REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

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1. REPORT DATE *(DD-MM-YYYY)* 18/01/2007	**2. REPORT TYPE** Final Report	**3. DATES COVERED** *(From - To)* 01/11/05 to 31/12/06

4. TITLE AND SUBTITLE **NATURE INSPIRED STRATEGIES FOR NEW ORGANIC MATERIALS**	**5a. CONTRACT NUMBER**
	5b. GRANT NUMBER FA9550-06-1-0007 [redacted]
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) Professor Karl A. Scheidt (researcher, author) Chris Galliford (researcher)	**5d. PROJECT NUMBER**
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Northwestern University Department of Chemistry 2145 Sheridan Road Evanston IL 60201	**8. PERFORMING ORGANIZATION REPORT NUMBER**
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of the Air Force Air Force Office of Sponsored Research 875 N. Randolph Street Arlington, Virginia 22203 Dr. Hugh DeLong/NL	**10. SPONSOR/MONITOR'S ACRONYM(S)**
	11. SPONSOR/MONITOR'S REPORT

AFRL-SR-AR-TR-07-0021

12. DISTRIBUTION / AVAILABILITY STATEMENT

Dist. A

13. SUPPLEMENTARY NOTES

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14. ABSTRACT

This report accounts for the technical accomplishments during the single year of funding for this program. It includes, but is not limited to, a list of publications, transitions, visits, and awards earned by the participating researchers. This grant has been instrumental in initiating organic materials research in the Scheidt laboratory. Key discoveries made in this small time period include the development of an efficient synthesis of bidentate organic "rods" to be used for material assembly. The basic fundamentals of the chemical reaction and the construction of various organic architectures were established. Furthermore, the interest in new methods and protocols to assemble tailor-made organic materials has been kindled and resulted in collaborations with additional high profile researchers at Northwestern University, including Chad Mirkin, Joe Hupp and SonBinh Nguyen.

15. SUBJECT TERMS

Catalysis, organic materials, self-assembly, nucleophilic acylation,

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			**19b. TELEPHONE NUMBER** *(include area code)*

AFOSR FINAL REPORT

NATURE INSPIRED STRATEGIES FOR NEW ORGANIC MATERIALS

Award Number FA:9550-06-1-007

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January 14, 2007

Period covered by this Report: 10/01/05 to 12/31/06

1. OBJECTIVES AND STATUS OF WORK

The objectives of this one year project were: 1) the investigation of new chemical methodology to construct extended organic materials with unique properties, 2) employ nature-inspired "carbene catalysis" to attach carbonyl functional groups to aromatic rings in an efficient manner, 3) synthesize rigid, aryl ring-based monomers that can be used in materials assembly, and 4) characterize and evaluate the electronic transport and spectroscopic properties of these materials.

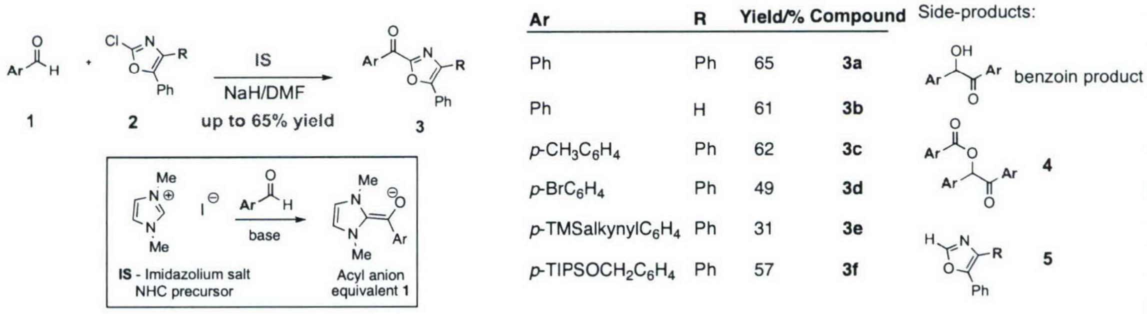
During the funding period (10/05 to 12/06), a new technique for the construction of key aryl-carbonyl bonds was discovered and developed. This protocol relies on the use of simple starting materials and generates the corresponding 2-acyl oxazoles in good to moderate yields. The basic chemical approaches to extended organic materials was refined and implemented to generate monomers capable of chelating metal ions.

