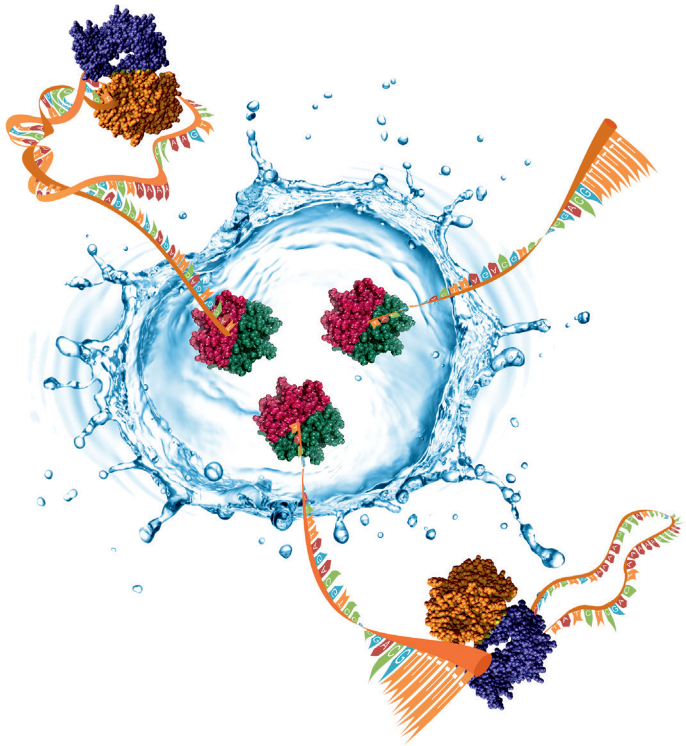
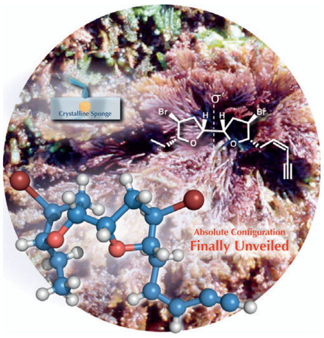
A simple paper-based device ...

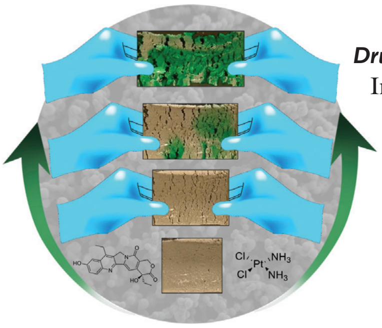


... for DNA amplification is described by J. D. Brennan, Y. Li, and co-workers in their Communication on page 2709 ff. The paper device is printed with all enabling reagents, such as DNA polymerase, circular DNA template, and small building blocks, for building long-chain DNA molecules for visual detection. DNA amplification is automatically activated upon addition of a test sample that contains the DNA or RNA sequence of interest.

Natural Products

The structure of natural elatenyne, which was first isolated from the red alga *Laurencia elata* 30 years ago, was determined by M. Fujita, S. Urban et al. in their Communication on page 2743 ff. with the help of a crystalline sponge.





Drug Delivery

In their Communication on page 2796 ff., M. W. Grinstaff et al. demonstrate how the stretching of a superhydrophobic multilayered device can be used for the strain-dependent release of various agents.

Nanocatalysis

In their Communication on page 2820 ff., X. Wang, T. Zhang et al. report a Rh sub-nanocluster supported on TiO_2 for the oxidation of CO at cryogenic temperatures.

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Editorial

"… I suggest two possible changes that might make better practices in scientific publishing. A mechanism is needed to recognize the valuable task that reviewers perform and I would also like to have a brief explanation of the individual author contributions to each manuscript …"
Read more in the Editorial by Richard N. Zare.

Service

Author Profile

"My favorite composer is Ludwig van Beethoven. My favorite painter is Qi Baishi (a famous Chinese painter) …"
This and more about Rui Wang can be found on page 2632.

News


L. An


Y. Li


Y. Liu


S.-G. Sun


W. Tan


Y. Tang


Z. Xi

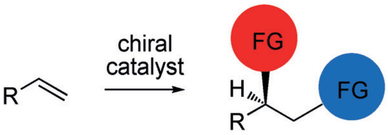

J. Yu


S. Zhang


R. H. Grubbs

Minireviews

Asymmetric Synthesis



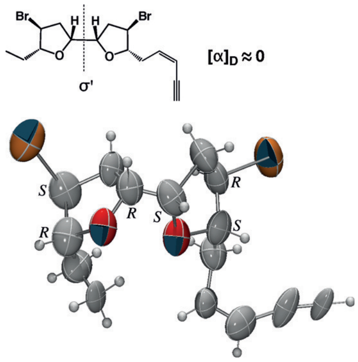
Reviews

Electrocatalysis

For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 101161, 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$ 16.862/14.051 (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

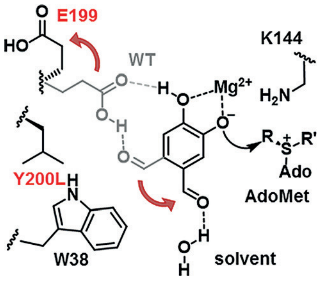
Natural Products



The structure of natural elatenyne, which was first isolated 30 years ago, was determined by the use of a porous coordination network (a crystalline sponge) capable of absorbing organic guests. The crystalline sponge differentiates between the two very similar alkyl side chains, and the absolute structure of elatenyne was thus reliably determined.

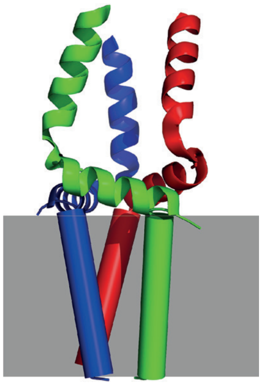
Frontispiece

Biocatalysis



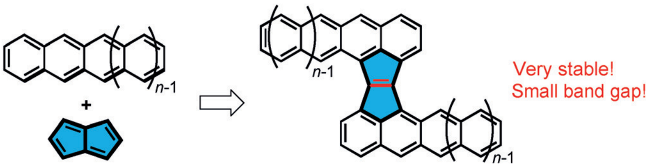
Old cat, new tricks: Protein engineering of catechol-*O*-methyltransferase generated mutants with improved regioselectivity, thus enabling *meta*- or *para*-methylation of substrates in significant regioisomeric excess. X-ray crystal structures elucidate the role of active-site residues and quaternary structure on enzyme regioselectivity. A one-pot tandem enzyme reaction was developed to regioselectively alkylate catechols by using AdoMet analogues.

HIV



The membrane-proximal external region (MPER) of HIV gp41 is an established target of antibodies that neutralize a broad range of HIV isolates. To evaluate the role of the transmembrane (TM) domain, synthetic MPER-derived peptides were incorporated into lipid nanoparticles and antibody affinity was measured. The studies suggest that neutralizing antibodies can bind the MPER when the TM domain is a three-helix bundle.

