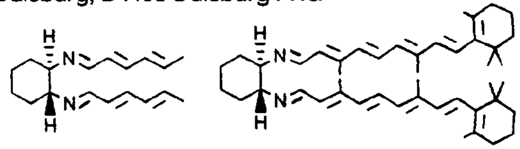
GRAPHICAL ABSTRACTS

Tetrahedron: Asymmetry **1993,** *4*, 1

UNEXPECTED BEHAVIOR OF THE RETINYLIDENE CHROMOPHORE IN THE EXCITON INTERACTION OF CHIRAL 1,2-CYCLOHEXANEDIAMINE SCHIFF BASES

Volker Buss*, Klaus Kolster, and Britta Görs
Fachgebiet Theoretische Chemie, Universität Duisburg, D4100 Duisburg FRG

Two bis-chromophoric Schiff Bases show opposite CD exciton coupling, without apparent reason.

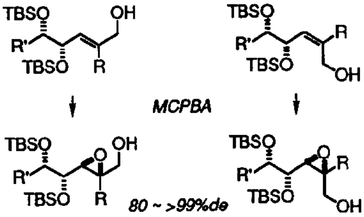


Tetrahedron: Asymmetry **1993,** *4*, 5

Vicinal Diol Controller Approach to Highly Diastereoselective Hydroxy-Directed MCPBA Epoxidations of Allylic Alcohols with Oxygen–Bearing Stereocenters

Seiki Saito,* Hiroyuki Itoh, Yukiji Ono, Kagetada Nishioka, and Toshio Moriwake*: *Department of Applied Chemistry, Faculty of Engineering, Okayama University, Tsushima, Okayama 700, Japan*

The diastereofaces of primary allylic alcohols bearing (4S,5S)-bis(*t*-butyldimethylsiloxy)–framework have been differentiated with high %de's in hydroxy-directed MCPBA epoxidations.

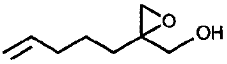


Tetrahedron: Asymmetry **1993,** *4*, 9

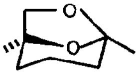
A NEW CHEMOENZYMATIC APPROACH TO ENANTIOMERICALLY PURE (R)- and (S)-2,3-EPOXY-2-(4-PENTENYL)-PROPANOL, A CHIRAL BUILDING BLOCK FOR THE SYNTHESIS OF (R)- and (S)-FRONTALIN.

*P. Ferraboschi, S. Casati, P. Grisenti, E. Santaniello**
Dipartimento di Chimica e Biochimica Medica, Universita' di Milano.

Racemic epoxyalcohol **1** has been resolved by *Pseudomonas fluorescens* lipase-catalyzed transesterification in CH_2Cl_2. The compound (S)-**1** is an intermediate for the preparation of (1S,5R)-frontalin **2**.



1



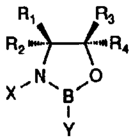
(1S,5R)-2

Tetrahedron: Asymmetry **1993,** *4*, 13

ENANTIOSELECTIVE REDUCTION OF ACETOPHENONE WITH 1,3,2-OXAZABOROLIDINES DERIVED FROM EPHEDRINE, PSEUDOEPHEDRINE, AND PHENYLGLYCINE

Ramon Berenguer, Jordi Garcia, Mercè Gonzàlez, and Jaume Vilarrasa
Department of Organic Chemistry, Faculty of Chemistry, University of Barcelona (III), 08028 Barcelona, Catalonia, Spain

The performance of several chiral 1,3,2-oxazaborolidines as catalysts in the reduction of acetophenone has been compared. The origin of the enantioselectivity is discussed.



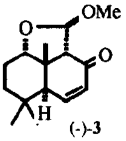
$R_1, R_2 = H, Me, Ph$
$R_3, R_4 = H, Ph$
$X = H, Me, CH_2Ph, CH_2Bu^t, SO_2Ph, SO_2Me$
$Y = H, Me, Bu$

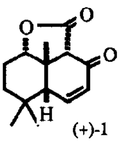
Resolution and Absolute Configuration of a Tricyclic Lactone. A Potentially Useful Precursor of Highly Functionalized Terpenoids.

