

Spotlight on Angewandte's Sister Journals

## Service

10216–10218

## Author Profile



*"My motto is 'simple is beautiful'.*

*My favorite drink is green tea ..."*

This and more about Chengde Mao can be found on page 10220.

Chengde Mao \_\_\_\_\_ 10220

## News



T. J. Marks



K. O. Christe



W. Tan



A. R. Wheeler

National Academy of Sciences Award in Chemical Sciences: T. J. Marks — 10221

Richard C. Tolman Award:  
K. O. Christe \_\_\_\_\_ 10221

Florida Award: W. Tan \_\_\_\_\_ 10221

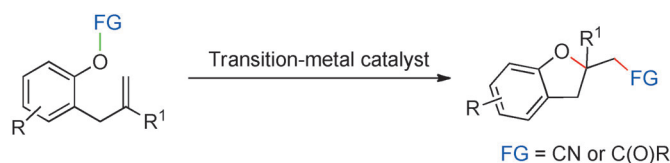
Heinrich Emanuel Merck Prize:  
A. R. Wheeler \_\_\_\_\_ 10221

## Books

Genentech

Sally Smith Hughes

reviewed by E.-L. Winnacker \_\_\_\_\_ 10222



**Functionalized dihydrobenzofuran derivatives** can be obtained by intramolecular alkoxyacylation and alkoxyacylation of alkenes (see scheme). In both transformations, selective activation of an O–FG

bond is accomplished by using a transition-metal catalyst. These transformations represent a conceptually new approach to metal-catalyzed alkene difunctionalization.

## Highlights

### Alkene Difunctionalization

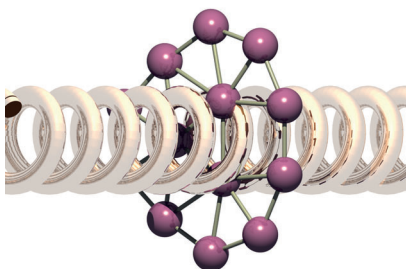
J. P. Wolfe\* \_\_\_\_\_ 10224–10225

Intramolecular Alkoxyacylation and Alkoxyacylation Reactions: New Types of Alkene Difunctionalizations for the Construction of Oxygen Heterocycles

## Molecular Motors

G. Merino,\* T. Heine\* — 10226–10227

And Yet It Rotates: The Starter for a Molecular Wankel Motor



**Gentlemen, start your engines!** A starter system for the smallest molecular motor known so far,  $B_{13}^+$ , has been prepared. An external laser field of circular polarized light with a tuned frequency is used to trigger the rotation of the inner and outer rings of the planar  $\pi$ -aromatic double-ring system (see picture). Can this idea be transferred to other systems in nanotechnology?

## Minireviews

### Coordination Chemistry

V. K. K. Praneeth, M. R. Ringenberg,  
T. R. Ward\* — 10228–10234

Redox-Active Ligands in Catalysis



**Juggling with both hands:** For sustainable energy, mastering multi-electron catalytic processes is the key feature. To address this challenge, nature combines redox-active metals with redox-active mediators or ligands. The resulting catalytic transformations (e.g. water splitting,  $CO_2$  reduction, C–H activation) proceed with low kinetic barriers. This Minireview highlights recent examples of homogeneous catalysis involving redox-active ligands.

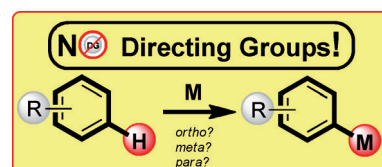
## Reviews

### C–H Activation

N. Kuhl, M. N. Hopkinson,  
J. Wencel-Delord,  
F. Glorius\* — 10236–10254

Beyond Directing Groups: Transition-Metal-Catalyzed C–H Activation of Simple Arenes

**Directionless?** Obtaining high levels of reactivity and selectivity is crucial for extending the scope of modern C–H activation chemistry. Whereas most of these transformations rely on the help of directing groups (DGs; leading to *ortho*-functionalized products and a remaining DG), the development of powerful alternative strategies is of utmost importance. Progress and trends of this evolving field are discussed.



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# Communications

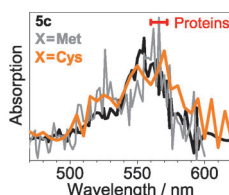
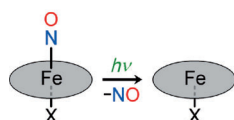
## Photobiophysics

J. A. Wyer,\*  
S. Brøndsted Nielsen — 10256–10260

Absorption by Isolated Ferric Heme  
Nitrosyl Cations In Vacuo

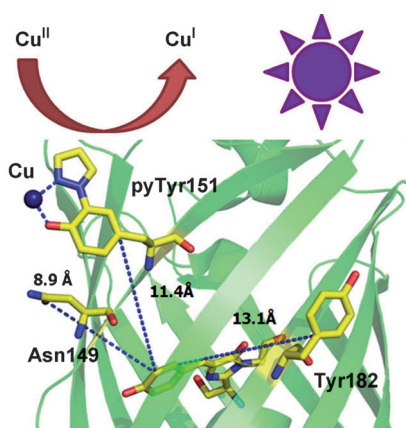


Frontispiece



**Almost innocent:** In photobiophysical studies of ferric heme nitrosyl complexes, the absorption spectra of six-coordinate complexes with NO and Met or Cys are similar to that of the five-coordinate complex ion Fe(heme)(NO)<sup>+</sup>. Since the

absorption spectra of related proteins with histidine as the proximal ligand are similar to those of the gaseous complexes, the protein microenvironment has little effect on the lowest-energy transition of the porphyrin macrocycle.



**ET encounters jellyfish:** Through the incorporation of the metal-chelating amino acid pyTyr into green fluorescent protein (GFP) from jellyfish, photoinduced electron transfer (ET) from the GFP chromophore to a bound Cu<sup>II</sup> ion was shown to occur within one nanosecond in a distance-dependent manner. The crystal structure of GFP with pyTyr at a specific position shows the structural basis for the nanomolar binding affinity of pyTyr to Cu<sup>II</sup> ions.

