



The following Communications have been judged by at least two referees to be “very important papers” and will be published online at [www.angewandte.org](http://www.angewandte.org) soon:

A. Patzer, M. Schütz, T. Möller, O. Dopfer\*

**IR Spectrum and Structure of the Adamantane Cation: Direct Evidence for Jahn–Teller Distortion**

C. Lux, M. Wollenhaupt, T. Bolze, Q. Liang, J. Köhler, C. Sarpe, T. Baumer\*

**Circular Dichroism in the Photoelectron Angular Distributions of Camphor and Fenchone from Multiphoton Ionization with Femtosecond Laser Pulses**

P. G. Schiro, M. Zhao, J. S. Kuo, K. M. Koehler, D. E. Sabath, D. T. Chiu\*

**Sensitive and High-Throughput Isolation of Rare Cells from Peripheral Blood with Ensemble-Decision Aliquot Ranking**

J. Lu, C. Aydin, N. D. Browning, B. C. Gates\*

**Imaging Gold Atom Catalytic Sites in Zeolite NaY**

## Editorial



*“... The past 30 years have seen an enormous effort to develop science and scientific institutions in China, and the last 20 years in particular have seen an active engagement in international cooperation ...”*

Read more in the Editorial by Chunli Bai.

C. Bai\* \_\_\_\_\_ 4318–4320

International Scientific Cooperation Is Key for The Chinese Academy of Sciences

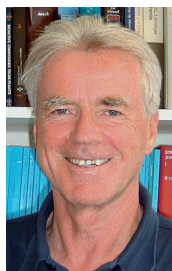
## Author Profile



*“My favorite saying is “Simple is best” (Occam’s razor). When I was eighteen I wanted to be a great chemist!”*  
This and more about Kazuaki Ishihara can be found on page 4268.

Kazuaki Ishihara \_\_\_\_\_ 4268

## News



B. Giese



N. Cramer



R. Gilmour



J. P. Maier

Paracelus Prize: B. Giese  
Werner Prize: N. Cramer  
Ružička Prize: R. Gilmour  
Erwin Schrödinger Gold Medal:  
J. P. Maier \_\_\_\_\_ 4269

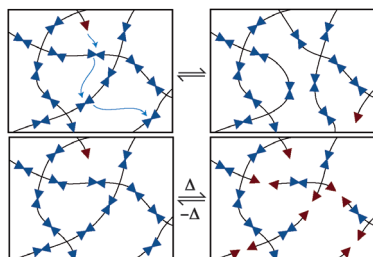
## Books

Organic Reactions

Scott E. Denmark

reviewed by M. Oestreich \_\_\_\_\_ 4270

## Highlights



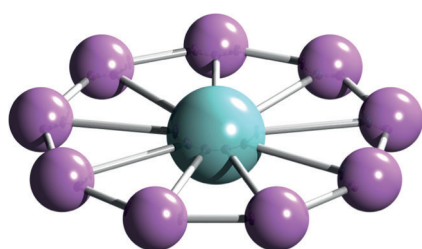
**Smart and responsive:** Reversible trans-esterification reactions were recently used within a polymer network to create a covalently crosslinked material that is capable of being processed as well as mended and recycled. This work is highlighted in the context of the covalent adaptable network approach and illustrates the bond cleavage and reformation mechanism that enable the adaptability of these materials (see picture).

### Adaptable Materials

C. N. Bowman,\*

C. J. Kloxin\* ————— 4272 – 4274

Covalent Adaptable Networks: Reversible Bond Structures Incorporated in Polymer Networks



**On a higher plane:** The combination of theoretical and experimental methods has been used to predict, produce, and detect systems with the highest coordination numbers so far known in planar clusters. With these planar  $MB_{10}^-$  wheels ( $M = Nb, Ta$ ; see picture), the world record for the highest coordination number is now set at ten.

### Coordination Numbers

T. Heine,\* G. Merino\* ——— 4275 – 4276

What Is the Maximum Coordination Number in a Planar Structure?



**King of the (nano)road:** Electrically powered unidirectional molecular motion across a metal surface has been demonstrated by using a unique design of molecule with multiple motor units. A scanning tunneling microscope tip is used to electrically excite the single mol-

ecule “nanocar”, driving it forward through vibrational and electronic excitation of its four chiral motor wheels. Helix inversion and double bond isomerization of the four motors leads to paddle-wheel like motion.

### Molecular Machines

E. C. H. Sykes\* ————— 4277 – 4278

Electric Nanocar Equipped with Four-Wheel Drive Gets Taken for its First Spin

#### For the USA and Canada:

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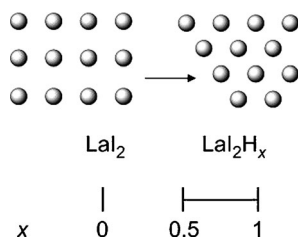
individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

## Minireviews

### Rare-Earth Metal Hydrides

A. Simon\* \_\_\_\_\_ 4280–4286

Oxidation by Hydrogen in the Chemistry and Physics of the Rare-Earth Metals



**Some do, some don't:** How do rare earth metals react with hydrogen? Some, such as La, don't, because electronic and electrostatic conditions mean they cannot take up hydrogen. Others use a trick: When  $\text{LaH}_2$ , for example, is treated with hydrogen, its quadratic net structure collapses into a densely packed triangular layer structure which can accommodate hydrogen (see picture).

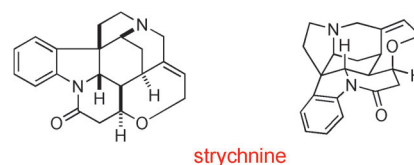
## Reviews

### Total Synthesis

J. S. Cannon,  
L. E. Overman\* \_\_\_\_\_ 4288–4311

Is There No End to the Total Syntheses of Strychnine? Lessons Learned in Strategy and Tactics in Total Synthesis

**Strychnine thrillers beyond Agatha Christie:** The complex indole alkaloid strychnine has engaged the chemical community since the 19th century. This Review examines why strychnine has been and still remains an important target for directed synthesis efforts. Selected syntheses of strychnine are discussed with the aim of identifying their influence on the evolution of the strategy and tactics of organic synthesis.



