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:

*T. Lewis, M. Faubel, B. Winter, J. C. Hemminger**
CO_2 Capture in an Aqueous Solution of an Amine: Role of the Solution Interface

*Y. H. Kim, S. Banta**
Complete Oxidation of Methanol in an Enzymatic Biofuel Cell by a Self-Assembling Hydrogel Created from Three Modified Dehydrogenases

*F. Freire, A. M. Almeida, J. D. Fisk, J. D. Steinkruger, S. H. Gellman**
Impact of Strand Length on the Stability of Parallel-β-Sheet Secondary Structure

*S.-H. Kim, D. A. Weitz**
One-Step Emulsification of Multiple Concentric Shells with Capillary Microfluidic Devices

*L. Furst, J. M. R. Narayanam, C. R. J. Stephenson**
Total Synthesis of (+)-Gliocladin C Enabled by Visible-Light Photoredox Catalysis

*Y. Kitagawa, H. Segawa, K. Ishii**
Magnetochiral Dichroism of Organic Compounds

*A. S. Pensado, A. A. Pádua**
Solvation and Stabilization of Metallic Nanoparticles in Ionic Liquids

*Y. Kou, Y. Xu, Z. Guo, D. Jiang**
Supercapacitive Energy Storage and Electric Power Supply Using an Aza-Fused Conjugated Microporous Framework

P. Höhn, F. Jach, B. Karabiyik, S. Agrestini, F. R. Wagner, M. Ruck, L. H. Tjeng, R. Kniep**
Highly Reduced Cobaltates $Sr_3[Co(CN)_3]$ and $Ba_3[Co(CN)_3]$: Crystal Structure, Chemical Bonding, and Conceptional Considerations

C.-Y. Chang, C.-E. Wu, S.-Y. Chen, C. Cui, Y.-J. Cheng, C.-S. Hsu, Y.-L. Wang,* Y. Li*
Enhanced Performance and Stability of a Polymer Solar Cell by Incorporating Vertically Aligned, Cross-Linked Fullerene Nanorods

Editorial

Author Profile

„What I look for first in a publication is the problem and then the data. If I won the lottery, I would continue doing science. …"
This and more about Ralph Weissleder can be found on page 8224.

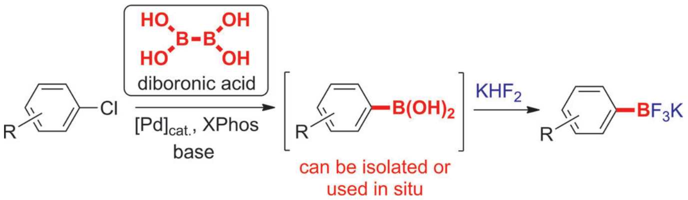
Books

Highlights

Boronic Acids

L. T. Pilarski, K. J. Szabó* — **8230 – 8232**

Palladium-Catalyzed Direct Synthesis of Organoboronic Acids

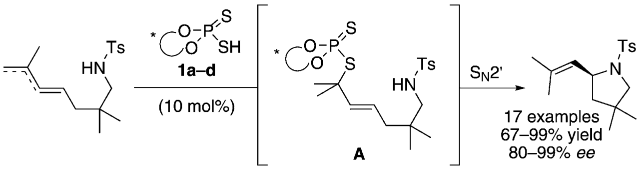


Diboronic acid in the spotlight: Molander et al. have developed an excellent method for the direct synthesis of aryl boronic acids from aryl chlorides (see scheme). In this palladium-catalyzed procedure, diboronic acid, a notably underutilized reagent, was used as the boron source. The boronic acid products can be isolated from the procedure, or used in one-pot reactions to give a wide range of boronates and biaryls.

Chiral Brønsted Acids

I. Dion, A. M. Beauchemin* **8233 – 8235**

Asymmetric Brønsted Acid Catalysis Enabling Hydroaminations of Dienes and Allenes



Acid treatment: Toste et al. recently unveiled a new pathway for asymmetric Brønsted acid catalysis of reactions involving dienes or allenes, and achieved highly efficient intramolecular hydroamination and hydroarylation reactions (see scheme). The P=S bond proved necessary for reactivity, and dithiophosphoric acids emerged as efficient catalysts. The association/displacement sequence led to chiral pyrrolidines and isoxazolidines in excellent yields and *ee* values.

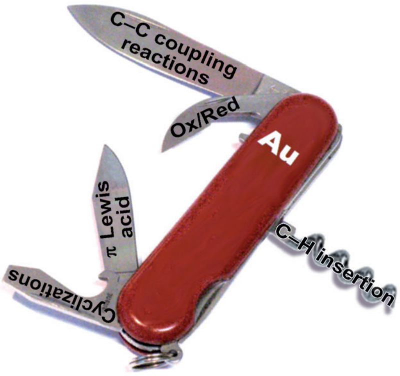
Minireviews

Gold Catalysis

H. A. Wegner,* M. Auzias — **8236 – 8247**

Gold for C–C Coupling Reactions: A Swiss-Army-Knife Catalyst?

More than just a pretty face: Gold excels as a catalyst for organic synthesis owing to its unique reactivity pattern: its π Lewis acidity as well as its ability to insert into C–H bonds and to undergo oxidation/reduction processes. This last property in particular offers an efficient means to construct C–C bonds. The current state of the art of gold-catalyzed C–C coupling is discussed along with mechanistic aspects of these reactions.



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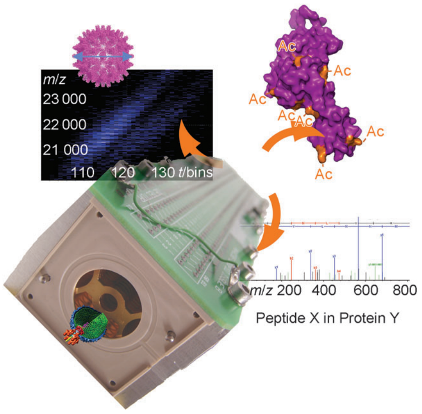
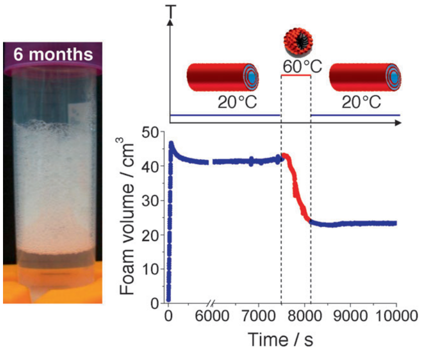
Reviews



Viruses on mass: Structural biology has profited greatly from modern biomolecular mass spectrometry (MS). In this Review a variety of mass spectrometry techniques, including proteomics, H/D exchange, chemical labeling, and native and ion mobility MS, are presented along with how they have contributed to structural-biology investigations, in particular of virus structure, assembly, and dynamics (see picture).

