GRAPHICAL ABSTRACTS

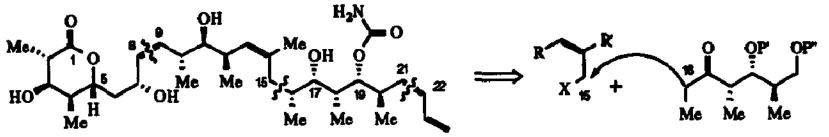
Tetrahedron Letters, **1994**, *35*, 1313

An Alkylative Strategy to the C-13 to C-21 Sector of Discodermolide.

Ge Yang and David C. Myles,* Department of Chemistry and Biochemistry, UCLA
Los Angeles, California 90024-1569, USA

An approach to the C-13 to C-21 sector of the immunosuppressive marine natural product discodermolide is described. The C-15 to C-16 bond is formed by diastereoselective alkylation of a ketone enolate. Either diastereomer of alkylation can be obtained by selecting the appropriate the counter ion.

Discodermolide (1)

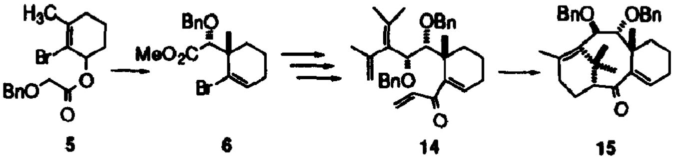


Tetrahedron Letters, **1994**, *35*, 1317

SYNTHESIS OF A C-1 EPI TAXININE INTERMEDIATE USING THE TYPE 2 INTRAMOLECULAR DIELS-ALDER APPROACH

Randy W. Jackson and Kenneth J. Shea*
Department of Chemistry, University of California, Irvine, California 92717

A highly functionalized type 2 intramolecular Diels-Alder precursor, 14, suited for use in the synthesis of taxane natural products, has been prepared. Its stereoselective preparation and cyclization to an epi-tricyclic taxane intermediate 15 are described.

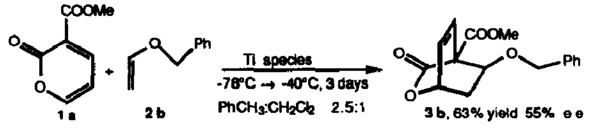


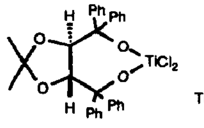
Tetrahedron Letters, **1994**, *35*, 1321

MILD, ASYMMETRIC DIELS-ALDER CYCLOADDITIONS OF ELECTRONICALLY MATCHED 2-PYRONES AND VINYL ETHERS

Gary H. Posner,* Jean-Christophe Carry, Jae Kyoo Lee, D. Scott Bull, and Haiyan Dai
Department of Chemistry, School of Arts and Sciences, The Johns Hopkins University, Baltimore, MD 21218, USA

Silica gel and a TADDOL-complexed titanium IV Lewis acid are shown to promote mild, practical, asymmetric [4+2]-cycloadditions of electron-poor 2-pyrone-3-carboxylates with electron-rich vinyl ethers to form isolable and useful bicyclic lactone adducts.





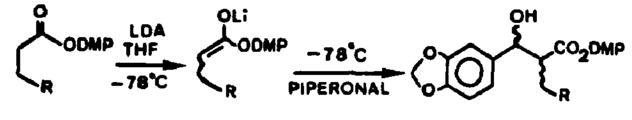
Ti species

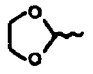
Tetrahedron Letters, **1994**, *35*, 1325

THE ALDOL ADDITION REACTION BETWEEN γ-OXYGENATED CARBOXYLIC ESTERS DERIVED FROM 2,6-DIMETHYLPHENOL AND PIPERONAL.

Paulo R.R. Costa,* Maria F.G. Fernandes and
Sergio Pinheiro,* NPPN/CCS/UFRJ, 21941-590, Rio de Janeiro, RJ, Brazil, GQO/IQ/UFF, 24210-150, Niteroi, RJ, Brazil.

The stereoselectivity of the aldolization of γ-oxygenated DMP-esters depends on the nature of the oxygenated function.



