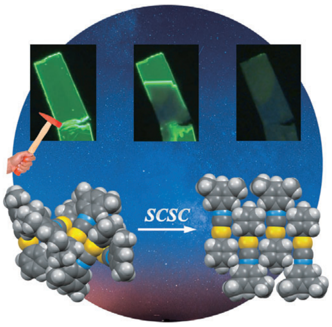
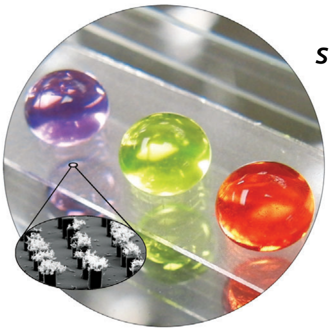
The potent and deadly neurotoxin ...

... caramboxin was extracted from star fruits, as N. Garcia-Cairasco, N. P. Lopes, et al. describe in their Communication on page 13067 ff. The main targets of caramboxin intoxication are the kidney and the brain. A worldwide awareness is needed for thousands of people who are exposed to this new phenylalanine-like neurotoxin. (Cover by N. Garcia-Cairasco)

Phase Transition

In their Communication on page 12828 ff., H. Ito et al. report a single-crystal-to-single-crystal (SCSC) phase transition of phenyl(3,5-dimethylphenyl isocyanide)gold(I). The transition was triggered by mechanical picking or solid seeding.



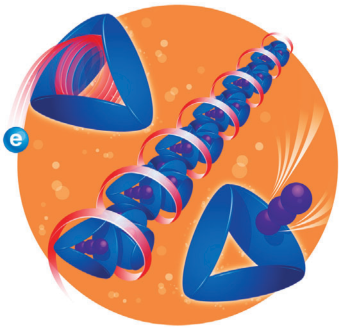


Surface Chemistry

A method for the fabrication of transparent hierarchically textured surfaces is described by A. Tuteja et al. in their Communication on page 13007 ff. The surfaces can repel essentially all liquids, including different oils and alcohols.

Anion-π Interactions

J. F. Stoddart, M. R. Wasielewski et al. show in their Communication on page 13100 ff. that π–π stacking of triiodide anions in the cavities of homochiral molecular prisms leads to single-handed supramolecular helices.



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Service

Author Profile

“The best advice I have ever been given is “Don’t panic!” I can never resist good food …”
This and more about Markus Kalesse can be found on page 12775.

News

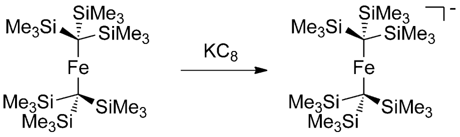
M. Schnell

S. Riedel

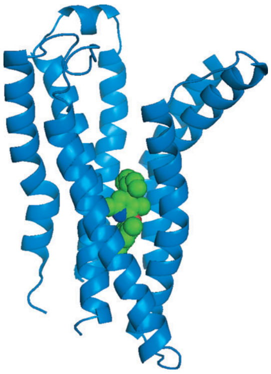
G.-J. Boons

Books

Highlights



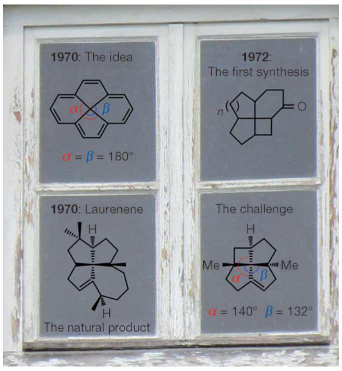
Not just any old iron ion: A linear, two-coordinate ionic Fe^{I} complex (see scheme) with a $S=3/2$ ground state has a large energy barrier for magnetization reversal, $U_{eff}=226\ cm^{-1}$, and undergoes slow magnetic relaxation in the absence of an applied magnetic field. The preparation of complexes with these properties is a step towards the eventual practical application of single-molecule magnets.



New members in the GPCR photo gallery! Crystal structures of class B G protein-coupled receptors, which bind peptide hormones, have been solved [see picture of the corticotropin-releasing factor receptor 1 (blue) and a bound allosteric nonpeptide antagonist (green)]. The structures provide a basis for a rational design of better drugs for diabetes, osteoporosis, migraine, or depression.

Minireviews

Highly strained: Four condensed cycles and a distorted tetracoordinated carbon center with bond angles greater than the regular 109.4° make the scaffold of fenestranes quite unique. A definition and nomenclature of these scaffolds is followed by a detailed overview over recent syntheses of these strained molecules, including their impact on the study of planar tetracoordinate carbon atoms.



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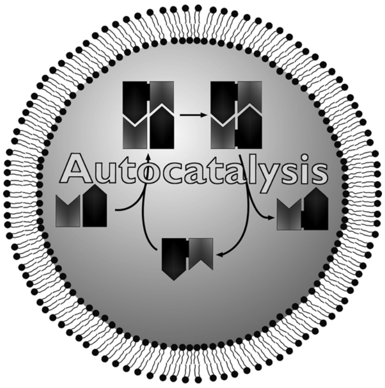
Reviews

Origins of Life

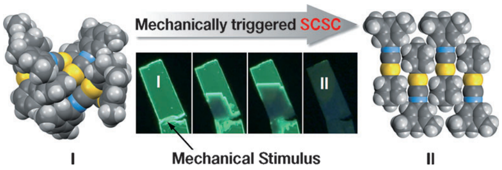


Self-replication is a fundamental concept which lies at the heart of the propagation of life and many other biological processes. Autocatalysis has been implicated in the origin of life itself. Diverse examples of autocatalytic chemical reactions are summarized, including the special case of absolute asymmetric autocatalysis, with special attention paid to their prebiotic relevance.

Communications

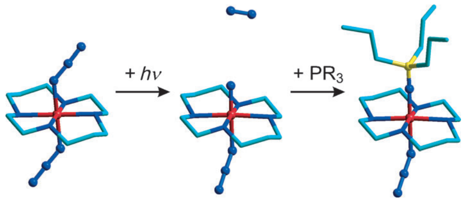
Molecular Domino Mechanism

Frontispiece



Green and blue polymorphs: A single-crystal-to-single-crystal (SCSC) phase transition of phenyl(3,5-dimethylphenyl isocyanide)gold(I) was triggered by mechanical picking or solid seeding and propagated spontaneously with a domino-like mechanism (see picture). As a result, one phase with intense green emission was transformed to another phase with weaker blue emission.

High-Valent Iron



Give me five: Time-resolved Fourier-transform IR spectroscopy is used to time-resolve the formation and the reaction dynamics of a fourfold symmetrical nitrido iron(V) complex (light blue C, red Fe, blue N) in liquid solution under physiological and technologically relevant conditions.


Quenching the thirst for knowledge
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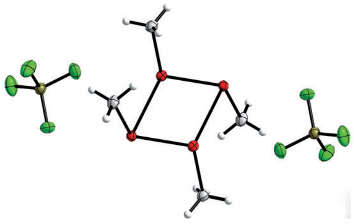
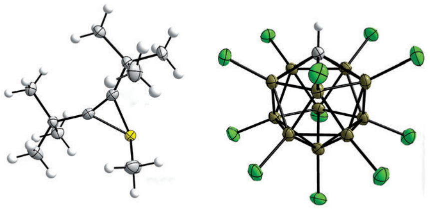
One-Electron Oxidants

H. Poleschner,*
K. Seppelt ______ 12838 – 12842

XeF$_2$/Fluoride Acceptors as Versatile One-Electron Oxidants


$Me_4Se_4^{2+}(BF_4^-)_2$

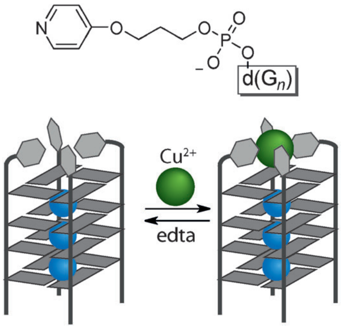

$[tBu_2C_2SMe]^+\ CHB_{11}Cl_{11}^-$

No phlogiston but xenon is released when XeF$_2$/F$^-$ acceptors act as new one-electron oxidants. F$^-$ acceptors are Lewis acids BF$_3$, B(C$_6$F$_5$)$_3$, and Al{OC(CF$_3$)$_3$}$_3$, and silyl derivatives TfOSiMe$_3$, Tf$_2$NSiMe$_3$, Me$_3$Si$^+$B(C$_6$F$_5$)$_4^-$, and Me$_3$Si$^+$CHB$_{11}$Cl$_{11}^-$. The anions BF$_4^-$, TfO$^-$, Tf$_2$N$^-$, FB(C$_6$F$_5$)$_3^-$, FAl{OC(CF$_3$)$_3$}$_3^-$, B(C$_6$F$_5$)$_4^-$, or CHB$_{11}$Cl$_{11}^-$ can be introduced into oxidation products of R$_2$E$_2$ (E = S, Se, Te), [FeCp$_2$], [(FeCpS)$_4$], tetrathiafulvalene, thianthrene, and (2,4-Br$_2$C$_6$H$_3$)$_3$N.

