## VIP 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 soon:

*A. C. Stelzer, J. D. Kratz, Qi Zhang, H. M. Al-Hashimi**
**RNA Dynamics by Design: Biasing Ensemble towards Ligand Bound States**

*Z. Zhang, Z. Wang, R. Zhang, K. Ding**
**Extremely Efficient Titanium Catalyst for the Enantioselective Cyanation of Aldehydes Using Cooperative Catalysis**

*Q. Wang, M. Zhang, C. Chen, W. Ma, J. Zhao**
**Photocatalytic Aerobic Oxidation of Alcohols on $TiO_2$: The Acceleration Effect of Bronsted Acids**

*Y. Fu, Q. Dai, W. Zhang, J. Ren, T. Pan,* C. He**
**AlkB Domain of Mammalian ABH8 Catalyzes Hydroxylation of 5-Methoxycarbonylmethyluridine at the Wobble Position of tRNA**

*H. Braunschweig,* K. Radacki, A. Schneider*
**Cyclodimerization of an Oxoboryl Complex Induced by *trans*-Ligand Abstraction**

*C. Apostolidis, B. Schimmelpfennig, N. Magnani, P. Lindqvist-Reis,* O. Walter, R. Sykora, A. Morgenstern, E. Colineau, R. Caciuffo, R. Klenze, R. G. Haire, J. Rebizant, F. Bruchertseifer, T. Fanghänel*
**$[An(H_2O)_9](CF_3SO_3)_3$ (An=U–Cm, Cf): Exploring Their Stability, Structural Chemistry, and Magnetic Behavior by Experiment and Theory**

*S. Rizzato, J. Bergès, S. A. Mason, A. Albinati, J. Kozelka**
**Dispersion-Driven Hydrogen Bonding: Theoretically Predicted H–bond between $H_2O$ and Platinum(II) Identified by Neutron Diffraction**

*D. R. Dreyer, H. Jia, C. W. Bielawski**
**Graphene Oxide: A Convenient Carbocatalyst for Facilitating Oxidation and Hydration Reactions**

*H. Amouri,* J. Moussa, A. K. Renfrew, P. J. Dyson, M. N. Rager, L.-M. Chamoreau*
**Metal Complex of Diselenobenzoquinone : Discovery, Structure, and Anticancer Activity**

## Author Profile

*„My favorite subjects at school were chemistry and mathematics.*
*If I could have dinner with three famous scientists from history, they would be Marie Curie, Louis Pasteur, and Alfred Werner …”*
This and more about Kim Renée Dunbar can be found on page 5408.

## Books

## Highlights

### Spider Silk

**How spiders enmesh their prey**: The NMR spectroscopic determination of the C-terminal non-repeat domain of *Araneus diadematus* fibroin 3 (ADF-3), a spider silk protein, was recently reported. At the same time, the X-ray structure determination of the N-terminal non-repeat domain was reported. Both structures provide key insights into fiber formation upon shear stress and pH changes, including the templating effect on fiber morphology.

### Fenton Polishing

G. Z. Chen* ______________ **5413 – 5415**

A Golden Episode Continues Fenton's Colorful Story

**Stimulating new studies** using Fenton's reagent to selectively dissolve asperities and hence knock out catalytic sites on the surface of gold, may present unknown fundamental and applied opportunities; for example, modification of the surfaces of micro- and nanoparticles of gold and other metals to enhance catalytic activity, thereby making the process more affordable (see figure).

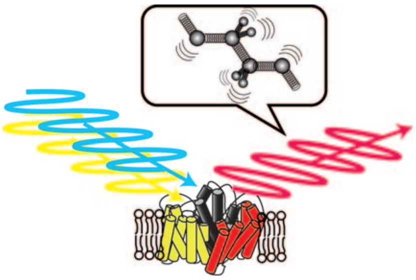
## Minireviews

### IR Spectroscopy on Biomolecules

K. Ataka, T. Kottke,
J. Heberle* ______________ **5416 – 5424**

Thinner, Smaller, Faster: IR Techniques To Probe the Functionality of Biological and Biomimetic Systems

**Good vibes**: Novel spectroscopic methodologies have been devised for the analysis of biomolecules. Recent developments in vibrational spectroscopy meet the need to measure in thinner (single monolayers), smaller (single molecules), and faster (femtoseconds) regimes. In this Minireview applications of surface techniques such as SEIRAS, SFG, and SNIM, and ultrafast techniques such as time-resolved 1D and 2D IR are described.

