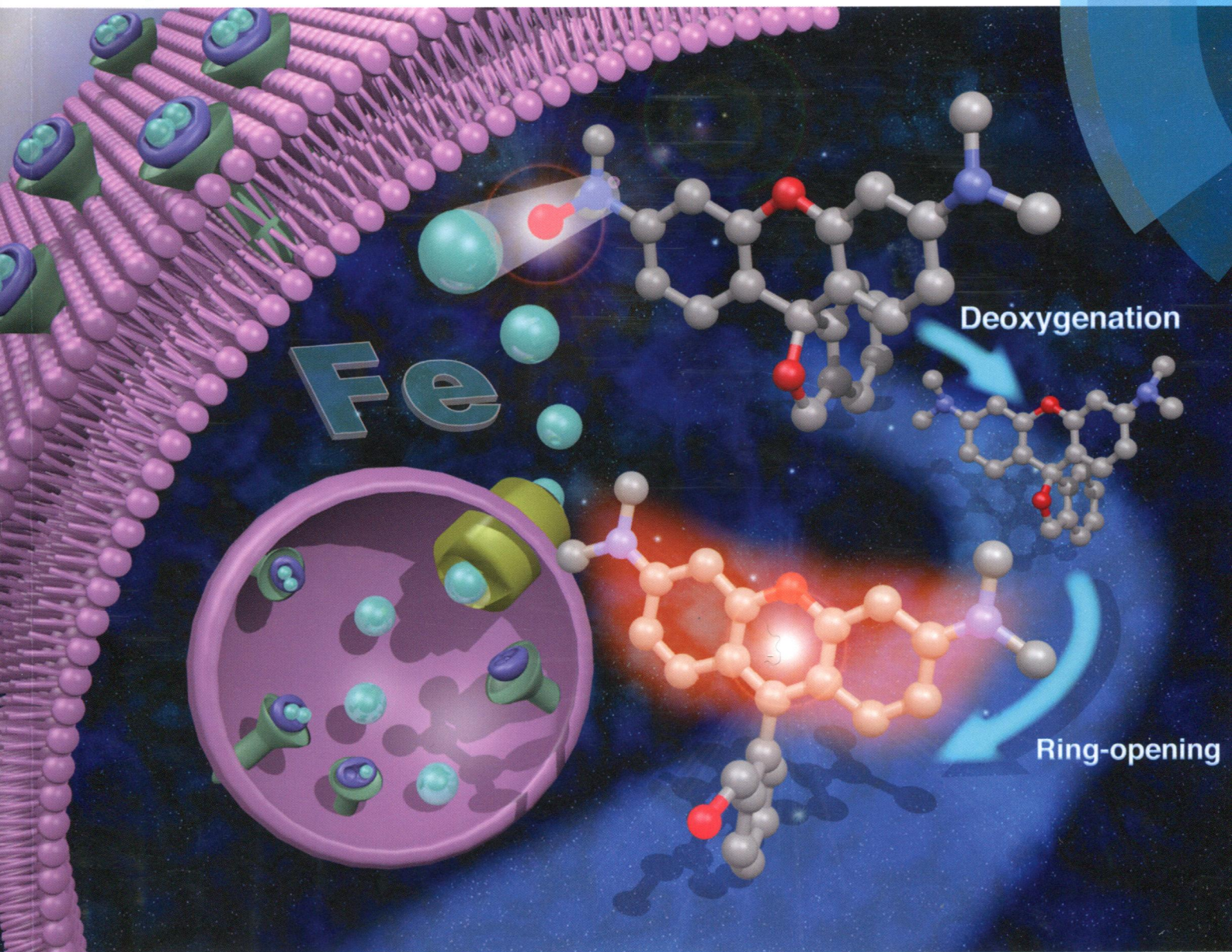


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Volume 12 | Number 34 | 14 September 2014 | Pages 6535–6746

# Organic & Biomolecular Chemistry

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ISSN 1477-0520



PAPER

Tasuku Hirayama, Hideko Nagasawa *et al.*

A new class of high-contrast Fe(II) selective fluorescent probes based on spirocyclized scaffolds for visualization of intracellular labile iron delivered by transferrin



