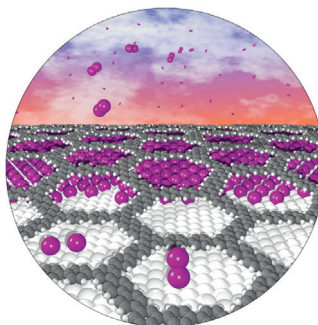


... play an important role in lipid, carbohydrate, and protein metabolism, neural development, as well as cardiovascular, renal, and brain functions. The prohormone L-thyroxine (T4) undergoes monodeiodination by deiodinase enzymes to produce the biologically active hormone T3. G. Mugesh and co-workers describe in their Review on page 7606 ff. the biosynthesis, transport, metabolism, and mechanism of action of thyroid hormones, as well as thyroid-related disorders.

## On-Surface Synthesis

M. Lackinger and co-workers show in their Communication on page 7650 ff. that iodine intercalation enables the post-synthetic decoupling of on-surface-synthesized covalent organic nanostructures from Ag(111).

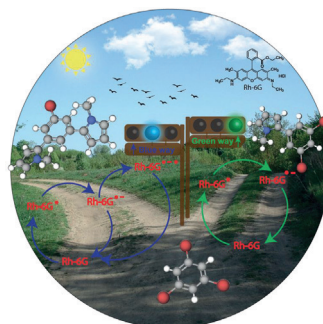


## Carbenoid Compounds

In their Communication on page 7712 ff., V. H. Gessner and S. Molitor report that the replacement of Li by Na or K in alkali metal carbenoids allows for unexpected control of the stability and reactivity of these usually highly reactive species.

## Photocatalysis

In their Communication on page 7676 ff., I. Ghosh and B. König report that the dye Rhodamine 6G shows different redox potentials under different colors of visible-light irradiation, which enables selective photocatalyst activation.



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... The next Angewandte Symposium, which is dedicated to chemical biology and bioorganic chemistry, will take place on July 13, 2016 during the CRSI National Symposium in Chemistry. This is an occasion to reflect on the international nature and societal responsibility of science, and to place the focus on chemical research in India. The number of Communications from India submitted to Angewandte Chemie has increased by 140% from 2010 to 2015, and the number published by as much as 325% ...

Read more in the Editorial by Thisbe Lindhorst.

## Editorial

T. K. Lindhorst\* ————— 7554 – 7555

Chemistry is a Key Science for the Future of India and the World

Spotlight on Angewandte's Sister Journals

7572 – 7575

## Service



"If I could be anyone for a day, I would be Roger Federer at Wimbledon.

My favorite musicians are Joe Bonamassa, David Gilmour, and Victor Wooten ..."

This and more about Peter R. Schreiner can be found on page 7576.

## Author Profile

Peter R. Schreiner ————— 7576 – 7577

## News



P. S. Mukherjee



D. B. Ramachary



T. Govindaraju



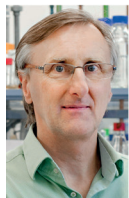
R. Gupta



S. Ghosh



C. M. Reddy



J. Buchner



T. A. M. Gulder



K. Pagel



F. Schüth



T. J. Marks



C. W. Kohlpaintner

CRSI Bronze Medals:

P. S. Mukherjee, D. B. Ramachary,  
T. Govindaraju, and R. Gupta — 7578

Swarnajayanti Fellowships:

S. Ghosh and C. M. Reddy — 7578

Albrecht Kossel Prize: J. Buchner — 7578

DECHEMA Early-Career Researcher

Prize: T. A. M. Gulder — 7579

Mattauch–Herzog Prize: K. Pagel — 7579

Honorary Doctorates:

F. Schüth and T. J. Marks — 7579

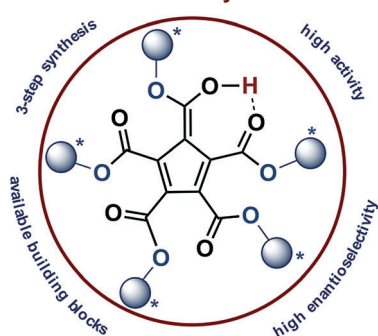
Karl Max von Bauernfeind Medal:

C. W. Kohlpaintner — 7579

## Highlights

## Organocatalysis

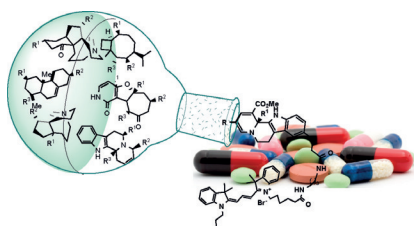
I. Fleischer\* — 7582 – 7584

Chiral Catalyst Design: Cyclopentadiene-  
Based Brønsted AcidsPCCPs: New Generation of Brønsted  
Acid Catalysts

The combination of  $-I$  and  $-M$  effects and the aromaticity of the conjugate base renders the chiral pentacarboxy-substituted cyclopentadienes (PCCPs) acidic. Their convenient synthesis together with substrates derived from the chiral pool and their performance in the tested reactions renders them prodigious candidates to become a new and highly competitive class of chiral Brønsted acid catalysts.

## Minireviews

## Scaffold Diversity

M. Garcia-Castro, S. Zimmermann,  
M. G. Sankar, K. Kumar\* — 7586 – 7605Scaffold Diversity Synthesis and Its  
Application in Probe and Drug Discovery

**Complexity and diversity:** The synthesis of compound libraries with a high degree of scaffold diversity has been addressed by transforming suitable common intermediates into various molecular frameworks or by using natural products as a source of scaffold diversity. In this Minireview, recent developments towards the construction of such libraries and their application in drug and probe discovery are summarized.

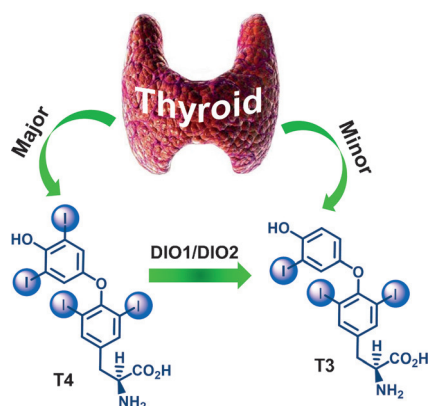
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ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 101161, 69451 Weinheim, Germany. US mailing agent: SPP, PO Box 437, Emigsville, PA 17318. Periodicals postage

paid at Emigsville, PA. US POSTMASTER: send address changes to *Angewandte Chemie*, John Wiley & Sons Inc., C/O The Sheridan Press, PO Box 465, Hanover, PA 17331. Annual subscription price for institutions: US\$ 16.862/14.051 (valid for print and electronic / print or

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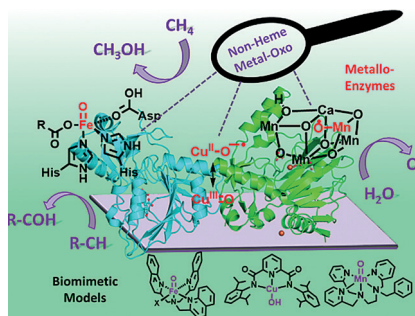


**A picture of health:** Thyroid hormones are essential to control body metabolism, heart rate, neural development, as well as cardiovascular, renal, and brain functions. This Review discusses the chemistry and biology involved in the biosynthesis, plasma transport, metabolic pathways, and receptor-mediated action of thyroid hormones in relation to thyroid related disorders and their treatment.

