

Tetrahedron Letters Vol. 46, No. 45, 2005

Contents

COMMUNICATIONS

Synthesis of 5-aza-analogues of angucyclines: manipulation of the 2-deoxy-*C*-glycoside subunit Nguyen Quang Vu, Gilles Dujardin,* Sylvain C. Collet,* Eun-Ang Raiber, André Y. Guingant* and Michel Evain

pp 7669-7673

A highly stereoselective reductive amination of 3-ketosteroid with amines: an improved synthesis of 3α -aminosteroid

pp 7675-7678

Sharaf Nawaz Khan, Seon-Yun Bae and Hong-Seok Kim*

A highly stereoselective reductive amination method was developed based on in situ generated sodium acyloxyborohydride and was successfully applied to a steroidal skeleton with various amine sources. High yield (96%) and a de of up to 95% were achieved by modifying the reducing reagent. The effect of this reagent will be discussed.

OTBS

Amine

NaBH(OCOR)₃, THF

1

2a:
$$\alpha$$
, R = COCH₃
2b: β , R = COCH₃
3a: α , R = spermidine
3b: β , R = spermide
4a: α , R = spermine
4b: β , R = spermine

The simple and selective synthesis of 3-amino-2,2-difluorocarboxylic esters and difluoro- β -lactams using ethyl bromodifluoroacetate in the presence of rhodium catalyst

pp 7679-7681

Kazuyuki Sato, Atsushi Tarui, Seiji Matsuda, Masaaki Omote, Akira Ando* and Itsumaro Kumadaki*

Treatment of imines (5) with ethyl bromodifluoroacetate (1) and Et_2Zn in the presence of $RhCl(PPh_3)_3$ in anhydrous medium gave difluoro- β -lactams (7) in good to excellent yields, while 3-amino-2,2-difluorocarboxylic esters (6) were obtained in good yields by adding $MgSO_4$ · $7H_2O$ to the reaction medium.



The first total synthesis of acutifolone A, a pinguisane-type sesquiterpenoid isolated from the Japanese liverwort *Porella acutifolia* subsp. tosana

pp 7683-7686

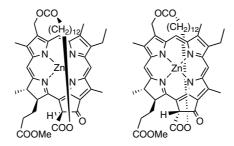
Junichi Shiina and Shigeru Nishiyama*

The first total synthesis of acutifolone A was achieved from the intermediate 6 by using the Mukaiyama aldol reaction as key step.

Synthesis of stereospecifically face-protected chlorophyll derivatives

pp 7687-7689

Shin-ichi Sasaki, Hiroshi Takebe, Tadashi Mizoguchi and Hitoshi Tamiaki*



(i)+

Regioselective alkylation of 3,4-dihydro-2*H*-pyran by xanthate-mediated free radical *nonchain* process

pp 7691-7694

Jaime Torres-Murro, Leticia Quintero* and Fernando Sartillo-Piscil*

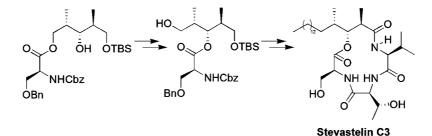
An intermolecular xanthate-mediated free radical *nonchain* reaction is introduced for the regioselective alkylation of 3,4-dihydro-2*H*-pyran. Additionally, we observed that the free radical *nonchain* reaction depends on the nature of the free radical precursor.

Synthesis of [13]-membered macrocyclic stevastelins via a transesterification reaction as the key step: total synthesis of stevastelin C3

pp 7695-7699

mixture of diastereoisomers

Francisco Sarabia,* Miguel García-Castro and Samy Chammaa



Substituent effects on the kinetics for the chemiluminescence reaction of 6-arylimidazo[1,2-a]-pyrazin-3(7H)-ones (*Cypridina* luciferin analogues): support for the single electron transfer (SET)-oxygenation mechanism with triplet molecular oxygen

pp 7701-7704

Hiroyuki Kondo, Takayuki Igarashi, Shojiro Maki, Haruki Niwa, Hiroshi Ikeda and Takashi Hirano*

Synthesis of streptorubin B core

pp 7705-7709

Meng-Yang Chang,* Chun-Li Pai and Hua-Ping Chen

(i)+

A novel chlorinated norsesquiterpenoid and two related new metabolites from the soft coral *Paralemnalia thyrsoides*

pp 7711-7714

Ho-Cheng Huang, Chih-Hua Chao, Ju-Hsiou Liao, Michael Y. Chiang, Chang-Feng Dai, Yang-Chang Wu and Jyh-Horng Sheu*

Selective alkylation of a 6,7-dihydroxyquinazoline

pp 7715-7719

Craig S. Harris,* Laurent F. Hennequin, Jason G. Kettle and Olivier A. Willerval

Mechanism of action of base-catalyzed oxygenation of phenol derivatives

pp 7721-7723

Duck-Hyung Lee, Jung Beom Son, Seokwon Jung, Jihey Song and Seung Wook Ham*

Mechanism of base-catalyzed autooxidation of phenol derivatives has been investigated by using cyclopropyl derivatives of 2,6-ditert-butylphenol as a mechanistic probe.

