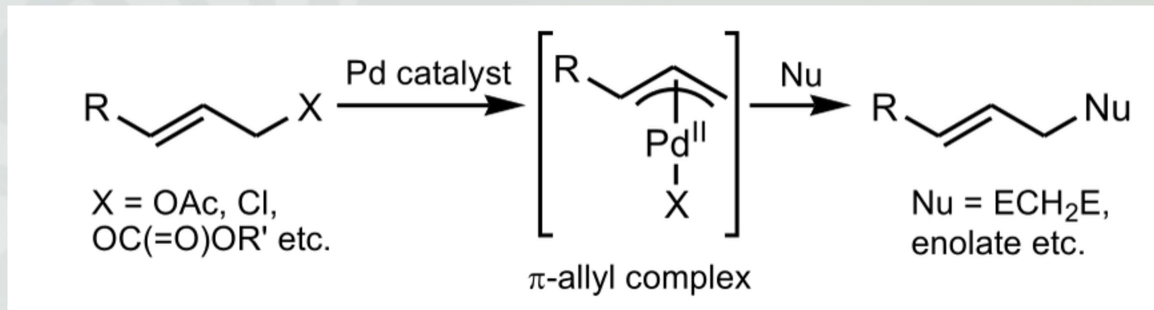
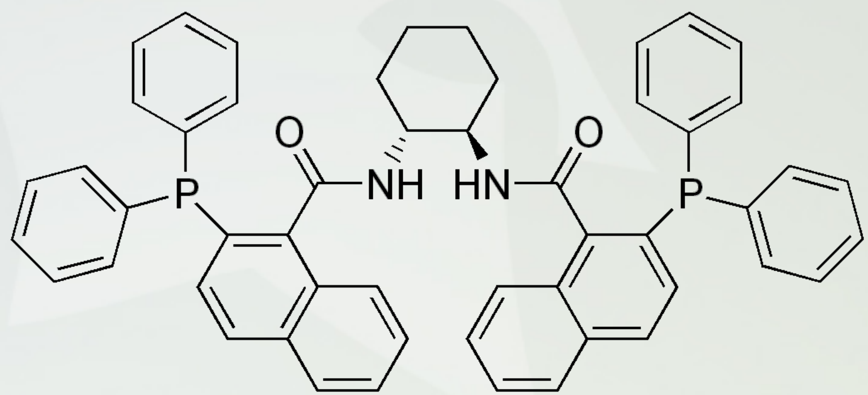
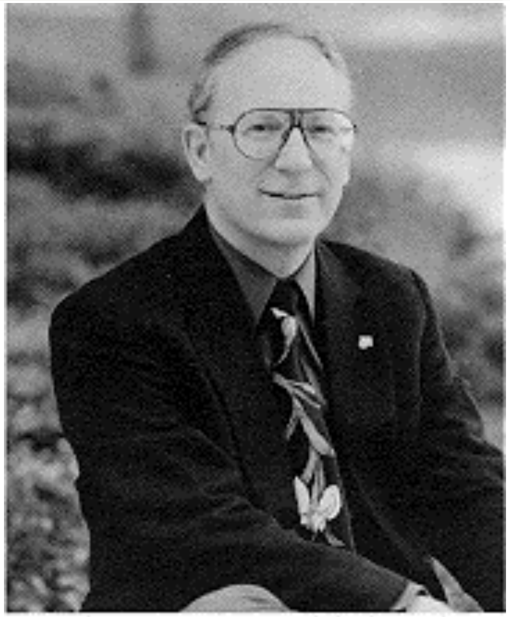
The Career of BARRY M. TROST





Yijing Dai @ Wulff's Group
Dec 12, 2014

Barry M. Trost



Birthplace & Date: Philadelphia, PA; June 13, 1941
Marital Status: Married; wife Susan, sons Aaron, Carey

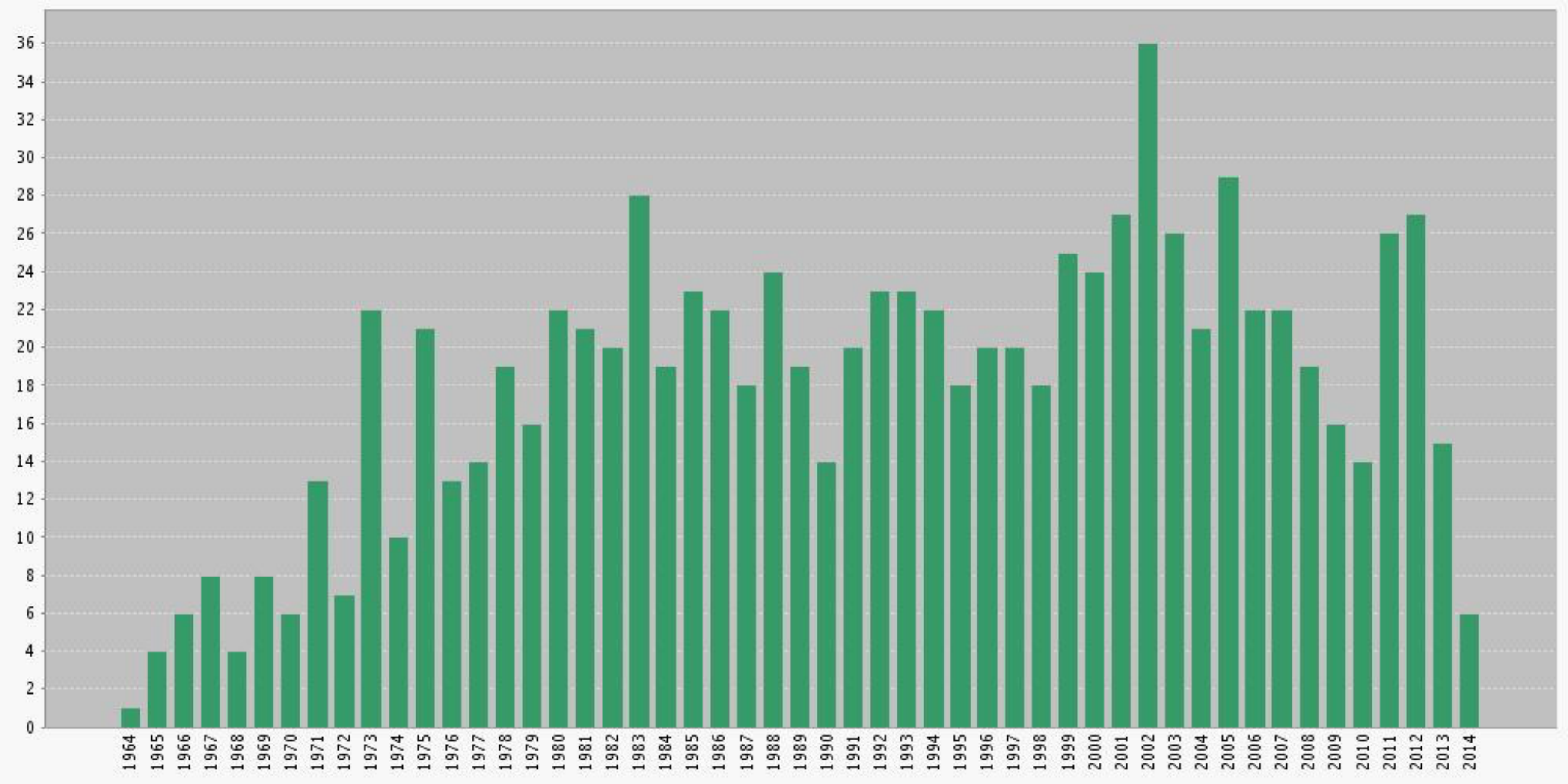
Education:
Undergraduate - B.A. University of Pennsylvania, 1962
Philadelphia Board of Education Scholarship 1959-1962
Graduate - Ph.D. Massachusetts Institute of Technology, 1965
Thesis Title: The Structure and Reactivity of Enolate Anions
Thesis Advisor: H.O. House
National Science Foundation Predoctoral Fellow 1963-1965

Appointments: University of Wisconsin:
Assistant Professor of Chemistry, 1965
Associate Professor of Chemistry, 1968
Professor of Chemistry, 1969

Appointments: Stanford University :
Professor of Chemistry, 1987.
Job and Gertrud Tamaki Professor in the School of Humanities and Sciences, 1990
Chair, 1996 – 2002

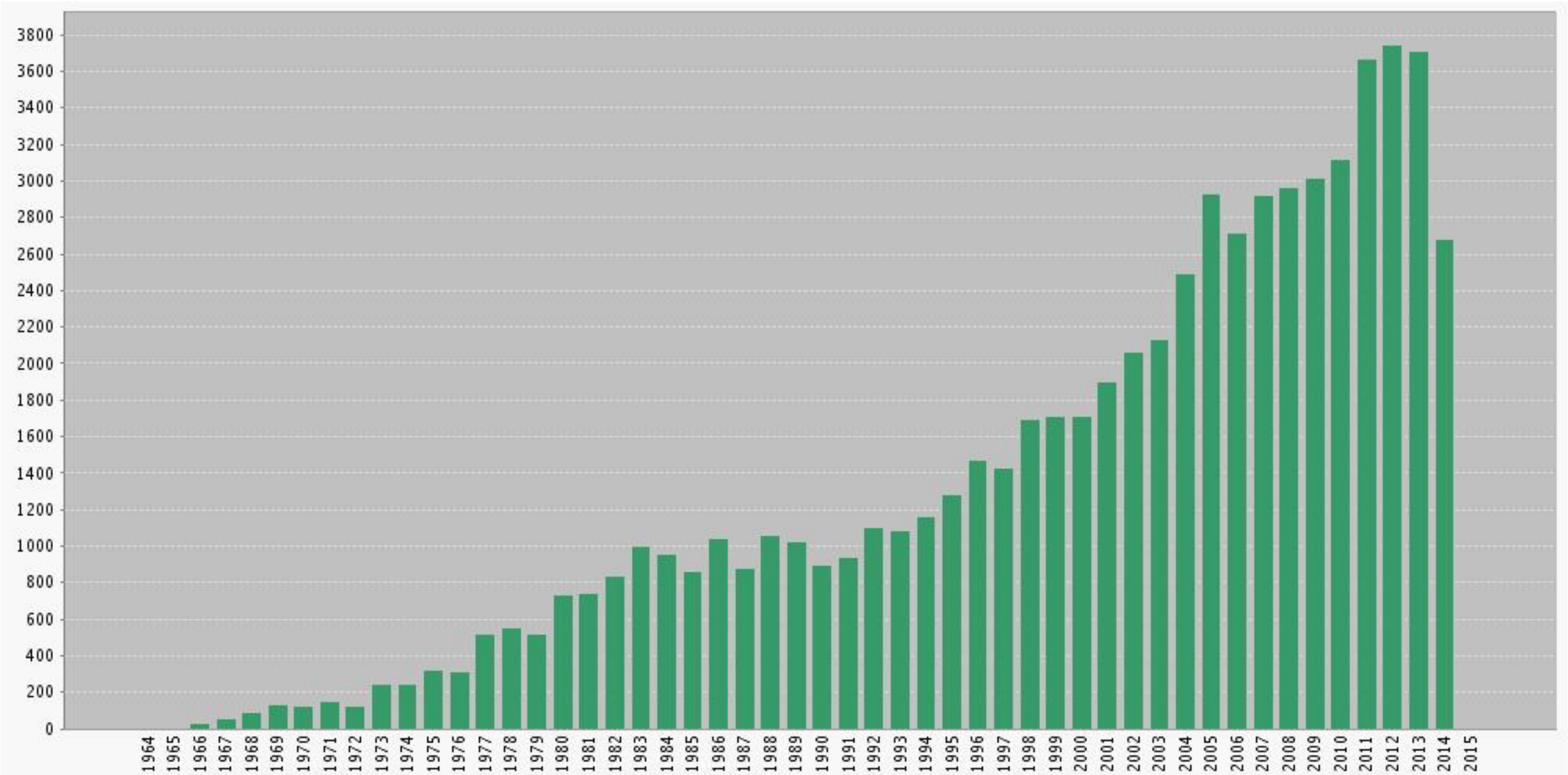
Publications

Total 925 (1064 in Scifinder and 967 in web of science database)



Web of Science

Citations of Each Year



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Top 10 Citations

MICHIGAN STATE UNIVERSITY

Title	Source Title	Publication Year	Total Citations	Average per Year
THE ATOM ECONOMY - A SEARCH FOR SYNTHETIC EFFICIENCY	SCIENCE	1991	2148	89.50
Asymmetric transition metal-catalyzed allylic alkylations	CHEMICAL REVIEWS	1996	1944	102.32
ATOM ECONOMY - A CHALLENGE FOR ORGANIC-SYNTHESIS - HOMOGENEOUS CATALYSIS LEADS THE WAY	ANGEWANDTE	1995	1558	77.90
Asymmetric transition-metal-catalyzed allylic alkylations: Applications in total synthesis	CHEMICAL REVIEWS	2003	1134	94.50
On inventing reactions for atom economy	ACCOUNTS OF CHEMICAL RESEARCH	2002	747	57.46
NEW RULES OF SELECTIVITY - ALLYLIC ALKYLATIONS CATALYZED BY PALLADIUM	ACCOUNTS OF CHEMICAL RESEARCH	1980	726	20.74
ON THE USE OF THE O-METHYLMANDELATE ESTER FOR ESTABLISHMENT OF ABSOLUTE-CONFIGURATION OF SECONDARY ALCOHOLS	JOC	1986	671	23.14
NEW SYNTHETIC REACTIONS - SULFENYLATIONS AND DEHYDROSULFENYLATIONS OF ESTERS AND KETONES	JACS	1976	628	16.10
Non-metathesis ruthenium-catalyzed C-C bond formation	CHEMICAL REVIEWS	2001	565	40.36
ORGANOPALLADIUM INTERMEDIATES IN ORGANIC-SYNTHESIS	TETRAHEDRON	1977	505	13.29

Web of Science

Category of Trost's Research Topics

MICHIGAN STATE UNIVERSITY

Categorize

1. Select a heading and category.

2. Select index terms of interest.

Category Heading	Category
All	Prepared substances (17697)
General chemistry	Reactants & reagents (12907)
Synthetic chemistry	**Reactions (228)**
Catalysis	Bio-prepared substances (44)
Physical chemistry	Manufactured substances (34)
Technology	Purified substances (21)
Genetics & protein chemistry	
Polymer chemistry	
Biotechnology	
Environmental chemistry	
Biology	
Analytical chemistry	

Index Terms

Page: 1 of 3

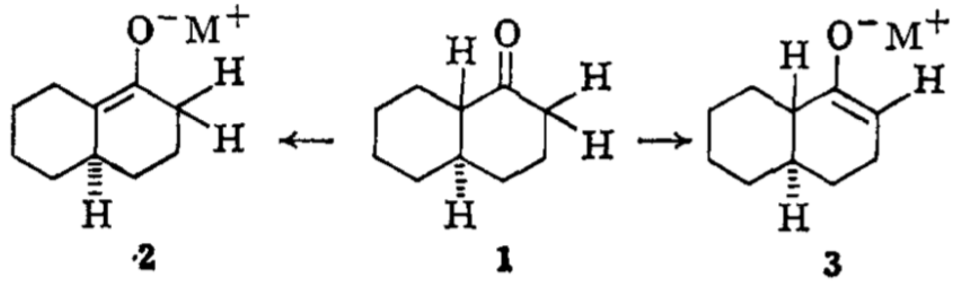
Select All Deselect All

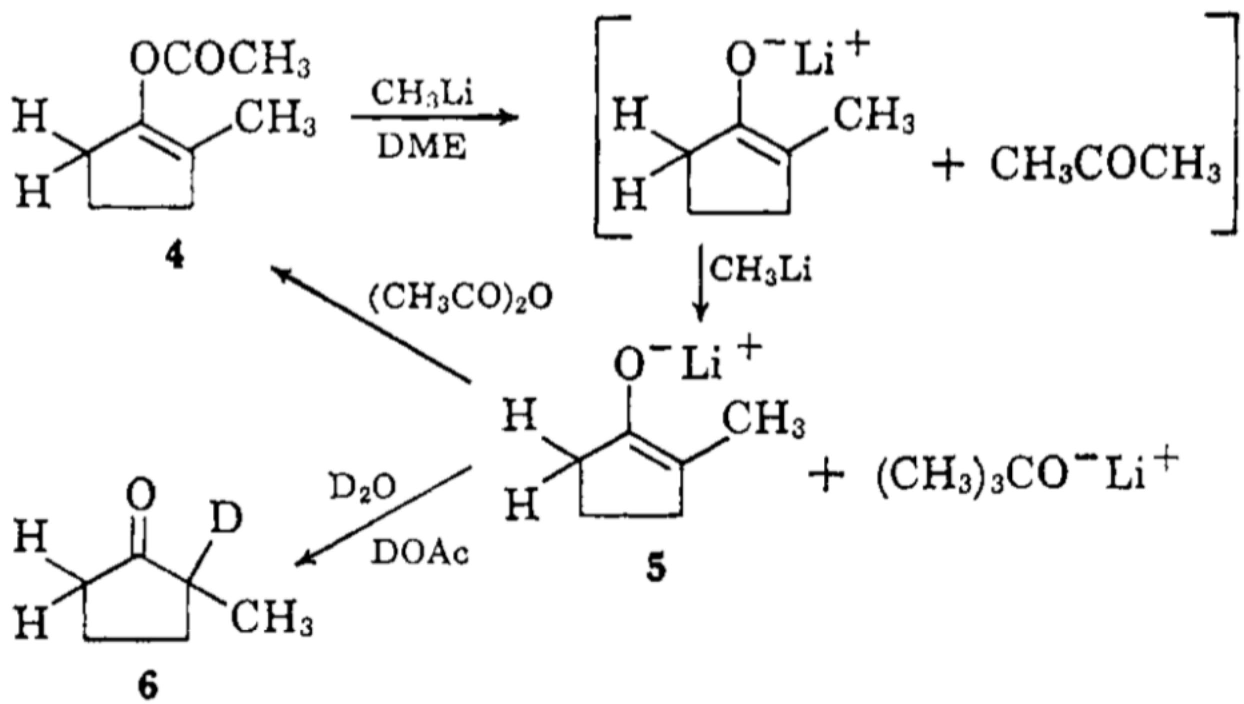
Stereoselective synthesis	220
Alkylation	175
Stereochemistry	175
Cyclization	121
Cycloaddition reaction	87
Regiochemistry	86
Addition reaction	61
Enantioselective synthesis	58
Isomerization	40
Coupling reaction	35
Diastereoselective synthesis	32
Ring opening	30
Diels-Alder reaction	28
Organic synthesis	26
Rearrangement	26

Scifinder

Alkylation in 70-80’s

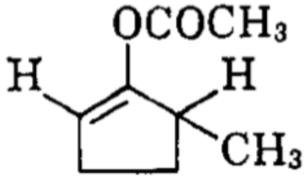
Alkylation of Unsymmetrical Ketone





JOC, **1965**, *30*, 1341; JOC, **1965**, *30*, 2502

Alkylation of Unsymmetrical Ketone



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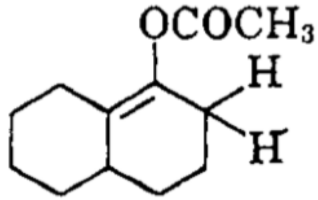

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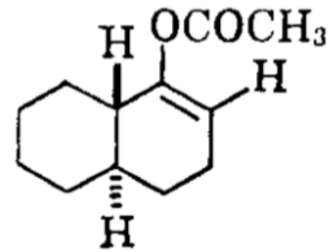

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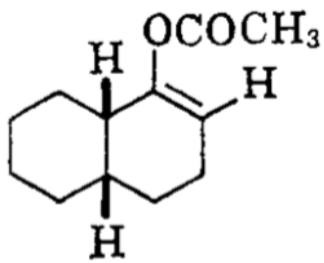

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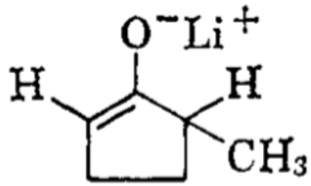

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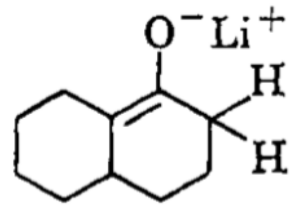

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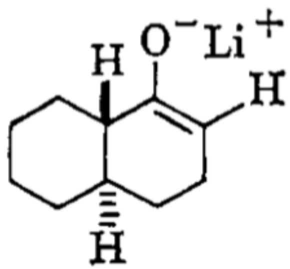

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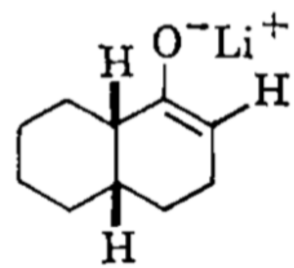

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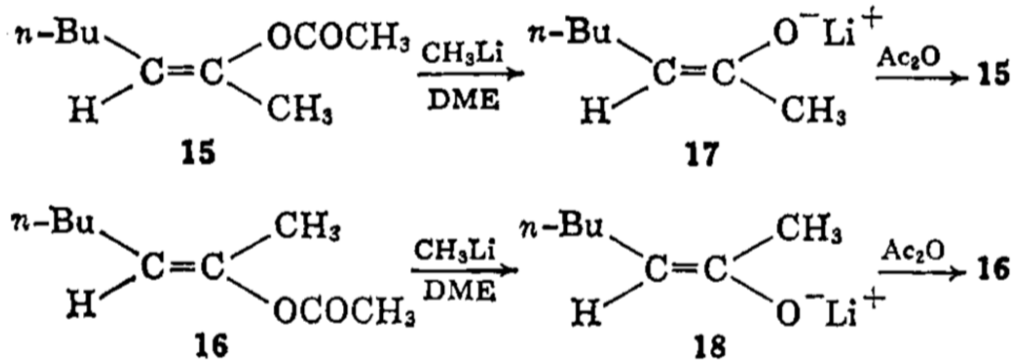
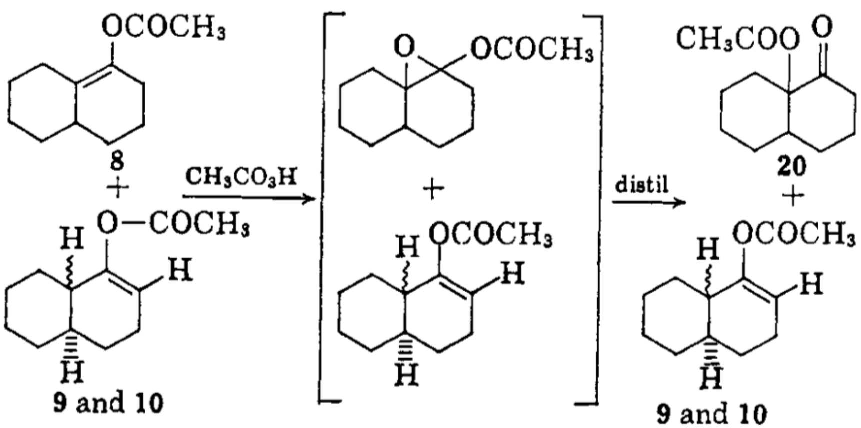
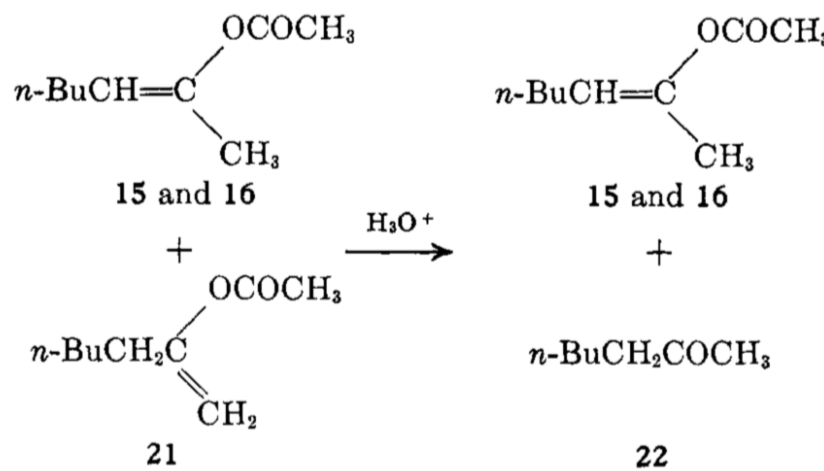
JOC, **1965**, *30*, 2502

Alkylation of Unsymmetrical Ketone

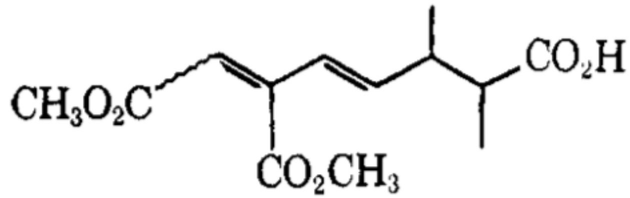






JOC, **1965**, *30*, 2502

Transfer Alkylation



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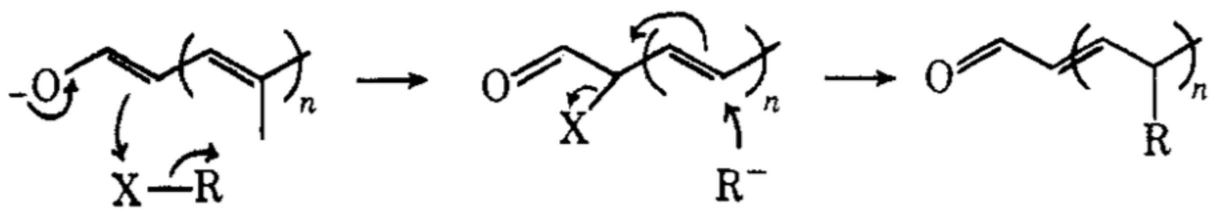

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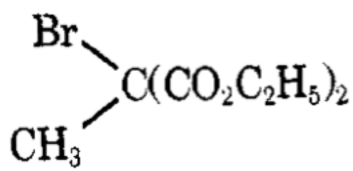

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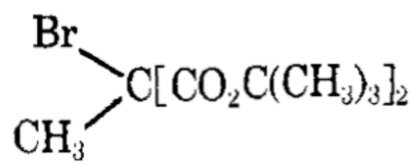

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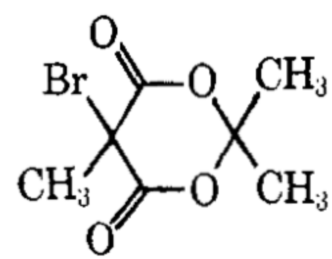

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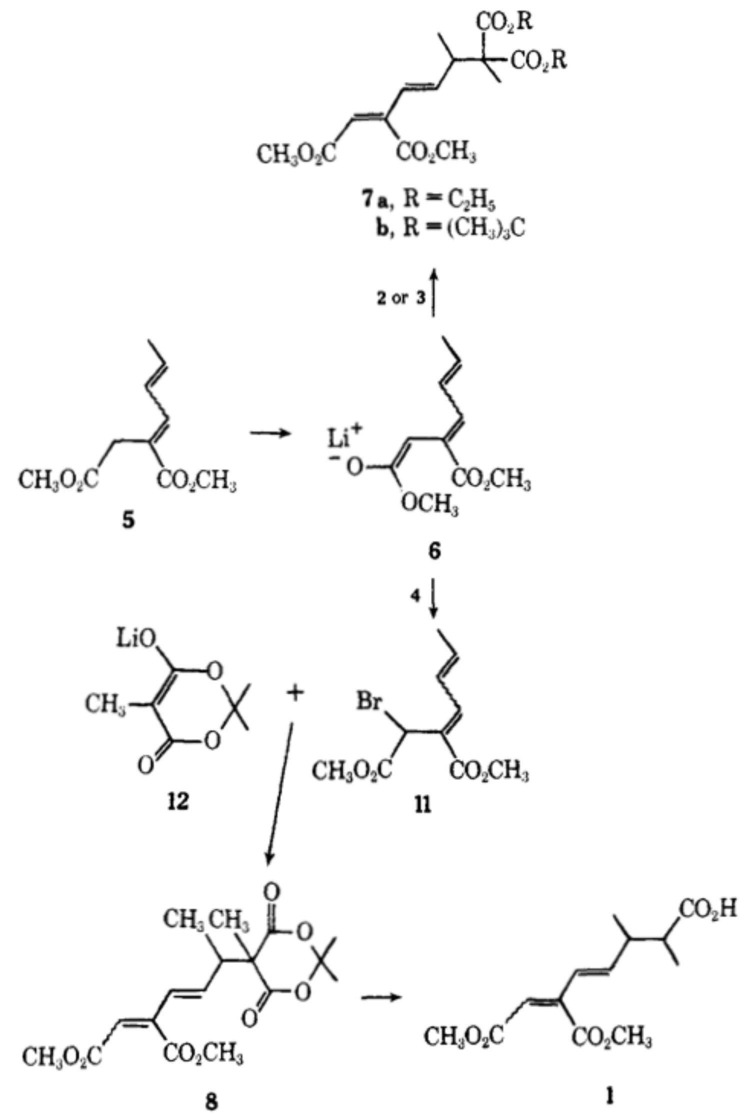
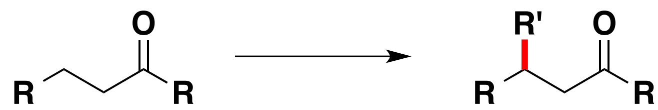
JACS, **1972**, *94*, 1970

