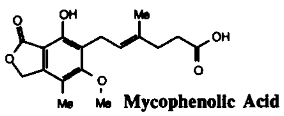
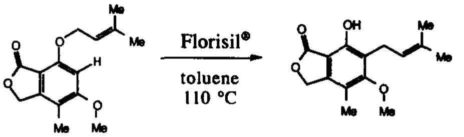
GRAPHICAL ABSTRACTS

Tetrahedron Letters, **1997**, *38*, 4725

The Florisil® Catalyzed [1,3]-Sigmatropic Shift of Allyl Phenyl Ethers - An Entryway Into Novel Mycophenolic Acid Analogues.

Francisco X. Talamás*, David B. Smith*, Alicia Cervantes, Fidencio Franco, Serena T. Cutler, David G. Loughhead, David J. Morgans, Jr., and Robert J. Weikert
Syntex, S. A. de C. V., División de Investigación, Apartado Postal 272 (CIVAC), Jiutepec, Morelos, México, cp 62500 and Roche Bioscience, Inflammatory Diseases Unit, 3401 Hillview Avenue, Palo Alto, CA 94304


Mycophenolic Acid



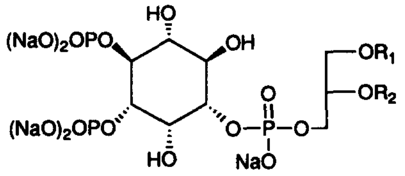
Florisil® was found to be effective in promoting the [1,3]-sigmatropic shift of mycophenolic acid related allyl phenyl ethers.

Tetrahedron Letters, **1997**, *38*, 4729

CONCISE SYNTHESIS OF L-α-PHOSPHATIDYL-D-*myo*-INOSITOL 3,4-BISPHOSPHATE, AN INTRACELLULAR SECOND MESSENGER.

K.Kishta Reddy, Josep Rizo, J. R. Falck*, Depts. Biochemistry and Pharmacology, Univ. Texas Southwestern Med. Center, Dallas, Tx 75235

Highly efficient syntheses of the title phospholipid, short chain diester, and cross-linkable aminodiether analogs are described.



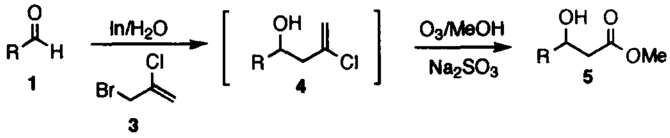
a : $R_1 = C(O)(CH_2)_{14}CH_3$
$R_2 = C(O)(CH_2)_{14}CH_3$
b : $R_1 = C(O)(CH_2)_6CH_3$
$R_2 = C(O)(CH_2)_6CH_3$
c : $R_1 = (CH_2)_7CH_2NHR$
$R_2 = (CH_2)_7CH_3$

Tetrahedron Letters, **1997**, *38*, 4731

Indium Mediated Reactions In Water: Synthesis of β-Hydroxyl Esters

*Xiang-Hui Yi, Yue Meng and Chao-Jun Li**
Department of Chemistry, Tulane University, New Orleans, LA 70118, USA

A variety of β-hydroxyl esters were synthesized efficiently through indium mediated carbon-carbon bond formation in water followed by ozonolysis.

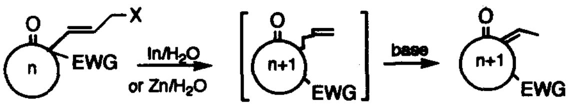


Tetrahedron Letters, **1997**, *38*, 4735

Indium and Zinc Mediated One-Atom Carbocycle Enlargement In Water

*John X. Haberman and Chao-Jun Li**
Department of Chemistry, Tulane University, New Orleans, LA 70118, USA

An one carbon-atom ring expansion was developed *via* indium or zinc mediated reactions in aqueous medium.

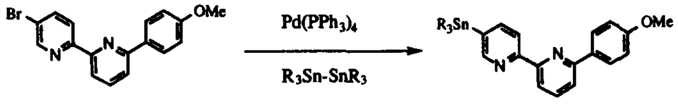


Tetrahedron Letters, **1997**, *38*, 4737

Synthesis of Pyridylstannanes from Halopyridines and Hexamethyl-distannane with Catalytic Palladium.

Maurizio Benaglia, Shinji Toyota, Craig R. Woods, and Jay S. Siegel,* Department of Chemistry, University of California, San Diego, La Jolla, California, 92093-0358,

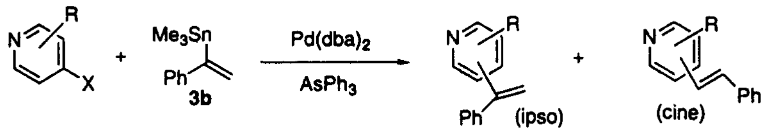
An easy method for direct stannylation of halopyridines and bipyridines by hexamethyldistannane is accomplished by Pd catalysis



Tetrahedron Letters, **1997**, *38*, 4741

On The Stille Vinylation Reactions With α-Styryltrimethyltin

Shu-Hui Chen
Vion Pharmaceuticals, Inc., Four Science Park, New Haven, CT 06511, USA



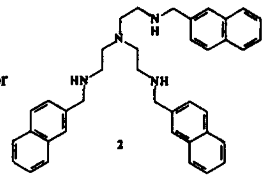
Stille vinylation reactions involving α-styryltrimethyltin **3b** and a series of chloro- or bromo-pyridine derivatives are described.

Tetrahedron Letters, **1997**, *38*, 4745

A New Heterotopic Allostere With Low Pre-Organization.

Gregory J. Arnold and Scott A. Van Arman, Department of Chemistry, Franklin and Marshall College, Lancaster, PA, USA 17604-3003.

A new molecule based on a branched polyamine is described that exhibits Zn(II) dependence for binding a second, fluorescent substrate in a hydrophobic binding site.

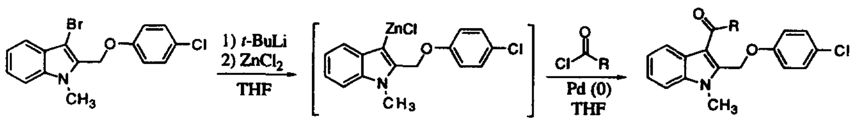


Tetrahedron Letters, **1997**, *38*, 4749

Palladium-Catalyzed Acylation of a 1,2-Disubstituted 3-Indolylzinc Chloride.

