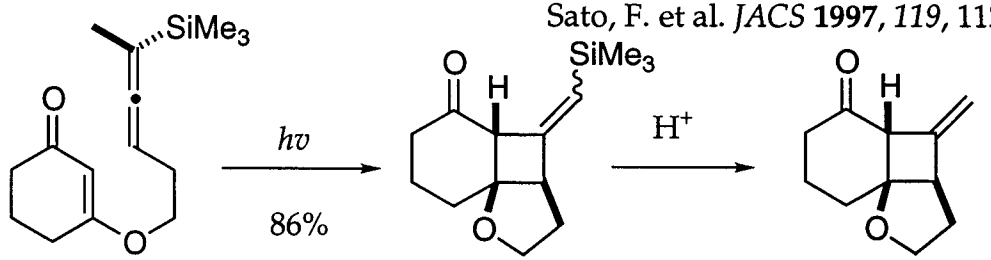


Marshall, J. A. *Chem. Rev.* **1996**, *96*, 31-47.



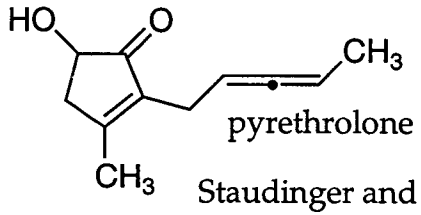
d.r. 93 / 7
yield 62%

Sato, F. et al. *JACS* **1997**, *119*, 11295-11305.



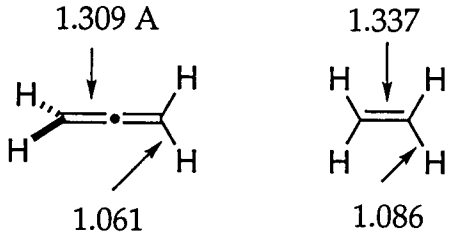
Carreira, E. M. el al. *JACS* **1997**,*119*, 2597-2605.

The first chiral allenic natural product



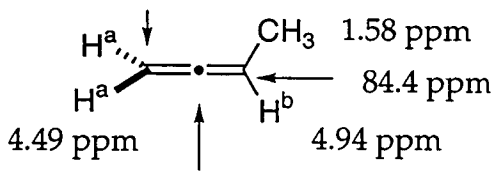
Staudinger and Ruzicka, 1924

cructure and Properties



UV_{max}	171 nm	175 nm
IR	1950-1960 cm^{-1}	
HOMO	-10.13 ev	-10.19 ev
LUMO	5.01 ev	5.05 ev

NMR 74.1 ppm



$J_{Ha, Hb} = 6.67$
$J_{H, CH3} = 3.37$

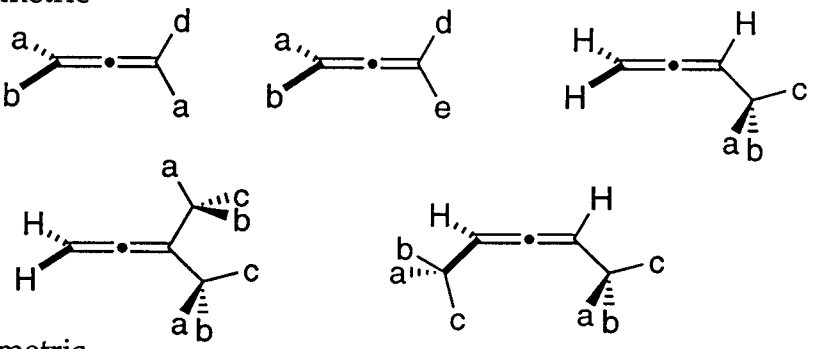
Allenes are like olefins in terms of chemical reactivities.

Ref. Allenes in Organic Synthesis,
Schuster H. F., Coppola G. M.
John Wiley & Sons. 1984

Chiral allene types

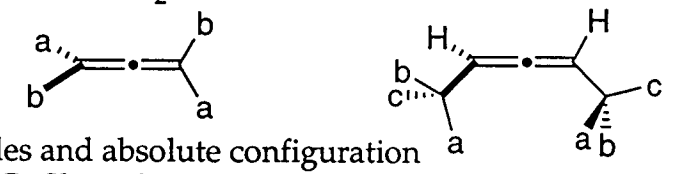
racemization barrier 46, 47 kcal/mol

asymmetric



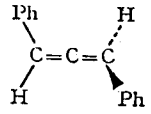
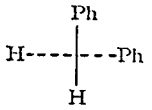
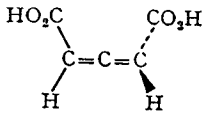
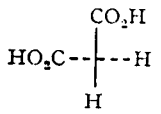
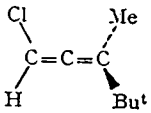
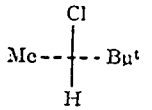
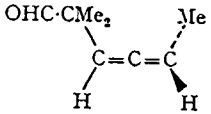
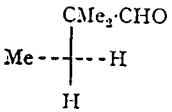
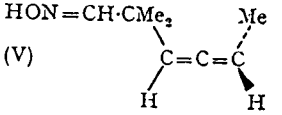
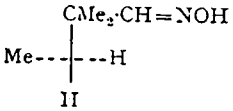
dissymetric

