Editorial


Bruce C. Gates


Tobin J. Marks

"… We assert that catalysis should be viewed as a coherent scientific field that requires defragmentation to maximize research progress in all catalytic fields and to attract the best young minds …"
Read more in the Editorial by Bruce C. Gates and Tobin J. Marks.

Service

Author Profile

"I like refereeing because I hope that our publications will also be refereed with the same amount of interest. Without this mutual willingness, scientific publication would be impossible.
The most significant scientific advance of the last 100 years has been quantum theory and the theory of relativity in terms of furthering knowledge, and computers and the internet in terms of changing our lives …"
This and more about Holger Braunschweig can be found on page 11670.

News


E. Zass


P. Knochel

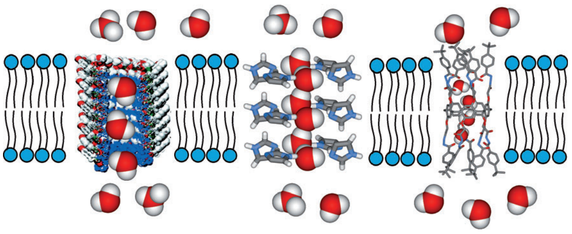

T. Akiyama


M. Terada

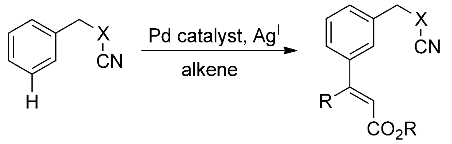

M. T. Reetz

Books

Highlights



Going through the channels: Synthetic scaffolds mimicking natural protein functions have been developed that allow water/proton or only water translocation pathways in bilayer membranes (see picture). The ion-exclusion behaviors of the synthetic systems are based on hydrophobic or dimensional steric effects, while hydrodynamic effects appear to be less important.



Give a direction: A rationally designed, removable *meta*-directing group enables the selective, remote functionalization of aromatic substrates (see scheme). The generality of the concept was shown with alkenylation reactions of hydrocinnamic acid derivatives, the selectivities of which were similar to the ones described for benzyl derivatives.

Essays

Modus operandi: There is increased interest and activity in drug discovery at universities and other non-profit organizations. The essay addresses challenges associated with progress in this area. Lead optimization and preclinical testing are identified as key bottlenecks.

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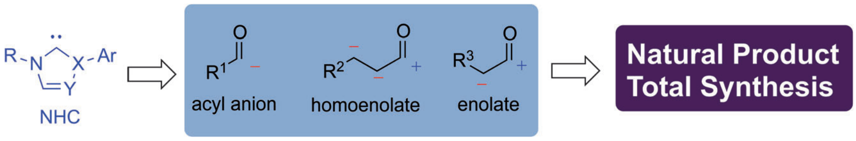
Minireviews

Natural Product Synthesis

J. Izquierdo, G. E. Hutson, D. T. Cohen,
K. A. Scheidt* ______ **11686 – 11698**

A Continuum of Progress: Applications of N-Hetereocyclic Carbene Catalysis in Total Synthesis



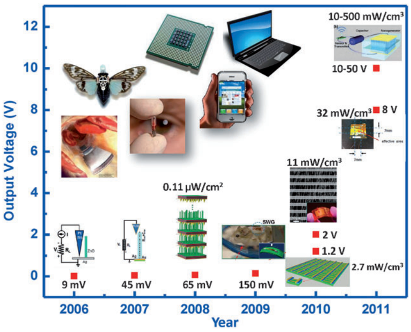
A modern touch: The field of N-heterocyclic carbene catalysis has grown rapidly over the last decade. This expansion has generated a wide variety of new asymmetric transformations including benzoin and Stetter reactions as well as the more modern homoenolate equivalent and aroylation coupling reactions, which have been used successfully in total syntheses (see scheme).

Reviews

Self-Powered Nanosystems

Z. L. Wang,* W. Wu ______ **11700 – 11721**

Nanotechnology-Enabled Energy Harvesting for Self-Powered Micro-/ Nanosystems



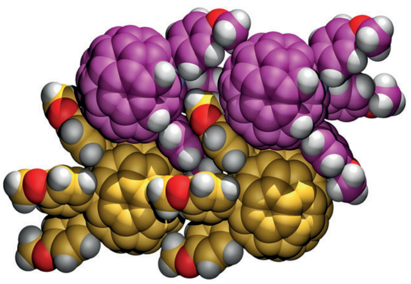
A bumper harvest, albeit on a small scale, is required for micro-/nanosystems (MNSs) to function reliably without an external power source. MNSs that can harvest energy from the environment in which they are used have wide-ranging potential applications in health, environmental, and infrastructure monitoring, as well as networking and defense technologies. This Review explores possibilities for energy harvesting to meet the future demand for MNSs.

Communications

Fullerene Chemistry

R. Neubauer, F. W. Heinemann,
F. Hampel, Y. Rubin,*
A. Hirsch* ______ **11722 – 11726**

Pentaarylazafullerenes and their Triaryldihydro and Tetraarylmonohydro Precursors



Give me five! The title compounds were isolated from the acid-catalyzed reaction of a $C_{59}N$ precursor with electron-rich aromatic compounds. Single-crystal X-ray diffraction on two compounds reveals characteristic packing motifs; the triaryldihydro derivative has a pseudo-stacked arrangement (C violet/yellow, N blue, O red, H white).

Frontispiece

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Susumu Kitagawa


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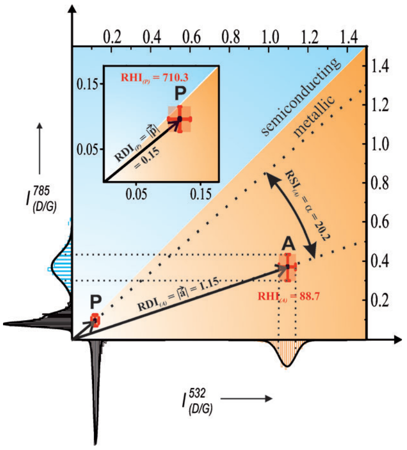
A powerful method based on statistical Raman analysis has been developed for the classification of the degree of functionalization, electronic selectivity, and sample homogeneity of functionalized carbon nanotubes (CNTs). The outcome of addition reactions to CNTs can easily be analyzed and quantitated by the determination of three characteristic Raman indices: the Raman defect (RDI), homogeneity (RHI), and selectivity index (RSI).