Margaret M. Faul* and Leonard L. Winneroski, Lilly Research Laboratories, A Division of Eli Lilly and Company, Chemical Process Research and Development Division, Indianapolis, IN 46285

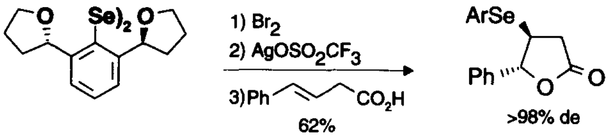
3-Acylindoles are prepared by Pd (0) catalyzed coupling of a 3-indolylzinc chloride with acid chlorides.



Tetrahedron Letters, **1997**, *38*, 4753

2,6-BIS[(2S)-TETRAHYDROFURAN-2-YL]PHENYL DISELENIDE: A VERY EFFECTIVE REAGENT FOR ASYMMETRIC ELECTROPHILIC ADDITION REACTIONS TO OLEFINS

Robert Déziel,* Eric Malenfant, Carl Thibault, Sylvie Fréchette and Michel Gravel
Bio-Méga Research Division, Boehringer Ingelheim (Canada) Ltd.

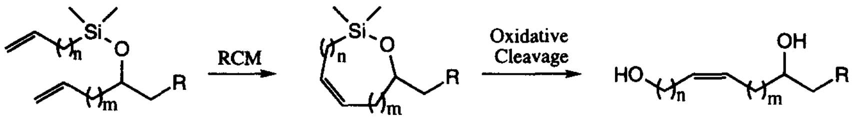


Tetrahedron Letters, **1997**, *38*, 4757

A Simple Method To Polyhydroxylated Olefinic Molecules Using Ring-Closing Olefin Metathesis.

Sukbok Chang and Robert H. Grubbs.* The Arnold and Marbel Beckman Laboratory of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125.

A sequential ring-closing metathesis (RCM) of silyloxy ether dienes and oxidative ring cleavage can be used to prepare a series of cis-olefinic polyhydroxy molecules.

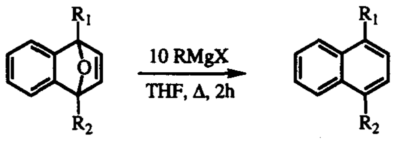


Tetrahedron Letters, **1997**, *38*, 4761

DEOXYGENATION OF 1,4-EPOXIDES BY GRIGNARD REAGENTS

David H. Blank and Gordon W. Gribble*
Department of Chemistry, Dartmouth College, Hanover, New Hampshire, 03755

Deoxygenation of benzo-fused 1,4-dihydro-1,4-epoxides is facilitated by treatment with ten equivalents of a Grignard reagent in refluxing THF.

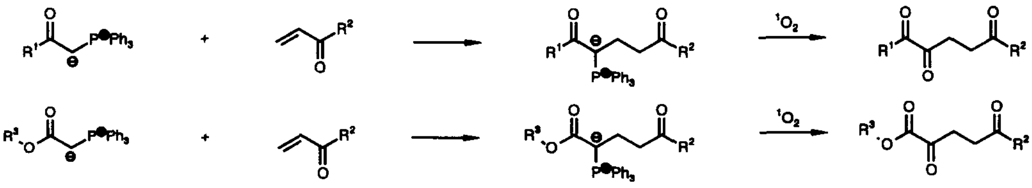


R_1, R_2 = H, Me

Tetrahedron Letters, **1997**, *38*, 4765

REACTIONS OF VINYLKETONES WITH STABILIZED PHOSPHONIUM YLIDS

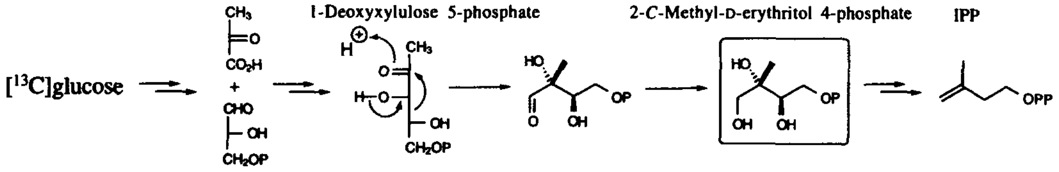
H. J. Bestmann*, A. Groß, Institut für Organische Chemie, Universität Erlangen-Nürnberg, Henkestr. 42, D-91054 Erlangen



Tetrahedron Letters, **1997**, *38*, 4769

Biosynthesis of 2-*C*-Methyl-D-erythritol, a Putative C5 Intermediate in the Mevalonate Independent Pathway for Isoprenoid Biosynthesis

Tore Duvold, Jean-Michel Bravo, Catherine Pale-Grosdemange and Michel Rohmer,*
Université Louis Pasteur/CNRS, Institut Le Bel, 4 rue Blaise Pascal, 67070 Strasbourg Cedex, France

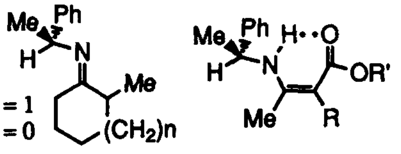


Tetrahedron Letters, **1997**, *38*, 4773

Condensation of Chiral Imines and Chiral β-Enaminoesters with Maleic and Citraconic Anhydrides

C. Cavé, A. Gassama, J. Mahuteau, J. d'Angelo, C. Riche
Unité de Chimie Organique Associée au CNRS, Faculté de Pharmacie, 92296 Châtenay-Malabry; Institut de Chimie des Substances Naturelles, CNRS, 91198 Gif-sur-Yvette, France.

Reactivity of six-and five-membered chiral imines **1** and **4**, and chiral enaminoesters **10** and **13** toward maleic and citraconic anhydrides were reported.



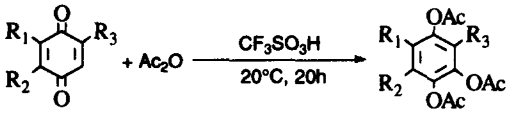
1: n = 1
4: n = 0
10: R = H
13: R = CH_3

Tetrahedron Letters, **1997**, *38*, 4777

Triflic Acid an Efficient Catalyst for Thiele-Winter Reaction.

