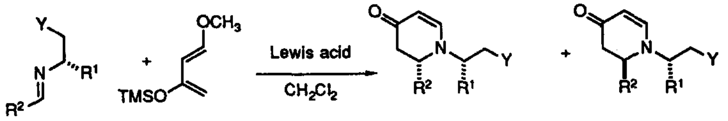
GRAPHICAL ABSTRACTS

Tetrahedron Lett. **1993**, *34*, 5827

Factors Influencing the Stereoselectivity in the Cycloaddition of Imino-Dienophiles Derived from Amino Ethers, Amino Alcohols, and Amino Acid Esters

Paul N. Devine, Michael Reilly and Taeboem Oh*
Department of Chemistry, State University of New York, Binghamton, NY 13902-6000

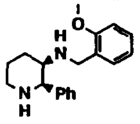


Tetrahedron Lett. **1993**, *34*, 5831

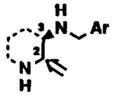
SYNTHESIS OF (±)-CP-99,994: A HIGHLY POTENT SUBSTANCE P ANTAGONIST

Manoj C. Desai*, Peter F. Thadeio and Sheri L. Lefkowitz
Central Research Division, Pfizer Inc., Groton, CT 06340

We report here the synthesis of racemic CP-99,994 *via* a method suitable for producing detailed structural activity relationship (SAR) about generic structure 1.



(±)-CP-99,994



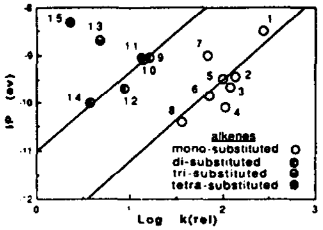
1

Tetrahedron Lett. **1993**, *34*, 5835

DIIMIDE REDUCTION OF REPRESENTATIVE ALKENES AND CORRELATION OF THEIR RELATIVE REACTION RATES WITH CORRESPONDING IONIZATION POTENTIALS.

Donna Nelson,* Robert Henley, Ziyun Yao, and Terrill Smith, Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK 73019

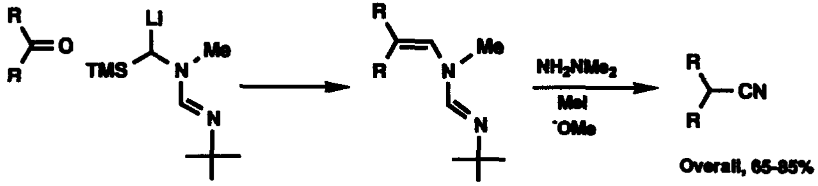
The plot of log k_{rel} of alkenes vs. IP's exhibits a natural separation into sterically similar groups, indicating the importance of steric effects. Within each group, a good correlation is observed with a lower IP corresponding to a higher rate, demonstrating electronic effects in sterically similar molecules.



Tetrahedron Lett. **1993**, *34*, 5839

Formamidine Anions in Synthesis. The One-Carbon Homologation of Aldehydes and Ketones to Nitriles

Braulio Santiago and A. I. Meyers*
Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523 U.S.A.



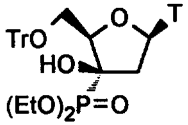
Overall, 65-85%

Tetrahedron Lett. **1993**, *34*, 5843

Synthesis of Nucleoside α-Hydroxy Phosphonates

Wenkui Lan McEldoon, Koo Lee and David F. Wiemer*
Department of Chemistry, University of Iowa, Iowa City, Iowa 52242

Nucleophilic addition of diethyl phosphite anion to 2'- or 3'-keto nucleosides results in an efficient synthesis of 2'-ß-hydroxy-2'-α-phosphono- or 3'-ß-hydroxy-3'-α-phosphononucleosides. The stereochemistry of one such adduct, 5'-O-trityl-3'-ß-hydroxy-3'-α-phosphonothymidine, was determined by single crystal diffraction analysis.

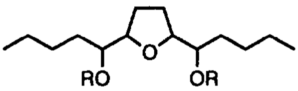


Tetrahedron Lett. **1993**, *34*, 5847

STEREOCHEMISTRY OF MONO-TETRAHYDROFURANYL MOIETY IN CYTOTOXIC POLYKETIDES.
PART A: SYNTHESIS OF MODEL COMPOUNDS

Jonathan B. Gale, Jing-Guang Yu, Xiufeng E. Hu, Anakshi Khare, David K. Ho and John M. Cassady*
Division of Medicinal Chemistry and Pharmacognosy, College of Pharmacy
The Ohio State University, Columbus, Ohio 43210, U. S. A.

