

Spotlight on Angewandte's Sister Journals

12154 – 12157

Service

Author Profile



"The principal aspect of my personality is I am enormously optimistic."

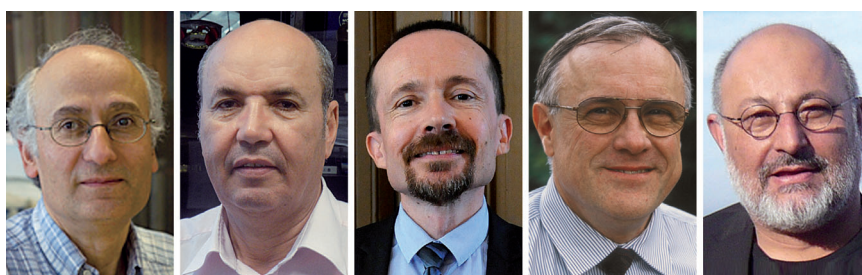
My motto is fully enjoy whatever I do ..."

This and more about Kyoko Nozaki can be found on page 12160.

Kyoko Nozaki _____ 12160 – 12161

News

Société Chimique de France 2012
Prize Winners _____ 12162 – 12163



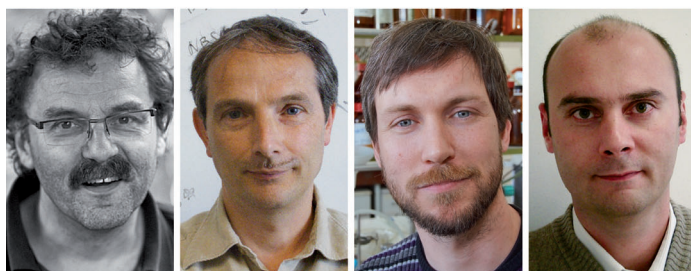
S. Z. Zard

L. Ouahab

P. Sautet

K. Müllen

M. W. Hosseini



Y. Journaux

J. Maddaluno

F. Gagosz

V. Gandon

Books

Sand and Silicon

Denis McWhan

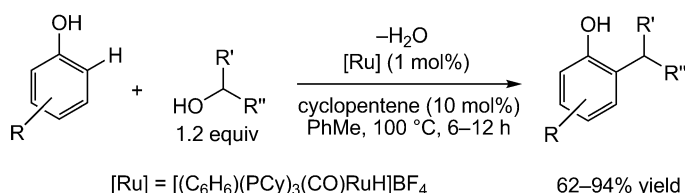
reviewed by P. O. Hahn _____ 12164

Highlights

Dehydrative Alkylation

J. W. Walton,
J. M. J. Williams* _____ 12166 – 12168

Ruthenium-Catalyzed *ortho*-Alkylation of Phenols with Alcohols by Dehydrative Coupling



Only water: Phenols have been shown to undergo a ruthenium-catalyzed *ortho*-alkylation reaction (see scheme; Cy = cyclohexyl). Unactivated alcohols are used

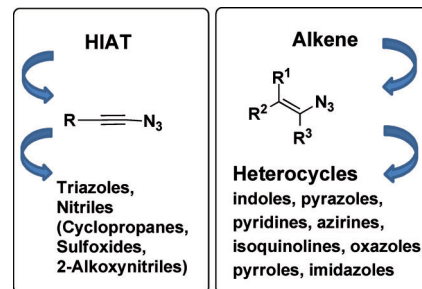
as the alkylating agents and water is the only by-product that is generated, making this transformation more atom-economical and greener than traditional methods.

1-Azidoalkenes and 1-Azidoalkynes

N. Jung,* S. Bräse* — 12169–12171

Vinyl and Alkynyl Azides: Well-Known Intermediates in the Focus of Modern Synthetic Methods

Getting real: Although 1-azidoalkenes are known as important intermediates for the formation of many nitrogen heterocycles, for a long time the existence of the corresponding 1-azidoalkynes could not be proven unequivocally. The recent synthesis and full characterization of 1-azidoethyne have provided incontrovertible verification of this substance class.

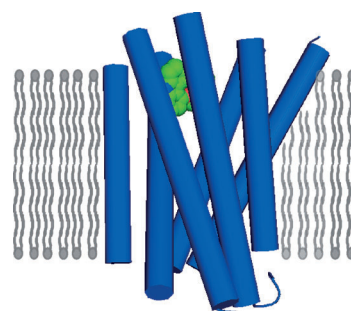


Nobel Prize for Chemistry 2012

F. Hausch,* F. Holsboer — 12172–12175

The Seven Pillars of Molecular Pharmacology: GPCR Research Honored with Nobel Prize for Chemistry

G protein-coupled receptors with seven transmembrane helices (see picture) are the most important drug targets in medicine. Their molecular and structural characterization has now been honored with the Nobel Prize for Chemistry to Robert J. Lefkowitz and Brian K. Kobilka.

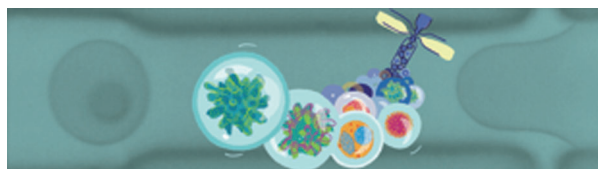


Reviews

Life in a Bubble

H. N. Joensson,*
H. Andersson Svahn — 12176–12192

Droplet Microfluidics—A Tool for Single-Cell Analysis



A one-off: Single-cell analysis is one of the most interesting applications for droplet microfluidics. Droplets provide robust compartments on the size scale of a single cell, and their ability to encapsulate and rapidly manipulate cells along

with their immediate environment in monodisperse compartments allows the possibility of automation. This Review focuses on single-cell analyses and applications in drug screening and genetic and enzyme analysis.

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Communications

Supramolecular Chemistry

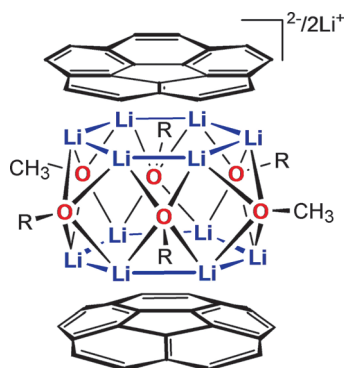


A. V. Zabula, S. N. Spisak, A. S. Filatov,
M. A. Petrukhina* — 12194–12198

Pentadecker Supramolecules with
a Lithium Alkoxo Nanobelt Sandwiched
between Two Highly Charged Buckybowl
Surfaces

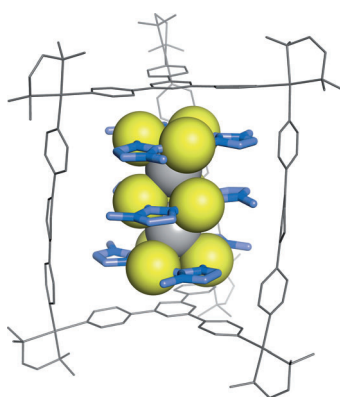


Frontispiece



Stack it up: Reduction of corannulene with an excess of lithium metal in dimethoxyethane (DME) results in the formation of remarkable multilayered supramolecular aggregates (see picture) having lithium alkoxo nanobelts encapsulated between two tetra-reduced corannulene bowls, $[\text{C}_{20}\text{H}_{10}^{4-}/\text{Li}_6(\text{OR})_6\text{Li}_6/\text{C}_{20}\text{H}_{10}^{4-}]^{2-}$. The alkoxo groups ($\text{R} = \text{CH}_3\text{O}$ or/and $\text{CH}_3\text{OCH}_2\text{CH}_2\text{O}$) are products of the Li-induced DME cleavage.