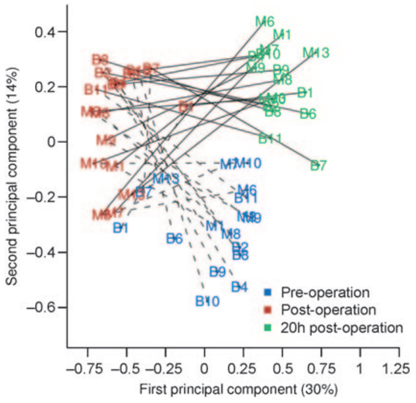


## Reviews

### Metabolites as Biomarkers

W. J. Griffiths, T. Koal, Y. Wang, M. Kohl,
D. P. Enot, H.-P. Deigner* _ **5426 – 5445**

Targeted Metabolomics for Biomarker Discovery



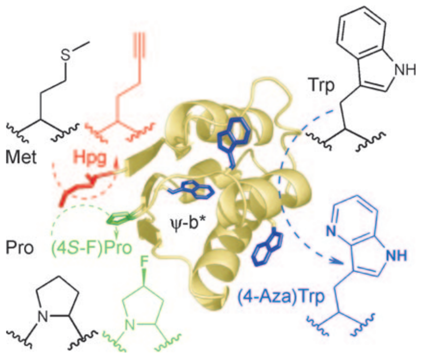
**An indication of interest**: In metabolomics, questions from the areas of pathobiochemistry, systems biology, medicine, and molecular diagnostics can be addressed by using analytical chemistry and statistical data analysis. The focus of this Review is the identification and qualification of biomarkers as well as the mass spectrometric approach to targeted metabolomics.

**For the USA and Canada:**
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Journal Customer Services, John Wiley & Sons Inc., 350 Main St., Malden, MA 02148-5020. Annual subscription price for institutions: US$ 9442/8583 (valid for print and electronic / print or electronic delivery); for 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.

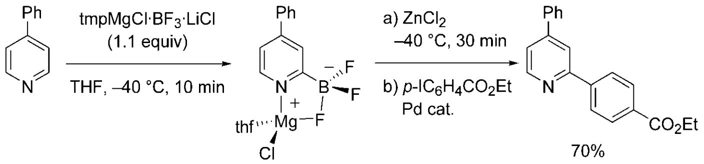
## Communications

### Engineering the Genetic Code

**Three in one**: A new method has been developed for the simultaneous in vivo incorporation of two or three different synthetic amino acids in a protein in a single expression experiment using polyauxotrophic *Escherichia coli* strains. The picture shows the model protein ψ-b* used and the synthetic amino acids incorporated.



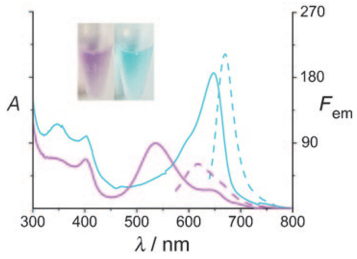
### Frustrated Lewis Pairs



**Efficient and selective**: Frustrated Lewis pairs based on $BF_3{\cdot}OEt_2$ and LiCl-complexed tmpMg or tmpZn amides (tmp = 2,2,6,6-tetramethylpiperidyl) allow the efficient and regioselective metalation of various functionalized N heterocycles (see scheme for examples). Moreover, such metalations carried out in the presence or absence of $BF_3{\cdot}OEt_2$ enable a complete switch of regioselectivity, thus allowing complementary functionalization.

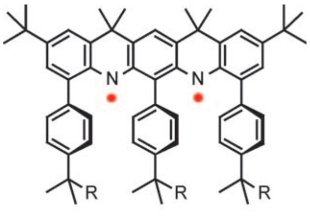
### Photoswitchable Proteins

**Lighting up and changing color**: Genes coding for apoprotein and chromophore biosynthesis from heme were combined in a single fused construct, thereby providing access, in vivo, to biliproteins. Persistently fluorescent biliproteins, as well as red–green photoswitchable biliproteins derived from a cyanobacteriochrome that have well-separated absorption and fluorescence maxima of the two states, were produced in *E. coli*.



### Reactive Intermediates

**Spin cycle**: A high-spin nitrogen-centered (aminyl) diradical with a triplet ($S = 1$) ground state (see picture) has a large singlet-triplet energy gap ($\Delta E_{ST}$). Effective shielding of the reactive aminyl radical centers provides stability at room temperature and maintains the planarity of the π system required for the triplet ground state and large $\Delta E_{ST}$ value. The diradical assembles in solution to form a π-dimer-like structure with weak exchange coupling.



