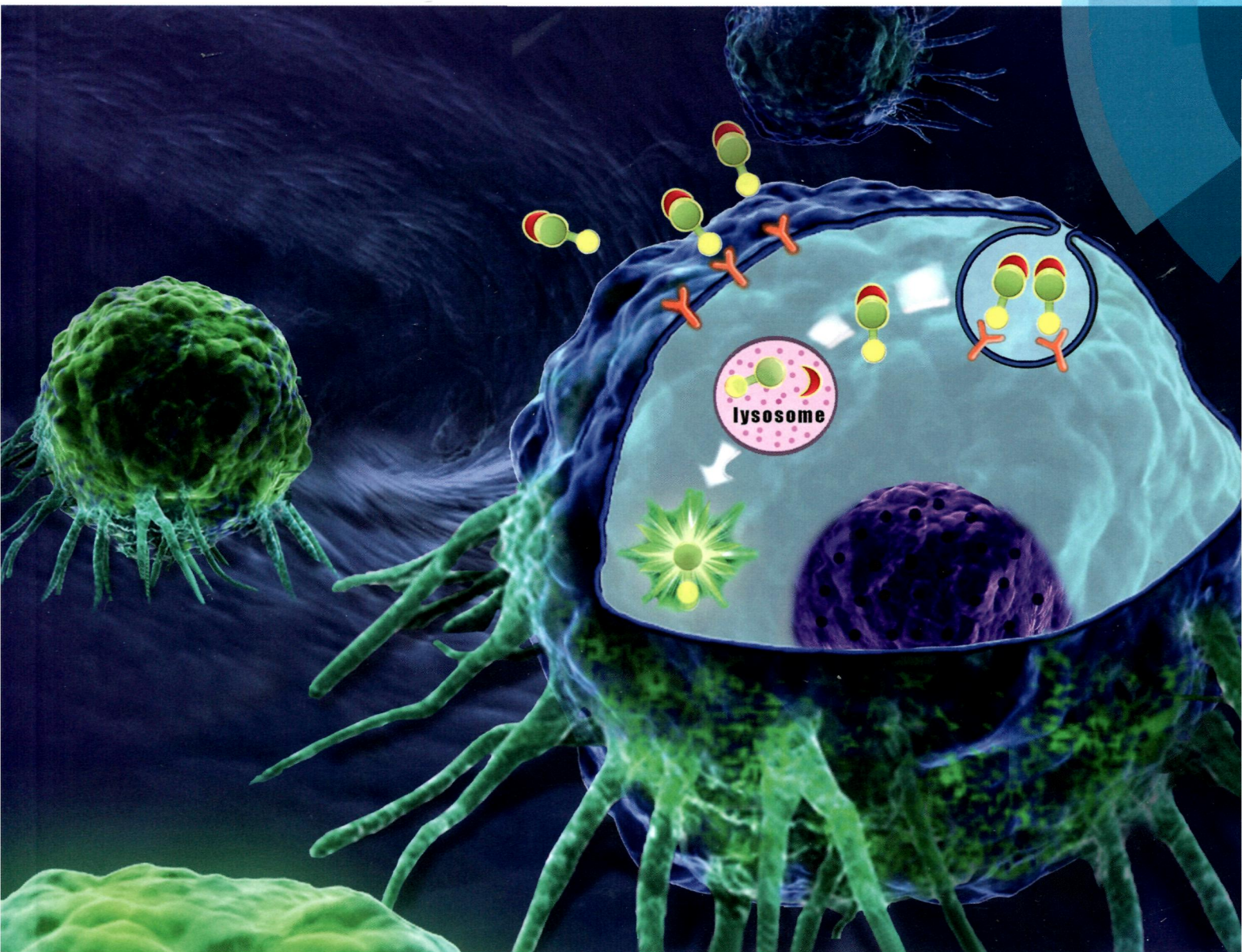


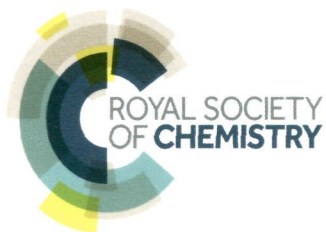
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# Organic & Biomolecular Chemistry

