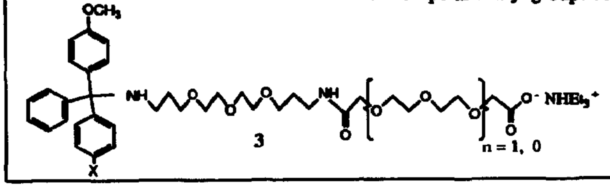
GRAPHICAL ABSTRACTS

Tetrahedron Letters, **1994**, *35*, 6777

The Preparation And Synthetic Application Of Heterobifunctional Biocompatible Spacer Arms

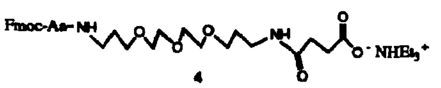
Ronald M. Cook, J. Howard Adams and Derek Hudson* *Biosearch Technologies, 40 Mark Drive, San Rafael, CA 94903*

Simple spacer arm molecules such as 3 (X = OCH_3, or H) and 4 which provide improved biomolecule synthesis and display are described. Initial functionalization with non-polar triaryl groups confers organic solvent solubility and facilitates isolation.



3

Aa = Nle, Lys(Fmoc), Lys(Boc), Lys(Aloc)



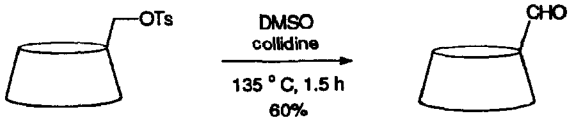
4

Tetrahedron Letters, **1994**, *35*, 6781

FACILE PREPARATION OF THE β-CYCLODEXTRINYL ALDEHYDE

Kristy A. Martin and Anthony W. Czarnik,* Department of Chemistry,
The Ohio State University, Columbus, Ohio 43210

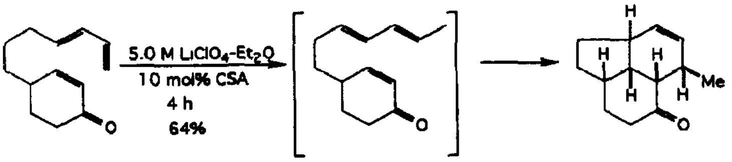
This paper describes the synthesis and characterization of the 1° - side β-Cyclodextrinyl Monoaldehyde in two steps from β-cyclodextrin.



Tetrahedron Letters, **1994**, *35*, 6783

ACID CATALYZED INTRAMOLECULAR DIELS-ALDER REACTIONS IN LITHIUM PERCHLORATE-DIETHYL ETHER: ACID PROMOTED MIGRATION OF TERMINAL DIENES PRIOR TO [4+2] CYCLOADDITION IN CONFORMATIONALLY RESTRICTED SUBSTRATES

P. A. Grieco,* J. P. Beck, S. T. Handy, N. Saito and J. F. Daeuble, Dept. of Chemistry, Indiana University, Bloomington, IN 47405

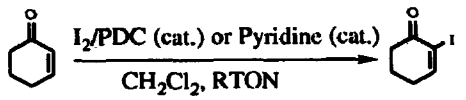


Tetrahedron Letters, **1994**, *35*, 6787

CONCERNING THE FORMATIONS OF α-IODOENONES

Pakorn Bovonsombat, Geetha J. Angara and Edward Mc Nelis *
Department of Chemistry, New York University, New York, New York 10003

The formations of α-iodoenones from secondary alkynols with NIS/HTIB (cat.), tertiary alkynols with I_2/PDC and enones with I_2/pyridine have been compared. In the latter two reactions the PDC and the pyridine have been found to be catalytic.

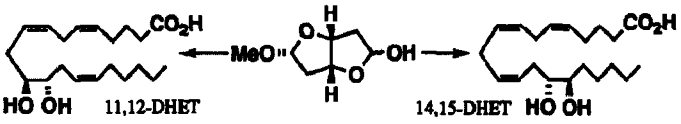


Tetrahedron Letters, **1994**, *35*, 6791

vic-DIOL CHIRONS: ENANTIOSPECIFIC SYNTHESIS OF 11,12- AND 14,15-DIHYDROXYEICOSATRIENOIC ACIDS

K. Chauhan[1], S. Aravind[1], S.-G. Lee[1], J.R. Falck*[1], J. H. Capdevila[2]
[1]Departments of Molecular Genetics and Pharmacology, Univ. of Texas Southwestern Medical Center, Dallas, TX 75235
[2]Departments of Medicine and Biochemistry, Vanderbilt Univ. Med. School, Nashville, TN 37205

A differentiated *vicinal*-diol chiron, from D-glucurono-6,3-lactone, was exploited for the asymmetric synthesis of the *erythro/threo*-isomers of the title eicosanoids.

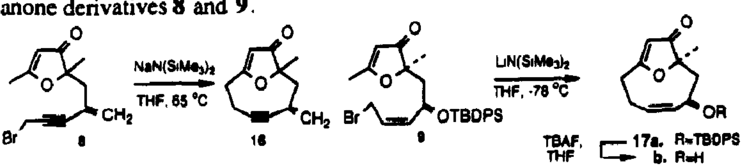


Tetrahedron Letters, **1994**, *35*, 6795

THE SYNTHESIS OF 11-OXABICYCLO[6.2.1]UNDECENONE DERIVATIVES.

