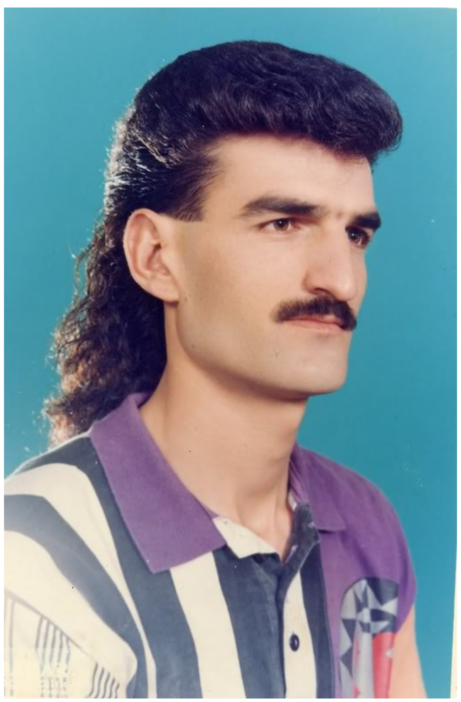
MUSIC TELEVISION®

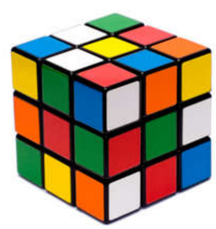
The most important organic chemistry of the 1980s



Dan Jansen

Shenvi Lab

12/6/2011



Methods

- Web of Science
- Search settings:
  - 1980-1989
  - Highest to lowest citation
  - JACS, JOC, Tet. Lett.

Organic chemistry as it was in 1980

- Heck, Suzuki, Negishi, and Stille cross-coupling reactions were recently developed (will not be covered in this review)
- W.C. Still's procedure for rapid column chromatography recently published in 1978
- Ernst publishes details on COSY NMR in *J Chem Phys* in 1976

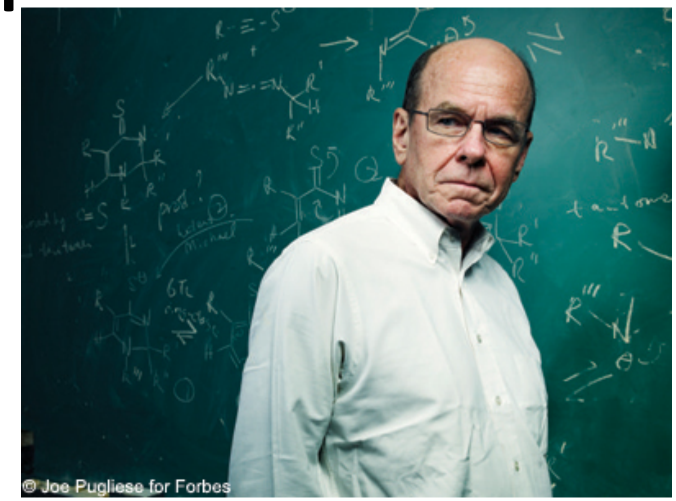
Biggest players in 1980s chemistry

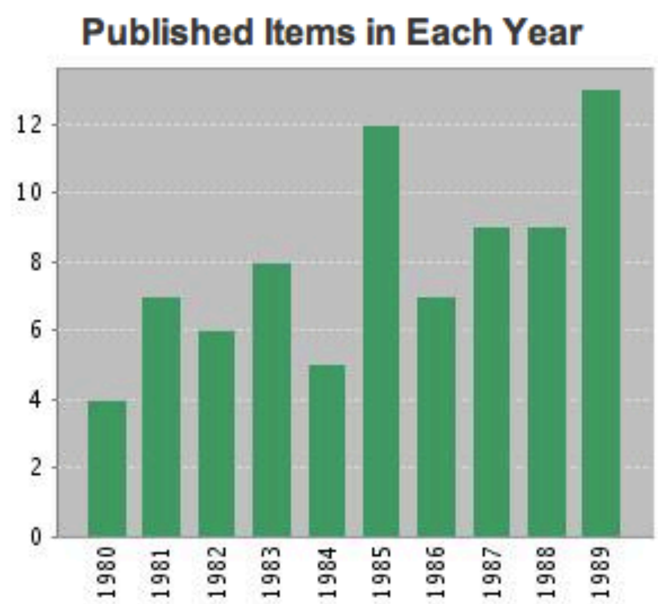
- Sharpless (asymmetric oxidations, practical methods)
- Corey (total synthesis, CBS catalyst)
- Noyori (asymmetric hydrogenation)
- Brown (boron chemistry)
- Evans (asymmetric/stereoselective enolate chemistry)
- Others:
  - Paquette, Still, Stille, Seebach

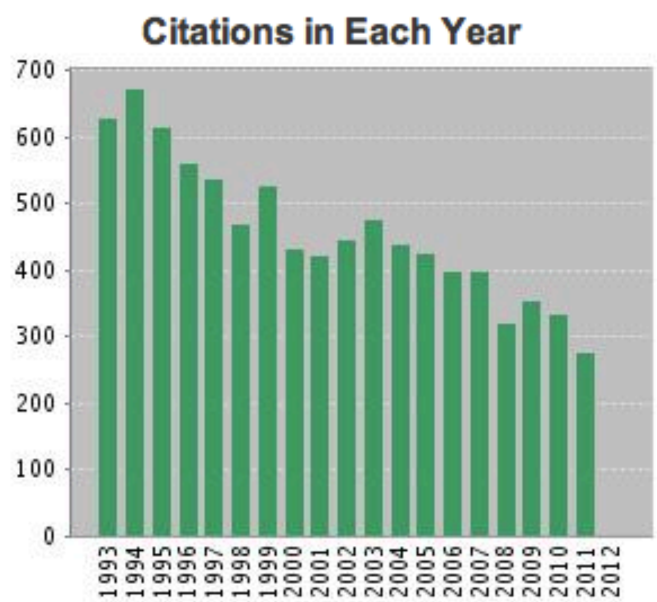
K. Barry Sharpless

Highest cited paper:

Title: THE 1ST PRACTICAL METHOD FOR ASYMMETRIC EPOXIDATION
Author(s): KATSUKI T; SHARPLESS KB
Source: JOURNAL OF THE AMERICAN CHEMICAL SOCIETY Volume: 102 Issue: 18 Pages: 5974-5976 DOI: 10.1021/ja00538a077
Published: 1980
Times Cited: 1,863 (from All Databases)







The latest 20 years are displayed.
View a graph with all years.

Results found: 80

Sum of the Times Cited [?] **:** 13434

Sum of Times Cited without self-citations [?] **:** 13234

Citing Articles[?] **:** 9300

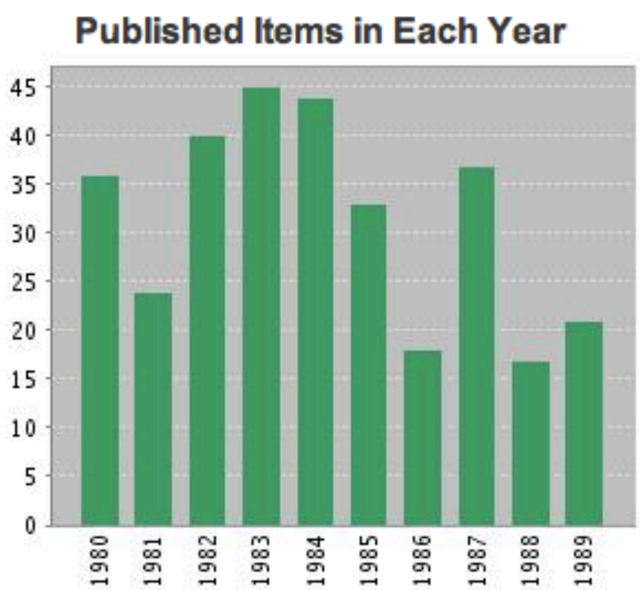
View Citing Articles
View without self-citations

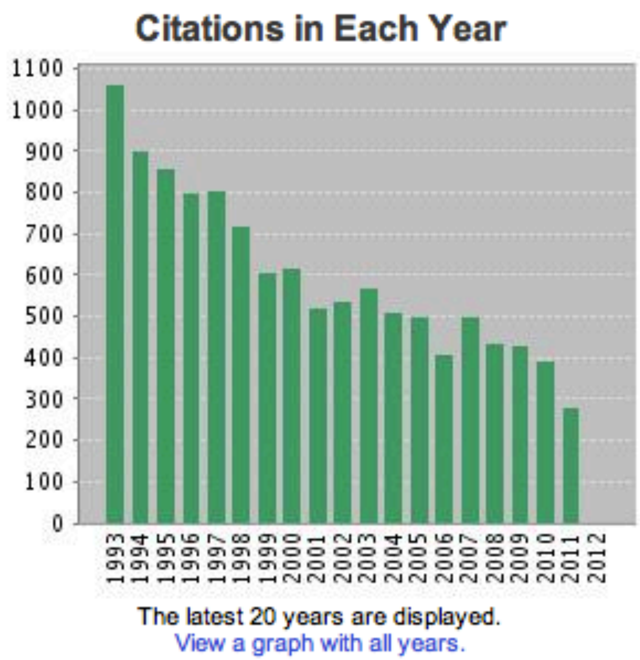
Average Citations per Item [?] **:** 167.93

h-index [?] **:** 44

E.J. Corey

Highest cited paper:
Title: HIGHLY ENANTIOSELECTIVE BORANE REDUCTION OF KETONES CATALYZED BY CHIRAL OXAZABOROLIDINES - MECHANISM AND SYNTHETIC IMPLICATIONS
Author(s): COREY EJ; BAKSHI RK; SHIBATA S
Source: JOURNAL OF THE AMERICAN CHEMICAL SOCIETY Volume: 109 Issue: 18 Pages: 5551-5553 DOI: 10.1021/ja00252a056
Published: SEP 2 1987
Times Cited: 962 (from All Databases)

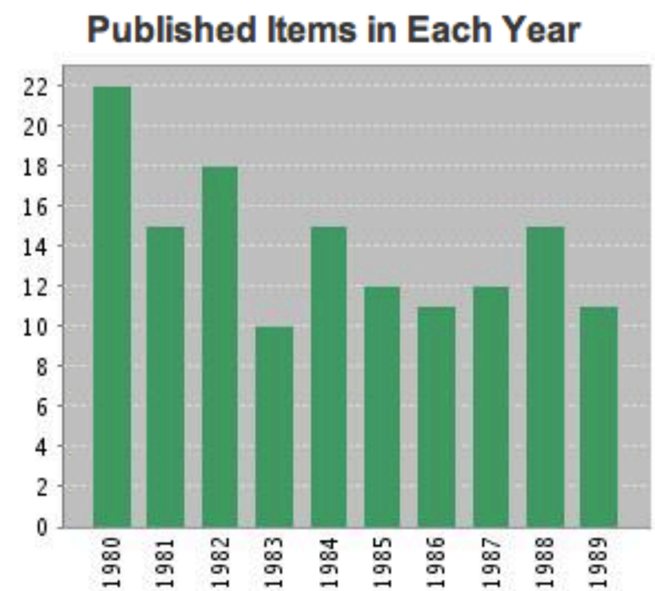


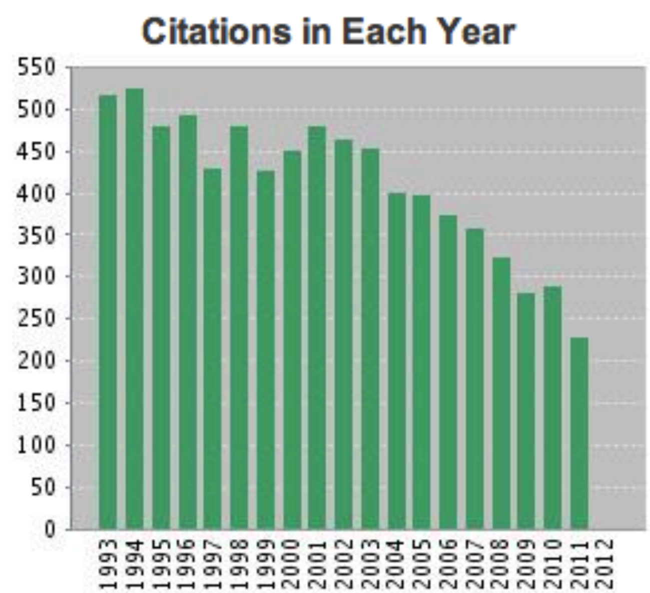


Results found:	315
Sum of the Times Cited [?] :	24592
Sum of Times Cited without self-citations [?] :	23677
Citing Articles[?] :	16304
View Citing Articles View without self-citations	
Average Citations per Item [?] :	78.07
h-index [?] :	81

Ryōji Noyori

Highest cited paper:
Title: SYNTHESIS OF 2,2'-BIS(DIPHENYLPHOSPHINO)-1,1'-BINAPHTHYL (BINAP), AN ATROPISOMERIC CHIRAL BIS(TRIARYL)PHOSPHINE, AND ITS USE IN THE RHODIUM(I)-CATALYZED ASYMMETRIC HYDROGENATION OF ALPHA-(ACYLAMINO)ACRYLIC ACIDS
Author(s): MIYASHITA A; YASUDA A; TAKAYA H; et al.
Source: JOURNAL OF THE AMERICAN CHEMICAL SOCIETY Volume: 102 Issue: 27 Pages: 7932-7934 DOI: 10.1021/ja00547a020
Published: 1980
Times Cited: 603 (from All Databases)



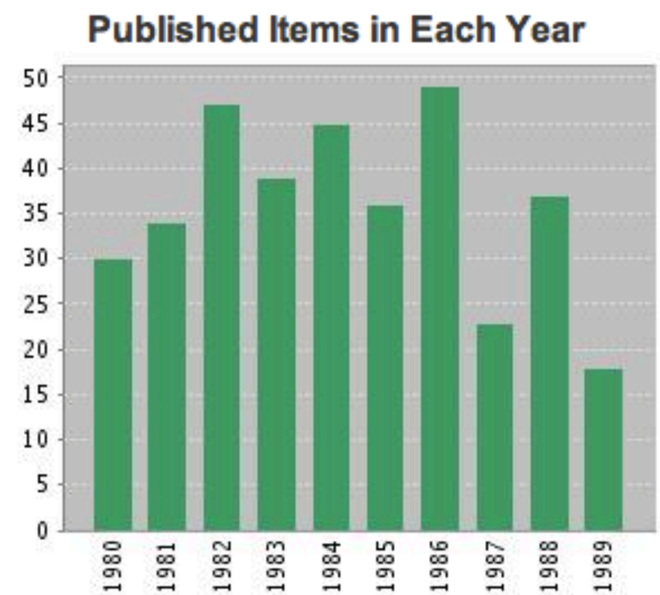


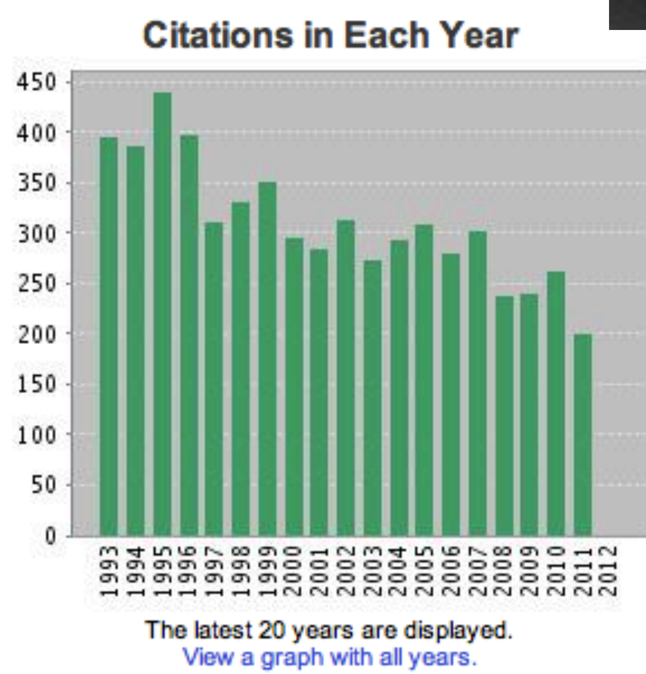
The latest 20 years are displayed.
View a graph with all years.