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ISSN 1477-0520



PAPER

Weiqliang Huang, Wenjie Wu, Zhangyong Hong *et al.*  
An intracellularly activatable, fluorogenic probe for cancer imaging

# Organic & Biomolecular Chemistry

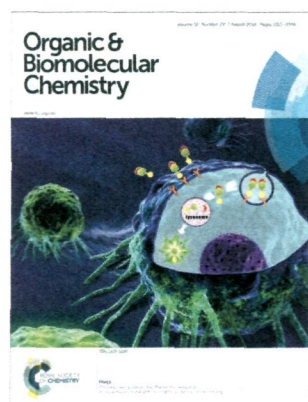
An international journal of synthetic, physical and biomolecular organic chemistry

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## IN THIS ISSUE

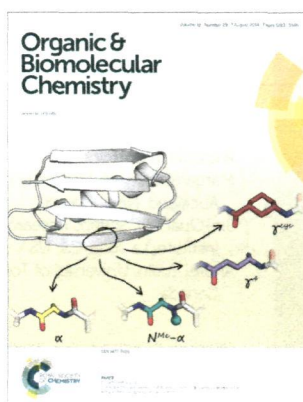
ISSN 1477-0520 CODEN OBCRAK 12(29) 5313-5546 (2014)



### Cover

See Weiqiang Huang, Wenjie Wu, Zhangyong Hong *et al.*, pp. 5365–5374.

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### Inside cover

See W. Seth Horne *et al.*, pp. 5375–5381.

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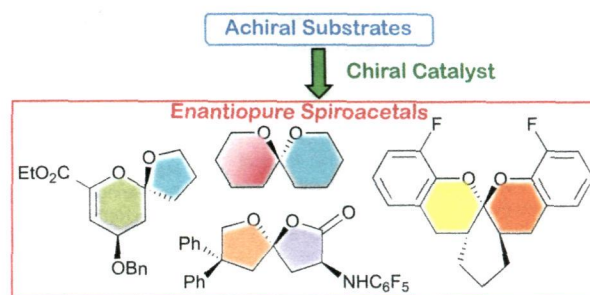
## PERSPECTIVE

5324

### Enantioselective synthesis of spiroacetals: the conquest of a long-sought goal in asymmetric catalysis

Lara Cala, Francisco J. Fañanás\* and Félix Rodríguez\*

This perspective article summarizes the few and recently reported methods on catalytic asymmetric synthesis of spiroacetal derivatives from achiral substrates.



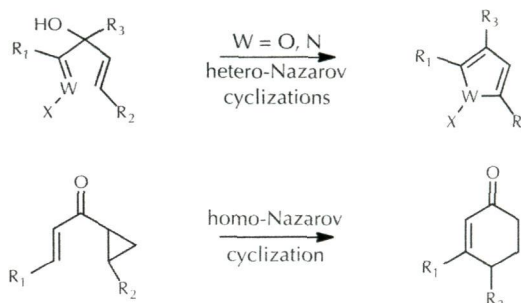
## REVIEW

5331

### Nazarov-like cyclization reactions

Martin J. Di Grandi

This review discusses novel Nazarov cyclization variations and their application to the synthesis of complex molecules.



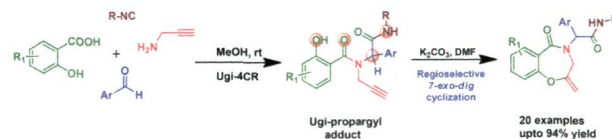
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Центральная научная библиотека  
Уральского отделения  
Российской академии наук (ЦНБ УрО РАН)

5346

### Base mediated 7-*exo-dig* intramolecular cyclization of Ugi–propargyl precursors: a highly efficient and regioselective synthetic approach toward diverse 1,4-benzoxazepine-5(2*H*)-ones

Shashi Pandey, S. Vinod Kumar, Ruchir Kant and Prem M. S. Chauhan\*

A metal-free facile and efficient two-step synthetic protocol for the preparation of 1,4-benzoxazepine-5(2*H*)-one derivatives has been developed.