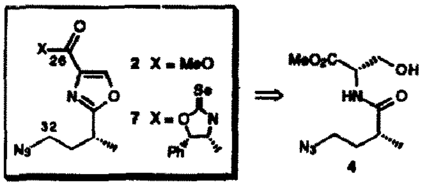
R	E : Z	ANTI : SYN
	34 : 66	34 : 66
CH_2OTBMS	90 : 10	90 : 10

Tetrahedron Letters, **1994**, *35*, 1329

CALYCULIN SYNTHETIC STUDIES. 3. ENANTIOMERIC PURITY DETERMINATION FOR THE C(26)-C(32) OXAZOLE SEGMENT VIA THE SILKS-ODOM ^{77}Se NMR METHOD

Brian A. Salvatore and Amos B. Smith, III*
Department of Chemistry, Laboratory for Research on the Structure of Matter, and Monell Chemical Senses Center, University of Pennsylvania, Philadelphia, Pennsylvania 19104, U.S.A.

An improved preparation of the C(26)-C(32) oxazole subunit of calyculin A is described. The enantiomeric purity was determined via the exceptionally sensitive Silks-Odom method, which can probe very remote stereocenters by ^{77}Se NMR analysis.



Tetrahedron Letters, **1994**, *35*, 1331

A Convenient Preparation of O-Alkyl Selenoesters from Esters

Stephen W. Wright
Pfizer Central Research, Eastern Point Road, Groton, CT 06340

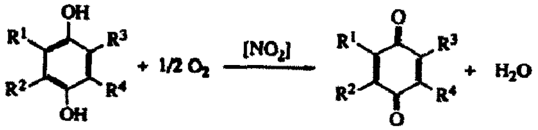
A new methodology is described for the one-flask synthesis of O-alkyl selenoesters directly from the corresponding esters. The ester is converted to the silyl ketene acetal with LDA and Me3SiCl, which is then treated with H2Se generated in situ from aluminum selenide and dilute HCl.

Tetrahedron Letters, **1994**, *35*, 1335

Convenient Preparation of Quinones via the Catalytic Autoxidation of Hydroquinones with Nitrogen Oxides

Rajendra Rathore, Eric Bosch and Jay K. Kochi
Chemistry Department, University of Houston,
Houston 77204-5641, Texas

An efficient, inexpensive, catalytic method for the autoxidation of hydroquinones utilizes the gaseous (NO_x) catalyst which allows a simple workup procedure for quinone isolation merely by solvent removal.

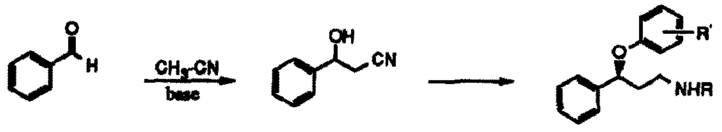


Tetrahedron Letters, **1994**, *35*, 1339

A CONVENIENT METHOD FOR PREPARING ENANTIOMERICALLY PURE NORFLUOXETINE, FLUOXETINE AND TOMOXETINE

Thomas M. Koenig and David Mitchell*
Lilly Research Laboratories, Eli Lilly and Company, Lilly Corporate Center, Indianapolis, Indiana 46285

A convenient synthesis for preparing enantiomerically pure norfluoxetine, fluoxetine and tomoxetine is described. All final products are derived from a common intermediate, 3-phenyl-3-hydroxypropylamine.

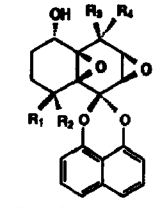


Tetrahedron Letters, **1994**, *35*, 1343

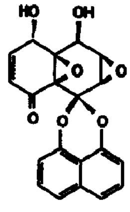
A NOVEL CLASS OF ANTITUMOR METABOLITES FROM THE FUNGUS *NATTRASSIA MANGIFERAE*

Min Chu*, Imbi Truumees, Mahesh Patel, Vincent Gullo,
Christine Blood, Ivan King, Jin-Keon Pai and Mohindar S. Puar
Schering-Plough Research Institute,
2015 Galloping Hill Road, Kenilworth, New Jersey 07033 U.S.A.

Three novel antitumor agents, Sch49210(1), Sch53514(2) and Sch53516(3), have been isolated and identified. In addition, 2 and 3 were also derivatized for the purposes of structure elucidation and biological evaluation.



1 R_1=H R_2=OH R_3=R_4=O
3 R_1=R_2=O R_3=OH R_4=H



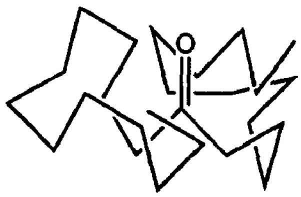
2

Tetrahedron Letters, **1994**, *35*, 1347

THE QUESTION OF REMOTE STERIC EFFECTS

F. M. Menger*and K. H. Nelson, Jr.
Department of Chemistry, Emory University, Atlanta, GA 30322 USA

The hypothesis that carbons on a long chain remote from a functional group can impede its reactivity has been tested with three systems designed to maximize the effect. No remote steric effects were observed in organic solvents.

