Tetrahedron: Asymmetry **1993**, *4*, 1711

Synthetic Routes to 2,5-Disubstituted Tetrahydrofurans

Jean-Christophe HARMANGE and Bruno FIGADERE*
Laboratoire de Pharmacognosie, associé au C.N.R.S. Faculté de Pharmacie 92296 Châtenay-Malabry (France)

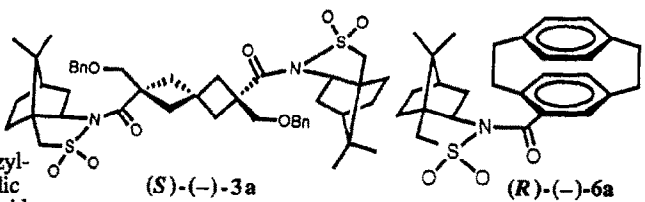
2,5-Disubstituted tetrahydrofurans are structural features commonly encountered in many natural products. The preparation of such valuable synthetic units, because of their implications in biological processes, has attracted particular attention from the organic synthetic chemists. The purpose of this review is to present in a concise format the main preparations of 2,5-disubstituted tetrahydrofurans, and to report the recent progresses in the stereocontrolled routes to such units.

Tetrahedron: Asymmetry **1993**, *4*, 1755

A Chiral Probe Useful for Optical Resolution and X-Ray Crystallographic Determination of the Absolute Stereochemistry of Carboxylic Acids

Nobuyuki Harada,* Tomomi Soutome, Shinji Murai, and Hisashi Uda
Institute for Chemical Reaction Science, Tohoku University, 2-1-1 Katahira, Aoba, Sendai 980, Japan

2,10-camphorsultam amides of 2,6-Bis(benzyloxymethyl)spiro[3.3]heptane-2,6-dicarboxylic acid and [2.2]Paracyclophane-4-carboxylic acid

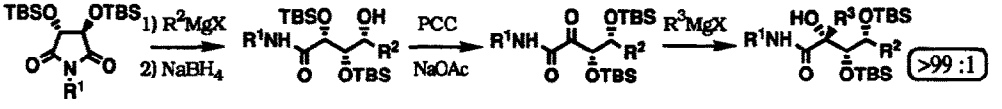


(*S*)-(−)-**3a** (*R*)-(−)-**6a**

Tetrahedron: Asymmetry **1993**, *4*, 1759

DIASTEREOMER DIFFERENTIATION DURING 1,2-ADDITION OF GRIGNARD REAGENTS UNDER ROTAMER DISTRIBUTION CONTROL

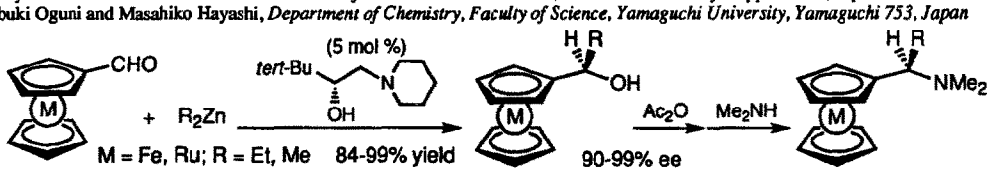
Hidemi Yoda,* Hidekazu Kitayama, Kunihiko Takabe,* and Akikazu Kakehi †
Department of Applied Chemistry, Faculty of Engineering, Shizuoka University, Hamamatsu 432, Japan
†Department of Chemistry and Material Engineering, Faculty of Engineering, Shinshu University, Nagano 380, Japan



Tetrahedron: Asymmetry **1993**, *4*, 1763

Enantioselective Synthesis of 1-Metallocenylalkanols by Catalytic Asymmetric Alkylation of Metallocenecarboxaldehydes with Dialkylzincs

