SYNTHESIS OF FERROCENYL QUINONES AND FERROCENYL BASED BURNING RATE CATALYSTS

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I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

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This is to certify that we have read this thesis and in our opinion it is full adequate, in scope and quality, as a thesis for the degree of Master of Science.

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ABSTRACT

SYNTHESIS OF FERROCENYL QUINONES AND FERROCENYL BASED BURNING RATE CATALYSTS

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Recently, considerable interest has been devoted to the synthesis of new ferrocene derivatives since properly functionalized ferrocene derivatives could be potential antitumor substances. For this purpose, we have investigated the synthesis of ferrocenyl quinones starting from squaric acid. Thermolysis of ferrocenyl-substituted cyclobutenones, which have been prepared from ferrocenyl cyclobutenediones and alkenyllithiums, affords hydroquinones, which furnish, upon oxidation, ferrocenyl quinones. Ferrocenyl cyclobutenediones have been prepared from known cyclobutenediones by nucleophilic addition of ferrocenyllithiumfollowed by hydrolysis, Pd/Cu-cocatalyzed cross-coupling with

(tri-n-butylstannyl)ferrocene or Friedel–Crafts alkylation with ferrocene. A mechanism involving electrocyclic ring opening of alkenyl substituted cyclobutenone to dienylketene and consequent electrocyclic ring closure to cyclohexadienone followed by enolization has been proposed to account for the formation of ferocenyl substituted hydroquinones.

Rocket design and production is one of the hottest topics in defense industry. On this subject, significant amount of investments have been done and excellent results were obtained. Among the burning rate catalysts for composite rocket propellants, ferrocene derivatives are one of the most famous ones. Although ferrocene derivatives are superior to some other burning rate catalysts, their use has some drawbacks arising from the tendency of migration in the bulk of the material and their sensitivity toward oxidation by air. With the aim of preventing the negative aspects of ferrocene derivatives, we have investigated the synthesis of EDA (ethylenediamine), TEP (tetraethylenepentamine) and DDI (dimeryl-diisocyanate) based ferrocene derivatives.

Keywords: Ferrocene, ferrocenyl quinone, cyclobutenedione, cyclobutenone, cyclobutenol, hydroquinone, electrocyclization, oxidation, burning rate catalyst, tetraethylenepentamine, dimeryldiisocyanate.

ÖZ

FERROSENİL KİNONLARIN VE FERROSEN BAZLI YANMA HIZI KATALİZÖRLERİNİN SENTEZİ

AÇIKALIN, SERDAR

Yüksek Lisans, Kimya Bölümü

Tez Yöneticisi: Doç. Dr. Metin Zora

Ağustos 2003, 105 sayfa

Uygun olarak işlevselleştirilmiş ferrosen türevlerinin potansiyel antitumor maddeler olduğunun bulunmasıyla yapılarında ferrosen birimi içeren maddelerin sentezi son yıllarda büyük önem kazanmıştır. Bu amaçla, ferrosenil kinonların sentezini skuarik asitten başlanarak incelenmiştir. Siklobütendionlar ve alkenillityumdan elde edilen ferrosenil sübstitüe siklobütenonların termolizi sonucu hidrokinonlar onların da yükseltgenmesiyle ferrosenil kinonlar elde edilmiştir. Ferrosenil siklobütendionlar bilinen siklobütendionların ferrosenlityumun nükleofilik eklenme ve hidroliz tepkimesi, Pd/Cu kokatalizörlüğünde (tri-n-butilkalay)ferrosen ile olan tepkimesi ve Friedel-Crafts alkilasyonu yöntemleriyle sentezlenmiştir. Ferrosenil sübstitüe hidrokinonun oluşumu alkenil sübstitüe

siklobütenonun dienilketen elektrosiklik halka açılması ve ardışık elektrosiklik halka kapanmasıyla oluşan siklohekzadienonun enolizasyonu ile açıklanmıştır.

Roket tasarımı ve üretimi savunma sanayisinin en güncel araştırma konularını teşkil etmektedir. Bu konuda büyük yatırımlar yapılmış ve önemli başarılar elde edilmiştir. Kompozit roket yakıtları için kullanılan yanma hızı katalizörleri arasında ferrosen türevleri en tanınmış olanlarındandır. Ferrosen türevleri birçok yanma hızı katalizörüne üstünlük sağlasa da, yakıt içerisinde yüzeye doğru göçe uğramaları ve havaya duyarlılıkları nedeniyle pek uygulama bulamamışlardır. Ferrosen türevlerinin bu olumsuz yönlerinin giderilmesi amacıyla, EDA (etilendiamin), TEP (tetraetilenpentamin) ve DDI (dimeril-diizosiyanat) bazlı ferrosen türevlerinin sentezleri incelenmiştir.

Anahtar Kelimeler: Ferrosen, ferrosenil kinon, siklobütendion, siklobütenon, siklobütenol, hidrokinon, electrocyclization, yükseltgenme, yanma hızı katalizörü, tetraetilenpentamin, dimeril-diizosiyanat.

Aileme,

To My Family,

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LIST OF ABBREVIATIONS

bp	boiling point
br	broad (spectral)
Bu	butyl
°C	degrees Celcius
Cp	cyclopentadienyl ligand
δ	chemical shift in parts per million downfield from tetramethylsilane
d	doublet (spectral)
Et	ethyl
FT	fourier transform
g	gram(s)
h	hour(s)
Hz	hertz
IR	infrared
i-Pr	isopropyl
J	coupling constant
m	multiplet (spectral)
mL	milliliter(s)
MHz	megahertz

min	minutes
mmol	millimole(s)
mp	melting point
NMR	nuclear magnetic resonance
Ph	phenyl
ppm	parts per million (in NMR)
Pr	propyl
q	quartet (spectral)
R_f	retention factor (in chromatography)
rt	room temperature
s	singlet (spectral)
t	triplet (spectral)
THF	tetrahydrofuran
TLC	thin layer chromatography
EDA	ethylenediamine
TEP	tetraethylenepentamine
DDI	dimeryl-diisocyanate

CHAPTER 1

INTRODUCTION

1.1. Synthesis of Ferrocenyl Quinones

One of the most attractive research areas in chemistry for recent years has involved studying the compounds which possess direct, more or less polar bonds between metal and carbon atoms. The field of organometallic chemistry combines aspects of classical organic chemistry and inorganic chemistry and has led to many important applications in synthetic community [1, 2].

Today a number of important industrial processes are fulfilled by the assistance of organometallic chemistry. Some of these processes are Wilkinson hydrogenation [3], Monsanto's acetic acid process [4], Ziegler-Natta polymerization [5], Wacker process [6], asymmetric hydrogenation [7] and many others [8]. Of course, catalytic processes are not the only contribution of organometallic chemistry to synthetic community and quality of life. The field has added powerful synthetic

methods in organic chemistry, too. In particular, metal carbene complexes are recognized as valuable reagents in organic synthesis since discovered by E. O. Fischer in 1964 [9]. Their importance is increasing with time because they are not only suitable as carbene-transfer agents but also undergo interesting cycloaddition reactions, producing a diverse array of compounds. For example, K. H. Dötz synthesized naphtyl compounds by the reaction of methoxy phenyl Fisher carbenes with an alkyne [10] (Figure 1). In the Dötz reaction, ten carbon atoms in the naphthalene ring is contributed by a CO ligand (1 atom), carbene ligand (7 atom), and acetylene reagent (2 atoms).

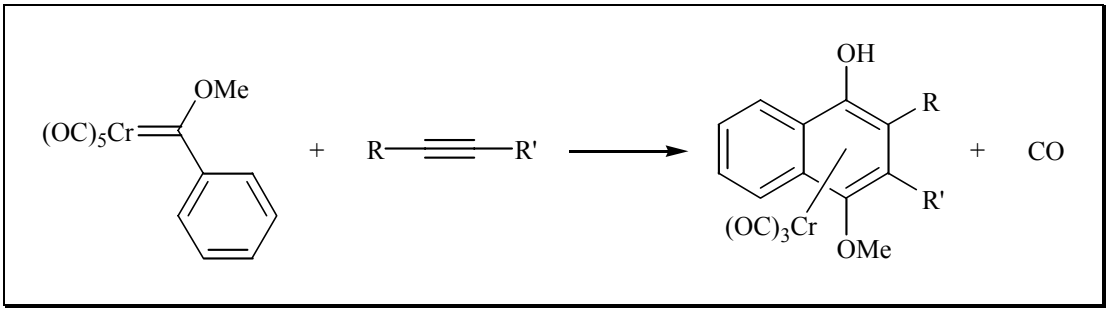


Figure 1. A representative example of Dötz reaction

Chemistry is increasingly influenced by biology as a result of advances in our understanding of the chemical basis of life [11]. Therefore, organometallic chemistry is beginning to make links with biochemistry. Now, it is clear that organometallic species also occur in biology, both as stable species and reaction intermediates. Nature uses organometallic chemistry sparingly, but it has been suggested that the examples known are relics from early life forms, which had to

live on simple molecules, such as H_2, CO, and CH_4 and may have used organometallic chemistry more extensively.

Biochemical reactions have to be kept under strict control. They must only happen as they are required, where they are required. One way of doing this is to employ reactions that can only happen when catalyzed. The catalysts of biology are called enzymes. More than half of the enzymes have metal ions in their structure. These are called metalloenzymes. Hence, metals have important roles in biological systems including energy storage and release, oxygen transport and storage, hydrolytic enzyme action, electron transfer, selective oxidation of carbon-hydrogen bonds, nitrogen fixation, and photosynthesis [12]. For many years biology and organometallic chemistry are viewed as two mutually separate fields of research. Most organometallic compounds are thought to be inherently sensitive to water and oxygen, which are substances essential for biology. However, as researchers went deeper into organometallic chemistry, they began to realize that much of this field is compatible with biology. The discovery that certain inorganic complexes such as *cis*-platin are effective against testicular cancer has led to increase in research on metal complexes as drugs [13].

Metallocenes are organometallic compounds which consist of a metal between two planar polyhapto rings [14]. They are informally called “sandwich compounds”. One of the ligands encountered in metallocenes is cyclopentadienyl. The cyclopentadienyl ligand (C_5H_5) has played a major role in the development of

organometallic chemistry and a huge number of metal cyclopentadienyl compounds are known today.

Ferrocene (**1**), an orange crystalline and diamagnetic solid, is one of the well-known and most popular organometallic compounds [15]. The sandwich structure of Cp_2Fe was discovered by G. Wilkinson, R. B. Woodward and E. O. Fischer independently [16]. They suggested a "double cone" structure with all five carbon atom of a cyclopentadienyl ligand interacting with the metal centre. In 1973, Wilkinson and Fischer were awarded the Nobel Prize for the subsequent synthesis of ferrocene (**1**) and its further complexes. With its 18 valance electrons, ferrocene is the most stable member of the metallocene series. It sublimes readily and is not attacked by air or water, but can be oxidized reversibly [17]. It undergoes Friedel-Crafts acylation and alkylation, mercuration and Vilsmeier formylation [18]. Ferrocene derivatives containing asymmetric substituents are used as ligands for asymmetric hydrogenation catalysts [19]. Some basic reactions of ferrocene are shown in Figure 2.

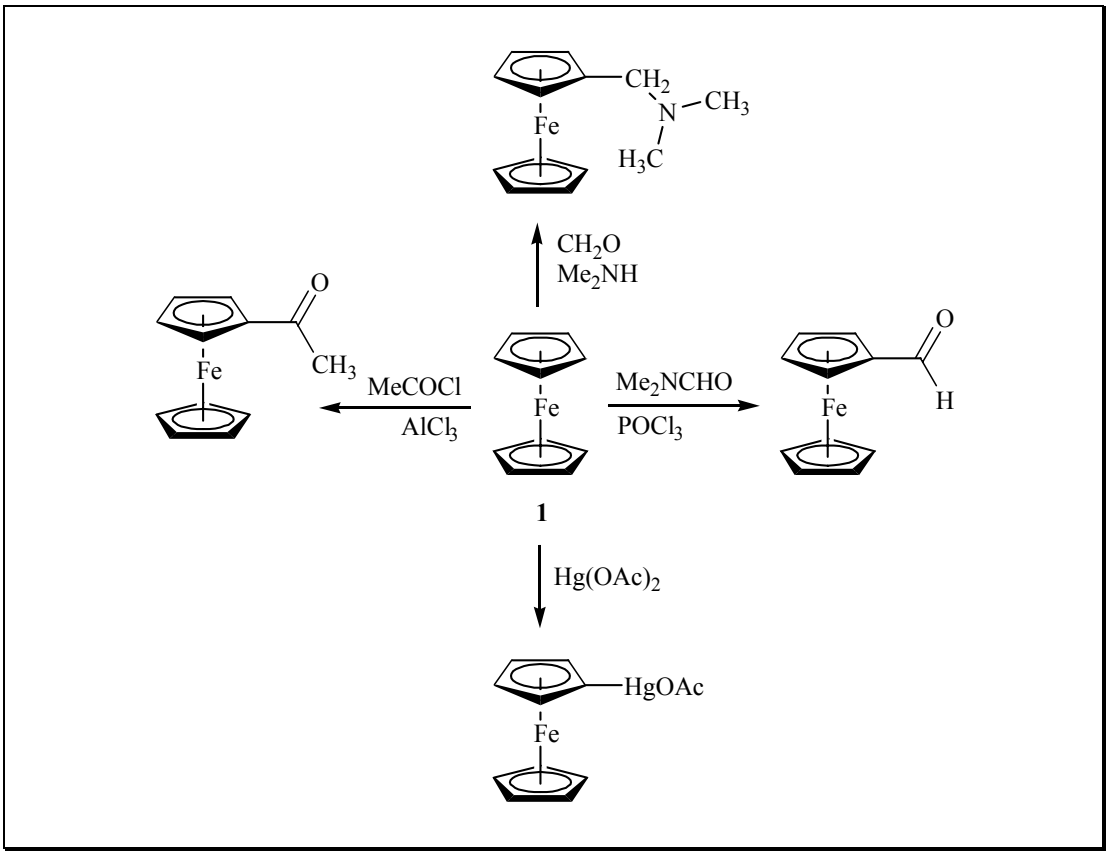


Figure 2. Typical electrophilic substitution reactions of ferrocene

Ferrocene (**1**) does not show any biological activity even if it is solubilized in water using heptakis(2,6-di-*O*-methyl)-β-cyclodextrin (dmβ-CD) [20]. There are some other methods in the literature to overcome the water solubility problem of ferrocene derivatives. As depicted in the Figure 3, first method is to create a salt form on the organic residue of ferrocene moiety and the second one is to form salt through oxidation of central iron atom. It has been reported that ferrocenium salts are exhibiting antitumor activity against number of tumors [21]. Although they have excellent solubility in water because of their ionic character, the inhibitory effect of ferrocenium salts **4** is independent of water solubility (Figure 4) . Their antitumor

activity is shown to be related to the oxidation state of the central iron atom of the ferrocene moiety, not the water solubility. Studies showed that only the ferrocenium salts, in which the central iron atoms have the oxidation state +3 (in ferrocenium cations) exhibit tumor inhibitory effects [20].

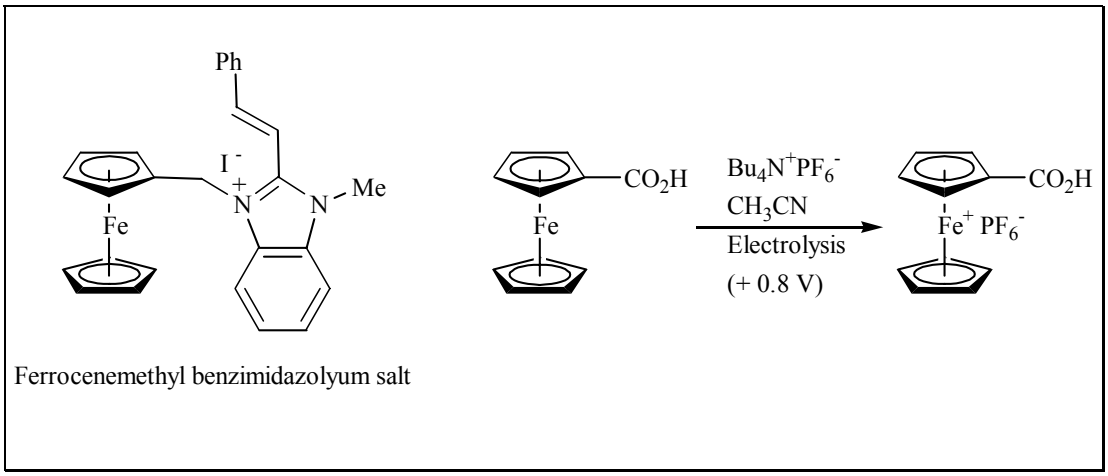


Figure 3. Ferrocenium salt formation

Tamoxifen (**2**) exhibits antitumor activity against breast cancer cells that are mediated by ER_α estrogen receptors (Figure 4) [22]. However, it is not effective on cancer cells that are mediated by ER_β estrogen receptors. In 2002, Jaouen and coworkers have investigated tamoxifen analogs that contain an organometallic moiety. When the phenyl group, which is geminal to ethyl group in tamoxifen (**2**), is replaced by ferrocenyl group, resulting ferrocifens (**3**) exhibited a strong effect against breast cancer cells that are mediated by both ER_α and ER_β estrogen receptors [23].

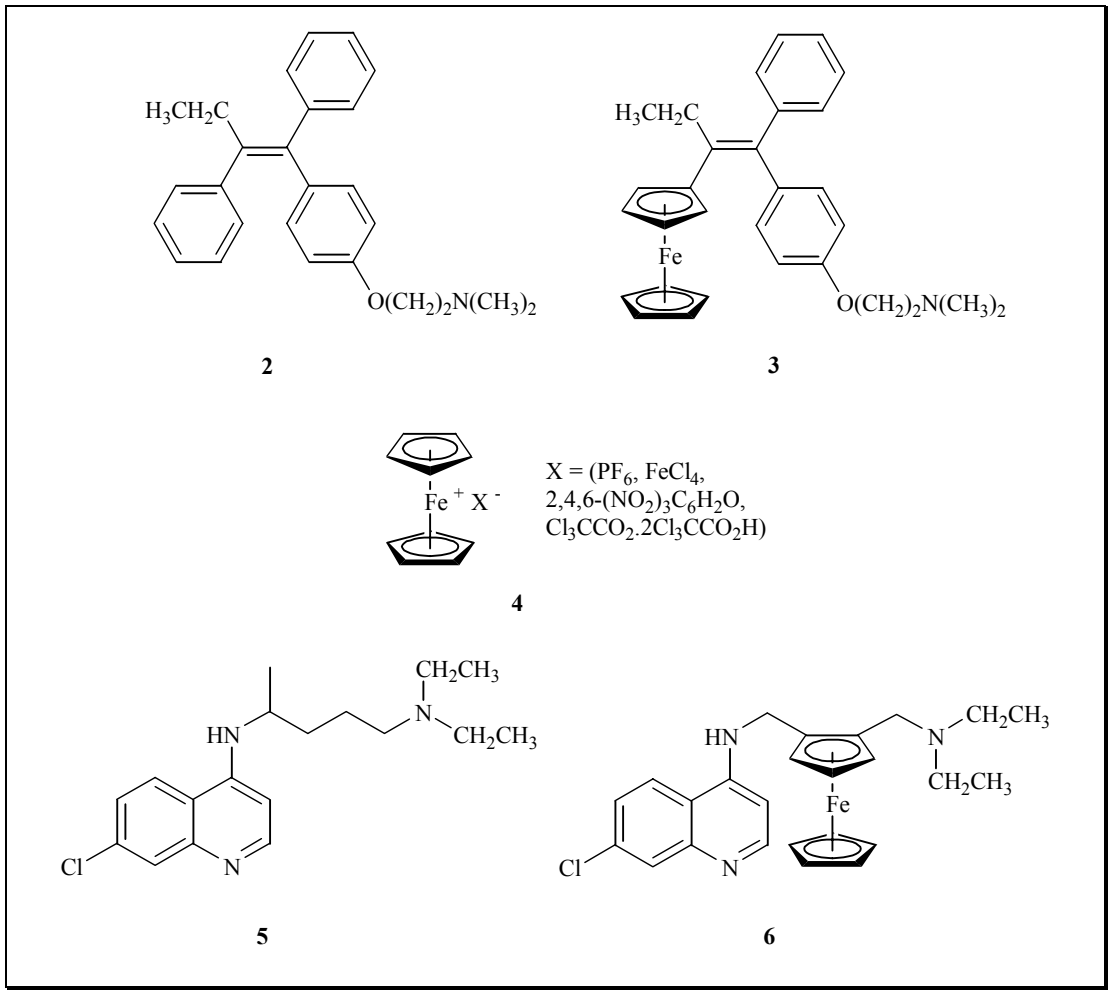


Figure 4. Some biologically active compounds

Cancers are not the only diseases that might be treatable using organometallic pharmaceuticals. Several drugs, such as chloroquine (**5**), are used against malaria parasite (Figure 4). Unfortunately, resistance to these drugs is increasing [24]. Brocard and coworkers inserted a ferrocenyl group into the side chain of the chloroquine (**5**), thus producing a hybrid compound called ferroquine (**6**) [25]. It is reported that ferroquine (**6**) is much more safe and effective in mice, as well as non-mutagenic [26].

Although ferrocene and its derivatives have found application in number of areas, the most notable of which are material chemistry and asymmetric catalysis [27, 28], relatively few studies on the biological properties of molecules bearing ferrocene moiety have been reported [29].

Quinones are important class of compounds in industry (*e.g.* anthraquinone dye-stuff), in organic synthesis as dehydrogenating agents, and in nature, where they have a vital role in electron transport in the respiratory and photosynthetic elements of biological systems. It is apparent that quinones play a variety of roles in our life cycle and that interest in their biological function has stimulated basic chemical research in several areas [30]. The use of quinones, in fact, dates to antiquity and the recorded and verifiable history of these compounds is perhaps longer than that of any other group of naturally occurring compounds [31]. Widely distributed in both plants and animals, quinones are important class of naturally occurring compounds, some of which are vitamin K_2 [32], danshexinkun A [33], daunomycinone [34], saframycin B [35], etc. Since many years *p*-benzoquinones (1,4-benzoquinones) are recognized as one of the most important class of compounds possessing a wide range of biological activities. For this reason, several methodologies have been developed for the construction of *p*-benzoquinone skeleton.

Quinones are easily prepared by oxidation of activated arenes. The activation normally arises from a hydroxyl, alkoxy or amino group [31]. Teuber reaction, which uses Fermy's salt (potassium nitrodisulfonate) as oxidizing reagent, has been one of the most widely used method since it gives good to excellent yields and

proceeds under mild conditions [36]. For example, monohydric phenols or aromatic amines are oxidized rapidly using two equivalents of the reagent in aqueous alcohol or acetone, buffered with phosphate or acetate (Figure 5) [37]. Teuber reaction is especially useful for the synthesis of heterocyclic quinones, where other oxidizing reagents fail [38].

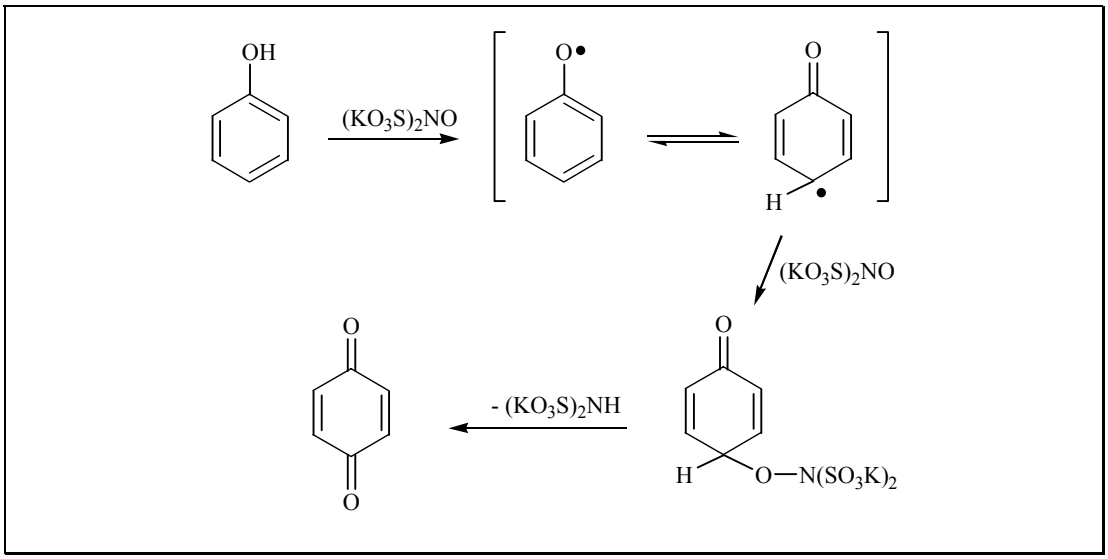


Figure 5. Mechanism of Teuber reaction

Cerium (IV) ammonium nitrate (CAN) is another oxidizing agent that has been used in the synthesis of quinones, particularly as a means of effecting oxidative demethylation of methoxyarenes [39]. Hart and Huang employed CAN oxidation in the penultimate step in their synthesis of pleurotin, an antitumor antibiotic (Figure 6) [40].

