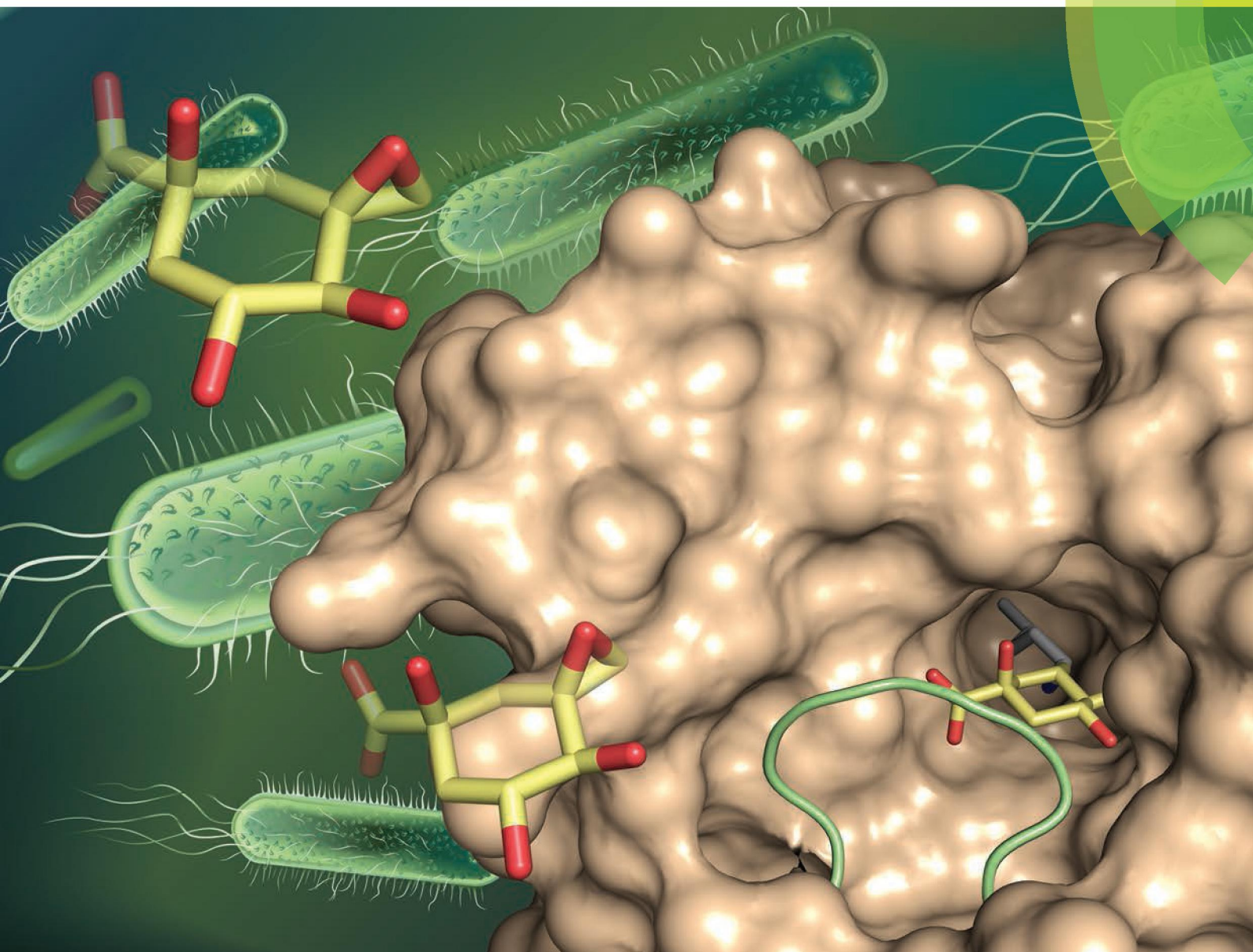


# Organic & Biomolecular Chemistry

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ISSN 1477-0520



**PAPER**

Concepción González-Bello *et al.*  
Irreversible covalent modification of type I dehydroquinase with a stable Schiff base

# Organic & Biomolecular Chemistry

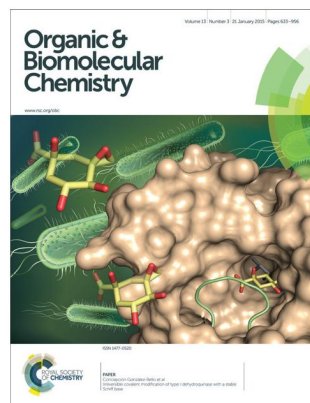
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## IN THIS ISSUE

ISSN 1477-0520 CODEN OBCRAK 13(3) 633–956 (2015)



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See Concepción González-Bello *et al.*, pp. 706–716.

