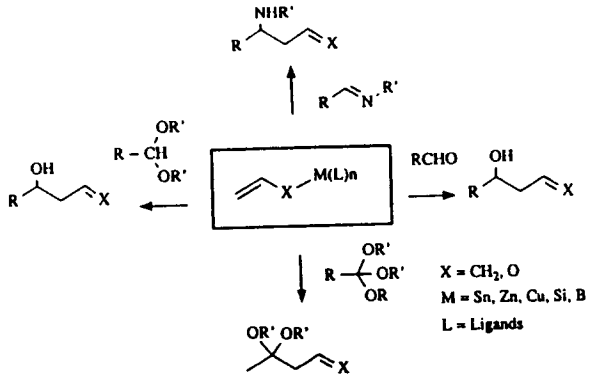


$$n\,C_8K + MX_n \longrightarrow M/\text{Graphite} + nKX$$

$MX_n = ZnCl_2 ; SnCl_2 ; FeCl_3 ; PdCl_2 ; TiCl_3$

M/Graphite = highly dispersed metal over the graphite grains

Advantages : large surface area, high activity,

all the facilities related to the use of reactives anchored on solid insoluble supports

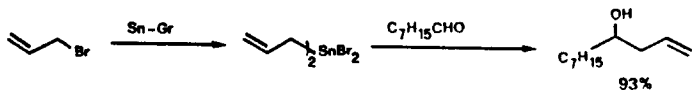
APPLICATIONS OF M/GRAPHITES

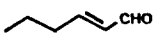
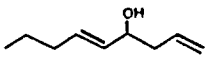
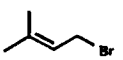
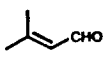
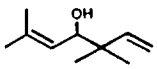
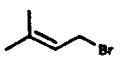
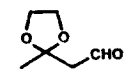
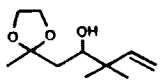
AS CATALYSTS FOR :

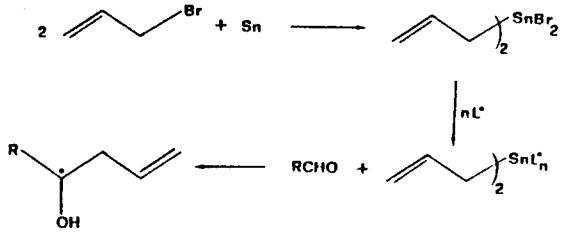
HYDROGENATION REACTIONS (Ni, Pd)
HECK REACTIONS (Pd)
ALLYLIC SUBSTITUTION REACTIONS (Pd)

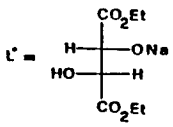
AS STOICHIOMETRIC REAGENTS FOR :

Mc MURRY REACTIONS (Ti)
DEBROMINATION REACTIONS (Fe)
REFORMASKII REACTIONS (Zn)
η^1- ALLYLIC COMPLEXES (Zn, Sn)



