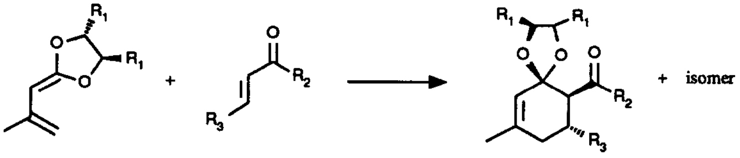
*Tetrahedron*, **1991**, *47*, 4519

## ENANTIOMERICALLY PURE VINYLKETENE ACETALS IN THE DIELS-ALDER REACTION. CATALYSIS AND FACIAL SELECTIVITY.

Mark A. Boehler and Joseph P. Konopelski*
*Department of Chemistry, University of California, Santa Cruz, CA 95064*

The synthesis and reactivity of a series of enantiomerically pure vinylketene acetals is presented.



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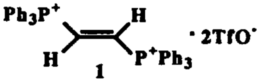
*Tetrahedron*, **1991**, *47*, 4539

## REACTION OF E-1,2-BIS[TRIPHENYL(TRIFLUOROMETHANESULFONYLOXY)PHOSPHO]ETHYLENE, $Ph_3PCH=CHPPh_3 \cdot 2OTf$ WITH BASES: UNUSUAL PRODUCTS AND EVIDENCE FOR $C_2$-DIYLIDE, $Ph_3P=C=C=PPh_3$, FORMATION

P.J. Stang*, A.M. Arif, V.V. Zhdankin Chemistry Department, University of Utah, Salt Lake City, Utah 84112

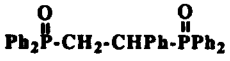
Bis-phosphonium salt 1 reacts with $Et_3N$ or NaH in wet $CH_3CN$ affording phosphineoxides 2 and 3 as a result of phenyl migration and related rearrangements in hydrolysed phosphonium moieties. The reaction of 1 with *t*-BuLi in $CH_2Cl_2$ results in nucleophilic vinylic substitution of the phosphonium group with the *t*-Bu anion. Evidence for the intermediate formation of the $C_2$-diylide 4 is obtained in the reaction of 1 with *n*-BuLi in $CH_2Cl_2$ via trapping with 3,4-dichlorobenzaldehyde.



1

$Ph_3P^+\text{-}CH_2\text{-}CHPh\text{-}\overset{O}{\overset{\|}{P}}Ph_2\ TfO^-$

2



$Ph_2\overset{O}{\overset{\|}{P}}\text{-}CH_2\text{-}CHPh\text{-}\overset{O}{\overset{\|}{P}}Ph_2$

3

$Ph_3P=C=C=PPh_3$

4

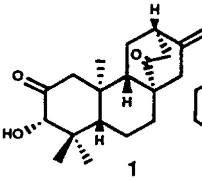
---

*Tetrahedron*, **1991**, *47*, 4547

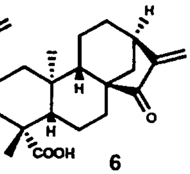
## HIV INHIBITORY NATURAL PRODUCTS. 3. DITERPENES FROM Homalanthus acuminatus and Chrysobalanus icaco

K.R. Gustafson, M.H.G. Munro, J.W. Blunt, J.H. Cardellina II, J.B. McMahon, R.J. Gulakowski, G.M. Cragg, P.A. Cox, L.S. Brinen, J. Clardy and M.R. Boyd*
Laboratory of Drug Discovery Research and Development,
National Cancer Institute-FCRDC, Frederick, MD 21702-1202

Diterpenes 1-4 were found in Homalanthus acuminatus, while two (6,7) were found in Chrysobalanus icaco. Compounds 1 and 6 were active in the anti-HIV screen; 1, 3 and 4 were previously unknown.



1



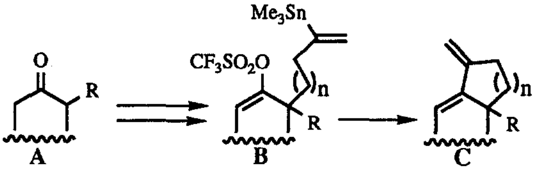
6

*Tetrahedron*, **1991**, *47*, 4555

## INTRAMOLECULAR PALLADIUM(O)-CATALYZED COUPLING OF ENOL TRIFLATE AND VINYLSTANNANE FUNCTIONS. NEW ANNULATION SEQUENCES LEADING TO BICYCLIC DIENE SYSTEMS

Edward Piers,* Richard W. Friesen, and Brian A. Keay, Department of Chemistry, University of British Columbia, 2036 Main Mall, University Campus, Vancouver, B. C., Canada V6T 1Y6

A new annulation method, the key step of which involves the Pd(O)-catalyzed cyclization of **B**, converts ketones (general formula A) into structurally novel dienes (general formula C).



