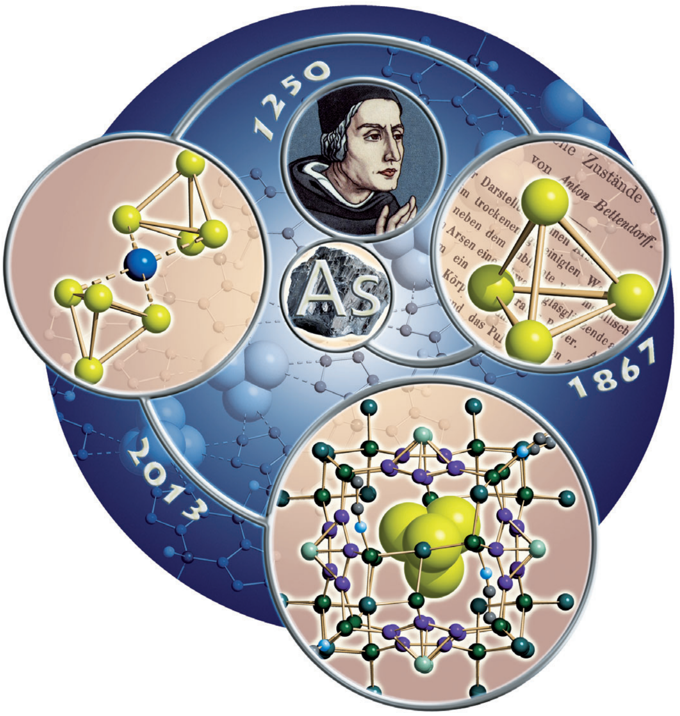
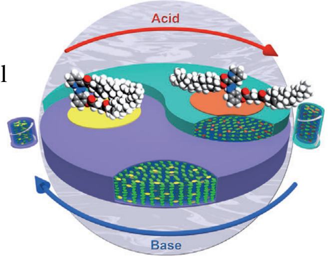
A new chapter in the history of arsenic ...



… has been opened up by M. Scheer et al. in their Communication on page 10887 ff. Long after the discovery of grey and yellow arsenic by Albertus Magnus and Anton Bettendorff, the structure of As_4 has finally been described by X-ray crystallographic techniques. Highly reactive yellow arsenic was embedded in a polymeric matrix, which minimizes molecular motion and therefore allows the determination of the As–As bond length.

Liquid Crystals

The helical pitch of a host liquid-crystalline material can be controlled by the acid/base-induced isomerization of a cholesterol-containing hydrazone, as I. Aprahamian et al. describe in their Communication on page 10734 ff.

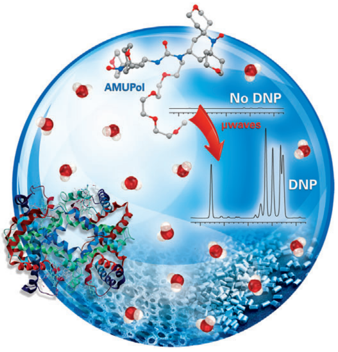


Main-Group Metal Complexes

In their Communication on page 10822 ff., Z. Xi et al. describe the synthesis of barium dibenzopentalenide by introducing Ba–C bonds into phenyl-substituted 1,4-dilithio-1,3-butadienyl skeletons.

Dynamic Nuclear Polarization

Two new polarizing agents for dynamic nuclear polarization NMR spectroscopy have been developed. The enhancement factors are 3.5 to 4 times larger than for the established agent TOTAPOL, as O. Ouari, P. Tordo et al. describe in their Communication on page 10858 ff.



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Author Profile

*"My favorite piece of research is 'the current potential of electrochemistry'.
If I were not a scientist, I would be a detective solving unsolved crimes by sifting through evidence for non sequiturs and clues …"*
This and more about Joel S. Miller can be found on page 10688.

News


R. V. Ulijn


T. Simpson


C. C. Cummins


R. A. Layfield


R. Luque


C. A. Mirkin


J. P. Attfield


J. Goodman

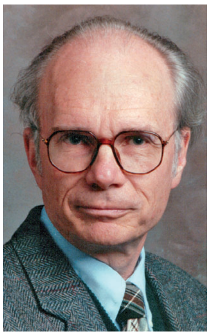

O. Scherman


M. C. White


J. A. Gladysz


J. M. Brown

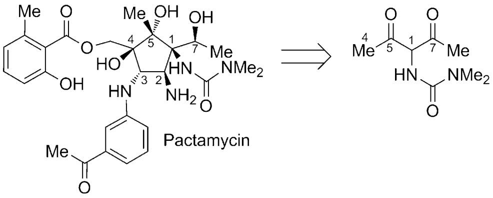
Obituaries



Duward F. Shriver passed away at the age of 78 on March 6, 2013. He was well-known to generations of inorganic and organometallic chemists from his classic textbooks.

Highlights

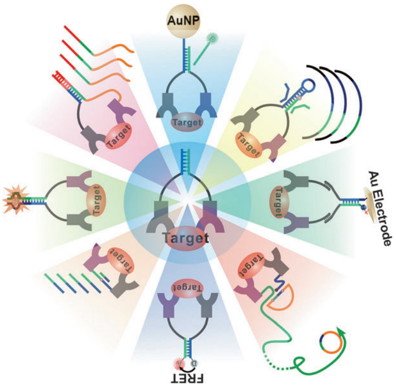
Total Synthesis



Inside insight: Pactamycin has long been recognized as a potent bioactive compound and a formidable target for chemical total synthesis. Recently, Johnson and co-workers published a 15-step enantioselective synthesis of pactamycin that capitalized on the recognition of latent symmetry in the core structure.

Minireviews

DNA Assembly



The concentration makes the difference: Binding of a target molecule to two affinity ligands brings the complementary oligonucleotides together, thereby dramatically increasing their local concentrations and enhancing the stability of the hybrids. The principle is used to generate binding-induced assembly of DNA probes containing various motifs and DNA-functionalized nanomaterials for ultrasensitive detection of specific proteins.

