

OCTOBER 3, 2014

VOLUME 79 ISSUE 19

JOCEAH 79(19) 8937–9440 (2014)

ISSN 0022-3263

Registered in the U.S. Patent and Trademark Office

© 2014 by the American Chemical Society

**ON THE COVER:** Understanding the reactivity of complex molecular architectures is often a central challenge in complex molecule synthesis. Oftentimes, complex intermediates display reactivity and stability patterns that differ widely from simpler molecules containing their isolated functional groups. This issue is discussed in the context of hasubanan and acutumine alkaloid syntheses. See King and Herzon, p 8937. Professor Herzon is the recipient of the 2014 Arthur C. Cope Scholar Award.

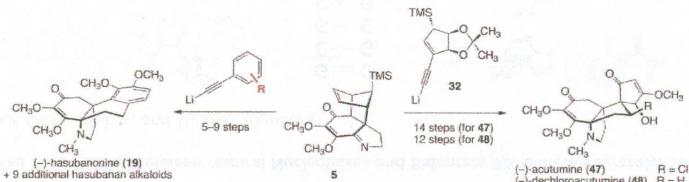
## Perspective

8937

[dx.doi.org/10.1021/jo501516x](http://dx.doi.org/10.1021/jo501516x)

### Substrate-Modified Functional Group Reactivity: Hasubanan and Acutumine Alkaloid Syntheses

Sandra M. King and Seth B. Herzon\*



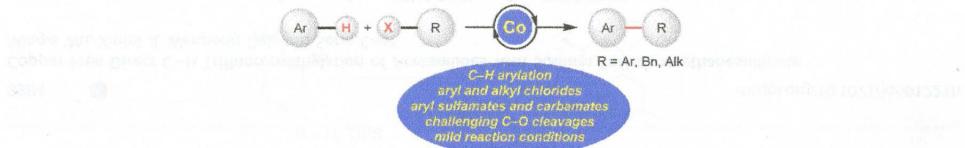
## JOC Synopsis

8948

[dx.doi.org/10.1021/jo501361k](http://dx.doi.org/10.1021/jo501361k)

### Cobalt-Catalyzed C–H Arylations, Benzylations, and Alkylations with Organic Electrophiles and Beyond

Lutz Ackermann\*



Volume 79, Number 19, October 3, 2014  
 ISSN 0022-3263 • DOI: 10.1021/jo501516x • Copyright © 2014 by the American Chemical Society  
 Printed in the United States of America

## Brief Communications

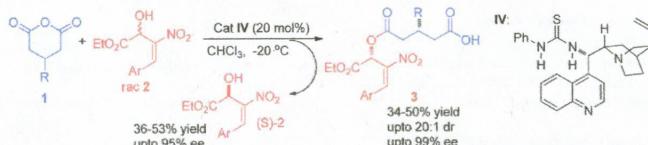
8955

S

[dx.doi.org/10.1021/jo501882q](https://doi.org/10.1021/jo501882q)

### Organocatalytic Kinetic Resolution of Racemic Secondary Nitroallylic Alcohols Combined with Simultaneous Desymmetrization of Prochiral Cyclic Anhydrides

Suparna Roy, Kan-Fu Chen, Ramani Gurubrahramam, and Kwunmin Chen\*



## Featured Articles

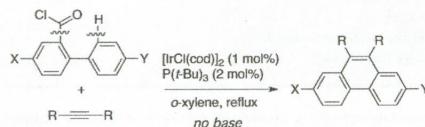
8960

S

[dx.doi.org/10.1021/jo501835u](https://doi.org/10.1021/jo501835u)

### Iridium-Catalyzed Annulative Coupling of 2-Arylbenzoyl Chlorides with Alkynes: Selective Formation of Phenanthrene Derivatives

Tomoya Nagata, Koji Hirano, Tetsuya Satoh, and Masahiro Miura\*



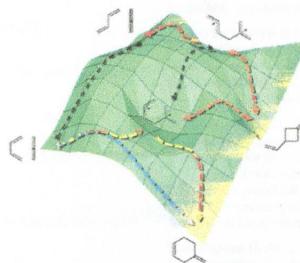
8968

S

[dx.doi.org/10.1021/jo502041f](https://doi.org/10.1021/jo502041f)

