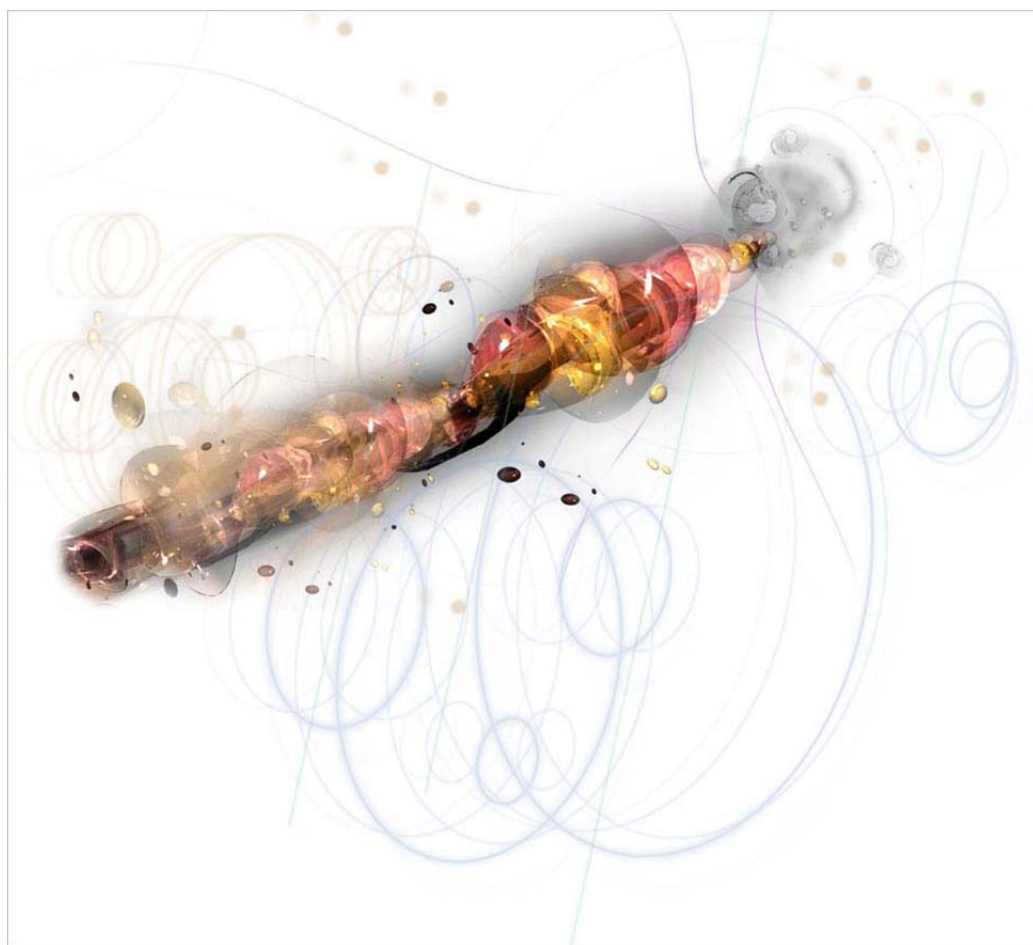


**Boston College
Undergraduate Research
in Chemistry and Biochemistry**



Poster Session
September 24, 2010
3:30 - 5:00 p.m.
Merkert Chemistry Center Foyer



The Chemistry Department at Boston College is dedicated to providing a challenging environment for our students. We are pleased that our students not only meet but often exceed our expectations when faced with the demands of their coursework and research experiences. Today, we acknowledge the accomplishments of our undergraduate Chemistry and Biochemistry majors. These enthusiastic and dedicated scholars exemplify the high standards of our department, and we look forward to observing their future contributions to the scientific community.

We extend a warm welcome to the families and friends of our undergraduate majors and share your deep pride in their scholarly achievements.