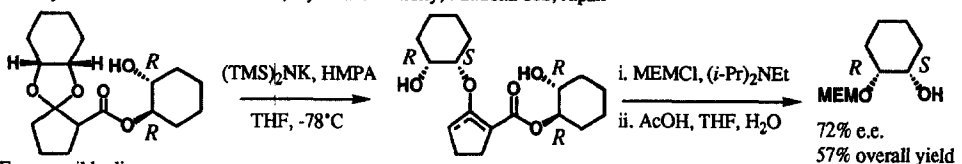
Yonetatsu Matsumoto, Akira Ohno, Shi-jie Lu, and Tamio Hayashi,*
Catalysis Research Center and Graduate School of Pharmaceutical Sciences, Hokkaido University, Sapporo 060, Japan
Nobuki Oguni and Masahiko Hayashi, *Department of Chemistry, Faculty of Science, Yamaguchi University, Yamaguchi 753, Japan*



Tetrahedron: Asymmetry **1993**, *4*, 1767

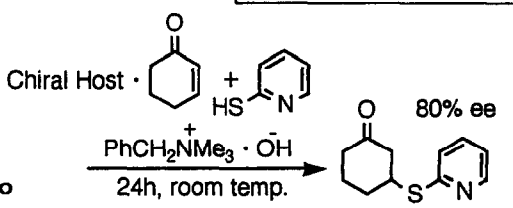
ASYMMETRIC INDUCTION TO *MESO*-CYCLOHEXANE-1,2-DIOL BASED ON DIASTEREOSELECTIVE ELIMINATION

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



Tetrahedron: Asymmetry **1993**, *4*, 1771

Enantioselective Michael Additions to Enones in Their Inclusion Crystals with Optically Active Host Compounds



F. Toda,* K. Tanaka, and J. Sato

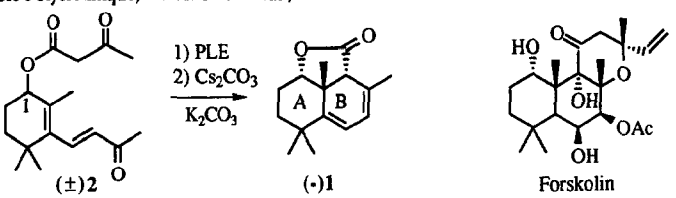
Department of Applied Chemistry, Faculty of Engineering,
Ehime University, Matsuyama, Ehime 790, Japan

Tetrahedron: Asymmetry **1993**, *4*, 1775

Easy Access to an Optically Pure Precursor of Forskolin.

J.-Y. Lallemand, M. Leclaire, R. Levet and G. Aranda.
Laboratoire de Synthèse Organique, Ecole Polytechnique, F-91128 Palaiseau, France.

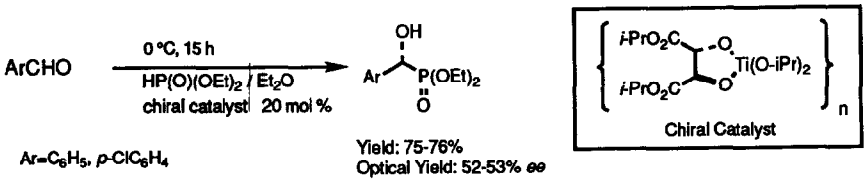
Enantioselective hydrolysis of racemic ester (±)2 by Pig Liver Esterase (PLE) allows separation of C-1 S enantiomer which can be easily cyclized into pure (-)-lactone 1, a precursor of natural compound, forskolin.



Tetrahedron: Asymmetry **1993**, *4*, 1779

Enantioselective Hydrophosphonylation of Aromatic Aldehydes Catalyzed by Chiral Titanium Alkoxides

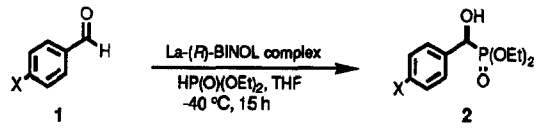
Tsutomu Yokomatsu, Takehiro Yamagishi, and Shiroshi Shibuya
Tokyo College of Pharmacy, 1432-1 Horinouchi, Hachioji, Tokyo 192-03, Japan



Tetrahedron: Asymmetry **1993**, *4*, 1783

Enantioselectivity for Hydrophosphonylation of Aromatic Aldehydes Catalyzed by Lanthanum Binaphthol Complex. Remarkable Electronic Effect of Aromatic Substituents