Drury Caine* and Mark E. Arant,
Department of Chemistry, University of Alabama, Tuscaloosa, AL 35487, USA

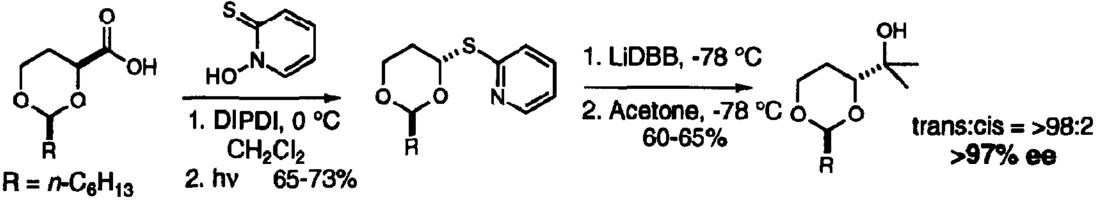
Oxabicycloundecenone derivatives 16 and 17 were prepared by base-promoted cycloalkylations of the monocyclic 3(2H)-furanone derivatives 8 and 9.



Tetrahedron Letters, **1994**, *35*, 6799

Reductive Lithiation of Alkyl 2-Thiopyridyl Ethers to Generate Optically Pure α-Alkoxylithium Reagents

Scott D. Rychnovsky,* Kevin Plzak, and Dacia Pickering
Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

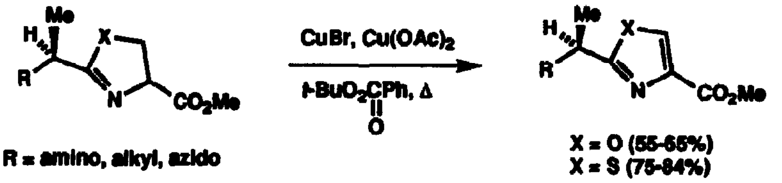


Tetrahedron Letters, **1994**, *35*, 6803

Further Studies on Oxazoline and Thiazoline Oxidations. A Reliable Route to Chiral Oxazoles and Thiazoles

Francis Tavares and A. I. Meyers*
Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523 USA

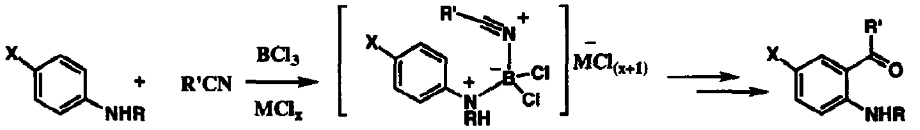
Radical oxidation leads to reproducible yields of oxazoles without affecting stereocenter.



Tetrahedron Letters, **1994**, *35*, 6807

In Situ NMR Spectroscopic Studies of Aniline *ortho* Acylation ("Sugasawa Reaction"): The Nature of Reaction Intermediates and Lewis Acid Influence on Yield.

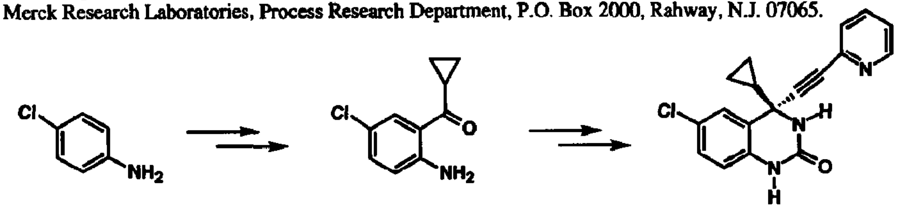
A.W. Douglas, N.L. Abramson, I.N. Houpis, S. Karady, A. Molina, L.C. Xavier, N. Yasuda.
Merck Research Laboratories, Process Research Department, P.O. Box 2000, Rahway, N.J. 07065.



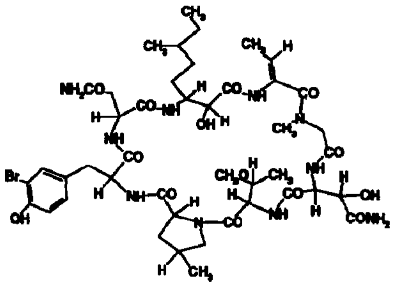
Tetrahedron Letters, **1994**, *35*, 6811

Synthesis of a New Generation Reverse Transcriptase Inhibitor via the $BCl_3/GaCl_3$-induced Condensation of Anilines with Nitriles (Sugasawa Reaction).

I. N. Houpis, A. Molina, A. W. Douglas, L. Xavier, J. E. Lynch, R.P. Volante and P. J. Reider
Merck Research Laboratories, Process Research Department, P.O. Box 2000, Rahway, N.J. 07065.



Tetrahedron Letters, **1994**, *35*, 6815



ISOLATION AND STRUCTURE ELUCIDATION OF PERTHAMIDE B, A NOVEL PEPTIDE FROM THE SPONGE *THEONELLA* SP.

Nanda K. Gulavita,* Shirley A. Pomponi, and Amy E. Wright, Division of Biomedical Marine Research, Harbor Branch Oceanographic Institution, Inc., 5600 US1 North, Ft. Pierce, Florida 34946
Donna Yarwood and Matthew A. Sills*, Ciba-Geigy Corporation, Research Department, 556 Morris Ave., Summit, NJ 07901

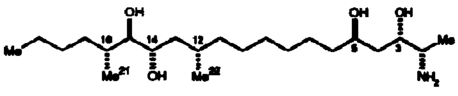
A cyclic octapeptide perthamide B, which weakly inhibited the binding of $[^{125}I]$IL-1β to intact EL4.6.1 cells with an IC_{50} of 27.6 µM, was isolated from a *Theonella* sp.

Tetrahedron Letters, **1994**, *35*, 6819

Relative and Absolute Stereochemistry of the Fumonisin B_2 Backbone

Jean-Christophe Harmange, Craig D. Boyle, and Yoshito Kishi*
Department of Chemistry, Harvard University,
Cambridge, Massachusetts 02138, U.S.A.

The relative and absolute stereochemistry of the backbone of fumonisin B_2 is established to be **7a**.



