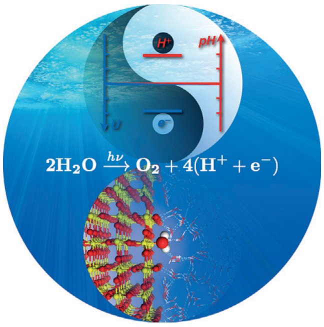
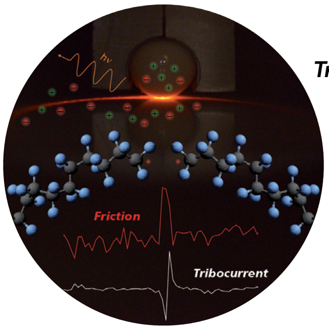
Structure–performance relationships ...

... of ceria in heterogeneous reactions are revealed by J. Pérez-Ramírez, A. Trovarelli, et al. in their Communication on page 12069 ff. The (111) surface prevalent in conventional polyhedral CeO_2 particles outperforms in hydrogenation, while the (100) surface that is exposed in nanocubes dominates in oxidation. Artwork: Amalia Gallardo (ArteLi) and Marcel Reich.

Proton-Coupled Electron Transfer

In their Communication on page 12046 ff., J. Cheng et al. propose the concept of protonic energy levels to visualize the thermodynamics of proton-coupled electron transfer. Their method helps to elucidate the electronic and protonic components of thermodynamic overpotentials in photocatalysis.



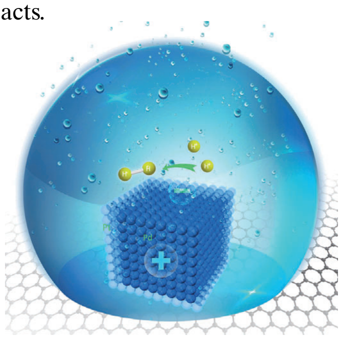


Triboelectrification

In their Communication on page 12101 ff., T. A. L. Burgo and A. Erdemir describe that friction force fluctuations and tribocurrent generation at metal–insulator interfaces show a strong correlation during sliding contacts.

Hydrogen Evolution Reaction

In their Communication on page 12120 ff., Y. Xiong and co-workers show how the surface polarization effect can be induced on Pt surfaces. As the thickness of the Pt layer decreases, the surface polarization boosts the hydrogen evolution reaction activity.



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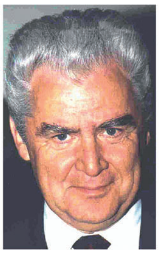
Service

Author Profile

"In a spare hour, I read a good science fiction novel. My favorite saying is "better late than never" …"
This and more about Kari Rissanen can be found on page 12012.

News

J. M. Thomas



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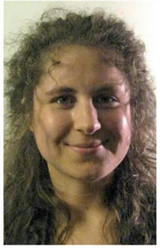
D. B. Werz



F. Schoenebeck

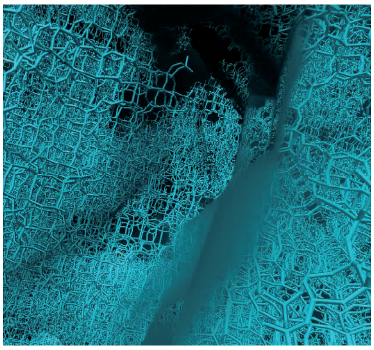
S. J. Rowan

Books

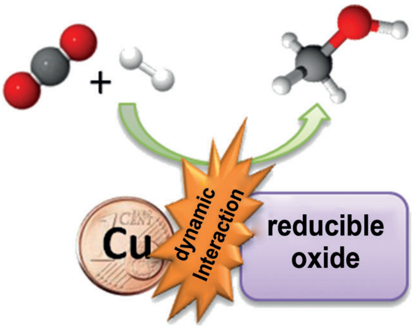
Highlights

Nanoporous Materials

A triad of complementary techniques, namely high-resolution gas adsorption coupled with hysteresis scanning and density functional theory, rotation electron diffraction, and electron tomography, has revealed the intracrystalline nature and connectivity of size-tailored mesopores in surfactant-templated mesostructured zeolite-Y with new clarity. This approach constitutes a significant advance in the elucidation of the structure of nanoporous solids.



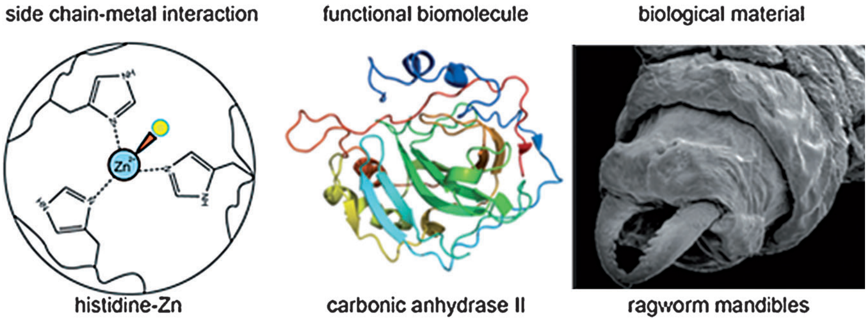
Heterogeneous Catalysis



Combined experimental and theoretical approaches resulted in a better understanding of the hydrogenation of CO_2 to methanol on copper-based catalysts. These results highlight the important role of the reducible oxide promoter for CO_2 activation.

Reviews

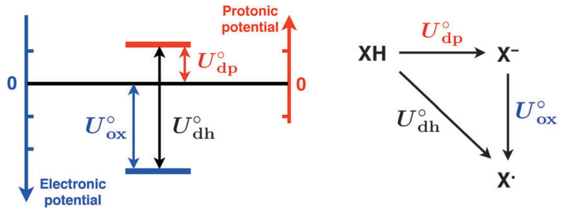
Biomaterials



Protein–metal interactions were traditionally regarded for their role in metabolic processes. Nowadays, they are also known to enhance the performance of certain biogenic materials, influencing properties such as hardness, toughness, adhesion, and self-healing. In this Review, recent advances in the understanding of the biological structure–function relationships are highlighted.

For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. US mailing agent: SPP, PO Box 437, Emigsville, PA 17318. Periodicals postage paid at Emigsville, PA. US POSTMASTER: send address changes to *Angewandte Chemie*, John Wiley & Sons Inc., C/O The Sheridan Press, PO Box 465, Hanover, PA 17331. Annual subscription price for institutions: US$ 11.738/10.206 (valid for print and electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

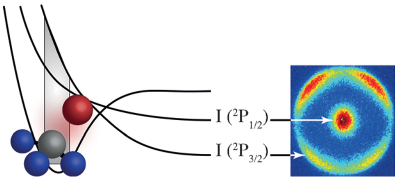
Communications



Scheming: A scheme for computing the thermochemistry of proton-coupled electron transfer (PCET) reactions at interfaces is described. In analogy with electronic energy levels, an appealing concept of protonic energy levels is proposed to visualize the thermodynamics of PCET in a level diagram. This diagram helps to elucidate the electronic and protonic components of thermodynamic overpotentials in photocatalysis.