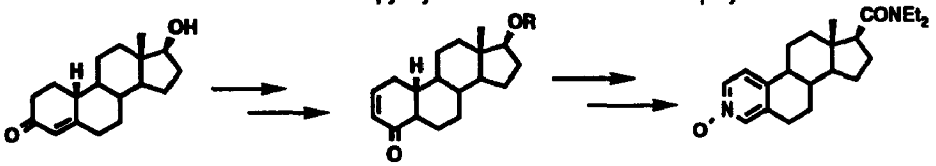


Tetrahedron Letters, **1994**, *35*, 1349

An Efficient Synthesis of 3-Pyridyl-N-Oxide Steroids: Inhibitors of 5 α-Reductase. Curt Haffner

Glaxo Inc. Research Institute, Five Moore Drive, Research Triangle Park,
North Carolina, 27709.

Nortestosterone was converted into a 3-pyridyl-N-oxide steroid via a 15 step synthesis.

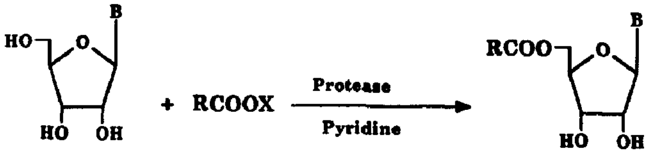


Tetrahedron Letters, **1994**, *35*, 1353

Manipulation of Enzyme Regioselectivity by Solvent Engineering: Enzymatic Synthesis of 5'-O-Acylribonucleosides

Haribansh K. Singh*[1], Gregory L. Cote[2], and Trina M. Hadfield[2]
[1]Department of Chemistry, Bradley University, Peoria, IL 61625. [2]Biopolymer Research Unit,
National Center for Agricultural Utilization Research, USDA-ARS, 1815 N. University St. Peoria, IL 61604, U.S.A.

Synthesis of 5'-O-acylribonucleosides by enzymatic regioselective esterification at the 5'-position of ribonucleosides.



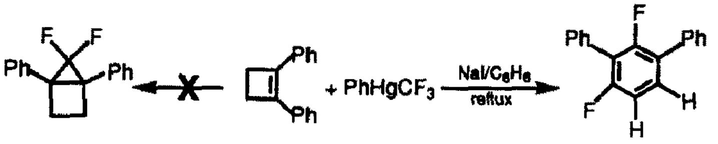
B = Pyrimidines and purines
RCO = Acyl group
X = CH_2CF_3 or $CH{=}CH_2$

Tetrahedron Letters, **1994**, *35*, 1357

ATTEMPTED PREPARATION OF 5,5-DIFLUORO-1,4-DIPHENYLBICYCLO[2.1.0]PENTANE – SERENDIPITOUS SYNTHESIS OF 1,3-DIFLUORO-2,4-DIPHENYLBENZENE.

Scott B. Lewis and Weston Thatcher Borden,* Department of Chemistry,
University of Washington, Seattle, WA 98195 USA

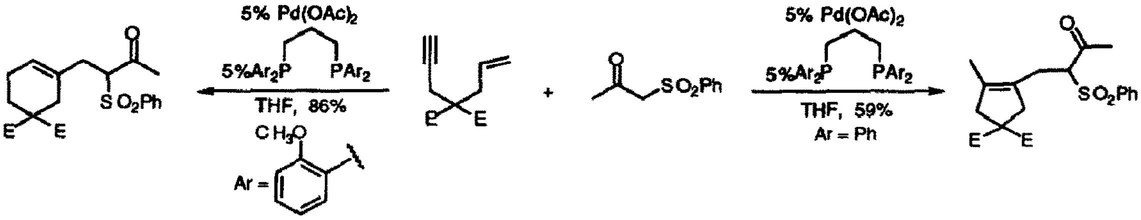
Addition of difluorocarbene to 1,2-diphenylcyclobutene, using $PhHgCF_3$, results in formation of 1,3-difluoro-2,4-diphenylbenzene. A mechanism for this reaction is proposed.



Tetrahedron Letters, **1994**, *35*, 1361

A Novel Cycloalkylation of 1,6- and 1,7-Enynes with Stabilized Pronucleophiles

Barry M. Trost, Lin Zhi and Katsuharu Imi
Department of Chemistry, Stanford University, Stanford, CA 94305-5080

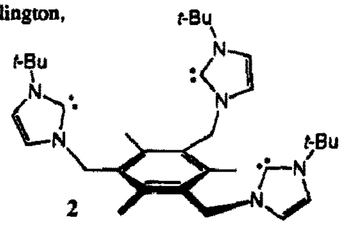


Tetrahedron Letters, **1994**, *35*, 1365

A STABLE TRIDENTATE CARBENE LIGAND

H. V. Rasika Dias* and Wiechang Jin
Department of Chemistry & Biochemistry, The University of Texas at Arlington,
Arlington, Texas 76019-0065, USA.

