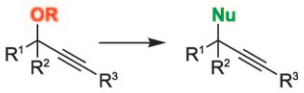
**VIP** *The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:*



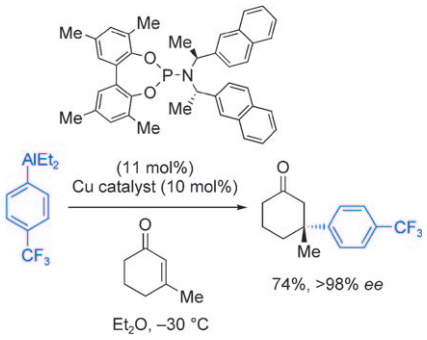
## Highlights


**Keen for a share in the glory**: Until recently, the title reaction stood in the shadows, its famous sister, catalytic allylic substitution, in the limelight. Catalytic propargylic substitution has now emerged as an efficient transformation that can be catalyzed by a variety of transition metals (see picture). Among the recent developments are copper-catalyzed asymmetric propargylic amination reactions.
Nu = nucleophile

### Catalytic Propargylation





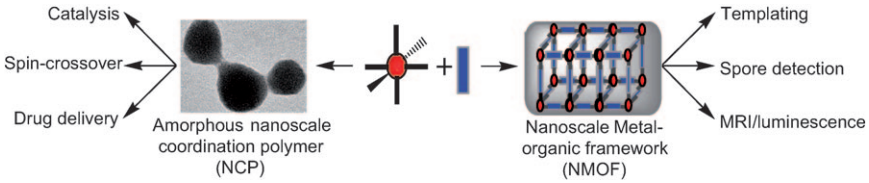

**Choosing the right metal for the job**: A broad range of asymmetric conjugate addition reactions are catalyzed efficiently by copper complexes, provided the appropriate organometallic reagent is used. With aluminum reagents, for example, quaternary stereogenic centers with functionalized aryl substituents can be generated with high enantioselectivity (see scheme).

### Conjugate Addition

# Contents

## Minireviews

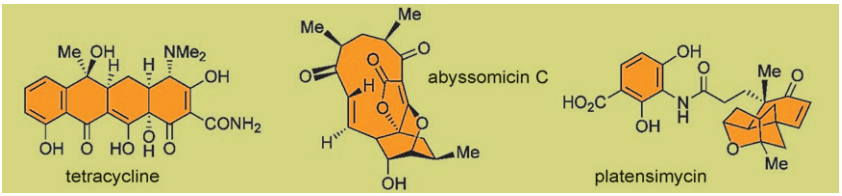





**Next-generation nanomaterials**: The coordination-directed assembly of metal ions and organic bridging ligands has afforded bulk-scale functional hybrid materials. Their scaling-down to the nano-regime has led to nanoscale coordination polymers and metal–organic frameworks which have been used in a broad range of applications including catalysis, spin-crossover, templating, biosensing, biomedical imaging, and anticancer drug delivery.

## Reviews

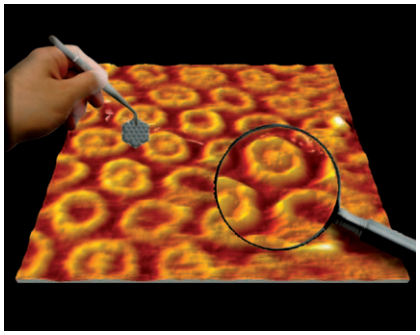





**Exciting developments** in the area of antibiotics are discussed in this stimulating review article as the authors present highlights of research carried out since the year 2000, emphasizing the pivotal role that total synthesis plays in moving the field forward and into new possibilities of drug design. The three compounds are shown as an illustration of the structural diversity of antibiotics.