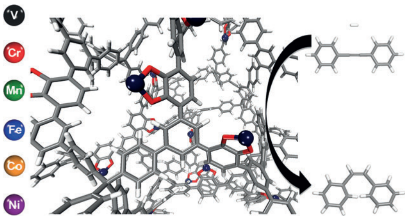
Thermodynamics

Frontispiece



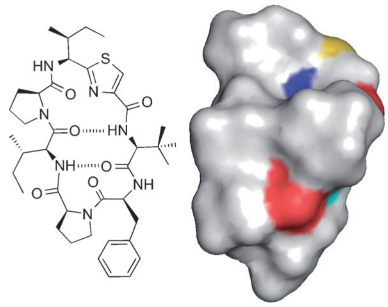
The spin calls the shots: Velocity slice imaging was used to study the dynamics of electron-induced dissociation of the potential plasma gas CF$_3$I (see picture). The changed spin state was found to switch the predominant diabatic path in the neutral CF$_3$I molecule to an adiabatic path in the CF$_3^-$ transient negative ion by opening a path through a conical intersection that is efficiently repressed by a required spin flip in the neutral molecule.

Dissociation Dynamics



POP around: Six first-row transition metals can be engineered into active and selective catalysts for alkyne hydrogenation upon incorporation into catechol porous organic polymers (POPs). These results highlight the advantages of using a POP platform to develop new catalysts which are otherwise difficult to achieve through traditional heterogeneous and homogeneous routes.

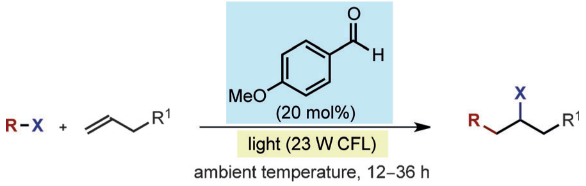
Heterogeneous Catalysis



The oral absorption and bioavailability of a cyclic heptapeptide in rats was improved by combining heterocyclic constraints, intramolecular hydrogen bonds, and branched amino acid side chains to shield polar backbone atoms. These improvements were solely guided by amide H–D exchange rates, NMR-derived structures, and solvent-exposed polar surfaces.

Orally Bioavailable Peptides

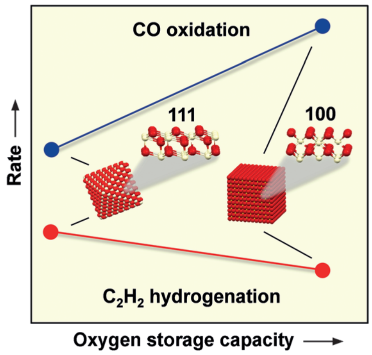
Photochemistry



Light and simple: An organic molecule as simple as *p*-anisaldehyde can efficiently catalyze the intermolecular atom-transfer radical addition of a variety of haloalkanes onto olefins. The protocol requires irradiation from a household 23 W compact fluorescent light (CFL) bulb to proceed, and ambient temperature is sufficient to functionalize olefins in a synthetically useful fashion.

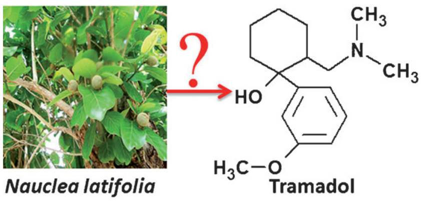
Crystal Morphology

Shape and face matter: The design of ceria catalysts for oxidation and hydrogenation reactions is governed by opposite criteria. Whereas oxygen vacancies, maximized on (100) nanocubes, promote oxidation, hydrogenation is favored by their minimization, requiring (111) face-enclosed polyhedral particles.

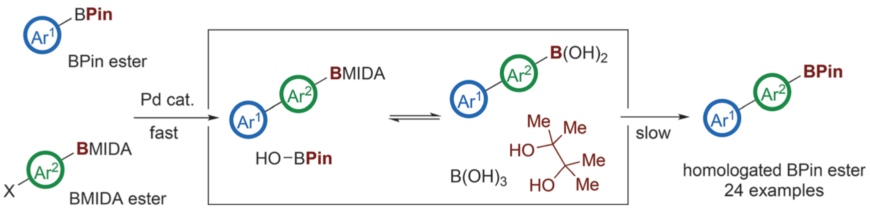


Anthropogenic Contamination

The root of the problem: Tramadol, a synthetic analgesic, was recently detected in the roots of the Cameroonian medicinal plant *Nauclea latifolia*. However, tramadol is not a natural product. Along with its major mammalian metabolites, tramadol is present in the roots of *N. latifolia* and other plant species, as well as in soil and local water sources in the Far North region of Cameroon as a result of anthropogenic contamination.

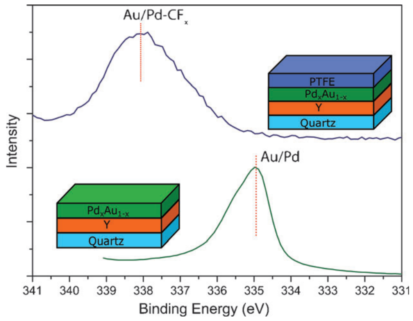


Cross-Coupling

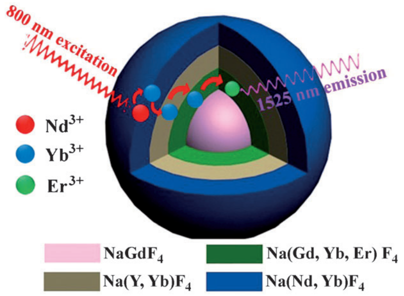


Under control: Controlling boron solution speciation during Suzuki–Miyaura cross-coupling enables the chemoselective synthesis of functionalized boronic acid pinacol esters. A rapid Suzuki–Miyaura reaction followed by controlled pinacol recycle enables the formal homologation of sp^2 boronic acid pinacol esters. The reaction can also be used for controlled oligomerization of sp^2-hybridized boronic esters. MIDA = *N*-methyliminodiacetic acid, Pin = pinacol.

Wonders of PTFE: Sputter deposition of few nanometer thick polymer films on Pd–Au alloy thin films led to the modification of the chemical properties of (sub)surface Pd atoms. The modification led to pronounced enhancements of their catalytic performance in Pd-based and Pd-catalyzed hydrogen sensing and hydrogen storage applications.