Results found:	141
Sum of the Times Cited [?] :	12229
Sum of Times Cited without self-citations [?] :	11761
Citing Articles[?] :	8379
View Citing Articles View without self-citations	
Average Citations per Item [?] :	86.73
h-index [?] :	53

H.C. Brown

Highest cited paper:
Title: ASYMMETRIC CARBON CARBON BOND FORMATION VIA BETA-ALLYLDIISOPINOCAMPHEYLBORANE - SIMPLE SYNTHESIS OF SECONDARY HOMOALLYLIC ALCOHOLS WITH EXCELLENT ENANTIOMERIC PURITIES
Author(s): BROWN HC; JADHAV PK
Source: JOURNAL OF THE AMERICAN CHEMICAL SOCIETY Volume: 105 Issue: 7 Pages: 2092-2093 DOI: 10.1021/ja00345a085 Published: 1983
Times Cited: 340 (from All Databases)

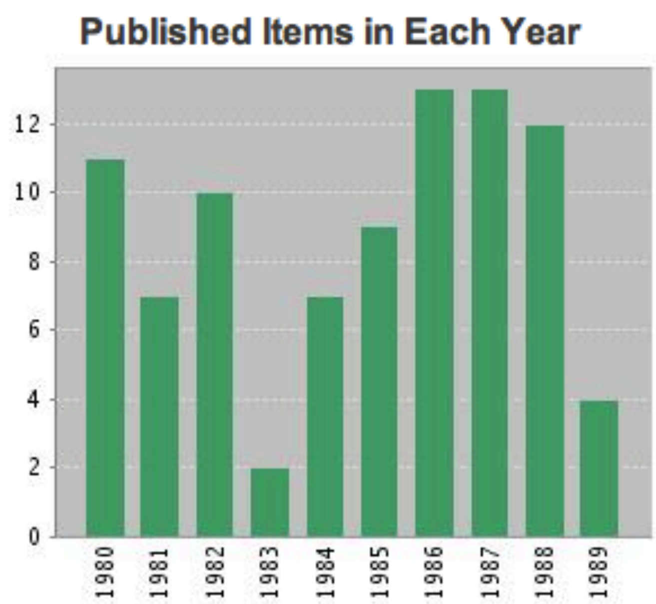


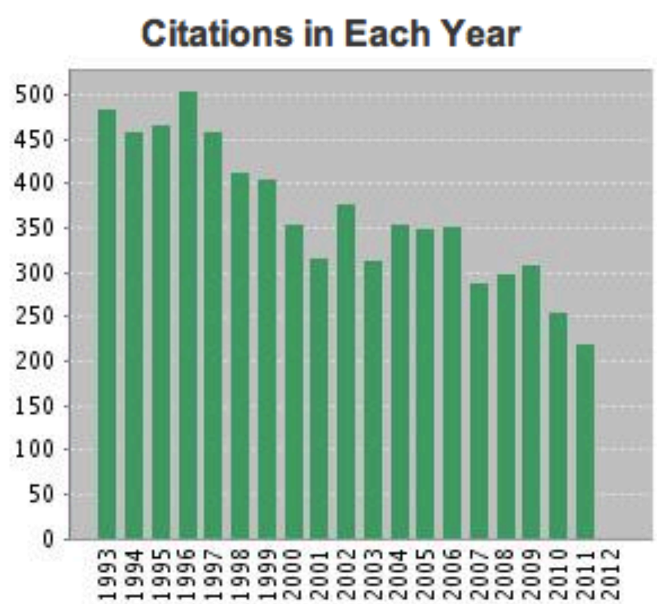


Results found:	358
Sum of the Times Cited [?] :	10418
Sum of Times Cited without self-citations [?] :	9274
Citing Articles[?] :	6032
View Citing Articles View without self-citations	
Average Citations per Item [?] :	29.10
h-index [?] :	51

Dave Evans

Highest cited paper:
Title: ENANTIOSELECTIVE ALDOL CONDENSATIONS .2. ERYTHRO-SELECTIVE CHIRAL ALOL CONDENSATIONS VIA BORON ENOLATES
Author(s): EVANS DA; BARTROLI J; SHIH TL
Source: JOURNAL OF THE AMERICAN CHEMICAL SOCIETY Volume: 103 Issue: 8 Pages: 2127-2129 DOI: 10.1021/ja00398a058 Published: 1981
Times Cited: 1,175 (from All Databases)





The latest 20 years are displayed.
View a graph with all years.

Results found:	88
Sum of the Times Cited [?] :	10085
Sum of Times Cited without self-citations [?] :	9967
Citing Articles[?] :	7121
View Citing Articles View without self-citations	
Average Citations per Item [?] :	114.60
h-index [?] :	45

1980's Highest cited

AM1: A New General Purpose Quantum Mechanical Molecular Model[1]

13,048 citations

Michael J. S. Dewar,* Eve G. Zoebisch, Eamonn F. Healy, and James J. P. Stewart

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. *Received October 29, 1984*

J. Am. Chem. Soc. **1985**, *107*, 3902–3909

2,228 citations

Linear Solvation Energy Relationships. 23. A Comprehensive Collection of the Solvatochromic Parameters, π^*, α, and β, and Some Methods for Simplifying the Generalized Solvatochromic Equation

Mortimer J. Kamlet,* José-Luis M. Abboud,* Michael H. Abraham,* and R. W. Taft*

Tetrahedron Letters, Vol.22, No.20, pp 1859 - 1862, 1981

DEOXYNUCLEOSIDE PHOSPHORAMIDITES—A NEW CLASS OF KEY INTERMEDIATES FOR DEOXYPOLYNUCLEOTIDE SYNTHESIS

1,641 citations

S. L. Beaucage and M. H. Caruthers*

Miscellaneous chemistry of the 1980s

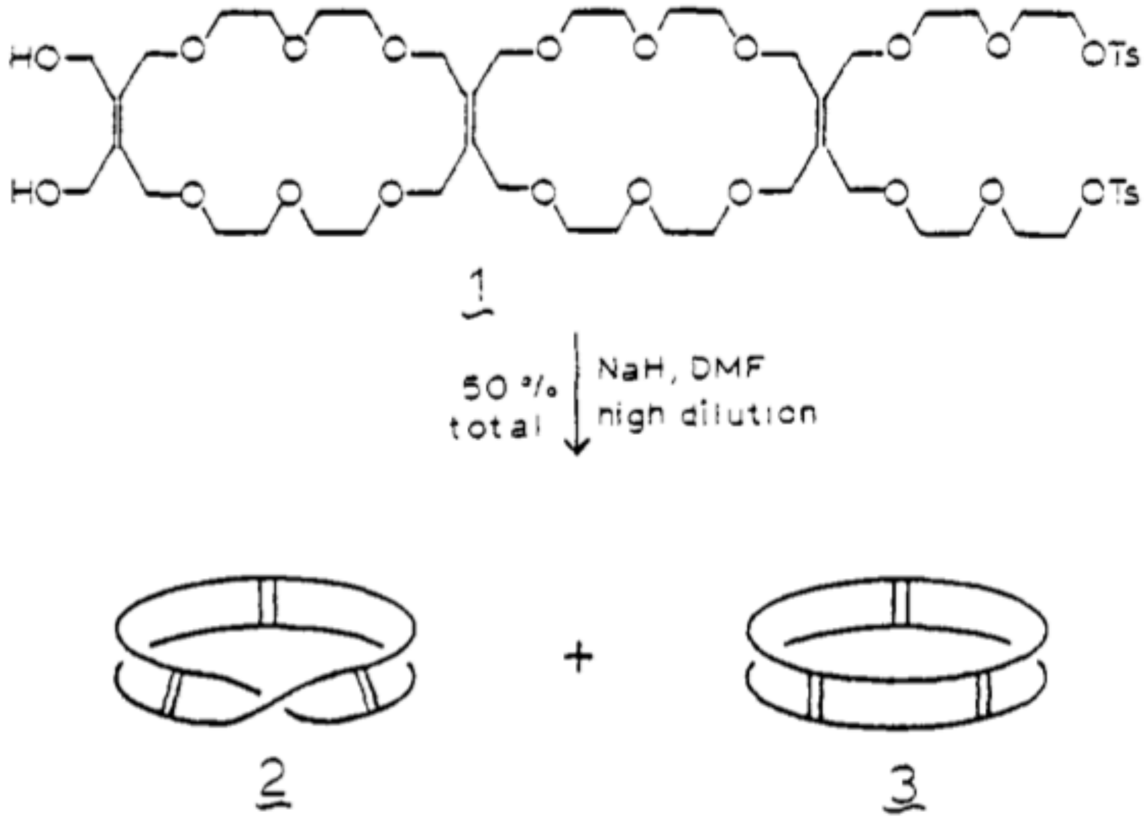
- Microwave chemistry starts to become in vogue in part due to a Tet. Lett. entitled "The Use of Microwave Ovens in Organic Synthesis" by Gedye and co-workers (1072 citations) *Tet. Lett.* **1986**, *27*, 279-282
- Lipase resolution of alcohols, esters, and acids
  J. Am. Chem. Soc. **1985**, *107*, 7072–7076
- Total synthesis of the first molecular Möbius strip
  J. Am. Chem. Soc. **1982**, *104*, 3219–3221
- Ultrasound use starts to become prevalent for accelerating organometallic formation
  J. Am. Chem. Soc. **1980**, *102*, 7926–7927
- Woodward's last total synthesis (Erythromycin) published 2 years after his death in 1979
  J. Am. Chem. Soc. **1981**, *103*, 3215–3217
- Tramontano, Janda, and Lerner publish work on catalytic antibodies *Science*, New Series, Vol. 234, No. 4783 (Dec. 19, 1986), pp. 1566-1570

Total Synthesis of the First Molecular Möbius Strip

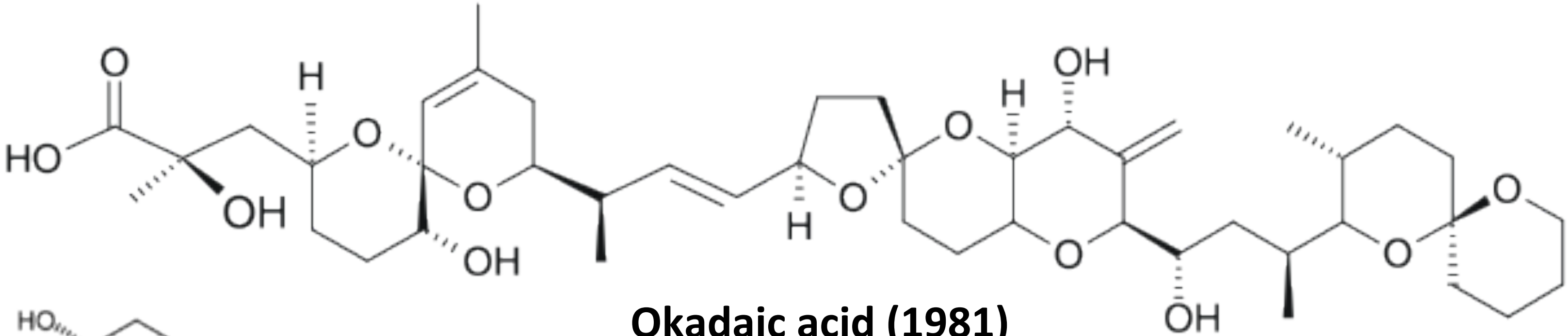
David M. Walba,* Rodney M. Richards, and
R. Curtis Haltiwanger

J. Am. Chem. Soc. **1982**, *104*, 3219–3221

Scheme I

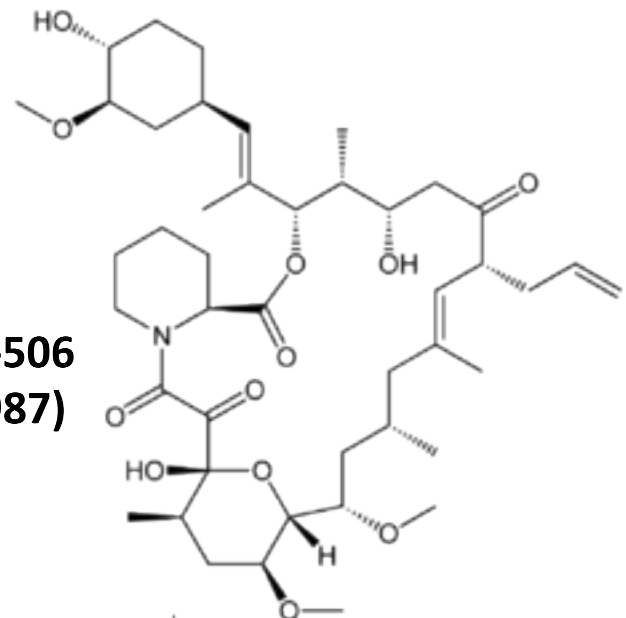


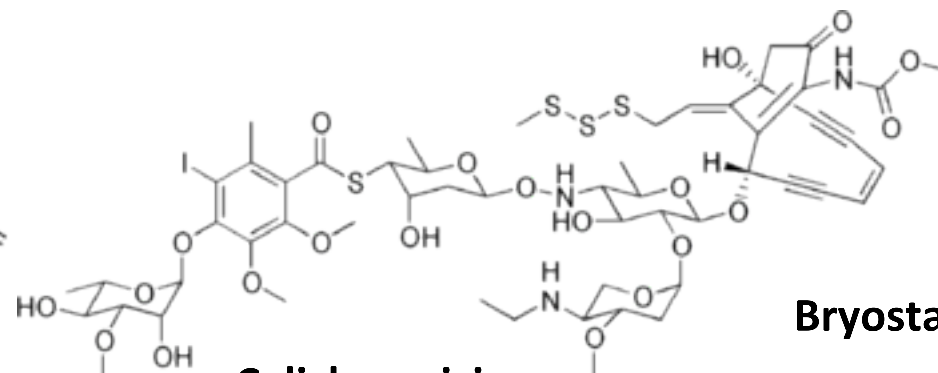
Natural Products of the 1980s



Okadaic acid (1981)

