

Spotlight on Angewandte's Sister Journals

8922 – 8924

Service

Author Profile



"When I was eighteen I wanted to be a chemical engineer. Looking back over my career, I am hopeful, based on the progress achieved so far, that molecular sieve films will become a widespread energy-efficient separation technology. ..."

This and more about Michael Tsapatsis can be found on page 8926.

Michael Tsapatsis _____ 8926

News



R. W. Hoffmann



J. Pérez-Ramírez



G. Hutchings



T. Tatsumi

Honorary Doctorate:
R. W. Hoffmann _____ 8927

Otto Roelen Medal:
J. Pérez-Ramírez _____ 8927

Alwin Mittasch Prize:
G. Hutchings and T. Tatsumi _____ 8927

Obituaries



Thomas Kauffmann (1924–2012)

The Kauffmann olefination for the transformation of keto groups with alkyl tungsten complexes into vinyl groups and the Kauffmann dimerization of organic groups by transfer to copper halides with subsequent thermolysis or oxidation are linked with Thomas Kauffmann, Emeritus Professor at the University of Münster, who passed away in February 2012.

H. J. Schäfer* _____ 8928

Books

Introduction to Strategies for Organic Synthesis

Laurie S. Starkey

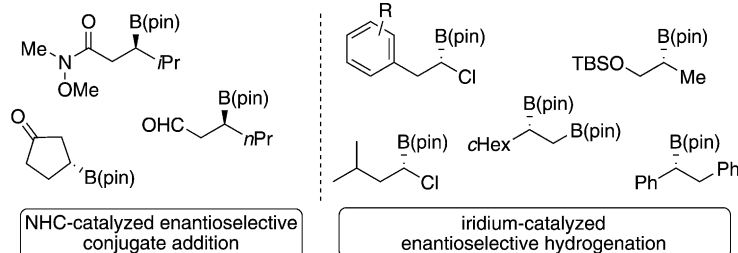
reviewed by M. Rizzacasa _____ 8929

Highlights

Asymmetric Catalysis

J. A. Bull* — 8930–8932

Catalytic Enantioselective Synthesis of Secondary Alkylboronate Building Blocks With and Without Metals



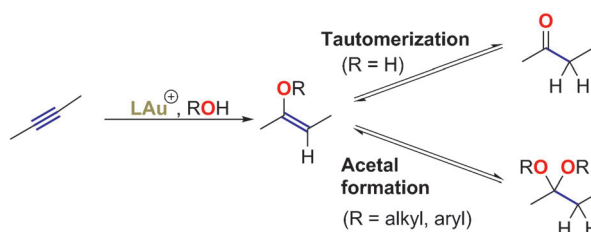
With or without you: Chiral secondary alkylboronates can now be accessed by highly enantioselective catalytic methods including conjugate addition under metal-free conditions with an NHC catalyst, and

also iridium-catalyzed hydrogenation. These methods reinforce the potential of secondary alkylboronates as ideal and universal chiral building blocks for bond formation to sp^3 carbon atoms.

Homogeneous Catalysis

W. E. Brenzovich, Jr.* — 8933–8935

Gold in Total Synthesis: Alkynes as Carbonyl Surrogates



Fields of gold: Recent developments in the field of gold catalysis, using an alkyne as a carbonyl equivalent is becoming an important chemical transformation, thus providing flexibility in synthetic planning

of complex and sensitive natural products. Understanding of the reaction and new catalyst designs are providing new conditions that are amenable for late-stage synthetic intermediates.

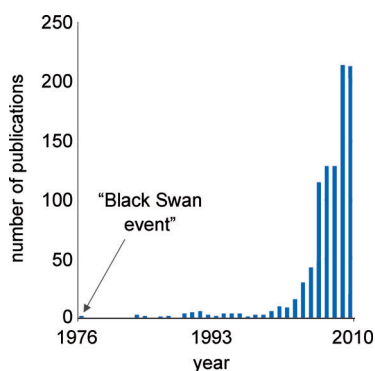
Essays

Organic Synthesis

W. A. Nugent* — 8936–8949



“Black Swan Events” in Organic Synthesis



When a research area “goes viral”, the event typically occurs in conjunction with a major change in “conventional wisdom”. In retrospect, the literature often contains earlier hints that the original judgment was not correct. These antecedents are referred to as “Black Swan” events. The picture shows research on homogeneous gold catalysis “going viral”.

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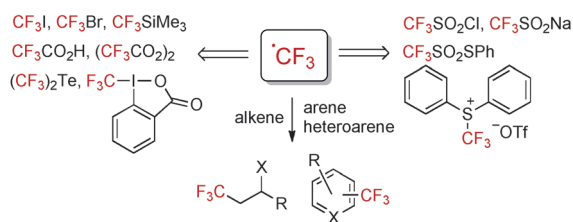
postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Journal Customer Services, John Wiley & Sons Inc., 350 Main St., Malden, MA 02148-5020. Annual subscription price for institutions: US\$ 11,738/10,206 (valid for print and electronic / print or electronic delivery); 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.

Minireviews

Trifluoromethylation

A. Studer* _____ 8950–8958

A “Renaissance” in Radical
Trifluoromethylation


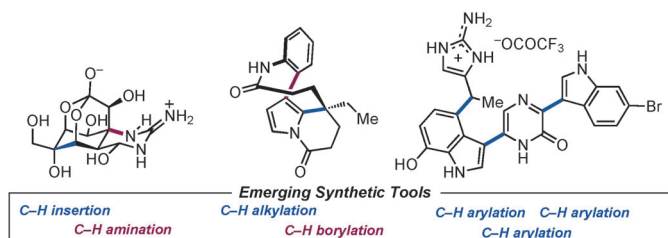
A **privileged moiety**, the CF₃ substituent can be found in many drugs, drug candidates, and agrochemicals. This Minireview highlights recent developments in

the radical trifluoromethylation of alkenes and arenes. Important older contributions are also discussed.

Reviews

Synthetic Strategy

J. Yamaguchi,* A. D. Yamaguchi,
K. Itami* _____ 8960–9009

C–H Bond Functionalization: Emerging
Synthetic Tools for Natural Products and
Pharmaceuticals


The ideal case: The direct functionalization of C–H bonds in organic compounds has recently emerged as a powerful and ideal method for the formation of carbon–carbon and carbon–heteroatom bonds.

