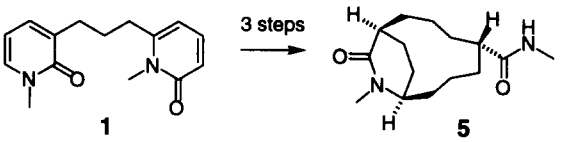
## GRAPHICAL ABSTRACTS

*Tetrahedron Letters*, **1997**, *38*, 8433

**BEYOND THE MEDIUM RING: A [4 + 4] CYCLOADDITION/FRAGMENTATION SYNTHESIS OF ELEVEN-MEMBERED RINGS**

Scott McN. Sieburth,* Taleb H. Al-Tel, and David Rucando, Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794-3400

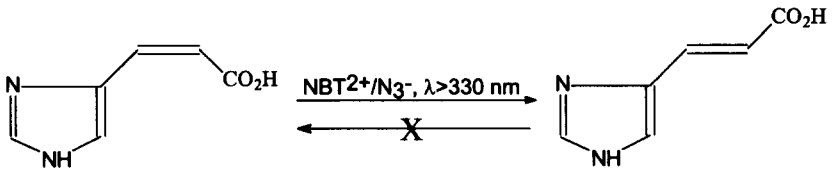
Intramolecular photo-[4 + 4] cycloaddition of bis-2-pyridone **1** yields a fused 5-8 ring system. Hydrogenation and lithium/ammonia reduction, leads to the bridged 11-membered ring **5**.




*Tetrahedron Letters*, **1997**, *38*, 8435

**Evidence for Azidyl Radical Initiated Olefin Isomerization. One-way Isomerization of (Z)-Urocanic Acid** Armah Kpissay, C. Nicole Kuhl, Taj Mohammad, Ken Haber and Harry Morrison*

Department of Chemistry, Purdue University West Lafayette, IN 47907-1393

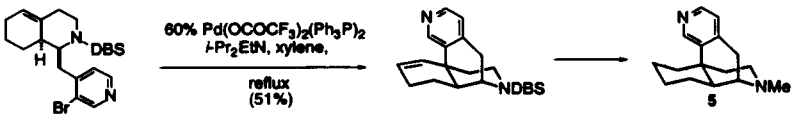



*Tetrahedron Letters*, **1997**, *38*, 8439

**Pyridinomorphinans: Asymmetric Synthesis of Either Enantiomer and Opioid Receptor Binding Selectivity.**

Chang Y. Hong, Larry E. Overman* and Alex Romero, Department of Chemistry, 516 Physical Sciences 1, University of California, Irvine, CA 92697-2025, USA

Either enantiomer of a new class of morphinans in which the aryl ring is replaced by a pyridine ring can be prepared by sequential iminium ion–allylsilane cyclization and intramolecular Heck insertion. Pyridinomorphinan **5** exhibits high affinity for the μ opioid receptor.

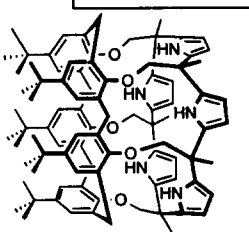



*Tetrahedron Letters*, **1997**, *38*, 8443

FIRST SYNTHESIS OF AN EXPANDED CALIXPYRROLE

Philip A. Gale, John W. Genge, Vladimír Král, M. Anthony McKervey,* Jonathan L. Sessler,* and Andrew Walker.
Department of Chemistry and Biochemistry,
University of Texas at Austin, Austin, Texas 78712-1167, USA.

The first example of a calix[5]pyrrole has been synthesized by the use of a calix[5]arene template.



