GRAPHICAL ABSTRACTS

Tetrahedron: Asymmetry **1993, *4*,** 2109

Application of Chiral Cyclic Diols to Asymmetric Synthesis

Kiyoshi Sakai* and Hiroshi Suemune
Faculty of Pharmaceutical Sciences, Kyushu University, Fukuoka 812, Japan

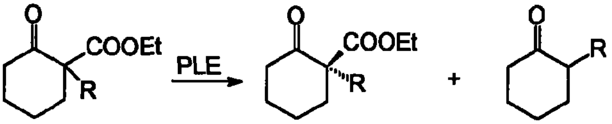
Tetrahedron: *Asymmetry* Report Number 15

The use of chiral cycloalkane-1,2-diol derivatives, for example, esters, acetals and enol ethers in asymmetric synthesis is reviewed.

Tetrahedron: Asymmetry **1993, *4*,** 2119

PLE-catalyzed Resolution of α substituted ß-Ketoesters Application to the Synthesis of (+)-Nitramine and (-)-Isonitramine

Bernhard Westermann, Hildegard Große Scharmann, Ina Kortmann
Universität-GH Paderborn, Fachbereich Chemie und Chemietechnik, Warburgerstr. 100, 33098 Paderborn, Germany



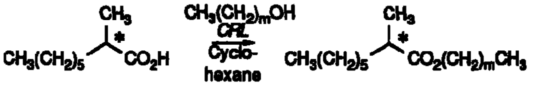
PLE catalyzed hydrolysis of substituted ß-ketoesters leads to optically pure compounds (8 examples, ee > 98%). (R = Alkyl, Alkylnitrile, Benzyl)

Tetrahedron: Asymmetry **1993, *4*,** 2123

Water Activity Influences Enantioselectivity in a Lipase-Catalysed Resolution by Esterification in an Organic Solvent

Hans-Erik Högberg*, Helen Edlund, Per Berglund, Erik Hedenström
Department of Chemistry, Mid-Sweden University, S-851 70 Sundsvall, Sweden.

The enantioselectivity of the *Candida rugosa* lipase-catalysed esterification of 2-methyloctanoic acid with *n*-alcohols in cyclohexane is dependent on water activity as judged from the ratios between the initial rates of the individual enantiomers at different water activities, a_w.



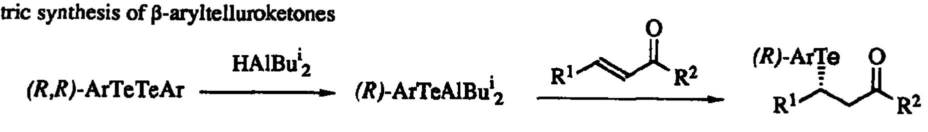
a_w :	0.76	0.15	dry enzyme a_w not fixed
E ≈ Initial rate ratios:	95	23	7

Tetrahedron: Asymmetry **1993, *4*,** 2127

Synthesis of Optically Active Tellurium-Containing Binaphtyls and their Use in the Asymmetric 1,4-Addition Reaction of α,β-Unsaturated Ketones.

M. Irie, Y. Doi, M. Ohsuka, Y. Aso, T. Otsubo and F. Ogura
Department of Applied Chemistry, Faculty of Engineering, Hiroshima University
Kagamiyama, Higashi-Hiroshima 724, Japan.

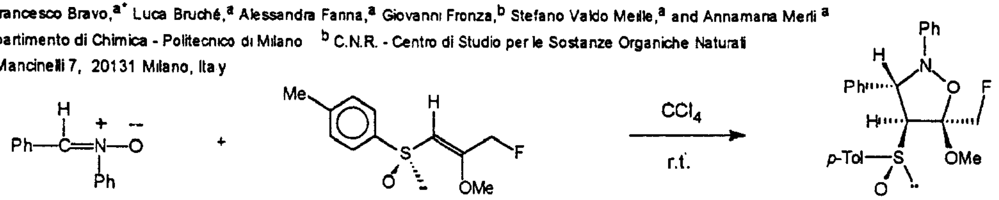
Asymmetric synthesis of β-aryltelluroketones



Tetrahedron: Asymmetry **1993**, *4*, 2131

Synthesis of Optically Pure Fluorosubstituted Isoxazolidines by 1,3-Dipolar Cycloaddition of Nitrones to Chiral Methyl Enol Ethers of 3-Fluoro-1-sulphinyl-2-propanones

