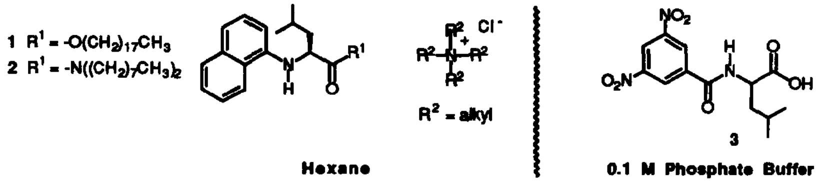
GRAPHICAL ABSTRACTS

Tetrahedron: Asymmetry **1994**, *5*, 773

PREPARATIVE SEPARATION OF ENANTIOMERS USING HOLLOW-FIBER MEMBRANE TECHNOLOGY.

William H. Pirkle* and William E. Bowen, School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801



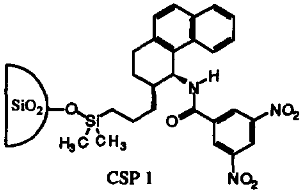
Chiral selectors (1, 2)have been used in a hollow-fiber membrane system (Sepracor) to separate the enantiomers of amino acid derivatives (3) in enantiomeric purities exceeding 95%.

Tetrahedron: Asymmetry **1994**, *5*, 777

Use of Simultaneous Face to Face and Face to Edge π-π Interactions to Facilitate Chiral Recognition

William H. Pirkle and Christopher J. Welch
School of Chemical Sciences, University of Illinois, Urbana, IL 61801

A recently developed HPLC chiral stationary phase (CSP 1) exhibits a general ability to resolve the enantiomers of compounds possessing both an electron rich conjugated π-system and a hydrogen bond acceptor located near the stereogenic center.



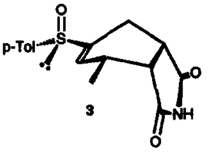
CSP 1

Tetrahedron: Asymmetry **1994**, *5*, 781

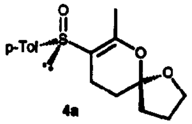
Asymmetric Intermolecular Diels-Alder Reactions of Enantiopure Sulfinyl-Homo- and -Hetero-Dienes: Preliminary Results.

Pascal Gosselin*[a], Eric Bonfand[a], Patricia Hayes[a], Richard Retoux[b] and Christian Maignan*[a]
a)Laboratoire de Synthèse Organique, URA CNRS 482, b) Laboratoire des Fluorures, URA CNRS 449,
Faculté des Sciences, Avenue Olivier Messiaen, BP 535, F-72017 Le Mans Cedex France

Reaction of (E)-(+)-(R)-2-*p*-tolylsulfinyl-1,3-pentadiene 1 with maleimide afforded 3 as a single adduct. Heterodiene (+)-(S)-3-*p*-tolylsulfinyl-3-butene-2-one 2 smoothly reacted with sensitive 2-methylenetetrahydrofuran yielding easily separable 1:1 diastereomeric dioxaspiroadducts **4a** and **4b**.



3

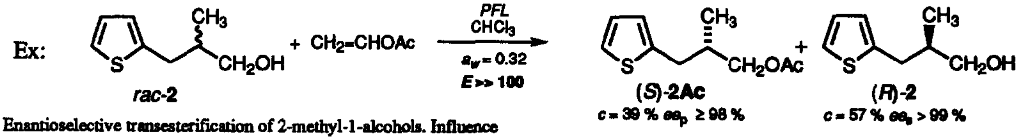


4a

Tetrahedron: Asymmetry **1994**, *5*, 785

Enantioselective Transesterifications of 2-Methyl-1-alcohols Catalysed by Lipases from *Pseudomonas*.

Ove Nordin, Erik Hedenström, Hans-Erik Högberg*
Chemistry, Department of Science and Engineering, Mid Sweden University, S-851 70 Sundsvall, Sweden.

