Highlight Review

1554  Cu–Rh Redox Relay Catalysts for Synthesis of Azaheterocycles via C–H Functionalization

Shunsuke Chiba
doi:10.1246/cl.2012.1554

This Highlight Review described the Cu–Rh bimetallic redox relay catalytic system that enables efficient synthesis of highly substituted isoquinolines and their derivatives from readily available aryl ketoximes or α-arylvinyl azides with internal alkynes via C–H bond functionalization. A preliminary mechanistic investigation revealed that both of Cu and Rh catalysts are prerequisites to achieve the present process, and play their particular roles with synergistic cooperation during the multistep sequence.

Letter

1560  Novel 4-Trifluoromethylthiazole-5-carboxylic Acid as Acceptor in Photosensitized Dyes

Satoru Iwata,* Misa Aoyama, Satoshi Uchida, and Kiyoshi Tanaka*
doi:10.1246/cl.2012.1560

The novel photosensitized dyes having 4-trifluoromethylthiazole-5-carboxylic acid as an acceptor are synthesized. The dyes with this acceptor show high performance as the dye-sensitized solar cells. The trifluoromethyl group is assumed to act as a suppressor of the electron back-donation from the TiO$_2$ conduction band to the electrolyte and as an accelerator of the charge separation in the photoexcited state.

Electronic Supporting Information
1563 Observation of $^{47,49}$Ti NMR Spectra of TiCl$_4$/MgCl$_2$ Catalysts under an Ultrahigh Magnetic Field

Ryutar"o Ohashi, Masayoshi Saito, Takashi Fujita, Toshihito Nakai, Hiroaki Utsumi, Kenzo Deguchi, Masataka Tansho, and Tadashi Shimizu*  
doi:10.1246/cl.2012.1563

1566 Nickel-catalyzed Decarbonylative Polymerization of 5-Alkynylphthalimides: A New Methodology for the Preparation of Polyheterocycles

Nickel-catalyzed decarbonylative cycloaddition was developed, where 5-alkynylphthalimides reacted to afford a new type of polyisoquinolones. It was demonstrated for the first time that decarbonylative cycloaddition can be an elementary process of polycondensation for preparation of heterocyclic polymers.

Makoto Takeuchi, Takuya Kuraishi,* and Seijiro Matsubara*  
doi:10.1246/cl.2012.1566  
Electronic Supporting Information

1569 Ammonia Chemiresistor Sensor Based on Poly(3-Hexylthiophene) Film Oxidized by Nitrosonium Hexafluorophosphate

An ammonia chemiresistor sensor is demonstrated on the basis of poly(3-hexylthiophene) film oxidized by nitrosonium hexafluorophosphate. The sensor gave a good response to ammonia, while was insensitive to a variety of organic vapors. The detection limit was estimated to be ca. 0.22 ppm. The redox reaction between ammonia and bipolarons was attributed to the sensor signals.

Yan Li, Yong-Qiang Liu, Li-Wei Liu, and Ge-Bo Pan*  
doi:10.1246/cl.2012.1569

1571 Unique Adsorption Behavior of Antimicrobial Poly(hexamethylenebiguanide hydrochloride) onto Solid-supported Lipid Films

Antimicrobial poly(hexamethylenebiguanide hydrochloride) (PHMB) showed the multilayer adsorption onto negatively charged lipid films above a threshold concentration of PHMB.

Takaaki Date, Yosuke Matsuoka, Nobuyuki Sakamoto, and Takeshi Serizawa*  
doi:10.1246/cl.2012.1571  
Electronic Supporting Information

1574 Peroxidase-like Enzymes Designed from Cytochrome $b_5$ Exhibit Enhanced Hydrolysis Activity

Rationally designed peroxidase-like enzymes, H39Q Cyt $b_5$ and H39S Cyt $b_5$, exhibit hydrolysis activity by catalyzing the hydrolysis of 4-nitrophenyl acetate.