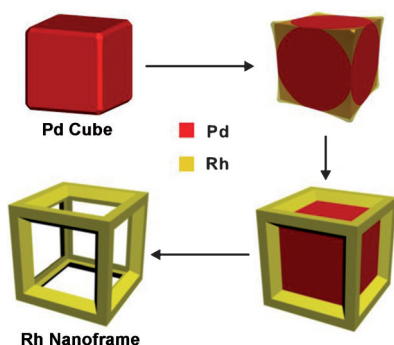
## Metalloprotein Engineering

X. H. Liu, J. S. Li, J. S. Dong, C. Hu,  
W. M. Gong,\* J. Y. Wang\* 10261–10265

Genetic Incorporation of a Metal-Chelating Amino Acid as a Probe for Protein Electron Transfer



Inside Cover



**The art of addition and subtraction:** By confining the nucleation and growth of Rh atoms only to the corners and edges of Pd cubic seeds, Pd-Rh core-frame nanocrystals were obtained with concave side faces. The Pd cores were then selectively removed by oxidative etching to generate Rh cubic nanoframes with a highly open structure (see picture).

## Bimetallic Nanocrystals

S. Xie, N. Lu, Z. Xie, J. Wang, M. J. Kim,  
Y. Xia\* — 10266–10270

Synthesis of Pd-Rh Core-Frame Concave Nanocubes and Their Conversion to Rh Cubic Nanoframes by Selective Etching of the Pd Cores





The German Chemical Society (GDCh) invites you to:



# Angewandte Anniversary Symposium

GDCh  
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

**Tuesday, March 12, 2013**

Henry Ford Building / FU Berlin

## Speakers



Carolyn R.  
Bertozzi



François  
Diederich



Alois  
Fürstner



Roald Hoffmann  
(Nobel Prize 1981)



Susumu  
Kitagawa



Jean-Marie Lehn  
(Nobel Prize 1987)



E.W. "Bert"  
Meijer



Frank  
Schirrmacher  
(Publisher, FAZ)



Robert  
Schlögl



George M.  
Whitesides



Ahmed Zewail  
(Nobel Prize 1999)

More information:

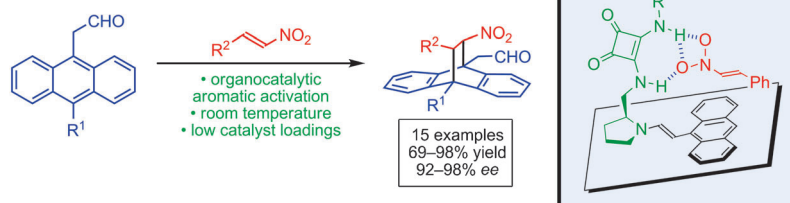


[angewandte.org/symposium](http://angewandte.org/symposium)



 **WILEY-VCH**

  
GESELLSCHAFT  
DEUTSCHER CHEMIKER



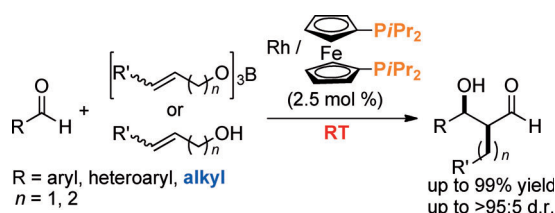
**The anglerfish catalyst:** The activation of anthracenes through aminocatalysis (see scheme) allows them to undergo [4+2] cycloadditions with concomitant breaking of the aromaticity at room temperature

and low catalyst loadings. A highly enantioselective Diels–Alder reaction of anthracenes has been developed using nitroalkenes as dienophiles.

## Asymmetric Catalysis

H. Jiang, C. Rodríguez-Escrich,  
T. K. Johansen, R. L. Davis,  
K. A. Jørgensen\* ————— 10271 – 10274

Organocatalytic Activation of Polycyclic Aromatic Compounds for Asymmetric Diels–Alder Reactions



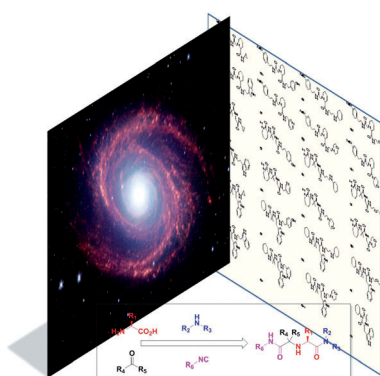
**Dip in!** A Rh/dppf catalyst generates aldehyde-derived enol boranes at ambient temperature by isomerization of allyloxy- and homoallyloxyboranes. A one-pot isomerization/cross-aldol sequence provides

aldehyde–aldehyde adducts in good yield with *syn* selectivity. Direct use of primary allylic and homoallylic alcohols was also achieved.

## Synthetic Methods

L. Lin, K. Yamamoto, S. Matsunaga,\*  
M. Kanai\* ————— 10275 – 10279

Rhodium-Catalyzed Cross-Aldol Reaction: In Situ Aldehyde–Enolate Formation from Allyloxyboranes and Primary Allylic Alcohols

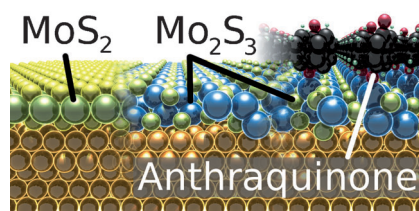


**Mix and match:** Similar to a galaxy consisting of millions of stars, a multicomponent reaction (MCR) system can result in millions of compounds. The MCR of  $\alpha$ -amino acids, oxo components, isocyanides, and amines leads to numerous and diverse compounds, thus having enormous potential for drug discovery or catalyst screening.