Surface Modification

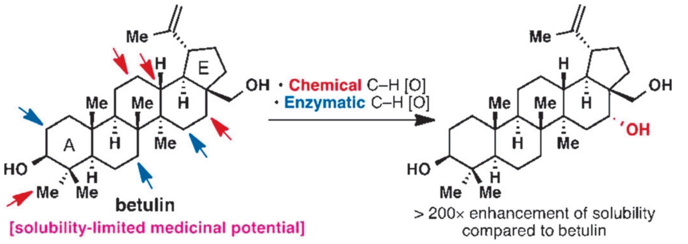


A multi-shell nanocrystal was synthesized and used as an effective probe for in vivo imaging. With emission in the short-wavelength infrared region at 1525 nm, the probe is detectable in tissues at depths of up to 18 mm with a low detection threshold.

Bioimaging

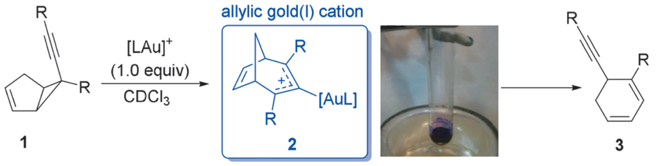
VIP

Inside Cover



A handle on [O]: A variety of C–H oxidation methods were explored on the betulin skeleton to improve the solubility of this bioactive, yet poorly water-soluble, natural product. The innate reactivity of the molecule, as well as the molecular handles present on the core, allowed oxidations at different positions. Solubility enhancement was observed for many of the synthesized compounds.

Terpenoids



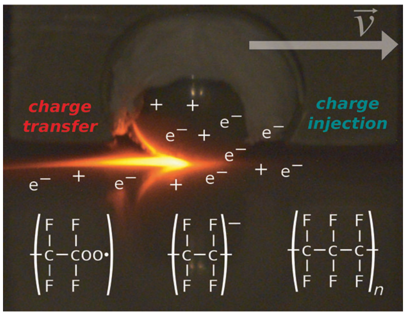
No longer elusive: The allylic gold(I) cation **2**, which has been proposed as an intermediate in the rearrangement of alkynylcyclopropanes (**1**) into alkynylcyclohexadienes (**3**), has been detected and characterized by NMR spectroscopy. Participation of **2** was supported experimentally and theoretically, and through these studies, a stable homo-antiaromatic carbocation was isolated and characterized.

Reactive Intermediates

Triboelectrification

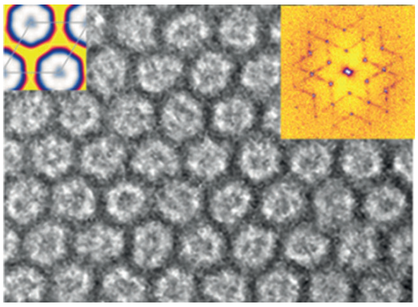
Inside Back Cover

Friction force fluctuation and tribocurrent generation at metal–insulator interfaces show a strong correlation during sliding contacts. The reported results suggest that these two phenomena have a common origin that must be associated with the occurrence of strong electrostatic interactions at the interface.

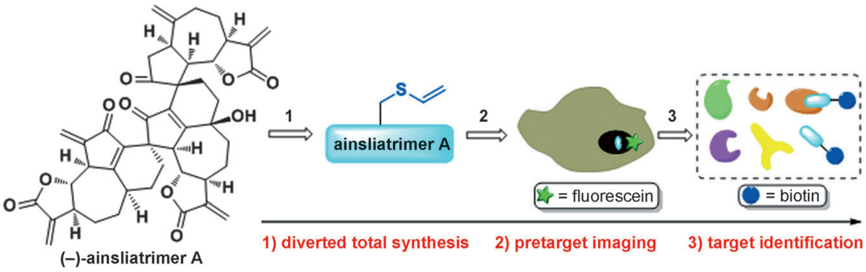


Template Synthesis

Templates with a twist: Chiral guanosine monophosphate (GMP) has been used as a supramolecular template for the synthesis of highly ordered silica mesoporous materials with trigonal symmetry and anisotropic channels. Electron microscopy studies revealed diffuse scattering patterns (see picture) corresponding to silica modulations associated with the chiral twisting of the GMP tetramers.

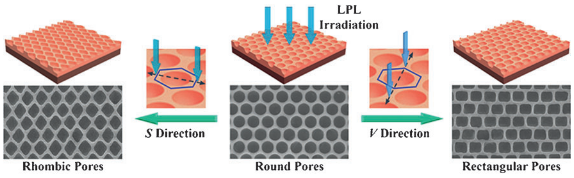


Target Identification



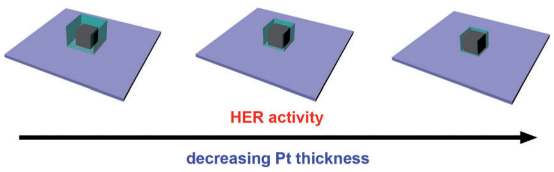
The target of the structurally complex natural product (−)-ainsliatrimer A has been identified by a systematic and efficient approach enabled by diverted total synthesis and bioorthogonal ligation. This approach enabled visualization of the subcellular localization of the natural product in live cells and identified activation of PPARγ as leading to the anticancer activity of ainsliatrimer A.

Porous Polymer Films



Directional photofluidization of azobenzene groups manipulates the shape transformation of the round pores in an ordered breath figure array. Depending on the irradiation time and polarization direction of the incident polarized light, rectangular, rhombic, or parallelogram-shaped pores can be obtained.

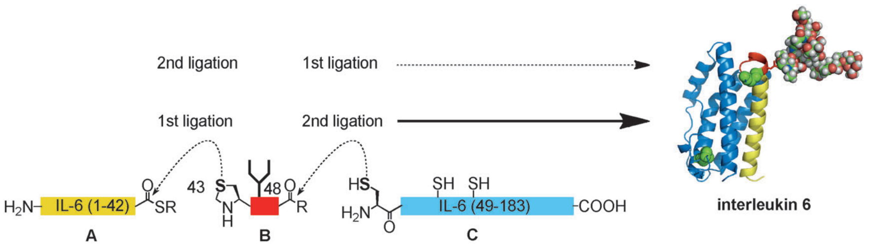
Nanostructures



Less is more: Pt–Pd–graphene stack structures (see picture) are prepared by a new method that allows control of the thickness of the Pt shell. This thickness correlates with performance in the hydrogen evolution reaction (HER). As a result of surface polarization, the HER activity actually increases with decreasing Pt thickness, opening possibilities of using less Pt.