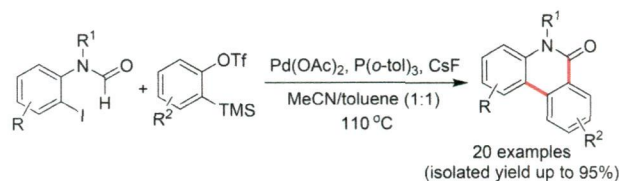


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### Palladium-catalyzed annulation of benzynes with *N*-substituted-*N*-(2-halophenyl)formamides: synthesis of phenanthridinones

Yuan Yang, Hui Huang, Lijun Wu and Yun liang\*

Palladium-catalyzed annulation of benzynes with *N*-(2-halophenyl)formamides afforded phenanthridinones *via* tandem C–C bond formation.

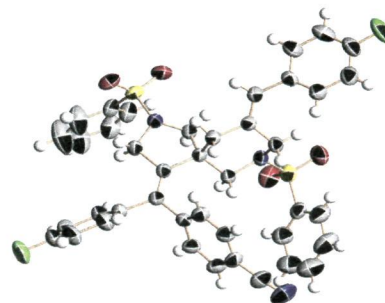


5356

### One-step synthesis of diazaspiro[4.5]decane scaffolds with exocyclic double bonds

Lidong Li, Qiong Hu, Pingping Zhou, Haifeng Xie, Xiaorong Zhang, Hao Zhang, Yadong Hu, Fei Yin and Yimin Hu\*

Unactivated yne-en-yne reacted with a range of substituted aryl halides in the presence of Pd(OAc)<sub>2</sub>–PPh<sub>3</sub> to afford diazaspiro[4.5]decane with exocyclic double bonds.

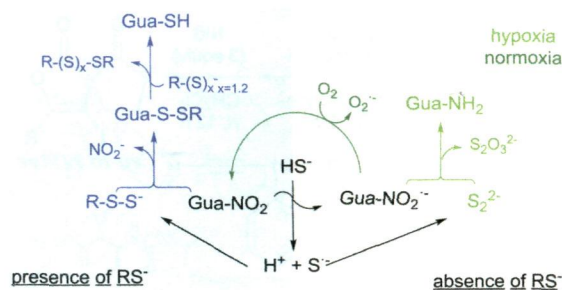


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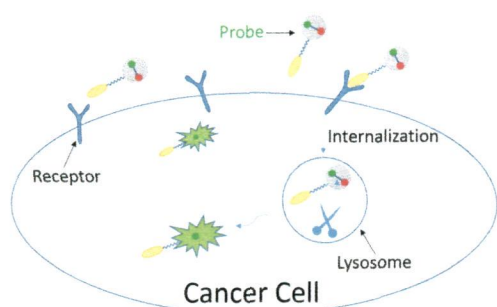
### Electrophilic sulfhydration of 8-nitro-cGMP involves sulfane sulfur

V. Terzić, D. Padovani, V. Balland, I. Artaud and E. Galardon\*

The complex chemistry taking place between the messenger 8-nitro-cGMP and the gaseous transmitter H<sub>2</sub>S is governed by dioxygen and thiols.



