Baran Group Meeting
3/27-2010

Organoaluminium in Synthesis

Mikkel Jessing

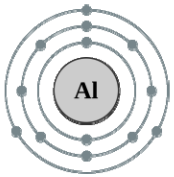
IUPAC:
Aluminium (or Aluminum)

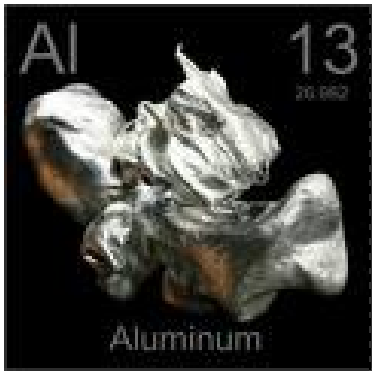
Atom number: 13

Oxidation states: (+I, +II) +III

Al-O bond ~138 kcal/mol

Reduction potential: -1.66 V



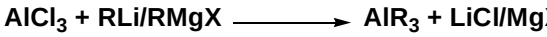


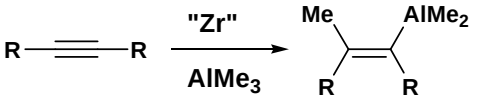
First isolated in impure form by Ørsted in 1825

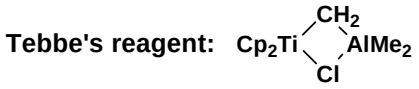
Aluminium is the most abundant (8.3% by weight) metallic element, in the Earth's crust, and the third most abundant of all elements (after oxygen and silicon). It is produced in over 30 mill. tons a year and is easy to recycle. Feldspars, the most common group of minerals in the Earth's crust, are aluminosilicates. It occurs in the minerals beryl, cryolite, garnet, spinel and turquoise. Impurities in Al_2O_3, such as chromium or cobalt yield the gemstones ruby and sapphire, respectively. Pure Al_2O_3, known as corundum, is one of the hardest materials known.

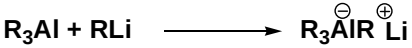
The Washington Monument was completed, with the 100 ounce (2.8 kg) aluminium capstone being put in place on December 6, 1884, in an elaborate dedication ceremony. It was the largest single piece of aluminium cast at the time, when aluminium was as expensive as silver. Aluminium has been produced in commercial quantities for just over 100 years.

Organoaluminums posses a rather low intrinsic nucleophilicity, conversion to (filled-octet) aluminates markedly increases the carbanion character

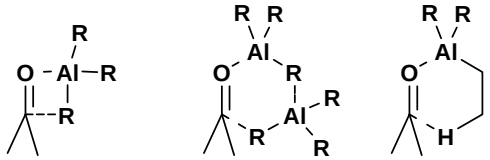








Four-membered/Six-membered/β-hydride transfer



Stoichiometry

Solvent dependable

Different reactivity for different alkyl-/arylgroups

airstable $AlMe_3$ reagent

Reviews:
Zweifel and Miller; Org. React. 1984, 375
Maruoka and Yamamoto; Tetrahedron, 1988, 5001
Negishi and Kondakov; Chem. Soc. Rev. 1996, 417
Negishi: Bull. Chem. Soc. Jpn., 2007, 233
von Zezschwitz; Synthesis, 2008, 1809

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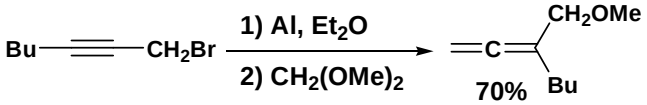
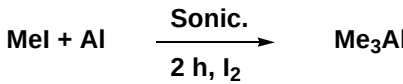
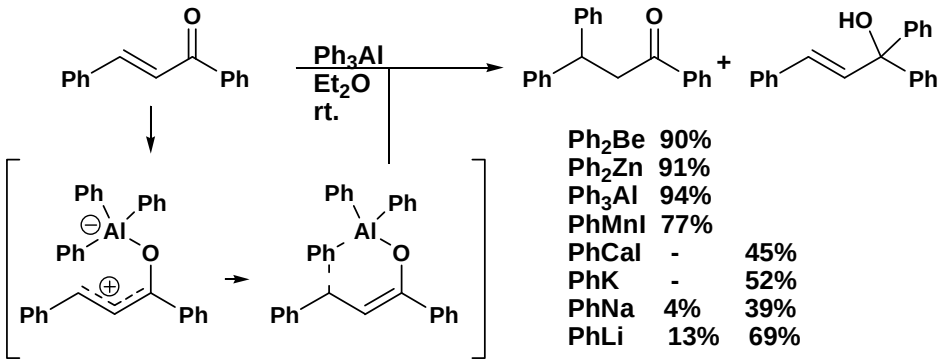


J. Organometal. Chem., 1986, 83

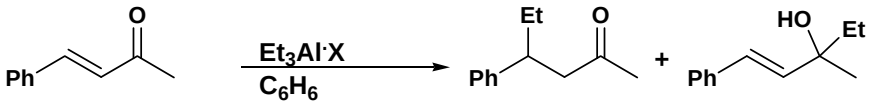


J. Organometal. Chem., 1986, 273



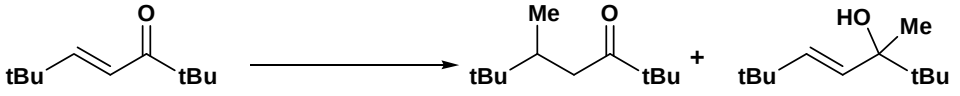
Ph_2Be	90%	
Ph_2Zn	91%	
Ph_3Al	94%	
PhMnI	77%	
PhCaI	-	45%
PhK	-	52%
PhNa	4%	39%
PhLi	13%	69%

JACS, 1941, 875



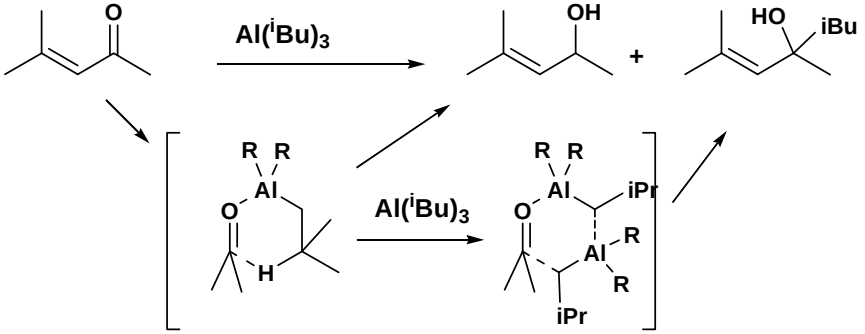
X: -	8%	69%
OEt_2	16%	48%
OPr_2	24%	61%
$OAmyl_2$	27%	53%

Bull. Chem. Soc. Jpn., 1968, 928



$AlMe_3$	C_6H_6	0:100	97%
Me_2AlCl	C_6H_6	7:93	70%
Me_2AlBr	C_6H_6	20:80	57%
Me_2AlI	C_6H_6	99:1	47%
$AlMe_3$	THF	0:100	75%
Me_2AlI	THF	98:2	42%