This Review provides an overview of C–H functionalization strategies for the rapid synthesis of biologically active compounds such as natural products and pharmaceutical targets.

Front Cover



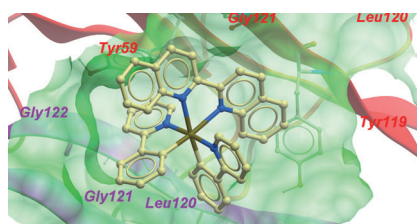
Communications

Bioorganometallic Chemistry

C.-H. Leung,* H.-J. Zhong, H. Yang,
Z. Cheng, D. S.-H. Chan, V. P.-Y. Ma,
R. Abagyan, C.-Y. Wong,
D.-L. Ma* _____ 9010–9014

A Metal-Based Inhibitor of Tumor
Necrosis Factor- α

Staying in the pocket: A cyclometalated iridium(III) biquinoline complex targets the protein–protein interface (see picture; C yellow, N blue, Ir dark green) of the tumor necrosis factor- α (TNF- α) trimer. Molecular-modeling studies confirm the nature of this interaction. Both enantiomers of the iridium complex display comparable in vitro potency to the strongest small-molecule inhibitor of TNF- α .



Frontispiece



The German Chemical Society (GDCh) invites you to:



Angewandte Anniversary Symposium

GDCh
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Tuesday, March 12, 2013

Henry Ford Building / FU Berlin

Speakers



Carolyn R.
Bertozzi



François
Diederich



Alois
Fürstner



Roald Hoffmann
(Nobel Prize 1981)



Susumu
Kitagawa



Jean-Marie Lehn
(Nobel Prize 1987)



E.W. "Bert"
Meijer



Frank
Schirmacher
(Publisher, FAZ)



Robert
Schlögl



George M.
Whitesides



Ahmed Zewail
(Nobel Prize 1999)

More information:

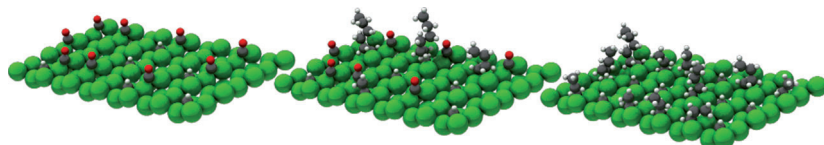


angewandte.org/symposium



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Long carbon chains: Self-assembly of monomeric carbon intermediates into long-chain hydrocarbons on catalytically reactive surface (see picture) was studied when full reversibility of the chain growth

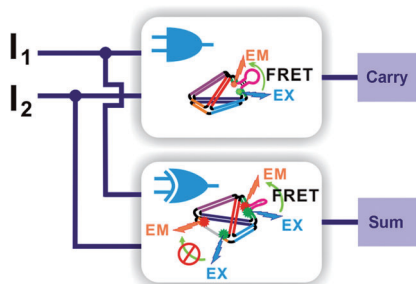
is included in the kinetic model. Using Brønsted–Evans–Polanyi relations, the maximum chain growth as a function of the surface reactivity is predicted.

Heterogeneous Catalysis

A. J. Markvoort,* R. A. van Santen,
P. A. J. Hilbers,
E. J. M. Hensen _____ 9015–9019

Kinetics of the Fischer–Tropsch Reaction

Inside Cover



Right out of the (logic) gate: Logic gates made from 3D DNA nanotetrahedra were constructed that are responsive to various ions, small molecules, and short strands of DNA. By including dynamic sequences in one or more edges of the tetrahedra, a FRET signal can be generated in the manner of AND, OR, XOR, and INH logic gates, as well as a half-adder circuit (see scheme). These DNA logic gates were also applied to intracellular detection of ATP.

DNA Computing

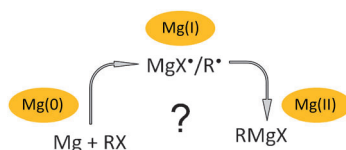
H. Pei, L. Liang, G. Yao, J. Li, Q. Huang,
C. Fan* _____ 9020–9024

Reconfigurable Three-Dimensional DNA Nanostructures for the Construction of Intracellular Logic Sensors

Inside Back Cover



Magnesium bromide radicals have to be prepared as high-temperature molecules and trapped as a metastable solution because a seemingly simple reduction of donor-free Grignard compounds failed. However, the essential role of magnesium(I) species during the formation of Grignard compounds could be demonstrated experimentally.



Radical Reactions

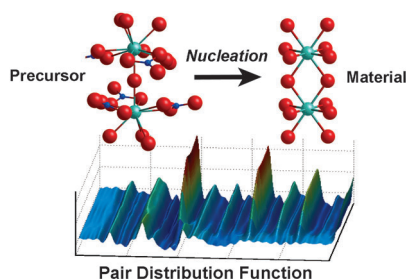
T. Kruczyński, N. Pushkarevsky, P. Henke,
R. Köppe, E. Baum, S. Konchenko,
J. Pikies, H. Schnöckel* _____ 9025–9029

Hunting for the Magnesium(I) Species: Formation, Structure, and Reactivity of some Donor-Free Grignard Compounds

Back Cover



Supercritical growth: The formation and evolution of ceria nanoparticles during hydrothermal synthesis was investigated by in situ total scattering and powder diffraction. The nucleation of pristine crystalline ceria nanoparticles originated from previously unknown cerium dimer complexes. The nanoparticle growth was highly accelerated under supercritical conditions.



