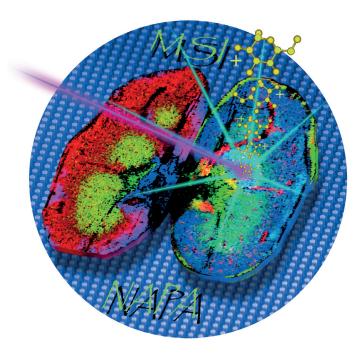
# Molecular tissue imaging ...

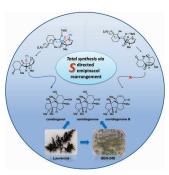


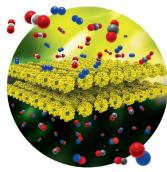


... by mass spectrometry is achieved by using nanostructured substrates. In their Communication on page 4482 ff., A. Vertes and co-workers show how laser desorption ionization from silicon nanopost arrays (NAPA) unlocks the metabolite and lipid distributions in biological tissues. The picture shows the laser pulse interacting with a mouse kidney tissue section and the underlying nanostructure to produce ions for mass spectrometry imaging (MSI).

### **Total Synthesis**

By installing a SPh "directing" group on the expected migratory carbon of the precursor, Y.-Q. Tu and co-workers in their Communication on page 4456 ff. perform the first total synthesis of cyclopiane class tetracyclic diterpenes.



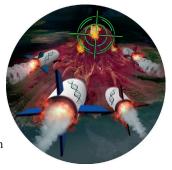


## Core-Shell Nanoparticles

In their Communication on page 4542 ff., H. J. Zhang, R. Jin, S. Song, and co-workers employ the biomolecule L-arginine to obtain high-quality Pd@CeO<sub>2</sub> core@shell nanocomposites with tunable Pd core sizes and shapes.

# **Drug Delivery**

J.-H. Choy et al. report an inorganic layered double hydroxide nanovector with a folic acid conjugated surface that showed siRNA-based cancer therapeutic efficacy in their Communication on page 4582 ff.



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"... The creation of robust biocatalysts with desired properties was previously challenging. Nowadays, knowledge of bioinformatics, protein engineering, molecular biology, high-throughput screening, as well as experience in biocatalysis and organic synthesis, are key skills to identify, develop, and implement novel synthetic routes ..."

Read more in the Editorial by Uwe T. Bornscheuer.

# **Editorial**

U. T. Bornscheuer\* \_\_\_\_\_ 4372 - 4373

Biocatalysis: Successfully Crossing Boundaries

Service

Spotlight on Angewandte's Sister Journals

4388 - 4391



"My favorite author (fiction) is Louis Paul Boon.
The downside of my job is spending too much time away from home..."

This and more about Geert-Jan Boons can be found on page 4392.

# **Author Profile**

Geert-Jan Boons \_\_\_\_\_\_ 4392







M. G. Kanatzidis

# News

Royal Australian Chemical Institute
Awards: C. Yu, J. G. Shapter, and
C. J. Jackson \_\_\_\_\_\_ 4393

Wilhelm Manchot Research
Professorship: M. G. Kanatzidis \_\_\_ 4393

J. G. Shapter

C. J. Jackson



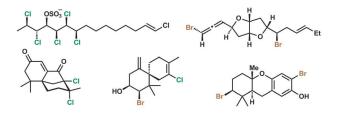


# Reviews

# Synthetic Methods

W.-j. Chung,\*
C. D. Vanderwal\* \_\_\_\_\_ 4396 – 4434

Stereoselective Halogenation in Natural Product Synthesis



With thousands of natural products containing halogen-bearing stereogenic centers, a wealth of methods have been developed for their stereocontrolled introduction in the context of total syn-

thesis. This Review highlights the creative ways in which organic chemists have dealt with the challenges of stereochemically rich, halogenated natural products.

# Hypervalent Iodine Compounds

Y. Li, D. P. Hari, M. V. Vita, J. Waser\* \_\_\_\_\_\_ 4436-4454

Cyclic Hypervalent Iodine Reagents for Atom-Transfer Reactions: Beyond Trifluoromethylation The exceptional reactivity of hypervalent iodine compounds make them privileged reagents in organic synthesis. Of them, cyclic derivatives stand apart because of their enhanced stability. The use of benziodoxol (on) es for trifluoromethylation (Togni's reagents) is now well recognized, but other transformations have also attracted strong interest recently. The progress in the area since 2011 is presented in this Review. Q = 8-aminoquinoline.