JOC, 1979, 4792



eq.	solvent			
0.5	pentane	86%	15%	(based on 53% conversion)
1.0	pentane	64%	36%	
2.0	pentane	24%	76%	
1.0	Et_2O	96%	-	

JOC, 1982, 4640

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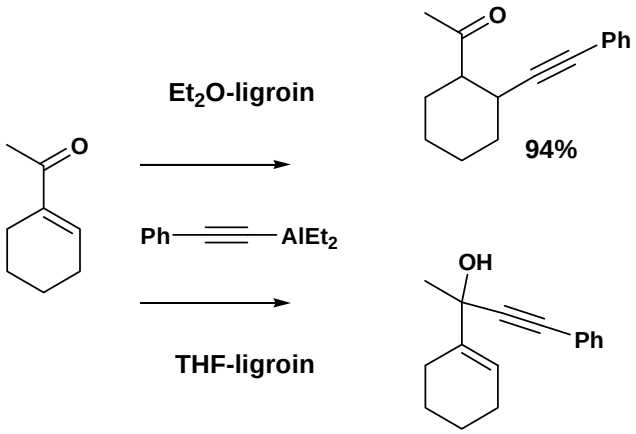
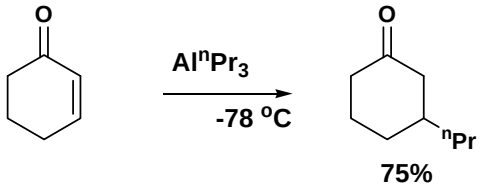
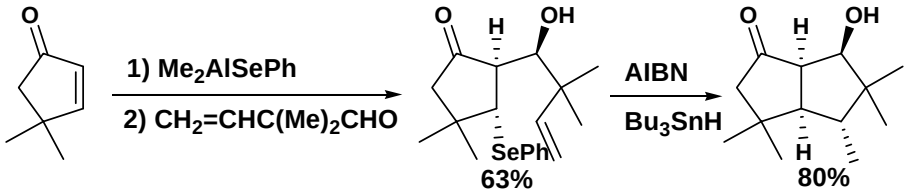


JACS, 1971, 7320

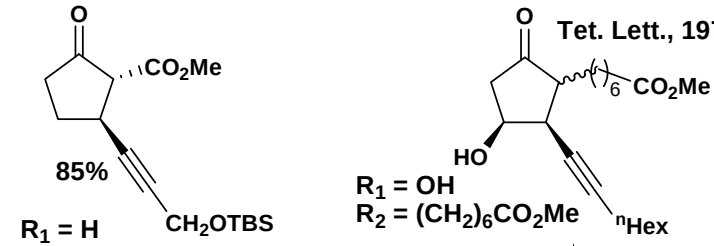


solvent independant
free radical mechanism

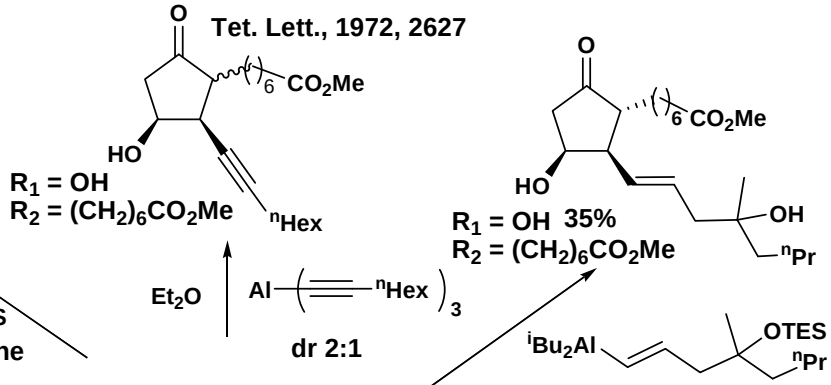
JACS, 1973, 4428



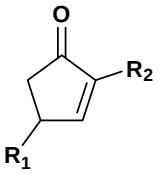
Tet. Lett., 1985, 6431

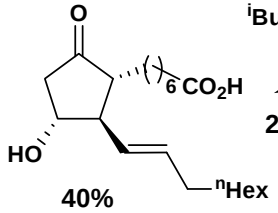


Tet. Lett., 1986, 2885

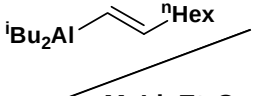


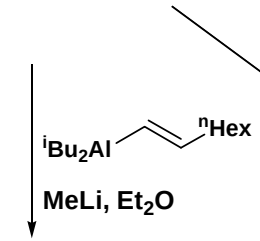
Tet. Lett., 1975, 4217



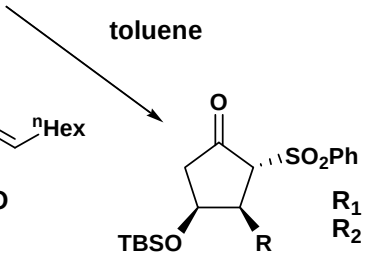


JOC, 1979, 1438





Tet. Lett., 1972, 4083



$AlMe_3$	cis	86%
$AlEt_3$	cis	65%
$AliBu_3$	cis	32%
$Et_2AlCCTMS$	31 cis:51 trans	100%

Synlett, 1999, 1313

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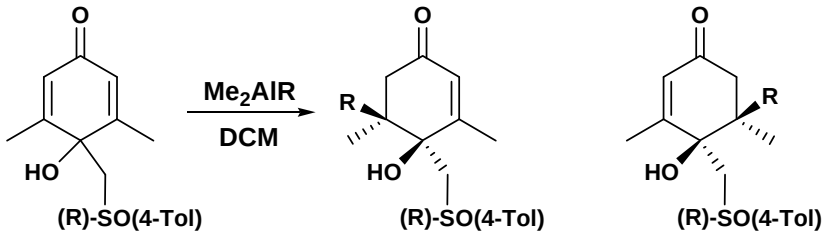
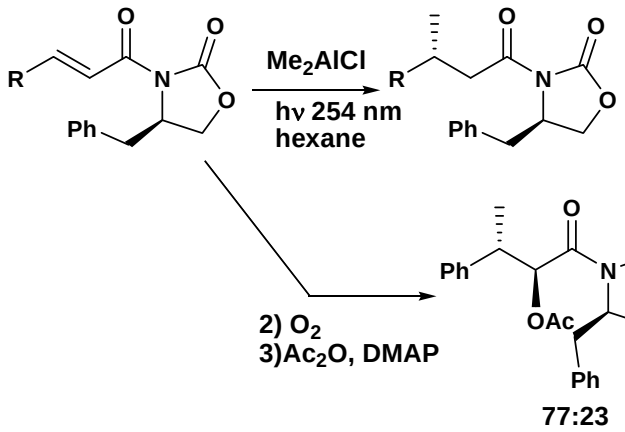