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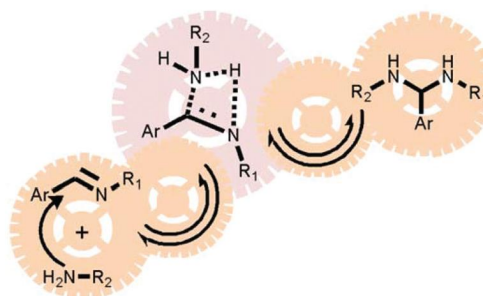
## REVIEWS

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### Mechanisms of imine exchange reactions in organic solvents

Maria Ciaccia and Stefano Di Stefano\*

Updated mechanisms operating in imine chemistry in organic solvents are reviewed and critically discussed.

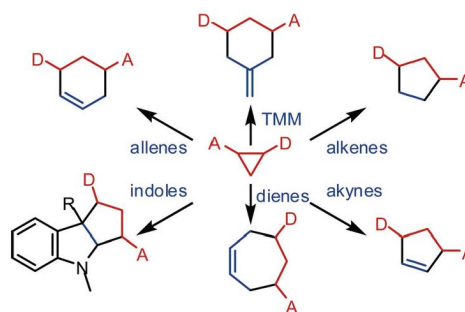


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### Carbocycles from donor–acceptor cyclopropanes

Huck K. Grover, Michael R. Emmett and Michael A. Kerr\*

Donor–acceptor cyclopropane annulations – not just for heterocycles.



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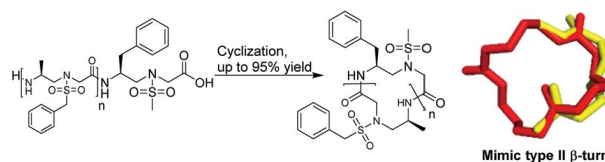
## COMMUNICATIONS

672

**The synthesis of head-to-tail cyclic sulfono- $\gamma$ -AApeptides**

Haifan Wu, Fengyu She, Wenyang Gao, Austin Prince, Yaqiong Li, Lulu Wei, Allison Mercer, Lukasz Wojtas, Shengqian Ma and Jianfeng Cai\*

Head-to-tail cyclic sulfono- $\gamma$ -AApeptides.

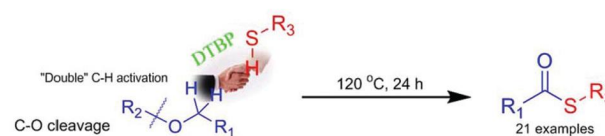


677

**Direct oxidative coupling of thiols and benzylic ethers via  $C(sp^3)$ -H activation and C-O cleavage to lead thioesters**

J. Feng, M.-F. Lv, G.-P. Lu and C. Cai\*

An unprecedented protocol for the synthesis of thioesters via C-H thioesterification and C-O cleavage was developed. This CDC protocol was found convenient and easy-to-handle involving the use of DTBP as the only green oxidant.

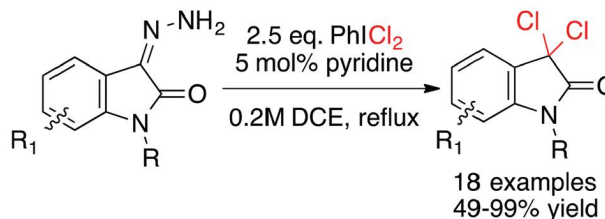


682

**Synthesis of 3,3-dichloroindolin-2-ones from isatin-3-hydrazones and (dichloroiodo)benzene**

Keith E. Coffey, Ryan Moreira, Farhana Z. Abbas and Graham K. Murphy\*

An operationally simple conversion from hydrazones to *gem*-dichlorides occurs with broad functional group compatibility in moderate to high yield.

