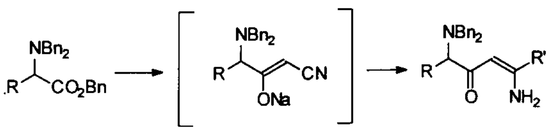
GRAPHICAL ABSTRACTS

Tetrahedron Letters, **1997**, *38*, 4191

A CONVENIENT SYNTHESIS OF ENAMINONES USING TANDEM ACETONITRILE CONDENSATION, GRIGNARD ADDITION.

Anthony R. Haight,* Timothy L. Stuk, Jerome A. Menzia, Timothy A. Robbins, Process Research, D54P, Abbott Laboratories, North Chicago, Illinois 60064 USA

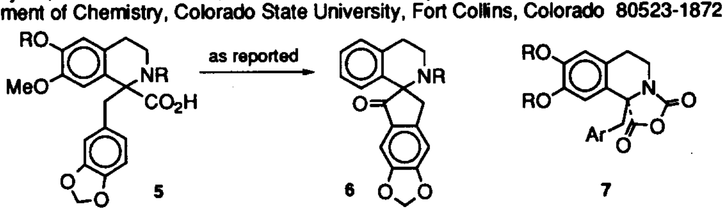
Tandem condensation of acetonitrile and Grignard reagents to α-aminoesters leads to enaminones in one pot.



Tetrahedron Letters, **1997**, *38*, 4195

A Reinvestigation of the Reported Synthesis of the Spirobenzyl Isoquinoline Alkaloid, Iso-Ochotensine

A. I. Meyers,* Atsushi Akahane, Vladimir Struzka, Joseph S. Warmus, Michael Gonzalez, and Guy Milot
Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523-1872 USA



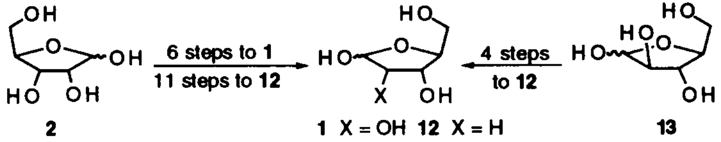
Only product obtained.

Tetrahedron Letters, **1997**, *38*, 4199

EFFICIENT SYNTHESES OF L-RIBOSE AND 2-DEOXY L-RIBOSE FROM D-RIBOSE AND L-ARABINOSE

Michael E. Jung* & Yue Xu, Department of Chemistry, University of California, Los Angeles, CA, USA 90095-1569

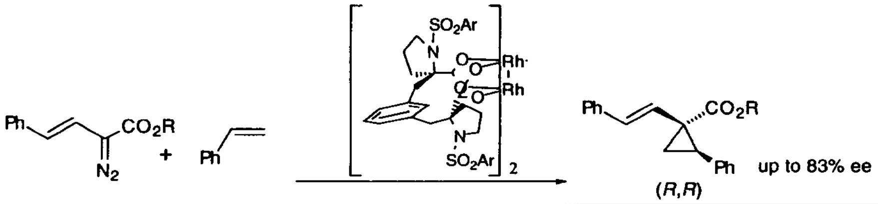
Interconversion of the ends of D-ribose **2** afforded in 6 steps and 45% overall yield L-ribose **1**, from which 2-deoxy L-ribose **12** was easily prepared. In addition, the inexpensive L-arabinose **13** was also converted into 2-deoxy L-ribose **12** via a reductive radical rearrangement of the arabinopyranosyl bromide **14**.



Tetrahedron Letters, **1997**, *38*, 4203

SYNTHESIS AND EVALUATION OF A NOVEL DIRHODIUM TETRAPROLINATE CATALYST CONTAINING BRIDGING PROLINATE LIGANDS

Huw M. L. Davies,* and Norman Kong
Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14260-3000

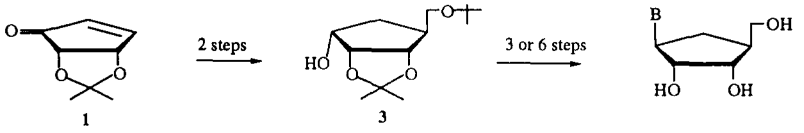


Tetrahedron Letters, **1997**, *38*, 4207

ASYMMETRIC SYNTHESIS OF L-CYCLOPENTYL CARBOCYCLIC NUCLEOSIDES

Peiyuan Wang[†], Luigi A. Agrofoglio[†], M. Gary Newton[‡] and Chung K. Chu*[†]
[†‡]The University of Georgia, Athens, GA 30602

Abstract: Enantiomeric synthesis of L-cyclopentyl nucleosides is described.