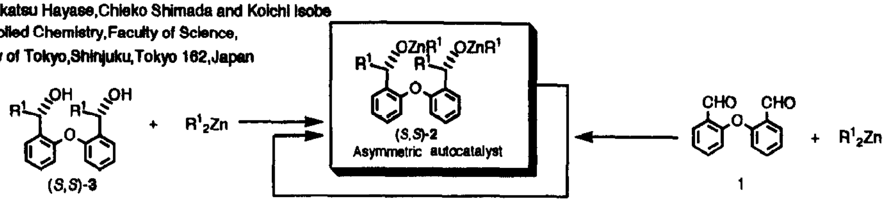


Enantioselective transesterification of 2-methyl-1-alcohols. Influence of water activity, solvent, substrate, acyl donor and immobilization.

Tetrahedron: Asymmetry **1994**, *5*, 789

Catalytic Asymmetric Synthesis of Chiral Diol, Bis[2-(1-hydroxyalkyl)phenyl]ether, an Asymmetric Autocatalytic Reaction

Kenso Soai*, Tadakatsu Hayase, Chieko Shimada and Koichi Isobe
Department of Applied Chemistry, Faculty of Science,
Science University of Tokyo, Shinjuku, Tokyo 162, Japan

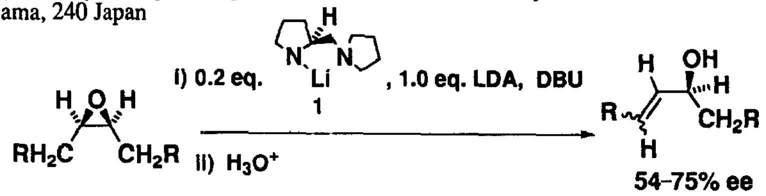


Tetrahedron: Asymmetry **1994**, *5*, 793

Catalytic Enantioselective Deprotonation of *meso*-Epoxides by the Use of Chiral Lithium Amide

Masatoshi Asami,* Tatsuya Ishizaki, and Seiichi Inoue
Department of Synthetic Chemistry, Faculty of Engineering, Yokohama National University,
Tokiwadai, Hodogaya-ku, Yokohama, 240 Japan

Enantioselective deprotonation of *meso*-epoxides was achieved using only a catalytic amount of chiral lithium amide **1** in the presence of excess LDA and DBU.

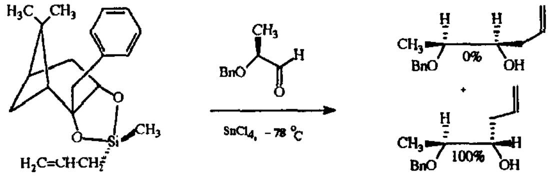


Tetrahedron: Asymmetry **1994**, *5*, 797

Chelation Controlled Allylation of Aldehydes with a Chiral Allylsilylene Derived from (—)-10-Phenylpinanediol.

Kirupathevy Shanmuganathan, Larry G. French and Bruce L. Jensen
Department of Chemistry, University of Maine, Orono, ME 04469 USA.

Asymmetric Allylation of (S)-2-(Benzyloxy)propanal with 10-Phenylpinanediol Allylmethylsilylene

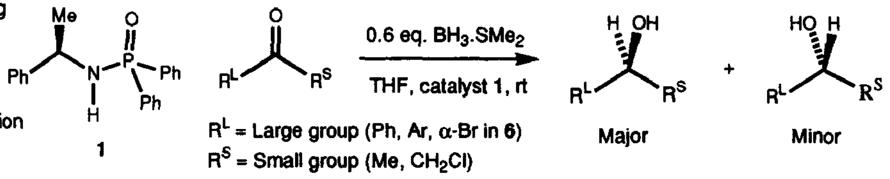


Tetrahedron: Asymmetry **1994**, *5*, 801

Stereoelectronic Requirements for a New Class of Asymmetric Ketone Reduction Catalysts Containing an N-P=O Structural Unit.

B. Burns, N. P. King, J. R. Studley. H. Tye and M. Wills.*
School of Chemistry, Bath University, Bath, UK, BA2 7AY.

Compounds containing an N-P=O structural unit, such as the phosphinamide **1**, are catalysts for the asymmetric reduction of ketones by borane.

