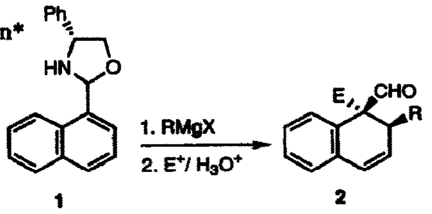
GRAPHICAL ABSTRACTS

Tetrahedron Letters, **1994**, *35*, 4267

A Single-Pot Synthesis of 1,1,2-Trisubstituted 1,2-Dihydronaphthalenes in High Enantiomeric Purity

Mohamed K. Mokhallalati, K. Raman Muralidharan, and Lendon N. Pridgen*
Synthetic Chemistry Department, SmithKline Beecham Pharmaceuticals,
Post Office Box 1539, King of Prussia, Pennsylvania 19406-0939

The tandem addition of Grignard reagents to the oxazolidines **1** followed by electrophile trapping of the intermediate, afforded the aldehydes **2** in high enantiosectivity.

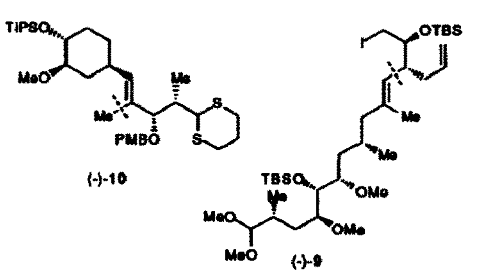


Tetrahedron Letters, **1994**, *35*, 4271

FORMAL TOTAL SYNTHESIS OF FK506. CONCISE CONSTRUCTION OF THE C(10)-C(34) SEGMENT VIA AN EFFECTIVE COUPLING TACTIC

Amos B. Smith, III,* Kwunmin Chen, Darius J. Robinson, Leif M. Laakso, and Karl J. Hale
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.

A formal total synthesis of the potent immunosuppressant FK506 has been achieved via a concise construction of the Merck advanced intermediate. Key features of the strategy include stereocontrolled σ-bond installation of the trisubstituted olefin moieties and an efficient coupling of dithiane (-)-**10** with α-silyloxy primary iodide (-)-**9**

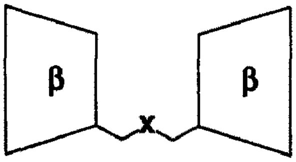


Tetrahedron Letters, **1994**, *35*, 4275

The Effect of Tether Length on the Affinity of Ligands for Bis(cyclodextrins)

C. T. Sikorski & R. C. Petter, Dept. of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260*

BisCDs linked by alkyl chains of varying lengths were prepared and their ability to bind to fluorophoric ligands (TNS and BNS) was evaluated.

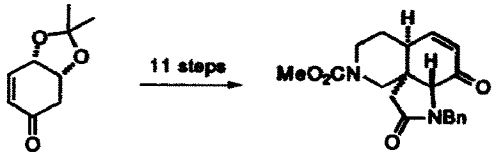


Tetrahedron Letters, **1994**, *35*, 4279

An Enantioselective Approach to the Synthesis of Manzamine A.

Theodore M. Kamenecka and Larry E. Overman* Department of Chemistry, University of California, Irvine, CA 92717-2025, USA

A new approach for asymmetric construction of the pyrrolo[2,3-i]isoquinoline core of manzamine A is described.

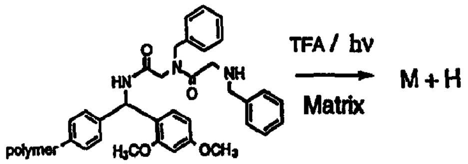


Tetrahedron Letters, **1994**, *35,* 4283

MICROCHEMICAL STRUCTURAL DETERMINATION OF A PEPTOID COVALENTLY BOUND TO A POLYMERIC BEAD BY MATRIX-ASSISTED LASER DESORPTION IONIZATION TIME-OF-FLIGHT MASS SPECTROMETRY.

Robert A. Zambias*[1], David A. Boulton[1] and Patrick R. Griffin[2],
Departments of Biophysical Chemistry[1] and Analytical Biochemistry[2] Merck Research Laboratories,
Rahway, New Jersey 07065

New methodology utilizing matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF MS) for the direct identification of a ligand covalently attached to a polymeric bead is reported.

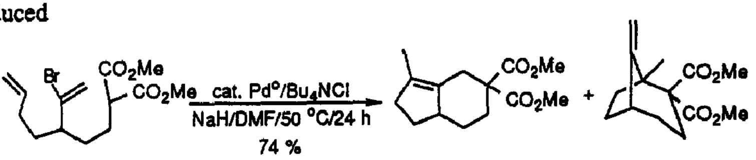


Tetrahedron Letters, **1994**, *35,* 4287

Consecutive Carbon-Carbon Bond Formation via the π-Allylpalladium Variant of the Heck Reaction

Christine S. Nylund, John M. Klopp, and Steven M. Weinreb*, Department of Chemistry, The Pennsylvania State University, University Park, PA 16802 USA

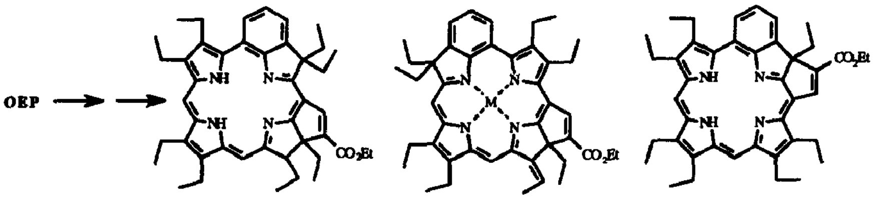
Two C-C bonds are readily formed by nucleophilic addition of stabilized carbanions to the π-allylpalladium intermediate regioselectively produced by the Heck reaction of a vinyl bromide and an unactivated olefin, producing functionalized carbobicyclic systems when performed intramolecularly.



Tetrahedron Letters, **1994**, *35,* 4291

SYNTHESIS OF BENZOPURPURINS, ISOBACTERIOBENZOPURPURINS AND BACTERIOBENZOPURPURINS.

Alan R. Morgan, Sapna Gupta, Department of Chemistry, University of Toledo, Toledo, OH 43606



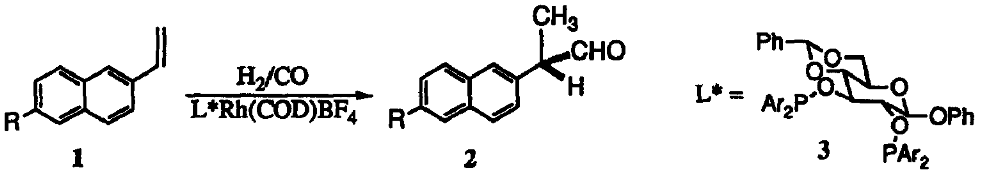
Cyclization of *meso*-substituted analogs of octaethylporphyrin under acidic conditions leads to formation of chlorins, bacteriochlorins or isobacteriochlorins, depending upon reaction conditions.

