



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. M. Scott, A. B. Ricks, M. T. Colvin, M. R. Wasielewski\*  
**Comparing Spin-Selective Charge Transport through Donor-Bridge-Acceptor Molecules having Different Oligomeric Aromatic Bridges**

D. Figgen, A. Koers, P. Schwerdtfeger\*  
**NWHCl: A Small and Compact Chiral Molecule with Large Parity Violation Effects in the Vibrational Spectrum**

C. Costentin, M. Robert, J. Savéant,\* C. Tard  
**Inserting a Hydrogen Bond Relay between Proton Exchanging Sites in Proton-Coupled Electron Transfers**

A. M. Nowicka,\* U. Hasse, G. Sievers, M. Donten, Z. Stojek, S. Fletcher, F. Scholz\*  
**Selective Knock-Out of Active Sites on a Gold Surface**

Q. Liu, G. Li, J. He, J. Liu, P. Li, A. Lei\*  
**Palladium-Catalyzed Aerobic Oxidation and Carbonylation of Arylboronate Esters under Mild Conditions**

A. C. Filippou,\* O. Chernov, K. W. Stumpf, G. Schnakenburg  
**Metal-Silicon Triple Bonds: The Molybdenum Silylidyne Complex  $[\text{Cp}(\text{CO})_2\text{Mo}=\text{SiR}]$**

K. Meister, J. Niesel, U. Schatzschneider,\* N. Metzler-Nolte,\* D. A. Schmidt, M. Havenith\*  
**Metal-Carbonyl Complexes as a Method for Label-Free Live-Cell Imaging by Raman Microspectroscopy**

A. C. M. Ferreón, C. R. Moran, J. C. Ferreón, A. A. Deniz\*  
**Parkinson's-Related Mutation Alters the  $\alpha$ -Synuclein Folding Landscape**



R. Huisgen



D. Guldi



S. Buchwald

## News

Organic Chemistry:  
 Huisgen Honored \_\_\_\_\_ 2658

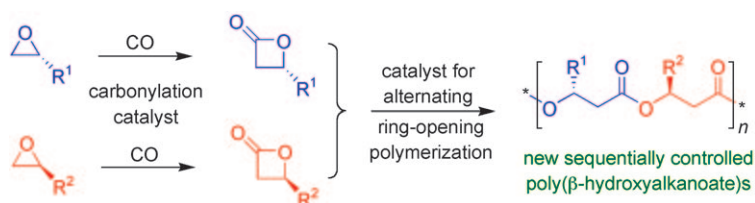
Physical Chemistry:  
 Guldi Awarded \_\_\_\_\_ 2658

Synthetic Methods:  
 Prize for Buchwald \_\_\_\_\_ 2658

Comprehensive Organic Name Reactions and Reagents Zerong Wang

## Books

reviewed by L. Hintermann \_\_\_\_\_ 2659



**Smart catalysts for new materials:** A syndiospecific yttrium catalyst that operates by a chain-end-control mechanism enabled the highly alternating ring-opening polymerization of a mixture of two different enantiomerically pure 4-substi-

tuted  $\beta$ -propiolactones of opposite absolute configuration (see scheme). This strategy offers access to original sequentially controlled poly( $\beta$ -hydroxyalkanoate)s.

## Highlights

### Polymerization Catalysis

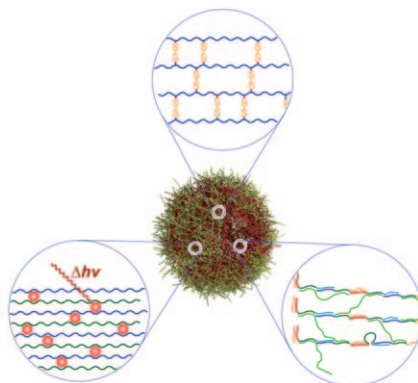
J.-F. Carpentier\* \_\_\_\_\_ 2662 – 2663