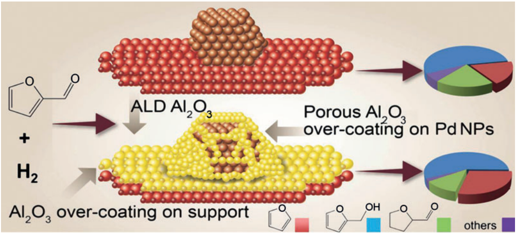
Back Cover

Native Chemical Ligation



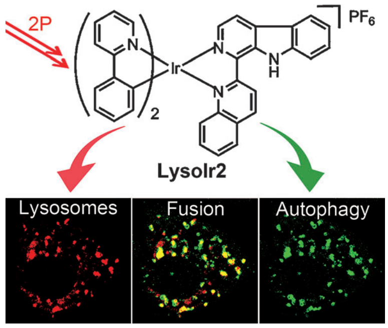
The sequence matters: The human cytokine interleukin 6 (IL-6) was synthesized in two glycoforms by sequential native chemical ligation from two recombinant fragments (**A**, **C**) and a synthetic glycopeptide (**B**). Only one of the possible sequences of ligations efficiently led to the IL variants because of the susceptibility of the peptide chain and the folded glycoprotein to nonphysiological conditions.

Selective Hydrogenation



Terrace versus step sites: Atomic layer deposition (ALD) overcoating was applied to cover the step sites of Pd nanoparticles with alumina, whereas the terrace sites remained as the active component for furfural hydrogenation. The modified catalyst exhibited an increased selectivity to furan, showing that this technique can be used to tune the catalytic properties of Pd nanoparticles.

Theranostic Iridium Complexes

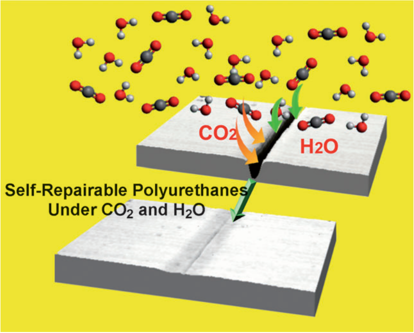


Kill Two Birds with One Stone: Two iridium(III) complexes can specifically image lysosomes and induce an autophagic response in live cells. The combination of these two intriguing properties makes them ideal theranostic agents to track lysosomal changes during autophagic processes. Additionally, these complexes display strong two-photon excited fluorescence, which is favorable for live cell imaging and in vivo applications.

Self-Repairing Materials

Y. Yang, M. W. Urban* ___ **12142 – 12147**

Self-Repairable Polyurethane Networks by Atmospheric Carbon Dioxide and Water

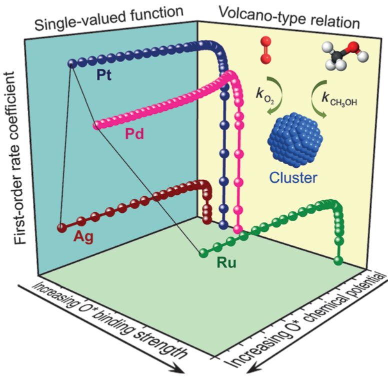


Self-repairing materials were obtained by reacting sugar moieties with hexamethylene diisocyanate trimer and polyethylene glycol to form cross-linked MGP-polyurethane networks. The repair process requires atmospheric amounts of CO_2 and H_2O, thus resembling plant behavior of carbon fixation during photosynthesis.

Oxidation Catalysis

W. Tu, Y.-H. Chin* ___ **12148 – 12152**

Catalytic Consequences of the Thermodynamic Activities at Metal Cluster Surfaces and Their Periodic Reactivity Trend for Methanol Oxidation

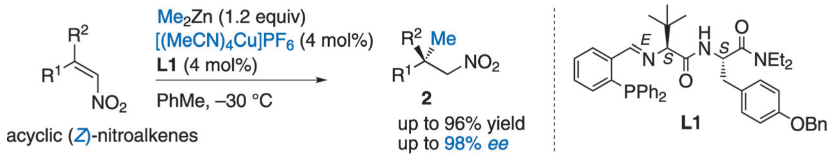


Oxidative dehydrogenation: The first-order rate coefficients for methanol oxidative dehydrogenation on metal clusters are a single-valued function of the O_2/CH_3OH ratio (see picture). The reactive collision frequency for CH_3OH activation on O*-covered surfaces varies with the oxygen-binding strength in a classical volcano-type relation.

Asymmetric Catalysis

X. Zeng,* J. J. Gao, J. J. Song, S. Ma, J.-N. Desrosiers, J. A. Mulder, S. Rodriguez, M. A. Herbage, N. Haddad, B. Qu, K. R. Fandrick, N. Grinberg, H. Lee, X. Wei, N. K. Yee, C. H. Senanayake ___ **12153 – 12157**

Remarkable Enhancement of Enantioselectivity in the Asymmetric Conjugate Addition of Dimethylzinc to (*Z*)-Nitroalkenes with a Catalytic $[(MeCN)_4Cu]PF_6$–Hoveyda Ligand Complex

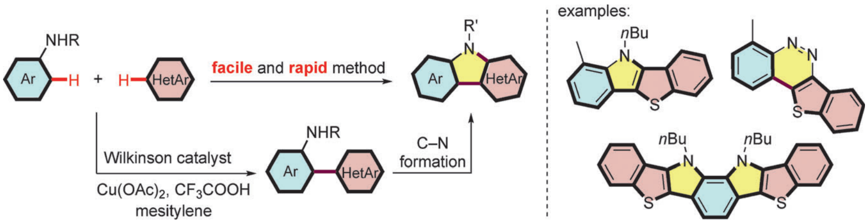


Don't forget Me! Challenging methyl-substituted all-carbon quaternary stereogenic centers were formed with high stereoselectivity by a copper-catalyzed asymmetric conjugate addition of Me_2Zn to (*Z*)-nitroalkenes (see scheme; Bn = benzyl). The key feature is the unprecedented use of $[(MeCN)_4Cu]PF_6$ in conjunction with ligand **L1** so that the undesired nitroalkene isomerization was minimized.

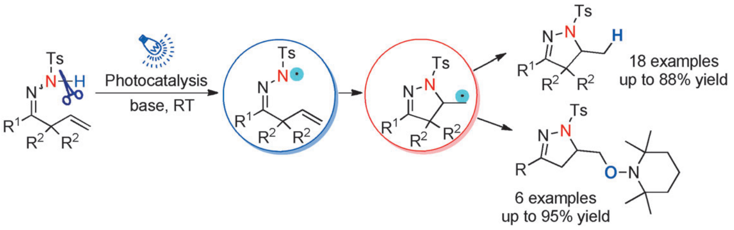
C–H Activation

Y. Huang, D. Wu, J. Huang, Q. Guo, J. Li, J. You* ___ **12158 – 12162**

Use of the Wilkinson Catalyst for the *ortho*-C–H Heteroarylation of Aromatic Amines: Facile Access to Highly Extended π-Conjugated Heteroacenes for Organic Semiconductors



An old favorite that can't be beat: An innovative system composed of the Wilkinson catalyst $[Rh(PPh_3)_3Cl]$ and CF_3COOH enabled the highly regioselective oxidative C–H/C–H cross-coupling of aromatic amines with heteroarenes (see scheme). The products could be conveniently transformed into highly extended π-conjugated heteroacenes with large HOMO–LUMO energy gaps and low-lying HOMO levels as promising organic semiconductors.