*Tetrahedron Letters*, **1997**, *38*, 8445

**Solid Phase Synthesis of Quinazolinones.**

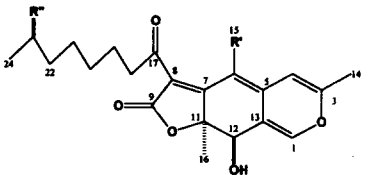
John P. Mayer*, George S. Lewis, Michael J. Curtis and Jingwen Zhang.
*Amgen Inc., 3200 Walnut St., Boulder, CO, 80301.*

*Tetrahedron Letters*, **1997**, *38*, 8449

**PITHOLIDES A-D, POLYKETIDES FROM A MARINE TUNICATE-DERIVED CULTURE OF PITHOMYCES SP.** Gui-Yang-Sheng Wang,

Bethel M. Borgeson and Phillip Crews*, Department of Chemistry and Biochemistry, University of California, Santa Cruz, CA 95064

Four new fungi pigments, pitholides A-D (**2-5**) were isolated from the salt water culture of the fungus *Pithomyces* sp. separated from the Indo-Pacific tunicate *Oxycorynia fasciculatis*. Their structures include the core of Austdiol (**6**), an *Aspergillus* metabolite.

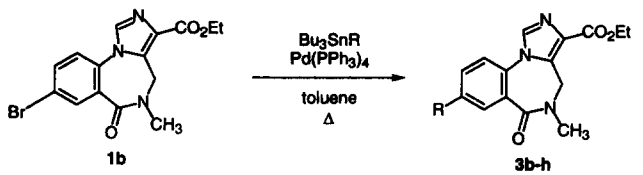


**2** R' = CHO, R" = OH
**3** R' = CHO, R" = H
**4** R' = H, R" = OH
**5** R' = H, R" = H

*Tetrahedron Letters*, **1997**, *38*, 8453

**The Synthesis of $GABA_A$ Active Ligands by the Stille Process**

Tong Gan, Scott G. Van Ornum and James M. Cook*
Department of Chemistry, University of Wisconsin-Milwaukee, Milwaukee, WI 53201



**1b**

**3b-h**

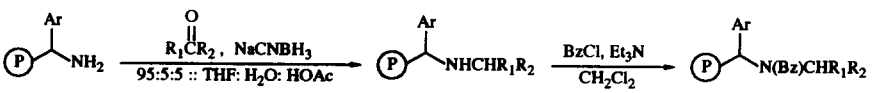
R = vinyl, allyl or aryl

*Tetrahedron Letters*, **1997**, *38*, 8457

**ALKYLATION OF RINK'S AMIDE LINKER ON POLYSTYRENE RESIN: A REDUCTIVE AMINATION APPROACH TO MODIFIED AMINE-LINKERS FOR THE SOLID PHASE SYNTHESIS OF N-SUBSTITUTED AMIDE DERIVATIVES.**

Edward G. Brown and John M. Nuss, Drug Discovery Research, Chiron Corporation, 4560 Horton Street, Emeryville, CA 94608.

Selective mono-alkylation of Rink's Linker is obtained using carbonyl compounds and $NaCNBH_3$ in aqueous, acidified THF.

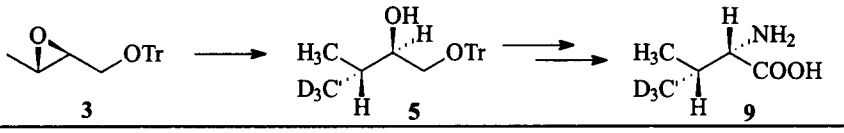


*Tetrahedron Letters*, **1997**, *38*, 8461

**THE PREPARATION OF L-(2*S*, 3*S*)-4,4,4-[$^2H_3$] VALINE.**

James C. Shattuck, Department of Chemistry, University of Hartford, 200 Bloomfield Ave., W. Hartford, CT 06117 USA,
Jerrold Meinwald*, Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, NY 14853 USA