## Molecular Diversity

K. Khoury, M. K. Sinha, T. Nagashima,  
E. Herdtweck,  
A. Dömling\* ————— 10280 – 10283

Efficient Assembly of Iminodicarboxamides by a “Truly” Four-Component Reaction



**An Mo<sub>2</sub>S<sub>3</sub> monolayer** grown on copper coexists with well-known MoS<sub>2</sub> patches and triangular islands. Imaging by scanning tunneling microscopy after exposure to anthraquinone shows the new structure to be far more active in adsorption, permitting even the formation of a compressed adsorbate layer before other surface areas, including the supposedly reactive brim areas of MoS<sub>2</sub> islands, capture this adsorbate.

## Adsorption

D. Sun, W. Lu, D. Le, Q. Ma, M. Aminpour,  
M. Alcántara Ortigoza, S. Bobek, J. Mann,  
J. Wyrick, T. S. Rahman,  
L. Bartels\* ————— 10284 – 10288

An MoS<sub>x</sub> Structure with High Affinity for Adsorbate Interaction

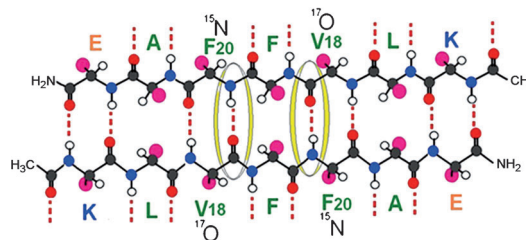


## Solid-State NMR

O. N. Antzutkin,\* D. Iuga, A. V. Filippov,  
R. T. Kelly, J. Becker-Baldus, S. P. Brown,  
R. Dupree ————— 10289 – 10292



Hydrogen Bonding in Alzheimer's  
Amyloid- $\beta$  Fibrils Probed by  $^{15}\text{N}\{^{17}\text{O}\}$   
REAPDOR Solid-State NMR Spectroscopy



**An exclusive label:**  $^{15}\text{N}\{^{17}\text{O}\}$  REAPDOR NMR was used to validate intermolecular  $\text{C}=\text{O}\cdots\text{H}-^{15}\text{N}$  hydrogen bonding in  $\text{Ac-A}\beta_{(16-22)}\text{-NH}_2$  (see scheme) and  $\text{A}\beta_{(11-25)}$  amyloid fibrils, which are associated with

Alzheimer's disease, by selectively labeling them with  $^{17}\text{O}$  and  $^{15}\text{N}$ . This method was effective for confirming the structure of these fibrils, and could be useful for a number of other biological samples.

## Bacterial Alkaloids

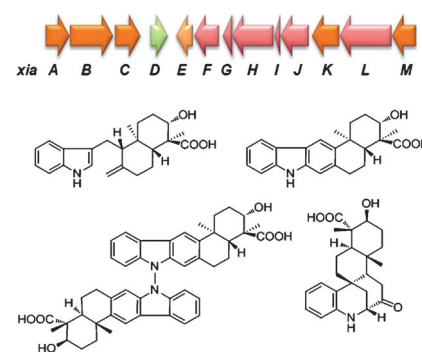
Z. Xu, M. Baunach, L. Ding,  
C. Hertweck\* ————— 10293 – 10297



Bacterial Synthesis of Diverse Indole  
Terpene Alkaloids by an Unparalleled  
Cyclization Sequence

### Getting indole terpenes into shape:

Genetic analysis, pathway dissection, and heterologous reconstitution provide first insights into bacterial indolosesquiterpene biosynthesis and unveil the involvement of a new type of terpene cyclase and an indole oxygenase in the formation of indospesene, xiamycin, and sespenine ring systems. Furthermore, heterologous pathway expression led to the discovery of C–C- and C–N-linked xiamycin dimers.



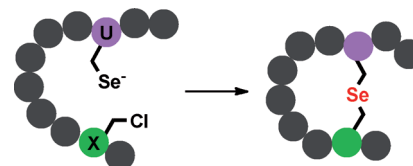
## Peptide Cyclization

A. D. de Araujo,\* M. Mobli, G. F. King,  
P. F. Alewood ————— 10298 – 10302



Cyclization of Peptides by using  
Selenolanthionine Bridges

**Selenocysteine does the job:** Lanthionine bridges are important structural elements in naturally occurring lantibiotics. They can be engineered into peptides to increase biological activity and metabolic stability. Macrocyclization of peptides by intramolecular thiolation of cysteine is often difficult but can be achieved by replacing cysteine with the more reactive isosteric selenocysteine amino acid.



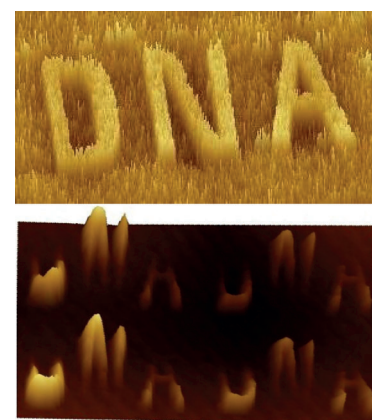
## DNA Nanostructures

M. N. Khan, V. Tjong, A. Chilkoti,  
M. Zharnikov\* ————— 10303 – 10306



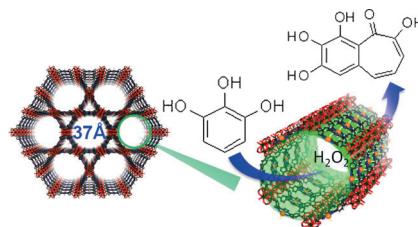
Fabrication of ssDNA/Oligo(ethylene glycol) Monolayers and Complex Nanostructures by an Irradiation-Promoted Exchange Reaction

**Creative design:** An approach to preparing mixed monolayers of thiolated single-stranded DNA (ssDNA) and oligo(ethylene glycol)s (OEG-AT) in a broad range of compositions as well as ssDNA/OEG-AT patterns of any required shape (see top figure) has been shown. A combination of this approach with surface-initiated enzymatic polymerization allows complex 3D DNA nanostructures to be sculpted with high spatial precision (bottom).