Exploitation of a Chain-End-Control Mechanism for the Synthesis of Alternating Copolymers

## Polymer Carriers

A. P. R. Johnston, G. K. Such,  
F. Caruso\* \_\_\_\_\_ 2664 – 2666

Triggering Release of Encapsulated Cargo



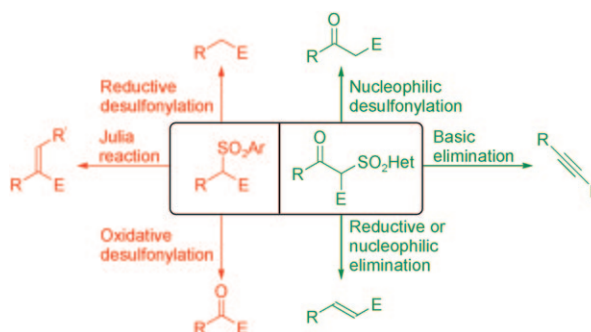
**Specific stimuli** can be used to trigger the release of cargo encapsulated in polymer carriers in applications ranging from drug delivery to catalysis. Current approaches can be categorized in two classes: application of an external stimulus, such as light, and exploitation of environmental changes, such as chemical and enzymatic degradation (see picture).

## Minireviews

### Asymmetric Catalysis

M. Nielsen, C. B. Jacobsen, N. Holub,  
M. W. Paixão,  
K. A. Jørgensen\* \_\_\_\_\_ 2668 – 2679

Asymmetric Organocatalysis with  
Sulfones



**Sulfone groups play** a significant role in asymmetric organocatalysis, which has become a powerful tool for the synthesis of optically active compounds. Sulfones have become important substrates in

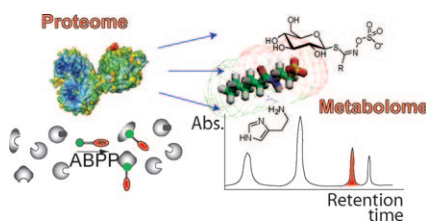
organocatalysis because of their ability to generate both nucleophilic and electrophilic reaction partners, and because they serve as a precursor to many functional groups (see scheme; E = electrophile).

## Reviews

### Proteomics/Metabolomics

T. Böttcher, M. Pitscheider,  
S. A. Sieber\* \_\_\_\_\_ 2680 – 2698

Natural Products and their Biological  
Targets: Proteomic and Metabolomic  
Labeling Strategies



**A marked profile:** Various methods have been developed in the field of proteomics and metabolomics in recent years to understand the action and function of proteins and small metabolites in organisms. These methods enable the identification of the targets of natural products in complex proteomes, the characterization of protein activity, and the determination of the function of specific metabolites.

**For the USA and Canada:**  
ANGEWANDTE CHEMIE International  
Edition (ISSN 1433-7851) is published weekly  
by Wiley-VCH, PO Box 191161, 69451 Wein-  
heim, 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 POST-  
MASTER: send address changes to *Angewandte  
Chemie*, Journal Customer Services, John  
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MA 02148-5020. Annual subscription price for  
institutions: US\$ 9442/8583 (valid for print and  
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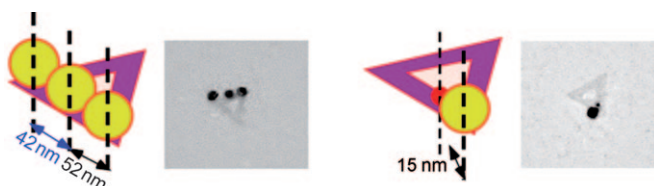
## Communications

### DNA Templates



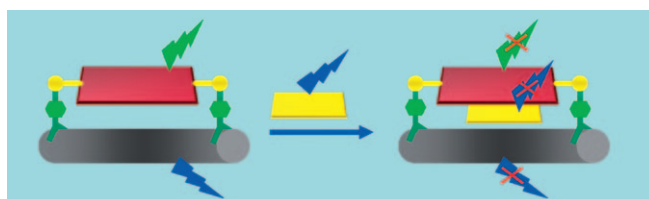
S. Pal, Z. Deng, B. Ding, H. Yan,\*  
Y. Liu\* 2700 – 2704