Crystal Growth

C. Tyrsted, K. M. Ørnsbjerg Jensen,
E. D. Bøjesen, N. Lock, M. Christensen,
S. J. L. Billinge,
B. Brummerstedt Iversen* _____ 9030–9033

Understanding the Formation and Evolution of Ceria Nanoparticles Under Hydrothermal Conditions



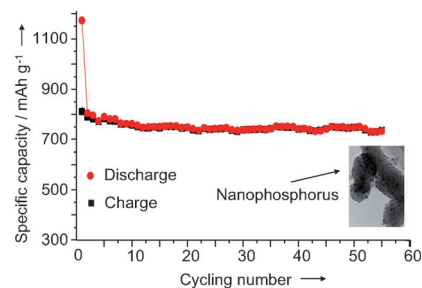
Lithium Batteries

L. Wang, X. M. He,* J. J. Li, W. T. Sun,
J. Gao, J. W. Guo, C. Y. Jiang **9034–9037**



Nano-Structured Phosphorus Composite
as High-Capacity Anode Materials for
Lithium Batteries

More than LiP service: The adsorption of red phosphorus into porous carbon provides a composite anode material for lithium-ion batteries. The amorphous nano phosphorus, in the carbon matrix, shows highly reversible lithium storage with high coulombic efficiencies and stable cycling capacity of 750 mAh per gram composite (see picture).



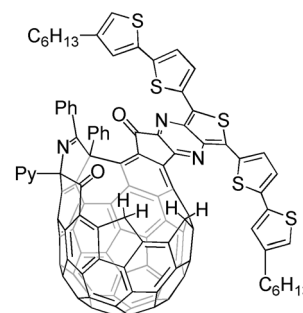
Fullerenes

Z. Xiao, G. Ye, Y. Liu, S. Chen, Q. Peng,*
Q. Zuo, L. Ding* **9038–9041**



Pushing Fullerene Absorption into the
Near-IR Region by Conjugately Fusing
Oligothiophenes

Fusing two in one: The π -electron systems of fullerene and an oligothiophene were conjugately fused by an open-cage process. This led to novel fullerene–oligothiophene chromophores with significantly enhanced light-absorbing capability, which covers a wide spectral range. The fullerene band gap could be tuned to about 1 eV by a chemical approach.

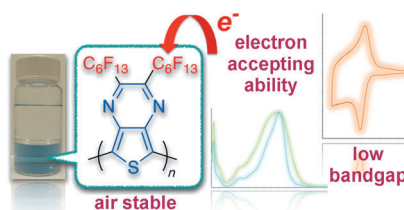


Molecular Devices

Y. Takeda, T. L. Andrew, J. M. Lobe, J. M. Mork, T. M. Swager* **9042–9046**



An Air-Stable Low-Bandgap n-Type
Organic Polymer Semiconductor
Exhibiting Selective Solubility in
Perfluorinated Solvents



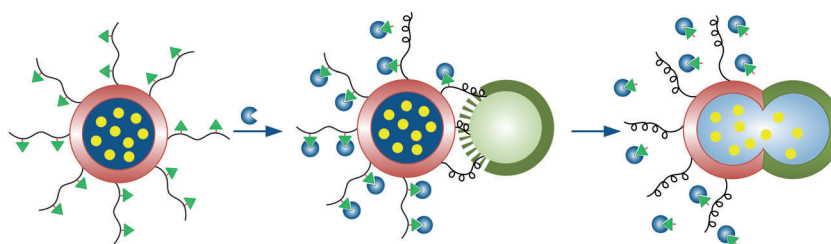
A thin-film transistor: An n-type polymer semiconductor, poly(2,3-bis(perfluorohexyl)thieno[3,4-*b*]pyrazine), was synthesized through a Pd-catalyzed polycondensation employing a perfluorinated multiphase solvent system. This is the first example of an n-type polymer semiconductor with exclusive solubility in fluorinated solvents. The fabrication of organic field effect transistors containing this new n-type polymer semiconductor is shown (see picture).

Drug Delivery

J. P. M. Motion, J. Nguyen,
F. C. Szoka* **9047–9051**

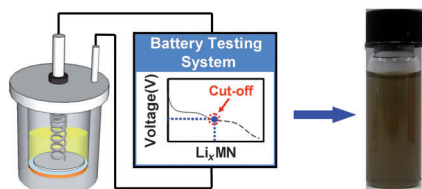


Phosphatase-Triggered Fusogenic
Liposomes for Cytoplasmic Delivery of
Cell-Impermeable Compounds



License to fuse! A phosphorylated fusion peptide can mediate membrane fusion when the phosphates (green triangles, see scheme) are removed by phosphatases

(blue spheres), delivering the contents of the liposome into the cytosol. This phosphatase-triggered approach may be useful to create target-specific lipid nanocarriers.



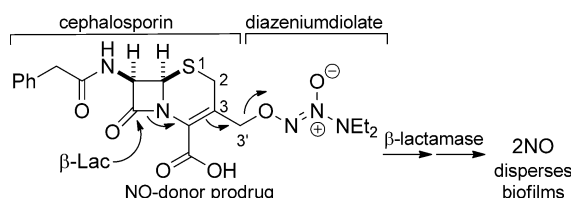
Intercalation and exfoliation of lithium:

Few-layer-thick inorganic nanosheets (BN, NbSe₂, WSe₂, Sb₂Se₃, and Bi₂Te₃) have been prepared from their layered bulk precursors by using a controllable electrochemical lithium intercalation process (see picture). The lithium intercalation conditions, such as cut-off voltage and discharge current, have been systematically studied and optimized to produce high-quality BN and NbSe₂ nanosheets.

Nanosheets

Z. Y. Zeng, T. Sun, J. X. Zhu, X. Huang, Z. Y. Yin, G. Lu, Z. X. Fan, Q. Y. Yan, H. H. Hng, H. Zhang* — 9052–9056

An Effective Method for the Fabrication of Few-Layer-Thick Inorganic Nanosheets



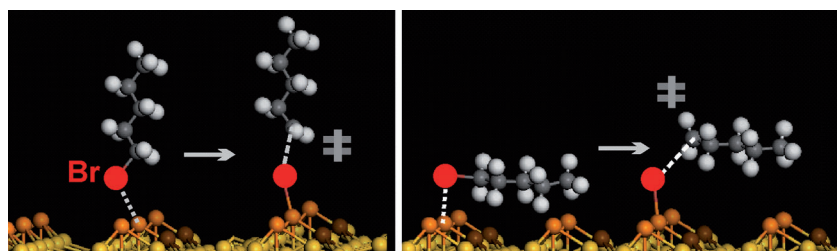
Just say NO to biofilms: NO-donors are used to disperse a bacterial biofilm so that co-administered antibiotics will kill the more susceptible unattached cells. The chemically stable cephalosporin-3'-diaze-

niumdiolate NO-donor prodrug (see scheme) is activated by bacterial β -lactamases and facilitates this two-step biofilm eradication.

