Part I: VIRTUAL LABORATORY versus TRADITIONAL LABORATORY: WHICH IS MORE EFFECTIVE FOR TEACHING ELECTROCHEMISTRY?

Part II: THE GREEN SYNTHESIS OF AURONES USING A DEEP EUTECTIC SOLVENT

By

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I dedicate this research to my wife who, through sacrifice and encouragement, made this work possible. I love you, Katie.

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Abstract

The role of the teaching laboratory in science education has been debated over the last century. The goals and purposes of the laboratory are still debated and while most science educators consider laboratory a vital part of the education process, they differ widely on the purposes for laboratory and what methods should be used to teach laboratory. One method of instruction, virtual labs, has become popular among some as a possible way of capitalizing on the benefits of lab in a less costly and more time-flexible format. The research regarding the use of virtual labs is limited and the few studies that have been done on general chemistry labs do not use the virtual labs as a substitute for hands-on experiences, but rather as a supplement to a traditional laboratory program. This research seeks to determine the viability of a virtual simulation as a replacement for a traditional hands-on electrochemistry lab in the general chemistry II course sequence. The data indicate that for both content knowledge and the development of hands-on skills, the virtual lab showed no significant difference in overall scores on the assessments, but that an individual item related to the physical set-up of a galvanic cell showed better scores for the hands-on labs over the virtual labs. Further research should be done to determine if these results are corroborated by experiments performed in other settings with the use of different virtual labs and how the virtual labs compare to other laboratories using different learning styles and learning goals.

One often-cited purpose of laboratory experiences in the context of preparing chemists is to simulate the experiences common in chemical research

laboratories. As a part of my graduate school requirements I worked for several years in an organic synthesis lab. This research experience provided the opportunity to complete an organic synthesis of aurones using a deep eutectic solvent. These solvents show unique properties that make them a viable alternative to ionic liquids. Aurones are a unique biological product in many plants and preliminary research has shown that these chemicals could be viable drug candidates. The use of the deep eutectic solvent provides a green and inexpensive way to make large numbers of different aurones quickly. In this dissertation, the synthesis of twelve different aurones is described.

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CHAPTER ONE: INTRODUCTION

At the beginning of my teaching career, I was hired as a science program coordinator and teacher at a very small private college with a total enrollment of roughly 350 students that was just beginning to design their fledgling science curriculum. As I worked to design the curriculum plans they had envisioned, I became aware of my lack of experience dealing with curriculum development and classroom design, as well as the daunting task of determining the best course of action for a science major curriculum at the college level. The most difficult thing for me was the design and implementation of laboratory activities. What sorts of methods would best serve a given class and what were the purposes and goals of the laboratory for each class? Does the way we teach laboratory really reflect “real-world” science? Should we place our students in research laboratories early on in their educational careers and eliminate teaching laboratories associated for each class? These are some of the questions I asked myself. Also, the cost of running a laboratory program in the way that I saw fit was not possible due to budget constraints, so the feasibility of providing comparable lab activities to our students as those from other higher institutions on a small budget became my ultimate goal. Early on as a teacher, I wondered what benefits my students received from their laboratory experiences. I can honestly say that some of this was due to my lack of preparation but as I gained more experience teaching labs in other settings including several years as a graduate student and several years as an adjunct at a nearby college, I realized that the problems I was facing were universal. Do students actually understand what they are doing in the laboratory or are they only concerned about finishing the work as soon as possible? Do students, or for that matter teachers, have a firm grasp on the purposes and expected outcomes of laboratories? Can the cost of the laboratory be reduced while still providing an adequate educational experience with respect to content and skills? These questions plagued me, and I became interested in researching them as I began my doctoral career. After reviewing the literature on laboratory education in chemistry specifically but also in science in general (see Chapter 2), I found that many of my problems and questions regarding laboratory were addressed by research articles that had been written on the purpose and usefulness of the laboratory component of the baccalaureate educational system in America. As I began to look at the costs of laboratory and possible ways of overcoming these barriers, I was introduced to the concept of virtual laboratories.

Virtual Laboratories

Virtual environments and computer simulations provide a means to give students a better understanding of the particulate world that we study in science classes, especially in chemistry. This is illustrated in the use of a variety of formats that allow students to view and manipulate chemicals at the molecular level in a three dimensional world. Programs such as Spartan, have been widely used for years in chemistry classes to enhance students understanding of the particulate world. The use of these computer programs to model reactions at the molecular level have led others to think of possibilities in which computer simulations can mimic laboratory experiments for students. These simulations were developed as tools to help students access and interact with information in different ways and recently some have suggested that these virtual experiences could possibly replace the expensive hands-on activities traditionally found in most undergraduate laboratories. Simulations have been used in other areas as well as a means to help students grasp an understanding before real hands-on applications were necessary. Just as computer simulations are used early on in pilot training, perhaps simulations could be used for laboratory experiences early in a student's education. Research investigating the effectiveness of virtual labs has been done since the 1970s but most of the recent studies have used virtual labs as a supplement to the regular curriculum rather than a replacement. Some of these programs have indicated that they have been used in a number of ways including replacement of labs and use for an online school but very few research papers have been published regarding the use of virtual labs as a replacement. Recently as well, the American Chemical Society (ACS), and The College Board have decided to encourage and promote the use of hands-on labs by implementing policies on the AP science courses and approved ACS chemistry bachelor's degrees. The College Board informed high schools that have AP (Advanced Placement) science classes that in order for the classes to be approved by them, a sufficient number of hands-on labs had to be performed. In the case of the chemistry AP classes, 16 hands-on labs must be performed (The

College Board, 2013). If the schools decided to use virtual labs to teach the lab portion of the class, then the classes could be conditionally approved with a statement made to the colleges reviewing their credit that indicated the nature of their lab. The ACS recently published a policy statement regarding their approval of more hands-on labs and the emphasis they place on its value (American Chemical Society, 2011). They also require 400 hours of hands-on labs in upper-level classes for chemistry majors to be ACS approved; however, these hours do not include the general chemistry labs, which are the largest chemistry classes in most schools. Several schools, including Oregon State, provide online courses with virtual lab components for non-major chemistry courses. Much of the original push in research and development of virtual labs was intended for high school and distance education courses in college settings. The ability to offer laboratories online would be extremely helpful for online degrees and online high school curricula. There currently is a lack of sufficient research in the area of virtual labs and simulations to make good decisions regarding their usefulness in education. A review on virtual lab research papers across the science disciplines and a book by the National Research Council indicates this lack of sufficient research (Honey, 2011; Ma & Nickerson, 2006). One of the concerns is that virtual labs will not be the best method to teach laboratory skills when it comes to measurement, use of tools (glassware, analytical balances, etc.), and any activity that requires hands-on manipulation of instrumentation. This raises the question of the purpose of laboratory and what goals we want to accomplish in lab. Could we use virtual labs in the General Chemistry class to reduce the costs of large enrollment courses and invest in the more expensive hands-on labs for students enrolled in higher-level college chemistry courses? In this dissertation, I wanted to compare virtual labs to traditional hands-on labs in an effort to determine the viability of a virtual lab as a replacement to the hands-on experience.

Electrochemistry Simulations

Dr. Thomas J. Greenbowe and his Chemical Education research group at Iowa State University have been researching the difficulties students experience with electrochemistry for years. Many graduate and undergraduate students have done research with electrochemistry concepts to determine the misconceptions students have and the possible teaching tools and approaches that could be used to eliminate those misconceptions. The design of some of these tools took on the form of virtual computer simulations to help students view the particulate and macroscopic aspects of the chemicals involved in an electrochemical cell. Many of these were written to be used as supplements or homework to help students learn the specifics of batteries and redox reactions. These virtual simulations also were posted on the Internet with worksheets to go along with the simulations for the students to fill out. As we began to study the use of virtual simulations as a replacement for some of our General Chemistry Labs, we realized that several of the simulations could replace each of the hands-on activities that our students were required to complete in the laboratory. Given the simplicity of the Greenbowe simulation of the electrochemistry laboratory, its no cost access, and the similarity between this simulation and our hands-on laboratory, we decided to use these simulations as the virtual lab option in the experiment to test the viability of a virtual lab as a replacement for a hands-on laboratory.

Organic Research

Since one of the purposes for the educational laboratory is to prepare students for future scientific lab research, as a teacher I knew it would be beneficial for me to have some experience in a research lab. Having the opportunity to work in Dr. Handy’s research lab has given me vital tools to use in structuring and developing a research laboratory in the future to help students get experience in a scientific research setting. While in Dr. Handy’s lab, I was able to synthesize several aurones in a new green and inexpensive way.

Aurones are a member of the flavonoid family of compounds found in plants that have been recently studied for their medicinal properties. Aurones are aromatic compounds that are found in plant flowers and contribute to the yellow colors. Since research suggests these compounds can serve as possible drug candidates, several methods of making aurones have been employed. We were interested in developing a way to make them quickly and cheaply with very little waste. The condensation reaction to make the Aurone was done using a new family of liquids called deep eutectic solvents. These solvents are solids that combine to form liquids with extremely depressed melting points which makes them viable alternatives to catalytic solvents such as ionic liquids (Ru & Konig, 2012). Using urea and choline chloride as a deep eutectic solvent, we synthesized aurones from coumaranone and several aromatic halides. This allowed us to create many different aurones quickly and easily with minimal waste and little purification necessary. This gives us a “green” method to make aurones for further study in the field of medicine and other possible uses.

Conclusion

Since the laboratory has become an important part of my preparation on a daily basis as I teach my undergraduate courses in science, the role of laboratory in science education has become a passion of mine. Through my research in the areas of virtual labs and organic synthesis, I have furthered my understanding of the role of laboratory and its importance in the educational careers of my students. The education of highly motivated and prepared scientists is important for our future and the role of laboratory in this educational process plays a vital role, but we need to figure out how to use the methods of laboratory education to our benefit in whatever ways we can determine work the best. Hopefully this research will spur future work in the areas of laboratory research so that the question of the role of laboratory and how to accomplish that role can become clearer.

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CHAPTER TWO: LABORATORY EDUCATION

The laboratory component has been a major part of science education since the beginning. Chemistry labs began as apprenticeship experiences and became part of the wider circle of education at the end of the 19th century. In order for us to understand the implications of the educational laboratory and its shortcomings as well as its benefits, we must understand the history of the lab in science education and its changes over the past century.

The Beginnings of Chemistry Laboratory in Education

Science education in America was originally known as the study of natural philosophy (Elliott, Stewart, & Lagowski, 2008). Early on in America's history, much emphasis was placed on science education due, in part, to early American patriots like Franklin and Jefferson (Fay, 1931; Newell, 1925). Chemistry education originally was taught as part of medical education and was taught in schools as early as the late 1700s by Benjamin Rush. Later, chemistry was considered a separate discipline when several schools began forming departments of chemistry in the late 1700s (Fay, 1931). Most early chemistry instruction, however, only included lecture and demonstrations but laboratories were not used in America for the purpose of instruction (Sheppard & Robbins, 2005). The use, dissemination, and method of laboratory education was not established in America until the middle of the 19th century. Understanding of the historical underpinning of laboratory education gives us insight into where we have been and how this has shaped where we are today.

While there were many chemistry labs both in the US and in Europe, the use of laboratory as an integral part of the educational endeavor has its roots in Germany (Good, 1936). There were teaching laboratories in the United States in the late 1700s, but the influence of the German scientist, Justus Von Liebig, had profound implications for the dissemination of laboratory education in America (Browne, 1941; Fay, 1931; Fife, 1975; Sheppard & Horowitz, 2006; Sheppard & Robbins, 2005). He also had great influence in Europe and even though many countries including Great Britain had chemistry departments, the influence of Liebig on the use of laboratory as a teaching tool disseminated across the world. Teaching science to a few in research lab settings was the standard, and many “scientists” learned their trade in apprenticeship-type settings when the need for skilled workers became necessary during the early industrial revolution (Reid & Shah, 2007). Liebig, however, receives a lot of credit for implementing the educational aspect of laboratory because of his analytical approach and his success in churning out successful research (Elliott et al., 2008). Liebig came to Germany after studying in Paris under Gay-Lussac and he began his tenure at the age of 21 at the school in Giessen in 1824 (Brand, 1941; Sommer, 1931). Liebig’s lab in Germany worked much like our graduate schools do now and his lab became a popular destination for American and European scientists in the middle of the 19th century (Pickering, 1993). Students entered his lab to learn the trade by accomplishing research tasks under Liebig’s qualified instruction. Each new student was to learn specific techniques in order for them to become skilled at performing the necessary tasks for chemical analysis (Elliott et al., 2008). After learning these techniques, students were then given several chemicals labeled with letters and the students were asked to identify these unknown compounds using the analysis methods they had previously learned. They learned these techniques and analyzed these unknowns under the watchful eyes of Liebig's research assistants. Students were expected to identify these compounds in a timely manner and the research assistants monitored their progress. Once students passed these tests they were then able to take on research projects under Liebig's tutelage (Sheppard & Horowitz, 2006). This method of analytical determination helped solidify the process of laboratory education and would be classified today as "inquiry' or "problem-based" laboratories (Domin, 1999; Elliott et al., 2008). Liebig's lab produced such a high quantity of quality research that many in Europe and America went to study under Liebig. Many of his students left his laboratory to go to other institutions and took with them his method of laboratory education. Some of his unknowns were published so that others could use this method for educating their students.

The influence of Liebig on American laboratory education can be seen through the influence of his methods on some of his students who came to America and their influence on their own students. Horsford, a student of Liebig's, brought Liebig's laboratory method of education to the United States when he became the science professor at Harvard and convinced Abbott Lawrence, a successful manufacturer, to support the creation of a laboratory and scientific school known as the Lawrence scientific school (Sheppard & Horowitz, 2006). This school modeled Liebig's approach and had great influence on a number of chemistry students. In 1850, Josiah Cooke became the chemistry instructor at Harvard after graduating from Harvard and created a chemistry laboratory much like the method used at the Lawrence scientific school. Cooke even wrote a book called *The Pamphlet* that included experiments and requirements for high school chemistry classes that he thought were necessary for students to undertake before coming to college (Rosen, 1956). A lack of funding and qualified teachers prevented many high schools from providing appropriate instruction in chemistry as defined by Cooke. At Harvard, one of Cooke's earliest students was Charles Eliot. Eliot gained an appreciation for the use of laboratory to teach aspects of chemistry and science in general (Sheppard & Horowitz, 2006). Eliot worked for Cooke for a few years after graduating, worked as a dean at the Lawrence scientific school, spent years abroad in Europe looking at their educational systems, and eventually ended up teaching at MIT with another chemist named Storer (T. L. Davis, 1929). Eliot again began implementing the laboratory education style he had been a product of for so many years. He eventually ended up becoming the president at Harvard and, along with Cooke; they influenced the American educational system in favor of laboratory. While Eliot was president of Harvard, he made great strides in changing Harvard's admission policies, which drastically changed the way high schools approached science, especially in the surrounding areas (Rosen, 1981). Many public high schools were just beginning to be built and many of them included science laboratories for the first time. Eliot also served on the Committee of Ten, which was a national education committee set up to help high schools and colleges work together to make recommendations for high school college preparatory education. Eliot's influence on the laboratory component of science education can be seen in the Committee of Ten's recommendations for science curriculum especially that of chemistry (Sheppard & Horowitz, 2006). Reading the list of recommendations shows the high value they placed on lab and most schools, even colleges today, would be hard pressed to meet all of their recommendations. Since high schools were just being built it was easier for schools to include facilities that made it possible to implement these recommendations (Sheppard & Horowitz, 2006). This set the table for laboratory education in America at the start of the 20th century.

The Committee of Ten's recommendations in 1893 were eventually used by the Committee on College Entrance requirements in 1899 to establish the requirements for high school graduates who were to be eligible for college entrance (Sheppard & Robbins, 2005). The new requirements from the Committee for high school graduates were less stringent and most high schools followed the requirement of only one science class for high school students. This was not the recommendation of the Committee of Ten, but schools were given electives that the Committee on College Entrance believed would be additional science courses. Biology became the primary science course taken in the 1920s by high school students and few students took other science courses. Debates about the number and sequence of science courses were developed in these committees. The Committee of Ten had very large goals and ideas about the sequence and number of science courses to be offered and other committees and high schools loosely followed these in the following years. Chemists like Eliot, Storer, and Cooke had written textbooks and lab books (*The Pamphlet*) to help high schools in their endeavors to provide good instruction (T. L. Davis, 1929). The lab books at that time appeared to focus on the qualitative aspect of chemistry and the learning of analytical techniques in the laboratory (Siebring & Schaff, 1977). Many other textbooks were also available, but around the turn of the century many high schools thought it was too difficult to teach chemistry as Cooke and Eliot wanted, and there was a backlash against the “ivory tower” educators in the colleges and universities and they refused to implement their recommendations (Rosen, 1956). While Eliot and Cooke placed a high value on a particular kind of science education, the other schools refused to implement this kind of science education because they felt that these professors were out of touch with the way things were in these institutions. This was due to a number of factors including huge enrollments in colleges and high schools, lack of funding, lack of qualified educators, and the educators though Eliot and Storer’s lack of emphasis on qualitative work and only on technique and quantitative data was not the correct approach (Kapuecinski, 1981; Rosen, 1956). For these reasons, after World War I, a debate began about the usefulness of laboratory education. Couldn’t scientists be taught by using demonstrations by the teachers only and not require students to have a hands-on laboratory component?

Laboratory versus Demonstration: the 1920s and 1930s

Around the 1920s and 1930s, many in the physical sciences began asking if instructional laboratories were necessary for students to gain an adequate understanding of the discipline. This was debated primarily for instruction at the high school and early college level. Some were advocating that the use of demonstrations and the use of supplied data for students to analyze would be sufficient in early education. Science departments became flooded with students at this time because of the industrial boom in America and the cost to educate these students was tremendous. Reasons for the debate varied. Those in favor of demonstrations suggested that individual laboratory instruction was costly, time-consuming, and lacked in the teaching of the scientific method (Kapuecinski, 1981). Many believed laboratories should be relegated to those who would work as chemists and needed the technical aspects of laboratory but not those who were going into other fields. They also believed that demonstrations had important educational benefits such as keeping all students together and not allowing poor students to fall behind (Kapuecinski, 1981). They argued that demonstrations gave students more time to think about the experiment instead of worrying about the set-up. Herbert Smith argued many of these points and seemed to think that students can very easily go through the laboratory portion of a course mechanically because they are not required to think and they usually have learned what the answers should be in lecture (Smith, 1927). Herschel Hunt argued along similar lines stating that the cost of lab is prohibitory to individual instruction (Hunt, 1935, 1936). On the other hand, those who argued for individual laboratory education instead of demonstrations cited better learning of chemistry concepts with hands-on experiences, increased retention of facts, and increased opportunities to experience real science. These proponents of laboratory further argued that professors could use laboratories to teach students how and what to observe (Kapuecinski, 1981). Bowers (1924) argued these points for the inclusion of laboratory work in 1924 and cited higher exam scores of those students in laboratory. Carmody (1935) and Schlesinger (1935) argued that the reason for the debate was that most of the current labs were so poorly designed and taught that they did not seem to be worth the effort. The debate raged from the 1920s until the early 1940s, and eventually led to several educational research studies comparing the two lab types but these studies showed little difference between students taught by these two methods. For instance, Payne (1932a-c) wrote a series of three articles in 1932 regarding the debate over demonstration versus individual laboratory instruction. In his first article, Payne outlines the literature and lists a series of seven studies, mainly in high schools, that showed varying statistical results comparing the two approaches (Payne, 1932a). While only a few of the studies showed significant results, they were evenly distributed with three showing favorable results for the demonstration method, three showing favorable results for the individual laboratory method, and one study showing no difference. One of the significant results cited was one by Horton who demonstrated that while written tests of chemical knowledge showed no difference, testing on students' ability to perform laboratory tasks was significantly different in favor of individual laboratory instruction (Horton, 1928). In the second article, Payne outlined the differences in lecture and laboratory offerings in general chemistry across several colleges and universities (Payne, 1932b). Then, in the last article, Payne did an experiment with almost 300 students from several institutions and found that students that were given a demonstration course in the first half of general chemistry followed by an individual laboratory instruction in the second half scored better on tests than did students in individual laboratory instruction for the whole year (Payne, 1932c). Debates continued for decades and many decided to retain the individual laboratory instruction even though little in the way of solid research suggested its supremacy when it came to educational practice and student outcomes (Adams, 1942).

Since the debate was mainly aimed at the inadequacy of the status quo, many on the side of individual laboratory instruction argued that the problem was not the laboratory itself, but the way in which it was taught (Carleton, 1930). Carmody, for instance, argued for the overhaul of the way laboratories were taught and he suggested the practice of including the purposes of each experiment into the mind of the instructor to ensure the developments of proper laboratories to reach each specific goal (Carmody, 1935). He advocated for three types of labs, one for the instruction of scientific methods, one for the instruction of laboratory techniques and one for the understanding of chemical principles and knowledge. He outlined each one and gave examples for others to follow. Siebring and Schaff (1977) also pointed out that lab manuals had undergone changes since the early 1900s. In the early part of the 20th century, the laboratory book was open ended with qualitative experiments and open-ended questions allowing students to pose ideas of their own, whereas in later laboratory books of the 1920s and 1930s, all the information was given to the student and they were only required to fill in the blanks. Even though the debates about the use of demonstrations versus individual lab instruction were prevalent in the research literature there was very little change when it came to actual practice in the high schools and colleges of America. As questions about the necessity of lab eventually began to diminish after World War II and the importance of science education became a premium once more, the laboratory component was reconsidered as a viable and valuable instruction method. This was probably due to the important discoveries made in science during the war. Questions about the laboratory turned to the proper way in which laboratory instruction should be conducted and in the 1960s with the overhaul of chemistry curriculum, the laboratory received new scrutiny.

Curriculum Changes and the New Debates Since the 1960s

Several decades after World War II, the Cold War led to a war of scientific innovations. The competition among nations to further their causes led to major discoveries and explorations in the field of science. As this enthusiasm for scientific discoveries continued, the ideas of science education began to change as well. A new creative sort of discovery-based curriculum was born and because of the wealth of information, an emphasis was placed on learning principles and concepts instead of individual reactions and factoids. These curriculum changes led many to believe that the education of scientists worldwide would be more uniform since the curriculum was put into practice into many of the nations of the world and they believed their new emphasis on creativity was superior to previous teaching methods of a more “cookbook” style. This led to nearly universal reform of science education as demonstrated by many conferences on science education that were international in scope including many European countries and the U.S. especially. These changes in curriculum were important across all levels of education but they again caused many to ask questions about the place of laboratory in the teaching of science. Since an emphasis was placed on being creative and the discovery of ideas, learning in the laboratory would seem to take a prime place in the education of scientists. In the 1970s, with the influence of changes in learning and teaching theories brought on by psychologists such as Piaget, the curriculum needed to be looked at again. Johnstone, who was one of the leading chemists in the curriculum changes of the 1960s, stated that the teachers were excited about the curriculum changes and thought that chemistry would be easier to learn (Johnstone, 1993) but the optimistic views of the outcomes that would be seen from this curriculum change soon waned. In fact, enrollments of chemistry majors in college specifically began to decline after the curriculum changes were made. Maybe the answer to science education lay in the new wave of psychological theories about the way students learned. Maybe we had been focusing on the wrong problem.

Johnstone (1982) believed that unlike the other science disciplines such as physics and biology, chemistry required some unique learning aspects that required students to relate the macroscopic world to the unseen chemical world (particulate) and the representations or symbols that we use to express that particulate world. Unlike biology and physics and even early chemistry education, the new conceptual understanding of chemistry required that students be able to understand that particulate world and apply this to their understanding of the macroscopic world that they could see and touch and be able to represent that world in the form of chemical formulas and equations. In earlier chemistry education, the main focus was on relating the macroscopic lab work to the representation of chemical reactions with little emphasis placed on visualizing or understanding the particulate world. With the new focus on the principles of chemistry and its underlying concepts, the laboratory's role in the educational endeavors of scientists became uncertain especially as educational emipirical research suggested that the laboratory was not useful in teaching concepts (Rowe, 1978).

To understand the role of the laboratory in science education after the curriculum changes of the 1960s, we need to look no further than the review of the literature by Hofstein and Lunetta (1982). They explained that many educators believed the lab was important but that many studies suggested little to no difference in outcomes of those students who participated in lab compared to those who didn’t perform labs, except in the area of hands-on skills. In fact, Rowe (1978) reviewed the literature in a book by the National Science Teachers Association and questioned the use of laboratory because of the lack of empirical evidence for its inclusion. Hofstein and Lunetta’s (1982) view was that the research regarding laboratory in science education was misssing due to a lack of defined goals for the lab, poorly designed studies with improper controls, a lack of proper assessment tools, and a limited number of participants in the studies conducted. They expressed their desire to see improvements in these areas of the research so that answers could be attained regarding the role of laboratory (Hofstein & Lunetta, 1982).

As changes were made in the philosophies of education due to the work of the psychologists like Piaget and Vygotski, the next few decades saw changes in laboratory education (Hofstein & Lunetta, 2004). This new constructivist approach can be seen in the call for science educators to develop the lab environment to include more opportunities for students to manipulate apparati and construct their knowledge of scientific concepts. These ideas, as well as the failure of the curriculum changes of the 1960s to boost science enrollments, new curriculum changes began in the US in the 1990s, but this time it started in the early educational grades and is making its way up to college level (Council, 1996, 2000). These changes involved standardizing the goals of education at each level - elementary to high school - to increase the level of education across the board. This shift in emphasis could be seen in the fact that many educators were proposing a lab that was more student-focused and inquiry driven than previous decades of teacher-focused lab directives (Tobin, 1990).

Twenty years later, Lunetta and Hofstien (2004), reviewed the literature again and noted the changes in lab education. The shift in philosophy was the most significant change, from a traditional style of teaching to a more student-focused classroom, including emphasis on inquiry and discovery as the research on psychology and cognition began to decifer the ways in which people learn. This lead to an emphasis on laboratory education since the laboratory was the most appropriate place to incorporate inquiry and discovery approaches. These new approaches, however, were hard to implement and an overall review of laboratory showed few improvements. In their review, Lunetta and Hofstein (2004) noted that while the new inquiry approaches were thought to be better, many lab manuals continued to use the old "cookbook" methods of laboratory education. Also, assessment of lab activities was still severely lacking and this was often due to the continued lack of specific goals. Without specific goals, the assessment of the outcomes of laboratory was impossible. Teachers and administrators also lacked knowledge and motivation about the uses of these approaches and they lacked the resources to gain an understanding of these new approaches and put them into practice. New technologies in virtual simulations and other tools gave teachers access to new possibilities but without knowledge of the specific goals of lab activities and the understanding of the use of these tools, little progress was achieved by these new technologies. As we strive to determine the best way to approach lab education the purposes of lab need to be defined, the approaches to lab educational models need to be understood, and the proper use and accumulation of resources needs to be developed.

Purposes of Lab

When ideas about laboratory education are discussed, the purposes of lab are of upmost importance. In the early years of lab education, the emphasis of laboratory was on the teaching of techniques and analytical skills related to reproducing results. In the early 1900s, the focus on lab changed to reproducing conceptual ideas in the lab and lab became a “cookbook” demonstration of the concepts in lecture. Many in the early debates over demonstration versus individual laboratory argued with different purposes in mind, indicating that the problem was not which method is best, but what do we want students to learn in lab. The defining of goals for the laboratory continues to be a problem. Lunetta and Hofstein (1982, 2004) pointed out that the purposes of lab are not defined specifically for the lab component of science education. While some have tried to define the goals of laboratory education, these goals tend to match the overall goals of science education in general and do not reflect the specific goals that need to be accomplished by laboratory work. Johnstone and Al-Shuaili (2001) for instance looked at the purposes of lab in English schools and stated that while these objectives were good they are ever-changing. Abraham (Abraham et al., 1997) demonstrated this when he used a survey to show how educators have changed their ranking of the goals for laboratory over the years. These differences can be seen across disciplines and can be seen in the validation of different styles of laboratory education.

While the number and importance of these goals has changed, the categories of goals outlined by several sources (Abraham et al., 1997; Bretz et. al., 2013; Bruck, Towns, & Bretz, 2010; Cheronis, 1962; Hofstein & Lunetta, 1982, 2004; Johnstone & Al-Shuaili, 2001) were as follows:

- Understanding and manipulation of instruments and materials in the lab (technique)
- Understanding of the scientific method and its processes of accumulating and evaluating information (method)
- Ability to design experiments, evaluate results, and problem solve (critical thinking)
- Understanding the underlying concepts of science (conceptual knowledge)
- Knowledge of facts regarding chemicals and materials (factual knowledge)
- Increase curiosity and positive attitudes toward science (positive attitudes)
- Ability to work in groups to problem solve (cooperative learning)
- Ability to read, write, and present orally in the discipline (communication skills)

These goals are not universal, as the research indicates, and many of the reasons for such a large amount of literature on the purposes of laboratory are an effort to define the goals and establish a standard of laboratory goals by which we can operate. However, as Hofstein and Lunetta (1982) pointed out in their earlier review, the problem is not that laboratory goals are elusive but that we rarely define them for the laboratory itself. The issue is that most educators do not define their goals for their own laboratories. Since goals for laboratory are ill-defined in the classroom, the instructor has little ability to decide on proper instructional styles to help accomplish these goals. As Abraham (1997) noted, each learning goal in the laboratory was probably taught best by using a specific lab style. The other issue regarding lab in general is its usefulness. As recently debated in the *Journal of Chemical Education* (Hawkes, 2005; Morton, 2005; Stephens, 2005), the opinions are varied as to the importance of laboratory in chemistry education at all. If we are to determine the usefulness of lab in education we must define our goals and then devise proper assessments to determine the lab's effectiveness at accomplishing these goals. It may very well be as many have said that laboratory is not the problem, it is the way we teach it.