Biomolecular Mass Spectrometry

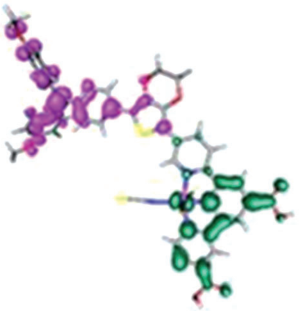
Communications



Smart foams: Ultrastable foams with an optimal foamability are obtained using hydroxy fatty acids tubes (see picture). The stabilization results from the adsorption of monomers at the air–water interface and from the presence of tubes in the plateau borders. Upon heating, tubes transform to micelles, leading to foam destabilization and thus to the first foams to exhibit temperature-tuneable stability.

Foams

VIP



Panchromatic sensitizers: A series of ruthenium(II) compounds was prepared that contain three thiocyanate ligands and a novel chelating terpyridine ligand. The latter (see picture: colors indicate orbital occupation) serves as an effective and versatile light-harvesting auxochrome. One compound has a solar conversion efficiency of up to 10.3 %.

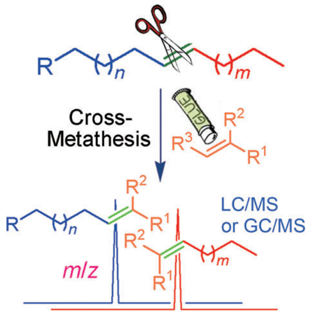
Dye-Sensitized Solar Cells

Contents

Structure Elucidation

Y. Kwon, S. Lee, D.-C. Oh,*
S. Kim* ______________ **8275 – 8278**

Simple Determination of Double-Bond Positions in Long-Chain Olefins by Cross-Metathesis



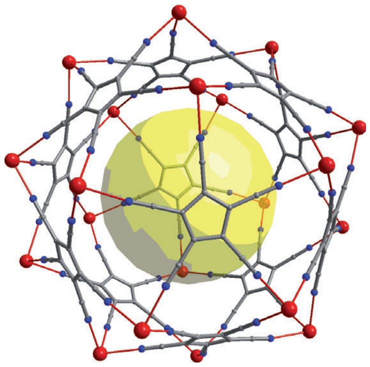
Cut, paste, and measure: The positions of double bonds in unsaturated long-chain compounds can be easily determined by chemical derivatization using a cross-metathesis reaction and chromatography–mass spectrometry. The produced olefins have distinct physicochemical properties suitable for LC/MS or GC/MS analysis that depend on the cross-metathesis partner used. This method is operationally simple and applicable at a sub-milligram scale.

Metal–Organic Frameworks

J. Bacsa, R. J. Less,* H. E. Skelton,
Z. Soracevic, A. Steiner, T. C. Wilson,
P. T. Wood,* D. S. Wright* _ **8279 – 8282**

Assembly of the First Fullerene-Type Metal–Organic Frameworks Using a Planar Five-Fold Coordination Node

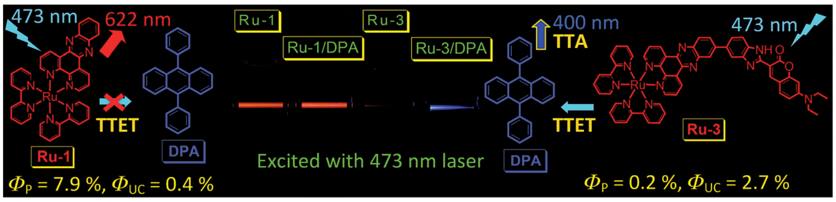
Pump up the volume: Slow crystallization of $Na[C_5(CN)_5]$, the unsolvated sodium salt of pentacyanocyclopentadienide, gives the first example of an anionic coordination network based on metal–fullerene units. The structure of this network is closely related to a type I gas clathrate (see picture) in which around 66 % of the unit cell volume is occupied by solvent molecules.



Photochemistry

S. Ji, H. Guo, W. Wu, W. Wu,
J. Zhao* ______________ **8283 – 8286**

Ruthenium(II) Polyimine–Coumarin Dyad with Non-emissive ^{3}IL Excited State as Sensitizer for Triplet–Triplet Annihilation Based Upconversion

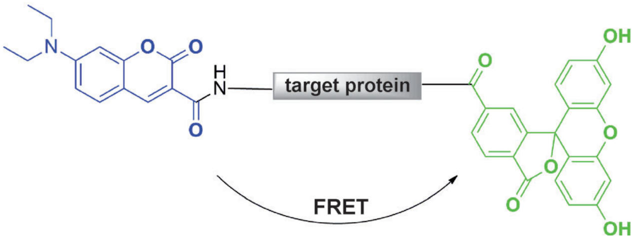


Light out of darkness? Most sensitizers for triplet–triplet annihilation (TTA) upconversion are strongly phosphorescent. A new Ru^{II}–coumarin dyad, on the other hand, has a non-emissive ^{3}IL excited state ($\Phi_P = 0.2\%$) but shows a good upconversion quantum yield ($\Phi_{UC} = 2.7\%$, see picture, TTET = triplet–triplet energy transfer).

Protein Chemistry

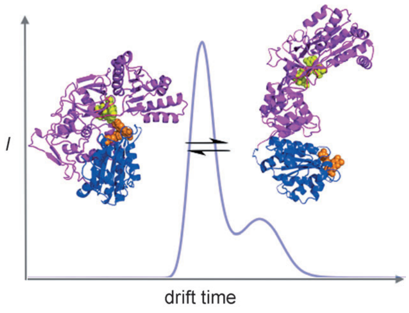
L. Yi, H. Sun, A. Itzen, G. Triola,
H. Waldmann, R. S. Goody,*
Y. W. Wu* ______________ **8287 – 8290**

One-Pot Dual-Labeling of a Protein by Two Chemoselective Reactions



Dual system for proteins: The site-specific two-color labeling of a Rab GTPase was achieved in a one-pot procedure by combination of chemoselective native chemical ligation and oxime ligation. This strategy could be a general, facile, and efficient method for specific multiple modifications of a given protein. The Rab GTPase biosensor was demonstrated for protein folding and protein–protein interaction studies.