Silver in a gold mine: A triple-decker $\text{Au}^{\text{I}}\text{--Ag}^{\text{I}}$ ion cluster was synthesized by alternate alignment of cyclic trinuclear Au^{I} complexes and Ag^{I} ions within a self-assembled cage. The box-shaped cavity of the cage is suitable not only for limiting the cluster number, but also for the stabilization of weakly associated metal ions, which cannot exist without the help of the cage.



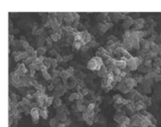
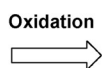
Metal Ion Clusters

T. Osuga, T. Murase,
M. Fujita* — 12199–12201

Triple-Decker $\text{Au}_3\text{--Ag--Au}_3\text{--Ag--Au}_3$ Ion
Cluster Enclosed in a Self-Assembled
Cage

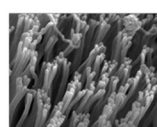


Solid Carbon Powders



Oxidized Carbon

Carbonization



Carbon Nanofibers

Carbon nanofibers were synthesized from common solid carbon sources (such as artificial graphites and acetylene black) in the presence of an iron catalyst by direct

carbonization. This inexpensive and simple method is expected to trigger a revolution in the preparation of nanocarbons.

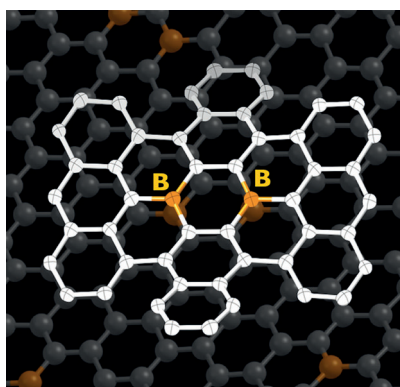
Nanostructures

Y. Shen, L. Yan, H. Song,* J. Yang, G. Yang,
X. Chen, J. Zhou, Z.-Z. Yu,
S. Yang — 12202–12205

A General Strategy for the Synthesis of
Carbon Nanofibers from Solid Carbon
Materials



BBC news: Two boron atoms have been incorporated into a carbon nanosheet by a bottom-up synthesis to give a “B-doped nanographene” (see picture) with a defined structure. The experimental and theoretical analyses revealed the important role of the two boron atoms in producing its characteristic properties, such as broad absorption bands covering the visible region and reversible redox processes.

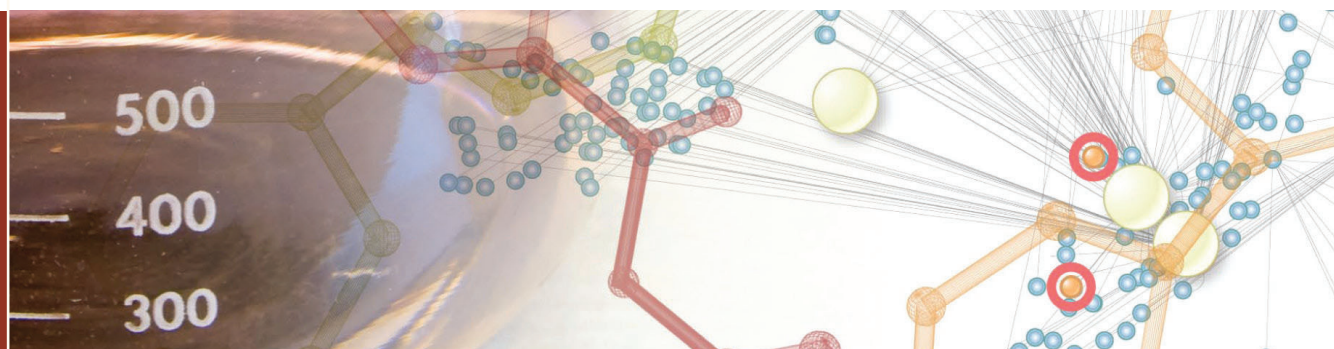


Graphene

C. Dou, S. Saito,* K. Matsuo, I. Hisaki,
S. Yamaguchi* — 12206–12210

A Boron-Containing PAH as
a Substructure of Boron-Doped Graphene





Novartis is pleased to announce the 2012 recipients of the Novartis Early Career Award in Organic Chemistry



Professor Sarah E. Reisman,
California Institute of Technology, Pasadena, CA, USA

Sarah Reisman earned her Ph.D. in 2006 from Yale University in the research group of Professor John Wood. For her postdoctoral work she pursued studies at Harvard University as a NIH fellow, working with Professor Eric Jacobsen. In 2008, Sarah began her independent career at the California Institute of Technology and has gone on to build an excellent reputation as one of the leaders in natural product synthesis, addressing complex total synthesis problems with innovative approaches as well as the development of new synthetic methods.



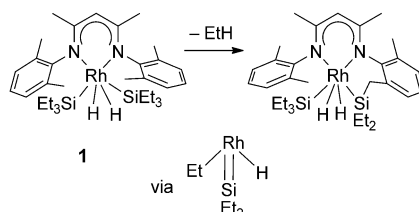
Professor Corey R. J. Stephenson,
Boston University, Boston, MA, USA

Corey Stephenson earned his Ph.D. in 2004 from the University of Pittsburgh working with Professor Peter Wipf. He went on to postdoctoral studies at ETH Zürich working with Professor Erick Carreira. In 2007 Corey joined the Department of Chemistry at Boston University as an Assistant Professor, and is a co-principle investigator for Boston University's Center for Methodologies and Library Development. Since this time he has emerged as a leader in the field of visible-light activated redox chemistry, developing new photocatalysts and synthetic methods for use in the synthesis of natural products.

The Novartis Early Career Award in Organic Chemistry is presented annually to outstanding scientists within 10 years of having established an independent academic research career, in the areas of organic or bioorganic chemistry in the broadest sense. Two winners are identified, from the Global Research community, each of whom receives an unrestricted research grant.