ALLYL BROMIDE	ALDEHYDE	PRODUCT	YIELD %
			86
			89
			84



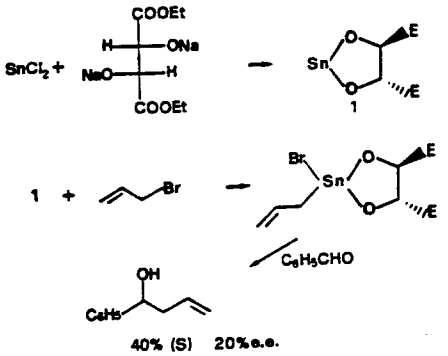


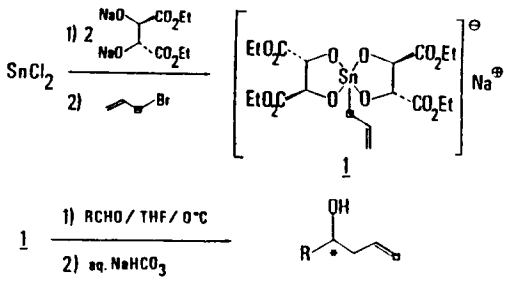
R = alkyl, aryl

HOMOALLYLIC ALCOHOLS FROM DIALLYLTIN DIBROMIDE

RCHO	Molar ratio	Yield %	e.e.	T °C
	A : B : C			
C_6H_5CHO	1 : 1 : 2	90	16	25
"	3 : 1 : 2	75	38	25
"	4 : 1 : 2	60	65	25
"	3 : 1 : 2	65	71	-55
$n\text{-}C_8H_{17}CHO$	3 : 1 : 2	70	46	-55
"	4 : 1 : 2	60	57	-55
$C_6H_5CH{=}CHCHO$	3 : 1 : 2	70	47	-55

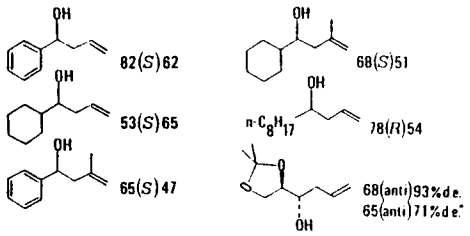
A = Diethyltartrate monosodium salt
B = Diallyltin dibromide
C = Aldehyde





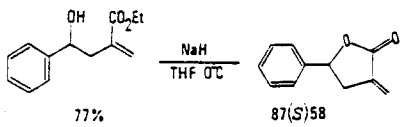
PRODUCTS yield%(config)e.e.%

from allyl and 2-methylallyl bromide

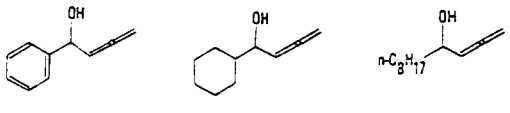


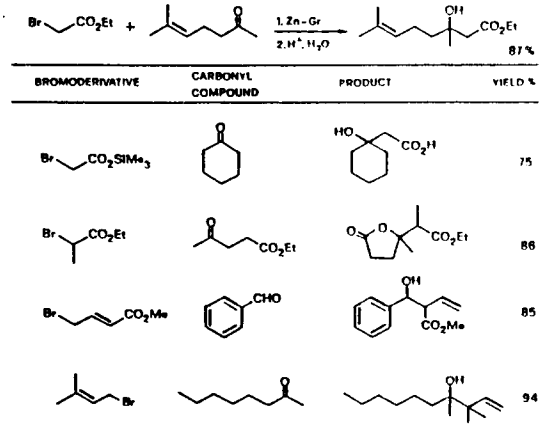
PRODUCTS yield%(config)e.e.%

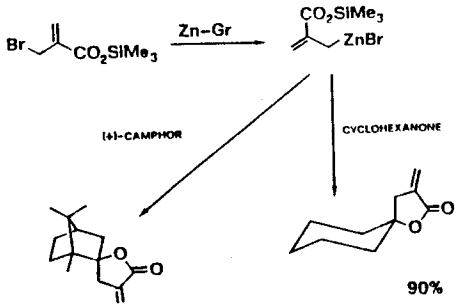
from 2-carbethoxy allyl bromide

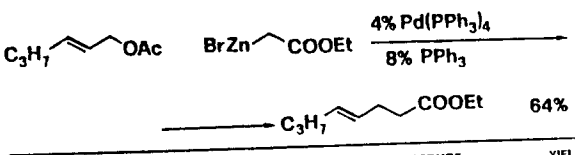


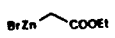
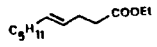
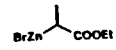
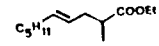
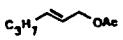
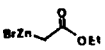
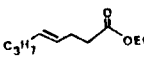
from propargyl bromide

