Contents

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:

*X. Xin, M. He, W. Han, J. Jung, Z. Lin**
Low-Cost Counter Electrodes for High-Efficiency Dye-Sensitized Solar Cells

Y. Filinchuk, Bo Richter, T. R. Jensen,* V. Dmitriev, D. Chernyshov, H. Hagemann*
Porous and Dense $Mg(BH_4)_2$ Frameworks: Synthesis, Stability, and Reversible Absorption of Guest Species

Editorial


F. Besenbacher


P. Krogsgaard-Larsen


P. Thostrup

Author Profile

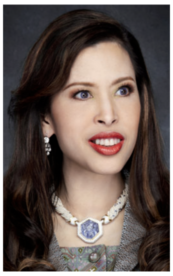
"Young people should study chemistry because they can learn how to cook.
My favorite time of day is reading literature. …"
This and more about Xinliang Feng can be found on page 10762.

News


L. De Cola


V. Gouverneur


K. Kohse-Höinghaus


C. Mahidol

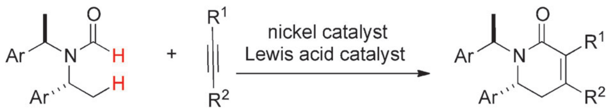

L. F. Nazar


A. E. Yonath

Books

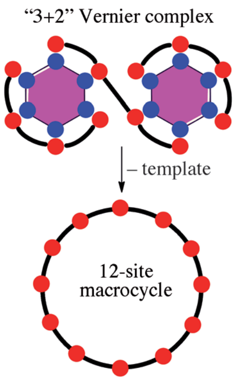
Highlights

Double C–H Activation



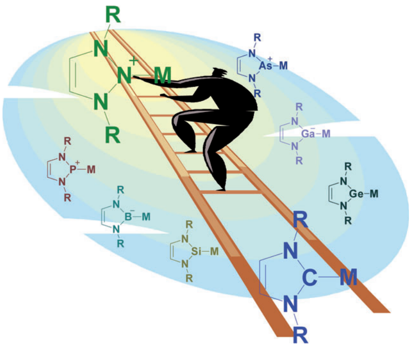
Double the fun: The future of cross-coupling chemistry lies in the development of cleaner synthetic methods for carbon–carbon bond formation. A recent advancement in the field of nickel-catalyzed $C(sp^2)$–$C(sp^3)$ cross-couplings (see scheme) via two C–H activations represents a major step forward.

Templating Giants



Growing bigger: A versatile approach toward the construction of nanosize π-conjugated macrocycles by Vernier templation has been demonstrated. The use of linear tetranuclear Zn^{II} porprhyrin complexes and a suitable and readily available six-site template leads to formation and isolation of a giant, monodisperse macrocycle in a limited amount of synthetic steps, marking Vernier complex formation a powerful and new tool for the creation of superstructures (see picture).

N-Heterocyclic Nitrenium Ligands



Pince me: N-heterocyclic nitrenium cations have been framed into pincer motifs to explore their unprecedented ligand behavior to transition metals. This work fills a long-standing gap in the series of main-group N-heterocyclic carbene-(NHC)-type ligands (see picture). Reasonable π-acceptor and weak σ-donor properties of these new ligands are expected to play a pivotal role in many organometallic reactions and in catalysis in the near future.

For the USA and Canada:
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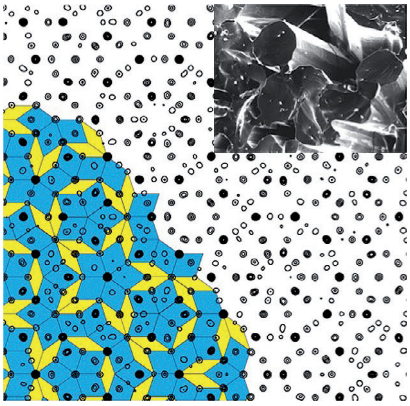
Contents

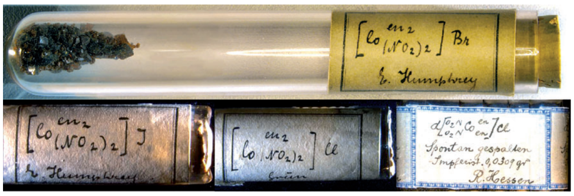
Nobel Prize in Chemistry 2011

Since the moment Dan Shechtman discovered a material with an ordered but aperiodic ("quasiperiodic") structure, which was believed to be impossible at the time, he began a long battle to convince his colleagues that his data were real. His efforts were finally rewarded with a Nobel Prize. The picture shows the projected electron density distribution function of decagonal Al-Co-Ni with Penrose tiling as an example of a quasicrystal.



Essays

Coordination Chemistry



Save your samples! The original compound $[Co(en)_2(NO_2)_2]Br$ prepared by Alfred Werner's student Edith Humphrey around 1900 did not crystallize as a conglomerate, but rather formed twinned crystals of both enantiomorphs. These findings, together with similar results for further samples from the Werner laboratory, provide new insight to the claim that Werner could have proved his coordination theory ten years earlier.

Minireviews

Oxidative Carbonylation

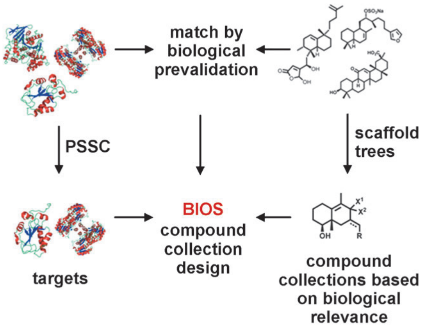
A new option: Classical carbonylation reactions employ organohalides as electrophiles to produce carbonyl compounds. Now a series of carbonylative derivatives can also efficiently synthesized by oxidative carbonylation reactions that have an enriched substrate scope and milder reaction conditions. This Minireview summarizes newly developed oxidative carbonylation reactions employing either R–M or R–H as the nucleophiles.

Reviews

Medicinal Chemistry

S. Wetzel, R. S. Bon, K. Kumar,
H. Waldmann* ________ 10800 – 10826

Biology-Oriented Synthesis



From nature with love! Biological relevance is the key argument in the search for small molecules that enable the chemical-biological analysis of biological systems or modulation of disease states. Biology-oriented synthesis (BIOS) uses this criterion to chart and navigate vast chemical structure space and to identify biologically relevant scaffold structures as guides for the synthesis of compound libraries (see picture).