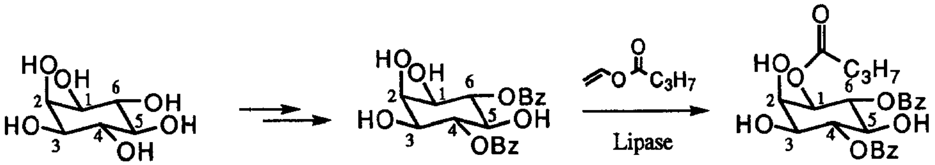
Pierfrancesco Bravo,[a*] Luca Bruché,[a] Alessandra Fanna,[a] Giovanni Fronza,[b] Stefano Valdo Meille,[a] and Annamaria Merli [a]
[a] Dipartimento di Chimica - Politecnico di Milano [b] C.N.R. - Centro di Studio per le Sostanze Organiche Naturali
Via Mancinelli 7, 20131 Milano, Italy



Tetrahedron: Asymmetry **1993**, *4*, 2135

Enzyme Assisted Synthesis of Enantiomerically Pure *myo* -Inositol Derivatives - Chiral Building Blocks for Inositol Polyphosphates

P.Andersch and M.P.Schneider *, FB 9 - Bergische Universität-GH-Wuppertal; 42097 Wuppertal , Germany

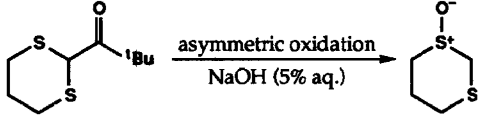


Tetrahedron: Asymmetry **1993**, *4*, 2139

ASYMMETRIC OXIDATION OF DITHIANE DERIVATIVES: ENANTIOMERICALLY PURE 1,3-DITHIANE 1-OXIDE

Philip C. Bulman Page,* M. Thomas Gareh and Roderick A. Porter[†]
Robert Robinson Laboratories, Department of Chemistry, University of Liverpool, Oxford Street, Liverpool, L69 3BX; †SmithKline Beecham Pharmaceuticals, The Frythe, Welwyn, Hertfordshire AL6 9AR

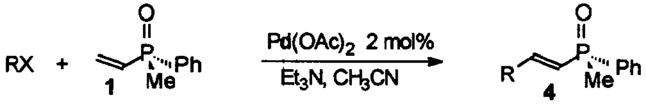
Enantiomerically pure 1,3-dithiane 1-oxide may be efficiently prepared in either absolute configuration through a three-step procedure involving a catalytic asymmetric sulphur oxidation.



Tetrahedron: Asymmetry **1993**, *4*, 2143

SYNTHESIS OF ENANTIOMERICALLY PURE STYRYL AND DIENYL PHOSPHINE OXIDES *VIA* PD-CATALYZED HECK COUPLING REACTION[1]

K. Michal Pietrusiewicz*, Maciej Kuznikowski and Marek Koprowski, Polish Academy of Science, Centre of Molecular and Macromolecular Studies, ul.Sienkiewicza 112, 90-363 Lodz, Poland.



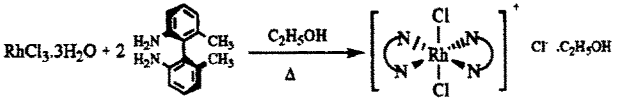
(S)-1 undergoes facile coupling with functionalized aryl and vinyl halides to provide new enantiomerically pure styryl and dienyl phosphine oxides 4 including also the corresponding symmetrical and nonsymmetrical bisphosphines.

Tetrahedron: Asymmetry **1993,** *4*, 2147

PREPARATION AND X-RAY STRUCTURE OF A RHODIUM(III)-(S)-6,6'-DIMETHYL-2,2'-DIAMINO-BIPHENYL COMPLEX.

Drorit Lew and Ibrahim Amer*,
Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel

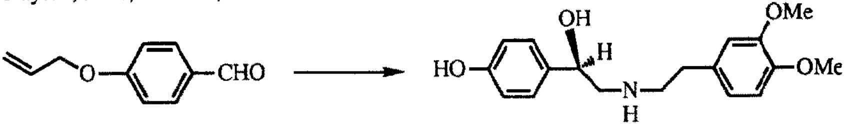
trans-Dichlorobis[(S)-6,6'-dimethyl-2,2'-diaminobiphenyl]rhodium(III) chloride was prepared, and its structure was determined by X-ray diffraction.



Tetrahedron: Asymmetry **1993,** *4*, 2149

A Synthesis of (-)-Denopamine.

Roger F.C.Brown, W. Roy Jackson and Tom D. McCarthy*
Department of Chemistry, Monash University, Wellington Road,
Clayton, 3168, Victoria, Australia.