Six dimesitoate esters of α,α-dibutyl-2,5-tetrahydrofuran-dimethanols of different relative stereochemistry were synthesized



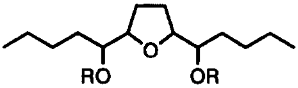
1 (*thr-cis-thr*)
2 (*ery-cis-ery*)
3 (*thr-cis-ery*)
4 (*thr-trans-thr*)
5 (*thr-trans-ery*)
6 (*ery-trans-ery*)

Tetrahedron Lett. **1993**, *34*, 5851

STEREOCHEMISTRY OF MONO-TETRAHYDROFURANYL MOIETY IN CYTOTOXIC POLYKETIDES.
PART B: APPLICATION OF PROTON CHEMICAL SHIFT PATTERNS

Jonathan B. Gale, Jing-Guang Yu, Anakshi Khare, Xiufeng E. Hu, David K. Ho and John M. Cassady*
Division of Medicinal Chemistry and Pharmacognosy, College of Pharmacy
The Ohio State University, Columbus, Ohio 43210, U. S. A.

Proton chemical shift patterns of six dimesitoate esters **1**–**6** is applied to the assignment of relative stereochemistry of the mono-tetrahydrofuranyl moiety of cytotoxic polyketides.



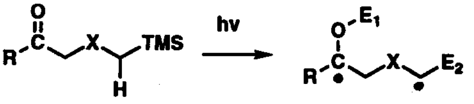
1 (*thr-cis-thr*)
2 (*ery-cis-ery*)
3 (*thr-cis-ery*)
4 (*thr-trans-thr*)
5 (*thr-trans-ery*)
6 (*ery-trans-ery*)

Tetrahedron Lett. **1993**, *34*, 5855

The Operation of H-Atom and TMS-Group Transfer Processes in the Photochemistry of Silylamidoalkyl- and Silylalkyl-Ketones and -Phthalimides.

Y. J. Lee, C. P. Lee, Y. T. Jeon, P. S. Mariano, U. C. Yoon,[+] D. U. Kim,[+] J. C. Kim,[+] J. G. Lee,[+] Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland, 20742, USA and [+]Department of Chemistry, Pusan National University, Pusan, 609-735, Korea.

Photoreactions occur by competitive H- and TMS-transfer mechanisms.



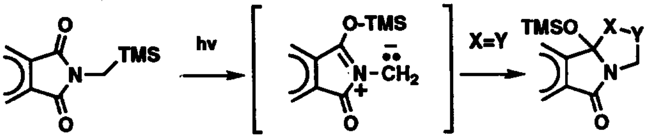
(E_1 or E_2 =H or TMS)

Tetrahedron Lett. **1993**, *34*, 5859

A Novel Azomethine Ylid Forming Photoreaction of N-Trimethylsilylmethylphthalimide.

U. C. Yoon, D. U. Kim, J. C. Kim, J. G. Lee, P. S. Mariano[+], Y. J. Lee[+], H. L. Ammon[+] Department of Chemistry, Pusan National University, Pusan, 609-735, Korea and [+]Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland, 20742, USA

Photoreaction leads to azomethine ylid by novel C to O TMS-migration process.

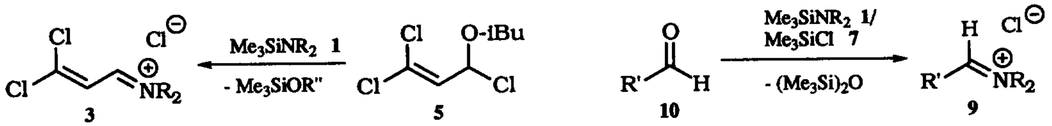


Tetrahedron Lett. **1993**, *34*, 5863

A NOVEL AND SIMPLE METHOD FOR THE PREPARATION OF IMINIUM SALTS

Ullrich Jahn and Werner Schroth*
Institut für Organische Chemie der Martin-Luther-Universität Halle-Wittenberg, D-06099 Halle/Saale

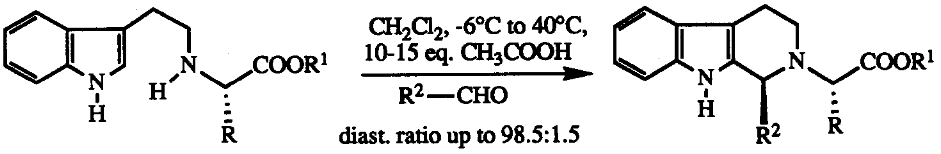
α-Chloroether 5 and carbonyl derivatives 10 are efficiently converted into iminium salts 3 and 9 by reaction with trimethylsilyl-N,N-dialkylamines 1 and the system trimethylsilyl-N,N-dialkylamine/trimethylchlorosilane, respectively.