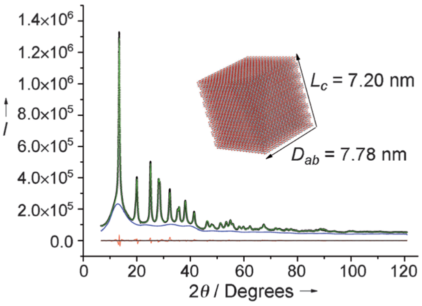
Communications

Nanocomposites

G. Cernuto, S. Galli, F. Trudu,
G. M. Colonna, N. Masciocchi,
A. Cervellino,*
A. Guagliardi* ________ 10828 – 10833

Investigating the Amorphous–Crystalline Interplay in SiO_2/TiO_2 Nanocomposites by Total Scattering Methods

Come together! A combined real- and reciprocal-space total scattering approach was realized by applying Debye and radial distribution functions to nanocrystalline and amorphous fractions within the same experimental pattern. The method allows for the quantitative description of microstructural features induced by the amorphous–crystalline interplay in silica–titania nanocomposites (see picture).

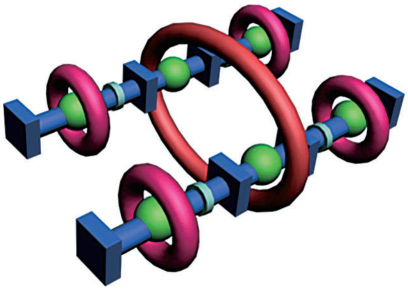


Rotaxanes

Z.-J. Zhang, H.-Y. Zhang, H. Wang,
Y. Liu* ________ 10834 – 10838

A Twin-Axial Hetero[7]rotaxane

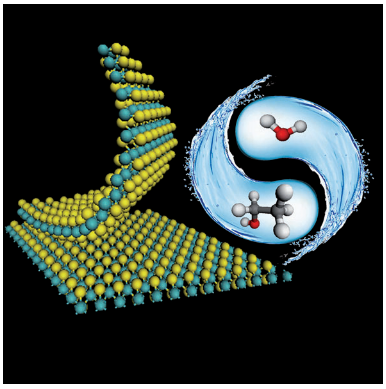
Two in one: Two pseudorotaxanes can be combined to form a twin-axial hetero[7]-rotaxane (see picture) by using the copper-catalyzed alkyne–azide "click" reaction. The synthetic route, in which twin-axial and single-axial rotaxanes are formed, combines self-assembly and the formation of covalent bonds to ensure the correct positioning of the two types of rings in the final product.



Inorganic Graphene Analogues

K.-G. Zhou, N.-N. Mao, H.-X. Wang,
Y. Peng, H.-L. Zhang* ___ 10839 – 10842

A Mixed-Solvent Strategy for Efficient Exfoliation of Inorganic Graphene Analogues



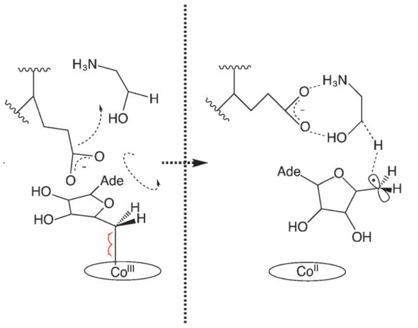
Two are better than one: A mixed-solvent method for liquid exfoliation of MoS_2, WS_2, and BN nanosheets is presented. Although ethanol and water are both poor solvents for this process, ethanol/water mixtures of appropriate composition, which can be predicted on the basis of Hansen solubility parameters, result in efficient exfoliation (see schematic) to give highly stable suspensions.

Contents

Enzymatic Reaction Dynamics

A. R. Jones,* S. J. O. Hardman, S. Hay, N. S. Scrutton* ______ **10843 – 10846**

Is There a Dynamic Protein Contribution to the Substrate Trigger in Coenzyme B_{12}-Dependent Ethanolamine Ammonia Lyase?



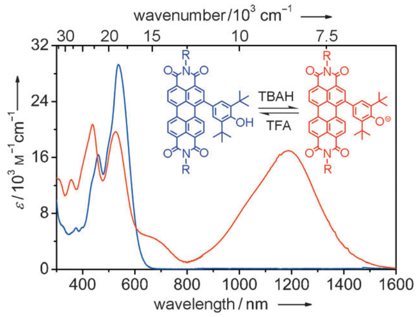
"Cohort-ry" in motion: The chemistry following Co–C bond homolysis in coenzyme B_{12}-dependent ethanolamine ammonia lyase is known to favor dissociation, but what of the protein contribution? Experiments reveal the radical pair reaction dynamics to be coupled to the ps–ns protein dynamics in B_{12} photolysis. This raises the possibility of a subtle, dynamic contribution to homolysis, which acts in cohort with electrostatics and H-abstraction from the substrate.

NIR Dyes

M.-J. Lin, B. Fimmel, K. Radacki, F. Würthner* ______ **10847 – 10850**

Halochromic Phenolate Perylene Bisimides with Unprecedented NIR Spectroscopic Properties

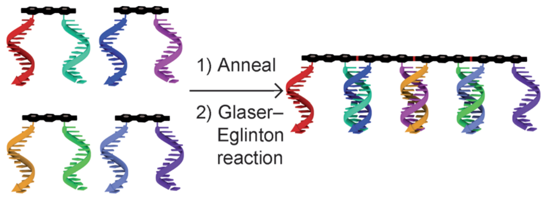
C–C coupling of 1,7-dibromoperylene bisimide with sterically hindered 2,6-di-*tert*-butylphenol by a carbon nucleophilic substitution reaction in the absence of transition-metal catalysts gave novel halochromic perylene bisimides (see picture). The corresponding phenolate ions of these compounds exhibit unprecedented NIR spectroscopic properties including strong absorption with maxima at around 1200 nm.



DNA-Directed Chemistry

J. B. Ravnsbæk, M. F. Jacobsen, C. B. Rosen, N. V. Voigt, K. V. Gothelf* ______ **10851 – 10854**

DNA-Programmed Glaser–Eglinton Reactions for the Synthesis of Conjugated Molecular Wires

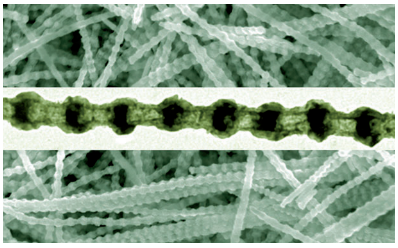


Wire self-assembly: Short oligo(phenylene ethynylene) modules (black structures, see picture) are assembled by attached DNA strands, which also direct the formation of 1,3-diyne linkages between the modules by the Cu-mediated Glaser–Eglinton reaction to selectively form dimer, trimer, and tetramer conjugated wires of up to 8 nm in length.

