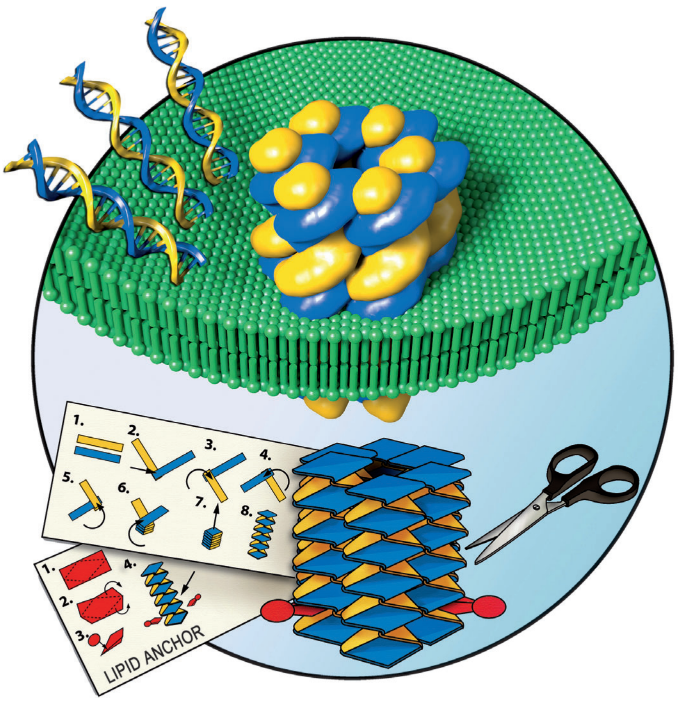
Membrane nanopores self-assembled from DNA …

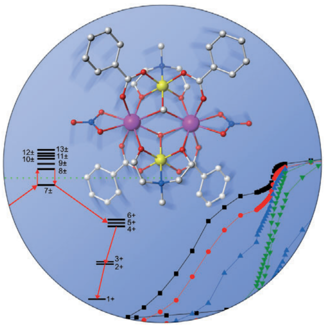
Angewandte
International Edition Chemie

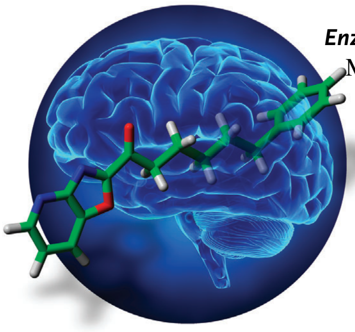


… are the most recent type of synthetic channels. Inserting negatively charged DNA origami structures into a hydrophobic membrane can be achieved with just two porphyrin-based lipid anchors, as shown by S. Howorka and co-workers in their Communication on page 12069 ff. Minimal chemical intervention paves the way to new DNA pores for label-free biosensing and research into single molecules and biomimetic nanoarchitectures. (Simplified illustration of origami pores by Silvio Bianco, Hugh Martin, Jonathan R. Burns.)

Single-Molecule Magnets

In their Communication on page 12014 ff., L. F. Chibotaru, K. S. Murray et al. describe the significant effect of Cr^{III} centers in Cr_2Dy_2 clusters upon exchange coupling, which results in long relaxation times (picture: Steven Morton).



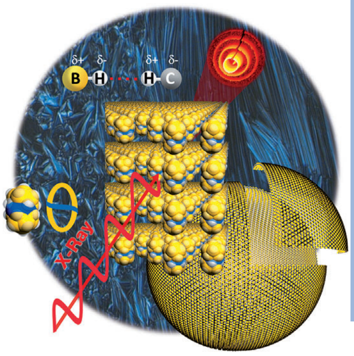


Enzyme Inhibitors

M. van der Stelt et al. present in their Communication on page 12081 ff. a new strategy for discovering selective hits by combining in silico screening and activity-based protein profiling in complex brain proteome.

Carborane Surfactants

In their Communication on page 12114 ff., P. Bauduin et al. show that intermolecular dihydrogen bonds are the key to understanding the aggregation of metallacarborane surfactants in water to give lamellar phases.



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Editorial

“ … Scientists need to be able to trust and rely on each other as a matter of care and responsibility towards our society. My further personal plea is that we have to give our students an awareness of good scientific practice and help them to find self-confidence …”
Read more in the Editorial by Katharina Al-Shamery.

Service

Author Profile

“My favorite place on earth is Hong Kong.
I lose track of time when I chat with my friends and students. …”
This and more about Chi-Ming Che can be found on page 11970 – 11971.

News

M. Karplus

M. Levitt

A. Warshel

Books

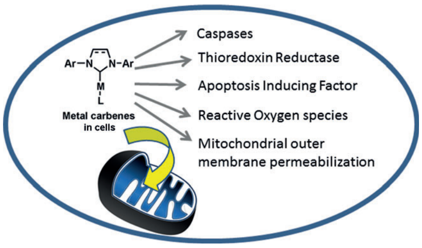
Symmetry Relationships between Crystal Structures | Ulrich Müller | *reviewed by U. Englert* ______ **11973**

Highlights

Membrane Transport

F. Cisnetti, A. Gautier* ___ **11976 – 11978**

The Tricky Task of Nitrate/Nitrite Antiport



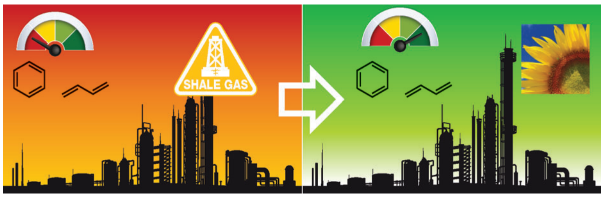
Subtle differences: Two recent crystal structures have provided the first insight into nitrate/nitrite exchangers (example shown with bound nitrite), which are crucial to bacterial metabolism. A direct comparison of the structures reveals how the proteins can distinguish between their highly similar substrates and translate this into a conformational change to translocate ions across the membrane.

Essays

Sustainable Chemistry

P. C. A. Bruijnincx,*
B. M. Weckhuysen* ______ **11980 – 11987**

Shale Gas Revolution: An Opportunity for the Production of Biobased Chemicals?



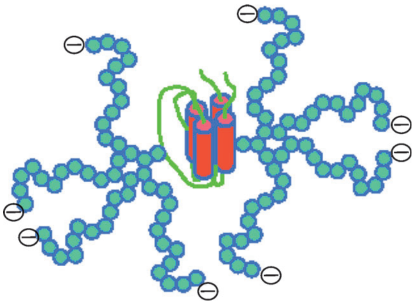
Saying a (bio)mass for the future: The shale gas revolution will strongly impact the availability of a number of key building blocks of the chemical industry, in particular butadiene and aromatics. These developments provide an opportunity for the on-purpose production of these bulk chemicals from renewable resources, such as biomass. Current efforts and developments from industry and academia in this direction are highlighted.