Tetrahedron Letters, **1994**, *35,* 4295

Electronic Effects in Asymmetric Catalysis: Hydroformylation of Olefins.

T. V. RajanBabu and Timothy A. Ayers, DuPont Central Research and Development, Experimental Station, E328 Wilmington, Delaware 19880-0328 USA

In the rhodium-catalyzed asymmetric hydroformylation of olefins 1 providing optically active aldehydes 2, substitution of electron-withdrawing aryl groups at phosphorus in carbohydrate derived diphosphinites 3 increases the enantioselectivity. Very high branched to linear ratios (>94%) for the product aldehydes were obtained with this catalyst system.



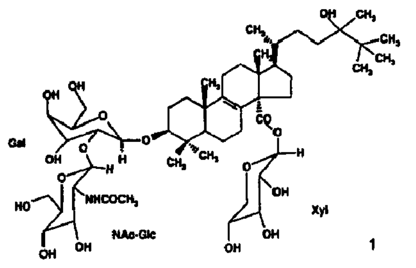
1 2 3

Tetrahedron Letters, **1994**, *35*, 4299

ERYLOSIDE E FROM AN ATLANTIC SPONGE *ERYLUS GOFFRILLERI*

Nanda K. Gulavita,* Amy E. Wright, Michelle Kelly-Borges, and Ross E. Longley
Harbor Branch Oceanographic Institution, Inc., 5600 US1, Ft. Pierce, Florida 34946
Donna Yarwood and Matthew A. Sills*
Ciba-Geigy Corporation, Research Department, 556 Morris Ave., Summit, NJ. 07901

A glycoside, eryloside E (1), was isolated from the marine sponge *Erylus goffrilleri* and characterized by spectroscopic methods. Eryloside E possesses a rare penasterol nucleus.

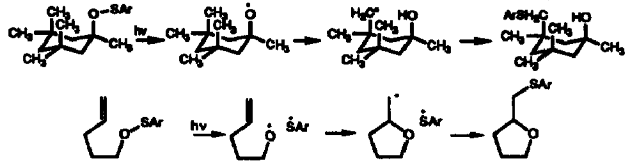


Tetrahedron Letters, **1994**, *35*, 4303

DEMONSTRATION OF THE SYNTHETIC UTILITY OF THE GENERATION OF ALKOXY RADICALS BY THE PHOTO-INDUCED, HOMOLYTIC DISSOCIATION OF ALKYL 4-NITROBENZENESULFENATES.

Daniel J. Pasto* and François Cottard, Department of Chemistry and Biochemistry, Univ. of Notre Dame, Notre Dame, IN 46556.

The facile generation of alkoxy radicals by the photo-induced homolytic dissociation of alkyl 4-nitrobenzenesulfenates is demonstrated by the reactions shown below giving the indicated products in 62-75% isolated yields.

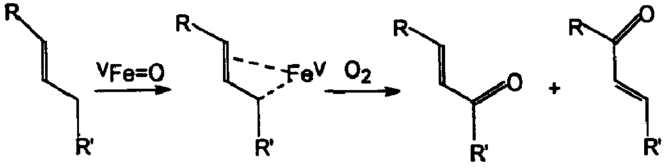


Tetrahedron Letters, **1994**, *35*, 4307

THE OXIDATION OF ALLYLIC METHYLENE GROUPS UNDER Fe^{III}-TBHP AND Fe^{III}-TBHP-PA CONDITIONS

Derek H. R. Barton* and Tie-Lin Wang*
Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255

Oxidation of allylic methylene groups under Fe^{III}-TBHP and Fe^{III}-TBHP-PA conditions gave α- and γ-ketonization products.

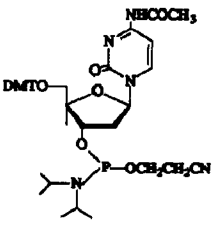


Tetrahedron Letters, **1994**, *35*, 4311

Fast Cleavage and Deprotection of Oligonucleotides

M. P. Reddy*, N. B. Hanna and Firdous Farooqui
Beckman Instruments Inc., 2500 Harbor Blvd., Fullerton, CA 92634.

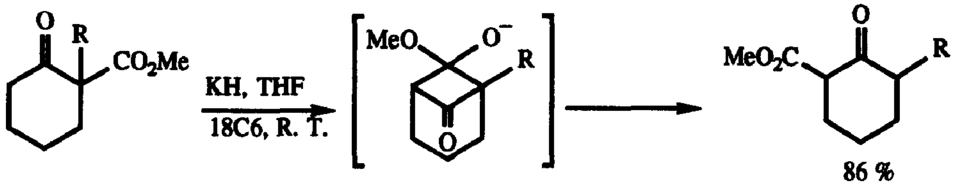
We have developed methylamine/ammonia used in conjunction with DMT dC^{ac} phosphoramidite as a fast cleavage and deprotection system which facilitates cleavage of oligonucleotides from the solid support in 5 min at room temperature and deprotection in 5 min at 65^{0}C.



Tetrahedron Letters, **1994**, *35*, 4315

EFFICIENT 1,3 ESTER SHIFT IN α-DISUBSTITUTED β-KETO-ESTER ENOLATES. REMARKABLE INFLUENCE OF THE METAL COUNTERION ON THE RATE OF REACTION.

A. Habi and D. Gravel, Department of Chemistry, Université de Montréal, P. O. Box 6128, Montreal QC, Canada, H3C 3J7

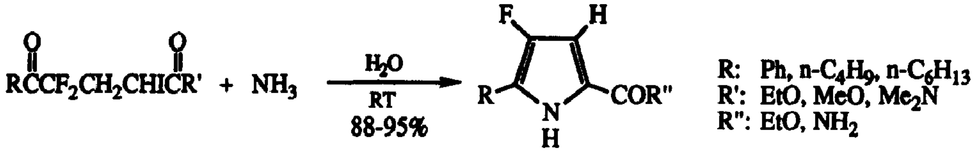


Tetrahedron Letters, **1994**, *35*, 4319

A NEW APPROACH TO THE SYNTHESIS OF β-FLUOROPYRROLE DERIVATIVES.

Zai-Ming Qiu and Donald J. Burton*, Department of Chemistry, The University of Iowa, Iowa City, IA 52242, U.S.A.

A new, high-yield preparation of β-fluoropyrroles is described. A mechanism is proposed.

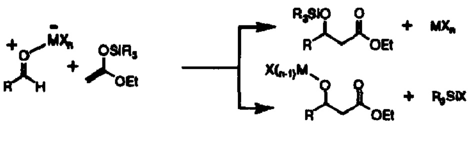


Tetrahedron Letters, **1994**, *35*, 4323

Metal Versus Silyl Triflate Catalysis in the Mukaiyama Aldol Addition Reaction

Erick M. Carreira* and Robert A. Singer, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

A mechanistic study of the Mukaiyama aldol addition of the ethyl acetate silyl ketene acetal mediated by BF3•OEt2, LiClO4, Yb(OTf)3, Sn(OTf)2, and Zn(OTf)2 is presented. The results of experiments conducted with doubly-labeled silyl ketene acetals establish that silicon is not transferred to the metal aldolate intramolecularly and implicate a Lewis acidic silicon species and not the metals as the catalyst in the Mukaiyama aldol addition reaction.