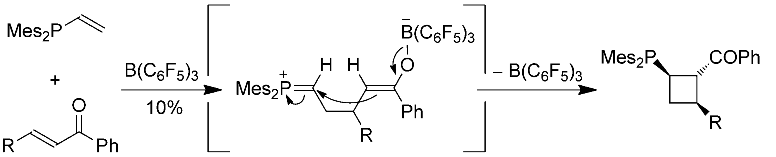


Centered on N: A visible-light-induced photocatalytic generation of N-centered hydrazonyl radicals has been accomplished for the first time. This approach allows efficient intramolecular addition of hydrazonyl radical to terminal alkenes, thus providing hydroamination and oxyamination products in good yields. Importantly, the protocol involves direct N−H oxidation under mild reaction conditions. Ts = 4-toluenesulfonyl.

Heterocycle Synthesis

X.-Q. Hu, J.-R. Chen,* Q. Wei, F.-L. Liu, Q.-H. Deng, A. M. Beauchemin, W.-J. Xiao* ——— **12163 – 12167**

Photocatalytic Generation of N-Centered Hydrazonyl Radicals: A Strategy for Hydroamination of β,γ-Unsaturated Hydrazones

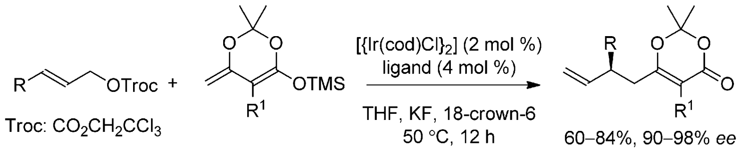


Vinyl phosphanes (ene–phosphanes) undergo B$(C_6F_5)_3$-induced phospha-Stork reactions with organic carbonyl compounds under frustrated Lewis pair conditions. The reactions proceed via methylene phosphonium intermediates.

Frustrated Lewis Pairs

Y. Hasegawa, C. G. Daniliuc, G. Kehr, G. Erker* ——— **12168 – 12171**

Developing Phospha-Stork Chemistry Induced by a Borane Lewis Acid



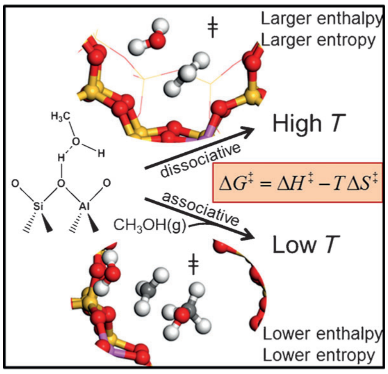
Keep on 'Troc'ing: The reported title reaction leads to the asymmetric allylation of a variety of allylic trichloroethyl carbonates with silyl dienolates. The γ-allylated products are produced selectively in 60–84 % yield and with 90–98 % *ee*. cod = 1,5-cyclooctadiene, THF = tetrahydrofuran, TMS = trimethylsilyl.

Asymmetric Catalysis

M. Chen, J. F. Hartwig* —— **12172 – 12176**

Iridium-Catalyzed Regio- and Enantioselective Allylic Substitution of Silyl Dienolates Derived from Dioxinones

Molecular crossroads: Associative routes prevail at low temperatures and high pressures for the reaction of methanol to dimethyl ether on zeolitic acids because they are mediated by larger transition states of lower enthalpy and entropy. A plausible sequence of elementary steps was established by rate and IR data during catalysis and confirmed by theoretical analysis using density functional theory with van der Waals interactions and transition-state theory formalisms.



Reaction Mechanisms

A. J. Jones, E. Iglesia* —— **12177 – 12181**

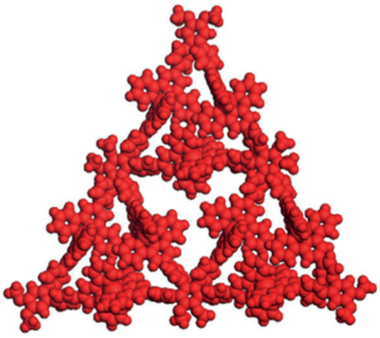
Kinetic, Spectroscopic, and Theoretical Assessment of Associative and Dissociative Methanol Dehydration Routes in Zeolites

Sierpiński Triangles

R. Sarkar, K. Guo, C. N. Moorefield,
M. J. Saunders, C. Wesdemiotis,*
G. R. Newkome* ______ 12182 – 12185

One-Step Multicomponent Self-Assembly of a First-Generation Sierpiński Triangle: From Fractal Design to Chemical Reality

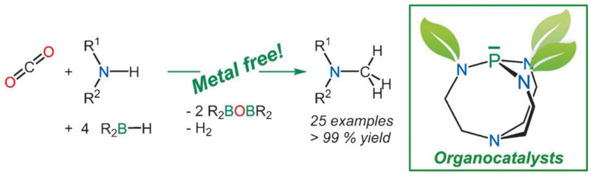
Mathematical mimicry leads to the synthesis of a Sierpiński triangle, which was obtained by multicomponent assembly and features terpyridine–Cd^{II}–terpyridine connectivity. Complementary ligand architecture and metal complex lability act in synergy to achieve the desired outcome.



Carbon Dioxide Reduction

E. Blondiaux, J. Pouessel,
T. Cantat* ______ 12186 – 12190

Carbon Dioxide Reduction to Methylamines under Metal-Free Conditions



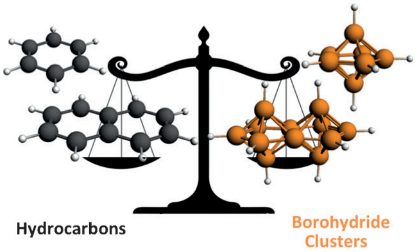
Organocatalysis: Proazaphosphatrane superbases prove to be highly active catalysts in the reductive functionalization of CO_2, in the presence of hydroboranes. The new method makes possible the methylation of N—H bonds in a wide variety of amines, including secondary amines (see picture), with increased chemoselectivity.

Cluster Compounds

J. Poater, M. Solà,* C. Viñas,
F. Teixidor* ______ 12191 – 12195

π Aromaticity and Three-Dimensional Aromaticity: Two sides of the Same Coin?