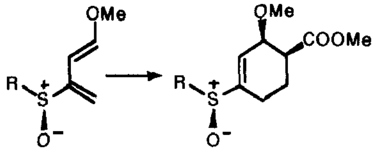


Tetrahedron: Asymmetry **1994**, *5*, 805

ASYMMETRIC DIELS-ALDER REACTIONS OF ENANTIOPURE 1-METHOXY-3-(PHENYL-2-HYDROXYETHYLSULFINYL)-1,3-BUTADIENES

Maria C. Aversa,[a]* Paola Bonaccorsi,[a] Placido Giannetto,[a] and D. Neville Jones[b]*
[a]Dipartimento di Chimica organica e biologica, Università, 98166 Messina, Italy
[b]Department of Chemistry, The University, Sheffield S3 7HF, U.K.

Enantiopure (E)- and (Z)-3-(1-phenyl- and 2-phenyl-2-hydroxyethylsulfinyl)-1-methoxy-1,3-butadienes are easily prepared from ethyl mandelate. Cycloadditions of **5a** and **6a** with $CH_2=CHCOOMe$, catalysed by $LiClO_4$ or $ZnCl_2$ in CH_2Cl_2 at RT, proceed with complete regioselectivity and very high *endo* diastereofacial selectivity.

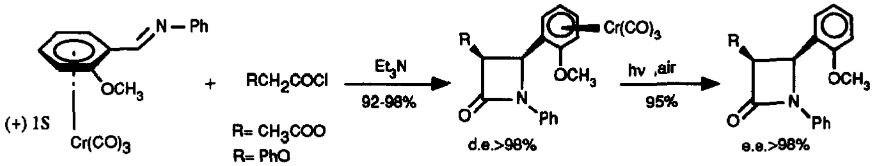


5a R = (S) $HOCH_2CH(Ph)$-
6a R = (S) $HOCH(Ph)CH_2$-

Tetrahedron: Asymmetry **1994**, *5*, 809

Tricarbonyl(η^{6}arene)chromium(0) complexes as Chiral Auxiliaries. Homochiral β-Lactams Synthesis "via" [2+2] Cycloaddition Reaction.

C. Baldoli, P. Del Buttero,* E. Licandro, S. Maiorana,* A. Papagni



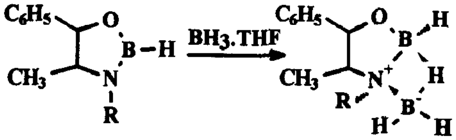
Moreover (+) 1S tricarbonyl[4-methoxy-N-(2-methoxycinnamylidene)aniline] gave the corresponding 3-acetoxy β-lactam in 56% d.e.

Tetrahedron: Asymmetry **1994**, *5*, 813

A Theoretical Investigation of Hydride Bridging in Chiral Oxazaborolidine-Borane Adducts: The Importance of Electron Correlation

Lynda P. Linney[a], Christopher R. Self[b] and Ian H. Williams[a]*.
[a] School of Chemistry, University of Bath, Claverton Down, Bath.
[b] Roche Research Center, P.O. Box 8, Welwyn Garden City, Herts.

Molecular-orbital calculations performed using the *ab initio* MP2/6-31G** and semi-empirical AM1 methods predict hydride bridging to be favoured in oxazaborolidine-borane adducts, in agreement with experiment but in contrast to the *ab initio* HF/6-31G** method.

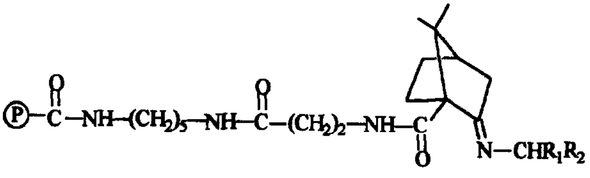


Tetrahedron: Asymmetry **1994**, *5*, 817

Asymmetric supported reactions : synthesis of chiral amines

Monique Calmes, Jacques Daunis, Ahmad Hanouneh, Robert Jacquier
URA 468 - Aminoacides et peptides, Université Montpellier II, Place E. Bataillon, 34095 Montpellier Cedex 05- France

Deracemization of various amines linked via Schiff bases to a chiral polyacrylic polymer facilitated reaction work up and afforded products in up to 72% ee.