Styles of Laboratory Education

Early in the history of lab education, most laboratories were set up like apprenticeships where students learned mainly techniques and were taught by following the instructors' specific directions. As laboratory education changed in the 1920s, the lab was taught with more "cookbook" style experiments where students just followed directions and with more emphasis on learning the techniques. In the 1960s, as curriculum changed to discovery and later on, inquiry styles of teaching became important in laboratory education as emphasis was placed on learning scientific methods and experimental designs and having students discover the concepts on their own.

Recently, Domin (1999) reviewed the laboratory styles of teaching and discussed their implications in laboratory. Domin lists four laboratory styles in his paper: expository (traditional), open-inquiry, discovery, and problem based. Domin explained the benefits and drawbacks to each style. Expository labs are what we would call “cook-book” labs and are definitely the most prevalent form for teaching labs in American colleges and schools. This style is seen in many commercially available lab manuals today. This was the style used early in chemistry lab education and little has changed in the way this style is taught. The other three methods are not used nearly as much in today’s educational system but may lead to better outcomes (Abraham et al., 1997). Open-inquiry labs consist of open questions and students must design and implement experiments to find the answers. This lab was first used as an implementation tool of the new constructivist approaches to education. Discovery labs have directions but leave students to interpret results and discover the concepts before they have been introduced in lecture. This style was formally a result of the curriculum changes in the 1960s (Richardson & Renner, 1970). Finally, problem based laboratories are labs in which the concepts have been introduced but students are given a new problem that they must come up with an experimental design to answer the question based on what they know (Cooper & Kerns, 2006; Sandi-Urena, Cooper, & Stevens, 2012). The method that works better depends on the goals and values for the laboratory. Many colleges use the expository method because it is generally considered safer and cheaper due to the fact that chemicals and procedures are determined in advance and because the labs are taught normally by graduate students. Abraham (1997) surveyed colleges and universities to determine the percentage that use the inquiry style versus the traditional or expository. He noted that more than 70% of instructors surveyed said they used expository labs. It may be that numbers of students, use of facilities, and cost savings become more of a factor for administrators than students' educational needs. However, the data needed to be clearer on the best ways to approach lab education. It could very well be that for different goals, we should use different approaches. The issue of cost however may be a prohibitive factor to proper education.

Cost of Laboratory Education

Recently due to standards outlined by the National Research Council on science education, there has been a push to increase the science standards in America (Council, 1996, 2000). This push in science education is due to the fact that America seems to be falling behind in math and science and that the production of technology produces valuable resources of income for the economy. However, with the increased emphasis in science education the costs may be too much to help students meet these new standards. A report in Great Britain in 2005 (R. C. Society, 2005) showed that many university chemistry departments have had to shut down due to lack of funds. Funding science programs can be very costly because of the facilities and equipment needed as well as the consumption of chemicals when compared to non-science programs. This has always been an issue in science education and chemistry in particular. The debate regarding the use of demonstrations instead of individual lab in the 1920s was primarily due to the increase in student populations in high schools and colleges and the expense to support these students was overwhelming administrators. Cost-cutting methods in chemistry laboratory education have been long sought after (Beach & Stone, 1988; Dyer, Chen, & Strawbridge, 1996; Neckers et. al., 1977; Payne & Smiley, 1931). Many methods have been considered from limiting the amount of chemicals used to designing green experiments to eliminate waste and recently designing virtual labs (Carnevale, 2003). While money for educational labs is not enough to support some curricula, it is also becoming harder to find financial support for research, as the NIH has had to cut budget spending over the past few years.

The costs of science laboratories appear to be mainly due to the use of facilities. In the Royal Society of Chemistry (2005) report, many of the chemistry departments are finding it hard to pay for facilities because of the need for both lecture and lab classrooms. This need for both types of facilities also requires that to get the best use out of the facilities they need to be used as much as possible. With enrollments skyrocketing in the last several years, colleges and universities are finding that funding for these students is becoming increasingly difficult to fund. If our goals for increasing our productivity in the sciences are to be realized, we will need to evaluate our cost efficiencies and find more sources of revenue for funding labs both in education and in research. One tool that may provide some benefit is the use of computers in lab education (Carnevale, 2003).

The Development, Use, and Research Regarding Virtual Laboratory Simulations

Since most schools are developing lower-cost ways to educate students, and since distance education has become an integral part of most colleges and universities, computers have been used in a number of ways to help with facilitating labs. Computer use in laboratory settings has increased over the past 50 years as most instrumentation has become automated and most data acquisition that is done in most modern labs requires computers. The use of computers in chemistry labs is evident by the use of simple graphing using spreadsheets, the use of probes to collect real-time data on computers, the use of computers to simulate molecular structures in organic chemistry with programs like ChemDraw and Spartan, and in many other aspects involving presentation and data analysis. Most science labs now include some use of computers. The use of computers varies from the use of spreadsheets to the virtual simulation of labs on a computer. Recently these virtual labs have garnered a lot of attention as online high schools and colleges seek ways to offer science courses online. Recent reports in the Chronicle of Higher Education and editorials in the New York Times have indicated the use of virtual labs are becoming more wide spread and that there are serious questions regarding the use of these labs

(Carnevale, 2003; Dillon, 2006). The use of virtual labs is not new and several studies using computers as lab replacements were carried out in the 1970s and 1980s (Cavin, Cavin, & Lagowski, 1978; L. N. Davis, Coffey, & Macero, 1973; Perone, 1970; Wilkins, 1975). Many colleges have designed their own virtual labs to help their students and the use of these labs is becoming a debated topic.

The reason many schools have shown interest in the ability to use virtual labs is because of the cost of hands-on labs (Carnevale, 2003; Josephsen & Kristensen, 2006; Woodfield et al., 2004). As mentioned before, many schools are finding it difficult to fund new facilities as well as the equipment and supplies. Colleges and schools need to have dedicated lab space in order to allow all the students to have lab in smaller groups. Most labs can only have about 25 to 30 students in them at one time, so this means that this space must be used constantly. Virtual labs offer opportunities to lower the costs of the lab due to less operating cost and the use of fewer chemicals. This does not mean that virtual labs come at no cost, since the up-keep of computers and equipment is still costly. Another reason that many schools are deciding to use virtual labs is the possibility of an increase in student population from on-line students. As enrollment in online courses keeps increasing, many schools are using online classes to increase their student enrollment and their funding. Online classes are beneficial because one professor can proctor a class of many students, which decreases teaching expenses, as well as decreases the amount of facilities necessary to carry out classes. There are some expenses to hire the technology staff to run the online format but this is still less expensive than the traditional format. Many for-profit schools make their living by offering online courses. The students enjoy them as well because of the ease of use and management of time. Several virtual labs have been designed with online or distance education in mind (Dalgarno et. al., 2009; Morozov, 2004; Yaron, 2003). One of these studies designed a virtual lab so that online students could become familiar with the chemistry lab before they came to the lab twice a semester and perform several experiments (Dalgarno et al., 2009). Some other labs were designed to help students with tough concepts in chemistry and were mainly used as supplementary tools to introduce new educational approaches to problems that might help the students understand the concepts (Climent-Bellido et. al., 2003; Coleman & Fedosky, 2006; Josephsen & Kristensen, 2006). These virtual labs were there to create an environment that students would not be able to see in a real chemistry lab. Most of these labs included simulations of how the molecules looked or reacted, which is impossible to accomplish in a real lab. This is an application of Johnstone’s triangle of chemical knowledge. He regarded the particulate world of chemistry to be the hardest for students to understand due to the lack of concrete ways to show this particulate world (Johnstone, 1982). These virtual labs are designed to help students visualize this particulate world and relate that to the macroscopic and representational world of chemistry as well. Virtual labs also have other advantages such as providing simulation of experiments that could not be done in normal labs. In Woodfield’s ChemLab design, he incorporated experiments about quantum chemistry that only a few labs in the country would have the machines or materials to accomplish

(Woodfield et al., 2005; Woodfield et al., 2004). In this case, students can perform experiments virtually that otherwise they would never be able to do. Virtual labs in this case can offer more educational approaches to increase the learning of concepts by students in lab.

If one were to survey the Internet for virtual labs, one would find a variety of designs and purposes for these virtual labs. Several of the virtual labs are designed with the purpose of helping students feel more confident when they actually visit the lab (Dalgarno et al., 2009), helping overcome some conceptual learning problems with chemistry (Coleman & Fedosky, 2006; Josephsen & Kristensen, 2006; Morozov, 2004), replicating real experiments, giving students some open-ended problems (Woodfield et al., 2004). These virtual simulations range from simple paragraphs with small applet pictures that depict the experiment to having a virtual lab where you can manipulate glassware and travel around the lab to get things. Each design is different and each design was created with different purposes in mind, and this makes it hard to compare virtual labs to each other for research purposes.

Since many of these virtual labs are designed differently and for different purposes, the determination of the usefulness of virtual labs in general is hard to verify. For instance, Josephsen and Kristensen (2006) designed a virtual lab known as Simulab and implemented the lab to increase student’s cognitive understanding of qualitative inorganic chemistry. They introduced the virtual lab to three successive groups of students (92 total students); all three groups answered a questionnaire and two groups took a pre- and post-test. The questionnaire indicated that students enjoyed working with the program and that most of them had a wonderful experience. The students also indicated that the virtual lab could not replace the hands-on labs. According to one group's scores, the virtual lab did increase the post-test scores.

Dr. Woodfield at Brigham Young University has created a virtual lab for many different disciplines, but his first virtual lab creation was for chemistry. His group created two virtual labs, one for general chemistry and the other for organic chemistry (Woodfield et al., 2005; Woodfield et al., 2004). In both studies, he had students take a questionnaire and a personality test and interviewed a few students. In the general chemistry virtual lab, they compared the student's personality and learning types with their responses on certain questions from the questionnaire (Woodfield et al., 2004). They found that students who are more cerebral (can approach problems from different perspectives) tended to enjoy the virtual lab more and explore them more than other students. Cerebral students also spent more time exploring the virtual lab. In the organic virtual chemistry lab, they also noticed that more students that semester had an A in the class at the end of the semester than in any previous semester they had taught the class (Woodfield et al., 2005). They also found correlations between the student's enjoyment of the virtual lab and their performance in the class. From both virtual labs, it is clear that learning styles play a role in the success of virtual labs. However, Woodfield concluded that virtual labs were the best when used as a supplement but they did not give the evidence to support that conclusion.

Dalgarno et. al. (2009) designed a virtual lab to help online students get acquainted with the real lab before they had to come on campus to perform the labs. They noticed that anxiety levels were high for online students who came to lab for the first time and they wanted to help these students by offering them a virtual environment that was designed to look exactly like the lab so that they could become familiar with it before they came to campus. In their first study, they used the virtual lab and the real lab to see whether students could appropriately find things in the real lab. They found that students who went through the real lab demonstration could identify the location of objects in lab a little better than the students who went through the virtual lab. They also saw that the majority online students who used the virtual lab demonstration thought that it helped, but only about a third of them said that it relieved their anxiety about lab or helped their confidence in their eventual lab work. One of the problems with this research however is that they made the virtual demonstration optional for online students, so only a few students chose to use it and only their data were used from the questionnaire portion.

The last two research reports used a testing source instead of only questionnaires. In the first paper, Climent-Bellido et. al. (2003) designed a full pedagogical computer program that had virtual labs as part of the teaching. This software contained several modules including a tutorial to teach concepts, virtual labs to demonstrate experiments, and an evaluation module for testing. This group chose four groups of students and placed two groups in the control group (traditional method) and two groups in the experimental group (virtual method).

The students either sat in a traditional class and listened to a teacher explain an experiment they were about to perform, or they went through the same tutorial on a computer looking at simulations of the lab. They then tested how well these students performed the actual lab in four categories: Set-up, quality of lab reports, results of experiment, and results of written test. They found that students in the control groups and students in the experimental groups scored about the same in all four categories. Students in the experimental group were better at understanding how to set up the experiment and what was to be learned by the experiment. This report was difficult to interpret since they did not explain how they did their evaluation and the virtual lab was only tested as a supplement (Climent-Bellido et al., 2003).

Liu (2006) used two classes with a total 33 students and split them into two groups. In these two groups, they both did the same hands-on and virtual labs but one group took the virtual lab first and the second group did the hands-on lab first. After each lab the students took a post-test. This experiment only tested them on one concept of gas laws. They also only tested conceptual learning in the form of the post-test. They found that students increased their conceptual knowledge significantly after the hands-on or the virtual lab. After both groups completed the other lab they also increased their scores. They conclude that it is better if students perform both the hands-on and virtual labs. However, they tested high school students who were somewhat more computer inclined and these students did not have as much science background knowledge, so their increase in post-test scores could be due to this lack of previous science experience.

Overall, the research suggests that virtual labs certainly can increase performance when used in conjunction with hands-on labs but very few experiments were conducted to test the ability of virtual labs to replace hands-on labs. One early study in the 1970s used virtual simulations as a replacement and researched both the conceptual learning by pre- and post-test comparisons and by looking at hands-on tasks that were tested as lab practical exam regarding one of the experiments they conducted. They determined that there was no significant difference in scores on any of the four experiments tested and on the practical exam regarding the use of a spectrophotometer (Cavin et al., 1978). This research presents a good approach to research but with the increased sophistication and accuracy of new computer simulations, new research on these virtual lab programs needs to be conducted. Overall the lack of sufficient research in this area is still an issue and needs to be addressed as several studies have suggested including further research designed to look at the purpose of lab and the concepts and skills that students should learn from these labs. Once we have a good understanding of the laboratory goals and purposes, we can better design educational research studies to determine the best teaching methods for these goals.

The recent use of virtual labs may also be an indictment of the current educational practices used in lab. It seems that many students just come to lab, follow the steps, and leave without ever really thinking about what they are learning or doing (Josephsen & Kristensen, 2006; Woodfield et al., 2004). This new use of virtual labs has led to increased debate on whether these computers can replace some real world hands-on training. Even this year, the college boards in several states voted to not accept college credit for science classes that did not involve a number of hours of hands-on experiments (College Board, 2013). The use of these virtual labs is still a matter of discussion, but many schools have implemented the use of virtual labs in their schools (Carnevale, 2003). One of the main questions that need to be answered with regard to science labs is what their purpose is. If professors and teachers are to effectively design and implement virtual or hands-on labs, they must have a clear purpose of the outcome of these labs. A recent review on the use of hands-on, virtual, and remote labs comes to this same conclusion (Ma & Nickerson, 2006). Ma and Nickerson suggested that one of the issues of using virtual labs has been the absence of clear purposes for the use of the labs in the research. They felt that researchers focused on four main purposes: Social skills, design skills, conceptual understanding, and professional skills. They also discovered that different studies resulted in varying conclusions. One of the reasons for these conflicting results is due to the fact that each study focused on different purposes. It seems that most people believe that virtual labs can be effective at improving conceptual learning (knowledge of facts and ideas) and design skills (critical thinking and problem solving) but might not be as effective at fostering social skills (solving problems within groups) or professional skills (technique of performing experiments). In fact, Woodfield specifically designed the virtual lab with the understanding that they would not teach students the technique of performing the labs and as a result left certain details out of his virtual lab software (Woodfield et al., 2005; Woodfield et al., 2004). In another study, Tsovaltzi et. al. (2010) added some features to their virtual lab software to increase the social collaborative process among the students that used it. In general, though there does not seem to be much empirical evidence to suggest what virtual labs and hands-on labs can and cannot do, and some of this may depend on the design of the virtual and hands-on labs. The use of new pedagogical approaches have been used both in hands-on and virtual labs and it may be hard to compare them because many of them use different approaches. Defining the purpose of lab, however, is probably the biggest problem with comparing different approaches to teaching lab. More research is necessary to define what should be accomplished in these chemistry labs and in science labs in general.

Conclusions

As we find ourselves today in a debate over the use of laboratory in chemistry education, it seems all too familiar to the debates of the 1920s and 1930s. After more than 100 years of laboratory education in the United States, we are still wondering what role laboratory should play in education and how lab should be taught. Hofstein and Lunetta (1982) concluded that with little emphasis on goals and with little to no standardized assessments for lab, it is difficult to answer these questions regarding the role of lab. We find ourselves asking similar questions as our predecessors with little to no concrete answers for them. What goals in science education are directly connected with laboratory? What methods of education work best in teaching these goals? At what levels of education should laboratory be taught? In what ways can we make use of limited resources to perform lab instruction well? Do all students need hands-on experiences to understand science? These questions have been asked by many generations of educators and if we are to answer them we must continue to improve our research in these areas so that we can be better instructors.

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CHAPTER THREE: VIRTUAL LABORATORY versus TRADITIONAL LABORATORY: WHICH IS MORE EFFECTIVE FOR TEACHING ELECTROCHEMISTRY?

Introduction

The laboratory in chemistry education has been a debated part of the curriculum since its beginning in the late 1800s and early 1900s. In the 1970s and 1980s, the empirical evidence for the validity and importance of laboratory education was lacking (Hofstein & Lunetta, 1982; Rowe, 1978). The usefulness of laboratory is still debated, even though most science educators would advocate for the importance of including the laboratory in chemistry education (Hawkes, 2004; Morton, 2005; Stephens, 2005). According to the literature, laboratory effectiveness is difficult to study due to a lack of agreed upon explicitly state purposes and goals (Hofstein & Lunetta, 1982, 2004; Rowe, 1978; Tobin, 1990). Many studies, both old and new, have tried to pinpoint the purposes of laboratory education from the instructors perspective finding little in the way of a consensus (Abraham et. al., 1997; Bretz et. al., 2013; Bruck et. al., 2010; Cheronis, 1962; Johnstone & Al-Shuaili, 2001). Without well-defined goals, it becomes difficult to evaluate what constitutes effective laboratory instruction.

Recent changes and developments in educational delivery particularly in the area of technology have led to questions regarding how best to design chemistry instruction (Casanova, Civelli, Kimbrough, Heath, & Reeves, 2006). Since distance education and online schools have become a prominent option at both the high school and especially college levels, new ways to teach and deliver content have become inevitable. This has led some to consider computer simulations as viable options for laboratory education. The use of computers to enhance or even replace certain laboratory activities is not new, and many laboratories use computers at a number of different levels to both analyze and even create data (Cavin et. al., 1978; Davis, Coffey, & Macero, 1973; Jones, 2000; Krause, 1988; Perone, 1970; Wilkins, 1975). However, there has been skepticism regarding the use of these tools as a replacement for hands-on laboratory experiences and both the American Chemical Society and the College Board have decided to endorse the hands-on laboratory activities as preferred over the virtual laboratories for chemistry majors at the college level and for high school Advanced Placement classes respectively (Board, 2013; Dillon, 2006; Society, 2011). Any attempt to compare hands-on laboratories and virtual laboratories are stymied due to the lack of sufficient research in the area of virtual or computer simulated labs as well as traditional hands-on laboratory (Hofstein & Lunetta, 2004; Honey, 2011; Ma & Nickerson, 2006). Recent studies using new computer simulations mainly as supplements have shown some evidence that these labs can be helpful in increasing lecture test scores, enhancing students' attitudes, improving preparedness for hands-on lab, and strengthing conceptual knowledge (Dalgarno, Bishop, Adlong, & Bedgood, 2009; X. Liu, 2006; Woodfield et al., 2005; Woodfield et al., 2004; Yaron, 2003). Since many of these virtual simulations are done in addition to the normal hands-on labs, these improvements may be mainly due to more time on task. A review of several studies using virtual labs in different science classes indicated that the results were varied in regards to the efficacy of virtual labs. The lack of a consistent message when looking at virtual laboratories is difficult to achieve at least in part because of the different goals that each research project focused on (Ma & Nickerson, 2006). One of the primary concerns regarding virtual laboratories was the inability to teach laboratory techniques and one of the advantages of virtual laboratoriess appeared to be the ability to help students properly understand the concepts in chemistry by allowing students to visualize the particulate nature of chemistry.

One study highlighting the use of virtual lab simulations as a tool to teach chemistry concepts comes from the lab of Dr. Thomas J. Greenbowe at Iowa State University. Several of Dr. Greenbowe's students have worked to understand the issues and misconceptions students have with electrochemistry. Dr. Michael Sanger conducted several research projects as part of Dr. Greenbowe's research group to identify student misconceptions and determine what language and ideas in the instructional materials and textbooks that contributed to the students' misconceptions (Sanger & Greenbowe, 1997a, 1997b, 1999). Electrochemistry is difficult due to complex terminology and the lack of students' connections between the macroscopic, sub-microscopic, and the symbolic natures of the concept. In the 1990's, Greenbowe's research group developed some simple animations to help students understand and view the particulate (sub-microscopic) aspect of chemistry and its implications for electrochemistry (Greenbowe, 1997; Greenbowe, Sanger, Burke, & Lynch, 1995). A few years later Burke and Liu continued the work with animations and used them to increase students' conceptual knowledge as well as understand the psychological differences between computer simulations and hands-on laboratories. (Burke, Greenbowe, & Windschitl, 1998; H.-C. Liu, 2005). These simulations were used in lecture to help students visualize the particulate view of matter and were successful in increasing students' performance on quizzes designed to test their concept knowledge (Sanger & Greenbowe, 1997a, 1997b). Later these animations and others were developed for web access so that students could view these out of class. Many of these virtual simulations were designed with worksheets to help the students work through the concepts. These lab simulations covered several areas of electrochemistry including: Redox reactions, voltaic cells, concentration cells, and electrolysis cells (Chemistry Education Group Iowa State University, 2005). Using several of these animations, we put together a virtual lab to help develop students' understanding of the concepts of electrochemistry including how to set-up a voltaic cell.

In order to test the efficacy of this virtual lab as a replacement for the hands-on laboratory normally used in General Chemistry II, students were randomly separated into two groups based on their laboratory section to perform either the hands-on lab on electrochemistry or the electrochemistry virtual lab simulation. The students were given both a pre- and post-test on conceptual knowledge and a final test on the hands-on setup of a voltaic cell.

Method

The General Chemistry II laboratory at a regional comprehensive university in the south in the Spring semester of 2011 consisted of 16 sections and approximately 336 students, 169 of which gave us consent to use their test scores. These students in the laboratories came from numerous lecture classes each with a different professor and each laboratory teaching assistant (TA) was randomly assigned to teach a given laboratory section. Six of the sections were chosen to use the simulations (experimental group) instead of the standard hands-on laboratory (control group) in electrochemistry. The hands-on laboratory requires students to run a direct reaction of zinc metal in copper sulfate to develop a better understanding of the direct reduction and oxidation reaction (Appendix A). They then build a Daniell cell, record the voltage, and draw a diagram of the cell. Students are required to write the molecular and net ionic equations for the half reactions and the total Daniell cell reaction. Students demonstrate the importance of a salt bridge (soaked filter paper) by measuring the voltage with and without it. They also measure the voltage for the cell when the leads are switched. Then students experiment with setting up an electrochemical cell with the highest possible voltage using iron, magnesium, and copper. For the highest voltage cell students are required to write down the half-reactions at each electrode and the overall reaction. Students then use their Daniell cell and change the concentration of solutions to note the changes in voltage associated with a non-standard cell. They finish the lab with the construction of an electrolytic cell consisting of two strips of copper in copper (II) sulfate solution with a voltage applied for 20 minutes. The students measure the weight of the copper strips before and after the application of the voltage and compare this difference to their calculated results. The virtual lab simulations apply each of these four parts: metal reactivity, voltaic cells (Daniell cell), concentration cells, and electrolytic cells (Appendix B). The only differences are that in the simulations they can run many different metal/solution direct reactions and they form a metal reactivity sequence. The virtual lab students also looked at the Daniell cell and tried many other voltaic cells but they were not required to enter any data from other voltaic cells. Virtual lab students were also given directions to note the salt bridge in the voltaic cell but the salt bridge was always present and did not need to be selected to run the simulation. Virtual lab students ran several concentration cells with the Daniell cell and the electrolysis cell used nickel instead of copper as in the hands-on labs. While there were a few differences in the specific tasks the students engaged in, the concepts are all covered in both laboratory activities.

Several weeks prior to the laboratory, students were given information about the research project and each student included in the study signed an informed consent. Each lab section completed either the virtual lab or the hands-on lab. Virtual lab sections met in the regular lab and then moved to the computer lab to complete the virtual simulations. Each virtual lab student turned in a lab report consisting of the worksheets. All students were required to complete the lab they were assigned to after completing a pre-test and providing some demographic information and a survey of their opinions regarding technology. The students completed the assigned laboratory in groups of two or three. These were the same lab groups they had been working in throughout the semester. The laboratory teaching assistants (TAs) were present during their laboratories as usual. Two weeks later, the students completed the normal final exam for the laboratory portion of the course and were given the post-test (same as the pre-test) after completing the final exam. Students were also given a hands-on task at the end of this lab exam time where they were asked to set up an electrochemical cell with the materials they were given. In order to minimize lack of effort on the pre- and post-tests, extra credit was given to individuals for completing the pre-test and for correct answers on the post-test. The pre- and post-tests were designed with 5 questions (Table 1). These questions focused on the zinc and copper reaction because both the hands-on and virtual labs used this cell as their model. Even though there were slight differences in the labs the material on the pre- and post-test was dealt with in the two laboratory activities.

In order to evaluate the students' answers to the pre- and post- tests points were assigned to the individual parts of each question. For the first three questions , students were given one point for the correct answer. In the written equations, students were given points for correct reactants, correct products, correct states of matter symbols, correct direction of reaction, and having electrons on the proper side of the equation. For the overall reaction, the points were given similarly but one point was given for correctly canceling out the

Table 1. Questions

Pre- and Post-Test Questions
1. You have a solution of copper ions (Cu2+) and when you place a strip of solid zinc in the solution you notice a copper color appearing on the piece of zinc. **a. Which metal is being oxidized?** **b. Which metal is being displaced?**
2. A voltaic cell is created using zinc metal and zinc ions in one half cell and copper metal and copper ions in the other half-cell. **a. Which metal is the anode?** **b. Write each half reaction and the overall reaction.** **c. Draw a diagram of the voltaic cell and label the solutions, the electrodes, and the flow of electrons.**
3. What would happen to the reaction above if I increased the concentration of the zinc ion in the overall equations above?
4. If we took the voltaic cell of zinc and copper from above and we added an external source of electricity, what would eventually happen as we increased the voltage of the external source?
Hands-on Activity Question
Using the supplies given to you (iron metal, copper metal, tin metal, copper sulfate, iron chloride, U-tube, soaked filter paper, anode label, and cathode label), construct a voltaic cell that would have the greatest voltage and label the cathode and anode. When you are done I will give you a voltmeter to test your results.

electrons in the equation. In the voltaic cell diagram, students earned points for having the correct labels on each electrode and each solution, having two separate solutions, having the solutions and metals matched correctly, having a salt bridge, having a wire connecting the metal electrodes, and labeling the correct direction of the electron movement in the wire. The equilibrium question was graded on a scale where two points were given to the students who identified the correct shift in equilibrium, one and a half points to students who identified one change that would occur but did not mention shift in equilibrium, one point for students who mentioned equilibrium but did not mention the direction of shift or students who had contradictory statements, a half of a point to students who shifted in the wrong direction, and zero points for all other answers. The electrolysis question was awarded one point for mentioning that the reaction is reversed when the power source overcame the cell voltage. The hands-on task was graded on five parts including anode cathode labels, correct metals and solutions, and the correct voltage determination. Using this point distribution each person could score thirty-one points on the pre- and post-test and five points for the hands-on task. In the end, data was collected for 84 students who completed the virtual lab, and 85 students who completed the hands-on lab.

Results

In order to compare the virtual lab to the hands-on lab, the pre-and post-test items were analyzed for their overall reliability using their corrected-item total correlation. Due to our corrected-item correlation analysis, we decided to dismiss the first two items about the direct reaction of zinc in copper solution and the last question about the addition of an external power source because these three items showed a corrected-item total correlation below 0.200 for both the pre- and post-test. When deleted, they brought the Cronbach Alpha score up from 0.900 to 0.912 and 0.893 to 0.903 in the pre- and post-test respectively. There were now 27 items that would be used in our comparison test. This made the pre-and post-test worth 28 points total.

Since our questions proved reliable, we proceeded to compare the pre-tests scores from each group. The t-test revealed that there was no significant difference between the pre-test scores for virtual lab students (*N*=84, *M*=9.04, *SD*=6.60) and for hands-on lab students (*N*=85, *M*=9.77, *SD*=6.77), *t*(167)=7.12, *p*=0.478 (Table 2) indicating that the groups were not significantly different in there understanding of electrochemistry prior to participating in the laboratory activities. The groups were then compared using a repeated measures ANOVA to see if the groups significantly increased their scores on the test from pre to post (Figure 1). Students' scores were significantly higher on the post-test (virtual

Table 2: T-Tests and Repeated Measures ANOVA

	Virtual		**Hands-on**		**T-Test**	
Measures	**Mean**	**N**	**Mean**	**N**	**T-score**	**Sig.**
Pre-Test	9.04	84	9.77	85	0.712	0.478
Post-Test	16.84	84	17.03	85	0.190	0.849
Hands-on	2.71	84	3.14	79	1.702	0.091
Post-Pre	7.80	84	7.26	85	-0.555	0.579
					Repeated Measures Anova	
					F	**Sig.**
Time	Post vs. Pre				241.427	<0.001

α = .05

M=16.84, *SD*=6.69, hands-on *M*=17.03, *SD*=6.51) than the pre-test *F*(1,167)=241.427, *p*<.001 (Table 2). This significant difference indicates that the students in both laboratories gained in their understanding of electrochemistry. Notice, however, that while the scores did significantly increase they still scored about 60% on the average, only scoring 16-17 out of 27, which is not the increase one might hope for in their students. However, students in the two lab groups were not significantly different on their post-test scores *t*(167)=.190, *p*=.849 (Table 2) when compared to each other. Each group significantly increased their scores between the pre-test and post-test similarly as indicated by the graph in figure 1.