A novel tridentate carbene ligand, 2, was synthesized and characterized.



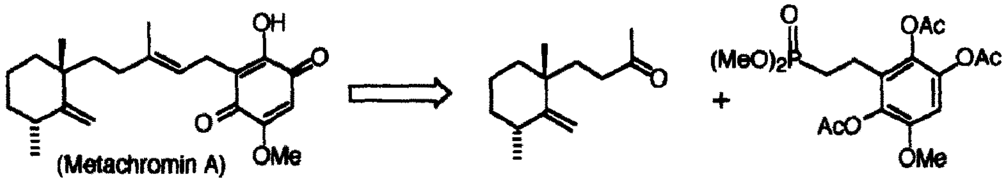
2

Tetrahedron Letters, **1994**, *35*, 1367

A Total Synthesis of the Sesquiterpene Quinone Metachromin-A

Wanda P. Almeida and Carlos Roque D. Correia.* Instituto de Química, Universidade Federal do Rio de Janeiro, RJ, 21945-970, Brasil and Instituto de Química, Universidade Estadual de Campinas, Campinas, SP, 13081-970, Brasil.

The first total synthesis of the sesquiterpene quinone metachromin A was accomplished employing the strategy depicted.

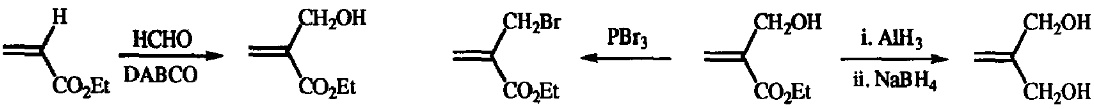


Tetrahedron Letters, **1994**, *35*, 1371

IMPROVED SYNTHESES OF ETHYL α-(BROMOMETHYL)ACRYLATE AND 2-METHYLENE-1,3-PROPANEDIOL VIA ETHYL α-(HYDROXY-METHYL)ACRYLATE.

Hoe-Sup Byun, Kasireddy Chandraprakash Reddy, and Robert Bittman,* Department of Chemistry & Biochemistry, Queens College of The City University of New York, Flushing, New York 11367-1597 USA

Ethyl α-(bromomethyl)acrylate (1) and 2-methylene-1,3-propanediol (2) have been prepared via formaldehyde addition to ethyl acrylate in the presence of DABCO, giving α,β-unsaturated ester 3. Reduction of hydroxy ester 3 with one equivalent of alane, then borohydride reduction of the resulting aldehyde 4 gives 2.

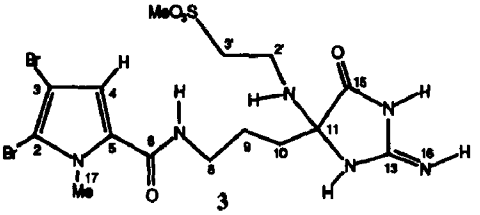


Tetrahedron Letters, **1994**, *35*, 1375

Mauritamide A and Accompanying Oroidin Alkaloids from the Sponge *Agelas mauritiana*.

Carlos Jiménez and Phillip Crews*
Dept. of Chemistry and Biochemistry and Inst. for Marine Sciences, Univ. of Calif., Santa Cruz, CA 95064

The alkaloid consitutents of a Fijian sponge, *Agelas mauritiana*, are described and consist of a new taurine containing compound, mauritamide A (3), accompanied by known oroidin alkaloids dibromophakellin (1) and midpacamide (2).



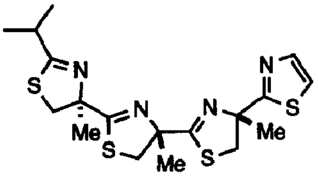
3

Tetrahedron Letters, **1994**, *35*, 1379

Revision of the Stereostructure of Mirabazole C.

Rodney L. Parsons, Jr. and Clayton H. Heathcock*, Department of Chemistry, University of California, Berkeley, CA 94720

The stereostructure of mirabazole C is revised to **11** on the basis of total synthesis.



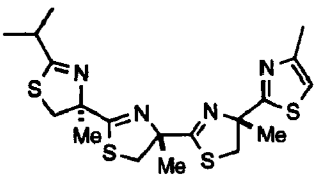
11

Tetrahedron Letters, **1994**, *35*, 1383

The Total Synthesis of Mirabazole B.

