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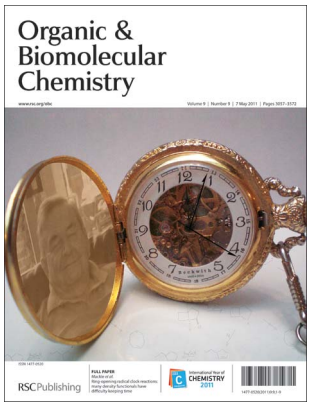
IN THIS ISSUE

ISSN 1477-0520 CODEN OBCRAK 9(9) 3057–3572 (2011)



Cover

See Mackie *et al.*, pp. 3158–3164.

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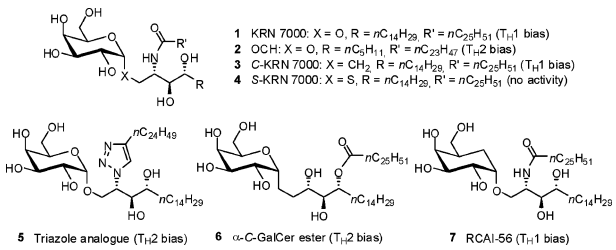
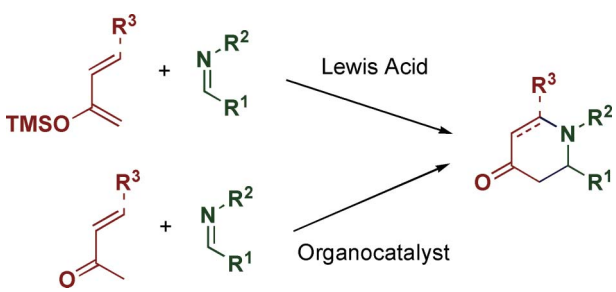
PERSPECTIVES





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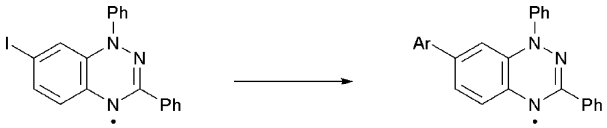
3122

Synthesis of 7-aryl/heteraryl-1,3-diphenyl-1,2,4-benzotriazinyls *via* palladium catalyzed Stille and Suzuki-Miyaura reactions

Christos P. Constantinides, Panayiotis A. Koutentis* and Georgia Loizou

Stille and Suzuki-Miyaura reactions of 7-iodo-1,3-diphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl are presented as rare examples of cross-coupling reactions with stable organic radicals.



Suzuki-Miyaura Conditions: $ArB(OH)_2$ (3 equiv.), $Pd(OAc)_2$ (5 mol%), K_2CO_3 (3 equiv.), 1 h, 47-93% 6 examples

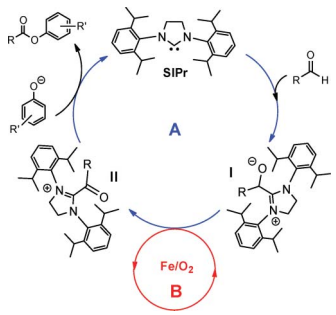
Stille Conditions: $ArSnBu_3$ (2 equiv.), $Pd(OAc)_2$ (5 mol%), 20-30 min, 82-93% 3 examples

3126

NHC/Iron cooperative catalysis: aerobic oxidative esterification of aldehydes with phenols

R. Sudarshan Reddy, João N. Rosa, Luís F. Veiros, Stephen Caddick and Pedro M. P. Gois*

An NHC/iron cooperative catalytic system mediates the aerobic oxidative esterification of aldehydes with phenols. The use of equimolar amounts of reactants led to good to excellent isolated yields of esters.

