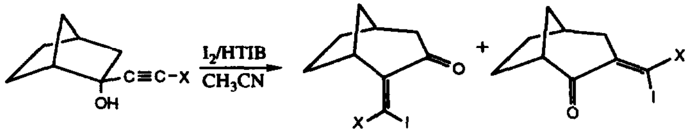
GRAPHICAL ABSTRACTS

Tetrahedron, **1994**, *50*, 11793

RING EXPANSIONS OF 2-HALOETHYNYL-2-NORBORNANOLS

Elsa Djuardi, Pakorn Bovonsombat and Edward Mc Nelis*
Department of Chemistry, New York University, New York, New York 10003

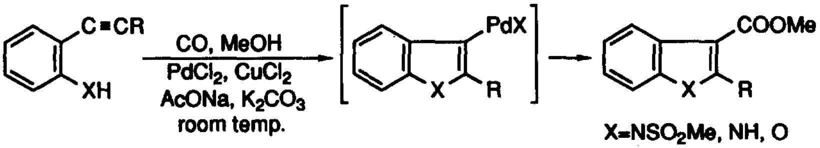
2-Haloethynyl-2-norbornanols react with iodine and Koser's reagent in acetonitrile to afford two ring-expanded products.



Tetrahedron, **1994**, *50*, 11803

CONDENSED HETEROAROMATIC RING SYSTEMS. XXIV. PALLADIUM-CATALYZED CYCLIZATION OF 2-SUBSTITUTED PHENYLACETYLENES IN THE PRESENCE OF CARBON MONOXIDE

Yoshinori Kondo, Futoshi Shiga, Naoko Murata, Takao Sakamoto*, and Hiroshi Yamanaka
Pharmaceutical Institute, Tohoku University, Aobayama, Aoba-ku, Sendai 980-77, Japan



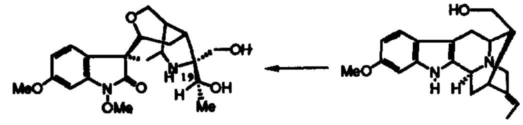
X=NSO_2Me, NH, O
R=Ph, Bu

Tetrahedron, **1994**, *50*, 11813

A Biomimetic Synthesis of a New Skeletal *Gelsemium* Alkaloid, 11-Methoxy-19(*R*)-hydroxygelselegine

Hiromitsu Takayama, Mariko Kitajima and Shin-ichiro Sakai*
Faculty of Pharmaceutical Sciences, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba 263, Japan

Based on a suggested biogenetic sequence, a sarpagine-type indole alkaloid, gardnerine (2), was stereoselectively converted to a new skeletal type *Gelsemium* alkaloid, 11-methoxy-19(*R*)-hydroxygelselegine (1).



11-Methoxy-19(*R*)-hydroxygelselegine 1   Gardnerine 2

Tetrahedron, **1994**, *50*, 11821

A New Enzymatic Synthesis of (*R*)-γ-Chloro-β-Hydroxybutyronitrile.

Tetsuji Nakamura,[1] Toru Nagasawa,[2] Fujio Yu,[1] Ichiro Watanabe,[1] and Hideaki Yamada[3]
Central Research Laboratory, Nitto Chemical Industry Co., Ltd., Yokohama 230,[1] Department of Applied Biological Sciences, Nagoya University, Nagoya 464,[2] Department of Agricultural Chemistry, Kyoto University, Kyoto 606,[3] Japan

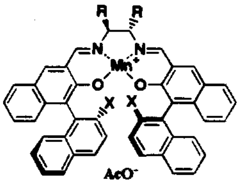
Enantioselective synthesis of (*R*)-γ-chloro-β-hydroxybutyronitrile with a cloned halohydrin hydrogen-halide-lyase (H-lyase)

Tetrahedron, **1994**, *50*, 11827

RATIONAL DESIGN OF Mn-SALEN CATALYST (2): HIGHLY ENANTIOSELECTIVE EPOXIDATION OF CONJUGATED *CIS*-OLEFINS

Hidehiko Sasaki, Ryo Irie, Tetsuya Hamada, Kenji Suzuki, and Tsutomu Katsuki*
Department of Chemistry, Faculty of Science, Kyushu University 33
Hakozaki, Higashi-ku, Fukuoka 812, Japan

Chiral (salen)manganese(III) complex (3) shows so far the best enantioselectivity in the epoxidation of various conjugated *cis*-olefins.