Tetrahedron Lett. **1993**, *34*, 5867

Asymmetric Pictet-Spengler Reactions Employing Amino Acid Esters as Mediators of Selectivity

Herbert Waldmann*, Gunther Schmidt, Martin Jansen and Jutta Geb
Universität Karlsruhe, Institut f. Organ. Chemie, R.-Willstätter-Allee 2, D-76128 Karlsruhe

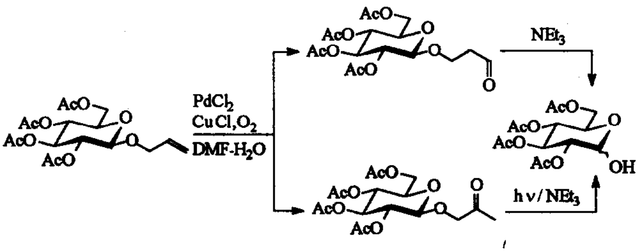


Tetrahedron Lett. **1993**, *34*, 5871

A NEW METHOD FOR THE CLEAVAGE OF ALLYL GLYCOSIDES

Joachim Lüning, Uwe Möller,
Norbert Debski, and Peter Welzel*
Fakultät für Chemie der Ruhr-Universität
D-44780 Bochum (Germany)

Allyl glycosides can be cleaved by Wacker oxidation followed by photolysis in the presence of triethylamine.

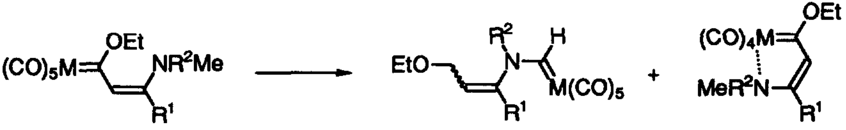


Tetrahedron Lett. **1993**, *34*, 5875

A NOVEL REARRANGEMENT OF THE CARBENE LIGAND IN (Z)-(2-DI-ALKYLAMINOETHENYL)CARBENE COMPLEXES.

Michael Duetsch, Frank Stein and Armin de Meijere,* Institut für Organische Chemie der Georg-August-Universität Göttingen, Tammannstraße 2, D-37077 Göttingen, Germany

(Z)-(2-Dialkylamino)carbene-chromium and -tungsten complexes rearrange to aminomethylene complexes and/or chelated tetracarbonyl complexes upon heating.

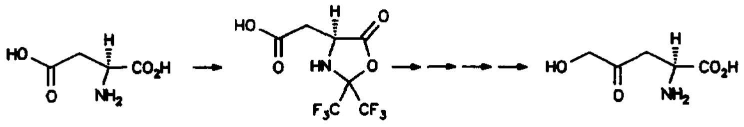


Tetrahedron Lett. **1993**, *34*, 5879

An Efficient Synthesis of 5-Hydroxy-4-oxo-L-norvaline from L-Aspartic Acid

Alexander Golubev, Norbert Sewald, and Klaus Burger*
Organisch-Chemisches Institut der Technischen Universität München, Lichtenbergstraße 4, D-85747 Garching, Germany

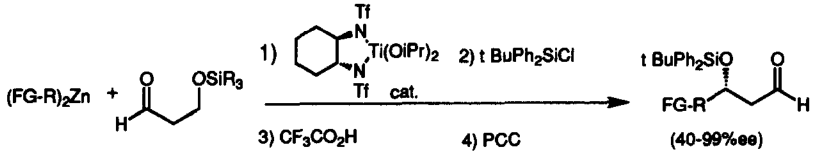
A synthesis of the antibiotic (-)-HON (5-hydroxy-4-oxo-L-norvaline, RI-331) from L-aspartic acid using hexafluoroacetone as protecting reagent is described.