Carbon Nanotubes

F. Hof, S. Bosch, J. M. Englert, F. Hauke, A. Hirsch* —— **11727 – 11730**

Statistical Raman Spectroscopy: An Method for the Characterization of Covalently Functionalized Single-Walled Carbon Nanotubes

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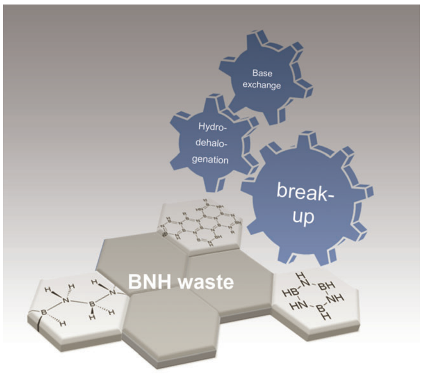
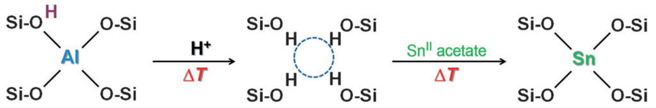


Recycling: A self-contained procedure for the recycling of BNH-waste, based on the three major steps: polymer break-up, amine supported catalytic hydrodehalogenation of boron halogens, and the base exchange in borane amine adducts, is developed (see picture). Beyond the original task of recycling spent ammonia borane, the process provides a new means to produce borohydride species efficiently, by the direct use of molecular hydrogen.

Hydrogen Storage

C. Reller, F. O. R. L. Mertens* —— **11731 – 11735**

A Self-Contained Regeneration Scheme for Spent Ammonia Borane Based on the Catalytic Hydrodechlorination of BCl_3



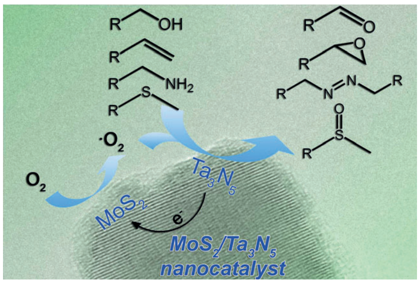
Tin goes in: The solid Lewis acid Sn-zeolite β is obtained in a simple and scalable procedure (see scheme). A high metal content can be obtained, without undesirable side-effects. The space-time-yields of the resulting catalysis are over one order-of-magnitude larger than those of the state-of-the-art materials for the Baeyer–Villiger oxidation of cyclohexanone and the synthesis of ethyl lactate from the triose dihydroxyacetone.

Zeolites

C. Hammond, S. Conrad, I. Hermans* —— **11736 – 11739**

Simple and Scalable Preparation of Highly Active Lewis Acidic Sn-β

Back Cover



Learning from nature: The development of an MoS_2/Ta_3N_5 nanocomposite as a catalyst for selective aerobic oxidation by O_2 activation was inspired by the nitrogenase enzymes in nature. The superior performance of this biomimetic catalyst, which shows potential for the selective oxidation of multifunctional substrates (see picture), results from the integration of Ta_3N_5 and MoS_2 at the nanoscale and the synergistic enhancement of their activity.

Functional Nanocomposites

Q. S. Gao,* C. Giordano, M. Antonietti —— **11740 – 11744**

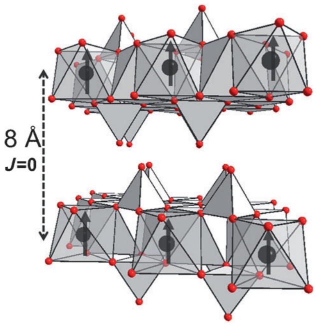
Biomimetic Oxygen Activation by MoS_2/Ta_3N_5 Nanocomposites for Selective Aerobic Oxidation

Magnetic Materials

H. Kabbour, R. David, A. Pautrat,
H.-J. Koo, M.-H. Whangbo, G. André,
O. Mentré* ______ 11745 – 11749

A Genuine Two-Dimensional Ising Ferromagnet with Magnetically Driven Re-entrant Transition

$BaFe_2(PO_4)_2$ consists of honeycomb layers containing high-spin d^6 Fe^{2+} ions. It is the first genuine two-dimensional oxide Ising ferromagnet (FM) with uniaxial magnetism parallel to the crystallographic threefold axis. $BaFe_2(PO_4)_2$ undergoes a re-entrant structural transition between 170 K and its FM critical temperature (65.5 K) owing to competition between the uniaxial magnetism and Jahn–Teller instability.

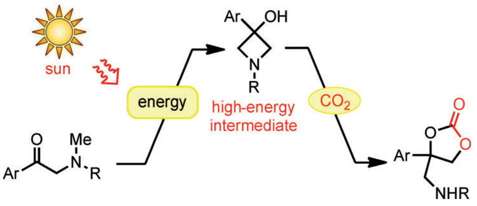


Solar Energy Utilization

N. Ishida, Y. Shimamoto,
M. Murakami* ______ 11750 – 11752

Solar-Driven Incorporation of Carbon Dioxide into α-Amino Ketones

Front Cover

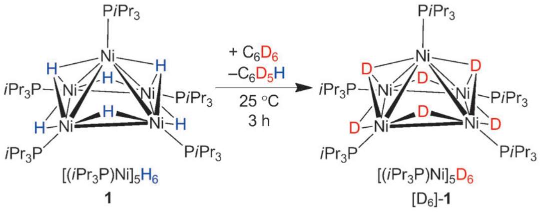


Power of the sun: Carbon dioxide was incorporated into α-amino ketones through a consecutive process consisting of a solar-energy-harvesting photocyclization reaction and a nucleophilic CO_2 incorporation reaction. The single-flask operation produced amino-substituted cyclic carbonates, thereby presenting a simple model of the chemical utilization of solar energy for CO_2 incorporation. R = sulfonyl group.