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



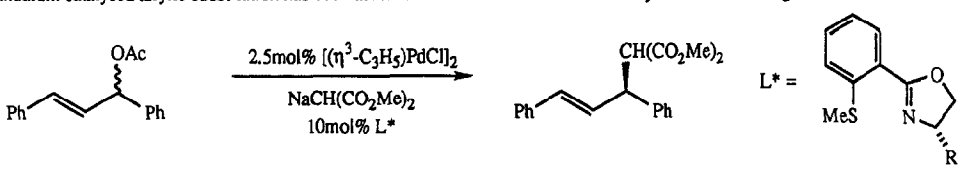
a: X=MeO; **b**: X=Me; **c**: X=H; **d**: X=Cl

Tetrahedron: Asymmetry **1993**, *4*, 1785

ENANTIOSELECTIVE PALLADIUM CATALYSED ALLYLIC SUBSTITUTION WITH SULFUR-CONTAINING OXAZOLINE LIGANDS

Christopher G. Frost and Jonathan M. J. Williams*
Department of Chemistry, Loughborough University of Technology, Loughborough, Leicestershire, LE11 3TU, UK.

Palladium catalysed allylic substitution has been achieved with 40-80% ee and 78-98% yield with novel ligands L*

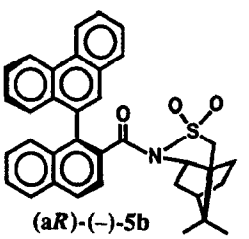


Tetrahedron: Asymmetry **1993**, *4*, 1789

Absolute Stereochemistry of 1-(9-Phenanthryl)-2-naphthoic Acid as Determined by CD and X-Ray Methods

Nobuyuki Harada,* Tetsutaro Hattori, Takatsugu Suzuki, Atsuko Okamura, Hiroshi Ono, Sotaro Miyano, and Hisashi Uda
Institute for Chemical Reaction Science and Faculty of Engineering, Tohoku University, Sendai 980, Japan

CD of 1-(9-phenanthryl)-2-naphthalenemethanol and X-ray of 2,10-camphorsultam amide of 1-(9-phenanthryl)-2-naphthoic acid



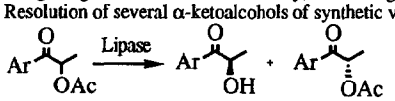
(a*R*)-(–)-5b

Tetrahedron: Asymmetry **1993**, *4*, 1793

ENZYMES IN ORGANIC SYNTHESIS: LIPASE CATALYZED RESOLUTION OF SECONDARY α-KETOALCOHOLS

Tsai-Hui Duh and Yi-Fong Wang*
School of Pharmacy, Kaohsiung Medical College, Kaohsiung City 80708 Taiwan, R.O.C.
Ming-Jung Wu* School of Chemistry, Kaohsiung Medical College.

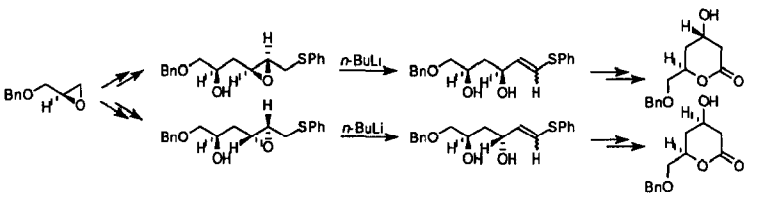
Resolution of several α-ketoalcohols of synthetic value using lipase as catalyst is described.



Tetrahedron: Asymmetry **1993**, *4*, 1795

Diastereodivergent Synthesis of Optically Active *trans*- and *cis*-6-Benzyloxymethyl-4-hydroxytetrahydro-2-pyrones *via* 3-Hydroxyalkenyl Phenyl Sulfides

Seiichi Takano, Yoshiaki Sugihara, and Kunio Ogasawara
Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980, Japan

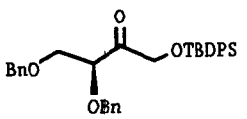


Tetrahedron: Asymmetry **1993**, *4*, 1799

Highly Diastereoselective Additions of Organometallic Reagents to 1-O-Silylated 3,4-di-O-Benzyl-L-Erythrulose Derivatives.