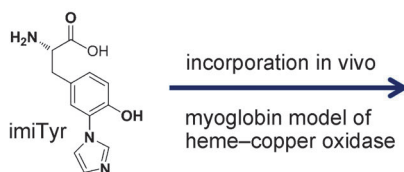
## Communications

### Enzyme Models

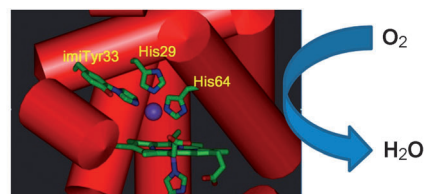
X. Liu, Y. Yu, C. Hu, W. Zhang, Y. Lu,\*  
J. Wang\* \_\_\_\_\_ 4312–4316



Significant Increase of Oxidase Activity through the Genetic Incorporation of a Tyrosine–Histidine Cross-Link in a Myoglobin Model of Heme–Copper Oxidase

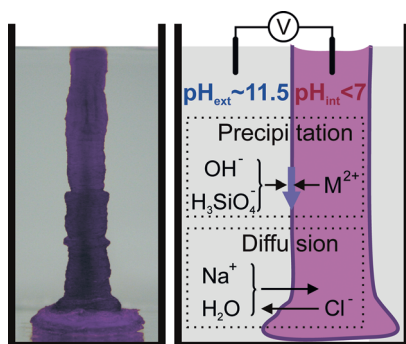


**Top model:** Heme–copper oxidase (HCO) contains a histidine–tyrosine cross-link in its heme  $a_3$ /Cu $_B$  oxygen reduction center. A functional model of HCO was obtained through the genetic incorporation of the unnatural amino acid imiTy, which



mimics the Tyr–His cross-link, and of the Cu $_B$  site into myoglobin (see picture). Like HCO, this small soluble protein exhibits selective O<sub>2</sub>-reduction activity while generating little reactive oxygen species.

**Frontispiece**



**Silica gardens** are well-known examples for the self-assembly of inorganic material (see figure). The growth of hollow tubes results in the spontaneous formation of two compartments with highly dissimilar pH and ion concentrations, which cause electrochemical potential differences across the membrane. Initially generated gradients are relieved over time through dynamic diffusion and precipitation processes.

## Chemical Gardens

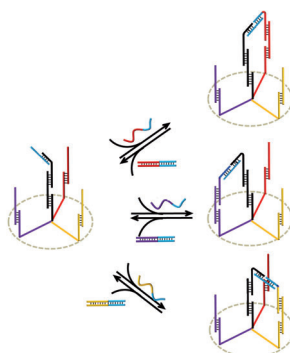
F. Glaab, M. Kellermeier, W. Kunz,\*  
E. Morallon,  
J. M. García-Ruiz\* ——— 4317 – 4321

Formation and Evolution of Chemical  
Gradients and Potential Differences  
Across Self-Assembling Inorganic  
Membranes



Inside Cover

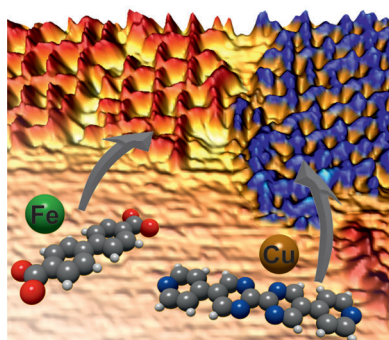
**Fuel for thought:** A DNA nanostructure consisting of a central axis and three footholds has been developed that acts as a dynamically programmed DNA nano-transporter in the presence of appropriate nucleic acids, fuel strands, and anti-fuel strands (see picture). The device consists of three interconvertible programs, where each program includes eight distinct states.



## Molecular Machines

Z.-G. Wang, J. Elbaz,  
I. Willner\* ——— 4322 – 4326

A Dynamically Programmed DNA  
Transporter



**Programmed:** A combination of chemical synthesis and scanning tunneling microscopy has demonstrated high selectivity in the formation of coordination nano-architectures from instructed metal–ligand mixtures under surface-confined conditions. Processing of the molecular information, here the coordination preferences of the two ligands and two metals, leads to the formation of two different regular networks (see picture).

## Systemic Chemistry

A. Langner, S. L. Tait,\* N. Lin,  
R. Chandrasekar, V. Meded, K. Fink,  
M. Ruben,\* K. Kern\* ——— 4327 – 4331

Selective Coordination Bonding in  
Metallo-Supramolecular Systems on  
Surfaces



**Mussel glue:** Bioinspired underwater chemical bonding with the possibility of phototriggered debonding is reported. A four-arm star-poly(ethyleneglycol) end-functionalized by nitrodopamine was synthesized. The nitrodopamine offered the reactivity of catechol and the chemistry of the photocleavable *o*-nitrophenyl ethyl group (see picture).



## Bioadhesion

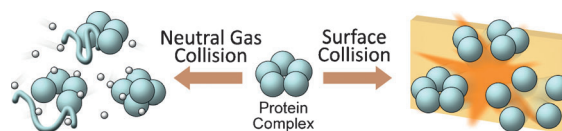
Z. Shafiq, J. Cui, L. Pastor-Pérez,  
V. San Miguel, R. A. Gropeanu, C. Serrano,  
A. del Campo\* ——— 4332 – 4335

Bioinspired Underwater Bonding and  
Debonding on Demand



## Protein Structures

M. Zhou, S. Dagan,  
V. H. Wysocki\* 4336–4339



Protein Subunits Released by Surface Collisions of Noncovalent Complexes: Nativelike Compact Structures Revealed by Ion Mobility Mass Spectrometry

**Crash survival:** Several noncovalent protein complexes were dissociated by surface collision and studied using ion mobility mass spectrometry. Most of the resulting monomer products and some undissociated precursors maintain the

overall size and shape of their native fold after surface impact. This result is in contrast to the unfolding of the structures observed for the commonly used activation involving neutral gas collisions.



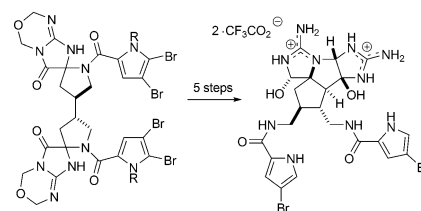
## Synthetic Methods

H. Ding, A. G. Roberts,  
P. G. Harran\* 4340–4343



Synthetic (±)-Axinellamines Deficient in Halogen

**Hiding in plain sight:** Tailored synthetic dimers of the natural product dispacamide exist as a dynamic set of structural isomers. These materials isomerize readily to unveil a spirocyclic glycohydrazide from which ring systems common to complex pyrrole/imidazole alkaloids can be derived. Fully synthetic axinellamine congeners have been prepared in this way (see scheme), wherein a host of unusual and unanticipated reactions are employed.