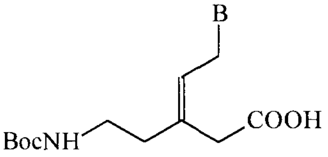
B
11: adenine
12: thymine

Tetrahedron Letters, **1997**, *38*, 4211

SYNTHESIS OF THE MONOMERIC BUILDING BLOCKS OF *Z*-OLEFINIC PNA (*Z*-OPA) CONTAINING THE BASES ADENINE AND THYMINE

Michel Cantin, Rolf Schütz and Christian J. Leumann, Department of Chemistry and Biochemistry, University of Berne, Freiestrasse 3, CH-3012 Berne.

The PNA analogs **11** and **19** are conveniently accessible via a Pd(0)-catalyzed coupling of a vinyl iodide with a *Reformatsky* reagent as the key step in the build-up of the carbon framework.



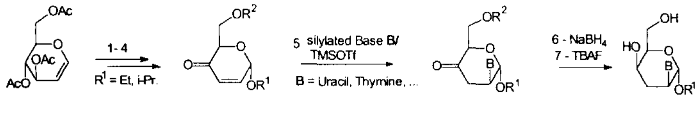
11, B = Thy
19, B = A^{Cbz}

Tetrahedron Letters, **1997**, *38*, 4215

ISONUCLEOSIDES BY MICHAEL ADDITION OF PYRIMIDINE BASES ON 2,6-DISUBSTITUTED 2*H*-PYRAN-3(6*H*)-ONES.

NATACHA PREVOST and FRANCIS ROUESSAC*, Laboratoire de Synthèse Organique, associé au CNRS, Faculté des Sciences, Université du Maine, 72085 Le Mans CEDEX 9, France

A short synthesis of isonucleosides is described, based on the Michael-type addition of silylated nucleobases with an appropriate pyran-3-one as a pyranosidic acceptor. This provide a new way to prepare title compounds in 7 steps from triacetylglucal (ov. yield 25%).

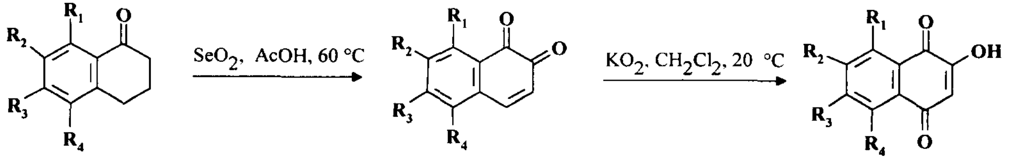


Tetrahedron Letters, **1997**, *38*, 4219

A CONVENIENT SYNTHESIS OF MONPAIN TRIMETHYLETHER.

Alain Bekaert,* Jean Andrieux, Michel Plat and Jean-Daniel Brion,
Laboratoire de Chimie Thérapeutique, Faculté de Pharmacie,Université Paris XI, rue J.B. Clément, F 92296 Châtenay-Malabry Cedex

SeO_2 regiospecific oxidation of 1-tetralones lead to the corresponding 1,2-naphtoquinones which undergo a further oxidation with potassium superoxide in dichloromethane into 2-hydroxy-1,4-naphtoquinones (yield = 60-75%).

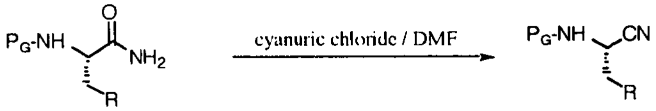


Tetrahedron Letters, **1997**, *38*, 4221

A SIMPLE PREPARATION OF N-PROTECTED CHIRAL α-AMINONITRILES FROM N-PROTECTED α-AMINO ACID AMIDES

Philippe Maetz and Marc Rodriguez, Neosystem, 7 rue de Boulogne, 67100 Strasbourg, France

N-protected α-amino-acid amides are converted to N-protected α-aminonitriles in good yields and with excellent purities by reaction of the corresponding primary amides with cyanuric chloride in DMF.

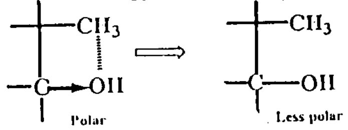


Tetrahedron Letters, **1997**, *38*, 4223

STUDIES OF STERIC EFFECTS. SPECTROSCOPIC EVIDENCE FOR THROUGH-SPACE INTERACTION IN CH_3 ----- O IN CROWDES ALCOHOLS

T. Tezuka*, M. Nakagawa, and K. Yokoi
Departemtn of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan
Y. Nagawa, T. Nakagaki, and H. Nakanishi*
Biomolecular Department, National Institute of Bioscience and Human Technology, Tsukuba, Japan

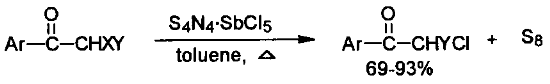
^{17}O and ^{13}C NMR chemical shifts revealed the existence of the CH_3 ---- O attractive interaction and the less polar C-O bond in crowded aliphatic alcohols.