G-Quadruplex DNA

D. M. Engelhard, R. Pievo,
G. H. Clever* ______ 12843 – 12847

Reversible Stabilization of Transition-Metal-Binding DNA G-Quadruplexes

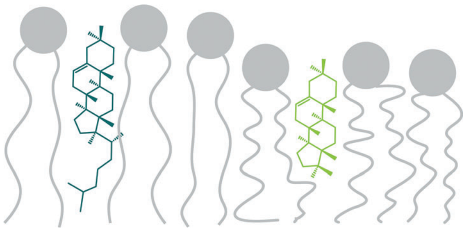


You can't top the CopperTop: Tetramolecular G-quadruplexes modified with terminal pyridine ligands exhibit metal-triggered stabilization as monitored by thermal denaturation studies, circular dichroism, and nondenaturing gel electrophoresis. Formation of the square-planar Cu^{II}(pyridine)$_4$ complex was confirmed by EPR measurements. The metal complexation is fully reversible by removal of the transition metal with ethylenediaminetetraacetic acid (edta).

Cholesterol

H. A. Scheidt, T. Meyer, J. Nikolaus,
D. J. Baek, I. Haralampiev, L. Thomas,
R. Bittman, P. Müller, A. Herrmann,
D. Huster* ______ 12848 – 12851

Cholesterol's Aliphatic Side Chain Modulates Membrane Properties

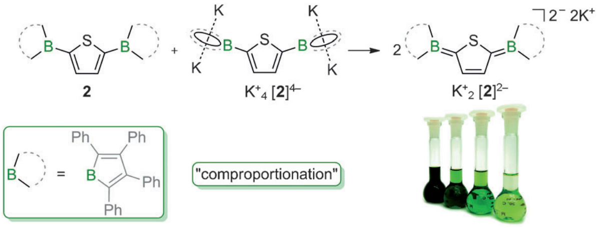


The influence of cholesterol's alkyl side chain on membrane properties was studied using a series of synthetic cholesterol derivatives without a side chain or with a branched side chain consisting of 5 to 14 carbon atoms. Cholesterol's side chain is crucial for all membrane properties investigated and therefore essential for the membrane properties of eukaryotic cells.

Bipolarons

H. Braunschweig,* V. Dyakonov,
B. Engels,* Z. Falk, C. Hörl, J. H. Klein,
T. Kramer, H. Kraus, I. Krummenacher,
C. Lambert, C. Walter ____ **12852 – 12855**

Multiple Reduction of 2,5-Bis(borolyl)thiophene: Isolation of a Negative Bipolaron by Comproportionation

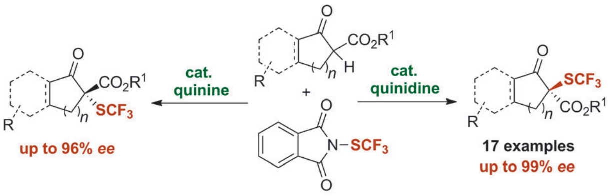


The 2,5-bis(borolyl)thiophene 2, a conjugated acceptor–π–acceptor system, can be reduced to the monoradical anion [**2**]$^{\bullet-}$, the dianion [**2**]$^{2-}$, and the tetraanion [**2**]$^{4-}$. The dianion [**2**]$^{2-}$ was also prepared by a comproportionation reaction (see scheme) and features an absorption maximum in the near-IR region (λ_{max} = 800 nm), which is characteristic of a bipolaron with a quinoidal structure.

Trifluoromethylsulfenylation

T. Bootwicha, X. Liu, R. Pluta, I. Atodiresei,
M. Rueping* ____________ **12856 – 12859**

N-Trifluoromethylthiophthalimide: A Stable Electrophilic SCF$_3$-Reagent and its Application in the Catalytic Asymmetric Trifluoromethylsulfenylation



Cinchona alkaloid catalysts in combination with air- and moisture-stable *N*-trifluoromethylthiophthalimide as electrophilic SCF$_3$ source enabled the catalytic enantioselective trifluoromethylsulfenylation. Thus, a series of α-SCF$_3$ esters that bear a quaternary carbon stereogenic center were obtained with excellent yield and enantioselectivity. Moreover, the products can be readily converted into valuable α-SCF$_3$ β-hydroxyesters.

Trifluoromethylthiolation

X. Q. Wang, T. Yang, X. Cheng,
Q. Shen* ______________ **12860 – 12864**

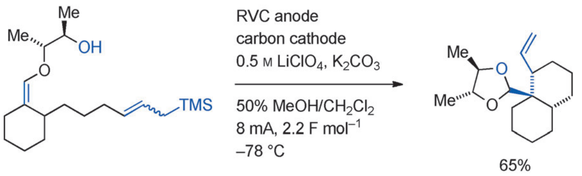
Enantioselective Electrophilic Trifluoromethylthiolation of β-Ketoesters: A Case of Reactivity and Selectivity Bias for Organocatalysis

A chiral Lewis base or a phase-transfer catalyst (PTC) can mediate the highly enantioselective trifluoromethylthiolation of β-ketoesters with the previously developed SCF$_3$ reagent (see scheme). Reactions of indanone-derived β-ketoesters occurred with high yield and excellent enantioselectivity with quinine as catalyst. Reactions of tetralone- or 1-benzosuberone-derived β-ketoesters occurred with moderate to good enantioselectivity with a quinine-derived PTC.

Anodic Cyclizations

A. Redden, R. J. Perkins,
K. D. Moeller* __________ **12865 – 12868**

Oxidative Cyclization Reactions: Controlling the Course of a Radical Cation-Derived Reaction with the Use of a Second Nucleophile

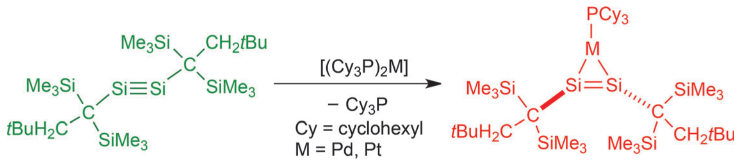


Construction of new ring systems: Oxidative cyclizations (see picture; RVC = reticulated vitreous carbon) have been conducted that use two separate intramolecular nucleophiles to trap an enol ether-derived radical cation intermediate. The reactions provide a means for rapidly trapping the radical cation intermediate in a manner that avoids competitive decomposition reactions.

Disilyne Complexes

S. Ishida,* R. Sugawara, Y. Misawa, T. Iwamoto* ______ **12869 – 12873**

Palladium and Platinum η²-Disilyne Complexes Bearing an Isolable Dialkyldisilyne as a Ligand

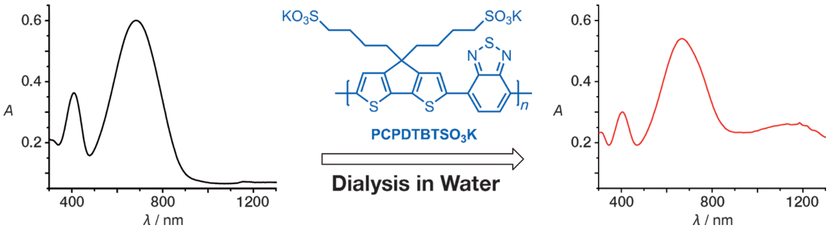


Not so alkyne like: A dialkyldisilyne (left, green) that can be isolated is synthesized and fully characterized. It coordinates to palladium and platinum in a η²-fashion giving complexes (red) with a *trans*-bent geometry, in contrast to η²-alkyne complexes. The complexes showed significant metallacycle character.

Conjugated Polyelectrolytes

C.-K. Mai, H. Zhou, Y. Zhang, Z. B. Henson, T.-Q. Nguyen, A. J. Heeger, G. C. Bazan* ______ **12874 – 12878**

Facile Doping of Anionic Narrow-Band-Gap Conjugated Polyelectrolytes During Dialysis

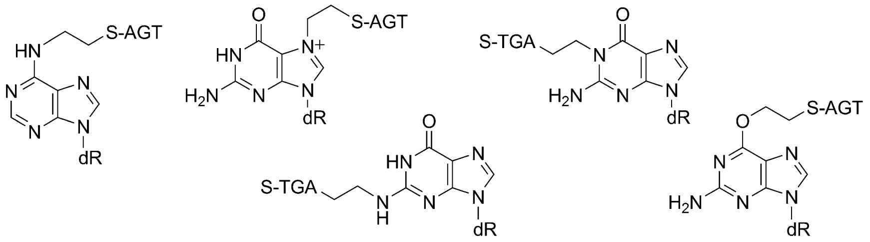


$PCPDTBTSO_3K$, an anionic, narrow-band-gap conjugated polyelectrolyte, was found to be doped after dialysis. The proposed doping mechanism involves protonation of the polymer backbone, followed by electron transfer from a neutral chain, to generate radical cations, which are stabilized by the pendant sulfonate anions. Formation of polarons is supported by spectroscopy and electrical-conductivity measurements.