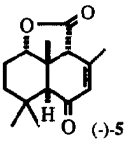
Tetrahedron: Asymmetry **1993,** *4*, 17

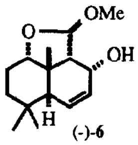
M.D. Preite, J. Zinczuk, M.I. Colombo, J.A. Bacigaluppo, M.González-Sierra and E.A. Rúveda,
Instituto de Química Orgánica de Síntesis (CONICET-UNR), Casilla de Correo 991, 2000 Rosario, Argentina.

Enantiomerically pure (-)-**3** was obtained by a sulfoximine assisted resolution. From (-)-**3** the tricyclic lactones (+)-**1** and (-)-**5** were then prepared. The absolute configuration of these optically active compounds was confirmed by application of the high field FT NMR Mosher method to alcohol (-)-**6**


(-)-3


(+)-1

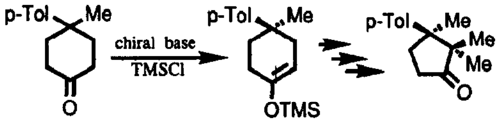

(-)-5


(-)-6

Tetrahedron: Asymmetry **1993,** *4*, 21

CONSTRUCTION OF A CHIRAL QUATERNERY CARBON CENTER BY ENANTIOSELECTIVE DEPROTONATION: APPLICATION TO THE FORMAL SYNTHESIS OF (+)-α-CUPARENONE

Toshio Honda,* Nobuaki Kimura and Masayoshi Tsubuki
Institute of Medicinal Chemistry, Hoshi University, Ebara 2-4-41, Shinagawa-ku, Tokyo 142, Japan



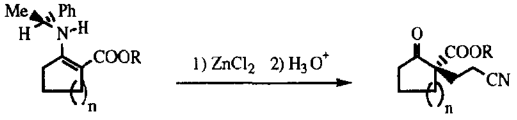
Formal synthesis of (+)-α-cuparenone has been achieved by employing an enantioselective deprotonation as a key reaction.

Tetrahedron: Asymmetry **1993,** *4*, 25

ASYMMETRIC NUCLEOPHILIC ADDITION OF CHIRAL β - ENAMINO ESTERS TO ACRYLONITRILE

A.Guingant and H.Hammami
Laboratoire de Synthèse Organique, Faculté des Sciences et des Techniques, 2 rue de la Houssinière, 44072 Nantes Cedex 03 (France)
Centre d'Etudes Pharmaceutiques, BIO C.I S , 5 rue Jean-Baptiste Clément, 92296 Chatenay-Malabry Cedex (France)

A preparation of optically active α,α – disubstituted β - keto esters via an asymmetric Michael addition of chiral β–enamino esters to acrylonitrile



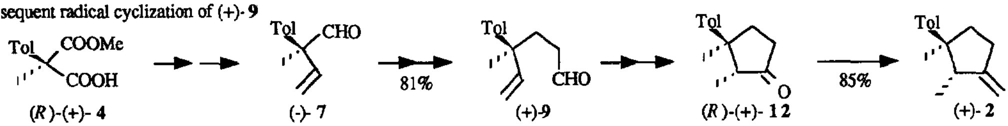
n = 1, R = COOMe; n = 2, R = COOEt

Tetrahedron: Asymmetry **1993,** *4*, 27

ASYMMETRIC CONSTRUCTION OF QUATERNARY CARBONS FROM CHIRAL MALONATES : TOTAL SYNTHESES OF (+)-EPILAURENE, AND (-)-ISOLAURENE

Antoine Fadel *, Jean-Louis Canet and Jacques Salaün
Laboratoire des Carbocycles, Associé au C.N.R.S., Institut de Chimie Moléculaire d'Orsay, Bât. 420
Université de Paris-Sud, 91405 ORSAY (France)

(+)-Epilaurene **2** was obtained from the chiral malonate (+)-**4** via the aldehyde (-)-**7** by double Wittig homologation under sonication and subsequent radical cyclization of (+)-**9**



Tetrahedron: Asymmetry 1993, 4, 31

ENANTIOMERIC EXCESS ANALYSIS OF SESQUITERPENE PRECURSORS THROUGH PROTON DECOUPLED DEUTERIUM NMR IN CHOLESTERIC LYOTROPIC LIQUID CRYSTAL.