Acenes



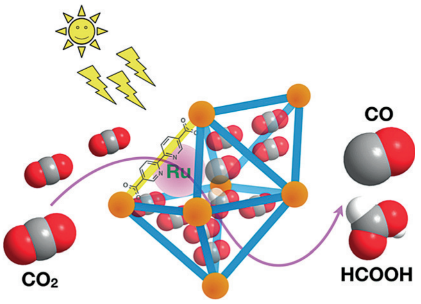
Stable acene dimers: The fusion of an anti-aromatic pentalene unit to the zigzag edges of acenes dramatically changed their electronic structure as a result of intramolecular donor–acceptor interactions, thus leading to materials having a small energy gap, amphoteric redox behavior, and largely enhanced photostability. X-ray crystallographic analyses revealed a slip-stack column structure, which guarantees their activity as field-effect transistors in thin films.

Microporous Materials

T. Kajiwara, M. Fujii, M. Tsujimoto,
K. Kobayashi, M. Higuchi, K. Tanaka,
S. Kitagawa* ———— **2697 – 2700**

Photochemical Reduction of Low Concentrations of CO_2 in a Porous Coordination Polymer with a Ruthenium(II)–CO Complex

A porous coordination polymer (PCP)-based catalyst containing both CO_2 adsorption and reduction sites has been synthesized by incorporation of a Ru^{II} complex into a PCP. The resulting PCP-Ru^{II} composite catalyzed photochemical CO_2 reduction to produce CO and HCOOH. Catalytic activity was maintained even under a 5 % CO_2/Ar gas mixture, thus revealing the synergistic effect between the adsorption sites and catalytically active sites.

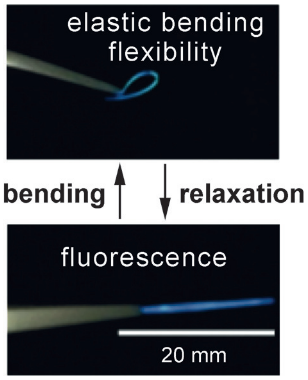


Crystal Engineering

S. Hayashi,* T. Koizumi —— **2701 – 2704**

Elastic Organic Crystals of a Fluorescent π-Conjugated Molecule

A long stretch: A large fluorescent single crystal of a π-conjugated molecule exhibits a fibril lamella morphology based on slip-stacked molecular wires, and is a remarkably elastic crystalline material. Mechanical bending–relaxation resulted in reversible change of the morphology and fluorescence. The crystal can be bent through more than 180° before returning to its original shape upon relaxation.

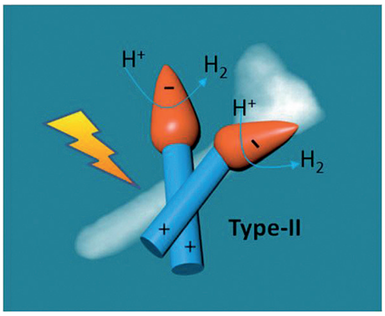


Photocatalysts

G. Prusty, A. K. Guria, I. Mondal, A. Dutta,
U. Pal, N. Pradhan* ———— **2705 – 2708**

Modulated Binary–Ternary Dual Semiconductor Heterostructures

Semiconducting tadpoles: A generic modular synthetic strategy for fabricating a series of group II-VI and I-III-VI coupled binary–ternary dual semiconductory heterostructures is reported. Among these, dispersive type-II semiconductors were explored as photocatalysts for the evolution of hydrogen from water.



VIP

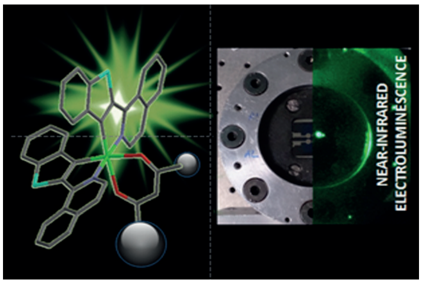
Point-of-Care Diagnostics

M. Liu, C. Y. Hui, Q. Zhang, J. Gu,
B. Kannan, S. Jahanshahi-Anbuhi,
C. D. M. Filipe, J. D. Brennan,*
Y. Li* ———————— **2709 – 2713**

Target-Induced and Equipment-Free DNA Amplification with a Simple Paper Device

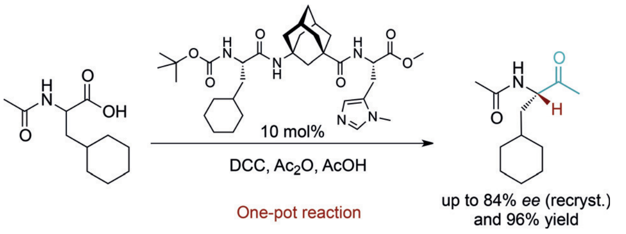
Front Cover

DNA amplification is better on paper: A highly functional, "all-in-one" DNA amplification based paper device allows for visual detection of DNA and microRNA with minimal human intervention, making this method particularly suitable for bioassays used in resource-poor settings.



Let’s glow: Heteroleptic benzo[*b*]thiophenyl isoquinolinate Ir^{III} complexes with diketonate ancillary ligands of increasing conjugation were prepared. The compounds are NIR emissive with high emission quantum yields (up to 16%). A solution-processed OLED fabricated with one of the complexes demonstrates a remarkable external quantum efficiency (EQE) of more than 3% with negligible efficiency roll-off.

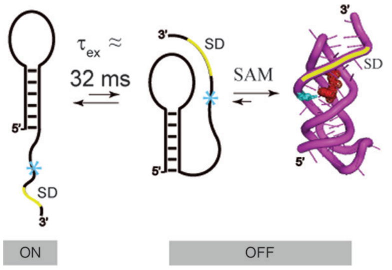
Photophysics



Nearly 90 years after its development the first enantioselective Dakin–West reaction is reported. The reaction produces valuable enantioenriched acetamido ketones. The key step is a dispersion-controlled enantioselective decarboxylative protonation by the catalyst. DCC = *N*,*N*′-dicyclohexylcarbodiimide.

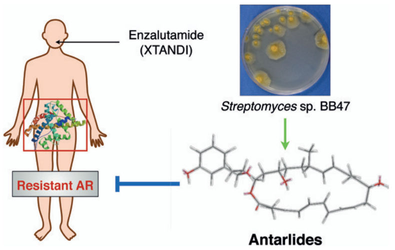
Organocatalysis

Decloaking invisible RNA worlds: RNAs code for multiple conformations that can be selected by various ligands to modulate signaling. Most of these functional states are transient and sparsely populated, but isotopic labeling and NMR dynamics studies promise to unveil these otherwise invisible conformations.



RNA Structures

The next generation: Advanced prostate cancer is treated with androgen receptor (AR) antagonists, but most patients experience disease progression after long-term treatment with these antagonists. Antarlides, isolated from *Streptomyces* sp. BB47, inhibited the transcriptional activity of mutant ARs, which are seen in patients with acquired resistance to the current clinically used drug enzalutamide (XTANDI).



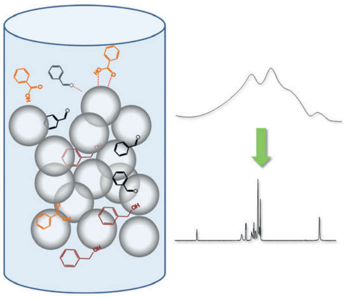
Drug Resistance

NMR Spectroscopy

T. González-García, T. Margola,
A. Silvagni, F. Mancin,
F. Rastrelli* __________ **2733 – 2737**

Chromatographic NMR Spectroscopy with Hollow Silica Spheres

A (w)hole lot better: Hollow silica microspheres made possible the use of solution-state NMR instruments to analyze mixtures of small molecules by chromatographic NMR spectroscopy (see picture). The silica microspheres clearly provide major advantages over conventional stationary phases.

