



3-2014

Synthesis and Polymerization of (E,E)-[6.2]- (2,5)furanophane-1,5-diene

Neil D. Doppler

Sacred Heart University, dopplerd@sacredheart.edu

Jeffrey H. Glans

Sacred Heart University, glansj@sacredheart.edu

Follow this and additional works at: http://digitalcommons.sacredheart.edu/chem_fac



Part of the [Polymer Chemistry Commons](#)

Recommended Citation

Doppler, Neil D. and Glans, Jeffrey H., "Synthesis and Polymerization of (E,E)-[6.2]-(2,5)furanophane-1,5-diene" (2014). *Chemistry Faculty Publications*. Paper 35.

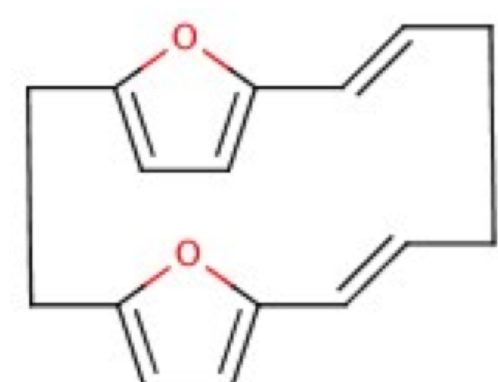
http://digitalcommons.sacredheart.edu/chem_fac/35

This Poster is brought to you for free and open access by the Chemistry Department at DigitalCommons@SHU. It has been accepted for inclusion in Chemistry Faculty Publications by an authorized administrator of DigitalCommons@SHU. For more information, please contact ferribyp@sacredheart.edu.



Abstract

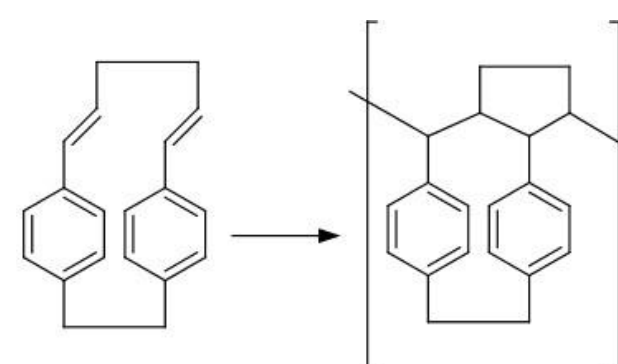
The goal of this research is to polymerize (E,E)-[6.2]-(2,5)furanophane to give a linear polymer. It will be synthesized by a 1,8-Hofmann Elimination using trimethyl-[(E)-3-(5-methyl-2-furyl)allyl] ammonium iodide.



This diene will then be polymerized. The resulting polymeric [3.2] furanophane will then be oxidized to form a polymeric macrocycle tetra ketone. This compound will be tested for cation complexation.