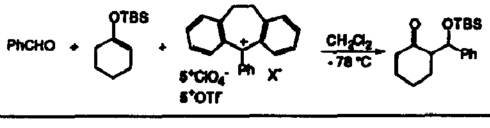


Tetrahedron Letters, **1994**, *35*, 4327

TRIARYLCARBENIUM IONS AS CATALYSTS IN THE MUKAIYAMA ALDOL ADDITION: A MECHANISTIC INVESTIGATION

Scott E. Denmark* and Chien-Tien Chen
Roger Adams Laboratory, Department of Chemistry, University of Illinois, Urbana, IL 61801, USA

1-Phenyl-2:3,6:7-dibenzosuberyl salts $5^+ClO_4^-$ and 5^+TfO^- are efficient catalysts in the aldol reaction between silyl enol ethers and benzaldehyde with moderate diastereoselectivity. Crossover experiments with doubly labeled silyl enol ethers and kinetic studies support the role of the catalyst as 5^+ rather than a Lewis acidic TBSX species in this transformation.

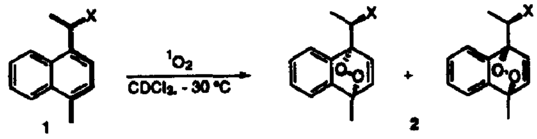


Tetrahedron Letters, 1994, 35, 4331

SUBSTITUENT EFFECTS IN THE DIASTEREOSELECTIVE [4+2] CYCLOADDITION OF CHIRAL NAPHTHALENE DERIVATIVES WITH SINGLET OXYGEN.

Waldemar Adam* and Michael Prein, Institut für Organische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg (Germany)

Stereoelectronic and not steric effects control the π-facial selectivity in the photooxygenation of naphthalenes **1**.



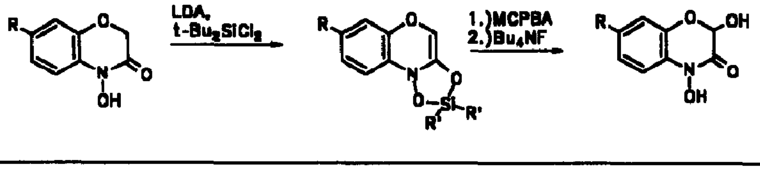
X = OH, OAc, OMe, $OSiMe_3$, tBu, $SiMe_3$, Cl, Br

Tetrahedron Letters, 1994, 35, 4335

α-Hydroxylation of Cyclic Hydroxamic Acids by Peroxide Oxidation : A Novel Approach to Allelochemicals from *Gramineae*

Holger Hartenstein and Dieter Sicker
Institute of Organic Chemistry, University of Leipzig, Talstraße 35, 04103 Leipzig, Germany

DIBOA and DIMBOA were synthesized by the first α-hydroxylation of N-hydroxylactams via *m*-chloroperbenzoic acid oxidation of corresponding cyclosilyl enol ethers

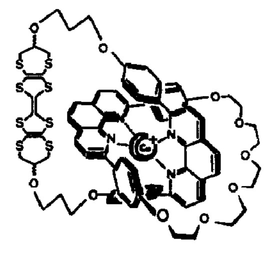


Tetrahedron Letters, 1994, 35, 4339

A COPPER(I) [2]-CATENATE INCORPORATING A TETRATHIAFULVALENE UNIT

Tine Jørgensen, Jan Becher
Department of Chemistry, Odense University, 5230 Odense M, Denmark.
Jean-Claude Chambron, Jean-Pierre Sauvage
Laboratoire de Chimie Organo-Minérale, CNRS UA 422, Faculté de Chimie, 1, rue Blaise Pascal, 67000 Strasbourg, France

A copper(I) [2]-catenate incorporating an electron-donor tetrathiafulvalene unit has been synthesized and characterized.



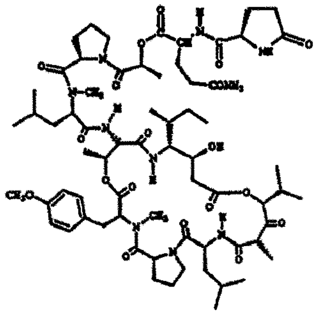
Tetrahedron Letters, 1994, 35, 4343

Synthesis of "CHO-CO-Peptides" by N-terminal Acylation with a Glyoxylyl Equivalent

Driss Qasmi, Loïc René and Bernard Badet
Institut de Chimie des Substances Naturelles, C.N.R.S., 91198 Gif-sur-Yvette, France

Activated esters of glyoxylic acid di-isopropylthioacetal were prepared by conventional procedures and used in the Solid Phase Peptide Synthesis of N-glyoxylyl-peptides (CHOCO-Peptides).

Tetrahedron Letters, **1994**, *35*, 4345



The Complete Spectral Assignment Of Didemnin H, A New Constituent Of The Tunicate *Tridideminum Cyanophorum*

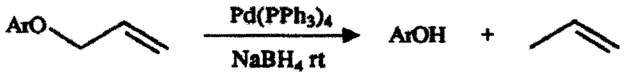
Anna Boulanger, Eliane Abou-Mansour, Ayoub Badre, Bernard Banaigs*, Georges Combaut and Christian Francisco. Groupe d'Etudes des Métabolites Marins d'Intérêt Biologique, Université de Perpignan, 66860 Perpignan cedex.

Complete ^{1}H and ^{13}C spectral assignments by 2D NMR means are presented for a new cyclodepsipeptide namely didemnin H, isolated from *Trididemnum cyanophorum* (Didemnidae).

Tetrahedron Letters, **1994**, *35*, 4349

REDUCTIVE DEPROTECTION OF ARYL ALLYL ETHERS WITH $Pd(PPh_3)_4/NaBH_4$

René Beugelmans, Sebastien Bourdet, Antony Bigot, Jieping Zhu*
Institut de Chimie des Substances Naturelles, CNRS, 91198 Gif-sur-Yvette, France



8 examples

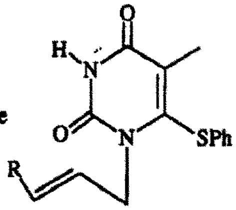
Treatment of Aryl allyl ethers with catalytic amounts of $Pd(PPh_3)_4$ and $NaBH_4$ at room temperature gave the parent phenols in high yield.