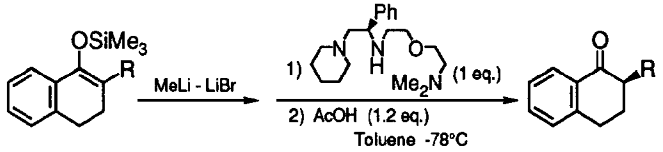
Jean-Louis Canet, Antoine Fadel * and Jacques Salaün
Laboratoire des Carbocycles, CNRS, Institut de Chimie Moléculaire d'Orsay, Bât. 420, Université de Paris-Sud, 91405 ORSAY (France)
Isabelle Canet-Fresse and Jacques Courtieu
Laboratoire de Chimie Structurale, CNRS, Institut de Chimie Moléculaire d'Orsay, Bât. 410, Université de Paris-Sud, 91405 ORSAY (France)

Polybenzyl L-glutamate (PBLG) lyotropic liquid crystal can be used as solvent for enantiomeric excess analysis through proton decoupled ^{2}H NMR spectroscopy. Deuterated (*R*) and (*S*) enantiomers of laurene and epilaurene precursors exhibit different deuterium quadrupolar splittings on their ^{2}H NMR spectra. This effect allows enantiomeric excess measurement.

Tetrahedron: Asymmetry 1993, 4, 35

Enantioselective Protonation of Achiral Lithium Enolates Using a Chiral Amine in the Presence of Lithium Bromide

Tatsuro Yasukata and Kenji Koga*
Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan



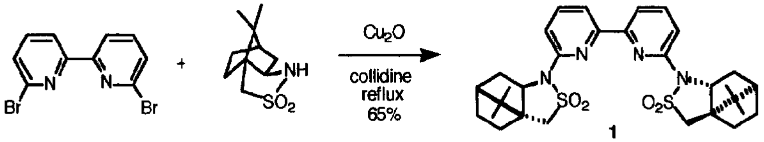
R = CH_3	91% e.e. (*S*)
R = $^nC_4H_9$	90% e.e. (*S*)
R = CH_2Ph	83% e.e. (*R*)
R = $^iC_3H_7$	67% e.e. (*R*)

Tetrahedron: Asymmetry 1993, 4, 39

EFFICIENT AND SHORT SYNTHESIS OF CAMPHOR SULTAM BASED CHIRAL BIPYRIDINES AND PHENANTHROLINES

Christof Kandzia[a], Eberhard Steckhan*[a] and Falk Knoch[b]
a Institut f. Organische Chemie und Biochemie der Universität Bonn, Gerhard-Domagk-Str.1, W-5300 Bonn, Germany
b Institut f.Anorganische Chemie II der Universität Erlangen-Nürnberg, Egerlandstraße 1, W-8520 Erlangen, Germany

For example, the copper catalyzed synthesis of the symmetrical bis sultam substituted bipyridin 1:



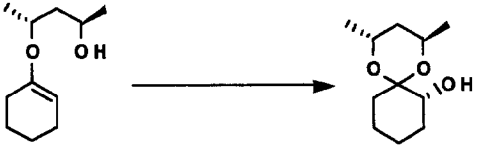
1

Tetrahedron: Asymmetry 1993, 4, 43

DIASTEREOFACE DIFFERENTIATING PERACID OXIDATION OF THE ENOL ETHER DERIVED FROM CYCLOHEXANONE AND 2,4-PENTANEDIOL: PREPARATION OF OPTICALLY PURE 2-HYDROXYCYCLOHEXANONE ACETAL.