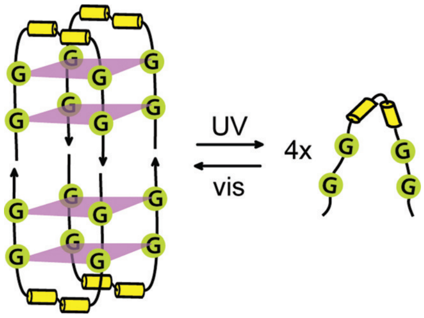


G-Quadruplexes

J. Thevarpadam, I. Bessi, O. Binas,
D. P. N. Gonçalves, C. Slavov,
H. R. A. Jonker, C. Richter, J. Wachtveitl,
H. Schwalbe,* A. Heckel* __ **2738 – 2742**

Photoresponsive Formation of an Intermolecular Minimal G-Quadruplex Motif

Switch and self-assemble: Three different azobenzene-containing bifunctional guanosine sequences were employed for the construction, upon UV/Vis irradiation, of a defined intermolecular two-tetrad G-quadruplex. The use of one azobenzene derivative enables photoswitching between a stacked, tetramolecular G-quadruplex and an unstructured state after *E*–*Z* isomerization.

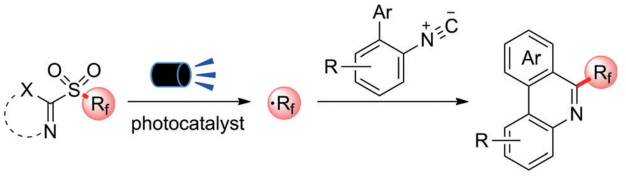


Photoredox Catalysis

J. Rong, L. Deng, P. Tan, C. Ni,* Y. Gu,
J. Hu* __________ **2743 – 2747**

Radical Fluoroalkylation of Isocyanides with Fluorinated Sulfones by Visible-Light Photoredox Catalysis

Inside Cover



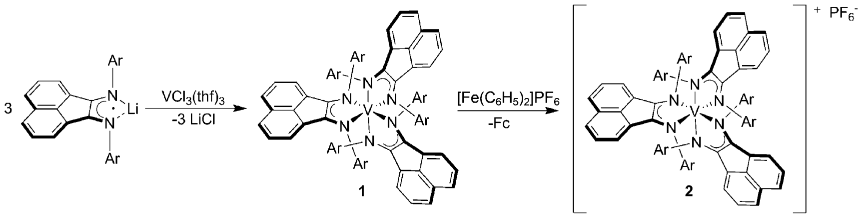
$R_f = CH_2F, CF_2H, CF_2Me, CF_2Ph, CF_3, CF_2COPh$

Sulfones in the spotlight: The radical fluoroalkylation of isocyanides with a wide range of readily available mono-, di-, and trifluoromethyl heteroaryl sulfones is enabled by visible-light photoredox catalysis. Fluorinated sulfones can thus be used as precursors of fluoroalkyl radicals.

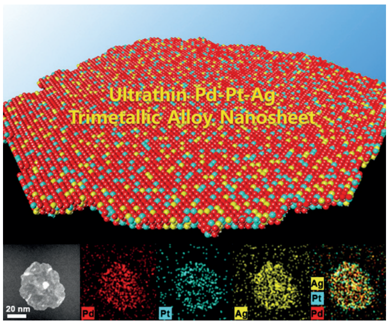
Noninnocent Ligands

J. Bendix, K. M. Clark* ____ **2748 – 2752**

Delocalization and Valence Tautomerism in Vanadium Tris(iminosemiquinone) Complexes



V unusual: Homoleptic vanadium complexes $[V(L)_3]$ (**1**) and monocation $[V(L)_3]PF_6$ (**2**; L = bis(arylimino) acenaphthene ligand, Ar = 3,5-$Me_2C_6H_3$) have a very rich electronic behavior. Complex **1** is a mixed-valence complex that displays strong electronic delocalization, whereas **2** exists as two discrete redox isomers, which is a rare example of valence tautomerism. Complex **2** also undergoes a spin transition with increasing temperature.

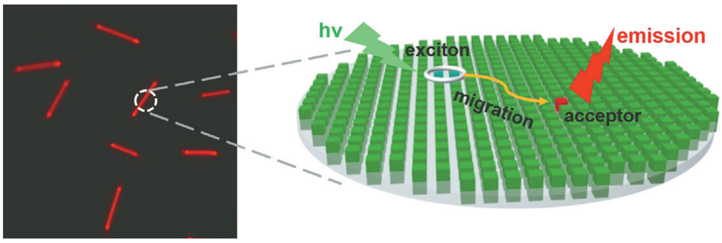


Ultrathin Pd-Pt-Ag nanosheets with a thickness of approximately 3 nm were successfully prepared by the co-reduction of suitable metal precursors in an appropriate molar ratio in the presence of CO. These nanosheets are superior catalysts of ethanol electrooxidation owing to their specific structural and compositional characteristics.

Electrocatalysis

J. W. Hong, Y. Kim, D. H. Wi, S. Lee, S.-U. Lee, Y. W. Lee, S.-I. Choi, S. W. Han* ________ **2753 – 2758**

Ultrathin Free-Standing Ternary-Alloy Nanosheets



Daylight saving: Uniform nanocrystals of organic difluoroboron chromophores with controlled donor/acceptor ratios were prepared by simple coassembly of the donors and acceptors in water. The light-harvesting system funneled the excitation energy with an energy transfer efficiency of 95 % at a donor/acceptor ratio as high as 1000:1. The acceptor was found to have a significant fluorescence at donor/acceptor ratios of up to 200 000:1.

Photochemistry VIP

P.-Z. Chen, Y.-X. Weng, L.-Y. Niu, Y.-Z. Chen, L.-Z. Wu, C.-H. Tung, Q.-Z. Yang* ________ **2759 – 2763**

Light-Harvesting Systems Based on Organic Nanocrystals To Mimic Chlorosomes

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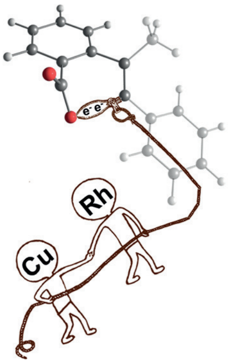

Joint effort: The reaction between benzoic acid and methylphenylacetylene to form an isocoumarin is catalyzed by Cp*Rh-$(OAc)_2$ in the presence of $Cu(OAc)_2(H_2O)$ as the oxidant. Its mechanism was elucidated by DFT calculations with the B97D functional, which showed that the overall transformation proceeds by cooperative reductive elimination with a transition state containing both rhodium and copper centers.

Reaction Mechanisms VIP

I. Funes-Ardoiz, F. Maseras* ________ **2764 – 2767**

Cooperative Reductive Elimination: The Missing Piece in the Oxidative-Coupling Mechanistic Puzzle

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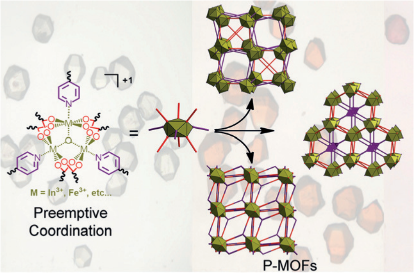


New traps for bio-anions. Using a preemptive coordination approach, highly porous cationic frameworks were made that allow immobilization of anionic nucleotides and coenzymes, in addition to charge- and size-selective capture and separation of organic dyes.