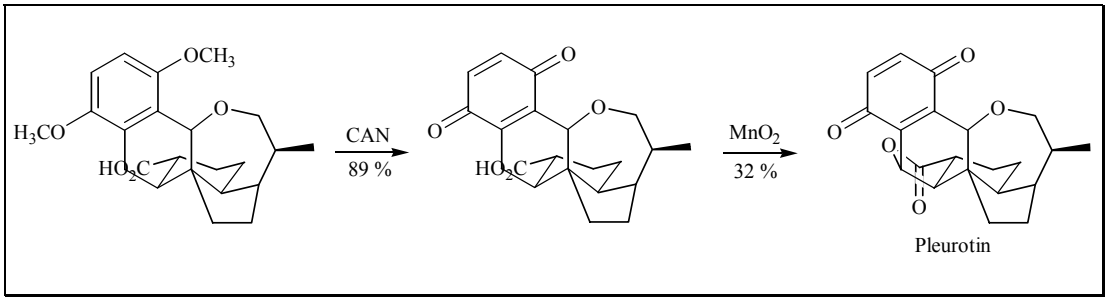


Figure 6. Synthesis of pleurotin

Hydroquinones can be easily oxidized to quinones in air if it is sufficiently activated towards oxidation [41]. An example of this is reported by Kelly et. al. in a short synthesis of diazaquinomycin A (Figure 7) [42]. Stirring the solution of diazaquinomycin B in an open flask affords the antibiotic diazaquinomycin A.

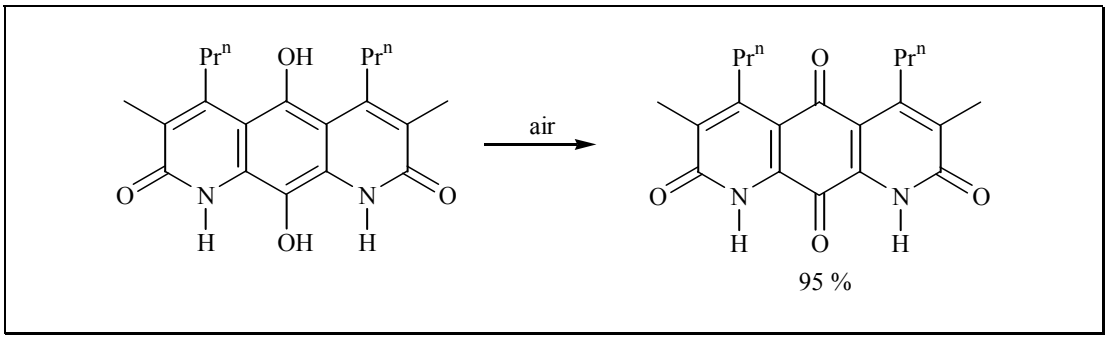


Figure 7. Air oxidation of diazaquinomycin B

There are numerous other examples of the synthesis of quinones employing reagents such as nitric acid [43], manganese oxide [44], salcomine/O_2 [45], silver oxide [46], chromium oxidants [47], benzene selenic anhydride [48] and DDQ [49].

An electrochemical method for the formation of quinones is the anodic oxidation of phenol derivatives. An example is shown in Figure 8 [50].

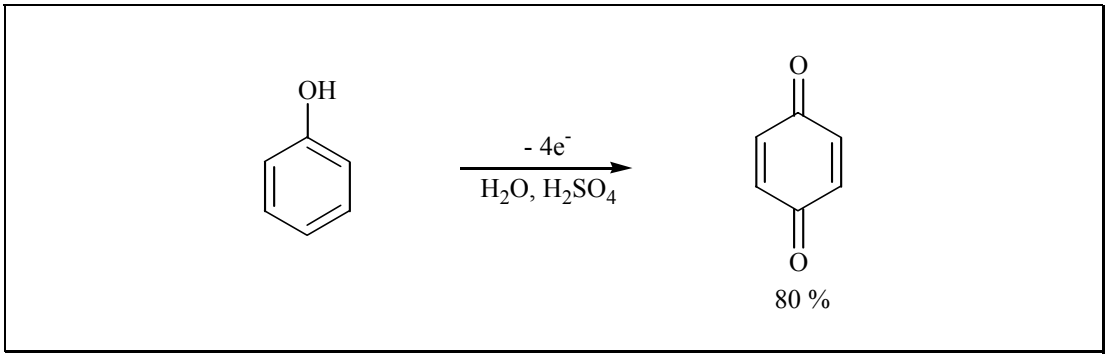


Figure 8. Electrochemical synthesis of quinones

Danheiser and coworkers employed vinylketene/alkyne cycloaddition reaction for quinone synthesis [51]. The sequence of the quinone transformation using vinylketene/alkyne cycloaddition starts with the irradiation of α,β-unsaturated α'-diazo ketone **7** (Figure 9). This generates a photochemical Wolff rearrangement which produces the vinylketene **8**. This then undergoes cycloaddition to the alkyne **9** to give cyclobutenone **10**. Electrocyclic ring opening of **10** gives the dienyl ketene **11**, which then undergoes six-electron electrocyclization followed by enolization to yield in phenol **12**. Oxidation subsequently furnishes corresponding quinone **13**.

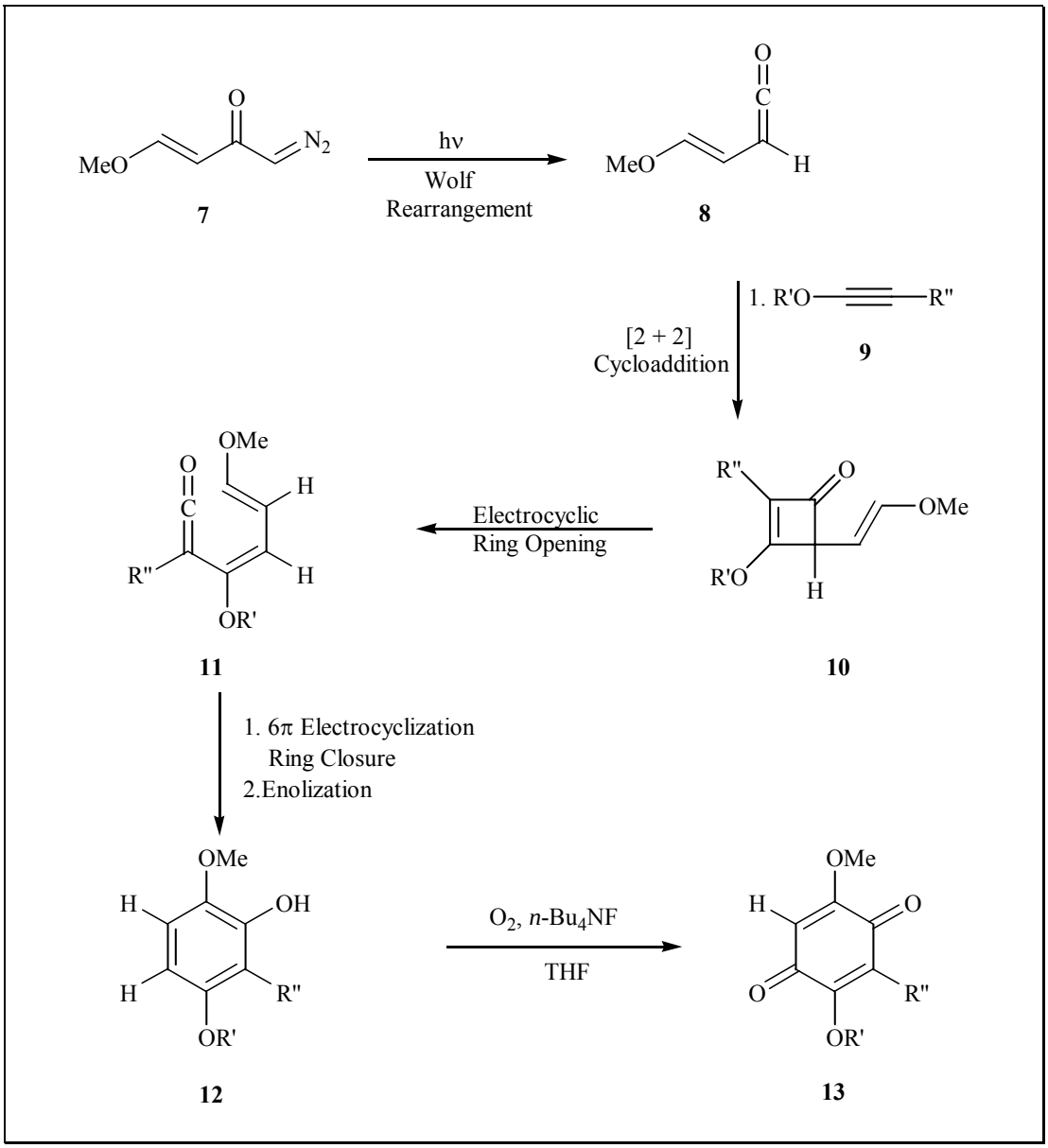


Figure 9. Quinone transformation using vinylketene/alkyne cycloaddition reaction

Quinones and their metal complexes were first isolated among the many products of the reaction of metal carbonyls and alkynes. Industrial development of metal catalyzed reactions of ethyne, CO and water using high pressures and temperatures produced hydroquinone in up to 70 % yield (Figure 10) [52]. An intermediate in this chemistry is maleoyl complex **14**.

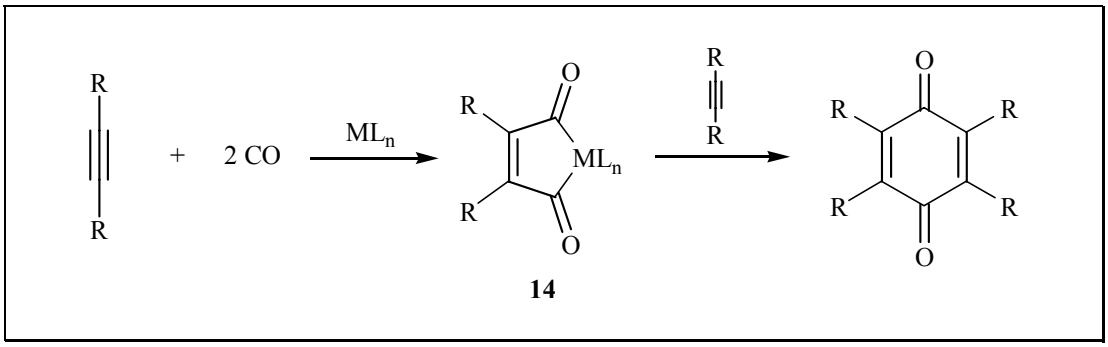


Figure 10. Metal catalyzed synthesis of quinones through maleoyl complex

However, a general synthesis of complicated quinone derivatives from alkynes was not possible until Liebeskind and coworkers found a controllable, alternative route to structures of type **14** and phthaloyl analogues **17** (Figure 11) [53].

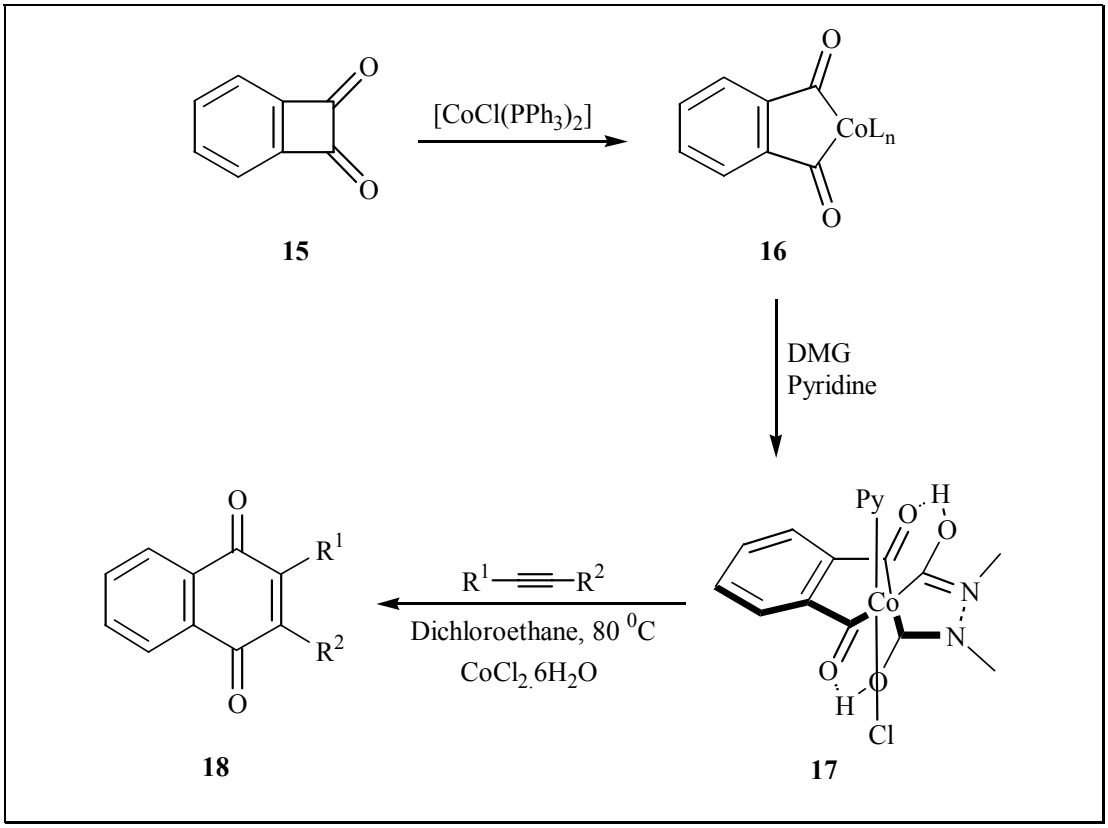


Figure 11. Transition metal catalyzed synthesis of naphtaquinones

Benzocyclobutenedione (**15**) reacts with the low valent cobalt complex $[CoCl(PPh_3)_2]$ to form phthaloylcobalt complex **16**. Subsequent treatment of **16** with one equivalent of dimethylglyoxime (DMG) in pyridine provides the dimethylglyoxime variant **17**. From the cobalt complex **17** naphtaquinones **18** are prepared simply by heating the complex **17** to 80 ^{0}C in the presence of an alkyne and a mild Lewis acid such as $CoCl_2.6H_2O$.

Similarly, benzoquinones are obtained from cyclobutenedione derivatives (Figure 12). Effective reaction rates can be achieved at room temperature in the presence of a strong Lewis acid such as $SnCl_4$ or $Zn(OSO_2CF_3)_2$ [54].

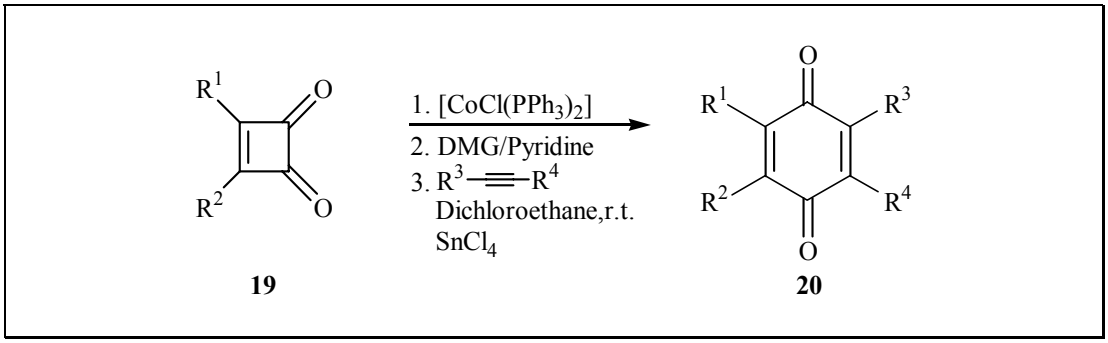


Figure 12. Transition metal catalyzed synthesis of quinones

Nanaomycin A (**22**), an antibiotic pyranonaphtaquinone, has been synthesized *via* this route starting from **21** (Figure 13) [55]. This method has also been applied to the synthesis of royleanone (**23**), an antitumor cytotoxicity, in which the highly substituted quinone skeleton has been efficiently constructed by using a maleoylcobalt complex **14** derivative [56].

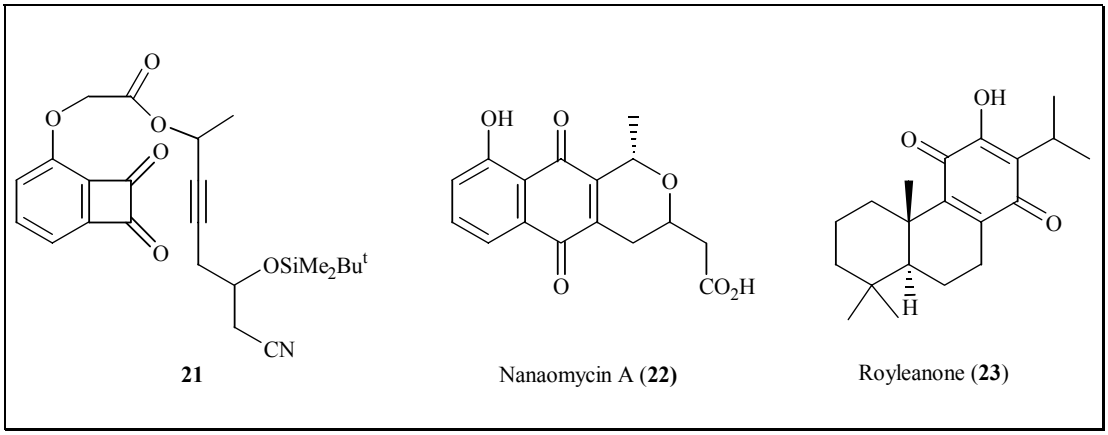


Figure 13. Some applications of transition metal catalyzed reactions of cyclobutenedione derivatives

In addition to conversion of cyclobutenediones to quinone products by transition metal catalyst, there is an electrocyclic pathway to quinones which employs cyclobutenones bearing an sp- or sp^2-carbon at the fourth position. 4-vinyl- and 4-alkynyl-cyclobutenones **24** and **27** having a hydroxyl group at the C-4 position furnishes quinones **26** or **29** upon thermolysis (Figure 14) [57]. Extension of this approach to 4-aryl (or heteroaryl) cyclobutenones **30** provides the synthesis of highly substituted quinones of general structure **32** and **34** [58].

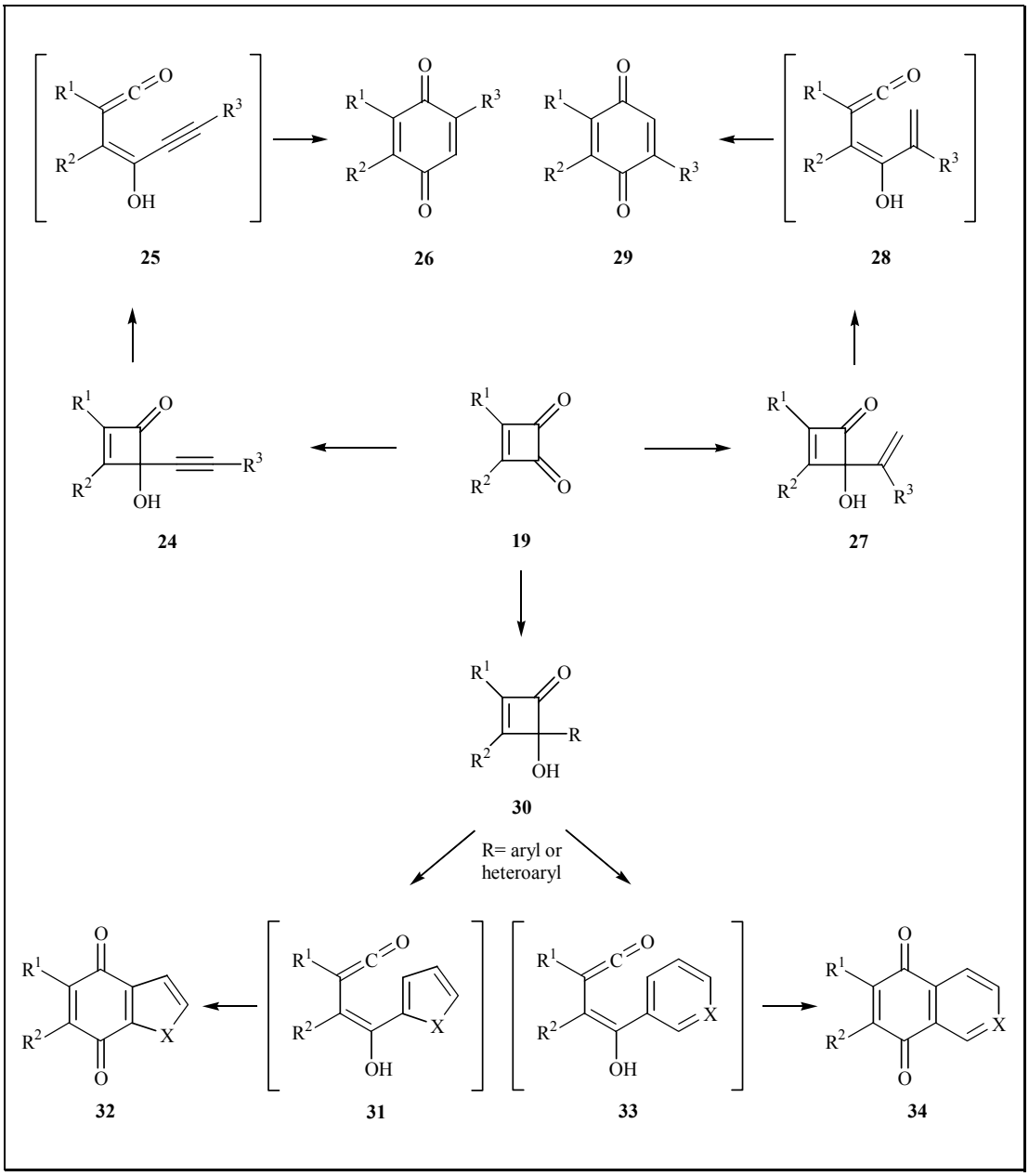


Figure 14. Transformations of cylobutenones into quinone

Among the rearrangements of cyclobutenones bearing an unsaturated substituent at the 4-position, mechanistically the most interesting one is the ring expansion of 4-alkynyl-4-hydroxycyclobutenones **24** to benzoquinones **26**. These are unique reactions since the intermediate enynylketens **25** undergo ring closure to previously unknown diradical intermediate **35**. These proceed to their corresponding quinones **26** via a process involving migration of the group on the oxygen (Figure 15).

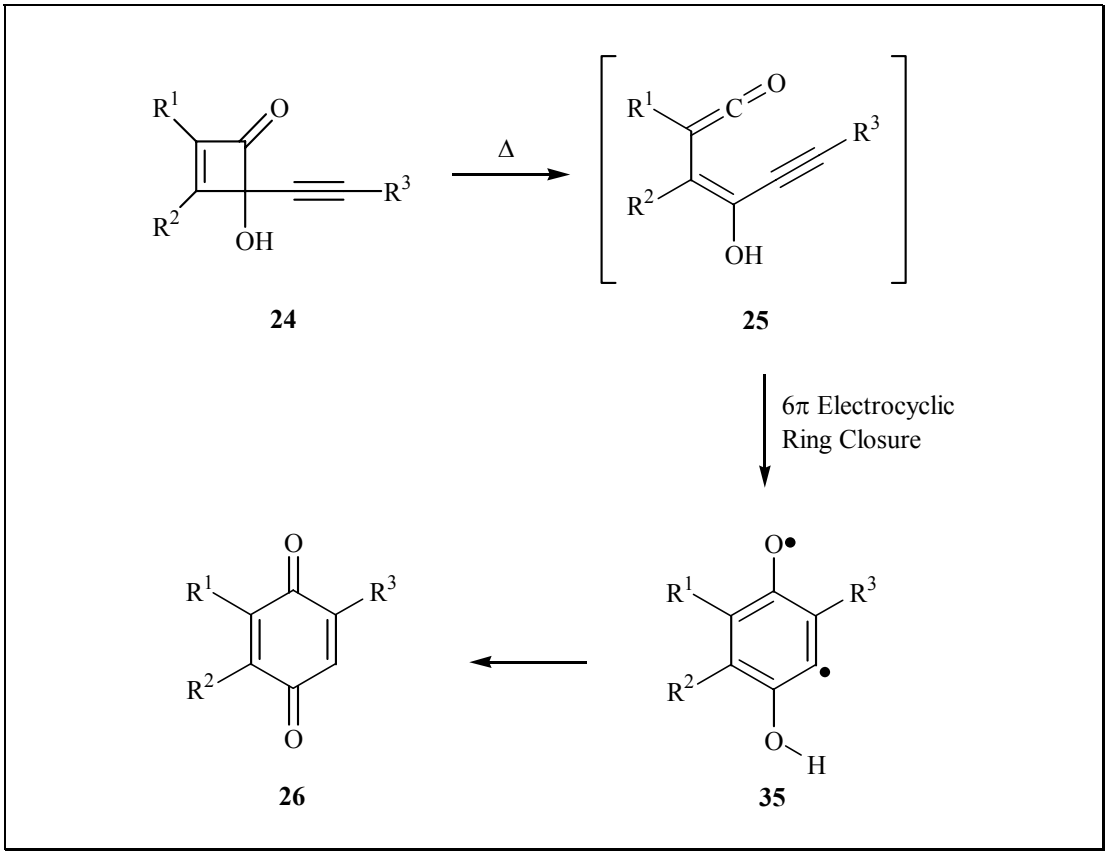


Figure 15. Mechanism of the transformation of 4-alkynylcyclobutenone into quinone upon thermolysis

The 4-alkenyl-4-hydroxycyclobutenones, like their 4-akynyl analogs, have also been shown to be versatile precursors to substituted quinone products [59]. The transformation of 4-alkenyl-4-hydroxycyclobutenone **27** into quinone **29** involves the ring expansion of cyclobutenone **27** to hydroquinone **37** (Figure 16). The cyclobutenones, obtained either by addition of alkenyl lithiums to cyclobutenediones **19** or [2 + 2] cycloaddition of vinyleketene/alkyne couple (Figure 9), undergo an electrocyclic ring opening upon thermolysis to form the dienylketenes **28**. These ketenes then undergo electrocyclic ring closure to generate cyclohexadienone **36**. The subsequent enolization gives the hydroquinone **37**, which can be easily converted into corresponding **29** upon oxidation.

