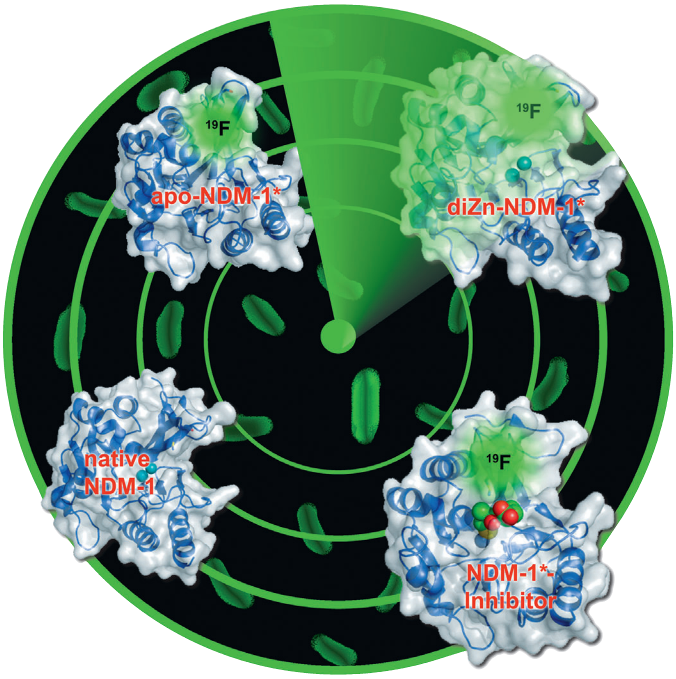
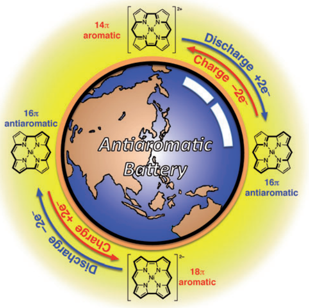
Increasing antibiotic resistance ...

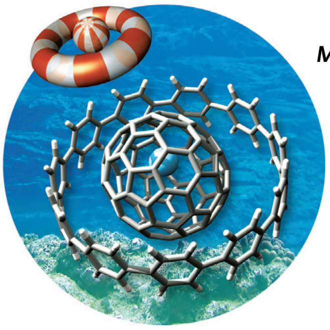


… is a global health concern. Metallo-β-lactamases catalyze the hydrolysis of almost all β-lactam antibiotics. T. D. W. Claridge, C. J. Schofield et al. show in their Communication on page 3129 ff. how ^{19}F NMR spectroscopy can be used to investigate the binding mode of inhibitors to the New Delhi Metallo-β-lactamase I (NDM-1). By labeling an active-site loop with ^{19}F, changes in the local chemical environment caused by inhibitor binding can be readily monitored by NMR spectroscopy.

Antiaromatic Batteries

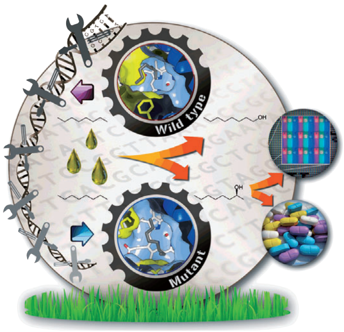
A rechargeable battery with an antiaromatic norcorrole Ni^{II} complex as a cathode-active material and a Li metal anode is described in the Communication by H. Yoshikawa, K. Awaga, H. Shinokubo and co-workers on page 3096 ff.





Metallofullerenes

K. Itami, H. Shinohara et al. describe in their Communication on page 3102 ff., a new strategy for the nonchromatographic extraction of metallofullerenes from solutions of arc-processed raw soot.



C–H Activation

In their Communication on page 3120 ff., Z. Li et al. describe the development of an enzyme by the directed evolution of terminal-selective P450pyr hydroxylase for the regio- and enantioselective subterminal hydroxylation of an alkane.

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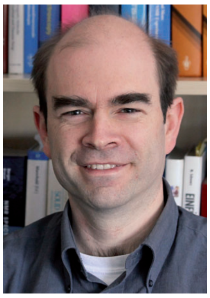


"I can never resist a piece of good chocolate. My favorite author (fiction) is Sir Arthur Conan Doyle ..." This and more about Burkhard Luy can be found on page 3058.

News

P. K. Chattaraj

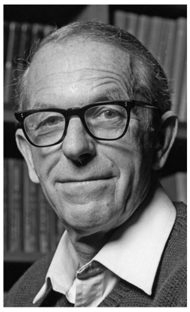
X.-M. Chen

S. Gao

M. Poliakoff

H. Tian

Obituaries



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Frederick (Fred) Sanger died on 19th November, 2013 aged 95. He is the only person to have been awarded two Nobel Prizes in Chemistry, in 1958 and 1980, for his development of methods for the sequencing of proteins and nucleic acids, respectively. He was a pivotal figure in 20th century science and the medical applications of what he made possible are only now beginning to be realized.

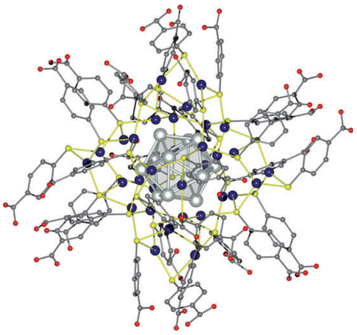
Books

Highlights

Cluster Compounds

A. Schnepf,* H. Schnöckel* **3064 – 3066**

Nanoscale Molecular Silver Cluster Compounds in Gram Quantities

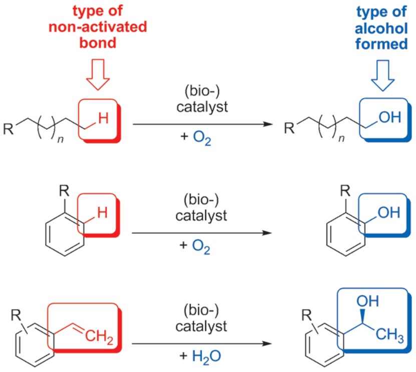


All that's nano is not gold: Definite, crystalline molecular compounds of noble metals have been known for gold for the last few years. Now a simple synthesis of a nanoscale silver cluster compound containing $[Ag_{44}(S\text{-}C_6H_4COOH)_{30}]^{4-}$ ions has been found leading to gram scales quantities. Synthetic, structural, and bonding aspects of this novel compound are discussed in the context of metalloid clusters in general.