Takashi Sugimura,* Norio Nishiyama, Akira Tai,* and Tadao Hakushi, Faculty of Science, Himeji Institute of Technology, Kanaji, Kamigori, Ako-gun, Hyogo 678-12 Japan, Faculty of Engineering, Himeji Institute of Technology, 2167 Shosha, Himeji, Hyogo 671-22 Japan

Oxidation of the chiral enol ether with *m*-chloroperbenzoic acid at -72 °C gave one diastereomer predominantly.



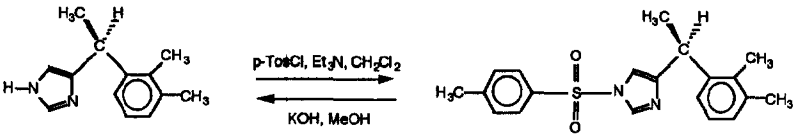
Tetrahedron: Asymmetry 1993, 4, 45

Crystal Structures and Absolute Configurations of Dexmedetomidine and Its Tosyl Derivative

Jussi H. Kivikoski,[a]* Kari T. Rissanen[a] and Seppo S.L. Parhi[b]

[a]Department of Chemistry, University of Jyväskylä, PO. Box 35, 40351 Jyväskylä, Finland
[b]Orion Corporation FARMOS, R&D Pharmaceuticals, 90650 Oulu, Finland

The absolute configuration of dexmedetomidine was determined by X-ray diffraction using its tosyl derivative as a reference.

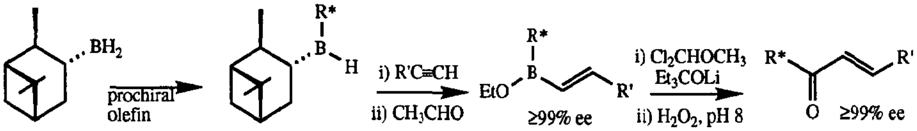


Tetrahedron: Asymmetry 1993, 4, 59

CHIRAL SYNTHESIS VIA ORGANOBORANES 37. ENANTIOSELECTIVE SYNTHESIS OF CONJUGATED ACYCLIC α-CHIRAL (*E*)-ALKENONES.

Herbert C. Brown* and Verinder K. Mahindroo
H.C. Brown and R.B. Wetherill Laboratories of Chemistry, Perdue University, West Lafayette, Indiana 47907, USA.

Conjugated acyclic α-chiral (*E*)-alkenones are synthesised in high enantiomeric purity (≥99% ee)

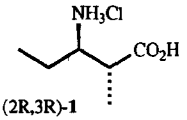


Tetrahedron: Asymmetry 1993, 4, 69

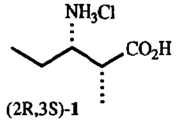
ASYMMETRIC SYNTHESES OF 3-AMINO-2-METHYLPENTANOIC ACIDS. CONFIGURATIONS OF THE β-AMINO ACID IN MAJUSCULAMIDE C, 57-NORMAJUSCULAMIDE C AND DOLASTATINS 11 and 12.

Robert B. Bates* and Sanjeev Gangwar
Department of Chemistry, University of Arizona, Tuscon, AZ 85721, USA

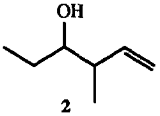
Asymmetric syntheses of all stereoisomers of 2. Conversion into (2R,3R)- and (2R,3S)-1. Natural 1 is (2S,3R).