STUDENT POSTERS

“Computational Studies of Polyelectrolyte Behavior of RNA and the Ribosome to Conformational Stability of Stapled p53 Peptides”

~**David Richards, Brian Stamm**, Zuojun Guo and Prof. Udayan Mohanty

“Expression and Purification of *T. maritima* Aspartate Transcarbamoylase”

~**Catherine Lancaster, David Machajewski, Michael Dolan** and Dr. Evan Kantrowtiz

“Retooling Nature’s Arsenal: the Modulation of Antimicrobial, Gramicidin A to Improve Selectivity and Solubility”

~**Patrick Wong**, Fang Wang and Dr. Jianmin Gao

“Regioselective and Enantioselective Hydroformylation of Homoallylic Sulfonamides”

~**Ka Cheng**, Kian L.Tan, Ph.D.

“Laboratory Studies of the Heterogeneous Oxidation of Humic-Like Substances (HULIS)”

~**Ross Crossdale** and Professor Paul Davidovits

“Laboratory Field-Deployable Potential Aerosol Mass (PAM) Flow Reactor for Real-Time Oxidative Aging Studies”

~**Justin Wright** and Professor Paul Davidovits

“Copper-Catalyzed Enantioselective Conjugate Additions of Alkyl Groups to Acyclic Enones”

~**Matthew Villaume**, Jennifer Dabrowski, Amir Hoveyda

Shape-Controlled Palladium Nanoparticles: Synthesis and Applications”

~**Casey Brodsky**, Brian Sneed, Yang Tang, Professor Chia-Kuang Tsung

“The Development of Cysteine-Reactive Triazine Probes”

~**Douglas Brown**, Ranjan Banerjee, Ph.D., Professor Eranthie Weerapana

“Synthesis of Morphologically Controlled Au-Pd Core-Shell Nanoparticles”

~**Leo Lamontagne**, Chun-Hong Kuo, Professor Chia-Kuang Tsung

“Mesoporous Zeolites Both Alone and as a Synergistic Coating on Metal Nanoparticles as Robust, Active Catalysts for Renewable Fuels”

~**Joseph Morabito** and Professor Chia-Kuang Tsung

Computational Studies of Polyelectrolyte Behavior of RNA and the Ribosome to Conformational Stability of Stapled p53 Peptides

David Richards, Brian Stamm, Zuojun Guo, and Udayan Mohanty
Merkert Chemistry Center, Boston College

Our lab has worked on three projects:

Free Energy of Magnesium Binding Sites in the Ribosome

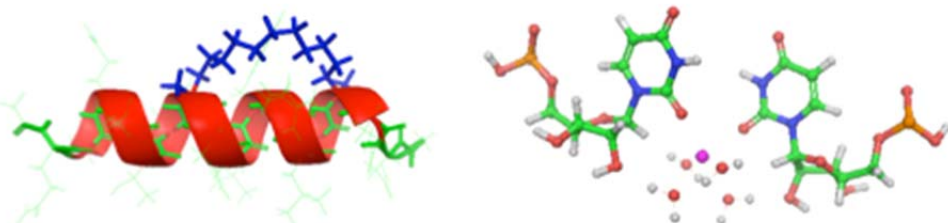
Magnesium ions play a critical role in the structural stability of the ribosome because they effectively neutralize the negative charge in the RNA phosphates. Magnesium ions are able to bind to different RNA and amino acids in the ribosome through a combination of site-specific binding and diffuse binding. The strength of the magnesium binding is reflected in the Gibbs free energy, which is composed of the interaction energy, the solvation energy, and entropy contributions. We present extensive results on the entropy of the magnesium binding sites in the ribosome using density functional theory, normal mode analysis, and constrained molecular dynamics.

Conformation Stability of Stapled p53 Peptides

Over-expression of the ubiquitin ligase MDM2 can lead to loss of p53 tumor suppressor activity, and is characteristic in some forms of cancer. One new method to fight this cancer involves targeting MDM2 with stapled-alpha-helical p53 peptide analogs. These peptides that have been experimentally proven to be able to enter the cell membrane, interact with MDM2 and re-activate the p53 cell apoptosis pathway. Our research has been focused on optimizing the structure of the p53 analog peptides in order to maintain the necessary alpha helix conformation over a variety of temperatures and conditions. Specifically, we have studied the conformations and structural stability of various stapled peptides with a saturated hydrocarbon staple in aqueous solvent via extensive Replica Exchange Molecular Dynamic all-atoms simulations.