# Organic & Biomolecular Chemistry

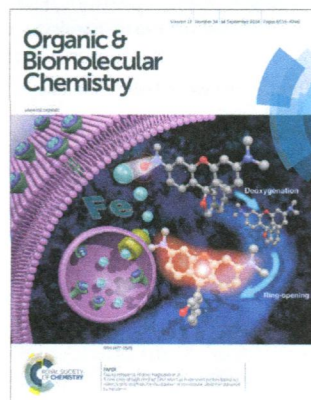
An international journal of synthetic, physical and biomolecular organic chemistry

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## IN THIS ISSUE

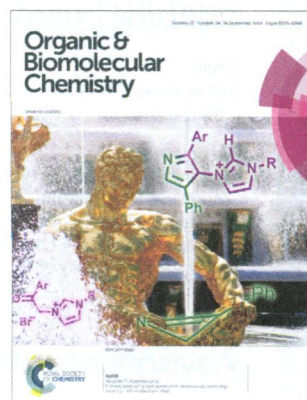
ISSN 1477-0520 CODEN OBCRAK 12(34) 6535–6746 (2014)



### Cover

See Tasuku Hirayama, Hideko Nagasawa *et al.*, pp. 6590–6597.

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### Inside cover

See Alexander F. Khlebnikov *et al.*, pp. 6598–6609.

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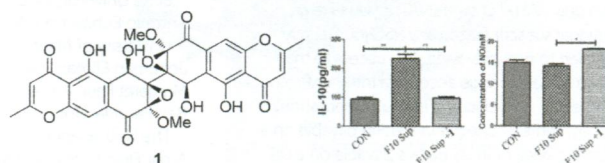
## COMMUNICATIONS

6545

### Diaporine, a novel endophyte-derived regulator of macrophage differentiation

Hao Chen Wu, Hui Ming Ge, Le Yun Zang, Yun Cheng Bei, Zhi Yuan Niu, Wei Wei, Xiu Jing Feng, Sen Ding, Seik Weng Ng, Ping Ping Shen\* and Ren Xiang Tan\*

Diaporine (**1**), an unprecedented symmetric polyketide, was characterized from the endophytic fungus *Diaporthe* sp. Diaporine was demonstrated to inhibit significantly the differentiation of macrophages.

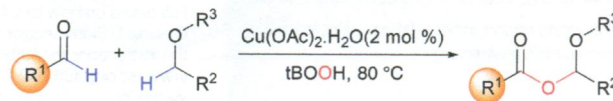


6549

### Copper catalyzed C–O bond formation via oxidative cross-coupling reaction of aldehydes and ethers

Quan Wang, Hao Zheng, Wen Chai, Dianyu Chen, Xiaojun Zeng, Renzhong Fu\* and Rongxin Yuan\*

A practical and efficient construction of C–O bonds via oxidative cross-coupling reaction of aldehydes and ethers has been realized under open air. When 2 mol% copper was used as the catalyst, various  $\alpha$ -acyloxy ethers were obtained with up to 93% isolated yield.



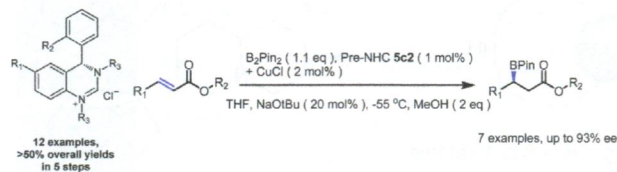
Федеральное государственное  
бюджетное учреждение науки  
Центральная научная библиотека  
Уральского отделения  
Российской академии наук (ЦНБ УрО РАН)

6554

### Asymmetric borylation of $\alpha,\beta$ -unsaturated esters catalyzed by novel ring expanded N-heterocyclic carbenes based on chiral 3,4-dihydroquinazolinium compounds

Liliang Huang, Yong Cao, Manping Zhao, Zhongfeng Tang and Zhihua Sun\*

A series of novel ring expanded N-heterocyclic carbene (NHC) precursors were synthesized, which showed excellent enantioselectivities for borylation of  $\alpha,\beta$ -unsaturated esters.