Metal–Organic Frameworks

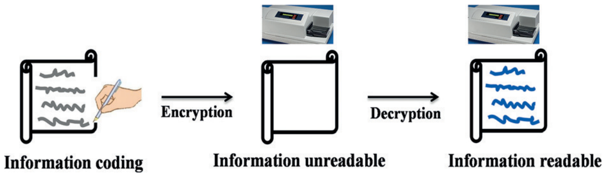
X. Zhao, C. Mao, K. T. Luong, Q. Lin, Q.-G. Zhai, P. Feng, X. Bu* **2768 – 2772**

Framework Cationization by Preemptive Coordination of Open Metal Sites for Anion-Exchange Encapsulation of Nucleotides and Coenzymes

Carbon Quantum Dots

Z. Song, T. Lin, L. Lin, S. Lin, F. Fu, X. Wang,* L. Guo* ———— **2773 – 2777**

Invisible Security Ink Based on Water-Soluble Graphitic Carbon Nitride Quantum Dots



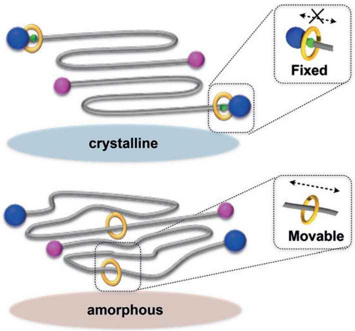
Secret communication: The information written by using carbon nitride dots as security ink is invisible under illumination with both ambient light and UV light. The encoded information is readable by a fluorescence microplate reader, and it can be further encrypted and decrypted by quenching and recovering the fluorescence of the security ink using H_2CO_4 and $NaHCO_3$, respectively.

Supramolecular Chemistry

Z. Chen, D. Aoki, S. Uchida, H. Marubayashi, S. Nojima, T. Takata* ———— **2778 – 2781**

Effect of Component Mobility on the Properties of Macromolecular [2]Rotaxanes

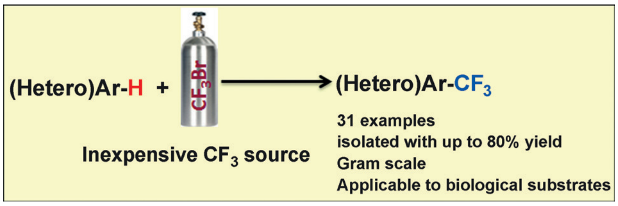
Stop and go: Macromolecular [2]rotaxanes, consisting of a polyester axle and crown ether wheel, were synthesized with either fixed or movable components and with various molecular weights to evaluate the effect of component mobility on the axle polymer properties. Crystallinity measurements revealed that the effect of mobility is significant, thus suggesting that the properties of the axle polymer depend on the mobility of the polyrotaxane components.



C–H Activation

K. Natte, R. V. Jagadeesh, L. He, J. Rabeah, J. Chen, C. Taeschler, S. Ellinger, F. Zaragoza, H. Neumann, A. Brückner, M. Beller* ———— **2782 – 2786**

Palladium-Catalyzed Trifluoromethylation of (Hetero)Arenes with CF_3Br

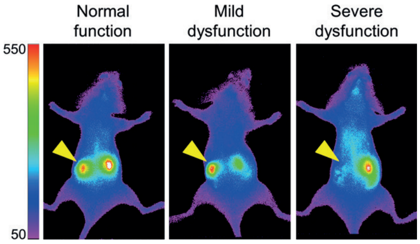


A cheaper source: A general and reliable palladium-catalyzed method for the synthesis of trifluoromethylated (hetero)arenes using CF_3Br has been developed. The products are isolated in good yields and the reaction proceeds under comparably mild reaction conditions with good regio- and chemoselectivity.

Fluorescence Imaging

M. X. Yu, J. C. Zhou, B. J. Du, X. H. Ning, C. Authement, L. Gandee, P. Kapur, J. T. Hsieh, J. Zheng* ———— **2787 – 2791**

Noninvasive Staging of Kidney Dysfunction Enabled by Renal-Clearable Luminescent Gold Nanoparticles

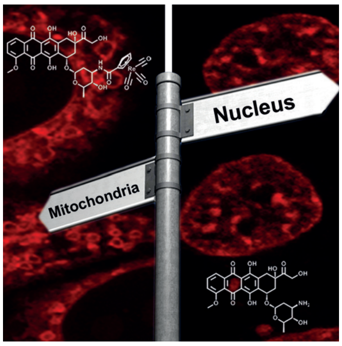


A noninvasive, inexpensive method for the noninvasive staging of kidney dysfunction is based on the use of renal-clearable near-infrared-emitting gold nanoparticles as imaging agents for in vivo fluorescence imaging. The various stages of kidney dysfunction could thus be readily differentiated in a unilateral-ureteral-obstruction mouse model.

Drug Targeting

S. Imstepf, V. Pierroz, R. Rubbiani,
M. Felber, T. Fox, G. Gasser,
R. Alberto* ______ **2792 – 2795**

Organometallic Rhenium Complexes Divert Doxorubicin to the Mitochondria



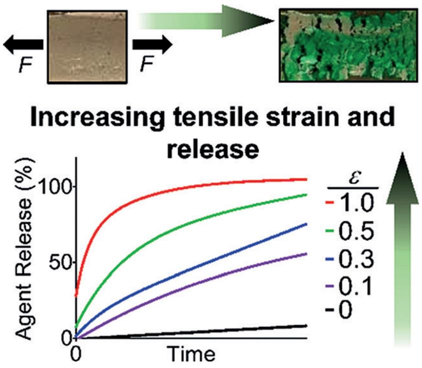
The road less travelled: Doxorubicin is a strong chemotherapeutic agent known for its exclusively nuclear accumulation. Two organometallic derivatives of Doxorubicin were found to display a novel and unexpected subcellular distribution, with significant uptake into mitochondria. First in vitro studies corroborate an influence on mitochondrial homeostasis. Such derivatives could be relevant in the ongoing quest for chemotherapeutic agents that can be better tolerated.

Drug Delivery

J. Wang, J. A. Kaplan, Y. L. Colson,
M. W. Grinstaff* ______ **2796 – 2800**

Stretch-Induced Drug Delivery from Superhydrophobic Polymer Composites: Use of Crack Propagation Failure Modes for Controlling Release Rates

Inside Back Cover

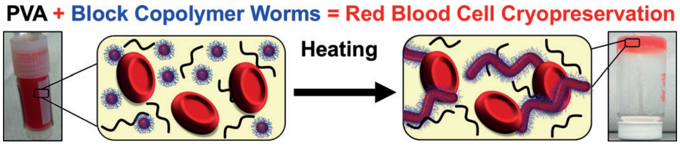


Mechanoresponsive delivery: Superhydrophobic composites were developed whose drug release rates can be controlled through the applied tensile strain. Strain-dependent in vitro delivery of anticancer agents (cisplatin and 7-ethyl-10-hydroxycamptothecin) to esophageal cancer cells and ex vivo delivery of fluorescein diacetate with an esophageal stent are demonstrated.

