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# Organic & Biomolecular Chemistry

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**PAPER**

Jason E. Camp *et al.*

Multifaceted catalysis approach to nitrile activation: direct synthesis of halogenated allyl amides from allylic alcohols



1477-0520 (2013) 11:43;1-4

# Organic & Biomolecular Chemistry

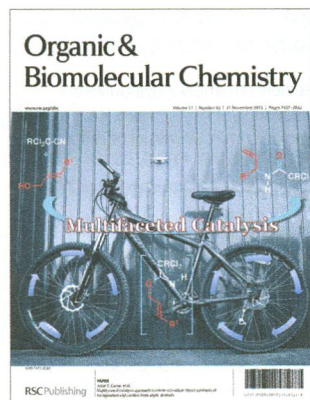
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## IN THIS ISSUE

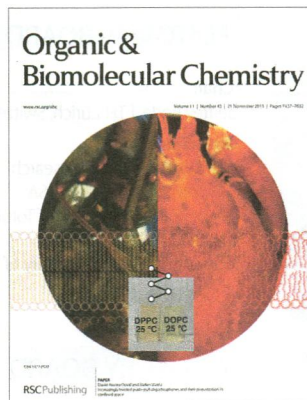
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### Cover

See Jason E. Camp *et al.*, pp. 7472–7476.

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### Inside cover

See David Alonso Doval and Stefan Matile, pp. 7467–7471.

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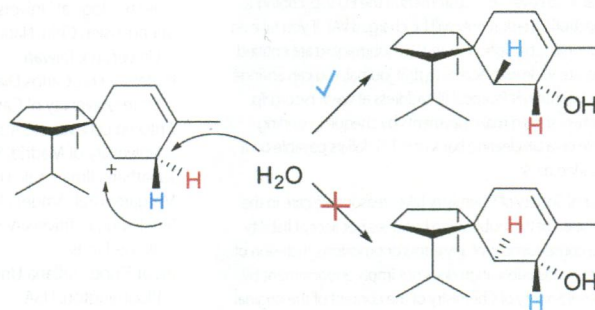
## COMMUNICATIONS

7447

### The stereochemical course of tricho-acorenol biosynthesis

Christian A. Citron and Jeroen S. Dickschat\*

The stereochemical course of tricho-acorenol biosynthesis in the fungus *Trichoderma harzianum* was investigated by feeding of stereospecifically deuterated mevalonolactone isotopomers.

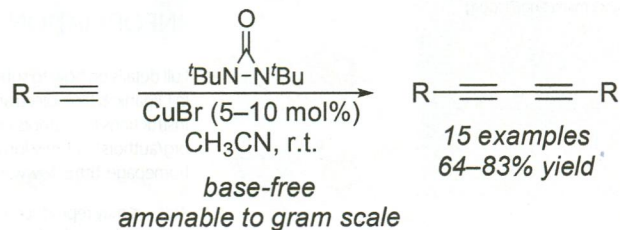


7451

### A facile copper(i)-catalyzed homocoupling of terminal alkynes to 1,3-diynes with diaziridinone under mild conditions

Yingguang Zhu and Yian Shi\*

A novel and efficient Cu(I)-catalyzed oxidative homocoupling of terminal alkynes with diaziridinone as an oxidant is described. Various terminal alkynes can be transformed into the corresponding 1,3-diynes in good yields. The reaction process is base-free, operationally simple, and amenable to the gram scale.

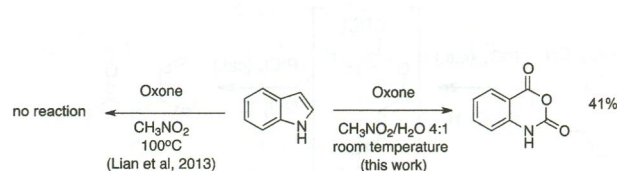


7455

### Is the 2,3-carbon–carbon bond of indole really inert to oxidative cleavage by Oxone? – Synthesis of isoic anhydrides from indoles

Amber C. Nelson, Emily S. Kalinowski,  
Nikolas J. Czerniecki, Taylor L. Jacobson and  
Peter Grundt\*

A recent report has indicated that the oxidizing agent Oxone does not possess the ability to cleave the 2,3-carbon–carbon bond of indole.