Front Cover



**High-valent Fe-, Mn-, and Cu-oxo cores** are proposed as reactive intermediates in biological oxidation reactions. The generation of well-characterized model compounds can provide vital insights into the mechanisms of such enzymatic reactions. This Review provides a comprehensive summary of recent advances in biomimetic high-valent metal-oxo complexes related to our understanding of biological systems.

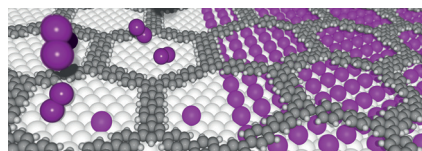


### Metal-Oxo Complexes

X. Engelmann, I. Monte-Pérez,  
K. Ray\* 7632–7649

Oxidation Reactions with Bioinspired Mononuclear Non-Heme Metal-Oxo Complexes

Inside Cover



**The go-between:** Post-synthetic exposure of covalent porous polyphenylene networks synthesized by on-surface polymerization on Ag(111) to iodine vapor leads to detachment through intercalation of a densely packed iodine monolayer. Consequently, the organic nanostructures become decoupled from the strongly interacting metal surface, as evident by changes in both the geometric and electronic structures toward freestanding networks.

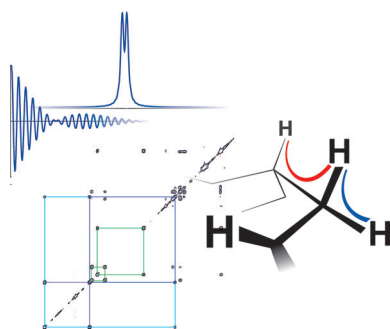
## Communications

### On-Surface Synthesis

A. Rastgoo-Lahrood, J. Björk, M. Lischka,  
J. Eichhorn, S. Kloft, M. Fritton,  
T. Strunskus, D. Samanta, M. Schmittel,  
W. M. Heckl, M. Lackinger\* 7650–7654

Post-Synthetic Decoupling of On-Surface-Synthesized Covalent Nanostructures from Ag(111)

Frontispiece



**A cozy COSY:** The COSY experiment is one of the fundamental two-dimensional NMR experiments. A severe drawback of state-of-the-art implementations is the complex line shape, demanding long data acquisitions. Clean in-phase COSY (CLIP-COSY) combines the unique information from COSY experiments with a simple line shape (as in NOESY-type spectra), and enables rapid acquisition and the combination with homonuclear decoupling.

### NMR Spectroscopy

M. R. M. Koos, G. Kummerlöwe,  
L. Kaltschnee, C. M. Thiele,  
B. Luy\* 7655–7659

CLIP-COSY: A Clean In-Phase Experiment for the Rapid Acquisition of COSY-type Correlations



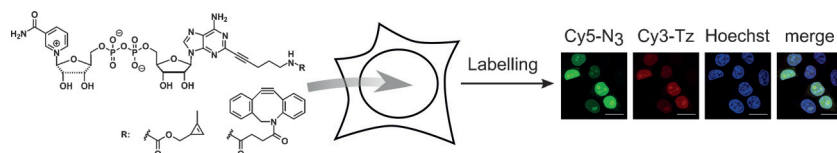


## ADP-Ribosylation

S. Wallrodt, A. Buntz, Y. Wang,  
A. Zumbusch, A. Marx\* — 7660 – 7664



Bioorthogonally Functionalized NAD<sup>+</sup>  
Analogues for In-Cell Visualization of  
Poly(ADP-Ribose) Formation



**Now you see it:** NAD<sup>+</sup> is metabolized and built into poly(ADP-ribose) by ADP-ribosyltransferases, and this PARylation affects various biological processes. Methods for the intracellular visualization of this process are rare and limited. To

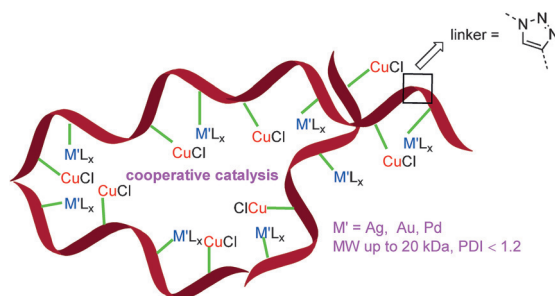
overcome this, new NAD<sup>+</sup> analogues functionalized with bioorthogonal reporter groups were developed and successfully applied to the selective two-color labeling of poly(ADP-ribose) formation in cells.

## Bifunctional Catalysts

W. Wang, L. Zhao, H. Lv, G. Zhang, C. Xia,  
F. E. Hahn,\* F. Li\* — 7665 – 7670



Modular “Click” Preparation of  
Bifunctional Polymeric Heterometallic  
Catalysts



**Clicked into place:** Alternating NHC-metal tethered polymers and heterobimetallic NHC complexes have been obtained by click linkage of complexes bearing NHCs with either *p*-azidophenyl or *p*-ethynyl-

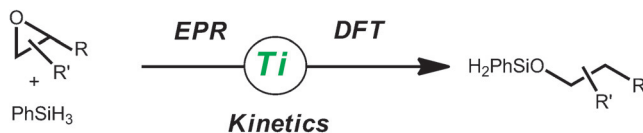
phenyl wingtips. The connection of the NHC-metal units led to active bifunctional catalysts for the alkylation of trifluoromethyl ketones.

## Homogeneous Catalysis

D. S. G. Henriques, K. Zimmer, S. Klare,  
A. Meyer, E. Rojo-Wiechel, M. Bauer,  
R. Sure, S. Grimme, O. Schiemann,\*  
R. A. Flowers II,\*  
A. Gansäuer\* — 7671 – 7675



Highly Active Titanocene Catalysts for  
Epoxide Hydrosilylation: Synthesis,  
Theory, Kinetics, EPR Spectroscopy



**A titanocene-catalyzed** epoxide hydrosilylation was developed that shows high activity, high regio- and diastereoselectivity, unusual kinetics, and an unexpected resting state. The combination of experi-

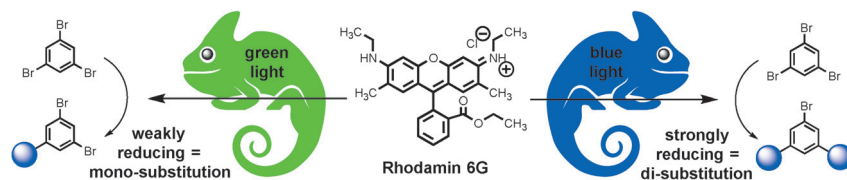
ment and theory permitted catalyst design and elucidation of the mechanism. The reaction provides an efficient access to anti-Markovnikov alcohols from epoxides.