DNA Damage

G. Chowdhury, S.-H. Cho, A. E. Pegg, F. P. Guengerich* ______ **12879 – 12882**

Detection and Characterization of 1,2-Dibromoethane-Derived DNA Crosslinks Formed with *O*⁶-Alkylguanine-DNA Alkyltransferase

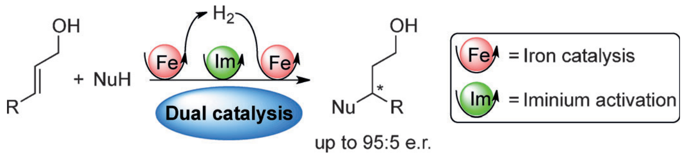


A combination of chemical modifications and LC-tandem MS was used for the structure elucidation of various ethylene crosslinks of DNA with *O*⁶-alkylguanine-DNA alkyltransferase (AGT, see picture). The elucidation of the chemical structures of such DNA–protein crosslinks is necessary to understand mechanisms of mutagenesis.

Dual Catalysis

A. Quintard,* T. Constantieux, J. Rodriguez* ______ **12883 – 12887**

An Iron/Amine-Catalyzed Cascade Process for the Enantioselective Functionalization of Allylic Alcohols

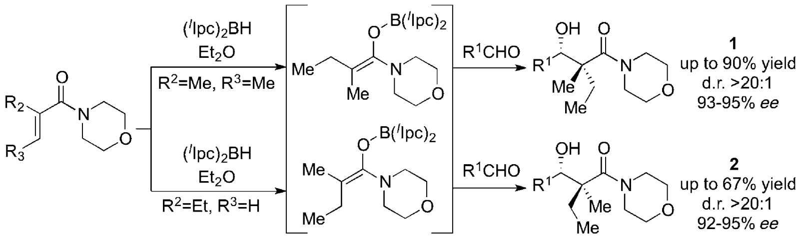


Three is a lucky number: An enantioselective transformation of allylic alcohols into β-chiral saturated alcohols has been developed by combining two distinct metal- and organocatalyzed catalytic cycles. This waste-free triple cascade process merges an iron-catalyzed borrowing-hydrogen step with an aminocatalyzed nucleophilic addition reaction.

Synthetic Methods

C. Allais, A. S. Tsai, P. Nuhant,
W. R. Roush* ________ **12888 – 12891**

Generation of Stereochemically Defined Tetrasubstituted Enolborinates by 1,4-Hydroboration of α,β-Unsaturated Morpholine Carboxamides with (Diisopinocampheyl)borane

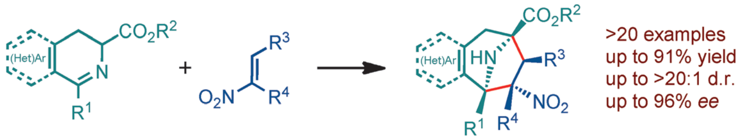


On all fours: The title reaction with $(Ipc)_2BH$ provides tetrasubstituted enolborinates which undergo aldol reactions with aldehydes to form products with all-carbon quaternary centers with exceptional diastereo- and enantioselectivity. A change to the substitution pattern of the starting amide leads to either diastereomer of the α-methyl-α-ethyl-β-hydroxy carboxamide (**1** or **2**).

Asymmetric Catalysis

R. Narayan, J. O. Bauer, C. Strohmann,
A. P. Antonchick,*
H. Waldmann* ________ **12892 – 12896**

Catalytic Enantioselective Synthesis of Functionalized Tropanes Reveals Novel Inhibitors of Hedgehog Signaling



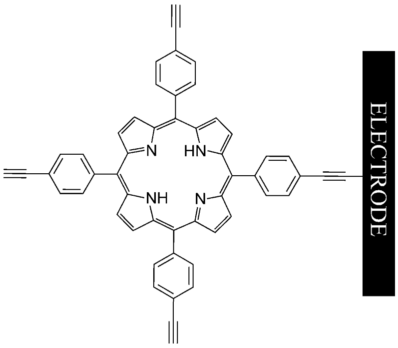
Dipolar cycloaddition: A highly efficient copper(I)-catalyzed enantioselective [3+2] cycloaddition reaction of 1,3-fused cyclic azomethine ylides and nitroalkenes has been developed. This method provides access to functionalized tropane scaffolds with several quaternary and tertiary stereocenters in a single step under mild reaction conditions.

Electrochemistry

M. V. Sheridan, K. Lam,
W. E. Geiger* ________ **12897 – 12900**

Covalent Attachment of Porphyrins and Ferrocenes to Electrode Surfaces through Direct Anodic Oxidation of Terminal Ethynyl Groups

One with the surface: A method is presented for electrode modification with terminal alkynes and alkenes. Direct oxidation of these moieties leads to efficient grafting onto glassy carbon, gold, platinum, and indium tin oxide surfaces. Various ferrocenes and 5,10,15,20-(4-ethynylphenyl)porphyrin were attached in this way.



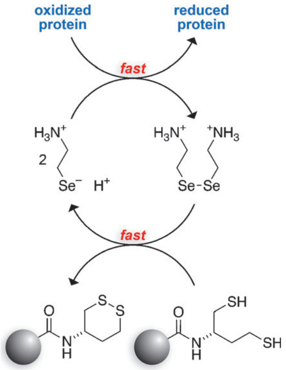
Thiol–Disulfide Interchange

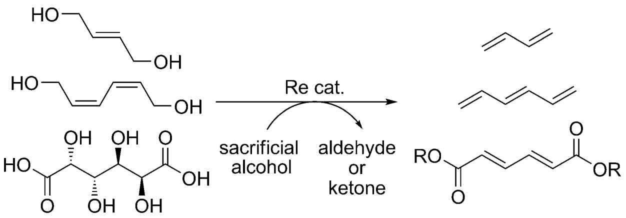
J. C. Lukesh, III, B. VanVeller,
R. T. Raines* ________ **12901 – 12904**

Thiols and Selenols as Electron-Relay Catalysts for Disulfide-Bond Reduction

Inside Cover

Pass them on! Dithiobutylamine immobilized on a resin is a useful reagent for the reduction of disulfide bonds. Its ability to reduce a disulfide bond in a protein is enhanced greatly if used along with a soluble strained cyclic disulfide or mixed diselenide that relays electrons from the resin to the protein. This electron-relay catalysis system provides distinct advantages over the use of excess soluble reducing agent alone.





New modes of DODH: Oxorhenium compounds act as deoxydehydration-(DODH)/acid dual-purpose catalysts to transform biomass-derived diol substrates into a variety of commodity chemical precursors. The power of this approach is highlighted by a tandem [1,3]-OH shift/DODH of 2-ene-1,4-diols and 2,4-diene-1,6-diols, and by a DODH/esterification sequence of sugar acids to unsaturated esters for the production of polymers and plasticizers.

Biomass Conversion

M. Shiramizu,
F. D. Toste* ———— **12905 – 12909**

Expanding the Scope of Biomass-Derived Chemicals through Tandem Reactions Based on Oxorhenium-Catalyzed Deoxydehydration

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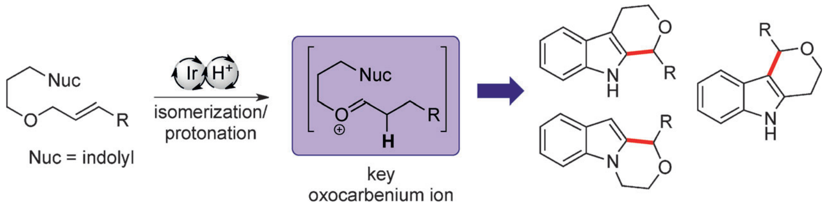


Working together: A mild and efficient isomerization/protonation sequence generates pyran-fused indoles by cooperative catalysis between cationic iridium(III) and Bi(OTf)$_3$. Three distinct cyclization manifolds lead to the corresponding bioactive scaffolds in good yields. In addition, N-substituted indoles can be synthesized enantioselectively in the presence of a chiral phosphate.