contains a C_2 axis

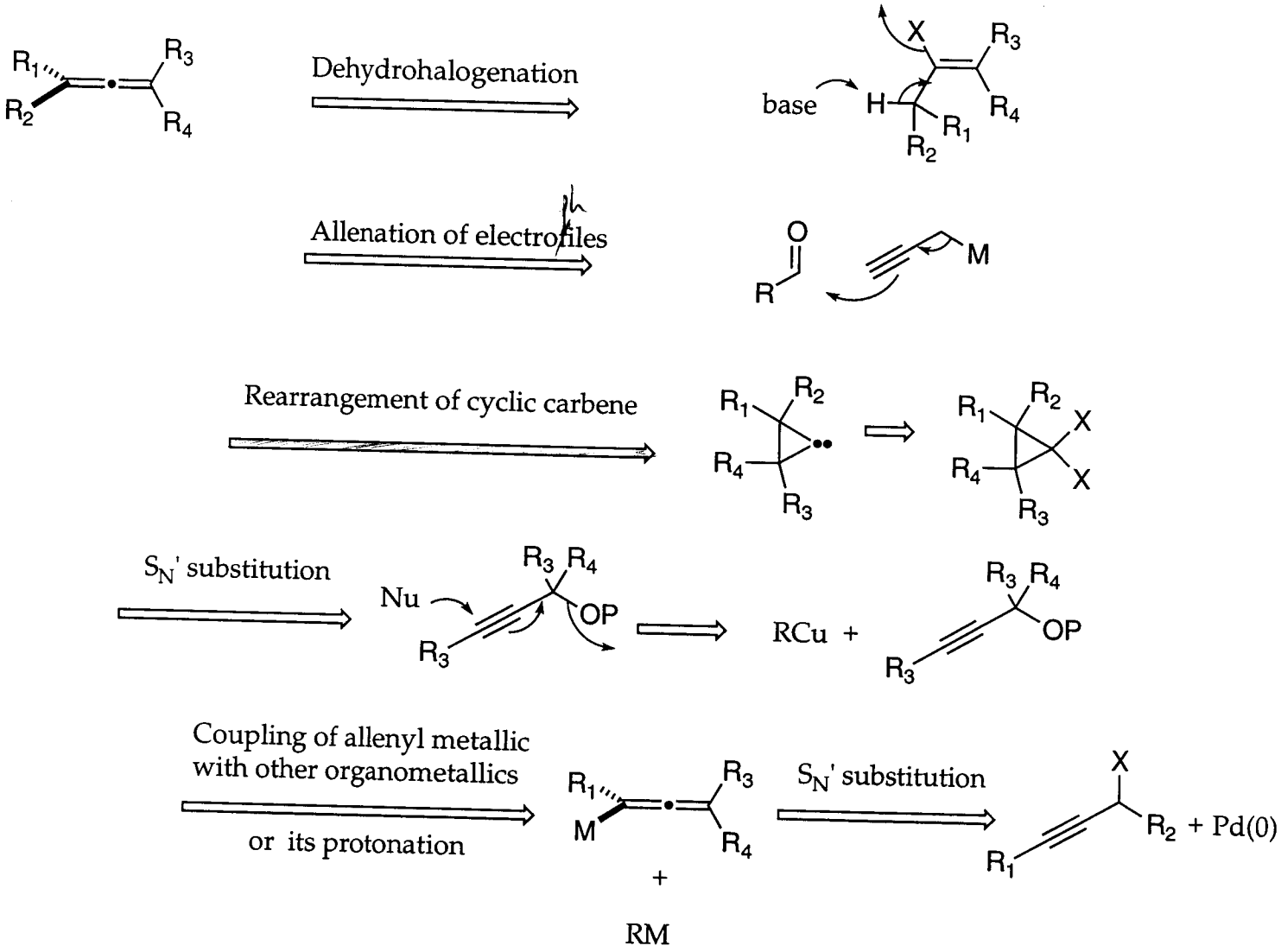


CIP rules and absolute configuration
Lowe, G. *Chem. Commun.* **1965**, 411

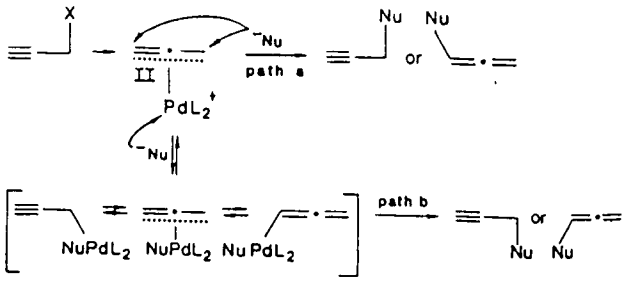
for 1,3-disubstituted allenes

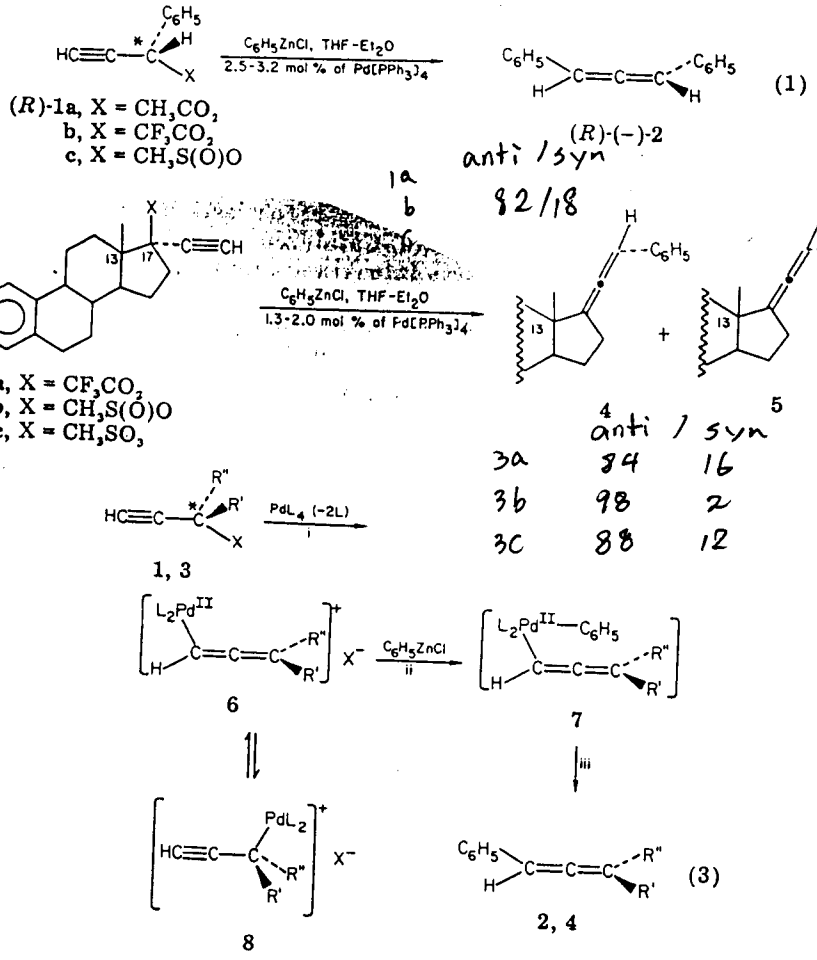
	Absolute Configuration of the Allene	*View along the Orthogonal axes*	*Screw pattern of Polarizability*	*Sign of* $[\alpha]_D$	*Configura Type*
(I)			clockwise	+ve	*S*
(II)			anticlockwise	−ve	*R*
(III)			anticlockwise	−ve	*S*
(IV)			anticlockwise	−ve	*R*
(V)			anticlockwise	−ve	*R*

Conceptually,



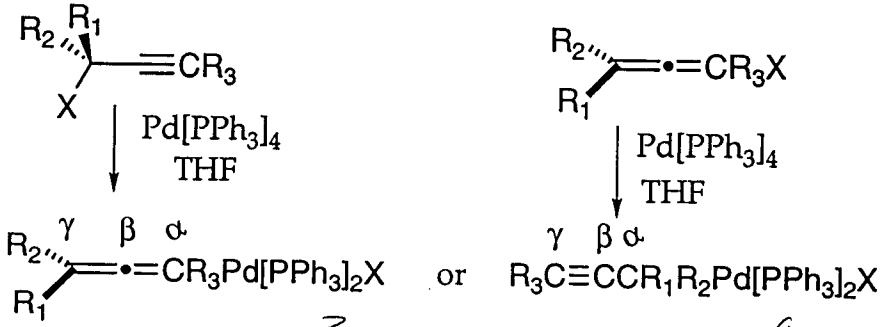
Anti stereoselectivity in Pd catalyzed allene synthesis



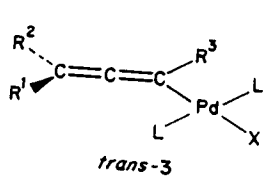


Vermeer P et al. *JOC* **1983**, *48*, 1103-1105.

Synthesis of σ-allenyl palladium complexes

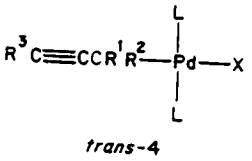


IR	1900 cm^{-1} ~ 3	2150 cm^{-1} ~ 4
^1H NMR	$R_3 = H$	
	$J_{P,H\alpha} = 6\sim9$ HZ	
^{13}C NMR	$C_\beta = 190-200$ ppm	$C\beta, C\gamma$ = 80 -100 ppm
^{31}P NMR	20 ppm, one sharp signal	



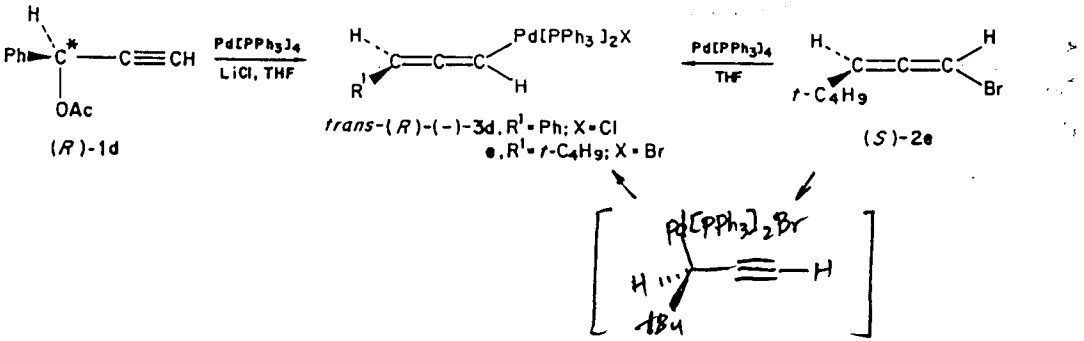
trans-3

1-4	R^1	R^2	R^3	X
1a, 2a, 3a	CH_3	CH_3	H	Cl
1b, 3b	C_5H_{10}		H	Cl
2c, 3c	t-C_4H_9	CH_3	H	Cl
1d, 3d	C_6H_5	H	H	Cl
2e, 3e	t-C_4H_9	H	H	Br
1f, 3f	CH_3	H	CH_3	Cl
1g, 4g	H	H	t-C_4H_9	Cl
1h, 4h	H	H	$Si(CH_3)_3$	Cl



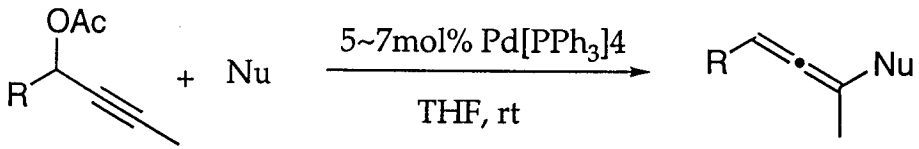
trans-4

Stereochemical outcome



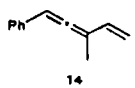
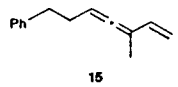
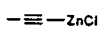
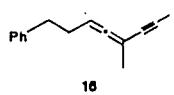
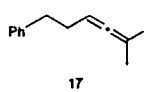
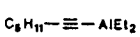
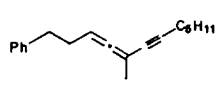
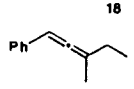
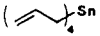
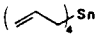
Vermeer P et al. *Organometallics* **1986**, *5*, 716-720.

