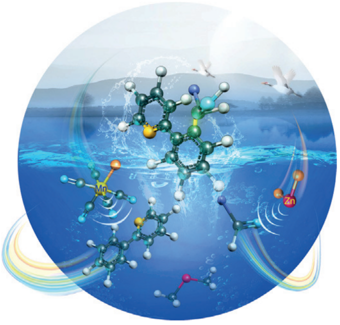
High-molar-mass poly(alkylphosphinoboranes) ...

… are currently not accessible by conventional metal-catalyzed dehydropolymerization. However, the mild thermolysis of a Lewis base stabilized phosphinoborane is an alternative metal-free approach. In their Communication on page 13782 ff., M. Scheer, I. Manners, and co-workers describe their successful synthesis of poly(*tert*-butylphosphinoborane) by this promising strategy.

Lead Generation

Activity-directed synthesis (ADS), a novel discovery approach in which bioactive molecules emerge in parallel with associated syntheses, is exploited by A. Nelson, S. Warriner et al. in their Communication on page 13538 ff.

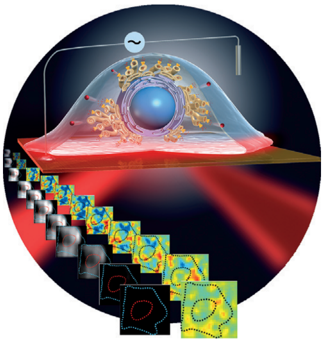


C–H Activation Reactions

In their Communication on page 13659 ff., C. Wang et al. achieve Grignard-type C–H nucleophilic addition to aldehydes and nitriles by merging C–H activation by a manganese catalyst and aldehyde/nitrile activation by zinc bromide.

Cell Signaling

J. Li and J. Lu investigate the calcium signaling activities at the early stage of GPCR stimulation by plasmonic-based electrochemical impedance microscopy and surface plasmon resonance in their Communication on page 13576 ff.



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Editorial

"… Taiwan has successfully developed semiconductor, and information and communication technology industries that earned Taiwan a good reputation and brought prosperity to the country. Now Taiwan has recognized the need for a disruptive change that will require the establishment of new industries. Basic research remains the major focus of the chemistry community …"
Read more in the Editorial by Chi-Huey Wong.

Service

Author Profile

"I celebrate success by working harder!
My biggest motivation is competition …"
This and more about Richard G. Compton can be found on page 13498.

News


T. K. Lindhorst


D. Seebach

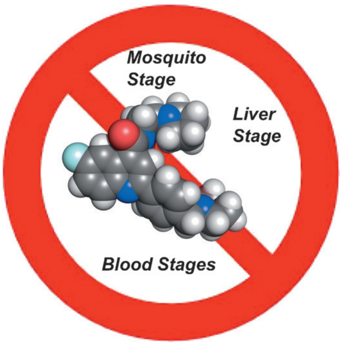

P. S. Baran


J. Cheon

Books

Highlights

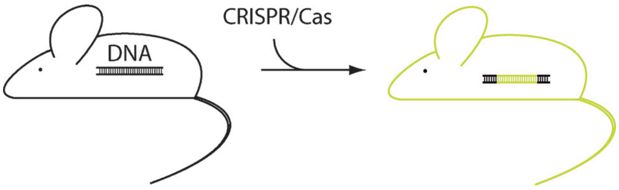
Drug Discovery



Putting a stop to malaria: Phenotypic screening against malaria parasites, hit identification, and efficient lead optimization have delivered the preclinical candidate antimalarial DDD107498. This molecule is distinctive in that it has potential for use as a single-dose cure for malaria and shows a unique broad spectrum of activity against the liver, blood, and mosquito stages of the parasite life cycle.

Minireviews

Genetic Engineering

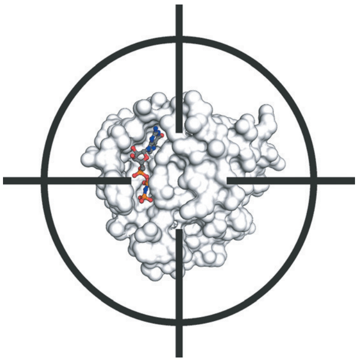


Talkin' 'Bout a Revolution: The field of biology has been revolutionized by the recent advancement of an adaptive bacterial immune system as a universal genome engineering tool. This has opened up new frontiers in genome engineering, including the potential to treat or cure human genetic disorders. Now the potential risks as well as the ethical, social, and legal implications of this powerful new technique move into the limelight.

Reviews

Drug Design

In the focus of drug discovery: Small GTPases are molecular switches and control a multitude of pivotal cellular processes and functions. As no modulators of small GTPase function are in clinical use, this protein class is considered "undruggable". This Review gives a comprehensive overview on the targeting of small GTPases and summarizes the recent advances in drug discovery.



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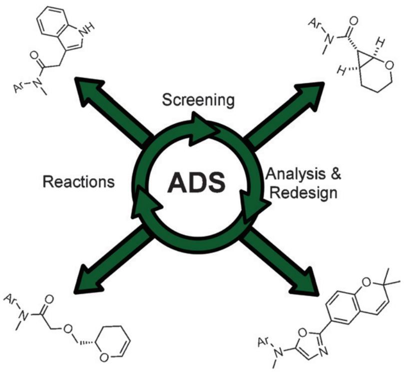
Lead Generation

G. Karageorgis, M. Dow, A. Aimon,
S. Warriner,* A. Nelson* _ 13538 – 13544

Activity-Directed Synthesis with Intermolecular Reactions: Development of a Fragment into a Range of Androgen Receptor Agonists



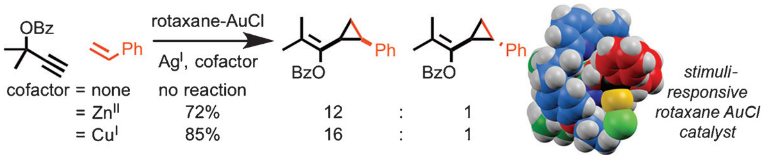
Activity-directed synthesis (ADS), a novel discovery approach in which bioactive molecules emerge in parallel with associated syntheses, was exploited to develop a weakly binding fragment into novel androgen receptor agonists. Harnessing promiscuous intermolecular reactions of carbenoid compounds enabled the highly efficient exploration of chemical space.

Frontispiece

Supramolecular Catalysts

M. Galli, J. E. M. Lewis,
S. M. Goldup* ________ 13545 – 13549

A Stimuli-Responsive Rotaxane–Gold Catalyst: Regulation of Activity and Diastereoselectivity



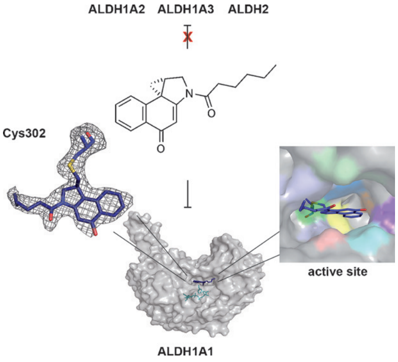
A group effort: A rotaxane-based Au catalyst was developed and the effect of the mechanical bond on its behavior was studied. Unlike the non-interlocked thread, the rotaxane requires a catalytically innocent cofactor, which significantly influences the yield and diastereoselectivity of the reaction. Under optimized conditions, Au^I (the catalyst), Ag^I (to abstract the Cl$^-$ ligand) and Cu^I (the cofactor) combine to produce a catalyst with excellent activity and selectivity.

Inhibitors

M. F. Koch, S. Harteis, I. D. Blank,
G. Pestel, L. F. Tietze, C. Ochsenfeld,
S. Schneider,*
S. A. Sieber* ________ 13550 – 13554

Structural, Biochemical, and Computational Studies Reveal the Mechanism of Selective Aldehyde Dehydrogenase 1A1 Inhibition by Cytotoxic Duocarmycin Analogues

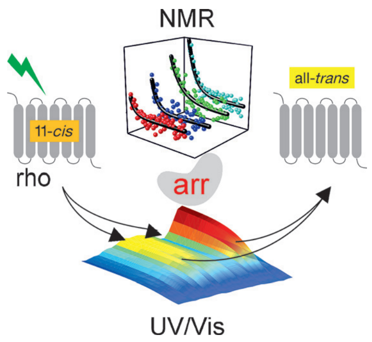
Fit for purpose: Duocarmycin analogues exhibit an unsurpassed selectivity for ALDH1A1. The molecular origin of this unique preference was revealed through cocrystallization, molecular dynamics calculations, mutational studies, and kinetic analysis. The molecule precisely fits into a customized binding pocket that is characteristic for ALDH1A1 but not closely related isoforms and it is stabilized in the pocket by π-stacking and van der Waals interactions.