Rodney L. Parsons, Jr. and Clayton H. Heathcock*, Department of Chemistry, University of California, Berkeley, CA 94720

The total synthesis of mirabazole B **3** is reported.



3

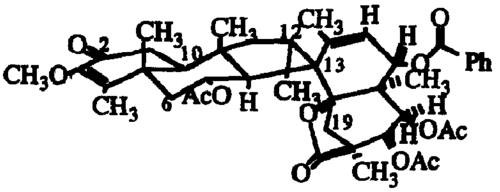
Tetrahedron Letters, **1994**, *35*, 1385

SPIROCARACOLITONE ISOLATED FROM A NEW GENUS SPECIES *RUPTILIOCARPON CARACOLITO*. THE FIRST CD SPIRO-TRITERPENOID.

Shawna L. MacKinnon*, Tony Durst*, John T. Arnason*, Corine Bensimon*, P.E. Sanchez-Vindas#, L. San Roman#, L. J. Poveda#, C. Hasbun#.

*Ottawa-Carleton Biology and Chemistry Institutes, Department of Chemistry, University of Ottawa, Canada K1N 6N5.

Universidad Nacional, Heredia, Costa Rica Apdo 86-3000

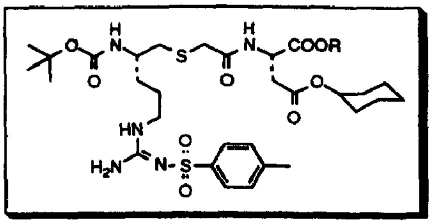


Tetrahedron Letters, **1994**, *35*, 1389

Arg-Gly Thiomethylene Dipeptide Surrogates: Synthesis and Incorporation into Arg-Gly-Asp Pseudotripeptides

Nancy K. Ham, Stephan J. Cripps, and Gilbert M. Rishton*
Tanabe Research Laboratories, 4540 Towne Centre Ct., San Diego, CA 92121.

Syntheses of thiomethylene containing Arg-Gly dipeptide surrogates and Arg-Gly-Asp type pseudotripeptides are described.

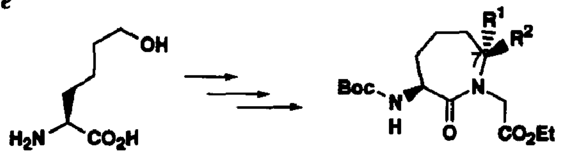


Tetrahedron Letters, **1994**, *35*, 1393

A Synthetic Route for the Generation of C-7 Substituted Azepinones

Jeffrey A. Robl and Maria P. Cimarusti*
Bristol-Myers Squibb Pharmaceutical Research Institute
P. O. Box 4000, Princeton, N. J. 08543-4000

A convenient method for the generation of 3-amino C-7 substituted azepinones 9 from L-ε-hydroxynorleucine is presented.

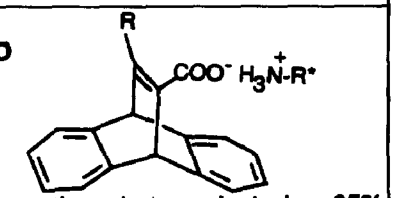


9

Tetrahedron Letters, **1994**, *35*, 1397

IONIC CHIRAL HANDLE-INDUCED SOLID STATE ASYMMETRIC SYNTHESIS: ORIGIN OF THE ASYMMETRIC INDUCTION ELUCIDATED THROUGH ABSOLUTE CONFIGURATION CORRELATION STUDIES

Anna D. Gudmundsdottir, John R. Scheffer* and James Trotter
Department of Chemistry, University of British Columbia
2036 Main Mall, Vancouver, Canada V6T 1Z1

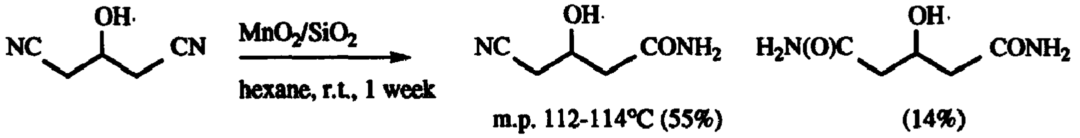


Irradiation of crystalline salts of the type shown above leads to optically active photoproducts in >95% enantiomeric excess, a process in which the optically active ammonium ion has acted as an "ionic chiral handle." By correlating the absolute configurations of reactant and photoproduct, the factors responsible for the high enantioselectivity are identified.