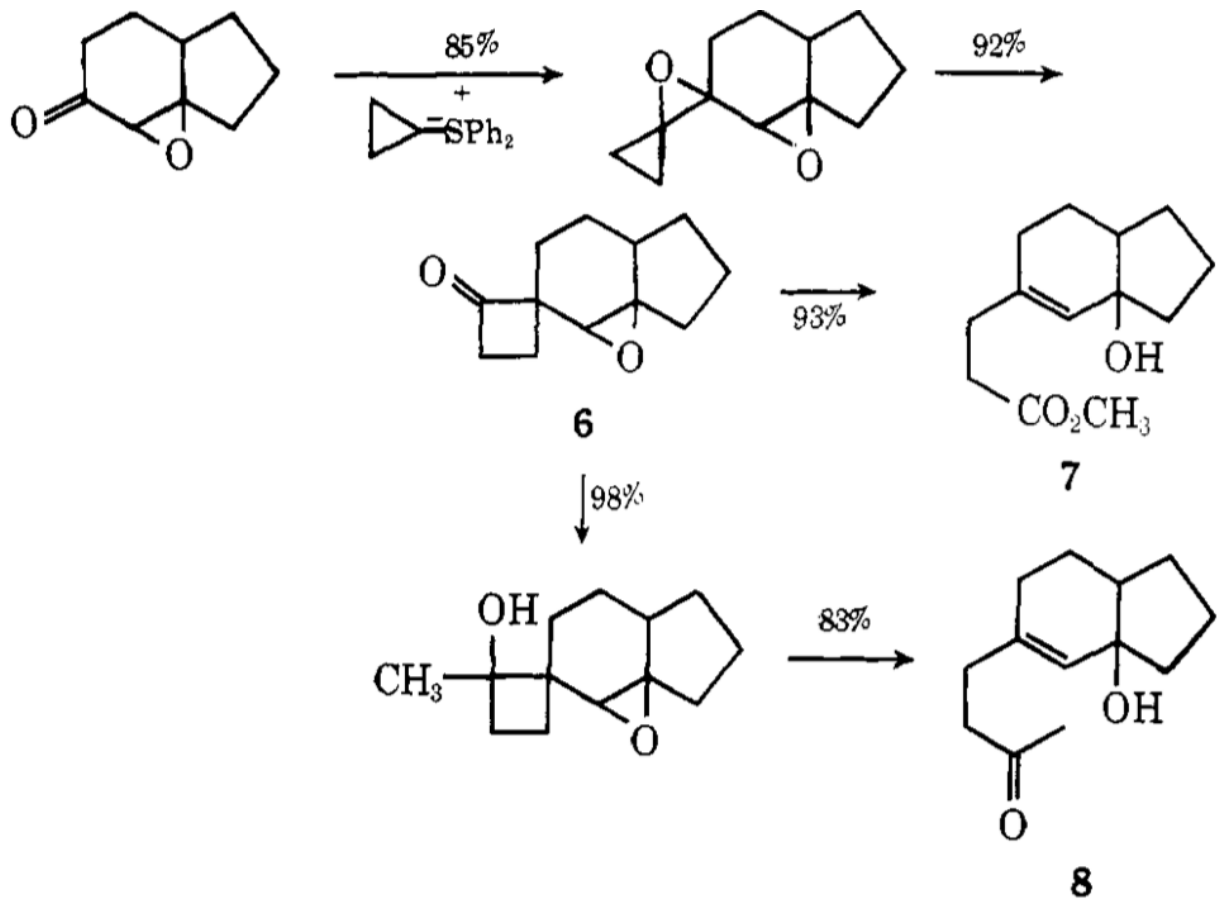
Transfer Alkylation



JACS, **1972**, *94*, 1970

Secoalkylation

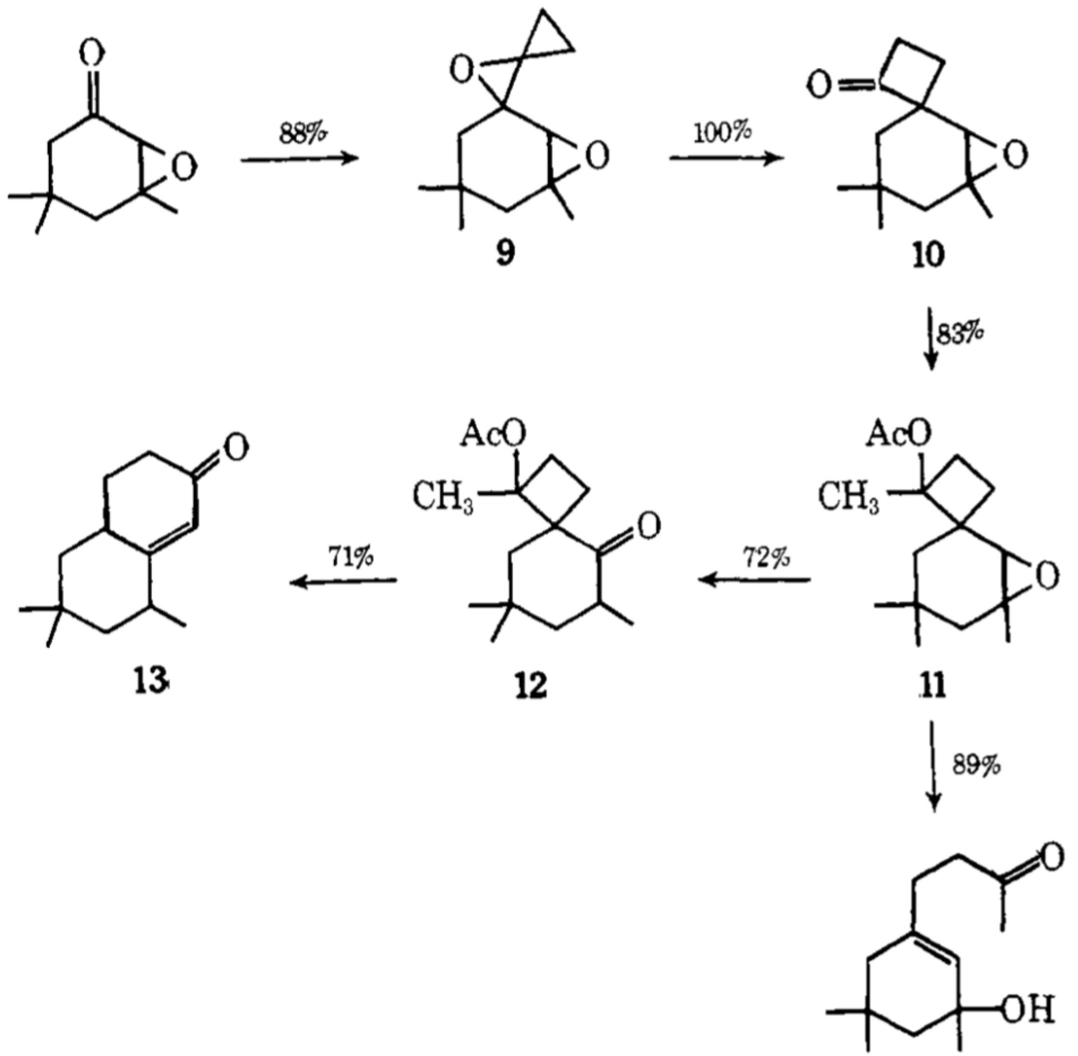




JACS, **1972**, *94*, 4777

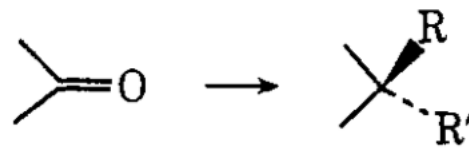
Secoalkylation

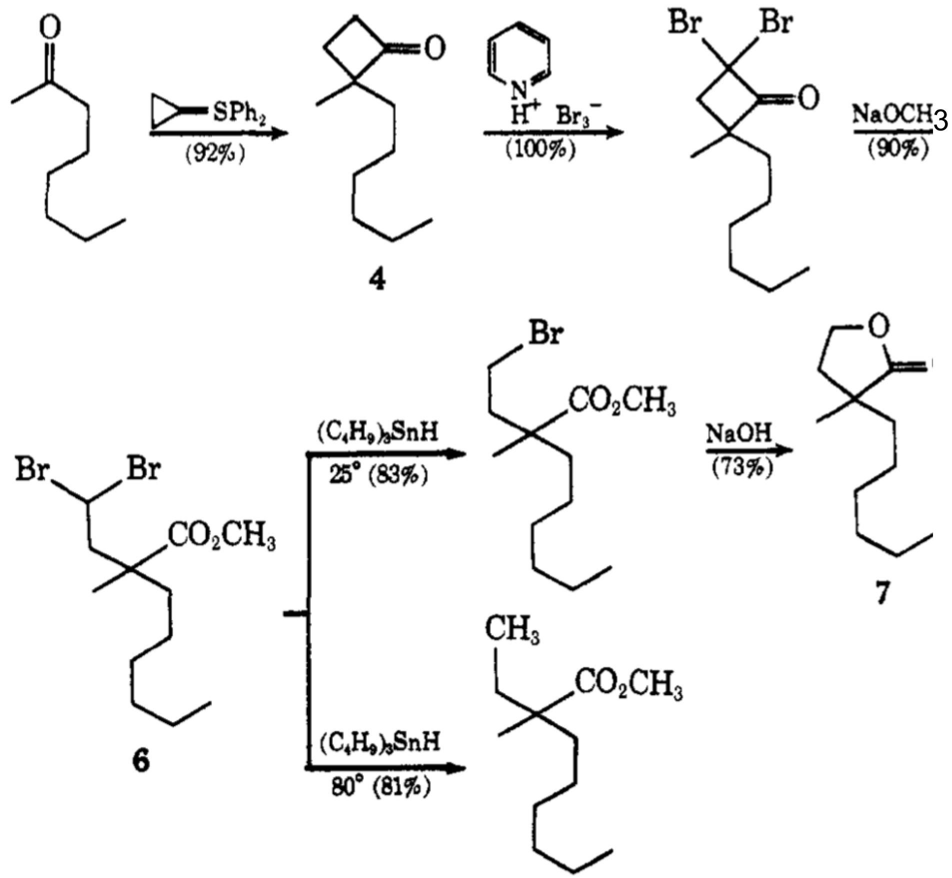
MICHIGAN STATE UNIVERSITY



JACS, **1972**, *94*, 4777

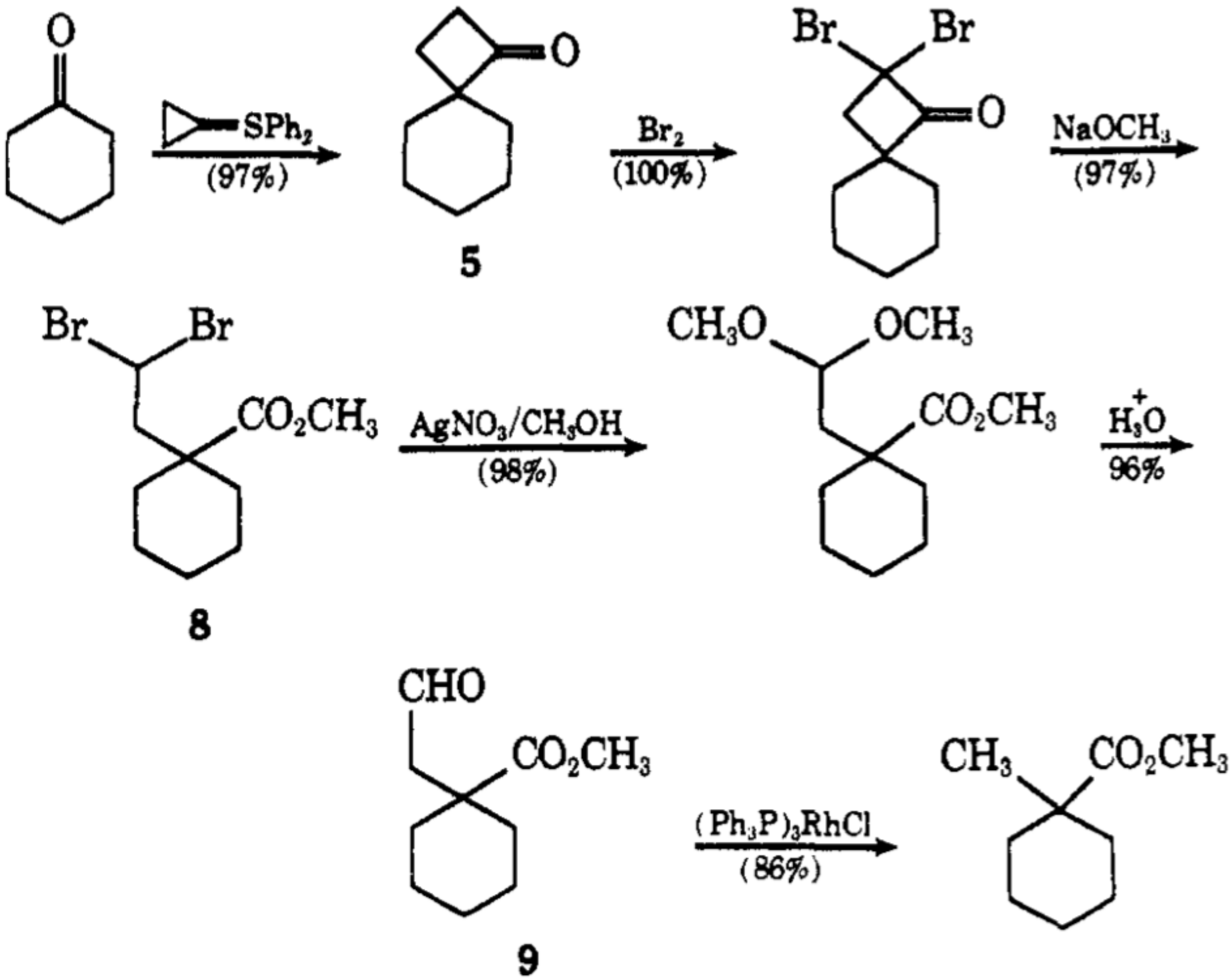
Geminal Alkylation





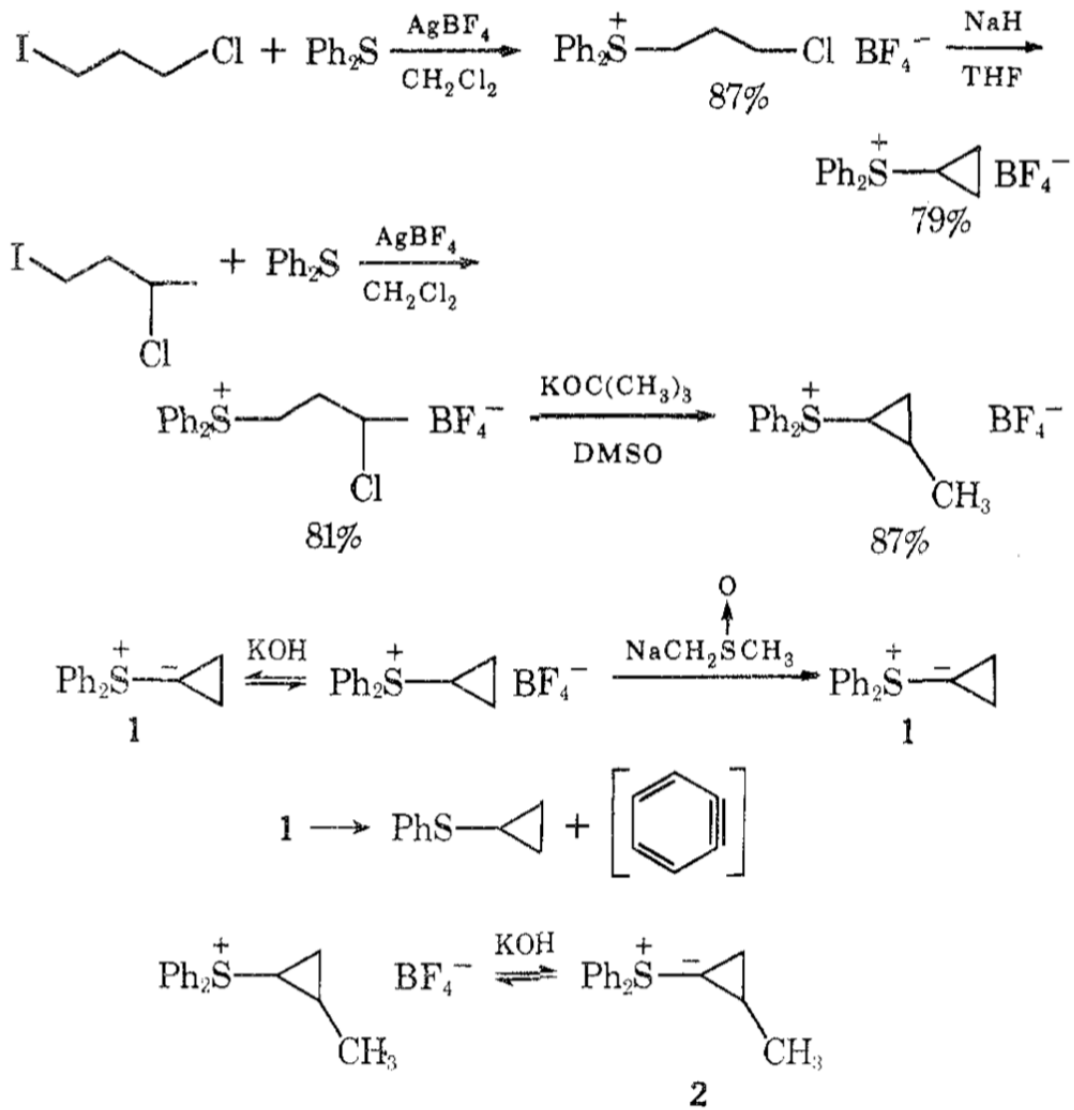
JACS, **1973**, *95*, 2038

Geminal Alkylation



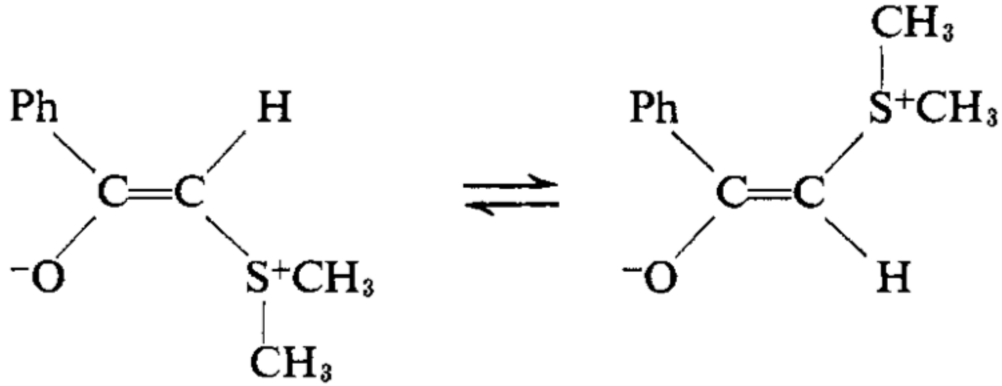
JACS, **1973**, *95*, 2038

Dimethylsulfonium Phenacylide



Accounts Chem. Res, **1974**, *7*, 85

Dimethylsulfonium Phenacylide



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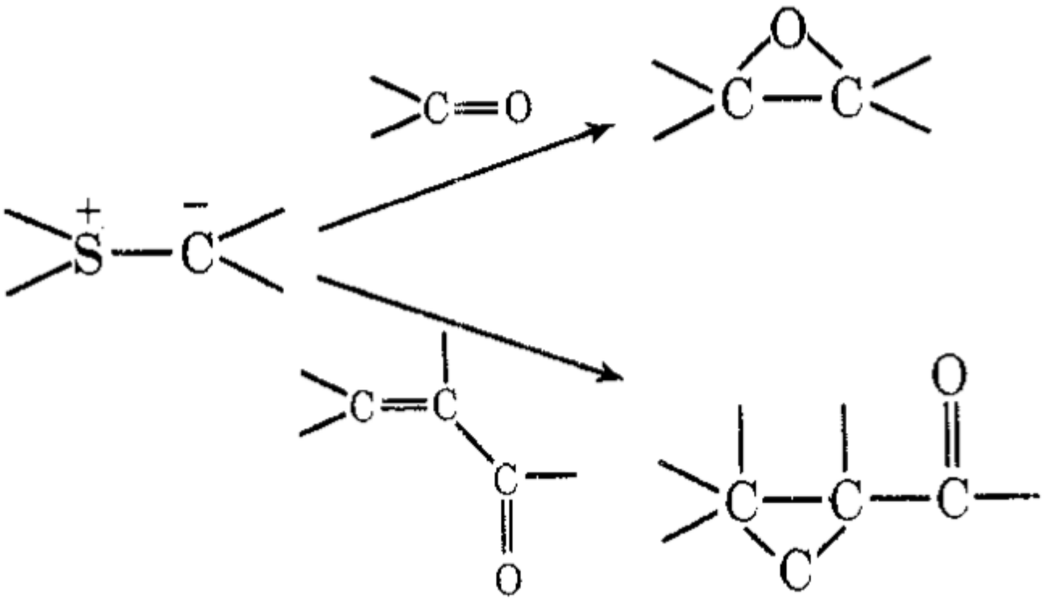
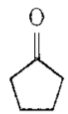
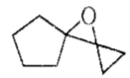
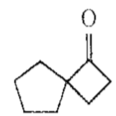
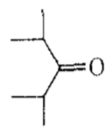
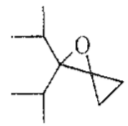
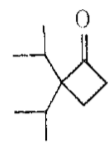
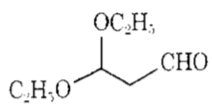
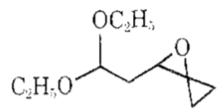
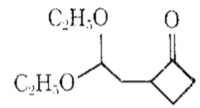
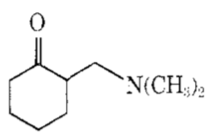
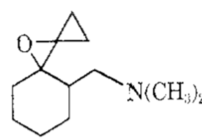
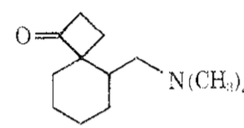
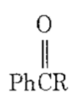
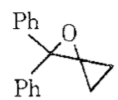
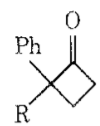
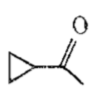
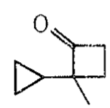
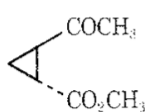
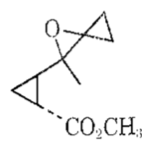
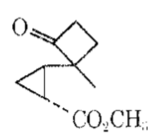


Trost, JACS, **1967**, *89*, 138

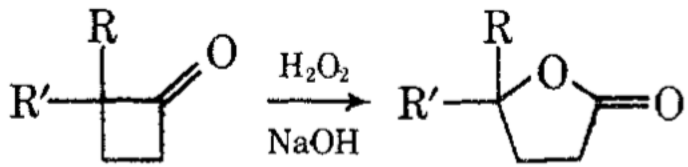
New Alkylation Methods

Formation of Selected Oxaspiropentanes and Cyclobutanones Utilizing 1

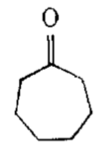
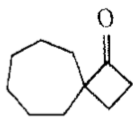
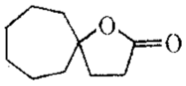
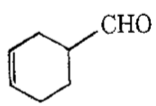
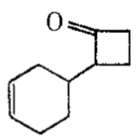
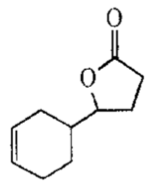
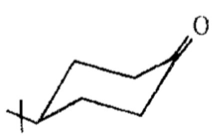
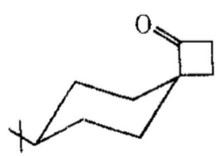
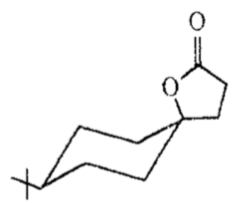
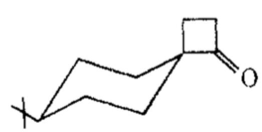
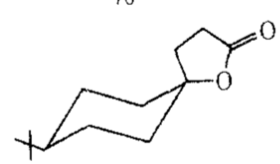
Entry	Aldehyde or ketone	Oxaspiropentanes	Cyclobutanones	Overall % yield
1		 (94)		(94)
2		 (59)		(59)
3				(59)
4				(44)
5		 (R = H, 87)		(R = H, 87) (R = Ph, 91)
6				(86)
7		 (87)		(71)

Accounts Chem. Res, **1974**, *7*, 85

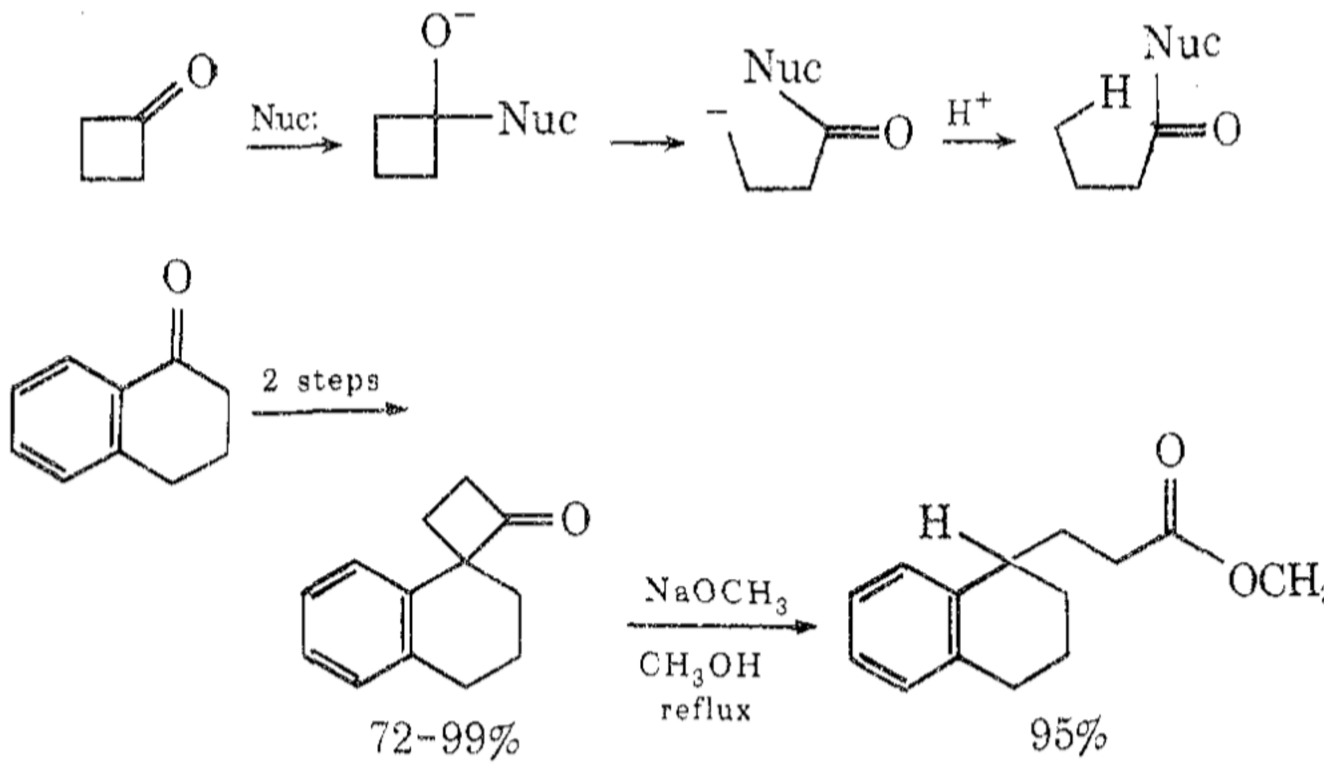
New Alkylation Methods



Representative Examples of Lactone Annelation

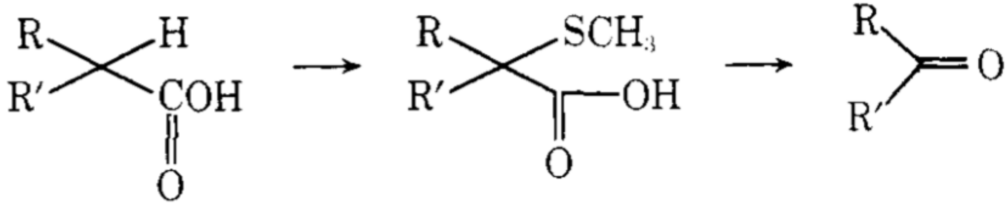
Entry	Ketone or aldehyde	Cyclobutanone	Lactone	Overall % yield
1				85
2				57
3		 70	 70	80
		 30	 30	

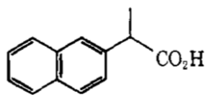
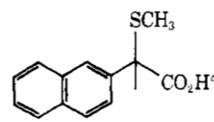
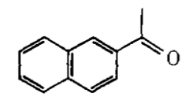
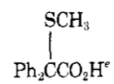
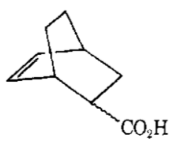
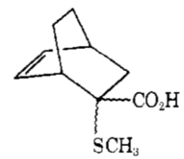
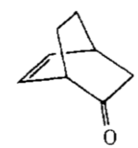
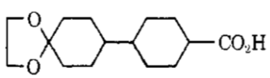
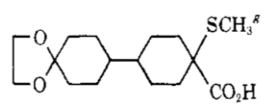
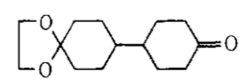
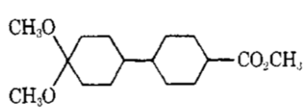
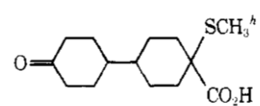
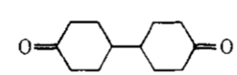
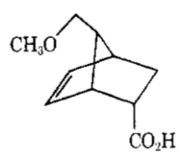
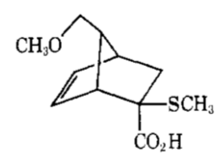
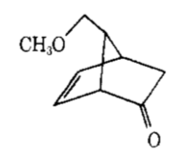
Accounts Chem. Res, **1974**, *7*, 85



Accounts Chem. Res, **1974**, *7*, 85

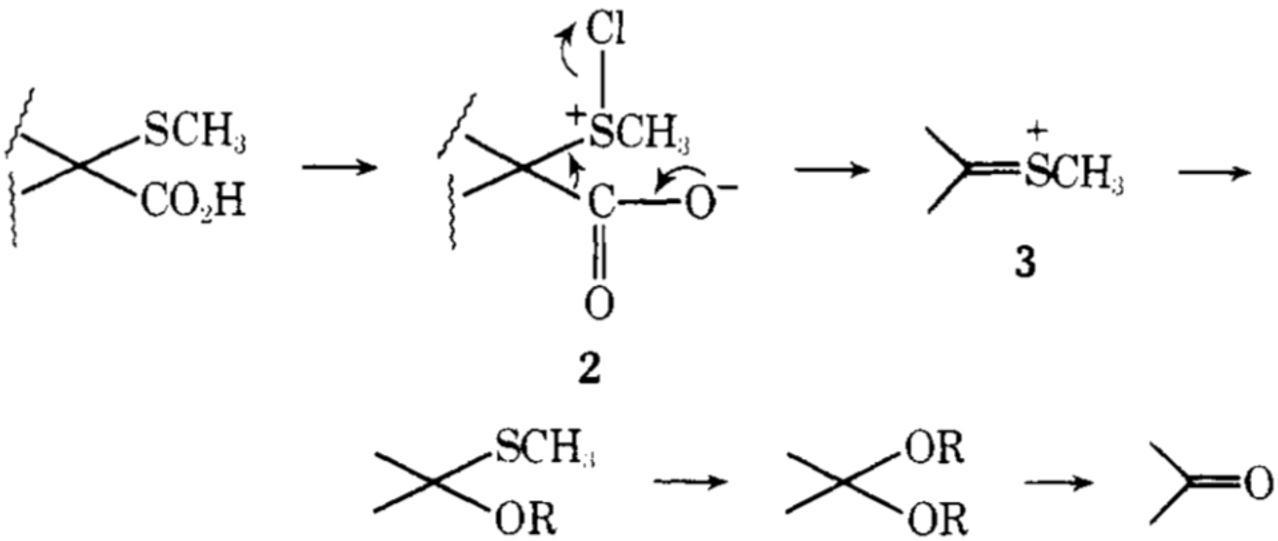
Oxidative Decarboxylation



Entry no.	Acid	Sulfenylation[a] temp (°C), time (min)	Sulfenylated acid	Oxidation time (hr)	Ketone	% yield[o]
1		−20, 20[b] 0, 30		1.25[i]		64[m]
2	Ph$_2$CHCO$_2$H	−20, 25[b] 0, 25		1.5[j]	Ph$_2$CO	57[m]
3		0, 40[c]		1.5–2.5[i]		44[n]
4		0, 30[c]		1.5[i]		78[m]
5		−20, 30[b] 0, 30 *p*, 5		3[i]		69[m]
6		0, 50[c]		2[i]		62–76[n]

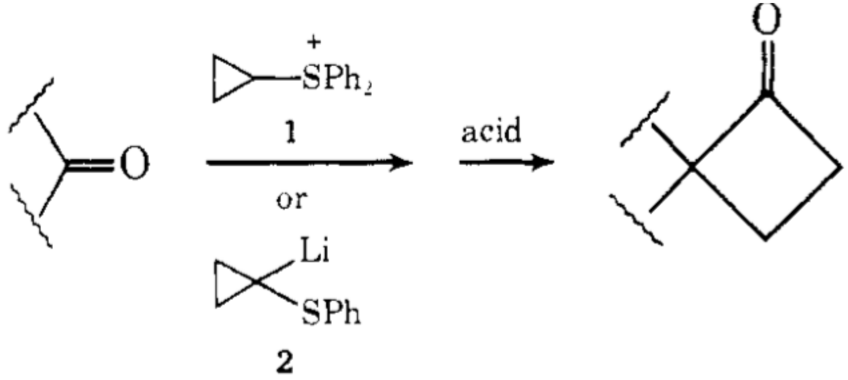
JACS, **1975**, *97*, 3528

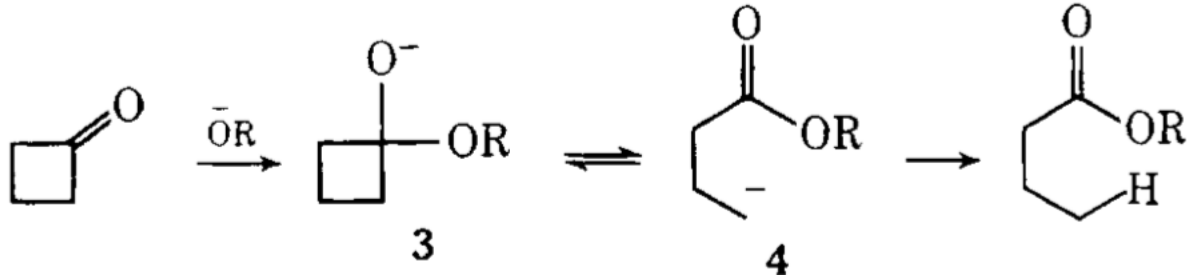
Oxidative Decarboxylation

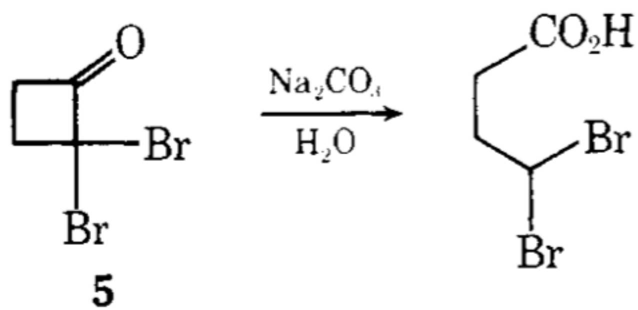


JACS, **1975**, *97*, 3528

Geminal and Reductive Alkylations

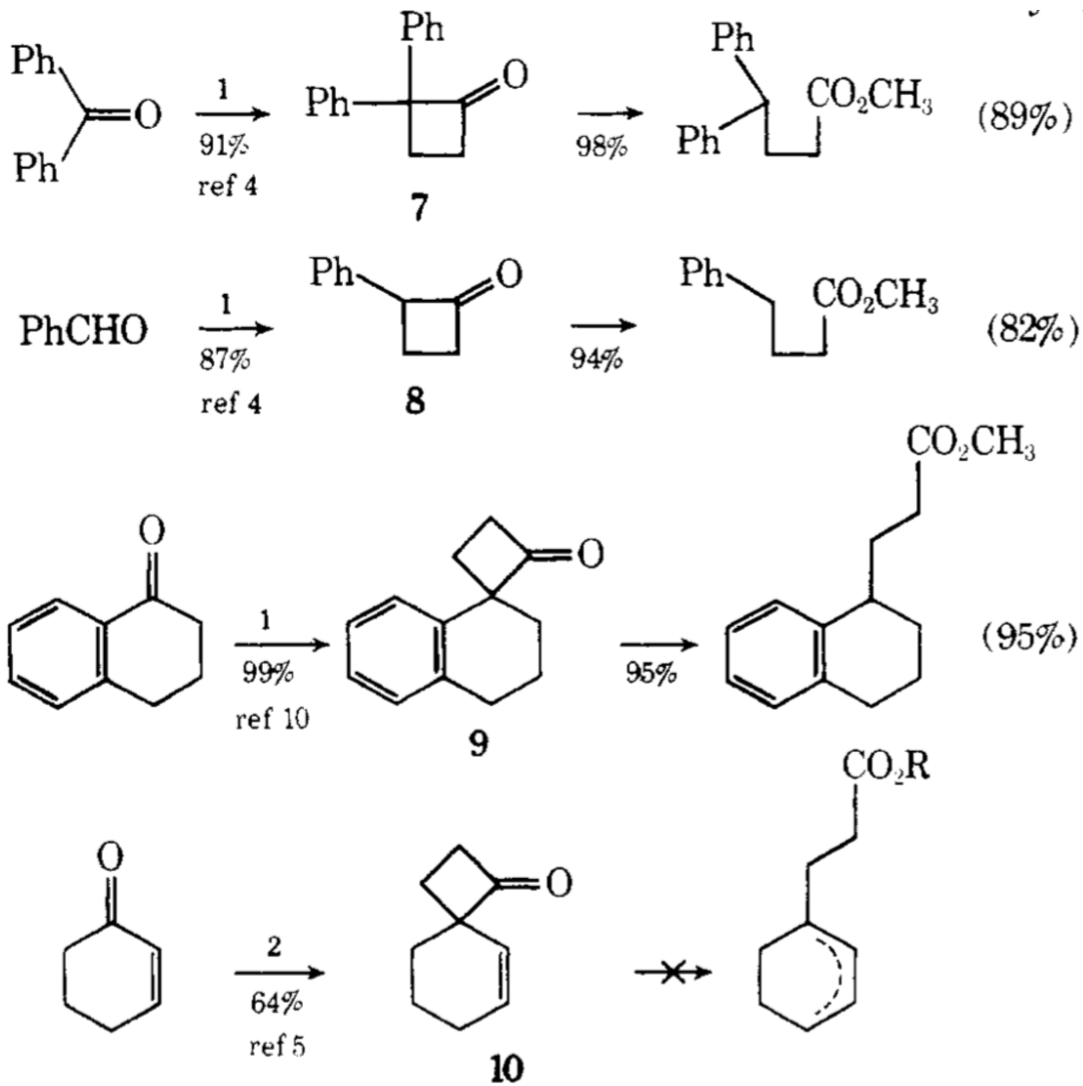






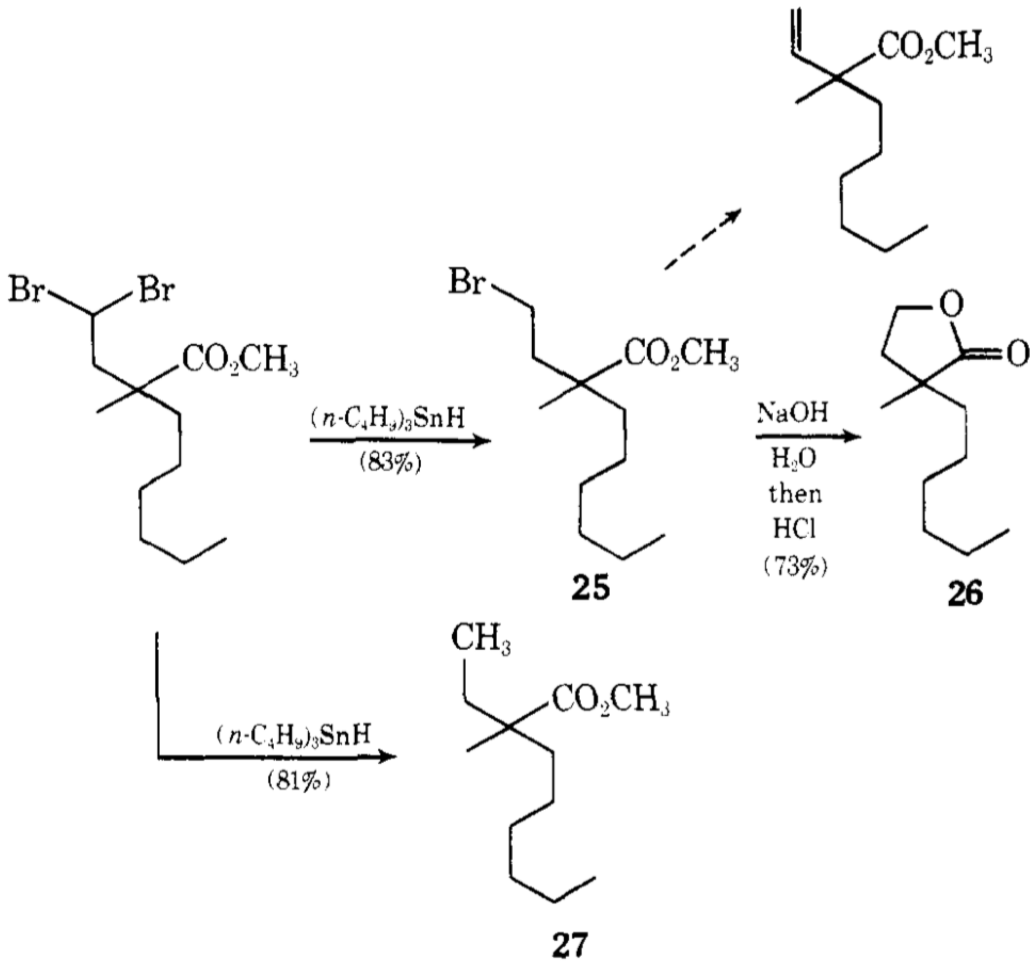
JACS, **1975**, *97*, 2218

Geminal and Reductive Alkylations



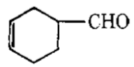
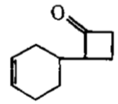
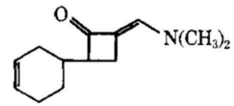
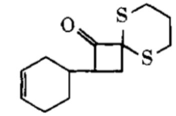
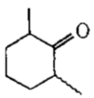
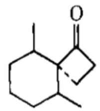
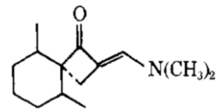
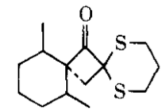
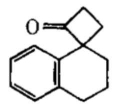
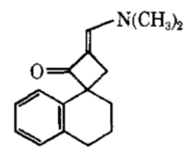
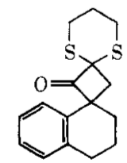
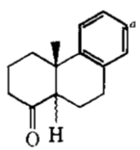
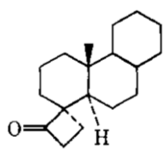
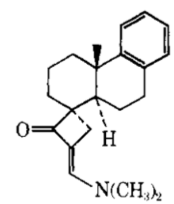
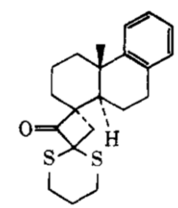
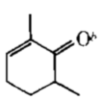
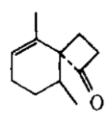
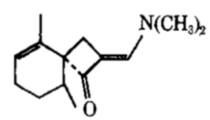
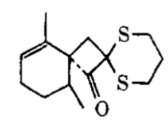
JACS, **1975**, *97*, 2218

Geminal and Reductive Alkylations



JACS, **1975**, *97*, 2218

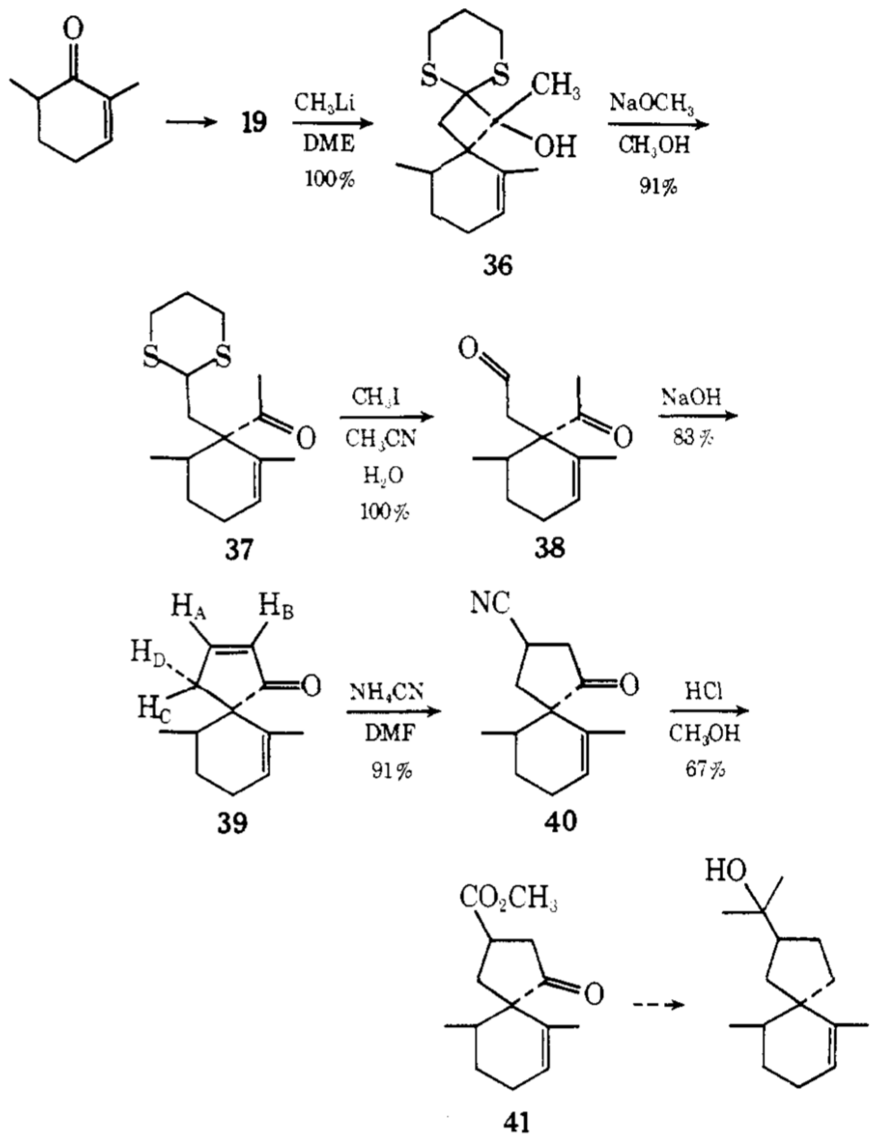
Geminal Alkylation via α-Trimethylenedithiocyclobutanones

Aldehyde or ketone	annel-ation[c]	Cyclobutanone	(% yield)[d]	Enamide	(% yield)[e]	dithiocyclo-butanone	(% yield)[d]
	A	 2	(70)[f,g]	 10	(98)	 15	(19)
	A	 3	(88)[f]	 11	(87)	 16	(37)
1-Tetralone	A	 4	(99)[f,g]	 13	(95)	 17	(62)
 7	A	 5	(99)[f,g]	 13	(100)	 18	(91)
	B	 6	(72)[h]	 14	(97)	 19	(53)

[a] G. Stork and A. Burgstahler, *J. Am. Chem. Soc.*, 73, 3544 (1951). [b] R. K. Smith, M.S. Thesis, University of Wisconsin, 1972. [c] Method A: diphenylsulfonium cyclopropylide, reversible conditions. Method B: 1-lithiocyclopropyl phenyl sulfide. [d] Yield of isolated pure product. [e] Yield of solid before recrystallization. Recrystallization unnecessary for further transformation. [f] This work. [g] See also reference 5. [h] Reference 6.