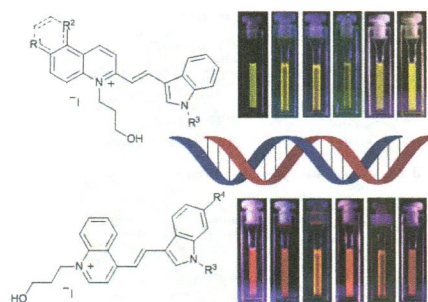


7458

### Synthesis and evaluation of cyanine–styryl dyes with enhanced photostability for fluorescent DNA staining

Peggy R. Bohländer and Hans-Achim Wagenknecht\*

The photostability of cyanine–styryl dyes of the indole–quinolinium type can be significantly improved by structural variations while the excellent optical properties including the bright fluorescence in the presence of DNA can be maintained or even improved, too.

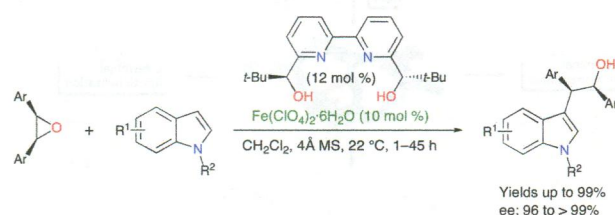


7463

### Highly enantioselective iron(II)-catalyzed opening reaction of aromatic *meso*-epoxides with indoles

Baptiste Plancq, Mathieu Lafantaisie, Simon Companys,  
Cendrella Maroun and Thierry Ollevier\*

A highly enantioselective method for the catalytic *cis*-stilbene oxide opening reaction with indole derivatives was developed. Various 2-(indol-3-yl)ethanol derivatives were obtained in good to excellent yields with excellent enantioselectivities (from 96 to >99% ee).



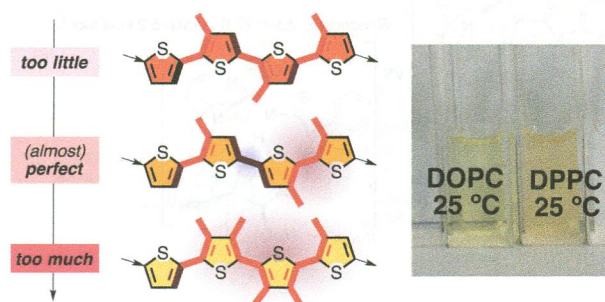
## PAPERS

7467

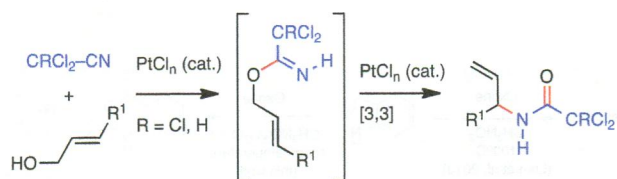
### Increasingly twisted push–pull oligothiophenes and their planarization in confined space

David Alonso Doval and Stefan Matile\*

Systematic deplanarization of push–pull oligothiophene amphiphiles affords conceptually innovative fluorescent probes for the sensing of different membrane environments.



7472

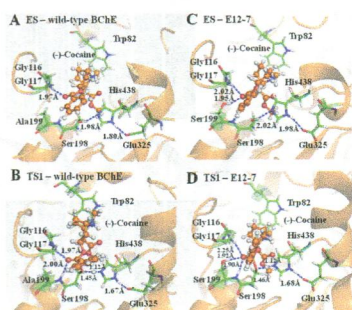


### Multifaceted catalysis approach to nitrile activation: direct synthesis of halogenated allyl amides from allylic alcohols

Roy P. Lester, Jay J. Dunsford and Jason E. Camp\*

The direct synthesis of halogenated allyl amides from allyl alcohols and nitriles was accomplished using a platinum multifaceted catalysis approach.

