Syntheses Using the Oxiranyl Anion Methodology

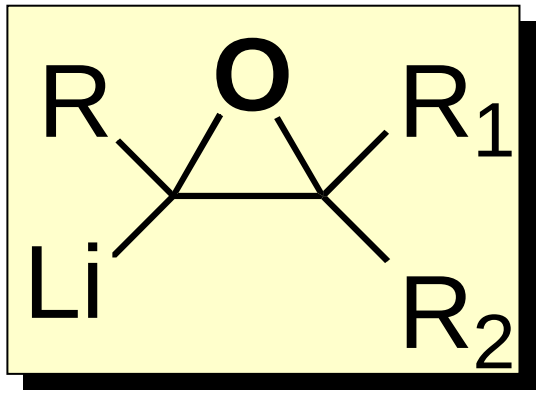
Saverio Florio

Dipartimento Farmaco-Chimico, Università degli Studi di Bari - Italy

florio@farmchim.uniba.it
www.farmchim.uniba.it/chimica_organica

IASOC-2006

α-Lithiated Oxiranes



Under investigation:

-generation

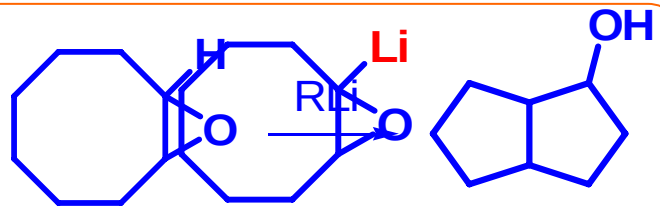
-nature (carbanion or carbenoid)

-chemical and configurational stability

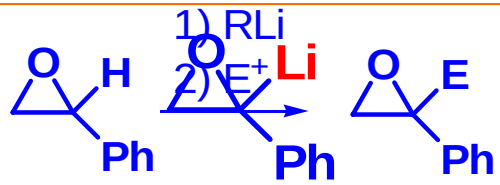
-stereochemistry

The History:

Cope and Crandall (late fifties)



Eisch and Galle (middle seventies)



Eisch, Molander, Pfaltz, Yamakawa, Satoh, Mori, Jackson, Doris and Dechoux, Hodgson, Malacria, Uneyama, Florio (nineties)

Reviews and Accounts:

Satoh, Chem. Rev. 1996, 96, 3303

Mori, Rev. Heter. Chem. 1997, 17, 183

Hodgson, Synthesis, 2002, 12, 1625

Hodgson, Synlett 2006, 1-22

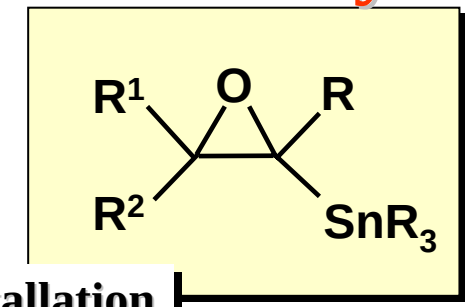
Florio, Tet. Symposia in Print, 2003, 9713

Florio, Synlett 2005, 9, 1359-1369

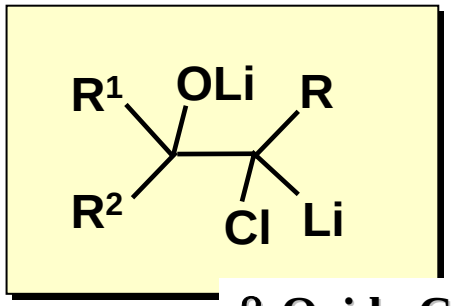
Chemlà, The Chemistry of Organolithium Compounds, Patai, 2004, Vol. 2, chap. 18

Oxiranyllithiums in Synthetic Organic Chemistry

A. Pfaltz, *Tet. Lett.* **1991**, *32*, 615

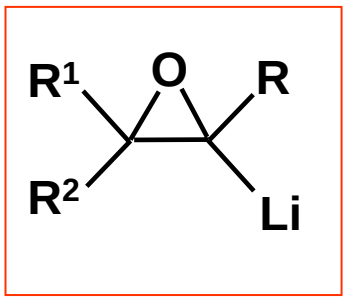


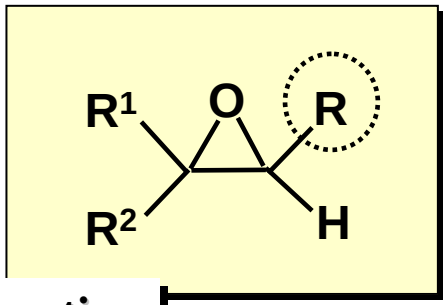
Transmetallation



β-Oxido Carbenoid

Shimizu, M. *Tet.* **2003**, 59, 9811



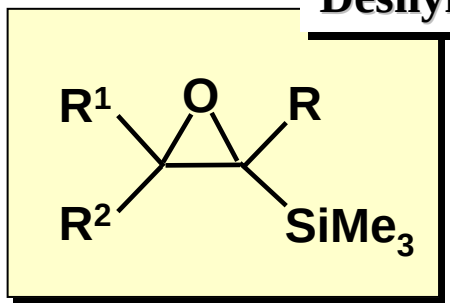


Deprotonation

R = EWG

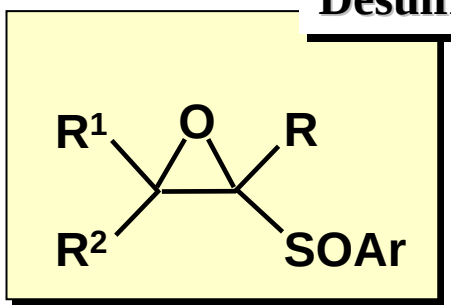
R = H, Alkyl

Desilylation



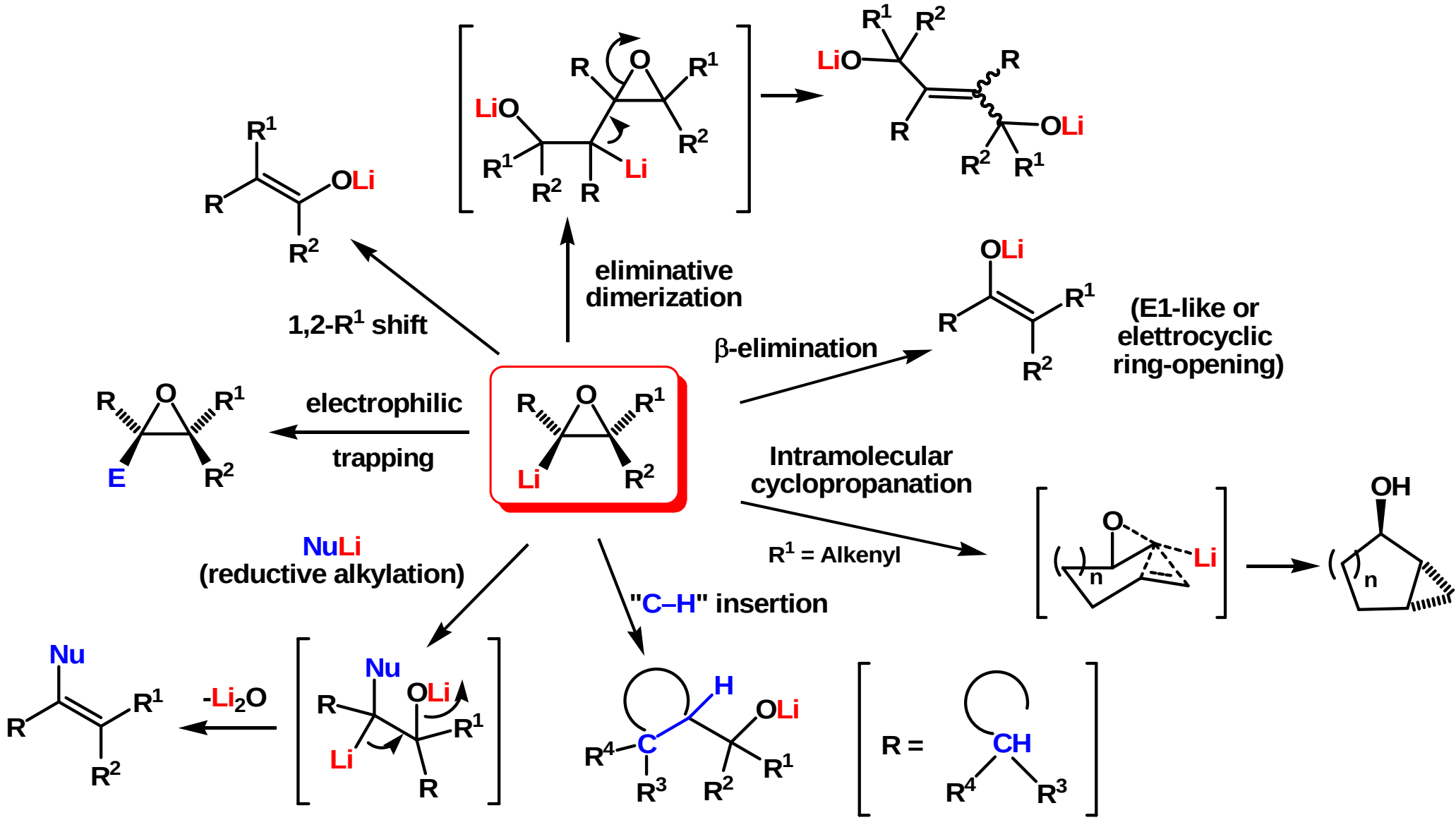
Kobayashi. *Tet. Lett.* **1999**, *40*, 7371

Desulfinylation

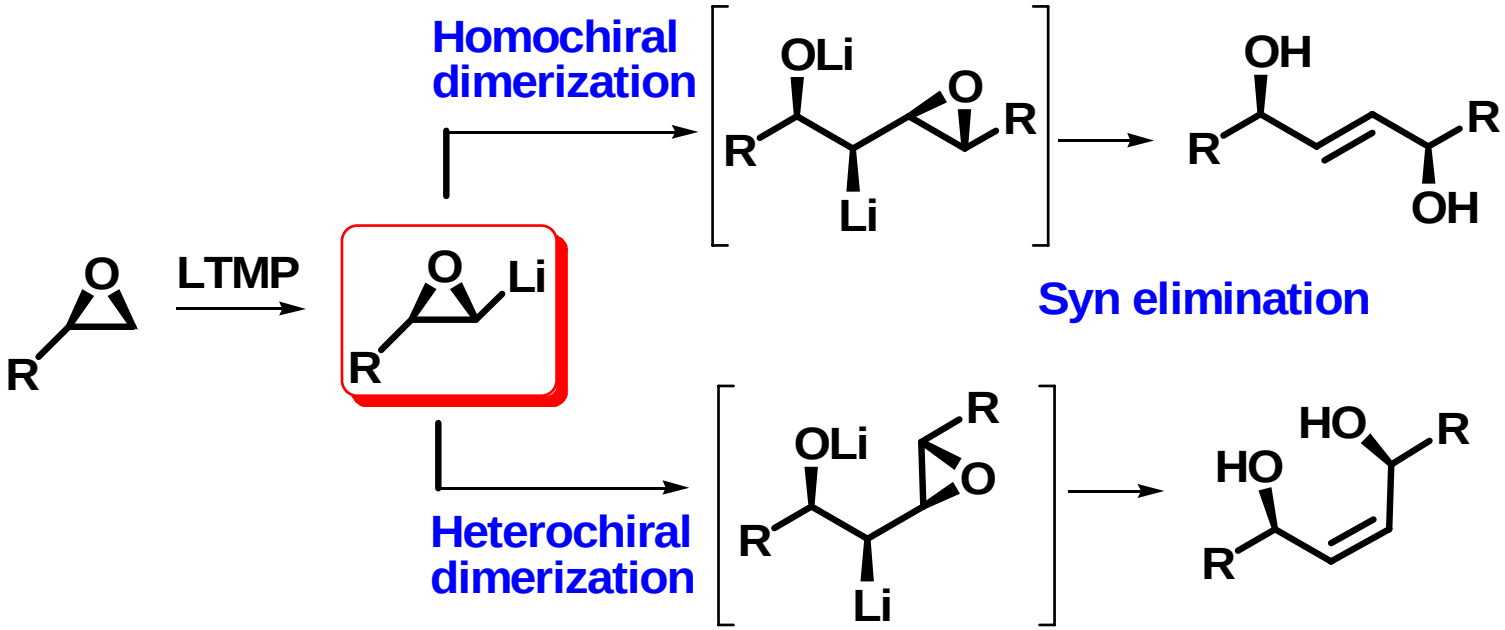


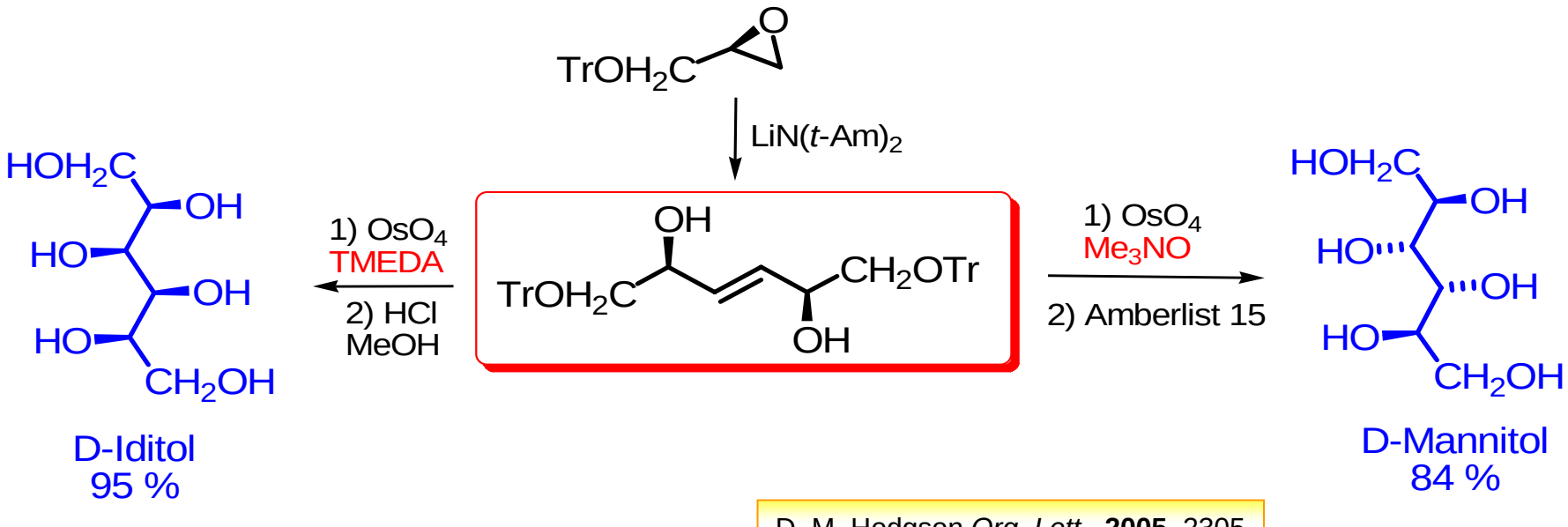
K. Yamakawa, *J. Org. Chem.* **1989**, *54*, 3130

Multifaceted Reactivity of Oxiranyllithiums: Carbanions and Carbenoids



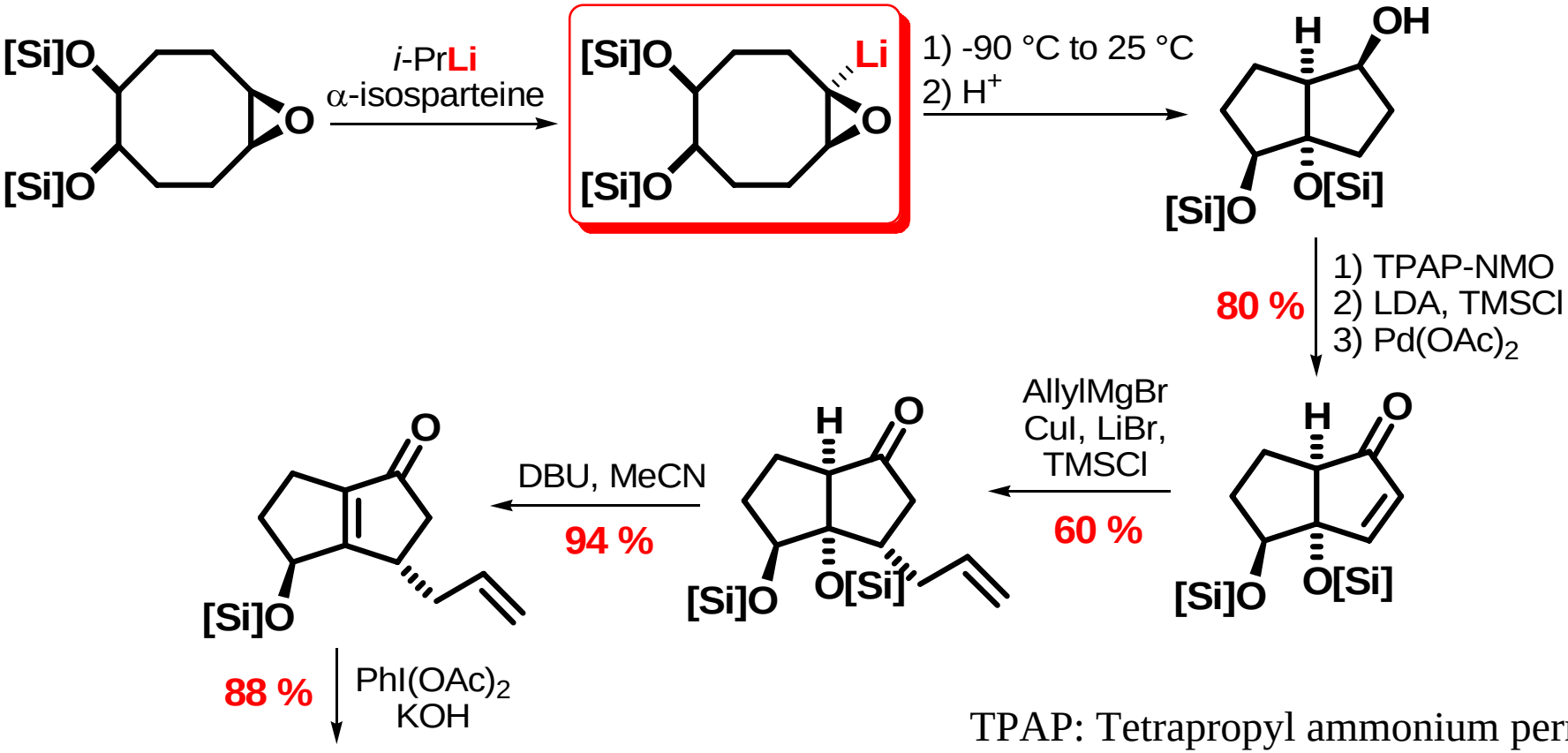
2-Ene-1,4-diols by Dimerization of Terminal Epoxides





D. M, Hodgson *Org. Lett.* **2005,** 2305

Oxiranyl anion methodology: synthesis of the natural product Xialenon A

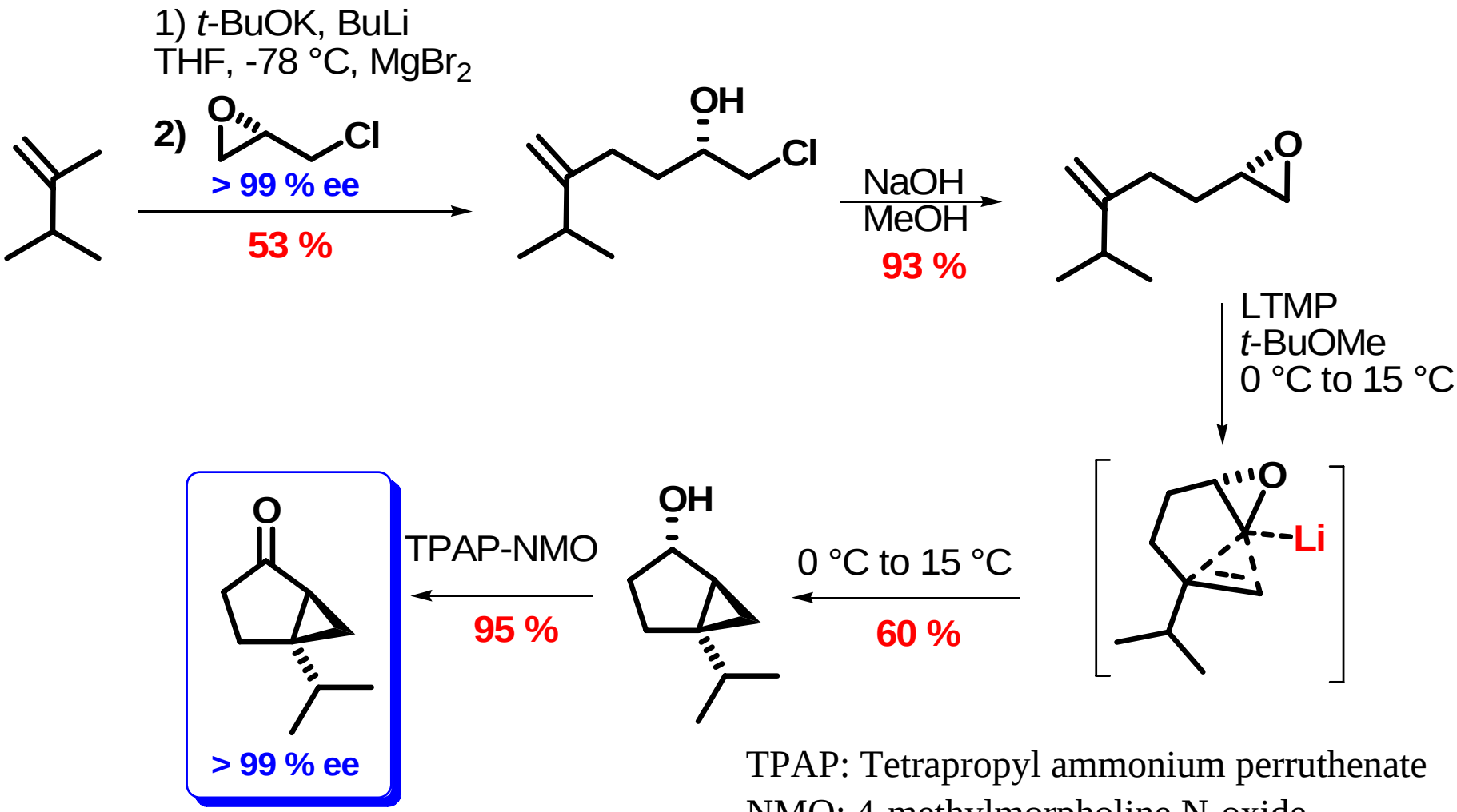


TPAP: Tetrapropyl ammonium perruthenate
NMO: 4-methylmorpholine N-oxide

Xialenon A

D. M, Hodgson *Synthesis* **2005,** 1

Oxiranyl anion mediated cyclopropanation: synthesis of (–)-Sabina ketone



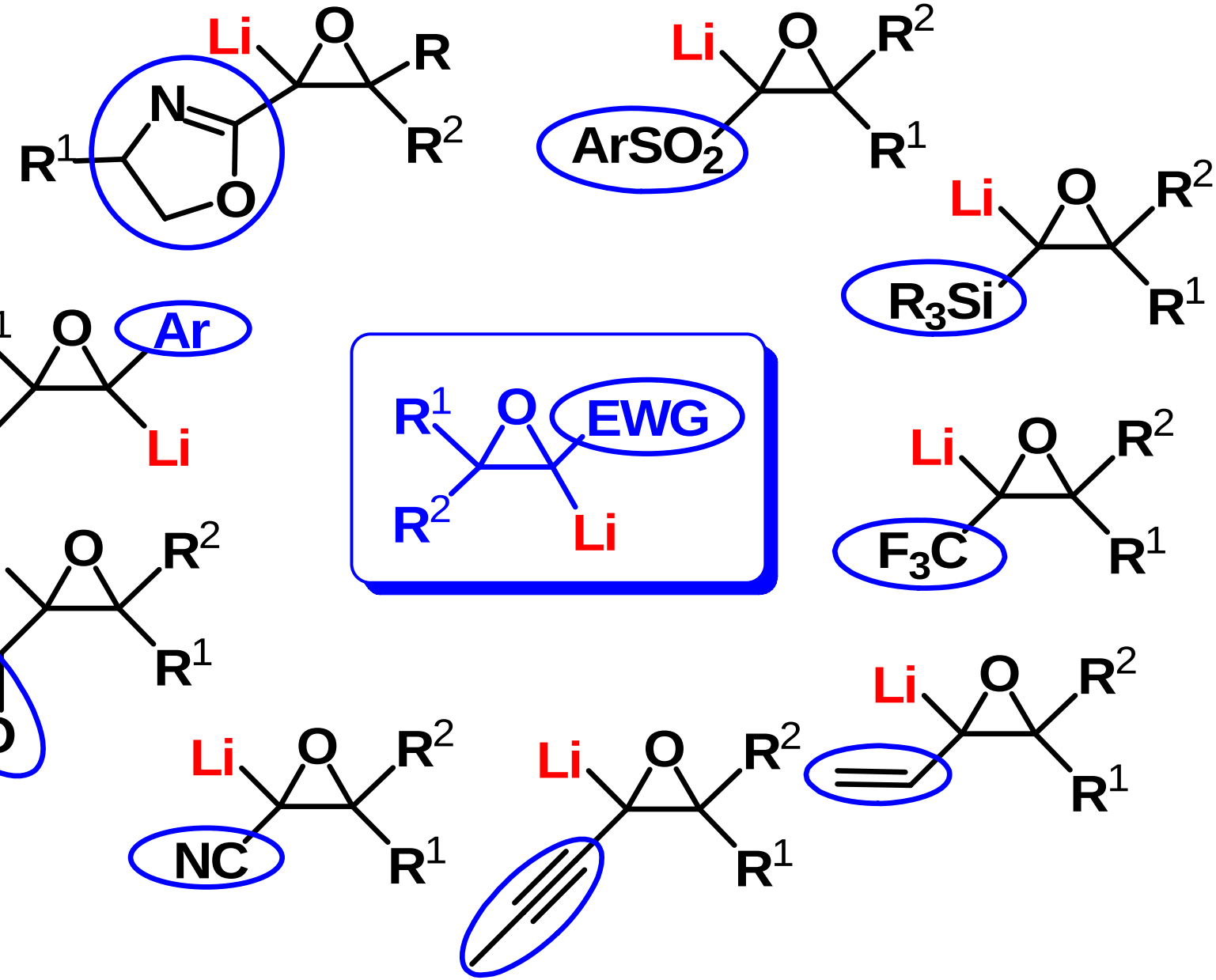
TPAP: Tetrapropyl ammonium perruthenate
NMO: 4-methylmorpholine N-oxide

(-)-Sabina Ketone

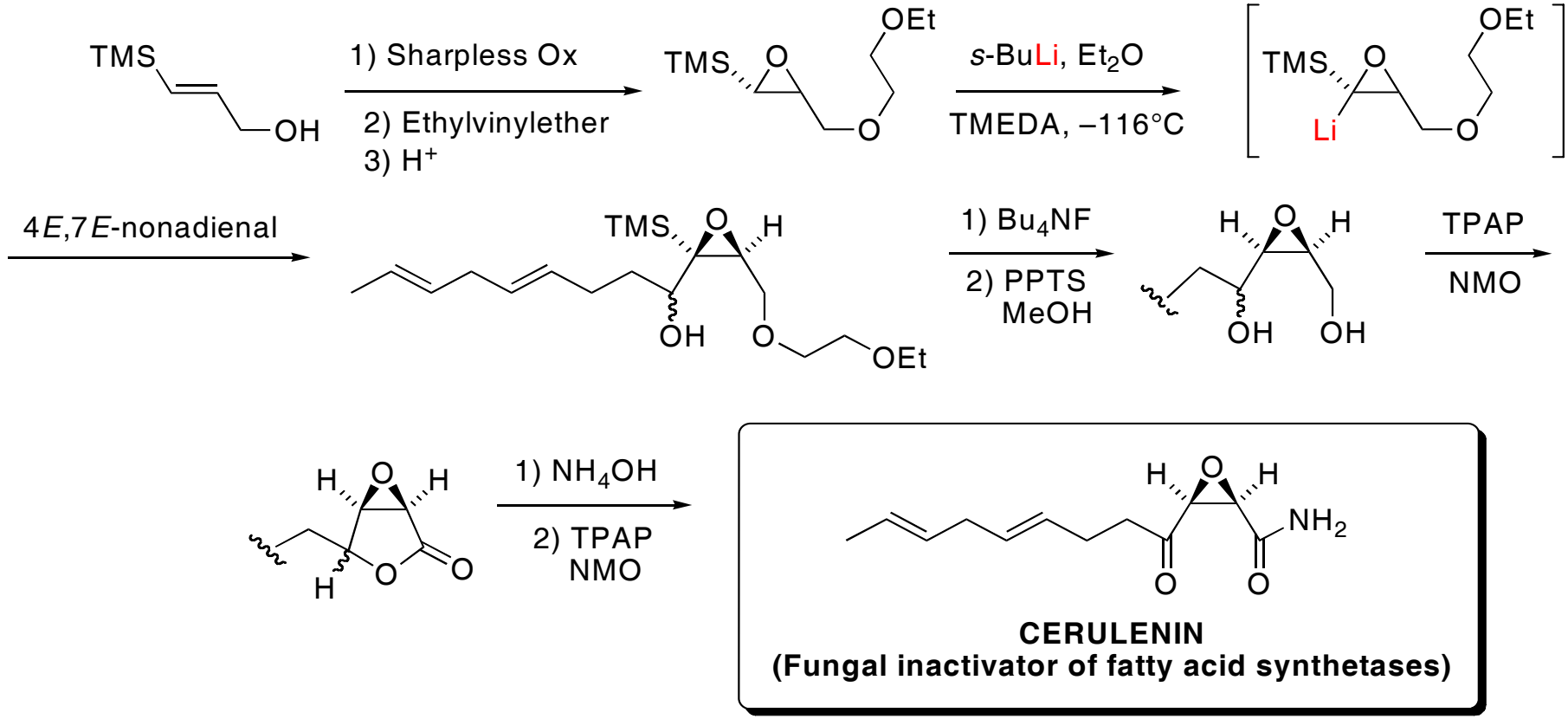
Precursor of important flavor chemical found in a variety of essential oils.