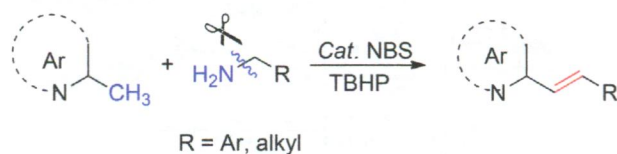


6557

### Metal-free oxidative olefination of primary amines with benzylic C–H bonds through direct deamination and C–H bond activation

Liang Gong, Li-Juan Xing, Tong Xu, Xue-Ping Zhu, Wen Zhou, Ning Kang and Bin Wang\*

An oxidative olefination reaction between aliphatic primary amines and benzylic  $sp^3$  C–H bonds has been achieved using *N*-bromosuccinimide as catalyst and *tert*-butyl hydroperoxide as oxidant.

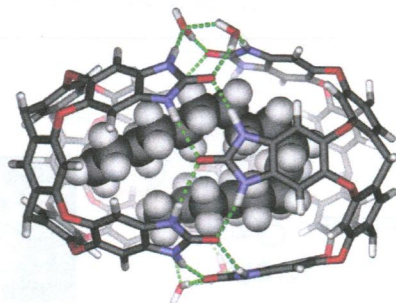


6561

### Folded alkyl chains in water-soluble capsules and cavitands

Jesse V. Gavette, Kang-Da Zhang, Dariush Ajami and Julius Rebek Jr.\*

A deep cavitand with ionic "feet" dimerizes around hydrophobic compounds in  $D_2O$ .

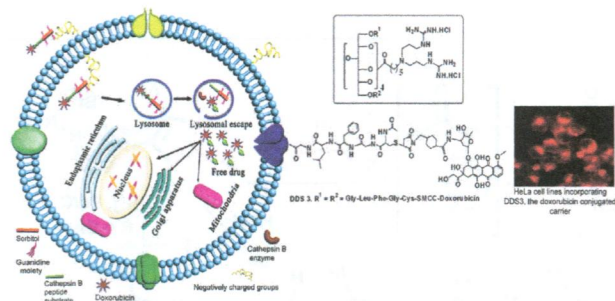


6564

### A lysosome-targeted drug delivery system based on sorbitol backbone towards efficient cancer therapy

Santhi Maniganda, Vandana Sankar, Jyothi B. Nair, K. G. Raghu and Kaustabh K. Maiti\*

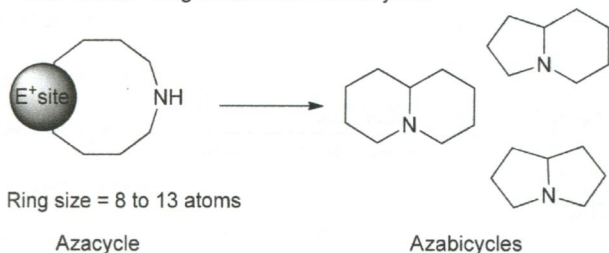
A lysosome-targeted drug delivery system utilizing sorbitol scaffold linked to octa-guanidine and to a peptide substrate of lysosomal cysteine protease, cathepsin B.





6570

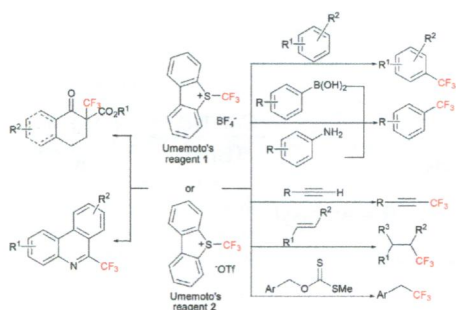
## Transannular Ring Contraction in Azacycles

Azabicycles construction: the transannular ring contraction with *N*-protected nucleophiles

Antonio Rizzo and Syuzanna R. Harutyunyan\*

Synthetic strategies are one of the most critical factors for the success of a synthetic campaign, but most importantly they are crucial for the economy and the efficiency of the sequence.

6580



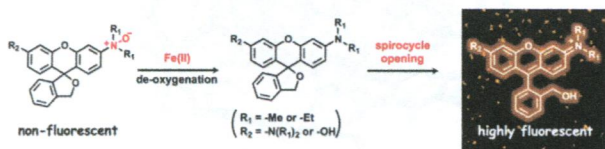
## Recent advances in trifluoromethylation of organic compounds using Umemoto's reagents

Cai Zhang

This review highlights recent developments in the direct introduction of a trifluoromethyl group into organic compounds with Umemoto's reagents.