7477

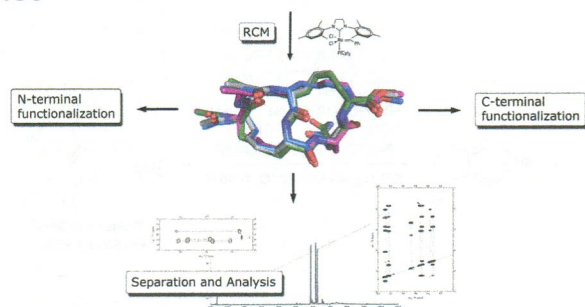


### Substrate selectivity of high-activity mutants of human butyrylcholinesterase

Shurong Hou, Liu Xue, Wenchao Yang, Lei Fang, Fang Zheng and Chang-Guo Zhan\*

Cocaine is one of the most addictive drugs, and there is still no FDA (Food and Drug Administration)-approved medication specific for cocaine.

7486

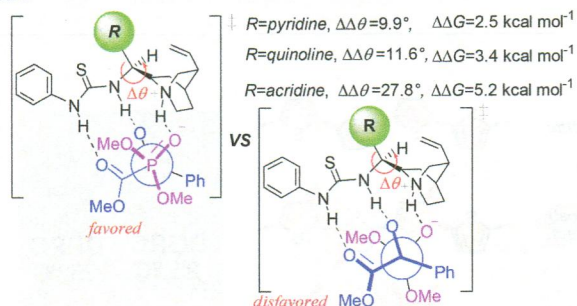


### Synthesis and structural characterization of the individual diastereoisomers of a cross-stapled alkene-bridged nisin DE-ring mimic

Jack C. Slootweg, Johan Kemmink, Rob M. J. Liskamp and Dirk T. S. Rijkers\*

A cross-stapled alkene-bridged octapeptide was synthesized to mimic the DE-ring of the lantibiotic nisin to access novel nisin-hybrids as antibiotic peptides.

7497



### Theoretical study on the mechanism and stereochemistry of the cinchona-thiourea organocatalytic hydrophosphonylation of an $\alpha$ -ketoester

Weiyi Li,\* Dongfeng Huang\* and Yajing Lv

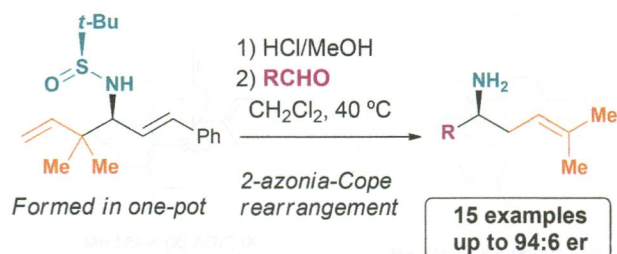
A larger R group could selectively make one of the competing transition states unstable by increasing the strain on the catalyst.

7507

### A general protocol to afford enantioenriched linear homoprenylic amines

Irene Bosque, Francisco Foubelo and Jose C. Gonzalez-Gomez\*

The reaction of a readily obtained chiral branched homoprenylammonium salt with a range of aldehydes, including aliphatic substrates, affords the corresponding linear isomers in good yields and enantioselectivities.

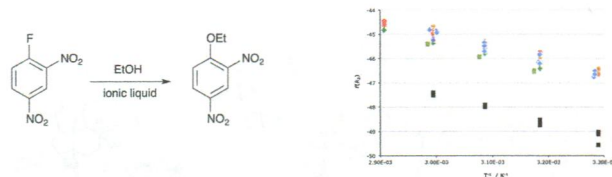


7516

### Probing the importance of ionic liquid structure: a general ionic liquid effect on an S<sub>N</sub>Ar process

Eden E. L. Tanner, Rebecca R. Hawker, Hon Man Yau, Anna K. Croft and Jason B. Harper\*

A general 'ionic liquid effect' is demonstrated on the aromatic substitution reaction shown above. Irrespective of the nature of the components of the ionic liquid, an increase in rate constant is seen relative to ethanol.