**Biomimetic MOF:** Extremely stable MOFs with different open metal sites and ultra-large 1D channels, PCN-222 (Fe, Mn, Co, Ni, Cu, and Zn), have been assembled with eight-connected  $Zr_6$  clusters and redox-active metalloporphyrin motifs. PCN-222(Fe) shows peroxidase-like activity in aqueous solution, exhibiting highly effective biomimetic oxidation on a number of substrates.

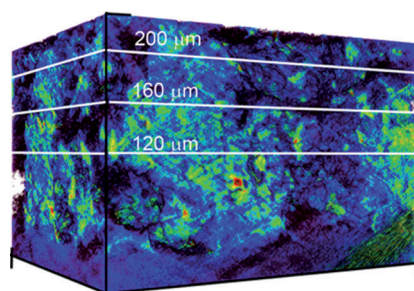


## Porous Coordination Networks

D. Feng, Z.-Y. Gu, J.-R. Li, H.-L. Jiang, Z. Wei, H.-C. Zhou\* — 10307 – 10310

Zirconium-Metalloporphyrin PCN-222: Mesoporous Metal–Organic Frameworks with Ultrahigh Stability as Biomimetic Catalysts

Front Cover

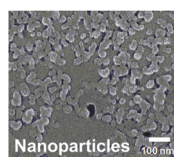


**Four-dimensional** visualization of Pt/C cathode catalyst layers in membrane electrode assemblies (MEAs) were successfully performed by a newly developed method, namely laminography–XAFS (X-ray absorption fine structure). The method not only enables imaging of the 3D distribution of Pt nanoparticle cathode catalysts, but also the chemical states of the Pt catalysts in fresh and degraded MEAs in a nondestructive manner.

## Visualization of Electrodes

T. Saida, O. Sekizawa, N. Ishiguro, M. Hoshino, K. Uesugi, T. Uruga, S. Ohkoshi, T. Yokoyama, M. Tada\* — 10311 – 10314

4D Visualization of a Cathode Catalyst Layer in a Polymer Electrolyte Fuel Cell by 3D Laminography–XAFS



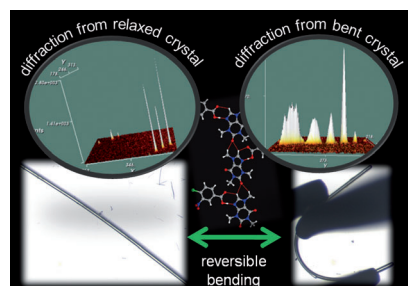
**A method for preparing** nanoparticles of a water-insoluble drug that are suitable for administration to the human body has been established. A reprecipitation method was used to fabricate 50 nm nanoparticles of dimerized SN-38, an

anticancer camptothecin derivative, that form stable aqueous dispersions and can penetrate into cancer cells to inhibit cell proliferation more potently than irinotecan.

## Nanotechnology

H. Kasai,\* T. Murakami, Y. Ikuta, Y. Koseki, K. Baba, H. Oikawa, H. Nakanishi, M. Okada, M. Shoji, M. Ueda, H. Imahori, M. Hashida — 10315 – 10318

Creation of Pure Nanodrugs and Their Anticancer Properties



**Crystalline spring:** Single crystals formed from caffeine, 4-chloro-3-nitrobenzoic acid, and methanol (1:1:<1) have an interlocked structure with weak interactions in the three perpendicular directions, as well as solvent channels, and display reversible elastic bending. Excellent conservation of long-range order even after many bending cycles is observed, thus demonstrating the opportunities for flexible organic materials.

## Crystal Engineering

S. Ghosh, C. M. Reddy\* — 10319 – 10323

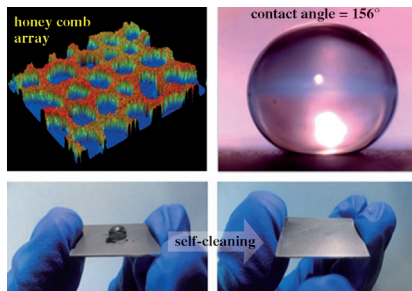
Elastic and Bendable Caffeine Cocrystals: Implications for the Design of Flexible Organic Materials

## Self-Cleaning Materials

M. B. Avinash, E. Verheggen,  
C. Schmuck,\*  
T. Govindaraju\* — 10324 – 10328



Self-Cleaning Functional Molecular  
Materials



**Clean and polish:** The spontaneous hierarchical molecular assembly of a naphthalenediimide derivative is used to form microarrays by a simple solution-processing technique. This method is further employed to fabricate a self-cleaning surface with very low slide angle ( $3^\circ$ ) and contact angle hysteresis ( $1^\circ$ ).

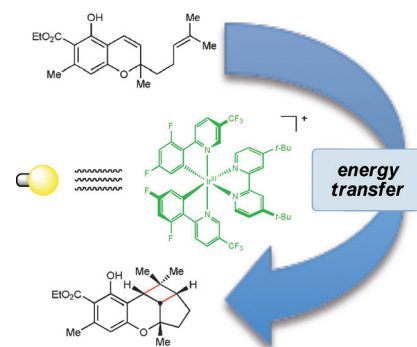
## Photocatalysis

Z. Lu, T. P. Yoon\* — 10329 – 10332



Visible Light Photocatalysis of [2+2]  
Styrene Cycloadditions by Energy Transfer

**Hip to be square:** Styrenes participate in [2+2] cycloadditions upon irradiation with visible light in the presence of an iridium(III) polypyridyl complex. In contrast to previous reports of visible light photoredox catalysis, the mechanism of this process involves photosensitization by energy transfer and not electron transfer.