Enzyme Catalysis

H. Gröger* **3067 – 3069**

Hydroxy Functionalization of Non-Activated C–H and C=C Bonds: New Perspectives for the Synthesis of Alcohols through Biocatalytic Processes



New perspectives through enzymes: Recent breakthroughs have been achieved in the selective hydroxy functionalization of non-activated C–H and C=C bonds. Enzymes turned out to be suitable catalysts for the ω-hydroxylation of (substituted) alkanes and regioselective hydroxylation of aromatic hydrocarbons with atmospheric oxygen as the oxidant, and the asymmetric addition of water to non-activated alkenes.

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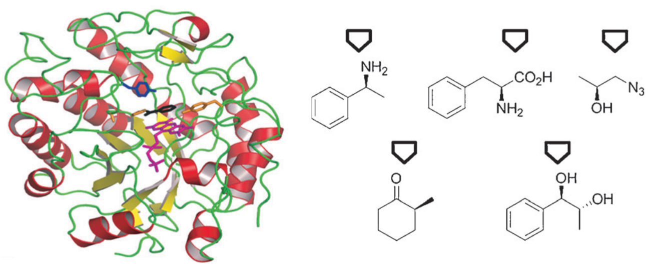
Reviews



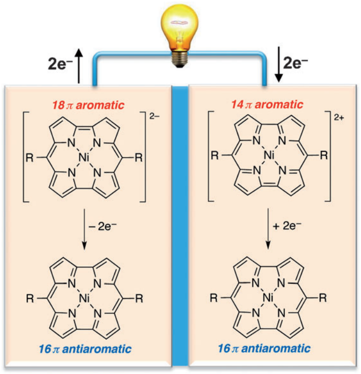
A dash of BIO-catalyst: A new generation of biocatalysts has entered modern organic synthesis. Recent advances in enzyme catalysis for the synthesis of challenging chemicals are presented in this Review.

Biocatalysis

B. M. Nestl, S. C. Hammer, B. A. Nebel,
B. Hauer* ______ **3070–3095**

New Generation of Biocatalysts for Organic Synthesis

Communications



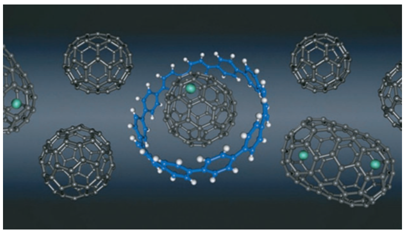
The balance of power: A discharge capacity of greater than 200 mA h g^{-1} over 100 charge/discharge cycles was found for a rechargeable battery with an antiaromatic norcorrole Ni^{II} complex (NiNC) as a cathode-active material and a Li metal anode. The bipolar redox property of NiNC also enabled the construction of a Li metal free rechargeable battery with high discharge capacity (see scheme) and good cycle performance.

Antiaromatic Batteries

J.-Y. Shin,* T. Yamada, H. Yoshikawa,*
K. Awaga,* H. Shinokubo* _ **3096–3101**

An Antiaromatic Electrode-Active Material Enabling High Capacity and Stable Performance of Rechargeable Batteries

Frontispiece



Complexation: A new strategy for the non-chromatographic extraction of metallofullerenes from solutions of arc-processed raw soot is based on the size-selective complexation with cycloparaphenylene (CPP). [11]CPP has a high affinity for $M_x@C_{82}$ ($x=1, 2$); for example, $Gd@C_{82}$ can be selectively extracted from a fullerene mixture by the addition of [11]CPP.

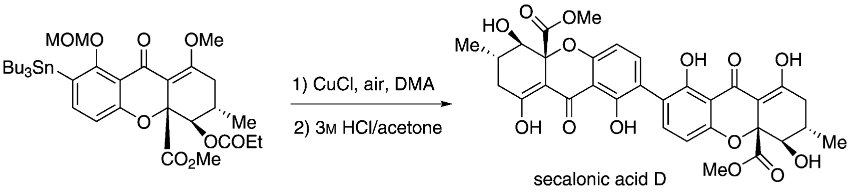
Metallofullerenes

Y. Nakanishi, H. Omachi, S. Matsuura,
Y. Miyata, R. Kitaura, Y. Segawa, K. Itami,*
H. Shinohara* ______ **3102–3106**

Size-Selective Complexation and Extraction of Endohedral Metallofullerenes with Cycloparaphenylene

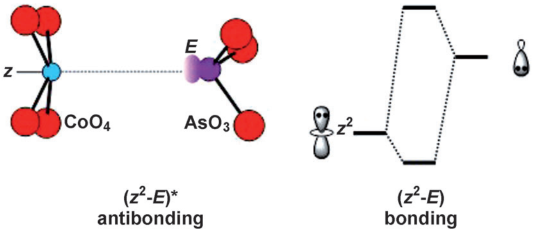
Inside Back Cover

Natural Product Synthesis



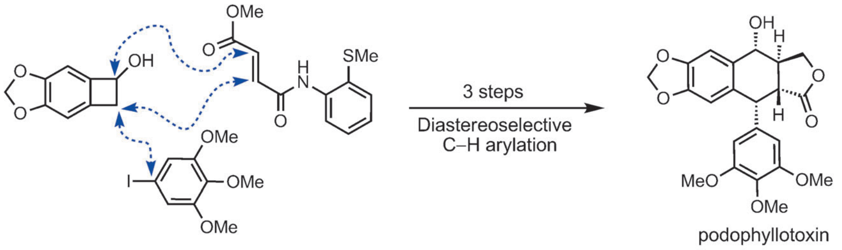
It takes two: Concise syntheses of the natural products secalonic acids A and D using copper(I)-mediated dimerization of complex aryl stannane monomers to construct the requisite 2,2′-biphenol linkage are reported. Highly efficient kinetic resolution of the monomeric tetrahydroxanthone core structures was achieved using homobenzotetramisole catalysis. DMA = *N*,*N*-dimethyl acetamide, MOM = methoxymethyl.