QHN 
$$R^{2}$$
  $R^{1}$   $R^{1}$   $R^{1}$   $R^{2}$   $R^{2}$   $R^{2}$   $R^{1}$   $R^{2}$   $R^{2}$ 

# **Communications**

# Natural Products Synthesis

S.-H. Hou, Y.-Q. Tu,\* S.-H. Wang, C.-C. Xi, F.-M. Zhang, S.-H. Wang, Y.-T. Li, L. Liu \_\_ **4456 – 4460**  HO Me Me Me conidiogenone





- · strained 6/5/5/5 tetracyclic framework
- 6-8 consecutive stereocenters
- 4 quaternary centers



Total Syntheses of the Tetracyclic Cyclopiane Diterpenes Conidiogenone, Conidiogenol, and Conidiogenone B



# **Frontispiece**

Three of a kind: The biologically important tetracyclic diterpenes conidiogenone, conidiogenol, and conidiogenone B (see scheme) were constructed by an efficient strategy involving an intramolecular [2+2] cyclization, a regio- and diastereoselective

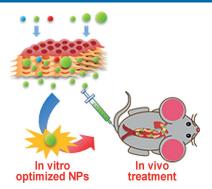
semipinacol rearrangement, and an intramolecular aldol cyclization as key steps. The synthesis also enabled the correction of the absolute configuration of naturally occurring conidiogenone B.

# For the USA and Canada:

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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.





Throw away the crystal ball: Threedimensional human-artery models allowed in vitro prediction of the in vivo behavior of drug-delivery nanoparticles. In vivo experiments with atherosclerotic mice suggested strong biological characteristics and potential treatment effects of nanoparticles optimized in vitro (see picture). This approach is a promising alternative to animal experiments for the optimization of nanomaterials.

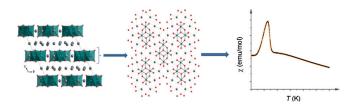
### Nanomaterials

P. Chetprayoon, M. Matsusaki, U. Yokoyama, T. Tejima, Y. Ishikawa,\*

M. Akashi\* \_\_\_\_ \_ 4461 - 4466

Use of Three-Dimensional Arterial Models To Predict the In Vivo Behavior of Nanoparticles for Drug Delivery





Magnetic attraction: β-Ag<sub>3</sub>RuO<sub>4</sub> was synthesized using hydrothermal conditions. The crystal structure is based on a hexagonal close packing of oxygen, and displays tetrameric polyoxoanions [Ru<sub>4</sub>O<sub>16</sub>]<sup>12-</sup> embedded in a 2D trigonal environment.

The Ru<sub>4</sub> diamonds are separated by silver, which suppress the frustrated antiferromagnetic exchange common to trigonal lattices. Strong interanionic antiferromagnetic interactions dominate instead. Key: Ag gray, Ru cyan, O red.

## Antiferromagnetic Materials

B. E. Prasad, P. Kazin, A. C. Komarek, C. Felser, M. Jansen\* \_\_\_\_\_ 4467 - 4471

 $\beta$ -Ag<sub>3</sub>RuO<sub>4</sub>, a Ruthenate(V) Featuring Spin Tetramers on a Two-Dimensional Trigonal













# **Drug Discovery**

K. Qvortrup, T. E. Nielsen\* 4472 - 4475

In-Bead Screening of Hydroxamic Acids for the Identification of HDAC Inhibitors

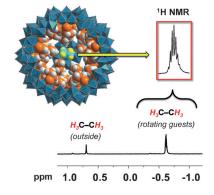


In-bead screening: A one bead-one compound screening format was developed. A combinatorial library of 55 800 hydroxamic acids were synthesized and readily

screened inside polymer beads, which led to the discovery of potent HDAC inhibitors with  $IC_{50}$  values in the nanomolar range.