### Diels–Alder Reactions of Allene with Benzene and Butadiene: Concerted, Stepwise, and Ambimodal Transition States

Hung V. Pham and K. N. Houk\*



## Articles

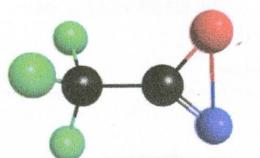
8977



dx.doi.org/10.1021/jo500664e

### Computational Rationalization for the Observed Ground-State Multiplicities of Fluorinated Acylnitrenes

Matthew P. Sherman and William S. Jenks\*



8984



dx.doi.org/10.1021/jo501221h

### Copper-Free Direct C–H Trifluoromethylation of Acetanilides with Sodium Trifluoromethanesulfinate

Mingxi Wu, Xinfei Ji, Wenpeng Dai, and Song Cao\*



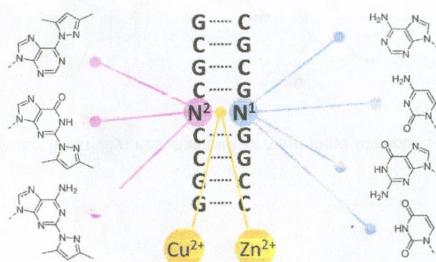
8990



dx.doi.org/10.1021/jo501237r

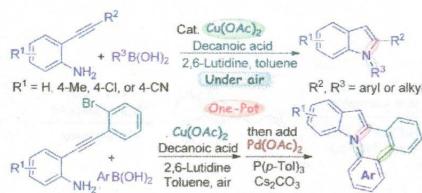
### Metal-Ion-Mediated Base Pairing between Natural Nucleobases and Bidentate 3,5-Dimethylpyrazolyl-Substituted Purine Ligands

Sharmin Taherpour, Oleg Golubev, and Tuomas Lönnberg\*



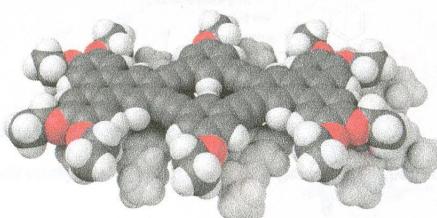
**One-Pot Approach to 1,2-Disubstituted Indoles via Cu(II)-Catalyzed Coupling/Cyclization under Aerobic Conditions and Its Application for the Synthesis of Polycyclic Indoles**

Jilong Gao, Yingying Shao, Jiaoyan Zhu, Jiaqi Zhu, Hui Mao, Xiaoxia Wang,\* and Xin Lv\*



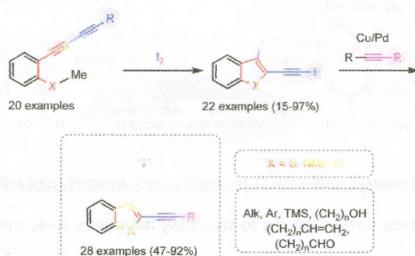
**Solution-Phase Dimerization of an Oblong Shape-Persistent Macrocycle**

Meng Chu, Ashley N. Scioneaux, and C. Scott Hartley\*



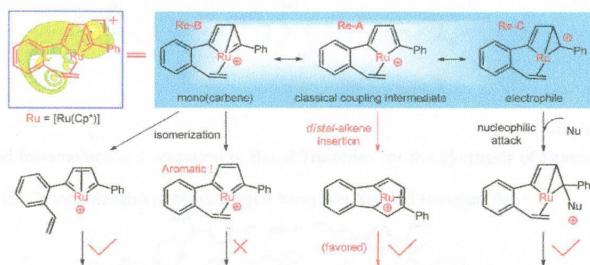
**Electrophilic Cyclization of Aryldiacetylenes in the Synthesis of Functionalized Enediynes Fused to a Heterocyclic Core**

N. A. Danilkina, A. E. Kulyashova, A. F. Khlebnikov, S. Bräse,\* and I. A. Balova\*



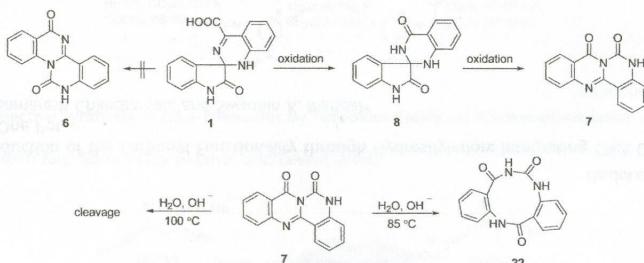
**Mechanistic Origins of Chemo- and Regioselectivity of Ru(II)-Catalyzed Reactions Involving *ortho*-Alkenylarylacetylene, Alkyne, and Methanol: The Crucial Role of a Chameleon-like Intermediate**