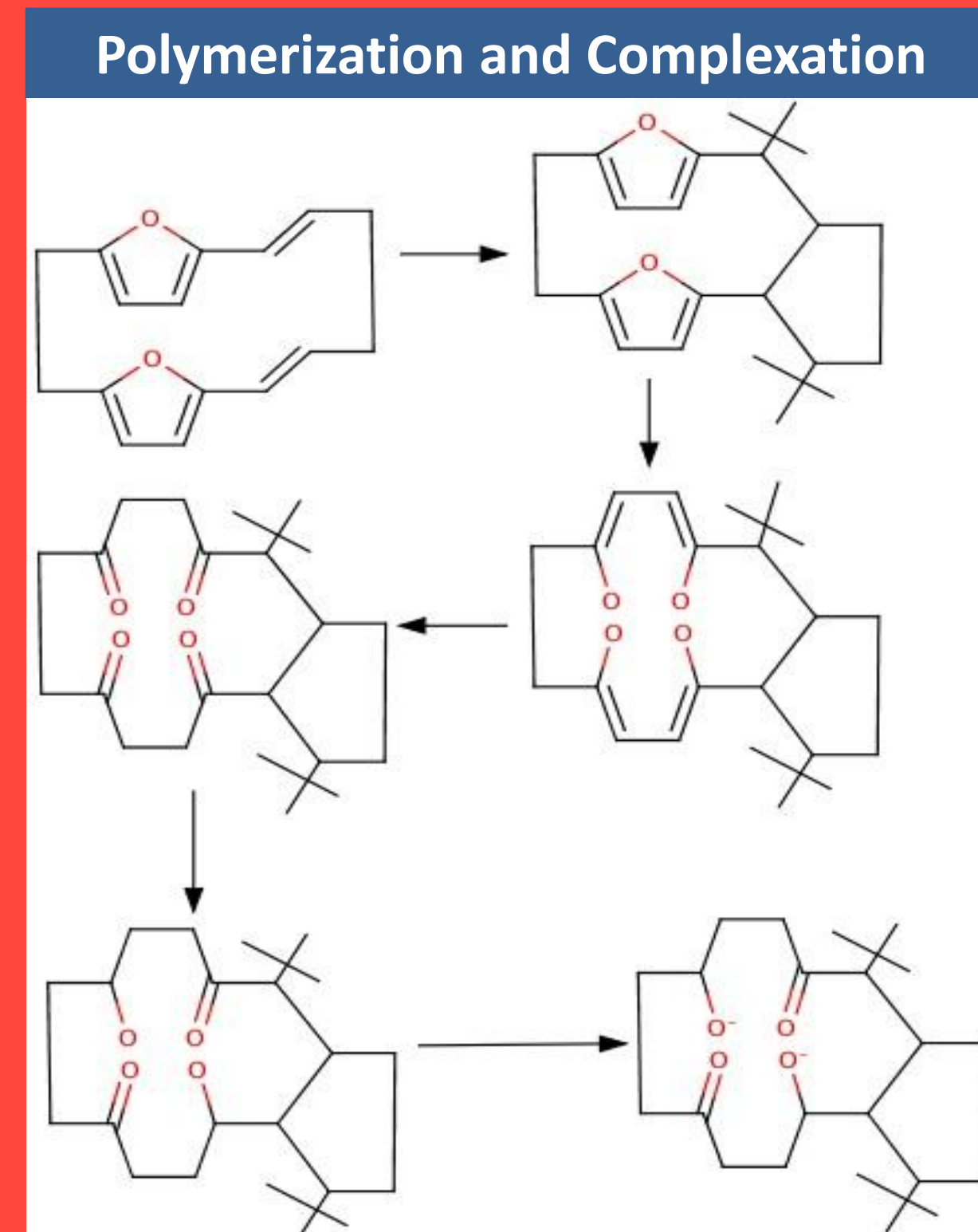
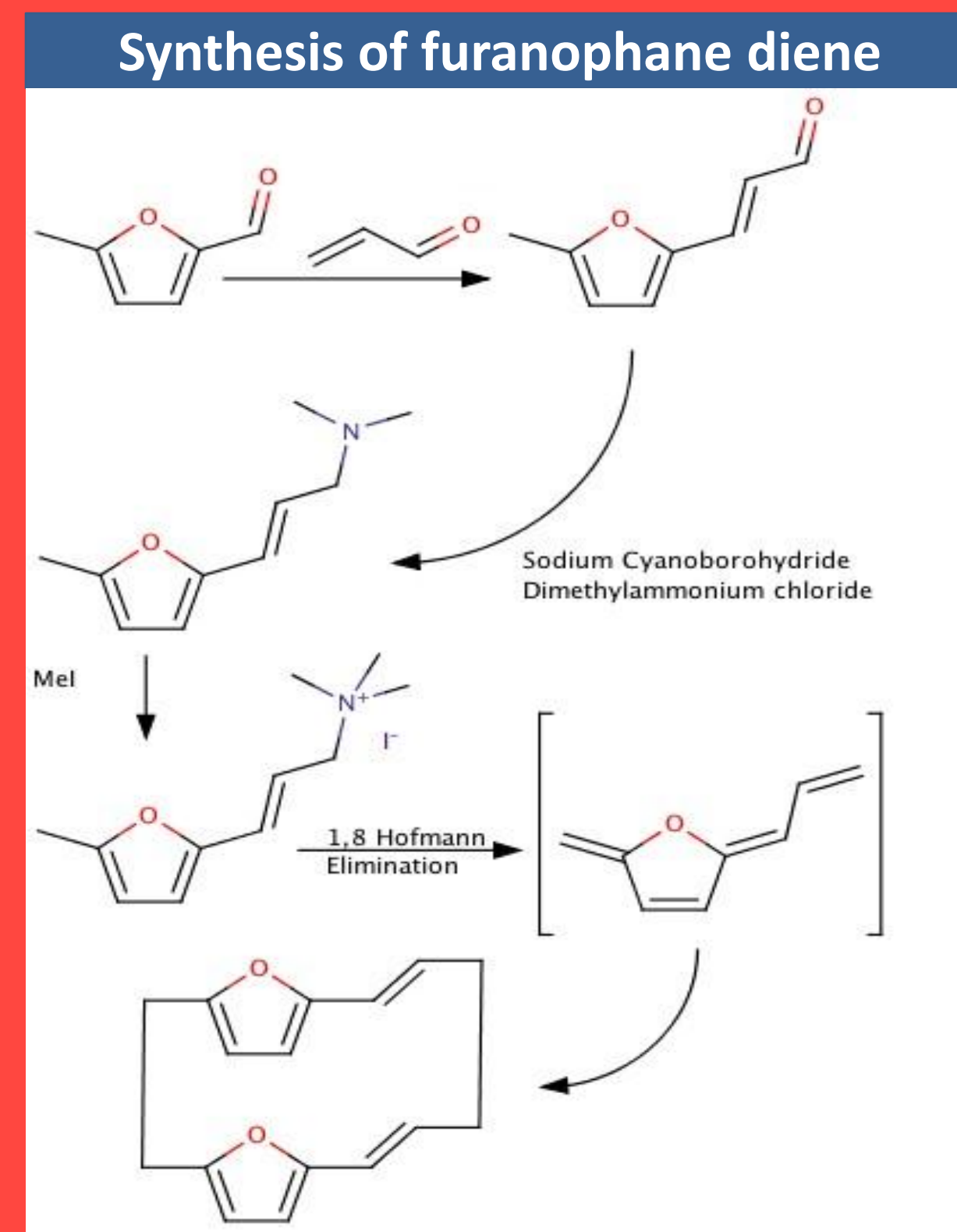
Introduction

