The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:

*A. Elahi, T. Fowowe, D. J. Caruana**
Dynamic Electrochemistry in Flame Plasma Electrolyte

*T. Köchner, T. A. Engesser, H. Scherer, D. A. Plattner, A. Steffani, I. Krossing**
Positive at Last: $[P_9]^+[Al(OR^F)_4]^-$, the First Pure Phosphorus Cation Salt

R. Liu, G. Yuan, C. L. Joe, T. E. Lightburn, K. L. Tan, D. Wang**
Silicon Nanowires as Photoelectrodes for Carbon Dioxide Fixation

*L. M. H. Lai, I. Y. Goon, K. Chuah, M. Lim, F. Braet, R. Amal, J. J. Gooding**
Biochemical Resistor: An Ultrasensitive Biosensor for Small Organic Molecules

*F. P. C. Binder, K. Lemme, R. C. Preston, B. Ernst**
Sialyl Lewis^x: A "Pre-organized Water Oligomer"?

*W. Chaladaj, M. Corbet, A. Fürstner**
Total Synthesis of Neurymenolide A Based on a New Gold-Catalyzed Synthesis of 4-Hydroxy-2-pyrones

*D. V. Kondratuk, L. M. A. Perdigao, M. C. O'Sullivan , S. Svatek, G. Smith, J. N. O'Shea, P. H. Beton, H. L. Anderson**
Two Vernier-Templated Routes to a 24-Porphyrin Nanoring

*V. Horvath, P. L. Gentili, V. K. Vanag, I. R. Epstein**
Pulse-Coupled Chemical Oscillators with Time Delay

Author Profile

"If I could be described as an animal it would be a white bull.
My motto is to accept my fate …"
This and more about Akio Baba can be found on page 6042.

Obituaries

D. Wayne Goodman (1945–2012)

Books

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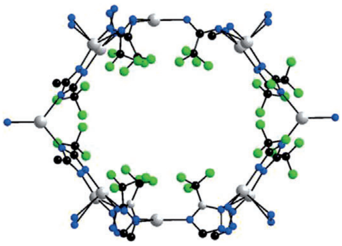
Highlights

Metal–Organic Frameworks



A new job: Highly fluorinated porous MOFs (see picture) that exhibit a superior hydrophobic character can possibly find an application as new superhydrophobic adsorbents in aqueous-phase separation processes.

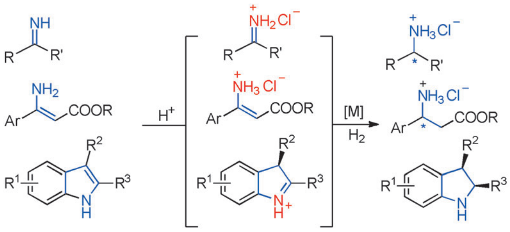
Essays

Coordination Chemistry

“Elusion, Confusion” could well be the title of the story of the discovery and rediscovery of the sandwich complexes, best represented by the accidentally found prototype ferrocene. The two most important competitors in this fiercely contested field, E. O. Fischer und G. Wilkinson, were reconciled (even in terms of dancing) only after they were jointly awarded the Nobel Prize. This keen competition in the 1950s contributed decisively to what R. S. Nyholm called the “Renaissance of Inorganic Chemistry”.

Minireviews

Asymmetric Catalysis



Protection free: Asymmetric hydrogenation of the title compounds has been realized under transition-metal catalysis by means of Brønsted acid activators (see scheme). Activation of the Lewis-basic substrates by protonation or hydrogen bonding with a Brønsted acid leads to highly enantioselective hydrogenation, thus providing efficient and atom-economical access to the corresponding chiral amines.

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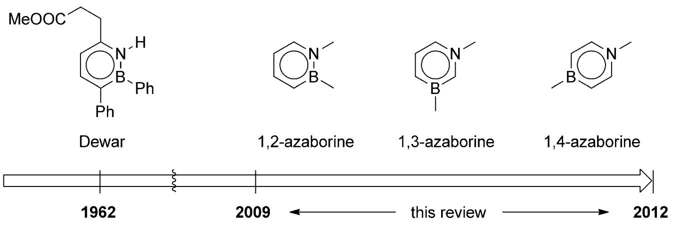
Reviews

B,N Heteroarenes

P. G. Campbell, A. J. V. Marwitz,
S.-Y. Liu* ________ 6074 – 6092

Recent Advances in Azaborine Chemistry

Back Cover



Ring around the boron: The BN/CC isosterism of arenes, which results in azaborine structures, has emerged as a viable strategy to increase the range of compounds relevant to biomedical research and materials science. As a tribute to Dewar's first synthesis of a monocyclic 1,2-azaborine 50 years ago, this review summarizes recent advances in the synthesis and characterization of carbon(C)–boron(B)–nitrogen(N)-containing heteroaromatics.

Communications

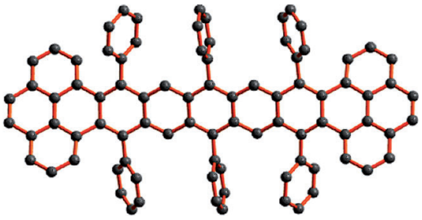
Oligotwistacene

J. Xiao, H. M. Duong, Y. Liu, W. Shi, L. Ji,
G. Li, S. Li, X.-W. Liu, J. Ma, F. Wudl,*
Q. Zhang* ________ 6094 – 6098

Synthesis and Structure Characterization of a Stable Nonatwistacene

Frontispiece

A clean reaction strategy based on thermally eliminating lactam bridges from a soluble acene precursor through a retro-Diels–Alder reaction, led to the synthesis and characterization of a novel, stable, green crystalline 6,8,10,17,19,21-hexaphenyl-1.22,4.5,11.12,15.16-tetrabenzononatwistacene. An analysis of the single crystal structure of the nonatwistacene indicates that this molecule is twisted at an angle of 25.44°.