D. M, Hodgson *Synthesis* **2005,** 1

Stabilized Oxiranyllithiums



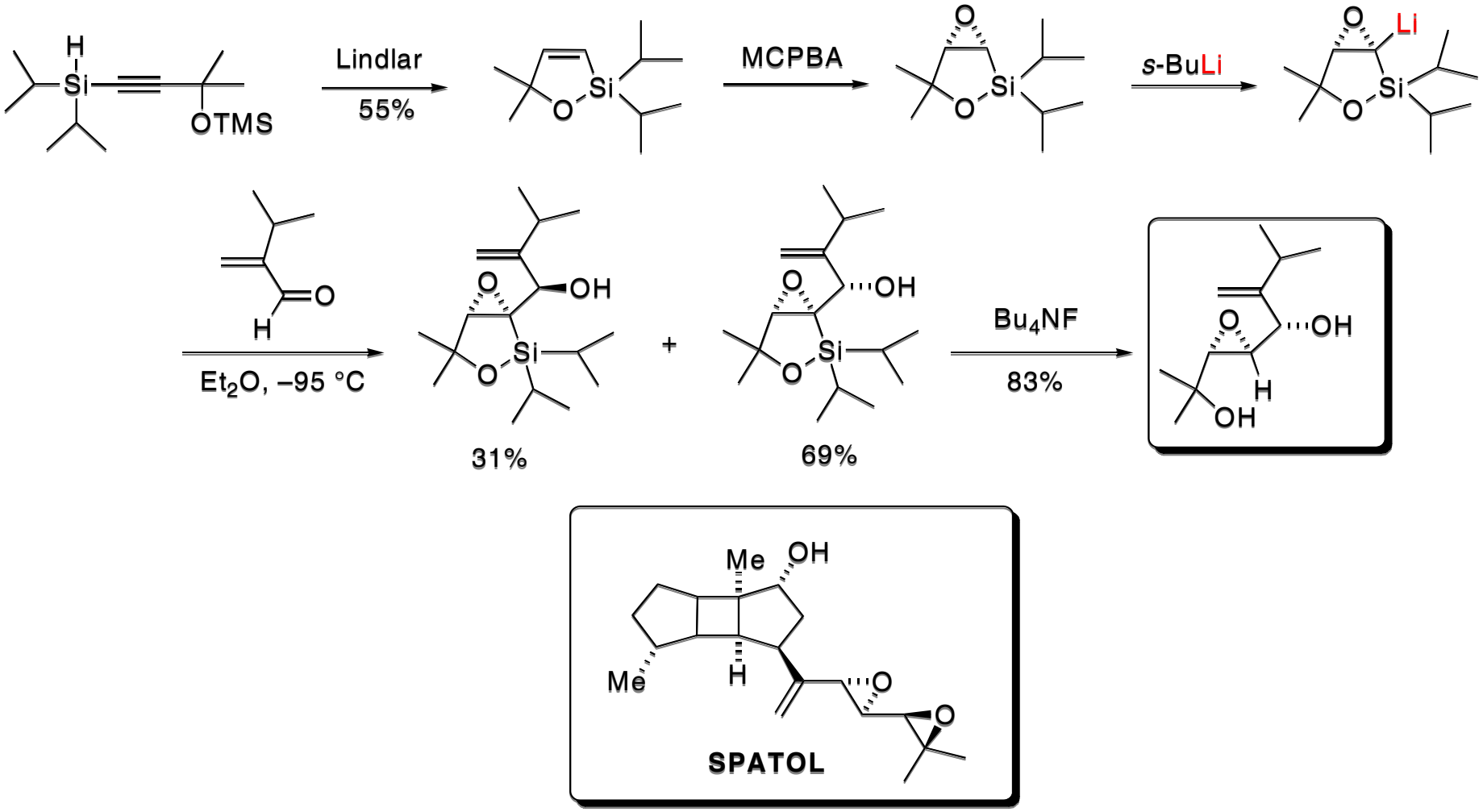
Silicon-Stabilized Oxiranyl Anions: Total Synthesis of Cerulenin



PPTS: Pyridinium p-toluensulfonate
TPAP: Tetrapropyl ammonium perruthenate
NMO: 4-Methyl morpholine *N*-oxide

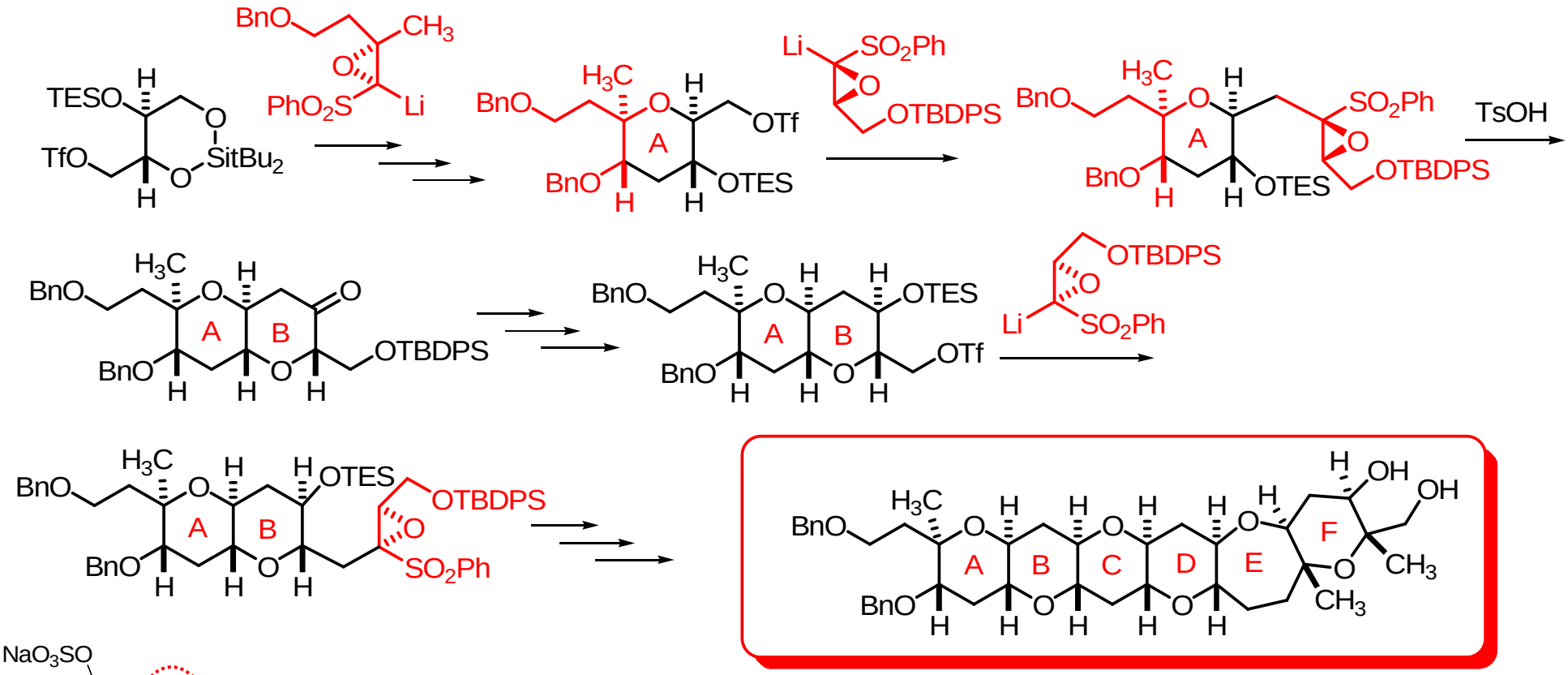
Mani, N. S. et al., *J. Org. Chem*. **1997**, 62, 636

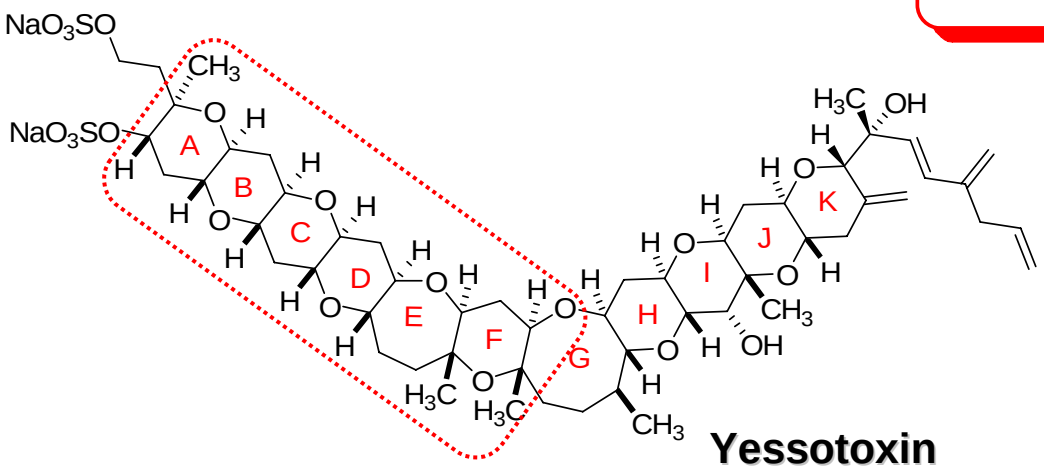
Synthesis of Spatol Analogues



Salomon, R. G. *Terahedron Lett*. **1994**, 35, 517

Oxiranyl anion methodology: Iterative synthesis of the ABCDEF-ring system of yessotoxin

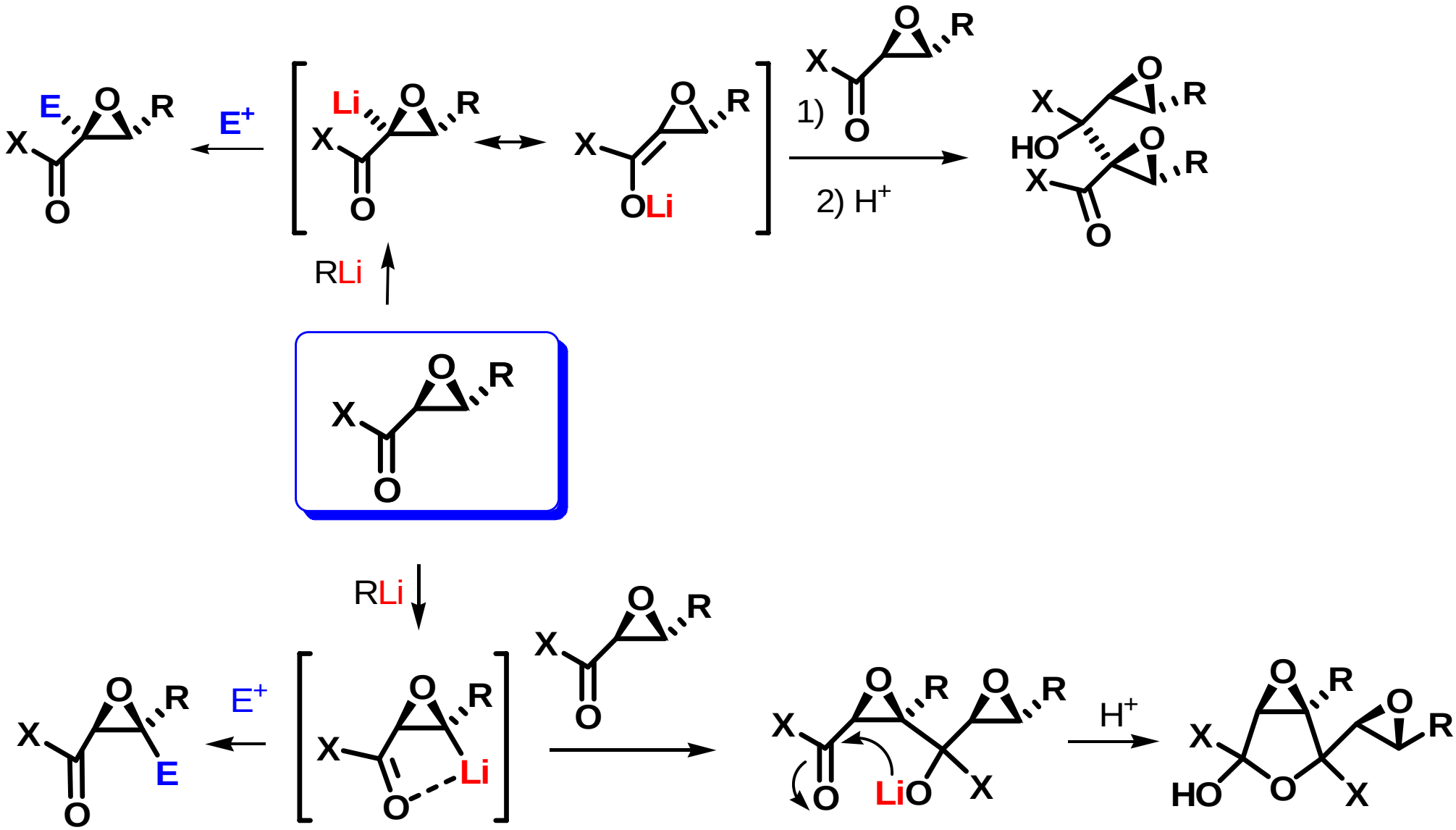




Yessotoxin

Mory, Y.; Noyori, R.; Takase, T.
Tetrahedron Lett. **2003,** 2319

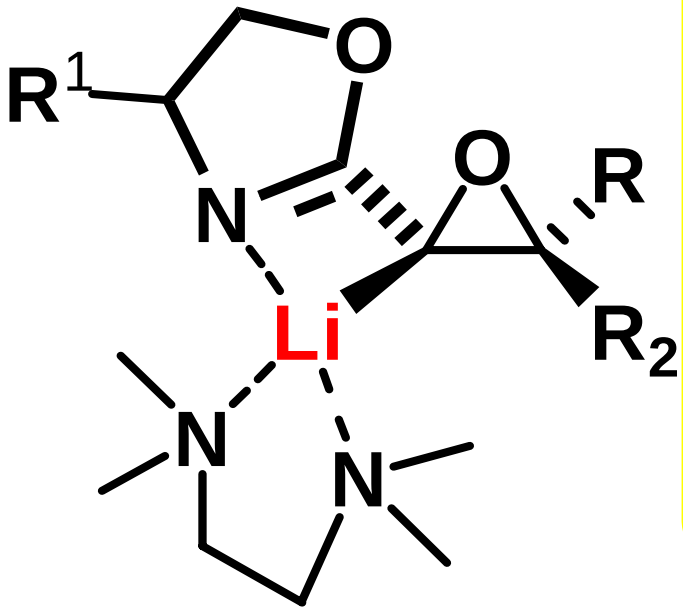
Carbonyl-stabilized oxiranyl anions

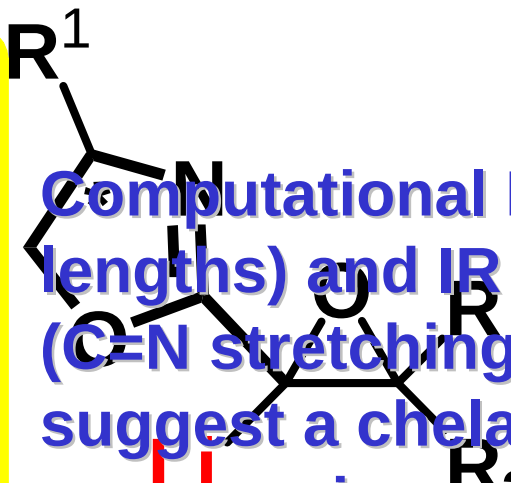


“Oxazolinyloxiranyllithiums particularly promising”

G. Molander, Pure & Appl. Chem. **1990**, *62*, 707-712

α-LITHIATED OXAZOLINYLOXIRANES

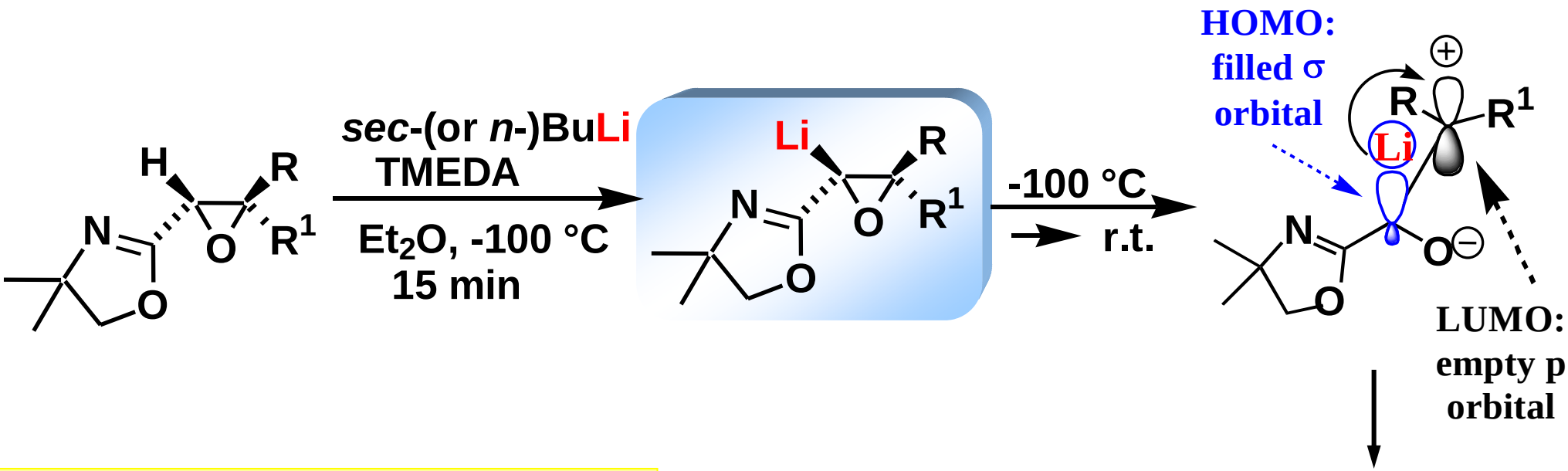




Computational DFT study (bond lengths) and IR spectroscopy (C=N stretching frequence) suggest a chelated tetrahedral monomeric aggregate.

-very easy generation (THF, s-BuLi/TMEDA),
-high chemical stability,
-amenable to synthetic elaboration

Lithiation of Oxazolinyloxiranes: Synthesis of Oxazolinyl Ketones

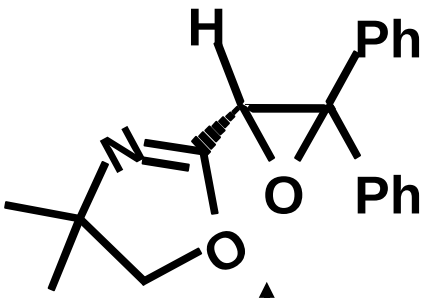


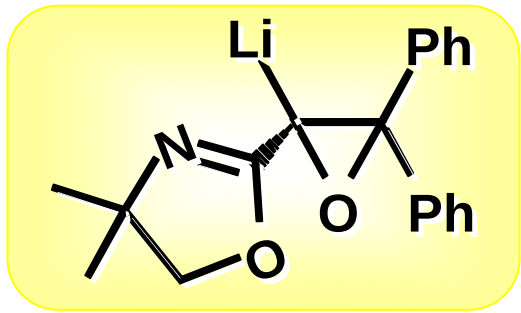
R	R^1	Yield, %
p-Me-C_6H_4	H	67
H	*p*-Me-C_6H_4	67
p-F-C_6H_4	*p*-F-C_6H_4	60
Ph	Ph	63
i-Pr	H	30
Me	Me	80
Et	Et	62
-$(CH_2)_4$-		62
-$(CH_2)_5$-		75
2-Adamantylidene		60

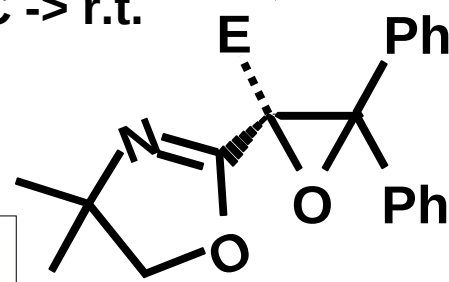
Tetrahedron Lett., **2000**, *41*, 8835

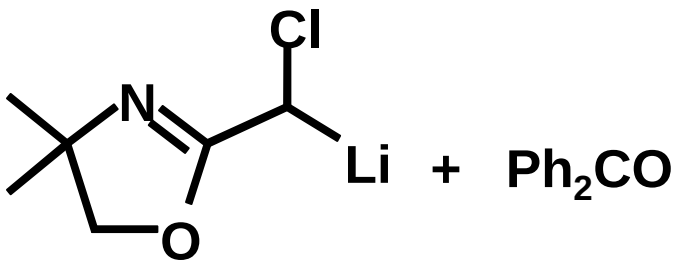
Peptidyl derivatives are HNE (Human Neutrophyl Elastase) Inhibithors

Oxazoline-Stabilized Oxiranyllithiums

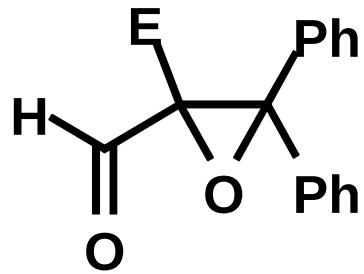








+ Ph_2CO



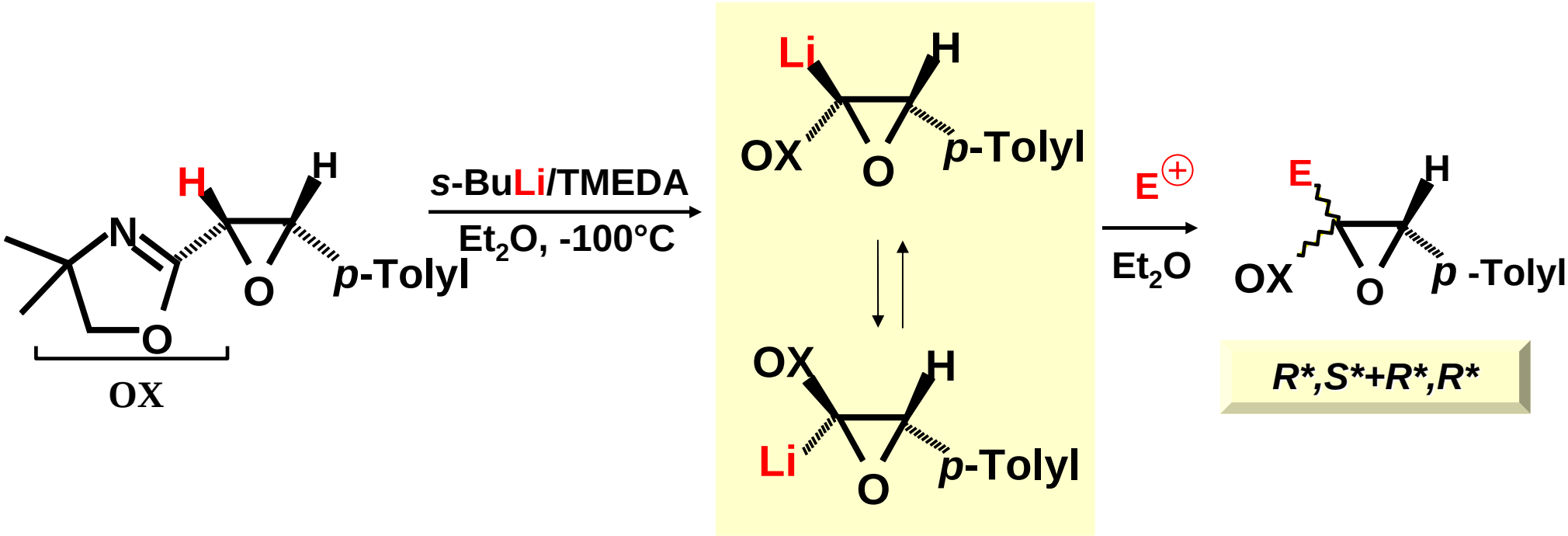
Electrophile	% Yield	*Syn*/*Anti*
$(CH_3)_3SiCl$	95	
$CH_2=CHCH_2$-Br	76	
CH_3I	62	
$(CH_3)_2CO$	67	
Cyclohexanone	79	
PhCHO	83	50/50
p-CH_3-C_6H_4-CHO	70	64/36
$(CH_3)_2CHCHO$	65	55/45
CH_3CHO	68	56/44

Tetrahedron Lett., ***1996***, *37, 4781*

Tetrahedron Lett., ***1998***, *39, 5639*

Eur. J. Org. Chem., ***1999***, *409-417*

Regio and Stereospecific Deprotonation-Trapping of *cis*-Oxazolinyl Epoxides



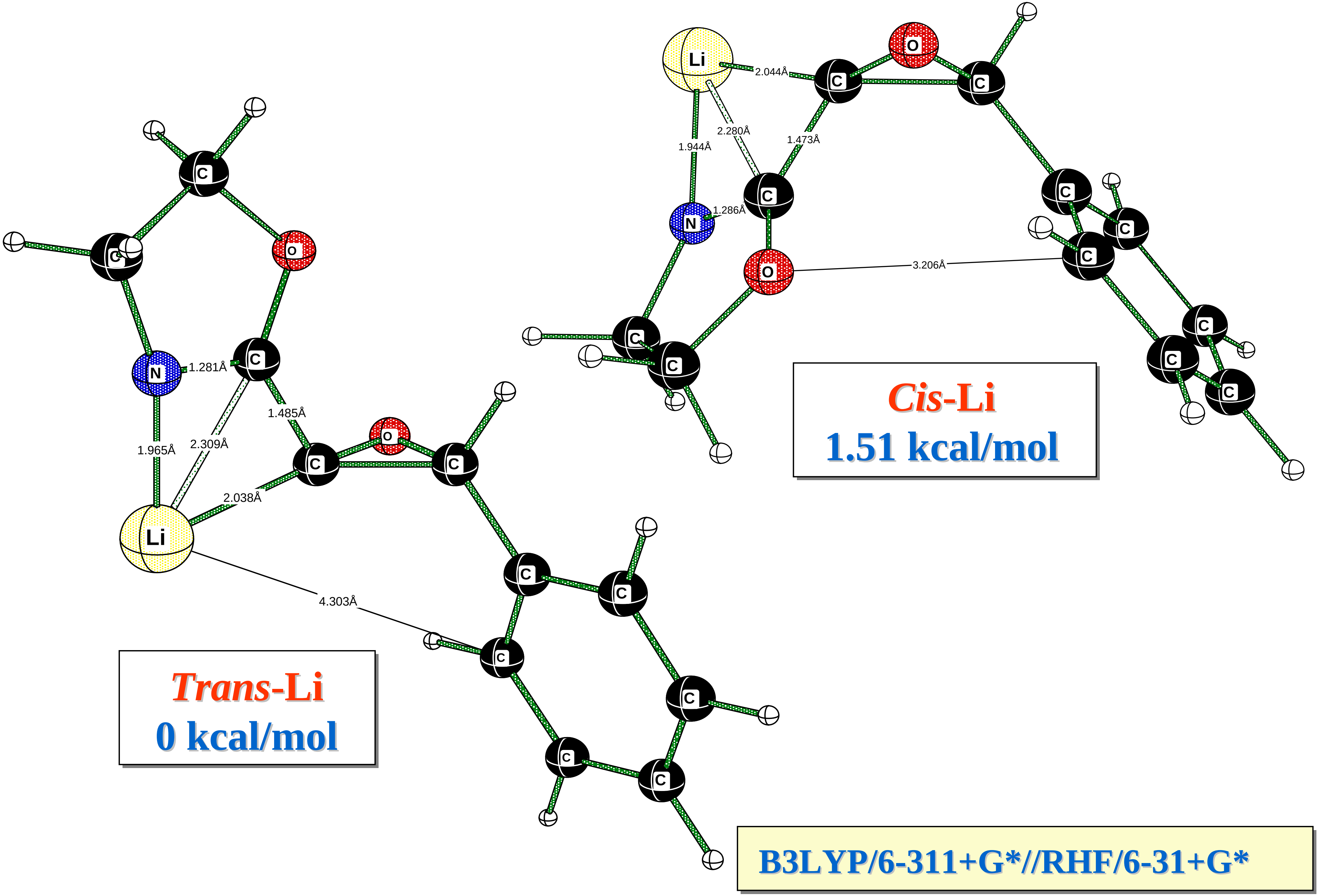
R,S*+R*,R**

E^+ = D_2O, MeI, PhCHO, MeCHO, Et_2CO

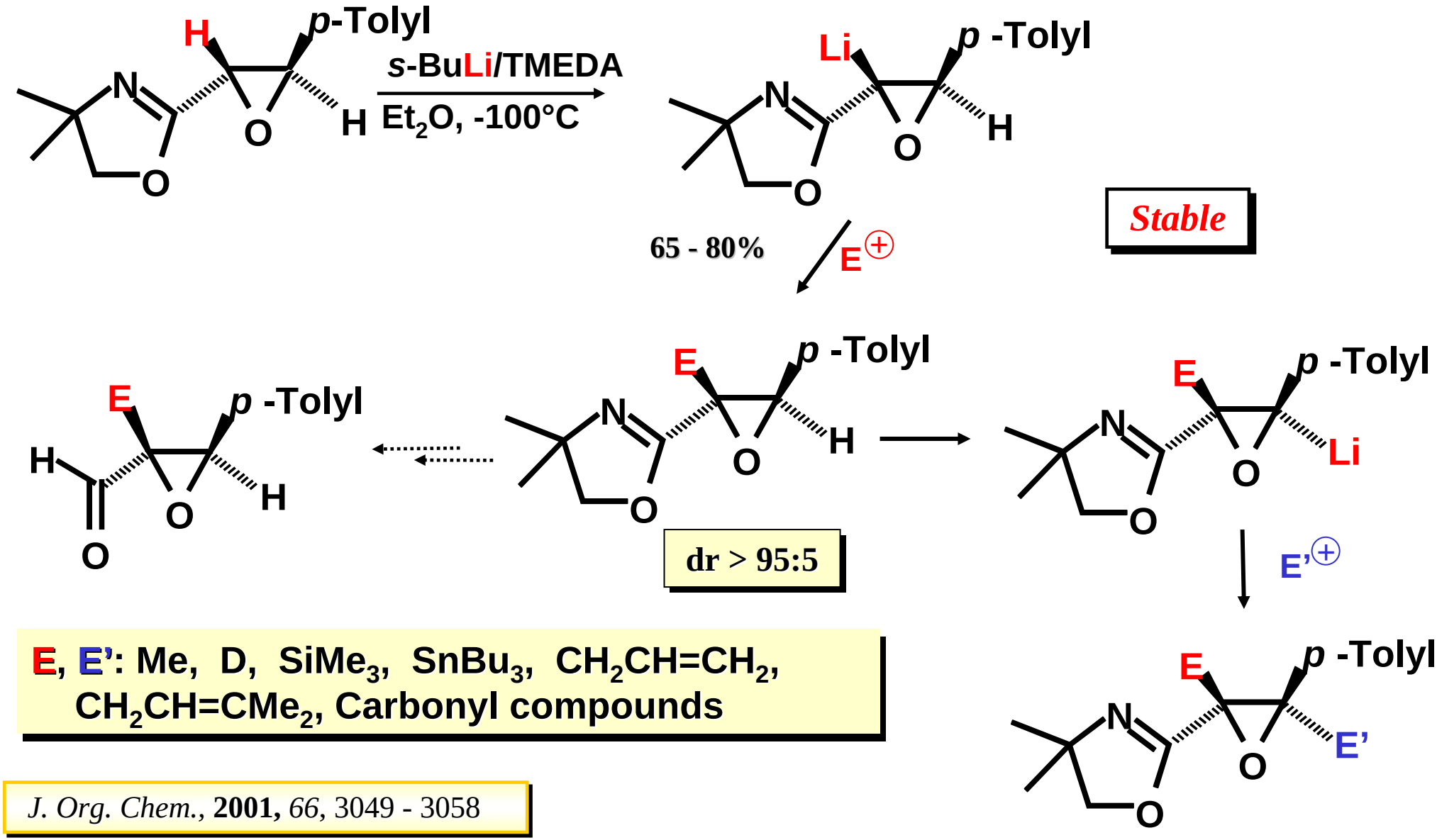
60-95% Yields

R*,S*/R*,R* **ratio: 80/20 - 95/5**

J. Org. Chem., **2001,** *66*, 3049 - 3058


Cis-Li
1.51 kcal/mol
2.044Å
1.944Å
2.280Å
1.473Å
1.286Å
3.206Å
Trans-Li
0 kcal/mol
1.281Å
1.485Å
1.965Å
2.309Å
2.038Å
4.303Å
B3LYP/6-311+G*//RHF/6-31+G*