Yanfeng Dang, Shuanglin Qu, Yuan Tao, Chunyu Song, and Zhi-Xiang Wang\*



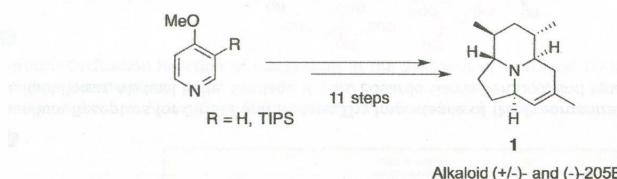
**Oxidative Ring Expansion of Spirocyclic Oxindole Derivatives**

Jan Bergman,\* Carl-Johan Arewång, and Per H. Svensson



**Total Synthesis of Alkaloid 205B**

Sergey V. Tsukanov and Daniel L. Comins\*



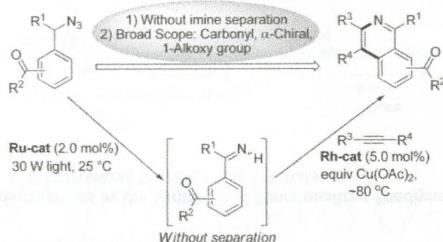
Theoretical Study To Explain How Chirality Is Stored and Evolves throughout the Radical Cascade Rearrangement of Enyne-allenes

Anouk Gaudel-Siri,\* Damien Campolo, Shovan Mondal, Malek Nechab, Didier Siri, and Michèle P. Bertrand



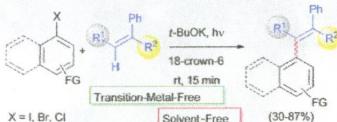
C–H Activation Guided by Aromatic N–H Ketimines: Synthesis of Functionalized Isoquinolines Using Benzyl Azides and Alkynes

Sreyaa Gupta, Junghoon Han, Yongjin Kim, Soon W. Lee, Young Ho Rhee,\* and Jaiwook Park\*



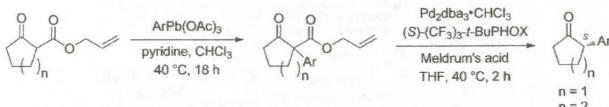
Room-Temperature and Transition-Metal-Free Mizoroki–Heck-type Reaction. Synthesis of E-Stilbenes by Photoinduced C–H Functionalization

Javier F. Guastavino, María E. Budén, and Roberto A. Rossi\*

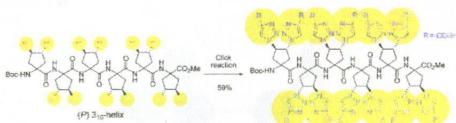


Catalytic Asymmetric Synthesis of Sterically Hindered Tertiary  $\alpha$ -Aryl Ketones

Robert Doran and Patrick J. Guiry\*

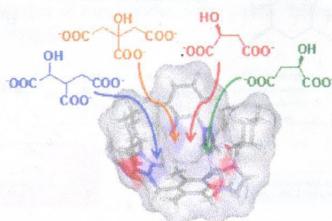


**Helical Peptide-Foldamers Having a Chiral Five-Membered Ring Amino Acid with Two Azido Functional Groups**  
 Makoto Oba, Hiroomi Takasaki, Naomi Kawabe, Mitsunobu Doi, Yosuke Demizu, Masaaki Kurihara, Hiromu Kawakubo, Masanobu Nagano, Hiroshi Suemune, and Masakazu Tanaka\*



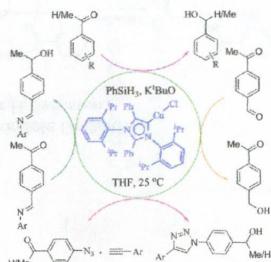
**Chiral Imidazolium Receptors for Citrate and Malate: The Importance of the Preorganization**

Enrico Faggi, Raúl Porcar, Michael Bolte, Santiago V. Luis, Eduardo García-Verdugo, and Ignacio Alfonso\*



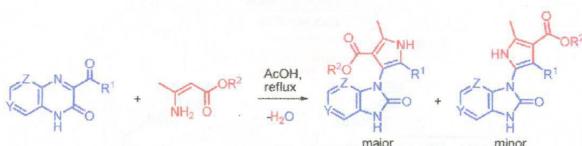
**Choselective Reduction of the Carbonyl Functionality through Hydrosilylation: Integrating Click Catalysis with Hydrosilylation in One Pot**