- Cyclophanes are macrocycles that contain aromatic rings within the greater ring structure¹.
- The penchant for cyclopolymerization was demonstrated previously with [6.2]paracyclophane-1,5-diene².



- Our research uses furan in place of the benzene ring in the macrocycle. These are termed "furanophanes".
- We are trying to polymerize the furanophane. The intermediate diene: [6.2] furanophane diene has already been reported³.
- Through oxidation of the furan ring, we will attempt to create an organometallic complex; fixing and binding a metal in the center of the macrocycle.

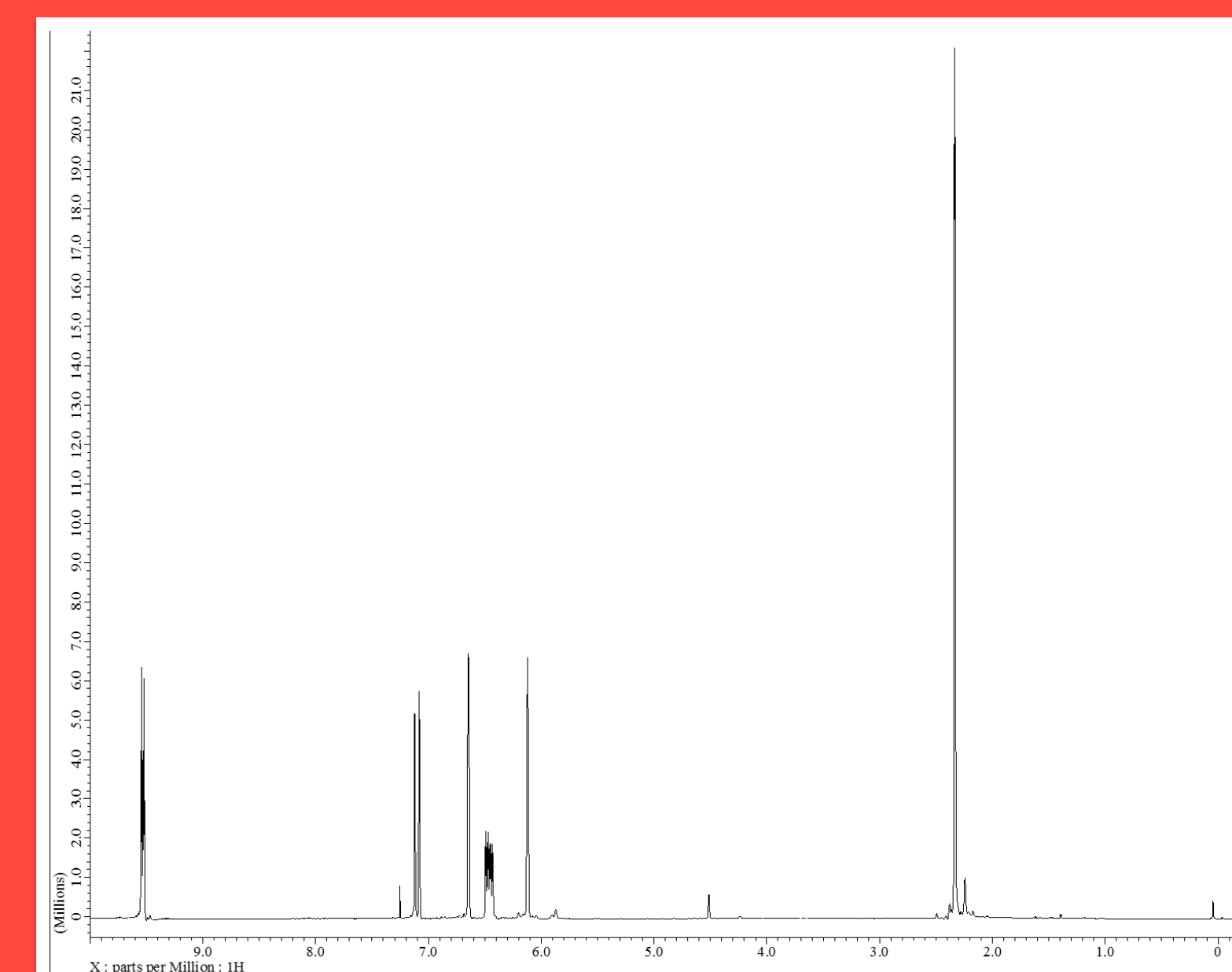
Reaction Scheme



Results

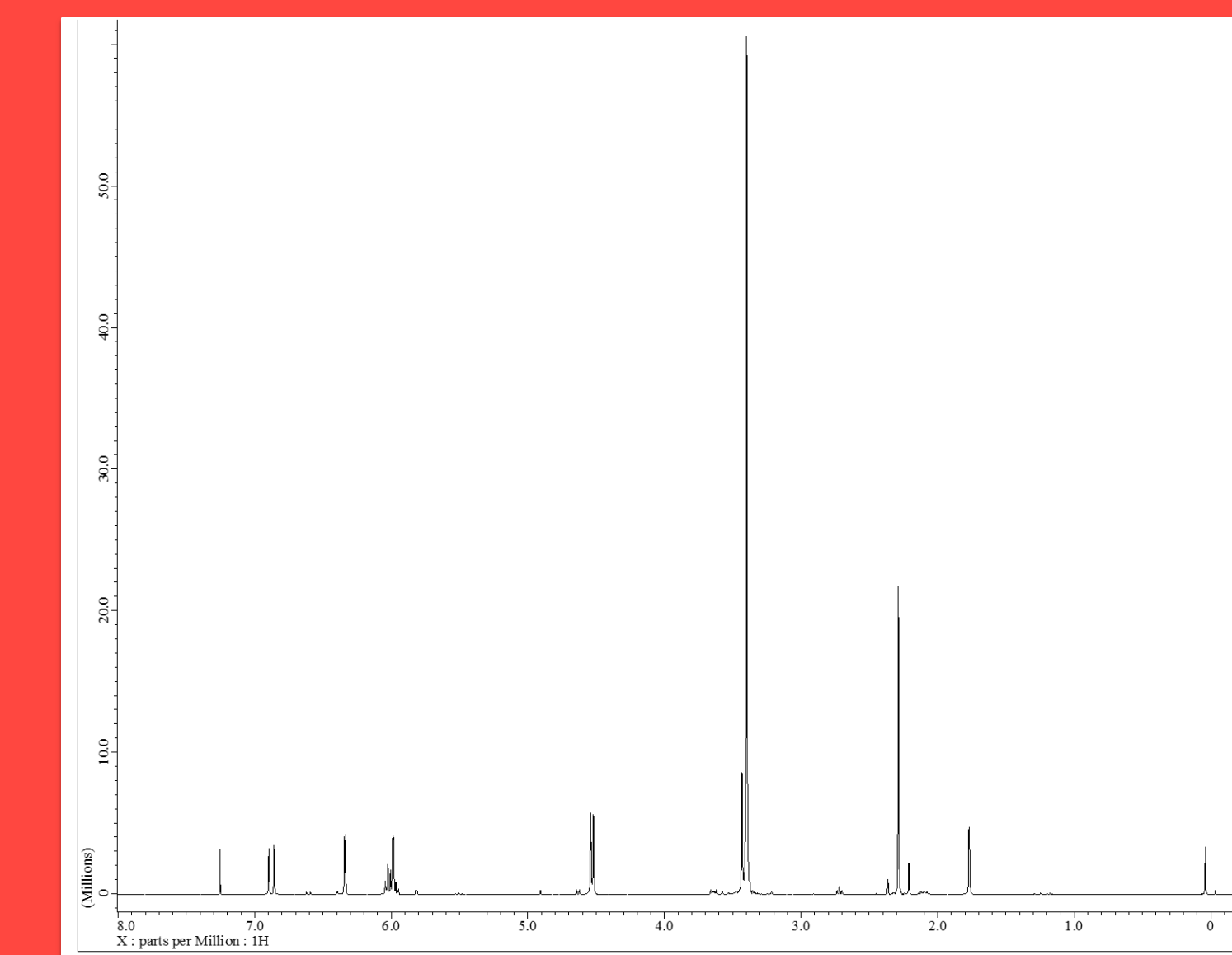
Synthesis of (E)-3-(5-methyl-2-furyl)prop-2-enal