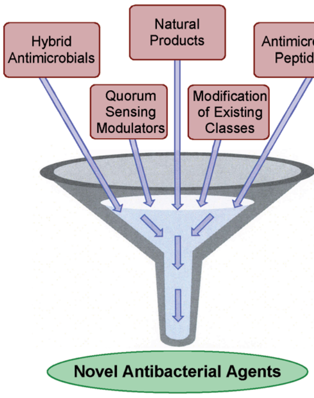
For the USA and Canada: ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Journal Customer Services, John Wiley & Sons Inc., 350 Main St., Malden, MA 02148-5020. Annual subscription price for institutions: US$ 11.738/10.206 (valid for print and electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

Reviews

Antibiotics

K. M. G. O'Connell, J. T. Hodgkinson, H. F. Sore, M. Welch, G. P. C. Salmond, D. R. Spring* ———— **10706 – 10733**

Combating Multidrug-Resistant Bacteria: Current Strategies for the Discovery of Novel Antibacterials



Resistance is futile: With bacterial resistance on the rise, a number of approaches are currently being explored to ensure that new drugs are being brought to the clinic. It is necessary for the next generation of antibacterials to not only have an improved drug profile but also overcome the latest bacterial resistance mechanisms. Insight into the current strategies being developed is discussed, in particular recent research within the area of quinolone quorum sensing modulators.

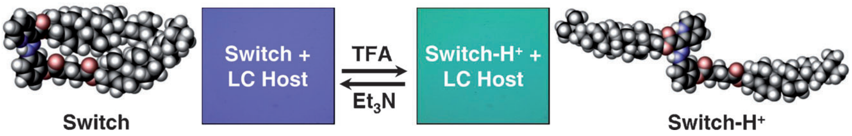
Communications

Liquid Crystals

X. Su, S. Voskian, R. P. Hughes, I. Aprahamian* ———— **10734 – 10739**

Manipulating Liquid-Crystal Properties Using a pH Activated Hydrazone Switch

Frontispiece

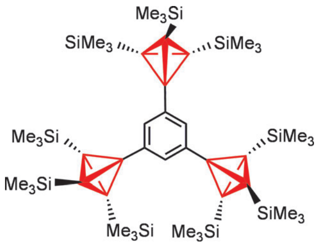


The long-range organization of a liquid crystal can be controlled by using an additive that consists of cholesterol units attached to a hydrazone switch. The acid/base-induced rotary motion in the switch is transmitted to the self-assembled supramolecular host, wherein this information is propagated and amplified. This process alters the photophysical properties of the host, which results in the change of the readout color from purple to green.

Small Ring Systems

Y. Kobayashi, M. Nakamoto, Y. Inagaki, A. Sekiguchi* ———— **10740 – 10744**

Cross-Coupling Reaction of a Highly Strained Molecule: Synthesis of σ–π Conjugated Tetrahedranes



Strain for an effect: The cross-coupling reaction of highly strained tetrahedranes with aryl halides has been investigated. In the presence of a palladium catalyst, tetrahedryllithium rapidly reacted with various aryl halides to form aryl-substituted tetrahedranes (see picture) in good to excellent yields. The UV/Vis absorption spectra suggest an extended σ–π conjugation between the σ orbital of the tetrahedrane core and the aryl π system.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Umwandlung von Triazolen in andere Heterocyclen
Kurzaufsatz von V. Gevorgyan und B. Chattopadhyay
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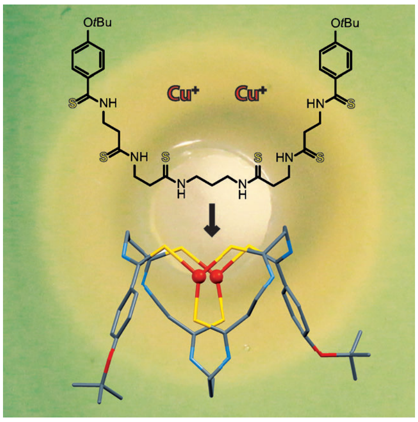


A metal chelator from the oxygen-free world: Multiple lines of experimental evidence show that closthioamide, the first antibiotic from a strictly anaerobic bacterium (*Clostridium*), is a selective copper(I) chelator. The geometry of the polythioamide complex, in which two copper ions in a trigonal-planar coordination stabilize the pitch of a helix-like arrangement, is unprecedented for natural products.

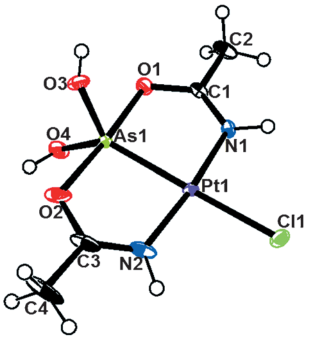
Natural Products

F. Kloss, S. Pidot, H. Goerls, T. Friedrich, C. Hertweck* ———— **10745 – 10748**

Formation of a Dinuclear Copper(I) Complex from the *Clostridium*-Derived Antibiotic Closthioamide

---

Anticancer drugs based on molecular adducts of platinum and arsenic (arsenoplatins) show an unanticipated structure, substitution chemistry, and cellular cytotoxicity. The Pt^{II}–As^{III} bonds in these complexes are stable in aqueous solution and strongly influence the lability of the *trans* ligand.



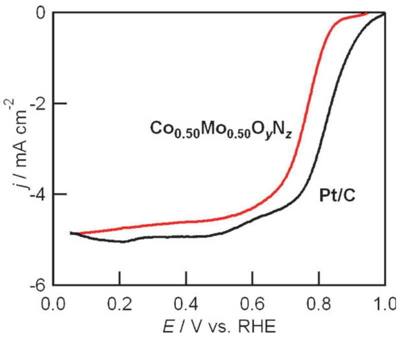
Antitumor Agents

Đ. U. Miodragović, J. A. Quentzel, J. W. Kurutz, C. L. Stern, R. W. Ahn, I. Kandela, A. Mazar, T. V. O'Halloran* ———— **10749 – 10752**

Robust Structure and Reactivity of Aqueous Arsenous Acid–Platinum(II) Anticancer Complexes

---

A non-noble metal electrocatalyst has been developed for the oxygen reduction reaction. Carbon-supported cobalt molybdenum oxynitride was simply prepared by impregnation followed by thermal ammonolysis. The oxynitride electrocatalytic activity nearly matched that of platinum in 0.1 M KOH solution. The catalyst structure and valence have been characterized using complementary local and bulk probes.