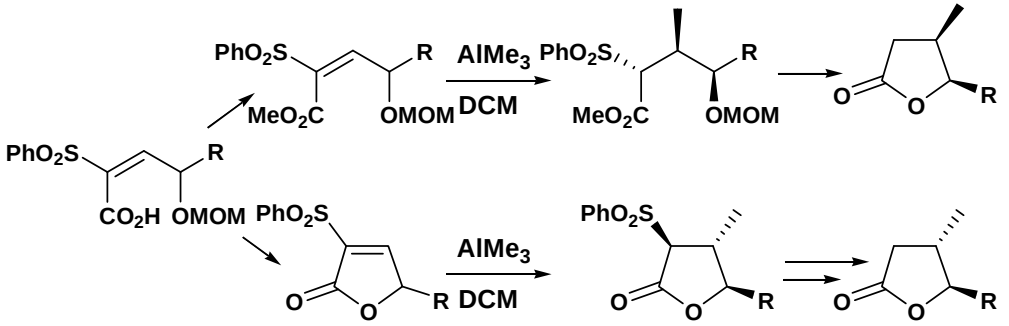
R = Me	>95:5	71%
^{n}Bu	>95:5	56%
^{n}Bu	>95:5	53%

JOC, 1996, 6758

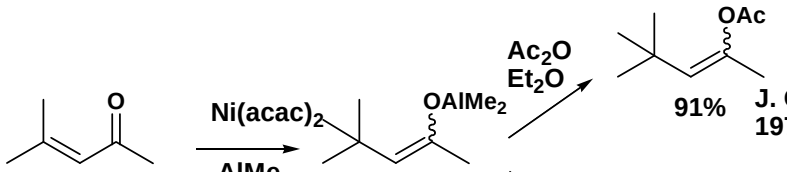


^{n}Pr	19:81	61%
Ph	88:12	63%
Ph	92:8	56%
4-ClPh	90:10	46%

ACIEE, 1991, 694

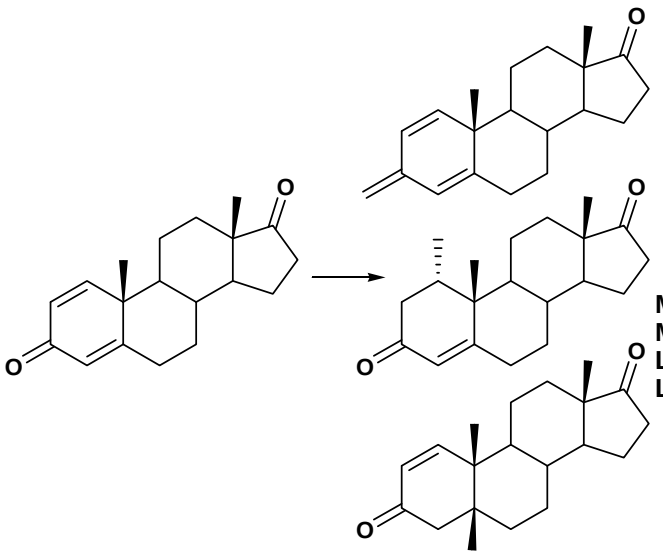


Tet. Lett. 1992, 7407



J. Organomet. Chem., 1974, 365

J. Organomet. Chem., 1974, 373



MeLi	cat. Cu	
MeMgX	cat. Cu	
Me_3Al	cat. Cu	70% 100:0
Me_3Al	cat. Ni	92% 64:36
$LiAlMe_4$	cat. Ni	90% 38:62
$LiAlMe_3OAr$	cat. Ni	90% 15:85

ACIEE, 1993, 1368

Chem. Ber., 1996, 963

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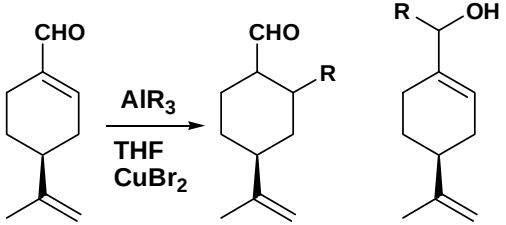
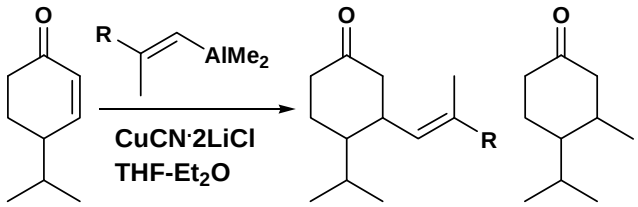
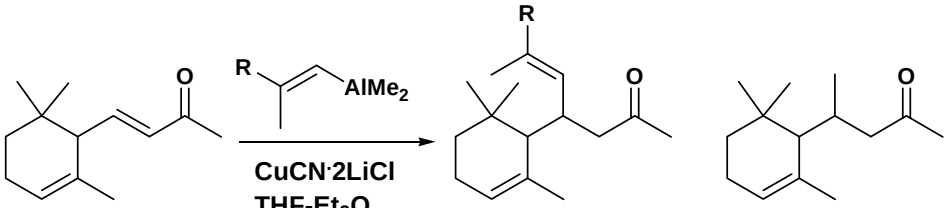


$AlMe_3$	95%	90:10
$AlMe_3$ (TMSCl)	89%	89:11
$AlEt_3$	74%	36:64
Al^iBu_3	69%	25:75