Nanostructures

Y. Yang,* L. Liu,* F. Güder, A. Berger, R. Scholz, O. Albrecht, M. Zacharias ______ **10855 – 10858**

Regulated Oxidation of Nickel in Multisegmented Nickel–Platinum Nanowires: An Entry to Wavy Nanopeapods

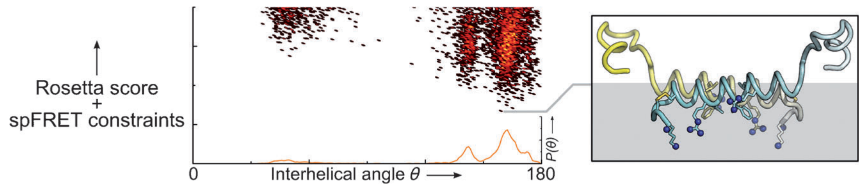


Split peas: Nanopeapods consisting of highly ordered, wavy NiO nanopods embedded with equally spaced Pt nanopeas were fabricated by the oxidation of multisegmented Ni/Pt nanowires at low temperatures. The Ni/Pt interface is an efficient platform for enhancing the outward diffusion of Ni during oxidation and for manipulating the nucleation of vacancies in Ni, which intrinsically behaves in an uncontrolled manner.

Peptide Structure

A. Nath, A. D. Miranker,*
E. Rhoades* ______ 10859 – 10862

A Membrane-Bound Antiparallel Dimer of Rat Islet Amyloid Polypeptide

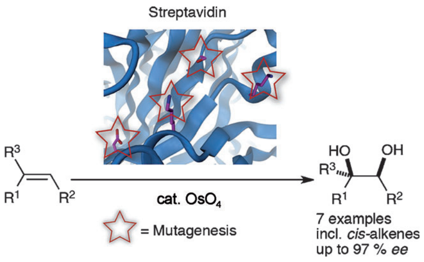


Gaining recognition: The structure of a previously unrecognized antiparallel dimer of rat islet amyloid polypeptide bound to anionic membrane nanodiscs was examined by using a combination of single-pair FRET and Rosetta model refinement. Models of the dimer showed a likely interface for lipid binding and suggest key interactions may also occur in the human isoform, thereby providing possible insights into fibril formation in type II diabetes.

Artificial Metalloenzymes

V. Köhler, J. Mao, T. Heinisch, A. Pordea,
A. Sardo, Y. M. Wilson, L. Knörr, M. Creus,
J.-C. Prost, T. Schirmer,*
T. R. Ward* ______ 10863 – 10866

OsO_4·Streptavidin: A Tunable Hybrid Catalyst for the Enantioselective *cis*-Dihydroxylation of Olefins

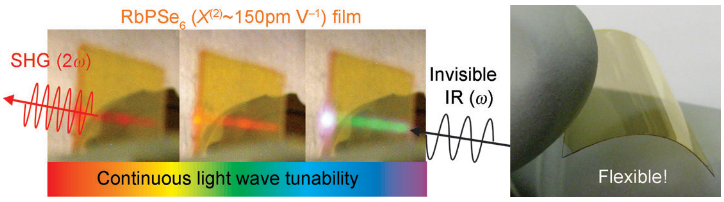


Taking control: Selective catalysts for olefin dihydroxylation have been generated by the combination of apo-streptavidin and OsO_4. Site-directed mutagenesis allows improvement of enantioselectivity and even inversion of enantiopreference in certain cases. Notably allyl phenyl sulfide and *cis*-β-methylstyrene were converted with unprecedented enantiomeric excess.

Nonlinear Optics

I. Chung, M. Kim, J. I. Jang, J. He,
J. B. Ketterson,
M. G. Kanatzidis* ______ 10867 – 10870

Strongly Nonlinear Optical Chalcogenide Thin Films of $APSe_6$ (A=K, Rb) from Spin-Coating



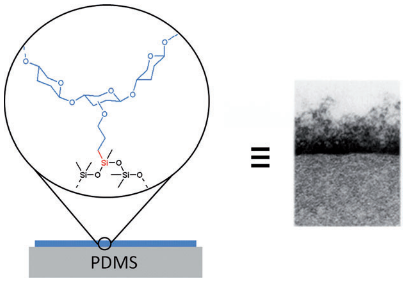
The first example of solution-based deposition of strongly nonlinear optical inorganic thin films at low temperatures of 125–250 °C is presented. The obtained glassy and crystalline films of highly nonlinear $APSe_6$ compounds (A = K, Rb; $\chi^{(2)} \approx 150\ \mathrm{pm\,V^{-1}}$) exhibit strong, inherent second harmonic and difference frequency generation (SHG and DFG) in the visible and near-IR spectral region at room temperature without the need of poling (see picture).

Surface Chemistry

W. Mussard, N. Kebir, I. Kriegel,
M. Estève, V. Semetey* ______ 10871 – 10874

Facile and Efficient Control of Bioadhesion on Poly(dimethylsiloxane) by Using a Biomimetic Approach

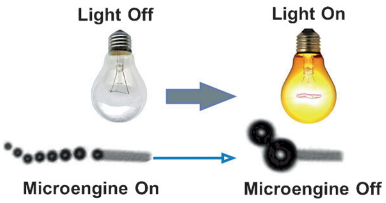
An antiadhesive nanofilm has been designed and prepared in one step in water onto commercial poly(dimethylsiloxane) (PDMS) by mimicking the external region of cell membranes. The resulting biomimetic surfaces are effective in suppressing protein adsorption as well as bacterial and mammalian cell adhesion.



Microengines

A. A. Solovev, E. J. Smith, C. C. Bof′ Bufon,
S. Sanchez,*
O. G. Schmidt ________ **10875 – 10878**

Light-Controlled Propulsion of Catalytic Microengines

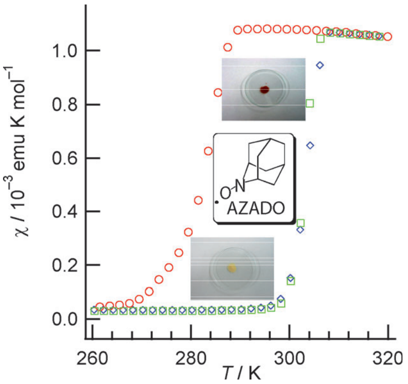


Turn off the light: A white-light source is used to control the propulsion of catalytic microengines powered by the local decomposition of hydrogen peroxide into oxygen and water. The influence of the wavelength of the light and intensity on the fuel conditions provides a remote control over the power of the self-propelled microengines (see picture).