## Photocatalysis

I. Ghosh,\* B. König\* — 7676 – 7679



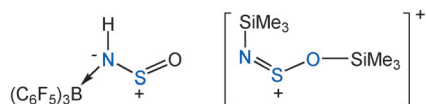
Chromoselective Photocatalysis:  
Controlled Bond Activation through Light-  
Color Regulation of Redox Potentials



**I see your two colors, shining through:** The xanthene dye rhodamine 6G is a moderately reducing photoredox catalyst if irradiated with green light, but provides an high reduction power of

–2.4 V vs. SCE upon blue-light irradiation. This allows control of the selectivity of photocatalytic C–H arylation reactions through changing the color of the light.

## Back Cover

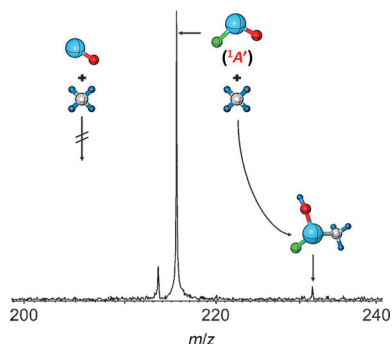


**Non-Standard Object:** Labile NSO species such as  $\text{H-NSO-LA}$  (LA = Lewis acid) and salts containing  $[\text{Me}_3\text{Si-NSO-SiMe}_3]^+$  ions were isolated and fully characterized.

### Main-Group Chemistry

R. Labbow, D. Michalik, F. Reiß,  
A. Schulz,\* A. Villingner — **7680 – 7684**

Isolation of Labile Pseudohalogen NSO Species



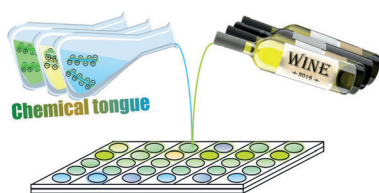
### I get by with a little help from halogens:

The thermal reactions of methane with  $[\text{HfO}]^+$  and  $[\text{XHfO}]^+$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) were investigated by using FT-ICR mass spectrometry complemented by high-level quantum chemical calculations. In contrast to the inertness of  $[\text{HfO}]^+$  towards methane (left; C gray, H blue, Hf turquoise, O red), the closed-shell oxide ions  $[\text{XHfO}]^+$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ) activate the  $\text{H}_3\text{C-H}$  bond to form the insertion products  $[\text{Hf}(\text{X})(\text{OH})(\text{CH}_3)]^+$  (right, X green).

### Gas-Phase Reactions

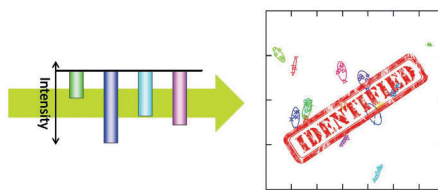
S. Zhou, J. Li, M. Schlangen,  
H. Schwarz\* — **7685 – 7688**

Thermal Activation of Methane by  $[\text{HfO}]^+$  and  $[\text{XHfO}]^+$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) and the Origin of a Remarkable Ligand Effect



**Cheers!** A system consisting of polyelectrolyte complex formed from one cationic and one anionic poly(*para*-phenyleneethynylene) (PPE), together with the simple ionic PPEs, was examined as a new type of array-based sensor. Without any

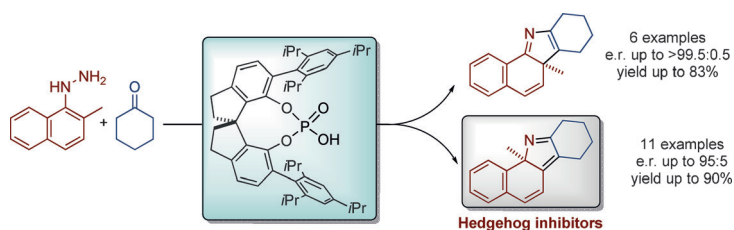
design efforts, these primitive and non-specific sensory elements can be used to differentiate white wines by subjecting the obtained fluorescence-response patterns to linear discriminant analysis.



### Sensors

J. Han, M. Bender, K. Seehafer,  
U. H. F. Bunz\* — **7689 – 7692**

Identification of White Wines by using Two Oppositely Charged Poly(*p*-phenyleneethynylene)s Individually and in Complex



**The versatility of pyrroles:** A Fischer indolization and a [1,5]-alkyl shift were used in the title reaction to obtain enantioenriched 2*H*- or 3*H*-pyrroles. The products could be generated in good to excellent yields and enantiomeric ratios by

using a chiral SPINOL-derived phosphoric acid derivative as catalyst. Biological evaluations revealed the novel 2*H*-pyrroles to be potent inhibitors of the Hedgehog signaling pathway.

### Pyrroles

L. Kötzner, M. Leutzsch, S. Sievers,  
S. Patil, H. Waldmann, Y. Zheng, W. Thiel,  
B. List\* — **7693 – 7697**

The Organocatalytic Approach to Enantiopure 2*H*- and 3*H*-Pyrroles: Inhibitors of the Hedgehog Signaling Pathway



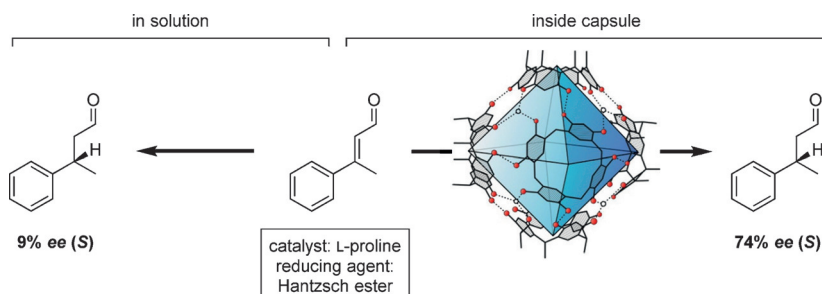


## Host-Guest Systems

T. M. Bräuer, Q. Zhang,  
K. Tiefenbacher\* — 7698 – 7701



Iminium Catalysis inside a Self-Assembled Supramolecular Capsule: Modulation of Enantiomeric Excess



**An accommodating host:** The iminium-catalyzed 1,4-reduction of unsaturated aldehydes can be performed inside a supramolecular host. Only catalytic amounts of the supramolecular capsule

are required. The intermolecular, noncovalent interactions inside the host system dramatically improve enantioselectivity for several amine catalysts.