DNA-Origami-Directed Self-Assembly of  
Discrete Silver-Nanoparticle Architectures



**Noble decoration:** DNA origami nanostructures (purple) were utilized as spatially addressable templates to organize noble-metal nanoparticles of silver (yellow

balls) and gold (red ball) into well-defined discrete architectures (see examples of nanostructure designs and TEM images of the assembled structures).



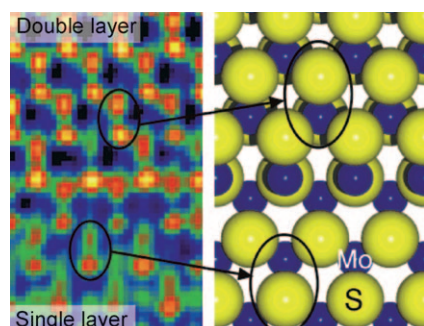
**Pickpocket:** Perylene can be detected by inorganic-organic nanomaterials comprising ZnO nanorods (gray cylinder) and perylene diimide derivatives (red rectangle). Intercalation of perylene (yellow

rectangle) in a molecular pocket at the inorganic-organic interface results in fluorescence quenching of the three components with a detection limit as low as  $10^{-12}$  M.

### Molecular Recognition

H. Liu,\* Z. Zuo, Y. Guo, Y. Li,  
Y. Li\* 2705 – 2707

Supramolecular Interactions at the  
Inorganic-Organic Interface in Hybrid  
Nanomaterials

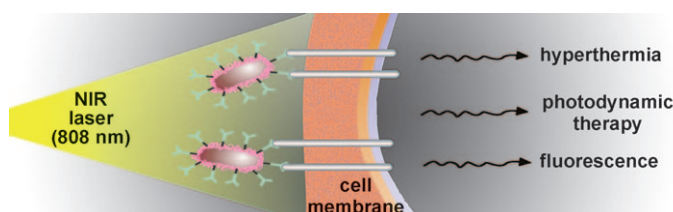


**Close up:** The atomic arrangement of industrial-style MoS<sub>2</sub> nanocatalysts can be scrutinized by using single-atom-sensitive electron microscopy (see picture). This technique, which provides an excellent agreement between simulation and experiment, allows element detection in compound materials and permits the type and the concentration of the catalytically important edge sites to be estimated.

### High-Resolution Microscopy

C. Kisielowski, Q. M. Ramasse,  
L. P. Hansen, M. Brorson, A. Carlsson,  
A. M. Molenbroek, H. Topsøe,  
S. Helveg\* 2708 – 2710

Imaging MoS<sub>2</sub> Nanocatalysts with Single-  
Atom Sensitivity



**The best of three worlds:** Gold nanorods coated with poly(styrene-*alt*-maleic acid) (see picture; pink), the photosensitizer indocyanine green (black), and antibodies (green “Y”) serve not only as photody-

namic therapy and hyperthermia agents to destroy malignant cells, but they also act as optical contrast agents to simultaneously monitor cells by imaging in the near-IR region.

### Nanotechnology

W. S. Kuo,\* C. N. Chang, Y. T. Chang,  
M. H. Yang, Y. H. Chien S. J. Chen,  
C. S. Yeh\* 2711 – 2715

Gold Nanorods in Photodynamic Therapy,  
as Hyperthermia Agents, and in Near-  
Infrared Optical Imaging