## Communications





**Finding the middle ground**: A 1:1 host–guest complex consisting of a hexa-*peri*-hexabenzocoronene molecule sitting in the middle of the free cavity of a giant π-conjugated carbazole macrocycle has been obtained (see STM image). The complex has been prepared by physisorption of a monolayer of macrocycles followed by gas-phase deposition of graphene molecules by pulsed laser deposition.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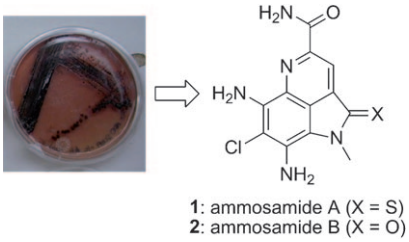


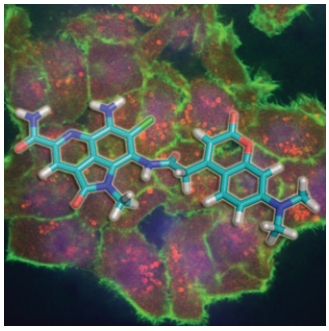

**1**: ammosamide A (X = S)
**2**: ammosamide B (X = O)

**From the ocean**: Ammosamides A (**1**) and B (**2**) were isolated from a marine-derived *Streptomyces* species collected in the Bahamas. The structures of these chlorinated tricyclic pyrroloquinoline alkaloids were solved using X-ray crystallographic techniques. Ammosamide A (**1**) was shown to contain an unusual thio-γ-lactam ring. Both metabolites show specific nanomolar cytotoxicity against selected cancer cell lines.

***Ammosamides, Biological Chemistry***

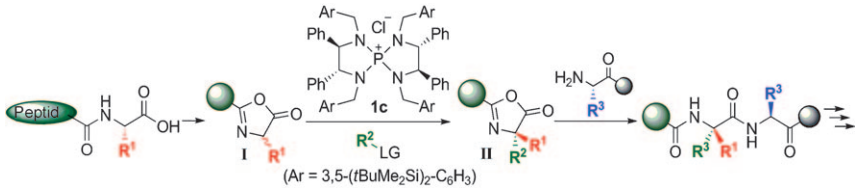


**The protein target** of the ammosamides, cytotoxic natural products from a marine-derived actinomycete, has been elucidated. An immunoaffinity fluorescent tag was used to construct a fluorescent molecular probe (see structure). First, uptake and localization of the probe in cells was visualized with fluorescence microscopy. The probe was then used to co-immunoprecipitate proteins that bound to the ammosamide core. Myosin was thus identified as a target.



***Ammosamides, Chemical Biology***



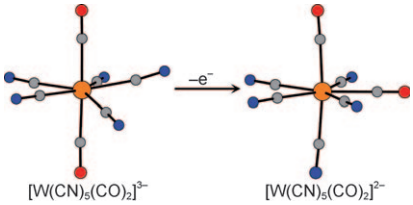



***Peptide Modification***



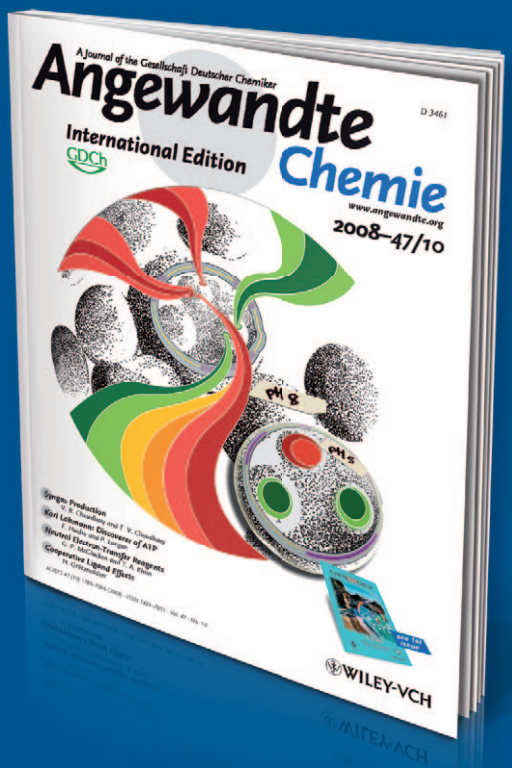
**Dual-purpose activation**: Peptide C-terminal azlactones **I** undergo stereoselective alkylation with high efficiency by the use of a newly devised chiral tetraaminophosphonium salt as a phase-transfer catalyst, and the alkylated azlactone products **II** can be employed directly for peptide ligation (see scheme, LG = leaving group). In this way, a wide range of chiral quaternary α-amino acid residues can be incorporated at specific sites of a peptide strand.