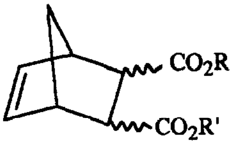


Tetrahedron: Asymmetry **1994**, *5*, 821

Diastereoselectivities in the Diels-Alder Reactions of Cyclopentadiene with Optically Active Dimenthyl Fumarate and Menthyl Methyl Fumarate in $LiClO_4$/Ether and on Alumina.

Satinder Bains, Richard M. Pagni,* and George W. Kabalka,* Department of Chemistry, University of Tennessee,
Knoxville, TN 37996-1600 U.S.A.

The title reactions afforded diastereomeric dialkyl bicyclo(2.2.1)hept-5-ene-2,3-dicarboxylates.

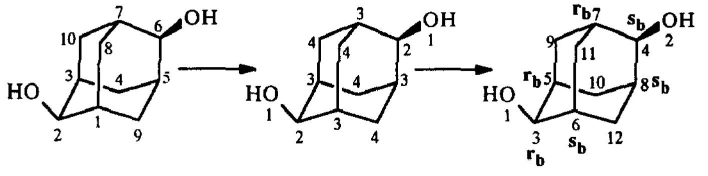


Tetrahedron: Asymmetry **1994**, *5*, 835

Stereochemistry and Sequence Rules. A Proposal for Modification of Cahn-Ingold-Prelog System.

Marko Perdih and Marko Razinger
National Institute of Chemistry, Hajdrihova 19, Ljubljana, Slovenia.

The asignment of the descriptors to 2,6-adamantanediol. The numbering of atoms in the rightmost formula is canonical. The ranking induced by canonical numbering determines the descriptors.

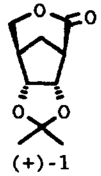


Tetrahedron: Asymmetry **1994**, *5*, 863

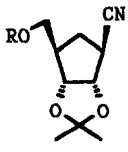
CHIRAL BUILDING BLOCKS FOR CARBOCYCLIC N- AND C- RIBONUCLEOSIDES THROUGH BIOCATALYTIC ASYMMETRISATION OF *meso*-CYCLOPENTANE-1,3-DIMETHANOLS.

Barbara Mohar[a], Anton Štimac[b], Jože Kobe[a]*
[a]*National Institute of Chemistry, Ljubljana and* [b]*Krka, Pharmaceutical and Chemical Works, Novo mesto, Slovenia*

Enantiomerically pure carbocyclic ribonucleoside synthons, Ohno's lactone (+)-1 and carbonitriles 10 (R=Ac) and 15 (R=^{t}BuCO), were prepared through a lipase catalysed enantioselective hydrolysis of *meso*-diesters 5a-c or transesterification of their parent diol 2 with vinyl acetate providing chiral monoesters 6a-c or *ent*-6a of >99% ee in the crucial step. The combined HLADH catalysed and chemical (PDC) oxidation of 2 resulted in (-)-1 of 74% ee.



(+)-1



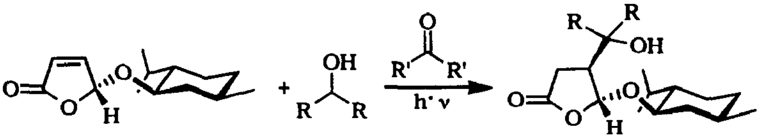
10,15

Tetrahedron: Asymmetry **1994**, *5*, 879

Highly Diastereoselective Addition of Photochemically Generated Radicals to (5R)-(-)-Menthyloxy-2-[5H]-furanone - Synthesis of (-)-Terebic Acid

Norbert Hoffmann
Institut für Organische Chemie der RWTH Aachen
Prof.-Pirlet-Str. 1, D-52054 Aachen, Germany.