Electrocatalysis

B. Cao, G. M. Veith, R. E. Diaz, J. Liu, E. A. Stach, R. R. Adzic, P. G. Khalifah* ———— **10753 – 10757**

Cobalt Molybdenum Oxynitrides: Synthesis, Structural Characterization, and Catalytic Activity for the Oxygen Reduction Reaction

---

Deep-sea chemistry: The electrochemical analysis of hydrothermal fluids and the ambient seawater with fuel cells installed in deep-sea hydrothermal vents provided evidence for the possibility of generating electricity in the deep sea. The illumination of light-emitting diodes in the dark environment also confirmed this prospect.

Electrochemistry

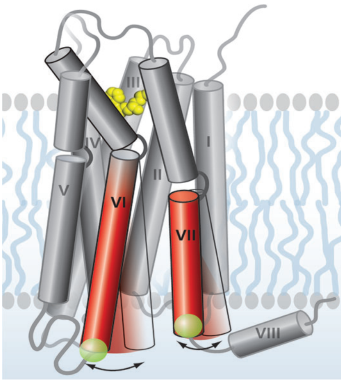
M. Yamamoto,* R. Nakamura,* K. Oguri, S. Kawagucci, K. Suzuki, K. Hashimoto, K. Takai ———— **10758 – 10761**

Generation of Electricity and Illumination by an Environmental Fuel Cell in Deep-Sea Hydrothermal Vents

Protein Dynamics

R. Horst, J. J. Liu, R. C. Stevens,
K. Wüthrich* ———— **10762 – 10765**

β_2-Adrenergic Receptor Activation by Agonists Studied with ^{19}F NMR Spectroscopy

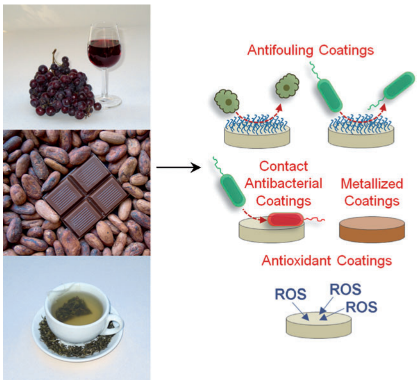


Proteins in slow motion: ^{19}F NMR studies indicate that equilibria between active and inactive states of the human β_2-adrenergic receptor require extensive structural rearrangements (arrows in picture). This was shown by an enthalpy difference of $\Delta H_o \approx 40\ \mathrm{kJ\,mol^{-1}}$ and a slow exchange rate, with $k_{ex} \ll 10\ \mathrm{s^{-1}}$.

Multifunctional Materials

T. S. Sileika, D. G. Barrett, R. Zhang,
K. H. A. Lau,
P. B. Messersmith* —— **10766 – 10770**

Colorless Multifunctional Coatings Inspired by Polyphenols Found in Tea, Chocolate, and Wine

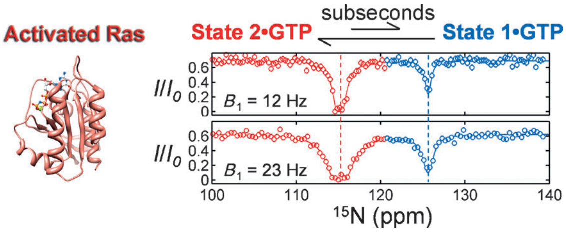


Polyphenolic compounds present in tea, red wine, and chocolate form thin adherent polyphenol films on substrates through spontaneous adsorption from solution. From this observation emerged a versatile and comprehensive approach to surface modification of a variety of solid, porous, and nanoparticulate substrates composed of metals, ceramics, and polymers (see picture; ROS = reactive oxygen species).

Protein Dynamics

D. Long, C. B. Marshall, G. Bouvignies,
M. T. Mazhab-Jafari, M. J. Smith, M. Ikura,
L. E. Kay* ———— **10771 – 10774**

A Comparative CEST NMR Study of Slow Conformational Dynamics of Small GTPases Complexed with GTP and GTP Analogues

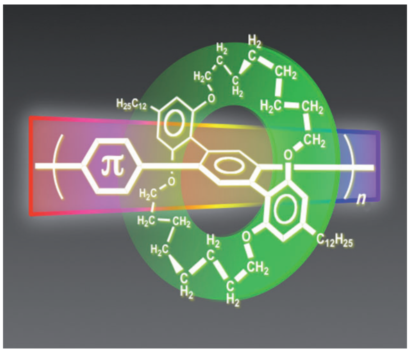


Conformational Exchange: Small GTPases, such as Ras and Rheb, exchange between major and minor conformers when bound to GTP, with different functional properties for each state (see picture). Two-dimensional ^{15}N CEST NMR spectroscopy is used to quantify the exchange parameters for both Ras and Rheb complexed with physiological GTP and the analogues GTPγS and GppNHp.

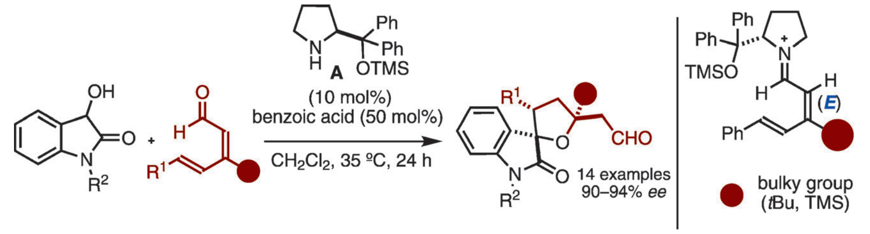
Materials Science

C. Pan, K. Sugiyasu,* Y. Wakayama,
A. Sato, M. Takeuchi* —— **10775 – 10779**

Thermoplastic Fluorescent Conjugated Polymers: Benefits of Preventing π–π Stacking



Molecular wires: Fluorescent conjugated polymers that are sheathed within their own cyclic side chains have been synthesized (see picture). Owing to the unique three-dimensional architecture, the polymers are light-emissive, even in the film state, miscible, allowing the combination of various fluorescence colors, and thermoformable, like conventional plastics.

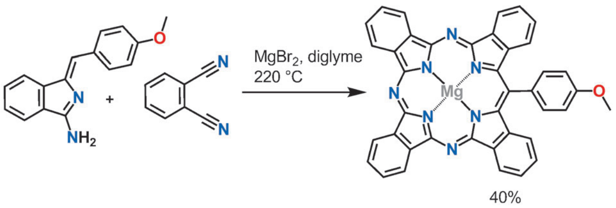


All about topology control: The title reaction yields valuable tetrahydrofuran spirooxindoles (see scheme; TMS = trimethylsilyl), and exemplifies a rare asymmetric 1,6-addition to linear 2,4-dienals proceeding with high δ-site- and stereoselectivity. A steering group at the β-dienal position ensured molecular preorganization of the catalytically active vinylogous iminium ion intermediate for highly predictable reaction outcomes.