Thermochromism

S. Matsumoto, T. Higashiyama,
H. Akutsu, S. Nakatsuji* _ **10879 – 10883**

A Functional Nitroxide Radical Displaying Unique Thermochromism and Magnetic Phase Transition

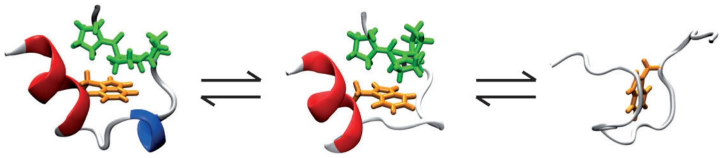


Thermochromic nitroxide: A nitroxide radical (AZADO) exhibits thermochromism with a structural change from a dimer at low temperature (4 °C) to paired monomers with large antiferromagnetic interaction at high temperature (35 °C). An hysteresis loop is observed in the magnetic data of this compound, revealing it to exhibit a first-order phase transition with room-temperature magnetic bistability.

Protein Folding

R. M. Culik, A. L. Serrano,
M. R. Bunagan,* F. Gai* _ **10884 – 10887**

Achieving Secondary Structural Resolution in Kinetic Measurements of Protein Folding: A Case Study of the Folding Mechanism of Trp-cage

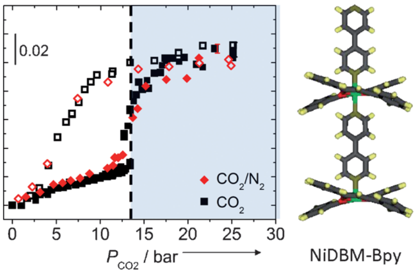


A new twist: A multi-probe and multi-frequency approach is shown for dissecting the folding dynamics of individual protein structural elements. In response to a temperature jump the 3_{10}-helix (blue in the picture) of the miniprotein Trp-cage unfolds before the global unfolding of the protein, whereas the formation of the cage structure depends on the folding of the α-helix (red).

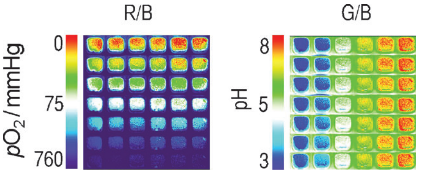
CO_2-Selective Adsorption

K. L. Kauffman, J. T. Culp, A. J. Allen,
L. Espinal, W. Wong-Ng, T. D. Brown,
A. Goodman, M. P. Bernardo,
R. J. Pancoast, D. Chirdon,
C. Matranga* ________ **10888 – 10892**

Selective Adsorption of CO_2 from Light Gas Mixtures by Using a Structurally Dynamic Porous Coordination Polymer



Flexibility provides selectivity: The selective adsorption of CO_2 from mixtures with N_2, CH_4, and N_2O in a dynamic porous coordination polymer (see monomer structure) was evaluated by ATR-FTIR spectroscopy, GC, and SANS. All three techniques indicate highly selective adsorption of CO_2 from CO_2/CH_4 and CO_2/N_2 mixtures at 30 °C, with no selectivity observed for the CO_2/N_2O system.



Two kinds of imaging: A fluorescent sensor membrane is presented that responds to pH and to pO_2 at different emission wavelengths. The fluorescence intensities can be imaged with a digital camera using the red-green-blue (RGB) data storage option.

Tissue Imaging

R. J. Meier, S. Schreml, X. D. Wang, M. Landthaler, P. Babilas, O. S. Wolfbeis* ________ **10893 – 10896**

Simultaneous Photographing of Oxygen and pH In Vivo Using Sensor Films

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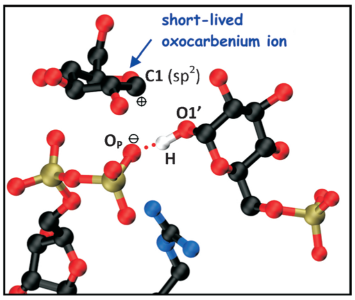
A quantum leap: By means of quantum mechanics/molecular mechanics metadynamics simulations, a front-face S_Ni-type reaction for glycosyl transfer with retention of the anomeric configuration is shown to be feasible. A short-lived oxocarbenium-like species (see picture; O red, P gold, N blue, C black) is identified and provides the complete itinerary of this long sought after molecular mechanism.



Reaction Mechanisms

A. Ardèvol, C. Rovira* ____ **10897 – 10901**

The Molecular Mechanism of Enzymatic Glycosyl Transfer with Retention of Configuration: Evidence for a Short-Lived Oxocarbenium-Like Species

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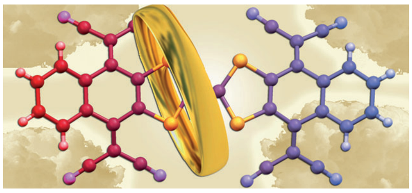
Happy marriage: For the first time, a fused TCNQ–TTF–TCNQ triad has been synthesized and structurally characterized. Strong bending is observed in both the TTF bridge and the benzo-TCNQ moieties, which prevents good packing for intermolecular charge transfer. The Vis/NIR and VT-EPR studies of the mixed-valence derivative of the triad indicate that the electrons are moving from one acceptor moiety to the other through the donor TTF bridge.



Organic Materials

F. Otón, V. Lloveras, M. Mas-Torrent, J. Vidal-Gancedo, J. Veciana, C. Rovira* ________ **10902 – 10906**

Coupling Tetracyanoquinodimethane to Tetrathiafulvalene: A Fused TCNQ–TTF–TCNQ Triad

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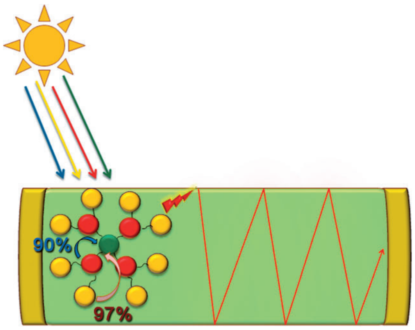


A polymer-embedded dendritic, bodipy-based panchromatic absorber with a built-in energy gradient concentrates incident solar radiation at a terminal chromophore, resulting in a monochromatized emission directed to the sides of the polymer waveguide (see picture). This particular design minimizes self-absorption losses from the peripheral antenna units with an impressive S factor of 10000.