Sudipta Raha Roy, Samaresh Chandra Sau, and Swadhin K. Mandal\*



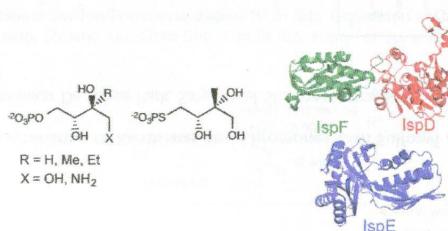
**Reaction for the Synthesis of Benzimidazol-2-ones, Imidazo[5,4-*b*]-, and Imidazo[4,5-*c*]pyridin-2-ones via the Rearrangement of Quinoxalin-2-ones and Their Aza Analogues When Exposed to Enamines**

Vakhid A. Mamedov,\* Nataliya A. Zhukova, Anastasiya I. Zamaletdinova, Tat'yana N. Beschastnova, Milyausha S. Kadyrova, Il'dar Kh. Rizvanov, Victor V. Syakaev, and Shamil K. Latypov



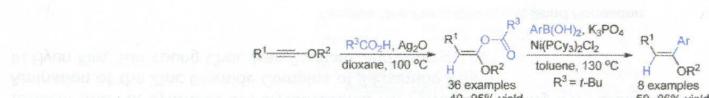
**Synthesis of Methyerythritol Phosphate Analogues and Their Evaluation as Alternate Substrates for IspDF and IspE from *Agrobacterium tumefaciens***

Sergiy G. Krasutsky, Marek Urbansky, Chad E. Davis, Christian Lherbet, Robert M. Coates,\* and C. Dale Poulter\*



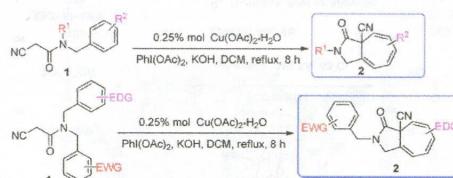
**Silver-Catalyzed Regio- and Stereoselective Addition of Carboxylic Acids to Ynol Ethers**

Jing Yin, Yihui Bai, Mengyi Mao, and Gangguo Zhu\*



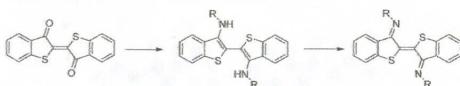
**In Situ-Generated Iodonium Ylides as Safe Carbene Precursors for the Chemoselective Intramolecular Buchner Reaction**

Shanyan Mo, Xinhao Li, and Jiaxi Xu\*

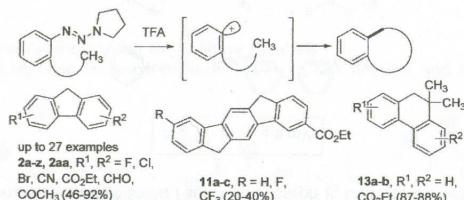


**Synthesis and Photophysics of Thioindigo Diimines and Related Compounds**

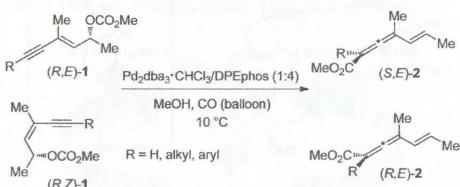
Geneviève Boice, Brian O. Patrick, Robert McDonald, Cornelia Bohne,\* and Robin Hicks\*

**Brönsted Acid-Mediated Intramolecular Cyclization of Biaryl Triazenes for the Synthesis of Fluorenes and 9,10-Dihydro-Phenanthrenes**

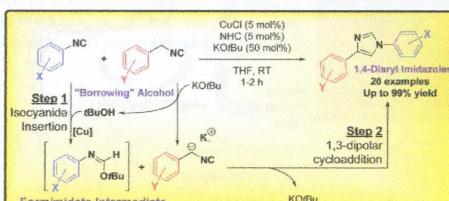
Lijun Xu, Weijun Yang, Lili Zhang, Maozhong Miao, Zhigen Yang, Xin Xu, and Hongjun Ren\*

**Regio- and Stereoselective Synthesis of 2,3,5-Trienoates by Palladium-Catalyzed Alkoxycarbonylation of Conjugated Enyne Carbonates**

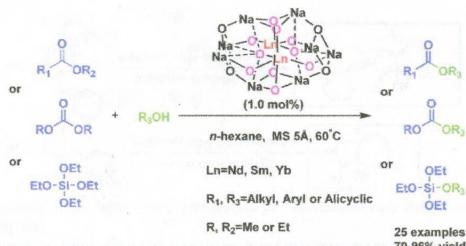
Ezgi Şule Karagöz, Melih Kuş, Gürkan Eray Akpinar, and Levent Artok\*

