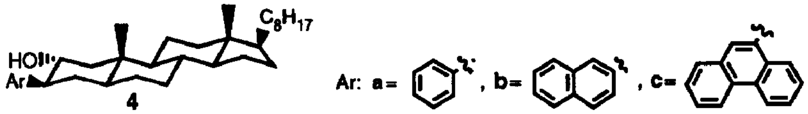
GRAPHICAL ABSTRACTS

Tetrahedron Letters, **1994**, *35*, 661

Novel Steroidal Chiral Auxiliaries: Enantioselective Synthesis of Chiral α-Hydroxy Acids

Deeng-Lih Huang* and Richard W. Draper
Chemical Process Research Department, Schering-Plough Research Institute, Kenilworth, NJ 07033, U.S.A.

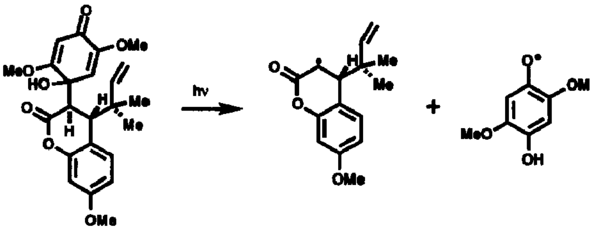
The synthesis is reported of three novel steroidal chiral auxiliaries (4) which were used to generate an α-hydroxy acid in high optical purity (90-98% ee).



Tetrahedron Letters, **1994**, *35*, 663

PREFERENCE FOR PHOTODISSOCIATION OVER INTERNAL [2 + 2]-CYCLOADDITION DURING IRRADIATION OF AN UNSATURATED α,β-ENONE

E. J. Corey and Laurence I. Wu
Department of Chemistry, Harvard University
Cambridge, Massachusetts, 02138

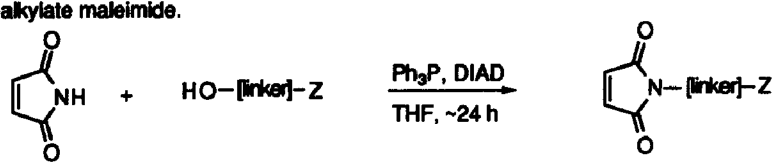


Tetrahedron Letters, **1994**, *35*, 665

The Mitsunobu Reaction: A Novel Method for the Synthesis of Bifunctional Maleimide Linkers

Michael A. Walker
Bristol-Myers Squibb Pharmaceutical Research Institute,
5 Research Parkway, Wallingford, CT 06492

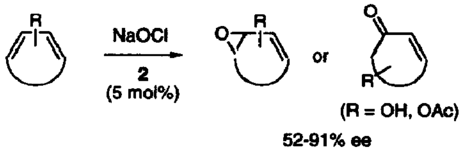
The synthesis of maleimido bifunctional linkers was accomplished using the Mitsunobu reaction to N-alkylate maleimide.



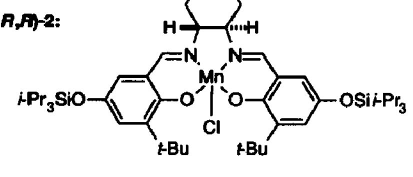
Tetrahedron Letters, **1994**, *35*, 669

ENANTIOSELECTIVE EPOXIDATION OF CYCLIC 1,3-DIENES CATALYZED BY A STERICALLY AND ELECTRONICALLY OPTIMIZED (SALEN)MN COMPLEX.

Sukbok Chang,[a] Richard M. Heid,[b] and Eric N. Jacobsen[a,*]
[a]Dept. of Chemistry, Harvard University, Cambridge, MA 02138 [b]Dept. of Chemistry, University of Illinois, Urbana, IL 61801



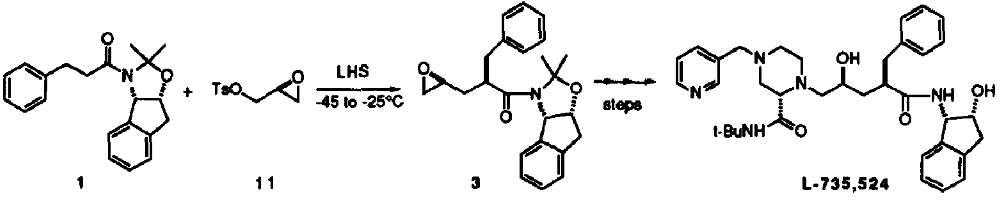
***(R,R)*-2:**



Tetrahedron Letters, **1994**, *35*, 673

Highly Diastereoselective Reaction of a Chiral, Non-Racemic Amide Enolate with (*S*)-Glycidyl Tosylate. Synthesis of the Orally Active HIV-1 Protease Inhibitor L-735,524 *D. Askin*, K. Eng*, K. Rossen*, R. Purick, K. Wells, R. Volante and P. Reider*

Department of Process Research, Merck Research Laboratories, P.O. Box 2000, Rahway, NJ 07065



1 11 3 L-735,524

Tetrahedron Letters, **1994**, *35*, 677

Sonochemistry in $S_{RN}1$ Reactions in Liquid Ammonia at Room Temperature

Pablo G. Manzo, Sara M. Palacios and Rubén A. Alonso*
CEQUIMAP, Fac. de Ciencias Químicas, Universidad Nacional de Córdoba.
Suc. 16, C.C. 61, 5016 Córdoba, Argentina.