Square-Planar Cobalt(II)



As on a plane: $BaCoAs_2O_5$ exhibits nearly square-planar $Co^{2+}O_4$ units that possess direct Co^{2+}—As^{3+} bonds (2.51 Å). Owing to the high-spin character of the Co^{2+} ion, the As—Co bond is stabilized by a two-orbital three-electron interaction between the filled d_{z2} Co^{2+} orbital and the lone pair (*E*) of As^{3+}.

Total Synthesis

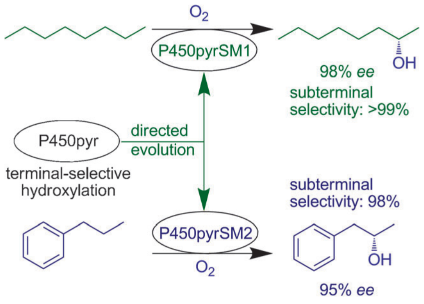


Testing a new tactic: In a concise synthesis of podophyllotoxin with a crucial palladium-catalyzed arylation step, subtle conformational effects govern reductive elimination pathways from the high-valent palladium center. This route to aryltetralin lignan derivatives may be of interest in drug discovery.

C—H activation

Back Cover

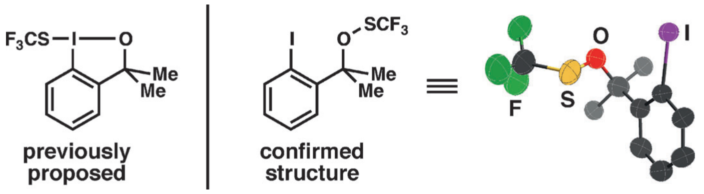
Get a handle on it: Highly regio- and enantioselective subterminal hydroxylation of *n*-octane and propylbenzene was observed with P450 enzymes obtained by the directed evolution of terminal-selective P450pyr hydroxylase (see scheme). The engineered enzymes with their fully altered selectivities are useful for the functionalization of alkanes and the preparation of enantiomerically pure alcohols.



Hypervalent Iodine Reagents

E. V. Vinogradova, P. Müller,
S. L. Buchwald* ——— 3125 – 3128

Structural Reevaluation of the Electrophilic Hypervalent Iodine Reagent for Trifluoromethylthiolation Supported by the Crystalline Sponge Method for X-ray Analysis



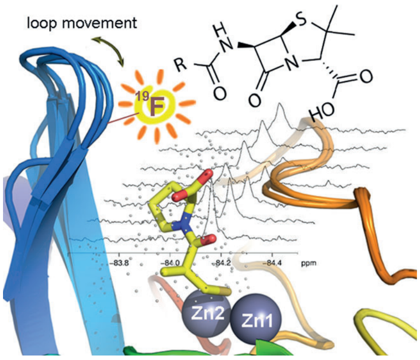
Not-so-hypervalent iodine: Studies of several benziodoxole thiolate derivatives revealed that these species lack the hypervalent iodine motif, instead adopting a thioperoxide configuration. Crystallographic analysis of a liquid trifluoromethylthiolation reagent trapped inside a metal–organic framework provided direct structural proof for the observed phenomenon. These thioperoxide reagents were also shown to be reactive in electrophilic substitution reactions.

Metallo-β-lactamases

A. M. Rydzik, J. Brem, S. S. van Berkel,
I. Pfeffer, A. Makena, T. D. W. Claridge,*
C. J. Schofield* ——— 3129 – 3133

Monitoring Conformational Changes in the NDM-1 Metallo-β-lactamase by ^{19}F NMR Spectroscopy

Front Cover



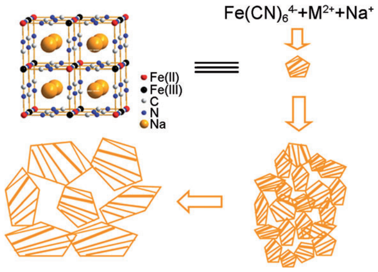
^{19}Follow the moves: ^{19}F NMR spectroscopy is used to monitor active-site loop movements in the New Delhi metallo-β-lactamase (NDM-1) following site-selective cysteine S-alkylation with CH_2COCF_3. The method discriminates between types of inhibition and enables determination of binding constants and will be useful in identifying inhibitors of clinically important metallo-β-lactamases.

Porous Materials

Y. Yue, A. J. Binder, B. Guo,* Z. Zhang,
Z.-A. Qiao, C. Tian, S. Dai* 3134 – 3137

Mesoporous Prussian Blue Analogues: Template-Free Synthesis and Sodium-Ion Battery Applications

Blue, blue, electric blue: Porous Prussian blue analogues with tailorable surface area and pore structure were synthesized through a facile template-free method at room temperature. This methodology could provide an alternative to the hard or soft templating methods for fabricating crystalline mesoporous materials. As cathodes for sodium-ion batteries, these porous Prussian blue analogues showed reversible capacity and excellent cycle stability.

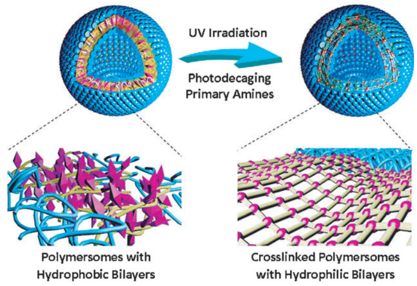


Polymersomes

X. Wang, G. Liu, J. Hu, G. Zhang,
S. Liu* ——— 3138 – 3142

Concurrent Block Copolymer Polymersome Stabilization and Bilayer Permeabilization by Stimuli-Regulated "Traceless" Crosslinking

Two processes in one: A stimuli-triggered crosslinking strategy was developed to concurrently crosslink and permeabilize block copolymer assemblies. Upon self-assembling into polymersomes (see picture), light-triggered self-immolative decaging reactions release primary amine moieties and lead to extensive amidation reactions.