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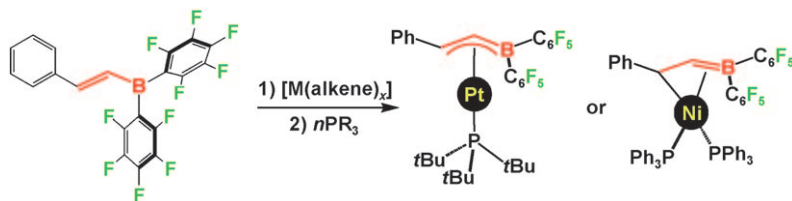
E. Amouyal, M. Che,  
F. C. De Schryver,  
A. R. Fersht, P. Göllitz,  
J. T. Hynes, J.-M. Lehn

## Topics

catalysis, biochemical imaging,  
chemical biology, bionanotechnology,  
proteomics, spectroscopy, solar cells



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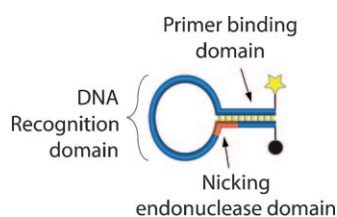
**Anyone for pi?** The vinylborane  $\text{PhHC}=\text{CH-B}(\text{C}_6\text{F}_5)_2$  reacts with zero-valent Group 10 transition-metal precursors to form  $\eta^3$ -vinylborane complexes. The platinum tri-*tert*-butylphosphine complex

exhibits an  $\eta^3$ -borataallyl-like coordination mode whereas the nickel bis(triphenylphosphine) complex tends towards alkyl/borataalkene coordination.

### Vinylborane Complexes

K. B. Kolpin,  
D. J. H. Emslie\* — 2716–2719

$\eta^3$ -Vinylborane Complexes of Platinum and Nickel: Borataallyl- and Alkyl/Borataalkene-Like Coordination Modes



**Not bad at all:** A simple biological circuit composed of two integrated molecular switches was developed for the detection and amplification of a specific nucleic acid in a biological extract. The nucleic acid is recognized by a molecular beacon, then a DNA polymerase and nicking endonuclease are used to rapidly amplify the signal for sensitive detection of the nucleic acid.

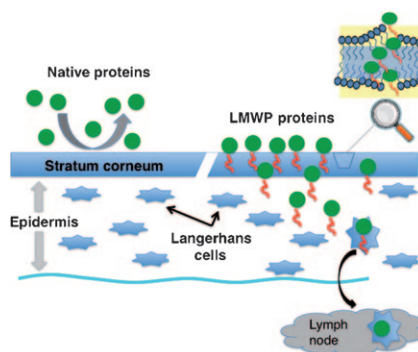
### Nanobiotechnology

A. R. Connolly,\* M. Trau — 2720–2723

Isothermal Detection of DNA by Beacon-Assisted Detection Amplification



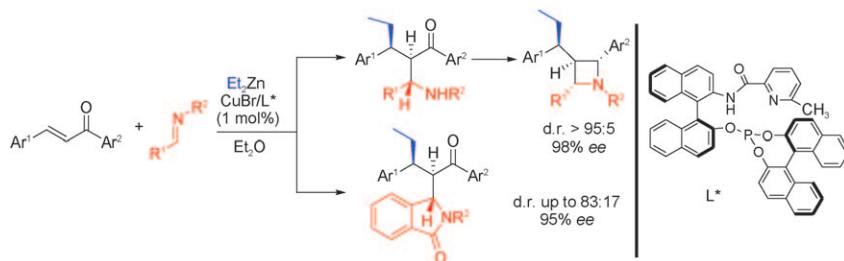
**More than skin-deep:** Synthetic skin-permeable antigens are constructed by conjugation of the cell-penetrating low-molecular-weight protamine (LMWP) peptide to protein antigens through cleavable disulfide bonds. Such artificial antigens can penetrate the stratum corneum barrier (see picture), thereby sensitizing the skin immune system to elicit robust immune responses.