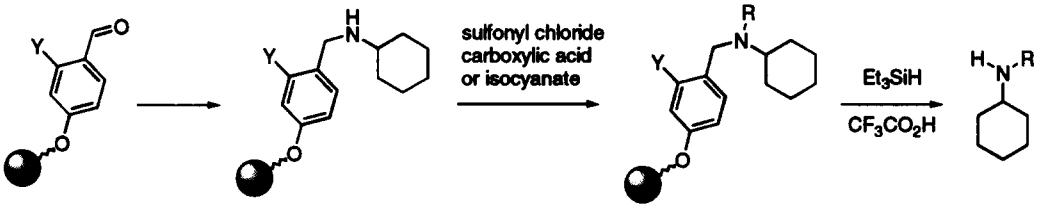
L-(2*S*, 3*S*)-4,4,4-[$^2H_3$] Valine has been synthesized using a short, versatile, enzyme-free procedure. The isotopic label is introduced with an organocuprate opening of a chiral epoxide. The stereochemistry of the starting epoxide can be manipulated using the Sharpless asymmetric epoxidation.




3 5 9

*Tetrahedron Letters*, **1997**, *38*, 8465

**SECONDARY AMIDE-BASED LINKERS FOR SOLID PHASE ORGANIC SYNTHESIS.** Eric E. Swayze, Isis Pharmaceuticals, 2292 Faraday Av., Carlsbad, CA 92008



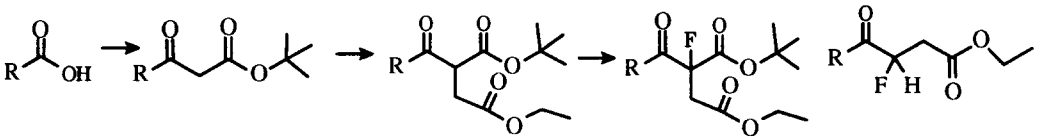

Y=H, OMe

*Tetrahedron Letters*, **1997**, *38*, 8469

A SHORT, EFFICIENT SYNTHESIS OF MONOFLUORO KETOMETHYLENE PEPTIDE ISOSTERE CORE UNITS

Robert V. Hoffman* and James E. Saenz
Department of Chemistry and Biochemistry, New Mexico State University, Las Cruces, NM 88003-0001

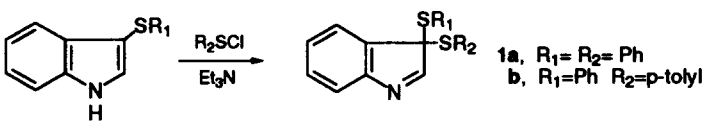
An efficient, four step synthesis of monofluoro ketomethylene peptide isostere core units is described.




*Tetrahedron Letters*, **1997**, *38*, 8473

**Isolation of 3H-Indole-3,3 Bis-Sulfides as Intermediates in the Second Sulfenylation of Indole.** Pierre Hamel, Merck Frosst Centre for Therapeutic Research, P.O. Box 1005, Pointe-Claire - Dorval, Quebec H9R 4P8

3H-Indole-3,3 bis sulfides have been isolated as probable intermediates in the second sulfenylation of indole with sulfenyl halides, which leads to indole 2,3-bis sulfides as end products.



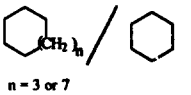

**1a**, $R_1 = R_2 = Ph$
**b**, $R_1 = Ph$ $R_2$=p-tolyl

*Tetrahedron Letters*, **1997**, *38*, 8491

**ON THE DISTINCTION BETWEEN RADICAL CHEMISTRY AND GIF CHEMISTRY.**

D.H.R. Barton*, F. Launay, V.N. Le Gloahec, T. Li and F. Smith
Department of Chemistry, Texas A&M University, College Station, TX 77843-3255, USA.

By simple competitive experiments between saturated hydrocarbons, a distinction between radical and Gif chemistry can be made.

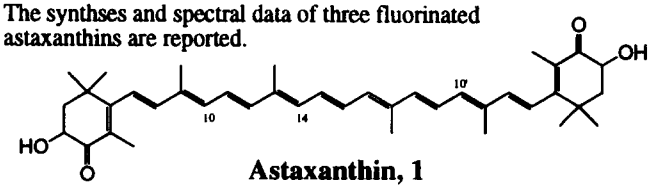



*Tetrahedron Letters*, **1997**, *38*, 8495

**Fluorinated Astaxanthins.**

Jin Liu, L. U. Colmenares and R. S. H. Liu
Department of Chemistry, University of Hawaii, Honol;ulu, HI, 96822 USA

The synthses and spectral data of three fluorinated astaxanthins are reported.



