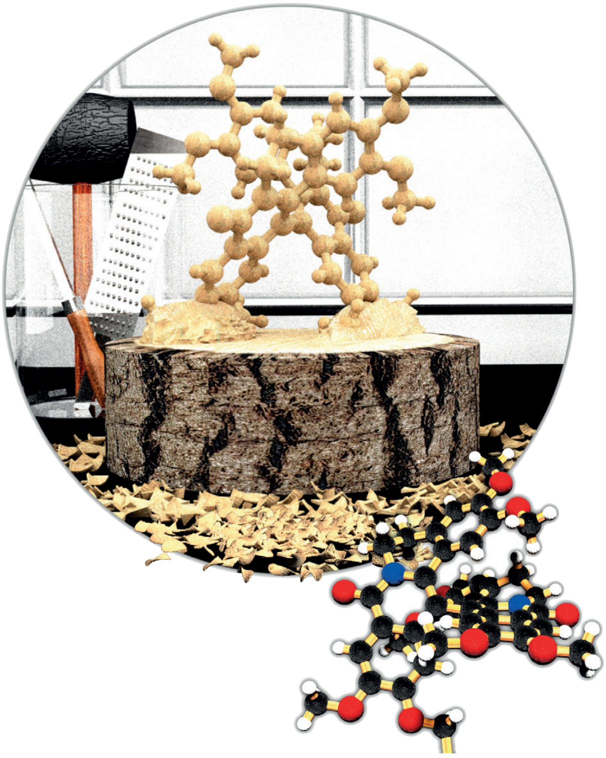
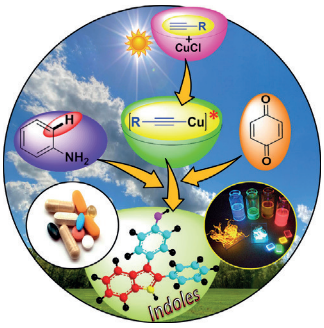
“Carving” molecules out of wood …

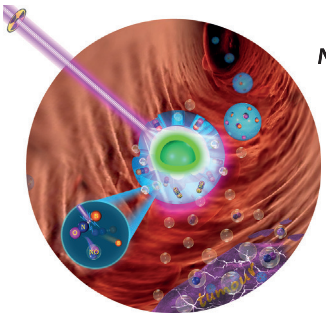


… The synthesis of chemical materials from sustainable resources in an environmentally responsible way is an important challenge for a modern chemical infrastructure. In their Communication on page 14187 ff., T. Opatz, A. J. Arduengo et al. tackle the first of the four aspects of xylochemistry. The cover image (Jason W. Runyon) metaphorically depicts the process of creating a natural product, ilicifoline B, exclusively from wood-based starting materials.

Heterocycles

In their Communication on page 13896 ff., K. C. Hwang et al. describe the regioselective one-step synthesis of functionalized indoles by coupling anilines, terminal alkynes, and benzoquinones in the presence of a CuCl catalyst and visible light.





Nanotheranostics

A nanotheranostic system based on X-ray radiation controlled NO release is described by W. Bu, J. Shi et al. in their Communication on page 14026 ff. The results enable the on-demand therapy of deep-seated solid tumors by simply manipulating the X-ray dose.

Metalation Reactions

In their Communication on page 14075 ff., R. E. Mulvey et al. show that metalation of a pendant arene present on an N-heterocyclic carbene along with a pre-inverse-crown template base induces three different metal–ligand contacts.

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Author Profile

"If I were not a scientist, I would be depressed. My worst nightmare is losing my sight! Chemistry is such a visual science! …"
This and more about Richmond Sarpong can be found on page 13852.

News

D. W C. MacMillan

P. S. Dittrich

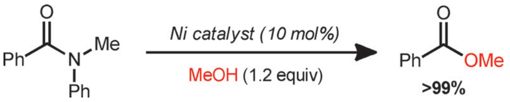
N. Maulide

Highlights

Synthetic Methods

S. A. Ruider, N. Maulide* **13856 – 13858**

Strong Bonds Made Weak: Towards the General Utility of Amides as Synthetic Modules



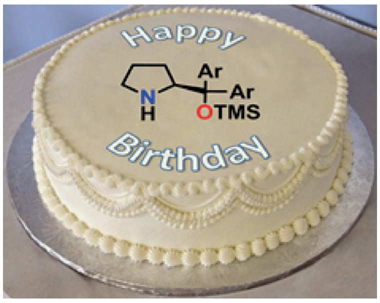
Breaking good: The amide bond is widely recognized as the strongest bond among the carboxylic acid derivatives. Therefore, the potential of amides to serve as synthetic building blocks has remained mostly untapped thus far. This Highlight describes a recent breakthrough that enables the catalytic conversion of amides into esters for the first time.

Minireviews

Organocatalysis

B. S. Donslund, T. K. Johansen, P. H. Poulsen, K. S. Halskov, K. A. Jørgensen* **13860 – 13874**

The Diarylprolinol Silyl Ethers: Ten Years After



Looking back—don't look back: After ten years of asymmetric organocatalysis with diarylprolinol silyl ethers, we look back over the history of this class of aminocatalysts and its impact. We outline the development of this area from reactions via enamine and iminium ion intermediates to remote functionalizations, combinatorial methods, and industrial applications, describing in which directions these catalysts have moved organocatalysis and where the field might be going.

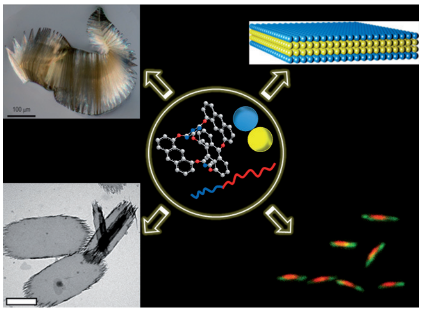
Reviews

2D Functional Materials

C. E. Boott, A. Nazemi, I. Manners* **13876 – 13894**

Synthetic Covalent and Non-Covalent 2D Materials

No plane, no gain: 2D structures have emerged as attractive functional materials over the past few decades. The development of new synthetic methods that allows their creation from a variety of building blocks, including small molecules, nanoparticles, and block copolymers, is expected to pave the way to a range of applications.



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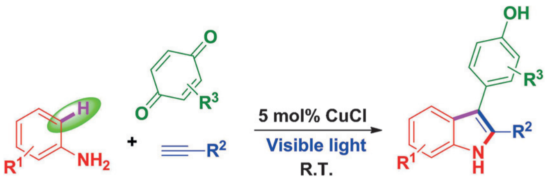
Communications

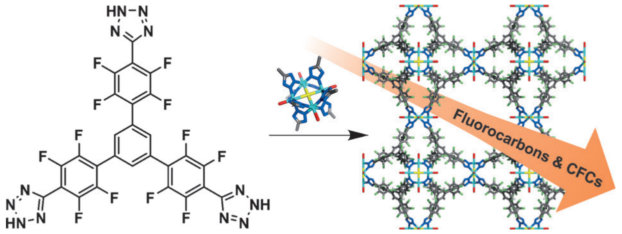
Heterocycles



Visibility: A facile visible-light initiated copper-catalyzed process leads to regioselectively functionalized indoles by the C–H annulation of simple arylamines with terminal alkynes and benzoquinone at room temperature. This transformation represents a sustainable and atom-economical approach for the preparation of substituted indoles from readily available substrates.

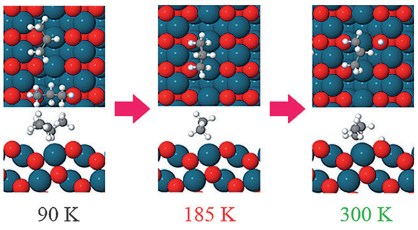
Frontispiece

Fluorocarbon Adsorption



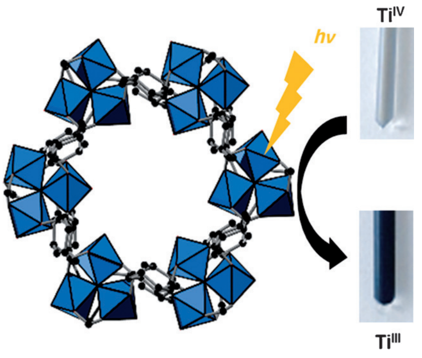
Putting the F into MOFs: Fluorinated aromatic tritopic linkers are used to construct the most porous fluorinated metal–organic framework (MOF) to date. It has an exceptionally high uptake of fluorocarbons and CFCs. Its highly polarized and fluorophilic pore surfaces and electron-deficient aromatic nuclei suggest highly fluorinated MOFs will have different properties from other MOFs.

Alkane Activation



The structural evolution of propane σ-complexes on PdO(101) was investigated by using reflection absorption infrared spectroscopy and DFT calculations. Favorable dative bonding with the surface palladium atoms causes an exceptionally high selectivity for the activation of primary C–H bonds.