5365

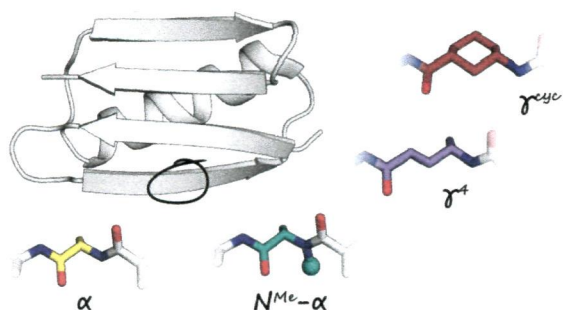


### An intracellularly activatable, fluorogenic probe for cancer imaging

Ruisong Tian, Mingjie Li, Jin Wang, Min Yu, Xiuqi Kong, Yupeng Feng, Zeming Chen, Yuxi Li, Weiqiang Huang,\* Wenjie Wu\* and Zhangyong Hong\*

A newly designed, dual-functional probe based on intracellular activation has been successfully developed for the detection of cancer cells.

5375

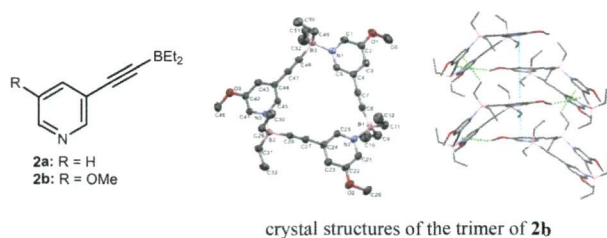


### Comparison of backbone modification in protein $\beta$ -sheets by $\alpha \rightarrow \gamma$ residue replacement and $\alpha$ -residue methylation

George A. Lengyel, Zachary E. Reinert, Brian D. Griffith and W. Seth Horne\*

Systematic backbone alteration of sheet secondary structure in a small protein yields unnatural mimics with native-like tertiary folding behavior.

5382

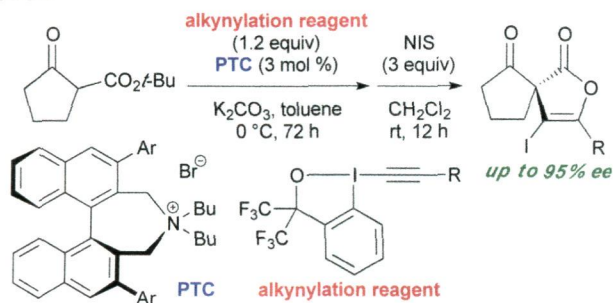


### The structure of 3-(diethylborylethynyl)pyridine: a nonplanarly arranged cyclic trimer

Shigeharu Wakabayashi,\* Mitsumi Kuse, Aimi Kida, Seiji Komeda, Kazuyuki Tatsumi and Yoshikazu Sugihara

The cyclic trimer of 3-(diethylborylethynyl)pyridine is conformationally flexible enough to be affected by the crystal packing.

5388



### Efficient asymmetric synthesis of spiro-2(3H)-furanones via phase-transfer-catalyzed alkylation

Xiangfei Wu, Seiji Shirakawa and Keiji Maruoka\*

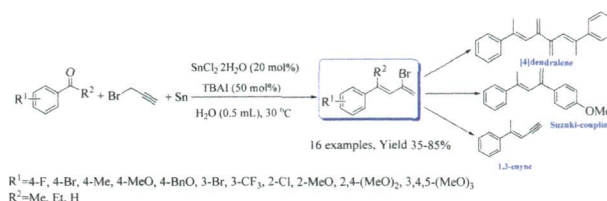
Efficient asymmetric synthesis of spiro-2(3H)-furanones was achieved via chiral phase-transfer-catalyzed alkylation.

5395

### The metal tin promoted cascade reaction of ketones in aqueous media for the construction of 2-bromo-4-aryl-1,3-pentadiene

Lingyan Liu,\* Yan Zhang, Hua Zhang, Kaimeng Huang, Bo-xin Gao, Min Zou, Xin Zhou, Hongkai Wang and Jing Li\*

A novel Barbier-type allenylation cascade reaction of carbonyl compounds promoted by tin was discovered, and afforded a new, highly functionalized 1,3-pentadiene.

