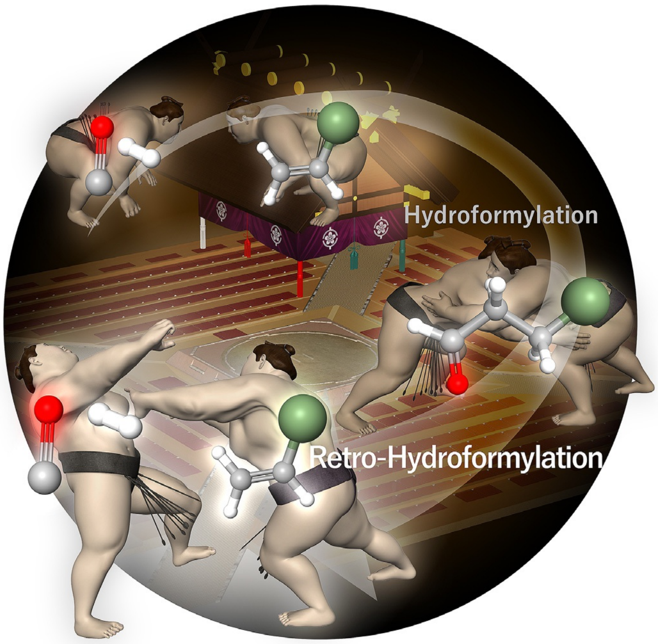
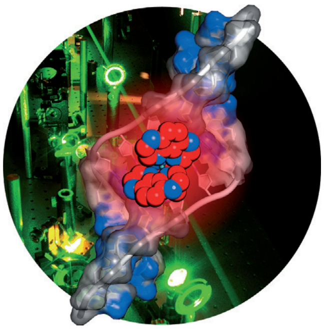


… an alkene captures synthesis gas ($CO+H_2$) to form an aldehyde. Since its discovery in 1938, knowledge on the hydroformylation reaction has continuously grown, and it is finally possible to push the reaction in the reverse direction. The first example of retro-hydroformylation, that is, the conversion of an aldehyde into the corresponding alkene and synthesis gas, is thus described by K. Nozaki et al. in their Communication on page 8458 ff.

DNA Photooxidation

Small changes in DNA sequence can have major biological effects. P. M. Keane, C. J. Cardin, J. M. Kelly et al. show on page 8364 ff. that the reversal of a single base-pair step has a dramatic effect on the guanine photooxidation by a DNA-intercalating Ru^{II} complex.

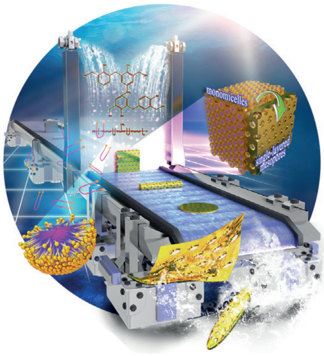


Natural Product Synthesis

A divergent approach featuring efficient stereoselective transformations from a common precursor, (*S*)-perillic acid, enables the synthesis of machaeriols and cannabinoids by A. Studer and F. Klotter in their Communication on page 8547 ff.

Mesoporous Layered Structures

In their Communication on page 8425 ff., G. F. Zheng, D. Y. Zhao, et al. present a new approach for the synthesis of single-layered mesoporous carbon films on substrates with different surface compositions and morphologies.



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Editorial

"... Inorganic chemistry has evolved from fundamental studies to the forefronts of interdisciplinary research. What was considered to be impossible or elusive has now become feasible. While we still keep our identity as inorganic chemists, the sharp demarcation between the divisions of different subject disciplines or subdisciplines is no longer relevant ..."
Read more in the Editorial by Vivian W.-W. Yam.

V. W.-W. Yam* ______ **8304–8305**

Inorganic Chemistry: A Prestigious History and a Bright Future

Service

Spotlight on Angewandte's Sister Journals **8324–8327**

Author Profile

"I get advice from my father and my colleagues. When I was eighteen I wanted to be a mathematician ..."
This and more about Mercouri G. Kanatzidis can be found on page 8328.

Mercouri G. Kanatzidis ______ **8328–8329**

News


G. A. Ozin


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A. N. Khlobystov


S. T. Liddle


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R. S. Paton


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Royal Society of Chemistry Prizes 2015 ______ **8330–8331**

Books

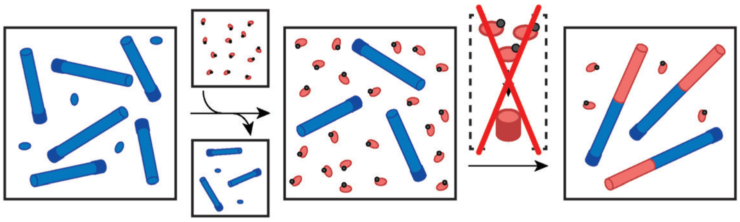
Modern Alkyne Chemistry — Barry M. Trost, Chao-Jun Li — *reviewed by M. M. Haley** ______ **8332**

Highlights

Supramolecular Polymerization

D. van der Zwaag, T. F. A. de Greef,
E. W. Meijer* ______ **8334–8336**

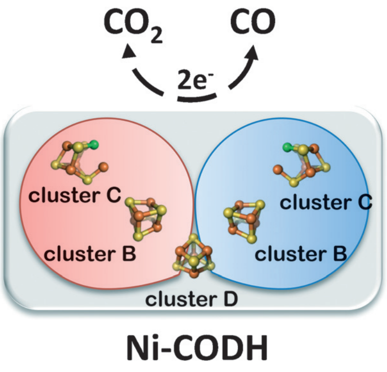
Programmable Supramolecular Polymerizations



Living large: Rational design of self-assembly pathways has been demonstrated in supramolecular polymers. By controlling the concentration of an aggregation-competent monomer through intramolecular interactions, living supramolecular polymerization conditions were achieved. This universal approach can be used to obtain aggregates of well-defined length and narrow dispersity, and allows access to new supramolecular polymer architectures.

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

Unexpected similarities: Atomic-resolution structures of CO_2- and NCO^--bound nickel-containing carbon monoxide dehydrogenases (Ni-CODHs) reveal that the reaction pathway of this enzyme involves an intermediate that is generated by two-electron reduction.

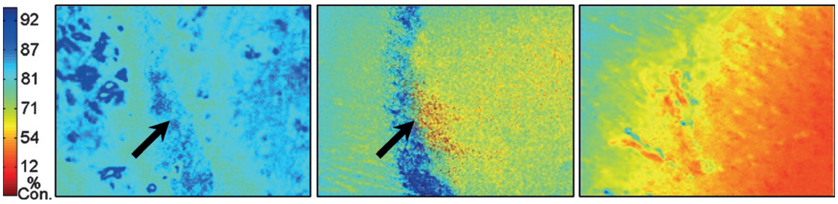


Enzyme Crystallography

M. W. Ribbe* ———— **8337 – 8339**

Insights into the Mechanism of Carbon Monoxide Dehydrogenase at Atomic Resolution

Reviews



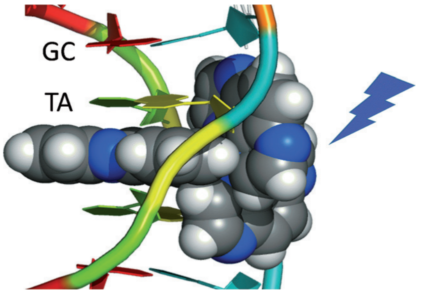
Tracking oxygen: To fully comprehend oxygen's critical role in the biochemistry of life, various techniques have been developed for the measurement of its physiological tensions in different environments. There have been exciting advances in both instrumentation and method development, leading to techniques that are capable of providing oxygenation information from sub-cellular to macroscopic tissue levels (image: changes in oxygen consumption in a full-thickness burn).