# In the porous metal oxide capsule

 $[\{Mo^{V_1}_{6}O_{21}(H_2O)_{6}\}_{12}\{(Mo^{V_2}O_4)_{30}(L)_{29}\}_{12}$  $(H_2O)_2$ ]<sup>41-</sup> (L = propionate), the ethyl tails of the endohedrally coordinated ligands form a spherical, hydrophobic shell, while their methyl end groups generate a hydrophobic cavity at the center of the capsule. Whereas  $C_7$  to  $C_3$  alkanes are tightly intercalated between the ethyl tails, two or three rapidly rotating ethane molecules reside in the central cavity.



# Porous Capsules

S. Kopilevich, H. Gottlieb, K. Keinan-Adamsky, A. Müller, I. A. Weinstock\* \_ 4476 - 4481

The Uptake and Assembly of Alkanes within a Porous Nanocapsule in Water: New Information about Hydrophobic Confinement



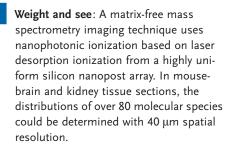


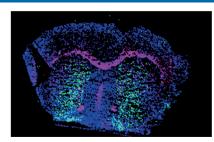
# Mass Spectrometry Imaging

S. A. Stopka, C. Rong, A. R. Korte,
S. Yadavilli, J. Nazarian, T. T. Razunguzwa,
N. J. Morris, A. Vertes\* \_\_\_\_\_ 4482 – 4486



Molecular Imaging of Biological Samples on Nanophotonic Laser Desorption Ionization Platforms







# Front Cover

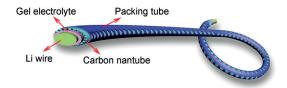


## Wearable Devices

Y. Zhang, L. Wang, Z. Guo, Y. Xu, Y. Wang, H. Peng\* \_\_\_\_\_\_ 4487 – 4491



High-Performance Lithium-Air Battery with a Coaxial-Fiber Architecture



Bendy batteries: A flexible, fiber-shaped lithium-air battery was developed from a gel polymer electrolyte and an aligned carbon nanotube sheet air electrode. It delivered a high specific capacity of

12470 mAh g<sup>-1</sup> and could work for 100 cycles in air. Its electrochemical performance was maintained during and after bending and it could be woven into textiles to power electronic devices.

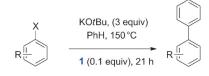
### **Reaction Mechanisms**

J. P. Barham, G. Coulthard, R. G. Kane, N. Delgado, M. P. John,

J. A. Murphy\* \_\_\_\_\_ 4492 – 4496



Double Deprotonation of Pyridinols Generates Potent Organic Electron-Donor Initiators for Haloarene–Arene Coupling Trigger happy: Transition-metal-free couplings of iodoarenes with arenes are triggered by the use of alkali metal alkoxides in the presence of an organic additive. Recently 1 was shown to extend the reaction to aryl bromides. Evidence is reported for the dianion (2), derived from 1, which serves as an electron donor to initiate the reaction. Routes by which electron-poor benzoyl derivatives can be transformed into electron donors to initiate these reactions are also proposed.



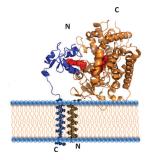
## **Membrane Proteins**

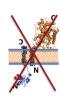
M. Zhang, R. Huang, R. Ackermann, S. Im, L. Waskell, A. Schwendeman,

A. Ramamoorthy\* \_\_\_\_\_ 4497 - 4499

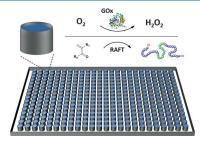


Reconstitution of the Cytb<sub>5</sub>-CytP450 Complex in Nanodiscs for Structural Studies using NMR Spectroscopy Stay on the right side: Co-reconstitution of the cytP450–cyt $b_5$  complex into a lipid membrane environment is achieved using peptide-based nanodiscs containing a planar lipid bilayer, completely obviating the need to use denaturing detergents. NMR experiments revealed effective interactions between the two proteins to form productive complexes where the proteins are properly oriented with respect to each other and to the lipid bilayer.









Micro-RAFTing: By using the enzyme glucose oxidase to effectively remove oxygen, highly controlled polymers are prepared in low volumes under ambient conditions on 384 well plates. This method enables the combinatorial synthesis of polymer libraries for high-throughput screening applications. RAFT = reversible addition—fragmentation chain transfer.