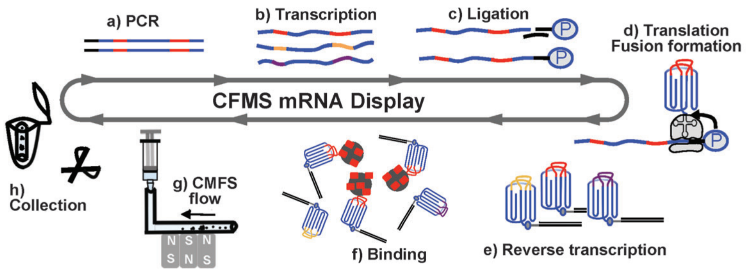
Conforming to convention: Evidence for compact and extended forms of cytochrome P450 reductase, believed to exist in dynamic equilibrium in solution, is found in the gas phase by using ion mobility spectrometry. The relative abundance of the two conformations (see picture) can be influenced by the ionic strength of the solution from which they are electrosprayed.



Protein Conformation

M. Jenner, J. Ellis, W.-C. Huang, E. Lloyd Raven, G. C. K. Roberts, N. J. Oldham* ——— 8291 – 8294

Detection of a Protein Conformational Equilibrium by Electrospray Ionisation-Ion Mobility-Mass Spectrometry

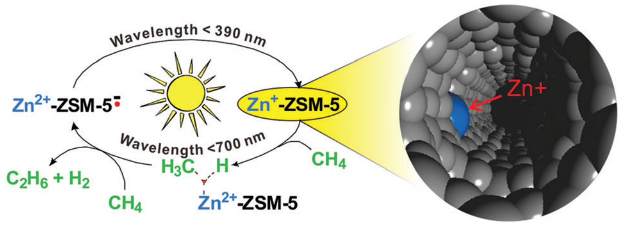


Even flow: Microfluidics technology can rapidly generate affinity reagents that bind to protein targets using mRNA display. The continuous-flow magnetic separation (CFMS) method (see scheme; steps a–h) offers reproducible means to impose stringent selection conditions without the need for a specialized device. The method yields approximately a 30-fold greater partition efficiency over conventional methods when using interleukin-6 as a model target.

Selection Methods

C. A. Olson, J. D. Adams, T. T. Takahashi, H. Qi, S. M. Howell, T. Wu, R. W. Roberts,* R. Sun,* H. T. Soh* ——— 8295 – 8298

Rapid mRNA-Display Selection of an IL-6 Inhibitor Using Continuous-Flow Magnetic Separation

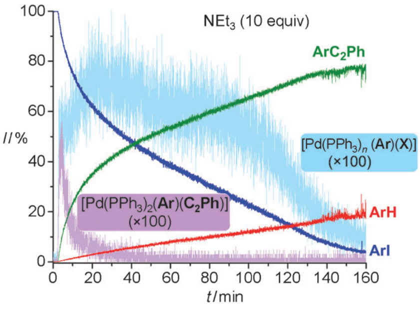


Sun bath: A Zn^+-modified zeolite catalyst showing superior photocatalytic activity for the activation of a C–H bond converted methane into ethane and hydrogen upon irradiation of sunlight (see picture). Light at wavelengths shorter than 390 nm transferred electrons from the zeolite framework to the zinc centers.

Methane Conversion

L. Li, G. D. Li, C. Yan, X. Y. Mu, X. L. Pan, X. X. Zou, K. X. Wang, J. S. Chen* ——— 8299 – 8303

Efficient Sunlight-Driven Dehydrogenative Coupling of Methane to Ethane over a Zn^+-Modified Zeolite



Keeping an eye on all the players: The combination of bulky phosphonium tags and pressurized sample infusion transforms electrospray ionization mass spectrometry into a tool capable of producing dense data on the relative concentrations of all components of a catalytic reaction, such as the palladium-catalyzed coupling of an aryl iodide with phenylacetylene (see graph).

Reaction Mechanisms

K. L. Vikse, Z. Ahmadi, C. C. Manning, D. A. Harrington, J. S. McIndoe* ——— 8304 – 8306

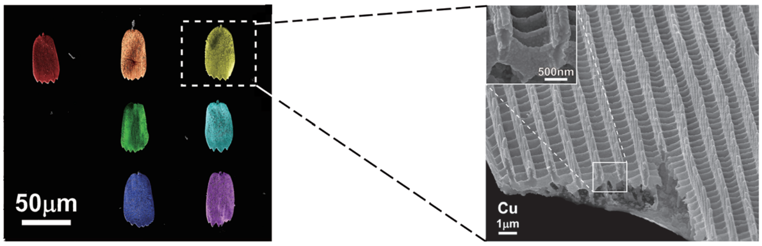
Powerful Insight into Catalytic Mechanisms through Simultaneous Monitoring of Reactants, Products, and Intermediates

Contents

3D Nanostructures

Y. W. Tan, J.-J. Gu,* X. N. Zang, W. Xu,
K. C. Shi, L. H. Xu,
D. Zhang* **8307–8311**

Versatile Fabrication of Intact Three-Dimensional Metallic Butterfly Wing Scales with Hierarchical Sub-micrometer Structures

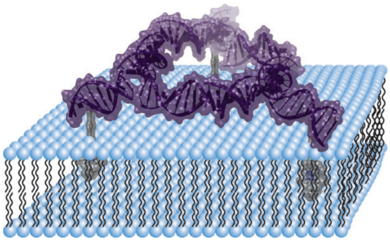


Spread your wings: Surface functionalization of butterfly wing scales and subsequent electroless deposition of different metals produces metallic replicas with 3D sub-micrometer structures (see picture). This approach converts complicated natural 3D bioorganic structures into various otherwise unavailable metal structures with optical, electronic, magnetic, thermal, or catalytic applications.