M. Carda,[a] F. González,[a] S. Rodríguez[a] and J. A. Marco[b]

[a]*Departamento de Química Orgánica, Colegio Universitario de Castellón, E-12080 Castellón, and* [b]*Departamento de Química Orgánica, Facultad de Químicas, Universidad de Valencia, E-46100 Burjassot, Valencia, Spain.*



1

(TBDPS = t-butyldiphenylsilyl Bn = benzyl)

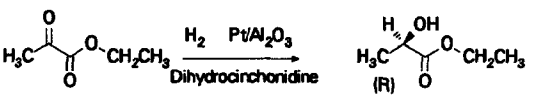
The diastereoselectivity of the addition of organometallic reagents to the carbonyl group of **1** is studied. A high diastereomeric excess is observed with some Grignard reagents.

Tetrahedron: Asymmetry **1993**, *4*, 1803

Enantioselective Heterogeneous Catalysis I. A Working Model For The Catalyst:Modifier:Substrate Interactions In Chiral Pyruvate Hydrogenations

Robert L. Augustine, Setrak K. Tanielyan and Lisa K. Doyle
Department of Chemistry, Seton Hall University, South Orange NJ 07079 USA

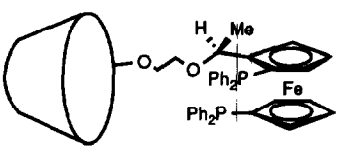
A study of the mode of surface modification to produce a chiral heterogeneous catalyst.

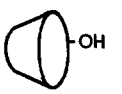


Tetrahedron: Asymmetry **1993**, *4*, 1829

Synthesis and Properties of a New Chiral Diphosphine Ligand Bearing a Cyclodextrin-Based Molecular Recognition Site and Its Palladium(II) Complex

Masaya Sawamura, Kenji Kitayama, and Yoshihiko Ito*
Department of Synthetic Chemistry, Kyoto University, Kyoto 606-01, Japan





heptakis(2,6-di-O-methyl)-β-cyclodextrin

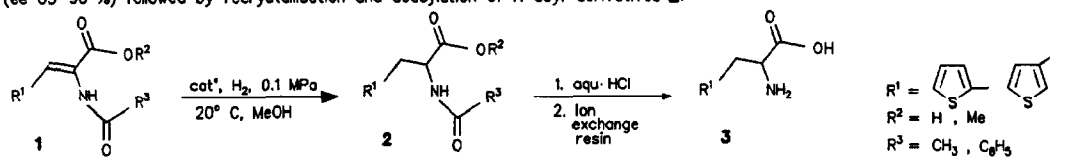
A new chiral diphosphine tethered to heptakis(2,6-di-O-methyl)-β-cyclodextrin was synthesized and converted to water soluble palladium(II) complex.

Tetrahedron: Asymmetry **1993**, *4*, 1833

UNUSUAL AMINO ACIDS–IV.
ASYMMETRIC SYNTHESIS OF THIENYLALANINES

Chr. Döbler, H.-J. Kreuzfeld, H.W. Krause, M. Michalik
Institut für Organische Katalyseforschung, D–2500 Rostock

Synthesis of 2–and 3–thienyl–α–alanines **3** (up to > 99 % ee) by homogeneous catalytic hydrogenations of (Z)–α–N–acylamino–β–thienylacrylic acid derivatives **1** using [Rh–PROPRAPHOS]$^+$ and [Rh–norbornane–aminophosphinephosphinite]$^+$ complexes (ee 65–90 %) followed by recrystallisation and deacylation of N–acyl–derivatives **2**.