Cluster Compounds

R. Beck, M. Shoshani,
S. A. Johnson* ______ 11753 – 11756

Catalytic Hydrogen/Deuterium Exchange of Unactivated Carbon–Hydrogen Bonds by a Pentanuclear Electron-Deficient Nickel Hydride Cluster

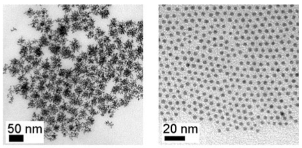


Exchangeable: The cluster $[(i\mathrm{Pr}_3\mathrm{P})\mathrm{Ni}]_5\mathrm{H}_6$ (**1**; see picture) was prepared by the addition of hydrogen gas to the dinuclear dinitrogen complex $[(i\mathrm{Pr}_3\mathrm{P})_2\mathrm{Ni}]_2(\mu\text{-}\mathrm{N}_2)$. This unprecedented first-row transition-metal cluster is electron deficient and highly reactive. Complex **1** undergoes hydrogen/deuterium exchange in deuterated benzene at room-temperature with a half-life of 27 minutes.

Metal Nanodendrites

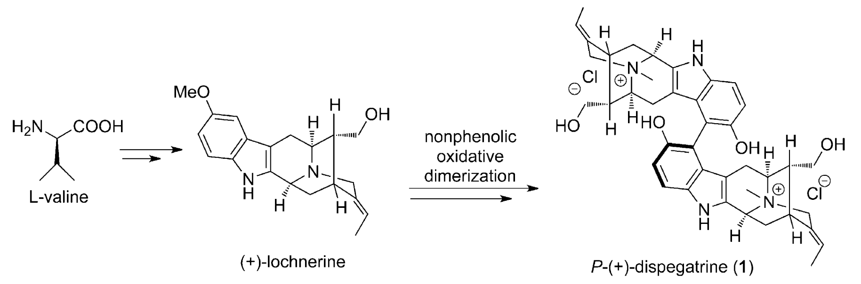
N. Ortiz, S. E. Skrabalak* 11757 – 11761

Manipulating Local Ligand Environments for the Controlled Nucleation of Metal Nanoparticles and their Assembly into Nanodendrites



nanodendrites nanoparticles

Branching out: A simple two-component system comprised of a Pd precursor and oleylamine has shown that both the rate of nanoparticle nucleation and growth can be controlled by manipulating the local ligand environment, thus allowing the facile selection of either Pd nanodendrites or monodisperse Pd nanoparticles (see TEM images). This ligand-controlled approach connects fundamental principles of coordination chemistry to nanostructure design.



All five: The first total synthesis of the C_2-symmetric indole alkaloid **1** involved a late-stage thallium(III) acetate-mediated intermolecular oxidative coupling to construct the C9–C9′ bond with complete regio- and stereocontrol. The formation of a single atropodiastereomer in this critical step arises from internal asymmetric induction. The first total synthesis of four other monomeric *sarpagine* indole alkaloids is also described.

Natural Product Synthesis

C. R. Edwankar, R. V. Edwankar,
J. R. Deschamps,
J. M. Cook* ———— **11762 – 11765**

Nature-Inspired Stereospecific Total Synthesis of *P*-(+)-Dispegatrine and Four Other Monomeric *Sarpagine* Indole Alkaloids

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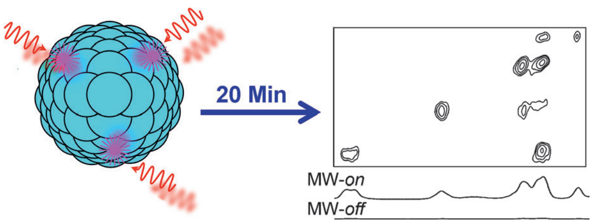

Ultra-fast: Substantial solid-state NMR sensitivity can be achieved using dynamic nuclear polarization and matrix-free sample preparation (that is, absence of solvent and cryoprotectant). This method avoids line-broadening, maximizes sample filling factor, and allows natural-abundance 2D ^{13}C–^{13}C dipolar correlation experiments to be carried out in tens of minutes. MW = microwaves.

NMR Spectroscopy

H. Takahashi, D. Lee, L. Dubois,
M. Bardet, S. Hediger,
G. De Paëpe* ———— **11766 – 11769**

Rapid Natural-Abundance 2D ^{13}C–^{13}C Correlation Spectroscopy Using Dynamic Nuclear Polarization Enhanced Solid-State NMR and Matrix-Free Sample Preparation

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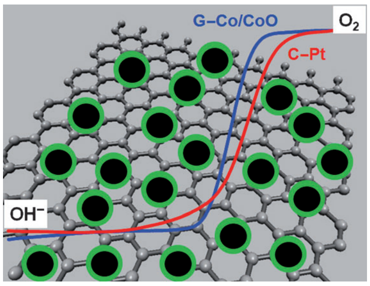

Good support: A solution-phase self-assembly approach leads to Co/CoO core/shell nanoparticles deposited on graphene (G–Co/CoO NPs). Their catalytic activity for the oxygen reduction reaction in O_2-saturated KOH solution depends on the thickness of the CoO shell (green in picture). The optimized G–Co/CoO NPs have a comparative activity and better stability than the commercial Pt NP catalyst supported on carbon (C–Pt).

Heterogeneous Catalysis

VIP

S. Guo, S. Zhang, L. Wu,
S. Sun* ———— **11770 – 11773**

Co/CoO Nanoparticles Assembled on Graphene for Electrochemical Reduction of Oxygen

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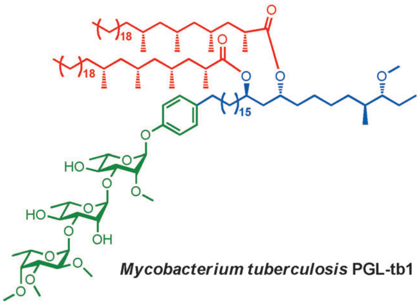
Complex: The synthesis of the glycolipid PGL-tb1 present in the outer membrane of hypervirulent strains of *Mycobacterium tuberculosis* has been accomplished for the first time by using a highly convergent strategy featuring a Sonogashira coupling to unite a phenolic trisaccharide with the phthiocerol. Efficient asymmetric Cu-catalyzed 1,4-additions to unsaturated thioesters and cyclic enones have been employed to introduce the methyl groups.