(-)-denopamine (5)

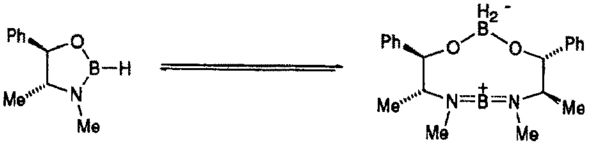
The homochiral cardiac drug, (-)-denopamine (5) is available in 68% overall yield from *para*-allyloxybenzaldehyde.

Tetrahedron: Asymmetry **1993,** *4*, 2151

Reversible Dimerisation of Ephedrine-derived Oxazaborolidines.

John M. Brown, Guy C. Lloyd-Jones and Timothy P. Layzell, Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY

On standing, 4R, 5R-3,4-dimethyl-5-phenyl-1,3,2-oxazaborolidine dimerises to a monocyclic species, reverting quantitatively on gentle thermolysis. Related oxazaborolidines show contrasting behaviour.

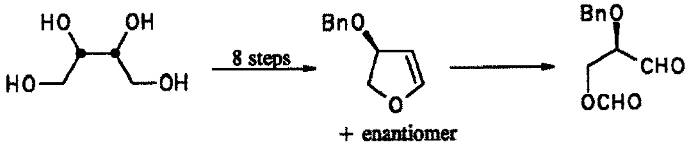


Tetrahedron: Asymmetry **1993,** *4*, 2155

Enantiomerically Pure (*R*)- and (*S*)-3-Benzyloxy-2,3-dihydrofuran: Versatile Precursors for the Synthesis of Protected Glycerinaldehydes.

Hans-Josef Altenbach and Eckardt Wolf
Bergische Universität-Gesamthochschule Wuppertal, Gaußstraße 20, D-42097 Wuppertal, Germany.

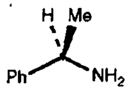
Synthesis of Both Enantiomers of 3-Benzyloxy-2,3-dihydrofuran and Conversion into 2-*O*-Benzyl-3-*O*-formylglycerinaldehyde



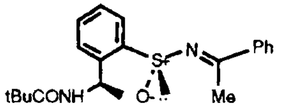
Tetrahedron: Asymmetry **1993**, *4*, 2159

Asymmetric Synthesis of Amines using a Chiral, Non-Racemic, Cyclic Sulphinamide

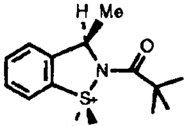
David R. J. Hose,[a] Tony Raynham[b] and Martin Wills.*[b]
a. School of Chemistry, Bath University, Bath, UK. b. Roche Products Ltd, Welwyn Garden City, UK.



R-(+)-α-methylbenzyl-amine-7 : 86% e.e.



R$_{(S)}$R-(-)-3



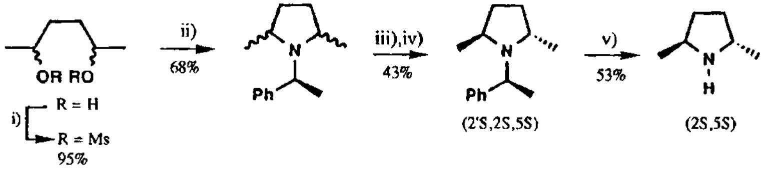
S$_{(S)}$R-(+)-1

Enantiomerically enriched **7** was prepared by asymmetric reduction of benylidenesulphinimide **3**, itself prepared in one step from the cyclic sulphinamide **1**.

Tetrahedron: Asymmetry **1993**, *4*, 2163

ASYMMETRIC SYNTHESIS OF TRANS-2,5-DIMETHYLPYRROLIDINE

M.E. Zwaagstra, A. Meetsma, B.L. Feringa,
University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

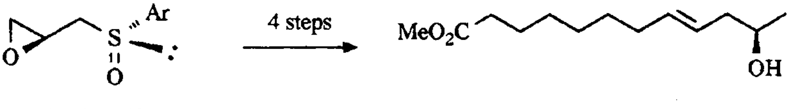


i) MsCl, Et$_3$N, CH$_2$Cl$_2$, -20°C. ii) (S)-1-Phenyl-ethylamine, 65°C, 18 hr. iii) picric acid, recrystallization from methanol. iv) NaOH. v) H$_2$, Pd/C, AcOH, 36 hr.

Tetrahedron: Asymmetry **1993**, *4*, 2173

Enantioselective Synthesis of methyl (+)-(R)-11-hydroxy-8(E)-dodecenoate, the seco-ester of (+)-(R)-recifeiolide, from [2(S),S(R)]-2-(p-tolylsulfinyl)methyl oxirane.