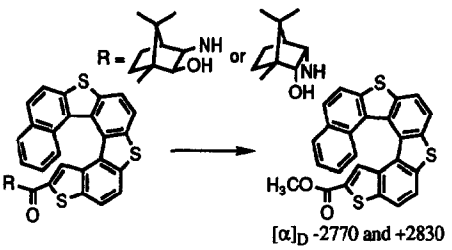


Tetrahedron: Asymmetry **1993**, *4*, 1843

Diastereocontrolled Synthesis of Optically Pure Functionalized Heterohelicenes

Kazuhiko Tanaka, Hideji Osuga, and Hitomi Suzuki
Department of Chemistry, Faculty of Science, Kyoto University, Kitashirakawa, Sakyo, Kyoto 606, Japan

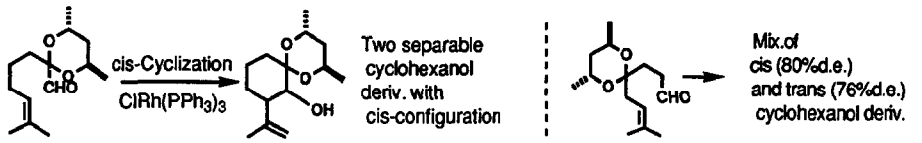
Diastereomeric aminoalcohols prepared from D-camphor were found to be efficient chiral auxiliaries for the preparation of optically pure functionalized heterohelicenes. The diastereoselectivities were controlled by the use of these diastereomeric chiral auxiliaries.



Tetrahedron: Asymmetry **1993**, *4*, 1857

INSIGHT INTO Rh(I)-CATALYZED CYCLIZATION OF 6-OCTEN-1-ALS WITH A CHIRAL PROTECTING GROUP

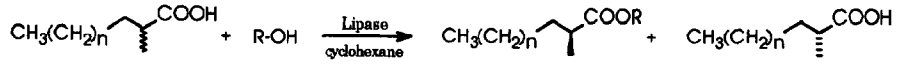
Ichiro Koga, Kazuhisa Funakoshi, Asako Matsuda, and Kiyoshi Sakai*
Faculty of Pharmaceutical Sciences, Kyushu University, Fukuoka 812, Japan



Tetrahedron: Asymmetry **1993**, *4*, 1869

2-Methylalkanoic Acids Resolved by Esterification Catalysed by Lipase from *Candida rugosa*: Alcohol Chain Length and Enantioselectivity

Per Berglund, Mats Holmquist, Erik Hedenström, Karl Hult, Hans-Erik Högberg
Department of Chemistry, University College of Sundsvall/Härnösand, S-851 70 Sundsvall, Sweden
Department of Biochemistry and Biotechnology, Royal Institute of Technology, S-100 44 Stockholm, Sweden



$E = 37 \pm 5$ (n = 6, R = n-C_7H_{15}), E > 100 (n = 4, R = n-$C_{16}H_{33}$)

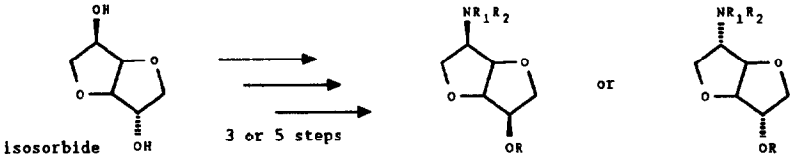
Multi gram scale preparation of (*R*)-2-methyldecanoic acid (> 99.8% *ee*) and (*S*)-2-methyl-1-decanol (96.7% *ee*)

Tetrahedron: Asymmetry **1993**, *4*, 1879

SYNTHESIS OF NEW CHIRAL AUXILIARIES DERIVED FROM ISOSORBIDE

Rodolphe TAMION, Francis MARSAIS, Pierre RIBEREAU and Guy QUEGUINER, *URA CNRS 1429 de l'IRCOF, INSA de Rouen, 76131 Mont Saint Aignan Cedex, France*

David ABENHAIM, André LOUPY and Laurent MUNNIER.
ICMO, URA CNRS 478 Université Paris Sud, Bt 410, 91405 Orsay Cedex, France



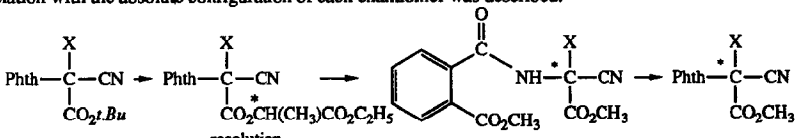
R= H, alkyl. R_1,R_2= H, alkyl, aryl.