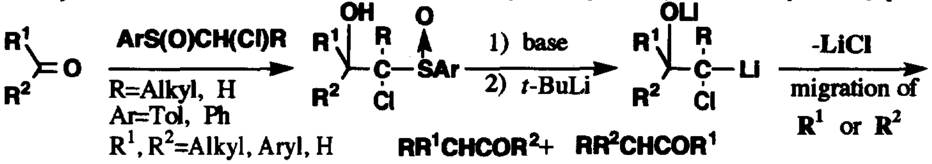


3: R= 3,5-$(CH_3)_2C_6H_3$, X= Ph

Tetrahedron, **1994**, *50*, 11839

New Method for Generation of β-Oxido Carbenoid via Ligand Exchange Reaction of Sulfoxides: A Versatile Procedure for One-Carbon Homologation of Carbonyl Compounds

Tsuyoshi Satoh, Norifumi Itoh, Kaoru Gengyo, Sae Takada, Naoyuki Asakawa, Yumi Yamani, and Koji Yamakawa*
Faculty of Pharmaceutical Sciences, Science University of Tokyo; Shinjuku-ku, Tokyo 162, Japan

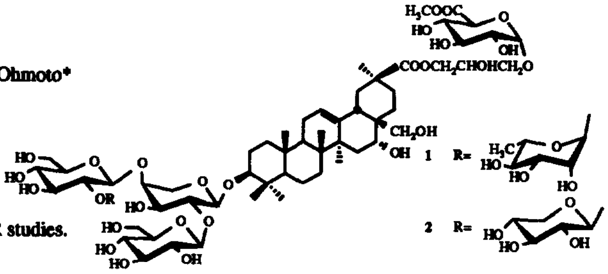


Tetrahedron, **1994**, *50*, 11853

Two Novel Triterpenoid Pentasaccharides with an Unusual Glycosyl Glycerol Side Chain from *Ardisia crenata*

Zhonghua Jia, Kazuo Koike, Tamotsu Nikaido, Taichi Ohmoto*
School of Pharmaceutical Sciences, Toho University,
Miyama 2-2-1, Funabashi, Chiba 274, Japan

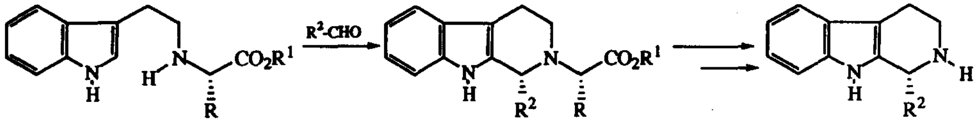
Two novel triterpenoid pentasaccharides, ardisicrenosides E (1) and F (2) were isolated from the roots of *Ardisia crenata*. Their structures were mainly established on the basis of high field NMR studies.



Tetrahedron, **1994**, *50*, 11865

Asymmetric Steering of the Pictet-Spengler Reaction by Means of Amino Acid Esters as Chiral Auxiliary Groups

Herbert Waldmann[a]*, Gunther Schmidt[a], Martin Jansen[b] and Jutta Geb[b]
a) Universität Karlsruhe, Institut für Organische Chemie, Richard-Willstätter-Allee 2, D-76128 Karlsruhe.
b) Universität Bonn, Institut für Anorganische Chemie, Gerhard-Domagk-Straße 1, D-53121 Bonn.



The Pictet-Spengler reaction of N-(β-3-indolyl)ethyl amino acid esters and various substituted benzaldehydes delivers tetrahydro-β-carbolines with isomer ratios up to 98.5:1.5.

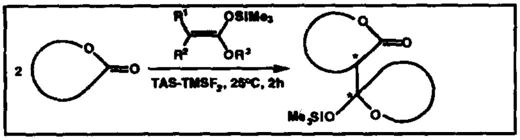
Tetrahedron, **1994**, *50*, 11885

DIASTEREOSELECTIVE DIMERISATION OF ALDONOLACTONES

RENÉ CSUK,[a*] MARTINA SCHAADE[a] AND ANDREA SCHMIDT[b]

[a] PHARMAZEUTISCH-CHEMISCHES INSTITUT, UNIVERSITÄT HEIDELBERG, Im Neuenheimer Feld 364, D-69120 Heidelberg, Germany;
[b] INSTITUT F. PHYSIKALISCHE CHEMIE, UNIVERSITÄT GRAZ, Heinrichstraße 28, A-8010 Graz, Austria

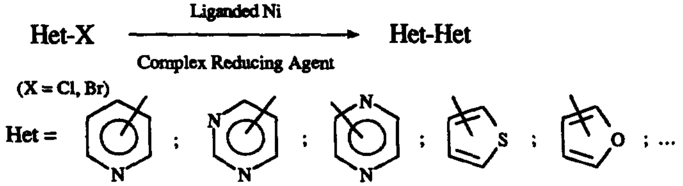
The TAS-TMSF$_2$ mediated reaction of dialkyl substituted trimethylsilyl ketene acetals with aldonolactones affords carbohydrate dimers. This as well as the reaction of the lactones with cyclic TMS ketene acetals results in the creation of two stereogenic centers in a diastereoselective manner.