**Mixed company**: The use of a mixed carbonyl/cyanide ligand set enables stabilization of two new heptacoordinate complexes: $[W(CN)_5(CO)_2]^{3-}$ and $[W(CN)_5(CO)_2]^{2-}$. In the trianionic complex the two carbonyl ligands occupy the axial positions. Remarkably, one-electron oxidation causes loss of this axial symmetry, as shown by X-ray crystallography (see picture, orange W, gray C, blue N, red O), IR, and EPR spectroscopy.




***Isomerization***

# Incredibly inexpensive,-




...!

Do chemistry journals really cost so much? Perhaps some do, but certainly not *Angewandte Chemie!* In 2008, an entire institution could subscribe through Wiley InterScience* for 5000 € and get access to 52 issues with over 1600 articles and all associated online search options, and for just 5 % more, the printed issues could be included as well. For full members of the German Chemical Society (GDCh), a personal subscription cost not much more than 300 €, and student GDCh members paid less than 150 €, which is just under 3 € per issue - a price that even compares with high-circulation newsstand publications!

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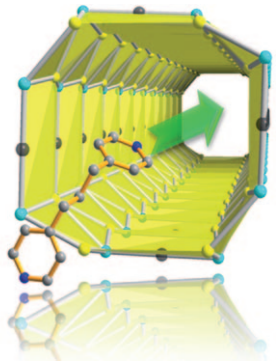
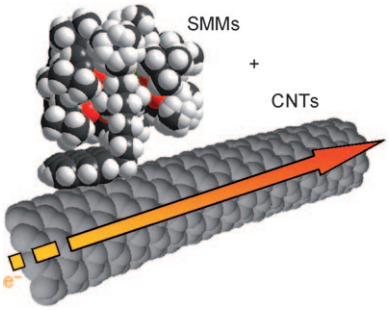


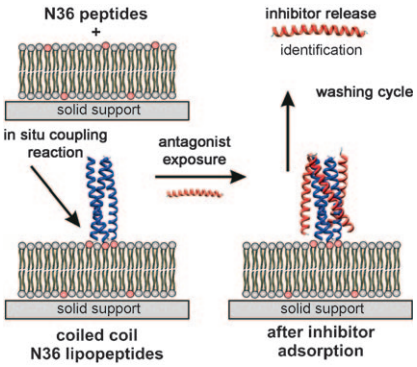
**Glowing with pride**: An activator-free gallium oxalatophosphite is a new class of color conversion phosphors for NUV and blue light-emitting diodes. It is synthesized by using an organic template and an environmentally friendly eutectic solvent in a reaction that shows efficient atom economy. The resulting material has a tubular structure (see picture) and intriguing luminescence properties.



**Devices and desires**: The self-assembly of single-molecule-magnet (SMM) carbon-nanotube (CNT) hybrids (see picture) in conditions compatible to the creation of electronic devices is described. The process is controlled at the single-molecule level, and the resulting CNT–field-effect transistors display single-SMM sensitivity at room temperature.



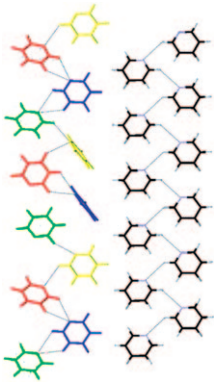



**A sheep in wolf's clothes?** Mimicking the crucial conformational step in viral fusion promises to be an efficient method to detect potential antagonists of retroviral infection (see scheme). Reconstituted lipopeptides derived from the N peptides of the class I virus fusion protein of SIV serve as receptors for potential inhibitors that function like the C peptides of the virus protein.



**Not so simple**: It is normally assumed that deuteration has only a minor effect on the stabilities of crystal structures. This assumption is wrong for pyridine. A low-temperature polymorph exists for $[D_5]$pyridine, but not for $[H_5]$pyridine, which adds a further twist to the already unusual structural chemistry of one of the simplest and most familiar laboratory chemicals.