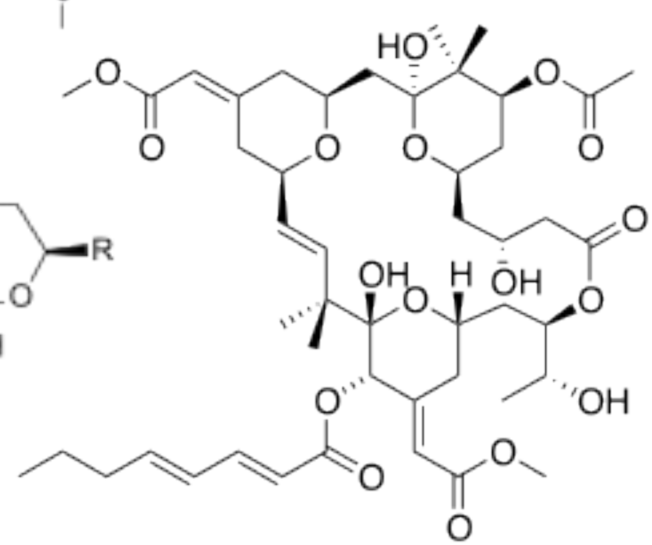
FK-506 (1987)

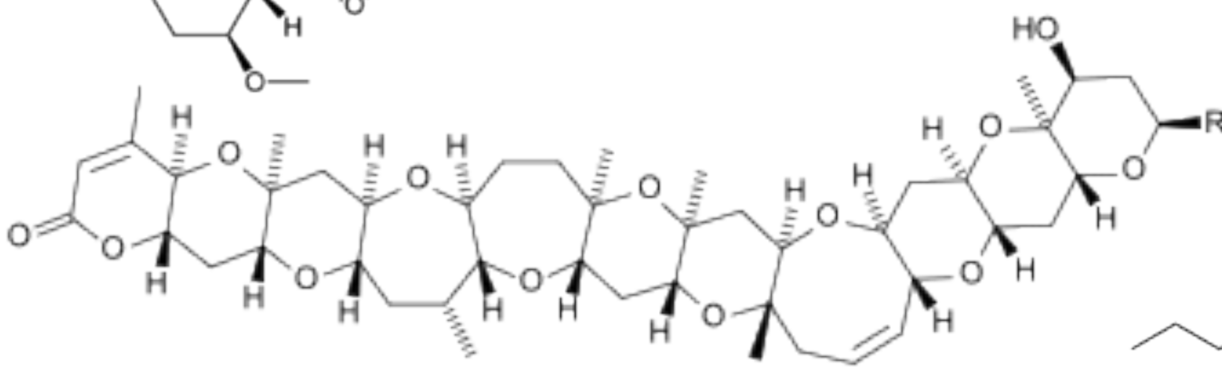




Calicheamicin (1987)

Bryostatin 1 (1982)





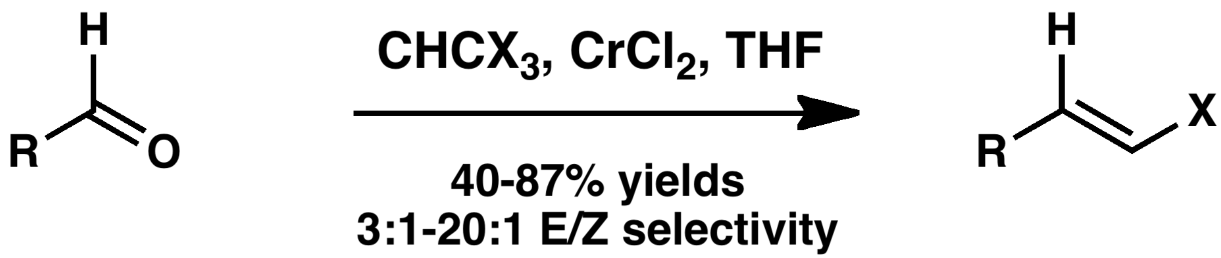
Brevetoxin B (1981)

Simple and Selective Method for RCHO → (*E*)-RCH=CHX Conversion by Means of a CHX_3–$CrCl_2$ System

520 citations

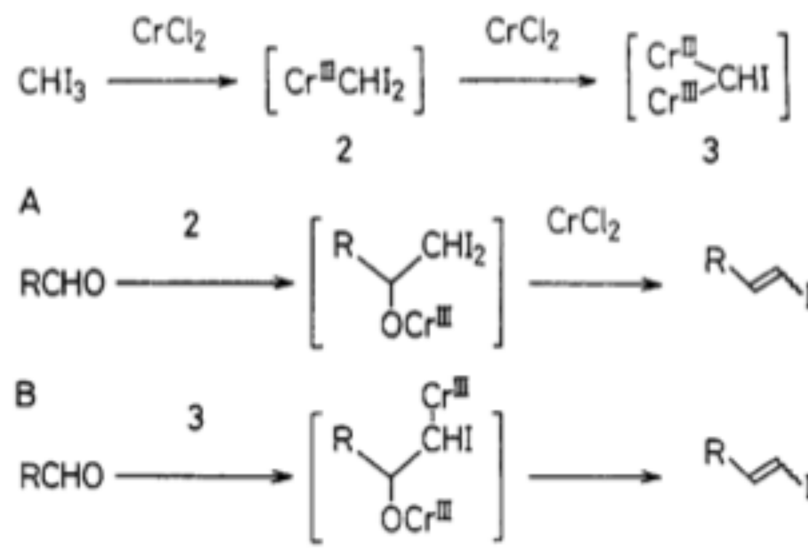
Kazuhiko Takai,* Kenji Nitta, and Kiitiro Utimoto

J. Am. Chem. Soc. **1986**, *108*, 7408–7410



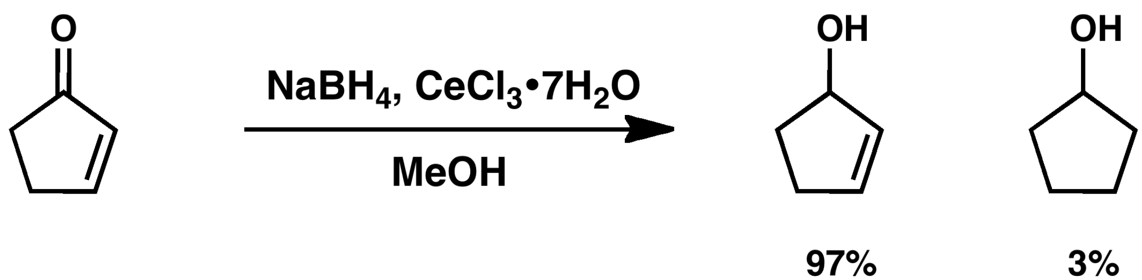
- Takai olefination
- Selective for aldehydes over ketones

Scheme III

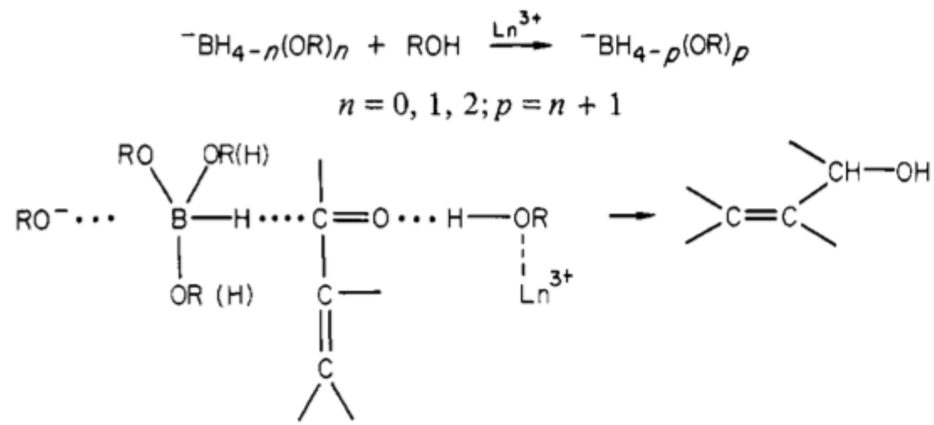


Lanthanoids in Organic Synthesis. 6. The Reduction of α-Enones by Sodium Borohydride in the Presence of Lanthanoid Chlorides: Synthetic and Mechanistic Aspects

André L. Gemal and Jean-Louis Luche* *J. Am. Chem. Soc.* **1981**, *103*, 5454–5459

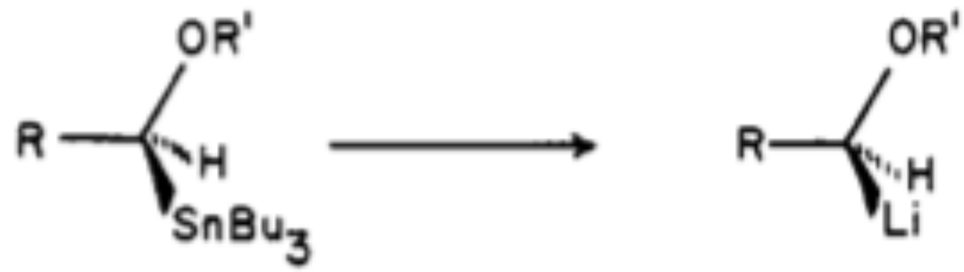


- Luche reduction
- Expands on previous methodology that allowed for selective reduction of aldehydes over ketones
- Selective 1,2 over 1,4 reduction

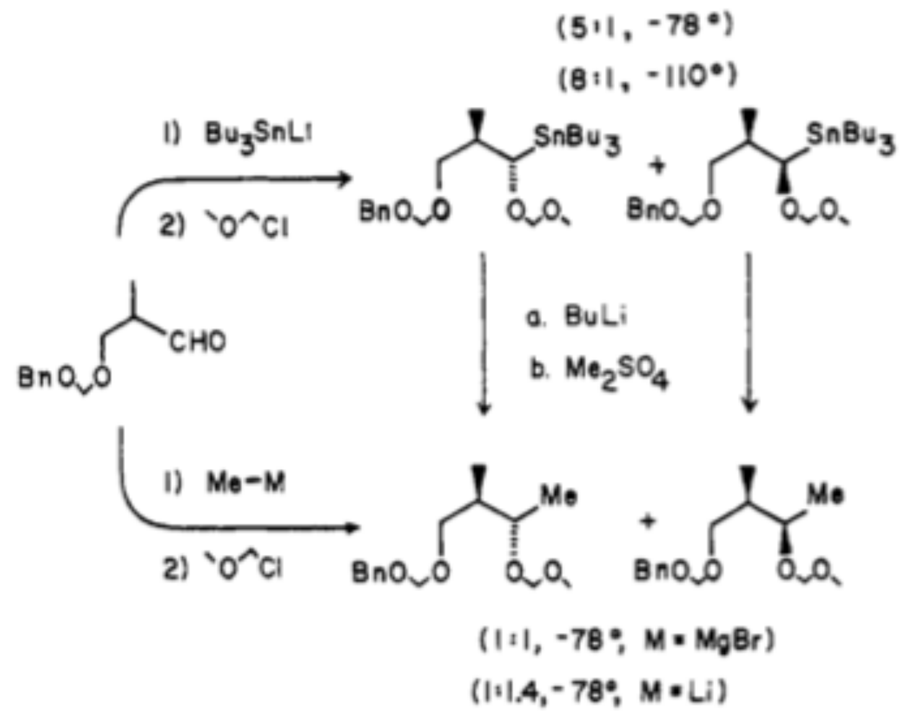


α-Alkoxyorganolithium Reagents. A New Class of Configurationally Stable Carbanions for Organic Synthesis

W. Clark Still,*[16] C. Sreekumar *J. Am. Chem. Soc.* **1980**, 102, 1201-1202.



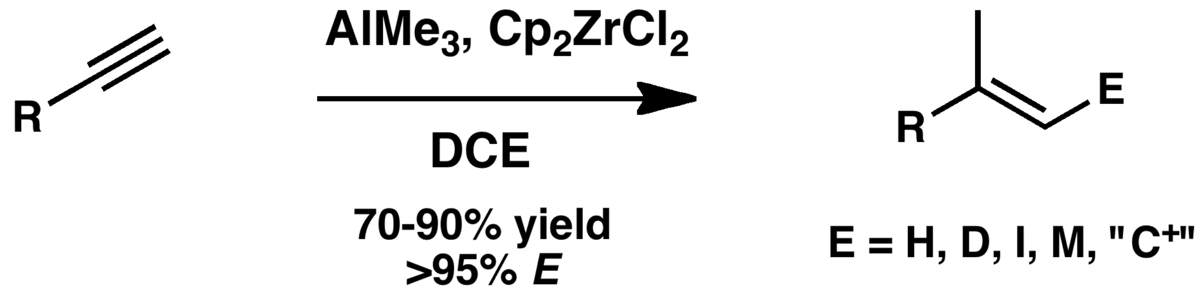
- Chiral organolithium species

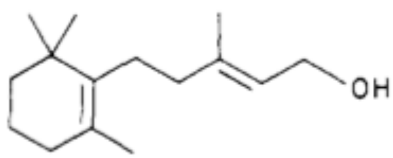


Carbometalation Reaction of Alkynes with Organoalane–Zirconocene Derivatives as a Route to Stereo- and Regiodefined Trisubstituted Alkenes[1]

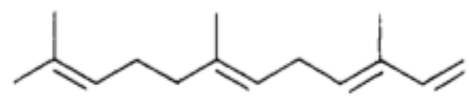
Ei-ichi Negishi,*[2] David E. Van Horn, and Tadao Yoshida

J. Am. Chem. Soc. **1985**, *107*, 6639–6647

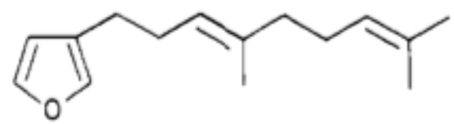




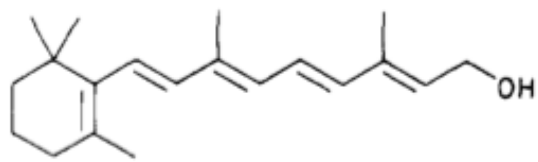
5



6



7



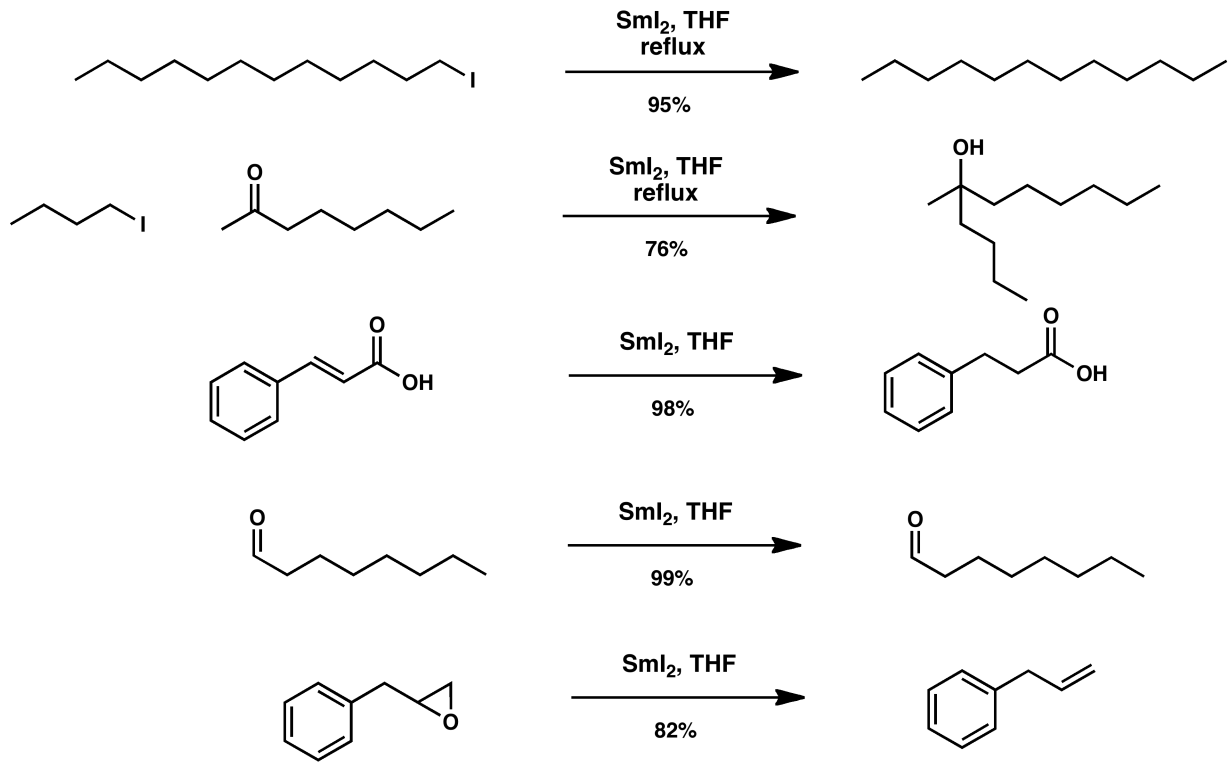
8

Divalent Lanthanide Derivatives in Organic Synthesis. 1. Mild Preparation of SmI_2 and YbI_2 and Their Use as Reducing or Coupling Agents[1]