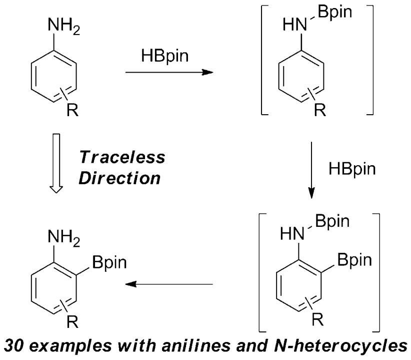
Synthetic Methods

V. M. Lombardo, C. D. Thomas,
K. A. Scheidt* ———— **12910 – 12914**

A Tandem Isomerization/Prins Strategy: Iridium(III)/Brønsted Acid Cooperative Catalysis

---

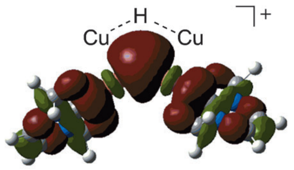
Not a trace: Borylation of the nitrogen in nitrogen heterocycles or anilines provides a traceless directing group for subsequent catalytic C–H borylation. Selectivities that previously required Boc protection can be achieved; furthermore, the NBpin directing group can be installed and removed in situ, and product yields are substantially higher. Boc = *tert*-butoxycarbonyl, pin = pinacolato.



C–H Functionalization

S. M. Preshlock, D. L. Plattner,
P. E. Maligres, S. W. Krska,*
R. E. Maleczka, Jr.,*
M. R. Smith, III* ———— **12915 – 12919**

A Traceless Directing Group for C–H Borylation



A bent dicopper–hydride cation that has an N-heterocyclic carbene supporting ligand has a Cu-H-Cu angle of 122° in the solid state. Density functional theory suggests an open three-centered metal–hydrogen interaction. The hydride reacts readily with methanol and with carbon dioxide; insertion of phenylacetylene affords a *gem*-dicopper vinyl complex.

Copper Hydrides

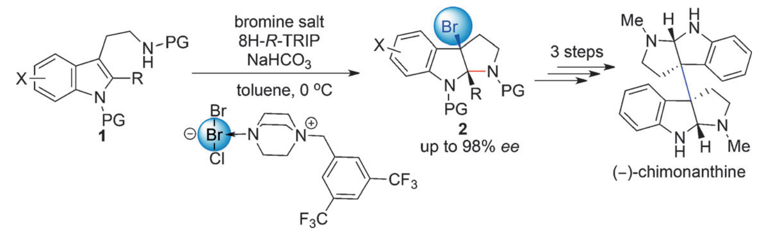
C. M. Wyss, B. K. Tate, J. Bacsa,
T. G. Gray,* J. P. Sadighi* **12920 – 12923**

Bonding and Reactivity of a μ-Hydrido Dicopper Cation

Total Synthesis

W. Xie,* G. Jiang, H. Liu, J. Hu, X. Pan, H. Zhang, X. Wan, Y. Lai,* D. Ma* ____ **12924 – 12927**

Highly Enantioselective Bromocyclization of Tryptamines and Its Application in the Synthesis of (−)-Chimonanthine



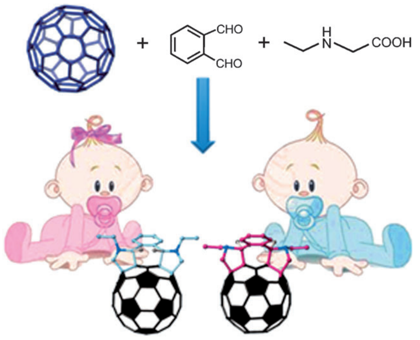
A shorter path: A highly enantioselective bromocyclization of tryptamine has been developed using an anionic chiral phase-transfer catalyst. This method provides a direct approach for preparing chiral 3-bromopyrroloindoline from tryptamine, which enables a four-step enantioselective synthesis of (−)-chimonanthine. PG = protecting group.

Fullerene Isomers

M. Izquierdo, M. R. Cerón, N. Alegret, A. J. Metta-Magaña, A. Rodríguez-Fortea, J. M. Poblet, L. Echegoyen* ____ **12928 – 12931**

Unexpected Isomerism in *cis*-2 Bis(pyrrolidino)[60]Fullerene Diastereomers

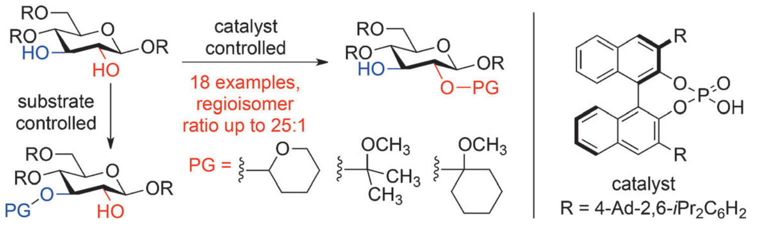
Similar yet different: A one-step regio- and diastereoselective synthesis of three new bis(pyrrolidine)[60]fullerenes, one *cis*-1 and two unprecedented *cis*-2 diastereoisomers, is reported (see scheme). The compounds are easily purified using simple chromatographic techniques, and were fully characterized by spectroscopic techniques and X-ray crystallography. A mechanism for the isomeric conversion observed is proposed.



Organocatalysis

E. Mensah, N. Camasso, W. Kaplan, P. Nagorny* ____ **12932 – 12936**

Chiral Phosphoric Acid Directed Regioselective Acetalization of Carbohydrate-Derived 1,2-Diols



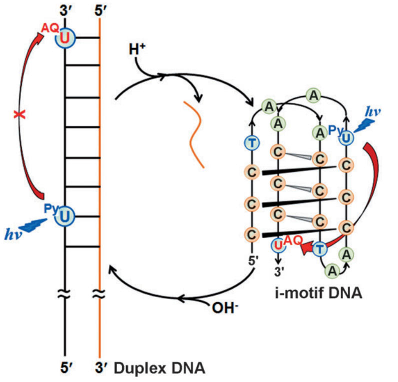
In control: A chiral phosphoric acid catalyst (see scheme) significantly enhances or completely overrides the inherent regioselective acetalization profiles exhibited by monosaccharide-derived 1,2-diol substrates. This study represents the first example of chiral-catalyst-directed regio- and enantioselective intermolecular acetalizations, which are complementary to existing methods for substrate-controlled functionalization of polyols.

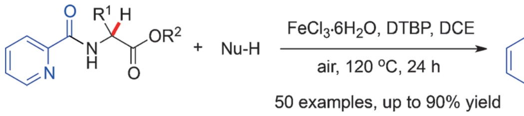
Bio-nanotechnology

J. Choi,* A. Tanaka, D. W. Cho, M. Fujitsuka, T. Majima* . **12937 – 12941**

Efficient Electron Transfer in i-Motif DNA with a Tetraplex Structure

Electron transfer through DNA: The electron-transfer dynamics of i-motif DNA conjugated with pyrene (Py) and anthraquinone (AQ) has been investigated by fluorescence up-conversion and transient absorption spectroscopic methods. Electron transfer (see red arrows) in i-motif DNA is more efficient than in duplex DNA, suggesting that i-motif DNA can be used as electron carrier in nanoelectronic devices.



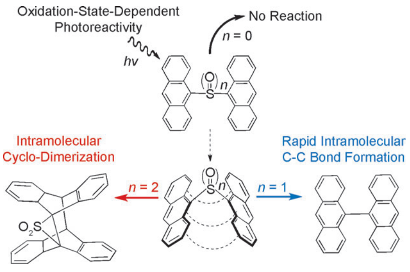


Fully loaded: A coordinating activation strategy has been developed to furnish α-quaternary α-amino acids through the iron(III)-catalyzed oxidative functionalization of α-C(sp^3)−H bonds of α-tertiary α-amino acid esters. The reaction exhibits a broad substrate scope for both α-amino acids and nucleophiles (Nu) as well as good functional-group tolerance (see scheme, DTBP = di-*tert*-butyl peroxide, DCE = 1,2-dichloroethane).

Oxidative Cross-Coupling

K. Li, G. Tan, J. Huang, F. Song, J. You* ———— **12942 – 12945**

Iron-Catalyzed Oxidative C−H/C−H Cross-Coupling: An Efficient Route to α-Quaternary α-Amino Acid Derivatives

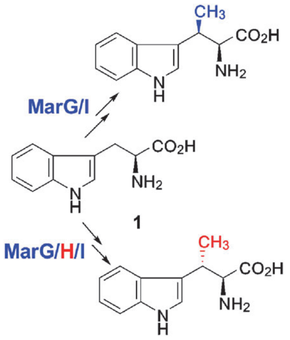


What's up sulfur? The photochemical reactivity, including a mechanistic study of sulfur-bridged anthracenes is reported. The oxidation state of the bridging sulfur (SO$_n$) dictates the excited-state behavior of these molecules (see picture).