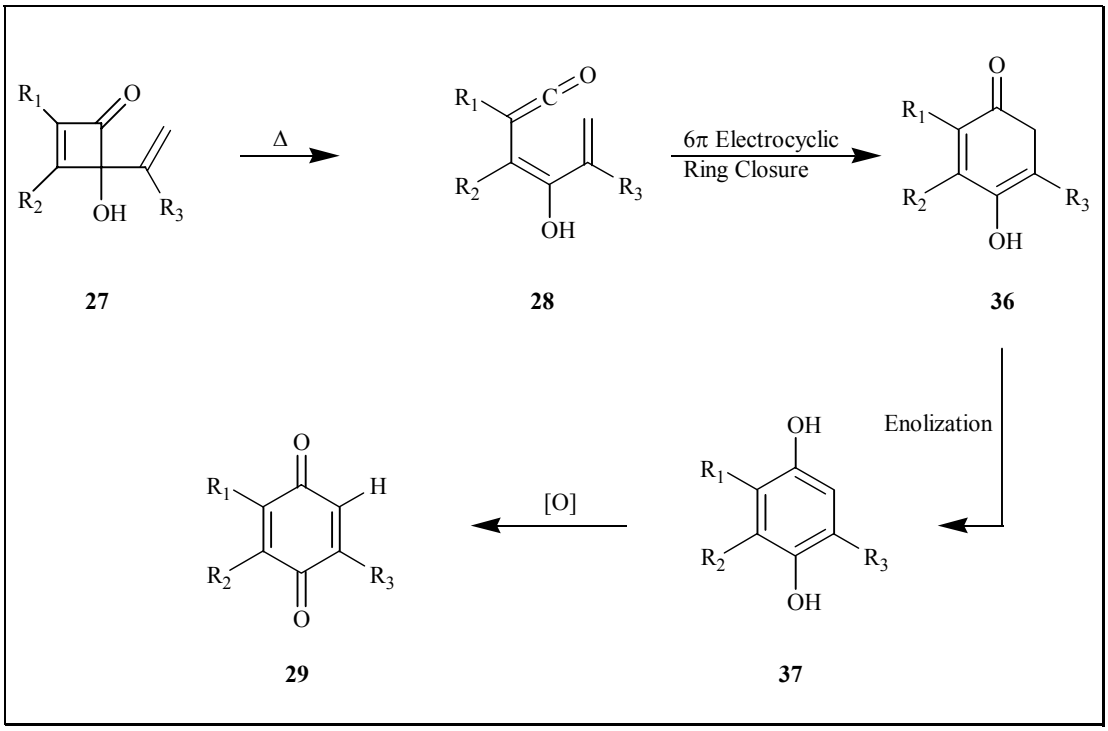


Figure 16. Transformation of 4-akenyl-4-hydroxycyclobutenone into quinone product upon thermolysis

Important complimentary regiochemical control for the synthesis of quinones is apparent when the ring expansions of 4-akynyl- and 4-alkenyl-4-hydroxycyclobutenones are compared (Figure 14) [60]. Cyclobutenedione **19** can be converted to **24** and **27** upon treatment with the respective alkynyl and alkenyl lithium reagents. Ring expansion of the later followed by oxidative workup gives the quinone **29** while the former gives the regio isomer **26** directly upon thermolysis.

While squaric acid (**38**) has unique characteristics [61] and has been applied for advanced materials [60], it has also received much attention from the synthetic point of view as a precursor of substituted cyclobutenones and cyclobutenediones, which can be transformed into important ring systems [57, 63] such as; quinone [53, 64], phenol [64], cyclopentendione [65], butenolide [66], polyquinane [67], and various heterocycles [68]. In order to perform such transformations generally and efficiently, selective and viable derivatization of squaric acid is a prerequisite. Therefore, a number of feasible methods were established based on the 1,2-addition of organolithiums [69] and palladium-catalyzed cross coupling of organotins [70].

Cyclobutenediones can be prepared from squaric acid with known literature procedures [67a,b]. The synthetic sequences are shown in the Figures 17 and 18. Basically, cyclobutenediones are obtained by treating diisopropyl squarate (**39**), a crystalline ester of squaric acid, with organolithium nucleophiles followed by hydrolysis with HCl, as depicted in Figure 17. Standard acid catalyzed hydrolysis allows the isopropyl group of **40** to be replaced with an alkyl substituent.

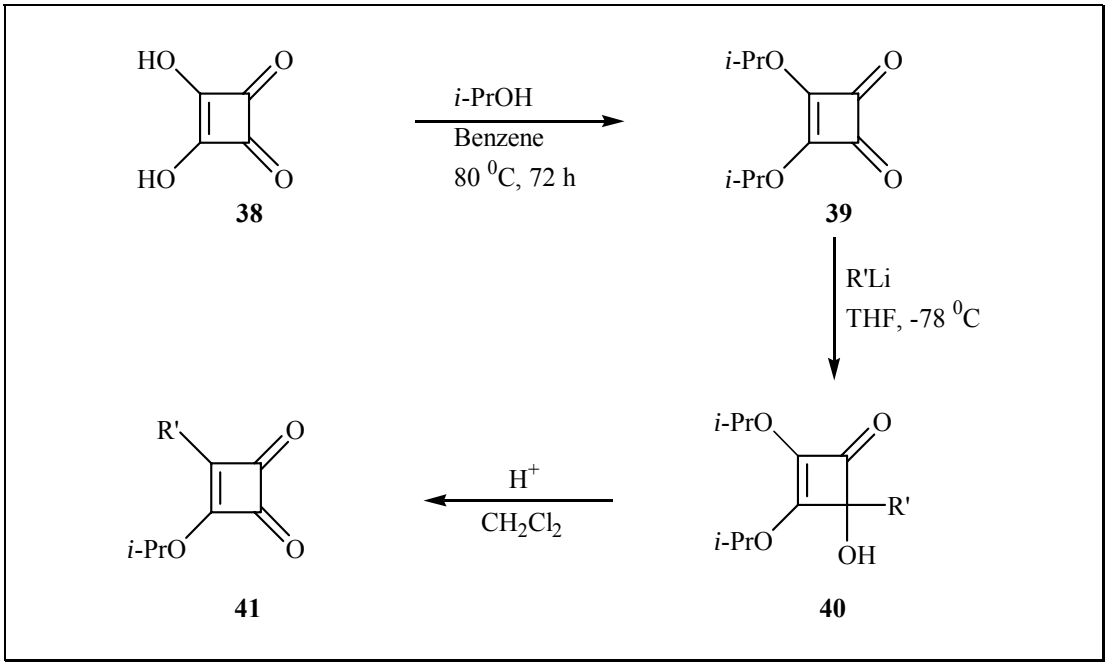


Figure 17. Derivatization of squaric acid into mono-substituted cyclobutenediones

Differentially di-substituted cyclobutenediones **44** are available by the sequential addition of two different organolithium reagents to diisopropyl squarate (**39**), as depicted in Figure 18 [69a,b]. Addition of organolithium nucleophile to diisopropyl squarate (**39**) gives isolable 1,2-adduct, which is then protected as *tert*-butyldimethylsilyl ether **42**. Addition of second organolithium reagent to cyclobutenone **42**, followed by acidic hydrolysis, provides differentially substituted cyclobutenediones **44** (Figure 18).

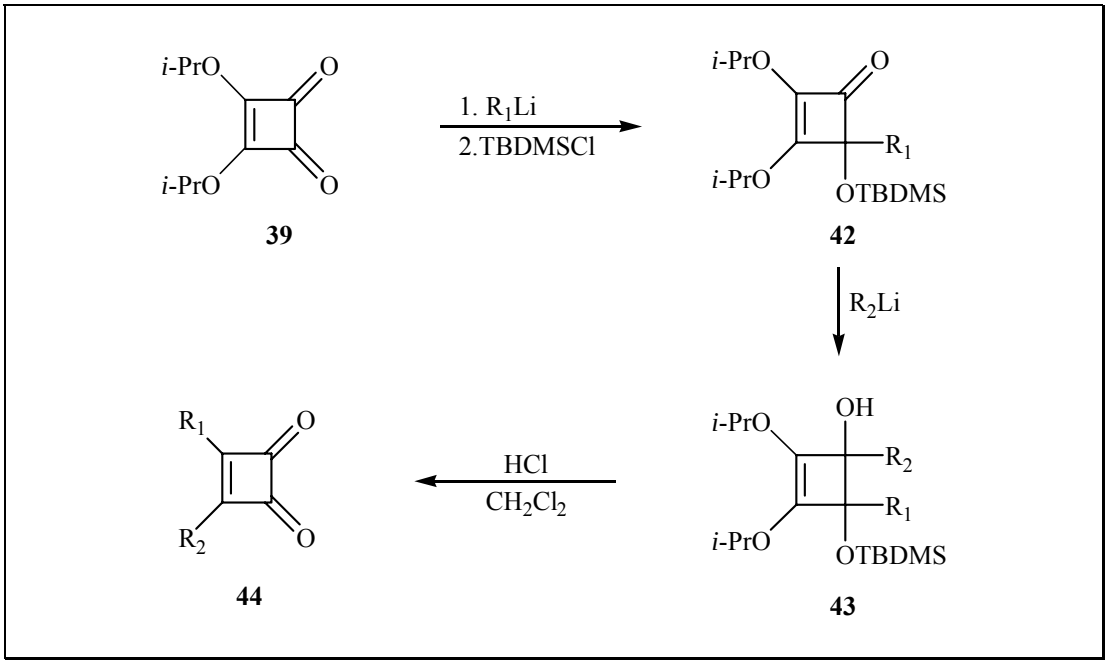


Figure 18. Derivatization of squaric acid into di-substituted cyclobutenediones

As mentioned previously, ferrocene does not show any biological activity despite all attempts. On the other hand, ferrocenium salts have exhibited antitumor activity against several tumors [20-23, 25, 26]. The results were encouraging and for the last few years, substitution of ferrocene moiety into biologically active compounds gained more interest in the synthetic community [29, 65a, 71]. The successful attempts made on tamoxifen (**2**) and chloroquine (**5**) were promising [23, 25].

Quinones are one of the most extensively studied classes of compounds due to their presence in antitumor quinone natural products [30]. This apparent importance of quinones and the discovery that ferrocene derivatives are effective against various kinds of tumors brings to mind that the combination of the structural

aspects of quinones with ferrocene moiety could furnish compounds with enhanced antitumor activities [21-23].

Amazingly, there are a small number of articles entitling the synthesis of ferrocenyl substituted quinones [72]. Therefore, a general and versatile synthetic methodology affording ferrocenyl quinones is considerable interest due to the fact that these compounds could be biologically active compounds with enhanced activity.

Hence, we have investigated the derivatization of squaric acid into ferrocenyl substituted cyclobutenones (Figure 19), and their rearrangements into ferrocenyl quinone derivatives as a part of our general involvement in ferrocene containing molecules [65a, 71].

In this work, the results concerning the scope, limitations and mechanisms of the reactions are discussed.

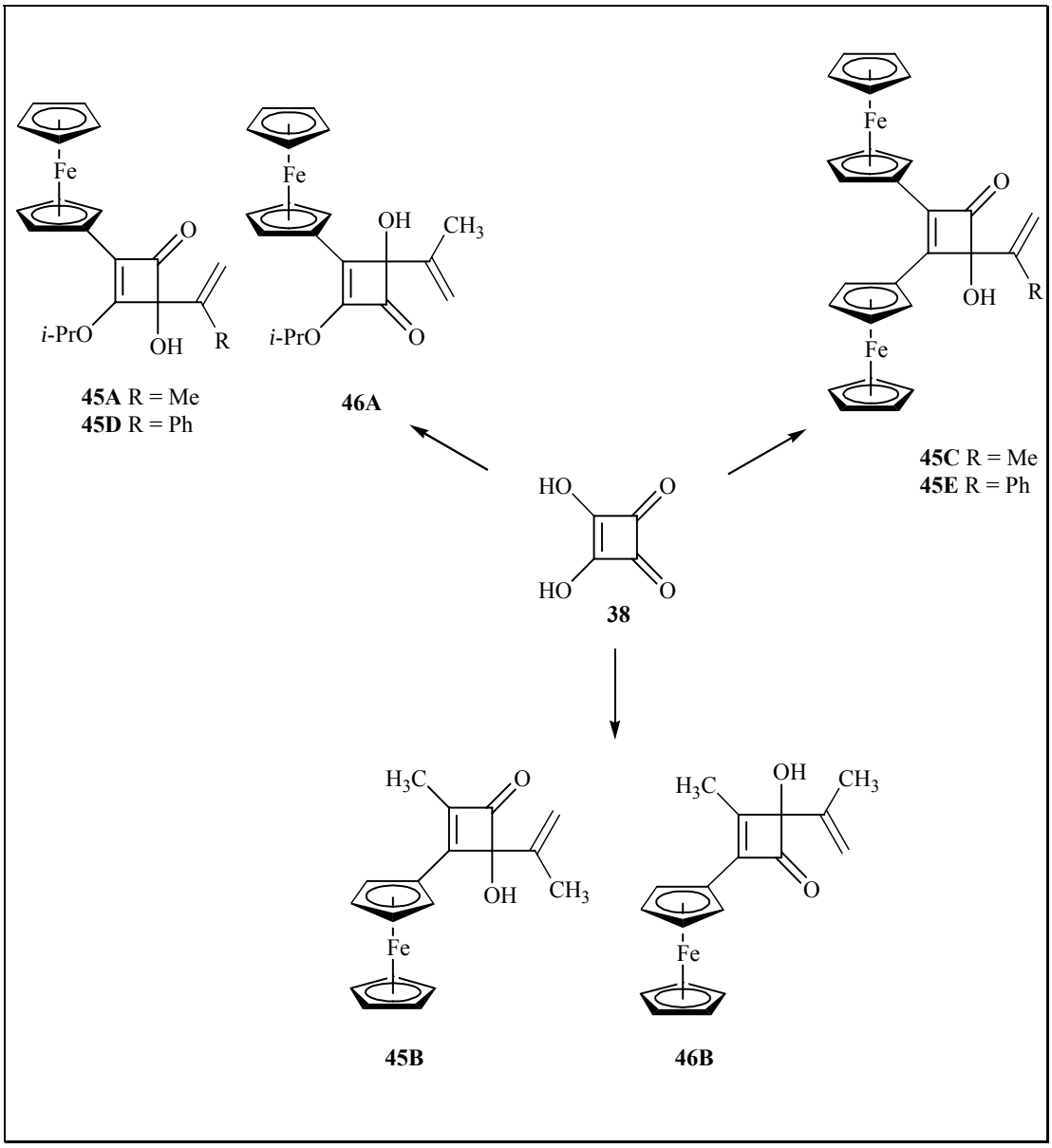


Figure 19. Targeted ferrocenyl cyclobutenones starting from squaric acid

1.2. Synthesis of Ferrocenyl Based Burning Rate Catalysts

Rocket design and production is one of the most recent research areas in defense industry. On this topic, significant amount of investments have been done and excellent results were obtained. Knowledge of propellant properties and production of desired and qualified propellants are the two principal aspects of rocket design. Most of the short and middle range rockets produced today are equipped with hydroxyl terminated polybutadiene (HTPB) and ammonium perchlorate (AP) based composite propellants. The uppermost ballistic element that should be taken into account in rocket design is the burning rate of the propellant employed. There are a number of ways to adjust the burning rate of composite rocket propellants [73]. Addition of transition metal oxides to composite propellant is the most widely utilized method [74]. The transition metal oxides used for this purpose reduce decomposition and burning temperatures of HTPB/AP based composite rocket propellants [75]. Although the mechanism is not clear, it is thought that transition metal oxide lower the activation energy of decomposition by donating electron to perchloric acid and ammonia molecules, which are formed through gas-phase decomposition of AP [76]. Iron (III) oxide is the most popular burning rate catalyst in HTPB/AP based composite rocket propellant [77]. As the particle size of iron (III) oxide decreases, its catalytic activity increases [78]. The materials that are capable of diffusing into the composite propellant homogeneously show higher catalytic activity. When the burning rate obtained with very small particle sized iron (III) oxide became insufficient, organometallic compounds bearing iron atoms inside are started to be explored. Among these organometallic compounds, ferrocene (**1**)

and its derivatives are found to be highly efficient burning rate catalysts for composite rocket propellants [27, 79]. Although ferrocene derivatives are superior to other transition metal compounds for this purpose, their use has some drawbacks arising from the tendency of migration in the bulk of the material and their sensitivity toward oxidation by air [80, 81] (Figure 20).

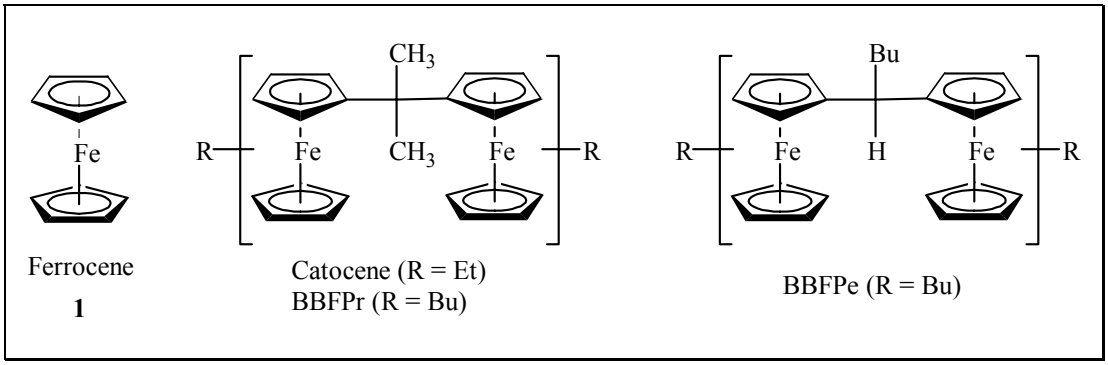


Figure 20. Ferrocene and some derivatives

In order to prevent the migration tendency completely, ferrocene (**1**) is bound to a polymeric binder or is a part of its polyurethane backbone. For this purpose, butacene has been synthesized, which contains ferrocene (**1**) chemically bound to HTPB polymer [81] (Figure 21). Among these ferrocene derivatives, butacene is proved to be screening the highest catalytic activity. The high price of catocene and butacene is the basic obstacle for their use as burning rate catalyst in composite rocket propellant applications.

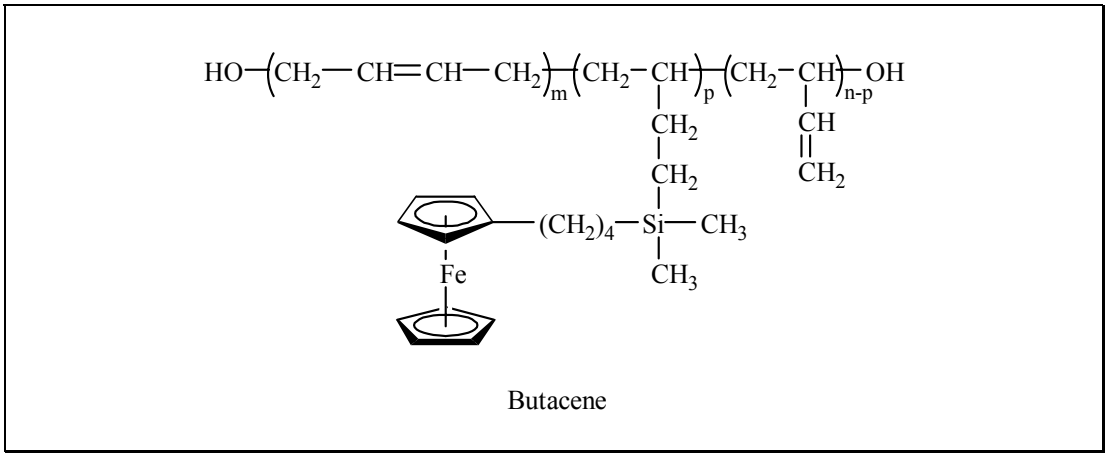


Figure 21. Butacene

In the most of the short and middle range rockets manufactured in our day, tetraethylenepentamine-acrylonitrile (TEPAN) is employed as binder in HTPB/AP based composite propellants. As a burning rate catalyst, TEPAN, TEP (tetraehylenepentamine, used in the synthesis of TEPAN) and EDA (ethylenediamine, a similar molecule to TEP) containing ferrocene units are unknown. Similarly, ferrocene containing catalyst derivatives of dimeryldiisocyanate (DDI), which are important propellant components, are unknown, as well.

Therefore, the design and synthesis of burning rate catalyst that disperse in the propellant matrix homogeneously but not migrate is a substantial research topic. For this purpose, ferrocene containing EDA and TEP based burning rate catalysts **47-50** were synthesized. Based on our literature knowledge and experience, it is expected that the burning rate catalysts **47-50** interact (or react) with TEPAN

equivalent, ammonium perchlorate (AP), and then react with other components of the propellant to function as a binder and catalyst in the course of burning process.

EDA based catalysts **47** and **48** are relatively simpler molecules than TEP based catalyst **49**. Structural determinations of the former catalysts are also simpler than that of later one (Figure 22). It is anticipated that DDI including catalyst **50** reacts with other components of the propellant so that it will avoid the migration tendency of the ferrocene derivatives in the bulk of the material and operate as burning rate catalyst throughout burning process (Figure 22).

In this work, the results concerning the scope, limitations and mechanisms of the reactions are discussed.

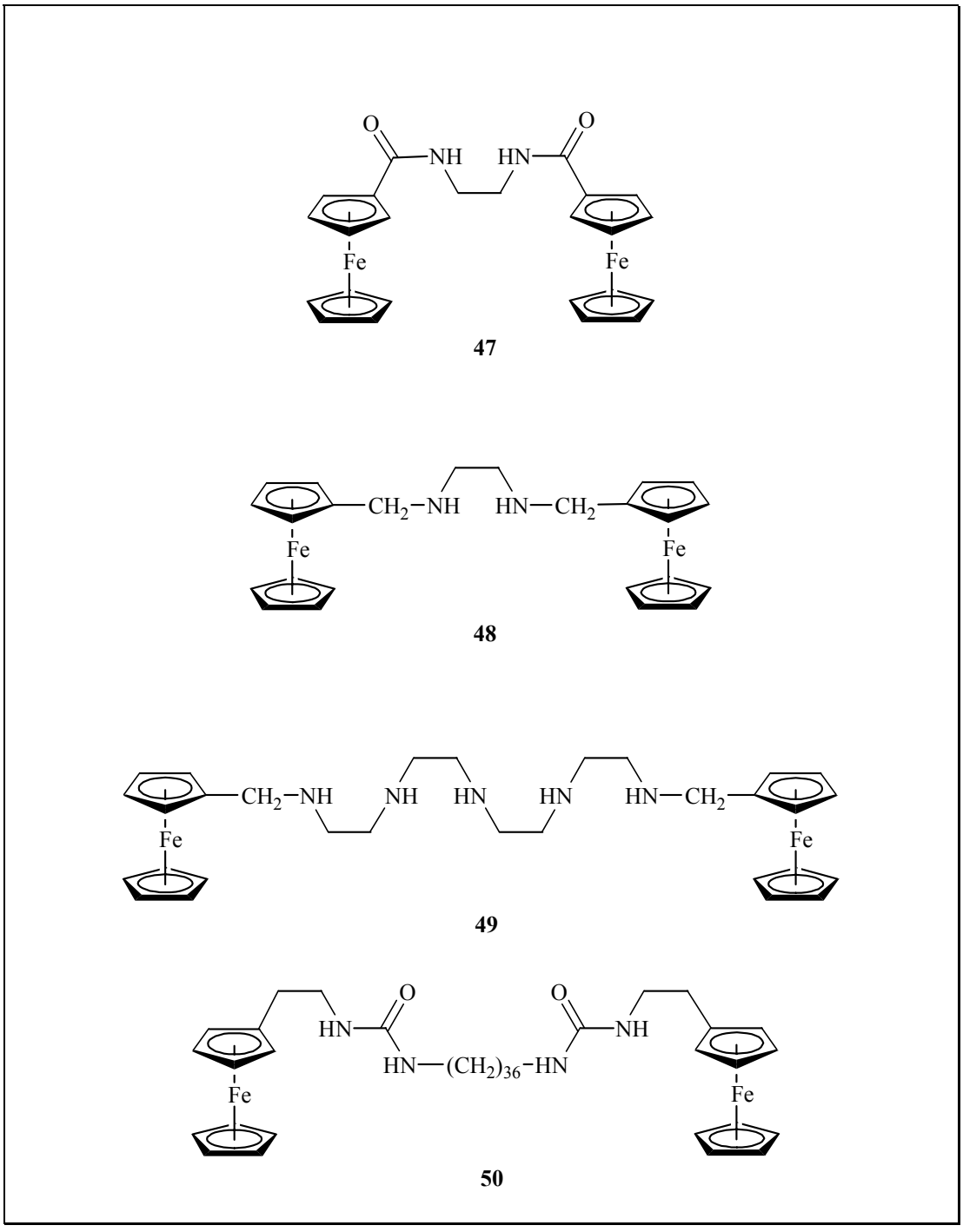


Figure 22. Target EDA, TEP and DDI based catalysts

CHAPTER 2

RESULTS AND DISCUSSION

2.1. SYNTHESIS OF FERROCENYL QUINONES

2.1.1. Synthesis of Cyclobutenedione Derivatives

In order to synthesize ferrocenyl substituted quinone derivatives, firstly ferrocenyl substituted cyclobutenedione derivatives were prepared starting from known cyclobutenediones. Squaric acid (**38**) was refluxed in isopropanol and benzene for 72 hours with continuous removal of the resulting water by using a Dean-Stark apparatus to produce diisopropyl squarate (**39**) (Figure 23) [69a]. Ferrocenyllithium (FcLi) [82] was reacted with diisopropyl squarate (**39**) to produce cyclobutenone **51**. Then cyclobutenone **51** was transformed into ferrocenyl substituted cyclobutenedione **52A** upon hydrolysis using HCl in CH_2Cl_2 at room temperature (Figure 24).