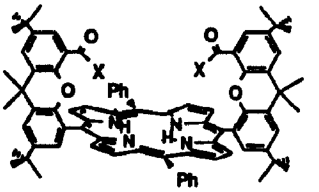
7a

New Synthetic Receptors Derived from Porphyrins.

Tetrahedron Letters, **1994**, *35*, 6823

Gerald Shipps, Jr. and Julius Rebek, Jr.*
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

Convergent functional groups attached to a porphyrin spacer are used to bind several guests.

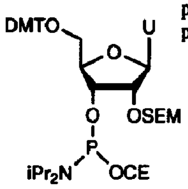


2'-(Trimethylsilyl)ethoxymethyl Protection of the 2'-Hydroxyl Group in Oligoribonucleotide Synthesis.

Tetrahedron Letters, **1994**, *35*, 6827

Francine E. Wincott and Nassim Usman,
Department of Chemistry & Biochemistry, Ribozyme Pharmaceuticals Inc., 2950 Wilderness Place, Boulder, CO 80301

2'-*O*-((Trimethylsilyl)ethoxymethyl)-5'-*O*-dimethoxytrityl uridine 3'-(2-cyanoethyl-*N*,*N*-diisopropyl phosphoramidite), synthesized from dimethoxytrityl uridine in two steps, was incorporated into a polymer. Removal of the SEM group was effected with $BF_3 \bullet OEt_2$ in 30 min.



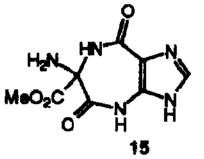
$$\longrightarrow (U^{SEM}p)_9U^{SEM} \xrightarrow{BF_3\bullet OEt_2} (Up)_9U$$

NOVEL INHIBITORS OF GUANASE

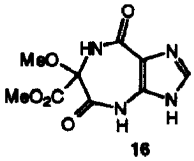
Tetrahedron Letters, **1994**, *35*, 6831

Anila Bhan and Ramachandra S. Hosmane*
Department of Chemistry and Biochemistry, University of Maryland Baltimore County, Baltimore, Maryland 21228

*Synthesis and guanase inhibitory activity of two novel 5:7-fused heterocycles, **15** and **16**, have been reported.*



15



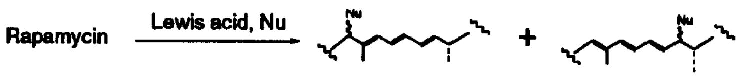
16

ACID CATALYZED FUNCTIONALIZATION OF RAPAMYCIN.

Tetrahedron Letters, **1994**, *35*, 6835

Alexander A. Grinfeld, Craig E. Caufield,* Robert A. Schiksnis, James F. Mattes and Kelvin W. Chan, Department of Chemical Sciences, Wyeth-Ayerst Research, Inc., CN 8000, Princeton, NJ 08543-8000 USA

Rapamycin rapidly undergoes demethoxylation at C-7 in the presence of Lewis acids ($BF_3 \cdot Et_2O$, $SnCl_4$) to give a highly stabilized carbocation. This intermediate is trapped by nucleophiles to give functionalized trienes or in the absence of nucleophiles, eliminates to form isomeric tetraenes

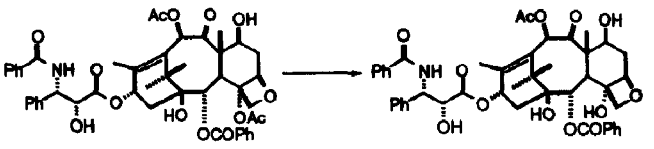


Tetrahedron Letters, **1994**, *35*, 6839

SYNTHESIS AND BIOLOGICAL EVALUATION OF 4-DEACETYLPACLITAXEL

Kurt A. Neidigh, Milind M. Gharpure, John M. Rimoldi and David G. I. Kingston,* Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061-0212
Yuan Qing Jiang and Ernest Hamel,* Laboratory of Molecular Pharmacology, Developmental Therapeutics Program, Division of Cancer Treatment, National Cancer Institute, National Institutes of Health, Bethesda, Maryland 20892

4-Deacetylpaclitaxel prepared from baccatin III via two synthetic approaches and from paclitaxel via one synthetic approach, has minimal effects on tubulin polymerization and is not cytotoxic to human CA46 Burkitt lymphoma cells.

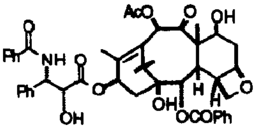


Tetrahedron Letters, **1994**, *35*, 6843

SYNTHESIS AND BIOLOGICAL EVALUATION OF 4-DEACETOXYPACLITAXEL.

Mahendra D. Chordia, Ashok G. Chaudhary and David G.I. Kingston,* Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0212,
Yuan Qing Jiang and Ernest Hamel* Laboratory of Molecular Pharmacology, Developmental Therapeutics Program, Division of Cancer Treatment, National Cancer Institute, NIH, Bethesda, MD 20892

4-Deacetoxypaclitaxel has been prepared in seven steps from paclitaxel It is significantly less active than paclitaxel in tubulin-assembly and cytotoxicity bioassays.

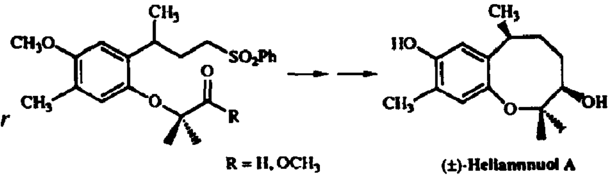


Tetrahedron Letters, **1994**, *35*, 6847

Total Synthesis of (±)-Heliannuol A

Erich L. Grimm*, Sylvain Levac and Laird A. Trimble
Merck Frosst Centre for Therapeutic Research,
P.O. Box 1005, Pointe Claire-Dorval, Quebec
H9R 4P8 Canada

(±)-Heliannuol A was synthesized via *intramolecular* Julia coupling and *intramolecular* sulfone ester cyclization.