(2R,3R)-1



(2R,3S)-1



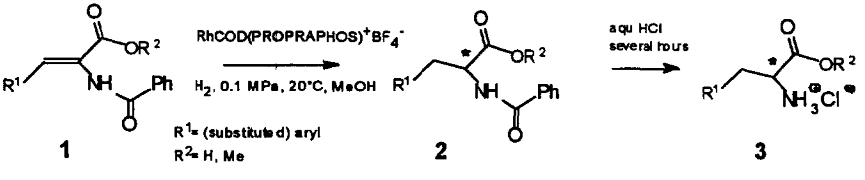
2

Tetrahedron: Asymmetry 1993, 4, 73

ASYMMETRIC SYNTHESIS OF 3-ARYLALANINES

Stefan Taudien and Klaus Schinkowski, Berlin-Chemie AG, D-1199 Berlin,
Hans-W. Krause*, Institut f. Organische Katalyseforschung, D-2500 Rostock,

Synthesis of the hydrochlorides of 3-Arylalanines 3 by homogeneous, catalytic hydrogenations of (Z)-α-N-benzoylamino-ß-arylacrylic acid derivatives 1 using [Rh-PROPRAPHOS]$^+$-complexes (ee 82-95%), followed by deacylation

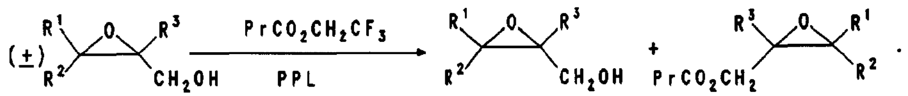


Tetrahedron: Asymmetry **1993,** *4*, 85

Biocatalytic Resolution of 2,3-Epoxyalcohols in Organic Solvents

Eero Vänttinen and Liisa T. Kanerva
Department of Chemistry, University of Turku, 20500 Turku, Finland

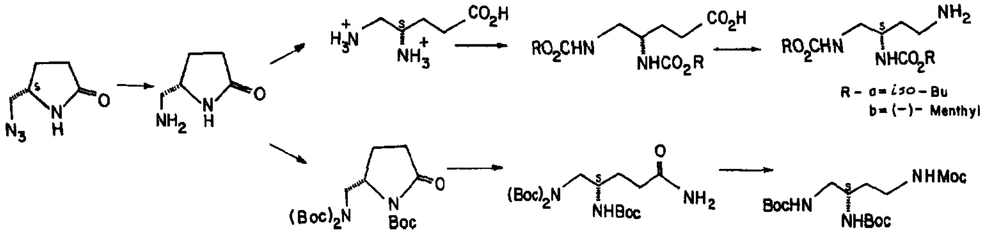
Resolution of 3-substituted *cis*- and *trans*-2,3-epoxyalcohols



Tetrahedron: Asymmetry **1993,** *4*, 91

The Synthesis of Chiral 1,2,4,-Triaminobutanes

Janina Altman and Dov Ben-Ishai
Department of Chemistry, Technion-Israel Institute of Technology,
Haifa 32000, ISRAEL

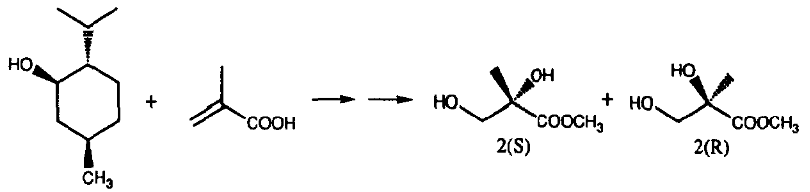


Tetrahedron: Asymmetry **1993,** *4*, 101

PREPARATION OF 2(R) AND 2(S) METHYL 2-METHYLGLYCERATES

Juan B. Rodriguez[a], Sanford P. Markey[a] and Herman Ziffer[b]
[a]Laboratory of Clinical Science. NIMH, National Institutes of Health, Bethesda, Md 20892.
[b]Laboratory of Chemical Physics. NIDDK, National Institutes of Health, Bethesda, Md 20892.

Diastereomeric (-)-menthyl esters of 2(R,S)-2-methylglycerate were chromatographically separated, hydrolyzed and methylated to yield optically pure (R) and (S) methyl 2-methylglycerate.