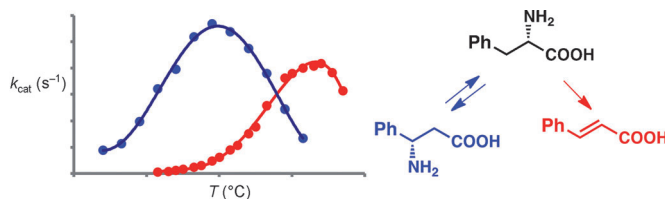


## Enzyme Catalysis

C. Chesters, M. Wilding, M. Goodall,  
J. Micklefield\* 4344–4348



Thermal Bifunctionality of Bacterial Phenylalanine Aminomutase and Ammonia Lyase Enzymes



**Enzymatic thermal switch:** The bacterial 4-methylideneimidazol-5-one (MIO) dependent enzymes AdmH and EncP are shown to display remarkable thermal bifunctionality: they act as mutases (blue graph) at lower temperatures but with

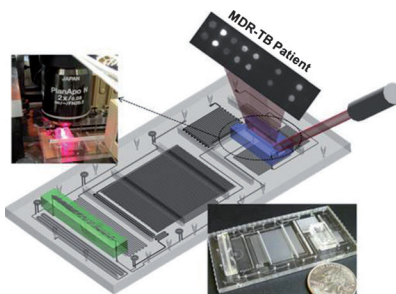
lyase (red graph) activity predominant at higher temperatures. This temperature-dependent switch in enzyme class also explains how these two similar enzymes can fulfill different catalytic functions in secondary metabolisms.

## Microfluidics

H. Wang, H.-W. Chen, M. L. Hupert,  
P.-C. Chen, P. Datta, T. L. Pittman,  
J. Goettert, M. C. Murphy, D. Williams,  
F. Barany, S. A. Soper\* 4349–4353

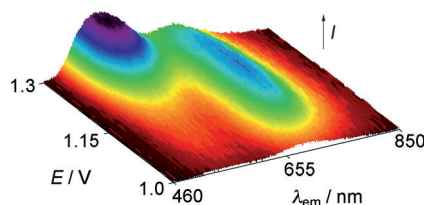


Fully Integrated Thermoplastic Genosensor for the Highly Sensitive Detection and Identification of Multi-Drug-Resistant Tuberculosis



**A modular system** for the reporting of drug-resistant strains of *Mycobacterium tuberculosis* (Mtb) in less than 30 min with full process automation was developed (see picture; MDR-TB = multi-drug-resistant tuberculosis). The fluidic cartridge uses a polymer chain reaction (PCR)/ligase detection reaction (LDR)/universal array assay that can detect, with high reliability, resistant strains that are a minority (less than 1%) from a mixed population.





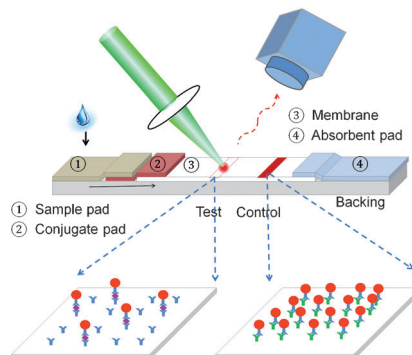
**ECL in 3D:** Selective electrogenerated chemiluminescence (ECL) of several ruthenium and iridium complexes simultaneously in solution can be controlled by electrode potential (see picture;  $\lambda_{em}$  = emission wavelength). These luminescent redox systems create a range of new possibilities for multi-analyte ECL detection, assessment of interdependent electrochemical/spectroscopic properties, and color tuning in light-emitting devices.

### Electrogenerated Chemiluminescence

E. H. Doeven, E. M. Zammit, G. J. Barbante, C. F. Hogan,\* N. W. Barnett, P. S. Francis\* **4354–4357**

Selective Excitation of Concomitant Electrochemiluminophores: Tuning Emission Color by Electrode Potential

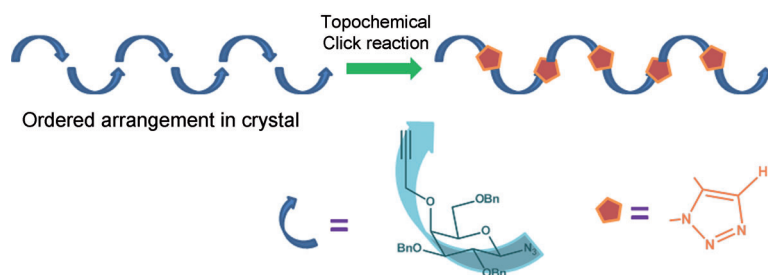
**Heat beyond visual:** The thermal contrast from the heating of gold nanoparticles upon laser stimulation can improve the analytical sensitivity of lateral flow assays (LFAs; see picture). A 32-fold improvement in sensitivity of an approved LFA for cryptococcal antigen (purple diamond) was shown, with the potential for further improvement by optimizing the backing material and the properties of the antibody-coated nanoparticles (red circle with blue Y).



### Bioassays

Z. Qin, W. C. W. Chan, D. R. Boulware, T. Akkin, E. K. Butler, J. C. Bischof\* **4358–4361**

Significantly Improved Analytical Sensitivity of Lateral Flow Immunoassays by Using Thermal Contrast



**No activation needed:** A topochemical click reaction that dispenses with catalyst, solvent, or other modes of activation takes place in crystals of a sugar derivative. The spontaneous, regiospecific

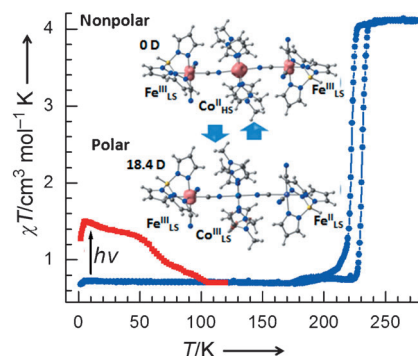
azide–alkyne cycloaddition gives linear polymers that are difficult to synthesize by conventional solution-state chemistry (see picture).