Virulence Factors

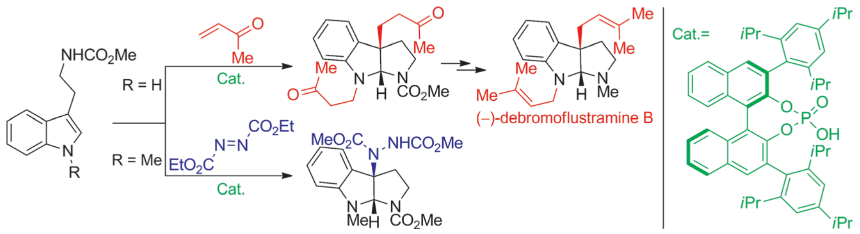
S. Barroso, R. Castelli, M. P. Baggelaar,
D. Geerdink, B. ter Horst, E. Casas-Arce,
H. S. Overkleeft, G. A. van der Marel,
J. D. C. Codée,*
A. J. Minnaard* ———— **11774 – 11777**

Total Synthesis of the Triglycosyl Phenolic Glycolipid PGL-tb1 from *Mycobacterium tuberculosis*

Asymmetric Catalysis

Z. Zhang, J. C. Antilla* ___ **11778 – 11782**

Enantioselective Construction of Pyrroloindolines Catalyzed by Chiral Phosphoric Acids: Total Synthesis of (−)-Debromoflustramine B

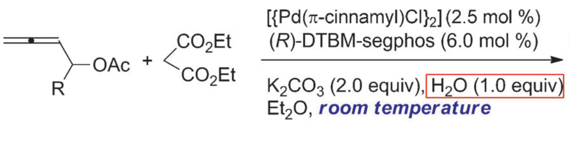


Acids in command: The asymmetric formation of pyrroloindolines with adjacent quaternary and tertiary carbon centers has been achieved through catalysis by a chiral phosphoric acid. Starting from readily available tryptamine, both Michael products and amination products were obtained in high yields and enantioselectivities. The significance of this study was further demonstrated by the total synthesis of (−)-debromoflustramine B.

Asymmetric Catalysis

Q. Li, C. Fu, S. Ma* ___ **11783 – 11786**

Catalytic Asymmetric Allenylation of Malonates with the Generation of Central Chirality



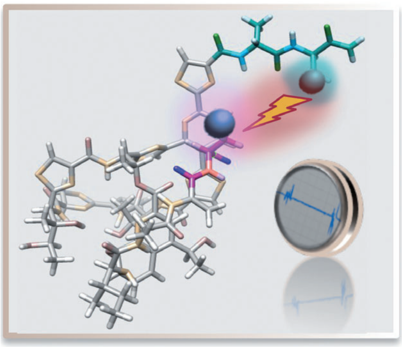
Water plays an important role in a palladium-catalyzed allenylation of diethyl malonate with 2,3-allenyl acetates to yield centrally chiral allenyl malonates bearing synthetically useful functional groups (see scheme). The products were formed with 92–96 % *ee* in the presence of a bulky, electron-rich biphenyl ligand at room temperature.

Hyperpolarization

F. Gruppi, X. Xu, B. Zhang, J. A. Tang, A. Jerschow,* J. W. Canary* ___ **11787 – 11790**

Peptide Hydrogenation and Labeling with Parahydrogen

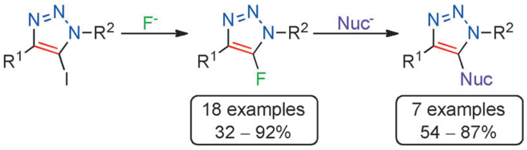
Site-specific spin polarization labeling of a peptide was conducted by homogeneous hydrogenation with parahydrogen. Surprisingly, polarization transfer to a remote alanine residue was observed. The diastereoselectivity of the hydrogenation reaction was determined, and these results show that parahydrogen can be used to enhance signals and elucidate the hydrogenation processes of dehydropeptide units in complex molecules.



Heterocycles

B. T. Worrell, J. E. Hein, V. V. Fokin* ___ **11791 – 11794**

Halogen Exchange (Halex) Reaction of 5-Iodo-1,2,3-triazoles: Synthesis and Applications of 5-Fluorotriazoles

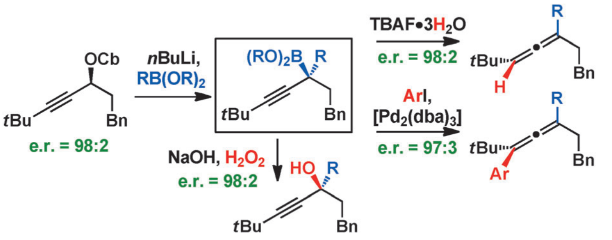


A good exchange: 5-Iodo-1,2,3-triazoles undergo facile substitution reactions with fluoride salts, thus providing ready access to 5-fluorotriazoles (see scheme). The latter can be further elaborated with various nucleophiles to furnish fully substituted 1,2,3-triazole compounds.

Enantioselective Synthesis

B. M. Partridge, L. Chausset-Boissarie,
M. Burns, A. P. Pulis,
V. K. Aggarwal* ________ **11795 – 11799**

Enantioselective Synthesis and Cross-Coupling of Tertiary Propargylic Boronic Esters Using Lithiation–Borylation of Propargylic Carbamates

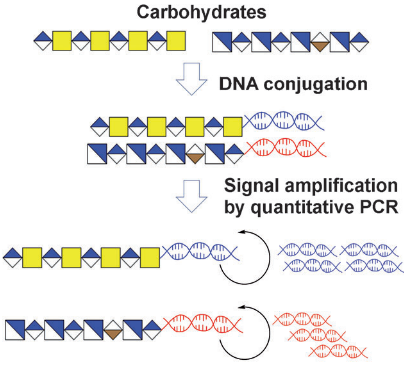


Lithiation–borylation of propargylic carbamates leads to tertiary propargylic boronic esters in very high e.r., provided that ethylene glycol boronic esters are used. These versatile intermediates undergo a range of highly stereoselective transformations, including protodeboronation to give tertiary allenes and Suzuki–Miyaura cross-couplings of tertiary boron species leading to tetrasubstituted allenes with high enantiospecificity.