Guy Solladié*, José Kovenski, Françoise Colobert
Ecole Européenne des Hautes Etudes des Industries Chimiques, 1 Rue B. Pascal, 67008-Strasbourg, France.



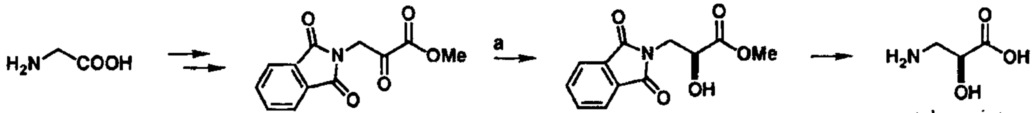
(+)-[2(S)S(R)]- 4

[8(E)11(R)]-1

Tetrahedron: Asymmetry **1993**, *4*, 2179

Enantioselective Synthesis of L- and D-Isoserine via Asymmetric Hydrogenation of Methyl *N*-Phthaloyl-3-amino-2-oxopropanoate

K. Nozaki, N. Sato, and H. Takaya
Division of Material Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan



L-Isoserine
100% *ee*

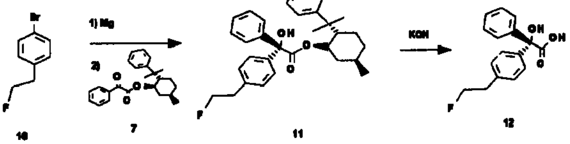
Asymmetric synthesis of L- and D-isoserine via catalytic hydrogenation

a: H$_2$ (100 kg•cm^{-2}), cat: [RuCl((*R*)-binap)(benzene)]Cl with HBF$_4$ (10 equiv. to the catalyst)

Tetrahedron: Asymmetry 1993, 4, 2183

Asymmetric Synthesis of Benzilic Acid Analogues Using 8-Phenylmenthol as a Chiral Auxiliary

Dale O. Kiesewetter. Positron Emission Tomography Department, Warren Grant Magnuson Clinical Center, Bldg 10, Rm 1C401, National Institutes of Health, 9000 Rockville Pike, Bethesda, MD 20892

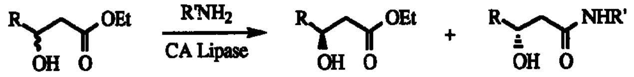


Tetrahedron: Asymmetry 1993, 4, 2199

PRACTICAL ENZYMATIC ROUTE TO OPTICALLY ACTIVE 3-HYDROXYAMIDES. SYNTHESIS OF 1,3-AMINOALCOHOLS

María J. García, Francisca Rebolledo and Vicente Gotor*
Departamento de Química Orgánica e Inorgánica. Universidad de Oviedo. 33071 Oviedo. Spain.

Candida antarctica lipase is a very efficient catalyst for the enantioselective aminolysis of different 3-hydroxyesters with aliphatic amines.

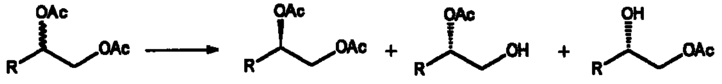


R = Me, Et, CH_2Cl, Ph

Tetrahedron: Asymmetry 1993, 4, 2211

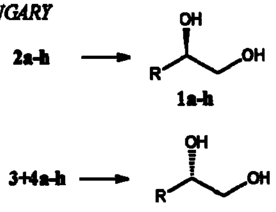
Lipase-Catalysed Enantiomer Selective Hydrolysis of 1,2-Diol Diacetates

László Poppe[a], Lajos Novák[b], Mária Kajtár-Peredy[a], Csaba Szántay[a,b]
[a]*Central Research Institute for Chemistry, H-1521 Budapest, PO Box 17., HUNGARY*
[b]*Institute for Organic Chemistry, Technical University Budapest, H-1521 Budapest, Gellért tér 4., HUNGARY*



rac-**2a-h** **2a-h** **3a-h** **4a-h**

a-h: R= $(CH_2)_nCH_3$ [n= 0,1,2,5,8], CH_2Cl, CH_2OMe, CH_2OBn



1a-h

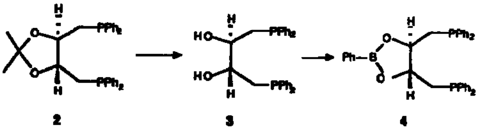
ent-**1a-h**

Resolution of 1,2-diols (*rac*-1a-h) was invesigated *via* enantiomer selective hydrolysis of their diacetates (*rac*-2a-h) by porcine pancreatic lipase.