Ying-Wu Lin,* Xiao-Xing You, Lie-Song Chen, and Yi-Mou Wu  
doi:10.1246/cl.2012.1574  
Electronic Supporting Information
1576  **Magnetic Orientation of Hexagonal Carbon Layers at High Temperatures**

Ayumi Sakaguchi, Atom Hamasaki,* Toyonari Sadatou, Yoshitaka Nishihara, Shou Yamamoto, Yuuya Sekinuma, and Sumio Ozeki*

doi:10.1246/cl.2012.1576

Magnetic-field dependence of (002) XRD peak intensities of coal tar pitch treated at 773 K, indicating that hexagonal carbon layers should orient cooperatively in parallel to magnetic fields.

1579  **Dipole Moments of Amino Acid Residues, Gly and Ala, in α-Helix: Quantum Chemical Building Blocks for Macrodipole Moment of α-Helical Polypeptide**

Shunsuke Mieda and Misako Aida*


Electronic Supporting Information

1581  **Reversible Phase Transfer of Ferromagnetic L10-FePt Nanoparticles**

Shinpei Yamamoto,* Yoshinori Tamada, Teruo Ono, and Mikio Takano

doi:10.1246/cl.2012.1581

Electronic Supporting Information

1584  **In Vivo Real-time Detection of Plant Response to Physical and Chemical Stresses by Spin Probe ESR**

Mami Endo, Hidehiro Kurosawa, Takahiro Kawai,* Tomohiro Ito, and Tateaki Ogata

doi:10.1246/cl.2012.1584

1586  **Mild Synthesis of Furans with a Quaternary Carbon Substituent at the 2-Position**

Akihisa Iwamoto, Aki Katori, Yoshiaki Sashihara, and Satoshi Kojima*

doi:10.1246/cl.2012.1586

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Hexamethoxytribenzocoronene, a Janus Double Concave Molecule to Selectively Assemble with Fullerene C_{60}

Zhongtao Li, Zhengpeng Hu, Xing Chen, Yinping Zhang, and Jianmin Zhang*
doi:10.1246/cl.2012.1588
Electronic Supporting Information

Phosphorescence Detection of the Singlet Molecular Oxygen Generated by Visible-light Irradiation on Gold-nanoparticle-deposited TiO₂ Photocatalysts

Hironobu Saito and Yoshio Nosaka*
doi:10.1246/cl.2012.1591

Mg²⁺ Storage in Organic Positive-electrode Active Material Based on 2,5-Dimethoxy-1,4-benzoquinone

Hikaru Sano, Hiroshi Senoh, Masaru Yao,* Hikari Sakaebe, and Tetsu Kiyobayashi
doi:10.1246/cl.2012.1594

Unexpected Extension of Usage of PPh₃/CBr₄, a Versatile Reagent: Isomerization of Aromatic Allylic Alcohols

Wanchun Gong, Yun Liu, Jijun Xue, Zhixiang Xie,* and Ying Li*
doi:10.1246/cl.2012.1597
Electronic Supporting Information

A Simple Rhodamine-based Naked-eye and Fluorescence “Off–On” Sensor for Cu(II) in Aqueous Solution

Shyamaprosad Goswami,* Abhishek Manna, Krishnendu Aich, and Sima Paul
doi:10.1246/cl.2012.1600
Electronic Supporting Information
In this paper, a novel strategy for preparing large-area, vertically aligned silicon nanotip arrays at near-room temperature by combining silver mirror reaction with metal-catalyzed electroless etching (MCEE) has been developed.

Yilan Jiang, Silu Tao,* Jianxiong Huang, Chun Zhou, Hua Zhao, and Weiming Zhao
doi:10.1246/cl.2012.1603

Healthy experimental rabbit was auricular vein injected with fresh $^{18}$F-radiolabeled nano-HAP suspension that dispersed in physiological saline. Nano-HAP biodistribution could be observed directly on PET images dynamically in real time. Great mass of nano-HAP deposited in regions of lung, liver, spleen, and stomach. Using the ROI tool, changes of nano-HAP aggregation level in different organs and special site could be traced and calculated. The current work may propose a new approach to investigate the biodistribution and pharmacokinetics of nano-HAP and the other related nanoparticles in vivo.

