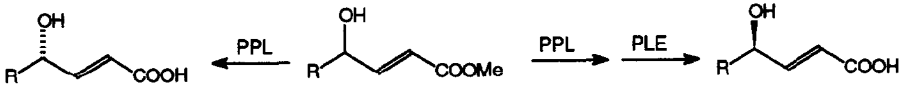
GRAPHICAL ABSTRACTS

Tetrahedron: Asymmetry **1993, *4*,** 1397

PREPARATION OF (*R*)- AND (*S*)-(*E*)-4-HYDROXY-2-UNSATURATED ACIDS BY ASYMMETRIC HYDROLYSIS OF THEIR RACEMIC ESTERS

Pietro Allevi, Mario Anastasia, Pierangela Ciuffreda, and Anna Maria Sanvito*
Department of Chemistry and Biochemistry Medical Via Saldini 50, 20133 - Milan (Italy)

Six unreported (*R*)- and (*S*)-(*E*)-4-hydroxyalk-2-enoic acids were prepared by asymmetric hydrolysis of their racemic esters mediated by porcine pancreas lipase (PPL) and porcine liver esterase (PLE).

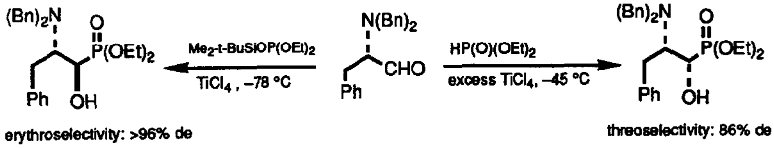


R = C_3H_7; C_4H_9; C_5H_{11}; C_6H_{13}; C_7H_{15}; C_8H_{17}

Tetrahedron: Asymmetry **1993, *4*,** 1401

Stereodivergent Synthesis of β-Amino-α-hydroxyphosphonic Acid Derivatives by Lewis Acid Mediated Stereoselective Hydrophosphonylation of α-Amino Aldehydes

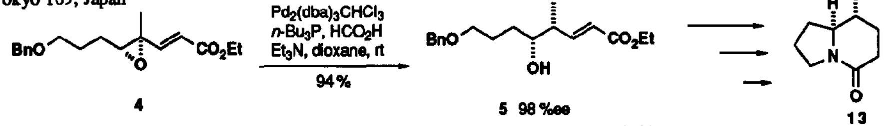
Tsutomu Yokomatsu, Takehiro Yamagishi, and Shiroshi Shibuya
Tokyo College of Pharmacy, 1432-1 Horinouchi, Hachioji, Tokyo 192-03, Japan



Tetrahedron: Asymmetry **1993, *4*,** 1405

A Chiral Synthesis of (*8R,8aS*)-Hexahydro-8-methyl-5(1H)-indolizinone

Akiharu Satake and Isao Shimizu*
Department of Applied Chemistry, School of Science and Engineering, Waseda University, Ookubo 3-4-1, Shinjuku, Tokyo 169, Japan



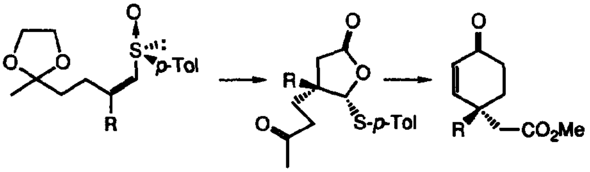
Enantioselective synthesis of (*8R,8aS*)-hexahydro-8-methyl-5(1H)-indolizinone((-)-13), a synthetic intermediate of 5,8-disubstituted indolizidine alkaloids, was carried out.

Tetrahedron: Asymmetry **1993, *4*,** 1409

A New Route to Enantiomerically Pure 4,4-Disubstituted Cyclohex-2-en-1-ones: Asymmetric Synthesis of (+)-Mesembrine

H. Kosugi,* Y. Miura, H. Kanna, and H. Uda
Institute for Chemical Reaction Science, Tohoku University,
Katahira, Sendai 980, JAPAN

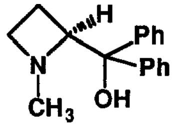
Optically pure 4,4-disubstituted cyclohex-2-en-1-ones were synthesized from cycloaddition of enantiomerically pure β,β-disubstituted vinyl sulfoxides with dichloroketene followed by intramolecular Aldol-type condensation.



Tetrahedron: Asymmetry **1993,** *4,* 1413

Catalytic Enantioselective Addition of Diethylzinc to Aldehydes: Synthesis and Application of a New Cyclic Catalyst

W. Behnen, Th. Mehler, J. Martens*
Fachbereich Chemie, Universität Oldenburg
Ammerländer Heerstr. 114-118, D-2900 Oldenburg



(*S*)-**4**

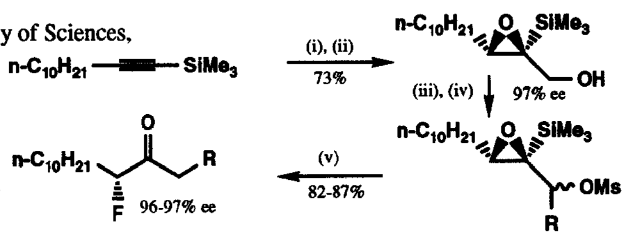
The new optically active β-amino alcohol (*S*)-1-methyl-2-(diphenylhydroxymethyl)azetidine (*S*)-**4** derived from (*S*)-azetidinecarboxylic acid catalyzes the enantioselective addition of diethylzinc to various aldehydes. The resulting chiral secondary alcohols **5a-h** are obtained in high optical yields up to 100 % under mild reaction conditions.

Tetrahedron: Asymmetry **1993,** *4,* 1417

Highly Enantioselective Synthesis of α-Fluoroketones *via* Allene Oxides

Marek M. Kabat
Institute of Organic Chemistry, Polish Academy of Sciences,
Kasprzaka 44, 01-224 Warszawa, Poland

α-Fluoroketones (96-97% ee) were obtained by the regioselective opening of allene oxides with anhydrous tetrabutylammonium fluoride.

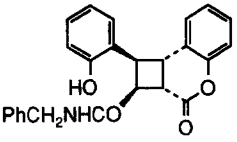


(i) ^{i}BuMgBr, cat. $(Cp)_2TiCl_2$, HCHO (ii) L(+)-DET, $Ti(O^iPr)_4$ ^{t}BuOOH (iii) PCC (iv) RMgX, MsCl (v) TBAF (2 eg)

Tetrahedron: Asymmetry **1993,** *4,* 1421

Determination of Enantiomeric Excesses of Chiral Amines by Using an Enantiomerically Pure *Anti* Head-to-Head Coumarin Dimer Derivative

Yutaka Adegawa, Takeshi Kashima, and Kazuhiko Saigo
Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113, Japan



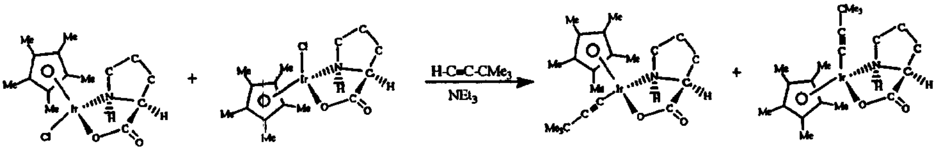
(-)-**2**

Monolactone-monoamide **2**, prepared from enantiomerically pure (*S,S,S,S*)-(-)-*anti* head-to-head coumarin dimer and an equimolar amount of benzylamine, was easily reacted with chiral amines to give mixtures of diastereomeric diamides without any condensing agent. The enantiomeric excesses of the chiral amines were successfully determined by ^{1}H NMR spectral and/or HPLC analysis of the mixtures of diastereomeric diamides .