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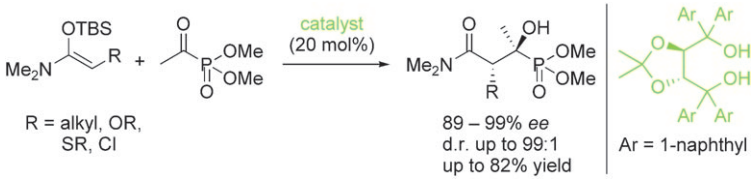
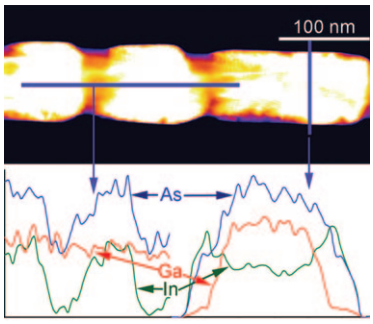



**Hydrogen-bond activation** by a diol promotes enantioselective Mukaiyama aldol reactions of acyl phosphonates. This mild and general method gives α-hydroxy phosphonate products having two chiral centers, one tertiary and one quaternary, formed with high diastereo- and enantioselectivity.

## Asymmetric Catalysis

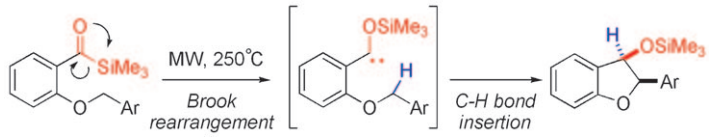





**Rings around the wire**: Novel hierarchical heterostructures, assembled by radial deposition of InAs on GaAs nanowires with nonplanar side walls, result in the formation of InAs nanorings. The mechanism of formation of such structures, determined by transmission electron microscopy, involves the preferential nucleation of InAs at concave regions of the GaAs surface by capillarity effects.

## Nanostructures

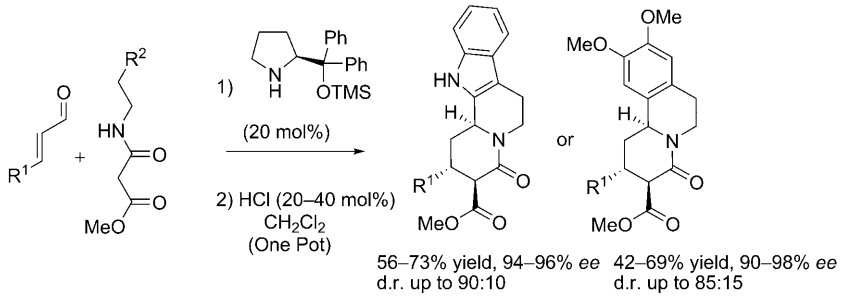





**Instant carbenes—that's hot**: The thermal 1,2-Brook rearrangement of acylsilanes generates siloxycarbene intermediates that can undergo intramolecular C–H bond insertion to provide benzofuran derivatives. This metal-free tandem reaction occurs in less than 10 minutes in the microwave.

## C–H Functionalization

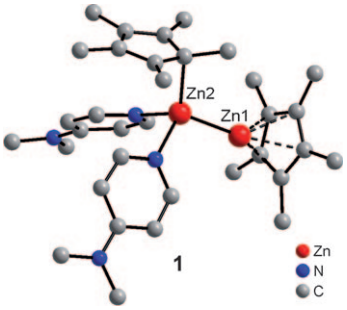





**One pot + two steps = three stereocenters**: A short enantioselective synthesis to access the indolo[2,3*a*]quinolizidine and the benzo[*a*]quinolizidine skeleton has been developed (see scheme; TMS = trimethylsilyl, $R^1$ = aromatic, $R^2$ = 3-indoyl or 3,4-dimethoxyphenyl). The sequence involves an organocatalytic conjugate addition and subsequent acid-catalyzed cyclization of the acyliminium ion.

## Asymmetric Catalysis

# Contents

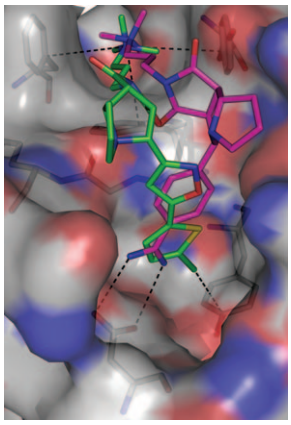



**Reaction without Zn–Zn rupture**: $[Cp^*_2Zn_2]$ reacts with a fourfold excess of the strong Lewis base 4-dimethylaminopyridine (dmap) to unexpectedly form the Lewis acid–base adduct **1**, in which both dmap molecules coordinate in a geminal binding mode to only one zinc atom. $Cp^* = C_5Me_5$.