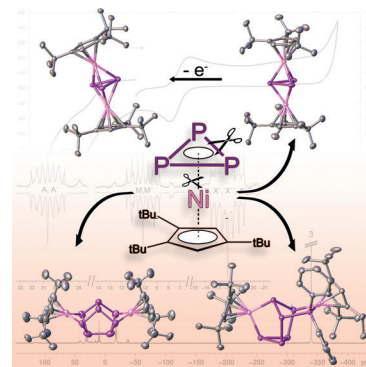
## Phosphorus Ligands

E. Mädl, G. Balázs, E. V. Peresypkina,  
M. Scheer\* — 7702 – 7707



Unexpected Reactivity of  $[(\eta^5-1,2,4-tBu_3C_5H_2)Ni(\eta^3-P_3)]$  towards Main Group Nucleophiles and by Reduction

**Stacking the deck:** The reaction of  $[(\eta^5-1,2,4-tBu_3C_5H_2)Ni(\eta^3-P_3)]$  with potassium leads to the formation of a realgar-like  $P_8$  ligand. Triple-decker sandwich complexes with a  $P_3$  middle deck or unprecedented bicyclic  $P_7$  ligands are formed with nucleophiles.



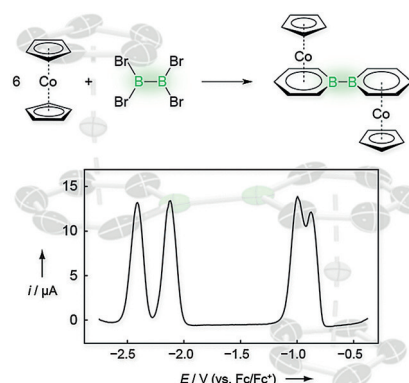
## Metal-Metal Interactions

H. Braunschweig,\* S. Demeshko,  
W. C. Ewing, I. Krummenacher,  
B. B. Macha, J. D. Mattock, F. Meyer,  
J. Mies, M. Schäfer,  
A. Vargas — 7708 – 7711



A Binuclear 1,1'-Bis(boratabenzene) Complex: Unprecedented Intramolecular Metal-Metal Communication through a B-B Bond

**Ground cobalt to major triplet:** Free and metal-bound borabenzene derivatives have traditionally featured electron-donating or neutral exocyclic boron substituents, limiting their potential use for materials applications. A boratabenzene species has now been synthesized bearing an exocyclic boron substituent in the form of a symmetrical bis(boratabenzene) derivative that has displayed unique conductive abilities not previously observed for these systems.

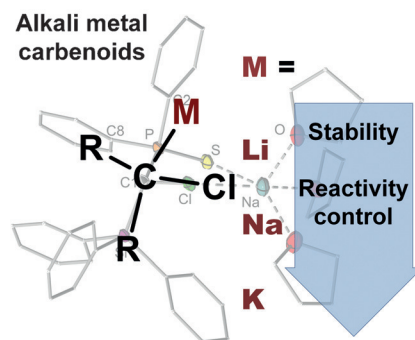


## Carbenoid Compounds

S. Molitor, V. H. Gessner\* — 7712 – 7716



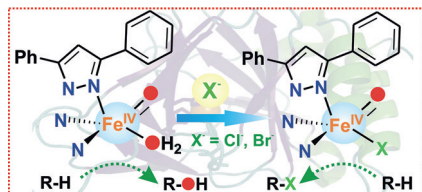
Alkali Metal Carbenoids: A Case of Higher Stability of the Heavier Congeners



**Heavy but stable:** The reactivity of s-block metal organyl compounds generally increases when going down the group of the periodic table, often limiting applications of the heavier congeners. However, the reverse of this trend has now been demonstrated for alkali metal carbenoids by replacement of Li by Na or K. The resulting compounds exhibit an increased thermal stability, which allows their isolation and selective application.

Inside Back Cover



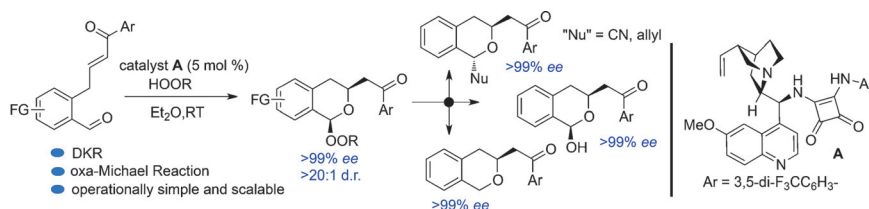


**An oxidative copycat:** An iron(II)–benzilate complex of a facial  $N_3$  ligand promoted the oxidative halogenation of aliphatic C–H bonds in the presence of a protic acid and a halide. An iron(IV)–oxo–halide species is proposed as the active oxidant in this biomimetic process (see scheme).

### Biomimetic Oxidation

S. Chatterjee, T. K. Paine\* — 7717–7722

Hydroxylation versus Halogenation of Aliphatic C–H Bonds by a Dioxygen-Derived Iron–Oxygen Oxidant: Functional Mimicking of Iron Halogenases



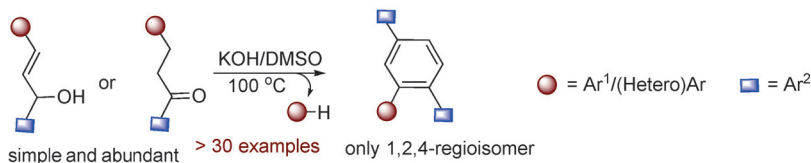
**O–O–H!** The title cascade reaction of *ortho*-formyl homochalcones has been developed using a cinchona-alkaloid-based chiral organocatalyst to provide the *cis*-configured *exo*-peroxyacetals, a new class of organic peroxide, with excellent

enantio- and diastereoselectivities. Furthermore, the displacement of the peroxide moiety with various nucleophiles proceeds without affecting the enantioselectivity.

### Asymmetric Synthesis

S. Maity, B. Parhi, P. Ghorai\* — 7723–7727

Enantio- and Diastereoselective Synthesis of *exo*-Peroxyacetals: An Organocatalyzed Peroxyhemiacetalization/oxa-Michael Addition Cascade



**Rings on rings:** An unprecedented approach for the synthesis of homo- and hetero-1,2,4-triaryl benzenes has been developed by a simple KOH/DMSO-mediated reaction of either  $\alpha$ -aryl cinnamyl alcohols or  $\alpha,\gamma$ -di-aryl propanones.

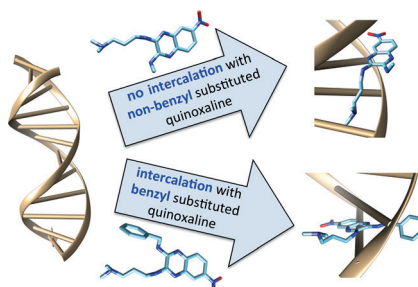
The salient feature of this strategy involves sequential hydride transfer, regioselective condensation, regioselective dearylation, and aromatization under metal-free reaction conditions. DMSO = dimethylsulfoxide.

### Arenes

M. Rehan, S. Maity, L. K. Morya, K. Pal, P. Ghorai\* — 7728–7732

Transition-Metal-Free Synthesis of Homo- and Hetero-1,2,4-Triaryl Benzenes by an Unexpected Base-Promoted Dearylation Pathway

**Flip the switch:** A benzyl group in a series of designed nitroquinoxaline derivatives is shown to alter or switch DNA binding modes. Without the benzyl group there is no intercalation, whereas with the benzyl group intercalation is accompanied with cooperative change in the DNA structure.