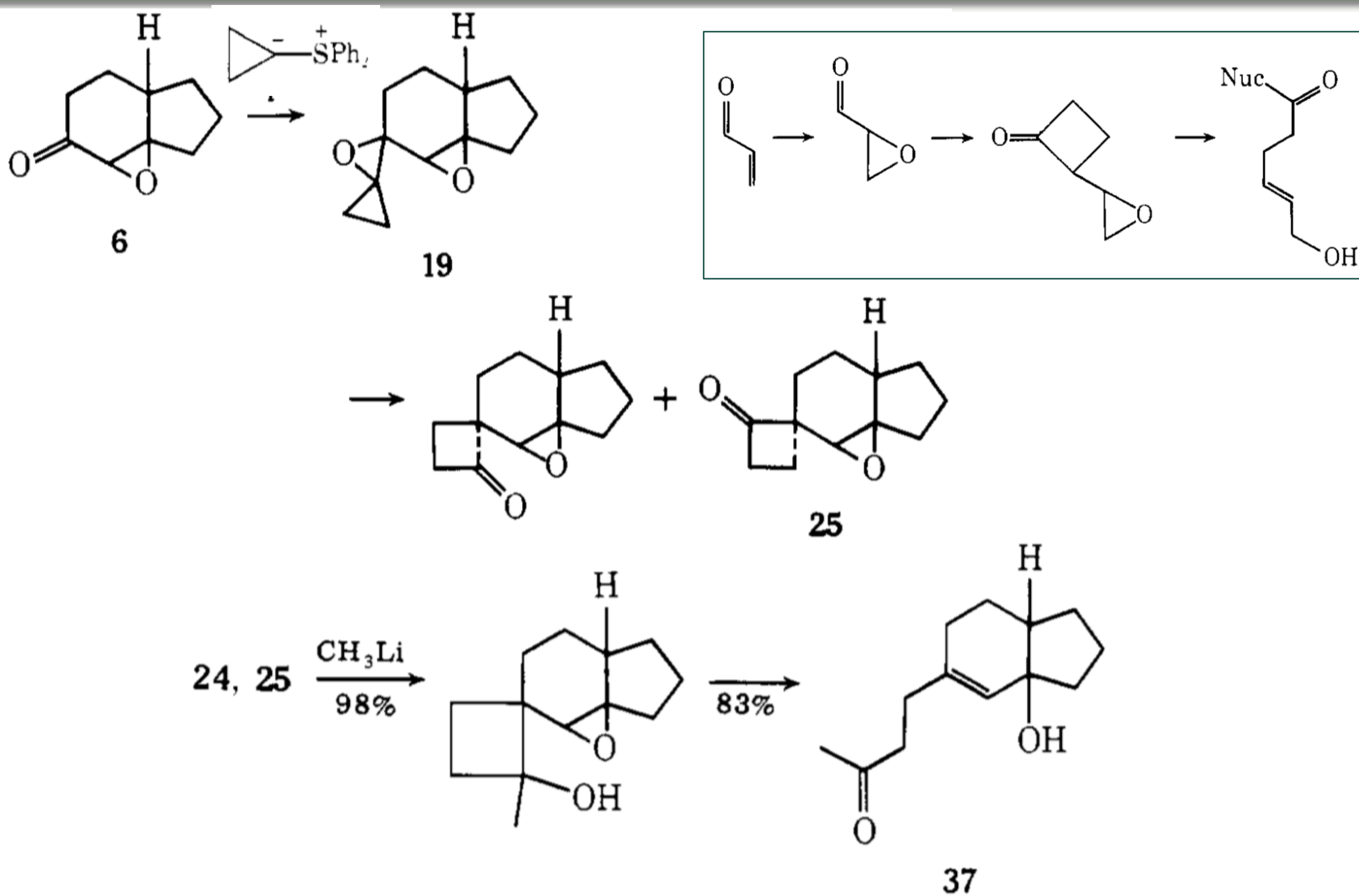
JACS, **1975**, *97*, 2224

Geminal Alkylation via α-Trimethylenedithiocyclobutanones



JACS, **1975**, *97*, 2224

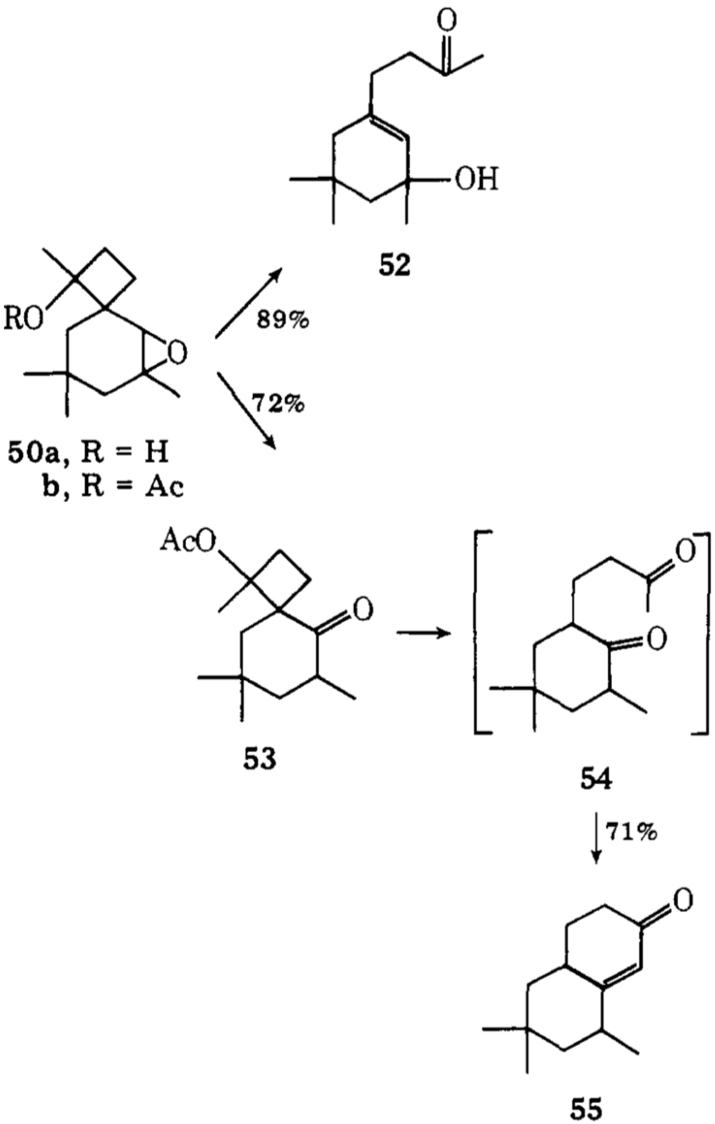
Oxasecoalkylation via Cyclobutanone Intermediates

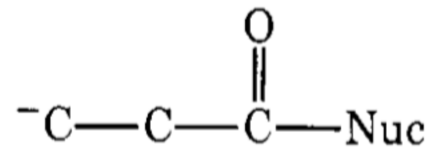


JACS, **1978**, *100*, 5512

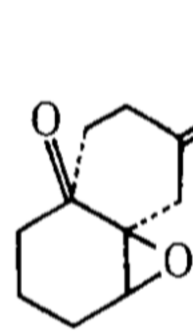
Oxasecoalkylation via Cyclobutanone Intermediates

MICHIGAN STATE UNIVERSITY

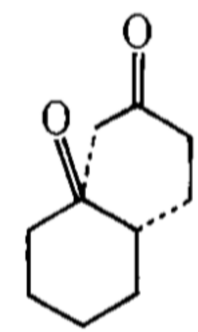




61



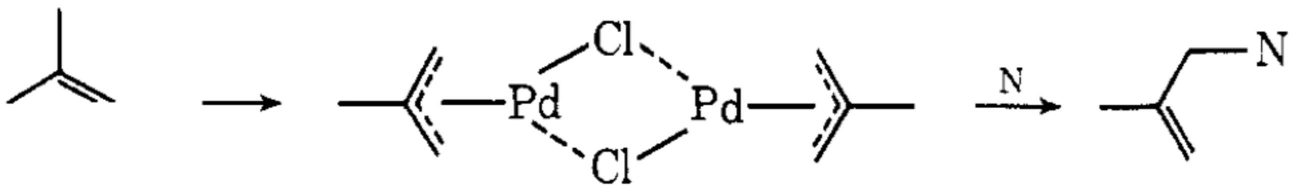
secoalkylation–
annelation



Robinson
annelation

JACS, **1978**, *100*, 5512

Allylic Alkylation



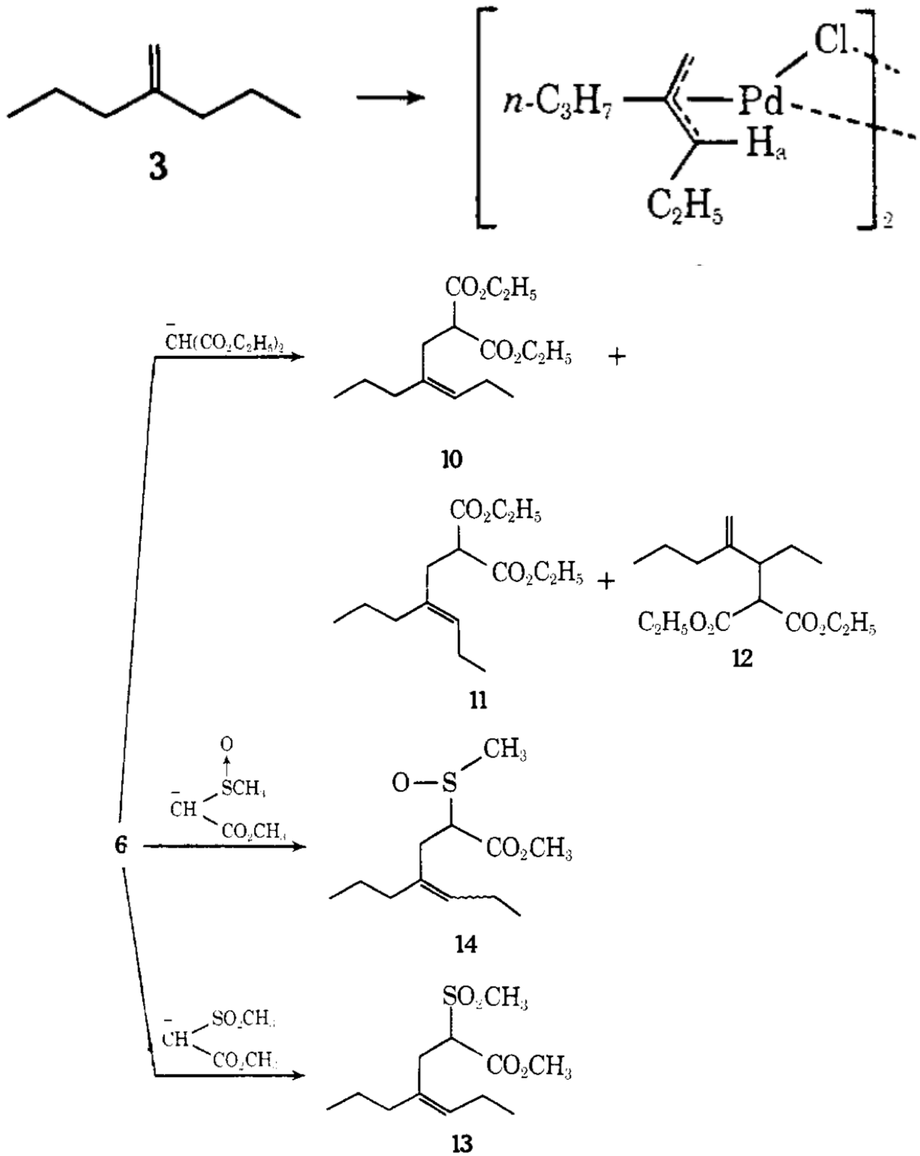
(1)

Formation of the Π-allyl complex directly from the olefin can be accomplished in high yields (80-100 %) by either treatment with palladium chloride in methylene chloride containing sodium carbonate (method **A**) or with palladium chloride and sodium chloride in acetic acid containing sodium acetate (method **B**).

JACS, **1973**, *95*, 292

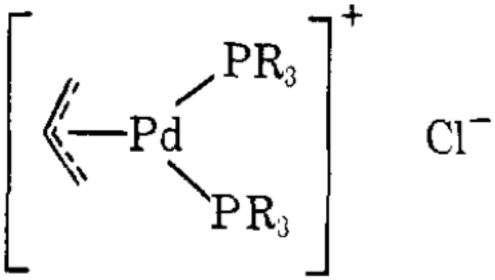
Allylic Alkylation

MICHIGAN STATE UNIVERSITY



JACS, **1973**, *95*, 292

Allylic Alkylation

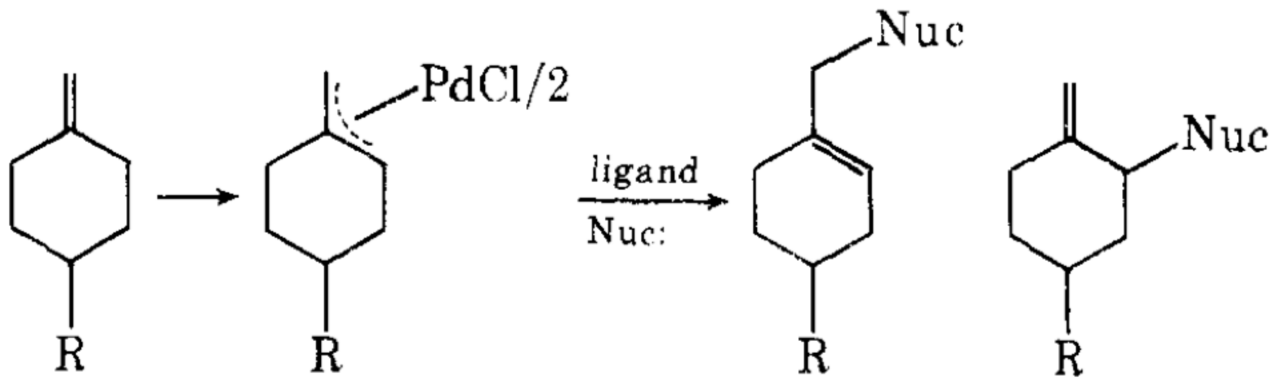


18

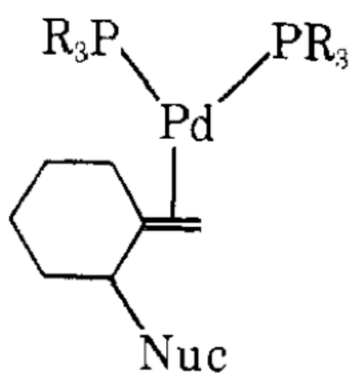
Although no definitive statements regarding the course of the alkylation can be made, the requirement of 4 equiv of phosphine per dimer and the use of a soft anion led us to suggest the ionic complex **18** as an inter- mediate.

JACS, **1973**, *95*, 292

Regio- and Stereoselectivity of Allylic Alkylation



1



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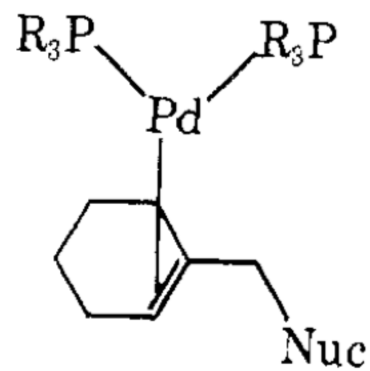
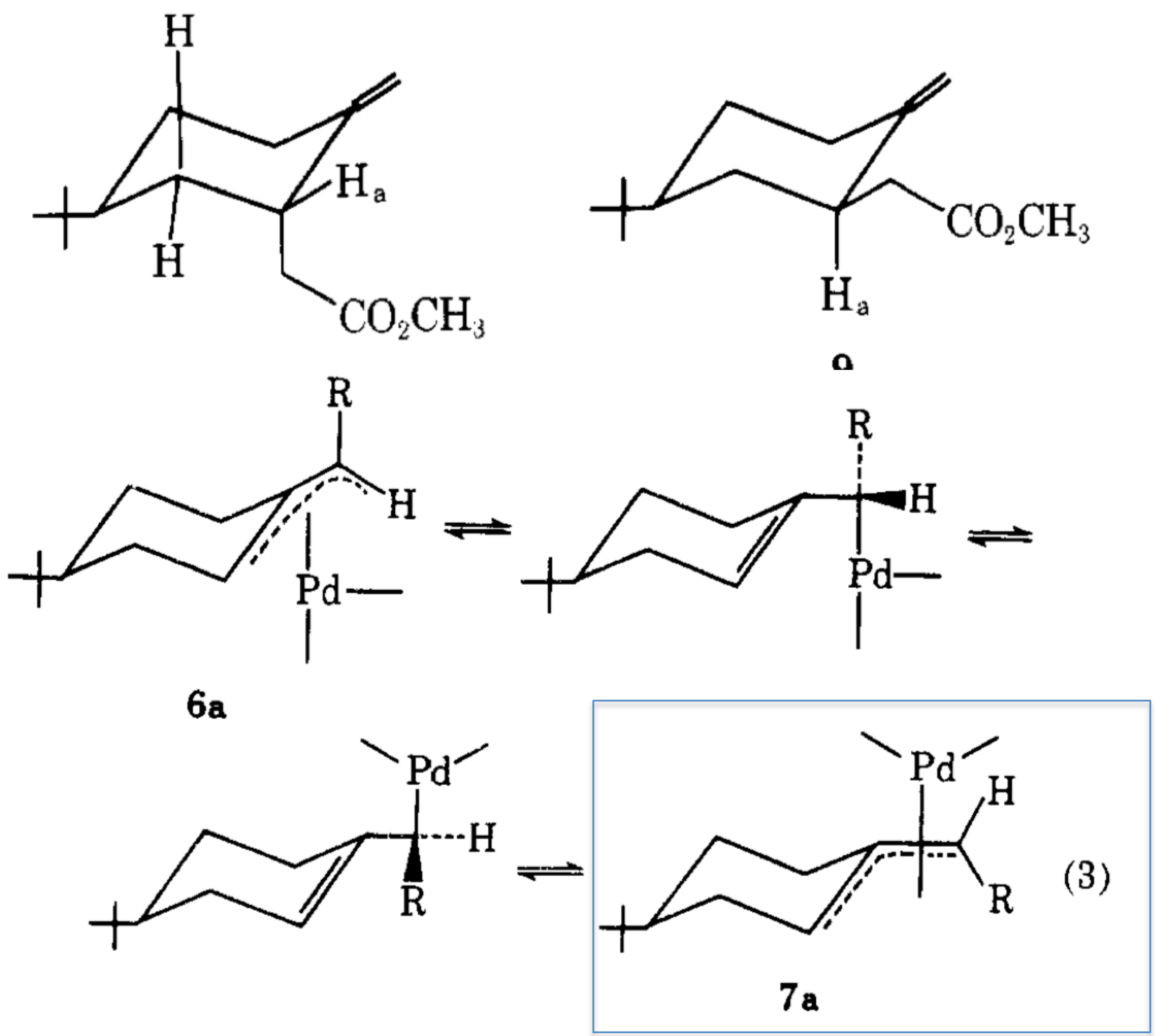


5

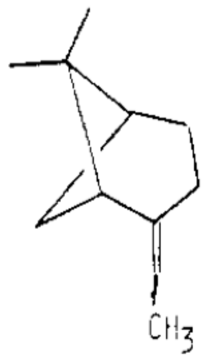
JACS, **1975**, *97*, 2534

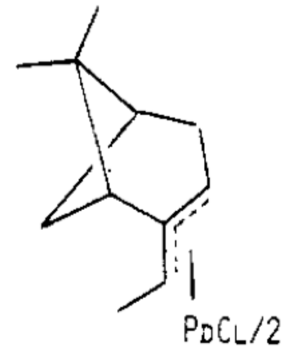
Regio- and Stereoselectivity of Allylic Alkylation



JACS, **1975**, *97*, 2534

Sterochemistry Allylic Alkylation





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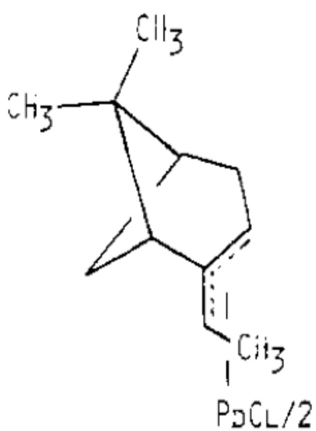
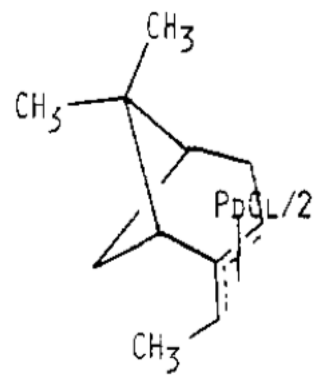
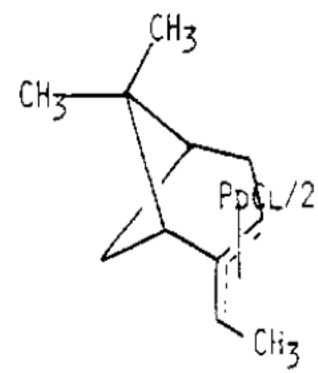


2b



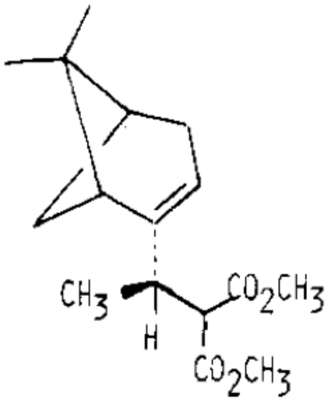
2c



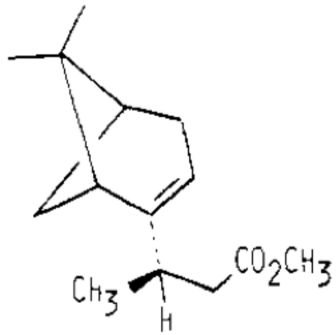
2d

JACS, **1975**, *97*, 1611

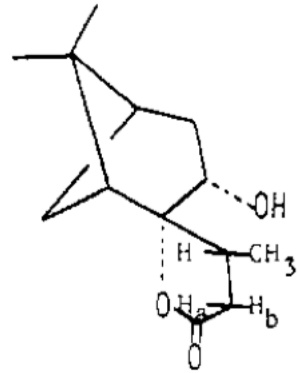
Sterochemistry Allylic Alkylation



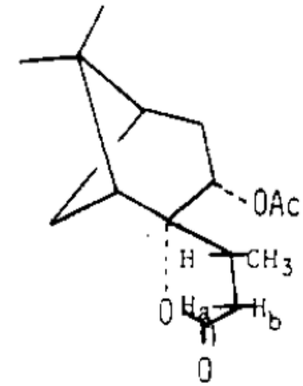
3a



4a



5a



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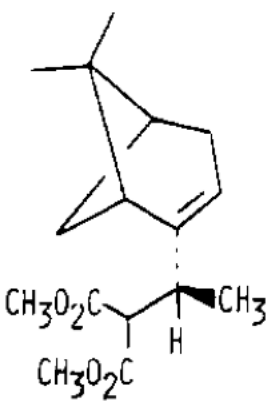
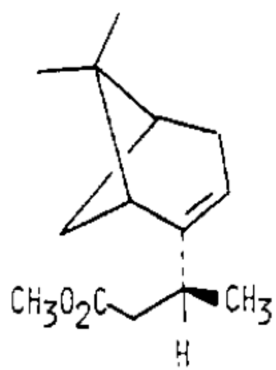


3b



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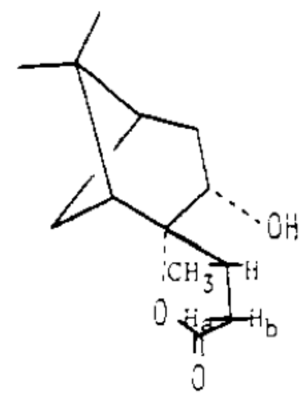
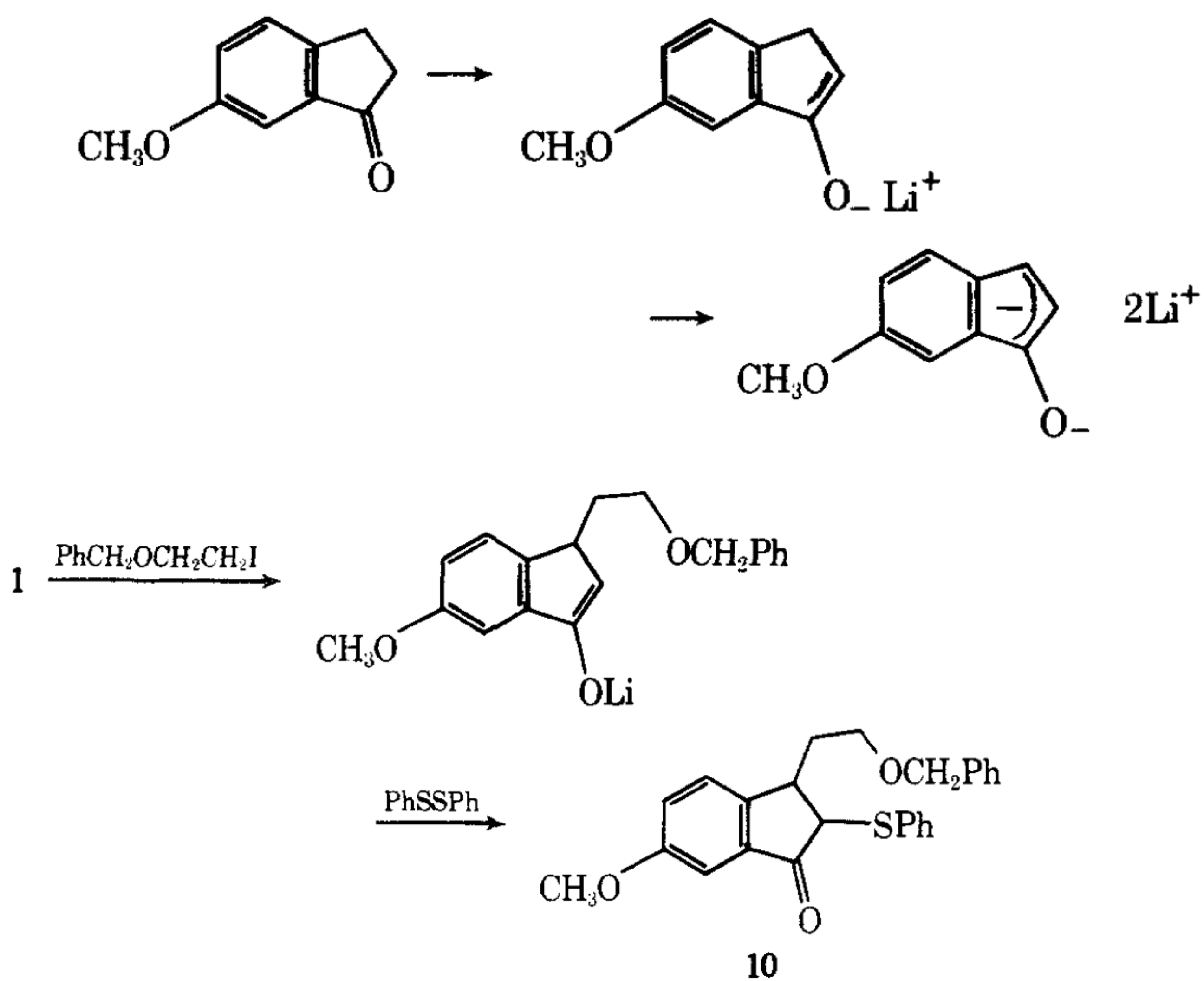


5b

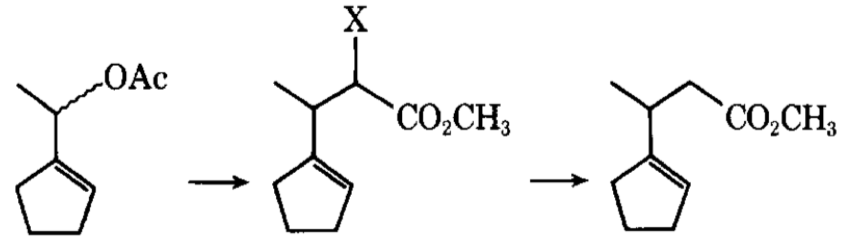
JACS, **1975**, *97*, 1611

Generation and Alkylation of the Dianion of 1-Indanone



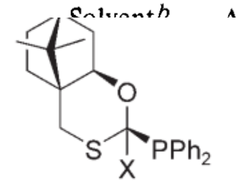
JOC, **1977**, *42*, 3212

Asymmetric Induction in Catalytic Allylic Alkylation

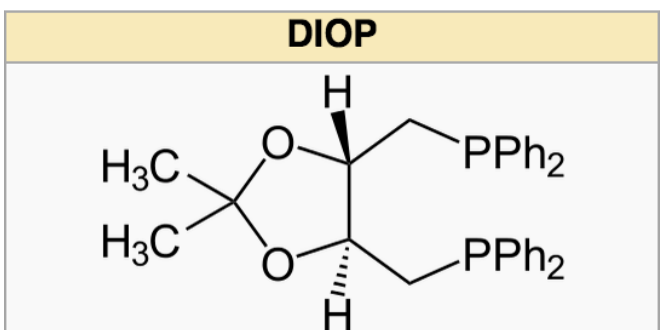


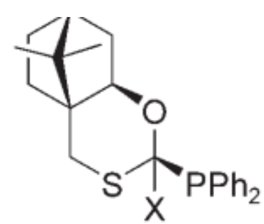
5 6 7

Entry	Ligand[a]	Nucleophile	Solvent[b]	Alkylation	Decarbomethoxylation or desulfonylation	Rotation of 7 (C, CCl_4)	Optical yield
1	(+) DIOP[c]	$NaCH(CO_2CH_3)_2$		57	94	+0.833 (3.85)	21
2	(+) DIOP[c]	$NaCH(CO_2CH_3)_2$		98	60	−1.5 (1.0)	37
3	(+) DIOP[c,f]	$NaCH(CO_2CH_3)_2$		82	74	+1.55 (2.75)	38
4	(−) DIPAMP[d]	$NaCH(CO_2CH_3)_2$		62	87	−0.65 (1.2)	16
5	(+) CAMPHOS[e]	$NaCH(CO_2CH_3)_2$		99	80	−1.50 (1.2)	37
6	(+) CAMPHOS[e]	$NaCH(SO_2Ph)(CO_2CH_3)$		76	78	−1.60 (2.25)	39
7	(+) DIOP[c]	$NaCH(SO_2Ph)(CO_2CH_3)$	DME	84	87	−1.86 (2.25)	46

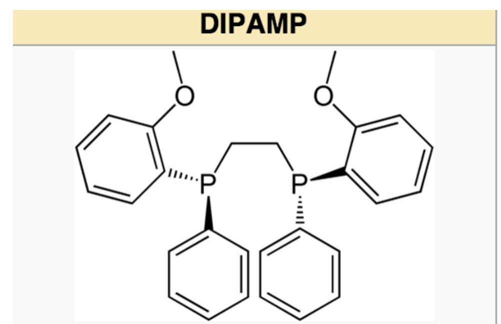


X = H CamPHOS



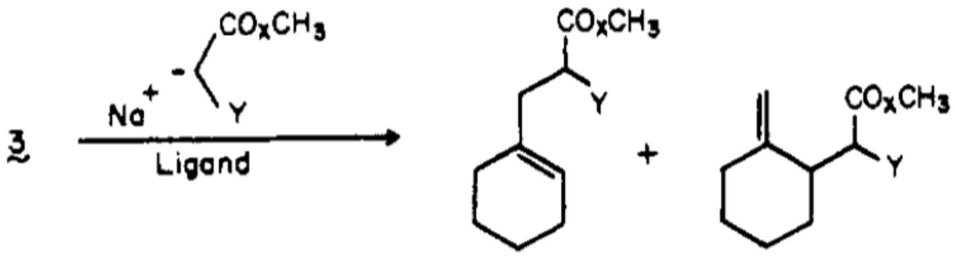


X = H CamPHOS



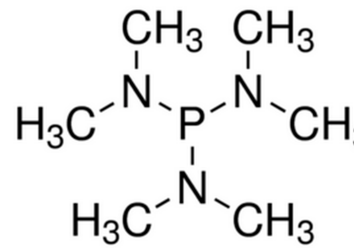
JACS, **1977**, *99*, 1649

Allylic Alkylation: Nature of the Nucleophile

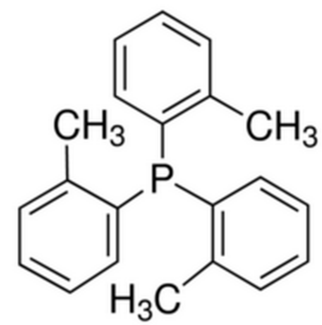


7   8

X	Y	Ligand	% yield	7	8
2	CO_2CH_3	HMPT[a]	74	79[c]	21[c]
2	CO_2CH_3	TOT[b]	57	26[c]	74[c]
2	$PhSO_2$	HMPT	73	95	5
2	$PhSO_2$	TOT	78	16	84
2	CH_3SO_2	HMPT	90	100[c]	*c*
2	CH_2SO_2	TOT	90	15[c]	85[c]
2	PhSO	HMPT	71	100	
1	PhS	HMPT	70	90	10
2	PhS	HMPT	*d*	52	43
2	PhS	TOT	15	<1	>99
2	CH_3S	HMPT	*e*		

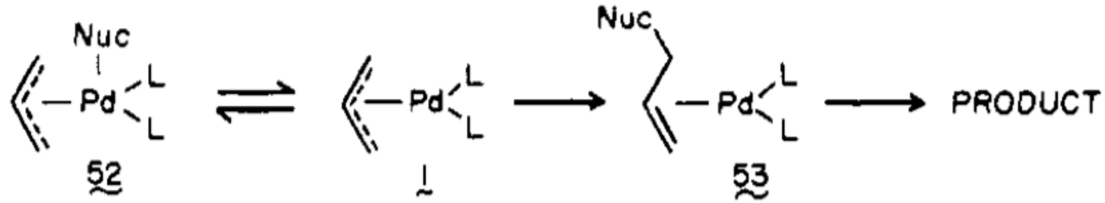


HMPT

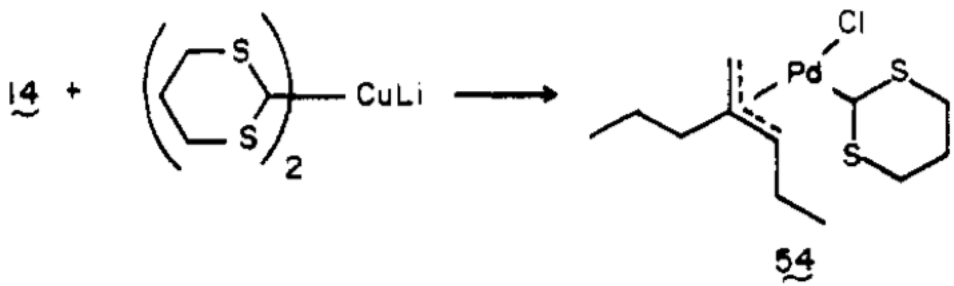


TOT

Allylic Alkylation: Nature of the Nucleophile



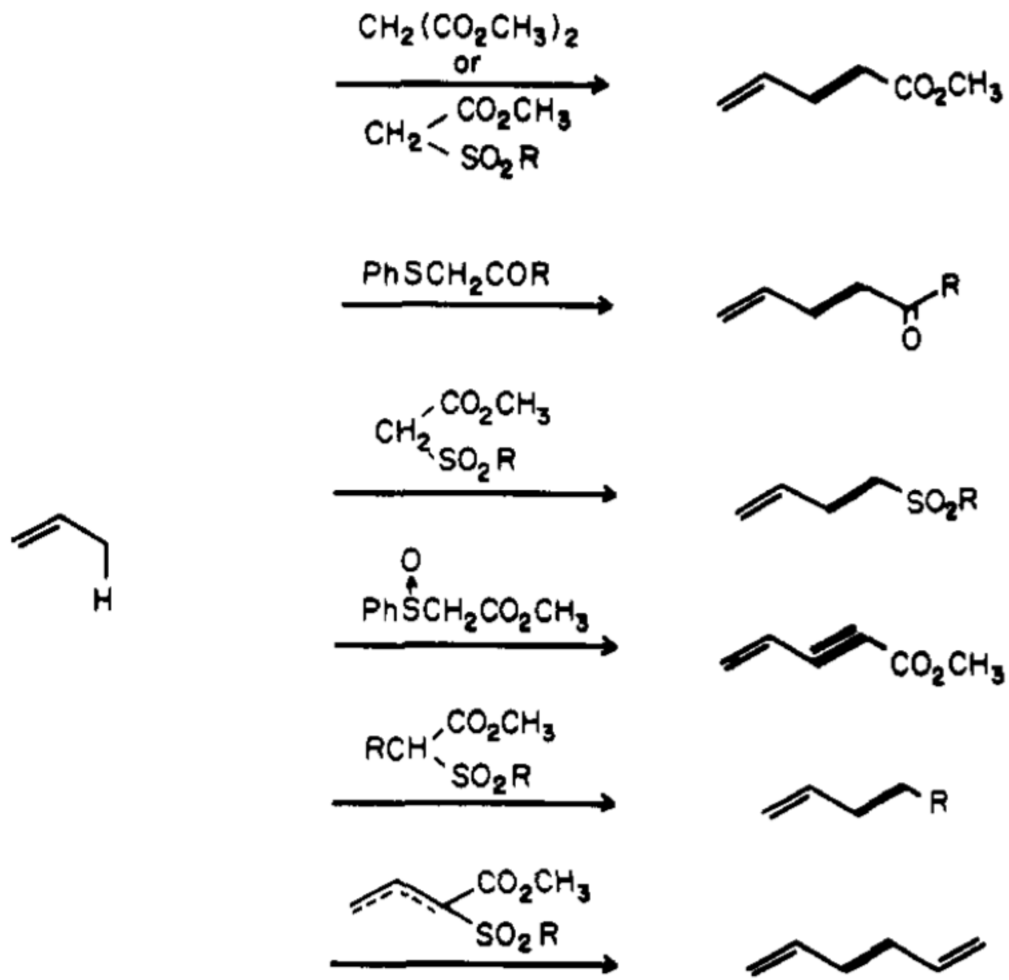
First, it is possible that kinetically reaction occurs initially at palladium. Subsequent C-alkylation then requires this initial reaction to be reversible. The lower the stability of the anion, the poorer the reversibility.



As the nucleophile becomes harder, charge distribution becomes more important in determining the regiochemistry. Since more positive charge resides at palladium rather than carbon, attack occurs there-ultimately leading to decomposition.

JACS, **1978**, *100*, 3426

Allylic Alkylation: Nature of the Nucleophile

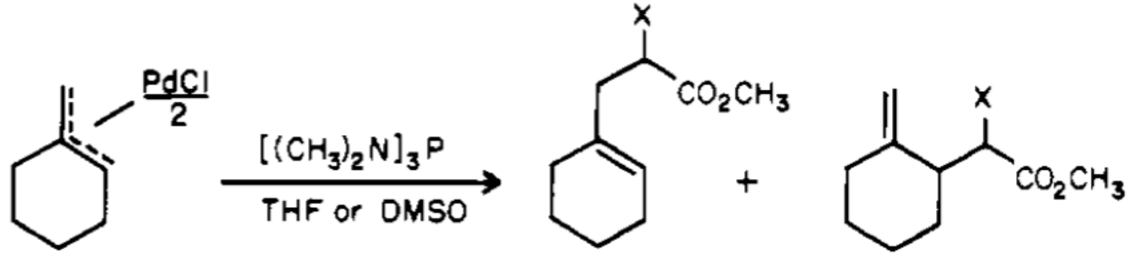


JACS, **1978**, *100*, 3426

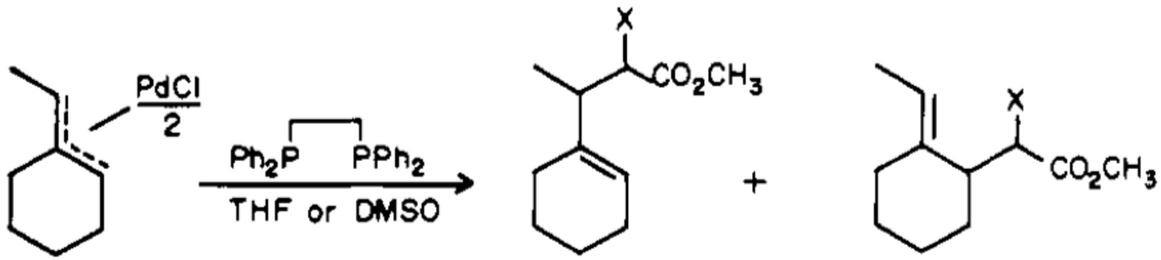
Allylic Alkylation: Nu attack on π-Allyl-Pd Complexes

$NaCH(CO_2R)_2$ $CH_3SO_2\overset{\ominus}{C}HCO_2CH_3$

2   6



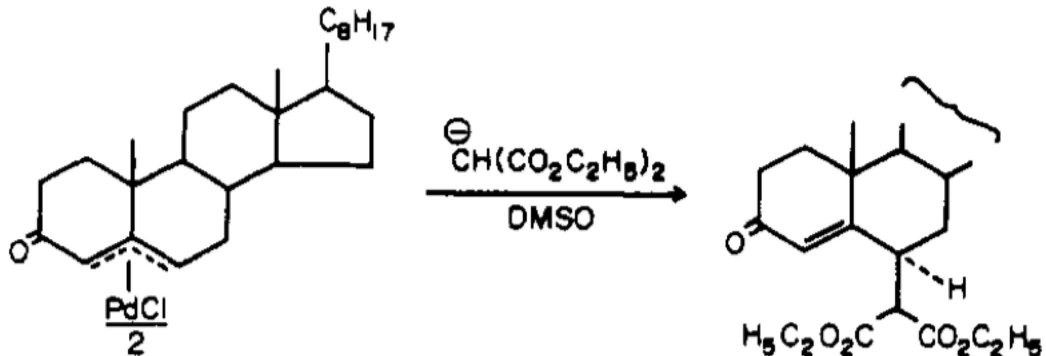
16	17	18
+2 (70%, X = CO_2CH_3)	79%	21%
+6 (58–90%)	100%	0%



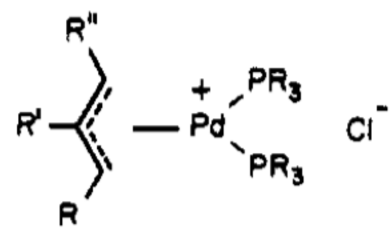
19	20	21
+2 (100%, X = CO_2CH_3)	47%	53%
+6 (54%, X = SO_2CH_3)	50%	50%

JACS, **1978**, *100*, 3461

Allylic Alkylation: Nu attack on π-Allyl-Pd Complexes



42

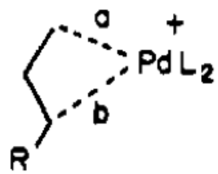


43

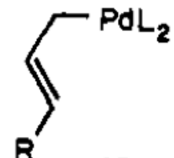
JACS, **1978**, *100*, 3461

$$\mathbf{16} \xrightarrow[\text{Me}_2\text{SO}]{\text{NaCH(CO}_2\text{CH}_3)_2} \mathbf{17} + \mathbf{18}$$

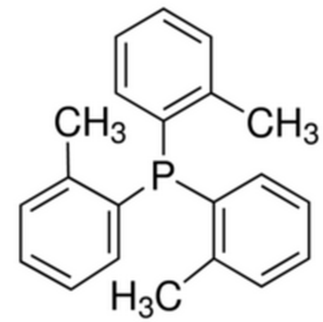
	17 X = CO_2CH_3	18 X = CO_2CH_3
HMPT (70%)	79%	21%
TOT (57%)	26%	74%



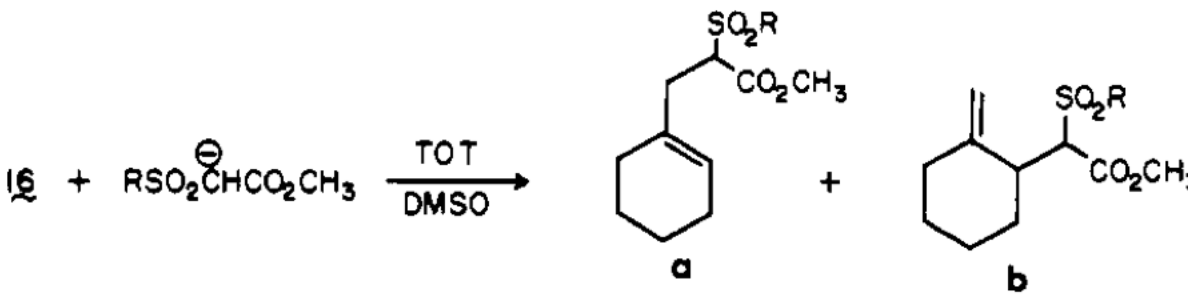
44



45



TOT



	a	b
R = CH_3	15%	85%
R = Ph	26%	74%

JACS, **1978**, *100*, 3461

Pd-Mediated Cycloaddition Approach to Cyclopentanoids

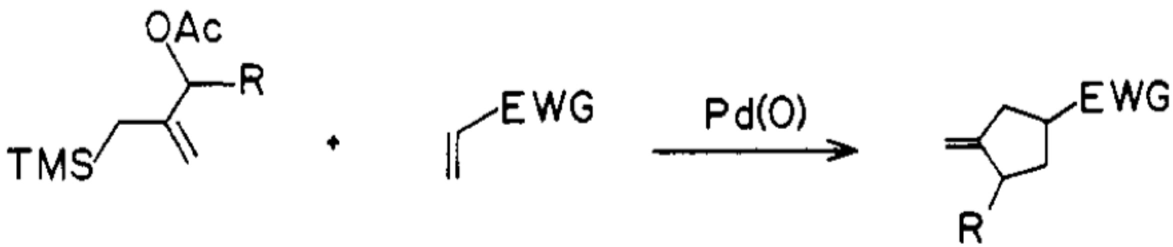
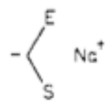
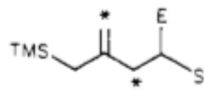
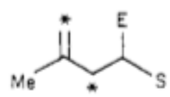
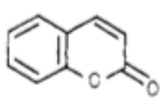
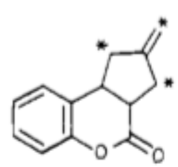
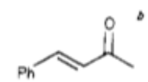
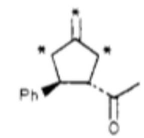
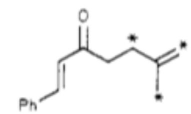
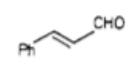
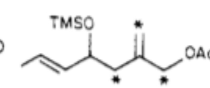


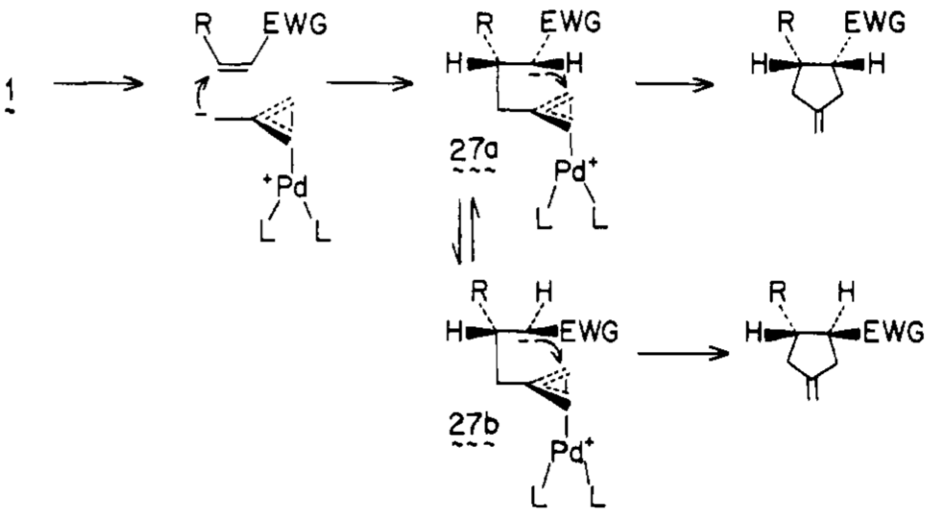
Table II. Reaction of 20 with Acceptors

entry	trap	product[e,f]	(yield)[d]
		A. Alkylation[b]	
1		 **21**	(74)
2		 **22**	(90) (92)[c]
		B. Cycloaddition	
3		 **23**	(52)
		C. Cycloaddition/Alkylation	
4	 [b]	 **24**	(30)
		 **25**	(15)
		D. Carbonyl Addition	
5		 **26**	(58)

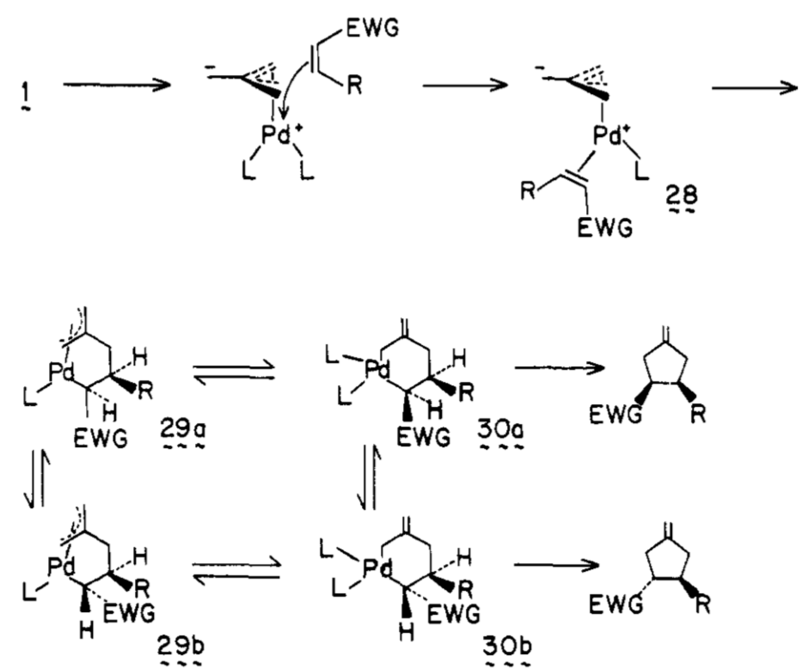
[a] Reactions are carried out with 1 equiv of **20**, 1.7–2.6 equiv of the trap, 5–9 mol % $(Ph_3P)_4Pd$, 1.7–2.8 mol % dppe in refluxing THF. [b] This reaction was performed in toluene at 110 °C. [c] This reaction was carried out at room temperature. [d] Isolated yields are based on amounts of **20** used. [e] *–carbon atom containing deuterium label. [f] Deuterium content of products was determined by mass spectroscopy. [g] E = CO_2CH_3, S = SO_2Ph.