2. ACCOMPLISHMENTS

A. *N*-Heterocyclic Carbene-Catalyzed Nucleophilic Acylation

2-chlorooxazoles are competent electrophiles for acyl anion equivalent **I**, providing access to bioactive keto-oxazoles (Scheme 1).[1-2] Treatment of benzaldehyde **1a** with 25 mol % of imidazolium salt **IS** in the presence of 2.0 equivalents of sodium hydride and 1.0 equivalent of chloro-oxazole **2** at room temperature yielded 65% yield of the keto-oxazole product **3.**

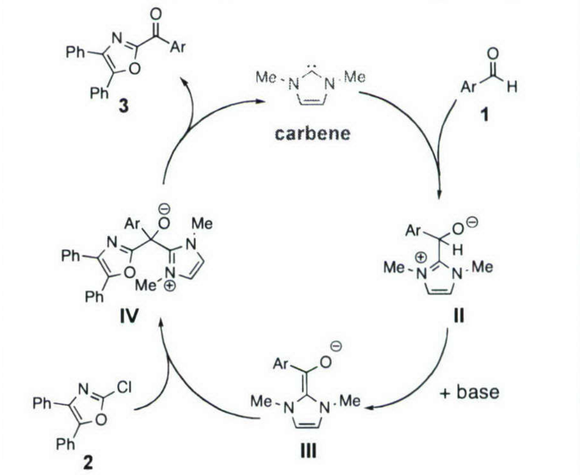
Scheme 1 **NHC-catalyzed Nucleophilic Acylation with Aldehydes**



Ar	R	Yield/%	Compound
Ph	Ph	65	**3a**
Ph	H	61	**3b**
p-$CH_3C_6H_4$	Ph	62	**3c**
p-BrC_6H_4	Ph	49	**3d**
p-TMSalkynylC_6H_4	Ph	31	**3e**
p-$TIPSOCH_2C_6H_4$	Ph	57	**3f**

The proposed catalytic cycle for this process is depicted in Scheme 2. The major side products of the reaction were identified as benzoin-type products (derived from the addition of intermediate **IV** to the starting aldehyde) and more importantly, the acylated benzoin adduct **4**, derived from three equivalents of the starting aldehyde (Scheme 1) and *des*-chloro-oxazole **5**. Using a deuterium labeling experiment (employing C_1-deuterated benzaldehyde) we were able to determine that the formation of **4** and **5** was the result of an interesting redox process. The deuterium atom was quantitatively transferred to the *des*-chloro-oxazole,

Scheme 2. Catalytic Cycle for the NHC-Catalyzed Acylation



supporting a mechanism involving a hydride transfer from the **II** (Scheme 2), formed from addition of NHC to the aldehyde (instead of the formal 1,2-hydrogen shift), to the chlorooxazole, followed by elimination of chloride ion. This kind of reductive process involving hydride transfer is precedented in a related NHC-catalyzed process.[2]

The ratio of **3**:**5** is strongly dependent on the structure of the aldehyde starting material. Our optimized reaction conditions are 20-25 mol% of the imidazolium salt with 2.0 equivalents of NaH at room temperature for 5 h. For benzaldehyde, this affords **3** and **5** in a ratio of 4.2:1, with an isolated yield of 65% of **3a** (Ar=R=Ph). In an attempt to circumvent the reduction pathway, benzoyltrimethylsilane as the nucleophilic component. The presence of **5** was not detected during the course of the reaction, however 4 equivalents of the acylsilane and 1 equivalent of **IS** are required to afford acceptable yields (**3a** in 64%). It appears that acylsilane–NHC intermediate is less nucleophilic (intermediate **III** and **IV** are presumably silylated in the acylsilane pathway). The exact nature of the intermediates in this reaction, and the factors governing their reactivity are currently under investigation.

Conclusion: *N-Heterocyclic carbenes can be used as catalysts to facilitate carbonyl anion additions of aromatic aldehydes to 2-chlorooxazoles to afford a unique binding motif, the 2-acyl oxazole. The fundamentals of this process have been outlined and the utility of the reaction has been demonstrated.*

B. Carbene catalysis approach to bidentate organic material monomers

Using the protocols developed in the Section A, novel bidentate dyad precursors have been readily prepared using the NHC-catalyzed acylation reaction. bis-ketooxazole ligands **6** and **7** have been prepared from **3d** and **3e** as dyads for use in metal organic frameworks (**MOFs**) (**6** from the facile Sonogashira coupling of **3d** and **3e**, **7** from **3d** and commercially available 1,4-diethynylbenzene). In each dyad, the keto-oxazole units are separated by a suitable spacer unit (Figure 1). Crystallization and metal-binding studies are currently underway for this promising new class of ligands. The potential scope for this facile and modular methodology for ligand synthesis is potentially unlimited, with illustrative examples of spacer units presented in Figure 1. Using our NHC-catalyzed acylation reaction followed by a homo or heterocoupling reaction to another keto-oxazole monomer, we hope to demonstrate high levels of control over the rigidity, length and spacing of the organic framework.