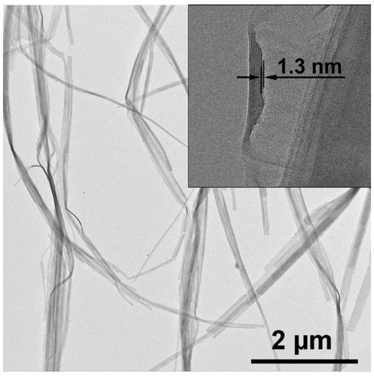
Making the rules: The Wade–Mingos $4n+2$ rule for three-dimensional *closo* boranes is equivalent to the Hückel $(4n+2)\pi$ rule for two-dimensional polycyclic aromatic hydrocarbons.



Nanocluster Self-Assembly

Z. N. Wu, Y. C. Li, J. L. Liu, Z. Y. Lu,
H. Zhang,* B. Yang ______ 12196 – 12200

Colloidal Self-Assembly of Catalytic Copper Nanoclusters into Ultrathin Ribbons

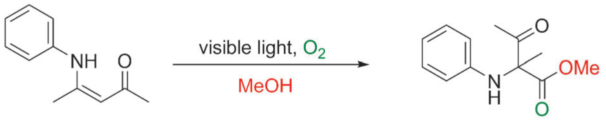


Cooperative forces: Ligand-capped copper nanoclusters are self-assembled into ribbons with single-cluster thickness in colloidal solution, a process controlled by tuning the cooperation between the dipolar interaction between nanoclusters and the van der Waals attraction between ligands. The self-assembled structures exhibit excellent catalytic activity and durability in oxygen reduction reactions.

Synthetic Methods

W. Fan, P. Li* ______ **12201 – 12204**

Visible-Light-Mediated 1,2-Acyl Migration: The Reaction of Secondary Enamino Ketones with Singlet Oxygen

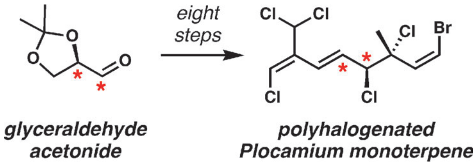


Singled out: Secondary enaminones were oxidized by photochemically generated singlet oxygen, and subsequent nucleophilic addition of an alcohol and with an 1,2-acyl migration afforded quaternary amino acid derivatives. An ene-type reaction pathway is proposed. It is distinctively different from the typical [2+2] addition of singlet oxygen to a C=C bond.

Natural Product Synthesis

C. V. Vogel, H. Pietraszkiewicz,
O. M. Sabry, W. H. Gerwick,
F. A. Valeriote,
C. D. Vanderwal* ______ **12205 – 12209**

Enantioselective Divergent Syntheses of Several Polyhalogenated *Plocamium* Monoterpenes and Evaluation of Their Selectivity for Solid Tumors

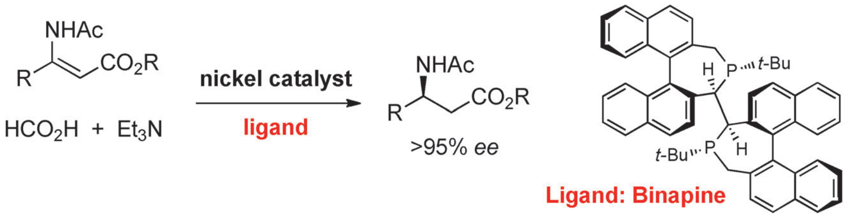


Glyceraldehyde acetonide serves as a chiral glyoxal equivalent and a linchpin for the enantioselective synthesis of several acyclic polyhalogenated monoterpenes from the red algae *Plocamium*. Several of these compounds demonstrate selective toxicity towards solid-tumor cell lines over leukemia cell lines, as well as low-micromolar cytotoxicity towards the HCT-116 human colon carcinoma cell line.

Asymmetric Hydrogenation

P. Yang, H. Xu,
J. (S.) Zhou* ______ **12210 – 12213**

Nickel-Catalyzed Asymmetric Transfer Hydrogenation of Olefins for the Synthesis of α- and β-Amino Acids

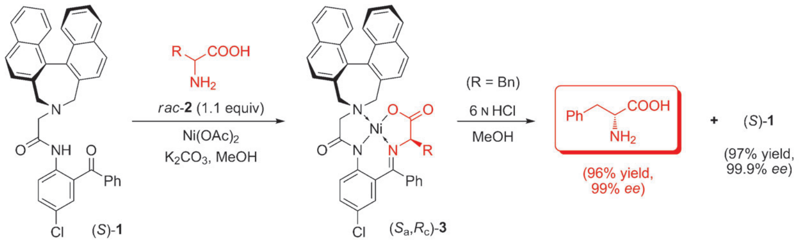


Nickel and dime for the asymmetric transfer hydrogenation of prochiral olefins to access α- and β-amino acids. Formic acid was used as the hydrogen source.

Diastereoselectivity

R. Takeda, A. Kawamura, A. Kawashima,
T. Sato, H. Moriwaki,* K. Izawa, K. Akaji,
S. Wang, H. Liu,* J. L. Aceña,
V. A. Soloshonok* ______ **12214 – 12217**

Chemical Dynamic Kinetic Resolution and *S*/*R* Interconversion of Unprotected α-Amino Acids

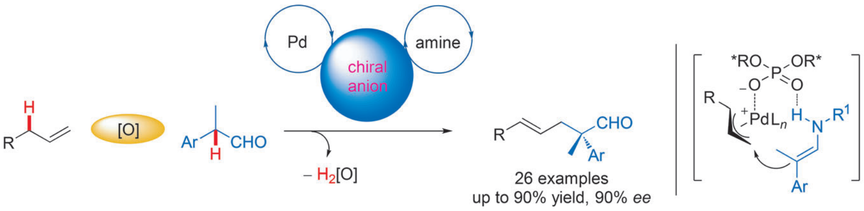


A new player for DKR: Dynamic kinetic resolution of α-amino acids has been achieved upon complexation with nickel(II) and a chiral ligand derived from optically active bis(naphthyl)amine under thermodynamic control, thus affording excellent diastereoselectivities and chemical yields. The *S* to *R* interconversion of α-amino acids is also described.

Synthetic Methods

P.-S. Wang, H.-C. Lin, Y.-J. Zhai, Z.-Y. Han,
L.-Z. Gong* ______ **12218 – 12221**

Chiral Counteranion Strategy for Asymmetric Oxidative C(sp^3)–H/C(sp^3)–H Coupling: Enantioselective α-Allylation of Aldehydes with Terminal Alkenes



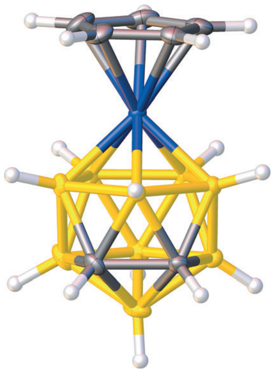
Go with the combo: The title reaction is realized by combining asymmetric counteranion catalysis and palladium-catalyzed allylic C–H activation. This method tolerates a wide scope of α-branched aromatic aldehydes and terminal alkenes, thus affording allylation products in high yields and with good to excellent levels of enantioselectivity.