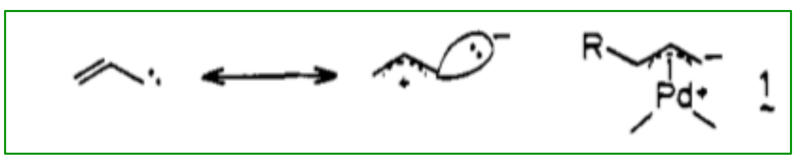
JACS, **1983**, *105*, 2326

Scheme III. Distal Approach Mechanism of Cycloaddition



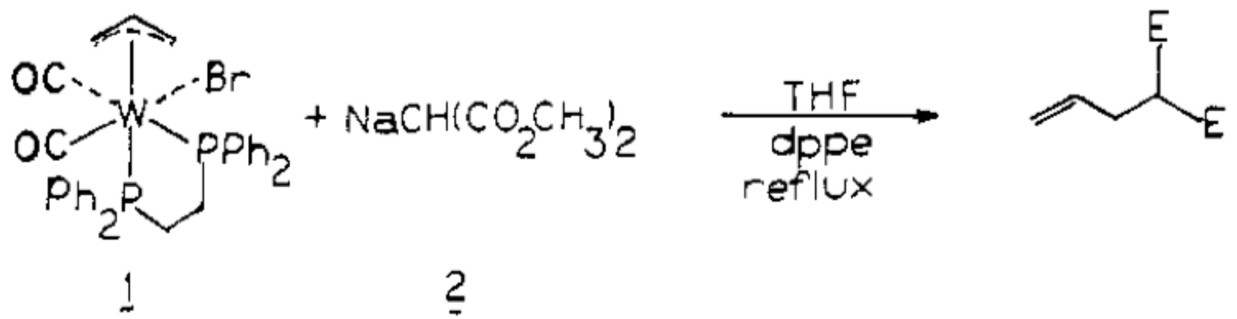
Scheme IV. Proximal Approach Mechanism of Cycloaddition





JACS, **1983**, *105*, 2326; JACS, **1983**, *105*, 5942

Tungsten-Catalyzed Allylic Alkylation



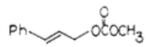
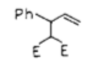
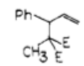
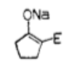
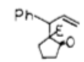
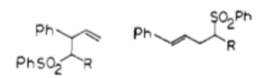
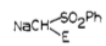
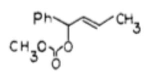
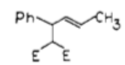
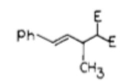
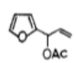
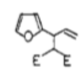
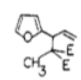
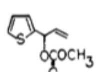
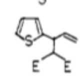
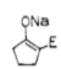
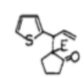
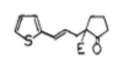
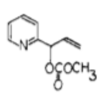
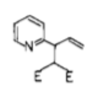
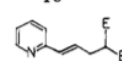
Five factors may be envisioned to affect the regioselectivity. **(1)** steric demands of the nucleophile, **(2)** steric demands of the Π-allyl substituents, **(3)** charge distribution of the π-allyl intermediate, **(4)** steric and electronic demands of the metal template, and **(5)** reactivity of the nucleophile. Rationalizing that factors **3** and **4** favor attack at the more substituted end, we envisioned that the steric demands imposed by a tungsten template may favor alkylation at the more substituted end.

JACS, **1973**, *95*, 292

Tungsten-Catalyzed Allylic Alkylation

MICHIGAN STATE UNIVERSITY

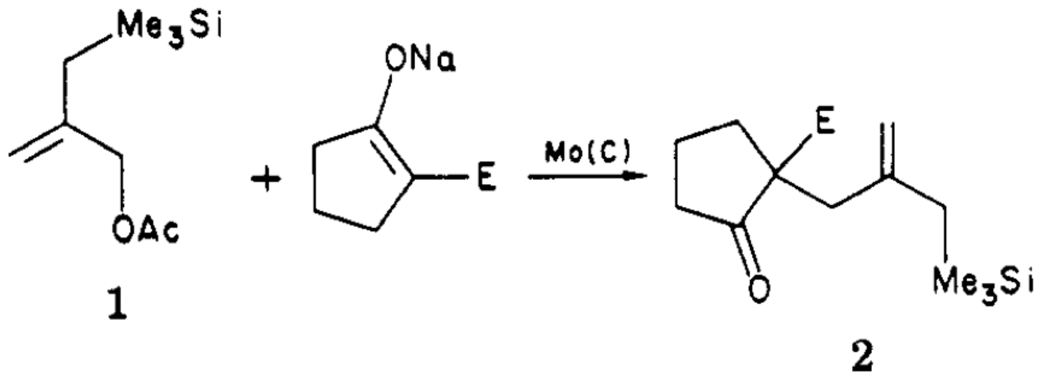
Table I. Tungsten-Catalyzed Alkylation of Aryl-Bearing Allylic Substrates

entry	allyl substrate	nucleophile[a]	time, h	product[b]	%[c]
1	 **4**	$NaCHE_2$	4		91[d]
2	**4**	$NaCH_3CE_2$	17		92[d]
3	**4**		15		87[d,e]
					
4	**4**		5	R=E 72[f] 28	78
5	**4**	$NaCH(SO_2Ph)_2$	9	$R=PhSO_2$ 53 47	67
6		$NaCHE_2$	4	 90  10	88
7	 **5**	$NaCHE_2$	6		81[d]
8	**5**	$NaCHE_2$	2		86
9	 **6**	$NaCHE_2$	4		70[g]
10	**6**		16.5	 84[h]  16	76
11		$NaCH_3CE_2$	14.5	 83  17	60

[a] The nucleophile was generated by treating the carbon acid with sodium hydride in THF. All reactions were run with 15 mol % $(CH_3CN)_3W(CO)_3$ and 15 mol % bpy[9] in refluxing THF. [b] All products have been fully characterized. [c] Isolated yields of pure products. [d] ≥98% a single regioisomer. [e] Threo/erythro 38/62. [f] Threo/erythro 42/58. [g] ≥95% a single regioisomer. [h] Threo/erythro 60/40.

JACS, **1983**, *105*, 7757

Regiochemical Control in Molybdenum Allylic Alkylation



25% mol% $Mo(CO)_6$, $PhCH_3$, reflux, **72** h   60%

Organometallics, **1983**, *2*, 1687

Regiochemical Control in Molybdenum Allylic Alkylation

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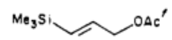
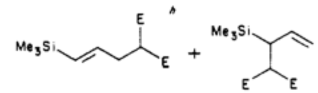
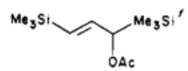
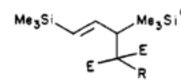
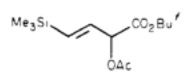
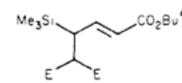
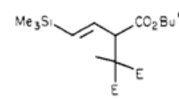
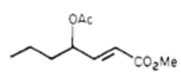
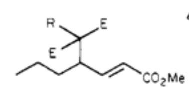
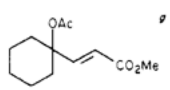
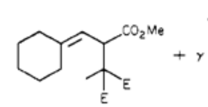
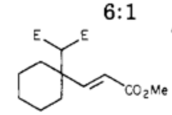
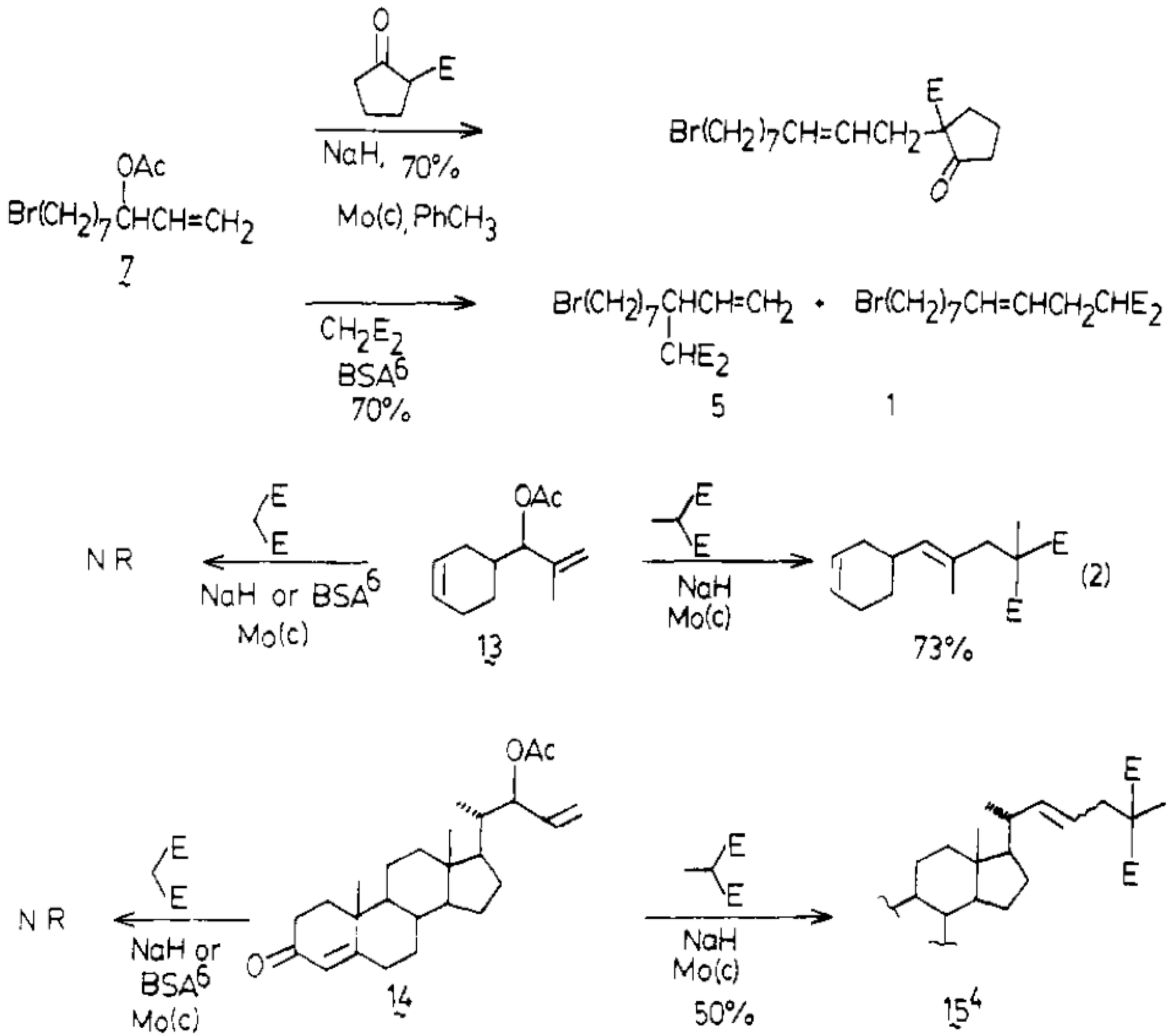
entry	allylic acetate	nucleophile	time, h	product[a]	% yield[b,c]
1		CH_2E_2	9	 1:1.2	35
2		CH_2E_2	2.5	 R = H or Me	49
3		CH_3CHE_2	2.5		58 (80)[i]
4		CH_2E_2	12		43
5		CH_3CHE_2	7		57
6		CH_2E_2	4	 R = H or Me	33 (66)[d]
7		CH_3CHE_2	2		60
8		CH_3CHE_2	1.5	 6:1	52
9		CH_2E_2	2.5		62

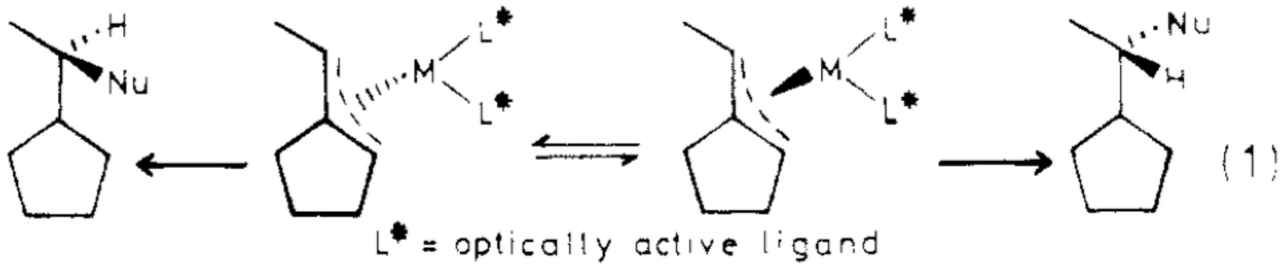
[a] All products have been identified by spectroscopic methods and by high resolution mass spectrometry. [b] Isolated yields of pure products. [c] These represent unoptimized yields. [d] Yield based on recovered starting material, longer reaction times led to destruction of product. [e] Only the trans stereoisomer was detected. [f] See ref 5. [g] See ref 9. [h] See ref 10. [i] See ref 11.

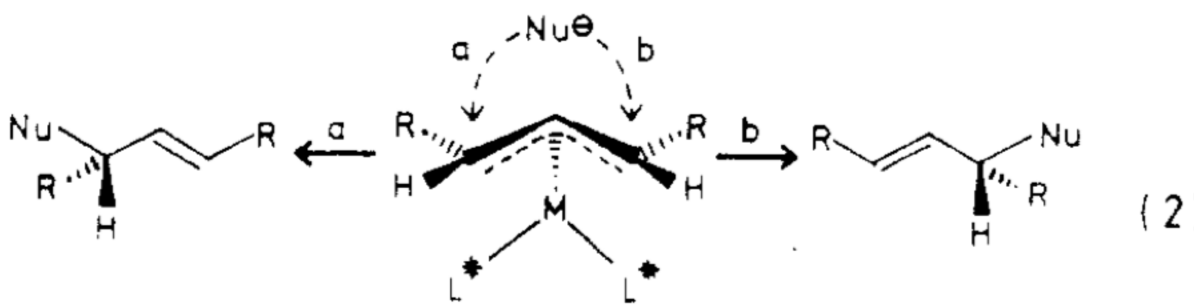
Organometallics, **1983**, 2, 1687



JACS, **1983**, *105*, 3343

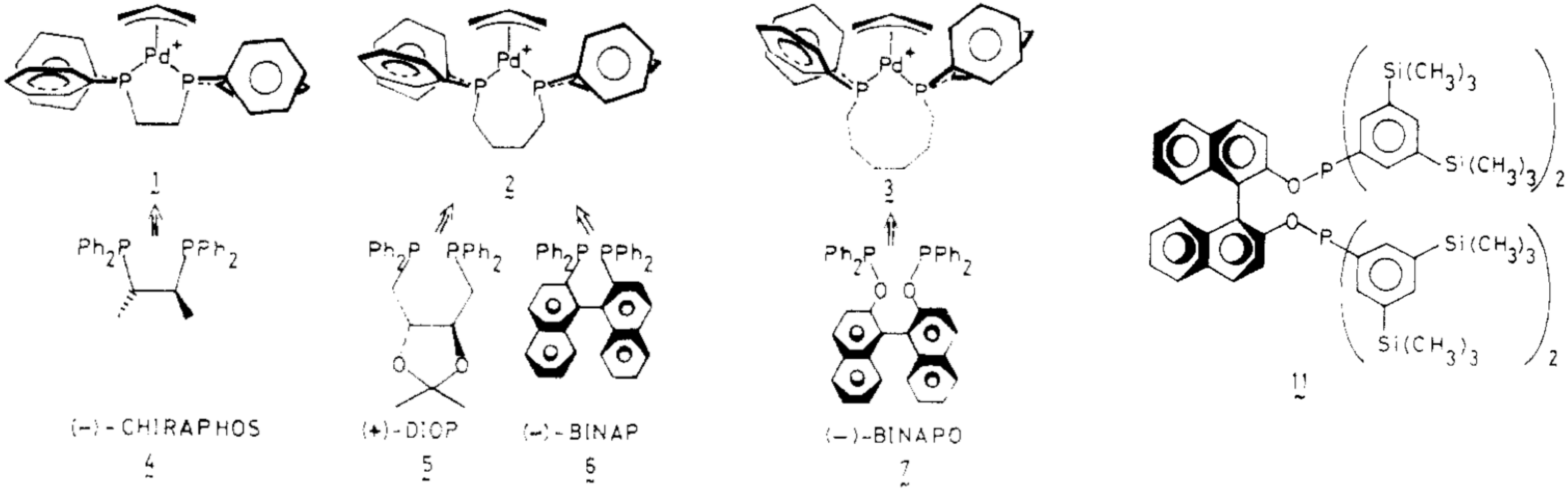
A Model for Metal –Templated Catalytic Asymmetric Induction via Π-Allyl Fragments

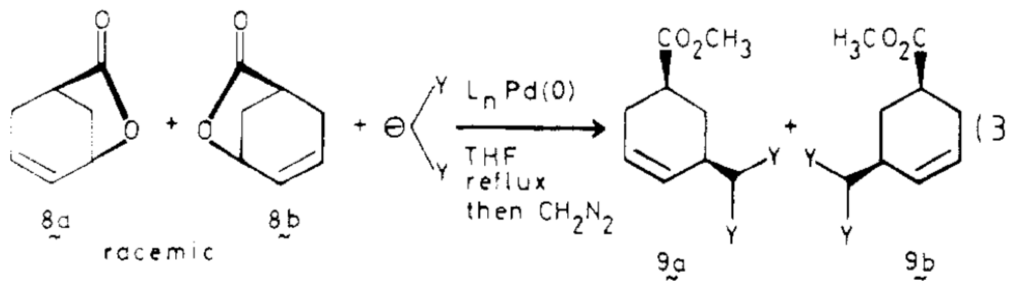




Organometallics, **1985**, *4*, 1143

A Model for Metal –Templated Catalytic Asymmetric Induction via Π-Allyl Fragments





L	Y	% 9a	% 9b	% ee	% yield
4	SO_2Ph	59	41	18	73
5	SO_2Ph	58	42	16	82
6	SO_2Ph	65	35	31	92
7	SO_2Ph	69	31	38	66
11	SO_2Ph	85	15	69	82

Organometallics, **1985**, *4*, 1143

Unusual Chemoselectivity Using Difunctional Allylic Alkylation Agents

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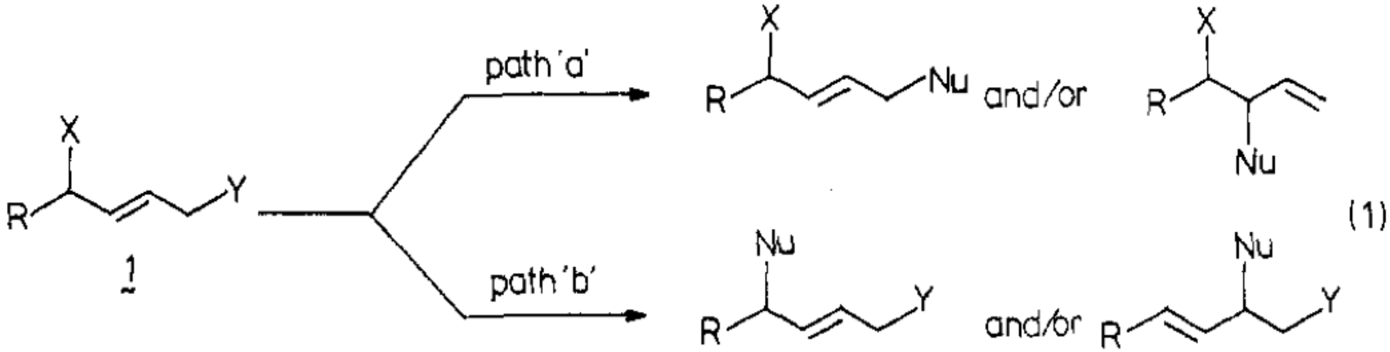
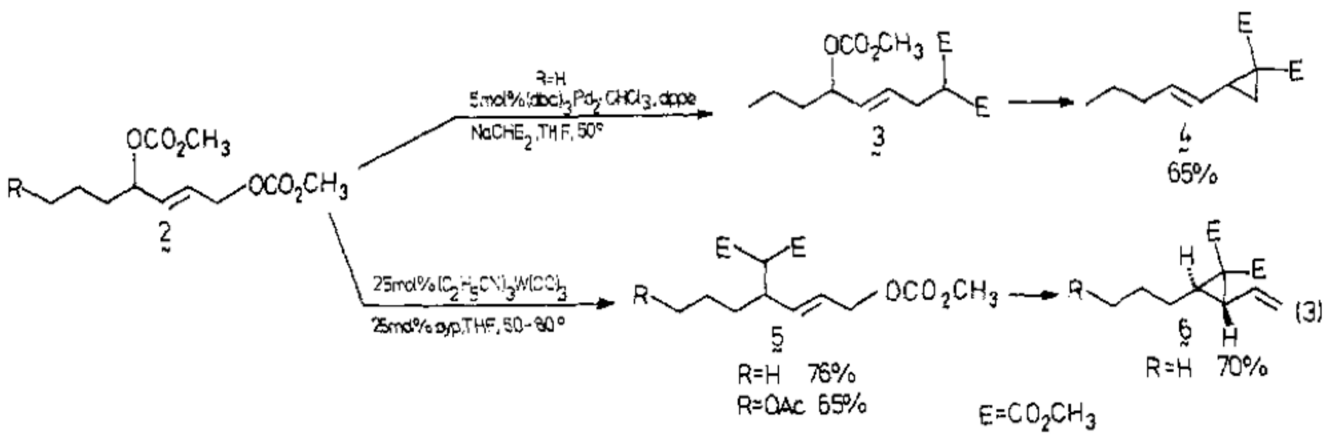
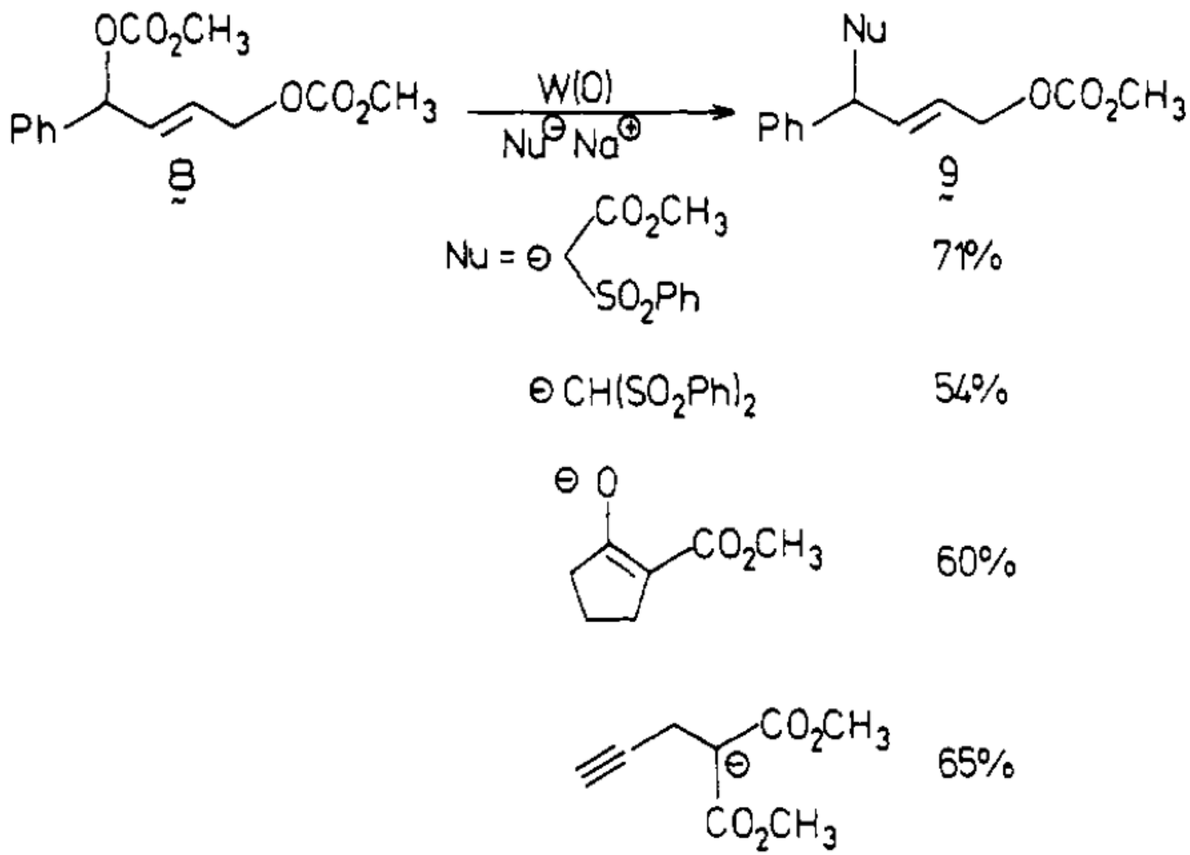




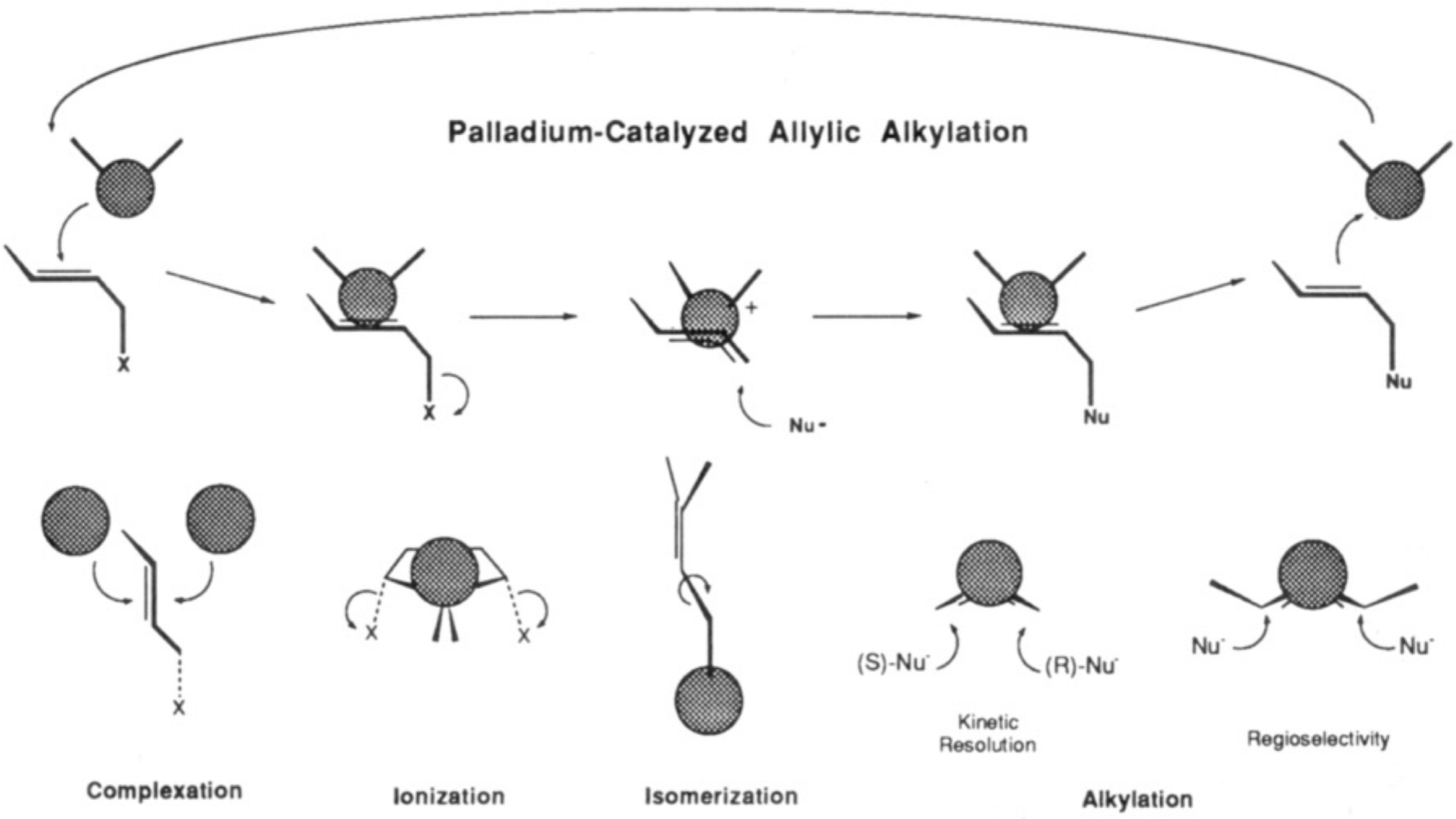
JACS, **1987**, *109*, 2176

Unusual Chemoselectivity Using Difunctional Allylic Alkylation Agents



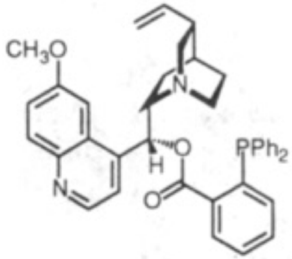
JACS, **1987**, *109*, 2176

A Modular Approach for Ligand Design for Asymmetric Allylic Alkylations



JACS, **1992**, 114, 9327

A Modular Approach for Ligand Design for Asymmetric Allylic Alkylations



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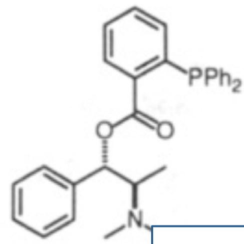

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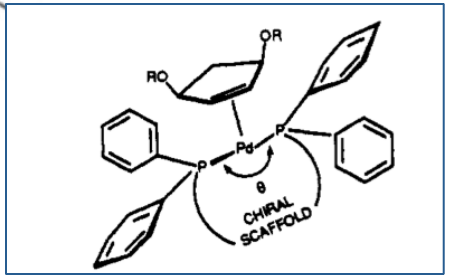

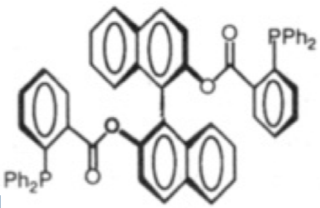

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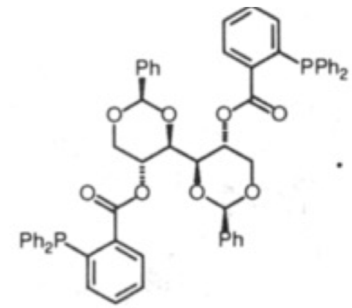
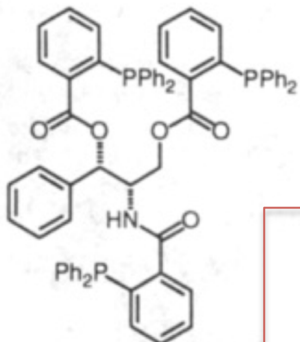


· 1/2 Et_2O

7



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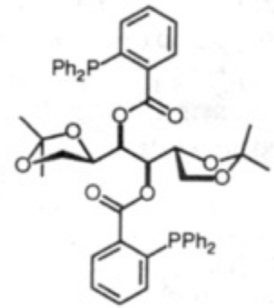

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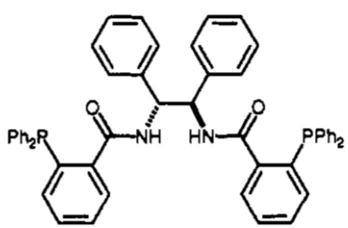

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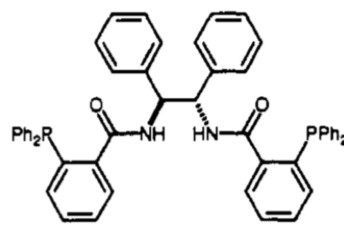

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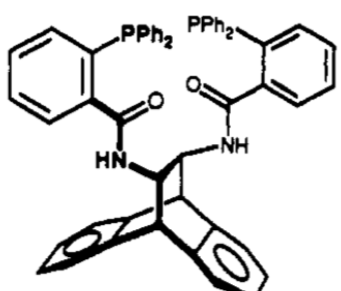

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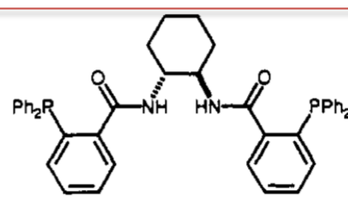

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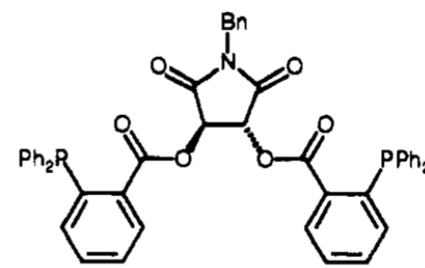

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JACS, **1992**, 114, 9327

A Modular Approach for Ligand Design for Asymmetric Allylic Alkylations

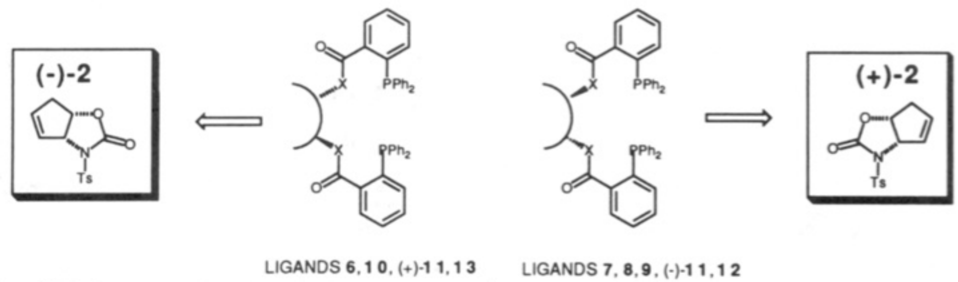


Figure 13. Correlation of absolute stereochemistry of the product with that of the variable chiral linker.

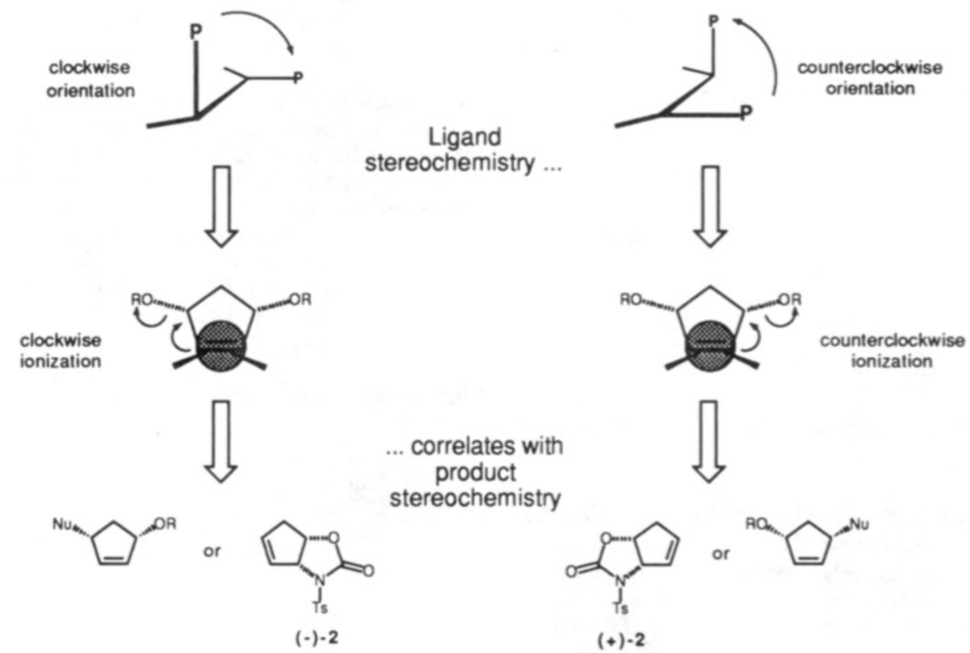
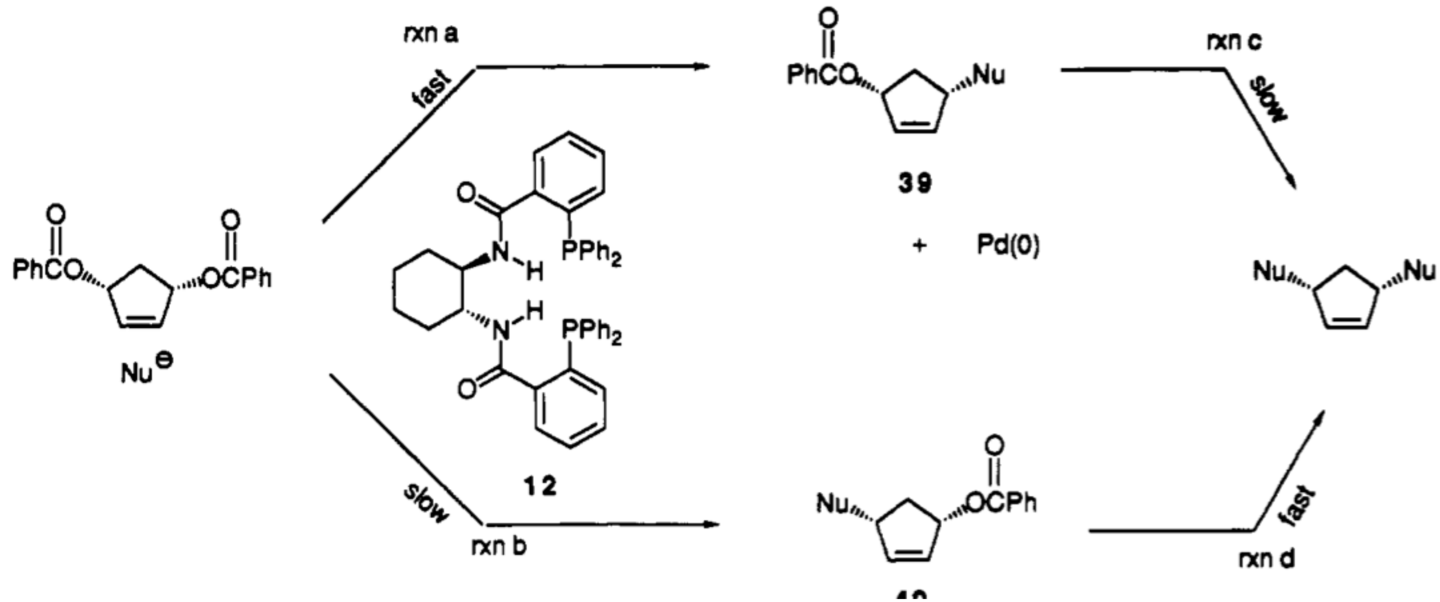


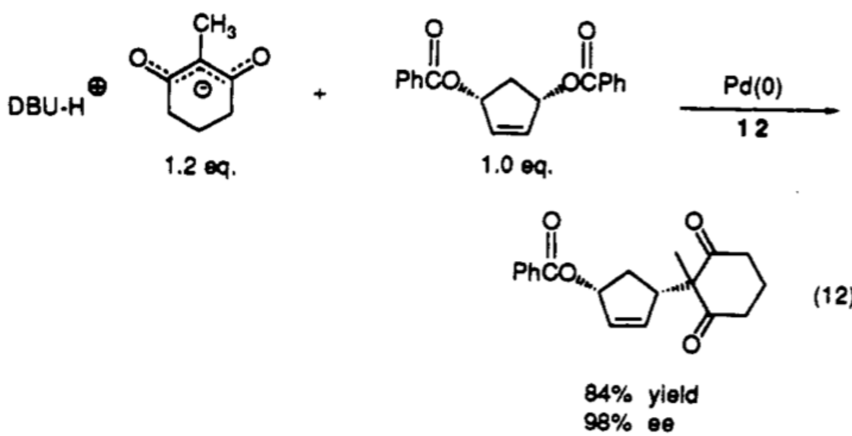
Figure 14. Mnemonic rule for ionization.