Synthetic Methods

M. Silvi, I. Chatterjee, Y. Liu,
P. Melchiorre* ———— **10780 – 10783**

Controlling the Molecular Topology of Vinylogous Iminium Ions by Logical Substrate Design: Highly Regio- and Stereoselective Aminocatalytic 1,6-Addition to Linear 2,4-Dienals



Up to now, hybrid structures that lie between the ubiquitous phthalocyanine and porphyrin scaffolds have been extremely difficult to prepare. A straightforward, high-yielding synthesis of meso-derivatized tetrabenzotriazaporphyrins (see scheme) is described, thus unlocking access to this underdeveloped class of materials.

Heterocycles

A. Díaz-Moscoso,* G. J. Tizzard,
S. J. Coles,
A. N. Cammidge* ———— **10784 – 10787**

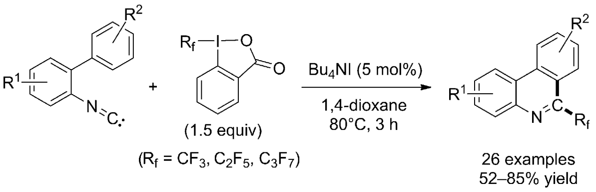
Synthesis of meso-Substituted Tetrabenzotriazaporphyrins: Easy Access to Hybrid Macrocycles

A monolithic material has marshmallow-like flexibility and superamphiphobic properties on any cutting surface. The two-step synthesis consists of a simple sol–gel process to obtain vinyl-modified superhydrophobic monolithic gels and grafting of perfluoroalkyl groups onto the pore surface to decrease surface energy. These superamphiphobic materials float on water and even on organic liquids with low polarity, such as alkanes.

Superamphiphobic Materials

G. Hayase, K. Kanamori,* G. Hasegawa,
A. Maeno, H. Kaji,
K. Nakanishi ———— **10788 – 10791**

A Superamphiphobic Macroporous Silicone Monolith with Marshmallow-like Flexibility



A radical approach toward 6-perfluoroalkylphenanthridines employs the Togni reagent or derivatives thereof as radical precursors and occurs in the absence of a transition metal. Bu_4NI is applied as radical initiator and phenanthridines are formed in good to excellent yields. In contrast to the currently intensively investigated trifluoromethylation of arenes, the arene core is formed during the trifluoromethylation in this approach.

Trifluoromethylation

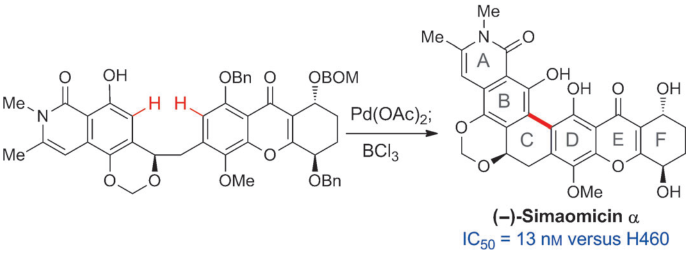
B. Zhang, C. Mück-Lichtenfeld,
C. G. Daniliuc, A. Studer* **10792 – 10795**

6-Trifluoromethyl-Phenanthridines through Radical Trifluoromethylation of Isonitriles

Total Synthesis

Y. Wang, C. Wang, J. R. Butler,
J. M. Ready* ———— **10796 – 10799**

Dehydrogenative Coupling to Enable the Enantioselective Total Synthesis of (−)-Simaomicin α

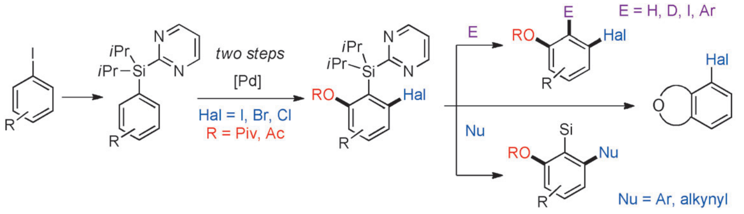


The anticancer natural product simaomicin α has been synthesized. Asymmetric synthesis allowed the assignment of absolute stereochemistry. The enantiomer of the naturally occurring substance shows potent cytotoxicity towards Gram-positive bacteria and human cancer cells. Bn = benzyl, BOM = benzyloxymethyl.

C–H Activation

D. Sarkar, F. S. Melkonyan, A. V. Gulevich,
V. Gevorgyan* ———— **10800 – 10804**

Twofold Unsymmetrical C–H Functionalization of PyrDipSi-Substituted Arenes: A General Method for the Synthesis of Substituted *meta*-Halophenols

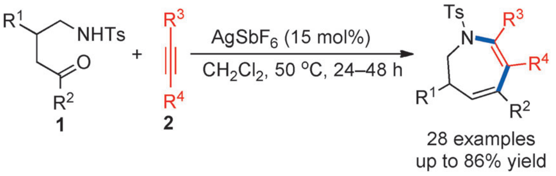


And the world is your oyster... Sequential halogenation/oxygenation reactions of 2-diisopropylsilylpyrimidine-substituted arenes provide a general and efficient synthesis of substituted *meta*-halophenols from simple aryl iodides (see scheme; Piv = pivaloyl). The products are poised to undergo diverse C–C, C–N, and C–O bond-forming reactions that enable the transformation of their framework and the introduction of valuable functionalities.

Cycloaddition reactions

M.-B. Zhou, R.-J. Song, C.-Y. Wang,
J.-H. Li* ———— **10805 – 10808**

Synthesis of Azepine Derivatives by Silver-Catalyzed [5+2] Cycloaddition of γ-Amino Ketones with Alkynes

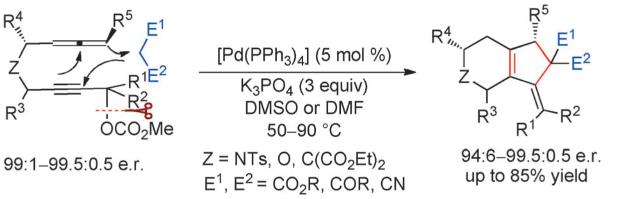


Silver forges the ring: A new and practical silver-catalyzed [5+2] cycloaddition method has been developed for the synthesis of azepines through the formation of four new chemical bonds between a γ-amino ketone and an alkyne in one step. This method provides a new hetero-[5+2] cycloaddition strategy for the construction of seven-membered ring systems.