Didier Villemin[a]*, Nathalie Bar[a], Mohamed Hammadi [b] ,[a]ISMRA, Université de Caen, équipe associée au CNRS, F-14050 Caen, France. [b]Institut National des Industries Manufacturières (INIM), 35000 Boumerdes (Algérie).

Triflic acid is a convenient and non hazardous acid for the Thiele-Winter reaction of quinones. The synthetic scope of Thiele-Winter reaction was increased by the use of triflic acid.

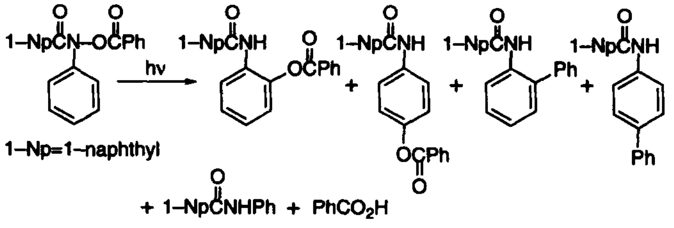


R=H, CH_3, Br, OC_2H_5
94-42%

Tetrahedron Letters, **1997**, *38*, 4779

NOVEL PHOTOREARRANGEMENT OF *N*-(1-NAPHTHOYL)-*N*-PHENYL-*O*-BENZOYLHYDROXYLAMINE IN MICELLAR MEDIA

Tsuyoshi Kaneko, Kanji Kubo and Tadamitsu Sakurai*
Department of Applied Chemistry,
Faculty of Technology, Kanagawa University,
Kanagawa-ku, Yokohama 221, Japan



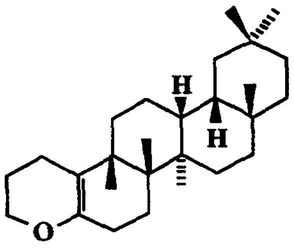
Tetrahedron Letters, **1997**, *38*, 4783

GRACILIPENE: A HETEROCYCLIC *SECO-TRISNOR*-TRITERPENE FROM *CALOPHYLLUM GRACILIPES* (GUTTIFERAE)

Shu-Geng Cao,[1] Keng-Yeow Sim,[1] Swee-Hock Goh,[1*] Feng Xue[2] and Thomas C.W. Mak[2*]

[1]*Department of Chemistry, National University of Singapor, 10 Kent Ridge Crescent, Singapore 119260*
[2]*Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong*

Gracilipene, a novel heterocyclic *trisnor*-triterpene from the leaves of *Calophyllum gracilipes*, shows an unprecedented rearranged *seco-trisnor*-oleanane structure with a dihydropyran ring-A.



Tetrahedron Letters, **1997**, *38*, 4787

EVIDENCE OF A STEPWISE ACYL-TRANSFER REACTION MECHANISM : NONLINEAR HAMMETT PLOTS FOR REACTIONS OF *p*-NITROPHENYL SUBSTITUTED BENZOATES WITH HYDROXIDE AND *p*-CHLOROPHENOXIDE.

Ik-Hwan Um,* Eun-Kyung Chung, and Dong-Sook Kwon, Department of Chemistry, Ewha Womans University, Seoul, 120-750, Korea

Nonlinear Hammett plots obtained in the title reactions support a stepwise acyl-transfer reaction mechanism.

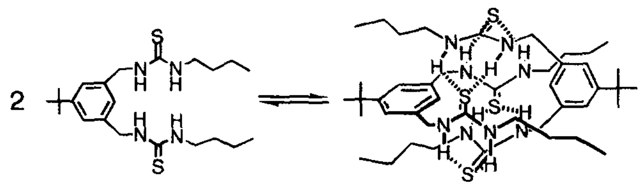
X = 4-MeO, 4-Me, 3-Me, H, 4-Cl, 3-Cl, 4-CN, 4-NO_2, 4-Cl-3-NO_2, 3,5-$(NO_2)_2$; Nu^- = OH^- , 4-$ClC_6H_4O^-$

Tetrahedron Letters, **1997**, *38*, 4791

NOVEL SELF-ASSEMBLY OF *m*-XYLYLENE TYPE DITHIOUREAS

Yoshito Tobe,* Shin-ichi Sasaki, Keiji Hirose, Koichiro Naemura,
Department of Chemistry, Faculty of Engineering Science,
Osaka University, Toyonaka, Osaka 560, Japan

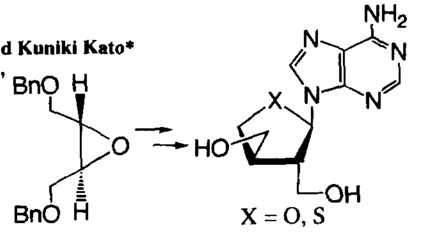
m-Xylylene type dithioureas self-assemble to form an orthogonal dimer through a novel intermolecular hydrogen bonding between the four thiourea groups.



Tetrahedron Letters, **1997**, *38*, 4795

Synthesis of 9-[2',3'-Dideoxy-2',3'-bis-*C*-hydroxymethyl-α-L-threofuranosyl]Adenine and its 4'-Thio Analog as Potential Antiviral Agents

Yoshiko Kikuchi, Hiroko Kurata, Shigeru Nishiyama, Shosuke Yamamura, and Kuniki Kato*
Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi, Yokohama 223, Japan
Research Laboratories, Pharmaceuticals Group, Nippon Kayaku Co. Ltd., Shimo, Kita-ku, Tokyo 115, Japan

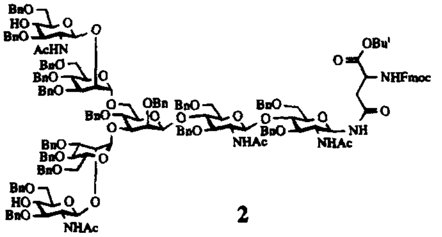


Tetrahedron Letters, **1997**, *38*, 4799

A Practical and Efficient Synthesis of Complex-type Biantennary Heptasaccharide-asparagine Conjugate, a Key Building Block for the Synthesis of Complex N-Linked Glycopeptides

Zhong-Wu Guo[a], Yoshiaki Nakahara[a*], Tomoya Ogawa[a,b*]
a. The Institute of Physical and Chemical Research (RIKEN), Wako-shi, Saitama; Japan; b. Graduate School for Agricultural and Life Sciences, The University of Tokyo, Tokyo, Japan

Compound **2** was synthesized from monosaccharide units **3**, **4**, **6**, **7** and **8** in 7 steps, 18.4% overall yield.