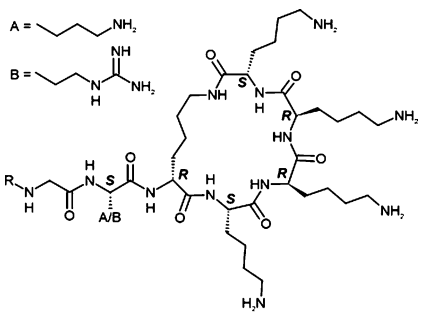


3130

Structure elucidation and biosynthesis of lysine-rich cyclic peptides in *Xenorhabdus nematophila*

Sebastian W. Fuchs, Anna Proschak, Thorsten W. Jaskolla, Michael Karas and Helge B. Bode*

The structures of thirteen novel cyclic lipoheptapeptides were elucidated from *Xenorhabdus nematophila* using a combination of different methods.

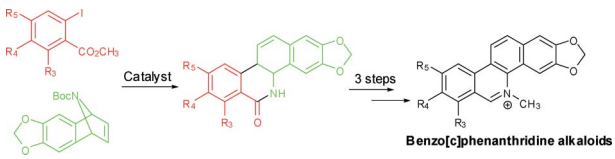


3133

Palladium-catalyzed tandem reaction to construct benzo[*c*]phenanthridine: application to the total synthesis of benzo[*c*]phenanthridine alkaloids

Pei Lv, Kanglun Huang, Longguan Xie and Xiaohua Xu*

Total synthesis of benzo[*c*]phenanthridine alkaloids was accomplished by palladium-catalyzed ring-opening coupling–cyclization.



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- **chemical biology**
- **chemical biology/ Biosynthesis**
- **chemical biology/ DNA nucleoside analogues**

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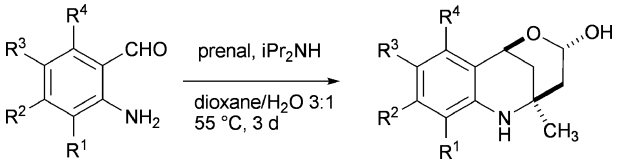
www.ichc2011.com

3136

Synthetic studies towards marmycins A and B: development of the vinylogous aldol–aza-Michael domino reaction

Emmanuel Bourcet, Manuel C. Bröhmer, Martin Nieger and Stefan Bräse*

The vinylogous aldol–aza-Michael domino reaction between 2-aminobenzaldehydes and prenal was developed to build up the core of natural products marmycin A and B without the need of protective groups.

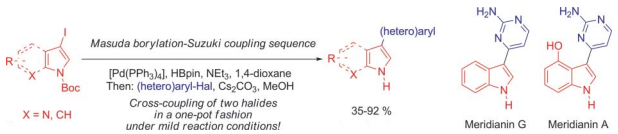


3139

Rapid synthesis of bis(hetero)aryls by one-pot Masuda borylation–Suzuki coupling sequence and its application to concise total syntheses of meridianins A and G

Eugen Merkul, Elisabeth Schäfer and Thomas J. J. Müller*

3-(Hetero)aryl substituted indoles, 7-azaindoles, and pyrroles can be obtained in a very concise fashion *via* a one-pot Masuda borylation–Suzuki coupling sequence.

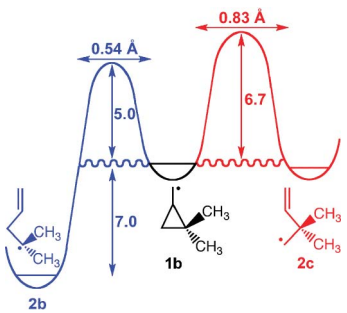


3142

Effects of geminal methyl groups on the tunnelling rates in the ring opening of cyclopropylcarbinyl radical at cryogenic temperature

Xue Zhang, David A. Hrovat, Ayan Datta and Weston Thatcher Borden*

Relative enthalpy changes for the two possible modes of ring opening of 2,2-dimethylcyclopropylcarbinyl radical. Tunnelling is indicated by wavy lines.