Recyclable ligand-free mesoporous heterogeneous Pd catalysts for Heck coupling

pp 7725-7728

Attila Papp, Gábor Galbács and Árpád Molnár*

R¹
$$\xrightarrow{+}$$
 X $\xrightarrow{\text{Pd-MCM41}}$ $\xrightarrow{+}$ NMP, base, 150 °C $\xrightarrow{+}$ Yields = 54–100% selectivites = 71–100% $=$ R² $=$ Ph, COOMe

Pd-MCM41 catalysts exhibit unprecedented stability among heterogeneous catalysts and can be reused at least 20 times to achieve complete conversion without any additional activation treatment.



Direct hydroxylation of substituted benzenes to phenols with air and CO using molybdovanadophosphates as a key catalyst

pp 7729-7732

Shuichi Mita, Takao Sakamoto, Shingo Yamada, Satoshi Sakaguchi and Yasutaka Ishii*

A direct synthetic method of cresols from toluene by hydroxylation with air using CO as a reducing agent was developed. The reaction of toluene with air (15 atm) and CO (5 atm) in the presence of catalytic amounts of $H_4PMo_{11}VO_{40}\cdot31H_2O$ and Pd/C in aqueous acetic acid at 120 °C for 2 h afforded a mixture of o-, m-, and p-cresols in 9.9% yield at 83% selectivity.

Semipermanent p-nitrobenzyloxycarbonyl (pNZ) protection of Orn and Lys side chains: prevention of undesired α -Fmoc removal and application to the synthesis of cyclic peptides

pp 7733–7736

Albert Isidro-Llobet, Mercedes Álvarez* and Fernando Albericio*

$$O_2N$$
 O PNZ group

Semipermanent side-chain protection of Orn and Lys with p-nitrobenzyloxycarbonyl (pNZ) for Fmoc/'Bu chemistry does not result in the unwanted removal of α -Fmoc that occurs when groups such as Alloc are used for the same application. Furthermore, pNZ can be used in conjuction with p-nitrobenzyl ester (pNB) to prepare cyclic peptides.

Use of p-nitrobenzyloxycarbonyl (pNZ) as a permanent protecting group in the synthesis of Kahalalide F analogs

pp 7737-7741

Pilar E. López, Albert Isidro-Llobet, Carolina Gracia, Luis J. Cruz, Andrés García-Granados, Andrés Parra, Mercedes Álvarez* and Fernando Albericio*

p-Nitrobenzyloxycarbonyl (*p*NZ) is used for the permanent protection of Orn in the synthesis of derivatives of the anti-tumor cyclodepsipeptide Kahalalide F that contain acid labile residues.

Heterogeneous Cu-catalysts for the reductive deoxygenation of aromatic ketones without additives

pp 7743-7745

Federica Zaccheria, Nicoletta Ravasio,* Mauro Ercoli and Pietro Allegrini

Environment friendly organic synthesis using bismuth compounds. An efficient method for carbonyl-ene pp 7747–7750 reactions catalyzed by bismuth triflate

Erin D. Anderson, Justin J. Ernat, Mai P. Nguyen, Ann C. Palma and Ram S. Mohan*

Synthesis and photoinitiated radical cyclization of allyl- and propynyloxymethyl substituted cyclopentanones to tetrahydrocyclopenta[c]furanols

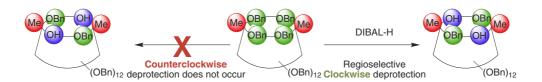
pp 7751-7755

Nikolay T. Tzvetkov and Jochen Mattay*

Diisobutylaluminium hydride (DIBAL-H) is promoting a selective clockwise debenzylation of perbenzylated 6^A , 6^D -dideoxy- α -cyclodextrin

pp 7757-7760

Olivia Bistri, Pierre Sinaÿ and Matthieu Sollogoub*





Aza-Michael reactions catalyzed by samarium diiodide

Iréna Reboule, Richard Gil* and Jacqueline Collin*

pp 7761–7764

$$R = CO_2Et, CH_3, C_3H_7, H$$

$$\frac{10\% \text{ Sml}_2(\text{THF})_2}{\text{CH}_2Cl}_2, \text{ rt}$$

$$\frac{\text{ArHN O ArHN O$$

Samarium diiodide catalyzes the Michael addition of aromatic amines onto α,β -unsaturated N-acyloxazolidinones to afford β -amino-N-acyloxazolidinone or β -aminoamide or a mixture of both products depending on the reaction conditions.