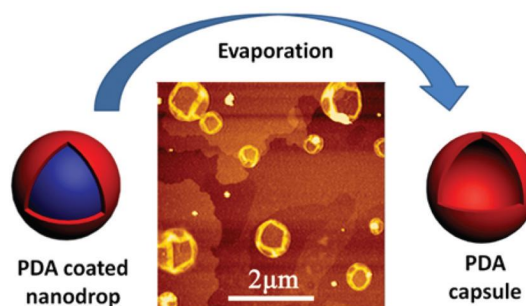


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**Preparation of polydopamine nanocapsules in a miscible tetrahydrofuran–buffer mixture**

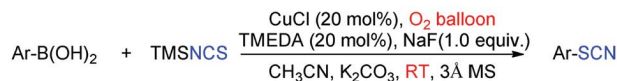
Yun-Zhou Ni, Wen-Feng Jiang, Gang-Sheng Tong, Jian-Xin Chen, Jie Wang, Hui-Mei Li, Chun-Yang Yu, Xiao-hua Huang\* and Yong-Feng Zhou\*

A non-emulsion soft template method based on a miscible tetrahydrofuran–tris buffer mixture has been used to fabricate polydopamine nanocapsules.



## COMMUNICATIONS

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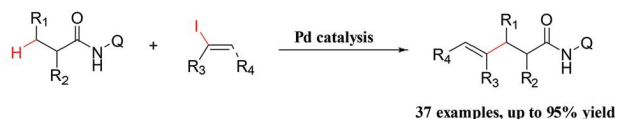


### A mild copper-catalyzed aerobic oxidative thiocyanation of arylboronic acids with TMSNCS

Nan Sun,\* Liusheng Che, Weimin Mo, Baoxiang Hu, Zhenlu Shen and Xinquan Hu\*

A facile and generalized synthesis of aryl thiocyanates has been established *via* the CuCl-catalyzed oxidative coupling of arylboronic acids with TMSNCS. The reaction could be conducted at RT and under an O<sub>2</sub> atmosphere.

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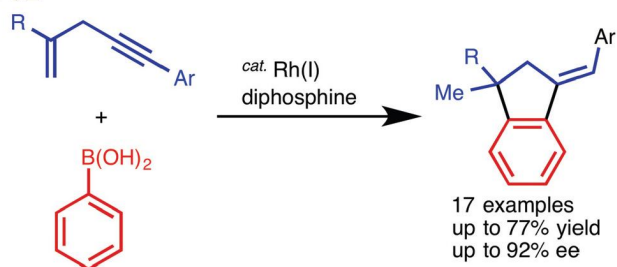


### Palladium-catalyzed unactivated $\beta$ -methylene C(sp<sup>3</sup>)-H bond alkenylation of aliphatic amides and its application in a sequential C(sp<sup>3</sup>)-H/C(sp<sup>2</sup>)-H bond alkenylation

Gang Shan, Guiyi Huang and Yu Rao\*

A palladium(II)-catalyzed  $\beta$ -methylene C(sp<sup>3</sup>)-H bond alkenylation of acyclic aliphatic amides with alkenyl halides has been developed. Solvent effect-promoted sequential C(sp<sup>3</sup>)-H bond alkenylation and C(sp<sup>2</sup>)-H bond alkenylation has also been studied.

702



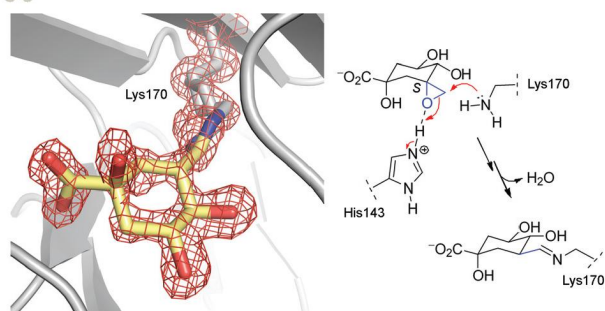
### Rhodium-catalysed arylation of 1,4-enynes with arylboronic acids

Takanori Matsuda\* and Shoichi Watanuki

Rhodium(I)-catalysed arylation of 1,4-enynes with arylboronic acids affords 1,1-disubstituted 3-(arylmethylene)indanes *via* an addition–1,4-rhodium migration–addition sequence.

## PAPERS

706



### Irreversible covalent modification of type I dehydroquinase with a stable Schiff base

Lorena Tizón, María Maneiro, Antonio Peón, José M. Otero, Emilio Lence, Sergio Poza, Mark J. van Raaij, Paul Thompson, Alastair R. Hawkins and Concepción González-Bello\*

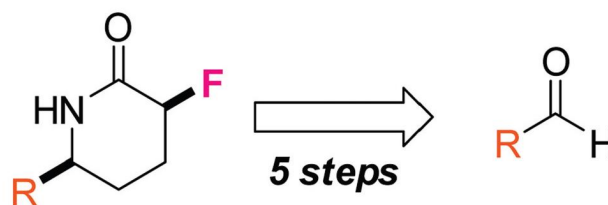
Structural and computational studies carried out with two epoxides provide insight into the irreversible inhibition of type I dehydroquinase.