Tetrahedron Lett. **1993**, *34*, 5881

A New Catalytic Asymmetric Approach to Polyfunctional Aldol Products Mediated by Zinc Organometallics

Paul Knochel*, Walter Brieden, Michael J. Rozema and Christina Eisenberg
Fachbereich Chemie der Philipps-Universität Marburg, Hans-Meerwein-Straße, 35043 Marburg (Germany)

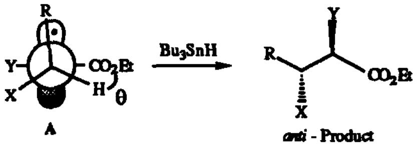


Tetrahedron Lett. **1993**, *34*, 5885

The Effect of Polar Substituents on the Conformation and Stereochemistry of Enolate Radicals

*B. Giese**, *W. Damm*, *F. Wetterich*, *H.G. Zeitz*, Department of Chemistry, University of Basel, 4056 Basel, Switzerland.
J. Rancourt, *Y. Guindon**, Biomega/Boehringer Ingelheim Research Inc., Laval, Québec, Canada H7S 2G5 and Department of Chemistry, Université de Montréal, Montréal, Québec, Canada H7S 2G5

Enolate radicals prefer conformation A. But the energy, the dihedral angle, and the stereoselectivity of the formation of the *anti*-product depend largely on polar effects of substituents X and Y.

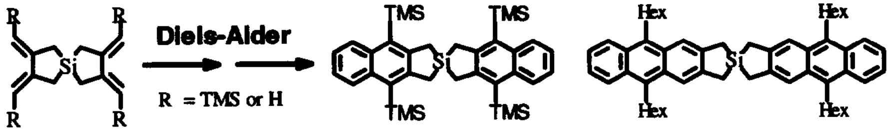


Tetrahedron Lett. **1993**, *34*, 5889

Orthogonal Connection of Acenes via Two-Fold Diels-Alder Reactions

Thomas Horn, Martin Baumgarten, Liletta Gerghel, Volker Enkelmann and Klaus Müllen,*
Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55021 Mainz, Germany

Synthesis of new bis-acenes, which stand almost orthogonal to one another; involving silicon-spiro tetraenes.



Tetrahedron Lett. **1993**, *34*, 5893

A Facile and Highly Chemoselective Protection of Primary Hydroxyl Groups with 2-Methyl-1-Butene

Bruno Figadère*, Xavier Franck and André Cavé
Laboratoire de Pharmacognosie, associé au CNRS (BIOCIS) Faculté de Pharmacie 92290 Châtenay-Malabry (France)

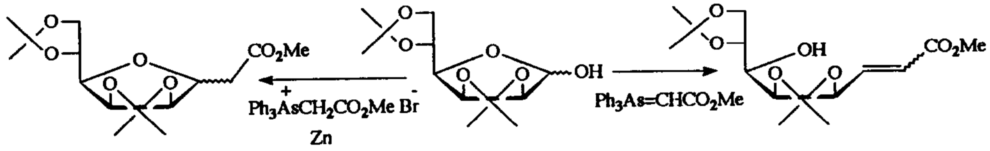
A new protection of primary hydroxyl groups is described, resulting of a highly chemoselective addition of primary hydroxyl groups with 2-methyl-1-butene, *via* a Markovnikov hydration, to give rise to *tert*-amyl ethers (= *tam*-ether).

$$\underset{\textbf{1 a-g}}{RCH_2OH} + CH_3CH_2C(CH_3){=}CH_2 \xrightarrow[CH_2Cl_2;\ 20°C;\ 24\ h]{BF_3.OEt_2\ cat.} \underset{\textbf{2 a-g}}{RCH_2OC(CH_3)_2CH_2CH_3} \equiv RCH_2OTAM$$

Tetrahedron Lett. **1993**, *34*, 5895

SYNTHESES DE C-GLYCOSIDES: UTILISATIONS D'UN DERIVE DE L'ARSENIC

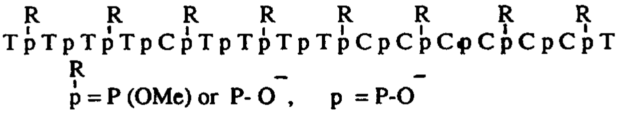
Lydie Dheilly, Catherine Lièvre, Catherine Fréchou et Gilles Demailly*, Laboratoire de Chimie Organique, Groupe de Valorisation des Glucides, Faculté des Sciences. 33 rue Saint Leu, 80039 Amiens (France)
Fax: (33) 22 82 75 76



Tetrahedron Lett. **1993**, *34*, 5899

Synthesis and Physicochemical Studies of Partially Phosphate-Methylated Oligodeoxyribonucleotides.