JACS, **1992**, 114, 9327

A Modular Approach for Ligand Design for Asymmetric Allylic Alkylations

Scheme V. Kinetic Enrichment of Enantioselectivity

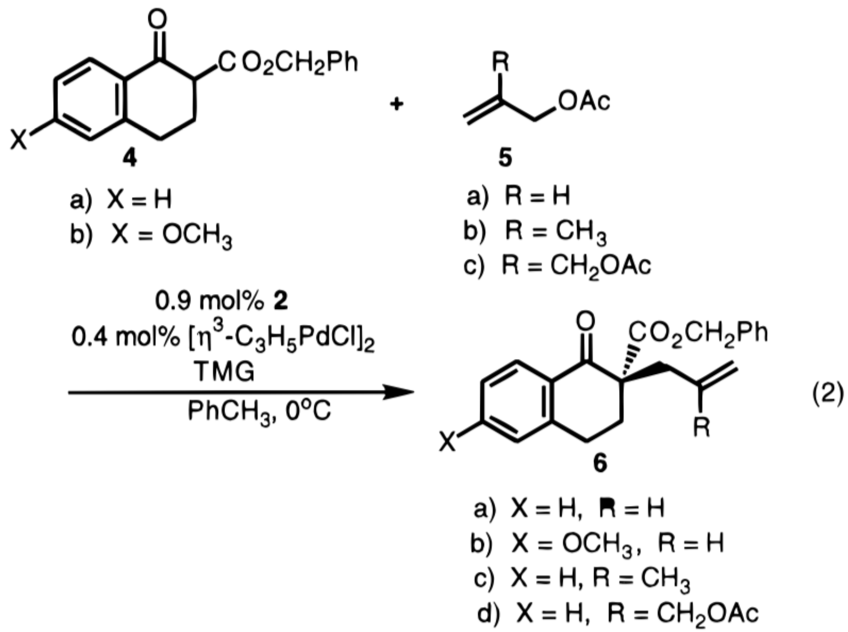


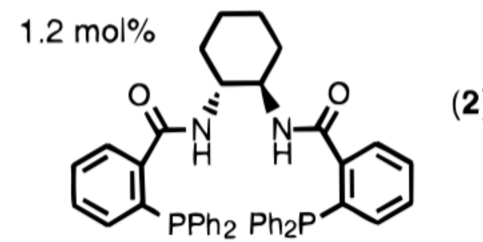


(12)

JACS, **1992**, 114, 9327

Asymmetric Alkylation of β-Ketoester



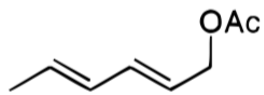


TMG: *N*,*N*,*N′*,*N′*-tetramethylguanidine.

entry	tetralone	allylic ester	time	product % yield	dr	ee (er)[b]
1	**4a**	**5a**	0.25	**6a**, 94%		89 (94.5: 5.5)
2	**4b**	**5a**	1	**6b**, 98%		91 (95.5:4.5)
3	**4a**	**5b**	3	**6c**, 81%		95 (97.5:2.5)
4	**4a**	**5c**	1.5	**6d**, 80%		94 (97:3)
5	**4a**	**7**	3	**8**, 71%	94:6	97[c] (98:2)
6	**4a**	**9a**	2	**10a**, 87%	99:1	96[c] (98:2)
7	**4a**	**9b**	3	**10b**, 91%	98:2	99[c] (99.5:0.5)

JACS, **1997**, *119*, 7879

On the Effect of the Nature of Ion Pairs As Nucleophile in Metal-Catalyzed Substitution Reaction



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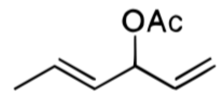

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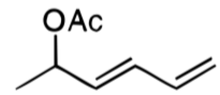

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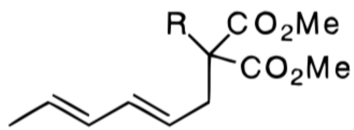
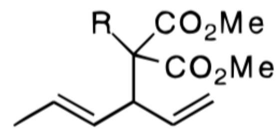
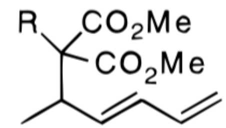


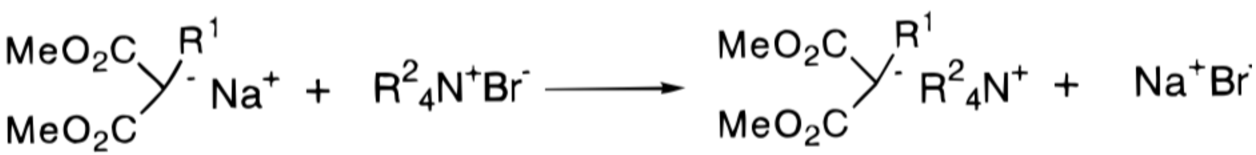
11a R = H
11b R = Bn



12a R = H
12b R = Bn



13a R = H
13b R = Bn



10a R^1 = H	$R^2 = CH_4$	(TMAB)
10b R^1 = Bn	$R^2 = n\text{-}C_6H_{13}$	(THAB)

JACS, **1998**, *120*, 70

On the Effect of the Nature of Ion Pairs As Nucleophile in Metal-Catalyzed Substitution Reaction

Table 2. Alkylations of **7−9** with Dimethyl Benzylmalonate Nucleophiles (**10b**) and Triphenylphosphine Ligands for Palladium

entry	substr[a]	counterion[b]	reactn time, h	yield (%)	product ratio (%)		
					11b	**12b**	**13b**
1	**7**	Na^+	1.5	81	78	20	2
2	**8**	Na^+	1.5	79	70	28	2
3	**9**	Na^+	1.5	87	57	33	10
4	**7**	TMA^+	4	75	80	18	2
5	**8**	TMA^+	4	80	60	38	2
6	**9**	TMA^+	4	96	56	36	8
7	**7**	THA^+	4	89	76	21	3
8	**8**	THA^+	4	99	72	25	3
9	**9**	THA^+	4	94	77	20	3
10	**7**	Cs^+	4	82	52	45	3
11	**8**	Cs^+	4	85	53	44	3
12	**9**	Cs^+	4	84	53	43	4

[a] Reaction conditions: 5% $(Ph_3P)_4Pd$, THF, 67 °C. [b] TMA, tetramethylammonium; THA, tetrahexylammonium.

JACS, **1998**, *120*, 70

Asymmetric O- and C- Alkylation of Phenols

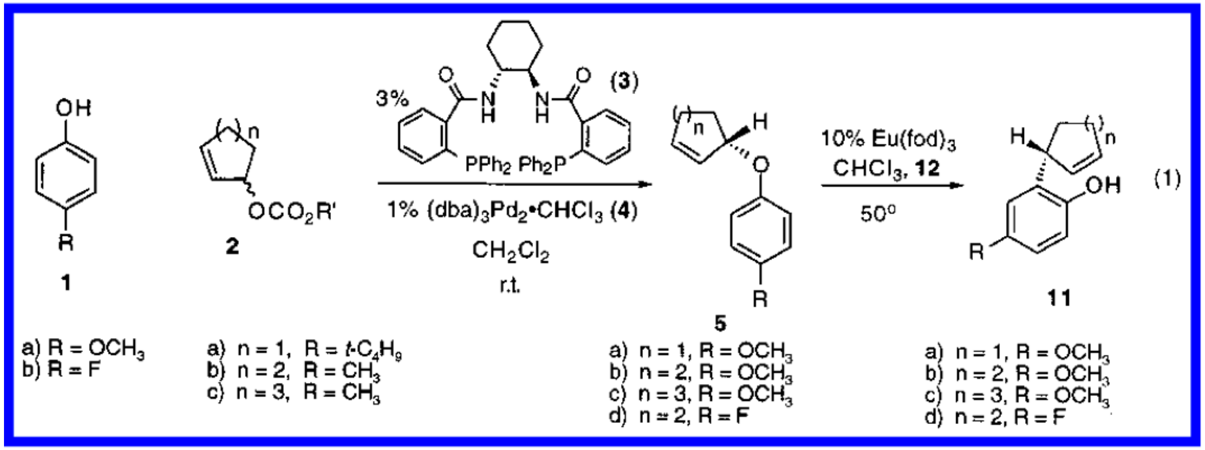
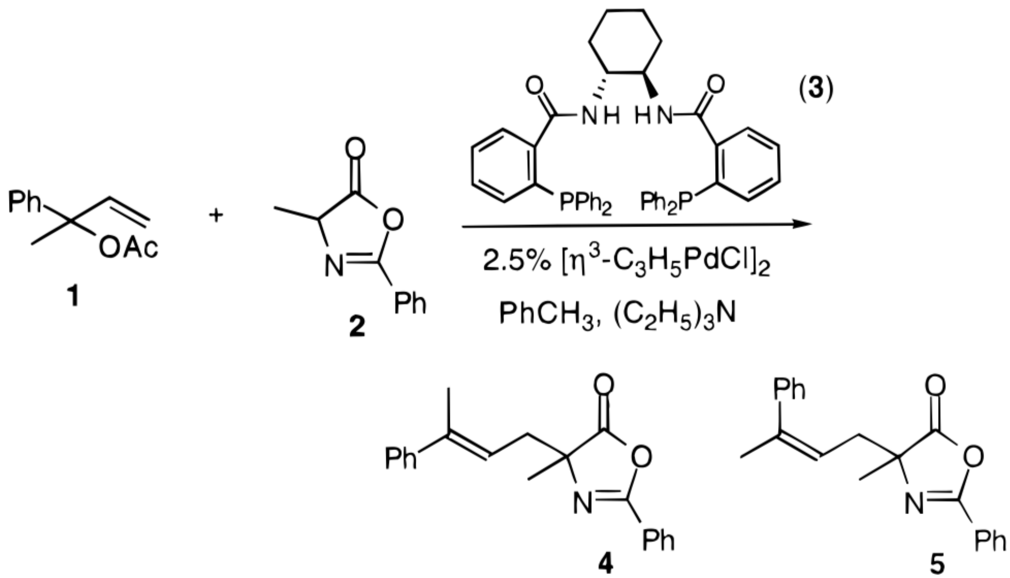


Table 1. Enantioselective Phenol Alkylations[a]

entry	phenol	allyl carb.	O-alk. temp (°C)	allyl ether (isol yield, %)	% ee[b]	rearr. temp (°C)	C-alk. (isol yield, %)	product ee (%)
1	**1**	**2a**	25	**5a** (96)	60			
2	**1**	**2a**	−40	**5a** (85)	85			
					94[c]	50	**11a** (86)	93
3	**1**	**2a**	−78	**5a** (82)	78			
4	**1**	**2b**	25	**5b** (88)	97	50	**11b** (79)	97
5	**1**	**2c**	25	**5c** (89)	92			
6	**1**	**2c**	0	**5c** (85)	93	50	**11c** (77)	96
7	**1b**	**2b**	25	**5d** (88)		80	**11d** (83)	94[h]
8	**6a**	**2b**	25	**7a** (89)	94	50	**13a** (81)	93
9	**6b**	**2b**	25	**7b** (90)	77			
10	**6b**	**2b**	0	**7b** (83)	85	80	**13b** (84)	80
11	**6c**	**2b**	25	**7c** (90)	95	50[d]	**13c**[e] (91)	93
12	**9**	**8**	25	**10** (89)	85	50	**14** (97)[f]	91[g]

JACS, **1998**, *120*, 815

Chiral Recognition for Control of Alkene Geometry In Allylic Alkylation



entry	ligand	isolated yield, %	E:Z[a]
1	*R,R*-**3**	88	50[b]:50[c]
2	*S,S*-**3**	97	55[d]:45[c]
3	*R,R*-**3** + *S,S*-**3**	83	15:85
4	Ph_3P	85	84:16

JACS, **1999**, *121*, 8667

Chiral Recognition for Control of Alkene Geometry In Allylic Alkylation

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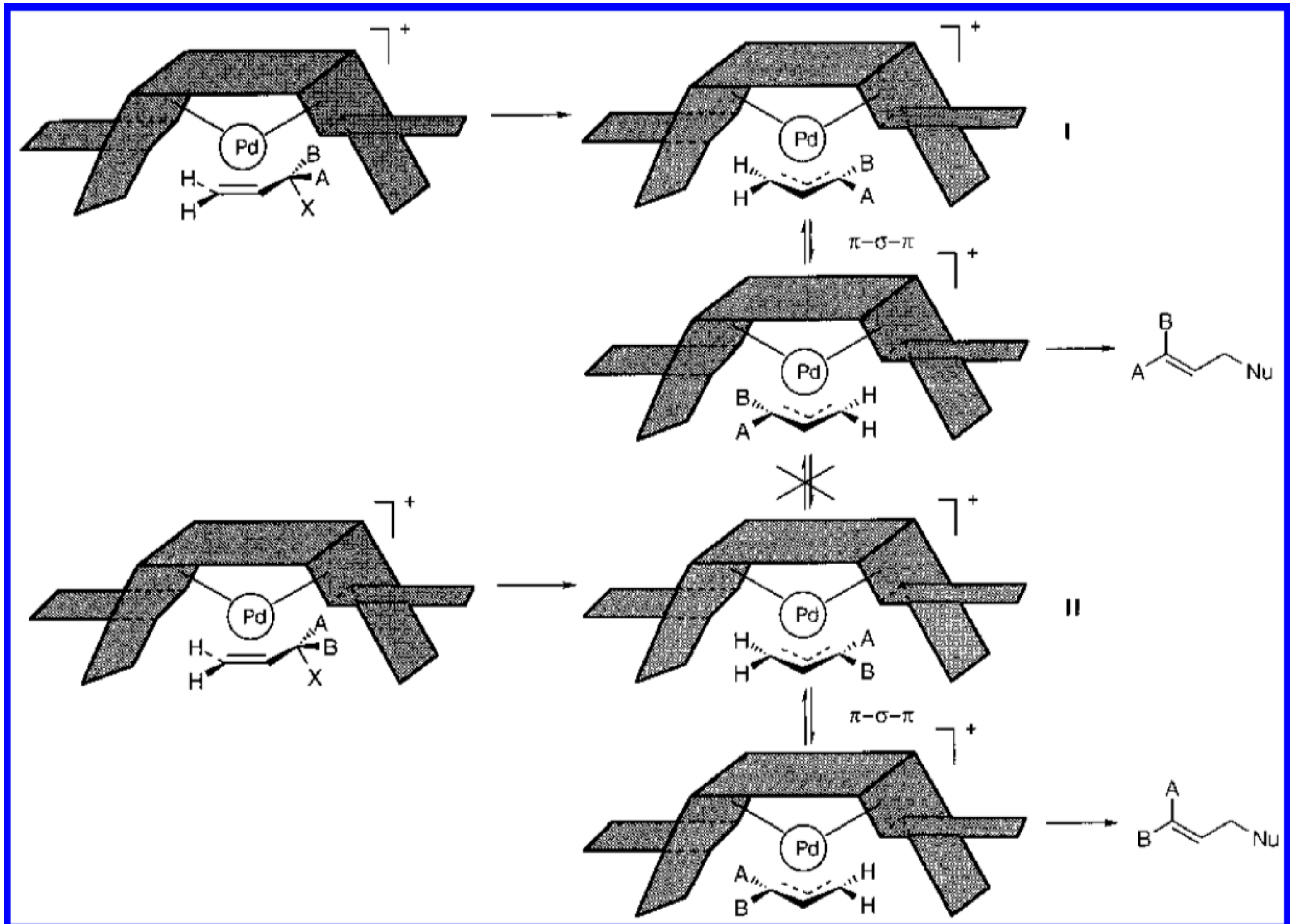

Figure 1. Cartoon representing the reaction of racemic allyl esters with enantiomerically pure catalyst.

JACS, **1999**, *121*, 8667

Chiral Recognition for Control of Alkene Geometry In Allylic Alkylation

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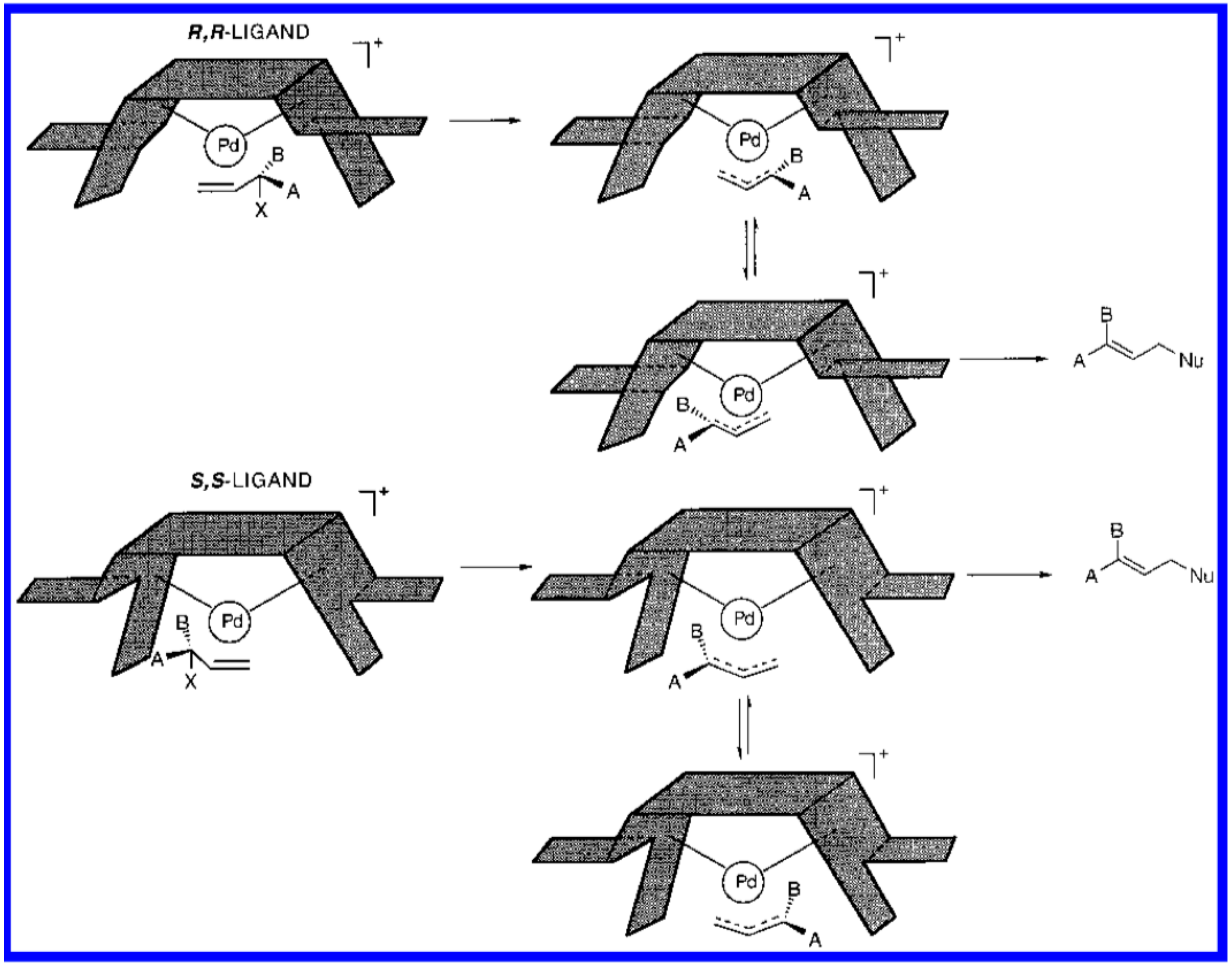
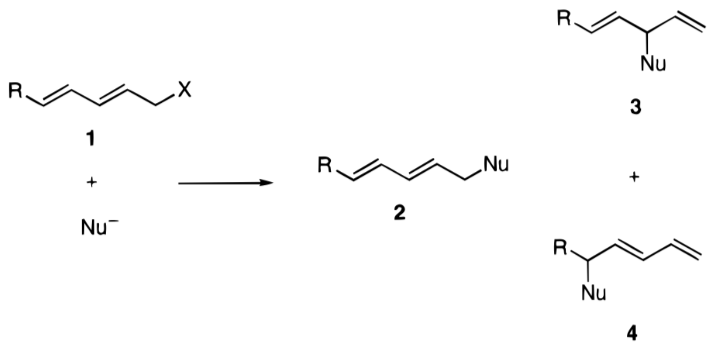
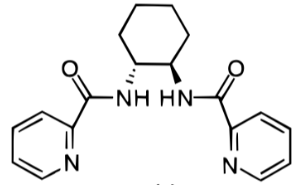


Figure 2. Cartoon representing the reaction of racemic allyl esters with racemic catalyst.

JACS, **1999**, *121*, 8667

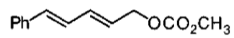
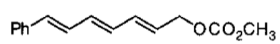
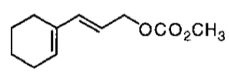
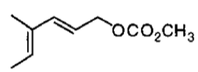
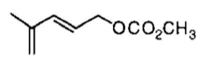
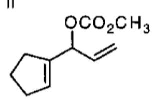
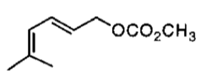
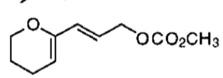
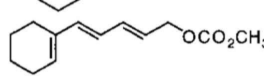
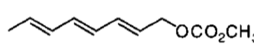
Regio- and Enantioselective Mo-Catalyzed Alkylations of Polyenyl Esters





11

$(CH_3CH_2CN)_3Mo(CO)_3$
(**8**)

Entry		Time	Yield[b]	Ratio[c] 3:2	ee (er)[d] 3
1		3 h[e]	95	6.1:1	98 (99:1)
2		4 h[e]	58 (92)	5.3:1	97 (98.5:1.5)
		3.5 h	68	6.1:1	>99 (>99:1)
3		3 h	91	11.5:1	94 (97:3)
4		3 h	89 (94)	49:1	98 (99:1)
		6 h[e]	87 (95)	15.7:1	97 (98.5:1.5)
5		3 h	81 (89)	8.1:1	80 (90:10)
6		2 h	94	11.5:1	87 (93.5:6.5)
		1.5 h[f]	88	13.3:1	86 (7:93)
7		2 h	96	15.7:1	86 (93:7)
		2 h[f]	94	15.7:1	91 (4.5:95.5)
8[g]		1.5 h	93	13.3:1	96 (98:2)
9		2 h	70 (79)	11.5:1	97 (98.5:1.5)
10		3 h	81 (85)	10.1:1	98 (99:1)

JACS, **1999**, *121*, 10416

Asymmetric Alkylation of Ketone Enolates

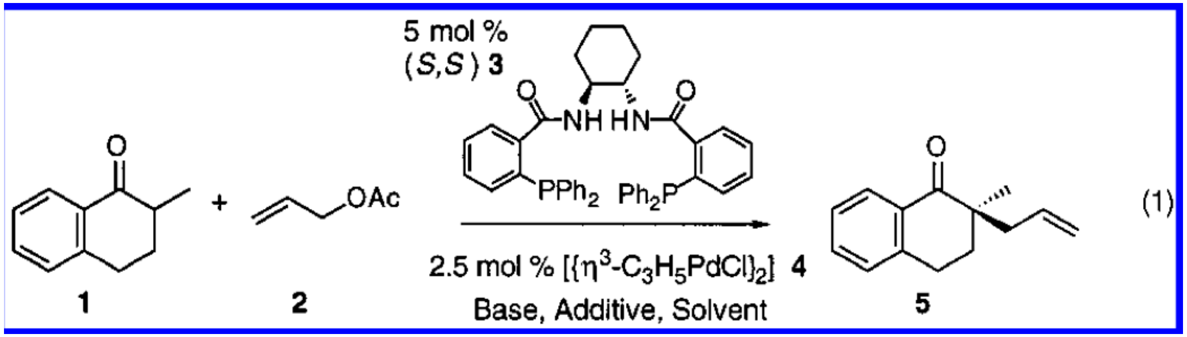
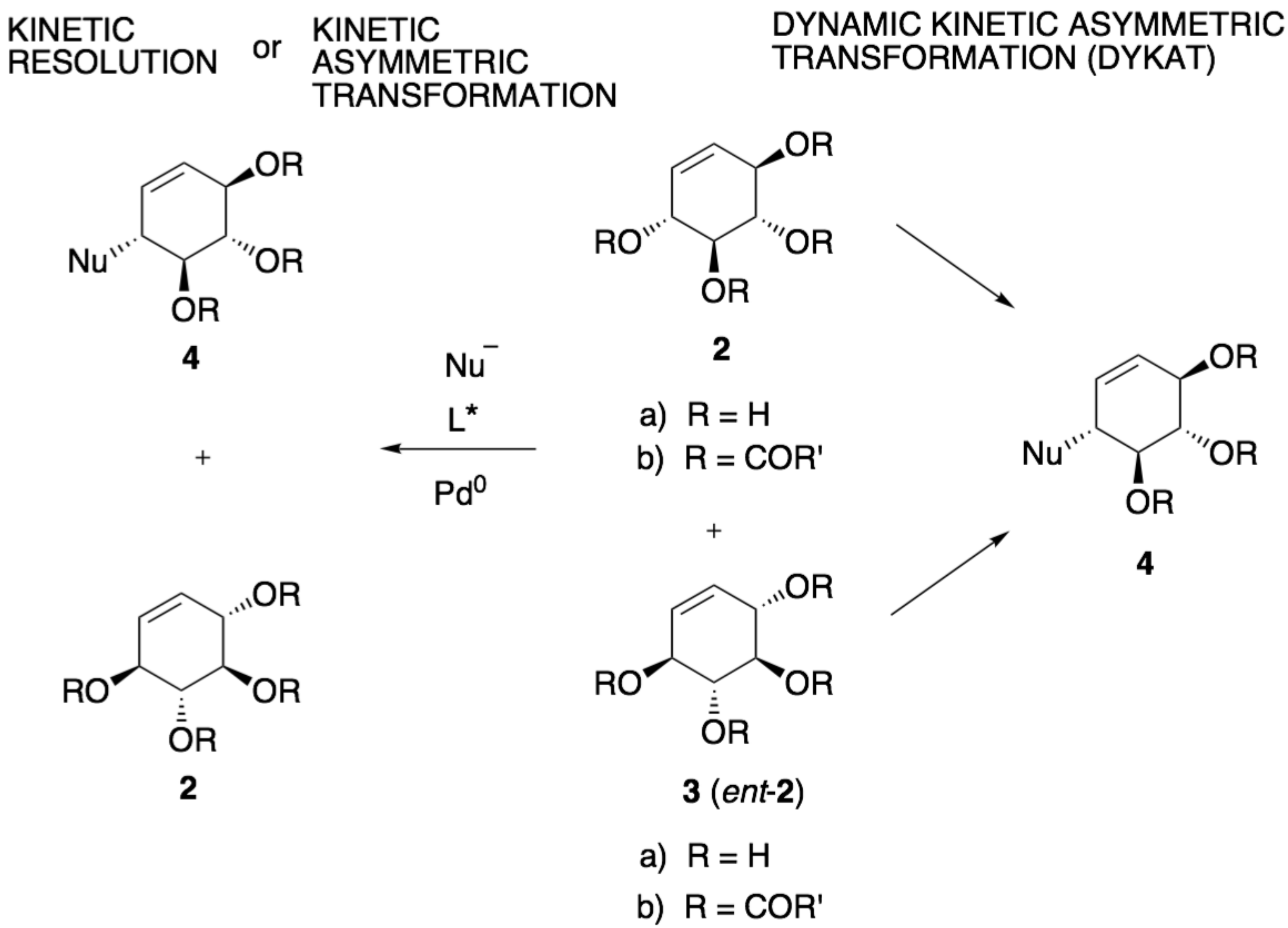


Table 1. Selected Optimization Studies[a]

entry	base (eq no.)	additive[b]	time (h)	% yield[c]	% ee[d]
1	LDA (1)	$(C_4H_9)_3SnOSO_2CF_3$	3	21	32
2	LDA (1)	$(C_4H_9)_3SnCl$	2	53	65
3	LDA (1)	$(CH_3)_3SnCl$	3	65	69
4	LDA (1.25)	$(CH_3)_3SnCl$	2.5	78	78
5	LDA (1.5)	$(CH_3)_3SnCl$	2.5	99	80
6	LDA (2)	$(CH_3)_3SnCl$	0.5	99	88
7	LDA (3)	$(CH_3)_3SnCl$	1.75	61	84
8	LiHMDS (2)	$(CH_3)_3SnCl$	2	94	71
9	LiTMP (2)	$(CH_3)_3SnCl$	0.5	99	86
10	LDA (2)	none	1	96	85

JACS, **1999**, *121*, 6759

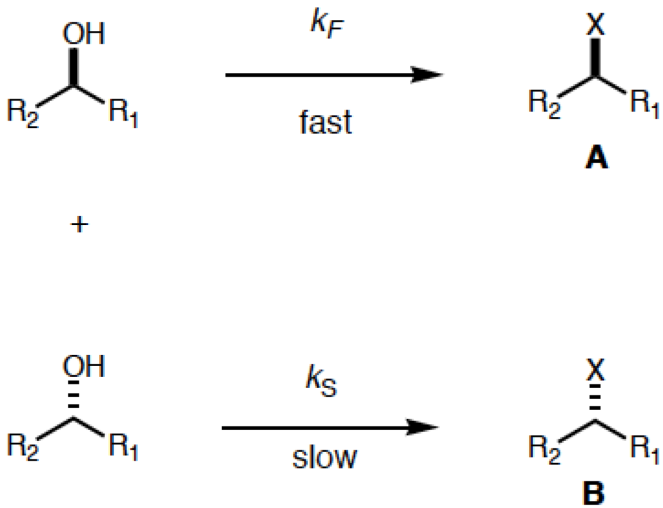
AAA in KAT/DYKAT Processes



Chem. Eur. J., **2001**, *7*, 3768

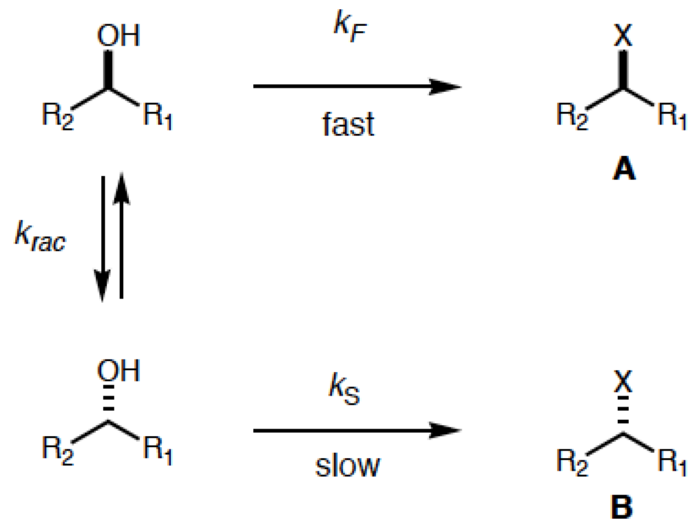
AAA in KAT/DYKAT Processes

Kinetic Resolution



50% theoretical yield of **A**

Dynamic Kinetic Resolution



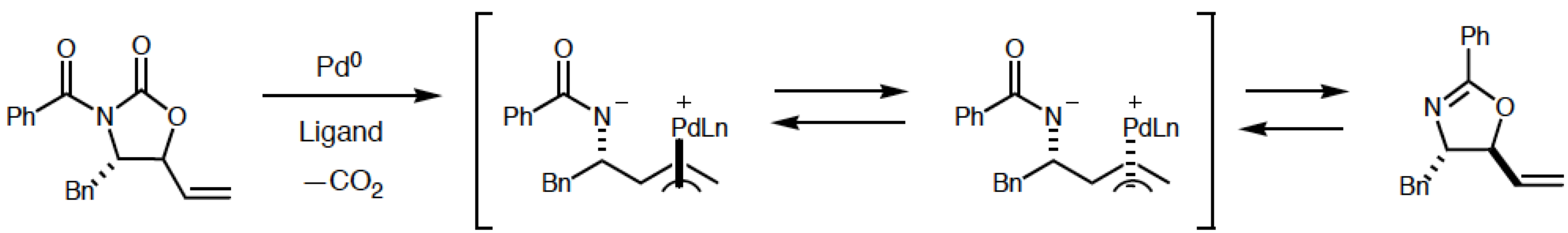
If $k_{rac} > k_F >> k_S$ 100% theoretical yield of **A**

- In a DKR, as with a classical KR, one enantiomer reacts slowly under the reaction conditions
- In a DKR, the rate of racemization of SM is fast relative the rate of the asymmetric transformation
- Thus, using DKR, possible to convert 100% of racemic SM to enantiopure product due to equilibrating racemization of SM

JACS, **1973**, *95*, 292

AAA in KAT/DYKAT Processes

- Enhanced diastereomeric ratio after internal trapping suggests rapid equilibration of Pd complexes

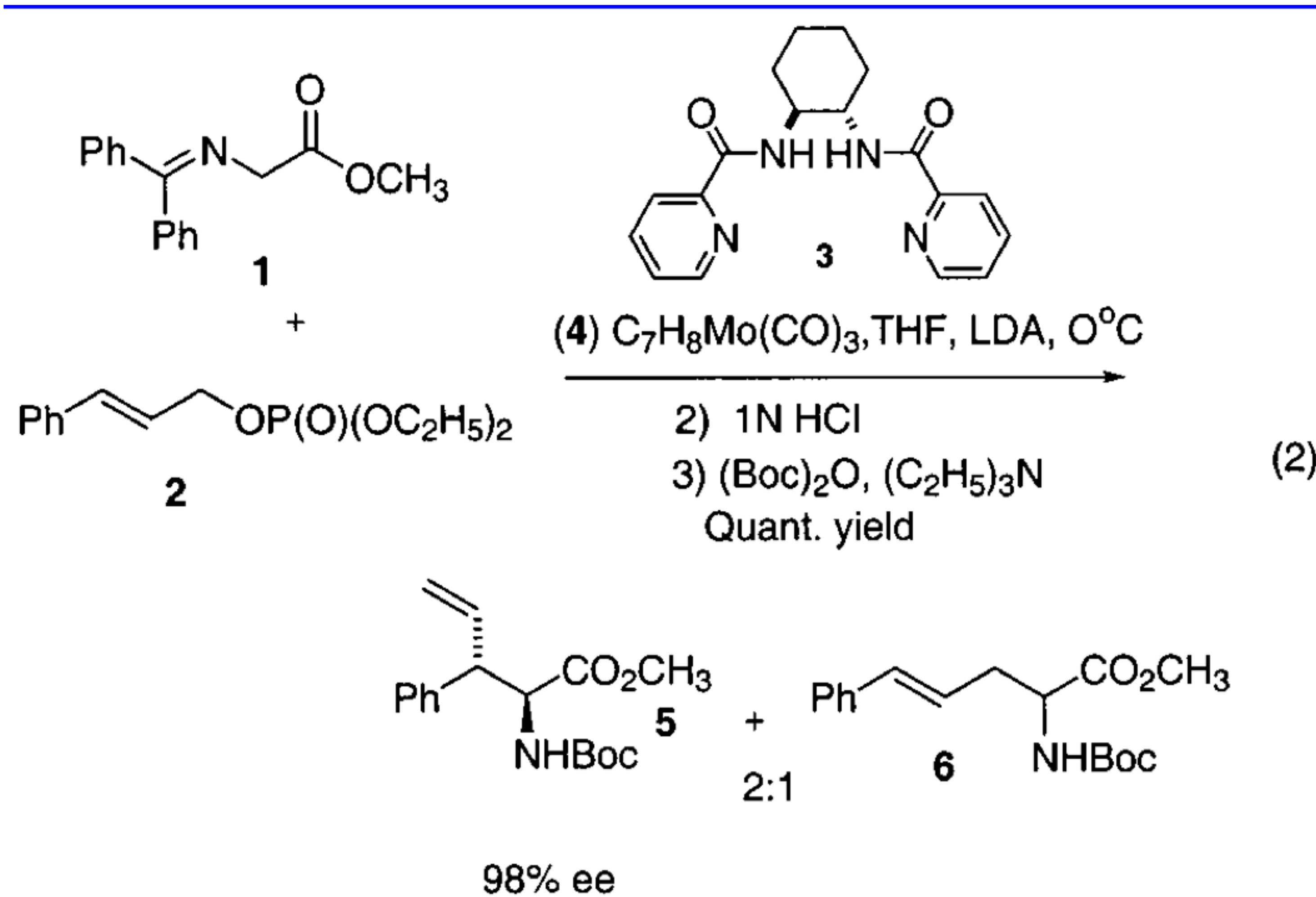


Low DR

Higher DR

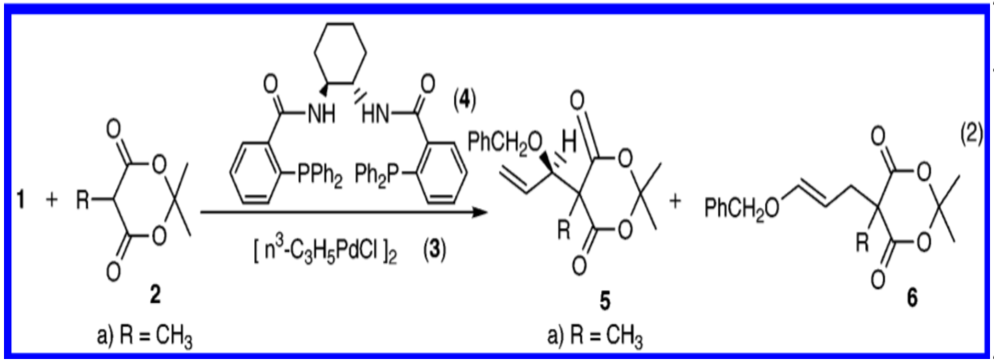
Cook, ACIEE, **1999**, *38*, 110

Synthesis of Quaternary Amino Acids Using Mo-Catalyzed AAA

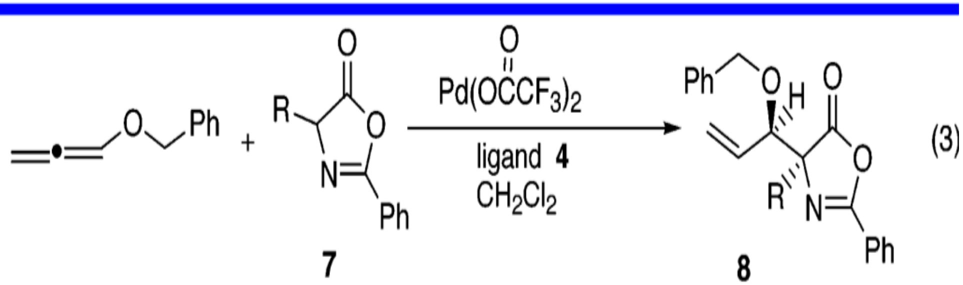


JACS, **2002**, *124*, 7256; Angew, ***2002***, 41, 1929

Pd-Catalyzed Asymmetric Addition of Pronucleophiles to Allene



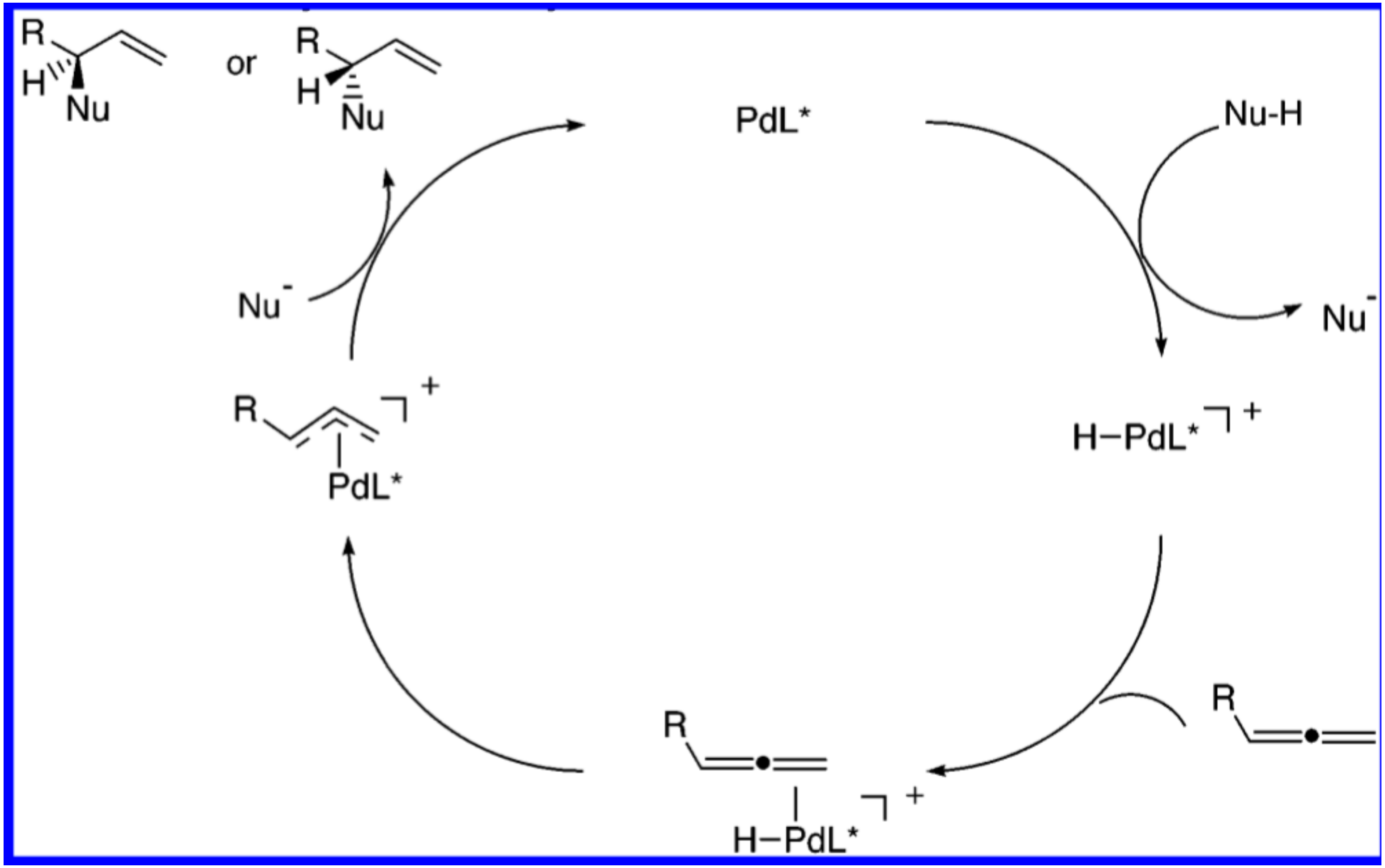
entry	**2** (R)	isolated yield **5**	ee[b]
1	CH_3 (a)	75% (a)	99%
2	$(CH_3)_2CHCH_2$ (b)	61% (b)	88%
3	$CH_2{=}CHCH_2$ (c)	82% (c)	96%
4	$PhCH_2$ (d)	90% (d)	91%
5	2-$C_4H_3OCH_2$ (e)	81% (e)	94%
6	HO (f)	63% (f)	82%



entry	**7** (R)	isolated yield **8**	dr **8**[b]	ee **8**[b]
1	CH_3 (a)	85% (a)	20:1	93%
2	$(CH_3)_2CHCH_2$ (b)	83% (b)	20:1	94%
3	$CH_2{=}CHCH_2$ (c)	85% (c)	20:1	90%
4	$PhCH_2$ (d)	87% (d)	16:1	93%
5	$CH_3S(CH_2)_3$ (e)	67% (e)	13:1	85%