Cryopreservation

D. E. Mitchell, J. R. Lovett, S. P. Armes,
M. I. Gibson* ______ **2801 – 2804**

Combining Biomimetic Block Copolymer Worms with an Ice-Inhibiting Polymer for the Solvent-Free Cryopreservation of Red Blood Cells

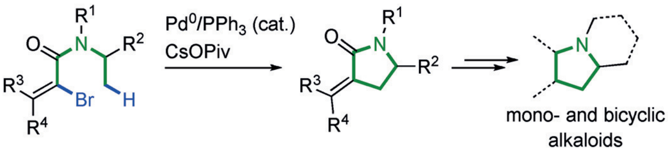


Antifreeze-free freezing: A wholly synthetic, solvent-free approach for cellular cryopreservation is based on the use of biomimetic block copolymer worms in combination with a well-known ice-recrystallization inhibitor, poly(vinyl alcohol). Upon thawing, red-blood-cell recoveries of up to 70% were achieved, and free-standing hydrogels were obtained by warming to ambient temperature.

C–H Activation

P. M. Holstein, D. Dailler, J. Vantourout,
J. Shaya, A. Millet,
O. Baudoin* ______ **2805 – 2809**

Synthesis of Strained γ-Lactams by Palladium(0)-Catalyzed C(sp^3)–H Alkenylation and Application to Alkaloid Synthesis

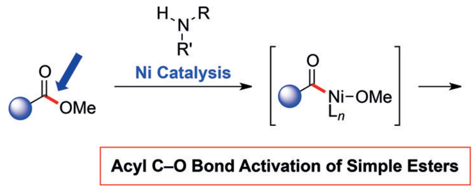


Strain away: A variety of strained α-alkylidene-γ-lactams were synthesized from easily accessible acyclic and monocyclic bromoalkene precursors. These lactams are valuable intermediates for accessing various classes of mono- and bicylic alkaloids containing a pyrrolidine ring, as illustrated with the synthesis of an advanced model of the marine natural product plakoridine A and of the indolizidine alkaloid δ-coniceine.

Nickel Catalysis

L. Hie, N. F. Fine Nathel, X. Hong,
Y.-F. Yang, K. N. Houk,*
N. K. Garg* **2810 – 2814**

Nickel-Catalyzed Activation of Acyl C–O Bonds of Methyl Esters

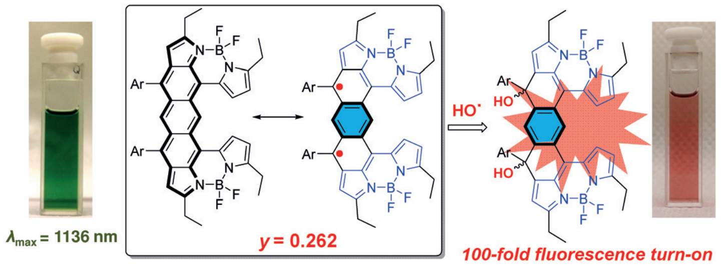


The acyl C–O bonds of methyl esters are activated through a nickel-catalyzed oxidative-addition process. The putative oxidative-addition adducts are trapped in situ to provide anilides. DFT calculations support the proposed mechanism, explain why decarbonylation does not occur competitively, and elucidate the beneficial role of $Al(OtBu)_3$ on the kinetics and thermodynamics of the reaction.

Near-Infrared Dyes

Y. Ni, S. Lee, M. Son, N. Aratani, M. Ishida,
A. Samanta, H. Yamada, Y.-T. Chang,
H. Furuta, D. Kim,* J. Wu* **2815 – 2819**

A Diradical Approach towards BODIPY-Based Dyes with Intense Near-Infrared Absorption around $\lambda = 1100$ nm



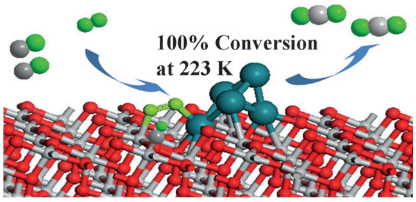
BODIPY sees red: *para*- and *meta*-quinodimethane-bridged BODIPY dimers (see example) absorb strongly around $\lambda = 1100$ nm and have a small amount of diradical character (y). The dyes were found to have large two-photon-absorption cross-sections in the NIR region and showed selective fluorescence turn-on for the hydroxyl radical over other reactive oxygen species.

Nanocatalysis

H. Guan, J. Lin, B. Qiao, X. Yang, L. Li,
S. Miao, J. Liu, A. Wang, X. Wang,*
T. Zhang* **2820 – 2824**

Catalytically Active Rh Sub-Nanoclusters on TiO_2 for CO Oxidation at Cryogenic Temperatures

Supported catalysts: A catalyst with unique configuration of Rh sub-nanoclusters supported on a TiO_2 surface was prepared. This catalyst exhibited an unprecedentedly high activity for CO oxidation at cryogenic temperatures.

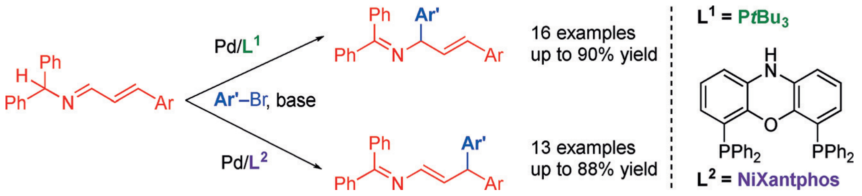


Back Cover

Synthetic Methods

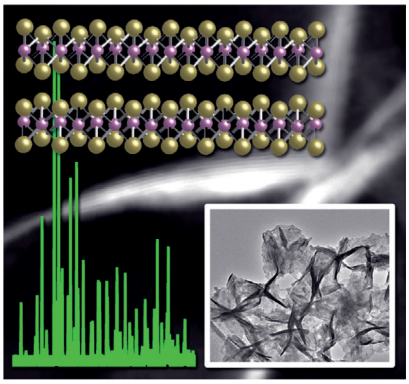
M. Li, M. González-Esguevillas, S. Berritt,
X. Yang, A. Bellomo,
P. J. Walsh* **2825 – 2829**

Palladium-Catalyzed C–H Arylation of α,β-Unsaturated Imines: Catalyst-Controlled Synthesis of Enamine and Allylic Amine Derivatives



A tale of two catalysts: One was the best α-arylation catalyst, one was the worst (it gave only γ-arylation). Their opposite regioselectivity in a unique umpolung C–H arylation of palladium azapentadienyl intermediates enabled the selective synthesis of allylic amine and enamine derivatives (see scheme). A cation–π interaction with the heterobimetallic Pd/Na NiXantphos catalyst is proposed to be responsible for the unusual γ-regioselectivity.

Metastable and compressed: Low-temperature solution synthesis yields uniform colloidal nanostructures containing few-layer nanosheets of 1T′-$MoTe_2$, a metastable layered transition-metal dichalcogenide of significant emerging interest for diverse applications. The 1T′-$MoTe_2$ nanomaterial exhibits a lattice compression of about 1 % relative to its bulk analogue.



