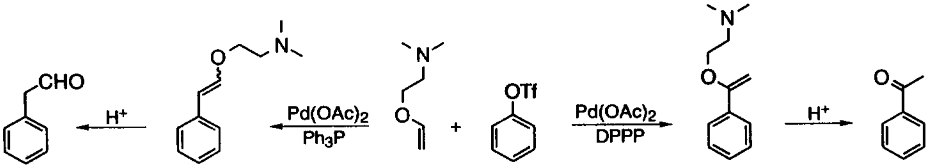
GRAPHICAL ABSTRACTS

Tetrahedron, **1994**, *50*, 285

Chelation-Controlled, Palladium-Catalyzed Arylation of Enol Ethers with Aryl Triflates. Ligand Control of Selection for α– or β–Arylation of [2-(Dimethylamino)ethoxy]ethene.

Mats Larhed[a], Carl-Magnus Andersson[b] and Anders Hallberg[a]*
[a]*Department of Organic Pharmaceutical Chemistry, Uppsala University, P. O. Box 574, S-751 23 Uppsala, SWEDEN*
[b]*Department of Medicinal Chemistry, Preclinical R & D, Astra Draco AB, P. O. Box 34, S-221 00 Lund, SWEDEN*

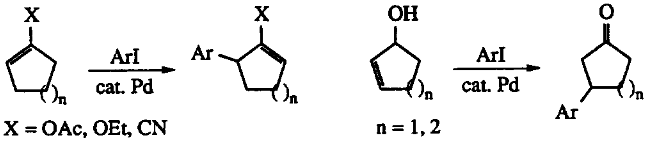


Tetrahedron, **1994**, *50*, 305

PALLADIUM-CATALYZED INTERMOLECULAR ARYLATION OF FUNCTIONALLY-SUBSTITUTED CYCLOALKENES BY ARYL IODIDES

Richard C. Larock, Eul K. Yum and Hoseok Yang, Department of Chemistry, Iowa State University, Ames, IA 50011

The palladium-catalyzed, intermolecular arylation of functionally-substituted cycloalkenes by aryl iodides affords a new synthetic route to a variety of arylated cyclic derivatives.



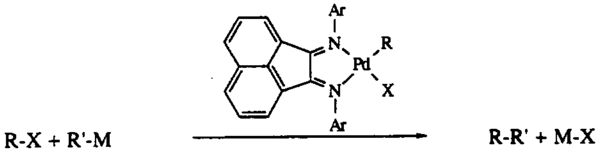
X = OAc, OEt, CN
n = 1, 2

n = 1, 2

Tetrahedron, **1994**, *50*, 323

PALLADIUM COMPLEXES CONTAINING RIGID BIDENTATE NITROGEN LIGANDS AS CATALYSTS FOR CARBON-CARBON BOND FORMATION

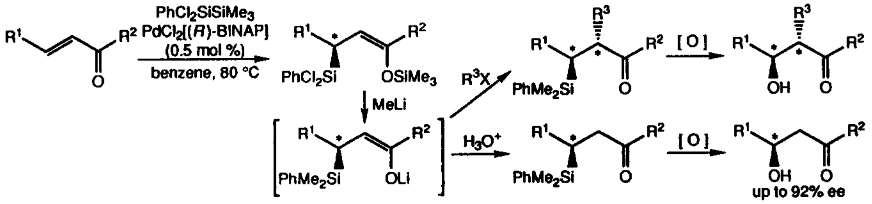
Rob van Asselt and Cornelis J. Elsevier
Anorganisch Chemisch Laboratorium, Universiteit van Amsterdam, Nieuwe Achtergracht 166,
1018 WV Amsterdam, The Netherlands



Tetrahedron, **1994**, *50*, 335

Catalytic Asymmetric Synthesis of β-Hydroxy Ketones by Palladium-Catalyzed Asymmetric 1,4-Disilylation of α,β-Unsaturated Ketones

Yonetatsu Matsumoto and Tamio Hayashi,* *Catalysis Research Center and Graduate School of Pharmaceutical Sciences, Hokkaido University, Sapporo 060, Japan*
Yoshihiko Ito,* *Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan*

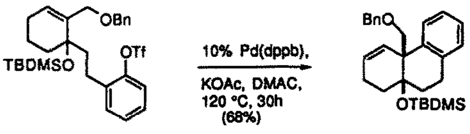


Application of Intramolecular Heck Reactions to the Preparation of Steroid and Terpene Intermediates Having cis A-B Ring Fusions. Model Studies for the Total Synthesis of Complex Cardenolides..