Tetrahedron Letters, **1997**, *38*, 4227

S_4N_4·$SbCl_5$ COMPLEX: A USEFUL REAGENT FOR CONVERSION OF STERICALLY LESS HINDERED α-BROMO KETONES TO α-CHLORO KETONES

Kil-Joong Kim and Kyongtae Kim*
Department of Chemistry, Seoul National University, Seoul 151-742, Korea



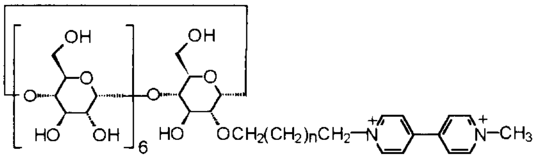
$$Ar-\overset{O}{\overset{\|}{C}}-CHXY \xrightarrow[\text{toluene, } \Delta]{S_4N_4\cdot SbCl_5} \underset{69\text{-}93\%}{Ar-\overset{O}{\overset{\|}{C}}-CHYCl} + S_8$$

X = Br, I ; Y = H, Me
Ar = aromatic, 1°~3° alkyl

Tetrahedron Letters, **1997**, *38*, 4231

SYNTHESIS AND REDOX PROPERTIES OF METHYLBIPYRIDINIO-ALKYL (VIOLOGEN)-MODIFIED β-CYCLODEXTRINS AT THE SECONDARY FACE.

Kwanghee Koh Park* and Sun Young Han. Department of Chemistry. Chungnam National University. Taejon 305-764. Korea
Youn-Hee Park and Joon Woo Park*. Department of Chemistry. Ewha Womans University. Seoul 120-750. Korea



2a: n = 2 **2b**: n = 6

Viologen-modified β-CDs at the secondary face. **2a** and **2b** are prepared and their redox properties are investigated.

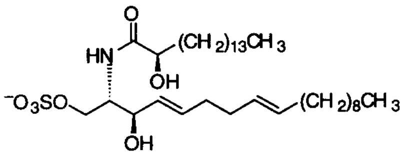
Tetrahedron Letters, **1997**, *38*, 4235

NOVEL CERAMIDE 1-SULFATES, POTENT DNA TOPOISOMERASE I INHIBITORS ISOLATED FROM THE BRYOZOA *WATERSIPORA CUCULLATA*

Makoto Ojika,* Yoshino Go, and Youji Sakagami*

Graduate School of Bioagricultural Sciences, Nagoya University,
Chikusa, Nagoya 464-01, Japan

Two ceramide 1-sulfates have been isolated from the Japanese Bryozoa *Watersipora cucullata* as new potent inhibitors of a human DNA topoisomerase I.



Tetrahedron Letters, **1997**, *38*, 4239

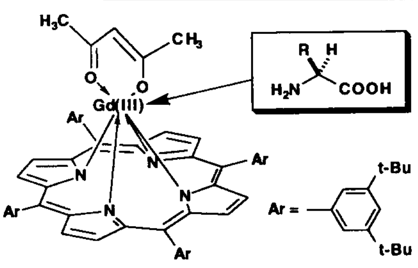
GADOLINIUM(III) PORPHYRIN AS A NOVEL CIRCULAR DICHROISM PROBE FOR CHIRALITY OF AMINO ACIDS

Hitoshi Tamiaki,*[a] Natsushi Matsumoto[a] and Hiroshi Tsukube[b]

[a]Department of Bioscience and Biotechnology, Faculty of Science and Engineering, Ritsumeikan University, Kusatsu, Shiga 525-77, Japan

[b]Department of Chemistry, Faculty of Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka, 558, Japan

Synthetic achiral gadolinium(III) porphyrin extracted chiral amino acids from an aqueous solution into a dichloromethane solution and the formed 1 : 1 complexes exhibited chirality-specific circular dichroism activities.