Rational Drug Design

N. Barraud, B. G. Kardak, N. R. Yepuri, R. P. Howlin, J. S. Webb, S. N. Faust, S. Kjelleberg, S. A. Rice, M. J. Kelso* — 9057–9060

Cephalosporin-3'-diazeniumdiolates: Targeted NO-Donor Prodrugs for Dispersing Bacterial Biofilms



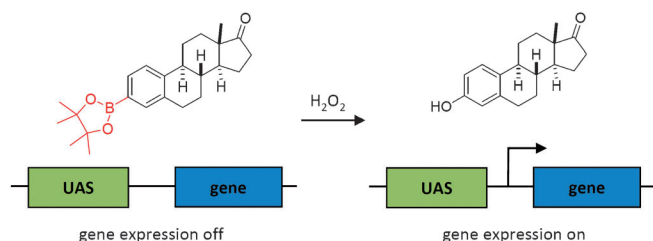
Bromine atom transfer to a silicon surface as a function of physisorbed adsorbate alignment (see picture: left, vertical 1-bromopentane; right, horizontal 1-bromopentane) of 1-bromopropane and

1-bromopentane on Si(111)-7 \times 7 has been studied by STM. In both thermal and electron-induced bromination reactions, the vertical alignment is more reactive.

Surface Science

K. Huang, I. R. McNab, J. C. Polanyi,* J. (S. Y.) Yang — 9061–9065

Adsorbate Alignment in Surface Halogenation: Standing Up is Better than Lying Down



Keeping the boron out of the ER: A genetic switch was engineered that activates gene expression in the presence of H₂O₂ (see scheme). The use of a boronate group on an estrone molecule allows for activation

of gene expression through binding of the estrogen receptor only when the boron group is oxidized by H₂O₂. This sensor is highly sensitive and specific for H₂O₂.

Reactive Oxygen Species

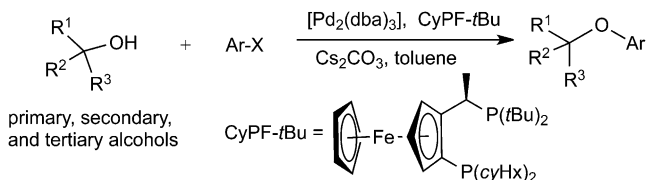
J. M. Govan, A. L. McIver, C. R. Riggsbee, A. Deiters* — 9066–9070

Hydrogen Peroxide Induced Activation of Gene Expression in Mammalian Cells using Boronate Estrone Derivatives



Cross-Coupling

P. E. Maligres,* J. Li,* S. W. Krska,
J. D. Schreier, I. T. Raheem* **9071–9074**

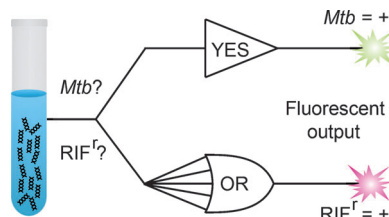


A robust and general catalyst system facilitates the alkoxylation of activated heteroaryl halides with primary, secondary, and select tertiary alcohols without the need for an excess of either coupling

partner (see scheme). This catalyst system displays broad functional-group tolerance and excellent regioselectivity, and is insensitive to the order of reagent addition.

DNA Logic Gates

E. M. Cornett, E. A. Campbell, G. Gulenay,
E. Peterson, N. Bhaskar,
D. M. Kolpashchikov* **9075–9077**

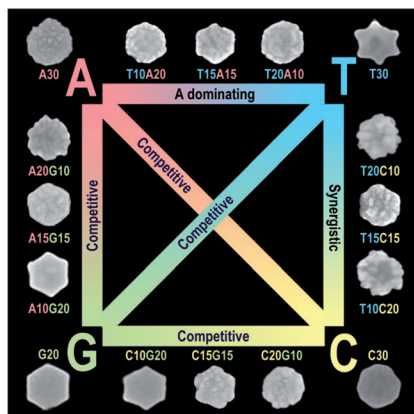


Elementary, Dr. Watson! A combination of YES and OR logic gates was applied to differentiate between DNA sequences of wild-type and rifampin-resistant (Rif^r) *Mycobacterium tuberculosis* (Mtb) in a multiplex real-time fluorescent assay.

Molecular Logic Gates for DNA Analysis:
Detection of Rifampin Resistance in
M. tuberculosis DNA

DNA Nanotechnology

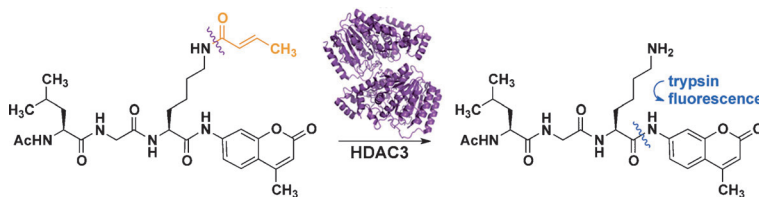
Z. Wang, L. Tang, L. H. Tan, J. Li,
Y. Lu* **9078–9082**



DNA is in control: Different combinations of DNA nucleotides can control the shape and surface roughness of gold nanoparticles during their synthesis. These nanoparticles were synthesized in the presence of either homogenous oligonucleotides or mixed-base oligonucleotides using gold nanoprisms as seeds. The effect of the individual DNA bases and their combinations on shape control are shown in the figure.

Enzyme Substrates

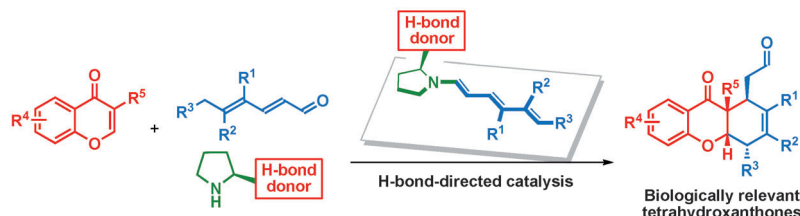
A. S. Madsen, C. A. Olsen* **9083–9087**



Profiling of Substrates for Zinc-dependent Lysine Deacetylase Enzymes: HDAC3 Exhibits Decrotonylase Activity In Vitro

Systematic screening of the activities of the eleven human zinc-dependent lysine deacetylases against a series of fluorogenic substrates (see scheme) as well as kinetic evaluation revealed substrates for screenings of histone deacetylases

HDAC10 and HDAC11 at reasonably low enzyme concentrations. Furthermore, HDAC3 in complex with nuclear receptor corepressor 1 (HDAC3–NCoR1) was shown to harbor decrotonylase activity in vitro.