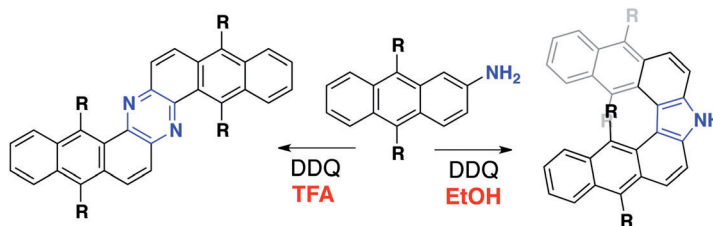


## Oligoacenes

K. Goto, R. Yamaguchi, S. Hiroto,\*  
H. Ueno, T. Kawai,  
H. Shinokubo\* — 10333 – 10336



Intermolecular Oxidative Annulation of  
2-Aminoanthracenes to Diazaacenes  
and Aza[7]helicenes



**Which way to go:** The product distribution in the efficient oxidation of 2-aminoanthracene derivatives to pyrazine- and pyrrole-fused bisanthracenes can be controlled by additives (see scheme; TFA =

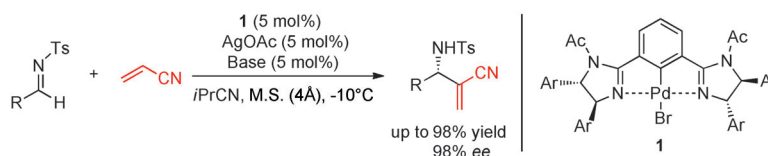
trifluoroacetic acid, DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone). The pyrrole-fused dimer can be regarded as an aza[7]helicene with a stable helical conformation.

## Asymmetric Synthesis

K. Hyodo, S. Nakamura,\*  
N. Shibata\* — 10337 – 10341



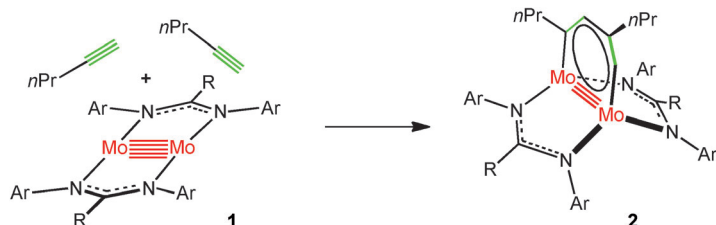
Enantioselective Aza-Morita–Baylis–Hillman Reactions of Acrylonitrile Catalyzed by Palladium(II) Pincer Complexes having  $C_2$ -Symmetric Chiral Bis(imidazoline) Ligands



**Simple and efficient:** The first highly enantioselective aza-Morita–Baylis–Hillman reaction between acrylonitrile and imines has been developed. Excellent yields and enantioselectivities were observed for the reaction of various

imines using chiral phebim/Pd<sup>II</sup> complexes (**1**; see scheme). This process offers a simple and efficient route for the synthesis of functionalized  $\alpha$ -methylene- $\beta$ -aminonitriles and their derivatives.





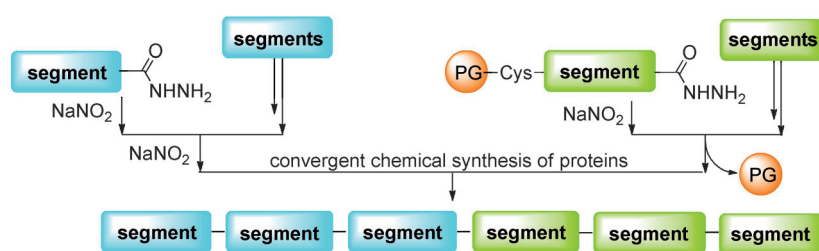
**High five!** The quintuply bonded molybdenum amidinate **1** reacts with two equivalents of 1-pentyne through a [2+2+2] cycloaddition reaction to give the first examples of the benzannulated

product **2**. The  $C_4Mo_2$  rings exhibit aromatic character. Treatment of **1** with internal alkynes afforded the 2:1 and 1:1 [2+2] cycloadducts, which are mechanistically associated with the formation of **2**.

## Aromaticity

H.-Z. Chen, S.-C. Liu, C.-H. Yen,  
J.-S. K. Yu,\* Y.-J. Shieh, T.-S. Kuo,  
Y.-C. Tsai\* — 10342 – 10346

Reactions of Metal–Metal Quintuple Bonds with Alkynes: [2+2+2] and [2+2] Cycloadditions



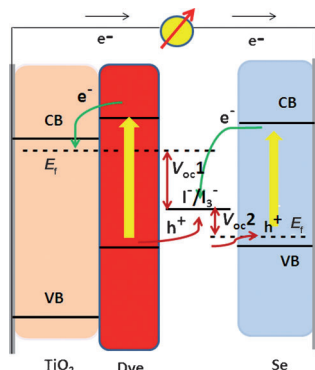
**Coming together:** A generally applicable strategy for convergent chemical synthesis of proteins from multiple peptide segments is developed on the basis of the ligation of peptide hydrazides. The pep-

tide hydrazide intermediates can be made at low cost and the new strategy is used in the synthesis of the 142 residue model protein RpS25 from six peptide segments. PG = protecting group.

## Total Synthesis

G.-M. Fang, J.-X. Wang,  
L. Liu\* — 10347 – 10350

Convergent Chemical Synthesis of Proteins by Ligation of Peptide Hydrazides

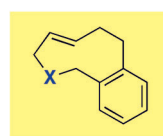


**High voltage:** A selenium-based photo-cathode has been developed for a photoelectrochemical solar cell with a high open-circuit voltage  $V_{oc}$  of 318 mV and an efficiency of 0.34 %. A higher  $V_{oc}$  of 940 mV was realized in a tandem solar cell with a conventional N719 dye-sensitized photoanode, giving an efficiency of 0.98 %.

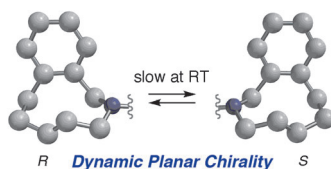
## Solar Cells

J. Qian, K.-J. Jiang,\* J.-H. Huang, Q.-S. Liu,  
L.-M. Yang,\* Y. Song\* — 10351 – 10354

A Selenium-Based Cathode for a High-Voltage Tandem Photoelectrochemical Solar Cell



1: X = CH<sub>2</sub>, O, NTs



**Just plain chiral:** The [7]orthocyclophanes **1**, having an *E*-olefinic ansa chain, exhibit planar chirality at ambient temperature and their stereochemical stabilities are highly dependent upon the embedded X

group in the ansa chain. Inter- and intra-molecular transformations of **1** (where X = NTs) provide a variety of nitrogen-containing chiral molecules in a stereo-specific manner. Ts = 4-toluenesulfonyl.