Tetrahedron: Asymmetry **1993**, *4*, 1891

Control of the Enantiomeric Purity and Correlation with the Absolute Configuration of N-Protected 2-Cyanoglycinates

P. Hudhomme and G. Duguay*, *Laboratoire de Synthèse Organique*, URA CNRS n°475, Faculté des Sciences et des Techniques, 2, rue de la Houssinière, 44072 Nantes Cedex 03, France.

The synthesis and enantiomeric purity of N-phthaloyl-2-cyanoglycine derivatives using ^{1}H NMR shift reagent have been reported. A useful correlation with the absolute configuration of each enantiomer was described.

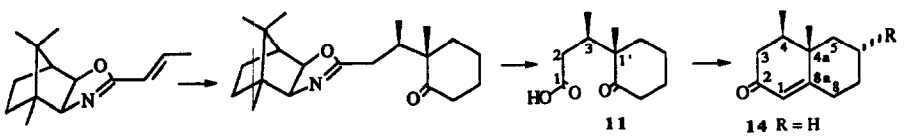


Tetrahedron: Asymmetry **1993**, *4*, 1901

Enantioselective Synthesis of (+)-De-Isopropenyl Nootkatone

Nathalie Dahuron and Nicole Langlois*
Institut de Chimie des Substances Naturelles, C.N.R.S., 91198 Gif-sur-Yvette, France

The absolute configuration of the δ-oxo acid **11** obtained through an asymmetric Michael-type reaction was established by comparison of the CD curves of **14** and natural (+)-nootkatone **15**.



11

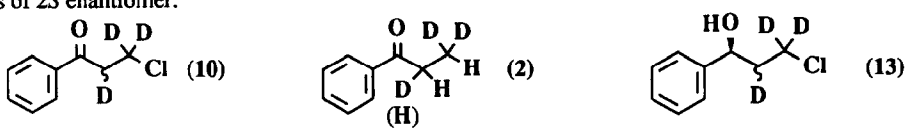
14 R = H
15 R = $C(CH_3)=CH_2$ [(+)-nootkatone]

Tetrahedron: Asymmetry **1993**, *4*, 1909

Stereochemical Features of Baker's Yeast Mediated Transformation of Racemic and Enantiomerically Pure 2-Deutero-3-Chloropropiophenone.

Giovanni Fronza, Claudio Fuganti and Piero Grasselli
Dipartimento di Chimica and CNR, Via mancinelli 7, Milano, Italy

Baker's Yeast reduction of **10** gives rise to **2** retaining ca. 70% deuterium and to **13** showing ca. 10% excess of 2*S* enantiomer.



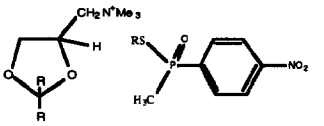
Tetrahedron: Asymmetry **1993**, *4*, 1917

Chiral Drug Potency: Pfeiffer's Rule and Computed Chirality Coefficients

Alon Seri-Levy and W. Graham Richards*

Physical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ, United Kingdom.

Using computer-aided molecular design (CAMD) methods, a quantitative structure activity relation (QSAR) is drawn between the potency ratio of two enantiomers and the chiral coefficient of the enantiomer pair. Pfeiffer's set and the homologous series of the two examples shown are analysed.