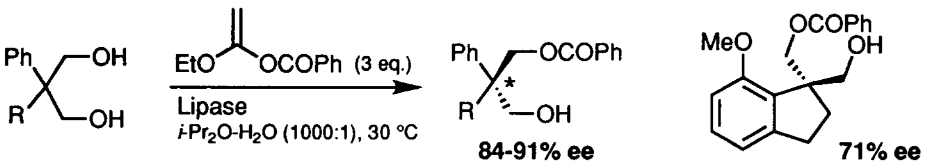


Tetrahedron Letters, **1997**, *38*, 4243

ENZYME-CATALYZED ASYMMETRIZATION OF 2,2-DISUBSTITUTED 1,3-PROPANEDIOLS USING 1-ETHOXYVINYL ESTERS

Shuji Akai, Tadaatsu Naka, Yasushi Takebe, and Yasuyuki Kita*

Faculty of Pharmaceutical Sciences, Osaka University, 1-6, Yamada-oka, Suita, Osaka 565, JAPAN



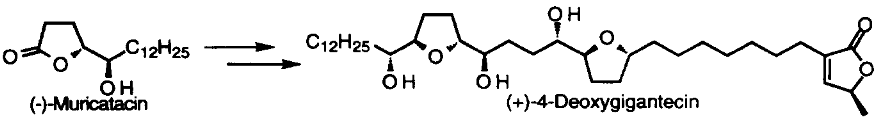
Tetrahedron Letters, **1997**, *38*, 4247

TOTAL SYNTHESIS OF (+)-4-DEOXYGIGANTECIN

Hidefumi Makabe, Akira Tanaka,[†]* and Takayuki Oritani

Department of Applied Biological Chemistry, Faculty of Agriculture and [†]Division of Environmental Bioremediation, Graduate School of Agriculture, Tohoku University, 1-1 Tsutsumidori-Amamiyamachi, Aoba-ku, Sendai 981, Japan

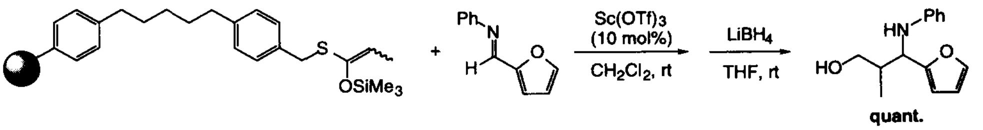
Natural (+)-4-deoxygigantecin belonging to non-adjacent bis-tetrahydrofuran annonaceous acetogenins was totally synthesized from (-)-muricatacin.



Tetrahedron Letters, **1997**, *38*, 4251

5-(4'-CHLOROMETHYLPHENYL)PENTYLPOLYSTYRENE RESIN (CMPP RESIN). A NEW LINKER RESIN FOR SOLID-PHASE ORGANIC SYNTHESIS UNDER LEWIS ACIDIC CONDITIONS

S. Kobayashi,* 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

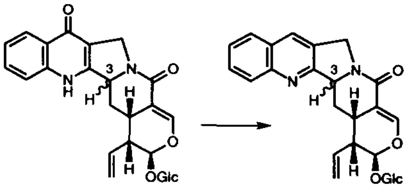


Tetrahedron Letters, **1997**, *38*, 4255

ISOLATION AND PARTIAL SYNTHESIS OF 3(*R*)- AND 3(*S*)-DEOXYPUMILOSIDE; STRUCTURAL REVISION OF THE KEY METABOLITE FROM THE CAMPTOTHECIN PRODUCING PLANT, *OPHIORRHIZA PUMILA*

Mariko Kitajima, Seiji Masumoto, Hiromitsu Takayama, and Norio Aimi*
Faculty of Pharmaceutical Sciences, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba 263, Japan

Both the 3(*R*)- and 3(*S*)-Deoxypumiloside were found in *Ophiorrhiza pumila*. The structure of each tetraacetate derivative was elucidated by spectroscopic analysis and partial syntheses.



3H-β : 3(*R*)-Pumiloside
3H-α : 3(*S*)-Pumiloside

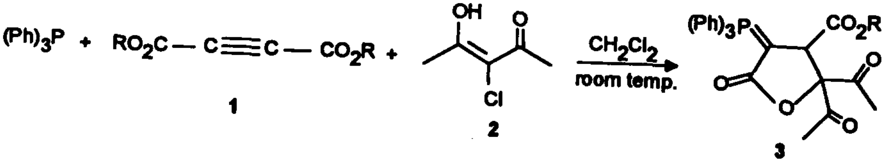
3H-β : 3(*R*)-Deoxypumiloside
3H-α : 3(*S*)-Deoxypumiloside

Tetrahedron Letters, **1997**, *38*, 4259

Vinyltriphenylphosphonium Salt Mediated One-pot Synthesis of Functionalized 3-(Triphenylphosphoranylidene)butyrolactones.