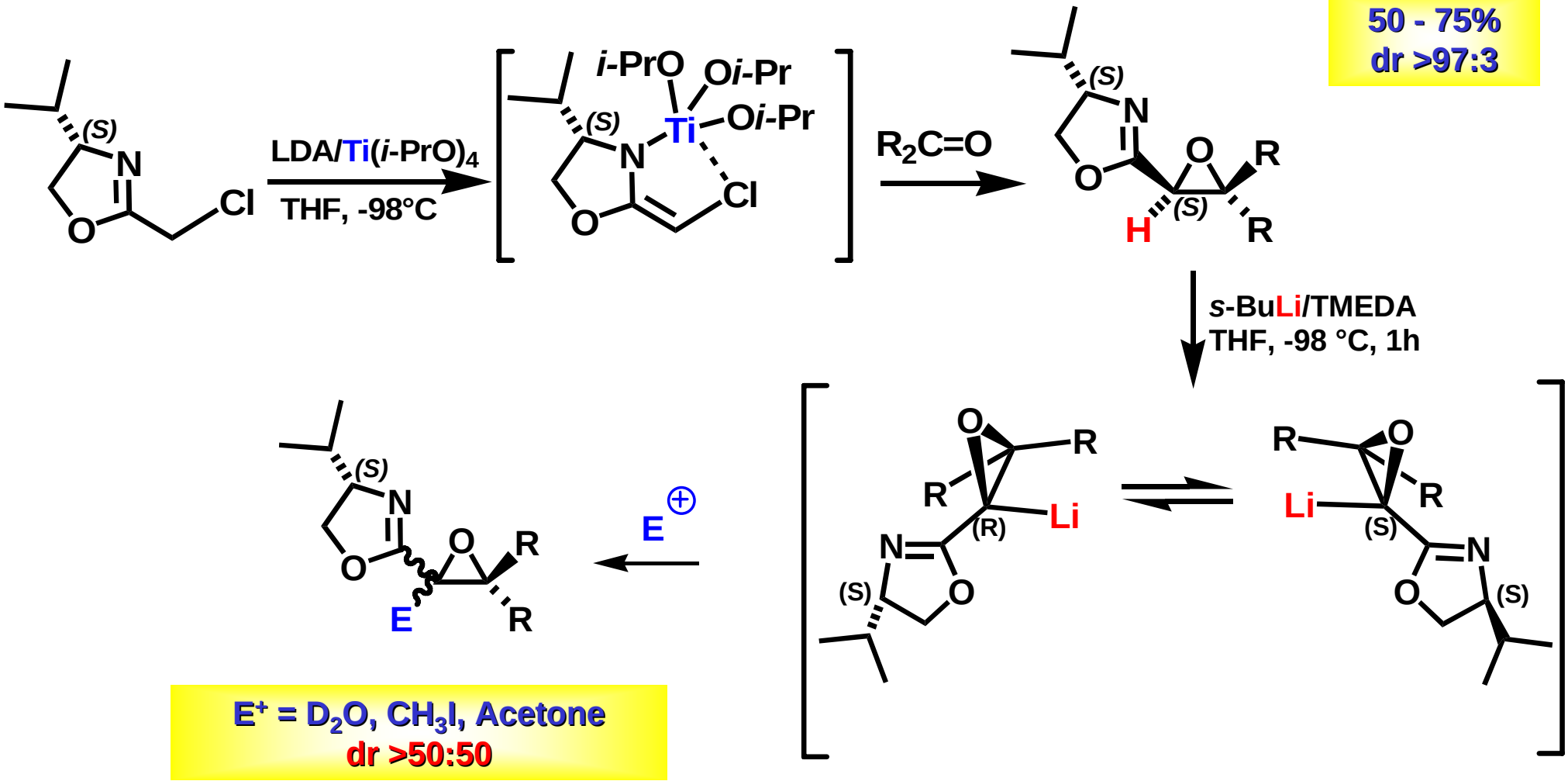
Regio and Stereospecific Deprotonation-Trapping of *trans*-Oxazolinyl Epoxides



E, E': Me, D, $SiMe_3$, $SnBu_3$, $CH_2CH{=}CH_2$, $CH_2CH{=}CMe_2$, Carbonyl compounds

J. Org. Chem., **2001,** *66*, 3049 - 3058

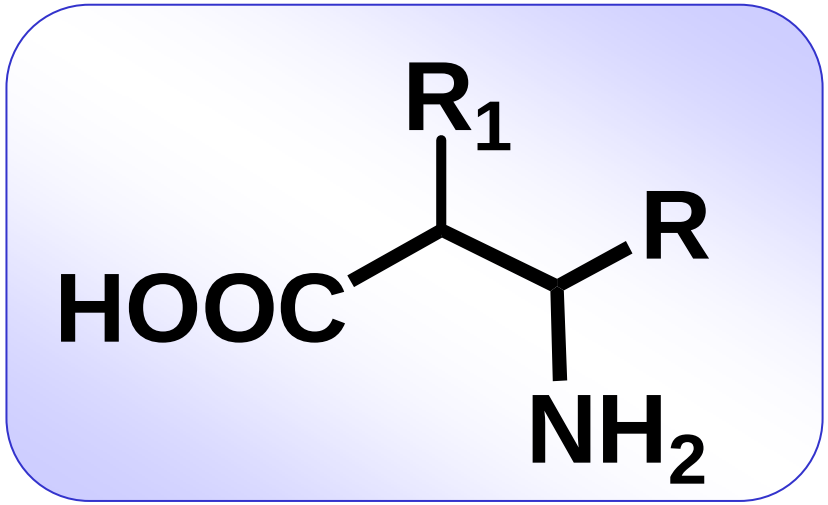
Lithiation of Chiral Oxazolinyloxiranes



• α-Lithiated Oxazolinyloxiranes are configurationally unstable

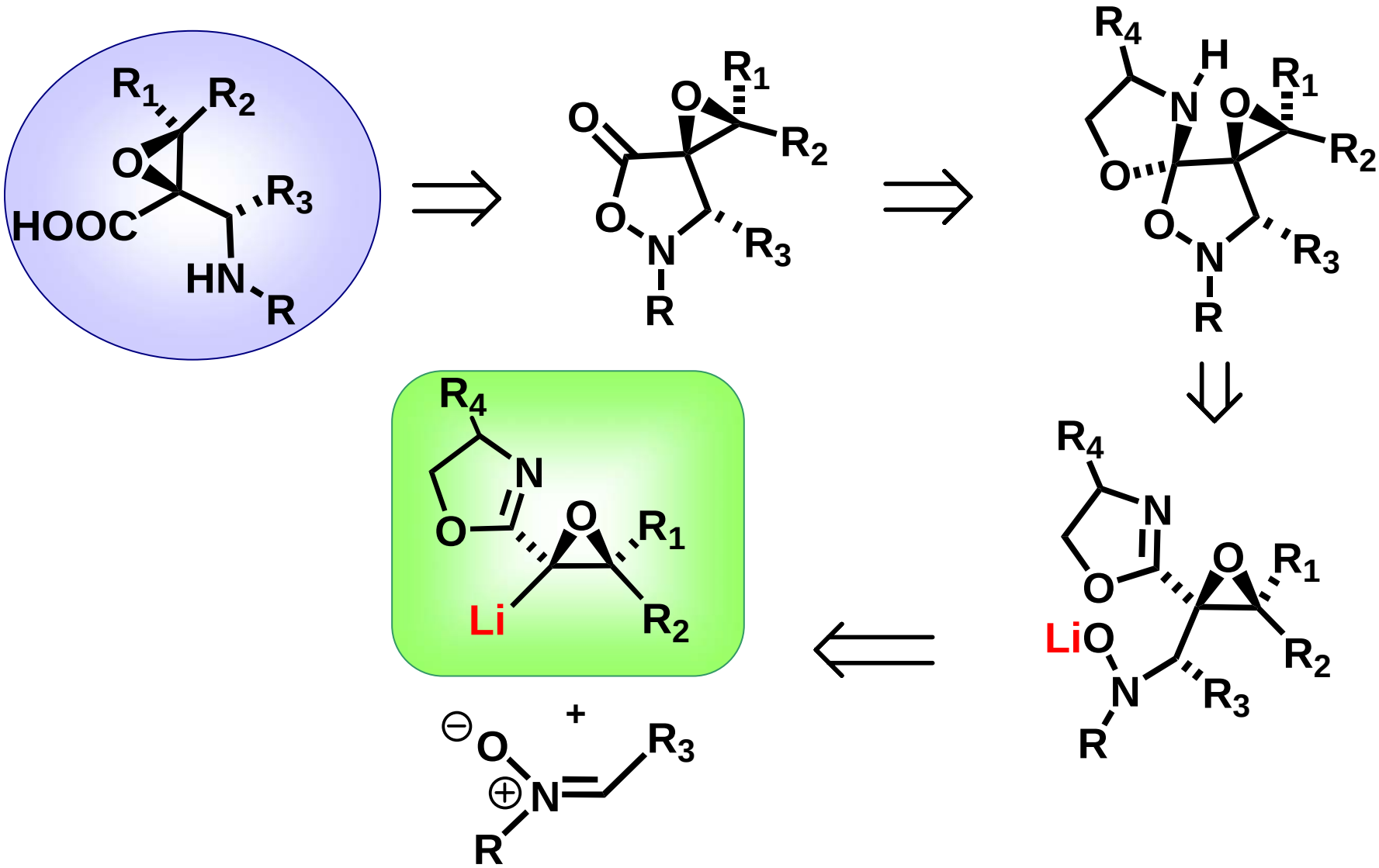
Tetrahedron. **2003**, 9707

β-Amino Acids

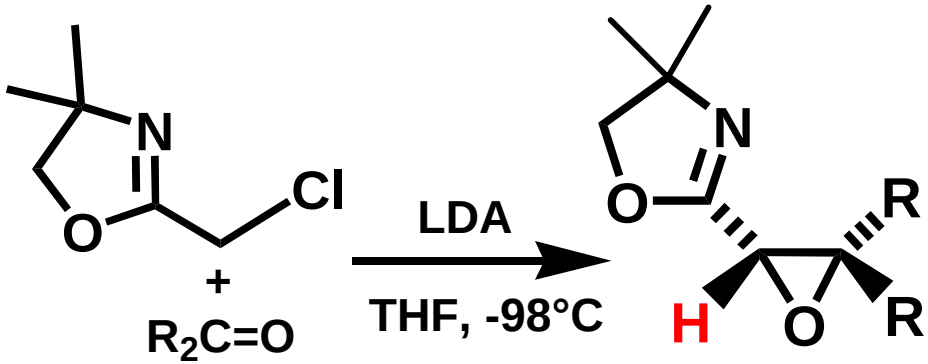


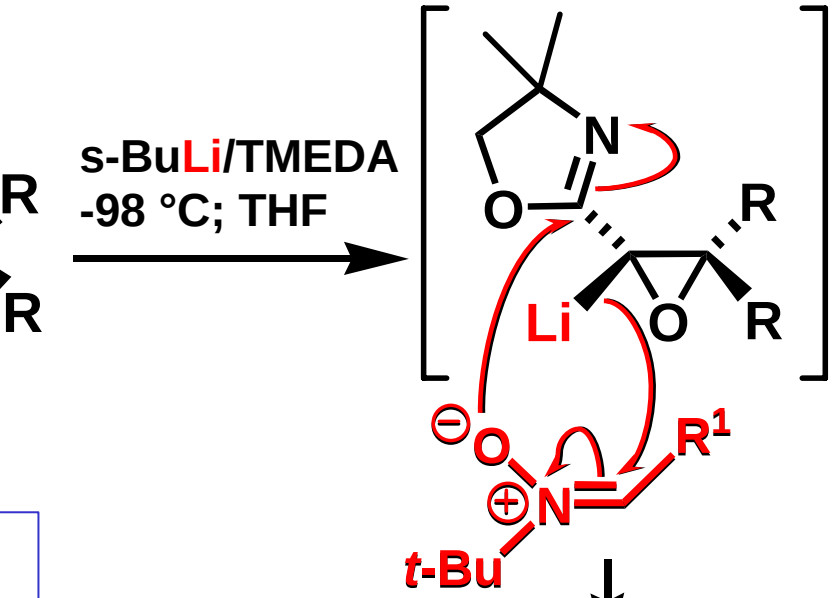
-present in natural products
-exhibit important biological properties
-valuable chiral building blocks for the asymmetric construction of β-lactam antibiotics
-incorporated into biologically active molecules enhance bioactivity and can probe mechanisms of action

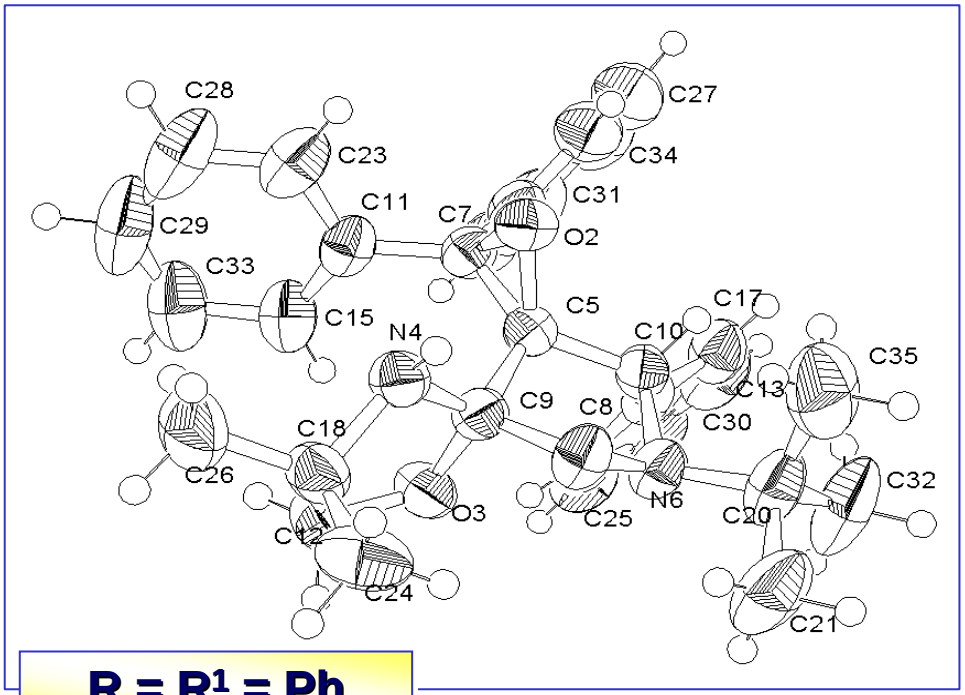
Retrosynthetic Approach to α-Epoxy-β-Amino Acids: Combining the Oxiranyllithium Methodology with the Chemistry of Nitrones and Oxazolines



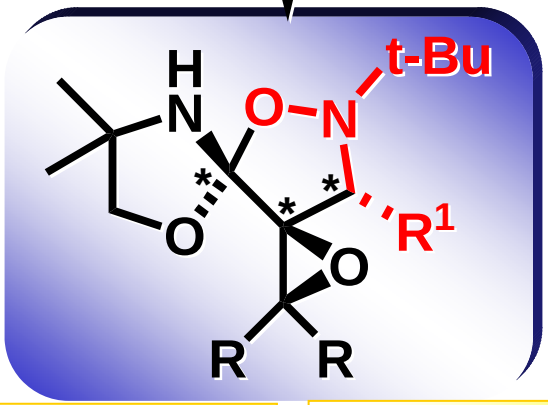
Reaction of Lithiated Oxazolinyloxiranes with Nitrones







R = R^1 = Ph

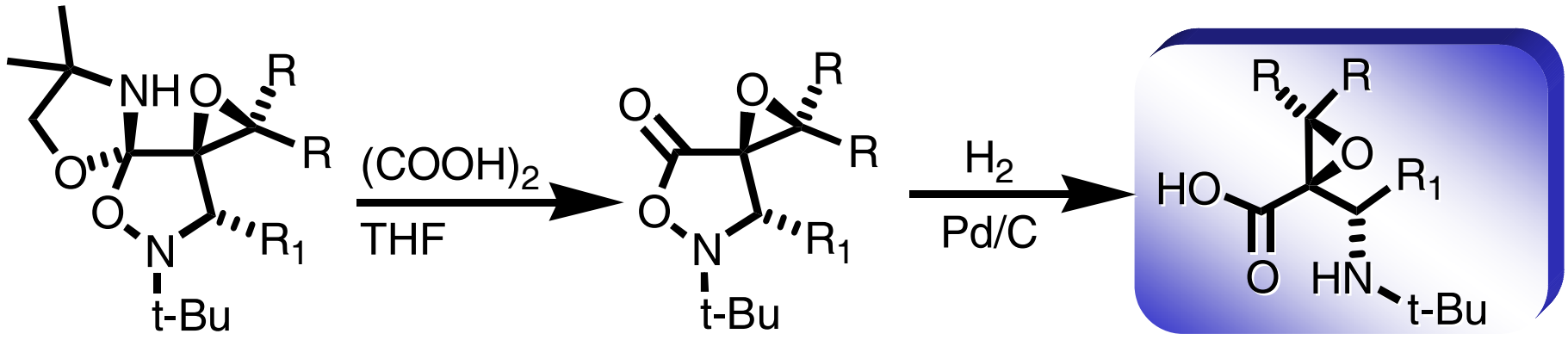


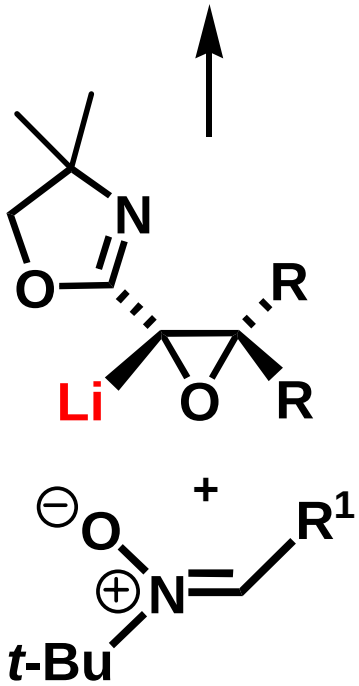
Yields 68 – 82 %

Single Diastereoisomer

Org. Lett. **2003**, 2723

Synthesis of α-Epoxy-β-Amino Acids

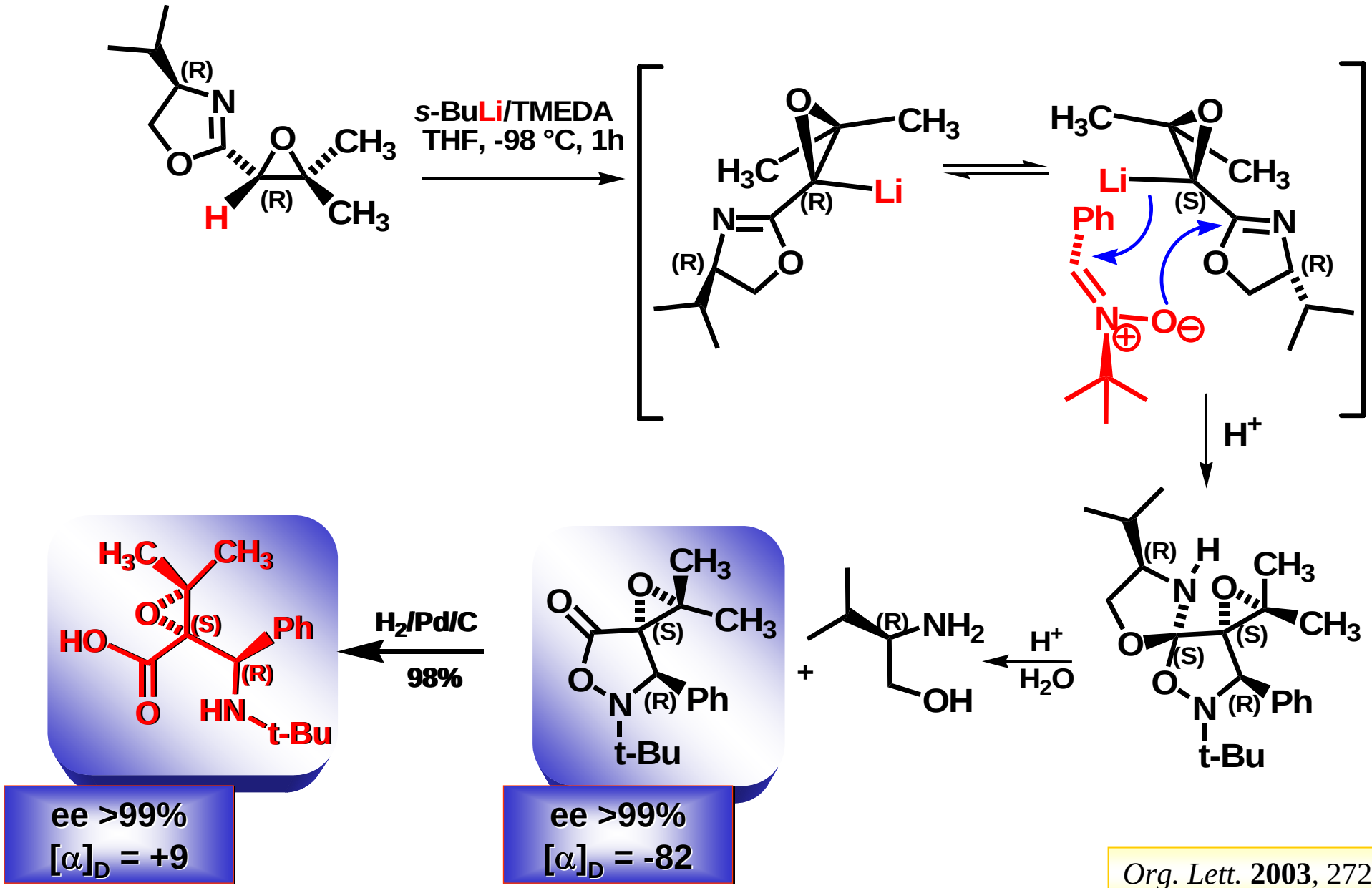




R	R^1	Oxazolidinone Yield %	Amino Acid Yield %
Me	Ph	68	98
"	*p*-$MeOC_6H_4$	85	98
"	*p*-$CF_3C_6H_4$	90	98
Et	Ph	72	98
-$(CH_2)_5$-	Ph	61	98

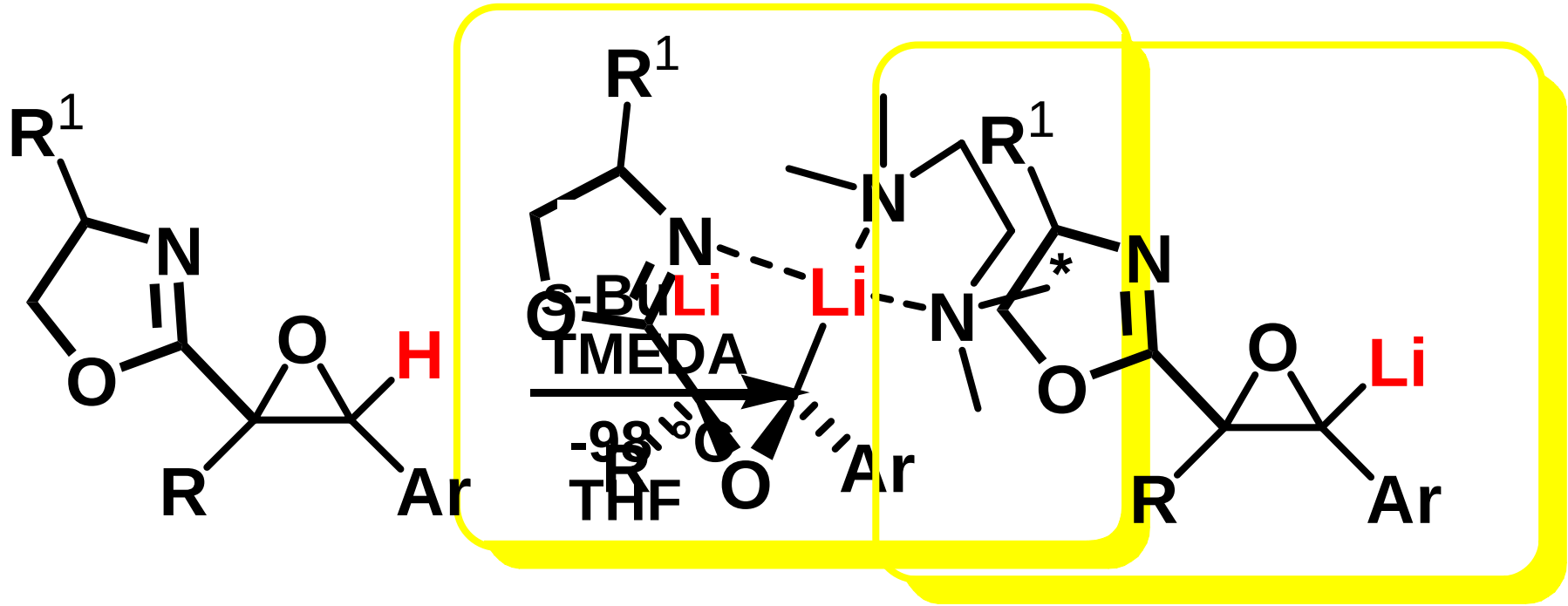
Org. Lett. **2003**, 2723

Enantioselective Synthesis of α-Epoxy-β-Amino Acids



Org. Lett. **2003**, 2723

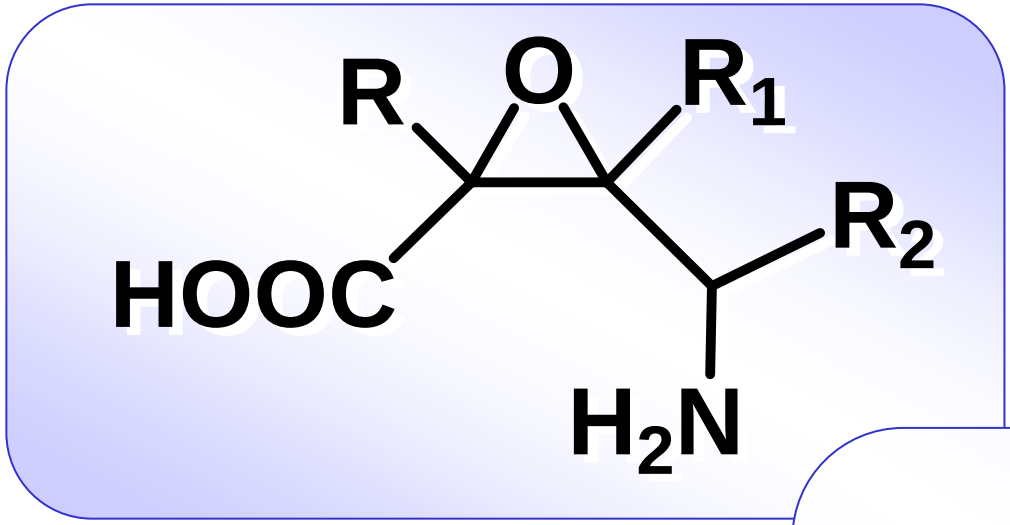
β-LITHIATED OXAZOLINYLOXIRANES



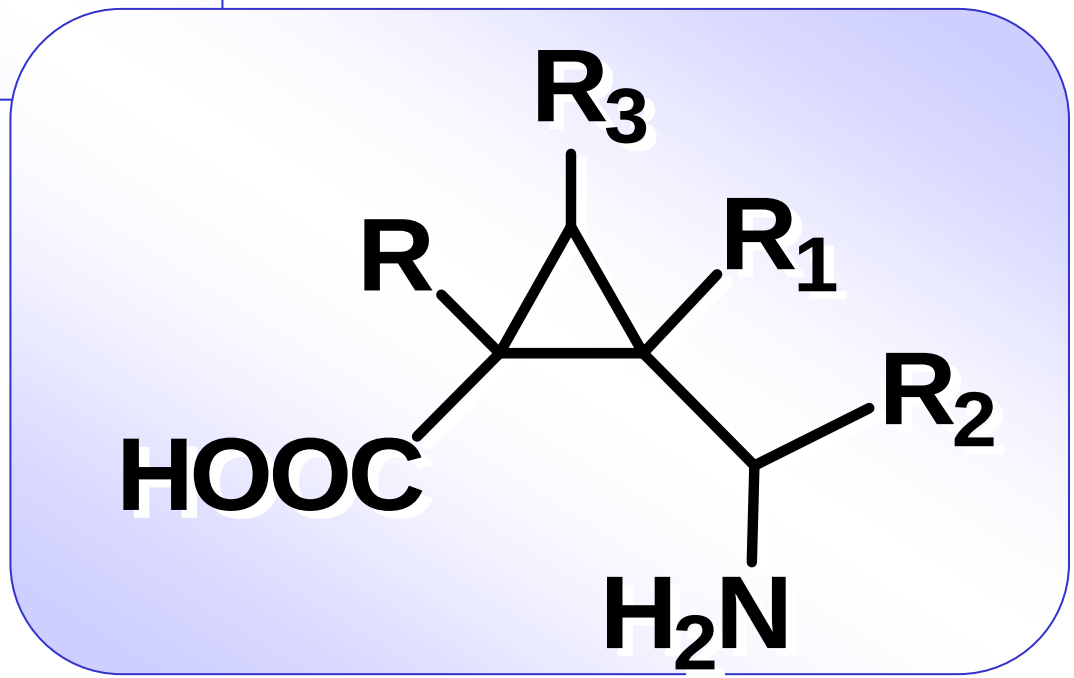
-very easy generation
-Chemically and configurationally stable !
-synthetically useful

γ-Amino Acids

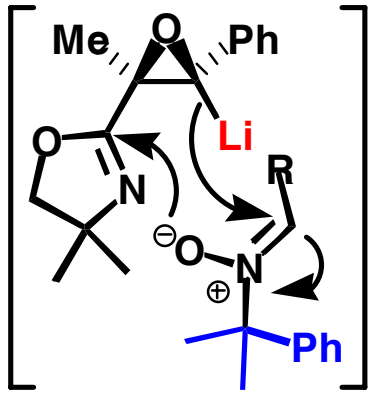
α,β-epoxy-γ-amino acids



α,β-cyclopropyl-γ-amino acids

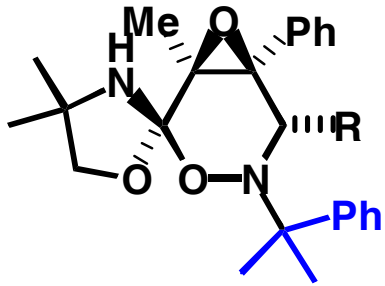


Stereoselective Synthesis of α,β-Epoxy-γ-Amino Acids and α,β-Epoxy-γ-Butyrolactams



NH_4Cl

51-78 %

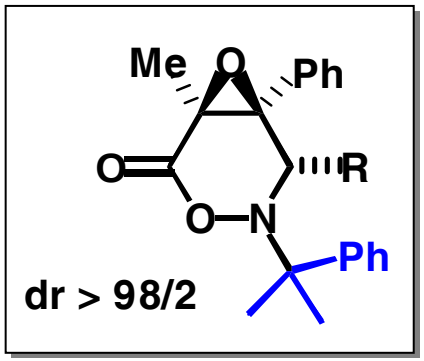


$Dioxane/H_2O$

TFA

R = Ph, *p*-ClC_6H_4, *p*-$MeOC_6H_4$, C_6H_{11}

40-71 %

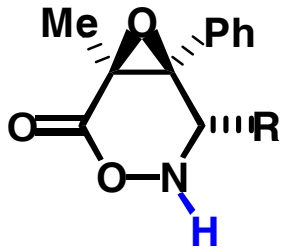


dr > 98/2

CH_2Cl_2/TFA

R = Ph, *p*-ClC_6H_4

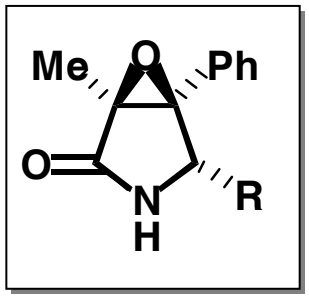
90 %



$HCOONH_4$, Pd/C

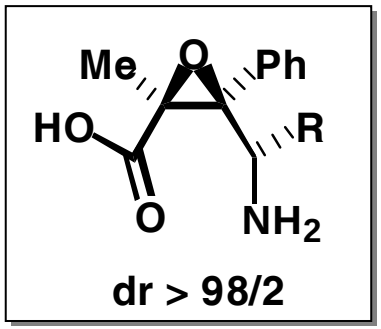
MeOH

R = Ph, 55 %



H_2, Pd/C

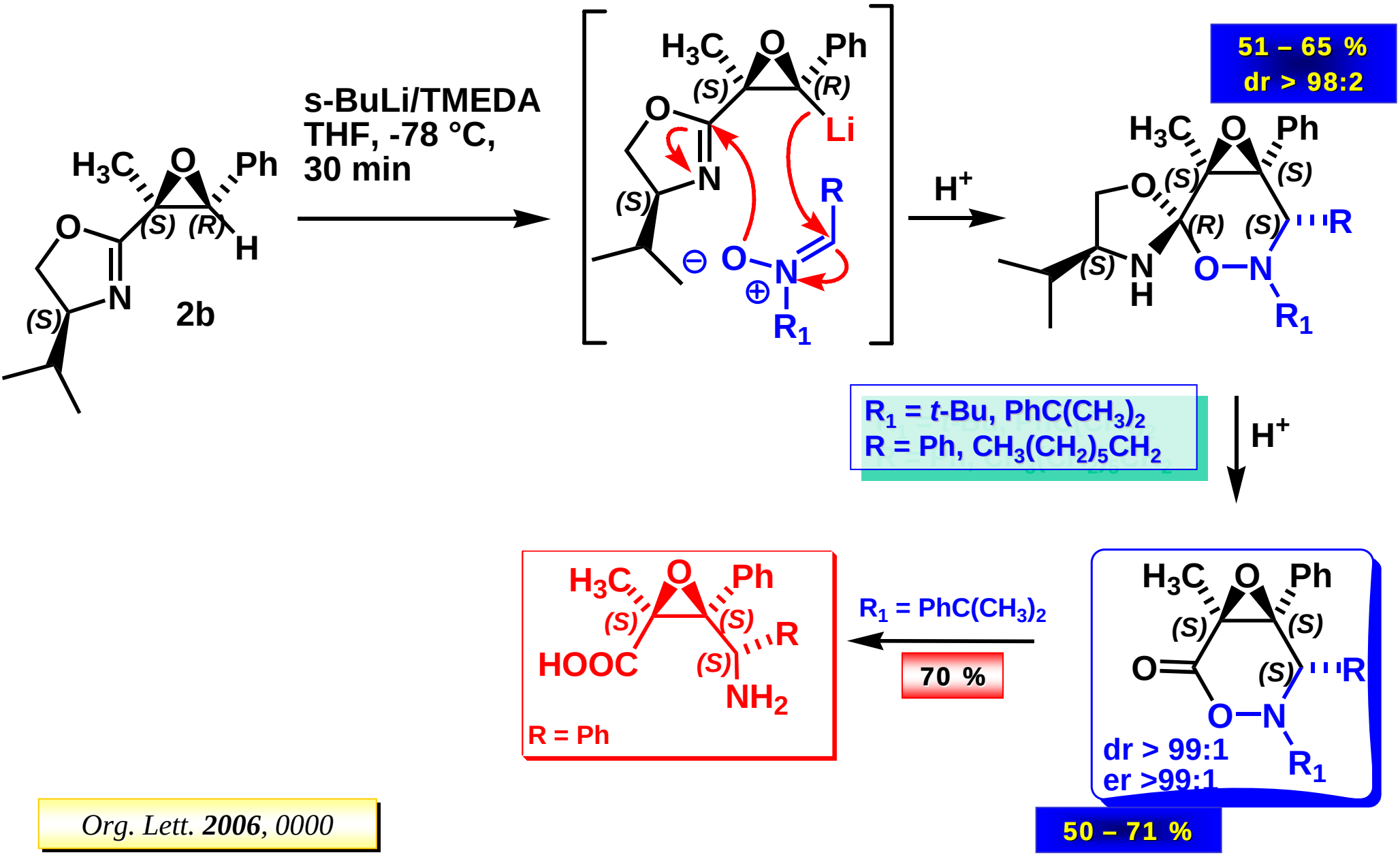
R = Ph, 70 %



dr > 98/2

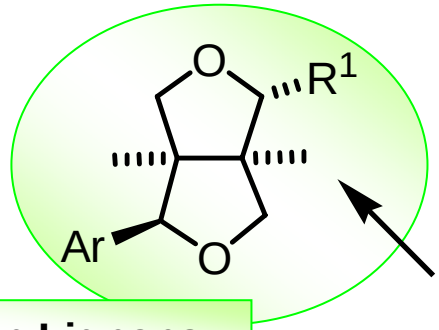
Org. Lett. ***2006***, *0000*

Enantioselective Synthesis of 4,5-Epoxy-1,2-Oxazin-5-ones



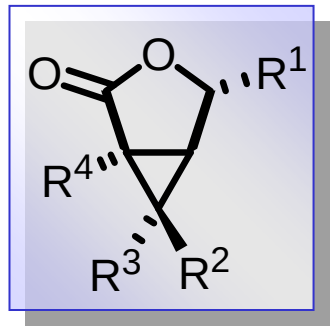
Org. Lett. ***2006***, *0000*

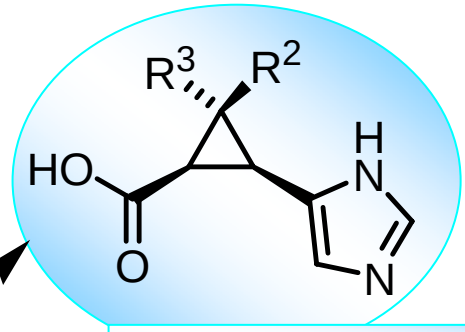
Cyclopropane-γ-lactones: Useful Precursors of Biologically Important Target Molecules



Furofuran Lignans

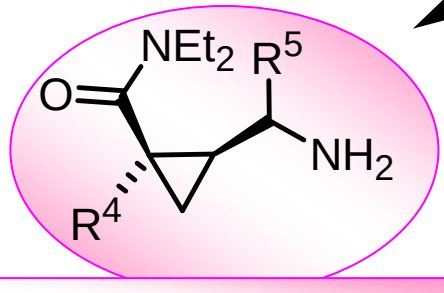
Brown, R. C. D. *et al.*
J. Org. Chem. 2004, *69*, 122.