Oxygen Sensing

E. Roussakis, Z. Li, A. J. Nichols,
C. L. Evans* ———— **8340 – 8362**

Oxygen-Sensing Methods in Biomedicine from the Macroscale to the Microscale

Communications



Small change, big impact: The reversal of a single base-pair step has a dramatic effect on the rates and yield of guanine photo-oxidation by a DNA-intercalating Ru^{II} complex. Identifying features in the time-resolved IR spectra also allows binding at GC sites to be distinguished from AT sites, showing that efficient electron transfer only occurs to adjacent guanines in this system.

DNA Photo-Oxidation

P. M. Keane,* F. E. Poynton, J. P. Hall,
I. V. Sazanovich, M. Towrie,
T. Gunnlaugsson, S. J. Quinn,
C. J. Cardin,* J. M. Kelly* —— **8364 – 8368**

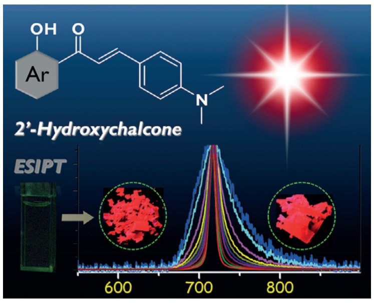
Reversal of a Single Base-Pair Step Controls Guanine Photo-Oxidation by an Intercalating Ruthenium(II) Dipyridophenazine Complex

Frontispiece

Near-Infrared Spectroscopy

X. Cheng, K. Wang, S. Huang, H. Zhang,
H. Zhang,* Y. Wang ________ **8369 – 8373**

Organic Crystals with Near-Infrared Amplified Spontaneous Emissions Based on 2′-Hydroxychalcone Derivatives: Subtle Structure Modification but Great Property Change

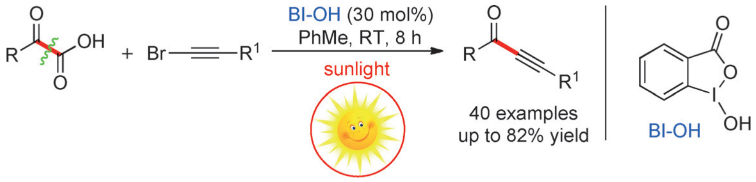


Highly efficient near-infrared fluorescent organic crystals with amplified spontaneous emissions have been achieved in large amounts based on structurally simple organic molecules. These findings also exemplify how the optical properties of organic crystals can be tuned in a rational and efficient way by controlling molecular packing mode and molecular conformation.

Photochemistry

H. Tan, H. Li,* W. Ji,
L. Wang* ________ **8374 – 8377**

Sunlight-Driven Decarboxylative Alkynylation of α-Keto Acids with Bromoacetylenes by Hypervalent Iodine Reagent Catalysis: A Facile Approach to Ynones



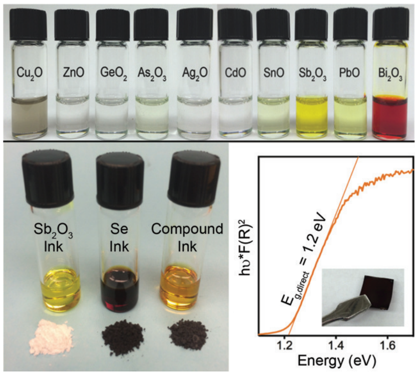
Under the sun: A novel and practical hypervalent iodine(III) reagent catalyzes the decarboxylative alkynylation of α-keto acids with bromoacetylenes under sunlight irradiation at room temperature. The product ynones are generated in good yields and mechanistic studies demonstrate that the reaction proceeds through a radical process.

Metal Chalcogenides

C. L. McCarthy, D. H. Webber,
E. C. Schueller,
R. L. Brutchey* ________ **8378 – 8381**

Solution-Phase Conversion of Bulk Metal Oxides to Metal Chalcogenides Using a Simple Thiol–Amine Solvent Mixture

It's in the mix: Conversion of bulk oxides to chalcogenides by ambient solution processing is demonstrated. Sulfides are recovered by low-temperature annealing of inks of bulk oxides dissolved in thiol–amine mixtures, while selenides and tellurides are synthesized from compound inks comprised of a dissolved oxide with Se or Te. The procedure was used to produce photoresponsive thin films and alloys with tunable band gaps.

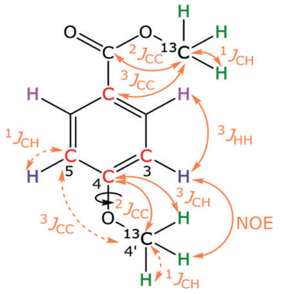


NMR Spectroscopy

N. G. A. Bell, A. A. L. Michalchuk,
J. W. T. Blackburn, M. C. Graham,
D. Uhrín* ________ **8382 – 8385**

Isotope-Filtered 4D NMR Spectroscopy for Structure Determination of Humic Substances

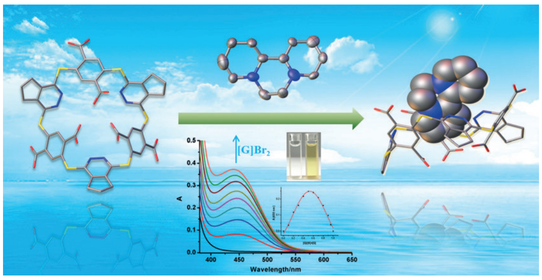
Unraveling the molecular make-up of chromatographically inseparable mixtures remains a significant analytical challenge. Illustrated here is the structure elucidation of phenolic aromatic moieties of a peat soil fulvic acid using *n*-dimensional NMR spectroscopy that uses tags to report directly on the identity of the tagged molecules.



Host–Guest Complexes

Q.-H. Guo, L. Zhao,
M.-X. Wang* ______ 8386 – 8389

Synthesis and Molecular Recognition of Water-Soluble S_6-Corona[3]arene[3]pyridazines



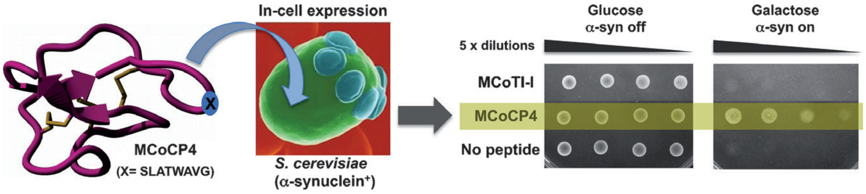
Waterproofed: Unprecedented water-soluble S_6-corona[3]arene[3]pyridazines were synthesized efficiently through a four-step reaction sequence. They act as powerful and selective macrocyclic hosts to form 1:1 complexes with electron-deficient guests with K_a up to $(1.18 \pm 0.06) \times 10^5\ \mathrm{M}^{-1}$ in water.