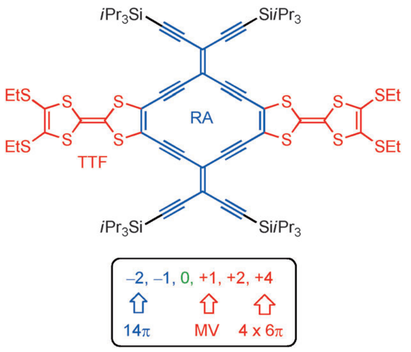


Annulenes

K. Lincke, A. Floor Frellsen, C. R. Parker,
A. D. Bond, O. Hammerich,
M. Brøndsted Nielsen* ________ 6099 – 6102

A Tetrathiafulvalene-Functionalized Radiaannulene with Multiple Redox States

Inside Cover



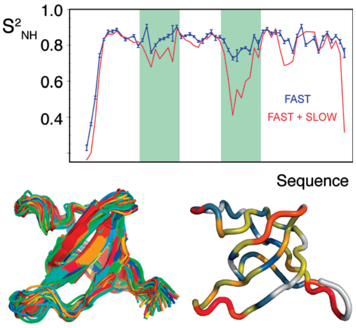
Multiple states: Fusing a central expanded radiaannulene (RA) core with two tetrathiafulvalene (TTF) units furnishes a molecule that can exist in several redox states with characteristic UV/Vis/IR absorptions. The radical cation was found to be of mixed valence (MV) character as reflected by a low-energy intervalence transition.

Protein Dynamics

L. Salmon, L. Pierce, A. Grimm,
J.-L. Ortega Roldan, L. Mollica,
M. R. Jensen, N. van Nuland,
P. R. L. Markwick, J. A. McCammon,
M. Blackledge* **6103 – 6106**

Multi-Timescale Conformational Dynamics of the SH3 Domain of CD2-Associated Protein using NMR Spectroscopy and Accelerated Molecular Dynamics

Inside Back Cover



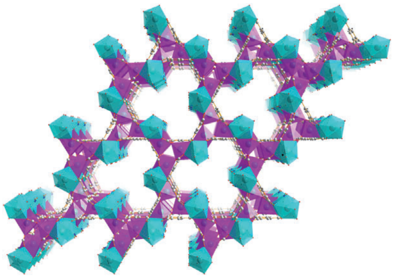
An extensive set of experimental NMR residual dipolar couplings (RDCs) has been used to determine the conformational behavior of the SH3 domain of CD2-associated protein. Analytical descriptions of the local dynamics were compared to restraint-free accelerated molecular dynamics simulation, providing a convergent and comprehensive description of conformational fluctuations on picosecond to millisecond time-scales.

Coordination Polymers

M. L. Foo, S. Horike, Y. Inubushi,
S. Kitagawa* **6107 – 6111**

An Alkaline Earth I^3O^0 Porous Coordination Polymer: $[Ba_2TMA(NO_3)(DMF)]$

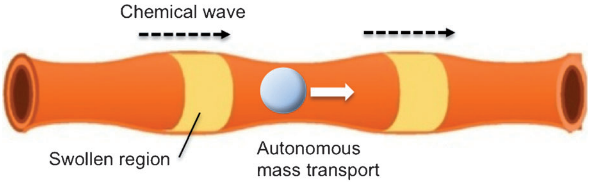
A CO_2 sieve: $[Ba_2TMA(NO_3)(DMF)]$ (DMF = dimethylformamide, H_3TMA = trimesic acid) is a main group, porous I^3O^0 coordination polymer that is connected in all three dimensions with barium-oxygen-barium bonds, leading to good thermal stability. The one-dimensional channels of this framework are decorated with protruding oxygen atoms and can separate carbon dioxide from methane under kinetic breakthrough conditions at 273 K.



Biomimetic Gels

Y. Shiraki, R. Yoshida* **6112 – 6116**

Autonomous Intestine-Like Motion of Tubular Self-Oscillating Gel



Totally tubular (chemical) wave! A tubular self-oscillating gel has been designed that converts the chemical energy of the Belousov–Zhabotinsky (BZ) reaction into a mechanical swelling–deswelling of the gel (see scheme). It exhibits peristaltic motion, similar to a living worm, with propagation of the chemical wave. In the gel tube, a bubble is autonomously transported by the peristaltic pumping motion.

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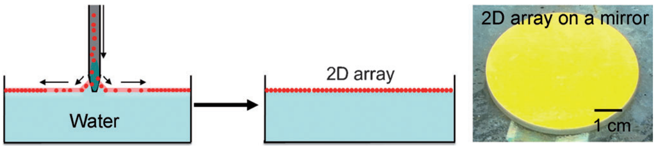
Polymers

J. T. Zhang, L. Wang, D. N. Lamont,
S. S. Velankar, S. A. Asher* **6117–6120**

Fabrication of Large-Area Two-Dimensional Colloidal Crystals

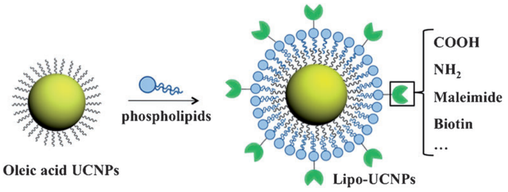


Nanoparticle coating: A suspension of colloidal particles in a water/propanol solution was layered onto a water surface, where the particles self-assembled into ordered two-dimensional hexagonal crystal arrays (> 280 cm^2) within two minutes. These arrays were transferred from the water surface to other substrates (see picture) and embedded in a chitosan hydrogel for visual detection of the pH value.

Imaging Agents

L. Li, R. Zhang, L. Yin, K. Zheng, W. Qin,
P. R. Selvin, Y. Lu* **6121–6125**

Biomimetic Surface Engineering of Lanthanide-Doped Upconversion Nanoparticles as Versatile Bioprobes



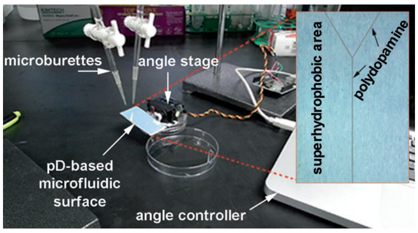
Coat of lipids: Water-dispersible and functionalizable upconverting nanoparticles (UCNPs) for selective imaging of live cancer cells were synthesized. The synthetic approach involves coating the surface of the UCNPs with a monolayer of phospholipids that contain different functional groups (see picture), thus allowing for conjugation of many molecules for applications in fields such as bioinspired nanoassembly, biosensing, and biomedicine.