Retinal Regeneration

D. Chatterjee, C. E. Eckert, C. Slavov,
K. Saxena, B. Fürtig, C. R. Sanders,
V. V. Gurevich, J. Wachtveitl,*
H. Schwalbe* ________ 13555 – 13560

Influence of Arrestin on the Photodecay of Bovine Rhodopsin

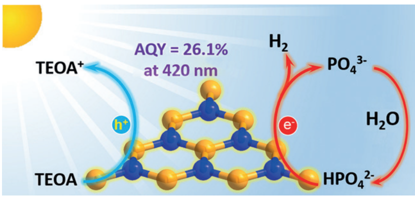


In the twilight: The influence of arrestin (arr) on the photokinetics of the mammalian visual dim-light photoreceptor rhodopsin is studied by time-resolved liquid-state NMR spectroscopy and flash photolysis spectroscopy. The data reveal the important role of arrestin in the retinal regeneration processes in the rod outer segments: Arrestin stabilizes the metarhodopsin III state and thus induces a twofold slower retinal release.

Photocatalysis

G. Liu, T. Wang, H. Zhang, X. Meng, D. Hao, K. Chang, P. Li,* T. Kako, J. Ye* ________ **13561 – 13565**

Nature-Inspired Environmental "Phosphorylation" Boosts Photocatalytic H_2 Production over Carbon Nitride Nanosheets under Visible-Light Irradiation



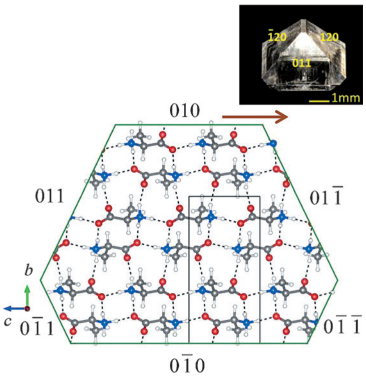
The right environment for success: A "phosphorylation" strategy inspired by natural photosynthesis was explored to boost photocatalytic H_2 production over g-C_3N_4 nanosheets. Thus, the addition of a phosphate led to a high apparent quantum yield (AQY). Experimental and theoretical results indicated that the large increase in activity was due to the synergy of enhanced proton reduction and improved hole oxidation (see picture; TEOA = triethanolamine).

Young's Moduli of Crystals

I. Azuri, E. Meirzadeh, D. Ehre, S. R. Cohen, A. M. Rappe, M. Lahav, I. Lubomirsky,* L. Kronik* ________ **13566 – 13570**

Unusually Large Young's Moduli of Amino Acid Molecular Crystals

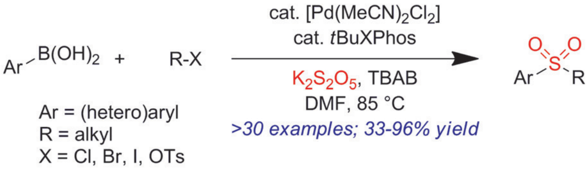
Exceptionally stiff amino acid crystals: Young's moduli of five prototypical amino acid crystals were determined using a combination of computational and experimental studies. The simple molecular solids possess surprisingly large Young's moduli, suggesting that the mechanical stiffness of the crystals may be determined by the orientation of the intermolecular hydrogen bond networks.



Alkylsulfonylation

A. Shavnya,* K. D. Hesp, V. Mascitti, A. C. Smith ________ **13571 – 13575**

Palladium-Catalyzed Synthesis of (Hetero)Aryl Alkyl Sulfones from (Hetero)Aryl Boronic Acids, Unactivated Alkyl Halides, and Potassium Metabisulfite



One-step alkylsulfonylation: A Pd-catalyzed one-step synthesis of (hetero)aryl alkyl sulfones from (hetero)arylboronic acids, $K_2S_2O_5$, and alkyl halides is described. This transformation is of broad scope, occurs under mild conditions, and employs readily available reactants. A stoichiometric experiment led to the isolation and characterization of a catalytically active dimeric Pd sulfinate complex.

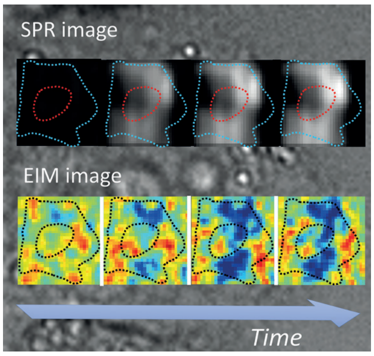
Cell Signaling

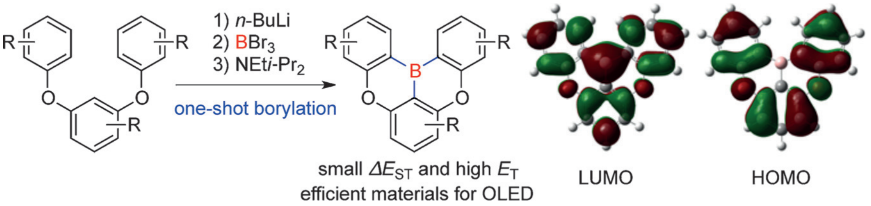
J. Lu, J. Li* ________ **13576 – 13580**

Label-Free Imaging of Dynamic and Transient Calcium Signaling in Single Cells

Back Cover

A plasmonic-based electrochemical impedance microscope with excellent temporal and subcellular resolution was developed for studying cell-signaling processes. The calcium signaling activities at the early stage of GPCR (G-protein-coupled receptor) stimulation could thus be elucidated.





Easy boryl LEDs: A one-step borylation of 1,3-diaryloxybenzenes has been developed. The resulting boron-containing aromatic compounds possess high singlet–triplet excitation energies as a result of localized frontier molecular orbitals induced by boron and oxygen. These compounds are efficient host and emitting materials for organic light-emitting diodes.

Light-Emitting Diodes

H. Hirai, K. Nakajima, S. Nakatsuka,
K. Shiren, J. Ni, S. Nomura, T. Ikuta,
T. Hatakeyama* ———— **13581 – 13585**

One-Step Borylation of 1,3-Diaryloxybenzenes Towards Efficient Materials for Organic Light-Emitting Diodes

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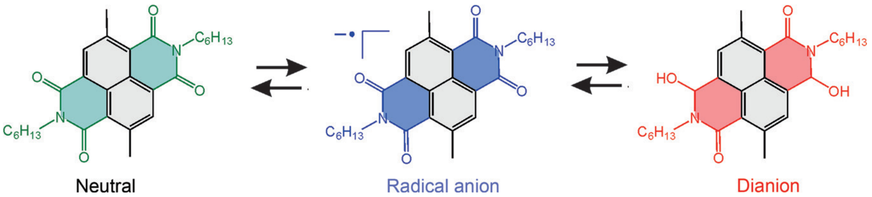


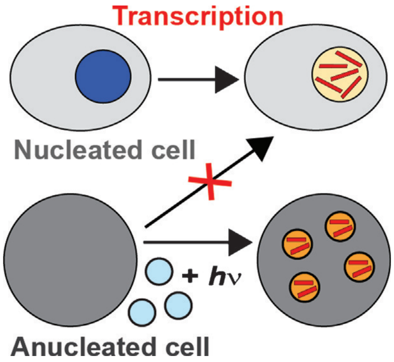
Charge-transport phenomena through core-substituted naphthalenediimide (NDI) single-molecule junctions have been studied using the electrochemical scanning-tunneling microscopy based break-junction technique in combination with DFT calculations. Three well-distinguished conductance states of the NDI molecule could be accessed, which can be reversibly switched by adjusting the potential.

Molecular Electronics

Y. Li, M. Baghernejad, A.-G. Qusiy,
D. Zsolt Manrique, G. Zhang, J. Hamill,
Y. Fu, P. Broekmann, W. Hong,*
T. Wandlowski, D. Zhang,*
C. Lambert* ———— **13586 – 13589**

Three-State Single-Molecule Naphthalenediimide Switch: Integration of a Pendant Redox Unit for Conductance Tuning

---



No nuclei required: Transcription without nuclei was accomplished by encapsulating components of a transcription reaction into nanoliposomes. These liposomes could controllably synthesize mRNA upon irradiation with white light after being internalized by anucleate platelets. This study is a step towards using extranucleate transcription in mammalian cells as a general tool in molecular biology and gene therapy.