1082 citations

P. Girard, J. L. Namy, and H. B. Kagan*
J. Am. Chem. Soc. **1980**, 102, 2693-2698.

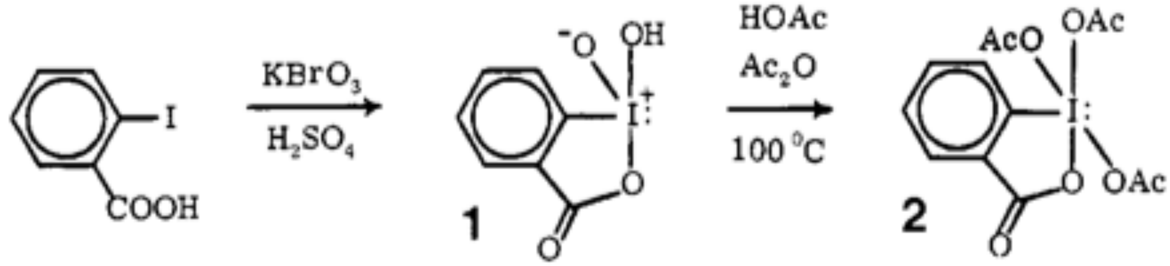
- Preparation, halide reduction, carbonyl reductive alkylation, olefin reduction, carbonyl reduction, deoxygenation



Readily Accessible 12-I-5[1] Oxidant for the Conversion of Primary and Secondary Alcohols to Aldehydes and Ketones

2011 citations

J. Org. Chem. 1983, *48*, 4155–4156



- DMP
- Hypervalent iodine oxidant
- Mild oxidation with high reproducibility

Table I. Oxidations of Alcohols to Aldehydes or Ketones with **2** in CH_2Cl_2 at 25 °C

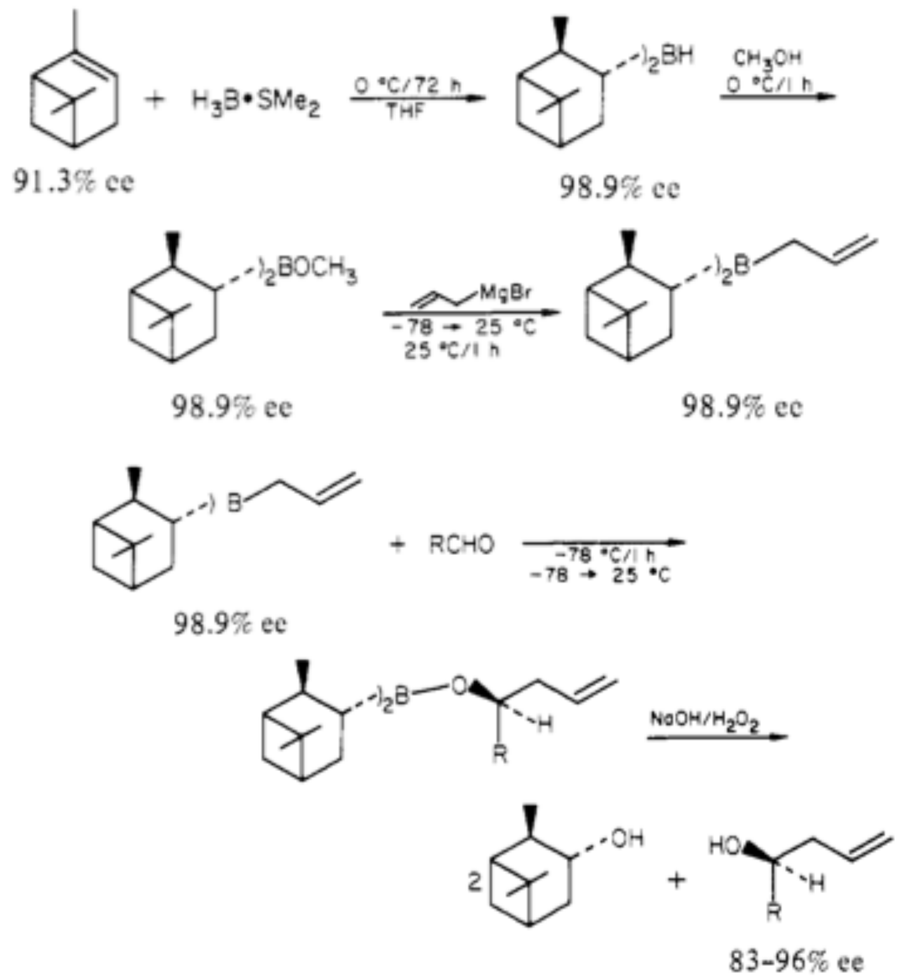
alcohol	equiv of **2**[d] (time, h)	added acid or base (concn, M)	yield, %
cyclohexanol	1.05 (0.5)	CF_3COOH (0.17)	90[a]
n-octanol	1.05 (0.5)	CF_3COOH (0.17)	83[a]
n-octanol	1.05 (1.0)	CF_3COOH (5.1×10^{-3})	94[a]
cyclooctanol	1.05 (1.0)	CF_3COOH (5.1×10^{-3})	99[a]
cyclooctanol	1.05 (1.0)	CH_3COOH (4.7×10^{-2})	84[b]
n-octanol	1.05 (1.0)	CH_3COOH (0.017)	93[a]
$PhCH_2OH$	1.05 (1.0)		91[a]
2,5-dimethoxybenzyl alcohol	1.10 (1.0)		94[b]
3,4,5-trimethoxybenzyl alcohol	1.10 (0.3)		94[b]
3,4,5-trimethoxybenzyl alcohol	1.10 (0.3)		90[b,c]
n-octanol	1.05 (1.0)	C_6H_5N (0.34)	86[a]

Asymmetric Carbon–Carbon Bond Formation via *B*-Allyldiisopinocampheylborane. Simple Synthesis of Secondary Homoallylic Alcohols with Excellent Enantiomeric Purities

J. Am. Chem. Soc. **1983**, *105*, 2092–2093

Herbert C. Brown* and Prabhakar K. Jadhav[1]

- Brown allylation
- High yield and high e.e.



R = CH_3, CH_3CH_2, $CH_3CH_2CH_2$, $(CH_3)_2CH$, $(CH_3)_3C$, Ph

Selective Reductions. 26. Lithium Triethylborohydride as an Exceptionally Powerful and Selective Reducing Agent in Organic Synthesis. Exploration of the Reactions with Selected Organic Compounds Containing Representative Functional Groups[1,2]

Herbert C. Brown,* S. C. Kim,[3] and S. Krishnamurthy

J. Org. Chem., *Vol. 45, No. 1, 1980*

$$LiH + Et_3B \xrightarrow{THF} \underset{100\%}{LiEt_3BH}$$

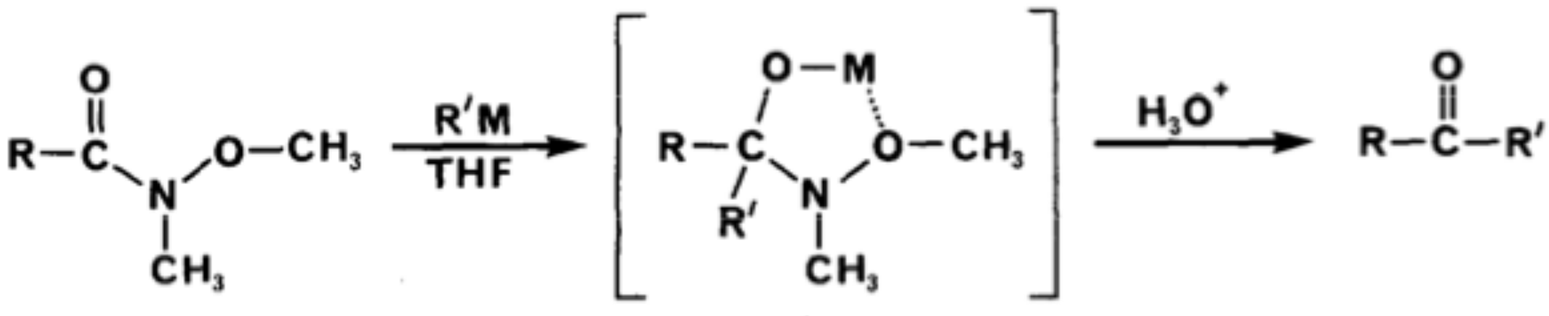
- **Superhydride**
- Aldehydes, ketones, acid chlorides and esters to alcohols
- Lactones to diols
- Acid anhydrides to alcohols
- α,β-enones by 1,4-addition to give lithium enolates
- Disulfides to thiols
- Tertiary amides to an alcohol
- High yield and high e.e.

Tetrahedron Letters, Vol.22, No.39, pp 3815 - 3818, 1981

1147 citations

N-METHOXY-N-METHYLAMIDES AS EFFECTIVE ACYLATING AGENTS

Steven Nahm and Steven M. Weinreb*

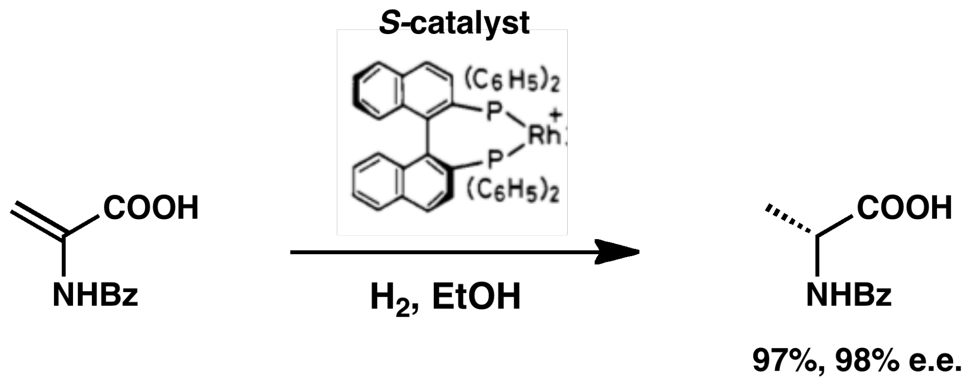


- Weinreb amide
- Prevents over-addition of organometallic agents to carbonyl groups with ester oxidation state
- High yields
- Simple formation from acid chloride or (later on) from aluminum reagent and N,O-dimethylhydroxylamine hydrochloride

Synthesis of 2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl (BINAP), an Atropisomeric Chiral Bis(triaryl)phosphine, and Its Use in the Rhodium(I)-Catalyzed Asymmetric Hydrogenation of α-(Acylamino)acrylic Acids

J. Am. Chem. Soc. **1980**, *102*, 7932–7934

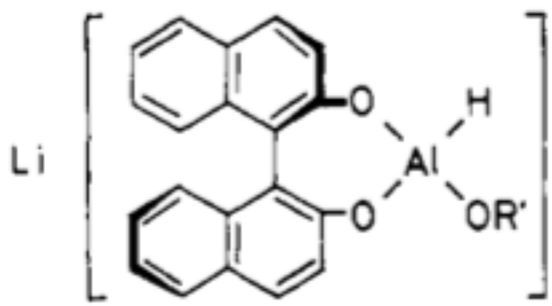
A. Miyashita, A. Yasuda, H. Takaya* K. Toriumi, T. Ito[17] T. Souchi, R. Noyori*



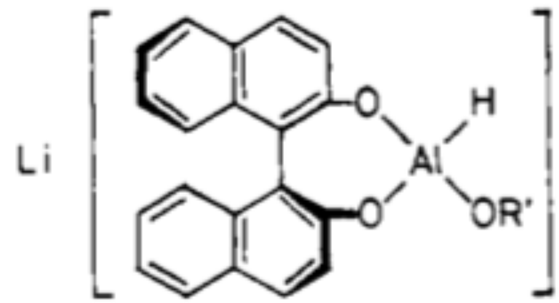
- Noyori’s highest cited paper of the decade
- First description of BINAP ligands in literature
- Basis for much of Noyori’s future work in asymmetric hydrogenations

Rational Designing of Efficient Chiral Reducing Agents. Highly Enantioselective Reduction of Aromatic Ketones by Binaphthol-Modified Lithium Aluminum Hydride Reagents[1]

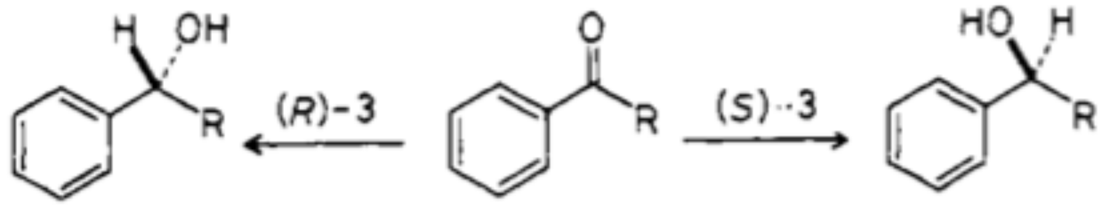
R. Noyori,* I. Tomino, Y. Tanimoto, and M. Nishizawa *J. Am. Chem. Soc.* **1984**, *106*, 6709–6716