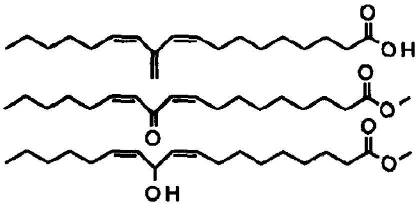


Tetrahedron Letters, **1994**, *35*, 6851

PREPARATION OF 11-SUBSTITUTED LINOLEIC ACIDS

Alexander V Muehldorf, Syntex Discovery Research
Mailstop R6-201, 3401 Hillview Ave., Palo Alto CA 94304

A concise, stereospecific synthesis of 11-substituted linoleic acids, potentially useful as 15-lipoxygenase inhibitors, is presented.



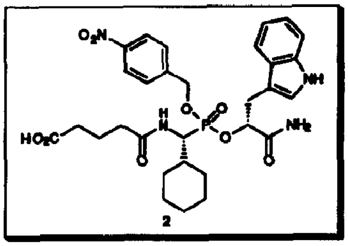
Tetrahedron Letters, 1994, 35, 6853

PEPTIDE BOND FORMATION VIA CATALYTIC ANTIBODIES: SYNTHESIS OF A NOVEL PHOSPHONATE DIESTER HAPTEN

Amos B. Smith, III,* Carol M. Taylor, Stephen J. Benkovic,* and Ralph Hirschmann*

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104 and Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania 16802

Phosphonate diester 2, a hapten recently employed to induce the first monoclonal catalytic antibodies capable of catalyzing peptide bond formation, was synthesized via elaboration of a scalemic α-amino phosphonate.



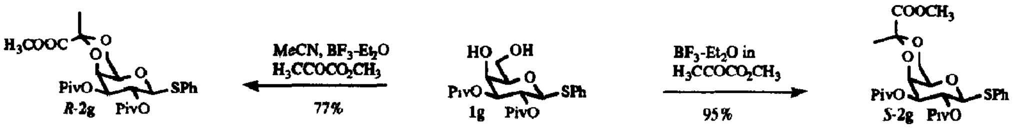
2

Tetrahedron Letters, 1994, 35, 6857

RHIZOBIAL SACCHARIDES 2. SELECTIVE SYNTHESIS OF BOTH DIASTEREOMERS OF 4,6-*O*-PYRUVYLATED D-GLYCOPYRANOSIDES

Thomas Ziegler, Institut für Organische Chemie und Isotopenforschung, Univ. Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

Condensation of 2,3-di-*O*-acyl-D-glycopyranosides 1 with methyl pyruvate and BF_3-diethylether complex gives exclusively the corresponding pyruvylated glycosides 2 having an *axial*- and *equatorial*-oriented carboxylate group, respectively, depending on the solvent.



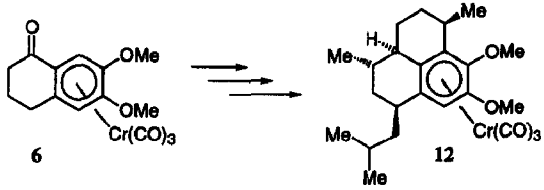
Tetrahedron Letters, 1994, 35, 6861

CHIRAL η^6-ARENE-Cr(CO)$_3$ COMPLEXES AS SYNTHETIC BUILDING BLOCKS: AN ENANTIO- AND DIASTEREOSELECTIVE APPROACH TO SUBSTITUTED HYDROPHENALENES RELATED TO HELIOPORIN E AND PSEUDOPTEROSIN G

Hans-Günther Schmalz*, Andrea Schwarz, and Gerd Dürner

Institut für Organische Chemie der Technischen Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany

The chiral building block 6 (> 97 % e.e.) is diastereoselectively converted in 12 steps and 10 % overall yield into the complex 12.



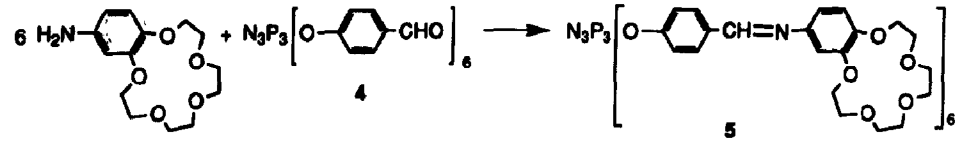
Tetrahedron Letters, 1994, 35, 6865

Facile Syntheses of Phosphorus Containing Multisite Receptors

Joëlle Mitjaville, Anne-Marie Caminade and Jean-Pierre Majoral*

Laboratoire de Chimie de Coordination du CNRS, 205 Route de Narbonne, 31077 Toulouse Cédex, FRANCE

Reaction of 4-aminobenzo-15-crown-5 with hexa(phenoxy-4-carboxaldehyde)cyclotriphosphazène 4 leads to the hexa crown ether 5

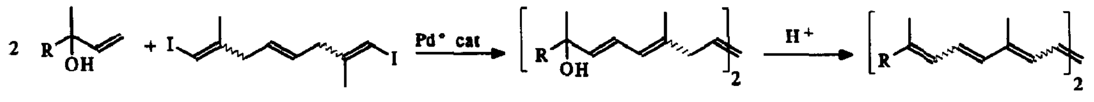


Tetrahedron Letters, **1994**, *35*, 6867

A CONVERGENT SYNTHESIS OF SYMMETRICAL CAROTENOIDS USING THE HECK REACTION.

Hugues Bienayme, Rhône-Poulenc, CRIT-C, BP 62, 69192 Saint-Fons Cedex, France.

Heck-type vinylation of allylic alcohols has proved to be an extremely effective method for the rapid construction of symmetrical carotenoids.

