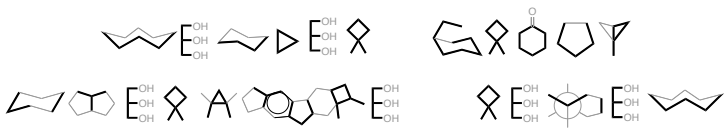


Volume 37 / Issue 03 15 March 2012

Next Due Date: Monday, 16 April 2012

Instructions for Authors (*Volume 37*)

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.

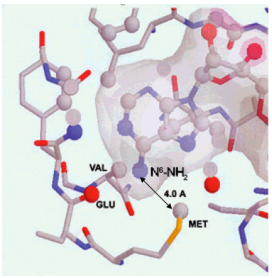
Include a brief textual summary of the article; an example of a completed abstract is shown below. The list of topics and subgroups on the right is useful to highlight which subgroups should pay attention to your abstract and roughly what kind of chemistry the article contains.

Please email the files to lmieuli@stanford.edu. Late abstracts will be included in the Lit Review for the following month. **PC Users should submit their abstracts as PDFs** or purchase a Mac.

Citation: Abeyweera, T.P.; Rotenberg, S.A. *Biochemistry* **2007**, *46*, 2364-2370

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 (1c-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.



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Citation: Dictionary.com (search term = "mook")

For those of you who always wanted to know what it meant....
mook **Pronunciation Key** (mk) *n. Slang*
An insignificant or contemptible person.

methods
synthesis

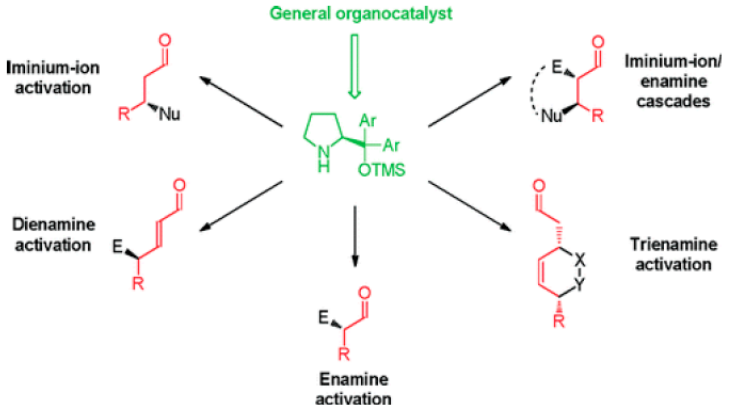
DON'T BE A MOOK!

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 not receive a printed copy of the Lit Review.
- You will get last choice when it's time to pick new journals.
- We will crack your corn (clean in half)

Citation: Jensen, K. L. *et al*. Acc. Chem. Res. 2011, 45, 248-264.

The Diarylprolinol Silyl Ether System: A General Organocatalyst.



http://pubs.acs.org/doi/abs/10.1021/ar200149w

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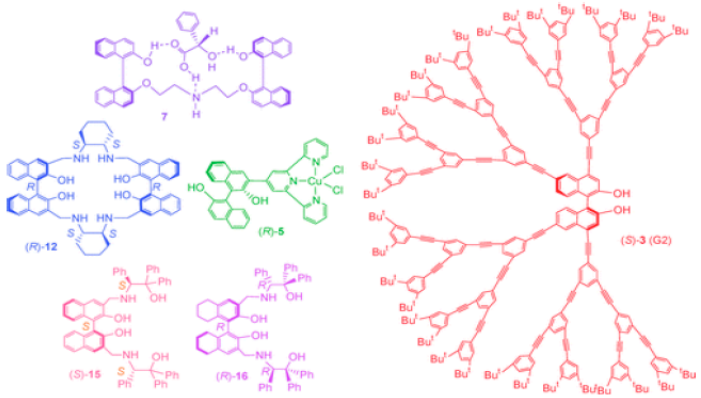
Prostratin

Citation: Pu, L. Acc. Chem. Res. 2011, 45, 150-163.

Enantioselective Fluorescent Sensors: A Tale of BINOL.



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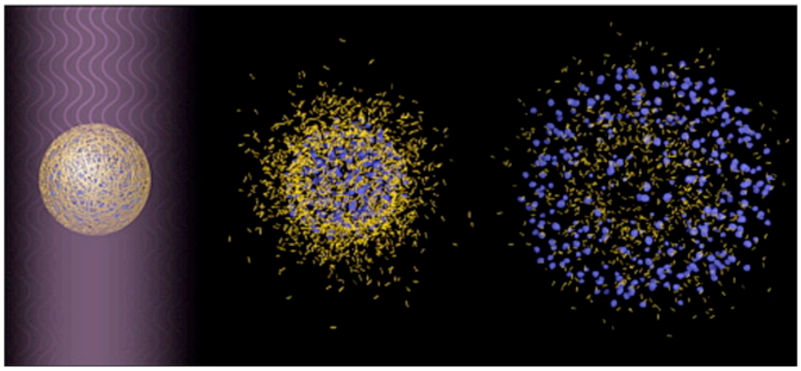
Citation: Fomina, N.; Sankaranarayanan, J.; Almutairi, A. *Adv. Drug Deliv. Rev.* **2012** *ASAP*

Photochemical Mechanisms of Light-Triggered Release from Nanocarriers



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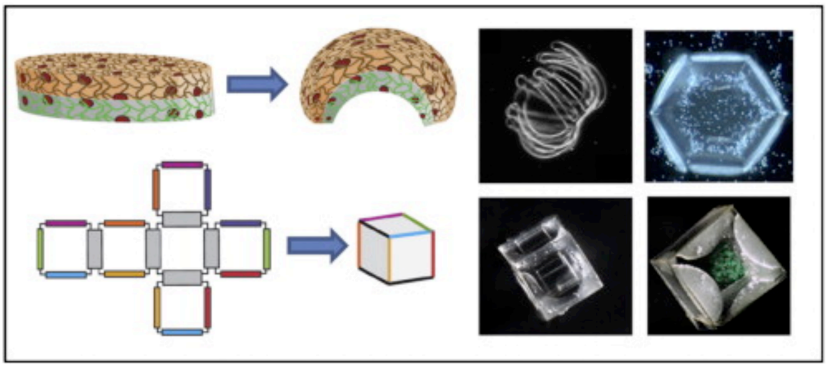
Citation: Fernandes, R.; Gracias, D.H. *Adv. Drug Deliv. Rev.* **2012** *ASAP*

Self-Folding Polymeric Containers for Encapsulation and Delivery of Drugs



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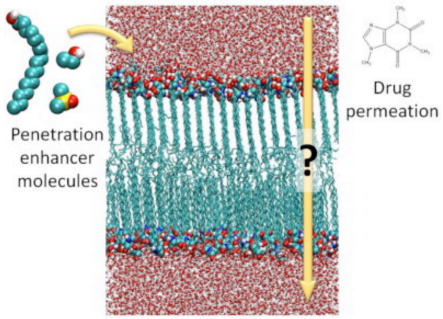
Citation: Notman, R.; Anwar, J. *Adv. Drug Deliv. Rev.* **2012** *ASAP*

Breaching the Skin Barrier - Insights from Molecular Simulation of Model Membranes



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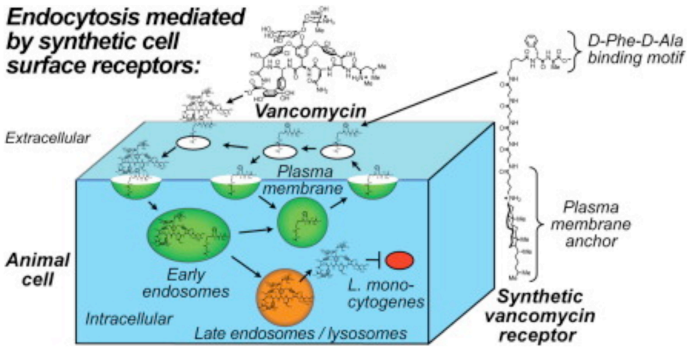
Citation: Hymel, D.; Peterson, B.R. *Adv. Drug Deliv. Rev.* **2012** *ASAP*

Synthetic Cell Surface Receptors for Delivery of Therapeutics and Probes



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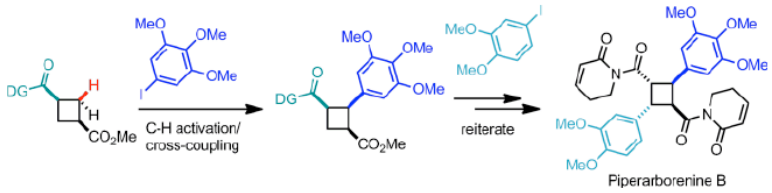
Citation: *Angew. Chem. Int. Ed.* **2012**, 51, 2815 – 2817.



Activate and reiterate: The activation of C(sp3)[BOND]H bonds is a highly desirable transformation because molecular complexity can be increased at the expense of the most simple and readily available organic linkage. In recent contributions this approach was used for coupling reactions with small all-carbon rings, as exemplified by the sequential C[BOND]H activation steps in an elegant total synthesis of the piperarborenines

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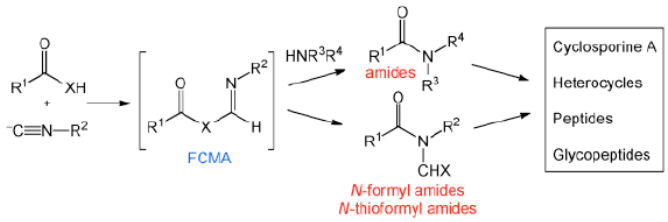
Citation: A*ngew. Chem. Int. Ed.* **2012**, 51, 2834 – 2848.



New take on an old classic: Recent explorations in the field of isonitrile chemistry led to the development of an array of broadly useful coupling methods for the formation of peptidyl and glycopeptidyl amide bonds. The methods were applied to the syntheses of complex systems, including the cyclic peptide cyclosporine A, constrained peptide systems, and heterocycles (see scheme; FCMA=formimidate carboxylate mixed anhydride).

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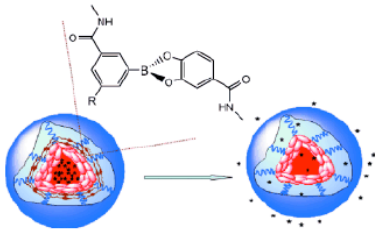
Citation: *Angew. Chem. Int. Ed.* **2012**, 51, 2864 –2869



Demand and deliver: Micelles reversibly crosslinked by boronate esters (see scheme) show in vitro and in vivo stability, and thus minimize premature drug release under physiological conditions. After reaching the tumor sites, drug (stars in scheme) release is activated by cleavage of the boronate esters by the acidic conditions around the tumor or in the target cells, or by the administration of mannitol.