- Aldol condensation of 5-methylfurfural and acetylaldehyde in basic conditions⁴
- Isolated by vacuum distillation (bp 68-74°C @ approximately 25 mmHg)
- 62.4% isolated yield
- Structure and purity confirmed by ¹H and ¹³C NMR.



Synthesis of trimethyl-[(E)-3-(5-methyl-2-furyl)allyl] ammonium iodide

- Synthesis was a reductive amination with sodium cyanoborohydride and dimethylamine hydrochloride⁵
- The ammonium salt was formed with methyl iodide
- Isolated through crystallization
- 50.7% yield isolated yield
- Structure and purity confirmed by ¹H and ¹³C NMR



Next Steps:

- Improve yields of the completed reactions.
- Use the ammonium salt product in a 1,8-Hofmann Elimination to undergo cyclopolymerization to form the [6.2] furanophane diene.
- Polymerize to the [3.2] furanophane containing polymer.
- Oxidize the [3.2] furanophane containing polymer.
- Attempt to form organometallic compound through the complexation of cations.

Acknowledgements

ND thanks the Undergraduate Research & Internships grant committee at Sacred Heart University for a research grant and travel grant.

Contact

Neil Doppler
Sacred Heart University
Email: dopplern@sacredheart.edu
Phone: (609) 781-0796

References

- Cram, Donald J.; Cram, Jane M. (1971). "Cyclophane chemistry: bent and battered benzene rings." *Accounts of Chemical Research*. **1971**, 4(6), 204-213.
- Longone, Daniel T.; Günzler, Daniel T. (1986). "Cyclopolymerization of (E,E)-[6.2]paracyclophane-1,5-diene." *Journal of Polymer Science Part A: Polymer Chemistry*. **1986**, 24(8), 1725-1733.
- Küselgus, S.H.; Longone, Daniel T. (1978). "A new vinylic-like intermediate: 2-allylidene-5-methylene-2,5-dihydrofuran. Synthesis of [6.2], [4.4], and [4.2] furanophanes." *Tetrahedron Letter*, **1978**, 27, 2391-2394.
- Brooks, D.W.; et al. "Furan and pyrrole containing lipogemase inhibiting compounds." US Patent 5,112,840 1992.
- Higberg, T.; Ulf, B. (1984). "Stereoconservative reductive methyl- and dimethylamination of isomeric 3,3-dialkylpropenals." *Synthetic and mechanistic studies on control of the stereochemistry.* *Journal of Organic Chemistry*. **1984**, 49, 4209-4214.