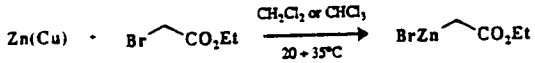


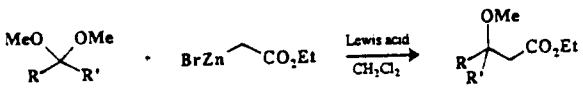




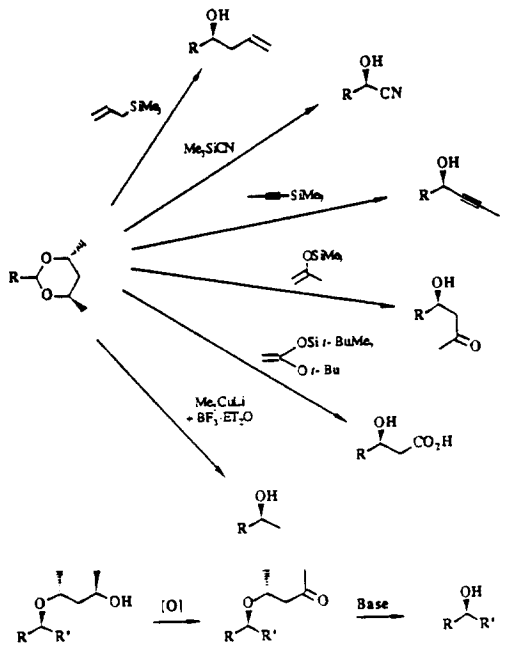


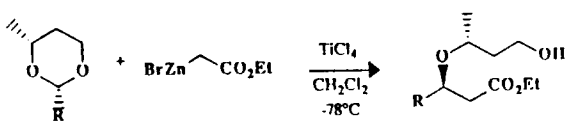
ALLYLIC ACETATE	ORGANOZINC DERIVATIVE	PRODUCT	YIELD %
			63
			65
			70



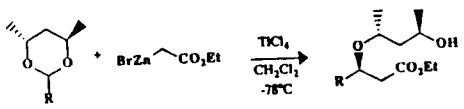


R	R'	Lewis acid	T (°C)	Yield
Ph	H	$TiCl_4$	-78	90
Ph	H	$BF_3{\cdot}Et_2O$	-60	87
n-C_7H_{15}	CH_3	$TiCl_4$	-78	80

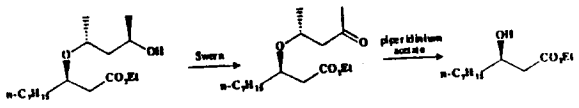




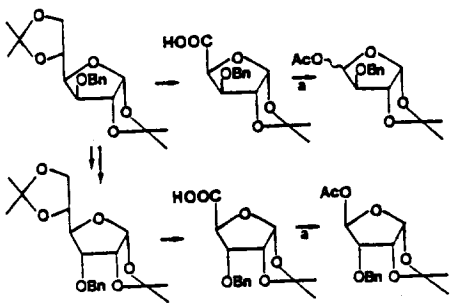
R	Yield %	d.e.
Ph	80	50
n-C_7H_{15}	70	62
Et	70	62
$(CH_3)_2CHCH_2$	80	60
$(C_2H_2)_2CH$	72	41



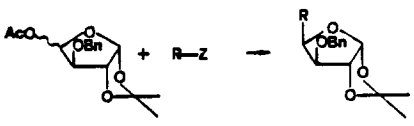
R	Yield %	d.e.
Ph	80	71
n-C_7H_{15}	70	84
Et	70	73



64% yield, 84% e.e.

