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The Onion	N/A	Steven Ryckbosch
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Next Due Date: Thursday May 15th, 2014

Instructions for Authors (*Volume 39)*

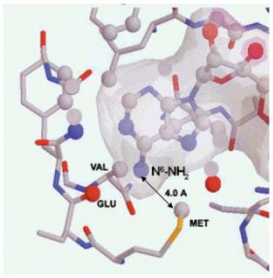
Identify articles to abstract in the journals you have been assigned. Try to pick things that the group (or specific subgroups) would like to read or should be aware of. This does not need to be limited to chemistry! If you encounter interesting pieces of media elsewhere (The Economist being a recent example) don't hesitate to let the group know. If you are splitting a journal with another group member, talk with him/her to be sure you are not reviewing redundantly. If you are not able to cover your journal for some reason, get someone to cover it for you—as if it were your group job.

Create an Abstract

Abstract submissions are usually prepared using ChemDraw. The editors of the *Lit Review* strongly encourage the copying of graphical material from PDF files and wish to point out the following. Graphics stored in PDF files are typically of postscript or >300 dpi quality. When an image is copied into a ChemDraw document, a screen snapshot is taken, and the image is captured at the present screen resolution. If the PDF file is being viewed zoomed-in, this typically results in the transfer of a high quality image. If the PDF is being viewed zoomed-out, a low quality image typically results. Text can be copied from a PDF file and pasted as text using the text select or column select tool. Once pasted, this text behaves as if it were input from the keyboard.

Include a brief textual summary of the article; an example of a completed abstract is shown below. The list of topics and subgroups on the right is useful to highlight which subgroups should pay attention to your abstract and roughly what kind of chemistry the article contains.

Please email the files to sryckbos@stanford.edu. Late abstracts will be included in the Lit Review for the following month**. PCs please send .pdf and macs please send .cdx files.**

<table>
<tr><td colspan="2">Citation: Abeyweera, T.P.; Rotenberg, S.A. Biochemistry 2007, 46, 2364-2370</td></tr>
<tr><td>Design and Characterization of a Traceable Protein Kinase C-alpha
Protein kinase CR (PKCR) is a critical component of pathways that govern cancer-related phenotypes such as invasion and proliferation. Proteins that serve as immediate substrates for PKCR offer potential targets for anticancer drug design. To identify specific substrates, a mutant of PKCR (M417A) was constructed at the ATP binding site such that it could bind a sterically large ATP analogue derivatized through the N6 amino group of adenosine (1ç-32Pl-N6-phenyl-ATP). Because this analogue could be utilized by the mutant kinase but not by wild-type PKCR (or presumably other protein kinase) to phosphorylate peptide or protein substrates, 32P-labeled products were the direct result of the mutant PKCR.
  </td><td>bioorganic
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Drug Deliv.</td></tr>
</table>

<table>
<tr><td colspan="2">Citation: Dictionary.com (search term = "mook")</td></tr>
<tr><td>For those of you who always wanted to know what it meant....
mook Pronunciation Key (mk) n. Slang
An insignificant or contemptible person.</td><td>methods
synthesis</td></tr>
</table>

DON'T BE A MOOK!

Lit Review MOOKS include those who:

- fail to submit their abstracts in a timely fashion (or at all), or
- claim there was nothing to abstract in *JACS*, *JOC*, *Org. Lett.*, etc.

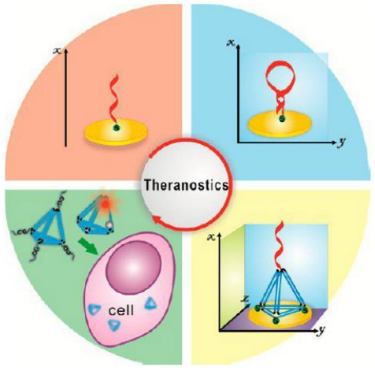
Penalties for being a Lit Review MOOK:

- You will get last choice when it's time to pick new journals.

Citation: Pei, H., Zuo, X., Zhu, D., Huang, Q., Fan, C. *Acc. Chem. Res.* 2014 (47) 550-559.

Functional DNA Nanostructures for Theranostic Applications

This article describes several potential uses of DNA nanostructures in diagnosis and therapy. DNA tetrahedra, for example, have sufficient structural stability to be used as anchors to secure other biomolecules to the surface of a gold nanoparticle. DNA tetrahedra are also cell-permeable and biocompatible.



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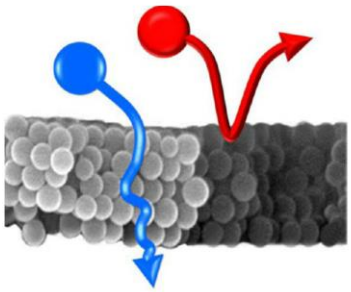
Drug Deliv.
Prostratin

Citation: Zharov, I., Khabibullin, A. *Acc. Chem. Res.* 2014 (47) 440-449.

Surface-Modified Silica Colloidal Crystals: Nanoporous Films and Membranes with Controlled Ionic and Molecular Transport

This account describes the synthesis, modification, and application of nanoporous membranes formed from colloidal silica crystals. These membranes can be functionalized with silanol chemistry. Flux and selectivity of across the membrane can be controlled with temperature, light, pH, and small-molecule binding. The membranes can therefore selectively separate macromolecules and chiral entities, and electrostatically gate ionic flux.



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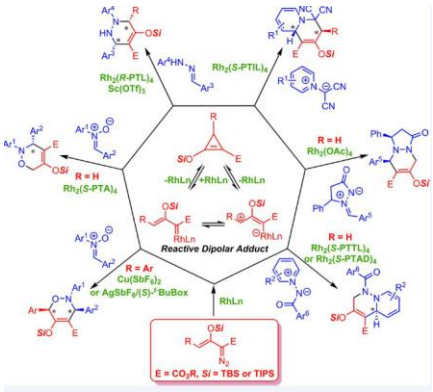
Citation: *Acc. Chem. Res.* 2014 (47) 1396-1405.

The [3+3]-Cycloaddition Alternative for Heterocycle Syntheses: Catalytically Generated Metalloenolcarbenes as Dipolar Adducts

This account reviews the development of [3+3] cycloadditions to access heterocycles over the last 20 years, originating from organometallic or vinyliminium ion chemistry. Key to [3+3] cycloadditions is the *in situ* formation of energetic dipolar adducts. Enoldiazoacetates or donor-acceptor cyclopropenes, for example, are good sources for generating metalloenolcarbenes to act as dipolar adducts.



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Citation: Zhu, Lei, *et al. ACS Chem. Biol.* **2014,** *9,* 510-516.

Rational Design of Matrix Metalloproteinase-13 Activatable Probes for Enhanced Specificity

Because of the important roles that matrix metalloproteinases (MMPs) play in tumor invasion and metastasis, various activatable optical probes have been developed to visualize MMP activities in vitro and in vivo. In this study, to further optimize the in vivo behavior of the proteinase activatable probe, the authors tracked and profiled the metabolites by a high-resolution liquid chromatography–mass spectrometry (LC–MS) system. Two major metabolites that contributed to the fluorescence recovery were identified. One was specifically cleaved between glycine (G4) and valine (V5) by MMP, while the other one was generated by nonspecific cleavage between glycine (G7) and lysine (K8). To visualize the MMP activity more accurately and specifically, a new probe, d-MMP-P12, was designed by replacing the l-lysine with d-lysine in the MMP substrate sequence. The metabolic profile of the new probe, d-MMP-P12, was further characterized by in vitro enzymatic assay, and no nonspecific metabolite was found by LC–MS.

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Citation: Patterson, D.M.; Nazarova, L.A.; Prescher, J.A. *ACS Chem. Biol.* **2014,** *9,* 592-605.

Finding the Right (Bioorthogonal) Chemistry

Bioorthogonal chemistries can be used to tag diverse classes of biomolecules in cells and other complex environments. With over 20 unique transformations now available, though, selecting an appropriate reaction for a given experiment is challenging. In this article, the authors compare and contrast the most common classes of bioorthogonal chemistries and provide a framework for matching the reactions with downstream applications. They also discuss ongoing efforts to identify novel biocompatible reactions and methods to control their reactivity. The continued expansion of the bioorthogonal toolkit will provide new insights into biomolecule networks and functions and thus refine our understanding of living systems.

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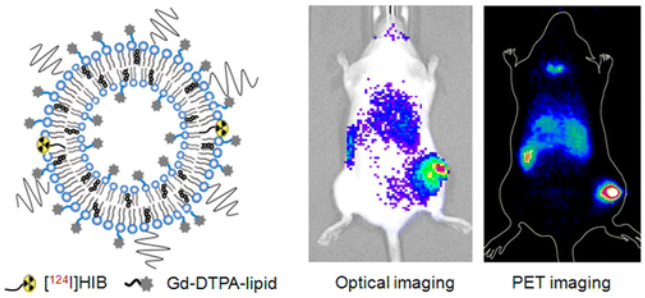
Citation: Kim, J. *et al. ACS. Med. Chem. Lett.* 2014, 5, 390-394.

Vivid Tumor Imaging Utilizing Liposome-Carried Bimodal Radiotracer

By developing a new bimodal radioactive tracer that emits both luminescence and nuclear signals, a trimodal liposome for optical, nuclear, and magnetic resonance imaging is efficiently prepared. Fast clearance of the radiotracer from reticuloendothelial systems enables vivid tumor imaging with minimum background



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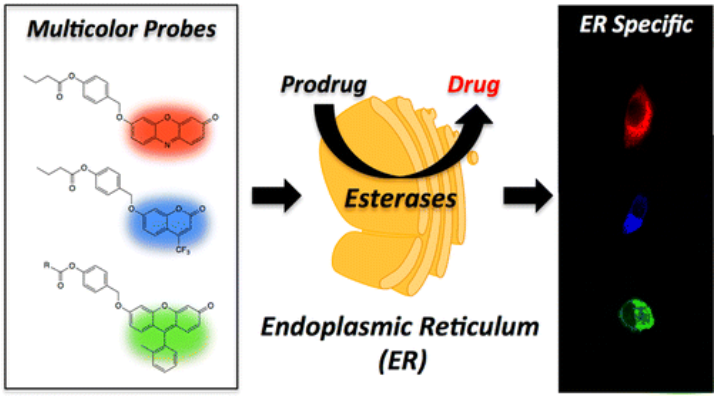
Citation: Hakamata, W. *et al. ACS. Med. Chem. Lett.* 2014, 5, 321-325.

Multicolor Imaging of Endoplasmic Reticulum-Located Esterase As a Prodrug Activation Enzyme

The carboxylesterase families of enzymes are key participants in phase I drug metabolism processes. Carboxylesterase families 1 and 2 are of particular clinical relevance. These enzymes produce endoplasmic reticulum localization signals, are primarily localized in the endoplasmic reticulum, and hydrolyze a wide range of ester-containing prodrugs into an activated form. In order to detect enzymes belonging to both families, we developed an optical multicolor imaging technique, which provides a distinct color window for multicolor imaging.



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Citation: Cui, J. *et al. ACS. Med. Chem. Lett.* 2014, 5, 272-274.

A New Challenging and Promising Era of Tyrosine Kinase Inhibitors

Protein kinases are key regulators that govern complex cellular processes. Dysregulation of kinase signaling is associated in many human diseases, particularly cancers and developmental and metabolic disorders. Tyrosine kinase inhibitors have achieved great success in molecular targeted therapies for cancer and now is expanding to other therapeutic areas. The onset of drug resistance to prolonged TKI treatment brings new challenges in TKI drug development. The deep understanding of disease pathologies related to TKs and drug resistance mechanisms will generate new waves for seeking highly selective, potent, and safe TKIs.