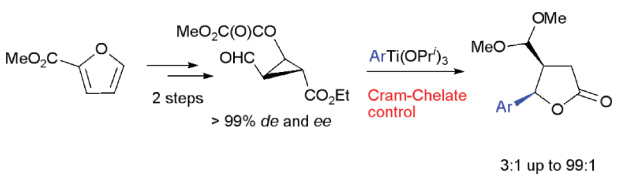


3146

Stereoselective routes to aryl substituted γ-butyrolactones and their application towards the synthesis of highly oxidised furanocembranoids

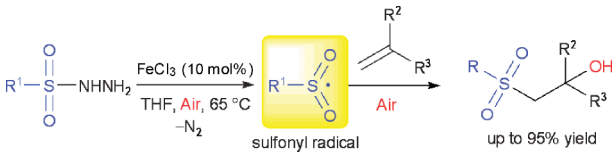
Allan Patrick G. Macabeo, Andreas Kreuzer and Oliver Reiser*

Addition of aryltitanium compounds to cyclopropylcarbaldehyde **6** leads to *cis*-aryl disubstituted γ-butyrolactones in up to 99% *de*, contrasting with additions of allylsilanes that proceed with high Felkin–Anh-control to the corresponding *trans* disubstituted γ-butyrolactones.



COMMUNICATIONS

3151

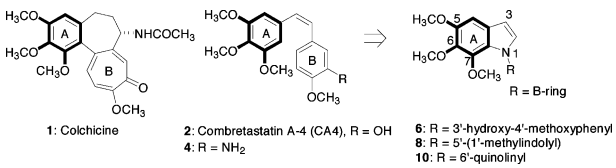


Iron-catalyzed sulfonyl radical formations from sulfonylhydrazides and oxidative addition to alkenes

Tsuyoshi Taniguchi,* Atsushi Idota and Hiroyuki Ishibashi

Sulfonyl radicals generate from sulfonylhydrazides in the presence of an iron catalyst and air. Addition of resultant radicals to alkenes affords β-hydroxysulfones in good yield.

3154



Concise syntheses of *N*-aryl-5,6,7-trimethoxyindoles as antimitotic and vascular disrupting agents: application of the copper-mediated Ullmann-type arylation

Hsueh-Yun Lee, Jang-Yang Chang, Ling-Yin Chang, Wen-Yang Lai, Mei-Jung Lai, Kuang-Hsing Shih, Ching-Chuan Kuo, Chi-Yen Chang and Jing-Ping Liou*

A series of *N*-aryl-5,6,7-trimethoxyindoles were synthesized *via* copper-catalyzed Ullmann-type *N*-arylation through the corresponding 5,6,7-trimethoxyindole and aryl halides; the synthesized compounds demonstrated potent antiproliferative activity.

PAPERS

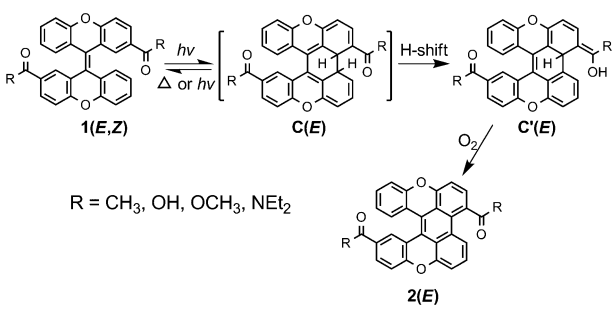
3158

Ring-opening radical clock reactions: many density functionals have difficulty keeping time

Iain D. Mackie and Gino A. DiLabio*

Many density-functional theory methods provide poor agreement to experimental rate constants for the ring opening of radical clock species.