Tetrahedron, **1994**, *50*, 347

Sabine Laschat, Frank Narjes and Larry E. Overman,*
Department of Chemistry, University of California, Irvine, California, USA 92717-2025.

The cis-hexahydrophenanthridine 22 is formed in good yield from Heck cyclization of the aryl triflate 21. This latter conversion demonstrates that allylic ether substitution is compatible with intramolecular Heck chemistry and suggests applications of this chemistry in the synthesis of highly oxidized cardenolides.



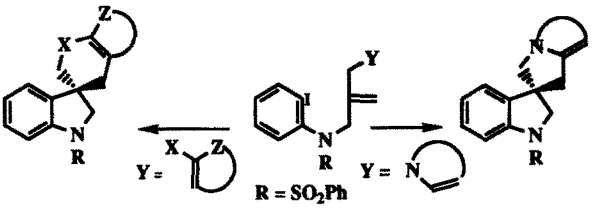
21 22

PALLADIUM CATALYSED SYNTHESIS OF SPIROINDOLINES

Tetrahedron, **1994**, *50*, 359

Ronald Grigg,[a,*] Paul Fretwell,[a] Clive Meerholtz,[b] and Visuvanathar Sridharan[a]
a. School of Chemistry, Leeds University,Leeds LS2 9JT
b. Glaxo Group Research, Greenford, Middlesex UB6 OHE

A series of Palladium catalysed bis - cyclisations of aryl iodides onto heterocyclic rings (both aromatic and non - aromatic) via an alkene relay furnishes spiroindolines in good yield.

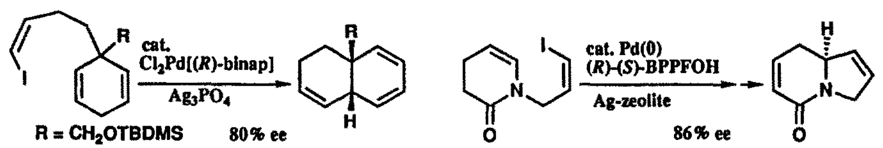


Asymmetric Heck Reaction of Alkenyl Iodides in the Presence of Silver Salts. Catalytic Asymmetric Synthesis of Decalin and Functionalized Indolizidine Derivatives

Tetrahedron, **1994**, *50*, 371

Yoshihiro Sato,[a] Seiji Nukui,[b] Mikiko Sodeoka,[b] and Masakatsu Shibasaki[b*]
Faculty of Pharmaceutical Sciences, [a]Hokkaido University, Sapporo 060, [b]University of Tokyo, Tokyo 113, Japan

The important role of silver salts in the asymmetric Heck reaction of alkenyl iodides is described, suggesting that Ag_3PO_4 or Ag-zeolite is the best silver salt.

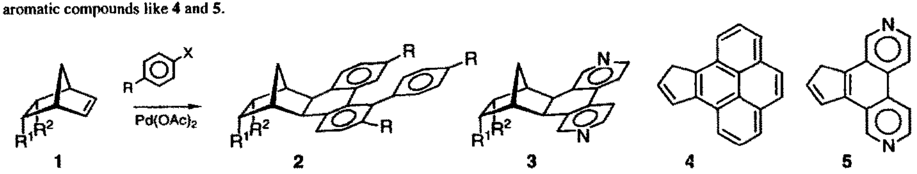


PALLADIUM-CATALYZED DOMINO COUPLING REACTIONS OF ARYL HALIDES WITH NORBORNENE AND NORBORNENE DERIVATIVES – A SIMPLE ROUTE TO POLYCYCLIC AROMATIC COMPOUNDS

Tetrahedron, **1994**, *50*, 383

Karsten Albrecht[a], Oliver Reiser[a], Martin Weber[b], Burkhard Knieriem[a], and Armin de Meijere[a*]
Institut für Organische Chemie der Georg-August-Universität Göttingen[a], Tammannstrasse 2, D-37077 Göttingen, Germany
Institut für Organische Chemie der Universität Hamburg[b], Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany

Under palladium-catalysis, norbornene and several norbornene derivatives 1 undergo a 1 : 3 domino coupling reaction with a variety of aryl bromides and iodides. Iodopyridines give only 1 : 2 coupling products 3. The adducts 2 and 3 can be transformed and cleaved to polycyclic aromatic compounds like 4 and 5.