Past Awardees: David Chen, Seoul National University (2011); David Spiegel, Yale University (2011); Karl Gademann, University of Basel (2010); Jin-Quan Yu, The Scripps Research Institute (2010); Magnus Rueping, RWTH Aachen University (2009); Christopher J. Chang, University of California, Berkeley (2009); Matthew J. Gaunt, University of Cambridge (2008); Jeffrey S. Johnson, University of North Carolina at Chapel Hill (2008); Lukas J. Goossen, Technische Universität Kaiserslautern (2007); Anna K. Mapp, University of Michigan Ann Arbor (2007); Armido Studer, University of Münster (2006); F. Dean Toste, University of California Berkeley (2006); Benjamin List, Max Planck Institute Mülheim (2005); Dirk Trauner, University of California Berkeley (2005); J. Stephen Clark, University of Nottingham (2004); Jonathan P. Clayden, University of Manchester (2004); Thorsten Bach, Technical University of Munich (2003); Bernhard Breit, University of Freiburg (2002); Thomas Carell, University of Munich (2002).

The coupling of HSiEt_3 and related silanes to β -diiminate ligands is achieved through a series of Si–H, C–H, and Si–C bond-breaking and bond-forming reactions. Complex **1** (see scheme) loses an Et(Si) group as ethane and couples the remaining SiEt_2H fragment to a benzylic methyl group of the ligand skeleton. According to DFT calculations, the reaction involves silylene intermediates.



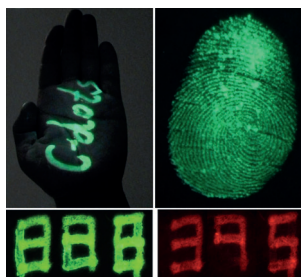
Si–C Activation

D. Zhu, D. J. Kozera, K. D. Enns,
P. H. M. Budzelaar* — 12211 – 12214

Cascade Activation of Si–H, C–H, and Si–C Bonds at a Rhodium β -Diiminate Complex



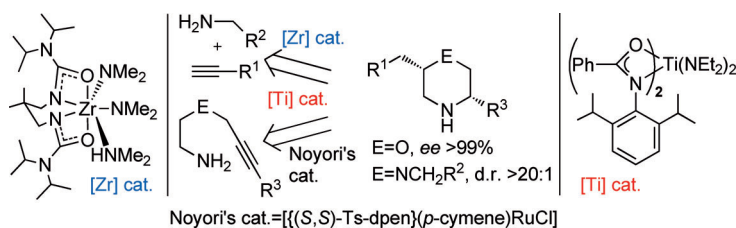
C-dots on hand: Luminescent carbon nanodots were synthesized and were shown to be biocompatible, have low toxicity, and distinctive photoluminescence properties. These C-dots are inexpensive to synthesize and could potentially be used for versatile applications, such as anticounterfeiting, information encryption, and information storage.



Carbon Nanodots

S. Qu, X. Wang, Q. Lu, X. Liu,*
L. Wang* — 12215 – 12218

A Biocompatible Fluorescent Ink Based on Water-Soluble Luminescent Carbon Nanodots



Noyori's cat. = $[(S,S)\text{-Ts-dpen}](p\text{-cymene})\text{RuCl}]$

Heterocycle Synthesis

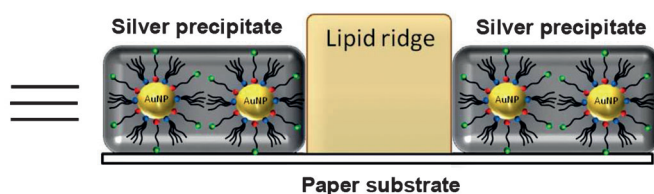
H. Zhai, A. Borzenko, Y. Y. Lau, S. H. Ahn,
L. L. Schafer* — 12219 – 12223

Catalytic Asymmetric Synthesis of Substituted Morpholines and Piperazines



Under two conditions: Hydroamination catalyzed by group 4 metals is featured in the modular and enantioselective syn-

thesis of 3-substituted morpholines and the diastereoselective synthesis of 2,5-substituted piperazines.



Don't sweat it: "Negative" fingerprints are developed on paper by the application of gold nanoparticles (gold circles) that are capped by a bifunctional ligand, and then silver precipitation. In this process,

paper is the substrate and the fingerprints serve as a mask. This approach may contribute to the successful recovery of latent fingerprints by law enforcement agencies.

Gold Nanoparticles

N. Jaber, A. Lesniewski, H. Gabizon,
S. Shenawi, D. Mandler,*
J. Almog* — 12224 – 12227

Visualization of Latent Fingerprints by Nanotechnology: Reversed Development on Paper—A Remedy to the Variation in Sweat Composition



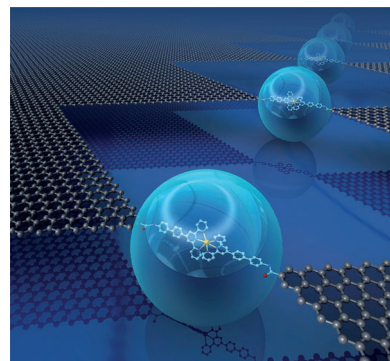
Molecular Electronics

Y. Cao, S. Dong, S. Liu, L. He, L. Gan,
X. Yu, M. L. Steigerwald, X. Wu, Z. Liu,
X. Guo* ————— 12228 – 12232



Building High-Throughput Molecular Junctions Using Indented Graphene Point Contacts

A molecular-scale gap array is introduced into a single-layer graphene sheet by a lithographic dash-line cutting process. Electrically active molecules are then covalently wired into these point contacts in high yield, thus forming stable molecular devices that for example are able to reversibly switch their conductance by chemical treatment.



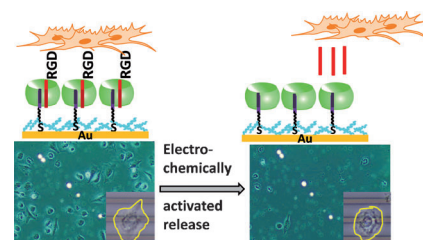
Host–Guest Systems

Q. An, J. Brinkmann, J. Huskens,
S. Krabbenborg, J. de Boer,
P. Jonkheijm* ————— 12233 – 12237



A Supramolecular System for the Electrochemically Controlled Release of Cells

Please release me: Electrochemically activated cell release is achieved using a redox-active supramolecular complex (see picture). Host molecule CB[8] (green) links surface-bound viologen (purple) with solution-exposed RGD peptides (red). Electrochemical reduction dissociates the complex, releases the peptides, and thus releases the cells from the substrates. This supramolecular strategy is also applicable to microelectrodes.