Metallacarboranes

W. Y. Man, S. Zlatogorsky, H. Tricas,
D. Ellis, G. M. Rosair,
A. J. Welch* ______ **12222 – 12225**

How to Make 8,1,2-*closo*-MC$_2$B$_9$ Metallacarboranes

The crystallographic characterization of three new examples of metallacarboranes with 8,1,2-*closo*-MC$_2$B$_9$ structure is reported. Consideration of the reactions in which they were formed as well as their coproducts led to a suggested mechanism. This mechanism was tested in the synthesis of 8-(η-C$_5$H$_5$)-8,1,2-*closo*-CoC$_2$B$_9$H$_{11}$ and found to be successful.

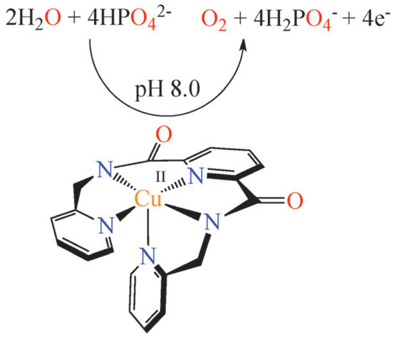


Electrocatalysis

M. K. Coggins, M.-T. Zhang, Z. Chen,
N. Song, T. J. Meyer* ______ **12226 – 12230**

Single-Site Copper(II) Water Oxidation Electrocatalysis: Rate Enhancements with HPO$_4^{2-}$ as a Proton Acceptor at pH 8

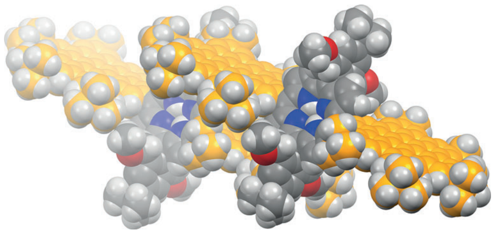
Metal-catalyzed water oxidation: Cu^{II}-(Py$_3$P) (**1**) is a water oxidation electrocatalyst in H$_2$PO$_4^-$/HPO$_4^{2-}$ buffered aqueous solutions (see picture). Electrolysis experiments with **1** at pH 8.0 and at a potential of 1.40 V versus the normal hydrogen electrode resulted in the formation of dioxygen (84% Faradaic yield) through multiple catalyst turnovers with minimal catalyst deactivation.



Carbon-Rich Porphyrins

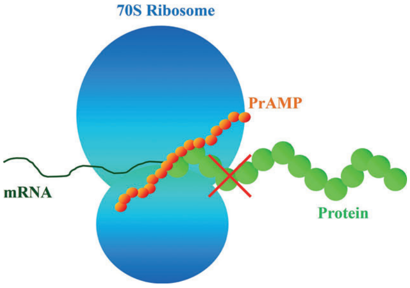
D. Lungerich, J. F. Hitzenberger,
M. Marcia, F. Hampel, T. Drewello,*
N. Jux* ______ **12231 – 12235**

Superbenzene–Porphyrin Conjugates



Super size me! The first porphyrin conjugate with two superbenzene units shows properties induced by the superbenzene and porphyrin moieties, but also behavior that differs distinctly from that of the individual buildung blocks. The molecule is characterized by standard spectroscopic methods and modern mass spectrometry, and the first X-ray structure of such a conjugate is presented.

Lost in translation: Proline-rich antimicrobial peptides (PrAMPs) inhibit bacterial protein translation by binding to the 70S ribosome of Gram-negative bacteria. This represents a novel killing mechanism for gene-encoded antimicrobial peptides. Alanine substitutions in the peptides additionally identified specific basic and hydrophobic residues as major interaction sites, which will enable the design of optimized compounds.



Antimicrobial Peptides

A. Krizsan, D. Volke, S. Weinert, N. Sträter, D. Knappe, R. Hoffmann* ________ **12236 – 12239**

Insect-Derived Proline-Rich Antimicrobial Peptides Kill Bacteria by Inhibiting Bacterial Protein Translation at the 70 S Ribosome

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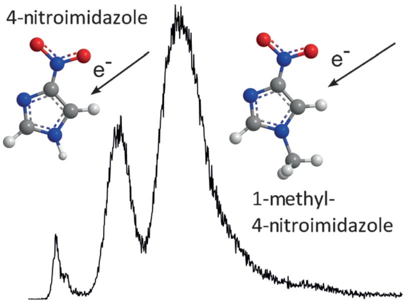

Low-energy electrons (LEEs) with energies of less than 2 eV effectively decompose the 4-nitroimidazole molecule by electron attachment. Thereby a variety of decomposition channels are observed involving simple bond cleavages but also complex reactions involving multiple bond cleavages and formation of new molecules. This rich chemistry induced by LEE is completely suppressed in the energy domain below 2 eV for the molecule in its methylated form.

Electron-Induced Decomposition

K. Tanzer, L. Feketeová,* B. Puschnigg, P. Scheier, E. Illenberger, S. Denifl* ________ **12240 – 12243**

Reactions in Nitroimidazole Triggered by Low-Energy (0–2 eV) Electrons: Methylation at N1-H Completely Blocks Reactivity

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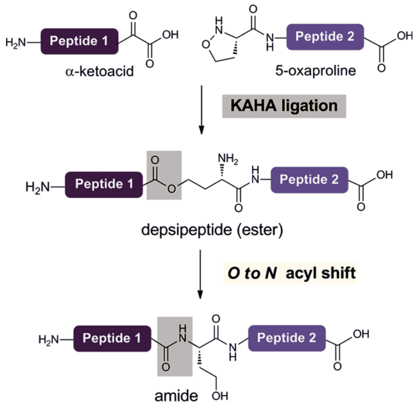
The primary products of the chemical ligations of α-ketoacids and 5-oxaproline peptides are esters, rather than the previously reported amides (see scheme). The depsipeptide products rapidly rearrange to the amides in basic buffers. The formation of esters sheds light on possible mechanisms for the type II KAHA ligations and opens a new avenue for the chemical synthesis of depsiproteins.