Ultrasound was used for the stimulation of $S_{RN}1$ reaction in liquid Ammonia at room temperature

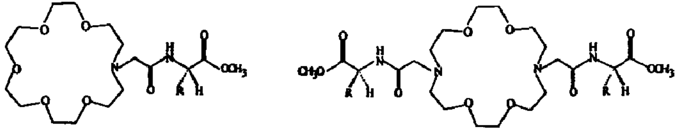
$$ArX + Ph_2P^- \xrightarrow[S_{RN}1]{)))} ArPPh_2 + X^-$$

X = p-Iodoanisole, 1-halonaphthalene(Cl,Br,I)

Tetrahedron Letters, **1994**, *35*, 681

EQUILIBRIUM CATION BINDING CONSTANTS OF THE DIPEPTIDE DERIVED LARIAT ETHERS IN METHANOL DETERMINED FROM CIRCULAR DICHROISM MEASUREMENTS. Danlin Gu, Birdella D. Kenney, Banita White Brown*, Department of Chemistry, University of North Carolina at Charlotte, Charlotte, NC 28223 USA

A new application of circular dichroism spectropolarimetry indicates high calcium binding for the ligands shown.

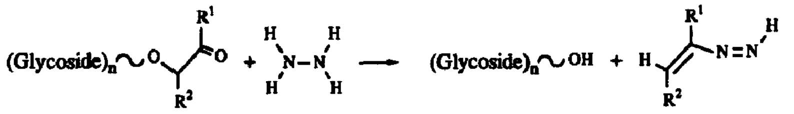


Tetrahedron Letters, **1994**, *35*, 685

SEQUENTIAL REMOVAL OF MONOSACCHARIDES FROM THE REDUCING END OF OLIGOSACCHARIDES. I. A REACTION BETWEEN HYDRAZINE AND SUGARS HAVING A GLYCOSIDIC SUBSTITUENT ON A CARBON ATOM ADJACENT TO THE CARBONYL GROUP

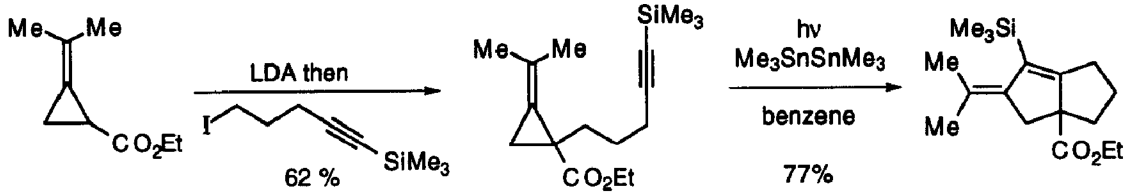
Brad Bendiak,* Mary Ellen Salyan and Mario Pantoja, The Biomembrane Institute and University of Washington, 201 Elliott Ave. West, Seattle, WA 98119 USA

Hydrazine reacts with sugars having a glycosidic substituent on a carbon atom adjacent to an aldehyde or keto group.



Tetrahedron Letters, **1994**, *35*, 689

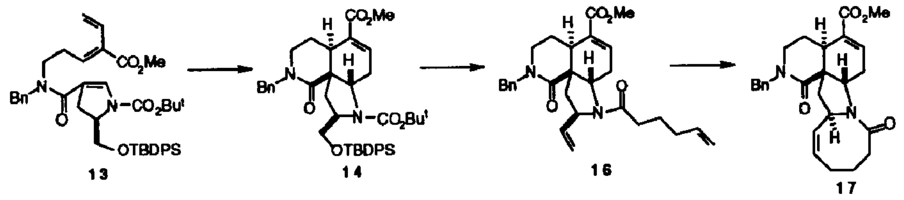
A CONJUNCTIVE DIQUINANE SYNTHESIS USING A FREE-RADICAL CATALYZED INTRAMOLECULAR [3 + 2] METHYLENECYCLOPENTANE ANNULATION. Chad C. Huval and Daniel A. Singleton*, Department of Chemistry, Texas A & M University, College Station, TX 77843-3255 USA



Tetrahedron Letters, **1994**, *35*, 691

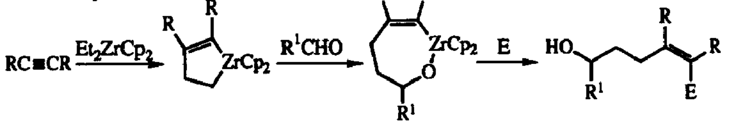
A NOVEL APPROACH TO THE ASYMMETRIC SYNTHESIS OF MANZAMINE A. CONSTRUCTION OF THE TETRACYCLIC ABCE RING SYSTEM.
S. F. Martin,* Y. Liao, Y. Wong and T. Rein, Department of Chemistry and Biochemistry, The University of Texas, Austin, TX 78712

The manzamine A ABCE ring subunit 17 was assembled using an intramolecular [4+2] reaction and an olefin metathesis as key steps.