(*R*)-3



(*S*)-3

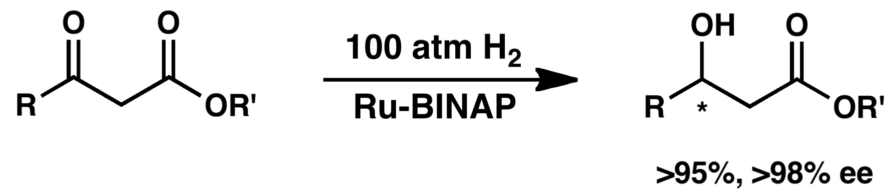


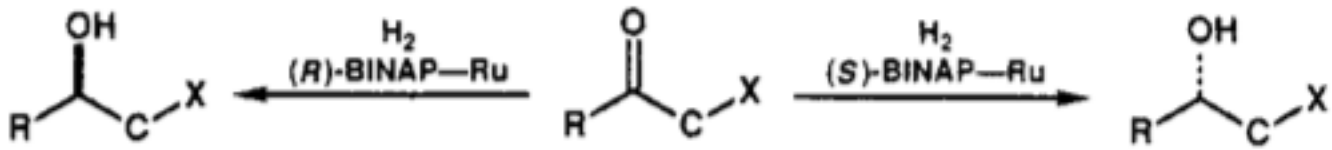
(*R*)-5 4 (*S*)-5

a, R = CH_3
b, R = C_2H_5
c, R = *n*-C_3H_7
d, R = *n*-C_4H_9
e, R = $CH(CH_3)_2$
f, R = $C(CH_3)_3$

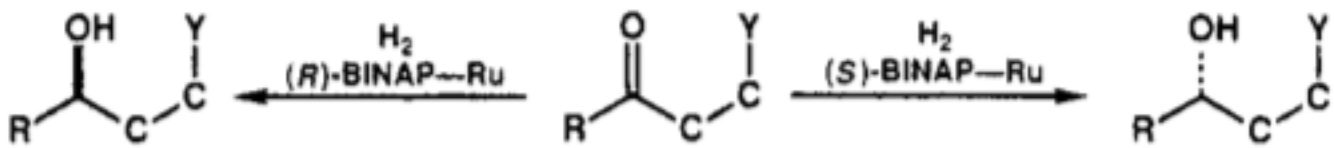
Asymmetric Hydrogenation of β-Keto Carboxylic Esters. A Practical, Purely Chemical Access to β-Hydroxy Esters in High Enantiomeric Purity

J. Am. Chem. Soc. 1987, 109, 5856–5858





(1)



(2)

Catalytic Asymmetric Induction. Highly Enantioselective Addition of Dialkylzincs to Aldehydes

M. Kitamura, S. Suga, K. Kawai, and R. Noyori*

J. Am. Chem. Soc. **1986**, *108*, 6071–6072

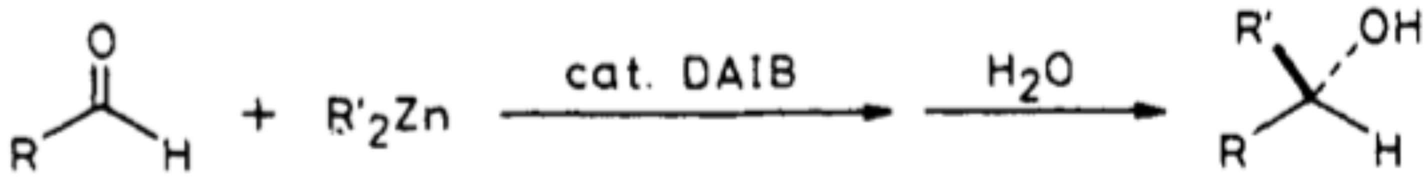
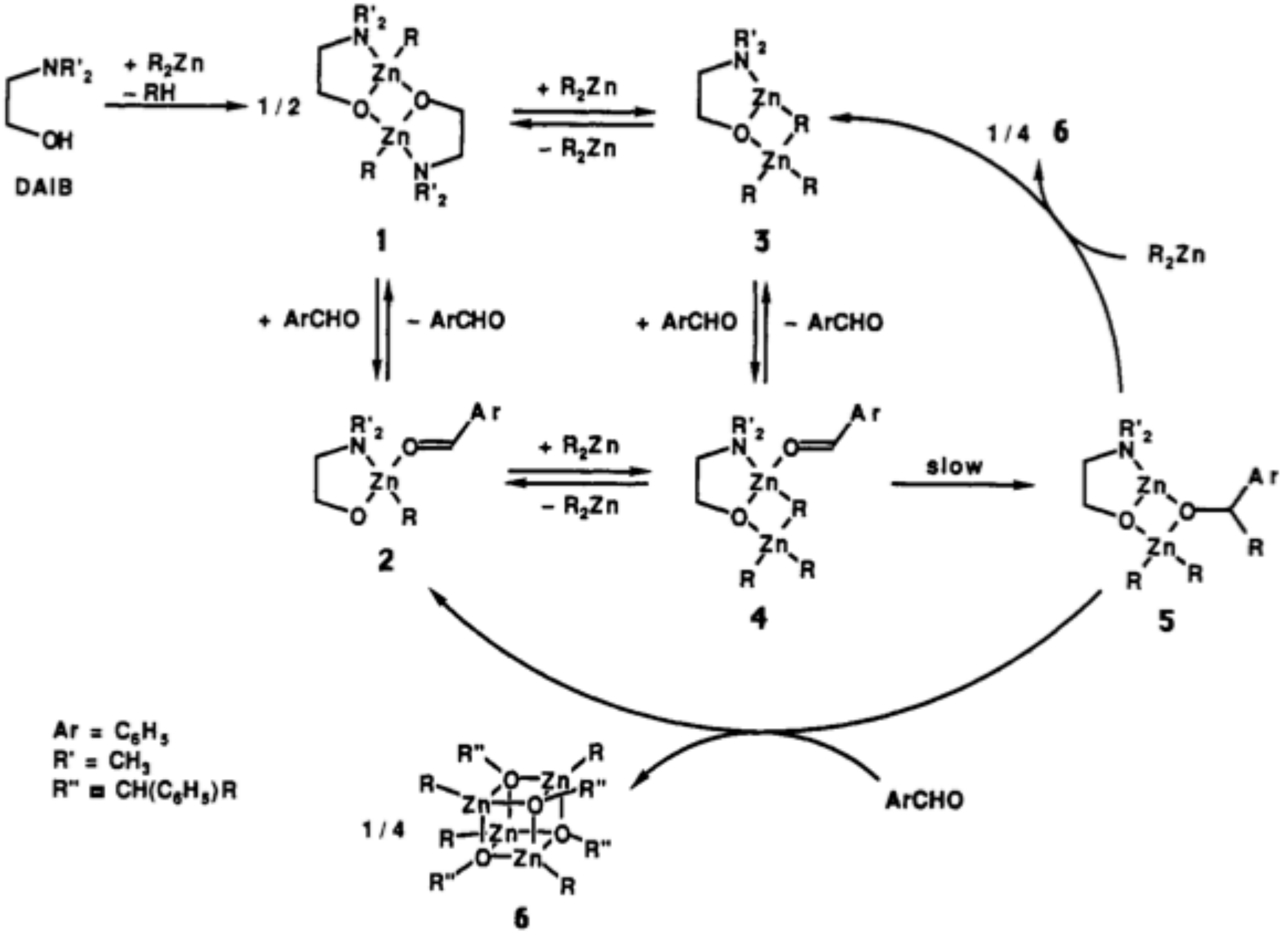


Table I. Enantioselective Addition of Dialkylzincs to Aldehydes[a]

aldehyde	alkylating agent	conditions: solvent	conditions: time, h	alkylated product: % yield[b]	alkylated product: $[\alpha]^{22}_{D}$, deg (*c*, solvent)	alkylated product: % ee[c] (confign)
C_6H_5CHO	$(C_2H_5)_2Zn$	toluene	6	97	−47.6 (6.11, $CHCl_3$)[d]	98 (*S*)[e]
C_6H_5CHO	$(C_2H_5)_2Zn$	hexane–toluene	6	94[f]		98 (*S*)
C_6H_5CHO	$(C_2H_5)_2Zn$	ether–toluene	6	98[f]		99 (*S*)
C_6H_5CHO	$(C_2H_5)_2Zn$	THF–toluene	64	44[f]		91 (*S*)
C_6H_5CHO	$(CH_3)_2Zn$	toluene	70	59[f]	−49.7 (2.01, *c*-C_5H_{10})[g]	91[h] (*S*)
p-ClC_6H_4CHO	$(C_2H_5)_2Zn$	toluene	12	86	−23.5 (0.82, C_6H_6)[i]	93 (*S*)
p-$CH_3OC_6H_4CHO$	$(C_2H_5)_2Zn$	toluene	12	96	−32.1 (1.25, C_6H_6)[i]	93 (*S*)
(*E*)-$C_6H_5CH{=}CHCHO$	$(C_2H_5)_2Zn$	toluene	6	81	−5.7 (100, $CHCl_3$)[j]	96 (*S*)
$C_6H_5CH_2CH_2CHO$	$(C_2H_5)_2Zn$	toluene	12	80	+23.9 (1.44, C_2H_5OH)[k]	90[l] (*S*)
n-$C_6H_{13}CHO$	$(C_2H_5)_2Zn$	toluene	24	81	+5.1 (1.31, $CHCl_3$)[m]	61[l] (*S*)

Enantioselective Addition of Dialkylzincs to Aldehydes Promoted by Chiral Amino Alcohols. Mechanism and Nonlinear Effect

M. Kitamura, S. Okada, S. Suga, and R. Noyori* *J. Am. Chem. Soc.* **1989**, *111*, 4028–4036

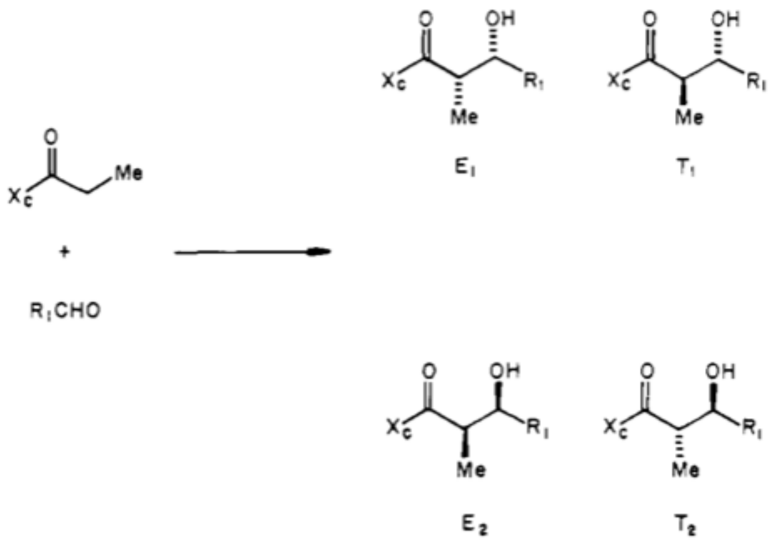


Enantioselective Aldol Condensations. 2. Erythro-Selective Chiral Aldol Condensations via Boron Enolates[1]

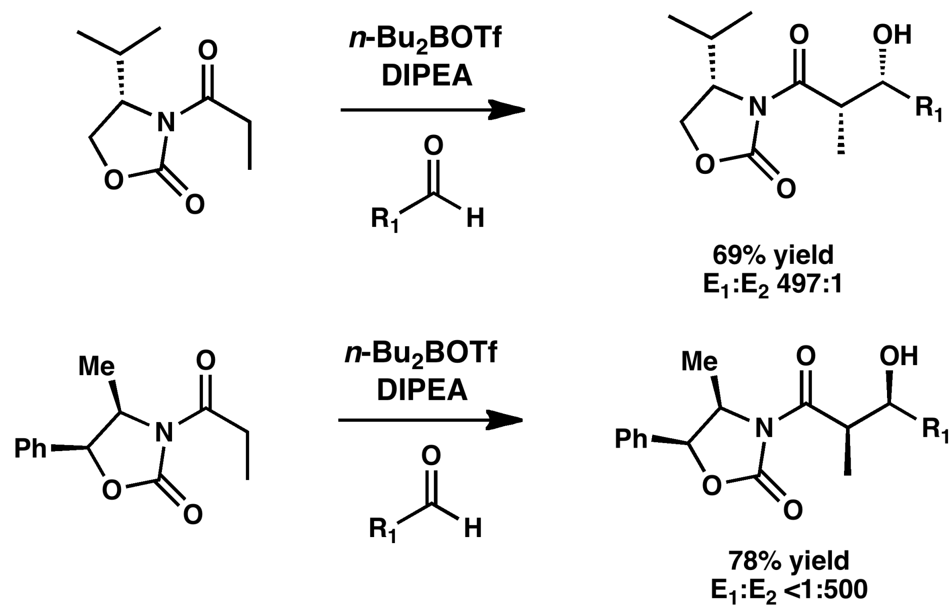
1175 citations

J. Am. Chem. Soc. **1981**, *103*, 2127–2129

D. A. Evans,* J. Bartroli, and T. L. Shih



Inherent problem of enantio and diastereoselection in aldol condensations



- Excellent erythro selectivity when different enantiomers of chiral oxazolidone auxiliary used
- One of many works by Evans with chiral auxiliaries

The First Practical Method for Asymmetric Epoxidation

Tsutomu Katsuki, K. Barry Sharpless*[18]

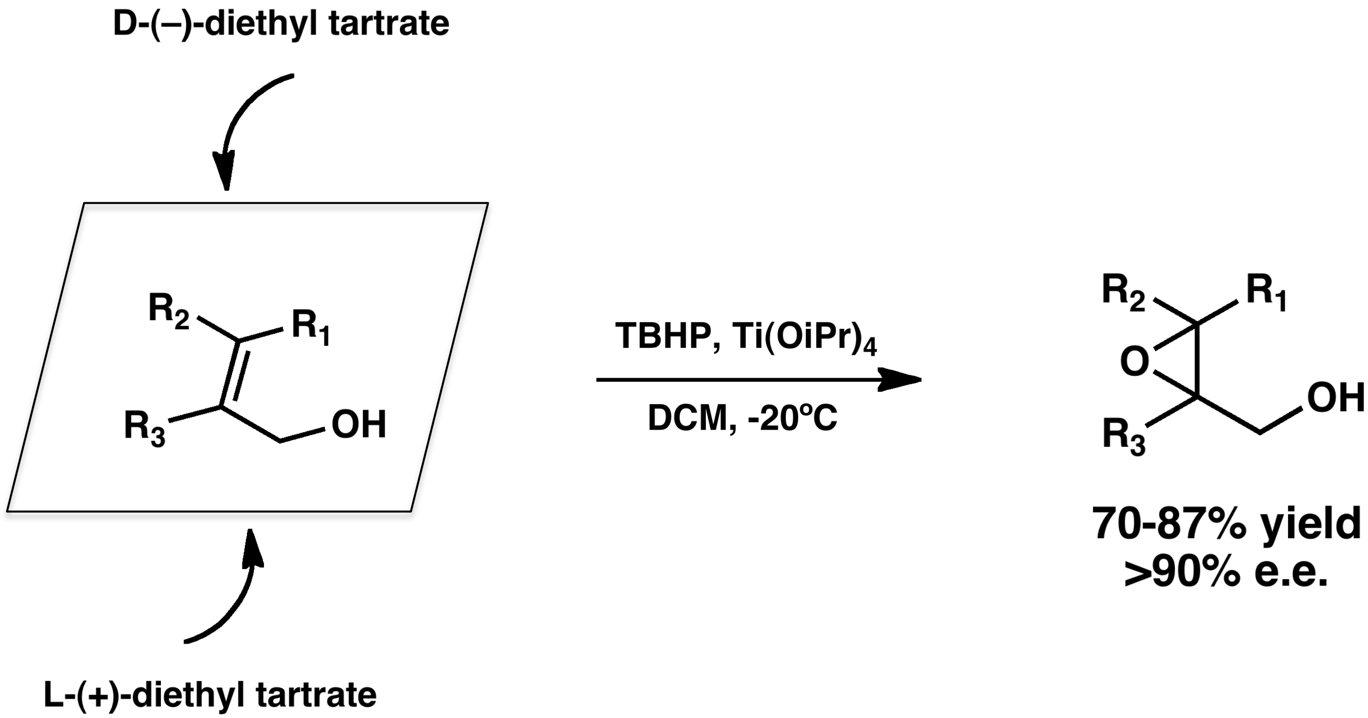
Department of Chemistry, Stanford University
Stanford, California 94305