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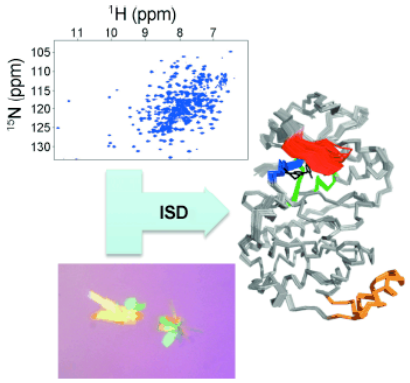
Citation: *Angew. Chem. Int. Ed.* **2012**, 51, 2359 –2362.



Complex problem: The crystal structure of p38? mitogen-activated protein kinase in complex with a dibenzo[a,d]cycloheptenone inhibitor was found to be incompatible with NMR data of the same complex in solution. By using inferential structure determination (ISD) with restraints from X-ray crystallography and NMR spectra, a structure that is compatible with both data sets and very close to the X-ray crystal structure was generated

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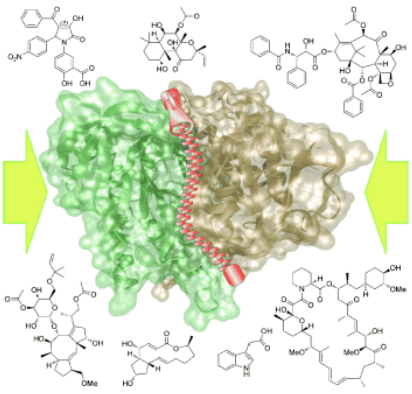
Citation: *Angew. Chem. Int. Ed.* **2012**, 51, 2012 – 2018



Doing it the other way round: The modulation of protein–protein interactions (PPIs) by small molecules has become increasingly popular over the last few decades. However, "modulation" has mainly been perceived as "inhibition" of protein–protein interactions, omitting the complementary strategy of stabilizing such macromolecular complexes. This Minireview highlights amazing examples and the potential of this constructive side of modulating PPIs.

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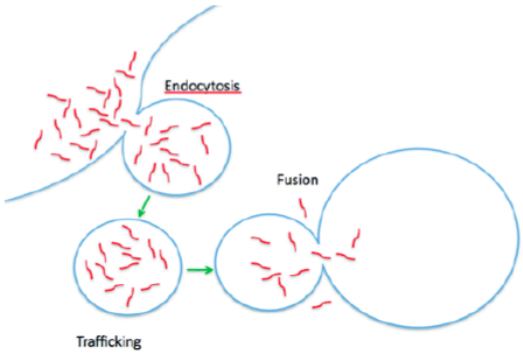
Citation: Juliano, R.L. et al. *Bioconjugate Chemistry* **2012** 23 (2), 147-157.

Review: Cellular Uptake and Intracellular Trafficking of Antisense and siRNA Oligonucleotides



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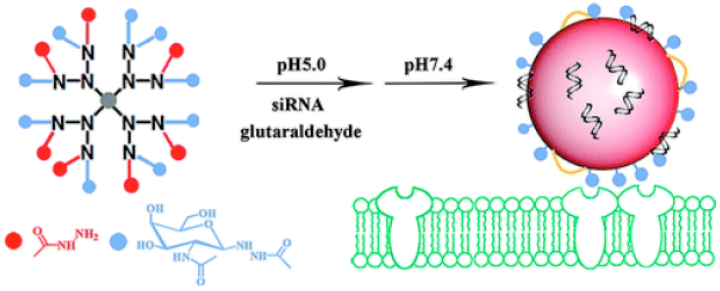
Citation: Liu, J. et al. *Bioconjugate Chemistry* **2012** 23 (2), 174-183.

SiRNA Delivery Systems Based on Neutral Cross-Linked Dendrimers



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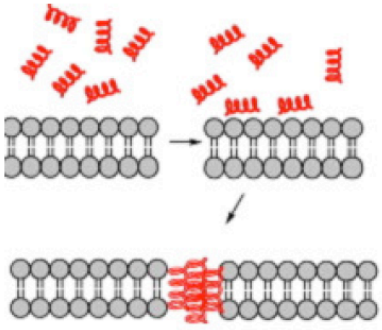
Citation: Russell, A. L. *et al. Bioorg. Med. Chem.* **2011**, *20* (5), 1723.

The effect of the length and flexibility of the side chain of basic amino acids on the binding of antimicrobial peptides to zwitterionic and anionic membrane model systems



The authors found that the hydrophobicity and charge distribution of amino acids in a spacer in the peptides contribute to their antimicrobial activity.

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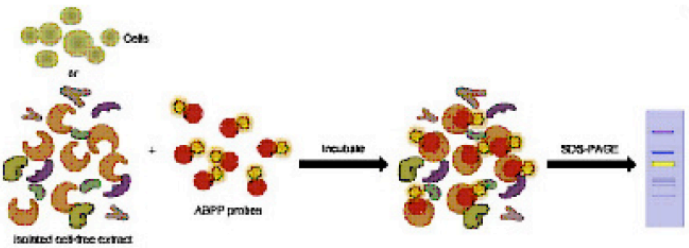
Citation: Azad, M. A.; Wright, G. D. *Bioorg. Med. Chem.* **2011**, *20* (6), 1929.

Determining the mode of action of bioactive compounds

Highlights challenges and advances in studying bioactive compound-target interactions.



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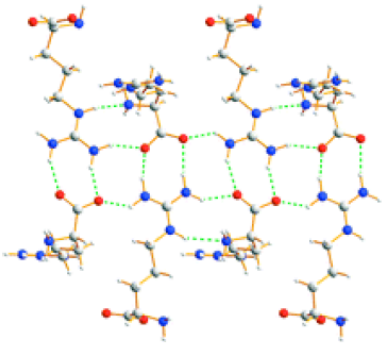
Citation: Courvoisier, E.; Williams, P. A.; Lim, G. K.; Hughes, C. E.; Harris, K. D. M. *Chem. Commun.* **2012**, *48* (22), 2761.

The crystal structure of L-arginine



The crystal structure of L-arginine was determined from powder X-ray diffraction data. Previously, L-arginine was one of the few natural amino acids whose crystal structure was unknown.

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Morrissey, S. R. *Chemical & Engineering News.* **2012**, *90* (8), 7.

Obama Continues R&D Support

President Barack Obama is requesting $140.8 billion for federal R&D in his fiscal 2013 budget, which was rolled out on Feb. 13. The total R&D budget—which includes defense and nondefense work—is 1.4%, or $2.0 billion, more than it was in fiscal 2012. It increases funding for basic science research and for science, technology, engineering, and mathematics (STEM) education.

The increases are significant because the discretionary part of the budget, which funds nonmandatory programs such as R&D, is frozen at 2011 levels. Discretionary funding represents about one-third of the overall $3.8 trillion proposed budget.

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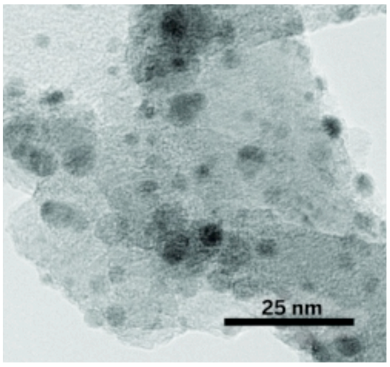
Jacoby, M. *Chemical & Engineering News*. **2012**, *90* (8), 9.



Iron Nanoparticles for Olefin Synthesis

A new iron-based carbon-carbon coupling catalyst may enable biomass to serve as an economically feasible source of the common feedstocks ethylene and propylene, according to a study conducted in the Netherlands (*Science,*DOI: **10.1126/science.1215614**). The advance could lead to environmentally attractive ways to produce the compounds, which are traditionally derived from petroleum sources.

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Schulz, W. G. *Chemical & Engineering News*. **2012**, *90* (9), 9.

Uncertain Path for H5N1 Research

How to move forward with controversial research on the H5N1 avian flu virus, including publication of two papers reporting on recent experimental work, has grown murkier in the wake of a Feb. 17 statement from the World Health Organization.

According to WHO, an expert panel it convened "reached consensus on two urgent issues related to the newly created H5N1 influenza viruses: extending the temporary moratorium on research with new laboratory-modified H5N1 viruses and recognizing that research on naturally occurring H5N1 influenza virus must continue in order to protect public health." The statement also says that the panel supports full publication of two research papers on the work, accepted by Nature and Science, "however, there are significant public health concerns surrounding this research that should first be addressed."

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Borman, S. *Chemical & Engineering News*. **2012**, *90* (9), 8.

Single-Atom Transistor

In work that could advance the development of quantum computers, researchers have created a transistor that consists of a single atom positioned precisely between two electrodes in a silicon substrate. Quantum computers could perform some calculations not possible on current computers, such as solving the Schrödinger equation for large molecules.

Quantum computing specialist **Michelle Y. Simmons** of the University of New South Wales, in Australia, and coworkers prepared the transistor. They used scanning tunneling microscopy, lithography, and phosphine chemistry to place, with single-lattice-site spatial accuracy, an individual phosphorus atom between electrodes in a silicon device (*Nat. Nanotechnol.,* DOI:**10.1038/nnano.2012.21**). Such precise positioning hadn't been achieved before.

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Mullin, R. *Chemical & Engineering News*. **2012**, *90* (10), 22-23.

Drugmakers Join to Study a Viral Threat

A unique consortium of five major drug companies is aiming at an extremely small target: progressive multifocal leukoencephalopathy (PML), a rare and often fatal viral brain infection associated with immunodeficiency that has primarily affected HIV/AIDS patients.

The PML Consortium—composed of **Biogen Idec**, **BMS**, **Elan**, **Pfizer**, and **Roche**—is unique in that it is not, at least currently, involved in drug development. Nor was its formation compelled by an interest in treating the disease itself, which occurs in an estimated 3 to 5% of patients with HIV/AIDS. Instead, the group was formed to pool patient information and fund academic research into the basic biology of the disease.

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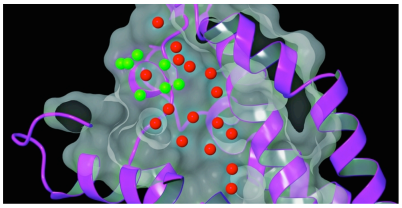
Wilson, E. K. *Chemical & Engineering News*. **2012**, *90* (11), 64-65.