## PAPERS

6590

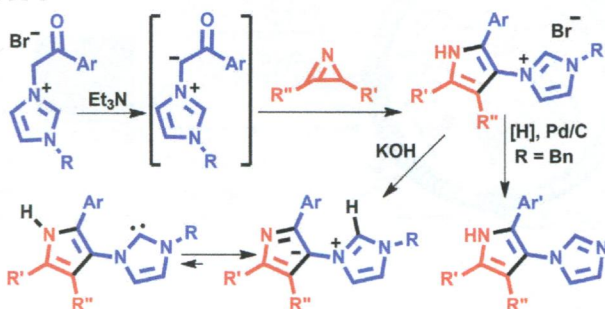


## A new class of high-contrast Fe(II) selective fluorescent probes based on spirocyclized scaffolds for visualization of intracellular labile iron delivered by transferrin

Masato Niwa, Tasuku Hirayama,\* Kensuke Okuda and Hideko Nagasawa\*

A new class of high-contrast Fe(II) selective fluorescent probes based on spirocyclized scaffolds were developed to visualize transferrin-delivered intracellular labile iron.

6598



## A simple approach to pyrrolylimidazole derivatives by azirine ring expansion with imidazolium ylides

Alexander F. Khlebnikov,\* Olesya A. Tomashenko, Liya D. Funt and Mikhail S. Novikov

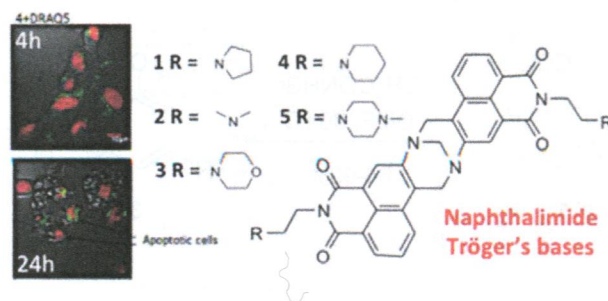
Versatile synthesis of 1-(1*H*-pyrrol-3-yl)-1*H*-imidazole derivatives by a domino reaction of 2*H*-azirines with 1-alkyl-3-phenacyl-1*H*-imidazolium bromides is reported.

6610

### Synthesis, photophysical and cytotoxicity evaluations of DNA targeting agents based on 3-amino-1,8-naphthalimide derived Tröger's bases

Samantha Murphy, Sandra A. Bright, Fergus E. Poynton, Thomas McCabe, Jonathan A. Kitchen, Emma B. Veale,\* D. Clive Williams\* and Thorfinnur Gunnlaugsson\*

The synthesis, spectroscopic and biological evaluation of five fluorescent Tröger's bases is described. These were shown to bind to DNA, being rapidly taken up into cancer cells and induce apoptosis after 4–24 hours.

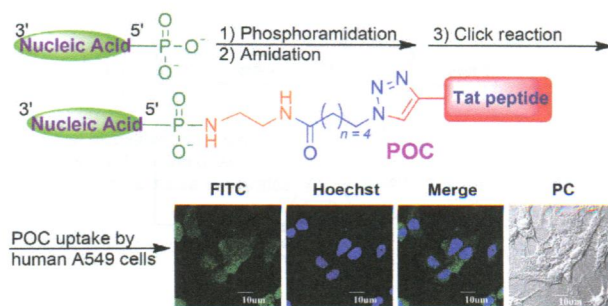


6624

### Azide–alkyne cycloaddition for universal post-synthetic modifications of nucleic acids and effective synthesis of bioactive nucleic acid conjugates

Yu-Chih Su, Yu-Lun Lo, Chi-Ching Hwang, Li-Fang Wang, Min Hui Wu, Eng-Chi Wang, Yun-Ming Wang and Tzu-Pin Wang\*

We have developed a universal approach for post-synthetic modifications of DNA/RNA by harnessing versatile phosphoramidation and powerful azide–alkyne cycloaddition reactions.