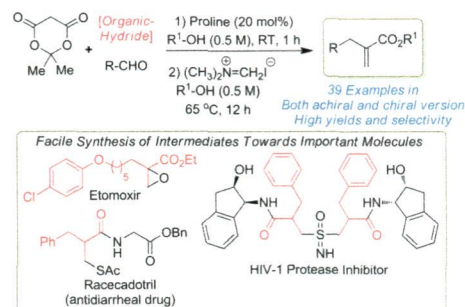


5400

### High-yielding sequential one-pot synthesis of chiral and achiral $\alpha$ -substituted acrylates via a metal-free reductive coupling reaction

Dhevalapally B. Ramachary,\* Chintalapudi Venkaiah and Y. Vijayendar Reddy

A variety of chiral and achiral  $\alpha$ -substituted acrylates were furnished in very good yields with excellent selectivity by using an organocatalytic reductive coupling reaction (TCRA) followed by an Eschenmoser methylenation.

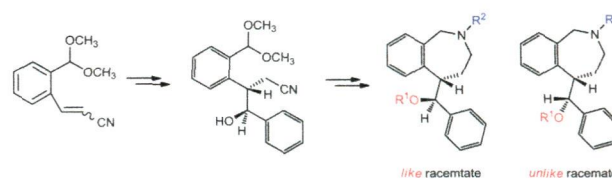


5407

### Synthesis and pharmacological evaluation of *like*- and *unlike*-configured tetrahydro-2-benzazepines with the $\alpha$ -substituted benzyl moiety in the 5-position

Peer Hasebein, Bastian Frehland, Kirstin Lehmkühl, Roland Fröhlich, Dirk Schepmann and Bernhard Wünsch\*

5-Substituted tetrahydro-2-benzazepines were prepared and the relationship between the structure, in particular the stereochemistry, and the  $\sigma_1$  affinity was analyzed.

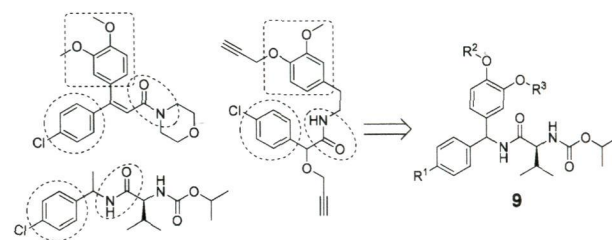


5412

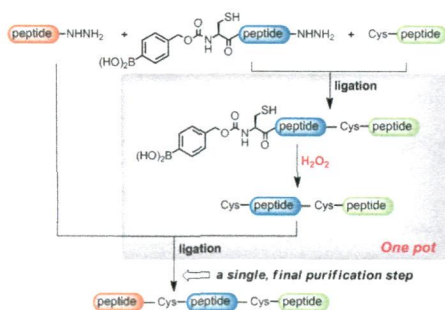
### Design, synthesis, and fungicidal activity of novel carboxylic acid amides represented by *N*-benzhydryl valinamide carbamates

Xiu-Jiang Du, Qiang Bian,\* Hong-Xue Wang, Shu-Jing Yu, Jun-Jie Kou, Zhi-Peng Wang, Zheng-Ming Li and Wei-Guang Zhao\*

A series of valinamide carbamate derivatives were designed and synthesized by introducing substituted aromatic rings into valinamide carbamate leads. Bioassays showed that some title compounds exhibited very good fungicidal activity.



5435

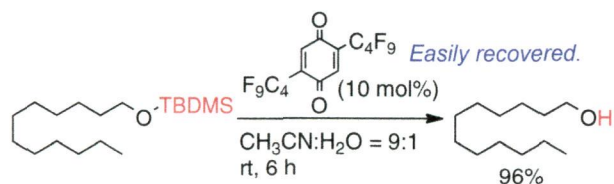


### One-pot native chemical ligation of peptide hydrazides enables total synthesis of modified histones

Jiabin Li, Yuanyuan Li, Qiaoqiao He, Yiming Li,\*  
Haitao Li and Lei Liu\*

One of the rising demands in the field of protein chemical synthesis is the development of facile strategies that yield the protein in workable quantities and homogeneity, with fewer handling steps.