Nanotechnology

K. Börjesson, E. P. Lundberg, J. G. Woller,
B. Nordén, B. Albinsson* **8312–8315**

Soft-Surface DNA Nanotechnology: DNA Constructs Anchored and Aligned to Lipid Membrane

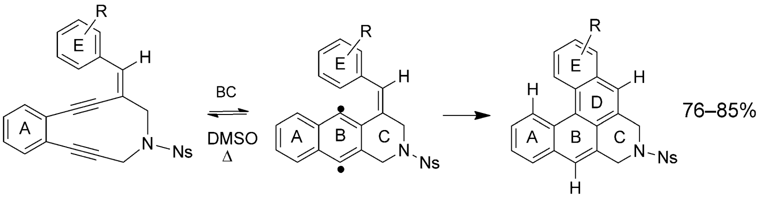


No strings attached: At least three attachment points are needed to align a two-dimensional DNA nanoconstruct to a soft lipid membrane surface with a porphyrin nucleoside as membrane anchor (see picture). The resulting freely diffusing DNA constructs can be reversibly assembled on the surface thus enabling the possibility of a self-repairing system.

Radical Reactions

S. Roy, A. Anoop, K. Biradha,
A. Basak* **8316–8319**

Synthesis of Angularly Fused Aromatic Compounds from Alkenyl Enediynes by a Tandem Radical Cyclization Process

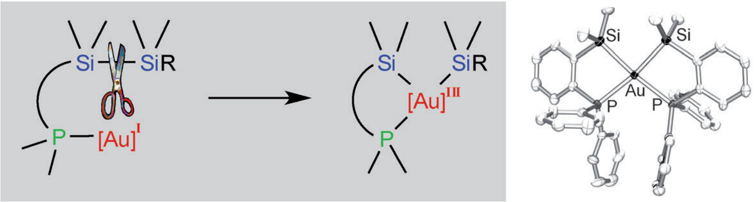


Let's get radical: A general synthetic route toward angularly *ortho*-fused polyaromatic [4]helicenes starting from aryl alkenyl N-substituted cyclic enediynes is described (see scheme; DMSO = dimethyl sulfoxide, Ns = 4-nitrobenzenesulfonyl). The process involved a Bergman cyclization (BC) as the key step of an unprecedented tandem radical reaction.

Gold Chemistry

P. Gualco, S. Ladeira, K. Miqueu,*
A. Amgoune,*
D. Bourissou* **8320–8324**

Spontaneous Oxidative Addition of σ-Si–Si Bonds at Gold

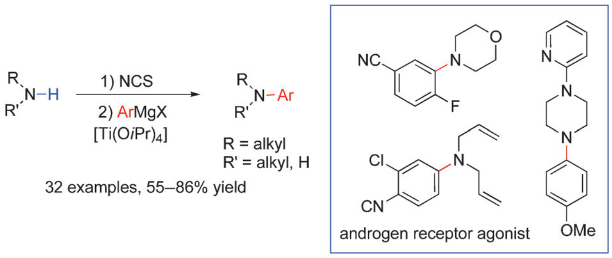


Gold can do it! The activation of disilanes at gold was observed experimentally and analyzed theoretically. Upon chelation with two or even only one phosphine donor, the oxidative addition of σ-Si–Si bonds proceeds readily at low temperatures. These results show an unexpected similarity between gold and the other late transition metals towards σ bond activation.

Amination Reactions

T. J. Barker, E. R. Jarvo* ____ 8325 – 8328

Titanium-Mediated Amination of Grignard Reagents Using Primary and Secondary Amines

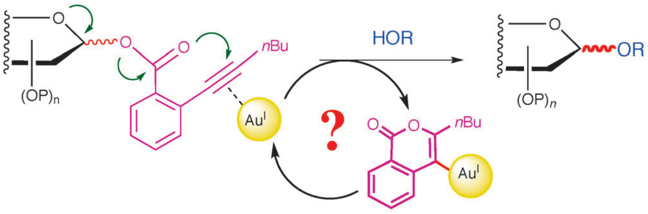


Make it, then break it: *N*-chlorosuccinimide (NCS) was employed as the oxidant in the synthesis of aniline derivatives using the title transformation (see scheme). Functionalization was well tolerated on both the amine and Grignard reagent. An androgen receptor agonist and several analogues were synthesized to demonstrate the utility of this method.

Glycosylation

Y. Zhu, B. Yu* ____ 8329 – 8332

Characterization of the Isochromen-4-yl-gold(I) Intermediate in the Gold(I)-Catalyzed Glycosidation of Glycosyl *ortho*-Alkynylbenzoates and Enhancement of the Catalytic Efficiency Thereof

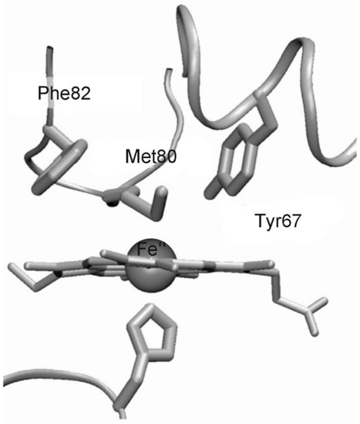


Gold standard: The title gold complex (see scheme) was characterized unambiguously as an important intermediate in the title reaction. Protonolysis of this vinyl gold(I) complex was critical for regeneration of the active gold(I) species for the catalytic cycle, and use of a protic acid co-catalyst significantly lowered the required catalyst loading to 0.5 mol%.

Protein Probes

J. Zimmermann, M. C. Thielges, Y. J. Seo, P. E. Dawson, F. E. Romesberg* ____ 8333 – 8337

Cyano Groups as Probes of Protein Microenvironments and Dynamics



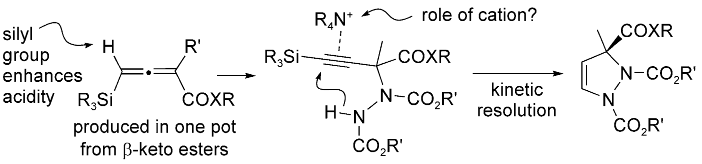
Probe probation: The cyano group is sensitive to its environment, absorbs in a unique region of protein IR spectra, and may be appended to an amino acid. When investigated in variants of cytochrome *c* (see picture: heme-pocket structure) by steady-state and time-resolved methods, it was found to be a useful site-specific probe of protein microenvironments and dynamics; however, it can also perturb its environment and destabilize the folded state of the protein.