Microfluidics

I. You, S. M. Kang, S. Lee, Y. O. Cho,
J. B. Kim, S. B. Lee, Y. S. Nam,*
H. Lee* **6126–6130**

Polydopamine Microfluidic System toward a Two-Dimensional, Gravity-Driven Mixing Device

Given path: A polydopamine-based, pump-free, two-dimensional microfluidic system is energy-efficiently operated by gravity (see picture). The device consists of polydopamine (pD) micro-patterns on nanostructured, superhydrophobic anodized aluminum oxide (AAO) surfaces on which liquid droplets move along the micro-patterned paths of the polydopamine.

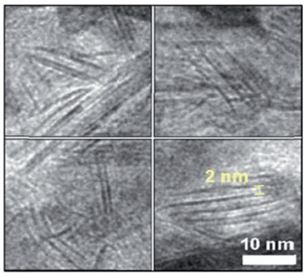


Heterogeneous Catalysis

W.-F. Chen, K. Sasaki,* C. Ma,
A. I. Frenkel, N. Marinkovic,
J. T. Muckerman, Y. Zhu,
R. R. Adzic **6131–6135**

Hydrogen-Evolution Catalysts Based on Non-Noble Metal Nickel–Molybdenum Nitride Nanosheets

Not noble but effective: A new class of heterogeneous hydrogen-evolving electrocatalysts based on inexpensive components was developed. The carbon-supported nickel–molybdenum nitride (NiMoN$_x$, see picture) catalyst had a nanoscale sheet structure comprising a few layers and an abundance of highly accessible reactive sites.



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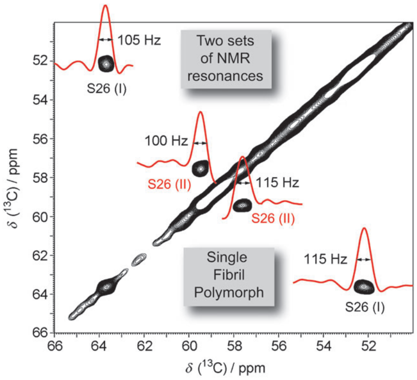
Two-faced culprit: Fibrils of recombinantly produced amyloid β peptides (Aβs; residues 1–40) gave well-resolved solid-state NMR spectra. Two sets of resonances corresponding to residues 12–40 and 21–38 of the Aβ primary sequence were observed (see picture). Statistical analysis of electron microscopy data revealed that it was composed of a single Aβ polymorph, thus indicating that this Aβ fibril is composed of an asymmetric dimer.



Amyloid β Peptides

J. M. Lopez del Amo, M. Schmidt, U. Fink, M. Dasari, M. Fändrich, B. Reif* —— **6136–6139**

An Asymmetric Dimer as the Basic Subunit in Alzheimer's Disease Amyloid β Fibrils

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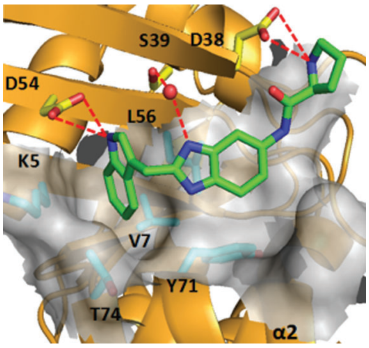


Looking for fragments: A fragment-based screen using NMR spectroscopy was applied to discover ligands that bind to the GTPase K-Ras and modulate the activity of the nucleotide exchange factor Sos. Structural data on how these fragment-derived hits bind to the guanosine diphosphate–K-Ras complex (see picture) provides a starting point for the future discovery of drugs that target K-Ras activation and signaling.

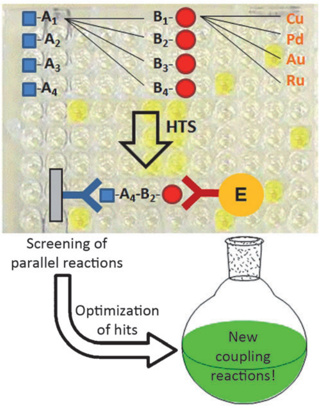
Fragment-Based Screening

Q. Sun, J. P. Burke, J. Phan, M. C. Burns, E. T. Olejniczak, A. G. Waterson, T. Lee, O. W. Rossanese, S. W. Fesik* —— **6140–6143**

Discovery of Small Molecules that Bind to K-Ras and Inhibit Sos-Mediated Activation

---

Mmm, a reaction sandwich… Using an immunoassay-based technique able to monitor any kind of cross-coupling reaction, a systematic and rapid evaluation of a large panel of random reactions was carried out. This approach led to the discovery of two new copper-promoted reactions: a desulfurization reaction of thioureas leading to isoureas and a cyclization reaction leading to thiazole derivatives from alkynes and *N*-hydroxy thioureas.

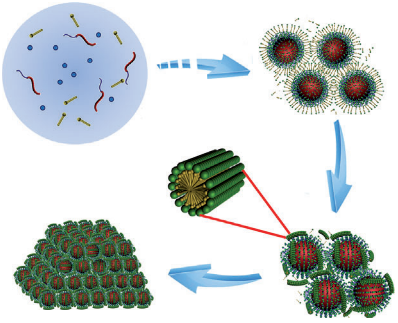


High-Throughput Screening

VIP

J. Quinton, S. Kolodych, M. Chaumonet, V. Bevilacqua, M.-C. Nevers, H. Volland, S. Gabillet, P. Thuéry, C. Créminon, F. Taran* —— **6144–6148**

Reaction Discovery by Using a Sandwich Immunoassay



It takes two: Ordered dual-mesoporous silica with two sets of well-configured pores can be synthesized by evaporation-induced step-by-step aggregating assembly in which the non-ionic block copolymer PEO-*b*-PMMA (red spheres) and the cationic surfactant alkyltrimethyl ammonium bromide (yellow rods) serve as co-templates in an acidic THF/H$_2$O solution containing tetraethyl orthosilicate as the silica source (SiO$_2$ oligomers shown as green balls in the picture).