Protein Expression

K. Jagadish, A. Gould, R. Borra,
S. Majumder, Z. Mushtaq, A. Shekhtman,
J. A. Camarero* ______ 8390 – 8394

Recombinant Expression and Phenotypic Screening of a Bioactive Cyclotide Against α-Synuclein-Induced Cytotoxicity in Baker's Yeast

Inside Cover



Bioactive folded cyclotides can be produced in eukaryotic microorganisms such as yeast *S. cerevisiae* by protein trans-splicing using highly efficient split inteins. This approach was used for the production of a novel cyclotide (MCoCP4) that was able to inhibit α-syn-induced cytotoxicity in live yeast cells.

Multicomponent Reactions

T. Flagstad, M. T. Petersen,
T. E. Nielsen* ______ 8395 – 8397

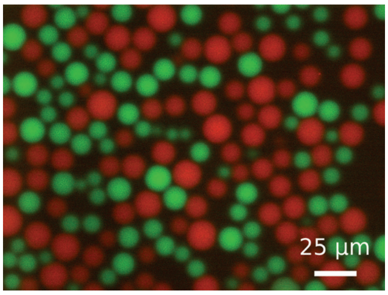
A Four-Component Reaction for the Synthesis of Dioxadiazaborocines

All together now: A four-component reaction was developed that combines a hydrazide, an α-hydroxy aldehyde, and two orthogonally reactive boronic acids to give structurally distinct enantio- and diastereomerically pure bicyclic boronates, termed dioxadiazaborocines. One boronic acid reacts as a carbon nucleophile and the other as a boron electrophile to provide heterocyclic boronates with multiple stereocenters in high yield.

Microfluidics

D. van Swaay, T.-Y. D. Tang, S. Mann,*
A. de Mello* ______ 8398 – 8401

Microfluidic Formation of Membrane-Free Aqueous Coacervate Droplets in Water



Stable dispersions of polymer/nucleotide or polymer/polysaccharide coacervate droplets with a narrow size distribution are prepared in water using microfluidic flow focusing. Two distinct populations of co-located coacervate droplets containing different DNA oligonucleotides are produced simultaneously, and shown to coexist in close proximity without exchange of genetic information for over six days.

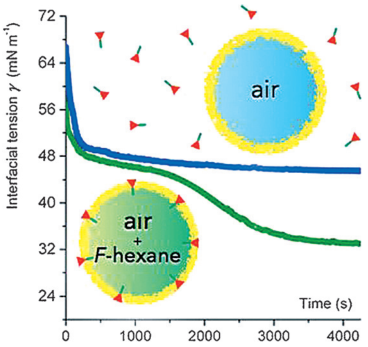
VIP

Transmembrane Molecular Recognition

G. Yang, M. O'Duill, V. Gouverneur,
M. P. Krafft* ____________ **8402 – 8406**

Recruitment and Immobilization of a Fluorinated Biomarker Across an Interfacial Phospholipid Film using a Fluorocarbon Gas

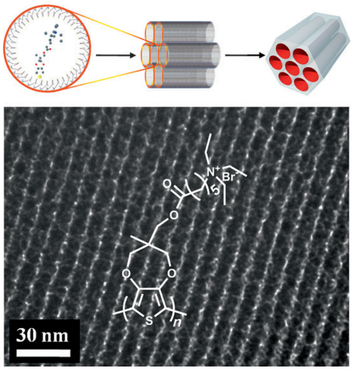
Attractive interactions can arise between a fluorocarbon gas and a C_2F_5-labeled compound (red triangle with green tail) across a phospholipid monolayer, allowing recruitment and immobilization of the fluorinated compound in the phospholipid layer. This new phenomenon allowed preparation of microbubbles loaded with a C_2F_5-labeled hypoxia biomarker.



Conducting Materials

J. Kim, B. Kim, C. Anand, A. Mano,
J. S. M. Zaidi, K. Ariga, J. You, A. Vinu,*
E. Kim* ____________ **8407 – 8410**

A Single-Step Synthesis of Electroactive Mesoporous ProDOT-Silica Structures

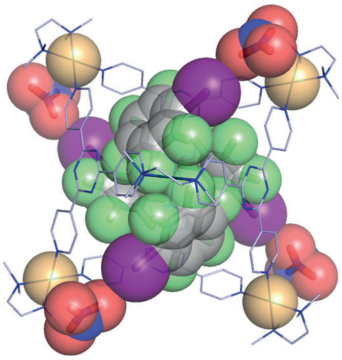


Pore over: Highly ordered mesoporous silica hybrid nanocomposites with ultralarge pores and high conductivity were synthesized in a single step. The method employs a novel cationic surfactant having a bulky 3,4-propylenedioxythiophene (ProDOT) tail group, and does not require high-temperature calcination or a washing procedure.

Host–Guest Complexes

H. Takezawa, T. Murase, G. Resnati,*
P. Metrangolo,* M. Fujita* **8411 – 8414**

Halogen-Bond-Assisted Guest Inclusion in a Synthetic Cavity

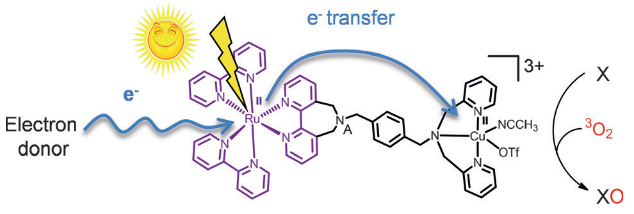


Close but comfortable: Iodoperfluorocarbons were efficiently included in a self-assembled cage owing to halogen bonding (XB) with NO_3^- anions or H_2O molecules (see picture: C gray, N blue, O red, F green, I purple, Pd brown). The confined cavity of the cage enhanced XB, as confirmed by NMR spectroscopy in solution and X-ray crystallography in the solid state. Pairwise selective XB between $C_6F_3I_3$ and $C_6H_5NMe_2$ within the cavity was also observed.

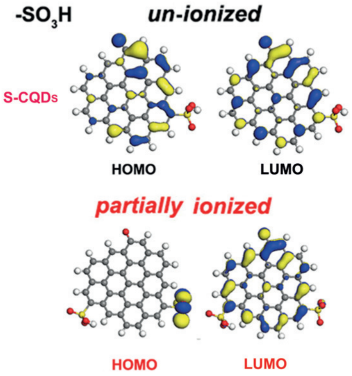
Photocatalysis

W. Iali, P.-H. Lanoe, S. Torelli,*
D. Jouvenot, F. Loiseau, C. Lebrun,
O. Hamelin,* S. Ménage __ **8415 – 8419**

A Ruthenium(II)–Copper(II) Dyad for the Photocatalytic Oxygenation of Organic Substrates Mediated by Dioxygen Activation



O_2 activation oxidation: A new Ru-Cu dyad has been isolated and confirmed to be efficient for the photocatalytic oxygenation of organic substrates. Mechanistic investigations confirmed a photoinduced electron transfer from the photosensitizer to the copper catalytic center prior to O_2 activation. X = substrate (sulfides, alkenes, phosphines).