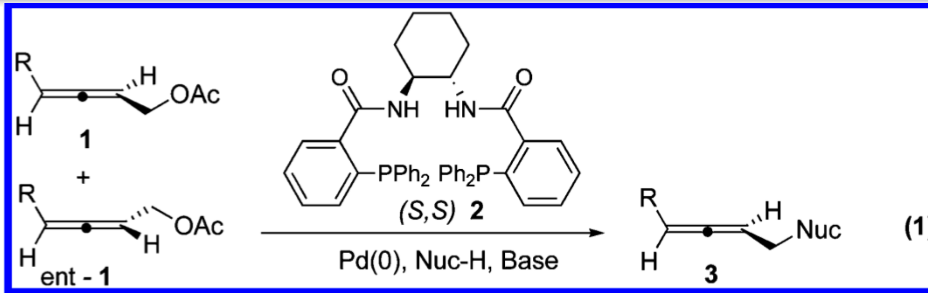
JACS, **2003**, *125*, 4438

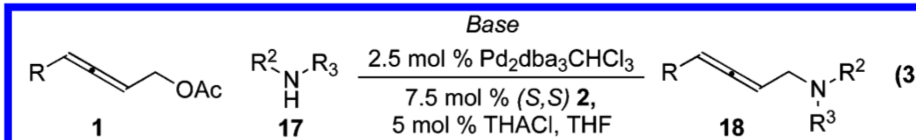
Pd-Catalyzed Asymmetric Addition of Pronucleophiles to Allene

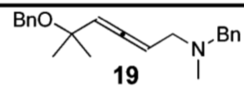
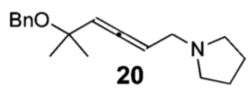
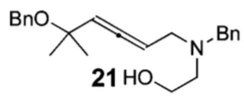
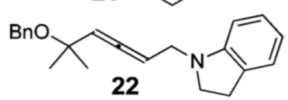
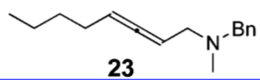


JACS, **2003**, *125*, 4438

Dynamic Kinetic AAA of Allenes



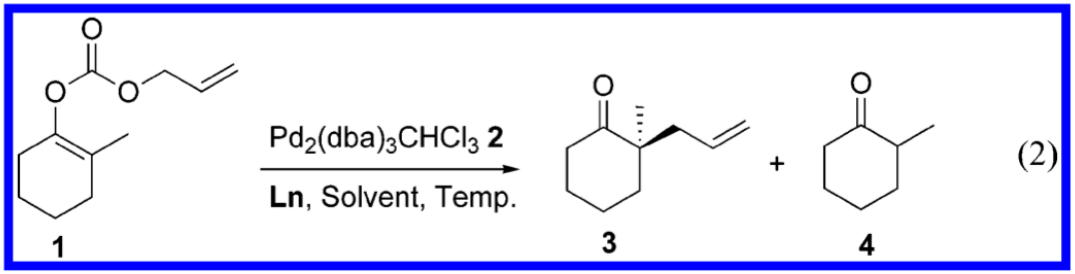


entry	Product	Condition[a]	ee[b] (Config)[c]	yield[d]
1	 19	A	95% (S)-(+)	98%
		B	65% (R)-(-)	91%
2	 20	A	89% (S)-(+)	86%
		B	28% (R)-(-)	90%
3[e]	 21	A	90% (S)-(+)	89%
		B	35% (R)-(-)	85%
4	 22	C	84% (R)-(-)	88%
5	 23	A[f]	~90% (S)-(+)[g]	56%

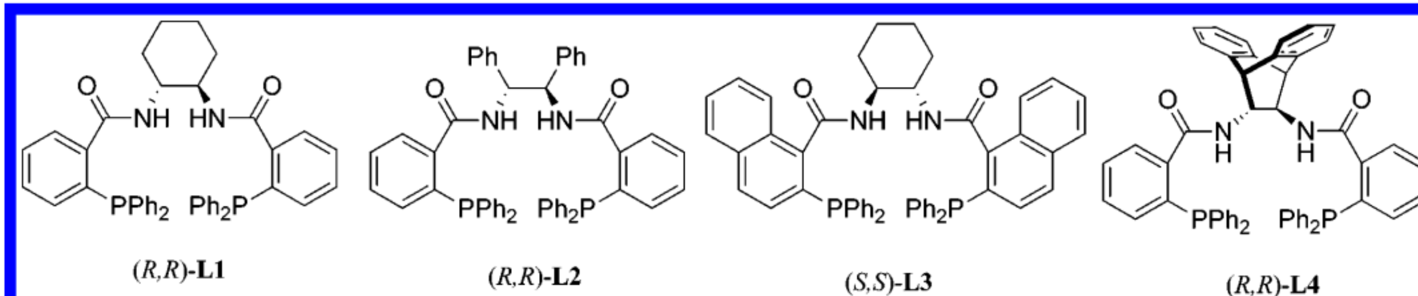
[a] Conditions: **A**. 1.1 equiv of amine to allene, 3 equiv of Cs_2CO_3, room temperature, 1 day. **B**. 2.2 equiv of amine to allene, room temperature, 1 day. **C**. 1.1 equiv of indoline to allene, 60 °C, 1 day. [b] Enantiomeric excess

JACS, **2005**, *127*, 14186

Regio- and Enantioselective Pd-Catalyzed AAA of ketones through Allyl Enol Carbonates



entry	ligand	solvent	ee[b]	yield[c] of **3**	yield[c] of **4**
1	**L1**	DME	66	81	8
2	**L3**	DME	76	87	2
3	**L1**	toluene	31	73	0
4	**L2**	toluene	61	73	2
5	**L3**	toluene	60	85	1
6	**L4**	toluene	85	88	0
7	**L4**	CH_2Cl_2	84	64	26
8	**L4**	dioxane	80	99	0
9	**L4**	DME	84	87	7
10	**L4**	THF	81	85	1
11	**L4**	DME (1%H_2O)	NA	20	3.7
12	**L3**	DME (1%H_2O)	NA	1.5	0



JACS, **2005**, *127*, 2846

Regio- and Enantioselective Pd-Catalyzed AAA of ketones through Allyl Enol Carbonates

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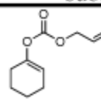
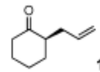
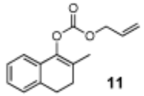
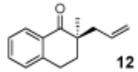
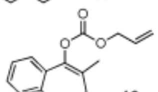
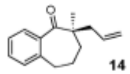
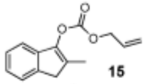
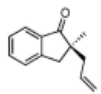
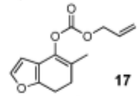
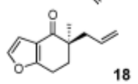
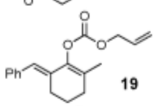
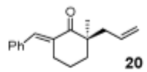
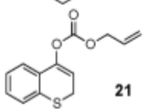
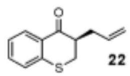
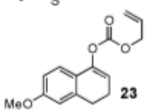
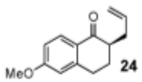
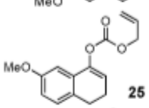
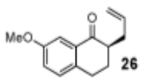
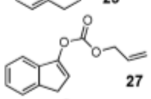
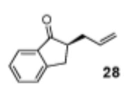
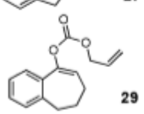
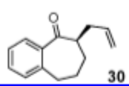
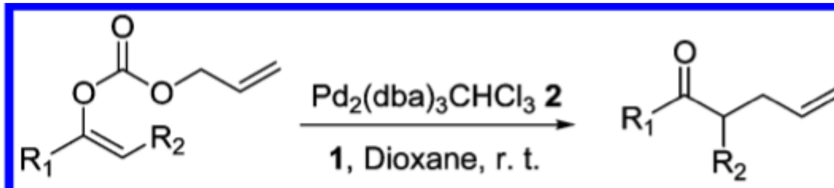
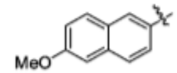
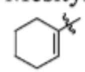
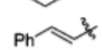
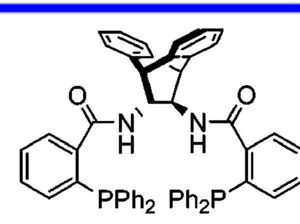
entry	substrate	product	yield[b]	ee[c]
1[d]	 9	 10	78%	78%[e]
2[d]	 11	 12	88%	>99%
3	 13	 14	94%	91%[e]
4[b]	 15	 16	98%	76%
5	 17	 18	64%	82%
6	 19	 20	99%	95%
7	 21	 22	89%	93%
8[f]	 23	 24	90%	>99%
9[f]	 25	 26	97%	97%
10	 27	 28	87%	81%
11[f]	 29	 30	93%	99%



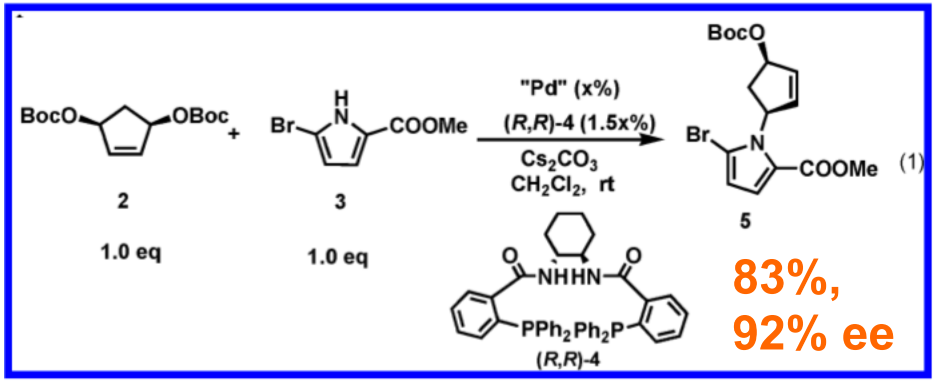
	R_1	R_2	Z/E[b]	time	yield	ee
1	Ph	Me	>98/2	2 h	94%	94%
2	Ph	Et	>98/2	2 h	94%	94%
3	Ph	C_5H_{11}	>98/2	16 h	93%	92%[c]
4	Ph	*i*-Pr	>98/2	24 h	30%	32%[c]
5	Ph	CH_2Ph	>98/2	1 h	75%	88%
6		Me	>98/2	1 h	90%	95%
7	2'-F-Ph	Me	>98/2	1 h	80%	94%
8	3'-Cl-Ph	Me	>98/2	1 h	97%	93%
9	4'-Br-Ph	Me	>98/2	1 h	94%	93%
10	2'-OMe-Ph	Me	>98/2	16 h	99%	98%[c]
11	Pyridyl	Me	>98/2	1 h	95%	73%[c]
12	3'-NO_2-Ph	Me	>98/2	1 h	83%	82%
13	Furyl	Me	>98/2	4 h	89%	88%
14	2'-CF_3-Ph	Me	>98/2	2 h	94%	92%
15	Mesityl	Me	5/95	6 h	99%	96%[c]
16	Mesityl	Me	96/4	16 h	trace	NA
17		Me	>98/2	5 h	94%	88%
18		Me	25/1	0.3h	93%	91%

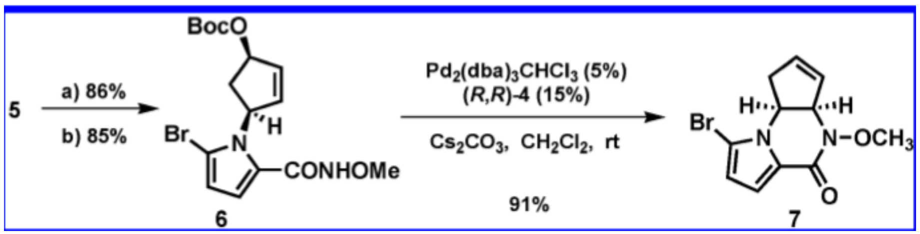


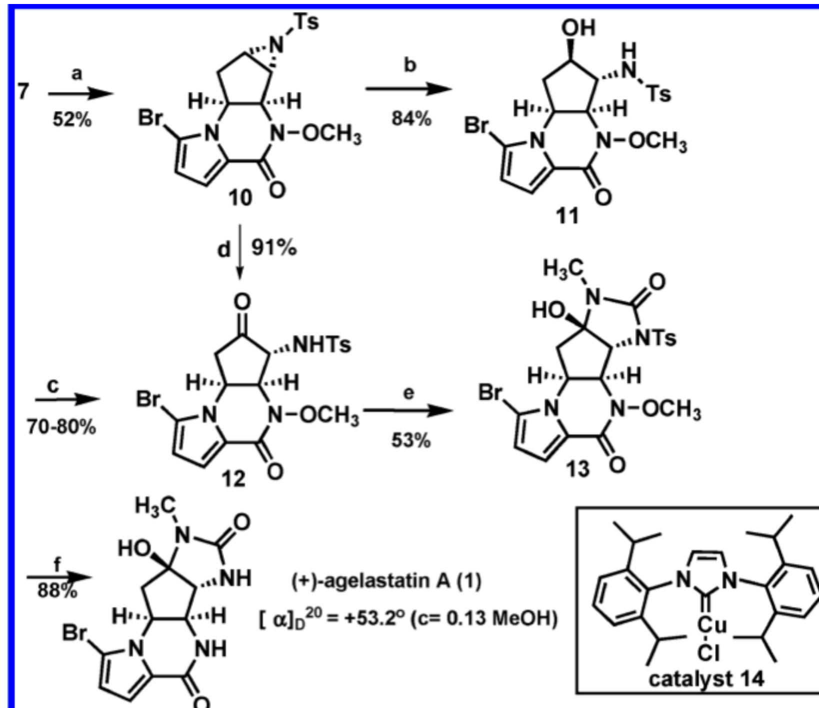
(*R*, *R*)-**1**

JACS, **2005**, *127*, 2846; JACS, **2005**, *127*, 17180

New Class of Nu for AAA
Total Synthesis of Agelastatin A

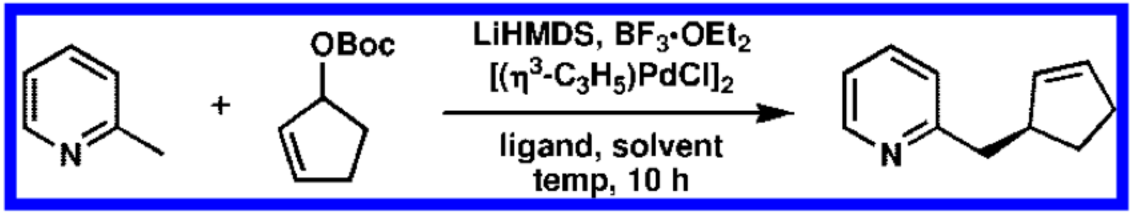




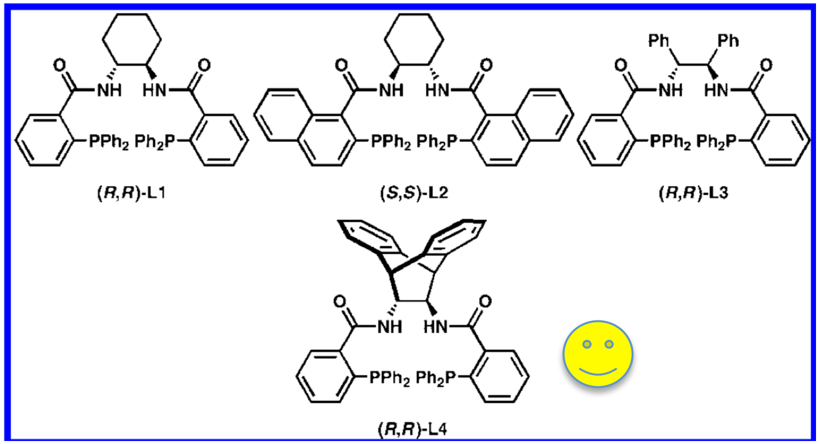


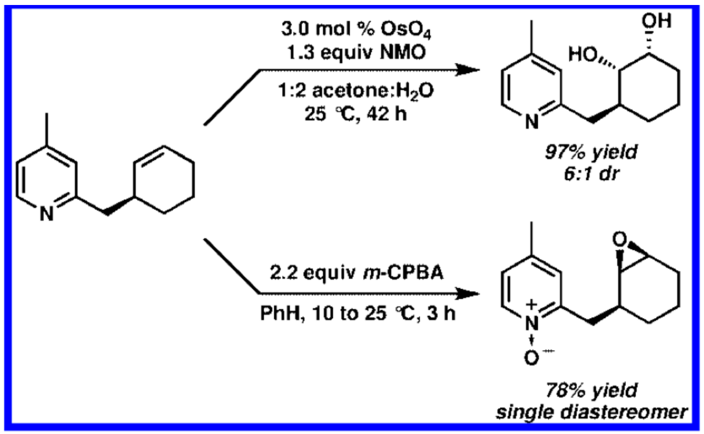
JACS, **2006**, *128*, 6054

Strategy for Employing Unstabilized Nu in AAA



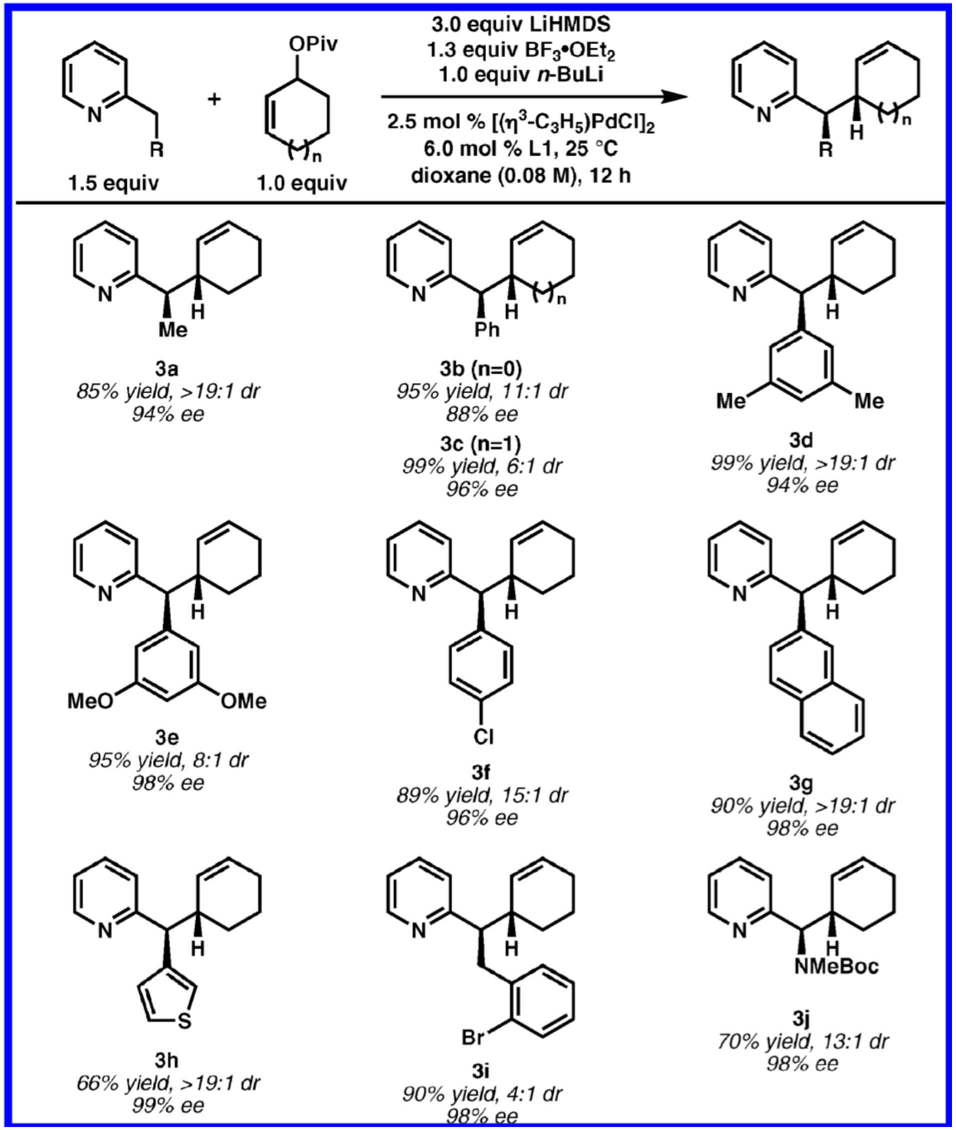
entry	ligand	solvent	temp (°C)	yield (%)[b]	ee (%)[c]
1	L1	THF	25	13	−30[d]
2	L1	THF	40	11	1.0
3	L1	THF	4	68	−8.4
4	L1	THF	−25	18	−4.0
5	L2	THF	25	55	−20
6	L3	THF	25	15	−43
7	L4	THF	25	70	86
8	L4	DME	25	50	94
9	L4	toluene	25	31	59
10	L4	dioxane	25	86	95

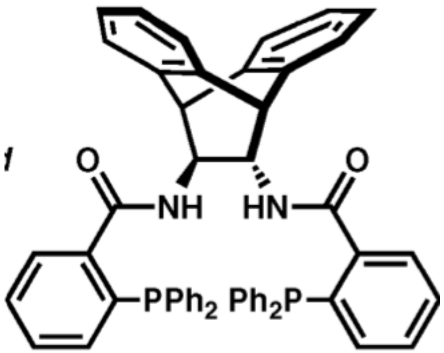




Pd-Catalyzed allylation of 2-Substituted Pyridines

MICHIGAN STATE UNIVERSITY

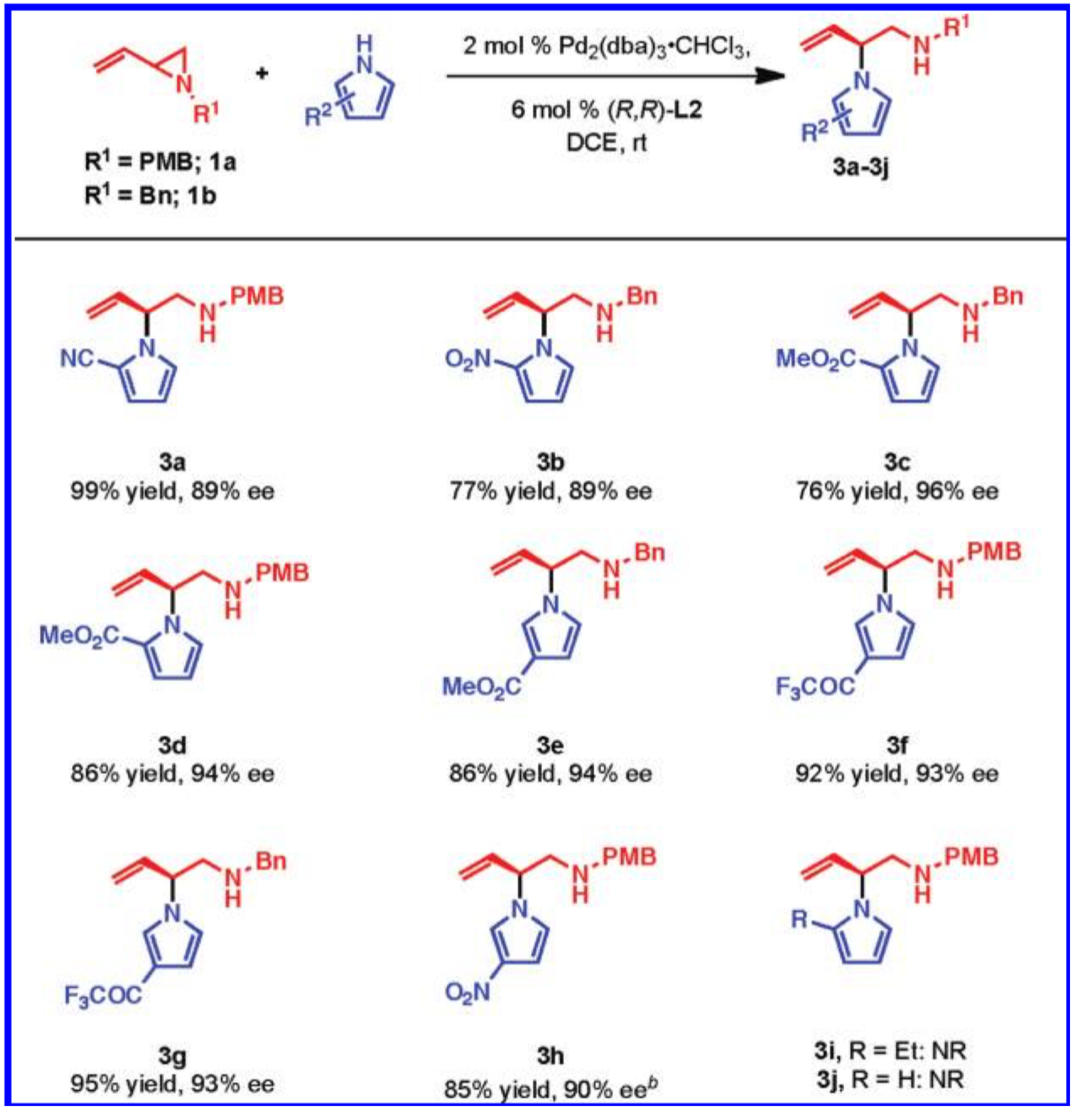


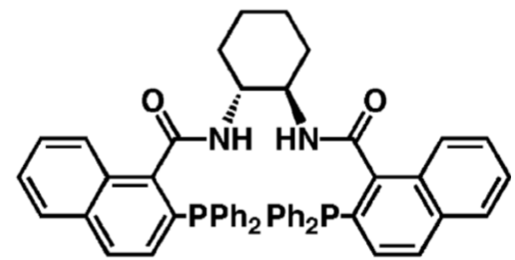


JACS, **2009**, *131*, 12056

Pd-DKAT of Vinyl Aziridines with N-Heterocycles

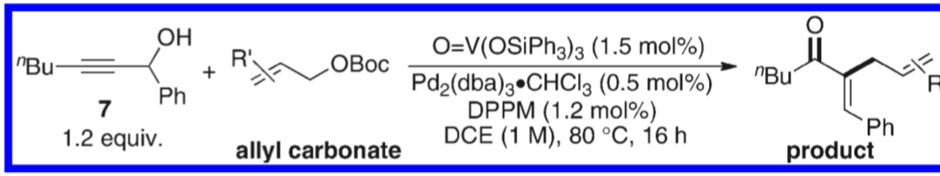
MICHIGAN STATE UNIVERSITY

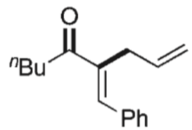
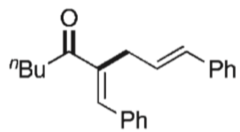
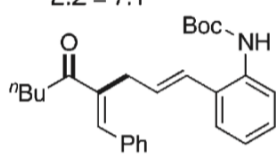
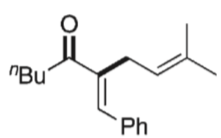
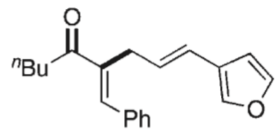
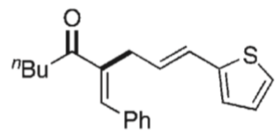
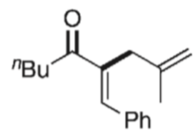
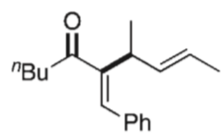




(R,R)-**L2**

Dual Catalysis by Coupling Highly Transient Nu and E Intermediates Generated in Situ

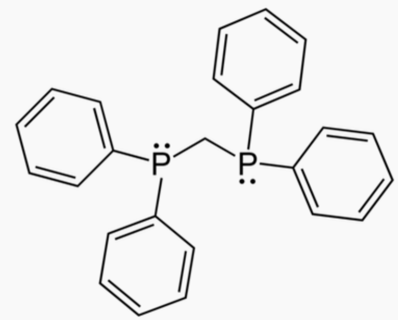


entry	product	yield (%)
1	 *E*:*Z* = 7:1	98
2	 *E*:*Z* = 7:1	92
3	 *E*:*Z* = 7:1	85
4	 *E*:*Z* = 7:1	57
5	 *E*:*Z* = 10:1	94
6	 *E*:*Z* = 6:1	76
7	 *E*:*Z* = 7:1	88
8[b]	 *E*:*Z* = 12:1	66

(Entries 5–8: entry[a])

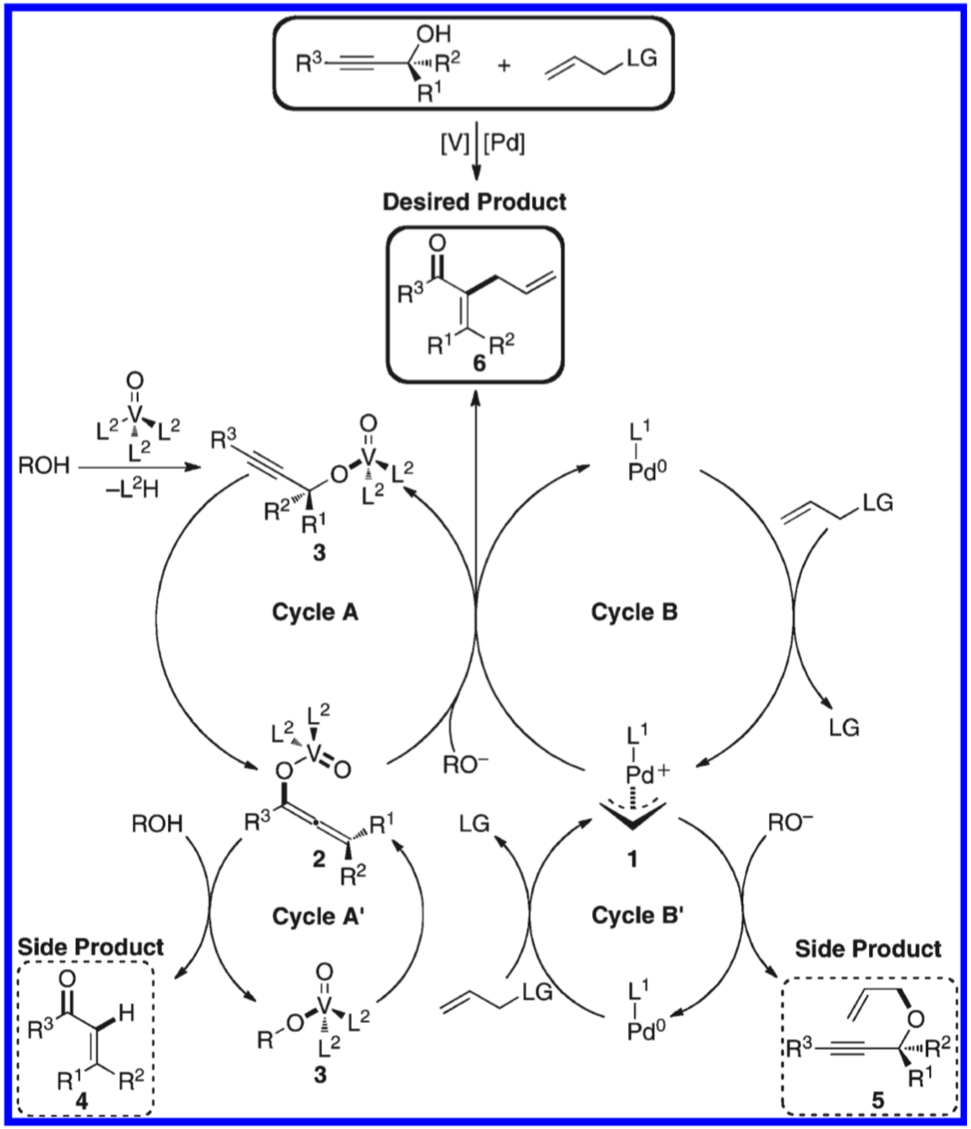
[a] Using 1.5 mol % $Pd_2(dba)_3 \cdot CHCl_3$, 3.6 mol % DPPM, and 4.5 mol % $O{=}V(OSiPh_3)_3$. [b] Using 1.5 equiv of 7 and a reaction time of 48 h.

1,1-bis(diphenylphosphino)methane



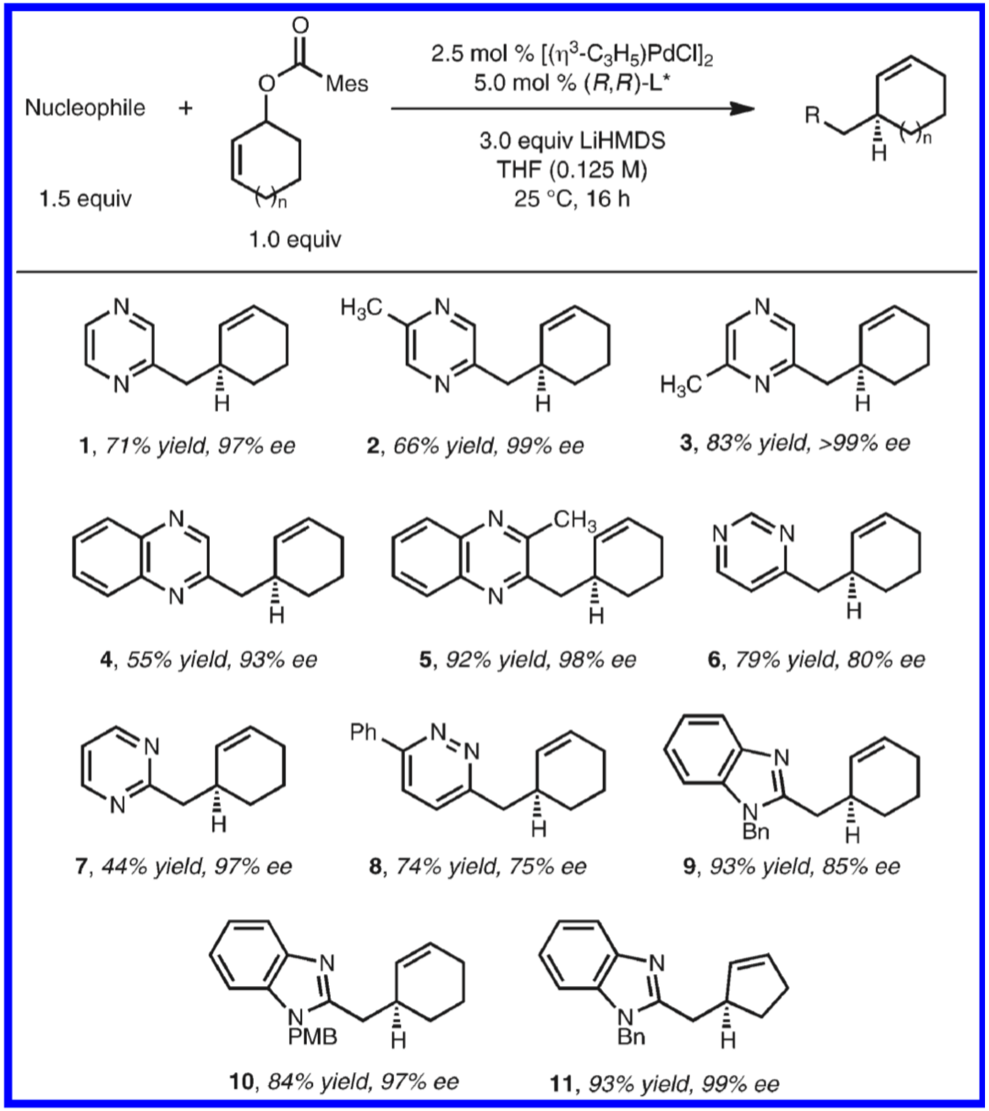
JACS, **2011**, *133*, 1706

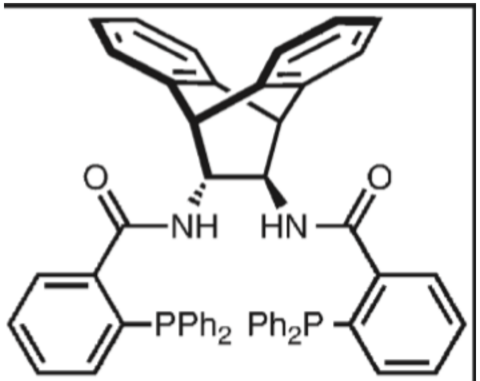
Dual Catalysis by Coupling Highly Transient Nu and E Intermediates Generated in Situ



JACS, **2011**, *133*, 1706

Pd-AAA of Polynitrogen-Containing Aromatic Heterocycles



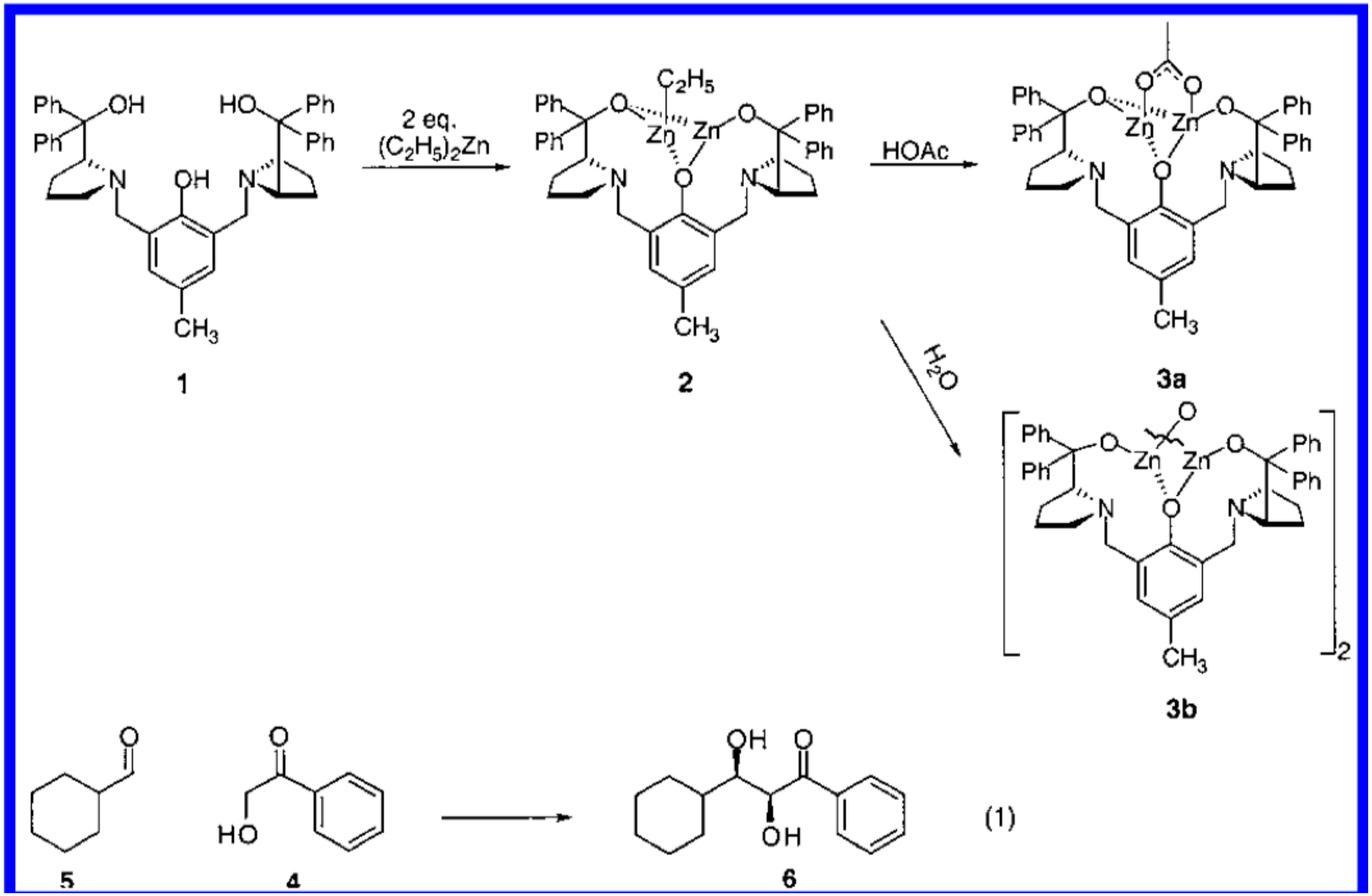


(R,R)-L*

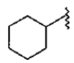
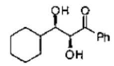
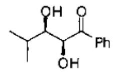
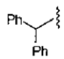
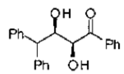
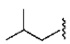
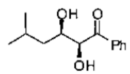
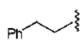
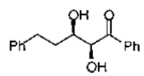
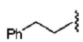
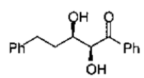
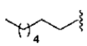
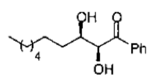
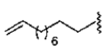
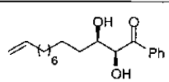
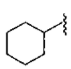
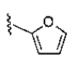
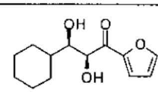
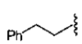
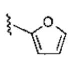
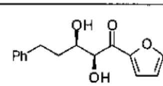
JACS,2011, *133*, 12439