Ester Ligation

T. G. Wucherpfennig, F. Rohrbacher, V. R. Pattabiraman, J. W. Bode* ________ **12244 – 12247**

Formation and Rearrangement of Homoserine Depsipeptides and Depsiproteins in the α-Ketoacid–Hydroxylamine Ligation with 5-Oxaproline

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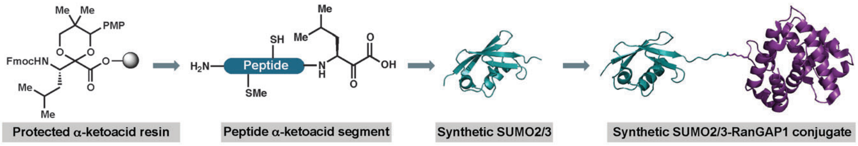


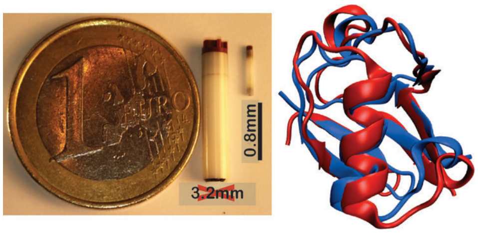
SUMO match! A protected α-ketoacid resin delivers C-terminal peptide α-ketoacids directly and accommodates the inclusion of all canonical amino acids, including cysteine and methionine. By using this approach, SUMO2 and SUMO3 proteins were prepared by KAHA ligation with 5-oxaproline. The synthetic SUMO proteins were recognized by and conjugated to RanGAP1 by SUMOylation enzymes in vitro.

Protein Ligation

T. G. Wucherpfennig, V. R. Pattabiraman, F. R. P. Limberg, J. Ruiz-Rodríguez, J. W. Bode* ________ **12248 – 12252**

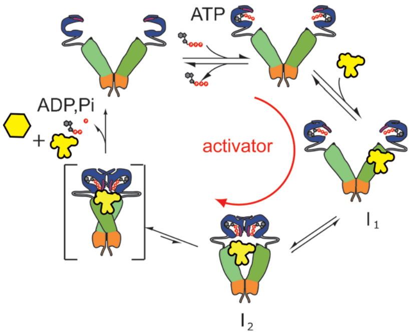
Traceless Preparation of C-Terminal α-Ketoacids for Chemical Protein Synthesis by α-Ketoacid–Hydroxylamine Ligation: Synthesis of SUMO2/3

Solid-State NMR Spectroscopy



Smaller and faster: The 3D structure of a model protein was determined with a protein sample one-fortieth of the usual amount thanks to 100 kHz magic-angle-spinning NMR spectroscopy.

Chaperones



Effective intervention: Novel small-molecule modulators of the molecular chaperone Hsp90 have been identified and characterized which mimic the effects of protein cofactors in accelerating changes in the conformation of Hsp90. This opens new perspectives for targeting Hsp90 to treat diseases such as cancer and viral infections.

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

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

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The Hot Papers are articles that the Editors have chosen on the basis of the referee reports to be of particular importance for an intensely studied area of research.

Angewandte Corrigendum

Nucleophilic Reactivity of a Copper(II)–Superoxide Complex

P. Pirovano, A. M. Magherusan,
C. McGlynn, A. Ure, A. Lynes,
A. R. McDonald* ———— **5946–5950**

Angew. Chem. Int. Ed. **2014**, *53*

DOI: 10.1002/anie.201311152

In this Communication, two sentences need to be corrected.
The sentence on page 5946, column 2, line 4 should read: “An Fe^{III}–superoxide intermediate in a mutated form of homoprotocatechuate 2,3-dioxygenase was recently trapped and spectroscopically characterized,[9] however, rather than display electrophilic HAA or nucleophilic reactivity, this species decayed through electron transfer.”
And the sentence on page 5948, column 1, line 18 should begin as follows: “The only model complex that displayed higher deformylation rates than **1** is $[Fe^{III}(\eta^1\text{-}OO^-)(TMCS)]$ (TMCS = 1-(2-mercaptoethyl)-4,8,11-trimethyl-1,4,8,11-tetraazacyclotetradecane), ... ”

Angewandte Corrigendum

In this Communication, the structure of salinosporamide A in Figure 1 has been incorrect. The correct structure is as follows.

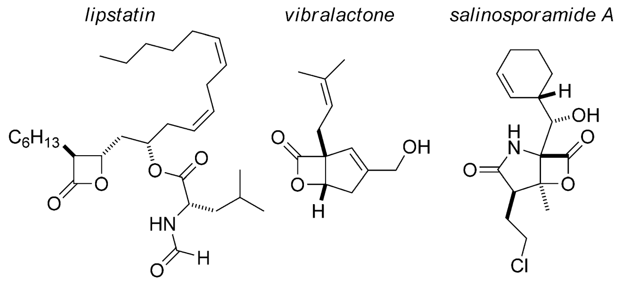

Figure 1. Biologically active β-lactones.

Asymmetric Synthesis of Highly Substituted β-Lactones through Oxidative Carbene Catalysis with LiCl as Cooperative Lewis Acid

S. Bera, R. C. Samanta, C. G. Daniliuc, A. Studer* ______________ **9622–9626**

Angew. Chem. Int. Ed. **2014**, *53*

DOI: 10.1002/anie.201405200

Angewandte Corrigendum

Upon further investigations of the KAHA ligations with 5-oxaproline the authors of this Communication have found that esters, rather than amides are the major products. The esters easily rearrange to the amide products in basic buffers. For further details and updated characterization data for the ligation products described in this paper, please see the Communication in Ref. [1].

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[1] T. G. Wucherpfennig, F. Rohrbacher, V. R. Pattabiraman, J. W. Bode, *Angew. Chem. Int. Ed.* **2014**, *53*, 12244; *Angew. Chem.* **2014**, *126*, 12441.

Chemical Protein Synthesis by Chemoselective α-Ketoacid–Hydroxylamine (KAHA) Ligations with 5-Oxaproline

V. R. Pattabiraman, A. O. Ogunkoya, J. W. Bode* ______________ **5114–5118**

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

DOI: 10.1002/anie.201200907

Angewandte Corrigendum

Upon further investigations of the KAHA ligations with 5-oxaproline, the authors of this Communication have found that esters, rather than amides are the major products. The esters easily rearrange to the amide products in basic buffers. For further details and updated characterization data for the ligation products described in this paper, please see the Communication in Ref. [1].

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[1] T. G. Wucherpfennig, F. Rohrbacher, V. R. Pattabiraman, J. W. Bode, *Angew. Chem. Int. Ed.* **2014**, *53*, 12244; *Angew. Chem.* **2014**, *126*, 12441.

Sequential α-Ketoacid-Hydroxylamine (KAHA) Ligations: Synthesis of C-Terminal Variants of the Modifier Protein UFM1

A. O. Ogunkoya, V. R. Pattabiraman, J. W. Bode* ______________ **9693–9697**

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

DOI: 10.1002/anie.201204144