Palladium Catalyzed Propargyl Alkylation

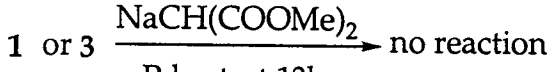


1, R = Ph; 3, R = $PhCH_2CH_2$

Table I. Palladium(0)-Catalyzed Propargylic Substitution[a]

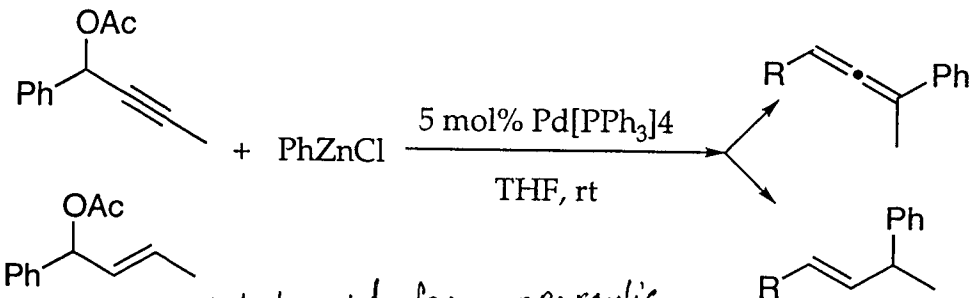
substrate	nucleophile	time (h)	product	yield (%)
1		0.8	 14	36
3		2	 15	68
3		96	 16	39
3	MeZnCl	40	 17	62
3		12	 18	87
1	Et_3Al	3	 19	68
1		48	no reaction	
3		72	no reaction	

[a] All reactions were carried out according to the general procedure given in the Experimental Section. Yields are of isolated products.



Keinan E. et al. *JOC.* **1986**, *51*, 4006-16.

Propargylic Alkylation vs allyl. ılkylation



latent period for propargylic alkylation

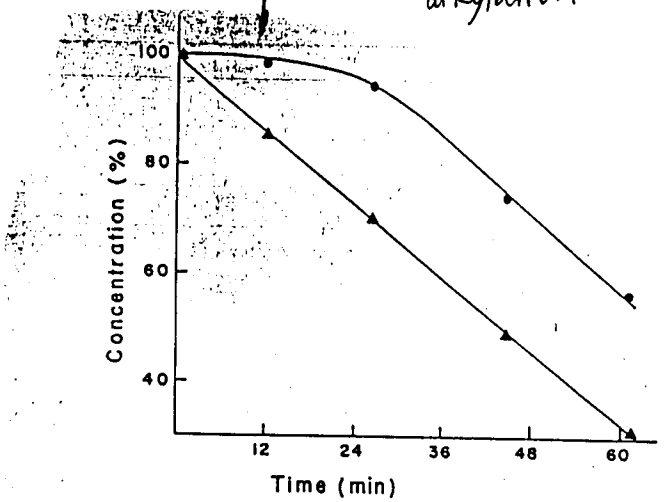
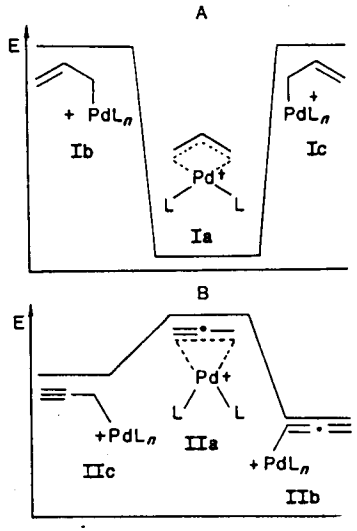


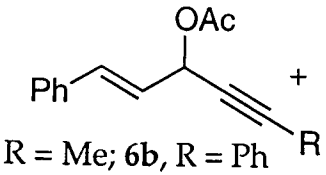
Figure 1. Pd(0)-catalyzed competitive substitution of 1 and 2 with PhZnCl: PhZnCl (1 mmol) was added to a 5-mL THF solution containing 1 and 2 (1 mmol each) and $Pd(PPh_3)_4$ (0.05 mmol) at room temperature. Disappearance of 1 (▲) and 2 (●) was detected by GC (10% SE-30 on Chromosorb W).

Scheme III. Hypothetical Relative Energies of Allyl Pd(II) (Scheme IIIA) and Propargyl Pd(II) Complexes (Scheme IIIB)



Keinan E. et al. *JOC.* **1986**, *51*, 4006-16.

Bifunctional Substrate Competition



6a R = Me; 6b, R = Ph

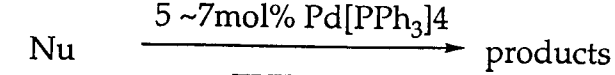
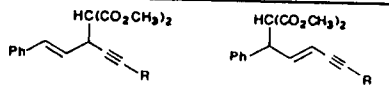
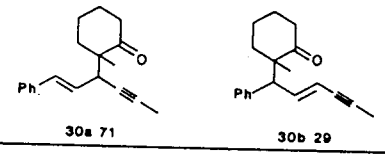
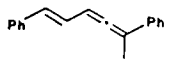
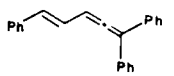
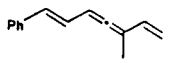
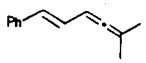
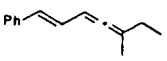
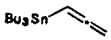
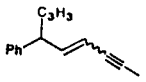
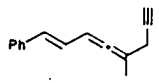
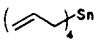
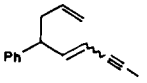
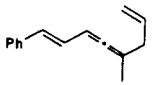
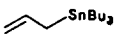
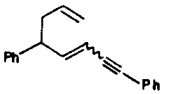
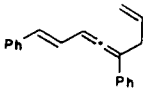
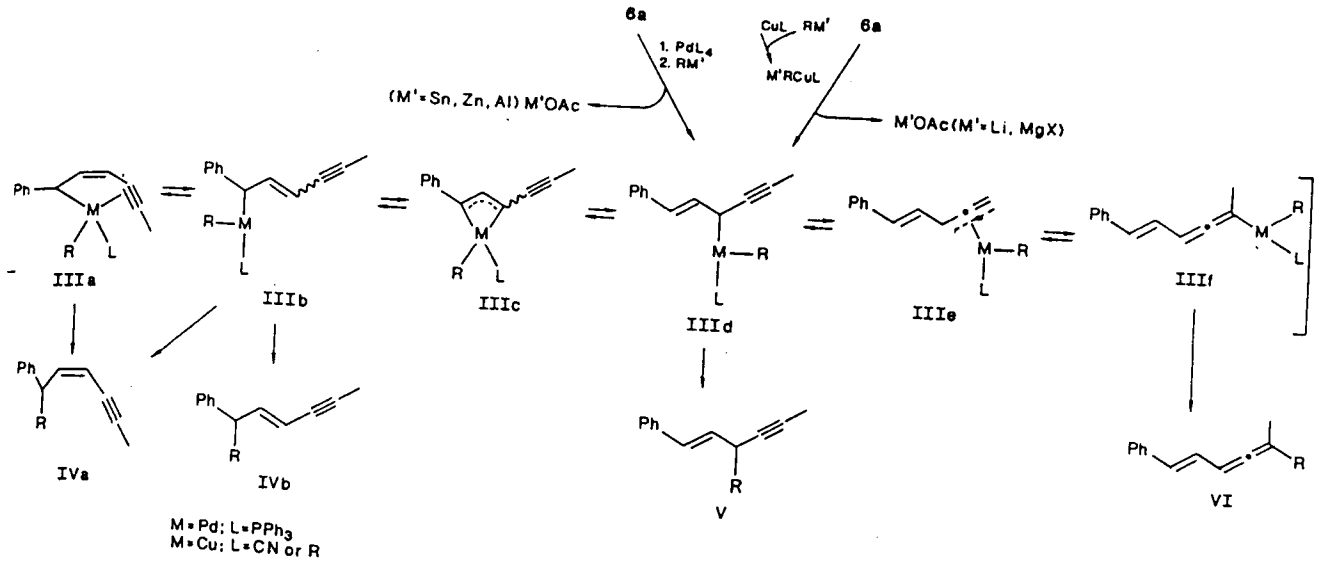