Issa Yavari* and Robabeh Baharfar
Chemistry Department, Tarbiat Modarres University, P.O.Box 14155-4838, Tehran, Iran

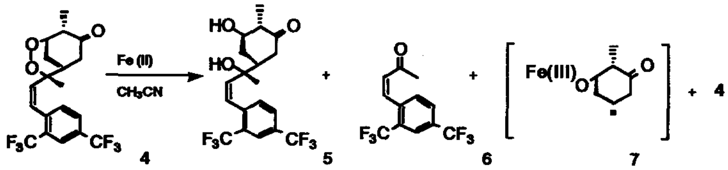
A single-step synthesis of functionalized butyrolactones 3 is described.



Tetrahedron Letters, **1997**, *38*, 4263

The Biomimetic Iron-Mediated Degradation of Arteflene (Ro-42-1611), an Endoperoxide Antimalarial: Implications for the Mechanism of Antimalarial Activity

Paul M. O' Neill,* Laurence P. Bishop, Natalie L. Searle, James L. Maggs, Stephen A. Ward, Patrick G. Bray, Richard C. Storr and B. Kevin Park, Departments of Pharmacology and Therapeutics and of Chemistry, Liverpool University, P.O. Box 147, Liverpool L69 3BX



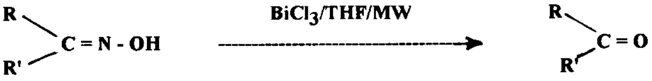
Arteflene in the presence of $FeCl_2.4H_2O$ or hemin/ N-acetylcysteine produces the diol **5** and the eneone **6**. The formation of **6** indicates that arteflene rearranges to a non-stabilised carbon centred radical **7**

Tetrahedron Letters, **1997**, *38*, 4267

REGENERATION OF CARBONL COMPOUNDS FROM OXIMES UNDER MICROWAVE IRRADIATIONS

Anima Boruah, Bipul Baruah, Dipak Prajapati and Jagir S Sandhu*
Regional Research Laboratory, Jorhat 785 006, Assam, India.

A new and efficient method for the cleavage of oximes 1 has been achieved by a simple reaction of a ketoxime or an aldoxime with bismuth trichloride in tetrahydrofuran under microwave irradiations.



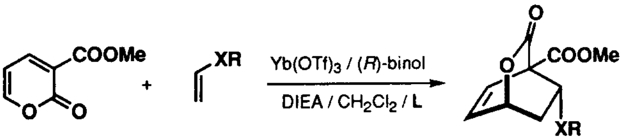
1

2

Tetrahedron Letters, **1997**, *38*, 4269

REMARKABLE EFFECT OF BASIC LIGANDS IN THE LANTHANIDE-CATALYSED ENANTIOSELECTIVE CYCLOADDITIONS OF 3-CARBOMETHOXY-2-PYRONE

István E. Markó*, Isabelle Chellé-Regnaut, Bernard Leroy and Stuart L. Warriner
Université catholique de Louvain, Laboratoire de Chimie Organique, Louvain-la-Neuve, Belgique.



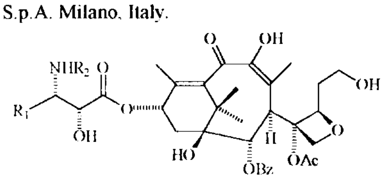
XR = OBu, SBu, OCy, SCy, SPh
L = H_2O, ^{t}BuOH, THF
ee = 65 to >95%

Tetrahedron Letters, **1997**, *38*, 4273

SYNTHESIS AND EVALUATION OF C-*SECO* PACLITAXEL ANALOGUES

G. Appendino.[a]* B. Danieli,[b]* J. Jakupovic,[c] E. Belloro,[a] G. Scambia[d] and E. Bombardelli[e] [a]Dip. Scienza Tecnologia del Farmaco, Torino, Italy. [b]Dip. Chimica Organica Industriale, Milano, Italy.[c] Inst. Organische Chemie, Technische Universität, Berlin, Germany. [d] Univ. Cattolica Sacro Cuore, Roma, Italy.[e] Indena S.p.A. Milano, Italy.

Starting from 10-dehydro-C-*seco*baccatin III, C-*seco* analogues of paclitaxel retaining biological activity were synthesised.

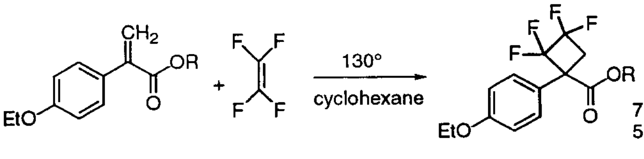


Tetrahedron Letters, **1997**, *38*, 4277

STEREOSELECTIVITY IN THE THERMAL CYCLOADDITION REACTIONS OF TETRAFLUOROETHYLENE TO DERIVATIVES OF α-(4-ETHOXY-PHENYL)ACRYLIC ACID.