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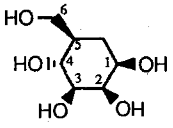
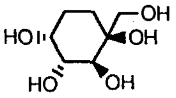
*Tetrahedron*, **1991**, *47*, 4571

## (-)-QUINIC ACID IN ORGANIC SYNTHESIS. 2. FACILE SYNTHESES OF PSEUDO-β-D-MANNOPYRANOSE AND PSEUDO-β-D-FRUCTOPYRANOSE.

Tony K. M. Shing*[a] and Ying Tang[b]
a Department of Chemistry, The Chinese University of Hong Kong, Shatin, Hong Kong.
b Department of Chemistry, The Victoria University of Manchester, Manchester M13 9PL, U.K.



(1)



(2)

Pseudo-b-D-mannopyranose (1) and pseudo-b-D-fructopyranose (2) have been obtained from quinic acid in 7 and 12 steps respectively.

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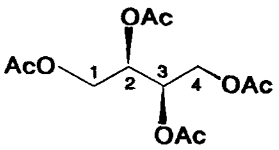
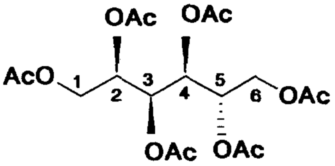
*Tetrahedron*, **1991**, *47*, 4579

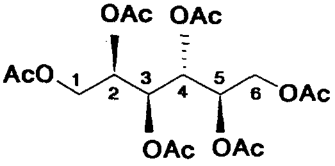
## ON THE POSSIBILITY OF DETERMINING STEREOCHEMISTRY IN ACYCLIC POLYHYDROXYLATED COMPOUNDS BY THE COMBINED VICINAL COUPLING CONSTANT/MOLECULAR MECHANICS METHOD. A TEST WITH ALDITOL PERACETATES

Eiji Osawa, Keisuke Imai, Teruyo Fujiyoshi-Yoneda, and Carlos Jaime, Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan, Philip Ma, and Satoru Masamune, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA.

**Relative configurations of multiple asymmetric centers in alditol peracetates can be determined with 92% confidence from vicinal H/H coupling constants along backbone chain and molecular mechanics calculations.**



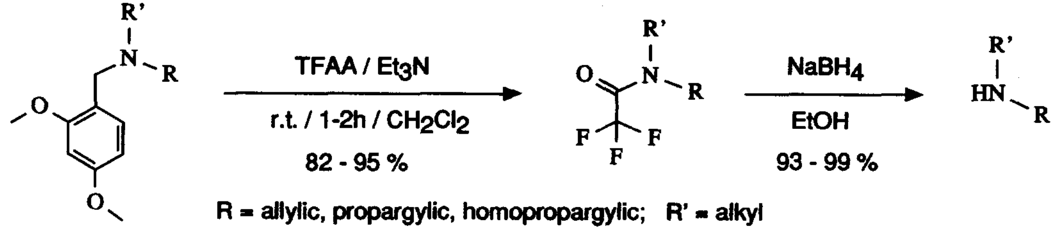




*Tetrahedron*, **1991**, *47*, 4591

# HIGHLY SELECTIVE TFAA-CLEAVAGE OF TERT. 2,4-DIMETHOXYBENZYLAMINES AND ITS USE IN THE SYNTHESIS OF SECONDARY AMINES

P. Nussbaumer*, K. Baumann, Th. Dechat, M. Harasek
Dept. of Dermatology, SANDOZ Forschungsinstitut Wien, Brunnerstrasse 59, A-1235 Wien, Austria



R = allylic, propargylic, homopropargylic; R' = alkyl

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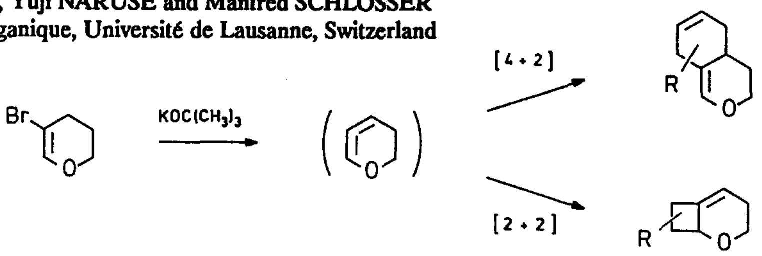
*Tetrahedron*, **1991**, *47*, 4603