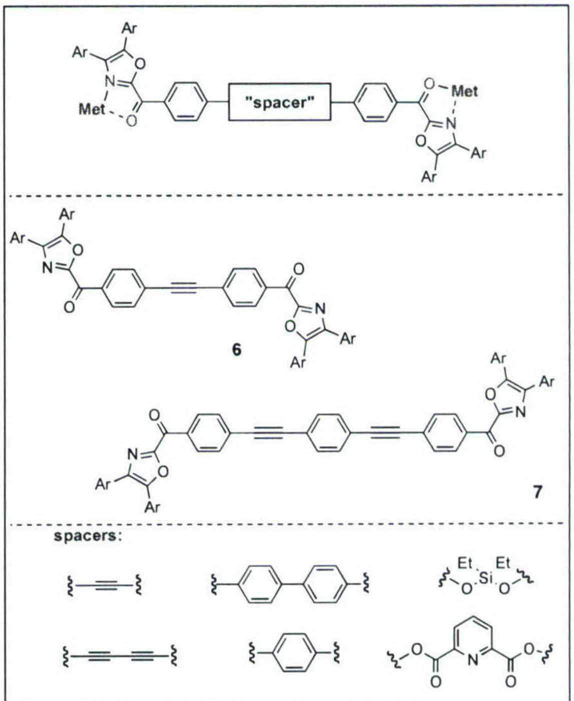


Figure 1. **NHC-Catalyzed Acylations for the Construction of New Metal Organic Framework Dyads**

Conclusion: *The nucleophilic acylation methodology developed in part A has been successfully applied to the development of conjugating bidentate monomers. These molecules are the basic building blocks that will be assembled using transition metals as lynch pins to construct conducting arrays of organic materials.*

The initial support for this research has realized a strong interest to merge the development of organic methodology with new material research. Ultimately, these new organic materials will be studied for their potential in the oxidation of organic feedstocks into easier to handle primary alcohols that can be used as fuel. A direct outcome of this work is the integration of our growing general interest in organic materials with the Mirkin, Hupp and Nguyen research groups culminating in the recent submission of MURI proposal entitled, "Bioinspired Supramolecular Enzymatic Systems" (BAA 06-02, FY07 MURI TOPIC 19).

Future Work:

The progress from the initial funding period has laid the foundation for further organic material studies. We are heavily engaged in the integration of new chemical methods and materials research. The research the Scheidt laboratory will continue in this area is focused on three distinct goals:

GOAL 1: The synthesis and assembly of monomers from Section B using divalent metal ions. Confirm structure by X-ray crystallography.

GOAL 2: Study the electronic and spectroscopic properties of the materials from Section B.

GOAL 3: Further develop the nucleophilic acylation chemistry to synthesize coiled systems of continuously conduction carbon fibers.

3. PERSONNEL SUPPORTED

Graduate student:	**% of Salary provided by grant**
Chris Galliford	80%

4. PUBLICATIONS

A. JOURNAL ARTICLES

1. Galliford, C. V; Myers, M. C.; Scheidt, K. A. "Nucleophilic Acylation of Oxazoles Catalyzed by N-Heterocyclic Carbenes," in preparation.
2. Galliford, C. V.; Scheidt, K. A. "Metal-Organic Frameworks From Bidentate 2-Acyl Oxazole Monomers," in preparation.

B. BOOKS AND/OR BOOK CHAPTERS

None

C. PROCEEDINGS ARTICLES

None

5. INTERACTIONS

A. PRESENTATIONS AT MEETINGS, CONFERENCES, AND SEMINARS

University of Missouri, September 2005

Merck Process Research, September 2005

University of New Hampshire (Organic Syntheses Lecture Series), September 2005
Abbott Laboratories, Abbott Park, September 2005
Illinois Institute of Technology, October 2005
University of Delaware, November 2005
University of Illinois-Chicago, January 2006
Bristol Myers Squibb, Princeton, February 2006
Abbott Process Research Laboratories, March 2006
University of Buffalo, April 2006
University of California, San Diego, April 2006
3M Corporation, April 2006
Irving Klotz Memorial Symposium, Northwestern University, April 2006
Wyeth Research, June 2006
Stereochemistry Gordon Conference, June 2006
Heterocyclic Compounds Gordon Conference, July 2006
Organic Reactions and Processes Gordon Conference, July 2006
Roche Pharmaceuticals, August 2006
Texas A&M University, August 2006
Amgen Pharmaceuticals, September 2006
Bayer, September 2006
University of Colorado, Boulder, October 2006
Yale University, October 2006
Columbia University, October 2006
University of Minnesota, October 2006
University of Iowa, October 2006
University of Wisconsin, November 2006
University of Pennsylvania, November 2006

B. CONSULTATIVE/ADVISORY FUNCTIONS

Scheidt consults for Abbott Laboratories

C. TRANSITIONS

N.A. for the period.

5. NEW DISCOVERIES, INVENTIONS AND PATENT DISCLOSURES

A. NEW DISCOVERIES

N. A. for the period.

B. INVENTIONS AND/OR PATENT DISCLOSURES

N.A. for the period.

6. HONORS/AWARDS

2006	Amgen Young Investigator Award (2006)
2005	Boehringer-Ingelheim New Investigator Award in Organic Chemistry (2005)
2005	Northwestern University Distinguished Teaching Award
2005	3M Nontenured Faculty Award
2005	Abbott Laboratories New Faculty Award