### DNA Intercalation

T. Mahata, A. Kanungo, S. Ganguly, E. K. Modugula, S. Choudhury, S. K. Pal, G. Basu,\* S. Dutta\* — 7733–7736

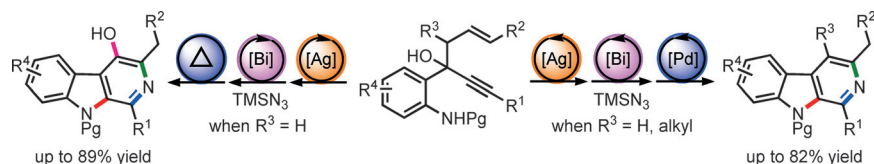
The Benzyl Moiety in a Quinoxaline-Based Scaffold Acts as a DNA Intercalation Switch

## Heterocycle Synthesis

S. Dhiman, U. K. Mishra,  
S. S. V. Ramasastry\* — 7737–7741



One-Pot Trimetallic Relay Catalysis: A Unified Approach for the Synthesis of  $\beta$ -Carbolines and Other [c]-Fused Pyridines



**All in the same pot:** An unprecedented one-pot approach based on triple relay catalysis was developed for the synthesis of unusual  $\beta$ -carboline derivatives (see scheme; Pg = protecting group). The strategy was also extended to the syn-

thesis of benzofuro[2,3-c]pyridines, benzothieno[2,3-c]pyridines, and isoquinolines. The methodologies described herein can provide rapid access to several natural products and therapeutically important compounds.

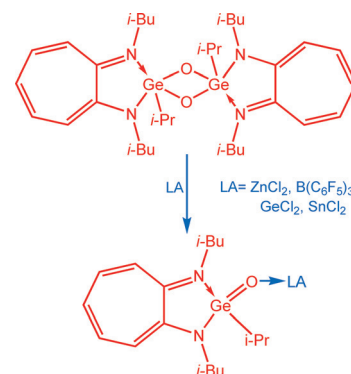
## Germanium Compounds

S. Sinhababu, D. Yadav, S. Karwasara,  
M. K. Sharma, G. Mukherjee,  
G. Rajaraman,  
S. Nagendran\* — 7742–7746



The Preparation of Complexes of Germanone from a Germanium  $\mu$ -Oxo Dimer

**An alternative path:** Complexes of germanone containing formal  $\text{Ge}=\text{O} \rightarrow \text{M}$  bonds ( $\text{M} = \text{Zn}, \text{B}, \text{Ge}, \text{Sn}$ ) were synthesized from a germanium  $\mu$ -oxo dimer, circumventing the need to prepare synthetically challenging germanones. The complexes were spectroscopically and structurally characterized. LA = Lewis acid.

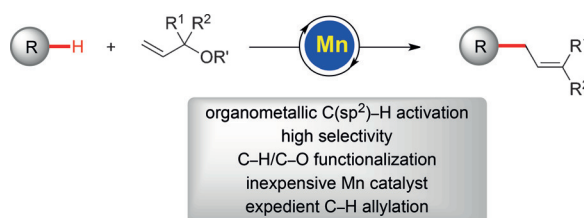


## C–H Activation

W. Liu, S. C. Richter, Y. Zhang,  
L. Ackermann\* — 7747–7750



Manganese(I)-Catalyzed Substitutive C–H Alkylation



**Manganese(I)** carboxylate catalysts allow step-economical C–H alkylations with broad substrate scope. The reaction proceeds through redox-neutral organome-

tallic  $\text{C}(\text{sp}^2)\text{-H}$  activation, which has the advantage of enabling the transformative late-stage diversification of functionalized molecules.

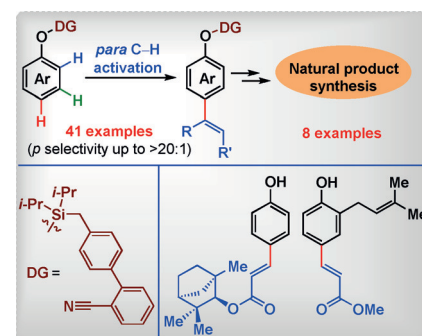
## C–H Activation

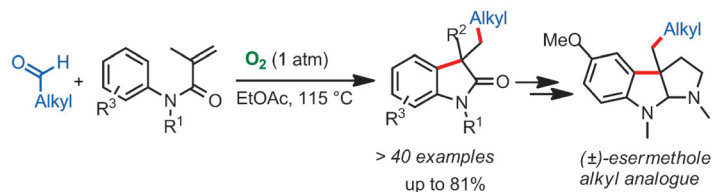
T. Patra, S. Bag, R. Kancherla, A. Mondal,  
A. Dey, S. Pimparkar, S. Agasti, A. Modak,  
D. Maiti\* — 7751–7755



Palladium-Catalyzed Directed *para* C–H Functionalization of Phenols

**The template-assisted *para* C–H olefination** of phenol derivatives was enabled by a silicon-containing directing group (DG; see scheme) in combination with a palladium catalyst. This method was also applied to the synthesis of different natural products.





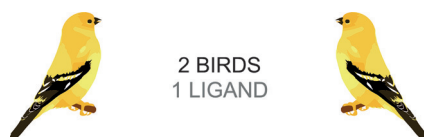
**A radical solution:** An efficient method for the aerobic radical-cascade alkylation/cyclization of  $\alpha,\beta$ -unsaturated amides to afford functionalized oxindoles with a C3 quaternary stereocenter is described. The method features a broad substrate

scope, inexpensive alkyl radical precursors, and  $\text{O}_2$  as the sole oxidant. It was successfully applied to the synthesis of alkyl analogues of the alkaloid natural product (±)-esermethole.

### Synthetic Methods

P. Biswas, S. Paul, J. Guin\* **7756–7760**

Aerobic Radical-Cascade Alkylation/Cyclization of  $\alpha,\beta$ -Unsaturated Amides: an Efficient Approach to Quaternary Oxindoles



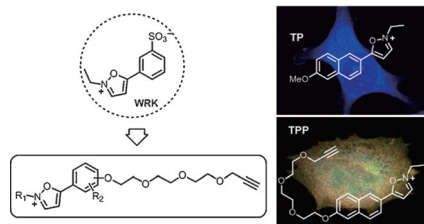
2 BIRDS  
1 LIGAND

**Two for one offer:** An efficient method based on copper(I)-catalyzed [3+2] cycloadditions has been developed for the enantiodivergent combination of natural product derived tropane and pyrrolidine scaffolds. The strategy enables the synthesis of two enantiopure products in a one-pot reaction with one chiral catalyst in high diastereo- and enantioselectivity.