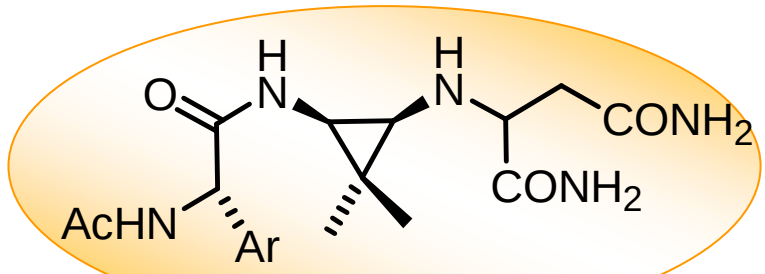
H_3 Histamine Receptor Ligands

Brana, M. F. *et al.Bioorg. Med. Chem. Lett.* 2002, *12*, 3561.



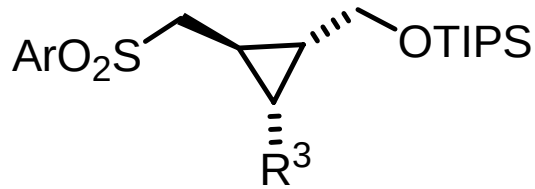
NMDA Receptor Antagonist

Shuto, S. *et al.*
Bioorg. Med. Chem. 2002, *10*, 3829.



Martin, S. F. *et al.*
Tetrahedron Lett. 2003, *59*, 1571.

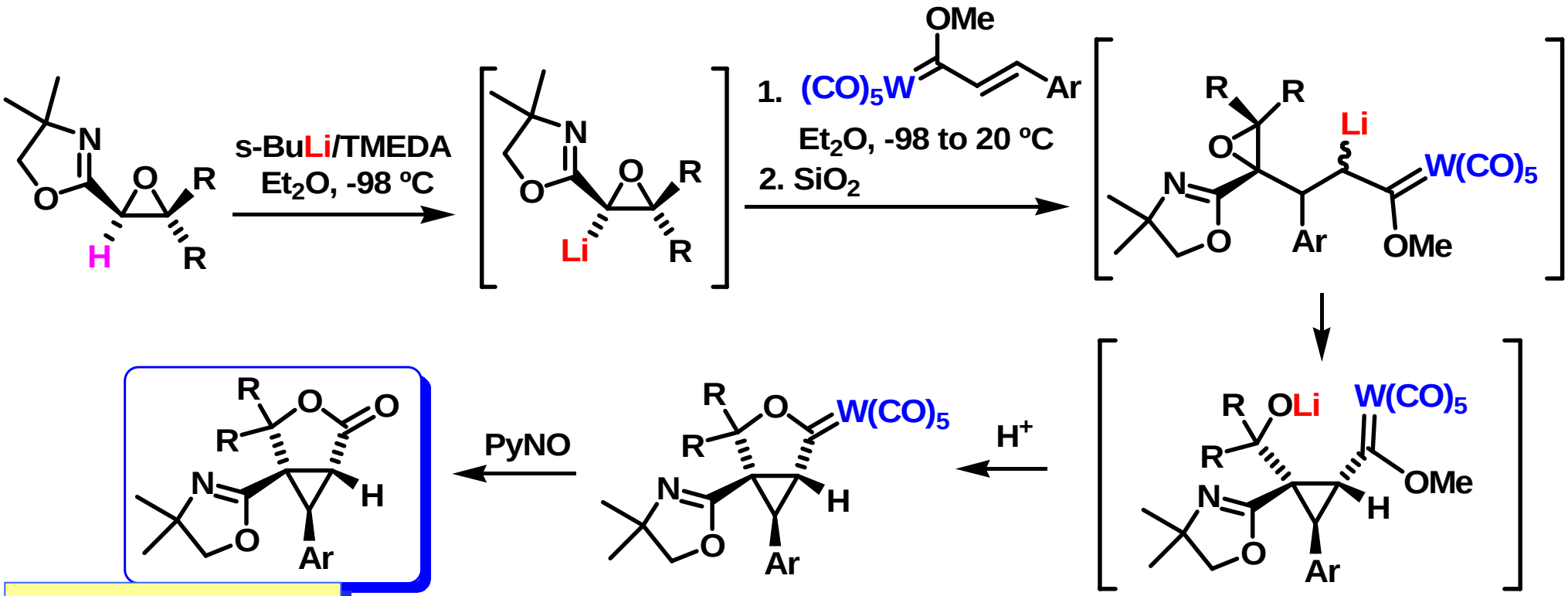
Mammalian Grb2-SH2 Antagonist



(+) Ambruticin S
Novel Antifungal

Martin, S. F. *et al.*
Tetrahedron 2003, *59*, 6819.

Synthesis of Cyclopropane-γ-lactones, precursors of cyclopropane-γ-amino acids

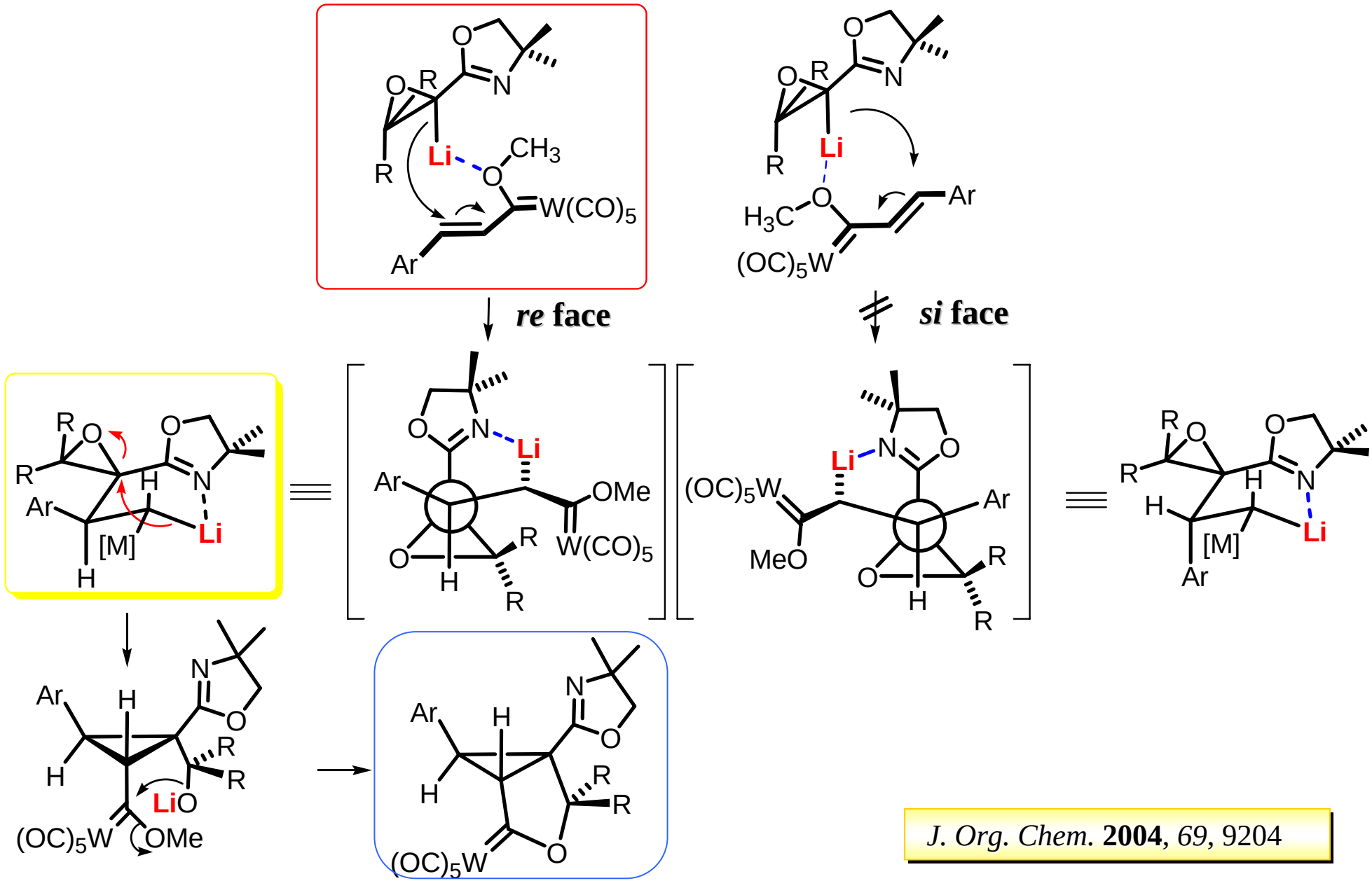


R	Ar	Yield (%)
Ph	Ph	80
"	2-Furyl	75
"	4-$MeOC_6H_4$	81
"	4-ClC_6H_4	83
Me	4-ClC_6H_4	61

Yield of Pentacarbonyl(3-oxa-2-bicyclo[3.1.0] hexylidene)-Tungsten Complexes

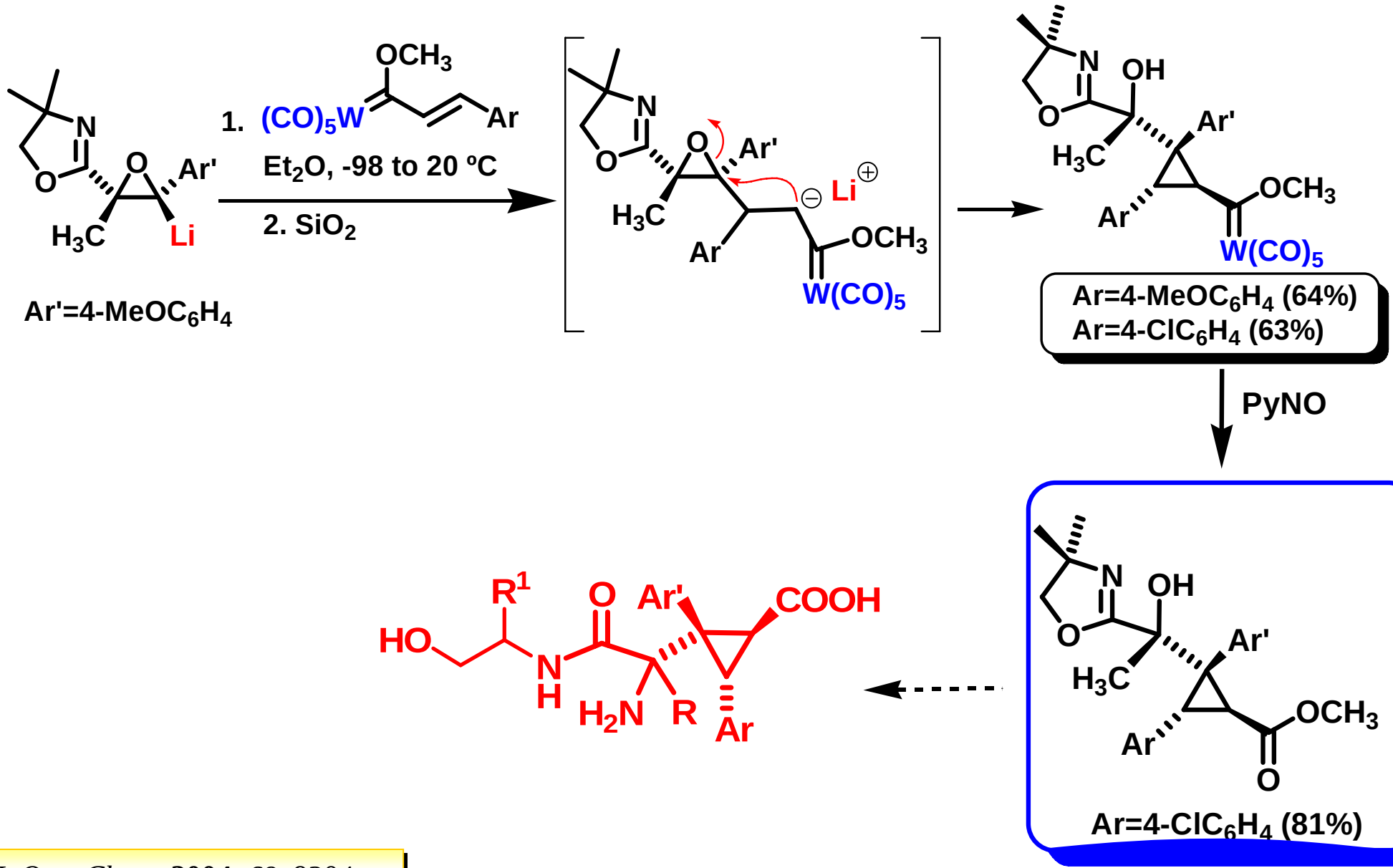
J. Org. Chem. **2004**, *69*, 9204

Cyclopropanation of Lithiated Oxazolinyloxiranes with Fischer Carbene Complexes: Synthesis of Cyclopropane-γ-lactones



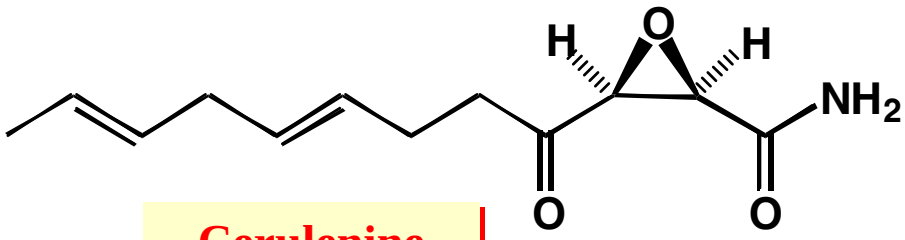
J. Org. Chem. **2004**, *69*, 9204

Cyclopropanation of Lithiated Oxazolinyloxiranes with Fischer Carbenes: Synthesis of cyclopropane-γ-hydroxy esters

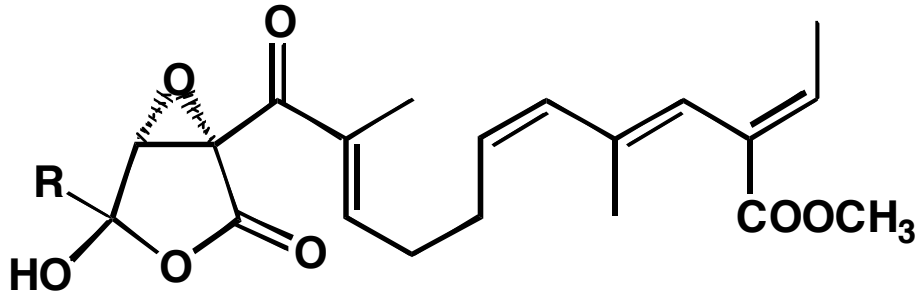


J. Org. Chem. **2004**, *69*, 9204

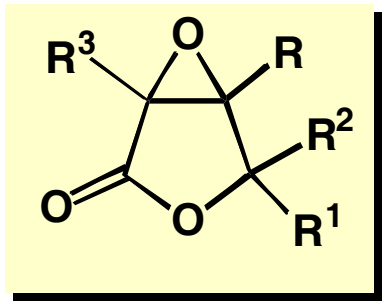
Synthetic Use of Epoxy Lactones

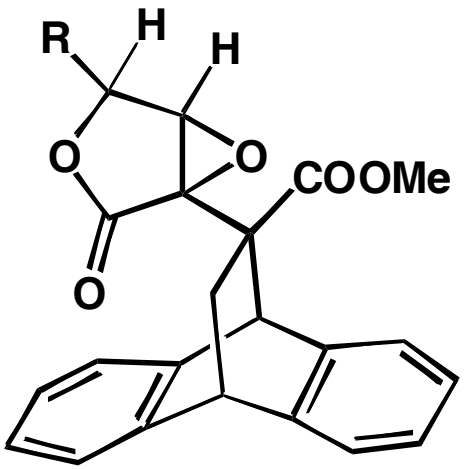


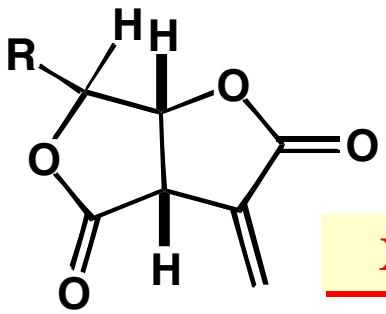
Cerulenine



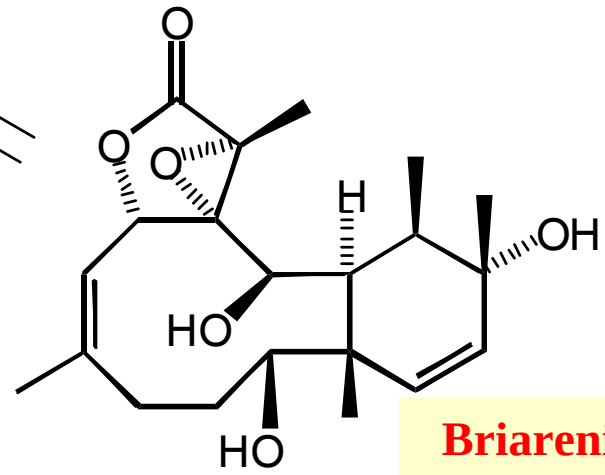
Epolactaene





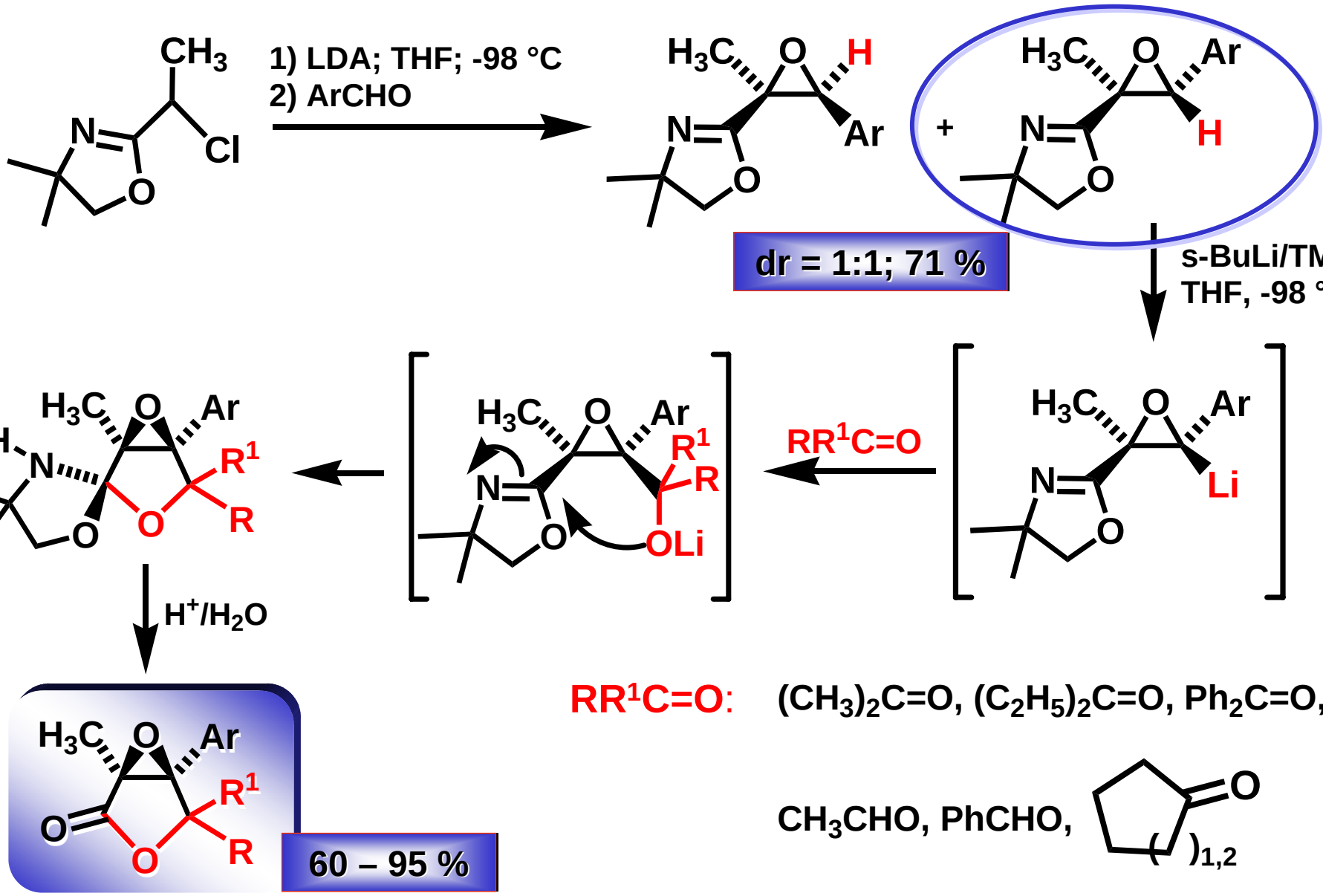


Xilobovide



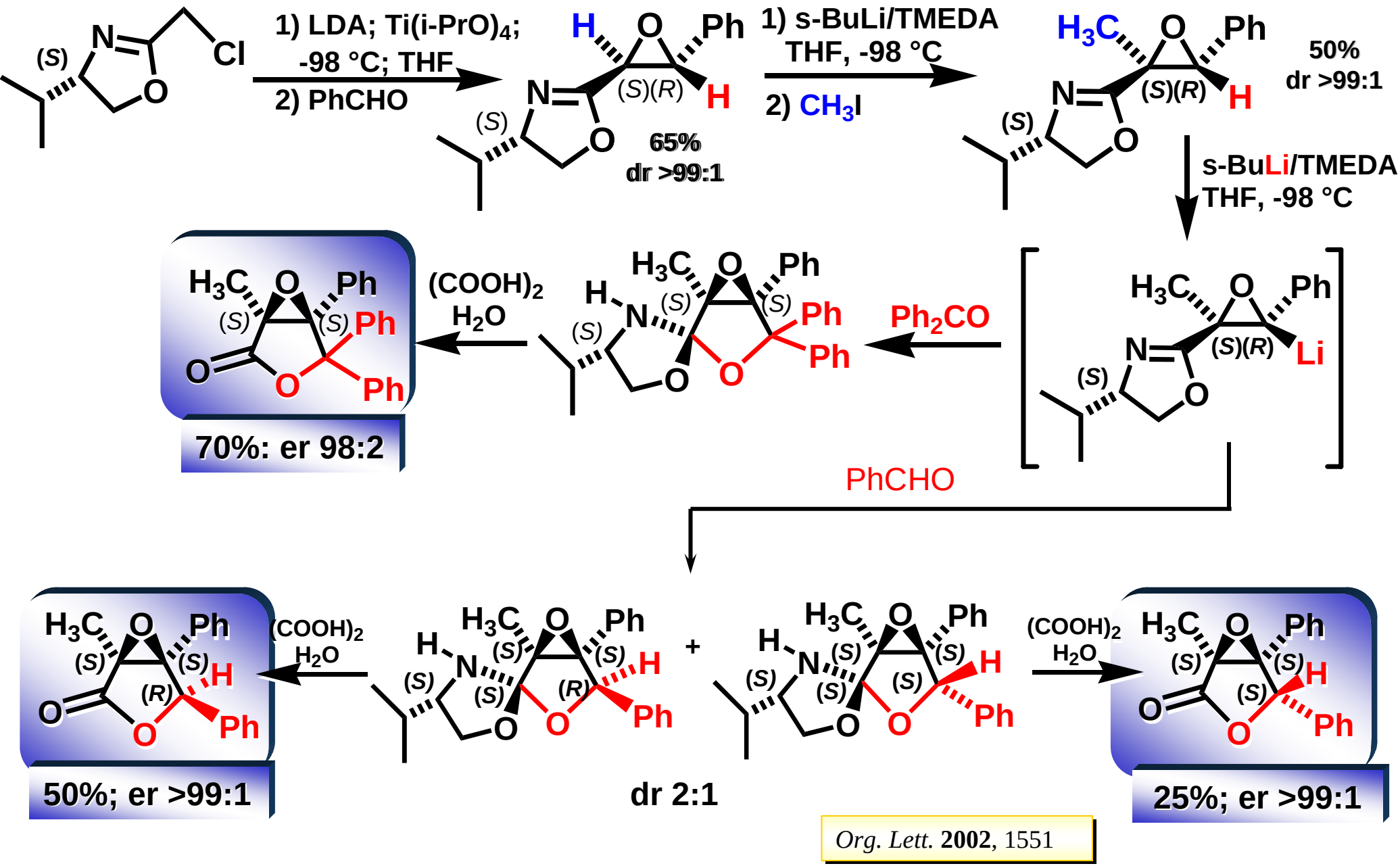
Briarenic diterpenes

Stereoselective Synthesis of α,β-Epoxy-γ-Butyrolactones



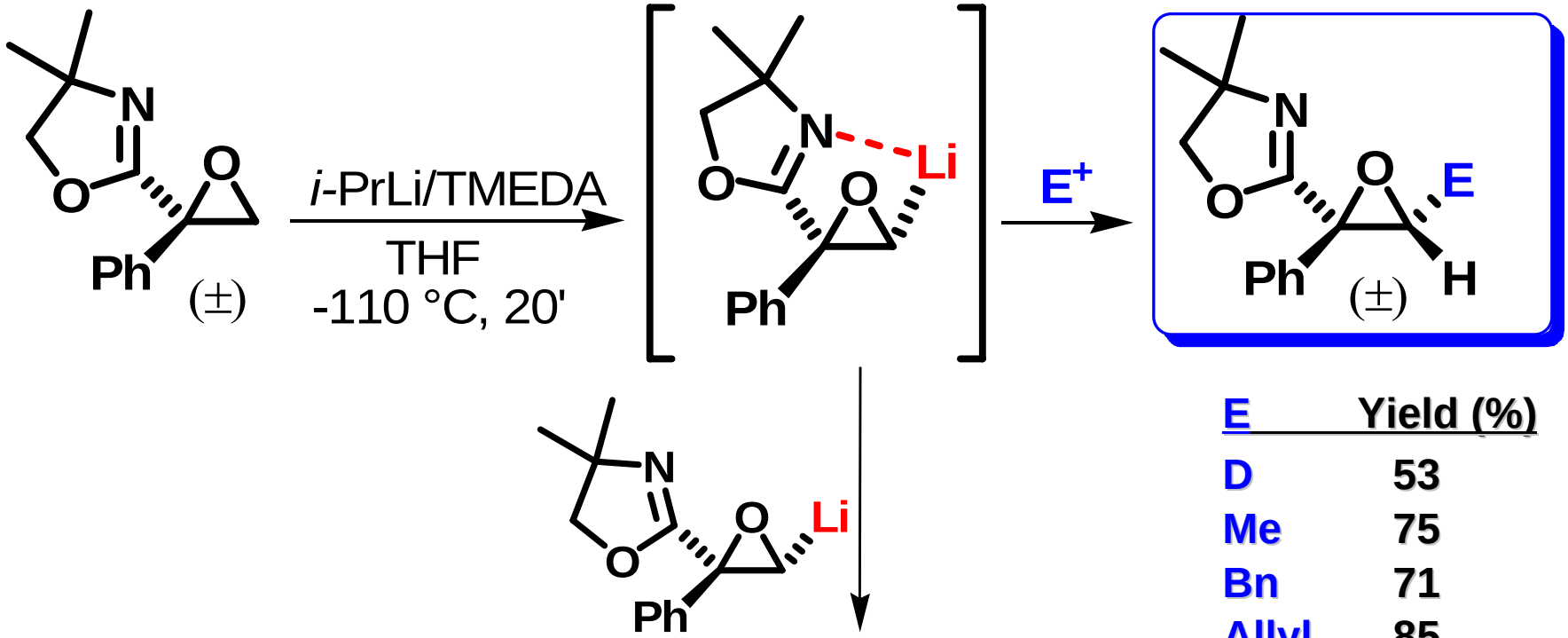
Org. Lett. **2002**, 1551

Enantioselective Synthesis of α,β-Epoxy-γ-Butyrolactones

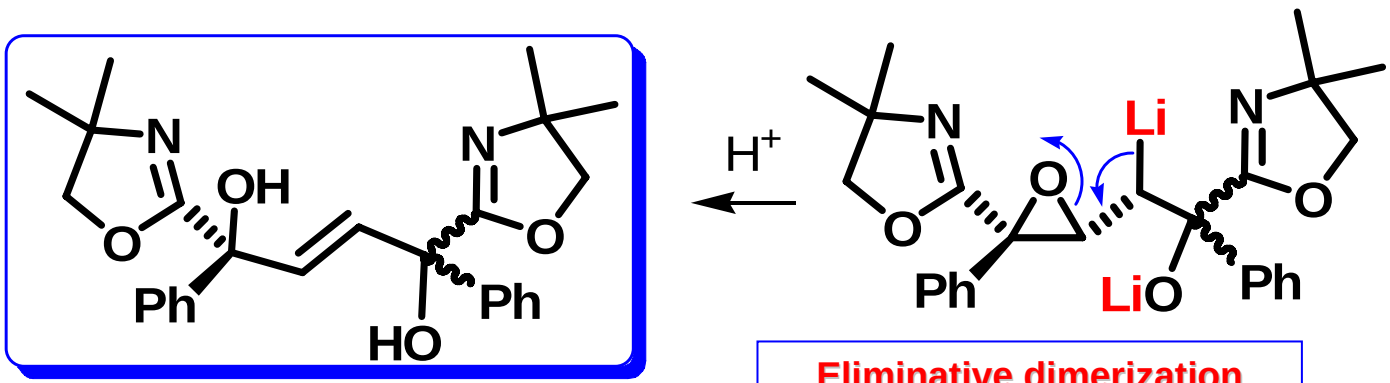


Org. Lett. **2002**, 1551

Regioselective lithiation of terminal Oxazolinyloxiranes



E	Yield (%)	
D	53	
Me	75	
Bn	71	
Allyl	85	
Me_3Si	90	In situ quench
Bu_3Sn	50	In situ quench