Carbon quantum dots (CQDs) decorated with small amounts of hydrogensulfate groups exhibit a photogenerated acidity that produces highly efficient acid catalysis of the ring-opening of epoxides with methanol and other primary alcohols. This reversible, light-switchable acidity is due to photoexcitation and charge separation in the carbon quantum dots, which create an electron-withdrawing effect from the acidic groups

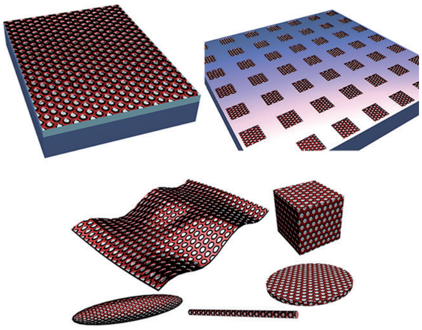
Photocatalysis

H. Li, C. Sun, M. Ali, F. Zhou, X. Zhang,
D. R. MacFarlane* ________ **8420 – 8424**

Sulfated Carbon Quantum Dots as Efficient Visible-Light Switchable Acid Catalysts for Room-Temperature Ring-Opening Reactions

---

Extremely thin and transparent: Single-layered 2D mesoporous polymer/carbon ultrathin films were grown by self-assembly of monomicelles at the interfaces of various kinds of substrates (see picture). This method is a general and common modification strategy for a large variety of substrate surfaces, and can be used for the preparation of thin films ranging from inch size to nanometer scale.

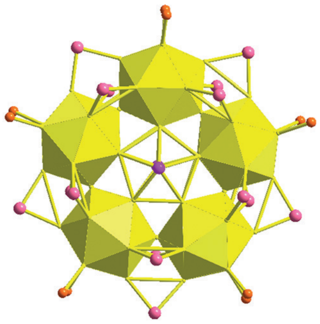


Mesoporous Carbon Materials

Y. Fang, Y. Y. Lv, J. Tang, H. Wu, D. S. Jia,
D. Feng, B. Kong, Y. Wang, A. A. Elzatahry,
D. Al-Dahyan, Q. Zhang, G. F. Zheng,*
D. Y. Zhao* ________ **8425 – 8429**

Growth of Single-Layered Two-Dimensional Mesoporous Polymer/Carbon Films by Self-Assembly of Monomicelles at the Interfaces of Various Substrates

Back Cover



The X-ray crystallographic structure of the [$Au_{60}Se_2(SePh)_{15}(Ph_3P)_{10}]^+$ nanocluster exhibits a closed gold ring that contains five icosahedral Au_{13} building blocks, which are clipped together by Au–Se–Au linkages. This new material can be used for optical limiting. These results offer a basis for a deeper understanding of how to control cluster-assembled materials for tailoring their functionalities.

Surface Chemistry

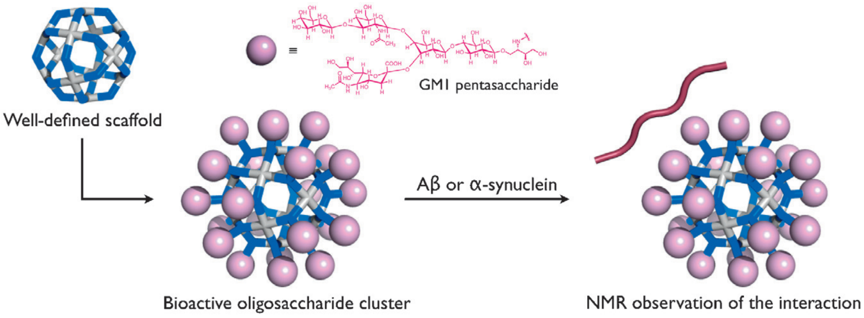
Y. Song, F. Fu, J. Zhang, J. Chai, X. Kang,
P. Li, S. Li, H. Zhou,
M. Zhu* ________ **8430 – 8434**

The Magic Au_{60} Nanocluster: A New Cluster-Assembled Material with Five Au_{13} Building Blocks

Self-Assembly

S. Sato,* Y. Yoshimasa, D. Fujita,
M. Yagi-Utsumi, T. Yamaguchi, K. Kato,*
M. Fujita* **8435–8439**

A Self-Assembled Spherical Complex Displaying a Gangliosidic Glycan Cluster Capable of Interacting with Amyloidogenic Proteins

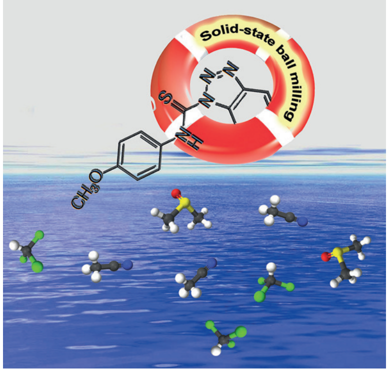


A pentasaccharide cluster derived from natural ganglioside was synthesized by chemical modification of self-assembled spherical scaffolds. The cluster interacts with amyloidogenic proteins, amyloid β (Aβ), or α-synuclein, demonstrating its inherent recognition abilities through clustering effect. This discrete cluster allows characterizing the early encounter stage of biomolecular interactions of pathological interest using NMR spectroscopy.

Mechanochemistry

V. Štrukil,* D. Gracin, O. V. Magdysyuk,
R. E. Dinnebier, T. Friščić* **8440–8443**

Trapping Reactive Intermediates by Mechanochemistry: Elusive Aryl *N*-Thiocarbamoylbenzotriazoles as Bench-Stable Reagents

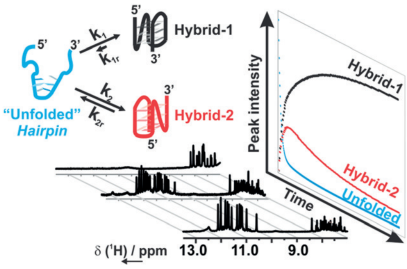


Saved from drowning in solvent: Switching from solution to mechanochemistry enabled the first-time isolation and structural characterization of aromatic *N*-thiocarbamoyl benzotriazoles, a family of reactive and previously thought unisolable intermediates of thiocarbamoylation reactions.

DNA Structures

I. Bessi, H. R. A. Jonker, C. Richter,
H. Schwalbe* **8444–8448**

Involvement of Long-Lived Intermediate States in the Complex Folding Pathway of the Human Telomeric G-Quadruplex

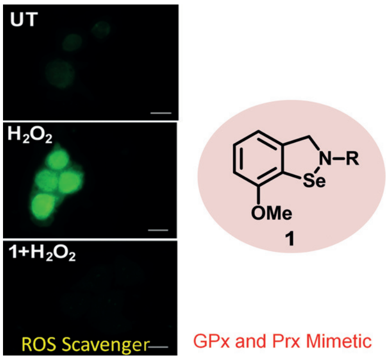


By NMR spectroscopy, three long-lived states were detected during the K^+-induced folding of human telomeric DNA: a major conformation (hybrid-1), a previously structurally uncharacterized minor conformation (hybrid-2), which is formed faster than the more stable hybrid-1 conformation, and a partially unfolded intermediate. The intermediate state can be described as an ensemble of hairpin-like structures.

Cytoprotection

D. Bhowmick, S. Srivastava, P. D'Silva,*
G. Mugesh* **8449–8453**

Highly Efficient Glutathione Peroxidase and Peroxiredoxin Mimetics Protect Mammalian Cells against Oxidative Damage

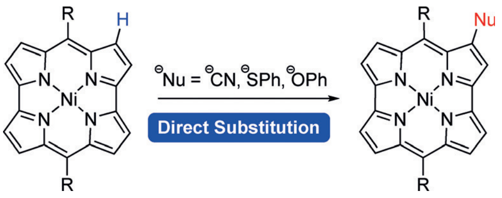


Isoselenazoles display high glutathione peroxidase (GPx) and peroxiredoxin (Prx) activities and provide remarkable cytoprotection to human cells, mainly by catalyzing the reduction of H_2O_2 in the presence of cellular thiols. These compounds thus have the potential to be used as therapeutic agents for disorders mediated by reactive oxygen species (ROS; UT = untreated).