Jun Zheng and Wei Zhou*
doi:10.1246/cl.2012.1606

Formation of Diphosphate in the Presence of Vanadium(IV)–tpen Complex

Kyouhei Sato, Kiyoshi Tsuge, and Kan Kanamori*
doi:10.1246/cl.2012.1608

A Coumarin-based Fluorescence Sensor for the Reversible Detection of Thiols

A Young Cho and Kihang Choi*
doi:10.1246/cl.2012.1611
Electronic Supporting Information

Organic Sensitizers Including π-Conjugated Fluorenone–Benzothiadiazole Bridge for Dye-sensitized Solar Cells

Mutsumi Kimura, Masayoshi Karasawa, Naoki Sasagawa, Keisuke Takemoto, Ryota Goto, and Shogo Mori
doi:10.1246/cl.2012.1613
Electronic Supporting Information
1616 Environmentally Friendly Inorganic Red Pigments Based on Bismuth Oxide

Wendusu, Toshiyuki Masui, and Nobuhiro Imanaka*
doi:10.1246/cl.2012.1616
Electronic Supporting Information

Novel environmentally friendly red pigments based on Bi$_2$O$_3$ were synthesized successfully using a conventional solid-state reaction method. The optimal red hue was obtained for [(Bi$_{0.72}$Er$_{0.28}$)$_{0.80}$Fe$_{0.20}$]$_2$O$_3$, which possessed a more reddish color than that of a commercially available Fe$_2$O$_3$ pigment.

1619 $\gamma$-Selective Addition to 1,1-Difluoroallenes: Three-component Coupling Leading to 2,2-Disubstituted 1,1-Difluoroalkenes

Kohei Fuchiibe, Mikiko Ueda, Misaki Yokota, and Junji Ichikawa*
doi:10.1246/cl.2012.1619
Electronic Supporting Information

1622 Synthesis and Characterization of 2,3,9,10-Tetradendronized Pentacene

Tomoyuki Tajima, Akio Yamakawa, Keitaro Fukuda, Yuuki Hayashi, Masahiko Nakano, and Yutaka Takaguchi*
doi:10.1246/cl.2012.1622
Electronic Supporting Information

1625 Immobilization of Trypsin on Graphene Oxide Nanosheets for Increased Proteolytic Stability

Masayo Sakata,* Asami Funatsu, Shohei Sonoda, Tatsuya Ogata, Takaaki Taniguchi, and Yasumichi Matsumoto
doi:10.1246/cl.2012.1625
Electronic Supporting Information

The high stability of trypsin–GONS is a result of stabilization of weak intermolecular forces and prevention of enzyme autolysis, when trypsin–GONS is sufficiently dispersed in solution.

1628 Carbon Dioxide-promoted Selective Reductive Amination of Aliphatic Ketones with Aniline and Hydrogen Using a Pt/C Catalyst

Shinichiro Ichikawa, Tsunetake Seki, and Takao Ikariya*
doi:10.1246/cl.2012.1628
Electronic Supporting Information

The product selectivity for the reductive amination of aliphatic ketones with aniline and H$_2$ over a 5% Pt/C catalyst was remarkably improved in the presence of CO$_2$. It is concluded that the in situ formed CO by the reverse water–gas shift reaction specifically poisoned the Pt sites active for undesired side reactions.
1630 Synthesis of 2-Pyridylphosphinate and Thio-phosphinate Derivatives by Nucleophilic Aromatic Substitution of N-Methoxypyridinium Tosylates

Natsuhisa Oka,* Kousuke Ito, Futoshi Tomita, and Kaori Ando
doi:10.1246/cl.2012.1630
Electronic Supporting Information

1633 Multicomponent Cascade Reactions for the Synthesis of 2,3-Dihydrobenzofuran Derivatives

Qu-Bo Li and Xiao-Chun Hu*
doi:10.1246/cl.2012.1633
Electronic Supporting Information