## Low-Valent Lewis Acids

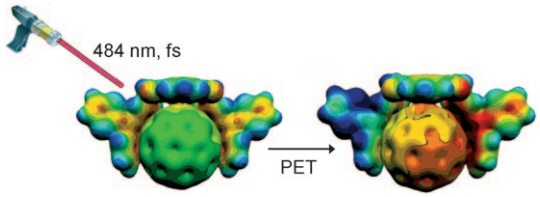


**In pocket**: A new class of potent inhibitors of factor Xa features a quaternary ammonium ion to fill the aromatic box in the S4 pocket and a 2-chlorothiophenyl group to occupy the S1 pocket (see picture; red O, blue N, yellow S, green Cl). Changing from a primary to a quaternary ammonium ion increases the binding affinity by a factor of 1000. The poor affinity in the former case suggests negligible cation–π interactions between Lys and Trp.



## Enzyme Inhibitors



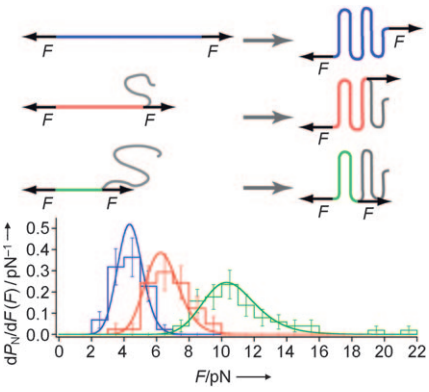



**On the ball**: Charge transfer occurs readily in tightly interacting complexes formed from π-extended tetrathiafulvalenes, which act as pincerlike receptors, and $C_{60}$ in a variety of solvents upon photoexcitation (see picture; PET = photoelectron transfer). It should be feasible to construct simple photovoltaic devices from systems based on similar recognition motifs.

## Electron Transfer



**The anisotropy of the folding-energy landscape** of proteins under force can be tested with cysteine engineering. The shorter the actively contracting polypeptide (see scheme, from blue to green), the higher the force at which the protein folds. The anisotropy of the folding mechanics can be described surprisingly simply with the help of a minimal model, mainly considering the entropic elasticity of the polypeptide.




## Protein Folding



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).

# Contents



## Service



# Corrigendum

High Internal Phase Emulsions Stabilized Solely by Functionalized Silica Particles


V. O. Ikem, A. Menner, A. Bismarck* — **8277–8279**



*Angew. Chem. Int. Ed.* **2008**, *47*

DOI 10.1002/anie.200802244


We would like to correct the following statement "*All previous reports on particle-stabilized emulsions deal with emulsions that have internal phase levels below 70 vol%.*" made in the introduction of our recent article. Since the publication of our communication, three papers[1–3] describing Pickering w/o and o/w emulsions with different internal phase levels and stabilities, which were not referenced in our paper, have been brought to our attention. Arditty et al.[2] describe silicone oil-in-water Pickering emulsions with up to 90 wt% internal phase and water-in-silicone oil Pickering emulsions having internal phase levels of up to 75 wt% stabilized using as received hydrophilic silica particles and silanized hydrophobic silica particles, respectively. Therefore, we should have stated "*Reports on particle stabilized w/o emulsions deal with emulsions having internal phase levels of up to 75 vol%. However, Arditty et al. reported on the preparation of o/w Pickering-HIPEs with up to 90% internal phase by manual shaking.*" Furthermore, we also stated in our communication that "*Binks and Lumsdon[11] further stated that particle-stabilized emulsions phase invert between volume fractions of 0.65 and 0.7, which means the major phase becomes the continuous phase.*" This statement is correct for the water-in-oil Pickering emulsions described in Ref. [4], however, Binks and Lumsdon[1] also provide examples of phase inversion occurring at different oil/water ratios starting from as low as 0.4. We would like to apologize to the authors of papers [1–3] for not acknowledging their research.


[1] B. P. Binks, S. O. Lumsdon, *Phys. Chem. Chem. Phys.* **2000**, *2*, 2959.
[2] S. Arditty, C. P. Whitby, B. P. Binks, V. Schmitt, F. Leal-Calderon, *Eur. Phys. J. E* **2003**, *11*, 273.
[3] B. P. Binks, J. A. Rodrigues, *Langmuir* **2003**, *19*, 4905.
[4] B. P. Binks, S. O. Lumsdon, *Langmuir* **2000**, *16*, 2539.