### Click Polymerization

A. Pathigoolla, R. G. Gonnade, K. M. Sureshan\* **4362–4366**

Topochemical Click Reaction: Spontaneous Self-Stitching of a Monosaccharide to Linear Oligomers through Lattice-Controlled Azide–Alkyne Cycloaddition

**A light change:** A linear cyanido-bridged  $\text{Fe}_2\text{Co}$  compound (see picture) exhibits a reversible, thermally induced cooperative charge transfer transition accompanying spin transition and polar–nonpolar transformation in the trinuclear cluster. The change in magnetic properties and polarity could also be induced by irradiation with light.



### Bistable Materials

T. Liu,\* D.-P. Dong, S. Kanegawa, S. Kang, O. Sato,\* Y. Shiota, K. Yoshizawa, S. Hayami, S. Wu, C. He, C.-Y. Duan\* **4367–4370**

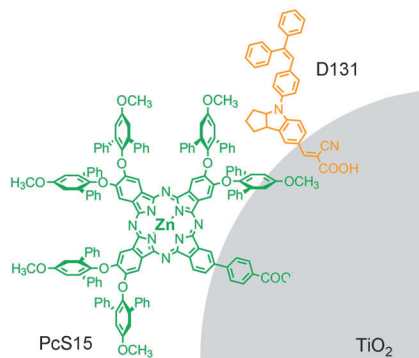
Reversible Electron Transfer in a Linear  $\{\text{Fe}_2\text{Co}\}$  Trinuclear Complex Induced by Thermal Treatment and Photoirradiation

## Energy Conversion

M. Kimura,\* H. Nomoto, N. Masaki,  
S. Mori\* 4371–4374



Dye Molecules for Simple Co-Sensitization Process: Fabrication of Mixed-Dye-Sensitized Solar Cells



**Sensitive kind of dye:** Co-sensitization of the TiO<sub>2</sub> electrode using PcS15 and the dye D131 results in a dramatic enhancement of the photocurrent response for the entire visible-light region. This method provides a simple design for accessing dye-sensitized solar cells.

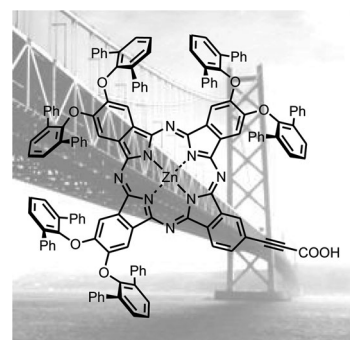
## Electron Transfer

M.-E. Ragoussi, J.-J. Cid, J.-H. Yum,  
G. de la Torre, D. Di Censo, M. Grätzel,\*  
M. K. Nazeeruddin,\*  
T. Torres\* 4375–4378



Carboxyethyl Anchoring Ligands: A Means to Improving the Efficiency of Phthalocyanine-Sensitized Solar Cells

**Bridge the gap:** Rigid  $\pi$ -conjugated bridges such as the ethynyl spacers, are effective for connecting the phthalocyanine  $\pi$  system to the conduction band of TiO<sub>2</sub>. A series of zinc phthalocyanine photosensitizers with carboxyethyl anchoring groups have been synthesized. Solar cells sensitized with the pictured compound exhibit record efficiencies of 5.5% and 6.1% under 100 (1 sun irradiation) and 9.5 mWcm<sup>-2</sup>, respectively.

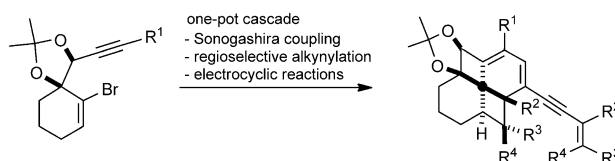


## Synthetic Methods

M. Charpenay, A. Boudhar, G. Blond,  
J. Suffert\* 4379–4382



An Expendious and Atom-Economical Synthesis of a New Generation of Substituted [4.6.4.6]Fenestradienes



**With finesse and strain:** Highly strained derivatives of fenestranes, [4.6.4.6]fenestradienes, have been prepared using a remarkable reaction cascade featuring

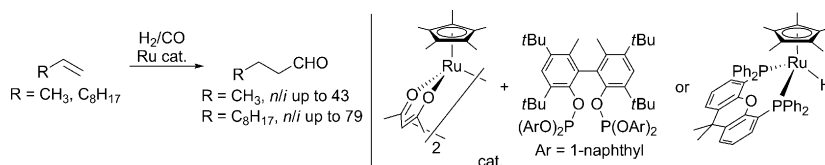
a 4-*exo*-dig cyclocarbopalladation, a Sonogashira-type coupling, a regioselective alkylation, and an 8 $\pi$ /6 $\pi$  electrocyclization sequence.

## Synthetic Methods

K. Takahashi, M. Yamashita,\* Y. Tanaka,  
K. Nozaki\* 4383–4387

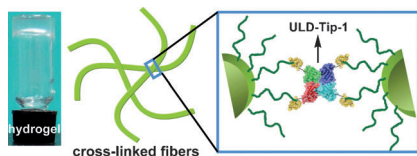


Ruthenium/C<sub>5</sub>Me<sub>5</sub>/Bisphosphine- or Bisphosphite-Based Catalysts for *normal*-Selective Hydroformylation



**A way into normality:** By using [Cp\**Ru*] complexes with bisphosphite or bisphosphine ligands, selective hydroformylation of propene and 1-decene to homologated *normal* aldehydes was accomplished with the highest levels of activity and selectivity

ever reported for ruthenium catalyst systems (see scheme). The reaction mechanism was investigated using stoichiometric amounts of [Cp\**Ru*(Xantphos)H] and [D<sub>2</sub>]-1-decene.

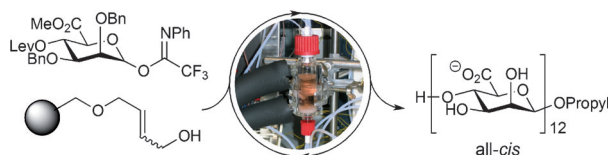


**Styling gels:** The fusion protein ULD-TIP-1 (ULD = ubiquitin-like domain, TIP-1 = Tax-interacting protein-1) enhances the interactions between self-assembled fibers formed by small molecules bearing a peptide that specifically binds to the ULD-TIP-1. The mechanical properties of the resulting hydrogels (see picture) are tuned by using peptides with different dissociation constants for the protein.