### Drug Delivery

Y. Huang, Y. S. Park, C. Moon, A. E. David,  
H. S. Chung, V. C. Yang\* — 2724–2727

Synthetic Skin-Permeable Proteins Enabling Needleless Immunization



**Michael and Mannich cooperate:** A rapid and reliable approach to highly functionalized chiral isoindolinone and azetidine

derivatives, possessing multiple contiguous stereogenic centers, has been achieved (see scheme).

### Tandem Reactions

S. Guo, Y. Xie, X. Hu, C. Xia,  
H. Huang\* — 2728–2731

Diastereo- and Enantioselective Catalytic Tandem Michael Addition/Mannich Reaction: Access to Chiral Isoindolinones and Azetidines with Multiple Stereocenters



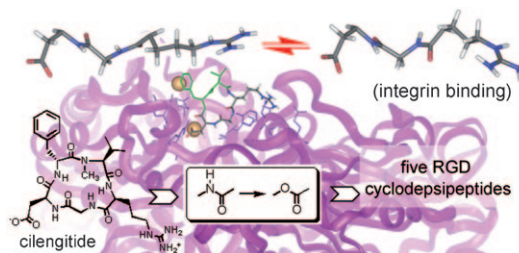


## Bioorganic Chemistry

T. Cupido,\* J. Spengler, J. Ruiz-Rodriguez,  
J. Adan, F. Mitjans, J. Piulats,  
F. Albericio\* 2732–2737



Amide-to-Ester Substitution Allows  
Fine-Tuning of the Cyclopeptide  
Conformational Ensemble



**Without affecting the overall 3D structure**, amide-to-ester backbone substitution (or ester scan) exerts a pronounced influence on the conformational equilibrium of the RGD cyclopeptide cilengitide and its

derivatives (see figure; RGD = Arg-Gly-Asp). The appropriate substitution, which stabilized the receptor-complementary conformations, improved the biological activity of this integrin antagonist.

## Quadruplex Sensors

K. Meguellati, G. Koripelly,  
S. Ladame\* 2738–2742



DNA-Templated Synthesis of Trimethine  
Cyanine Dyes: A Versatile Fluorogenic  
Reaction for Sensing G-Quadruplex  
Formation



**A healthy glow:** Fluorogenic peptide nucleic acids (PNAs) functionalized with indoline derivatives are used to specifically sense G-quadruplex formation. Upon hybridization of both PNAs to the single-stranded flanking arms of quadruplex

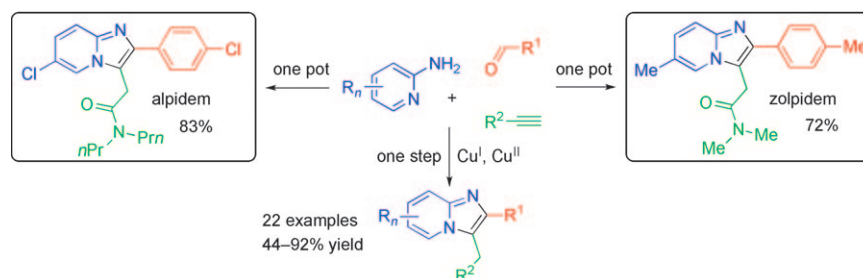
DNA (see scheme), the synthesis of a trimethine cyanine dye is templated. Dye formation can be detected by the appearance of a characteristic fluorescence signal.

## Multicomponent Reactions

N. Chernyak, V. Gevorgyan\* 2743–2746



General and Efficient Copper-Catalyzed  
Three-Component Coupling Reaction  
towards Imidazoheterocycles: One-Pot  
Synthesis of Alpidem and Zolpidem



**Three is not a crowd:** A method for the construction of imidazopyridine, imidazoquinoline, and imidazoisquinoline frameworks has been developed. The

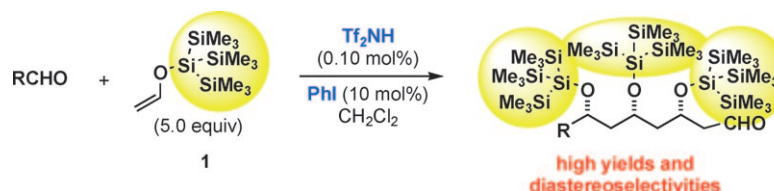
synthetic utility of this method was demonstrated in a highly efficient one-pot synthesis of the drugs alpidem and zolpidem (see scheme).