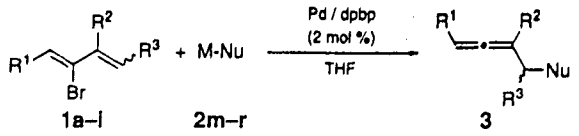
Table II. Palladium(0)-Catalyzed Substitution of Conjugated Bifunctional Substrates 6[a]

group	substrate	nucleophile	time (h)	products	yield (%)
A	6a (R = Me)	$NaCH(CO_2CH_3)_2$	10	 28a 97 28b 3	70
	6b (R = Ph)	$NaCH(CO_2CH_3)_2$	1	29a 70 29b 30 (*E*:*Z* = 1:3)	90
	6a		1	 30a 71 30b 29	91
B	6a	PhZnCl	2	 31	94
	6b	PhZnCl	0.2	 32	86
	6a		1.3	 33	68
	6a	MeZnCl	48	 34	71
	6a	Et_3Al	1	 35	63
C	6a		2	 36a,b 20 (*E*:*Z* = 3:1)  36c 80	73
	6a		3	 37a 36 (*E*:*Z* = 1:3)  37b 64	75
	6b		24	 38a 33 (*E*:*Z* = 1:3)  38b 67	57

General Mechanism

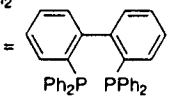


π-Allyl Palladium Catalyzed Sy...nesis Of Allenes



1a : R^1 = Ph, R^2 = R^3 = H
1b : R^1 = $PhCH_2$, R^2 = R^3 = H
1c : R^1 = (*E*)-PhCH=CH, R^2 = R^3 = H
1d : R^1 = *i*Pr, R^2 = R^3 = H
1e : R^1 = n-C_7H_{15}, R^2 = R^3 = H
1f : R^1 = Ph, R^2 = Me, R^3 = H
1g : R^1 = R^2 = Ph, R^3 = H
1h : R^1 = H, R^2 = Ph, R^3 = H
1i : R^1 = Ph, R^2 = H, R^3 = Me

2m: $Na[CMe(COOMe)_2]$
2n : $Na[CH(COOMe)_2]$
2o : Na[CMe(COMe)(COOEt)]
2p : $K[CMe(COMe)_2]$
2q : NaOPh
2r : $KN(Boc)_2$
2s : $LiPPh_2$

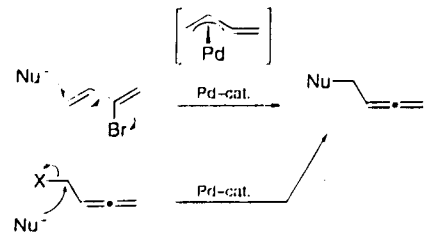
dpbp = 

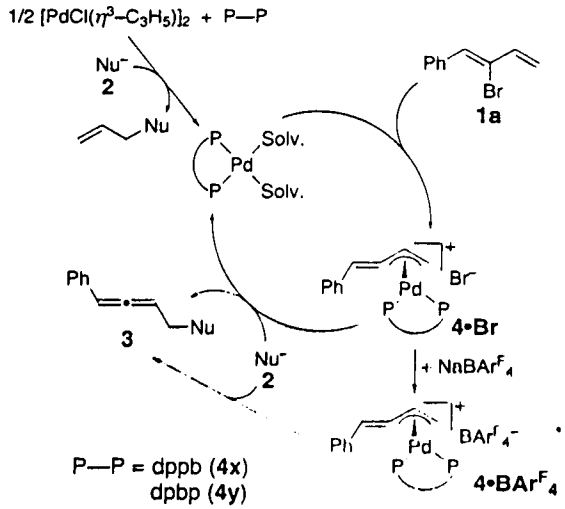
Scheme 2. π-Allylpalladium-mediated catalytic synthesis of functionalized allenes.

Table 1. Palladium-catalyzed synthesis of allenes 3 from bromodiene 1 and nucleophile 2.[a]

Entry	Bromodiene	Nucleophile	T [°C]	t [h]	Yield [%][b]
1	**1a**	**2m**	23	12	91 (**3am**)
2	**1a**	**2n**	23	12	79 (**3an**)[c]
3	**1a**	**2o**	23	12	93 (**3ao**)[d]
4	**1a**	**2p**	23	6	96 (**3ap**)
5	**1a**	**2q**	23	24	83 (**3aq**)
6	**1a**	**2r**	23	12	89 (**3ar**)
7	**1a**	**2s**	0	3	62 (**3as**)[e]
8	**1b**	**2m**	23	12	91 (**3bm**)
9	**1c**	**2m**	23	12	92 (**3cm**)
10	**1d**	**2m**	23	6	88 (**3dm**)
11	**1e**	**2m**	23	6	93 (**3em**)
12	**1f**	**2m**	23	12	90 (**3fm**)
13	**1g**	**2m**	23	12	95 (**3gm**)
14	**1h**	**2m**	23	6	93 (**3hm**)
15	**1i**[f]	**2m**	23	60	80[g](**3im**)[h]

[a] Reaction was carried out in THF in the presence of 2 mol% of the catalyst generated from $[PdCl(\eta^3\text{-}C_3H_5)]_2$ and dpbp. [b] Yield of isolated product after column chromatography on silica gel. [c] Doubly reacted products, *rac*- and *meso*-**3an'**, were isolated in 19% yield (based on **1a**) as a *rac*/*meso* = 47/53 mixture. [d] Mixture of two diastereomers (50/50). [e] The product was oxidized during an aerobic work-up and isolated as a corresponding phosphane oxide. [f] Mixture of two isomers (*E*/*Z* = 5/1). [g] 18% of **1i** was recovered (*E*/*Z* = 6/1). [h] Mixture of two diastereomers (50/50).

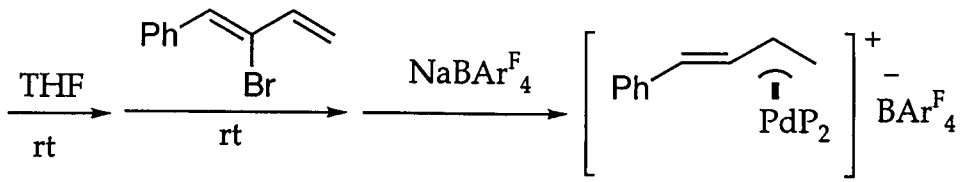




Scheme 3. Catalytic cycle of the allene synthesis reaction (Solv. = solvent)

Synthesis of intermediates

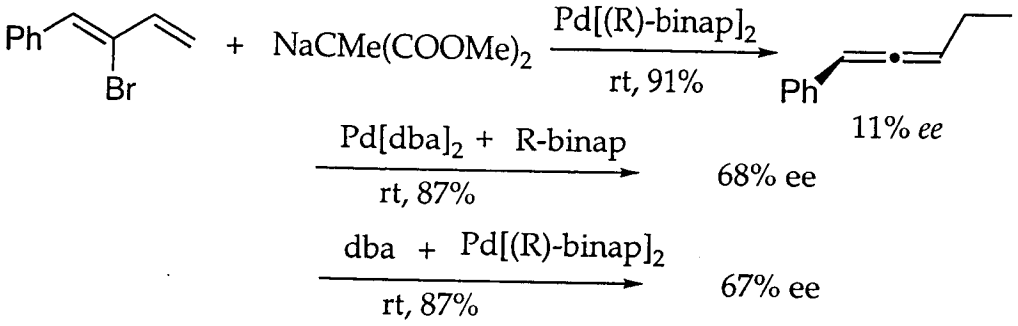
$[PdCl(n\text{-allyl})]2$ + (R)-binap + $NaCMe(COOMe)_2$



Hayashi, T. et al. *ACIEE.* **2000**, *39*, 1042-4.