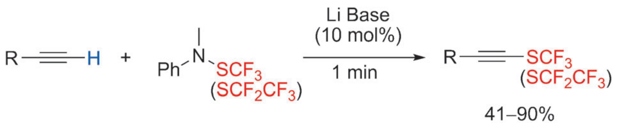
Synthetic Methods

J. Ye, S. Ma* ———— **10809 – 10813**

Allene Relay: Palladium-Catalyzed Bicyclization of Allene-Propargylic Carbonates with Geminal Bis(nucleophile)s



Pass the baton: The title reaction affords synthetically attractive bicyclo[4.3.0] skeletons in up to 85 % yield by three consecutive C–C bond formations in a single operation (see scheme; DMF = *N*,*N*-dimethylformamide, DMSO = dimethyl sulfoxide, Ts = 4-toluenesulfonyl). The challenge of efficient axial-to-central chirality transfer involving π-allyl palladium intermediates has been also realized. Mechanistic studies are discussed.



Pin the tail on the alkyne: CF_3S- or CF_3CF_2S-alkynes can be simply and quickly obtained by mixing terminal alkynes with a trifluoromethanesulfenamide reagent. The reaction uses easy-to-handle reagents, and functions under mild conditions without activation by transition metals.

Trifluoromethylthiolation

S. Alazet, L. Zimmer,
T. Billard* ——— **10814 – 10817**

Base-Catalyzed Electrophilic Trifluoromethylthiolation of Terminal Alkynes

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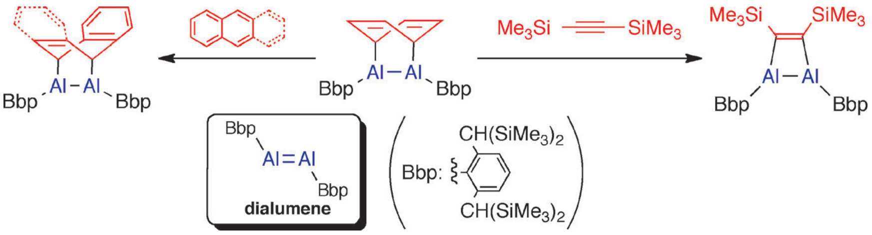

Bonding with Al: Treatment of a dialumene-benzene adduct (**1**) with naphthalene and anthracene afforded the corresponding dialumene-arene adducts at room temperature. A 1,2-dialuminacyclobutene derivative was also obtained by the exchange of the C_6H_6 moiety of **1** with bis(trimethylsilyl)acetylene. These findings exhibit the potential of **1** as a synthetic equivalent of a dialumene.

Main-Group Chemistry

T. Agou, K. Nagata,
N. Tokitoh* ——— **10818 – 10821**

Synthesis of a Dialumene-Benzene Adduct and Its Reactivity as a Synthetic Equivalent of a Dialumene

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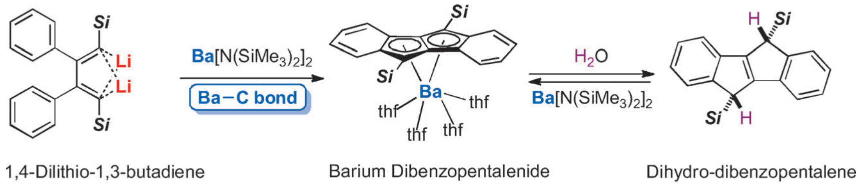


Transmetalation of 1,4-dilithio-1,3-butadienes with $Ba[N(SiMe_3)_2]_2$ gave barium dibenzopentalenides, which were structurally characterized by single-crystal X-ray analysis. A preliminary study of the reaction chemistry of thus obtained barium dibenzopentalenides demonstrated that synthetically useful applications can be expected.

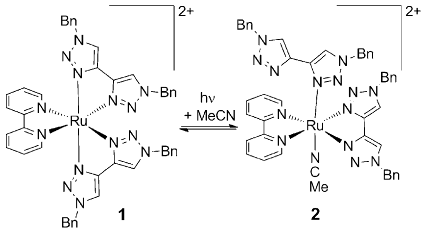
Main-Group Metal Complexes

H. Li, B. Wei, L. Xu, W.-X. Zhang,
Z. Xi* ——— **10822 – 10825**

Barium Dibenzopentalenide as a Main-Group Metal η^8 Complex: Facile Synthesis from 1,4-Dilithio-1,3-butadienes and $Ba[N(SiMe_3)_2]_2$, Structural Characterization, and Reaction Chemistry

Inside Back Cover

Hanging in there: Unprecedented quantitative formation of a long-lived intermediate **2** that contains a monodentate N^N ligand has been observed and the species characterized. Photoreactive ligand loss from a ruthenium(II) tris(chelate) complex **1** leads to **2**, which has a half-life of 14 hours. Bn = benzyl.

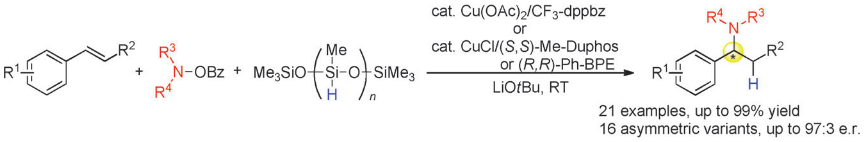


Photochemistry

C. E. Welby, C. R. Rice,
P. I. P. Elliott* ——— **10826 – 10829**

Unambiguous Characterization of a Photoreactive Ligand-Loss Intermediate

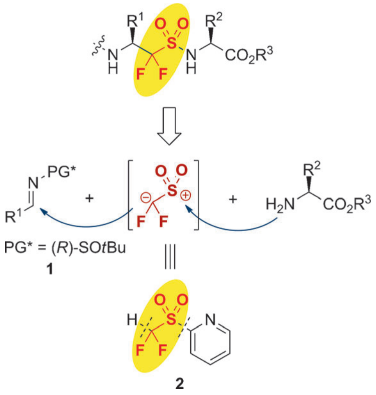
Synthetic Methods



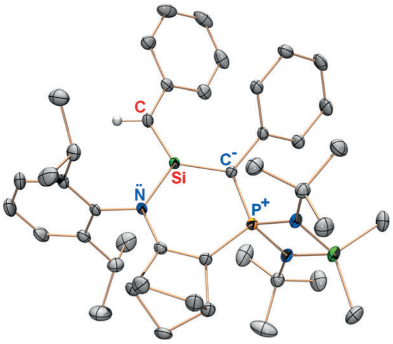
Playing Reversi with H and N: A copper-catalyzed intermolecular regioselective hydroamination of styrenes with polymethylhydrosiloxane and hydroxylamine derivatives has been developed. The catalysis accommodates challenging β-substituted substrates. Moreover, the chiral biphosphine-ligated copper complex successfully forms benzylamines with good enantiomeric ratios.