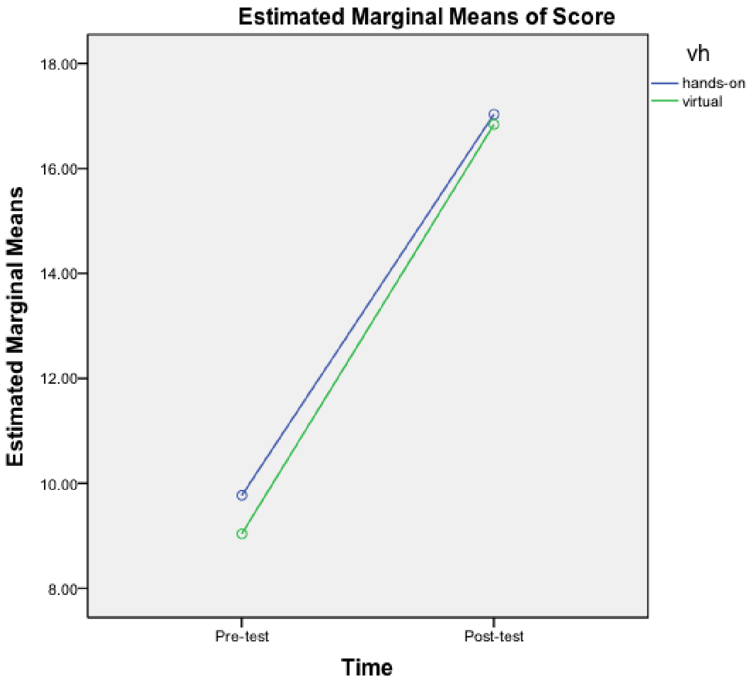

Figure 1: Pre-test (1) and Post-test (2) Scores of Hands-on labs (blue) and Virtual labs (green)

Since the students in lab were separated into different lecture groups, we wondered if the lecture group had any effect on their pre- and post-test scores. We ran an ANOVA to compare the differences that might arise based on the lecture instructor (Figure 2). The lecture groups had significantly different scores for both the pre-test, $F(5,163)=7.673$, $p<.001$, and post-test, $F(5,163)=8.199$, $p<.001$. This indicates that the differences in the students' scores could be attributed to variation in lecture rather than variation in laboratory type.

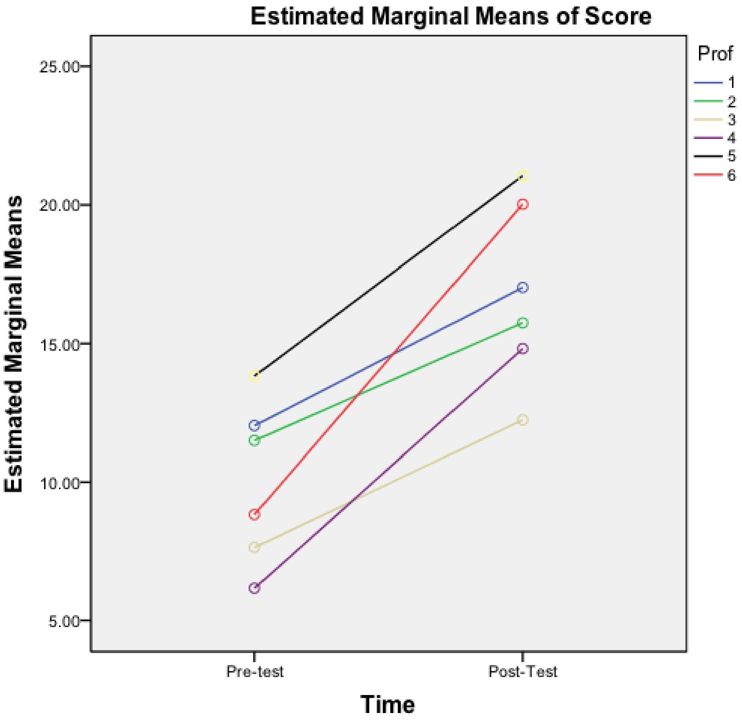

Figure 2: Pre-test (1) and Post-test (2) scores of the lecture sections (colors)

One of the criticisms of virtual labs is the fact that they do not teach laboratory techniques and manipulative skills well. We included the hands-on set-up to see if there was a difference in the two laboratory methods in teaching manipulative (hands-on) skills although this lab does not require extensive techniques. We decided to have the students set up of a voltaic cell with the materials given (Sn, Fe, and Cu metals, Cu and Fe solutions, filter paper, U-tube, anode and cathode labels, and voltmeter). Students were graded on correct metals used to create the highest voltage, the use of a salt bridge, correctly placing the anode and cathode labels, placement of voltmeter leads on metals, and correct positive voltage reading. Hands-on activity scores were not significantly different between the virtual (N=84, M=2.71, SD=1.65) and the hands-on (N=79, M=3.14, SD=1.53) laboratory groups $t(161)=1.702$, $p=.091$ (Table 2). Also there was no significant difference in the hands-on activity scores between the lecture groups $F(5, 157)=.910$, $p=.476$. Since hands-on activity scores would have been significant at the 90% confidence level we decided to run Mantel-Haenszel Chi-Square analysis and t-tests on the individual items (Table 3) to see if we could identify the potential difference. The students who were in the hands-on laboratory group were significantly more likely to correctly use the salt bridge in the hands-on activity (virtual 66.7% correct, hands-on 91.1%) $X^2(1, N=163)=12.97$, $p<.001$. It also showed a significant value on the t-test $t(167)=4.016$, $p<.001$. Since the individual chi-square and t-tests revealed something when applied to the individual hands-on items, we ran chi-square analysis and t-tests on the individual items of the pre- and post-test (Table 3).

The use of a salt bridge in the written diagram of the voltaic cell had a chi-square of 3.60 and a *p*-value of 0.058, but the t-test was significant (*t*(167)=2.087, *p*=0.039). The use of the salt bridge was the only significant difference between lab groups on the assessments we used. As students performed the hands-on activity in our presence we began to notice some differences between the two lab groups. First we gave the students two options for a salt bridge, a U-tube and filter paper. The hands-on lab used filter paper for the salt bridge during the original laboratory whereas the virtual lab only saw a U-tube in the simulation. Those virtual students who used a salt bridge in the hands-on assessment used the U-tube as their salt bridge 93% of the time, compared to hands-on students who used the U-tube only 50% of the time. Secondly, we noticed that the hands-on lab students kept placing the leads of the voltmeter into the solutions rather than on the electrodes only - 34% of hands-on students placed the voltmeter leads into the solution versus 15% of virtual lab students. In trying to understand the reason for placing the metal leads into the solutions, we realized that the hands-on students had been given such small metal samples during the instructional lab that they had to place the metals around the leads down into the solutions or they fell into the solutions due to the small size of the electrodes so many believed that was necessary.

Table 3: Individual Item Analysis

	Mantel-Haenszel Chi Square		T-Test	
Measures	X^2	Sig.	T-score	Sig.
Post-Test				
Correct Anode	2.312	0.128	1.692	.093
Reaction Equations				
Zn in half	0.027	0.869	-0.365	0.716
Zn^{2+}, e$^-$ in half	-	-	-0.949	0.344
Zn half states	-	-	-0.245	0.807
Zn e$^-$ correct side	0.159	0.690	-0.553	0.581
Zn half direction	-	-	1.177	0.241
Cu in half	0.054	0.816	0.428	0.670
Cu^{2+}, e$^-$ in half	-	-	-0.325	0.746
Cu half states	-	-	-0.061	0.951
Cu e$^-$ correct side	0.287	0.592	0.694	0.489
Cu half direction	-	-	0.704	0.482
Overall Cu & Zn	-	-	0.148	0.882
Overall states	-	-	-0.565	0.573
Overall direction	-	-	0.182	0.856
No e$^-$ in Overall	0.141	0.707	0.530	0.597
Overall direction	-	-	-0.150	0.881
Diagram				
Cu2+ solution	-	-	0.552	0.582
Cu metal	-	-	-0.509	0.611
Zn2+ solution	-	-	-0.159	0.874
Zn metal	0.884	0.347	-1.107	0.270
Metals in solution	1.329	0.249	-1.356	0.177
Two solutions	0.184	0.668	0.843	0.400
Metal ions correct	-	-	-1.030	0.305
Salt bridge	3.603	0.058	2.085	0.039
Wire connection	-	-	-0.047	0.963
e- flow	0.149	0.700	-0.538	0.591
Equilibrium				
Identified Equ.	-	-	1.201	0.231
Hands-on				
Solutions and metals	0.689	0.407	1.010	0.314
Salt Bridge	12.965	<0.001	4.016	<0.001
Anode, Cathode	1.510	0.219	1.390	0.166
Leads on metals	0.684	0.408	-9.84	0.327
Positive Voltage	0.639	0.424	0.959	0.339

Discussion

Since the advent of online high schools and colleges, the use of virtual science labs has seen major growth. These labs have been used as introductory tools, as supplements, and as replacements. Skepticism remains in many science disciplines regarding the use of virtual laboratories as replacements for traditional hands-on laboratory activities. This could be due to philosophical reasons or to the concern that virtual laboratories do a poor job of teaching laboratory techniques. Since most of the research is limited to the use of virtual laboratoriess as supplements, we wanted to determine the effect of using virtual labs as a substitute for a traditional laboratory so that we could see if they work as replacements in our setting, and determine if there are ways in which our normal hands-on labs fall short of our goals for lab education.

In this study, we looked at the use of virtual labs as a replacement to our normal hands-on lab, to determine the efficacy of virtual labs to help students learn the concepts and set-up of materials of electrochemical cells. We were using a comparison to our own labs and these results are only valid in relation to this context. Also the use of electrochemistry lab as a measurement tool for technique learning is limited since the set-up of materials to form voltaic cells is not necessarily indicative of technique learning, but this did provide some data regarding the ability to learn hands-on concepts in a virtual environment. Many virtual pre-lab exercises involve teaching students the proper way to use machines and chemical apparatus in the lab. With these goals and limitations in mind, the study showed that there was no significant difference between the two lab teaching methods when it came to the pre- and post-test data which focused primarily on conceptual understanding of the electrochemical cells. One of the main goals of lab is to teach content knowledge but according to this study the methods used here did not affect the scores on the tests. When comparing lecture sections to one another, however, we did find significant differences between the pre- and post-test scores, but not in the hands-on activity scores. This may indicate that the lecture is the main place where students learn conceptual and factual knowledge. We did not ask any descriptive questions regarding lab materials such as the color of the solutions or the metals. It may be that laboratories play an important role in providing this descriptive information but since we did not assess them on this we were unable to say anything about the development of this knowledge. The virtual lab was designed to include accurate macroscopic representations regarding colors of solutions and colors of metals. More research needs to be conducted to discover what uses or methods are the best for these goals.

When comparing the hands-on task, we did not find a significant difference between either the lab groups or the lecture groups. However, the p-value was significant at the 0.10 alpha, we decided to do an item analysis on the pre- post- and hands-on activity test. The only items that showed a significant difference between the lab groups was the placement of a salt bridge in their hands-on voltaic cell activity and the correct addition of a salt-bridge to the cell diagram. The virtual lab students left the salt bridge out more than the hands-on students in the hands-on activity. This may be due to the fact that the simulation did not require the students to place the salt bridge in the cell but placed it for them in the simulation, whereas in the hands-on lab students had to place the salt bridge correctly to get any results. In fact in the hands-on laboratory, they are asked to make a measurement without the salt bridge specifically to help them understand the importance of the salt bridge. The inclusion of a salt bridge in the pre- and post-test diagrams of the cell also revealed a difference in the two groups of students and the t-test was significant at the 95% confidence interval level but the chi-square was only significant at the 90% confidence interval level. If the simulation was redone to include the placement of the salt bridge we may see different results. It is possible that merely including this consideration in the virtual lab would close this gap in performance.

In observing the labs and specifically grading the hands-on task, we noticed an abundance of students putting the voltmeter leads into the solution on the metals. This was cause for concern and we looked at the data to determine if one group placed the leads into the solution more than the other. The data revealed that more students in the hands-on lab placed their leads in the solutions, but this difference did not lead to a significant difference in the item analysis for this question. One explanation for the difference was that in the hands-on laboratory, we used such small pieces of metal that it became impossible for our students to attach the electrodes to them without having the leads in the solutions as well. This led to corrosion of the electrodes and may have led students to believe that proper placement of the electrodes was in the solution. This idea may give us some insight into proper technique training. While it is believed that hands-on labs teach technique better than virtual labs, techniques can be improperly taught if students are not observed and corrected during the lab and if the materials given to the students are not proper for the tasks at hand. In order to have students do the labs with less cost and time we may be sacrificing the teaching of technique due to our shortcuts. This idea could also be seen in the use of different types of salt bridges used in the two labs. The hands-on lab used soaked filter paper, whereas, the virtual simulations and the textbooks use U-tubes. These subtle differences may not be well understood by the students and so misconceptions would occur by not understanding the role the equipment plays in the facilitation of the laboratory experiments.

Virtual laboratories are a tool that, when used properly, can be very beneficial. The difficulty is knowing when they are appropriate for a particular situation. In order for us to identify the strengths and weaknesses of virtual laboratories, we need to have clearly stated goals and conduct controlled research in these areas that focus on the agreed upon goals. This study showed that a virtual lab simulation was just as good as the normal hands-on general chemistry laboratory at teaching concepts and voltaic cell set-up in electrochemistry. More research needs to be done to determine virtual laboratories efficacy as a replacement for more traditional hands-on laboratory experiences.

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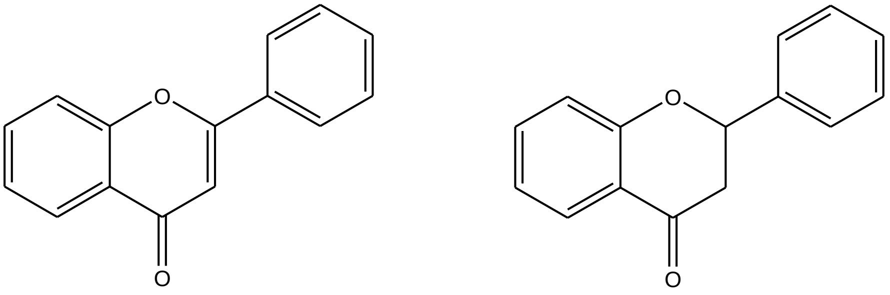
CHAPTER FOUR: GREEN SYNTHESIS OF AURONES USING A DEEP EUTECTIC SOLVENT

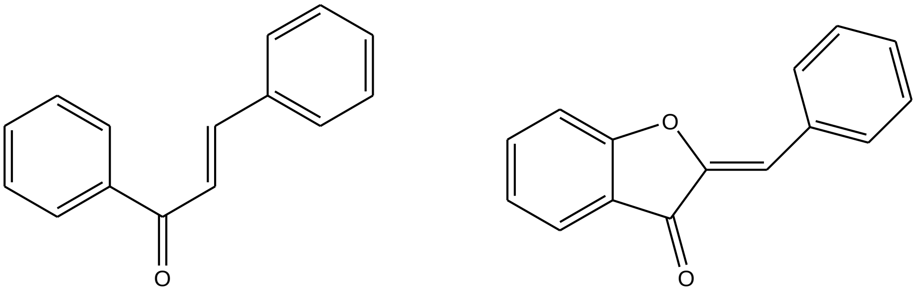
Introduction

Aurones are a family of natural compounds that are found in plants and are part of a larger family of natural products known as flavonoids (Boumendjel, 2003; Haudecoeur & Boumendjel, 2012; Zwergel et al., 2012). This family consists of flavones, isoflavones, chalcones, and aurones and are mainly secondary metabolites of plants found in fruits and flowers. (Figure 3) Aurones in particular have been found to be involved in the coloring of fruits and flowers (Harborne & Williams, 2000). While flavones and chalcones have been well studied over the years for various therapeutic effects; aurones have not been as well studied. In early studies, aurones have been found to be possibly beneficial in anti-cancer therapies (Lawrence et. al., 2003), in the treatment of malaria (Kayser et. al., 2001), and in microbial infections (Bandgar et al., 2010). Aurones have shown higher activities in these assays when compared with the corresponding flavones and chalcones. These early studies show promise in the use of aurones in many different medical applications (Haudecoeur & Boumendjel, 2012; Zwergel et al., 2012)



Flavone

Flavanone



Chalcone

Aurone

Figure 3: Some Flavonoid Sub-classes

Aurones are synthesized in plants by oxidation, cyclization, and rearrangement of chalcones by an enzyme called aureusidin synthase (Nakayama et al., 2001; Nakayama et al., 2000). In the lab, however, several methods have been employed. One of the older methods involves the condensation of an aldehyde with coumaranone. The coumaranone fragment in turn can be formed several ways, including Friedel-Crafts acylation of phenol derivatives (Adams & Main, 1992). The compound is then hydrolyzed to a ketone and then cyclization takes place forming the coumaranone derivative. (Figure 4)

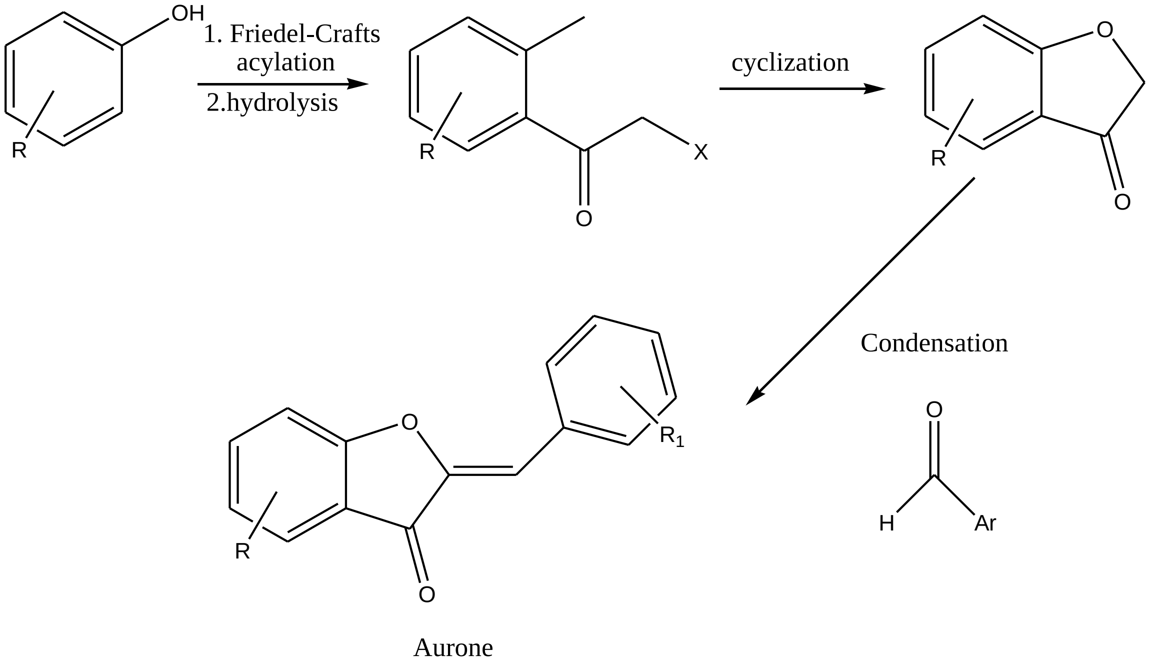


Figure 4: Coumaranone (Benzofuran-3(2H)-one) Method

An alternate approach is based upon the biosynthetic pathway and follow the same procedure of oxidation followed by cyclization of the aurone (D. Donnelly, Donnelly, & Keegan, 1977; Varma & Varma, 1992). (Figure 5) Chalcones can also be brominated first and then cyclization occurs in a KOH/EtOH solvent (Bose et. al., 2001) Also the use of thallium (III) nitrate in oxidative rearrangement of chalcones (Thakkar & Cushman, 1994) and the use of gold catalyzed cyclization of 2-(1-hydroxyprop-2-ynyl)phenols have been reported recently (Harkat et.al., 2008). Returning to the condensation

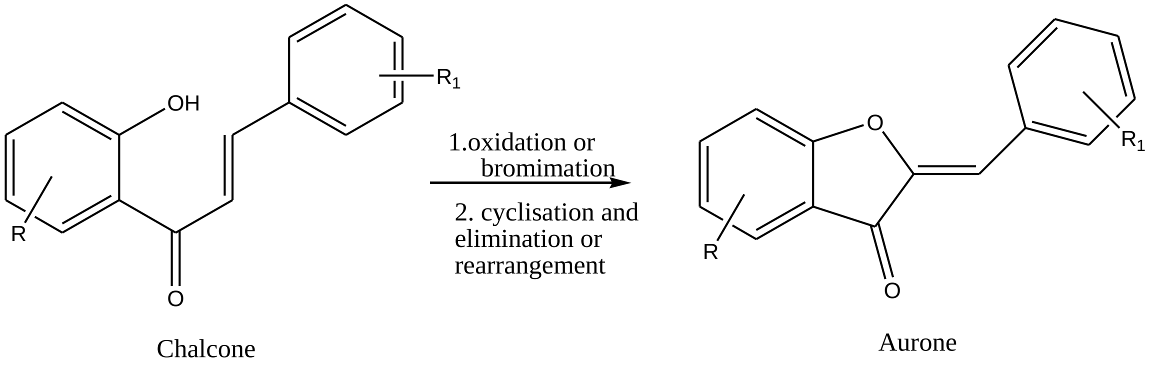


Figure 5: Biosynthetic and Biomimetic pathway

approach, the reaction between coumaranone and an aldehyde involves the use of acid or base catalyzed conditions. Among the many possible variations, one of the milder is the use of neutral alumina to mediate the condensation (Varma & Varma, 1992). Pratically all synthesized aurones appear in the Z conformation which is the thermodynamically stable isomer (Boumendjel, 2003). Here we report the synthesis of aurones by the condensation of coumaranone with arylaldehydes using the deep eutectic solvent of choline chloride and urea. (Figure 6)

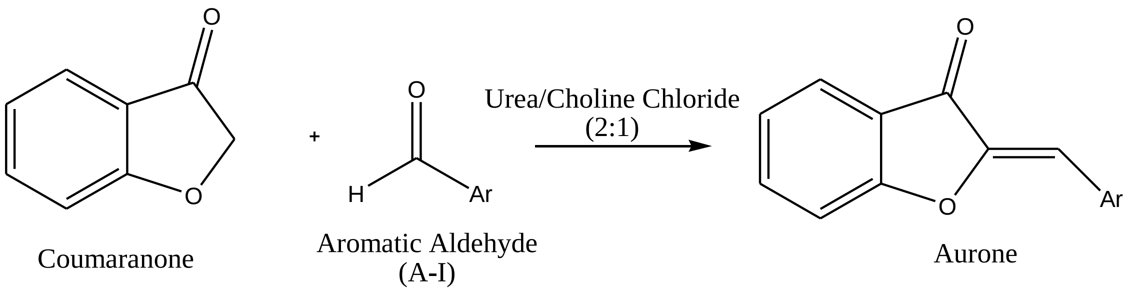


Figure 6: Coumaranone Condensation with Deep Eutectic Solvent

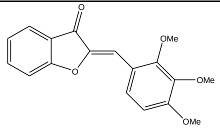
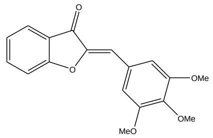
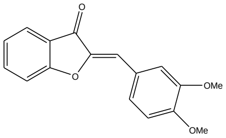
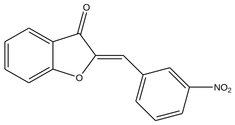
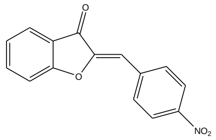
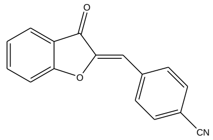
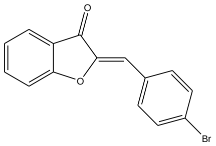
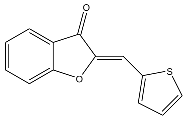
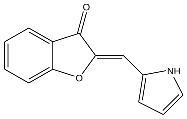
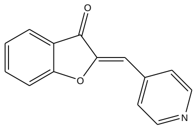
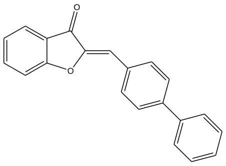
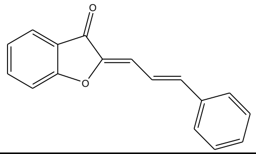
Deep Eutectics

Deep eutectic solvents are solvents composed of two or more materials where the melting point is drastically reduced compared to that of the original two components (Russ & Koenig, 2012). The choline chloride/urea (CC/U) deep eutectic solvent is quite interesting and has been extensively studied for several reasons. First, the two components are inexpensive, readily available in large quantities, and non-toxic. Further, it can be seen as a much less expensive alternative to room temperature ionic liquids. To date, deep eutectic solvents have been most extensively explored in areas such as metal extraction and electroplating (Abbott et. al., 2011). The use of a mixture of choline chloride and urea forms a very inexpensive solvent and a wide range of solutes have high solubilities in this mixture. Abbott et. al. have looked specifically at choline chloride and urea mixtures and determined that it is one of the few deep eutectic solvents that have freezing points below ambient temperatures (Abbott et. al., 2004; Abbott et. al., 2003). This makes it a useful solvent for ambient temperature reactions. Abbott et. al. also established the molar ratio of urea to choline chloride of 1:2 results in the optimal eutectic with a freezing point of 12°C. Despite their promising attributes, deep eutectic solvents remain virtually unexplored as reaction solvents in Organic synthesis (Pawar, Jarag, & Shankarling, 2011; Phadtare & Shankarling, 2010; Russ & Koenig, 2012; Singh, Lobo, & Shankarling, 2011).

Results and Discussion

Intrigued by the potential to employ the choline chloride/urea deep eutectic as a green solvent in Organic synthesis, we explored a number of simple condensation reactions, including that of coumaranone with aldehydes. (Table 4) Gratifyingly, the reaction proceeded cleanly in a relatively short time to afford the anticipated aurone products. Neither additional acid nor base was required, so the reactions proceed under effectively neutral conditions. The mild nature of these reaction conditions could certainly be of use in synthesizing aurones with more sensitive functionality, while the simplicity of the reaction conditions renders the method quite user friendly: mixing the coumaranone, and aryl aldehydes in the urea/choline chloride solvent overnight at 80°C. This reaction is easily accomplished for most of the aryl aldehydes overnight and because the coumaranone is heat labile the aldehyde is the only other material potentially remaining. Product isolation can be readily accomplished by simple partitioning between methylene chloride and water. Most of the reactions required no further purification. This procedure makes it easy to make numerous aurones in a short amount of time with little effort. The choline chloride/urea solvent is inexpensive and presents a wonderful alternative to standard ionic liquid catalyzed reactions. This condensation reaction displays the possible future utility of deep eutectic solvents as catalysts and solvents.

Table 4: Aurone Synthesis Results

Entry	Aryl Aldehyde	Aurone Product	% Yield(hr)	MP (°C)
1	2,3,4-Trimethoxy-benzaldehyde		68%(12)	115-120
2	3,4,5-Trimethoxy-benzaldehyde		17%(48)	175-178
3	3,4-Dimethoxy-benzaldehyde		66%(12)	123-130
4	3-Nitrobenzaldehyde		40%(12)	163-166
5	4-Nitrobenzaldehyd		12%(48)	165-170
6	4-Cyanobenzaldehyde		41%(12)	181-185
7	4-Bromobenzaldehyde		8.6%(48)	152-158
8	Thiophene-2-carboxaldehyde		46%(12)	92-96
9	Pyrrole-2-carboxaldehyde		60%(12)	138-142
10	Pyridine-4-carboxaldehyde		34%(36)	89-93
11	4-Phenylbenzaldehyde		53%(12)	63-68
12	Trans-cinnamaldehyde		78%(12)	57-64

In previous papers it was reported that most aurones are synthesized in the Z conformation and this is determined by the olefinic hydrogen shift (~6.7ppm for Z isomer, > 7 ppm for E isomer) (Bandgar et al., 2010; Thakkar & Cushman, 1995). According to our proton NMR spectra, all of our aurones synthesized are in the Z conformation except for the thiophene benzaldehyde addition. This spectra does not contain a peak in the 6.7 ppm range and could be considered the E isomer. However, earlier studies on aurones regarded the proton NMR as inconclusive in determining the isomer because of the small change in shift of the olefinic hydrogens (~.3ppm) (Brady, Kennedy, & Osulliva, 1973; Pelter, Ward, & Heller, 1979). Carbon NMR spectra was also used and they found that the olefinic carbon in the Z isomer appeared at ~111 ppm and in the E isomer this was shifted by 9-10 ppm (Pelter et al., 1979). In our 2-(thiophen-2-ylmethylene)benzofuran-3(2H)-one spectra, we did see a carbon peak around 112 ppm and this may be the olefinic carbon indicating the Z isomer, but more spectra needs to be done to confirm this isomer.

It is worth noting that the same reaction has been explored in an alternative deep eutectic solvent: choline chloride/glycerol. Under the same reaction conditions (time and temperature), a much slower reaction occurs, affording roughly 40% conversion of the aldehyde to the aurone product. For this reason, we propose that the choline chloride/urea deep eutectic solvent catalyzes the reaction via hydrogen-bonding activation of the aldehyde. Urea is known to be a weak organocatalyst, with its activity largely diminished due to intermolecular hydrogen-bonding (Schreiner, 2003). Still, the very high concentrations of urea present in the deep eutectic can likely overcome this weakness and result in effective catalysis. The stronger hydrogen-bonding capabilities and preorganized nature of urea compared to glycerol account for the difference in activity of the two deep eutectic solvents observed in this study. Further applications and confirmation of this hypothesis are underway and will be reported in due course.

Conclusion

Aurones are an interesting, but little studied member of the flavanoid family of natural products. Of the various methods available for their synthesis, the simplest involves the condensation of a coumaranone with an aldehyde. This reaction can be performed under acidic or basic conditions. We have recently discovered an effectively neutral set of conditions that employ the deep eutectic solvent comprised of choline chloride and urea as both solvent and catalyst. Modest to good yields can be achieved for a range of aldehydes, thereby facilitating further study of aurones from both a biological as well as a spectroscopic perspective.