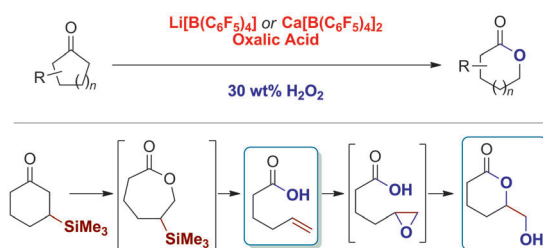
Right direction: The presented enantioselective strategy for the preparation of diversely functionalized tetrahydroxanthones is based on a trienamine-mediated cycloaddition between 2,4-dieneals and

activated chromones. It is possible to control the stereochemical outcome of such reactions by employing an H-bond-directing aminocatalyst.

Asymmetric Catalysis

Ł. Albrecht, F. Cruz Acosta, A. Fraile, A. Albrecht, J. Christensen, K. A. Jørgensen* — 9088 – 9092

Enantioselective H-Bond-Directing Approach for Trienamine-mediated Reactions in Asymmetric Synthesis



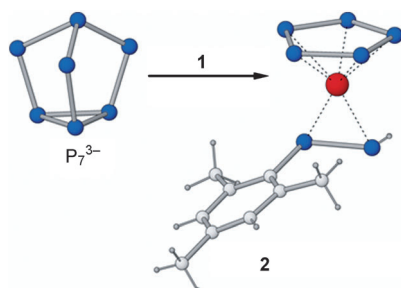
Efficient and selective: Two lipophilic catalysts were used for Baeyer–Villiger (BV) oxidations to give lactones in high yields (see scheme). Cascade reactions

involving this BV oxidation were used to selectively obtain either unsaturated carboxylic acids or hydroxylactones in high yields from β -silyl cyclohexanones.

Synthetic Methods

M. Uyanik, D. Nakashima, K. Ishihara* — 9093 – 9096

Baeyer–Villiger Oxidation and Oxidative Cascade Reactions with Aqueous Hydrogen Peroxide Catalyzed by Lipophilic $\text{Li}[\text{B}(\text{C}_6\text{F}_5)_4]$ or $\text{Ca}[\text{B}(\text{C}_6\text{F}_5)_4]_2$

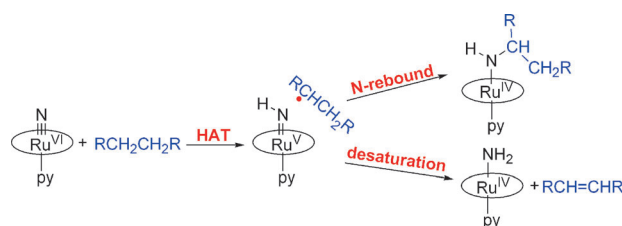


A carbon copy: The chemical activation of the heptaphosphide trianion with $[\text{Co}(\text{PEt}_2\text{Ph})_2(\text{mes})_2]$ (see picture; **1**) yields the novel phospho-organometallic complex $[\text{Co}(\eta^5\text{-P}_5)\{\eta^2\text{-P}_2\text{H}(\text{mes})\}]^{2-}$ (**2**). The reaction product maintains the nuclearity of the parent cluster, but extensive cage fragmentation takes place to yield a diamagnetic “inorganometallic” cobalt complex.

Phosphorus Complexes

C. M. Knapp, B. H. Westcott, M. A. C. Raybould, J. E. McGrady, J. M. Goicoechea* — 9097 – 9100

$[\text{Co}(\eta^5\text{-P}_5)\{\eta^2\text{-P}_2\text{H}(\text{mes})\}]^{2-}$: A Phospho-Organometallic Complex Obtained by the Transition-Metal-Mediated Activation of the Heptaphosphide Trianion



Kinetic and mechanistic studies on the intermolecular activation of strong C–H bonds of alkanes by a (salen)ruthenium(VI) nitride were performed. The initial, rate-limiting step, the hydrogen

atom transfer (HAT) from the alkane to $\text{Ru}^{\text{VI}}\equiv\text{N}$, generates $\text{Ru}^{\text{V}}=\text{NH}$ and $\text{R}\dot{\text{C}}\text{HCH}_2\text{R}$. The following steps involve N-rebound and desaturation.

C–H Activation

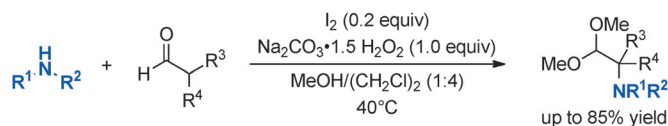
W. L. Man, W. W. Y. Lam, H. K. Kwong, S. M. Yiu, T. C. Lau* — 9101 – 9104

Ligand-Accelerated Activation of Strong C–H Bonds of Alkanes by a (Salen)ruthenium(VI)–Nitrido Complex



Oxidative Amination

J. S. Tian, K. W. J. Ng, J. R. Wong,
T. P. Loh* — 9105–9109



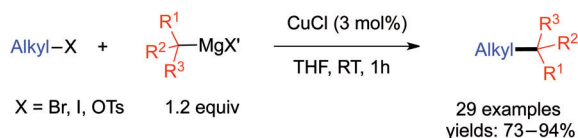
α -Amination of Aldehydes Catalyzed by
In Situ Generated Hypiodite

The metal-free amination of different aldehydes is catalyzed by hypiodite, which is generated by employing commercially available sodium percarbonate as the co-oxidant. This approach has several advantages: it is a metal-free

oxidation that works under mild reaction conditions; furthermore, it has a wide substrate scope and does not give toxic by-products from the co-oxidant that is used.