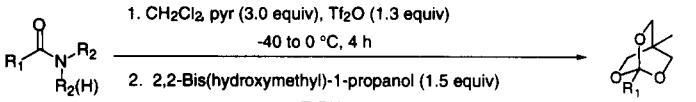

**Astaxanthin, 1**

**2**: 10,10'-difluoro
**3**: 10-fluoro-
**4**: 14-fluoro-

*Tetrahedron Letters*, **1997**, *38*, 8499

**A NEW METHOD FOR THE CONVERSION OF SECONDARY AND TERTIARY AMIDES TO BRIDGED ORTHOESTERS**

André B. Charette,* Peter Chua. Département de Chimie, Université de Montréal, Montréal, Québec, Canada, H3C 3J7.



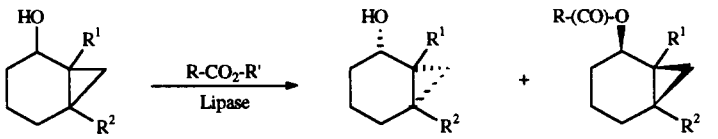

$R_1$ = alkyl, aryl, cyclopropyl
$R_2$ = alkyl

59 - 88%

*Tetrahedron Letters*, **1997**, *38*, 8503

**Enzymatic resolution of endo-bicyclo[4.1.0]heptan-2-ols**

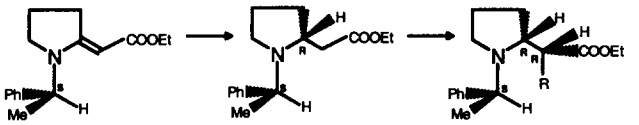
Jean-Pierre Barnier, Vincent Rayssac, Véronique Morisson, Luis Blanco
Laboratoire des Carbocycles (Associé au C.N.R.S.), Institut de Chimie Moléculaire d'Orsay, Bât. 420, Université de Paris-Sud, 91405 Orsay (France)



*Tetrahedron Letters*, **1997**, *38*, 8507

**CHIRAL CYCLIC β-AMINO ESTERS. PART I : SYNTHESIS BY DIASTEREOSPECIFIC ALKYLATION.**

A. Bardou, J. P. Célérier, and G. Lhommet*
Université Pierre et Marie Curie. Laboratoire de Chimie des Hétérocycles. associé au CNRS. 4, Place Jussieu, 75252 Paris cedex 05, France



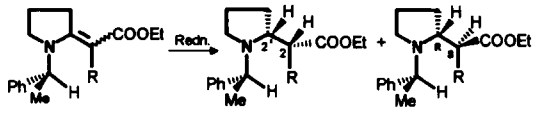
Chiral cyclic β-amino esters can be enantiospecifically prepared by a kinetically controled alkylation α to the ester function of β-amino esters.

*Tetrahedron Letters*, **1997**, *38*, 8511

**CHIRAL CYCLIC β-AMINO ESTERS. PART II: SYNTHESIS BY DIASTEREOSELECTIVE REDUCTION OF ENAMINO ESTERS.**

J. Blot[a], A. Bardou[a], C. Bellec[a], M.C. Fargeau-Bellassoued[a], J.P. Célérier[a], G. Lhommet[a], D. Gardette[b] J. C. Gramain[b].
[a]Université P. et M. Curie. Laboratoire de Chimie des Hétérocycles, 4 Place Jussieu, 75252 Paris cedex 05, France.
[b]Université B. Pascal. Laboratoire de Chimie des Substances Naturelles 63177 Aubière cedex, France.