Ion Atmosphere Around a Polyelectrolyte in Aqueous Salt Solution

The condensation of counterions, such as Na^+ and Mg^{2+} , enables the folding of polyelectrolytes, i.e. DNA and RNA, through the neutralization of backbone negative phosphate charges. It is well-determined that ions with a smaller size and higher charge density are more effective agents in the collapse of these biomolecules. Brownian simulations are conducted in an effort to determine the concentration dependence for the folding event. The model consists of a 120-monomer polyelectrolyte neutralized fully via Na^+ counterions and exposed to varying concentrations of divalent and trivalent cations.



(left): a p53 peptide analog with a hydrocarbon staple (blue)

(right): Mg 42 (magenta) coordinated to two Uracil bases and four water molecules

Expression and Purification of *T. maritima* Aspartate Transcarbamoylase

Catherine Lancaster, David Machajewski, Michael Dolan, and Dr. Evan Kantrowitz

Merkert Chemistry Center, Boston College

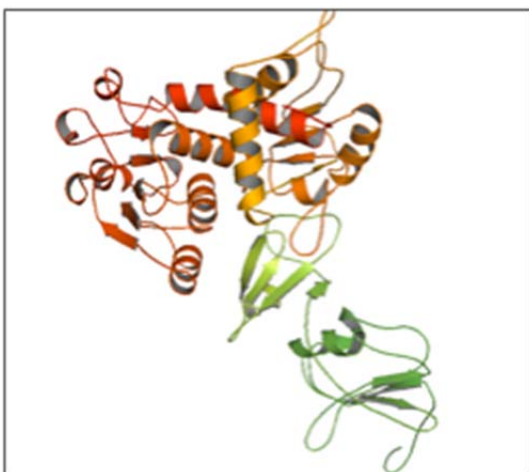


Figure 1: *T. maritima* ATCase, shown as modeled by alignment with *E. coli* ATCase

Aspartate transcarbamoylase (ATCase) is an allosteric enzyme that catalyzes the reaction between carbamoyl phosphate and L-aspartate to form N-carbamoyl-L-aspartate, which is the committed step in the pyrimidine biosynthesis pathway. In *Escherichia coli*, ATCase is made up of two catalytic trimers and three regulatory dimers. Pyrimidines and purines are the two types of nucleotides that make up deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). The pyrimidines—thymine, uracil, and cytosine—are characterized by their single-ring structure, while the purines—guanine and adenine—are heterocyclic. *Thermotoga maritima* is a rod-shaped thermophilic bacteria that grows optimally between 80°C and 90°C. *T. maritima* ATCase is of particular interest because, unlike in *E. coli*, the regulatory and catalytic regions are linked on the same polypeptide. The high temperatures at which it thrives also raise interesting questions because carbamoyl phosphate has a half-life of less than two seconds at 80°C, introducing the possibility of transient complex formation between the enzymes in the *de novo* pyrimidine biosynthesis pathway. The *T. maritima* ATCase was expressed in two *E. coli* expression systems, one that used a plasmid with the T7 promoter and another that utilized the arabinose promoter. The expression was optimized by testing different growth medias, growth times, and expression temperatures. The enzyme was purified by a heat step followed by ion-exchange chromatography, and the purity was evaluated by gel electrophoresis and size-exclusion chromatography (SEC). Thus far, a pure sample of the protein has not been obtained. Based on SEC testing, it seems the quaternary structure of the protein—presumed to be a trimer or hexamer, based on previous ATCase studies—is not forming correctly. The ultimate goal of this project is to obtain crystals of pure *T. maritima* ATCase and to elucidate the structure using x-ray diffraction analysis and to potentially investigate the formation of any complexes of the enzymes of pyrimidine biosynthesis.