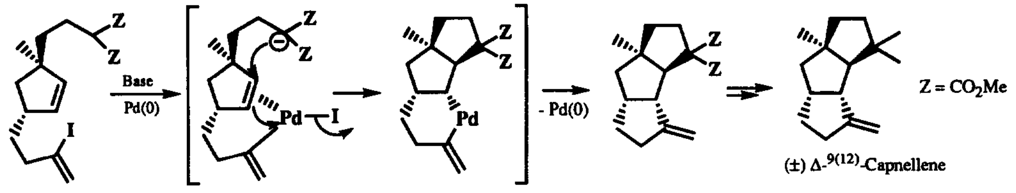


1 2 3 4 5

(±) Δ $^{9(12)}$CAPNELLENE WAS SYNTHESIZED VIA A NEW PALLADIUM-CATALYZED BIS-CYCLISATION STEP

Tetrahedron, **1994**, *50*, 403

Geneviève Balme* and Didier Bouyssi
Laboratoire de Chimie Organique 1, associé au CNRS, Université Claude Bernard, Bât 308, 43, Bd du 11 Novembre 1918, 69622 Villeurbanne, France.

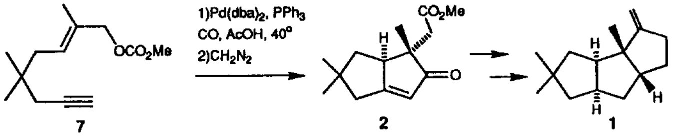


SYNTHESIS OF (±)-HIRSUTENE BY A CATALYTIC ALLYLPALLADIUM-ALKYNE CYCLIZATION/ CARBONYLATION CASCADE

Tetrahedron, **1994**, *50*, 415

Wolfgang Oppolzer* and Chantal Robyr
Département de Chimie Organique, Université de Genève, CH-1211 Genève 4, Switzerland

The tricyclic terpenoid (±)-hirsutene (**1**) has been synthesized starting from 2-hydroxy-4,4-dimethyltetrahydropyrane. In the key step, acyclic enynyl carbonate **7** afforded bicyclooctenone **2** *via* a 85 % diastereoselective palladium catalyzed metallo-ene/carbonylation reaction cascade.

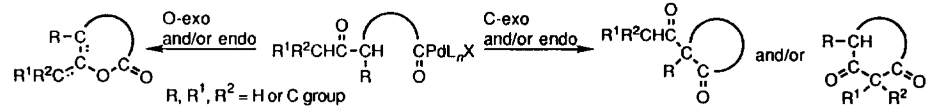


7 **2** **1**

PALLADIUM-CATALYZED CARBONYLATIVE CYCLIZATION VIA TRAPPING OF ACYLPALLADIUM DERIVATIVES WITH INTERNAL ENOLATES. ITS SCOPE AND FACTORS AFFECTING THE C-TO-O RATIO

Tetrahedron, **1994**, *50*, 425

Ei-ichi Negishi,* Christophe Copéret, Takumichi Sugihara, Izumi Shimoyama, Yantao Zhang, Guangzhong Wu, and James M. Tour
Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, U.S.A.

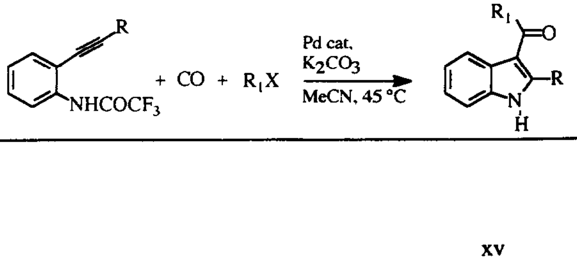


Intramolecular trapping of acylpalladium species by C- or O-enolates preferentially gives 5- or 6-membered rings. In a competition between O- and C-processes of the same ring size, the O-process dominates.