Received May 5, 1980

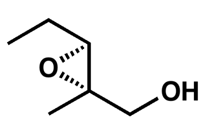
J. Am. Chem. Soc. **1980**, *102*, 5974–5976

- 1863 citations to date (14th highest in *JACS*, arguably the highest cited methodology/ synthesis paper of the decade in *JACS*)
- Inspired several more papers that improved procedure, rendered the reaction catalytic, proved its usefulness to natural product synthesis, and added a kinetic resolution aspect

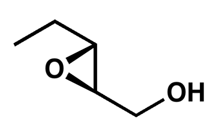
Sharpless Asymmetric Epoxidation



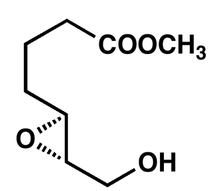
J. Am. Chem. Soc. **1981**, *103*, 464–465



methmycin precursor



erythromycin precursor



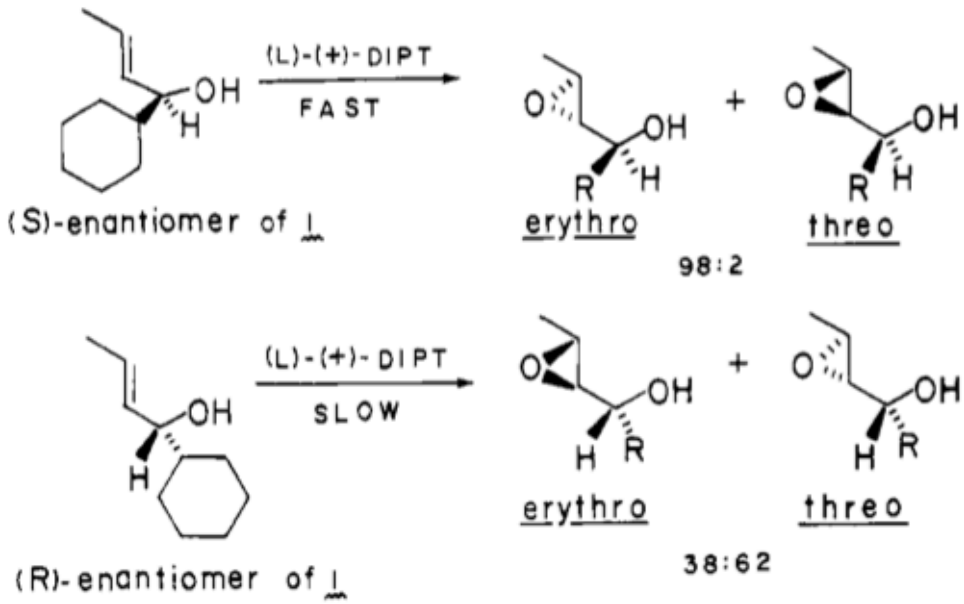
leukotriene C-1 precursor

Kinetic Resolution of Racemic Allylic Alcohols by Enantioselective Epoxidation. A Route to Substances of Absolute Enantiomeric Purity?[†,‡]

Victor S. Martin, Scott S. Woodard, Tsutomu Katsuki, Yasuhiro Yamada, Masanori Ikeda, and K. Barry Sharpless*

J. Am. Chem. Soc. **1981**, *103*, 6237–6240

Scheme I. Differential Erythro–Threo Selectivity[a] for Enantiomers of **1**



[a] Erythro–threo ratios were determined in separate experiments by using the pure enantiomers.

- 720 citations to date (4th highest cited paper)
- Allows for kinetic resolution of racemic secondary allylic alcohols
- Yields are typically 30-45% with >95% e.e.

Catalytic Asymmetric Epoxidation and Kinetic Resolution: Modified Procedures Including in Situ Derivatization†

J. Am. Chem. Soc. **1987**, *109*, 5765–5780

Yun Gao, Robert M. Hanson, Janice M. Klunder, Soo Y. Ko, Hiroko Masamune, and K. Barry Sharpless*

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received July 11, 1986*

- 1819 citations to date (2nd highest cited paper)
- Originally reported in a 1986 JOC article, the introduction of molecular seives rendered the epoxidation reaction catalytic and highly reproducible with excellent e.e.
- Sharpless describes five key advantages over previous procedure: (1) cost savings from decreased amount of catalyst components; (2) higher yields due to less decomposition of sensitive epoxy substrates; (3) simplified isolation procedures; (4) higher substrate concentrations; (5) in situ derivitization

Asymmetric Dihydroxylation via Ligand-Accelerated Catalysis†

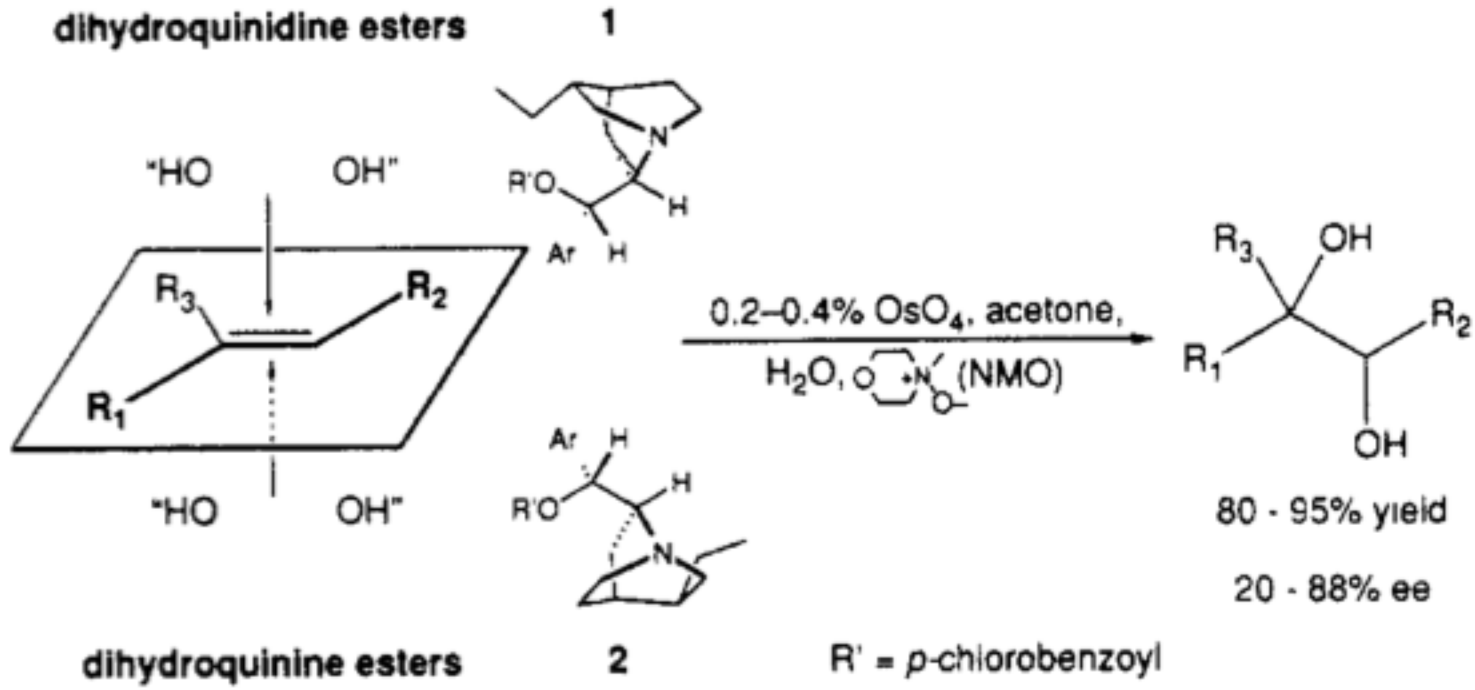
Eric N. Jacobsen, István Markó, William S. Mungall, Georg Schröder, and K. Barry Sharpless*

J. Am. Chem. Soc. **1988**, *110*, 1968–1970

- 535 citations to date (5th highest cited paper)
- Requires no directing group
- Very low osmium loading
- Uses two readily available cinchona alkaloids as ligands
- Performed in the presence of air and water, high concentration, very scalable

Sharpless Asymmetric dihydroxylation

Scheme I



J. Org. Chem. 1981, *46*, 3936–3938

A Greatly Improved Procedure for Ruthenium Tetraoxide Catalyzed Oxidations of Organic Compounds

Per H. J. Carlsen, Tsutomu Katsuki
Victor S. Martin, K. Barry Sharpless*[21]

Table I. RuO_4 Oxidation of (*E*)-5-Decene[a]

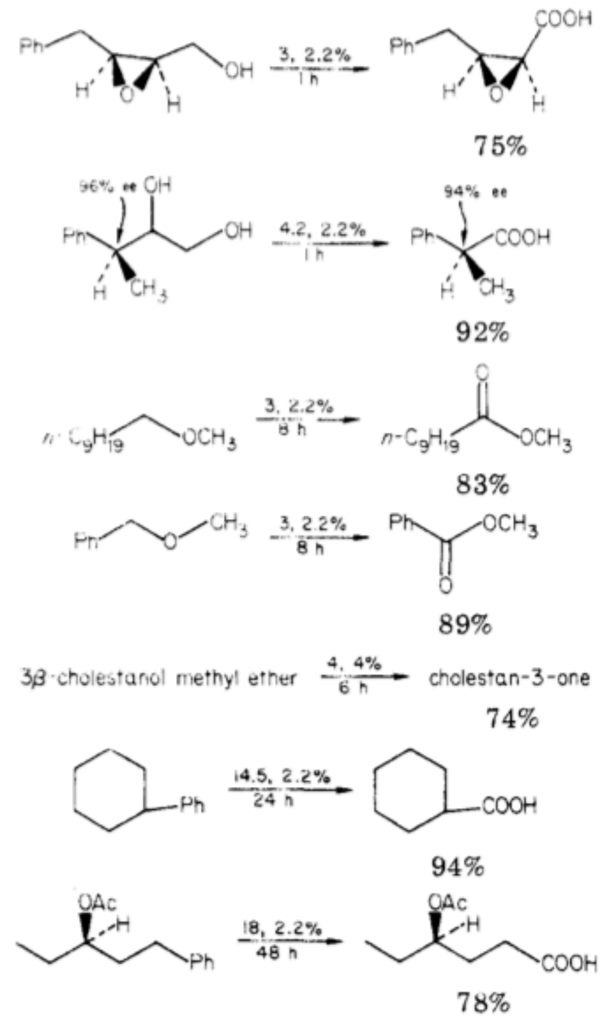
solvent	products[b] recovered olefin, %	*n*-pentanal, %	*n*-pentanoic acid, %
1. CCl_4, H_2O (1:1)	80	17	
2. acetone, H_2O (5:1)	74	20	3
3. CCl_4, CH_3CN, H_2O (2:2:3)[8]			88

[a] Reactions were performed at 25 °C for 2 h, using 0.022 mol equiv of $RuCl_3 \cdot (H_2O)_n$ and 4.1 mol equiv of $NaIO_4$. [b] Yields: entries 1 and 2 by GLC; entry 3 is an isolated yield.

Table II. Cleavage of Olefins by Improved Method[a]

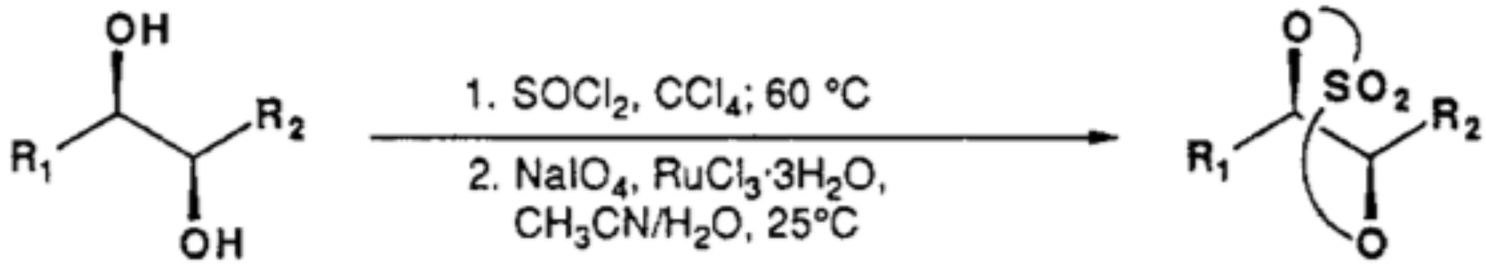
olefin	$NaIO_4$, equiv	time, h	% yield carboxylic acid
1-decene	4.5	2	89 [b]
(*E*)-5-decene	4.1	2	88 [c]
(*Z*)-5-decene	4.1	1	87 [c]
cyclooctene	4.5	1	75 [b]
citronellyl acetate	3.1	0.5	83 [b]
2,3-dimethyl-2-octene	2.1	6	>95 [d]

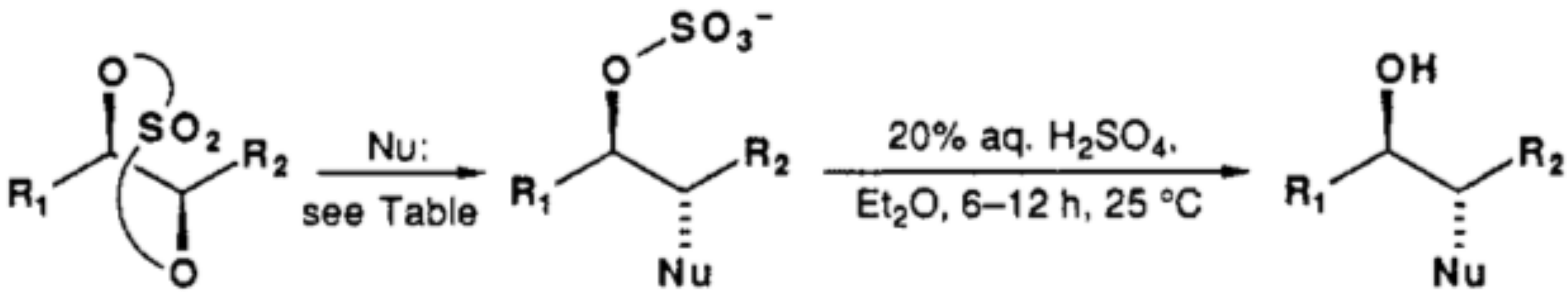
Scheme II. Oxidations of Alcohols, Ethers, and Aromatic Rings[a]