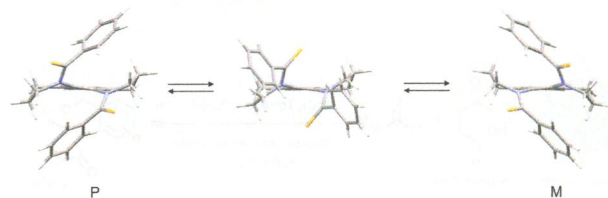


7522

### Helicity discrimination in *N,N'*-dibenzoyl-1,2,3,4,7,8,9,10-octahydro-1,10-phenanthrolines and their thiono- and selenocarbonyl analogues by inclusion complexation with chiral diols

Teresa Olszewska,\* Artur Sikorski, Aleksander Herman and Tadeusz Połński

The optically active thiono- and selenoamides are configurationally labile compounds and gradually racemize in solution but they are stable in the form of the inclusion complexes.

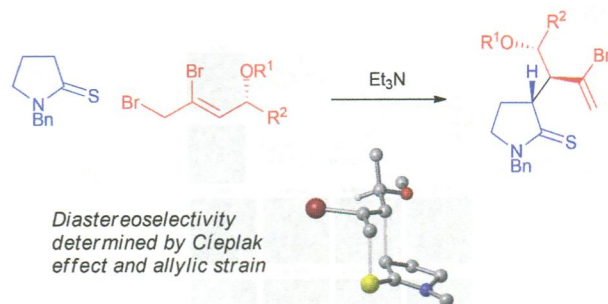


7530

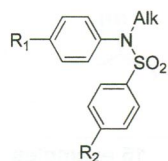
### Reversal of facial selectivity in a thia-Claisen rearrangement by incorporation of a vinylic bromine substituent

Adam R. Ellwood, Anne J. Price Mortimer, Jonathan M. Goodman and Michael J. Porter\*

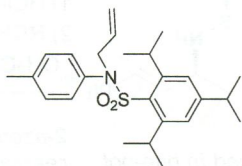
A reversal in the diastereoselectivity of thia-Claisen rearrangements upon bromination has been observed, and the stereoselectivity rationalised using DFT calculations.



7540



Ki (hCA IX) = 8.3 - 451 nM  
selectivity hCA II / hCA IX > 1000



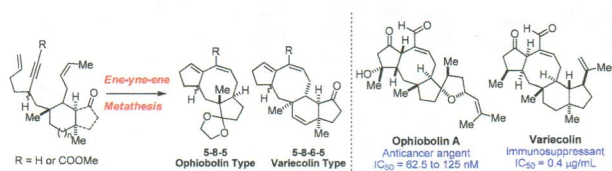
Ki (hCA IX) = 451 nM  
selectivity hCA I / hCA IX > 1000  
selectivity hCA II / hCA IX > 1000

### Superacid synthesized tertiary benzenesulfonamides and benzofused sultams act as selective hCA IX inhibitors: toward understanding a new mode of inhibition by tertiary sulfonamides

Benoît Métayer, Agnès Martin-Mingot, Daniella Vullo, Claudiu. T. Supuran\* and Sébastien Thibaudeau\*

Superacid synthesized tertiary benzenesulfonamides show strong selectivity toward tumor-associated hCA IX, confirming the non-zinc binding mode of this class of sulfonamides.

7550



R = H or COOMe

5-8-5 Ophiobolin Type

5-8-6-5 Variecolin Type

Ophiobolin A  
Anticancer agent  
IC<sub>50</sub> = 62.5 to 125 nM

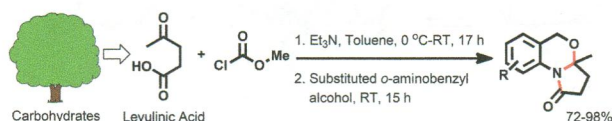
Variecolin  
Immunosuppressant  
IC<sub>50</sub> = 0.4 μg/mL

### Construction of the basic skeleton of ophiobolin A and variecolin

Ke Li, Cheng Wang, Gang Yin and Shuanhu Gao\*

Ophiobolin and variecolin type sesterterpenoids belong to cyclooctane-containing natural products. Both sesterterpenoids have challenging structures and appealing biological activities. We envisioned that a key tandem ring closing metathesis of dienynes could provide the basic skeleton of ophiobolin A and variecolin. We report herein the detailed reactivities of the dienynes which furnished the 5-8-5 and 5-8-6-5 rings efficiently.