General Experimental

FT-IR was performed on Varian 800 FT-IR. NMR was performed on a JEOL ECA-500 500MHz spectrometer.

General Procedure for Production of Urea/Choline Chloride Solvent

Choline Chloride (7 g, 50 mmol) and Urea (6 g, 100 mmol) were combined in a vial and heated with shaking overnight at 80 C.

General Procedure for Condensation of Coumaranone and Aryl Aldehydes

To coumaranone (1mmol) was added the aryl aldehyde (1mmol) and 2mL of Choline Chloride/Urea solvent in 5mL sealed vial. The reaction was stirred at 80 C for specified time. The reaction mixture was then diluted with water (10 mL) and extracted with methylene chloride (3 x 10 mL). The organic layer was then concentrated *in vacuo* to afford the product. In most cases, this product was spectroscopically pure, except where noted. See Appendix D for the spectra.

1. (Z)-2-(2,3,4-trimethoxybenzylidene)benzofuran-3(2H)-one (Imafuku, Honda, & Mcomie, 1987): IR v=1702, 1645, 1589, 1496, 1464, 1285, 1204, 1191, 1131, 1092, 1008, 910, 885, 802, 759, 732, 696cm-1; ^{1}H NMR (500 MHz, $CDCl_3$): δ= 3.86 (s, 3H), 3.90 (s, 3H), 3.94 (s, 3H), 6.77 (d, *J*=9.15Hz , 1H), 7.17 (t, *J*=7.45Hz, 1H), 7.24-7.28 (m, 2H), 7.58 (t, *J*=1.15Hz 1H), 7.77 (d, *J*=6.3Hz, 1H), 8.06 (d, *J*=8.6Hz, 1H); ^{13}C NMR (500 MHz, $CDCl_3$): δ=56.13, 60.96, 61.96, 107.61, 112.86, 119.21, 121.92, 123.31, 124.63, 127.37, 136.52, 142.27, 146.61, 153.92, 155.62, 165.57, 184.38.

2. (Z)-2-(3,4,5-trimethoxybenzylidene)benzofuran-3(2H)-one (Morimoto et. al., 2007): solid required further purification on a silica column with 50% CH_2Cl_2/Hexanes followed by a wash with 10% EtOAc/Hexanes. IR v=1708, 1647, 1602, 1581, 1505, 1460, 1336, 1296, 1244, 1189, 1151, 1125, 1098, 1005, 879, 758, 668, 640cm-1; ^{1}H NMR (500 MHz, $CDCl_3$): δ=3.85 (s, 1H), 3.88 (s, 6H), 6.74 (s, 1H), 7.10 (s, 2H), 7.15 (t, J=7.45Hz, 1H), 7.23 (d, J=8Hz, 1H), 7.57 (t, J=6.9Hz, 1H), 7.73 (d, J=6.85Hz, 1H); ^{13}C NMR (500 MHz, $CDCl_3$): δ=56.15 (2C), 60.97, 108.85 (2C), 112.82, 113.30, 121.65, 123.48, 124.63, 127.62, 136.71, 140.08, 146.34, 153.27 (2C), 165.84, 184.48.

3. (Z)-2-(3,4-dimethoxybenzylidene)benzofuran-3(2H)-one (Detsi et. al., 2009; Morimoto et al., 2007): IR v=1705, 1595, 1522, 1463, 1296, 1269, 1248, 1202, 1153, 1124, 1019, 885, 758, 731, 645cm-1; ^{1}H NMR (500 MHz, $CDCl_3$): δ= 3.86 (s, 3H), 3.89 (s, 3H), 6.78 (s, 1H), 6.86 (d, J=8.6Hz, 1H), 7.13 (t, J=7.4Hz, 1H), 7.23 (d, J=8.6Hz, 1H), 7.41 (d, J=10.3Hz, 1H), 7.45 (d, J=1.7Hz, 1H), 7.56 (t, J=8.55Hz, 1H), 7.72 (d, J=7.45Hz, 1H); ^{13}C NMR (500 MHz, $CDCl_3$): δ=111.13, 112.79, 113.67 (2C), 121.81, 123.30, 124.54, 125.20, 125.98, 136.51, 145.86, 148.98, 150.82, 165.70, 184.43.

4. (Z)-2-(3-nitrobenzylidene)benzofuran-3(2H)-one (J. Donnelly & Emerson, 1990): IR v= 1708, 1655, 1601, 1531, 1475, 1458, 1347, 1303, 1191, 1132, 1098, 885, 810, 757, 734, 699, 675cm-1; ^{1}H NMR (500 MHz, $CDCl_3$): δ= 6.86 (s, 1H), 7.25 (t, J=7.75Hz, 1H), 7.38 (d, J=8Hz, 1H), 7.62 (t, J=8Hz, 1H), 7.69 (t,

J=8.55Hz, 1H), 7.80 (d, J=8.6Hz, 1H), 8.13 (d, J=7.45Hz, 1H), 8.22 (d, J=8Hz, 1H), 8.79 (s, 1H); ^{13}C NMR (500 MHz, $CDCl_3$): δ=109.62, 113.11, 121.07, 123.95, 124.04, 124.88, 125.52, 129.79, 133.91, 136.71, 137.55, 147.86, 148.59, 166.23, 184.52.

5. (Z)-2-(4-nitrobenzylidene) benzofuran-3(2H)-one (J. Donnelly & Emerson, 1990; Patonay, Bognar, & Litkei, 1984; Pelter et al., 1979): solid required further purification on silica column with 50% CH_2Cl_2/Hexanes. IR v=1711, 1603, 1517, 1476, 1458, 1343, 1322, 1299, 1204, 1188, 1130, 1111, 1097, 1033, 889, 860, 760, 688, 647cm-1; ^{11}H NMR (500 MHz, $CDCl_3$): δ=6.85 (s, 1H), 7.26 (t, J=7.45Hz, 1H), 7.35 (d, J=8.05Hz, 1H), 7.69 (t, J=8.65Hz, 1H), 7.82 (d, J=6.85Hz, 1H), 8.04 (d, J=9.15Hz, 2H), 8.28 (d, J=8.6Hz, 2H); ^{3}C NMR (500 MHz, $CDCl_3$): δ=109.35, 113.01, 120.97, 123.85 (2C), 124.22, 125.06, 131.61 (2C), 137.29, 138.60, 148.37, 166.30, 184.94, 206.98.

6. (Z)-4-((3-oxobenzofuran-2(3H)-ylidene)methyl)benzonitrile (Patonay et al., 1984): IR v= 1703, 1650, 1602, 1475, 1461, 1302, 1190, 1130, 1108, 885, 833, 755, 734, 699, 664, 645, 626cm-1; ^{1}H NMR (500 MHz, $CDCl_3$): δ=6.79 (s, 1H), 7.24 (t, J=6.85Hz, 1H), 7.32 (d, J=8.6Hz, 1H), 7.65-7.70 (m, 3H), 7.79 (d, J=7.45, 1H), 7.97 (d, J=8.55, 2H); ^{13}C NMR (500 MHz, $CDCl_3$): δ=110.09, 112.65, 113.10, 118.65, 121.20, 124.17, 125.04, 131.61 (2H), 132.56 (2H), 136.83, 137.64, 148.21, 166.34, 184.65.

7. (Z)-2-(4-bromobenzylidene)benzofuran-3(2H)-one (Manjulatha et al., 2012; Patonay et al., 1984): solid required further purification on silica column with 50% CH$_2$Cl$_2$/Hexanes. IR v= 1714, 1655, 1601, 1487, 1474, 1460, 1298, 1205, 1186, 1128, 1112, 1099, 1071, 1008, 884, 821, 756, 697, 653, 626cm-1; ^{1}H NMR (500 MHz, CDCl$_3$): δ=6.81 (s, 1H), 7.24 (t, J=7.45Hz, 1H), 7.34 (d, J=8Hz, 1H), 7.58 (d, J=8.6Hz, 2H), 7.67 (t, J=8.6Hz, 1H), 7.78 (d, J=8.6Hz, 2H), 7.81 (d, J=8.6Hz, 1H); ^{13}C NMR (500 MHz, CDCl$_3$): δ=111.47, 112.87, 121.39, 123.57, 124.21, 124.66, 131.03, 132.07 (2C), 132.61 (2C), 136.99, 146.99, 165.99, 184.58.

8. 2-(thiophen-2-ylmethylene)benzofuran-3(2H)-one (D. Donnelly, Donnelly, & Philbin, 1972): IR v=1698, 1684, 1645, 1593, 1504, 1475, 1458, 1417, 1391, 1328, 1295, 1232. 1185, 1124, 1095, 992, 881, 846, 756, 710, 695, 625cm-1; ^{1}H NMR (500 MHz, CDCl$_3$): δ=7.17 (t, J=4Hz, 1H), 7.20 (s, 1H), 7.24 (t, J=7.45Hz, 1H), 7.27 (s, 1H), 7.36 (d, J=8.55, 1H), 7.57 (d, J=3.45Hz, 1H), 7.63 (d, J=5.15Hz, 1H), 7.66 (t, J=8.55Hz, 1H), 7.81 (d, J=7.45Hz, 1H); ^{13}C NMR (500 MHz, CDCl$_3$): δ=107.12, 112.92, 122.25, 123.52, 124.58, 128.09, 131.54, 133.17, 135.55, 136.71, 145.33, 165.65, 183.85.

9. (Z)-2-((1H-pyrrol-2-yl)methylene)benzofuran-3(2H)-one: IR v=1687, 1635, 1594, 1477, 1458, 1430, 1319, 1300, 1195, 1143, 1125, 1100, 1039, 885, 868, 819, 756, 725, 696cm-1; ^{1}H NMR (500 MHz, CDCl$_3$): δ= 6.72 (s, 1H), 6.96 (s, 1H), 7.03 (s, 1H), 7.14 (s, 1H), 7.19-7.23 (m, 1H), 7.30 (d, J=8Hz, 1H), 7.60-7.63 (m, 1H), 7.79 (d, J=1.15Hz, 1H), 9.56 (bs, 1H); ^{13}C NMR (500 MHz, CDCl$_3$):

δ=105.16, 111.43, 112.58, 118.43, 122.62, 123.37, 124.23, 124.61, 126.10, 136.00, 143.70, 164.53, 183.00.

10. (Z)-2-(pyridine-4-ylmethylene)benzofuran-3(2H)-one (Bobbitt et. al., 1968): IR v= 1647, 1599, 1474, 1464, 1416, 1378, 1300, 1201, 1130, 828, 756, 734, 697, 675, 660c,-1; ^{1}H NMR (500 MHz, $CDCl_3$): δ=6.87 (s, 1H), 7.43 (t, J=7.45Hz, 2H), 7.57 (d, J=8.6Hz, 1H), 7.71 (d, J=7.45Hz, 1H), 7.75 (d, J=5.75Hz, 2H), 8.20 (d, J=6.3hz, 1H), 8.79 (d, J=6.3Hz, 1H); ^{13}C NMR (500 MHz, $CDCl_3$): δ=109.34, 118.24, 119.86 (2C), 124.07, 124.73, 125.86, 134.43, 150.78 (2C), 156.20, 160.59, 178.22.

11. (Z)-2-(biphenyl-4-ylmethylene)benzofuran-3(2H)-one (Jimenez, Miranda, & Tormos, 1997): IR *v*=1702, 1646, 1597, 1486, 1461, 1299, 1209, 1185, 1150, 1128, 1109, 1007, 886, 838, 755, 729, 696cm-1; ^{1}H NMR (500MHz, $CDCl_3$): δ= 6.95 (s, 1H), 7.24 (t, J=7.45Hz, 2H), 7.35-7.71 (m, 8H), 7.82 (d, J=8.55Hz, 1H), 8.01 (d, J=8.05Hz, 2H). ^{13}C NMR (500MHz, $CDCl_3$): δ=112.84, 112.96, 121.67, 123.50, 124.70, 127.08, 127.36, 127.40, 127.52, 127.92, 128.26, 128.77, 128.93, 131.28, 132.04, 136.90, 140.08, 142.52, 146.94, 166.08, 184.75.

12. (Z)-2-((E)-3-phenylallylidene)benzofuran-3(2H)-one IR v=1699, 1638, 1608, 1475, 1462, 1298, 1198, 1149, 1117, 970, 879, 753, 698, 669cm-1; ^{1}H NMR (500MHz, $CDCl_3$): δ=6.78 (d, J=11.45Hz, 1H) 7.02 (d, J=16.05Hz, 1H), 7.18 (t, J=7.45Hz, 1H), 7.24-7.38 (m, 6H), 7.54 (d, J=7.45Hz, 1H), 7.62 (t, J=8.6Hz, 1H),

7.76 (d, J=7.45Hz, 1H); ^{13}C NMR (500 MHz, $CDCl_3$): δ=112.58, 114.44, 120.79, 122.42, 123.34, 124.62, 127.55 (2H), 128.98 (2H), 129.46, 136.39, 136.80, 141.52, 147.46, 165.52, 183.91.

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CHAPTER FIVE: CONCLUSIONS AND FUTURE IMPLICATIONS

Introduction

The state of laboratory in American science education has been one of constant flux. While many educators would contend that laboratory is a vital part of the science education curriculum, there are those who debate its usefulness particularly in light of the associated cost. The issue has been that significant quantitative evidence to support the educational benefit of laboratory has been difficult to find. Several reviews point out the lack of conclusive evidence in support of the use of laboratory (Elliott, Stewart, & Lagowski, 2008; Hofstein & Lunetta, 1982, 2004; Lagowski, 1982; Tobin, 1990). Many believe the issue is that laboratory education is not given enough attention by instructors in high schools and colleges. Many of the stated goals of laboratory are the same as the goals for lecture. Without unique goals for laboratory itself it is hard to assess the outcomes of laboratory education. In recent years, the advent of online and distance education has presented new challenges for laboratory and some computer simulations and virtual environments have been used and studied as possible alternatives. As is true for laboratory education research in general, the use of these labs as an alternative to hands-on labs has not revealed conclusive evidence (Ma & Nickerson, 2006). In this research project, I wanted to use a virtual lab as a replacement to study its efficacy at teaching the conceptual knowledge of electrochemistry and its ability to help students learn the correct set-up of a voltaic cell.

Virtual Laboratory and Hands-on Laboratory

Students in the virtual laboratory did not perform significantly different than students in the hands-on laboratory on the post-test questions designed to assess their conceptual knowledge of electrochemistry at the 95% confidence interval level. When students were given materials to set-up an electrochemical cell, the virtual laboratory student did not perform significantly different than the hands-on laboratory students at the 95% confidence interval. However, if we were using a 90% confidence interval level, there would have been a significant difference in favor of the hands-on group. In order to better understand the differences in the overall scores, we performed an item analysis. The only significant differences at the 95% confidence interval in the individual items appeared in the use of the salt bridge for both the electrochemical set-up and the post-test diagram of a Daniell cell. These differences indicated that the virtual laboratory students did not learn the significance of the salt bridge in completing the circuit and they forgot to use the salt bridge in their diagrams and battery set-up significantly more times than the hands-on students. We thought that this was probably due to the fact that the virtual lab had the salt bridge already in place for each reaction and did not require students to select it as part of the virtual lab set-up. If the virtual lab was redesigned, these students may score similarly to the hands-on laboratory with regards to the use of a salt bridge.

In our research we showed that our virtual lab was sufficient for teaching conceptual knowledge as it was evaluated by the post-test on electrochemistry. One of the reasons why these virtual simulations were designed in the first place was to allow students to visualize the sub-microscopic nature of the chemicals in these electrochemical cells in order to alleviate some misconceptions that had been identified. This is one area in which virtual laboratories may present a benefit and more research into the area of virtual labs as tools for developing greater understanding of the sub-microscopic nature of chemistry is needed. However, since there were significant differences in the scores from the different lecture groups, it could be that the students were learning the concepts in lecture and not in laboratory and since our students were equally distributed among the lab groups we saw no significant difference in the scores between these groups More work needs to be done to determine the part that laboratory plays in the learning of concepts and future work could include data from post-tests for students who did not attend the electrochemistry laboratory.

Virtual laboratories are believed by many to be inappropriate for teaching laboratory technique. In our study the virtual laboratory students placed the salt-bridge in the hands-on activity significantly less times than the hands-on lab group. However, future changes to the virtual laboratory environment may prove that this difference was only due to the fact that in the virtual lab students were not required to select the salt bridge. One lab is also insufficient to determine the efficacy of virtual labs as a teaching technique since the setting up of an electrochemical cell in an the lab is not necessarily a demanding technique and only requires the proper positioning of materials. While other techniques, such as the use of instrumentation or the manipulation of glassware, may require more difficult hands-on skills, we need to determine the ability of a virtual lab to teach these skills.

Teaching techniques, such as titrations, filtering, chromatography, and the like, can also be a challenge because as technology changes the techniques have changed. For instance the use of instrumentation is certainly different depending on the model or the computer programs that run the instrument. While exposure to the use of these instruments is important, it may be the understanding of the method in which the instrument acquires data and does analysis that is more important than actually learning the exact procedure used to run any given instrument. As Johnstone points out in his review of the laboratory, each instrument requires knowledge regarding the use of that particular instrument and students still require several uses of an instrument to become familiar enough to learn the manipulative skills (techniques) necessary to work with that instrument (Johnstone & Al-Shuaili, 2001). He also points out that what is most important is that students understand the use of the instrument and how to read and interpret the data that is collected by the instrument. While I myself believe that students benefit from having hands-on learning when it comes to the laboratory, it may prove beneficial to use virtual laboratories to teach these techniques before students come to a hands-on laboratory. One such study showed that students could use a spectrophotometer just as well after having completed a simulation as compared to a hands-on laboratory (Cavin, Cavin, & Lagowski, 1978). While it is true that science majors need hands-on experience with certain instruments, we might be able to use virtual labs as a cheaper alternative to hands-on labs as a tool to teach techniques in introductory classes.

One future area of study that we are hoping to review is a qualitative study of the conversations of student groups in a hands-on laboratory and a virtual laboratory. While conducting this research we collected data from 4 groups of students from each laboratory where we recorded their conversations as they completed the labs. This evidence may give us insight into the time on task each student group spent on the lab itself and if topics of conversation differed among these groups. Hopefully this qualitative study can shed light on the differences in students' learning between the two laboratory methods and can help us understand the benefits and drawbacks of these two laboratory teaching methods.

Synthesis of Aurones Using a Deep Eutectic Solvent

We have also shown here the ability to synthesize aurones using a condensation reaction method with the simple, green, inexpensive deep eutectic solvent of urea and choline chloride. These new solvents show promise in replacing ionic liquids as a means to catalyze reactions and produce biodegradable wastes. The synthesis of aurones in particular is helpful as these compounds have shown promise in antibiotic and anti-cancerous assays. These solvents could also be important for use in laboratory education, where the costs of chemicals and chemical waste disposal are becoming more and more expensive. With future research such as this, more inexpensive and greener options for chemical synthesis and analysis are possible and could provide new experiments for laboratory education.

The Future of Laboratory Education Research

As laboratory education has changed in the past, we know that future changes in education are important and necessary. As I have reviewed the literature on laboratory education, however, it seems that we keep asking the same questions over and over again. Which method is the best method to teach laboratory, is it demonstration, or “cookbook” labs, or inquiry-based labs, or even virtual labs? The reasons there are no concrete answers regarding the teaching of laboratory are numerous and it may be useful for each institution to determine their own answers for how they will teach the laboratory based on their specific institutional goals. One problem that has been mentioned before is the lack of clear laboratory goals. I believe it is necessary for each school or department needs to specify the specific goals that they have for laboratory education and assess those goals to see if the methods they are using are the most efficacious to meet those goals. While this may not create a universal consensus on the use of laboratory in science education, it can create a backdrop for good research. In a review of the literature on virtual laboratory studies across the sciences, Ma and Nickerson (2006) determined that the main reason why so many studies seemed to contradict one another in their use of virtual laboratories was that each study was looking at different purposes and goals but these were not clearly stated in the literature. When we begin with clearly stated goals and purposes for the lab, we can better determine the usefulness of methods in teaching such laboratories. As we have shown in this study, future work is still necessary to determine whether virtual labs are useful alternatives and this must be done with clear goals in mind. We began by looking at a virtual laboratory's efficacy in replacing a hands-on laboratory when it comes to electrochemistry conceptual knowledge and the physical set-up of an electrochemical cell. In the future more studies will be necessary to determine the best methods of teaching laboratory for individual concepts and purposes. One method might work better for teaching concepts, whereas another is better for a particular technique.

Another issue is the lack of emphasis in laboratory education in most colleges and schools. Most students spend almost as much time in laboratory as they do in lecture in a given week in most colleges. However, the emphasis of teaching and organizing the laboratory is far less than the average time spent on the lecture portion of the class. If we say we value laboratory as an integral part of the science education curriculum then we need to treat the lab with as much importance as we do the lecture materials. Hopefully in the next couple of years, I can help my students appreciate the laboratory and make it a much better learning experience by doing nothing more than giving my time to work on making it better. The often neglected aspect of science education is the laboratory and so it makes sense that it would be difficult to quantitatively give evidence for its extreme importance in the students learning experience (Elliott et al., 2008; Lagowski, 1982).

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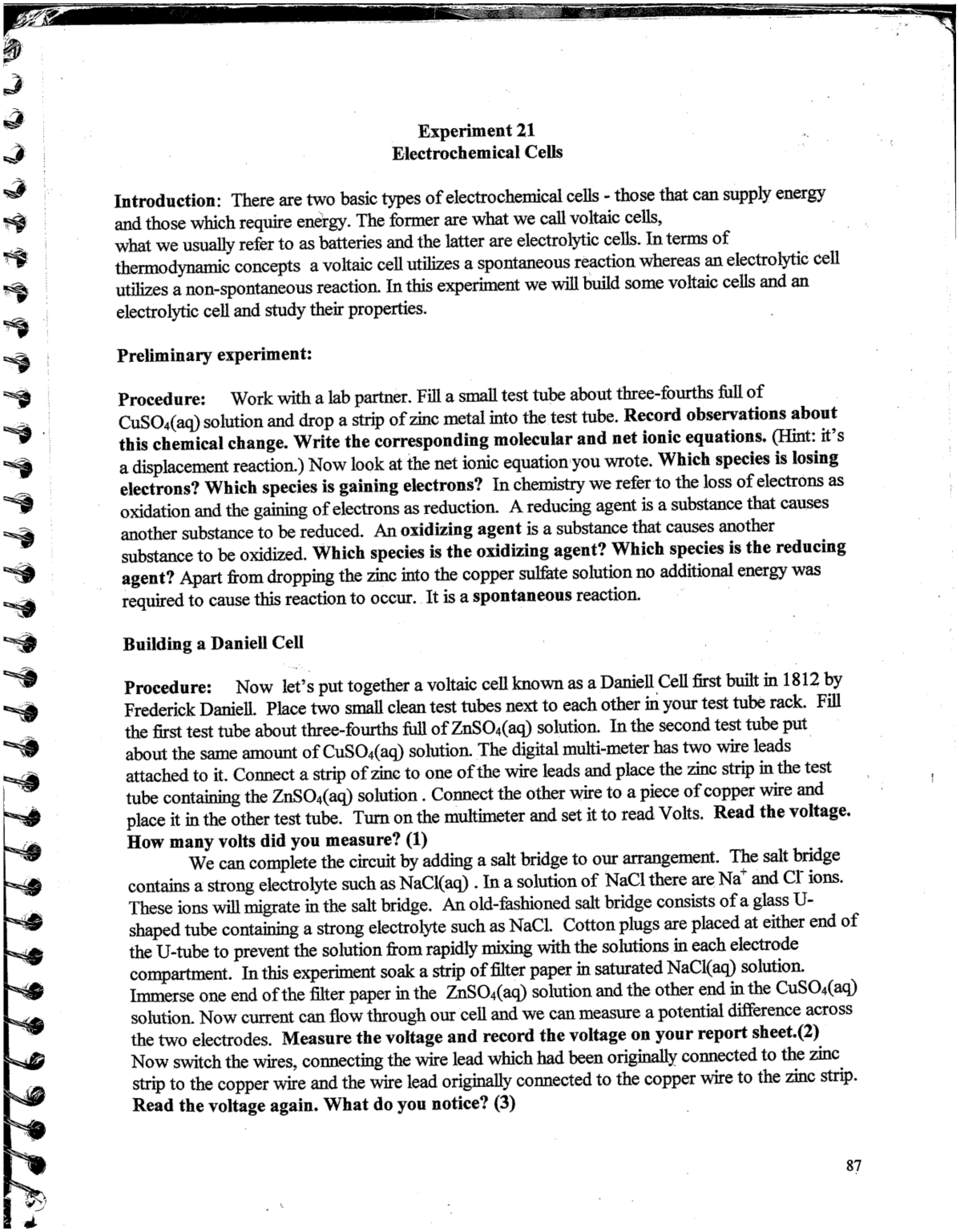
Appendices

Appendix A: Traditional Lab



Experiment 21
Electrochemical Cells

Introduction: There are two basic types of electrochemical cells - those that can supply energy and those which require energy. The former are what we call voltaic cells, what we usually refer to as batteries and the latter are electrolytic cells. In terms of thermodynamic concepts a voltaic cell utilizes a spontaneous reaction whereas an electrolytic cell utilizes a non-spontaneous reaction. In this experiment we will build some voltaic cells and an electrolytic cell and study their properties.

Preliminary experiment:

Procedure: Work with a lab partner. Fill a small test tube about three-fourths full of $CuSO_4(aq)$ solution and drop a strip of zinc metal into the test tube. **Record observations about this chemical change. Write the corresponding molecular and net ionic equations.** (Hint: it's a displacement reaction.) Now look at the net ionic equation you wrote. **Which species is losing electrons? Which species is gaining electrons?** In chemistry we refer to the loss of electrons as oxidation and the gaining of electrons as reduction. A reducing agent is a substance that causes another substance to be reduced. An **oxidizing agent** is a substance that causes another substance to be oxidized. **Which species is the oxidizing agent? Which species is the reducing agent?** Apart from dropping the zinc into the copper sulfate solution no additional energy was required to cause this reaction to occur. It is a **spontaneous** reaction.

Building a Daniell Cell

Procedure: Now let's put together a voltaic cell known as a Daniell Cell first built in 1812 by Frederick Daniell. Place two small clean test tubes next to each other in your test tube rack. Fill the first test tube about three-fourths full of $ZnSO_4(aq)$ solution. In the second test tube put about the same amount of $CuSO_4(aq)$ solution. The digital multi-meter has two wire leads attached to it. Connect a strip of zinc to one of the wire leads and place the zinc strip in the test tube containing the $ZnSO_4(aq)$ solution . Connect the other wire to a piece of copper wire and place it in the other test tube. Turn on the multimeter and set it to read Volts. **Read the voltage. How many volts did you measure? (1)**

We can complete the circuit by adding a salt bridge to our arrangement. The salt bridge contains a strong electrolyte such as NaCl(aq) . In a solution of NaCl there are Na^+ and Cl^- ions. These ions will migrate in the salt bridge. An old-fashioned salt bridge consists of a glass U-shaped tube containing a strong electrolyte such as NaCl. Cotton plugs are placed at either end of the U-tube to prevent the solution from rapidly mixing with the solutions in each electrode compartment. In this experiment soak a strip of filter paper in saturated NaCl(aq) solution. Immerse one end of the filter paper in the $ZnSO_4(aq)$ solution and the other end in the $CuSO_4(aq)$ solution. Now current can flow through our cell and we can measure a potential difference across the two electrodes. **Measure the voltage and record the voltage on your report sheet.(2)** Now switch the wires, connecting the wire lead which had been originally connected to the zinc strip to the copper wire and the wire lead originally connected to the copper wire to the zinc strip. **Read the voltage again. What do you notice? (3)**

The reaction taking place inside this voltaic cell is identical to the one in the preliminary experiment except that it only takes place when the cell delivers electricity. The electrode at which oxidation takes place is called the anode and the electrode at which reduction takes place is called the cathode. The electrons flow from the anode to the cathode. A common convention is to assign a negative sign to the anode and a positive sign to the cathode. **On your report sheet make a diagram of this cell labeling the anode and the cathode. Underneath each test tube write down the half reaction which occurs in each. Assign positive and negative signs to the electrodes.**

The main event:

Procedure: Now that you've had practice in constructing a voltaic cell we'll move on to another problem. Using iron, magnesium, and copper as materials for electrodes construct a voltaic cell which generates the **largest** voltage. To simplify this task, for each metal you should use the corresponding aqueous solution as the liquid phase of the electrode. In other words use magnesium sulfate as the aqueous phase with a strip of magnesium, use iron chloride as the aqueous phase for iron metal etc... **On your report sheet make a list of the cells you've constructed and the voltage generated for each cell.** Once you've figured out the pair of electrodes which produces the largest voltage **draw a diagram of this cell, labeling the cathode and the anode . Write down the half reaction which occurs at each electrode.**

A concentration cell:

Procedure: The voltage that a voltaic cell produces under standard conditions is denoted E^{o}_{cell}. The superscript refers to standard conditions which in thermodynamics means 1 atm, any temperature (usually 25°C), and 1 M concentration. The voltage a cell produces depends upon the concentrations of reactants and products. Using the Daniell Cell you constructed change the concentrations of reactants or products to increase the voltage of the cell by a minimum of 0.05 V. Use any of the reagents available in the lab. If you need a particular reagent that is not available ask your lab instructor to see if is available from the stockroom. Explain the results you obtained using LeChatelier's principle. Hint for this part: The cell voltage will increase if the reaction will proceed to the product side as a result of an increase or decrease in concentration. A good starting place would be to examine the net ionic equation you wrote in the preliminary exercise and determine what could be done to the concentrations of either reactants or products to make that reaction proceed more to the right hand side. Then carry out those changes in concentrations.

Electrolytic cells:

Procedure: Sometimes we may wish a particular chemical reaction to occur which is non-spontaneous. We can get this reaction to occur if we supply enough energy. One way to do this is to construct an electrolytic cell.