**Tandem Insertion–Cyclization Reaction of Isocyanides in the Synthesis of 1,4-Diaryl-1*H*-imidazoles: Presence of N-Arylformimidate Intermediate**

Benjamin Pooi, Jeongbin Lee, Kyujin Choi, Hajime Hirao,\* and Soon Hyek Hong\*

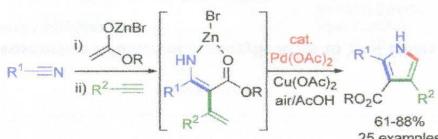


**Heterobimetallic Dinuclear Lanthanide Alkoxide Complexes as Acid–Base Difunctional Catalysts for Transesterification**  
 Ruijie Zeng, Hongting Sheng,\* Yongcang Zhang, Yan Feng,\* Zhi Chen, Junfeng Wang, Man Chen, Manzhou Zhu, and  
 Qingxiang Guo



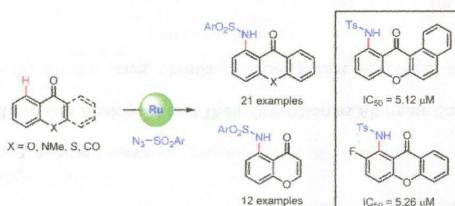
**Tandem One-Pot Synthesis of Polysubstituted NH-Pyrroles Involving the Palladium-Catalyzed Intramolecular Oxidative Amination of the Zinc Bromide Complex of  $\beta$ -Enamino Esters**  
 Ju Hyun Kim, Suh Young Choi, Jean Bouffard, and Sang-gi Lee\*

**Tandem One-Pot C–C/C–C/C–N Bond Formation**



**Ru(II)-Catalyzed Selective C–H Amination of Xanthones and Chromones with Sulfonyl Azides: Synthesis and Anticancer Evaluation**

Youngmi Shin, Sangil Han, Umasankar De, Jihye Park, Satyasheel Sharma, Neeraj Kumar Mishra, Eui-Kyung Lee, Youngil Lee, Hyung Sik Kim, and In Su Kim\*



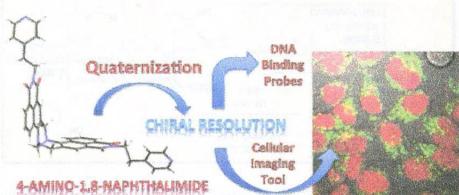
9272

S

[dx.doi.org/10.1021/jo501711g](https://doi.org/10.1021/jo501711g)

**Supramolecular Approach to Enantioselective DNA Recognition Using Enantiomerically Resolved Cationic 4-Amino-1,8-naphthalimide-Based Tröger's Bases**

Swagata Banerjee, Sandra A. Bright, Jayden A. Smith, Jeremy Burgeat, Miguel Martinez-Calvo, D. Clive Williams, John M. Kelly,\* and Thorfinnur Gunnlaugsson\*



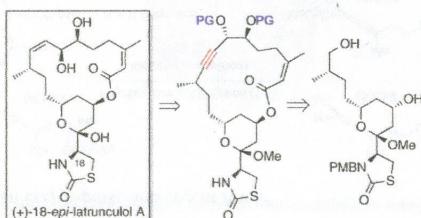
9284

S

[dx.doi.org/10.1021/jo501733m](https://doi.org/10.1021/jo501733m)

**Total Synthesis of (+)-18-*epi*-Latrunculol A: Development of a Synthetic Route**

Brett D. Williams and Amos B. Smith III\*



9297

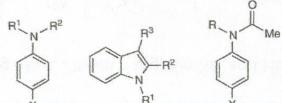
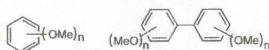
S

[dx.doi.org/10.1021/jo501761c](https://doi.org/10.1021/jo501761c)

**Accurate Oxidation Potentials of 40 Benzene and Biphenyl Derivatives with Heteroatom Substituents**

Pu Luo, Adam M. Feinberg, Gonzalo Guirado,\* Samir Farid,\* and Joseph P. Dinnocenzo\*

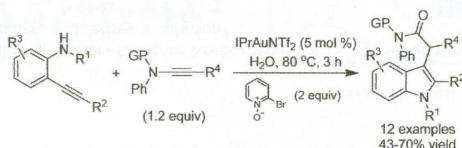
$E_{\text{ox}}^{\text{CH}_3\text{CN}}$  to  $< \pm 6$  mV