Dendritic Solar Concentrators

O. Altan Bozdemir, S. Erbas-Cakmak, O. O. Ekiz, A. Dana, E. U. Akkaya* ________ **10907 – 10912**

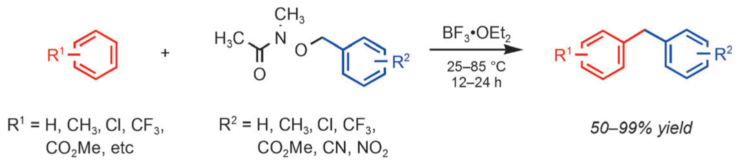
Towards Unimolecular Luminescent Solar Concentrators: Bodipy-Based Dendritic Energy-Transfer Cascade with Panchromatic Absorption and Monochromatized Emission

Contents

Arene Functionalization

G. Schäfer, J. W. Bode* ___ **10913 – 10916**

Friedel–Crafts Benzylation of Activated and Deactivated Arenes

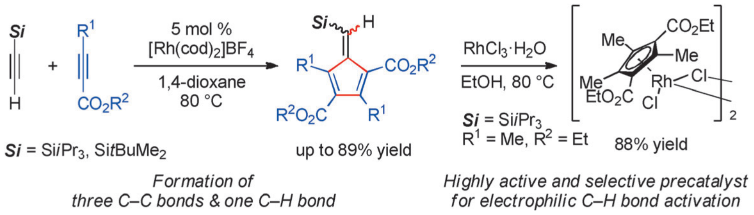


NO going back makes possible facile Friedel–Crafts benzylations with moderate reaction temperatures, simple reaction workups, and improved substrate scope for the formation of synthetically important diarylmethanes (see scheme). Upon complexation with BF_3·OEt_2, hydroxamates serve as reversible leaving groups that stabilize highly reactive carbocations. Even deactivated arenes and electron-deficient benzylhydroxamates react cleanly under these conditions.

Fulvene Synthesis

Y. Shibata, K. Tanaka* ___ **10917 – 10921**

Catalytic [2+2+1] Cross-Cyclotrimerization of Silylacetylenes and Two Alkynyl Esters To Produce Substituted Silylfulvenes

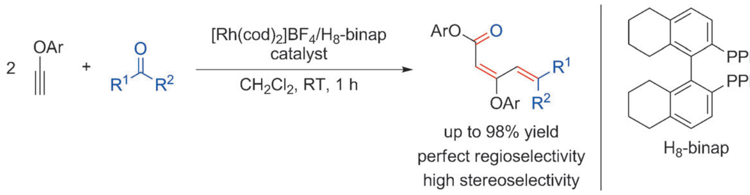


Three become one: The cationic rhodium(I) complex $[Rh(cod)_2]BF_4$ catalyzes the [2+2+1] cross-cyclotrimerization of silylacetylenes and two alkynyl esters, leading to substituted silylfulvenes (see scheme; cod = 1,5-cyclooctadiene). The reductive complexation of the silylfulvene product with $RhCl_3$ in EtOH furnished the corresponding dinuclear electron-deficient cyclopentadienyl rhodium(III) complex.

[2+2+2] Cross-Trimerization

Y. Miyauchi, M. Kobayashi, K. Tanaka* ___ **10922 – 10926**

Rhodium-Catalyzed Intermolecular [2+2+2] Cross-Trimerization of Aryl Ethynyl Ethers and Carbonyl Compounds To Produce Dienyl Esters



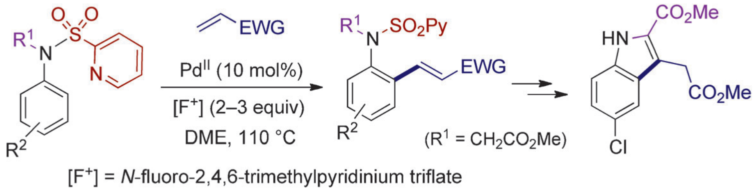
Positive thinking: A cationic rhodium(I)/H_8-binap complex catalyzes the chemo-, regio-, and stereoselective completely intermolecular [2+2+2] cross-trimerization of two aryl ethynyl ethers with both electron-deficient and electron-rich carbonyl compounds (see scheme; cod = 1,5-cyclooctadiene). This reaction proceeded at room temperature to give aryloxy-substituted dienyl esters in good yields.

VIP

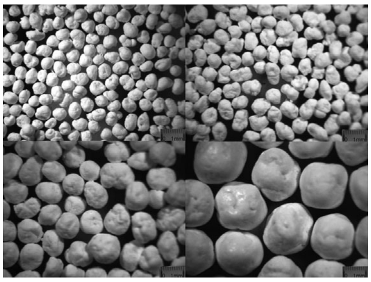
C–H activation

A. García-Rubia, B. Urones, R. Gómez Arrayás,* J. C. Carretero* ___ **10927 – 10931**

Pd^{II}-Catalyzed C–H Olefination of *N*-(2-Pyridyl)sulfonyl Anilines and Arylalkylamines



Flexible friend: The *N*-(2-pyridyl)sulfonyl group acts as a removable directing group in the Pd^{II}-catalyzed aryl C–H *ortho* alkenylation of *N*-alkyl aniline, benzylamine, and phenethylamine derivatives with electron-poor alkenes. The products were obtained in high yields (70–90%) and with complete regiocontrol. The mild reductive *N*-sulfonyl removal enables the construction of a variety of nitrogen heterocycles. EWG = electron-withdrawing group.

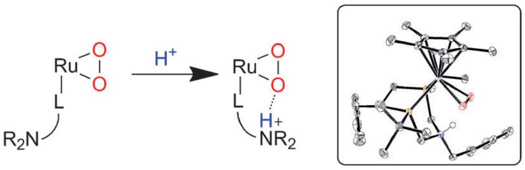


Partial to particular particles: The morphology of the polymer particles can be controlled in ethylene/CO copolymerization by pressurizing catalyst-containing 1-octanol droplets dispersed in water. The palladium catalyst should be harnessed with lipophilic long alkyl chains. Polymer particles of 0.5–1.0 mm size (see micrographs) with bulk densities of 0.2–0.3 $g\,mL^{-1}$ are produced without reactor fouling.

Polyketone Synthesis

J. H. Park, K. H. Oh, S. H. Kim, A. Cyriac,
J. K. Varghese, M. W. Hwang,
B. Y. Lee* ______ **10932 – 10935**

Morphology Control of Polymer Particles in Ethylene/Carbon Monoxide Copolymerization



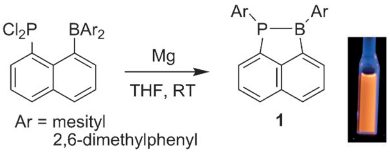
Proton relay: A side-on Ru–O_2 complex with pendent amines in the ligand backbone has been synthesized to model proton delivery in O_2 reduction (see scheme and structure; red O, purple Ru, blue N, yellow P). Protonation occurs at the amine near the O_2 ligand, forming a hydrogen bond between the ammonium ion and the O_2 ligand, leading to a small increase in O—O bond length.