### [3+2] Cycloaddition

H. Xu, C. Golz, C. Strohmann, A. P. Antonchick,\*  
H. Waldmann\* **7761–7765**

Enantiodivergent Combination of Natural Product Scaffolds Enabled by Catalytic Enantioselective Cycloaddition

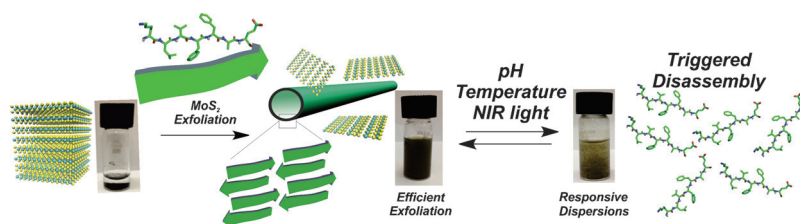


**Old dog—new tricks:** Woodward's reagent K (WRK) is a reactive heterocyclic compound known to covalently and unspecifically label proteins. A range of WRK-derived activity-based probes were synthesized and shown to be fairly selective for a few proteins in the human proteome.

### Activity-Based Probes

Y. Qian, M. Schürmann, P. Janning, C. Hedberg,\*  
H. Waldmann\* **7766–7771**

Activity-Based Proteome Profiling Probes Based on Woodward's Reagent K with Distinct Target Selectivity



**MoS<sub>2</sub> exfoliation by amyloids:** Powdered MoS<sub>2</sub> can be efficiently exfoliated in aqueous medium by cross- $\beta$ -amyloid nanotubes. The peptide sequence featured the nucleating core <sup>17</sup>LVFFA<sup>21</sup> of  $\beta$ -amyloid (A $\beta$  1–42). Notably, owing to the

properties of amyloid and MoS<sub>2</sub>, the hybrid dispersions showed multistimuli-responsive properties to various inputs, such as from temperature, pH, light, and ions.

### Layered Compounds

N. Kapil, A. Singh, M. Singh, D. Das\* **7772–7776**

Efficient MoS<sub>2</sub> Exfoliation by Cross- $\beta$ -Amyloid Nanotubes for Multistimuli-Responsive and Biodegradable Aqueous Dispersions

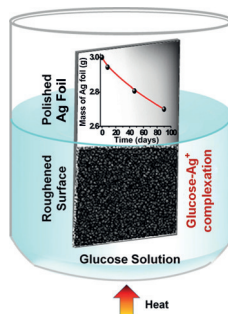


## Silver Extraction

A. Baksi, M. Gandhi, S. Chaudhari, S. Bag,  
S. S. Gupta, T. Pradeep\* — 7777–7781



Extraction of Silver by Glucose



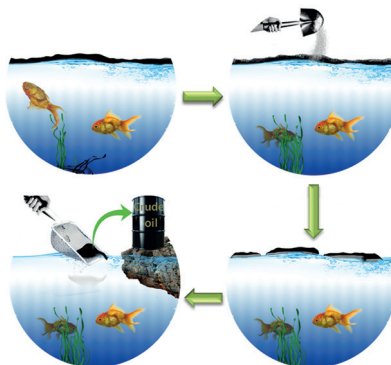
**A spoon full of sugar...** Direct silver extraction from metallic silver using glucose is possible. The dissolution of silver occurs in the ionic form and consequent complexation with glucose facilitates more silver leaching into the solution. The leaching is strongly dependent on the counter anion present in the solution. Dissolution of silver leads to microscopic roughening on the surface making it SERS active.

## Gelators

A. M. Vibhute, V. Muvvala,  
K. M. Sureshan\* — 7782–7785



A Sugar-Based Gelator for Marine Oil-Spill Recovery



**Solid solidifier:** Simple, cheap, and easy-to-prepare sugar-based phase-selective gelators were prepared that can selectively congeal oil from a mixture of oil and water and can be spread in solid powder form. Efficient crude-oil recovery from a mixture of water and crude oil was demonstrated.

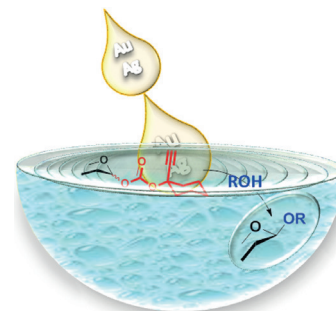
## Glycosidation

B. Mishra, M. Neralkar,  
S. Hotha\* — 7786–7791



Stable Alkynyl Glycosyl Carbonates: Catalytic Anomeric Activation and Synthesis of a Tridecasaccharide Reminiscent of *Mycobacterium tuberculosis* Cell Wall Lipoarabinomannan

**Donors that just keep giving:** Stable alkynyl carbonate glycosides were identified as excellent glycosyl donors that can be activated by a Au–Ag bimetallic catalyst for the rapid synthesis of glycosides, nucleosides, and oligosaccharides under mild conditions. Repeated glycosidation reactions with carbonate glycosyl donors enabled the highly convergent synthesis of a target tridecasaccharide.



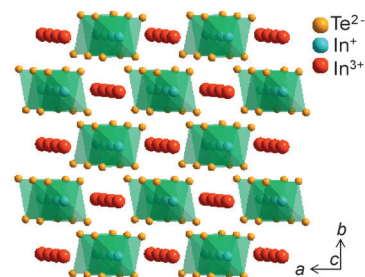
## Thermal Conductivity

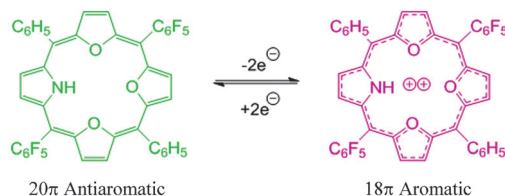
M. K. Jana, K. Pal, U. V. Waghmare,  
K. Biswas\* — 7792–7796



The Origin of Ultralow Thermal Conductivity in InTe: Lone-Pair-Induced Anharmonic Rattling

**It's in the rattle:** An ultralow lattice thermal conductivity (ca.  $0.4 \text{ W m}^{-1} \text{ K}^{-1}$ ) is found in mixed-valent InTe, which has an intrinsic bonding asymmetry with coexistent covalent and ionic substructures. The phonon dispersion of InTe reveals the rattling vibrations of  $\text{In}^+$  cations along the columnar ionic substructure, which are strongly anharmonic and scatter the heat-carrying acoustic phonons through strong anharmonic phonon–phonon interactions.





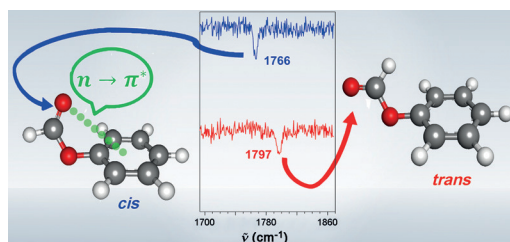
**Pyrrole with a bias:** Partial core modification of a porphyrin to a monopyrrole macrocycle yields a 20π antiaromatic isophlorin. It undergoes two-electron ring

oxidation with either  $[\text{Et}_3\text{O}]^+[\text{SbCl}_6]^-$  or  $[\text{NO}]^+[\text{BF}_4]^-$ , without deprotonating the pyrrole NH, to yield the 18π aromatic dication.