Tetrahedron, 1995, 743

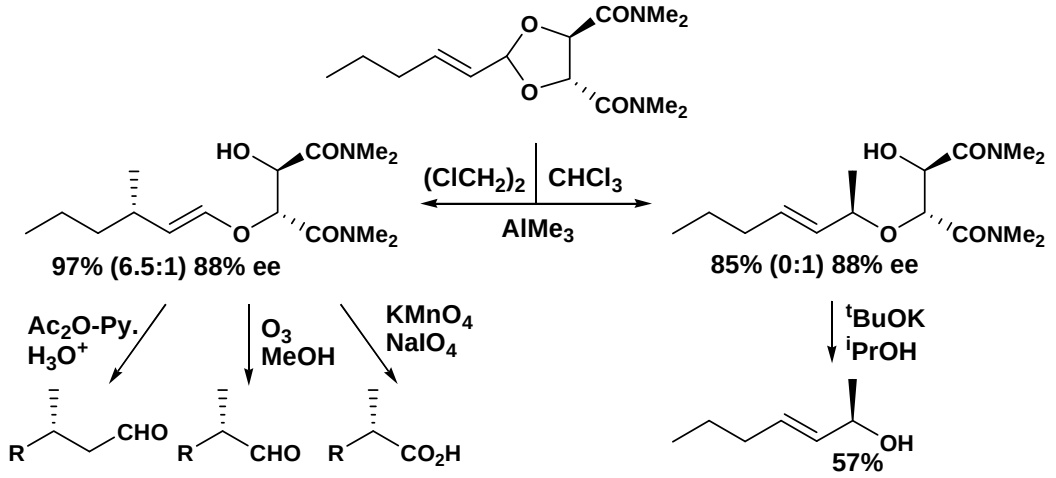


R = $(CH_2)_4OTIPS$	76%	10%
$(CH_2)_4OTBS$	7%	87%



R = $(CH_2)_4OH$	79%	
$(CH_2)_4OTBDPS$	-	

JOC, 1991, 5761

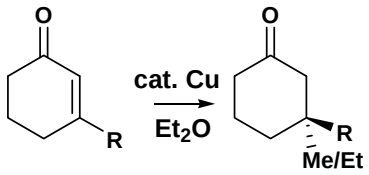


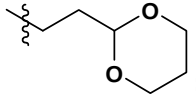
97% (6.5:1) 88% ee

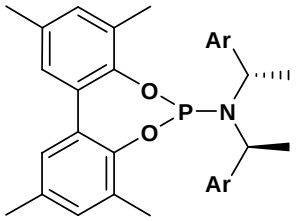
85% (0:1) 88% ee

57%

JACS, 1984, 5004
Synthesis, 1986, 130



Me:	$AlEt_3$	(>95%)	97% ee
Et:	$AlEt_3$	(84%)	96% ee
$(CH_2)_2CH=CH_2$:	$AlMe_3$	80%	95% ee
	$AlMe_3$	81%	95% ee
^iBu:	$AlMe_3$	85%	98% ee
Ph:	$AlMe_3$	(70%)	72% ee



ACIEE, 2005, 1376

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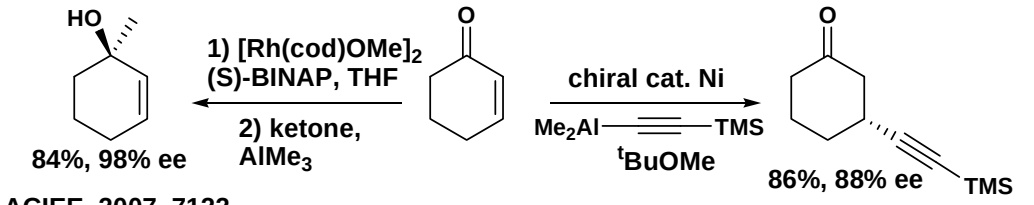
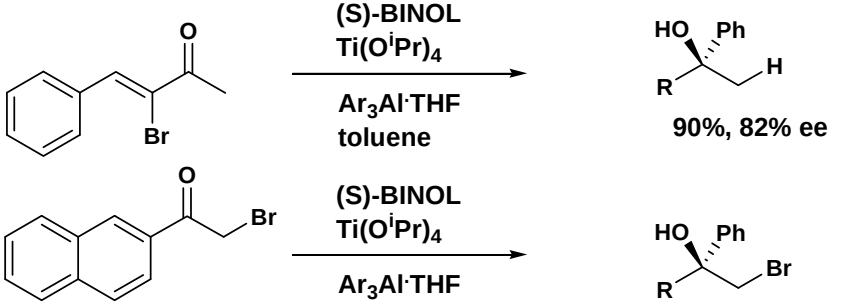