1636 Effect of Low-voltage Pulse on Cell Elimination

Hidenori Otsuka,* Saya Okimura, Masako Nagamura, Daisuke Matsukuma, Koichi Kutsuzawa, Naoki Matsuda, Tatsuro Nakashima, and Hirotaka Okabe
doi:10.1246/cl.2012.1636
Electronic Supporting Information

1639 3D-ordered Nanoporous LiMPO₄ (M = Fe, Mn)–Carbon Composites with Excellent Charging–Discharging Rate-capability

Isamu Moriguchi,* Shohei Nabeyoshi, Mayato Izumi, and Hirotoshi Yamada
doi:10.1246/cl.2012.1639

1642 A Molecular Orbital Study of the Dipole Moment of HF, LiH, and HeH⁺

Hiroyuki Teramae,* Shin-ichi Nagaoka, and Umpei Nagashima
doi:10.1246/cl.2012.1642

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1644 Synthesis and Solvatochromic Properties of Azulene-substituted Donor–Acceptor-type Polymethine Dyes

The synthesis of azulene-substituted polymethine dyes 3–6 by the Zincke-type ring-opening reaction of pyridinium salt 2 with several secondary amines, followed by the alumina-catalyzed Knoevenagel condensation reaction with malononitrile. The intramolecular charge-transfer interactions from both azulene and amine moieties to dicyanomethylidene acceptor unit were investigated by UV–vis spectroscopy.

Taku Shoji,* Atsuyo Yamamoto, Yuta Inoue, Erika Shimomura, Shunji Ito, Junya Higashi, and Noboru Morita
doi:10.1246/cl.2012.1644

1647 Selective Uptake of Lithium Ion from Brine by H_{1.33}Mn_{1.67}O_4 and H_{1.6}Mn_{1.6}O_4

Ramesh Chittrakar, Yoji Makita, Kenta Ooi, and Akinari Sonoda*
doi:10.1246/cl.2012.1647

1650 Synthesis and Characterization of Reduction-responsive Cyclophane Dimer Based on Disulfide Linkage

Osamu Hayashida* and Kazuaki Ichimura
doi:10.1246/cl.2012.1650
Electronic Supporting Information

1652 Flexible Silacyclophanes with Two Tricyclic Aromatic Units Linked by Two Disilanyl Pillars

Waka Nakanishi, Sho Kamata, Shunpei Hitosugi, and Hiroyuki Isobe*
doi:10.1246/cl.2012.1652
Electronic Supporting Information

1655 Simple Method to Fabricate an Biocompatible Antibacterial Surface on a Versatile Substrate through an Antiadhesion Approach

Feng Zhang, Siwei Liu,* Yi Zhang, Jiarui Xu,* and Yen Wei
doi:10.1246/cl.2012.1655

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**Synthesis of Poly(3,4-ethylendioxythiophene)-Palladium Nanocomposite-coated Polymer Particles by Chemical Oxidative Seeded Dispersion Polymerization**

Hiroyuki Hamasaki, Yuya Maekawa, Soichiro Matsuzawa, Atushi Ohtaka, Yoshinobu Nakamura, and Syuji Fujii*  
doi:10.1246/cl.2012.1658  
Electronic Supporting Information

**SPR Signals of Three-dimensional Antibody-immobilized Gel Layers Formed on Sensor Chips by Atom Transfer Radical Polymerization**

Yoshiaki Kuriu, Michiko Ishikawa, Akifumi Kawamura, Tadashi Uragami, and Takashi Miyata*  
doi:10.1246/cl.2012.1660  
Electronic Supporting Information

**Pore-size Tuning of Highly Selective Organic–Inorganic Hybrid Silica Membranes by Solid-phase Post-treatment at Low Temperature**

Jinhui Wang, Genghao Gong, Masakoto Kanezashi, Tomohisa Yoshioka, Kenji Ito, and Toshinori Tsuru*  
doi:10.1246/cl.2012.1663  
Electronic Supporting Information