Cyclic β-aminoesters are obtained by reduction of corresponding tetrasubstituted β-enaminoesters in good to moderate diastereoisomer excesses.

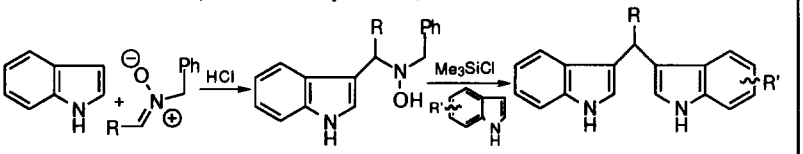


*Tetrahedron Letters*, **1997**, *38*, 8515

**THE REACTION OF NITRONES WITH INDOLES. SYNTHESIS OF ASYMMETRICAL DIINDOLYLALCANES**

Jean-Noël Denis, Hélène Mauger and Yannick Vallée*. L.E.D.S.S., Université Joseph Fourier, 38041 Grenoble, France.

The reaction of indoles with nitrones has been applied to the synthesis of various *N*-hydroxylamines, symmetrical and asymmetrical diindolylalcanes and three natural bis-indoles.

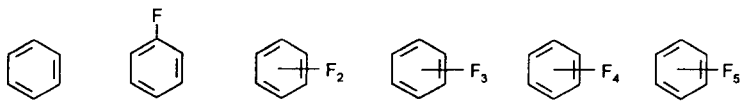


*Tetrahedron Letters*, **1997**, *38*, 8519

**ADDITIVITY OF SUBSTITUENT EFFECTS IN THE FLUOROARENE SERIES : EQUILIBRIUM ACIDITY IN THE GAS PHASE AND DEPROTONATION RATES IN ETHEREAL SOLUTION**

H. Büker, N.M.M. Nibbering, D. Espinosa, F. Mongin, M. Schlosser *
Universities of Amsterdam (NL) and Lausanne (CH)

*Gas Phase Acidity and Proton Mobility in Solution :*

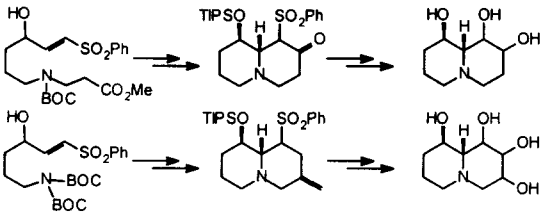


*Tetrahedron Letters*, **1997**, *38*, 8537

## A Stereoselective Approach to Polyhydroxylated Quinolizidine Alkaloids

Juan C. Carretero*, Ramón Gómez Arrayás and Isabel Storch de Gracia

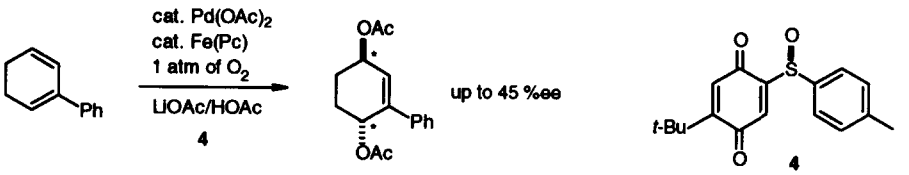
Departamento de Química Orgánica
Facultad de Ciencias
Universidad Autónoma de Madrid
28049 Madrid. Spain




*Tetrahedron Letters*, **1997**, *38*, 8541

**Asymmetric Palladium(II) Catalyzed 1,4-Oxidation of 2-Phenyl-1,3-Cyclohexadiene.**

Atli Thorarensen, Andreas Palmgren, Kenichiro Itami and Jan-E. Bäckvall*
Department of Organic Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden

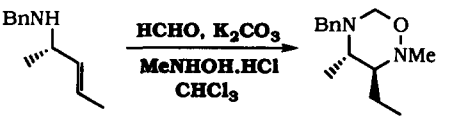



*Tetrahedron Letters*, **1997**, *38*, 8545

**Factors Influencing the Reverse-Cope Approach to 1,2,5-Oxadiazinanes from Allylamines and Nitrones : Optimization of a New Vicinal Diamine Synthesis**

K.E. Bell, M.P. Coogan, M.B. Gravestock, D.W. Knight and S.R. Thornton, Chemistry Departments, Nottingham University , Nottingham, NG7 2RD, UK and Cardiff University, P.O. Box 912, Cardiff, CF1 3TB, UK.