Tetrahedron Letters, **1994**, *35*, 695

REACTION OF 3-ZIRCONA-1-CYCLOPENTENES AND ZIRCONACYCLOPENTANES WITH ALDEHYDES. A SELECTIVE AND CONVENIENT SYNTHESIS OF 4-PENTEN-1-OLS, (Z)-5-IODO-4-PENTEN-1-OLS, AND RELATED ALKANOLS. Christophe Copéret, Ei-ichi Negishi,* Zhenfeng Xi, and Tamotsu Takahashi* *Department of Chemistry, Purdue University, West Lafayette, Indiana 47906, U.S.A. and Coordination chemistry Laboratories, Institute of Molecular Science, Myodaiji, Okazaki 444, Japan*



R, R^1= alkyl and aryl
E = H^+ and I_2
≥ 98% isomerically pure

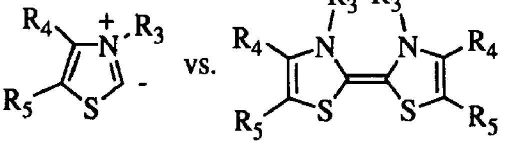
Selective one-pot procedure for the preparation of tri- and tetrasubstituted 4-alken-1-ols from alkynes and related reactions of alkenes, dienes, and diynes.

Tetrahedron Letters, **1994**, *35*, 699

The Thiazolium Catalyzed Benzoin Condensation with Mild Base Does not Involve a "Dimer" Intermediate

Ronald Breslow* and Ronald Kim
Department of Chemistry, Columbia University
New York, New York 10027

Kinetic studies show that the benzoin condensation catalyzed by 3,4,5-trimethylthiazolium iodide and triethylamine in DMSO does not involve thiazolium dimers as the catalytic species, as has been proposed.

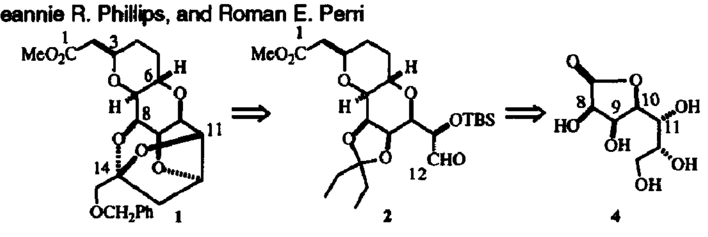


Tetrahedron Letters, **1994**, *35*, 703

An Expeditious Synthesis of the C(1)-C(14) Subunit of Halichondrin B

Steven D. Burke,* Kyung Woon Jung, Jeannie R. Phillips, and Roman E. Perri
Department of Chemistry, University of Wisconsin, Madison, WI 53706, USA

The C(1)-C(14) segment 1 of halichondrin B was constructed very efficiently from 4 in 15 steps. The synthesis of the C(1)-C(12) subunit 2 features a pinacol rearrangement and an intramolecular Michael addition.

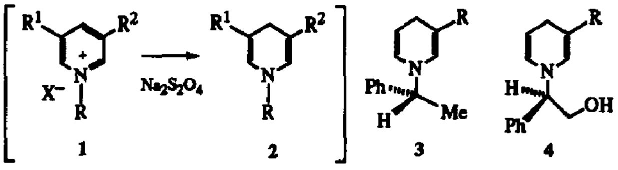


Tetrahedron Letters, **1994**, *35*, 707

1,4-Dihydropyridines from Dithionite Reduction of Pyridinium Salts without Electron-Withdrawing Groups as Substituents.

Yung-Sing Wong, Christian Marazano,* Dino Gnecco and Bhupesh C. Das, *Institut de Chimie des Substances Naturelles, C.N.R.S., 91198 Gif-su-Yvette Cedex, France.*

Sodium dithionite reduction of pyridinium salts 1, lacking EWGs offers a convenient access to 1,4-dihydropyridines 2, in particular, chiral derivatives such as 3 and unstable intermediates 4 (R, R^1, R^2= H or alkyl groups).

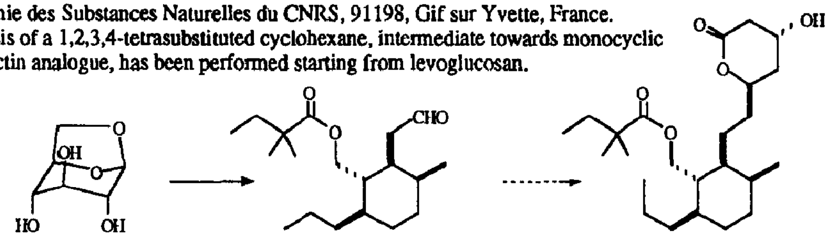


Tetrahedron Letters, **1994**, *35*, 711

STEREOSELECTIVE SYNTHESIS OF THE TETRASUBTITUTED CYCLOHEXANE CORE OF A MONOCYCLIC MEVINIC ACID ANALOGUE.