**Label-free Fluorescent Detection of Loop-mediated Isothermal Amplification of Nucleic Acid Using Pyrophosphate-selective Xanthene-based Zn(II)-coordination Chemosensor**

Ekkachai Kittiloespaisan, Akio Ojida, Itaru Hamachi, Yortyot Seetang-Nun, Wansika Kiatpathomechai,* and Jirarat Wongkongkatep*  
doi:10.1246/cl.2012.1666  
Electronic Supporting Information

**Stereochemical Structure of the Complex of (−)-Epigallocatechin 3-Gallate and Caffeine**

Hiroyuki Tsutsumi, Takashi Sato, and Takashi Ishizu*  
doi:10.1246/cl.2012.1669  
Electronic Supporting Information
### 1672 Transition-metal-free Benzylic C–H Bond Intermolecular Amination Utilizing Chloramine-T and I₂

Youhei Takeda, Junpei Hayakawa, Kazuki Yano, and Satoshi Minakata*
doi:10.1246/cl.2012.1672
Electronic Supporting Information

### 1675 Chiral Guanidine-catalyzed 1,4-Addition Reaction of 5H-Oxazol-4-ones to Alkynes

Tonomori Misaki,* Nari Jin, Kei Kawano, and Takashi Sugimura*  
doi:10.1246/cl.2012.1675
Electronic Supporting Information

### 1678 Effective Synthesis and Crystal Structure of a 24-Membered Cyclic Decanedisulfide Dimer

Yukihiro Tada, Takuya Yamamoto,* Yasuyuki Tezuka,* Tadashi Kawamoto, and Takehiko Mori  
doi:10.1246/cl.2012.1678
Electronic Supporting Information

### 1681 Downsizing of YVO₄:Bi⁺³⁺,Eu⁺³⁺ Nanoparticles through Hydrophobization by Surface Modification with Primary Alkylamines

Yoshiki Iso, Satoru Takeshita,* and Tetsuhiko Isobe*  
doi:10.1246/cl.2012.1681
Electronic Supporting Information

### 1684 Structural Insights for Design of Inhibitors against RISC Function

Asako Yamayoshi,* Yukiko Yamada, Akio Kobori, and Akira Murakami  
doi:10.1246/cl.2012.1684
Evaluation of Acyclic Form Content and Molar Absorption Coefficient of Carbonyl Group of Ketohexoses in Aqueous Solution

Kazuhiro Fukada,* Masakazu Okamitsu, and Masashi Sato
doi:10.1246/cl.2012.1686

Microflow-driven Temporal Self-assembly of Amphiphilic Molecules

Munenori Numata,* Momoko Takayama, Sunao Shoji, and Hitoshi Tamiaki
doi:10.1246/cl.2012.1689
Electronic Supporting Information

High Yield of Ordered and Straight Poly-pyrrole Microwires Synthesized through a (Hydroxyethyl)cellulose Template

Li Wang, Luyan Wang, Hailu Wang, Yue Zhang, and Meishan Pei*
doi:10.1246/cl.2012.1692

Selective Uptake by Akaganeite (β-FeOOH) and Ferr hydrite of Phosphate Ions from Real Spent Electroless Nickel Plating Baths

Ramesh Chittrakar, Yoji Makita, and Akinari Sonoda*
doi:10.1246/cl.2012.1694

Luminescent Properties of Rare-earth Complexes Embedded in Phenol–AOT Organogels Designed for Visible Color Tuning

Katsura Nishiyama,* Yasuhiro Watanabe, Keiichi Watanabe, and Takashi Harada*
doi:10.1246/cl.2012.1697
Electronic Supporting Information

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Toshiaki Shiomi, Tsukasa Nakahodo, and Hisashi Fujihara

doi:10.1246/cl.2012.1700

Electronic Supporting Information

Practical Synthesis of Ethyl 1-(tert-Butoxy-carbonyl)-4-(1-pyrrolidinyl)-4-piperidineacetate, an Intermediate of a Novel Antiarteriosclerotic, Utilizing Aza-Michael Addition Promoted by LiBr

Akira Iida,* Naohiro Onodera, and Tatsuro Yasukata

doi:10.1246/cl.2012.1703

Fabrication of Graphene-based Electrodes for Supercapacitors in Magnetic Fields

Graphene sheets are induced to align perpendicular to mesh in perpendicular magnetic field, while parallel magnetic fields induce sheets to align parallel to mesh.