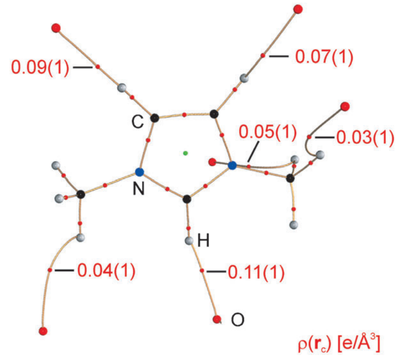


VIP

Ionic Liquids

W. Beichel, N. Trapp, C. Hauf, O. Kohler,
G. Eickerling, W. Scherer,*
I. Krossing* ______ 3143 – 3146

Charge-Scaling Effect in Ionic Liquids from the Charge-Density Analysis of *N*,*N*′-Dimethylimidazolium Methylsulfate

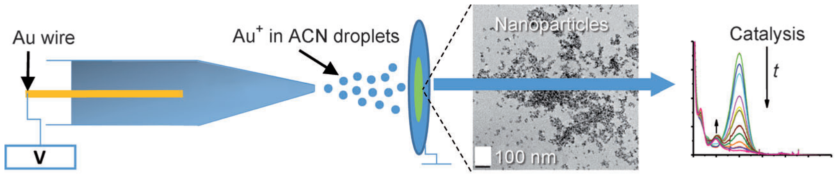


In charge? The (down-)scaling of partial charges in non-polarizable force fields is commonly applied for the simulation of ionic liquids. Analyses of charge densities, employing the quantum theory of atoms in molecules, on the prototype ionic liquid [C_1MIM][C_1SO_4] are shown to provide an experimental justification for such a treatment.

Nanoparticles by Spray Ionization

A. Li, Q. Luo, S. Park,
R. G. Cooks* ______ 3147 – 3150

Synthesis and Catalytic Reactions of Nanoparticles formed by Electrospray Ionization of Coinage Metals



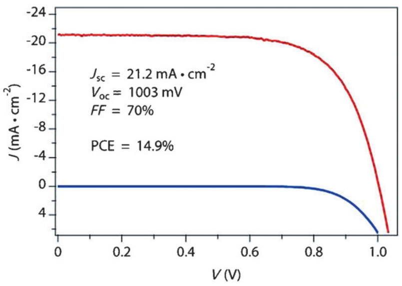
High catalytic activity: Copper, silver, and gold solids are ionized to the +1 oxidation state ions by electrospray in acetonitrile (ACN) as an anhydrous organic solvent. Collection of the solvated ions leads to formation of nanoparticles that serve as catalysts for bulk reactions, for example the reduction of *p*-nitrophenol by $NaBH_4$.

Perovskite Solar Cells

N. Pellet, P. Gao, G. Gregori, T.-Y. Yang,
M. K. Nazeeruddin, J. Maier,
M. Grätzel* ______ 3151 – 3157

Mixed-Organic-Cation Perovskite Photovoltaics for Enhanced Solar-Light Harvesting

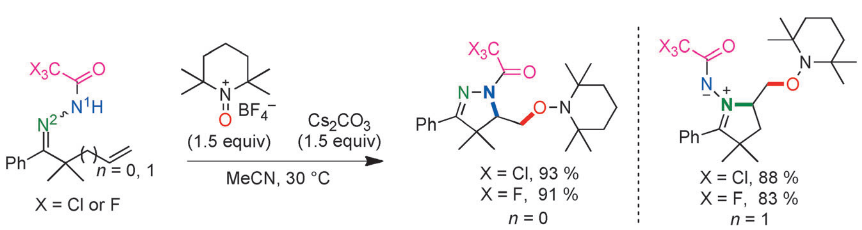
A productive partnership: Perovskite solar devices with mixed organic cations could outperform the standard methylammonium lead iodide pigment owing to extended light absorption and a higher carrier-diffusion length. Thus, the best optoelectronic features of methylammonium and formamidinium cations were combined in a perovskite solar cell with a striking 14.9% power-conversion efficiency (red curve: in simulated sunlight; blue curve: in the dark).



Radical Cyclization

X.-Y. Duan, N.-N. Zhou, R. Fang,
X.-L. Yang, W. Yu, B. Han* _ 3158 – 3162

Transition from π Radicals to σ Radicals: Substituent-Tuned Cyclization of Hydrazonyl Radicals

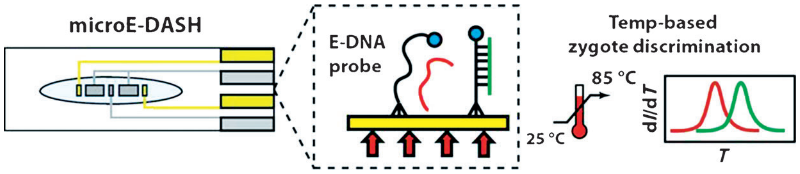


Time for a radical career change? Known for their π character, hydrazonyl radicals can be tuned to act as σ radicals with the spin density delocalized on both nitrogen atoms by attaching a trifluoroacetyl or trichloroacetyl group to the N^1 atom. The hydrazonyl σ radicals derived from the corresponding *N*-acyl-substituted β,γ- and γ,δ-unsaturated hydrazones underwent $C-N^1$ and $C-N^2$ bond-forming 5-*exo*-trig cyclization, respectively (see scheme).

Molecular Diagnostics

A. H. J. Yang, K. Hsieh, A. S. Patterson,
B. S. Ferguson, M. Eisenstein,
K. W. Plaxco, H. T. Soh* ____ 3163 – 3167

Accurate Zygote-Specific Discrimination of Single-Nucleotide Polymorphisms Using Microfluidic Electrochemical DNA Melting Curves

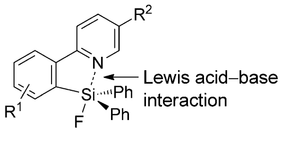


Rapid DNA identification: A novel microfluidic electrochemical system for the detection of single-nucleotide polymorphisms (SNPs) uses surface-immobilized DNA probes to accurately discriminate homozygous and heterozygous genotypes using real-time melting-curve analysis. Two clinically relevant SNPs in the apolipoprotein E gene were characterized and all six possible *ApoE* allele combinations were distinguished.