Tetrahedron, **1994**, *50*, 11893

A Convenient Synthetic Route to bis-Heteroaromatic and bis Heterocyclic Compounds Promoted by Liganded Nickel Complex Reducing Agents.

Yves Fort, Sandrine Becker and Paul Caubère. Laboratoire de Chimie Organique I, URA CNRS 457,
INCM FU CNRS 0008, Faculté des Sciences, Université H. Poincaré, Nancy I, BP239, 54506 Vandoeuvre les Nancy, France.

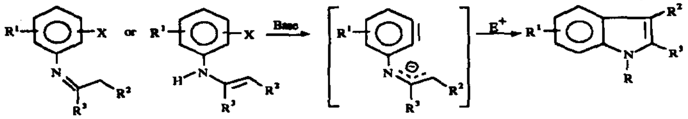


Tetrahedron, **1994**, *50*, 11903

Aggregative Activation and Heterocyclic Chemistry I. Complex Bases promoted Arynic Cyclisation of Imines or Enaminoketones ; Regiochemical Synthesis of Indoles

Catherine Caubère,[†] Paul Caubère,[†] ,Sandra Ianelli,[#]
Mario Nardelli[#] and Brigitte Jamart-Grégoire[†*]

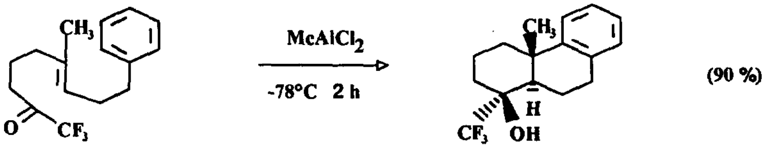
[†]Laboratoire de Chimie Organique I, URA CNRS 457, INCM FU CNRS 0008, Faculté des Sciences,Université Henri Poincaré, Nancy I, BP 239, F-54506 Vandoeuvre-les-Nancy, France [#] Istituto di Chimica Generale, Universita degli Studi di Parma, Centro di Studio CNR per la Strutturistica Diffrattometrica, Viale delle Scienze, I-43100 Parma, Italy.



Tetrahedron, **1994**, *50*, 11921

TANDEM CARBONYL ENE CYCLIZATION-CYCLOALKYLATION: A ROUTE TO TRIFLUOROMETHYL DITERPENOIDS

Ahmed Abouabdellah and Danièle Bonnet-Delpon
BIOCIS-CNRS, Centre d'Etudes Pharmaceutiques, Rue J.B. Clément, F-92296 Châtenay-Malabry, France.

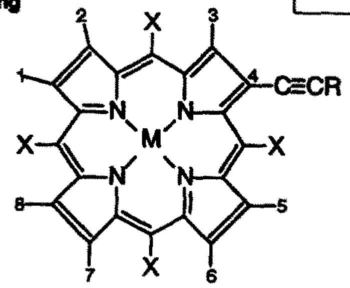


Tetrahedron, **1994**, *50*, 11933

Synthesis of β-Substituted Porphyrins Using Palladium Catalysed Reaction

Hasrat Ali and Johan E. van Lier
MRC Group in the Radiation Sciences
Fac. of Med., Univ. of Sherbrooke
Sherbrooke, QC, Canada J1H5N4

The palladium(II)-catalysed carbon-carbon coupling reaction between a variety of metalated β-halosubstitued porphyrins and a series of terminally substitued acetylenic derivatives, is reported.



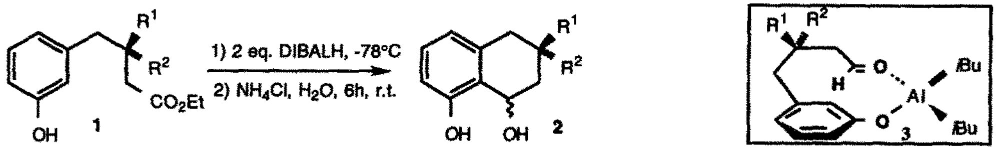
X= H; 1,2,3,5,8=Me; 2(4)=H
6,7=$CH_2CH_2CO_2CH_3$
X= H; 1,2,3,5,6,7,8=Et
X= Ph;1,2,3,5,6,7,8=H
R= Ph, $(CH_2)_nY$
n= 2-10
Y= H, OH, CN

Tetrahedron, **1994**, *50*, 11945

REGIOSELECTIVE SYNTHESIS OF 1,8-DIHYDROXYTETRALINS THROUGH A TANDEM REDUCTION / INTRAMOLECULAR HYDROXY-ALKYLATION OF 4-(3-HYDROXYPHENYL)ALKANOATES.