Cross-Coupling

P. Ren, L. A. Stern,
X. L. Hu* — 9110–9113



Copper-Catalyzed Cross-Coupling of
Functionalized Alkyl Halides and
Tosylates with Secondary and Tertiary Alkyl
Grignard Reagents

Added value: A copper-based method is highly efficient for the cross-coupling of alkyl electrophiles with secondary and tertiary alkyl Grignard reagents. The

method is distinguished by its broad substrate scope and high functional group tolerance.

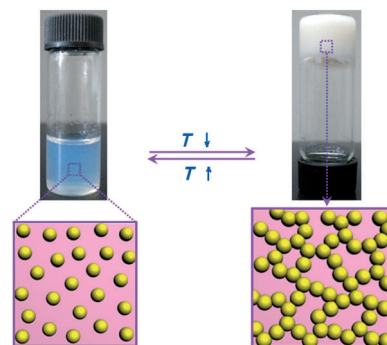
Ionic Gels

Y. Xiong,* J. Liu, Y. Wang, H. Wang,
R. Wang* — 9114–9118



One-Step Synthesis of Thermosensitive
Nanogels Based on Highly Cross-Linked
Poly(ionic liquid)s

A gel for all seasons: Thermosensitive nanogels based on highly cross-linked poly(ionic liquid)s (CLPNs) were prepared in one step by the copolymerization of imidazolium-based monomers with cross-linkers in selective solvents. Reversible nanogel–macrogel transitions of CLPNs in methanol could be achieved by changing the temperature (see picture).



Imaging Agents

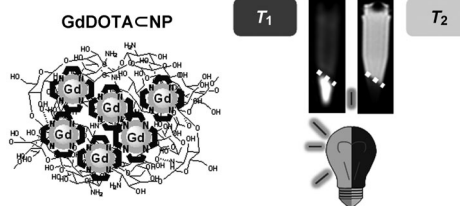
T. Courant, V. G. Roullin,* C. Cadiou,
M. Callewaert, M. C. Andry, C. Portefaix,
C. Hoeffel, M. C. de Goltstein, M. Port,
S. Laurent, L. V. Elst, R. N. Muller,
M. Molinari, F. Chuburu* — 9119–9122

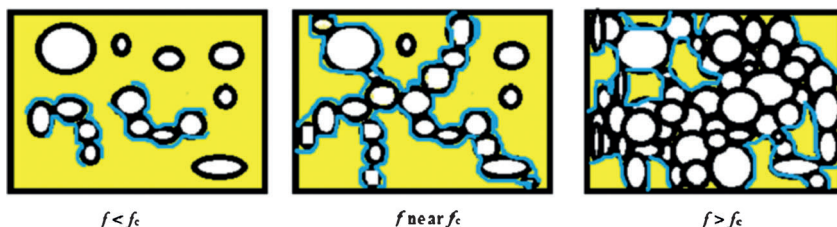


Hydrogels Incorporating GdDOTA:
Towards Highly Efficient Dual T_1/T_2 MRI
Contrast Agents

Do not tumble dry: Gadolinium-DOTA encapsulated into polysaccharide nanoparticles (GdDOTA@NPs) exhibited high relaxivity ($r_1 = 101.7 \text{ s}^{-1} \text{ mm}^{-1}$ per Gd^{3+} ion at 37°C and 20 MHz). This high relaxation rate is due to efficient Gd loading, reduced

tumbling of the Gd complex, and the hydrogel nature of the nanoparticles. The efficacy of the nanoparticles as a T_1/T_2 dual-mode contrast agent was studied in C6 cells (see picture).





The **dielectric constant** and electrical conductivity of a composite of two insulators, poly(1,1-difluoroethylene) (yellow) and K_2CO_3 (white), increased dramatically near the percolation threshold f_c ($f = \text{con-}$

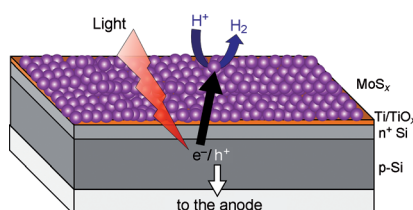
centration of K_2CO_3). This intriguing phenomenon can be interpreted in terms of interface percolation caused by the formation of chemically activated interfaces.

Interfaces

M. S. Wang, J. L. Zhu,* W. L. Zhu, B. Zhu, J. Liu, X. H. Zhu, Y. T. Pu, P. Sun, Z. F. Zeng, X. H. Li, D. Q. Yuan, S. Y. Zhu, G. Pezzotti* _____ **9123–9127**

The Formation of Percolative Composites with a High Dielectric Constant and High Conductivity

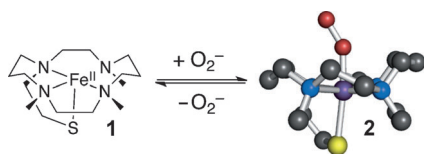
A low-cost substitute: A titanium protection layer on silicon made it possible to use silicon under highly oxidizing conditions without oxidation of the silicon. Molybdenum sulfide was electrodeposited on the Ti-protected n^+p -silicon electrode. This electrode was applied as a photocathode for water splitting and showed a greatly enhanced efficiency.



Photoelectrolysis

B. Seger, A. B. Laursen, P. C. K. Vesborg, T. Pedersen, O. Hansen, S. Dahl, I. Chorkendorff* _____ **9128–9131**

Hydrogen Production Using a Molybdenum Sulfide Catalyst on a Titanium-Protected n^+p -Silicon Photocathode

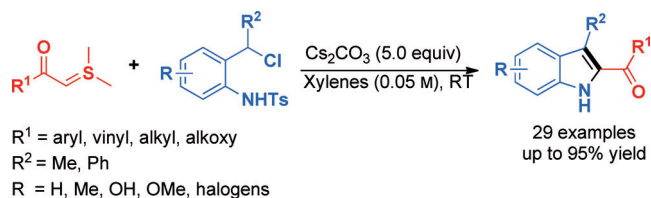


Nucleophilic oxidant: The reaction between a thiolato iron(II) complex **1** and superoxide in aprotic solvent at -90°C yields a novel thiolato iron(III) peroxide intermediate **2**, which exhibits unusually high nucleophilic reactivity. Compound **2** is an isomer of the thiolato iron(II) superoxide intermediate that is invoked in the reaction between superoxide reductase and superoxide.