# 1-OXA-2,3-CYCLOHEXADIENE ("2*H*-ISOPYRAN") : A STRAINED HETEROCYCLIC ALLENE UNDERGOING CYCLOADDITION REACTIONS WITH CHARACTERISTIC TYPO-, REGIO- AND STEREOSELECTIVITIES

Renzo RUZZICONI, Yuji NARUSE and Manfred SCHLOSSER*
Institut de Chimie organique, Université de Lausanne, Switzerland



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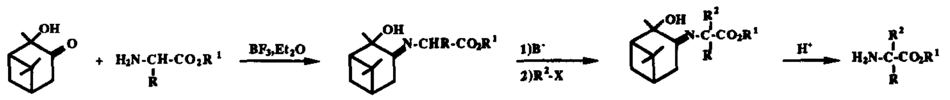
*Tetrahedron*, **1991**, *47*, 4611

# ALKYLATION AND PROTONATION REACTIONS OF CHIRAL SCHIFF BASES : DIASTEREOSELECTIVITY AS A FUNCTION OF THE NATURE OF REACTANTS

Mohamed TABCHEH, Abdelrhani EL ACHQAR, Louis PAPPALARDO, Marie-Louise ROUMESTANT and Philippe VIALLEFONT
Laboratoire de Synthèse et d'Etudes Physicochimiques U.R.A. 468 - Université Montpellier II
34095 - Montpellier cedex 5 - FRANCE.

The factors controlling the diastereoselective alkylation and protonation reactions of chiral Schiff bases are reported.

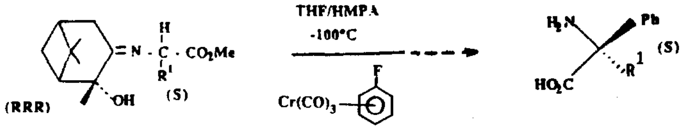


*Tetrahedron*, **1991**, *47*, 4619

## REACTIONS OF FLUOROBENZENE TRICARBONYLCHROMIUM COMPLEXES WITH ANIONS FROM SCHIFF BASES OF α-AMINO ESTERS : ENANTIOSELECTIVE SYNTHESIS OF α-ARYL AMINO ACIDS

Mohamed Chaari, Aîcha Jenhi, Jean-Pierre Lavergne* and Philippe Viallefont
Laboratoire de Synthèse et d'Etudes Physicochimiques d'aminoacides et de peptides, URA 468, Université de Montpellier II, 34095 - MONTPELLIER Cedex 5, France

A synthesis of α-substituted aryl amino acids via the addition of α-imino esters to fluorobenzene tricarbonylchromium complexes is described.



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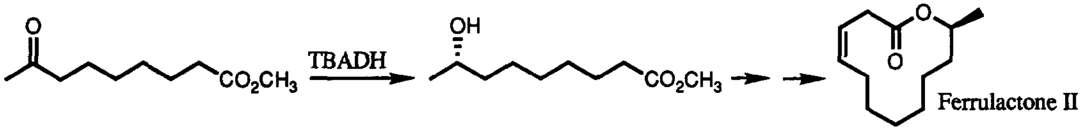
*Tetrahedron*, **1991**, *47*, 4631

## THERMOSTABLE ENZYMES IN ORGANIC SYNTHESIS, 5. TOTAL SYNTHESIS OF S-(+)-Z-DODEC-3-EN-11-OLIDE (FERRULACTONE II) USING A TBADH-GENERATED BIFUNCTIONAL CHIRON.

Ehud Keinan*, Subhash C. Sinha and Surendra P. Singh
Department of Chemistry, Technion - Israel Institute of Technology, Technion City, Haifa 32000, Israel.

The total synthesis of ferrulactone II, one of several synergistic aggregation pheromones produced by *Cryptolestes ferrugineus* was achieved in a five-step synthesis in very high optical purity (>99% ee), starting from a chiral building block that was obtained by *Thermoanaerobium brockii* alcohol dehydrogenase (TBADH)-catalyzed ketone reduction.



