

## GRAPHICAL ABSTRACTS

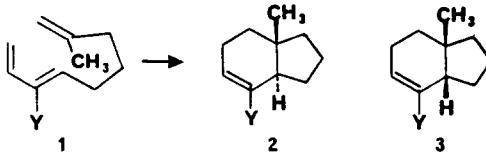
**Tetrahedron Lett.** 27, 6291 (1986)

**N,N-DIMETHYLANILINE AS A SOLVENT FOR INTRAMOLECULAR DIELS ALDER REACTIONS. IMPROVED YIELDS AND CHANGES IN STEREOISOMER RATIOS.**

Kathlyn A. Parker\* and Tahir Iqbal

Department of Chemistry, Brown University, Providence, RI 02912

The yields of product mixtures from the cycloaddition of nonatrienes **1** and the ratios of trans:cis hydrindene (**2:3**) in those mixtures are solvent dependent.



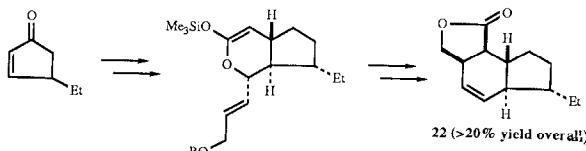
**Tetrahedron Lett.** 27, 6295 (1986)

**NOT THE ENOLATE CLAISEN REARRANGEMENT. A SURPRISING ROUTE TO THE "RIGHT-WING" OF INDANOMYCIN (X-14547A)**

Steven D. Burke,\* David M. Armistead, and K. Shankaran

Department of Chemistry, University of South Carolina, Columbia, SC 29208 USA

A tandem cycloreversion/cycloaddition process supersedes an intended Claisen rearrangement route to the ionophore synthon **22**.



**Tetrahedron Lett.** 27, 6299 (1986)

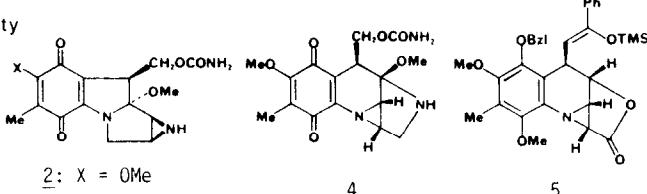
**SYNTHETIC APPROACHES TOWARD MITOMYCINS. I.**

**STEREOSELECTIVE SYNTHESIS OF A TETRACYCLIC INTERMEDIATE.**

Tohru Fukuyama\* and Lihu Yang

Department of Chemistry, Rice University  
Houston, Texas 77251

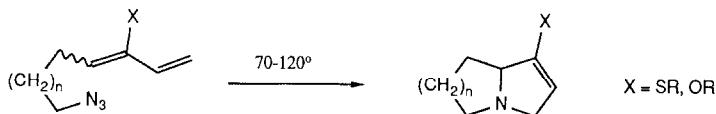
A highly efficient synthesis of a tetracyclic intermediate **5** to the antitumor antibiotic AX-2 **4**, a mitomycin A **2** equivalent, is described.



**Tetrahedron Lett.** 27, 6301 (1986)

**INTRAMOLECULAR AZIDE-DIENE CYCLOADDITIONS. AN APPROACH TO FUSED BICYCLIC 3-PYRROLINES BASED ON A ONE-POT NITRENE-DIENE CYCLOADDITION EQUIVALENT.**

William H. Pearson,\* Joseph E. Celebuski, Yam-Foo Poon, Brian R. Dixon, Jeffrey H. Glans  
Department of Chemistry, University of Michigan, Ann Arbor, MI 48109



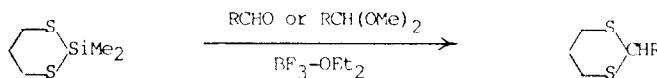
**A RAPID, EFFICIENT AND SELECTIVE CONVERSION OF ALDEHYDES AND ACETALS TO THEIR 1,3-DITHIANE DERIVATIVES WITH 2,2-DIMETHYL-2-SILA-1,3-DITHIANE**

Tetrahedron Lett. 27, 6305 (1986)

John A. Soderquist\* and Edgar I. Miranda

Department of Chemistry, University of Puerto Rico, Rio Piedras, Puerto Rico 00931

Aldehydes and acetals are cleanly and rapidly converted to the corresponding dithianes with 2,2-dimethyl-2-sila-1,3-dithiane and stoichiometric amounts of boron trifluoride etherate.