## Hydrogels

X. Zhang, X. Chu, L. Wang, H. Wang, G. Liang, J. Zhang, J. Long,\*  
Z. Yang\* ————— 4388 – 4392

Rational Design of a Tetrameric Protein to Enhance Interactions between Self-Assembled Fibers Gives Molecular Hydrogels



**A big step towards routine:** The title synthesis provides mannuronic acid alginic acid fragments featuring up to 12 *cis*-mannosidic linkages, in multi-milligram quantities (see scheme; Bn = benzyl, Lev = levulinoyl). Mannuronic acid build-

ing blocks were used in a second-generation carbohydrate synthesizer to secure the stereoselective introduction of the  $\beta$ -mannosidic bonds in a fully automated fashion.

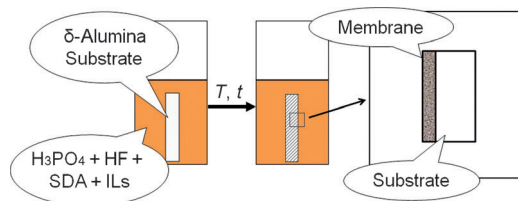
## Carbohydrates

M. T. C. Walvoort, H. van den Elst, O. J. Plante, L. Kröck, P. H. Seeberger, H. S. Overkleeft, G. A. van der Marel,\*  
J. D. C. Codée\* ————— 4393 – 4396

Automated Solid-Phase Synthesis of  $\beta$ -Mannuronic Acid Alginates



Back Cover



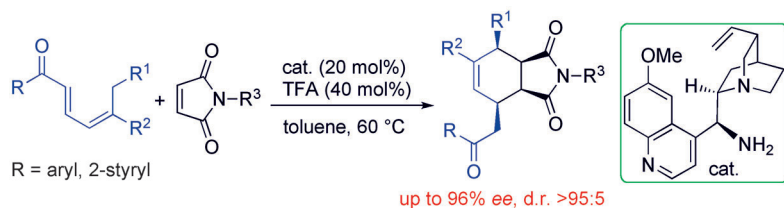
**A dual role** as a support and a source of Al is played by the alumina substrate in an ionothermal method for ambient-pressure synthesis of aluminophosphate molecular sieve membranes through substrate-sur-

face conversion (see picture; IL: ionic liquid, SDA: structure-directing agent). Aluminophosphate membranes with CHA, AEL, AFI, and LTA structure types could be obtained.

## Ionothermal Synthesis

K. Li, Z. Tian,\* X. Li, R. Xu, Y. Xu, L. Wang, H. Ma, B. Wang, L. Lin — 4397 – 4400

Ionothermal Synthesis of Aluminophosphate Molecular Sieve Membranes through Substrate Surface Conversion



**A tri-ing reaction:** An asymmetric Diels-Alder cycloaddition of  $\delta,\delta$ -disubstituted 2,4-dienones is possible through the tri-amine catalysis of cinchona-based primary amines (see scheme). An array of electron-deficient dienophiles, such as N-

substituted maleimides and 3-alkenyl oxindoles, were tolerated, and multifunctional cyclohexene derivatives were obtained in excellent stereoselectivity and with high diastereomer ratios.

## Asymmetric Catalysis

X.-F. Xiong, Q. Zhou, J. Gu, L. Dong, T.-Y. Liu, Y.-C. Chen\* — 4401 – 4404

Trienamine Catalysis with 2,4-Dienones: Development and Application in Asymmetric Diels-Alder Reactions



Front Cover

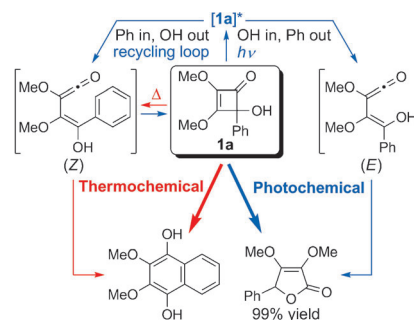


**Photochemistry**

D. C. Harrowven,\* M. Mohamed,  
T. P. Gonçalves, R. J. Whitby, D. Bolien,  
H. F. Sneddon ——— 4405 – 4408

An Efficient Flow-Photochemical  
Synthesis of 5*H*-Furanones Leads to an  
Understanding of Torquoselectivity in  
Cyclobutenone Rearrangements

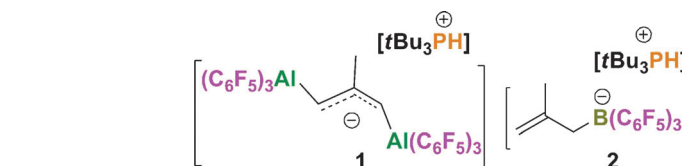
**Go with the flow:** 4-Hydroxycyclobutenones were efficiently transformed into 5*H*-furanones using an inexpensive flow-photochemical setup. The results challenge the notion that this and the related thermochemical rearrangement display torquoselectivity in their electrocyclic opening to a vinylketene intermediate. Selectivity in the photochemical rearrangement is due a dichotomous reactivity of the (*E*)- and (*Z*)-vinylketene intermediates (see scheme).



**C–H Activation**

G. Ménard, D. W. Stephan\* — 4409 – 4412

C–H Activation of Isobutylene Using  
Frustrated Lewis Pairs: Aluminum and  
Boron  $\sigma$ -Allyl Complexes



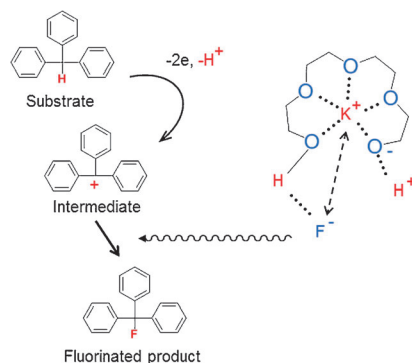
**Activation frustration:** The frustrated Lewis pairs derived from the Lewis base,  $t\text{Bu}_3\text{P}$ , and the Lewis acids,  $\text{Al}(\text{C}_6\text{F}_5)_3$  and  $\text{B}(\text{C}_6\text{F}_5)_3$ , react with isobutylene to give complexes **1** and **2**, respectively. Compound **1** reacts with ethylene to give the

insertion product,  $\text{CH}_2=\text{C}(\text{CH}_3)(\text{CH}_2)_3\text{Al}(\text{C}_6\text{F}_5)_2$ , and  $[\text{tBu}_3\text{PH}][\text{Al}(\text{C}_6\text{F}_5)_4]$  as the major products, and the zwitterion  $t\text{Bu}_3\text{PCH}_2\text{CH}_2\text{Al}(\text{C}_6\text{F}_5)_3$  and residual  $\text{Al}(\text{C}_6\text{F}_5)_3$  as the minor products.