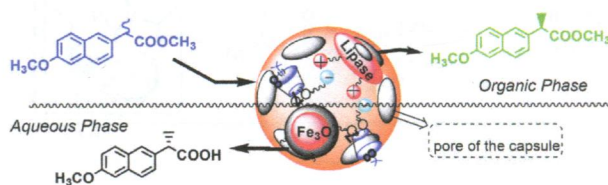


6634

### Enhanced catalysis and enantioselective resolution of racemic naproxen methyl ester by lipase encapsulated within iron oxide nanoparticles coated with calix[8]arene valeric acid complexes

Serkan Sayin, Enise Akoz and Mustafa Yilmaz\*

In this study, two types of nanoparticles have been used as additives for the encapsulation of *Candida rugosa* lipase via the sol–gel method.

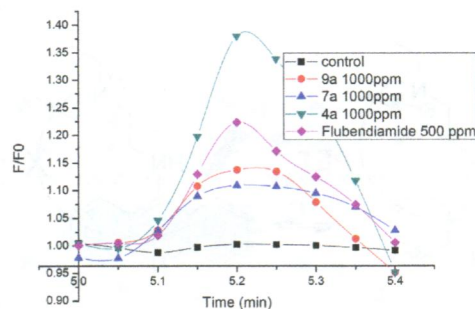


6643

### Novel phthalamides containing sulfiliminyll moieties and derivatives as potential ryanodine receptor modulators

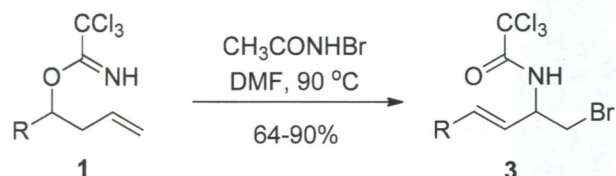
Sha Zhou, Tao Yan, Yuxin Li, Zhehui Jia, Baolei Wang, Yu Zhao, Yuanyuan Qiao, Lixia Xiong, Yongqiang Li and Zhengming Li\*

The present work firstly reported that the new diamides incorporating sulfiliminyll moieties are potential candidate structures for new ryanodine receptor modulators.





6653

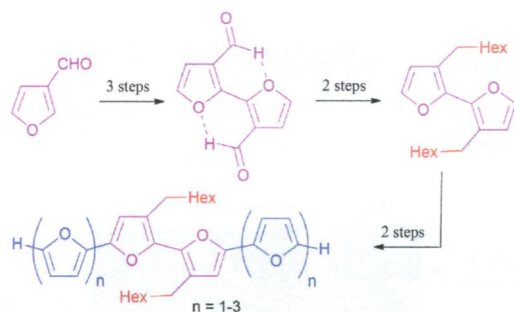


### *N*-Bromoacetamide-mediated domino cyclization and elimination of homoallylic trichloroacetimidates: a novel approach toward the synthesis of 1-bromo-2-amino-3-butene derivatives

Rui Zhu, Kai Yu and Zhenhua Gu\*

Allylic amides **3** were synthesized efficiently from homoallylic trichloroacetimidates **1** via domino bromo-cyclization and elimination reactions.

6661

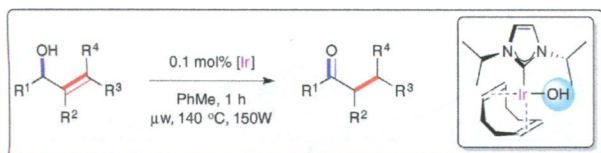


### Convenient access to readily soluble symmetrical dialkyl-substituted $\alpha$ -oligofurans

Edward E. Korshin,\* Gregory M. Leitus and Michael Bendikov

A combination of heteroatom directed lithiation/ $\text{CuCl}_2$ -induced homocoupling, Wittig olefination/ $\text{Pd}$ -catalyzed transfer hydrogenation followed by Suzuki–Miyaura or Stille cross-coupling enables convenient access to dialkyl-substituted  $\alpha$ -oligofurans of potential interest for organic electronics.