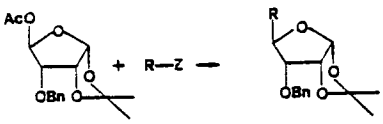


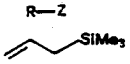
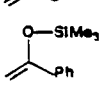
a= $Pb(OCOCH_3)_4$



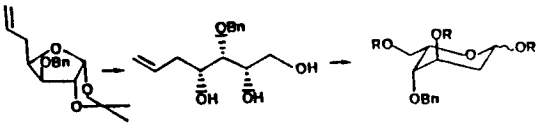
R—Z	Yield %	Ratio α/β
	90	15/85
	88	5/95
	85	20/80

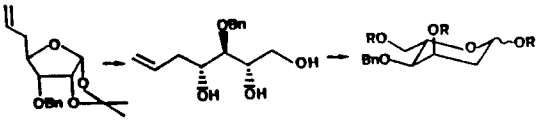
$MgBr_2$ as Lewis acid

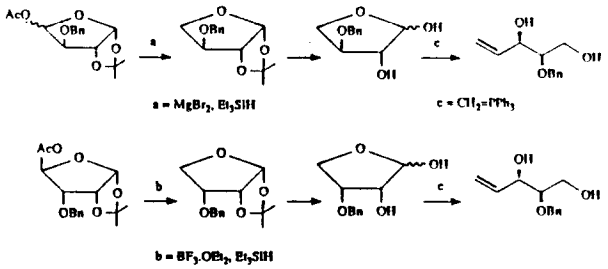


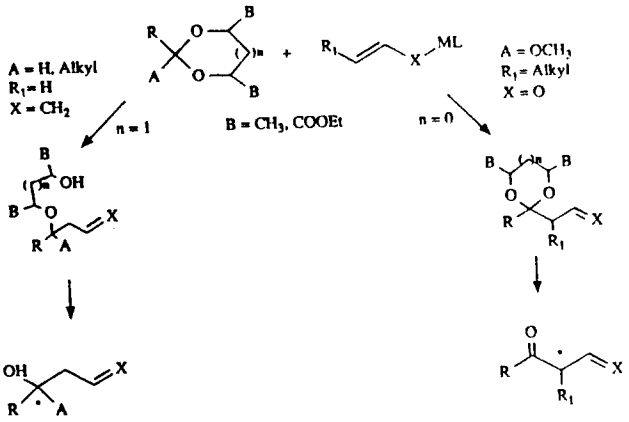
R—Z	Yield %	Ratio α/β
	90	2/98
	84	10/90

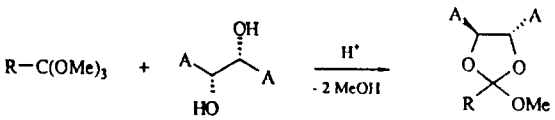
$BF_3 \cdot OEt_2$ as Lewis acid







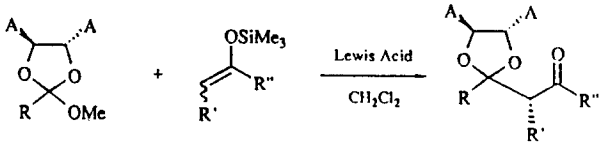


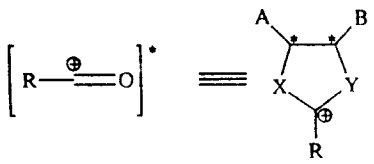


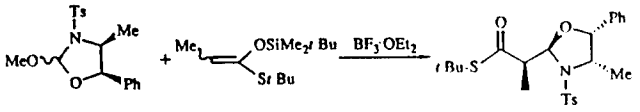
R = Me, Et, Ph

A = $-CO_2Me$, $-CO_2Et$, $-CO_2i$ Pr
-Ph, $-CH_2OPh$, $-CONMe_2$
≠ $-CH_2OBn$

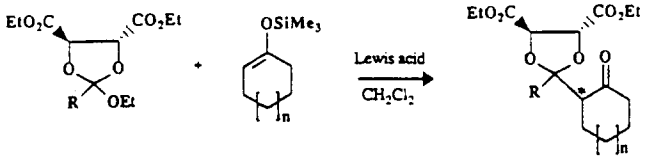
60+100%

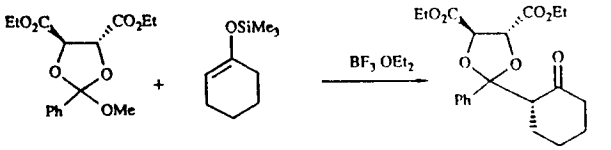






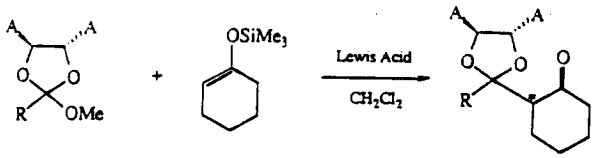
C. Scolastico et al., *Tetrahedron Lett.*, 1990, *31*, 2779