Carbohydrate Detection

S. J. Kwon, K. B. Lee, K. Solakyildirim,
S. Masuko, M. Ly, F. Zhang, L. Li,
J. S. Dordick,
R. J. Linhardt* ________ **11800 – 11804**

Signal Amplification by Glyco-qPCR for Ultrasensitive Detection of Carbohydrates: Applications in Glycobiology

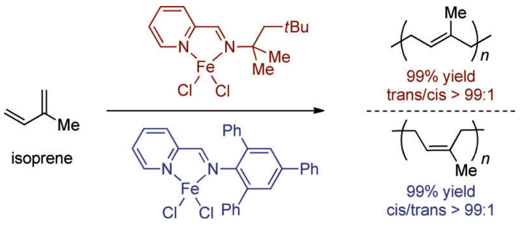


Tiny amounts of carbohydrates (ca. 1 zmol) can be detected quantitatively by a real-time method based on the conjugation of carbohydrates with DNA markers (see picture). The proposed method (glyco-qPCR) provides uniform, ultrasensitive detection of carbohydrates, which can be applied to glycobiology, as well as carbohydrate-based drug discovery.

Iron Catalysis

J. Raynaud, J. Y. Wu,
T. Ritter* ________ **11805 – 11808**

Iron-Catalyzed Polymerization of Isoprene and Other 1,3-Dienes

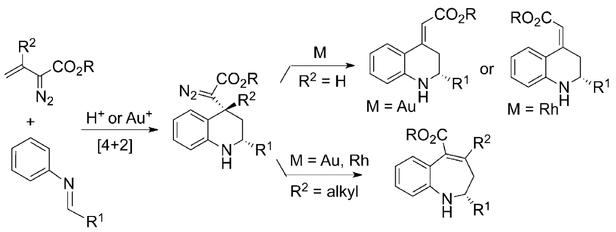


Ironing rubber: Iminopyridine-based $FeCl_2$ catalysts catalyze the polymerization of 1,3-dienes and provide stereoselective access to elastomers such as polyisoprenes, polymyrcenes, and polyfarnesenes. The choice of ligand determines the double-bond geometry in the polymer repeating unit, which can be varied from *trans*/*cis* > 99:1 to < 1:99 (see scheme).

Synthetic Methods

A. M. Jadhav, V. V. Pagar,
R.-S. Liu* ________ **11809 – 11813**

Development of a Povarov Reaction/Carbene Generation Sequence for Alkenyldiazocarbonyl Compounds

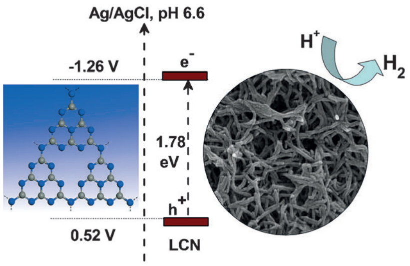


Rings aplenty: A HOTf-catalyzed (Tf = trifluoromethanesulfonyl) Povarov reaction of alkenyldiazo species has been developed and delivers diazo-containing cycloadducts stereoselectively (see scheme). The resulting cycloadducts provide access to six- and seven-membered azacycles through the generation of metal carbenes as well as the functionalization of diazo group.

Solution Processing

Y. Cui, Z. Ding, X. Fu,
X. Wang* ________ **11814–11818**

Construction of Conjugated Carbon Nitride Nanoarchitectures in Solution at Low Temperatures for Photoredox Catalysis

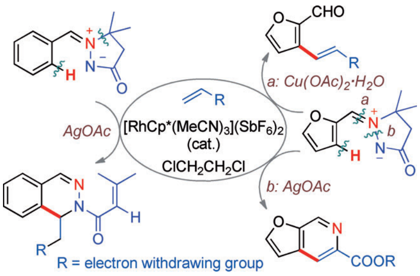


Hot: Conjugated carbon nitride polymers (LCNs) are synthesized by hot-fluid annealing in one pot. The LCNs possess a narrow band gap, have a complex nanostructure, and show enhanced photochemical performances. The described synthesis approach will allow the rational creation of a wide variety of polymeric carbon nitride semiconductors at low temperature in solutions, with control of structural complexity, electronic structure, and surface functionality.

C–H Activation

W. Zhen, F. Wang, M. Zhao, Z. Du,
X. Li* ________ **11819–11823**

Rhodium(III)-Catalyzed Oxidative C–H Functionalization of Azomethine Ylides

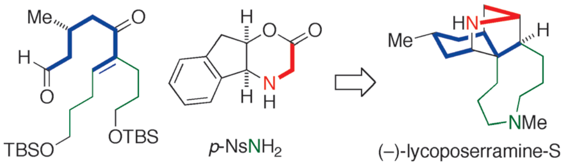


Put it on a ring: A rhodium(III) complex can catalyze the oxidative coupling of azomethine imines with olefins, leading to the synthesis of 1,2-dihydrophthalazines, olefinated aldehydes, or fused pyridines, depending on the conditions used.

Natural Product Synthesis

N. Shimada, Y. Abe, S. Yokoshima,
T. Fukuyama* ________ **11824–11826**

Total Synthesis of (−)-Lycoposerramine-S

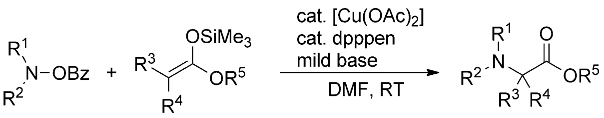


To the core: The first total synthesis of (−)-lycoposerramine-S has been accomplished in 14 steps. The synthesis features the facile construction of the tetracyclic core through an intramolecular 1,3-dipolar cycloaddition of an azomethine ylide, with unexpected stereoselectivity, an 5-*exo-trig* radical cyclization, and an alkylation of *p*-nosyl (Ns) amide. TBS = *tert*-butyldimethylsilyl.

Synthetic Methods

N. Matsuda, K. Hirano,* T. Satoh,
M. Miura* ________ **11827–11831**

Copper-Catalyzed Amination of Ketene Silyl Acetals with Hydroxylamines: Electrophilic Amination Approach to α-Amino Acids



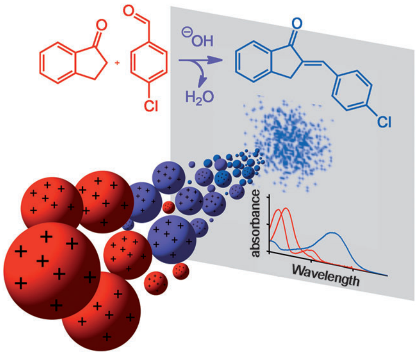
Role reversal: The title reaction has been developed to deliver α-amino acids under very mild reaction conditions (see scheme; dpppen = 1,5-bis(diphenylphosphino)pentane). The catalysis provides a new C–N bond-forming approach for the synthesis of α-amino acids by using an umpolung, electrophilic amination strategy.