84%, 98% ee

ACIEE, 2007, 7122

86%, 88% ee

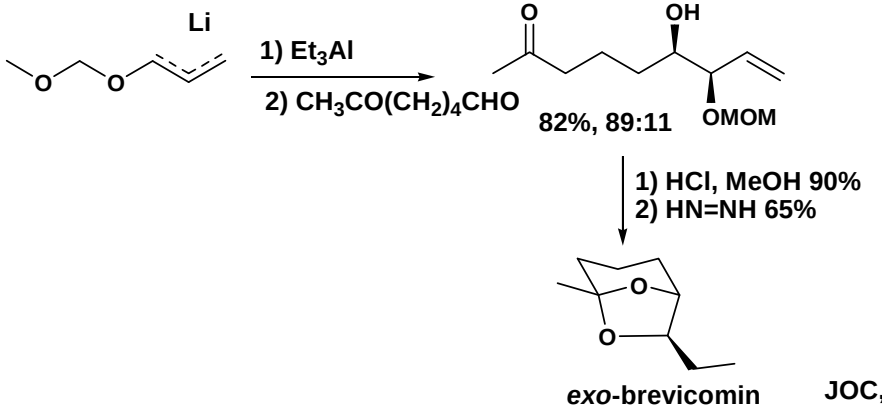
Org. Lett., 2004, 3385



90%, 82% ee

91%, 87% ee

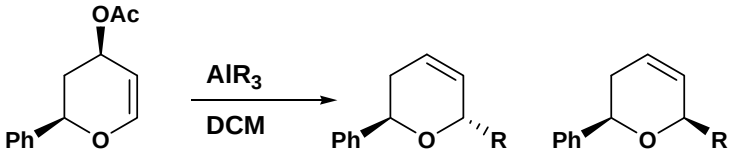
JACS, 2006, 14808



82%, 89:11

exo-brevicomin

JOC, 1984, 1096

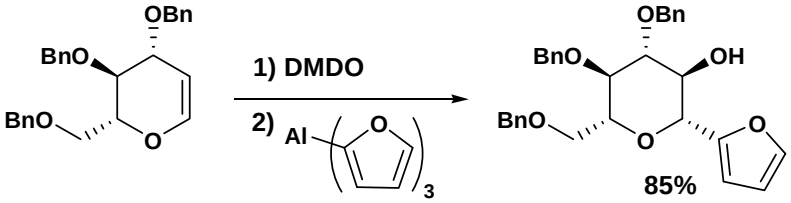


Me_3 96%, 96:4

$^{i}Bu_3$ 74%, 94:6

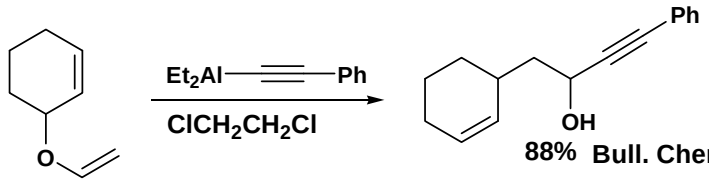
Et_2Al—≡—Bu 85%, 100:0

Chem. Lett., 1987, 2215

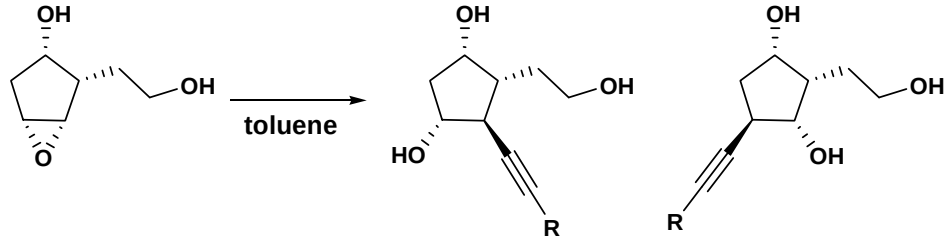


85%

Org. Lett. 2000, 2707



88% Bull. Chem. Soc. Jpn., 1986, 446



Me_2Al—≡—$CH(O^tBu)(CH_2)_4CH_3$ 3.3:1

$LiMe_2Al$—(≡—$CH(O^tBu)(CH_2)_4CH_3)_2$ 1:5

JOC, 1985, 3923

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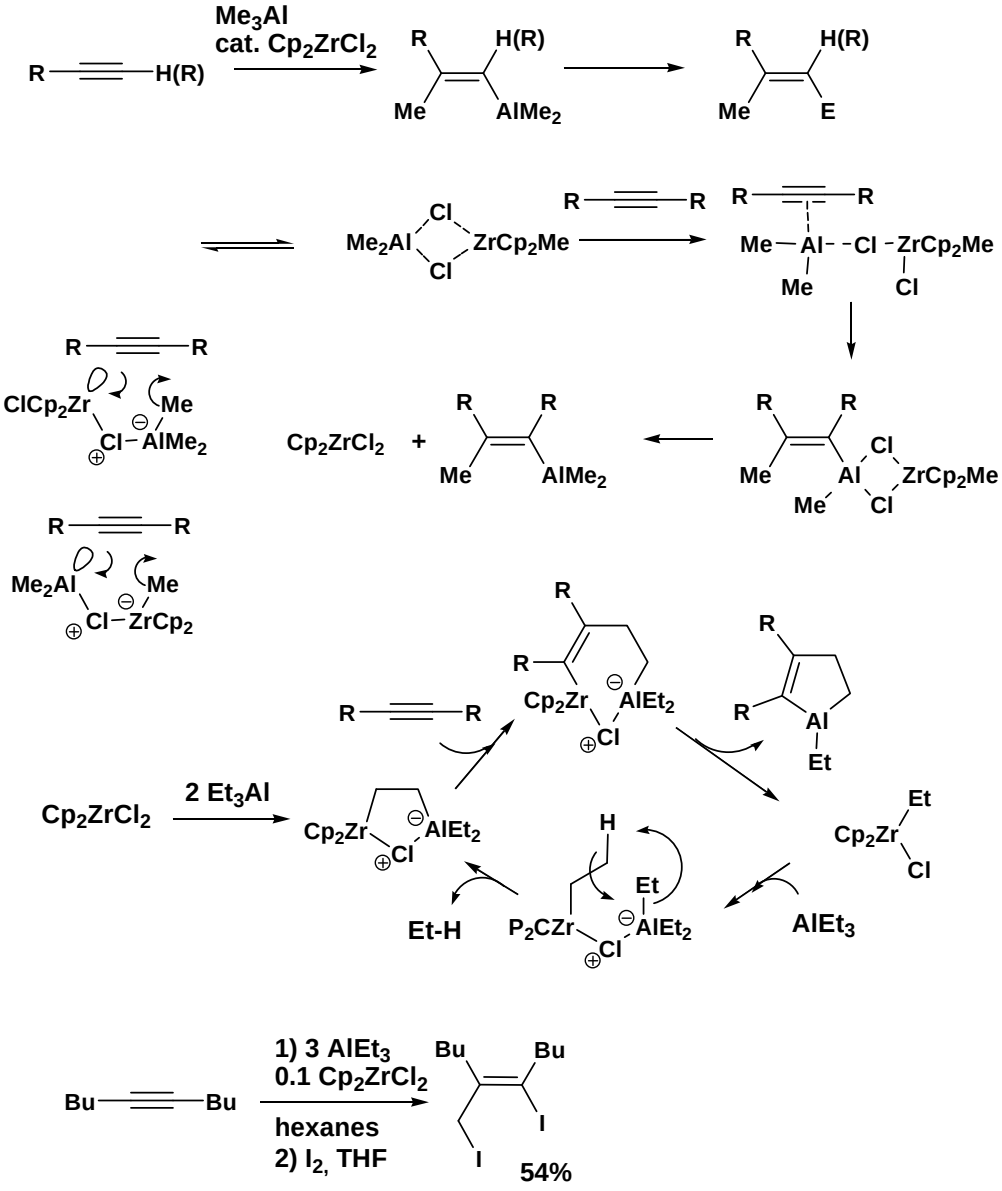
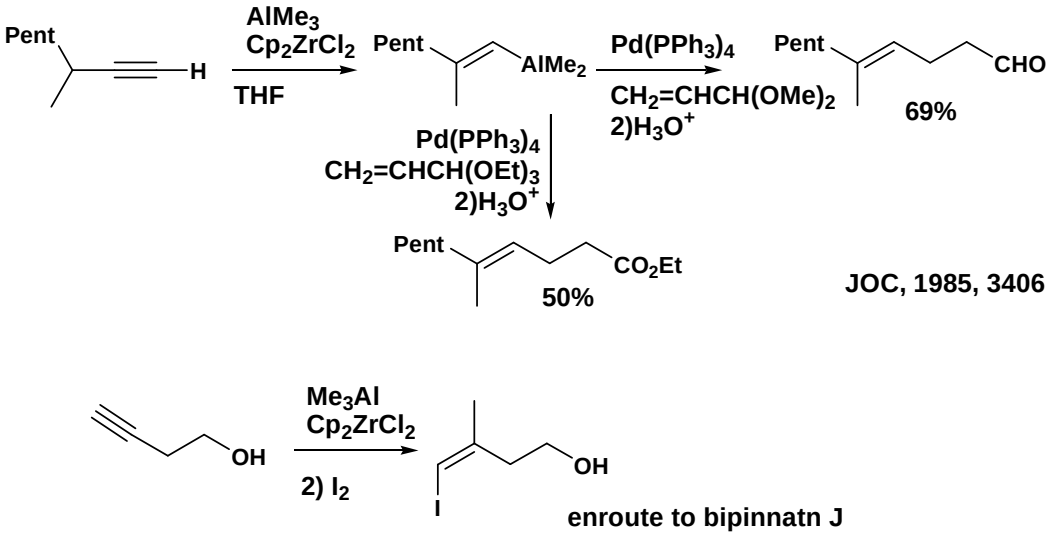


Chem. Soc. Rev., 1996, 417



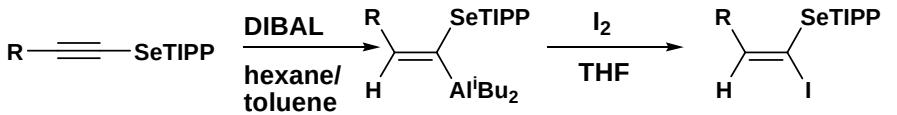
JOC, 1985, 3406

enroute to bipinnatn J

Org. Lett., 2006, 345

Explain double bond geometry:

JOC, 1997, 784

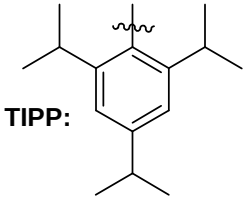


82%- 95%

enroute to tetrahydropyran subunit of polycavernoside

Tetrahedron, 2006, 2331

TIPP:



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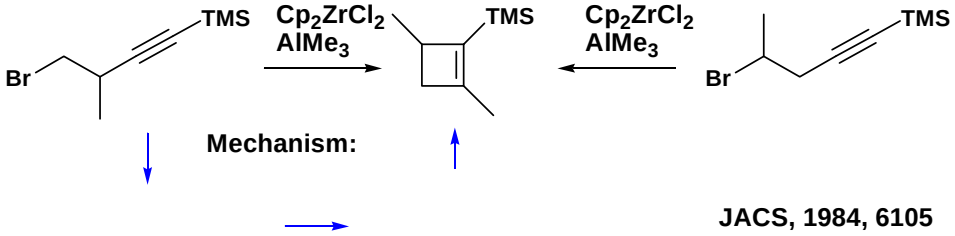
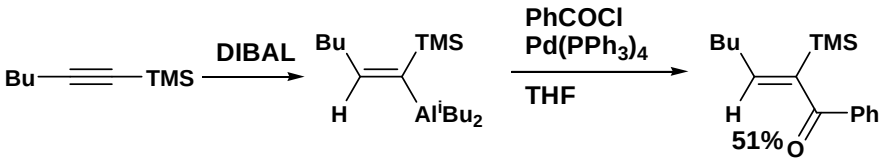
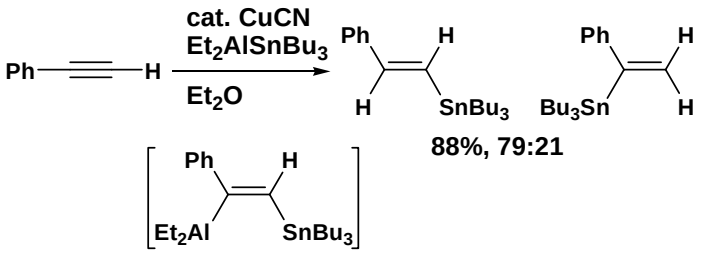


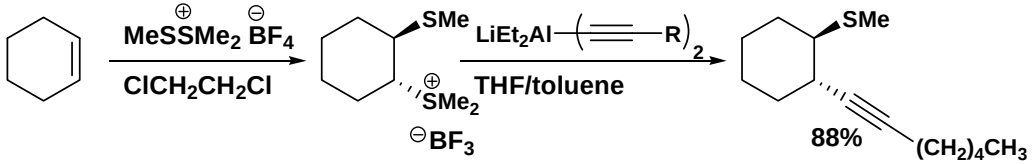
JACS, 1984, 6105



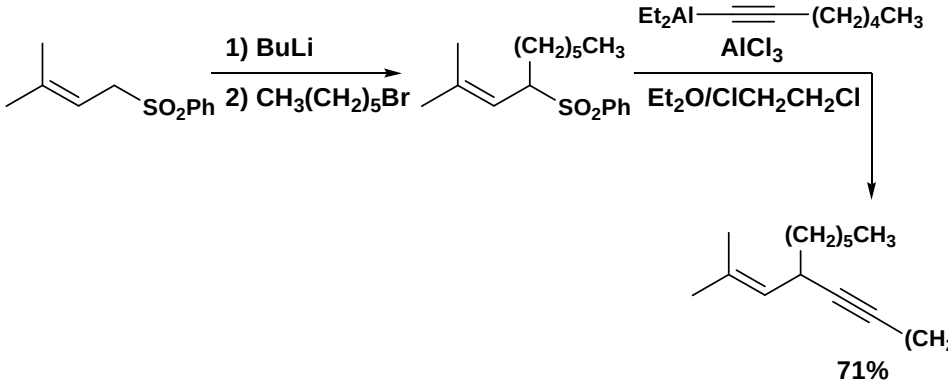
Bull. Chem. Soc. Jpn., 1985, 2425



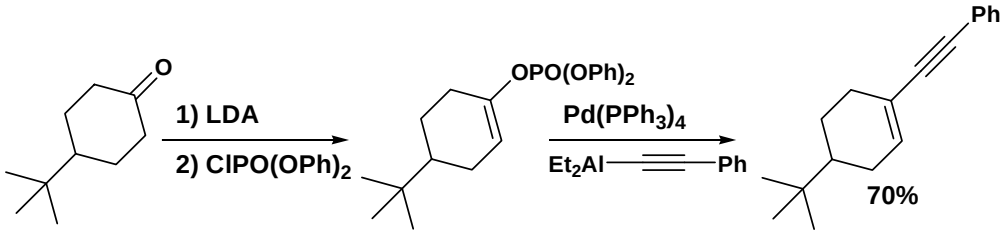
Tet. Lett., 1984, 2151



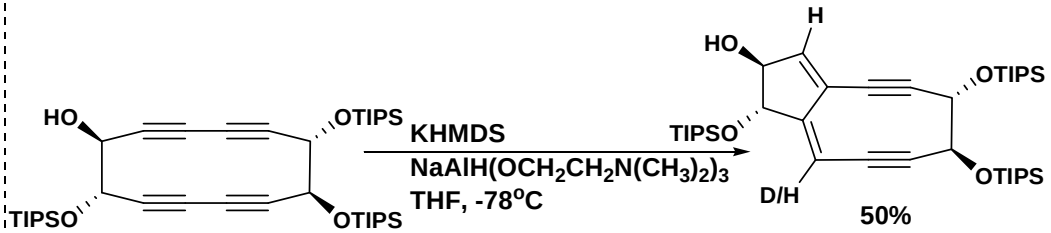
JACS, 1984, 4623



JACS, 1986, 1098



Bull. Chem. Soc. Jpn., 1984, 108



enroute to the Kedarcidin core

Tett. Lett., 1998, 9633

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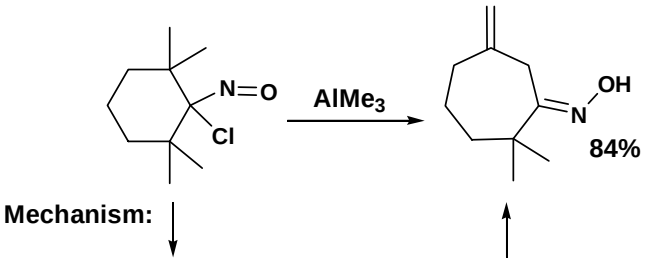
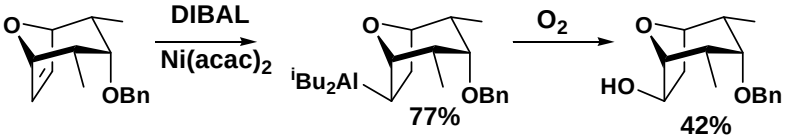
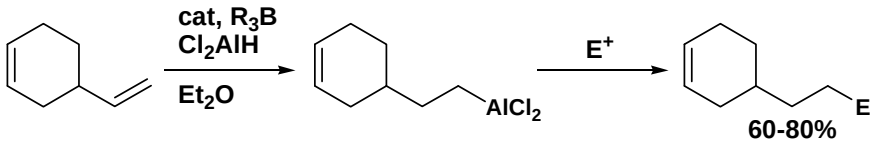