Metal–Organic Frameworks

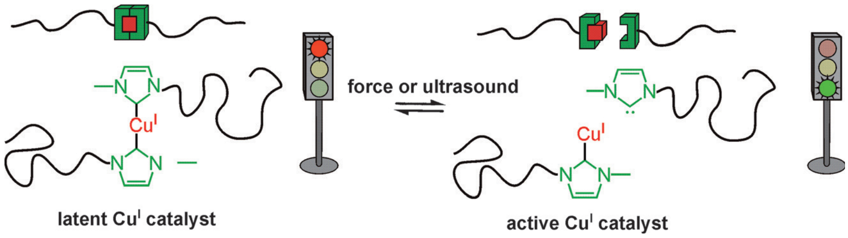


A breath of fresh air: Titanocene dichloride was used as the metal source in an innovative synthetic approach to titanium-based metal–organic frameworks (MOFs). In this way, a breathing Ti MOF (designated COK-69) featuring a photoactive trinuclear cluster was built up from *trans*-1,4-cyclohexanedicarboxylate and an unprecedented, photoactive $[Ti^{IV}{}_3$-$(\mu_3\text{-O})(COO)_6]$ inorganic building unit (see picture).

Click Chemistry

P. Michael, W. H. Binder* **13918 – 13922**

A Mechanochemically Triggered "Click" Catalyst

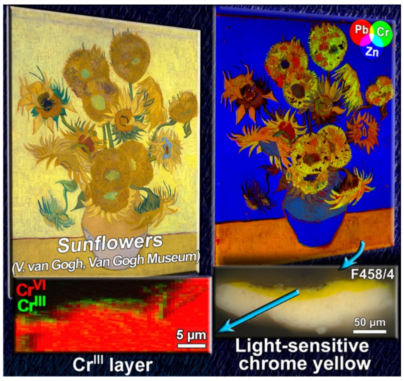


Feeling the pressure: A pressure-sensitive homogeneous Cu^{I} "click" catalyst activated by mechanical force through attached polymer chains has been developed. The attached polymer chains transmit the mechanical force directly to the central catalytic Cu carbene, which in turn activates the "click" reaction, both in solution and in the solid state.

Pigments

L. Monico,* K. Janssens, E. Hendriks, F. Vanmeert, G. Van der Snickt, M. Cotte, G. Falkenberg, B. G. Brunetti, C. Miliani **13923 – 13927**

Evidence for Degradation of the Chrome Yellows in Van Gogh's *Sunflowers*: A Study Using Noninvasive In Situ Methods and Synchrotron-Radiation-Based X-ray Techniques



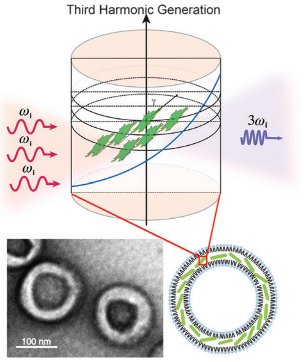
Why is the yellow darkening? Firm evidence that chrome yellow pigments darken through the Cr^{VI}→Cr^{III} reduction is provided by the use of complementary analytical techniques. Different types of chrome yellow, that is, the lightfast PbCrO$_4$ and the light-sensitive sulfur-rich PbCr$_{1-x}$S$_x$O$_4$ ($x \approx 0.5$), are shown to be present, and spots of the painting with the highest risk of color change have been identified.

Fluorescent Nanoparticles

L. Cui, D. Tokarz, R. Cisek, K. K. Ng, F. Wang, J. Chen, V. Barzda, G. Zheng* **13928 – 13932**

Organized Aggregation of Porphyrins in Lipid Bilayers for Third Harmonic Generation Microscopy

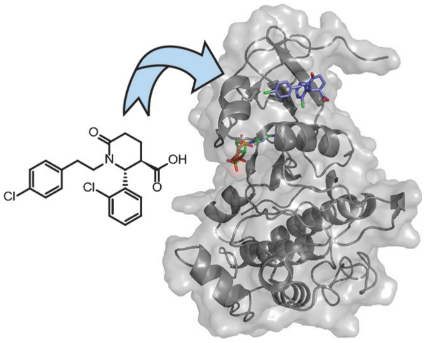
The assembly and characterization of an organized aggregation of porphyrins (OAP) for nonlinear optical microscopy is reported. Its structure-dependent photoproperty switch between harmonic (OAP-intact) and fluorescence (OAP-disrupted) generation permitted nanoparticle tracking in living cells. Green bars = porphyrin aggregates.



Inhibitors

E. Kroon, J. O. Schulze, E. Süß, C. J. Camacho, R. M. Biondi, A. Dömling* **13933 – 13936**

Discovery of a Potent Allosteric Kinase Modulator by Combining Computational and Synthetic Methods



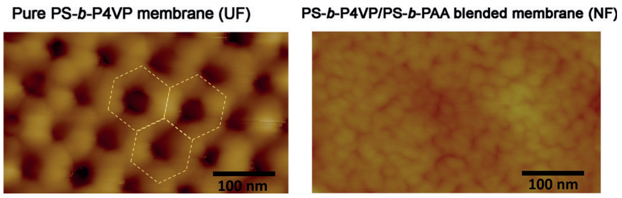
Piece of cake: Virtual pharmacophore-based screening of a large multicomponent reaction database followed by one-step synthesis yielded a potent allosteric modulator of the protein kinase PDK1. In addition to structure–activity relationship studies, a cocrystal structure was solved for the best-performing compound in complex with PDK1.

Membranes

H. Z. Yu, X. Y. Qiu, N. Moreno, Z. W. Ma, V. M. Calo, S. P. Nunes, K. V. Peinemann* ______ **13937 – 13941**

Self-Assembled Asymmetric Block Copolymer Membranes: Bridging the Gap from Ultra- to Nanofiltration

Inside Cover



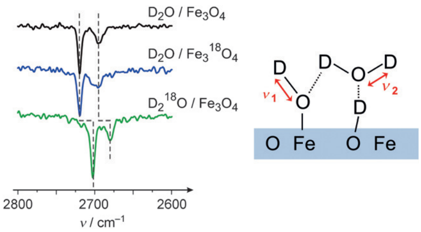
Blends of two chemically interacting copolymers bridge the gap from ultra- (UF) to nanofiltration (NF) as such membranes with pore sizes below 5 nm have been synthesized without post-treatment. Simulations of the membrane formation process by dissipative particle dynamics were used to explain the dramatic observed pore size reduction combined with an increase in water flux.

Surface Science

P. Dementyev, K.-H. Dostert, F. Ivars-Barceló, C. P. O'Brien, F. Mirabella, S. Schauermann,* X. Li, J. Paier,* J. Sauer, H.-J. Freund ______ **13942 – 13946**

Water Interaction with Iron Oxides

The adsorption of water on Fe_3O_4 surfaces is experimentally and theoretically investigated. Calorimetric and IR spectroscopy measurements under ultrahigh vacuum conditions combined with state-of-the-art density functional calculations show that adsorbed water molecules on the Fe_3O_4-(111) surface tend to form dimer-like complexes consisting of one intact and one dissociated water molecule (see picture).

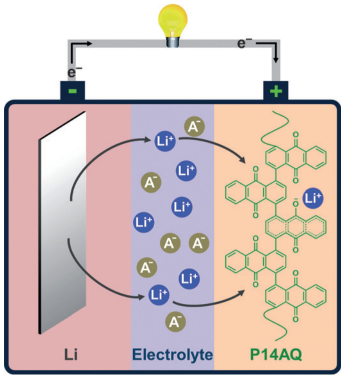


Lithium Batteries

Z. Song, Y. Qian, M. L. Gordin, D. Tang, T. Xu, M. Otani, H. Zhan, H. Zhou,* D. Wang* ______ **13947 – 13951**

Polyanthraquinone as a Reliable Organic Electrode for Stable and Fast Lithium Storage

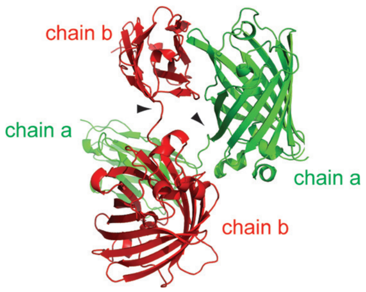
No compromises! An ideal polymer electrode based on anthraquinone, poly(1,4-anthraquinone) (P14AQ), was applied as a cathode for rechargeable lithium batteries (see picture). Unrivaled by other organic electrodes, it showed exceptional performance, including stable cycling (99.4% capacity retention after 1000 cycles) and fast discharge/charge ability (releasing 69% of the low-rate capacity or 64% of the energy in just 2 min).