Orthogonal Transcription

V. Chan, S. K. Novakowski, S. Law,
C. Klein-Bosgoed,
C. J. Kastrup* ———— **13590 – 13593**

Controlled Transcription of Exogenous mRNA in Platelets Using Protocells

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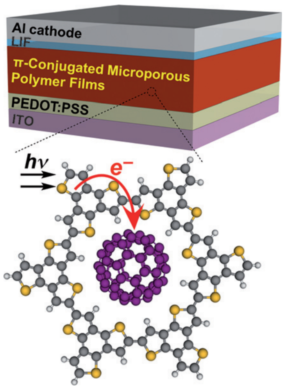


Film formation: A general strategy for synthesizing thin films of π-conjugated microporous polymers is described (see picture). Using a thiophene-based high-throughput electropolymerization it was possible to control the thickness of the films. The π-conjugated microporous polymers are shown to be outstanding conductors with a high carrier mobility and photoactive layers for efficient conversion of photoenergy.

Semiconducting Films

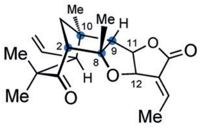
C. Gu, N. Huang, Y. Chen, L. Qin, H. Xu,
S. Zhang, F. Li, Y. Ma,
D. Jiang* ———— **13594 – 13598**

π-Conjugated Microporous Polymer Films: Designed Synthesis, Conducting Properties, and Photoenergy Conversions

Natural Products

B. Huang, L. Guo, Y. Jia* **13599 – 13603**

Protecting-Group-Free Enantioselective Synthesis of (−)-Pallavicinin and (+)-Neopallavicinin



(−)-pallavicinin (*11R,12R*)
(+)-neopallavicinin (*11S,12S*)

1) Protecting-group-free synthesis
2) Unprecedented LiBHEt$_3$-Induced fragmentation/protonation
- C8 carbonyl
- C9 tertiary stereocenter

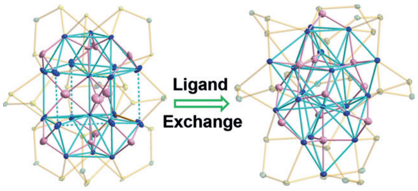
3) Palladium catalysis
- C10 quaternary stereocenter
- C2–C8 bond of [3.2.1] bicyclic system

Unprotected: The first enantioselective synthesis of (−)-pallavicinin and (+)-neopallavicinin has been achieved without the use of protecting groups. The palladium-catalyzed reactions were employed to form the chiral all-carbon quaternary stereocenter, and assemble the [3.2.1]bicyclic moiety. An unprecedented LiBHEt$_3$-induced fragmentation/protonation of an α-hydroxy epoxide to form the desired C9 stereocenter was discovered.

Chiral Copper Hydrides

R. S. Dhayal, J.-H. Liao, X. Wang, Y.-C. Liu, M.-H. Chiang, S. Kahlal, J.-Y. Saillard, C. W. Liu* ______ **13604 – 13608**

Diselenophosphate-Induced Conversion of an Achiral [$Cu_{20}H_{11}\{S_2P(OiPr)_2\}_9$] into a Chiral [$Cu_{20}H_{11}\{Se_2P(OiPr)_2\}_9$] Polyhydrido Nanocluster



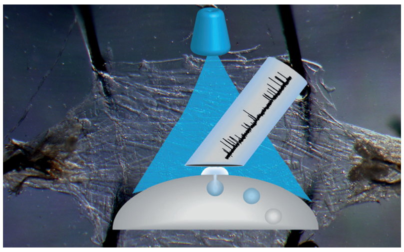
Well-coordinated: A five-coordinated H atom in a trigonal-bipyramidal cavity was observed by neutron diffraction in an intrinsically chiral, homometallic hydride cluster with a distorted cuboctahedral Cu_{13} metal core capped along the C_3 axis by a Cu_6 cupola on one side and a Cu atom on the other. This polyhydrido nanocluster with a chiral core was formed from an achiral nanocluster by ligand exchange (see picture; Cu blue, H pink).

Electrochemical Physiology

S. Majdi, E. C. Berglund, J. Dunevall, A. I. Oleinick, C. Amatore, D. E. Krantz, A. G. Ewing* ______ **13609 – 13612**

Electrochemical Measurements of Optogenetically Stimulated Quantal Amine Release from Single Nerve Cell Varicosities in *Drosophila* Larvae

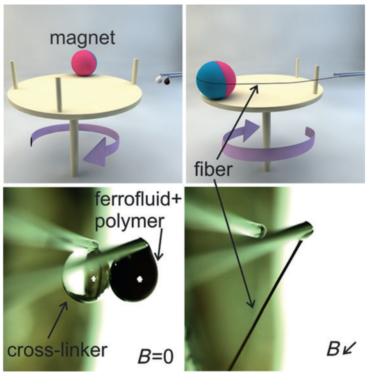
Recording single neurovesicle release: Measuring octopamine release from individual varicosities at a well-defined peripheral synapse has been achieved in *Drosophila* neuromuscular junctions by amperometry. The method is able to quantify octopamine release in in vivo larval muscle preparations. The different types of release observed are proposed to be related to the mechanism of opening of the vesicle to make the nanometer fusion pore.



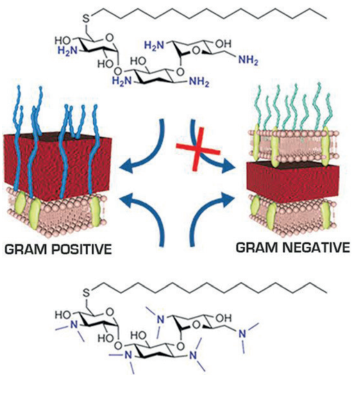
Nanostructures

A. Tokarev, O. Trotsenko, D. Asheghali, I. M. Griffiths, H. A. Stone, S. Minko* ______ **13613 – 13616**

Reactive Magnetospinning of Nano- and Microfibers



A new spin: Magnetic forces experienced by a droplet of polymer solution (for example, alginate in water) loaded with Fe_3O_4 nanoparticles are used to pull the droplet through another droplet of solution loaded with a cross-linker (for example, Ca^{2+} ions), rapidly mix the droplets, form a liquid thread, and stretch it into a fiber (see figure). This method can be used to produce nano- and microfibers that are free of magnetic particles.

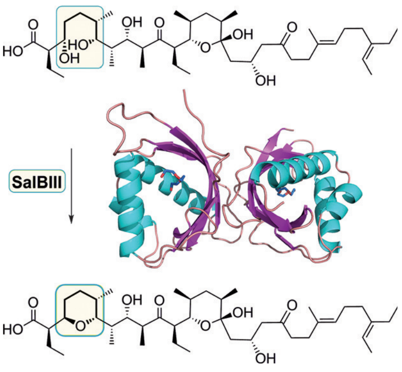


Antimicrobial amphiphilic aminoglycosides: Methylation of the primary amines of anti-Gram-positive amphiphilic aminoglycosides improved their antimicrobial activity and broadened their spectrum to Gram-negative bacteria.

Antibacterial Compounds

R. I. Benhamou, P. Shaul, I. M. Herzog, M. Fridman* ———— **13617 – 13621**

Di-*N*-Methylation of Anti-Gram-Positive Aminoglycoside-Derived Membrane Disruptors Improves Antimicrobial Potency and Broadens Spectrum to Gram-Negative Bacteria

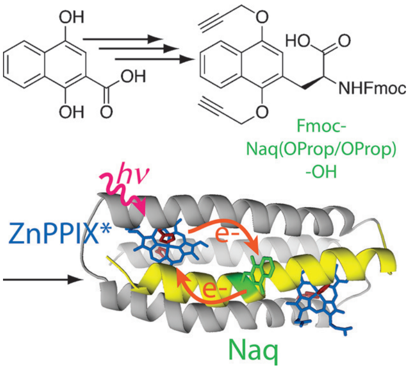


It takes two: X-ray crystallography, mutagenesis, and in vitro studies of the enzyme SalBIII in the salinomycin biosynthetic pathway identify it as a pyran synthase and highlight the role of a catalytic dyad. SalBIII is a promising candidate for chemoenzymatic synthesis.