Porphyrinoids

R. Nozawa, K. Yamamoto, J.-Y. Shin, S. Hiroto, H. Shinokubo* ___ 8454–8457

Regioselective Nucleophilic Functionalization of Antiaromatic Nickel(II) Norcorroles



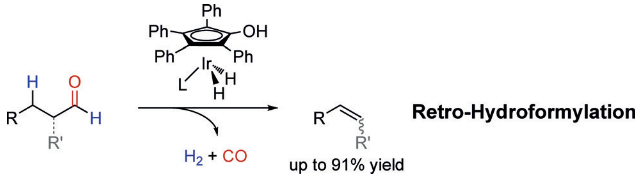
At the core: Cyanide, phenylthiolate, and phenoxide anions react with an antiaromatic nickel(II) norcorrole complex in the absence of a catalyst to yield substitution products. The reaction takes place regioselectively at the β-positions proximal to the meso substituents. The distinct antiaromatic property of the norcorrole core is retained in the functionalized products.

Iridium Catalysis

S. Kusumoto, T. Tatsuki, K. Nozaki* ___ 8458–8461

The Retro-Hydroformylation Reaction

Front Cover

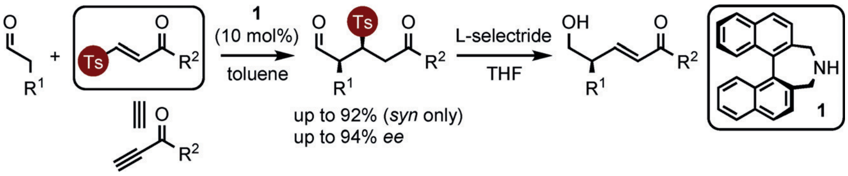


The reverse reaction of hydroformylation, a so-called retro-hydroformylation, has been developed. In the presence of an iridium catalyst, alkenes were obtained from aliphatic aldehydes in up to 91 % yield along with the quantitative evolution of synthesis gas. Mechanistic studies suggest that this reaction indeed proceeds by a retro-hydroformylation mechanism.

Asymmetric Catalysis

T. Kano, H. Sugimoto, H. Maruyama, K. Maruoka* ___ 8462–8465

Regio- and Stereoselective Conjugate Addition of Aldehydes to β-Tosyl Enones under the Catalysis of a Binaphthyl-Modified Chiral Amine

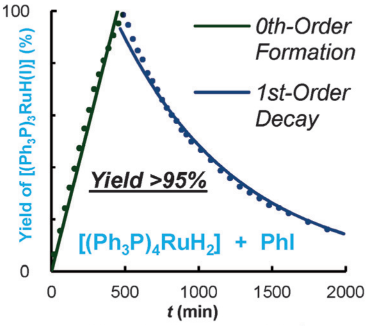


A good substitute: The regio-, diastereo-, and enantioselective conjugate addition of aldehydes to β-tosyl enones, which serve as ynone surrogates, was promoted by a simple axially chiral amine catalyst. The conjugate adducts were readily converted into less accessible enones with a γ stereogenic center through β elimination of the tosyl group (see scheme) and could thus be used in a further conjugate addition reaction.

Reaction Mechanisms

F. M. Miloserdov, D. McKay, B. K. Muñoz, H. Samouei, S. A. Macgregor,* V. V. Grushin* ___ 8466–8470

Exceedingly Facile Ph–X Activation (X = Cl, Br, I) with Ruthenium(II): Arresting Kinetics, Autocatalysis, and Mechanisms



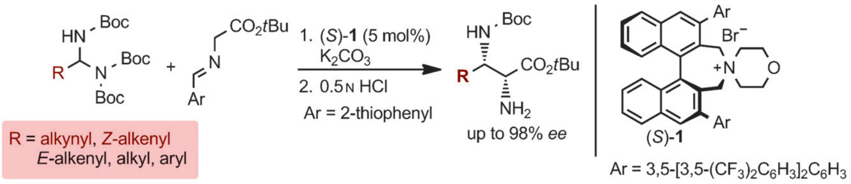
How is that possible?

Ph–X activation (X = Cl, Br, I) with simple Ph_3P-ligated Ru^{II} complexes is possible at as low as room temperature. The reaction of PhI activation with $[(Ph_3P)_4RuH_2]$ displays a striking kinetic profile (see scheme), initially suggesting zeroth order. The kinetic behavior, however, originates from a well-masked autocatalysis; this was recognized, thoroughly studied, and understood in considerable detail.

Asymmetric Catalysis

T. Kano, R. Kobayashi,
K. Maruoka* ______ 8471 – 8474

Versatile In Situ Generated *N*-Boc-Imines: Application to Phase-Transfer-Catalyzed Asymmetric Mannich-Type Reactions

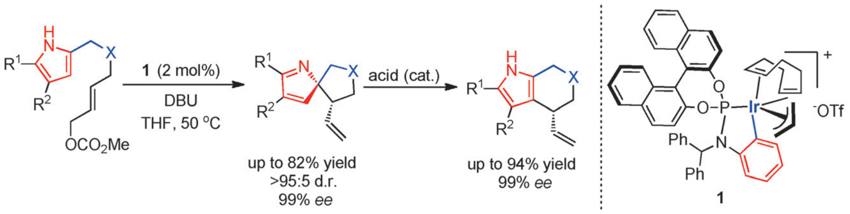


Going Mannich: Boc-protected aminals serve as versatile imine precursors in phase-transfer-catalyzed Mannich reactions with glycine and alanine Schiff bases. The reaction also worked well for the less-accessible alkenyl- and alkynyl-substituted imines. Boc = *tert*-butoxycarbonyl.

Asymmetric Dearomatization

C.-X. Zhuo, Q. Cheng, W.-B. Liu, Q. Zhao,
S.-L. You* ______ 8475 – 8479

Enantioselective Synthesis of Pyrrole-Based Spiro- and Polycyclic Derivatives by Iridium-Catalyzed Asymmetric Allylic Dearomatization and Controllable Migration Reactions

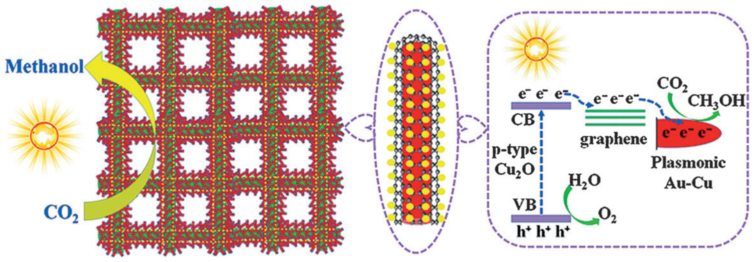


It's all under control: The highly diastereo- and enantioselective synthesis of five-membered spiro-2*H*-pyrroles was achieved using an Ir-catalyzed asymmetric allylic dearomatization. The spiro-2*H*-pyrrole derivatives readily undergo a stereospecific allylic migration under acid catalysis, providing polycyclic pyrrole derivatives in excellent yields and *ee* values.