## Chirality

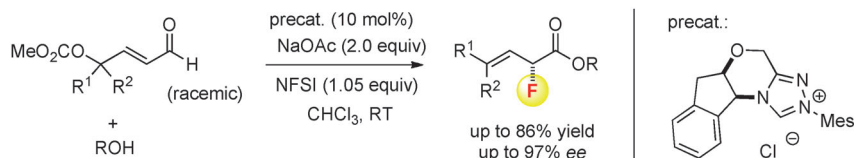
K. Tomooka,\* C. Iso, K. Uehara,  
M. Suzuki, R. Nishikawa-Shimono,  
K. Igawa — 10355 – 10358

Planar-Chiral [7]Orthocyclophanes



## Asymmetric Fluorination

Y.-M. Zhao, M. S. Cheung, Z. Lin,\*  
J. Sun\* 10359–10363



Enantioselective Synthesis of  
 $\beta,\gamma$ -Unsaturated  $\alpha$ -Fluoroesters Catalyzed  
by N-Heterocyclic Carbenes

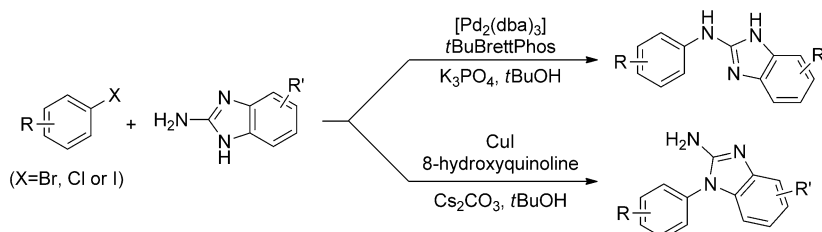
**NHC meets F:** NHC-bound enolates undergo a catalytic asymmetric fluorination reaction to  $\beta,\gamma$ -unsaturated  $\alpha$ -fluoroesters, which are obtained with good efficiency and stereoselectivity (see scheme, NFSI = *N*-fluorobenzenesulfoni-

mide). The strategy overcomes possible challenges, such as fluorination in the  $\gamma$  position and difluorination. Experimental evidence combined with DFT calculations provides insight into the reaction mechanism.

## Synthetic Method

S. Ueda, S. L. Buchwald\* 10364–10367

Catalyst-Controlled Chemoselective  
Arylation of 2-Aminobenzimidazoles



**What N would you like?** The chemoselective and complementary Pd- and Cu-catalyzed N-arylation of 2-aminobenzimidazoles is described. Selective N-arylation of the amino group was achieved with

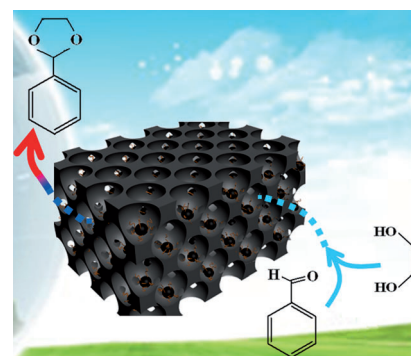
a Pd-catalyzed method, while selective N-arylation of azole nitrogen was achieved with a Cu-catalyzed procedure (see scheme).

## Confined Nanocatalysts

Q. Yue, M. H. Wang, J. Wei, Y. H. Deng,\*  
T. Y. Liu, R. C. Che, B. Tu,  
D. Y. Zhao\* 10368–10372

A Template Carbonization Strategy to  
Synthesize Ordered Mesoporous Silica  
Microspheres with Trapped Sulfonated  
Carbon Nanoparticles for Efficient  
Catalysis

**A facile template** carbonization strategy has been used for the synthesis of ordered mesoporous silica microspheres with sulfonated carbon nanoparticles trapped inside by combining solvent-evaporation-induced aggregating assembly, in situ carbonization, and sulfonation treatments. The obtained SO<sub>3</sub>H-bearing microspheres show an excellent catalytic performance in the condensation reaction of benzaldehyde with ethylene glycol.

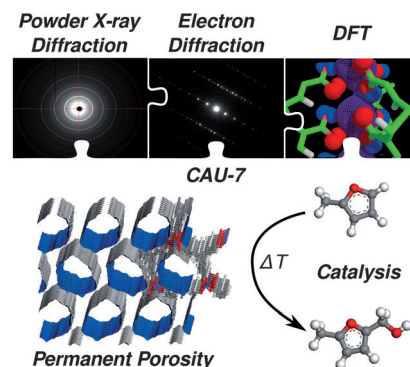


## Metal–Organic Frameworks

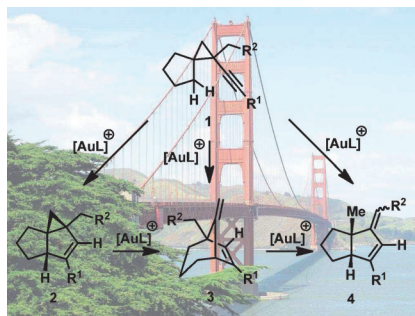
M. Feyand, E. Mugnaioli, F. Vermoortele,  
B. Bueken, J. M. Dieterich, T. Reimer,  
U. Kolb,\* D. de Vos,  
N. Stock\* 10373–10376

Automated Diffraction Tomography for  
the Structure Elucidation of Twinned, Sub-  
micrometer Crystals of a Highly Porous,  
Catalytically Active Bismuth Metal–  
Organic Framework

**A combined approach:** A permanent highly porous bismuth-containing metal–organic framework (CAU-7) has been synthesized and its structure determined by a combination of electron diffraction, Rietveld refinement, and DFT calculations. The compound is catalytically active in the hydroxymethylation of furan (see picture).