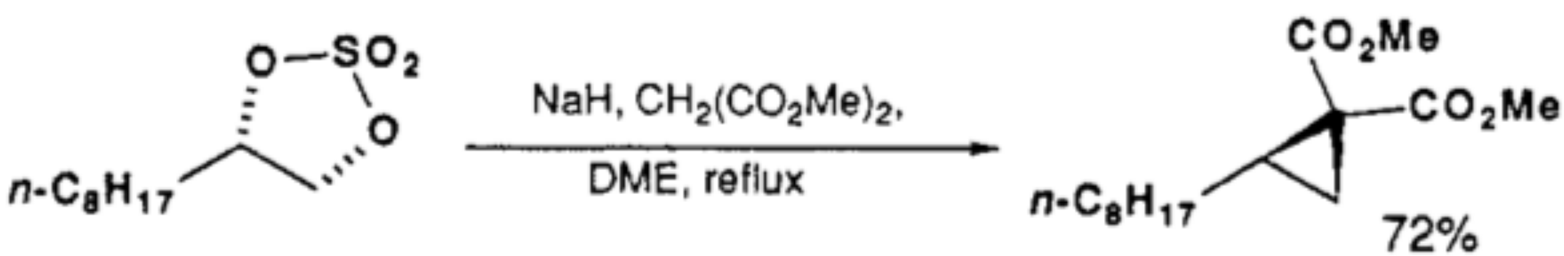
Vicinal Diol Cyclic Sulfates: Like Epoxides Only More Reactive

Yun Gao and K. Barry Sharpless* *J. Am. Chem. Soc.* **1988**, *110*, 7538–7539





2 3 4

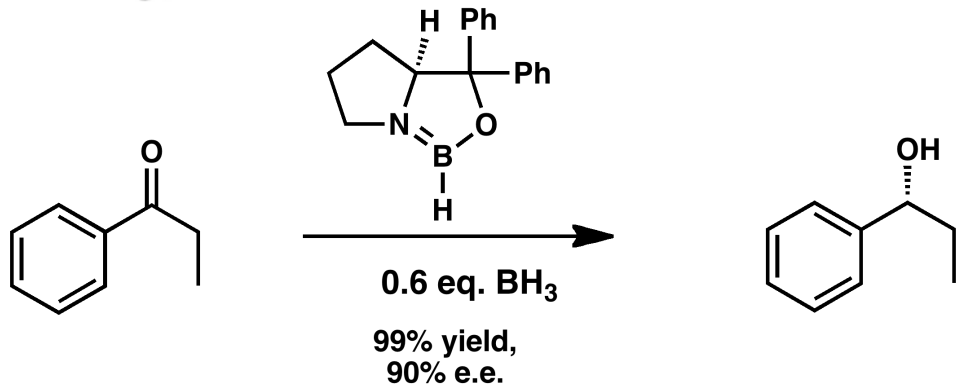


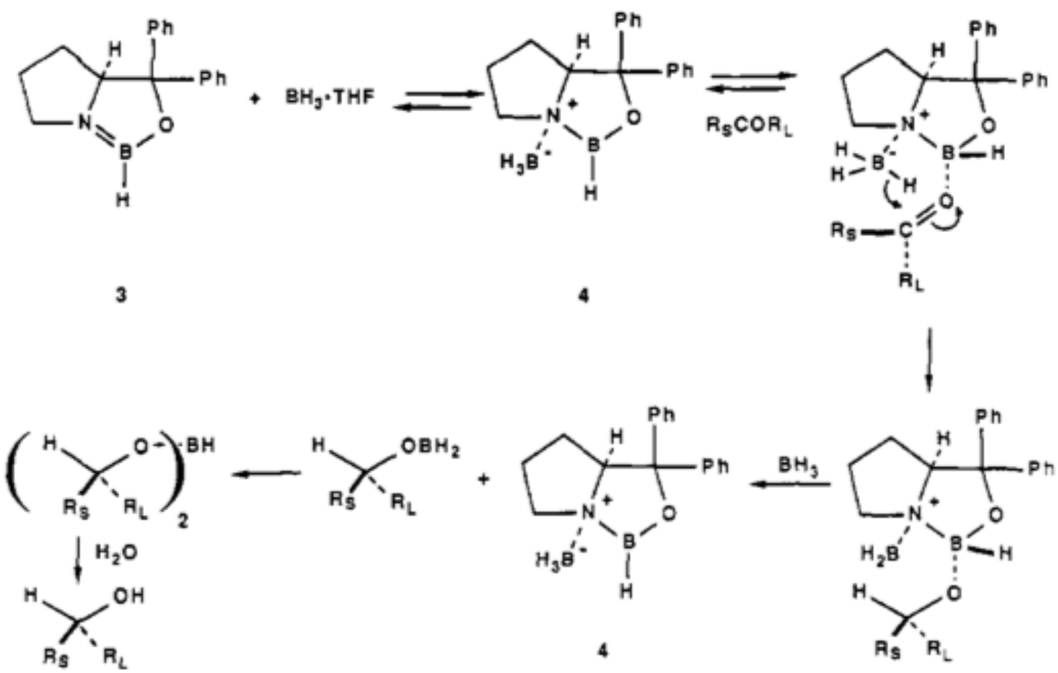
2d 5

Highly Enantioselective Borane Reduction of Ketones Catalyzed by Chiral Oxazaborolidines. Mechanism and Synthetic Implications *J. Am. Chem. Soc.* **1987**, *109*, 5551–5553

962 citations

E. J. Corey,* Raman K. Bakshi, and Saizo Shibata





- highest cited paper in a chemistry journal
- Precursor to CBS catalyst

A Stable and Easily Prepared Catalyst for the Enantioselective Reduction of Ketones. Applications to Multistep Syntheses

J. Am. Chem. Soc. **1987**, *109*, 7925–7926

E. J. Corey,* Raman K. Bakshi, Saizo Shibata, Chung-Pin Chen, and Vinod K. Singh

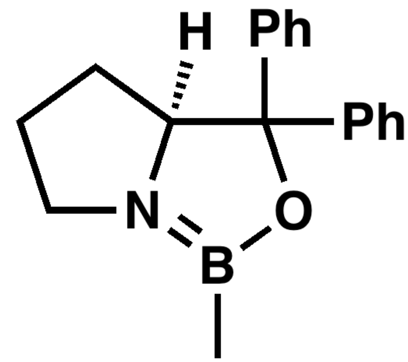
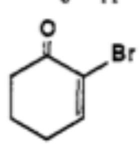
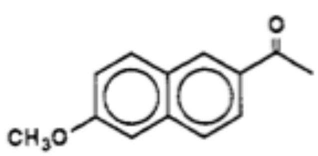


Table I. Borane Reduction of Ketones Catalyzed by (*S*)-**2**

$$2R_1R_2CO + BH_3 \xrightarrow[2\ min]{\mathbf{2},\ THF} (R_1R_2CH\text{-}O)_2BH \rightarrow R_1R_2CHOH$$

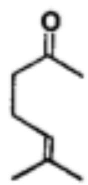
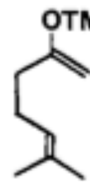
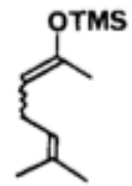
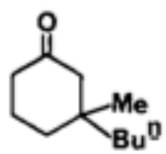
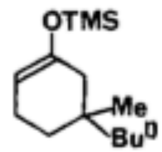
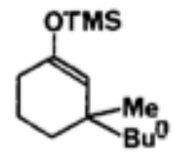
ketone	equiv BH_3	equiv **2**	reaction temp, °C	config of product[a] (% ee)[b]
$C_6H_5COCH_3$	0.6	0.1	2	*R* (96.5)
$C_6H_5COC_2H_5$	0.6	0.1	−10	*R* (96.7)
$C_6H_5COCH_2Cl$	0.6	0.1	32	*S* (95.3)
t-$BuCOCH_3$	0.6	0.1	−10	*R* (97.3)
α-tetralone	0.6	0.1	−10	*R* (83.3)
α-tetralone	0.6	0.25	−10	*R* (86.0)
c-$C_6H_{11}COCH_3$	0.6	0.1	−10	*R* (84)
	0.6	0.1	23	*R* (91)[c,d,e]
	0.6	0.1	23	*R* (97.6)[f]
$C_6H_5CO(CH_2)_2CO_2CH_3$	0.6	0.1	0	*R* (94)[f,g]
$C_6H_5CO(CH_2)_3CO_2CH_3$	0.6	0.1	0	*R* (96.7)[f,g]

- 2nd highest cited paper in a chemistry journal
- CBS catalyst
- Methyl group greatly increases stability

Tetrahedron Letters,Vol.25,No.5,pp 495-498,1984

HIGHLY SELECTIVE, KINETICALLY CONTROLLED ENOLATE FORMATION USING LITHIUM DIALKYLAMIDES IN THE PRESENCE OF TRIMETHYLCHLOROSILANE

E. J. Corey and Andrew W. Gross

SUBSTRATE	ENOL ETHER A	ENOL ETHER B	A:B[a] (A:B)[b] LDA	A:B[a] (A:B)[b] LOBA
$n\text{-}C_5H_{11}C(=O)CH_3$	$n\text{-}C_5H_{11}C(OTMS)=CH_2$	$n\text{-}C_4H_9CH=C(OTMS)CH_3$	95.5 (86:14)	97.5:2.5 (86 :14)
$n\text{-}C_6H_{13}C(=O)CH_3$	$n\text{-}C_6H_{13}C(OTMS)=CH_2$	$n\text{-}C_5H_{11}CH=C(OTMS)CH_3$	95:5 (94:6)[5]	97.5:2.5
			95:5	>97.5:<2.5
			90:10 (85:15)[6]	97:3 (95:5)
$C_6H_5CH_2C(=O)CH_3$	$C_6H_5CH_2C(OTMS)=CH_2$	$C_6H_5CH=C(OTMS)CH_3$	50:50 (0:100)	50:50

a) Internal quench

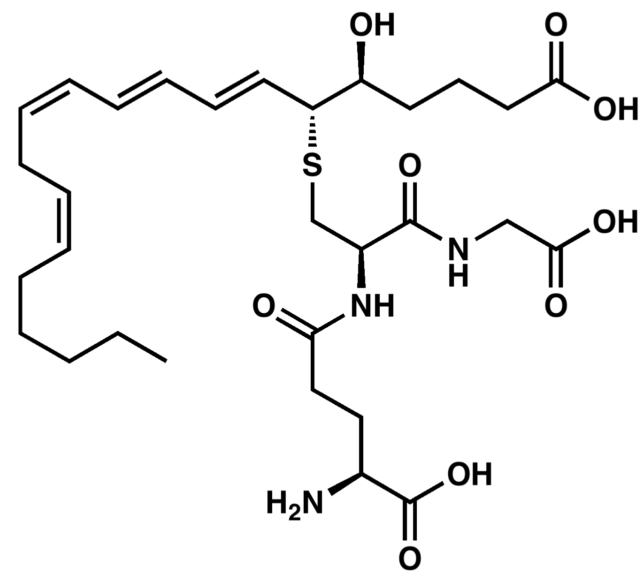
b) Two step procedure

Stereospecific Total Synthesis of a "Slow Reacting Substance" of Anaphylaxis, Leukotriene C-1

E. J. Corey,* David A. Clark, Giichi Goto
Anthony Marfat, Charles Mioskowski
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

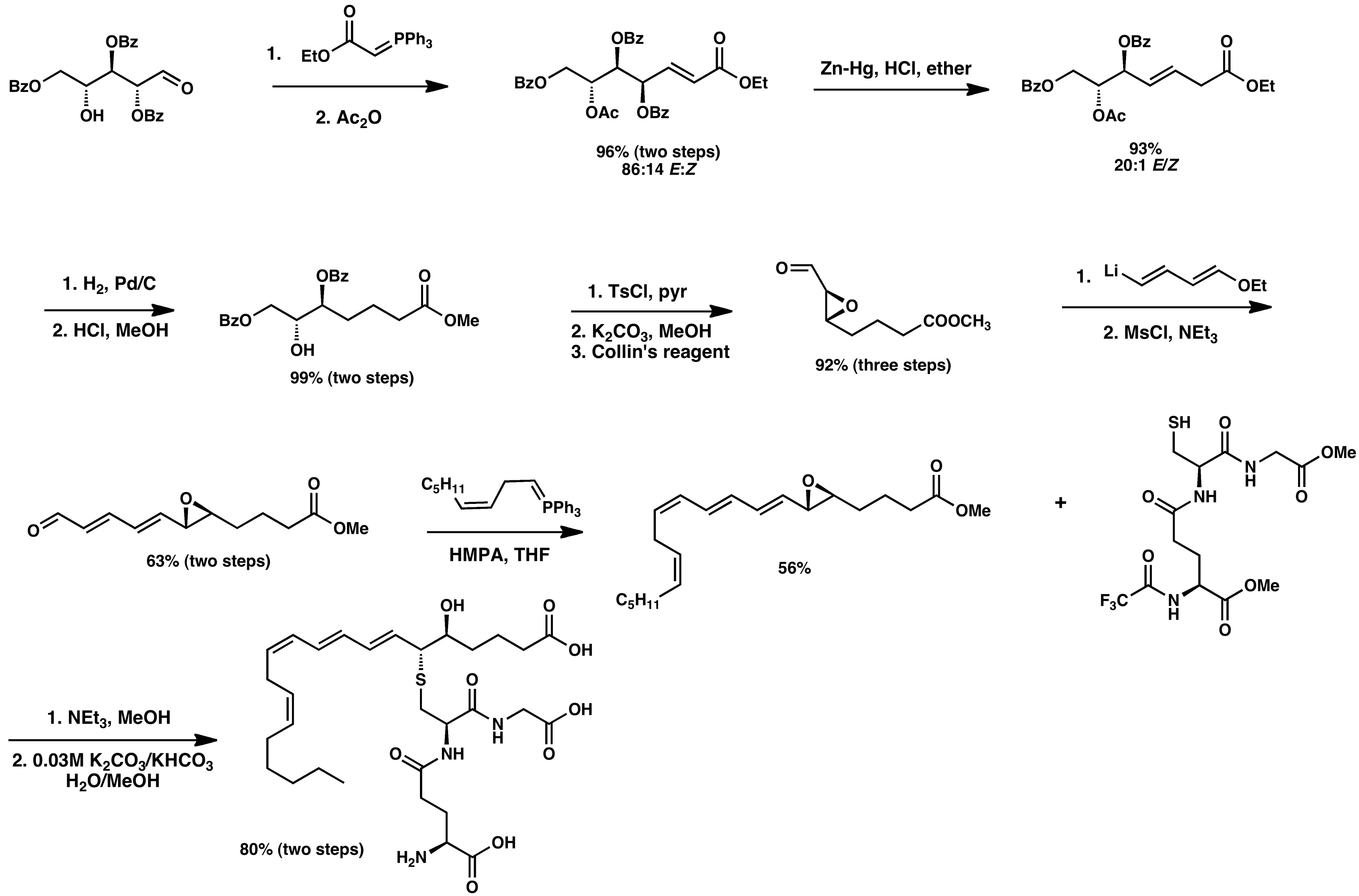
Bengt Samuelsson, Sven Hammarström
Department of Chemistry, Karolinska Institutet
S-104 01 Stockholm, Sweden
Received November 30, 1979