Carbon Dioxide Photoreduction

J. G. Hou,* H. J. Cheng, O. Takeda,
H. M. Zhu* ______ 8480 – 8484

Three-Dimensional Bimetal-Graphene-Semiconductor Coaxial Nanowire Arrays to Harness Charge Flow for the Photochemical Reduction of Carbon Dioxide

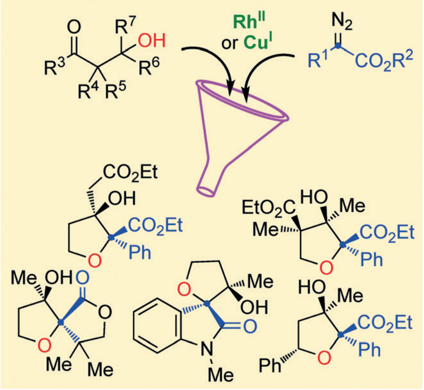


A copper–gold nanoalloy supported on a three-dimensional ultrathin graphene shell encapsulating a p-type Cu_2O coaxial nanowire array promotes the stable photochemical reduction of CO_2 to methanol by the synergetic catalytic effect of interfacial modulation and charge-transfer channel design.

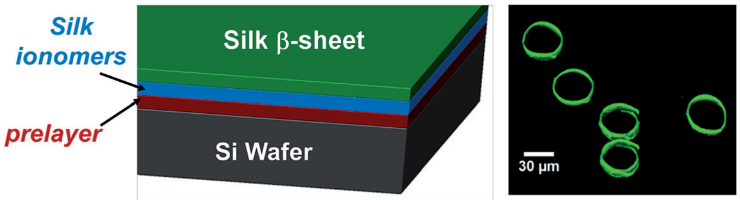
Tetrahydrofurans

S. M. Nicolle, W. Lewis, C. J. Hayes,
C. J. Moody* ______ 8485 – 8489

Stereoselective Synthesis of Highly Substituted Tetrahydrofurans through Diverted Carbene O–H Insertion Reaction



Gone astray: Copper- or rhodium-catalyzed reactions of diazocarbonyl compounds with β-hydroxyketones give highly substituted tetrahydrofurans with excellent diastereoselectivity. The single-step reaction proceeds under mild conditions, starting as a carbene O–H insertion reaction, but then diverting to an intramolecular aldol reaction.



Silk origami: Self-folding structures can be fabricated from silk-on-silk nanofilms with readily controlled morphologies and reversible folding/unfolding responses that are triggered by pH changes. The shapes of the resulting structures can be determined by fine-tuning the film geometry, and include microscopic rings, tubules, and helical tubules.

Biomaterials

C. Ye, S. V. Nikolov, R. Calabrese, A. Dindar, A. Alexeev, B. Kippelen, D. L. Kaplan, V. V. Tsukruk* **8490–8493**

Self-(Un)rolling Biopolymer Microstructures: Rings, Tubules, and Helical Tubules from the Same Material

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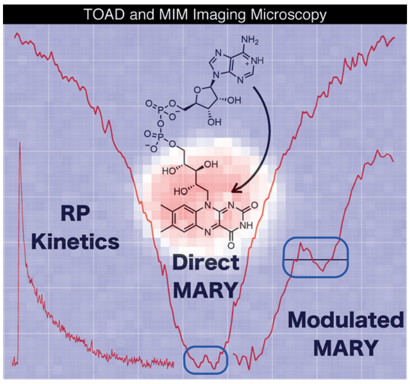
Imaging radicals: Direct spatial imaging of photochemically generated transient radicals with high sensitivity and submicrometer resolution is demonstrated for the photoexcited electron transfer reaction of flavin adenine dinucleotide along with selective imaging of magnetic field sensitive spin-correlated radical pairs. A low field effect on this photoreaction is clearly resolved with important implications for biological magnetoreception.



Laser Spectroscopy

J. P. Beardmore, L. M. Antill, J. R. Woodward* **8494–8497**

Optical Absorption and Magnetic Field Effect Based Imaging of Transient Radicals

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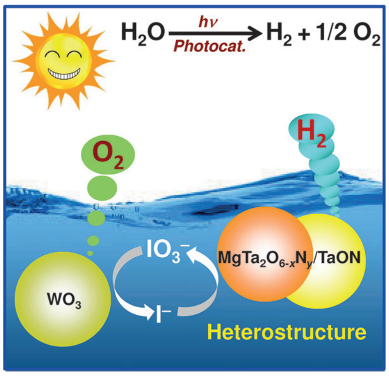

A MgTa$_2$O$_{6-x}$N$_y$/TaON heterostructure, fabricated by a one-pot nitridation strategy, effectively suppresses the recombination of carriers by efficient spatial charge separation and decreased defect density. By employing Pt-loaded MgTa$_2$O$_{6-x}$N$_y$/TaON as a H_2-evolving photocatalyst, a highly efficient Z-scheme overall water splitting system with an apparent quantum efficiency (AQE) of 6.8% at 420 nm was constructed.

Photocatalysis

S. Chen, Y. Qi, T. Hisatomi, Q. Ding, T. Asai, Z. Li, S. Ma, F. Zhang,* K. Domen, C. Li* **8498–8501**

Efficient Visible-Light-Driven Z-Scheme Overall Water Splitting Using a MgTa$_2$O$_{6-x}$N$_y$/TaON Heterostructure Photocatalyst for H_2 Evolution

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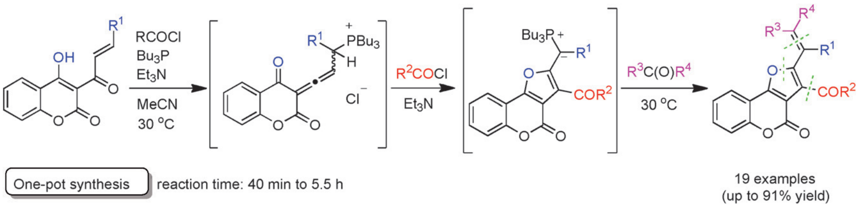


Building rings: The preparation of furo[3,2-*c*]coumarins with appending phosphorus ylides is realized through a Bu_3P-mediated cyclization reaction of 3-cinnamoyl-4-hydroxy-2H-chromen-2-ones by electrophilic addition of acyl chlorides as the key step. These in situ generated ylide intermediates can efficiently react with carbonyl electrophiles to synthesize alkenyl-substituted furo[3,2-*c*]coumarins in moderate to high yields.