Catalytic Enantioselective S. .hesis Of Allenes

Effect of DBA ligand on enantioselectivities



Scheme 2. Catalytic Cycle of the Enantioselective Synthesis Reaction of Allenes

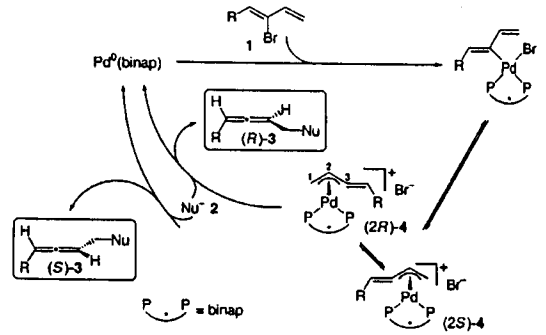
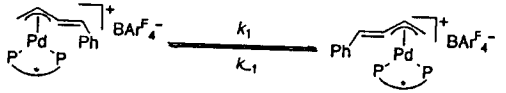


Table 1. Isomerization Rates between the Two Diastereoisomers of [(Benzylidene-π-allyl)Pd(binap)]BAr^F_4 (5) in $CDCl_3$[a]



temp/°C	[DBA]	k_1[b]/s^{-1}	k_{-1}[c]/s^{-1}	k_1/k_{-1}	[major]/[minor][d]
20	0	0.19	0.086[e]	2.2	1.9
	2 equiv	2.4	1.3	1.9	1.9
40	0	0.49	0.25	2.0	1.9
	2 equiv	>12[f]	5.4	>2.2	1.9

[a] The absolute configurations of the major and the minor isomers have not been determined. [b] The rate constants from the minor isomer to the major. [c] The rate constants from the major isomer to the minor. [d] The relative concentration of both isomers determined by ^1H NMR. [e] Due to the slowness of the exchange, the value contains some degree of uncertainty. [f] Due to the quickness of the exchange, the value contains some degree of uncertainty.

Scheme 1

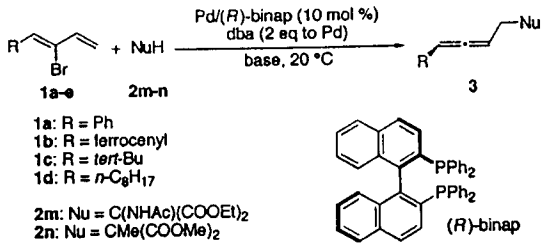


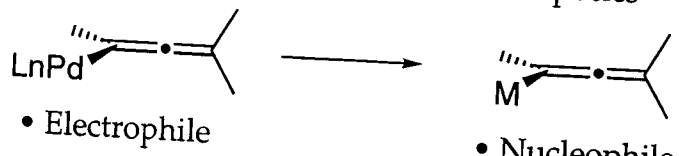
Table 2. Palladium-Catalyzed Asymmetric Synthesis of Allenes 3 from Bromodiene 1 and Nucleophile 2[a]

entry	diene	NuH	base	solvent	yield[b]/%	% ee[c] (config)	$[\alpha]^{20}_D$ (c in $CHCl_3$)
1	**1a**	**2m**	NaH	CH_2Cl_2	59 (**3am**)	52 (*R*)	
2	**1a**	**2m**	KO^{t}Bu	CH_2Cl_2	98 (**3am**)	75 (*R*)	
3	**1a**	**2m**	CsO^{t}Bu	CH_2Cl_2	75 (**3am**)	89 (*R*)	−141 (0.66)
4	**1a**	**2m**	CsO^{t}Bu	THF	77 (**3am**)	58 (*R*)	
5	**1a**	**2m**	CsO^{t}Bu	toluene	61 (**3am**)	41 (*R*)	
6	**1a**	**2n**	NaH	THF	88 (**3an**)	68 (*R*)	−87 (0.50)
7	**1b**	**2m**	CsO^{t}Bu	CH_2Cl_2	34 (**3bm**)	80 (*R*)	−314 (0.64)
8	**1c**	**2m**	CsO^{t}Bu	CH_2Cl_2	74 (**3cm**)	75 (*R*)	−29 (0.50)
9	**1d**	**2m**	CsO^{t}Bu	CH_2Cl_2	73 (**3dm**)	54 (*R*)	−33 (1.00)

[a] The reaction was carried out with bromodiene **1** (0.50 mmol), Nu-H **2** (0.55 mmol), and base (0.60 mmol) in a given solvent (5.0 mL) at 20 °C for 24 h in the presence of 10 mol % of the catalyst generated from $Pd(dba)_2$ and (*R*)-binap or Pd[(*R*)-binap]$_2$ and dba. [b] Isolated yield by silica gel or alumina chromatography. [c] Determined by HPLC analysis with chiral stationary phase columns: Daicel Chiralcel OJ (**3am**), AD (**3an**, **3cm**, **3dm**), and OD-H (**3bm**).

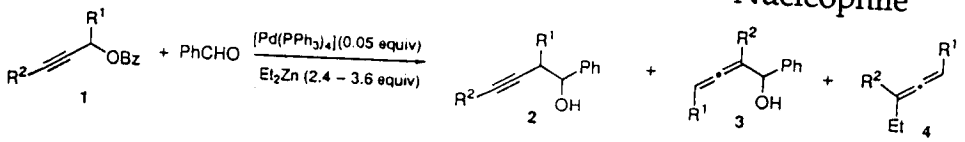
Hayashi, T. et al. *JACS*. **2001**, *123*, 2089-90.

Umpolung Allenyl Palladium Species



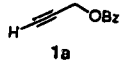
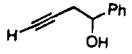
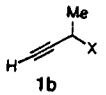
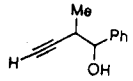
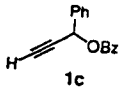
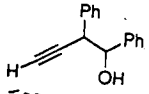
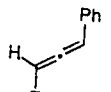
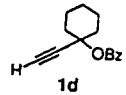
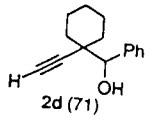
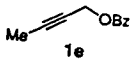
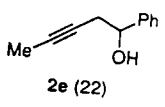
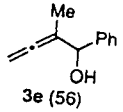
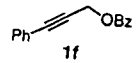
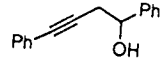
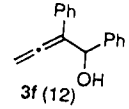
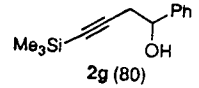
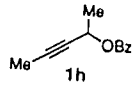
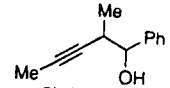
• Electrophile

• Nucleophile

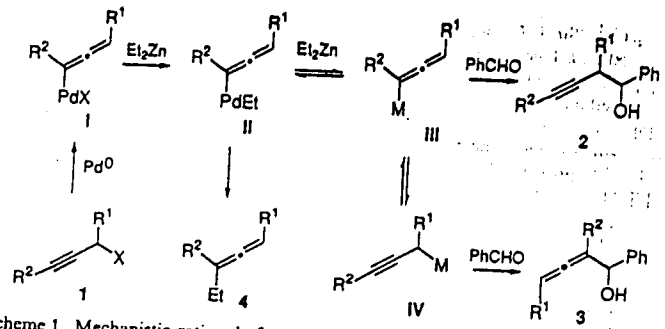


1 2 3 4

Table 1. Palladium-catalyzed propargylations of benzaldehyde according to Equation (a).

Run	1	mmol Et_2Zn	t [h] [a]	Products (Yield [%]) [b]
	 1a	3.6	7	 2a (57)
d]	 1b X = OBz X = OTs X = OCO_2Me X = Br	3.6, [3.6] 3.6 3.6 3.6	 3, [1] 1.5 7 0.2	2b (70) [c], [90] 2b (55) [c] 2b (72) [c] 2b (88) [c]
	 1c	3.6	1	 2c (79) [c]  4c (20)
	 1d	3.6	2.5	 2d (71)
	 1e	2.4	24	 2e (22)  3e (56)
9	 1f	2.4	75	 2f (57)  3f (12)
10	 1g	2.4	96	 2g (80)
11	 1h	2.4	30	 2h (60) [c]

[a] Reaction conditions: 1 (1.2 mmol), benzaldehyde (1.0 mmol), diethylzinc (indicated amount), $[Pd(PPh_3)_4]$ (0.05 mmol) in THF (5 mL) at room temperature under N_2. [b] Yields for the spectroscopically homogeneous products based on the amounts of benzaldehyde used. [c] Mixture of *syn* and *anti* isomers in a ratio of about 1:1. [d] The conditions and yields for a reaction carried out in benzene/THF (5 mL/1.6 mL) are given in square brackets.

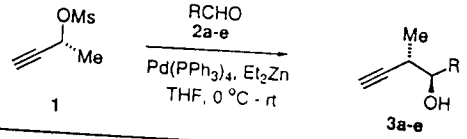


I II III 2 1 4 IV 3

Scheme 1. Mechanistic rationale for the propargylation and allenylation of benzaldehyde according to Equation (a).

Tamaru, Y. et al. *ACIEE.* **1996**, *35*, 878-879.