Tetrahedron: Asymmetry **1993,** *4,* 1425

OPTICAL RESOLUTION OF THE CHIRAL IRIDIUM(III) α-AMINO ACIDATO COMPLEX $[(\eta^5\text{-}C_5Me_5)Ir(L\text{-}Prolinate)(C{\equiv}C\text{-}CMe_3)]$

Daniel Carmona, Fernando J. Lahoz, Reinaldo Atencio, Luis A. Oro, M. Pilar Lamata and Emilio San José
Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, 50009 Zaragoza, Spain

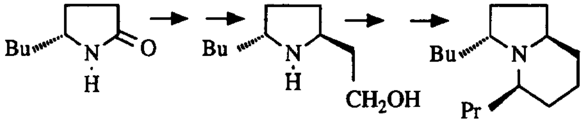


Tetrahedron: Asymmetry **1993**, *4*, 1429

ENANTIOSELECTIVE SYNTHESIS OF (-)-GEPHYROTOXINE 223AB [(3R,5R,9R)-3-BUTYL-5-PROPYLOCTAHYDROINDOLIZINE]

Anne Fleurant, Jean Pierre Célérier, and Gérard Lhommet*
Université P. et M. Curie. Laboratoire de Chimie des Hétérocycles
C.N.R.S. ERS 73. 4 Place Jussieu, 75252 Paris cedex 05. France

A highly enantioselective synthesis of the dendrobatid indolizine alkaloid 223AB is described using a chiral amino acid as starting material.

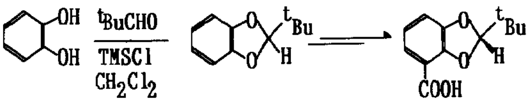


Tetrahedron: Asymmetry **1993**, *4*, 1431

(+)-Tert-BUTYL-1,3-BENZODIOXOLE-4-CARBOXYLIC ACID: FLUORESCENT CHIRAL CARBOXYLIC ACID WITH A 1,3-BENZODIOXOLE SKELETON

Y. Nishida, M. Abe, H. Ohrui and H. Meguro
Deapartment of Applied Biological Chemistry, Faculty of Agriculture, Tohoku University, Tsutsumidohri-Amamiyamachi 1-1, Sendai 981, Japan

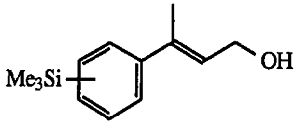
The new chiral carboxylic acid was prepared from catechol and trimethylacetaldehyde via carbonylation with n-BuLi and CO₂ and found to show high separations of D,L-amino acid derivatives on TLC.



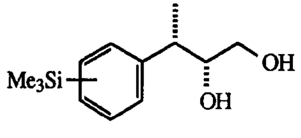
Tetrahedron: Asymmetry **1993**, *4*, 1435

Asymmetric Synthesis of Ibuprofen and Ketoprofen

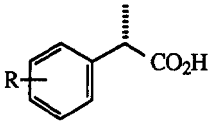
David P.G. Hamon, Ralph A. Massy-Westropp and Josephine L. Newton
Department of Organic Chemistry, University of Adelaide, GPO Box 498, Adelaide, South Australia, 5001.



(5a) ; *p*
(5b) ; *m*



(2*R*,3*S*)-(**7a**) ; *p*
(2*R*,3*S*)-(**7b**) ; *m*



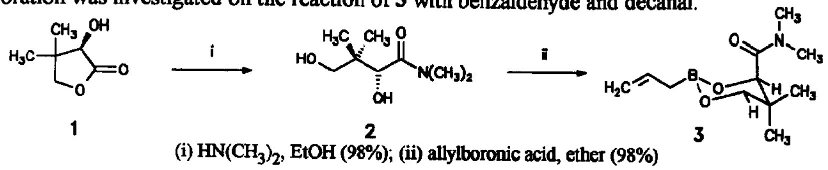
(*S*)-(+)-ibuprofen (1); R = isobutyl
(*S*)-(+)-ketoprofen (2); R = benzoyl

Tetrahedron: Asymmetry **1993**, *4*, 1439

A New Alkylboronate Reagent from Pantolactone

Frank Hoeper and Franz-Peter Montforts
Institut für Organische Chemie, Universität Bremen, Bremen, Germany

A new enantiomerically pure six membered cyclic allylboronate 3 has been prepared from pantolactone 1. The enantioselectivity of the allylboration was investigated on the reaction of 3 with benzaldehyde and decanal.



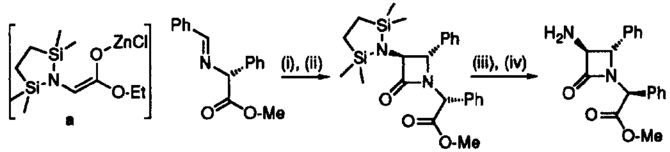
(i) HN(CH$_3$)$_2$, EtOH (98%); (ii) allylboronic acid, ether (98%)

Tetrahedron: Asymmetry **1993**, *4*, 1441

(*R*)-2-PHENYLGLYCINE AS A CHIRAL AUXILIARY IN THE ASYMMETRIC SYNTHESIS OF 2-AZETIDINONES.

Hendrik L. van Maanen, Johann T.B.H. Jastrzebski, Jan Verweij, Antonius P.G. Kieboom, Anthony L. Spek and Gerard van Koten
Department of Metal-Mediated Synthesis, Debye Institute, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands.

Enantioselective synthesis of (3*S*, 4*S*, α*S*)-1-[(methoxy-carbonyl)(phenyl)]methyl-3-amino-4-phenyl-2-azetidinone (e.e. = 97%) via the ester enolate-imine condensation, using double activation by $ZnCl_2$.



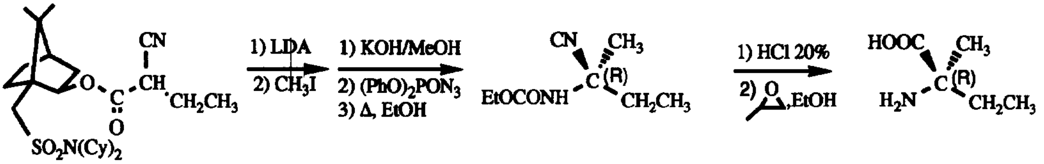
(i) $ZnCl_2$, THF, -30 °C; (ii) a, THF, -70 °C -> r.t.; (iii) HCl / H_2O, THF; (iv) NH_3 / H_2O, CH_2Cl_2

Tetrahedron: Asymmetry **1993**, *4*, 1445

SYNTHESIS OF *(R)*- and *(S)*-2-AMINO-2-METHYLBUTANOIC ACID (IVA) IN ENANTIOMMERICALLY PURE FORM

Carlos Cativiela*, María D. Díaz-de-Villegas and José A. Gálvez
Instituto de Ciencia de Materiales de Aragón. Departamento de Química Orgánica. Universidad de Zaragoza-CSIC. Zaragoza. Spain.