Synthesis using a Mass Spectrometer

T. Müller,* A. Badu-Tawiah,
R. G. Cooks* ____________ **11832 – 11835**

Accelerated Carbon–Carbon Bond-Forming Reactions in Preparative Electrospray

Inside Back Cover



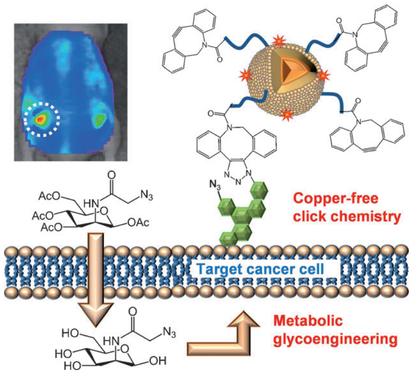
From analysis towards synthesis: Charged microdroplets act as microreaction vessels, extending the use of electrospray mass spectrometry from chemical analysis to synthesis. Application of this unique reaction conditions allows microscale carbon–carbon bond forming reactions to be performed rapidly and in high yields (see picture).

Nanoparticles

H. Koo, S. Lee, J. H. Na, S. H. Kim,
S. K. Hahn, K. Choi, I. C. Kwon, S. Y. Jeong,
K. Kim* ______________ **11836 – 11840**

Bioorthogonal Copper-Free Click Chemistry In Vivo for Tumor-Targeted Delivery of Nanoparticles

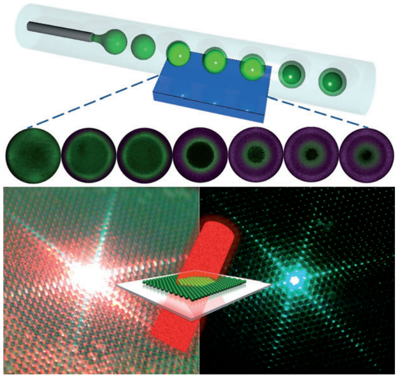
Right on target: An in vivo tumor-targeting strategy using nanoparticles has been developed. An unnatural sialic acid (green, see scheme) with azide groups is artificially generated on the target site by metabolic glycoengineering. These groups then effectively enhance the accumulation of nanoparticles in the target tumor site by an in vivo bioorthogonal copper-free click reaction.



Photochemistry

J.-H. Kang,
E. Reichmanis* ____________ **11841 – 11844**

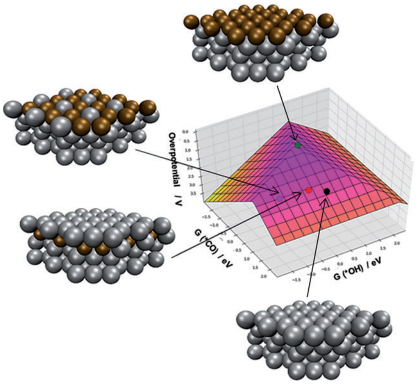
Low-Threshold Photon Upconversion Capsules Obtained by Photoinduced Interfacial Polymerization



Nonlinear optics: Photoinduced interfacial polymerization within a microfluidic channel is shown to be an effective method to prepare microcapsules that provide for photon upconversion by triplet–triplet annihilation (see picture). In this approach, an elastomeric shell formed on the inner surface of the microcapsules served as an efficient protective shield, whereas a liquid core promoted the required energy transfer for the upconverted luminescence.

Electrocatalysis

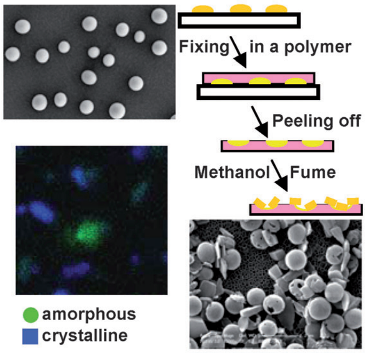
Inside Cover



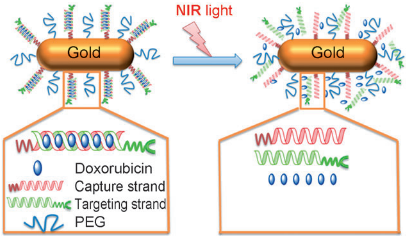
I could never be without Cu: An active site has been designed for the catalysis of CO electroxidation. This was achieved by incorporating submonolayer amounts of Cu (orange spheres) into a single crystal of Pt (gray spheres). The electrochemical reactivity of this surface was highly sensitive to the exact position of Cu (see scheme).

Amorphous/Crystalline Materials

Growth in a confined environment: A protocol for the amorphous-to-crystalline transformation (ACT) of nanoparticles has been developed, the critical step being the partial confinement of the particles by fixing in a polymer thin film and solvent vapor fuming. The ACT of a diaminodicyanoquinodimethane-based nanoparticle is accompanied by substantial fluorescence enhancement and switching of the emission color.

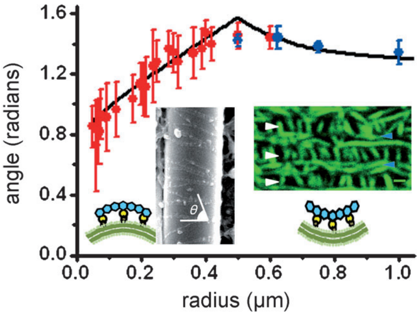


Drug Delivery

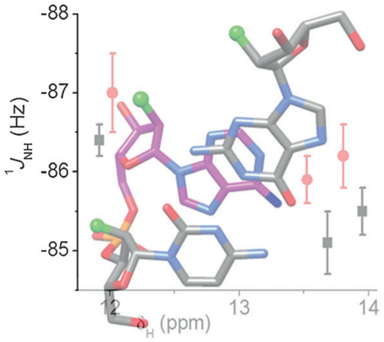


Targeted cancer therapy: Inspired by the ability of DNA hybridization, a targeted near-infrared (NIR) light-responsive delivery system has been developed through simple DNA self-assembly (see picture; PEG = polyethylene glycol). This DNA-based platform shows the ability of releasing therapeutics upon near-infrared irradiation, and remarkable targeted thermo- and chemotherapeutic efficacy in vitro and in vivo.