Heterocycles

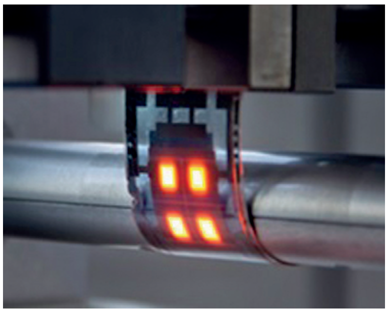
C.-J. Lee, C.-C. Tsai, S.-H. Hong, G.-H. Chang, M.-C. Yang, L. Möhlmann, W. Lin* **8502–8505**

Preparation of Furo[3,2-*c*]coumarins from 3-Cinnamoyl-4-hydroxy-2*H*-chromen-2-ones and Acyl Chlorides: A Bu_3P-Mediated C-Acylation/Cyclization Sequence

Conducting Polymers

A. I. Hofmann, W. T. T. Smaal,
M. Mumtaz, D. Katsigiannopoulos,
C. Brochon, F. Schütze, O. R. Hild,
E. Cloutet,*
G. Hadziioannou* ________ **8506 – 8510**

An Alternative Anionic Polyelectrolyte for Aqueous PEDOT Dispersions: Toward Printable Transparent Electrodes

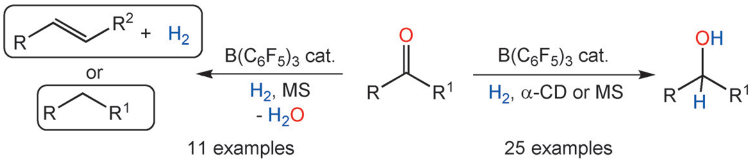


Flexible and transparent: Polyanions were used to stabilize PEDOT in aqueous dispersions. The highly viscous PEDOT:polyanion dispersions were easily processed into thin, conductive, and transparent films, which could be integrated as transparent electrodes into flexible organic electronic devices.

Frustrated Lewis Pairs

T. Mahdi, D. W. Stephan* __ **8511 – 8514**

Facile Protocol for Catalytic Frustrated Lewis Pair Hydrogenation and Reductive Deoxygenation of Ketones and Aldehydes

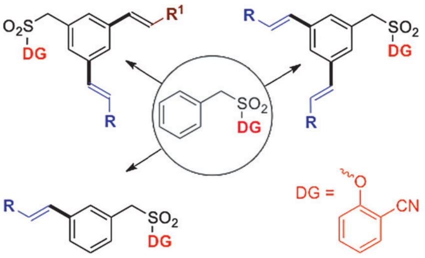


Should O stay or should O go? A series of ketones and aldehydes are reduced in toluene under H_2 in the presence of 5 mol% $B(C_6F_5)_3$ and either cyclodextrin (CD) or molecular sieves (MS) affording a facile metal-free protocol for reduction to alcohols. Similar treatment of aryl ketones resulted in metal-free deoxygenation yielding aromatic hydrocarbons.

C–H Activation

M. Bera, A. Maji, S. K. Sahoo,
D. Maiti* ______________ **8515 – 8519**

Palladium(II)-Catalyzed *meta*-C–H Olefination: Constructing Multisubstituted Arenes through Homo-Diolefination and Sequential Hetero-Diolefination

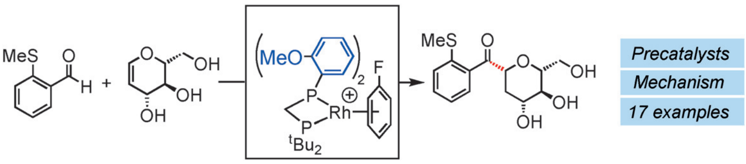


Jockeying for position: Reported herein is the palladium-catalyzed synthesis of mono- and divinylbenzenes by *meta*-C–H olefination of benzyl sulfones. Successful sequential olefinations in a position-selective manner provided a novel route for the synthesis of hetero-dialkenylated products, which are difficult to access using conventional methods. DG = directing group.

Hydroacylation

A. Prades, M. Fernández, S. D. Pike,
M. C. Willis,* A. S. Weller* _ **8520 – 8524**

Well-Defined and Robust Rhodium Catalysts for the Hydroacylation of Terminal and Internal Alkenes

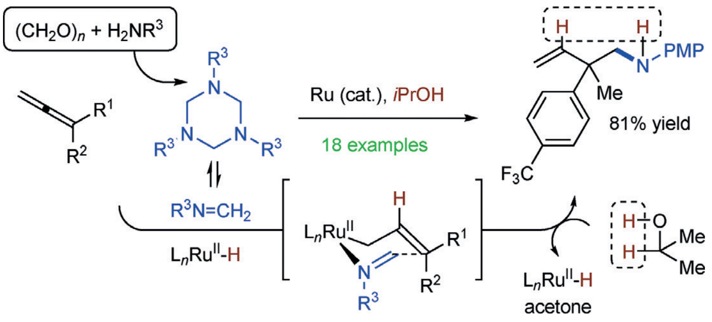


The asymmetric ligand $^tBu_2PCH_2P(o\text{-}C_6H_4OMe)_2$ in a Rh-catalyst system is shown to promote the hydroacylation of challenging internal alkenes with β-substituted aldehydes. Mechanistic studies indicate the stabilizing role of both excess alkene and the OMe-group.

Synthetic Methods

S. Oda, B. Sam,
M. J. Krische* ______ 8525 – 8528

Hydroaminomethylation Beyond Carbonylation: Allene–Imine Reductive Coupling by Ruthenium-Catalyzed Transfer Hydrogenation

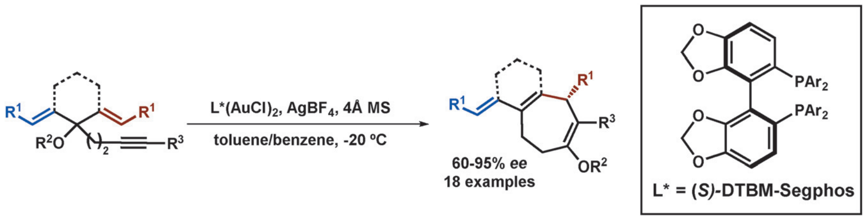


No CO: Ruthenium(II)-catalyzed hydrogen transfer from 2-propanol mediates reductive coupling of 1,1-disubstituted allenes with formaldimines with complete branch-regioselectivity. This reaction represents a new method for hydroaminomethylation beyond the classical hydroformylation/reductive amination.

Asymmetric Synthesis

H. Wu, W. Zi, G. Li, H. Lu,*
F. D. Toste* ______ 8529 – 8532

Gold(I)-Catalyzed Desymmetrization of 1,4-Dienes by an Enantioselective Tandem Alkoxylation/Claisen Rearrangement

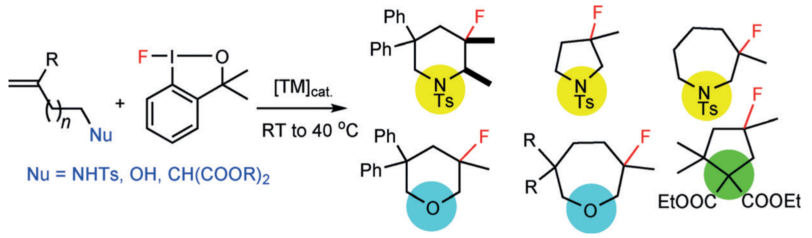


An enantioselective gold(I)-catalyzed alkoxylation/Claisen rearrangement of dienynes has been developed. This method provides substituted cycloheptenes in high yield and enantioselectivity from the desymmetrization of 1,4-dienes.

Homogeneous Catalysis

W. Yuan, K. J. Szabó* ______ 8533 – 8537

Catalytic Intramolecular Aminofluorination, Oxyfluorination, and Carbofluorination with a Stable and Versatile Hypervalent Fluoroiodine Reagent

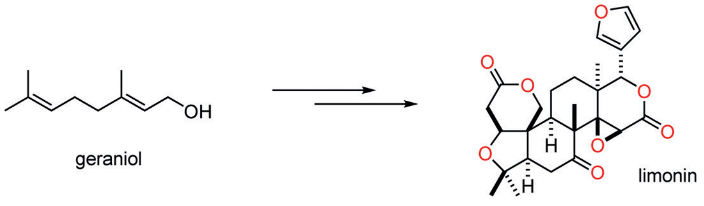


Multitasking: The use of a new hypervalent fluoroiodine reagent for fluorocyclization reactions is reported. In the presence of a transition-metal (TM) catalyst the fluoroiodine reagent can be used for aminofluorination, oxyfluorination, and carbofluorination reactions to deliver hetero- and isocyclic compounds containing a tertiary fluorine substituent. Ts = 4-toluenesulfonyl.