Giuseppe Guanti,* Luca Banfi, and Renata Riva. Istituto di Chimica Organica e C.N.R., corso Europa 26, 16132 Genova (Italy).

Reaction of esters **1** with DIBALH (2 eq.), followed by aqueous work-up, gave a totally regioselective intramolecular hydroxyalkylation, probably through chelated transition state **3**.

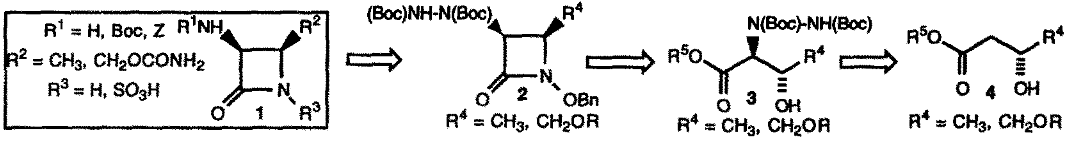


Tetrahedron, **1994**, *50*, 11967

ENANTIOSPECIFIC AND DIASTEREOSELECTIVE SYNTHESIS OF *CIS* MONOBACTAMS THROUGH ELECTROPHILIC AMINATION OF CHIRAL 3-HYDROXYESTERS.

Luca Banfi,[a] Giuseppe Cascio,[b] Giuseppe Guanti,[a]* Elso Manghisi,[b] Enrica Narisano,[a] and Renata Riva.[a] [a] Itituto di Chimica Organica e C.N.R., corso Europa 26, 16132 Genova (Italy). [b] Luso Farmaco s.p.a., Milano (Italy).

Cis azetidinones **1** have been synthesized by a new strategy, based on reaction of β-hydroxyesters **4** with di-*tert*-butyl azodicarboxylate.

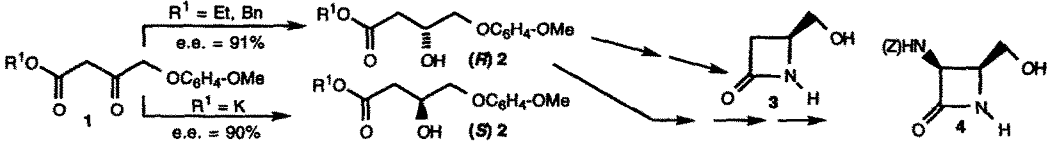


Tetrahedron, **1994**, *50*, 11983

MICROBIOLOGICAL ENANTIOSELECTIVE SYNTHESIS OF (*S*) AND (*R*) 4-(*p*-ANISYLOXY)-3-HYDROXYBUTYRATES AS NEW CHIRAL BUILDING BLOCKS FOR THE SYNTHESIS OF β-LACTAM ANTIBIOTICS.

Luca Banfi,[a] Giuseppe Cascio,[b] Chiara Ghiron,[a] Giuseppe Guanti,[a]* Elso Manghisi,[b] Enrica Narisano,[a] and Renata Riva.[a] [a] Istituto di Chimica Organica e C.N.R., corso Europa 26, 16132 Genova (Italy). [b]Luso Farmaco s.p.a., Milano(Italy).

Reduction of β-ketoesters or β-ketocarboxylates **1** with immobilized baker's yeast gave (*R*) or (*S*) **2**, as new useful chiral building blocks.

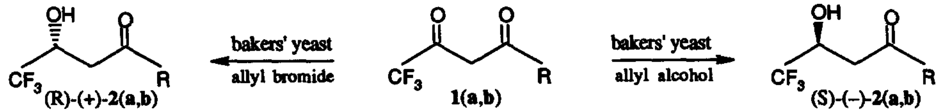


Tetrahedron, **1994**, *50*, 11995

STEREOCHEMICAL CONTROL IN YEAST REDUCTION OF FLUORINATED β-DIKETONES

Arrigo Forni,* Irene Moretti, Fabio Prati, Giovanni Torre.
Dipartimento di Chimica, Università di Modena, via Campi 183, 41100, Modena, Italy.