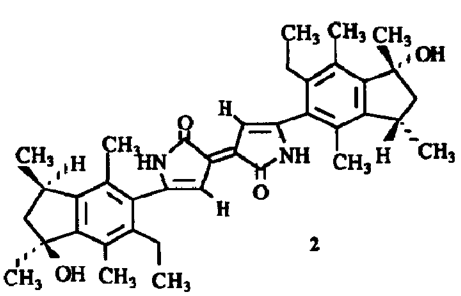


Tetrahedron Letters, **1994**, *35*, 6869

TRIKENDIOL, AN UNUSUAL RED PIGMENT FROM THE SPONGE *TRIKENTRION LOEVE*, ANTI-HIV-1 METABOLITE

Ali Loukaci and Michèle Guyot.
Laboratoire de Chimie, associé au C.N.R.S., M. N. H. N.,
63 rue Buffon, 75005 Paris, France.

Trikendiol **2**, an unusual red pigment has been isolated from the sponge*Trikentrion loeve*. The structure was determined from interpretation of spectral data. Trikendiol was shown to be anti-HIV-I



Tetrahedron Letters, **1994**, *35*, 6873

PHENYLTHIOACETYLENE AS A SOURCE OF STEREODEFINED TRISUBSTITUTED ALKENES.

Isabelle Creton, Ilane Marek* , Denis Brasseur, Jean-Luc Jestin, Jean-F. Normant*
Laboratoire de Chimie des Organoéléments, associé au C.N.R.S., Université P. et M. Curie, 4 Place Jussieu, F-75231 Paris Cedex 05, France

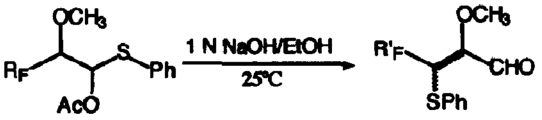
A 1,2-metal-ate rearrangement leads to stereodefined trisubstituted alkenes, via stereoselective creation of three C-C bonds as single isomers in a easy and straightforward one-pot procedure from a common starting material

Tetrahedron Letters, **1994**, *35*, 6877

SYNTHESIS OF 3-*F*-ALKYL-2-METHOXY-3-PHENYLTHIOPROPENALS

Ahmed Hedhli,[a] Ahmed Baklouti*[a] and Aimé Cambon[b]
[a]Laboratoire de Chimie Organique Structurale, Faculté des Sciences de Tunis, Département de Chimie, Campus Universitaire, 1060 Tunis, Tunisia
[b]Laboratoire de Chimie Organique du Fluor, UFR Sciences, Université de Nice- Sophia Antipolis, Parc Valrose, BP 71, F-06108 Nice cedex2, France

Contrary to the non-fluorinated analogous, the *F*-alkylated sulfides are hydrolysed into α,β-unsaturated aldehydes in satisfactory yield.



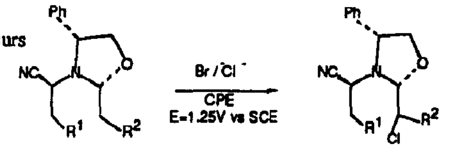
R_F: C_4F_9, C_6F_{13}, C_8F_{17} R'_F: C_3F_7, C_5F_{11}, C_7F_{15}

Tetrahedron Letters, **1994**, *35*, 6879

ANODIC OXIDATION OF THE N-CYANOMETHYL-OXAZOLIDINE SYSTEM: REGIOSELECTIVE CHLORINATION α TO THE N,O-ACETAL FUNCTION.

Thierry Martens[a], Florence Souquet[a] and Jacques Royer[b] a) Laboratoire de Chimie Analytique et d'Électrochimie, URA 1310 du CNRS, Université René Descartes, Faculté de Pharmacie, 75782 Paris cedex 06 b) Institut de Chimie des Substances Naturelles, CNRS, 91198 Gif-sur-Yvette cedex. France

Anodic oxidation of the N-cyanomethyl-oxazolidine system regioselectively occurs α to the N,O-acetal fonction to give mono or bis-chlorinated derivatives

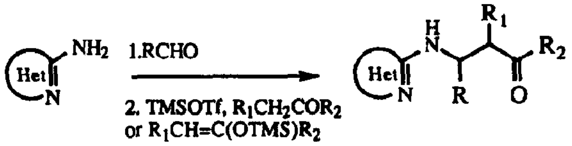


Tetrahedron Letters, **1994**, *35*, 6883

TMSO-TRIFLATE-ASSISTED ADDITION OF ENOLS TO HETERO-AROMATIC IMINES OR HYDROXYAMINAL INTERMEDIATES.

J. L. MOUTOU, M. SCHMITT, C. G. WERMUTH and J. J. BOURGUIGNON,
Laboratoire de Pharmacochimie Moléculaire, associé au CNRS, Centre de Neurochimie du CNRS, 5, Rue Blaise Pascal
67084 STRASBOURG-Cedex (France)

TMSO-Triflate-promoted reaction of heteroaromatic imines or hydroxyaminal intermediates with various enolisable ketones are reported.

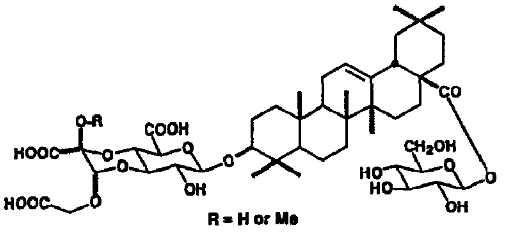


Tetrahedron Letters, **1994**, *35*, 6887

Achyranthosides A and B, Novel Cytotoxic Saponins from *Achyranthes fauriei* Root

Yoshiteru IDA,* Masumi KATSUMATA (nee OHTSUKA), Yohko SATOH, Mariko KATOH, Miki NAGASAO, Kentaro YAMAGUCHI, Hideo KAMEI and Junzo SHOJI.