Dioxygen Activation

T. A. Tronic, M. Rakowski DuBois,
W. Kaminsky, M. K. Coggins, T. Liu,
J. M. Mayer* ______ **10936 – 10939**

Directing Protons to the Dioxygen Ligand of a Ruthenium(II) Complex with Pendent Amines in the Second Coordination Sphere

On the move: The title compounds **1**, which are unique heterocyclic systems containing a P—B bond, have been synthesized by the reduction of 1-diarylboryl-8-dichlorophosphinonaphthalene derivatives (see scheme). Both experimental and theoretical results for **1** revealed an effective interaction between the phosphorus atom, boron atom, and naphthyl moiety. Furthermore, **1** exhibits orange fluorescence in solution.

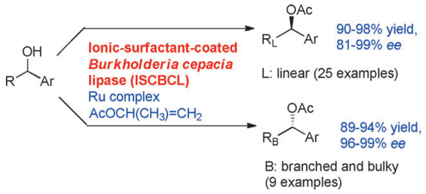


Heterocyclic Compounds

A. Tsurusaki, T. Sasamori,* A. Wakamiya,
S. Yamaguchi, K. Nagura, S. Irle,
N. Tokitoh* ______ **10940 – 10943**

Synthesis of 1-Phospha-2-bora-acenaphthenes: Reductive 1,2-Aryl Migration of 1-Diarylboryl-8-dichlorophosphinonaphthalenes

With a coat for activity: A highly active enzyme was prepared by coating *Burkholderia cepacia* lipase with an ionic surfactant for use in dynamic kinetic resolution (DKR). Important features of this enzyme include: the fastest DKR of 1-phenylethanol, the highly enantioselective DKR of a wide range of secondary alcohols (RCH(OH)Ar), and the switching of lipase enantioselectivity in DKR depending on the shape of the aliphatic chain (R).



Dynamic Kinetic Resolution

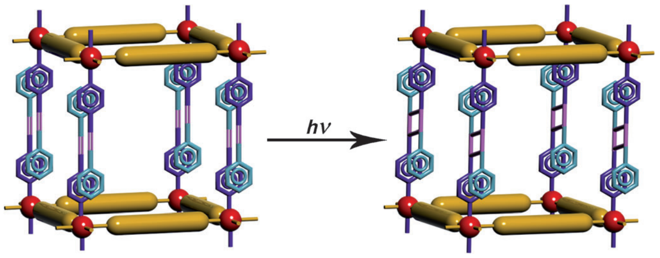
H. Kim, Y. K. Choi, J. Lee, E. Lee, J. Park,*
M.-J. Kim* ______ **10944 – 10948**

Ionic-Surfactant-Coated *Burkholderia cepacia* Lipase as a Highly Active and Enantioselective Catalyst for the Dynamic Kinetic Resolution of Secondary Alcohols

Metal–Organic Frameworks

R. Medishetty, L. L. Koh, G. K. Kole,
J. J. Vittal* ______________ **10949 – 10952**

Solid-State Structural Transformations from 2D Interdigitated Layers to 3D Interpenetrated Structures

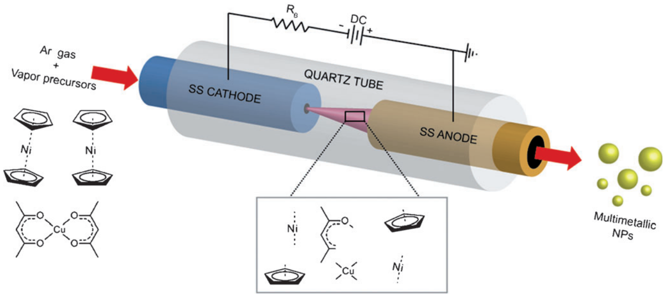


Construction by shining light! A [2+2] cycloaddition reaction in a 2D coordination polymer accompanied by single-crystal-to-single-crystal structural transformation to a 3D structure highlights the retrosynthesis of a 3D structure from a 2D layer compound (see scheme, Zn red, 4-styrylpyridine blue/turquoise).

Nanotechnology

P. A. Lin,
R. M. Sankaran* ________ **10953 – 10956**

Plasma-Assisted Dissociation of Organometallic Vapors for Continuous, Gas-Phase Preparation of Multimetallic Nanoparticles

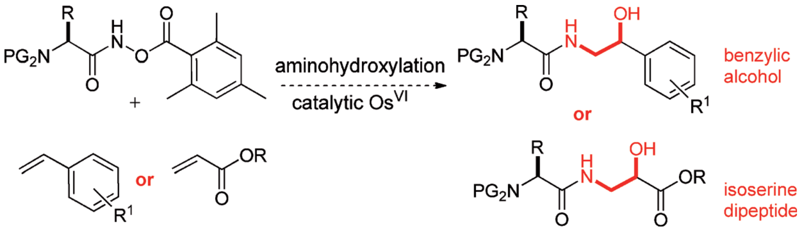


Vapor-sized: In a plasma-based route to multimetallic nanoparticles (NPs), vapor mixtures of organometallic compounds are dissociated in an atmospheric-pressure microplasma (see picture). The size and composition of the particles is controlled by the relative vapor concentrations of the precursors.

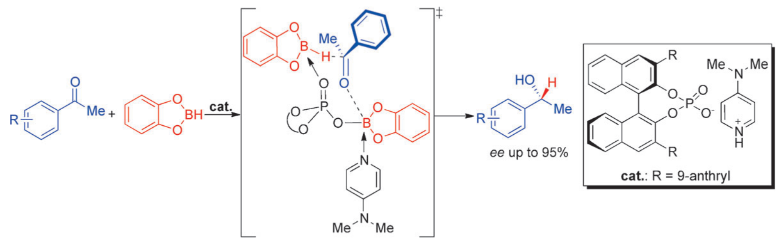
Amino Acids as Nitrogen Sources

T. J. Donohoe,* C. K. A. Callens, A. Flores,
S. Mesch, D. L. Poole,
I. A. Roslan ______________ **10957 – 10960**

Amino Acid-Based Reoxidants for Aminohydroxylation: Application to the Construction of Amino Acid–Amino Alcohol Conjugates



A viable nitrogen source for the aminohydroxylation reaction of terminal alkenes: By adding a N-O based reoxidant onto an amino acid acyl carbon atom, compounds were obtained that facilitated catalytic turnover and also promoted the conjugation of an amino acid with an alkene. High levels of regioselectivity were observed, as well as good stereoselectivity induced by catalytic amounts of a chiral ligand.