Mikhail S.Ermolenko*, Alain Olesker and Gabor Lukacs. Institut de Chimie des Substances Naturelles du CNRS, 91198, Gif sur Yvette, France.

Synthesis of a 1,2,3,4-tetrasubstituted cyclohexane, intermediate towards monocyclic Compactin analogue, has been performed starting from levoglucosan.

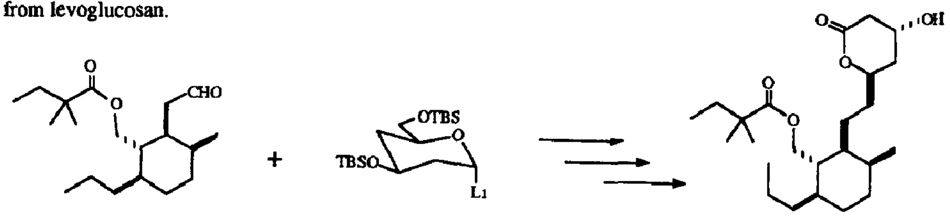


Tetrahedron Letters, **1994**, *35*, 715

TOTAL SYNTHESIS OF A MONOCYCLIC ANALOGUE OF COMPACTIN.

Mikhail S.Ermolenko*, Alain Olesker and Gabor Lukacs. Institut de Chimie des Substances Naturelles du CNRS, 91198, Gif sur Yvette, France.

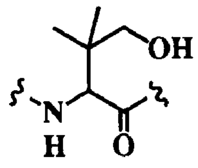
Total synthesis of Karanewsky's monocyclic Compactin analogue has been accomplished from levoglucosan.



Tetrahedron Letters, **1994**, *35*, 719

Polytheonamides, Unprecedented Highly Cytotoxic Polypeptides, from the Marine Sponge *Theonella swinhoei* 1. Isolation and Component Amino Acids

Toshiyuki Hamada, Takeo Sugawara, Shigeki Matsunaga, and Nobuhiro Fusetani*
Laboratory of Marine Biochemistry, Faculty of Agriculture, The University of Tokyo
Bunkyo-ku, Tokyo 113, Japan



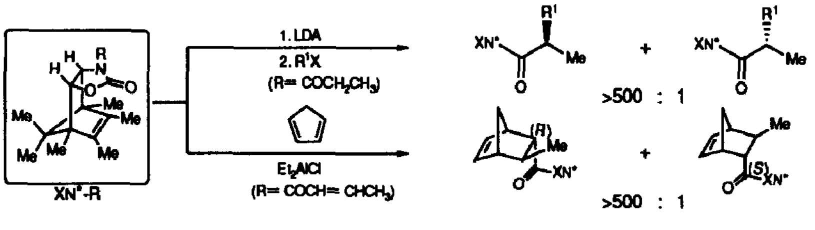
OH-*t*-Leu

Highly cytotoxic polypeptides, polytheonamides A-C, have been isolated from the marine sponge *Theonella swinhoei*. They contained unusual amino acids such as *t*-Leu, β-methylGlx, β-methylIle, β-hydroxyVal, β-hydroxyAsx and γ-hydroxy-*t*-Leu.

Tetrahedron Letters, **1994**, *35*, 721

Highly Efficient Chiral 2-Oxazolidinone Auxiliaries Derived from Methylcyclopentadienes and 2-Oxazolone

Noriaki Hashimoto, Tadao Ishizuka and Takehisa Kunieda*
Faculty of Pharmaceutical Sciences, Kumamoto University

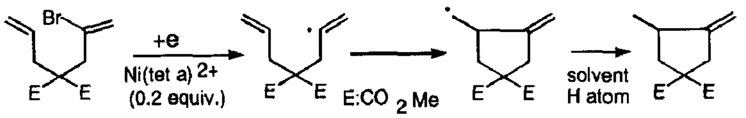


Tetrahedron Letters, **1994**, *35*, 725

CYCLIZATIONS OF VINYL AND ARYL RADICALS GENERATED BY A NICKEL(II) COMPLEX CATALYSED ELECTROREDUCTION

Faculty of Pharmaceutical Sciences, Osaka University, 1-6, Yamadaoka, Suita, Osaka-fu,565 Japan
Shigeko Ozaki, Ikuo Horiguchi, Hidenori Matsushita and Hidenobu Ohmori

Radical cyclization of vinyl and aryl halides was performed by indirect electroreduction using a nickel(II) complex as an electron-transfer catalyst.