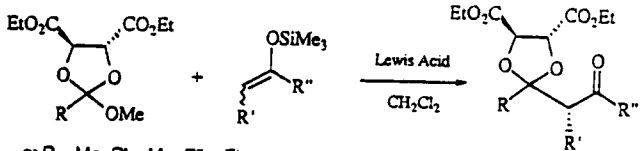


T. Basile, L. Longobardo, E. Tagliavini, C. Trombini and A. Umani-Ronchi; *J. Chem. Soc., Chem. Commun.* 1990, 759

R	n	Lewis acid	T (°C)	t (h)	Yield %	d.e.
Me	1	$TiCl_4$	-78	2	80	83
Me	1	BF_3·Et_2O	-60	3	70	80
Et	1	BF_3·Et_2O	-50	8	75	73
Ph	1	BF_3·Et_2O	-60	8	93	90
Me	0	BF_3·Et_2O	-20	24	34	43
Me	2	BF_3·Et_2O	-60	2	85	71



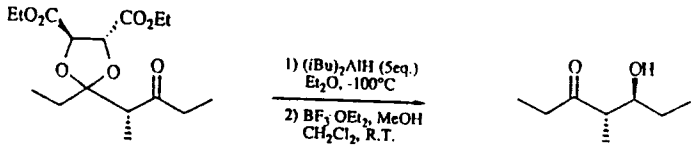
A	R	Lewis Acid	T(°C)	t(h)	Yield %	d. e. %
CO_2Me	Me	$BF_3{\cdot}OEt_2$	-60	3	80	78
CO_2Et	Me	$BF_3{\cdot}OEt_2$	-60	3	80	80
$CO_2i\,Pr$	Me	$BF_3{\cdot}OEt_2$	-60	4	80	80
Ph	Me	$BF_3{\cdot}OEt_2$	-60	5	65	33
CH_2OPh	Me	$BF_3{\cdot}OEt_2$	-60	5	69	48
$CONMe_2$	Me	$TiCl_4$	-60	15	70	60



a: R = Me, R' = Me, R" = Et
b: R = Me, R' = Et, R" = *n*Pr
c: R = Me, R' = Et, R" = Et

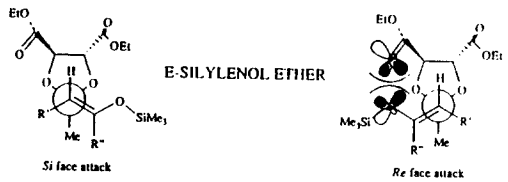
d: R = Me, R' = *n*Pr, R" = *n*Pr
e: R = Ph, R' = *n*Pr, R" = *n*Pr

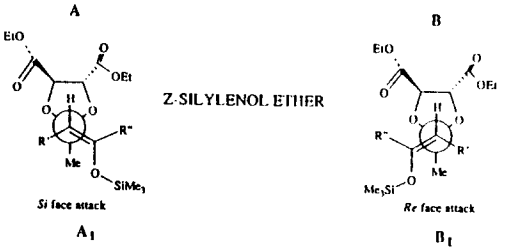
	E/Z	Lewis acid	T(°C)	Yield%	d. e.%
a	2/98	$TiCl_4$	-78	65	0
b	2/98	$BF_3{\cdot}OEt_2$	-60	61	0
c	95/5	$BF_3{\cdot}OEt$	-60	70	90
d	95/5	$BF_3{\cdot}OEt$	-60	60	90
e	95/5	$BF_3{\cdot}Et_2O$	-60	90	88