Enzyme Mechanisms

H. Luhavaya, M. V. B. Dias, S. R. Williams, H. Hong, L. G. de Oliveira, P. F. Leadlay* ———— **13622 – 13625**

Enzymology of Pyran Ring A Formation in Salinomycin Biosynthesis

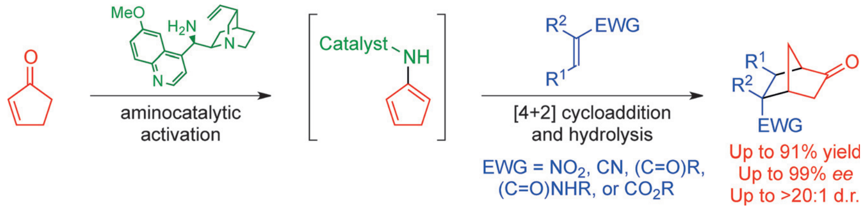


Copycat: To recapitulate and surpass the performance of natural proteins by designing manmade redox proteins, intein-based protein semisynthesis is used to pair a synthetic naphthoquinone amino acid (Naq) with the histidine-ligated photoactive metal–tetrapyrrole cofactors heme and Zn-protoporphyrin IX (ZnPPIX). Using this strategy, a charge separation unit akin to photosynthetic reaction centers is formed.

Protein Engineering

B. R. Lichtenstein, C. Bialas, J. F. Cerda, B. A. Fry, P. L. Dutton, C. C. Moser* ———— **13626 – 13629**

Designing Light-Activated Charge-Separating Proteins with a Naphthoquinone Amino Acid



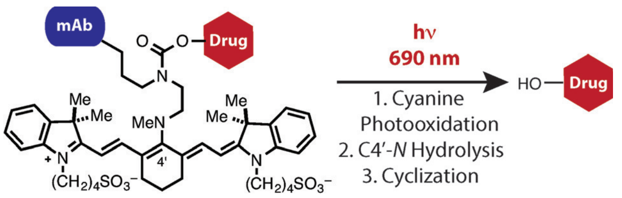
One organocatalyst fits all: A diversity-oriented approach has been employed to prepare a variety of important 5,6-substituted norcamphor scaffolds. The molecules were synthesized by means of asymmetric organocatalytic reactions between amino-activated cyclopentenones and many common classes of electron-deficient olefins.

Organocatalysis

R. Mose, M. E. Jensen, G. Preegel, K. A. Jørgensen* ———— **13630 – 13634**

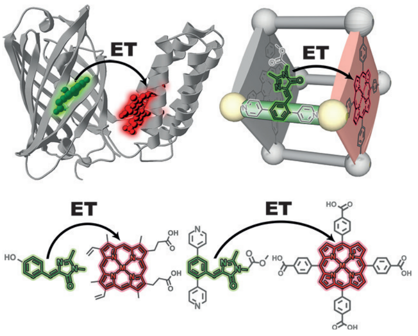
Direct Access to Multifunctionalized Norcamphor Scaffolds by Asymmetric Organocatalytic Diels–Alder Reactions

Antibody–Drug Conjugates



Near-IR ADC cleavage: Near-IR light mediated antibody-drug cleavage has been accomplished using cyanine photocages. This approach allows small molecules to be released from targeting antibodies with spatiotemporal control using easily accessible fluence of tissue-penetrating 690 nm light.

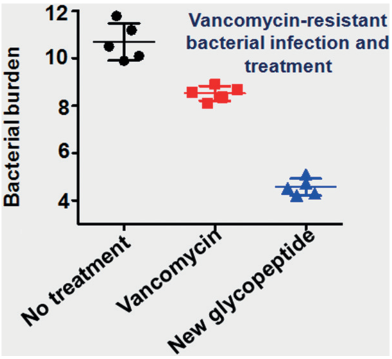
Metal–Organic Frameworks



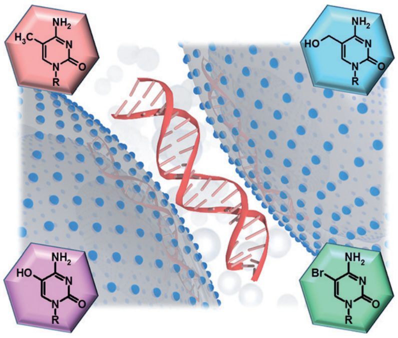
Energy pinball: Efficient chromophore coupling achieved in a protein scaffold was successfully mimicked by integration of chromophores inside metal–organic frameworks (MOFs). The ligand-to-ligand energy-transfer (ET) efficiency calculated based on the experimental time-resolved photoluminescence data was found to be the highest value achieved so far between two coordinatively immobilized ligands in a MOF matrix.

Drug Design

Glycopeptide antibiotics: Newly developed glycopeptide antibiotics demonstrated high activity against multidrug-resistant bacteria and showed the ability to stall bacterial resistance development because of incorporation of a novel membrane-disrupting mechanism and enhanced inhibition of the cell-wall synthesis. The results emphasize that this multipronged approach could be used clinically to develop the next generation of glycopeptide antibiotics.

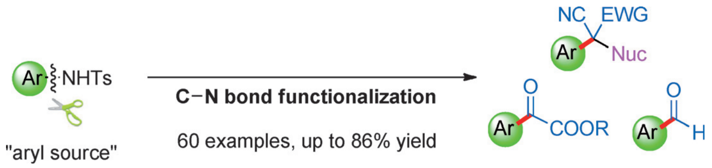


Adductomics



Chasing nucleobase variants: Direct, label-free high-throughput SERS analysis in combination with chemometrics and microfluidics enables the detection and quantification of different cytosine modifications in both single and double-stranded DNA sequences. The minute amount of DNA required per measurement, in the sub-nanogram regime, removes the necessity of pre-amplification or enrichment steps.

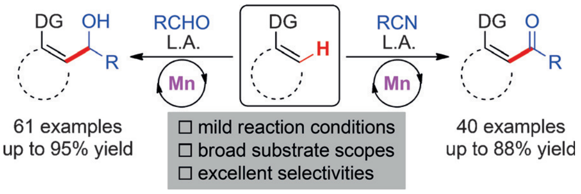
Synthetic Methods



Arene functionalization: An aromatic carbon–nitrogen bond functionalization reaction using a simple dearomatization strategy is reported (see picture). Through this process *para*-substituted aniline molecules served as a potential aryl source in the construction of a range of functionalized aromatic molecules, such as quaternary carbon centers, α-keto esters, and aldehydes.

C–H Activation

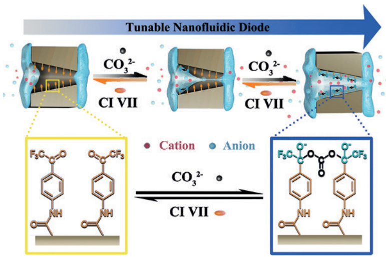
Inside Back Cover



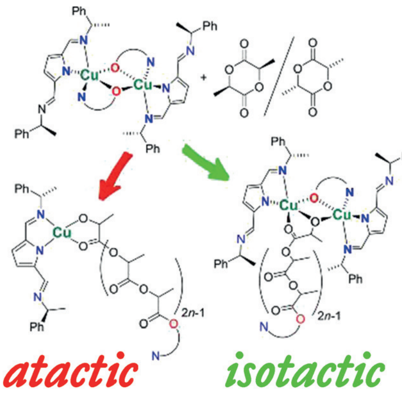
Dual activation: In the title reaction inert C(sp^2)–H bonds add to aldehydes and nitriles by a dual activation strategy. The reaction features mild reaction conditions, a wide substrate scope, and excellent regio- and stereoselectivity. The reaction mechanism is also discussed. DG = directing group, L.A. = Lewis acid.

Nanofluidic Diodes

Carbonate is the key: A smart nanofluidic diode that exhibits both ion gating and ion current rectification has been developed using a conical nanochannel whose switch-like property can be tuned by controlling the wettability and charge distribution with carbonate ions. The nanodevice shows excellent switchability and tunability in ion gating and rectification and may find potential applications in mass delivery.