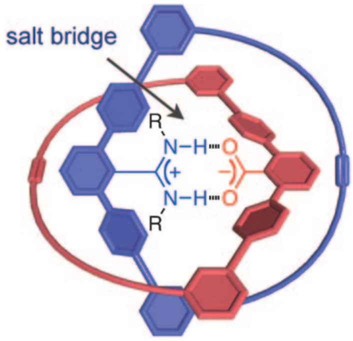
R = $n$-$C_8H_{17}$

# Contents

### Supramolecular Chemistry

Y. Nakatani, Y. Furusho,*
E. Yashima* ______________ **5463 – 5467**

Amidinium Carboxylate Salt Bridges as a Recognition Motif for Mechanically Interlocked Molecules: Synthesis of an Optically Active [2]Catenane and Control of Its Structure



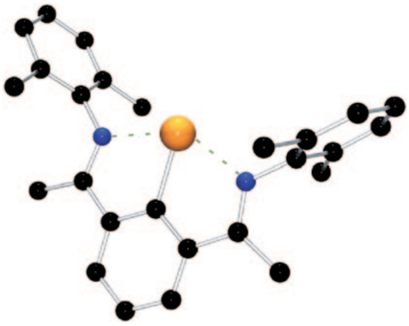
**Salty catenane**: An optically active [2]catenane was synthesized by utilizing an amidinium carboxylate salt bridge (see picture). The relative motion of the two macrocyclic components was completely controlled by an acid/base or Zn$^{2+}$/cryptand couple.

### Main-Group Chemistry

P. Šimon, F. de Proft, R. Jambor,
A. Růžička, L. Dostál* ______ **5468 – 5471**

Monomeric Organoantimony(I) and Organobismuth(I) Compounds Stabilized by an NCN Chelating Ligand: Syntheses and Structures

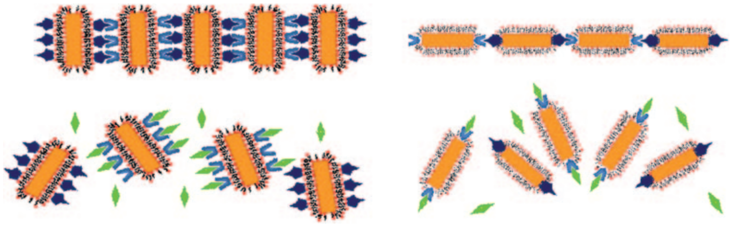
**One on one**: A combination of steric effects and M–N interactions of a rigid NCN pincer ligand allows the isolation and characterization of monomeric stibinidene and bismuthinidene compounds. The structure and bonding was confirmed by crystallographic studies (see picture; Sb or Bi yellow, N blue) and calculations.



### Nanotechnology

L. Wang, Y. Zhu, L. Xu, W. Chen, H. Kuang,
L. Liu, A. Agarwal, C. Xu,*
N. A. Kotov* ______________ **5472 – 5475**

Side-by-Side and End-to-End Gold Nanorod Assemblies for Environmental Toxin Sensing

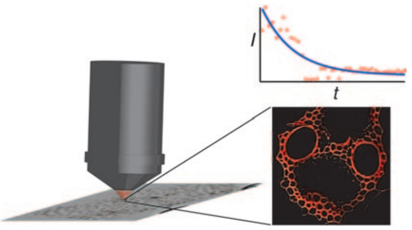


**Parallel or angle parked**: Gold nanorods (see picture) were selectively modified either on the sides or ends using complementary microcystin (MC-LR) antibody and antigen (blue). Fast detection of MC-LR (green) was successfully achieved with these assemblies, and both sensitivity and detection ranges were markedly better for the end-to-end motif (right) than the side-to-side variant (left).

### Chemical Imaging

B. G. Saar, Y. Zeng, C. W. Freudiger, Y. Liu,
M. E. Himmel, X. S. Xie,*
S. Ding* ______________ **5476 – 5479**

Label-Free, Real-Time Monitoring of Biomass Processing with Stimulated Raman Scattering Microscopy

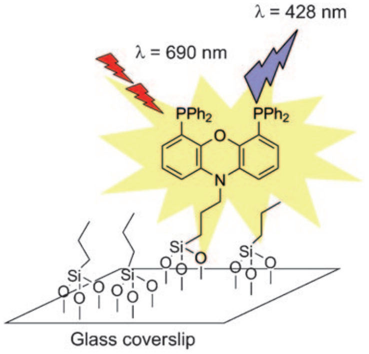


**Label-free "chemical movies"** of lignin and cellulose in fresh plant tissue were recorded during a step in the breakdown of biomass to produce biofuels by using stimulated Raman scattering microscopy. The technique allows the degradation of lignin in the cell wall to be monitored with high sensitivity, sub-micrometer spatial resolution, and high temporal resolution.

## Rational Catalyst Design

F. Marras, A. M. Kluwer,*
J. R. Siekierzycka, A. Vozza, A. M. Brouwer,
J. N. H. Reek* ———— **5480 – 5484**

Phosphorus Ligand Imaging with Two-Photon Fluorescence Spectroscopy: Towards Rational Catalyst Immobilization

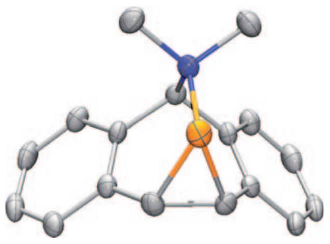


**Spotless catalysts**: Ligand immobilization was studied by two-photon fluorescence microscopy with a fluorescent nixantphos ligand as probe (see picture). In the immobilization process ligand aggregates form in solution and are deposited on the support, where they appear as bright spots in fluorescence images. Preventing their formation leads to “spotless” catalysts with superior catalytic properties.