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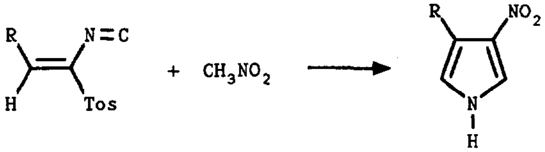
*Tetrahedron*, **1991**, *47*, 4639

## AN EFFICIENT SYNTHESIS OF 3-NITROPYRROLES

Daan van Leusen, Ernst Flentge and Albert M. van Leusen.

*Department of Organic Chemistry, Groningen University*
*Nijenborgh 16, 9747 AG, The Netherlands*

3-Nitropyrroles are prepared in high yield from nitromethane and 1-isocyano-1-tosyl-1-alkenes.

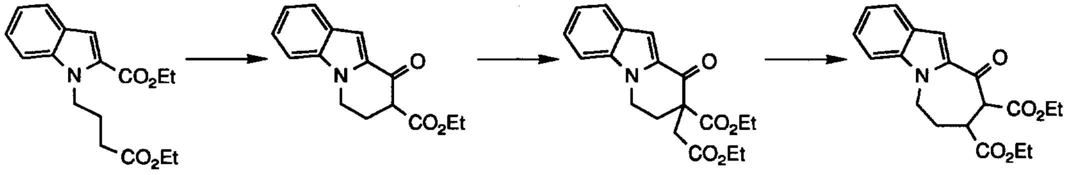


*Tetrahedron*, **1991**, *47*, 4645

### A DIECKMANN/RING EXPANSION APPROACH TO TETRAHYDROPYRIDO- AND TETRAHYDROAZEPINO-[1,2-a]INDOLES

Rino A. Bit, Peter D. Davis, Christopher H. Hill*, Elizabeth Keech and David R. Vesey
Roche Products Ltd., P. O. Box 8, Welwyn Garden City, Herts., AL7 3AY, UK.

*A general Dieckmann/ring expansion approach to fused [1,2-a]indole systems is reported.*



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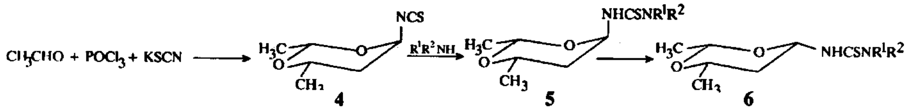
*Tetrahedron*, **1991**, *47*, 4665

### SIMPLE PREPARATION OF EPIMERIC 2,6-DIMETHYL-4-(N'-SUBSTITUTED THIOUREIDO)-1,3-DIOXANES AND CRYSTAL STRUCTURE OF *rel*-2S,4S,6S-2,6-DIMETHYL-4-(N'-BENZYLTHIOUREIDO)-1,3-DIOXANE

*Juraj Bernát [a], Ladislav Kniežo [a*], Gabriela Birošová [a], Ján Imrich [a], Jaroslav Podlaha [b], Miloš Buděšínsky [c], Jaromír Novák [d] and Tibor Liptaj [e]*
*[a] Department of Organic Chemistry, P.J.Safarik University, 04167 Kosice, CSFR.*

One-pot reaction of acetaldehyde, $POCl_3$ and KSCN affords isothiocyanate **4** in good yield. Compound **4** reacts with primary amines to give thioureas **5** which are spontaneously epimerized in acetone solution under formation of thioureas **6** ,



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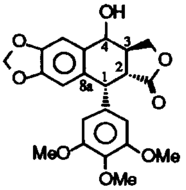
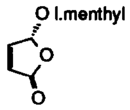
*Tetrahedron*, **1991**, *47*, 4675

### ENANTIOSELECTIVE TOTAL SYNTHESIS OF (-)-EPI-PODOPHYLLOTOXIN AND (-)-PODOPHYLLOTOXIN

R. Van Speybroeck, H. Guo, J. Van der Eycken, and M. Vandewalle* State University of Gent, Department of Organic Chemistry, Laboratory for Organic Synthesis, Krijgslaan, 281 (S.4), B-9000 GENT (Belgium).