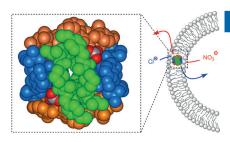
## High-Throughput Screening

R. Chapman, A. J. Gormley, M. H. Stenzel, M. M. Stevens\* 4500 – 4503

Combinatorial Low-Volume Synthesis of Well-Defined Polymers by Enzyme Degassing



A cyclic octapeptide has been shown to fold into a "V-shaped" conformation that allows the selective recognition of anions such as chloride, nitrate, and carbonate. The selective anion recognition process involves the simultaneous assembly of six cyclic peptide subunits and four anions to give a supramolecular cluster that efficiently facilitates transmembrane transport of the anions.



# Anion Recognition

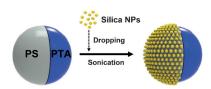


N. Rodríguez-Vázquez, M. Amorín,
I. Alfonso, J. R. Granja\* \_\_\_\_ 4504 – 4508

Anion Recognition and Induced Self-Assembly of an  $\alpha,\gamma$ -Cyclic Peptide To Form Spherical Clusters



Colloidal anisotropies: Bicompartmentalized Janus microparticles were synthesized using seeded polymerization.
Selectively patching the silica nanoparticles onto one of the bulb surfaces allowed the Janus particles to assemble at the oilwater interface with a designated level of adhesion, thus producing structurally stable Pickering emulsions.



# Colloid Interfaces

J. W. Kim, J. Cho, J. Cho, B. J. Park,\*
Y. J. Kim, K. H. Choi,
J. W. Kim\* \_\_\_\_\_\_ 4509 – 4513

Synthesis of Monodisperse Bi-Compartmentalized Amphiphilic Janus Microparticles for Tailored Assembly at the Oil-Water Interface



**Tunable H<sub>2</sub>S supply**: Prodrugs that release hydrogen sulfide upon esterase-mediated cleavage of an ester group followed by lactonization are described (see example). By modifying the ester group and thus its

susceptibility to esterase  $H_2S$  release rates can be tuned. The anti-inflammatory effects of one candidate were examined by studying its ability to inhibit TNF- $\alpha$  production in RAW 264.7 cells.

## H<sub>2</sub>S Release

Y. Zheng, B. Yu, K. Ji, Z. Pan, V. Chittavong, B. Wang\* \_\_\_\_\_\_ 4514 - 4518



Esterase-Sensitive Prodrugs with Tunable Release Rates and Direct Generation of Hydrogen Sulfide



Inside Cover





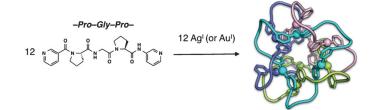




## Macrocycles



Peptide [4]Catenane by Folding and Assembly



It's all about topology: Upon complexation with silver(I) the tripeptide ligand (Pro-Gly-Pro) simultaneously folds into an  $\Omega$ -looped conformation and self-assembles into a discrete peptide [4]catenane

with the crossing number of 12. Within the [4] catenane each of the four equivalent  $M_3L_3$  macrocycles is interlocked with the other three rings with tetrahedral symmetry.



# CO<sub>2</sub> Adsorption

R. S. Patil, D. Banerjee, C. Zhang,
P. K. Thallapally,
J. L. Atwood\* \_\_\_\_\_\_ 4523 – 4526



Selective CO<sub>2</sub> Adsorption in a Supramolecular Organic Framework



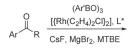
**SOFly, SOFly:** Two supramolecular organic frameworks (SOFs) based on *C*-pentylpyrogallol[4]arene ( $PgC_5$ ) with spacer molecules, such as 4,4'-bipyridine, are prepared. Their highly optimized and symmetric intermolecular hydrogenbonding interactions give robust extended frameworks. One of the evacuated frameworks shows excellent affinity for carbon dioxide over other gases.

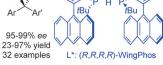
# Asymmetric Catalysis

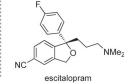
L. Huang, J. Zhu, G. Jiao, Z. Wang, X. Yu, W.-P. Deng,\* W. Tang\* \_\_\_\_\_ 4527 – 4531



Highly Enantioselective Rhodium-Catalyzed Addition of Arylboroxines to Simple Aryl Ketones: Efficient Synthesis of Escitalopram







Wing it: The title reaction has been achieved for the first time with a Rh/(R,R,R,R)-WingPhos catalyst, providing a range of chiral diaryl alkyl carbinols with

excellent *ee* values and yields. The method was applied for a concise synthesis of the antidepressant drug escitalopram.