## Cascade Reactions

B. J. Albert, H. Yamamoto\* 2747–2749

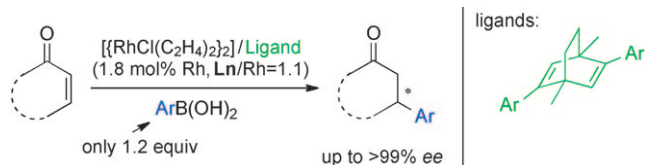


A Triple-Aldol Cascade Reaction for the  
Rapid Assembly of Polyketides



**Triple play:** The title reaction of **1** with simple aldehydes gives 3,5,7-trisilyloxy aldehydes in high yields and diastereoselectivities with extremely low catalyst loading (see scheme). Iodobenzene facil-

itates the third aldol reaction by apparently acting as a Lewis base towards the silyl catalyst. Tf = trifluoromethanesulfonyl.



**On your bi(cycle)ke!** A series of 1,4-dimethyl bicyclic [2.2.2] diene ligands with tunable substitution at the bridge positions was accessed using a lipase resolution and a high yielding six step

sequence (see scheme). The bridgehead methyl groups improve efficiency allowing less aryl boronic acid to be used in the title reaction.

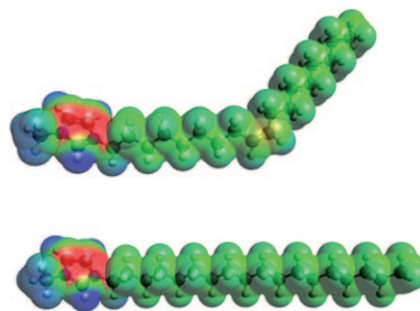
## Asymmetric Catalysis

Y. Luo, A. J. Carnell\* — 2750–2754

Chemoenzymatic Synthesis and Application of Bicyclo[2.2.2]octadiene Ligands: Increased Efficiency in Rhodium-Catalyzed Asymmetric Conjugate Additions by Electronic Tuning



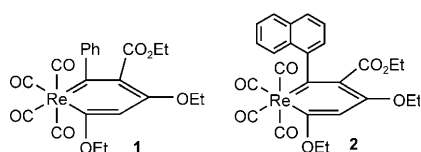
**Defying conventional wisdom:** Ionic liquids (ILs) with long, unsaturated alkyl appendages (see top structure) defy established trends that link long ion-bound alkyl groups to higher melting points. The new ILs are also less viscous than a saturated standard (see bottom structure) at the same temperature. These features parallel those that underpin homeoviscous adaptation in certain organisms and are indirectly supportive of a fluid-mosaic-like nanoscale character.



## Lipidlike Ionic Liquids

S. M. Murray, R. A. O'Brien, K. M. Mattson, C. Ceccarelli, R. E. Sykora, K. N. West,\* J. H. Davis, Jr.\* — 2755–2758

The Fluid-Mosaic Model, Homeoviscous Adaptation, and Ionic Liquids: Dramatic Lowering of the Melting Point by Side-Chain Unsaturation

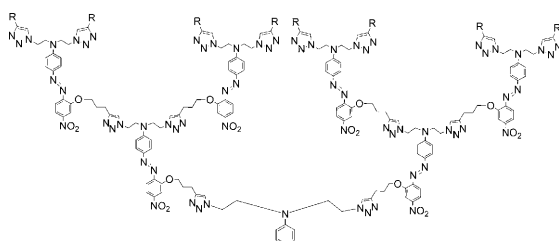


**Do the Maca-Rhena:** Although there are many known stable metallabenzene that contain a late transition metal, there are no examples of the direct observation of metallabenzene that contain an early or middle transition metal. The isolation and structural characterization of air-stable rhenabenzenes **1** and **2** (see scheme) are reported.