2-SUBSTITUTED-3-ACYLINDOLES THROUGH THE Pd-CATALYSED CARBONYLATIVE CYCLIZATION OF 2-ALKYNYLTRIFLUOROACETANILIDES WITH ARYL HALIDES AND VINYL TRIFLATES

Tetrahedron, **1994**, *50*, 437

Antonio Arcadi,[a] Sandro Cacchi,[b*] Veronica Carnicelli,[c] Fabio Marinelli[c]
[a] Istituto di Chimica Organica della Facoltà di Scienze, Università di Urbino, P.za della Repubblica 13, I-61020 Urbino, Italy.
[b] Dipartimento di Studi di Chimica e Tecnologia delle Sostanze Biologicamente Attive, Università degli Studi "La Sapienza", P.le A. Moro 5, I-00185 Roma, Italy.[c] Dipartimento di Chimica, Ingegneria Chimica e Materiali, Università degli Studi, V. Assergi 4, I-67100 L'Aquila, Italy.



X = I, OTf
R = alkyl, vinyl, aryl
R$_1$ = vinyl, aryl

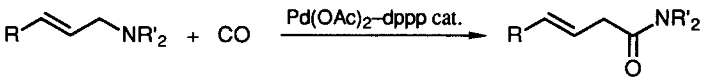
Tetrahedron, **1994**, *50*, 453

PALLADIUM-CATALYZED CARBONYLATION OF ALLYLAMINES. SYNTHESIS OF β,γ-UNSATURATED AMIDES BY ONE-CARBON HOMOLOGATION OF ALLYLAMINES

Shun-Ichi Murahashi,* Yasushi Imada, and Koichi Nishimura

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

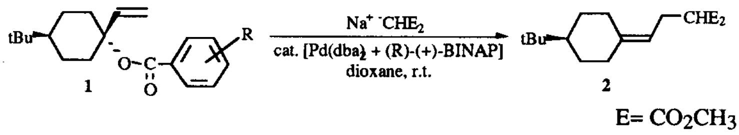
Carbonylation of allylamines proceeds smoothly in the presence of palladium-phosphine catalyst under CO (50 atm) at 110 °C to give the corresponding β,γ-unsaturated amides with high regioselectivity at the less substituted carbon of allyl unit.



Tetrahedron, **1994**, *50*, 465

ELECTRONIC CONTROL OF ENANTIOSELECTIVITY IN THE PALLADIUM-CATALYZED ASYMMETRIC ALLYLIC SUBSTITUTION OF 4-*t*BUTYL-1-VINYLCYCLOHEXYL BENZOATES

Jean-Yves Legros and Jean-Claude Fiaud, Laboratoire de Synthèse Asymétrique Associé au C.N.R.S., Bâtiment 420, Université de Paris-Sud, 91405 Orsay, France.

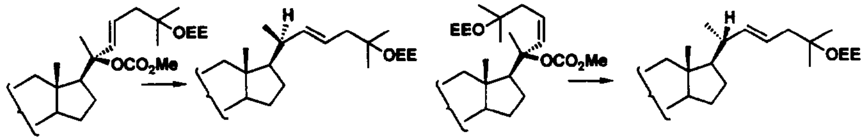


ee of **2** from 22% (**1**, R = 4-NO_2) to 90% (**1**, R = 4-OMe)

Tetrahedron, **1994**, *50*, 475

A novel Method for Stereospecific Generation of Natural C-17 Stereochemistry and either C-20 Epimer in Steroid Side Chains by Palladium-Catalyzed Hydrogenolysis of C-17 and C-20 Allylic Carbonates

Tadakatsu Mandai, Takaji Matsumoto, Mikio Kawada, and Jiro Tsuji
Department of Applied Chemistry, Okayama University of Science, Ridai-cho, Okayama, 700 Japan

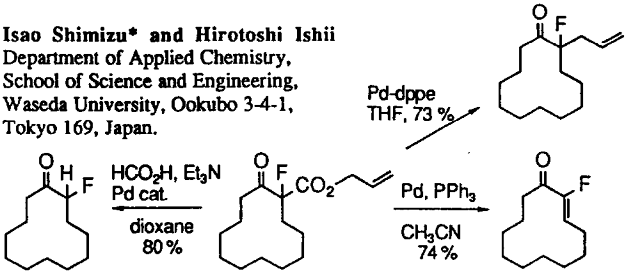


Control of stereochemistry at C-17 and C-20 of steroid side chains was achieved by the palladium-catalyzed stereospecific hydrogenolysis of allylic carbonates with formate.