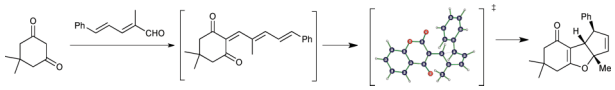
3165

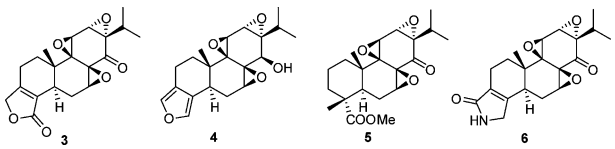


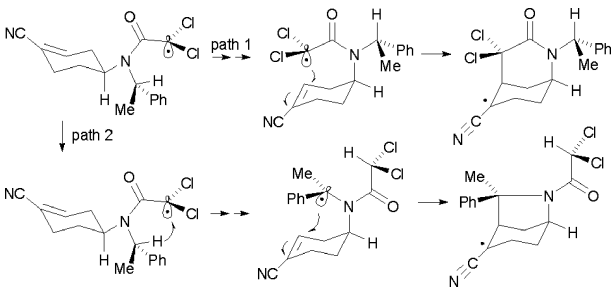
Highly efficient and regiospecific photocyclization of 2,2′-diacyl bixanthenylidenes

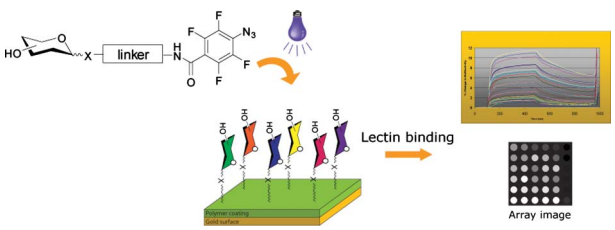
Mao Mao, Qing-Qing Wu, Ming-Guang Ren and Qin-Hua Song*

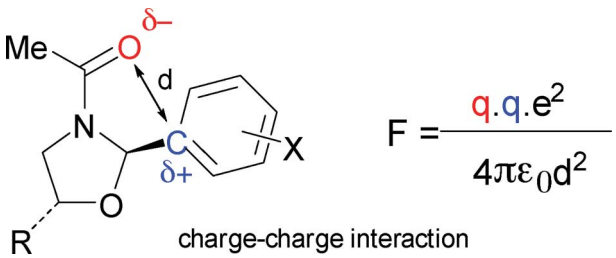
We report the conclusive mechanism for rationalizing the regioselectivity and efficiency in the photocyclization of synthesized 2,2′-substituted bixanthenylidenes.