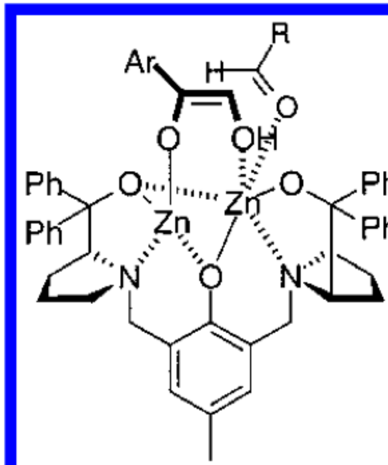
Alkylation via A Dinuclear Zn Catalyst

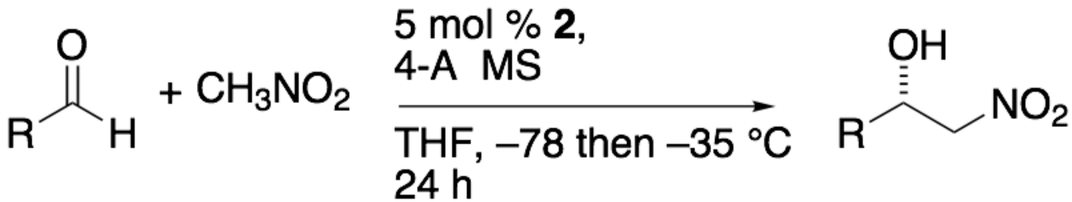
Asymmetric Aldol Reaction via a Dinuclear Zinc Catalyst

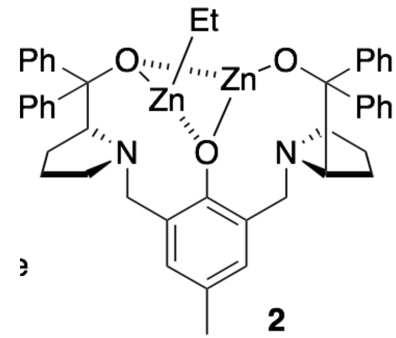


Asymmetric Aldol Reaction via a Dinuclear Zinc Catalyst

entry	R	Ar	Major Product[b]	isolated yield (%)	dr[c]	ee (%)[d]
1	 a b[e]	Ph		83 97	30:1 5:1	92 90
2a b[e] c[e,f]		Ph		89 93 72	13:1 5:1 6:1	93 86 93
3a b[e]		Ph		74 97	ONLY ONE 13:1	96 81
4a b[e] c[e,f]		Ph		65 96 79	35:1 3:1 4:1	94 88 93
5a b[e]		Ph		78 98	9:1 3:1	91 90
6[e,g]		Ph		62	3.5:1	96
7[e]		Ph		89	5:1	86
8[e]		Ph		91	5:1	87
9a[e,h] b[e,f]				90 77	6:1 6:1	96 98
10[e,h]				97	3.4:1	95

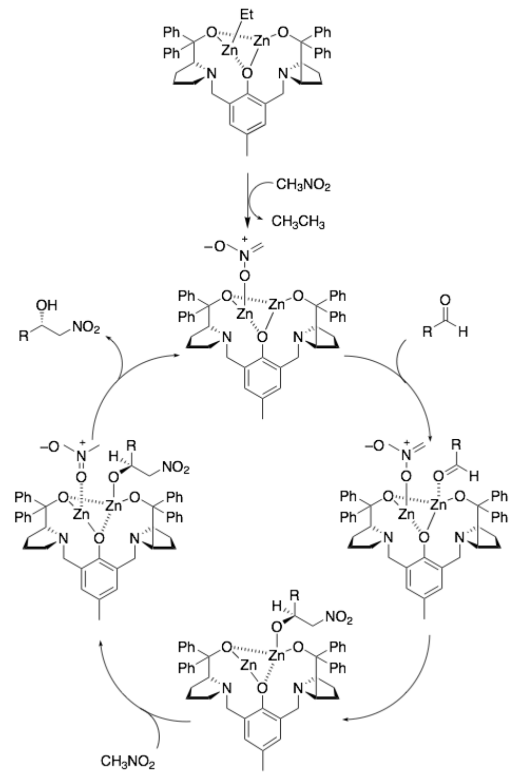




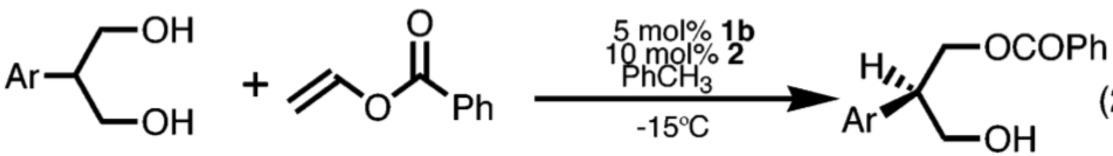


2

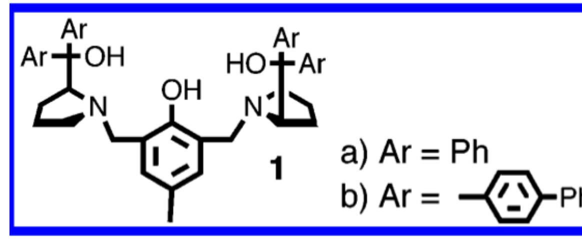
Entry	R	Product	Yield [°C]	*ee* [%][b]
1		3	75	85
2[c]		4	58	88
3[c]		5	88	93
4		6	90	92
5		7	84	87
6a[d]	Ph	8[f]	56	85
6b[e]			59	84
7[d]	BnO	9	56	86
8		10	75	91
9		11	71	93
10	MeO, OMe	12	69	78
11	Boc	13[11]	79	90

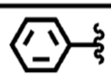
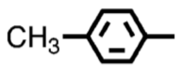
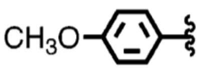
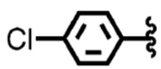
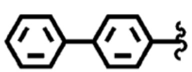
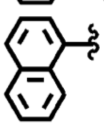
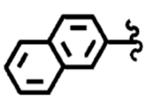
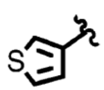


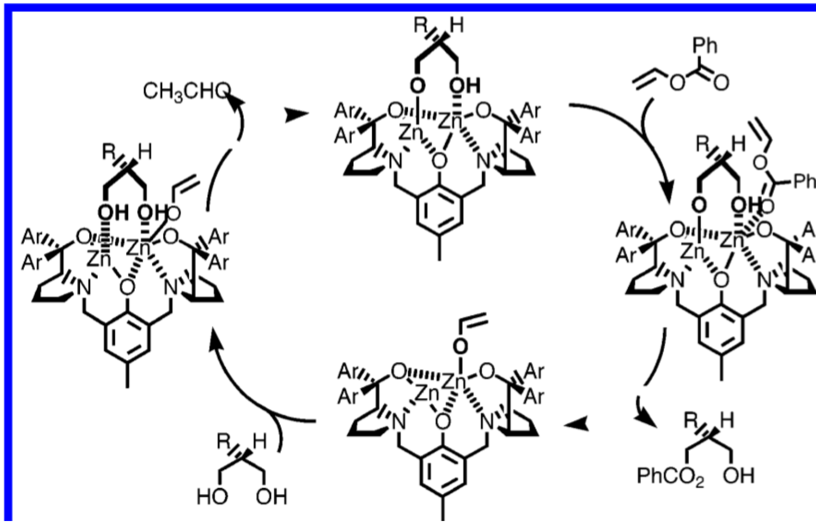
Desymmetrization of Meso Diols



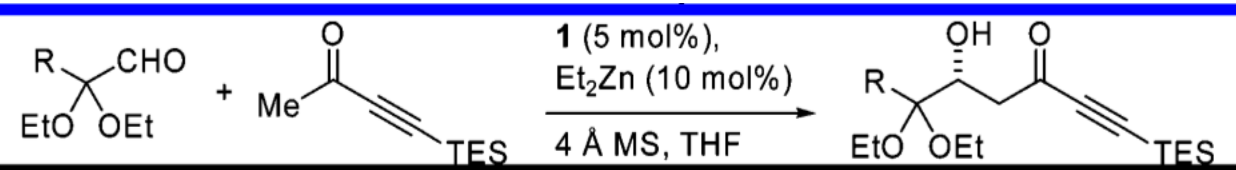
(2)

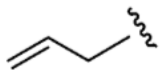
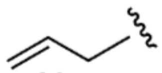
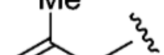


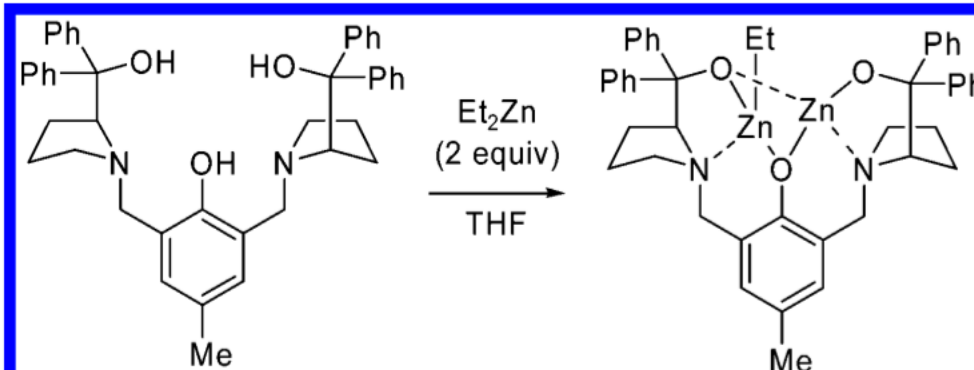
Entry	Ar	Mol% cat	Time	Yield[b]	ee[c]
1		5	24h	94%	91%[d]
2		5	24h	98%	91%
3		5	24h	99%	93%
4		10	18h	89%	90%
		5	24h	70%	83%
5		10	18h	83%	86%
		5	24h	48%	83%
6		10	18h	99%	59%
		5	30h	68%	38%
7		10	18h	97%	93%
		5	24h	60%	86%
8		10	20h	88%	74%
		5	24h	45%	63%
9		10	20h	78%	70%



Asymmetric Aldol Addition of Methyl Ynones



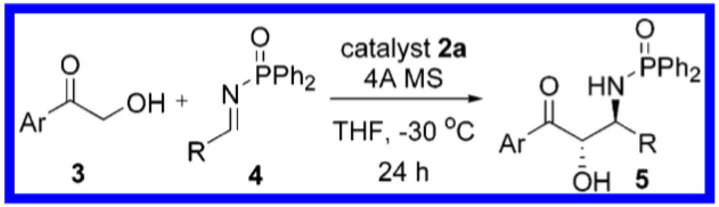
Entry	R	Equiv **4**	T (°C)	Time (h)	Yield (%)[b]	ee (%)[3c]
1		2.5	0	17.5	76	> 98
2		2.0	25	4	75	> 98
3		2.5	0	14	79	> 98
4	$TBSOCH_2$	2.5	0	6	84	> 95
5[d]	$TBSOCH_2$	1.2	25	5	73	> 98
6	EtO_2C	2.5	0	4.25	68	37

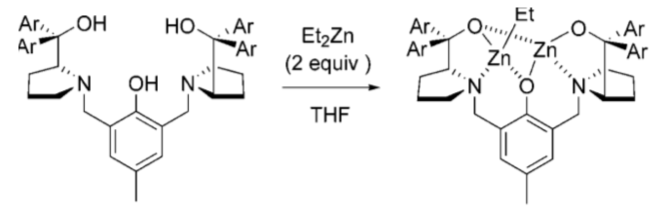


1

JACS, **2004**, *126*, 2660

Asymmetric Mannich-type Reaction via a Dinuclear Zinc Catalyst





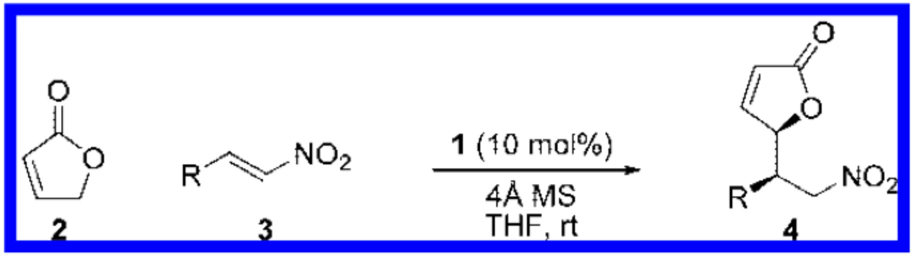
1a Ar = phenyl

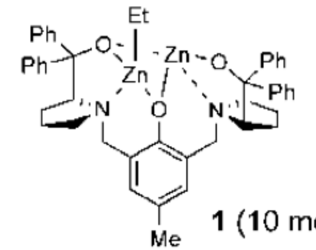
2a

entry	Ar		R		product	yield[b] (%)	dr[c] (*anti*:*syn*)	ee[d] (%) (*anti*)
1	Ph	**3a**	*cyclo*-hexyl	**4a**	**5a**	86	5:1	94
2	Ph	**3a**	*cyclo*-propyl	**4b**	**5b**	79	5:1	83
3	Ph	**3a**	*i*-propyl	**4c**	**5c**	83	6:1	>99
4	Ph	**3a**	*i*-butyl	**4d**	**5d**	80	5:1	96
5	Ph	**3a**	$PhCH_2CH_2$	**4e**	**5e**	76	4:1	96
6	Ph	**3a**	*n*-hexyl	**4f**	**5f**	71	4:1	96
7	2-furyl	**3b**	*cyclo*-hexyl	**4a**	**5g**	73	3:1	83
8[e]		**3b**		**4a**	**5g**	85	4:1	90
9	2-$MeOC_6H_4$	**3c**	*cyclo*-hexyl	**4a**	**5h**	65	2:1	56
10[e]		**3c**		**4a**	**5h**	70	1:1	57
11	1-naphthyl	**3d**	*i*-propyl	**4c**	**5i**	71	3:1	87
12[e]		**3d**		**4c**	**5i**	74	4:1	88
13	2-naphthyl	**3e**	*i*-propyl	**4c**	**5j**	69	3:1	(−)-86
14[e]		**3e**		**4c**	**5j**	77	4:1	(−)-95
15[f]		**3e**		**4c**	**5j**	74	4:1	(+)-95

JACS, **2006**, *128*, 2778

Asymmetric Michael Addition to Nitroalkenes



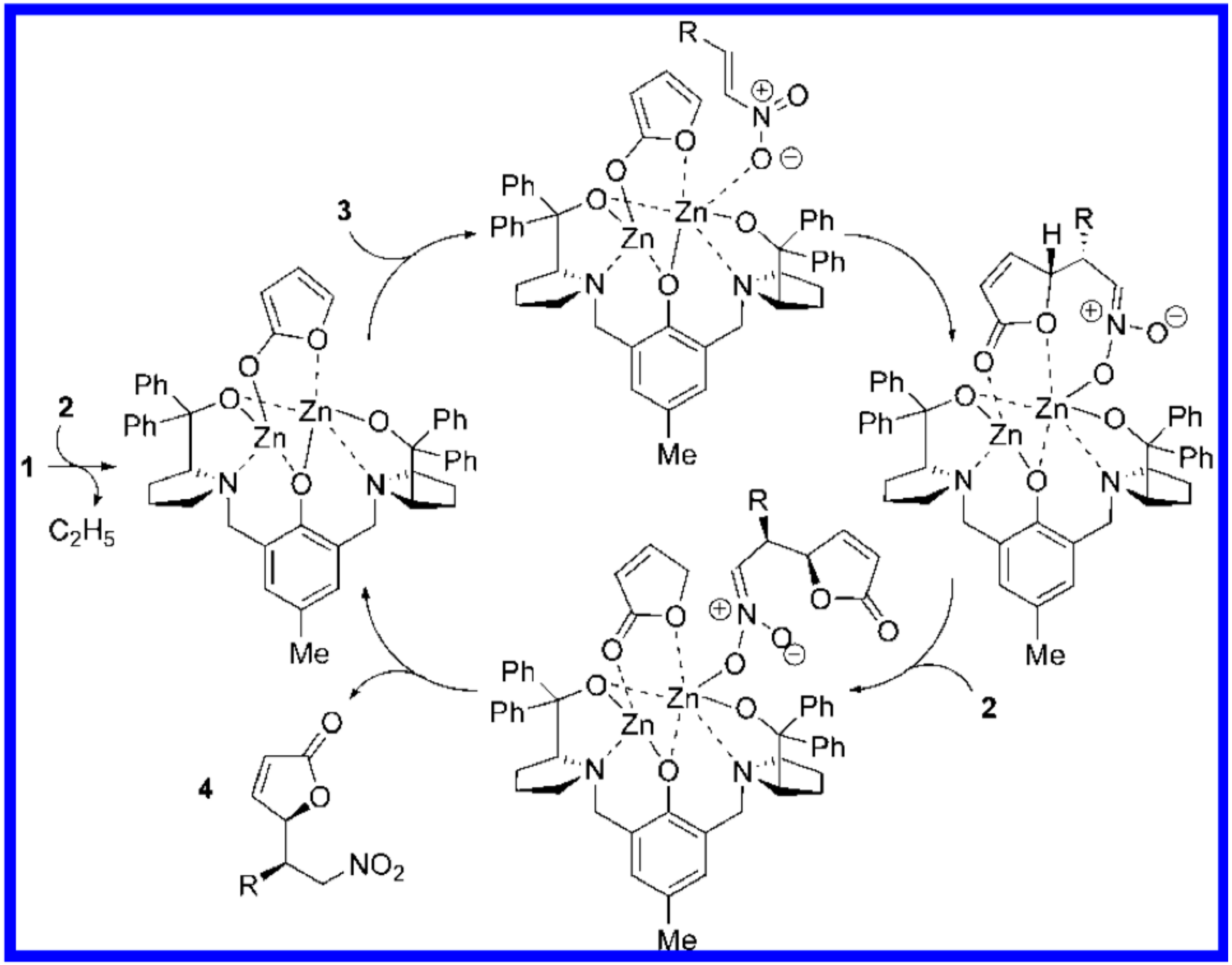


1 (10 mol%)

entry	R	product	yield (%)[b]	dr[c]	ee (%)[d]
1	2-Me-Ph (**3b**)	**4b**	74	8:1	92
2	4-Me-Ph (**3c**)	**4c**	70	17:1	95
3	4-MeO-Ph (**3d**)	**4d**	78	20:1	96
4	4-Cl-Ph (**3e**)	**4e**	70	9:1	90
5	3-Br-Ph (**3f**)	**4f**	72	7:1	87
6	1-naphthyl (**3g**)	**4g**	75	>20:1	94
7	2-furanyl (**3h**)	**4h**	77	18:1	95
8	3-furanyl (**3i**)	**4i**	65	14:1	95
9	2-thiophenyl (**3j**)	**4j**	69	>20:1	94
10	3-thiophenyl (**3k**)	**4k**	71	17:1	95
11[e,f]	*N*-Boc-3-indolyl (**3l**)	**4l**	73	6:1	85
12[e]	$PhCH_2CH_2$ (**3m**)	**4m**	47	4:1[g]	83
13[e]	PhCHCH (**3n**)	**4n**	52	3:1	91

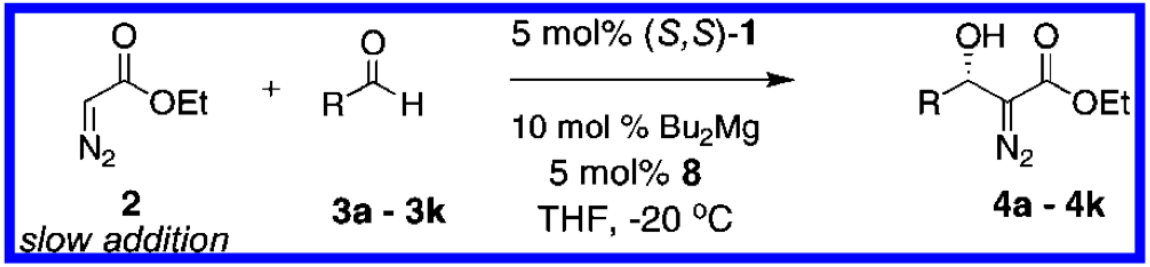
JACS, **2009**, *131*, 4572

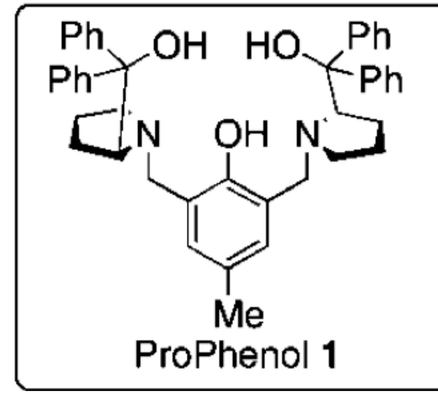
Asymmetric Michael Addition to Nitroalkenes



JACS, **2009**, *131*, 4572

Mg-Catalyzed Asymmetric Aldol Addition of EDA



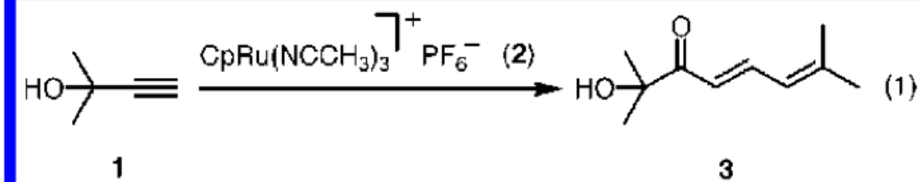


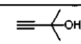
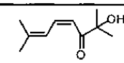
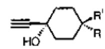
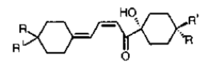
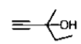
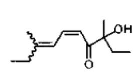
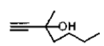
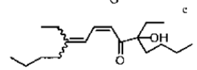
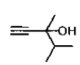
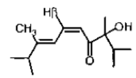
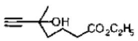
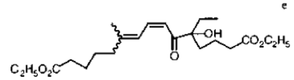
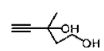
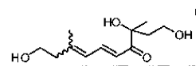
entry	R	product	time (h)	yield[b]	% ee[c]
1	Ph (**3a**)	**4a**	18	92	95
2	*m*-$CH_3OC_6H_4$ (**4b**)	**4b**	18	83	90
3	*p*-$CH_3OC_6H_4$ (**3c**)	**3c**	18	70	87
4	*o*-ClC_6H_4 (**3d**)	**4d**	18	91	89
5	*m*-ClC_6H_4 (**3e**)	**4e**	18	88	98
6	*p*-ClC_6H_4 (**3f**)	**4f**	18	78	93
7	2-furyl (**3g**)	**4g**	18	83	96
8[d]	$(CH_3)_2CH$ (**3h**)	**4h**	24	56	97
9[d]	$CH_3(CH_2)_3$ (**3i**)	**4i**	24	50	97
10[d]	$PhCH_2CH_2$ (**3j**)	**4j**	24	76	90
11	PhCHCH (**3k**)	**4k**	18	50	94

Some Other Reactions

Ru-Catalyzed Dimerization of Propargyl Alcohols

MICHIGAN STATE UNIVERSITY

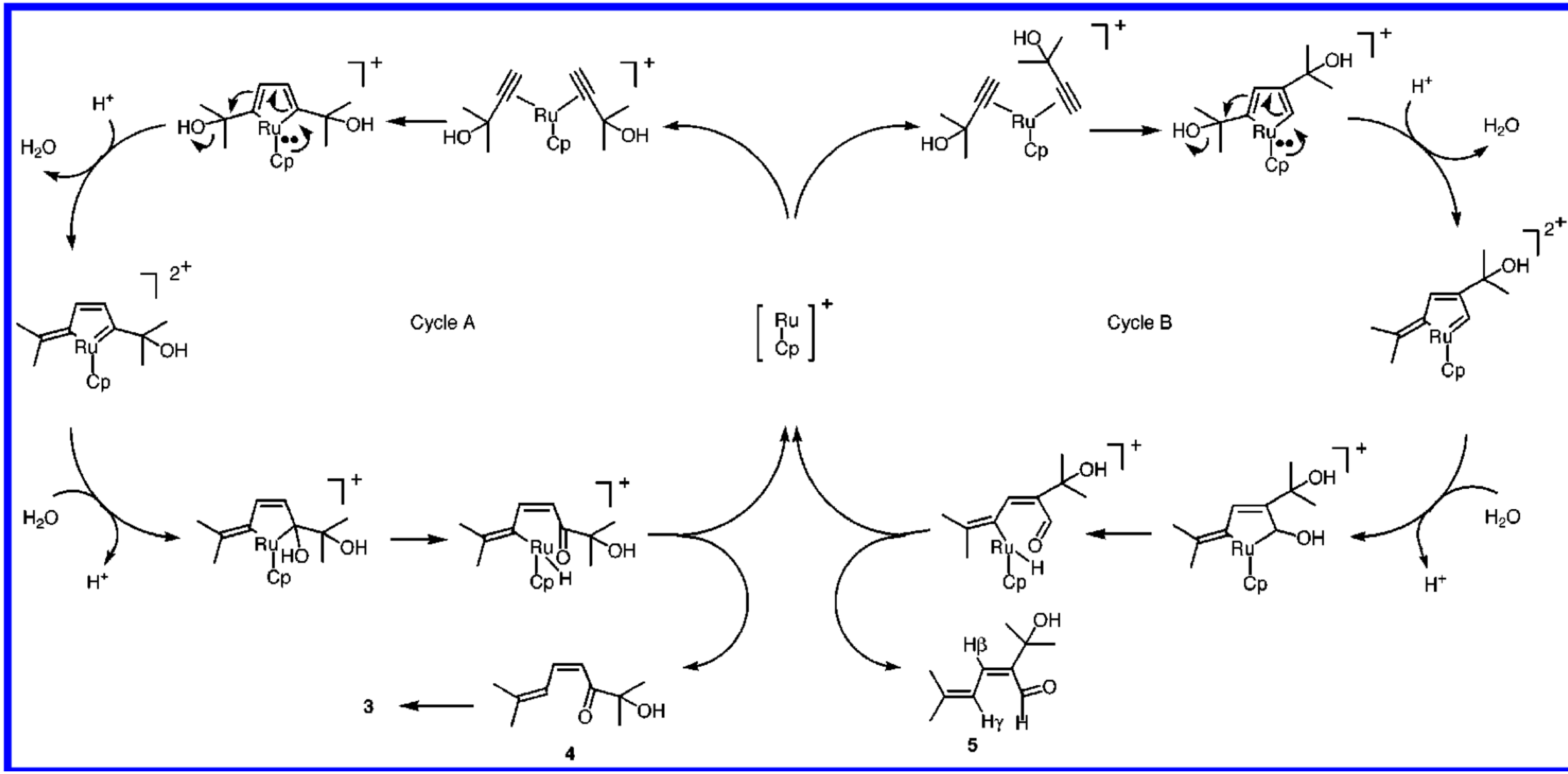


Entry	Propargyl Alcohol	Method	Product	Yield[g]
1		A[a]		77%
				
2	R = R' = H	B[b]	R = R' = H	55%
3	R, R' = OCH$_2$CH$_2$O	C[c]	R, R' = OCH$_2$CH$_2$O	65%
4	R = Ph, R' = H	C[c]	R = Ph, R' = H	76%
5	R = CN, R' = H	D[d]	R = CN, R' = H	60%
6	R = H, R' = CN	D[d]	R = CN, R' = H	55%
7	R, R' = O	C[c]	R, R' = O	70%
8		A[a]	 [e]	55%
9		B[b]	 [e]	65%
10		B[b]		65%
11		C[c]	 [e]	63%
12		C[c]	 [f]	70%

[a] Reaction performed at 3 M using 7 mol % **2** in 10 vol % acetone in THF, 1 equiv H_2O, −20°, 4 h. [b] As in footnote *a*, but using 10 mol % **2.** [c] As in footnote *a*, but using 10 mol % **2** at 0°. [d] As in footnote *a*, but using 10 mol % **2** at 60° and 0.1 M. [e] A 1:1 *E* :*Z* mixture at the γ,δ double bond. [f] A 2:1 *E* :*Z* mixture at the γ,δ double bond. [g] Isolated yield of pure product.

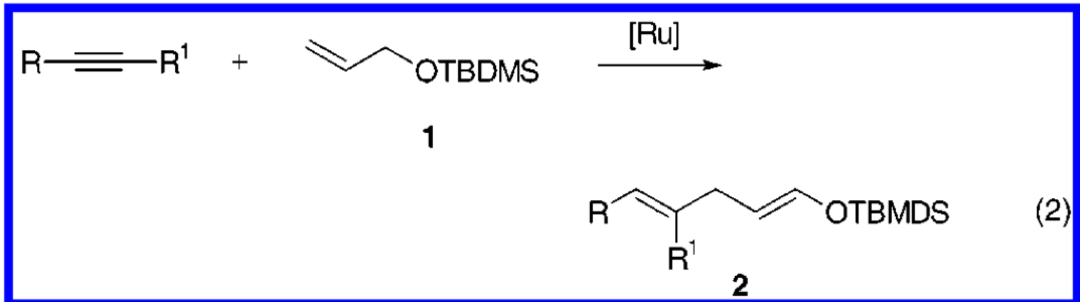
JACS, **2001**, *123*, 8862

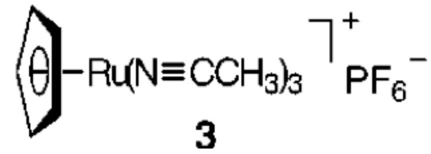
Ru-Catalyzed Dimerization of Propargyl Alcohols

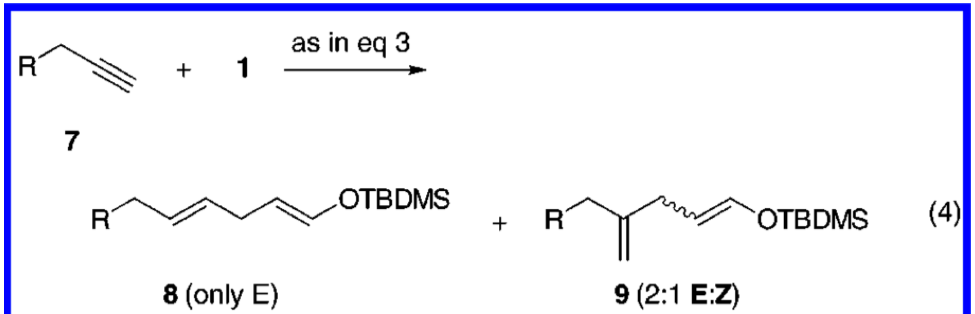


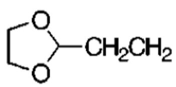
JACS, **2001**, *123*, 8862

Three-Carbon Chain Extension of Alkynes To form *E*-Enol silanes



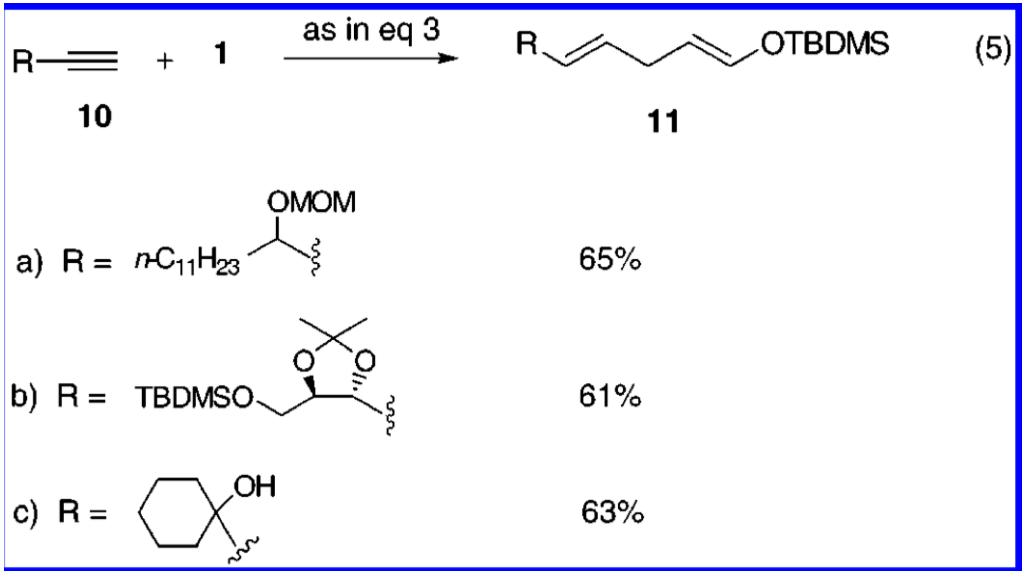


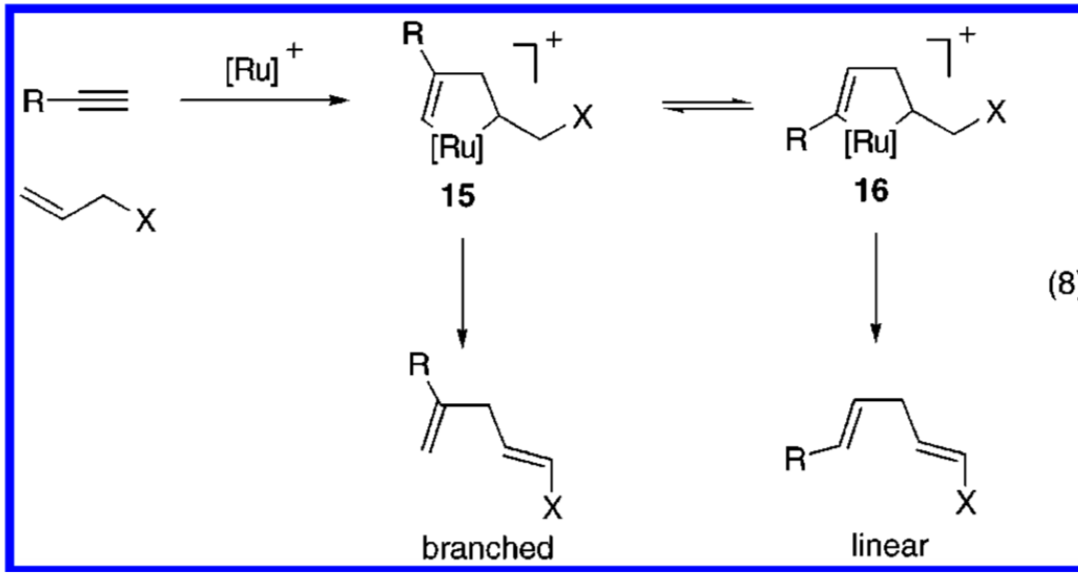


a) R = 	76%	**8:9**	3.4:1
b) R = $NCCH_2CH_2$	82%	**8:9**	3.6:1
c) R = CH_3COCH_2	51%	**8:9**	3.6:1
d) R = $TsNHCH_2$	83%	**8:9**	2.3:1
e) R = $TsN(Boc)CH_2$	79%	**8:9**	3.4:1

JACS, **2001**, *123*, 2897

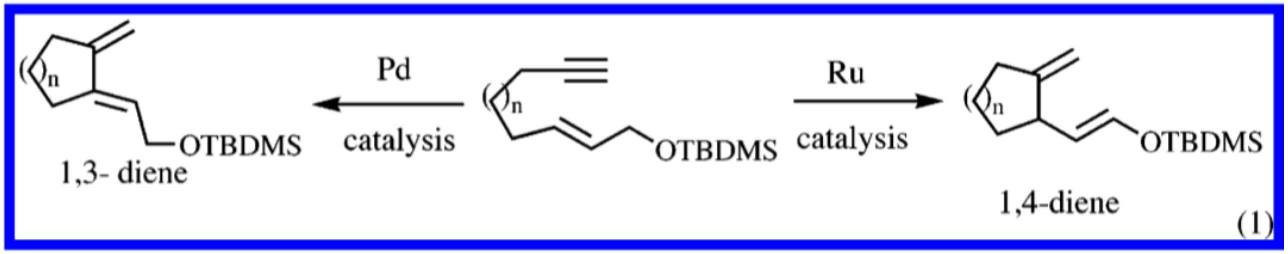
Three-Carbon Chain Extension of Alkynes To form *E*-Enol silanes