Protein Dimerization

M. Eshaghi, G. Sun, A. Grüter, C. L. Lim, Y. C. Chee, G. Jung, R. Jauch, T. Wohland, S. L. Chen* ______ **13952 – 13956**

Rational Structure-Based Design of Bright GFP-Based Complexes with Tunable Dimerization

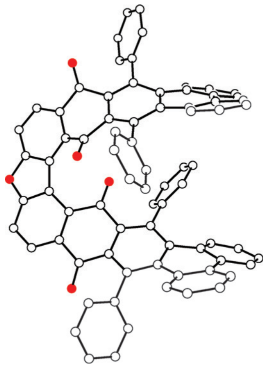


The "vGFP strategy" enables control of dimerization for GFP and other proteins while enhancing fluorescence, acid resistance, and redox robustness. The new vsfGFP variants are drop-in replacements for nearly all GFP applications and provide 50–200% increased brightness. The vGFP strategy should generalize to enable controlled dimerization for directed improvement of arbitrary proteins.

Helicenes

X. Geng, J. P. Donahue, J. T. Mague,
R. A. Pascal Jr.* ________ **13957 – 13960**

The Hairpin Furans: Easily Prepared Hybrids of Helicenes and Twisted Acenes

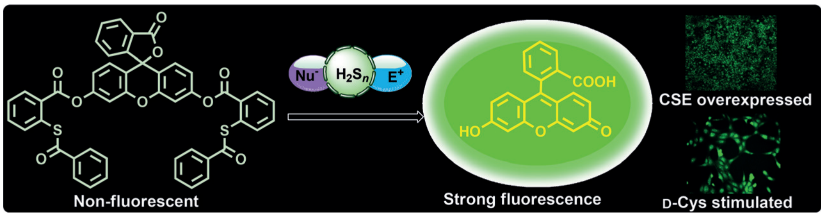


A new twist on furans: The hairpin furans are chiral molecular ribbons consisting of two longitudinally twisted aromatic polycycles fused to a heteropentahelicene. The one-step synthesis of hairpin furans is reported.

Fluorescent Probes

W. Chen, E. W. Rosser, T. Matsunaga,
A. Pacheco, T. Akaike,
M. Xian* ____________ **13961 – 13965**

The Development of Fluorescent Probes for Visualizing Intracellular Hydrogen Polysulfides



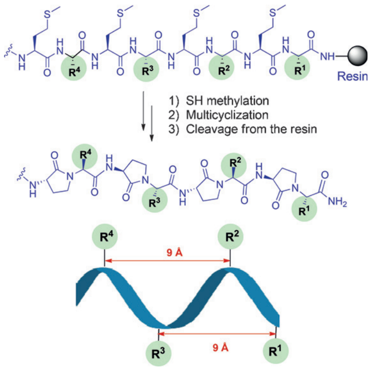
Bringing H_2S_n to light: The dual reactivity of hydrogen polysulfides (H_2S_n), which can act as both an electrophile and a nucleophile, is exploited in the development of highly sensitive and selective fluorescent probes. One of the probes was applied in the visualization of exogenous and endogenous H_2S_n in cells. CSE = cystathionine γ-lyase.

Peptide Foldamers

V. Martin, B. Legrand, L. L. Vezenkov,
M. Berthet, G. Subra, M. Calmès,
J.-L. Bantignies, J. Martinez,
M. Amblard* ________ **13966 – 13970**

Turning Peptide Sequences into Ribbon Foldamers by a Straightforward Multicyclization Reaction

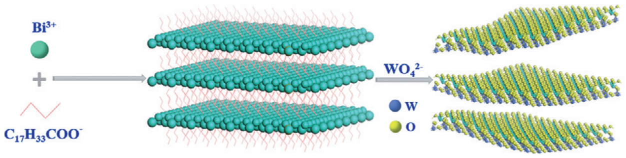
Ribbons on resin: A straightforward solid phase method for turning conventional peptide sequences into γ-lactam-containing oligomers displaying a ribbon-like structure is described. The controlled and periodic distribution of functional groups on both sides of the ribbon is simply encoded by the peptide sequence, offering highly versatile structured tools for biomedical applications and material sciences.



Solar CO_2 Reduction

L. Liang, F. Lei, S. Gao, Y. Sun,* X. Jiao,
J. Wu, S. Qamar, Y. Xie* _ **13971 – 13974**

Single Unit Cell Bismuth Tungstate Layers Realizing Robust Solar CO_2 Reduction to Methanol

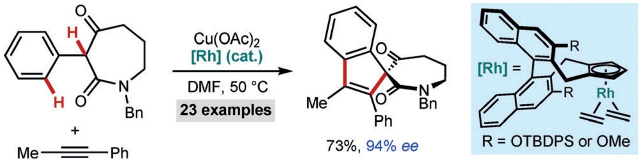


Single unit cell Bi_2WO_6 layers (right) are synthesized by virtue of a lamellar Bi-oleate intermediate (middle). Benefiting from the ultrahigh fraction of surface atoms and increased DOS, the single-unit-cell Bi_2WO_6 layers achieve a methanol formation rate of 75 $\mu mol\,g^{-1}\,h^{-1}$, 125-times higher than that of the bulk Bi_2WO_6 and also over 10-times higher than that of previously reported TiO_2-loaded zeolite and Ag/TiO_2.

Asymmetric Catalysis

S. Reddy Chidipudi, D. J. Burns, I. Khan, H. W. Lam* ——— 13975 – 13979

Enantioselective Synthesis of Spiroindenes by Enol-Directed Rhodium(III)-Catalyzed C—H Functionalization and Spiroannulation



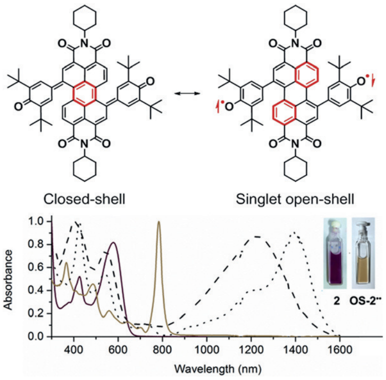
Take the high rhod: Chiral cyclopentadienyl rhodium complexes promote enantioselective enol-directed C(sp^2)–H functionalization and oxidative annulation with alkynes to give spiroindenes containing all-carbon quaternary stereocenters. High selectivity between two directing groups, as well as control of the direction of rotation in the isomerization of a rhodium enolate intermediate, appear to be critical for high enantiomeric excesses.

Biradical Chemistry

D. Schmidt, M. Son, J. M. Lim, M.-J. Lin, I. Krummenacher, H. Braunschweig, D. Kim,* F. Würthner* ——— 13980 – 13984

Perylene Bisimide Radicals and Biradicals: Synthesis and Molecular Properties

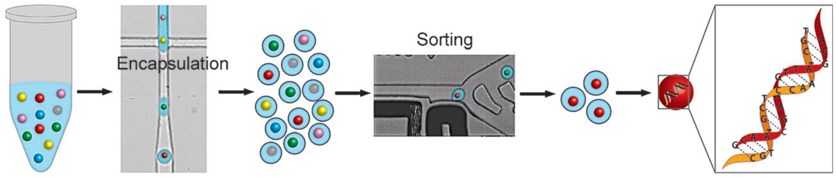
Stable biradicals: A singlet open-shell perylene bisimide (PBI) biradical was generated by facile chemical oxidation of a 4-hydroxyaryl-substituted PBI. The remarkable stability of **OS-2$^{\bullet\bullet}$** facilitates its unambiguous characterization, revealing a large singlet biradical character of $y = 0.72$.



Viruses

H.-S. Han, P. G. Cantalupo, A. Rotem, S. K. Cockrell, M. Carbonnaux, J. M. Pipas, D. A. Weitz* ——— 13985 – 13988

Whole-Genome Sequencing of a Single Viral Species from a Highly Heterogeneous Sample



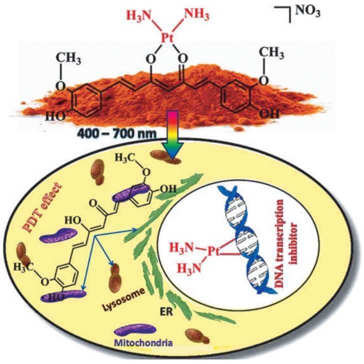
On a drop-in basis: A new platform that integrates drop-based microfluidics and computational analysis was developed for purification of a single viral species from a mixed sample and retrieval of its complete genome sequence. This method was used to retrieve the genome sequence of SV40 spiked into wastewater with more than 96% sequence coverage and 99.8% sequence identity. The platform can also be used to detect and identify unknown viruses.