Fluorescent Heterocycles

Q. Xiao, X. Meng, M. Kanai,*
Y. Kuninobu* ____ 3168 – 3172

Palladium-Catalyzed C—H Fluorosilylation of 2-Phenylpyridines: Synthesis of Silafluorene Equivalents



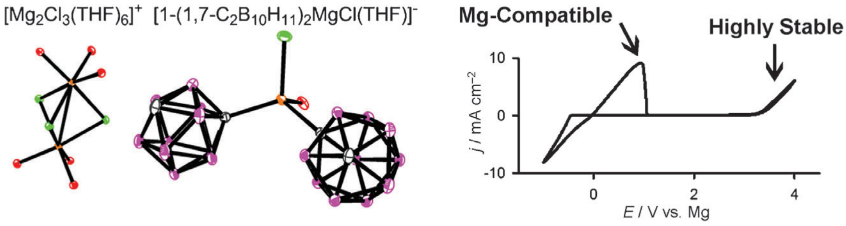
silafluorene equivalent

Treatment of 2-phenylpyridines with amino(1,3,2-dioxaborolan-2-yl)diphenylsilane produced fluorosilylated 2-phenylpyridines in good to excellent yields under palladium catalysis. This reaction is the first example of C—H fluorosilylation. A Lewis acid–base interaction exists between the silicon and nitrogen atoms, and the obtained fluorosilylated products can be regarded as silafluorene equivalents.

Magnesium Batteries

T. J. Carter, R. Mohtadi,* T. S. Arthur,
F. Mizuno, R. Zhang, S. Shirai,
J. W. Kampf ____ 3173 – 3177

Boron Clusters as Highly Stable Magnesium-Battery Electrolytes

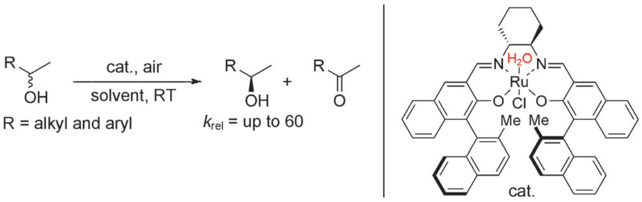


A b(o)rilliant improvement: An electrolyte incorporating an unprecedented magnesium-centered complex anion was developed for use in rechargeable magnesium batteries. The carboranyl magnesium halide (see structure; B purple, Cl green, O red, C white, Mg orange) exhibited compatibility with magnesium-metal anodes as well as remarkable oxidative stability (3.2 V vs. Mg) on non-noble-metal electrodes.

Kinetic Resolution

H. Mizoguchi, T. Uchida,
T. Katsuki* ____ 3178 – 3182

Ruthenium-Catalyzed Oxidative Kinetic Resolution of Unactivated and Activated Secondary Alcohols with Air as the Hydrogen Acceptor at Room Temperature

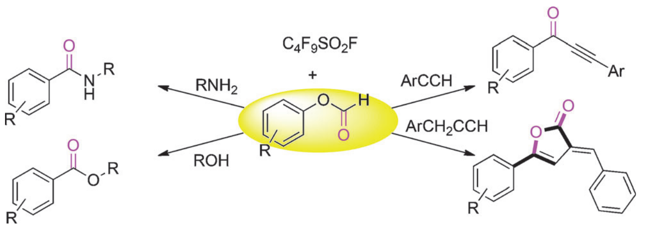


Alcohol resolution: An (aqua)ruthenium salen complex catalyzes the efficient oxidative kinetic resolution of both activated and unactivated secondary alcohols with air as the hydrogen acceptor at room temperature. The reaction is compatible with various functional groups, including halogen, ether, silyl ether, and ester groups. The reaction rate is lower at higher substrate concentrations as a result of substrate inhibition.

Cross-Coupling

H. Li, H. Neumann, M. Beller,*
X.-F. Wu* ——— 3183 – 3186

Aryl Formate as Bifunctional Reagent: Applications in Palladium-Catalyzed Carbonylative Coupling Reactions Using In Situ Generated CO

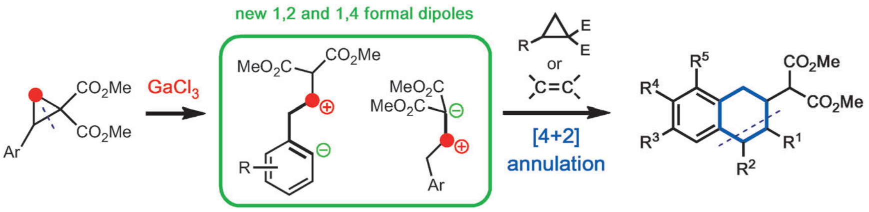


Transformers: A versatile and practical protocol for carbonylation reactions involve the cooperation of phenyl formate and nonaflate with generation of CO in situ. This protocol has a high functional-group tolerance and could be applied in carbonylative couplings with C, N, and O nucleophiles. The corresponding amides, alkynones, furanones, and aryl benzoates were synthesized in good yield.

Carbocycles

R. A. Novikov, A. V. Tarasova,
V. A. Korolev, V. P. Timofeev,
Y. V. Tomilov* ——— 3187 – 3191

A New Type of Donor–Acceptor Cyclopropane Reactivity: The Generation of Formal 1,2- and 1,4-Dipoles

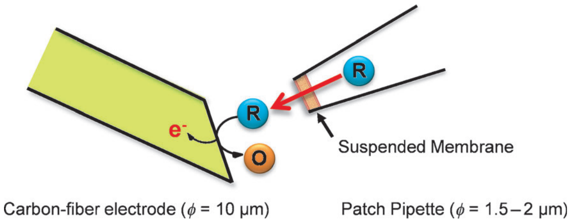


Old ring, new reactivity: A new type of donor–acceptor cyclopropane reactivity has been discovered. On treatment with anhydrous $GaCl_3$, they react as sources of even-numbered 1,2- and 1,4-dipoles instead of the classical odd-numbered 1,3-dipoles owing to the migration of positive charge from the benzyl center.

Lipid Membranes

P. Messina, F. Lemaître, F. Huet,
K. A. Ngo, V. Vivier, E. Labbé, O. Buriez,*
C. Amatore* ——— 3192 – 3196

Monitoring and Quantifying the Passive Transport of Molecules Through Patch–Clamp Suspended Real and Model Cell Membranes

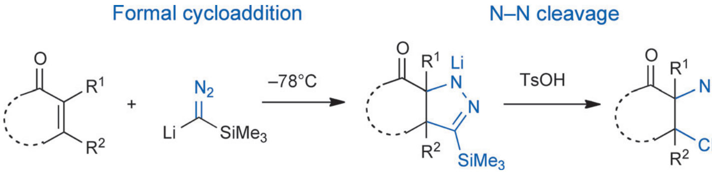


More than patched up: Electrochemical detection of molecular species crossing suspended membranes is possible by a novel integration of patch–clamp and amperometry. This approach provides a powerful means for quantifying, in real time, fluxes of molecular species across real cell and artificial membranes.