Mesoporous Materials

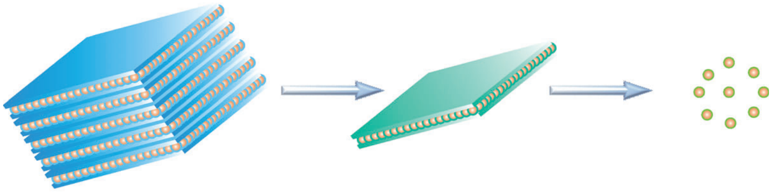
J. Wei, Q. Yue, Z. K. Sun, Y. H. Deng,* D. Y. Zhao* —— **6149–6153**

Synthesis of Dual-Mesoporous Silica Using Non-Ionic Diblock Copolymer and Cationic Surfactant as Co-Templates

Nanoclusters

Y. Wang, Y. H. Liu, Y. Zhang, F. Wang,
P. J. Kowalski, H. W. Rohrs, R. A. Loomis,
M. L. Gross, W. E. Buhro* — **6154–6157**

Isolation of the Magic-Size CdSe Nanoclusters $[(\mathrm{CdSe})_{13}(n\text{-octylamine})_{13}]$ and $[(\mathrm{CdSe})_{13}(\text{oleylamine})_{13}]$

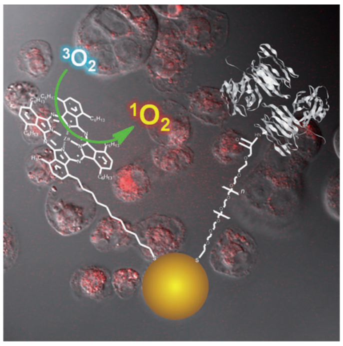


Pure magic: CdSe nanoclusters with a magic size have previously been obtained only as mixtures. Two ligated forms of $(\mathrm{CdSe})_{13}$ have now been isolated by exfoliation of nanocluster–*n*-octylamine bilayer aggregates followed by release of $[(\mathrm{CdSe})_{13}(n\text{-octylamine})_{13}]$ or freely soluble $[(\mathrm{CdSe})_{13}(\text{oleylamine})_{13}]$ nanoclusters by ligand exchange.

Photosensitizers

G. Obaid, I. Chambrier, M. J. Cook,
D. A. Russell* — **6158–6162**

Targeting the Oncofetal Thomsen–Friedenreich Disaccharide Using Jacalin-PEG Phthalocyanine Gold Nanoparticles for Photodynamic Cancer Therapy



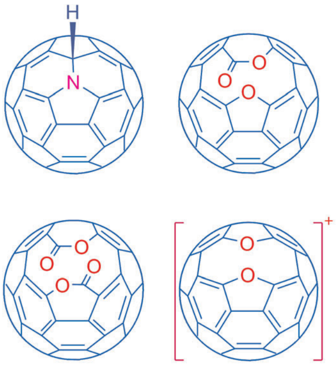
Light-sensitive: Targeted photodynamic therapy is achieved by using gold nanoparticles that are stabilized by a mixed monolayer of a hydrophobic zinc phthalocyanine photosensitizer, which produces cytotoxic singlet oxygen, and a water-soluble thiol-functionalized poly(ethylene glycol) carrying the lectin jacalin, which targets the Thomsen–Friedenreich disaccharide antigen at the surface of cancer cells.

Heterofullerenes

N. N. Xin, H. Huang, J. X. Zhang,
Z. F. Dai, L. B. Gan* — **6163–6166**

Fullerene Doping: Preparation of Azafullerene $C_{59}NH$ and Oxafulleroids $C_{59}O_3$ and $C_{60}O_4$

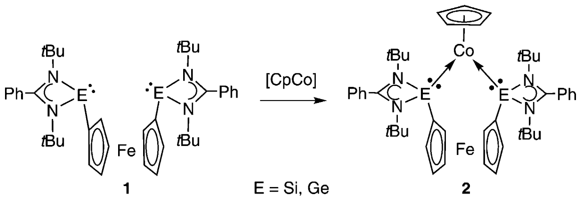
Breaking the surface: Replacement of a fullerene cage carbon with a nitrogen or oxygen atom is achieved by reactions mediated with fullerene peroxide. Similar procedures have also generated oxafulleroids with oxygen atoms inserted into the cage skeleton. The dioxafullerene $C_{58}O_2$ was selectively generated in the gas phase under MALDI-TOF conditions.



Chelate Ligands

W. Wang, S. Inoue,* S. Enthaler,*
M. Driess* — **6167–6171**

Bis(silylenyl)- and Bis(germylenyl)-Substituted Ferrocenes: Synthesis, Structure, and Catalytic Applications of Bidentate Silicon(II)–Cobalt Complexes



Strong bite: The two respective $\mathrm{Si^{II}}$ and $\mathrm{Ge^{II}}$ centers in ferrocene-containing bis(silylene) and bis(germylene) ligands **1** can serve as excellent σ donors, as shown in the formation of Co complexes **2** (see scheme, Cp = η^5-cyclopentadienyl). Unexpectedly, only the bis(silylene)–Co complex **2** is a precatalyst for the [2+2+2] cycloaddition of phenylacetylene and MeCN, possibly because of a stronger coordination of the $\mathrm{Ge^{II}}$ donor centers to Co.

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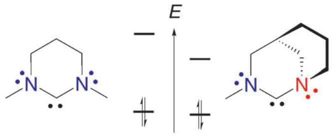
Stable Carbenes

D. Martin, N. Lassauque, B. Donnadieu, G. Bertrand* ———— **6172 – 6175**

A Cyclic Diaminocarbene with a Pyramidalized Nitrogen Atom: A Stable N-Heterocyclic Carbene with Enhanced Electrophilicity

An anti-Bredt NHC! Placing one of the adjacent nitrogen atoms of an NHC in the bridgehead position of a bicyclic scaffold prevents the donation of its lone pair. Thus, the π-electron-accepting properties of the carbene center are enhanced, while the strong σ-electron-donating properties of classical NHCs are retained.

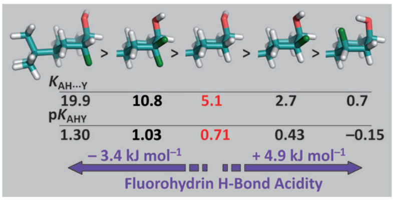


Hydrogen Bonding

J. Graton,* Z. Wang, A.-M. Brossard, D. Gonçalves Monteiro, J.-Y. Le Questel, B. Linclau* ———— **6176 – 6180**

An Unexpected and Significantly Lower Hydrogen-Bond-Donating Capacity of Fluorohydrins Compared to Nonfluorinated Alcohols

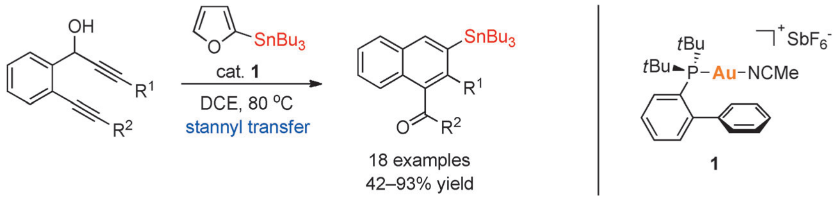
Rewriting the rules as fluorination does not always increase hydrogen-bond acidity: while the strongly electron-withdrawing fluorine significantly enhances alcohol H-bond acidity in *anti*-vicinal fluorohydrins, an intramolecular F···HO interaction overrules completely the inductive effect. This leads to an overall decrease in alcohol H-bond acidity, compared to the corresponding nonfluorinated alcohol.