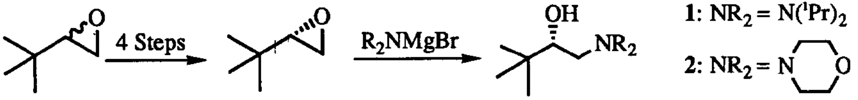
Diastereoselective alkylation of chiral 2-cyanoesters, subsequent Curtius rearrangement and hydrolysis of the cyanouretane afforded chiral 2-amino-2-methylbutanoic acid



Tetrahedron: Asymmetry **1993**, *4*, 1449

A Facile Enzyme Assisted Route to (*R*) - and (*S*)-*t*-Butyloxiranes and related β-Amino Alcohols - Catalysts for the Enantioselective Addition of Dialkylzinc Reagents to Aldehydes

A. Chadha, U. Goergens and Manfred P. Schneider*, FB 9 - Bergische Universität GH Wuppertal, W-5600 Wuppertal 1, Germany



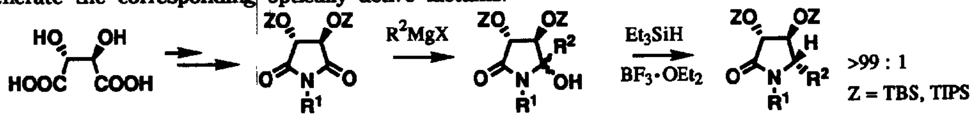
(±)-3　(*S*)-3　(*S*)-1,2

Tetrahedron: Asymmetry **1993**, *4*, 1451

NOVEL SYNTHETIC STRATEGY TO CHIRAL ALKYLATED LACTAMS EMPLOYING CYCLIC IMIDES WITH C_2-SYMMETRY

Hidemi Yoda,* Hidekazu Kitayama, Wataru Yamada, Takao Katagiri, and Kunihiko Takabe*
Department of Applied Chemistry, Faculty of Engineering, Shizuoka University, Hamamatsu 432, Japan

Unprecedented *trans*-selective deoxygenation of quarternary α-hydroxy lactams was developed to generate the corresponding optically active lactams.

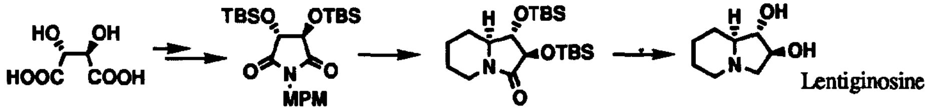


Tetrahedron: Asymmetry 1993, *4*, 1455

SYNTHESIS OF NATURAL LENTIGINOSINE EMPLOYING A CYCLIC IMIDE WITH C_2-SYMMETRY DERIVED FROM L-TARTARIC ACID

Hidemi Yoda,* Hidekazu Kitayama, Takao Katagiri, and Kunihiko Takabe*
Department of Applied Chemistry, Faculty of Engineering,
Shizuoka University, Hamamatsu 432, Japan

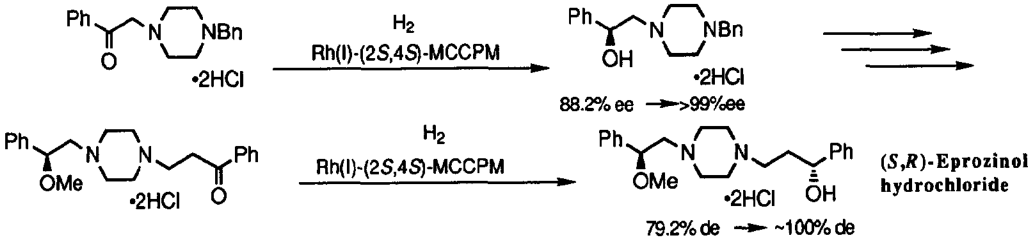
Synthesis of a *trans*-dihydroxyindolizidine alkaloid, lentiginosine was accomplished using deoxygenation of the quarternary α-hydroxy lactam prepared from a chiral C_2-imide.



Tetrahedron: Asymmetry 1993, *4*, 1457

An Efficient Synthesis of Optically Active Eprozinol

Shunji Sakuraba, Noriya Nakajima and Kazuo Achiwa*
School of Pharmaceutical Sciences, University of Shizuoka, 52-1 Yada, Shizuoka 422, Japan

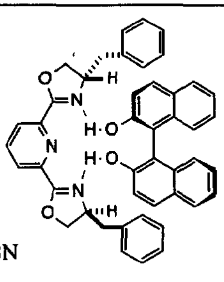


Tetrahedron: Asymmetry 1993, *4*, 1461

CHIRALITY RECOGNITION OF 1,1'-BI-2-NAPHTHOL WITH OPTICALLY ACTIVE BIS(OXAZOLINYL)PYRIDINES

Hisao Nishiyama,* Tomonori Tajima, Masahiro Takayama, and Kenji Itoh
School of Materials Science, Toyohashi University of Technology, Tempaku-cho, Toyohashi 441, JAPAN

Optically active 2,6-bis[(*S*)-4'-benzyloxazolin-2'-yl)pyridine, pybox-(*S,S*)-*bz* (**1**), proved to make a well-matched base-acid pair with the (*S*)-enantiomer of 1,1'-bi-2-naphthol [(*S*)-BN]on the basis of NMR study.



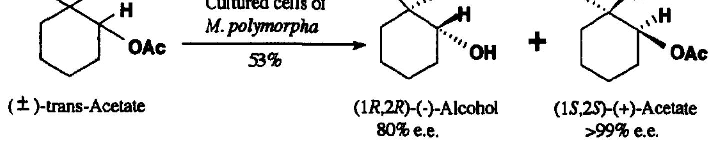
1+ (*S*)-BN

Tetrahedron: Asymmetry 1993, *4*, 1465

Enantioselective Hydrolysis of 2-Methylcyclohaxanyl Acetates with the Cultured Cells of *Marchantia polymorpha.*

Toshifumi Hirata,* Shunsuke Izumi, Kenji Akita, Hiroaki Yoshida, and Shisei Gotoh
Department of Chemistry, Faculty of Science, Hiroshima University, Kagamiyama, Higashi-hiroshima 724, Japan

Enantioselective hydrolysis of *trans*- and *cis*-2-methylcyclohexanyl acetates

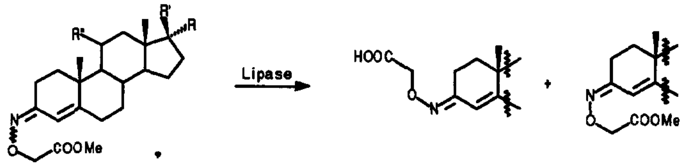


Tetrahedron: Asymmetry **1993**, *4*, 1467

Lipase Mediated Diastereoselective Hydrolysis of Steroidal 3-(O-Carboxymethyl) Oxime Methyl Esters

Maciej Adamczyk, Yon-Yih Chen, Jeff R. Fishpaugh, and John C. Gebler
Abbott Diagnostics Division, Abbott Laboratories, Abbott Park, Illinois 60064

Lipase mediated hydrolysis of **1-4** was preferential for the *anti* isomer.