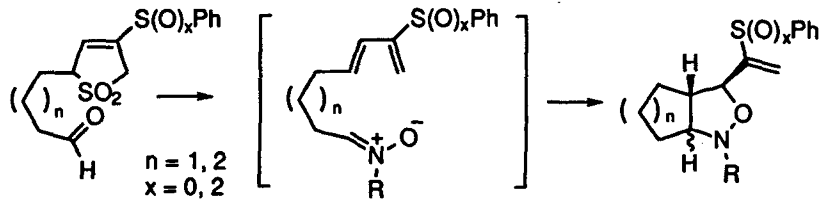


2

Tetrahedron Letters, **1997**, *38*, 4803

INTRAMOLECULAR CYCLOADDITION OF NITRONES WITH SULFUR-SUBSTITUTED DIENES AND ITS SYNTHETIC APPLICATIONS

Shang-Shing P. Chou* and Yu-Ju Yu, Department of Chemistry, Fu Jen Catholic University
Taipei, Taiwan 242, Republic of China



Tetrahedron Letters, **1997**, *38*, 4807

PALLADIUM-CATALYZED AMINATION OF ARYL CHLORIDES.

Nagavelli Prabhakar Reddy and Masato Tanaka
National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305, Japan

$Pd(PCy_3)_2Cl_2$ efficiently catalyzed the amination of aryl chlorides with secondary amines.

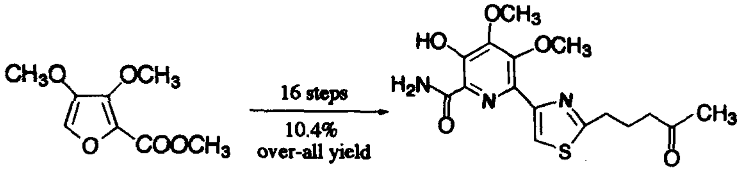
$$\text{Ar-Cl} + \text{R'(R)NH} \xrightarrow[\text{NaO}^t\text{Bu, toluene, 120 °C, 6-12 h}]{Pd(PCy_3)_2Cl_2} \text{Ar-N(R)R'}$$

Tetrahedron Letters, **1997**, *38*, 4811

TOTAL SYNTHESIS OF ANTIBIOTIC KARNAMICIN B1

Kazuyuki Umemura,* Koichi Watanabe, Kazumasa Ono, Masanori Yamaura, and Juji Yoshimura

College of Science and Engineering,
Iwaki Meisei University, Iwaki,
Fukushima 970, Japan



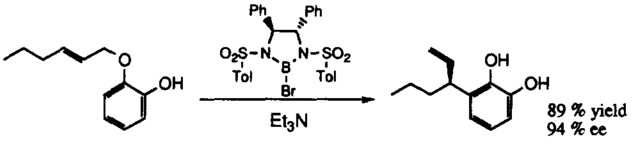
Karnamicin B1

Tetrahedron Letters, **1997**, *38*, 4815

ENANTIOSELECTIVE AROMATIC CLAISEN REARRANGEMENT

Hisanaka Ito, Azusa Sato, and Takeo Taguchi*
Tokyo University of Pharmacy and Life Science, 1432-1 Horinouchi, Hachioji, Tokyo 192-03, Japan

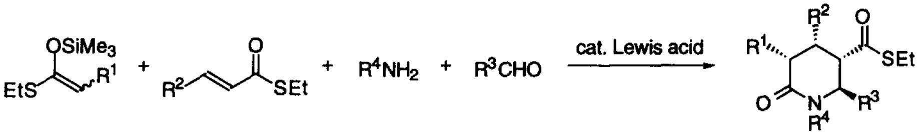
The development of a highly enantioselective aromatic Claisen rearrangement was achieved by the reaction of catechol mono allylic ethers with the chiral boron reagent.



Tetrahedron Letters, **1997**, *38*, 4819

THREE-COMPONENT OR FOUR-COMPONENT COUPLING REACTIONS LEADING TO δ-LACTAMS. FACILE SYNTHESI OF γ-ACYL-δ-LACTAMS FROM SILYL ENOLATES, α,β-UNSATURATED THIOESTERS, AND IMINES or AMINES AND ALDEHYDES VIA TANDEM MICHAEL-IMINO ALDOL REACTIONS,

S. Kobayashi,* R. Akiyama, M. Moriwaki, Department of Applied Chemistry, Faculty of Science, Science University of Tokyo (SUT), and CREST, Japan Science and Technology Corporation (JST), Kagurazaka, Shinjuku-ku, Tokyo 162

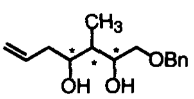


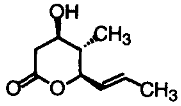
Tetrahedron Letters, **1997**, *38*, 4823

ENANTIOSELECTIVE PREPARATION OF 1-BENZYLOXY-3-METHYL-6-HEPTENE-2,4-DIOLS: TOTAL SYNTHESIS OF (+)-PRELACTONE C

Tomoyuki Esumi, Hiroko Fukuyama, Reiko Oribe, Kaori Kawazoe,
Yoshiharu Iwabuchi, Hiroshi Irie, and Susumi Hatakeyama*
Faculty of Pharmaceutical Sciences, Nagasaki University, Nagasaki 852, Japan

All stereoisomers of 1-benzyloxy-3-methyl-6-heptene-2,4-diol were prepared in enantiomerically pure forms and the first total synthesis of (+)-prelactone C was achieved utilizing the (2*S*,3*S*,4*R*)-isomer as a chiral building block.