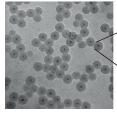
MTBE = *tert*-butyl methyl ether.

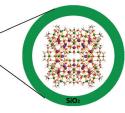
## Magnetic Clusters

D.-P. Liu, X.-P. Lin, H. Zhang, X.-Y. Zheng, G.-L. Zhuang,\* X.-J. Kong,\* L.-S. Long,\* L.-S. Zheng \_\_\_\_\_\_ 4532 – 4536



Magnetic Properties of a Single-Molecule Lanthanide-Transition-Metal Compound Containing 52 Gadolinium and 56 Nickel Atoms

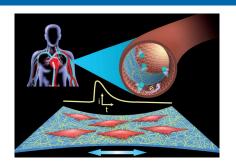




**Molecular magnet**: A single-molecule metal compound of 1a encapsulated in a silica nanosphere  $(1a = [Gd_{52}Ni_{56} - (IDA)_{48}(OH)_{154}(H_2O)_{38}]^{18+})$  was prepared through a facile one-pot microemulsion

method (see picture). The single-mole-cule high-nuclearity lanthanide—transition-metal compound showed experimentally and theoretically magnetic interactions.





Biomedical sensor: A highly controllable strategy has been developed for synthesizing Au nanotubes with a large aspect ratio. The nanotubes were used to construct an effective stretchable electrochemical sensor and to realize real-time monitoring of mechanically sensitive cells and tissues.

## Biosensors

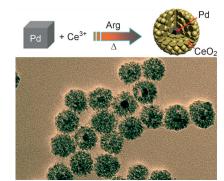


Y.-L. Liu, Z.-H. Jin, Y.-H. Liu, X.-B. Hu, Y. Qin, J.-Q. Xu, C.-F. Fan, W.-H. Huang\* \_\_\_\_ 4537 - 4541



Stretchable Electrochemical Sensor for Real-Time Monitoring of Cells and Tissues

Strictly structured: The biomolecule Larginine triggered CeO<sub>2</sub> crystal growth and self-assembly on Pd nanoparticles. Following the initial formation of cerium-L-arginine precursors on the Pd surface, heat treatment led to the production of high-quality Pd/CeO2 nanostructures (see picture). By controlling the synthetic conditions, it was possible to tune the core size and shape, nanostructure, and sheath thickness of the resulting nanospheres.



# Core-Shell Nanoparticles

X. Wang, Y. Zhang, S. Song, \* X. Yang, Z. Wang, R. Jin,\* H. J. Zhang\* -4542 – 4546



L-Arginine-Triggered Self-Assembly of CeO<sub>2</sub> Nanosheaths on Palladium Nanoparticles in Water





Powerful electrophiles: properly substituted keteniminium ions, simply generated by acidic treatment of the corresponding ynamides, can induce a remarkably efficient [1,5]-hydride shift from

unactivated C-H bonds. This triggers a cationic cyclization which gives, within minutes, highly functionalized tetrahydropyridine and piperidine derivatives.

# Heterocyclic Synthesis





Harnessing the Electrophilicity of Keteniminium Ions: A Simple and Straightforward Entry to Tetrahydropyridines and Piperidines from Ynamides



# cycloaddition cvcloaddition

End of the tether: The first catalytic and highly enantioselective synthesis of tribenzothiepin derivatives was achieved. Two types of intermolecular cycloadditions, either using diphenyl-sulfide-tethered diynes or 2-phenyl sulfanylbenzene tethered diynes with a monoalkyne, led to chiral multisubstituted tribenzothiepins in good to excellent ee values under mild reaction conditions. The present protocol was used to prepare a chiral tribenzoselenepin.