Minireviews

Synthetic Erythropoiesis Protein

S. B. H. Kent* ______ **11988 – 11996**

Bringing the Science of Proteins into the Realm of Organic Chemistry: Total Chemical Synthesis of SEP (Synthetic Erythropoiesis Protein)



The glycoprotein mimetic SEP (synthetic erythropoiesis protein) was prepared in homogenous form by total chemical synthesis. SEP had full biological activities and improved pharmacokinetic properties compared with first-generation recombinant human EPO. This work demonstrated that synthetic chemistry can be employed to systematically improve the properties of a protein biotherapeutic by the use of designed chemical moieties not found in nature.

For the USA and Canada:
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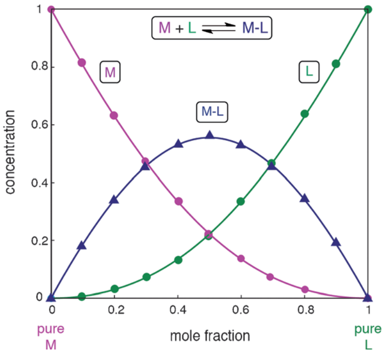
Reviews

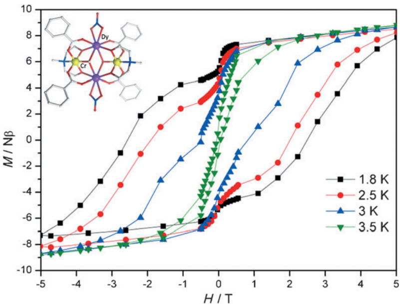
Lending a hand: Job plots, also known as the method of continuous variations (MCV), are used extensively throughout chemistry and biochemistry to study molecular associations. This review serves as a tutorial on using Job plots and a survey of the surprisingly few applications in organometallic chemistry.



Job Plots

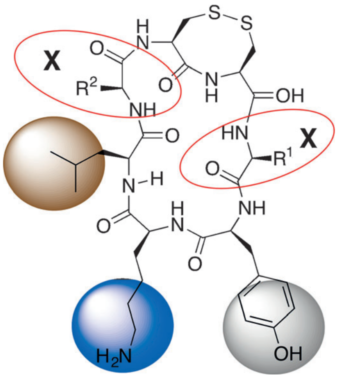
Communications

Butterfly magnet: The replacement of diamagnetic Co^{III} for Cr^{III} in a 3d-4f butterfly complex results in vastly improved single-molecule magnet properties. Longer relaxation times are found, with magnetic hysteresis observed. This is due to exchange interactions between the Dy^{III} and Cr^{III} ions, resulting in a multilevel exchange barrier with significantly reduced quantum tunneling of the magnetization.



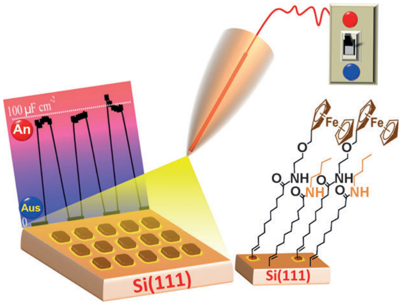
Single-Molecule Magnets

Frontispiece



Loopy peptides: Peptide turn mimetics of a clinically relevant norepinephrine reuptake inhibitor were developed employing a high-throughput synthesis approach to generate peptide thioesters, with subsequent cyclization through native chemical ligation. The vicinal disulfide constrained cyclic peptidomimetics (see scheme) show high structural and functional similarity to the parent peptide, though with superior metabolic stability.

Cyclic Peptides



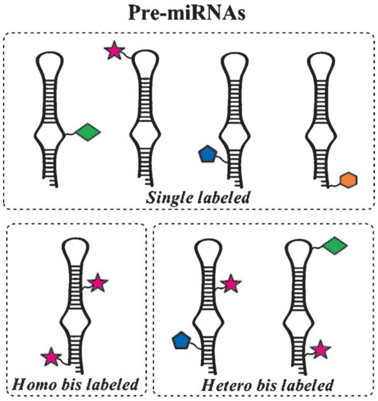
Ultrahigh-capacity molecular AND gates provide the potential for the next-generation dynamic random access memory. The ferrocene-terminated monolayer on oxide-free silicon system allows a highly stable and independent switching with both light and potential, yielding precisely such an AND gate (see picture).

Surface Chemistry

Pre-MicroRNA Labeling

U. Pradère, A. Brunschweiger,
L. F. R. Gebert, M. Lucic, M. Roos,
J. Hall* ——— 12028 – 12032

Chemical Synthesis of Mono- and Bis-Labeled Pre-MicroRNAs



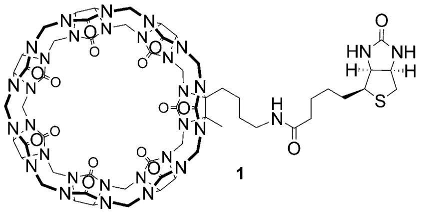
A chemical method for the post-synthetic labeling of pre-miRNAs on solid support using easily accessible reagents was developed. The procedure was employed to generate a library of 31 pre-microRNAs carrying labels commonly used in chemical biology, including Cy3, trioxalen, biotin, and BHQ-1.

Drug Delivery

L. Cao, G. Hettiarachchi, V. Briken,*
L. Isaacs* ——— 12033 – 12037

Cucurbit[7]uril Containers for Targeted Delivery of Oxaliplatin to Cancer Cells

Stay on target: The cucurbit[7]uril derivative **1**, which bears a covalently attached biotin targeting ligand allows for the efficient delivery of oxaliplatin as its **1**·oxaliplatin complex to cancer cells resulting in enhanced cytotoxicity relative to oxaliplatin alone.

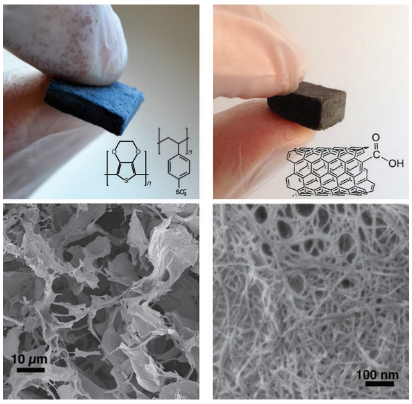

1

Functional Aerogels

M. Hamedi,* E. Karabulut, A. Marais,
A. Herland, G. Nyström,
L. Wågberg ——— 12038 – 12042

Nanocellulose Aerogels Functionalized by Rapid Layer-by-Layer Assembly for High Charge Storage and Beyond

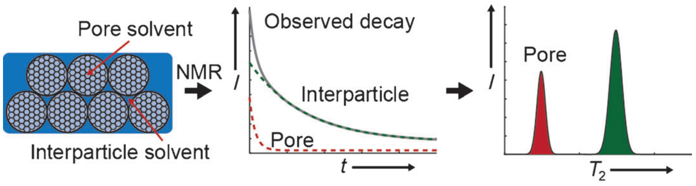
Step by step: A robust and rapid method for the layer-by-layer assembly of polymers and nanoparticles on strong and elastic aerogels has been developed. Thin films of biomolecules, conducting polymers, and carbon nanotubes were assembled, which resulted in aerogels with a number of functions, including a high charge-storage capacity.