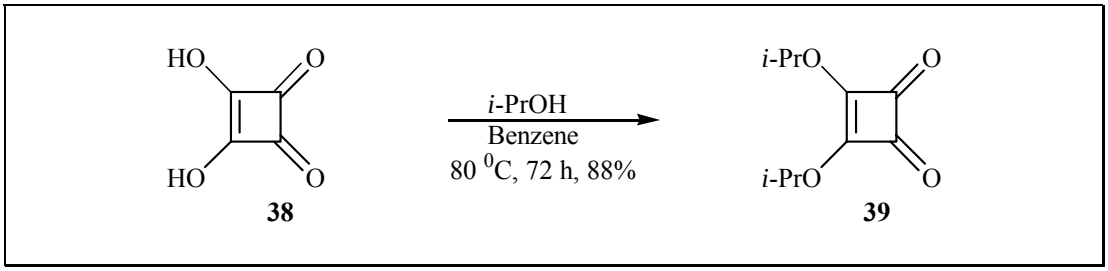


Figure 23. Synthesis of diisopropyl squarate (**39**) from squaric acid (**38**)

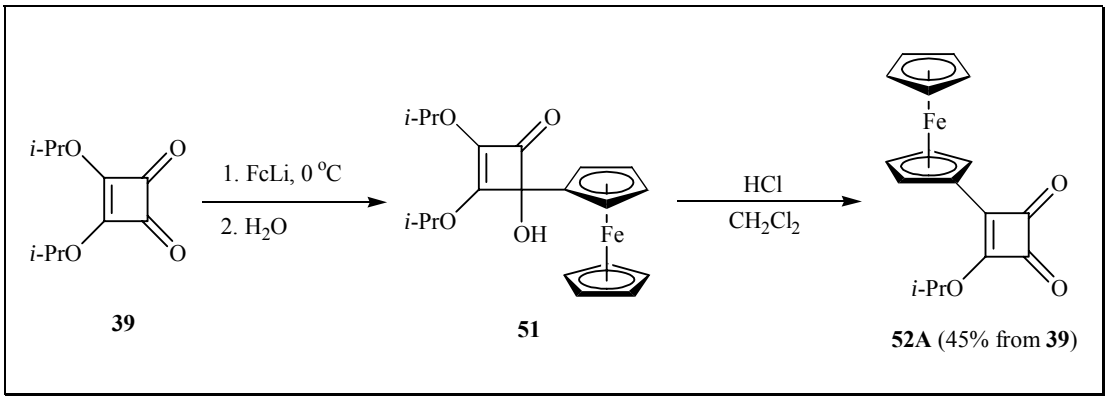


Figure 24. Synthesis of Ferrocenyl Cyclobutenedione **52A**

Addition of methyllithium to diisopropyl squarate (**39**) led to the formation of cyclobutenone **53** (94%), which upon hydrolysis afforded cyclobutenedione **54** in 92% yield (Figure 25) [69b]. The resulting cyclobutenedione **54** was refluxed in 6 N HCl and hexane for 36 hours to supply cyclobutenedione **55** (82%) (Figure 26) [63, 69b]. Reaction of cyclobutenedione **55** with thionyl chloride in presence of DMF furnished semisquaric chloride **56** (68%) [83]. Semisquaric chloride **56** underwent Pd-catalyzed coupling reaction with (tri-*n*-butylstannyl)ferrocene to yield in ferrocenyl substituted cyclobutenedione **52B** with the yield of 17% (Figure 26).

Synthesis of (tri-*n*-butylstannyl)ferrocene was accomplished according to known literature procedures [84].

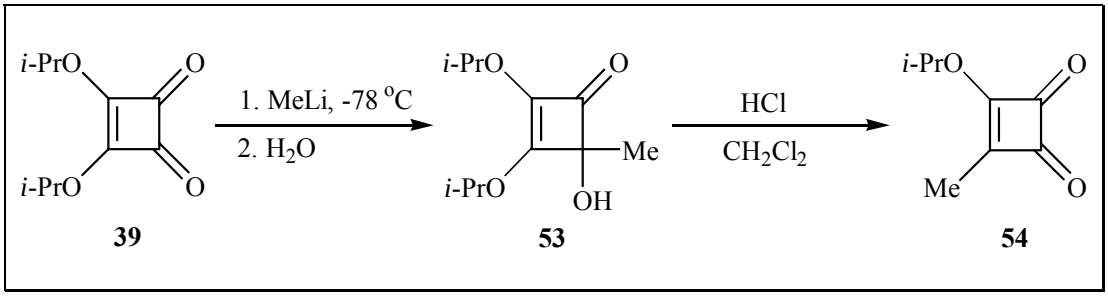


Figure 25. Synthesis of Cyclobutenedione **54**

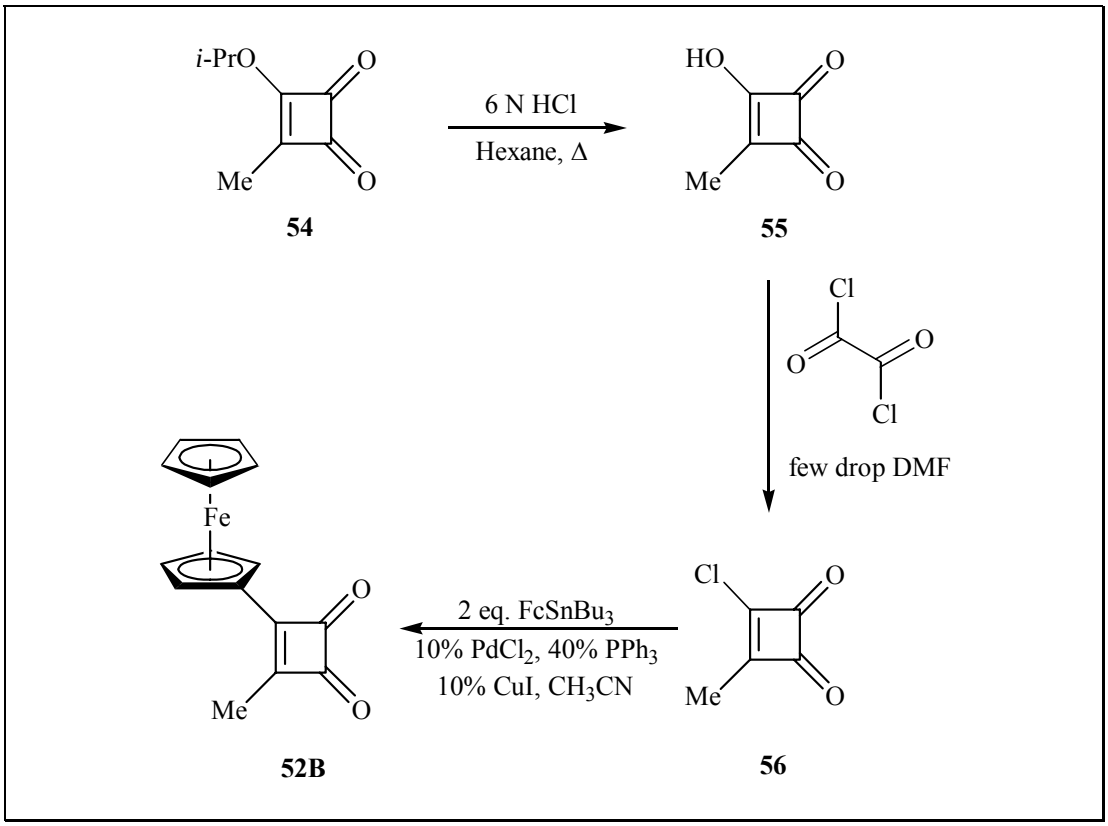


Figure 26. Synthesis of Ferrocenyl Cyclobutenedione **52B**

For the synthesis of diferrocenyl substituted cyclobutenedione **52C**, squaric dichloride (**57**) was employed [74a]. For this purpose, squaric acid (**38**) was refluxed with thionyl chloride in trace amount of DMF for 2.5 hours. Starting from squaric dichloride (**57**), diferrocenyl substituted cyclobutenedione **52C** was synthesized by both Pd-catalyzed coupling and Friedel-Crafts alkylation with the yields of 19% and 15% respectively (Figure 27). The mono substituted product, **52D**, was also isolated from both reactions (10% and 8% respectively).

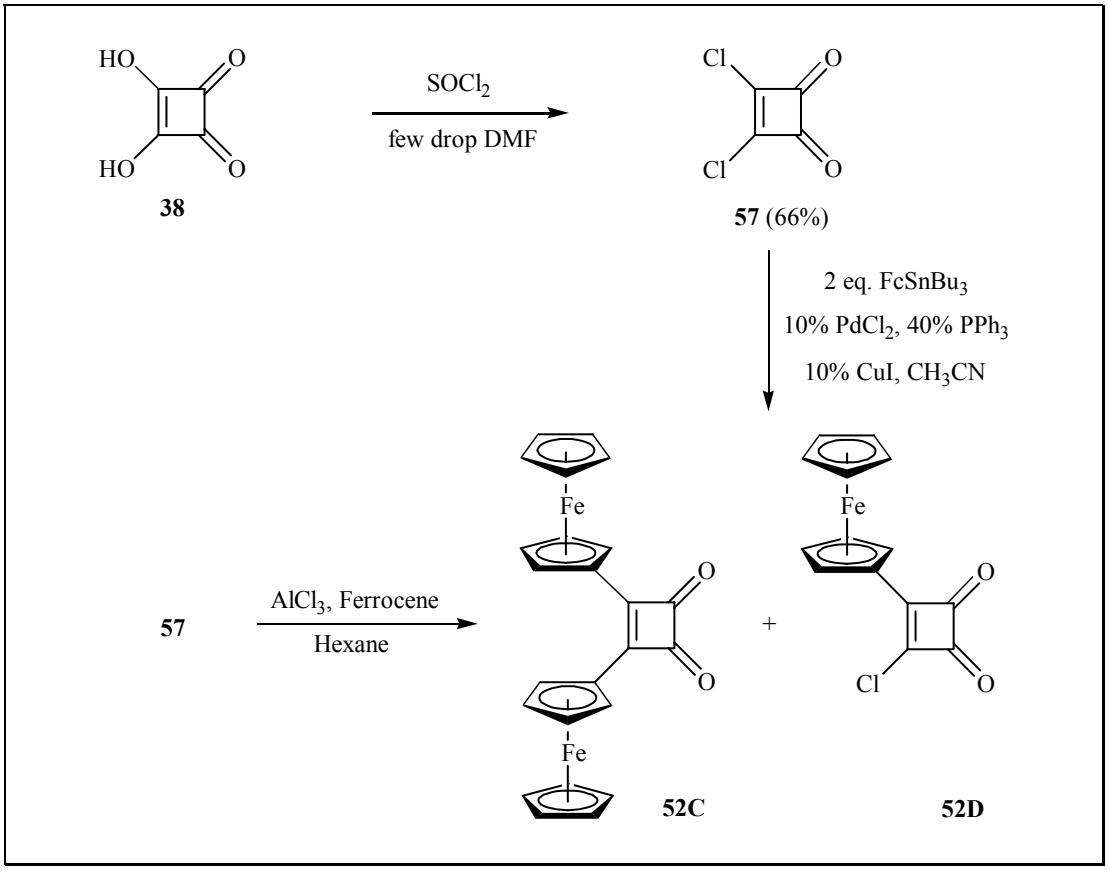
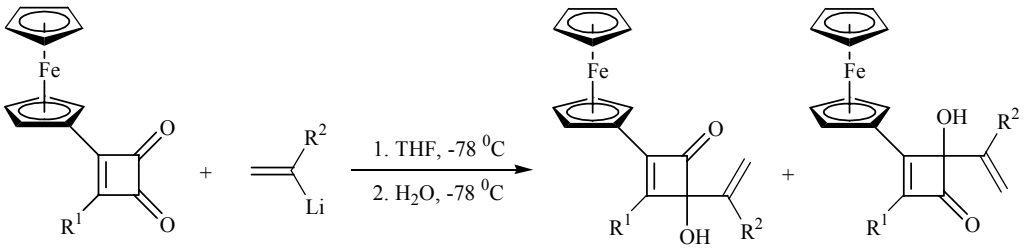


Figure 27. Synthesis of Diferrocenyl Cyclobutenedione **52C**

2.1.2. Synthesis of Cyclobutenone Derivatives

The obtained cyclobutenedione derivatives **52A-C** were then used as starting materials in the preparation of vinyl-substituted cyclobutenone derivatives **45** and **46**, as outlined in the Table 1. For this purpose, the cyclobutenedione derivatives **52A-C** were treated with vinyllithium (**58**) reagent in THF at -78 ^{0}C, leading to the formation of 4-hydroxycyclobutenone derivatives **45** and **46**.

Table 1. Syntheses of 4-vinylcyclobutenone derivatives **45** and **46** from cyclobutenedione derivatives **52**.[a]



52A (R^1 = *i*-PrO) **58A** (R^2 = Me) **45** **46**
52B (R^1 = Me) **58B** (R^2 = Ph)
52C (R^1 = Fc)

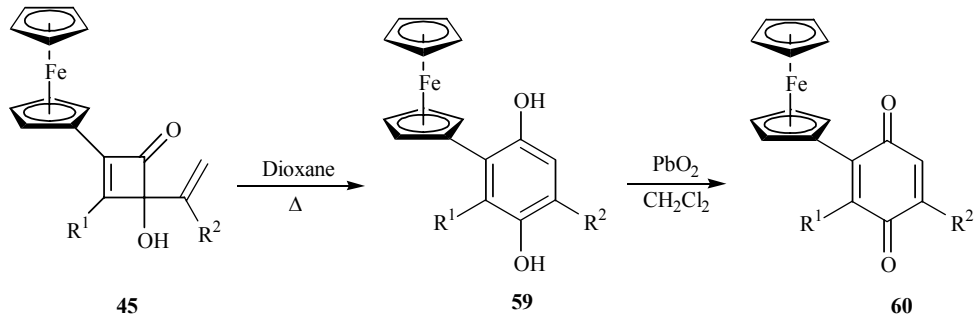
Entry[a]	R^1	R^2	Yield of **45** (%)	Yield of **46** (%)
A	*i*-PrO	Me	94	5
B	Me	Me	57	4
C	Fc	Me	65	0
D	*i*-PrO	Ph	40	0
E	Fc	Ph	47	0

[a] Entry letters define R^1 and R^2 for the compounds **45** and **46**.

2.1.3. Synthesis of Ferrocenyl Quinones

The synthesis of ferrocenyl quinones was accomplished through the thermolysis reactions of the cyclobutenones **45** and **46** in dioxane. Thermolysis afforded hydroquinone **59**, which was then oxidized to ferrocenyl quinone **60** using a mild oxidizing agent, such as lead dioxide (PbO_2) (Table 2).

Table 2. Synthesis of Ferrocenyl Quinones **60**[a]



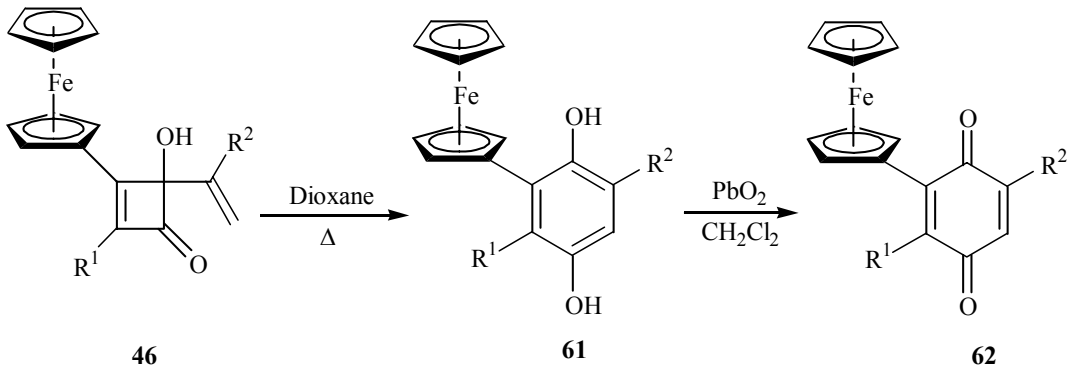
45 **59** **60**

Entry[a]	R^1	R^2	Yield of **45** from **57** (%)
A	*i*-PrO	Me	85
B	Me	Me	71
C	Fc	Me	56
D	*i*-PrO	Ph	61
E	Fc	Ph	75

[a] Entry letters define R^1 and R^2 for the compounds **45, 59** and **60**.

Regioisomeric 4-hydroxycyclobutenone derivatives **46** were converted to ferrocenyl substituted quinone products **62** in the same manner. Thermolysis of **58** furnished the formation of hydroquinone **61**. Subsequent oxidation of hydroquinone **61** using PbO_2 gave ferrocenyl quinone **62**, as depicted in the Table 3.

Table 3. Synthesis of regioisomeric Ferrocenyl Quinones **62**[a]



46 **61** **62**

Entry[a]	R^1	R^2	Yield of **62** from **46** (%)
A	*i*-PrO	Me	77
B	Me	Me	70

[a] Entry letters define R^1 and R^2 for the compounds **46, 61** and **62**.

2.1.4. Mechanism

We have demonstrated that 4-alkenyl-4-hydroxycyclobutenone derivatives **45** are versatile precursors for synthesis of ferrocenyl substituted quinone derivatives **60**. The reaction mechanism for the formation of ferrocenyl substituted quinone **60** from 4-alkenyl-cyclobutenone **45** is depicted in Figure 28. Upon heating in dioxane cyclobutenone **45** undergoes electrocyclic ring opening to form the vinylketene **63**, which then affords cyclohexadienone **64** through a 6π electrocyclic ring closure. Enolization of **64** gives ferrocenyl substituted hydroquinone **59**. Oxidation of hydroquinone **59** furnishes ferrocenyl quinone **60** easily. The transformation of regioisomeric 4-hydroxycyclobutenone derivatives **46** to quinones **62** occurs via the same mechanism as shown in Figure 28.

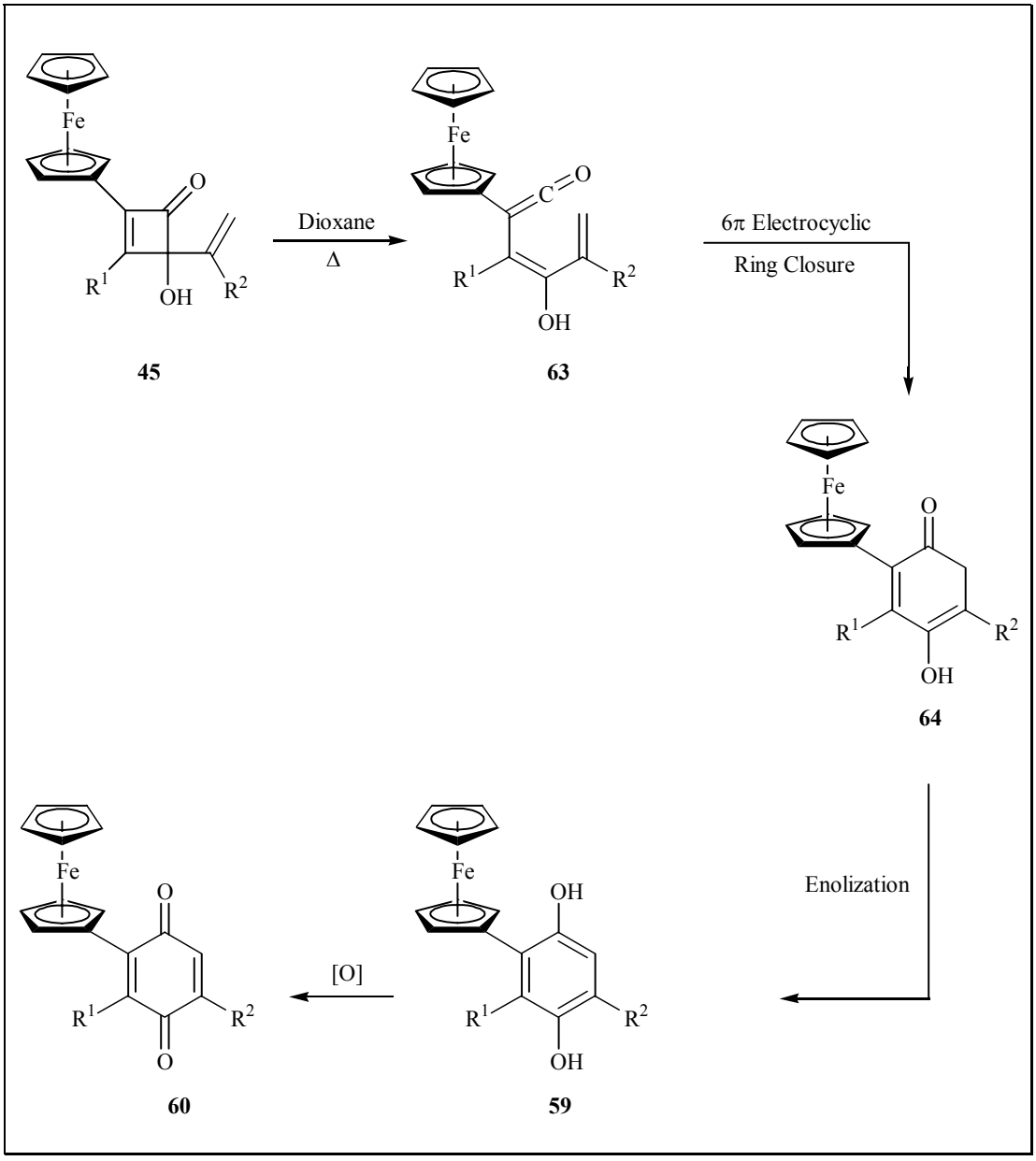


Figure 28. The mechanism for the formation of ferrocenyl quinone **60**

2.2. Synthesis of Ferrocenyl Based Burning Rate Catalysts

For the synthesis of catalyst **47**, firstly, ferrocene (**1**) was treated with *tert*-butyllithium to produce ferrocenyllithium [82], which was then reacted with dry ice (CO_2) and lastly with dilute HCl solution to afford ferrocene carboxylic acid (**65**) (45%) [85]. Treatment of **65** with oxalyl chloride provided ferrocenyl acid chloride (**66**) [86]. Finally, two equivalents of **66** was dissolved in *N*,*N*-dimethylformamide (DMF) and treated with one equivalent of ethylenediamine (EDA) to provide catalyst **47** (75%) [81a] (Figure 29).