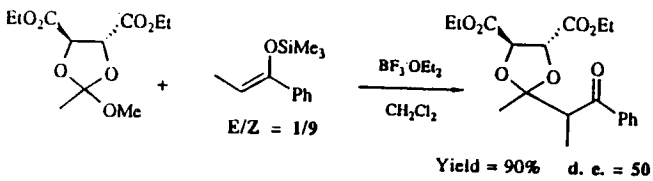


d. e. = 72%

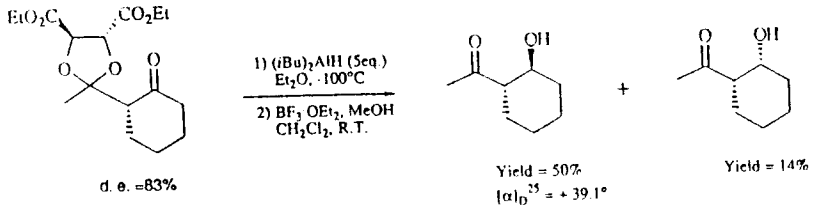
anti/syn = 5/1, e. e. = 68%
$[\alpha]_D^{25}$ = +24.2 (c 0.8 in Et_2O)

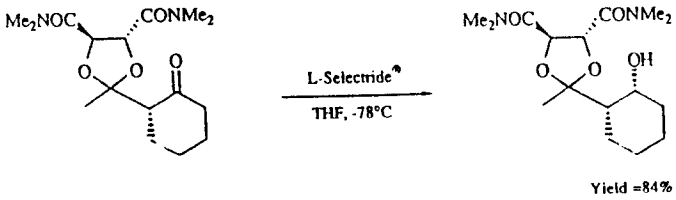


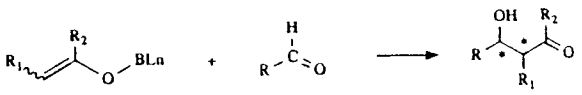




Yield = 90% d. e. = 50%

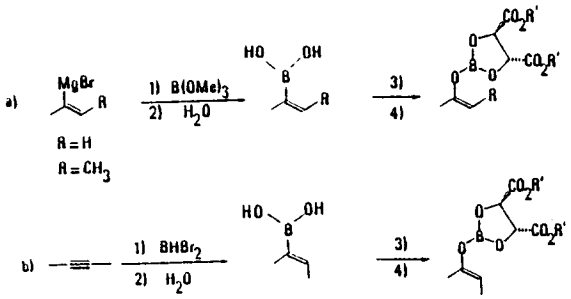


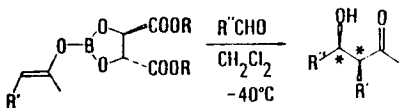




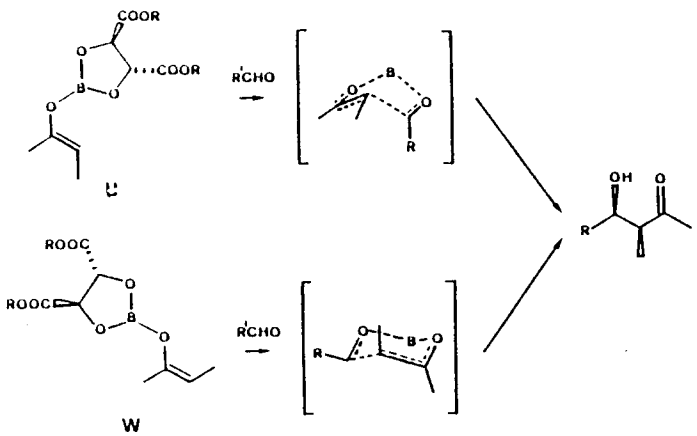
Ln = CHIRAL LIGANDS DERIVED FROM DIETHYL TARTRATE (n = 1

OR α-PINENE (n = 2)