NMR Porosity Screening

J. J. Chen,* X. Kong, K. Sumida,
M. A. Manumpil, J. R. Long,
J. A. Reimer ——— 12043 – 12046

Ex Situ NMR Relaxometry of Metal–Organic Frameworks for Rapid Surface-Area Screening



Taking a relaxed approach: The NMR relaxation behavior of imbibed solvent has been used to estimate the surface area of a variety of microporous metal–organic frameworks and zeolites. This NMR technique is amenable to automation and can expedite the characterization of microporous materials by identifying any nonporous or low-surface-area structures.

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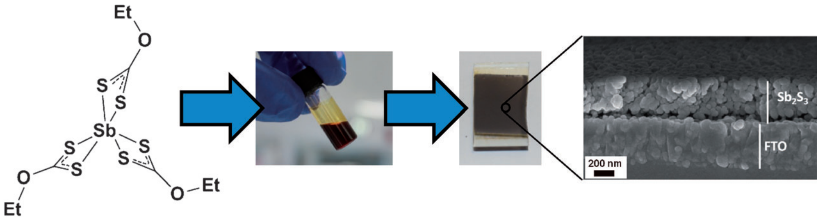
Hybrid Photovoltaics

F. T. F. O'Mahony, U. B. Cappel,
N. Tokmoldin, T. Lutz, R. Lindblad,
H. Rensmo, S. A. Haque* **12047 – 12051**

Low-Temperature Solution Processing of Mesoporous Metal–Sulfide Semiconductors as Light-Harvesting Photoanodes



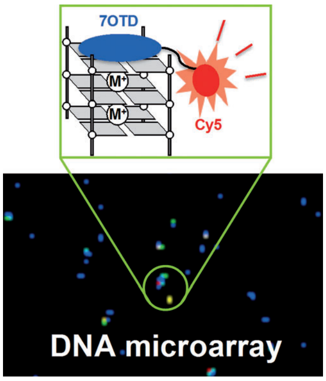
Structured absorbers: Mesoporous films of highly crystalline Sb_2S_3 are prepared from a doctor-bladed precursor paste that is thermally annealed. This facile and versatile processing route allows for control of the pore size through variation of the annealing temperature. The resulting high surface area allows for efficient charge transfer to a polymeric hole acceptor; hence, such films could form the basis of a novel hybrid organic–inorganic photovoltaic device.

G-Quadruplexes

K. Iida, T. Nakamura, W. Yoshida, M. Tera,
K. Nakabayashi, K. Hata, K. Ikebukuro,*
K. Nagasawa* ________ **12052 – 12055**

Fluorescent-Ligand-Mediated Screening of G-Quadruplex Structures Using a DNA Microarray

Inside Cover



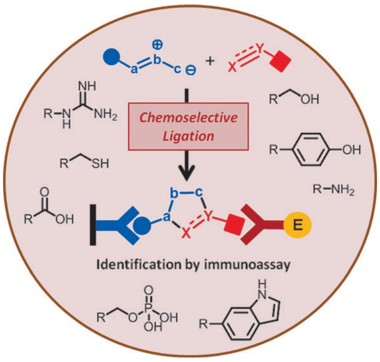
Light up, G-quadruplexes! A fast high-throughput screening for the discovery of novel G-quadruplex-forming oligonucleotides (GFOs) has been developed. By using a fluorescent G-quadruplex ligand and a DNA microarray, 1998 novel GFO candidates in CpG islands were disclosed. (CpG = cytosine-phosphate-guanosine).

Click Chemistry

S. Kolodych, E. Rasolofonjatovo,
M. Chaumontet, M.-C. Nevers,
C. Créminon, F. Taran* __ **12056 – 12060**

Discovery of Chemoselective and Biocompatible Reactions Using a High-Throughput Immunoassay Screening

An immunoassay-based method was used to screen numerous combinations of dipoles and dipolarophiles for their ability to undergo chemoselective and biocompatible [3+2] cycloaddition reactions. The approach fulfills most of the requirements of the click concept and led to the discovery of a copper-catalyzed reaction that generates pyrazoles from sydnone and alkyne reagents.

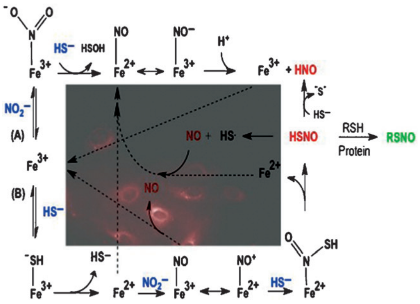


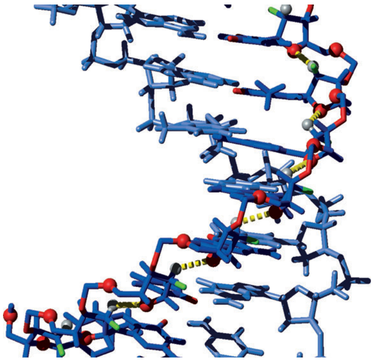
Nitrite Reduction

J. L. Miljkovic, I. Kenkel,
I. Ivanović-Burmazović,*
M. R. Filipovic* ________ **12061 – 12064**

Generation of HNO and HSNO from Nitrite by Heme-Iron-Catalyzed Metabolism with H_2S

Taking NO for an answer: A mechanistic study has shown that a heme-iron-catalyzed pathway (see scheme) could lead to the nitrite-/sulfide-induced formation of NO and HNO within mitochondria, and suggests that H_2S may be the elusive thiol responsible for the reduction of nitrite. This study offers an answer to the decades-old question on the role of nitrite in the treatment of H_2S poisoning.





Polarizing C–H···O hydrogen bonds: The structure of oligonucleotides containing alternating and contiguous tracts of 2′F-RNA and 2′F-ANA nucleotides reveals that nonconventional FC–H···O hydrogen bonds have a strong stabilizing effect on 2′-fluorinated duplexes.