The presence of additives in bakers' yeast reductions of fluorinated β-diketones turns the stereochemistry of the reaction towards the (R) or (S) enantiomers of the corresponding ketols.



(R)-(+)-2(a,b)

1(a,b)

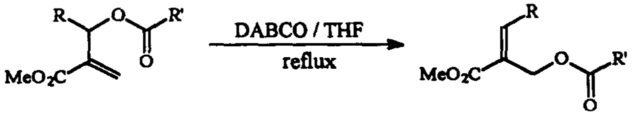
a) R = CH_3; b) R = thienyl

(S)-(–)-2(a,b)

Tetrahedron, **1994**, *50*, 12001

SOME MECHANISTIC AND SYNTHETIC ASPECTS OF THE DABCO CATALYSED REARRANGEMENT OF ALLYLIC ESTERS.

Paul H. Mason and Neville D. Emslie*. Department of Chemistry, University of Natal, Private Bag X01, Scottsville, 3209, Republic of South Africa.



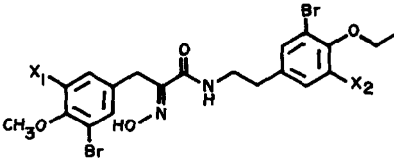
The DABCO (1,4-diazabicyclo-[2,2,2]-octane) catalysed rearrangement of allylic esters has been shown to proceed *via* a two-path mechanism.

Tetrahedron, **1994**, *50*, 12009

Marine Products from Bay of Bengal : Constituents of the Sponge Psammaplysilla purpurea.

S.C.Pakrashi*, B.Achari, P.K.Dutta, A.K.Chakrabarti, C.Giri, S.Saha (Indian Institute of Chemical Biology, Calcutta-700032) and S.C.Basa (Regional Research Laboratory, Bhubaneswar-751013, India).

Abstract: New bromotyrosine derived secondary metabolites **1a,b**(R=H) of the sponge Psammaplysilla purpurea have been identified through spectroscopic analyses of their acetates **1a,b**(R=Ac).



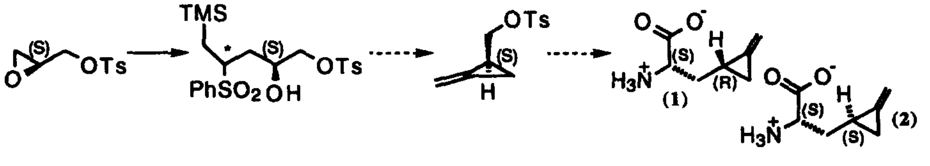
1.a $X_1 = X_2 = H$
b $X_1 = Br, X = H$
c $X_1 = H, X_2 = Br$
d $X_1 = X_2 = Br$

Tetrahedron, **1994**, *50*, 12015

ASYMMETRIC TOTAL SYNTHESIS OF THE INDIVIDUAL DIASTEREOISOMERS OF HYPOGLYCIN A.

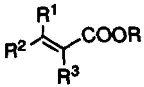
Jack. E. Baldwin, Robert M. Adlington, David Bebbington and Andrew T. Russell.
Dyson Perrins Laboratory and the Oxford Centre for Molecular Sciences, South Parks Road, Oxford, OX1 3QY, UK.

The individual diastereoisomers that constitute the unusual methylenecyclopropane containing α-amino acid hypoglycin A, (1) and (2), have been synthesised utilising the Sharpless epoxidation to permit an asymmetric methylenecyclopropane synthesis.



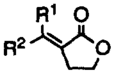
Tetrahedron, **1994**, *50*, 12029

SYNTHESIS OF VARIOUSLY 2-SUBSTITUTED ALKYL (*Z*)- AND (*E*)-2-ALKENOATES AND (*Z*)- and (*E*)-α-YLIDENE-γ-BUTYROLACTONES VIA PALLADIUM-MEDIATED CROSS-COUPLING REACTIONS BETWEEN ORGANOSTANNANES AND ORGANIC HALIDES. Fabio Bellina, Adriano Carpita, Massimo De Santis and Renzo Rossi *. Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Risorgimento 35, I-56126 Pisa, Italy.



(*Z*)-**7** : R^1 = alkyl, aryl; R_2 = H; R^3 = alkenyl, (hetero)aryl, $COCH_3$, CH_3

(*E*)-**7** : R^1 = H; R^2 = alkyl, aryl; R^3 = alkenyl, aryl



(*Z*)-**8** : R^1 = alkyl, aryl; R^2 = H

(*E*)-**8** : R^1 = H; R^2 = alkyl, aryl