Synthetic Methods

Making chains: An efficient method has been developed for the synthesis of previously unknown enantiopure difluorinated β-amino sulfinic and sulfonic acids from (*R*)-*N*-*tert*-butanesulfinyl imines (**1**) and difluoromethyl 2-pyridyl sulfone (**2**). The present protocol is expected to be suitable for constructing difluorinated peptidosulfonamides of biological interest.

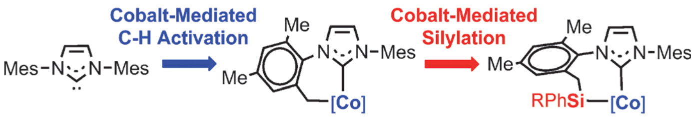


Silenes



Keen to donate: A stable and isolable silene with two π-donating groups on the silicon center has been synthesized. This silicon-substituted silene shows totally different π-substituent effects compared to those of related carbon-substituted silenes, and it presents intrinsic silene properties with an enhanced electron-donating character, making it an excellent ligand for transition metals.

Carbene Complexes

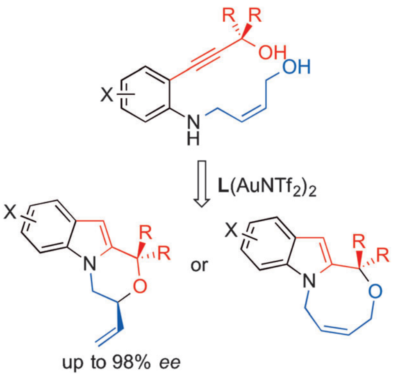


Pep up your carbene catalyst: A sequential cobalt-mediated C–H activation and silylation protocol has been developed for the preparation of novel silyl-donor-functionalized NHC complexes (see scheme; Mes = mesityl; R = H, Me, Ph). The resulting cobalt complexes exhibited high activity and selectivity as catalysts for the hydrosilylation of olefins.

Asymmetric Catalysis

M. Chiarucci, R. Mocci, L.-D. Syntrivanis, G. Cera, A. Mazzanti, M. Bandini* ________ **10850 – 10853**

Merging Synthesis and Enantioselective Functionalization of Indoles by a Gold-Catalyzed Asymmetric Cascade Reaction

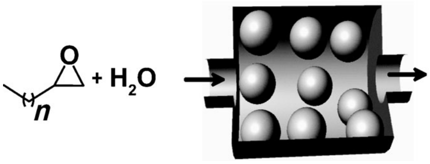


All at once: The simultaneous synthesis and enantioselective functionalization of an indole core is achieved with the assistance of chiral cationic Au^I complexes. A range of vinyloxazino-[4,3-*a*]-indoles is obtained by a cascade process in a highly enantioselective manner (see scheme; **L** = chiral diphosphine).

Heterogeneous Catalysis

M. Shakeri, R. J. M. Klein Gebbink, P. E. de Jongh, K. P. de Jong* ________ **10854 – 10857**

Tailoring the Window Sizes to Control the Local Concentration and Activity of (salen)Co Catalysts in Plugged Nanochannels of SBA-15 Materials



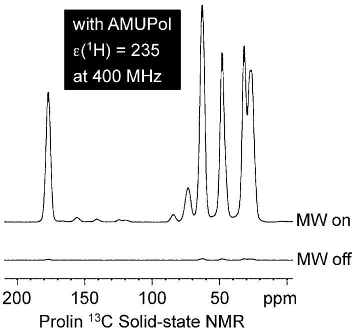
Ship shape! Chiral (salen)Co^{III} complexes (spheres) inside plugged nanochannels of SBA-15 materials is achieved using a ship-in-a-bottle synthesis technique. The local concentration of the metal complexes and the catalytic activity (such as the hydrolytic kinetic resolution of 1,2-epoxyalkanes; see scheme) showed a strong dependence on the size of the window.

NMR Spectroscopy

C. Sauvée, M. Rosay, G. Casano, F. Aussenac, R. T. Weber, O. Ouari,* P. Tordo* ________ **10858 – 10861**

Highly Efficient, Water-Soluble Polarizing Agents for Dynamic Nuclear Polarization at High Frequency

Back Cover

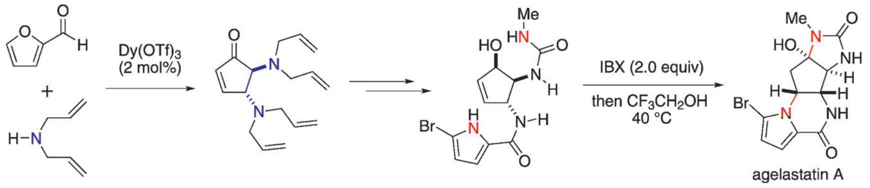


Well polarized: Two new polarizing agents PyPol and AMUPol soluble in glycerol/water mixtures are used for dynamic nuclear polarization (DNP) NMR spectroscopy. The enhancement factors (ε) are about 3.5 to 4 times larger than for the established agent TOTAPOL at 263 and 395 GHz. For AMUPol, the temperature dependence of ε allows DNP experiments to be performed at temperatures significantly higher than for typical high-field DNP NMR experiments.