Cell Imaging

K. Mitra, S. Gautam, P. Kondaiah,* A. R. Chakravarty* ——— 13989 – 13993

The *cis*-Diammineplatinum(II) Complex of Curcumin: A Dual Action DNA Crosslinking and Photochemotherapeutic Agent

Double duty: The title complex shows dual cellular activity by photorelease of curcumin as a photodynamic therapy (PDT) agent and formation of a cisplatin analogue as a transcription inhibitor (IC$_{50}$ ≈ 15 µM). Cellular platinum estimation suggests a DNA crosslink formation and fluorescence images reveal cytosolic localization.



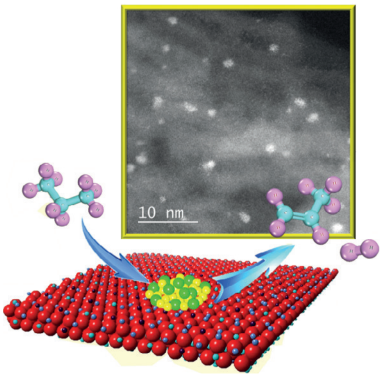
VIP

Dehydrogenation

L. Shi, G.-M. Deng, W.-C. Li, S. Miao, Q.-N. Wang, W.-P. Zhang, A.-H. Lu* ———— **13994 – 13998**

Al$_2$O$_3$ Nanosheets Rich in Pentacoordinate Al^{3+} Ions Stabilize Pt-Sn Clusters for Propane Dehydrogenation

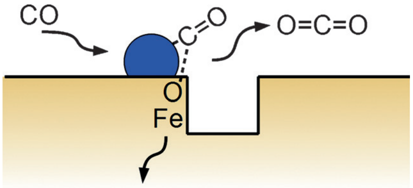
Stable and selective: γ-Al$_2$O$_3$ nanosheets rich in pentacoordinate Al^{3+} ions can well disperse and stabilize raft-like Pt-Sn clusters, which results in an increase of the electron density of the Pt sites. This material catalyzes the conversion of propane into propylene with > 99 % selectivity, and minimizes coke formation and sintering processes.



Supported Catalysts

R. Bliem, J. van der Hoeven, A. Zavodny, O. Gamba, J. Pavelec, P. E. de Jongh, M. Schmid, U. Diebold, G. S. Parkinson* ———— **13999 – 14002**

An Atomic-Scale View of CO and H$_2$ Oxidation on a Pt/Fe$_3$O$_4$ Model Catalyst

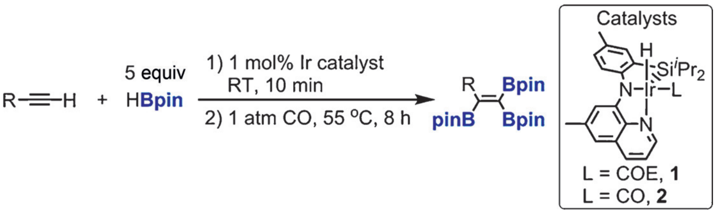


Scanning tunneling microscopy reveals that the etching and regrowth of an iron oxide support occurs in the vicinity of Pt clusters during CO and H$_2$ oxidation. The Pt clusters catalyze reduction/oxidation reactions that would only occur on the bare support at higher temperatures.

Homogeneous Catalysis

C.-I Lee, W.-C. Shih, J. Zhou, J. H. Reibenspies, O. V. Ozerov* ———— **14003 – 14007**

Synthesis of Triborylalkenes from Terminal Alkynes by Iridium-Catalyzed Tandem C—H Borylation and Diboration

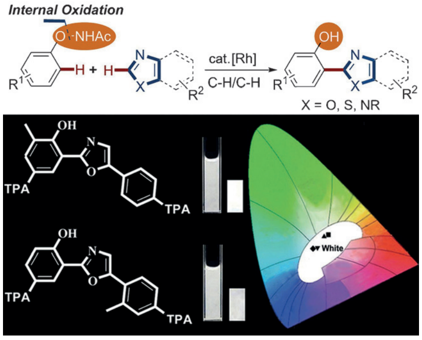


A two-step reaction that converts terminal alkynes into tris(boryl)alkenes is reported. In the first step, the terminal alkyne and pinacolborane (HBpin) are converted into an alkynylboronate by **1**, and then treatment of the reaction mixture with CO generates a new catalyst **2** which mediates dehydrogenative diboration of alkynylboronate with pinacolborane. COE = *cis*-cyclooctene.

Materials Science

B. Li, J. Lan,* D. Wu, J. You* ———— **14008 – 14012**

Rhodium(III)-Catalyzed *ortho*-Heteroarylation of Phenols through Internal Oxidative C—H Activation: Rapid Screening of Single-Molecular White-Light-Emitting Materials

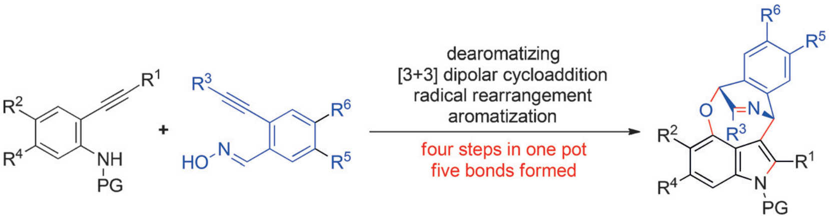


White out: A rhodium(III)-catalyzed C—H/C—H cross-coupling of phenols with azoles has been accomplished to construct highly functionalized 2-(2-hydroxyphenyl)azoles through a traceless oxidation directing strategy. The method presents an opportunity to rapidly screen white-light-emitting molecules. TPA = triphenylamine substituent.

Heterocycles

D. Han, Q. He,* R. Fan* **14013 – 14016**

Aniline Dearomatization and Silver-Catalyzed [3+3] Dipolar Cycloaddition: Efficient Construction of Oxocino[4,3,2-*cd*]indoles from 2-Alkynylanilines and 2-Alkynylbenzaldoximes

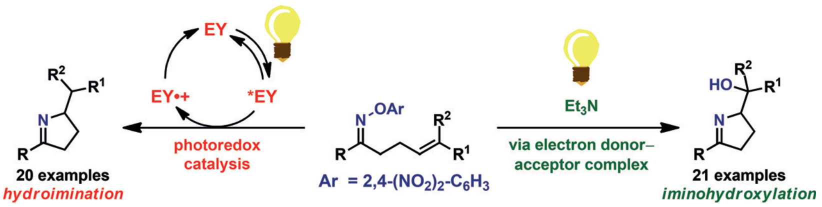


Ring-fusion event: A one-pot, stepwise procedure is reported for the efficient construction of multisubstituted oxocino[4,3,2-*cd*]indoles. The method comprises the oxidative dearomatization of 2-alkynylanilines, the silver-catalyzed [3+3] cycloaddition with 2-alkynylbenzaldoximes, and subsequent thermal radical skeletal rearrangement and aromatization. PG = protecting group.

Photoredox Catalysis

J. Davies, S. G. Booth, S. Essafi, R. A. W. Dryfe, D. Leonori* **14017 – 14021**

Visible-Light-Mediated Generation of Nitrogen-Centered Radicals: Metal-Free Hydroimination and Iminohydroxylation Cyclization Reactions

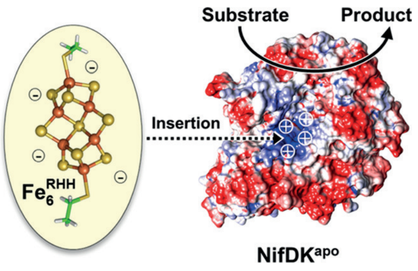


Divergent SET: Visible-light irradiation of *O*-aryl oximes leads to the generation of N-centered radicals. Depending on the reaction conditions, these radicals cyclize either in a photoredox-catalyzed hydroimination or in an iminohydroxylation via electron donor–acceptor complexes (EY = eosin Y).

Artificial Enzyme

K. Tanifuji, C. C. Lee, Y. Ohki, K. Tatsumi, Y. Hu,* M. W. Ribbe* **14022 – 14025**

Combining a Nitrogenase Scaffold and a Synthetic Compound into an Artificial Enzyme

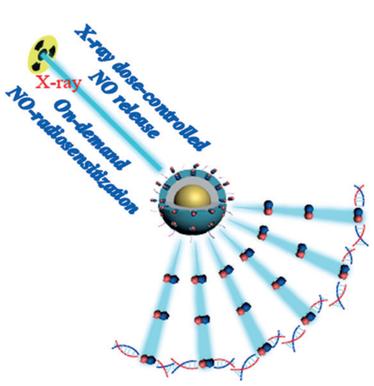


Mutual attraction: A negatively charged synthetic model complex (Fe$_6^{RHH}$), which mimics the topology of the nitrogenase cofactor, can be inserted into the catalytic component of nitrogenase (NifDK^{apo}) through a positively charged insertion path, resulting in an artificial enzyme that is capable of ATP-dependent and -independent reduction of C_2H_2 to C_2H_4, as well as ATP-independent reduction of CN^- to C_1–C_3 hydrocarbons.