Back Cover

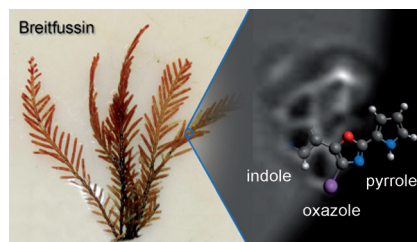


Natural Products

K. Ø. Hanssen, B. Schuler, A. J. Williams,
T. B. Demissie, E. Hansen, J. H. Andersen,
J. Svenson, K. Blinov, M. Repisky, F. Mohn,
G. Meyer, J.-S. Svendsen, K. Ruud,
M. Elyashberg, L. Gross, M. Jaspars,*
J. Isaksson* ————— 12238 – 12241



A Combined Atomic Force Microscopy and Computational Approach for the Structural Elucidation of Breitfussin A and B: Highly Modified Halogenated Dipeptides from *Thuiaria breitfussi*



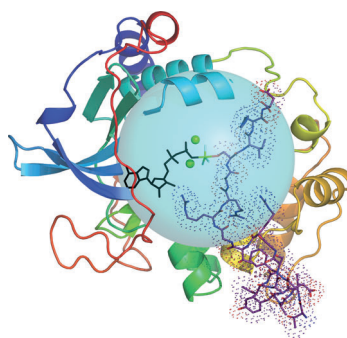
Turning a new leaf: The first structures isolated from *Thuiaria breitfussi*, the breitfussins, are presented. This structural class consists of indole–oxazole–pyrrole units. Limited quantities prevented crystallization; therefore, the structures were solved using a novel combination of AFM, computer-aided structure elucidation (CASE), and DFT calculations. Visualization by AFM determined all the connection points of the cyclic systems and the other substituents.

Enzyme Catalysis

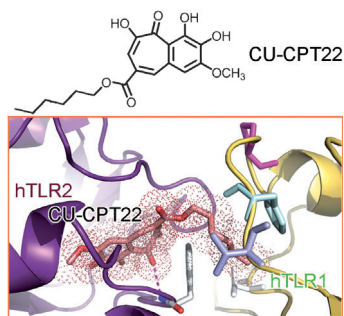
Y. Jin, M. J. Cliff, N. J. Baxter,
H. R. W. Dannatt, A. M. Hounslow,
M. W. Bowler, G. M. Blackburn,*
J. P. Waltho* ————— 12242 – 12245



Charge-Balanced Metal Fluoride Complexes for Protein Kinase A with Adenosine Diphosphate and Substrate Peptide SP20



Well-balanced: ^{19}F NMR spectroscopy defined a trifluoromagnesate complex for protein kinase A (multicolored) with adenosine diphosphate (black), the MgF_3^- ion (green), and the SP20 peptide substrate (purple with dots). A sphere (cyan) centered on the MgF_3^- ion embraces all catalytic components and much of the SP20 substrate. The content of the sphere is uncharged conforming to the charge balance hypothesis.



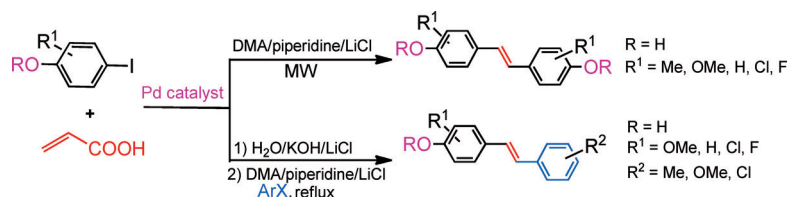
An important regulator of innate immunity, the protein complex of Toll-like receptors 1 and 2 (TLR1/TLR2) provides an attractive target for the treatment of various immune disorders. The novel compound CU-CPT22 can compete with the binding of the specific lipoprotein ligand to TLR1/TLR2 (see picture) with high inhibitory activity and specificity. Repression of downstream signaling from TNF- α and IL-1 β was also observed.

Drug Discovery

K. Cheng, X. H. Wang, S. T. Zhang,
H. Yin* 12246–12249

Discovery of Small-Molecule Inhibitors of the TLR1/TLR2 Complex

Inside Back Cover



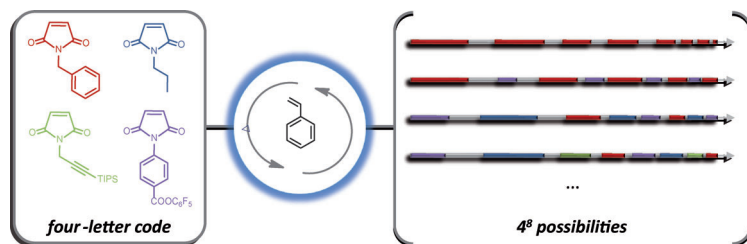
Ride the (micro)wave: The title strategy has been developed for the synthesis of various symmetric or unsymmetric hydroxylated stilbenoids utilizing 4-halo-phenols and acrylic acid as coupling

partners (see scheme; DMA = *N,N*-dimethylacetamide, MW = microwave). Protecting groups are not necessary and a single palladium catalyst is used.

Cross-Coupling

A. Shard, N. Sharma, R. Bharti,
S. Dadhwal, R. Kumar,
A. K. Sinha* 12250–12253

Tandem Heck/Decarboxylation/Heck Strategy: Protecting-Group-Free Synthesis of Symmetric and Unsymmetric Hydroxylated Stilbenoids



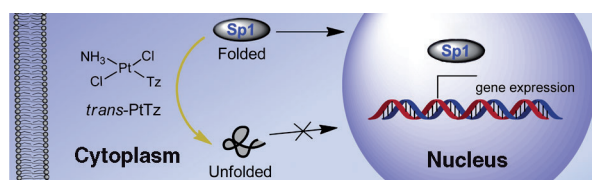
The automated sequence-controlled copolymerization of styrene and *N*-substituted maleimides allowed the production of unprecedented polymer microstructures (up to 65536 possible micro-

structural arrangements). Highly complex monomer sequence patterns were prepared using four *N*-substituted maleimides (see picture).

Sequence-Controlled Polymerization

D. Chan-Seng, M. Zamfir,
J.-F. Lutz* 12254–12257

Polymer-Chain Encoding: Synthesis of Highly Complex Monomer Sequence Patterns by Using Automated Protocols



No trafficking: The antitumor-active *trans*-platinum/thiazole complex *trans*-PtTz demonstrated high reactivity to the transcription factor Sp1, which is over-expressed in tumor cells. The binding of

trans-PtTz disrupts the DNA interaction with Sp1 in vitro and prevents the protein trafficking from the cytoplasm into the nucleus (see picture).

Protein Expression

S. Chen, D. Xu, H. Jiang, Z. Xi, P. Zhu,
Y. Liu* 12258–12262

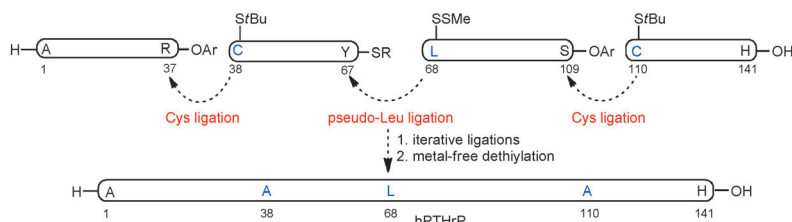
Trans-Platinum/Thiazole Complex Interferes with Sp1 Zinc-Finger Protein

Protein Synthesis

J. Li, S. Dong, S. D. Townsend, T. Dean,
T. J. Gardella,
S. J. Danishefsky* — 12263 – 12267



Chemistry as an Expanding Resource in
Protein Science: Fully Synthetic and Fully
Active Human Parathyroid Hormone-
Related Protein (1–141)



The convergent synthesis of human parathyroid hormone-related protein (hPTHrP, see scheme) has been accomplished through iterative peptide ligations fol-

lowed by global metal-free deethylation. The biological activity of synthetic PTHrP has been demonstrated.