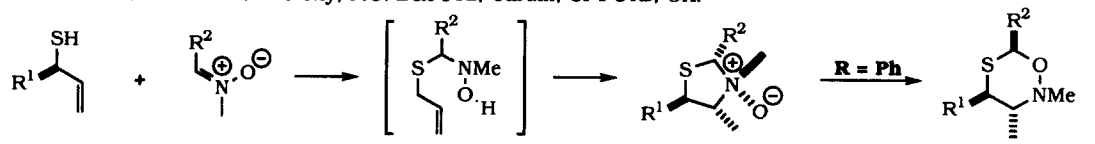
Nitrones derived *in situ* from formaldehyde and a hydroxylamine and especially suited to the reverse-Cope~ Meisenheimer sequence leading to 1,2,5-oxadiazinanes and thence to vicinal diamines.




*Tetrahedron Letters*, **1997**, *38*, 8549

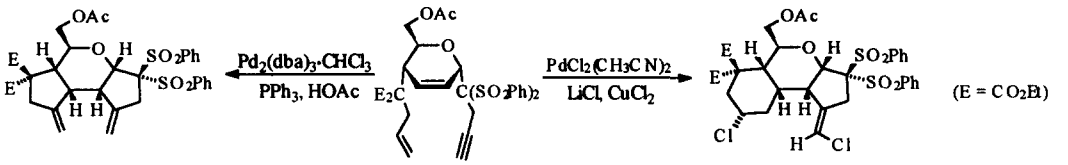
**Reverse-Cope Cyclisations of Thiahydroxylamines Derived from the Addition of Allylic Thiols to Nitrones : Synthesis of 1,3-Thiazolidine-*N*-oxides and 1,5,2-Oxathiazinanes**

M.P. Coogan, M.B. Gravestock, D.W. Knight and S.R. Thornton, Chemistry Departments, Nottingham University, Nottingham, NG7 2RD UK and Cardiff University, P.O. Box 912, Cardiff, CF1 3TB, UK.



*Tetrahedron Letters*, **1997**, *38*, 8585

**PALLADIUM-CATALYSED CASCADE REACTIONS OF UNSATURATED CARBOHYDRATE DERIVATIVES. SYNTHESIS OF ENANTIOPURE TRICYCLIC COMPOUNDS.** Cedric W. Holzapfel* and Lizel Marais, Department of Chemistry and Biochemistry, Rand Afrikaans University, PO Box 524, Auckland Park, 2006, South Africa

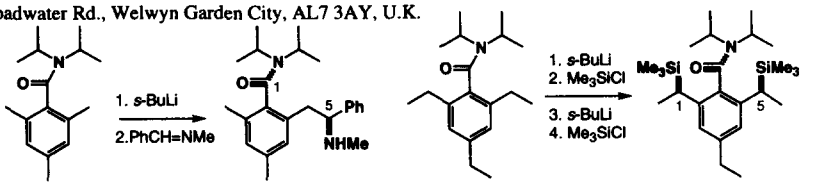



*Tetrahedron Letters*, **1997**, *38*, 8587

**REMOTE STEREOCONTROL USING ROTATIONALLY RESTRICTED AMIDES: (1,5)-ASYMMETRIC INDUCTION**

Jonathan Clayden,* Megan Darbyshire, Jennifer H. Pink, Neil Westlund and Francis X.Wilson[a]
Department of Chemistry, University of Manchester, Oxford Rd., Manchester, M13 9PL, U.K. and
[a]Roche Products Ltd., 40 Broadwater Rd., Welwyn Garden City, AL7 3AY, U.K.