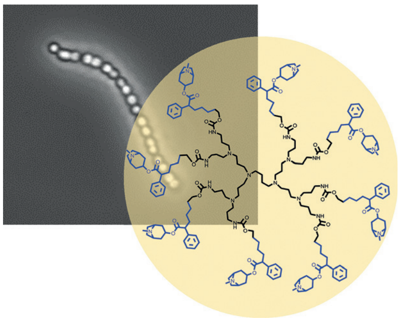


Polymerization



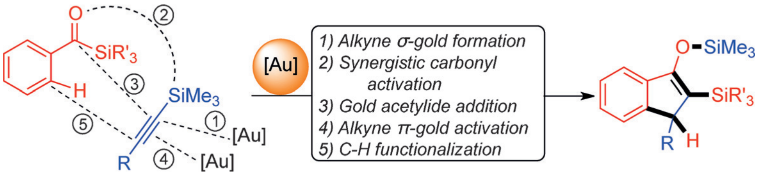
It takes two: Diiminopyrrolide copper alkoxide complexes, LCuOR (OR^1 = *N,N*-dimethylamino ethoxide, OR^2 = 2-pyridyl methoxide), are active for the polymerization of rac-lactide at ambient temperature in benzene. While LCuOR^1 provides only atactic polylactide, LCuOR^2 produces partially isotactic polylactide. The difference in stereocontrol is attributed to a dinuclear active species for LCuOR^2 in contrast to a mononuclear species for LCuOR^1.

Antimicrobial Resistance



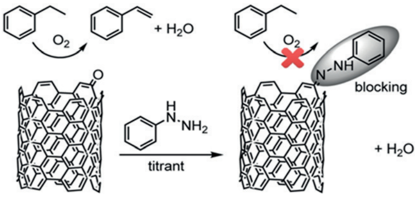
Bicycle race: Novel esters of bicyclic amines with aromatic groups inhibit the binding of pneumococcal choline-binding proteins to the bacterial cell wall, inducing growth arrest, bacterial lysis, a decrease in cell viability, and in vivo protection from infection. Multivalent display on dendrimers dramatically enhance their activity.

Gold Catalysis



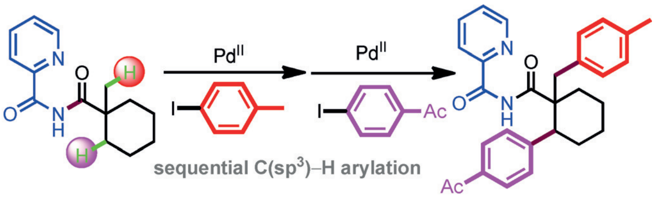
The elegant way: A gold(I)-catalyzed synthesis of indanones from trimethylsilylacetylenes and acylsilanes was developed. The reaction involves a synergistic acylsilane activation–gold acetylide formation and consecutive alkyne σ-gold(I) addition, π-activation, and 1,2-silyl migration. Mechanistic studies suggest the participation of a gold(I) carbenoid intermediate.

Heterogeneous Catalysis



Active duty: An in situ titration process, using phenyl hydrazine as the titrant, is employed to quantify the number of active sites on nanocarbon catalysts for alkane oxidative dehydrogenation reactions. Using this method, the turnover frequency for conversion of the ethyl benzene substrate is used as a reliable kinetic parameter to evaluate the intrinsic activity of the nanocarbon catalysts.

C–H Activation

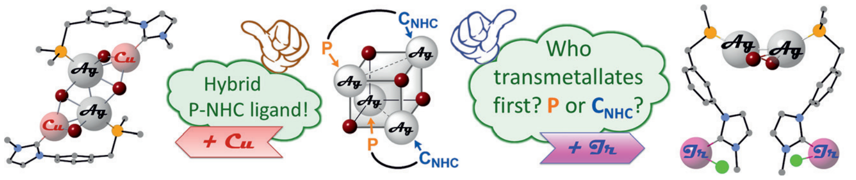


Director's cut: 2-Piconimide, prepared from commercially available 2-picolinamide/2-picolic acid as precursors, was used for the first time to direct C–H arylation/alkenylation by palladium catalysis. The directing group promotes a sequential primary and secondary C(sp^3)–H arylation with different aryl iodides in one substrate and can be easily removed.

Chemoselective NHC Transmetallation

T. Simler, P. Braunstein,*
A. A. Danopoulos* ______ **13691 – 13695**

Relative Lability and Chemoselective Transmetallation of NHC in Hybrid Phosphine-NHC Ligands: Access to Heterometallic Complexes

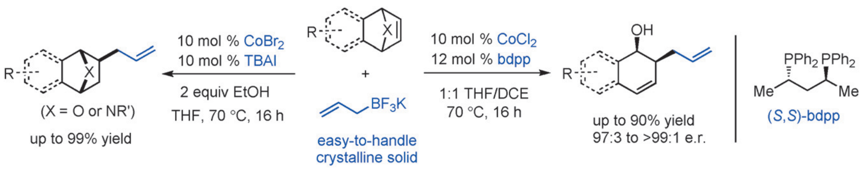


Who wins the transmetallation competition: NHC or phosphine donors? Hybrid ligands provide some answers and the first heterometallic Cu/Ag/NHC and Ag/Ir/NHC complexes have been structurally characterized.

Allylic Compounds

Y. Huang, C. Ma, Y. X. Lee, R.-Z. Huang,
Y. Zhao* ______ **13696 – 13700**

Cobalt-Catalyzed Allylation of Heterobicyclic Alkenes: Ligand-Induced Divergent Reactivities

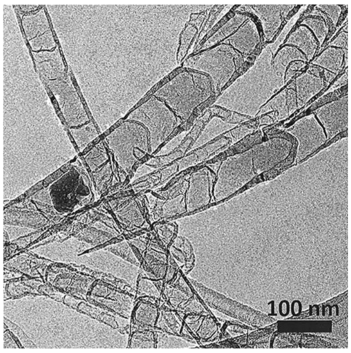


Phos and Co.: By using an inexpensive cobalt salt as the catalyst and potassium allyltrifluoroborate as the reagent, an unprecedented formal hydroallylation of bicyclic alkenes is realized in high efficiency. When a chiral cobalt/bis(phosphine) complex is used instead, the alternative ring-opening products can be obtained in high yield with excellent enantioselectivity. TBAI = tetra-*n*-butylammonium iodide.

Carbon Dioxide Fixation

P. P. Sharma, J. Wu, R. M. Yadav, M. Liu,
C. J. Wright, C. S. Tiwary, B. I. Yakobson,
J. Lou,* P. M. Ajayan,*
X.-D. Zhou* ______ **13701 – 13705**

Nitrogen-Doped Carbon Nanotube Arrays for High-Efficiency Electrochemical Reduction of CO_2: On the Understanding of Defects, Defect Density, and Selectivity

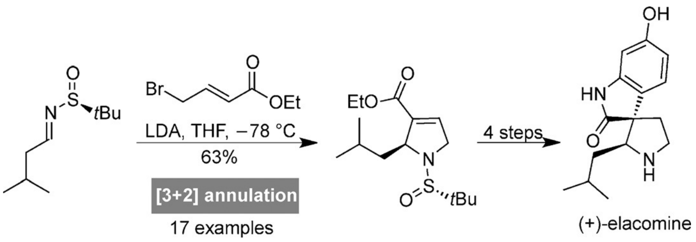


Useful defects: The electrochemical activity of nitrogen-doped multiwalled carbon nanotubes (see picture) used for the reduction of CO_2 was improved by tuning the nitrogen defect sites in the wall structure. Pyridinic nitrogen defects supported the selective formation of CO. DFT calculations confirmed the experimental results.

Synthetic Methods

I. Chogii,
J. T. Njardarson* ______ **13706 – 13710**

Asymmetric [3+2] Annulation Approach to 3-Pyrrolines: Concise Total Syntheses of (−)-Supinidine, (−)-Isoretronecanol, and (+)-Elacomine

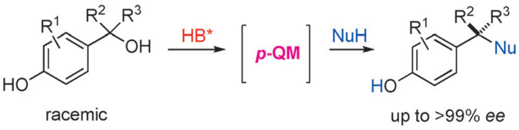


Caught in a trap: In the title reaction deprotonated ethyl 4-bromocrotonate is selectively trapped with Ellman imines, at the α-position, to yield enantiopure 3-pyrroline products. The efficacy of the method is showcased by short asymmetric total syntheses of (−)-supinidine, (−)-isoretronecanol, and (+)-elacomine (see scheme).

Asymmetric Catalysis

Z. Wang, Y. F. Wong,
J. Sun* ——————— **13711 – 13714**

Catalytic Asymmetric 1,6-Conjugate Addition of *para*-Quinone Methides: Formation of All-Carbon Quaternary Stereocenters

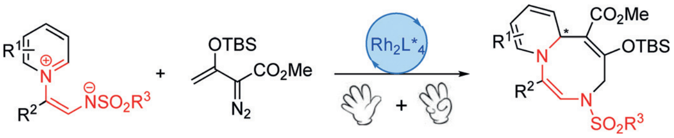


Remote control: A new catalytic asymmetric 1,6-conjugate addition reaction of *para*-quinone methides is disclosed. It is a new addition to the small family of asymmetric reaction of *p*-QMs. With chiral Brønsted acid catalysis, remarkable remote stereocontrol can be achieved for a range of in situ formed *p*-QMs to form all-carbon quaternary stereocenters with high efficiency and enantioselectivity.