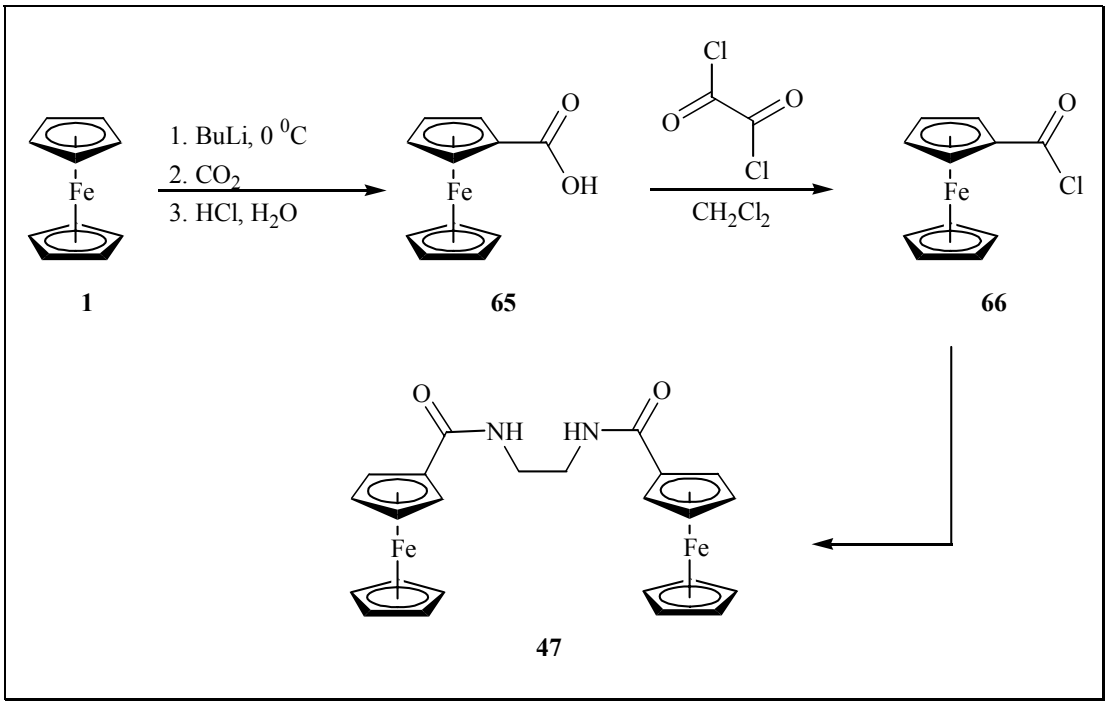


Figure 29. Synthesis of catalyst **47**

So as to acquire the catalysts **48** and **49**, ferrocenecarbaldehyde (**67**) and ferrocenedicarbaldehyde (**68**) were synthesized. For this purpose, ferrocenyllithium was prepared according to the method mentioned above and reacted first with DMF and then dilute HCl solution to yield in ferrocenecarbaldehyde (**67**) (82%) [87] (Figure 30). Treatment of ferrocene (**1**) with *n*-butyllithium in the presence of tetramethylethylenediamine (TMEDA) furnished dilithioferrocene. Ferrocenedicarbaldehyde (**68**) was prepared with the yield of 80% by the reaction of dilithioferrocene with DMF and dilute HCl solution (Figure 30) [87, 88].

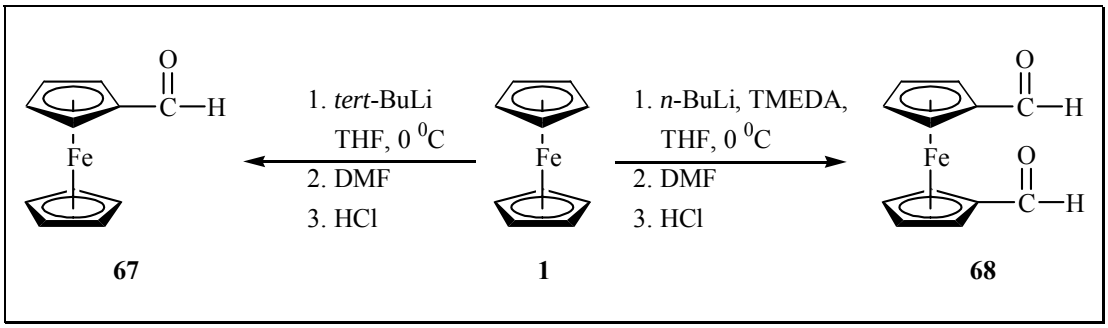


Figure 30. Syntheses of ferrocene derivatives **67** and **68**

Catalyst **48** and **49** were synthesized starting from ferrocenecarbaldehyde (**67**) (Figures 31 and 32). The condensation reaction of two equivalents of ferrocenecarbaldehyde (**67**) with one equivalent of ethylenediamine (EDA) in ethyl alcohol furnished compound **69** (83%) [89]. The synthesis of catalyst **48** was accomplished by reduction of compound **69** using lithium aluminum hydride as depicted in Figure 31 (95%) [89]. Likewise, when two equivalents of ferrocenecarbaldehyde (**67**) was condensed with one equivalent of

tetraethylenepentamine (TEP), compound **70** was obtained. Lithium aluminum hydride reduction of **70** gave catalyst **49** in 85% yield [90] (Figure 32).

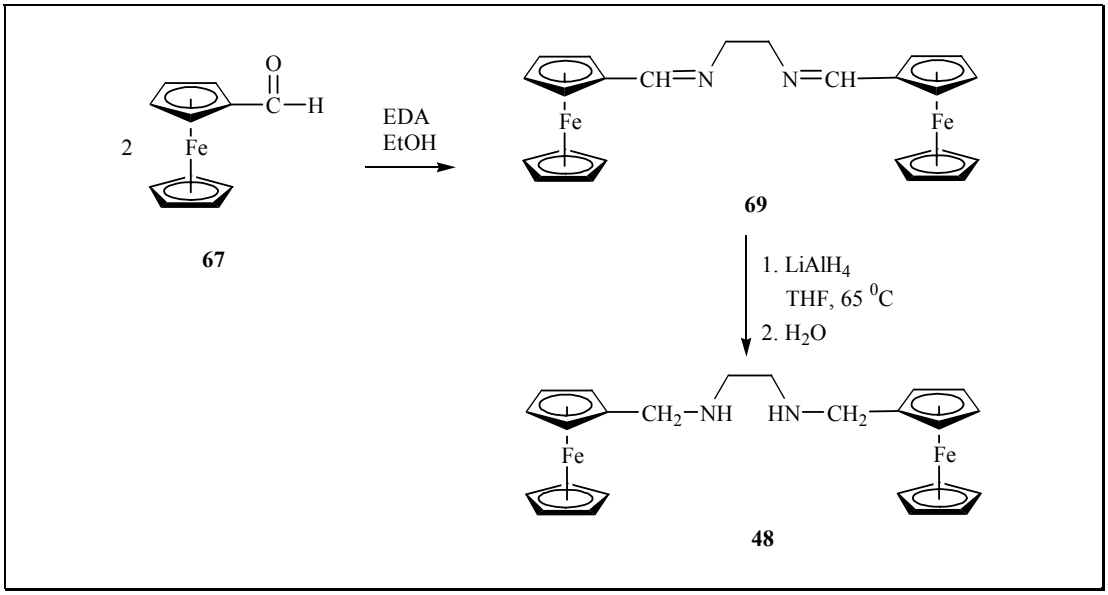


Figure 31. Synthesis of catalyst **48**

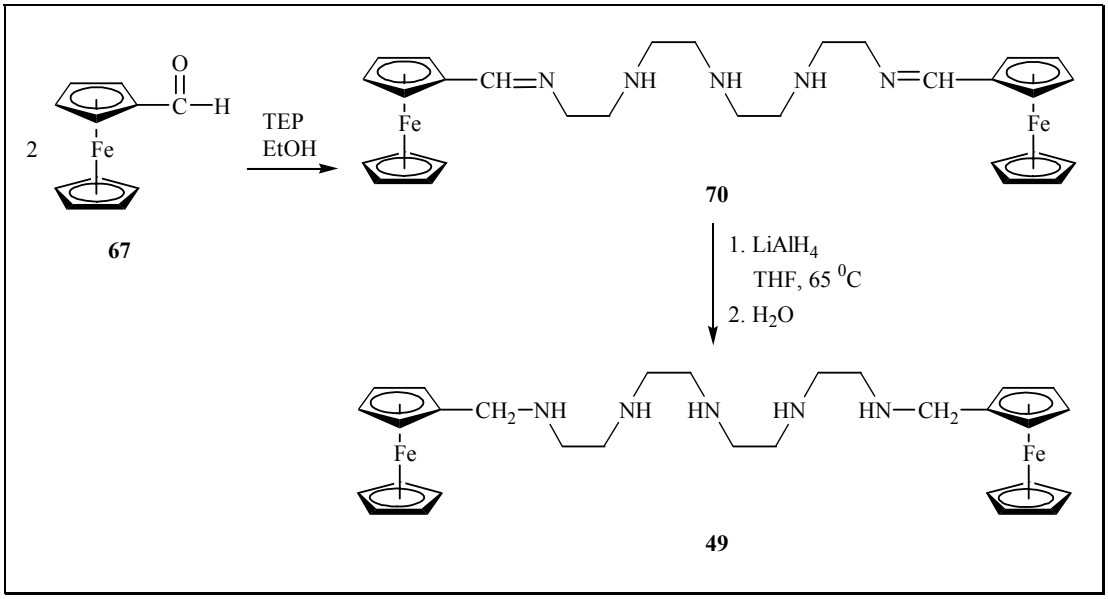


Figure 32. Synthesis of catalyst **49**

Ferrocenyl amine derivative **74** was produced for the synthesis of catalysts **50**. Treatment of ferrocene (**1**) with phosphoric and acetic acids in the presence tetramethylmethanediamine afforded ferrocene derivative **71** [92]. Ferrocene salt **72** was attained in 81% yield by means of reacting compound **71** with methyl iodide [92]. When the salt **72** was treated with potassium cyanide, ferrocene derivative **73** was obtained (77%) [93]. Reaction of compound **73** with lithium aluminum hydride gave ferrocenyl amine **74** (86%) [94] (Figure 33).

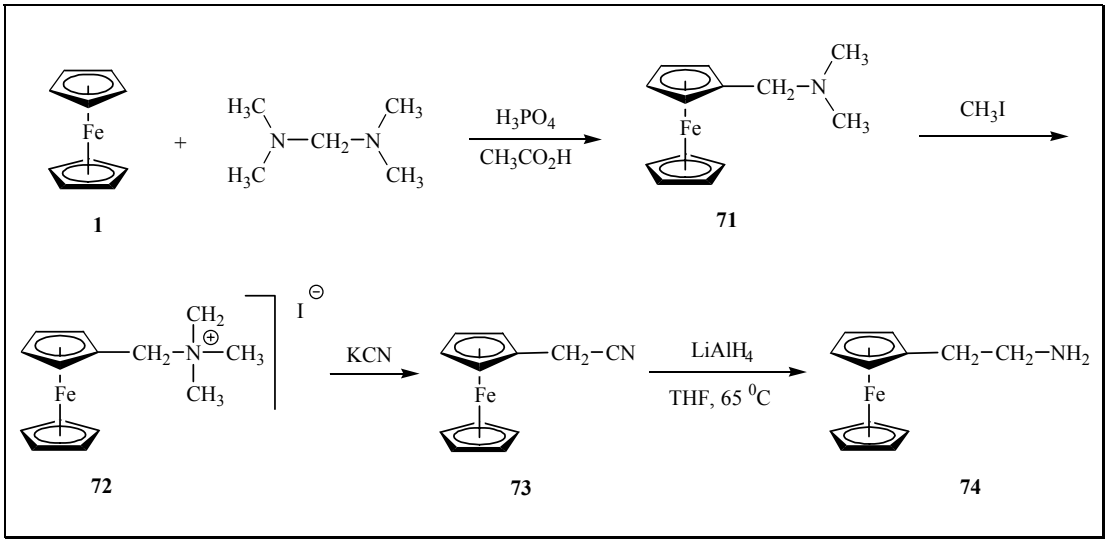


Figure 33. Synthesis of ferrocene amine derivative **74**

In fact, ferrocenyl amine derivative **74** is a potential burning rate catalyst due to the fact that if added to the propellant matrix, these derivatives of ferrocene react with mainly isocyanide derivatives and other appropriate components of propellant to bind ferrocene moiety in the bulk of propellant. Therefore, these compounds demonstrate catalytic property in the course of burning. If urethane derivatives that

are produced from these reactions are incorporated with ferrocene moiety, the resulting compounds are expected to be potential burning rate catalysts. Consequently, the reaction between ferrocenyl amine **74** and DDI was investigated. DDI treatment of ferrocenyl amine **74** in THF produced catalyst **50** with 94% yield (Figure 34).

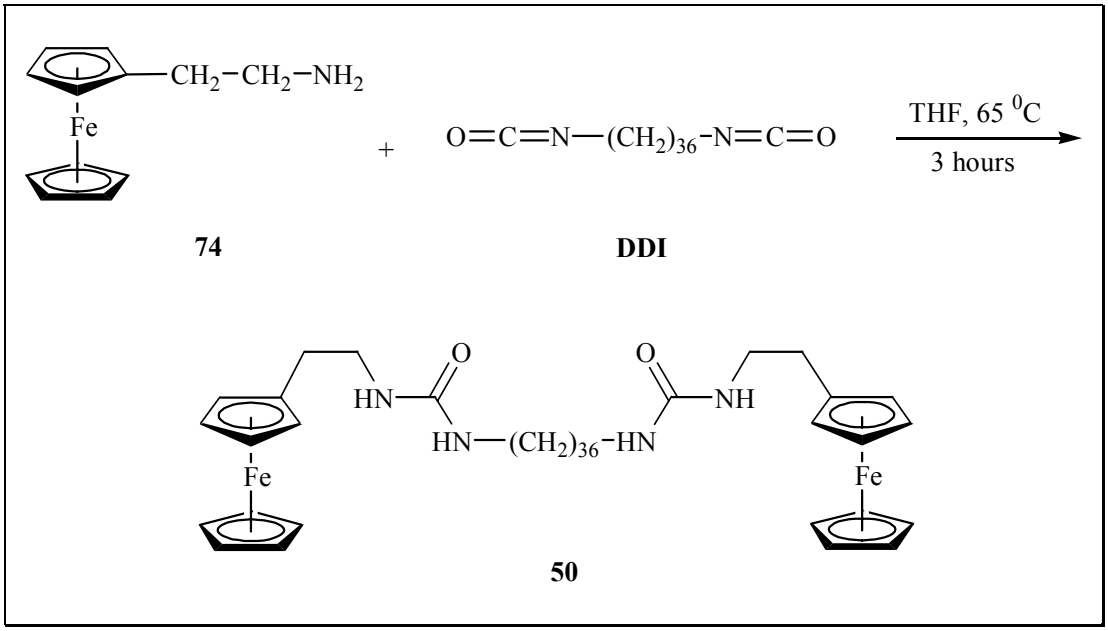


Figure 34. Condensation of **58** with DDI to produce catalyst **48**

CHAPTER 3

CONCLUSION

We have investigated the synthesis of ferrocenyl substituted quinones starting from squaric acid (**38**). As expected, cyclobutenone derivatives **45** and **46**, derived from squaric acid (**38**) gave the desired ferrocenyl quinones **60** and **62** upon thermolysis.

The reaction of cyclobutenediones **52** with alkenyllithium reagents **58** produced the cyclobutenone derivatives **45**. A complication in this reaction was the formation of the regioisomeric cyclobutenone **46A**. This low yield cyclobutenone couple **45A** and **46A** are characterized indirectly by comparison of HMBC-NMR spectra of their quinone products **60A** and **62A**. The regiochemistry of **60A** and **62A** was determined on account of such a comparison. In the HMBC-NMR spectrum of **60A**, hydrogens of both methyl groups (δ 2.12 and 2.05 ppm) give a three-bond coupling ($^3J_{CH}$) with the same carbonyl groups (δ 188.1 ppm). On the other hand, in the related spectrum of quinone **62A**, the hydrogens of each methyl

group (δ 2.05 and 2.04 ppm) make three-bond coupling interaction ($^3J_{CH}$) with different carbonyl groups (δ 187.7 and 187.4 ppm, respectively).

Thermolysis reactions were performed using variety of solvents. The highest amount of conversions was obtained utilizing dioxane as the reaction solvent. Subsequent to the thermolysis reaction of cyclobutenone **45A**, we isolated hydroquinone **59A** and ferrocenyl quinone **60A** in 72% and 17% yields, respectively. As can be figured out, the major product of the reaction was hydroquinone **59A**.

In the second part of the study, we have studied the synthesis of burning rate catalysts that include ferrocene moiety. Starting from ferrocene (**1**), four types of burning rate catalysts were synthesized. It should be noted that ferrocene moiety was incorporated in to propellant matrix through binding to EDA or TEP host. Consequently, migration tendency of ferrocene unit was prevented completely. The synthetic methodology described here can be extended for an industrial scale synthesis of the catalysts **47-50**.

CHAPTER 4

EXPERIMENTAL

General. Nuclear Magnetic Resonance (^{1}H and ^{13}C) spectra were recorded on a Bruker Spectrospin Avance DPX400 Ultrashield (400 MHz) spectrometer. Chemical shifts are reported in parts per million (δ) downfield from an internal tetramethylsilane reference. Coupling constants (*J* values) are reported in hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). DEPT ^{13}C-NMR information is given in parenthesis as C, CH, CH_2 and CH_3. Infrared spectra were recorded on a Perkin Elmer 1600 Series FT-IR spectrometer. Band positions are reported in reciprocal centimeters (cm^{-1}). Band intensities are reported relative to the most intense band and are listed as: br (broad), vs (very strong), s (strong), m (medium), w (weak), vw (very weak). Mass spectra (MS) were obtained on a Micromass UK Platform-II spectrometer using electron impact (EI); *m/e* values are reported, followed by the relative intensity in parentheses. Flash column chromatography was performed using thick-walled glass columns and "flash grade" silica (Merck 230-400 mesh). Routine

thin layer chromatography (TLC) was effected by using precoated 0.25 mm silica gel plates purchased from Merck. The relative proportions of solvents in mixed chromatography solvents refers to the volume:volume ratio. All commercially available reagents and reactants were obtained in reagent grade and used without purification. All reaction solvents were distilled for purity. Diethyl ether, THF, and dioxane were distilled from sodium/benzophenone kettle. The inert atmosphere created by slight positive pressure (ca. 0.1 psi) of argon.

4.1. Synthesis of Ferrocenyl Quinones

4.1.1. 3,4-Diisopropoxy-3-cyclobutene-1,2-dione (Diisopropyl squarate)

(**39**). 3,4-dihydroxy-3-cyclobutene-1,2-dione (Squaric acid) (**38**) (20.00 g, 175.40 mmol) was sluried in 100 mL of 1:1 benzene/2-propanol in a round-bottomed flask equipped with a Dean-Stark apparatus. The suspension was heated to reflux with continuous removal of the azeotrope over a period of 72 h. As the azeotrope was removed, 1:1 benzene/2-propanol was replenished. The reaction mixture was cooled to room temperature, and the solvents were removed on a rotary evaporator. The resulting oil was dissolved in diethyl ether (350 mL). The organic layer was washed with saturated aqueous sodium bicarbonate solution (2 × 20 mL) and once with saturated aqueous sodium chloride solution (20 mL). After drying over sodium sulfate, the solvent was removed on a rotary evaporator. The resulting viscous oil (R_f = 0.30 in 4:1 hexane/ethyl acetate) gave crystals of diisopropyl squarate (**39**) after standing overnight under argon (mp. 43-44 ^{o}C, 30.74 g, 88.4%). The product was pure according to TLC and ^{1}H-NMR.

39: ^{1}H-NMR ($CDCl_3$): δ 5.35 (septet, 2H, *J* = 6.1 Hz), 1.46 (d, 12H, *J* = 6.1 Hz); IR (CCl_4): 2986 (w), 1809 (m), 1736 (s), 1606 (vs), 1468 (w), 1406 (vs), 1388 (s), 1377 (m), 1331 (m), 1102 (s) cm^{-1}. The spectral data are in agreement with those reported previously for this compound [69c].

4.1.2. 3-Ferrocenyl-4-isopropoxy-3-cyclobutene-1,2-dione (52A). To a solution of ferrocene (**1**) (2.00 g, 10.75 mmol) in THF (10 mL) at room temperature under argon was added via syringe *tert*-butyllithium (5.3 mL of a 1.7 M of cyclohexane-ether solution, 9.00 mmol) over a period of 15 min. The resulting mixture was stirred for 1.5 hours at room temperature and then transferred via cannula to a solution of diisopropyl squarate (**39**) (1.43 g, 7.20 mmol) in THF (5.0 mL) at room temperature. After overnight stirring, the reaction mixture was diluted with 15 mL water and extracted with ether (3 × 150 mL). The ether layer was removed on a rotary evaporator. 4-ferrocenyl-4-hydroxy-2,3-diisopropoxy-2-cyclobuten-1-one (**51**) was obtained as crude product.

The crude material was dissolved in dichloromethane (20 mL) and concentrated hydrochloric acid (4 drops, ca 0.20 mL) was added. The mixture was stirred at room temperature approximately for a period of 30 min. (The progress of the reaction was monitored by routine TLC for disappearance of the starting compound). The reaction mixture was then diluted with dichloromethane (20 mL) and the layers were separated. The organic layer was washed with water (2 × 10 mL), and the aqueous layer was extracted with dichloromethane (2 × 50 mL). Combined organic layers were dried over sodium sulfate. Final purification was achieved by flash chromatography on silica gel using 9:1 hexane/ethyl acetate as

eluent. The red solid (R_f = 0.17 in 9:1 hexane/ethyl acetate) was collected to give 3-ferrocenyl-4-isopropoxy-3-cyclobutene-1,2-dione (**52A**) (1.05 g, 45%).

52A: ^{1}H-NMR ($CDCl_3$): δ 5.52 (septet, 1H, *J* = 6.2 Hz), 4.94 (ps, 2H), 4.63 (ps, 2H), 4.15 (s, 5H), 1.51 (d, 6H, *J* = 6.2 Hz); ^{13}C-NMR: ($CDCl_3$): δ 193 (C), 192.1 (C), 191.5 (C), 180.9 (C), 79.3 (CH), 73.2 (CH), 70.9 (CH), 69.2 (CH), 68 (C), 23.4 (CH_3); IR (CH_2Cl_2): 2984 (vw), 1786 (s), 1736 (vs), 1593 (vs), 1465 (s), 1385 (m), 1337 (m), 1092 (m), 1014 (w); MS (EI): 324 ($[M]^+$, 34), 279 (58), 277 (85), 226 (64), 201 (65), 175 (54), 157 (76), 125 (100), 117 (37), 99 (91); HRMS (EI): Calc. for. $C_{17}H_{16}{}^{56}FeO_3$: 324.0448. Found: 324.0439.

4.1.3. 3-Isopropoxy-4-methyl-3-cyclobutene-1,2-dione (54). To a solution of diisopropyl squarate (**39**) (2.20 g, 11.1 mmol) in THF (15 mL) at -78 ^{0}C under argon was added via syringe methyllithium (8.8 mL of a 1.5 M of cyclohexane-ether solution, 13.2 mmol) over a period of 15 min. The mixture was stirred for 3 hours and then diluted with 15 mL water and extracted with ether (3 × 150 mL). The ether layer was removed on a rotary evaporator.

The obtained crude product, 4-methyl-4-hydroxy-2,3-diisopropoxy-2-cyclobuten-1-one (**53**), was dissolved in dichloromethane (20 mL) and concentrated hydrochloric acid (4 drops, ca 0.20 mL) was added. The mixture was stirred at room temperature approximately for a period of 30 min. (The progress of the reaction was monitored by routine TLC for disappearance of the starting compound). The reaction mixture was then diluted with saturated sodium bicarbonate solution (20 mL) and the layers were separated. The organic layer was washed with water (2 × 10 mL), and the aqueous layer was extracted with dichloromethane (2 × 50 mL).

Combined organic layers were dried over sodium sulfate. After chromatographic purification, a single fraction (R_f = 0.26 in 4:1 hexane/ethyl acetate) was isolated and defined as compound **54** (1.58 g, 92%).

54: ^{1}H-NMR ($CDCl_3$): δ 5.40 (septet, 1H, *J* = 6.0 Hz), 2.22 (s, 3H), 1.48 (d, 6H,); IR (neat): 2985 (vw), 2359 (vw), 1799 (vs), 1750 (vs), 1597 (vs), 1399 (s), 1331 (m), 1098 (m), 1072 (w), 977 (vw), 897 (vw), 730 (w) cm^{-1}. The spectral data are in agreement with those reported previously for this compound [69c].

4.1.4. 3-Ferrocenyl-4-methyl-3-cyclobutene-1,2-dione (52B). 3-Isopropoxy-4-methyl-3-cyclobutene-1,2-dione (**54**) (1.7 g, 11.1 mmol) was dissolved in hexane (10 mL) and aqueous HCl (10 mL, 6 N) was added. The resulting two-phase system was refluxed with vigorous magnetic stirring for 36 hours. After cooling, the solvents were removed on a rotary evaporator. The gummy, light brown solid was dissolved in water (200 mL) and extracted with dichloromethane (5 × 20 mL) to remove impurities (the product remains in the water layer). The aqueous layer was evaporated, dried on a vacuum pump, dissolved in reagent grade acetone (30 mL), and filtered through celite. The acetone filtrate was evaporated to a volume of approximately 15 mL and crystallization was induced by addition of pentane (30 mL) directed into the acetone solution. The off-white, crystalline material was collected on a glass frit and washed with pentane. The filtrate was evaporated and recrystallized from acetone/pentane. The crystalline was collected to give 3-methyl-4-hydroxy-3-cyclobutene-1,2-dione (**55**) (0.7 g, 56.3%).

Into a round bottom flask 3-methyl-4-hydroxy-3-cyclobutene-1,2-dione (**55**) (0,8 g, 7.14 mmol) was placed and then dichloromethane (5.0 mL) and DMF

(catalytic amount) was added. After adding oxalylchloride (4.29 mL, 2.0 M, 8.6 mmol), reflux condenser was placed. The mixture was refluxed for 2-2.5 hours. After cooling, the reaction mixture was added ether (2 × 30 mL) and decanted to remove any residual cyclobutenedione **55**. The solvent was evaporated on rotary evaporator. Final purification was achieved by vacuum distillation (90 ^{0}C, 0.1 mmHg). A single fraction was isolated and identified as 3-chloro-4-methyl-3-cyclobutene-1,2-dione (**56**) (0.64 g, 68%).