Algirdas K. Serelis and Gregory W. Simpson,* CSIRO Division of Chemicals and Polymers, Private Bag 10, Clayton Sth MDC, Clayton VIC 3169, Australia

Esters of chiral auxiliaries with α-(4-ethoxyphenyl)acrylic acid undergo diastereoselective addition reactions with tetrafluoroethylene at 170° to afford tetrafluorobutane esters.



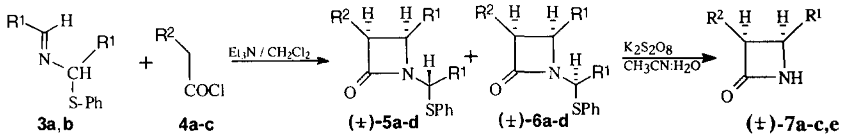
70% yield
57% d.e.

Tetrahedron Letters, **1997**, *38*, 4281

SYNTHESIS OF N^{1}-SUBSTITUTED β-LACTAMS : INTRODUCING N^{1}-(1′-THIOPHENYL)BENZYL AS AN N-PROTECTING GROUP

K. Karupaiyan, V. Srirajan, A. S. A. R. Deshmukh and B. M. Bhawal*, Division of Organic Chemistry (Synthesis), National Chemical Laboratory, Pune 411 008, India.

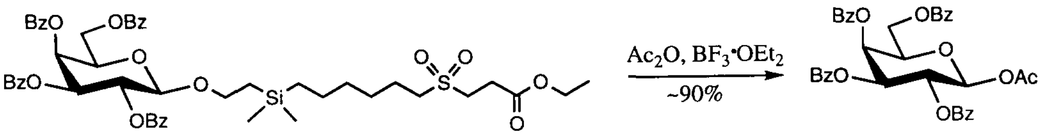
A diastereoselective synthesis of (±) *cis*-β-lactams (**5** & **6**) *via* cycloaddition reaction of N^{1}-(α-thiophenyl)benzyl imines (**3**) with acid chlorides (**4**) is described. The β-lactams **5** & **6** on oxidation with potassium persulfate gave NH- β-lactams (**7**) in good yields.



Tetrahedron Letters, **1997**, *38*, 4285

A 2-SILYLETHANOL-BASED ANOMERIC LINKER FOR CARBOHYDRATES; TRANSFORMATION INTO 1-O-ACYL DERIVATIVES

Andreas Wållberg, Dirk Weigelt, Niklas Falk, and Göran Magnusson*, Organic chemistry 2, Center for Chemistry and Chemical Engineering, The Lund Institute of Technology, Lund University, P. O. Box 124, S-221 00 Lund, Sweden.

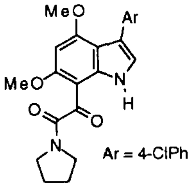


Tetrahedron Letters, **1997**, *38*, 4287

SELF-ASSEMBLY OF AN INDOLYL-GLYOXYLAMIDE BY UNUSUAL HYDROGEN BONDING

David StC. Black, Donald C. Craig, Darryl B. McConnell
School of Chemistry, The University of New South Wales, Sydney, 2052, Australia

The tertiary indol-7-ylglyoxylamide, 2-(3′-(4″-chlorophenyl)-4′,6′-dimethoxyindol-7′-yl)glyoxyl-1-pyrrolidide self-assembles into a "step" shaped hydrogen bonded dimer in the crystalline state *via* the preferential use of π-hydrogen bonding from an indole NH to a carbonyl acceptor.

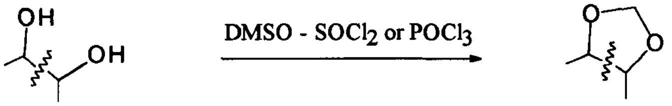


Tetrahedron Letters, **1997**, *38*, 4291

METHYLENE ACETALS AS PROTECTING GROUPS - AN IMPROVED PREPARATION METHOD

Marcella Guiso*, Carmela Procaccio, Maria Rosaria Fizzano, Francesco Piccioni.,
Dipartimento di Chimica, Università "La Sapienza", Piazzale Aldo Moro 5, I-00185 Roma, Italy .