Dry and weigh two lengths of copper wire .**Write the masses on your report sheet.** Fill a 100 mL beaker about three-fourths full of Cu^{2+} solution. Hang the copper strips on either side of the beaker so that they are suspended in the solution. **Do not let the electrodes touch each**

other. Connect the positive terminal of the power supply to one copper strips and the negative terminal of the power supply to the other copper strip. Plug in the power supply . **Watch for any changes that occur.** Let the cell run for about 20 minutes. **While you're waiting read the following discussion.**

We can calculate the weight of the mass deposited at one of the electrodes with the following formula.

weight deposited in grams= MIt/(96,500 n)

where M is the molar mass of the compound deposited, I is the current applied and t is the time in seconds. The number 96500 comes from Faraday's constant which is the magnitude of charge on a mole of electrons . n is the number of moles of electrons transferred per mol of substance deposited. For example in the half-reaction
$Ni^{2+} + 2e \rightarrow Ni$ the number of moles of electrons transferred is 2.

Turn off the power supply and remove the metal electrodes from your voltaic cell. Carefully dry the electrodes and then weigh them. **Record the results. Identify the metal deposited. Use the formula above to calculate how much metal deposited given the current and time you used. Compare this calculated value to your experimental results. Which electrode gains mass?**

Name	Date
Lab Partner	Lab Instructor

Experiment 21
Electrochemical Cells

Preliminary exercise:

Observations	
Molecular equation	
Net ionic equation	
Species losing electrons	Species gaining electrons

Building a Daniell Cell

1 Voltage
2 Voltage
3 Voltage

Draw a diagram of the Daniell Cell

The main event:

Cells constructed	Voltage generated

Draw a diagram of the cell which produces the largest voltage

Concentration Cell:

The voltage of the non-standard Daniell Cell is

Which reactant or product concentration(s) did you change?

Describe the method you used to change the concentration?

Explain using LeChatelier’s principle why the change in concentration increased the cell voltage.

Electrolytic cell:

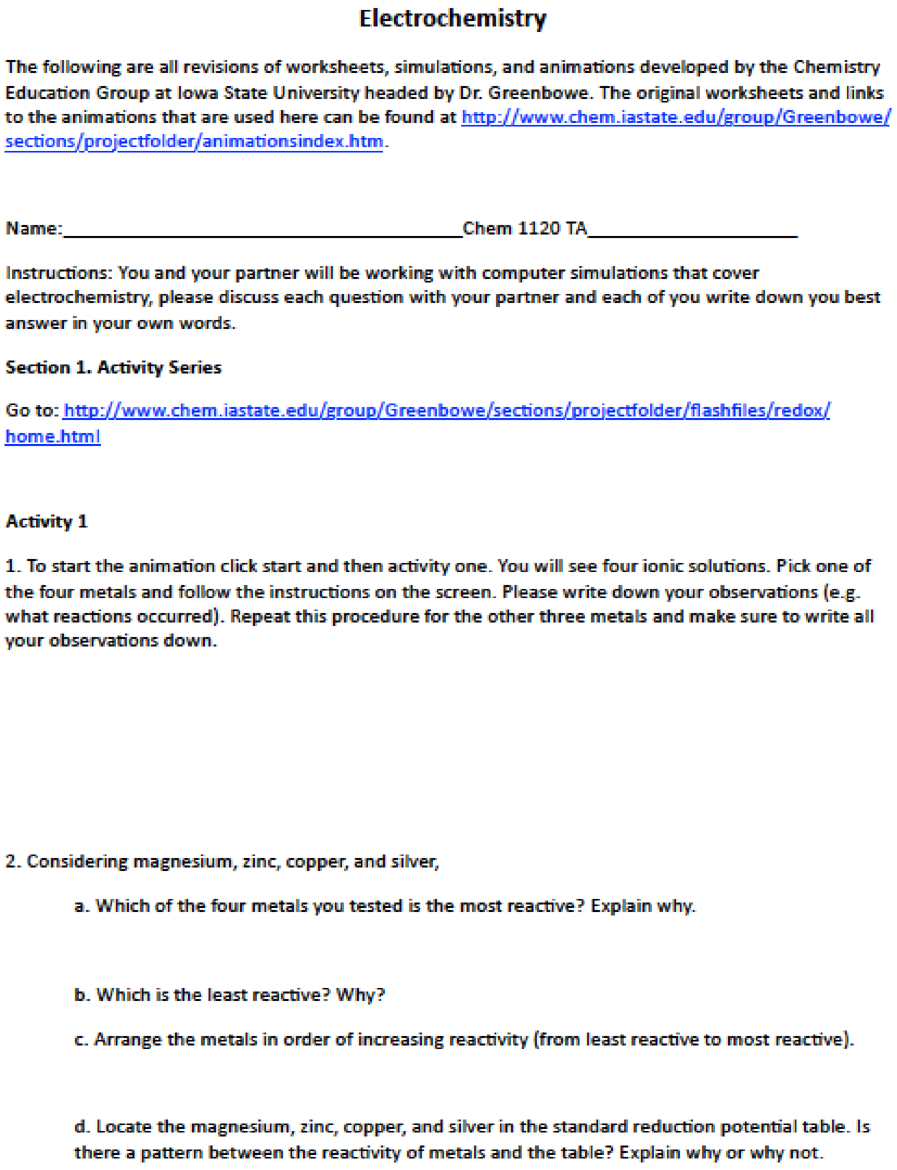
Mass of one electrode		Mass of other electrode	
before electrolysis	after electrolysis	before electrolysis	after electrolysis

The metal deposited is __________

Calculated mass. Assume the current is 0.50 A.

The electrode which gains mass is

Appendix B: Virtual Lab



Electrochemistry

The following are all revisions of worksheets, simulations, and animations developed by the Chemistry Education Group at Iowa State University headed by Dr. Greenbowe. The original worksheets and links to the animations that are used here can be found at http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/animationsindex.htm.

Name:____Chem 1120 TA_____________________

Instructions: You and your partner will be working with computer simulations that cover electrochemistry, please discuss each question with your partner and each of you write down you best answer in your own words.

Section 1. Activity Series

Go to: http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/flashfiles/redox/home.html

Activity 1

1. To start the animation click start and then activity one. You will see four ionic solutions. Pick one of the four metals and follow the instructions on the screen. Please write down your observations (e.g. what reactions occurred). Repeat this procedure for the other three metals and make sure to write all your observations down.

2. Considering magnesium, zinc, copper, and silver,

   a. Which of the four metals you tested is the most reactive? Explain why.

   b. Which is the least reactive? Why?

   c. Arrange the metals in order of increasing reactivity (from least reactive to most reactive).

   d. Locate the magnesium, zinc, copper, and silver in the standard reduction potential table. Is there a pattern between the reactivity of metals and the table? Explain why or why not.

Section 2. Electrochemical Cells

Oxidation: A process in which a substance loses one or more electrons
Reduction: A process in which a substance gains one or more electrons
Anode: an electrode at which oxidation occurs
Cathode: an electrode at which reduction occurs

Activity 2

Go to: http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/flashfiles/electroChem/voltaicCell20.html

1. Begin by assembling a zinc-copper cell. Click on the Metals tab on the left and choose copper. Click on the Solutions tab on the left and choose copper nitrate. Click on the Metals tab on the left and choose zinc. Click on the Solutions tab on the right and choose zinc nitrate. Click on the "ON" button for the voltmeter and observe what happens. Notice the salt bridge that connects the two solutions. After answering the questions feel free to try other combinations.

2. Complete the following table

	Zinc	**Copper**
Is there an electron transfer between species?		
Mark the species that loses electrons		
Mark the species that gains electrons		
Write down the reduction half reaction under the species that is undergoing reduction.		
Write down the oxidation half reaction under the species that is undergoing oxidation		
Mark the cathode		
Mark the anode		

3. Is this a spontaneous reaction? Explain your reasoning.

4. Write the complete balanced equation for the reaction.

Name ______________________________ Chem 1120 Spring 2011 TA ____________

Concentration Electrochemical Cells Lab Work in groups. GOTO:

http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/flashfiles/electroChem/voltaicCellEMF.html

1. Start the software and construct a zinc-copper electrochemical cell using 1.0 M Zn^{2+} and 1.0 M Cu^{2+} solutions.

a. What is the EMF of this cell (include units)? ___________________

b. For the voltage that you are measuring, is this $E°_{cell}$ or E_{cell}? ________. Explain.

c. Write the chemical equation that represents the reaction occurring in this cell.

d. Is this a spontaneous or non-spontaneous reaction? ______________________. Explain.

e. Draw a cell diagram for this electrochemical cell.

f. What is the oxidation half-reaction that occurs and where does it occur? Look at the molecular level animation. The anode is _________.

2. Construct another cell using zinc and copper as before except use a 2.0 M Zn^{2+} solution and a 0.001 M Cu^{2+} solution.

a. Do you expect the voltage to increase, decrease, or stay the same as the 1.0M solutions in the previous electrochemical cell? ____________________Why?

b. What is the EMF of this cell?_____________ Was your prediction correct?_____

c. Based on the chemical equation you wrote for 1c, explain why changing the concentration of the solutions changed the voltage.

3. Construct another cell using zinc and copper but now use 0.001M Zn^{2+} solution and a 2.0 M Cu^{2+} solution.

a. What do you expect to happen to the voltage now?______________

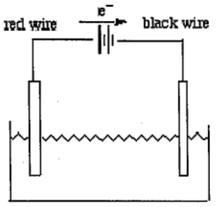
b. Explain the change in the voltage.

NAME______________________________ **Chem 1120 Spring 2011 T.A.** ________________

ELECTROLYSIS LAB ASSIGNMENT

Go to:
http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/flashfiles/electroChem/electrolysis10.html

a) Will nickel metal spontaneously react with aqueous nickel(II) nitrate? Set-up an electrolysis experiment. Connect two strips of nickel metal to a power supply and immersed the electrodes in aqueous nickel(II) nitrate. Select the mass of each electrode and record the initial mass of each electrode.



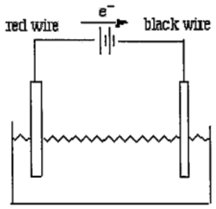
b) Your goal is to cause a non-spontaneous reaction to occur. Before running the simulation, predict what will happen when the power is turned on. Complete the diagram. Identify the metal used for each electrode. Indicate the direction of the flow of electrons in the wire and indicate what will happen at each electrode. Identify the anode and the cathode. Write the half-reactions that will occur.

b) Set the voltage and the current on the power supply. Select the amount of time you want the current to flow. Turn on the power supply. At the end of the experiment, record the final mass of each electrode. Did your predictions match what happened?

Initial ______g Initial_______g

Final _______g Final________g

c) Will nickel metal spontaneously react with aqueous iron(II) nitrate? Set-up another electrolysis experiment. Use a nickel electrode and an iron electrode immersed in aqueous iron(II) nitrate. Your goal is to set-up the electrodes so that iron metal will be deposited on the nickel electrode when the power supply is turned on. Complete the diagram. Indicate the direction of the flow of electrons in the wire and indicate what will happen at each electrode. Identify the metal used for each electrode. Identify the anode and the cathode. Write the half-reactions and the balanced chemical equation. What is the minimum voltage, Eš, necessary to cause this reaction to occur?



Appendix C: Pre-Test and Post-Test

Pre Exam Extra Credit Name:________________________TA

1. You have a solution of copper ions (Cu 2+) and when you place a strip of solid zinc in the solution you notice a copper color appearing on the piece of zinc.

    a. Which metal is being oxidized?

    b. Which metal is being displaced?

2. A voltaic cell is created using zinc metal and zinc ions in one half cell and copper metal and copper ions in the other half cell.

    a. Which metal is the anode?

    b. Write each half reaction and the overall reaction?

    c. Draw a diagram of the voltaic cell and label the solutions, the electrodes, and the flow of electrons.

3. What would happen to the reaction if I increased the concentration of the zinc ion in the overall equation above?

4. If we took the voltaic cell of zinc and copper from above and we added an external source of electricity, what would eventually happen as we increased the voltage of the external source?

Post Exam Extra Credit Name:________________________TA

1. You have a solution of copper ions (Cu 2+) and when you place a strip of solid zinc in the solution you notice a copper color appearing on the piece of zinc.

   a. Which metal is being oxidized?

   b. Which metal is being displaced?

2. A voltaic cell is created using zinc metal and zinc ions in one half cell and copper metal and copper ions in the other half cell.

   a. Which metal is the anode?

   b. Write each half reaction and the overall reaction?

   c. Draw a diagram of the voltaic cell and label the solutions, the electrodes, and the flow of electrons.

3. What would happen to the reaction if I increased the concentration of the zinc ion in the overall equation above?

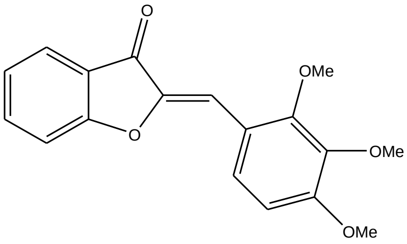
4. If we took the voltaic cell of zinc and copper from above and we added an external source of electricity, what would eventually happen as we increased the voltage of the external source?

5. Using the supplies given to you, construct a voltaic cell that would have the greatest voltage and label the cathode and anode. When you are done I will give you a voltmeter to test your results.

For the professor: CS ☐, SB☐ - UT☐ FP ☐, CAC☐, VC ☐

Appendix D: Spectroscopy of Aurones

1. (Z)-2-(2,3,4-trimethoxybenzylidene)benzofuran-3(2H)-one



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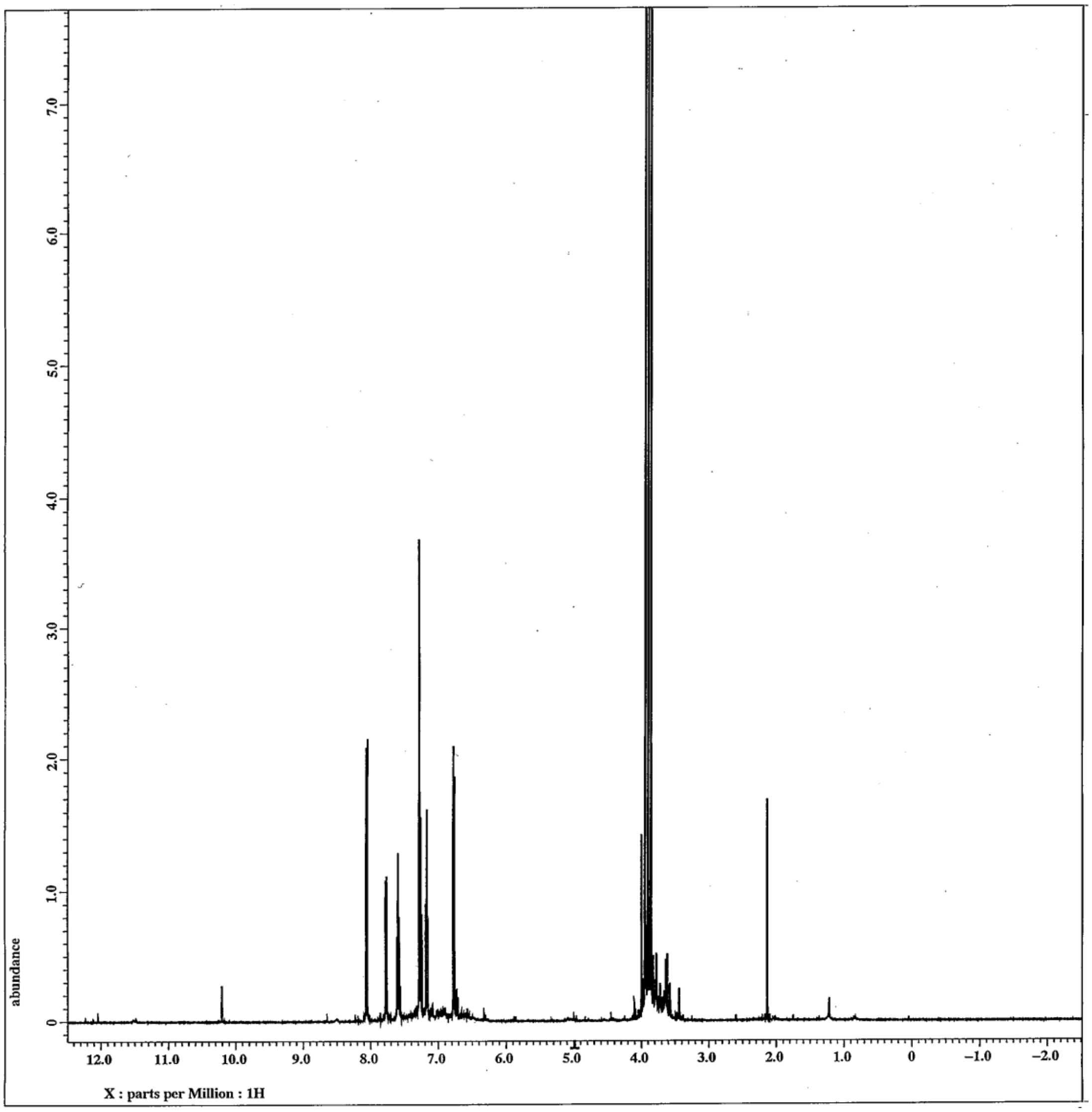

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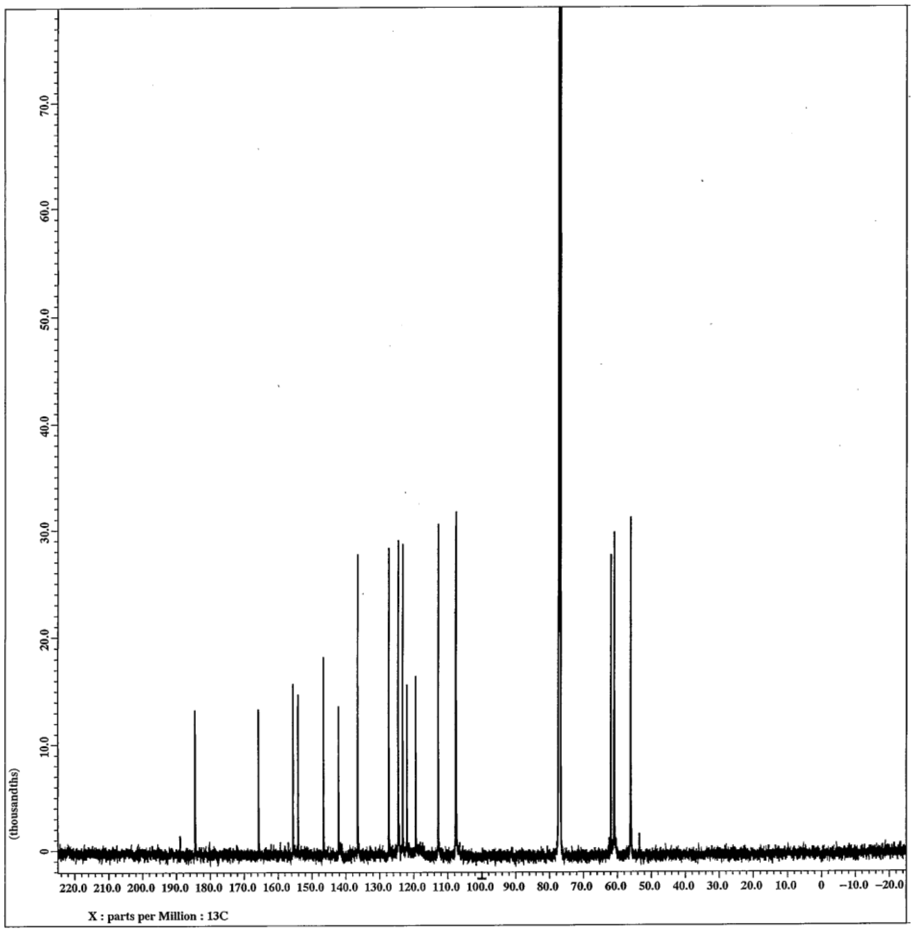
(thousandths)
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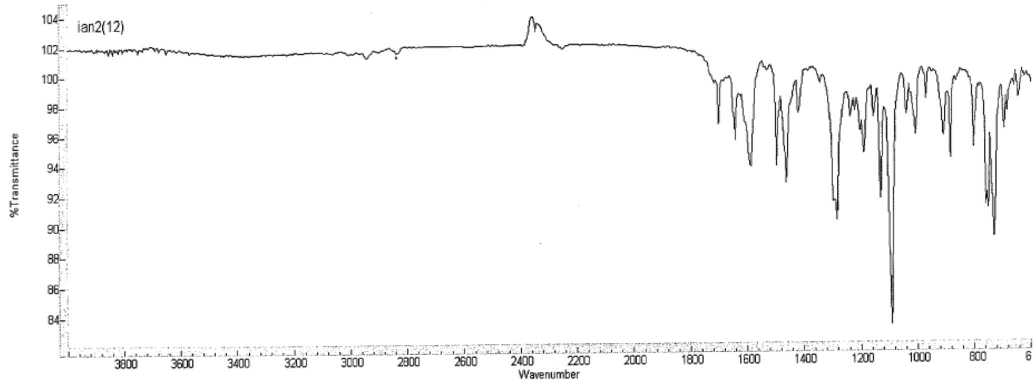
20.0
30.0
40.0
50.0
60.0
70.0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0
X : parts per Million : 13C

IR


ian2(12)
%Transmittance
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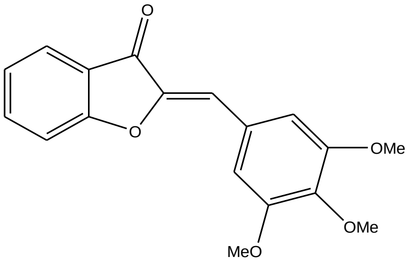
102
100
98
96
94
92
90
88
86
84
3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 6
Wavenumber

2. (Z)-2-(3,4,5-trimethoxybenzylidene)benzofuran-3(2H)-one



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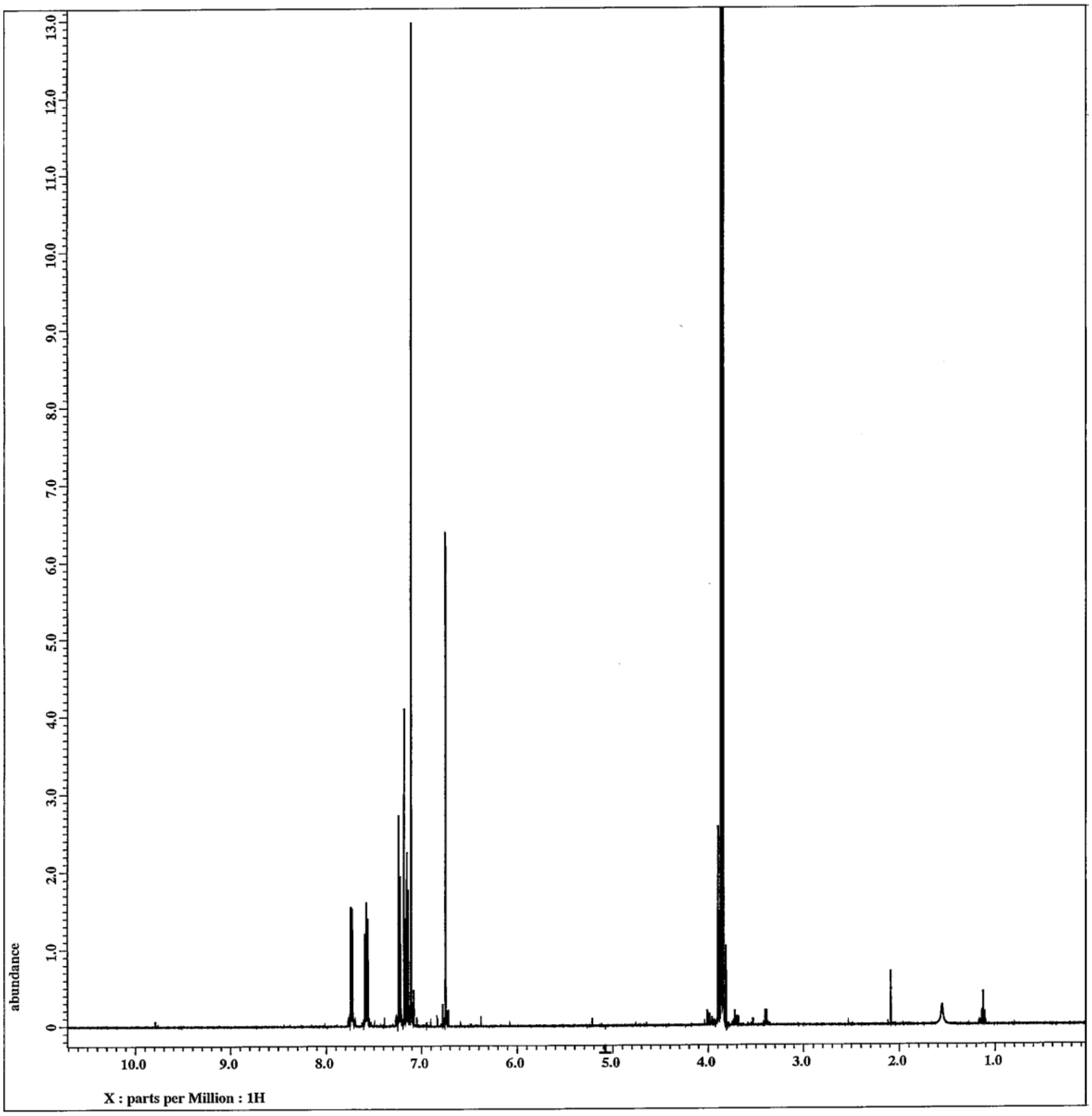

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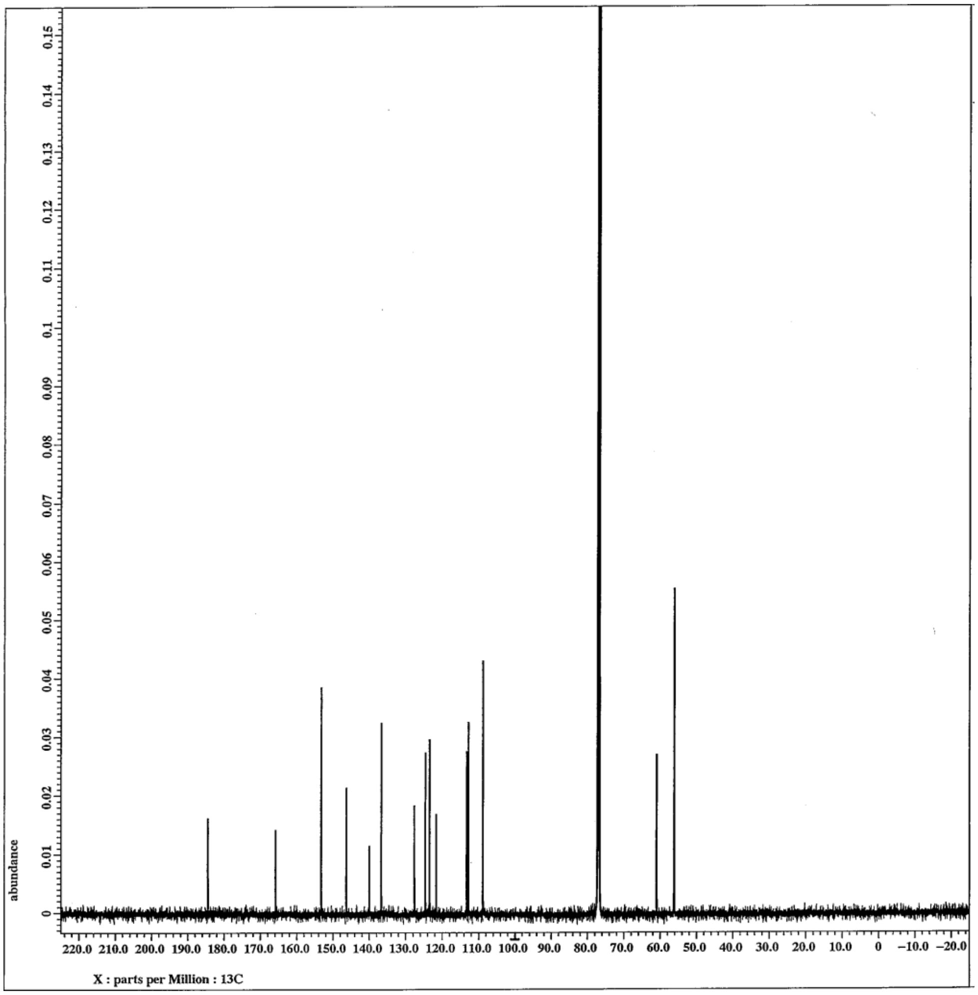
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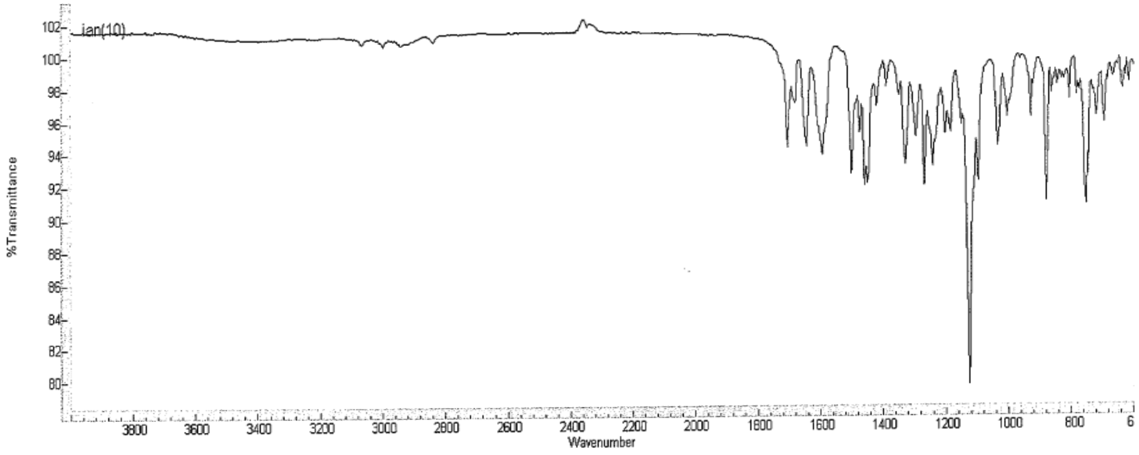
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0
X : parts per Million : 13C