$FcSnBu_3$ (2.18 g, 4.60 mmol), 3-chloro-4-methyl-3-cyclobutene-1,2-dione (0.60 g, 4.60 mmol), $PdCl_2$ (81 mg, 10%, 0.46 mol), PPh_3 (0.48 g, 40%, 1.83 mmol), CuI (87.6 g, 10%, 0.46 mol), CH_3CN (30 mL) were placed in a round bottom flask equipped with reflux condenser and stirred at room temperature for 42 hours under inert atmosphere. At the end of the period, the reaction mixture was added KF solution (15 mL). The mixture was extracted with ether (3 × 100 mL). The organic layer was washed with KF solution (2 × 20 mL) and dried over sodium sulfate. The solvent was removed on a rotary evaporator. Final purification was achieved by flash chromatography on silica gel using 9:1 hexane/ethyl acetate as eluent. The red solid (R_f =0 0.11 in 9:1 hexane/ethyl acetate) was isolated and assigned as 3-ferrocenyl-4-methyl-3-cyclobutene-1,2-dione (**52B**) (0.22 g, 17%).

52B: ^{1}H-NMR: ($CDCl_3$): δ 4.96 (s, 2H) , 4.73 (s, 2H), 4.17 (s, 5H), 2.36 (s, 3H); ^{13}C-NMR: ($CDCl_3$): δ 197.7 (C), 197.0 (C), 196.9 (C), 188.5 (C), 73.7 (CH), 70.5 (CH), 69.2 (CH), 67.8 (C), 11.8 (CH_3); IR (CH_2Cl_2): 1781 (vs), 1756 (s), 1590 (vs), 1454 (w), 1381 (w), 1312 (m), 1259 (m), 1201 (w), 1100 (w), 1044 (m), 908 (m) cm^{-1}.

4.1.5. 3,4-Dichloro-3-cyclobuten-1,2-dione (57). A mixture of squaric acid (**38**) (4.0 g, 35 mmol), thionyl chloride (5.1 mL, 70 mmol), and DMF (catalytic amount), was placed into a two necked round bottom flask and refluxed for 2.5 hours. After cooling the reaction mixture was added ether (20 mL) and decanted to sublimation flask. The solvents were removed on a rotary evaporator. Final purification was achieved by vacuum sublimation at (50 ^{0}C, 0.1 mmHg). The yellow crystals were collected to 3,4-dichloro-3-cyclobutene-1,2-dione (**57**) (3,47 g, 66%) [74a].

4.1.6. 3,4-Diferrocenyl-3-cyclobuten-1,2-dione (52C) with Stille Coupling Method. $FcSnBu_3$ (2.1 g, 4.42 mmol), 3,4-dichloro-3-cyclobuten-1,2-dione (0.3 g, 1.99 mmol), $PdCl_2$ (39 mg, 0.22 mmol), PPh_3 (229.2 mg, 0.84 mmol), CuI (41.4 mg, 0.22 mmol) were placed in a round bottom flask equipped with a reflux condenser and acetonitrile (50 mL) was added. The reaction mixture was stirred for 48 hours at room temperature under argon. The reaction mixture was then added KF solution and extracted with ether (3 × 100 mL). After drying the combined organic layers over sodium sulfate, the solvents were removed on a rotary evaporator. The red solid was purified by flash chromatography on silica gel. Two fractions were isolated. The first fraction (R_f = 0.43 in 9:1 hexane/ethyl acetate) was isolated and defined as 3-chloro-4-ferrocenyl-3-cyclobutene-1,2-dione (**52D**) (60.1 mg, 10%). The red fraction (R_f = 0.29 in 9:1 hexane/ethyl acetate) was isolated and assigned as 3,4-diferrocenyl-3-cyclobuten-1,2-dione **52C** (0.17 g, 19%).

52C: ^{1}H-NMR: ($CDCl_3$): δ 5.14 (s, 4H) , 4.74 (s, 4H), 4.22 (s, 10H); ^{13}C-NMR: ($CDCl_3$): δ 196.5 (C), 187.4 (C), 73.6 (CH), 71.0 (CH), 70.1 (CH), 69.8 (C);

IR (CH_2Cl_2): 2958 (m), 2927 (s), 2867 (m), 1734 (vs), 1578 (m), 1483 (m), 1375 (m), 1247 (s), 1045 (m) cm^{-1}.

52D: ^{1}H-NMR: ($CDCl_3$): δ 5.15 (s, 2H), 4.87 (s, 2H), 4.23 (s, 5H); ^{13}C-NMR: ($CDCl_3$): δ 196.1 (C), 195.0 (C), 190.7 (C), 174.4 (C), 75.2 (CH), 71.6 (CH), 70.2 (CH), 66.2 (C); IR (CH2Cl2): 3057 (vw), 2957 (vw), 1772 (vs), 1577 (vs), 1269 (m), 1134 (m), 1061 (vw) cm^{-1}.

4.1.7. 3,4-Diferrocenyl-3-cyclobuten-1,2-dione (52C) with Friedel-Craft Method. To a solution of ferrocene (**1**) (3.08 g, 16.6 mmol) and 3,4-dichloro-3-cyclobuten-1,2-dione (1.00 g, 6.62 mmol) in dichloromethane (45 mL) aluminum chloride (2.65 g, 19.9 mmol) was added. The reaction was stirred for overnight at room temperature. The reaction mixture was poured onto water and extracted with ether (3 × 100 mL). The ether layer was washed with water. The combined organic layers were dried over sodium sulfate, and the solvents were removed on rotary evaporator. Final purification was achieved by flash chromatography on silica gel using 19:1 hexane/ethyl acetate as eluent. The first fraction (R_f = 0.43 in 9:1 hexane/ethyl acetate) was cyclobutenedione **52D** (0.16 g, 8%). The second fraction (R_f = 0.29 in 9:1 hexane/ethyl acetate) was collected to give the 3,4-diferrocenyl-3-cyclobuten-1,2-dione (**52C**) (0.45 g, 15%).

4.1.8. General Procedure 1. Synthesis of 4-vinylcyclobutenones 45A-E and 46A-B (Table 1). To a solution of cyclobutenedione derivative (**52A-C**) (1.11 mmol) in THF (15 mL) at -78 ^{0}C under argon was added corresponding vinyllithium reagent (**58A-B**) (1.33 mmol) which was prepared *in situ* by reacting *tert*-

butyllitihum and vinylbromide reagent. The reaction mixture was stirred at -78 ^{0}C for 3 h and then quenched with water (10 mL) at -78 ^{0}C. The mixture was allowed to warm to room temperature and diluted with ether (50 mL). The layers were separated and the aqueous layer was extracted with ether (2 × 50 mL). The combined organic layers were dried over Na_2SO_4 and the solvents were removed on a rotary evaporator. Final purification was achieved by flash chromatography on silica gel using 9:1 hexane/ethyl acetate followed by 4:1 hexane/ethyl acetate as eluent.

4.1.9. 2-Ferrocenyl-4-hydroxy-4-isopropenyl-3-isopropoxy-2-cyclobutene-1-one (45A) (Table 1, Entry A). General Procedure 1 was followed using cyclobutenedione **52A** (360 mg, 1.11 mmol) and 2-lithiopropene (**58A**), which was prepared *in situ* using 2-bromo-1-propene (0.12 mL, 1.33 mmol) in THF (10 mL) and *tert*-butyllithium (1.5 mL of a 1.7 M of hexane-ether solution, 2.55 mmol) at -78 ^{0}C. After chromatographic purification two fractions were isolated. The first fraction (R_f = 0.22 in 9:1 hexane/ethyl acetate) was isolated and assigned as 3-ferrocenyl-4-hydroxy-4-isopropenyl-2-isopropoxy-2-cyclobutene-1-one (**46A**) (20.3 mg, 5%). The second fraction (R_f = 0.16 in 9:1 hexane/ethyl acetate) was isolated and assigned as compound **45A** (382 mg, 94%).

45A: ^{1}H-NMR: ($CDCl_3$): δ 5.31 (s, 1H), 5.10 (ps, 1H), 4.85 (septet, 1H, *J* = 1.1 Hz), 4.58 (ps, 1H), 4.55 (ps, 1H), 4.16 (t, 2H, *J* = 1.8 Hz), 4.08 (s, 5H), 3.44 (s, 1H), 1.80 (s, 3H), 1.40 (d, 3H, *J* = 6.2 Hz), 1.33 (d, 3H, *J* = 6.2 Hz); ^{13}C-NMR: ($CDCl_3$): δ 187.8 (C), 177.9 (C), 141.3 (C), 126.6 (C), 114.5 (CH_2), 95.9 (C), 78.4 (CH), 70.9 (C), 69.6 (CH), 69.1 (CH), 68.0 (CH), 67.8 (CH), 23.4 (CH_3), 23.3

(CH_3), 20.2 (CH_3); IR (CH_2Cl_2): 3564 (vw), 3364 (br), 1753 (s), 1631 (vs), 1471 (s), 1384 (s), 1330 (m), 1095 (s) cm^{-1}; MS (EI): 366 ($[M]^+$, 100), 324 (53), 258 (42), 257 (83), 229 (22); HRMS (EI): Calc. for. $C_{20}H_{22}{}^{56}FeO_3$: 366.0918. Found: 366.0926.

46A: ^{1}H-NMR: ($CDCl_3$): δ 5.30 (s, 1H), 5.07 (s, 1H), 4.98 (septet, 1H, *J* = 6.0 Hz), 4.69 (s, 1H), 4.54 (s, 1H), 4.42 (s, 1H), 4.38 (s, 1H), 4.14 (s, 5H), 2.49 (s, 1H), 1.70 (s, 1H), 1.33 (d, 3H, *J* = 6.0 Hz), 1.28 (d, 3H, *J* = 6.0 Hz); ^{13}C-NMR: ($CDCl_3$): δ 187.5 (C), 156.2 (C), 150.0 (C), 143.3 (C), 114.0 (CH_2), 90.9 (C), 74.3 (CH), 71.8 (CH), 71.4 (CH), 71.3 (C), 70.6 (CH), 69.4 (CH), 68.7 (CH), 23.4 (CH_3), 20.3 (CH_3); IR (CH_2Cl_2): 3574 (br), 2980 (w), 1749 (vs), 1620 (s), 1463 (m), 1380 (m), 1328 (m), 1260 (m), 1104 (m) cm^{-1}; MS (EI): 366 ($[M]^+$, 100), 338 (42), 324 (44), 296 (73), 257 (65), 250 (80), 229 (49), 121 (24); HRMS (EI): Calc. for. $C_{20}H_{22}{}^{56}FeO_3$: 366.0918. Found: 366.0901.

4.1.10. 2-Ferrocenyl-4-hydroxy-4-isopropenyl-3-methyl-2-cyclobutene-1-one (45B) (Table 1, Entry B). General Procedure 1 was followed using cyclobutenedione **52B** (230 mg, 0.82 mmol) and 2-lithiopropene (**58A**), which was prepared *in situ* using 2-bromo-1-propene (0.087 mL, 0.99 mmol) in THF (10 mL) and *tert*-butyllithium (1.1 mL of a 1.7 M of hexane-ether solution, 1.89 mmol) at -78 ^{0}C. After chromatographic purification two fractions were isolated. The first fraction (R_f = 0.12 in 9:1 hexane/ethyl acetate) was isolated and assigned as 3-ferrocenyl-4-hydroxy-4-isopropenyl-2-methyl-2-cyclobutene-1-one (**46B**) (10.6 mg, 4%). The second fraction (R_f = 0.11 in 9:1 hexane/ethyl acetate) was isolated and assigned as compound **45B** (151 mg, 57%).

45B: ^{1}H-NMR: ($CDCl_3$): δ 5.21 (s, 1H), 5.08 (s, 1H), 4.68 (s, 1H) 4.61 (s, 1H), 4.33 (s, 2H), 4.14 (s, 5H), 2.31 (s, 3H), 1.81 (s, 3H).

46B: ^{1}H-NMR: ($CDCl_3$): δ 5.23 (s, 1H), 5.10 (s, 1H), 4.70 (s, 1H), 4.63 (s, 1H), 4.35 (s, 2H), 4.16 (s, 5H), 2.56 (s, 1H), 2.22 (s, 3H), 1.83 (s, 3H); IR (CH_2Cl_2): 3570 (m), 3439 (br), 1755 (vs), 1639 (m), 1460 (w), 1336 (w), 1380 (w), 1105 (m), 824 (m) cm^{-1}.

4.1.11. 2,3-Diferrocenyl-4-hydroxy-4-isopropenyl-2-cyclobutene-1-one (45C) (Table 1, Entry C). General Procedure 1 was followed using cyclobutenedione **52C** (266 mg, 0.59 mmol) and 2-lithiopropene (**58A**), which was prepared *in situ* using 2-bromo-1-propene (0.063 mL, 0.71 mmol) in THF (10 mL) and *tert*-butyllithium (0.8 mL of a 1.7 M of hexane-ether solution, 1.36 mmol) at -78 ^{0}C. After chromatographic purification a single fraction was isolated and assigned as compound **45C** (187 mg, 65%).

45C: ^{1}H-NMR: ($CDCl_3$): δ 5.41 (s, 1H), 5.16 (s, 1H), 4.92 (s, 1H), 4.91 (s, 1H), 4.85 (s, 1H), 4.83 (s, 1H), 4.62 (s, 1H), 4.58 (s, 1H), 4.41 (s, 2H), 4.28 (s, 5H), 4.21 (s, 5H), 2.55 (s, 1H), 1.84 (s, 3H).

4.1.12. 2-Ferrocenyl-4-hydroxy-3-isopropoxy-4-(1-phenylvinyl)-2-cyclobutene-1-one (45D) (Table 1, Entry D). General Procedure 1 was followed using cyclobutenedione **52A** (200 mg, 0.62 mmol) and α-lithiostyrene (**58B**), which was prepared *in situ* using α-bromostyrene (0.01 mL, 0.68 mmol) in THF (5 mL) and *tert*-butyllithium (0.84 mL of a 1.7 M of hexane-ether solution, 1.43 mmol) at -78 ^{0}C. After chromatographic purification a single fraction was isolated as

cyclobutenone **45D** (106 mg, 40%). Compound **45D** was not stable enough to be analyzed spectrally.

4.1.13. 2,3-Diferrocenyl-4-hydroxy-4-(1-phenylvinyl)-2-cyclobutene-1-one (45E) (Table 1, Entry E). General Procedure 1 was followed using cyclobutenedione **52C** (100 mg, 0.22 mmol) and α-lithiostyrene (**58B**), which was prepared *in situ* using α-bromostyrene (0.036 mL, 0.28 mmol) in THF (5 mL) and *tert*-butyllithium (0.32 mL of a 1.7 M of hexane-ether solution, 0.54 mmol) at -78 ^{0}C. After chromatographic purification a single fraction was isolated and assigned as cyclobutenone **45E** (66 mg, 47%).

45E: ^{1}H-NMR: ($CDCl_3$): δ 7.49 (m, 2H), 7.31-7.18 (m, 3H), 5.49 (s, 1H), 5.30 (s, 1H), 4.93 (s, 1H), 4.85 (s, 1H), 4.75 (s, 1H), 4.72 (s, 1H), 4.58 (s, 1H), 4.54 (s, 1H), 4.32 (s, 2H), 4.19 (s, 5H), 3.97 (s, 5H), 2.72 (s, 1H); ^{13}C-NMR: ($CDCl_3$): δ 190.2 (C), 168.0 (C), 148.7 (C), 143.6 (C), 139.2 (C), 129.9 (CH), 128.8 (CH), 128.7 (CH), 128.5 (CH), 128.3 (CH), 116.8 (CH_2), 96.9 (C), 72.6 (CH), 72.1 (CH), 72.0 (C), 71.9 (C), 71.1 (CH), 71.0 (CH), 70.1 (CH), 70.0 (CH), 69.9 (CH), 69.6 (CH),69.4 (CH), 68.5 (CH); IR (CH_2Cl_2): 3565 (w), 3046 (w), 2955 (w), 1743 (vs), 1616 (s), 1488 (s), 1381 (m), 1308 (m), 1104 (m), 1026 (m) cm^{-1}.

4.1.14. General Procedure 2. Synthesis of Ferrocenyl Quinones 60A-E (Table 2) and 62A-B (Table 3). A dioxane (15 mL) solution of cyclobutenone **45A-E, 46A-B** (0.75 mmol) was heated to reflux under argon for a period of 5 h. The mixture was allowed to cool to room temperature and the solvent was removed on a rotary evaporator. Without purification, the reaction mixture was dissolved in

CH_2Cl_2 (5 mL) and added PbO_2 (525.8 mg, 2.20 mmol). The resulting mixture was allowed to stir at room temperature for 30 minute. After filtration, the solvent was removed on a rotary evaporator. Final purification was achieved by flash chromatography on silica gel using 9:1 hexane/ethyl acetate as eluent. (Note that, if otherwise stated, hydroquinones were not isolated).

4.1.15. 2-Ferrocenyl-3-isopropoxy-5-methyl-[1,4]-benzoquinone (60A) (Table 2, Entry A). General Procedure 2 was followed using cyclobutenone **45A** (275 mg, 0.75 mmol) with an exception that hydroquinone was isolated before oxidation step. Final purification was achieved by flash chromatography on silica gel using 19:1 hexane/ethyl acetate as the eluent. Two fractions were isolated. First fraction (R_f = 0.56 in 9:1 hexane/ethyl acetate) was assigned as **60A** (green solid, 46.5 mg, 17%). The second fraction (R_f = 0.44 in 9:1 hexane/ethyl acetate) was identified as **59A** (bright yellow crystals, 198 mg, 72%). Oxidation of **59A** (80 mg, 0.22 mmol) to **60A** was achieved according to the oxidation procedure stated in the General Procedure 3. Final purification was achieved by flash chromatography on silica gel using 9:1 hexane/ethyl acetate as eluent. A single fraction (R_f = 0.56 in 9:1 hexane/ethyl acetate) was collected to give **60A** (74.8 mg, 94%).

59A: ^{1}H-NMR: ($CDCl_3$): δ 7.13 (brs, 1H), 6.51 (s, 1H), 5.40 (s, 1H), 4.66 (s, 2H), 4.52 (s, 2H), 4.32 (s, 5H), 3.67 (septet, 1H, J = 6.1 Hz), 2.24 (s, 3H), 1.11 (d, 6H, J = 6.1 Hz); ^{13}C-NMR: ($CDCl_3$): δ 147.2 (C), 142.1 (C), 142.0 (C), 124.1 (C), 113.1 (C), 112.7 (CH), 75.5 (CH), 69.9 (Fc peaks as multiplet), 22.5 (CH_3), 16.1 (CH_3); IR (CH_2Cl_2): 3523 (br), 3374 (br), 2977 (m), 2928 (m), 2870 (vw), 1461 (vs), 1331 (m), 1203 (vs), 1104 (m), 1050 (s) cm^{-1}; MS (EI): 366 ([M]$^+$, 100), 323 (40),

257 (95), 229 (18); HRMS (EI): Calc. for. $C_{20}H_{22}{}^{56}FeO_3$: 366.0918. Found: 366.0901.

60A: ^{1}H-NMR: ($CDCl_3$): δ 6.52 (s, 1H), 5.14 (s, 2H), 4.73 (septet, 1H, *J* = 6.1 Hz), 4.51 (s, 2H), 4.14 (s, 5H), 2.08 (s, 3H), 1.27 (s, 3H, *J* = 6.1 Hz), 1.27 (s, 3H); ^{13}C-NMR: ($CDCl_3$): δ 187.7 (C), 183.9 (C), 152.7 (C), 143.9 (C), 134.4 (CH), 134.0 (C), 76.3 (CH), 74.6 (C), 72.8 (CH), 70.7 (CH), 70.4 (CH), 23.1 (CH_3), 15.6 (CH_3); IR (CH_2Cl_2): 2981 (w), 1650 (vs), 1571 (w), 1380 (w), 1357 (w), 1188 (w), 1099 (m), 1064 (w) cm^{-1}; MS (EI): 364 ([M]$^+$, 69), 322 (100), 294 (92), 257 (44), 229 (31), 121 (13); HRMS (EI): Calc. for. $C_{20}H_{20}{}^{56}FeO_3$: 364.0761. Found: 364.0750.

4.1.16. 2-Ferrocenyl-3,5-dimethyl-[1,4]-benzoquinone (60B) (Table 2, Entry B). General Procedure 2 was followed using cyclobutenone **45B** (110 mg, 0.34 mmol). Final purification was achieved by flash chromatography on silica gel using 9:1 hexane/ethyl acetate as eluent. A single fraction (R_f = 0.64 in 9:1 hexane/ethyl acetate) was collected to give **60B** (78 mg, 71%).

60B: ^{1}H-NMR: ($CDCl_3$): δ 6.54 (d, 1H, *J* = 1.1 Hz), 4.67 (s, 2H), 4.49 (s, 2H), 4.13 (s, 5H), 2.12 (s, 3H), 2.05 (d, 3H, *J* = 1.1 Hz); ^{13}C-NMR: ($CDCl_3$): δ 188.1 (C), 187.0 (C), 145.4 (C), 143.6 (C), 139.3 (C), 134.2 (CH), 77.6 (C), 72.9 (CH), 70.5 (CH), 70.4 (CH), 16.2 (CH_3), 15.5 (CH_3); IR (CH_2Cl_2): 3098 (w), 2961 (w), 2924 (w), 1650 (vs), 1636 (vs), 1580 (s), 1413 (m), 1270 (s), 1058 (m) cm^{-1}; MS (EI): 320 ([M]$^+$, 100), 256 (85), 181 (5), 69 (9); HRMS (EI): Calc. for. $C_{18}H_{16}{}^{56}FeO_2$: 320.0499. Found: 320.0490.

4.1.17. 2,3-Diferrocenyl-5-methyl-[1,4]-benzoquinone (60C) (Table 2, Entry C). General Procedure 2 was followed using cyclobutenone **45C** (174 mg, 0.35 mmol). Final purification was achieved by flash chromatography on silica gel using 9:1 hexane/ethyl acetate as eluent. A single fraction (R_f = 0.51 in 9:1 hexane/ethyl acetate) was collected to give **60C** (97 mg, 56%).

60C: ^{1}H-NMR: ($CDCl_3$): δ 6.54 (s, 1H), 4.32 (brs, 8H), 4.01 (s, 5H), 3.99 (s, 5H), 2.10 (s, 3H); ^{13}C-NMR: ($CDCl_3$): δ 186.2 (C), 185.7 (C), 145.4 (C), 141.8 (C), 141.5 (C), 133.6 (CH), 79.5 (C), 79.1 (C), 72.6 (CH), 70.1 (CH), 70 (CH), 69.6 (CH), 69.5 (CH), 16.0 (CH_3); IR (CH_2Cl_2): 3098 (w), 2926 (w), 1650 (vs), 1542 (w), 1457 (s), 1306 (m), 1270 (w), 1216 (w), 1002 (w) cm^{-1}; MS (EI): 490 ($[M]^+$, 100), 422 (46), 360 (10), 304 (14), 245 (8), 186 (8); HRMS (EI): Calc. for. $C_{27}H_{22}{}^{56}Fe_2O_2$: 490.0318. Found: 490.0326.

4.1.18. 2-Ferrocenyl-3-isopropoxy-5-phenyl-[1,4]-benzoquinone (60D) (Table 2, Entry D). General Procedure 2 was followed using cyclobutenone **45D** (49 mg, 0.12 mmol). Final purification was achieved by flash chromatography on silica gel using 9:1 hexane/ethyl acetate as eluent. A single fraction (R_f = 0.41 in 9:1 hexane/ethyl acetate) was collected to give **60D** (30 mg, 61%).

60D: ^{1}H-NMR: ($CDCl_3$): δ 8.25 (m, 2H), 7.45 (m, 3H), 7.37 (s, 1H), 6.00 (septet, 1H, J = 6.0 Hz), 5.38 (s, 2H), 4.55 (s, 2H), 4.11 (s, 5H), 1.47 (d, 6H, J = 6.0 Hz); ^{13}C-NMR: ($CDCl_3$): δ 188.3 (C), 187.6 (C), 161.6 (C), 140.4 (C), 137.7 (CH), 133.7 (C), 133.4 (CH), 131.7 (CH), 128.9 (CH), 128.6 (C), 77.6 (C), 75.4 (CH), 71.9 (CH), 70.7 (CH), 70.5 (CH), 23.9 (CH_3); IR (CH_2Cl_2):3069 (w), 2361 (vw), 1712 (w), 1667 (vs), 1625 (s), 1580 (m), 1451 (m), 1382 (m),1358 (w), 1333 (w), 1094

(m) cm^{-1}; MS (EI): 426 ($[M]^+$, 37), 384 (100), 385 (25), 319 (11); HRMS (EI): Calc. for. $C_{25}H_{22}{}^{56}FeO_3$: 426.0918. Found: 426.0921.

4.1.19. 2,3-Diferrocenyl-5-phenyl-[1,4]-benzoquinone (60E) (Table 2, Entry E). General Procedure 2 was followed using cyclobutenone **45E** (20 mg, 0.04 mmol). Final purification was achieved by flash chromatography on silica gel using 9:1 hexane/ethyl acetate as eluent. A single fraction (R_f = 0.61 in 9:1 hexane/ethyl acetate) was collected to give **60E** (15 mg, 75%).