Contents

Alkyne Activation

P. Maity, S. D. Lepore* —— **8338–8341**

Catalytic Synthesis of Nonracemic Azaproline Derivatives by Cyclization of β-Alkynyl Hydrazines under Kinetic Resolution Conditions

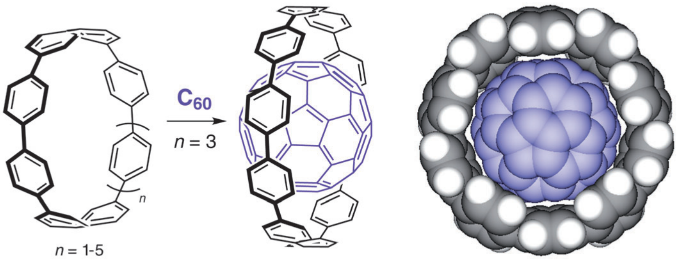


No metals required: Starting from readily accessible γ-silyl allenyl esters, β-alkynyl hydrazines were prepared in one step and subsequently cyclized in the presence of ammonium and phosphonium catalysts leading to dehydroazaproline products (see scheme; $X=O$, S). These heterocycles were also produced in high enantiomeric excesses using chiral ammonium phase-transfer catalysts by a kinetic resolution.

Host–Guest Chemistry

T. Iwamoto, Y. Watanabe, T. Sadahiro, T. Haino, S. Yamago* —— **8342–8344**

Size-Selective Encapsulation of C_{60} by [10]Cycloparaphenylene: Formation of the Shortest Fullerene-Peapod



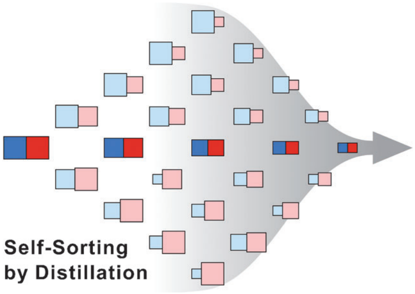
For sorting peas: When a mixture of cycloparaphenylenes (CPPs) is treated with C_{60}, [10]CPP selectively encapsulates C_{60} forming the shortest fullerene-peapod, $[10]CPP\supset C_{60}$ (see picture). Such complementary host–guest complexes could be useful for the size- and shape-selective separation of higher fullerenes and carbon nanotubes.

Dynamic Covalent Chemistry

K. Osowska, O. Š. Miljanić* **8345–8349**

Self-Sorting of Dynamic Imine Libraries during Distillation

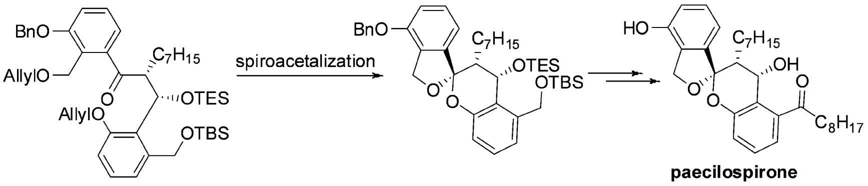
Keep it simple: The reaction of n aldehydes with n amines leads to a dynamic library of $[n\times n]$ imines. Slow distillation of the library amplifies the most volatile imine, whereby the most volatile aldehyde and amine are extracted from all other library components. Iterative repetition of the process enabled the self-sorting of the dynamic library into n mechanically separated imines, which were obtained in high yield.



Natural Product Synthesis

T.-Y. Yuen, S.-H. Yang, M. A. Brimble* —— **8350–8353**

Total Synthesis of Paecilospirone

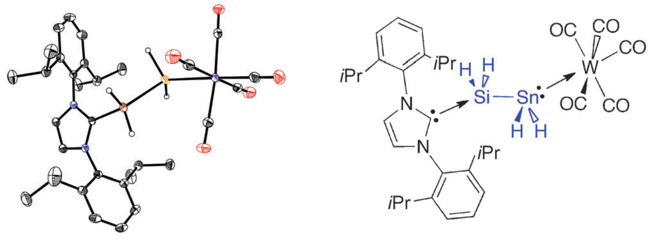


Neutrality is the best policy: Key features of the first total synthesis of paecilospirone include an *anti*-selective, lactate-derived aldol reaction, and a double deallylation/spirocyclization conducted at neutral pH to construct the sensitive hydroxy-substituted benzannulated spiroacetal (see scheme; Bn = benzyl, TBS = *tert*-butyldimethylsilyl, TES = triethylsilyl).

Main-Group Compounds

S. M. I. Al-Rafia, A. C. Malcolm, R. McDonald, M. J. Ferguson, E. Rivard* ______ **8354 – 8357**

Trapping the Parent Inorganic Ethylenes H_2SiGeH_2 and H_2SiSnH_2 in the Form of Stable Adducts at Ambient Temperature

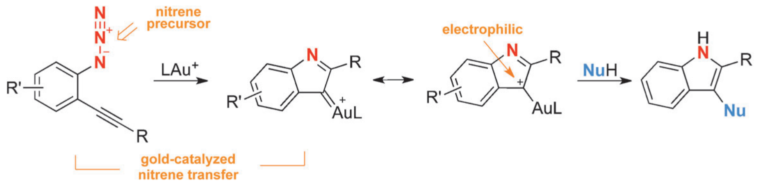


Putting on some weight: A series of stable adducts featuring the hitherto unknown mixed heavy ethylene analogues H_2SiGeH_2 and H_2SiSnH_2 (see picture) were prepared using a versatile donor–acceptor method.

Heterocycles

B. Lu, Y. Luo, L. Liu, L. Ye, Y. Wang, L. Zhang* ______ **8358 – 8362**

Umpolung Reactivity of Indole through Gold Catalysis

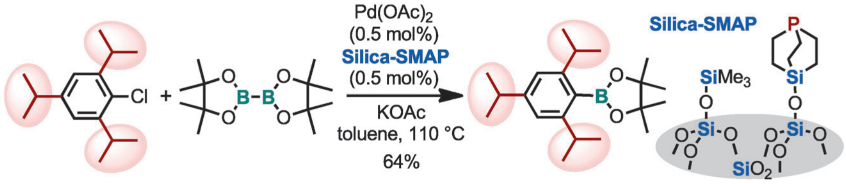


Electrophilic indole? Indoles, which are typically nucleophilic, can be made electrophilic through gold catalysis. By using an *ortho*-azido group to deliver a nitrene intramolecularly, an arylalkyne is converted into a gold carbene intermediate containing an indole skeleton that is highly electrophilic at the 3-position. A range of functionalized indoles is readily accessed by utilizing this strategy.