Gold Catalysis

Y.-F. Chen, M. Chen, Y.-H. Liu* ———— **6181 – 6186**

Gold-Catalyzed Cyclization of 1,6-Diyne-4-en-3-ols: Stannyl Transfer from 2-Tributylstannylfuran Through Au/Sn Transmetalation



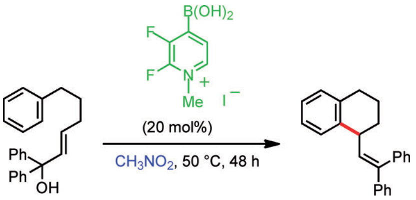
1

Gold-tinted: A gold catalyzed cyclization reaction of 1,6-diyne-4-en-3-ols, incorporating an in situ stannyl transfer reaction involving 2-tributylstannylfuran, gives synthetically valuable 2-stannylnaphthalenes (see scheme; DCE = dichloroethane). A *gem*-diaurated furan complex, was isolated and fully characterized by X-ray crystallographic analysis, and provides strong evidence for a tin to gold transmetalation step.

Homogeneous Catalysis

H. Zheng, S. Ghanbari, S. Nakamura, D. G. Hall* ———— **6187 – 6190**

Boronic Acid Catalysis as a Mild and Versatile Strategy for Direct Carbo- and Heterocyclizations of Free Allylic Alcohols



BAC to the future: Boronic acid catalysis (BAC) was applied to the direct activation of alcohols leading to the preparation of carbocycles (see scheme), benzofurans, tetrahydrofurans, pyrrolidines, pyrans, piperidines, and various polycyclic compounds. The reactions proceed under mild conditions that circumvent the use of reactive leaving groups like halides.

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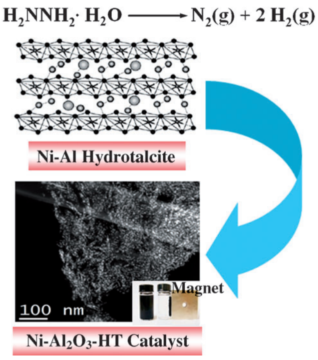
Heterogeneous Catalysis

L. He, Y. Huang, A. Wang, X. Wang, X. Chen, J. J. Delgado, T. Zhang* ______ **6191 – 6194**

A Noble-Metal-Free Catalyst Derived from Ni-Al Hydrotalcite for Hydrogen Generation from $N_2H_4{\cdot}H_2O$ Decomposition

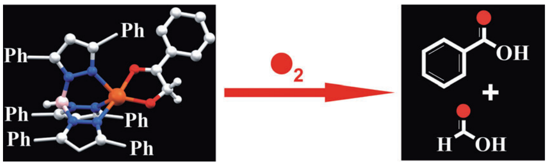
Free of nobility: A supported nickel catalyst derived from Ni-Al hydrotalcite is a promising candidate to replace noble metals for hydrogen generation from the catalytic decomposition of $N_2H_4{\cdot}H_2O$ under ambient conditions. The catalyst produces H_2 at 30 °C in 93 % selectivity. The catalytic function is due to the cooperation of highly dispersed Ni nanoparticles and strong basic sites located nearby.



Biomimetic Model

S. Paria, P. Halder, T. K. Paine* ______ **6195 – 6199**

Oxidative Carbon–Carbon Bond Cleavage of a α-Hydroxy Ketone by a Functional Model of 2,4′-Dihydroxyacetophenone Dioxygenase

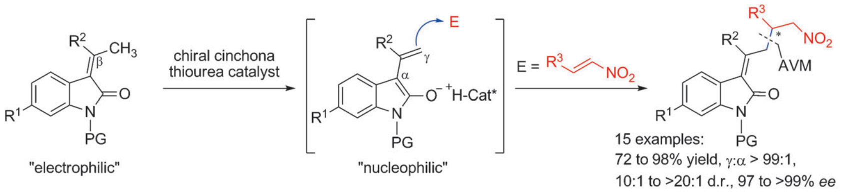


Bond cleavage: An iron(II)–α-hydroxy ketone complex of a facial tridentate nitrogen donor ligand undergoes a C–C bond cleavage reaction in the presence of dioxygen to form two equivalents of carboxylic acids. This reaction is a functional model of 2,4′-dihydroxyacetophenone dioxygenase.

Organocatalysis

C. Curti,* G. Rassu,* V. Zambrano, L. Pinna, G. Pelosi, A. Sartori, L. Battistini, F. Zanardi, G. Casiraghi* ______ **6200 – 6204**

Bifunctional Cinchona Alkaloid/Thiourea Catalyzes Direct and Enantioselective Vinylogous Michael Addition of 3-Alkylidene Oxindoles to Nitroolefins

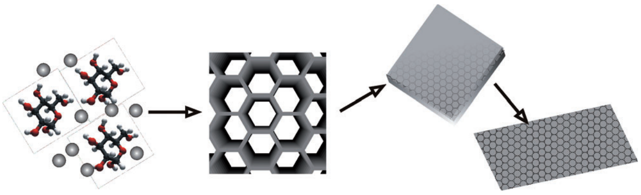


Vinylogy: Advances in asymmetric catalysis using the bifunctional cinchona alkaloid/thioureas enabled an umpolung of the classical C_β reactivity of 3-alkylidene oxindoles, thus allowing the development of the first and sole example of a direct, organocatalytic asymmetric vinylogous Michael (AVM) reaction with nitroolefins.