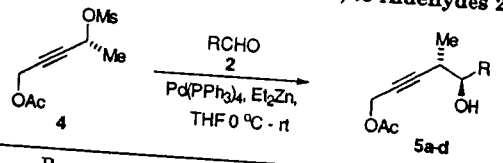
Table 1. Additions of an Allenylzinc Reagent, Generated in Situ from Propargylic Mesylate 1, to Aldehydes 2a–e



R	yield, %	anti:syn[a]	ee,[a–c] %
c-C_6H_{11}, **a**	85	95:5	95
C_6H_{13}, **b**	70	88:12	90
$TBSOCH_2CH_2$, **c**	56	86:14	86[d]
(*E*)-BuCH=CH, **d**	71	77:23	88
1-octynyl, **e**	60	68:32	90

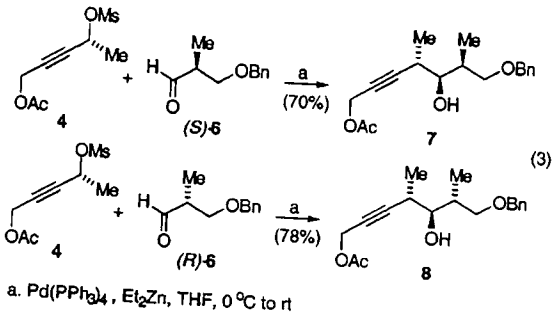
[a] Analysis by gas chromatography. [b] For the anti isomer. [c] Corrected for the ee of the starting material. [d] Analyzed as the diol.

Table 2. Addition of an Allenylzinc Reagent, Generated in Situ from Propargylic Mesylate 4, to Aldehydes 2a–d



R	yield, %	anti:syn[a]	ee,[b,c] %
c-C_6H_{11}, **a**	51	95:5	96
C_6H_{13}, **b**	57	90:10	89
i-Pr, **c**	47	95:5	96
(*E*)-BuCHd CH, **d**	57	70:30	d

[a] ^1H NMR analysis. [b] ^1H NMR analysis of the *O*-methyl mandelate[8] of the the anti isomer. [c] Corrected for the ee of the starting material. [d] Not determined.



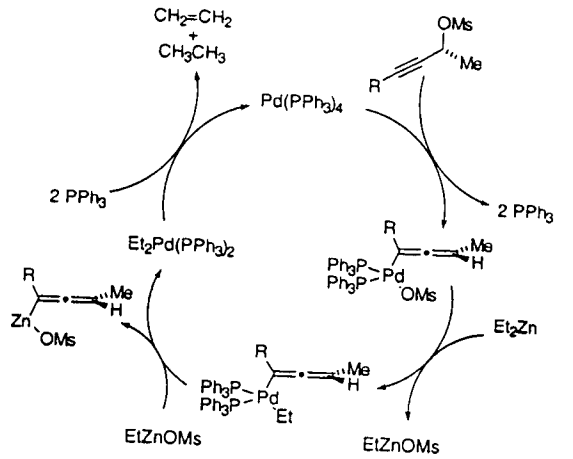
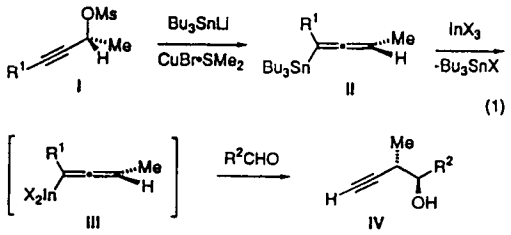


Figure 1. Possible catalytic cycle for Pd(0)-catalyzed zincatio of propargylic mesylates.

Marshall, J. A. et al. JOC. **1998**, *63*, 3812-13.



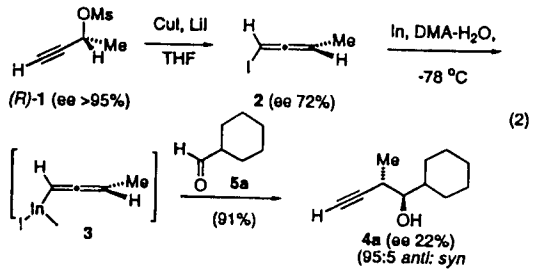
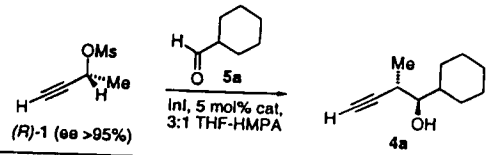


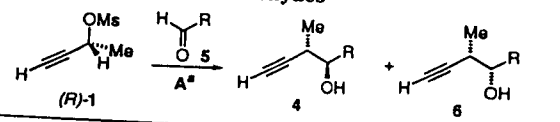
Table 1. Variation of Catalyst and Solvent in Additions of Allenylindium Reagents Derived From Mesylate (*R*)-1 to Cyclohexanecarboxaldehyde



catalyst	yield, %	*anti:syn*[a]	ee, %[a]
none	66	96:4	0
$Pd(dppf)Cl_2$	76	95:5	95
$Pd(dppf)Cl_2$[b]	63	87:13	87
$Pd(dppf)Cl_2$[c]	80	91:9	90
$Pd(dppf)Cl_2$[d]	66	93:7	91
$Pd(OAc)_2 \cdot PPh_3$	75	95:5	91

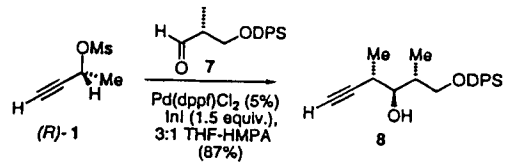
[a] Ratios and ee values were determined by GC analysis. [b] 3:1 THF–DMPU as the solvent. [c] 1:1 THF–DMPU as the solvent. [d] 20:1 THF–HMPA as the solvent.

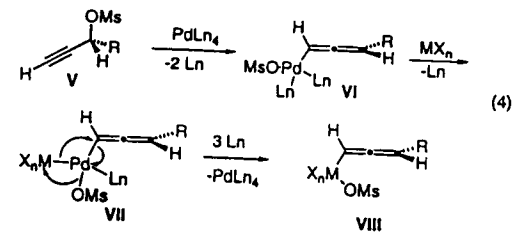
Table 2. Additions of Transient Chiral Allenylindium Reagents from Mesylate (*R*)-1 to Representative Achiral Aldehydes



R	yield, %	*anti:syn*	ee, %
c-C_6H_{11} (**5a**)	76	95:5[b]	95[b]
C_6H_{13} (**5b**)	73	82:18[b]	96[b]
$DPSOCH_2CH_2$ (**5c**)	88	88:12[c]	*d*
(E)-BuCH=CH (**5d**)	68	71:29[b]	96[b]
1-heptynyl (**5e**)	62	72:28[b]	95[b]
Ph (**5f**)	85	45:55[b]	92[b]

[a] 5 mol % $Pd(dppf)Cl_2$, 1 equiv of InI, 3:1 THF–HMPA, room temp. [b] Analysis by gas chromatography on a β-cyclodextrin column. [c] Calculated from the ^1H NMR spectrum. [d] Not determined.





Palladium Mediated Reductio. f Propargylic Phosphates

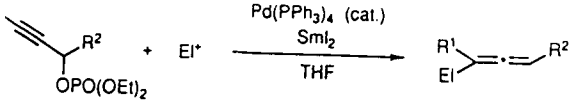
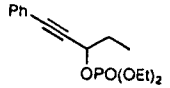
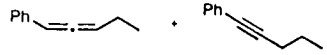
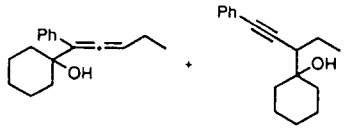
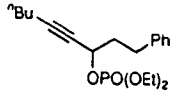
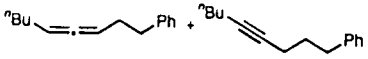
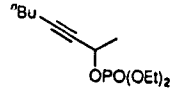
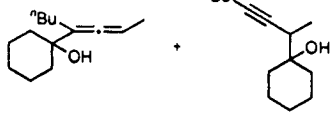
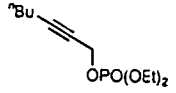
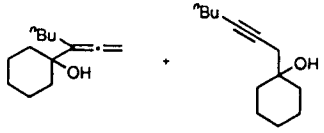
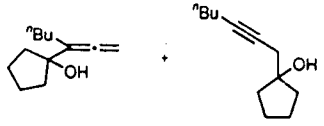


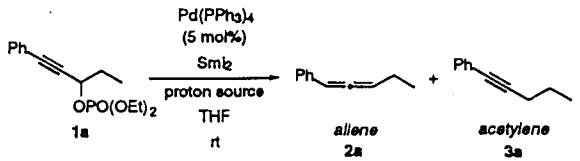
Table 1. Pd(0)-Catalyzed Reaction of Propargylic Esters with SmI_2.