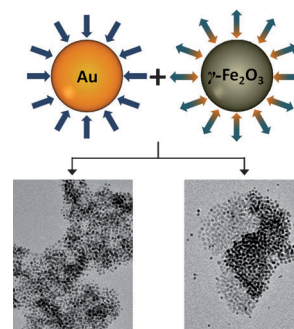
Nanostructures

M. Boterashvili, M. Lahav, T. Shirman,
D. Freeman,
M. E. van der Boom* — 12268 – 12271



Integrated and Segregated Au/ γ -Fe₂O₃
Binary Nanoparticle Assemblies

To mix or not to mix: Integrated (left) and segregated (right) assemblies were obtained upon treating functionalized γ -Fe₂O₃ nanoparticles (NPs) with AuNPs. Their binary nature is controlled by the capping layer of the γ -Fe₂O₃ NPs and the AuNP initial aggregation state. The segregated assembly formation is induced by AuNP aggregates which act as nucleation sites for growth of the γ -Fe₂O₃ NP domains.



Fingerprints

M. Wood, P. Maynard,* X. Spindler,
C. Lennard, C. Roux — 12272 – 12274



Visualization of Latent Fingermarks Using
an Aptamer-Based Reagent



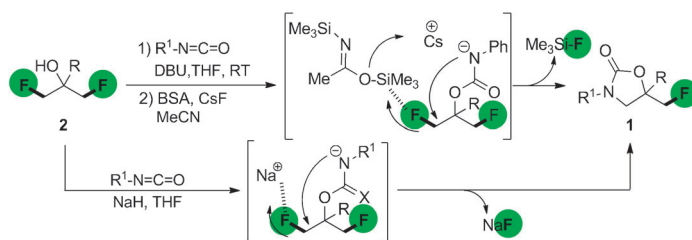
Don't touch! Aptamers selected against lysozyme are transformed into aptamer-based reagents, with which latent fingermarks can be developed with high selectivity and sensitivity. The design of aptamers targeting components of latent fingermarks opens up a new range of detection methods that previously have not been explored.

Organofluorine Chemistry

G. Haufe,* S. Suzuki, H. Yasui, C. Terada,
T. Kitayama, M. Shiro,
N. Shibata* — 12275 – 12279

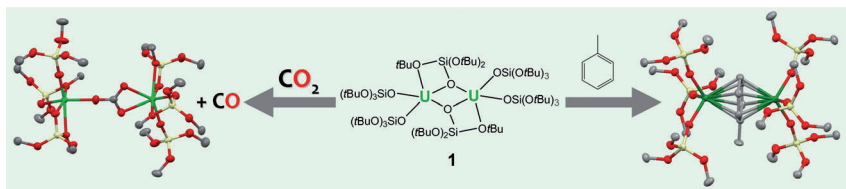


C–F Bond Activation of Unactivated
Aliphatic Fluorides: Synthesis of
Fluoromethyl-3,5-diaryl-2-oxazolidinones
by Desymmetrization of 2-Aryl-1,3-
difluoropropan-2-ols



How to lose fluorine: Biologically relevant oxazolidinones **1** were synthesized through the desymmetrization of unactivated aliphatic difluorides by Si-induced catalytic C–F bond-cleavage using BSA/CsF (BSA = bis(trimethylsilyl)acetamide).

The direct transformation of **2** with isocyanates into **1** by cascade carbamoylation/cyclization, in which cyclization is induced by Na-assisted C–F bond activation, was also achieved.



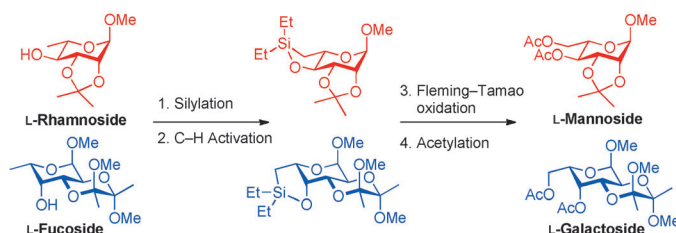
Siloxides can support U! ...in the reduction of small molecules with uranium complexes. The treatment of $[U\{N(SiMe_3)_2\}_3]$ with $HOSi(OtBu)_3$ (3 equiv) yielded a novel homoleptic uranium(III)

siloxide complex **1**, which acted as a two-electron reducing agent toward CS_2 and CO_2 (see scheme). Complex **1** also reduced toluene to afford a diuranium inverted-sandwich complex.

Uranium Siloxides

V. Mougel, C. Camp, J. Pécaut, C. Copéret, L. Maron, C. E. Kefalidis, M. Mazzanti* 12280–12284

Siloxides as Supporting Ligands in Uranium(III)-Mediated Small-Molecule Activation



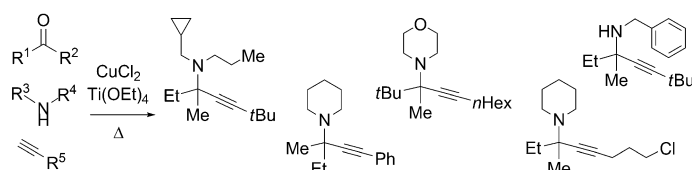
Rare sugars by CH activation: The title compounds have been prepared from the corresponding 6-deoxysugars by an intramolecular C–H activation in high yields. Diethyl silane is attached to the 4-OH

group followed by formation of a Si–C bond; both transformations are catalyzed by iridium in a one-pot fashion. The subsequent Fleming–Tamao oxidation provided the L-sugars.

Sugar Synthesis

T. G. Frihed, M. Heuckendorff, C. M. Pedersen,* M. Bols* 12285–12288

Easy Access to L-Mannosides and L-Galactosides by Using C–H Activation of the Corresponding 6-Deoxysugars



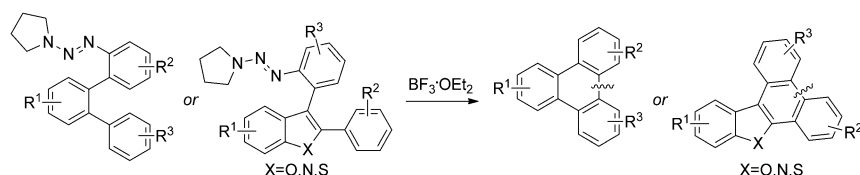
Three-component coupling, with a pair: The combination of Cu^{II} and Ti^{IV} catalyzes the first three-component coupling of unactivated ketones with a diverse range of amines and terminal alkynes. Tetrasubstituted propargylamines are formed

under green, solvent-free conditions (see scheme). This dual metal system overcomes the barrier to ketimine formation and subsequent attack, opening a new path to multicomponent reactions of ketone electrophiles.