6672

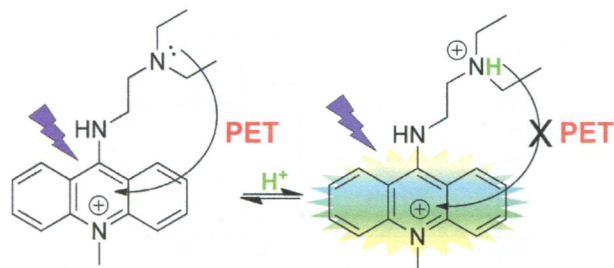


### Iridium(i) hydroxides in catalysis: rearrangement of allylic alcohols to ketones

David J. Nelson, José A. Fernández-Salas, Byron J. Truscott and Steven P. Nolan\*

The iridium(i) hydroxide complex  $[\text{Ir}(\text{OH})(\text{COD})(\text{l}^i\text{Pr})]$  has been shown to be a competent catalyst for the rearrangement of allylic alcohols to ketones.

6677



### An acridinium-based sensor as a fluorescent photoinduced electron transfer probe for proton detection modulated by anionic micelles

Stefano Basili, Tiziana Del Giacco,\* Fausto Elisei and Raimondo Germani

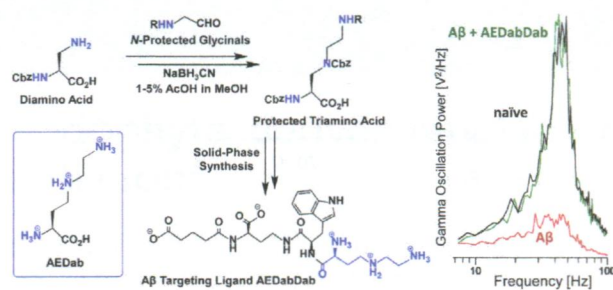
Photoinduced electron transfer has been demonstrated to be the quenching mechanism for the fluorescent pH sensor based on the 9-amino-10-methylacridinium chromophore. The presence of anionic micelles causes a significant increase in the detection sensitivity of pH.

6684

### Synthesis and evaluation of antineurotoxicity properties of an amyloid- $\beta$ peptide targeting ligand containing a triamino acid

D. Honcharenko,\* P. P. Bose, J. Maity, F. R. Kurudenkandy, A. Juneja, E. Flöistrup, H. Biverstål, J. Johansson, L. Nilsson, A. Fisahn and R. Strömberg\*

A new triamino acid enables synthesis of an amyloid- $\beta$  peptide ( $A\beta$ ) targeting ligand with additional  $A\beta$ -ligand interactions that gives protection towards  $A\beta$ -induced reduction of gamma oscillations in hippocampal slice preparation.

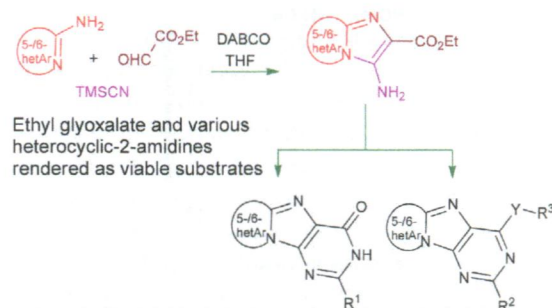


6694

### Desilylative activation of TMSCN in chemoselective Strecker–Ugi type reaction: functional fused imidazoles as building blocks as an entry route to annulated purines

Sankar K. Guchhait\* and Vikas Chaudhary

Nucleophilic activation of TMSCN as an isocyanide equivalent by DABCO–THF in the Strecker–Ugi reaction facilitates the synthesis of functional imidazoles which, as building blocks, afford access to C8–N9 annulated purines.