717

### Short and efficient synthesis of fluorinated $\delta$ -lactams

Thomas J. Cogswell, Craig S. Donald, De-Liang Long and Rodolfo Marquez\*

The diastereoselective synthesis of fluorinated  $\delta$ -lactams.

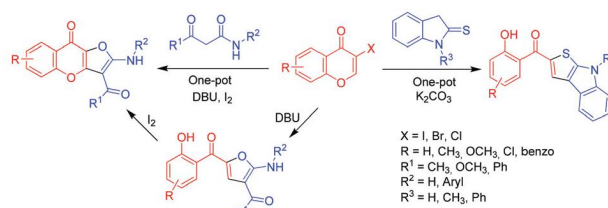


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### Synthesis of functionalized 2-salicyloylfurans, furo-[3,2-*b*]chromen-9-ones and 2-benzoyl-8*H*-thieno-[2,3-*b*]indoles by one-pot cyclizations of 3-halochromones with $\beta$ -ketoamides and 1,3-dihydroindole-2-thiones

I. Savych, T. Gläsel, A. Villinger, V. Y. Sosnovskikh, V. O. Iaroshenko\* and P. Langer\*

Domino reactions of 3-halochromones with  $\beta$ -ketoamides and 1,3-dihydroindole-2-thiones provided a convenient approach to various heterocyclic systems.

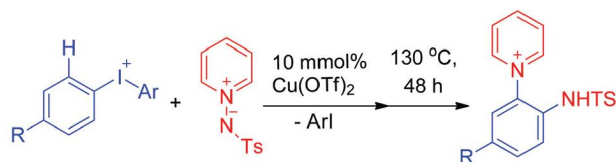


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### Exploiting the narrow gap of rearrangement between the substituents in the vicinal disubstitution reactions of diaryliodonium salts with pyridine *N*-sulfonamidates

Yong Wang, Ming Li,\* Lirong Wen, Peng Jing, Xiang Su and Chao Chen\*

The vicinal disubstitution reactions of diaryliodonium salts with pyridine *N*-sulfonamidates were studied fully to give *o*-pyridinium anilines.

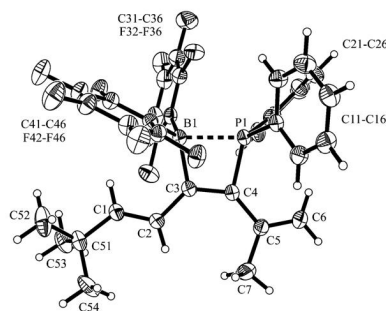


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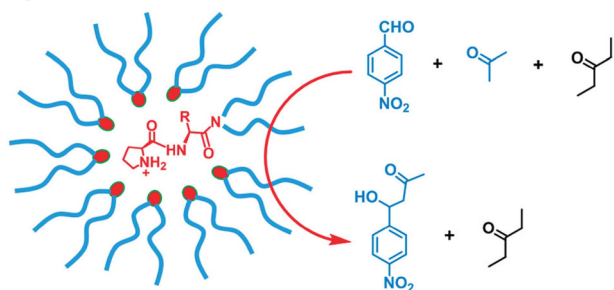
### 1,1-Alkenylboration of diarylphosphino-enynes: convenient synthetic entry to vicinal P/B Lewis pairs at extended conjugated $\pi$ -frameworks

Guo-Qiang Chen, Gerald Kehr, Constantin G. Daniliuc and Gerhard Erker\*

Alkenylboranes R-CH=CH-B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> undergo carbon-carbon coupling by means of 1,1-alkenylboration with diarylphosphino-enynes to give conjugated hexatriene derivatives that bear a vicinal pair of B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> and PAr<sub>2</sub> functionalities at the framework.



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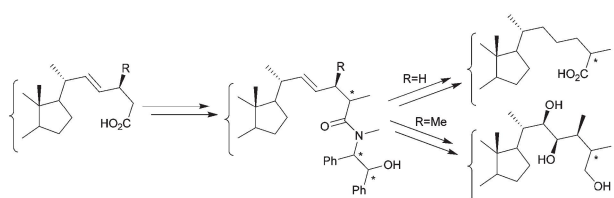


### Interfacial catalysis of aldol reactions by prolinamide surfactants in reverse micelles

Premkumar Rathinam Arivalagan and Yan Zhao\*

Aggregation of prolinamide surfactants in nonpolar solvents enhanced their catalytic activity and gave unusual substrate selectivity in aldol condensations.