Water's Role in Drug Discovery



Computational chemists are advancing in their ability to account for water in molecular simulations for drug discovery. At a recent meeting, theorists described new developments in computational chemistry software that allow them to include water in simulations of protein-drug binding that are more explicit and more widely usable than ever before.

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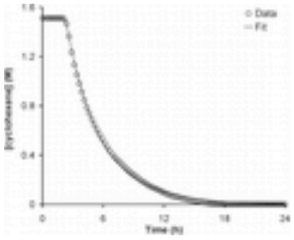
Citation: Crabtree, R. H., *Chem. Rev*. **2012**, 112, 1536-1554.

Resolving Heterogeneity Problems and Impurity Artifacts in Operationally Homogeneous Transition Metal Catalysts



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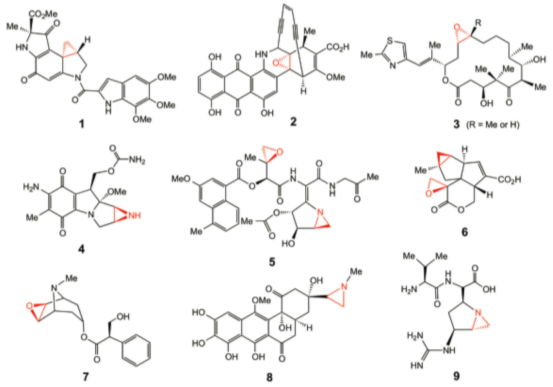
Citation: Thibodeaux, C. J.; Chang, W-C.; Liu, H-W., *Chem. Rev*. **2012**, 112, 1681-1709

Enzymatic Chemistry of Cyclopropane, Epoxide, and Aziridine Biosynthesis



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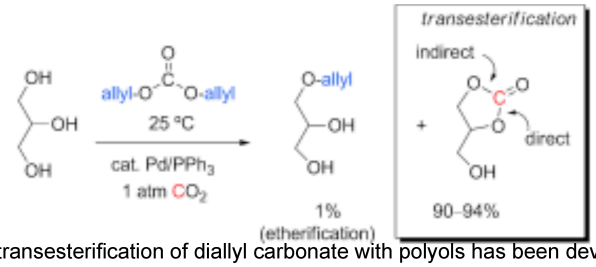
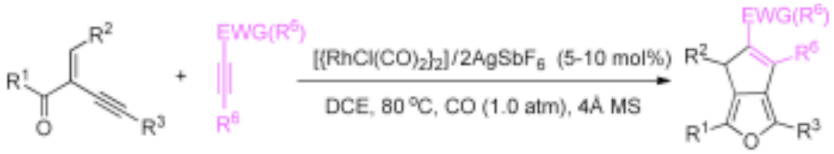
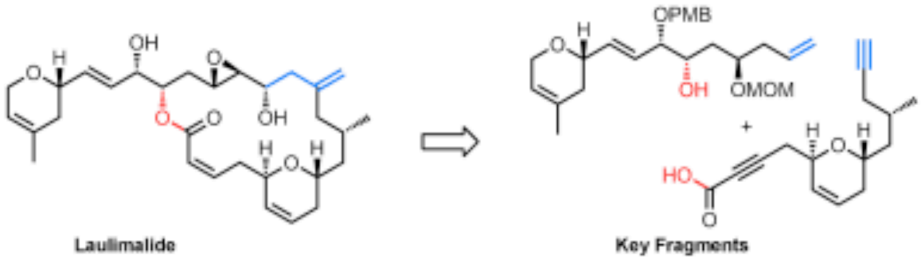
Citation: Chemistry - A European Journal, Volume 18, Issue 9, pages 2660–2665	
Pd-Catalyzed Reaction of Allyl Carbonate with Polyols: The Role of CO2 in Transesterification versus Etherification of Glycerol Dr. Alvaro Gordillo, Prof., Dr. Guy C. Lloyd-Jones  "A Pd-catalyzed transesterification of diallyl carbonate with polyols has been developed. The CO_2 concentration is shown to control the relative rates of etherification and transesterification. Kinetic and isotopic labeling studies suggest that intermediate η^1-allyl Pd alkoxides mediate indirect intermolecular transesterification. The higher polyols erythritol and threitol selectively generate monocarbonates."	bioorganic **methods** synthesis mechanism review other OM Bryo DDO Hybrid Drug Deliv. Prostratin

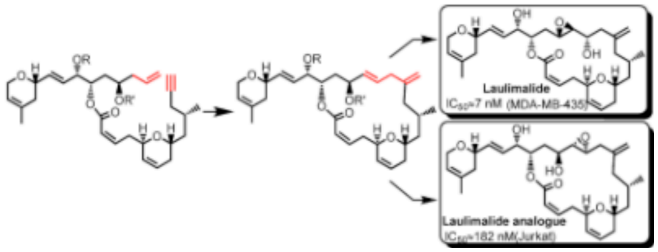
Citation: Chemistry - A European Journal, Volume 18, Issue 10, pages 2777–2782	
Cationic Rhodium(I)-Catalyzed Regioselective Tandem Heterocyclization/[3+2] Cycloaddition of 2-(1-Alkynyl)-2-alken-1-ones with Alkynes Hongyin Gao, Prof., Dr. Junliang Zhang  "A RhI-catalyzed tandem heterocyclization/[3+2] cycloaddition reaction was developed that provides rapid, efficient, and stereoselective access to highly substituted cyclopenta[c]furans from readily available 2-(1-alkynyl)-2-alken-1-ones and alkynes (see scheme). The cationic RhI acts as both a Lewis acid and a conventional transition-metal catalyst, providing the first example of a RhI species acting as a Lewis acid."	bioorganic **methods** synthesis mechanism review other **OM** Bryo DDO Hybrid Drug Deliv. Prostratin

Citation: Chemistry - A European Journal, Volume 18, Issue 10, pages 2948–2960	
Total Synthesis of Laulimalide: Synthesis of the Northern and Southern Fragments Prof. Barry M. Trost, Dr. W. Michael Seganish, Dr. Cheol K. Chung, Dr. Dominique Amans  "The synthesis of two equal-sized fragments of laulimalide is described (see scheme). A key Rh-catalyzed cycloisomerization reaction allowed for an efficient synthesis of the endocyclic dihydropyran and a stereoselective acylpyrrole Zn-aldol reaction allowed for the formation of the syn-diol."	bioorganic methods **synthesis** mechanism review other OM Bryo DDO Hybrid Drug Deliv. Prostratin **Laulimalide**

Citation: Chemistry - A European Journal, Volume 18, Issue 10, pages 2961–2971

Total Synthesis of Laulimalide: Assembly of the Fragments and Completion of the Synthesis of the Natural Product and a Potent Analogue

Prof. Barry M. Trost, Dr. Dominique Amans, Dr. W. Michael Seganish, Dr. Cheol K. Chung



"Efforts to couple the northern and southern building blocks, synthesized in the preceding paper, along with modifications required to lead to a successful synthesis of laulimalide are discussed. Interestingly, the designed synthetic route also allowed the preparation of an analogue of the natural product that possesses significant cytotoxic activity (see scheme). A more concise, second-generation route to the natural product is also described."

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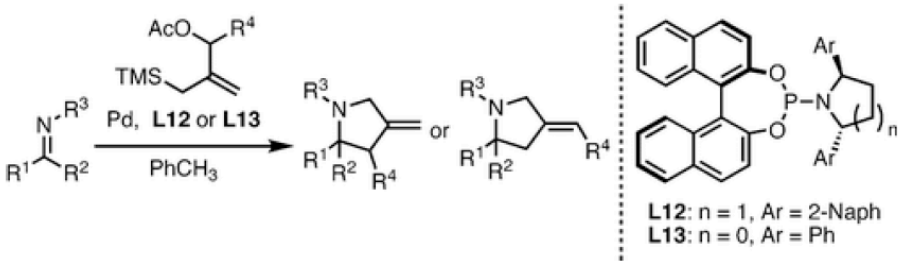
Citation: Trost, B.M.; Silverman, S.M. J. Am. Chem. Soc., 2012, 134 (10), pp 4941–4954

Enantioselective Construction of Pyrrolidines by Palladium-Catalyzed Asymmetric [3 + 2] Cycloaddition of Trimethylenemethane with Imines



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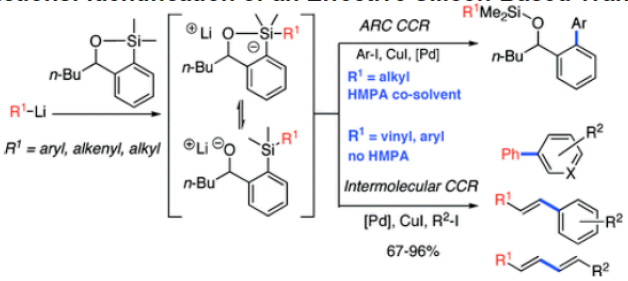
Hybrid
Gnid/ Kirk
Laulimalide
Drug Deliv.

Citation: Smith, III, A.B.; Hoye, A.T.; Martinez-Solorio, D.; Kim, W-S.; Tong, R. J. Am. Chem. Soc., 2012, 134 (10), pp 4533–4536

Unification of Anion Relay Chemistry with the Takeda and Hiyama Cross-Coupling Reactions: Identification of an Effective Silicon-Based Transfer Agent



These results provide a practical solution for intermolecular cross-coupling of organolithium reagents without the problematic lithium–halogen exchange and/or undesired homocoupling that has kept organolithium cross-couplings from achieving the same level of utility asother palladium-mediated methods (e.g., Suzuki organoboron, Negishi organozinc, Stille organotin, Kumada organomagnesium, etc.).