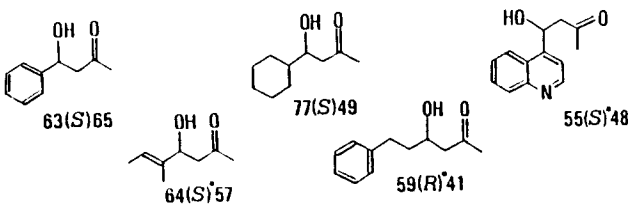


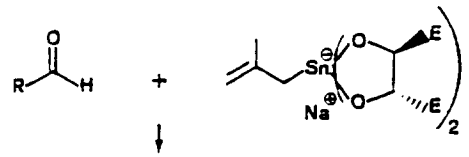


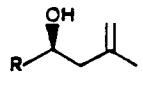
R' = H, CH_3



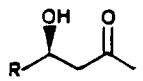
PRODUCTS yield% (config) e.e.%

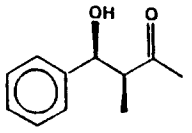






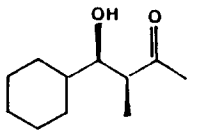
R = Ph



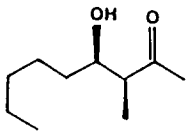


75% (3S,4S) 68% e.e.

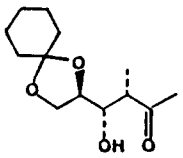
(78% (3S,4S) 39% e.e. using the Z enolate)

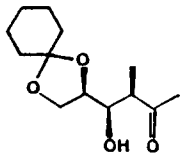


64% (3S,4R) 54% e.e.



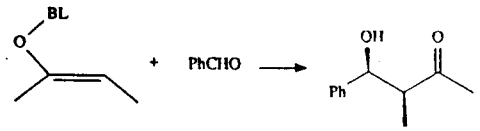
70% (3S,4R) 72% e.e.



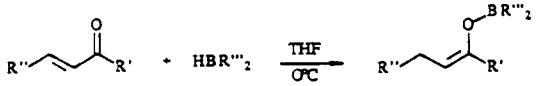


Enolate	Tartrate		
E	R,R	99	1
E	S,S	68	32
Z	R,R	99	1
Z	S,S	75	25

EFFECT OF THE CHIRAL LIGANDS



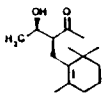
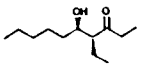
L	$[\alpha]_D$	e.e.
DICYCLOHEXYLTARTRATE	-33.3	65%
(S,S)1,4-DITOSYLOXYBUTANE-2,3-DIOL	+15.5	30%
(S,S)1,4-DIPHENYLOXYBUTANE-2,3-DIOL	+2.0	4%

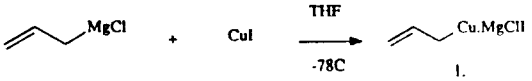


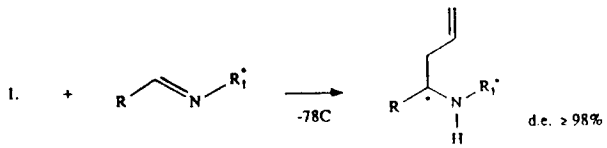
R''' = dicyclohexyl or diisopinocampheyl

d.e. ≥ 98%

R''' = dicyclohexyl or diisopinocampheyl

Ketone	Aldehyde	Solvent	Aldol	Yield %	e.e. %
	PhCHO	THF		90	91
	PhCHO	THF		77	75
"	PhCHO	CH_2Cl_2		70	62
"	CH_3CHO	THF		60	75
	PhCHO	$CHCl_3$		65	64
"	PhCHO	$CHCl_3$		57	(Chx_2BH)
"	$n\text{-}C_5H_{11}CHO$	THF		75	65





$R = C_6H_5 ; C_5H_{11}$ $R_1 = (CH_3)_2\dot{C}HCHCOOCH_3 ; C_6H_5\dot{C}HCH_3$