Total Synthesis

S. Yamashita,* A. Naruko, Y. Nakazawa,
L. Zhao, Y. Hayashi,
M. Hirama ______ 8538 – 8541

Total Synthesis of Limonin

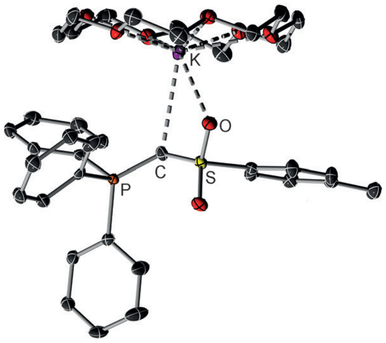


Limonin, not limonene: The flagship congener of the limonoid natural-product family, limonin, was synthesized for the first time. Geraniol was employed as the starting material, and key reactions for the efficient construction of the limonin framework included a tandem radical cyclization, a singlet-oxygen cycloaddition, Baeyer–Villiger oxidation, and a Suárez reaction.

Ylide Ligands

T. Scherpf, R. Wirth, S. Molitor,
K.-S. Feichtner,
V. H. Gessner* ________ **8542 – 8546**

Bridging the Gap between Bisylides and Methandiides: Isolation, Reactivity, and Electronic Structure of an Yldiide



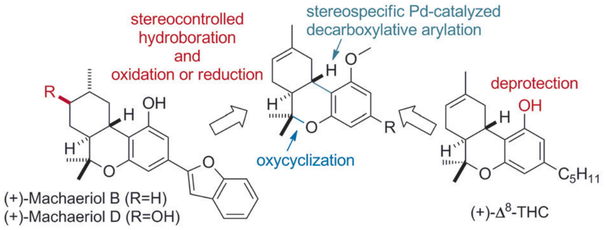
Metalation makes a difference. The metalation of a stabilized phosphorus ylide yields the isolable yldiide [Ph_3P-C-$SO_2Tol]^-$, which was isolated with different alkali metal counterions. Its electronic structure shows a clear relation to other divalent carbon species such as bisylides. Reactivity studies demonstrate the strong nucleophilicity of the yldiide and its capability to act both as a σ- and π-donor.

Natural Product Synthesis

F. Klotter, A. Studer* ________ **8547 – 8550**

Short and Divergent Total Synthesis of (+)-Machaeriol B, (+)-Machaeriol D, (+)-Δ^8-THC, and Analogues

Inside Back Cover

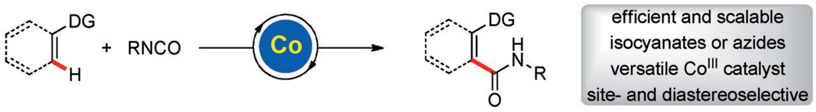


Just 4 or 5 steps! A short and divergent synthesis that is based on highly efficient stereoselective transformations provides machaeriols and cannabinoids from commercially available (*S*)-perillic acid. The five-step synthesis leads to (+)-machaeriol B, (+)-machaeriol D, and related analogues whereas (+)-Δ^8-THC and an analogue are prepared in a four-step sequence.

C–H Activation

J. Li, L. Ackermann* ________ **8551 – 8554**

Cobalt(III)-Catalyzed Aryl and Alkenyl C–H Aminocarbonylation with Isocyanates and Acyl Azides



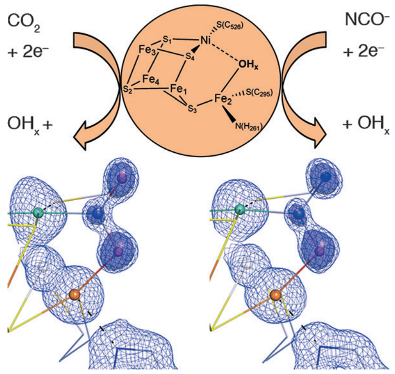
Clever cobalt: C–H aminocarbonylation of (hetero)arenes and alkenes was achieved by means of a user-friendly cobalt(III) catalyst. The reaction shows excellent chemo-, site-, and diastereoselectivity, as well as ample substrate scope.

Photolysis

N. Kretschy, A.-K. Holik, V. Somoza,
K.-P. Stengele,
M. M. Somoza* ________ **8555 – 8559**

Next-Generation *o*-Nitrobenzyl Photolabile Groups for Light-Directed Chemistry and Microarray Synthesis

High-speed photolysis: The highly light-sensitive groups benzoyl- and thiophenyl-NPPOC (NPPOC = 2-(2-nitrophenyl)propoxycarbonyl) were used for light-directed, spatio-selective synthesis. Their photolytic efficiencies are two- and twelvefold greater than that of NPPOC, respectively.



Two sides of the same coin: CO_2 and NCO^- are both activated at Ni and Fe2 of the [$NiFe_4S_4$] cluster of CO dehydrogenase and bind as bridging ligands between the two metal atoms. Insights from true atomic resolution structures draw a clear picture of the chemical nature of the ligands: activation of both the substrate CO_2 and the inhibitor NCO^- occurs by formal two-electron reduction.

Biocatalysis VIP

J. Fesseler, J.-H. Jeoung,
H. Dobbek* ______ **8560–8564**

How the [$NiFe_4S_4$] Cluster of CO Dehydrogenase Activates CO_2 and NCO^-

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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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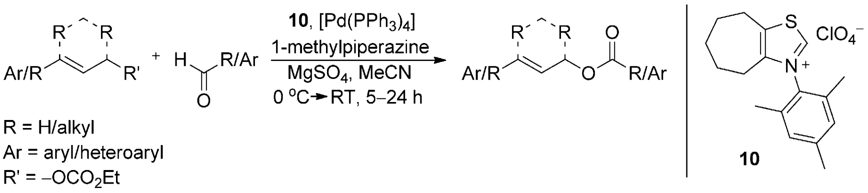
Angewandte Corrigendum

The authors of this Communication have been alerted regarding a structural assignment mistake. A double-check of the data revealed that the major isolated products were allyl esters and not the expected allyl ketones (see scheme). Plausibly the formed acyl anions were oxidized under the reaction conditions to the corresponding carboxylates, leading to the esters as the major product. The presence of an additional oxygen atom in the product was not realized, probably because the analytical (HRMS: The observed $M+K$ was actually M (for ester)+Na) and spectral data (close δ values in ^1H and ^{13}C NMR spectra) were misinterpreted and initially compared with data for a wrong known compound. Apart from this wrong structural assignment, all yields, data, copies of spectra, and the experimental sections reported in the manuscript and the supporting information remain valid.

The authors wish to thank Professor T. Rovis and Professor R. Lundgren for bringing this matter to their attention. They sincerely apologize to the scientific community for this severe inadvertent mistake.



Direct Allylation of In Situ Generated Aldehyde Acyl Anions by Synergistic NHC and Palladium Catalysis

M. M. Ahire, S. B. Mhaske* **7038–7042**

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