5442

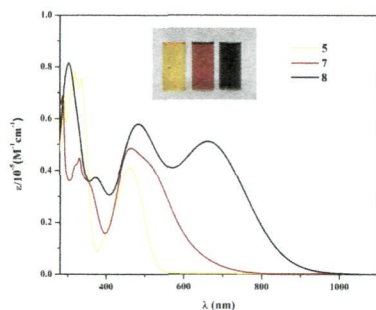


### Synthesis and properties of fluoruous benzoquinones and their application in deprotection of silyl ethers

Hiroshi Matsubara,\* Takahiko Maegawa, Yasuaki Kita,  
Takato Yokoji and Akihiro Nomoto

1,4-Benzoquinone derivatives bearing perfluoroalkyl groups were prepared and used as a recyclable catalyst in the selective desilylation of silyl ethers.

5448

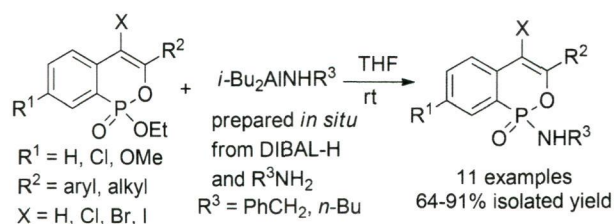


### Tuning of the HOMO–LUMO gap of donor-substituted symmetrical and unsymmetrical benzothiadiazoles

Rajneesh Misra\* and Prabhat Gautam

This article reports the design and synthesis of donor-substituted symmetrical and unsymmetrical benzothiadiazoles (BTDs) **5–12** of type D– $\pi$ –A–D, D<sub>1</sub>– $\pi$ –A–D<sub>2</sub>, D<sub>1</sub>–A<sub>1</sub>–A<sub>2</sub>–D<sub>2</sub>, D–A<sub>1</sub>–A<sub>2</sub>–D and D–A<sub>1</sub>–A<sub>2</sub>–A<sub>1</sub>–D by Ullmann, Suzuki and cycloaddition–retroelectrocyclization reactions.

5458



### Synthesis of phosphaisocoumarin amidates via DIBAL-H-mediated selective amidation of phosphaisocoumarin esters

Yu-Juan Guo, Pei-Jiang Chen, Bo Wang and Ai-Yun Peng\*

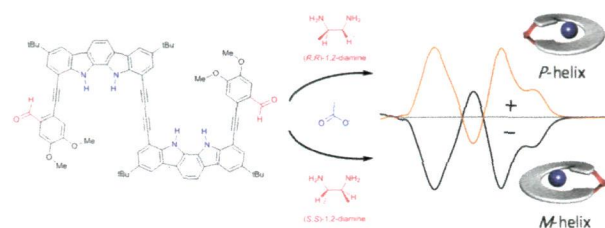
A series of phosphaisocoumarin amidates were synthesized *via* DIBAL-H-mediated selective amidation of phosphaisocoumarin esters in good to excellent yields. In each case, the phostone ring was intact and only the exocyclic ethoxy group was amidated.

5464

### An indolocarbazole dimer as a new stereodynamic probe for chiral 1,2-diamines

Hae-Geun Jeon, Min Jun Kim and Kyu-Sung Jeong\*

An indolocarbazole dimer functions as a new stereodynamic probe determining the absolute configurations of chiral 1,2-diamines.

