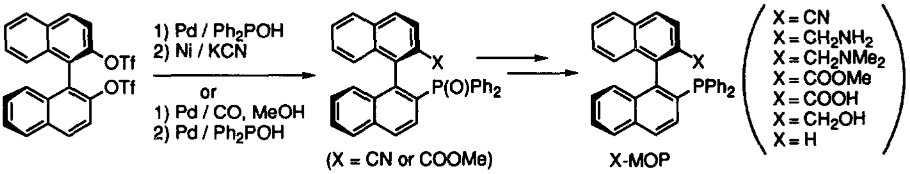
GRAPHICAL ABSTRACTS

Preparation of Optically Active Binaphthylmonophosphines (MOP's) Containing Various Functional Groups

Tetrahedron, **1994**, *50*, 4293

Yasuhiro Uozumi, Nobuhiro Suzuki, Aya Ogiwara, and Tamio Hayashi*
Catalysis Research Center, Hokkaido University, Kitaku, Sapporo 060, Japan

Optically active 2-functionalized-2'-diphenylphosphino-1,1'-binaphthyls (MOP's) were prepared. Cyano, aminomethyl, methoxycarbonyl, carboxy, and hydroxymethyl groups were introduced on the MOP skeleton by transition metal-catalyzed transformation of aryl triflates.

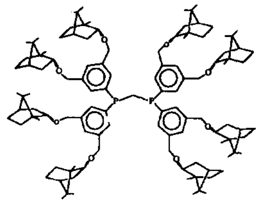


Optically Active Expanded Chelate Phosphines Derived from 1,ω-Bis(dichlorophosphino)alkanes

Tetrahedron, **1994**, *50*, 4303

Henri Brunner* and Josef Fürst
Institut für Anorganische Chemie, Universität Regensburg, 93040 Regensburg, Germany.

Optically active expanded chelate phosphines were synthesised by reaction of bromotolyl, bromoxylyl and bromodiphenylmethane derivatives with 1,ω-bis(dichlorophosphino)alkanes. The bromotolyl, bromoxylyl and bromodiphenylmethane ethers were obtained from the corresponding bromo(bromomethyl)arenes and the optically active alcohol (-)-borneol.

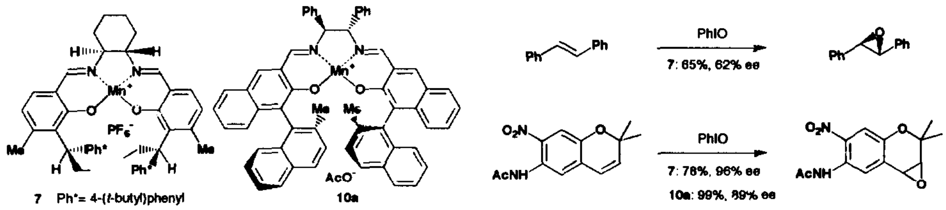


RATIONAL DESIGN OF Mn-SALEN EPOXIDATION CATALYSTS: PRELIMINARY RESULTS

Tetrahedron, **1994**, *50*, 4311

Naoki Hosoya,† Akira Hatayama,† Ryo Irie, Hidehiko Sasaki, and Tsutomu Katsuki*
Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashi-ku, Fukuoka 812, Japan

(Salen)manganese complexes **7** and **10a** were found to be effective catalysts for the epoxidation of unfunctionalized olefins, especially for *cis*-olefins.

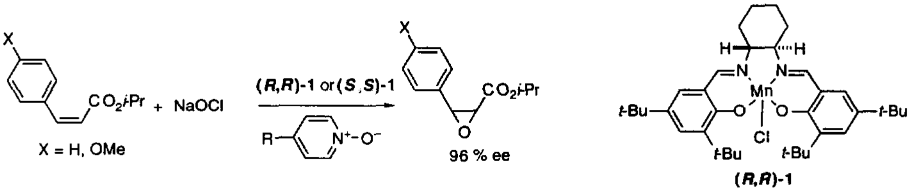


ENANTIOSELECTIVE CATALYTIC EPOXIDATION OF CINNAMATE ESTERS

Tetrahedron, **1994**, *50*, 4323

Eric N. Jacobsen,* Li Deng, Yoshiro Furukawa, and Luis E. Martínez
Department of Chemistry, Harvard University, Cambridge, MA 02138

The asymmetric epoxidation of cis-cinnamate esters catalyzed by **1** is sensitive to the steric properties of the ester group, with bulkier esters affording highest ee's. Application of the AE to the synthesis of dilitazem is described.