Reactive Intermediates

A. R. McDonald, K. M. Van Heuvelen, Y. Guo, F. Li, E. L. Bominaar, E. Münck,* L. Que, Jr.* _____ **9132–9136**

Characterization of a Thiolato Iron(III) Peroxy Dianion Complex



Batting the ylides: A simple procedure carried out under mild conditions allows the direct and efficient synthesis of structurally diverse indoles. This approach

involves a cascade reaction of sulfur ylides and *N*-(*ortho*-chloromethyl)aryl amides (see scheme).

Indole Synthesis

Q.-Q. Yang, C. Xiao, L.-Q. Lu, J. An, F. Tan, B.-J. Li, W.-J. Xiao* _____ **9137–9140**

Synthesis of Indoles through Highly Efficient Cascade Reactions of Sulfur Ylides and *N*-(*ortho*-Chloromethyl)aryl Amides

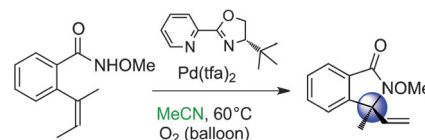
Asymmetric Catalysis

G. Yang, C. Shen,
W. Zhang* 9141–9145



An Asymmetric Aerobic Aza-Wacker-Type Cyclization: Synthesis of Isoindolinones Bearing Tetrasubstituted Carbon Stereocenters

It's all in the solvent: An enantioselective variant of an aza-Wacker-type cyclization that gives isoindolinones containing tetrasubstituted carbon centers α to the nitrogen atom has been developed (see scheme; tfa = trifluoroacetate). The use of a highly coordinating solvent is crucial for the activity of the catalyst and the stereoselectivity the reaction (up to 99% ee).

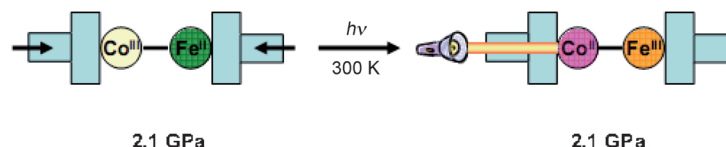


Photoinduced Electron Transfer

J.-D. Cafun, J. Lejeune, F. Baudelet,
P. Dumas, J.-P. Itié,
A. Bleuzen* 9146–9148



Room-Temperature Photoinduced Electron Transfer in a Prussian Blue Analogue under Hydrostatic Pressure



In from the cold: The $\text{Co}^{\text{III}}\text{Fe}^{\text{II}}$ state of a CoFe Prussian blue analogue undergoes a $\text{Co}^{\text{III}}-\text{Fe}^{\text{II}} \rightarrow (\text{Co}^{\text{II}}-\text{Fe}^{\text{III}})^*$ electron transfer at room temperature when irradiated by visible light (532 nm; see scheme). This

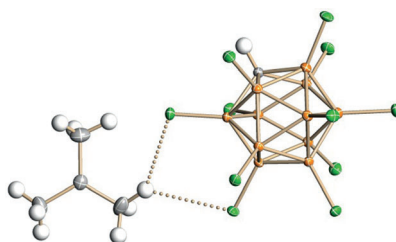
property was confirmed using energy-dispersive X-ray absorption spectroscopy at the Co and Fe K-edges of the piezo-induced $\text{Co}^{\text{III}}\text{Fe}^{\text{II}}$ state.

Noncovalent Interactions

E. S. Stoyanov,* I. V. Stoyanova,
F. S. Tham, C. A. Reed* 9149–9151



Evidence for C–H Hydrogen Bonding in Salts of *tert*-Butyl Cation



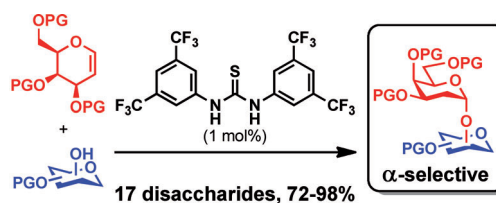
Environmentally sensitive: A combination of C–H...anion hydrogen bonding and hyperconjugative charge delocalization explains the sensitivity of the IR spectrum of the *tert*-butyl cation to its anion (see high-resolution X-ray structure with a $\text{CHB}_{11}\text{Cl}_{11}^-$ counterion). The ν_{CH} vibration of the cation scales linearly with the basicity of carborane anions on the ν_{NH} scale. The same also holds for the C_6H_7^+ benzenium ion.

Organocatalysis

E. I. Balmond, D. M. Coe, M. C. Galan,*
E. M. McGarrigle* 9152–9155

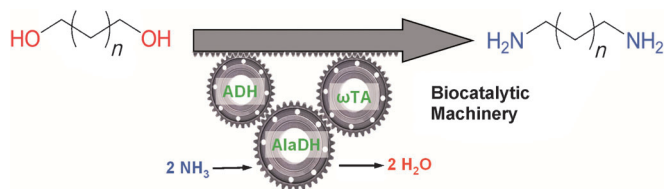


α -Selective Organocatalytic Synthesis of 2-Deoxygalactosides



Alpha rules: A thiourea acts as an efficient organocatalyst for the glycosylation of protected galactals to form oligosaccharides containing a 2-deoxymonosaccharide

moiety (see scheme). The reaction is highly stereoselective for α -linkages and proceeds by way of a *syn*-addition mechanism.



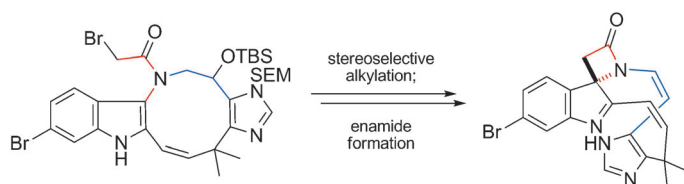
Driving the machinery: A biocatalytic redox-neutral cascade for the preparation of terminal primary amines from primary alcohols at the expense of ammonia has been established in a one-pot one-step

method (see picture). Applying this artificial biocatalyst network, long-chain 1,ω-alkanediols were converted into diamines, which are building blocks for polymers, in up to 99% conversion.