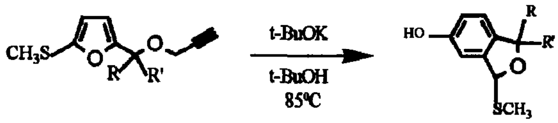


Tetrahedron Letters, **1994**, *35*, 729

INTRAMOLECULAR DIELS-ALDER REACTION OF FURANS WITH ALLENYL ETHERS FOLLOWED BY METHYLTHIO GROUP 1,4-REARRANGEMENT

Hsien-Jen Wu*, Wei-Dar Shao and Fu-Hsing Ying
Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan, ROC.

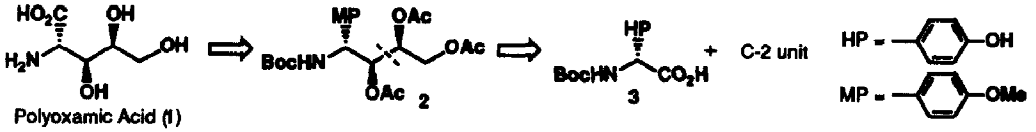
A novel reaction involving an intramolecular Diels-Alder reaction of furans with allenyl ether followed by a methylthio group 1,4-rearrangement was discovered.



Tetrahedron Letters, **1994**, *35*, 733

An Efficient Synthesis of Polyoxamic Acid Utilizing the Aryl Group as the Carboxyl Synthon. A New Approach to Polyhydroxyamino Acids.

Fumiyoshi Matsuura, Yasumasa Hamada,* and Takayuki Shioiri*
Faculty of Pharmaceutical Sciences, Nagoya City University, Tanabe-dori, Mizuho-ku, Nagoya 467, JAPAN



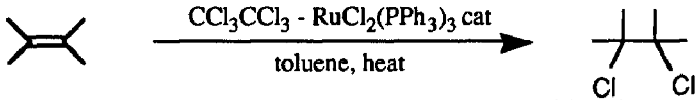
Polyoxamic Acid (1)

Polyoxamic acid (1), an amino acid moiety of antifungal antibiotics polyoxins, has been efficiently synthesized from Boc-(R)-4-hydroxyphenylglycine (3) utilizing its aryl group as the carboxyl synthon.

Tetrahedron Letters, **1994**, *35*, 737

A NEW SELECTIVE DICHLORINATION OF C-C DOUBLE BONDS

Kunikazu Sakai,* Kikuo Sugimoto, Sanae Shigeizumi, and Kiyosi Kondo, Sagami Chemical Research Center, Nishi-Ohnuma 4-4-1, Sagamihara, Kanagawa 229, Japan



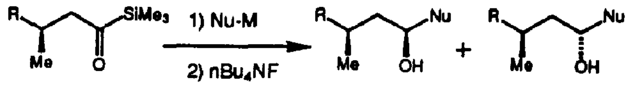
The reaction proceeded at the existence of various kinds of functional groups, such as hydoxy, carboxyl, ester phenyl, of active methylene in the structure.

Tetrahedron Letters, **1994**, *35*, 741

NON-CHELATION CONTROLLED 1,3-ASYMMETRIC INDUCTION IN β-CHIRAL ACYLSILANES

Masahisa Nakada, Yasuharu Urano, Susumu Kobayashi, and Masaji Ohno*
Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

Non-chelation controlled 1,3-asymmetric induction is examined, and our method is applied to the stereoselective synthesis of calcitriol lactone, major metabolite of vitamine D_3.



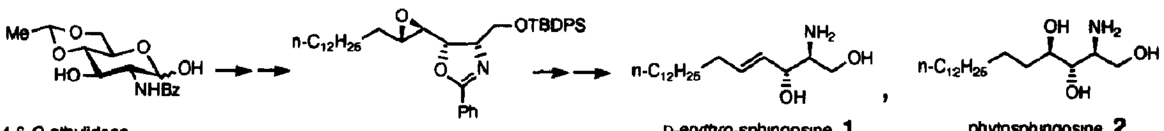
syn : *anti* = 1 : 1 - 36 : 1

R = Ph, Cyclohexyl, ${}^tBu$, Steroidal *syn* *anti*

Tetrahedron Letters, **1994**, *35*, 745

Regio- and Stereocontrolled Synthesis of D-*erythro*-Sphingosine and Phytosphingosine from D-Glucosamine

Teiichi Murakami,* Hiroyuki Minamikawa, and Masakatsu Hato
National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan



4,6-*O*-ethylidene-*N*-benzoyl-D-glucosamine **3**

10

D-*erythro*-sphingosine **1**

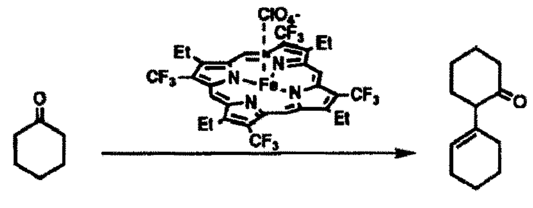
phytosphingosine **2**

Tetrahedron Letters, **1994**, *35*, 749

Aldol Condensation Catalyzed by Highly Electron Deficient Iron Porphyrin

Yasuhisa Kuroda*, Yasuhiko Suzuki, and Hisanobu Ogoshi*
Department of Synthetic Chemistry, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606, Japan

The perchlorate complex of 2,4,6,8-tetratrifluoromethyl-1,3,5,7-tetraethyl-porphyrin•Fe(III) catalyzes the aldol condensation of cyclohexanone.