Tetrasubstituted Carbon Centers

C. J. Pierce, M. Nguyen, C. H. Larsen* 12289–12292

Copper/Titanium Catalysis Forms Fully Substituted Carbon Centers from the Direct Coupling of Acyclic Ketones, Amines, and Alkynes



Rings, rings, rings: A Friedel–Crafts intramolecular arylation for the synthesis of polycyclic aromatic hydrocarbons from aryl triazenes has been achieved. Poly-

cyclic aromatic compounds consisting of five-, six-, and seven-membered rings can be prepared using this method.

Polycyclic Hydrocarbons

J. Zhou, W. Yang, B. Wang, H. Ren* 12293–12297

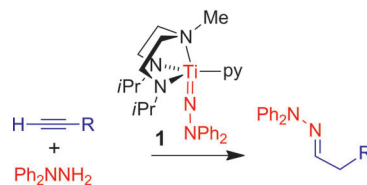
Friedel–Crafts Arylation for the Formation of C_{sp^2} – C_{sp^2} Bonds: A Route to Unsymmetrical and Functionalized Polycyclic Aromatic Hydrocarbons from Aryl Triazenes

Catalytic Intermediates

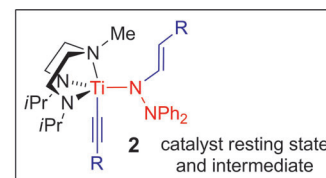
A. D. Schwarz, C. S. Onn,
P. Mountford* 12298 – 12302



A Remarkable Switch from a Diamination to a Hydrohydrazination Catalyst and Observation of an Unprecedented Catalyst Resting State



A small change with a big effect: Reaction of the titanium complex **1** with terminal alkynes gave the unusual acetylide–vinylhydrazide(**1**–) compounds **2** (R = 4-C₆H₄X (X = Me, CF₃, OMe), C₆F₅, SiMe₃) as hydrohydrazination intermediates. In



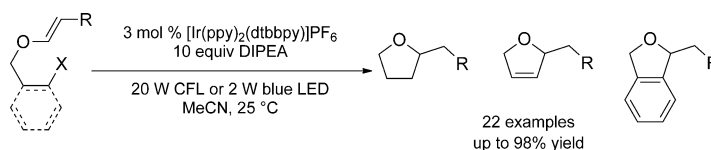
contrast, a complex similar to **1** with bulkier trimethylsilyl substituents in place of the isopropyl groups is known to catalyze the 1,2-diamination of alkynes with hydrazines.

Photocatalysis

H. Kim, C. Lee* 12303 – 12306



Visible-Light-Induced Photocatalytic Reductive Transformations of Organohalides



A photo opportunity: A visible-light-excited iridium catalyst delivers electrons from an amine to an organohalide. The electron transfer then induces reductive scission of the carbon–halogen bond,

generating the corresponding alkyl, alkenyl, and aryl radical that can undergo cyclization and hydrodehalogenation reactions.

DOI: 10.1002/anie.201207322

50 Years Ago ...

Angewandte Chemie International Edition was first published in 1962, the mother journal first in 1888. In this monthly flashback, we feature some of the articles that appeared 50 years ago. This look back can open our eyes, stimulate discussion, or even raise a smile.

A series of Reviews dedicated to Otto Bayer on his 60th birthday reads like a “Who’s Who” of German chemistry at the time. The authors include Hans Meerwein et al., who wrote about ionic hydrogenations and dehydrogenations, Fritz Kröhnke et al., who discussed the synthesis of substituted pyridines by the Michael addition of pyridinium salts, and Siegfried Hünig et al., who outlined the synthesis of azo dyes by oxidative coupling. Otto Bayer founded the field of polyurethane chemistry and was Research Director of Bayer AG, but was not related to the Bayer family that

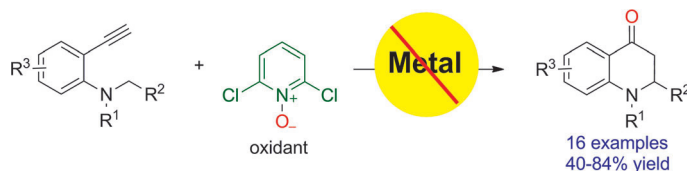
founded the company. He was also on the Editorial Board of *Angewandte Chemie*. His contribution to chemistry is commemorated by the Otto Bayer Award (see *Angew. Chem. Int. Ed.* **2012**, *51*, 6310).

The synthesis of oxazole was described by H. Bredereck and R. Bangert in a Communication. The route involved heating a hydroxyketosuccinic ester with formamide and reaction of the resulting di(alkoxycarbonyl)oxazole in situ to form oxazole. This procedure was reported to be relatively simple com-

pared to that reported by Cornforth 15 years earlier.

G. Manecke and W. Storck described how redox resins comprising cross-linked polymers of 2-vinyl-9,10-anthraquinone and styrene were obtained by thermal copolymerization in dimethyl sulfoxide with divinylbenzene as the cross-linking agent. The resins were pH-stable and had a very low redox potential

[Read more in Issue 12/1962](#)



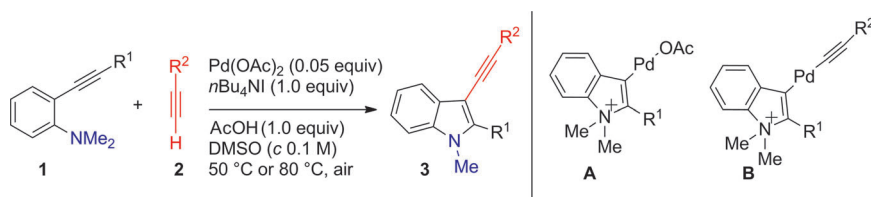
Externally yours: 2,3-Dihydroquinolin-4(1H)-ones are obtained in moderate to good yields (40–84%, see scheme) in a metal-free oxidation/C(sp³)–H functionalization of unactivated aryl alkynes.

2,6-Dichloropyridine-*N*-oxide is used as an external oxidant. In the reaction, a Brønsted acid, not a metal, plays a key role in the triple C–C bond activation.

C–H Activation

D.-F. Chen, Z.-Y. Han, Y.-P. He, J. Yu, L.-Z. Gong* — 12307 – 12310

Metal-Free Oxidation/C(sp³)–H Functionalization of Unactivated Alkynes Using Pyridine-*N*-Oxide as the External Oxidant



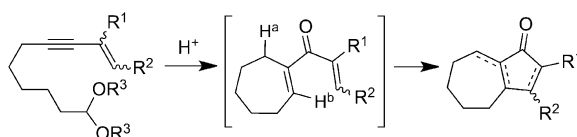
Two nucleophiles, one triple bond: Under aerobic conditions, palladium-catalyzed direct coupling of *o*-alkynylanilines and terminal alkynes took place smoothly to afford the 2,3-disubstituted 3-alkynyl-

indoles **3** in good to excellent yields. The intermediate **A** was characterized and a retro-aminopalladation of **B** was observed for the first time.