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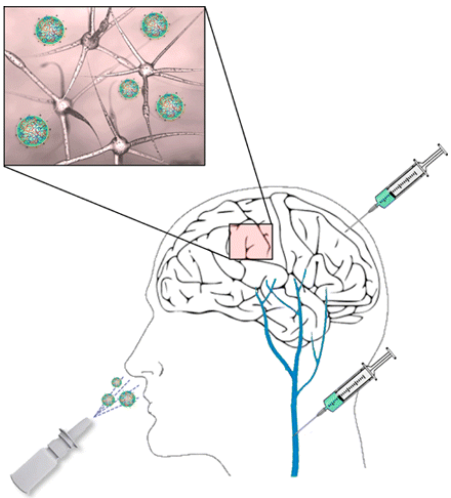
Citation: Goldsmith,M., et. al. *ACS Nano*, **2014**, 8, 1958–1965



Precision Nanomedicine in Neurodegenerative Diseases

The treatment of neurodegenerative diseases remains a tremendous challenge due to the limited access of molecules across the blood–brain barrier, especially large molecules such as peptides and proteins. Development of noninvasive approaches, such as nanostructured protein delivery carriers and intranasal administration, seem to be the most promising strategies for the treatment of chronic diseases, which require long-term interventions. These approaches are both target-specific and able to rapidly bypass the blood–brain barrier. The authors detail and discuss some of the potential pitfalls and opportunities in this field.

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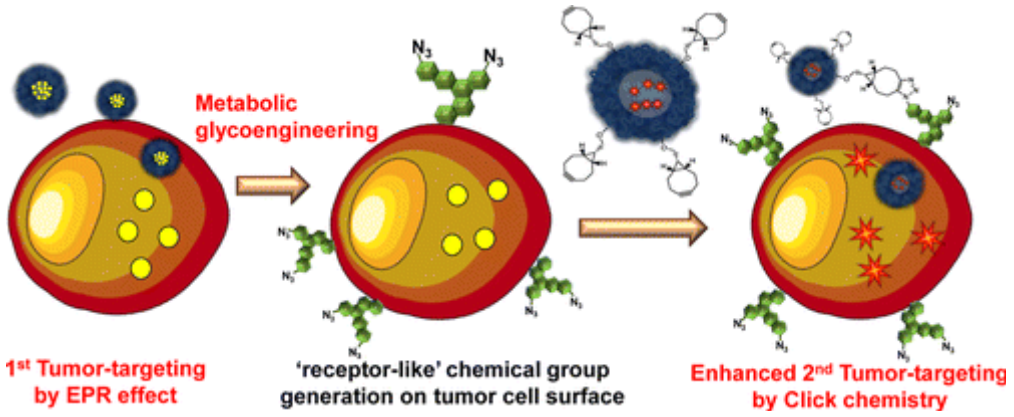
Citation: Lee, S., et. al. *ACS Nano*, **2014**, 8, 2048–2063

Chemical Tumor-Targeting of Nanoparticles Based on Metabolic Glycoengineering and Click Chemistry



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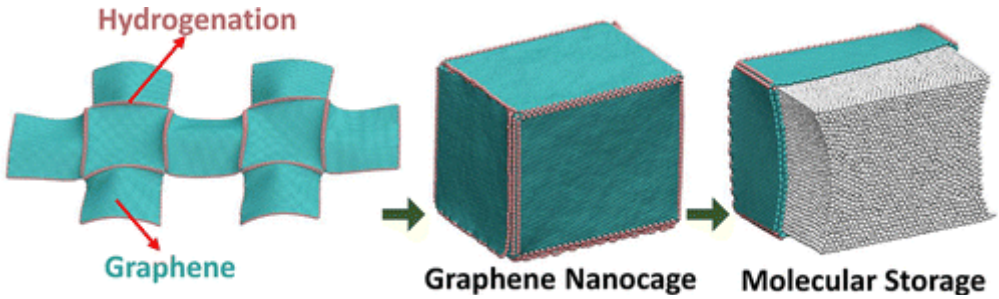
Citation: Zhu, S., et. al. *ACS Nano*, **2014**, 8, 2864–2872

Hydrogenation-Assisted Graphene Origami and Its Application in Programmable Molecular Mass Uptake, Storage, and Release



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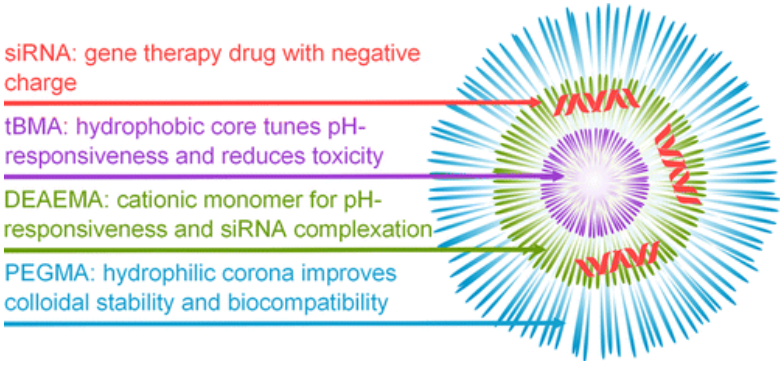
Citation: Forbes, D.C, et. al. **ACS Nano**, **2014**, 8, 2908–2917

Polycationic Nanoparticles for siRNA Delivery: Comparing ARGET ATRP and UV-Initiated Formulations



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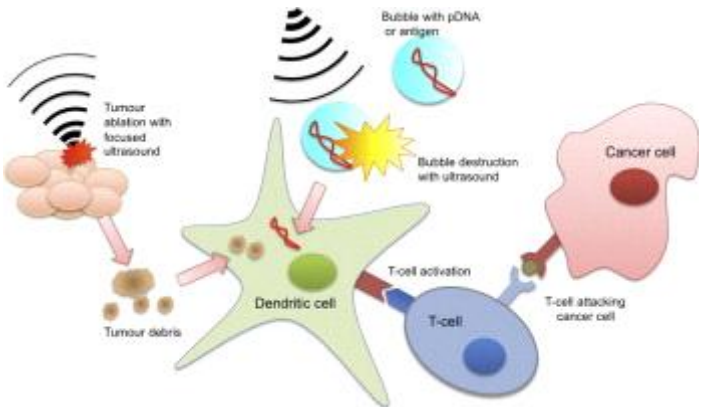
Citation: Unga, J.; Hashida, M. *Adv. Drug Del. Revs.* **2014,** *in press.*

Ultrasound induced cancer immunotherapy



Recently ultrasound has been used to expose debris from tumor tissue to immune cells to cause an immune response.

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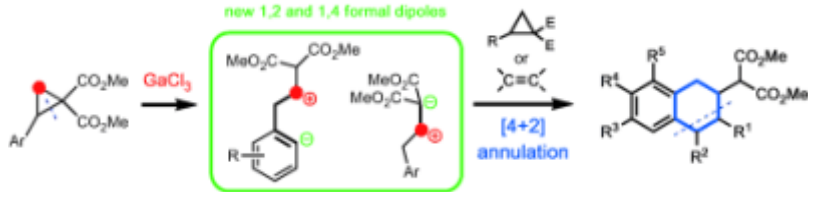
Citation: Novikov, R.; et al. *Angew. Chem. Int. Ed.* **2014**, *53 (12)*, 3187-3191.

A New Type of Donor–Acceptor Cyclopropane Reactivity: The Generation of Formal 1,2- and 1,4-Dipoles

A new type of donor–acceptor cyclopropane reactivity has been discovered. On treatment with anhydrous GaCl3, they react as sources of even-numbered 1,2- and 1,4-dipoles instead of the classical odd-numbered 1,3-dipoles owing to the migration of positive charge from the benzyl center.



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Prostratin

Citation: Trauner, D.; et al. *Angew. Chem. Int. Ed.* **2014**, *53 (12)*, 3264-3267.

A Photochromic Agonist for μ-Opioid Receptors

Photofentanyl-2 is a photochromic version of the well-known analgesic fentanyl. It is a potent agonist in the dark (or when illuminated with blue light) and loses activity when irradiated with UV light. It can be used to optically control the μ-opioid receptor, converting a G-protein-coupled receptor (GPCR) into a photoreceptor.

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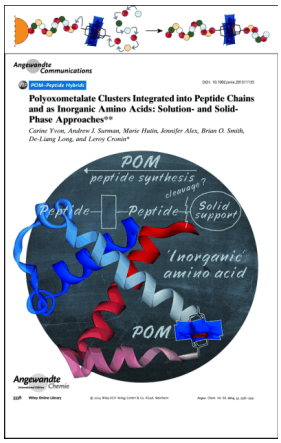
Citation: Cronin, L.; et al. *Angew. Chem. Int. Ed*. **2014**, *53 (13)*, 3336-3341.

Polyoxometalate Clusters Integrated into Peptide Chains and as Inorganic Amino Acids: Solution- and Solid-Phase Approaches

The incorporation of polyoxometalates (POMs) into peptides was realized by the use of activated precursors. Using a solution-phase approach, pre-synthesized peptides can be grafted onto the metal oxide cluster to produce hybrids of unprecedented scale. An adapted solid-phase method allows direct incorporation of these clusters during peptide synthesis as hybrid unnatural amino acids.



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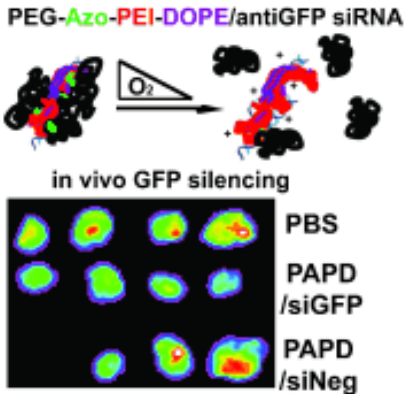
Laulimalide
Colin

Citation: Torchilin, V.; et al. *Angew. Chem. Int. Ed*. **2014**, *53 (13)*, 3362-3366.

Hypoxia-Targeted siRNA Delivery

Self-assembled nanoformulations like PEG-Azobenzene-PEI-DOPE/siRNA (PAPD/siRNA) achieved hypoxia-specific GFP downregulation in vitro and GFP downregulation in GFP-expressing tumors in vivo after intravenous administration and charge exposure (see picture). By contrast, no hypoxia specificity was observed with the nonresponsive PEG-PEI-DOPE/siRNA complexes.



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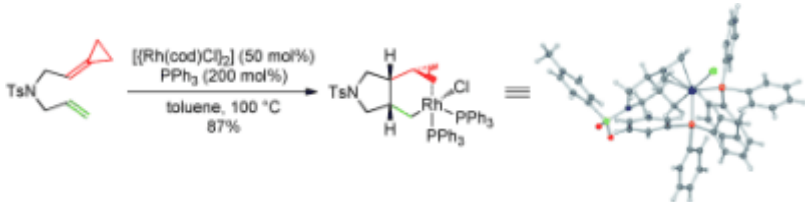
Laulimalide
Pharma

Citation: Evans, P.; et al. *Angew. Chem. Int. Ed*. **2014**, *53 (15)*, 3952-3956.

The Isolation and Characterization of a Rhodacycle Intermediate Implicated in Metal-Catalyzed Reactions of Alkylidenecyclopropanes

A rhodacycle intermediate implicated in rhodium-catalyzed reactions of alkylidenecyclopropanes (ACPs) was isolated and characterized. The structure of the metallacycle, which was unambiguously determined by X-ray crystallography, is catalytically competent in the rhodium-catalyzed carbocyclization and ene-cycloisomerization reactions of ACPs.



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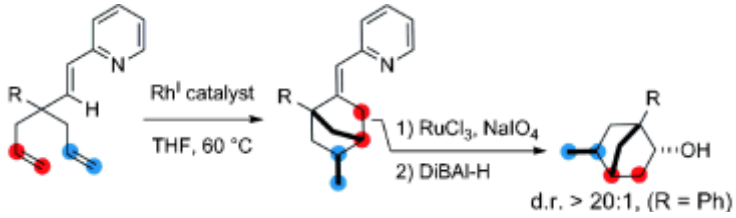
Laulimalide
Drug Deliv.