Nanotheranostics

W. Fan, W. Bu,* Z. Zhang, B. Shen, H. Zhang, Q. He, D. Ni, Z. Cui, K. Zhao, J. Bu, J. Du, J. Liu, J. Shi* **14026 – 14030**

X-ray Radiation-Controlled NO-Release for On-Demand Depth-Independent Hypoxic Radiosensitization



A novel nanotheranostic system based on X-ray radiation-controlled NO-release enables simultaneous luminescent imaging and controllable NO-sensitized radiation enhancement effects without depth dependence. The results will lead to the on-demand therapy of deep-seated solid tumors with very few adverse effects by simply manipulating the appropriate X-ray dose.

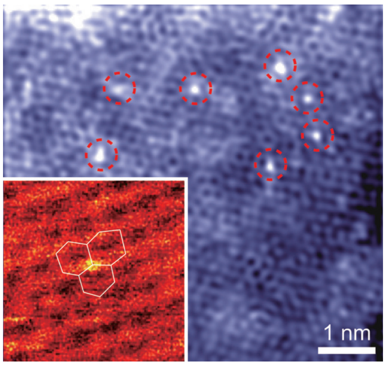
Inside Back Cover

Hydrogen Evolution Reaction

H.-J. Qiu, Y. Ito, W. Cong, Y. Tan, P. Liu, A. Hirata, T. Fujita, Z. Tang,* M. Chen* ______ **14031 – 14035**

Nanoporous Graphene with Single-Atom Nickel Dopants: An Efficient and Stable Catalyst for Electrochemical Hydrogen Production

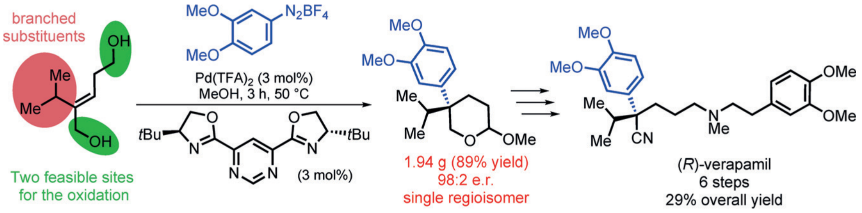
Single-atom nickel dopants anchored to three-dimensional nanoporous graphene show superior catalytic activities towards the hydrogen evolution reaction (HER) in acidic solutions. Experimental and theoretical investigations suggest that the unusual catalytic performance of this catalyst is due to sp–d orbital charge transfer between the Ni dopants and the surrounding carbon atoms.



Asymmetric Heck Reactions

C. C. Oliveira, A. Pfaltz,* C. R. D. Correia* ______ **14036 – 14039**

Quaternary Stereogenic Centers through Enantioselective Heck Arylation of Acyclic Olefins with Aryldiazonium Salts: Application in a Concise Synthesis of (*R*)-Verapamil



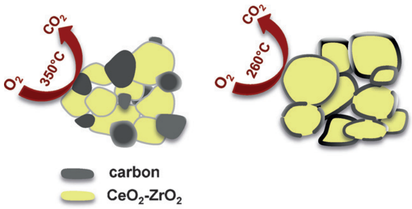
The combination of designed chiral N,N-based ligands and aryldiazonium salts allowed the enantioselective construction of all-carbon quaternary stereocenters through a Heck reaction with acyclic olefins. The molecular complexity provided by this new method enabled a concise total synthesis of (*R*)-verapamil.

Heterogeneous Catalysis

E. Aneggi, V. Rico-Perez, C. de Leitenburg, S. Maschio, L. Soler, J. Llorca,* A. Trovarelli* ______ **14040 – 14043**

Ceria–Zirconia Particles Wrapped in a 2D Carbon Envelope: Improved Low-Temperature Oxygen Transfer and Oxidation Activity

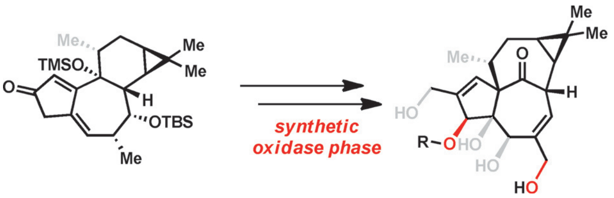
Soot combustion: The intimate contact of ceria–zirconia particles with a thin carbon layer promoted the transfer of lattice/surface oxygen atoms. The oxidation temperatures of soot were significantly lowered (see picture).



C–H Oxidation

Y. Jin, C.-H. Yeh, C. A. Kuttruff, L. Jørgensen, G. Dünstl, J. Felding, S. R. Natarajan, P. S. Baran* ______ **14044 – 14048**

C–H Oxidation of Ingenanes Enables Potent and Selective Protein Kinase C Isoform Activation



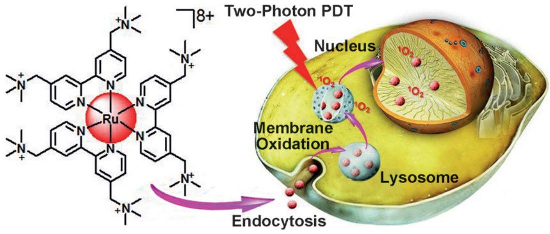
Ingenious access: Ingenol derivatives with varying degrees of C–H oxidation were prepared by two-phase terpene synthesis to give analogues that cannot be prepared by semisynthesis from ingenol. Since interaction with protein kinase C (PKC) was found to be dependent on oxidation level, this enabled PKC isoform selectivity, wherein PKCδ-driven activation of keratinocytes is strongly reduced while PKCβII-driven activation of neutrophils is retained.

Photodynamic Therapy

VIP

H. Huang, B. Yu, P. Zhang, J. Huang,
Y. Chen, G. Gasser,* L. Ji,
H. Chao* **14049–14052**

Highly Charged Ruthenium(II) Polypyridyl Complexes as Lysosome-Localized Photosensitizers for Two-Photon Photodynamic Therapy

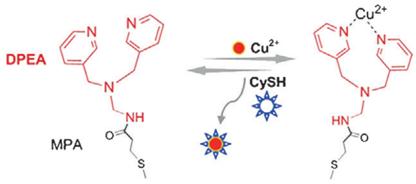


Very positive: The title complexes can be used for two-photon photodynamic therapy (PDT). They selectively accumulate in lysosomes through endocytosis and exhibit high phototoxicity against 2D monolayer cancer cells and 3D multicellular tumor spheroids upon two-photon laser irradiation.

Biosensors

Y. Luo, L. Zhang, W. Liu, Y. Yu,
Y. Tian* **14053–14056**

A Single Biosensor for Evaluating the Levels of Copper Ion and L-Cysteine in a Live Rat Brain with Alzheimer's Disease

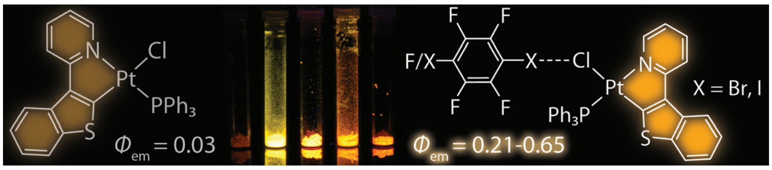


Copper on my mind: By designing the amine DPEA for specific recognition of Cu^{2+} and synthesizing Methylene Blue-DNA for an inner reference, a single biosensor based on Au nanoleaves was developed for evaluating the levels of Cu^{2+} and CySH in rat brains with Alzheimer's disease.

Halogen Bonding

V. V. Sivchik, A. I. Solomatina, Y.-T. Chen,
A. J. Karttunen, S. P. Tunik, P.-T. Chou,*
I. O. Koshevoy* **14057–14060**

Halogen Bonding to Amplify Luminescence: A Case Study Using a Platinum Cyclometalated Complex

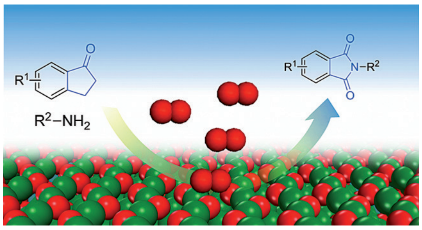


Hal-lighted: A weakly luminescent Pt complex readily cocrystallizes with fluorinated bromo- and iodoarenes (halogen-bond donors) to form compounds with significantly increased emission quantum yields (Φ_{em}). The effect is attributed to the combination of enhanced spin–orbit coupling and structural rigidity in the cocrystallized compound that suppresses the nonradiative decay rate.