A Mild Hydration of Nitriles into Amides

Tetrahedron Letters, **1994**, *35*, 1401

P. Breuilles, R. Leclerc, and D. Uguen*
Laboratoire de Synthèse Organique, Ecole Européenne des Hautes Etudes des Industries Chimiques
1 rue Blaise Pascal, 67008 Strasbourg (France)

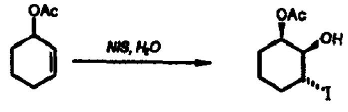


Tetrahedron Letters, **1994**, *35*, 1405

Diastereospecific Hydroxyiodination of 1-Acetoxycyclohex-2-ene via Intramolecular Delivery of Oxygen

Johannes Bange, Alan F. Haughan and J.B. Sweeney*
School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, U.K.

The reaction of acetoxycyclohex-2-ene with NIS is diastereospecific, in contrast to the reaction of NPSP with the same substrate.

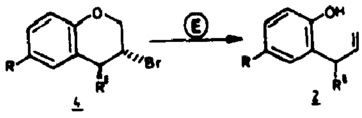


Tetrahedron Letters, **1994**, *35*, 1409

NOVEL ELECTROCHEMICAL ROUTE TO 2(α-ALKOXYALLYL)-PHENOLS-CATHODIC ELIMINATIVE RING OPENING REACTION.

N.Bhuvaneswari, C.S.Venkatachalam* and K.K.Balasubramanian*
Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

Electrochemical reduction of 4-alkoxy-3-bromochromans in acetonitrile afforded the respective 2(α-alkoxyallyl)phenols in good yield.



R : H,Cl,Me

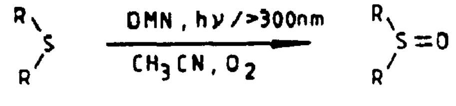
R': OMe, OEt

Tetrahedron Letters, **1994**, *35*, 1413

NOVEL PHOTOOXIDATION OF ORGANIC SULPHIDES TO SULPHOXIDES SENSITIZED BY 1,4-DIMETHOXYNAPHTHALENE

Uday T. Bhalerao* and Madabhushi Sridhar
Organic Division II, Indian Institute of Chemical Technology, Hyderabad-500 007, INDIA.

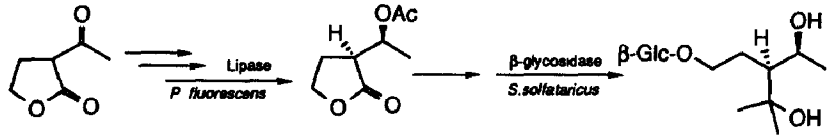
Efficient and controlled photooxidation of organic sulphides to sulphoxides has been achieved under 1,4-dimethoxynaphthalene(DMN) sensitization.



Tetrahedron Letters, **1994**, *35*, 1415

CHEMOENZYMATIC SYNTHESIS AND STEREOCHEMISTRY OF ALEPPOTRIOLOSIDE, A NATURALLY OCCURRING GLUCOSIDE.

Antonio Trincone[a]*, Edoardo Pagnotta[a] and Guido Sodano[b]
[a]Istituto per la Chimica di Molecole di Interesse Biologico CNR Via Toiano 6, 80072 Arco Felice (Naples) Italy
[b]Dipartimento di Fisica Università di Salerno, 84081, Baronissi Salerno

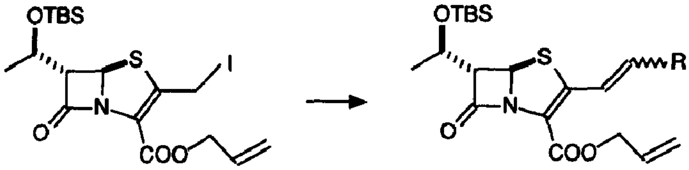


Tetrahedron Letters, **1994**, *35*, 1417

2-(IODOMETHYL) PENEMS AS USEFUL SUBSTRATES IN THE WITTIG OLEFINATION: SYNTHESIS OF 2-ARYLETHENYL PENEMS

Maria Altamura and Enzo Perrotta*
"A. Menarini" Industrie Farmaceutiche Riunite S.r.l., Via dei Sette Santi 3, I-50131 Firenze (Italy)

Wittig olefination on the new (2-iodomethyl) penems gave (2-arylethenyl) penems, with different E/Z selectivity depending on the aldehyde substituent position and electronic effect.