Photochemistry

P. R. Christensen, B. O. Patrick, É. Caron, M. O. Wolf* ———— **12946 – 12950**

Oxidation-State-Dependent Photochemistry of Sulfur-Bridged Anthracenes

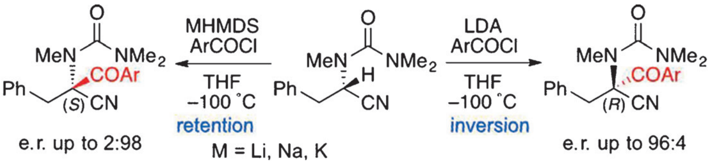


Make the switch: The three-enzyme cassette MarG/H/I is responsible for stereospecific biosynthesis of β-methyltryptophan from L-tryptophan (**1**). MarG/I convert **1** into (2*S*,3*R*)-β-methyltryptophan, while MarG/I combined with MarH convert **1** into (2*S*,3*S*)-β-methyltryptophan. MarH serves as a stereochemical switch by catalyzing the stereoinversion of the β-stereocenter.

Amino Acid Synthesis

Y. Zou, Q. Fang, H. Yin, Z. Liang, D. Kong, L. Bai, Z. Deng, S. Lin* —— **12951 – 12955**

Stereospecific Biosynthesis of β-Methyltryptophan from L-Tryptophan Features a Stereochemical Switch



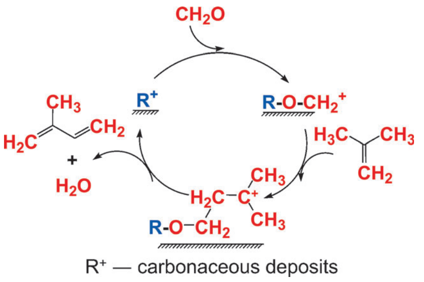
Back to 'base'ics: The title reaction of enantioenriched α-ureidonitriles was found to proceed in a highly enantiodivergent manner despite the intermediacy of stereolabile α-nitrile metallocarbanions. Enantiodivergence is dependent upon the base used. For the less basic hexamethyldisilazides (HMDS), deprotonation in which a metal (M) cation is precomplexed with an electrophile is proposed. LDA = lithium diisopropylamide.

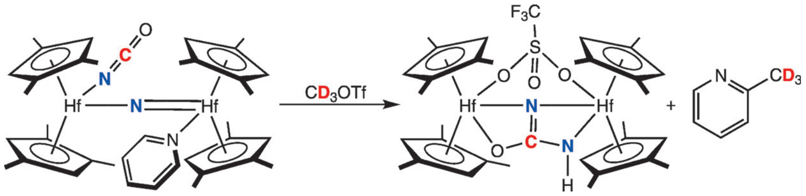
Carbanions

M. Sasaki, T. Takegawa, K. Sakamoto, Y. Kotomori, Y. Otani,* T. Ohwada, M. Kawahata, K. Yamaguchi, K. Takeda* ———— **12956 – 12960**

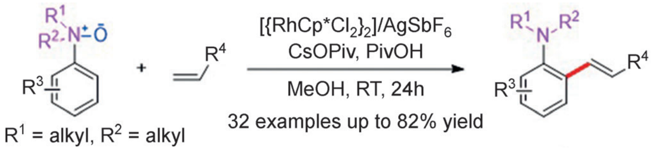
Enantiodivergent Deprotonation/Acylation of α-Amino Nitriles

A help rather than a hindrance: Carbonaceous deposits have been found to play a key role in the selective synthesis of isoprene from formaldehyde and isobutene over solid catalysts. They accumulate on the catalyst surface during the induction period and promote the interaction of the substrates at the steady state. The proposed mechanism (see scheme) shows the way forward for the design of efficient solid catalysts for the synthesis of isoprene.

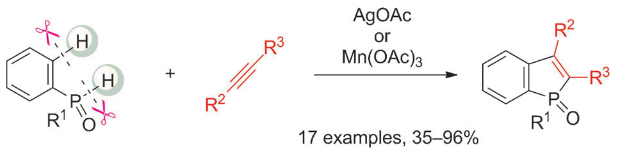




Better by Hf: Anion coordination to a bridging hafnocene nitride complex, prepared from CO-induced N_2 cleavage, increases the nucleophilicity of the nitrogen atom, thus promoting additional N–C bond formation with a typically inert terminal isocyanate ligand. This cascade sequence allows synthesis of otherwise challenging mono-substituted ureas using N_2, CO, and an appropriate electrophile.

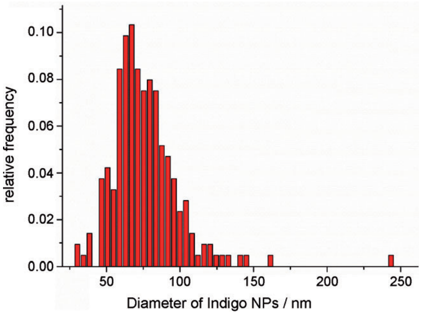


Double role: A traceless directing group also acts as an internal oxidant in a novel Rh^{III}-catalyzed protocol developed for the synthesis of *ortho*-alkenylated tertiary anilines (see scheme). A five-membered cyclometalated Rh^{III} complex is proposed as a plausible intermediate and confirmed by X-ray crystallographic analysis.



Benzophosphole construction was achieved through the Ag^{I}-mediated dehydrogenative annulation of phenylphosphine oxides with internal alkynes in a process involving C–C and C–P bond formation. A wide range of asymmetrical phenylacetylenes could be employed and the reactions proceeded with perfect regioselectivity. Moreover, the annulation could be conducted even at room temperature when a Mn^{III} promoter was used in place of Ag^{I}.

The size of organic nanoparticles (NPs) can be electrochemically determined by Faradaic charge transfer when nanoparticles strike an electrode. Indigo NPs were used as a model (see distribution of the NP diameter). This strategy could be used for monitoring the size of a wide range of organic nanoparticles.

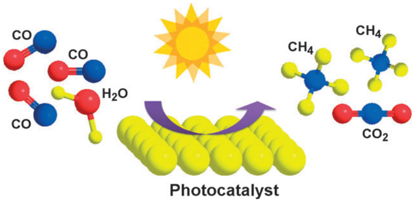


Electrochemistry

W. Cheng, X.-F. Zhou,
R. G. Compton* ________ 12980 – 12982

Electrochemical Sizing of Organic Nanoparticles

Solar Fuels: Different n- and p-type semiconductors have been investigated for sustainable solar fuel production. p-Type semiconductors, such as NiO, Fe_3O_4, Co_3O_4, and CuO, are able to reduce carbon monoxide by water or hydrogen to methane (see picture). The highest CH_4 yield achieved was 17.26 mmol of CH_4 per gram of catalyst using NiO in an excess of H_2.



Photocatalysis

F. Sastre, A. Corma,*
H. García* ____________ 12983 – 12987

Visible-Light Photocatalytic Conversion of Carbon Monoxide to Methane by Nickel(II) Oxide

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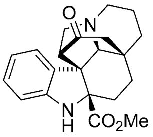

All caged up: The first total synthesis of *N*-decarbomethoxychanofruticosinate (see figure) is achieved by using a SmI_2-mediated intramolecular Reformatsky-like reaction to create the seven-membered ring, and an intramolecular oxidative coupling to install the caged and strained ring system.

Natural Product Synthesis

Y. Wei, D. Zhao, D. Ma* _ 12988 – 12991

Total Synthesis of the Indole Alkaloid (±)- and (+)-Methyl *N*-Decarbomethoxychanofruticosinate

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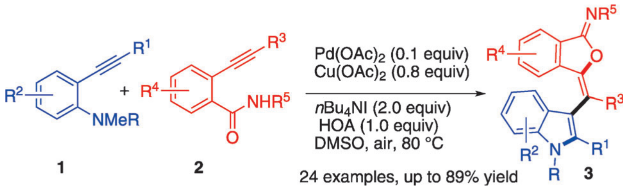


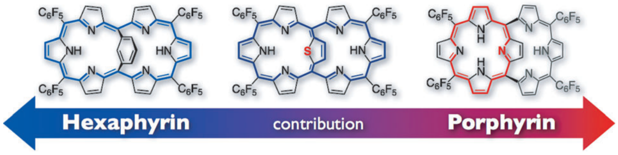
Born to couple: The $Pd(OAc)_2$-catalyzed reaction of *o*-alkynylanilines (**1**) with *o*-alkynylbenzamides (**2**) affords the cyclizative cross-coupling products **3** in good to excellent yields. Three bonds are created in the formation of two heterocycles tethered by a tetrasubstituted double bond. Mechanistic studies indicate that the reaction is initiated by aminopalladation with subsequent oxypalladation, N-demethylation, and reductive elimination.