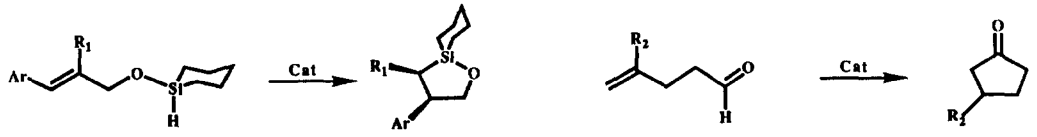


ASYMMETRIC CATALYSIS. ASYMMETRIC CATALYTIC INTRAMOLECULAR HYDROSILATION AND HYDROACYLATION.

Tetrahedron, **1994**, *50*, 4335

Richard W. Barnhart, Xianqi Wang, Pedro Noheda, Steven H. Bergens, John Whelan, and B. Bosnich*
Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637, U.S.A.

The catalyst [Rh(binap)]$^+$, efficiently promotes the two intramolecular cyclizations with very high enantiomeric excesses.

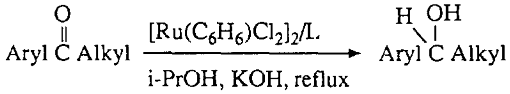


SCHIFF BASES AS ADDED CHIRAL LIGANDS FOR THE $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ CATALYZED HYDROGEN TRANSFER REDUCTION OF KETONES WITH ISOPROPANOL

Tetrahedron, **1994**, *50*, 4347

Pavel Krasik and Howard Alper*
Department of Chemistry, University of Ottawa,Ottawa, Ontario, Canada K1N 6N5

The asymmetric hydrogen transfer reduction of alkyl aryl ketones by isopropanol can be effected in up to 40% ee using $[Ru(C_6H_6)Cl_2]_2$ and a chiral Schiff base.



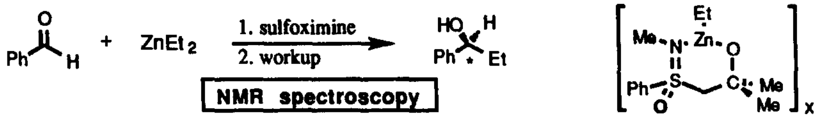
$$\text{Aryl}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{Alkyl} \xrightarrow[\text{i-PrOH, KOH, reflux}]{[Ru(C_6H_6)Cl_2]_2/L} \text{Aryl}\overset{\text{H OH}}{\overset{\backslash\,|}{\text{C}}}\text{Alkyl}$$

Spectroscopic Studies on the β-Hydroxysulfoximine-Catalyzed Enantioselective Alkylation of Aldehydes

Tetrahedron, **1994**, *50*, 4355

Carsten Bolm* and Jürgen Müller
Department of Chemistry, University of Basel, St. Johanns-Ring 19, CH-4056 Basel (Switzerland)

The asymmetric β-hydroxysulfoximine-catalyzed alkyl transfer from diethylzinc to benzaldehyde has been studied by NMR spectroscopy.

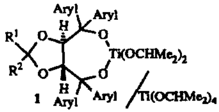


Tetrahedron, **1994**, *50*, 4363

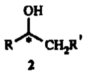
ENANTIO- AND DIASTEREOSELECTIVE TITANIUM-TADDOLate CATALYZED ADDITION OF DIETHYL AND BIS(3-BUTEN-1-YL) ZINC TO ALDEHYDES
A FULL ACCOUNT WITH PREPARATIVE DETAILS

Dieter Seebach*, Albert K. Beck, Beat Schmidt, Yan Ming Wang
Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule, ETH-Zentrum, Universitätstr. 16
CH-8092 Zürich, Switzerland.

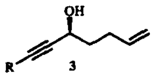
Secondary alcohols of type 2 and 3 of very high enantiopurity are obtained by addition of diethyl and dibutenyl zinc to achiral aldehydes in the presence of the Ti-TADDOLate 1 (0.05 - 0.2 equiv.) and $Ti(OCHMe_2)_4$ (1.2 equiv.). With chiral aldehydes such as myrtenal, epimeric products can be prepared with high diastereoselectivity (see 4a and 4b).