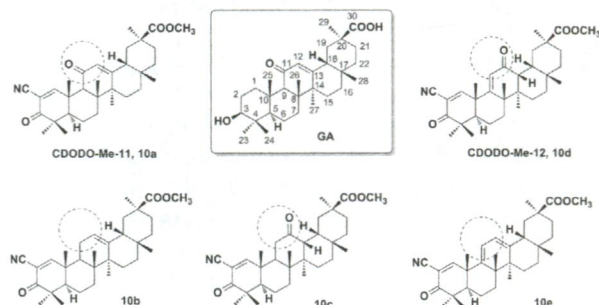


6706

### Synthesis of methyl 2-cyano-3,12-dioxo-18 $\beta$ -olean-1,9(11)-dien-30-oate analogues to determine the active groups for inhibiting cell growth and inducing apoptosis in leukemia cells

Xiaojing Li, Yuetong Wang, Yuan Gao, Lei Li, Xin Guo, Dan Liu, Yongkui Jing\* and Linxiang Zhao\*

A series of CDODO-Me-12 analogues were synthesized with improved ability to inhibit cell growth and induce apoptosis in HL-60 cells.

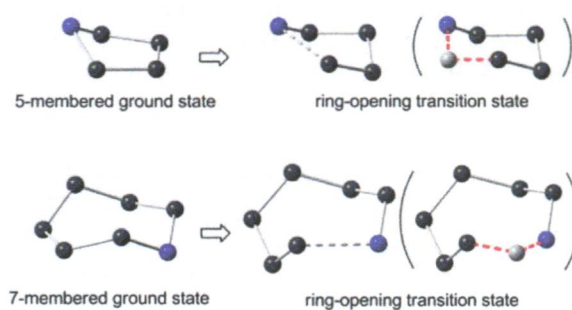


6717

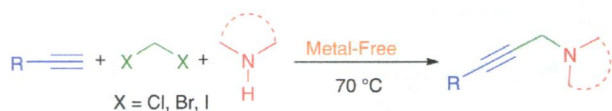
### $S_N2$ regioselectivity in the esterification of 5- and 7-membered azacycloalkane quaternary salts: a DFT study to reveal the transition state ring conformation prevailing over the ground state ring strain

Akihiro Kimura, Susumu Kawauchi,\* Takuya Yamamoto and Yasuyuki Tezuka\*

$S_N2$  regioselectivity in 5- and 7-membered azacycloalkanes quaternary salts is directed by the transition state ring conformation.



6725

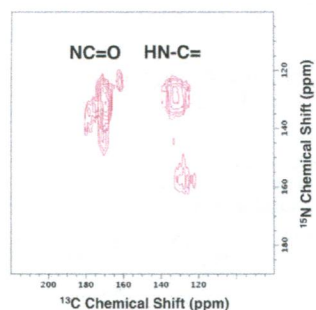


### Catalyst-free activation of methylene chloride and alkynes by amines in a three-component coupling reaction to synthesize propargylamines

Vikas S. Rawat, Thulasiram Bathini, S. Govardan and Bojja Sreedhar\*

Propargylamines are synthesized *via* metal-free activation of the C–halogen bond of dihalomethanes and the C–H bond of terminal alkynes in a three-component coupling without catalyst or additional base and under mild reaction conditions.

6730

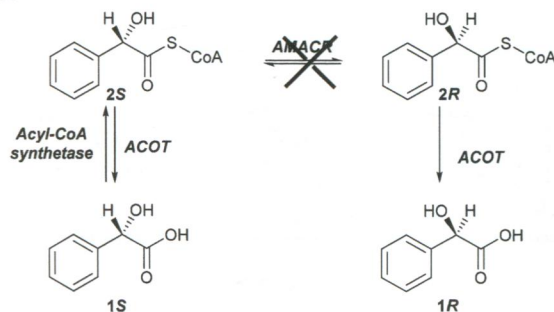


### Demonstration of a common indole-based aromatic core in natural and synthetic eumelanins by solid-state NMR

Subhasish Chatterjee,\* Rafael Prados-Rosales, Sindy Tan, Boris Itin, Arturo Casadevall and Ruth E. Stark\*

Comparing natural and synthetic eumelanin pigment structures: high-field 2D solid-state NMR reveals a common indole-based aromatic core for ubiquitous protective pigments that inspire engineered materials.

6737



### A study on the chiral inversion of mandelic acid in humans

Maksims Yevglevskis, Catherine R. Bowskill, Chloe C. Y. Chan, Justin H.-J. Heng, Michael D. Threadgill, Timothy J. Woodman and Matthew D. Lloyd\*

Mandelic acid **1** undergoes uni-directional chiral inversion in mammalian cells by a separate pathway to that of Ibuprofen **3**.