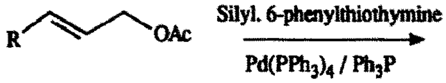
Tetrahedron Letters, **1994**, *35*, 4351

SYNTHESIS OF DEOXY-ANALOGS of HEPT *via* a Pd(0) CATALYZED COUPLING

Renée Pontikis, and Claude Monneret*, Laboratoire de Chimie associé au CNRS
Institut Curie, Section de Biologie, 26 rue d'ulm, 75231 Paris Cedex 05

A series of deoxy-analogs of HEPT has been synthesized by coupling allylic acetates with the bis-silylated 6-phenylthiothymine in the presence of tetrakis(triphenylphosphine)palladium.





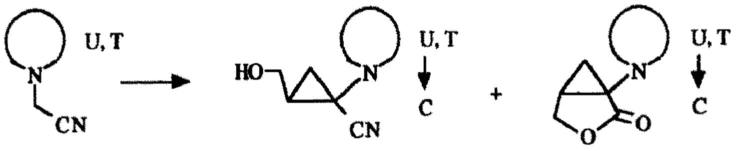
R = Ph, pyridine, thiophene, and furanne

Tetrahedron Letters, **1994**, *35*, 4355

SYNTHESIS OF NOVEL CYCLOPROPANE NUCLEOSIDE ANALOGUES

Géraldine Grangier, David J. Aitken, Dominique Guillaume and Henri-Philippe Husson*
Laboratoire de Chimie Thérapeutique, URA 1310 du CNRS, Faculté des Sciences Pharmaceutiques et Biologiques,
4 Avenue de l'Observatoire, 75270 Paris cedex 06, France.

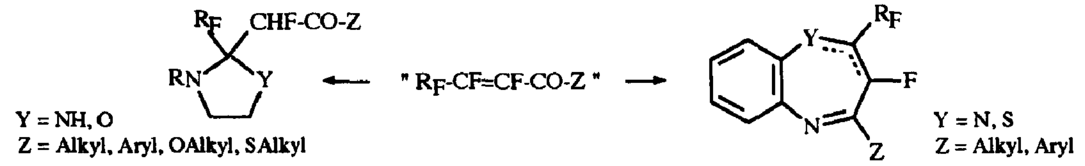
Preparation of the following cyclopropane derivatives is described for the pyrimidine bases uracil, thymine and cytosine.



Tetrahedron Letters, **1994**, *35*, 4357

SELECTIVITY IN THE SYNTHESIS OF FLUORINATED HETEROCYCLES FROM α,β-UNSATURATED PERFLUOROACYL DERIVATIVES (OR THEIR SYNTHETIC EQUIVALENTS) AND 1,2-BIS-NUCLEOPHILES.

B. Dondy, P. Doussot, M. Iznaden, M. Muzard, C. Portella* *Laboratoire des Réarrangements Thermiques et Photochimiques, Associé au CNRS, U.F.R. Sciences, B.P. 347, 51062 REIMS cedex. France*

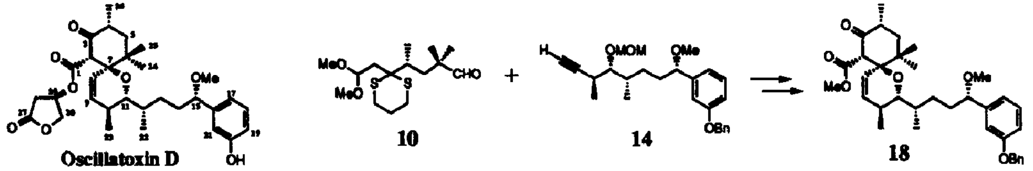


Tetrahedron Letters, **1994**, *35*, 4361

SYNTHETIC STUDY ON OSCILLATOXIN D: CONSTRUCTION OF THE C_1-C_{26} SPIROETHER SEGMENT BY INTRAMOLECULAR ALDOL CONDENSATION AND MICHAEL-TYPE ADDITION.

Hiroaki Toshima,* Takashi Goto, and Akitami Ichihara*
Department of Bioscience and Chemistry, Faculty of Agriculture, Hokkaido University, Sapporo 060, Japan

The C_1-C_{26} spiroether segment (18) of oscillatoxin D has been synthesized from two optically active segments (10 and 14).

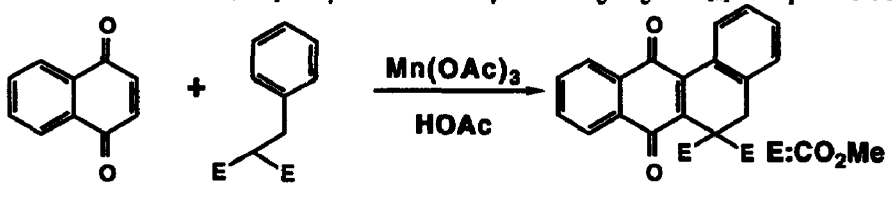


Tetrahedron Letters, **1994**, *35*, 4365

Manganese(III) Acetate Initiated Oxidative Free Radical Reaction Between 1,4-Naphthoquinone And α-Benzylmalonates

Che-Ping Chuang* and Sheow-Fong Wang
Department of Chemistry, National Cheng Kung University, Tainan, Taiwan, 70101, R.O.C.

The free radical reaction between 1,4-naphthoquinone and α-benzylmalonates giving benzo[a]anthraquinones is described.

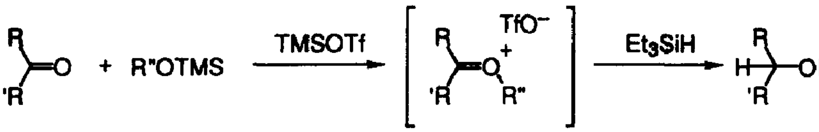


Tetrahedron Letters, **1994**, *35*, 4367

Efficient Reductive Etherification of Carbonyl Compounds with Alkoxytrimethylsilanes

Susumi HATAKEYAMA*, Hisato MORI, Kaori KITANO, Hidetoshi YAMADA, and Mugio NISHIZAWA*
Faculty of Pharmaceutical Sciences, Tokushima Bunri University, Yamashiro-cho, Tokushima 770, Japan

An efficient TMSOTf catalyzed ether synthesis from carbonyl compounds and alkokxytrimethylsilanes *via* triethylsilane-reduction is described.

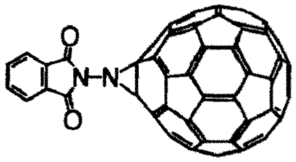


Tetrahedron Letters, **1994**, *35*, 4371

Synthesis and Structure of Nitrene-C_{60} Adduct, C_{60}NPhth (Phth = Phthalimido).

Shin-ya Kuwashima, Masayuki Kubota, Katsuhiko Kushida,[†] Takayuki Ishida, Mamoru Ohashi, and Takashi Nogami, Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofugaoka, Chofu, Tokyo 182, Japan. [†]Varian Japan Ltd., Sumitomo Shibaura Bldg., 4-16-36 Shibaura, Minato-ku, Tokyo 108, Japan.