A new path to chiral alcohols: Asymmetric reduction of ketones was achieved utilizing a chiral Brønsted acid as precatalyst for the first time. Using catecholborane as the reducing agent, a highly enantioselective formation of chiral secondary alcohols was found with a broad substrate scope. Mechanistic studies indicate that phosphoryl catechol borate derived from the reaction of the Brønsted acid with catecholborane produced the active catalyst (see scheme).

Asymmetric Catalysis

Z. Zhang, P. Jain,
J. C. Antilla* ———— 10961 – 10964

Asymmetric Reduction of Ketones by Phosphoric Acid Derived Catalysts

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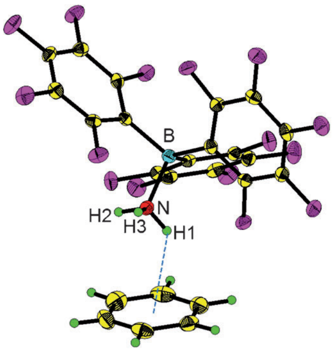

O/N−H⋯π hydrogen bonds: Water–benzene and ammonia–benzene complexes are stabilized by the Lewis acid $B(C_6F_5)_3$ and provide rare structural (X-ray) and infrared spectroscopic data for water–benzene and ammonia–benzene complexes in the solid state (see picture). The infrared spectra of the complexes showed that the O−H and N−H stretching frequencies decrease significantly on benzene complexation.

Hydrogen Bonds

X. Wang,* P. P. Power* — 10965 – 10968

Structural Characterization, Infrared Spectroscopy, and Theoretical Calculations for $B(C_6F_5)_3$-Stabilized Benzene–Ammonia and Benzene–Water Complexes

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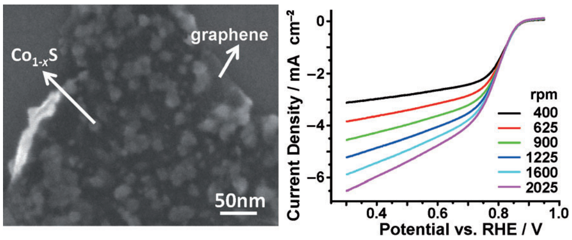


A hybrid electrocatalyst for the oxygen reduction reaction (ORR), consisting of $Co_{1-x}S$ nanoparticles directly nucleated and grown on sheets of reduced graphene oxide (RGO; see SEM image), was prepared by a mild solution-phase reaction followed by an annealing step. The $Co_{1-x}S$–RGO hybrid has the highest catalytic performance of all cobalt chalcogenide based ORR catalysts, as revealed inter alia by measurements with a rotating-disk electrode (see picture; RHE = reversible hydrogen electrode).

Oxygen Reduction

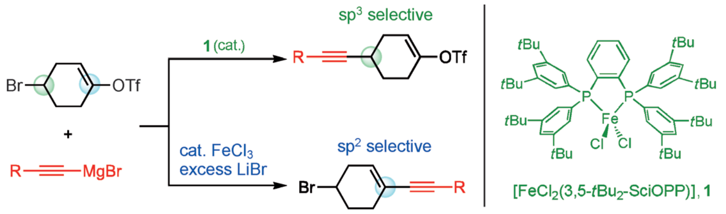
H. Wang, Y. Liang, Y. Li,
H. Dai* ———— 10969 – 10972

$Co_{1-x}S$–Graphene Hybrid: A High-Performance Metal Chalcogenide Electrocatalyst for Oxygen Reduction

Cross-Coupling

T. Hatakeyama, Y. Okada, Y. Yoshimoto,
M. Nakamura* ———— **10973 – 10976**

Tuning Chemoselectivity in Iron-Catalyzed Sonogashira-Type Reactions Using a Bisphosphine Ligand with Peripheral Steric Bulk: Selective Alkynylation of Nonactivated Alkyl Halides

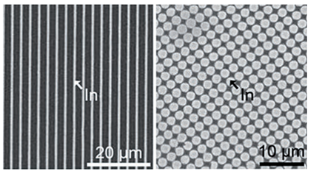


The incredible bulk: A highly C_{sp^3}-center-selective alkynylation of nonactivated alkyl halides with the corresponding Grignard reagents is achieved by using the iron-phosphine complex **1**. Primary and secondary alkyl iodides, bromides, and chlorides take part in the reaction to give the substituted alkynes in good to excellent yields. Sequential cyclization/cross-coupling reactions are also demonstrated.

Lithography

M. Park, Y. Xia, U. Jeong* **10977 – 10980**

Patterning Materials through Viscoelastic Flow and Phase Separation

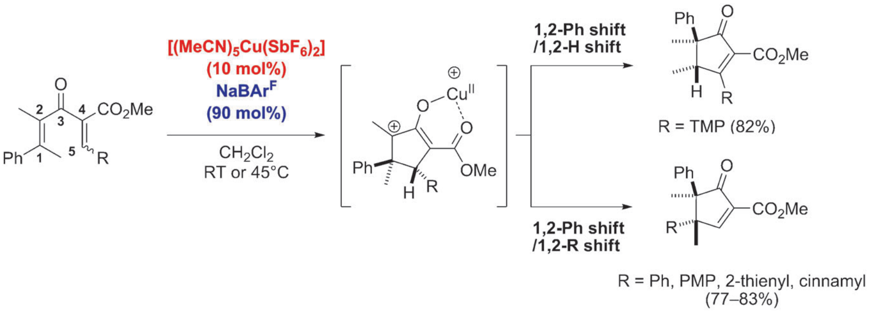


Going with the flow: Patterning of various inorganic materials was achieved by phase separation between the nanomaterials and a polymer melt as well as concentrating the nanomaterials in defined areas by a polymer melt flow. This technique generated micro- and nanostructured patterns of metals and semiconductors (see picture).

Synthetic Methods

D. Lebœuf, J. Huang, V. Gandon,
A. J. Frontier* ———— **10981 – 10985**

Using Nazarov Electrocyclization to Stage Chemoselective [1,2]-Migrations: Stereoselective Synthesis of Functionalized Cyclopentenones

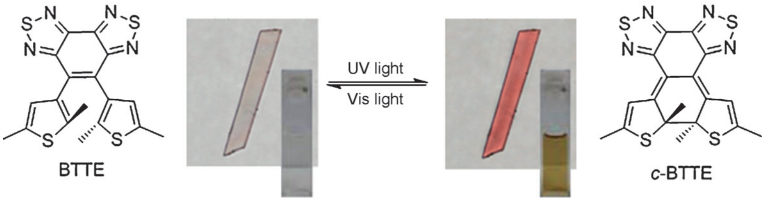


Highly functionalized cyclopentenones have been prepared stereospecifically through a chemoselective copper(II)-mediated Nazarov/Wagner–Meerwein rearrangement sequence. After the initial 4π electrocyclization, this reaction involves two sequential [1,2]-migrations depending upon both migratory ability and steric bulk of the substituents at C1 and C5 (see scheme). The proposed mechanism of the reaction is supported by DFT studies.