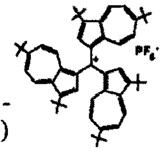


Tetrahedron Letters, **1994**, *35*, 751

Tris(3,6-di-t-butyl-1-azulenyl)methyl Cation; Hydrocarbon Cation with the Highest p$K_R$$^+$ Value

Shunji Ito, Noboru Morita and Toyonobu Asao*
Department of Chemistry, Faculty of Science, Tohoku University, Kawauchi, Aoba-ku, Sendai 980 Japan

Tris(3,6-di-*t*-butyl-1-azulenyl)methyl (**5**), tri(3-*t*-butyl-1-azulenyl)methyl (**10**), and tri(6-*t*-butyl-1-azulenyl)methyl (**11**) hexafluorophosphates were synthesized. Their pK_R^+ values were determined as 14.3, 13.2, and 13.7, respectively.



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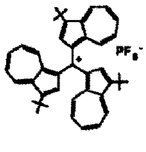
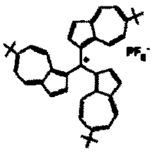


10



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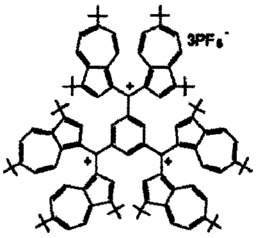
Tetrahedron Letters, **1994**, *35*, 755

Synthesis of Trication Stabilized by Azulene Rings

Shunji Ito, Noboru Morita and Toyonobu Asao*
Department of Chemistry, Faculty of Science, Tohoku University, Kawauchi, Aoba-ku, Sendai 980 Japan

Extraordinary stable trication **6** was synthesized, and the pK_R^{+++}, pK_R^{++} and pK_R^+ values were determined as 9.1, 10.9, and 12.7, respectively.

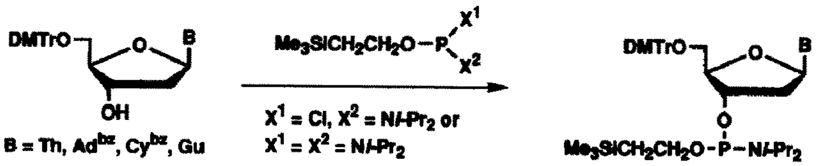


6

Tetrahedron Letters, **1994**, *35*, 757

2-(Trimethylsilyl)ethyl as a Phosphate Protecting Group in Oligonucleotide Synthesis

Takeshi Wada and Mitsuo Sekine*
Department of Life Science, Faculty of Bioscience and Biotechnology, Tokyo Institute of Technology, Nagatsuta, Midoriku, Yokohama 227, Japan

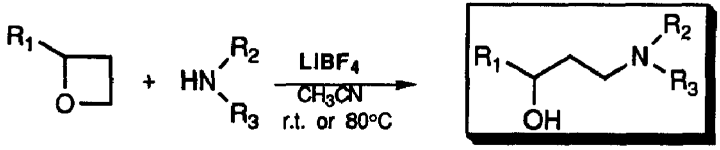


Tetrahedron Letters, **1994**, *35*, 761

MILD LiBF4-PROMOTED AMINOLYSIS OF OXETANES

Marco Chini, Paolo Crotti,* Lucilla Favero, and Franco Macchia
Dipartimento di Chimica Bioorganica, Università di Pisa, via Bonanno 33, 56126 Pisa, Italy

$LiBF_4$ in CH_3CN efficiently catalyzes the aminolysis of trimethylene oxide and 2-octyl oxetane under mild conditions (r.t. or 80 °C) to give the corresponding γ-amino alcohols in very good yields.

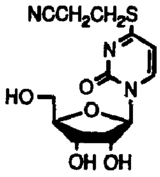


Tetrahedron Letters, **1994**, *35*, 765

A CONVENIENT SYNTHESIS OF *S*-CYANOETHYL-PROTECTED 4-THIOURIDINE AND ITS INCORPORATION INTO OLIGORIBONUCLEOTIDES.

Chris J. Adams*, James B. Murray, John R. P. Arnold and Peter G. Stockley, Department of Genetics, University of Leeds, Leeds LS2 9JT, UK.