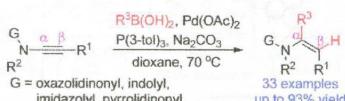
**Organocatalytic Asymmetric Inverse-Electron-Demand 1,3-Dipolar Cycloaddition of *N,N'*-Cyclic Azomethine Imines**  
Ren-Yi Zhu, Cong-Shuai Wang, Jian Zheng, Feng Shi,\* and Shu-Jiang Tu



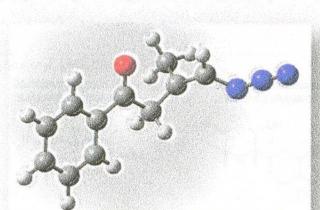
**Gold-Catalyzed Tandem Cycloisomerization/Functionalization of in Situ Generated  $\alpha$ -Oxo Gold Carbenes in Water**  
Cang-Hai Shen, Long Li, Wei Zhang, Shuang Liu, Chao Shu, Yun-Er Xie, Yong-Fei Yu, and Long-Wu Ye\*



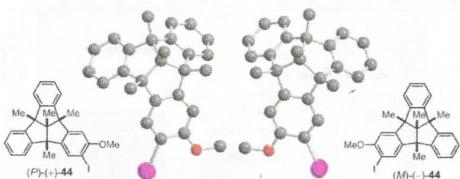
**Preparation of (*Z*)- $\alpha,\beta$ -Disubstituted Enamides via Palladium-Catalyzed Addition of Boronic Acids to Ynamides**  
Yuanfa Yang, Lina Wang, Fang Zhang, and Gangguo Zhu\*



**Triplet Sensitized Photolysis of a Vinyl Azide: Direct Detection of a Triplet Vinyl Azide and Nitrene**  
Sridhar Rajam, Abhijit V. Jadhav, Qian Li, Sujan K. Sarkar, Pradeep N. D. Singh, Ahleah Rohr, Tamara C. S. Pace, Rui Li, Jeanette A. Krause, Cornelia Bohne, Bruce S. Ault, and Anna D. Gudmundsdottir\*

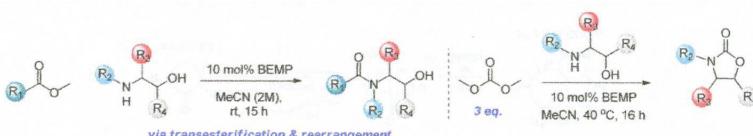


**Regiocontrolled Synthesis and Optical Resolution of Mono-, Di-, and Trisubstituted Tribenzotriquinacene Derivatives: Key Building Blocks for Further Assembly into Molecular Squares and Cubes**  
 Wen-Rong Xu, Hak-Fun Chow,\* Xiao-Ping Cao,\* and Dietmar Kuck\*



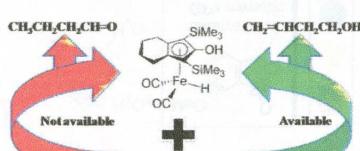
**Amidation of Esters with Amino Alcohols Using Organobase Catalysis**

Nicola Caldwell, Peter S. Campbell, Craig Jamieson,\* Frances Potjewyd, Iain Simpson, and Allan J. B. Watson



**High Chemoselectivity of an Advanced Iron Catalyst for the Hydrogenation of Aldehydes with Isolated C=C Bond: A Computational Study**

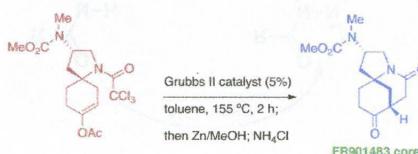
Xi Lu, Runjiao Cheng, Nicholas Turner, Qian Liu, Mingtao Zhang,\* and Xiaomin Sun\*



## Notes

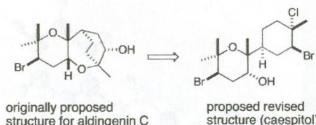
**Atom Transfer Radical Cyclization of Trichloroacetamides to Electron-Rich Acceptors Using Grubbs' Catalysts: Synthesis of the Tricyclic Framework of FR901483**