A facile method to protect *vic* diols, 1,3 diols and other hydroxyl functions as methylene acetals is achieved by treating the relative substrates with $POCl_3$ or $SOCl_2$ in DMSO. The good yields obtained, the good solubility of many organic compounds in DMSO and the easy hydrolysis of the 1,3,5-trioxaepane derivatives prepared from *trans vic* diols make useful this protecting method.

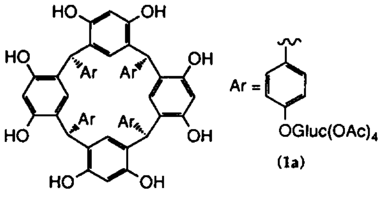


Tetrahedron Letters, **1997**, *38*, 4295

NOVEL CALIX[4]RESORCINARENE GLYCOSIDES

Anthony D.M. Curtis
Department of Chemistry, Keele University,
Keele, Staffordshire ST5 5BG UK

The calix[4]resorcinarene glycoside (**1a**) was prepared from the condensation of the corresponding glycosidic aldehyde (**2a**) and resorcinol using Lewis acid catalysis.



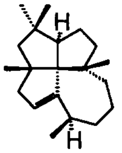
(**1a**)

Tetrahedron Letters, **1997**, *38*, 4297

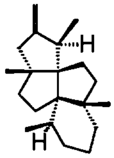
WAIHOENSENE. A NEW LAURENENE-RELATED DITERPENE FROM *PODOCARPUS TOTARA VAR WAIHOENSIS.*

Don B. Clarke, Simon F.R. Hinkley and Rex T. Weavers.
Department of Chemistry, University of Otago, Box 56, Dunedin, New Zealand.

New sources of the rosettane diterpene, laurenene, and the structure of a new laurenene-related, diterpene hydrocarbon, waihoensene, are reported.



Laurenene

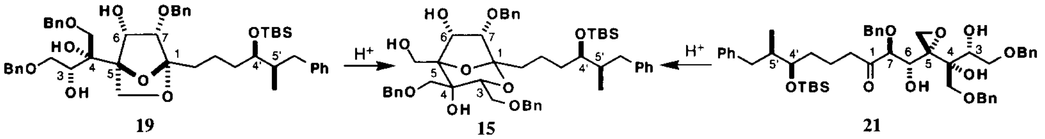


Waihoensene

Tetrahedron Letters, **1997**, *38*, 4301

STUDIES TOWARDS THE SYNTHESIS OF THE ZARAGOZIC ACIDS: SYNTHESIS OF THE BICYCLIC ACETAL CORE OF ZARAGOZIC ACID C.

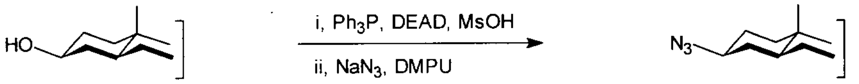
Ian Paterson,* Klaus Feßner and M. Raymond V. Finlay
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.



Tetrahedron Letters, **1997**, *38*, 4305

Mitsunobu Reactions with Methanesulfonic Acid; The Replacement of Equatorial Hydroxyl Groups by Azide with Net Retention of Configuration

Anthony P. Davis,* Stephan Dresen and Laurence J. Lawless
Department of Chemistry, Trinity College, Dublin 2, Ireland



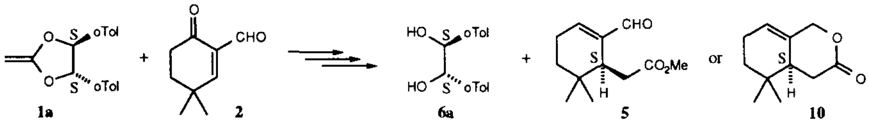
Method is applied to 5α and 5β steroids, giving overall yields of 74 - 87%

Tetrahedron Letters, **1997**, *38*, 4309

THE USE OF HOMOCHIRAL 2-METHYLENE-4,5-DIARYL-1,3-DIOXOLANES AS RECYCLABLE ACETIC ESTER ENOLATE EQUIVALENTS: ASYMMETRIC SYNTHESIS OF TERPENOIDS

Roy Hayes, Ke-Dong Li, Peter Leeming and Timothy W. Wallace*
Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, U.K.

Two α-cyclocitral derivatives can be prepared in homochiral form using the C_2-symmetric diol **6a** as a recyclable auxiliary. The key step is the heterodiene cycloaddition of 2-methylene-4,5-*bis*(*o*-tolyl)-1,3-dioxolane **1a** to the cyclohexenal **2**.