Heterogeneous Catalysis

M. Wang, J. M. Lu, J. P. Ma, Z. Zhang,
F. Wang* **14061–14065**

Cuprous Oxide Catalyzed Oxidative C—C Bond Cleavage for C—N Bond Formation: Synthesis of Cyclic Imides from Ketones and Amines

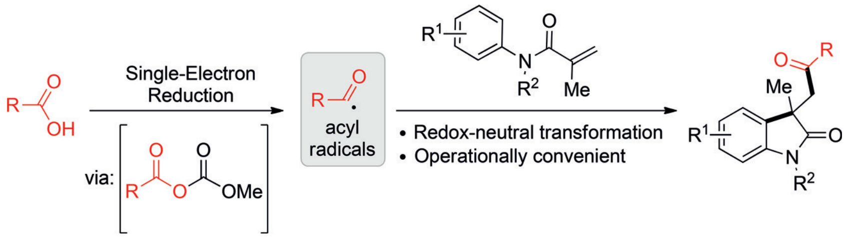


On the surface: A new reaction for the synthesis of cyclic imides from ketones and amines was developed. Cuprous oxide catalyzes the oxidative C—C bond cleavage for C—N bond formation. The reaction mechanism is also discussed.

Acyl Radicals

G. Bergonzini, C. Cassani,
C.-J. Wallentin* ———— 14066 – 14069

Acyl Radicals from Aromatic Carboxylic Acids by Means of Visible-Light Photoredox Catalysis

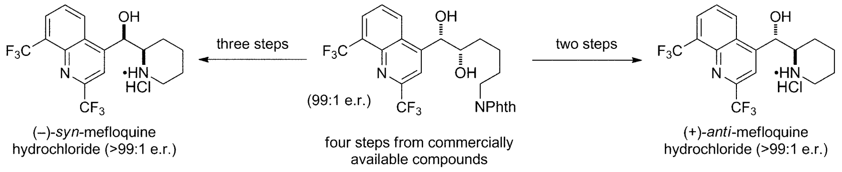


A mild method for C–C bond formation: Acyl radicals have been accessed from simple aromatic carboxylic acids under visible-light photoredox catalysis. The method offers mild entry to high-value heterocyclic compounds without the need of high-energy UV irradiation, stoichiometric oxidants, high CO pressure, or high temperature.

Total Synthesis

E. J. Rastelli,
D. M. Coltart* ———— 14070 – 14074

A Concise and Highly Enantioselective Total Synthesis of (+)-*anti*- and (−)-*syn*-Mefloquine Hydrochloride: Definitive Absolute Stereochemical Assignment of the Mefloquines

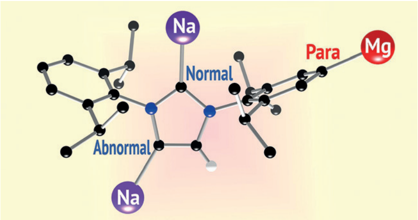


A common intermediate: The concise asymmetric total synthesis of (+)-*anti*- and (−)-*syn*-mefloquine hydrochloride is based on the Sharpless dihydroxylation of an olefin that is accessed in three steps from commercially available materials. The diol is then converted into either a *trans* or *cis* epoxide, which are subsequently transformed into the two mefloquine diastereomers.

Metalation

A. J. Martínez-Martínez, M. Á. Fuentes,
A. Hernán-Gómez, E. Hevia,
A. R. Kennedy, R. E. Mulvey,*
C. T. O'Hara ———— 14075 – 14079

Alkali-Metal-Mediated Magnesiations of an N-Heterocyclic Carbene: Normal, Abnormal, and "Paranormal" Reactivity in a Single Tritopic Molecule



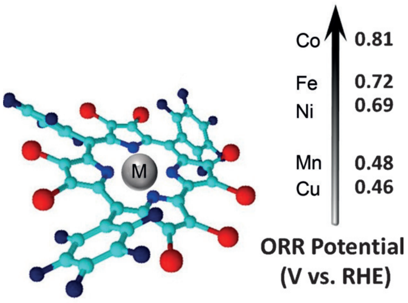
Paranormal NHC: When an N-heterocyclic carbene (NHC) encounters a pre-inverse-crown template base, an extraordinary event occurs, thus generating a dative C–Na bond at the normal C2-position, sodiation at the abnormal C4-position, and magnesiation at the *para*-position of a diisopropylphenyl (Dipp) substituent on N. Structure elucidation and steps towards the target compound are discussed.

Back Cover

Oxygen Reduction Reaction

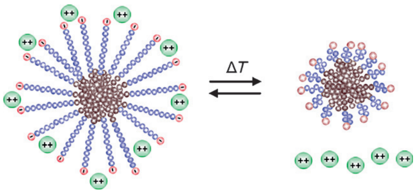
N. Levy, A. Mahammed, M. Kosa,
D. T. Major, Z. Gross,*
L. Elbaz* ———— 14080 – 14084

Metallocorroles as Nonprecious-Metal Catalysts for Oxygen Reduction



Money-saving measures: A series of first-row transition-metal corroles were investigated as electrocatalysts for the oxygen reduction reaction (ORR). The best catalytic performance was obtained for the Co^{III} corrole, which had an onset potential of 0.81 V versus the reversible hydrogen electrode (RHE), comparable to the performance of precious-metal catalysts used by the fuel-cell industry. Br red, N dark blue, C light blue.

Shifting affections: A micellar system consisting of polystyrene–poly(methoxy diethyleneglycol acrylate) block copolymers modified with carboxylic acid end groups could be reversibly switched between the adsorption and desorption of Ca^{2+} ions by a mild temperature trigger (see picture). Such materials are needed for the removal of multivalent ions from aqueous streams without the inconvenience of brine regeneration.



Smart Materials

J. P. A. Custers, S. F. G. M. van Nispen, A. Can, V. R. de La Rosa, S. Maji, U. S. Schubert, J. T. F. Keurentjes, R. Hoogenboom* ______ 14085 – 14089

Reversible Calcium(II)-Ion Binding through an Apparent pK_a Shift of Thermosensitive Block-Copolymer Micelles

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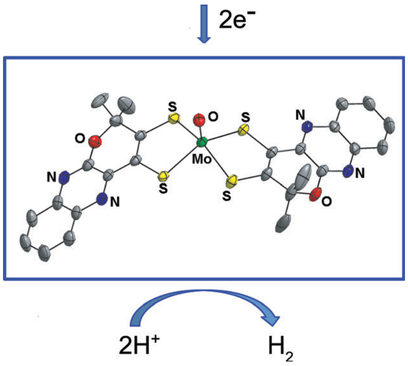
Second nature: A bioinspired molybdenum complex employing a quinoxaline–pyran-fused dithiolene ligand has been synthesized for the first time. The complex was found to be an efficient and stable catalyst for the photo- and electroreduction of protons to form hydrogen. As suggested by DFT calculations, the oxo ligand plays a key role in facilitating protonation of a Mo–hydride intermediate and H_2 formation.



Bioinorganic Chemistry

J.-P. Porcher, T. Fogeron, M. Gomez-Mingot, E. Derat, L.-M. Chamoreau, Y. Li,* M. Fontecave* ______ 14090 – 14093

A Bioinspired Molybdenum Complex as a Catalyst for the Photo- and Electroreduction of Protons

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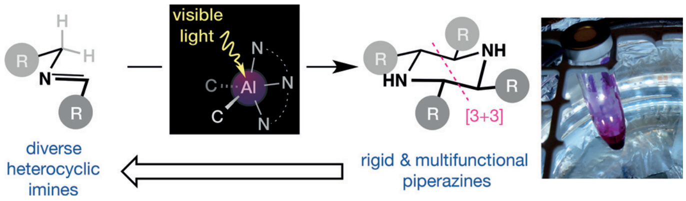

Al-umination: A new synthesis of polyfunctional piperazine ligands has been developed using visible-light irradiation and an aluminum alkyl promoter. This system reverses the reactivity commonly found in azomethine ylide chemistry, introduces the concept of using visible-light photochemistry of main-group organometallics, and sets the basis for new promising C–H oxidation catalysts.

Cycloaddition

S. Suárez-Pantiga, K. Colas, M. J. Johansson, A. Mendoza* ______ 14094 – 14098

Scalable Synthesis of Piperazines Enabled by Visible-Light Irradiation and Aluminum Organometallics

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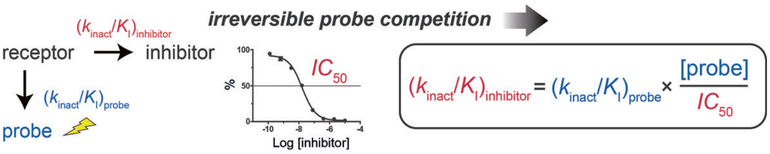


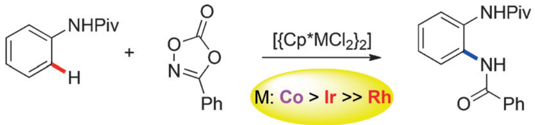
No going back: The potency metric of irreversible inhibitors is k_{inact}/K_I not IC_{50}. A simple approach was developed that makes use of an irreversible probe for competitive assays run to completion against test compounds. In this system, k_{inact}/K_I of the test compound is equal to $(k_{inact}/K_I)_{probe} \times [probe]/IC_{50}$. Advantages include simplicity, high throughput, and application to all target classes, and it only requires an in-depth kinetic evaluation of the probe.