**Synthetic Methods**

T. Sawamura, K. Takahashi, S. Inagi,  
T. Fuchigami\* ——— 4413 – 4416

Electrochemical Fluorination Using Alkali-  
Metal Fluorides



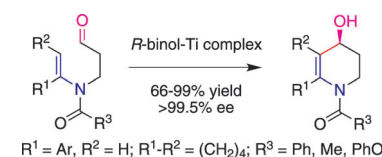
**Charged up:** The selective electrochemical fluorination of organic compounds using the alkali-metal fluoride KF under very mild reaction conditions has been accomplished (see scheme). The long-standing problems of low solubility of metal fluorides in organic solvent and low nucleophilicity of fluoride ions for fluorination have been overcome by the use of poly(ethylene glycol).

**Asymmetric Catalysis**

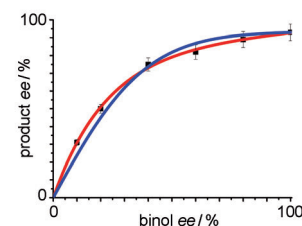
S. Tong, D.-X. Wang, L. Zhao, J. Zhu,  
M.-X. Wang\* ——— 4417 – 4420

Enantioselective Synthesis of 4-  
Hydroxytetrahydropyridine Derivatives by  
Intramolecular Addition of Tertiary  
Enamides to Aldehydes

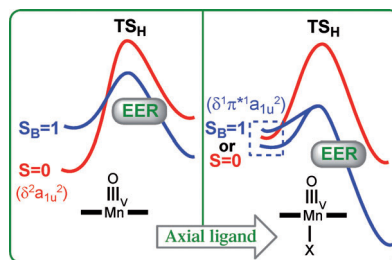
**Stable tertiary** enamides and enecarbamates undergo highly enantioselective intramolecular nucleophilic addition to aldehyde units catalyzed by chiral binol–Ti complexes under mild conditions to produce the title compounds in up to 99.5% or greater enantiomeric excess. A positive nonlinear effect was detected and the formation of binol–Ti aggregates suggests an intricate asymmetric catalytic pathway.



$\text{R}^1 = \text{Ar}$ ,  $\text{R}^2 = \text{H}$ ;  $\text{R}^1\text{--R}^2 = (\text{CH}_2)_4$ ;  $\text{R}^3 = \text{Ph}$ ,  $\text{Me}$ ,  $\text{PhO}$



**Spin-state effects:** In [(Cz)Mn<sup>VO</sup>] complexes, even with singlet closed-shell ground states, the reactive state is the open-shell triplet B state ( $S_B = 1$ ) that has a high oxyl radical character and a transition state (TS) stabilized by exchange-enhanced reactivity (EER; see picture). The dramatic axial ligand effect originates in the EER of this state.

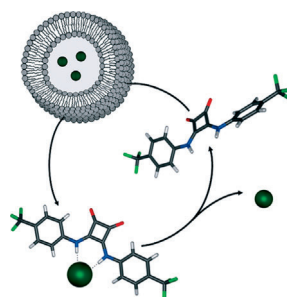


## Ligand Effects

D. Janardanan, D. Usharani,  
S. Shaik\* 4421–4425

The Origins of Dramatic Axial Ligand Effects: Closed-Shell Mn<sup>VO</sup> Complexes Use Exchange-Enhanced Open-Shell States to Mediate Efficient H Abstraction Reactions

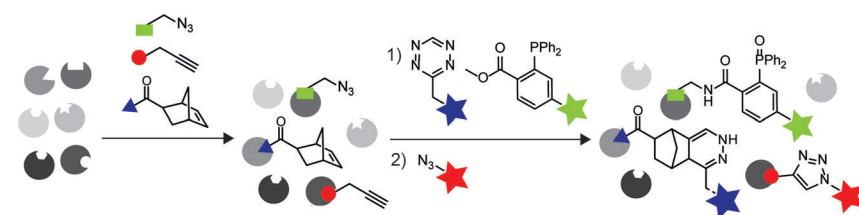
**Square peg in a round ball:** Squaramides are shown to be potent transmembrane anion transporters for both chloride and bicarbonate, performing better than the thiourea and urea analogues. Studies into the nature of this transport point to a mobile carrier mechanism, where the squaramide delivers the anion cargo across the lipid bilayer (see scheme, green sphere = anion). These drug-like molecules provide a platform for the development of a new generation of anion-transport systems.



## Anion Transport

N. Busschaert, I. L. Kirby, S. Young,  
S. J. Coles, P. N. Horton, M. E. Light,  
P. A. Gale\* 4426–4430

Squaramides as Potent Transmembrane Anion Transporters



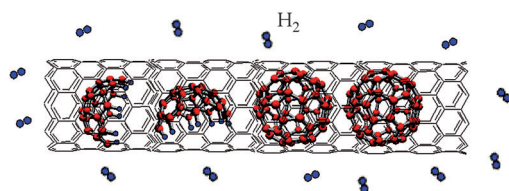
**Three at the same time:** A ligation strategy combining tetrazine–norbornene cycloaddition, Staudinger–Bertozzi ligation, and copper(I)-catalyzed click reaction was used to label the three catalytic activities

of the proteasome simultaneously in a single experiment. The orthogonality of the three ligation reactions enables selective monitoring of multiple targets at the same time in complex biological samples.

## Activity-Based Profiling

L. I. Willems, N. Li, B. I. Florea, M. Ruben,  
G. A. van der Marel,  
H. S. Overkleeft\* 4431–4434

Triple Bioorthogonal Ligation Strategy for Simultaneous Labeling of Multiple Enzymatic Activities



**A small intruder:** The reaction of C<sub>60</sub> peapods with hydrogen was studied at elevated pressure and temperature and compared with the reaction of bulk C<sub>60</sub> powder. At temperatures above 500 °C the reaction results in a collapse of the full-

erene cage structure and formation of various hydrocarbon molecules. Direct evidence was given for the surprising ability of hydrogen to penetrate into the inner space of C<sub>60</sub> peapods and to react with the fullerenes (see picture).