Serge Vinogradov⁺, Ulysse Asseline and Nguyen Thanh Thuong
Centre de Biophysique Moléculaire, 1A Avenue de la Recherche Scientifique-45071 Orléans Cedex 2, France.
⁺*The Research Center of Molecular Diagnostics and Therapy, 8 Simpheropolsky Bd. 113149 Moscow. Russia.*



$$T\overset{R}{p}TpT\overset{R}{p}TpC\overset{R}{p}TpT\overset{R}{p}TpT\overset{R}{p}CpC\overset{R}{p}CpC\overset{R}{p}CpC\overset{R}{p}T$$

$$\overset{R}{p} = P\,(OMe) \text{ or } P\text{-}\bar{O}, \quad p = P\text{-}\bar{O}$$

Tetrahedron Lett. **1993**, *34*, 5903

Substituent Effect on Gas Phase Basicity of 1-Phenylpropyne. Thermodynamic Stability and Resonance Demand of 1-Phenylpropenyl Cations

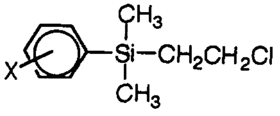
Shinjiro KOBAYASHI,* Takatsugu MATSUMOTO, Hiroshi TANIGUCHI, Masaaki MISHIMA,†* Mizue FUJIO,†† and Yuho TSUNO††*
Department of Chemical Science and Technology, Faculty of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812, Japan
†Institute for Molecular Science, Okazaki 444, Japan
††Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812, Japan

Tetrahedron Lett. **1993**, *34*, 5907

SUBSTITUENT EFFECT ON SOLVOLYSIS OF 2-(ARYLDIMETHYLSILYL)ETHYL CHLORIDES

Ryoji Fujiyama and Toshihiro Munechika
Department of Chemistry, Faculty of Science, Kochi University
Akebono-cho, Kochi, 780 Japan

The analysis of Yukawa-Tsuno LArSR equation on the solvolysis of 3 suggests that the β-silicon effect of 3 is attributed to the cyclic transition state with a positive charge on silicon.



3

Tetrahedron Lett. **1993**, *34*, 5911

A Novel Synthesis of Cyanoalkynes via Iodide-Catalyzed Cyanation of Terminal Acetylenes with Cuprous Cyanide

Fen-Tair Luo* and Ren-Tzong Wang
Institute of Chemistry, Academia Sinica, Nankang, Taipei, Taiwan, ROC

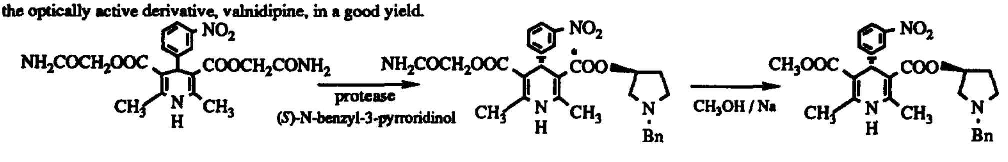
$$\text{R-C}\equiv\text{C-H} \xrightarrow[\substack{\text{cat. NaI, DMSO/CH}_3\text{CN} \\ 50^{\circ}\text{C}}]{\text{CuCN, TMSCl, H}_2\text{O}} \text{R-C}\equiv\text{C-CN}$$

Tetrahedron Lett. **1993**, *34*, 5915

CARBAMOYLMETHYL GROUP AS AN ACTIVATED GROUP IN PROTEASE- AND BASE-CATALYZED TRANSESTERIFICATION OF 1,4-DIHYDROPYRIDINES : A NOVEL ASYMMETRIC SYNTHESIS OF VALNIDIPINE

Yoshihiko Hirose*, Kinya Kariya, Ikuharu Sasaki and Yoshiaki Kurono, Amano Pharmaceutical Co., Ltd., Nishiharu, Nishikasugai, Aichi 481, Japan Kazuo Achiwa*, School of Pharmaceutical Sciences, University of Shizuoka, 52-1 Yada, Shizuoka 422, Japan

The protease-catalyzed and successive base-catalyzed enantioselective transesterifications of 1,4-dihydropyridine were proceeded to give the optically active derivative, valnidipine, in a good yield.