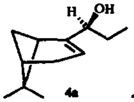
1



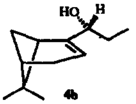
2



3



4a



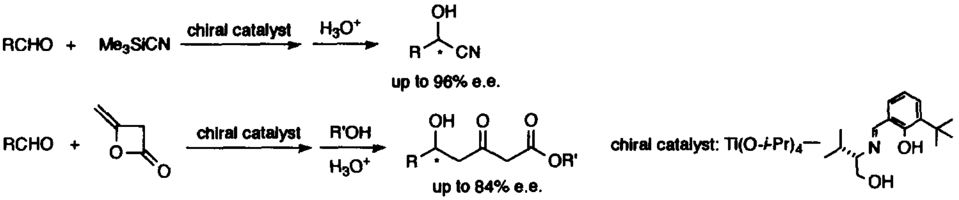
4b

Asymmetric Carbon-Carbon Bond Forming Reactions Catalyzed by Chiral Schiff Base-Titanium Alkoxide Complexes

Tetrahedron, **1994**, *50*, 4385

Masahiko Hayashi, Tetsuya Inoue, Yasunori Miyamoto, and Nobuki Oguni*
Department of Chemistry, Faculty of Science, Yamaguchi University, Yamaguchi City, Yamaguchi 753, Japan

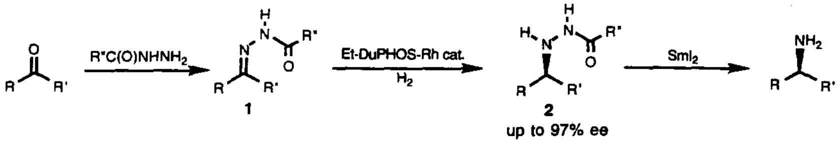
Optically active cyanohydrins and 5-hydroxy-3-oxoesters can be prepared by using a chiral Schiff base--titanium alkoxide catalyst in high optical yield.



CATALYTIC ASYMMETRIC REDUCTIVE AMINATION OF KETONES VIA HIGHLY ENANTIOSELECTIVE HYDROGENATION OF THE C=N DOUBLE BOND

Tetrahedron, **1994**, *50*, 4399

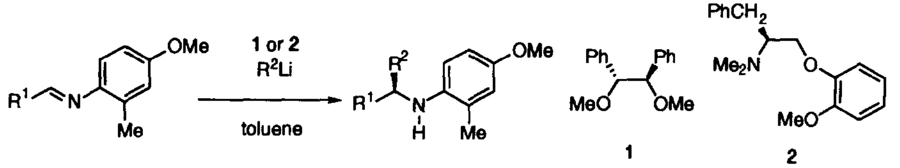
Mark J. Burk*[1], Jose P. Martinez[1], John E. Feaster[2], and Nick Cosford[3]
1. Department of Chemistry, Duke University, Durham, NC 27706. 2. The DuPont Company, Central Research and Development, Experimental Station, Wilmington, DE 19880. 3. The DuPont Merck Pharmaceutical Company, Experimental Station, Wilmington, DE 19880.



ASYMMETRIC 1,2-ADDITION OF ORGANOLITHIUMS TO ALDIMINES CATALYZED BY CHIRAL LIGAND

Tetrahedron, **1994**, *50*, 4429

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]ISIR, Osaka University, Ibaraki, Osaka 567, Japan

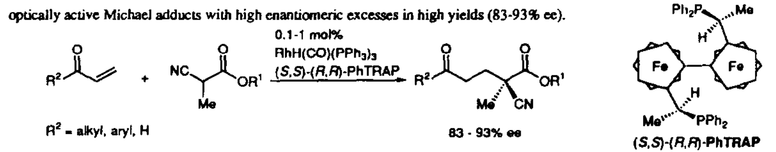


Tetrahedron, **1994**, *50*, 4439

Asymmetric Michael Reaction of α-Cyano Carboxylates Catalyzed by a Rhodium Complex with Trans-Chelating Chiral Diphosphine PhTRAP

Masaya Sawamura, Hitoshi Hamashima, and Yoshihiko Ito*
Department of Synthetic Chemistry and Biological Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606-01, Japan

Asymmetric Michael reaction of 2-cyanopropionates with electrophiles in the presence of 0.1-1 mol% of Rh(I)-PhTRAP catalyst gave optically active Michael adducts with high enantiomeric excesses in high yields (83-93% ee).