Inhibitors

I. Miyahisa,* T. Sameshima, M. S. Hixon ______ 14099 – 14102

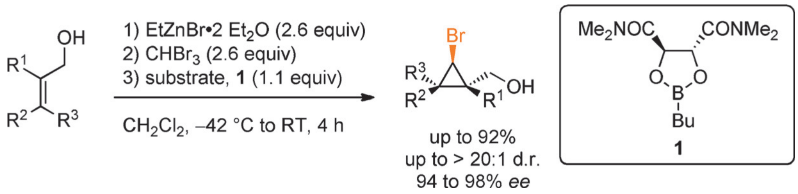
Rapid Determination of the Specificity Constant of Irreversible Inhibitors (k_{inact}/K_I) by Means of an Endpoint Competition Assay

Cobalt Catalysis



Pick of the bunch: A variety of arenes, including anilides, underwent direct C–H amidation with dioxazolones in the presence of a cobalt catalyst with a Cp* ligand under mild and straightforward reaction conditions (see scheme; Piv = pivaloyl). A comparative study of Group 9 [Cp*M^{III}] complexes revealed the unique ability of the cobalt catalyst to promote this transformation efficiently.

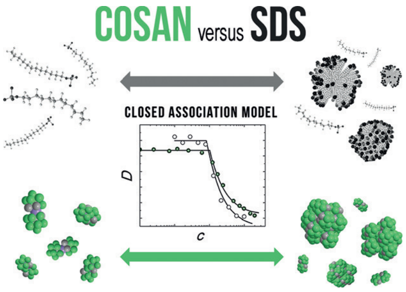
Carbenoids



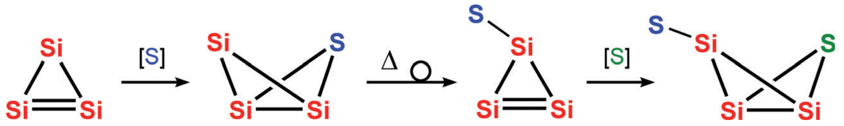
Finding the right carbenoid: In-depth NMR experiments led to an understanding of the mechanism of the formation and the nature of a dibromomethylzinc carbenoid, thus permitting development of an efficient bromocyclopropanation reaction for allylic alcohols. The desired bromo-substituted cyclopropanes were isolated in high yields and excellent diastereo- as well as enantioselectivities using readily available reagents.

Self-Assembly

Spot the difference: The metallacarborane anion [3,3′-Co(C$_2$B$_9$H$_{11}$)$_2$]$^-$ ([COSAN]$^-$), which can be considered as a nonclassical 3D-aromatic amphiphile, undergoes self-assembly in water. As is the case for classical surfactants such as sodium dodecylsulfate (SDS), the self-assembly process obeys the mechanism of closed association. However, in contrast to classical surfactants, COSAN$^-$ aggregation is enthalpy-driven. D = diffusion coefficient.

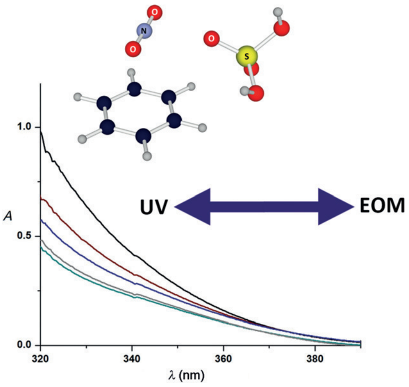


Valence Isomerism



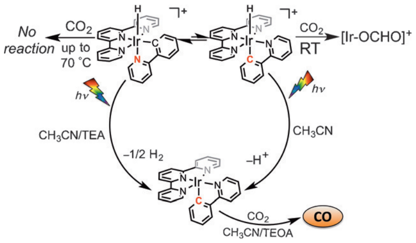
Back-and-forth and in-between: The back-and-forth interconversion between the cyclotrisilenes and thiatrisilabicyclo[1.1.0]butanes is presented, allowing for the synthesis of highly reactive organometallic compounds. The peculiar structural and bonding features of the newly synthesized compounds, as well as their isomerization mechanism, are verified both experimentally and computationally.

A new intermediate in an old reaction: Experimental evidence is presented for the first intermediate in benzene nitration with mixed acid. Both experiment and theory show that no charge transfer accompanies the formation of the π-complex. EOM = Equation of motion.



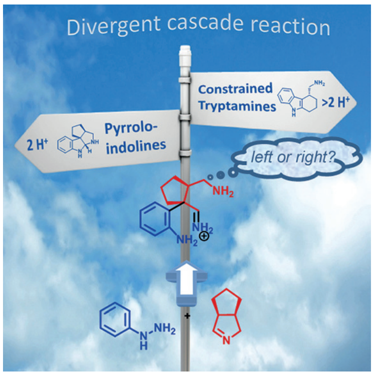
Computational Chemistry

Two geometric isomers of [Ir(tpy)(ppy)H]$^+$ were prepared and their ground- and excited-state properties towards reaction with CO_2, as well as their hydricities, were characterized using experimental and computational methods.

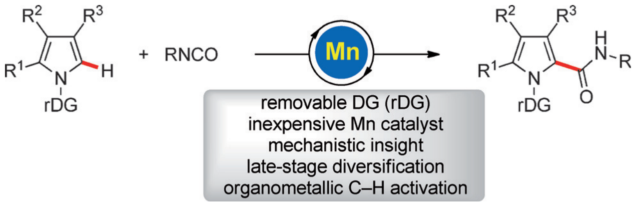


CO_2 Reduction

One way or the other: The interrupted Fischer indole synthesis of arylhydrazines and chiral bicyclic imines selectively affords either tetracyclic pyrroloindolines or tricyclic tryptamine analogues depending on the reaction conditions. The products were obtained in high optical purity and readily elaborated to medicinally important compounds.



Asymmetric Synthesis



Heteroaromatic amides were obtained by a step-economical, manganese(I)-catalyzed C–H aminocarbonylation reaction between heteroarenes and aryl and alkyl isocyanates. The catalytic cycle was initiated by a facile organometallic C–H manganesation step, followed by a rate-determining migratory insertion. DG = directing group.

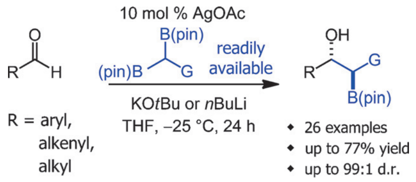
C–H Activation

Homogeneous Catalysis

M. V. Joannou, B. S. Moyer,
M. J. Goldfogel,
S. J. Meek* ____________ 14141 – 14145

Silver(I)-Catalyzed Diastereoselective Synthesis of *anti*-1,2-Hydroxyboronates

Bor(o)n to add: A catalytic protocol for the title reaction is described. The process provides access to secondary alkyl organoboron compounds. The deborylative 1,2-addition reactions of alkyl 1,1-diboronates proceed in the presence of a silver(I) salt with either KO*t*Bu or *n*BuLi as an activator. The catalytic diastereoselective protocol can be extended to aryl, alkenyl, and alkyl aldehydes. G = attached group.

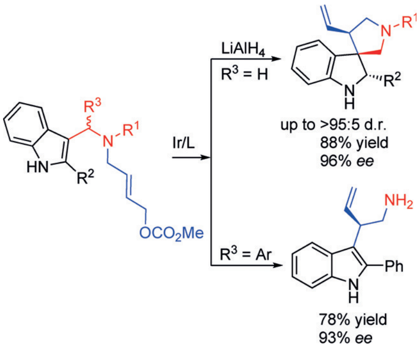


Asymmetric Catalysis

C.-X. Zhuo, Y. Zhou, Q. Cheng, L. Huang,
S.-L. You* ____________ 14146 – 14149

Enantioselective Construction of Spiroindolines with Three Contiguous Stereogenic Centers and Chiral Tryptamine Derivatives via Reactive Spiroindolenine Intermediates

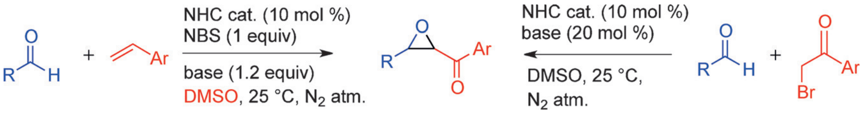
On a tryp: The highly efficient synthesis of enantioenriched spiroindolines by an iridium-catalyzed asymmetric allylic dearomatization and reduction has been realized. The spiroindolines contain three contiguous chiral centers and are obtained with excellent diastereo- and enantioselectivities. Furthermore, a chiral tryptamine derivative could also be accessed with excellent enantioselectivity.