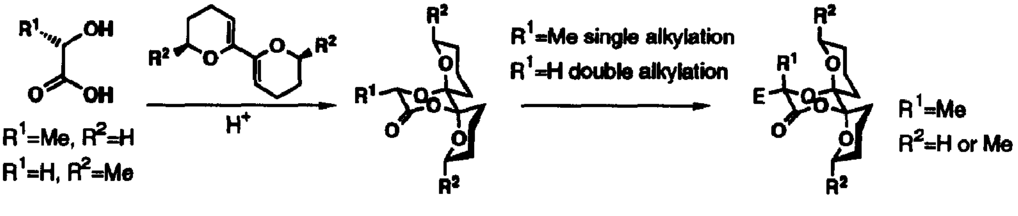
Synthesis of S^4-cyanoethyl-4-thiouridine and its incorporation into oligoribonucleotides using current phosphoramidite methodology.



Tetrahedron Letters, **1994**, *35*, 769

DISPIROKETALS IN SYNTHESIS (PART 6): HIGHLY STEREOSELECTIVE ALKYLATION OF DISPIROKETAL PROTECTED LACTATE AND GLYCOLATE ENOLATES.

Robert Downham, Kun Soo Kim, Steven V. Ley*, and Martin Woods. Department of Chemistry, Cambridge University, Lensfield Road, Cambridge, CB2 1EW, UK.

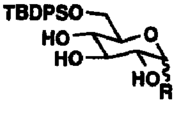


Tetrahedron Letters, **1994**, *35*, 773

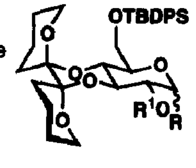
DISPIROKETALS IN SYNTHESIS (PART 7): PROTECTION OF D-GLUCOPYRANOSE SUBSTRATES.

Andrew B. Hughes, Steven V. Ley*, Henning W.M. Priepke, and Martin Woods, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK.

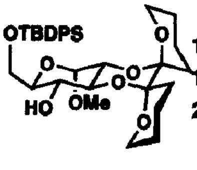
The efficient formation of 1,8,13,16-tetraoxadispiro[5.0.5.4]hexadecanes of various D-glucopyranosyl substrates is described.



10 R = α OMe
13 R = β SEt
17 R = α SEt



11 R = α OMe, R^1 = H
14 R = β SEt, R^1 = H
20 R = α SEt, R^1 = Ac



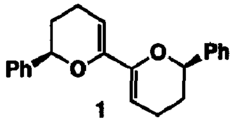
12 R = α OMe, R^1 = H
15 R = β SEt, R^1 = H
21 R = α SEt, R^1 = Ac

DISPIROKETALS IN SYNTHESIS (PART 8): REGIOSELECTIVE PROTECTION OF D-GLUCOPYRANOSE SUBSTRATES.

Tetrahedron Letters, **1994**, *35*, 777

David A. Entwistle, Andrew B. Hughes, Steven V. Ley,* and Giuseppina Visentin, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK.

The dienes **1** and **2** are able to recognise enantiomeric *trans* 1,2-diols. Acid catalysed reaction of **1** and **3** or **2** and **3** gives dispiroketals **4** or **10** respectively. Novel conditions for the deprotection of **4** and **10** and a related allyl substituted dispiroketal **12** are presented.



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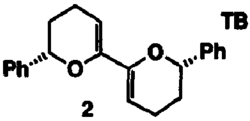

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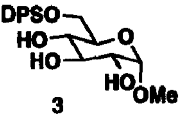

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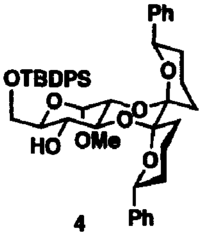

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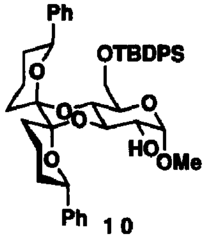


10

Polystyrene-Supported $RhCl_3$-Quaternary Ammonium Ion Pair as a Long-Lived, Efficient and Recyclable Catalyst.

Tetrahedron Letters, **1994**, *35*, 781

Merav Setty-Fichman, Jochanan Blum*, Yoel Sasson* and Moris Eisen

The Hebrew University, Jerusalem 91904, Israel; and Israel Institute of Technology, Haifa 32000, Israel

The ion pair generated from Dowex^R 1 and $RhCl_3$ is an efficient and recyclable catalyst for the following reactions:

$PhCH_2CH=CH_2 \rightarrow$ *E*- and *Z*-PhCH=CHMe

$C_5H_{11}CH(OH)CH=CH_2 \rightarrow C_5H_{11}COEt$

$2C_6H_8 \rightarrow C_6H_{10} + PhH$

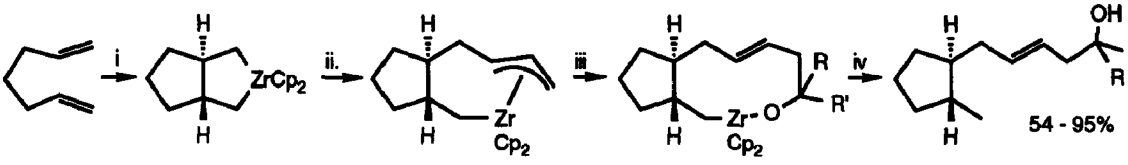
$3C_6H_4C\equiv CH \rightarrow$ 1,2,4- and 1,3,5-$C_6H_3Ph_3$

catalyst: $[\text{polystyrene-}CH_2NMe_3]^+[RhCl_4(H_2O)_n]^-$

Elaboration of Zirconacyclopentanes by Sequential Insertion of Lithium Chloroallylide and Ketones or Aldehydes.