Homogeneous Catalysis

B. Yao, Q. Wang, J. Zhu* . 12992 – 12996

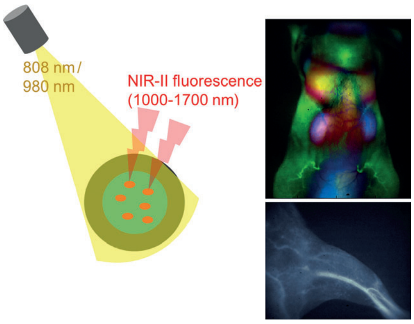
Palladium(II)-Catalyzed Cyclizative Cross-Coupling of *ortho*-Alkynylanilines with *ortho*-Alkynylbenzamides under Aerobic Conditions

Porphyrinoids



Internal bridges: [26]Hexaphyrins with an aromatic strap in 5,20 position have two potentially cyclic conjugated networks, that is, [18]porphyrin and [26]hexaphyrin (see picture), and show a formal analogy with [18]annuleno[18]annulens. 1,3-Phenylene-, 2,5-thienylene-, and 2,5-pyrrylene-bridged [26]hexaphyrins have been synthesized and characterized.

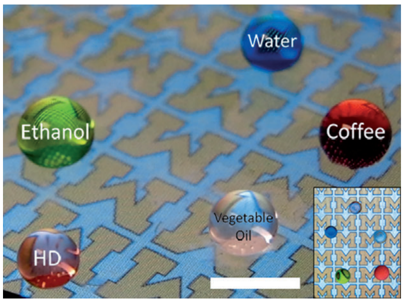
Near-Infrared Imaging



Embedded in a polymer: A hydrophobic organic molecule that fluoresces in the near-infrared II (NIR-II) region was made water-soluble and biocompatible by its embedment in a polymer nanoparticle, which was then coated with hydrophilic poly(ethylene glycol) chains. The resulting nanoparticles exhibit bright fluorescence in the NIR-II window and high photostability in aqueous media and were used for in vivo imaging in mice.

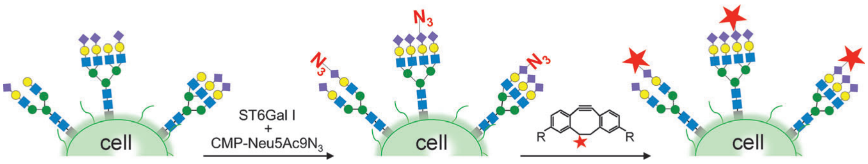
Surface Chemistry

Inside Back Cover



See-through surfaces: High transparency is required to use superomniphobic surfaces, which can be self-cleaning, stain-proof, anti-bio-fouling, drag-reducing, or anti-fogging, for smartphone screens (see picture), eye glasses, windshields, or flat panel displays. A spray-based method has now been developed that can fabricate transparent, flexible, and highly superomniphobic surfaces. HD = hexadecane.

Bio-orthogonal Chemistry

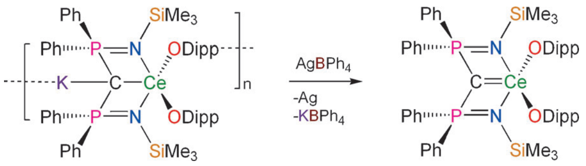


A game of tag: N-Glycans on the surface of living cells were selectively tagged by exogenously administering recombinant ST6Gal I sialyltransferase and azide-modified CMP-Neu5Ac. This modification was followed by a strain-promoted cycloaddition using a biotin-modified dibenzylcyclooctynol (red star = biotin). The methodology will make it possible to dissect the mechanisms that underlie altered glycoconjugate recycling and storage in disease.

Multiple Bonding

M. Gregson, E. Lu, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle* —— **13016 – 13019**

A Cerium(IV)–Carbon Multiple Bond



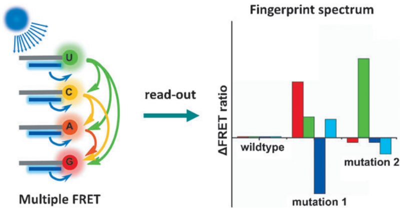
Straightforward access to a cerium(IV)–carbene complex was provided by one-electron oxidation of an anionic "ate" cerium(III)–carbene precursor, thereby avoiding decomposition reactions that plague oxidations of neutral cerium(III) compounds. The cerium(IV)–carbene complex is the first lanthanide(IV)–element multiple bond and involves a two-fold bonding interaction of two electron pairs between cerium and carbon.

Biosensors

J. Song, J. Zhang, F. Lv,* Y. Cheng, B. Wang, L. Feng, L. Liu, S. Wang* —— **13020 – 13023**

Multiplex Detection of DNA Mutations by the Fluorescence Fingerprint Spectrum Technique

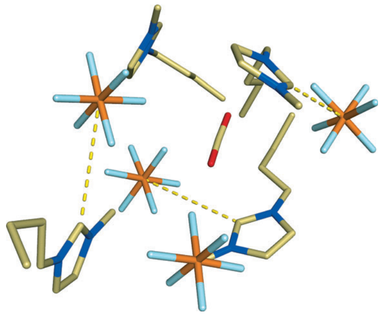
A fingerprint spectrum technique that utilizes cationic conjugated-polymer-based fluorescence resonance energy transfer (FRET) is used for multiplex detection of DNA mutations. This method detects as low as 5% mutation of the total DNA. Ten *PIK3CA* mutations originating from 30 clinical breast cancer samples could be detected.



CO_2 Sequestration

M. C. Corvo, J. Sardinha, S. C. Menezes, S. Einloft, M. Seferin, J. Dupont, T. Casimiro, E. J. Cabrita* **13024 – 13027**

Solvation of Carbon Dioxide in $[C_4mim][BF_4]$ and $[C_4mim][PF_6]$ Ionic Liquids Revealed by High-Pressure NMR Spectroscopy

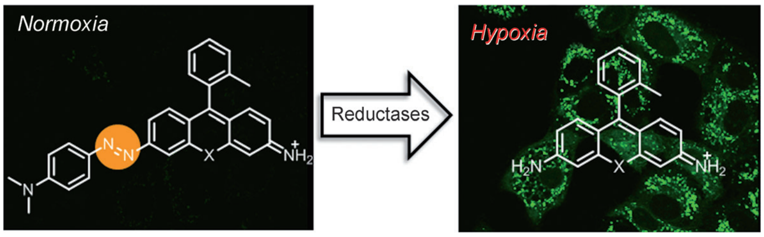


Where is CO_2? The intermolecular interactions of $[C_4mim]BF_4$ and $[C_4mim]PF_6$ ionic liquids and CO_2 have been determined by high-pressure NMR spectroscopy in combination with molecular dynamic simulations. The anion and the cation are both engaged in interactions with CO_2. A detailed picture of CO_2 solvation in these ILs is provided. CO_2 solubility is essentially determined by the microscopic structure of the IL.

Fluorescent Probes

W. Piao, S. Tsuda, Y. Tanaka, S. Maeda, F. Liu, S. Takahashi, Y. Kushida, T. Komatsu, T. Ueno, T. Terai, T. Nakazawa, M. Uchiyama, K. Morokuma, T. Nagano, K. Hanaoka* —— **13028 – 13032**

Development of Azo-Based Fluorescent Probes to Detect Different Levels of Hypoxia

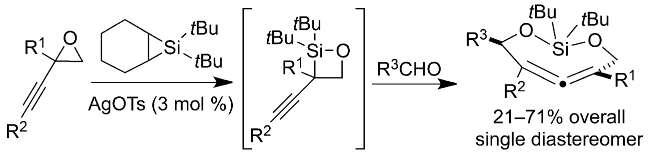


Let it shine: New hypoxia-sensitive fluorescent probes were developed; they consist of a rhodamine moiety with an azo group directly conjugated to the fluorophore. Because of an ultrafast conformational change around the N=N bond, the compounds are nonfluorescent under normoxia. However, under hypoxia, the azo group is reduced, and a strongly fluorescent rhodamine derivative is released.