Citation: Aissa, C.; et al. *Angew. Chem. Int. Ed*. **2014**, *53 (16)*, 4209-4212.

Diastereoselective Carbocyclization of 1,6-Heptadienes Triggered by Rhodium-Catalyzed Activation of an Olefinic C-H Bond

Described is the first example of a rhodium(I)-catalyzed functionalization of an olefinic C-H bond with a 1,6-heptadiene reagent. This carbocyclization is completely diastereoselective and creates at least three stereogenic centers from simple prochiral substrates. The directing group can easily be converted into other functional groups.



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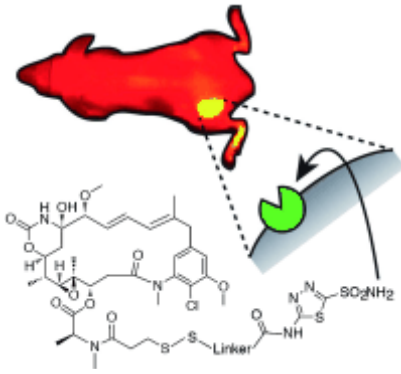
Citation: Neri, D.; et al. *Angew. Chem. Int. Ed*. **2014**, *53 (16)*, 4231-4235.

A Small-Molecule Drug Conjugate for the Treatment of Carbonic Anhydrase IX Expressing Tumors

Antibodies are currently the most widely used vehicles for drug-delivery applications. Small-molecule ligands, however, may have improved pharmacokinetics and better tissue penetration. Targeted small-molecule drug conjugates directed against the tumor marker carbonic anhydrase IX were synthesized, characterized in vitro, and tested in vivo.



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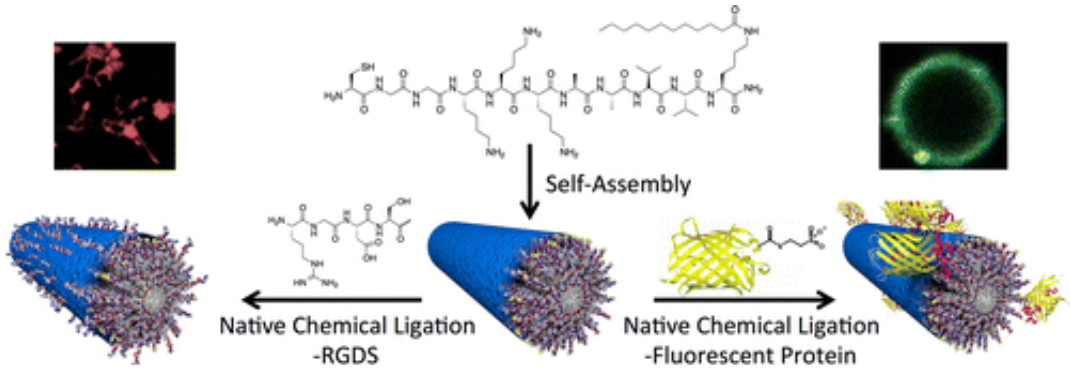
Citation: Khan, S., et. al. *Bioconjugate Chem*., **2014**, 25, 707–717

Post-Assembly Functionalization of Supramolecular Nanostructures with Bioactive Peptides and Fluorescent Proteins by Native Chemical Ligation



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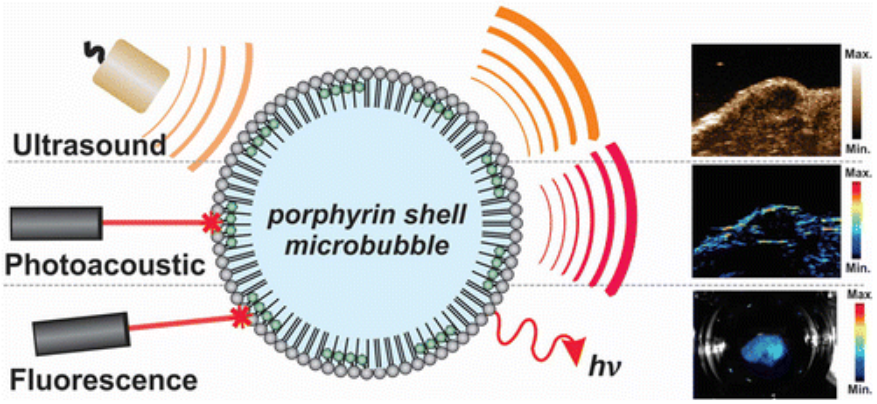
Citation: Huynh, E., et. al. *Bioconjugate Chem.*, 2014, 25, 796–801

Aggregate Enhanced Trimodal Porphyrin Shell Microbubbles for Ultrasound, Photoacoustic, and Fluorescence Imaging



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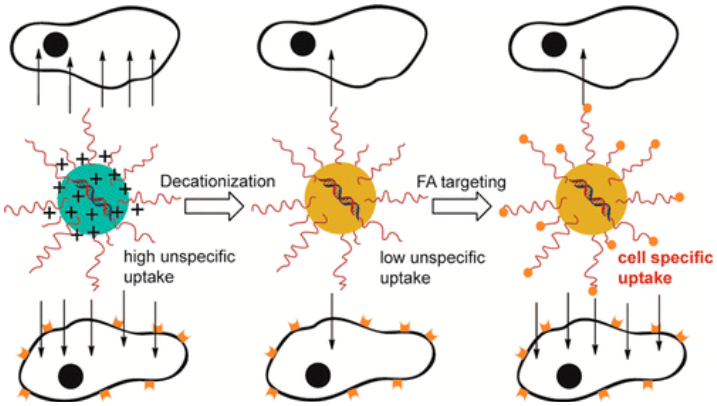
Citation: Novo, L., et.al. *Bioconjugate Chem.*, **2014**, 25, 802–812

Targeted Decationized Polyplexes for Cell Specific Gene Delivery

Decationized polyplexes have previously shown unique features, especially regarding their excellent cytocompatibility and very low degree of nonspecific cellular uptake. In the present study, targeted disulfide cross-linked decationized polyplexes were composed of a core of disulfide cross-linked poly(hydroxypropyl methacrylamide) (pHPMA) stably entrapping plasmid DNA (pDNA) and a shell of poly(ethylene glycol) (PEG) decorated with folate molecules. Folate was used as targeting ligand because of its high binding affinity to its receptor, which is overexpressed in many tumors.



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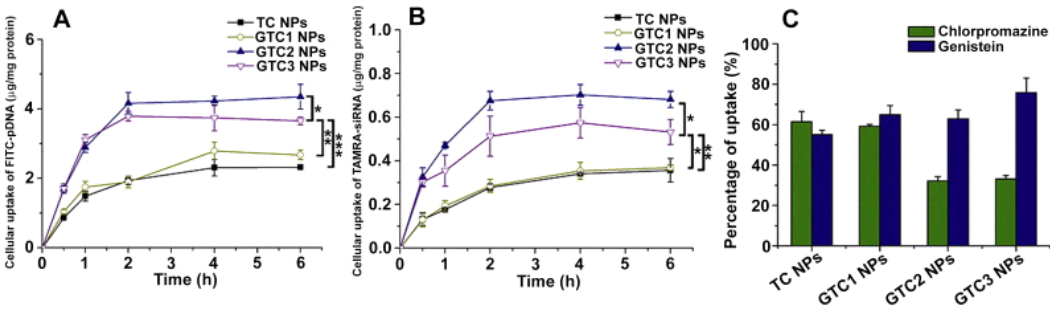
Citation: Han, L.; Tang, C.; Yin, C. Biomaterials 2014, 35, 4589–4600.

Oral delivery of shRNA and siRNA via multifunctional polymeric nanoparticles for synergistic cancer therapy



bioorganic
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DDO
Hybrid
Drug Deliv.
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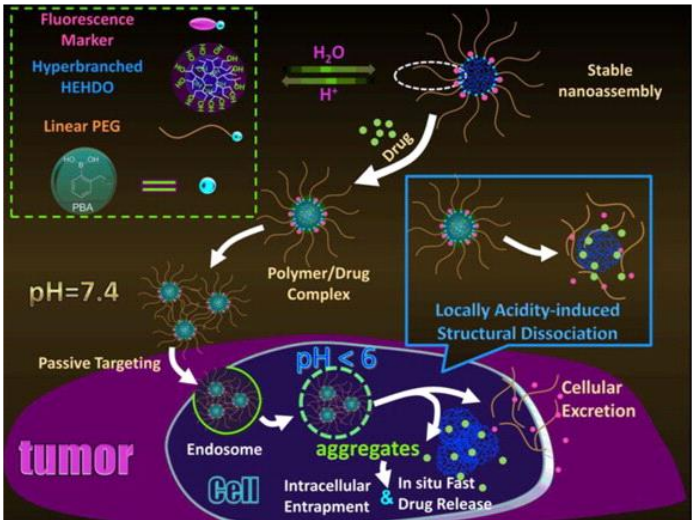
Citation: Jia, H.; Zhu, J.; Wang, X.; Cheng, H.; Chen, G.; Zhao, Y.; Zeng, X.; Feng, J.; Zhang, X.; Zhuo, R.Biomaterials 2014, 35, 5240–5249.

A boronate-linked linear-hyperbranched polymeric nanovehicle for pH-dependent tumor-targeted drug delivery



bioorganic
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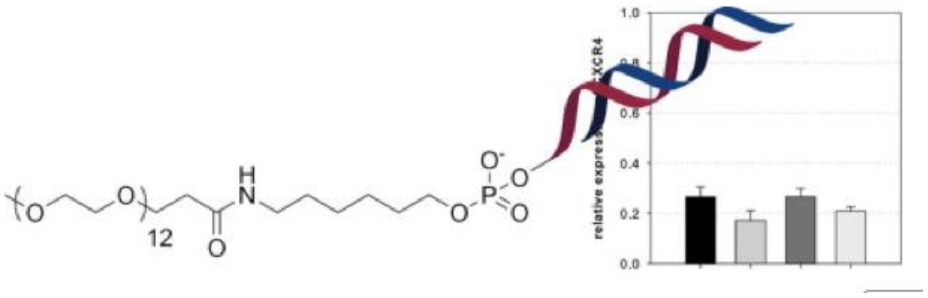
Citation:Winkler, J.; et al. *Bioorg. Med. Chem*., 22, (2014) 2320-2326

Chemically defined polyethylene glycol siRNA conjugates with enhanced gene silencing effect



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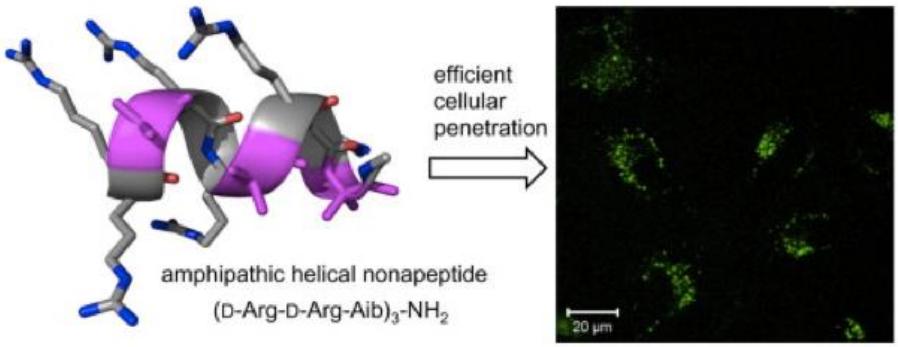
Citation: Yamashita, H.; et al. *Bioorg. Med. Chem*., 22, (2014) 2403-24083

Amphipathic short helix-stabilized peptides with cell-membrane penetrating ability



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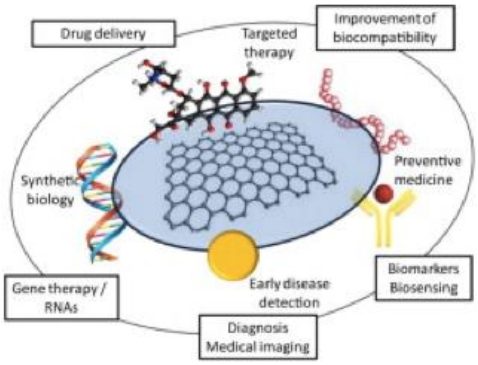
Citation: Servant, A.; et al. *Bioorg. Med. Chem. Lett.*, 24, (2014) 1638-1649

Graphene for multi-functional synthetic biology: The last 'zeitgeist' in nanomedicine



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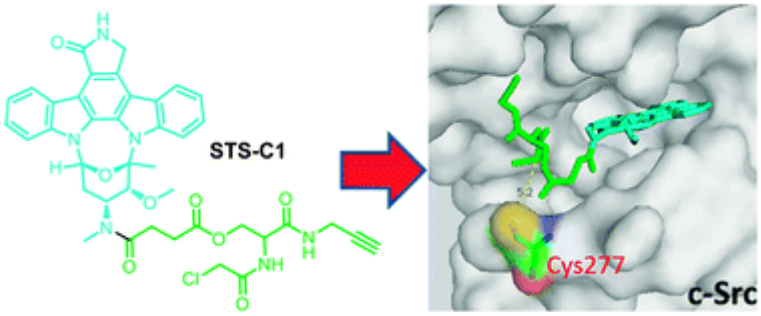
Prostratin

Citation: Cheng, X.; *et al. Chem. Commun.* **2014**, *50,* 2851.