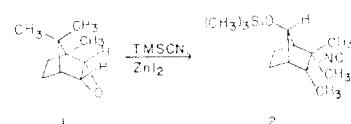


**MECHANISTIC INSIGHTS INTO THE OPENING OF EPOXIDES WITH TRIMETHYLSILYL CYANIDE - ZINC IODIDE**

Paul G. Gassman,\* Kentaro Okuma, Aline Lindbeck, and Richard Allen

Department of Chemistry, University of Minnesota, Minneapolis, MN 55455 USA

Reaction of **1** with TMSCN - ZnI<sub>2</sub> gave 72% of **2** in addition to 25% of a mixture of eight other products. The formation of **2** and of other rearrangement products required an ionic component for this epoxide ring opening process.

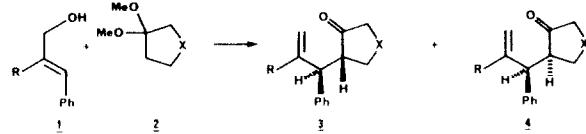


**THE STEREOSELECTIVITY OF KETAL CLAISEN REARRANGEMENTS WITH KETALS OF SIMPLE CYCLIC KETONES**

G. William Daub\* and David A. Griffith

Department of Chemistry, Harvey Mudd College, Claremont, California 91711 USA

Claisen rearrangements of the ketals of simple cycloalkanones (**2**, X=1-3) give mixtures of *syn* (**3**) and *anti* (**4**) products favoring the *syn* isomer by as much as 19:1. Competing enolization processes reduce the selectivity in some cases.

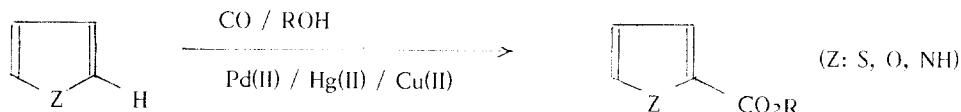


**PALLADIUM-CATALYZED, ONE-POT CARBONYLATION OF HETEROCYCLIC COMPOUNDS INTO THEIR ESTERS.**

Tetrahedron Lett. 27, 6315 (1986)

R: Jaouhari, P.H. Dixneuf (Université de Rennes, France)

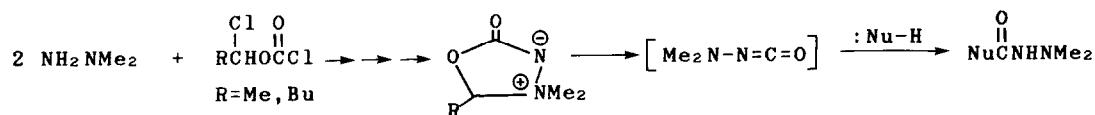
S: Lecolier (SNPE-Le Bouchet, France)



**CYCLIC CARBALKOXY AMINIMIDES. SYNTHESIS AND THERMAL DECOMPOSITION TO GIVE N,N-DIMETHYLAMINO ISOCYANATE**

Jean-Pierre Senet\*, Guy Selaine Vergne, and Gary P. Wooden  
SNPE, Centre de Recherches du Bouchet, 91710 Vert-le-Petit, FRANCE

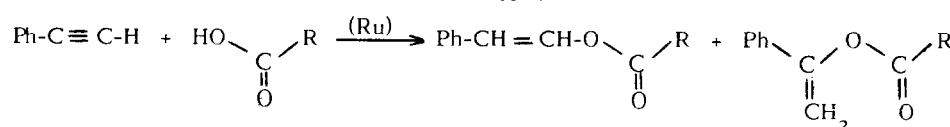
Five membered ring carbalkoxy aminimides are prepared from dimethylhydrazine and  $\alpha$ -chloroalkyl chloroformates. These give high yields of N,N-dimethylamino isocyanate which dimerizes or can be trapped in the presence of a nucleophile.