Regioselective boron trichloride-mediated aromatic Claisen rearrangement of resorcinol allyl ethers

pp 7765-7767

Fumihiro Ito, Takuya Kumamoto* and Tsutomu Ishikawa

RO O BCI₃,
$$CH_2CI_2$$
-50 °C, 3 h

RO OH OH OH OH OR (6%)

 (76%)
 (76%)
 (76%)
 (76%)
 (76%)
 (76%)
 (76%)
 (76%)
 (76%)
 (76%)
 (76%)
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A versatile protocol for the preparation of substituted 1- and 2-naphthyl piperazines from aminonaphthols

pp 7769-7771

Ana B. Bueno,* Claire J. Flynn, Jeremy Gilmore, Alicia Marcos, Carlos Montero, Warren Porter and Andrew C. Williams

Aminonaphthols are easily transformed into a variety of 1- and 2-naphthyl piperazines using a sequence of diazotization reaction, iodide substitution and Pd(0) catalyzed coupling reaction.

Microwave-promoted synthesis of chiral pyridinium salts

pp 7773-7776

Gustavo H. R. Viana, Itamar C. Santos, Rosemeire B. Alves, Laurent Gil, Christian Marazano and Rossimiriam P. F. Gil*

The synthesis of several chiral pyridinium salts via Zincke's reaction can be easily accomplished by microwave oven irradiation. Yield enhancements, shorter reaction times, and less racemization were observed under microwave heating when compared to conventional heating.

i) Conventional heating: 15 h, yields from 29 to 100%; ii) Microwave heating (less racemization): 5-10 min, yields from 61 to 100%.

Catalytic ketone olefination with methyltrioxorhenium

Filipe M. Pedro, Sebastian Hirner and Fritz E. Kühn*

pp 7777-7779

$$R^{1} = C = O + PPh_{3} + N_{2} = CHCO_{2}Et$$

$$R^{2} = O + PPh_{3} + N_{2} = CHCO_{2}Et$$

$$R^{2} = O + PPh_{3} + N_{2} = CHCO_{2}Et$$

$$R^{2} = O + PPh_{3} + N_{2} = CHCO_{2}Et$$

$$R^{2} = O + PPh_{3} + N_{2} = CHCO_{2}Et$$

Efficient syntheses of new chiral peptidomimetic macrocycles through a configurationally driven preorganization

pp 7781-7785

Miriam Bru, Ignacio Alfonso, M. Isabel Burguete and Santiago V. Luis*

Configurational preorganization drives a [2+2] macrocyclization reaction of new chiral peptidomimetic compounds.

Michael addition approach for the synthesis of novel spiro compounds and 2-substituted malonic acid derivatives from Meldrum's acid

pp 7787-7792

Madhukar S. Chande* and Rahul R. Khanwelkar

Novel routes for the synthesis of spiro derivatives of Meldrum's acid and 2-substituted malonic acid derivatives using Michael addition reactions are reported.

Synthesis of the floresolide B hydroquinone lactone core using ring-closing metathesis

pp 7793-7796

Timothy F. Briggs and Gregory B. Dudley*

floresolide B

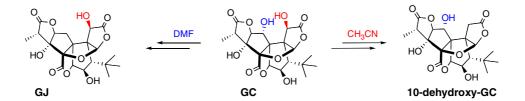
The hydroquinone lactone core of the floresolides was synthesized through a ring-closing metathesis (RCM) approach. Optimal RCM efficiency was obtained at *higher* reaction concentration. An unexpected Lewis acid-promoted rearrangement of the hydroquinone is also discussed.



Regioselective thionocarbonation of ginkgolides: facile preparation of ginkgolide J

pp 7797-7799

Sergei V. Dzyuba,* Sergei Bolshakov and Koji Nakanishi*

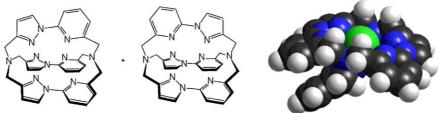




Direct synthesis of new cryptates based on the N,C-pyrazolylpyridine motif

pp 7801-7805

Ernesto Brunet,* Olga Juanes, Miguel Angel Rodríguez-Blasco, Suzana Pereira Vila-Nueva, David Garayalde and Juan Carlos Rodríguez-Ubis*



An expeditious synthesis of new cryptands derived from N,C-pyrazolylpyridine and their full characterization is reported. Emission lifetimes of the europium and terbium cryptates were in the range of milliseconds and terbium quantum yield was high.