IR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90
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86
84
82
80
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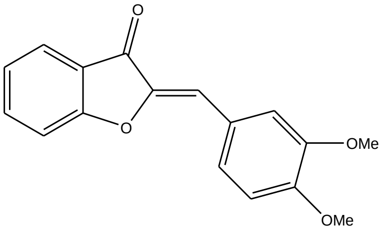
Wavenumber

3. (Z)-2-(3,4-dimethoxybenzylidene)benzofuran-3(2H)-one



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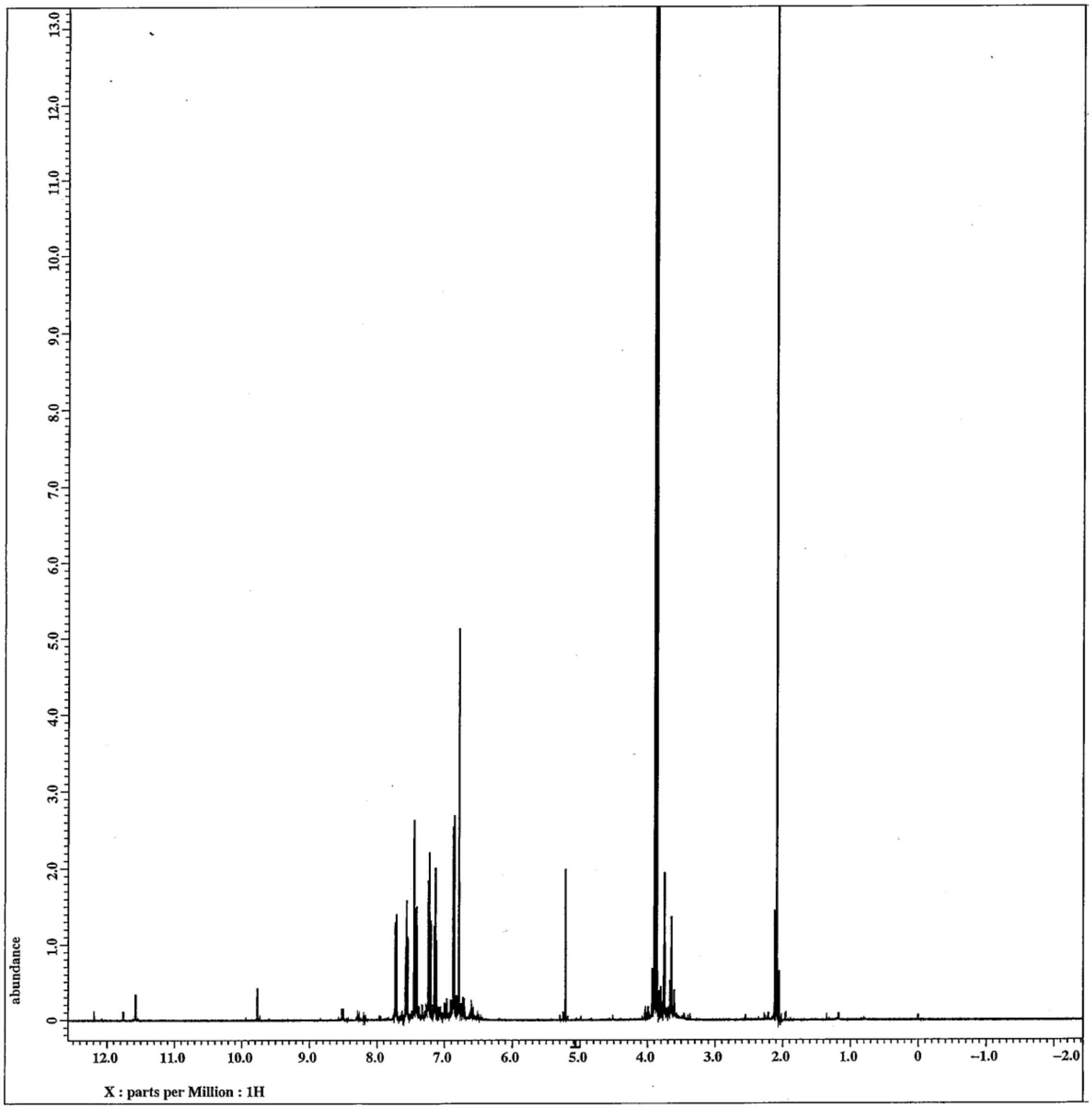

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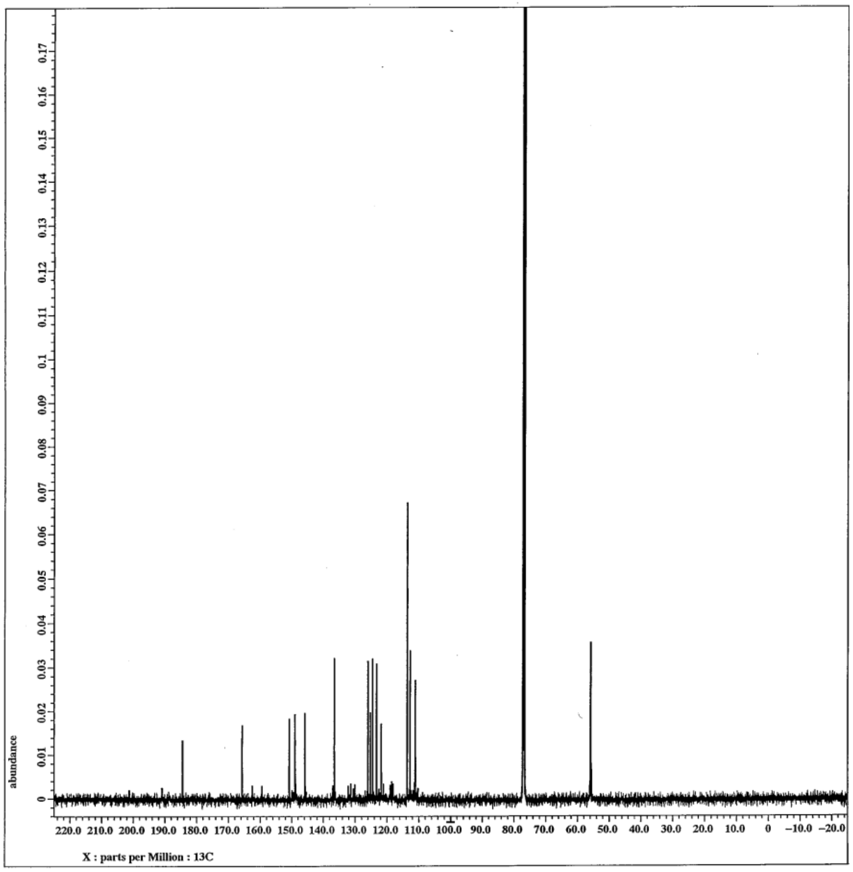
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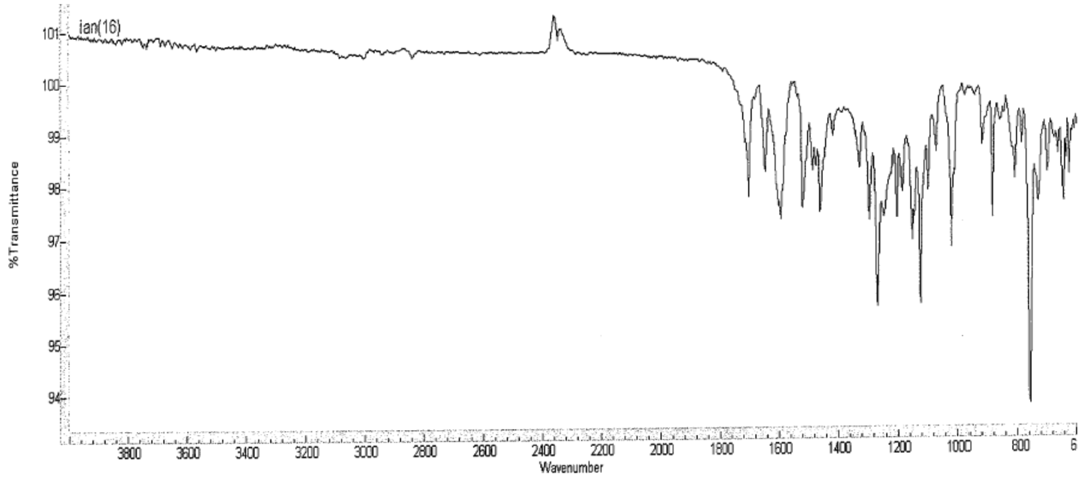
X : parts per Million : 13C

IR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%Transmittance
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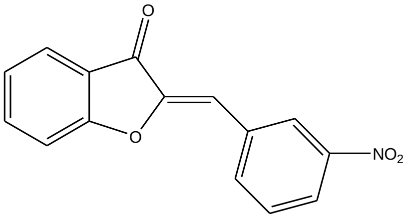
Wavenumber

4. (Z)-2-(3-nitrobenzylidene)benzofuran-3(2H)-one



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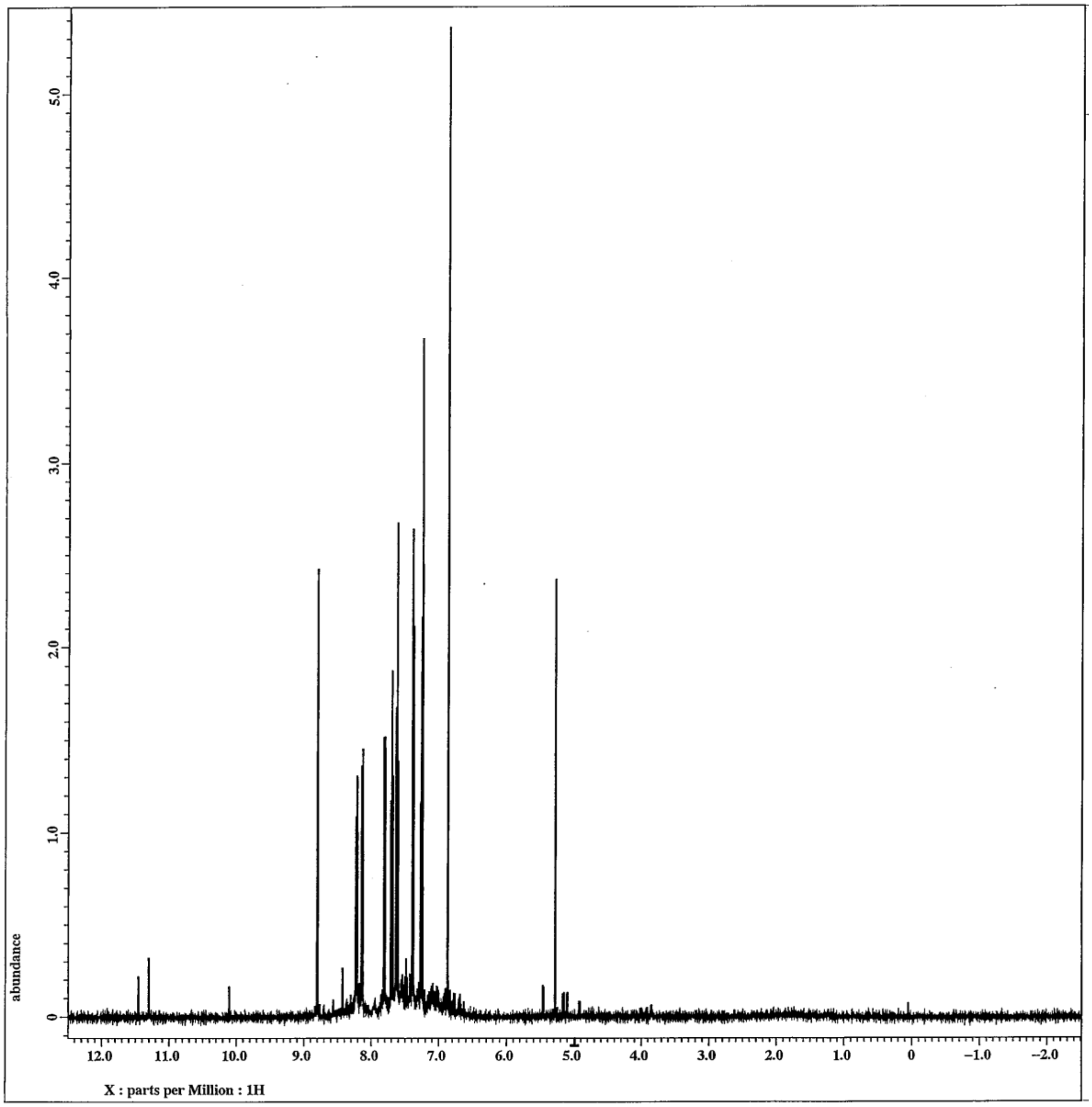

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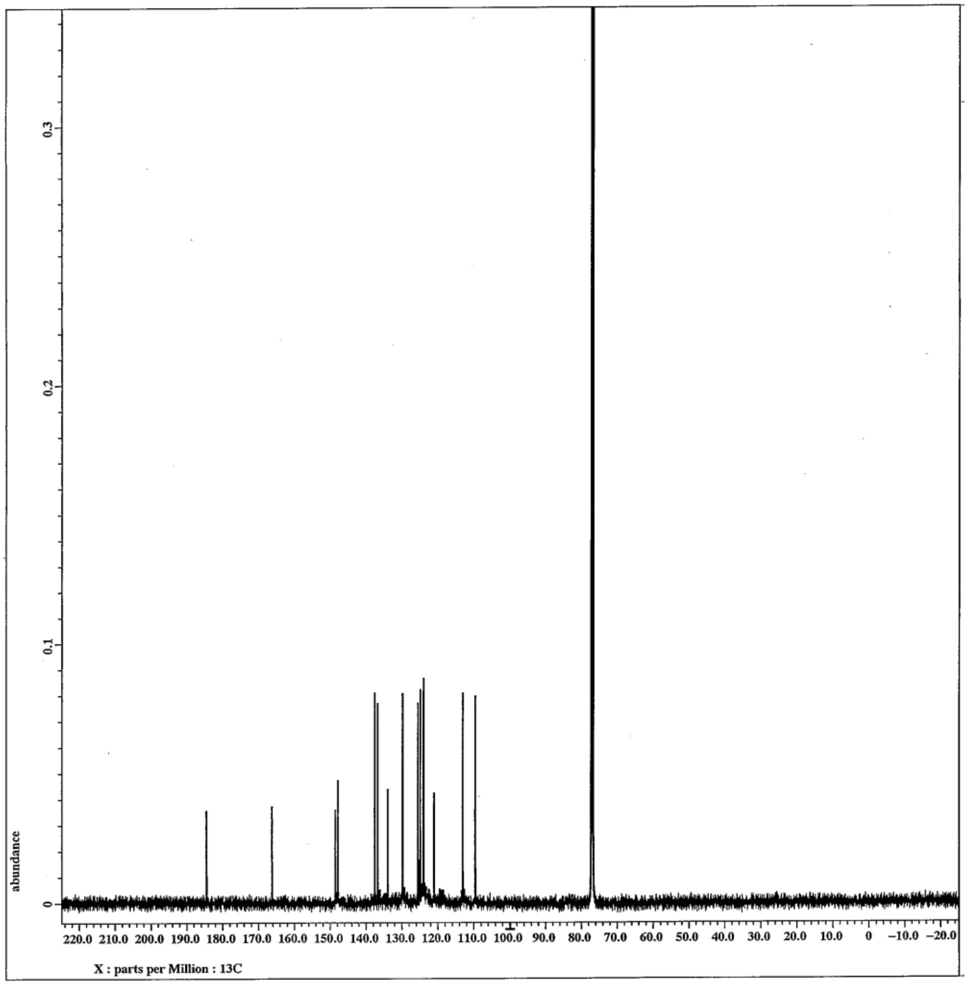
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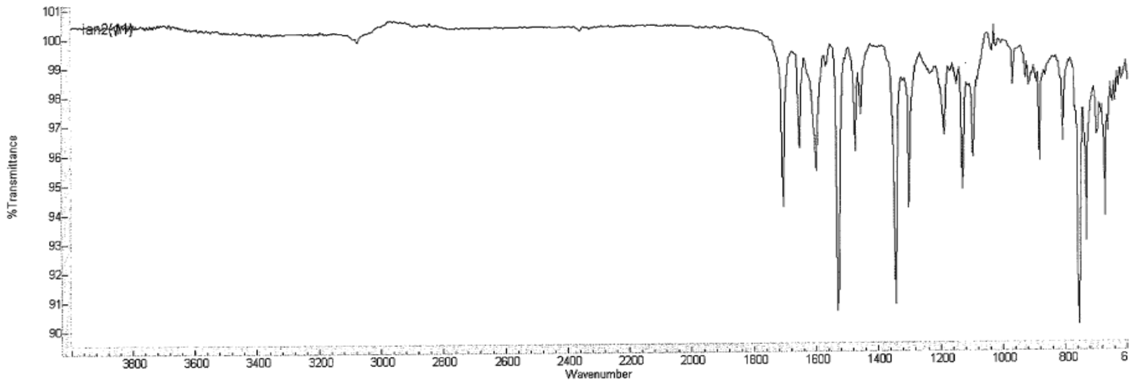
0.3
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0
X : parts per Million : 13C

IR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%Transmittance
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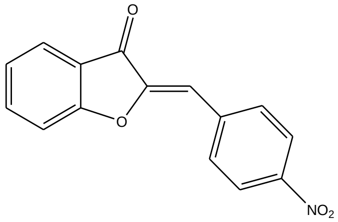
Wavenumber

5. (Z)-2-(4-nitrobenzylidene) benzofuran-3(2H)-one



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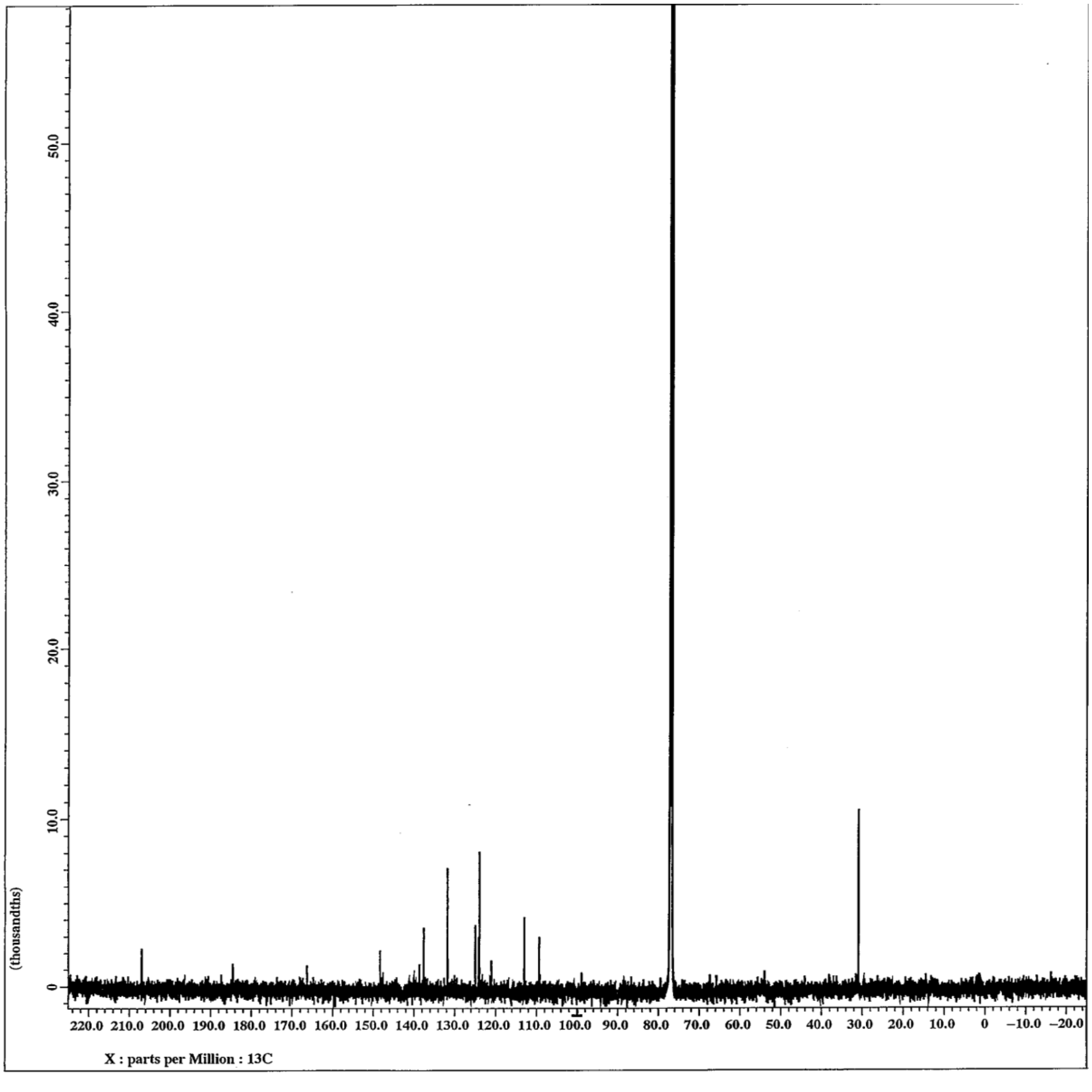

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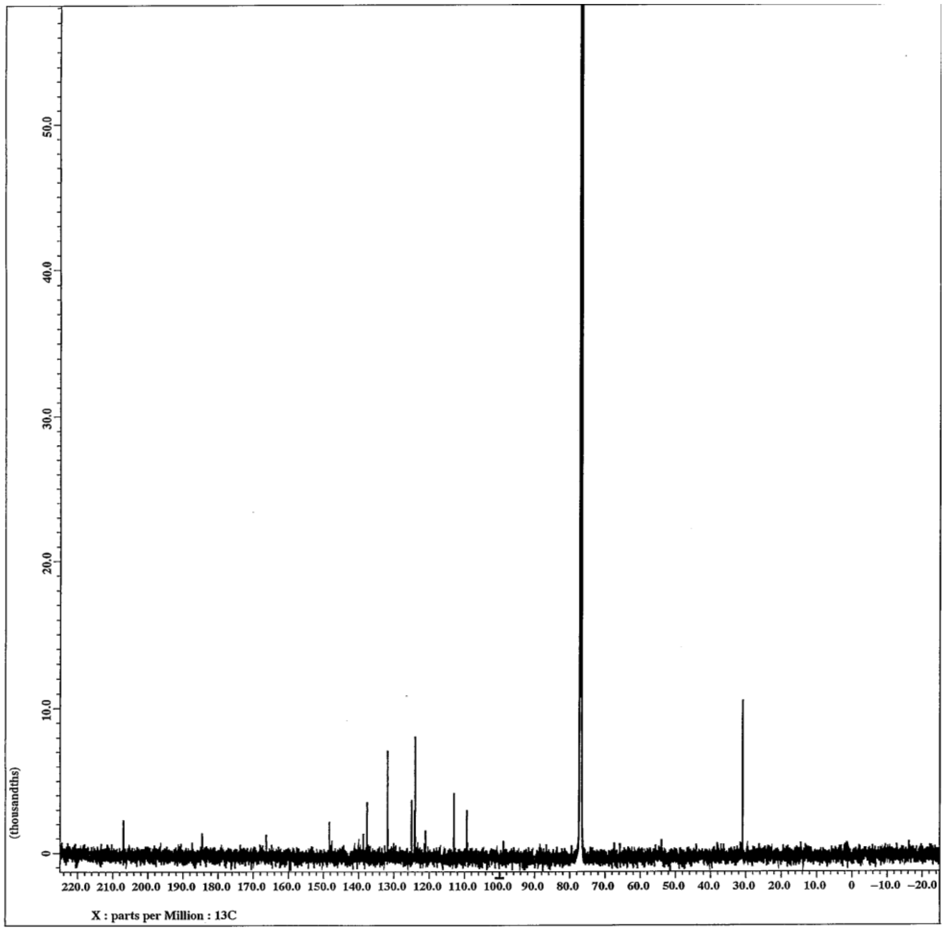
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50.0
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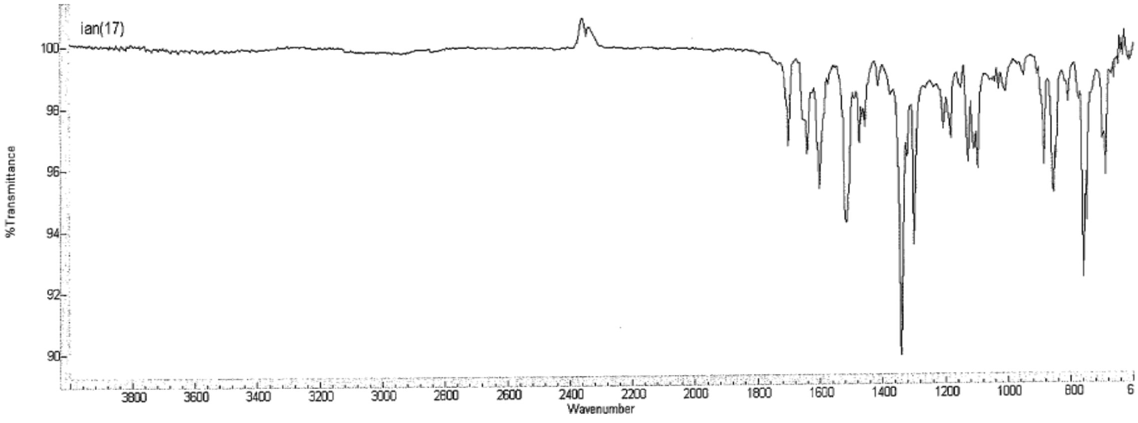
X : parts per Million : 13C

IR


ian(17)
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94
92
90
%Transmittance
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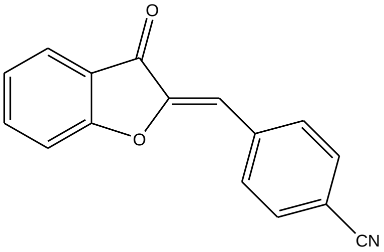
Wavenumber

6. (Z)-4-((3-oxobenzofuran-2(3H)-ylidene)methyl)benzonitrile



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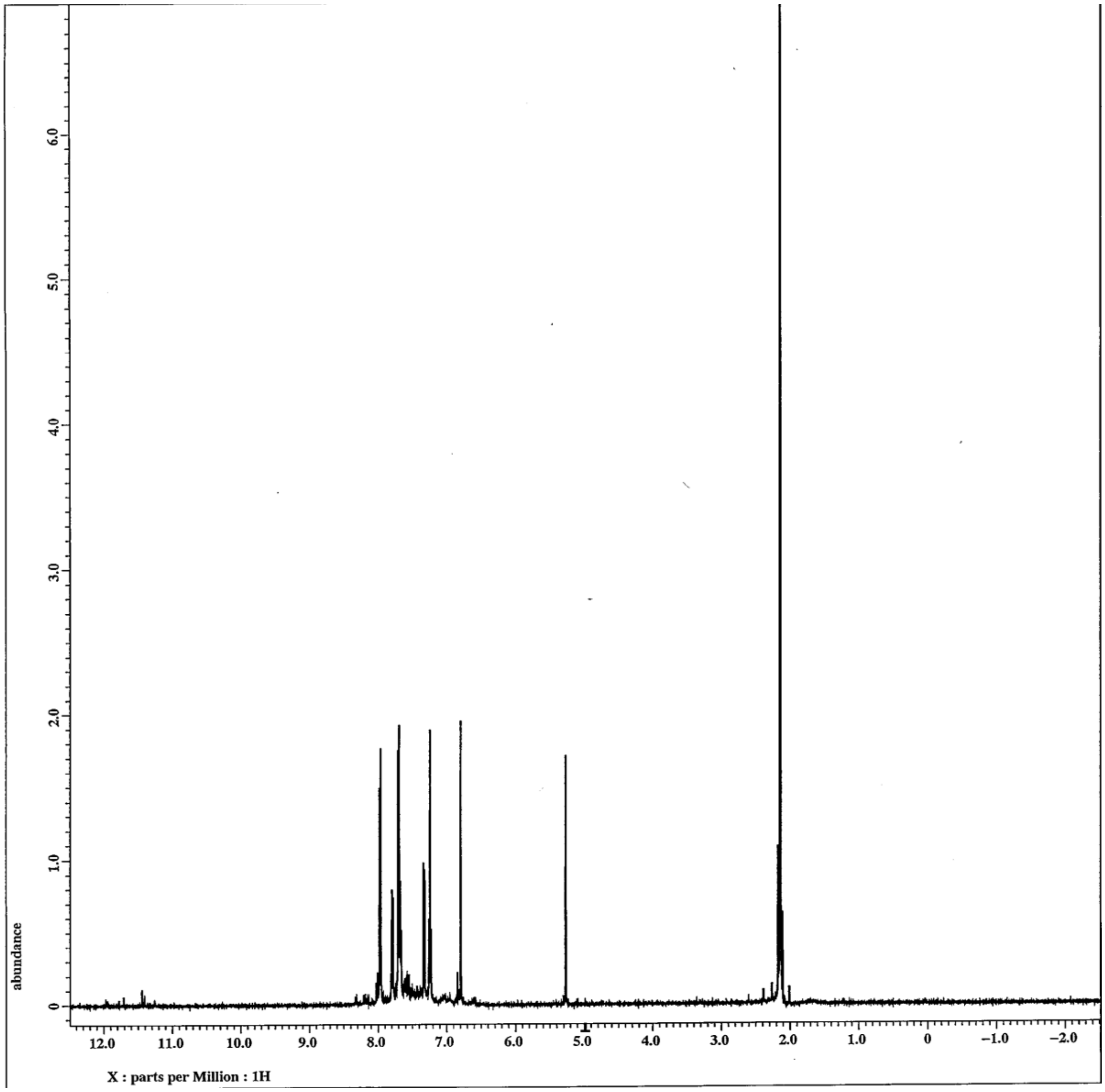