Carbenes

R. N. Reddi, P. K. Prasad,
A. Sudalai* ____________ 14150 – 14153

N-Heterocyclic Carbene Catalyzed Oxidative Coupling of Alkenes/α-Bromoacetophenones with Aldehydes: A Facile Entry to α,β-Epoxy Ketones

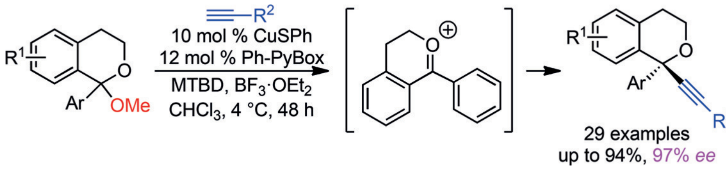


Two routes can be taken: The title reaction between styrenes and aldehydes enables the regioselective synthesis of α,β-epoxy ketones in the presence of NBS/DBU/DMSO as an oxidative system at ambient conditions. Also, the first NHC-catalyzed Darzens reaction of α-bromoketones and aldehydes under mild reaction conditions is described. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, DMSO = dimethylsulfoxide, NBS = *N*-bromosuccinimide.

Oxygen Heterocycles

S. Dasgupta, T. Rivas,
M. P. Watson* ____________ 14154 – 14158

Enantioselective Copper(I)-Catalyzed Alkynylation of Oxocarbenium Ions to Set Diaryl Tetrasubstituted Stereocenters

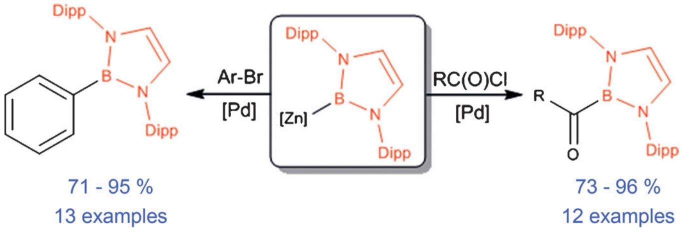


Face time: By distinguishing the faces of a diaryl-substituted oxocarbenium ion through a tether, high enantioselectivities are achieved in a copper-catalyzed alkynylation. This reaction enables formation of challenging diaryl, tetrasubstituted stereocenters within oxygen heterocycles and incorporates a useful alkyne functional group. MTBD = 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene, PyBox = pyridine bis(oxazoline).

Borylation

J. Campos,* S. Aldridge* **14159 – 14163**

Catalytic Borylation Using an Air-Stable Zinc Boryl Reagent: Systematic Access to Elusive Acylboranes

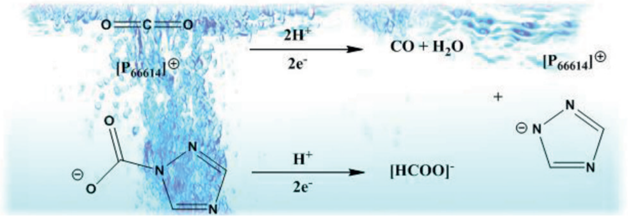


Borylzinc reagents are used in palladium-catalyzed borylation chemistry, that is, a C–B coupling protocol analogous to well-known Negishi chemistry. This approach also enabled the systematic preparation of acylboranes, whose conversion into synthetically useful acyltrifluoroboronates has also been demonstrated.

Ionic Liquids

N. Hollingsworth, S. F. R. Taylor,
M. T. Galante, J. Jacquemin, C. Longo,
K. B. Holt, N. H. de Leeuw,
C. Hardacre* **14164 – 14168**

Reduction of Carbon Dioxide to Formate at Low Overpotential Using a Superbase Ionic Liquid

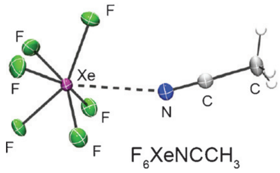


The superbasic RTIL (room-temperature ionic liquid) $[P_{66614}]$[124Triz] provides an alternative low-energy pathway for conversion of CO_2 into formate. This is the first time chemical binding of the CO_2 molecule to the anion of a RTIL has been shown to decrease the activation energy for electrochemical reduction, by distortion of the CO_2 geometry from linear to bent.

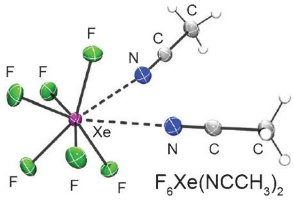
Xenon Fluorides

K. Matsumoto, J. Haner, H. P. A. Mercier,
G. J. Schrobilgen* **14169 – 14173**

Syntheses and Structures of $F_6XeNCCH_3$ and $F_6Xe(NCCH_3)_2$



$F_6XeNCCH_3$



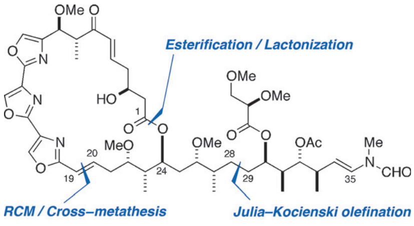
$F_6Xe(NCCH_3)_2$

Xe^{VI}–N bonds at last: Two shock-sensitive, highly explosive adducts of the potent oxidant XeF_6 and CH_3CN have been synthesized and characterized at low temperatures. Crystal structures and Raman spectra confirm that the title compounds represent the first examples of Xe^{VI}–N bonds and a well-isolated XeF_6 (C_{3v}) moiety in the solid state. Calculations were used to assign vibrational frequencies and determine binding energies.

Total Synthesis

M. Kita,* H. Oka, A. Usui, T. Ishitsuka,
Y. Mogi, H. Watanabe, M. Tsunoda,
H. Kigoshi* **14174 – 14178**

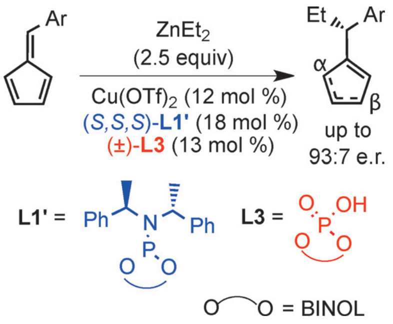
Total Synthesis of Mycalolides A and B through Olefin Metathesis



Mycalolide B

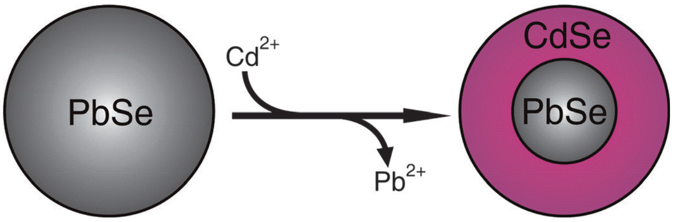
From start to finish: An asymmetric total synthesis of the trisoxazole macrolides, mycalolides A and B, is described. The synthesis involves the convergent assembly of C1–C19 trisoxazole and C20–C35 side-chain segments using olefin metathesis and esterification as key steps.

C–C Coupling



Something to zinc about: The use of a combined phosphoramidite–phosphate ligand system allows the demanding catalytic asymmetric carbozincation of pentafulvenes to be realized (see scheme; BINOL = 2,2′-dihydroxy-1,1′-binaphthyl). A simple phosphoric acid additive has a profound effect on the rate of the carbozincation reaction. Titanocene dichloride derivatives of the cyclopentadienyl products are useful biological probes.

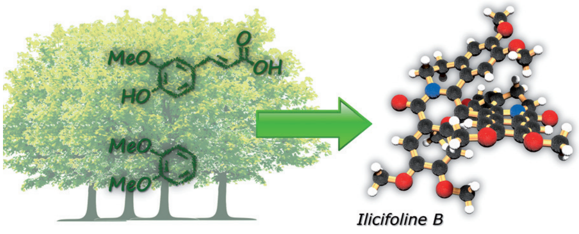
Nanoparticles



Lead astray: Ion exchange and transport in nanocrystals is studied on the molecular scale. The cation exchange from PbSe with Cd^{2+} showed that the exchange occurred exclusively by diffusion via the interstitial sites and subsequent expulsion of individual ions from lattice sites without the formation of vacancies.

Sustainable Chemistry

Front Cover



A chip off the old block: A xylochemical approach for the total syntheses of ilicifoline B and morphinans was developed. All of the carbon centers in the final product originate from wood-based starting materials. These results demonstrate the feasibility and advantages of a xylochemical approach to a sustainable chemical economy and meet the first of four grand challenges in developing a new chemical infrastructure that employs renewable resources.

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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