The reaction of C_{60} and phthalimidonitrene gave $C_{60}(NPhth)_n$ (Phth = phthalimido, n=1-4). The structure, electron-accepting properties, and aziridine inversion of C_{60}NPhth are described.

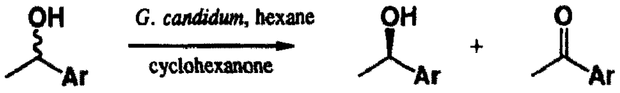


Tetrahedron Letters, **1994**, *35*, 4375

Enantioselective Microbial Oxidation of 1-Arylethanol in an Organic Solvent

K. Nakamura, Y. Inoue, and A. Ohno
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611 Japan

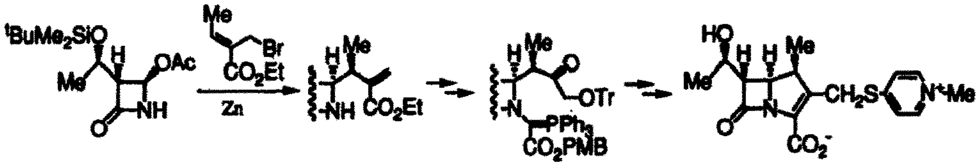
Reactivity in enantioselective oxidation of 1-arylethanol by *G. candidum* is improved when the microbe is entrapped with a water-adsorbent polymer and the reaction is conducted in hexane. Cyclohexanone enhances enantioselective oxidation.



Tetrahedron Letters, **1994**, *35*, 4377

Practical, Stereocontrolled Synthesis of 2-Functionalized-methyl-1β-methylcarbapenems

Shoichiro Uyeo* and Hikaru Itani, Shionogi Research Laboratories, Shionogi & Co., Ltd., Fukushima-ku, Osaka 553, Japan

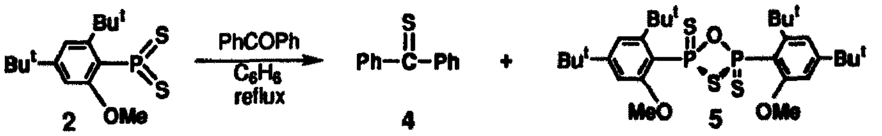


Tetrahedron Letters, **1994**, *35*, 4379

2,4-Di-*t*-butyl-6-methoxyphenyldithioxophosphorane as a Probe for the Mechanistic Studies of Lawesson's Reagent

M. Yoshifuji,* D.-L. An, K. Toyota, and M. Yasunami
Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Sendai 980, Japan

2,4-Di-*t*-butyl-6-methoxyphenyldithioxophosphorane (2) reacted with benzophenone to give thiobenzophenone (4) and 5.

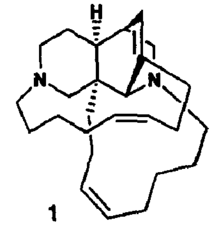


Tetrahedron Letters, **1994**, *35*, 4383

Keramaphidin B, a Novel Pentacyclic Alkaloid from a Marine Sponge *Amphimedon* sp. : A Plausible Biogenetic Precursor of Manzamine Alkaloids

Jun'ichi Kobayashi*, Masashi Tsuda, Naoko Kawasaki, Keita Matsumoto[a], and Takashi Adachi[a]
Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060, Japan, and [a]Research Center, Taisho Pharmaceutical Co., Ltd., Omiya 330, Japan.

Keramaphidin B (1), a novel cytotoxic alkaloid possessing a 1,4-etheno-2,7-decahydronaphthylidine core with two macrocyclic rings has been isolated from an Okinawan marine sponge *Amphimedon* sp.



1

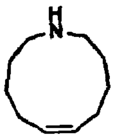
Tetrahedron Letters, **1994**, *35*, 4387

Keramaphidin C and Keramamine C, Plausible Biogenetic Precursors of Manzamine C from an Okinawan Marine Sponge

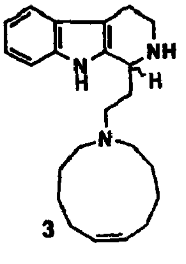
Masashi Tsuda, Naoko Kawasaki, and Jun'ichi Kobayashi*

Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060, Japan

Two plausible biogenetic precursors of manzamine C, named keramaphidin C (2) and keramamine C (3), have been isolated from the Okinawan marine sponge *Amphimedon* sp.



2

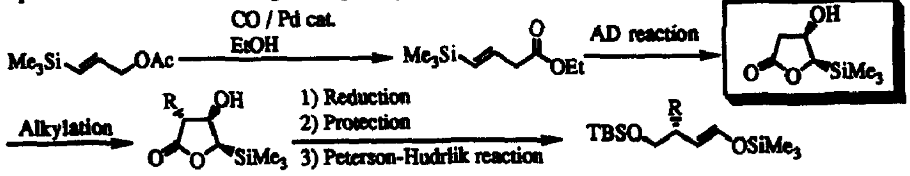


3

Tetrahedron Letters, **1994**, *35*, 4389

Synthesis of β-Hydroxy-γ-trimethylsilyl-γ-butyrolactone as Key Chiral Building Block for Preparation of Four-Carbon Chain Units Having Tertiary Stereogenic Carbon

Yasushi Miyazaki, Hiroyasu Hotta and Fumie Sato*
Department of Biomolecular Engineering, Tokyo Institute of Technology, Midori-ku, Yokohama 227, JAPAN

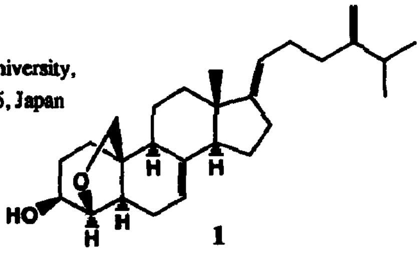


Tetrahedron Letters, **1994**, *35*, 4393

The Structure of Abscisterol A: A Novel 21-Nor-$\Delta^{17(20)}$-unsaturated Sterol from *Cryptosporiopsis abietina*

Hiroshi Yada[a], Hiroji Sato[a,*], Shigeru Kaneko[b], and Akitami Ichihara[a,*]
[a]Department of Bioscience and Chemistry, Faculty of Agriculture, Hokkaido University, Sapporo 060, Japan [b]Forestry and Forest Product Research Institute, Ibaraki 305, Japan

The structure of abscisterol A (1), isolated from *C. abietina*, was determined from a series of 1D and 2D NMR experiments and an advanced Mosher method.