Cycloaddition

D. J. Lee, D. Ko, E. J. Yoo* **13715 – 13718**

Rhodium(II)-Catalyzed Cycloaddition Reactions of Non-classical 1,5-Dipoles for the Formation of Eight-Membered Heterocycles

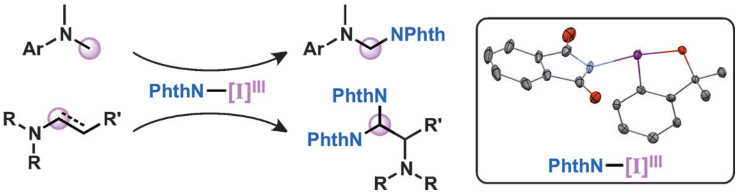


Up-to-eight: A practical [5+3] cycloaddition for the synthesis of eight-membered heterocycles was developed. This rhodium(II)-catalyzed cycloaddition of pyridinium zwitterions and enol diazoacetates is characterized by high selectivity, mild reaction conditions, and a wide substrate scope.

Amination Reactions

K. Kiyokawa,* T. Kosaka, T. Kojima,
S. Minakata* ——————— **13719 – 13723**

Synthesis and Structure of Hypervalent Iodine(III) Reagents Containing Phthalimidate and Application to Oxidative Amination Reactions



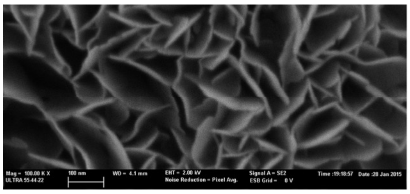
Hyper-active: Benziodoxole-based hypervalent iodine reagents containing phthalimidate have been prepared and found to be reasonably stable in both the solid and solution states. These reagents resulted in the oxidative amination of C(sp^3)—H bonds of *N*,*N*-dimethylanilines and were also applicable to an oxidative amination with rearrangement of trialkylamines and of enamines that were prepared in situ from secondary amines and aldehydes.

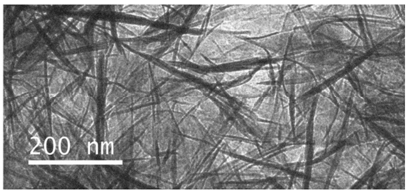
VIP

Zeolites

V. J. Margarit, M. E. Martínez-Armero,
M. T. Navarro, C. Martínez,
A. Corma* ——————— **13724 – 13728**

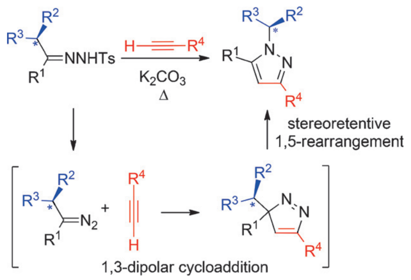
Direct Dual-Template Synthesis of MWW Zeolite Monolayers





The direct synthesis of a delaminated MWW zeolite was achieved by using two organic structure-directing agents. The resultant material consists of approximately 70% single and double layers with well preserved structural integrity and was found to be an excellent catalyst for the liquid-phase alkylation of benzene with propylene.

Maintaining a (con)figur(ation): Retention of configuration in [1,5] sigmatropic shifts are predicted by the Woodward–Hoffmann rules, but are not well-documented experimentally. Such shifts are observed in the reactions of α-chiral tosylhydrazones with terminal alkynes. The chiral pyrazole products are formed by a 1,3-dipolar cycloaddition and subsequent site-, regio-, and stereospecific [1*s*,5*s*] sigmatropic rearrangement. Ts = 4-toluenesulfonyl.



Diazo Compounds

M. C. Pérez-Aguilar,
C. Valdés* ______ 13729 – 13733

Synthesis of Chiral Pyrazoles: A 1,3-Dipolar Cycloaddition/[1,5] Sigmatropic Rearrangement with Stereoretentive Migration of a Stereogenic Group

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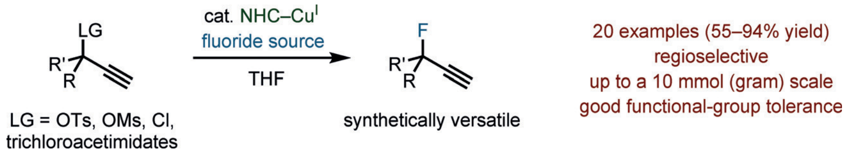

A carbene can: A Cu(NHC)-catalyzed nucleophilic fluorination of propargylic electrophiles was found to be suitable for the synthesis of secondary and tertiary propargylic fluorides without the formation of isomeric fluoroallenes (see scheme; NHC = N-heterocyclic carbene, Ms = methanesulfonyl, Ts = *p*-toluenesulfonyl). Preliminary mechanistic investigations suggest that fluorination proceeds via copper acetylides and involves cationic species.

Synthetic Methods

L.-J. Cheng, C. J. Cordier* 13734 – 13738

Catalytic Nucleophilic Fluorination of Secondary and Tertiary Propargylic Electrophiles with a Copper–N-Heterocyclic Carbene Complex

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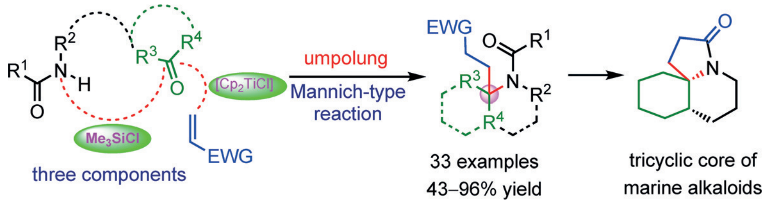

Three parts to one: By using the title method, N-substituted γ-amido-acid derivatives and γ-amido ketones can be prepared efficiently. The extension of the method to ketoamides leads to the formation of piperidine skeletons with α-amino quaternary carbon centers, and provides a concise approach to the tricyclic core of marine alkaloids. Cp = cyclopentadienyl, EWG = electron-withdrawing group.

Multicomponent Reactions

X. Zheng,* J. He, H.-H. Li, A. Wang,
X.-J. Dai, A.-E Wang,
P.-Q. Huang ______ 13739 – 13742

Titanocene(III)-Catalyzed Three-Component Reaction of Secondary Amides, Aldehydes, and Electrophilic Alkenes

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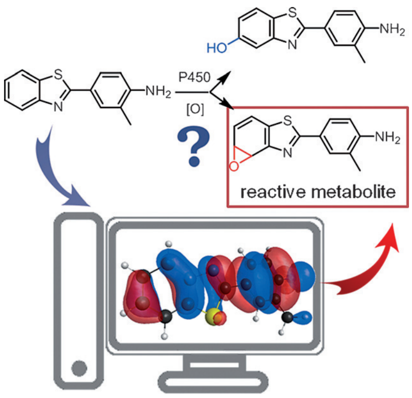
The prediction of the metabolism of a compound will enable to speed up the drug discovery process by discarding potentially toxic drug candidates at an early stage. This study focuses on the oxidation of small molecules by cytochrome P450 enzymes, which metabolize most drugs. The metabolites formed by this bio-transformation can be identified directly from the molecular orbitals of a compound.