# Heterocycles

Y. Tahara, R. Matsubara, A. Mitake, T. Sato, K. S. Kanyiva, T. Shibata\* \_\_ 4552 - 4556

Catalytic and Enantioselective Synthesis of Chiral Multisubstituted Tribenzothiepins by Intermolecular Cycloadditions





## Synthetic Methods

J. He, Y. Shi, W. Cheng, Z. Man, D. Yang, C.-Y. Li\* \_\_\_\_\_ 4557 – 4561



Rhodium-Catalyzed Synthesis of 4-Bromo-1,2-dihydroisoquinolines: Access to Bromonium Ylides by the Intramolecular Reaction of a Benzyl Bromide and an  $\alpha$ -Imino Carbene

$$R^2$$
 $N = N$ 
 $N - R^1$ 
 $R^3$ 
 $R^3$ 

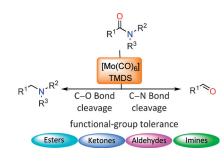
Illustrious ylides: 4-Bromo-1,2-dihydroisoquinolines were obtained conveniently from 4-(2-(bromomethyl)phenyl)-1-sulfonyl-1,2,3-triazoles 1 through the formation of bromonium ylides from  $\alpha$ -imino rhodium carbene intermediates and subsequent rearrangement (see scheme). The versatile products participated as intermediates in a series of one-pot reactions and were converted into valuable polycyclic systems.

## Reduction

F. Tinnis,\* A. Volkov, T. Slagbrand, H. Adolfsson\* \_\_\_\_\_ 4562 – 4566



Chemoselective Reduction of Tertiary Amides under Thermal Control: Formation of either Aldehydes or Amines The choice is yours: [Mo(CO)<sub>6</sub>] is demonstrated to be an efficient catalyst for the chemoselective reduction of tertiary amides in the presence of a large number of reducible groups, including imines and aldehydes. The reaction is tunable by variation of the temperature, and either an amine or an aldehyde can be obtained as the major product from the corresponding amide. TMDS = 1,1,3,3-tetramethyldisiloxane.



# Cross-Coupling

S. I. Arlow, J. F. Hartwig\* \_\_\_ 4567 - 4572



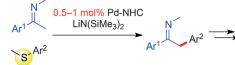
Synthesis of Aryldifluoroamides by Copper-Catalyzed Cross-Coupling

Double the eFFect: A copper-catalyzed coupling of aryl, heteroaryl, and vinyl iodides with  $\alpha$ -silyldifluoroamides is reported. The reaction forms  $\alpha$ ,  $\alpha$ -difluoro- $\alpha$ -aryl amides from electron-rich, electronpoor, and sterically hindered aryl iodides

in high yield and tolerates a variety of functional groups. The aryldifluoroamide products can be further transformed to provide access to a diverse array of difluoroalkylarenes. TMS = trimethylsilyl.

# Palladium Catalysis

K. Gao, H. Yorimitsu,\* A. Osuka \_



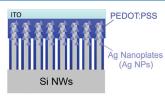


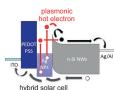
 $\alpha$ -Arylation of Ketimines with Aryl Sulfides at a Low Palladium Catalyst Loading

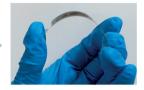
Aryl sulfides, although typically poisonous to transition-metal catalysts, serve as aryl electrophiles in the catalytic  $\alpha$ -arylation of ketimines. Low catalyst loadings (down to 0.5 mol%) of a Pd-NHC complex are

sufficient for efficient arylation.  $\alpha$ -Arylated ketimine products were used to synthesize various azaarenes including 2,3-diarylpyrroles.









Flexible friend: The quantum efficiency of flexible photovoltaic devices in the nearinfrared spectral region has been improved by integrating Si nanowire arrays with plasmonic Ag nanoplates. The Ag nanoplates can directly harvest and

convert NIR light into plasmonic hot electrons for injection into Si, while the Si nanowire arrays allow light trapping. The flexible devices show excellent durability over 50 flexing cycles.

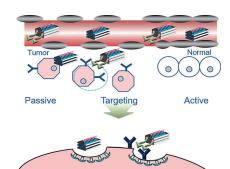
# Light Harvesting



D. Liu, D. Yang, Y. Gao, J. Ma, R. Long, C. Wang, Y. Xiong\* \_\_\_\_\_ 4577 - 4581

Flexible Near-Infrared Photovoltaic Devices Based on Plasmonic Hot-Electron Injection into Silicon Nanowire Arrays





Cancer therapy: An inorganic layered double hydroxide (LDH) nanovector with a folic acid (FA) conjugated surface showed siRNA-based cancer therapeutic efficacy in vivo through receptor-mediated active targeting (see picture). A 1.2-fold higher accumulation of the drug was achieved in tumor tissue, resulting in 3.0fold higher suppression of tumor volume.