Heterocycles

B. Yao, Q. Wang, J. Zhu* — 12311 – 12315

Palladium-Catalyzed Coupling of *ortho*-Alkynylanilines with Terminal Alkynes Under Aerobic Conditions: Efficient Synthesis of 2,3-Disubstituted 3-Alkynylindoles



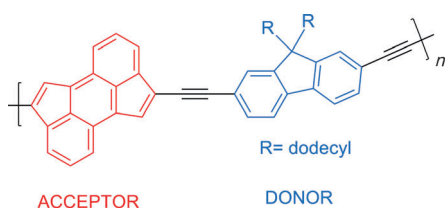
Ring the changes: Enyne acetals were easily converted into hydroazulene skeletons by a new and efficient metal-free route involving a Brønsted acid promoted carbocyclization and a subsequent ste-

reospecific Nazarov cyclization (see scheme). The versatility of this transformation also allowed assembly of interesting heteroaromatic tricyclic systems.

Domino Reactions

L. Escalante, C. González-Rodríguez, J. A. Varela, C. Saá* — 12316 – 12320

Tandem Brønsted Acid Promoted and Nazarov Carbocyclizations of Enyne Acetals to Hydroazulenones



The Sonogashira cross-coupling polymerization of a dibrominated cyclopenta[hi]aceanthrylene and a diethynylfluorene derivative produced a donor–acceptor copolymer composed solely of cyclopenta-fused polycyclic aromatic hydrocarbons.

The resulting polymer displays low band gaps (<1.5 eV), dual absorption bands, and electron-accepting behavior as demonstrated through fluorescence quenching of poly(3-hexylthiophene).



Polycyclic Aromatic Hydrocarbons

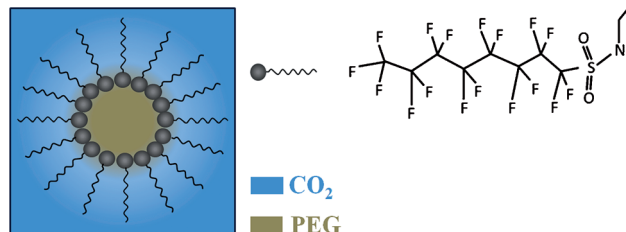
J. L. Jellison, C.-H. Lee, X. Zhu, J. D. Wood, K. N. Plunkett* — 12321 – 12324

Electron Acceptors Based on an All-Carbon Donor–Acceptor Copolymer



Micelles

Z. Xue, J. Zhang,* L. Peng, J. Li, T. Mu,
B. Han,* G. Yang — 12325 – 12329



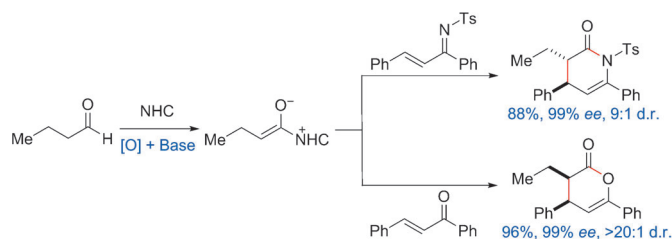
Nanosized Poly(ethylene glycol) Domains
within Reverse Micelles Formed in CO₂

Tiny reactors: By using a surfactant (see picture), domains of poly(ethylene glycol) (PEG) at the nanometer scale are dispersed within reverse micelles formed in supercritical CO₂. The size and properties

of the PEG domains are tuneable by changing the PEG content. Furthermore, the PEG domains have been used as nanoreactors to synthesize highly dispersed gold nanocrystals.

Heterocycles

X. Zhao, K. E. Ruhl,
T. Rovis* — 12330 – 12333



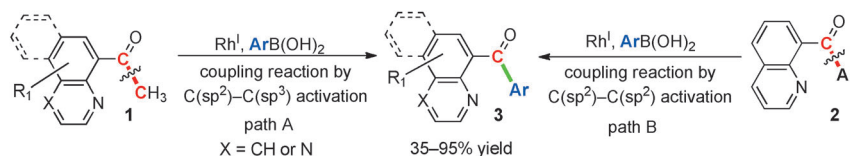
N-Heterocyclic-Carbene-Catalyzed
Asymmetric Oxidative Hetero-Diels–Alder
Reactions with Simple Aliphatic
Aldehydes

An efficient enantioselective approach to form *trans* lactams and *cis* lactones in up to 98 % yield with greater than 99 % *ee*, and greater than 20:1 d.r. using simple aliphatic aldehydes has been developed.

The process involves a new pathway to generate enolate intermediates from aliphatic aldehydes by oxidation and deprotonation. NHC = N-heterocyclic carbene, Ts = 4-toluenesulfonyl.

C–C Activation

J.-J. Wang, W. Chen, S. Zuo, L. Liu,
X. Zhang, J.-H. Wang* — 12334 – 12338



Direct Exchange of a Ketone Methyl or Aryl
Group to Another Aryl Group through
C–C Bond Activation Assisted by
Rhodium Chelation

Swapped: Commercially available quinoline derivatives (**1** or **2**, see scheme) were reacted with arylboronic acids in the presence of a Rh complex to give aryl-(quinolin-8-yl)methanone products **3** in

medium to good yields. A mechanism that involves the in situ oxidation of Rh^I to Rh^{III} by O₂ in the presence of CuI was proposed.

Asymmetric Catalysis

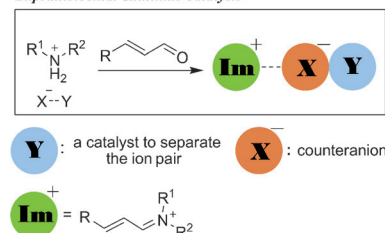
Y. Wang, T.-Y. Yu, H.-B. Zhang, Y.-C. Luo,
P.-F. Xu* — 12339 – 12342



Hydrogen-Bond-Mediated
Supramolecular Iminium Ion Catalysis

Mod squad: Multiple small molecules appear to spontaneously self-assemble to form supramolecular amine catalysts that have high reactivity, good efficiency, and enhanced turnover numbers. These modular organocatalysts should be applicable to many iminium as well as hydrogen-bond catalytic reactions and provide new insights into asymmetric catalysis.

Supramolecular Iminium Catalysis





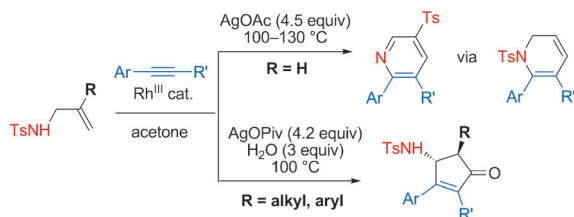
General solution: An efficient rhodium-catalyzed dual C–H bond activation and cyclization of *N*-methoxybenzamides **1** with aryl boronic acids **2** (see scheme; Cp* = Me₅C₅) provides a straightforward and general approach to the phenanthri-

dinone structure, which occurs widely in natural products and drugs. Highly regio-selective C–C and C–N bond formation under mild conditions afforded a wide range of substituted phenanthridinones **3**.