A tuned affinity-based staurosporine probe for in situ profiling of protein kinases



A clickable and cell-permeable affinity-based probe (AfBP) was designed from staurosporine, by incorporating an electrophilic chloroacetamide warhead to facilitate in situ proteome labeling of a range of potential kinase targets.

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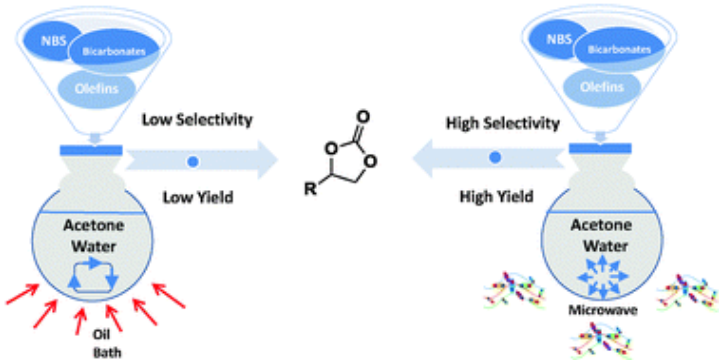
Citation: Yang, X.; *et al. Chem. Commun.* **2014** 50, 3245.

Microwave assisted synthesis of cyclic carbonates from olefins with sodium bicarbonates as the C1 source



An effective transformation of alkenes into cyclic carbonates has been achieved using NaHCO3 as the C1 source in acetone–water under microwave heating, with selectivities and yields significantly surpassing those obtained using conventional heating.

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Citation: *C&EN.* **2014**, 92(13), 29.

Patent Picks: Chinese Drug Industry

A look at recent patenting activity in the Chinese drug industry, brought to you by C&EN and CAS

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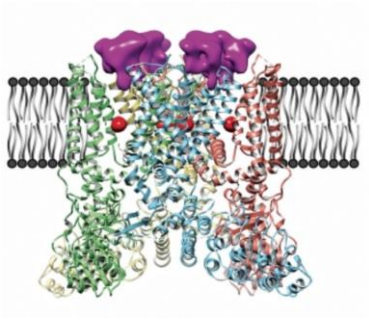
Citation: Wolf, L. *C&EN.* **2014**, 92(4), 37-39.

Drugmakers Tune To New Channels



Medicinal chemists set their sights on sensory ion channels to find pain, cancer, asthma treatments

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Citation: Duzdevich, D.; Redding, S.; Greene, E.C. Chem. Rev., 2014, 114 (6), pp 3072–3086

DNA Dynamics and Single-Molecule Biology

Recognition of DNA Sequences and Structures
DNA Structure
Single-Molecule Studies of Protein–DNA Interactions
RNA Polymerase
Nucleosomes

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Citation: Pitchiaya, S.; Heinicke, L.A.; Custer, T.C.; Walter*, N.G. Chem. Rev., 2014, 114 (6), pp 3224–3265

Single Molecule Fluorescence Approaches Shed Light on Intracellular RNAs

Cell Biology of RNA
Principles of Intracellular Single Molecule Fluorescence Microscopy of RNA
Recent Applications of Single Molecule Approaches to RNA in Cellulo

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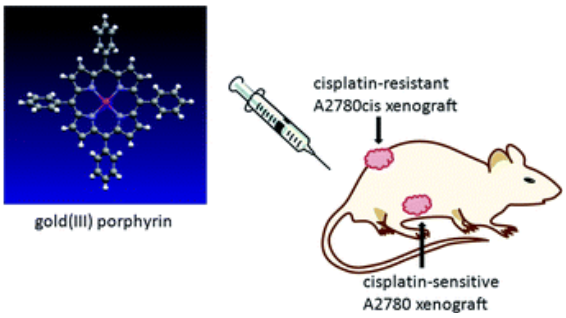
Citation: Che, C.-M., *et al.*, Chemical Science, 2014, 5, 1579-1584

Gold(III) complexes inhibit growth of cisplatin-resistant ovarian cancer in association with upregulation of proapoptotic PMS2 gene



Taken together, this work demonstrates the prospect of gold(III) complexes for the treatment of cisplatin-resistant/relapsed ovarian cancers.

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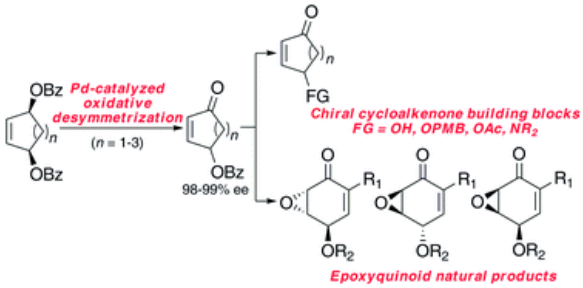
Citation: Trost, B. *et. al.*, Chemical Science, 2014, 5, 1354-1360

Asymmetric synthesis of chiral cycloalkenone derivatives via palladium catalysis



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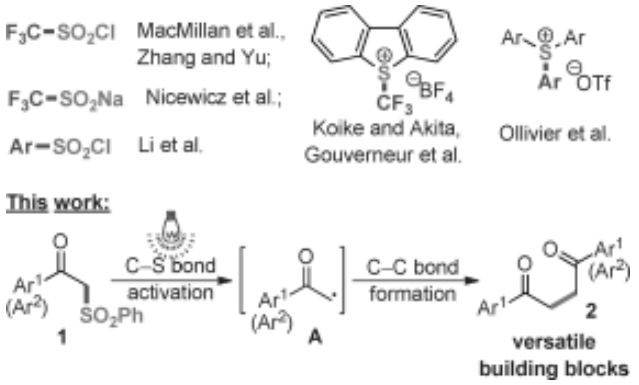
Citation: Xuan, *et al.* *Chem. Eur. J.* **2014,** 20, 3045-3049.

Visible-Light-Induced C-S Bond Activation: Facile Access to 1,4-Diketones from b-Ketosulfones

A novel method for the synthesis of 1,4-diketones from b-ketosulfones was developed by means of a visible light-induced C-S bond activation process. Symmetrical and unsymmetrical 1,4-diketones can be easily prepared in moderate to good yields



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Citation: Li, L. *et al.* *Chem. Eur. J.* **2014,** 20, 3050-3060.

Urea-Based Porous Organic Frameworks: Effective Supports for Catalysis in Neat Water

Two urea-based porous organic frameworks, UOF-1 and UOF-2, were synthesized through a urea-forming condensation of 1,3,5-benzenetriisocyanate with 1,4-diaminobenzene and benzidine, respectively. UOF-1 and UOF-2 possess good hydrophilic properties and high scavenging ability for palladium. Their palladium polymers, PdII/UOF-1 and PdII/UOF-2, exhibit high catalytic activity and selectivity for Suzuki–Miyaura cross-coupling reactions and selective reduction of nitroarenes in water. The catalytic reactions can be efficiently performed at room temperature. Palladium nanoparticles with narrow size distribution were formed after the catalytic reaction and were well dispersed in UOF-1 and UOF-2. XPS analysis confirmed the coordination of the urea oxygen atom with palladium. SEM and TEM images showed that the original network morphology of UOF-1 and UOF-2 was maintained after palladium loading and catalytic reactions

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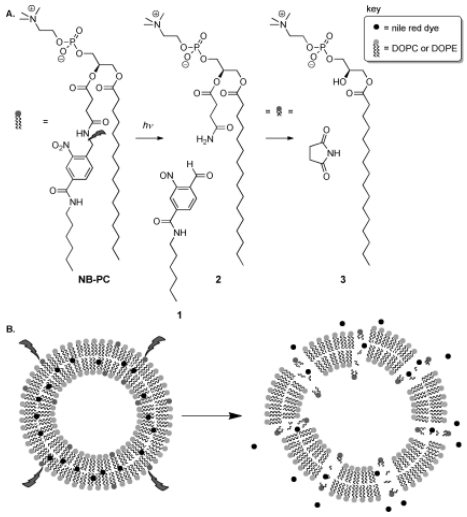
Citation: Bayer, A. *et al.* *Chem. Eur. J.* **2014,** 20, 3350-3357.

Triggered Liposomal Release through a Synthetic Phosphatidylcholine Analogue Bearing a Photocleavable Moiety Embedded within the sn-2 Acyl Chain

Liposomes represent promising carriers for drug delivery applications. To maximize this potential, there has been significant interest in developing liposomal systems encapsulating molecular cargo that are highly stable until their contents are released remotely in a controlled manner. Herein, we describe the design, synthesis, and analysis of a photocleavable analogue of the ubiquitous lipid phosphoatidylcholine (PC) for the development of highly stable and controllable photodisruptable membranes. Our strategy was to develop a lipid that closely mimics the structure of PC to optimize favorable properties including biocompatibility and stability of subsequent liposomes when mixed with lipids possessing a broad range of physicochemical properties.



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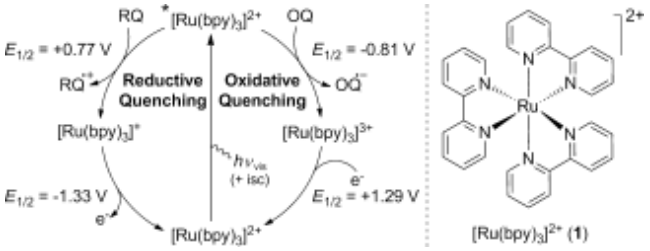
Citation: Hopkinson, M. *et al. Chem. Eur. J.* **2014,** 20, 3874-3886.

Dual Catalysis Sees the Light: Combining Photoredox with Organo-, Acid, and Transition-Metal Catalysis

The photoredox activation of organic substrates with visible light is a powerful methodology that generates reactive radical species under very mild conditions. When combined with another catalytic process in a dual catalytic system, novel, visible-light-promoted transformations have been realized that do not proceed using either catalyst in isolation. In this minireview, the state of the art in organic reactions mediated by dual catalytic systems merging photoredox activation with organo-, acid or metal catalysis is discussed.



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Citation: Moo, J. *et al. Chem. Eur. J.* **2014,** 20, 4292-4296.

Biomimetic Artificial Inorganic Enzyme-Free Self-Propelled Microfish Robot for Selective Detection of Pb2+ in Water

Anthropogenic pollutants of water, such as heavy-metal ions, are major problems in water contamination. The toxicity assays used range from cell assays to animal tests. Herein, we replace biological toxicity assays, which use higher organisms, with artificial inorganic self-propelled microtubular robots. The viability and activity of these robots are negatively influenced by heavy metals, such as Pb2+, in a similar manner to that of live fish models. This allows the establishment of a lethal dose (LD50) of heavy metal for artificial inorganic microfish robots. The self-propelled microfish robots show specific response to Pb2+ compared to other heavy metals, such as Cd2+, and can be used for selective determination of Pb2+ in water. It is a first step towards replacing the biological toxicity assays with biomimetic inorganic autonomous robotic systems.