Drug Metabolism Modeling

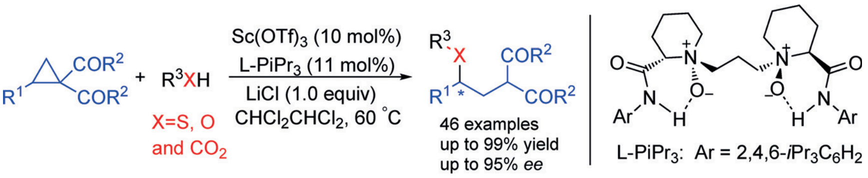
A. Tomberg, J. Pottel, Z. Liu, P. Labute,
N. Moitessier* ______ 13743 – 13747

Understanding P450-mediated Bio-transformations into Epoxide and Phenolic Metabolites

Asymmetric Ring Opening

Y. Xia, L. L. Lin, F. Z. Chang, X. Fu,
X. H. Liu,* X. M. Feng* — **13748 – 13752**

Asymmetric Ring-Opening of Cyclopropyl Ketones with Thiol, Alcohol, and Carboxylic Acid Nucleophiles Catalyzed by a Chiral *N*,*N*′-Dioxide–Scandium(III) Complex



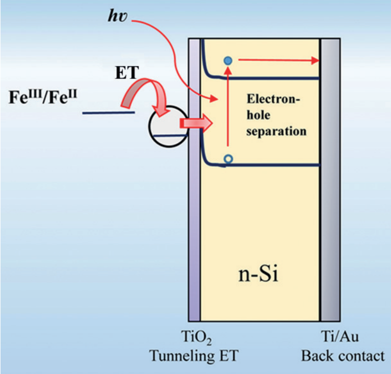
The highly efficient title reaction supplied a variety of chiral sulfides, ethers, and esters in excellent outcomes (up to 99% yield, 95% *ee*). The products could be efficiently converted to a series of γ-substituted carbonyl compounds. Pi = pipecolic acid.

Electrochemistry

H. S. Ahn, A. J. Bard* —— **13753 – 13757**

Single-Nanoparticle Collision Events: Tunneling Electron Transfer on a Titanium Dioxide Passivated n-Silicon Electrode

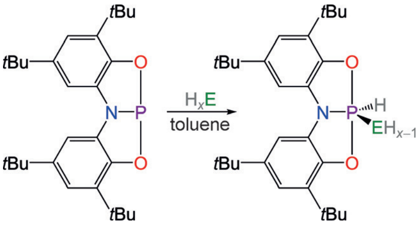
Collision course: Single-nanoparticle collisions result in tunneling electron transfer (ET) from platinum nanoparticles through a thin insulating oxide layer to an n-type silicon electrode (see figure). Single-nanoparticle collisions can be observed on large electrodes ($d > 100$ μm), and this technique avoids photocorrosion and current decay that are experienced with unprotected n-Si surfaces.



Small-Molecule Activation

T. P. Robinson, D. M. De Rosa,
S. Aldridge,*
J. M. Goicoechea* ——— **13758 – 13763**

E–H Bond Activation of Ammonia and Water by a Geometrically Constrained Phosphorus(III) Compound

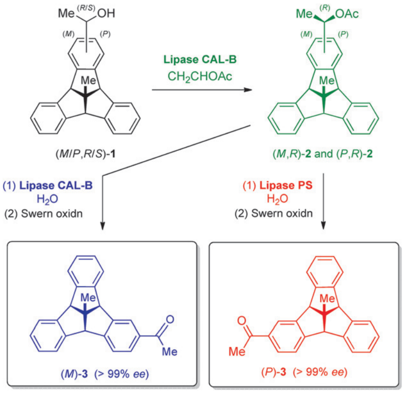


Divide and conquer: A phosphorus(III) compound bearing a tridentate *N*,*N*-bis(3,5-di-*tert*-butyl-2-phenoxy)amide ligand is reported. This species has been found to react with ammonia and water activating the E−H bonds (E = N and O, respectively) in both substrates to afford the corresponding phosphorus(V) compounds. In the case of water, both O−H bonds can be activated.

Enzyme Catalysis

W. Greschner, B. Neumann,
H.-G. Stammler, H. Gröger,*
D. Kuck* ———— **13764 – 13768**

Enantiomerically Pure Tribenzotriquinacenes through Stereoselective Synthesis

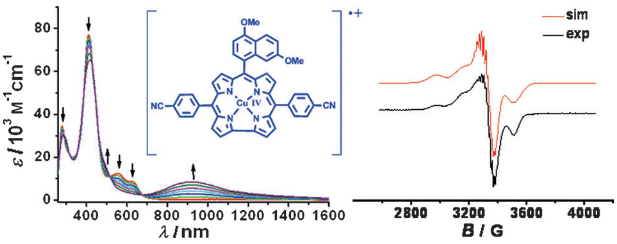


Bowls go bio! Enzymes accept the bowl-shaped hydrocarbon core of tribenzotriquinacene (TBTQ)-based secondary and even primary benzylic alcohols and facilitate their highly enantio- and diastereoselective esterification and the hydrolysis of the corresponding acetates. Lipases CAL-B and PS act complementarily with regard to the configuration of the TBTQ core, allowing for the biocatalytic synthesis of enantiomerically pure TBTQ building blocks.

Copper(IV) Complexes

W. Sinha, M. G. Sommer, N. Deibel,
F. Ehret, M. Bauer, B. Sarkar,*
S. Kar* ________ 13769 – 13774

Experimental and Theoretical Investigations of the Existence of Cu^{II}, Cu^{III}, and Cu^{IV} in Copper Corrolato Complexes

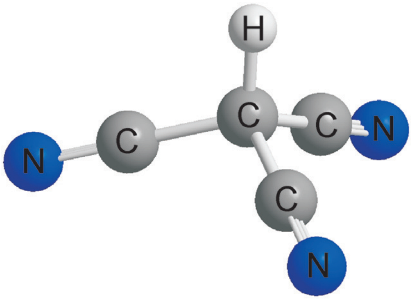


Fly high: Electrochemical, UV/Vis/NIR/EPR spectroelectrochemical, and XANES measurements as well as DFT calculations point to the existence of three distinct redox states in the title compounds as oxidation states of +II, +III, and +IV can be invoked for the copper centers. These results thus represent the first spectroscopic and theoretical investigation of a Cu^{IV} species.

Cyanoform

T. Soltner, J. Häusler,
A. J. Kornath* ________ 13775 – 13776

The Existence of Tricyanomethane

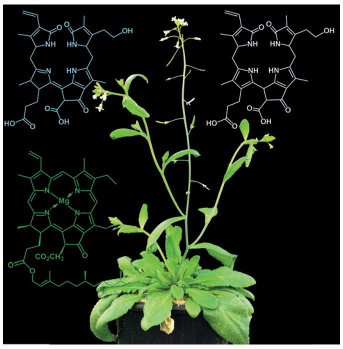


After searching for the tricyanomethane molecule for more than one century, the synthesis of the elusive molecule has now been accomplished by the simple reaction of calcium tricyanomethanide with anhydrous hydrogen fluoride at low temperature.

Biodegredation Pathways

I. Süssenbacher, S. Hörtensteiner,
B. Kräutler* ________ 13777 – 13781

A Dioxobilin-Type Fluorescent Chlorophyll Catabolite as a Transient Early Intermediate of the Dioxobilin-Branch of Chlorophyll Breakdown in *Arabidopsis thaliana*



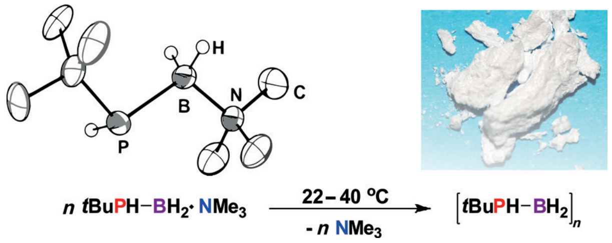
Chlorophyll breakdown in higher plants leads to phyllobilins, which are first formed as 1-formyl-19-oxobilins. An enzyme-catalyzed deformylation of the fleetingly existent "fluorescent catabolites" has been proposed for the subsequent generation of 1,19-dioxobilin-type catabolites. A 1,19-dioxobilin-type fluorescent catabolite that rapidly isomerizes to the nonfluorescent 1,19-dioxobilin was identified as a breakdown intermediate in *Arabidopsis thaliana*.

Main-Group-Element Polymers

C. Marquardt, T. Jurca, K.-C. Schwan,
A. Stauber, A. V. Virovets, G. R. Whittell,
I. Manners,* M. Scheer* _ 13782 – 13786

Metal-Free Addition/Head-to-Tail Polymerization of Transient Phosphinoboranes, $RPH\text{-}BH_2$: A Route to Poly(alkylphosphinoboranes)

Front Cover



$$n\ t\mathrm{BuPH{-}BH_2 \cdot NMe_3} \xrightarrow[-\,n\ \mathrm{NMe_3}]{22\text{–}40\ ^\circ\mathrm{C}} [t\mathrm{BuPH{-}BH_2}]_n$$

Mild thermolysis of Lewis base stabilized phosphinoborane monomers provides a convenient new route to oligo- and polyphosphinoboranes. The polymerization appears to proceed by the addition/head-to-tail polymerization of short-lived phosphinoborane monomers. This method offers access to high-molar-mass poly(alkylphosphinoboranes), which are currently inaccessible by transition-metal-catalyzed routes.