Layered Compounds

Y. Sun, Y. Wang, D. Sun, B. R. Carvalho, C. G. Read, C. Lee, Z. Lin, K. Fujisawa, J. A. Robinson, V. H. Crespi, M. Terrones,* R. E. Schaak* ______ **2830 – 2834**

Low-Temperature Solution Synthesis of Few-Layer 1T′-$MoTe_2$ Nanostructures Exhibiting Lattice Compression

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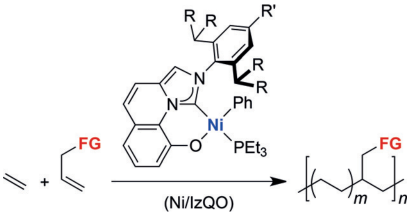
So long: A series of neutral nickel complexes bearing imidazo[1,5-*a*]quinolin-9-olate-1-ylidene (IzQO) ligands is reported. The Ni/IzQO system can catalyze ethylene polymerization at 50–100 °C in the absence of any co-catalyst, whereas most known nickel-based catalysts are deactivated at this temperature range. This was successfully applied to the copolymerization of ethylene with allyl monomers to obtain the corresponding copolymers with high molecular weight.



Polymerization

W-J. Tao, R. Nakano, S. Ito, K. Nozaki* ______ **2835 – 2839**

Copolymerization of Ethylene and Polar Monomers by Using Ni/IzQO Catalysts

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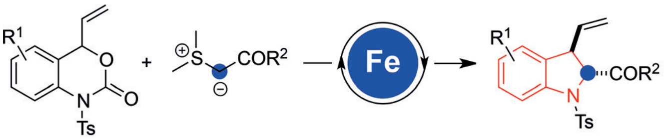

54–95% yields, up to >95:5 d.r.

Going in reverse: The first example of iron-catalyzed decarboxylative formal (4+1) cycloaddition reactions, which exploit the reverse reactivity of ambident iron-stabilized intermediates, was developed. By using this method, a wide range of functionalized indoline products were facilely prepared in generally good yields and high stereoselectivities from easily available starting materials. Ts = 4-toluenesulfonyl.

Heterocycle Synthesis

Q. Wang, X. Qi, L.-Q. Lu,* T.-R. Li, Z.-G. Yuan, K. Zhang, B.-J. Li, Y. Lan,* W.-J. Xiao* ______ **2840 – 2844**

Iron-Catalyzed Decarboxylative (4+1) Cycloadditions: Exploiting the Reactivity of Ambident Iron-Stabilized Intermediates

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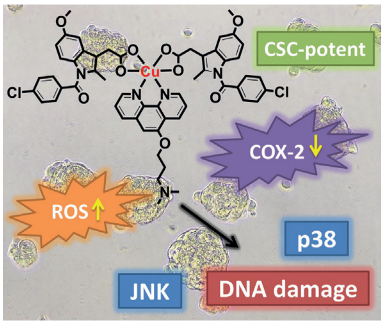
Coppers lock up cancer: Effective treatments of breast cancer often require compounds that can destroy the breast cancer stem cells (CSCs). A series of Cu^{II}-phenanthroline complexes bearing the anti-inflammatory drug, indomethacin, selectively kills breast CSCs by elevating intracellular reactive oxygen species levels and inhibiting cyclooxygenase-2.

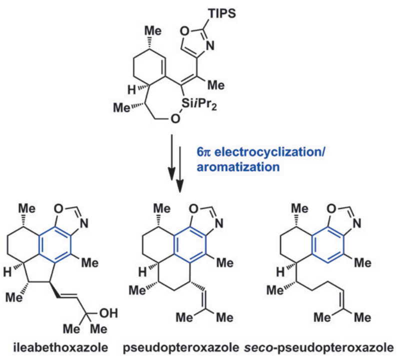


Anticancer Agents

J. N. Boodram, I. J. Mcgregor, P. M. Bruno, P. B. Cressey, M. T. Hemann, K. Suntharalingam* ______ **2845 – 2850**

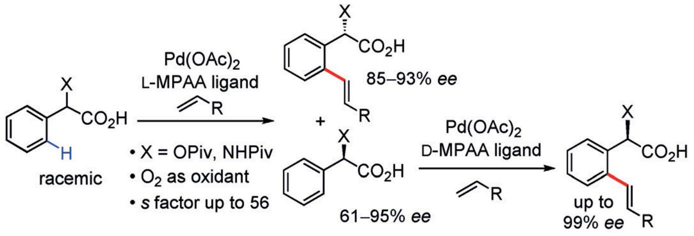
Breast Cancer Stem Cell Potent Copper(II)–Non-Steroidal Anti-Inflammatory Drug Complexes

Natural Products



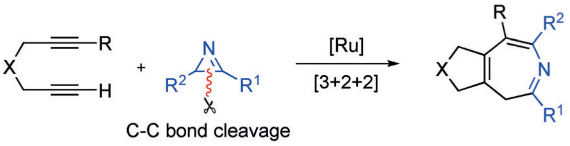
The antituberculosis diterpenoids ileabethoxazole, pseudopteroxazole, and *seco*-pseudopteroxazole were prepared by total synthesis. An important triene intermediate was obtained by an alkyne carbopalladation/Stille reaction cascade and then subjected to a one-pot 6π electrocyclization/aromatization process to assemble the multisubstituted aromatic core.

C–H Activation



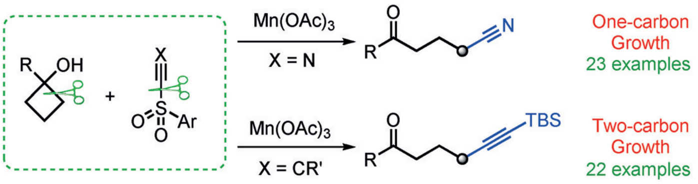
Quick to react: A palladium(II)-catalyzed enantioselective C–H olefination of racemic α-hydroxy and α-amino phenylacetic acids by kinetic resolution has been developed using mono-N-protected amino acids (MPAAs) as chiral ligands. The installation of an olefin unit can lead to a novel class of chiral mandelic acid and phenylglycine derivatives.

Heterocycle Synthesis

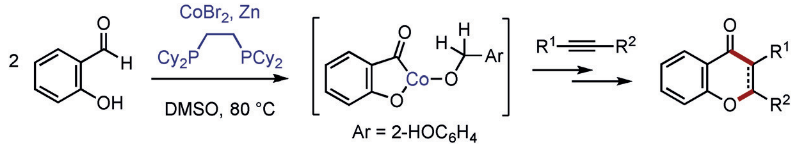


Fusion rings: The ruthenium-catalyzed [3+2+2] cycloaddition of 2*H*-azirines with diynes has been established. This approach features an unprecedented metal-catalyzed C–C bond cleavage of 2*H*-azirines at room temperature, and achieves the challenging construction of aza-seven-membered rings from diynes.

C–C Bond-Forming Reactions



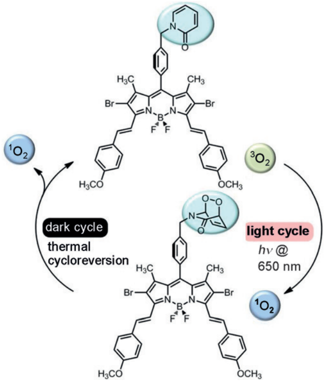
Chain extension: A novel C–C bond-forming strategy employing manganese-catalyzed ring opening of cyclobutanol substrates, followed by cyanation or ethynylation, is described. A cyano C1 unit and ethynyl C2 unit are regiospecifically introduced to the γ-position of ketones at room temperature, thus providing a mild yet powerful tool for the production of elusive aliphatic nitriles and alkynes.