Aminocyanation

C. Sun, M. J. O'Connor, D. Lee,*
D. J. Wink, R. D. Milligan — 3197 – 3200

Formal Aminocyanation of α,β-Unsaturated Cyclic Enones for the Efficient Synthesis of α-Amino Ketones

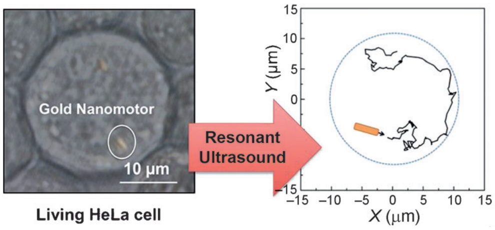


Make and break: 1,2-Aminocyanation was achieved through a formal dipolar cycloaddition of cyclic α,β-unsaturated ketones with lithium trimethylsilyldiazomethane to generate pyrazoline followed by protonolytic N–N bond cleavage. This reaction provides an efficient method for the synthesis of a diverse array of structurally complex and novel α-amino ketones.

Nanomotors

W. Wang, S. Li, L. Mair, S. Ahmed,
T. J. Huang,* T. E. Mallouk* **3201 – 3204**

Acoustic Propulsion of Nanorod Motors Inside Living Cells

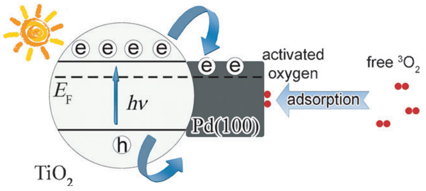


Ultrasonic propulsion: Metallic nanomotors can be internalized by incubation with HeLa cells for periods longer than 24 h (see picture). Once inside the cells, the nanomotors can be activated by resonant ultrasound operating at 4 MHz, and show axial propulsion as well as spinning. The HeLa cells remain viable.

Catalytic Materials

R. Long, K. Mao, M. Gong, S. Zhou, J. Hu,
M. Zhi, Y. You, S. Bai, J. Jiang, Q. Zhang,*
X. Wu,* Y. Xiong* **3205 – 3209**

Tunable Oxygen Activation for Catalytic Organic Oxidation: Schottky Junction versus Plasmonic Effects

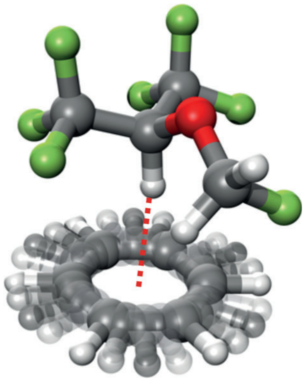


All things in moderation: The charge state of the Pd surface is critical to the ability of Pd nanocrystals to promote oxygen activation (see picture). Thus, the catalytic efficiency of Pd nanocrystals in organic oxidation reactions can be tuned by simply varying the intensity of light shed on palladium–semiconductor hybrid structures. Under strong illumination, a plasmonic effect may cause the reverse migration of electrons from Pd to TiO_2.

Weak Hydrogen Bonds

N. A. Seifert, D. P. Zaleski, C. Pérez,
J. L. Neill, B. H. Pate,* M. Vallejo-López,
A. Lesarri,* E. J. Cocinero, F. Castaño,
I. Kleiner **3210 – 3213**

Probing the C−H⋯π Weak Hydrogen Bond in Anesthetic Binding: The Sevoflurane–Benzene Cluster

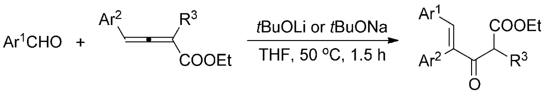


Cooperation is force: The cooperativity between a primary C−H⋯π hydrogen bond and multiple C−H⋯F weak interactions defines the dynamic nonbonding union between sevoflurane and benzene. The structure and internal rotation was determined with broadband rotational spectroscopy.

Synthetic Methods

M. Wang, Z. Fang, C. Fu,
S. Ma* **3214 – 3217**

Metal Alkoxide Promoted Regio- and Stereoselective C=O and C=C Metathesis of Allenoates with Aldehydes



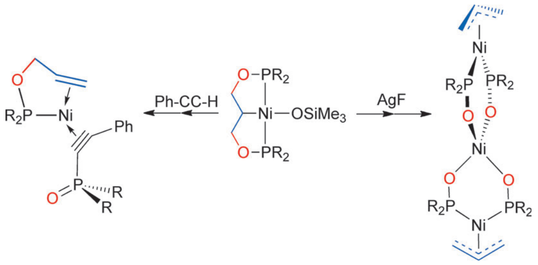
1

All’ene’ all: The reaction of aldehydes with 2,3-allenoates in the presence of *t*BuOM (M = Li or Na) affords the stereodefined, highly functionalized γ,δ-unsaturated β-ketoesters **1** in good to excellent yields with *E* stereoselectivity. The reactivity of 5-hydroxy-2,3-allenoates and the isolation of 3,4-diaryloxetanes led to a rationale for the mechanism of the reaction.

Quasi-Stable Pincer Ligands

J. Hao, B. Mougang-Soumé, B. Vabre,
D. Zargarian* ________ 3218 – 3222

On the Stability of a POC$_{sp3}$OP-Type Pincer Ligand in Nickel(II) Complexes

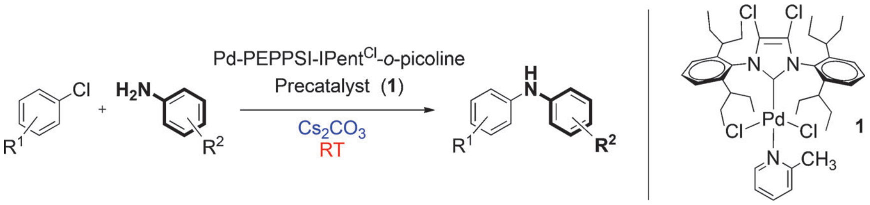


Survival of the fittest: One or both of the C–O linkages in the complex [(POC$_{sp3}$-OP)Ni(OSiMe$_3$)] break under fairly mild conditions to generate unprecedented mono- and trinuclear species. These decomposition processes can serve as models for predicting the stabilities of these complexes in catalytic settings.