**SYNTHESIS OF ENOL ESTERS FROM TERMINAL ALKYNES  
CATALYZED BY RUTHENIUM COMPLEXES.**

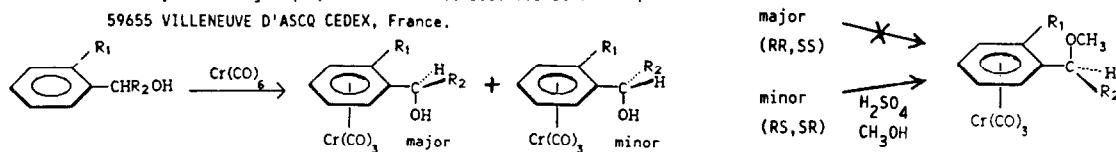
Christophe Ruppin and Pierre H. Dixneuf

Campus de Beaulieu, Université de Rennes, 35042 Rennes (France)



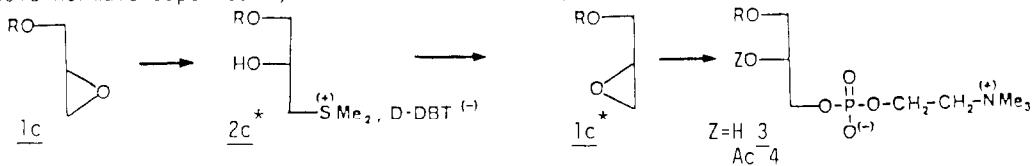
**COMPLEXATION DIASTEROSELECTIVE D'ALCOOLS BENZYLIQUES  
PAR LE CHROME HEXACARBONYLE. DIFFERENCE DE REACTIVITE  
DES DIASTEROISOMERES EN MILIEU ACIDE.**

Jacques BROCARD, Jacques LEBIBI, Lydie PELINSKI et Madani MAHMOUDI  
Laboratoire de Synthèse Organique, Université des Sciences et Techniques de Lille  
59655 VILLENEUVE D'ASCQ CEDEX, France.



**RESOLUTION OF OXIRANES, APPLICATION TO  
THE SYNTHESIS OF THE PLATELET AGGREGATION FACTOR**

Bernard Cimetière, Laurent Jacob et Marc Julia  
Ecole Normale Supérieure, Laboratoire de Chimie, 24 rue Lhomond, 75231 Paris Cedex 05



**ONE-STEP SYNTHESIS OF VINYL CARBAMATES  
CATALYZED BY MONONUCLEAR RUTHENIUM COMPLEXES.**

R. Mahé, P.H. Dixneuf (Université de Rennes, France)

S. Lécolier (SNPE, Le Bouchet, France)



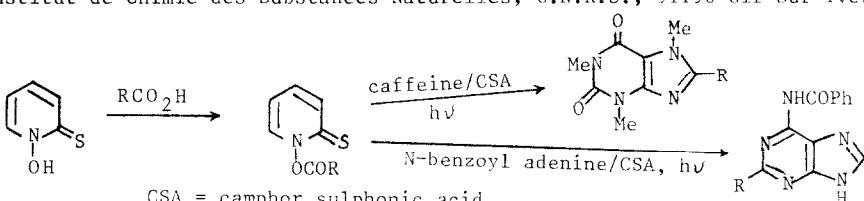
DECARBOXYLATIVE RADICAL ADDITION ONTO PROTONATED HETEROAROMATIC SYSTEMS INCLUDING PURINE BASES

Enzo Castagnino and Stefano Corsano

Istituto di Chimica Farmaceutica, Università di Perugia, via Del Liceo, 06100 Perugia, Italy

Derek H.R. Barton and Samir Z. Zard

Institut de Chimie des Substances Naturelles, C.N.R.S., 91190 Gif-sur-Yvette, France

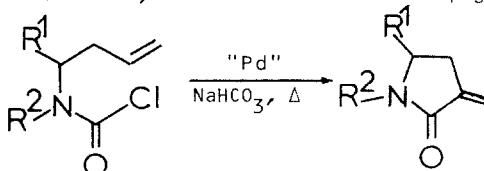


Palladium-Catalysed Synthesis of  $\alpha$ -Methylene  $\gamma$ -Butyro-Lactams via Cyclisation of Homoallylic Chloroformamides

F. HENIN, J. MUZART and J.P. PETE

Laboratoire de Photochimie, Unité Associée au CNRS n° 459, Université de Reims Champagne-Ardenne, 51062 Reims Cedex, France

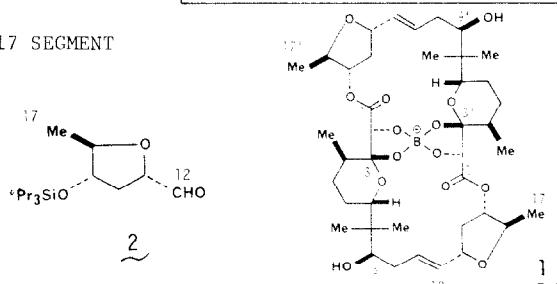
3-Methylene 2-pyrrolidinones were prepared by intramolecular cyclisation of homoallylic chloroformamides catalysed by  $\text{Pd}^{II}$  or  $\text{Pd}^0$  complexes.