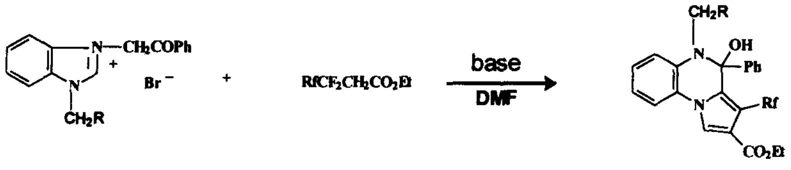


(+)-prelactone C

Tetrahedron Letters, **1997**, *38*, 4827

A NEW APPROACH TO PYRROLO[1,2-a]QUINOXALINE DERIVATIVES

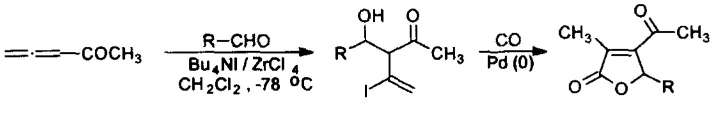
Xue-chun Zhang , Wei-yuan Huang *Shanghai Institute of Organic Chemistry,*
Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China



Tetrahedron Letters, **1997**, *38*, 4831

A CONVENIENT SYNTHESIS OF 3-IODOHOMOALLYLIC ALCOHOLS AND THE FURTHER TRANSFORMATION TO α,β-UNSATURATED γ-LACTONES

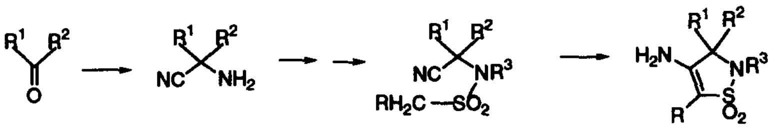
Chunming Zhang and Xiyan Lu*, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences,
354 Fenglin Lu, Shanghai 200032, China



Tetrahedron Letters, **1997**, *38*, 4835

FROM α,α-DISUBSTITUTED α-AMINONITRILES TO HETEROCYCLES: SYNTHESIS OF DERIVATIVES OF 4-AMINO-2,3-DIHYDROISOTHIAZOLE 1,1-DIOXIDE, A NEW HETEROCYCLIC RING SYSTEM

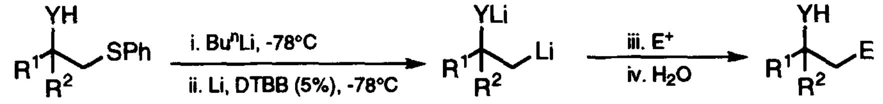
**José L. Marco* and Simon Ingate. Instituto de Química Orgánica General (CSIC),
Juan de la Cierva, 3; 28006-Madrid, Spain.**



Tetrahedron Letters, **1997**, *38*, 4837

β-FUNCTIONALISED ORGANOLITHIUM COMPOUNDS THROUGH A SULFUR-LITHIUM EXCHANGE

F. Foubelo, A. Gutiérrez and M. Yus*
Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Alicante, Apdo. 99, 03080 Alicante, Spain



1 **2** **3** (24-99%)

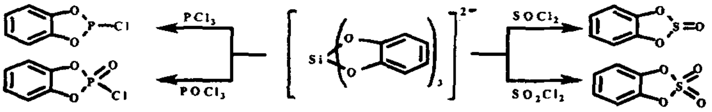
[Y = O, PhN; E^+ = D_2O, Bu^tCHO, PhCHO, Me_2CO, $(CH_2)_5CO$]

Tetrahedron Letters, **1997**, *38*, 4841

HIGH YIELD SYNTHESIS OF CYCLIC PHOSPHITES, PHOSPHATES, SULPHITES AND SULPHATES OF CATECHOL AND GLYCOL MEDIATED BY HYPERVALENT SILICON CENTRES.

J.V. Kingston and M.N. Sudheendra Rao*, Department of Chemistry,
Indian Institute of Technology, Madras 600 036, INDIA

Reactions of catecholato/glycolato hypervalent silicon species with PCl_3. $POCl_3$. $SOCl_2$ and SO_2Cl_2 afford high yield and convenient synthesis of the corresponding cyclic derivatives

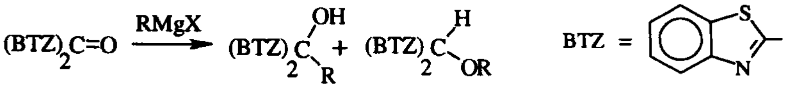


Tetrahedron Letters, 1997, 38, 4845

Unexpected Regioselectivity in the Attack of Vinyl Grignard Reagents to Bis(2-benzothiazolyl) Ketone

Carla Boga*, Luciano Forlani and Paolo E. Todesco
Dipartimento di Chimica Organica "A. Mangini", Università di Bologna,
Viale Risorgimento 4, 40136, Bologna Italia.

The addition of vinyl Grignard reagents to bis(2-benzothiazolyl) ketone affords the unexpected *O*-alkylation products in very high yields.



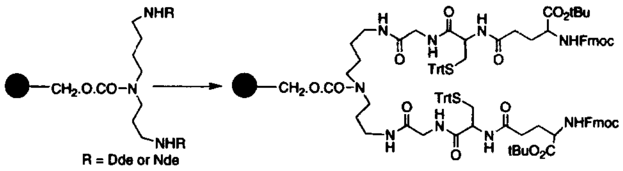
$(BTZ)_2C{=}O \xrightarrow{RMgX} (BTZ)_2C(OH)R + (BTZ)_2C(H)OR$

Tetrahedron Letters, 1997, 38, 4849

SOLID PHASE APPLICATIONS OF Dde AND THE ANALOGUE Nde: SYNTHESIS OF TRYPANOTHIONE DISULPHIDE

Barrie Kellam, Barrie W. Bycroft* and Siri Ram Chhabra
Department of Pharmaceutical Sciences, University of Nottingham,
University Park, Nottingham NG7 2RD, England

An efficient solid phase synthesis of trypanothione disulphide utilizing *bis*-Dde and Nde spermidine derivatives selectively protected on the primary amines and attached via the secondary amine to the HMPA resin is described.

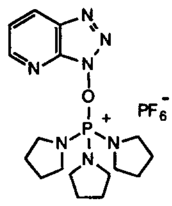


Tetrahedron Letters, 1997, 38, 4853

ON THE USE OF PyAOP, A PHOSPHONIUM SALT DERIVED FROM HOAt, IN SOLID-PHASE PEPTIDE SYNTHESIS

F. Albericio, M. Cases, J. Alsina, S.A. Triolo, L.A. Carpino, and S.A. Kates
Department of Organic Chemistry, University of Barcelona, E-08028 Barcelona, Spain
Departament of Chemistry, University of Massachusetts, Amherst, MA-01003, U.S.A.
PerSeptive Biosystems, Inc. 500 Old Connecticut Path, Framingham, MA-01701, U.S.A.