Protein Modification

D. Schumacher, J. Helma, F. A. Mann,
G. Pichler, F. Natale, E. Krause,
M. C. Cardoso, C. P. R. Hackenberger,*
H. Leonhardt* ________ **13787 – 13791**

Versatile and Efficient Site-Specific Protein Functionalization by Tubulin Tyrosine Ligase

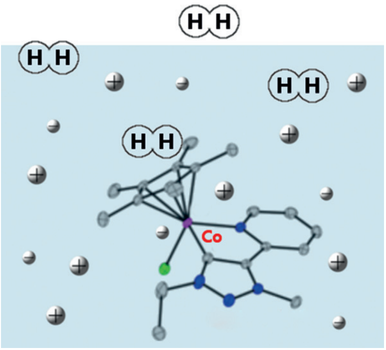
Tub-tag labeling: Tubulin tyrosine ligase was repurposed for the site-specific labeling any protein of interest. The enzyme adds unnatural tyrosine derivatives to the C terminus of proteins containing a short tubulin-derived recognition sequence (Tub-tag), which can subsequently be modified through bioorthogonal chemistry. The technique is compatible with a broad variety of bioorthogonal reactions for site-specific protein modification.

Dihydrogen Production

M. van der Meer, E. Glais, I. Siewert,*
B. Sarkar* ________ **13792 – 13795**

Electrocatalytic Dihydrogen Production with a Robust Mesoionic Pyridylcarbene Cobalt Catalyst

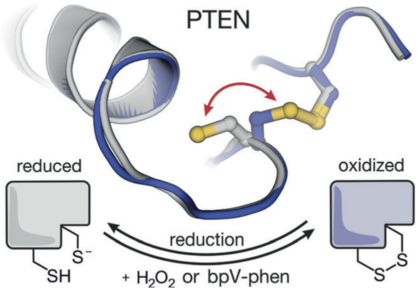
A Co^{III} complex with a mesoionic pyridylcarbene ligand is presented. This complex acts as a potent catalyst for electrocatalytic H_2 production, delivering high turnover frequencies at low overpotentials. The present results thus open new avenues for carbene-based ligands for generating functional models for hydrogenases.



Phosphatase Inhibition

C.-U. Lee, G. Hahne, J. Hanske, T. Bange,
D. Bier, C. Rademacher, S. Hennig,
T. N. Grossmann* ________ **13796 – 13800**

Redox Modulation of PTEN Phosphatase Activity by Hydrogen Peroxide and Bisperoxidovanadium Complexes



An important tumor suppressor, the phosphatase PTEN, is crucially involved in regenerative processes. Based on protein crystallography, mass spectrometry, and NMR spectroscopy, the molecular basis of PTEN inhibition by H_2O_2 and bisperoxidovanadium complexes has been elucidated. Both inhibit PTEN via oxidative mechanisms resulting in the formation of the same intramolecular disulfide, therefore enabling the reactivation of PTEN under reductive conditions.

Carbenes

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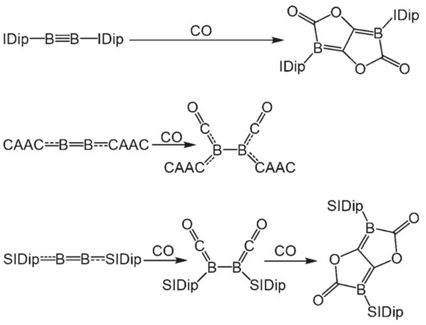
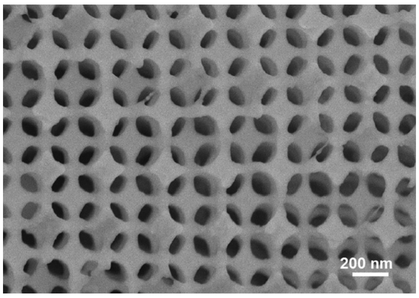
J. Mies ________ **13801 – 13805**

The Synthesis of $B_2(SIDip)_2$ and its Reactivity Between the Diboracumulenic and Diborynic Extremes

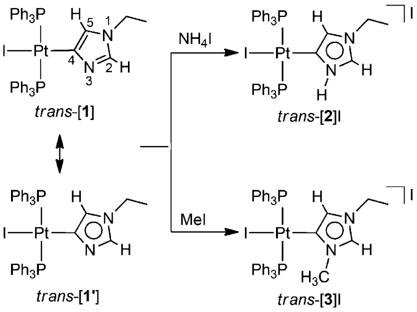


A happy middle ground: The synthesis and characterization of $B_2(SIDip)_2$ shows the capacity of carbene ligands to control the chemistry in which they are involved. The SIDip carbene, having a π-acidity lying between those of the commonly used CAAC and IDip carbenes, allows the syntheses of compounds with structures and reactivities intermediate between those found in compounds constructed of CAAC or IDip.

Porous perovskite: A series of organometal halide perovskite inverse opals were fabricated by using a colloidal crystal templating method. The perovskite inverse opal not only preserved the advantage of band gap engineering but also showed sensitive photocurrent generation. These perovskite inverse opals could be promising materials for optoelectronic device and photocatalysis.



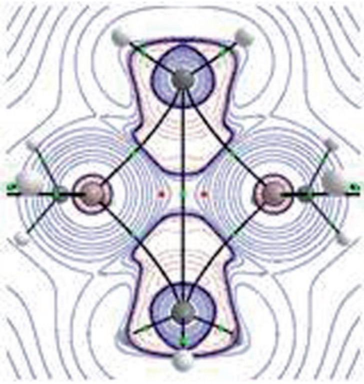
Perovskites



The oxidative addition of neutral 4-iodo-*N*-ethylimidazole to [Pt(PPh$_3$)$_4$] yields the complex *trans*-[**1**] bearing an anionic C4-bound heterocycle. Complex *trans*-[**1**] can be N3-protonated and N3-methylated giving complexes with protic and conventional *a*NHC ligands, respectively. (aNHC = abnormal N-heterocyclic carbene; NHC = N-heterocyclic carbene).

Abnormal N-Heterocyclic Carbenes

“C—C or Al—Al, if at all” is the short version of characterizing the bonding situation in trimethylaluminum, which is now characterized by studies of the experimental charge density as well as the calculated charge and current density topologies.



Chemical Bonding

Inside Cover

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

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

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Angewandte Apology

Readily Removable Directing Group Assisted Chemo- and Regioselective C(sp^3)—H Activation by Palladium Catalysis

Y.-F. Zhang, H.-W. Zhao, H. Wang, J.-B. Wei, Z.-J. Shi* ______ **13686–13690**

Angew. Chem. Int. Ed. **2015**, *54*

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In this Communication a most important prior work was not acknowledged. In 2014, Baran and Gutekunst had already described the use of picolinimide as a directing group in C—H activation.[1] They articulated the reasons for inventing this directing group, used it in the particularly challenging case of a direct indolylation of cyclobutane carboxylic acid derivatives, and obtained an X-ray crystal of a palladium–picolinimide complex. They also reported simple and mild conditions for removal of this directing group.

Thus, Scheme 1 of this Communication should be revised as shown below. The authors deeply apologize for this error.

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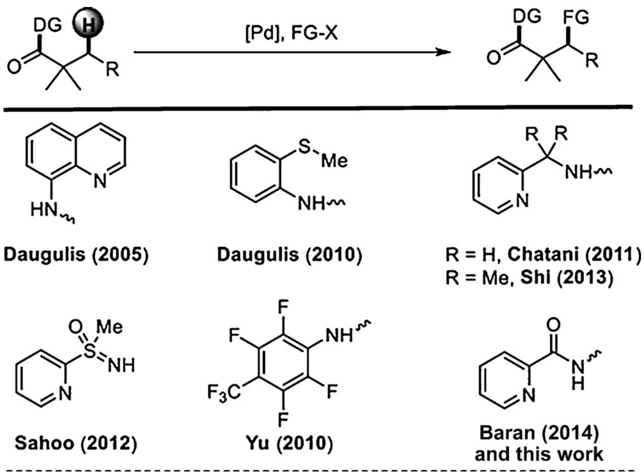
[1] W. R. Gutekunst, P. S. Baran, *J. Org. Chem.* **2014**, *79*, 2430–2452.



Scheme 1. Directing groups for functionalization of carboxylic acid derivatives by palladium catalysis. FG = functional group.