Tetrahedron: Asymmetry 1993, 4, 2219

A BORON ANALOG OF DIOP : SYNTHESIS AND PROPERTIES

A. BÖRNER, J. WARD, K. KORTUS, H. B. KAGAN*, Laboratoire de Synthèse Asymétrique, Institut de Chimie Moléculaire d'Orsay, Université Paris-Sud, URA CNRS n° 1497, 91405 Orsay, France



The synthesis of bisphosphines 3 and 4 derived from DIOP 2 and their utilisation in asymmetric reduction has been described.

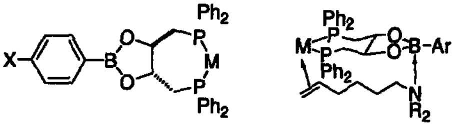
Tetrahedron: Asymmetry **1993, *4*, 2229**

Synthesis and Characterization of Chiral Bimetallic Complexes Bearing Hard and Soft Lewis Acidic Sites.

Lisa B. Fields[1] and Eric N. Jacobsen[2]

[1] Department of Chemistry, University of Illinois
[2] Department of Chemistry, Harvard University

Preparation of a new class of optically active heterobimetallic complexes is described. Evidence for cooperative binding of difunctional substrates to the bimetallic system is presented.

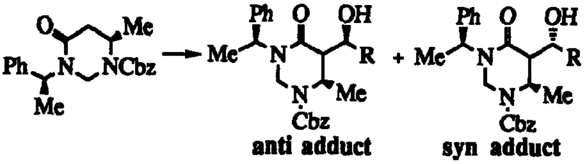


Tetrahedron: Asymmetry **1993, *4*, 2241**

Metal-Assisted Aldol Condensation of Chiral 6-Methyl Perihydropyrimidin-4-ones

Rosa Amoroso, Giuliana Cardillo,* Giovanna Mobbili and Claudia Tomasini - Dipartimento di Chimica "G. Ciamician" Università di Bologna - Via Selmi, 2 - 40126 Bologna - ITALY

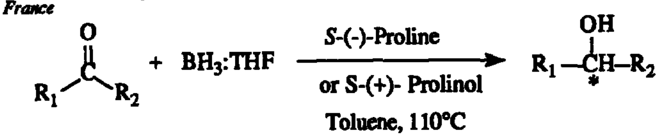
The aldol condensation of various metal enolates of (1'*S*,6*R*) and (1'*S*,6*S*) 6-methyl perihydropyrimidin-4-ones with benzaldehyde and acetaldehyde is reported. All reactions afford complete facial diastereoselectivity and good simple diastereoselectivity.



Tetrahedron: Asymmetry **1993, *4*, 2255**

Enantioselective Reduction of Ketones with Borane, Catalyzed by (*S*)-(–)-Proline or (*S*)-(+)-Prolinol

Jean Michel Brunel, Michel Maffei and Gérard Buono
ENSSPICAM, URA 1410 Réativité Catalyse, Université Aix-Marseille III, Avenue Escadrille Normandie Niemen, 13397 Marseille Cedex 13, France



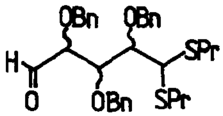
In the presence of 10 mol % of proline, the e.e. for the alcohols range from 81 to >95% in refluxing toluene. A mechanistic rationale based on the reactive species isolated is proposed.

Tetrahedron: Asymmetry **1993, *4*, 2261**

Pentodialdose Mercaptal Derivatives: New Chiral C_5 Synthetic Building Blocks.

Imre Kovács, Zoltán Tóth, Pál Herczegh, Ferenc Sztaricskai
Research Group for Antibiotics of the Hungarian Academy of Sciences, H-4010 Debrecen, P.O.B. 70, Hungary

Three tribenzyloxy derivatives of the title compounds with D-*xylo*, D-*arabino* and D-*lyxo* configuration were prepared from naturally abundant hexoses in five steps.



Enzymatic Resolution of Butanoic Esters of 1-Phenyl, 1-Phenylmethyl, 1-[2-Phenylethyl] and 1-[2-Phenoxyethyl] Ethers of 3-Methoxy-1,2-Propanediol

Tetrahedron: Asymmetry **1993**, *4*, 2265

Viggo Waagen[1], Ingjerd Hollingsæter[1], Vassilia Partali[1], Olav Thorstad[2] and Thorleif Anthonsen[1]
1, Department of Chemistry, The University of Trondheim, N-7055 Dragvoll, Norway
2, Norsk Hydro, Research Center, N-3901 Porsgrunn, Norway

R = Ph, E = 55
R = CH_2Ph, E = 20
R = CH_2CH_2Ph, E > 100
R = OCH_2CH_2Ph, E > 55