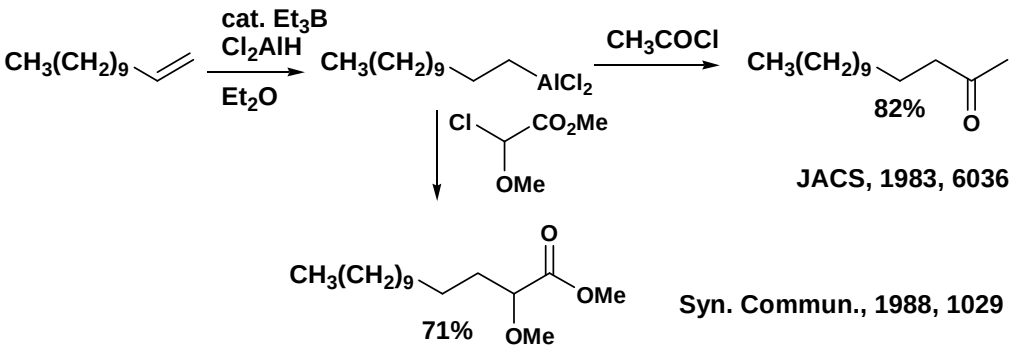
Tetrahedron, 1988, 5001



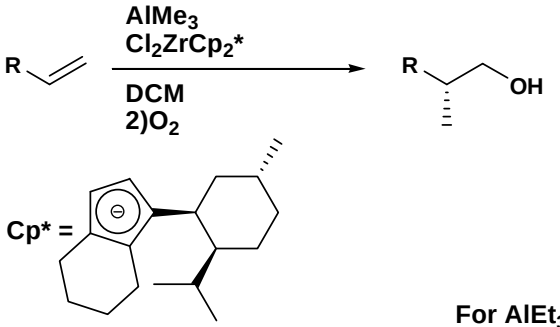
JACS, 1997, 6478



JACS, 1983, 6036



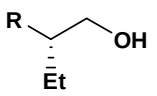
Syn. Commun., 1988, 1029



$CH_3(CH_2)_5$	88% 72% ee
^{i}Bu	92% 74%ee
c-Hex	80% 65% ee
Bn	77% 70% ee
$HO(CH_2)_4$	79% 75% ee
$Et_2N(CH_2)_3$	68% 71% ee

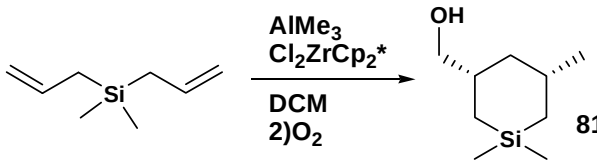
JACS, 1995, 10771

For $AlEt_3$:



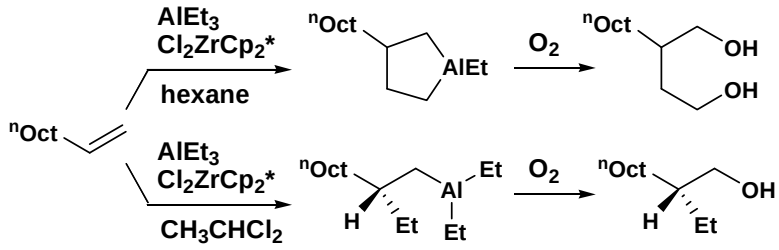
$CH_3(CH_2)_5$	64% 92% ee
^{i}Bu	77% 90%ee
Bn	69% 93% ee
$Et_2N(CH_2)_3$	56% 95% ee

JACS, 1996, 1577



81% 74% ee JACS, 1995, 10771

For $AlEt_3$: 66% 96% ee JACS, 1996, 1577



JACS, 1996, 1577

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3/27-2010

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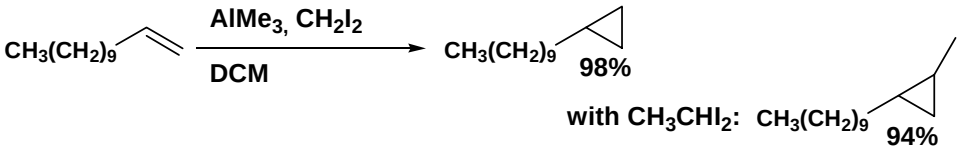
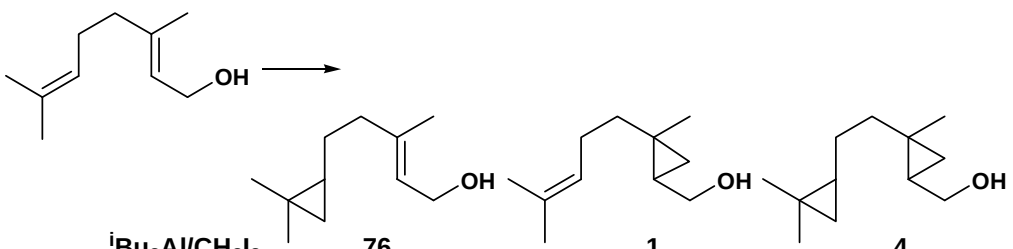
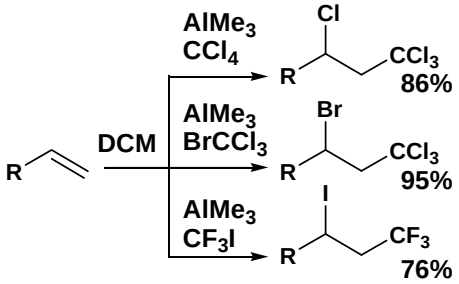


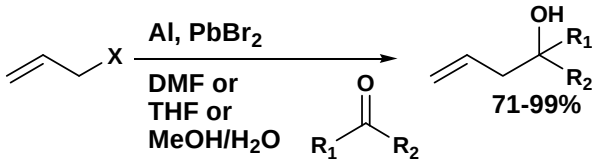
JOC, 1985, 4412



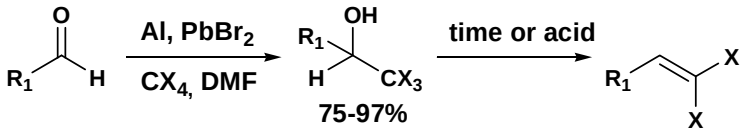
JOC, 1985, 4412

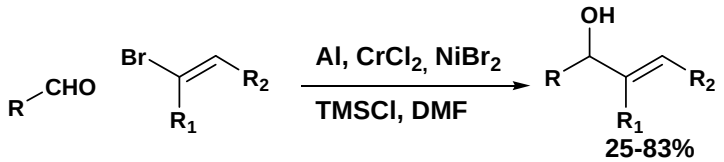


Chem. Lett., 1985, 1689

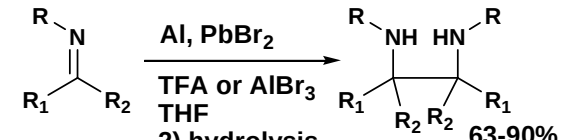


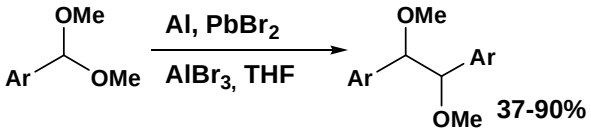
Other electrophiles:
CHO
CO_2Me (2 allyls)
CN (2 allyls)
$RN=R_1R_2$
$CH(OMe)_2$ (1 or 2)