School of Pharmaceutical Sciences, Showa University, Hatanodai, Shinagawa-ku, Tokyo 142, Japan

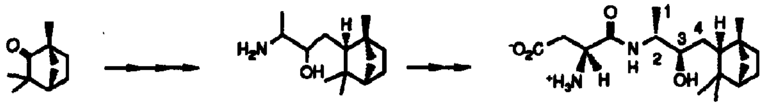


Tetrahedron Letters, **1994**, *35*, 6891

THE SWEETNESS AND STEREOCHEMISTRY OF L-ASPARTYL-FENCHYLAMINOALCOHOL DERIVATIVES.

Yoshifumi Yuasa,* Akira Nagakura, and Haruki Tsuruta, Central Research Laboratory, Takasago International Corporation, 1-4-11 Nishiyawata, Hiratsuka City, Kanagawa 254, Japan

Four L-aspartyl-fenchylaminoalcohols were derived from (+)-fenchone. Only L-aspartylaminoalcohol, having the (2*R*, 3*R*) of abosolute configuration, showed potent sweetness.

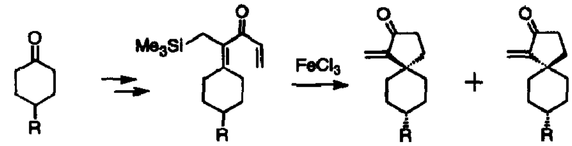


Tetrahedron Letters, **1994**, *35*, 6895

SYNTHESIS OF SPIRO[4.5]DECANE RING SYSTEM THROUGH ALLYLSILANE PROMOTED SPIROANNULATION.

Chiaki Kuroda and Yukari Hirono, Department of Chemistry, Rikkyo University, Nishi-Ikebukuro, Toshima-ku, Tokyo 171, Japan

Spiro[4.5]decane ring system was synthesized using Nazarov cyclization of α-(trimethylsilylmethyl)divinyl ketone derivatives.

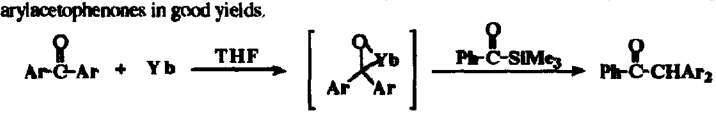


Tetrahedron Letters, **1994**, *35*, 6897

NOVEL DEOXYGENATIVE ACYLATION OF DIARYL KETONES WITH ACYLSILANES MEDIATED BY LANTHANOID METALS

Yuki Taniguchi,* Akihiro Nagafuji, Yoshikazu Makioka, Ken Takaki,* and Yuzo Fujiwara,* Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima 724, Japan

The reaction of diaryl ketones and benzoyltrimethylsilane is mediated by lanthanoid metals such as ytterbium to give the deoxygenatively acylated product, 1,1-diarylacetophenones in good yields.

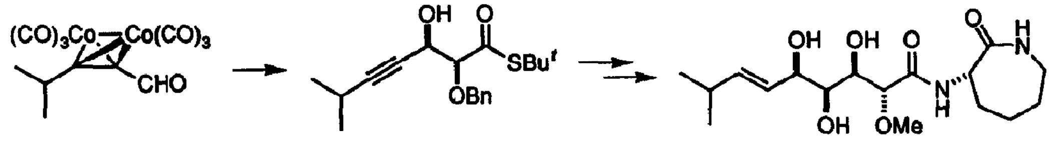


Tetrahedron Letters, **1994**, *35*, 6899

A Cobalt-Complexed Propynal in Organic Synthesis: A Highly Stereoselective Total Synthesis of Bengamide E.

Chisato Mukai, Osamu Kataoka, and Miyoji Hanaoka, Faculty of Pharmaceutical Sciences, Kanazawa University, Takara-machi, Kanazawa 920 Japan

A highly stereoselective aldol reaction of cobalt-complexed 4-methylpent-2-ynal **2** provided the *syn*-aldol product **3**, which was subsequently converted to bengamide E in a highly stereoselective manner.

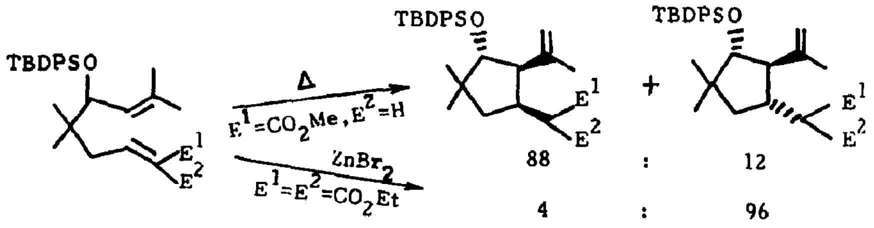


2 **3** (+)-Bengamide E

Tetrahedron Letters, **1994**, *35*, 6903

INTRAMOLECULAR ALDER ENE REACTION OF ACTIVATED 1,6-DIENES : STEREOCHEMICAL CONTROL OVER THREE CONTIGUOUS STEREOGENIC CENTRES.

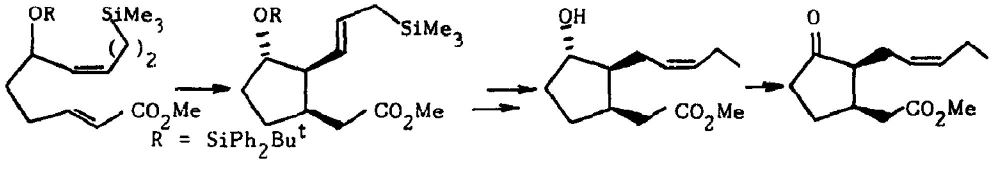
Tarun K. Sarkar*, Binay K. Ghorai, Sandip K. Nandy and Bireswar Mukherjee, Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, India



Tetrahedron Letters, **1994**, *35*, 6907

INTRAMOLECULAR ALDER ENE APPROACH TO STEREOCHEMICAL CONTROL OVER THREE CONTIGUOUS STEREOGENIC CENTRES : SYNTHESIS OF (±) - METHYL CUCURBATE AND (±) - METHYL EPIJASMONATE.