## Fullerene Peapods

A. V. Talyzin,\* S. M. Luzan, I. V. Anoshkin,  
A. G. Nasibulin, H. Jiang,  
E. I. Kauppinen 4435–4439

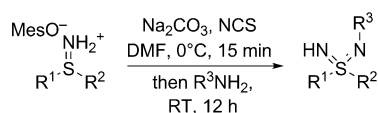
Hydrogen-Driven Collapse of C<sub>60</sub> Inside Single-Walled Carbon Nanotubes

## Synthetic Methods

M. Candy, C. Guyon, S. Mersmann,  
J.-R. Chen, C. Bolm\* — 4440–4443



Synthesis of Sulfondiimines by  
N-Chlorosuccinimide-Mediated Oxidative  
Imination of Sulfiliminium Salts



R<sup>1</sup> = aryl, alkyl  
R<sup>2</sup> = aryl, alkyl  
R<sup>3</sup> = aryl, alkyl,  
H, CN, SO<sub>2</sub>Ar

29 examples  
31–80% yield

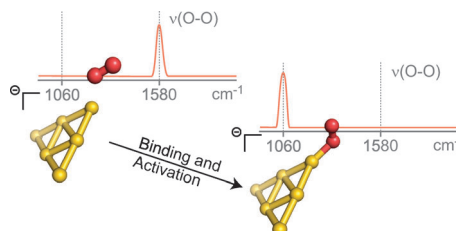
**Access to sulfondiimines:** The oxidative one-pot chlorination–imination sequence of in situ generated free sulfilimines by N-chlorosuccinimide (NCS) allows the preparation of N-monosubstituted sulfondiimines under mild reaction conditions with excellent functional-group tolerance (see scheme; Mes = 2,4,6-trimethylphenylsulfonyl)

## Oxygen Activation

A. P. Woodham, G. Meijer,  
A. Fielicke\* — 4444–4447



Activation of Molecular Oxygen by Anionic Gold Clusters



**A golden opportunity:** Molecular oxygen is found to be converted into a superoxo (O<sub>2</sub><sup>−</sup>) species upon complexation to gold-cluster anions containing an even number of Au atoms. Vibrational spectra (see

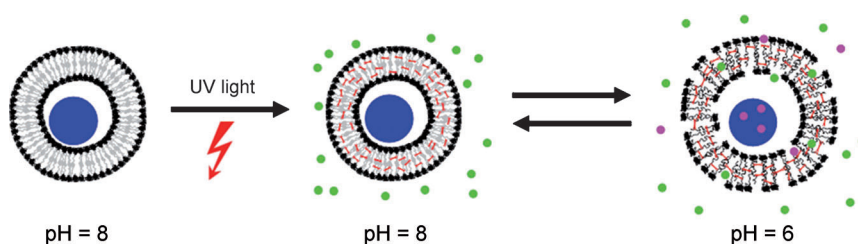
scheme) reveal small variations in the extent of O–O bond activation dependent upon the electron affinity of the parent cluster.

## Nanoreactors

J. Gaitzsch, D. Appelhans, L. Wang,  
G. Battaglia,\* B. Voit\* — 4448–4451



Synthetic Bio-nanoreactor: Mechanical  
and Chemical Control of Polymersome  
Membrane Permeability



**pH-sensitive polymersomes** have been stabilized by UV cross-linking after incorporation of an enzyme in a synthetic bio-nanoreactor without transmembrane proteins. This stabilization allows the reversible swelling and deswelling of the poly-

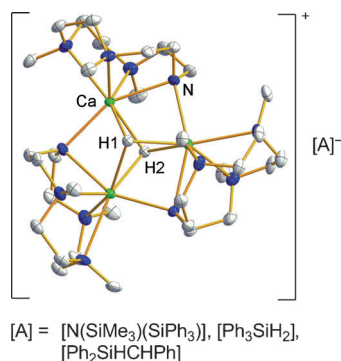
mersomes upon changes in the pH value. The controlled reaction of the enclosed enzyme could be monitored selectively at pH 6, when the substrate could penetrate the membrane.

## Calcium Hydrides

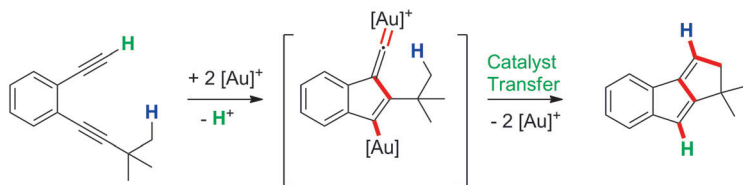
P. Jochmann, J. P. Davin, T. P. Spaniol,  
L. Maron,\* J. Okuda\* — 4452–4455



A Cationic Calcium Hydride Cluster  
Stabilized by Cyclen-Derived Macrocyclic  
N,N,N,N Ligands



**Cationic calcium hydride** complexes with a [Ca<sub>3</sub>(μ<sub>3</sub>-H)<sub>2</sub>] core were prepared from different organocalcium precursors and Ph<sub>2</sub>SiH<sub>2</sub>. The hydride complexes were found to be active in the catalytic hydrosilylation and hydrogenation of 1,1-diphenylethene.



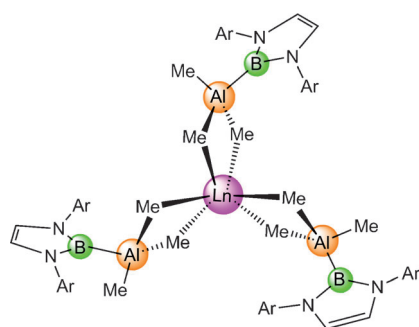
**Alkyl-substituted diynes** deliver benzofulvenes in a unique gold-catalyzed reaction. The catalytic cycle involves the formation of gold acetylides by alkynyl C–H activation, the formation of vinylidene gold(I) intermediates by dual activation, and alkyl

C–H activation by the vinylidene gold(I) species. *gem*-Diaurated species obtained from the catalysis reactions prove to be highly active catalysts for these conversions.