Biocatalysis

J. H. Sattler, M. Fuchs, K. Tauber,
F. G. Mutti, K. Faber, J. Pfeffer, T. Haas,
W. Kroutil* 9156–9159

Redox Self-Sufficient Biocatalyst Network
for the Amination of Primary Alcohols



What a core-ker! The title synthesis was achieved using a route featuring an intramolecular Mitsunobu reaction of a nosyl amide, stereoselective construction of the β-lactam, and formation of an enamide moiety by selenoxide elimination. The

stereochemistry of the alkylation for the formation of the β-lactam was controlled by a secondary hydroxy group on the ten-membered ring. SEM = 2-(trimethylsilyl)ethoxymethyl; TBS = *tert*-butyldimethylsilyl.

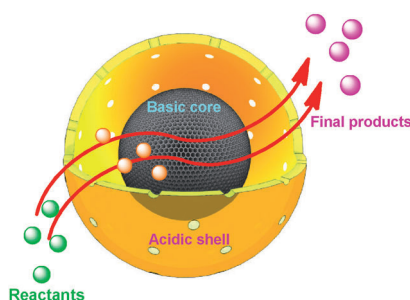
Natural Products

K. Iwasaki, R. Kanno, T. Morimoto,
T. Yamashita, S. Yokoshima,
T. Fukuyama* 9160–9163

Synthetic Studies on Chartelline C:
Stereoselective Construction of the Core
Skeleton



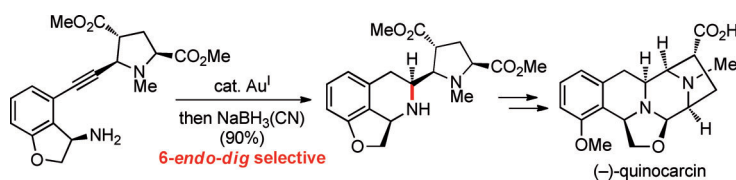
Smart yolk–shell nanoparticles (hollow nanoparticles with a movable core) with an acidic shell and a basic core were fabricated through an organosilane-assisted selective etching method and acted as efficient nanoreactors for catalyzing a deacetalization–Henry cascade reaction with high activity and high selectivity. This strategy is very promising for the design of multifunctional nanoreactors for cascade reactions.



Nanostructures

Y. Yang, X. Liu, X. B. Li, J. Zhao, S. Y. Bai,
J. Liu,* Q. H. Yang* 9164–9168

A Yolk–Shell Nanoreactor with a Basic
Core and an Acidic Shell for Cascade
Reactions



In control: The novel and enantioselective total synthesis of (–)-quinocarcin includes the highly stereoselective preparation of the 2,5-*cis*-pyrrolidine by intramolecular amination, a selective sub-

strate-controlled 6-*endo-dig* intramolecular alkyne hydroamination with a cationic Au^I catalyst, and Lewis-acid-mediated ring-opening/halogenation sequence.

Natural Products

H. Chiba, S. Oishi, N. Fujii,*
H. Ohno* 9169–9172

Total Synthesis of (–)-Quinocarcin by
Gold(I)-Catalyzed Regioselective
Hydroamination

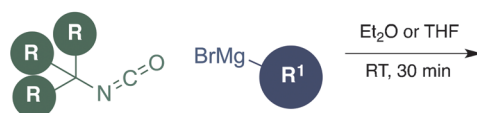


Amide Formation

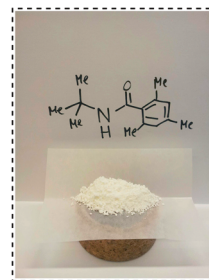
G. Schäfer, C. Matthey,
J. W. Bode* 9173–9175



Facile Synthesis of Sterically Hindered and Electron-Deficient Secondary Amides from Isocyanates



- Extremely hindered amides accessible
- No excess of reagents necessary
- Rapid reactions at RT
- Robust and scalable



The big easy: The direct coupling of Grignard reagents to isocyanates provides a facile and robust solution for the synthesis of sterically hindered and electron-

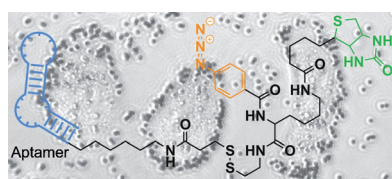
deficient secondary amides. The products are obtained in high yields without the need for excess reagents or chromatographic purification.

Aptamer Affinity Labeling

J. L. Vinkenborg, G. Mayer,
M. Famulok* 9176–9180



Aptamer-Based Affinity Labeling of Proteins



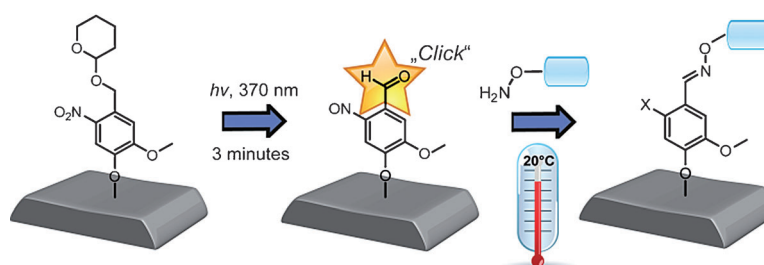
A most able label: Labeled aptamers (see picture) can be cross-linked to their target structures in a light-dependent and highly specific manner as a result of a new strategy termed aptamer-based affinity labeling (ABAL) of proteins. The aptamer–protein complexes can be enriched in vitro, from a cellular lysate and from the surface of living cells, opening new ways to study aptamer interactions in biological contexts.

Photoreactions on Surfaces

T. Pauloeuhl, G. Delaittre, M. Bruns,
M. Meißler, H. G. Börner, M. Bastmeyer,
C. Barner-Kowollik* 9181–9184



(Bio)Molecular Surface Patterning by Phototriggered Oxime Ligation



Making light work of ligation: A novel method utilizes light for oxime ligation chemistry. A quantitative, low-energy photodeprotection generates aldehyde, which subsequently reacts with aminooxy

moieties. The spatial control allows patterning on surfaces (see scheme) with a fluoro marker and GRGSR peptide, and can be imaged by time-of-flight secondary-ion mass spectrometry.



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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