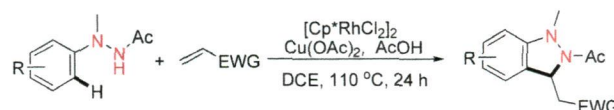


5469

### Synthesis of 2,3-dihydro-1*H*-indazoles by Rh(III)-catalyzed C–H cleavage of arylhydrazines

Jinzhong Yao, Ruokun Feng, Cong Lin, Zhanxiang Liu\* and Yuhong Zhang\*

A rhodium-catalyzed efficient method for the synthesis of 2,3-dihydro-1*H*-indazoles is described.

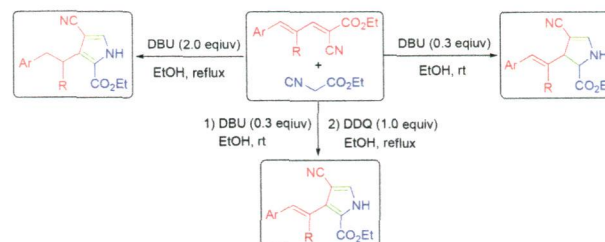


5477

### Divergent synthesis of 2,3-dihydro-1*H*-pyrroles, 3-alkyl-1*H*-pyrroles and 3-alkenyl-1*H*-pyrroles from 2,4-pentadienenitriles and isocyanides

Xiaoqing Xin, Xu Liu, Dingyuan Zhang, Rui Zhang, Yongjiu Liang,\* Fushe Han and Dewen Dong\*

A facile and divergent synthesis of 2,3-dihydro-1*H*-pyrroles, 3-alkyl-1*H*-pyrroles and 3-alkenyl-1*H*-pyrroles has been developed via a formal [2 + 3] annulation of 2,4-penta-dienenitriles and ethyl isocyanoacetate by the variation of reaction conditions.

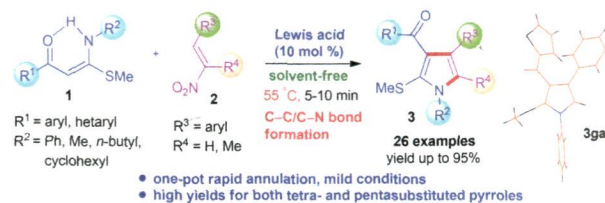


5494

### In(OTf)<sub>3</sub>-catalysed one-pot versatile pyrrole synthesis through domino annulation of α-oxoketene-*N,S*-acetals with nitroolefins

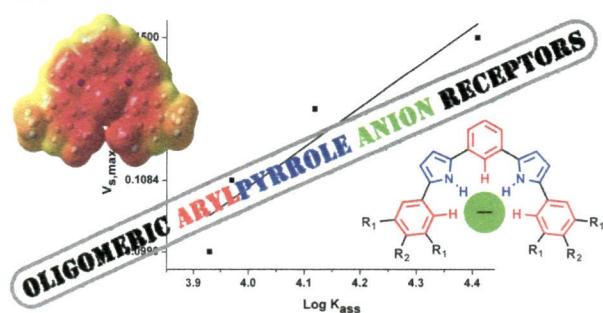
Abhijeet Srivastava, Gaurav Shukla, Anugula Nagaraju, Girijesh Kumar Verma, Keshav Raghuvanshi, Raymond C. F. Jones and Maya Shankar Singh\*

An operationally simple and efficient one-pot direct access to pyrroles has been achieved by annulation of α-oxoketene-*N,S*-acetals with β-nitrostyrenes catalyzed by In(OTf)<sub>3</sub> under solvent-free conditions.



- one-pot rapid annulation, mild conditions
- high yields for both tetra- and pentasubstituted pyrroles

5482

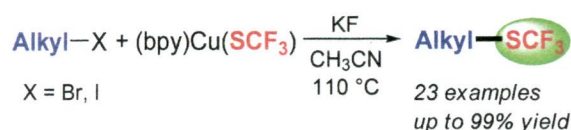


### Arylpyrrole oligomers as tunable anion receptors

Wim Van Rossom,\* Tatyana G. Terentyeva, Keitaro Sodeyama, Yoshitaka Matsushita, Yoshitaka Tateyama, Katsuhiko Ariga and Jonathan P. Hill\*

A novel class of oligomeric arylpyrrole receptors has been designed, prepared and analysed for their affinity towards anionic guests.