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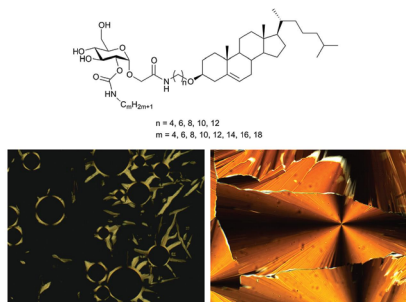


### Formation of the steroidal C-25 chiral center via the asymmetric alkylation methodology

Yu. V. Ermolovich, V. N. Zhabinskii\* and V. A. Khripach

A novel approach for the preparation of steroids containing a chiral center at C-25 is reported. The key stereochemistry inducing step was asymmetric alkylation of pseudoephedrine amides of steroidal C-26 acids. The developed methodology was successfully applied to the synthesis of (25*R*)- and (25*S*)-cholestenoic acids as well as (25*R*)- and (25*S*)-26-hydroxy brassinolides.

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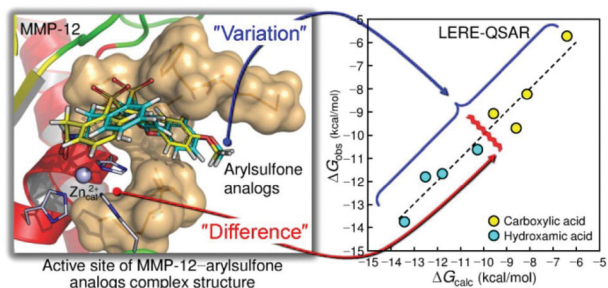


### Self-organizing behaviour of glycoconjugated bolaphiles: insights into lipidic microsegregation

R. Xu, F. Ali-Rachedi, N. M. Xavier, S. Chambert, F. Ferkous, Y. Queneau,\* S. J. Cowling,\* E. J. Davis and J. W. Goodby

The synthesis of glycoconjugated bolaphile biomimics are described along with the liquid-crystalline behaviours as a function of increasing aliphatic composition.

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### A QSAR study on the inhibition mechanism of matrix metalloproteinase-12 by arylsulfone analogs based on molecular orbital calculations

Seiji Hitaoka, Hiroshi Chuman\* and Kazunari Yoshizawa\*

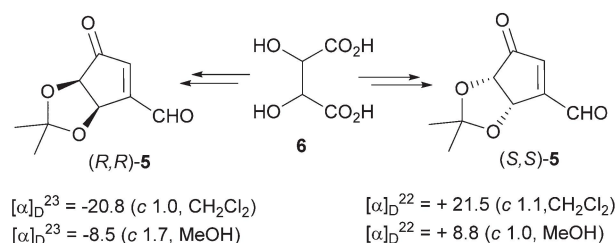
The inhibition mechanism of matrix metalloproteinase-12 by arylsulfone analogs is revealed using a comprehensive computational approach including docking simulations, molecular orbital calculations, and QSAR.

807

### Synthesis and the absolute configuration of both enantiomers of 4,5-dihydroxy-3-(formyl)-cyclopent-2-enone acetonide as a new chiral building block for prostanoid synthesis

Beata Łukasik, Marian Mikołajczyk, Grzegorz Bujacz and Remigiusz Żurawiński\*

Starting from optically inactive *meso*-tartaric acid (**6**) the synthesis of both enantiomers of a new cyclopentenone building block **5** was developed.

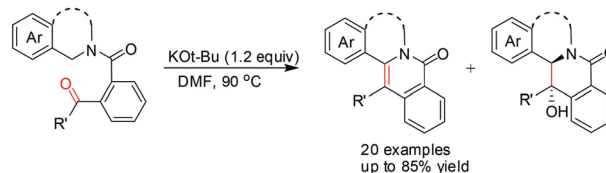


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### Rapid synthesis of isoquinolinones by intramolecular coupling of amides and ketones

Wen-Tao Wei, Yu Liu, Lin-Miao Ye, Rong-Hui Lei, Xue-Jing Zhang and Ming Yan\*

Isoquinolinones were prepared in good yields *via* the intramolecular coupling of amides and ketones in the presence of KOt-Bu/DMF.