## Charged Phosphiranes

H. Jansen, F. B. Läng, J. C. Slootweg,
A. W. Ehlers, M. Lutz, K. Lammertsma,*
H. Grützmacher* ———— **5485 – 5488**

Synthesis, Structure, and Reactivity of a Stabilized Phosphiranylium Salt

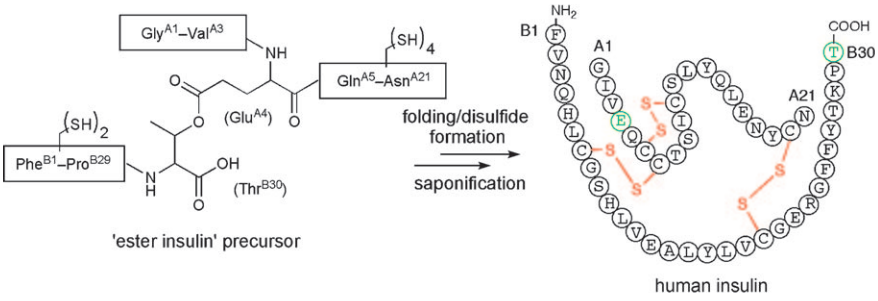


**Charged!** Combining $^{Me}$BABAR-Phos and methyl triflate affords an amino-stabilized phosphiranylium ion (see picture; C gray, N blue, P orange), which undergoes various nucleophilic addition reactions to give P-substituted phosphiranes and an N-heterocyclic carbene stabilized phosphiranylium cation.

## Protein Folding

Y. Sohma,* Q.-X. Hua, J. Whittaker,
M. A. Weiss, S. B. H. Kent* **5489 – 5493**

Design and Folding of [Glu$^{A4}$(O$^{\beta}$Thr$^{B30}$)]Insulin (“Ester Insulin”): A Minimal Proinsulin Surrogate that Can Be Chemically Converted into Human Insulin

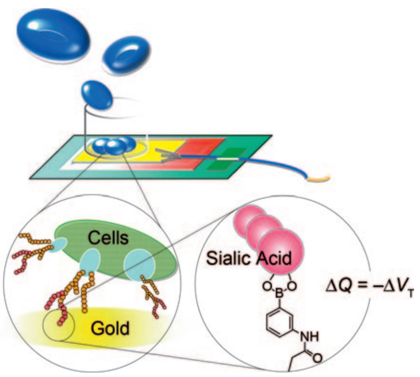


**Insulin folding**: An ester-linked polypeptide proinsulin surrogate folded efficiently with concomitant disulfide bond formation, and saponification gave native insulin having full biological activity. This strategy overcomes the low yield combination of individual insulin A and B chains, and provides a simple and effective approach to the total chemical synthesis of human insulin and its analogues.

## Carbohydrate Detection

A. Matsumoto, H. Cabral, N. Sato,
K. Kataoka, Y. Miyahara* —— **5494 – 5497**

Assessment of Tumor Metastasis by the Direct Determination of Cell-Membrane Sialic Acid Expression



**In a world without labels...** A self-assembled phenylboronic acid monolayer on the surface of a gold electrode enabled the potentiometric detection of cell-membrane sialic acid (SA; see diagram) and differentiation of healthy pneumocytes from metastatic melanoma cells on the basis of altered SA expression. This approach to the diagnosis of tumoral malignancy or the degree of metastasis holds promise for label-free, noninvasive, real-time cytology.

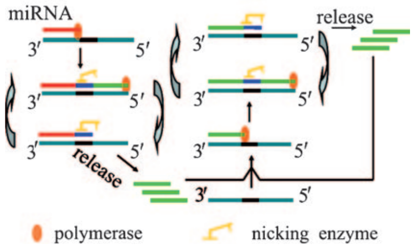
# Contents

### Biomolecule Detection

H. X. Jia, Z. P. Li,* C. H. Liu,
Y. Q. Cheng ———— **5498 – 5501**

Ultrasensitive Detection of microRNAs by Exponential Isothermal Amplification

**Tiny amounts** of a given miRNA (0.1 zmol) can be detected accurately and quantitatively by a real-time method based on an exponential amplification reaction (see picture). The proposed method has a wide dynamic range of more than 10 orders of magnitude, can be carried out within 30 minutes under isothermal conditions, and requires no modified DNA probes. It clearly discriminates miRNA sequences that differ by one base.