Synthetic Biology



Bending over backward: Despite their small size, bacteria display highly organized cytoskeletal structures. Using microfabricated supports for model membranes, mechanical features of FtsZ (blue hexagons) filaments, a key component of bacterial cell division, can be addressed. Studying the curvature of an FtsZ filament into a groove or around a capillary (see picture) helps to understand its mechanics.

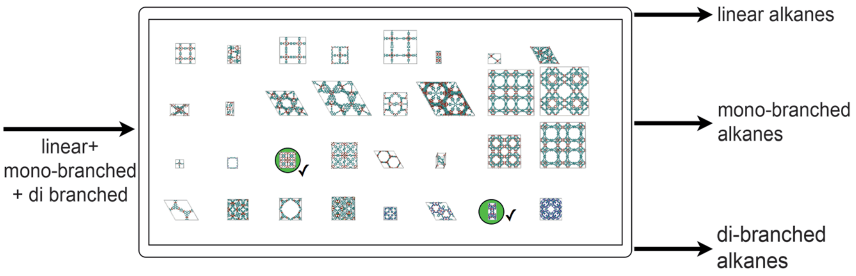


The way it is: Incorporation of 2′-deoxy-2′-fluororibonucleotides (2′-F RNA) into RNA oligomers leads to a marked increase in duplex stability. Using NMR spectroscopy (see picture) with native (red circles) and 2′-F modified (black squares) RNA duplexes, and UV melting and osmotic stress experiments the higher stability of 2′-F RNA relative to RNA is shown to be the result of both increased Watson–Crick H-bonding strength and favorable base stacking.

RNA Thermodynamics

A. Patra, M. Paolillo, K. Charisse, M. Manoharan, E. Rozners,* M. Egli* ______ **11863 – 11866**

2′-Fluoro RNA Shows Increased Watson–Crick H-Bonding Strength and Stacking Relative to RNA: Evidence from NMR and Thermodynamic Data



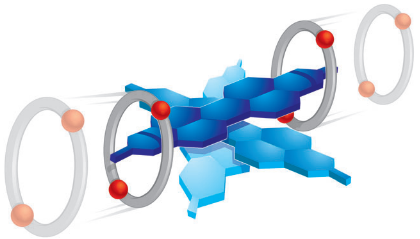
A matter of degree: Separation of di-branched alkanes from their linear and mono-branched isomers is important in producing high-octane gasoline. Using computational techniques to screen a large variety of adsorbent materials (see scheme), ZIF-77 emerges as the best adsorbent. It has the unique ability to fractionate isomer mixtures according to the degree of branching.

Alkane Separation

D. Dubbeldam,* R. Krishna, S. Calero, A. Ö. Yazaydın ______ **11867 – 11871**

Computer-Assisted Screening of Ordered Crystalline Nanoporous Adsorbents for Separation of Alkane Isomers

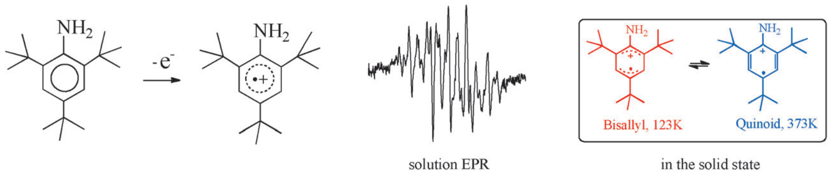
Two for the price of one! The diazaperopyrenium dication behaves dichotomously in a homo- and heterophilic manner, allowing for complexation with itself and a variety of π-electron-rich donors. This chameleonic characteristic, in addition to its electronic properties, leads to self-assembled nanowires in the solid state, as well as to its acting as a template for aromatic crown ethers to form a [3]- and two [2]rotaxanes (see picture).



Noncovalent Interactions

A. N. Basuray, H.-P. Jacquot de Rouville, K. J. Hartlieb, T. Kikuchi, N. L. Strutt, C. J. Bruns, M. W. Ambrogio, A.-J. Avestro, S. T. Schneebeli, A. C. Fahrenbach, J. F. Stoddart* ______ **11872 – 11877**

The Chameleonic Nature of Diazaperopyrenium Recognition Processes



Feeling the heat: The aniline radical cation TBA$^{\bullet+}$ (TBA = 2,4,6-tBu$_3$C$_6$H$_2$NH$_2$) has been successfully stabilized both in solution and in the solid state. It exists as two isomers in the crystal lattice that interchange with temperature, and features an exceptionally long C–N bond beyond theoretical prediction.

Radical Cation Structures

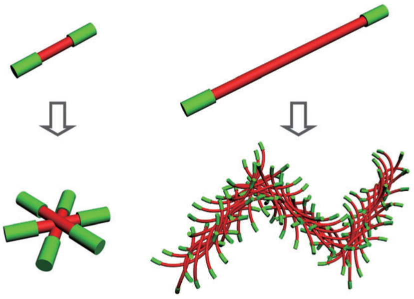
X. Chen, X. Wang, Y. Sui, Y. Li, J. Ma,* J. Zuo, X. Wang* ______ **11878 – 11881**

Synthesis, Characterization, and Structures of a Persistent Aniline Radical Cation

Hierarchical Structures

H. Qiu, G. Russo, P. A. Rupar,
L. Chabanne, M. A. Winnik,*
I. Manners* ____________ 11882 – 11885

Tunable Supermicelle Architectures from the Hierarchical Self-Assembly of Amphiphilic Cylindrical B–A–B Triblock Co-Micelles

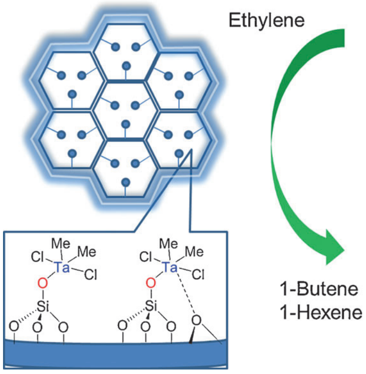


Crossing the block: Amphiphilic cylindrical B–A–B triblock co-micelles, micelle analogues of bolaamphiphiles, can be prepared by the crystallization-driven living self-assembly of diblock copolymers with core-forming polyferrocenylsilane blocks. These novel co-micelle building blocks form regular crossed or spherical supermicelles or elongated networks in polar media depending on the relative lengths of the A and B segments (see picture).