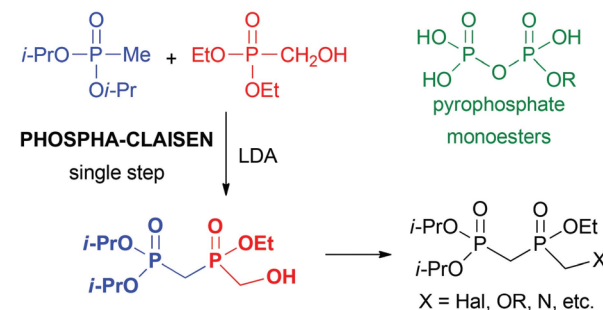


825

### Synthesis of (phosphonomethyl)phosphinate pyrophosphate analogues *via* the phospho-Claisen condensation

Fabien Gelat, Claire Lacomme, Olivier Berger, Laurent Gavara and J.-L. Montchamp\*

Pyrophosphate analogues are of great importance especially for the design of biologically active molecules.

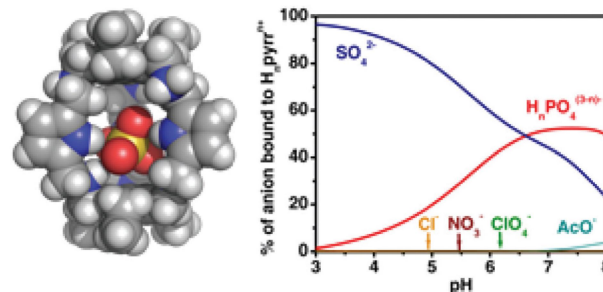


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### Sulfate recognition by a hexaaza cryptand receptor

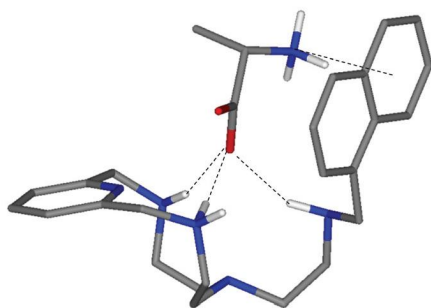
Pedro Mateus,\* Rita Delgado,\* Vânia André and M. Teresa Duarte

A polypyrrolic polyammonium macrobicyclic receptor encapsulates sulfate with very high association constants and selectivity in the presence of other anions.





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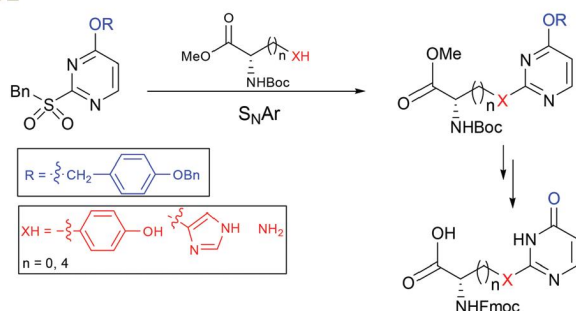


### A thermodynamic insight into the recognition of hydrophilic and hydrophobic amino acids in pure water by aza-scorpian type receptors

Salvador Blasco, Begoña Verdejo,\* Carla Bazzicalupi, Antonio Bianchi,\* Claudia Giorgi, Concepción Soriano and Enrique García-España\*

Thermodynamic studies about the interaction of scorpian aza-macrocycles with amino acids in water show entropy driven stabilisations often associated with solvation/desolvation processes.

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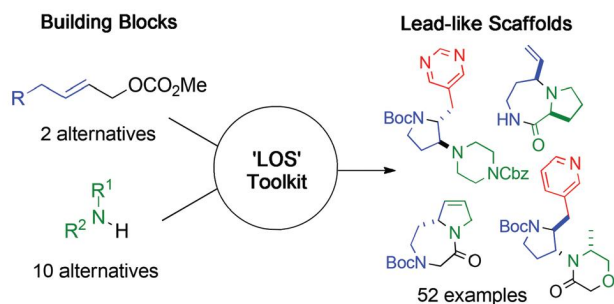


### Synthesis of new unnatural $N^{\alpha}$ -Fmoc pyrimidin-4-one amino acids: use of the *p*-benzyloxybenzyloxy group as a pyrimidinone masking group

Abdellatif ElMarrouni and Montserrat Heras\*

The *p*-benzyloxybenzyloxy group is used to mask the oxo function of the 4(3*H*)-pyrimidinone ring in the synthesis of new unnatural amino acids.