Tetrahedron Letters, **1994**, *35*, 785

Tim Luker and Richard J. Whitby*, Department of Chemistry, The University, Southampton, SO9 5NH, U.K.



i. Cp_2ZrBu_2, r.t., 1h; ii. $CH_2{=}CHCH_2Cl$ / R_2NLi, -78°C; iii. RR'CO, Δ or $BF_3.Et_2O$; iv. MeOH, $NaHCO_3$aq

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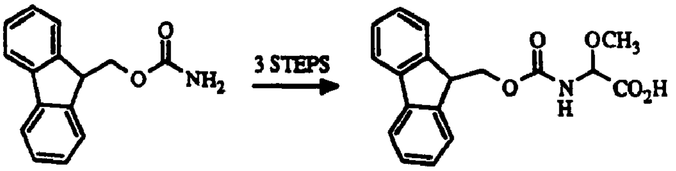
Tetrahedron Letters, **1994**, *35*, 789

SOLID PHASE SYNTHESIS OF α-HYDROXYGLYCINE EXTENDED PEPTIDES - BIOLOGICAL PRECURSORS OF PEPTIDE AMIDES.

Angus R. Brown and Robert Ramage, Edinburgh University, Department of Chemistry, West Mains Road, Edinburgh, EH9 3JJ, Scotland.

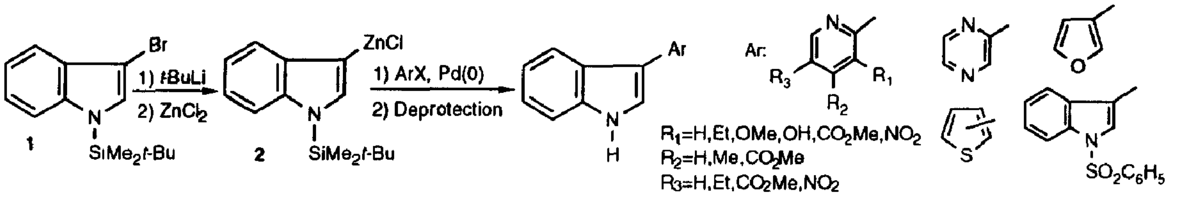
The first solid phase synthesis of α-hydroxyglycine extended peptides is described.



Palladium-Catalyzed Heteroarylation of 1-(*tert*-Butyldimethylsilyl)-3-indolylzinc Chloride. Efficient Synthesis of 3-(2-Pyridyl)indoles.

Tetrahedron Letters, **1994**, *35*, 793

Mercedes Amat, Sabine Hadida, and Joan Bosch
Laboratory of Organic Chemistry, Faculty of Pharmacy, University of Barcelona, 08028-Barcelona, Spain

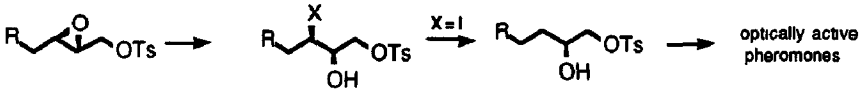


Ring Opening of 2,3-Epoxy 1-Tosylates to Halohydrins and Subsequent Elaboration to Asymmetrical Alcohols

Tetrahedron Letters, **1994**, *35*, 797

Carlo Bonini[a]*, Lucia Chiummientu[a], Maria Funicello[a], Giuliana Righi[b]*,Chiara Federici[b],Leucio Rossi[b]
[a]Dipartimento di Chimica,Università degli Studi della Basilicata,Via N. Sauro 85, 85100 Potenza. [b]Centro C.N.R. per lo Studio della Chimica delle Sostanze Organiche Naturali, c/o Dipartimento di Chimica, Università "La Sapienza", P.le A. Moro 5, 00185 Roma, ITALY

2,3 epoxy alcohols tosylates are regio and chemoselectively opened to the corresponding 3-halohydrins (I, Br, Cl): the iodohydrins have been successfully elaborated, via reduction to the 1,2-diols-1-tosylates and replacement of the tosyl group. The application of the protocol leads to a straightforward synthesis of optically active naturally occurring pheromones.



CYCLISATION OF STILBENES TO PHENANTHRENES BY FLASH VACUUM PYROLYSIS

Tetrahedron Letters, **1994**, *35*, 801

M. John Plater
Department of Chemistry, Aberdeen University, Meston Walk, Old Aberdeen, Scotland AB9 2UE, UK

Flash Vacuum Pyrolysis of 1-chlorostilbene and other derivatives gives phenanthrenes in reasonable yields.