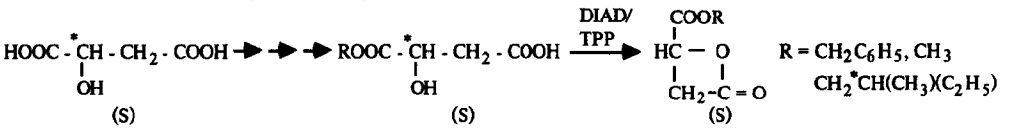
Tetrahedron: Asymmetry **1993**, *4*, 1925

A NOVEL SYNTHESIS OF OPTICALLY ACTIVE 4-BENZYL-OXY- AND 4-ALKYLOXYCARBONYL-2-OXETANONES

Sandrine Cammas, Isabbelle Renard, Karine Boutault and Philippe Guérin *

Laboratoire de Chimie Biologique et Macromoléculaire, URA CNRS 1467, Ecole Nationale Supérieure de Chimie de Rennes, Avenue du Général Leclerc, 35 700 RENNES, FRANCE.

Starting from L-(S)-malic, (R)- β-substituted- β-lactones have been prepared with enantiomeric excesses > 98 %.

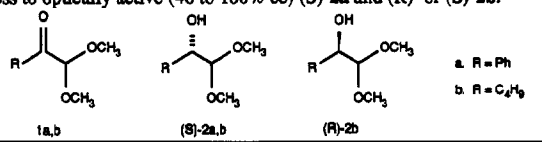


Tetrahedron: Asymmetry **1993**, *4*, 1931

MICROBIAL REDUCTION OF 2-KETO ACETALS AS A BIOCATALYTIC APPROACH TO THE ENANTIOSELECTIVE SYNTHESIS OF OPTICALLY ACTIVE 2-HYDROXY ACETALS.

P. Ferraboschi,[a] *E. Santaniello,*[a] *M. Tingoli,*[b] *F. Aragozzini,*[a] *F. Molinari*[a]- [a]Dipartimenti di Chimica e Biochimica Medica e di Scienze e Tecnologie Alimentari e Microbiologiche, Universita' di Milano. [b]Istituto di Chimica Organica, Universita' di Perugia-Italy

The reduction of the 2-keto acetals **1a** and **1b** by means of different microorganism constitutes the biocatalytic access to optically active (46 to 100% ee) (S)-**2a** and (R)- or (S)-**2b**.

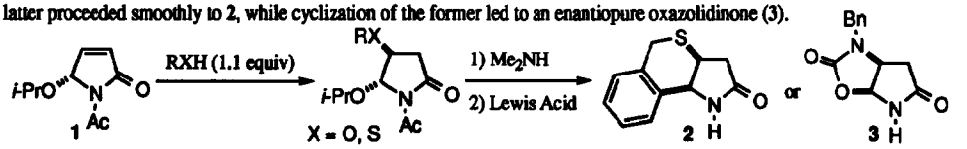


Tetrahedron: Asymmetry **1993**, *4*, 1941

Conjugate Addition of Amines and Thiols to (*R*)-1-Acetyl-5-isopropoxy-3-pyrrolin-2-one; Preparation of Enantiopure *N*-Acyliminium Ion Precursors

Wim-Jan Koot, Henk Hiemstra,* and W. Nico Speckamp*, Laboratory of Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands

The 1,4-addition reaction of amines and thiols to enantiopure γ-lactam **1** proceeded with high *trans*-stereoselectivity. Deacetylation of the *t*-Boc protected benzylamine adduct and the benzyl mercaptan adduct afforded the enantiopure *N*-acyliminium precursors. Cyclization of the latter proceeded smoothly to **2**, while cyclization of the former led to an enantiopure oxazolidinone (**3**).

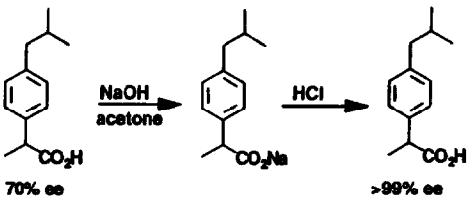


Tetrahedron: Asymmetry **1993**, *4*, 1949

Optical Purification of Profen Drugs

Thanikavelu Manimaran and G. Patrick Stahly*
Ethyl Technical Center, Ethyl Corp., P. O. Box 14799, Baton Rouge, LA 70898

Ibuprofen and naproxen are optically purified by crystallization of their sodium salts from optically enriched mixtures. Calculated melting point phase diagrams of ibuprofen, naproxen, and their sodium salts are presented.



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