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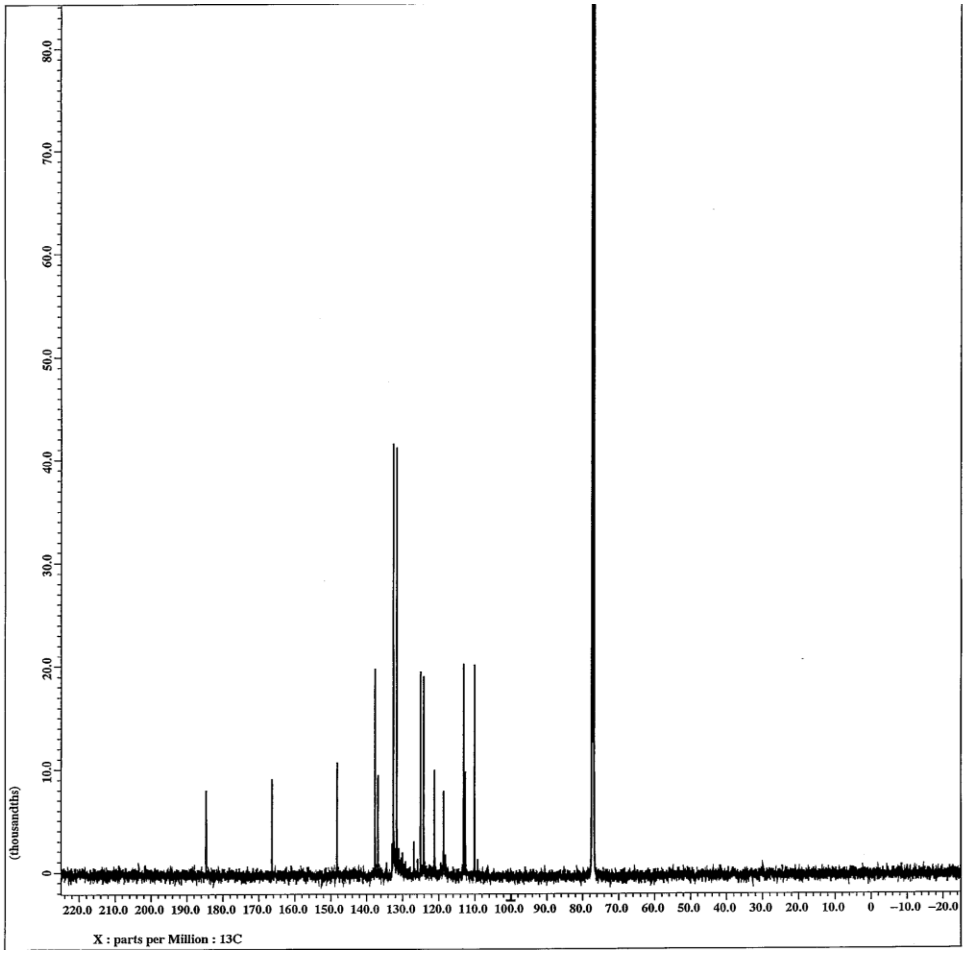
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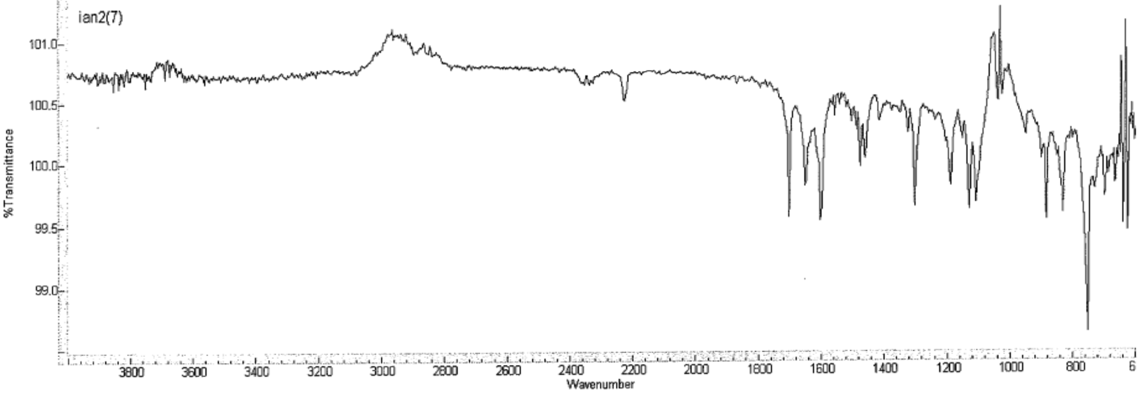
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0
X : parts per Million : 13C

IR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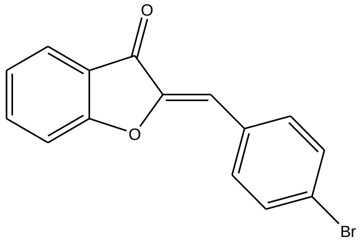
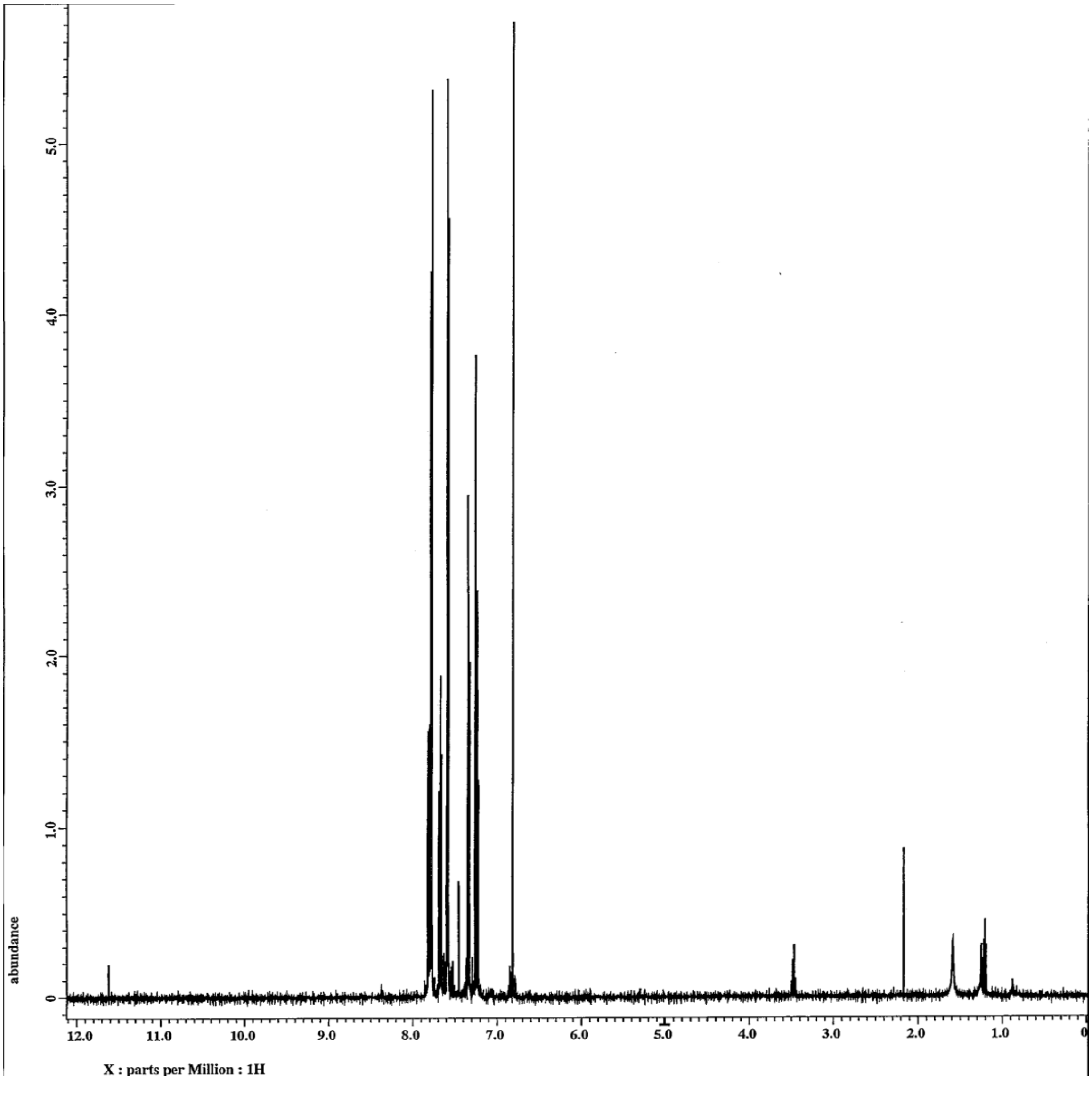
99.0
%Transmittance
3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 6
Wavenumber

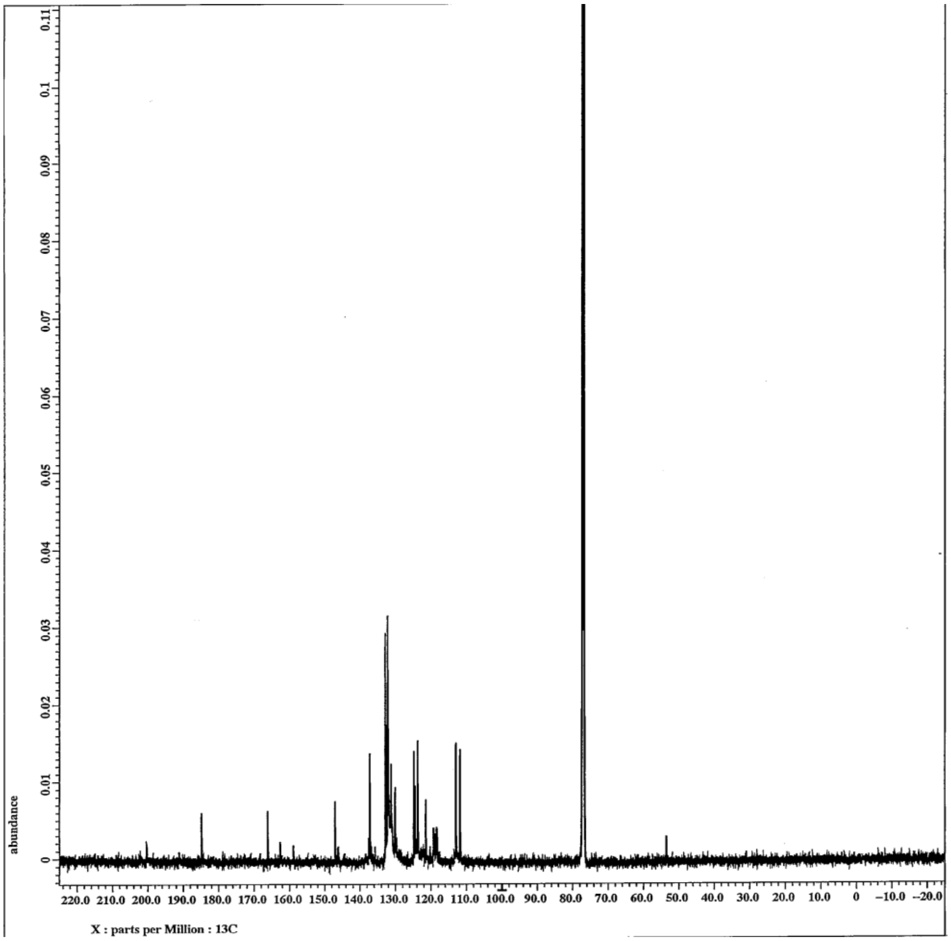
7. (Z)-2-(4-bromobenzylidene)benzofuran-3(2H)-one



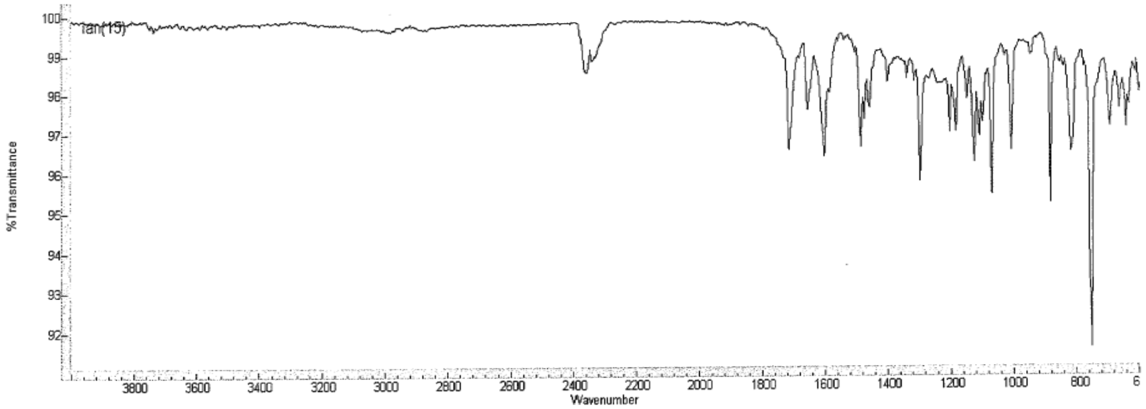
^{1}H-NMR



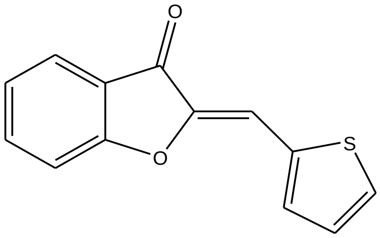
^{13}C-NMR


abundance
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
0.11
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0
X : parts per Million : 13C

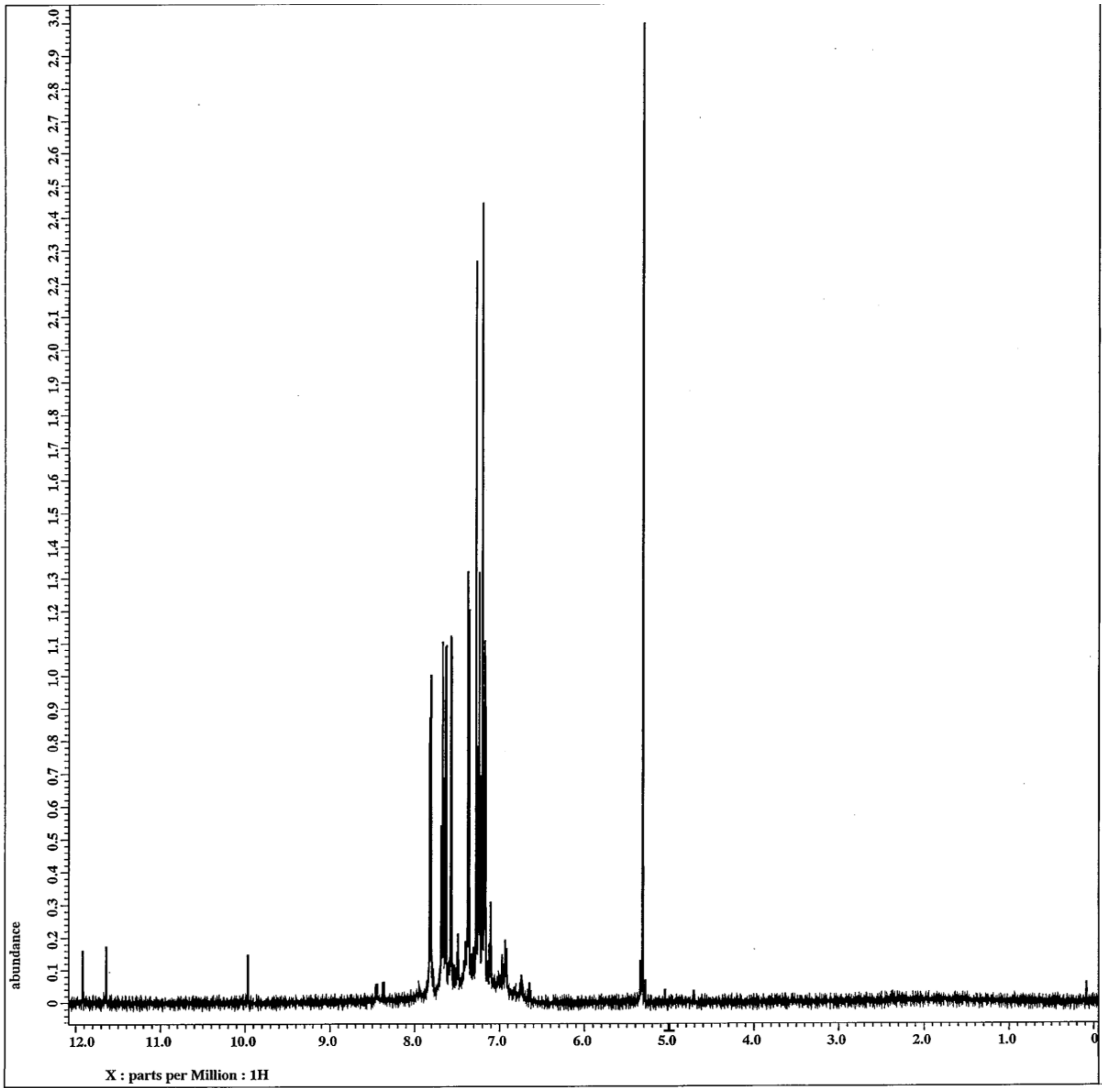
IR


Tan(15)
%Transmittance
100
99
98
97
96
95
94
93
92
3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 6
Wavenumber

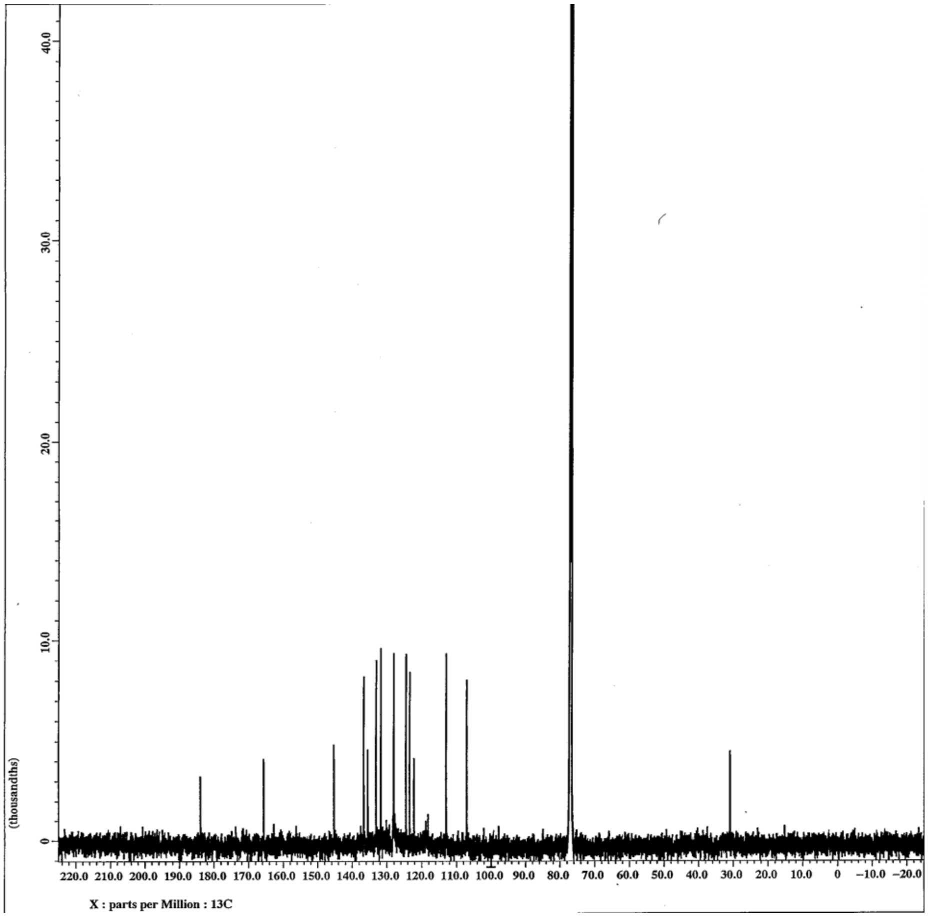
8. 2-(thiophen-2-ylmethylene)benzofuran-3(2H)-one



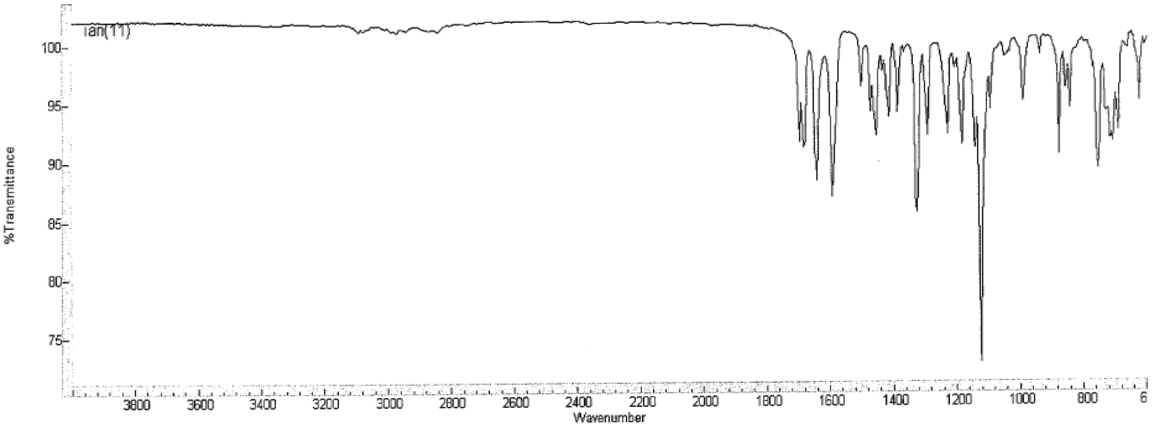
^{1}H-NMR



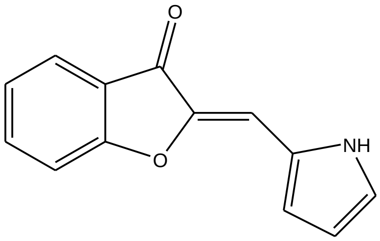
^{13}C-NMR


40.0
30.0
20.0
10.0
0
(thousandths)
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0
X : parts per Million : 13C

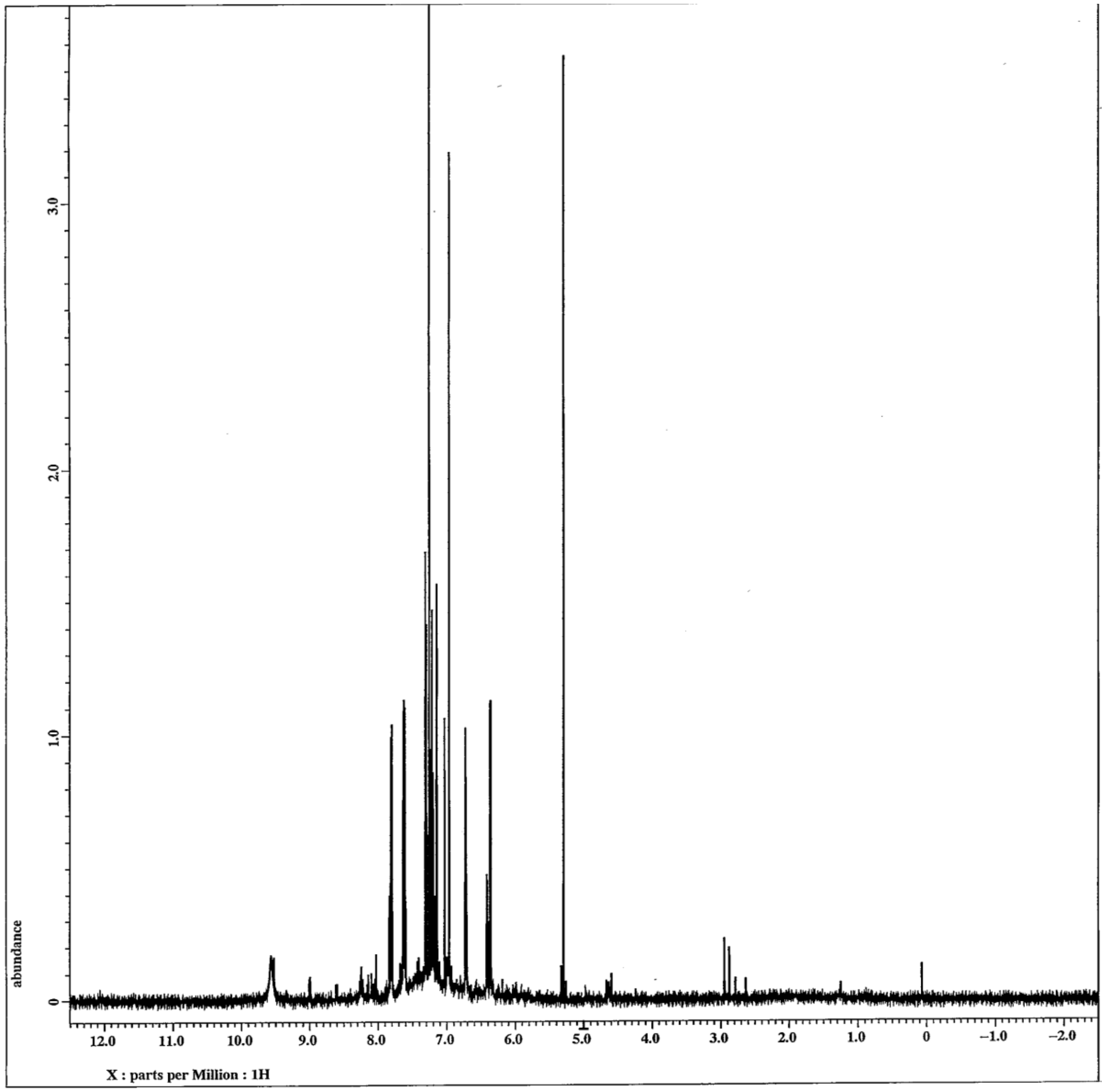
IR


Ian(11)
100
95
90
85
80
75
%Transmittance
3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 6
Wavenumber

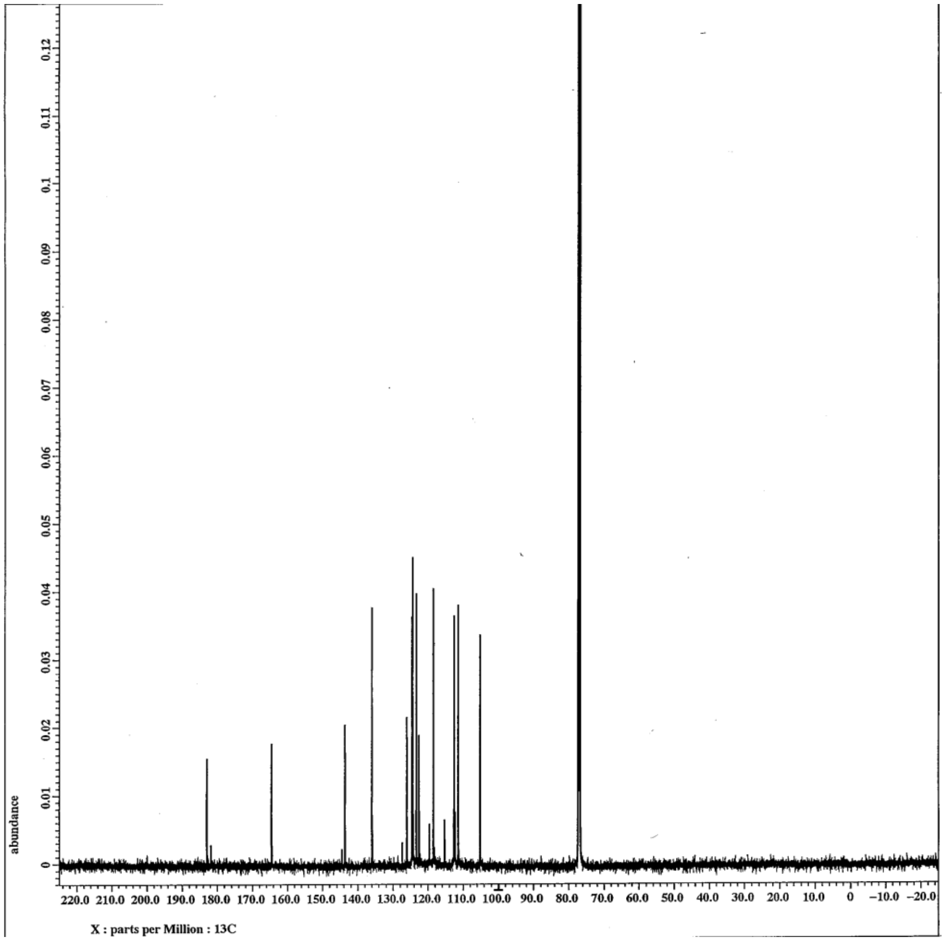
9. (Z)-2-((1H-pyrrol-2-yl)methylene)benzofuran-3(2H)-one