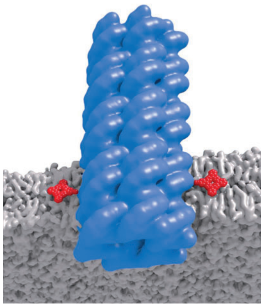
Nonconventional Hydrogen Bonding

N. Martin-Pintado, G. F. Deleavey, G. Portella, R. Campos-Olivas, M. Orozco, M. J. Damha,* C. González* ________ **12065 – 12068**

Backbone FC–H···O Hydrogen Bonds in 2′F-Substituted Nucleic Acids

---

Holding tight: An artificial membrane nanopore assembled from DNA oligonucleotides carries porphyrin tags (red), which anchor the nanostructure into the lipid bilayer. The porphyrin moieties also act as fluorescent dyes to aid the microscopic visualization of the DNA nanopore.

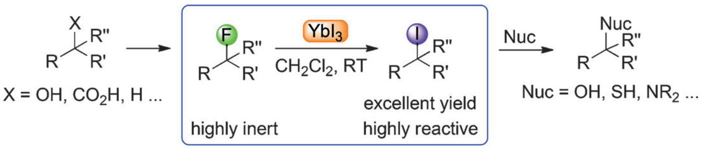


DNA Nanotechnology

J. R. Burns, K. Göpfrich, J. W. Wood, V. V. Thacker, E. Stulz, U. F. Keyser, S. Howorka* ________ **12069 – 12072**

Lipid-Bilayer-Spanning DNA Nanopores with a Bifunctional Porphyrin Anchor

Front Cover

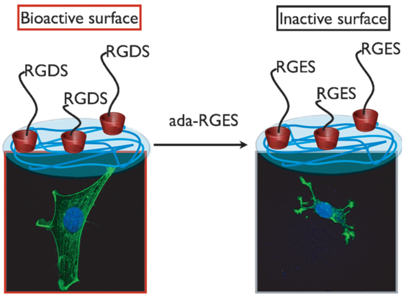


Synthetic Methods

A. M. Träff, M. Janjetovic, L. Ta, G. Hilmersson* ________ **12073 – 12076**

F makes the break: The carbon–fluorine single bond is quite strong, thus making aliphatic C–F bond scission unusually challenging. A new methodology utilizing YbI_3 leads to the conversion of a C–F bond into a C–I bond, and is compatible with various functional groups. The reaction is exceptionally selective towards alkyl fluorides and proceeds under mild conditions.

Selective C–F Bond Activation: Substitution of Unactivated Alkyl Fluorides using YbI_3



A molecular host, β-cyclodextrin (CD), covalently attached to an alginate matrix enables dynamic control of cue display through exchange of guest molecules. Addition of soluble RGDS-containing guest molecules to culture medium induced focal adhesion formation and spreading of 3T3 fibroblasts on the otherwise non-spreading alginate surface. The spreading could be reversed by adding competitive guest molecules bearing the mutated non-bioactive sequence RGES.

Biological Signaling

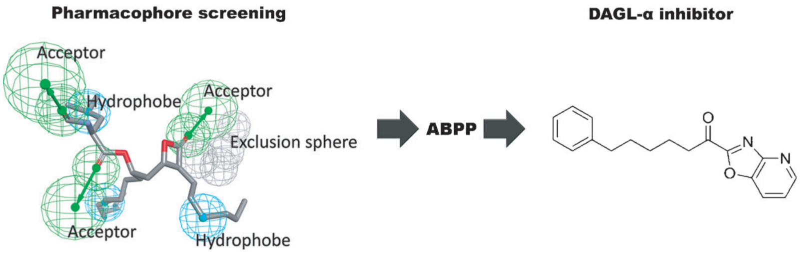
J. Boekhoven, C. M. Rubert Pérez, S. Sur, A. Worthy, S. I. Stupp* ________ **12077 – 12080**

Dynamic Display of Bioactivity through Host–Guest Chemistry

Enzyme Inhibition

M. P. Baggelaar, F. J. Janssen, A. C. M. van Esbroeck, H. den Dulk, M. Allarà, S. Hoogendoorn, R. McGuire, B. I. Florea, N. Meeuwenoord, H. van den Elst, G. A. van der Marel, J. Brouwer, V. Di Marzo, H. S. Overkleeft, M. van der Stelt* ———— **12081 – 12085**

Development of an Activity-Based Probe and In Silico Design Reveal Highly Selective Inhibitors for Diacylglycerol Lipase-α in Brain



A model method: A strategy that combines a knowledge-based in silico design approach and the development of novel activity-based probes (ABPs) for the detection of endogenous diacylglycerol lipase-α (DAGL-α) is presented. This approach resulted in the rapid identification of new DAGL-α inhibitors with high selectivity in the brain proteome. ABPP = activity-based protein profiling.

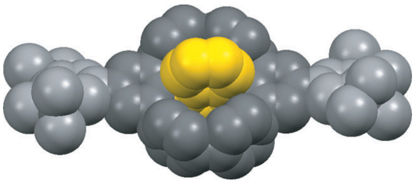
Inside Back Cover

Strained Aromatic Compounds

G. Ohlendorf, C. W. Mahler, S.-S. Jester, G. Schnakenburg, S. Grimme,* S. Höger* ———— **12086 – 12090**

Highly Strained Phenylene Bicyclophanes

Bending the rules: Strained bicyclophanes (see structure) with highly bent biphenylene units and a central aromatic moiety (yellow) forced into a perpendicular position were accessible in high yields by cyclization of the appropriate bromides by Yamamoto condensation. They were able to bind to graphite cutouts in solution and were adsorbed at the liquid/highly oriented pyrolytic graphite (HOPG) interface to form extended 2D structures.

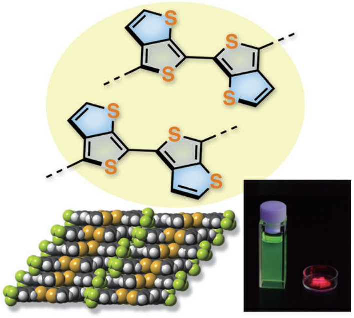


π-Electron Systems

A. Fukazawa,* D. Kishi, Y. Tanaka, S. Seki, S. Yamaguchi* ———— **12091 – 12095**

Diarylated Bi(thieno[2,3-*c*]thiophene)s: A Ring-Fusing Strategy for Controlling the Molecular Alignment of Oligoarenes

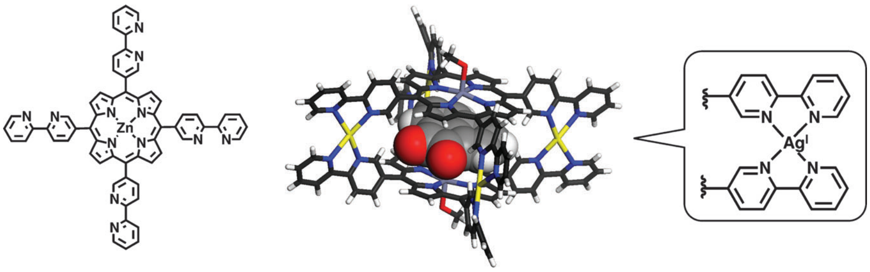
Red means go: The dense π stacking of thiophene-fused bithiophene derivatives in the crystalline state led to significantly red-shifted absorption and fluorescence bands (see the photograph of one compound in solution and in the solid state under UV irradiation). The π-stacking structure could be altered by changing the orientation of one of the fused thiophene rings.