### Macrocycles

S. P. Panchal, S. C. Gadekar,  
V. G. Anand\* — 7797 – 7800

Controlled Core-Modification of  
a Porphyrin into an Antiaromatic  
Isophlorin



**Here's the proof:** Direct spectroscopic evidence for an  $n \rightarrow \pi^*$  interaction was provided for the first time by probing the carbonyl stretching frequency in *cis* and *trans* conformers of phenyl formate using

gas-phase IR spectroscopy. The *cis* form of the molecule, in which an  $n \rightarrow \pi^*$  interaction occurs, was found to be more stable than the *trans* isomer.

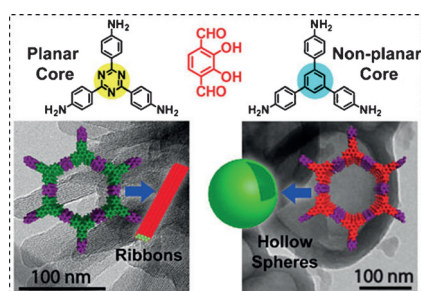
### $n \rightarrow \pi^*$ Interaction

S. K. Singh, K. K. Mishra, N. Sharma,  
A. Das\* — 7801 – 7805

Direct Spectroscopic Evidence for an  
 $n \rightarrow \pi^*$  Interaction



**Two self-templated,** morphologically diverse (ribbon and hollow sphere) crystalline porous polymers (CPPs) are characterized. Surprisingly, these polymers reflect how a slight change in torsion angles of the linker core dramatically affects the overall crystallinity, surface area, and the final morphology in the CPPs.



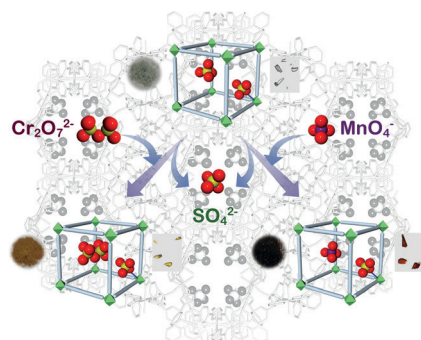
### Layered Compounds

A. Halder, S. Kandambeth, B. P. Biswal,  
G. Kaur, N. C. Roy, M. Addicoat,  
J. K. Salunke, S. Banerjee, K. Vanka,  
T. Heine, S. Verma,  
R. Banerjee\* — 7806 – 7810

Decoding the Morphological Diversity in  
Two Dimensional Crystalline Porous  
Polymers by Core Planarity Modulation



**Selective uptake:** A 3D water-stable cationic metal–organic framework (MOF) containing free  $\text{SO}_4^{2-}$  ions has been synthesized. The compound exhibits rapid, selective, and colorimetric aqueous-phase capture of environmentally toxic oxoanions. This system is the first example of a MOF-based adsorbent of both  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{MnO}_4^-$  ions, with the latter acting as a model for the radioactive contaminant  $\text{TcO}_4^-$ .



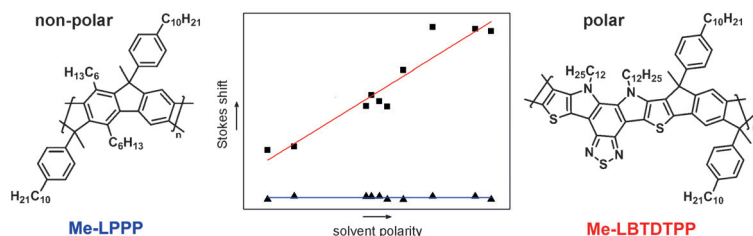
### Metal–Organic Frameworks

A. V. Desai, B. Manna, A. Karmakar,  
A. Sahu, S. K. Ghosh\* — 7811 – 7815

A Water-Stable Cationic Metal–Organic  
Framework as a Dual Adsorbent of  
Oxoanion Pollutants



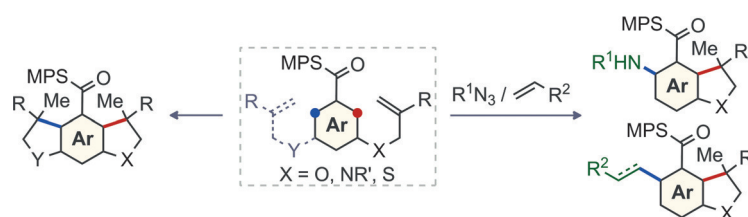
## Ladder Polymers

K.-J. Kass, M. Forster,  
U. Scherf\* — 7816–7820Incorporating an Alternating Donor–  
Acceptor Structure into a Ladder Polymer  
Backbone

**Up on the ladder:** The donor–acceptor structure of an alternating conjugated copolymer was incorporated into a rigid ladder polymer backbone. The resulting ladder polymers show optical features

typical of rigid ladder polymers, but present an increased Stokes shift corresponding to charge transfer processes during excitation, leading to a positive solvatochromism.

## Annulations

K. Ghosh, R. K. Rit, E. Ramesh,  
A. K. Sahoo\* — 7821–7825Ruthenium-Catalyzed Hydroarylation and  
One-Pot Twofold Unsymmetrical C–H  
Functionalization of Arenes

**In a single shot:** A methyl phenyl sulfoximine (MPS) is used as a directing group in the ruthenium-catalyzed intramolecular hydroarylation of alkene-tethered benzoic acid derivatives to afford dihydrobenzo-

furans and indolines in excellent yields. A one-pot, unsymmetrical, twofold C–H functionalization involving intramolecular C–C and intermolecular C–C/C–N bond formations is successfully demonstrated.



## Ruthenium Catalysis

M. Peña-López, H. Neumann,  
M. Beller\* — 7826–7830(Enantio)selective Hydrogen  
Autotransfer: Ruthenium-Catalyzed  
Synthesis of Oxazolidin-2-ones from Urea  
and Diols

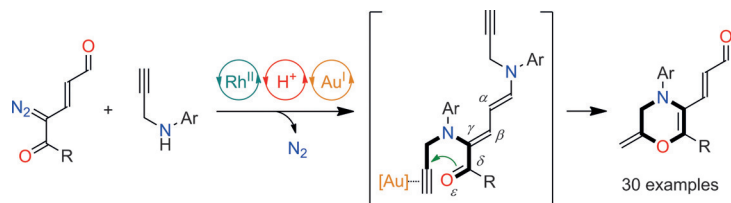
**Chiral version:**  $\text{Ru}_3(\text{CO})_{12}$   
 $\text{R}^1 = \text{aryl, alkyl}$   
 $\text{R}^2 = \text{H, Me}$   
 $\text{XR}^3 = \text{NH}_2$   
 23 examples  
 up to 78% yield  
 53–66% yield  
 82–93% ee

**Oxazolidin-2-ones** were synthesized from vicinal diols and urea or carbamates in a ruthenium-catalyzed process. The sequential formation of one C–O and one C–N bond takes place in a highly chemo-

and regioselective, atom-efficient domino process, which can be rendered enantioselective when an appropriate chiral ligand is used.