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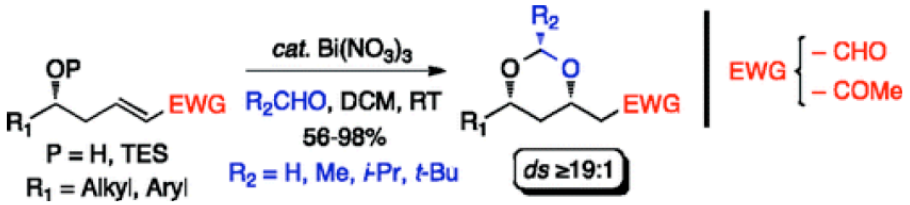
Citation: Evans, P.A.; Grisin, A.; Lawler, M.J. J. Am. Chem. Soc., 2012, 134 (6), pp 2856–2859

Diastereoselective Construction of syn-1,3-Dioxanes via a Bismuth-Mediated Two-Component Hemiacetal/Oxa-Conjugate Addition Reaction



The key advantages of this protocol are its operational simplicity and its ability to directly access electron-withdrawing groups without recourse to oxidation state adjustments.

bioorganic **methods** synthesis mechanism review other

OM Bryo Gnid/Kirk Hybrid Drug Deliv. Prostratin

Citation: Gadzikwa, T.; Bellini, R.; Dekker, H.L.; Reek, J.N.H. J. Am. Chem. Soc., 2012, 134 (6), pp 2860–2863

Self-Assembly of a Confined Rhodium Catalyst for Asymmetric Hydroformylation of Unfunctionalized Internal Alkenes

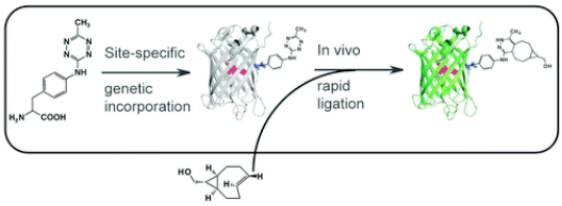
A chiral supramolecular ligand has been assembled and applied to the rhodium-catalyzed asymmetric hydroformylation of unfunctionalized internal alkenes. Spatial confinement of the metal center within a chiral pocket results in reversed regioselectivity and remarkable enantioselectivities.

bioorganic methods synthesis mechanism review other

OM Bryo Gnid/Kirk Hybrid Drug Deliv. Prostratin

Citation: Mehl, R.A.; et al. J. Am. Chem. Soc., 2012, 134 (6), pp 2898–2901

Genetically Encoded Tetrazine Amino Acid Directs Rapid Site-Specific in Vivo Bioorthogonal Ligation with trans-Cyclooctenes



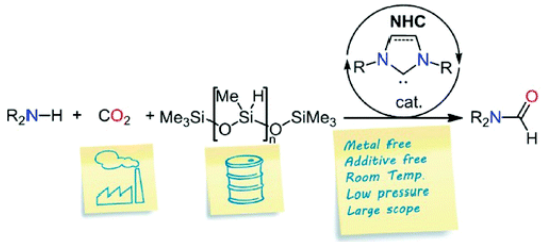
We have developed a tetrazine-containing amino acid, 1, that is stable inside living cells. We have site-specifically genetically encoded this unique amino acid in response to an amber codon allowing a single 1 to be placed at any location in a protein. We have demonstrated that protein containing 1 can be ligated to a conformationally strained trans-cyclooctene in vitro and in vivo with reaction rates significantly faster than most commonly used labeling methods.

bioorganic methods synthesis mechanism review other

OM Bryo Gnid/Kirk Hybrid Drug Deliv. Prostratin

Citation: Jacquet, O.; Gomes, C.D.N.; Ephritikhine, M.; Cantat, T. J. Am. Chem. Soc., 2012, 134 (6), pp 2934–2937

Recycling of Carbon and Silicon Wastes: Room Temperature Formylation of N–H Bonds Using Carbon Dioxide and Polymethylhydrosiloxane



A highly active organocatalytic system based on N-heterocyclic carbenes has been designed for the formylation of N–H bonds in a large variety of nitrogen molecules and heterocycles, using two chemical wastes: CO_2 and polymethylhydrosiloxane (PMHS).

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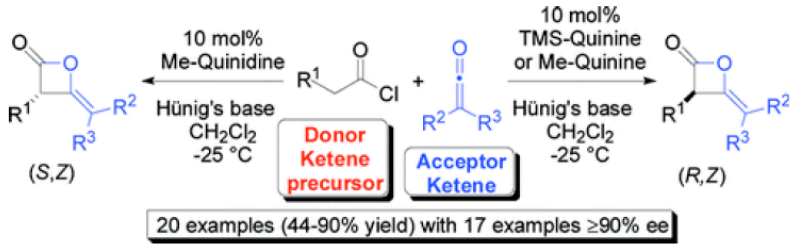
Citation: Ibrahim, A.A.; Nalla, D.; Van Raaphorst, M.; Kerrigan, N.J. J. Am. Chem. Soc., 2012, 134 (6), pp 2942–2945

Catalytic Asymmetric Heterodimerization of Ketenes



The alkaloid-catalyzed method provides access to ketene heterodimer ß-lactones and allows even two different monosubstituted ketenes to be cross-dimerized, with excellent enantioselectivity (17 examples with $=_{90}$% ee) and excellent heterodimer regioselectivity observed in all cases.

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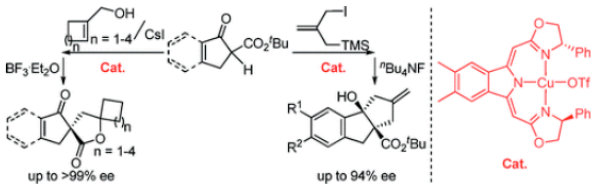
Citation: Deng, Q-H.; Wadepohl, H.; Gade, L.H. J. Am. Chem. Soc., 2012, 134 (6), pp 2946–2949

Highly Enantioselective Copper-Catalyzed Alkylation of ß-Ketoesters and Subsequent Cyclization to Spirolactones/Bi-spirolactones



Cu-catalyzed enantioselective alkylation of ß-ketoesters using alcohols for in situ preparation of alkylating reagents is reported. A number of functionalized ß-ketoesters containing a quaternary carbon stereocenter are obtained with up to 99% ee. The alkylation products derived from 2-substituted allylic alcohols or their corresponding iodides can then be converted to spirolactones, bi-spirolactones, and related chiral target products.

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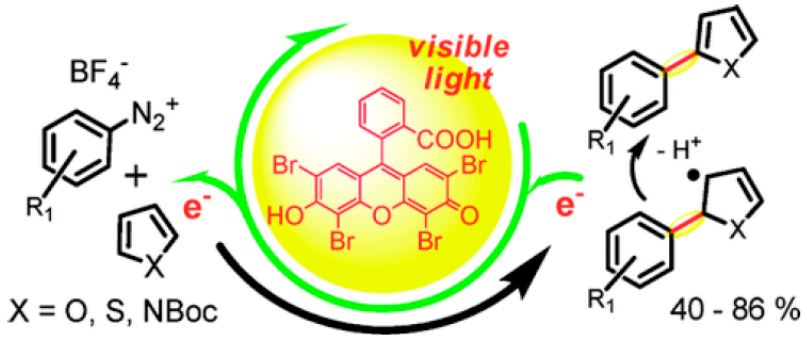
Citation: Hari, D.P.; Schroll, P.; König, B. J. Am. Chem. Soc., 2012, 134 (6), pp 2958–2961

Metal-Free, Visible-Light-Mediated Direct C–H Arylation of Heteroarenes with Aryl Diazonium Salts



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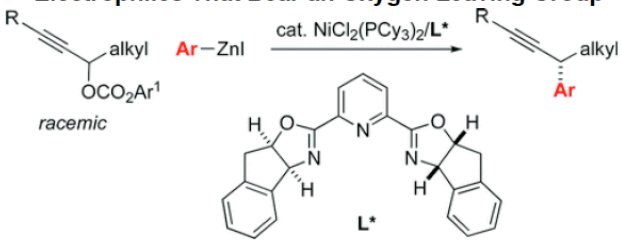
Citation: Oelke, A.J.; Sun, J.; Fu, G.C. J. Am. Chem. Soc., 2012, 134 (6), pp 2966–2969

Nickel-Catalyzed Enantioselective Cross-Couplings of Racemic Secondary Electrophiles That Bear an Oxygen Leaving Group



To date, effective nickel-catalyzed enantioselective cross-couplings of alkyl electrophiles that bear oxygen leaving groups have been limited to reactions of allylic alcohol derivatives with Grignard reagents. However, in the presence of a nickel/pybox catalyst, a variety of racemic propargylic carbonates are suitable partners for asymmetric couplings with organozinc reagents.

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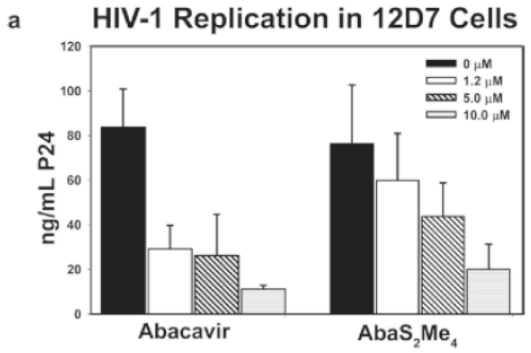
Citation: Chmielewski, J.; et al. J. Am. Chem. Soc., 2012, 134 (6), pp 2976–2980

Toward Eradicating HIV Reservoirs in the Brain: Inhibiting P-Glycoprotein at the Blood–Brain Barrier with Prodrug Abacavir Dimers



Dimeric prodrugs of abacavir were designed to have two functions: inhibit P-gp efflux at the BBB and revert to monomeric therapeutic within cellular reducing environments. The prodrug dimers are potent P-gp inhibitors in cell culture and in a brain capillary model of the BBB. Significantly, these agents demonstrate anti-HIV activity in two T-cell-based HIV assays, a result that is linked to cellular reversion of the prodrug to abacavir.