SYNTHETIC STUDIES ON (+)-APLASMOMYCIN. 1.  
STEREOSELECTIVE SYNTHESIS OF THE C-12~C-17 SEGMENT

T. Nakata, K. Saito, and T. Oishi  
RIKEN, Wako-shi, Saitama 351-01, Japan

The C-12~C-17 segment 2 of (+)-aplasmomycin (1) was synthesized.

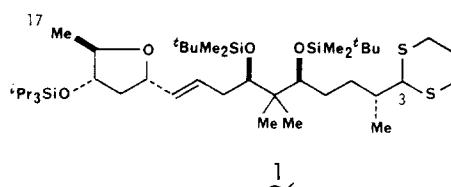


## SYNTHETIC STUDIES ON (+)-APLASMOMYCIN. 2.

## STEREOSELECTIVE SYNTHESIS OF COREY'S KEY INTERMEDIATE, A FOMAL TOTAL SYNTHESIS

T. Nakata,<sup>\*</sup> K. Saito, and T. Oishi<sup>\*</sup>  
RIKEN, Wako-shi, Saitama 351-01, Japan

The C-3~C-17 segment 1 of (+)-aplasmomycin was synthesized.

1

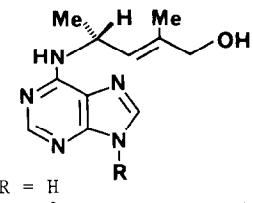
## SYNTHESSES AND ABSOLUTE CONFIGURATIONS OF THE CYTOKININS

## 1'-METHYLZEATIN AND ITS 9-RIBOSIDE

Taisuke Itaya,<sup>†</sup> Tozo Fujii,<sup>\*,†</sup> Antonio Evidente,<sup>‡</sup> Giacomo Randazzo,<sup>‡</sup> Giuseppe Surico,<sup>§</sup> and Nicola S. Iacobellis<sup>§</sup>

<sup>†</sup>Faculty of Pharmaceutical Sciences, Kanazawa University, Kanazawa 920, Japan, <sup>‡</sup>Dipartimento di Chimica Organica e Biologica, Università di Napoli, 80134 Napoli, Italy, and <sup>§</sup>Istituto Tossine e Micotossine da Parassiti Vegetali del C.N.R., 70126 Bari, Italy

The structures of the cytokinins 1'-methylzeatin and its 9-riboside have been established as shown.



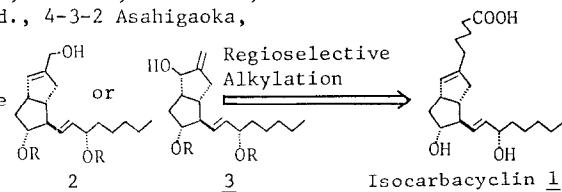
R = H  
R =  $\beta$ -D-ribofuranosyl

## IMPROVED SYNTHESIS OF ISOCARBACYCLIN USING REGIOSELECTIVE ALKYLATION OF ALLYLIC ALCOHOLS

K. Bannai, T. Tanaka, N. Okamura, A. Hazato, S. Sugiura, K. Manabe, K. Tomimori, and S. Kurozumi\*

Institute for Bio-Medical Research, Teijin Ltd., 4-3-2 Asahigaoka, Hino, Tokyo 191, Japan

Two efficient syntheses of isocarbacyclin (1) have been realized using highly regioselective direct alkylation of both *endo*- and *exo*-allylic alcohols (2 and 3).