Borylation

S. Kawamorita, H. Ohmiya, T. Iwai, M. Sawamura* ______ **8363 – 8366**

Palladium-Catalyzed Borylation of Sterically Demanding Aryl Halides with a Silica-Supported Compact Phosphane Ligand



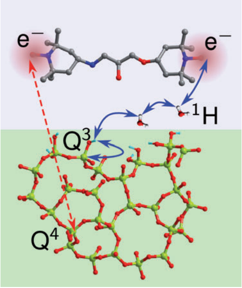
Immobile but active: A silica-supported "compact" phosphane, Silica-SMAP, can be used in the Pd-catalyzed borylation of aryl chlorides or bromides with bis(pinacolato)diboron (see scheme). The Silica-SMAP/Pd system significantly expands the substrate scope of the borylation toward sterically and electronically challenging aryl halides.

NMR Spectroscopy

O. Lafon,* M. Rosay, F. Aussenac, X. Lu, J. Trébosc, O. Cristini, C. Kinowski, N. Touati, H. Vezin, J.-P. Amoureux ______ **8367 – 8370**

Beyond the Silica Surface by Direct Silicon-29 Dynamic Nuclear Polarization

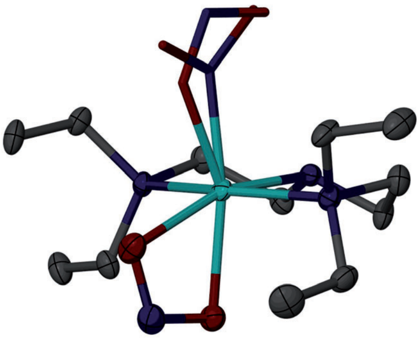
Buried truth: High-field magic angle spinning dynamic nuclear polarization (MAS DNP) enhances the sensitivity of solid-state NMR spectroscopy, but only for protonated surfaces. Direct ^{29}Si DNP using the biradical TOTAPOL (see picture) circumvents this limitation by producing a 30-fold enhancement of subsurface ^{29}Si NMR signals in mesoporous silica, a material with applications in photonics, nanotechnology and catalysis.



Isomerization

L. E. Hatcher, M. R. Warren, D. R. Allan, S. K. Brayshaw, A. L. Johnson,* S. Fuertes, S. Schiffers, A. J. Stevenson, S. J. Teat, C. H. Woodall, P. R. Raithby* ______ **8371 – 8374**

Metastable Linkage Isomerism in [Ni(Et$_4$dien)(NO$_2$)$_2$]: A Combined Thermal and Photocrystallographic Structural Investigation of a Nitro/Nitrito Interconversion



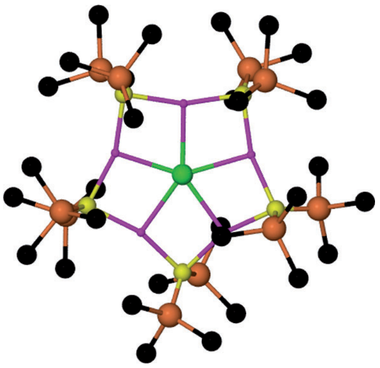
One way or another: The N-bound NO$_2$ group in [Ni(Et$_4$dien)(η^2-O,ON)(η^1-NO$_2$)] (see structure Ni turquoise, N blue, O red) has been shown to undergo reversible conversion into the O-bound nitrito linkage isomer under both thermal and photoactivation of a single crystal. Et$_4$dien = *N*,*N*,*N*′,*N*′-tetraethyldiethylenetriamine.

Metal Anionic Crowns

A. R. Kennedy, R. E. Mulvey,* C. T. O'Hara,* G. M. Robertson, S. D. Robertson ______ **8375 – 8378**

Mixed Lithium Amide–Lithium Halide Compounds: Unusual Halide-Deficient Amido Metal Anionic Crowns

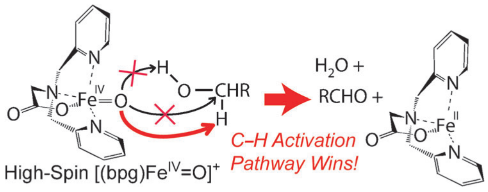
Molecular salt cellars: The addition of substoichiometric quantities of lithium halides to the lithium hexamethyldisilazide was studied. Surprisingly, a novel class of mixed amido-halide macrocyclic complexes, namely metal anionic crowns (MACs) was revealed (see picture: Li pink, N yellow, Cl green, Si orange, C black).



High-Spin Non-Heme Iron Complex

W. A. Donald, C. J. McKenzie, R. A. J. O'Hair* ______ **8379 – 8383**

C–H Bond Activation of Methanol and Ethanol by a High-Spin Fe^{IV}O Biomimetic Complex

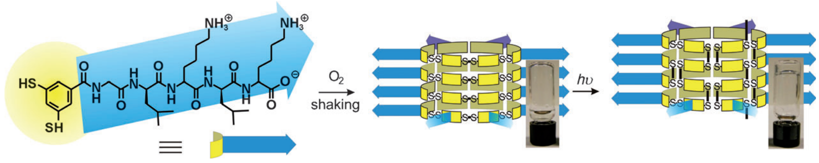


C–H vs O–H vs C–O bond activation? The non-heme complex [(bpg)Fe^{IV}O]$^+$ activates the αC–H bond of primary alcohols in vacuum through H abstraction by the FeO group in the rate-determining step. Although this effect counteracts any enhancement of reactivity that results from increasing the formal oxidation state of Fe, it increases the reaction selectivity.

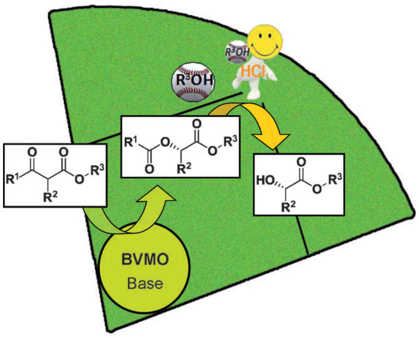
Dynamic Combinatorial Chemistry

J. Li, J. M. A. Carnall, M. C. A. Stuart, S. Otto* ______ **8384 – 8386**

Hydrogel Formation upon Photoinduced Covalent Capture of Macrocycle Stacks from Dynamic Combinatorial Libraries



Stacks of macrocycles, assembled using reversible disulfide-bond formation, are covalently captured by photoinitiated exchange of disulfide bonds, inducing the formation of hydrogels (see picture). This strategy allows access to structures beyond the thermodynamic minima traditionally targeted by dynamic combinatorial chemistry.