Retooling Nature's Arsenal: the Modulation of Antimicrobial, Gramicidin A to Improve Selectivity and Solubility

Patrick Wong, Fang Wang and Dr. Jianmin Gao
Merkert Chemistry Center, Boston College

To combat the growing prevalence of antibiotic-resistant strains of infectious bacteria, our lab has endeavored to expand upon the antimicrobial properties of the amphipathic and channel-forming peptide, Gramicidin A (gA) (Formyl-L-Val-Gly-Ala-D-Leu-Ala-D-Val-L-Val-D-Val-L-Trp-D-Leu-L-Trp-D-Leu-L-Trp-D-Leu-L-Trp-D-Leu-L-Trp-Ethanolamine). Its bactericidal mechanism differs from conventional drugs in that common medications typically target a distinct enzyme; gA attacks the membrane, a largely universal motif across all bacterial species. The goals of this long-term project comprise: increasing its solubility in aqueous solutions, conferring greater selectivity for bacterial targets, and retaining its innately powerful, membrane-lytic ability- potent even in the nanomolar range. Ultimately, the goal of this project would be to create an effective, peptide-antibiotic that would provide a preferable alternative to modern drugs.

To these ends, our lab has specifically substituted various residues along the 15 amino acid sequence in order to attain the aforementioned and desired attributes. Our method thus far has been to selectively substitute the tryptophan "anchors" and the leucine "spacers" with natural and unnatural amino acids of our own design. These mutants were subsequently evaluated with regards to their bactericidal activity (MIC) against four distinct species of bacteria, and their respective solubilities in aqueous solutions determined. Additionally, we intend to identify the consequent, structural changes in protein folding that contribute to the differential activities of each mutant.

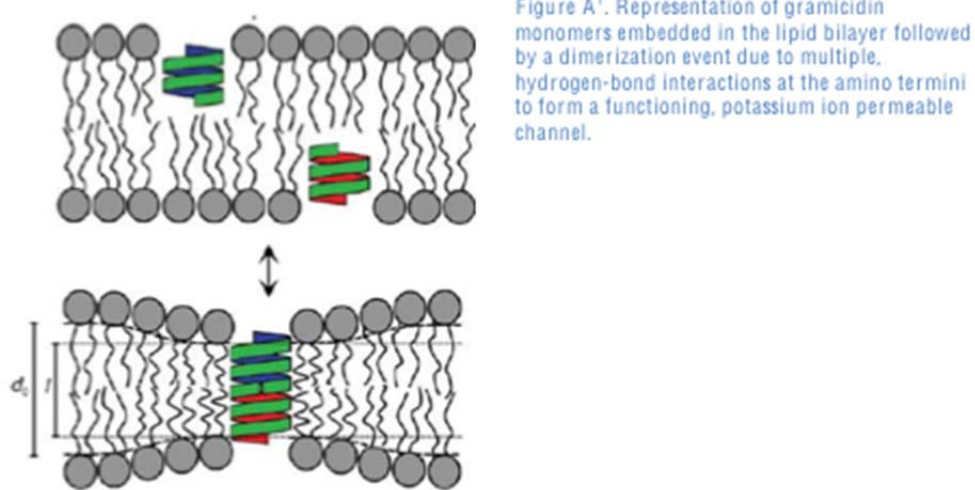


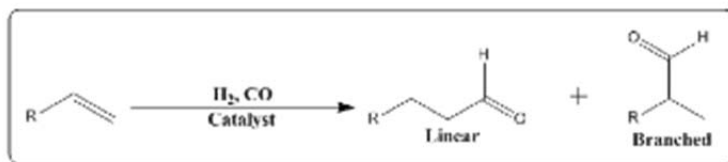
Figure A¹. Representation of gramicidin monomers embedded in the lipid bilayer followed by a dimerization event due to multiple, hydrogen-bond interactions at the amino termini to form a functioning, potassium ion permeable channel.