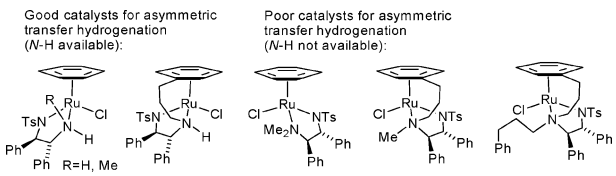


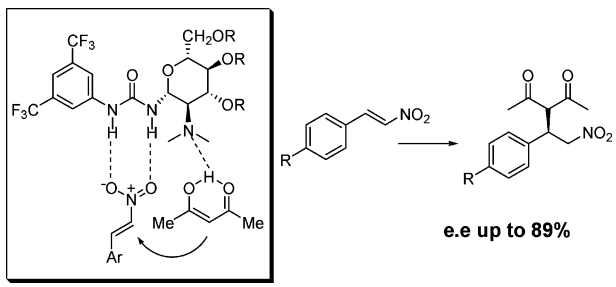


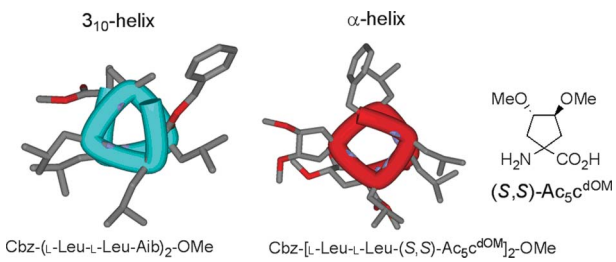












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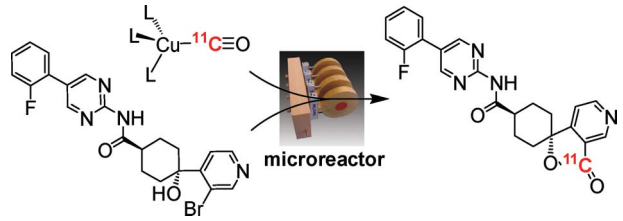
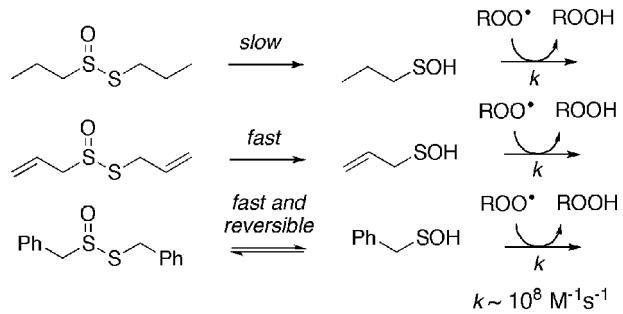


Microfluidic reactions using [^{11}C]carbon monoxide solutions for the synthesis of a positron emission tomography radiotracer

Steven Kealey, Christophe Plisson, T. Lee Collier, Nicholas J. Long, Stephen M. Husbands, Laurent Martarello and Antony D. Gee

A copper(I)-[^{11}C]CO solution has been used to perform carbonylation reactions for the synthesis of [^{11}C]MK-0233, a radioligand for the neuropeptide Y Y5 receptor, using both microfluidics and conventional techniques.

3320

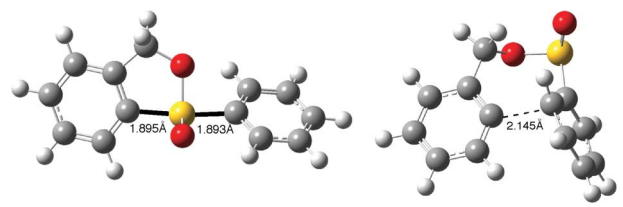


The mechanism of radical-trapping antioxidant activity of plant-derived thiosulfinates

Philip T. Lynett, Krista Butts, Vipraja Vaidya, Graham E. Garrett and Derek A. Pratt*

The ease with which plant-derived thiosulfinates undergo Cope elimination to form the corresponding sulfenic acids accounts for their differences in antioxidant activity.

3331

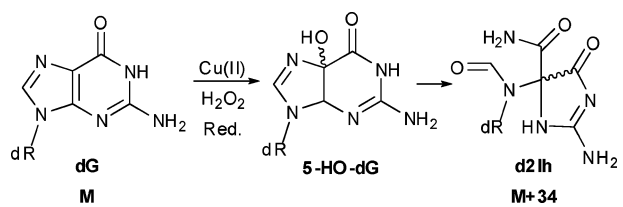


Intramolecular homolytic substitution of sulfinates and sulfinamides – a computational study

Sara H. Kyne,* Heather M. Aitken, Carl H. Schiesser, Emmanuel Lacôte, Max Malacria, Cyril Ollivier and Louis Fensterbank*

BHandHLYP/6-311++G(d,p) calculations predict that intramolecular homolytic substitution by aryl radicals at the sulfur atom in phenylsulfinates and sulfinamides competes with intramolecular addition to the phenyl ring.

3338



Characterization of 2′-deoxyguanosine oxidation products observed in the Fenton-like system Cu(II)/H_2O_2/reductant in nucleoside and oligodeoxynucleotide contexts

Aaron M. Fleming, James G. Muller, Insun Ji and Cynthia J. Burrows*

Copper-mediated Fenton oxidation of 2′-deoxyguanosine leads to predominant formation of 5-carboxamido-5-formamido-2-iminohydantoin (**d2Ih**) *via* C5 hydroxylation.