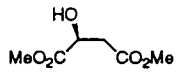
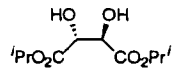
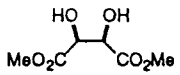
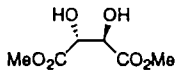
entry	substrate	electrophile	products (ratio)[a]	% yield[b]
1		H^+ (*i*-PrOH)	 (98 : 2)	66
2		H^+ (*t*-BuOH)	(>99 : <1)	80
3			 (94 : 6)	71
4[c]		H^+ (*i*-PrOH)	 (>99 : <1)	84
5[c]		H^+ (*t*-BuOH)	(>99 : <1)	89
6			 (94 : 6)	49
7			 (2 : 98)	84
8			 (4 : 96)	45

[a] Determined by 300- or 400-MHz ^1H NMR and/or GC-MS analysis. [b] Combined yield. [c] The reaction was carried out at 40°C.

Mikami, K. et al. *TL.* **1995**, *36*, 907-8.

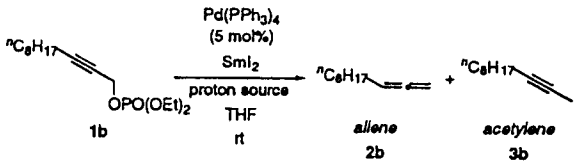
Table 1. Secondary propargylic phosphates as substrates

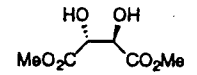


entry	proton source	% yield	*allene/acetylene* [a]
1	*t*-BuOH	80	>99 : <1
2	*i*-PrOH	66	98 : 2
3	H_2O	70	56 : 44
4		86	90 : 10
5		56	84 : 16
6		46	36 : 64
7		59	37 : 63
8		81	15 : 85
9[b]		22	10 : 90

[a] Determined by ^1H NMR analysis.
[b] Reaction was performed at 0 °C for 4.5 h

Table 2. Primary propargylic phosphates as substrates



entry	proton source	% yield	*allene/acetylene* [a]
1	*t*-BuOH	50	6 : 94
2	H_2O	33	19 : 81
3		63	55 : 45

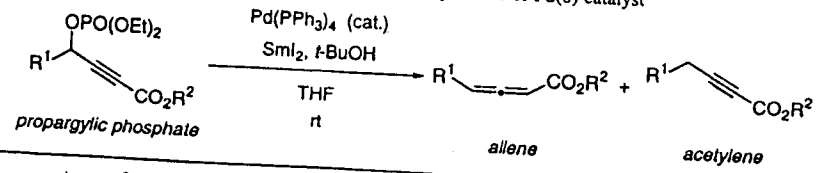
[a] Determined by ^1H NMR analysis

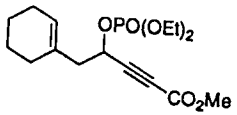
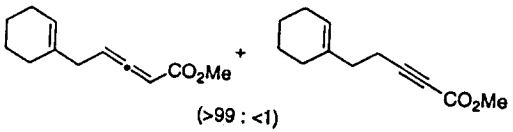
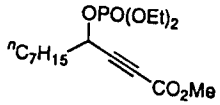
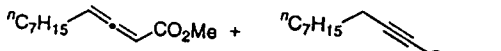
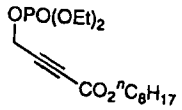
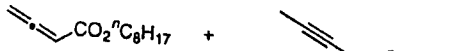
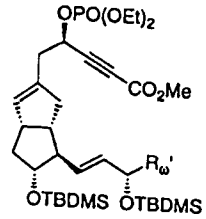
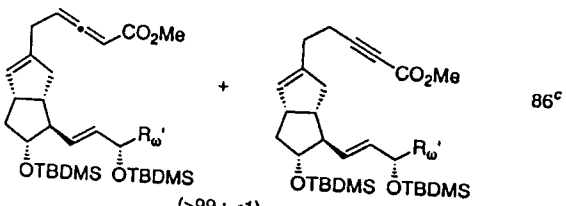
Mikami, K. et al. *SynLett.* **1997**, 1375-6.

Allenic ester substrates

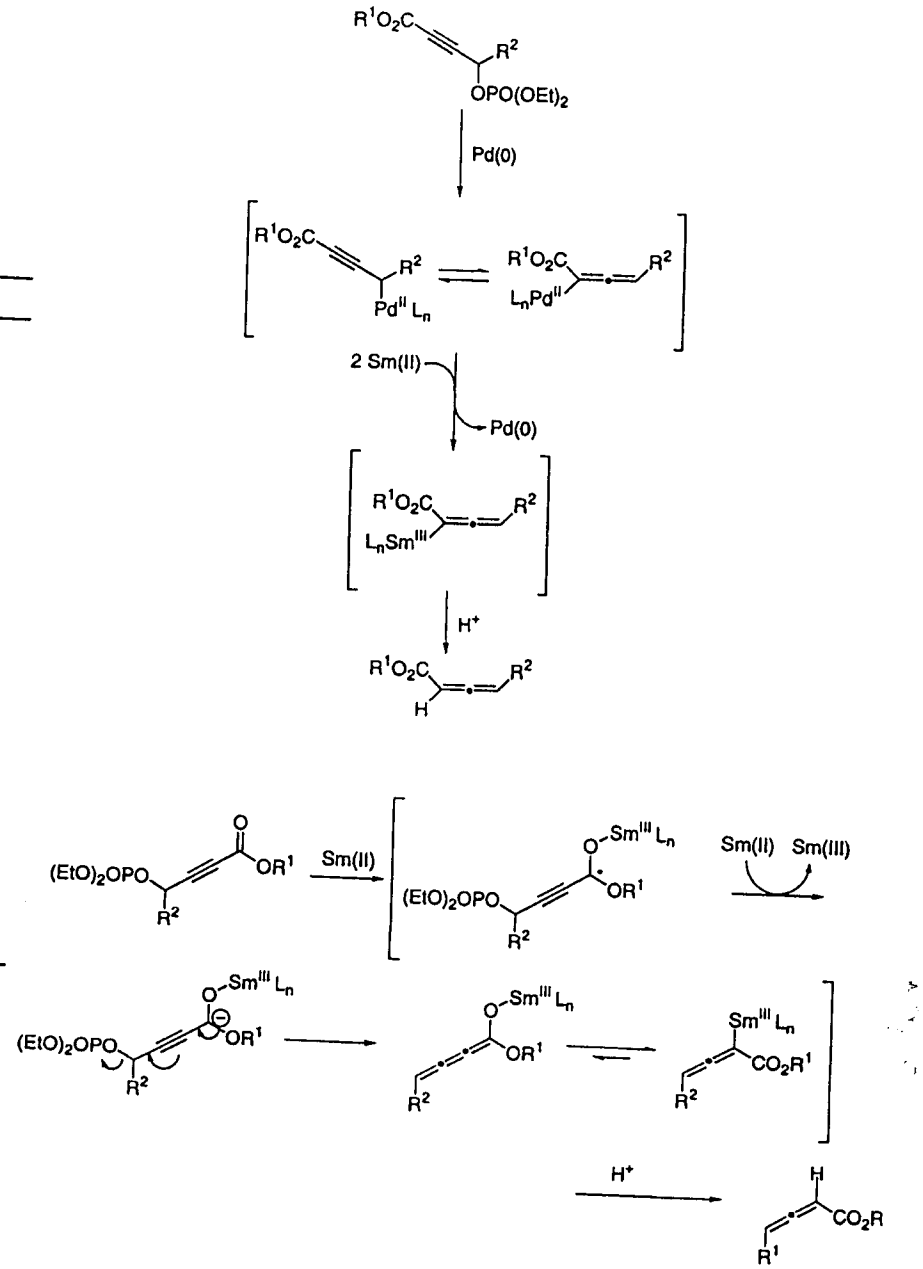
Two possible mechanisms

Table 1. Regioselective reduction–protonation of propargylic phosphates in the presence of Pd(0) catalyst



substrate[a]	product (ratio)[a,b]	% yield
	 (>99 : <1)	53
	 (>99 : <1)	100
	 (>99 : <1)	83
	 (>99 : <1)	86[c]

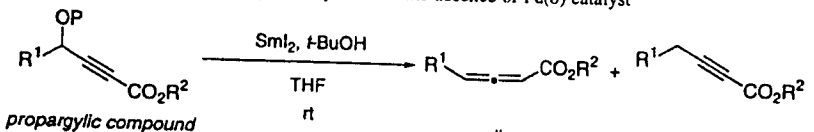
[a] R_ω'=(2*R*)–$CH_2CH(CH_3)(CH_2)_2CH{=}C(CH_3)_2$.
[b] Determined by ^1H NMR analysis.
[c] See Ref. 13.