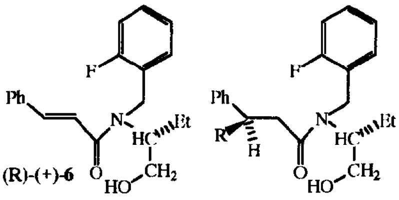
R,R', R": **1.** OH, C(O)Me, H **2.** H, C(O)Me, H **3.** H, OH, H **4.** OH, C(O)CH_2OH, OH

Tetrahedron: Asymmetry **1993**, *4*, 1469

Enantioselective Michael Additions of Grignard Reagents to Cinnamamides deriving from N-Fluoroalkyl (R)-(-)-2-Aminobutan-1-ol. Determination of Diastereomeric Excess by means of ^{19}F NMR

Joël Touet, Christelle Le Grumelec, François Huet and Eric Brown
Laboratoire de Synthèse Organique (URA-CNRS 482), Faculté des Sciences, Avenue Olivier Messiaen, BP 535, 72017 Le Mans, France

Michael additions of n-alkylmagnesium halides to the cinnamamide (R)-(+)-**6**, deriving from (R)-(-)-2-(2-fluorobenzylamino)butan-1-ol **4**, afforded the corresponding (R,R) adducts **8a-e** with 92-97% diastereomeric excesses.



(R)-(+)-**6**

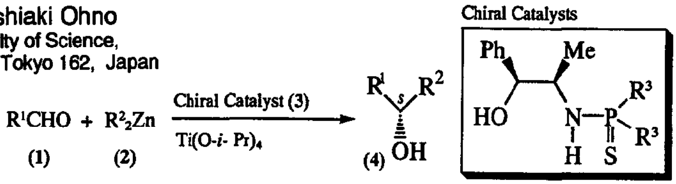
(R,R)-**8**
a R=Et;
b R=n-Bu;
c R=n-C_5H_{11};
d R=n-C_6H_{13};
e R=n-C_8H_{17}

Tetrahedron: Asymmetry **1993**, *4*, 1473

Chiral Dialkyl Thiophosphoramidates as Highly Enantioselective Catalysts for the Alkylation of Aldehydes

Kenso Soai, Yuji Hirose and Yoshiaki Ohno
Department of Applied Chemistry, Faculty of Science,
Science University of Tokyo, Shinjuku, Tokyo 162, Japan

Enantioselective addition of dialkylzincs to aldehydes catalyzed by chiral dialkyl thiophosphoramidates.

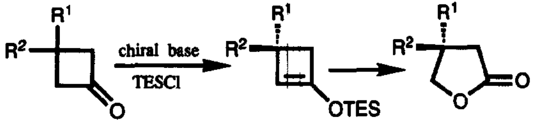


(1*S*,2*R*)-(3)

Tetrahedron: Asymmetry **1993**, *4*, 1475

CHIRAL SYNTHESIS OF 3-SUBSTITUTED AND 3,3-DI-SUBSTITUTED γ-BUTYROLACTONES BY ENANTIOSELECTIVE DEPROTONATION STRATEGY

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



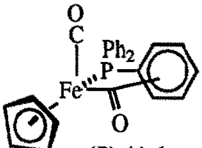
Chiral synthesis of γ-butyrolactones has been established by employing an enantioselective deprotonation as a key reaction.

Tetrahedron: Asymmetry **1993, *4***, 1479

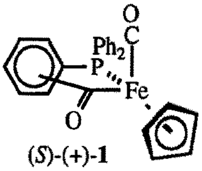
Resolution of the Chiral Iron Acetyl Complex [$(C_5H_5)Fe(CO)(PPh_3)COCH_3$]

Robert W. Baker and Stephen G. Davies*
The Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY, UK.

A novel resolution procedure for the iron acetyl complex **1** is described.



(*R*)-(-)-**1**

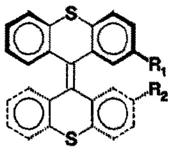


(*S*)-(+)-**1**

Tetrahedron: Asymmetry **1993, *4***, 1481

Sterically Overcrowded Alkenes;Synthesis, Resolution and Circular Dichroism Studies ofSubstituted Bithioxanthenylidenes

Wolter F. Jager, Ben de Lange, Anne Marie Schoevaars, Fré van Bolhuis and Ben L. Feringa*
Department of Organic and Molecular Inorganic Chemistry, University of Groningen,
Nijenborgh 4, 9747 AG Groningen The Netherlands



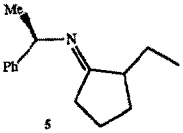
Bithioxanthenylidenes with small substituents at positions 2 and 2' (R_1, R_2= H, CH_3, OCH_3) have been synthesized and resolved by chiral HPLC. UV and CD studies of several bithioxanthylidenes are presented. The CD spectra of these molecules can be described qualitatively by subtracting the CD spectra of both differently sensed helices (M and P) present in the molecule.

Tetrahedron: Asymmetry **1993, *4***, 1499

FORMAL SYNTHESIS OF (-)-VALLESAMIDINE A 2,2,3-TRIALKYLINDOLINE ALKALOID

P.R.R. Costa, R.N. Castro, F.M.C. Farias, O.A.C. Antunes and L.Bergter
Nucleo de Pesquisas de Produtos Naturais, Universidade Federal do Rio de Janeiro (UFRJ),
Centro de Ciencias da Saede, Bloco H, Ilha da Cidade Universitaria, 21941 Rio de Janeiro, RJ Brasil

(S)-(+)-2-ethyl-2[2'-carboxymethyl]cyclopentanone 6 was prepared regio- and enantioselectively (ee = 90%) by "deracemizing alkylation" of the chiral imine 5 with methylacrilate. Compound 6 was transformed into the bycyclic imine (R)-(+)-3. This intermediate was used by Heathcock, in the racemic form, to the total synthesis of (±)-Vallesamidine (1), a 2,2,3-trialkylindoline alkaloid.