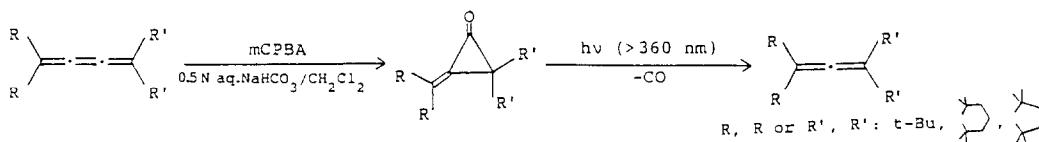


## OXIDATION OF 1,2,3-BUTATRIENES:

## A FACILE FORMATION OF METHYLENECYCLOPROPANONES AND THEIR SUBSEQUENT PHOTODECARBONYLATION

Wataru Ando, Hiroshi Hayakawa, Norihiro Tokitoh

Department of Chemistry, University of Tsukuba, Sakuramura, Niiharigun, Ibaraki 305, Japan

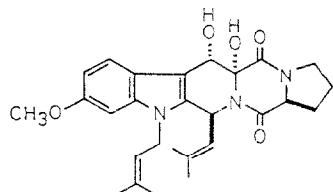


TOTAL SYNTHESIS OF FUMITREMORGIN B.

Shin-ichi Nakatsuka,\* Katsunori Terenishi, and Toshio Goto

Laboratory of Organic Chemistry, Faculty of Agriculture, Nagoya University, Nagoya 464, Japan

Tetrahedron Lett. 27, 6361 (1986)



Total synthesis of fumitremorgin B was achieved in 7 steps.

Fumitremorgin B

NOVEL CHIRAL PORPHYRINS WITH  $C_2$  SYMMETRY

H. Ogoshi,\* K. Saita, K. Sakurai, T. Watanabe,  
H. Toi, and Y. Aoyama\*

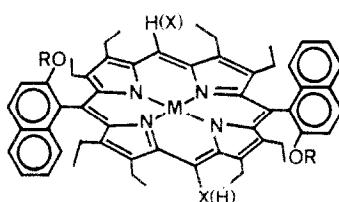
Department of Materials Science and Technology,  
Technological University of Nagaoka, Kamitomioka,  
Nagaoka, Niigata 940-21, Japan

Yoshio Okamoto

Department of Chemistry, Faculty of Engineering Science,  
Osaka University, Toyonaka, Osaka 560, Japan

Preparation and optical resolution of 5,10,15-tri-  
substituted chiral porphyrins.

Tetrahedron Lett. 27, 6365 (1986)

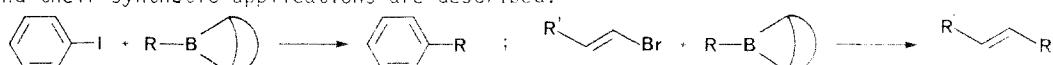


PALLADIUM-CATALYZED CROSS-CO尤LING REACTIONS OF B-ALKYL-9-BBN OR TRIALKYLBORANES WITH ARYL AND 1-ALKENYL HALIDES.

Norio Miyaura, Tatsuo Ishiyama, Masako Ishikawa, and Akira Suzuki\*

Department of Applied Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060,  
Japan

Alkylation of 1-alkenyl and aryl halides with organoboranes in the presence of  $PdCl_2(dppf)$   
and their synthetic applications are described.



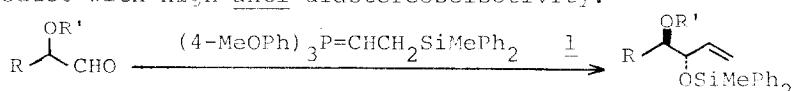
Tetrahedron Lett. 27, 6373 (1986)

CARBONYL ADDITION REACTION BY MEANS OF  $\beta$ -SILYL-PHOSPHOROUS YLDE. ANTI-DIASTEROSELECTIVE

VINYLYATION OF  $\alpha$ -ALKOXY ALDEHYDE.

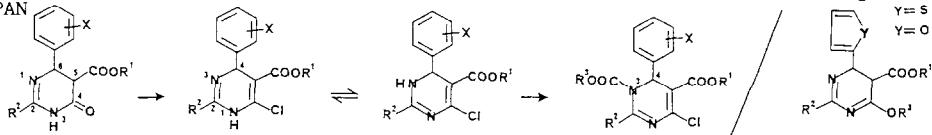
Hideo Iio,\* Tsukasa Mizobuchi, Masamitsu Tsukamoto, and Takashi Tokoroyama\*  
Faculty of Science, Osaka City University Sumiyoshi-ku, Osaka 558, Japan

$\beta$ -Silylphosphorous ylide 1 reacts with  $\alpha$ -alkoxy aldehydes to give exclusively  
vinylyation product with high anti-diastereoselectivity.