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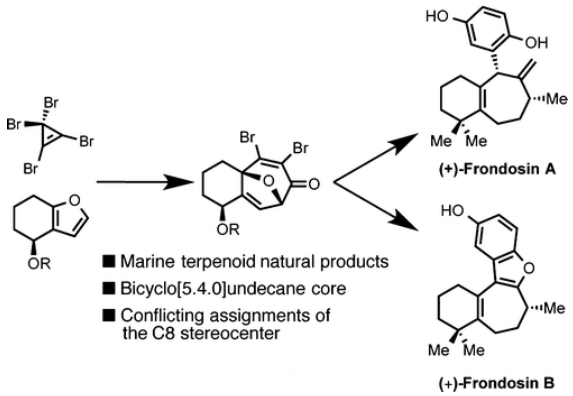
Citation: Oblak, E.Z.; VanHeyst, M.D.; Li, J.; Wiemer, A.J.; Wright, D.L. *J. Am. Chem. Soc.*, **2014**, *136* (11), 4309-4315.

Cyclopropene Cycloadditions with Annulated Furans: Total Synthesis of (+)- and (-)-Frondosin B and (+)-Frondosin A



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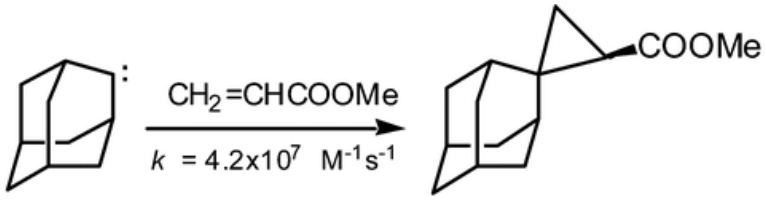
Citation: Moss, R.A.; Wang, L.; Krogh-Jespersen, K. *J. Am. Chem. Soc.*, **2014**, *136* (13), 4885-4888.

The Nucleophilicity of a Dialkylcarbene: Unusual Activation Parameters for Additions of Adamantanylidene to Simple Alkenes



E_a = -3.6 kcal/mol; $\Delta H^{\ddagger}$ = -4.1 kcal/mol; $\Delta S^{\ddagger}$ = -38 e.u.; $\Delta G^{\ddagger}$ = 7.1 kcal/mol. Adamantanylidene reacts as a *nucleophilic* carbene toward common alkenes

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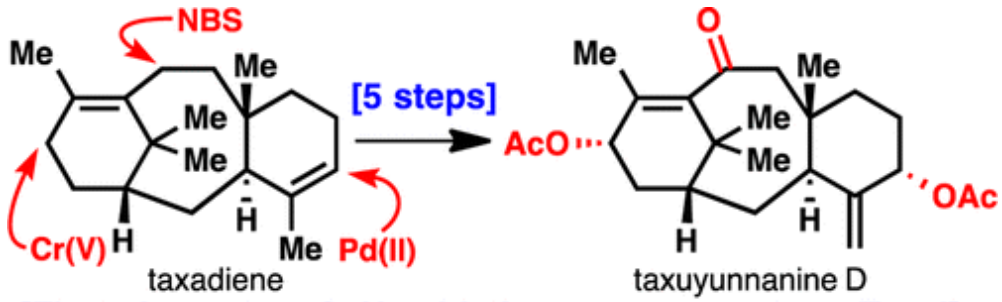
Citation: Wilde, N.C.; Isomura, M.; Mendoza, A.; Baran, P.S. *J. Am. Chem. Soc.*, **2014**, *136* (13), 4909-4912.

Two-Phase Synthesis of (-)-Taxuyunnanine D



[First elementary C–H oxidation steps en route to Taxol]

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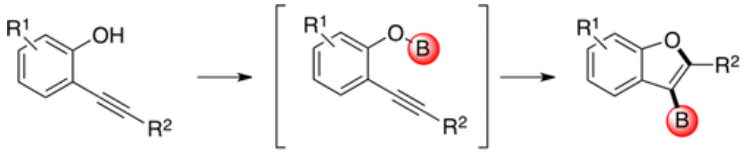
Citation: Hirner, J. J. et al. J. Am. Chem. Soc., 2014, 136 (12), pp 4740–4745

Alkoxyboration: Ring-Closing Addition of B-O sigma Bonds across Alkynes



- B–O σ bond activation
- previously unavailable organoboron products
- up to 83% yield
- gram-scale reactivity

An alkoxyboration reaction, the addition of boron–oxygen sigma bonds to alkynes, was reported. Functionalized O-heterocyclic boronic acid derivatives are produced using this transformation, which is mild and exhibits broad functional group compatibility.

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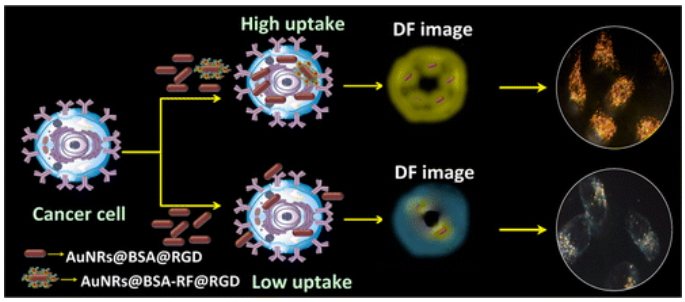
Citation: Ali, M. R. K. J. Am. Chem. Soc., 2014, 136 (12), pp 4464–4467



Rifampicin (RF) is known for its ability to enhance the accumulation of anticancer drugs in multidrug resistant (MDR) cancer cells. RF-conjugated AuNPs can greatly enhance the rate as well as efficiency of endocytosis of NPs and hence their concentration inside the cancer cell. Cell viability results showed a remarkable enhancement in the photothermal therapeutic effect of Au nanorods in presence of RF.

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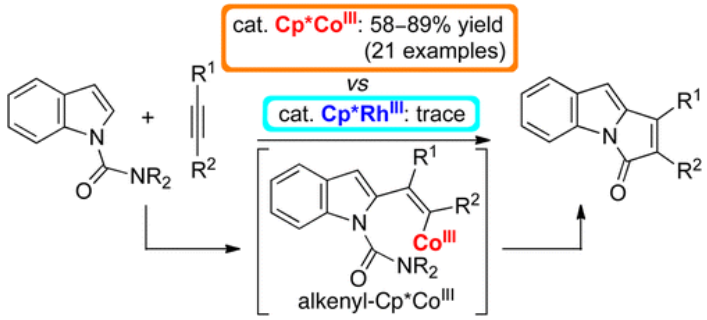
Citation: Ikemoto, H. et al. J. Am. Chem. Soc., 2014, 136 (14), pp 5424–5431



A C2-selective indole alkenylation/annulation sequence proceeded smoothly with catalytic amount of a [Cp*CoIII(C6H6)](PF6)2 complex and KOAc. Intramolecular addition of an alkenyl-Cp*Co species to a carbamoyl moiety gave pyrroloindolones in 58–89% yield in one pot. Clear difference was observed between the catalytic activity of the Cp*CoIII complex and those of Cp*RhIII complexes, highlighting the unique nucleophilic activity of the organocobalt species.

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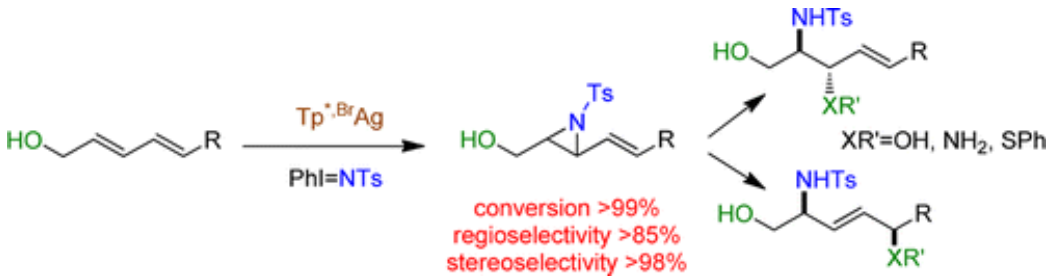
Citation: Llaveria, J. et al. J. Am. Chem. Soc., 2014, 136 (14), pp 5342–5350

Chemo-, Regio-, and Stereoselective Silver-Catalyzed Aziridination of Dienes: Scope, Mechanistic Studies, and Ring-Opening Reactions



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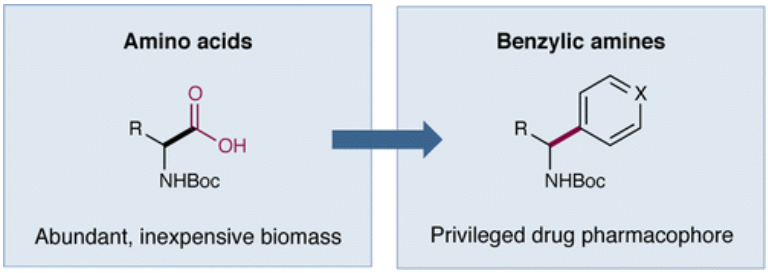
Citation: Zuo, Z.; MacMillan, D. W. C. J. Am. Chem. Soc., 2014, 136 (14), pp 5257–5260

Decarboxylative Arylation of a-Amino Acids via Photoredox Catalysis: A One-Step Conversion of Biomass to Drug Pharmacophore



The direct decarboxylative arylation of a-amino acids has been achieved via visible light-mediated photoredox catalysis. This method offers rapid entry to prevalent benzylic amine architectures from an abundant biomass, specifically a-amino acid precursors. Significant substrate scope is observed with respect to both the amino acid and arene components.

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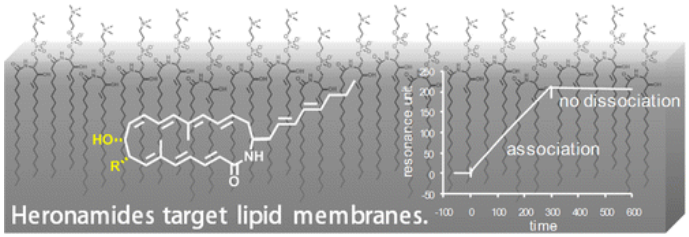
Citation: Sugiyama, R. et. al. J. Am. Chem. Soc., 2014, 136 (14), pp 5209–5212

Structure and Biological Activity of 8-Deoxyheronamide C from a Marine-Derived Streptomyces sp.: Heronamides Target Saturated Hydrocarbon Chains in Lipid Membranes



8-deoxyheronamide C, a new 20-membered polyene macrolactam from a marine-derived actinomycete Streptomyces sp., is a unique membrane binder. 8-Deoxyheronamide C showed a characteristic sensitivity profile against fission yeast sterol mutant cells, indicating that the metabolite targets cell membranes. Tight physical interaction between heronamides including 8-deoxyheronamide C and heronamide C and saturated hydrocarbon chains in lipid membranes was detected using surface plasmon resonance experiments.