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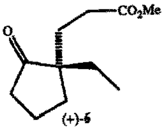
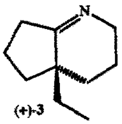


(+)-6

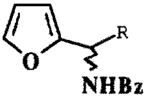


(+)-3

Tetrahedron: Asymmetry **1993, *4***, 1501

Circular Dichroic Method for Determination of Absolute Configuration of α-Furfuryl Amines

Wei-Shan Zhou, *[a] Xue-You Zhu [b] and Jie-Fei Cheng [a]
a State key laboratory of bioorganic and natural products chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China; b Department of Biological Engineering, Sichuan University, Chengdu, Sichuan, China



R = Me, n-propyl, i-butyl

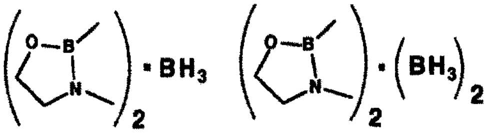
An unambiguous assignment of absolute configuration of α-furfuryl amines by using the circular dichroic method is described.

Tetrahedron: Asymmetry **1993,** *4*, 1505

Quantum Chemical Modeling of Chiral Catalysis. Part 9. On the Aggregation Reactions of Borane and Chiral Oxazaborolidines Used as Catalysts in the Enantioselective Reduction of Ketones

Vesa Nevalainen, Department of Chemistry, P.O. Box 6, SF-00014 University of Helsinki, Finland.

Aggregates consisting of borane and oxazaborolidine type of catalysts [1,3,2-oxazaborolidine and H_2N-B(H)-OH as models of the catalysts] were studied by means of *ab initio* MO methods. The behaviour of oxazaborolidines, as they react with intermediates of the CBS reduction, was found to resemble that of ketones or Lewis basic solvents (the polar B^{-}=N^{+} bond of oxazaborolidine behaves as the C=O bond of ketone; nitrogen of oxazaborolidine behaves as a Lewis base).

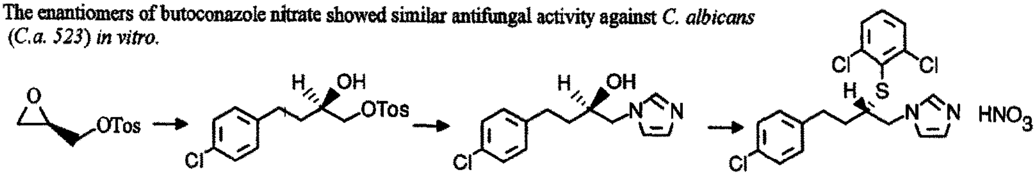


Tetrahedron: Asymmetry **1993,** *4*, 1521

The Synthesis and Antifungal Activity of the Enantiomers of Butoconazole Nitrate.

David M. Rotstein and Keith A. M. Walker
Syntex Research, 3401 Hillview Avenue, Palo Alto, California 94304, U.S.A.

The enantiomers of butoconazole nitrate showed similar antifungal activity against *C. albicans* *(C.a. 523) in vitro.*



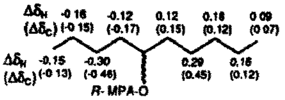
R-(-)-4 *R*-6 *R*-(+)-8 *S*-(+)-2 >99.4% e.e.

Tetrahedron: Asymmetry **1993,** *4*, 1527

DETERMINATION OF THE ABSOLUTE CONFIGURATION OF CHIRAL SECONDARY ALCOHOLS; NEW ADVANCES USING ^{13}C- AND 2D-NMR SPECTROSCOPY

T. Pehk,[a] E. Lippmaa,[a] M. Lopp,[b] A. Paju,[b], B.C. Borer[c] and R.J.K. Taylor[c]
[a] Institute of Chemical Physics and Biophysics, EE0001 Tallinn, Rävala puiestee 10, Estonia.
[b] Institute of Chemistry, EE0108 Tallinn, Akadeemia tee 15, Estonia.
[c] School of Chemical Sciences, University of East Anglia, Norwich, NR4 7TJ, U.K.

The use of 2D correlation experiments substantially enhance the potential of the NMR procedure for determining the absolute configuration of chiral secondary alcohols *via* their diastereomeric MPA and/or MTPA esters. *Phenyl ring current effects are observed over remarkably long distances and* comparable effects are seen for both ^{13}C and ^{1}H chemical shifts.

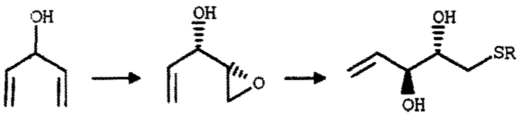


Tetrahedron: Asymmetry **1993,** *4*, 1533

One-pot Synthesis of α,β-dihydroxy Sulfides via Titanium-promoted Oxirane Ring Opening

Guo-qiang Lin*, Zhi-cai Shi, and Chun-min Zeng
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences
345 Lingling Lu, Shanghai 200032, China

The one-pot synthesis of α,β-dihydroxy sulfides via titanium-promoted oxirane ring opening of (2R,3S)-1,2-epoxy-4-penten-3-ol is described.

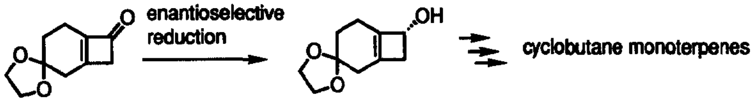


Tetrahedron: Asymmetry **1993**, *4*, 1537

PREPARATION OF CHIRAL CYCLOBUTANE DERIVATIVES: ENANTIOSELECTIVE SYNTHESES OF THE KEY INTERMEDIATES FOR CYCLOBUTANE MONOTERPENES, GRANDISOL AND LINEATIN

Tetsuya Toya, Hiromasa Nagase, and Toshio Honda*
Ageo Research Laboratory, Nippon Kayaku Co., Ltd., Koshikiya 225-1, Ageo, Saitama, Japan and
Institute of Medicinal Chemistry, Hoshi University, Ebara 2-4-41, Shinagawa-ku, Tokyo 142, Japan

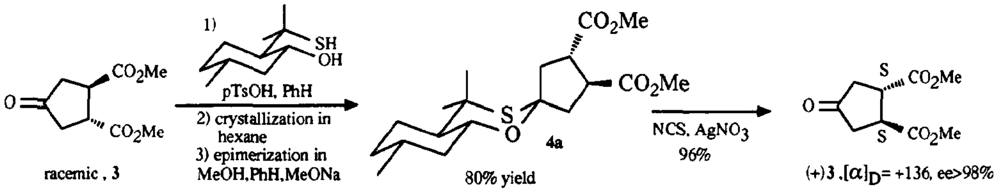
Enantioselective reduction of the cyclobutenone gave the chiral cyclobutenol, which was converted into the key intermediates for cyclobutane monoterpenes, grandisol and lineatin



Tetrahedron: Asymmetry **1993**, *4*, 1547

New Reagent for the Optical Resolution of Ketones : (-) (1R, 2R, 5R)-5-methyl-2-(1-mercapto-1-methylethyl)-cyclohexanol. Application to Trans dimethyl Cyclopentanone-3,4-Dicarboxylate.

Guy Solladié*, Olivier Lohse.
Ecole Européenne des Hautes Etudes des Industries Chimiques, 1 Rue Blaise Pascal, 67008-Strasbourg, France.