Supramolecular Chemistry

T. Nakamura, H. Ube,
M. Shionoya* ―――― 12096 – 12100

Silver-Mediated Formation of a Cofacial Porphyrin Dimer with the Ability to Intercalate Aromatic Molecules

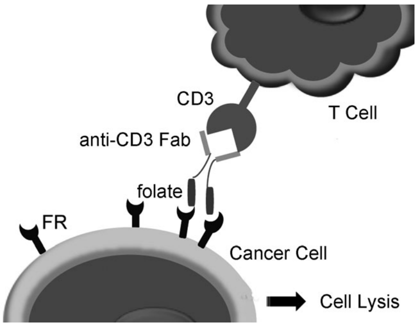


Guests welcome: Complex formation between Ag^I ions and a Zn-porphyrin ligand (**L**) possessing four 2,2′-bipyridyl groups produced a dimeric complex $[Ag_4\mathbf{L}_2]^{4+}$, wherein the interplane distance between the Zn-porphyrin groups was ideal for intercalation of aromatic molecules through π–π interactions. The cofacial dimer $[Ag_4\mathbf{L}_2]^{4+}$ serves as an excellent receptor for π-electron-deficient guests.

Cancer Immunotherapy

S. A. Kularatne, V. Deshmukh,
M. Gymnopoulos, S. L. Biroc, J. Xia,
S. Srinagesh, Y. Sun, N. Zou, M. Shimazu,
J. Pinkstaff, S. Ensari, N. Knudsen,
A. Manibusan, J. Y. Axup, C. H. Kim,
V. V. Smider, T. Javahishvili,
P. G. Schultz* ―――― 12101 – 12104

Recruiting Cytotoxic T Cells to Folate-Receptor-Positive Cancer Cells

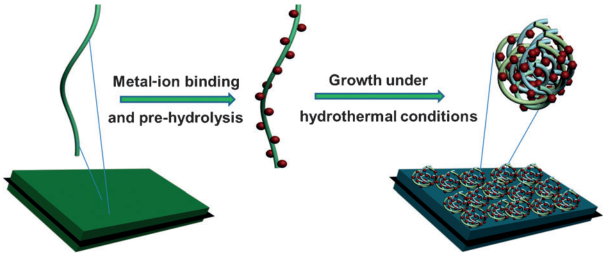


A Fab-ulous killer: An anti-CD3 Fab-folate conjugate that targets cytotoxic T cells to folate-receptor-positive (FR^+) tumors results in efficient killing of tumor cells by activated T cells. This chemical approach to the synthesis of bispecific antibodies using unnatural amino acids with orthogonal chemical reactivity affords homogenous conjugates with precise control over the relative geometry of the antibody binding sites in excellent yields.

Multifunctional 2D Nanohybrids

S. Li, D. Wu, C. Cheng, J. Wang, F. Zhang,
Y. Su,* X. Feng* ―――― 12105 – 12109

Polyaniline-Coupled Multifunctional 2D Metal Oxide/Hydroxide Graphene Nanohybrids

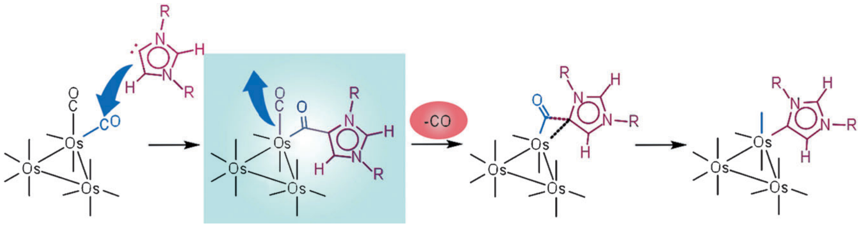


Particles and sheets: Polyaniline is used as a linker to couple metal oxides and hydroxides to graphene sheets. Hydrothermal treatment converts these coupled hybrids into nitrogen-doped 2D carbon nanosheets integrated with size-controlled metal nanoparticles. This structure gives these 2D nanohybrids promising electrochemical behavior in supercapacitors and oxygen-reduction reactions.

Reaction Mechanisms

Y. Liu, R. Ganguly, H. V. Huynh,*
W. K. Leong* ―――― 12110 – 12113

Direct Evidence for the Attack of a Free N-Heterocyclic Carbene at a Carbonyl Ligand: A Zwitterionic Osmium Carbonyl Cluster



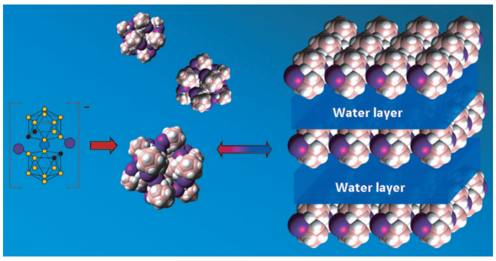
A key suspect arrested: The initial site of attack of a free N-heterocyclic carbene (NHC) on the triosmium carbonyl cluster $[Os_3(CO)_{12}]$ was found to be a carbonyl ligand. The stable zwitterionic species thus formed (blue background in the scheme) was characterized crystallographically. CO substitution proceeds from this intermediate by the loss of a CO group and migratory deinsertion.

Boron Cluster Lamellar Phases

D. Brusselle, P. Bauduin,* L. Girard,
A. Zaulet, C. Viñas, F. Teixidor, I. Ly,
O. Diat ______ **12114 – 12118**

Lyotropic Lamellar Phase Formed from Monolayered θ-Shaped Carborane-Cage Amphiphiles

Back Cover

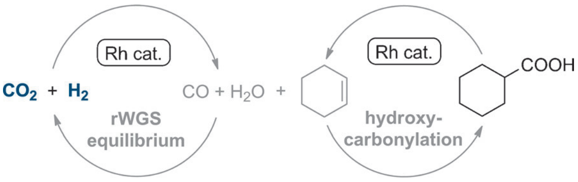


B in phase: Lyotropic lamellar phases can not only be formed from alkyl-chain-based surfactants with a well-defined amphiphilic structure, now they can be obtained from metallacarborane clusters, described as θ-shaped amphiphiles. The lamellae formed are unique as they have a monomolecular thickness.