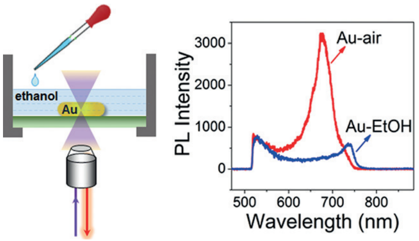
An unexpected outcome: A cobalt(I)–diphosphine catalyst has been employed for the coupling of salicylaldehyde and internal alkynes to afford, depending on the alkyne substituents, chromone or 4-chromanone derivatives. These annulation reactions feature aldehyde C–H oxidative addition and subsequent hydrometalation of another aldehyde as key steps.

Cobalt Catalysis

The power of the dark side: A BODIPY-based photosensitizer with a tethered 2-pyridone moiety effectively "stores" singlet oxygen under photosensitization conditions (by conversion of the pyridone fragment into an endoperoxide) and releases it thermally in the dark. This approach could hold significant potential in fractional photodynamic therapy, in which light must to be applied in intervals. BODIPY = boron–dipyrromethene.

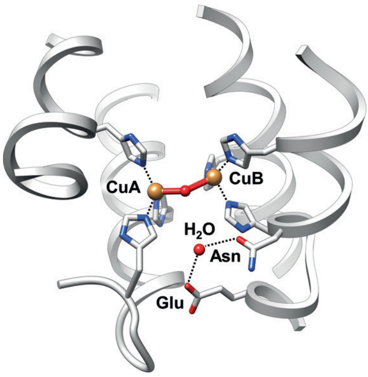


Photodynamic Therapy



Surface plasmons: Using plasmonic photoluminescence spectroscopy, a novel sensing method was developed for catalytic ethanol oxidation reactions at the single-nanoparticle level (see picture). A catalytic ethanol oxidation reaction occurred on the surface of a single Au nanorod and resulted in a clear quenching phenomenon of the photoluminescence of the Au nanorod.

Nanocatalysis



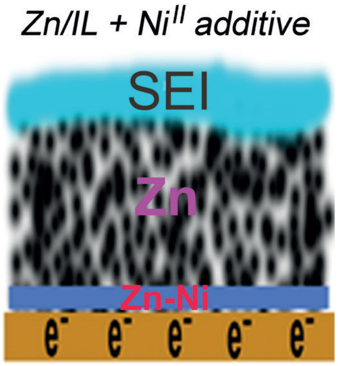
Mystery solved: The long-debated reactivity difference between tyrosinases and catechol oxidases can be traced back to one asparagine, which in tyrosinases is required to deprotonate monophenolic substrates via a conserved water molecule but is absent in catechol oxidases.

Oxidases

Electrodeposition

Z. Liu, T. Cui, G. Pulletikurthi, A. Lahiri,
T. Carstens, M. Olschewski,
F. Endres* ________________ **2889 – 2893**

Dendrite-Free Nanocrystalline Zinc Electrodeposition from an Ionic Liquid Containing Nickel Triflate for Rechargeable Zn-Based Batteries

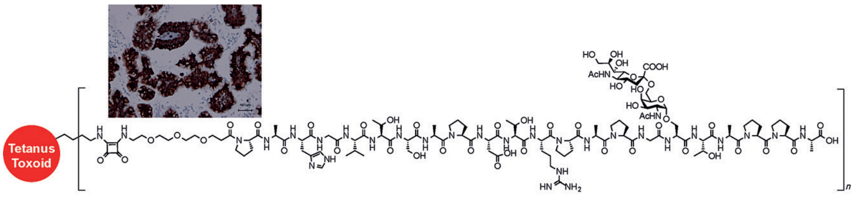


Deposits and returns: A dendrite-free zinc deposit with a nanocrystalline structure is obtained when nickel triflate is used as an additive in a zinc triflate containing ionic liquid (IL). The formation of a thin layer of Zn–Ni alloy and a solid electrolyte interface (SEI) layer on the electrode affect the nucleation and growth of zinc.

Medicinal Chemistry

B. Palitzsch, N. Gaidzik, N. Stergiou,
S. Stahn, S. Hartmann, B. Gerlitzki,
N. Teusch, P. Flemming, E. Schmitt,*
H. Kunz* ________________ **2894 – 2898**

A Synthetic Glycopeptide Vaccine for the Induction of a Monoclonal Antibody that Differentiates between Normal and Tumor Mammary Cells and Enables the Diagnosis of Human Pancreatic Cancer



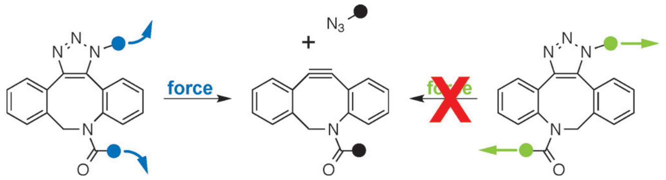
A

Synthetic antitumor vaccines obtained by the coupling of MUC1 glycopeptides of varied sequence and glycosylation to a tetanus toxoid induce very strong immune responses in mice, but antibodies of distinctly different binding to tumor cells. From a mouse immunized with vaccine **A**, a monoclonal IgG1 antibody was generated that differentiates between normal und tumor human mammary cells and selectively recognizes the tumor cells in human pancreas tumor tissues.

Mechanochemistry

M. J. Jacobs, G. Schneider,
K. G. Blank* ________________ **2899 – 2902**

Mechanical Reversibility of Strain-Promoted Azide–Alkyne Cycloaddition Reactions

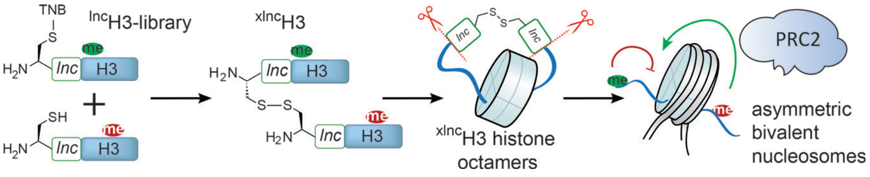


Broken by you: Mechanical cycloreversion of triazoles depends on the direction of the applied force (shearing vs. unzipping) acting on the triazole unit. Computational screening of a number of triazoles formed from strained alkynes shows that cycloreversion only occurs when the force acts in the unzipping geometry and identifies azadibenzylcyclooctyne (DIBAC) as a promising strained alkyne for mechanically reversible triazole structures.

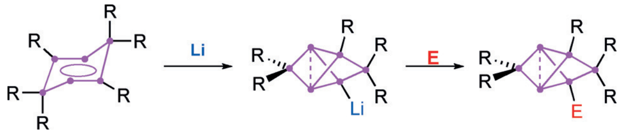
Post-translational Modifications

C. C. Lechner, N. D. Agashe,
B. Fierz* ________________ **2903 – 2906**

Traceless Synthesis of Asymmetrically Modified Bivalent Nucleosomes

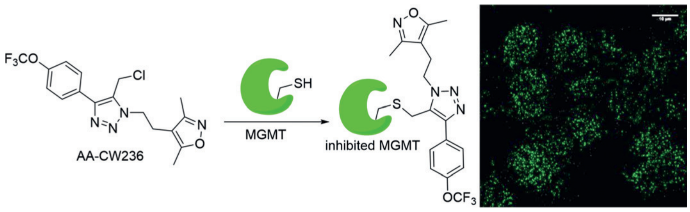


Make and break: A facile and traceless method to assemble asymmetric post-translationally modified nucleosomes was developed. By using a cleavable peptide tag (the Inc-tag), a library of asymmetric bivalent nucleosomes was generated, which allowed investigation of the intra-nucleosomal crosstalk between two modifications in the regulation of the histone methyltransferase PRC2.