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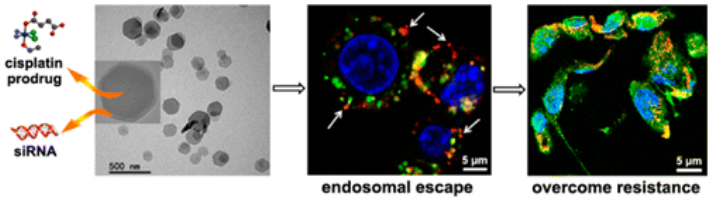
Citation: He, C. et. al. J. Am. Chem. Soc., 2014, 136 (14), pp 5181–5184

Nanoscale Metal–Organic Frameworks for the Co-Delivery of Cisplatin and Pooled siRNAs to Enhance Therapeutic Efficacy in Drug-Resistant Ovarian Cancer Cells



Nanoscale metal–organic frameworks (NMOFs) was used for co-delivery of cisplatin and pooled small interfering RNAs (siRNAs) to enhance therapeutic efficacy by silencing multiple drug resistance (MDR) genes and resensitizing resistant ovarian cancer cells to cisplatin treatment. UiO NMOFs with hexagonal-plate morphologies were loaded with a cisplatin prodrug and MDR gene-silencing siRNAs (Bcl-2, P-glycoprotein [P-gp], and survivin) via encapsulation and surface coordination, respectively. NMOFs protect siRNAs from nuclease degradation, enhance siRNA cellular uptake, and promote siRNA escape from endosomes to silence MDR genes in cisplatin-resistant ovarian cancer cells. Co-delivery of cisplatin and siRNAs with NMOFs led to an order of magnitude enhancement in chemotherapeutic efficacy in vitro.

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Citation: Laufer, S.; Bajorath, J. *J. Med. Chem.* **2014**, *57* (6), 2167.

New Frontiers in Kinases: Second Generation Inhibitors

A brief editorial mentioning that four journals (ACS Chemical Biology, ACS Medicinal Chemistry Letters, Biochemistry, and the Journal of Medicinal Chemistry) will publish special issues dedicated to New Frontiers in Kinases in the first quarter of 2015.

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Gnid/Kirk
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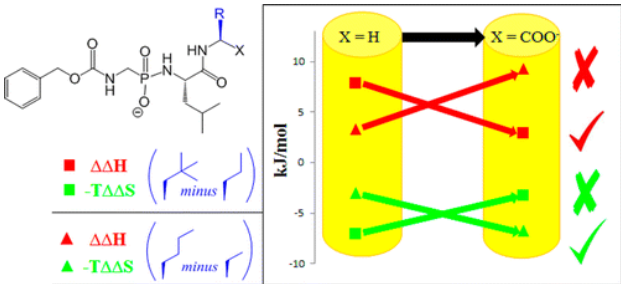
Citation: Nasief, N. N.; Hangauer, D. *J. Med. Chem.* **2014**, *57* (6), 2315.

Influence of Neighboring Groups on the Thermodynamics of Hydrophobic Binding: An Added Complex Facet to the Hydrophobic Effect

The thermodynamic consequences of systematic modifications in a ligand side chain that binds in a shallow hydrophobic pocket, in the presence and absence of a neighboring ligand carboxylate group, were evaluated using isothermal titration calorimetry (ITC). This study could improve our understanding of the hydrophobic effect and may enhance our ability to design potent ligands that are capable of modulating biological processes.



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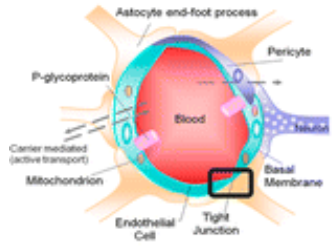
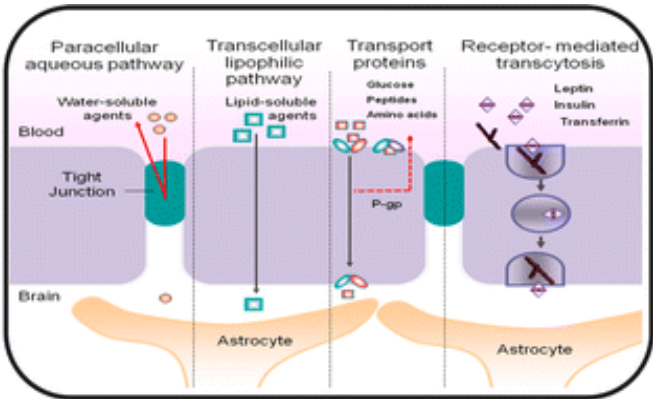
OM
Bryo
Gnid/Kirk
Hybrid
Drug Deliv.
Prostratin

Citation: Lalatsa, A.; Schatzlein, A. G.; Uchegbu, I. F. Mol. Pharmaceutics 2014, 11, 1081–1093.

Strategies To Deliver Peptide Drugs to the Brain





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DDO
Hybrid
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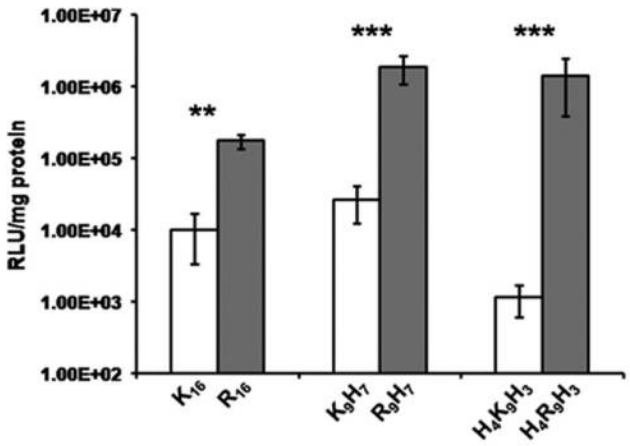
Prostratin

Citation: Mann, A.; Shukla, V.; Khanduri, R.; Dabral, S.; Singh, H.; Ganguli, M. . Mol. Pharmaceutics 2014, 11, 683–696.



Linear Short Histidine and Cysteine Modified Arginine Peptides Constitute a Potential Class of DNA Delivery Agents

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Hybrid
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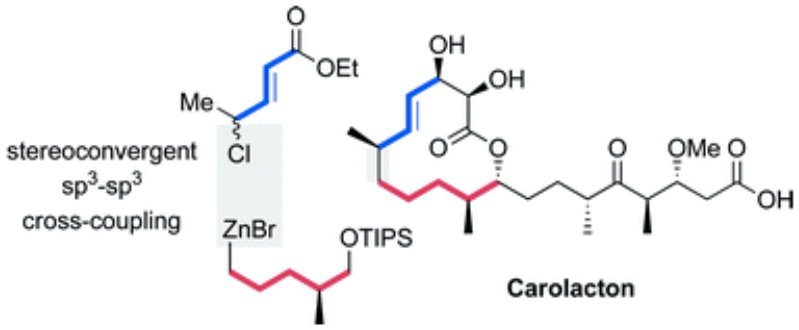
Citation: Geist, E., Kirsching, A., Schmidt, T., *Nat. Prod. Rep.* 31 (2014) 441-448

sp3-sp3 Coupling reactions in the synthesis of natural products and biologically active molecules



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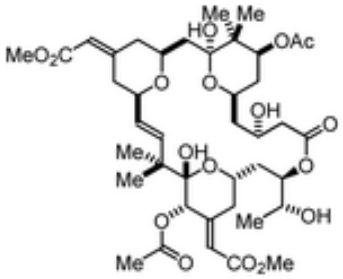
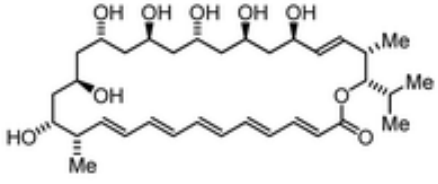
Citation: Kriche, M. J.; et al. *Nat. Prod. Rep.,* 31 (2014) 504-513

Polyketide construction via hydrohydroxyalkylation and related alcohol C–H functionalizations: reinventing the chemistry of carbonyl addition



BRYOSTATIN 7
20 Steps (LLS), 5 C-C Bonds Formed
via Hydrogen Mediated C-C Coupling



(+)-ROXATICIN
20 Steps (LLS), 8 C-C Bonds Formed
via Hydrogen Mediated C-C Coupling

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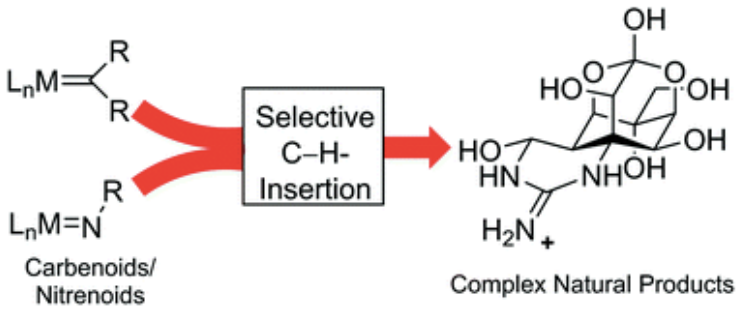
Citation: Egger, J., Carreira, E.M., *Nat. Prod. Rep.*, 31 (2014) 449-455

Efficient synthesis strategies by application of transition metal-catalyzed carbene/nitrene insertions into C–H bonds



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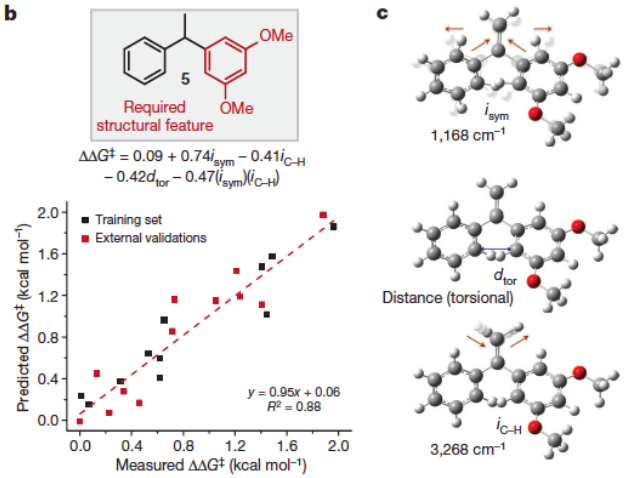
Citation: Milo, A.; Bess, E.N.; Sigman, M.S. *Nature*. **2014**, *507*, 210.

Interrogating selectivity in catalysis using molecular vibrations



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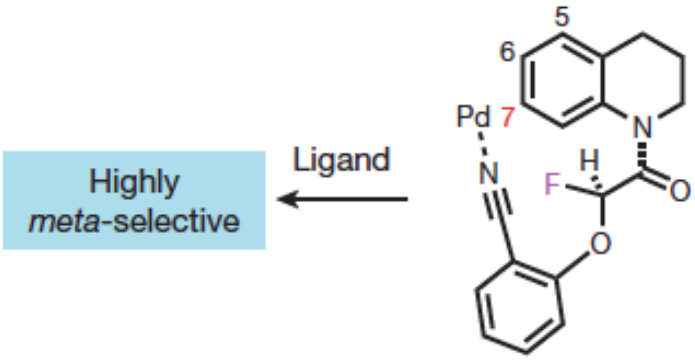
Citation: Tang, R.-Y.; Li, G.; Yu, J.-Q. *Nature*. **2014**, *507*, 215.

Conformation-induced remote *meta*-C-H activation of amines



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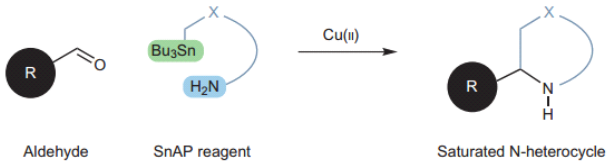
Citation: Vo, C.-V., T.; Luescher, M.U.; Bode, J.W. Nature Chemistry 6, 310–314 (2014)

SnAP reagents for the one-step synthesis of medium-ring saturated N-heterocycles from aldehydes



We describe the development of SnAP (Sn amino protocol) reagents for the transformation of aldehydes into seven-, eight- and nine-membered saturated N-heterocycles. This process occurs under mild, room-temperature conditions and offers exceptional substrate scope and functional-group tolerance. Air- and moisture-stable SnAP reagents are prepared on a multigram scale from inexpensive starting materials by simple reaction sequences. These new reagents and processes allow widely available aryl, heteroaryl and aliphatic aldehydes to be converted into diverse N-heterocycles, including diazepanes, oxazepanes, diazocanes, oxazocanes and hexahydrobenzoxazonines, by a single synthetic operation.