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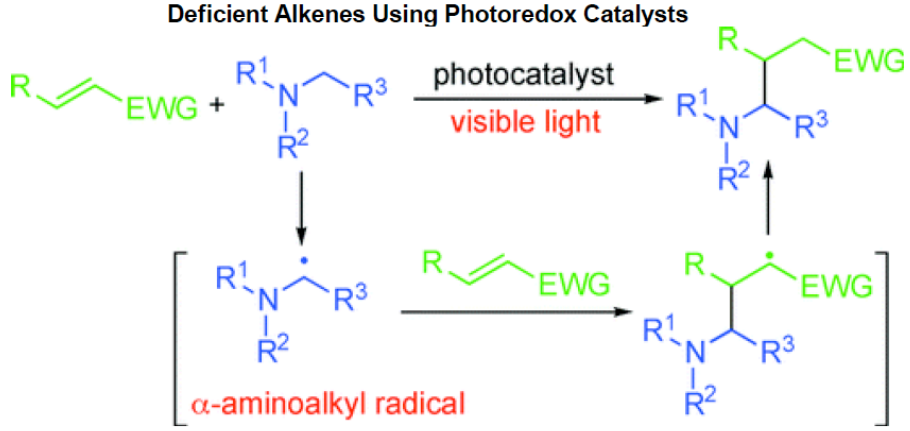
Citation: Miyake, Y.; Nakajima, K.; Nishibayashi, Y. J. Am. Chem. Soc., 2012, 134 (7), pp 3338–3341

Visible-Light-Mediated Utilization of a-Aminoalkyl Radicals: Addition to Electron-Deficient Alkenes Using Photoredox Catalysts



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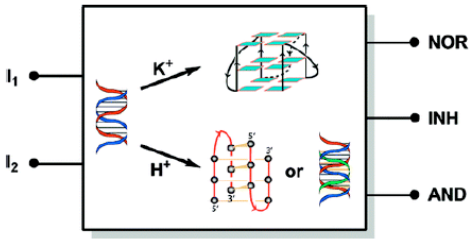
Citation: Li,T.; Ackermann, D.; Hall, a.M.; Famulok, M. J. Am. Chem. Soc., 2012, 134 (7), pp 3508–3516

Input-Dependent Induction of Oligonucleotide Structural Motifs for Performing Molecular Logic



The K^+–H^+-triggered structural conversion of multiple nucleic acid helices involving duplexes, triplexes, G-quadruplexes, and i-motifs is studied by gel electrophoresis, circular dichroism, and thermal denaturation. The G4/hemin complexes catalyze the H_2O_2-mediated oxidation of peroxidase substrates, resulting in a fluorescence or color change. Depending on the nature of the respective peroxidase substrate, distinct output signals can be generated, allowing one to operate multiple logic gates such as NOR, INH, or AND.

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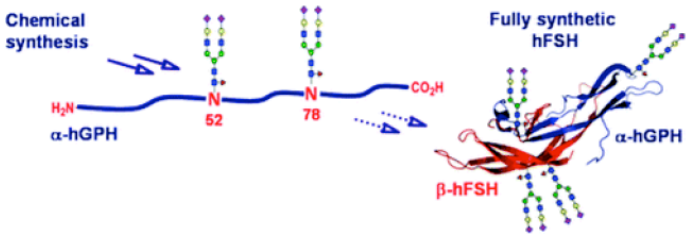
Citation: Danishefsky, S.J.; et al. J. Am. Chem. Soc., 2012, 134 (7), pp 3532–3541

Total Synthesis of the a-Subunit of Human Glycoprotein Hormones: Toward Fully Synthetic Homogeneous Human Follicle-Stimulating Hormone



Described herein is the first total chemical synthesis of the unique a-subunit of the human glycoprotein hormone (a-hGPH). Unlike the biologically derived glycoprotein hormones, which are isolated as highly complex mixtures of glycoforms, a-hGPH obtained by chemical synthesis contains discrete homogeneous glycoforms.

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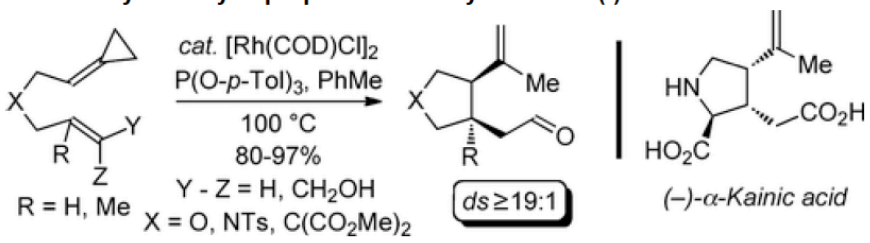
Citation: Evans, P.A.; Inglesby, P.A. J. Am. Chem. Soc., 2012, 134 (8), pp 3635–3638

Diastereoselective Rhodium-Catalyzed Ene-Cycloisomerization Reactions of Alkenylidenecyclopropanes: Total Synthesis of (-)-a-Kainic Acid



A key and striking feature of this protocol is that the alkene geometry does not impact the efficiency and diastereocontrol, which provides excellent synthetic versatility. For instance, (E)- and (Z)-allylic alcohols furnish the corresponding aldehydes with similar efficiency and selectivity. This process facilitates the construction of a key intermediate in an eight-step total synthesis of (-)-a-kainic acid.

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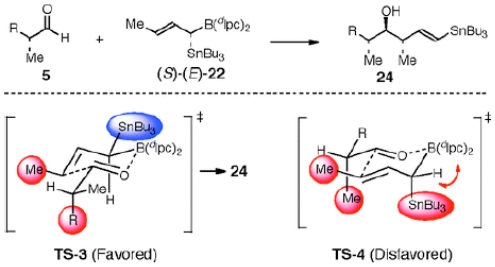
Citation: Chen, M.; Roush, W.R. J. Am. Chem. Soc., 2012, 134 (8), pp 3925–3931

Highly Stereoselective Synthesis of anti,anti-Dipropionate Stereotriads: A Solution to the Long-Standing Problem of Challenging Mismatched Double Asymmetric Crotylboration Reactions



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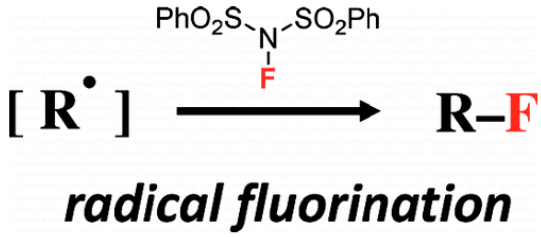
Citation: Sammis, G.M.; et al. J. Am. Chem. Soc., 2012, 134 (9), pp 4026–4029

Fluorine Transfer to Alkyl Radicals



This approach is successful for a broad range of alkyl radicals, including primary, secondary, tertiary, benzylic, and heteroatom-stabilized radicals.

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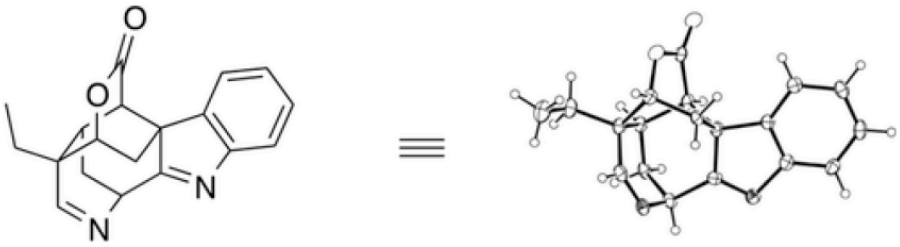
Citation: Adams, G.L.; Carroll, P.J.; Smith, III, A.B. J. Am. Chem. Soc., 2012, 134 (9), pp 4037–4040

Total Synthesis of (+)-Scholarisine A



(+)-Scholarisine A

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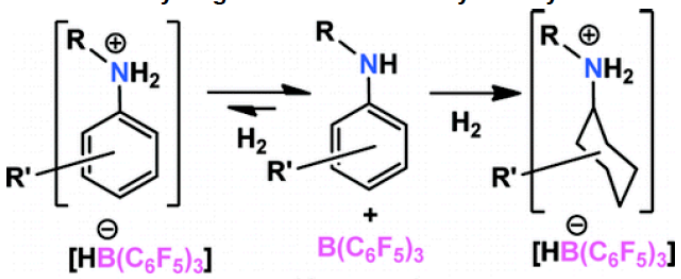
Citation: Mahdi, T.; Heiden, Z.M.; Grimme, S.; Stephan, D.W. J. Am. Chem. Soc., 2012, 134 (9), pp 4088–4091

Metal-Free Aromatic Hydrogenation: Aniline to Cyclohexyl-amine Derivatives



13 examples

Hydrogenation of the N-bound phenyl rings of amines, imines, and aziridine is achieved in the presence of H_2 and $B(C_6F_5)_3$, affording the corresponding N-cyclohexylammonium hydridoborate salts.

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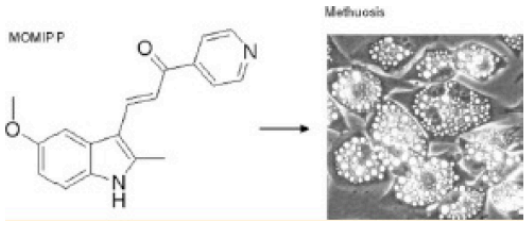
Citation: Robinson, M. W.; Overmeyer, J. H. et al. *J. Med. Chem.* **2012**, 55, 1940-1956.

Synthesis and Evaluation of Indole-Based Chalcones as Inducers of Methuosis, a Novel Type of Nonapoptotic Cell Death

Synthesis and SAR of indole-based chalcones reported. These induce methuosis - cell death caused by massive accumulation of vacuoles - in cancer cells.



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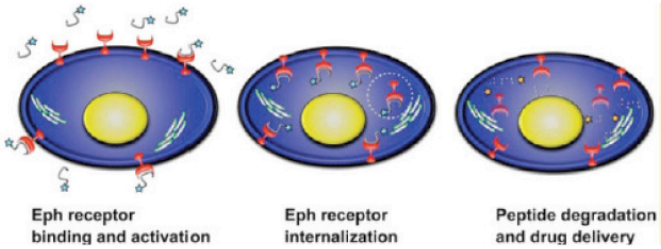
Citation: Wang, S.; Placzek, W. J. et al. *J. Med. Chem.* **2012**, 55, 2427-2436.

Novel Targeted System To Deliver Chemotherapeutic Drugs to EphA2-Expressing Cancer Cells



A 12 amino acid targeting peptide delivers paclitaxel to cancer cells, exploiting the EphA2 receptor.

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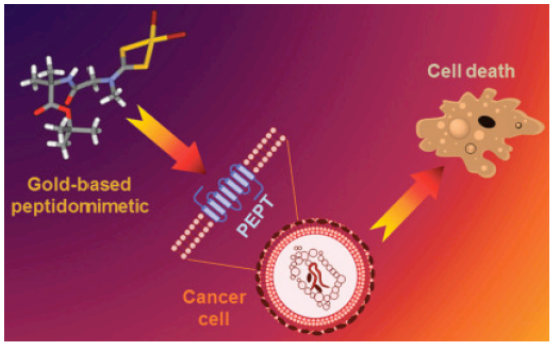
Citation: Kouodom, M. N.; Ronconi, L. et al. *J. Med Chem.* **2012**, 55, 2212-2226.

Toward the Selctive Delivery of Chemotherapeutics into Tumore Cells by Targeting Peptide Transporters: Tailored Gold-Based Anticancer Peptidomimetics

Gold-based peptidomimetics specifically targeting PEPT1 and PEPT2 were designed and synthesized. They inhibit tumor cell proliferation.