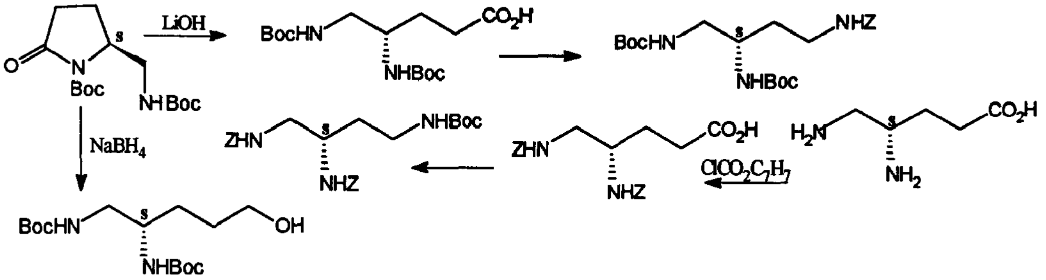
Photochemically generated radicals are added to (5R)-menthyloxy-2[5H]-furanone at the ul-side with a diastereoselectivity >95 %. (-)-Terebic acid is synthesized.



Tetrahedron: Asymmetry **1994**, *5*, 887

Selectively Protected Chiral 1,2,4-Triaminobutanes and Chiral Vicinal 1,2-Diamines

Janina Altman, Dov Ben-Ishai and Wolfgang Beck

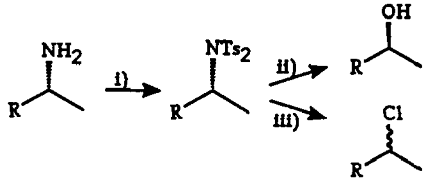


Tetrahedron: Asymmetry **1994**, *5*, 895

Nucleophilic Substitution of Chiral Amine *N,N*-Ditosylderivatives, Chiral Analysis.

Hilde Oppedal, Inger Cathrine Tveit and Anne Fiksdahl*.
Organic Chemistry Laboratories, University of Trondheim-NTH,
N-7034 Trondheim, Norway.

Transformation of optically active amines to the corresponding alcohol and chloride via the nucleophilic substitution of the *N,N*-ditosylimides;
Inversion degree of substitution products:
- alcohol, 85-100%,
- chlorides, 0-34%.



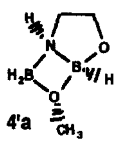
i) TsCl, NaH; ii) KOH, NH_4OAc or NH_4OBz; iii) NH_4Cl

Tetrahedron: Asymmetry **1994**, *5*, 903

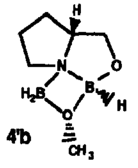
Quantum Chemical Modeling of Chiral Catalysis. Part 19. Strain and Stability - Oxazadiboretanes Potentially Involved in the Enantioselective Reduction of Ketones Promoted by Chiral Oxazaborolidines

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

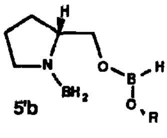
Abstract: Relative stabilities of oxazadiboretane derivatives (e.g. **4'a** and **4'b**) were studied by means of *ab initio* MO (RHF) methods. Reactions of analogs of **4'b** giving rise to the regeneration of the catalyst were found to require ≈ 20 kJ mol^{-1} (MP2/6-31G//6-31G) more energy than those of **4'a**. Cleavages of **4'b** leading to the rupture of both the oxazaborolidine and oxazadiboretane rings (e.g. **4'b** -> **5'b**) required ≈ 30 kJ mol^{-1} (MP2/6-31G//6-31G) more energy than those of **4'a**.