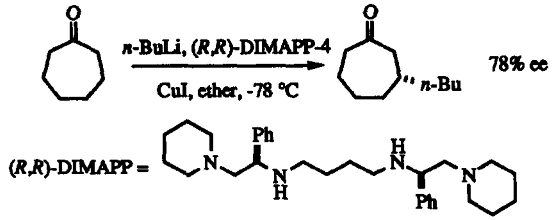


Tetrahedron, **1994**, *50*, 4455

Enantioselective Conjugate Addition, Part V. Synthesis and Testing of Scalemic Tetraamines as Chiral Cuprate Ligands.

Nicole M. Swingle, K. Vasavi Reddy, and Bryant E. Rossiter*
Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah 84602-4672

Enantioselective conjugate addition of *n*-butyl to cyclic enones using scalemic amidocuprates derived from copper(I) iodide, *n*-butyllithium and a homologous series of 5 scalemic tetraamines is reported. Enantioselectivities up to 78% were found.

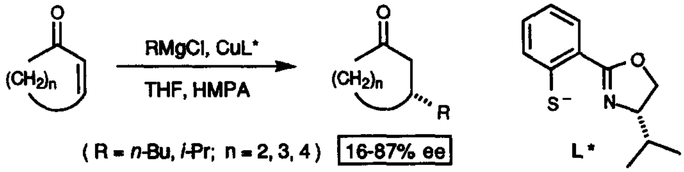


Tetrahedron, **1994**, *50*, 4467

Chiral Mercaptoaryl-oxazolines as Ligands in Enantioselective Copper-Catalyzed 1,4-Additions of Grignard Reagents to Enones.

Qi-Lin Zhou and Andreas Pfaltz*
Institut für Organische Chemie, Universität Basel, St. Johanns-Ring 19, CH-4056 Basel, Switzerland

Copper(I) thiolate complexes derived from chiral mercaptoaryl-oxazolines have been studied as enantioselective catalysts for the conjugate addition of Grignard reagents to cyclic enones.

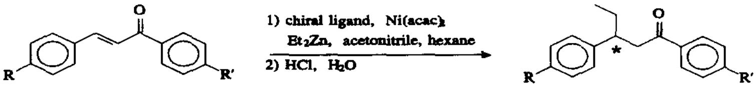


Tetrahedron, **1994**, *50*, 4479

ENANTIOSELECTIVE CONJUGATE ADDITION OF DIETHYLZINC TO CHALCONES CATALYSED BY CHIRAL Ni(II) AMINOALCOHOL COMPLEXES

André H.M. de Vries, Johan F.G.A. Jansen, Ben L. Feringa*
Department of Organic and Molecular Inorganic Chemistry, Groningen Centre for Catalysis and Synthesis
University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands

Conjugate addition of diethylzinc to chalcones is catalysed by complexes prepared *in situ* from Ni(acac)$_2$ and chiral aminoalcohols. The products are obtained with enantioselectivities up to 84 %.

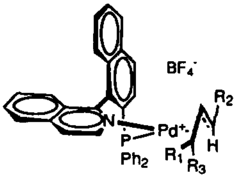


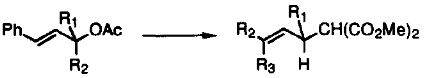
Tetrahedron, **1994**, *50*, 4493

Mechanistic and Synthetic Studies in Catalytic Allylic Alkylation with Palladium Complexes of 1-(2-Diphenylphosphino-1-naphthyl)isoquinoline

John M. Brown, David I. Hulmes, and Patrick J. Guiry.
The Dyson Perrins Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QY, U.K.

The title reaction occurs in 98% e.e and solution NMR studies permit the absolute configuration of the intermediate allyl complexes to be defined.