60E: ^{1}H-NMR: ($CDCl_3$): δ 7.55 (m, 2H), 7.47 (m, 3H), 6.80 (s, 1H), 4.43 (s, 2H), 4.38 (s, 2H), 4.36 (s, 4H), 4.06 (s, 10H); ^{13}C-NMR: ($CDCl_3$):δ 185.9 (C), 185.6 (C), 146.2 (C), 143.0 (C), 141.5 (C), 133.9 (CH), 133.4 (CH), 130.2 (CH), 129.6 (CH), 128.9 (CH), 73.5 (CH), 73.4 (CH), 71.2 (C), 71.0 (C), 70.9 (CH), 70.8 (CH), 70.7 (CH), 70.6 (CH). (It should be noted that carbon peaks are related to ferrocene appeared as multiplet); IR (CH_2Cl_2): 3099 (vw), 2928 (vw), 1650 (vs), 1457 (m), 1310 (m), 1150 (m), 1043 (m) cm^{-1}; MS (EI): 552 ($[M]^+$, 100), 484 (23), 422 (9), 366 (21), 186 (6); HRMS (EI): Calc. for. $C_{32}H_{24}{}^{56}Fe_2O_2$: 552.04750. Found: 552.0498.

4.1.20. 3-Ferrocenyl-2-isopropoxy-5-methyl-[1,4]-benzoquinone (62A) (Table 3, Entry A). General Procedure 2 was followed using cyclobutenone **46A** (15 mg, 0.04 mmol). Final purification was achieved by flash chromatography on silica gel using 9:1 hexane/ethyl acetate as eluent. A single fraction (R_f = 0.57 in 9:1 hexane/ethyl acetate) was collected to give **62A** (11.5 mg, 77%).

62A: ^{1}H-NMR: ($CDCl_3$): δ 6.41 (s, 1H), 5.01 (s, 2H), 4.72 (septet, 1H, J = 6.2 Hz), 4.40 (s, 2H), 4.03 (s, 5H), 2.00 (s, 3H), 1.18 (d, 6H, J = 6.2 Hz); ^{13}C-NMR: ($CDCl_3$): δ 187.9 (C), 183.8 (C), 152.6 (C), 146.5 (C), 133.9 (C), 132.0 (CH), 76.4 (CH), 74.9 (C), 72.7 (CH), 70.5 (CH), 70.4 (CH), 23.1 (CH_3), 16.7 (CH_3); IR (CH_2Cl_2): 2979 (w), 1651 (vs), 1572 (w), 1380 (w), 1096 (m), 909 (s) cm^{-1}; MS (EI): 364 ($[M]^+$, 91), 322 (99), 294 (100), 257 (72), 229 (12), 69 (17); HRMS (EI): Calc. for. $C_{20}H_{20}{}^{56}FeO_3$: 364.0761. Found: 364.0748.

4.1.21. 3-Ferrocenyl-2,5-dimethyl-[1,4]-benzoquinone (62B) (Table 3, Entry B). General Procedure 2 was followed using cyclobutenone **46B** (10 mg, 0.03 mmol). Final purification was achieved by flash chromatography on silica gel using 9:1 hexane/ethyl acetate as eluent. A single fraction (R_f = 0.61 in 9:1 hexane/ethyl acetate) was collected to give **62B** (7 mg, 70%).

62B: ^{1}H-NMR: ($CDCl_3$): δ 6.56 (s, 1H), 4.67 (s, 2H), 4.49 (s, 2H), 4.13 (s, 5H), 2.05 (s, 3H), 2.04 (s, 3H); ^{13}C-NMR: ($CDCl_3$): δ 187.7 (C), 187.4 (C), 146.2 (C), 143.8 (C), 139.2 (C), 133.4 (CH), 77.6 (C), 72.9 (CH), 70.6 (CH), 70.4 (CH), 16.6 (CH_3), 15.1 (CH_3); IR (CH_2Cl_2): 2364 (w), 1650 (vs), 1632 (vs), 1583 (s), 1443 (m), 1372 (m), 1305 (s), 1051 (m) cm^{-1}; MS (EI): 320 ($[M]^+$, 100), 294 (10), 256 (67), 121 (8); HRMS (EI): Calc. for. $C_{18}H_{16}{}^{56}FeO_2$: 320.0499. Found: 320.0495.

4.2. Synthesis of Ferrocenyl Based Burning Rate Catalysts

4.2.1. Ferrocenecarboxylic acid (65). In a round bottom flask under argon, ferrocene (**1**) (7.5 g, 40 mmol) was dissolved in THF and cooled to 0 ^{0}C. To this solution *tert*-butyllithium (22.0 mL, 1.85 M pentane solution, 40 mmol) was added via syringe during 15 minutes. The resulting mixture was allowed to stir at 0 ^{0}C for 15 minutes and then at room temperature for one and half hours. At the end of the period, the flask was opened to air and added dry ice (3.6 g, 80 mmol). Resulting mixture was added 6 N HCl until ferrocenecarboxylic acid (**65**) precipitated. The precipitate was filtrated and washed with cold water. Final purification was achieved by flash chromatography on silica gel using 1:1 hexane/ethyl acetate as eluent. A yellow fraction was collected to give **65** (4.2 g, 45%).

65: ^{1}H NMR ($CDCl_3$): δ 4.87 (s, 2H), 4.47 (s, 2H), 4.26 (s, 5H) (Due to deuterium-hydrogen exchange, acidic proton was not observed); IR (CH_2Cl_2): 3100-2500 (br, s), 1722 (m), 1675 (vw), 1478 (m), 1296 (m).

4.2.2. Ferrocenyl acid chloride (66). Into a two-necked round bottom flask equipped with reflux condenser under argon, ferrocenecarboxylic acid (**65**) (7.5g, 33 mmol) was placed and dissolved in CH_2Cl_2 (15 mL). After addition of oxalyl chloride (6.5 mL, 2.0 M CH_2Cl_2 solution, 12.0 mmol), the resulting mixture was refluxed at room temperature for one hour. After cooling to room temperature, the solvents were removed on rotary evaporator.

66: ^{1}H NMR ($CDCl_3$): δ 4.92 (t, 2 H, *J* = 2.0 Hz), 4.64 (t, 2 H, *J* = 2.0 Hz), 4.34 (s, 5 H). Due to the fact that this compound in not very stable, it was not further characterized. Prior to its isolation, it was used for the synthesis of catalyst **47**.

4.2.4. *N*,*N*'-bis[ferrocenylcarbonyl]ethylenediamine (47). Ferrocenyl acid chloride (**66**) (as crude) was added DMF (3 mL) and cooled to 0 ^{0}C. To this mixture ethylenediamine (0.12 mL, 1.8 mmol) was added via syringe. Resulting mixture was stirred at 0 ^{0}C for 30 minutes and three hour at room temperature. At the completion of the time period, cold water (80 mL) was added to the reaction mixture. The formed precipitate was filtrated and washed with cold water. The isolated compound was assigned as *N*,*N*-bis[ferrocenylcarbonyl]ethylenediamine (**47**) (0.65 g, 75%).

47: ^{1}H NMR ($CDCl_3$): δ 6.77 (br s, 2H), 4.74 (s, 4H), 4.36 (s, 4H), 4.18 (s, 10H), 3.6 (s, 4H); ^{13}C NMR ($CDCl_3$): δ 172.1 (C), 75.6 (C), 70.6 (CH), 69.8 (CH), 68.3 (CH), 40.9 (CH_2).

4.2.5. Ferrocenecarbaldehyde (67). In a round bottom flask equipped with reflux condenser, THF (60 mL) solution of ferrocene (**1**) (4.0 g, 21.5 mmol) was prepared and this solution is cooled to -20 ^{0}C using methanol and ice. *tert*-Butyllithium (19.0 mL, 1.7 M pentane solution, 32.3 mmol) was added in 15 minutes via syringe. The resulting mixture was allowed to warm to 10 ^{0}C and stirred for 30 minutes. Then DMF (3.4 mL, 43.0 mmol) was added. The color of the mixture turned red, and in a few minutes yellow precipitate formed. Then dilute HCl solution was added. The reaction mixture was diluted and extracted with CH_2Cl_2 (2 × 50 mL). The collected organic layers were dried over magnesium sulfate and the

solvents were removed on a rotary evaporator. Final purification was performed using flash column chromatography using 9:1 hexane/ethyl acetate as eluent. A single fraction (R_f = 0.41, 4:1 hexane/ethyl acetate) was collected and assigned as ferrocenecarbaldehyde (**67**) (3.77 g, 82%).

67: ^{1}H-NMR: ($CDCl_3$): δ 9.96 (s, 1H), 4.80 (t, 2H, *J* = 1.8 Hz), 4.61 (t, 2H, *J* = 1.8 Hz), 4.28 (s, 5H); IR (CH_2Cl_2): 3099 (vw), 3058 (vw), 2960 (vw), 2824 (w), 2763 (w), 1680 (s), 1455 (s), 1373 (w), 1269 (s), 1246 (m), 1036 (w), 827 (m) cm^{-1}. The spectral data are in agreement with those reported previously for this compound [73].

4.2.6. Ferrocene-1,1'-dicarbaldehyde (68). A hexane (75 mL) solution of ferrocene (**1**) (4.0 g, 21.5 mmol) was prepared in a round bottom flask. After addition of TMEDA (5.0 mL, 53.0 mmol), the reaction mixture was added n-butyllithium (19.2 mL, 2.5 M hexane solution, 48 mmol) in 15 minutes via syringe. The resulting mixture was stirred over night. To this solution ether (15 mL) solution of DMF (3.6 mL, 45.5 mmol) was added and allowed to stir for 10 minutes. Afterward, HCl solution (14%, 60 mL) was added. The reaction mixture was diluted and extracted with CH_2Cl_2 (3 × 30 mL). The collected organic layers were dried over magnesium sulfate and the solvents were removed on a rotary evaporator. Final purification was performed using flash column chromatography using 9:1 hexane/ethyl acetate as eluent. A single fraction (R_f = 0.44, 1:1 hexane/ethyl acetate) was collected and assigned as ferrocene-1,1'-dicarbaldehyde (**68**) (4.16 g, 80%).

68: ^{1}H-NMR: ($CDCl_3$): δ 9.95 (s, 2H), 4.89 (t, 4H, *J* = 1.8 Hz), 4.61 (t, 2H, *J* = 1.8 Hz), 4.28 (s, 5H); IR (CH_2Cl_2): 3099 (vw), 3058 (vw), 2960 (vw), 2824 (w),

2763 (w), 1680 (s), 1455 (s), 1373 (w), 1269 (s), 1246 (m), 1036 (w), 827 (m) cm^{-1}. The spectral data are in agreement with those reported previously for this compound [73, 76].

4.2.7. 1,6-Diferrocene-2,5-diazahexa-1,5-diene (69). Potassium carbonate (0.97 g, 7.0 mmol), ethylenediamine (0.47 mL, 7.0 mmol), ferrocenecarbaldehyde (**67**) (3.0 g, 14.0 mmol) and dry methanol (15 mL) were placed in a round bottom flask with reflux condenser and the mixture was refluxed for 2 hours. At the end, the solvents were removed on a rotary evaporator. The crude product was recrystallized from ethyl alcohol to form red-orange crystals of compound **69** (2.3 g, 83%) as a pure solid.

69: ^{1}H-NMR: ($CDCl_3$): δ 8.14 (s, 2H), 4.60 (t, 4H, J = 1.9 Hz), 4.30 (t, 4H, J = 1.9 Hz), 4.14 (s, 10H), 3.75 (s, 4H); IR (KBr pellet): 1636 (vs) cm^{-1}. The spectral data are in agreement with those reported previously for this compound [75].

4.2.8. 1,6-Diferrocene-2,5-diazahexane (48). Compound **69** (2.0 g, 5.0 mmol), ether (150 mL) and lithium aluminum hydride (0.46 g, 12.0 mmol) was placed in a round bottom flask equipped with reflux condenser and the mixture was refluxed for 2 hours. Latterly, the reaction mixture was quenched with water slowly, and the resulting mixture was diluted and extracted with CH_2Cl_2 (2 × 40 mL). After removal of solvent on rotary evaporator, the crude product was recrystallized from toluene to form yellow crystals of compound **48** (1.82 mg, 95%) as a pure solid.

48: ^{1}H-NMR: ($CDCl_3$): δ 4.17 (t, 4H, J = 1.9 Hz), 4.11 (s, 10H), 4.09 (t, 4H, J = 1.9 Hz), 3.52 (s, 4H), 2.74 (s, 4H), 1.76 (br s, 2H); IR (KBr pellet): 3401 (vw),

1641 (w) cm^{-1}. The spectral data are in agreement with those reported previously for this compound [75].

4.2.9. 1,15-Diferrocene-2,5,8,11,14-pentaazapentadeca-1,5-diene (70). Into a round bottom flask equipped with reflux condenser, ferrocenecarbaldehyde (**67**) (3.0 g, 14.0 mmol), tetraethylenepentamine (0.47 mL, 7.0 mmol), potassium carbonate (0.97 g, 7.0 mmol) and dry ethanol (15 mL) was refluxed for 2 hours. The crude product was recrystallized from ethyl alcohol to form red-orange crystals of compound **70**. Due to its sensitivity, compound **70** was used directly for the synthesis of **49** without further purification.

4.2.10. 1,15-Diferrocene-2,5,8,11,14-pentaazadodecane (49). Compound **70** (2.0 g, 5.0 mmol), ether (150 mL) and lithium aluminum hydride (0.46 g, 12.0 mmol) was placed in a round bottom flask equipped with reflux condenser and the mixture was refluxed for 2 hours. Then, the reaction mixture was quenched with water slowly, and the resulting mixture was diluted and extracted with CH_2Cl_2 (2 × 40 mL). After removal of solvent on rotary evaporator, the crude product was recrystallized from toluene to form yellow crystals of compound **49** (1.71 mg, 85%) as a pure solid.

49: ^{1}H-NMR: ($CDCl_3$): δ 4.18 (s, 4H, J = 1.9 Hz), 4.13 (s, 10H), 4.10 (s, 4H,), 3.50 (s, 4H), 2.72 (br s, 8H), 2.71 (br s, 8H), 1.75 (br s, 5H); IR (KBr pellet): 3401 (vw), 1641 (w) cm^{-1}. The compound **49** is so polar and viscous material that further purification was not achievable.

4.2.11. *N*,*N*-dimethylaminoferrocene (71). Into a round bottom flask, acetic acid (40 mL), bis(dimethylamino)methane (4.32 g, 42.2 mmol) and phosphoric acid (4.32 g) was placed and stirred well. Then, ferrocene (**1**) (4.64 g, 25.0 mmol) was added to this mixture. Resulting suspension was heated for 5 hours in a water bath under argon. After cooling room temperature, the mixture was diluted with water (55 mL). Unreacted ferrocene (**1**) was removed through extraction with ether (3 × 30 mL). Water layer was cooled in ice bath and made basic using sodium hydroxide (24.5 g). Formed tertiary amine **71** became a black colored oily layer. The mixture was then extracted with ether (3 × 50 mL). After drying the combined organic layers over sodium sulfate, the solvents were removed on a rotary evaporator. The red solid was used in the synthesis of **72** directly without purification [92].

4.2.12. *N*,*N*-dimethylaminomehtylferrocene methyl iodide (72). The crude tertiary amine **71** was dissolved in methanol (5.4 mL) and this solution was added methyl iodide (12.3 g, 87.0 mmol). The resulting mixture was heated for 5 minutes and after cooling to room temperature added ether (80 mL). after precipitation of the salt **72** it was filtered through Büchner funnel and washed with ether. Resulting orange color solid was found to be *N*,*N*-dimethylaminomehtylferrocene (**72**) (7.8 g, 81%) [92].

4.2.13. Ferrocenylacetonitrile (73). Potassium cyanide (5.7 g, 88.0 mmol) was dissolved in water (60 mL) in a round bottom flask equipped with reflux condenser. To this solution, ferrocene salt **72** (5.8 g, 15.0 mmo) was added and resulting mixture was refluxed for 2 hours. At the end of time period, the mixture

was filtered and the liquid part was extracted with ether (3 × 15 mL). Crude ferrocenylacetonitrile (**73**) was obtained as solid by distilling solvents. The crude product was added onto boiling hexane (20 mL). While the solution was still hot, it was filtered to remove some black impurities. The collected hexane solution was allowed to cool to room temperature and ferrocenylacetonitrile (**73**) was obtained as yellow crystals (m.p. 79-82 ^{0}C, 2.6 g, 77%) [93].

4.2.14. β-Ferrocenylethylamine (74). Ether (35 mL) suspension of lithium aluminum hydride (0.65 g, 17.0 mmol) was refluxed for 1 hour. Ether (16 mL) solution of **73** (2.5 g, 11.0 mmol) was added to ether-lithium aluminum hydride suspension and refluxed for 2 hours. At the end of the time period, the mixture was cooled to 0 ^{0}C in an ice bath and then added water (20 mL), sodium bicarbonate solution (20%, 15 mL), water (20 mL) respectively. Ether layer was decanted and collected organic layers were saturated with hydrogen chloride. Resulting salt filtered under argon. Solid part was added sodium hydroxide (2 N, 20 mL) and extracted with ether (3 × 15 mL). Ether layer was dried over sodium sulfate and removed on a rotary evaporator. The oily crude product was purified by vacuum distillation (120 ^{0}C, 0.5 mmHg) to give β-Ferrocenylethylamine (**74**) (b.p. 118-120 ^{0}C, 2.11 g, 9.46 mmol, 86%) [94].

74: ^{1}H-NMR: ($CDCl_3$): δ 4.04 (s, 5H), 4.01 (s, 2H), 4.00 (s, 2H), 2.74 (t, 2H, *J* = 6.7 Hz), 2.42 (t, 2H, *J* = 6.7 Hz), 1.60 (br s, 2H). The spectral data are in agreement with those reported previously for this compound [94].

4.2.15. 1-(2-ferrocenylethyl)-3-{36-[3-(2-ferrocenylethyl)ureido] hexatriontyl}urea (50). Into a round bottom flask equipped with reflux condenser, **74** (78.0 mg, 0.34 mmol) and DDI (0.1 g, 0.17 mmol) and THF (10 mL) were placed and refluxed for 3 hours. At the end of the time period, solvents were removed on rotary evaporator to give **50** (131 mg, 0.16 mmol, 94%).

50: ^{1}H-NMR: ($CDCl_3$): δ 4,03 (s, 5H), 4.00 (s, 2H), 3.99 (s, 2H), 3.67, 3.19, 3.03, 2.45, 1.77, 1.38, 1.19, 0.81; ^{13}C-NMR: ($CDCl_3$): δ 159.0 (C), 86.1 (C), 69.0 (CH), 68.7 (CH), 68.3 (CH), 42.0 (CH), 40.9 (CH_2), 32.3 (CH_2), 30.9 (CH_2), 30.7 (CH_2), 30.4 (CH_2), 30.0 (CH_2), 29.7 (CH_2), 27.4 (CH_2), 26.0 (CH_2), 23.1 (CH_2), 14.5 (CH_3); IR (CH_2Cl_2): 3400 (w), 3095 (vw), 2927 (vs), 2855 (s), 1670 (s), 1533 (s), 1464 (m), 907 (s), 822 (w) cm^{-1}.