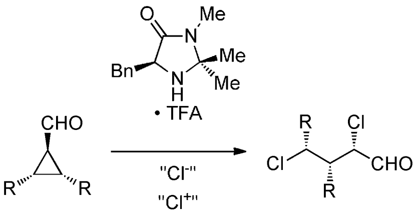


BVMOs make a play: The dynamic kinetic resolution of racemic α-alkyl-β-ketoesters was performed through a selective Baeyer–Villiger oxidation employing different Baeyer–Villiger monooxygenases (BVMOs) in mild basic media. The product diesters were obtained with excellent yields and enantioselectivities, and used as precursors for optically active α-hydroxy esters.

Biocatalysis

A. Rioz-Martínez, A. Cuetos, C. Rodríguez, G. de Gonzalo, I. Lavandera, M. W. Fraaije, V. Gotor* ____ **8387 – 8390**

Dynamic Kinetic Resolution of α-Substituted β-Ketoesters Catalyzed by Baeyer–Villiger Monooxygenases: Access to Enantiopure α-Hydroxy Esters

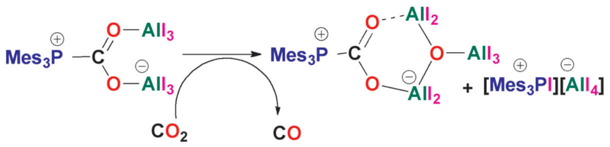


Trick the iminium! The concept of cyclopropyl iminium activation for the organocatalytic desymmetrization of *meso*-cyclopropylcarbaldehydes is presented. A combination of nucleophilic and electrophilic chlorinating reagents leads to a formal addition of Cl_2 across one of the cyclopropyl bonds giving access to 1,3-dichlorides in an enantioselective, catalytic fashion.

Reaction Design

C. Sparr,* R. Gilmour* ____ **8391 – 8395**

Cyclopropyl Iminium Activation: Reactivity Umpolung in Enantioselective Organocatalytic Reaction Design



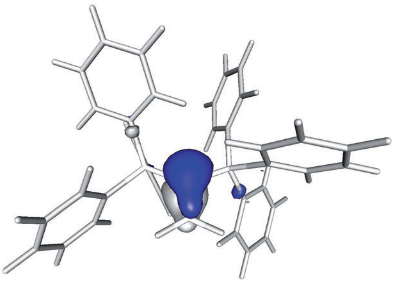
Reducing frustration: The reaction of $Mes_3P(CO_2)(AlI_3)_2$ in the presence of a CO_2 atmosphere results in the formation of $Mes_3P(CO_2)(O(AlI_2)_2)(AlI_3)$ and $[Mes_3PI][AlI_4]$ (Mes = 2,4,6-$Me_3C_6H_2$) with the evolution of CO.

CO_2 Reduction

G. Ménard, D. W. Stephan* ____ **8396 – 8399**

Stoichiometric Reduction of CO_2 to CO by Aluminum-Based Frustrated Lewis Pairs

Bottled! The employment of hexaphenylcarbodiphosphorane as ancillary ligand has allowed the isolation of the otherwise transient dihydrido borenium cation.



Borenium Cations

B. Inés, M. Patil, J. Carreras, R. Goddard, W. Thiel, M. Alcarazo* ____ **8400 – 8403**

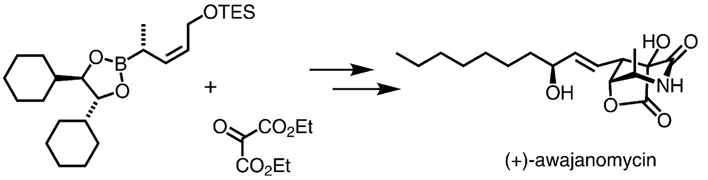
Synthesis, Structure, and Reactivity of a Dihydrido Borenium Cation

Contents

Total Synthesis

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

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



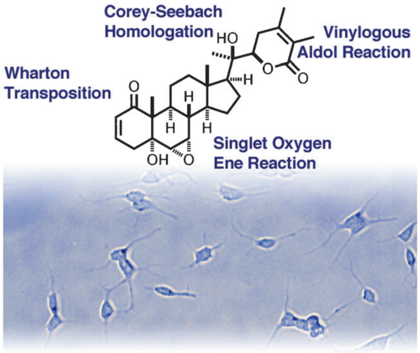
To the core: An efficient total synthesis of (+)-awajanomycin was achieved starting with an asymmetric allylboration of a *vic*-tricarbonyl compound (see scheme; TES = triethylsilyl). A stereoselective alkene dihydroxylation followed by a differentiation of diastereotopic ester groups and a subsequent lactamization gave the bicyclic core structure.

Neurosteroids

C. K. Jana, J. Hoecker, T. M. Woods,
H. J. Jessen, M. Neuburger,
K. Gademann* ______ **8407 – 8411**

Synthesis of Withanolide A, Biological Evaluation of Its Neuritogenic Properties, and Studies on Secretase Inhibition

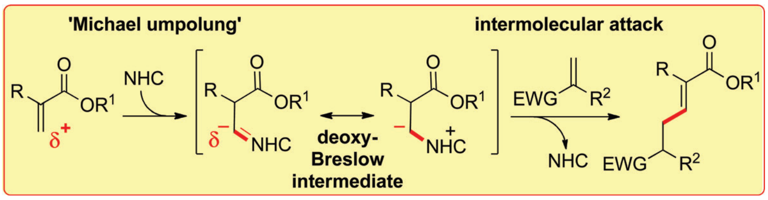
Neurons on steroids: A stereoselective synthesis of the neuritogenic steroid lactone withanolide A was achieved by singlet oxygen ene reaction, Wharton transposition, a Corey–Seebach homologation, and a vinylogous aldol reaction. Biological evaluation demonstrated neurite outgrowth, which supports the potential neuritogenic role of this compound in traditional Indian medicine.