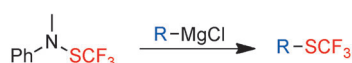
**A Golden Gate:** Alkynylspirocyclopropanes served as a template for the development of gold-catalyzed hydride transfer from unactivated C(sp<sup>3</sup>)–H bonds to electronically neutral alkynes. A variety of interesting carbocyclic structures can be accessed selectively with the appropriate choice of the reaction conditions. Mechanistic studies support a sequential gold-catalyzed cleavage of C–H and C–C bonds.



## Gold Catalysis

J. Barluenga,\* R. Sigüeiro, R. Vicente, A. Ballesteros,\* M. Tomás, M. A. Rodríguez ————— 10377–10381

Gold-Catalyzed Functionalization of Unactivated C(sp<sup>3</sup>)–H Bonds by Hydride Transfer Facilitated by Alkynylspirocyclopropanes



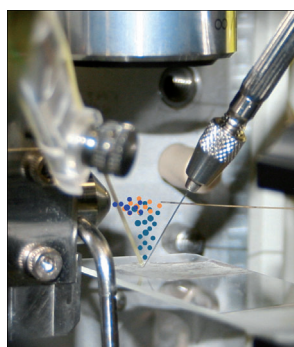
**It's so easy!** Direct trifluoromethanesulfanylation reactions remain difficult to perform because of the lack of reagents that are stable and easy to handle. Trifluoromethanesulfonamides are

reagents which, in combination with readily available Grignard reagents, can be used by those without experience in fluorine chemistry to easily synthesize trifluoromethylthioethers.

## Organometallic Chemistry

F. Baert, J. Colomb, T. Billard\* ————— 10382–10385

Electrophilic Trifluoromethanesulfanylation of Organometallic Species with Trifluoromethanesulfonamides



**Getting to the point:** Cell microdissection and analysis by the title technique was used to study the compartmentalization of metabolites within subcellular domains. Experiments performed on plant epidermal cells imply that there are significant differences between the metabolite composition in the nucleus and the cytoplasm. This technique is applicable to other cell types and may give insight into the mechanisms of disease and drug delivery.

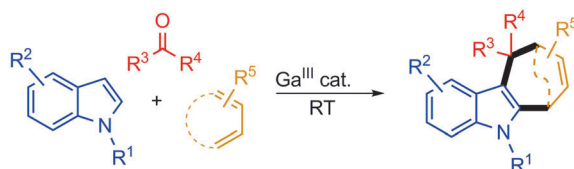
## Analytical Methods

J. A. Stolee, B. Shrestha, G. Mengistu, A. Vertes\* ————— 10386–10389

Observation of Subcellular Metabolite Gradients in Single Cells by Laser Ablation Electrospray Ionization Mass Spectrometry



**Back Cover**



**Direct approach to indoles:** The title reaction generates cyclohepta[b]indole derivatives in a single step at room temperature (see scheme). Exclusion of air or moisture is not required. DFT

calculations support a stepwise cyclization event, and the versatility of the method is demonstrated by providing quick access to a library of cyclohepta[b]indole analogues.

## Heterocycles

X. Han, H. Li, R. P. Hughes, J. Wu\* ————— 10390–10393

Gallium(III)-Catalyzed Three-Component (4+3) Cycloaddition Reactions

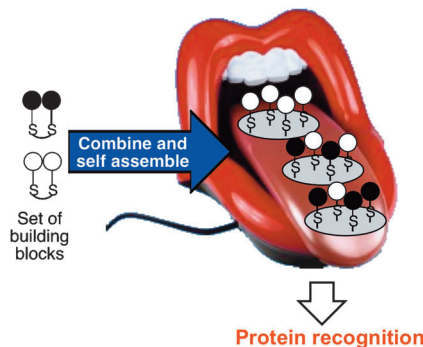


## Biosensors

Y. Hou,\* M. Genua, D. Tada Batista, R. Calemczuk, A. Buhot, P. Fornarelli, J. Koubachi, D. Bonnaffé,\* E. Saesen, C. Laguri, H. Lortat-Jacob, T. Livache\* — 10394 – 10398



Continuous Evolution Profiles for Electronic-Tongue-Based Analysis



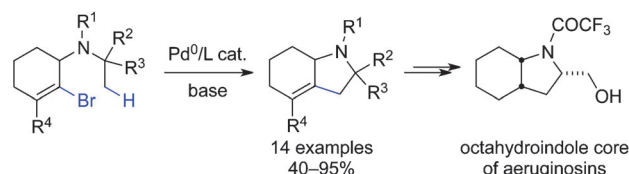
**Licking the problem:** A new type of electronic tongue was constructed by self-assembly on the surface of a surface plasmon resonance (SPR) imaging prism with combinations of simple building blocks. The resulting combinatorial array was used to detect proteins in solution (see scheme) by using SPR imaging to monitor the interactions. The signal from each spot was dependent on its composition and the protein infused, and correlated with the response of its neighbors.

## C–H Activation

J. Sofack-Kreutzer, N. Martin, A. Renaudat, R. Jazzar, O. Baudoin\* — 10399 – 10402



Synthesis of Hexahydroindoles by Intramolecular  $C_{sp^3}$ –H Alkenylation: Application to the Synthesis of the Core of Aeruginosins



**Give me five:** Pd-catalyzed intramolecular  $C_{sp^3}$ –H arylations have been successfully extended to alkenylations. This method shows remarkable selectivity and gives

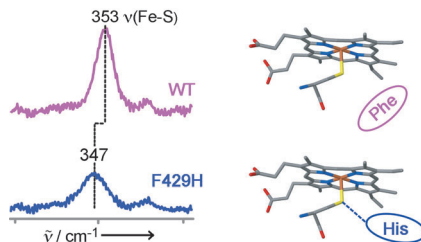
synthetically useful hexahydroindoles, as illustrated with the synthesis of the octahydroindole core of the aeruginosin family of natural products (see picture).