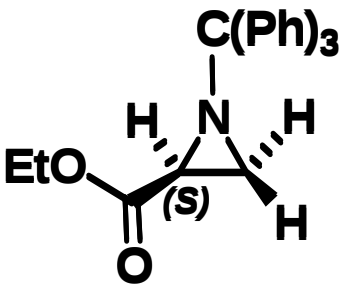


Mixture of Diastereomers

Eliminative dimerization

Unpublished Results

Regioselective lithiation of terminal Oxazolinylaziridines

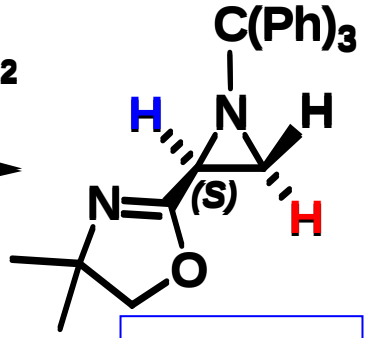


er > 98 : 2

1) HO, NH2

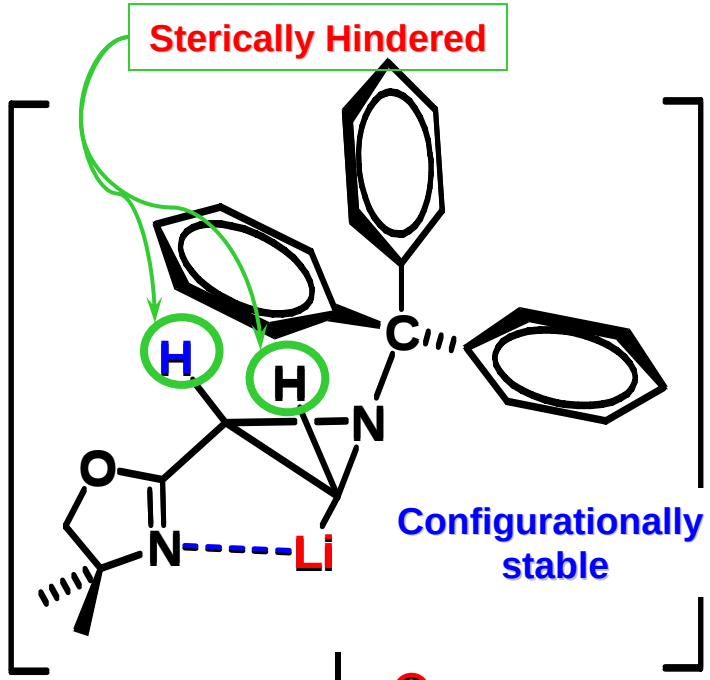
2) DAST

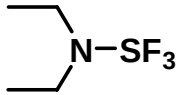
80 %



er > 98 : 2

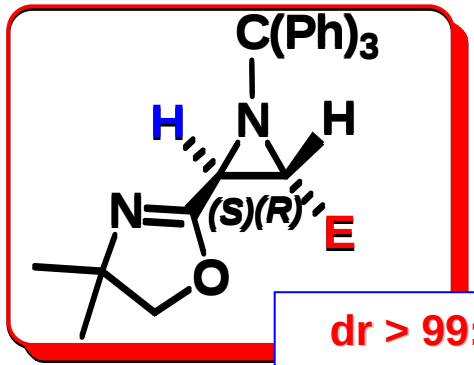
s-BuLi
TMEDA
THF, -78 °C
4h



DAST = 

E^+	Yield %
D_2O	75
MeI	75
EtI	60
BnBr	45
AllylBr	66
$Me_2AllylSiCl$	70
Bu_3SnCl	75
Et_2CO	44

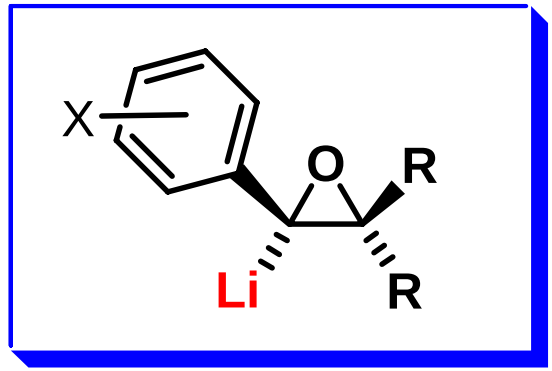
$E^{\oplus}$



dr > 99:1
er > 98:2

Unpublished results

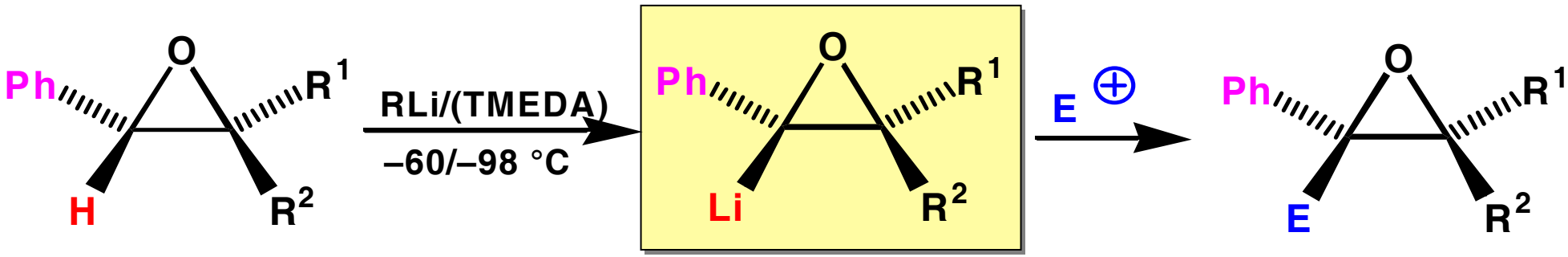
Lithiated Aryloxiranes:



-Chemically and configurationally stable

-Synthetically useful

Lithiated Aryloxiranes

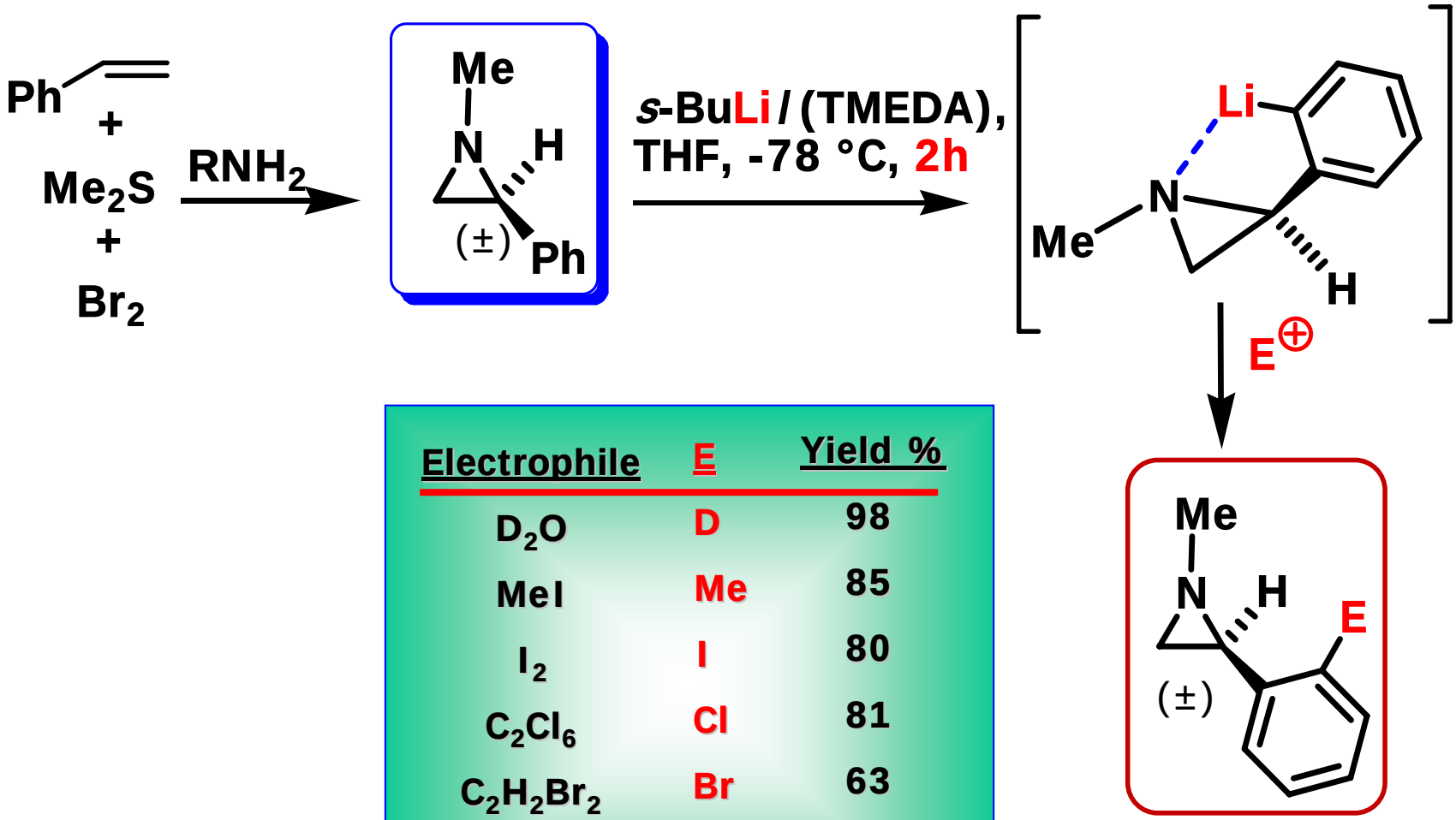


Lifetime : 30 min-2h

Chemically and configurationally stable

R^1, R^2 = H, Me, Ph, 2-oxazolin-2-yl

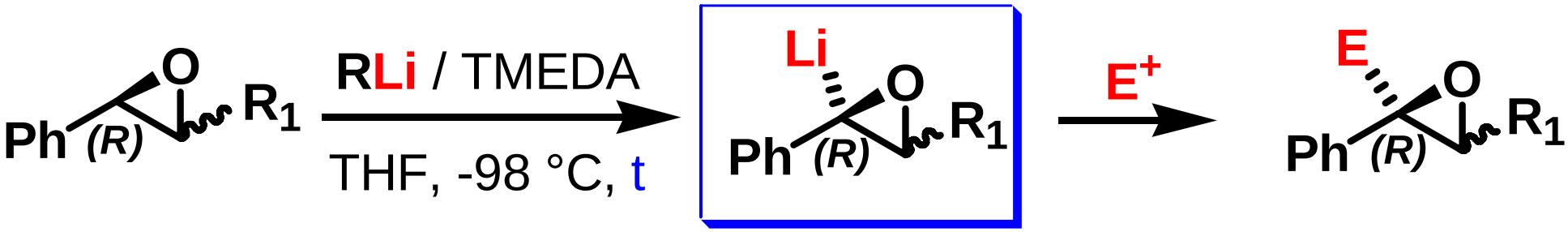
Trapping of *ortho*-lithiated N-methylphenylaziridine



Electrophile	E	Yield %
D_2O	D	98
MeI	Me	85
I_2	I	80
C_2Cl_6	Cl	81
$C_2H_2Br_2$	Br	63
DMF	CHO	98
PhCONH(OMe)	PhCO	50

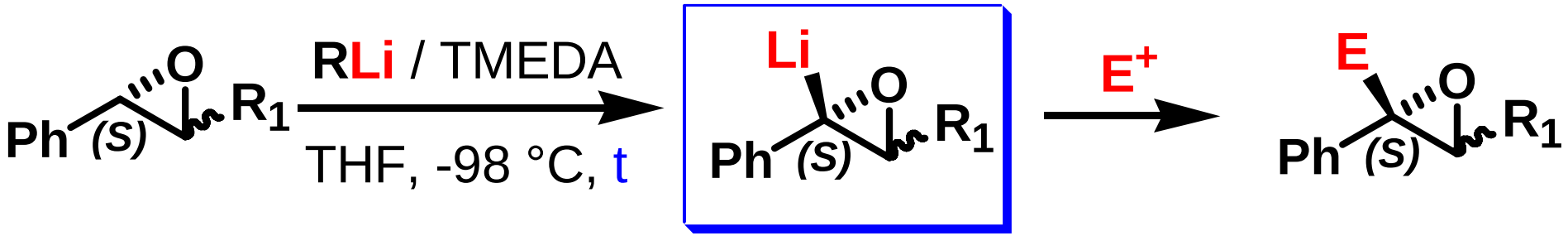
Org. Lett. **2005**, 7, 3749-3752

Stereospecific Synthesis of Substituted Aryloxiranes



R_1 = H, CH_3, Ph
RLi = s-BuLi, n-BuLi;
t = 0.5 – 2h

Chemically and Configurationally Stable



E^+ = D_2O; CH_3I; CH_3CH_2I; CH_2=$CHCH_2Br$; $PhCH_2Br$; MetallylCl
$(CH_3)_2CO$; $PhCON(CH_3)_2$; PhCHO; Cyclopentanone;
Yields: 51 – 98 %; dr: > 98:2; er = 97:3 – 99:1

Org. Lett. **2002**, 2445

J. Org. Chem. **2004**, 3330

Lithiated Aryloxiranes:

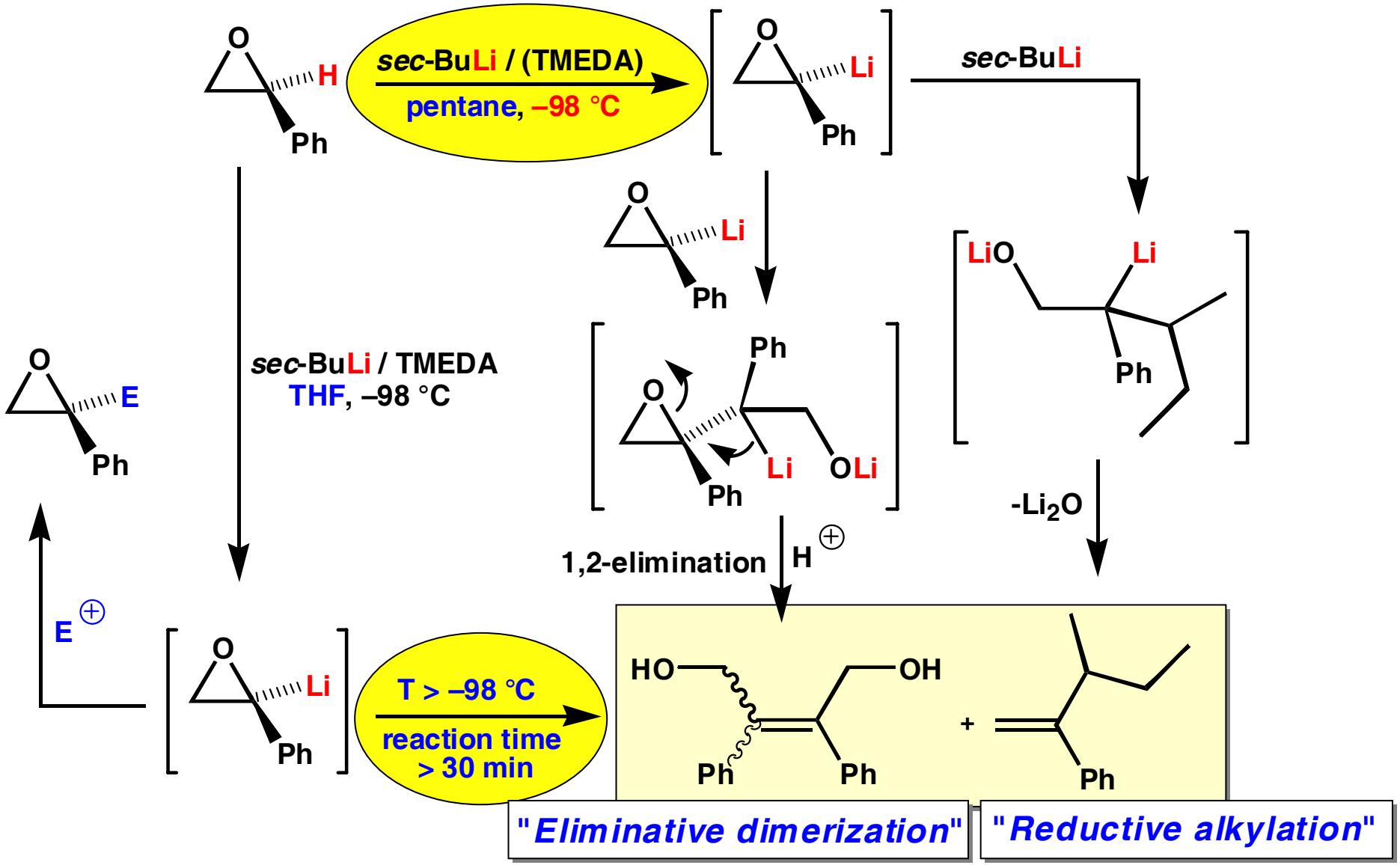
-Are they carbanions or carbenoids?

-Does the aryl group provide stability to the lithiated oxirane?

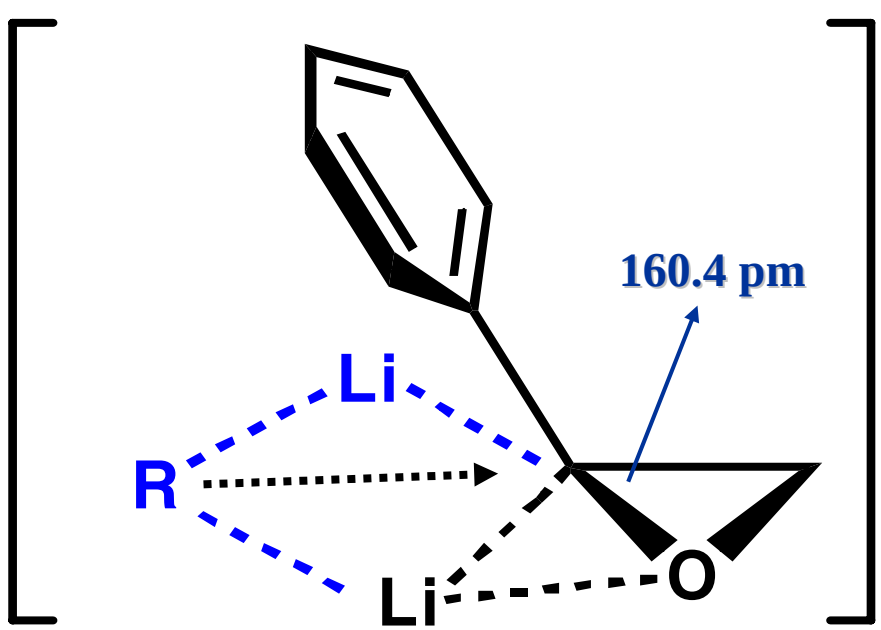
-Chemical Experiments

-Ab initio Calculations

Carbenoid Character of α-Lithiated Styrene Oxide



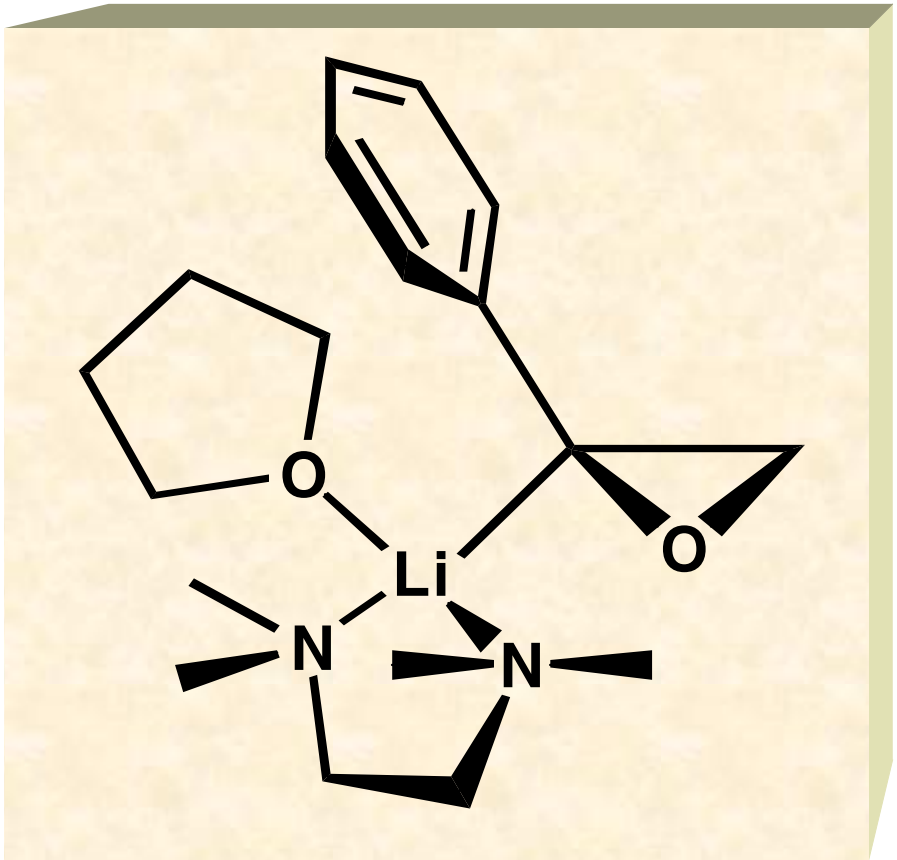
Transition State Model of the Reaction of α-Lithiated Styrene Oxide with RLi in Non-Donor Solvents and in the Absence of Ligands



Metal Assisted Ionization ("MAI") Effect

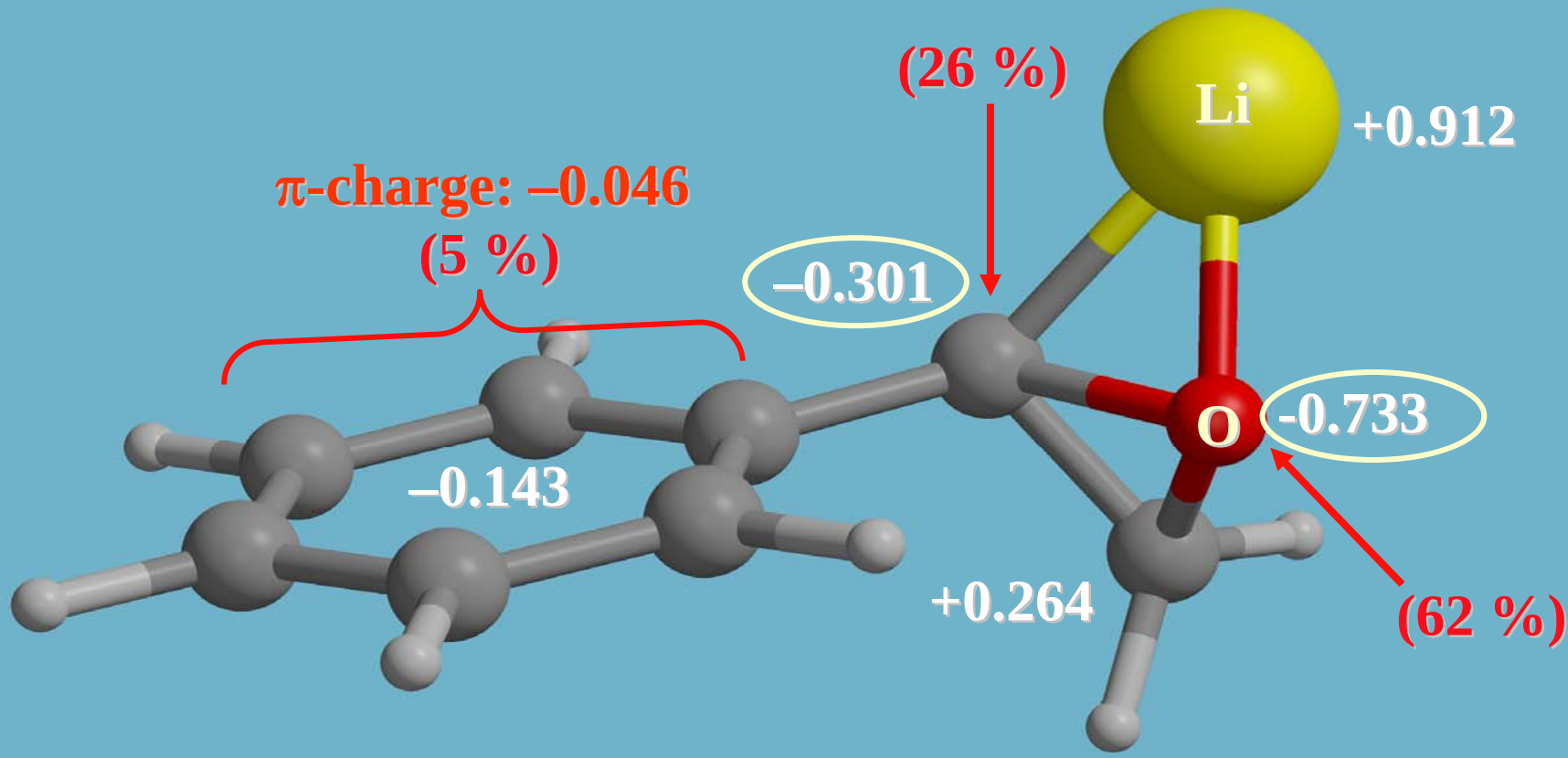
The bridging Li could help to cleave the C–O bond "Metal-Assisted Ionization"

Lithiated Styrene Oxide might be "Terminally Bonded" in Good Donor Solvents and in the Presence of Ligands



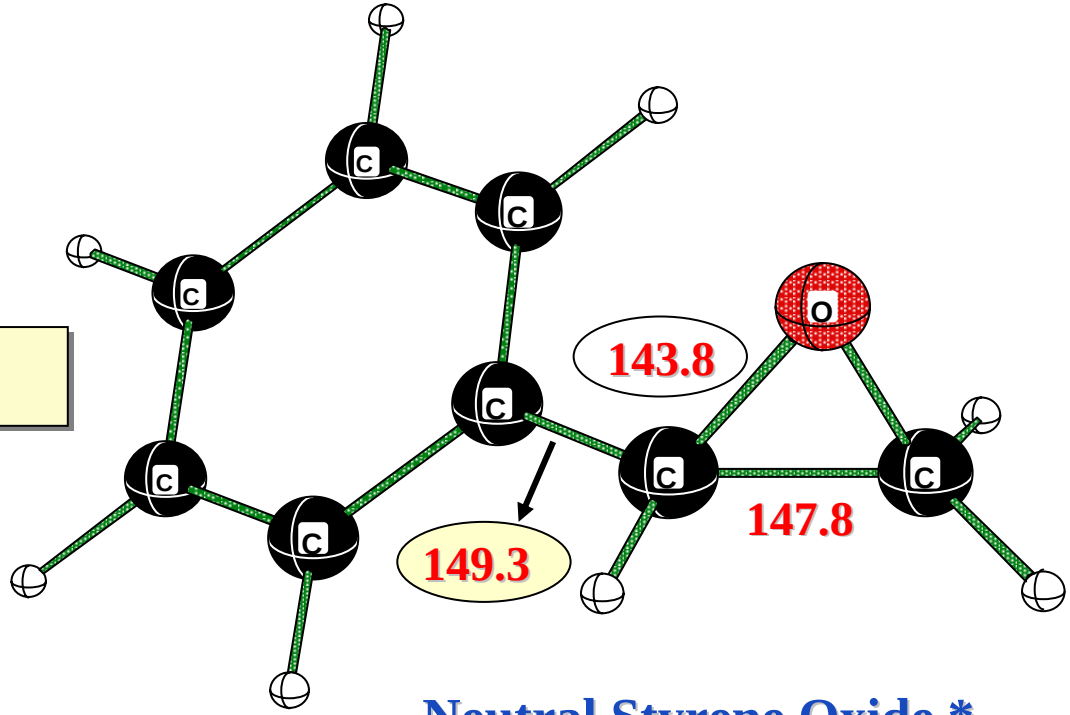
Donor solvents (e.g. THF) and ligands (e.g. TMEDA) could compete successfully with Li–C–O bridges favouring tetrahedral isomers with "less carbenoid" character.