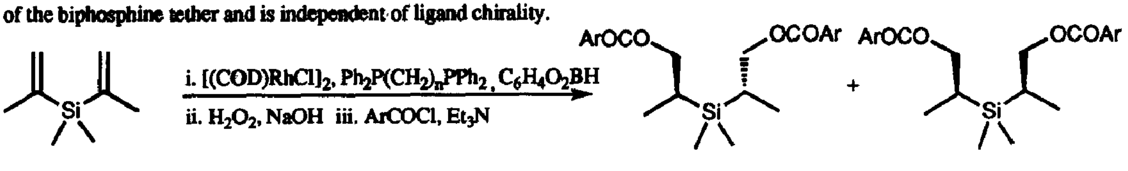


Tetrahedron Letters, **1994**, *35*, 1421

LIGAND CONTROLLED DIASTEREOSELECTIVITY IN THE RHODIUM CATALYSED HYDROBORATION OF DIVINYLSILANES

Jennifer L. Matthews and Patrick G. Steel*
Department of Chemistry, Science Laboratories, South Road, Durham DH1 3LE

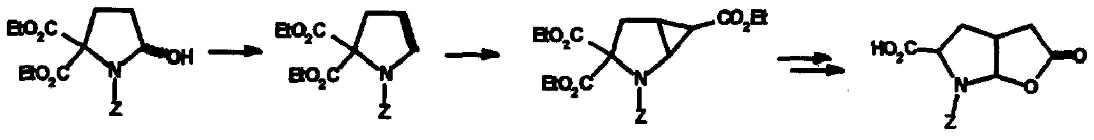
The diastereoselectivity of the rhodium catalysed double hydroboration of di(2-propenyl)dimethylsilane depends upon the length of the biphosphine tether and is independent of ligand chirality.



Tetrahedron Letters, **1994**, *35*, 1425

Synthesis of 1-Azabicyclo[3.1.0]hexane Tricarboxylate and its Transformation into a New Proline-γ-acetic Acid Equivalent

Loredana Arenare,[a] Paolo De Caprariis,[a] Maura Marinozzi,[b] Benedetto Natalini,[b] Roberto Pellicciari *[b]
[a] Dipartimento di Chimica Farmaceutica e Tossicologica, Università di Napoli, [b] Istituto di Chimica Farmaceutica e Tecnica Farmaceutica, Università di Perugia, Italy.

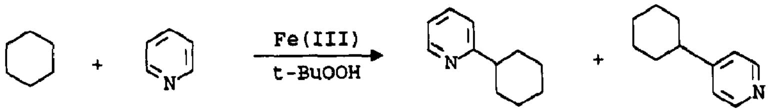


Tetrahedron Letters, **1994**, *35*, 1427

MECHANISM OF THE GIF-BARTON TYPE ALKANE FUNCTIONALIZATION BY HALIDE AND PSEUDOHALIDE IONS.

Francesco Minisci* and Francesca Fontana
Dipartimento di Chimica del Politecnico; via Mancinelli,7; I-20131 Milano, Italy.

Free-radical mechanism of the reaction



Tetrahedron Letters, **1994**, *35*, 1431

Comments on An Article by Francesco Minisci and Francesca Fontana.

Derek H. R. Barton* and David R. Hill
Department of Chemistry, Texas A&M University, College Station, TX 77843-3255, USA.

$$R_2CH_2 \xrightarrow{{}^{V}Fe{=}O} R_2HC{-}Fe^{V}L_n \longrightarrow R_2HC{-}X$$

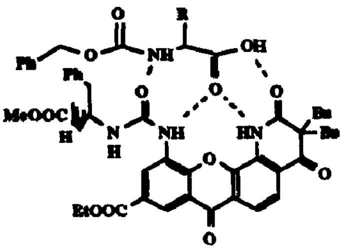
Evidence is summarized to show that the latest aspects of Gif chemistry do not involve Fenton-type radical chemistry.

Tetrahedron Letters, **1994**, *35*, 1435

CHIRAL RECEPTOR FOR N-BENZYLOXYCARBONYL AMINOACID DERIVATIVES

Mercedes Crego, Anselmo Partearroyo, César Raposo, M. Luisa Mussons,
J. Luis Lopez, Victoria Alcázar and Joaquín R. Morán*
Departamento de Química Orgánica, Universidad de Salamanca,
37008 Salamanca , Spain.

Cleft type receptors for N-benzyloxycarbonyl aminoacids have been prepared. The association constants have been measured in chloroform and have been corrected due to the presence of a receptor dimer, leading to only a modest chiral recognition.