**1** 4 α-OH
**2** 4 β-OH



**13**

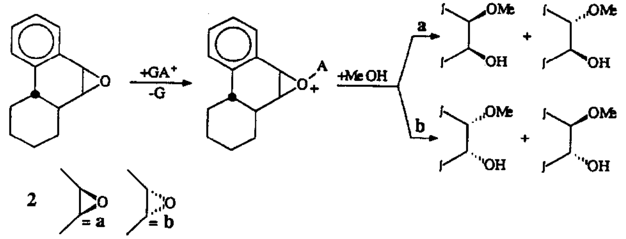
(-)-Epipodophyllotoxin (**2**) and (-)-podophyllotoxin (**1**) are obtained via the butenolide **13** as chiral template and a stereoselective formation of the 1-8a bond

*Tetrahedron*, **1991**, *47*, 4683

## Gas-Phase Acid-Induced Ring Opening in Diastereoisomeric 9,10-Oxides derived from *trans*-1,2,3,4,4a,10a-Hexahydrophenantrene

Patrizio Cecchi,[a] Marco Chini,[b] Paolo Crotti,[b*] Adriano Pizzabiocca,[c] Gabriele Renzi [c*] and Maurizio Speranza.[a]
[a] Università della Tuscia, I-01100 Viterbo, Italy. [b] Università di Pisa, I-56100 Pisa, Italy. [c] Università di Camerino, I-62032 Camerino, Italy.

The stereochemistry of the ring opening process in systems 2a and 2b was studied in the gas-phase.



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*Tetrahedron*, **1991**, *47*, 4693

## SPECTROSCOPIC, KINETIC AND SEMIEMPIRICAL MOLECULAR ORBITAL STUDIES ON 8-AMINO-, 8-METHYLAMINO- & 8-DIMETHYLAMINO-ADENOSINES

J. Hovinen, C. Glemarec, A. Sandström, C. Sund, & J. Chattopadhyaya*
*Department of Bioorganic Chemistry, Box 581, Biomedical Center,*
*University of Uppsala, S-751 23 Uppsala, Sweden*

Relative rates of acidic depurination of 8-amino, 8-methylamino or 8-dimethylaminoadenosine are respectively 2.7, 2 and 429-fold with respect to adenosine. Structural consequence of 8-amino substitution in adenosine have been therefore studied by $^{15}N$- and $^{1}H$-NMR spectroscopy in neutral and acidic solutions and also by Semiempirical Molecular Orbital calculations (AM1) in order to shade light on steric, electronic and conformational factors dictated by 8-amino, 8-methylamino or 8-dimethylamino group to the purine and the pentose rings.

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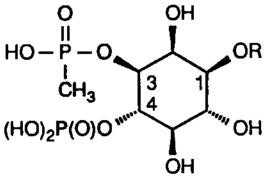
*Tetrahedron*, **1991**, *47*, 4709

## SYNTHESIS OF RACEMIC 3-METHYLPHOSPHONATE ANALOGUES OF *MYO*-INOSITOL 3,4-*BIS*- AND 1,3,4-*TRIS*PHOSPHATE

C.E. Dreef, R.J. Tuinman, A.W.M. Lefeber, C.J.J. Elie, G.A. van der Marel and J.H. van Boom
*Gorlaeus Laboratories, P.O. Box 9502, 2300 RA Leiden, The Netherlands*

The title compounds I and II were readily prepared from properly protected *myo*-inositol derivatives by sequential methylphosphonylation, removal of the temporary protecting group(s), phosphorylation and deprotection.

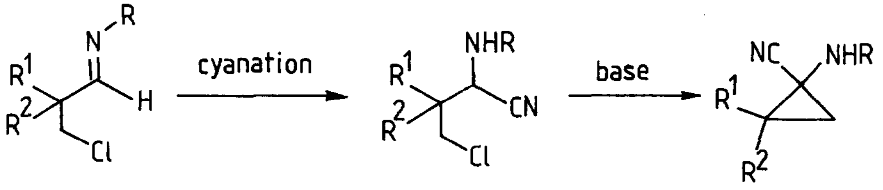


I R = H II R = $P(O)(OH)_2$

*Tetrahedron*, **1991**, *47*, 4723

## SYNTHESIS OF 1-AMINO-2,2-DIALKYLCYCLOPROPANECARBOXYLIC ACIDS FROM β-CHLOROALDIMINES

N. DE KIMPE, P. SULMON and C. STEVENS
Laboratory of Organic Chemistry, Faculty of Agricultural Sciences, State University of Gent, Coupure Links 653, B-9000 GENT, Belgium



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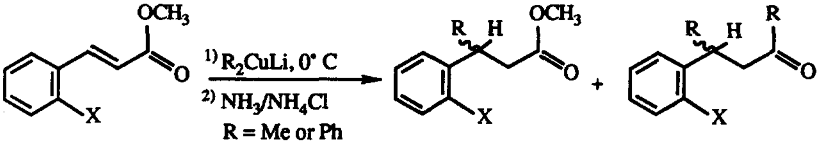
*Tetrahedron*, **1991**, *47*, 4739

## Stereoselective Addition of $R_2CuLi$ to *ortho*-Substituted Methyl Cinnamates. Intramolecular Assistance and Solvent Effects.