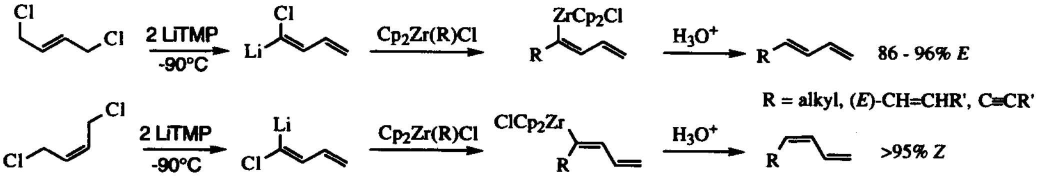
Phosphonium derivatives of HOAt such as PyAOP are useful for the solid-phase preparation of a range of peptides that include those incorporating hindered amino acids, difficult short sequences, and cyclic systems. An advantage relative to uronium salts is that excess PyAOP does not undergo the detrimental side-reaction at the amino terminus which blocks further chain assembly.



Tetrahedron Letters, 1997, 38, 4857

ZIRCONIUM MEDIATED SYNTHESIS. CONVERGENT ACCESS TO TERMINAL TRIENES, DIENES, AND DIENYNES.

Aleksandr Kasatkin and Richard J. Whitby*, Department of Chemistry,
The University, Southampton, SO17 1BJ, U. K.

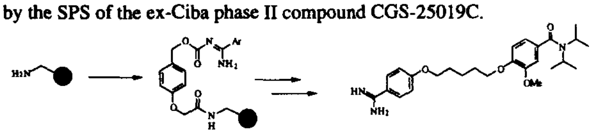


Tetrahedron Letters, **1997**, *38*, 4861

A Linker for Amidines in Solid Phase Synthesis.

Patrick Roussel[a], Mark Bradley*[a], Ian Matthews[b] and Peter Kane[b].
Department of Chemistry, University of Southampton, Southampton SO17 1BJ, U.K.[a]
Novartis Pharmaceuticals, Horsham, Sussex, U.K.[b]

The development of a linker for the important amidine pharmacophore is reported. Utility is demonstrated by the SPS of the ex-Ciba phase II compound CGS-25019C.

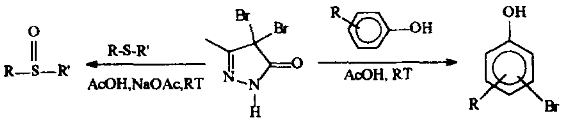


Tetrahedron Letters, **1997**, *38*, 4865

4,4-DIBROMO-3-METHYLPYRAZOL-5-ONE: NEW APPLICATIONS FOR SELECTIVE MONOBROMINATION OF PHENOLS AND OXIDATION OF SULFIDES AND SULFOXIDES.

Sabir H. Mashraqui*, Chandrashekar D. Mudaliar and Harini Hariharasubrahmanian,
Department of Chemistry, University of Mumbai, Vidyanagari, Santacruz (E), Mumbai-400098, INDIA.

Dibromopyrazolone 1 selectively monobrominated phenols and oxidised sulfides to sulfoxides in high yields.



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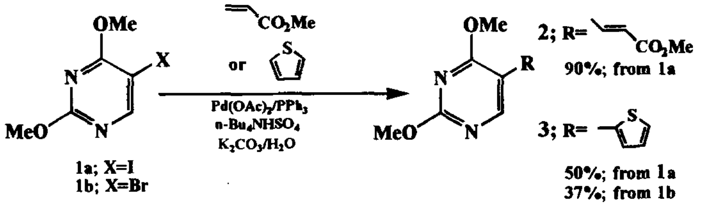
Tetrahedron Letters, **1997**, *38*, 4869

Palladium catalysed Carbomethoxyvinylation and Thienylation of 5-Iodo(Bromo)-2,4-Dimethoxypyrimidine in Water

I.Basnak, S.Takatori, R.T.Walker*, School of Chemistry, The University of Birmingham, Birmingham B15 2TT, UK.

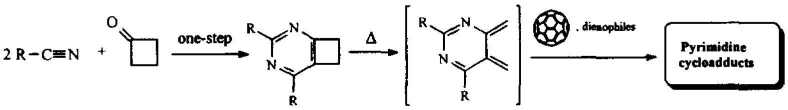


Tetrahedron Letters, **1997**, *38*, 4873

AN EXPEDITIOUS PROCEDURE FOR THE GENERATION OF PYRIMIDINE *ORTHO*-QUINODIMETHANES.

Antonio Herrera,* Roberto Martínez, Beatriz González, Nazario Martín, * Carlos Seoane and Beatriz Illescas, Departamento de Química Orgánica I
Facultad de Ciencias Químicas, Universidad Complutense, Madrid, E-28040 Spain.

One step synthesis of 2,4-dialkyl and 2,4-diaryl substituted 5,6-dihydrocyclobuta[*d*]pyrimidines as new precursors for pyrimidine *ortho*-quinodimethanes and their trapping with different dienophiles and C_{60} is reported.



Tetrahedron Letters, **1997**, *38*, 4877

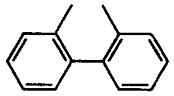
PREPARATION AND ^{13}C NMR SPECTROSCOPY OF ^{13}C-1 LABELLED 2,2-DIARYL-1-FLUORO-1-LITHIOALKENES

By Andrew Pelter*[a] and Jaroslav Kvicala[b]

[a]Department of Chemistry, University of Wales Swansea, Singleton Park, Swansea, SA2 8PP, UK.
[b]Department of Organic Chemistry, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic.

First synthesis and ^{13}C NMR of $Ar_2C = {}^{13}CLiF$

$Ar_2 = Ph_2$ or



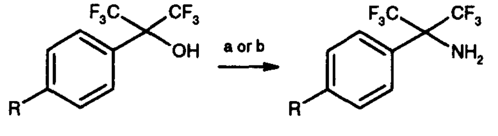
Tetrahedron Letters, **1997**, *38*, 4881

GENERATION OF DOUBLY TRIFLUOROMETHYLSUBSTITUTED CARBOCATIONS:

SYNTHESIS OF α,α-BIS(TRIFLUOROMETHYL)BENZYLAMINES.