Faïza Diaba,\* Agustín Martínez-Laporta, and Josep Bonjoch\*

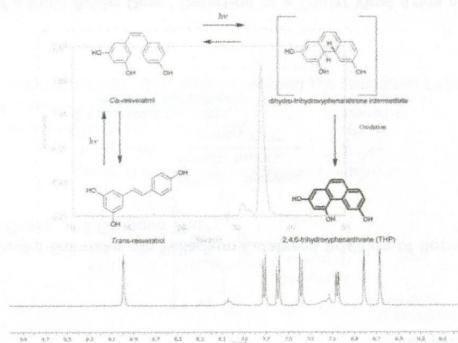


**Synthesis and Structural Revision of a Brominated Sesquiterpenoid, Aldingenin C**

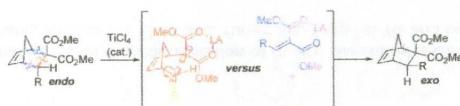
Shunya Takahashi,\* Masayuki Yasuda, Takemichi Nakamura, Ken Hatano, Koji Matsuoka, and Hiroyuki Koshino\*

**Isolation and Identification of 2,4,6-Trihydroxyphenanthrene as a Byproduct of *trans*-Resveratrol Photochemical Isomerization and Electrocyclization**

Antonio Franciosi,\* Alberto Boffi, Claudio Villani, Lucio Manzi, Maria D'Erme, Alberto Macone, and Luciana Mosca

**Experiments Probing the Viability of Donor–Acceptor Norbornenes for (5 + 2)-Annulation**

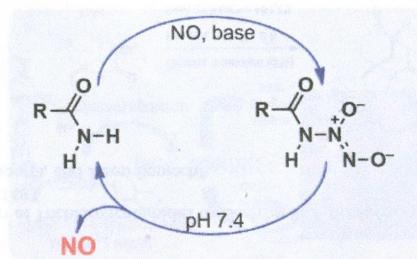
Morgan M. Walker, C. Guy Goodman, and Jeffrey S. Johnson\*



**Direct Reaction of Amides with Nitric Oxide To Form Diazeniumdiolates**

Ryan J. Holland,\* John R. Klose, Jeffrey R. Deschamps, Zhao Cao, Larry K. Keefer, and Joseph E. Saavedra

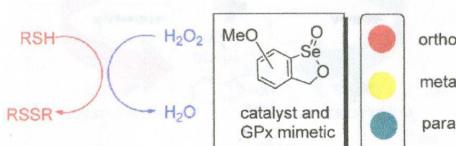
dx.doi.org/10.1021/jo501670e



dx.doi.org/10.1021/jo501689h

**Effects of Methoxy Substituents on the Glutathione Peroxidase-like Activity of Cyclic Seleninate Esters**

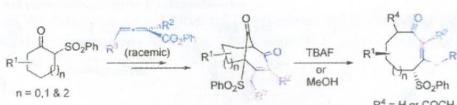
David J. Press, Nicole M. R. McNeil, Miranda Hambrook, and Thomas G. Back\*



dx.doi.org/10.1021/jo501700c

**Annulation Reactions of Allenyl Esters: An Approach to Bicyclic Diones and Medium-Sized Rings**

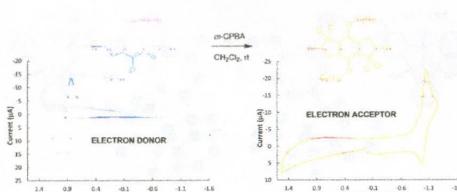
Bilal A. Bhat, Samantha L. Maki, Elijah J. St.Germain, Pradip Maity, and Salvatore D. Lepore\*



dx.doi.org/10.1021/jo5017585

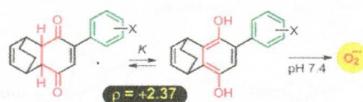
**Synthesis and Electronic Properties of Oxidized Benzo[1,2-*b*:4,5-*b'*]dithiophenes**

Ted M. Pappenfus,\* Daniel T. Seidenkranz, Matthew D. Lovander, Travis L. Beck, Brandon J. Karel, Katsu Ogawa, and Daron E. Janzen



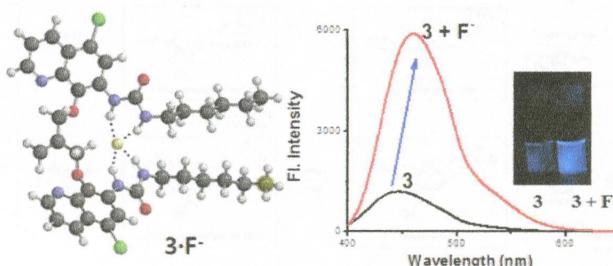
**Substituent Effects on Reactive Oxygen Species (ROS) Generation by Hydroquinones**  
Allimuthu T. Dharmaraja, Charu Jain, and Harinath Chakrapani\*

dx.doi.org/10.1021/jo501796z



**Bis-ureidoquinoline as a Selective Fluoride Anion Sensor through Hydrogen-Bond Interactions**  
Yunhee Jo, Nagesh Chidalla, and Dong-Gyu Cho\*