### Gold Catalysis

A. S. K. Hashmi,\* I. Braun, P. Nösel, J. Schädlich, M. Wietek, M. Rudolph, F. Rominger ————— **4456–4460**

Simple Gold-Catalyzed Synthesis of Benzofulvenes—*gem*-Diaurated Species as “Instant Dual-Activation” Precatalysts

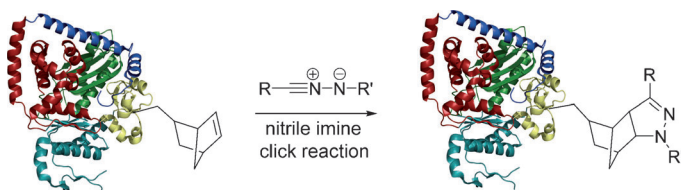


**Al B there for Lu:** Boryllithium (THF)<sub>2</sub>Li{B(NArCH)<sub>2</sub>} (Ar = C<sub>6</sub>H<sub>3</sub>iPr<sub>2</sub>-2,6) reacts with excess AlMe<sub>3</sub> to give dimeric {Me<sub>2</sub>Al[B(NArCH)<sub>2</sub>]}<sub>2</sub>, which readily adds to [LnMe<sub>3</sub>]<sub>n</sub> forming homoleptic Ln-[AlMe<sub>3</sub>B(NArCH)<sub>2</sub>]<sub>3</sub> (Ln = Y, Lu, see picture). The reaction with [LnMe<sub>3</sub>]<sub>n</sub> underlines the high methyl mobility and strong Al–B bonding in heteroleptic {Me<sub>2</sub>Al[B(NArCH)<sub>2</sub>]}<sub>2</sub>, which is also evidenced by NMR spectroscopy.

### Boryl Complexes

N. Dettenrieder, H. M. Dietrich, C. Schädle, C. Maichle-Mössmer, K. W. Törnroos, R. Anwander\* ————— **4461–4465**

Organoaluminum Boryl Complexes



**Built in for clicks:** A specially evolved pyrrolysyl-tRNA synthetase from *Methanocaldococcus jannaschii* was used to incorporate a norbornene amino acid into proteins in

*E. coli*. This unit can be site-selectively modified under mild physiological conditions using a [3+2] cycloaddition reaction with nitrile imines (see scheme).

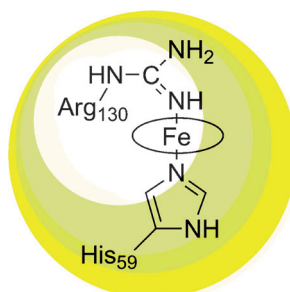
### Protein Labeling

E. Kaya, M. Vrabl, C. Deiml, S. Prill, V. S. Fluxa, T. Carell\* ————— **4466–4469**

A Genetically Encoded Norbornene Amino Acid for the Mild and Selective Modification of Proteins in a Copper-Free Click Reaction



**Prestidigitation:** In a mutant of the heme protein nitrophorin 4, the first binding of guanidine to iron in a porphyrin is observed (see structure). The protein pocket has two effects that aid this binding: its overall structure holds the ligands together providing binding energy from the chelate effect and it facilitates the deprotonation of the highly basic guanidine residue.



### Heme Complexes

C. He, M. R. Fuchs, H. Ogata,\* M. Knipp\* ————— **4470–4473**

Guanidine-Ferroheme Coordination in the Mutant Protein Nitrophorin 4(L130R)





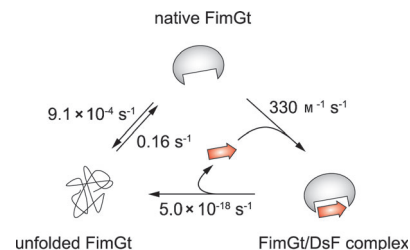
## Protein Purification

C. Giese, F. Zosel, C. Puorger,  
R. Glockshuber\* — 4474–4478



The Most Stable Protein–Ligand Complex:  
Applications for One-Step Affinity  
Purification and Identification of Protein  
Assemblies

**An alternative to tagging:** The thermodynamically most stable protein–ligand complex known to date ( $K_D = 1.5 \times 10^{-20}$  M) consists of the two components FimGt and DsF, portions of two different subunits of the type 1 pilus protein complex. The first technical applications of this new complex are the single-step purification and identification of multi-protein complexes from cell extracts.



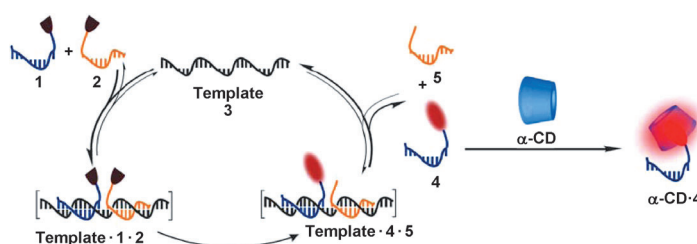
Inside Back Cover

## DNA-Templated Reactions

X.-H. Chen, A. Roloff,  
O. Seitz\* — 4479–4483



Consecutive Signal Amplification for DNA  
Detection Based on De Novo Fluorophore  
Synthesis and Host–Guest Chemistry



**Two is more than one:** A method has been developed in which a DNA template triggers a Wittig reaction that leads to transfer of a benzylidene group from a DNA-linked phosphonium salt to

a DNA-linked benzaldehyde. A synthetic receptor such as  $\alpha$ -cyclodextrin then encapsulates the newly formed stilbene and triggers further signal increases.

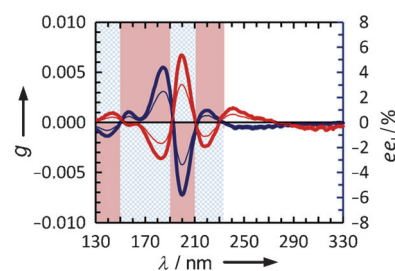
## Homochirality

C. Meinert, J. H. Bredehöft, J.-J. Filippi,  
Y. Baraud, L. Nahon, F. Wien, N. C. Jones,  
S. V. Hoffmann,  
U. J. Meierhenrich\* — 4484–4487



Anisotropy Spectra of Amino Acids

**Light on chirality:** To predict the enantiomeric enrichment that can be induced into racemic organic molecules with the help of circularly polarized light, the anisotropy factor  $g$  is essential. Anisotropy spectra  $g = f(\lambda)$  recorded for proteinaceous amino acids provide crucial information on the transfer of chirality from light to matter.



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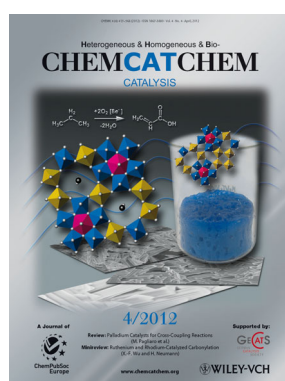
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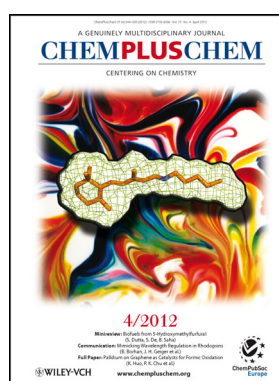
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