B. Christenson[a], G. Hallnemo[b] and C. Ullenius[a,*]; [a]Chalmers University of Technology, Göteborg, (Sweden), [b]Astra Research Centre AB, Södertälje, (Sweden).



+ high molecular weight products

X = $-CH_2OCH_3$, $-CH(CH_3)OCH_3$, $-CH_2N(CH_3)_2$, $-CH(CH_3)N(CH_3)_2$

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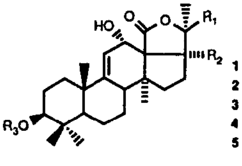
*Tetrahedron*, **1991**, *47*, 4753

## HOLOTHURINOSIDES: NEW ANTITUMOUR NON-SULPHATED TRITERPENOID GLYCOSIDES FROM THE SEA CUCUMBER *HOLOTHURIA FORSKALII*

JAIME RODRIGUEZ, RITA CASTRO and RICARDO RIGUERA*
Departamento de Química Orgánica, Facultad de Química, Universidad de Santiago de Compostela, Spain.

Five new saponins (1-5) have been isolated from the aqueous-methanolic extract from the echinoderm *Holothuria forskalii*. They were shown to have antitumour and antiviral activity.

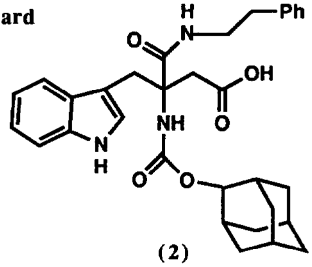


1 $R_1$= A $R_2$ = OH $R_3$ = β-D-3-O-Me-GLU (1 → 3) β-D-GLU (1 → 4) β-D-QUI (1 → 2) β-D XYL (4 → 1) β-D GLU
2 $R_1$= B $R_2$ = OH $R_3$ = β-D-3-O-Me-GLU (1 → 3) β-D-GLU (1 → 4) β-D-QUI (1 → 2) β-D XYL (4 → 1) β-D GLU
3 $R_1$= A $R_2$ = H $R_3$ = β-D-3-O-Me-GLU (1 → 3) β-D-GLU (1 → 4) β-D-QUI (1 → 2) β-D XYL
4 $R_1$= A $R_2$ = OH $R_3$ = β-D-3-O-Me-GLU (1 → 3) β-D-GLU (1 → 4) β-D-QUI (1 → 2) β-D XYL
5 $R_1$= A $R_2$ = H $R_3$ = β-D-QUI (1 → 2) β-D XYL

*Tetrahedron*, **1991**, *47*, 4763

## SYNTHESIS OF AN α-$CH_2CO_2H$ FUNCTIONALIZED TRYPTOPHAN AND ITS INCORPORATION INTO AN ANALOGUE OF CHOLECYSTOKININN.

**Gregory T. Bourne, David C. Horwell*, and Martyn C. Pritchard**
**Parke-Davis Research Unit , Addenbrookes Hospital Site,**
**Hills Road, Cambridge CB2 2QB, U.K.**



(2)

**Synthesis of an α,α-disustituted tryptophan (2) is described via the alkylation of an isonitrile derivative**

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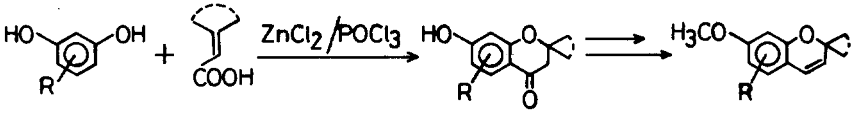
*Tetrahedron*, **1991**, *47*, 4775

## A NEW AND EFFICIENT GENERAL METHOD FOR THE SYNTHESIS OF 2-SPIROBENZOPYRANS: FIRST SYNTHESIS OF CYCLIC ANALOGUES OF PRECOCENE I AND RELATED COMPOUNDS.

Suneel Y Dike[*a], Jaysukhlal R Merchant[*b] and Niteen Y Sapre[b]
a: Alchemie Research Centre, PO Box 155, Thane-Belapur Road,
Thane - 400 601, Maharashtra, INDIA.
b: D G Ruparel College, Bombay 400 016, INDIA.



Starting from cycloalkylidene acetic acid novel synthesis of 2-spirobenzopyrans has been accomplished.