Tarun K. Sarkar,[a]* Binay K. Ghorai [a] and Asoke Banerji [b], [a]Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, India ; [b]Bio-Organic Division, Modular Laboratory, B.A.R.C., Bombay 400085, India

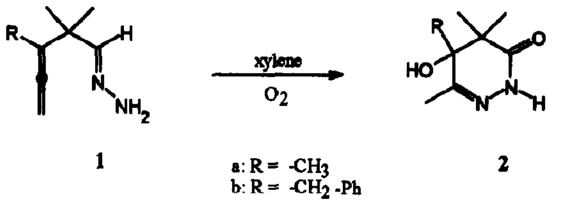


Tetrahedron Letters, **1994**, *35*, 6909

NOVEL TANDEM CYCLIZATION-OXIDATION REACTION OF 2,2-DIMETHYLPENTA-3,4-DIENAL HYDRAZONES

Radek Marek, Milan Potáček, Jaromír Marek
Department of Chemistry, Masaryk University
Kotlářská 2, CZ-611 37 Brno, Czech Republic

Alex De Groot
Department of Chemistry, Antwerp University
Groenenborgerlaan 171, B-2020 Antwerp, Belgium



1

a: R = -CH3
b: R = -CH2 -Ph

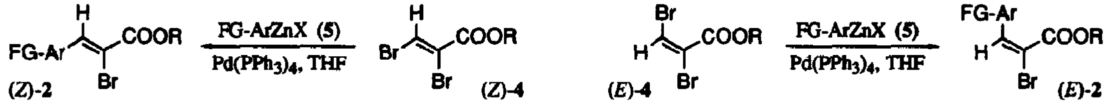
2

Tetrahedron Letters, **1994**, *35*, 6913

HIGHLY REGIOSELECTIVE PALLADIUM-MEDIATED SYNTHESIS OF STEREOISOMERICALLY PURE (*Z*)- AND (*E*)-ALKYL 2-BROMO-3-(HETERO)ARYLPROPENOATES.

Fabio Bellina, Adriano Carpita, Massimo De Santis and Renzo Rossi *, Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Risorgimento 35, I-56126 Pisa, Italy.

Stereoisomerically pure (*Z*)- and (*E*)-2 were synthetized by Pd(0)-mediated reaction between (hetero)arylzinc halides, 5, and compounds (*Z*)- and (*E*)-4, respectively. Compounds (*Z*)- and (*E*)-2 are precursors to stereodefined trisubstituted α,β-unsaturated esters.

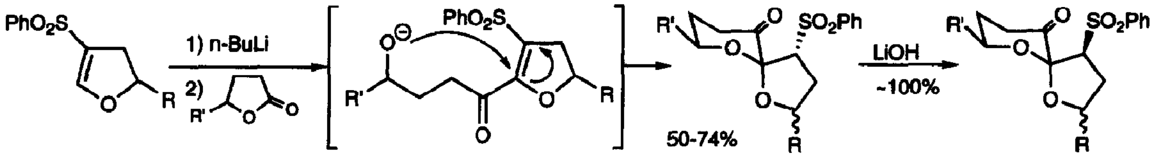


(*Z*)-2 (*Z*)-4 (*E*)-4 (*E*)-2

Tetrahedron Letters, **1994**, *35*, 6917

ONE-STEP SYNTHESIS OF FUNCTIONALIZED DIOXASPIRO[4,5]DECANES FROM β-PHENYLSULFONYL DIHYDROFURANS AND γ-LACTONES

Juan C. Carretero*, Nuria Díaz and Javier Rojo
Departamento de Química. Universidad Autónoma de Madrid.
Cantoblanco. 28049-Madrid. Spain

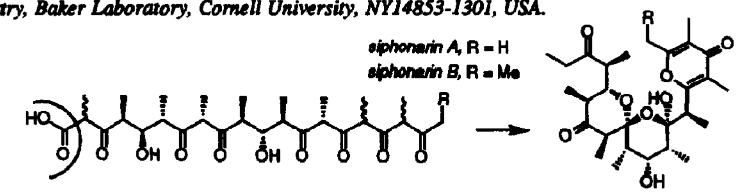


Tetrahedron Letters, **1994**, *35*, 6921

BIOSYNTHETIC STUDIES ON POLYPROPIONATES: A STEREOCHEMICAL MODEL FOR SIPHONARINS A AND B FROM THE PULMONATE LIMPET *SIPHONARIA ZELANDICA*.

Mary J. Garson*[a], David D. Jones[a], Christopher J. Small[b], Jun Liang[c] and Jon Clardy[c] [a]*Department of Chemistry, The University of Queensland, Brisbane QLD 4072, Australia.* [b]*Department of Chemistry, University of Wollongong, Wollongong NSW 2500, Australia.* [c]*Department of Chemistry, Baker Laboratory, Cornell University, NY14853-1301, USA.*

Biosynthetic precursors for siphonarins A and B are defined following revision of absolute configuration and determination of polypropionate chain building direction.

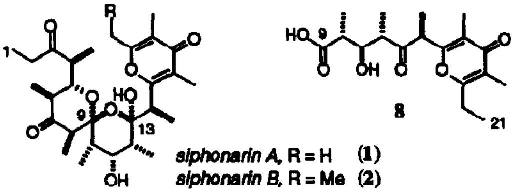


Tetrahedron Letters, **1994**, *35*, 6925

ASSIGNMENT OF THE ABSOLUTE CONFIGURATION OF THE SIPHONARINS AND BACONIPYRONES. ENANTIOCONTROLLED SYNTHESIS OF A γ-PYRONE SUBUNIT.