Charge Mapping by Natural Population Analysis

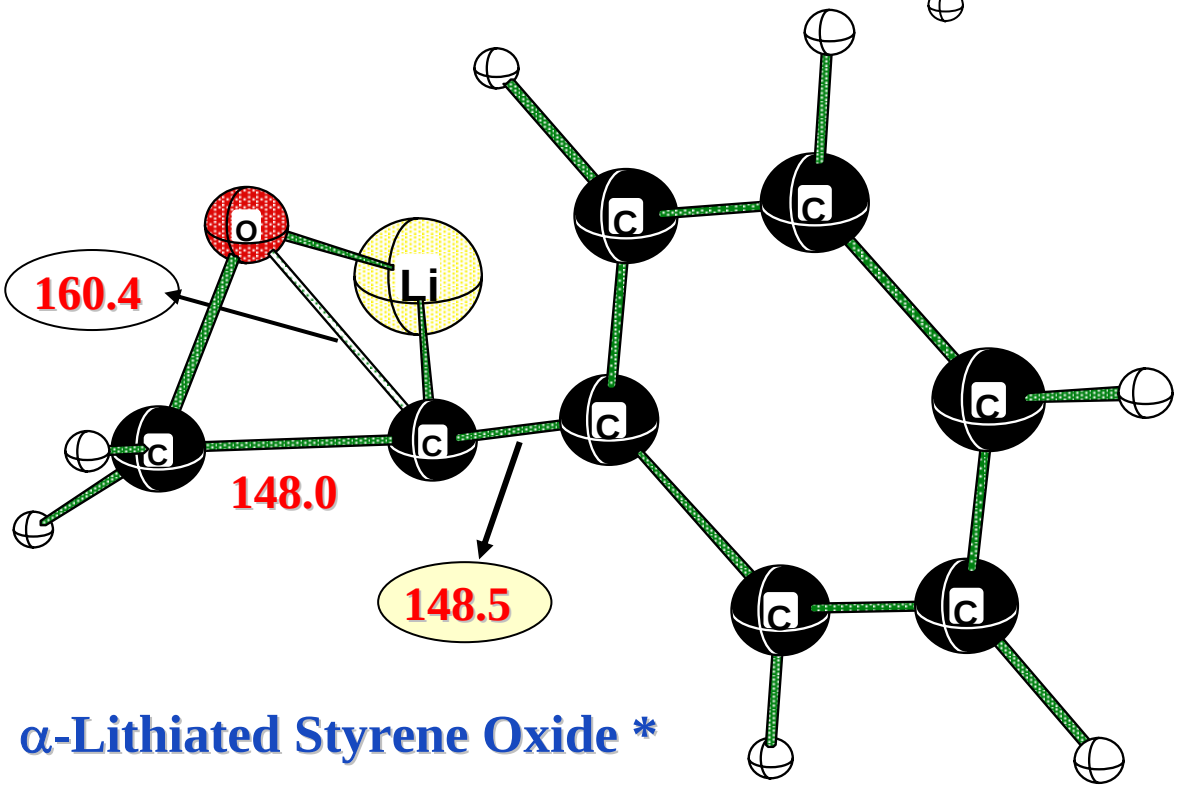


B3LYP/6-311+G*// B3LYP/6-31+G*

B3LYP/6-311+G*// B3LYP/6-31+G*



Neutral Styrene Oxide *

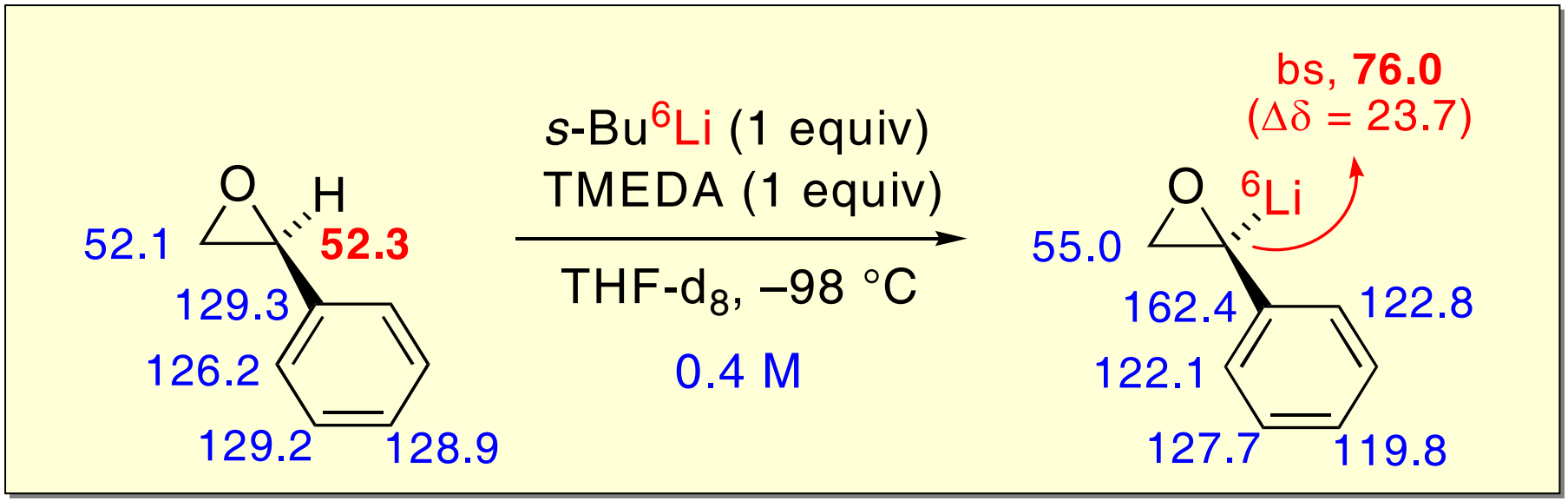


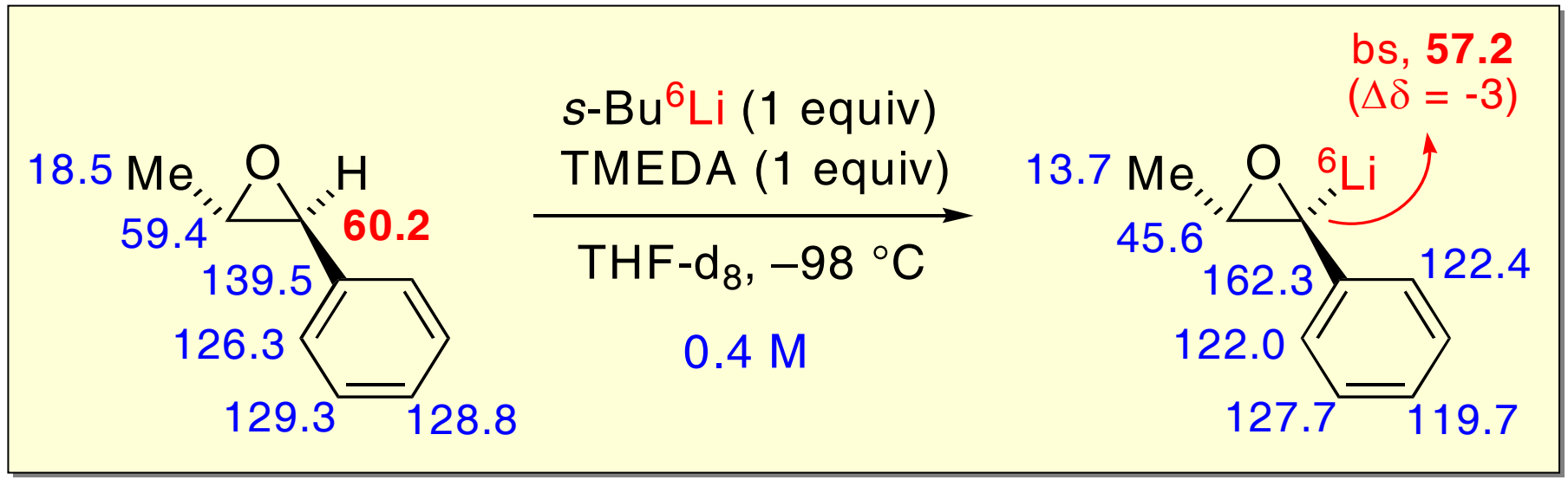
α-Lithiated Styrene Oxide *

The σ_{C-O} bond is weakened and thus more easily attacked by a nucleophile !

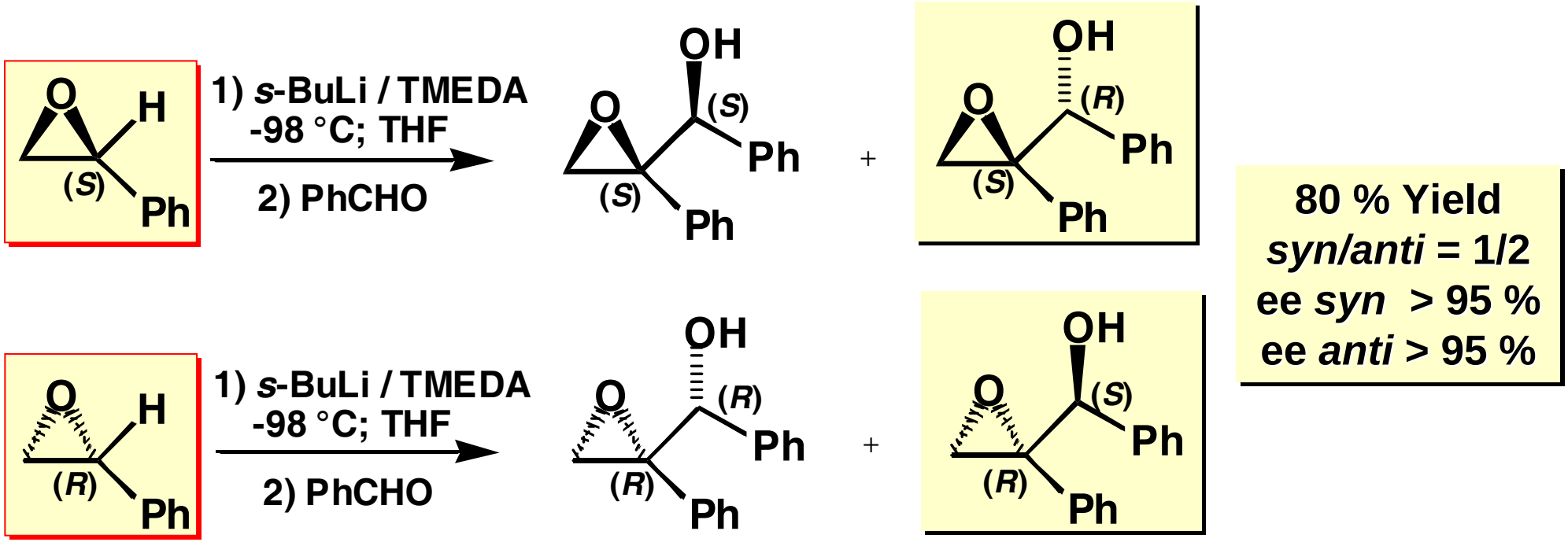
* Bond-lengths in pm

Lithiated Styrene Oxide:
a Multinuclear NMR Investigation





Stereospecific Deprotonation of Styrene Oxides

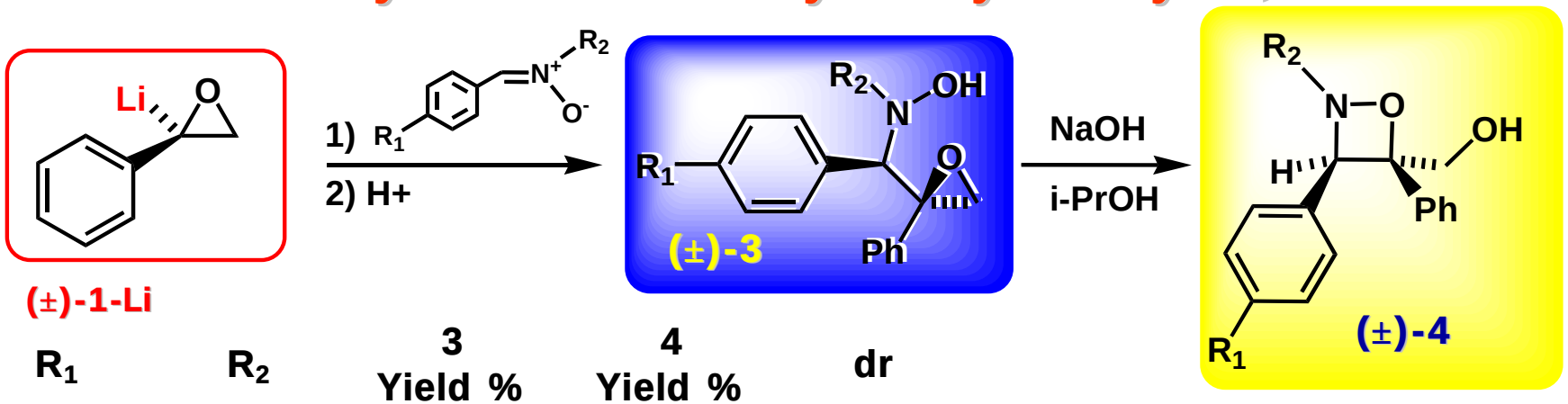


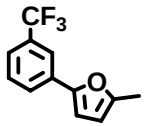
80 % Yield
syn/anti = 1/2
ee *syn* > 95 %
ee *anti* > 95 %

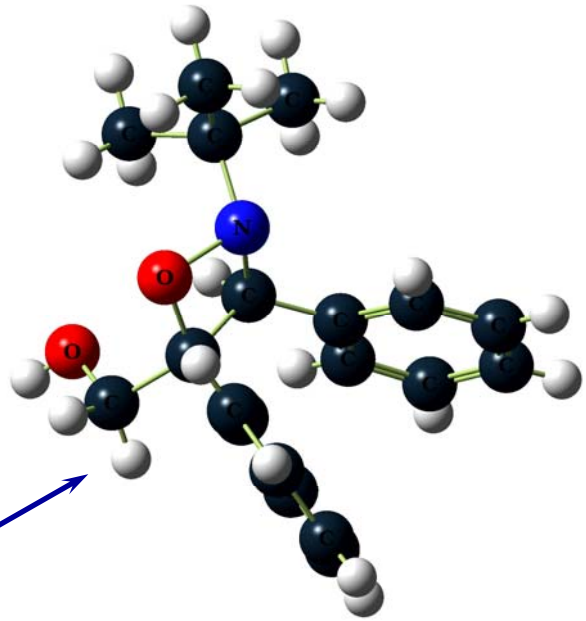
Optically active Styrene Oxide is not an Asymmetry Inductor

Org. Lett. **2002**, 2445

Stereoselective Synthesis of 4-Hydroxymethyl-1,2-oxazetidines

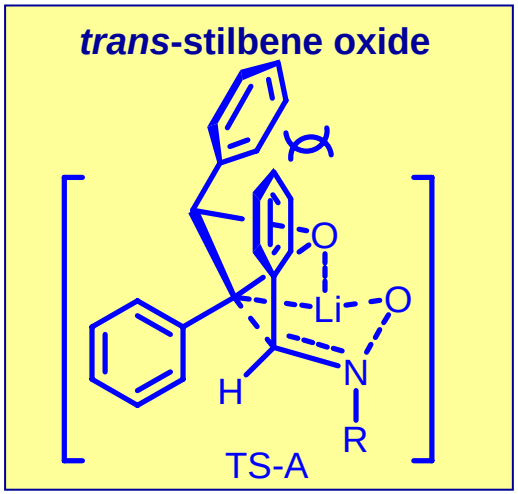


R_1	R_2	3 Yield %	4 Yield %	dr
Me	$PhCMe_2$	42	70	>98/2
Cl	$PhCMe_2$	50	70	>98/2
2-Furyl	$PhCMe_2$	82	62	>98/2
H	$PhCMe_2$	60	50[a]	>98/2
MeO	$PhCMe_2$	54	40[a]	>98/2
	$PhCMe_2$	82	65	>98/2
CF_3	t-Bu	60	50	90/10
H	t-Bu	63	58[a]	>98/2
Cl	t-Bu	78	>95	>98/2
H	$PhCH_2$	no reaction	-	-



Org. Lett. **2006**, 8, 3923-3926

Mechanistic Hypothesis



re

si

TS-A

TS-B

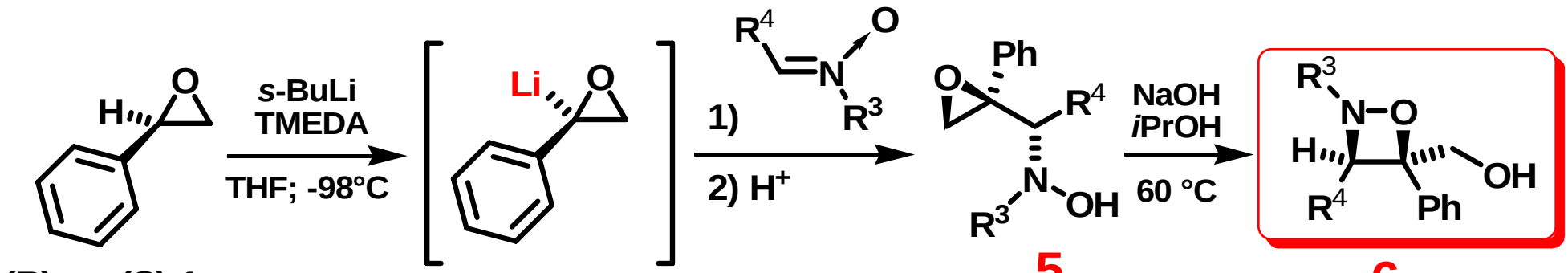
$H^{\oplus}$

S_N2

4-exo-tet

Org. Lett. **2006**, 8, 3923-3926

Asymmetric Synthesis of 1,2-Oxazetidines



(R)- or (S)-1

er = 98/2

configurationally stable

5

er = 98/2

6

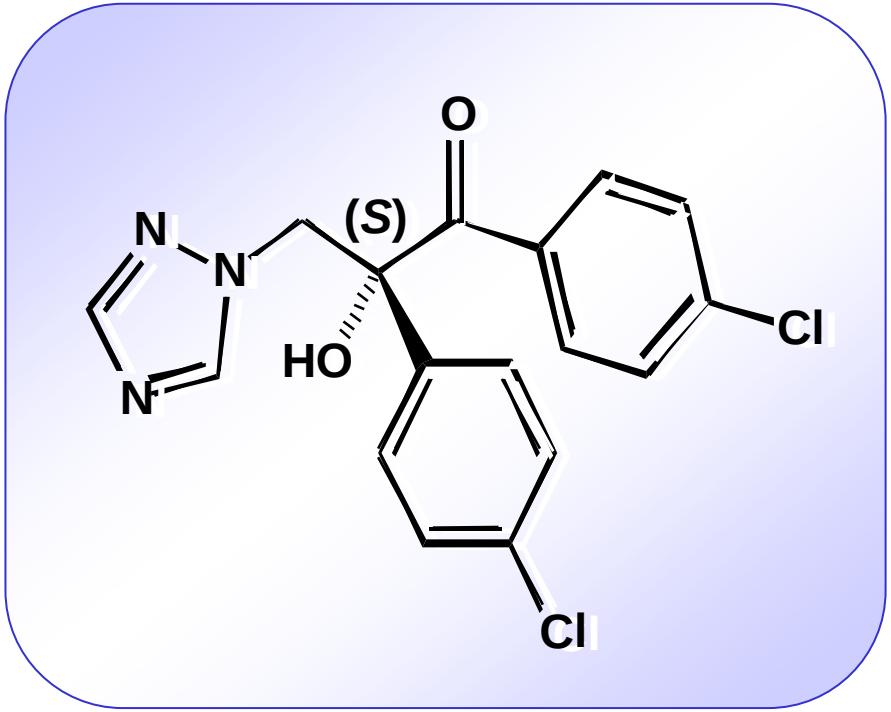
er = 98/2

R^4	R^3	5 Yield %	6 Yield %	er	dr
4-ClC_6H_4	Cumyl	78	78	98/2	>98/2
2-Furyl	Cumyl	60	62	98/2	>98/2
Ph	*t*-Butyl	63	80[a)]	98/2	>98/2
Ph	*t*-Butyl	60	75[a)]	98/2	>98/2

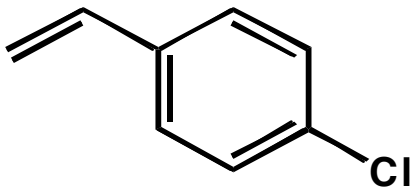
a) Reaction performed at room temperature

Org. Lett. **2006**, 8, 3923-3926

Triazole Antifungal Agents

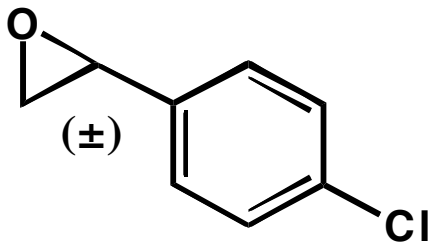


Hydrolitic Kinetic Resolution of 4-Chlorostyrene Oxide



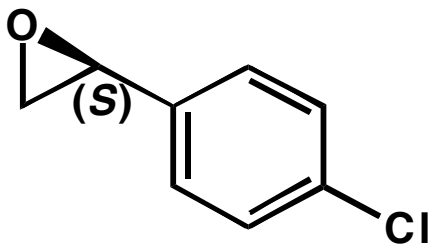
H_2O_2, CF_3COCH_3
pH = 11

quant.



(*S*,*S*)-(salen)$Co^{III}OAc$

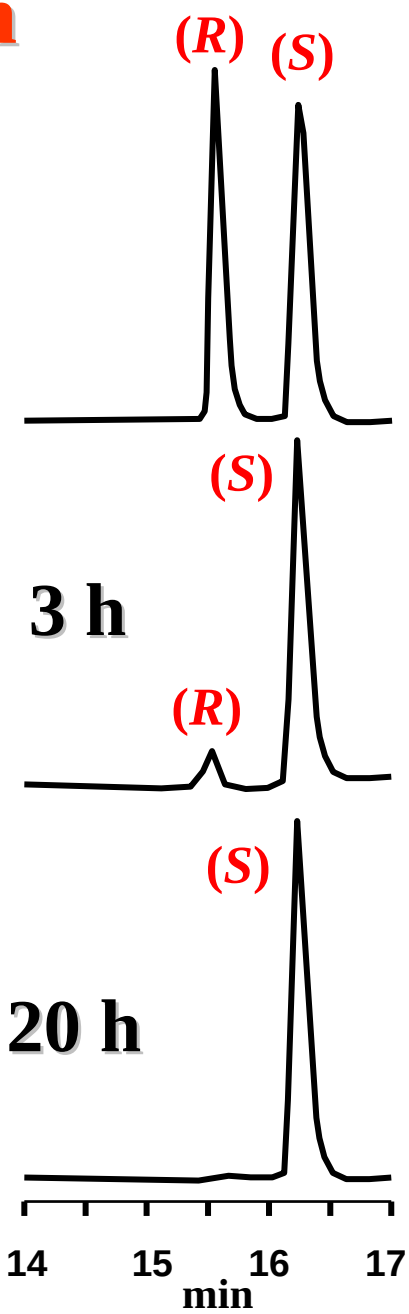
H_2O, 24 h
38 %



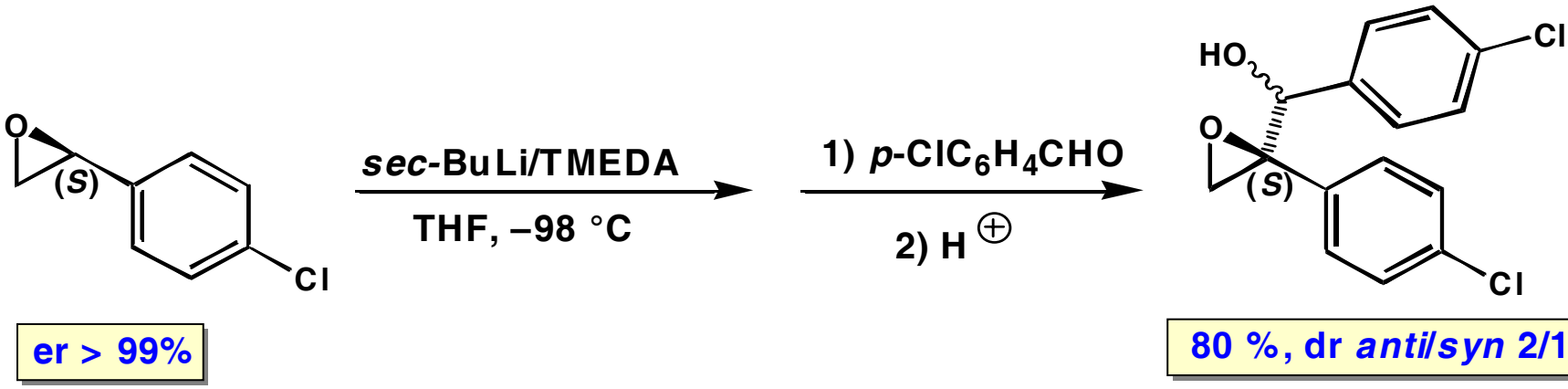
er > 99%

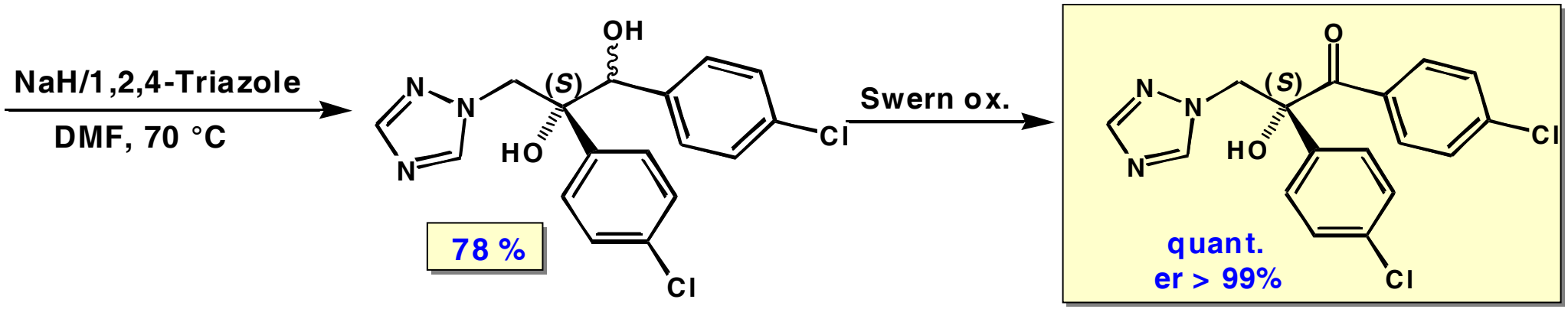
Org. Lett. **2002**, 2445

HKR monitored by chiral GC



Synthesis of an Optically Active Triazole Antifungal Agent



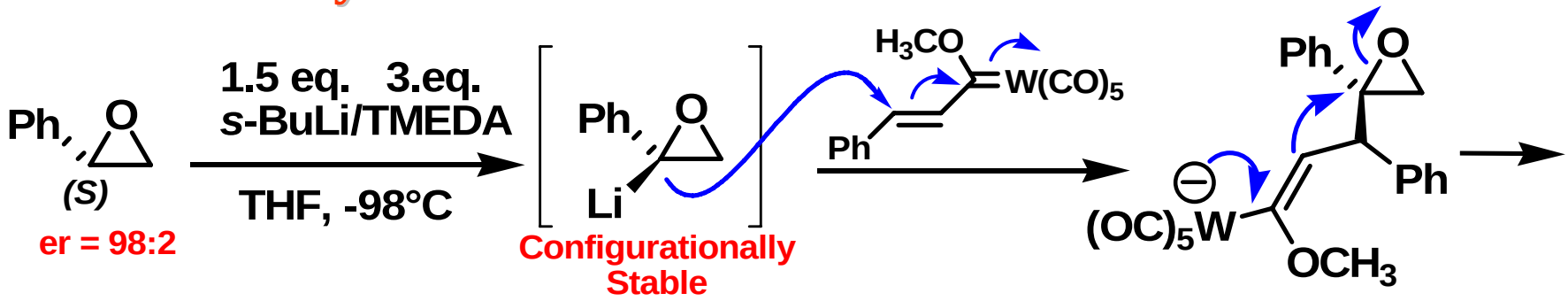


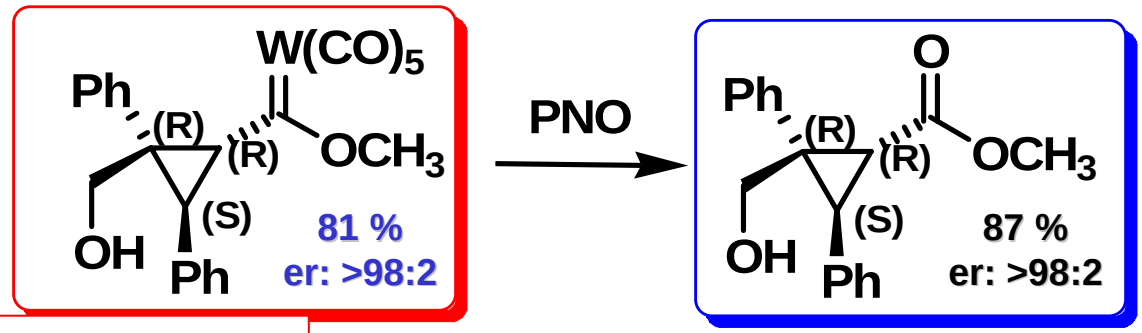
$[\alpha]_D$ = +113.5
lit. $[\alpha]_D$ = +117.3

Org. Lett. **2002**, 2445

Synthesis of Optically Enriched Cyclopropanes

Cyclopropanation Reaction of Optically Active Lithiated Styrene Oxide with Fischer Carbenes

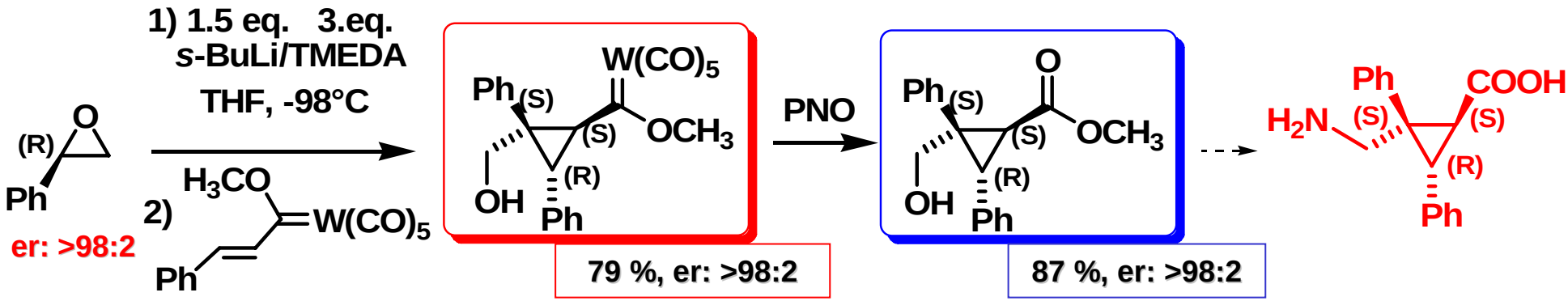




Single Diastereomer

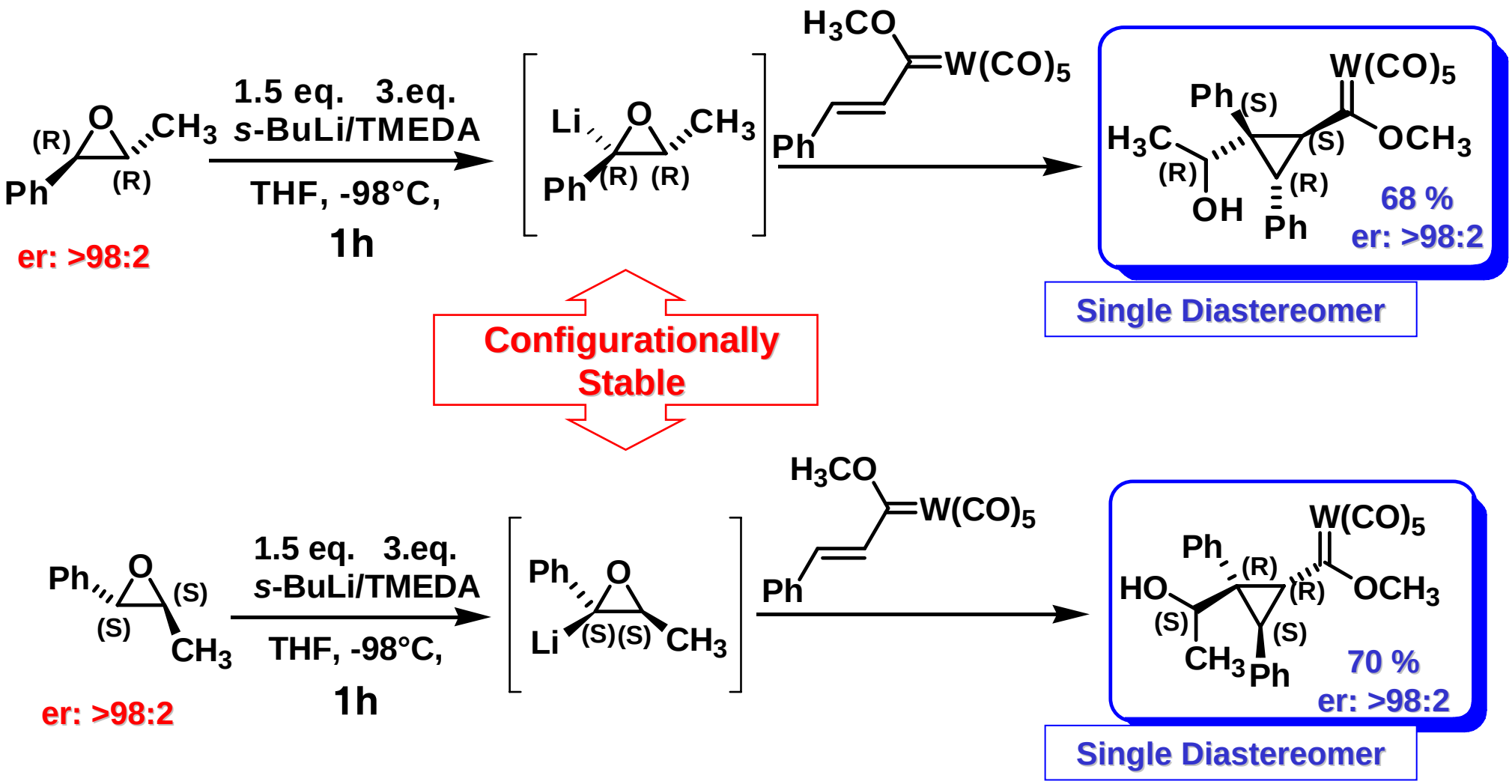
Li-Styrene oxide Induces asymmetry

PNO = Pyridine *N*-oxide



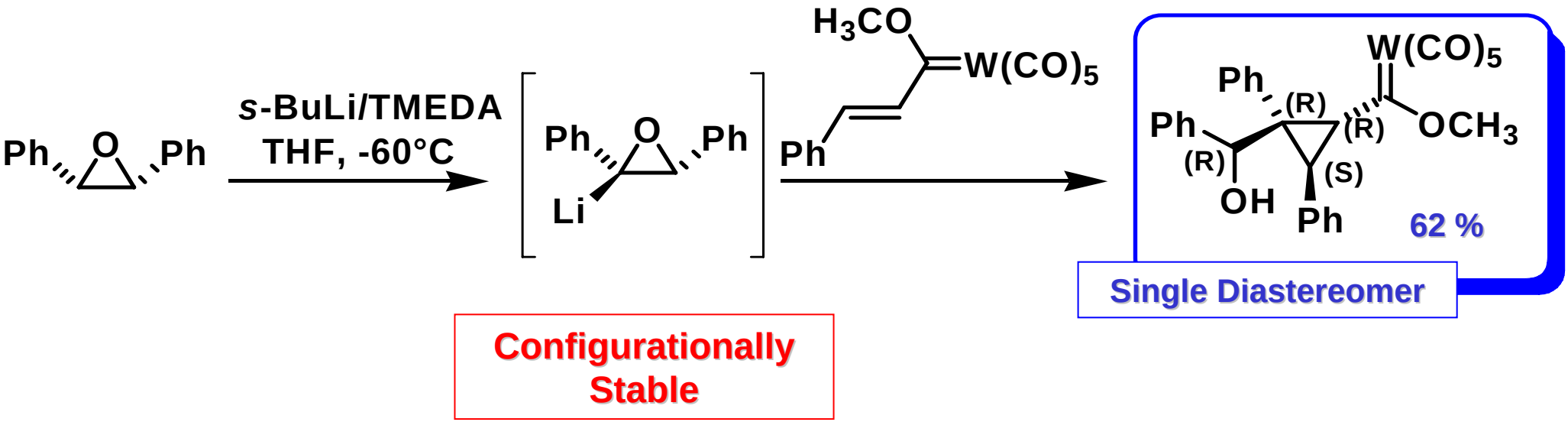
J. Org. Chem. ***2005***, *70,5852-5858*