Amination

M. Pompeo, J. L. Farmer, R. D. J. Froese,
M. G. Organ* ________ 3223 – 3226

Room-Temperature Amination of Deactivated Aniline and Aryl Halide Partners with Carbonate Base Using a Pd-PEPPSI-IPent^{Cl}-*o*-Picoline Catalyst

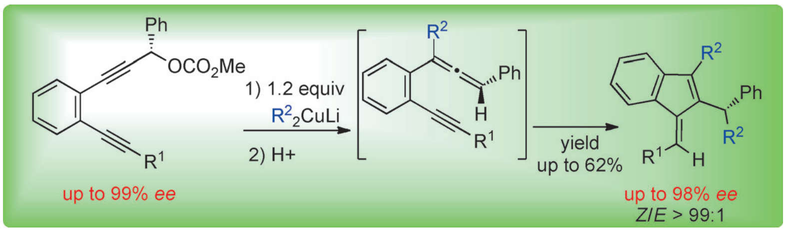


Running mild: An N-heterocyclic carbene complex of palladium (**1**) was systematically designed to enable the amination of strongly deactivated substrates (R^1 can be strongly electron donating, R^2 can be strongly electron-withdrawing) when using the most mild of bases (carbonate) at room temperature. This catalyst was used to produce elaborate, richly functionalized products for use in life-, health-, and material-science applications.

Synthetic Methods

D. Campolo, T. Arif, C. Borie, D. Mouysset,
N. Vanthuyne J.-V. Naubron,
M. P. Bertrand,*
M. Nechab* ________ 3227 – 3231

Double Transfer of Chirality in Organocopper-Mediated bis(Alkylating) Cycloisomerization of Enediynes

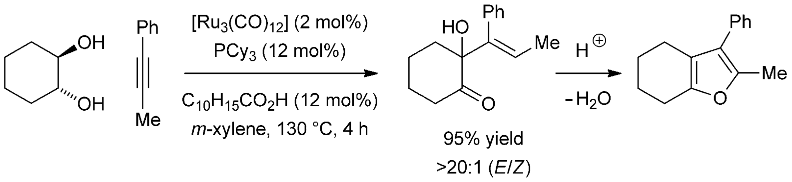


Double duty: An original synthesis of chiral benzofulvenes was developed through the highly chemo-, regio-, diastereo-, and enantioselective double transfer of alkyl groups to electrophilic enediynes. This organocopper-triggered cycloisomerization proceeds with double transfer of chirality (central-to-axial-to-central).

C–C Coupling

E. L. McInturff, K. D. Nguyen,
M. J. Krische* ________ 3232 – 3235

Redox-Triggered C–C Coupling of Diols and Alkynes: Synthesis of β,γ-Unsaturated α-Hydroxyketones and Furans by Ruthenium-Catalyzed Hydrohydroxyalkylation

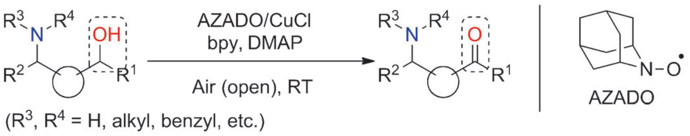


More alcohol, more fun: Diols and alkynes engage in ruthenium(0)-catalyzed hydrohydroxyalkylation to form β,γ-unsaturated ketones with good to complete levels of regioselectivity and control of alkene geometry. Exposure of the reaction products to *p*-toluenesulfonic acid results in cyclodehydration to form tetrasubstituted furans.

Chemoselectivity

Y. Sasano, S. Nagasawa, M. Yamazaki,
M. Shibuya, J. Park,
Y. Iwabuchi* ——— **3236 – 3240**

Highly Chemoselective Aerobic Oxidation of Amino Alcohols into Amino Carbonyl Compounds

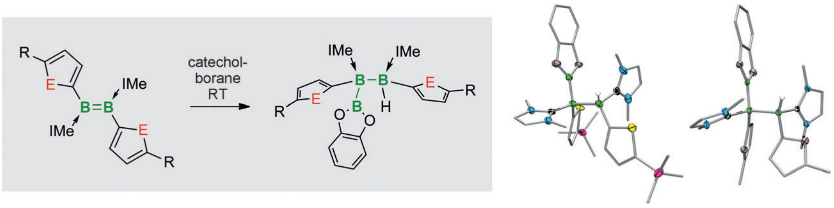


Strong as an ox: The highly chemoselective aerobic oxidation of unprotected amino alcohols to their corresponding amino carbonyl compounds has been achieved by using 2-azaadamantane *N*-oxyl (AZADO)/copper catalysis. This catalytic system oxidizes not only alcohols with tertiary amino groups but also those with secondary and primary amines in good to high yield at ambient temperature in air. bpy = 2,2-bipyridyl, DMAP = 4-(*N*,*N*-dimethylamino)pyridine.

Hydroboration

H. Braunschweig,* R. D. Dewhurst,
C. Hörl, A. K. Phukan, F. Pinzner,
S. Ullrich ——— **3241 – 3244**

Direct Hydroboration of B=B Bonds: A Mild Strategy for the Proliferation of B–B Bonds

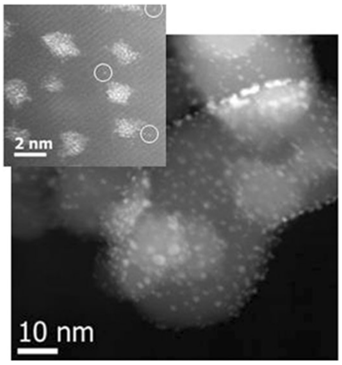


H. C. Brown meets diborenes: The few existing strategies for the construction of electron-precise boron chains involve either strongly reducing reagents or transition-metal catalysts; both have distinct disadvantages. Thus, the direct hydroboration of diborenes to form new B–B bonds and B_3 chains is presented. The reaction is diastereoselective and proceeds under mild conditions without the use of strong reducing agents or transition-metal catalysts. IMe = 1,3-dimethylimidazol-2-ylidene; E = O, S.