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Citation: Li, J.; Yu, J.; Zhao, J.; Wang, J.; Zheng, S.; Lin, S.; Chen, L.; Yang, M.; Jia, S.; Zhang, X.; Chen, P.R. Nature Chemistry 6, 352–361 (2014)

Palladium-triggered deprotection chemistry for protein activation in living cells

Employing small molecules or chemical reagents to modulate the function of an intracellular protein, particularly in a gain-of-function fashion, remains a challenge. In contrast to inhibitor-based loss-of-function approaches, methods based on a gain of function enable specific signalling pathways to be activated inside a cell. Here we report a chemical rescue strategy that uses a palladium-mediated deprotection reaction to activate a protein within living cells. We identify biocompatible and efficient palladium catalysts that cleave the propargyl carbamate group of a protected lysine analogue to generate a free lysine. The lysine analogue can be genetically and site-specifically incorporated into a protein, which enables control over the reaction site. This deprotection strategy is shown to work with a range of different cell lines and proteins. We further applied this biocompatible protection group/catalyst pair for caging and subsequent release of a crucial lysine residue in a bacterial Type III effector protein within host cells, which reveals details of its virulence mechanism.

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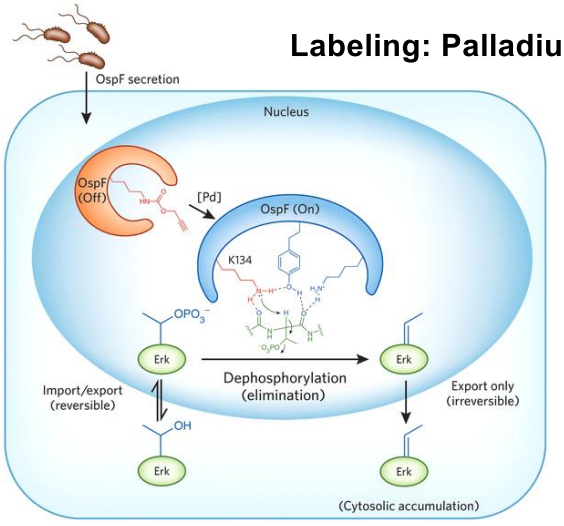
Citation: Qian, K. et. al. *Nature Chemical Biology*. **2014**, 10, 328–330

Labeling: Palladium brings proteins to life



A bioorthogonal decaging strategy, mediated by small-molecule palladium compounds, can recover the lysine-dependent activity of cellular proteins. This activation technique could be generally applicable for controlling and probing function of a protein target in living cells.

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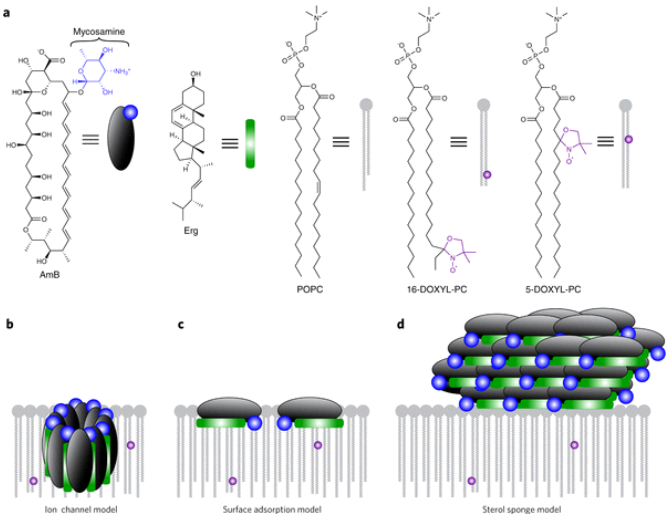
Citation: Anderson, T.M., *Nature Chemical Biology*. **2014**, 10, 400–406.

Amphotericin forms an extramembranous and fungicidal sterol sponge

Amphotericin remains a powerful but highly toxic last line of defense in treating life-threatening fungal infections. In the widely accepted ion channel model for its mechanism of cytocidal action, amphotericin forms aggregates inside lipid bilayers that permeabilize and kill cells. In contrast, we report that amphotericin exists primarily in the form of large, extramembranous aggregates that kill yeast by extracting ergosterol from lipid bilayers. These findings reveal that extraction of a polyfunctional lipid underlies the resistance-refractory antimicrobial action of amphotericin.



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Citation: http://www.nytimes.com/2014/04/08/business/cancer-analysis-tools-circumvent-biopsies.html

Sidestepping the Biopsy With New Tools to Spot Cancer

For people with cancer or suspected cancer, a biopsy is a necessary evil - an uncomfortable and somewhat risky procedure to extract tissue for diagnosis or analysis. Telltale traces of a tumor are often present in the blood. These traces - either intact cancer cells or fragments of tumor DNA - are present in minuscule amounts, but numerous companies are now coming to market with sophisticated tests that can detect and analyze them such as liquid biopsies, which can be easier to repeat, and can potentially track the disease as it evolves.

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Citation: http://www.nytimes.com/2014/04/09/business/international/japanese-drug-maker-ordered-to-pay-6-billion-over-cancer-claims.html?_r=0

Jury Awards $9 Billion in Damages in Drug Case

In one of the biggest damages verdicts ever imposed, a jury in Louisiana has ordered a Japanese drug maker and its American partner to pay a combined $9 billion in punitive damages over a diabetes drug that has been linked to cancer.
Jurors in a district court tiral in Lafayette, La., ordered the Japanese company, Takeda Pharmaceutical, to pay $6 billion in punitive damages on Monday after finding that the company had hidden the cancer risks of its drug, Actos. The jury also ordered Takeda's partner, Eli Lilly, which once marketed the drug in the US, to pay $3 billion.

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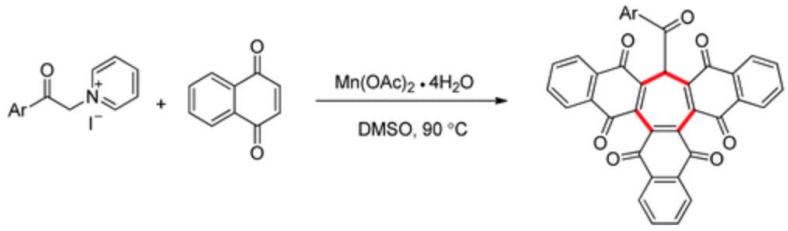
Citation: Wu, A-X.; et al. *Org. Lett.* **2014**, 16 (5), 1286-1289

An Efficient Synthesis of Novel Fused Cycloheptatrienes through Mn(II)-Mediated Formal Intermolecular [2 + 2 + 2 + 1] Cycloaddition



A new method for manganous acetate tetrahydrate mediated formal intermolecular [2 + 2 + 2 + 1] cycloaddition was developed for the synthesis of fused cycloheptatriene derivatives from *N*-(acylmethyl)pyridinium iodides and naphthoquinone. This method provides an innovative route for the efficient and convenient construction of fused seven-membered carbocycles from simple starting materials.

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Citation: Dong, L.; et al. *Org. Lett.* **2014**, 16 (6), 1684-1687.

Highly Functionalized Pyridines Synthesis from *N*-Sulfonyl Ketimines and Alkynes Using the N–S Bond as an Internal Oxidant

The N-S bond-based internal oxidant offers a distinct approach for the synthesis of highly functionalized pyridines. A novel Rh(III)-catalyzed one-pot process undergoes an efficient C-C/C-N bond formation along with desulfonylation under very mild conditions. The method is quite simple, general, and efficient.

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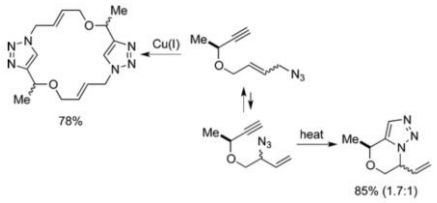
Citation: Aube, J.; et al. *Org. Lett.* **2014**, 16 (7), 1844-1847

A Concomitant Allylic Azide Rearrangement/Intramolecular Azide-Alkyne Cycloaddition Sequence



An intramolecular Huisgen cycloaddition of an interconverting set of isomeric allylic azides with alkynes affords substituted triazoles in high yield. The stereoisomeric vinyl-substituted triazoloxazines formed depend on the rate of cycloaddition of the different allylic azide precursors when the reaction is carried out under thermal conditions. In contrast, dimerized macrocyclic products were obtained when the reaction was done using copper(I)-catalyzed conditions, demonstrating the ability to control the reaction products through changing conditions.

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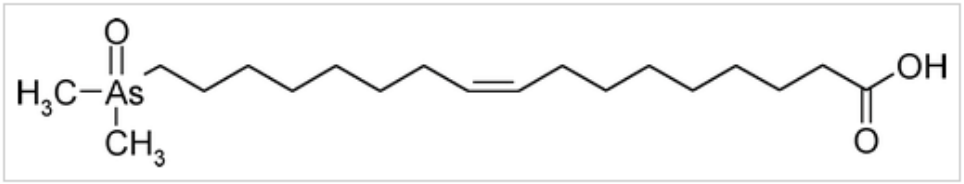
Citation: Taleshi, M.S. et al. *Organometallics*. **2014**, *33*, 1397.

Synthesis and Characterization of Arsenolipids: Naturally Occurring Aresnic Compounds in Fish and Algae



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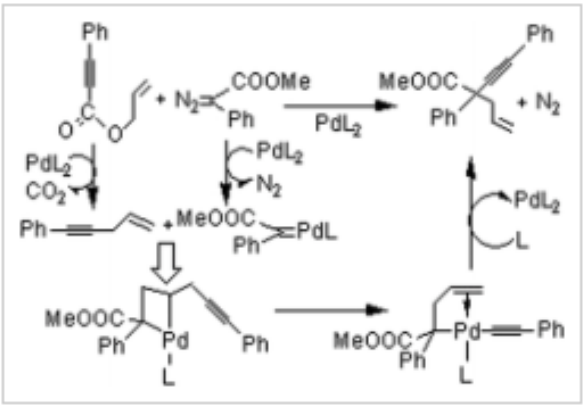
Citation: Wang, H.; Yang, X.; Liu, Y.; Bi, S. *Organometallics*. **2014**, *33*, 1404.

Theoretical Studies on a New Class of C-C Bond Formation: Palladium-Catalyzed Reactions of a-Diazocarbonyl Compounds with Allylic Esters



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Citation: Bertozzi, et al. PNAS **April 15, 2014** vol. 111 no. 15 **5456-5461**

Imaging bacterial peptidoglycan with near-infrared fluorogenic azide probes

Fluorescent probes designed for activation by bioorthogonal chem- istry have enabled the visualization of biomolecules in living systems. Such activatable probes with near-infrared (NIR) emission would be ideal for in vivo imaging but have proven difficult to engineer. The authors present the development of NIR fluorogenic azide probes based on the Si-rhodamine scaffold that undergo a fluorescence enhancement of up to 48-fold upon reaction with terminal or strained alkynes. They used the probes for mammalian cell surface imaging and, in con- junction with a new class of cyclooctyne D-amino acids, for visualiza- tion of bacterial peptidoglycan without the need to wash away unreacted probe.

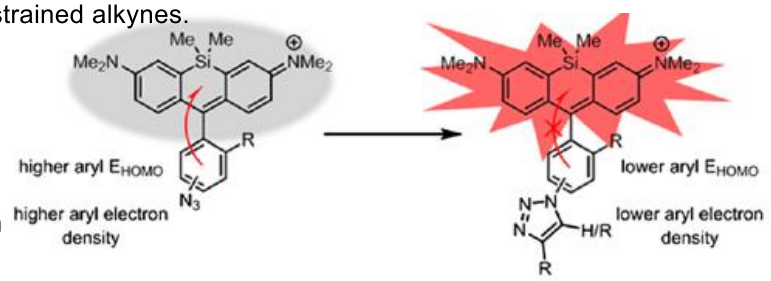

Fig. 1. Design of a PeT-based fluorogenic azido Si-rhodamine.