Xiao-meng Ren, Yuan-sheng Wang,* and Te He

doi:10.1246/cl.2012.1706

Novel Synthesis of Submicrometric LiNi0.5-Mn1.5O4 by Electrospinning Method

Mingjuan Li, Lijun Sun, Kai Sun, Shihua Yu, Rongshun Wang,* and Haiming Xie*

doi:10.1246/cl.2012.1709

A Novel Double-shelled LiNi0.5Co0.2Mn0.3O2 Cathode Material for Li-ion Batteries

A novel double-shelled Li[(Ni0.8Co0.1Mn0.1)2/7(Ni1/3Co1/3Mn1/3)3/14(Ni0.4Co0.2Mn0.4)1/2]O2 material with the composition of LiNi0.5Co0.2Mn0.3O2 was synthesized via coprecipitation route. Compared with the non-core-shell LiNi0.5Co0.2Mn0.3O2 material, the double-shelled material displayed higher capacity, more excellent cycling performance, and thermal stability.

Peyyu Hou, Jian Guo, Dawei Song, Jun Zhang, Enlou Zhou, and Lianqi Zhang*

doi:10.1246/cl.2012.1712
1715 Desorption of Cs⁺ Ions Intercalated in Vermiculite Clay through Cation Exchange with Mg²⁺ Ions

Kazuya Morimoto,* Toshihiro Kogure, Kenji Tamura, Saki Tomofuji, Akihiko Yamagishi, and Hisako Sato
doi:10.1246/cl.2012.1715
Electronic Supporting Information

1718 Novel Magnetic Gold Electrode Applied for Direct Capture and Sensitive Detection of DNA Targets

Zhengqi Pan,* Yan Zhao, Qisheng Yang, Xiaobing Song, and Xiang Wang
doi:10.1246/cl.2012.1718
Electronic Supporting Information

1720 Selective Hydrogenolysis of Glycerol to 1,3-Propanediol Catalyzed by Pt Nanoparticles–Al₂O₃/WO₃

Tomoo Mizugaki, Takayuki Yamakawa, Rachandhi Arundhati, Takato Mitsudome, Koichiro Jitsukawa, and Kiyotomi Kaneda*
doi:10.1246/cl.2012.1720
Electronic Supporting Information

1723 Synthesis of 2′-Modified Cyclic Bis(3′–5′)diadenylic Acids (c-di-AMPs) and Their Promotion of Cell Division in a Freshwater Green Alga

Takafumi Tezuka,* Noritaka Suzuki, Keigo Ishida, Kin-ichi Oyama, Setsuyuki Aoki, and Masaki Tsukamoto*
doi:10.1246/cl.2012.1723
Electronic Supporting Information

Three 2′-modified cyclic bis(3′–5′)diadenylic acids (c-di-AMPs) were synthesized from commercially available adenosine phosphoramidites and the effects of c-di-AMP derivatives on the cell division of *Chlamydomonas reinhardtii*, a kind of freshwater green algae, were investigated. This structure–activity relationship study suggests that the 2′-O-dimethyl-c-di-AMP showed the highest activity and that 2′-substituents influenced the cell division of *C. reinhardtii*. DNA quantification occurs via a three-step procedure. Firstly, the GMNBs modified with capture DNA probe are dispersed into the sample and hence brought directly to the target DNA. As the GMNBs diffuse through the sample, they are able to capture the target DNA. Finally, the application of the gold magnetic electrode brings the GMNBs back to its surface, where the amount of target DNA bound can be detected electrochemically by using Methylene Blue (MB) as a label-free indicator. The current response of MB is decreased as the concentration of target DNA is increased due to the different affinity of MB to ssDNA and dsDNA.