Tetrahedron, **1994**, *50*, 487

SYNTHESIS OF α-FLUOROKETONES BASED ON PALLADIUM -CATALYZED DECARBOXYLATION REACTION OF ALLYL β-KETO CARBOXYLATES

Isao Shimizu* and Hirotoshi Ishii
Department of Applied Chemistry,
School of Science and Engineering,
Waseda University, Ookubo 3-4-1,
Tokyo 169, Japan.

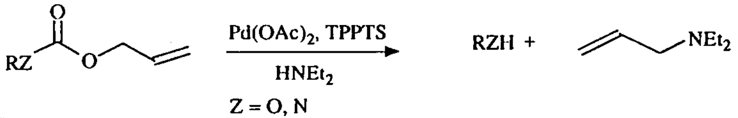


Practical Palladium-Mediated Deprotective Method of Allyloxycarbonyl in Aqueous Media.

Tetrahedron, **1994**, *50*, 497

Jean Pierre Genêt*, Errol Blart, Monique Savignac, Stéphane Lemeune, Sandrine Lemaire-Audoire, Jean-Marc Paris**and J.M. Bernard**
* Laboratoire de Synthèse Organique associé au CNRS, Ecole Nationale Supérieure de Chimie de Paris
11, rue Pierre et Marie Curie - 75231 Paris - France
** Rhône Poulenc Rorer - Centre de recherche Vitry-Alfortville - 13 Quai Jules Guesde - 94403 Vitry sur Seine

The allyloxycarbonyl (Alloc) moiety is removed smoothly and selectively from allylic esters and carbamates (including carbamates derived from secondary amines) in aqueous media by Pd(0) generated in situ from $Pd(OAc)_2$ and TPPTS (triphenylphosphine meta trisulfonate). In a two phase system the catalyst is efficiently recycled.

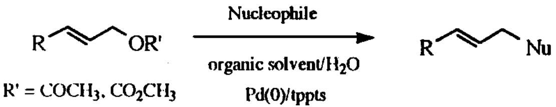


PALLADIUM(0)-CATALYZED SUBSTITUTION OF ALLYLIC SUBSTRATES IN AN AQUEOUS-ORGANIC MEDIUM

Tetrahedron, **1994**, *50*, 505

Errol Blart,[a] Jean Pierre Genêt,[a*] Mohamed Safi,[b] Monique Savignac[a] and Denis Sinou[b*]
[a] *Laboratoire de Synthèse Organique, associé au CNRS, Ecole Nationale Supérieure de Chimie de Paris, 11, rue Pierre et Marie Curie, 75231 Paris, France*
[b] *Laboratoire de Synthèse Asymétrique, associé au CNRS, ESCIL, Université Claude Bernard Lyon I, 43, boulevard du 11 Novembre 1918, 69622 Villeurbanne Cédex, France*

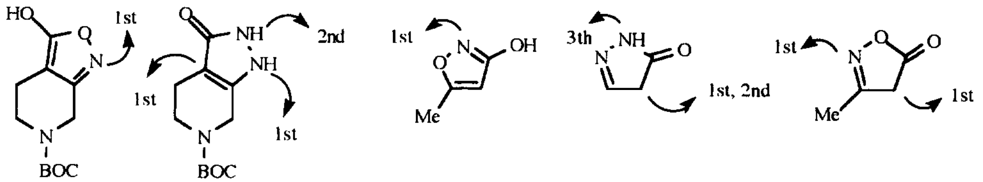
A palladium(0)-water soluble catalyst prepared from $Pd(OAc)_2$ and the sulfonated triphenylphosphine $PP(C_6H_4\text{-}m\text{-}SO_3Na)_3$ (or tppts) is an efficient catalyst for allylic substitution with various carbon and heteronucleophiles in an aqueous-organic medium.