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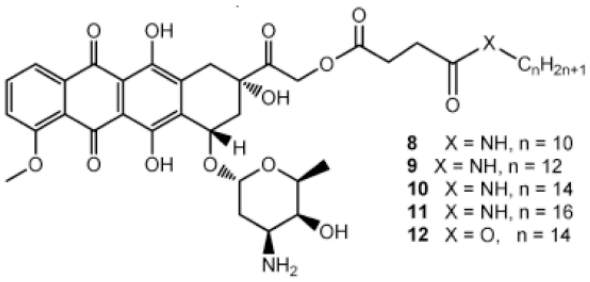
Prostratin

Citation: Chhikara, B. S.; Mandal, D. et al. *J. Med. Chem.* **2012**, 55, 1500-1510.

Synthesis, Anticancer Activities, and Cellular Uptake Studies of Lipophilic Derivatives of Doxorubicin Succinate



8 X = NH, n = 10
9 X = NH, n = 12
10 X = NH, n = 14
11 X = NH, n = 16
12 X = O, n = 14

14-substituted derivatives of doxorubicin were synthesized to enhance the lipophilicity, cellular uptake and cellular retention for sustained anticancer activity.

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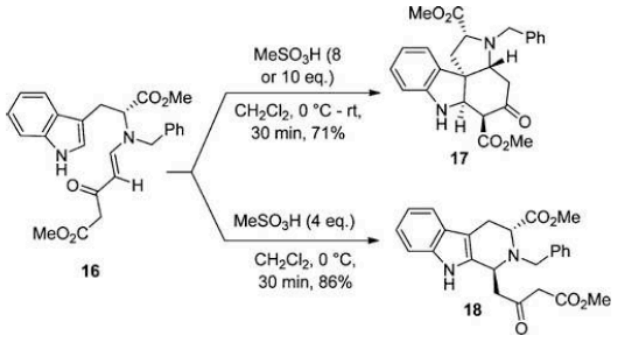
Citation: *J. Nat. Prod.* **2012**, 75, 181-188

Brønsted Acid Mediated Cyclization of Enaminones. Rapid and Efficient Access to the Tetracyclic Framework of the Strychnos Alkaloids



bioorganic
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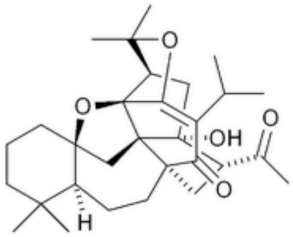
Bryo
DDO
Hybrid
Drug Deliv.
Prostratin

Citation: Hill R. A.; Sutherland, A. *Nat. Prod. Rep.* **2012**, *29*, 435-439.

Hot off the press

A personal selection of 31 recent papers is presented covering various aspects of current developments in bioorganic chemistry and novel natural products such as hydrangenone from *Salvia hydrangea*.



hydrangenone

bioorganic
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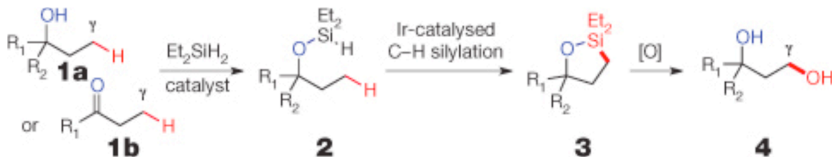
Hybrid
Drug Deliv.
Prostratin

Citation: Simmons, E.M.; Hartwig, J.F. *Nature* **2012** *483*, 70.

Catalytic Functionalization of Unactivated Primary C-H Bonds Directed by an Alcohol



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mechanism
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DDO
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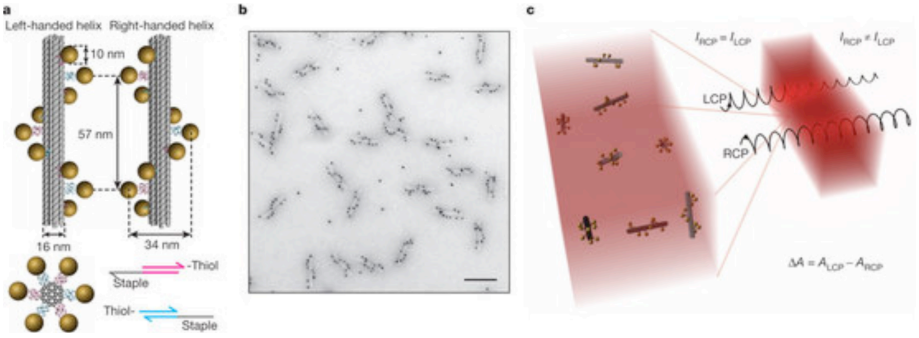
Citation: Kuzyk, A. *et al*. *Nature* **2012**, *483*, 311.

DNA-Based Self-Assembly of Chiral Plasmonic Nanostructures with Tailored Optical Response



bioorganic
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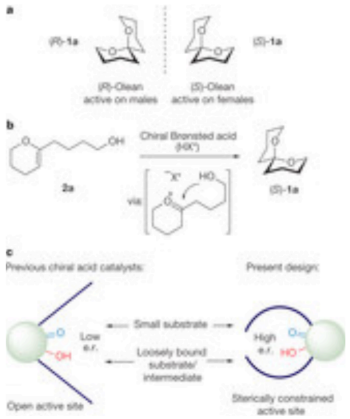
Prostratin

Citation: Coric, I.; List, B. *Nature* **2012**, *483*, 315.

Asymmetric Spiroacetalization Catalysed by Confined Bronsted Acids



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Hybrid
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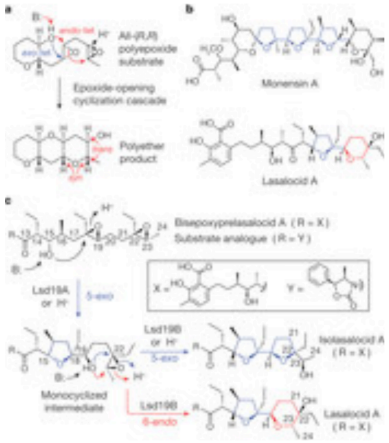
Citation: Hotta, K. *et al. Nature* **2012** *483*, 355.

Enzymatic Catalysis of Anti-Baldwin Ring Closure in Polyether Biosynthesis



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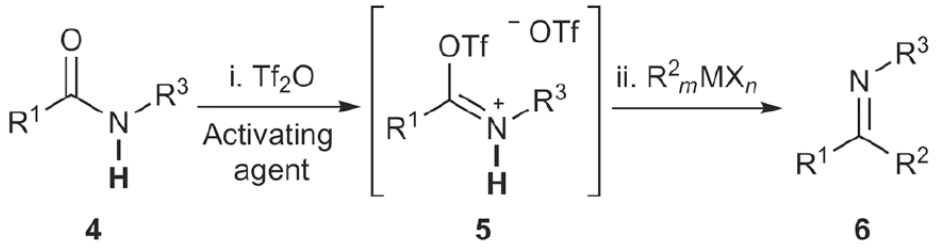
Citation: Bechara, W.S.; Pelletier, G.; Charette, A.B. *Nature Chem.*, **2012**, *4*, 228-234.

Chemoselective synthesis of ketones and ketimines by addition of organometallic reagents to secondary amides



4 **5** **6**

R^1 contains aldehydes, ketones, esters, amides

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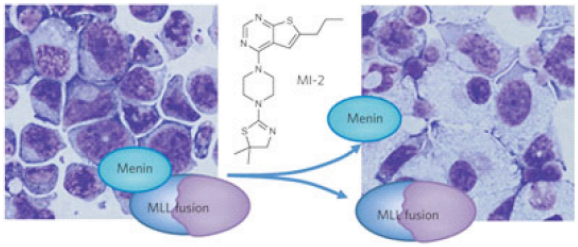
Citation: Grembecka, J.; He, G. et al. *Nat. Chem. Bio.* **2012** 8, 277-284

Menin-MLL Inhibitors Reverse Oncogenic Activity of MLL Fusion Proteins in Leukemia



The first small-molecule inihibitors of the menin-MLL fusion protein interaction are reported. They selectively induce apoptosis in leukemia cells with MLL translocations.

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Citation: *The Onion*, http://www.theonion.com/articles/new-biography-reveals-einstein-devised-theory-of-r,27313/

New Biography Reveals Einstein Devised Theory Of Relativity On Paper Because He Wasn't Smart Enough To Invent Microsoft Word

PRINCETON, NJ—A new biography by science historian Tanya Medel has rocked the physics world with the revelation that theoretical physicist Albert Einstein wasn't smart enough to invent Microsoft Word and use it to devise his theory of relativity. "The name Einstein has become synonymous with intelligence, but as I researched my book, it became clear he was incapable of devising a simple word-processing program with which to type up his findings," Medel said Thursday of the physicist whose work revolutionized science and fundamentally changed the way people think about space and time. "He had to scrawl everything out by hand, like some dumbo. It's a wonder people could even make heads or tails out of it without simple bullet points and auto-numbering." Medel also revealed that the famous photo of Einstein with his tongue sticking out was not a pose made for the sake of humor, but was instead the way he looked all the time because he was just that stupid

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Citation: *The Onion*, http://www.theonion.com/articles/new-study-finds-humans-may-have-some-capacity-for,27245/

New Study Finds Humans May Have Some Capacity For Compassion

TUCSON, AZ—A University of Arizona study published this week in the American Journal Of Sociology suggests that some adult humans may occasionally feel compassion, a trait scientists have long considered beyond the capacity of the species. "A small percentage of the roughly 900 subjects we observed seemed at times to exhibit genuine empathy toward another person experiencing either psychological or physical pain," said the study's lead author, Dr. Benjamin Trumble, who later added that these individuals did not appear as though they were looking to gain anything from their compassionate reactions, but, to the surprise of researchers, were simply concerned about another person's well-being. "Of course, we'll need to conduct further tests to rule out the possibility that these demonstrations weren't the result of statistical noise or the expression of some sort of very, very rare genetic mutation." The study also reaffirmed previous research indicating that 95 percent of individuals are capable of convincingly feigning compassion.

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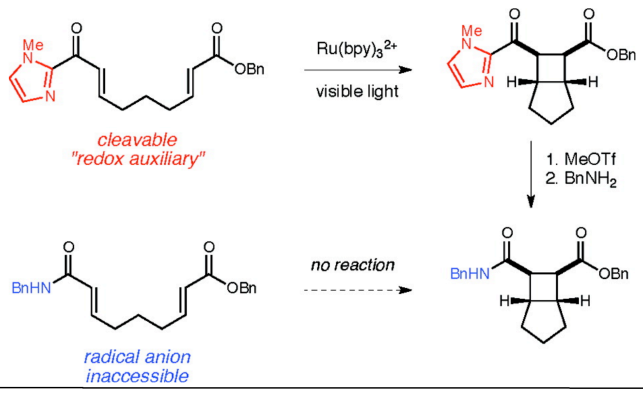
Tyson, E. L.; Farney, E. P.; Yoon, T. P. *Org. Lett.* **2012**, *14*, 1110-1113.