Marcella Nesi*, Maria Gabriella Brasca, Antonio Longo, Walter Moretti, Achille Panzeri; Pharmacia & Upjohn, Viale Pasteur 10, 20014 Nerviano (MI), Italy

α,α-Bis(trifluoromethyl)benzyltriflates offer a convenient access to the corresponding amines through either an azide desplacement or a Ritter type reaction.

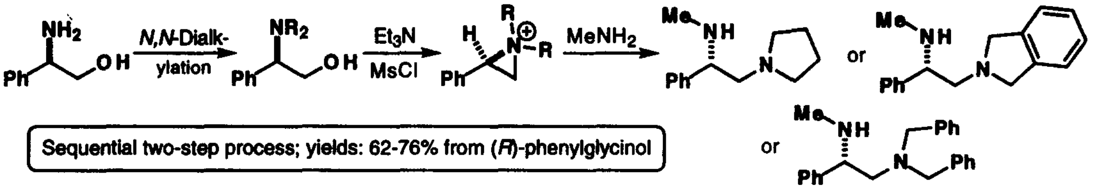


a) (1) MeOK, $(CF_3SO_2)_2O$, Toluene; (2) NaN_3, TFA, r.t.; (3) Raney-Ni.
b) (1) CH_3CN, TFA, TFAA; (2) 98% H_2SO_4, reflux.

Tetrahedron Letters, **1997**, *38*, 4885

AZIRIDINIUM IONS FROM PHENYLGLYCINOL – A NEW APPROACH TO THE SYNTHESIS OF CHIRAL DIAMINES

Simon E. de Sousa and Peter O'Brien*
Department of Chemistry, University of York, Heslington, York YO1 5DD UK



Sequential two-step process; yields: 62-76% from (*R*)-phenylglycinol

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Tetrahedron Letters, **1997**, *38*, 4889

THE ABSOLUTE STEREOCHEMISTRY OF THE NEW ZEALAND SHELLFISH TOXIN GYMNODIMINE

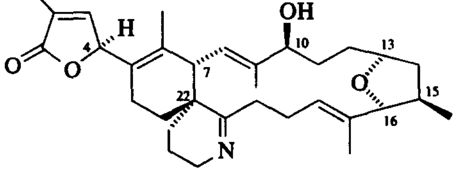
Michael Stewart[a], John W Blunt[a], Murray H G Munro[a], Ward T Robinson[a] & Donald J Hannah[b]

[a] Department of Chemistry, University of Canterbury, Private Bag 4800, Christchurch, New Zealand

[b] Institute of Environmental Science & Research Ltd, PO Box 30-547, Lower Hutt, New Zealand

The absolute stereochemistry of gymnodimine has been determined as 4*S*, 7*S*, 10*S*, 13*R*, 15*R*, 16*R*, 22*R* from the crystal structure of the *p*-bromobenzamide derivative of gymnodamine, formed on reduction of gymnodimine.

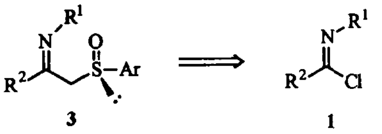
gymnodimine



Tetrahedron Letters, **1997**, *38*, 4891

A NEW AND GENERAL SYNTHESIS OF *N*-SUBSTITUTED FLUORINATED β-IMINOSULFOXIDES

Santos Fustero,* Antonio Navarro, and Amparo Asensio
Departamento de Química Orgánica, Facultad de Farmacia, Avda. Vicente Andrés Estellés s/n, 46100 Burjassot, Valencia, Spain.



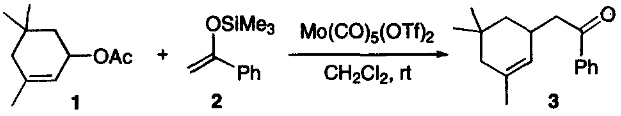
γ-Fluorinated *N*-substituted β-iminosulfoxides 3 are obtained by reaction of metalated methyl sulfoxides 2 with fluorinated imidoyl chlorides 1 in high yields.

Tetrahedron Letters, **1997**, *38*, 4895

MOLYBDENUM(II)-CATALYZED ALLYLIC SUBSTITUTION

A. V. Malkov, I. Baxendale, D. J. Mansfield, and P. Kočovský*
Department of Chemistry, University of Leicester, Leicester LE1 7RH, U.K.

The new Mo(II) triflate complex $Mo(CO)_5(OTf)_2$ has been found to catalyze the C-C bond forming allylic substitution with silyl enol ethers derived from β-dicarbonyls and from simple ketones (e.g., 1 + 2 → 3; 65%) as nucleophiles.

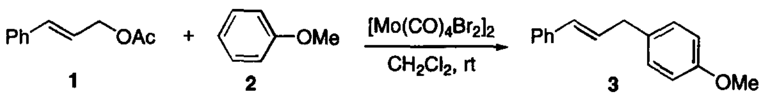


Tetrahedron Letters, **1997**, *38*, 4899

MOLYBDENUM(II)-CATALYZED ALKYLATION OF ELECTRON-RICH AROMATICS WITH ALLYLIC ACETATES

A. V. Malkov, S. L. Davis, W. L. Mitchell, and P. Kočovský*
Department of Chemistry, University of Leicester, Leicester LE1 7RH, U.K.

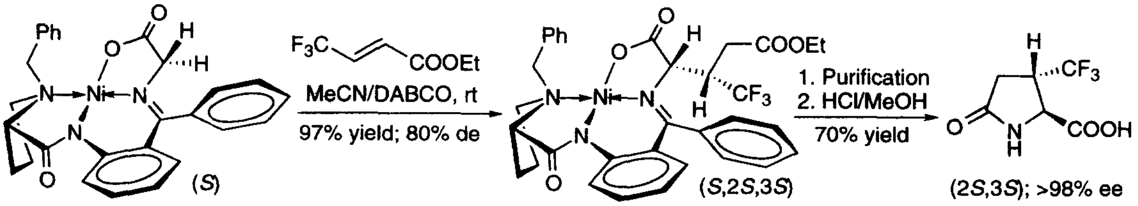
The molybdenum(II) complex $[Mo(CO)_4Br_2]_2$ has been found to catalyze allylic substitution with aromatic ethers, e.g., anisole (2), as nucleophiles. The reaction is remarkably *para*-selective (e.g., 1 + 2 → 3; 68%).