Surface Organometallics

Y. Chen, E. Callens, E. Abou-Hamad,
N. Merle, A. J. P. White, M. Taoufik,
C. Copéret, E. Le Roux,*
J.-M. Basset* ____________ 11886 – 11889

$[(\equiv\text{SiO})\text{Ta}^{\text{V}}\text{Cl}_2\text{Me}_2]$: A Well-Defined Silica-Supported Tantalum(V) Surface Complex as Catalyst Precursor for the Selective Cocatalyst-Free Trimerization of Ethylene



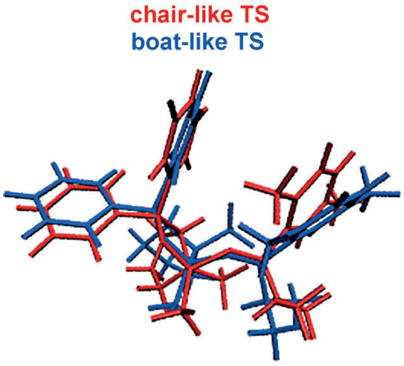
On the surface of it: In the absence of cocatalyst, a well-defined silica-supported surface organometallic complex $[(\equiv\text{SiO})\text{Ta}^{\text{V}}\text{Cl}_2\text{Me}_2]$ selectively catalyzes the oligomerization of ethylene. The use of surface organometallic species allows three different pathways to be determined for the reduction of Ta^{V} to Ta^{III} species under pressure of ethylene.

Stereoselection

H. Zhu, D. J. O'Leary,
M. P. Meyer* ____________ 11890 – 11893

Stereoselection in the Corey–Bakshi–Shibata Reduction: Insight from Kinetic Isotope Effects and Transition-Structure Modeling

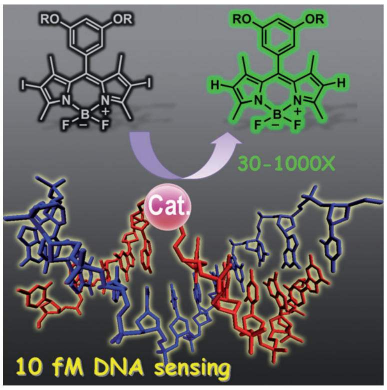
Flexible but demanding: Significant steric demand is isolated to the small (*i*Pr) substituent in the oxazaborolidine-catalyzed borane (CBS) reduction of 2′,5′-dimethylisobutyrophenone. Computed transition-structure models (see picture) demonstrate that nearly equivalent steric demand can be achieved from conformationally distinct transition structures.



DNA Sensing

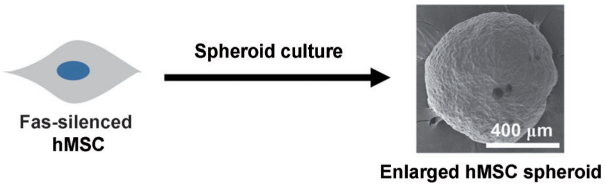
D. K. Prusty, M. Kwak, J. Wildeman,
A. Herrmann* ____________ 11894 – 11898

Modular Assembly of a Pd Catalyst within a DNA Scaffold for the Amplified Colorimetric and Fluorimetric Detection of Nucleic Acids



Phosphine ligands were covalently tethered to short oligonucleotide strands such that active palladium complexes formed in the presence of a specific nucleic acid target. This catalytic center on the double-stranded DNA then converted water-soluble iodo-BODIPY dyes, present in excess, into highly emissive deiodinated reporters (see picture). This approach is suitable for the rapid colorimetric or fluorimetric detection of nucleic acid targets with a lower detection limit of just 10 pM.

Intracellular Delivery



Larger is better: Fas-silencing siRNA can be delivered into the cytoplasm of human mesenchymal stem cells (hMSCs) by a bioreducible polymer (see picture). The enhanced anti-apoptotic activity of the Fas-silenced hMSCs means that they can be readily formulated as enlarged spheroids to significantly enhance angiogenic efficacy as compared to their smaller counterparts.

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 Retraction

The following article from *Angewandte Chemie International Edition*, "Total Syntheses of Hexacyclinol, 5-*epi*-Hexacyclinol, and Desoxohexacyclinol Unveil an Antimalarial Prodrug Motif" by James J. La Clair, published online on February 9, 2006 in Wiley Online Library (http://onlinelibrary.wiley.com), has been retracted by agreement between the author, the journal Editor in Chief, Peter Gölitz, and Wiley-VCH Verlag GmbH & Co. KGaA. The retraction has been agreed due to lack of sufficient Supporting Information. In particular, the lack of experimental procedures and characterization data for the synthetic intermediates as well as copies of salient NMR spectra prevents validation of the synthetic claims. The author acknowledges this shortcoming and its potential impact on the community.

Total Syntheses of Hexacyclinol, 5-*epi*-Hexacyclinol, and Desoxohexacyclinol Unveil an Antimalarial Prodrug Motif

J. J. La Clair* ________ 2769–2773

Angew. Chem. Int. Ed. **2006**, *45*

DOI: 10.1002/anie.200504033

Angewandte Corrigendum

In this communication, the second affiliation applies to S. J. Lee, not S. Y. Lee. This affiliation must read correctly:

S. J. Lee, Dr. Y. Choi
School of Life Science and Biotechnology, Korea University (Korea)

Tumor-Homing Poly-siRNA/Glycol Chitosan Self-Cross-Linked Nanoparticles for Systemic siRNA Delivery in Cancer Treatment

S. J. Lee, M. S. Huh, S. Y. Lee, S. Min,
S. Lee, H. Koo, J.-U. Chu, K. E. Lee,
H. Jeon, Y. Choi, K. Choi, Y. Byun,
S. Y. Jeong, K. Park, K. Kim,*
I. C. Kwon* ________ 7203–7207

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

DOI: 10.1002/anie.201201390

Angewandte Corrigendum

The ortho and *meta* Magnesiation of Functionalized Anilines and Amino-Substituted Pyridines and Pyrazines at Room Temperature

G. Monzón, I. Tirotta,
P. Knochel* ———— **10624–10627**

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

DOI: 10.1002/anie.201205465

The authors wish to add another co-author for this communication. Working in the laboratory in Munich, Yuji Nishii has contributed to some of the experiments that are described in this manuscript. Therefore, the author list must read correctly:

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