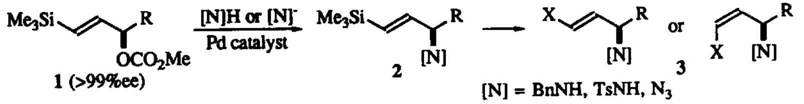


Tetrahedron Lett. **1993**, *34*, 5919

A REGIOCHEMICAL CONTROL IN THE π-ALLYLPALLADIUM SUBSTITUTION. PREPARATION OF OPTICALLY ACTIVE γ-SILYLALLYLAMINES

Hiroshi Inami, Takayori Ito, Hirokazu Urabe, and Fumie Sato*
Department of Biomolecular Engineering, Tokyo Institute of Technology,
4259, Nagatsuta-cho, Midori-ku, Yokohama 227, Japan

Optically active γ-trimethysilylallylamine derivatives 2 were prepared from γ-trimethylsilylallyl carbonates 1. Conversion of 2 to several γ-functionalized allylamine derivatives 3 was also demonstrated.

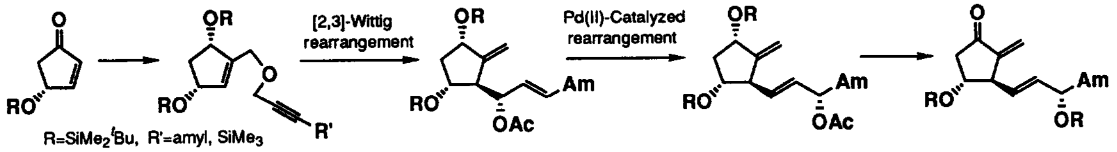


[N] = BnNH, TsNH, N_3

Tetrahedron Lett. **1993**, *34*, 5923

A New Approach to Asymmetric Synthesis of Stork's Prostaglandin Intermediate

M. Nakazawa, Y. Sakamoto, and T. Takahashi*
K. Tomooka, K. Ishikawa, and T. Nakai*
Department of Chemical Technology, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, JAPAN

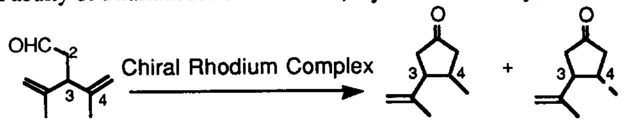


R=$SiMe_2{}^tBu$, R'=amyl, $SiMe_3$

Tetrahedron Lett. **1993**, *34*, 5927

HIGHLY DIASTEREOSELECTIVE, ENANTIOSELECTIVE CYCLIZATION OF SYMMETRICAL 3,4-DISUBSTITUTED 4-PENTENAL USING CHIRAL RHODIUM(I)-COMPLEX

Xiao-Ming Wu, Kazuhisa Funakoshi, Kiyoshi Sakai*
Faculty of Pharmaceutical Sciences, Kyushu University, Fukuoka 812, Japan



Neutral RhCl(R-BINAP) :
97(cis; 3S,4R; >99%e.e.):3(trans)

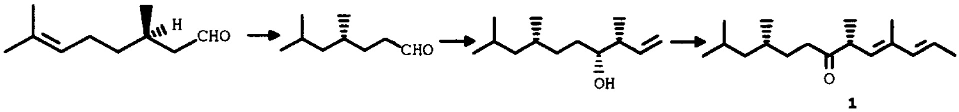
Cationic Rh(R-BINAP)ClO_4 :
3(cis):97(trans; 3S,4S; >99%e.e.)

Tetrahedron Lett. **1993**, *34*, 5931

Enantioselective Synthesis of All Four Stereoisomers of (2*E*, 4*E*)-4,6,10,12-Tetramethyl-2,4-tridecadien-7-one, The Sex Pheromone of *Matsucoccus* Pine Bast Scale

Lin Guo-qiang* and Xu Wei-chu,
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, China

A facile enantioselective synthesis of all four stereoisomers of (2*E*, 4*E*)-4,6,10,12-tetramethyl-2,4-tridecadien-one 1, the primary sex pheromone of *matsucoccus* pine bast scale is described.

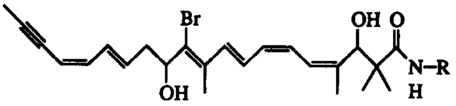


1

Tetrahedron Lett. **1993**, *34*, 5935

CLATHRYNAMIDES A, B, AND C: NOVEL AMIDES FROM A MARINE SPONGE *CLATHRIA* SP. THAT INHIBIT CELL DIVISION OF FERTILIZED STARFISH EGGS

Shinji Ohta,* Hironobu Okada,† Hiroki Kobayashi,† Jose M. Oclarit,†
and Susumu Ikegami*,†
Instrument Center for Chemical Analysis, Hiroshima University,
1-1-89 Higashisenda-machi, Naka-ku, Hiroshima 730, Japan.
†Department of Applied Biochemistry, Hiroshima University,
1-4-4 Kagamiyama, Higashi-Hiroshima, Hiroshima 724, Japan.