- Synthesized by Corey along with many other leukotrienes and eicosanoids
- Definitively proved the structure of the "slow reacting substance" of anaphylaxis
- Chemical synthesis inspires: 1000+ cited paper in NEJM, 700+ cited paper in PNAS, two 500+ and two 400+ cited papers (along with Corey's CBS papers, there are his highest cited paper's of the decade)



J. Am. Chem. Soc. **1980**, 102, 1436-1439.

Synthesis

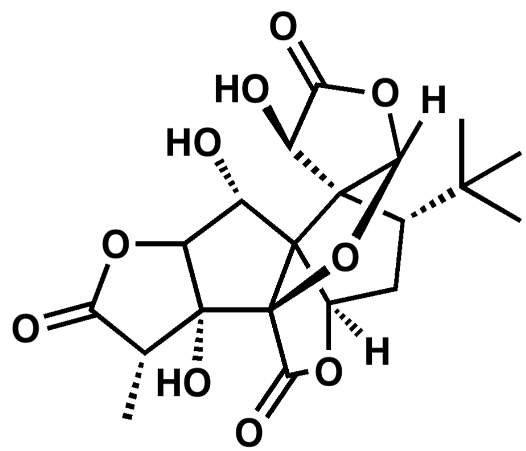


OBz
BzO
OH
OBz
O
1.
EtO
PPh$_3$
2. Ac$_2$O
OAc
OEt
96% (two steps)
86:14 *E*:*Z*
Zn-Hg, HCl, ether
93%
20:1 *E/Z*
1. H$_2$, Pd/C
2. HCl, MeOH
OMe
99% (two steps)
1. TsCl, pyr
2. K$_2$CO$_3$, MeOH
3. Collin's reagent
COOCH$_3$
92% (three steps)
1. Li
2. MsCl, NEt$_3$
63% (two steps)
C$_5$H$_{11}$
HMPA, THF
56%
+
SH
NH
H
F$_3$C
1. NEt$_3$, MeOH
2. 0.03M K$_2$CO$_3$/KHCO$_3$
H$_2$O/MeOH
S
OH
H$_2$N
80% (two steps)

Total Synthesis of (±)-Ginkgolide B

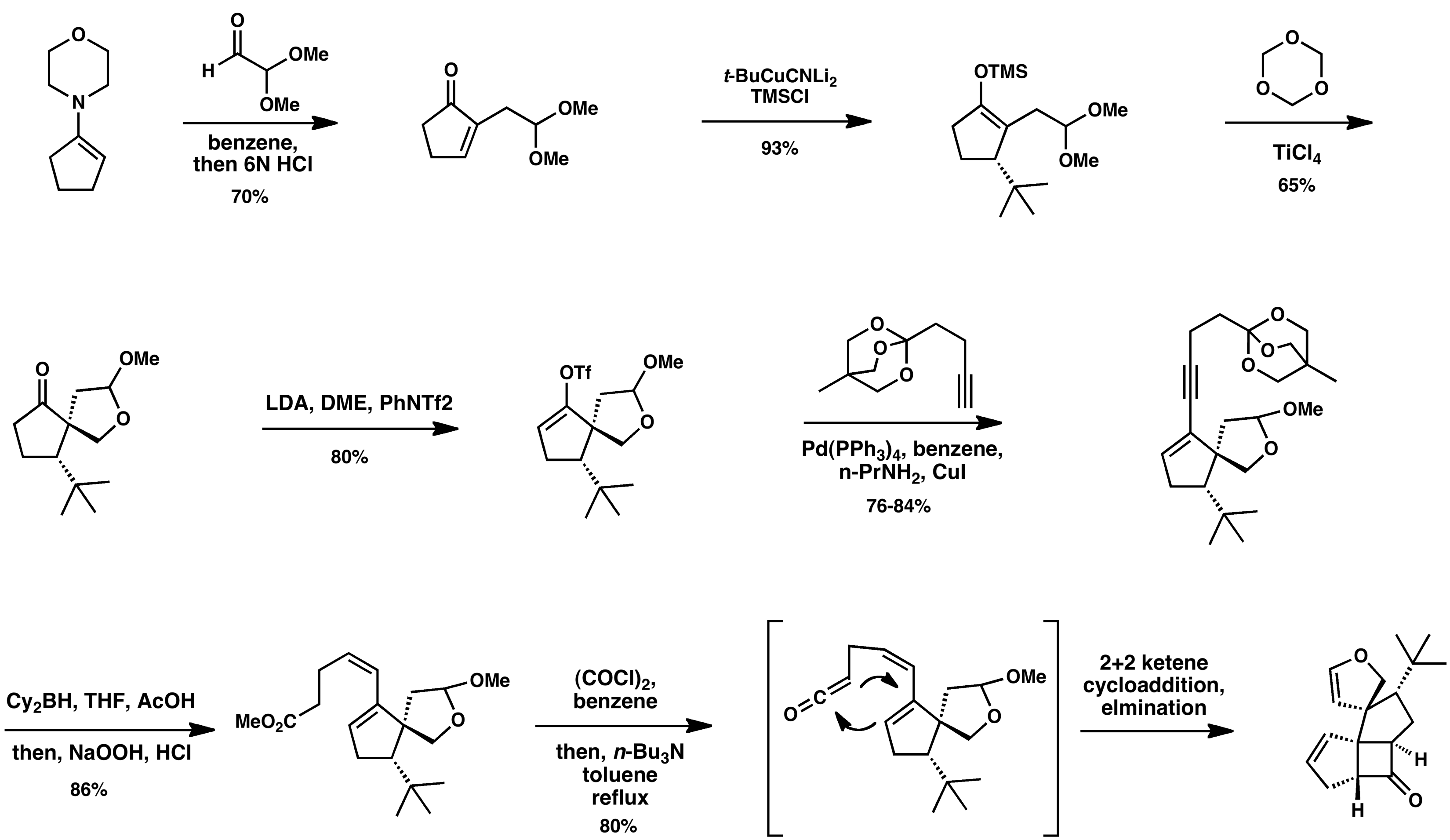
E. J. Corey,* Myung-chol Kang, Manoj C. Desai,
Arun K. Ghosh, and Ioannis N. Houpis

J. Am. Chem. Soc. **1988**, *110*, 649–651

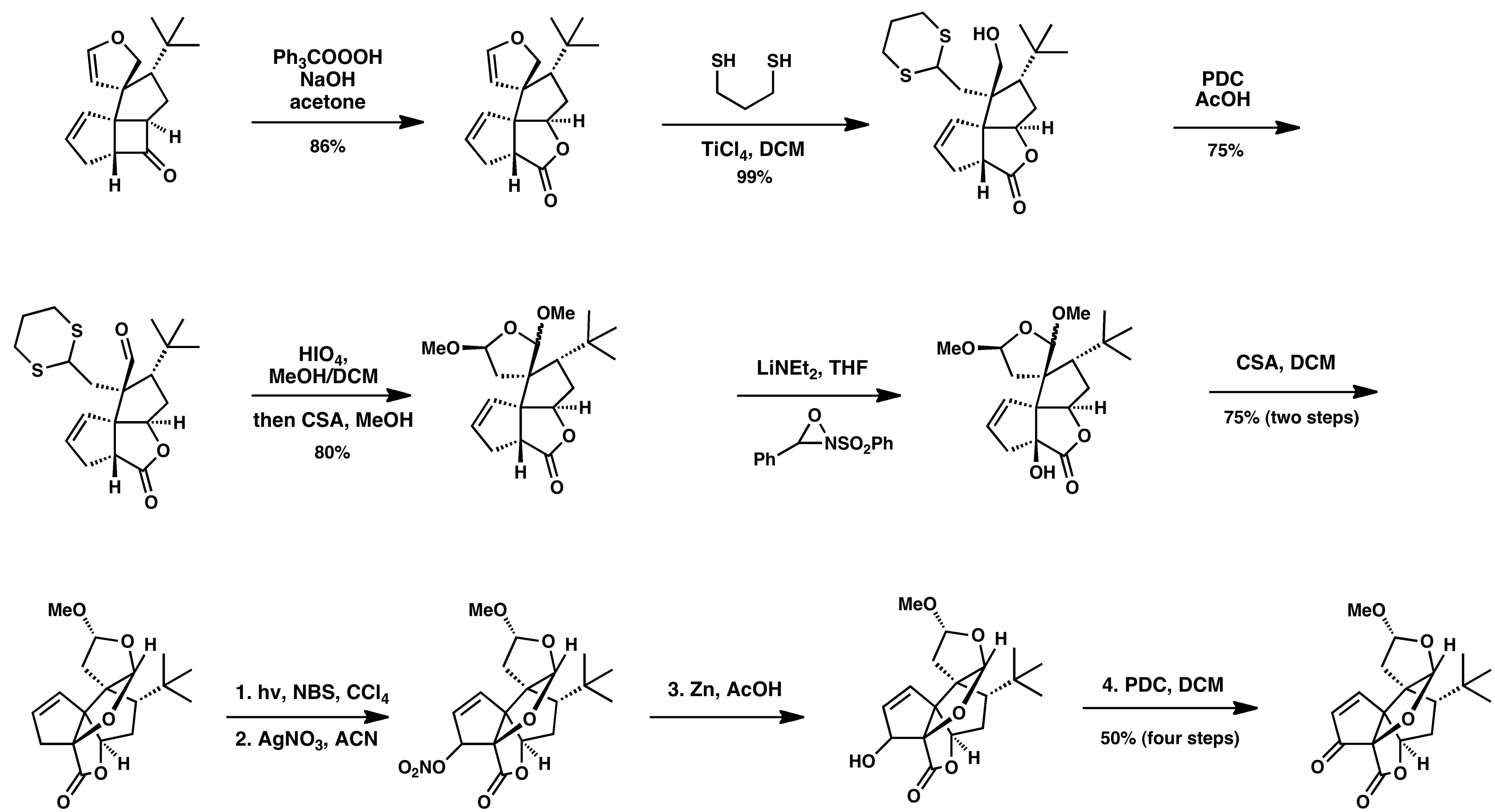


- 129 citations
- Featured in *Classics in Total Synthesis*

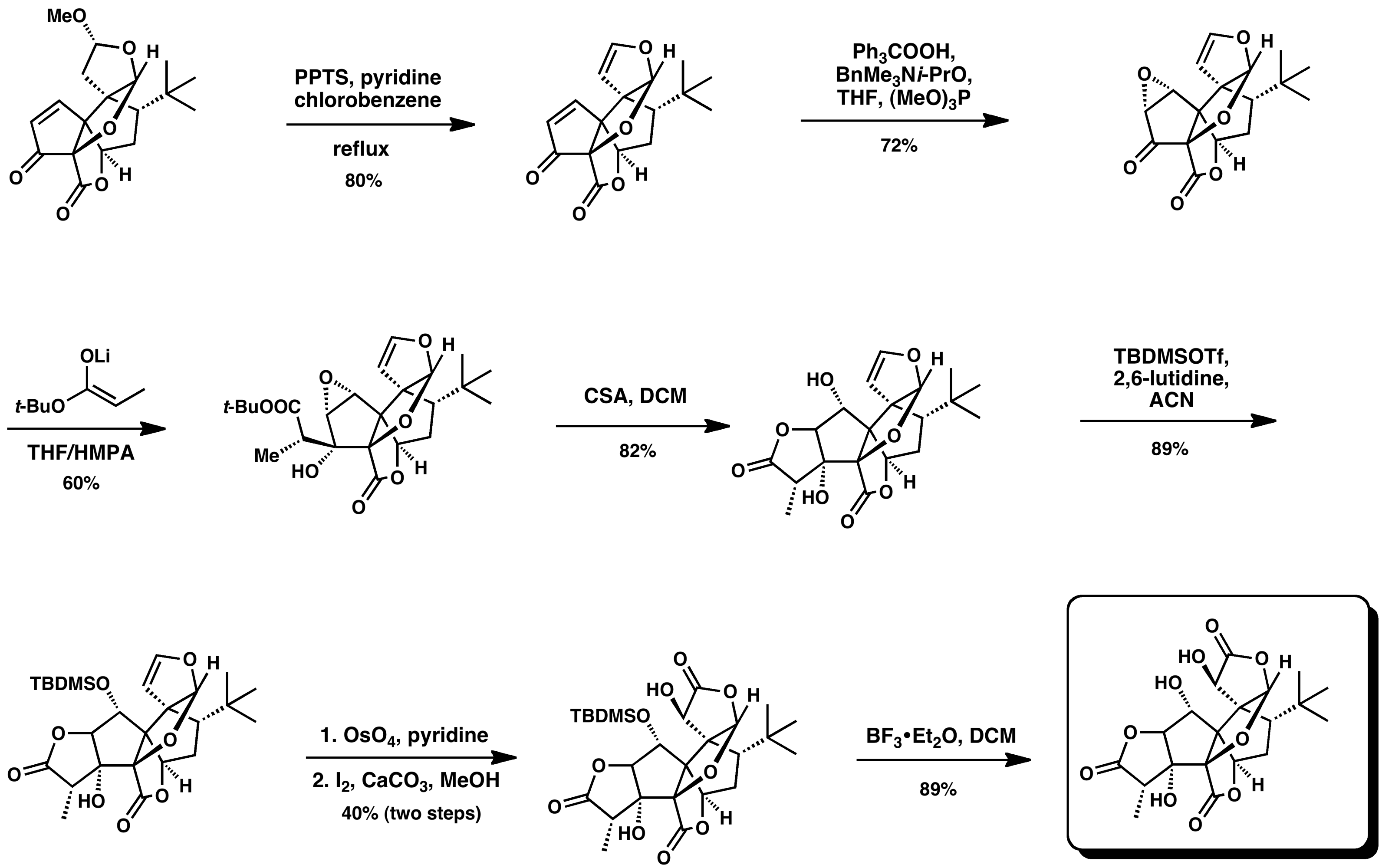
Synthesis


O
N
O
H
OMe
OMe
benzene,
then 6N HCl
70%
O
OMe
OMe
t-BuCuCNLi2
TMSCl
93%
OTMS
OMe
OMe
O
O
O
TiCl4
65%
O
OMe
O
LDA, DME, PhNTf2
80%
OTf
OMe
O
O
O
O
Pd(PPh3)4, benzene,
n-PrNH2, CuI
76-84%
O
O
O
OMe
O
Cy2BH, THF, AcOH
then, NaOOH, HCl
86%
MeO2C
OMe
O
(COCl)2,
benzene
then, n-Bu3N
toluene
reflux
80%
O=C=C
OMe
O
2+2 ketene
cycloaddition,
elmination
O
H
H
O

Synthesis


O
H
H
O
Ph3COOOH
NaOH
acetone
86%
SH SH
TiCl4, DCM
99%
S
S
HO
PDC
AcOH
75%
HIO4,
MeOH/DCM
then CSA, MeOH
80%
OMe
MeO
LiNEt2, THF
Ph
NSO2Ph
OH
CSA, DCM
75% (two steps)
MeO
1. hv, NBS, CCl4
2. AgNO3, ACN
O2NO
3. Zn, AcOH
HO
4. PDC, DCM
50% (four steps)

Synthesis



(+/-)-ginkolide B

Summary

- Corey and Sharpless arguably make their biggest contributions to chemical literature during the 1980s
- Asymmetric synthesis boomed
- Many practical methods developed
- Too much chemistry to cover in one group meeting