Tetrahedron: Asymmetry **1993**, *4*, 1553

THE OXIDATION OF BENZALDEHYDE TO BENZOIC ACID CATALYSED BY CYCLO-[(S)-HIS-(S)-PHE], AND ITS IMPLICATIONS FOR THE CATALYTIC ASYMMETRIC ADDITION OF HCN TO ALDEHYDES.

David J.P. Hogg, Michael North*, Robert B. Stokoe, and William G. Teasdale
Department of Chemistry, University of Wales, Bangor, Gwynedd, LL57 2UW

$$\mathrm{PhCHO} \xrightarrow[O_2]{cyclo\text{-}[(S)\text{-His-}(S)\text{-Phe}]} \mathrm{PhCOOH}$$

$$\mathrm{PhCHO} \xrightarrow[\mathrm{HCN}]{cyclo\text{-}[(S)\text{-His-}(S)\text{-Phe}]} (R)\text{-}\mathrm{PhCH(OH)CN}$$

Tetrahedron: Asymmetry **1993**, *4*, 1559

SINGLE-STEP SYNTHESIS OF KYOTORPHIN IN FROZEN SOLUTIONS BY CHYMOTRYPSIN

Helle Meos,Vello Tôugu, Mati Haga,Aavo Aaviksaar[a],Matthias Schuster[b]
and Hans-Dieter Jakubke[b]
Institutes of Chemical Physics and Biophysics and [a]Experimental Biology
of the Estonian Academy of Sciences,Estonia;[b]University of Leipzig,FRG

A method of Kyotorphin (H-Tyr-Arg-OH) synthesis by chymotrypsin(CT)-catalyzed aminolysis in frozen mixtures,

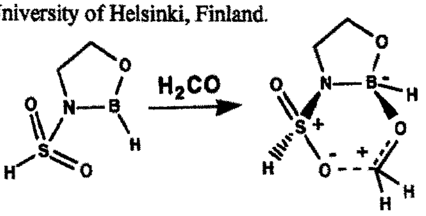
H-Tyr-OEt + CT-OH ⇌ H-Tyr-OEt·CT-OH → H-Tyr-O-CT + Et-OH
H-Tyr-O-CT + H-Arg-OH → H-Tyr-Arg-OH + CT-OH

Tetrahedron: Asymmetry **1993,** *4,* 1565

Quantum Chemical Modeling of Chiral Catalysis. Part 10. On the Complexes of Carbonyl Compounds with Chiral N-Sulfonylated 1,3,2-Oxazaborolidines Used as Catalysts in the Enantioselective Diels-Alder Reactions

Vesa Nevalainen, Division of Organic Chemistry, P.O. Box 6, SF-00014 University of Helsinki, Finland.

Abstract: - Formation of complexes of carbonyl compounds ($H_2C{=}O$ as a model) with *N*-sulfonylated 1,3,2-oxazaborolidines was investigated by means of *ab initio* molecular orbital methods (RHF). The oxygen of formaldehyde was found to be bound to the boron of oxazaborolidine and the carbon to one of oxygens of the *N*-sulfonyl-group.

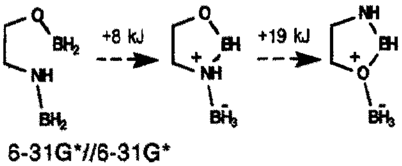


Tetrahedron: Asymmetry **1993,** *4,* 1569

Quantum Chemical Modeling of Chiral Catalysis. Part 11. Isomerism in Borane Adducts of Chiral Oxazaborolidines Used as Catalysts in the Enantioselective Reduction of Ketones ?

Vesa Nevalainen, Division of Organic Chemistry, P.O. Box 6, SF-00014 University of Helsinki, Finland.

Abstract: - The relative stability of isomers of borane adducts of 1,3,2-oxazaborolidines was investigated by means of *ab initio* molecular orbital methods. One open-chain isomer was found to be more stable than the corresponding borane *N*-adduct whereas the borane *N*-adduct turned out to be more stable than the corresponding *O*-adduct. Geometry of the ring oxygen of the *O*-adduct appeared to be practically planar.

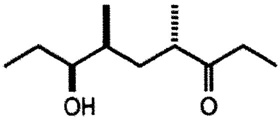


Tetrahedron: Asymmetry **1993,** *4,* 1573

Enantioselective Synthesis of (-)-Serricornin, a Sex Pheromone of a Female Cigarette Beetle (*Lasioderma serricorne* F.)

Masaaki Miyashita, Yuuko Toshimitsu, Tomonori Shiratani, and Hiroshi Irie

Faculty of Pharmaceutical Sciences, Nagasaki University, Bunkyo-machi, Nagasaki 852, Japan



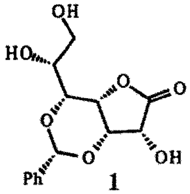
(-)-Serricornin, a sex pheromone of a cigarette beetle (*Lasioderma serricone* F.) has been synthesized highly stereoselectively by employing two stereospecific methylation reactions as key steps.

Tetrahedron: Asymmetry **1993,** *4,* 1579

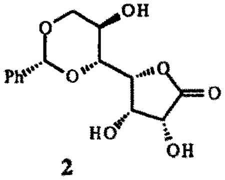
BENZYLIDENE ACETALS OF HEPTONOLACTONES

C. J. F. Bichard,[a] I. Bruce,[a] D. J. Hughes,[a] A. Girdhar,[b] G. W. J. Fleet,[a]* and D, J. Watkin[b]
[a]Dyson Perrins Laboratory, Oxford Centre for Molecular Sciences, South Parks Road,Oxford OX1 3QY, UK
[b]Chemical Crystallography Laboratory, Oxford University, 9, Parks Road, Oxford OX1 3PD, UK

An efficient synthesis of the readily available heptonolactone benzylidene derivative (1) is described. The preparation of other benzylidene acetals of heptonolactones, such as (2), are reported.



1

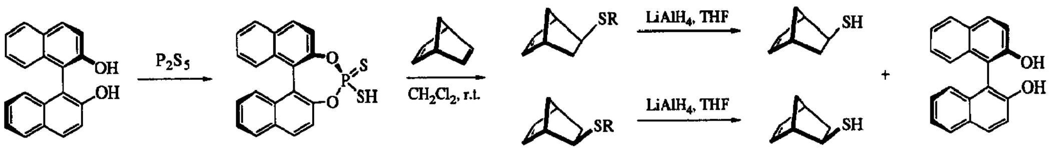


2

Tetrahedron: Asymmetry **1993**, *4*, 1591

Thiophosphonates of 1,1'-Binaphthol as Chiral Equivalents of H_2S. Preparation of 2-Mercaptonorbornanes and 2-Mercaptonorbornenes

Davide Fabbri,[a] Giovanna Delogu,[b] and Ottorino De Lucchi*[c]
[a]*Dipartimento di Chimica, Università di Sassari, via Vienna 2, I-07100 Sassari - Italy,* [b]*Istituto CNR IATCAPA, via Vienna 2, I-07100 Sassari, Italy,* [c]*Dipartimento di Chimica, Università di Venezia, Dorsoduro 2137, I-30123 Venezia - Italy*

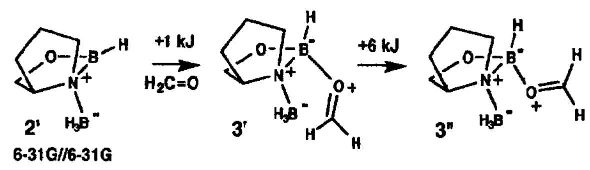


Tetrahedron: Asymmetry **1993**, *4*, 1597

Quantum Chemical Modeling of Chiral Catalysis. Part 12. On the Influence of the Nature of the Ring System on Binding in Ketone - Borane Complexes of Chiral Oxazaborolidines Used as Catalysts in the Enantioselective Reduction of Ketones

Vesa Nevalainen, Division of Organic Chemistry, P.O. Box 6, SF-00014 University of Helsinki, Finland.