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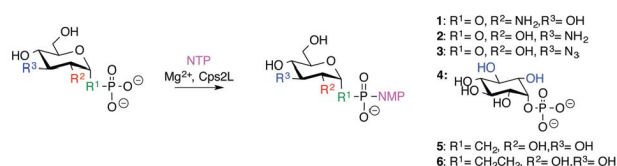


### A unified lead-oriented synthesis of over fifty molecular scaffolds

Richard G. Doveston, Paolo Tosatti, Mark Dow, Daniel J. Foley, Ho Yin Li, Amanda J. Campbell, David House, Ian Churcher, Stephen P. Marsden\* and Adam Nelson\*

Sourcing large numbers of lead-like compounds is a major challenge; a unified synthetic approach enabled the efficient synthesis of 52 diverse lead-like molecular scaffolds from just 13 precursors.

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### Kinetic evaluation of glucose 1-phosphate analogues with a thymidyltransferase using a continuous coupled enzyme assay

S. M. Forget, A. Jee, D. A. Smithen, R. Jagdhane, S. Anjum, S. A. Beaton, D. R. J. Palmer, R. T. Syvitski and D. L. Jakeman\*

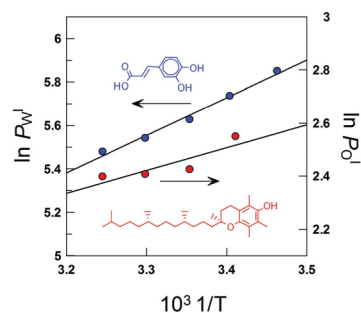
We have developed a continuous spectrophotometric kinetic assay for the detection of PP<sub>i</sub> and have applied the assay to evaluate Cps2L, a nucleotidyltransferase, kinetics with five synthetic substrate analogues (**2–6**).

876

### Transfer of antioxidants at the interfaces of model food emulsions: distributions and thermodynamic parameters

Sonia Losada-Barreiro, Verónica Sánchez-Paz and Carlos Bravo-Díaz\*

Caffeic acid and  $\alpha$ -tocopherol (vitamin E) incorporate spontaneously into the interfacial regions of emulsions and their transfer processes are entropy driven.

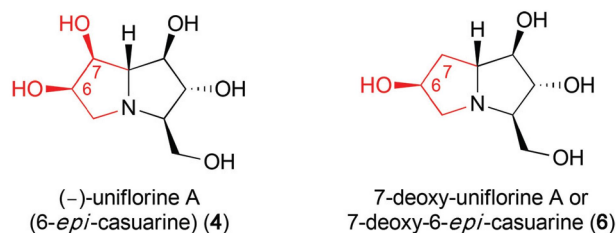


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### New synthesis and biological evaluation of uniflorine A derivatives: towards specific insect trehalase inhibitors

Giampiero D'Adamio, Antonella Sgambato, Matilde Forcella, Silvia Caccia, Camilla Parmeggiani, Morena Casartelli, Paolo Parenti, Davide Bini, Laura Cipolla, Paola Fusi\* and Francesca Cardona\*

(-)-Uniflorine A and 7-deoxy-uniflorine A are selective inhibitors of insect trehalases from *C. riparius* and *S. littoralis*.



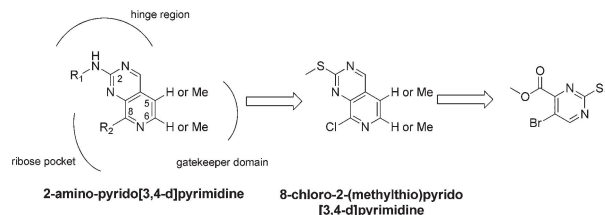
*Selective inhibitors of insect trehalases!*

893

### Expanding the scope of fused pyrimidines as kinase inhibitor scaffolds: synthesis and modification of pyrido[3,4-d]pyrimidines

Paolo Innocenti, Hannah Woodward, Lisa O'Fee and Swen Hoelder\*

A versatile and efficient entry into 2-amino-pyrido[3,4-d]-pyrimidines was developed. Our strategy hinges on the concise preparation and derivatisation of 8-chloro-2-(methylthio)pyrido[3,4-d]pyrimidine intermediates to yield putative kinase inhibitors.

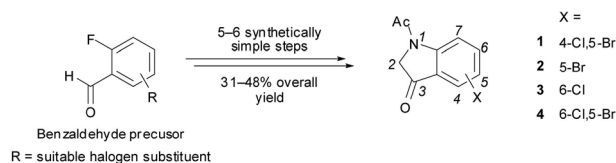


905

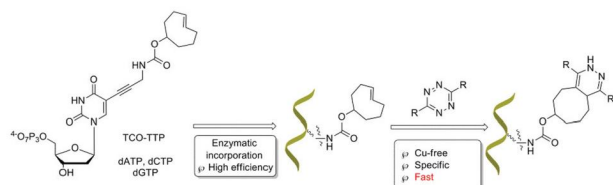
### A simple and robust preparation of N-acetylindoxyls: precursors for indigogenic substrates

Michael N. Gandy, Lindsay T. Byrne and Keith A. Stubbs\*

A generalised, simple and efficient synthesis of N-acetyl-5-bromo-4-chloroindoxyl and related analogues required for the synthesis of indigogenic substrates to probe for biological activities is reported.