Cyclopropanation Reaction of Optically Active Lithiated *trans*-Phenylpropylene Oxide with Fischer Carbenes



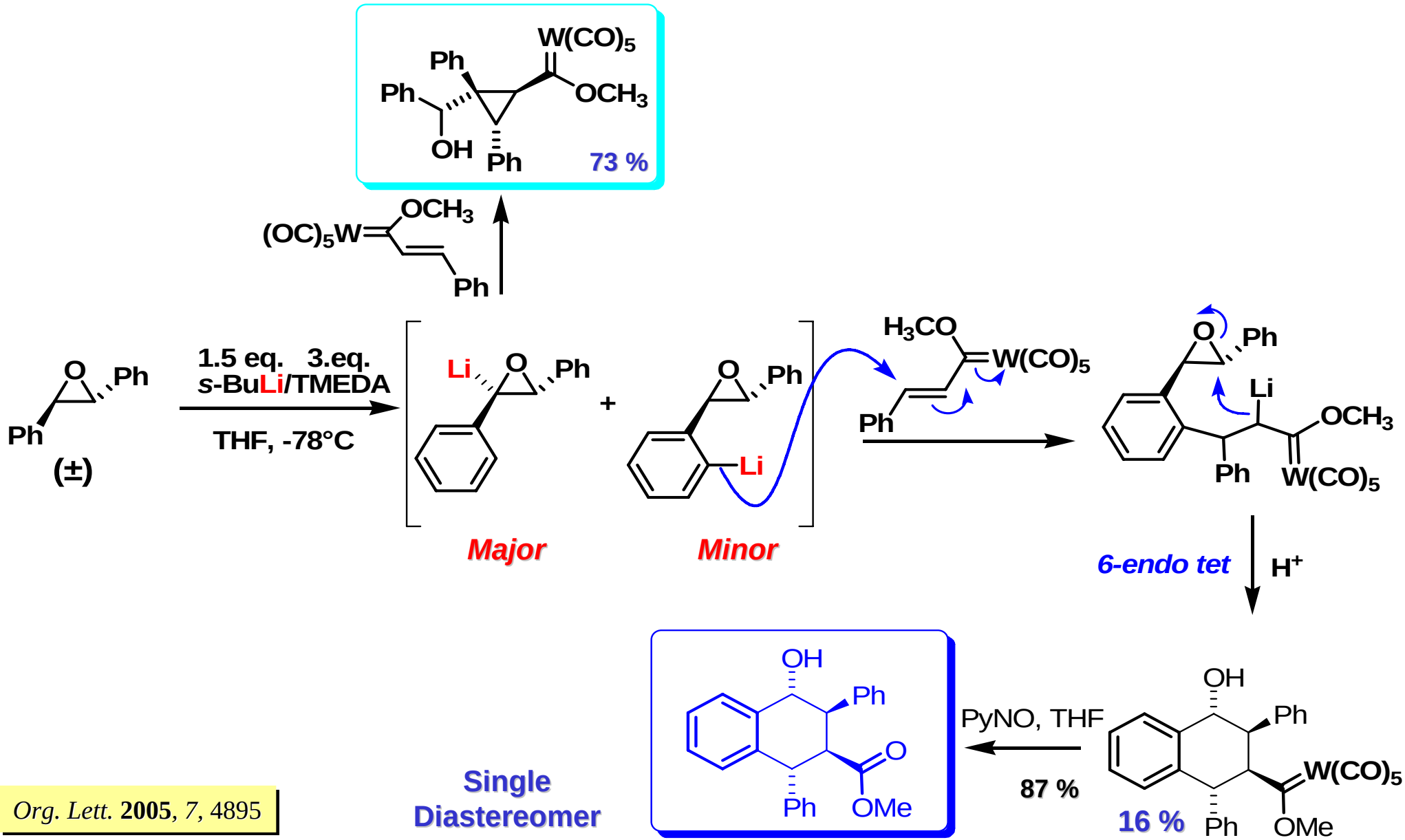
JOC **2005**, *70*, 5852

Cyclopropanation Reaction of Lithiated *cis*- Stylbene Oxide with Fischer Carbenes



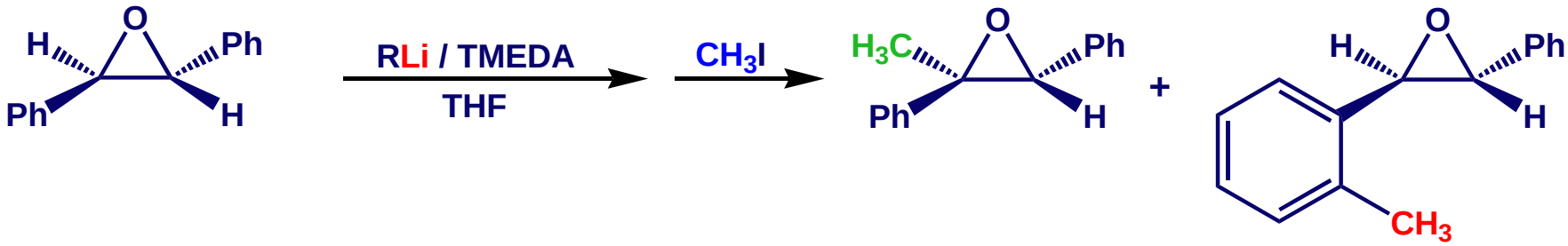
J. Org. Chem. ***2005***, *70, 5852-5858*

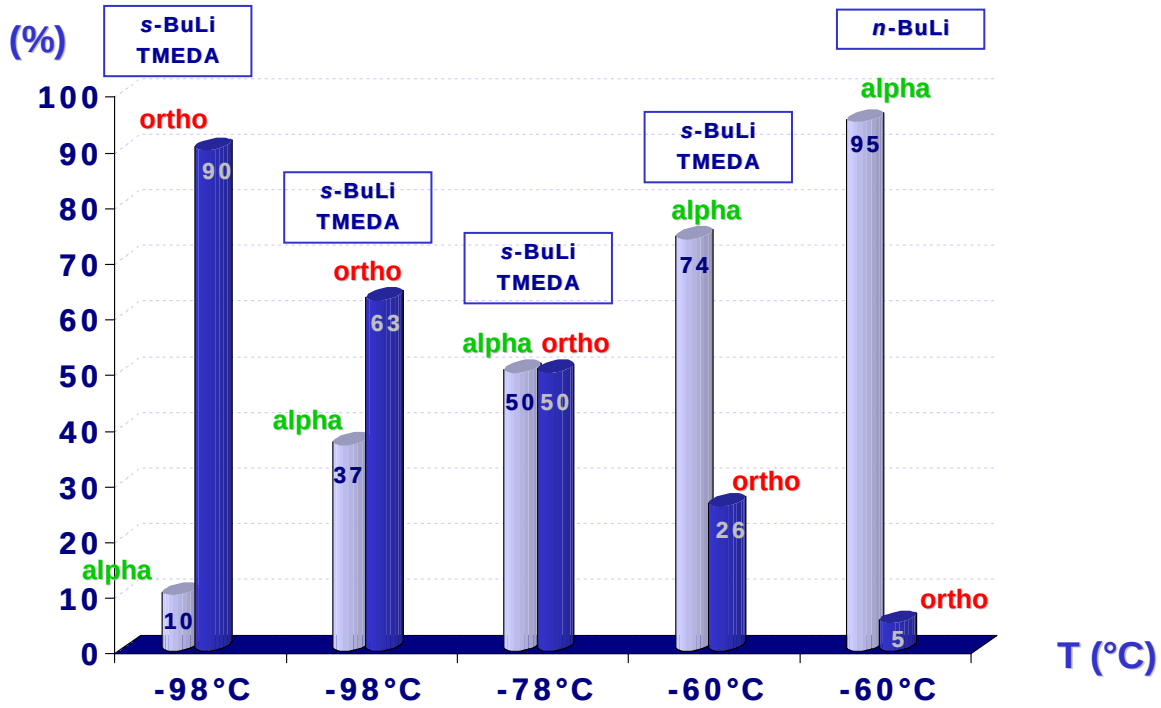
Deprotonation of *trans*-Stilbene Oxide: *ortho*-Lithiation vs. α-Lithiation

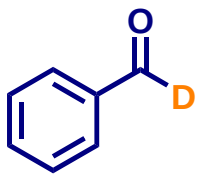


Org. Lett. **2005**, *7*, 4895

Lithiation of *trans*-Stilbene Oxide : Alpha vs Ortho



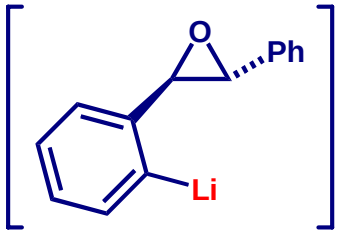




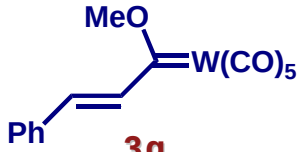
Deprotonation of
trans-Stilbene oxide-d_2

Org. Lett. **2004**, *6*, 4191.

Enantiospecific Synthesis of Tetrahydronaphthols



(*R*,*R*)-1a-Li

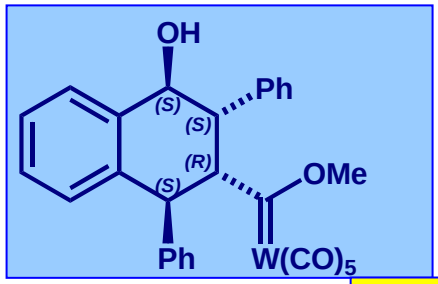


3g

THF, -78°C, 30 min

1) -78°C → R.T.

2) H^+

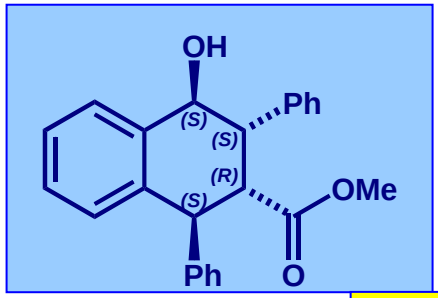


(+)-4a

$[\alpha]_D$ = +245°

ee >95 %

PyNO
THF

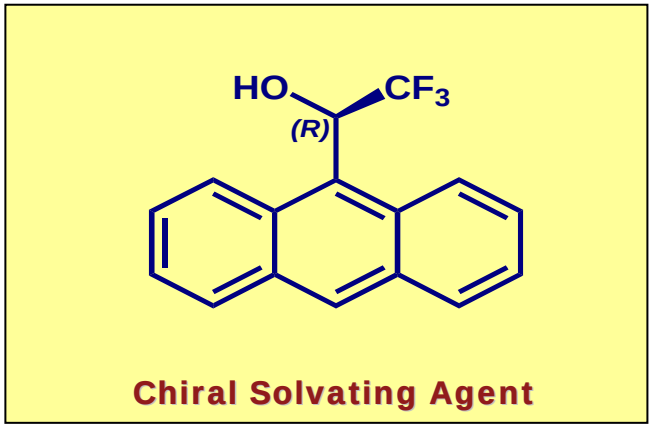


(+)-5a

$[\alpha]_D$ = +104°

ee >95 %

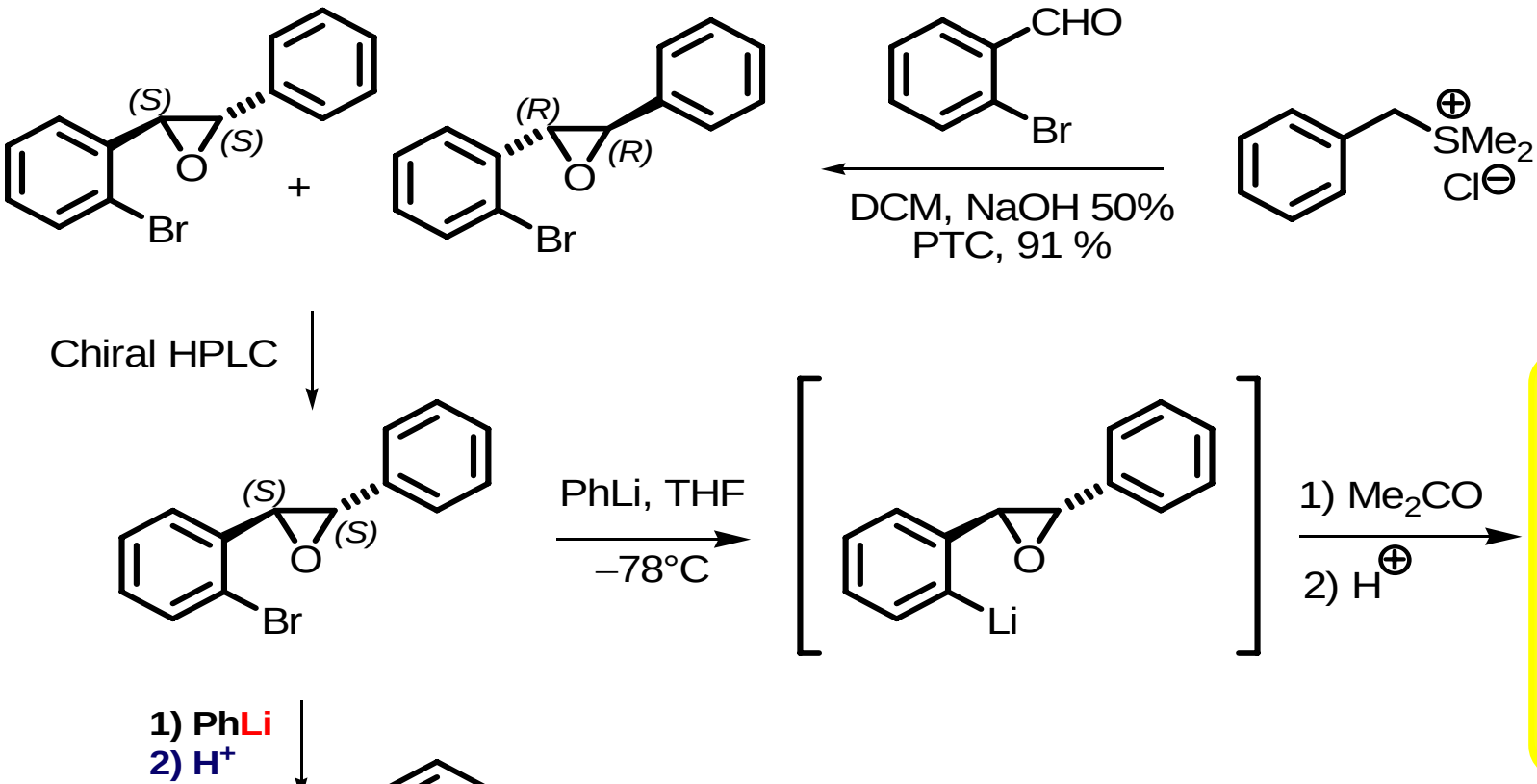
Ee determination via ^{1}H-NMR



Chiral Solvating Agent

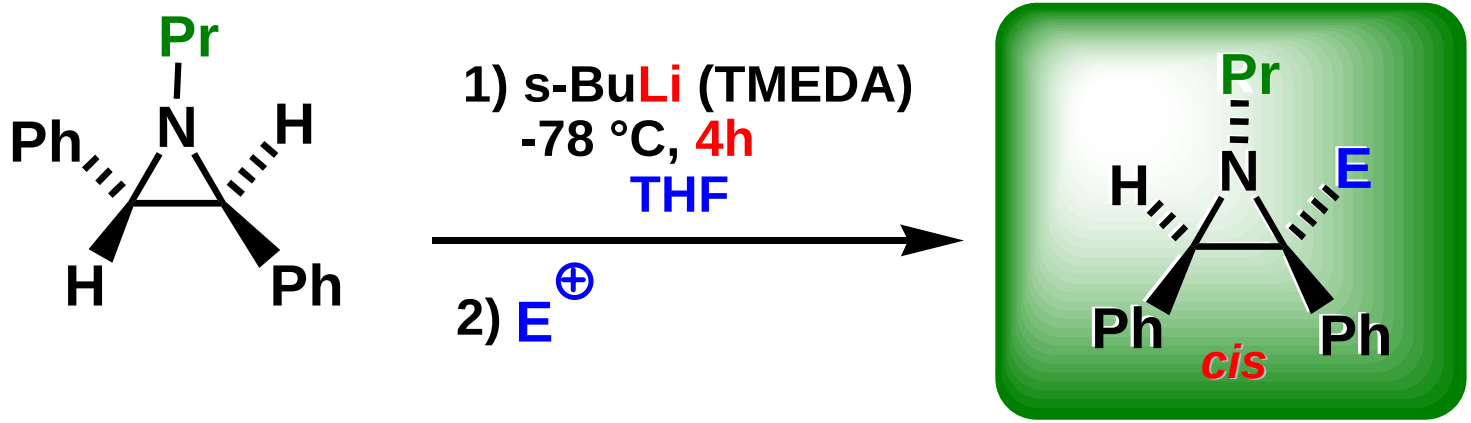
Org. Lett. **2005**, *7*, 4895

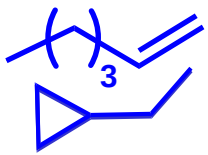
Enantiospecific Synthesis of Dihydrobenzo[c]furans (Phthalans)



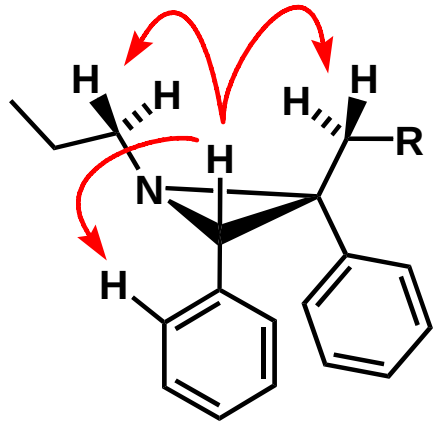
J. Org. Chem. **2006**, *71*, *3984-3987*

α-Lithiation of trans-N-Alkyl-2,3-diphenylaziridines:
Stereospecific Synthesis of functionalized Aziridines



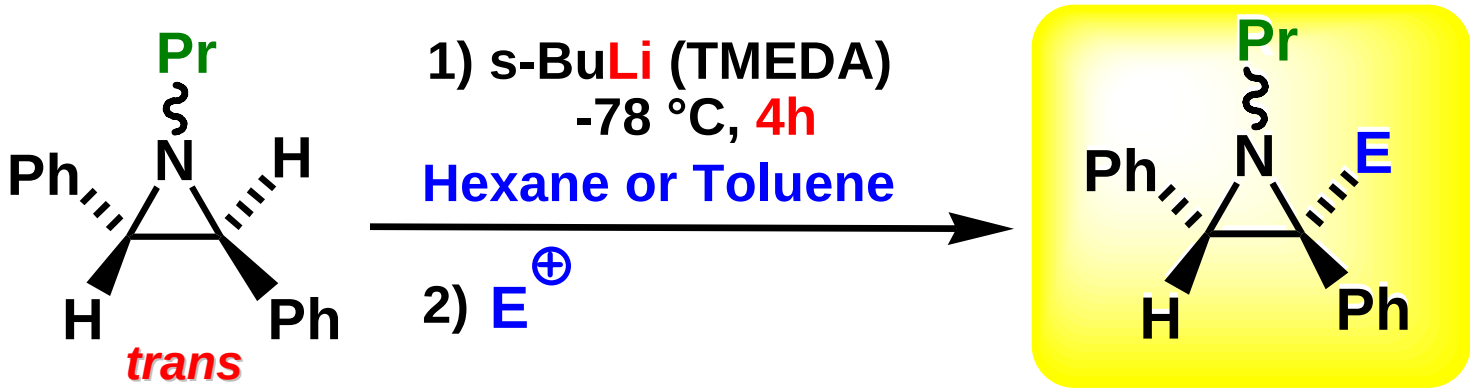
E	dr Cis/Trans	Yield %
Me	> 98/2	98
Et	> 98/2	92
Bn	> 98/2	70
Allyl	> 98/2	92
	> 98/2	48
	> 98/2	38

Selected NOE interaction



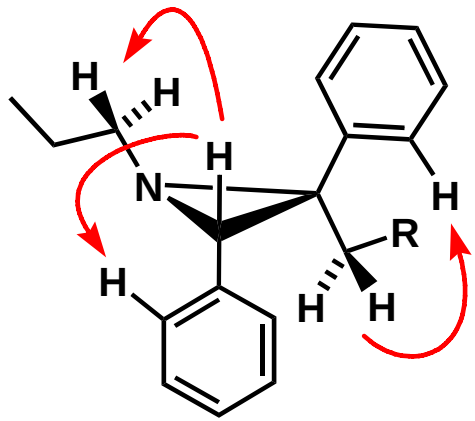
Unpublished results

α-Lithiation of trans-N-Alkyl-2,3-diphenylaziridines:
Stereospecific Synthesis of functionalized Aziridines



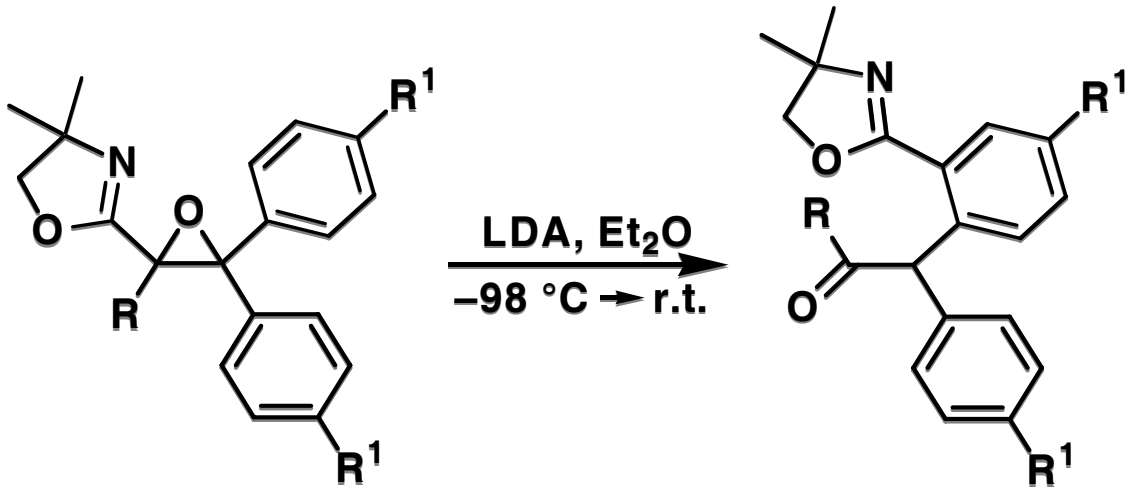
E^+	dr Trans/Cis	Yield %
MeI	> 98/2	64
EtI	> 98/2	95
$SnBu_3Cl$	> 98/2	80

Selected NOE interaction

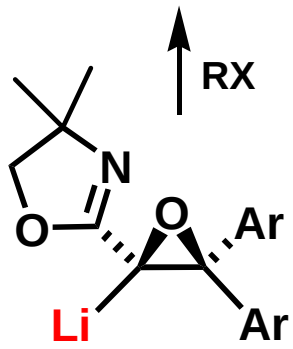


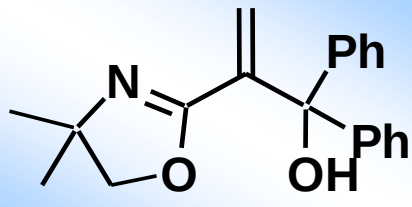
Unpublished results

Isomerization of Oxazolinyl Aryl Oxiranes: Synthesis of Oxazolinylarylalkanones



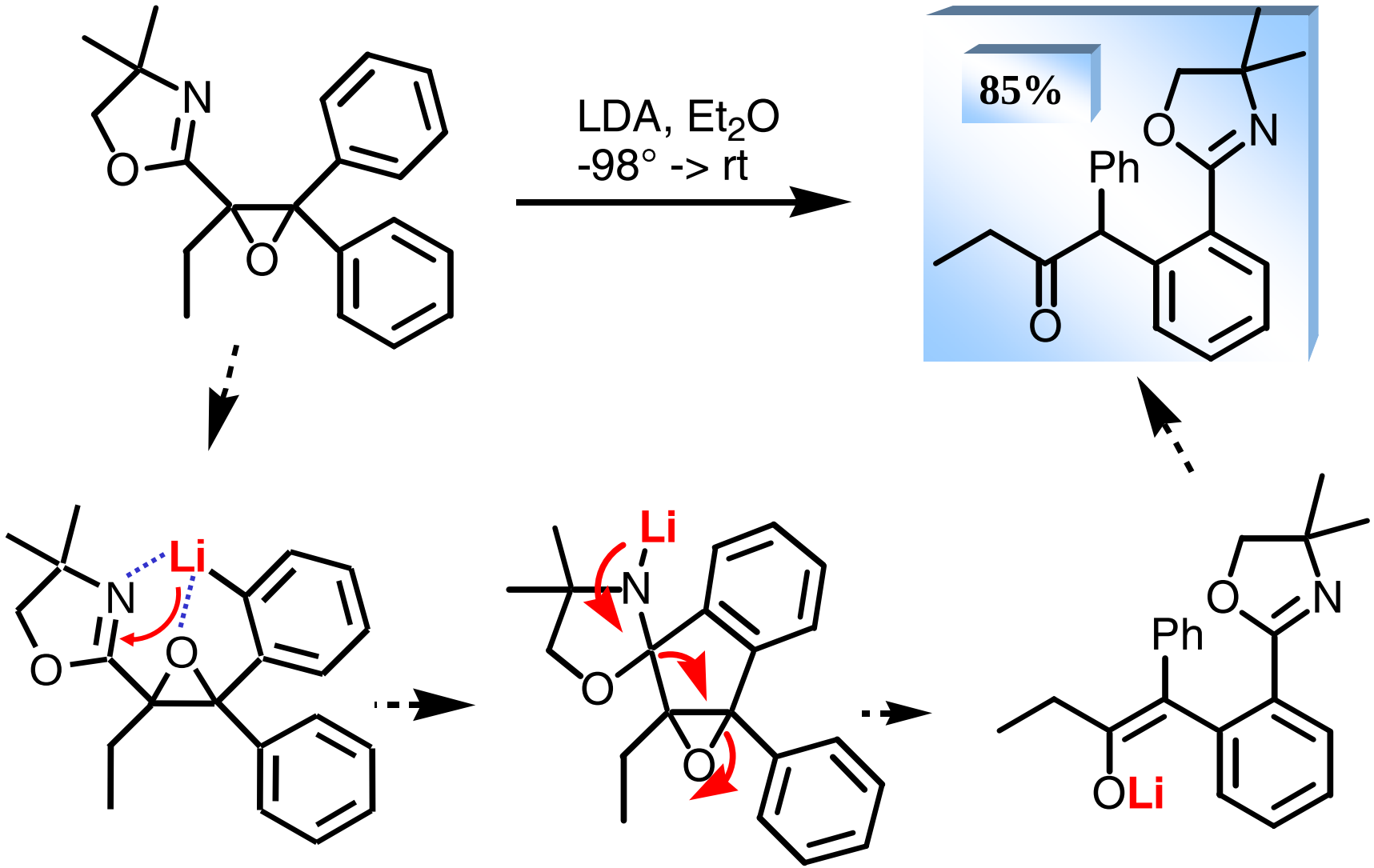
R	R^1	Yield
Et	H	85
Me	H	10
Et	Cl	95
Et	F	79
Et	Me	85
Et	OMe	88
n-Pr	H	85





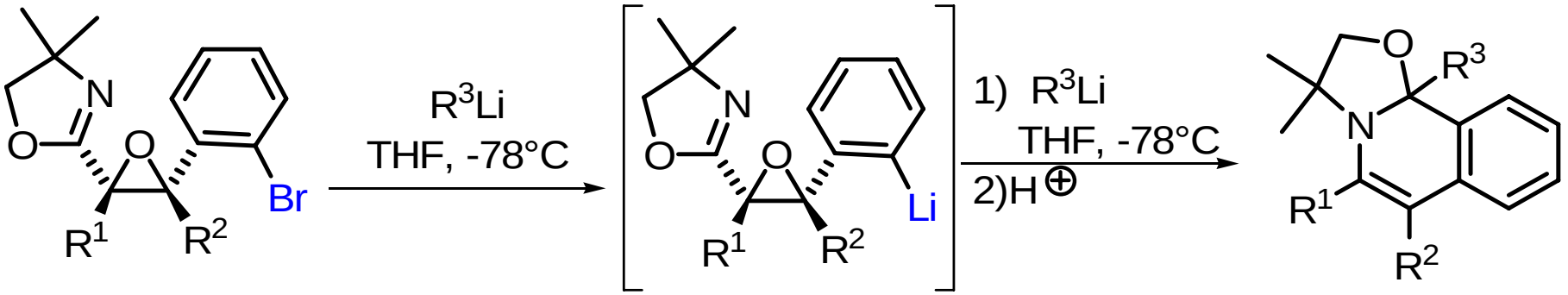
Tetrahedron Lett., **2002**, *43*, 7739

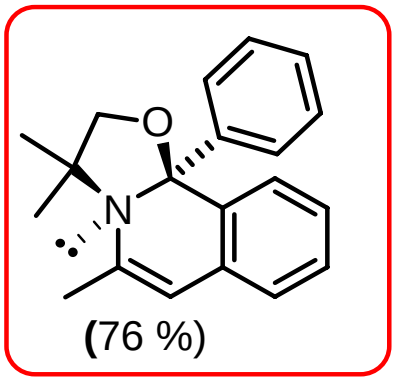
Isomerization of Oxazolinyl Aryl Oxiranes: Synthesis of Oxazolinylarylalkanones