1: R = H
2: $R = CH(CH_3)CH_2CH_2CH(OH)CH_3$
3: $R = CH(CH_3)CH_2CH_2COCH_3$

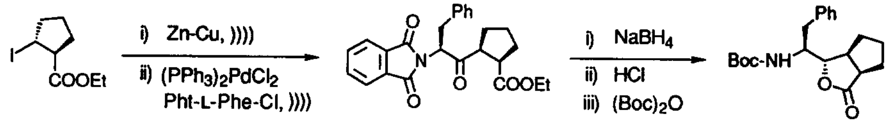
Three novel bromine-containing amides, clathrynamides A (1), B (2), and C (3), were isolated from a marine sponge *Clathria* sp. Their structures were established by spectroscopic data.

Tetrahedron Lett. **1993**, *34*, 5939

A NEW SYNTHETIC ROUTE FOR THE γ-LACTONE PRECURSORS OF HYDROXYETHYLENE DIPEPTIDE ISOSTERES.

Mitsuya Sakurai,*[a] Tadashi Hata,[b] and Yuichiro Yabe,[a] New Lead Research,[a] and Analytical and Metabolic Research Laboratories,[b] Sankyo Co. Ltd., 1-2-58 Hiromachi, Shinagawa-ku, Tokyo, 140, Japan.

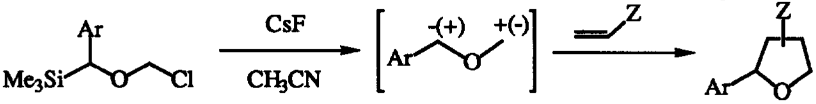
The γ-lactone precursors of Phe-ψ[H.E.]-Ala and Phe-ψ[H.E.]-Pro were obtained from β-iodoesters via δ-phthalimido-γ-ketoesters.



Tetrahedron Lett. **1993**, *34*, 5943

New Access to Carbonyl Ylides by the Silicon-Based 1,3-Elimination and their [3 + 2] Cycloadditions to Activated Alkenes and Alkynes: One-step Synthesis of Dihydrofurans and Tetrahydrofurans

Makoto Hojo, Masakazu Ohkuma, Naruyasu Ishibashi, and Akira Hosomi*
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan



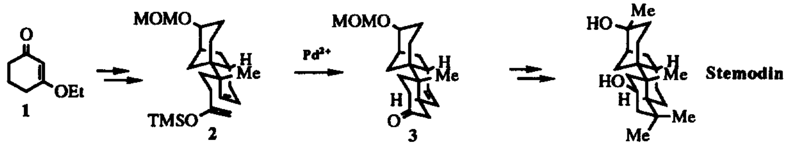
Fluoride ion-promoted 1,3-elimination of ethers provides the new method for the generation of carbonyl ylides.

Tetrahedron Lett. **1993**, *34*, 5947

Pd^{2+}-promoted Cyclization in Tetracyclic Diterpene Synthesis Highly Diastereoselective Formal Total Synthesis of (±)-Stemodin

Masahiro Toyota, Takashi Seishi, and Keiichiro Fukumoto*
Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980, Japan

Pd^{2+}-promoted cyclization reaction (2 → 3) is used as a key step in the synthesis of (±)-stemodin.

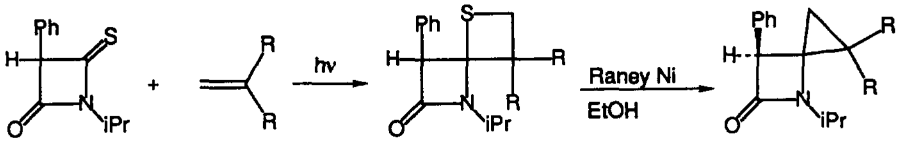


Tetrahedron Lett. **1993**, *34*, 5951

A Novel Synthesis of 4-Spirocyclopropyl β-Lactams.

Hiromu Aoyama*, Hiroyuki Sagae, and Akira Hosomi,
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki, 305 Japan

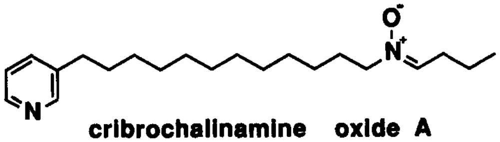
4-Spirocyclopropyl β-lactams were synthesized from a 4-thioxoazetidin-2-ones as shown below.