Tetrahedron Letters, **1997**, *38*, 4903

An Efficient Asymmetric Synthesis of (2*S*,3*S*)-3-Trifluoromethylpyroglutamic Acid

V.A.Soloshonok,* *National Industrial Research Institute of Nagoya, Japan*; D.V.Avilov, V.P.Kukhar *Institute of Bioorganic Chemistry and Petrochemistry, Ukraine*; Luc Van Meervelt, N. Mischenko *K. U. Leuven - Department of Chemistry, Belgium*



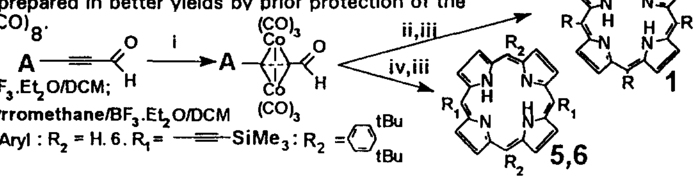
Tetrahedron Letters, **1997**, *38*, 4905

IMPROVED SYNTHESIS OF 10,20-BIS AND 5,10,15, 20-TETRA ETHYNYLPORPHYRINS VIA ETHYNYL PROTECTION WITH DICOBALT OCTACARBONYL.

Lionel R. Milgrom, Robert D. Rees, and Gokhan Yahioglu,
Department of Chemistry, Brunel University, Uxbridge, Middlesex, UB8 3PH, UK.

Compounds **1**, **5**, and **6** are prepared in better yields by prior protection of the precursor ethynal with $Co_2(CO)_8$.

A = Aryl or $SiMe_3$



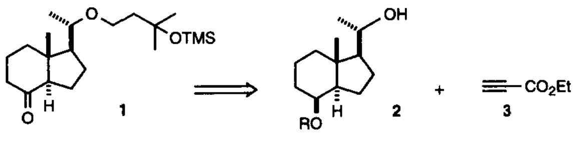
i, $Co_2(CO)_8$/THF/RT; ii, pyrrole/BF_3.Et_2O/DCM;
iii, $Fe(ClO_4)_3$/MeOH; iv, 5-R_2-dipyrromethane/BF_3.Et_2O/DCM
1. R = —≡—Aryl. 5. R_1 = —≡—Aryl : R_2 = H. 6. R_1 = —≡—$SiMe_3$: R_2 =

Tetrahedron Letters, **1997**, *38*, 4909

A NEW APPROACH TO THE SYNTHESIS OF THE 25-HYDROXY-22-OXAVITAMIN D_3 SIDE CHAIN.

Yagamare Fall
Departamento de Química Orgánica y Unidad Asociada al CSIC,
Facultad de Química, Universidad de Santiago de Compostela
15706 Santiago de Compostela, Spain.

An efficient new method for the construction of 25-hydroxy-22-oxavitaminD_3side chains is described which is based on the reaction of ethyl propiolate with alcohol **2** in the presence of a tertiary amine.

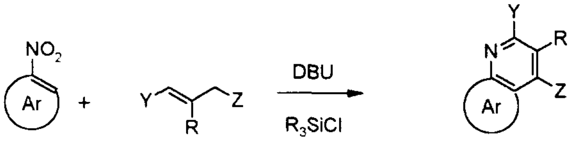


Tetrahedron Letters, **1997**, *38*, 4913

NEW CONCEPT IN SYNTHESIS OF FUSED SIX-MEMBERED NITROGEN HETEROCYCLES. SILANE- MEDIATED DIRECT CONDENSATION OF NITROARENES WITH ALLYLIC CARBANIONS.

Zbigniew Wróbel, Institute of Organic Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, PL-01-224, Poland.

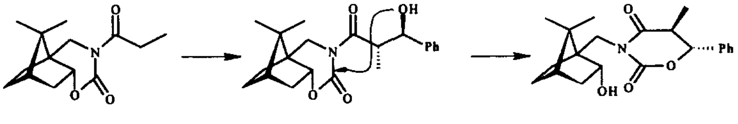
Six-membered nitrogen heterocycles were synthesized *via* DBU/ silane mediated double condensation of the allylic CH-acids with nitroarenes.



Tetrahedron Letters, **1997**, *38*, 4917

INTRAMOLECULAR RING CLEAVAGE OF CHIRAL TERPENOID-DERIVED OXAZINONE *VIA* ASYMMETRIC *ANTI*-ALDOL REACTION : UNEXPECTED ENTRY TO A *N*-SUBSTITUTED TETRAHYDRO-1,3-OXAZINE-2,4-DIONE DERIVATIVE.

Tariq Abbas[a], J.I.G. Cadogan[b], Allan A. Doyle[a], Ian Gosney[a], Philip K.G. Hodgson[c], Garnet E. Howells[a], Alison N. Hulme[a], Simon Parsons[a] and Ian H. Sadler[a], [a]Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland; [b]Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, England; [c]B.P.Chemicals Ltd, Research Laboratory, Dunstan Building, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN, England



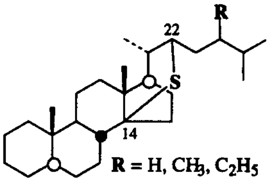
Tetrahedron Letters, **1997**, *38*, 4921

14β,22*R*-EPITHIOSTERANES, A NOVEL SERIES OF FOSSIL STEROIDS WIDESPREAD IN SEDIMENTS

Anke Behrens, Philippe Schaeffer and Pierre Albrecht.

Laboratoire de Géochimie Organique, URA 31 du CNRS, Institut de Chimie,
Université Louis Pasteur, 1 rue Blaise Pascal, 67000 Strasbourg, France.

A novel series of 14β,22*R*-epithiosteranes **1** was identified by NMR in a sulfur-rich sediment. They presumably result from intramolecular incorporation of sulfur on steradiene precursors of algal origin.



R = H, CH_3, C_2H_5

14β,22*R*-Epithiosteranes **1**