CO_2 Utilization

T. G. Ostapowicz, M. Schmitz, M. Krystof,
J. Klankermayer,
W. Leitner* ______ **12119 – 12123**

Carbon Dioxide as a C_1 Building Block for the Formation of Carboxylic Acids by Formal Catalytic Hydrocarboxylation

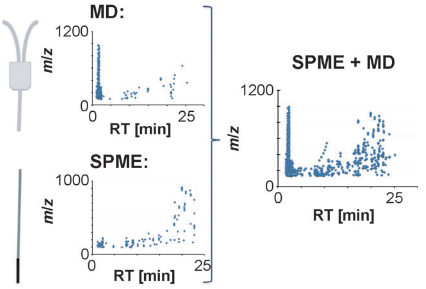


A happy marriage of two processes: An effective catalytic system was identified for the direct synthesis of carboxylic acids from non-activated olefins or alcohols, CO_2, and H_2. Detailed analysis together with labeling studies indicated that the overall hydrocarboxylation of simple olefins results from a combination of the reverse water–gas shift (rWGS) reaction and a hydroxycarbonylation step, each promoted by a rhodium catalyst (see scheme).

Analytical Methods

E. Cudjoe, B. Bojko, I. de Lannoy,
V. Saldivia, J. Pawliszyn* _ **12124 – 12126**

Solid-Phase Microextraction: A Complementary In Vivo Sampling Method to Microdialysis



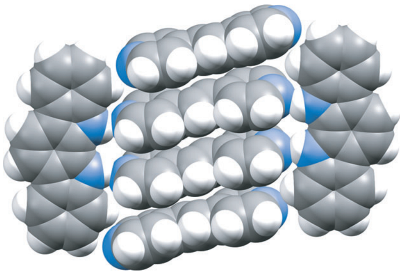
Two's compliment: Solid-phase microextraction (SPME) was validated against microdialysis (MD) in simultaneous targeted analysis of selected neurotransmitters in brain tissue. Complementary data was obtained from global brain profiling with both methods. MD extracts primarily polar species, and SPME detects semi hydrophobic and hydrophobic compounds, including lipids related to neurodegenerative diseases. RT = retention time.

Supramolecular Chemistry

J. Stojaković, A. M. Whitis,
L. R. MacGillivray* ______ **12127 – 12130**

Discrete Double-to-Quadruple Aromatic Stacks: Stepwise Integration of Face-to-Face Geometries in Cocrystals Based on Indolocarbazole

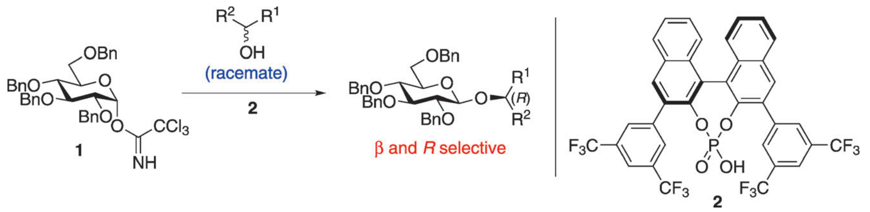
One, two, three, four: An indolocarbazole organizes double, triple, and quadruple stacks of aromatic molecules within multicomponent solids. The aromatic units are sequentially integrated into discrete assemblies and undergo [2+2] photodimerization.



Carbohydrates

T. Kimura, M. Sekine, D. Takahashi,
K. Toshima* ______ 12131 – 12134

Chiral Brønsted Acid Mediated Glycosylation with Recognition of Alcohol Chirality

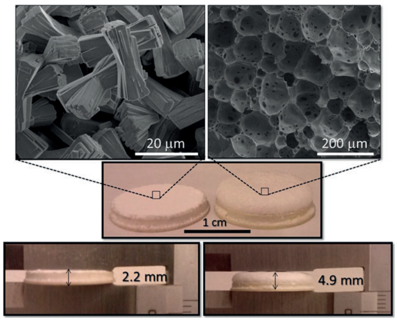


Sugar sugar: In the glycosylation of racemic alcohols with **1** using the chiral phosphoric acid **2** as an activator, one enantiomer of the racemic alcohol selectively reacts with **1** to give the corresponding glycoside with good to excellent α/β-stereo- and diastereoselectivity in high yield. The reaction was successfully applied to the synthesis of a chiral natural flavan glycoside using a racemic aglycon.

Polyamorphism

S. Ferdov* ______ 12135 – 12138

Low-Density Macroporous Foams Obtained from a Molecular Sieve by Temperature-Induced Amorphization

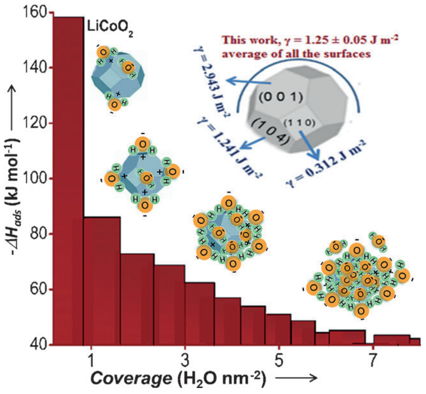


Featherweight foams: Uncommon polyamorphism in silicate molecular sieves is described. This finding is used for the synthesis of hierarchical macroporous foams with controllable density.

Lithium Ion Batteries

P. S. Maram, G. C. C. Costa,
A. Navrotsky* ______ 12139 – 12142

Experimental Confirmation of Low Surface Energy in $LiCoO_2$ and Implications for Lithium Battery Electrodes

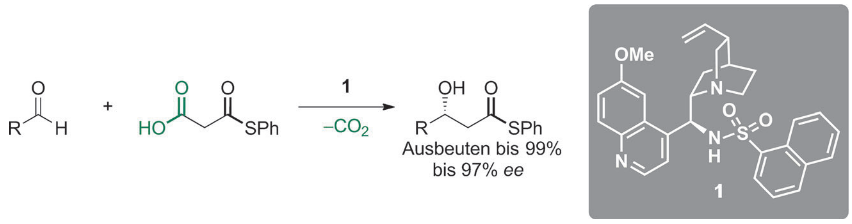


Water adsorption on the surface of $LiCoO_2$ nanoparticles was investigated. As the water coverage increases the adsorption enthalpy decreases reaching the enthalpy of water condensation (−44 kJ mol⁻¹). The experimentally observed average surface energy corresponding to all facets agree well with those reported from DFT calculations. The observed low surface energy is attributed to the surface Co^{3+} spin transition in nanophase $LiCoO_2$.