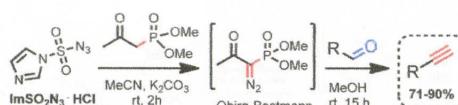
dx.doi.org/10.1021/jo501767g



dx.doi.org/10.1021/jo501803f

**In Situ Generation of the Ohira–Bestmann Reagent from Stable Sulfonyl Azide: Scalable Synthesis of Alkynes from Aldehydes**

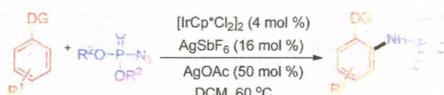
Tue Heesgaard Jepsen and Jesper Langgaard Kristensen\*



dx.doi.org/10.1021/jo5018052

**Iridium-Catalyzed Phosphoramidation of Arene C–H Bonds with Phosphoryl Azide**

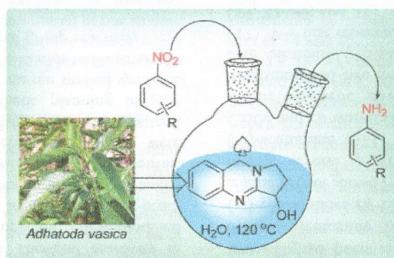
Changduo Pan, Ning Jin, Honglin Zhang, Jie Han, and Chengjian Zhu\*



DG = pyridinyl, pyrazoyl, quinolinyl

**Metal-Free Transfer Hydrogenation of Nitroarenes in Water with Vasicine: Revelation of Organocatalytic Facet of an Abundant Alkaloid**

Sushila Sharma, Manoranjan Kumar, Vishal Kumar, and Neeraj Kumar\*



Organocatalysis has emerged as a powerful tool for the synthesis of complex molecules. <sup>1–3</sup> In this context, the use of natural products as organocatalysts has been explored in various fields of organic chemistry. <sup>4–10</sup> Among them, alkaloids have received significant attention due to their unique properties and potential applications in pharmaceuticals, agrochemicals, and materials science. <sup>11–14</sup> Vasicine, an indole alkaloid, is one such compound that has been reported to exhibit various biological activities, including anti-inflammatory, <sup>15</sup> antidiabetic, <sup>16</sup> and antimicrobial properties. <sup>17</sup> It has also been shown to possess organocatalytic activity in the asymmetric synthesis of chiral molecules. <sup>18</sup> Despite these promising features, the use of vasicine in organic transformations is still limited. <sup>19</sup> In this work, we report the use of vasicine as an organocatalyst for the metal-free transfer hydrogenation of nitroarenes in water at 120 °C.

## INTRODUCTION

Nitroarenes are important organic compounds due to their unique properties and wide range of applications in various fields of organic chemistry. <sup>20–22</sup> They are often used as precursors for the synthesis of other functionalized molecules through various chemical reactions. <sup>23–25</sup> However, the conventional methods for the reduction of nitroarenes, such as the use of transition metals or strong reducing agents, often lead to side products and environmental issues. <sup>26–28</sup> Therefore, there is a need for developing more efficient and eco-friendly methods for the reduction of nitroarenes.

In recent years, the use of natural products as organocatalysts has gained significant interest due to their unique properties and potential applications in various fields of organic chemistry. <sup>29–31</sup> Among them, alkaloids have received significant attention due to their unique properties and potential applications in pharmaceuticals, agrochemicals, and materials science. <sup>32–34</sup> Vasicine, an indole alkaloid, is one such compound that has been reported to exhibit various biological activities, including anti-inflammatory, <sup>35</sup> antidiabetic, <sup>36</sup> and antimicrobial properties. <sup>37</sup> It has also been shown to possess organocatalytic activity in the asymmetric synthesis of chiral molecules. <sup>38</sup>

In this work, we report the use of vasicine as an organocatalyst for the metal-free transfer hydrogenation of nitroarenes in water at 120 °C. The results show that vasicine can effectively reduce nitroarenes to their corresponding aromatic amines without the use of any transition metals or strong reducing agents. This work provides a new perspective for the development of sustainable and eco-friendly methods for the reduction of nitroarenes.

\* Supporting Information available via online article.