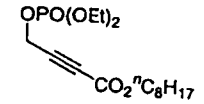
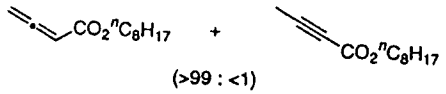
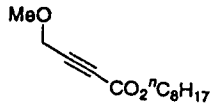
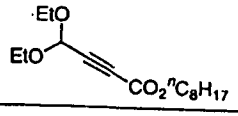
Mikami, K. et al. *Tetrahedron* **2001**, *57*, 889-898.

Sm(II) rec tion of propargylic phosphates

ıble 2. Regioselective reduction–protonation of propargylic compounds in the absence of Pd(0) catalyst

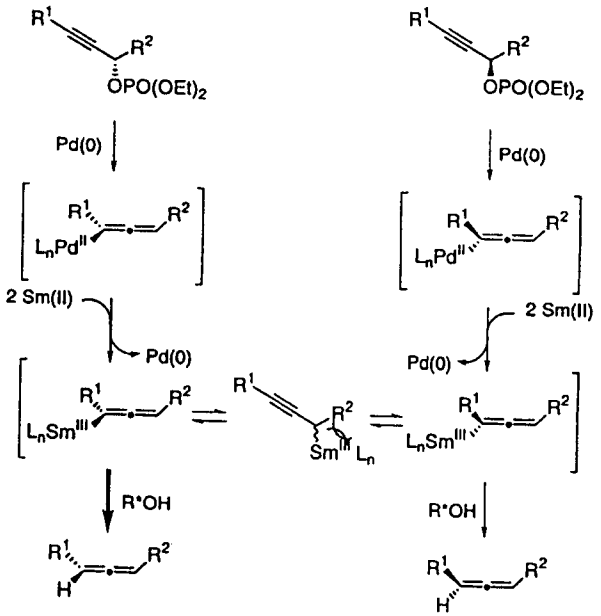


propargylic compound *allene* *acetylene*

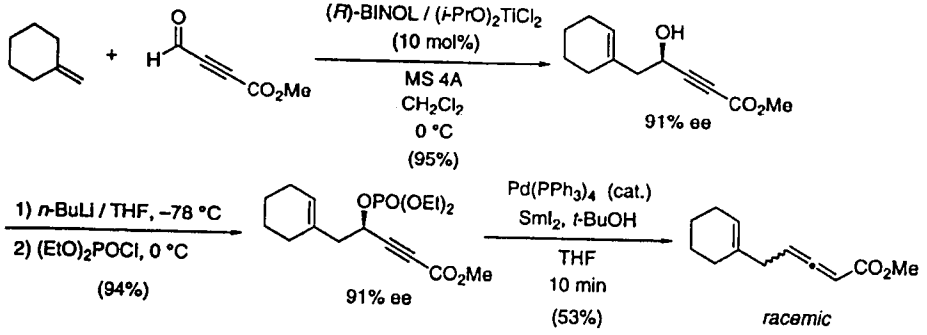
substrate	product (ratio)[a]	% yield
	 (>99 : <1)	79
	 (>99 : <1)	84
	no reaction	—

ermined by ^{1}H NMR analysis.

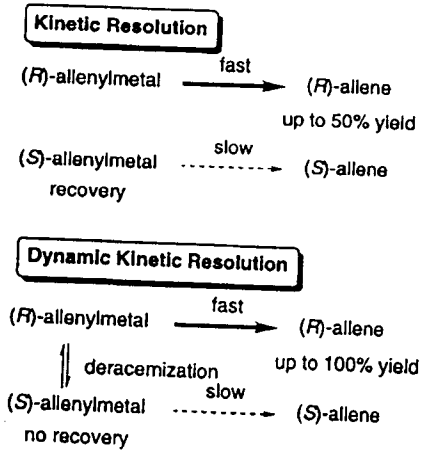
Mechanism for racemization

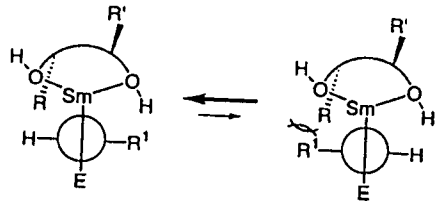


Results with optically active phosphate



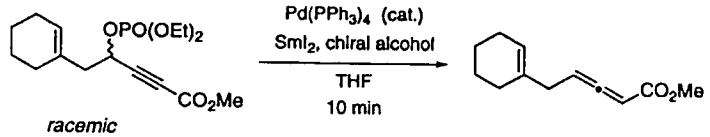
Possible dynamic kinetic resolution process

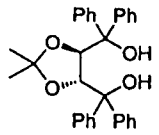
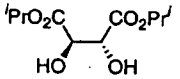
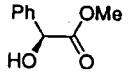
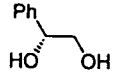
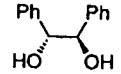
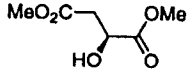
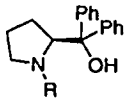
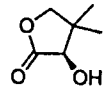




Mikami 2001

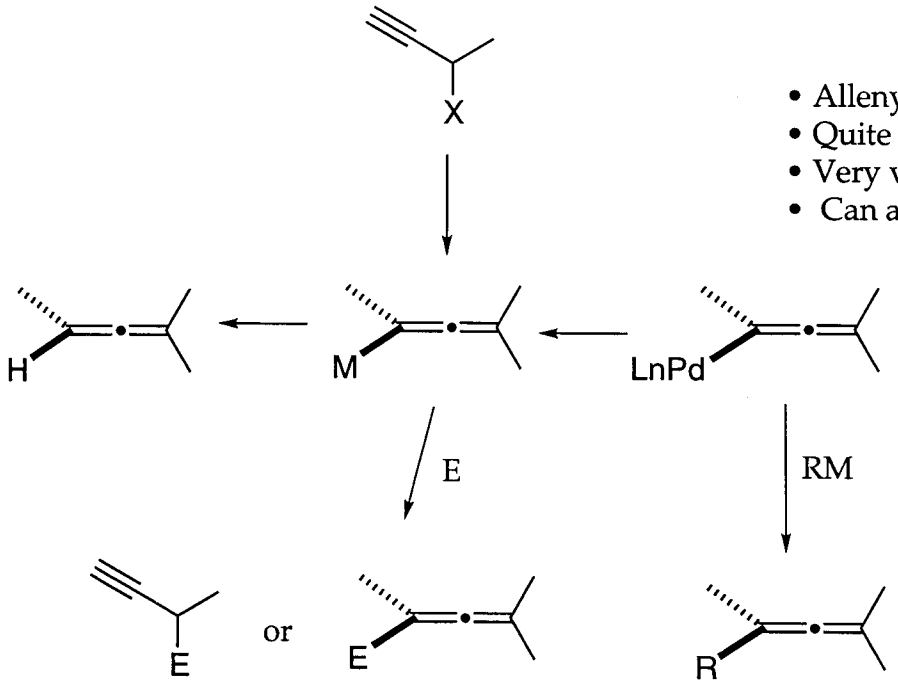
Table 3. Regio- and enantioselective reduction–protonation of propargylic phosphate



entry	chiral alcohol	% yield	% ee[a]	config.[b]
1	 TADDOL	52	41	*R*
2[c]		70	24	*S*
3		71	67	*S*
4		86	13	*R*
5		71	86	*R*
6		46	24	*S*
7	 R = H	25	45	*R*
8	R = Me	24	80	*R*
9		68	95	*R*

[a] Determined by LIS-NMR analysis using $Eu(hfc)_3$.
[b] Determined by Lowe–Brewster's rule.
[c] Acetylene-type product was also obtained in 9% yield.

Summary



- Allenylpalladium species can be easily generated
- Quite stable species, even configurationally
- Very versatile intermediate
- Can act as both electrophile or nucleophile (transmetallation)

Other new methods towards chiral allenes:

Bergman, G. et al. *ACIEE.* **2000**, *39*, 2339-2343.

Nelson, S. G. el al. *JACS*, **2000**, *122*, 10470-1

Tillack, A. et al. *J. Organomet.* **2000**, *603*, 116-21.

Myers, A. G. et al. *JACS*, **1996**, *118*, 4492-3

Ito, Y. et al. *JOC.* **1996**, *61*, 4884-5.

Review: Pd-Catalyzed Reactions of Propargylic Compounds in Organic Synthesis,
Tsuji J., Mandai, T. *ACIEE*, **1995**, *34*, 2589-2612.