## Proximal Side Control

P. J. Mak, Y. Yang, S.-C. Im, L. A. Waskell,\* J. R. Kincaid\* — 10403 – 10407



Experimental Documentation of the Structural Consequences of Hydrogen-Bonding Interactions to the Proximal Cysteine of a Cytochrome P450



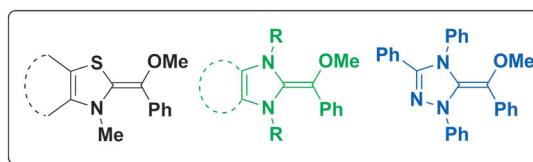
**Reactivity control:** Resonance Raman spectroscopy is used to document, for the first time, a  $6\text{ cm}^{-1}$  decrease of the Fe–S stretch by introducing an H-bond donor into the proximal pocket of a cytochrome P450, which interacts with the cysteine thiolate axial ligand (see picture). The anticipated *trans*-effect on bound exogenous ligands is also confirmed.

## Organocatalysis

B. Maji, H. Mayr\* — 10408 – 10412



Structures and Reactivities of O-Methylated Breslow Intermediates



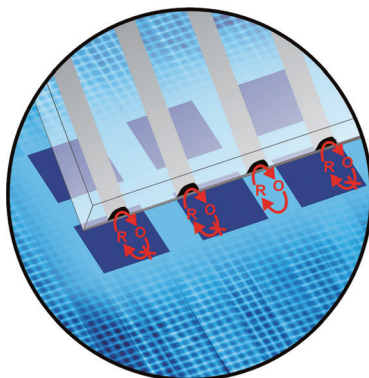
**As close as you can get:** Since Breslow intermediates usually exist in their keto form, their O-protected tautomers may be considered as their closest isolable rela-

tives. A series of these compounds have been synthesized, their structures determined, and the kinetics of their reactions with electrophiles investigated.

- Syntheses
- Structures
- Reactivities



Reagents were generated locally on an array of eight individually addressable electrodes in order to modify self-assembled monolayers. Since the array was manufactured in a soft polymer material, it can have mechanical contact with a delicate sample without inducing defects. Lengthy leveling procedures are not necessary and the scan times can be shortened.



### Self-Assembled Monolayers

A. Lesch, B. Vaske, F. Meiners,  
D. Momotenko, F. Cortés-Salazar,  
H. H. Girault,  
G. Wittstock\* \_\_\_\_\_ **10413–10416**

Parallel Imaging and Template-Free  
Patterning of Self-Assembled Monolayers  
with Soft Linear Microelectrode Arrays



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on [www.angewandte.org](http://www.angewandte.org)  
(see article for access details).



A video clip is available as Supporting  
Information on [www.angewandte.org](http://www.angewandte.org)  
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## Angewandte Addition

The authors of this Communication wish to add the following acknowledgement:

“[\*\*] Financial support from the Deutsche Forschungsgemeinschaft is gratefully acknowledged.”

Reaction of Frustrated Lewis Pairs with  
Conjugated Ynones—Selective  
Hydrogenation of the Carbon–Carbon  
Triple Bond

B.-H. Xu, G. Kehr, R. Fröhlich,  
B. Wibbeling, B. Schirmer, S. Grimme,  
G. Erker\* \_\_\_\_\_ **7183–7186**

*Angew. Chem. Int. Ed.* **2011**, *50*

DOI: 10.1002/anie.201101051

# Angewandte Corrigendum



## The Benzyne Aza-Claisen Reaction

A. A. Cant, G. H. V. Bertrand,  
J. L. Henderson, L. Roberts,  
M. F. Greaney\* — 5199–5202

Angew. Chem. Int. Ed. 2009, 48

DOI: 10.1002/anie.200901410

Compounds **14a**, **14b**, and **14c** in Table 3 of this communication were incorrectly reported as having the alkene *E* configuration. The correct configuration is *Z*. The correct table is shown below and a revised Supporting Information accompanies this corrigendum. The authors apologize for this mistake.

**Table 3:** Synthesis of medium-ring amines using the benzyne aza-Claisen rearrangement.<sup>[a]</sup>

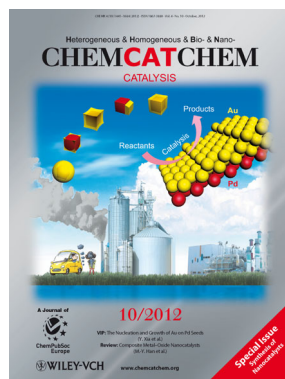
Entry	Amine	Product	Yield [%] <sup>[b]</sup>
1			41
2 <sup>[c]</sup>			40
3			28

[a] Reaction conditions: *o*-trimethylsilylphenyl triflate (1 equiv), amine (1.5 equiv), and CsF (3 equiv) in toluene (0.75 mL) and MeCN (0.25 mL). Reactions were carried out on a 0.2 mmol scale and were stirred for 24 hours at room temperature and then heated at reflux for 48 hours in a sealed tube. [b] Yield of isolated product. [c] 2 equivalents of *o*-trimethylsilylphenyl triflate to 1 equivalent of amine was used. Bn = benzyl.

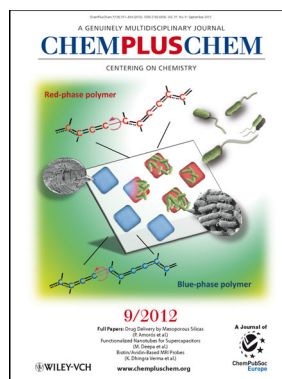
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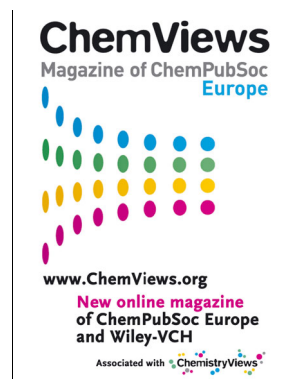
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