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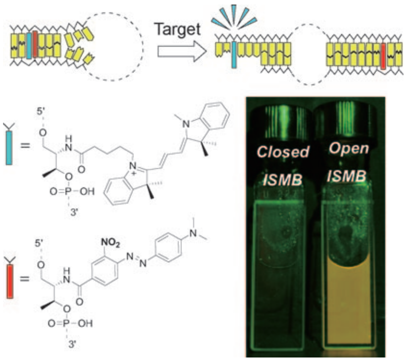
### Coherent Quenching

Y. Hara, T. Fujii, H. Kashida, K. Sekiguchi,
X. G. Liang, K. Niwa, T. Takase, Y. Yoshida,
H. Asanuma* ———— **5502 – 5506**

Coherent Quenching of a Fluorophore for the Design of a Highly Sensitive In-Stem Molecular Beacon

**Excitonic interaction** was utilized to design a highly sensitive in-stem molecular beacon (ISMB) in which both a fluorophore and a quencher on D-threoninols are incorporated as a pseudo base pair (see scheme; optimized combination with Cy3 and modified Methyl Red). Minimization of the difference between $\lambda_{max}$ of the fluorophore and quencher maximized quenching efficiency.



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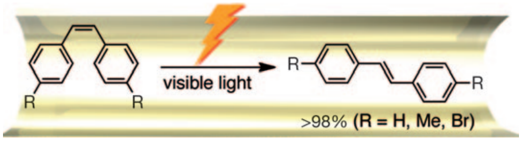
### Photoisomerization

K. Ohara, Y. Inokuma,
M. Fujita* ———— **5507 – 5509**

The Catalytic *Z* to *E* Isomerization of Stilbenes in a Photosensitizing Porous Coordination Network



**One way only**: The *Z*→*E* photoisomerization of stilbene under visible light occurs within a porous coordination network (see picture). The reaction proceeds through the photoexcitation of a charge-transfer complex between the highly electron-deficient ligand and the stilbene in the pore. The in situ formed *E* isomer rapidly exchanges with unreacted *Z* isomer in solution, hence a catalytic amount of the network is sufficient to promote the reaction.

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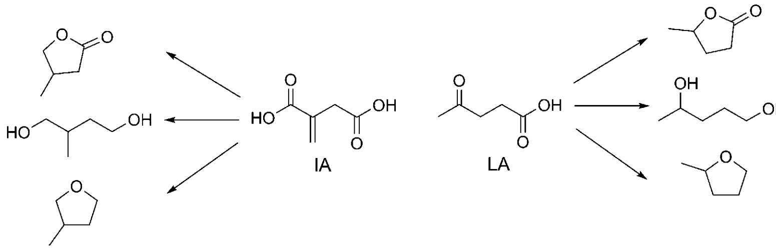
### Biorefinery

F. M. A. Geilen, B. Engendahl,
A. Harwardt, W. Marquardt,
J. Klankermayer,*
W. Leitner* ———— **5510 – 5514**

Selective and Flexible Transformation of Biomass-Derived Platform Chemicals by a Multifunctional Catalytic System

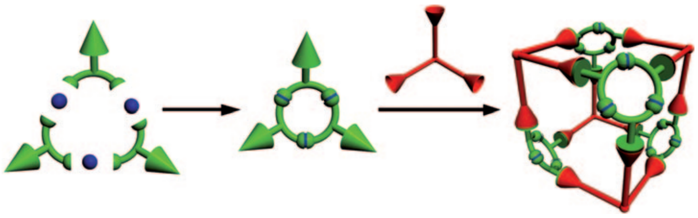


**A sustainable supply chain**: The controlled transformation of the biomass-derived platform compounds levulinic acid (LA) and itaconic acid (IA) into the corresponding lactones, diols, or cyclic ethers (see picture) by using a multifunctional molecular catalyst is described.

## Nanostructures

A. Granzhan, T. Riis-Johannessen,
R. Scopelliti, K. Severin* ____ 5515–5518

Combining Metallasupramolecular Chemistry with Dynamic Covalent Chemistry: Synthesis of Large Molecular Cages



**Ru-built cube**: By combining metallasupramolecular chemistry with dynamic covalent chemistry, complex nanostructures can be formed. Large cages are synthesized by reaction of trinuclear metallamacrocycles containing pendant aldehyde groups (see picture; Ru blue, aldehyde linkers green) with triamines (red).

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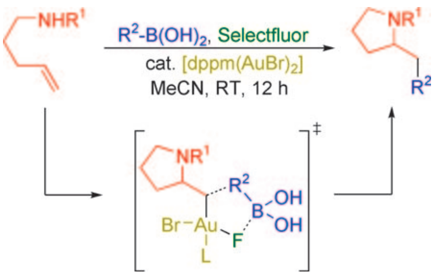
## Gold Catalysis

W. E. Brenzovich, Jr., D. Benitez,
A. D. Lackner, H. P. Shunatona,
E. Tkatchouk, W. A. Goddard, III,
F. D. Toste* ____ 5519–5522

Gold-Catalyzed Intramolecular Aminoarylation of Alkenes: C–C Bond Formation through Bimolecular Reductive Elimination



**Gold-ilocks and the 3 mol% catalyst**: Bimetallic gold bromides allow the room temperature aminoarylation of unactivated terminal olefins with aryl boronic acids using Selectfluor as an oxidant. A catalytic cycle involving gold(I)/gold(III) and a bimolecular reductive elimination for the key C–C bond-forming step is proposed. dppm = bis(diphenylphosphanyl)methane.