¹Andersen, O. S. Gramicidin Channels. *IEEE T NANOBIOSCI* 2005, 4, 10-20

Regioselective and Enantioselective Hydroformylation of Homoallylic Sulfonamides

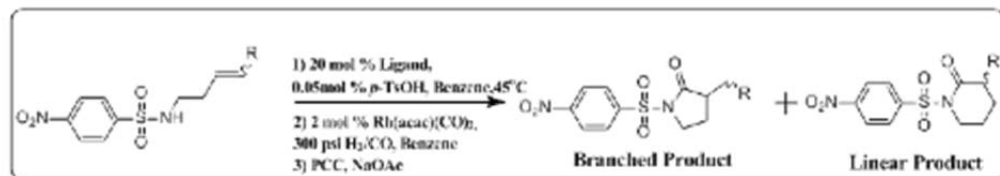
Ka Cheng, Kian L. Tan, Ph.D.

Merkert Chemistry Center, Boston College

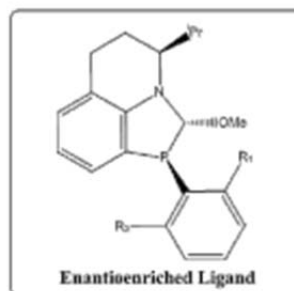
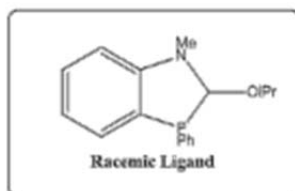


1

Hydroformylation (1), first discovered by Otto Roelen in 1938, involves the addition of carbon monoxide and hydrogen gas to an olefin to produce aldehydes. It is industrially significant because the aldehyde products are easily reduced to alcohols, which can then be converted to detergent or esterified to yield plasticizers. This research has focused around achieving excellent regioselectivity and enantioselectivity in the hydroformylation of homoallylic sulfonamides by using phosphine-based ligands designed by the Tan group. A model system (2) was chosen, and pressure, rhodium catalyst loading, and acid concentration were screened. It was found that good conversion (70%) and excellent regioselectivity (95:5) were achieved under mild conditions. Present work is focusing on further optimization of current conditions, as well as the exploration of enantioenriched ligands to achieve high levels of enantioselectivity.



2



**Laboratory Studies of the Heterogeneous Oxidation
of Humic-Like Substances (HULIS)**

Ross Croasdale and Prof. Paul Davidovits
Merkert Chemistry Center, Boston College

HULIS are macromolecular, highly oxygenated aromatic compounds found in soils and river beds. They are often used as surrogates for oxygenated organic aerosols (OOA) formed in the atmosphere. However, effects of heterogeneous oxidation on OOA properties have not been systematically studied.

In this work, six HULIS were exposed to OH radicals in a Potential Aerosol Mass (PAM) flow tube. The resulting refractory nature, chemical composition, and CCN activity were characterized.

**Laboratory Field-Deployable Potential Aerosol Mass (PAM) Flow Reactor
for Real-Time Oxidative Aging Studies**

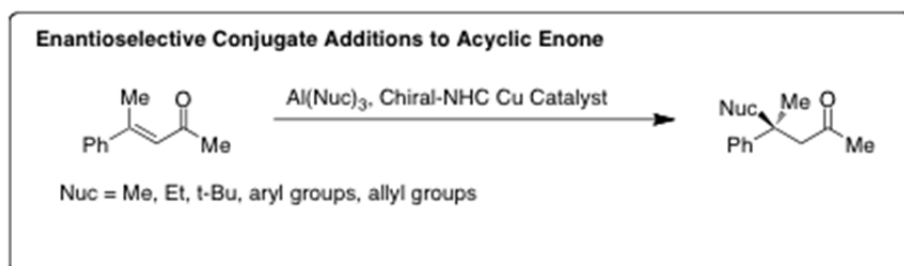
Justin Wright and Prof. Paul Davidovits
Merkert Chemistry Center, Boston College

In the atmosphere, oxidative aging of gas-phase and/or condensed-phase organic precursors produces oxygenated organic aerosol (OOA), that is continually modified as a result of dilution, mixing, and aging. In particular, the chemical composition of OOA over multiple generations of oxidation is not well characterized.