7559



Carbohydrates

Levulinic Acid

1. Et<sub>3</sub>N, Toluene, 0 °C-RT, 17 h  
2. Substituted o-aminobenzyl alcohol, RT, 15 h

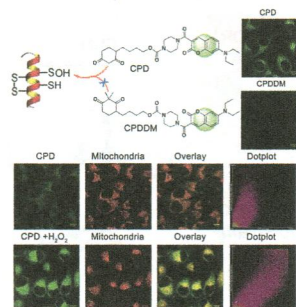
72-98%

### Transition metal-free one-pot cascade synthesis of 7-oxa-2-azatricyclo[7.4.0.0<sup>2,6</sup>]trideca-1(9),10,12-trien-3-ones from biomass-derived levulinic acid under mild conditions

Amitabh Jha,\* Ajaya B. Naidu and Ashraf M. Abdelkhalik

The reaction of keto acids with methyl chloroformate and substituted o-aminobenzyl alcohols using triethylamine as a base in toluene at room temperature gave good to excellent yields of the title compounds.

7566



### In situ visualization and detection of protein sulfenylation responses in living cells through a dimedone-based fluorescent probe

Qin Yin, Chusen Huang, Chao Zhang, Weiping Zhu,\* Yufang Xu,\* Xuhong Qian and Yi Yang\*

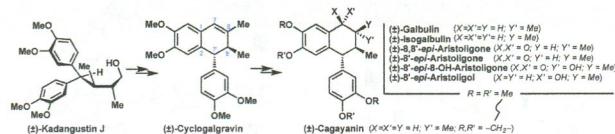
Small fluorescent probe (CPD and CPDDM) based live-cell-labelling technology for the visualization of protein sulfenylation in living cells has been developed.

7574

### Collective synthesis of several 2,7'-cycloignans and their correlation by chemical transformations

Yu Peng,\* Zhen-Biao Luo, Jian-Jian Zhang, Long Luo and Ya-Wen Wang

Collective synthesis of anti-malarial 2,7'-cycloignans has been stereoselectively achieved employing ( $\pm$ )-cyclogalgravin as a linchpin.

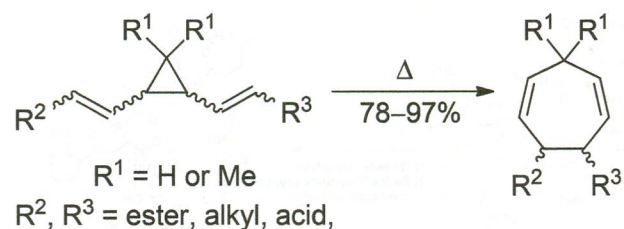


7587

### The Cope rearrangement of *gem*-dimethyl substituted divinylcyclopropanes

Jonathan D. Osler, William P. Unsworth and Richard J. K. Taylor\*

A detailed mechanistic study into the Cope rearrangement of *gem*-dimethyl substituted divinylcyclopropanes.

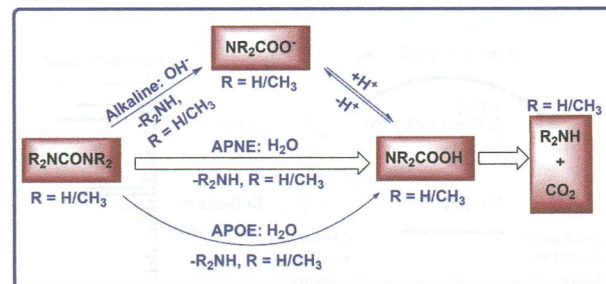


7595

### Reaction pathways and free energy profiles for spontaneous hydrolysis of urea and tetramethylurea: unexpected substituent effects

Min Yao, Wenlong Tu, Xi Chen\* and Chang-Guo Zhan\*

Computational studies on competing reaction pathways for non-enzymatic hydrolysis of urea and tetramethylurea reveal an unexpected mechanism and substituent effects.