Photochromism

W. Zhu,* Y. Yang, R. Métivier, Q. Zhang,
R. Guillot, Y. Xie, H. Tian,
K. Nakatani* ———— **10986 – 10990**

Unprecedented Stability of a Photochromic Bisthienylethene Based on Benzobisthiadiazole as an Ethene Bridge



An open and closed case: The photochromic bisthienylethene BTTE based on benzobisthiadiazole exhibits excellent photochromic performance in both solution and single crystals (see picture). BTTE shows excellent thermal stability, which is comparable to the widely known five-membered hexafluorocyclopentene-based counterpart.

Twisted organization: Pyrolysis of nanocrystalline cellulose (NCC)/silica composite films leads to mesoporous carbon materials with long-range chiral organization (see picture). The NCC acts as a template and the resulting mesoporous carbon has a high specific surface area ($>1400\ m^2g^{-1}$) and accurately replicates the left-handed helical structure of the chiral nematic NCC films.

Chiral Nanomaterials

VIP

K. E. Shopsowitz, W. Y. Hamad,
M. J. MacLachlan* ______ **10991 – 10995**

Chiral Nematic Mesoporous Carbon Derived From Nanocrystalline Cellulose

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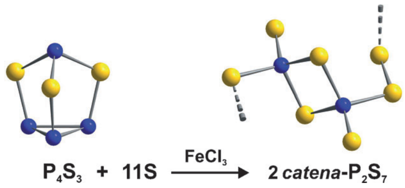
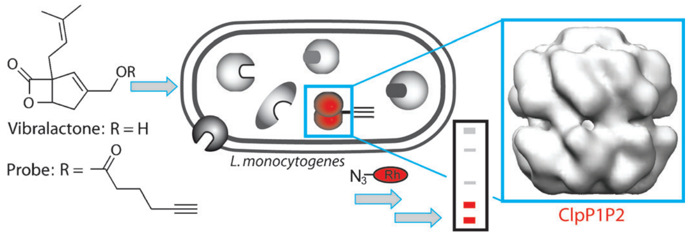
Sulfur, so good: Crystallization of phosphorus polysulfides *catena*-P_2S_7 is enhanced by catalytic amounts of anhydrous $FeCl_3$ (see scheme, P blue, S yellow). The formation of polysulfide bridges is observed which is typical for vulcanization reactions.



Phosphorus Polysulfides

T. Rödl, R. Weihrich, J. Wack, J. Senker,
A. Pfitzner* ______ **10996 – 11000**

Rational Syntheses and Structural Characterization of Sulfur-Rich Phosphorus Polysulfides: α-P_2S_7 and β-P_2S_7

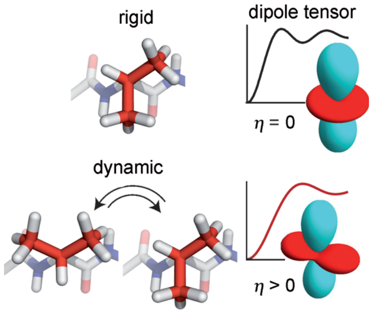


The Clp proteolytic machinery has important functions in many bacteria such as *L. monocytogenes*. Some organisms encode for two uncharacterized ClpP isoforms. Vibralactone was used to study the activity and assembly of ClpP1 and ClpP2 subunits in a hetero-oligomeric complex. Electron microscopic images reveal that the tetradecameric assembly is made up of two stacked homoheptameric ClpP1 and ClpP2 rings.

Heterooligomeric Complexes

E. Zeiler, N. Braun, T. Böttcher,
A. Kastenmüller, S. Weinkauf,
S. A. Sieber* ______ **11001 – 11004**

Vibralactone as a Tool to Study the Activity and Structure of the ClpP1P2 Complex from *Listeria monocytogenes*



Nonsymmetric motion: Solid-state NMR measurements of dipolar coupling tensors provide insight into protein dynamics. The hitherto ignored asymmetry of the dipolar coupling tensor contains valuable information about motional asymmetry, which was used in the first direct site-resolved measurement of such tensors. Important motions such as rotamer jumps can now be directly detected in the solid state.

Protein NMR Spectroscopy

P. Schanda, M. Huber, J. Boisbouvier,
B. H. Meier,* M. Ernst* ___ **11005 – 11009**

Solid-State NMR Measurements of Asymmetric Dipolar Couplings Provide Insight into Protein Side-Chain Motion

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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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Contents

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Corrigendum

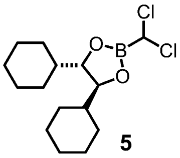
Asymmetric Allylboration of *vic*-Tricarbonyl Compounds: Total Synthesis of (+)-Awajanomycin

M. Wohlfahrt, K. Harms, U. Koert* ———— **8404–8406**

Angew. Chem. Int. Ed. **2011**, *50*

DOI 10.1002/anie.201103679

The absolute configurations of compounds **5**, **6**, and **8** as drawn in Scheme 2 of this communication were incorrect. The correct structures are shown below.



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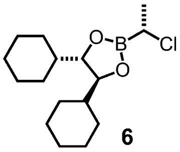

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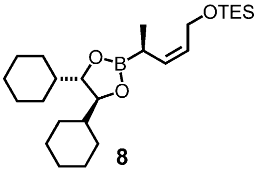

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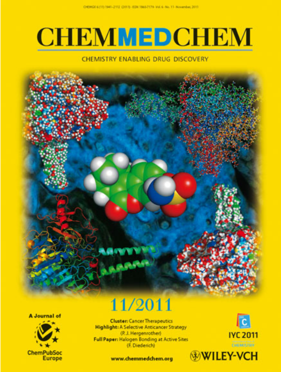

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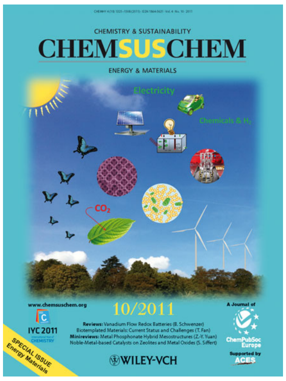

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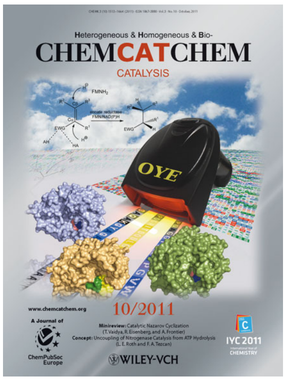

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