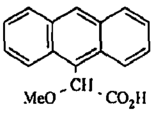


1

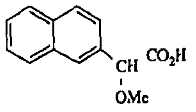
Tetrahedron Letters, **1994**, *35*, 4397

New Chiral Anisotropic Reagents, NMR Tools to Elucidate the Absolute Configurations of Long-chain Compounds

T. Kusumi,* H. Takahashi, X. Ping,' T.Fukushima,'' Y. Asakawa,'''
T. Hashimoto,''' Y. Kan''' and Y. Inouye''''
Faculty of Pharmaceutical Sciences, The University of Tokushima, Tokushima 770, Japan. 'School of Pharmaceutical Sciences, Beijing Medical University, Beijing 100083, China. ''Applied Plant Research Laboratory, Yokohama Center, Japan Tabacco Inc., Kanagawa 227, Japan.'''Faculty of Pharmaceutical Sciences, Tokushima Bunri University, Tokushima 770, Japan. ''''Department of Chemistry, University of Tsukuba,Tsukuba 305, Japan



1; 9ATMA



2; 2NMA

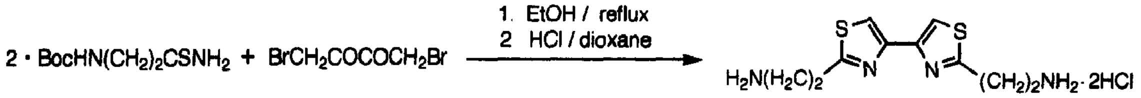
The chiral anisotropic reagents, 1 and 2, have bee applied to elucidate the absolute configurations of secondary alcohols included in long-chain compounds such as methyl 9-hydroxystearate.

Tetrahedron Letters, **1994**, *35*, 4401

2,2'-BIS(2-AMINOETHYL)-4,4'-BITHIAZOLE SYNTHESIS OF A NOVEL DNA CLEAVING AGENT ACTIVATED BY Co(II).

Hideaki Sasaki
Faculty of Pharmaceutical Sciences, Kobe Gakuin University, Ikawadani, Nishi-ku, Kobe 651-21, Japan

2,2'-Bis(2-aminoethyl)-4,4'-bithiazole at 10μM concentration showed a significant DNA cleavage only in the presence of Co(II).

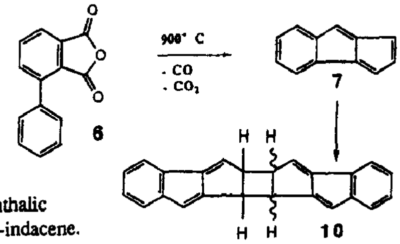


Tetrahedron Letters, **1994**, *35*, 4405

CYCLOPENT[a]INDENE (BENZOPENTALENE): GENERATION BY FLASH VACUUM PYROLYSIS AND SUBSEQUENT DIMERISATION.

Roger F.C. Brown,[a] Neil Choi,[a] Karen J. Coulston,[a] Frank W. Eastwood,[a]
Ulfert E. Wiersum[b] and Leonardus W. Jenneskens.[c]

[a] Department of Chemistry, Monash University, Clayton, Victoria 3618, Australia.
[b] Akzo Research Laboratories Arnhem, Corporate Research, Arnhem, The Netherlands.
[c] Debye Institute, Department of Physical Organic Chemistry, Utrecht University, The Netherlands.



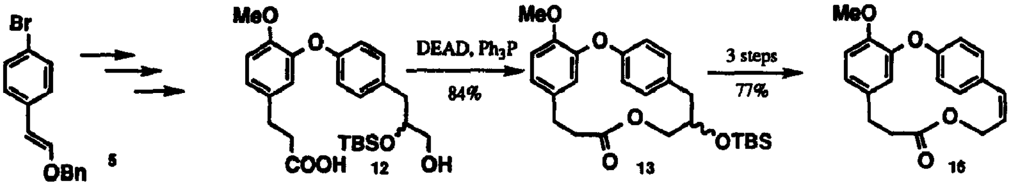
Cyclopent[*a*]indene (benzopentalene, 7) is generated by flash vacuum pyrolysis of 3-phenylphthalic anhydride (6). It dimerises readily above -70 °C, but it does not equilibrate at 900 °C with *as*-indacene.

Tetrahedron Letters, **1994**, *35*, 4409

SYNTHESIS OF COMBRETASTATIN D-2. AN EFFICIENT ROUTE TO CAFFRANE MACROLACTONES.

Elias A. Couladouros* and Ioanna C. Soufli,
Department of Chemistry, Agricultural University of Athens, Iera Odos 75, Athens 11855, Greece.

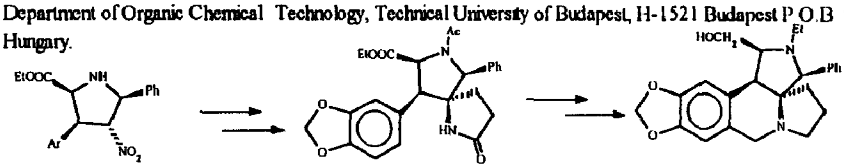
Using the saturated intermediate 12, caffrane 16 was prepared in 10 steps (45% total yield) from 5.



Tetrahedron Letters, **1994**, *35*, 4413

1,3-DIPOLAR CYCLOADDITION APPROACH TOWARDS THE STEREOSELECTIVE PREPARATION OF AZA-CEPHALOTAXINE SKELETON.

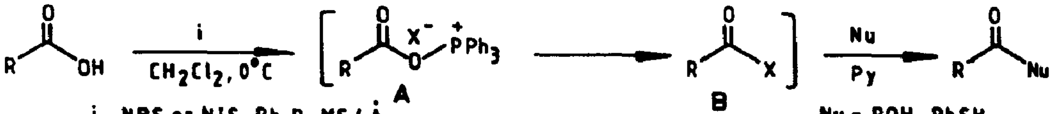
Miklós Nyerges, István Bitter, István Kádas, Gábor Tóth, and László Tõke *
Department of Organic Chemical Technology, Technical University of Budapest, H-1521 Budapest P.O.B 91, Hungary.



Tetrahedron Letters, **1994**, *35*, 4415

A Novel, General Route to the Synthesis of Carboxylic Acid Esters and Thiolesters

K. Sucheta, G.S.R. Reddy, D. Ravi and N. Rama Rao*
Birla Institute of Scientific Research, Malakpet, Hyderabad - 500 036, India.



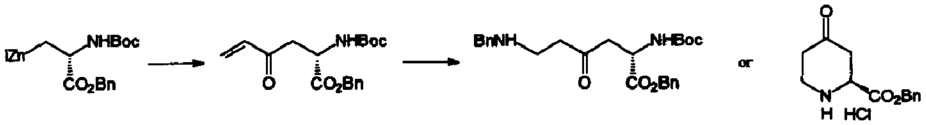
i, NBS or NIS, Ph_3P, MS 4Å

Nu = ROH, PhSH

Tetrahedron Letters, **1994**, *35*, 4417

SYNTHESIS OF PROTECTED 4-OXOPIPECOLIC ACID AND 4-OXOLYSINE USING A PALLADIUM-CATALYSED COUPLING PROCESS

Richard F.W. Jackson,* Lisa J. Graham and Alan B. Rettie
Department of Chemistry, Bedson Building, The University of Newcastle, Newcastle upon Tyne, NE1 7RU, UK

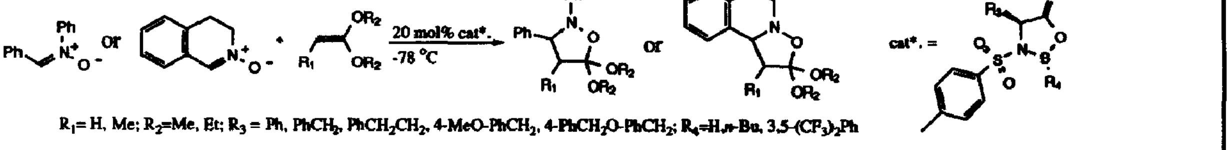


Tetrahedron Letters, **1994**, *35*, 4419

ASYMMETRIC 1,3-DIPOLAR CYCLOADDITION OF NITRONES WITH KETENE ACETALS CATALYZED BY CHIRAL OXAZABOROLIDINES.