5500

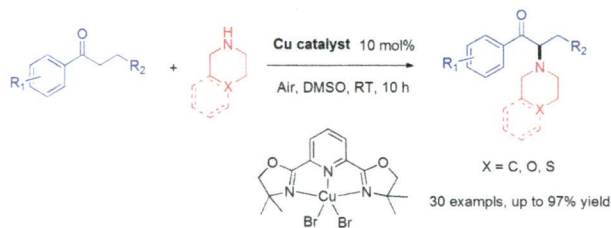


### Efficient C(sp<sup>3</sup><sub>alkyl</sub>)–SCF<sub>3</sub> bond formations via copper-mediated trifluoromethylthiolation of alkyl halides

Quanfu Lin, Li Chen, Yangjie Huang, Mingguang Rong, Yaofeng Yuan and Zhiqiang Weng\*

An efficient synthesis of alkyl trifluoromethyl sulfides via copper-mediated trifluoromethylthiolation of primary and secondary alkyl halides was described.

5509

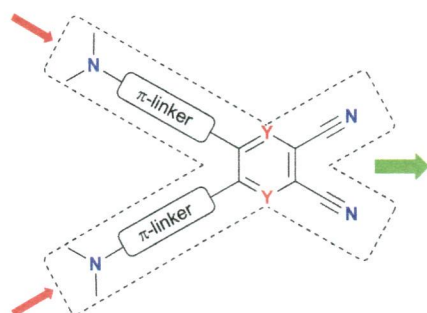


### Synthesis and characterization of bisoxazolines- and pybox-copper(II) complexes and their application in the coupling of $\alpha$ -carbonyls with functionalized amines

Wei-Guo Jia,\* Dan-Dan Li, Yuan-Chen Dai, Hui Zhang, Li-Qin Yan, En-Hong Sheng,\* Yun Wei, Xiao-Long Mu and Kuo-Wei Huang\*

[(Dm-Pybox)CuBr<sub>2</sub>] is efficient in catalyzing  $\alpha$ -amination of ketones and esters, which tolerates functionality on the carbonyl and amine reaction components.

5517



### Dicyanobenzene and dicyanopyrazine derived X-shaped charge-transfer chromophores: comparative and structure–property relationship study

L. Dokládlová, F. Bureš,\* W. Kuzník, I. V. Kityk, A. Wojciechowski, T. Mikysek, N. Almonasy, M. Ramaiyan, Z. Padělková, J. Kulhánek and M. Ludwig

Structure–property relationships in X-shaped push–pull molecules with dicyanobenzene and dicyanopyrazine acceptors.

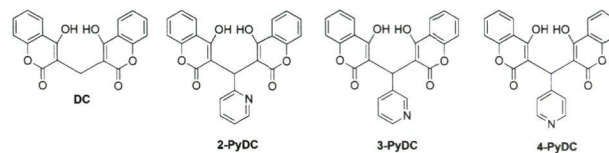


5326

### Synthesis, antibacterial activities, and theoretical studies of dicoumarols

Jing Li, Zheng Hou, Guang-Hui Chen, Fen Li, Ying Zhou, Xiao-Yan Xue, Zhou-Peng Li, Min Jia, Zi-Dan Zhang, Ming-Kai Li\* and Xiao-Xing Luo\*

In this work, we report the synthesis, evaluation of antibacterial activity and theoretical study of dicoumarols including DC, 2-PyDC, 3-PyDC and 4-PyDC.



5336

### Solid phase oxime ligations for the iterative synthesis of polypeptide conjugates

Isidore E. Decostaire, Dominique Lelièvre, Vincent Aucagne and Agnès F. Delmas\*

All on-resin! An efficient C-to-N iterative strategy for solid phase chemical ligations (SPCL).