Who's who in *Chemical Science*

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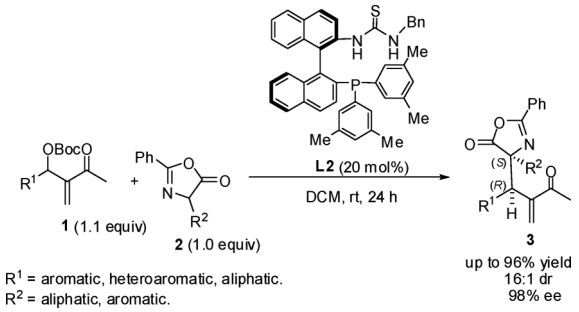
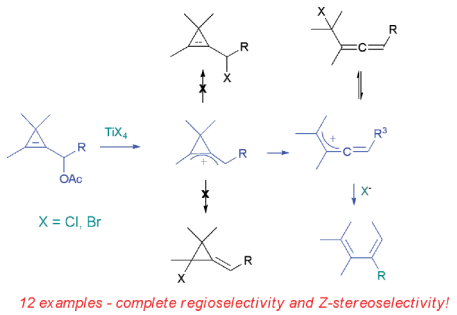


Multifunctional chiral phosphines-catalyzed highly diastereoselective and enantioselective substitution of Morita–Baylis–Hillman adducts with oxazolones

Yuan-Liang Yang, Cheng-Kui Pei and Min Shi*

Multifunctional chiral phosphine (phosphine–thiourea type) **L2**-catalyzed allylic substitutions of MBH adducts **1** with oxazolones **2** produce the corresponding optically active adducts **3** in good to excellent yields and ee's as well as moderate to good de's under mild conditions.

3359

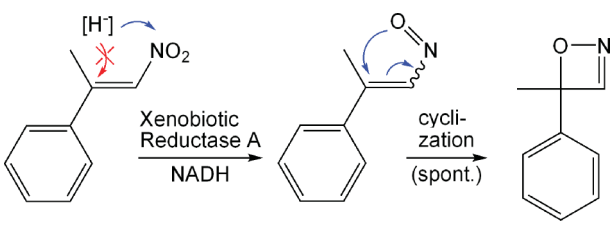


Titanium-mediated rearrangement of cyclopropenylmethyl acetates to (*E*)-halodienes

Gary Gallego, Alireza Ariafard,* Kiet Tran, David Sandoval, Leera Choi, Yi-Hsun Chen, Brian F. Yates, Fu-Ming Tao and Christopher J. T. Hyland*

$TiCl_4$ and $TiBr_4$ rapidly transform cyclopropenylmethyl acetates to (*E*)-halodienes with complete regio- and stereoselectivity.

3364

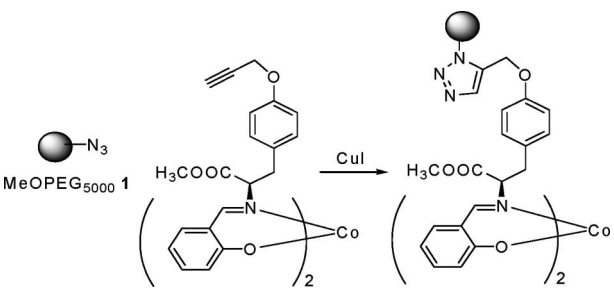


Reductive biotransformation of nitroalkenes *via* nitroso-intermediates to oxazetes catalyzed by xenobiotic reductase A (XenA)

Katharina Durchschein, Walter M. F. Fabian, Peter Macheroux, Klaus Zangger, Gregor Trimmel and Kurt Faber*

Bioreduction of a nitroalkene by xenobiotic reductase A (XenA) furnished the corresponding nitrosoalkene, which underwent electrocyclisation to yield a highly strained 1,2-oxazete derivative.

3370



Polyethylene glycol clicked Co(II) Schiff base and its catalytic activity for the oxidative dehydrogenation of secondary amines

Praveen K. Khatri, Suman L. Jain,* L. N. Sivakumar K. and Bir Sain*

Click reaction provided an efficient synthesis of PEGylated Co(II) Schiff base for the oxidative dehydrogenation of secondary amines in high yield.