Organocatalysis

A. T. Biju, M. Padmanaban, N. E. Wurz,
F. Glorius* ______ **8412 – 8415**

N-Heterocyclic Carbene Catalyzed Umpolung of Michael Acceptors for Intermolecular Reactions

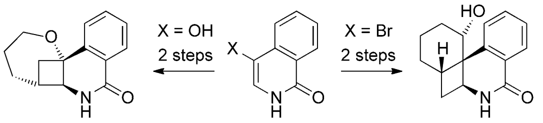


leahciM! The N-heterocyclic carbene catalyzed umpolung of Michael acceptors proceeds through the formation of a deoxy-Breslow intermediate (see scheme; EWG = electron-withdrawing group). This nucleophilic species can react with other Michael acceptors in an intermolecular fashion, thereby resulting in the formation of homo- or heterodimeric olefins. This “Michael umpolung” should become a valuable method for the formation of densely functionalized olefins.

Photochemistry

K. A. B. Austin, E. Herdtweck,
T. Bach* ______ **8416 – 8419**

Intramolecular [2+2] Photocycloaddition of Substituted Isoquinolones: Enantioselectivity and Kinetic Resolution Induced by a Chiral Template



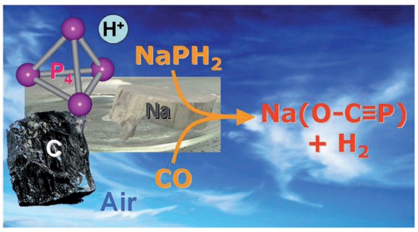
2 (96% *ee*) **1** **3** (53% *ee*)

From simple to complex: Starting from easily accessible isoquinolones **1** (X = Br, OH), complex cyclobutane photoproducts such as compound **2** can be obtained with high enantioselectivity (88–96% *ee*) through the use of a chiral template. Compound **3**, which was isolated in 53% *ee* starting from a racemic substrate, is the product of a unique, unprecedented kinetic resolution process.

Low-Valent Phosphorus

F. F. Puschmann, D. Stein, D. Heift,
C. Hendriksen, Z. A. Gal,
H.-F. Grützmacher,*
H. Grützmacher* ______ 8420 – 8423

Phosphination of Carbon Monoxide: A Simple Synthesis of Sodium Phosphaethynolate (NaOCP)



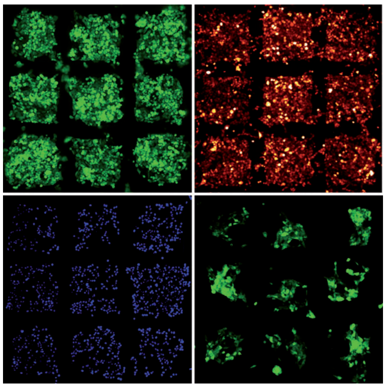
Simple basic ingredients are at the origin of the synthesis of Na(O−C≡P), the phosphorus analogue of sodium cyanate. Na(O−C≡P) is obtained from $NaPH_2$ (made from Na, P, and a proton source) and CO (from carbon and air). This salt is remarkably stable, in complete contrast to H−C≡P discovered 50 years ago.

High-Density Cell Microarrays

F. L. Geyer, E. Ueda, U. Liebel, N. Grau,
P. A. Levkin* ______ 8424 – 8427

Superhydrophobic–Superhydrophilic Micropatterning: Towards Genome-on-a-Chip Cell Microarrays

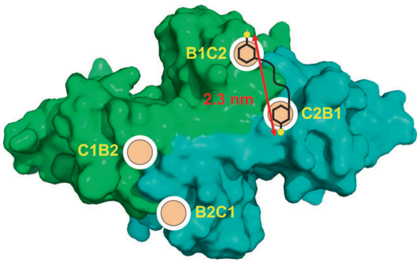
High-density cell microarrays based on superhydrophilic microspots separated by superhydrophobic barriers have been realized. The microspots absorb water solutions, while the barriers prevent cross-contamination, thus allowing the spots to be used as reservoirs for transfection mixtures and preventing cell proliferation and cell migration between the microspots. The picture shows four cell types after two days of culturing on the microarray.



Chemical Glycobiology

P. Braun, B. Nägele, V. Wittmann,*
M. Drescher ______ 8428 – 8431

Mechanism of Multivalent Carbohydrate–Protein Interactions Studied by EPR Spectroscopy

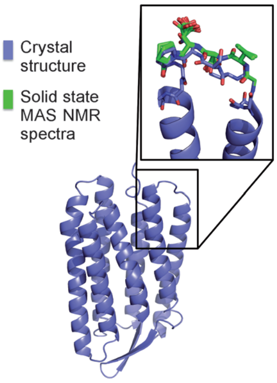


From a distance: Distance measurements in the nanometer range by means of spin-label electron paramagnetic resonance provide structural evidence for multivalent protein–ligand interactions in solution (see picture; protein subunits: blue/green, ligand: black, spin labels: yellow circles, binding sites: yellow letters). The data show a detailed picture of the binding of divalent ligands to a lectin.

Membrane Protein Structure

V. A. Higman, K. Varga, L. Aslimovska,
P. J. Judge, L. J. Sperling, C. M. Rienstra,
A. Watts* ______ 8432 – 8435

The Conformation of Bacteriorhodopsin Loops in Purple Membranes Resolved by Solid-State MAS NMR Spectroscopy



Making complements: Solid-state MAS NMR spectra of bacteriorhodopsin in its native purple membrane environment can be used to complement crystallographic studies of the protein by validating and redefining the (possibly distorted) loop structures. Backbone dihedral angles were extracted from the chemical shifts and compared to the crystal structures. Where there are conformational differences, the dihedral angles were used to recalculate the loop structure (see picture).

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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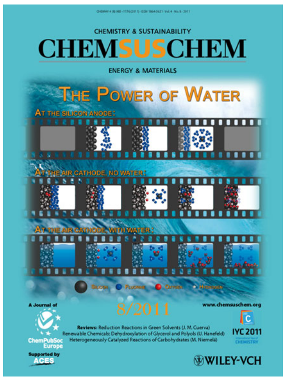

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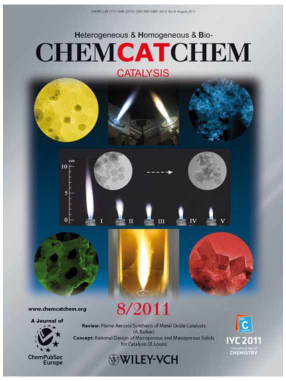

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