NHK catalytic in Cr





Curr. Org. Chem., 2004, 1027

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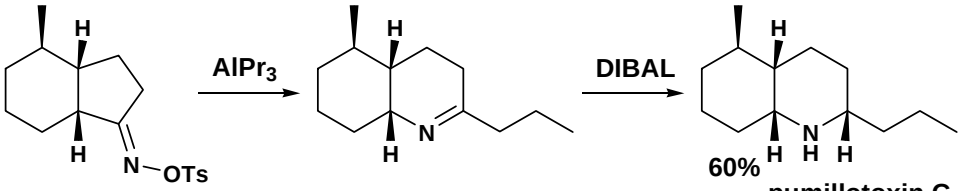
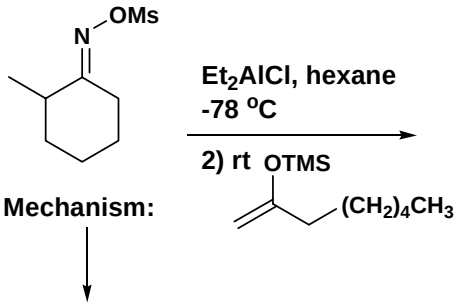
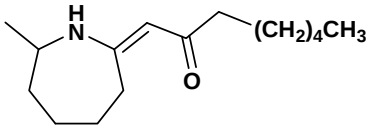


60%

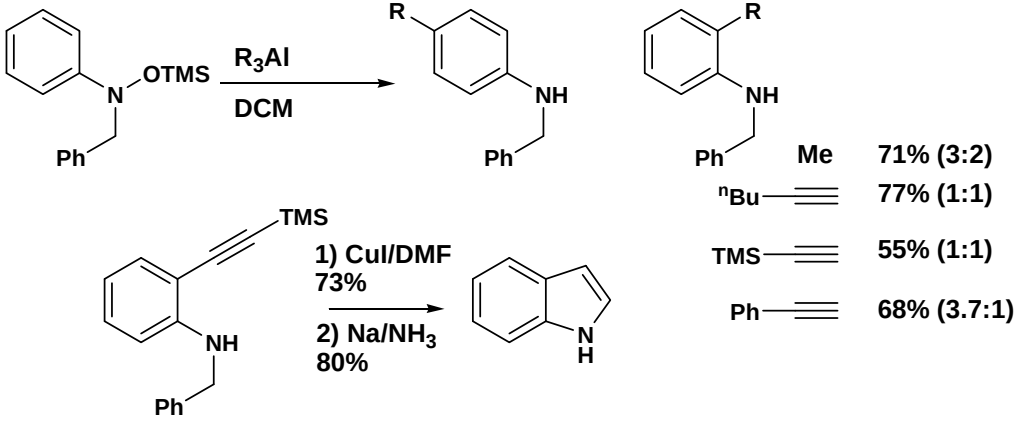
pumillotoxin C

JACS, 1983, 2831

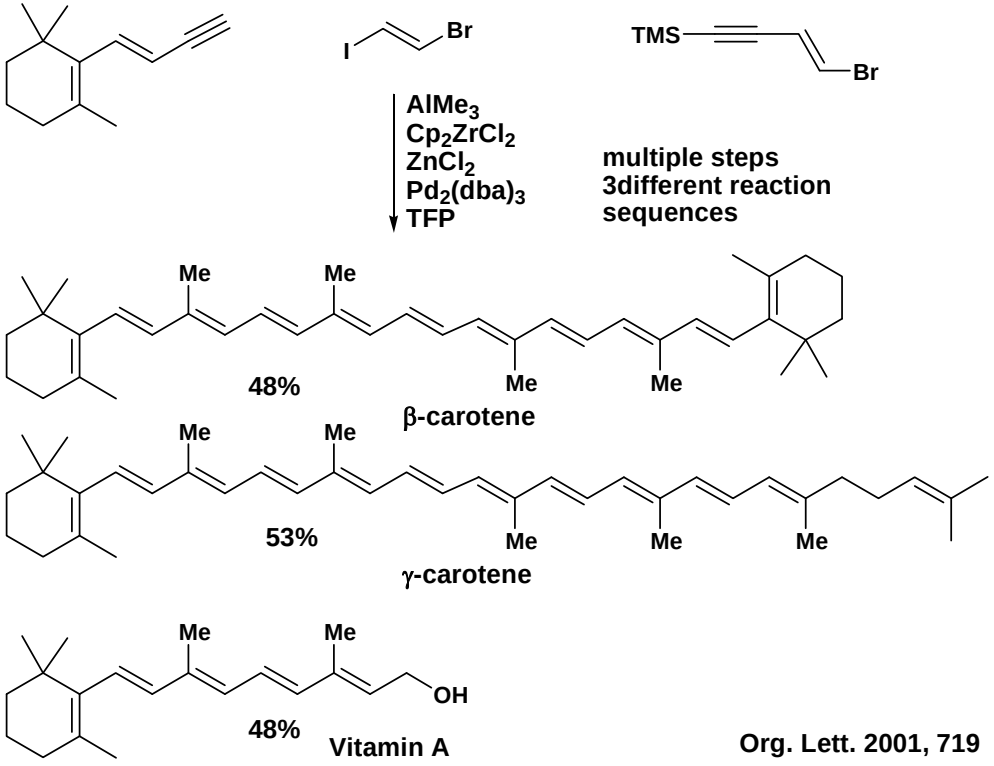




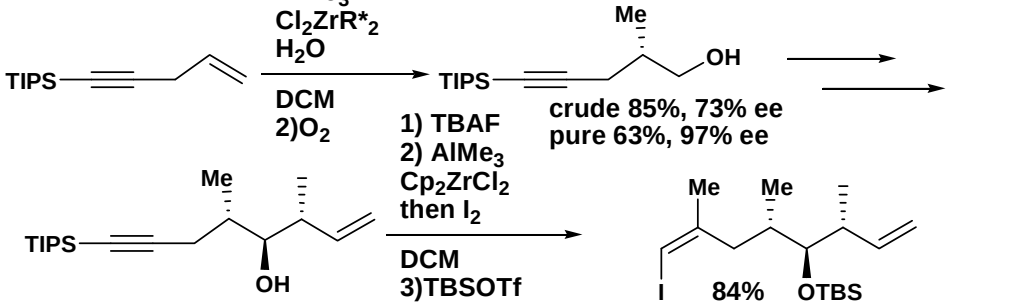
90%



Pure & Appl. Chem., 1983, 1853



Org. Lett. 2001, 719



Chem. Eur. J., 2008, 311