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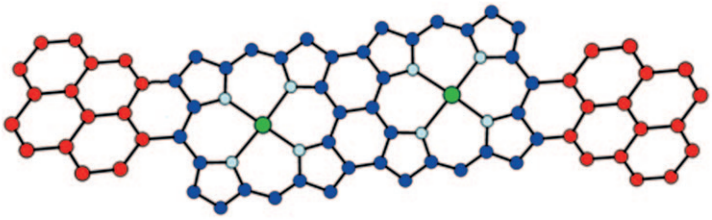
## Fused-Ring Systems

V. V. Diev, K. Hanson,
J. D. Zimmerman, S. R. Forrest,
M. E. Thompson* ____ 5523–5526

Fused Pyrene–Diporphyrins: Shifting Near-Infrared Absorption to 1.5 μm and Beyond



**Sticking together**: Direct fusion of pyrene rings with diporphyrins can be achieved without prior activation of aromatic rings. This simple method gives pyrene–diporphyrin hybrids (see picture, C (pyrene) red, C (porphyrin) dark blue, N light blue, Zn green) with a high near-infrared (NIR) absorption that reaches the wavelengths required for use in telecommunications.

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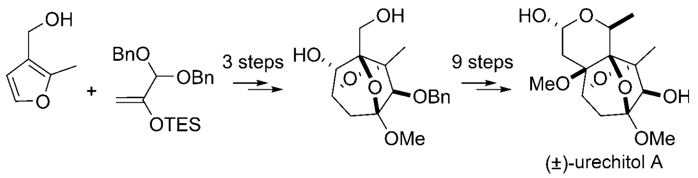
## Total Synthesis

T. Sumiya, K. Ishigami,
H. Watanabe* ____ 5527–5528

Stereoselective Total Synthesis of (±)-Urechitol A

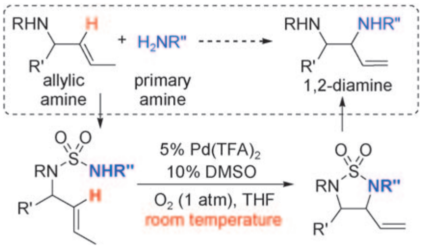


**I want to ride my tricycle**: Urechitol A was synthesized as a racemate by using a [4+3] cycloaddition reaction and methanol assisted intramolecular epoxide opening as the key steps for the efficient construction of the core tricyclic framework. The overall yield was 2.3% over 12 steps. Bn = benzyl, TES = triethylsilyl.

### Oxidative Amination

R. I. McDonald, S. S. Stahl* **5529 – 5532**

Modular Synthesis of 1,2-Diamine Derivatives by Palladium-Catalyzed Aerobic Oxidative Cyclization of Allylic Sulfamides



**Allylic sulfamides** undergo aerobic oxidative cyclization at room temperature, mediated by a $Pd(O_2CCF_3)_2$/DMSO catalyst system in tetrahydrofuran. The cyclic sulfamide products are readily converted into 1,2-diamines, and substrates derived from chiral allylic amines cyclize with very high diastereoselectivity.

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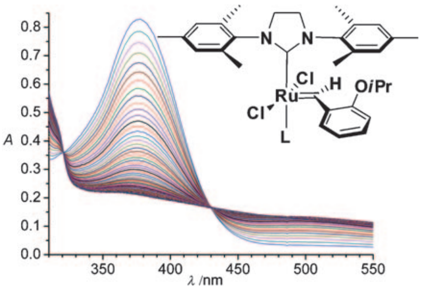
### Homogeneous Catalysis

T. Vorfalt, K.-J. Wannowius, H. Plenio* **5533 – 5536**

Probing the Mechanism of Olefin Metathesis in Grubbs–Hoveyda and Grela Type Complexes

**The more the better**: Kinetic data derived from UV/Vis spectroscopy (see picture) provide conclusive evidence for participation of the olefinic substrate in the rate-limiting step of the initiation reaction of Grubbs–Hoveyda type olefin metathesis catalysts, and for a second olefin-independent step, which is rate-limiting only at very high olefin concentrations.