## Metallacycles

K. C. Poon, L. Liu, T. Guo, J. Li, H. H. Y. Sung, I. D. Williams, Z. Lin,\* G. Jia\* — 2759–2762

Synthesis and Characterization of Rhenabenzenes



**Click it in:** Forth and fifth generation dendrimers (see structure), bearing 30 and 62 azobenzene chromophore moieties, respectively, are conveniently pre-

pared in satisfactory yields through a combination of divergent and convergent approaches by using the powerful Sharpless “click” reaction.

## Dendrimers

Z. Li, W. Wu, Q. Li, G. Yu, L. Xiao, Y. Liu, C. Ye, J. Qin, Z. Li\* — 2763–2767

High-Generation Second-Order Nonlinear Optical (NLO) Dendrimers: Convenient Synthesis by Click Chemistry and the Increasing Trend of NLO Effects

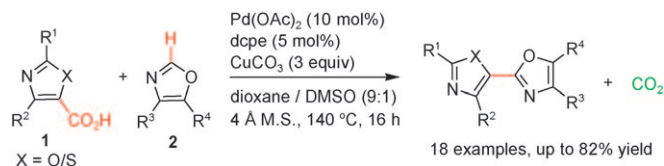


## Decarboxylative C–H Activation

F. Zhang, M. F. Greaney\* — 2768–2771



Decarboxylative C–H Cross-Coupling of Azoles



**Côte d'Azole:** The title reaction demonstrates the use of diverse oxazoles **2** as suitable substrates in cross-coupling reactions with azole-5-carboxylic acids **1** under palladium catalysis in the presence of copper carbonate. The reaction is

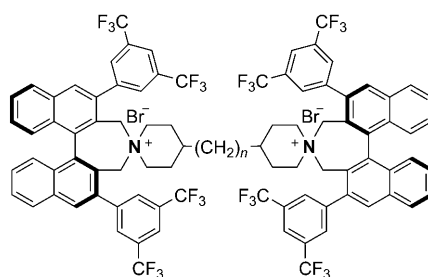
successful for the synthesis of a range of bis(azole)s, and has been applied to the convergent synthesis of challenging poly azoles (dcpe = bis(dicyclohexylphosphino)ethane, DMSO = dimethyl sulfoxide, M.S. = molecular sieves).

## Phase-Transfer Catalysis

M.-Q. Hua, H.-F. Cui, L. Wang, J. Nie, J.-A. Ma\* — 2772–2776



Reversal of Enantioselectivity by Tuning the Conformational Flexibility of Phase-Transfer Catalysts



### Towards perfect asymmetric catalysis:

When binol-derived *N*-spiro quaternary ammonium salts were used as phase-transfer catalysts in the conjugate addition of nitroalkanes to chalcones and its analogues, an intriguing reversal of enantioselectivity was observed. Novel chiral catalysts have been designed and synthesized (see structure).

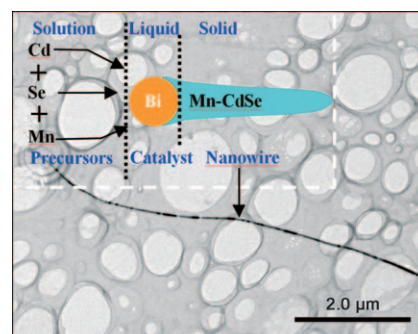
## Doped Nanostructures

Z. Li,\* L. N. Cheng, Q. Sun, Z. H. Zhu, M. J. Riley, M. Aljada, Z. X. Cheng, X. L. Wang, G. R. Hanson, S. Z. Qiao, S. C. Smith, G. Q. Lu\* — 2777–2781