Ian Paterson* and Alison S. Franklin *University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.*

The synthetic γ-pyrone acid **8** was found to be enantiomeric to that obtained by degradation of dihydrosiphonarin B, leading to the assignment of the absolute configuration of the siphonarins shown.

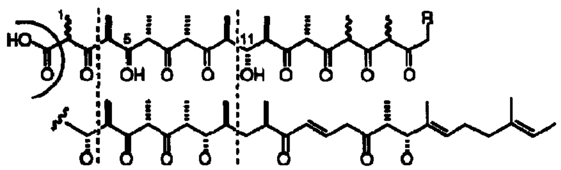


Tetrahedron Letters, **1994**, *35*, 6929

A CONFIGURATIONAL MODEL FOR SIPHONARIID POLYPROPIONATES DERIVED FROM STRUCTURAL AND BIOSYNTHETIC CONSIDERATIONS

Mary J. Garson*[a], Jonathan M. Goodman[b] and Ian Paterson*[b] [a]*Department of Chemistry, The University of Queensland, Brisbane QLD 4072, Australia.* [b]*University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.*

A configurational model for siphonariid metabolites is proposed which rationalises the stereochemistry of their acyclic precursors. It contains a tetrapropionate unit common to the Cane-Celmer-Westley PAPA model for polyether antibiotics of bacterial origin.



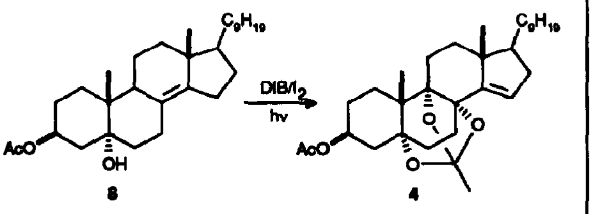
Tetrahedron Letters, **1994**, *35*, 6933

HYPERVALENT IODINE REAGENTS: SYNTHESIS OF A STEROIDAL ORTHOACETATE BY A RADICAL REACTION

Alicia Boto,[a] Carmen Betancor,[b] Ernesto Suárez*[a]

[a]Instituto de Productos Naturales y Agrobiología del C.S.I.C., Carretera de La Esperanza, 2, 38206-La Laguna, Tenerife, Spain. [b]Departamento de Química Orgánica, Universidad de La Laguna, Tenerife, Spain

The reaction of steroidal alcohol (**8**) with (diacetoxyiodo)benzene (DIB) and iodine under irradiation with visible light afforded, in addition to the expected β-fragmentation diene (**2**), the orthoacetate (**4**) in moderate yield.

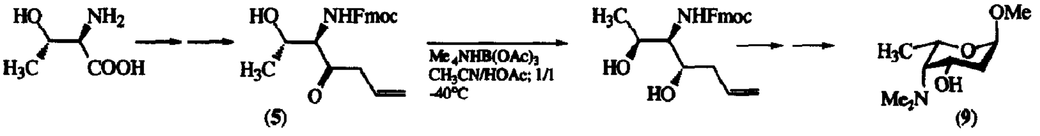


Tetrahedron Letters, **1994**, *35*, 6937

DIASTEREOSELECTIVE SYNTHESIS OF METHYL α-KEDAROSAMINIDE, A CARBOHYDRATE MOIETY OF THE ENEDIYNE ANTITUMOR ANTIBIOTIC KEDARCIDIN CHROMOPHORE.

Tatjana Vuljanic, Jan Kihlberg* and Peter Somfai*, Organic Chemistry 2, Lund Institute of Technology, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden

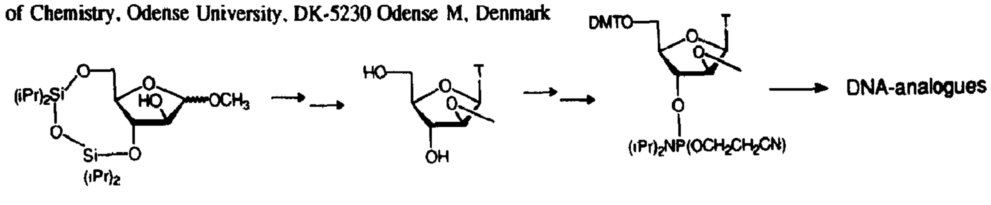
Methyl α-kedarosaminide (9) was synthesised from D-threonine, via the key diastereoselective reduction of the allyl ketone (5).



Tetrahedron Letters, **1994**, *35*, 6941

NOVEL OLIGODEOXYNUCLEOTIDE ANALOGUES CONTAINING A 2'-*O*-METHYLARABINONUCLEOSIDE

Charlotte H. Gotfredsen, Jens Peter Jacobsen, and Jesper Wengel*
Department of Chemistry, Odense University, DK-5230 Odense M, Denmark



Tetrahedron Letters, **1994**, *35*, 6945

EFFECTS OF ADDITIONAL STEREOGENIC CENTRES AND CATION IN THE NUCLEOPHILIC EPOXIDATION OF VINYLSULFOXIMINES WITH METAL ALKYLPEROXIDES

Andrew D. Briggs,[a] Richard F.W. Jackson,[a*] William Clegg,[a] Mark R.J. Elsegood,[a]
Josephine Kelly,[a] and Paul A. Brown[b]
[a] Department of Chemistry, Bedson Building, The University of Newcastle, Newcastle upon Tyne, NE1 7RU, UK
[b] Roche Products Limited, Research Centre, Welwyn Garden City, Hertfordshire, AL7 3AY, UK