Tetrahedron Lett. **1993**, *34*, 5953

Cribrochalinamine oxides A and B, Antifungal β-Substituted Pyridines with an Azomethine *N*-Oxide from a Marine Sponge *Cribrochalina* sp.

Shigeki Matsunaga, Katsumi Shinoda, and Nobuhiro Fusetani*
Laboratory of Marine Biochemistry
Faculty of Agriculture, The University of Tokyo
Bunkyo-ku, Tokyo 113, Japan

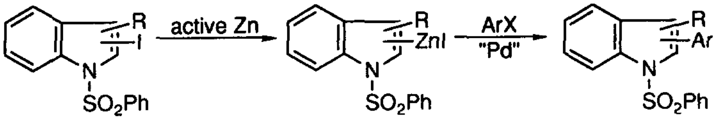


cribrochalinamine oxide A

Tetrahedron Lett. **1993**, *34*, 5955

INDOLYLZINC IODIDES BY OXIDATIVE ADDITION OF ACTIVE ZINC WITH IODOINDOLES

Takao Sakamoto,* Yoshinori Kondo, Nobuo Takazawa and Hiroshi Yamanaka
Pharmaceutical Institute, Tohoku University
Aobayama, Aoba-ku, Sendai 980, Japan

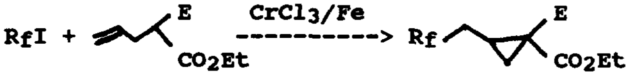


Tetrahedron Lett. **1993**, *34*, 5957

A Novel Method for the Preparation of Perfluoroalkylmethyl Substituted Electrophilic Cyclopropane Derivatives

Chang-Ming Hu* and Jian Chen
Shanghai Institute of Organic Chemistry, Academia Sinica,
345 LingLing Lu, Shanghai 200032, China.

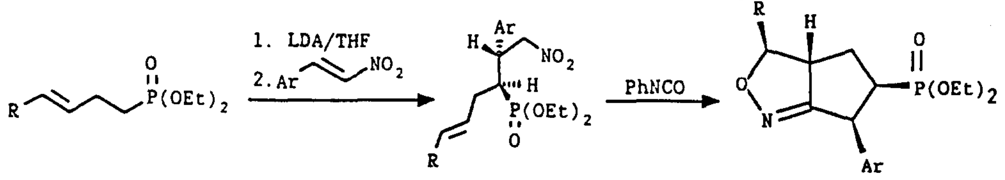
Perfluoroalkyl-containing cyclopropane derivatives were readily synthesized from perfluoroalkyl iodides with allylmalonate and its analogues.



Tetrahedron Lett. **1993**, *34*, 5959

STUDIES ON ORGANOPHOSPHORUS COMPOUNDS 80. STEREOSELECTIVE SYNTHESIS OF FUSED CARBOCYCLIC AND ISOXAZOLINE RINGS VIA INTRAMOLECULAR CYCLOADDITION OF NITRILE OXIDES DERIVED FROM α-NITROALKENES

Chengye Yuan* and Chaozhong Li, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China.

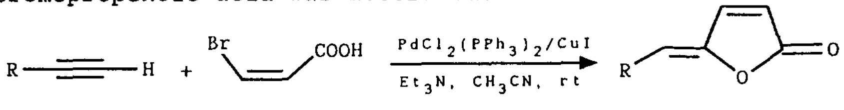


Tetrahedron Lett. **1993**, *34*, 5963

A CONVENIENT SYNTHESIS OF γ-(Z)-ALKYLIDENE BUTENOLIDES

Xiyan Lu*, Xiaoling Huang and Shengming Ma
Shanghai Institute of Organic Chemistry, Academia Sinica
345 Lingling Lu, Shanghai 200032, China

A convenient synthesis of γ-(Z)-alkylidene butenolides starting from (Z)-3-bromopropenoic acid was described.



Tetrahedron Lett. **1993**, *34*, 5967

A New Synthesis of the Pyrrole Ring

Galina P.Shkil and Reva S.Sagitullin
Department of Organic Chemistry, Omsk State University
Omsk, 644077, Russia

Abstract: Treatment of a quaternary 3-amino-5-nitrocollidinium salt with aqueous methylamine at room temperature leads to the formation of a nitroacetylpyrrole.