Natural Product Total Synthesis

P. A. Duspara, R. A. Batey* ________ **10862 – 10866**

A Short Total Synthesis of the Marine Sponge Pyrrole-2-aminoimidazole Alkaloid (±)-Agelastatin A

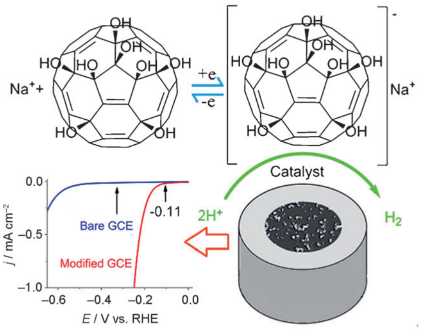


Ring by ring: (±)-Agelastatin A has been synthesized through the use of domino and one-pot reactions while minimizing protecting group usage. The core was accessed through a stereoselective domino condensation/ring-opening/4π-conrotatory electrocyclization and elaborated using newly developed protocols for urea and amide formation. Oxidation of an unprotected pre-agelastatin A and an intramolecular aza-Michael reaction completed the synthesis in only six steps.

Electrocatalysis

J. Q. Zhuo, T. Y. Wang, G. Zhang, L. Liu, L. B. Gan,* M. X. Li* —— **10867 – 10870**

Salts of $C_{60}(OH)_8$ Electrodeposited onto a Glassy Carbon Electrode: Surprising Catalytic Performance in the Hydrogen Evolution Reaction



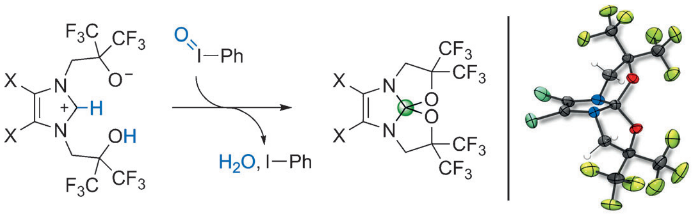
Full(erene) of surprises: The first isomerically pure multi-hydroxylated fullerene, $C_{60}(OH)_8$, shows a reduction peak and a reoxidation peak in aqueous solution. With surprising catalytic performance in the hydrogen evolution reaction (HER), when electrodeposited on a glassy carbon electrode (GCE), salts of $C_{60}(OH)_8$ may prove to be effective molecular catalysts for conducting the HER without transition metals.

Fused Heterocycles

A. J. Arduengo, III,* G. Gurau, S. P. Kelley, W. J. Marshall, J. W. Runyon* —— **10871 – 10873**

Fused Spirocyclic Imidazolone Ketals

Inside Cover



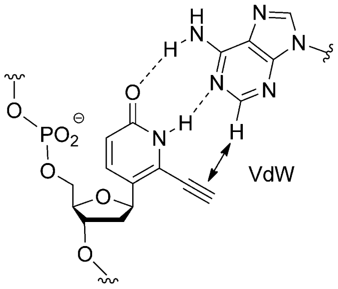
A Twist of Fate: Under oxidative conditions with iodosobenzene, a previously reported zwitterion meets a twisted fate. Oxidative cyclization of a series of imidazolium fluoroalkoxides provides access to a new class of fused imidazolone ketals.

Base Pairing

M. Minuth, C. Richert* —— **10874 – 10877**

A Nucleobase Analogue that Pairs Strongly with Adenine

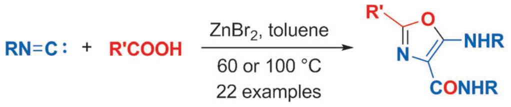
Shaping up for an A: Adenine is the only canonical nucleobase that does not offer a third hydrogen-bonding functionality at its Watson–Crick face, making it difficult to bind with high affinity. A 6-ethynyl-2-pyridone binds more tightly and with greater sequence fidelity than thymine. VdW = van der Waals interactions.



Domino Reactions

Y. Odabachian, S. Tong, Q. Wang, M.-X. Wang,* J. Zhu* —— **10878 – 10882**

Zinc Bromide Promoted Coupling of Isonitriles with Carboxylic Acids To Form 2,4,5-Trisubstituted Oxazoles



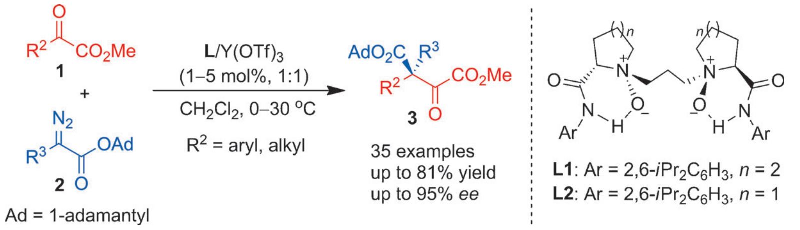
R: alkyl (including functionalized alkyl groups)
R': aromatic, heteroaromatic, olefinic, or aliphatic

Deviant behavior: In a deviation from “normal” reactivity, isocyanides underwent co-trimerization with carboxylic acids in the presence of $ZnBr_2$ to smoothly provide oxazoles (see scheme). The reaction is thought to occur by initial nucleophilic addition of the carboxylic acid to a ligated isonitrile molecule, followed by a sequence involving double migratory insertion, metal-salt elimination, acyl migration, cyclization, and dealkylation.

Asymmetric Catalysis

W. Li, X. H. Liu, F. Tan, X. Y. Hao,
J. F. Zheng, L. L. Lin,
X. M. Feng* ______ **10883 – 10886**

Catalytic Asymmetric Homologation of α-Ketoesters with α-Diazoesters: Synthesis of Succinate Derivatives with Chiral Quaternary Centers

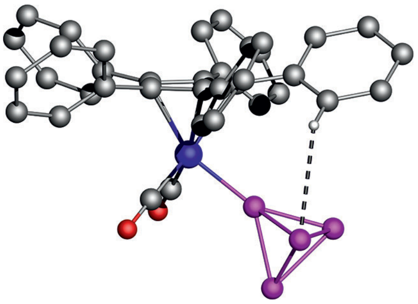


Y not? In the presence of the **L**/Y(OTf)$_3$ catalyst, the first catalytic asymmetric homologation of α-ketoesters with α-alkyl-α-diazoesters through either a 1,2-aryl or 1,2-alkyl shift was accomplished. Highly functionalized succinate derivatives containing a quaternary stereocenter were obtained in excellent yield and enantioselectivity under mild reaction conditions. Tf = trifluoromethanesulfonyl.