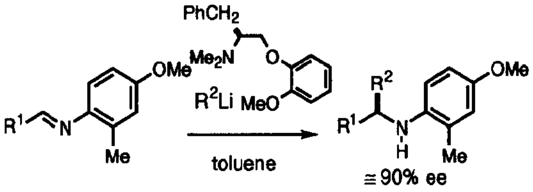
Coordination of formaldehyde to the borane *N*-adduct 2' leading to the formation of complexes 3' and 3'' was investigated by means of *ab initio* molecular orbital methods. Energies of the formation of 3' and 3'' were more positive than those of the corresponding less-strained and less-rigid oxazaborolidines.



Tetrahedron: Asymmetry **1993**, *4*, 1603

Steric Tuning in Chiral Ligand Mediated Enantioselective Alkylation of Imines

Isao Inoue,[a] Mitsuru Shindo,[b] Kenji Koga,[b] and Kiyoshi Tomioka[c]*
[a]Organic Chemistry Research Laboratory, Tanabe Seiyaku Co. Ltd., Toda, Saitama 335,
[b]Faculty of Pharmaceutical Sciences, University of Tokyo, Bunkyo-ku, Tokyo 113,
[c]The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567, Japan

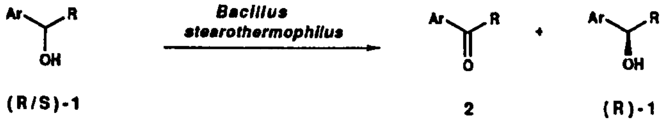


Tetrahedron: Asymmetry **1993**, *4*, 1607

MICROBIAL OXIDATION WITH BACILLUS STEAROTHERMOPHILUS: HIGH ENANTIOSELECTIVE RESOLUTION OF 1-HETEROARYL AND 1-ARYL ALCOHOLS

G. Fantin, M. Fogagnolo, A. Medici, P. Pedrini, S; Poli, F. Gardini,[a] Dipartimento di Chimica, Università di Ferrara, Italy ;
[a]Dipartimento di Protezione e Valorizzazione Agroalimentare, Università di Bologna, Italy

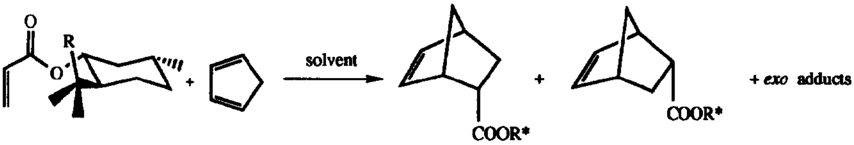
The kinetic resolution of racemic 1-aryl and 1-heteroaryl ethanols via oxidation by *Bacillus stearothermophilus* to give the R-enantiomer is reported.



Tetrahedron: Asymmetry **1993**, *4*, 1613

FLUORINATED ALCOHOLS AS SOLVENTS FOR DIELS-ALDER REACTIONS OF CHIRAL ACRYLATES

C.Cativiela, J.I. García, J.A. Mayoral*, A.J. Royo, L. Salvatella.
Dpto Qª Orgánica. I.C.M.A. Universidad de Zaragoza-C.S.I.C. 50009-Zaragoza (Spain)



3 4

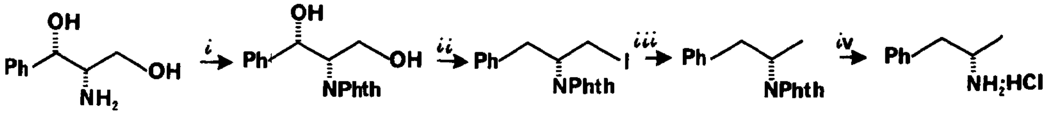
R=H , HFIP increases the *endo* %de with respect to toluene from 9.5 to 26.4. 4 is the major product
$R{=}C_6H_5$, HFIP decreases the *endo* %de with respect to toluene from 38.8 to 8. 3 is the major product

---

Tetrahedron: Asymmetry **1993**, *4*, 1619

An Efficient Synthesis of S-(+)-Amphetamine

Maria D.Rozwadowska, Faculty of Chemistry
A.Mickiewicz University, 60-780 Poznań, Poland



i:Phtalic anhydride;ii:PPh_3,I_2,toluene;iii:H_2/Pd-C,Et_3N,EtOAc;iv:$NH_2NH_2{\cdot}H_2O$,n-butanol

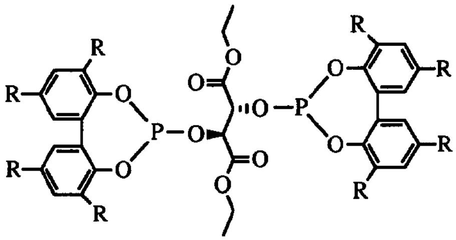
---

Tetrahedron: Asymmetry **1993**, *4*, 1625

Rhodium Catalyzed Asymmetric Hydroformylation with Chiral Diphosphite Ligands

Godfried J.H. Buisman, Paul C.J. Kamer, Piet W.N.M. van Leeuwen

Chiral diphosphites ligands have been synthesized and used in the asymmetric hydroformylation of styrene. High regioselectivities (>95%) and low e.e.'s (20%) have been obtained under mild conditions.



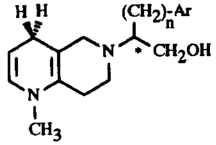
e.g. Diphosphite ligands with C_2 symmetry
based on *L*- tartaric acid (R = H, t-Bu)

Tetrahedron: Asymmetry **1993**, *4*, 1635

Variations of the Nature of the Chiral Auxiliary with a Highly Enantioselective Chiral NADH Model.

Yves Combret, Jack Duflos, Georges Dupas, Jean Bourguignon and Guy Quéguiner
Laboratoire de Chimie Organique Fine et Hétérocyclique de l'IRCOF.
URA CNRS 1429. INSA de Rouen, BP 08, 76131 Mont Saint Aignan Cédex (France).

Various chiral amino alcohols have been used as chiral auxiliaries for a highly enantioselective NADH model. Some of these are new reagents which have been obtained by an enzymic resolution method.