Medium-Ring Compounds

C. Z. Rotsides, C. Hu,
K. A. Woerpel* ________ 13033 – 13036

Diastereoselective Synthesis of Eight-Membered-Ring Allenes from Propargylic Epoxides and Aldehydes by Silylene Insertion into Carbon–Oxygen Bonds

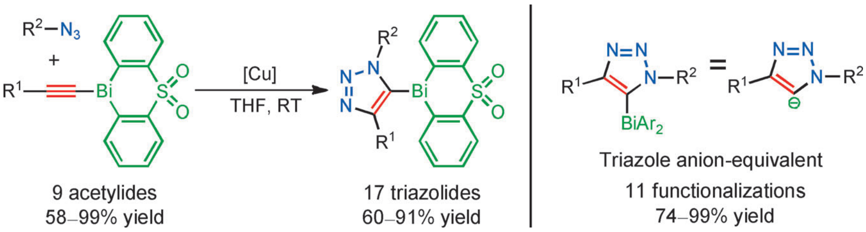


Bent out of shape: Silver-catalyzed insertions of silylenes into propargylic C–O bonds of epoxides regioselectively form 1,2-silaoxetanes, which add to aldehydes to give the title allenes as single diastereomers (see scheme; Ts = 4-toluenesulfonyl). An X-ray crystal structure confirmed the stereochemistry of the allene, which is bent significantly from linearity (164°).

Click Chemistry

B. T. Worrell, S. P. Ellery,
V. V. Fokin* ________ 13037 – 13041

Copper(I)-Catalyzed Cycloaddition of Bismuth(III) Acetylides with Organic Azides: Synthesis of Stable Triazole Anion Equivalents

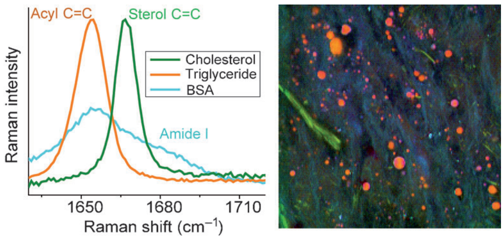


Fully loaded: Readily accessible and shelf-stable 1-bismuth(III) acetylides react rapidly and regiospecifically with organic azides in the presence of a copper(I) catalyst (see scheme). The reaction tolerates many functional groups and gives excellent yields of the previously unreported 5-bismuth triazolides. This uniquely reactive intermediate is functionalized under mild reaction conditions to give fully substituted 1,2,3-triazoles.

Chemical Imaging

P. Wang, J. Li, P. Wang, C. Hu, D. Zhang,
M. Sturek,* J.-X. Cheng* _ 13042 – 13046

Label-Free Quantitative Imaging of Cholesterol in Intact Tissues by Hyperspectral Stimulated Raman Scattering Microscopy

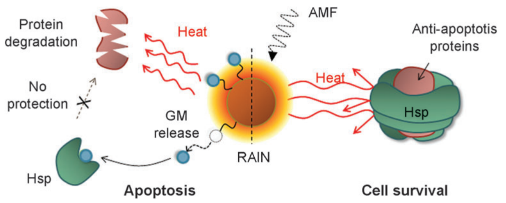


A finger on the pulse: Current molecular analysis of cells and tissues routinely relies on separation, enrichment, and subsequent measurements by various assays. Now, a platform of hyperspectral stimulated Raman scattering microscopy has been developed for the fast, quantitative, and label-free imaging of biomolecules in intact tissues using spectroscopic fingerprints as the contrast mechanism.

Cancer

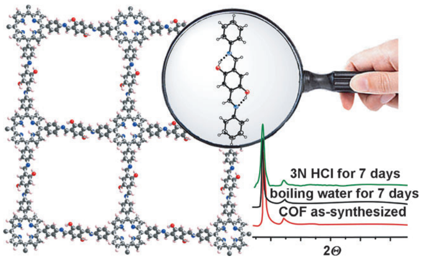
D. Yoo, H. Jeong, S.-H. Noh, J.-H. Lee,
J. Cheon* ________ 13047 – 13051

Magnetically Triggered Dual Functional Nanoparticles for Resistance-Free Apoptotic Hyperthermia



Overcoming resistance: Heat-treated cancer cells possess a protective mechanism for resistance and survival. Resistance-free apoptosis-inducing magnetic nanoparticles (RAINs) successfully promote hyperthermic apoptosis, obstructing cell survival by triggering two functional units of heat generation and the release of geldanamycin (GM) for heat shock protein (Hsp) inhibition under an alternating magnetic field (AMF).

A strong bond: A strategy based on intramolecular hydrogen-binding interactions in 2D covalent organic frameworks (COFs) is shown to improve the crystallinity, porosity, and chemical stability of the material (see picture). The concept is validated by removing the hydrogen-bonding interaction in the methoxy analog which showed a lower stability and crystallinity.



Mesoporous Materials

S. Kandambeth, D. B. Shinde, M. K. Panda, B. Lukose, T. Heine, R. Banerjee* ———— **13052 – 13056**

Enhancement of Chemical Stability and Crystallinity in Porphyrin-Containing Covalent Organic Frameworks by Intramolecular Hydrogen Bonds

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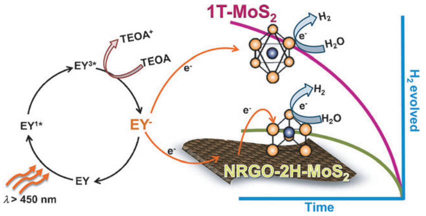

Two sorts of MoS$_2$: A single-layer, metallic form of MoS$_2$ (1T-MoS$_2$) and a nanocomposite of a second form of MoS$_2$ (few-layer 2H-MoS$_2$) with heavily nitrogenated reduced graphene oxide (NRGO; N content ca. 15%) show outstanding performance in the production of H$_2$ under visible-light illumination.

Hydrogen Generation with MoS$_2$

U. Maitra, U. Gupta, M. De, R. Datta, A. Govindaraj, C. N. R. Rao* ———— **13057 – 13061**

Highly Effective Visible-Light-Induced H$_2$ Generation by Single-Layer 1T-MoS$_2$ and a Nanocomposite of Few-Layer 2H-MoS$_2$ with Heavily Nitrogenated Graphene

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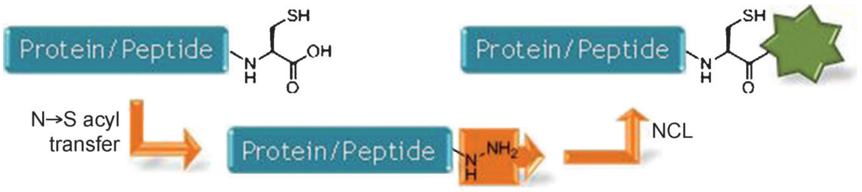

Tagging the terminus: N→S acyl transfer in native peptides and proteins can be reliably intercepted with hydrazine. The method allows selective labeling and ligation, without recourse to the use of protein-splicing elements. NCL = native chemical ligation.

N→S Acyl Transfer

A. L. Adams, B. Cowper, R. E. Morgan, B. Premdjee, S. Caddick, D. Macmillan* ———— **13062 – 13066**

Cysteine Promoted C-Terminal Hydrazinolysis of Native Peptides and Proteins

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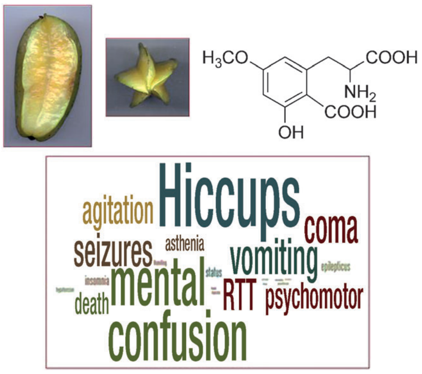


Caramboxin: Patients suffering from chronic kidney disease are frequently intoxicated after ingesting star fruit. The main symptoms of this intoxication are named in the picture. Bioguided chemical procedures resulted in the discovery of caramboxin, which is a phenylalanine-like molecule that is responsible for intoxication. Functional experiments in vivo and in vitro point towards the glutamatergic ionotropic molecular actions of caramboxin, which explains its convulsant and neurodegenerative properties.

Natural Products

N. Garcia-Cairasco,* M. Moyses-Neto, F. Del Vecchio, J. A. C. Oliveira, F. L. dos Santos, O. W. Castro, G. M. Arisi, M. Dantas, R. O. G. Carolino, J. Coutinho-Netto, A. L. A. Dagostin, M. C. A. Rodrigues, R. M. Leão, S. A. P. Quintiliano, L. F. Silva, Jr., L. Gobbo-Neto, N. P. Lopes* ———— **13067 – 13070**

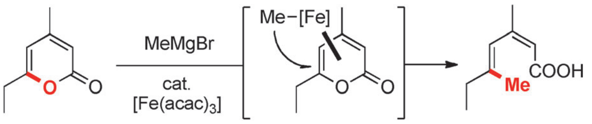
Elucidating the Neurotoxicity of the Star Fruit

Front Cover

Heterocycles

C.-L. Sun, A. Fürstner* ___ **13071 – 13075**

Formal Ring-Opening/Cross-Coupling Reactions of 2-Pyrones: Iron-Catalyzed Entry into Stereodefined Dienyl Carboxylates



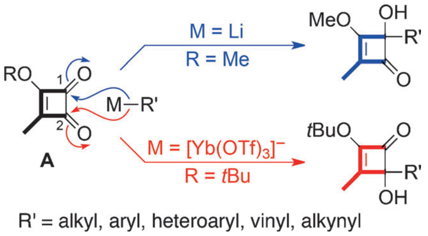
Open access: Despite the exceptional level of sophistication in cross-coupling chemistry, reactions of substrates that incorporate the leaving group as an integral part into a heterocyclic scaffold are scarce. The title reaction outlines the utility of this reaction format (see scheme; acac = acetylacetonate), provides a convenient entry into stereodefined diene carboxylates, and adds a new chapter to the field of iron catalysis.