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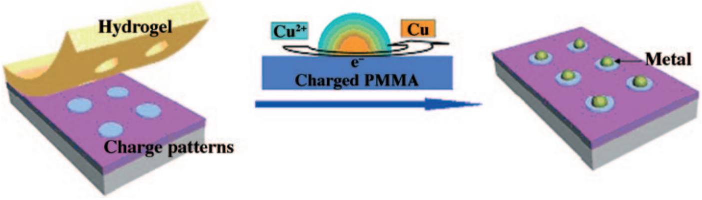
### Electrets

X. Ma, D. Zhao, M. Xue, H. Wang, T. Cao* **5537 – 5540**

Selective Discharge of Electrostatic Charges on Electrets Using a Patterned Hydrogel Stamp



**Paint with water**: A topographically patterned agarose hydrogel stamp transfers and prints water onto uniformly charged PMMA electrets for selectively discharging electrostatic charges. The high-resolution electrostatic charge patterns produced by this simple approach can induce the reduction of metal ions and allow the fabrication of micro- and nanoscale metallic arrays.

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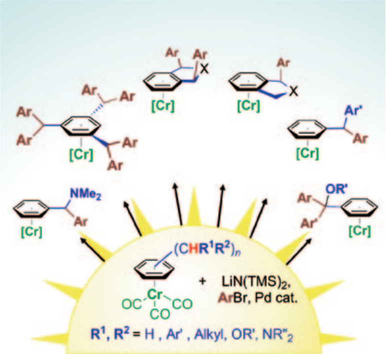
### Polyarylated Methanes

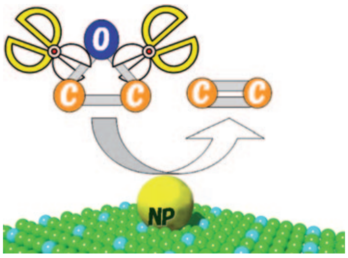
G. I. McGrew, J. Temaismithi, P. J. Carroll, P. J. Walsh* **5541 – 5544**

Synthesis of Polyarylated Methanes through Cross-Coupling of Tricarbonylchromium-Activated Benzyllithiums

**Support group**: Coordinated to the tricarbonylchromium fragment, a typically unstable benzylic organolithium can participate directly in cross-coupling reactions with aryl bromides to form polyarylated methane derivatives (see scheme). $Cr(CO)_3$ assistance leads to reactivity with a variety of coordinated substrates and—given multiple benzylic sites—can effect up to six coupling events per arene.



**Taking the 'O'**: Supported gold and silver nanoparticles (NPs), which are well-known epoxidation catalysts, were found to have intrinsic catalytic ability for the deoxygenation of epoxides into alkenes using alcohol as a reductant (see picture). The selectivity for all the alkenes were over 99%, and an excellent turnover number was achieved. Furthermore, these supported gold and silver nanoparticles were recyclable.



## Heterogeneous Catalysis

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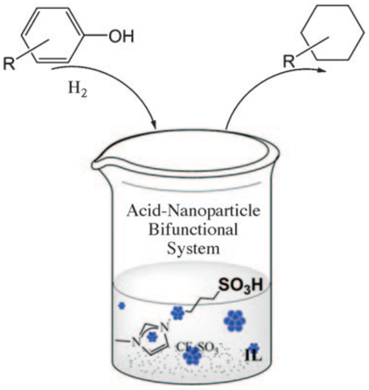
**Oxy-gone in a tandem**: A catalytic system composed of metal nanoparticles (NPs) and a functionalized Brønsted acidic ionic liquid (IL), both of which are immobilized in a nonfunctionalized IL, is highly efficient in upgrading lignin-derived phenolic compounds into alkanes; the hydrogenation and dehydration reactions take place in tandem.



## Nanoparticle Catalysis

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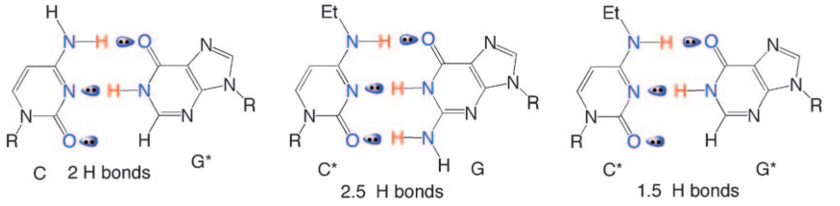

**Discerning in their choice of partner**: The DNA of a self-avoiding molecular-recognition system (SAMRS) binds to natural DNA but not to members of the same SAMRS. Multiplexed PCR with an SAMRS based on 2-aminopurine (A*), 2-thiothymine (T*), 2′-hypoxanthine (G*), and $N^4$-ethylcytosine (C*; see examples) showed the benefits of such systems for clinical analysis, which requires many DNA molecules to interact with target DNA but not with each other.