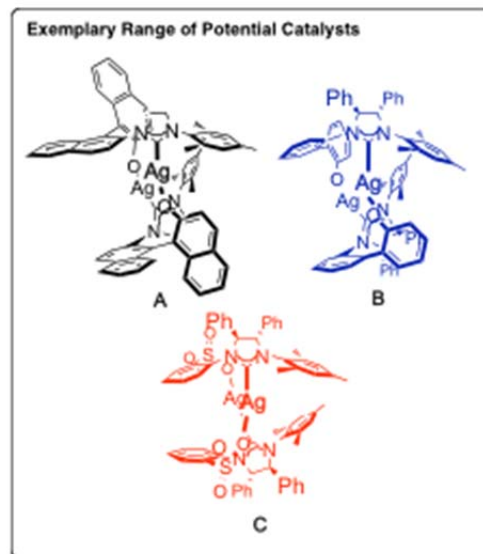
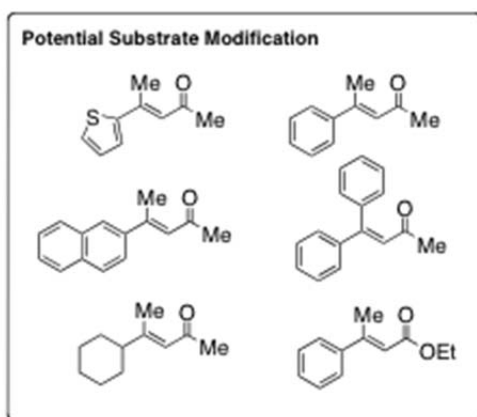
In the present work, ambient air was sampled through a Potential Aerosol Mass (PAM) flow reactor to simulate in the laboratory, in real time days to weeks of oxidative aging. OH exposures ranging from 6.2×10^{11} to 1.5×10^{12} molec cm^{-3} s^{-1} were used, corresponding to 5 to 12 days of atmospheric exposure at typical ambient OH levels. Chemical composition of the aerosol was characterized with an Aerodyne time-of-flight aerosol mass spectrometer (ToF-AMS). Results were compared to laboratory measurements of secondary organic aerosol (SOA) to elucidate possible sources of OOA.

Copper-Catalyzed Enantioselective Conjugate Additions of Alkyl Groups to Acyclic Enones

Matthew Villaume, Jennifer Dabrowski, Amir Hoveyda



This project seeks to develop a methodology for performing copper-catalyzed conjugate additions to acyclic systems, using the previously developed and rigorously explored N-Heterocyclic Carbene ligands used in the Hoveyda Research Group. To develop this methodology, a wide range of substrates were explored. These substrates contain a range of steric and electronic modifications, shedding light on the possible range for this reaction. A range of aluminum reagents were used to assess the effect of the nucleophile on the conjugate additions. This project is scientifically interesting as these acyclic conjugate addition products have never before been synthesized in an enantiopure process.



Shape-Controlled Palladium Nanoparticles: Synthesis and Applications

Casey Brodsky, Brian Sneed, Yang Tang, Chia-Kuang Tsung
Merkert Chemistry Center, Boston College

Nanomaterials have a number of advantages in catalysis when compared to their bulk counterparts. As metal particle size reaches the nano scale, the surface area to volume ratio greatly increases along with the percentage of atoms occupying catalytically active corner and edge sites.

In the last fifty years, much of nanomaterials research has focused on the size and shape control of transition metal nanoparticles. Because different shapes can better catalyze different reactions, nanomaterial shape control has become a vital step in the search for alternative energy. Nanoparticles have the potential to catalyze reactions necessary for solar cells, water splitting, fuel cells, and the production of hydrocarbons.

In this study, shape-controlled palladium nano-octahedrons and nano-cubes (Figure 1) of various sizes were synthesized, via both single-step and seed-mediated growth methods. The as-prepared palladium nanoparticles were then used as seeds in a rhodium overgrowth procedure, yielding particles with palladium cores and dendritic rhodium shells (Figure 2). Rhodium is an extremely catalytically active metal, but it is difficult to manipulate into shape-controlled structures. To resolve this problem, palladium seed particles are used as structure-directing templates. The palladium seeds have a controlled shape, and the rhodium that grows over the palladium acquires an identical shape.