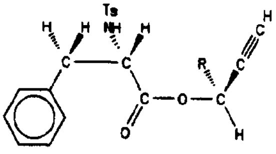
Tetrahedron: Asymmetry **1993, *4*, 1645**

SYNTHESIS OF OPTICALLY PURE ALKYNOLS

Th. Künstler, D. Schollmeyer, H. Singer*and M. Steigerwald
Fachbereich Chemie, Universität Mainz, J. J. Becherweg 34, D 55099 Mainz

Separation of (R,S)-1-alkyl-prop-2-yn-1-ols by a recrystallisation of their N-p-tosyl-(L)-phenylalanine esters

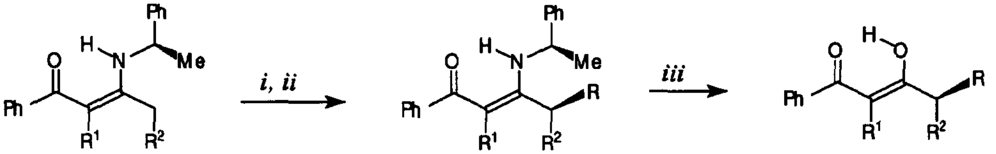
R: -methyl, -ethyl, -octyl,
-i-propyl, -t-butyl, -phenyl



Tetrahedron: Asymmetry **1993, *4*, 1651**

Stereoselective Alkylation of Cyclic and Acyclic Chiral β-Enamino Ketones Lithium Dianions: Synthesis of Either (*R*)- or (*S*)-Chiral 1,3-Diketones.

Giuseppe Bartoli, Marcella Bosco, Cristina Cimarelli, Renato Dalpozzo, Giovanni De Munno, and Gianni Palmieri *



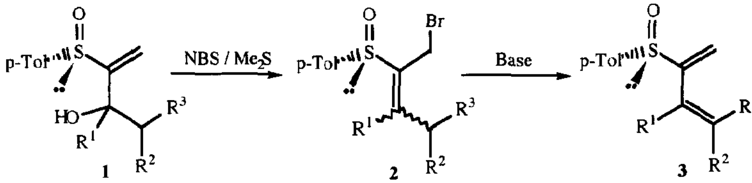
i: 2.5 MeLi/2.5 HMPA/THF, 0 to 30°C, 30'; ii: 1.5 RX/THF, -100°C, 30'; iii: HCl 2N/THF, r.t., 24 h.

Tetrahedron: Asymmetry **1993, *4*, 1667**

An Easy Synthesis of Chiral Sulfinyl Allylic Bromides and their Use in the Preparation of (R)- and (S)-2-p-Tolylsulfinyl-1,3-alkadienes

Eric Bonfand, Pascal Gosselin and Christian Maignan
Laboratoire de Synthèse Organique, Université du Maine, BP 535,
F-72017 Le Mans (France)

(R)- and (S)-2-p-Tolylsulfinyl-1,3-alkadienes 3 were readily prepared from chiral primary allylic sulfinylbromides 2



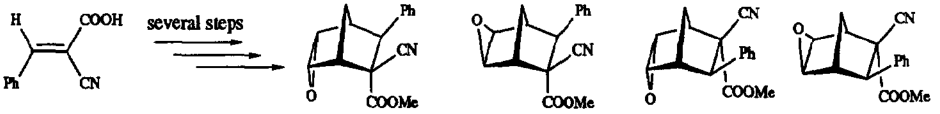
1 2 3

Tetrahedron: Asymmetry **1993, *4*, 1677**

SYNTHESIS OF METHYL 2-EXO-CYANO-3-EXO-PHENYL-5,6-ENDO(or EXO)-EPOXYBICYCLO[2.2.1]HEPTANE-2-ENDO-CARBOXYLATES IN ENANTIOMERICALLY PURE FORM

C. Cativiela*. Department of Organic Chemistry. Instituto de Ciencia de Materiales de Aragón. Universidad de Zaragoza-CSIC. 50009 Zaragoza. Spain. A. Avenoza and J. M. Peregrina. Department of Chemistry (Organic Chemistry). Edificio Científico-Técnico. Sección Ciencias. Universidad de La Rioja. 26001 Logroño. Spain.

The four enantiomerically pure methyl 2-exo-cyano-3-exo-phenyl-5,6-endo(and exo)epoxybicyclo[2.2.1]heptane-2-endo-carboxylates were prepared by divergent synthesis starting from (E)-2-cyanocinnamic acid.

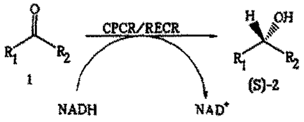


Tetrahedron: Asymmetry **1993,** *4*, 1683

Synthetic applications of the carbonyl reductases isolated from *Candida parapsilosis* and *Rhodococcus erythropolis*

Jörg Peters, Thomas Zelinski, Torsten Minuth and Maria-Regina Kula
Institut für Enzymtechnologie, Heinrich-Heine-Universität Düsseldorf, Postfach 2050, 5170 Jülich

(S)-configurated hydroxy compounds (2) were obtained from prochiral keto compounds (1) by enzymatic reduction. NADH was regenerated in situ by two different methods.



$R_1 = CH_3, CH_2Cl$

$R_2 = CH(OCH_3)_2, CH_2COOCH_3, CH_2COOC_2H_5, (CH_2)_2COOC_2H_5, (CH_2)_3COOC_2H_5, Ph$

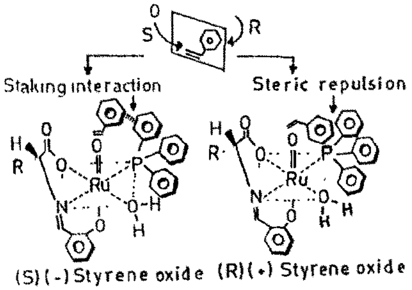
Tetrahedron: Asymmetry **1993,** *4*, 1693

Asymmetric Epoxidation of Styrene by novel Chiral Ru(II) Schiff base Complexes, Synthesis and Characterization

R.I.Kureshy, N.H.Khan, S.H.R.Abdi and K.N.Bhatt

Discipline of Coordination Chemistry
C.S.M.C.R.I., Bhavnagar 364 002, INDIA

Chiral Ru(II) complexes, $[RuL(PPh_3)(H_2O)_2]$ where L = Chiral Schiff bases derived from Salicylaldehyde and L-aminoacids, were synthesised, characterised and were evaluated for the enantioselective epoxidation of styrene. Possible mechanism of epoxidation reaction is discussed.



Tetrahedron: Asymmetry **1993,** *4*, 1703

THE SYNTHESIS OF (R) -γ-PHENYL-γ-(TRIFLUOROMETHYL)-BUTYROLACTONE AND (2R,3S)-1,1,1-TRIFLUORO-2-METHOXY-2 PHENYL-3,4-EPOXYBUTANE IN HOMOCHIRAL FORMS

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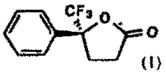
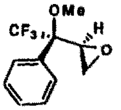
The syntheses of the homochiral butyrolactone (1) and the epoxide (2), carrying a CF₃ group at the tertiary chiral centre, are outlined.



(1)



(2)