One-pot synthesis of α -amino phosphonates from α -amino acids and β -amino alcohols

Alicia Boto,* Juan Antonio Gallardo, Rosendo Hernández* and Carlos Javier Saavedra

pp 7807-7811

Synthesis of a constrained tricyclic scaffold based on trans-4-hydroxy-L-proline

pp 7813-7816

Andrea Trabocchi, Massimo Rolla, Gloria Menchi and Antonio Guarna*

$$BnO$$
 CO_2Me
 HO
 CO_2Me

Synthesis of novel fluorinated 4-aminoquinoline derivatives

pp 7817-7821

Maurice Médebielle,* Stéphane Hohn, Etsuji Okada, Hidehiko Myoken and Dai Shibata

Selective displacement of aryl fluorides with hydroquinone: synthesis of 4-phenoxyphenols

pp 7823-7826

Benjamin F. Marcune,* Michael C. Hillier, Jean-François Marcoux and Guy R. Humphrey

Catalytic enantioselective aryl transfer: asymmetric addition of boronic acids to aldehydes using pyrrolidinylmethanols as ligands

pp 7827-7830

Antonio L. Braga,* Diogo S. Lüdtke, Paulo H. Schneider, Fabricio Vargas, Alex Schneider, Ludger A. Wessjohann and Márcio W. Paixão

B(OH)₂ + Et₂Zn
$$\frac{1. \text{ Ligand (20 mol\%)}}{2. \text{ Work-up}}$$
 $\frac{Ar}{OH}$ Up to 98% ee

Pyrrolidinylmethanols, easily accessible from readily available (S)-proline, were applied in zinc-catalyzed addition of arylboronic acids to aromatic aldehydes; the reaction is found to proceed in excellent yields and high enantioselectivities (up to 98% ee).

A highly enantioselective catalyst for asymmetric hydroformylation of [2.2.1]-bicyclic olefins

pp 7831-7834

Jinkun Huang,* Emilio Bunel,* Alan Allgeier, Jason Tedrow, Thomas Storz, J. Preston, Tiffany Correll, Deana Manley, Troy Soukup, Randy Jensen, Rashid Syed, George Moniz, Robert Larsen, Michael Martinelli and Paul J. Reider

Rh(CO)₂(acac)/TangPhos was found to be a highly enantioselective catalyst for asymmetric hydroformylation of norbornylene under mild conditions. Application of the protocol to the desymmetrization of other [2.2.1]-bicyclic olefins gave moderate to excellent enantioselectivity (55–92% ee).

Deuterium kinetic isotope effects in homogeneous decatungstate catalyzed photooxygenation of 1,1-diphenylethane and 9-methyl-9*H*-fluorene: evidence for a hydrogen abstraction mechanism Ioannis N. Lykakis and Michael Orfanopoulos*

pp 7835-7839

A green protocol for chemoselective O-acylation in the presence of zinc oxide as a heterogeneous, reusable and eco-friendly catalyst

pp 7841-7844

Fatemeh Tamaddon,* Mohammad Ali Amrollahi and Leily Sharafat

Synthesis and oxidation of 'non-annulated' vitamin E-like compounds

pp 7845-7848

Thomas Rosenau* and Amnon Stanger

Two model compounds with a substitution pattern typical of vitamin E, but without ring annulation, were synthesized and oxidized. No preference for one of the two *ortho*-quinone methides was found, confirming that the oxidation regioselectivity is not governed by electronic substituent effects of the annulated ring.

Auxiliary strategies for the preparation of β -amino alcohols with reductive cross-coupling and a synthesis of (–)-cytoxazone

pp 7849-7852

Xiangjie Lin, Paul A. Bentley* and Hexin Xie



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*Corresponding author

** Supplementary data available via ScienceDirect

COVER

The cover figure shows acutifonone A, a sesquiterpenoid carrying the bicylo[4.3.0]nonane structure, which was successfully synthesized from the corresponding tri-cyclic Diels-Alder product. Details can be found in *Tetrahedron Letters* **2005**, *46*, 7683–7686. © 2005 S. Nishiyama. Published by Elsevier Ltd.



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