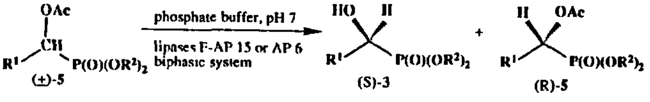


Tetrahedron: Asymmetry **1993,** *4*, 109

Enzymes in Organic Chemistry, Part 1: Enantioselective Hydrolysis of α-(Acyloxy)phosphonates by Esterolytic Enzymes

Yong-Fu Li, Friedrich Hammerschmidt
Institut für Organische Chemie der Universität Wien, Währingerstrasse 38, A-1090 Wien, Austria

Lipases were used to enantioselectively hydrolyze α-(acyloxy)phosphonates (±)-**5**. The absolute configurations of the α-hydroxyphosphonates **3** were assigned by Horeau´s method and ^{1}H-NMR spectroscopy of Mosher´s derivatives.



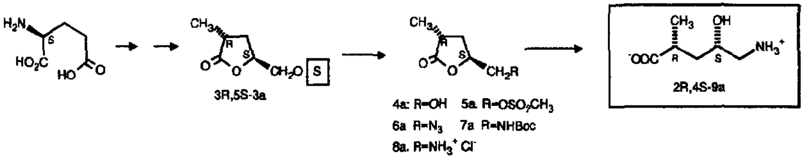
Tetrahedron: Asymmetry **1993,** *4*, 121

Enantiopure DAVA-Derivatives.

Synthesis of All 4 Stereoisomers of 2-Methyl-4-hydroxy-5-aminopentanoic Acid (2-Me-4-OH-DAVA)

Claus Herdeis and Karen Lütsch
Institut für Pharmazie und Lebensmittelchemie der Universität 8700 Würzburg, Am Hubland.

A synthesis of all 4 stereoisomers of **9** via the lactones **3-8** is presented.

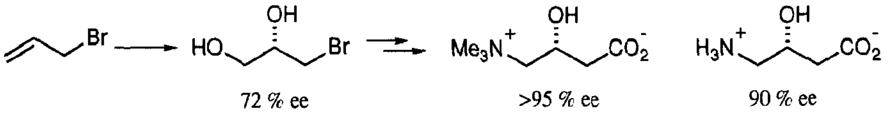


Tetrahedron: Asymmetry **1993,** *4*, 133

Short and Practical Syntheses of (*R*)-(–)-Carnitine and (*R*)-(–)-γ-Amino-β-hydroxybutyric Acid (GABOB)

Hartmuth C. Kolb, Youssef L. Bennani and K. Barry Sharpless*
Department of Chemistry, The Scripps Research Institute, 10666 N. Torrey Pines Road, La Jolla, CA 92037, U.S.A.

Short and practical syntheses of (*R*)-(–)-carnitine and (*R*)-(–)-γ-amino-β-hydroxybutyric acid have been developed, both commencing with the catalytic asymmetric dihydroxylation of allyl bromide

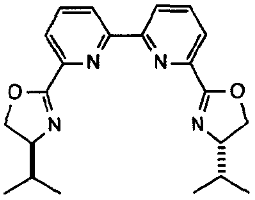


Tetrahedron: Asymmetry **1993,** *4*, 143

NEW CHIRAL BIS(OXAZOLINYL)BIPYRIDINE LIGAND (BIPYMOX): ENANTIOSELECTION IN THE ASYMMETRIC HYDROSILYLATION OF KETONES

Hisao Nishiyama,* Shinobu Yamaguchi, Soon-Bong Park, and Kenji Itoh
School of Materials Science, Toyohashi University of Technology, Tempaku-cho, Toyohashi 441, **JAPAN**

A homochiral chiral 6,6'-bis(oxazolinyl)-2,2'-bipyridine ligand, bipymox (**1**), and its rhodium complex were synthesized to examine the enantioselectivity in the asymmetric hydrosilylation of ketones.



Bipymox-(S,S)-ip **1**