P_4 Coordination

S. Heinl, E. V. Peresypkina,
A. Y. Timoshkin, P. Mastrorilli, V. Gallo,
M. Scheer* ______ **10887 – 10891**

Intact P_4 Tetrahedra as Terminal and Bridging Ligands in Neutral Complexes of Manganese

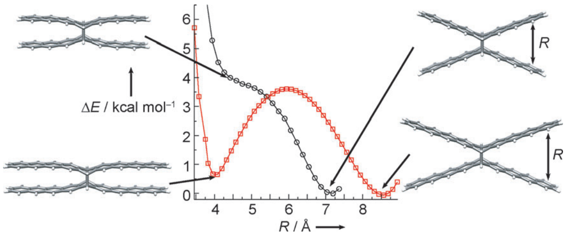


Static dynamic: Neutral, end-on bound white-phosphorus complexes with unprecedented stability in the solid state and solution were synthesized (see structure: gray C, blue Mn, red O, violet P). While the $C_5(4\text{-}n\text{BuC}_6\text{H}_4)_5$ ligands are stationary at low temperature on the NMR timescale, the P_4 ligands rotate rapidly. Despite the unfavorable γ_P/γ_H ratio, a heteronuclear Overhauser effect between the protons in *ortho* position and the basal P atoms was detected.

Conformational Analysis

S. Ehrlich, H. F. Bettinger,
S. Grimme* ______ **10892 – 10895**

Dispersion-Driven Conformational Isomerism in σ-Bonded Dimers of Larger Acenes



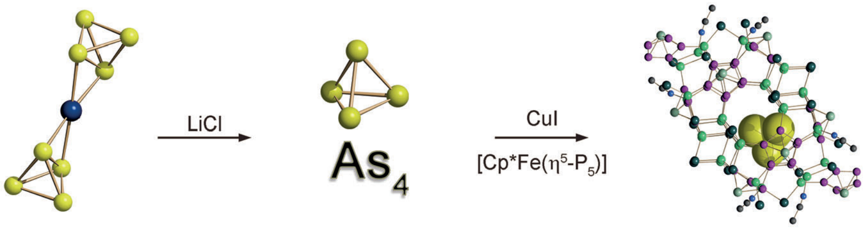
The σ-bonded butterfly structure of the nonacene dimer shows unusual dispersion-driven conformational isomerism that is due to strong intramolecular dispersion interactions between the wings of annulated aromatic rings. High-level LPNO-CEPA and DFT-D3 ab initio calculations are in good mutual agreement, whereas dispersion-devoid DFT and the MP2 method completely fail.

Yellow Arsenic

C. Schwarzmaier, A. Schindler, C. Heindl, S. Scheuermayer, E. V. Peresypkina, A. V. Virovets, M. Neumeier, R. Gschwind, M. Scheer* ____________ **10896 – 10899**

Stabilization of Tetrahedral P_4 and As_4 Molecules as Guests in Polymeric and Spherical Environments

Front Cover



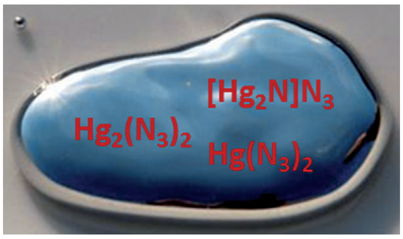
As you like it: $[Ag(\eta^2\text{-}As_4)_2]^+[pftb]^-$ can be used to store yellow arsenic (As_4). From it, As_4 can be easily released to give concentrated, light-stable solutions. These As_4 solutions, and those of white phosphorus (P_4), allowed molecular As_4 and P_4 to be encapsulated inside giant, spherical aggregates and polymeric matrices, enabling the first determination of their E–E (E = P, As) bond lengths by diffraction methods.

Mercury Azides

H. Lund, O. Oeckler, T. Schröder, A. Schulz,* A. Villinger* _ **10900 – 10904**

Mercury Azides and the Azide of Millon's Base

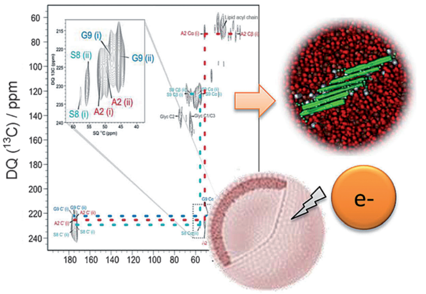
Always look on the bright azide of life: The synthesis of Millon's base azido salt $[Hg_2N]N_3$, and the metastable β-$Hg(N_3)_2$, along with their full characterization is possible for the first time and closes an open gap in azide chemistry.



NMR Spectroscopy

E. J. Koers, M. P. López-Deber, M. Weingarth, D. Nand, D. T. Hickman, D. Mlaki Ndao, P. Reis, A. Granet, A. Pfeifer, A. Muhs, M. Baldus* ____________ **10905 – 10908**

Dynamic Nuclear Polarization NMR Spectroscopy: Revealing Multiple Conformations in Lipid-Anchored Peptide Vaccines



Sensitivity is the key: Dynamic nuclear polarization NMR spectroscopy provides structural information on liposomal vaccines targeting Alzheimer's disease. DMPC/DMPG/Cholesterol mainly stabilizes extended structures of the lipid-anchored peptide, while in DMTAP/Cholesterol liposomes the peptide adopts a multitude of conformations including random-coil and extended structures.

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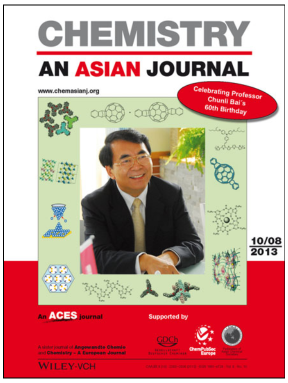

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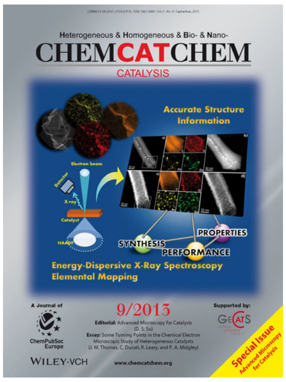

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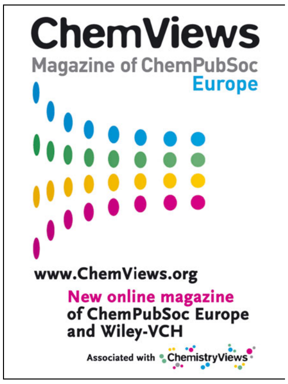

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In the abstract, the **motivation** for the work, the **methods** applied, the **results**, and the **conclusions** drawn should be presented (maximum 1000 characters). The abstract should contain several keywords to aid finding the paper online, and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