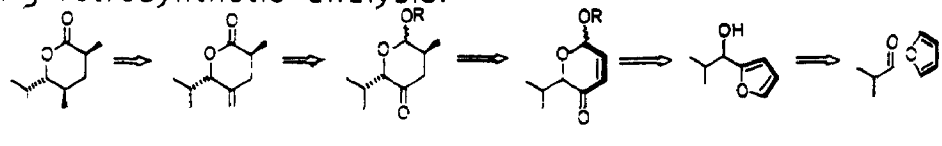


Tetrahedron Letters, **1994**, *35*, 1439

SYNTHESIS OF SEX PHEROMONE 3,5-*cis*-DIMETHYL-6-*trans*-*iso*PROPYL-3,4,5,6-TETRAHYDROPYRAN-2-ONE

Satya V.N.Raju and Bipin Pandey*
National Chemical Laboratory, Pune-411 008, INDIA.

An efficient synthesis of the title compound is described as per following retrosynthetic analysis:

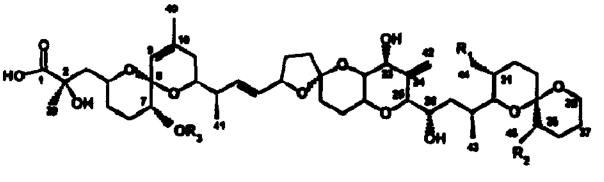


Tetrahedron Letters, **1994**, *35*, 1441

STUDIES ON THE BIOSYNTHESIS OF THE POLYETHER MARINE TOXIN DINOPHYSISTOXIN-1 (DTX-1)

Manuel Norte, Agustín Padilla and José J. Fernández.
Institute of Bioorganic Chemistry, University of La Laguna. 38206 La Laguna, Tenerife, Spain.

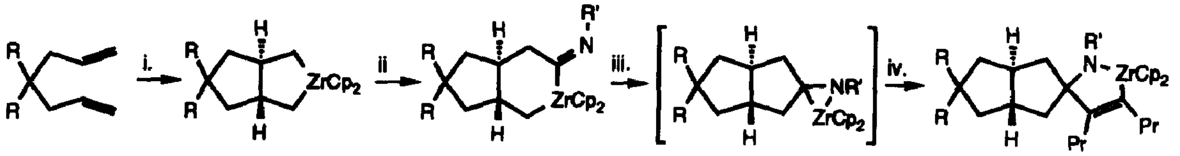
Abstracts: The biosynthetic origin of the marine toxin DTX-1 is establish on the basis of the NMR spectral data of samples obtained by addition of labelled [1-$^{13}C_1$], [2-$^{13}C_1$] and [1,2-$^{13}C_2$] sodium acetate to artificial cultures of the dinoflagellate *Prorocentrum lima*.



Tetrahedron Letters, **1994**, *35*, 1445

Synthesis of Cyclopentylamines using Zirconium Chemistry

Jeremy M. Davis, Richard J. Whitby*, Department of Chemistry, The University, Southampton, SO9 5NH, U.K.
Albert Jaxa-Chamiec, Medicinal Chemistry II, Glaxo Group Research, Greenford Road, Middlesex, UB6 OHE, U.K.



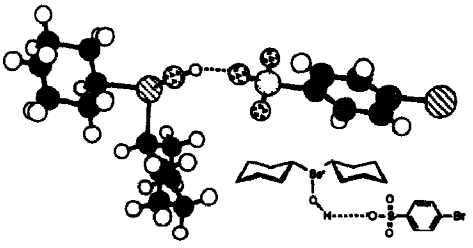
i. Cp_2ZrBu_2, THF, r.t., 1h; ii.R'NC, R' = Bu, c-C_6H_{11}, $SiMe_3$; iii. 67°C, 16h; iv. PrC≡CPr.

Tetrahedron Letters, **1994**, *35*, 1449

SELENOXIDE-SULFONIC ACIC ADDUCTS; A NEW CLASS OF STABLE, SELENOXIDE-BASED OXIDANTS

D. John Procter and Christopher M. Rayner*
School of Chemistry, University of Leeds, Leeds LS2 9JT, U.K.

Abstract: The preparation and characterisation of a novel class of adducts of selenoxides with sulfonic acids are described. They are considerably more stable, and show superior reactivity to the parent selenoxides. Their structure has been confirmed by ^1H NMR spectroscopy and X-ray crystallography.



Tetrahedron Letters, **1994**, *35*, 1453

A STRAIGHTFORWARD AND PRACTICAL FORMAL SYNTHESIS OF LAVENDAMYCIN ETHYL ESTER.

Pedro Molina*, Fernando Murcia, Pilar M. Fresneda
Departamento de Química Orgánica, Universidad de Murcia
Campus de Espinardo, 30071, Murcia, Spain

An iminophosphorane-mediated β-carboline formation is the key step in a practical new synthesis of lavendamycin ethyl ester.