Nakedness tolerated by functionaries: An unsaturated silicon cluster (siliconoid) with a negatively charged vertex efficiently transfers the intact siliconoid motif to various electrophilic substrates. Surprisingly, the "naked" silicon atoms are tolerated by functional groups, even by a carbonyl moiety, otherwise known to be extremely reactive towards low-coordinate silicon compounds (magenta dots = Si; R = 2,4,6-triisopropylphenyl, E = electrophile).

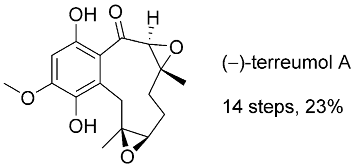
Main-Group Clusters



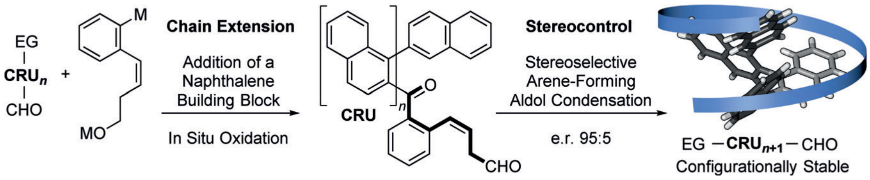
Don't fix what is broken: MGMT is an important DNA repair protein, but it also repairs DNA damage caused by chemotherapy in cancer cells. Chloromethyl triazoles (CMTs) are a novel, readily available chemical scaffold for cysteine-reactive covalent inhibitors. Synthesis of a small collection of CMTs leads to the identification of AA-CW236 as the first potent and selective non-pseudosubstrate inhibitor of MGMT.

Drug Discovery

The cytotoxic meroterpenoids (−)-terreumol A and C from the mushroom *Tricholoma terreum* were synthesized for the first time. The key step of the enantioselective total synthesis of terreumol C is a ring-closing metathesis to form a trisubstituted *Z* double bond embedded in a 10-membered ring.



Total Synthesis



Keep in good shape: The stereoisomers of configurationally stable oligo-1,2-naphthylenes were obtained by repeated building block addition and stereoselective arene-forming aldol condensations. The helix sense of the secondary structure was induced with 95:5 enantiocontrol by a natural amino acid as catalyst, and quaternaphthalene diastereoisomers featuring two chirality axes were accessible. CRU: constitutional repeating unit; EG: end group.

Aldol Reactions

Process Development

T. Gaide, J. M. Dreimann, A. Behr,
A. J. Vorholt* ______ 2924 – 2928

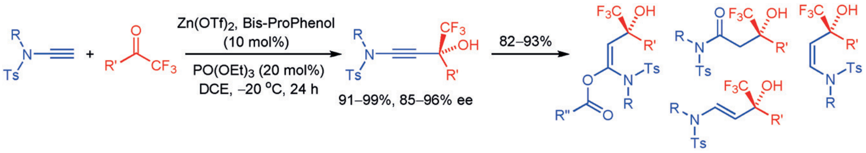
Overcoming Phase-Transfer Limitations in the Conversion of Lipophilic Oleo Compounds in Aqueous Media—A Thermomorphic Approach

Bringing cat and dog together: The intelligent selection of solvents facilitates both the reaction and the recovery of the Rh/SulfoXantphos catalyst. Green solvents (water and 1-butanol) and the use of a renewable feedstock contribute to the development of sustainable processes.

Asymmetric Synthesis

A. M. Cook, C. Wolf* ______ 2929 – 2933

Efficient Access to Multifunctional Trifluoromethyl Alcohols through Base-Free Catalytic Asymmetric C—C Bond Formation with Terminal Ynamides

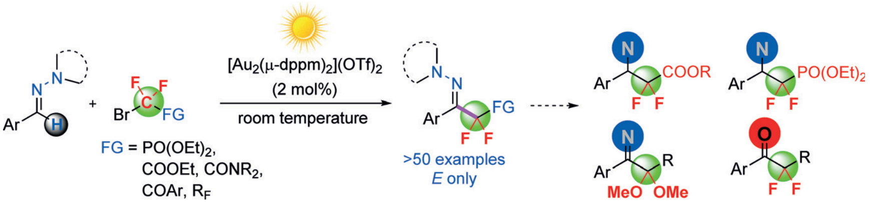


The asymmetric addition of terminal ynamides to trifluoromethyl ketones with a chiral zinc catalyst gives CF_3-substituted propargylic alcohols. The β-hydroxy-β-trifluoromethyl ynamides undergo selective transformations to chiral *Z*- and *E*-enamides, an amide, and N,O-ketene acetals. Regioselective hydration, stereoselective reduction, and hydroacyloxylation of the β-hydroxy ynamides proceed in high yields and without loss of the enantiomeric excess.

Fluoroalkylation

J. Xie, T. Zhang, F. Chen, N. Mehrkens,
F. Rominger, M. Rudolph,
A. S. K. Hashmi* ______ 2934 – 2938

Gold-Catalyzed Highly Selective Photoredox C(sp^2)—H Difluoroalkylation and Perfluoroalkylation of Hydrazones

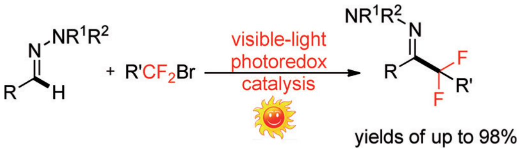


The radical C—H fluoroalkylation of hydrazones in the presence of a gold photoredox catalyst is compatible with a broad range of functional groups and provides access to *E*-configured products that can be converted into useful synthetic building blocks. A radical intermediate was trapped and analyzed by EPR spectroscopy.

Photocatalysis

P. Xu, G. Wang, Y. Zhu, W. Li, Y. Cheng,
S. Li,* C. Zhu* ______ 2939 – 2943

Visible-Light Photoredox-Catalyzed C—H Difluoroalkylation of Hydrazones through an Aminyl Radical/Polar Mechanism



Grab an electron from an aminyl radical: The unprecedented title reaction involving aldehyde-derived hydrazones was developed. A variety of versatile difluorinated hydrazones were synthesized under mild reaction conditions and in good to excellent yields. Mechanistic analysis and theoretical calculations suggest an aminyl radical/polar crossover mechanism.

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

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

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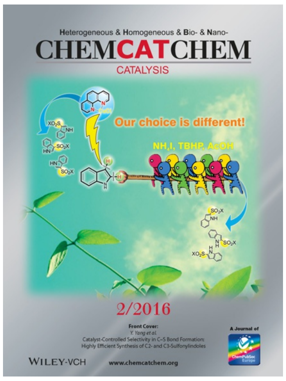

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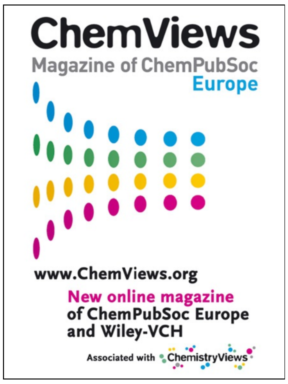

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