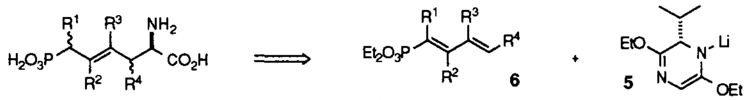


Tetrahedron Letters, **1997**, *38*, 4311

CONJUGATE ADDITION OF LITHIATED SCHÖLLKOPF'S BISLACTIM ETHER TO 1*E*,3*E*-BUTADIENYLPHOSPHONATES: STEREOCONTROLLED ACCESS TO 2,3-*ANTI*-4*E* 2-AMINO-6-PHOSPHONO-4-HEXENOIC ACID DERIVATIVES

Vicente Ojea, Susana Conde, María Ruiz, Mª Carmen Fernández and José Mª Quintela*, Departamento de Química Fundamental e Industrial, Facultade de Ciencias, Universidade da Coruña, Campus A Zapateira s/n, A Coruña 15071, Spain.

1,6-Addition of lithiated bislactim ether **5** to 1*E*,3*E*-butadienylphosphonates **6** allows a direct and stereocontrolled access to semi-rigid AP6 analogues, the 2,3-*anti*-4*E* 2-amino-6-phosphono-4-hexenoic acid derivatives **4**.



4, semi-rigid D-AP6 analogues

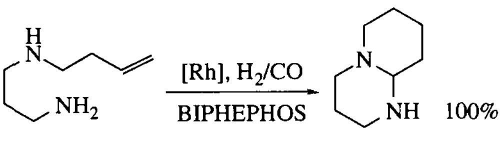
R^1,R^2,R^3,R^4 = H,Me,Ph,SnBu$_3$

Tetrahedron Letters, **1997**, *38*, 4315

Control of Chemo- and Regio-Selectivity in Rhodium Catalysed Reactions of Unsaturated Amines with H_2/CO

David J. Bergmann, Eva M. Campi, W. Roy Jackson, Quentin J. McCubbin and Antonio F. Patti,
Department of Chemistry, Monash University, Clayton,Victoria 3168, Australia.

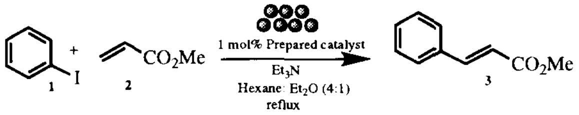
Rhodium catalysed reactions of N-alkenylamines with H_2/CO using the hindered bisphosphite ligand and BIPHEPHOS are chemo- and regioselective for terminal hydroformylation leading to quantitative formation of diazabicyclic compounds



Tetrahedron Letters, **1997**, *38*, 4319

PALLADIUM CATALYSED HECK REACTIONS AND ALLYLIC SUBSTITUTION REACTIONS USING GLASS BEAD TECHNOLOGY

Louise Tonks,[a] Michael S Anson,[c] Klaus Hellgardt,[b] Amin R Mirza,[a] David F Thompson,[a] and Jonathan M J Williams*[a]
[a]School of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, UK.
[b]Department of Chemical Engineering, Loughborough University, Loughborough, Leicestershire, LE11 3TU, UK.
[c]GlaxoWellcome Research and Development, Medicines Research Centre, Gunnels Wood Road, Stevenage, Herts, SG1 2NY, UK

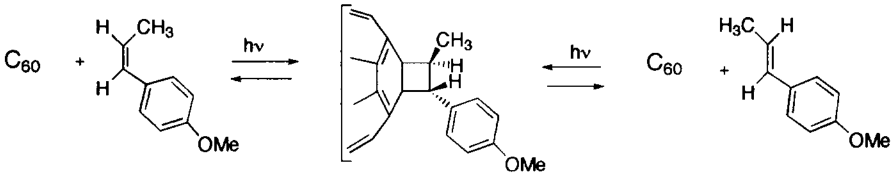


Using palladium catalysts in a supported liquid phase and controlled pore glass beads, this Heck reaction can be achieved with good yield (75%) and low levels of palladium leaching (0.2ppm)

Tetrahedron Letters, **1997**, *38*, 4323

[2+2] PHOTOCYCLOADDITIONS OF *cis/trans*-4-PROPENYL ANISOLE TO C_{60}. A STEP-WISE MECHANISM.

Georgios Vassilikogiannakis and Michael Orfanopoulos*
Department of Chemistry, University of Crete, Iraklion, 71409, Greece.



Tetrahedron Letters, **1997**, *38*, 4327

CONCISE SYNTHESIS OF THE CELL CYCLE INHIBITOR DEMETHOXYFUMITREMORGIN C.

Haishan Wang and Arasu Ganesan,*
Institute of Molecular and Cell Biology, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260

The natural product was synthesized in 3 steps from L-tryptophan methyl ester.