Photocatalytic [2+2] Cycloadditions of Enones with Cleavable Redox Auxiliaries



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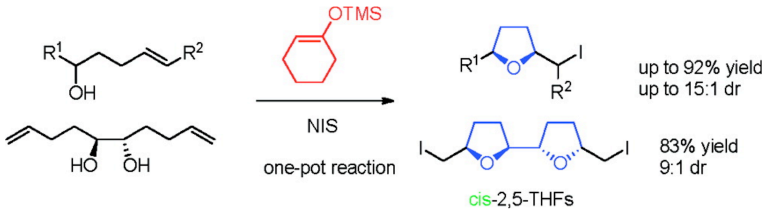
Fujioka, H.; Maehata, R.; Wakamatsu, S.; Nakahara, K.; Hayashi, T.; Oki, T. *Org. Lett.* **2012**, *14*, 1054-1057.

Stereoselective Synthesis of *cis*-2,5-Disubstituted THFs: Application to Adjacent Bis-THF Cores of Annonaceous Acetogenins



The iodocyclization of γ,δ-unsaturated alcohols in the presence of a silyl enol ether produced *cis*-2,5-disubstituted tetrahydrofurans in one pot via siloxy intermediates. *N*-Iodosuccinimide (NIS) effectively worked as an activator of the double bonds in the substrates and the silyl enol ether. Application to an expedient synthesis of the adjacent bis-tetrahydrofuran core of Annonaceous acetogenins with a *cis*/*threo*/*cis* relative stereochemistry is also described.

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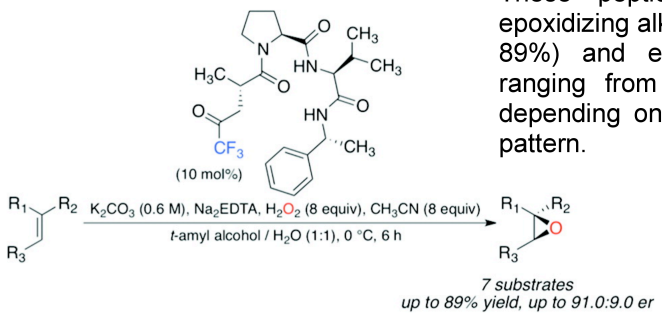
Romney, D. K.; Miller, S. J. *Org. Lett.* **2012**, *14*, 1138-1141.

A Peptide-Embedded Trifluoromethyl Ketone Catalyst for Enantioselective Epoxidation



The active catalyst is a chiral trifluoromethyl ketone (Tfk) with a pendant carboxylic acid that can be readily incorporated into a peptide. These peptides were capable of epoxidizing alkenes in high yield (up to 89%) and enantiomeric ratios (er) ranging from 69.0:31.0 to 91.0:9.0, depending on the alkene substitution pattern.

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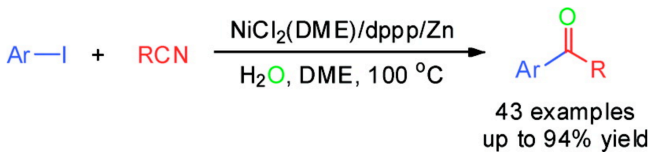
Hsieh, J.-C.; Chen, Y.-C.; Cheng, A.-Y.; Tseng, H.-C. *Org. Lett.* **2012**, *14*, 1282-1285.

Nickel-Catalyzed Intermolecular Insertion of Aryl Iodides to Nitriles: A Novel Method to Synthesize Arylketones



A novel procedure for the $NiCl_2$(DME)/dppp/Zn system catalyzed intermolecular insertion of aryl iodides to nitriles was developed, which afforded variously substituted arylketone derivatives in moderate to good yields with tolerance of a wide variety of functional groups.

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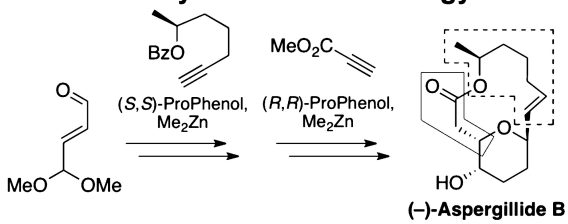
Trost, B. M.; Barlett, M. J. *Org. Lett.* **2012**, *14*, 1322-1325.

Transition-Metal-Catalyzed Synthesis of Aspergillide B: An Alkyne Addition Strategy



(–)-Aspergillide B

A catalytic enantioselective formal total synthesis of aspergillide B is reported. This linchpin synthesis was enabled by the development of new conditions for Zn-ProPhenol catalyzed asymmetric alkyne addition. This reaction was used in conjunction with ruthenium-catalyzed trans-hydrosilylation to affect the rapid construction of a late-stage synthetic intermediate of aspergillide B to complete a formal synthesis of aspergillide B in a highly efficient manner.

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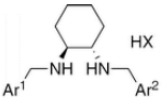
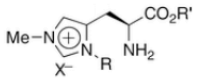
Citation: Zgonnik, V.; Gonella, S.; Mazieres, M.; Guillen, F.; Coquerel, G.; Saffon, N.; Plaquevent, J. *Org. Process Res. Dev.*, **2012**, *16(2)*, 277-285.

Design and Scalable Synthesis of New Chiral Selectors. Part 2: Chiral Ionic Liquids Derived from Diaminocyclohexane and Histidine

We disclose the conception and synthesis of new chiral selectors useful for enantioselective liquid–liquid extraction processes (ELLE). We report synthetic methods giving access to substantial amounts of the compounds, at least at the multigram scale. Two series are examined, i.e. ionic liquids based on diaminocyclohexane (DACH) and histidine, respectively.



Ar^1, Ar^2 = Ph, 2-pyridyl, 3-pyridyl, 4-pyridyl
X = Cl, BF_4, PF_6, NTf_2



R = Bu, Oct, Dodecyl
R' = Me, H
X = NTf_2

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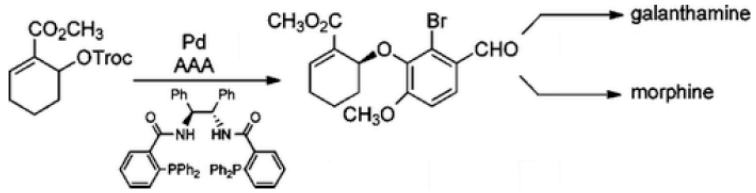
Citation: Trost, B.M. *Org. Process Res. Dev.*, **2012**, *16(2)*, 185-194.

Pd- and Mo-Catalyzed Asymmetric Allylic Alkylation

A unique aspect of asymmetric metal-catalyzed processes is the fact that many mechanisms exist for stereoinduction. Furthermore, with the use of the same catalyst system, many types of bonds including but not limited to C–C, C–N, C–O, C–S, C–P, and C–H can be formed asymmetrically. An overview of this process using palladium- and molybdenum-based metals being developed in my laboratories and how it influences strategy in synthesizing bioactive molecular targets is presented.



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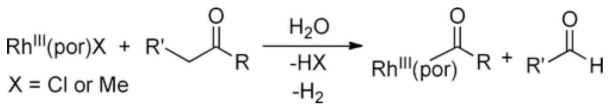
Citation: Hong Sang Fung, Bao Zhu Li, and Kin Shing Chan *Organometallics,* **2012**, *31*, 570-579.

Mild and Selective C(CO)-C(α) Bond Cleavage of Ketones by Rhodium(III) Porphyrins: Scope and Mechanism

Rhodium(III) porphyrins were found to undergo selective C(CO)-C(α) bond activation (CCA) of ketones promoted by water at temperatures as low as 50 °C. The acyl group of the ketone was transferred to the rhodium center, and the alkyl fragment was oxidized to a carbonyl moiety accordingly. The hydroxyl group of water is transferred to the rhodium porphyrin through hydrolysis of the kinetic (α-carbon,Äìhydrogen bond activation (α-CHA) product to give Rh^{III}(ttp)OH (ttp = 5,10,15,20-tetratolylporphyrinato dianion), which subsequently cleaves the C(CO)-C(α) bond of ketone.



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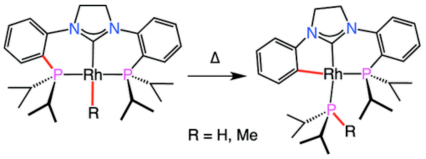
Citation: Bryan K. Shaw, Brian O. Patrick, and Michael D. Fryzuk *Organometallics,* **2012**, *31*, 783-786.

Thermal Rearrangement via P–C Bond Cleavage of a Tridentate Diphosphine–N-Heterocyclic Carbene Ligand System Coordinated to Rhodium

The synthesis of a series of rhodium complexes, [PCP]RhX, where X = Cl, H, CH_3 and PCP is a tridentate ligand that contains a central, saturated NHC donor flanked by two *o*-phenylenediisopropylphosphino groups, is described. These complexes were characterized by NMR spectroscopy (^1H, ^{13}C, and ^{31}P) and, in the case of the X = Cl derivative, by X-ray crystallography. Investigation of the thermal reactivity of these complexes uncovered an unexpected ligand rearrangement process (for X = H, CH_3) resulting from intramolecular P–C bond cleavage between one of the phosphine donors and the aryl linker of the ligand backbone. The structures of the P–C activation products are confirmed through X-ray diffraction analysis, and preliminary rate data in the case of the rhodium hydride are presented.



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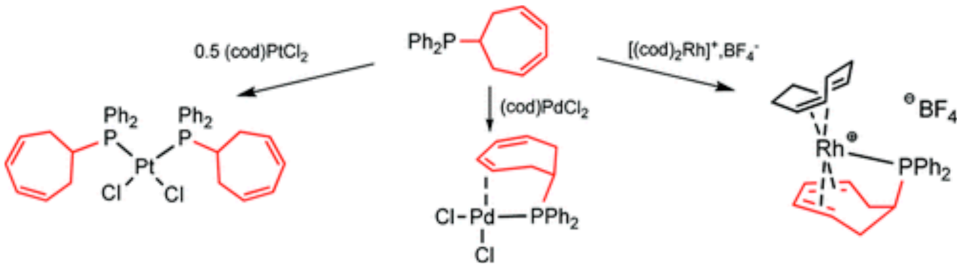
Citation: Alexandre Massard, Vincent Rampazzi, Arnaud Perrier, Ewen Bodio, Michel Picquet, Philippe Richard, Jean-Cyrille Hierso, and Pierre Le Gendre *Organometallics,* **2012**, *31*, 947-958.