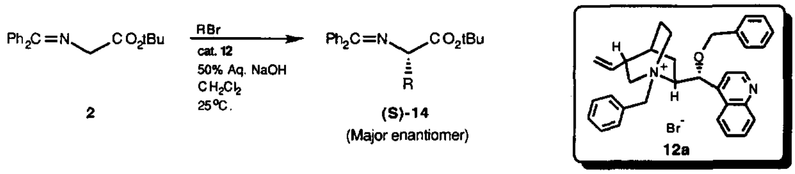


A NEW ACTIVE CATALYST SPECIES FOR ENANTIOSELECTIVE ALKYLATION BY PHASE-TRANSFER CATALYSIS

Tetrahedron, **1994**, *50*, 4507

Martin J. O'Donnell,[a]* Shengde Wu[a] and John C. Huffman[b]
[a]Department of Chemistry, Indiana-Purdue University at Indianapolis, Indianapolis, IN 46205 and [b]Department of Chemistry, Indiana University, Blomington, IN 47405

A new active catalyst (**12**) is proposed for the asymmetric phase-transfer catalytic alkylation of active methylene compounds (**2**).

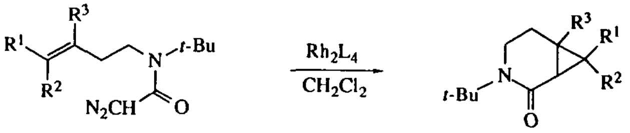


ENANTIOSELECTIVE INTRAMOLECULAR CYCLOPROPANATION OF *N*-ALLYLIC- AND *N*-HOMOALLYLIC DIAZOACETAMIDES CATALYZED BY CHIRAL DIRHODIUM(II) CATALYSTS.

Tetrahedron, **1994**, *50*, 4519

Michael P. Doyle*, Michail Y. Eismont‡, Marina N. Protopopova, and Michelle M. Y. Kwan, Department of Chemistry, Trinity University, San Antonio, Texas 78212, U.S.A. ‡N.D. Zelinski Institute of Organic Chemistry, Moscow, Russia.

Diazodecomposition of *N*-homoallylic diazoacetamides catalyzed by chiral dirhodium(II) catalysts forms the products from intramolecular cyclopropanation in good yields with enantiomeric excess of 60-90%.

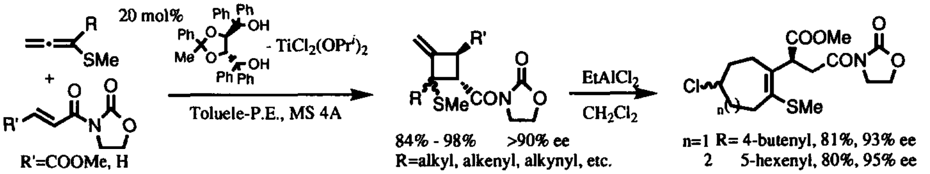


Asymmetric Synthesis of Methylenecyclobutanes and Their Transformation to Medium-sized Carbocyclic Compounds.

Tetrahedron, **1994**, *50*, 4529

Koichi NARASAKA, Kazuhiro HAYASHI, and Yujiro HAYASHI
Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113, Japan

Various chiral methylenecyclobutanes are synthesized by the catalytic asymmetric [2+2] cycloaddition reaction of 1,2-propadienylsulfides, and some of the products are transformed to medium-sized carbocyclic compounds.

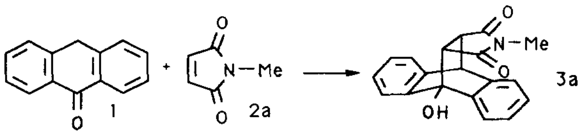


ASYMMETRIC BASE-CATALYZED CYCLOADDITION BETWEEN ANTHRONE AND DIENOPHILES

Tetrahedron, **1994**, *50*, 4543

Olivier Riant [1], Henri B. Kagan* [1], Louis Ricard [2]
1. Laboratoire de Synthèse Asymétrique - Institut de Chimie Moléculaire d'Orsay - Université Paris-Sud - 91405 ORSAY CEDEX - FRANCE
2. Laboratoire de Chimie du Phosphore et des Eléments de Transition - DCPH - Ecole Polytechnique - 91128 PALAISEAU - FRANCE

Anthrone reacts with N-methylmaleimide in presence of various β-aminoalcohols to give **3a**. Several features of this base-catalyzed Diels-Alder reaction have been studied. Quinidine leads to optically active **3a** (ee up to 61 %) whose absolute configuration has been established.



Tetrahedron, **1994**, *50*, 4557

Catalytic Asymmetric Diels-Alder Reactions of 2-Pyrone Derivatives.

István E Markó,* Graham R Evans and Jean-Paul Declercq
Université Catholique de Louvain, B-1348 Louvain-La-Neuve, Belgium