Nanostructures

J. Ge, H. Ding, X. Xue* ______ **6205 – 6208**

A Nanosheet-Structured Three-Dimensional Macroporous Material with High Ionic Conductivity Synthesized Using Glucose as a Transforming Template

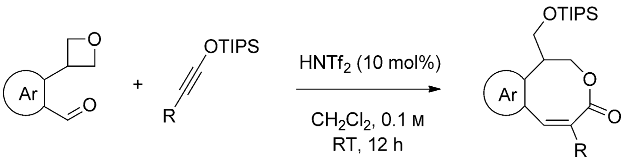


Building with sugar: Glucose acts as a transforming template for the synthesis of the three-dimensional macroporous oxide $Sm_{0.2}Ce_{0.8}O_{1.9}$. The material has a two-dimensional nanosheet microstructure and has a high surface area and great potential for the fabrication of gas-tight membranes with high ionic conductivity.

Homogeneous Catalysis

W. Zhao, Z. Wang, J. Sun* **6209 – 6213**

Synthesis of Eight-Membered Lactones: Intermolecular [6+2] Cyclization of Amphoteric Molecules with Siloxy Alkynes

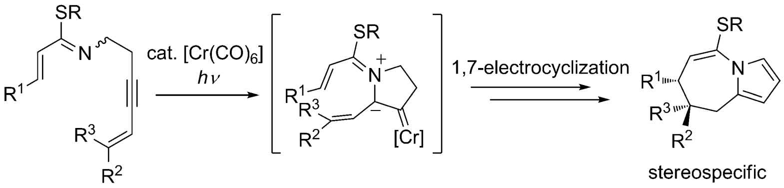


That's about the size of it: The title molecules react with siloxy alkynes in the presence of a Brønsted acid to deliver medium-sized lactones through a [6+2] cyclization (see scheme; TIPS = triisopropylsilyl). This process is the first intermolecular synthesis of such lactones and involves a sequence of several selective ring-opening/ring-closing events.

Synthetic Methods

Y. Karibe, H. Kusama, N. Iwasawa* **6214 – 6218**

Chromium(0)-Catalyzed Tandem Cyclization of α,β-Unsaturated Thioimidates Containing an Enyne Moiety

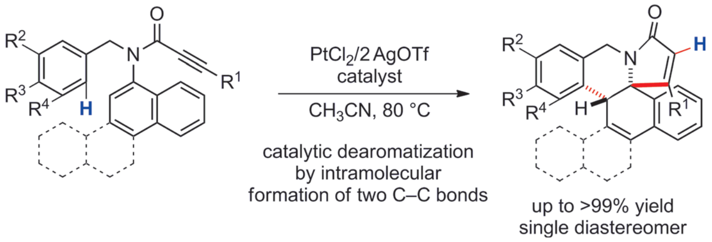


Bicyclic: The diastereoselective synthesis of functionalized 1-azabicyclo[5.3.0]decane derivatives proceeds through 1,7-electrocyclization of the zwitterionic intermediates that are formed in the cyclization of α,β-unsaturated thioimidates containing an enyne moiety (see scheme). Furthermore 1,4-addition of nucleophiles to α,β-unsaturated carbene complex intermediates was also achieved.

Dearomatization Reaction

T. Shibuya, K. Noguchi, K. Tanaka* **6219 – 6222**

Dearomatization of Fused Arenes Using Platinum-Catalyzed Intramolecular Formation of Two C–C Bonds

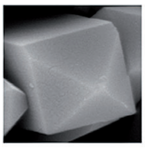


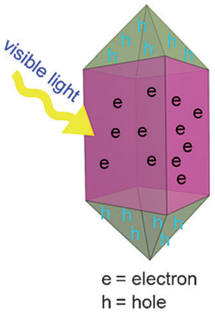
The (de)aroma of success: A cationic platinum(II) complex generated in situ catalyzes dearomatization of fused arenes by forming two intramolecular C–C bonds (see scheme). Mechanistic studies reveal that this reaction could proceed through alkyne activation by the cationic platinum(II) complex followed by a Friedel–Crafts-type reaction.

Photocatalysis

F. Zuo, K. Bozhilov, R. J. Dillon, L. Wang, P. Smith, X. Zhao, C. Bardeen, P. Feng* **6223 – 6226**

Active Facets on Titanium(III)-Doped TiO$_2$: An Effective Strategy to Improve the Visible-Light Photocatalytic Activity





Partially reduced TiO$_2$ with highly active facets has been fabricated: Ti^{3+} was successfully incorporated without any additional reducing agent and surfactant, and highly active facets developed preferentially. The product shows improved photocatalytic activity in H$_2$ production over previously reported material. Photocatalytic activity over an extended time period demonstrates the stability of reduced TiO$_2$ made by this approach.

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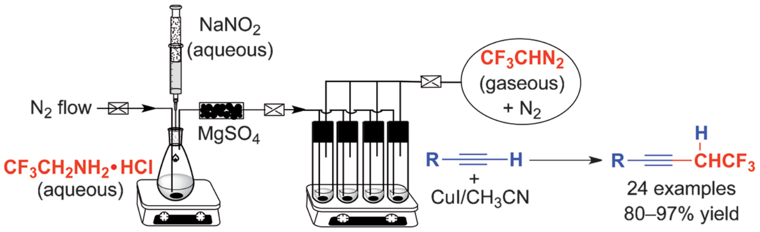
Fluorine Chemistry

C.-B. Liu, W. Meng, F. Li, S. Wang, J. Nie, J.-A. Ma* **6227 – 6230**

A Facile Parallel Synthesis of Trifluoroethyl-Substituted Alkynes

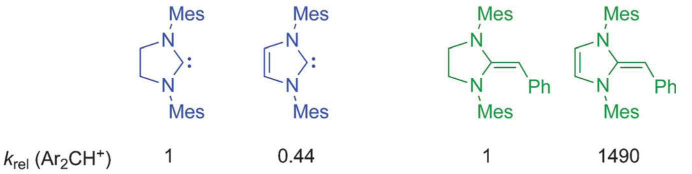


Trifluoroethylation made easy: The ease of execution of the reaction (see scheme), which runs under mild conditions and without the need for additional base or ligands, allows for the rapid parallel synthesis of a broad variety of trifluoroethylated alkynes. Both experimental and theoretical analyses indicate that the trifluoromethylcarbene could undergo concerted insertion into the C_{sp}—H bond of the alkyne.