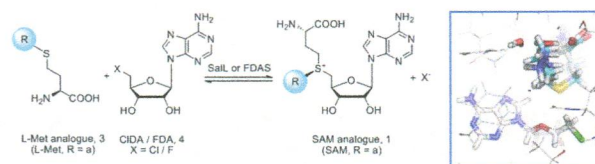


7606

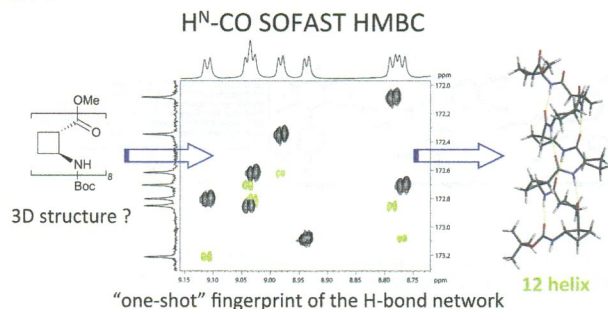
### Chemoenzymatic synthesis and *in situ* application of *S*-adenosyl-L-methionine analogs

Marie Thomsen, Stine B. Vogensen, Jens Buchardt, Michael D. Burkart\* and Rasmus P. Clausen\*

Chemoenzymatic synthesis of unnatural *S*-adenosyl-L-methionine analogs using bacterial halogenases was explored and implemented *in situ* with PRMT1.



7611

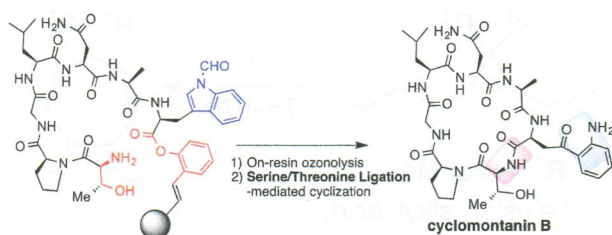


### Fast-pulsing NMR techniques for the detection of weak interactions: successful natural abundance probe of hydrogen bonds in peptides

Amandine Altmayer-Henzien, Valérie Declerck, David J. Aitken, Ewen Lescop, Denis Merlet and Jonathan Farjon\*

The SOFAST HMBC experiment is proposed for boosting the sensitivity at natural abundance for detecting H bonds in peptidomimetics.

7616

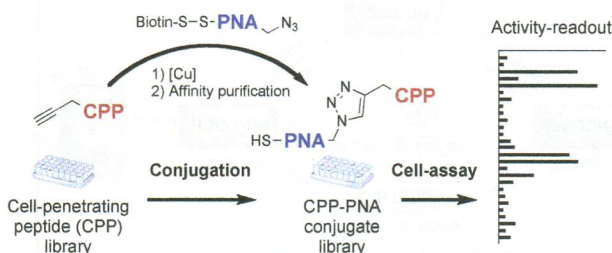


### Effective synthesis of kynurenine-containing peptides via on-resin ozonolysis of tryptophan residues: synthesis of cyclomontanin B

Clarence T. T. Wong, Hiu Yung Lam and Xuechen Li\*

Synthesis of cyclomontanin B has been described, wherein on-resin ozonolysis allows for the simultaneous generation of peptide salicylaldehyde ester and kynurenine.

7621



### Parallel synthesis and splicing redirection activity of cell-penetrating peptide conjugate libraries of a PNA cargo

Peter J. Deuss, Andrey A. Arzumanov, Donna L. Williams and Michael J. Gait\*

A novel method for the parallel synthesis of peptide-biocargo conjugates was developed and applied to synthesize cell-penetrating peptide (CPP)-PNA705 conjugate libraries for screening in a splicing redirection assay.