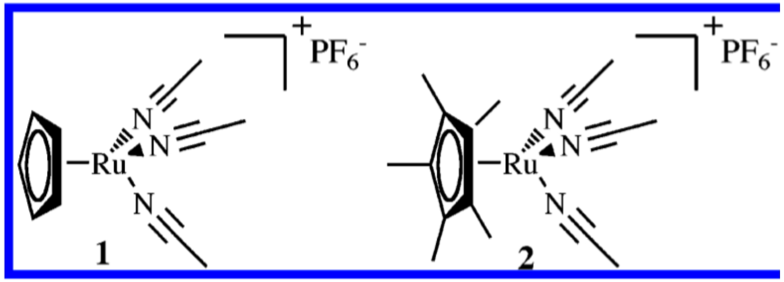


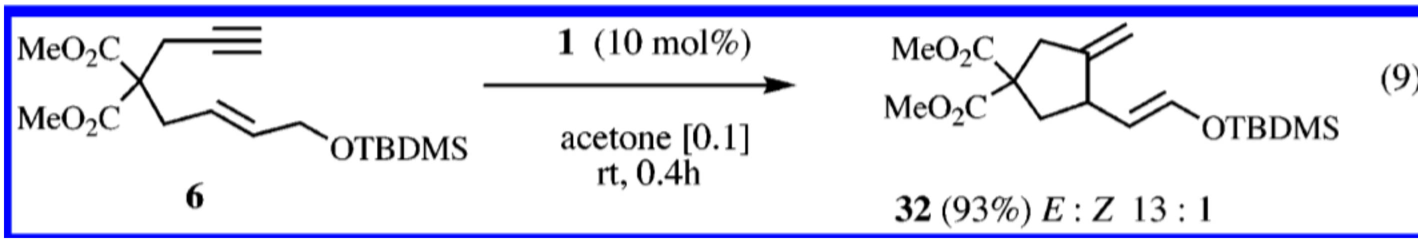


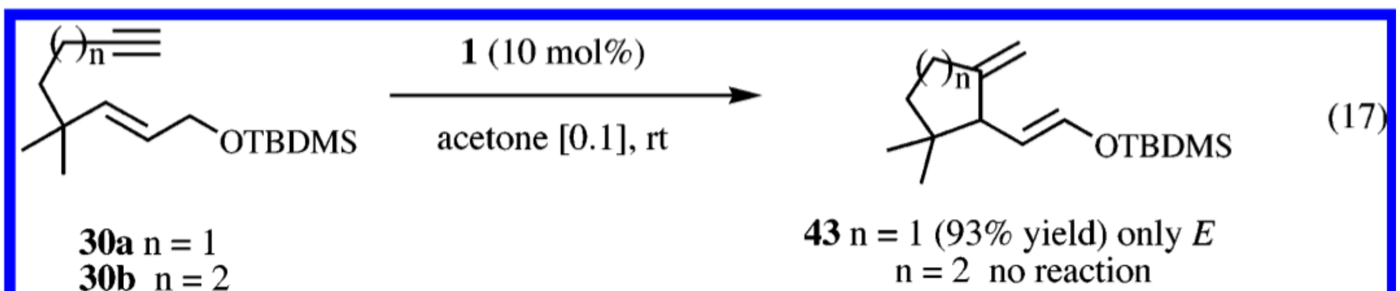
JACS, **2001**, *123*, 2897

Ru-Catalyzed Enyn Cycloisomerization



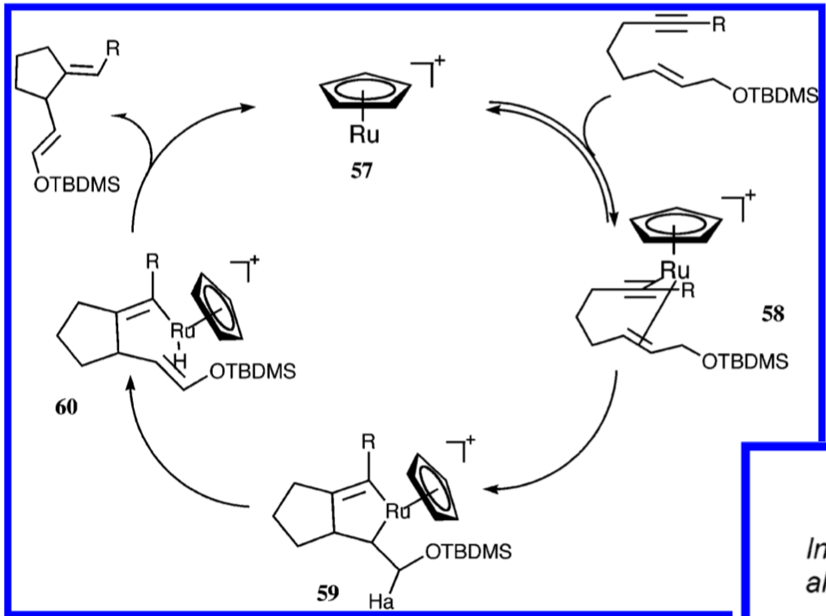


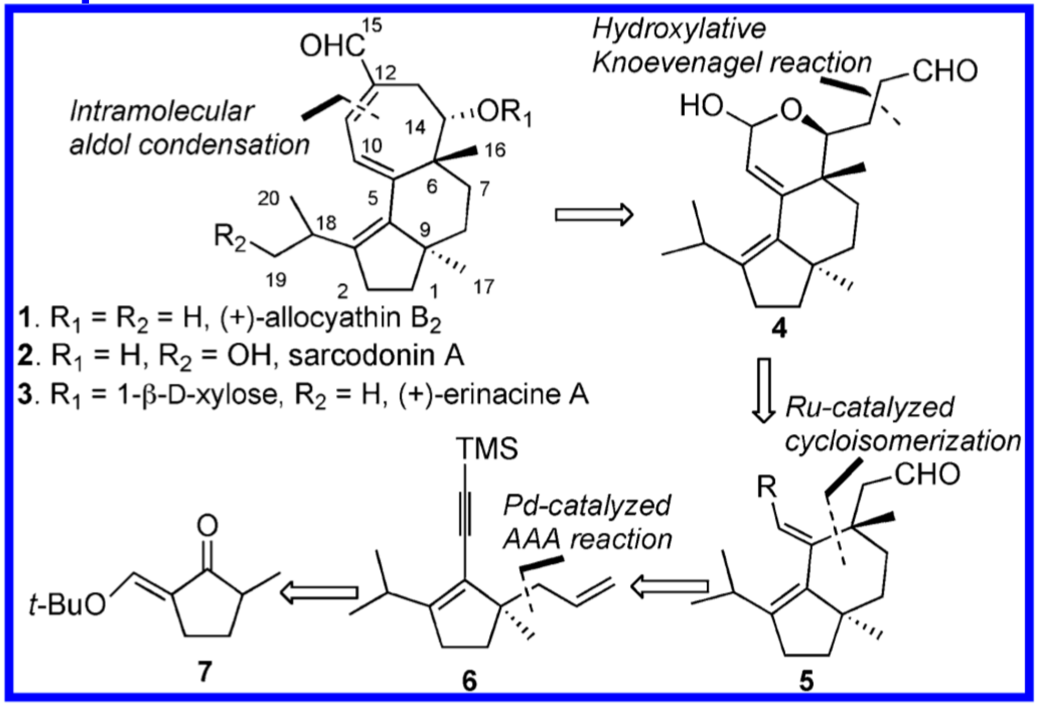




JACS, **2004**, *126*, 15592

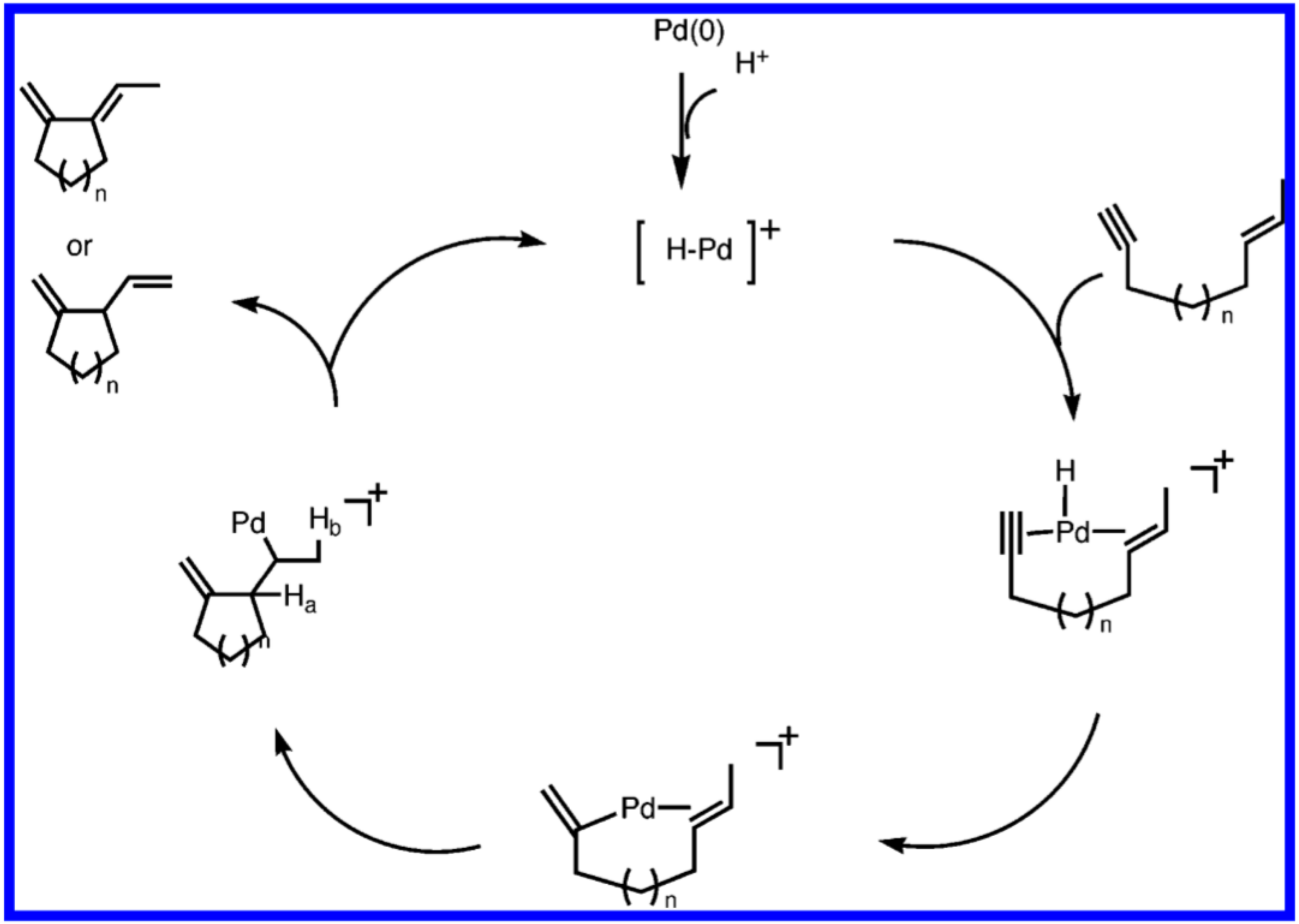
Allylic Alkylation





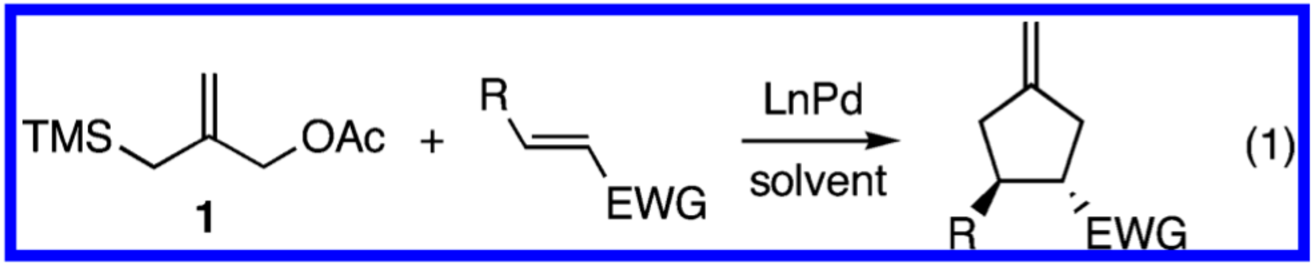
JACS, **2004**, *126*, 15592; JACS, **2005**, *127*, 10259

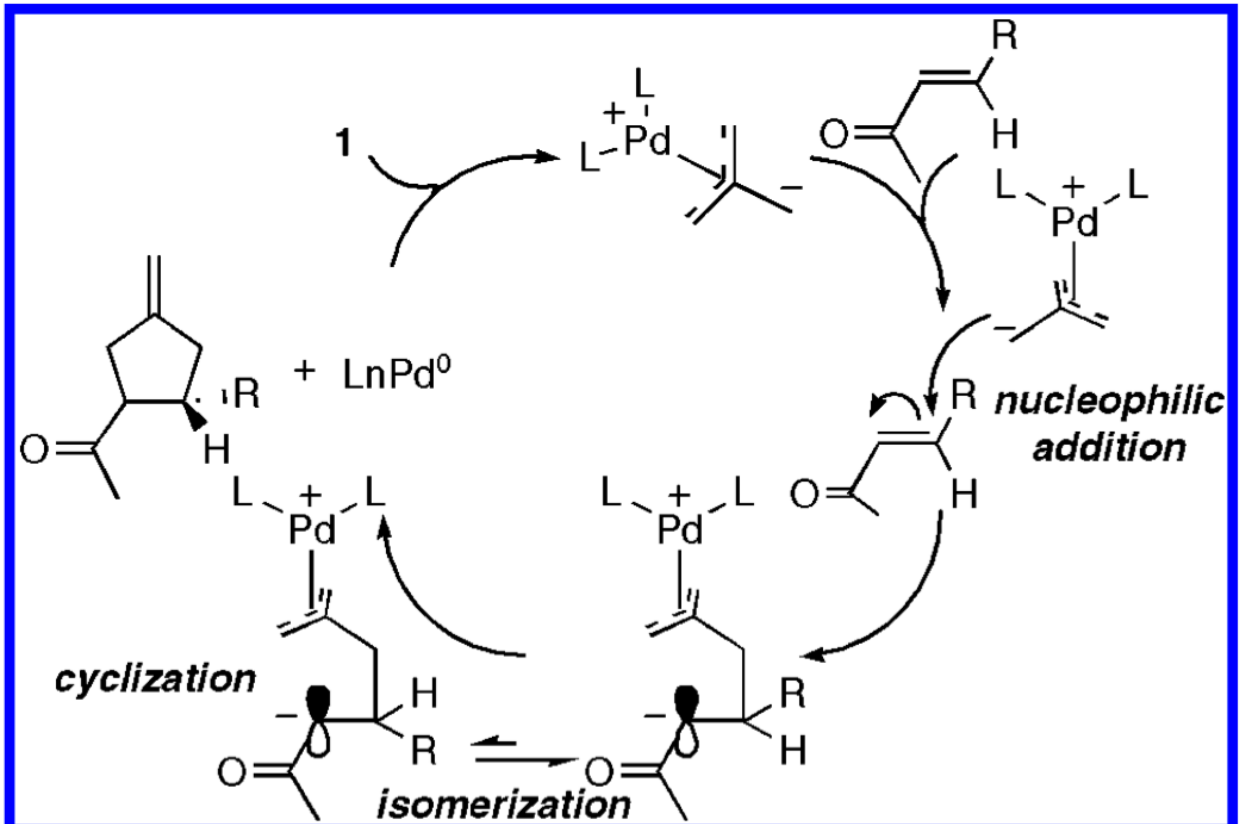
Ru-Catalyzed Enyn Cycloisomerization



JACS, **2005**, *127*, 10259

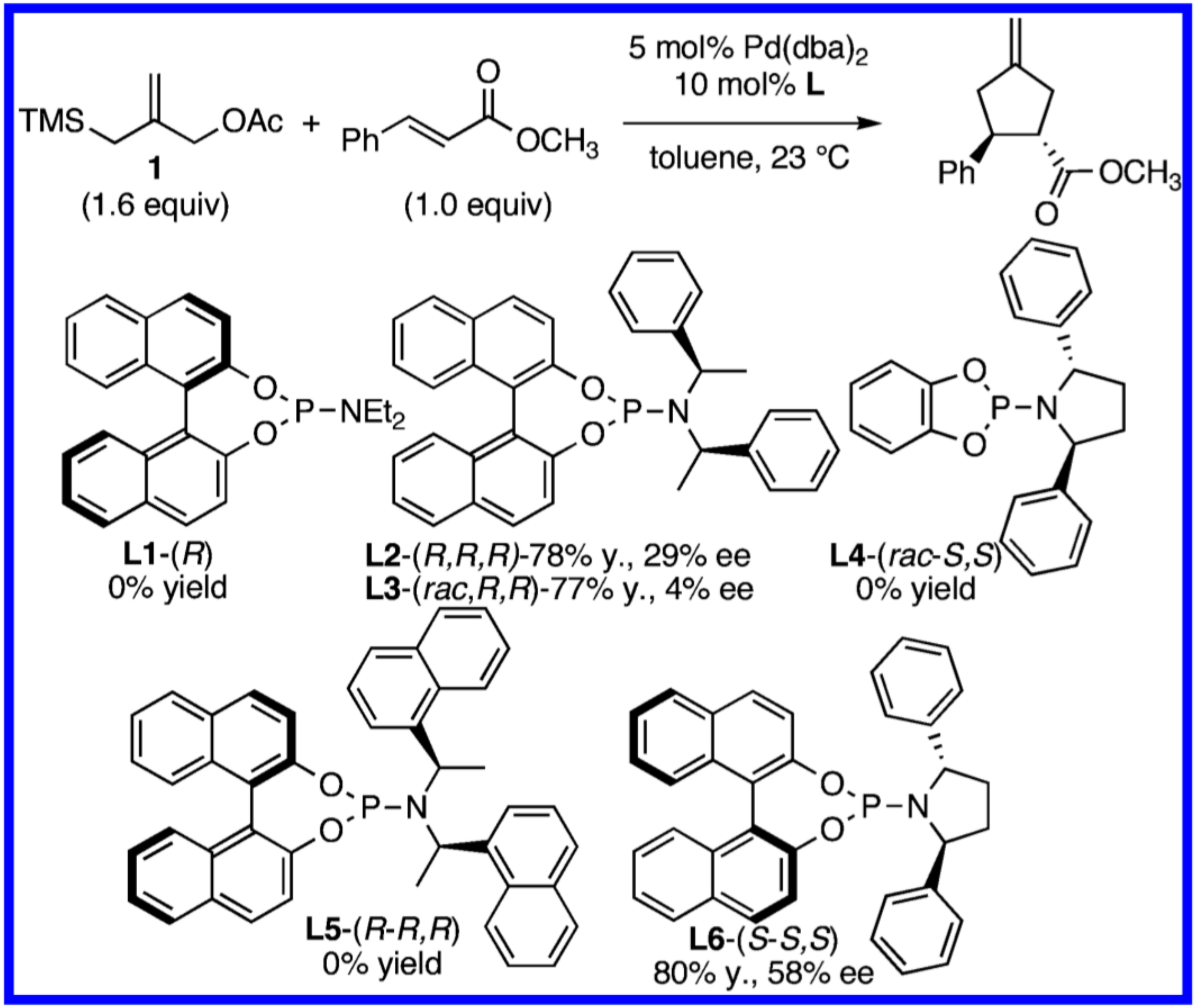
Pd-Catalyzed Asymmetric [3+2] Trimethylenemethane Cycloaddition





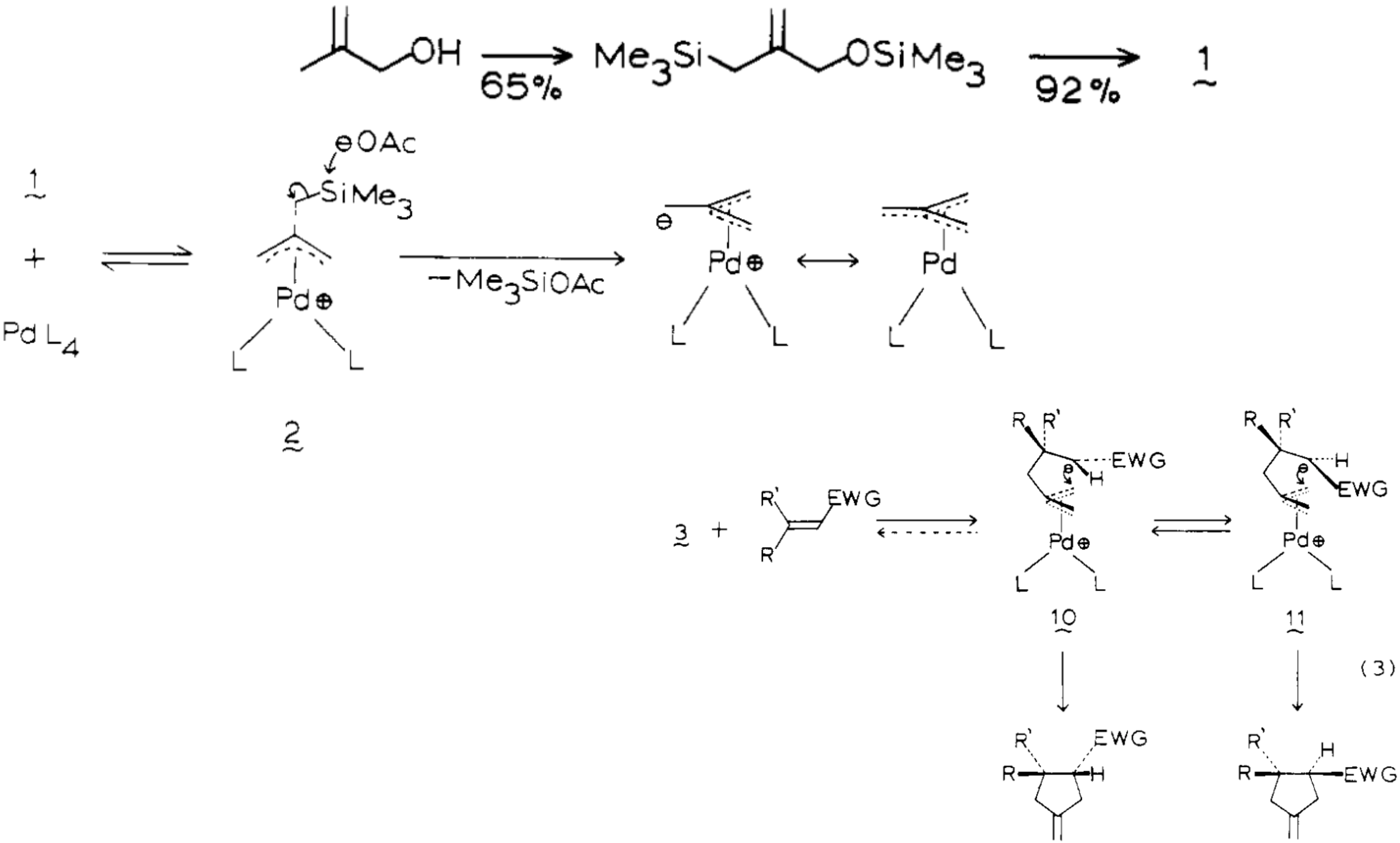
JACS, **2006**, *128*, 13328

Pd-Catalyzed Asymmetric [3+2] Trimethylenemethane Cycloaddition



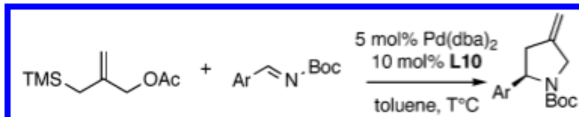
JACS, **2006**, *128*, 13328

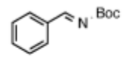
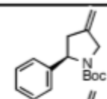
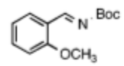
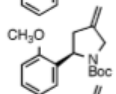
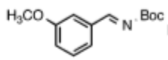
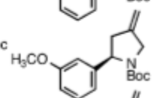
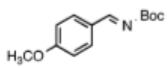
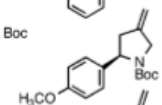
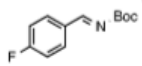
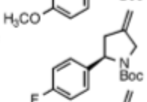
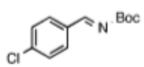
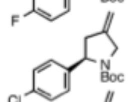
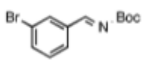
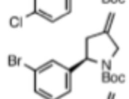
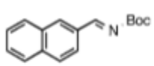
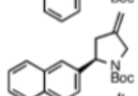
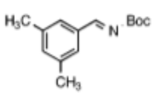
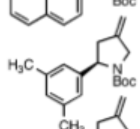
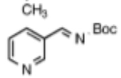
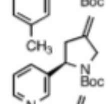
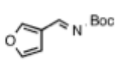
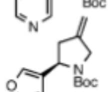
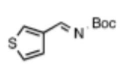
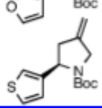
Pd-Catalyzed Asymmetric [3+2] Trimethylenemethane Cycloaddition

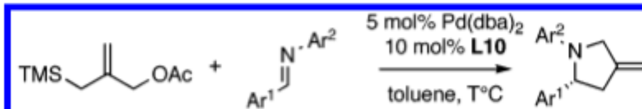


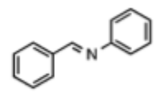
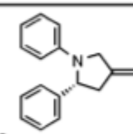
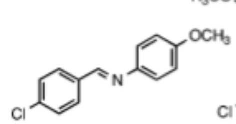
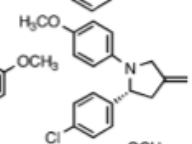
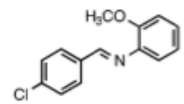
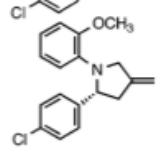
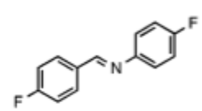
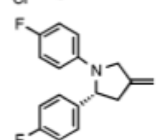
JACS, **1979**, *101*, 6429; JACS, **1979**, *101*, 6433;

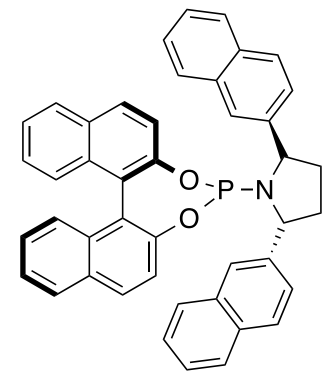
Pd-Catalyzed Asymmetric [3+2] Cycloaddition of Trimethylenemethane With Imines



Entry	Substrate	Product	T(°C)	Yield (%)[a]	ee(%)
1			4	84	91
2			4	80	92
3			-15	73	90
4			4	94	93
5			4	91	90
6			4	96	91
7			-15	94	86
8[b]			4	86	85
9			-15	65	90
10			4	75	86
11			4	71	91
12			-15	60	90

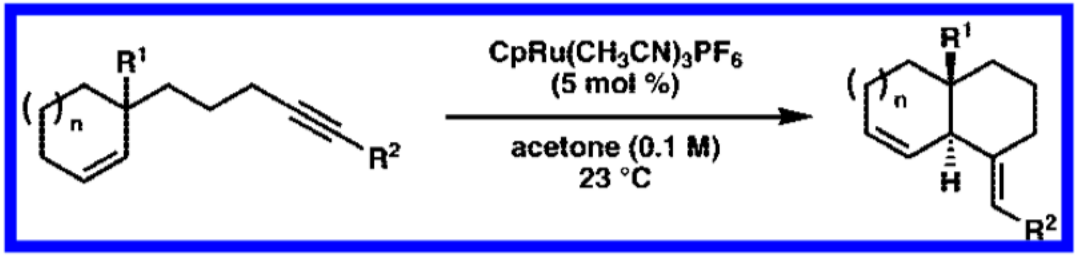


Entry	Substrate	Product	T(°C)	Yield (%)[a]	ee(%)
1[b]			45	80	82
2			45	80	84
3			45	87	83
4			4	83	83



JACS, **1973**, *95*, 292

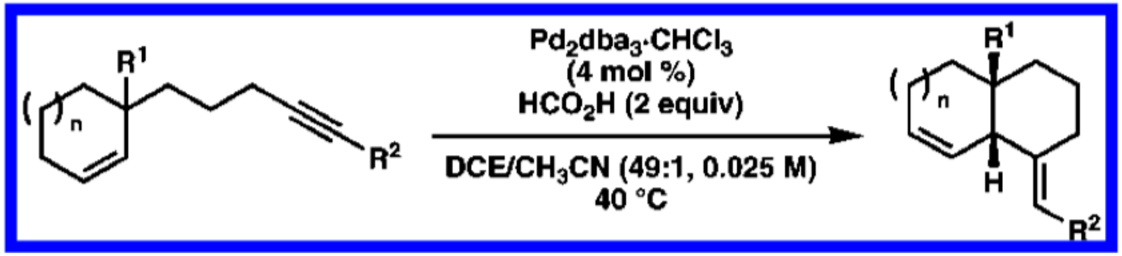
Ru- and Pd-Catalyzed Enyne Cycloisomerizations



entry	R^1	R^2	*n*	yield, time (%, h)[a]	dr[b]
1	CO_2Me	CO_2Me	1	90, 3	>19:1
				82, 3[c]	>19:1
2	CHO	CO_2Me	1	88, 2	>19:1
3	CON(OMe)Me	CO_2Me	1	79, 3	>19:1
4	CO_2H	CO_2Me	1	95, 3	>19:1
5	CH_2OH	CO_2Me	1	86, 6[d]	>19:1
6	CO_2Me	CO_2Me	2	99, 3	>19:1
7	CHO	CO_2Me	2	87, 5[e]	>19:1
8	CON(OMe)Me	CO_2Me	2	99, 4	>19:1
9	CO_2Me	CO*i*-Pr	1	70, 6[e]	>19:1
10	CO_2Me	$CONEt_2$	1	70, 3[d,f]	>19:1

JACS, **2008**, *130*, 16176

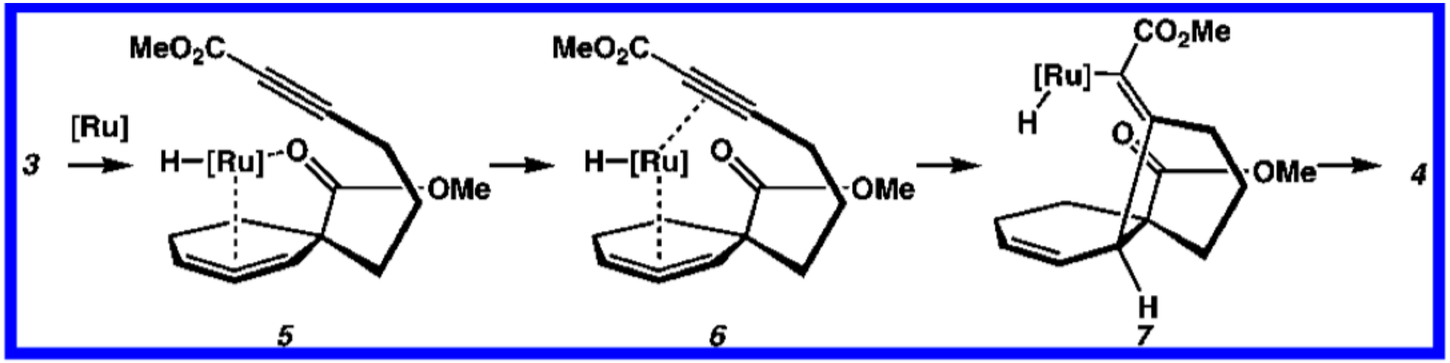
Ru- and Pd-Catalyzed Enyne Cycloisomerizations

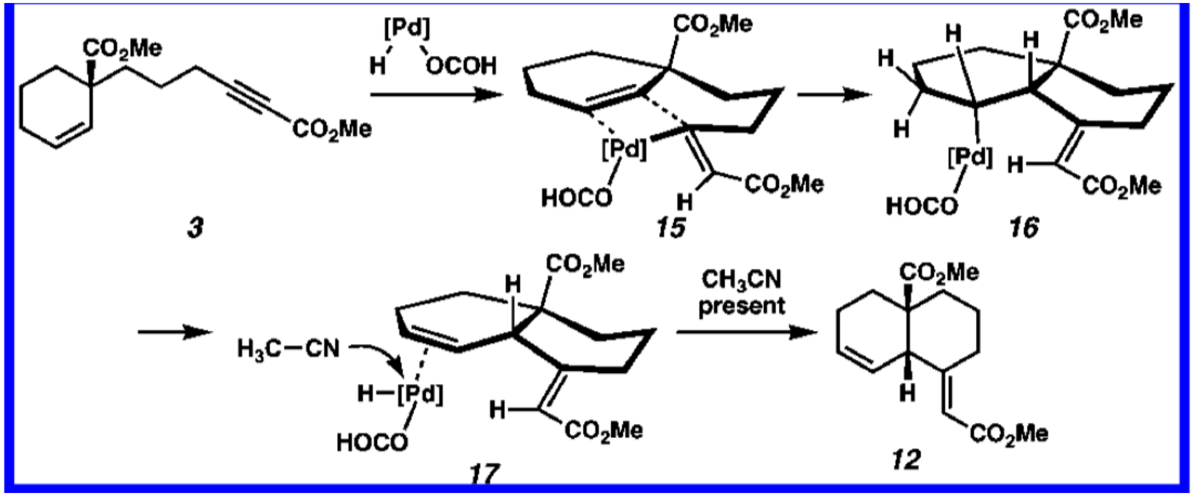


entry	R^1	R^2	*n*	yield, time (%, h)[a]	dr[b]
1	CO_2Me	CO_2Me	1	92, 4	>19:1
2	CHO	CO_2Me	1	73, 5	>19:1
3	CON(OMe)Me	CO_2Me	1	68, 15	>19:1
4	CO_2H	CO_2Me	1	NR	--
5	CH_2OH	CO_2Me	1	83, 2.5	>19:1
6	CO_2Me	CO_2Me	2	95, 3	>19:1
7	CHO	CO_2Me	2	92, 4	>19:1
8	CON(OMe)Me	CO_2Me	2	95, 2.5	>19:1
9	CO_2Me	CO*i*-Pr	1	67, 12	>19:1
10	CO_2Me	$CONEt_2$	1	NR	--

JACS, **2008**, *130*, 16176

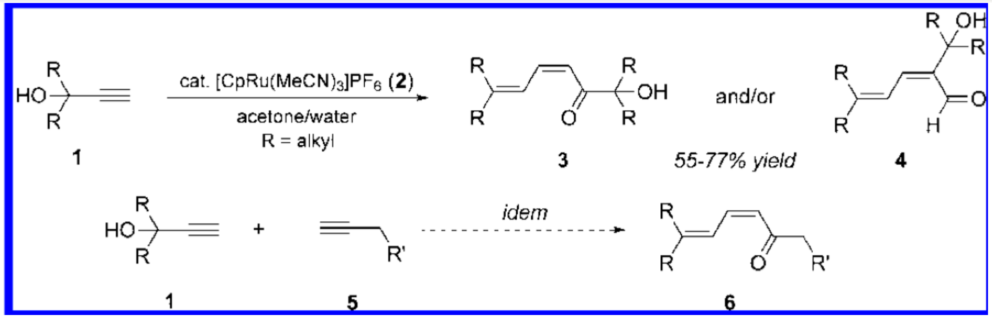
Ru- and Pd-Catalyzed Enyne Cycloisomerizations

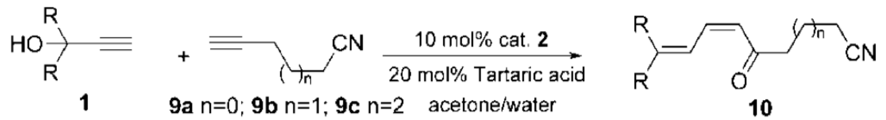


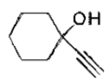
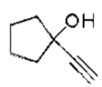
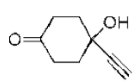
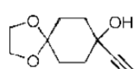


JACS, **2008**, *130*, 16176

Ru-Catalyzed Cross-Coupling of Tertiary Propargyl Alcohols With ω-Alkynenitriles

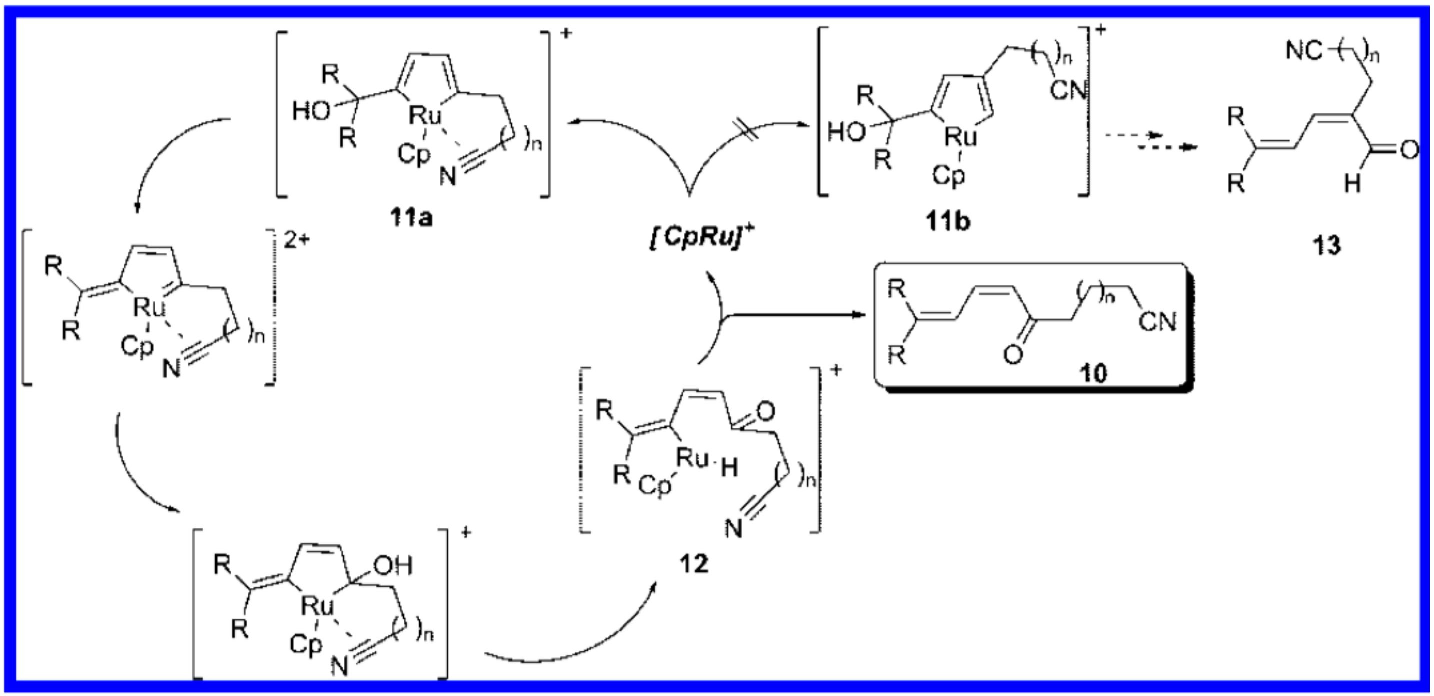




Entry	R	Nitrile	Product	Yield[a,b]
1	Me (1a)	9a	10a	65%
2		9b	10b	69%
3		9c	10c	75%
4	 (1b)	9b	10d	70%
5		9c	10e	68%
6	 (1c)	9a	10f	60%
7		9c	10g	52% (63)
8	 (1d)	9b	10h	68%
9	 (1e)	9a	10i	50% (62)
10		9c	10j	63%

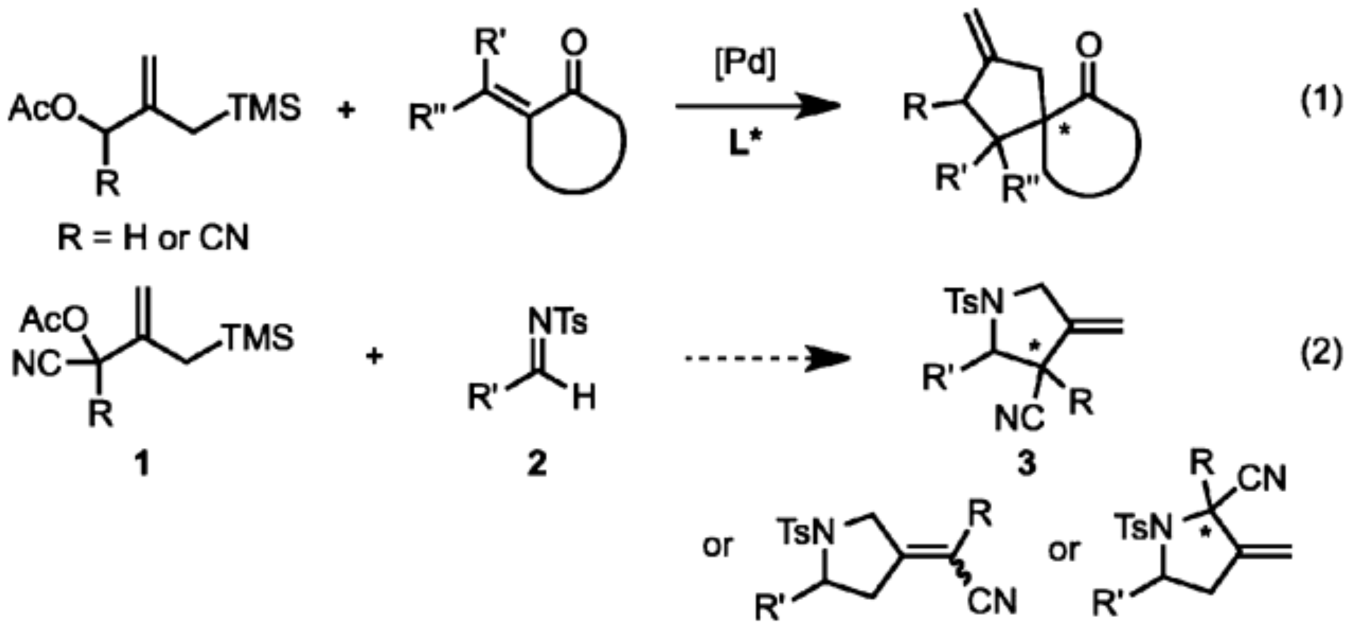
JACS, **2009**, *131*, 420

Ru-Catalyzed Cross-Coupling of Tertiary Propargyl Alcohols With ω-Alkynenitriles



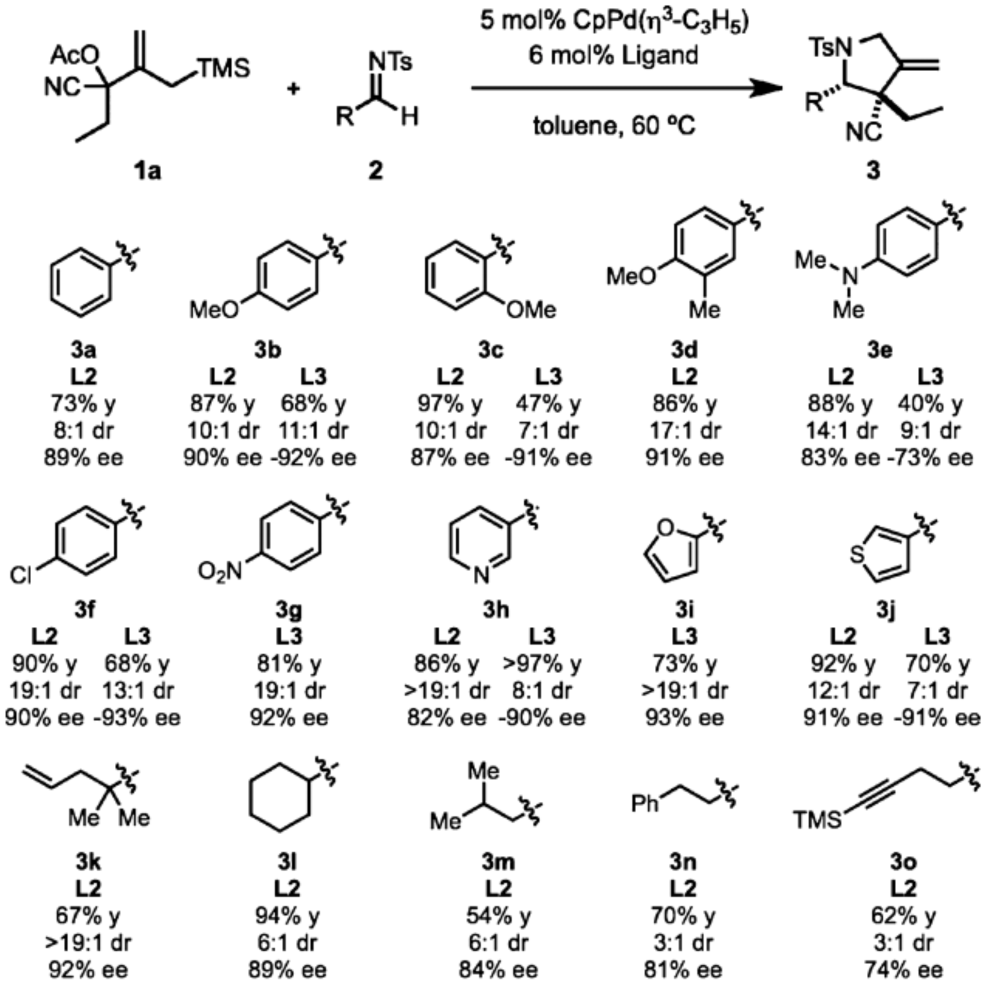
JACS, **2009**, *131*, 420

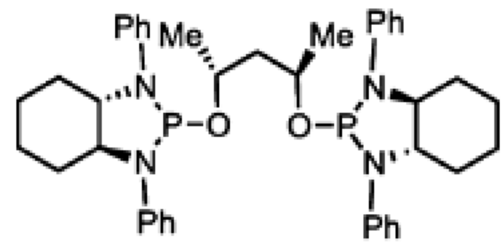
Allylic Alkylation



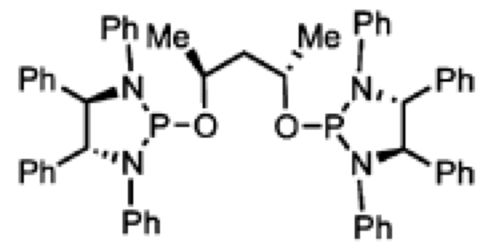
JACS, **2006**, *128*, 13328; JACS, **2013**, *135*, 2459

Pd-Catalyzed Asymmetric [3+2] Cycloaddition of Trimethylenemethanes





(*S*,*S*,*R*,*R*,*S*,*S*)-**L2**



(*R*,*R*,*S*,*S*,*R*,*R*)-**L3**

JACS, **2013**, *135*, 2459

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SPARTANS WILL.

THE END

THANK YOU