Synthetic Methods

E. Packard, D. D. Pascoe, J. Maddaluno, T. P. Gonçalves, D. C. Harrowven* ___ **13076 – 13079**

Organoytterbium Ate Complexes Extend the Value of Cyclobutenediones as Isoprene Equivalents

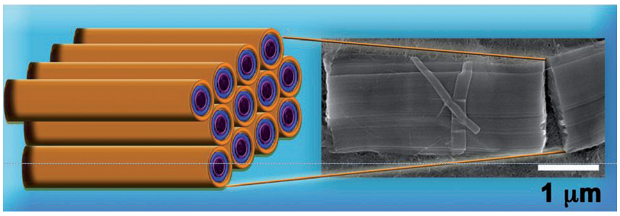
Changing course: While organolithium and Grignard reagents favor addition to C1 of **A** (R = Me), the corresponding organoytterbium reagents add to C2 (R = *t*Bu). Computational studies provide insights into the nature of organoytterbium species and their reactivity, and a total synthesis of (−)-mansonone B illustrates the utility of the method in terpenoid synthesis. Tf = trifluoromethanesulfonyl.



Organized Nanotubes

J.-H. Olivier, P. Deria, J. Park, A. Kumbhar, M. Andrian-Albescu, M. J. Therien* ___ **13080 – 13085**

Ionic Self-Assembly Provides Dense Arrays of Individualized, Aligned Single-Walled Carbon Nanotubes

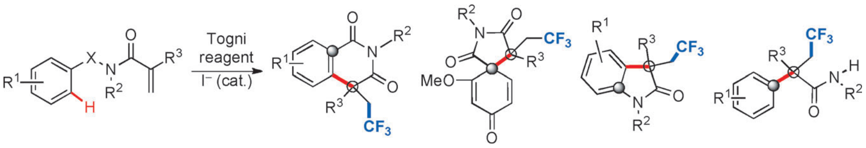


Wrap and stack: Polyanionic [arylene]-ethynylene polymers that helically wrap single-walled carbon nanotubes (SWNTs) enable the production of functionalized SWNTs that are soluble in organic solvents. These SWNTs can assemble into structures featuring aligned nanotubes that maintain the optoelectronic properties of individual SWNTs.

Aryltrifluoromethylation

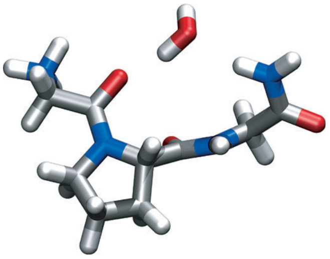
W. Kong, M. Casimiro, N. Fuentes, E. Merino, C. Nevado* ___ **13086 – 13090**

Metal-Free Aryltrifluoromethylation of Activated Alkenes



Metal-free: The first metal-free aryltrifluoromethylation of activated alkenes has been developed. With this method, trifluoromethylated isoquinolinediones, spirobicycles, oxindoles, and α-aryl-β-trifluoromethylamides were obtained with high control of the regioselectivity.

Water-mediated bond formation: The structure of the peptide GPG-NH_2 (see picture) has been investigated in aqueous solution to understand the role of water in the formation of a β-turn. Using a combination of neutron diffraction enhanced by isotopic substitution, NMR spectroscopy, and computer simulations, it was found that water is an essential component to initiate folding in solution.



Structure Elucidation

S. Busch, C. D. Bruce, C. Redfield,
C. D. Lorenz,
S. E. McLain* ———— **13091 – 13095**

Water Mediation Is Essential to Nucleation of β-Turn Formation in Peptide Folding Motifs

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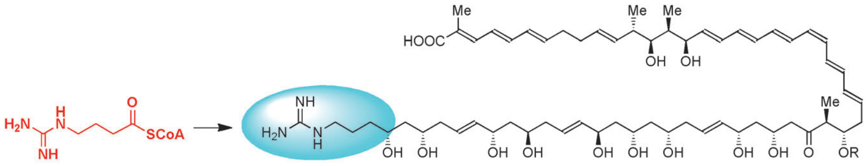

Desulfoclethramycin, R = H
Clethramycin, R = SO_2OH

Polyketide Biosynthesis

H. Hong,* T. Fill,
P. F. Leadlay* ———— **13096 – 13099**

A Common Origin for Guanidinobutanoate Starter Units in Antifungal Natural Products

Keeping it basic: Arginine provides the exotic 4-guanidinobutanoate starter unit for two different types of zwitterionic polyketide (an example for one type is shown in the picture) produced by the same *Streptomyces* bacterium. The three-step precursor pathway is initiated by a remarkable decarboxylating monooxygenase with high specificity for arginine.

Stacking on a full belly: Triangular molecular prisms display electron sharing among their triangularly arranged naphthalenediimide (NDI) redox centers. Their electron-deficient cavities encapsulate linear triiodide anions, leading to the formation of supramolecular helices in the solid state. Chirality transfer is observed from the six chiral centers of the filled prisms to the single-handed helices.

Anion–π Interactions

VIP

S. T. Schneebeli, M. Frasconi, Z. Liu,
Y. Wu, D. M. Gardner, N. L. Strutt,
C. Cheng, R. Carmieli, M. R. Wasielewski,*
J. F. Stoddart* ———— **13100 – 13104**

Electron Sharing and Anion–π Recognition in Molecular Triangular Prisms

Back Cover

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

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Angewandte Corrigendum

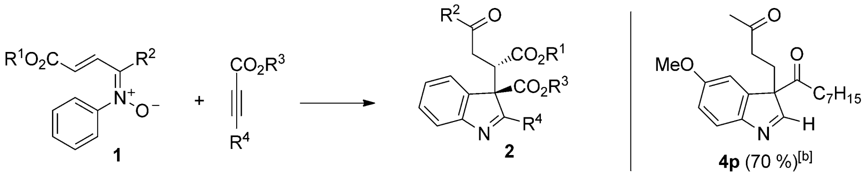
Diastereoselective Synthesis of C3-Quaternary Indolenines Using α,β-Unsaturated *N*-Aryl Ketonitrones and Activated Alkynes

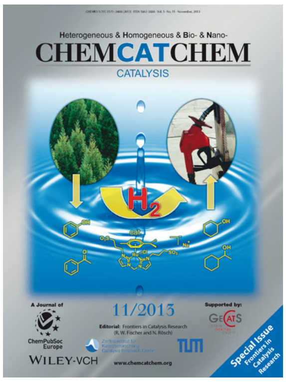
C. B. Huehls, T. S. Hood, J. Yang* ________________ **5110–5113**

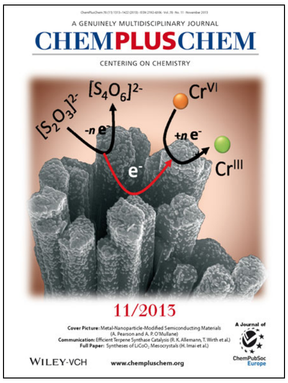
Angew. Chem. Int. Ed. **2012**, *51*

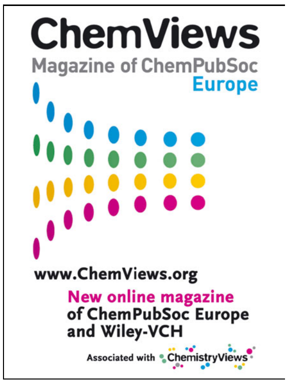
DOI: 10.1002/anie.201200860

The authors of this Communication wish to correct mistakes in two of the original Schemes. To clarify, the acetylene in the general reaction of Scheme 3 does not contain a methyl group but a substituent labeled R^4 as shown below. The structure of **4p** in Scheme 4 was missing the 5-OMe group. The data and structure shown in the Supporting Information is correct.









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In the abstract, the **motivation** for the work, the **methods** applied, the **results**, and the **conclusions** drawn should be presented (maximum 1000 characters). The abstract should contain several keywords to aid finding the paper online, and it should not mention graphical elements, tables, or references within the paper.