Electrophilic quench of lithiated atropisomeric 2-alkyl or 2-keto benzamides or naphthamides can lead to complete (1,5)-asymmetric induction

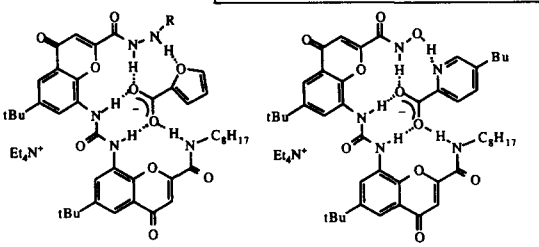



*Tetrahedron Letters*, **1997**, *38*, 8591

**RECEPTORS FOR CARBOXYLATES DERIVED FROM 2-FUROIC AND FUSARIC ACIDS**

Mª Fe de la Torre, Silvia González, Eduardo G. Campos, Mª Luisa Mussons, Joaquín R. Morán and Mª Cruz Caballero
Departamento de Química Orgánica, Universidad de Salamanca, 37008 Salamanca, Spain

New hydrogen bonding receptors have been prepared for complexing carboxylates derived from 2-furoic and fusaric acids.

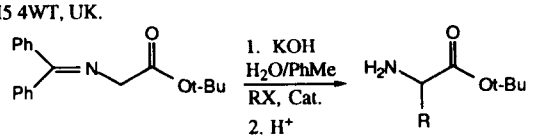



*Tetrahedron Letters*, **1997**, *38*, 8595

**A NEW CLASS OF ASYMMETRIC PHASE-TRANSFER CATALYSTS DERIVED FROM *CINCHONA* ALKALOIDS - APPLICATION TO THE ENANTIOSELECTIVE SYNTHESIS OF α-AMINO ACIDS.**

**Barry Lygo* and Philip G. Wainwright,**
Department of Chemistry, University of Salford, Salford, M5 4WT, UK.

New asymmetric phase-transfer catalysts have been developed allowing the alkylation of glycine imines with high enantioselectivity (67-94% e.e.).

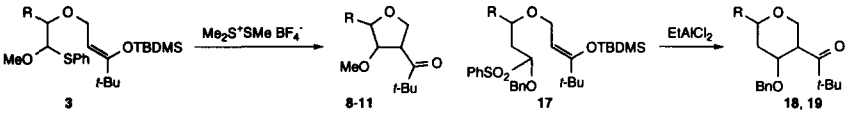


*Tetrahedron Letters*, **1997**, *38*, 8599

**HETEROCYCLIC SYNTHESIS BY C–C BOND FORMATION. TETRAHYDROFURAN AND TETRAHYDROPYRAN SYNTHESIS via OXONIUM ION-MEDIATED CYCLISATION REACTIONS**

Donald Craig,*[a] N. Paul King[a] and Anthony N. Shaw[b]
[a]Department of Chemistry, Imperial College of Science, Technology and Medicine, London SW7 2AY, U.K.
[b]SmithKline Beecham Pharmaceuticals, The Frythe, Welwyn, Hertfordshire AL6 9AR, U.K.

Dithioacetal–enol ethers **3** undergo cyclisation to give tetrahydrofurans **8-11** on treatment with $Me_2S^+SMe\ BF_4^-$. Sulfones **17** enter into related cyclisation reactions on exposure to $EtAlCl_2$.




*Tetrahedron Letters*, **1997**, *38*, 8603

**THE FIRST CHEMO- AND REGIOSPECIFIC PALLADIUM-CATALYZED ENYNE-DIYNE [4+2] INTERMOLECULAR *CROSS*-BENZANNULATION: AN EFFECTIVE ROUTE TO POLYSUBSTITUTED BENZENES.**

Vladimir Gevorgyan, Naoki Sadayori, and Yoshinori Yamamoto*, Department of Chemistry
Graduate School of Science, Tohoku University, Sendai 980-77, Japan