Organocatalysis

H. Y. Bae, J. H. Sim, J.-W. Lee, B. List,*
C. E. Song* ______ 12143 – 12147

Organocatalytic Enantioselective Decarboxylative Aldol Reaction of Malonic Acid Half Thioesters with Aldehydes

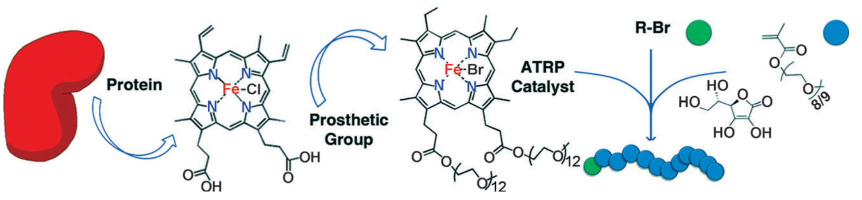


Copycat: A highly enantioselective biomimetic aldol reaction of malonic acid half thioesters with a variety of aldehydes affords optically active β-hydroxy thioesters by employing the cinchona-derived sulfonamide organocatalyst **1**. The synthetic utility of this protocol was demonstrated by performing formal syntheses of the antidepressants (*R*)-fluoxetine, (*R*)-tomoxetine, (−)-paroxetine, and (*R*)-duloxetine.

Polymerization

A. Simakova, M. Mackenzie, S. E. Averick, S. Park,
K. Matyjaszewski* ______ **12148 – 12151**

Bioinspired Iron-Based Catalyst for Atom Transfer Radical Polymerization

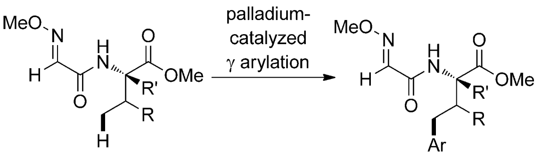


Naturally occurring hemin, an iron-containing porphyrin, and its synthetic derivatives were used as atom transfer radical polymerization (ATRP; see picture) catalysts. The effects of the halide salt concentration, attachment of poly(ethylene glycol) moieties, and hydrogenation of the hemin vinyl groups on the catalyst performance were studied.

C–H Activation

M. Fan, D. Ma* ______ **12152 – 12155**

Palladium-Catalyzed Direct Functionalization of 2-Aminobutanoic Acid Derivatives: Application of a Convenient and Versatile Auxiliary

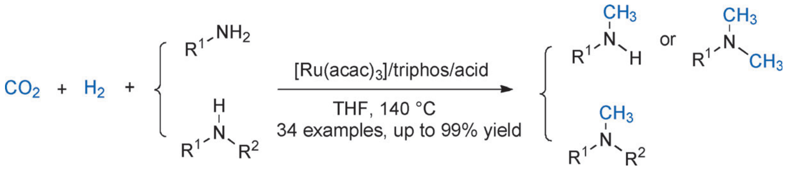


New group on the block: 2-Methoxyiminoacetyl is a readily available auxiliary for promoting palladium-catalyzed γ arylation of $C(sp^3)$–H bonds. This auxiliary can be easily removed by either treatment with 1 N KOH at room temperature, or converted into a glycine moiety for peptide synthesis.

Homogeneous Catalysis

Y. Li, I. Sorribes, T. Yan, K. Junge,
M. Beller* ______ **12156 – 12160**

Selective Methylation of Amines with Carbon Dioxide and H_2

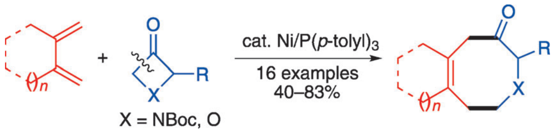


Put a label on it: Carbon dioxide with H_2 is shown to be an efficient and selective methylation reagent for aromatic and aliphatic amines (see scheme; acac = acetylacetonate, triphos = 1,1,1-tris(diphenylphosphanylmethyl)ethane). A variety of functionalized amines including ^{13}C-labelled drugs were obtained with good yields and functional-group tolerance.

Heterocycles

A. Thakur, M. E. Facer,
J. Louie* ______ **12161 – 12165**

Nickel-Catalyzed Cycloaddition of 1,3-Dienes with 3-Azetidinones and 3-Oxetanones

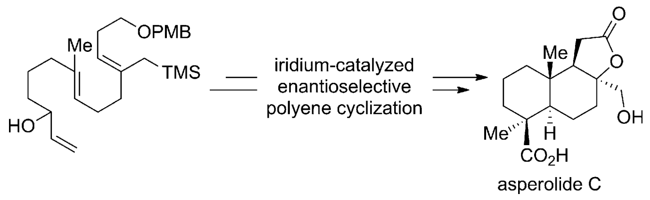


A growth and expansion strategy: A Ni/P(p-tol)$_3$-catalyzed cycloaddition of 1,3-dienes with 3-azetidinones and 3-oxetanones produced eight-membered heterocycles with a variety of substituents (see scheme; Boc = *tert*-butoxycarbonyl). The synthesis of the reduced azocine and oxocine derivatives involved the challenging steps of $C(sp^2)$–$C(sp^3)$ bond activation and $C(sp^3)$–$C(sp^3)$ reductive elimination.

Natural Product Synthesis

O. F. Jeker, A. G. Kravina,
E. M. Carreira* ———— **12166 – 12169**

Total Synthesis of (+)-Asperolide C by Iridium-Catalyzed Enantioselective Polyene Cyclization

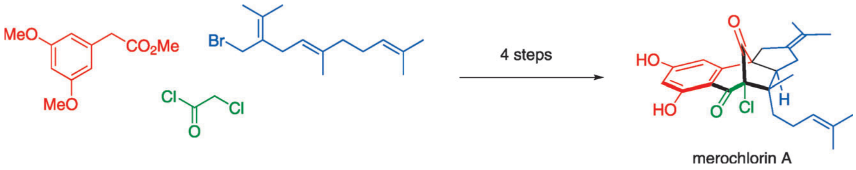


Domino rings: A general synthetic entry into labdane-type diterpenoids has been developed based on an iridium-catalyzed enantioselective polyene cyclization cascade. The potential of this process is demonstrated in the first total synthesis of the tetranorlabdane diterpene asperolide C (PMB = *p*-methoxybenzyl, TMS = trimethylsilyl).

Biomimetic Synthesis

H. P. Pepper,
J. H. George* ———— **12170 – 12173**

Biomimetic Total Synthesis of (±)-Merochlorin A

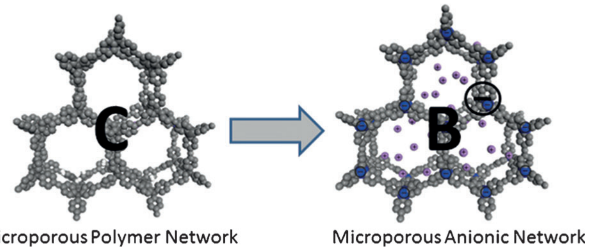


Inspired: The proposed biosynthetic pathway toward the potent antibiotic meroterpenoid (±)-merochlorin A inspired its concise total synthesis. The key steps in the synthesis are a one-pot aromatization–alkylation reaction, followed by a biomimetic oxidative dearomatization of a highly functionalized naphthalene derivative, which forms two rings and four contiguous stereocenters in a single step.