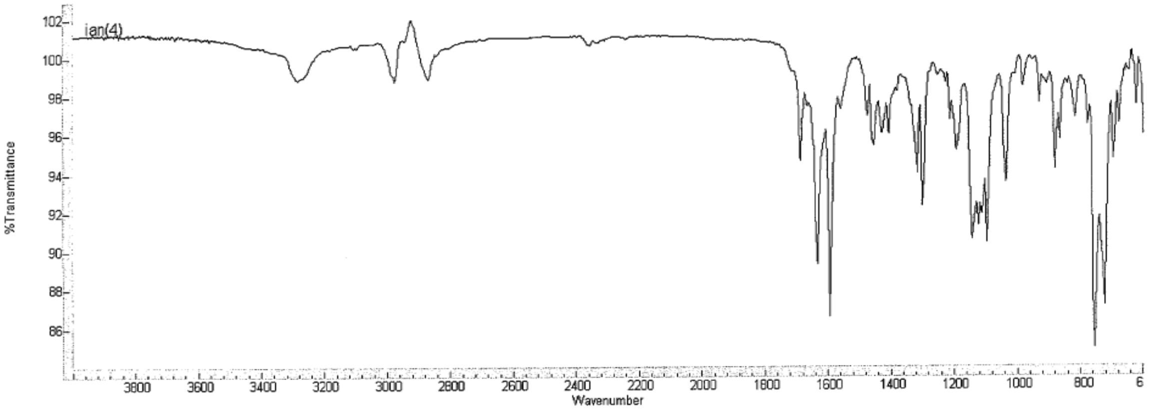
^{1}H-NMR



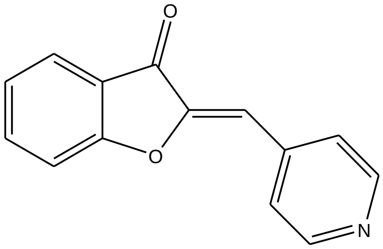
^{13}C-NMR


abundance
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
0.11
0.12
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0
X : parts per Million : 13C

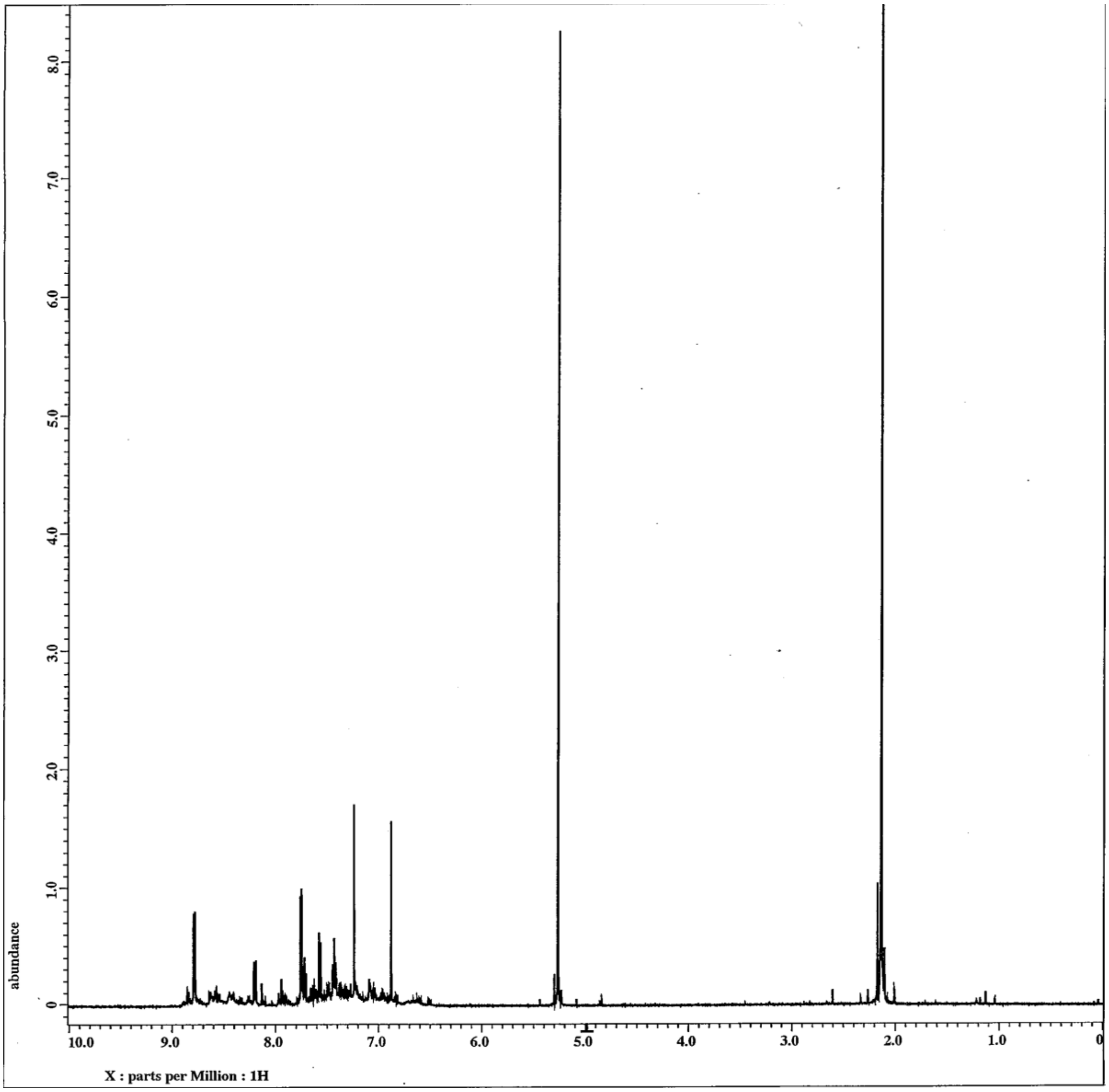
IR


ian(4)
%Transmittance
102
100
98
96
94
92
90
88
86
3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 6
Wavenumber

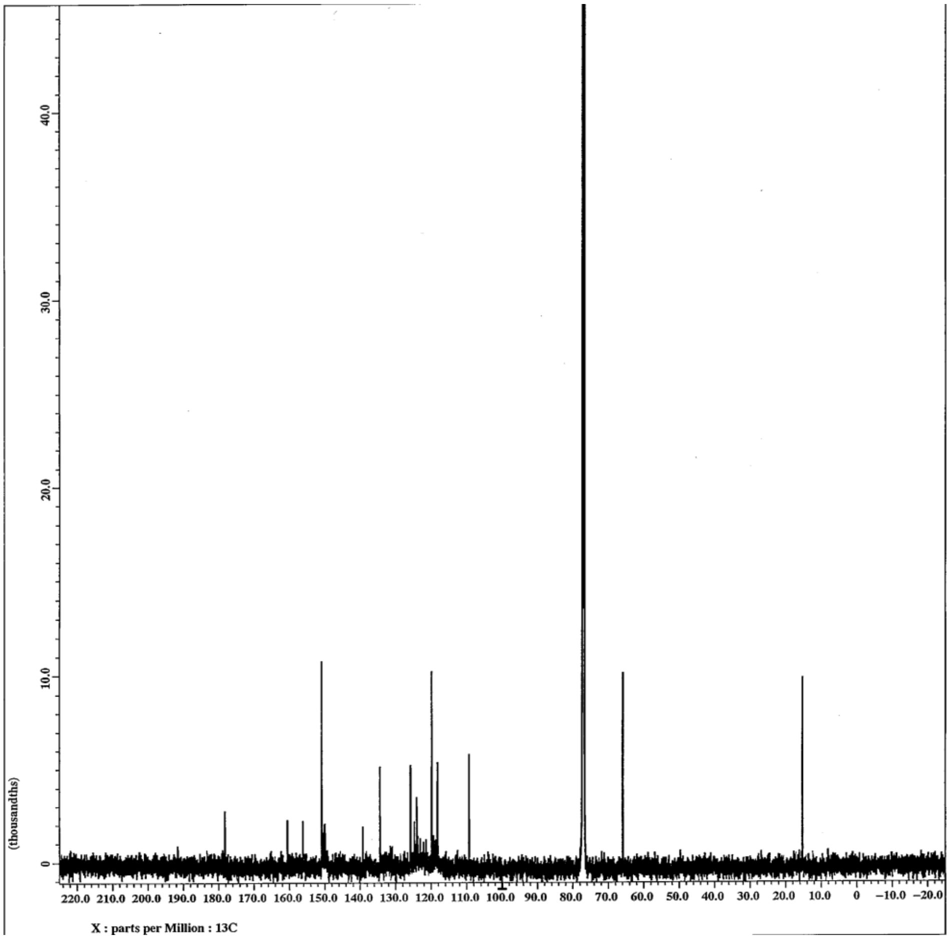
10. (Z)-2-(pyridine-4-ylmethylene)benzofuran-3(2H)-one



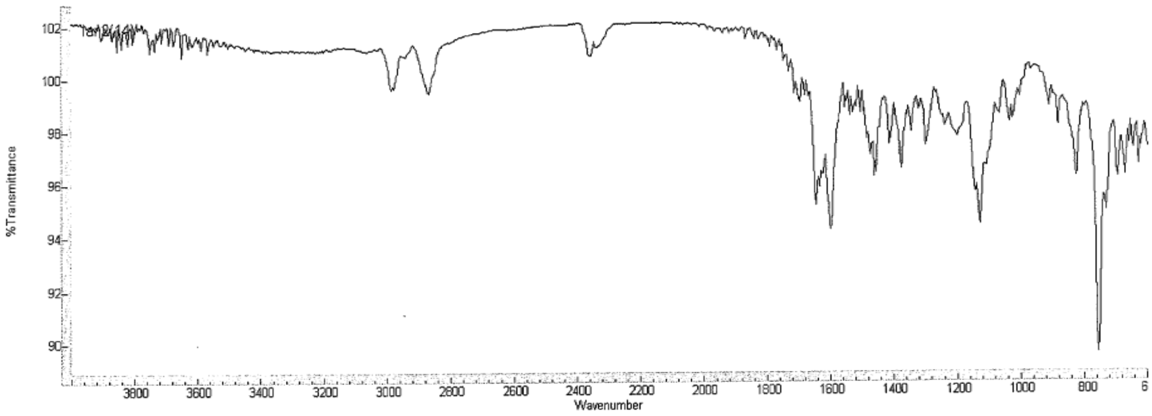
^{1}H-NMR



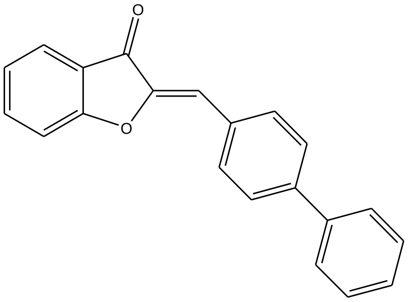
^{13}C-NMR


(thousandths)
0
10.0
20.0
30.0
40.0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0
X : parts per Million : 13C

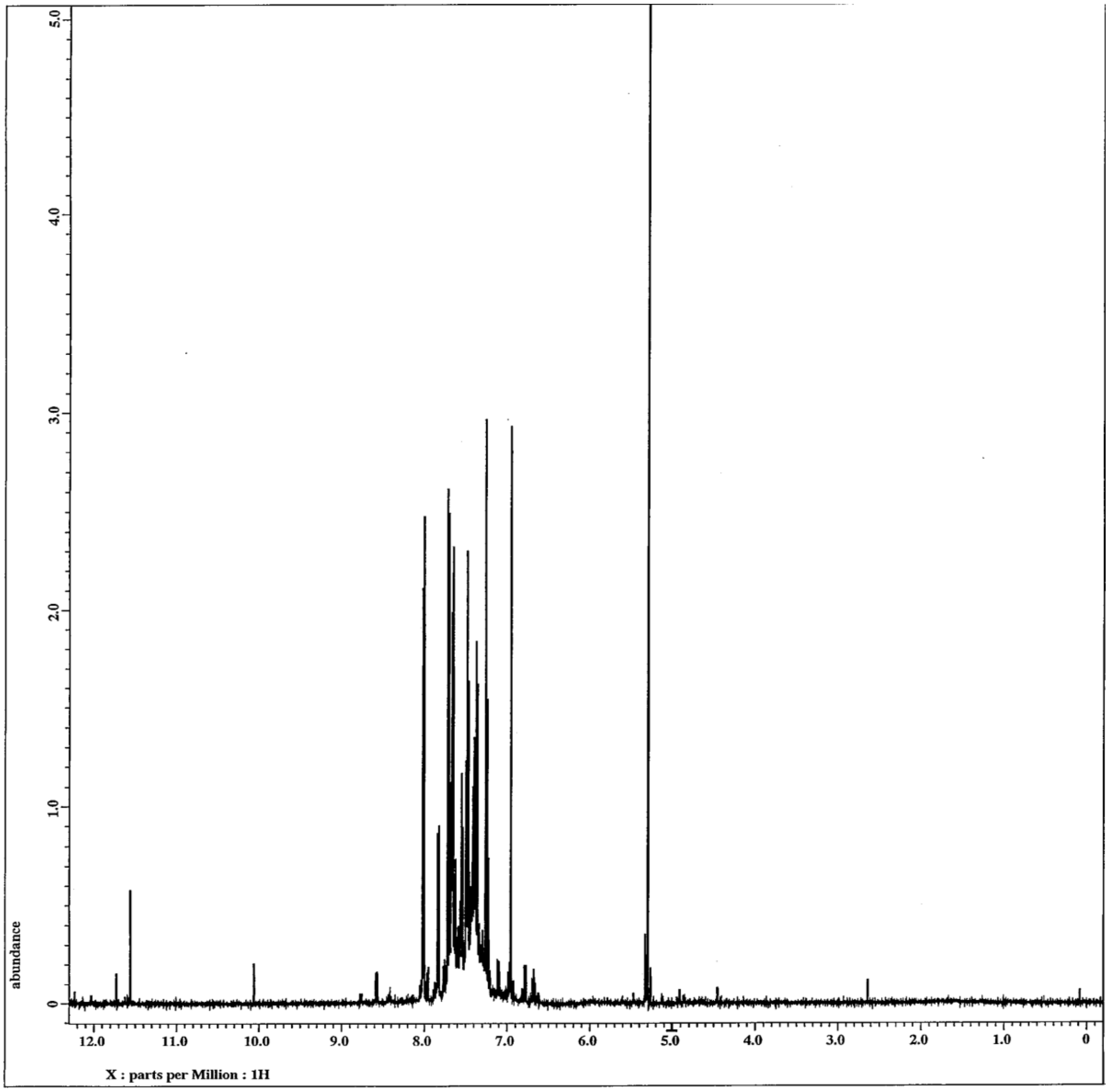
IR


%Transmittance
102
100
98
96
94
92
90
3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 6
Wavenumber

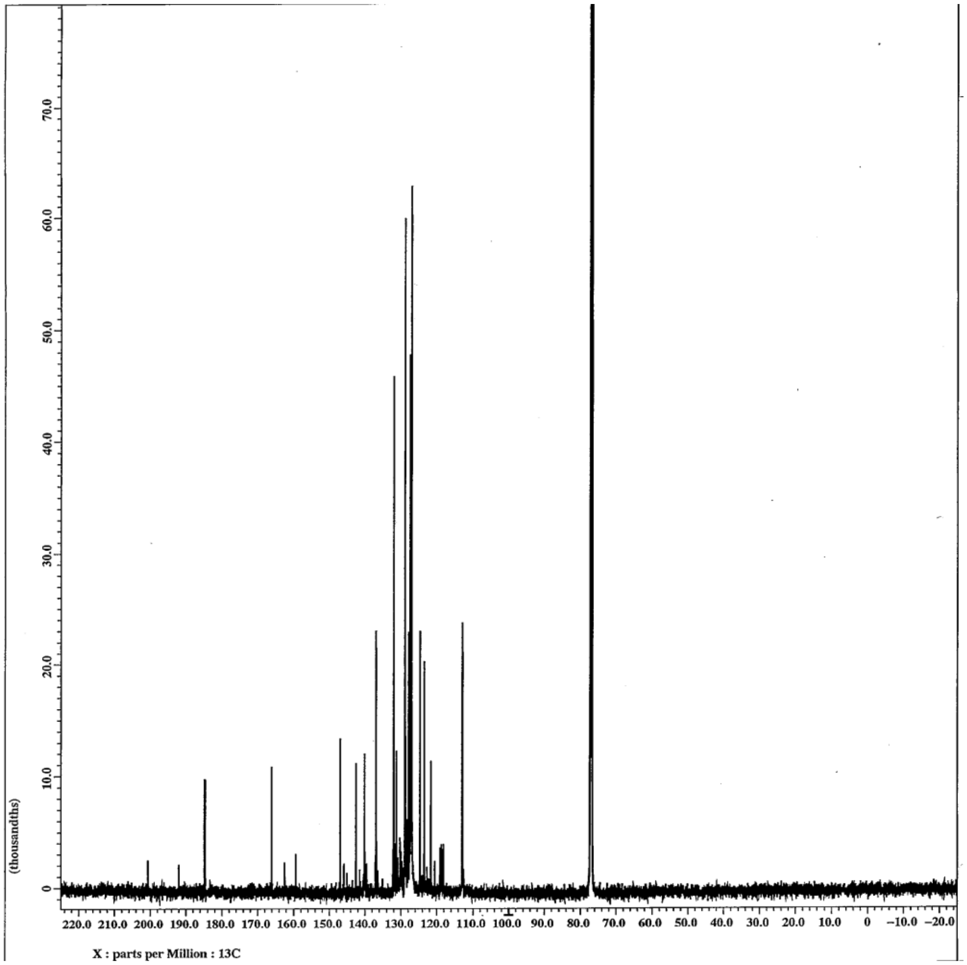
11. (Z)-2-(biphenyl-4-ylmethylene)benzofuran-3(2H)-one



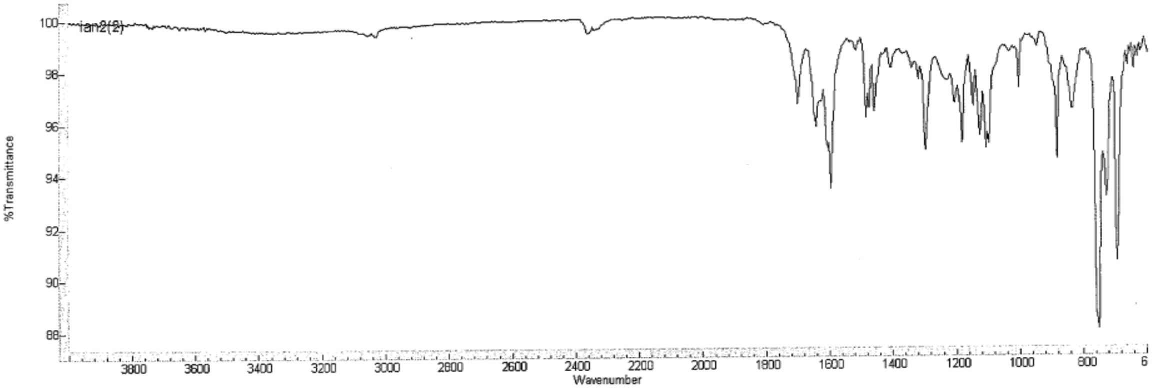
^{1}H-NMR



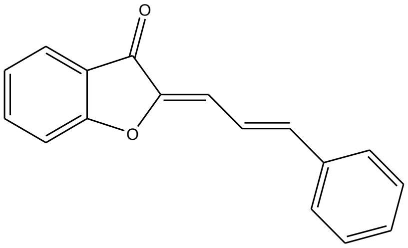
^{13}C-NMR


(thousandths)
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0
X : parts per Million : 13C

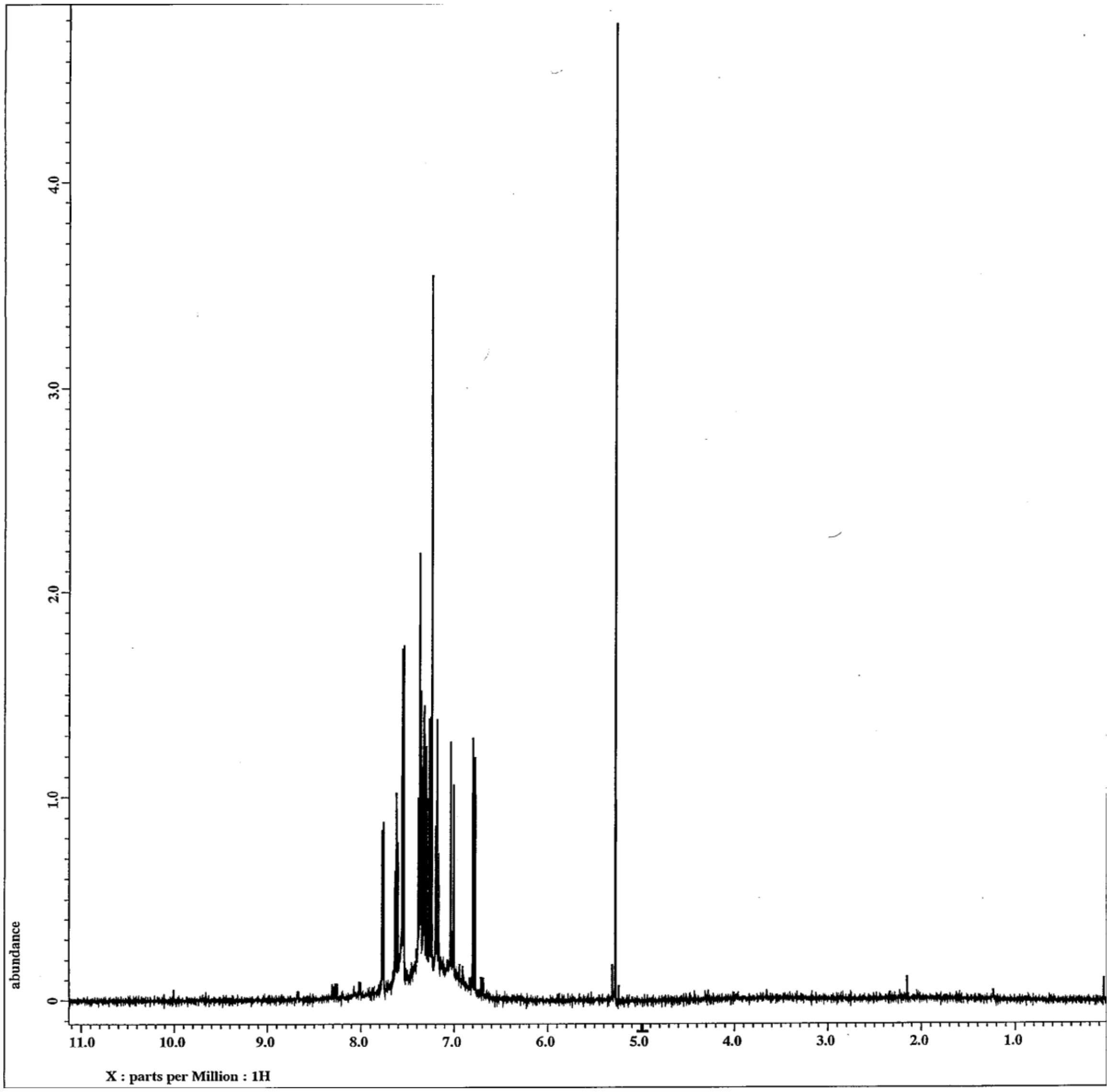
IR


Ian2(2)
%Transmittance
100
98
96
94
92
90
88
3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 6
Wavenumber

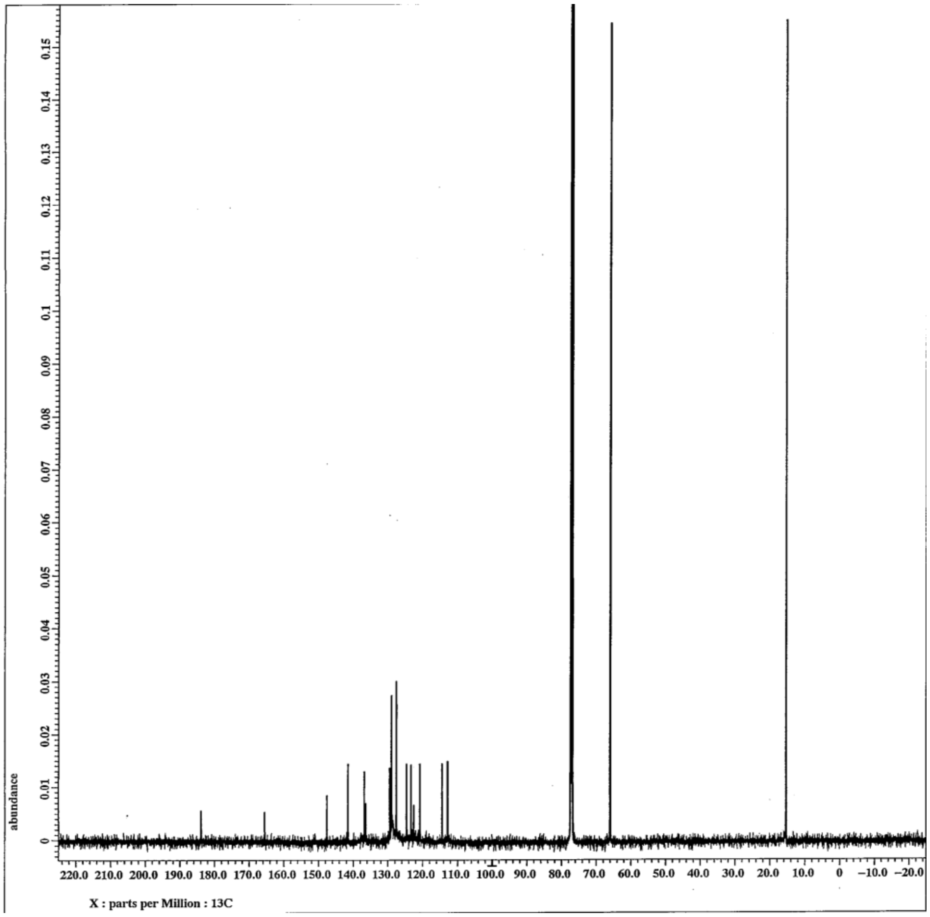
12. (Z)-2-((E)-3-phenylallylidene)benzofuran-3(2H)-one



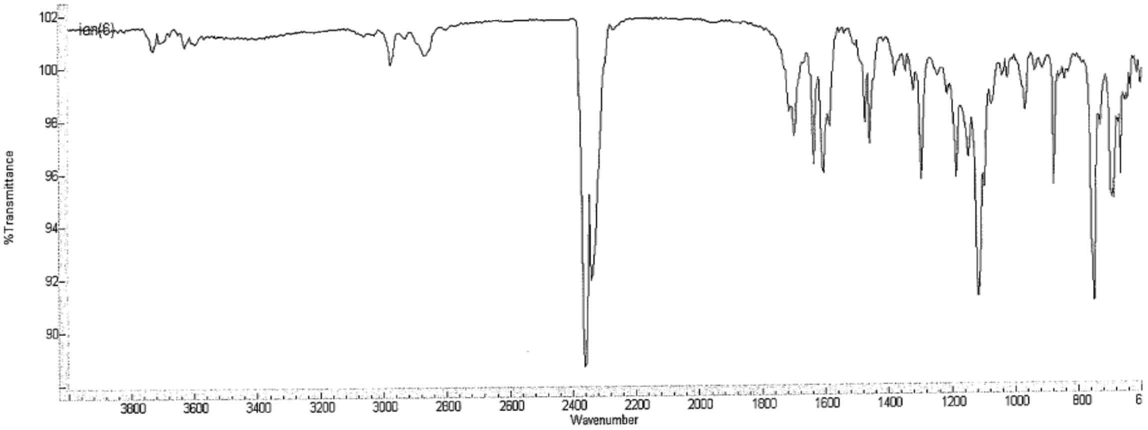
^{1}H-NMR



^{13}C-NMR


abundance
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
0.11
0.12
0.13
0.14
0.15
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0
X : parts per Million : 13C

IR


ian(6)
%Transmittance
102
100
98
96
94
92
90
3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 6
Wavenumber

Appendix E: IRB Approval Letter

MIDDLE TENNESSEE
STATE UNIVERSITY

February 29, 2012

Ian Hawkins, Dr. Amy Phelps
Department of Chemistry
ich2c@mtmail.mtsu.edu, Amy.Phelps@mtsu.edu

Protocol Title: "The Use of Virtual Labs in General Chemistry"

Protocol #: 11-207

Dear Investigator(s),
I have reviewed your research proposal identified above and your request for continuation. Approval for continuation is granted for three (3) years from the date of this letter.

You will need to submit an end-of-project report to the Office of Compliance upon completion of your research. Should the research not be complete by the expiration date, **February 29, 2015**, please submit a Progress Report for continued review prior to the expiration date.

According to MTSU Policy and Procedure, a researcher is defined as anyone who works with data or has contact with participants. Therefore, should **any individuals be added to the protocol that would constitute them as being a researcher, please identify them and provide their certificate of training to the Office of Compliance**. Any change to the protocol must be submitted to the IRB before implementing this change.

Please note that any unanticipated harms to subjects or adverse events must be reported to the Office of Compliance at (615) 494-8918.

Also, all research materials must be retained in a secure location by the PI or **faculty advisor (if the PI is a student) for at least three (3) years** after study completion. Should you have any questions or need additional information, please do not hesitate to contact me.

Sincerely,

Tyler Hubbard
Graduate Assistant to:
Emily Born
Compliance Officer
494-8918
eborn@mtsu.edu

Appendix F: Copyright Approval Letter for the Virtual Laboratory

WELCH
COLLEGE

Ian Hawkins <ihawkins@welch.edu>

Dissertation

Greenbowe, Thomas J [CHEM] <tgreenbo@iastate.edu> Tue, Jun 4, 2013 at 8:26 PM
To: Ian Hawkins <ihawkins@fwbbc.edu>

Ian,

Permission granted to use the simulations in your research project.

Thomas J. Greenbowe, Ph.D.
Professor of Chemistry
3051 Gilman Hall
Department of Chemistry
Iowa State University
Ames, IA 50011-3111
(515) 294-4050

From: Ian Hawkins [ihawkins@fwbbc.edu]
Sent: Tuesday, June 04, 2013 2:46 PM
To: tgreenbo@iastate.edu
Subject: Dissertation
[Quoted text hidden]