## Synthetic Biology

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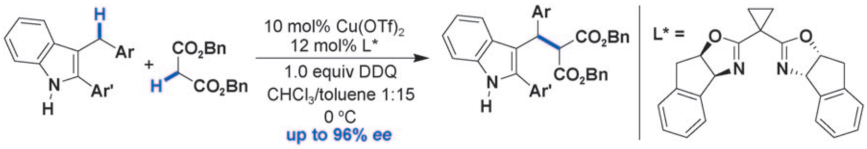


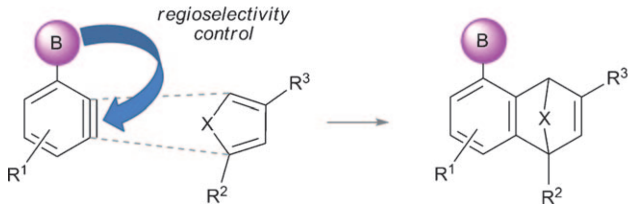
**A highly enantioselective** C–H-activation-based oxidative coupling reaction of 3-arylmethylindole derivatives with dibenzyl malonate by using chiral Lewis acid bonded nucleophiles provided an approach to indole derivatives (see scheme; DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, OTf = trifluoromethanesulfonate).

## C–H Activation

## Arynes

T. Ikawa, A. Takagi, Y. Kurita, K. Saito, K. Azechi, M. Egi, K. Kakiguchi, Y. Kita, S. Akai* ______ **5563 – 5566**

### Preparation and Regioselective Diels–Alder Reactions of Borylbenzynes: Synthesis of Functionalized Arylboronates



**B + [4 + 2]**: 3-Borylbenzynes undergo Diels–Alder reactions with substituted furans and pyrroles to give highly functionalized arylboronic acid derivatives with either good or exclusive regioselectivities (see picture). The effect of the boryl group on the regioselectivity arises from electronic rather than steric effects.

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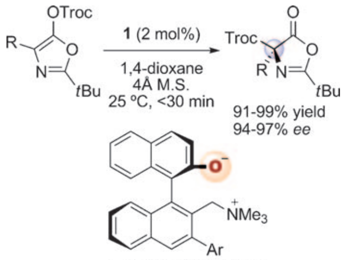
## Nucleophilic Catalysis

D. Uraguchi, K. Koshimoto, S. Miyake, T. Ooi* ______ **5567 – 5569**

### Chiral Ammonium Betaines as Ionic Nucleophilic Catalysts

**Catalyst debut**: The chiral ammonium betaine **1** has been successfully applied to the asymmetric Steglich rearrangement as an ionic nucleophilic catalyst. The catalyzed reaction results in record levels of product enantioselectivity, and has a broad substrate scope. M.S. = molecular sieves, Troc = 2,2,2-trichloroethoxycarbonyl.



**1**, Ar = 3,5-$(CF_3)_2C_6H_3$

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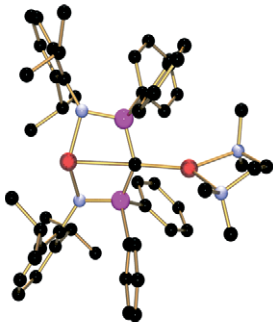
## Planar Four-Coordinate Carbon

O. J. Cooper, A. J. Wooles, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle* ______ **5570 – 5573**

### A Monomeric Dilithio Methandiide with a Distorted *trans*-Planar Four-Coordinate Carbon

**It's plain to see**: A monomeric dilithio methandiide features a distorted *trans*-planar four-coordinate carbon atom. The nature of this compound as established by an X-ray diffraction study (see picture: C black, N blue, P magenta, Li red) and supported by calculations.



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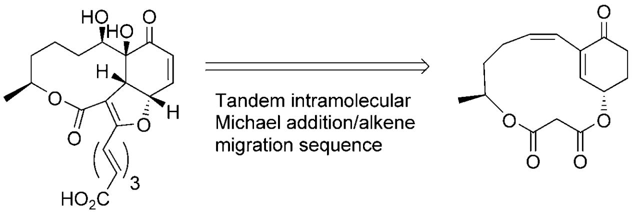
## Natural Product Synthesis

A. R. Burns, G. D. McAllister, S. E. Shanahan, R. J. K. Taylor* ______ **5574 – 5577**

### Total Synthesis and Structural Reassignment of (+)-Dictyosphaeric Acid A: A Tandem Intramolecular Michael Addition/Alkene Migration Approach



(+)-Dictyosphaeric acid A

**The acid test?** The synthetic route to the title compound features a *Z*-selective ring-closing metathesis reaction and an *E*-selective tandem intramolecular Michael addition/alkene migration sequence as the key transformations. The stereochemical configuration of the product was reassigned based on NMR studies.

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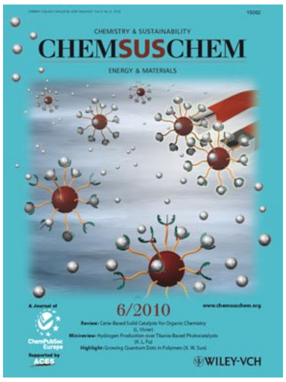

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