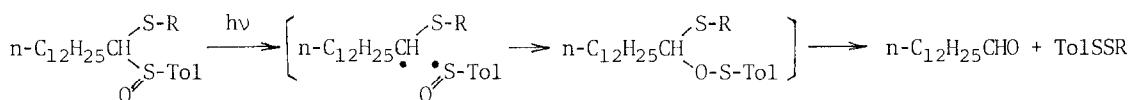
SYNTHESIS OF NOVEL 1,4-, 3,4- AND 4,5-DIHYDROPYRIMIDINES:  
FIRST SUCCESSFUL  $\text{POCl}_3$  CHLORINATION AND REGIOSELECTIVE  
ALKOXYCARBONYLATION

Hidetsura Cho\*, Yoshiko Ohnaka, Mariko Hayashimatsu, Masaru Ueda, and Keiyuu Shima  
Suntory Institute for Biomedical Research, 1-1-1, Wakayamadai, Shimamoto-cho, Mishima-gun,  
Osaka, 618, JAPAN



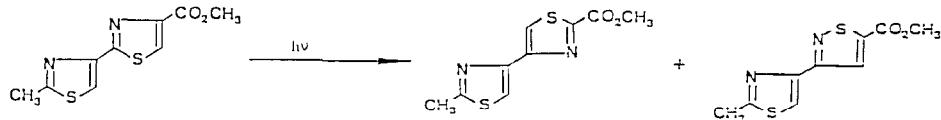
PHOTOCHEMICAL TRANSFORMATION OF A DITHIOACETAL S-OXIDE INTO THE CORRESPONDING ALDEHYDE

Katsuyuki Ogura\*, Shigeyuki Itoh, Kazumasa Takahashi, and Hirotada Iida  
Department of Synthetic Chemistry, Faculty of Engineering, Chiba University  
Yayoicho 1-33, Chiba 260, Japan



RING-SELECTIVE PHOTOREARRANGEMENT OF BITHIAZOLES  
Isao Saito\*, Takashi Morii, Yukihisa Okumura, Satoru Mori,  
§ Kizashi Yamaguchi and Teruo Matsuura

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan  
§ Department of Chemistry, Faculty of Engineering Science, Osaka University, Osaka 560, Japan

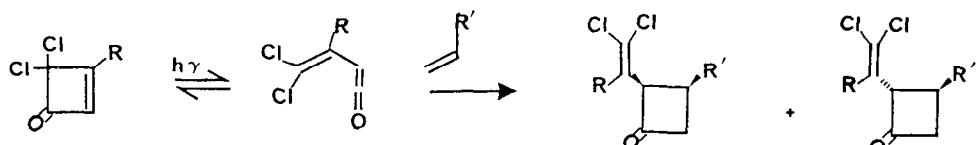


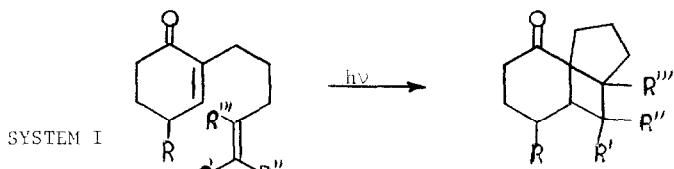
PHOTOCHEMICAL GENERATION OF VINYLKETENES BY ELECTROCYCLIC  
OPENING OF CYCLOBUTENONES

Alfred Hassner\*, Simha Naidorf

Department of Chemistry, Bar-Ilan University, Ramat-Gan 52100, Israel

Photolytic generation of vinylketenes as a route for preparation of 2-vinylcyclobutanones.





The stereoselectivity of the [2+2] intramolecular photoaddition of System I was studied.

PALLADIUM-CATALYSED REDUCTIVE ADDITION OF ARYL IODIDES TO ARYL AND ALKYLETHYNYL SILANES: A STEREO AND REGIOSELECTIVE ROUTE TO FUNCTIONALIZED 2,2-DISUBSTITUTED VINYL SILANES

A. Arcadi<sup>a</sup>, S. Cacchi<sup>b\*</sup>, F. Marinelli<sup>a</sup>

a) Dipartimento di Chimica, Ing. Chimica e Materiali, Via Assergi 4, 67100 L'Aquila (Italy)  
b) Istituto di Chimica Organica, Via del Castro Laurenziano 9, 00161 Roma (Italy)

Aryl and alkylethynyl silanes are stereo and regioselectively converted into 2,2-disubstituted vinylsilanes by a Pd-catalysed reaction