C–H Activation

J. Karthikeyan, R. Haridharan,
C.-H. Cheng* 12343 – 12347

Rhodium(III)-Catalyzed Oxidative C–H Coupling of *N*-Methoxybenzamides with Aryl Boronic Acids: One-Pot Synthesis of Phenanthridinones



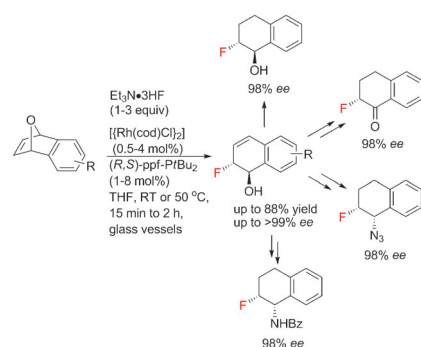
Olefinic C–H activation of *N*-allyl sulfonamides in the presence of [{RhCp*Cl₂]₂} (Cp* = Me₅C₅) enabled their oxidative coupling with alkynes to generate 1,2-dihydropyridines, pyridines, and cyclo-

pentenones (see scheme; Ts = *p*-toluene-sulfonyl). The type of highly substituted product formed was controlled by the substitution of the allyl group and the reaction conditions.

C–H Activation

D. Wang, F. Wang, G. Song,
X. Li* 12348 – 12352

Diverse Reactivity in a Rhodium(III)-Catalyzed Oxidative Coupling of *N*-Allyl Arenesulfonamides with Alkynes

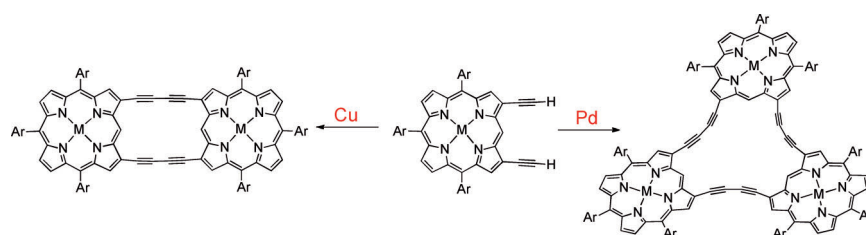


Done with 'F'lair: Enantioselective fluorination was achieved by Rh^I-catalyzed ring opening of oxabicyclic alkenes using Et₃N·3 HF. The chiral fluorinated scaffolds were obtained under mild reaction conditions in standard glass vessels, and served as useful building blocks for various chiral fluorinated targets. cod = cycloocta-1,5-diene, ppf = phenylphosphinoferrocene, THF = tetrahydrofuran.

Asymmetric Synthesis

J. Zhu, G. C. Tsui,
M. Lautens* 12353 – 12356

Rhodium-Catalyzed Enantioselective Nucleophilic Fluorination: Ring Opening of Oxabicyclic Alkenes



And palladium makes three: In contrast to the formation of cyclic dimers in the Cu-mediated reaction, Pd-catalyzed oxidative coupling of 2,18-diethynylporphyrins preferentially produced cyclic trimers (see

scheme). A porphyrin hexamer with a doubly 1,3-butadiyne-bridged conjugated trimeric core and directly *meso*-appended peripheral porphyrin substituents was also synthesized.

Porphyrin Macrocycles

S. Tokuji, H. Yorimitsu,*
A. Osuka* 12357 – 12361

Preferential Formation of Cyclic Trimers by Palladium-Catalyzed Oxidative Coupling Reactions of 2,18-Diethynylporphyrins

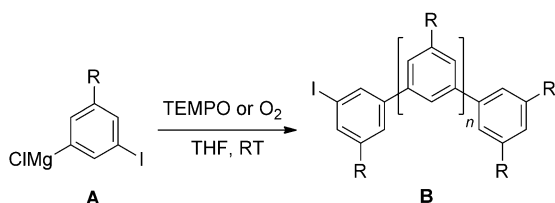
Inside Cover

Polymer Synthesis

S. Murarka, A. Studer* — 12362 – 12366



Radical/Anionic $S_{RN}1$ -Type Polymerization for Preparation of Oligoarenes



Radicals and anions: The TEMPO-mediated oxidation of magnesiated iodoarenes **A** provides highly regioregular poly(*m*-phenylenes) by strictly alternating anionic/radical cross-over chain-growth polymerization. Poly(*m*-phenylenes) with mean molecular weight (M_n) of up to

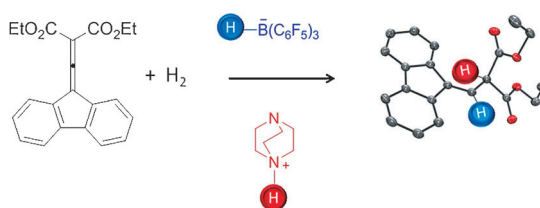
20 000 g mol^{-1} can be prepared under mild conditions by this method. The approach is a new concept for transition-metal-free polyarene synthesis. TEMPO = 2,2,6,6-tetramethylpiperidine-*N*-oxyl radical.

Frustrated Lewis Pairs

B. Inés, D. Palomas, S. Holle, S. Steinberg, J. A. Nicasio, M. Alcarazo* — 12367 – 12369



Metal-Free Hydrogenation of Electron-Poor Allenes and Alkenes



The poorer, the better: A metal-free catalytic procedure for the reduction of electron-poor allenes and alkenes has been developed. The method employs a frus-

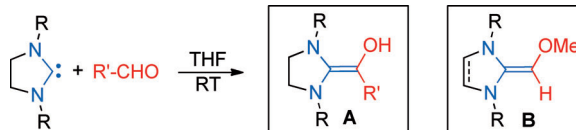
trated Lewis pair based catalyst. 1,4-Diazabicyclo[2.2.2]octane (DABCO)/ $\text{B}(\text{C}_6\text{F}_5)_3$ was shown to be the best combination in optimization studies.

Organocatalysis

A. Berkessel,* S. Elfert, V. R. Yatham, J.-M. Neudörfl, N. E. Schlörer, J. H. Teles — 12370 – 12374



Umpolung by N-Heterocyclic Carbenes: Generation and Reactivity of the Elusive 2,2-Diamino Enols (Breslow Intermediates)



54 years later: Saturated imidazolidin-2-ylidenes react with aldehydes to smoothly produce the elusive 2,2-diamino enols **A** ("Breslow intermediates", first postulated in 1958) of carbene-catalyzed umpolung

reactions. The 2,2-diamino enols **A** react with additional aldehyde in a cross-benzoin reaction. The methylated Breslow intermediates **B** are accessible by deprotonation of methoxymethyl azolium salts.

Front 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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