# **Drug Delivery**



D.-H. Park, J. Cho, O.-J. Kwon, C.-O. Yun, J.-H. Choy\* \_\_\_\_\_ 4582 – 4586

Biodegradable Inorganic Nanovector: Passive versus Active Tumor Targeting in siRNA Transportation



**Back Cover** 



catalytic deracemization of an organometallic reagent

Converging on a moving target: The first enantioconvergent palladium-catalyzed Fukuyama cross-coupling of racemic benzylic organozinc reagents with thioesters has been developed. The reaction

furnishes acyclic  $\alpha$ , $\alpha$ -disubstituted ketone products in good yields and high enantioselectivities, under mild reaction conditions which prevent racemization of the potentially labile tertiary stereocenter.

# **Cross-Coupling**

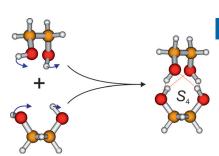
R. Oost, A. Misale, N. Maulide\* \_ 4587 - 4590

Enantioconvergent Fukuyama Cross-Coupling of Racemic Benzylic Organozinc Reagents



Click and lock: By twisting the OH groups in ethylene glycol, the molecule is prepared for a symmetric four-fold hydrogenbond lock with its transient enantiomer, resulting in an outstandingly stable dimer which has so far been elusive in both theory and experiment.

Angew. Chem. Int. Ed. 2016, 53, 4375-4384



# Vibrational Spectroscopy

F. Kollipost, K. E. Otto, M. A. Suhm\* \_\_\_\_\_ 4591 – 4595



A Symmetric Recognition Motif between Vicinal Diols: The Fourfold Grip in Ethylene Glycol Dimer









## Bis(carboranes)

W. Y. Man, D. Ellis, G. M. Rosair, A. I. Welch\* \_\_\_ 4596 – 4599



Carborane Substituents Promote Direct Electrophilic Insertion over Reduction-Metalation Reactions

Take two: Two-electron reduction of 1.1'bis(o-carborane) and subsequent metalation with  $\{Ru(mes)\}^{2+}$  results in a 4,1,8-RuC<sub>2</sub>B<sub>10</sub> species. A further two-electron reduction allows a direct electrophilic insertion reaction promoted by the carborane substituent for the addition of a second metal fragment and the formation of 1,13,2,9-Ru<sub>2</sub>C<sub>2</sub>B<sub>10</sub>. A mechanism is proposed to rationalize the observed fluxionality of the products.



# Heterocycles

C. C. J. Loh, M. Schmid, B. Peters, X. Fang, M. Lautens\* \_\_ 4600 - 4604



Exploiting Distal Reactivity of Coumarins: A Rhodium-Catalyzed Vinylogous Asymmetric Ring-Opening Reaction



**Gamma style**: While  $\gamma$ -functionalization is well established in the setting of aldol, Mannich, and Michael reactions, γ-reactivity is scarce in other reaction classes. By using the newly developed vinylogous reactivity involving the release of ring

strain in the rhodium-catalyzed asymmetric ring opening (ARO) the privileged coumarin motif was incorporated into the hydronaphthalene scaffold enantioselec-

## Synthetic Methods

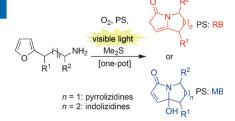
D. Kalaitzakis, M. Triantafyllakis,

M. Sofiadis, D. Noutsias,

G. Vassilikogiannakis\* \_\_\_ **4605 – 4609** 



Photooxygenation of Furylalkylamines: Easy Access to Pyrrolizidine and Indolizidine Scaffolds



Singlet oxygen is able to transform unprotected primary furylalkylamines into the important pyrrolizidine and indolizidine scaffolds. The outcome of the onepot sequences can be readily tailored to need by varying the choice of sensitizer. The synthetic utility of this method was demonstrated in the rapid synthesis of five natural products. PS: Photosensitizer. RB: rose Bengal. MB: Methylene blue.



Supporting information is available on www.angewandte.org (see article for access details).



This article is accompanied by a cover picture (front or back cover, and inside or outside).



A video clip is available as Supporting Information on www.angewandte.org (see article for access details).



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