PALLADIUM-CATALYZED ALLYLATION OF 3-HYDROXYISOXAZOLE, 5-ISOXAZOLONE AND 5-PYRAZOLONE SYSTEMS

Tetrahedron, **1994**, *50*, 515

M. Moreno-Mañas, M. Pérez and R. Pleixats
Department of Chemistry. Universitat Autònoma de Barcelona. Bellaterra. 08193-Barcelona. Spain.

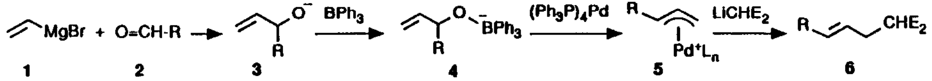


PALLADIUM(0)-CATALYZED ALLYLIC SUBSTITUTION WITH ALLYLIC ALKOXIDES AS SUBSTRATES

Tetrahedron, **1994**, *50*, 529

I. Starý,[*,a] I. G. Stará,[a] and P. Kočovský [*,b]
[a]Institute of Org. Chem. & Biochem, AVČR, 16610 Prague 6, Czech Republic
[b]Department of Chemistry, University of Leicester, Leicester LE1 7RH, UK

While allylic esters have frequently been used as substrates for the Pd(0)-catalyzed allylic substitution, the parent alcohols are much less reactive. We have now developed a new method which allows the substitution to occur between the alcohols and malonates: on reaction with Ph_3B, the allylic alkoxide **3** is first converted in situ into the more reactive species **4** which then undergoes a Pd(0)-catalyzed reaction with $LiCH(CO_2Et)_2$ via the (π-allyl)-Pd-complex **5**. Allylic alkoxides can be generated in situ either by Grignard raction (**1** + **2** → **3**) or by a DIBAH reduction of the corresponding ketones. The whole sequence can be carried out as a one-pot procedure and is particularly suitable for sensitive allylic alcohols. Mono- and bis-allylation has been observed with sterically less hindered substrates.

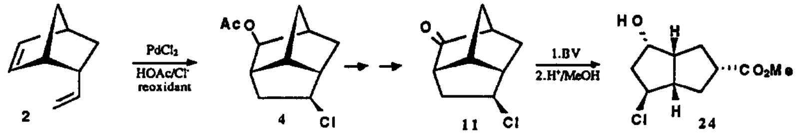


1 **2** **3** **4** **5** **6**

Direct Access to Substituted Brendane Derivatives by Palladium-Copper Mediated Cyclisation of *endo*-5-Vinyl-2-norbornene. X-ray Structure of the σ–π Intermediate Palladium Complex. Further Evolution (Baeyer-Villiger Oxidation) to the Quinane System

Tetrahedron, **1994**, *50*, 539

Andreas Heumann*, Serge. Kaldy and Alphonse Tenaglia
Université d'Aix-Marseille, Faculté de St.-Jérôme, URA - CNRS 1410 & 1411; F 13013 MARSEILLE - FRANCE



Disusbtitued brendane 4, easily prepared by Wacker type oxidation of 2 is an interesting synthetic intermediate for the obtention of functionalised quinanes *via* 11. The palladium-catalyzed cyclisation and Baeyer-Villiger ring cleavage proceed with complete regioselectivity and high stereocontrol of the 5 chiral carbons in 24.

Palladium-Catalyzed Oxaspirocyclizations

Tetrahedron, **1994**, *50*, 559

Pher G Andersson,* Ylva I. M. Nilsson and Jan-E. Bäckvall,*
Department of Organic Chemistry,
University of Uppsala, Box 531, S-751 21 Uppsala, Sweden

Palladium-catalyzed oxidation of 1-(3-hydroxyalkyl) and 1-(4-hydroxyalkyl)-1,3-cycloalkadienes results in a stereocontrolled oxaspirocyclization. The reaction proceeds via a spirocyclic (π-allyl)palladium intermediate, which is attacked by an acetate or a chloride nucleophile leading to an overall 1,4-addition across the diene. The oxaspirocyclization was applied to the total synthesis of theaspirone.