(Cycloheptadienyl)diphenylphosphine: A Versatile Hybrid Ligand

(3,5-Cycloheptadienyl)diphenylphosphine is easily synthesized from the reaction of diphenylphosphine with 1,3,5-cycloheptatriene. This new phosphine-diene has been coordinated as a monodentate P ligand with Pt, Pd, Au, Ni, and Ru; as a bidentate (P, olefin) ligand with Pt and Pd; and as a tridentate (P, diene) ligand with Rh. Fluxional properties of several complexes have been studied via NMR experiments and theoretical consideration.



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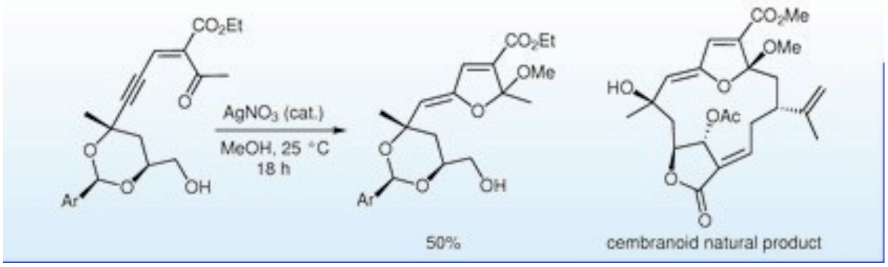
Citation: Pattenden, G.; Winne, J. M., *Syn. Lett*. **2012**, 723-726.

An approach to exo-Enol Ether - Cyclic Ketal Structures Found in Marine Cembranoids, Based on Silver-Assisted Cyclisations of Enynone Precursors



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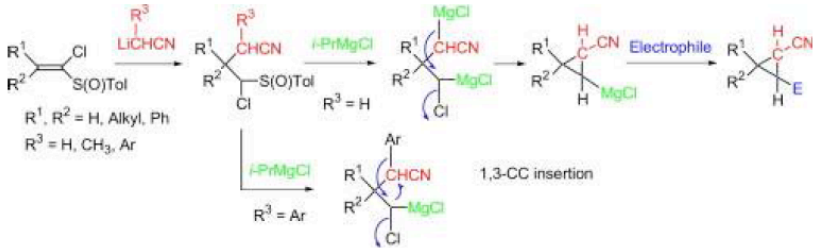
H. Saitoh et al, *Tetrahedron* **68** (2012) 2481-2495.

New synthesis of multisubstituted cyanocyclopropanes by the intramolecular SN2 alkylation and 1,3-CC insertion reaction of magnesium carbenoids as the key reactions



Addition reaction of 1-chlorovinyl p-tolyl sulfoxides derived from ketones and aldehydes with lithium α-cyano carbanions gave nitrile adducts in high to quantitative yields.

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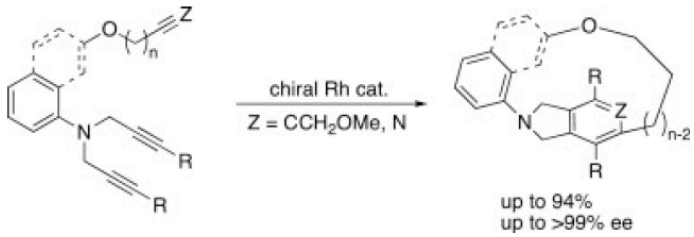
T. Shibata et al, *Tetrahedron* **68** (2012) 2679-2686.

Enantioselective synthesis of tripodal cyclophanes and pyridinophanes by intramolecular [2+2+2] cycloaddition



An enantioselective intramolecular [2+2+2] cycloaddition of 2-aminophenol-tethered triynes and diyne-nitriles proceeded using the chiral Rh catalysts, and tripodal cyclophanes and pyridinophanes with a long ansa chain (up to [16]pyridinophane) were obtained in acceptable yield with high to almost perfect ee.

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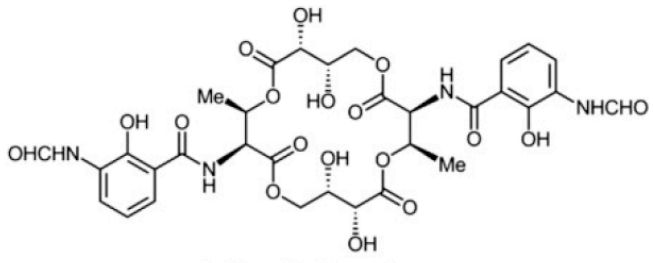
A. Arsianti et al, Tetrahedron **68** (2012) 2884-2891.

Synthesis and anticancer activity of polyhydroxylated 18-membered analogue of antimycin A3



Antimycin A_3 analogue

A novel polyhydroxylated 18-membered analogue of antimycin A3 was synthesized. The analogue exhibited a greater anticancer activity against HeLa cells, breast MDA-MB-231 cells, and prostate PC-3 cells compared to the original antimycin A3.

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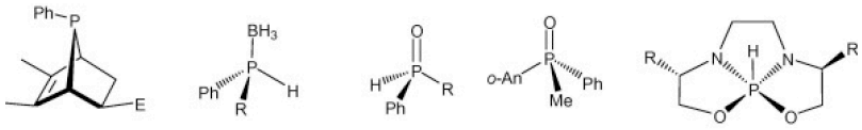
O. Kolodiazhnyi, *Tetrahedron Asymmetry* **15** (2012) 1-46.

Recent developments in the asymmetric synthesis of *P*-chiral phosphorus compounds



This review discusses methods for the asymmetric synthesis of P-chiral tri-, tetra- and pentacoordinated organophosphorus compounds with many applications in stereoselective synthesis and in asymmetric catalysis with reference to updated literature findings as well as the author's original research.

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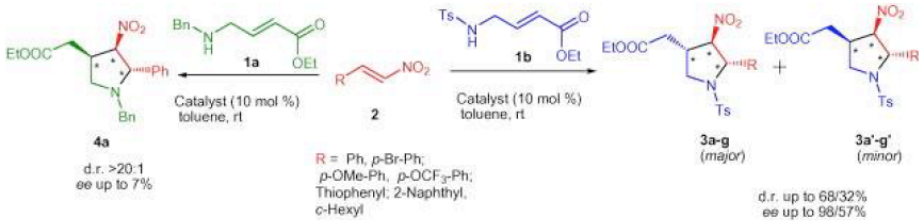
A. Nuoole et al, *Tetrahedron Asymmetry* **15** (2012) 188-198.

Organocatalytic asymmetric synthesis of trisubstituted pyrrolidines via a cascade reaction



A new bifunctional thiourea catalyzed methodology was developed for the synthesis of chiral trisubstituted pyrrolidines using 4-aminocrotonate 1a/1b and nitroolefins 2a–g as starting materials.

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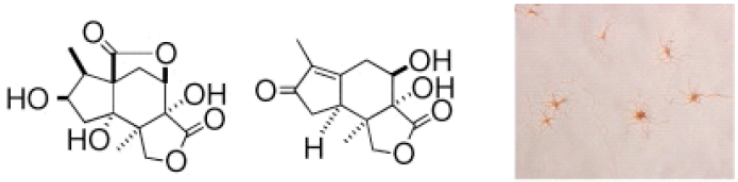
Citation: Kubo, M. *et al*. Tetrahedron Letters 2012, 53, 1231-1235.

The first examples of seco-prezizaane-type norsesquiterpenoids with neurotrophic activity from Illicium jiadifengpi.



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http://www.sciencedirect.com/science/article/pii/S0040403911022696

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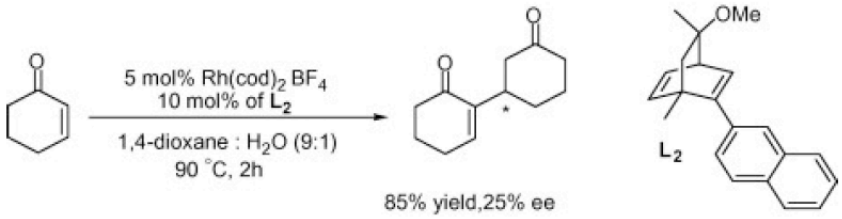
Citation: Kumaraswamy, G.; Rambabu, D. Tetrahedron Letters 2012, 53, 1042-1044.

Hydroxy-rhodium(I) catalyzed regioselective Michael addition of cyclic enones.



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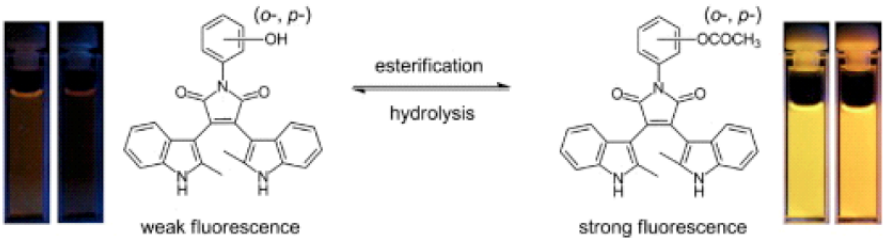
Citation: Li, X.; Xu, Y.; Wang, B.; Son, Y.-A. Tetrahedron Letters 2012, 53, 1098-1101.

Toggle-switchable fluorescence of bisindolylmaleimide derivatives by reversible esterification/hydrolysis.



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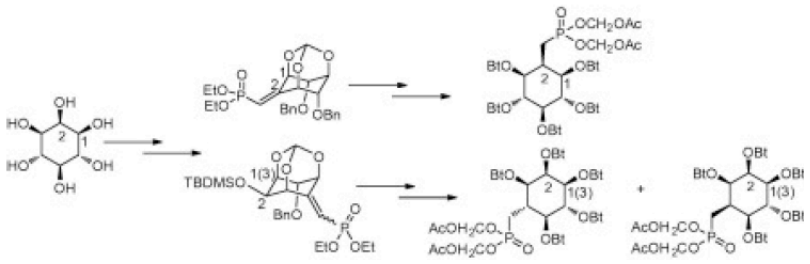
Citation: Song, F. *et al*. Tetrahedron Letters 2012, 53, 1102-1104.

Synthesis and antitumour activity of inositol phosphonate analogues.



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