## Annulations

J. Kalepu, S. Katukojvala\* — 7831–7835

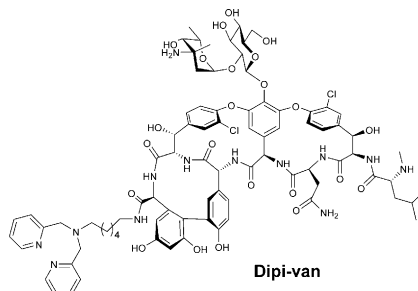
Dienamine Activation of Diazoenals:  
Application to the Direct Synthesis of  
Functionalized 1,4-Oxazines

**Rh/Au Co-op:** A new rhodium-catalyzed dienamine activation of diazoenals results in conformationally stable,  $\gamma$ -functionalized donor–acceptor dienamines. The synthetic importance of these dienamines

was demonstrated in a cooperative  $\text{Rh}^{\text{II}}$ /Brønsted acid and  $\text{Au}^{\text{I}}$ -catalyzed [3+3] annulation of diazoenals with N-propargyl anilines to give enal-functionalized substituted 1,4-oxazines.



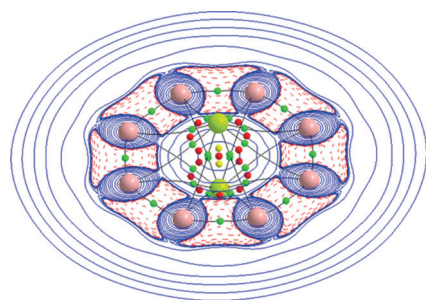
**The glycopeptide antibiotic Dippi-van**, with a zinc-binding dipicolyl moiety, is highly active against vancomycin-resistant bacteria as it binds to pyrophosphate groups of cell-wall lipids by the formation of zinc complexes while maintaining its inherent binding ability for the pentapeptide termini of cell-wall precursors. Cell-wall biosynthesis is thus inhibited.



## Antibiotics

V. Yarlagadda, P. Sarkar, S. Samaddar, J. Halder\* **7836–7840**

A Vancomycin Derivative with a Pyrophosphate-Binding Group: A Strategy to Combat Vancomycin-Resistant Bacteria



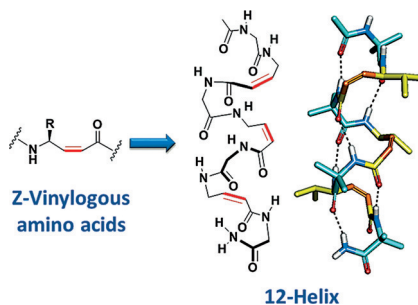
**Very close but not bonded:** The disc-shaped molecules  $\text{Be}_2\text{B}_8$  and  $\text{Be}_2\text{B}_7^-$  possess double ( $6\sigma$  and  $6\pi$ ) aromaticity and extremely short Be–Be distances of 1.9 Å without a chemical bond between these atoms.  $\text{Be}_2\text{F}_2$ , on the other hand, has a Be–Be bond length of 2.05 Å and displays a record-high bond dissociation energy of  $76.9 \text{ kcal mol}^{-1}$ .

## Bonding Analysis

Z.-h. Cui, W.-s. Yang, L. Zhao,\* Y.-h. Ding,\* G. Frenking\* **7841–7846**

Unusually Short Be–Be Distances with and without a Bond in  $\text{Be}_2\text{F}_2$  and in the Molecular Discs  $\text{Be}_2\text{B}_8$  and  $\text{Be}_2\text{B}_7^-$

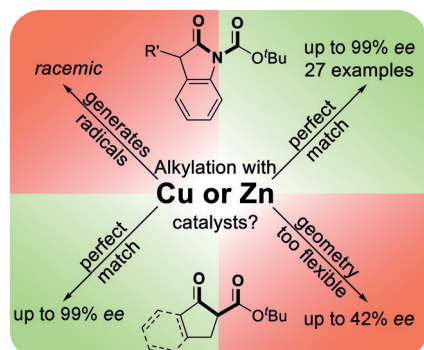
**Do the twist:** The design, synthesis, and solution and single-crystal conformations of hybrid helices containing *cis* carbon–carbon double bonds in the backbone are presented. The results reveal that *cis* double bonds can be accommodated into the helix without deviation from the overall helical fold.



## Foldamers

M. Ganesh Kumar, V. J. Thombare, M. M. Katariya, K. Veeresh, K. M. P. Raja, H. N. Gopi\* **7847–7851**

Non-classical Helices with *cis* Carbon–Carbon Double Bonds in the Backbone: Structural Features of  $\alpha,\gamma$ -Hybrid Peptide Foldamers



**The choice of metal** for an enantioselective catalyzed process depends on its preferred coordination geometry, redox reactivity, and the possible metal–substrate interactions. These are well matched in the boxmi/ $\text{Cu}^{\text{II}}$ -catalyzed electrophilic alkylation of  $\beta$ -ketoesters, whereas oxindoles react in an unselective radical process. However, they can be converted with excellent enantioselectivity in the presence of  $\text{Zn}^{\text{II}}$  catalysts.

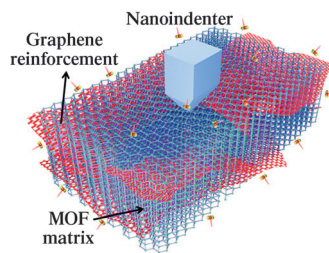
## Enantioselective Catalysis

T. Bleith, Q.-H. Deng, H. Wadeppohl, L. H. Gade\* **7852–7856**

Radical Changes in Lewis Acid Catalysis: Matching Metal and Substrate

## Graphene-Reinforced MOFs

R. Kumar, D. Raut, U. Ramamurty,  
C. N. R. Rao\* ————— 7857 – 7861



**A blend of strength:** Reinforcing a metal–organic framework (MOF) matrix with graphene significantly enhances its mechanical properties and CO<sub>2</sub> uptake. This strategy of strengthening a mechanically labile MOF matrix with graphene does not perturb the MOF's intrinsic microporosity.



Remarkable Improvement in the Mechanical Properties and CO<sub>2</sub> Uptake of MOFs Brought About by Covalent Linking to Graphene



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

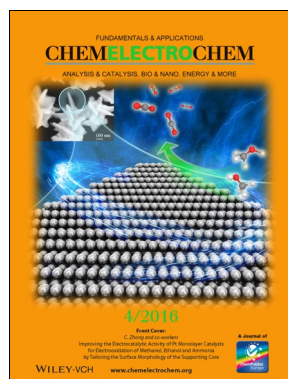


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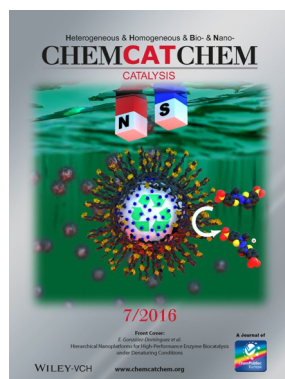


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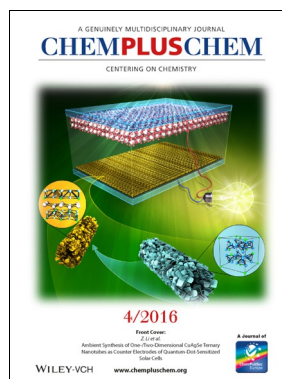
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