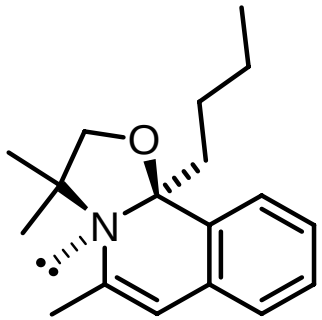


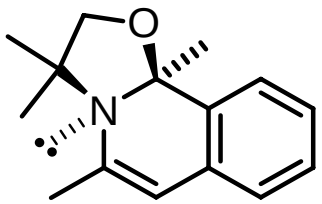
Tetrahedron Lett., **2002**, *43*, 7739

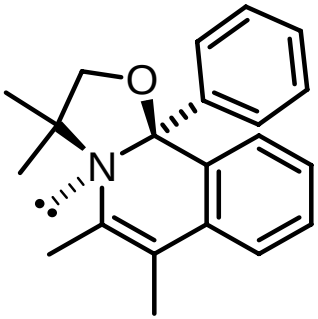
Synthesis of Substituted Isoquinoline Derivatives

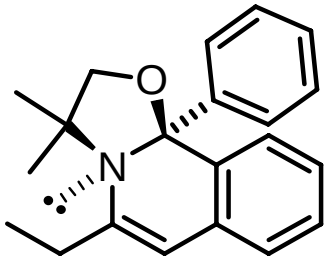


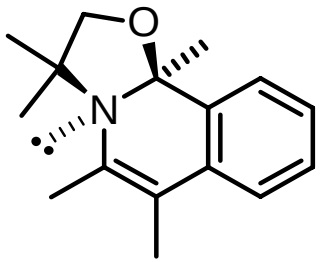

(76 %)


(69 %)


(69 %)

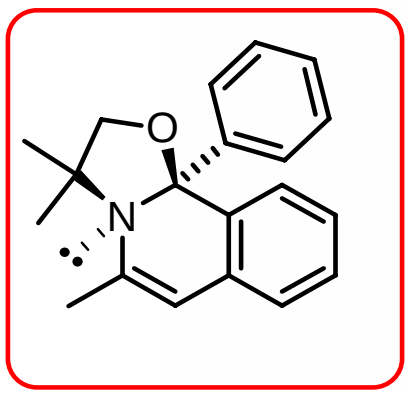

(70 %)

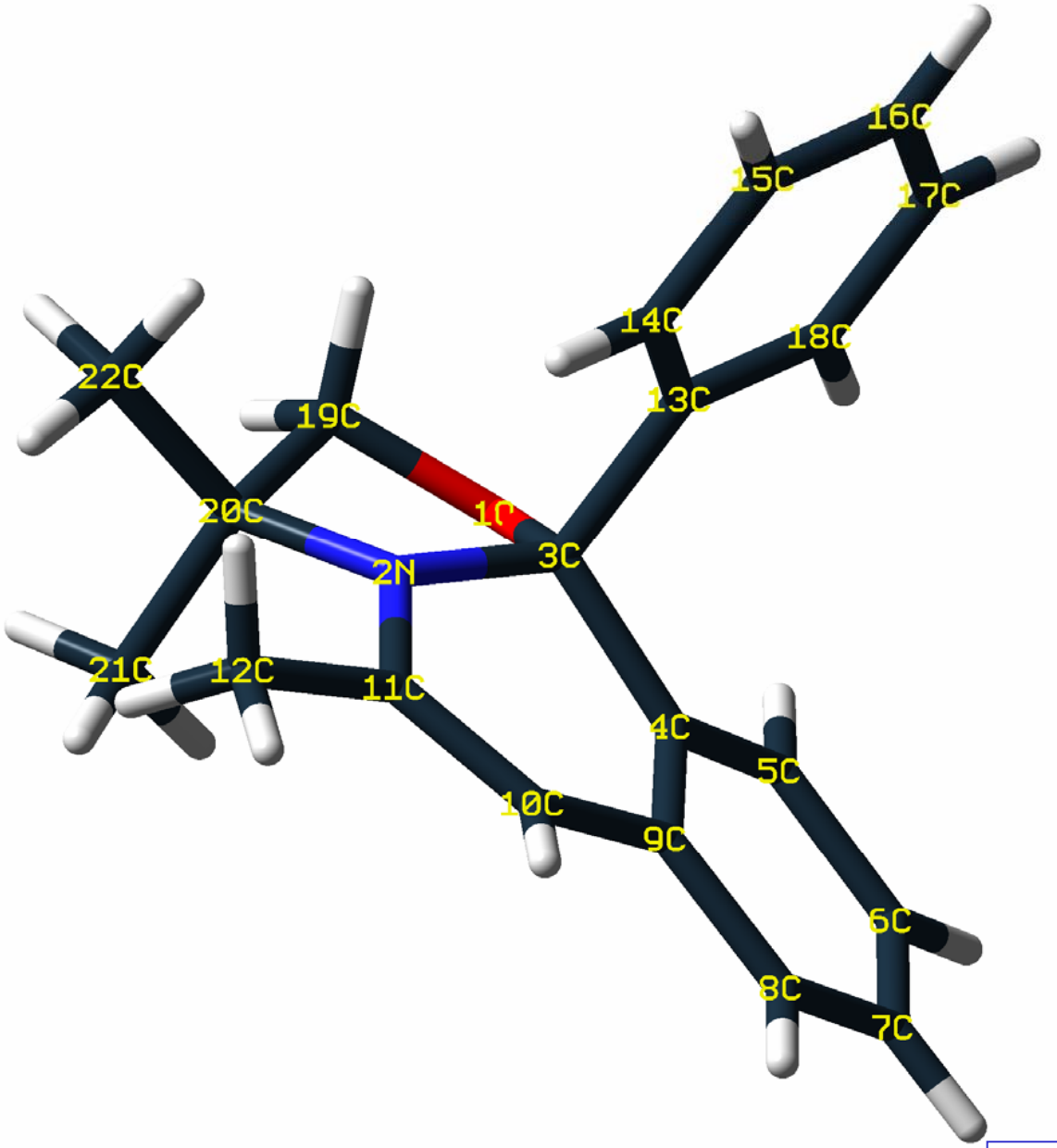

(74 %)


(67 %)

Unpublished results

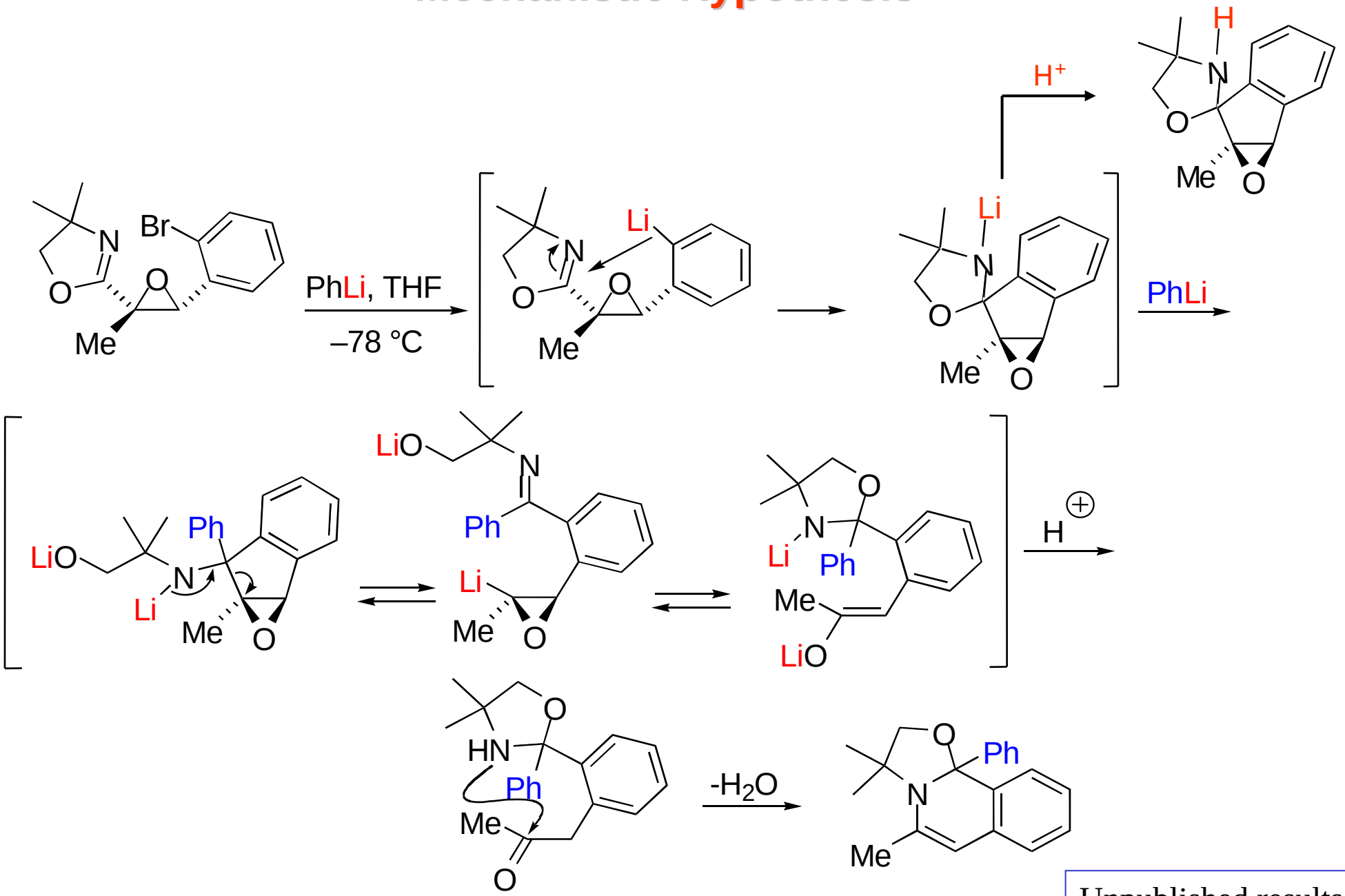
Synthesis of Substituted Isoquinoline Derivatives





Unpublished results

Mechanistic Hypothesis



Acknowledgements

Prof. V. Capriati
Prof. R. Luisi
Dr. L. Degennaro
Dr. F. M. Perna
Dr. A. Salomone

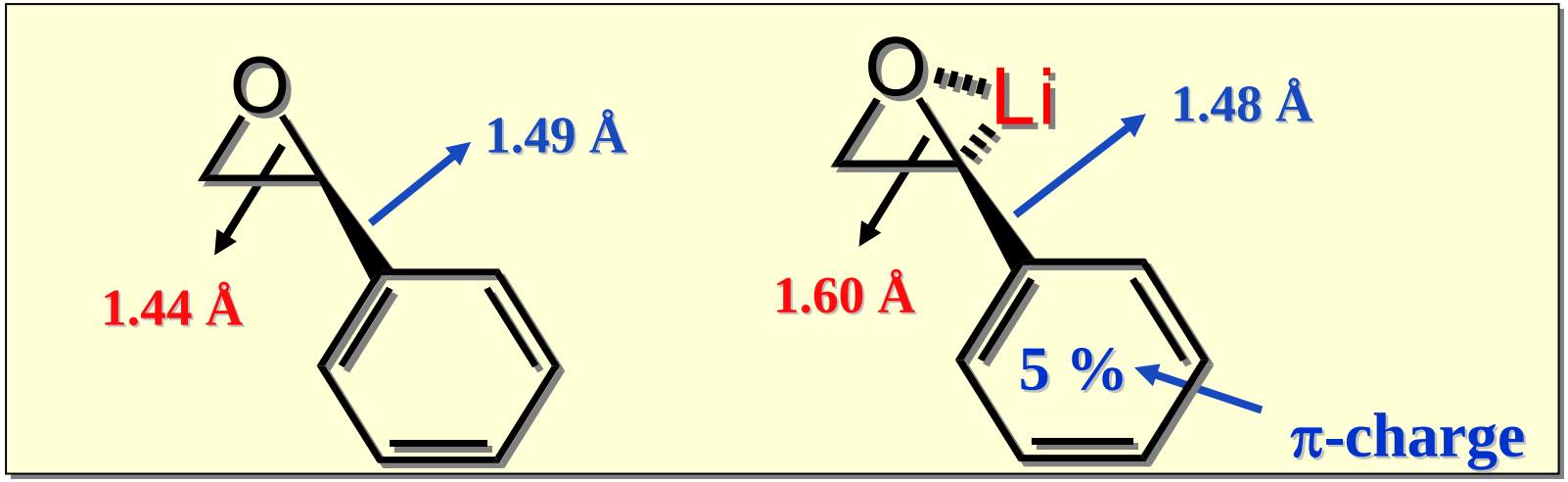
PhD Students:
Dr. I. Nuzzo
Dr. B. Musio
Dr. R. Mansueto
Dr. C. Carlucci

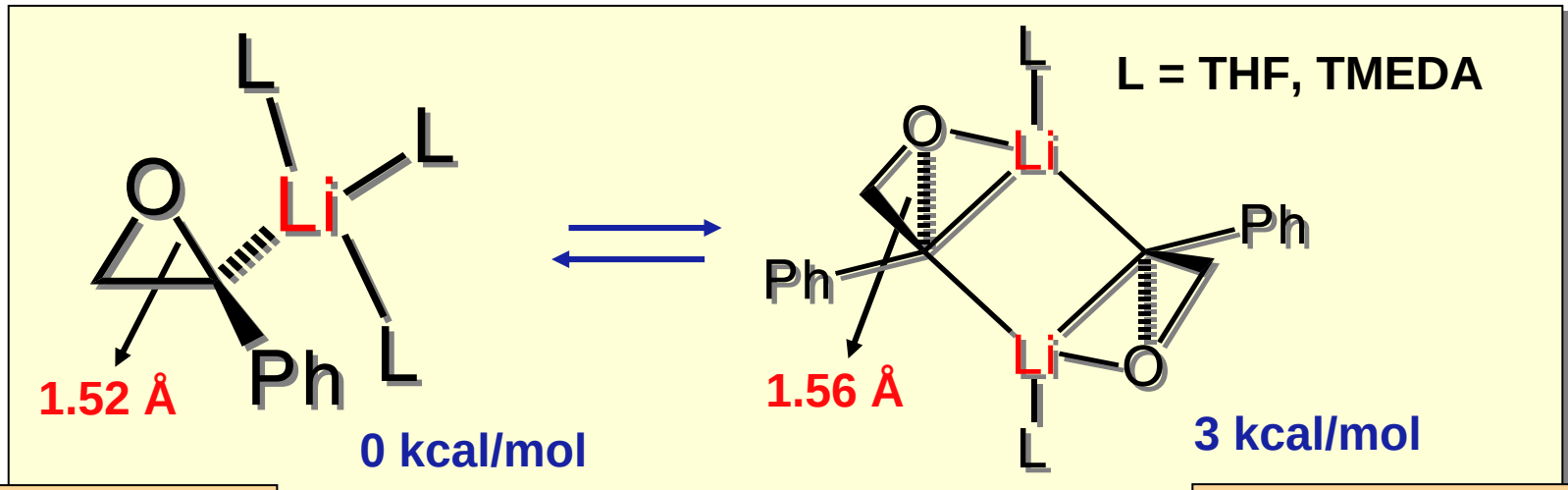
Dr. P. Di Cunto

MIUR, FIRB
C.I.N.M.P.I.S
DOMPE' (L'Aquila)
ANGELINI (Pomezia)

Lithiated Styrene Oxide:

a Computational Investigation at DFT Level



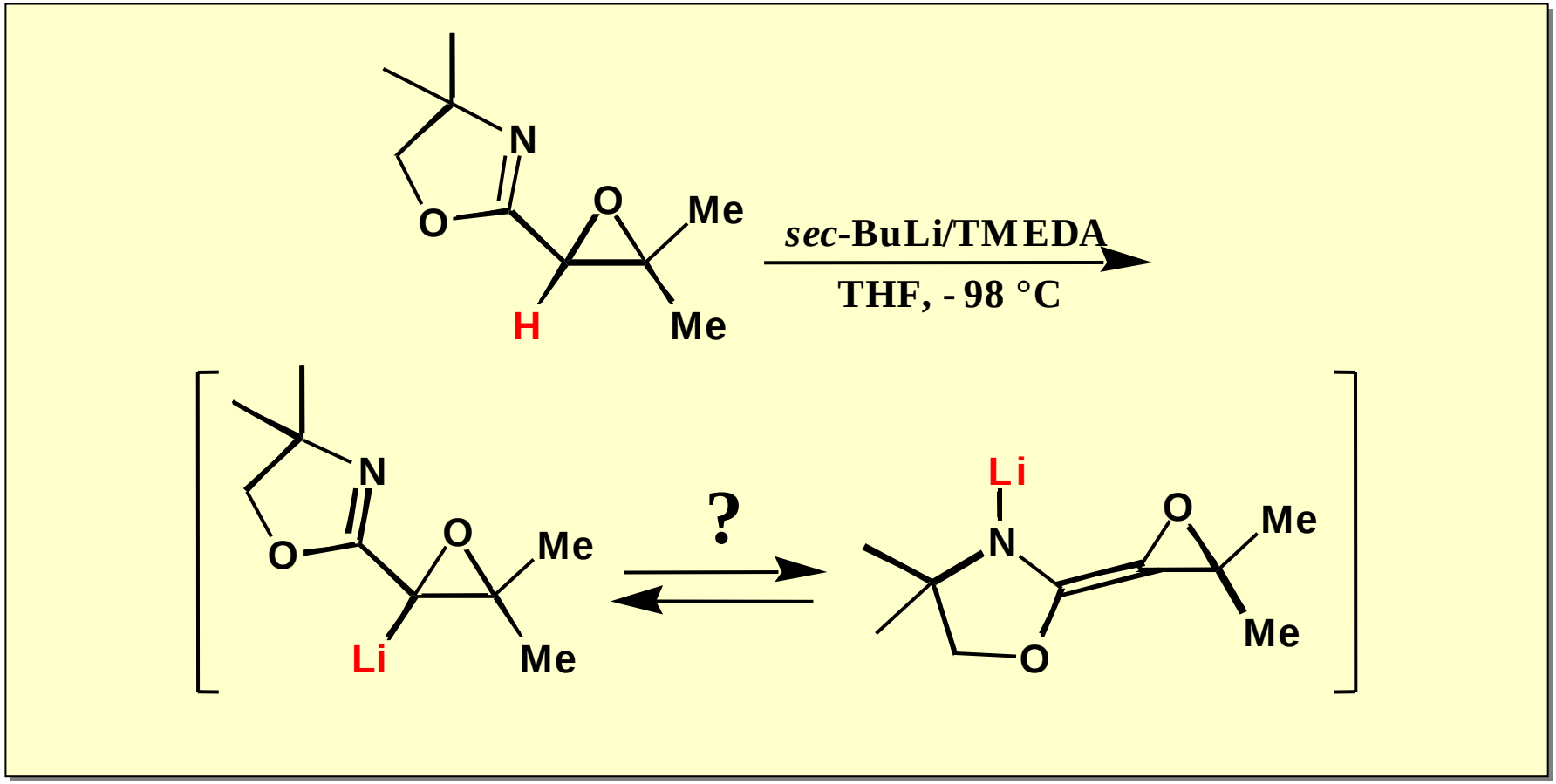


"Tetrahedral structure" in donor solvents, in the presence of TMEDA

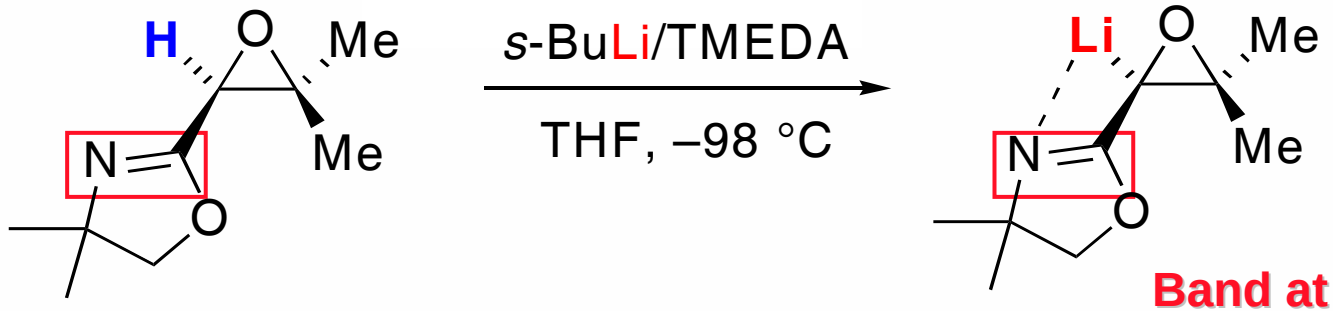
B3LYP/6-311+G*// B3LYP/6-31+G*

"Bridged structure" in nondonor solvents, in absence of ligands

Oxazolinyloxiranyllithium: Carbanion or Azaenolate?
-An IR-Spectroscopic Study-

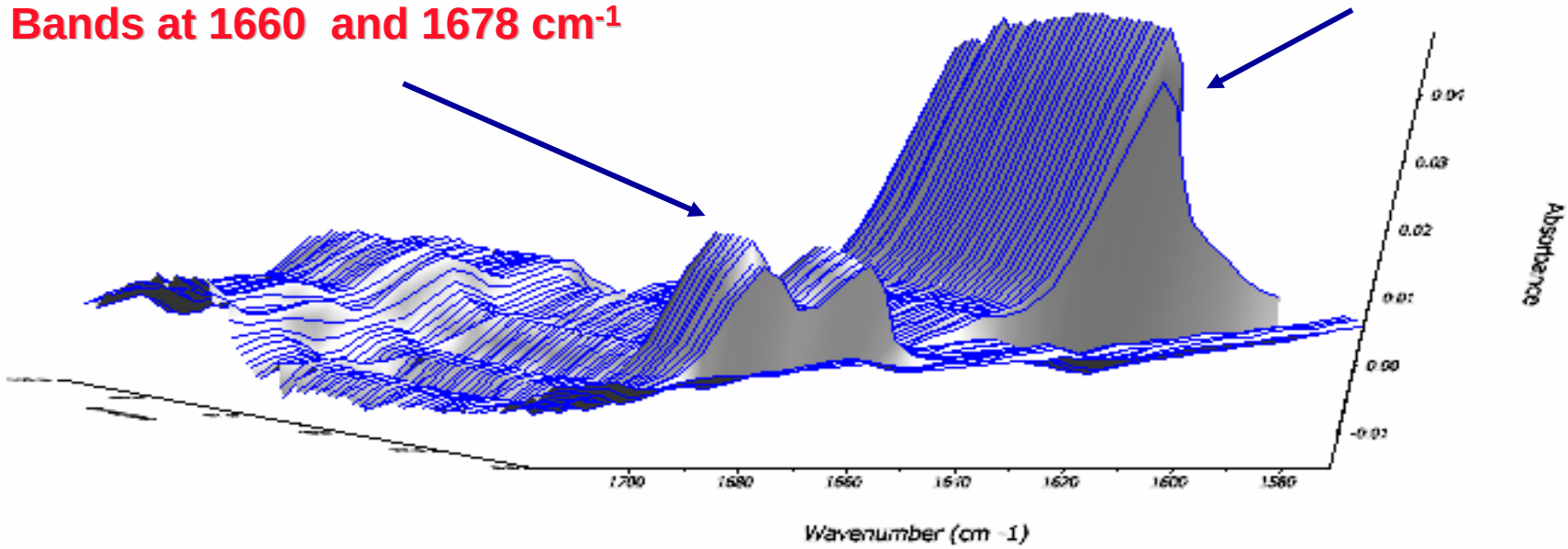


α-Lithiated Oxazolinyloxiranes: an *in situ* React-IR Investigation



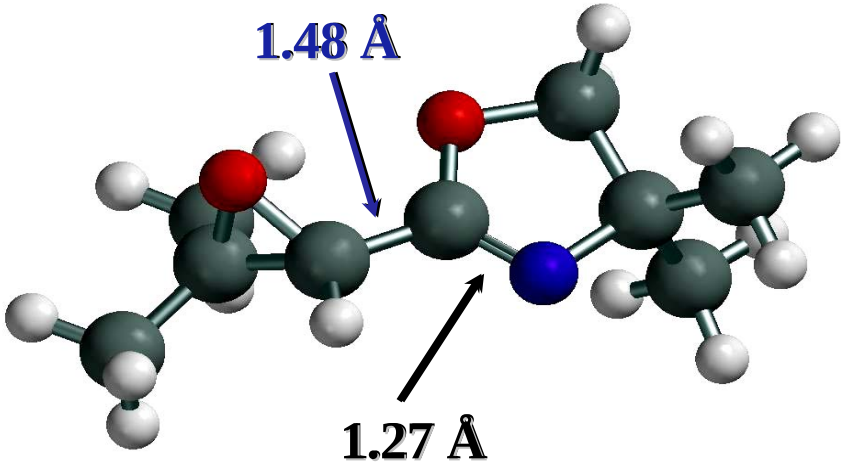
Band at 1600 cm^{-1}

Bands at 1660 and 1678 cm^{-1}

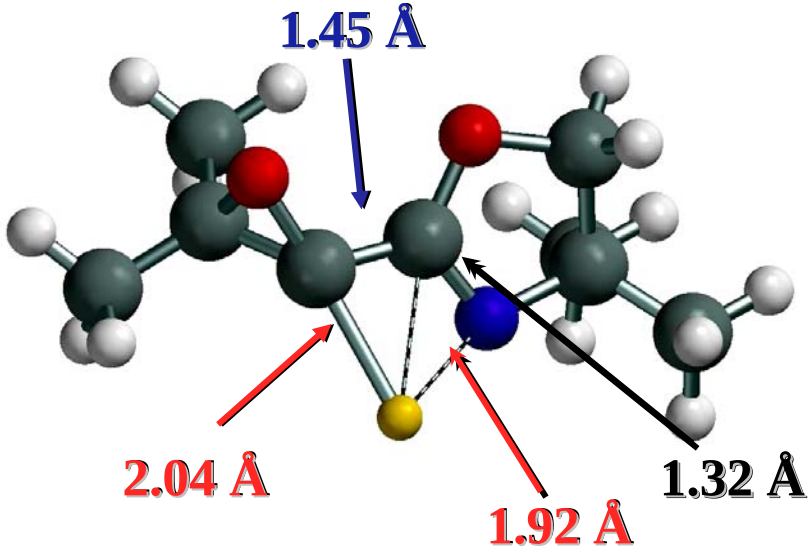


Unpublished results

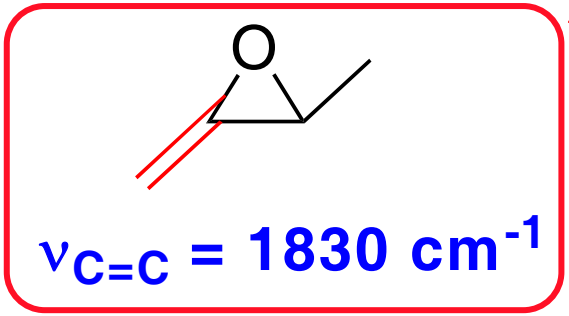
A DFT study: B3LYP/6-31+G*//PM3



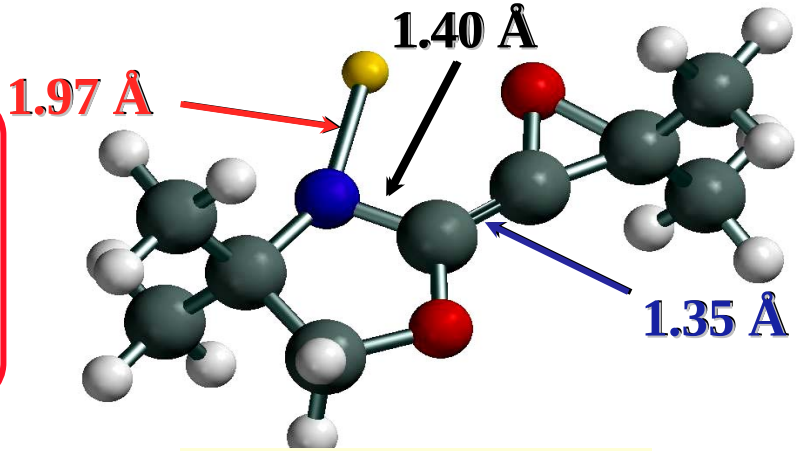
Neutral $\nu_{C=N}$ = 1727 cm^{-1}



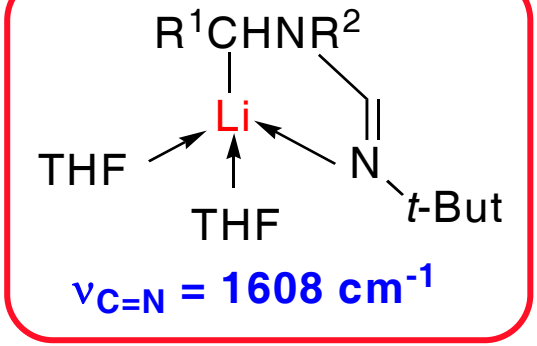
Oxiranyllithium
$\nu_{C=N}$ = 1550 cm^{-1}



$\nu_{C=C}$ = 1830 cm^{-1}



Planar Azaenolate
$\nu_{C=C}$ = 1844 cm^{-1}

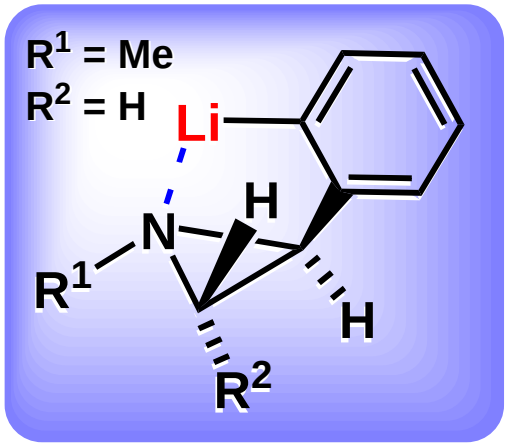


$\nu_{C=N}$ = 1608 cm^{-1}

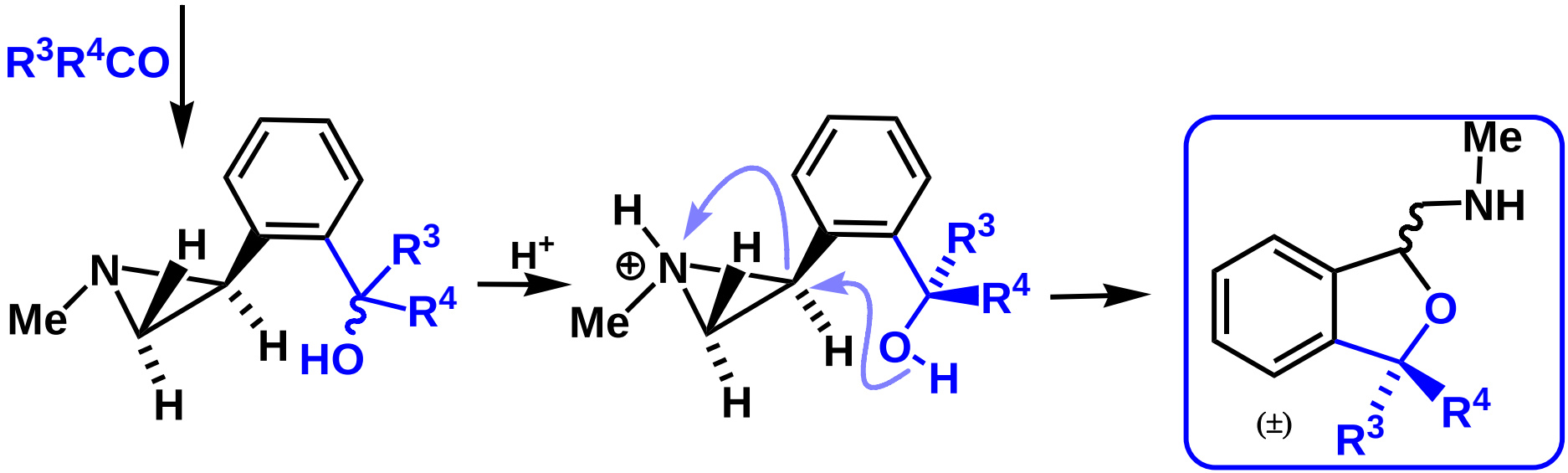
Org. Lett. **2004**, 403

J. Am. Chem. Soc. **1983**, 105, 2082

Trapping of *ortho*-lithiated N-methylphenylaziridine



R³R⁴CO: $(CH_3)_2CO$ (*89 %*), PhCHO (*47 %, dr = 1:1*), Ph_2CO (*52 %*), *n*-PrCOPh (*55 %, dr = 1:1*)



Org. Lett. 2005, 7, 3749-3752