Electrocatalysis is commonly utilized to test the catalytic activity of transition metal nanoparticles. In this study, palladium nanoparticles were used to catalyze the oxidation of dissolved carbon monoxide to carbon dioxide. The data for these reactions was recorded using cyclic voltammetry (Figure 3), and the resulting graphs were analyzed to obtain information about both the morphology and catalytic efficiency of the particles being tested.

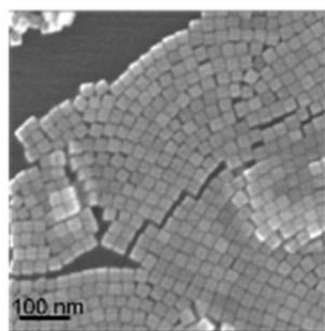


Figure 1

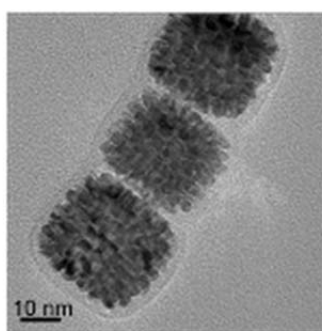


Figure 2

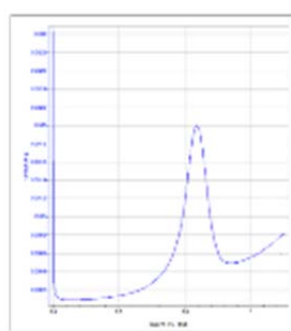
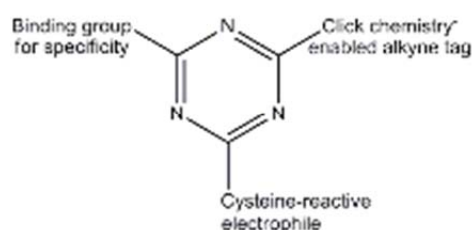


Figure 3

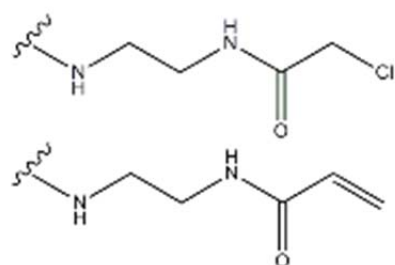
The Development of Cysteine-Reactive Triazine Probes
Douglas Brown, Ranjan Banerjee, Ph.D., Eranthie Weerapana, Ph.D.
Merkert Chemistry Center, Boston College

Bacteria require inordinately strong redox regulation because their high rate of metabolism necessitates frequent proteomic interaction with oxygen. Numerous species rely on thiol-dependent oxidoreductase enzymes to repair resulting oxidative damage, and hindering this redox system could potentially be lethal for bacteria. Cysteine-reactive electrophiles were linked to click chemistry-enabled triazine scaffolds in order to build a bioactive synthetic library that would identify protein targets for antibiotic research. Because these molecules covalently bind to the functional cysteine within the oxidoreductase, they are capable of effectively inhibiting its homeostatic activity. A variety of binding groups and electrophiles were utilized in order to increase diversity and augment specificity.

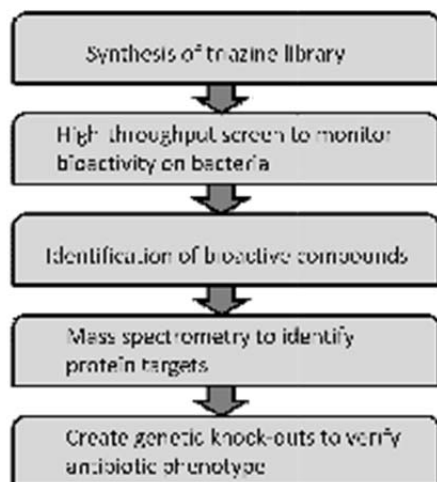
General Structure of Library Molecules



Cysteine-reactive electrophiles



Project Design Scheme





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