Organocatalysis

B. Maji, M. Horn, H. Mayr* **6231 – 6235**

Nucleophilic Reactivities of Deoxy Breslow Intermediates: How Does Aromaticity Affect the Catalytic Activities of N-Heterocyclic Carbenes?

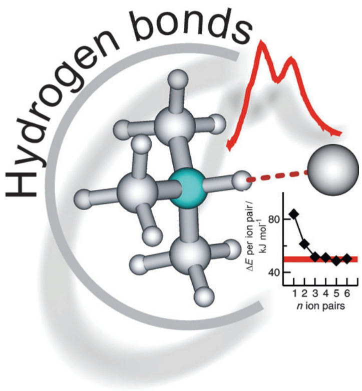


Aromatic or nonaromatic? Kinetic investigations show that structurally analogous saturated and unsaturated N-heterocyclic carbenes have almost identical nucleophilic reactivities, while the corresponding deoxy Breslow intermediates differ dramatically.

Hydrogen Bonds

K. Fumino, E. Reichert, K. Wittler, R. Hempelmann, R. Ludwig* **6236 – 6240**

Low-Frequency Vibrational Modes of Protic Molten Salts and Ionic Liquids: Detecting and Quantifying Hydrogen Bonds



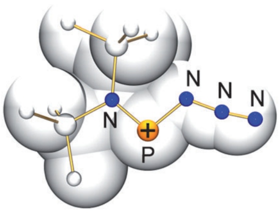
The subtle balance between Coulomb forces, hydrogen bonds, and dispersion forces is important for the understanding of the unique properties of molten salts and ionic liquids. Vibrational modes with peak frequencies falling in the 140–180 cm^{-1} range of far-infrared spectra were assigned unequivocally to hydrogen bonds, which are local and directional in nature, but almost insensitive to the molecular weight of the ions.

Phosphorus Azides

C. Hering, A. Schulz,* A. Villinger **6241 – 6245**

Low-Temperature Isolation of An Azidophosphenium Cation

Trapped in the cold: The synthesis and structural characterization of a $GaCl_4^-$ salt bearing an azidophosphenium cation is presented for the first time. This formal phosphapentacenium ion with a planar molecular skeleton is only stable at temperatures below −30 °C.



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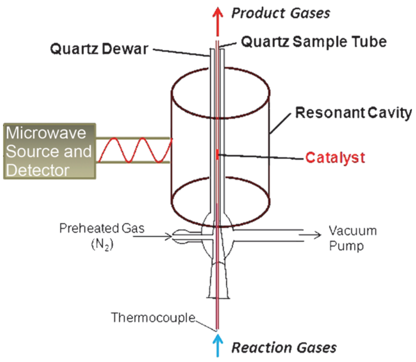
Heterogeneous Catalysis

M. Eichelbaum,* M. Hävecker, C. Heine,
A. Karpov, C.-K. Dobner, F. Rosowski,
A. Trunschke, R. Schlögl ____ **6246 – 6250**

The Intimate Relationship between Bulk Electronic Conductivity and Selectivity in the Catalytic Oxidation of *n*-Butane

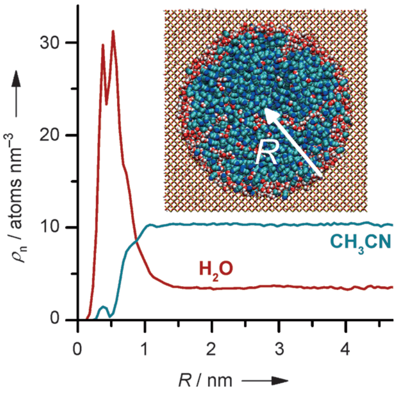


Don't touch! Without electrode contacts, but contact-free with microwaves in a resonant cavity the electronic conductivity of a VPO powder catalyst could be measured under the reaction conditions of the selective oxidation of *n*-butane to maleic anhydride. As a result, a linear correlation between conductivity and formation rate of maleic anhydride was observed.

Liquid Chromatography

S. M. Melnikov, A. Höltzel,
A. Seidel-Morgenstern,
U. Tallarek* ____________ **6251 – 6254**

A Molecular Dynamics Study on the Partitioning Mechanism in Hydrophilic Interaction Chromatography



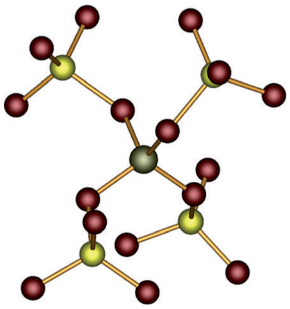
The retention mechanism in hydrophilic interaction chromatography is supposed to involve partitioning of analytes between a mostly organic mobile phase and a water layer at the surface of the stationary phase. By molecular dynamics simulations, in which a 9 nm diameter bare silica pore is fed with H_2O/CH_3CN mixtures (see picture: 10:90 (v/v)), the water layer is elucidated and interpreted regarding the retention of hydrophilic analytes.

Borosulfates

H. A. Höppe,* K. Kazmierczak, M. Daub,
K. Förg, F. Fuchs,
H. Hillebrecht ____________ **6255 – 6257**

The First Borosulfate $K_5[B(SO_4)_4]$

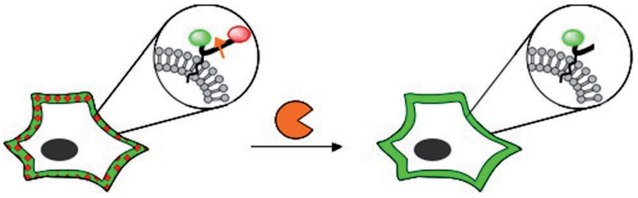
The first of its kind: $K_5[B(SO_4)_4]$, the first example of a borosulfate, comprises non-condensed $[B(SO_4)_4]^{5-}$ anions in which the boron atoms are tetrahedrally coordinated to sulfate tetrahedra (see picture; B brown, O red, S yellow). The compound, which crystallizes in a polar space group, was investigated by X-ray diffraction, vibrational spectroscopy, and calculations.



Neutrophil Elastase

S. Gehrig, M. A. Mall,
C. Schultz* ____________ **6258 – 6261**

Spatially Resolved Monitoring of Neutrophil Elastase Activity with Ratiometric Fluorescent Reporters



Finding NEmo: In a mouse model for lung inflammation, the lipidated peptide-based ratiometric fluorescent reporter NEmo-2 indicates that neutrophil elastase (NE) activity is mainly associated with the surface of neutrophils (see scheme), whereas a soluble reporter variant showed no activity in the lung fluid, likely because of the abundance of antiproteases. Targeting the localization of NE activity has great potential for the development of improved antiinflammatory drugs.