909

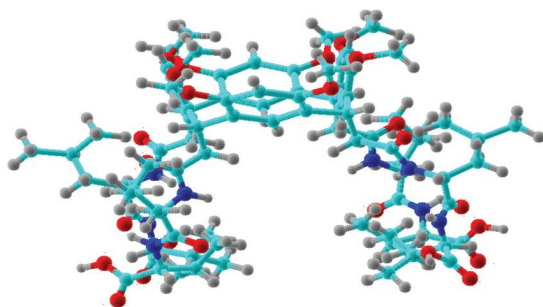


### Post-synthesis DNA modifications using a *trans*-cyclooctene click handle

Ke Wang, Danzhu Wang, Kaili Ji, Weixuan Chen, Yueqin Zheng, Chaofeng Dai and Binghe Wang\*

Efficient enzymatic DNA incorporation of *trans*-cyclooctene thymidine triphosphate (TCO-TTP) is reported. The general handle of *trans*-cyclooctene can undergo a rapid bioorthogonal cycloaddition with tetrazine, which is suitable for further DNA labeling work.

916

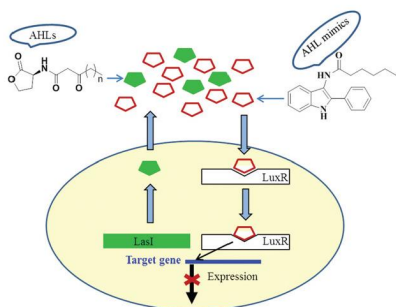


### Hydrolytic inhibition of $\alpha$ -chymotrypsin by 2,8,14,20-tetrakis(D-leucyl-D-valinamido)resorcin[4]-arene carboxylic acid: a spectroscopic NMR and computational combined approach

Gloria Uccello-Barretta,\* Federica Balzano, Federica Aiello, Letizia Vanni, Mattia Mori, Sergio Menta, Andrea Calcaterra and Bruno Botta

A rationale for the inhibition of hydrolytic efficiency of  $\alpha$ -chymotrypsin by a resorcin[4]arene derivative was obtained by NMR spectroscopy and molecular modeling.

925

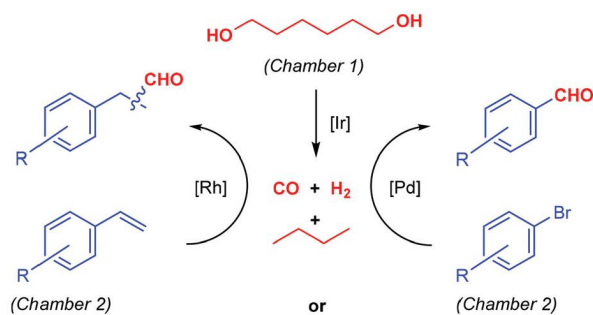


### Indole-based novel small molecules for the modulation of bacterial signalling pathways

Nripendra Nath Biswas, Samuel K. Kutty, Nicolas Barraud, George M. Iskander, Renate Griffith, Scott A. Rice, Mark Willcox, David StC. Black and Naresh Kumar\*

Indole based *N*-acylated L-homoserine lactone (AHL) mimics were developed as quorum sensing (QS) inhibitors for Gram-negative bacteria *Pseudomonas aeruginosa* and can be used as novel antimicrobial agents.

938



### Hydroformylation of olefins and reductive carbonylation of aryl halides with syngas formed *ex situ* from dehydrogenative decarbonylation of hexane-1,6-diol

Stig Holden Christensen, Esben P. K. Olsen, Jascha Rosenbaum and Robert Madsen\*

Carbon monoxide and molecular hydrogen are liberated from hexane-1,6-diol in a two-chamber reactor and employed for either a hydroformylation of olefins or a reductive carbonylation of aryl halides.

946

## Interactions of arene ruthenium metallaprisms with human proteins

Lydia E. H. Paul, Bruno Therrien\* and Julien Furrer\*

Interactions between three hexacationic arene ruthenium metallaprisms and human proteins have been studied using NMR spectroscopy, mass spectrometry and circular dichroism spectroscopy, showing that proteins are potential biological targets for these metallaprisms.