Jean-Paul G. Seerden, Anita W.A. Scholte op Reimer, Hans W. Scheeren*, Department of Organic Chemistry, NSR Center for Molecular Structure, Design and Synthesis, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

Asymmetric 1,3-dipolar cycloaddition of nitrones with ketene acetals catalyzed by chiral oxazaborolidines yields stereoselectively 5,5-dialkoxy-isoxazolidines in high yield with moderate enantioselectivity up to 62% ee.



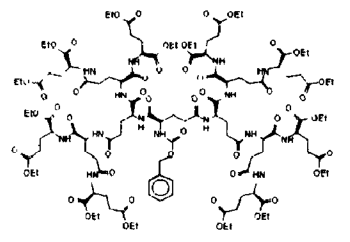
R_1= H, Me; R_2=Me, Et; R_3 = Ph, $PhCH_2$, $PhCH_2CH_2$, 4-MeO-$PhCH_2$, 4-$PhCH_2O$-$PhCH_2$; R_4=H, n-Bu, 3,5-$(CF_3)_2Ph$

Tetrahedron Letters, **1994**, *35*, 4423

THE SYNTHESIS OF CHIRAL DENDRITIC MOLECULES BASED ON THE REPEAT UNIT L-GLUTAMIC ACID

Lance J. Twyman, Anthony E. Beezer and John C. Mitchell* *The Chemical Laboratory, University of Kent, Canterbury, Kent CT2 7NH.*

The convenient synthesis of a glutamate dendrimeric molecule is reported. This chiral, unsymmetrical dendrimer contains 15 chiral centres all with identical configurations (L).

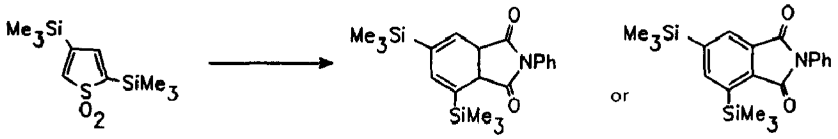


Tetrahedron Letters, **1994**, *35*, 4425

PREPARATION AND CYCLOADDITION REACTIONS OF SILYLATED THIOPHENE 1,1-DIOXIDES.

Allison R. M. O'Donovan and Michael K. Shepherd,* School of Applied Chemistry, University of North London, London N7 8DB, UK.

Cycloaddition reactions of the title compounds with N-phenylmaleimide give cyclohexadiene derivatives in xylene and the corresponding aromatisation products in DMF, eg:



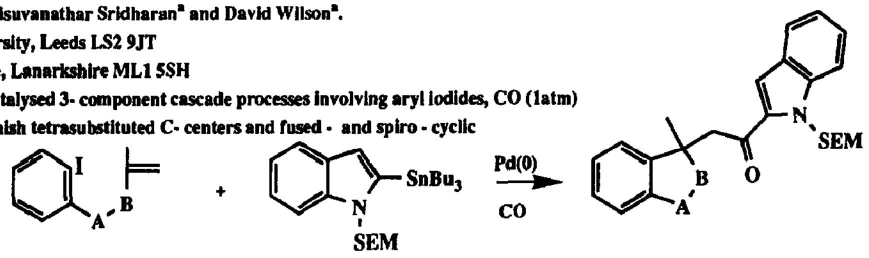
Tetrahedron Letters, **1994**, *35*, 4429

THREE COMPONENT PALLADIUM CATALYSED CYCLISATION - CARBONYLATION - ANION CAPTURE PROCESSES

Ronald Grigg,*[a] James Redpath[b], Visuvanathar Sridharan[a] and David Wilson[a].
a.School of Chemistry, Leeds University, Leeds LS2 9JT
b. Organon Laboratories, Newhouse, Lanarkshire ML1 5SH

Regio - and stereo - specific Pd(0) catalysed 3- component cascade processes involving aryl iodides, CO (1atm) and Sn(IV)R or B(III) reagents furnish tetrasubstituted C- centers and fused - and spiro - cyclic rings in excellent yield.

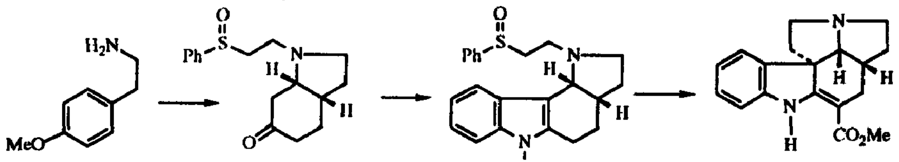
A = O, B = CH$_2$
A = NCH$_2$Ph, B = CO



Tetrahedron Letters, **1994**, *35*, 4433

THE PUMMERER CYCLIZATION ROUTE TO THE IBOPHYLLIDINE ALKALOIDS. TOTAL SYNTHESIS OF (±)-DEETHYLIBOPHYLLIDINE.

Juanlo Catena, Nativitat Valls, Joan Bosch*, and Josep Bonjoch*, Laboratory of Organic Chemistry, Faculty of Pharmacy, University of Barcelona, 08028-Barcelona, Spain.



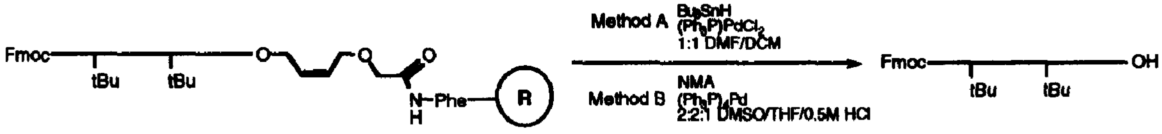
4 6 1

Regioselective Fischer indolization of ketone 4 followed by Pummerer cyclization of 6 and photochemical rearrangement of the methoxycarbonyl group leads to deethylibophyllidine (1).

Tetrahedron Letters, **1994**, *35*, 4437

SOLID-PHASE SYNTHESIS OF PEPTIDES USING ALLYLIC ANCHORING GROUPS 2.PALLADIUM-CATALYSED CLEAVAGE OF FMOC-PROTECTED PEPTIDES

Paul Lloyd-Williams,[a] Ahmed Merzouk,[a, b] François Guibé,[b] Fernando Albericio,[a, c] and Ernest Giralt [a]*
[a] Departament de Química Orgànica, Universitat de Barcelona, E-08028 Barcelona, Spain. [b] Institut de Chimie Moléculaire d'Orsay, Orsay Cedex, France. [c] Millipore Corporation, Peptide Research Group, 75A Wiggins Avenue, Bedford, MA 01730, USA.