Heterogeneous Catalysis

W. Grünert,* D. Großmann, H. Noei,
M.-M. Pohl, I. Sinev, A. De Toni, Y. Wang,
M. Muhler ——— **3245 – 3249**

Low-Temperature Oxidation of Carbon Monoxide with Gold(III) Ions Supported on Titanium Oxide

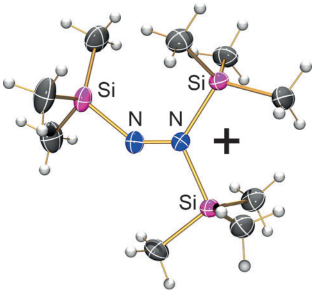


Ionic or metallic: Au^{3+} ions on TiO_2 (see HAADF-STEM image of a freshly prepared sample) can catalyze the oxidation of CO at low temperatures. The reaction rates at Au^{3+}-containing centers are similar to those found at metallic gold clusters. However, the apparent activation energies are very low, which is probably due to the opposing influence of the true activation energy and the adsorption enthalpy of CO on Au^{3+} centers.

Diazenium Ions

W. Baumann, D. Michalik, F. Reiß,
A. Schulz,* A. Villinger* ——— **3250 – 3253**

Isolation of a Labile Homoleptic Diazenium Cation



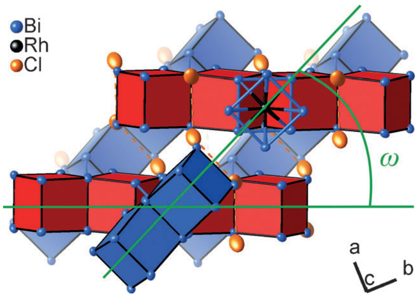
Cold, blue, and positive: The first homoleptic diazenium cation has been formed by treating mercury(II) dihydrazide with $Ag[GaCl_4]$ at low temperature. While numerous attempts at the direct silylation of diazene failed, this alternative new two-electron oxidation of the trisilylated hydrazide ion affords blue, highly labile $[(Me_3Si)_2N{=}N\text{-}SiMe_3]^+$ ions in almost quantitative yield.

Topochemistry

M. Kaiser, B. Rasche,
M. Ruck* ______________ 3254 – 3258

The Topochemical Pseudomorphosis of a Chloride into a Bismuthide

Inside Cover

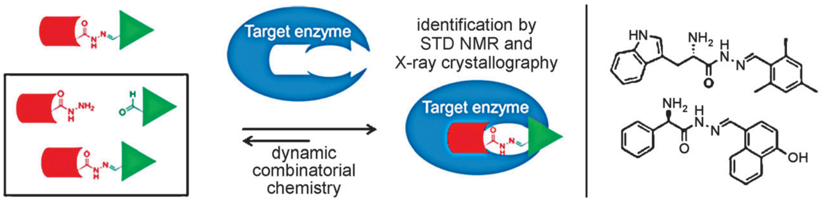


Breathe in: In the dense structure of $Bi_{12}Rh_3Cl_2$, chloride ions are replaced by bismuth atoms in the course of a heterogeneous topochemical reaction. The vast mass transport through the crystal at only 70 °C is enabled by a breathing mode of the intermetallic framework, which opens diffusion paths by varying the inclination ω (see picture). The complete exchange yields the metastable superconductor $Bi_{12}Rh_3Bi_2$.

Enzyme Inhibitors

M. Mondal, N. Radeva, H. Köster, A. Park,
C. Potamitis, M. Zervou, G. Klebe,*
A. K. H. Hirsch* ______________ 3259 – 3263

Structure-Based Design of Inhibitors of the Aspartic Protease Endothiapepsin by Exploiting Dynamic Combinatorial Chemistry



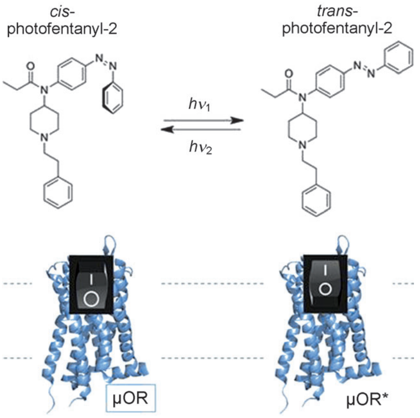
The dynamic duo: The combination of de novo structure-based design and dynamic combinatorial chemistry has been applied to the identification of novel acylhydrazone-based inhibitors for the aspartic protease endothiapepsin. ^{1}H-STD-NMR spectroscopy has been used to identify the binders from the dynamic combinatorial libraries. Proposed binding modes of the most potent inhibitors have been confirmed by X-ray crystallography.

Photopharmacology

M. Schönberger,
D. Trauner* ______________ 3264 – 3267

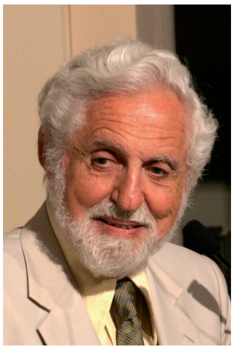
A Photochromic Agonist for μ-Opioid Receptors

Lighting up the opioid receptor: Photofentanyl-2 is a photochromic version of the well-known analgesic fentanyl. It is a potent agonist in the dark (or when illuminated with blue light) and loses activity when irradiated with UV light. It can be used to optically control the μ-opioid receptor, converting a G-protein-coupled receptor (GPCR) into a photoreceptor.



And Finally

In honor of the 90th birthday of Professor Carl Djerassi, J. I. Seeman has assembled a collection of poignant quotes and excerpts from Djerassi's writings which embody his remarkable life experiences, his philosophies of life, and his unique personality.



Carl Djerassi

J. I. Seeman* ______ **3268 – 3279**

Carl Djerassi: In His Own Words

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 Addendum

The authors of this Communication on the analysis of HK97 capsid particles by native electrospray mass spectrometry have been made aware that capsid particles of HK97 have been analyzed before by using cryodetection MALDI TOF mass spectrometry. The authors are happy to direct the readers to this study.[1]

Studying 18 MDa Virus Assemblies with Native Mass Spectrometry

J. Snijder, R. J. Rose, D. Veesler,
J. E. Johnson, A. J. R. Heck* **4020–4023**

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

DOI: 10.1002/anie.201210197

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[1] D. M. Sipe, A. Ozdemir, B. Firek, R. W. Hendrix, M. E. Bier, *Analysis of Viral Capsid HK97 via Cryodetection MALDI TOF in the MegaDalton Mass Range*, 56th ASMS Conference on Mass Spectrometry and Allied Topics, Denver, CO, USA, 1–5 June, **2008**. # 571.