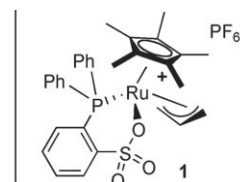
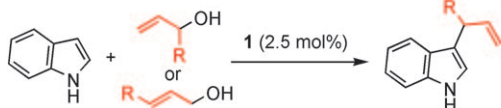
Diluted Magnetic Semiconductor Nanowires Prepared by the Solution–Liquid–Solid Method

**Wiry frame:** Manganese-doped cadmium selenide (Mn–CdSe) colloidal nanowires (see picture) exhibit ferromagnetism and good conductivity without any change to their optical properties. The nanowires are synthesized by a novel solution–liquid–solid approach that offers a low-cost route towards magnetically active quantum wires with excellent potential applications in electronics, photonics, and spintronics.



## Homogeneous Catalysis

B. Sundararaju, M. Achard, B. Demerseman, L. Toupet, G. V. M. Sharma, C. Bruneau\* — 2782–2785



Ruthenium(IV) Complexes Featuring P,O-Chelating Ligands: Regioselective Substitution Directly from Allylic Alcohols

**Branching out:** A new ruthenium(IV) complex (**1**), containing a P,O-chelating ligand, is an efficient precatalyst for

regioselective allylations starting from various allylic alcohol derivatives.



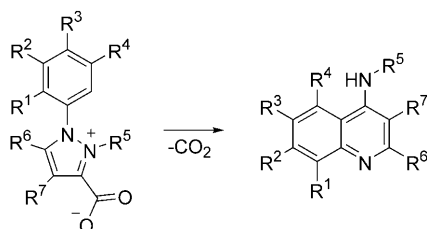


**Hyper-reactive:** A highly reactive, fully fluorinated hypervalent iodine reagent (see formula) mediates new transformations (e.g. the one-pot conversion of sulfides to sulfoximines) and serves as a stoichiometric oxidant in well-established reactions (e.g. C–C bond cleavage and the conversion of alcohols into aldehydes).

### Hypervalent Iodine Compounds

S. Schäfer, T. Wirth\* \_\_\_\_\_ 2786–2789

A Versatile and Highly Reactive Polyfluorinated Hypervalent Iodine(III) Compound



**Thermal decarboxylation** of 1-phenylpyrazolium-3-carboxylates from the meso-meric betaine class of substances leads to pyrazole-N-heterocyclic carbenes, which immediately rearrange to multiply substituted 4-aminoquinolines (see scheme). These species are of interest for the synthesis of heterocycles and pharmacologically active compounds.

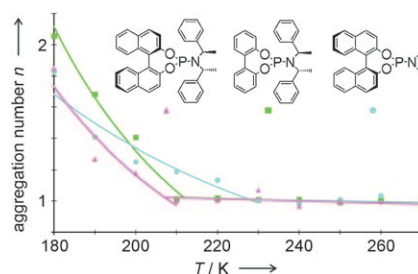
### N-Heterocyclic Carbenes

A. Schmidt,\* N. Münster,  
A. Dreger \_\_\_\_\_ 2790–2793

Functionalized 4-Aminoquinolines by Rearrangement of Pyrazole N-Heterocyclic Carbenes



**DOSY awakening:** The aggregation trends of phosphoramidite transition-metal complexes, which can catalyze highly enantioselective reactions, can be predicted by a DOSY NMR screening of the free ligands (see picture). This method is valuable for catalyst optimization as no structural knowledge of the complexes is required.



### Catalyst Optimization

K. Schober, E. Hartmann, H. Zhang,  
R. M. Gschwind\* \_\_\_\_\_ 2794–2797

<sup>1</sup>H DOSY Spectra of Ligands for Highly Enantioselective Reactions: A Fast and Simple NMR Method to Optimize Catalytic Reaction Conditions



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



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The issues for March 2010 appeared online on the following dates

Issue 10: February 22 • Issue 11: March 3 • Issue 12: March 10 • Issue 13: March 17 • Issue 14: March 23