Microporous Polymers

S. Fischer, J. Schmidt, P. Strauch,
A. Thomas* ———— **12174 – 12178**

An Anionic Microporous Polymer Network Prepared by the Polymerization of Weakly Coordinating Anions

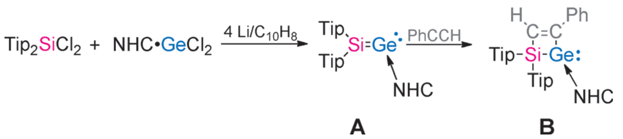


Organic zeolite: A microporous, covalent organic network with high surface area was synthesized by polymerization of $[B(C_6F_4Br)_4]^-$. The countercations, located within the pore channels, are highly accessible and can be easily exchanged, comparable to the extra-framework cations in zeolites. In this way a $[Mn^{II}(bpy)]^{2+}$ complex can be synthesized and immobilized in the network.

Main-Group Chemistry

A. Jana, V. Huch,
D. Scheschkewitz* ———— **12179 – 12182**

NHC-Stabilized Silagermenylidene: A Heavier Analogue of Vinylidene

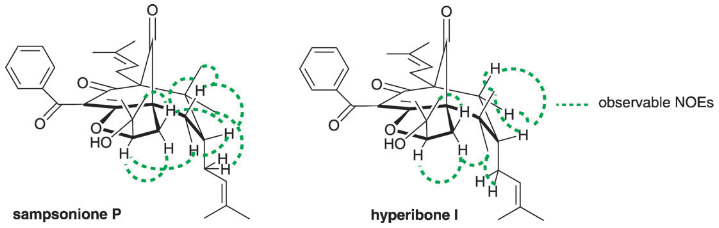


Stable vinylidene analogue: The synthesis of the first representative of a new compound class of low-valent Group 14 elements, namely silagermenylidene **A**, is achieved by reduction of Tip_2SiCl_2 and $NHC\cdot GeCl_2$ ($Tip = 2,4,6\text{-}iPr_3C_6H_2$; NHC = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene). The potential of **A** as a synthon is demonstrated by the formal [2+2] cycloaddition with phenylacetylene to afford NHC-stabilized cyclic germylene **B**.

Natural Product Synthesis

K. Lindermayr,
B. Plietker* ______ **12183 – 12186**

The Bidirectional Total Synthesis of Sampsonione P and Hyperibone I

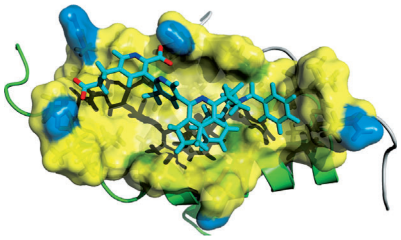


Make it simple: The separation of framework-decorating from framework-constructing steps facilitated the selective introduction of one prenyl group next to allyl groups. The selective epoxidation of the more electron-rich prenyl group led to the efficient formation of the tetrahydrofuran moiety in the title compounds. Spectroscopic analysis of hyperibone I and comparison with literature data led to a revision of the original structure.

Helix Mimetics

G. Schäfer, J. Milić, A. Eldahshan, F. Götz, K. Zühlke, C. Schillinger, A. Kreuchwig, J. M. Elkins, K. R. Abdul Azeez, A. Oder, M. C. Moutty, N. Masada, M. Beerbaum, B. Schlegel, S. Niquet, P. Schmieder, G. Krause, J. P. von Kries, D. M. F. Cooper, S. Knapp, J. Rademann, W. Rosenthal, E. Klussmann* ______ **12187 – 12191**

Highly Functionalized Terpyridines as Competitive Inhibitors of AKAP–PKA Interactions



A good fit: Interactions between A-kinase anchoring proteins (AKAPs) and protein kinase A (PKA) play key roles in a plethora of physiologically relevant processes whose dysregulation causes or is associated with diseases such as heart failure. Terpyridines have been developed as α-helix mimetics for the inhibition of such interactions and are the first biologically active, nonpeptidic compounds that block the AKAP binding site of PKA.

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

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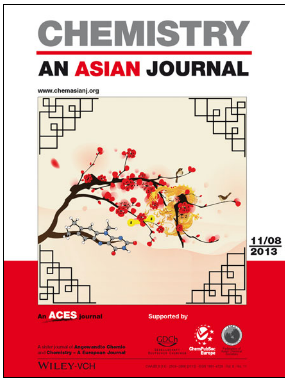

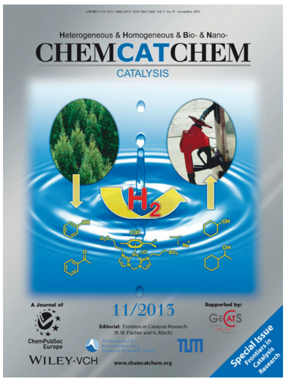

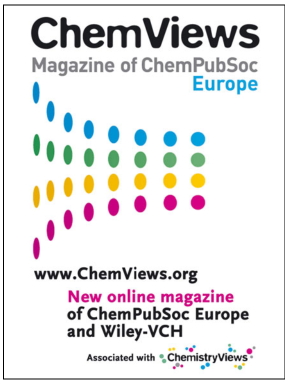

Angewandte Corrigendum

Upon further examination of the NMR spectra for the products of the reduction of the *Se*-phenyl 1-methoxybicyclo[2.2.2]oct-5-ene-2-carboselenoate **5 f** the authors of this Communication have found that the reaction did not give the expected 1-methoxybicyclo-[2.2.2]oct-2-ene **6 f** in 67% yield as reported in Table 1 (entry **f**). Instead, three major products were obtained in a combined yield of 67%: the expected product **6 f** (16%) along with the two products of cyclopropylcarbinyl radical rearrangement, the *endo* (major, 57%) and the *exo* (minor, 27%) isomers of 2-methoxybicyclo[3.2.1]oct-6-ene, the former being a known compound.[1]

Se-Phenyl Prop-2-eneselenoate: An Ethylene Equivalent for Diels–Alder Reactions

M. E. Jung,* F. Perez, C. F. Regan, S. W. Yi, Q. Perron ——— **2060–2062**

Angew. Chem. Int. Ed. **2013**, *52*

DOI: 10.1002/anie.201208294

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[1] a) M. A. Battiste, J. M. Coxon, A. J. Jones, R. W. King, G. W. Simpson, P. J. Steel, *Tetrahedron Lett.* **1983**, *24*, 307–310; b) M. A. Battiste, J. M. Coxon, G. W. Simpson, P. J. Steel, A. J. Jones, *Tetrahedron* **1984**, *40*, 3137–44.

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