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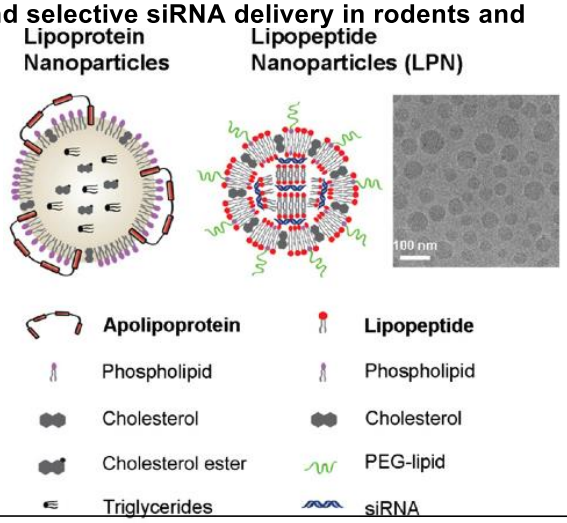
Citation: Langer et al. PNAS **March 18, 2014** vol. 111 no. 11 **3955-3960**

Lipopeptide nanoparticles for potent and selective siRNA delivery in rodents and nonhuman primates

siRNA therapeutics have promise for the treatment of a wide range of genetic disorders. Motivated by lipoproteins, we report lipopeptide nanoparticles as potent and selective siRNA carriers with a wide therapeutic index. These particles were shown to be extremely potent and selective for hepatocytes in both mouse and primate models.



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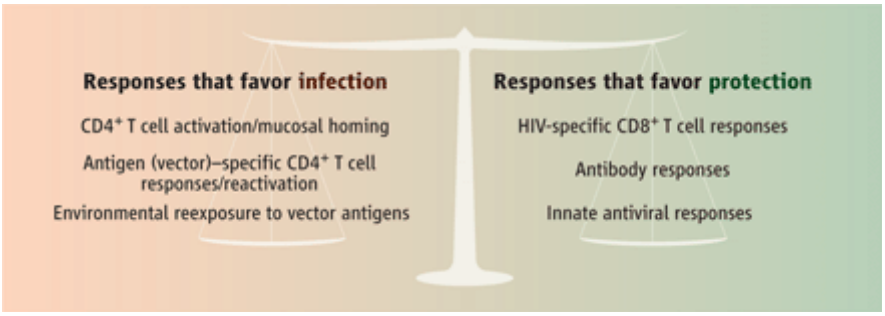
Citation: Fauci, A.S., et. al. *Science*. **2014**, 344, 49-51

Immune Activation with HIV Vaccines



Immune activation associated with HIV vaccination theoretically can lead to increased infection due to the activation of CD4+ T cells during the immune response. The level of protection seen with a vaccine can be viewed as the balance between the responses to the vaccine that lead to susceptibility to infection and by the responses that favor protection.

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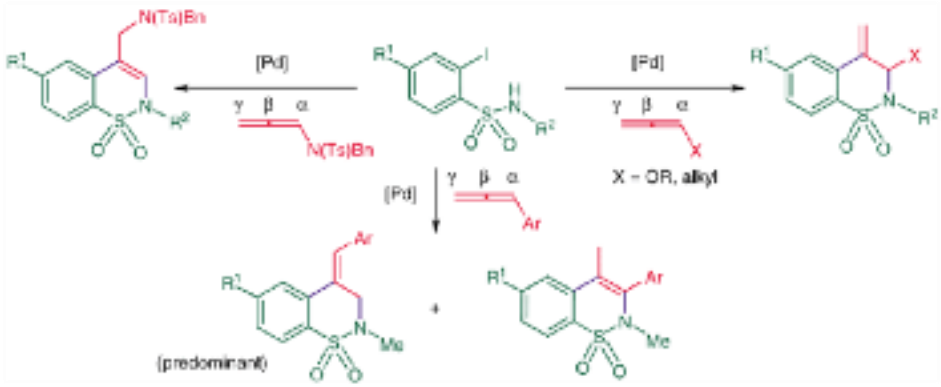
Citation: Nagarjuna Reddy, M.; Kumara Swamy, K. C. *Synthesis*, **2014**, 46(08), 1091.

Palladium-Catalyzed Reactions of Allenes with 2-Iodobenzenesulfonamides: Simple Synthesis of Benzosultams under Green Conditions



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Citation: Qian, Zhen-Chao; Zhou, Jun; Li, Bo; Shi, Bing-Feng; *Synlett*, **2014**, 07(25), 1036.

Efficient Synthesis of Isoquinolines via Rh(III)-Catalyzed Oxidative Annulation of Picolinamides with Alkynes

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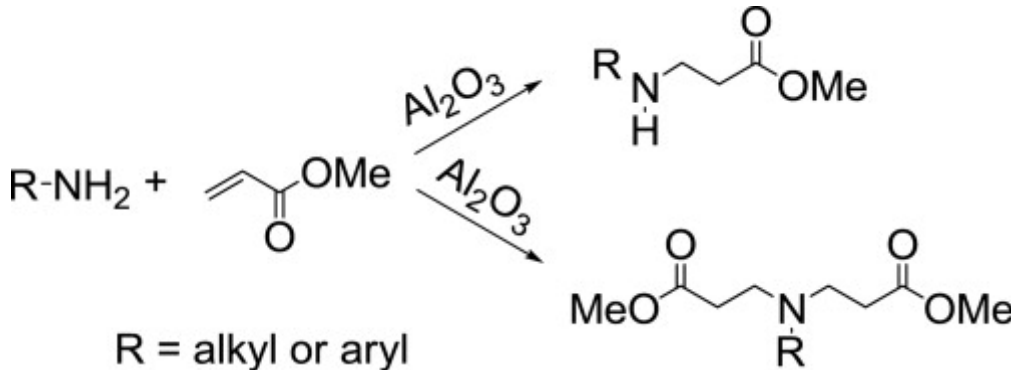
Citation: Bosica, Giovanna; Spiteri, Jonathan; Borg, Caroline *Tetrahedron* 70 (**2014**) 2449–2454

Aza-Michael reaction: selective mono- versus bis-addition under environmentally-friendly conditions



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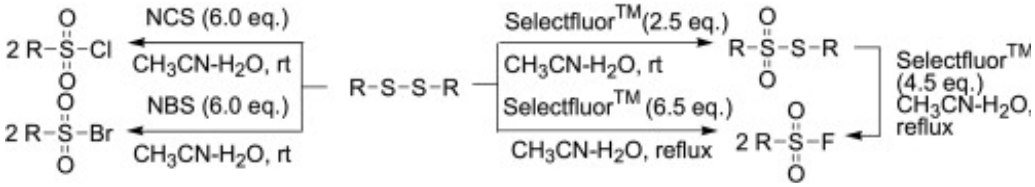
Citation: Kirihara, Masayuki; Naito, Sayuri; *et al.* *Tetrahedron*. 70 (**2014**) 2464–2471

Oxidation of disulfides with electrophilic halogenating reagents: concise methods for preparation of thiosulfonates and sulfonyl halides



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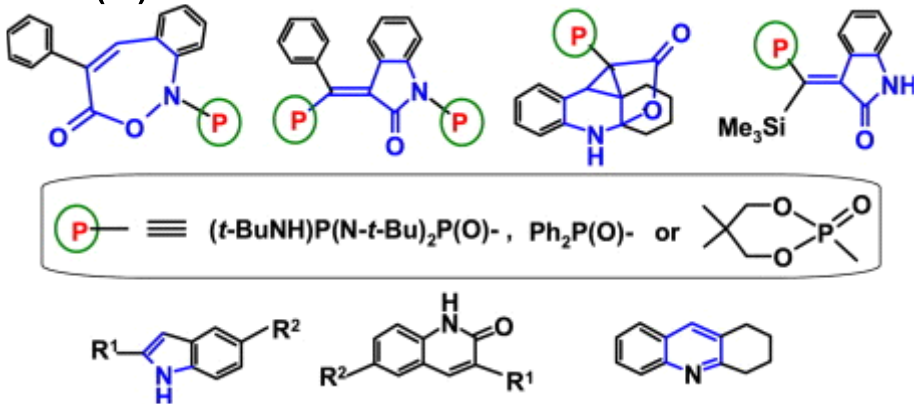
Citation: Gangadhararao, G.; Swamy, K.C. Kumara. *Tetrahedron* **2014**, 70, 2643–2653

Unusual nitrogen based heterocycles via allenic intermediates from the reaction of propargyl alcohols with P(III) substrates



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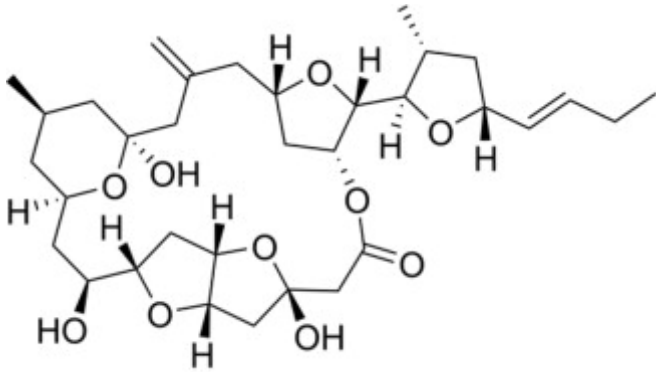
Citation: Tominagab, Akira; Tsuda, Masashi; *et al*. *Tetrahedron* **2014** 70, 2962–2965

Iriomoteolide-13a, a cytotoxic 22-membered macrolide from a marine dinoflagellate Amphidinium species



Iriomoteolide-13a

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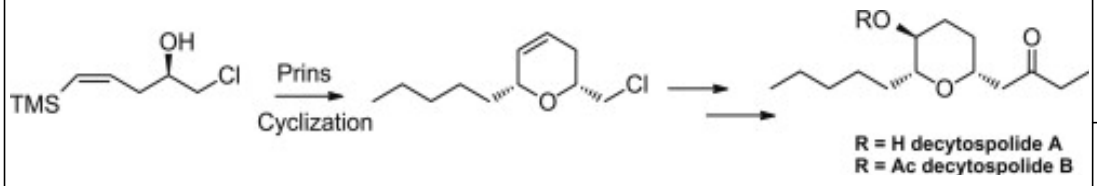
Citation: Clarisse, D.; Fache, F.; Tetrahedron Letters, 2014, 55 (14), 2221-2222

Application of Prins cyclization to the total synthesis of (+)-decytospolides A and B



(+)-Decytospolides A and B, natural products containing the tetrahydropyran skeleton, were synthesized via Prins cyclization as the key step.

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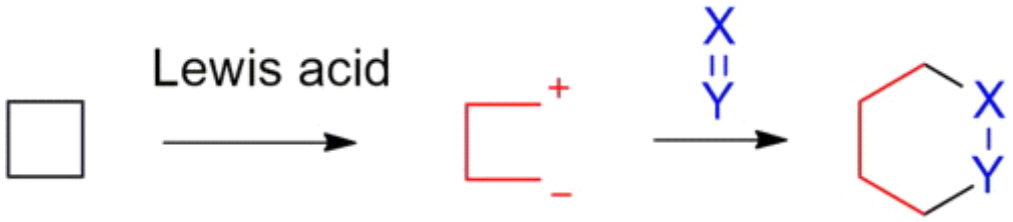
Citation:Matsuo, J.; Tetrahedron Letters, 2014, 55 (16), 2589-2595

1,4-Zwitterionic intermediates formed by cleavage of a cyclobutane ring and their cycloaddition reactions



Cycloaddition reaction is an efficient organic reaction because all of the substrate components are introduced into a product skeleton. Recently, more than six-membered rings have been synthesized by Lewis acid-promoted ring cleavage of a cyclobutane ring followed by addition to an unsaturated bond. Typical examples in the literature of these types of reactions using 1-donor–2-acceptor cyclobutanes and 3-donor cyclobutanones with Lewis acids are presented in this Letter.

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