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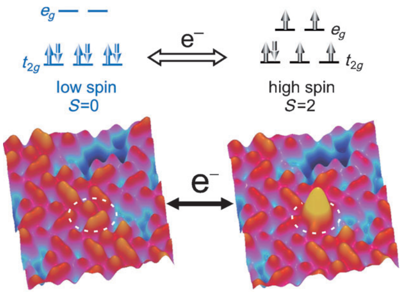
Spin Crossover

T. G. Gopakumar,* F. Matino, H. Naggert,
A. Bannwarth, F. Tuczek,
R. Berndt ______ 6262 – 6266

Electron-Induced Spin Crossover of Single Molecules in a Bilayer on Gold

Single molecules of the iron(II) complex [Fe(bpz)$_2$phen] (phen = 1,10-phenanthroline, bpz = dihydrobis(pyrazolyl)borate) are reversibly switched between low spin and high spin by electron-induced spin crossover (ELIESST) in a bilayer on gold, as revealed by STM.



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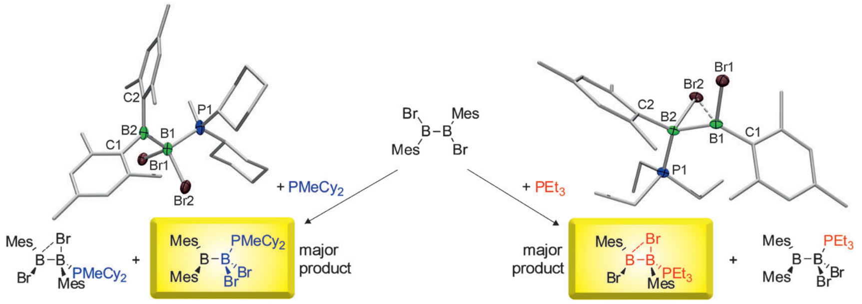
sp^2–sp^3 Diboranes

H. Braunschweig,* A. Damme,
J. O. C. Jimenez-Halla, T. Kupfer,
K. Radacki ______ 6267 – 6271

Phosphine Adducts of 1,2-Dibromo-1,2-dimesityldiborane(4): Between Bridging Halides and Rearrangement Processes



To bridge or not to bridge depends on the size of the Lewis base in mixed sp^2–sp^3 phosphine adducts of $Br_2B_2Mes_2$. Whereas reaction with bulky PMeCy$_2$ induced a 1,2-rearrangement to afford the 1,1-dimesityl adduct as the major component, the “normal” 1,2-dimesityl adduct was favored for the smaller PEt$_3$ molecule. The latter contains an uncommon B–Br–B bridge and a rare dative B–Hal bonding interaction to the sp^2 boron center.

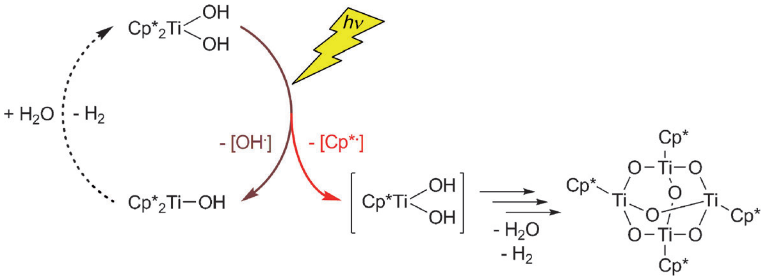
VIP

Water Splitting

M. Kessler, S. Schüler, D. Hollmann,
M. Klahn, T. Beweries, A. Spannenberg,
A. Brückner, U. Rosenthal* _ 6272 – 6275

Photoassisted Ti–O Activation in a Decamethyltitanocene Dihydroxido Complex: Insights into the Elemental Steps of Water Splitting

Front Cover



Step by step: Irradiation of the decamethyltitanocene(IV) dihydroxido complex [Cp*$_2$Ti(OH)$_2$] (Cp* = η^5-C$_5$Me$_5$) induces dissociation of Cp* and a rare homolytic Ti–O bond cleavage, most likely by elimination of an OH radical. Two independent reaction pathways are present, yielding the mononuclear Ti^{III} monohydroxy complex [Cp*$_2$Ti(OH)] as well as two tetranuclear Ti^{IV} complexes.

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

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

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The authors of this Communication wish to add an extra sentence to their acknowledgment:

"We thank Dr. Andreas Rummel and Jasmin Strotmeier (Institute of Toxicology, Hannover Medical School) for the measurements of CD spectra."

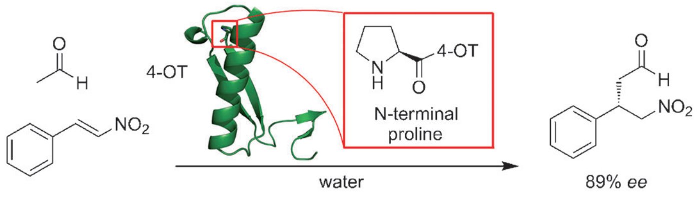
Isolation and Total Synthesis of Icumazoles and Noricumazoles—Antifungal Antibiotics and Cation-Channel Blockers from *Sorangium cellulosum*

J. Barbier, R. Jansen, H. Irschik, S. Benson, K. Gerth, B. Böhlendorf, G. Höfle, H. Reichenbach, J. Wegner, C. Zeilinger, A. Kirschning,* R. Müller* ———— **1256–1260**

Angew. Chem. Int. Ed. **2012**, *51*

DOI: 10.1002/anie.201106435

In the Table of Contents picture for this Communication, the nitroaldehyde product was erroneously displayed as the *R* enantiomer. The correct picture with the *S*-configured product is shown below.



Bridging between Organocatalysis and Biocatalysis: Asymmetric Addition of Acetaldehyde to β-Nitrostyrenes Catalyzed by a Promiscuous Proline-Based Tautomerase

E. Zandvoort, E. M. Geertsema, B.-J. Baas, W. J. Quax, G. J. Poelarends* ———— **1240–1243**

Angew. Chem. Int. Ed. **2012**, *51*

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