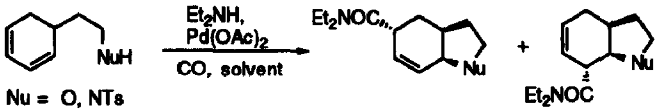


Tetrahedron Letters, **1994**, *35*, 4441

PALLADIUM-MEDIATED STEREO- AND REGIOSELECTIVE TANDEM-CYCLIZATION- CARBONYLATIONS OF 1,3-DIENES.

Pher G. Andersson* and Attila Aranyos
Department of Organic Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden

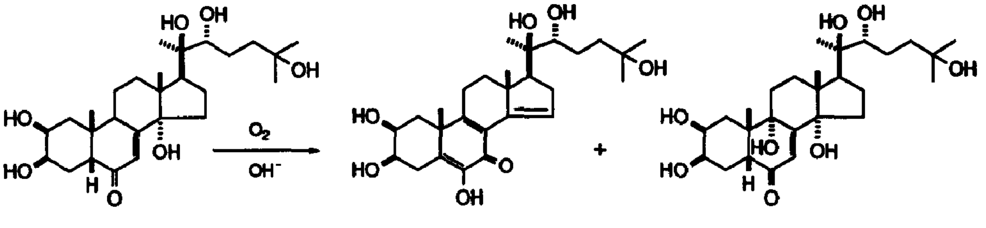
A new palladium-mediated tandem cyclization-carbonylation of 1,3-dienes is described. It was possible to control the regiochemical outcome of the reaction by proper choice of conditions.



Tetrahedron Letters, **1994**, *35*, 4445

BASE-CATALYZED AUTOXIDATION OF 20-HYDROXYECDYSONE : SYNTHESIS OF CALONYSTERONE AND 9,20-DIHYDROXYECDYSONE.

Apichart Suksamrarn*, Penpan Ganpinyo and Chatriwat Sommechai, Department of Chemistry, Faculty of Science, Ramkhamhaeng University, Bangkok 10240, Thailand.

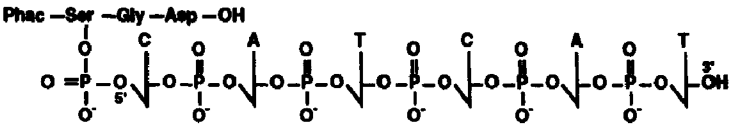


Tetrahedron Letters, **1994**, *35*, 4449

STEPWISE SOLID-PHASE SYNTHESIS OF NUCLEOPEPTIDE Phac-Ser(p5'CATCAT)-Gly-Asp-OH FROM ADENOVIRUS-2 NUCLEOPROTEIN

Jordi Robles, Enrique Pedroso and Anna Grandas*
Departament de Química Orgànica, Universitat de Barcelona, Martí i Franquès 1, 08028 Barcelona, Spain

The target nucleopeptide



was obtained by oligonucleotide chain elongation at the serine hydroxyl group of the resin-linked peptide

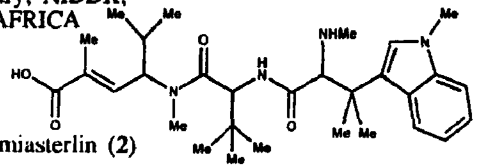
Tetrahedron Letters, 1994, 35, 4453

HEMIASTERLIN AND GEODIAMOLIDE TA; TWO NEW CYTOTOXIC PEPTIDES FROM THE MARINE SPONGE HEMIASTERELLA MINOR (KIRKPATRICK)

R. TALPIR[1], Y. KASHMAN[1], Y. BENAYAHU[2], L. PANNELL[3] AND M. SCHLEYER[4]

[1]School of Chemistry and [2]Department of Zoology, Tel Aviv University,
Tel Aviv 69978, ISRAEL[3], Laboratory of Analytical Chemistry, NIDDK,
NIH, Bethesda, MD 20892, USA[4], O.R.I. Durban, SOUTH AFRICA

Hemiasterella minor was found to contain jaspamide, geodiamolide TA and hemiasterlin (2).
Compound 2 emodies two new natural amino acids.



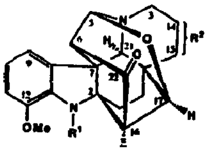
hemiasterlin (2)

Tetrahedron Letters, 1994, 35, 4457

KOPSINITARINES A, B AND C, NOVEL CAGE ALKALOIDS FROM A MALAYSIAN *KOPSIA*

Toh-Seok Kam*, K. Yoganathan and Cheng-Hock Chuah
Department of Chemistry, University of Malaya, 59100 Kuala Lumpur, Malaysia.

The structures of three novel octacyclic indole alkaloids, kopsinitarines A 2, B 3, and C 4, possessing an unprecedented cage skeletal system were elucidated mainly by 2-D NMR methods.



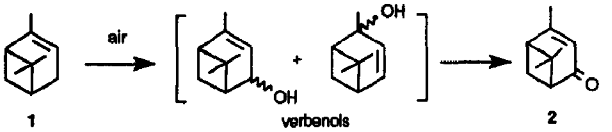
2 $R^1 = CO_2Me$, $R^2 = \Delta^{14,15}$
3 $R^1 = H$, $R^2 = \Delta^{14,15}$
4 $R^1 = H$, $R^2 = 15\text{-}\alpha\text{-}OH$

Tetrahedron Letters, 1994, 35, 4461

Co(II)-Catalysed Allylic Oxidation of α-Pinene by Molecular Oxygen; Synthesis of Verbenone

Marja Lajunen* and Ari M.P. Koskinen
Department of Chemistry, University of Oulu, Linnanmaa, SF-90570 Oulu, Finland

A facile, high-yield, catalytic air-oxidation entry to verbenone (2) from α-pinene (1) by is presented.



Tetrahedron Letters, 1994, 35, 4465

ROLE OF THE ISOMERIZATION PATHWAYS IN THE STAUDINGER REACTION. A THEORETICAL STUDY ON THE INTERACTION BETWEEN ACTIVATED KETENES AND IMIDATES.

Ana Arrieta, Jesus M. Ugalde, and Fernando P. Cossío*. Kimika Fakultatea. Euskal Herriko Unibertsitatea. P.K. 1072, 20080 San Sebastián-Donostia. Spain. Begoña Lecea. Farmazi Fakultatea. Euskal Herriko Unibertsitatea. Lasarteko ataria z/g. 01007 Vitoria-Gasteiz. Spain.

Theoretical (AM1) studies on the Staudinger reaction between ketenes and imidates provide an explanation for the unusual *trans* stereoselectivity observed.