4'a



4'b



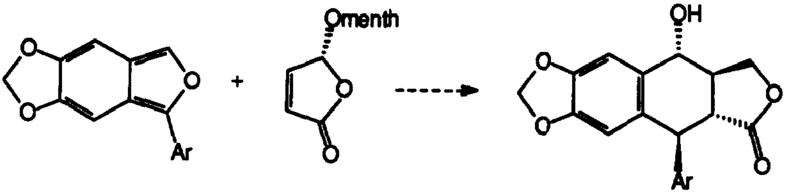
5'b

Tetrahedron: Asymmetry **1994**, *5*, 909

AN ASYMMETRIC SYNTHESIS OF ISOPODOPHYLLOTOXIN

By Andrew Pelter, Robert S. Ward, Li Qianrong and Jaroslav Pis
(Chemistry Department, University of Wales, Swansea, Singleton Park, Swansea SA2 8PP, U.K.)

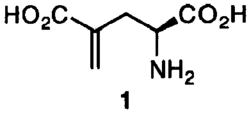
(-)-Isopodophyllotoxin has been synthesised *via* an asymmetric Diels Alder reaction of an isobenzofuran.

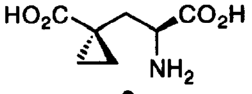


Tetrahedron: Asymmetry **1994**, *5*, 921

EFFICIENT SYNTHESIS OF 4-METHYLENE-L-GLUTAMIC ACID AND ITS CYCLOPROPYL ANALOGUE

J.Ezquerra,[a] C. Pedregal,[a*] C. Najera,[b*] I. Micó[b]
[a] Centro de Investigación Lilly, S. A. Paraje de la Cruz s/n. 28130 Valdeolmos, Madrid, Spain.
[b]Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Alicane. Spain.


1


2

4-Methylene-L-glutamic acid **1** and its cyclopropyl derivative **2** have been prepared in 2 and 3 steps respectively from the common precursor 4-methylene-*N*-BOC ethylpyroglutamate

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Tetrahedron: Asymmetry **1994**, *5*, 927

A practical Synthesis of (*R*)- and (*S*)-(*E*)-4-Hydroxyalk-2-enals, Cytotoxic Products of the Microsomial Lipid Peroxidation

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

Both *R* and *S* enantiomers of some biologically important (*E*)-4-hydroxyalk-2-enals have been efficiently synthesised starting from the Depezay's diepoxides derived from D-mannitol.

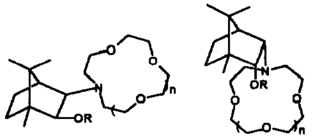
R = CH_3; C_2H_5; C_5H_{11}

Tetrahedron: Asymmetry **1994**, *5*, 935

NEW CHIRAL CROWN ETHERS DERIVED FROM CAMPHOR AND THEIR APPLICATION TO ASYMMETRIC MICHAEL ADDITION. FIRST ATTEMPTS TO RATIONALIZE ENANTIOSELECTION BY AM1 AND AMBER CALCULATIONS

Ernesto Brunet*, Ana M. Poveda, Dolores Rabasco, Enrique Oreja, Luis M. Font, Manohar Singh Batra and Juan C. Rodríguez Ubis *Departamento de Química, C-I. Facultad de Ciencias. Universidad Autónoma de Madrid, 28049-Madrid, Spain* Fax 34 1 397 3966

Catalysis by the title compounds (R=H,Me, n=1-3) is discussed in terms of the relative basicity of their complexes with Na^+ or K^+, which leads to a kinetic *vs.* theromodynamic control in the formation of the ion-pairs between the complexes and phenylacetate enolate with a different stereochemical outcome. AM1 and AMBER calculations support the discussion.



Tetrahedron: Asymmetry **1994**, *5*, 949

Synthesis of Homochiral Cyclopentane Derivatives by Beckmann Fragmentation of 1-Substituted 2-Norbornanoximes

A. García Martínez, E. Teso Vilar, A. García Fraile,
S. de la Moya Cerero, C. Díaz Oliva, L. R. Subramanian.
Fac. C.C. Químicas, Dpto. Quím. Orgánica I, Universidad Complutense, 28040-Madrid, Spain.

	R^1	R^2	R^3	R^4
a	H	H	H	H
b	H	H	CH_3	CH_3
c	CH_3	CH_3	H	H