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APPENDIX

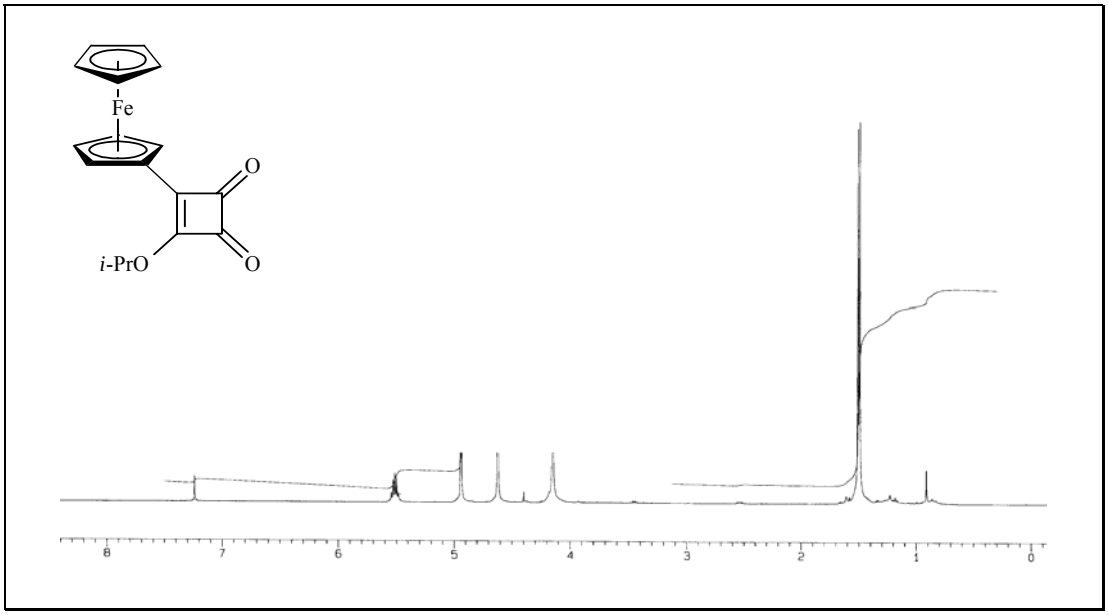

Figure A1. ^{1}H-NMR Spectrum (400 MHz) of ferrocenyl cyclobutenedione **52A**

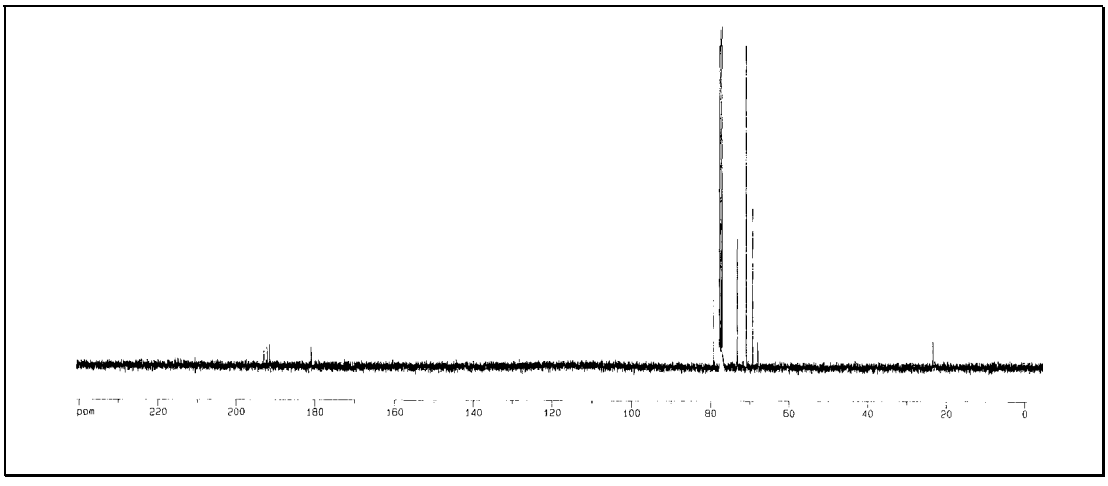

Figure A2. ^{13}C-NMR Spectrum (100 MHz) of ferrocenyl cyclobutenedione **52A**

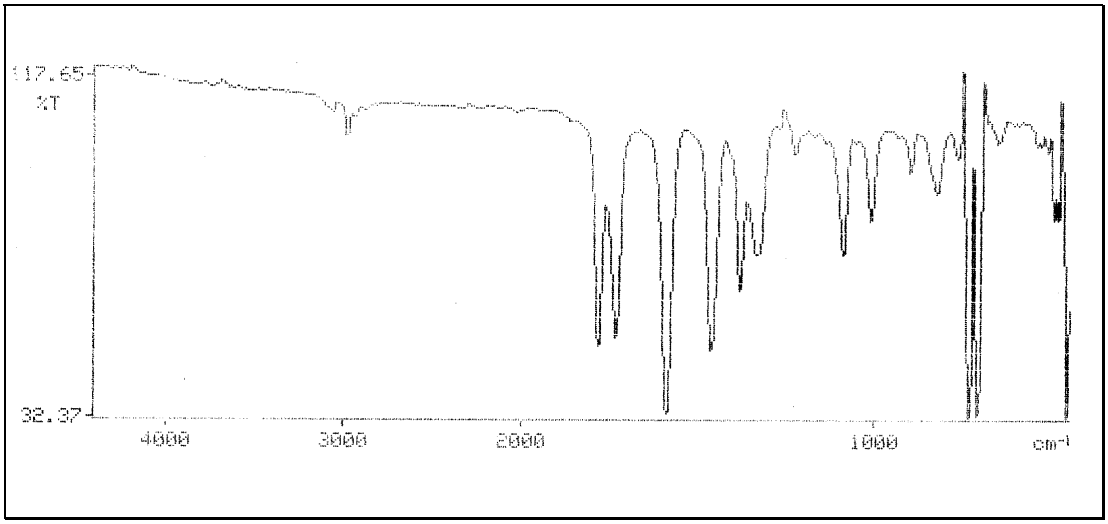

Figure A3. FT-IR Spectrum of ferrocenyl cyclobutenedione **52A**

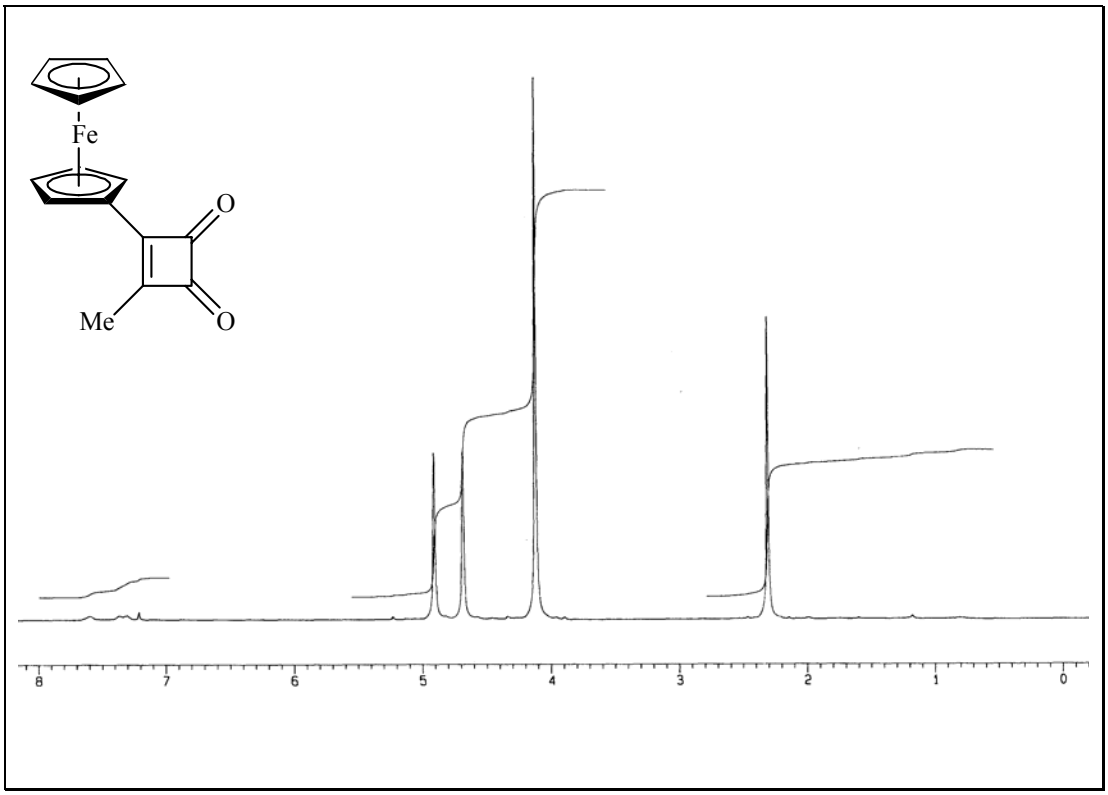

Figure A4. ^{1}H-NMR Spectrum (400 MHz) of ferrocenyl cyclobutenedione **52B**

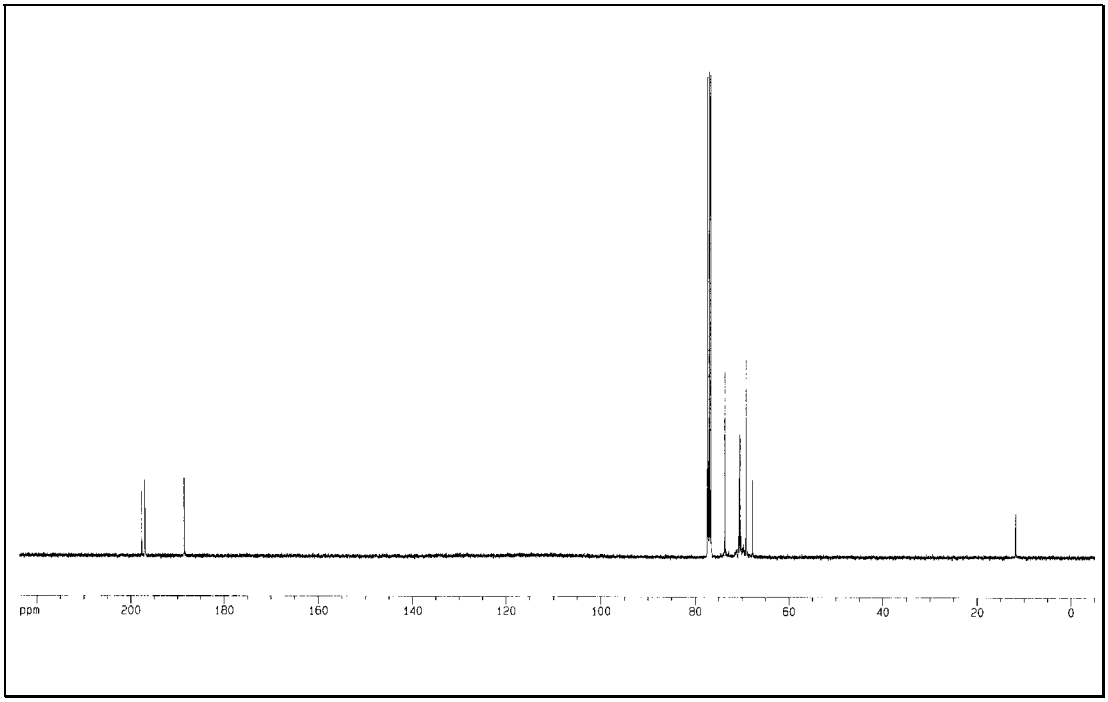

Figure A5. ^{13}C-NMR Spectrum (100 MHz) of ferrocenyl cyclobutenedione **52B**

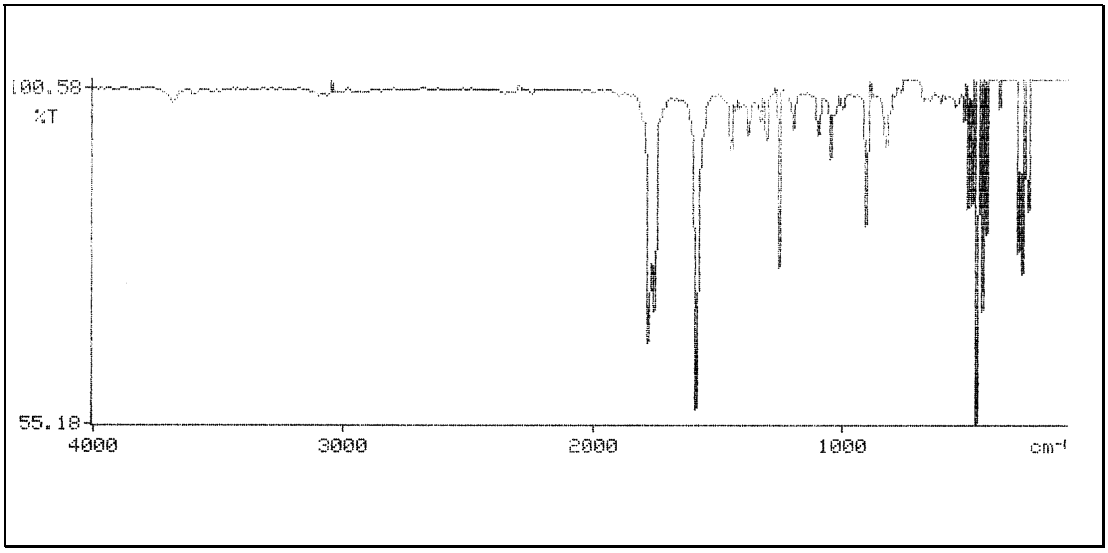

Figure A6. FT-IR Spectrum of ferrocenyl cyclobutenedione **52B**

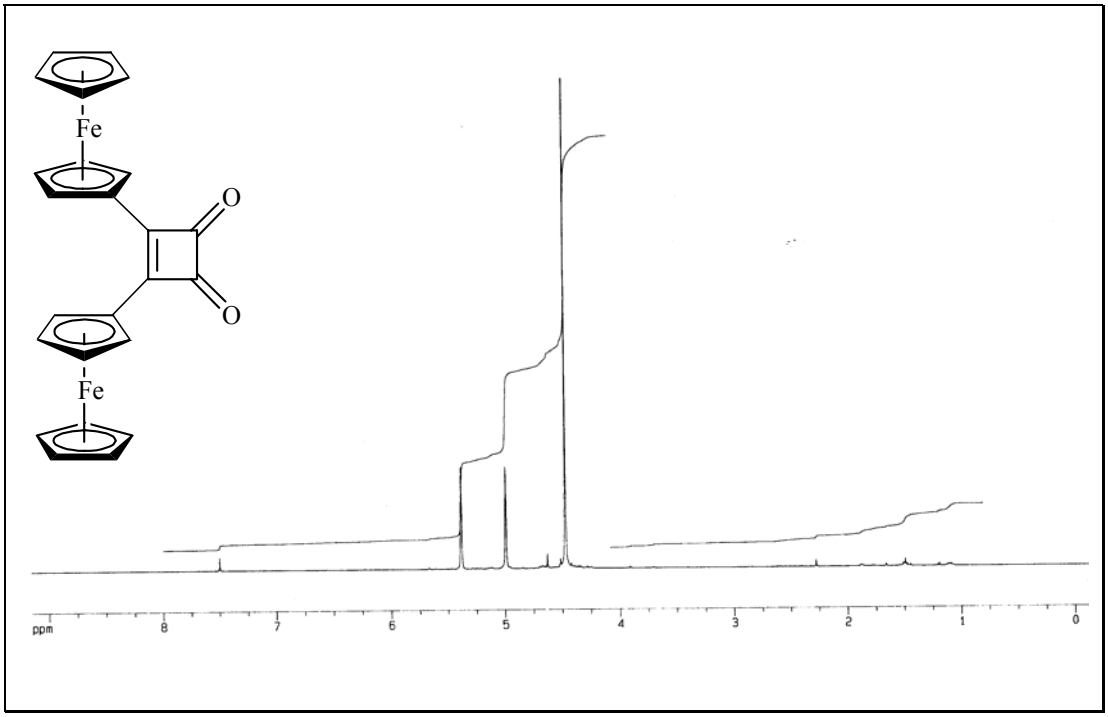

Figure A7. ^{1}H-NMR Spectrum (400 MHz) of ferrocenyl cyclobutenedione **52C**

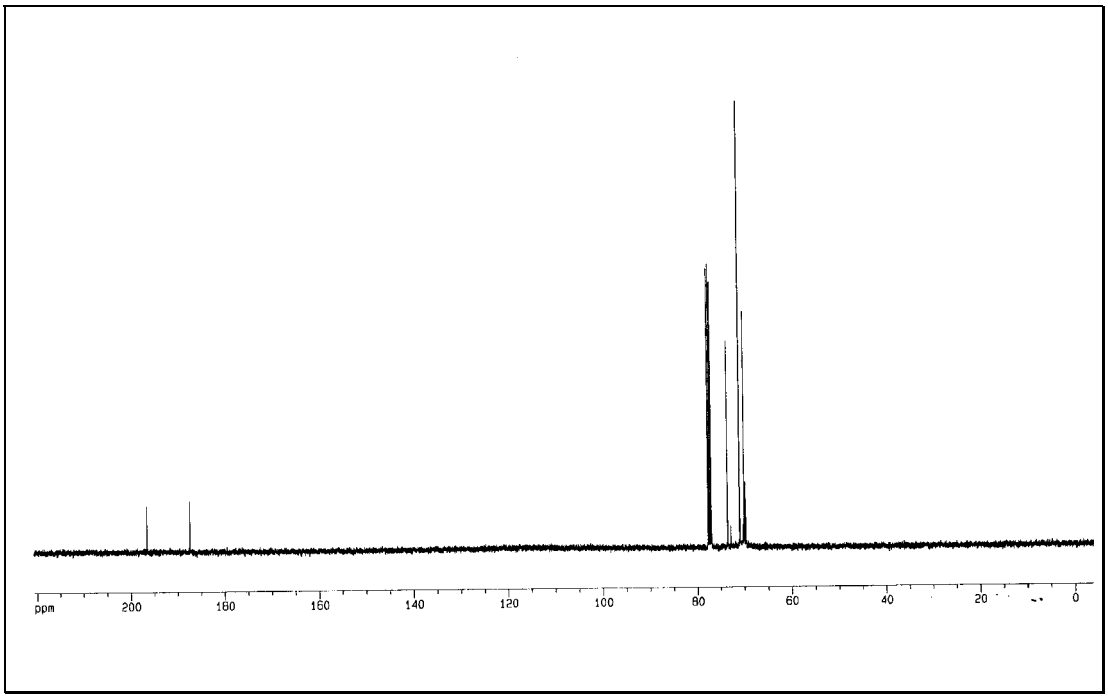

Figure A8. ^{13}C-NMR Spectrum (100 MHz) of ferrocenyl cyclobutenedione **52C**

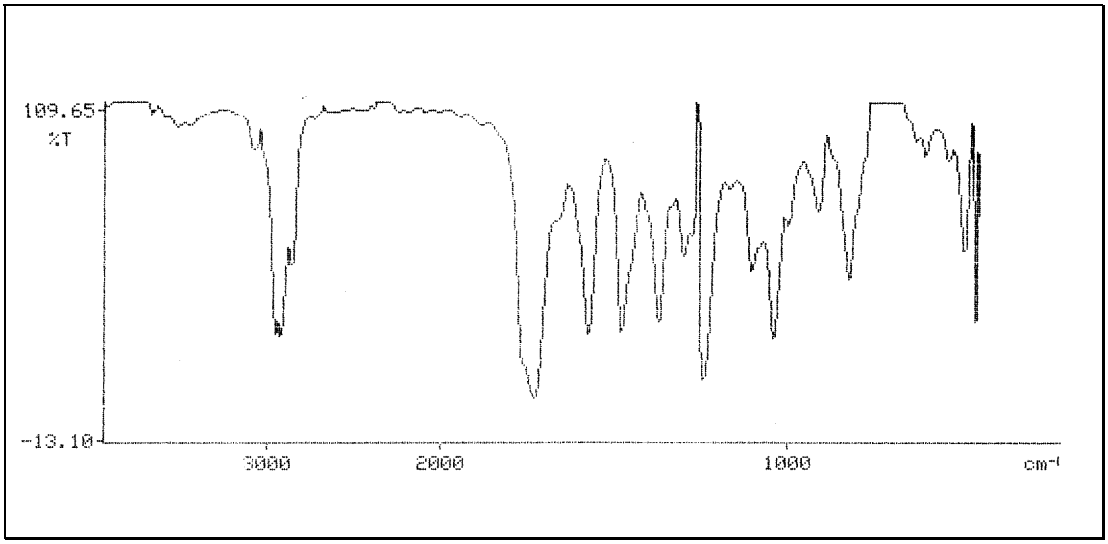

Figure A9. FT-IR Spectrum of ferrocenyl cyclobutenedione **52C**

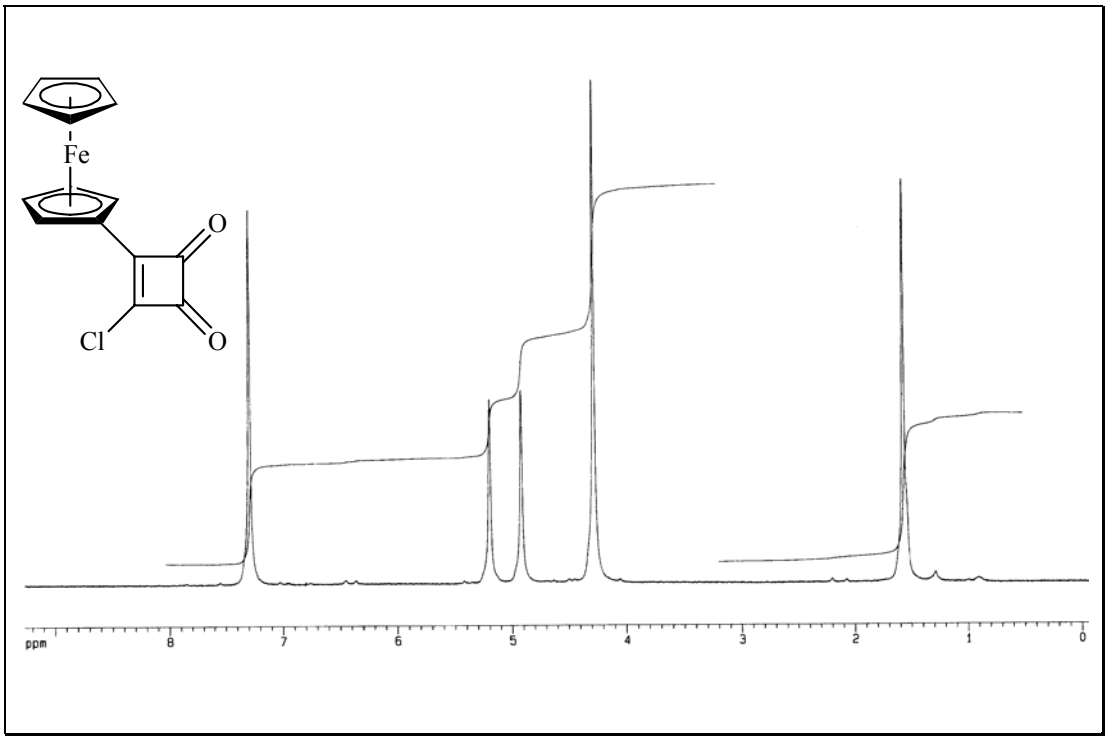

Figure A10. ^{1}H-NMR Spectrum (400 MHz) of ferrocenyl cyclobutenedione **52D**

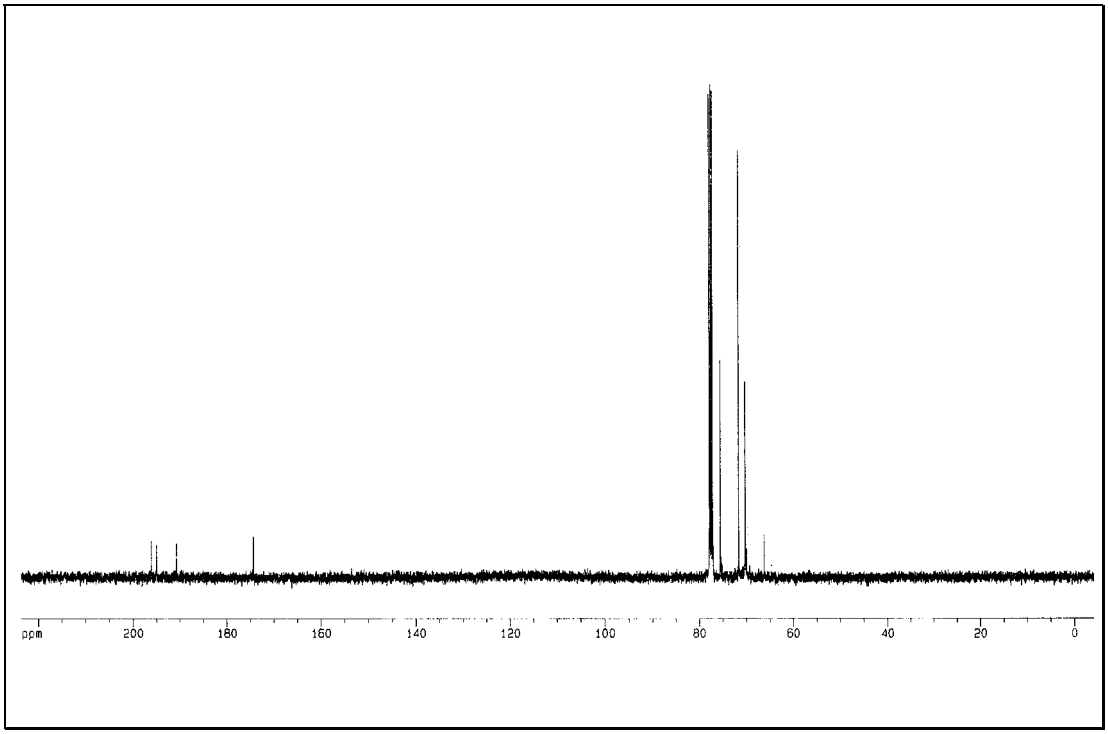

Figure A11. ^{13}C-NMR Spectrum (100 MHz) of ferrocenyl cyclobutenedione **52D**

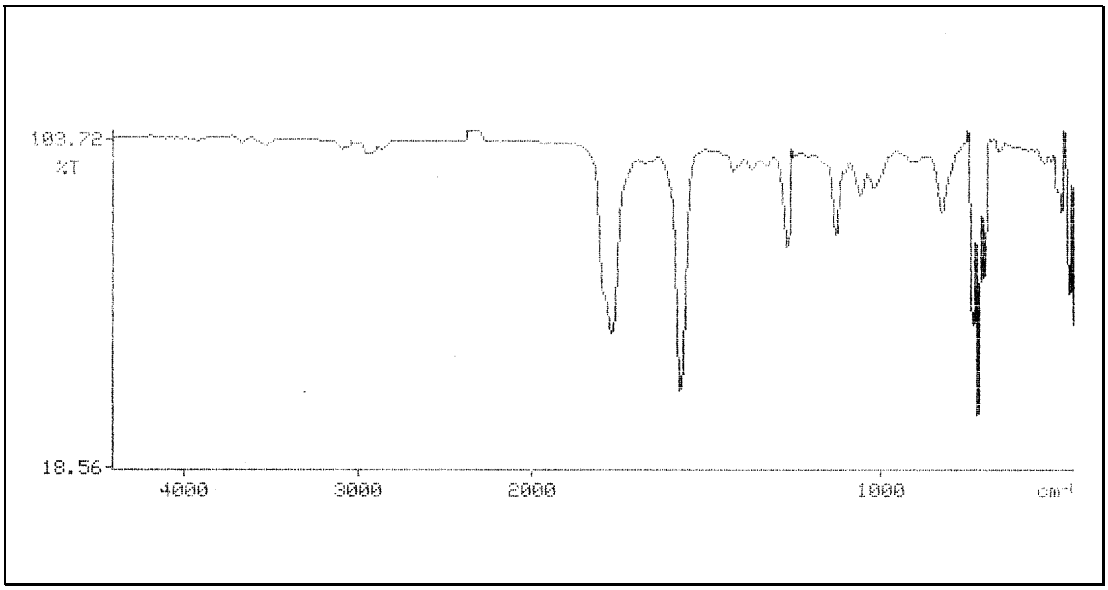

Figure A12. FT-IR Spectrum of ferrocenyl cyclobutenedione **52D**

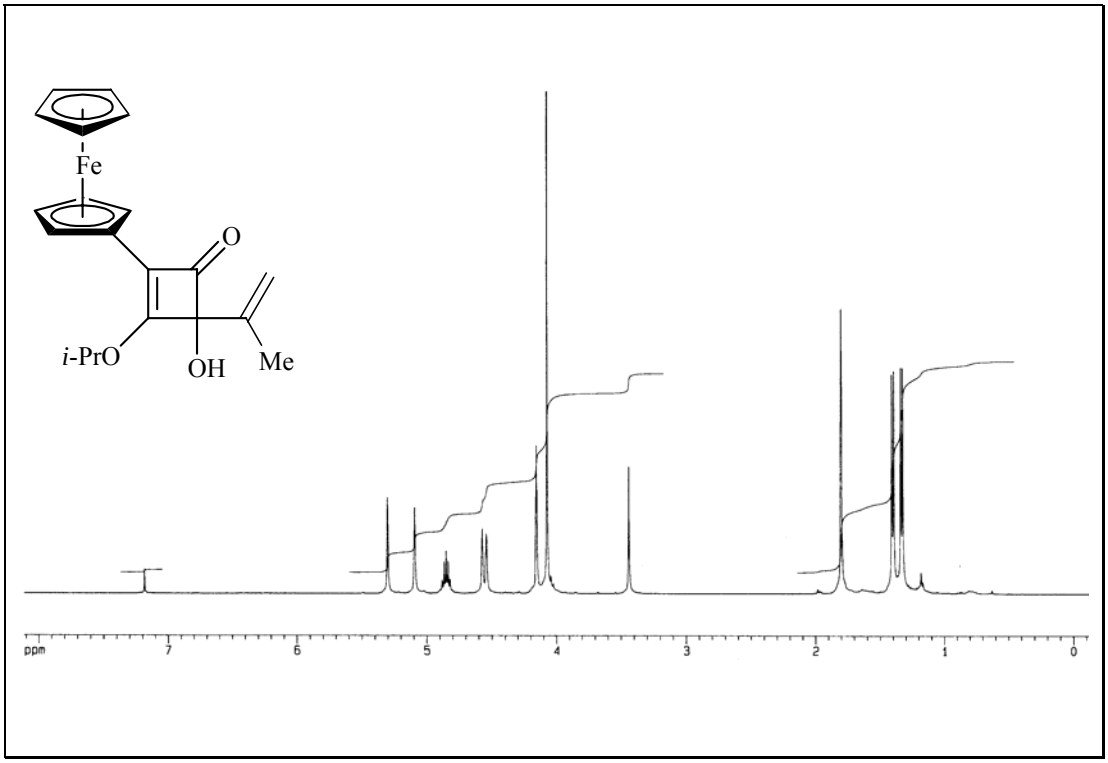

Figure A13. ^{1}H-NMR Spectrum (400 MHz) of ferrocenyl cyclobutenone **45A**

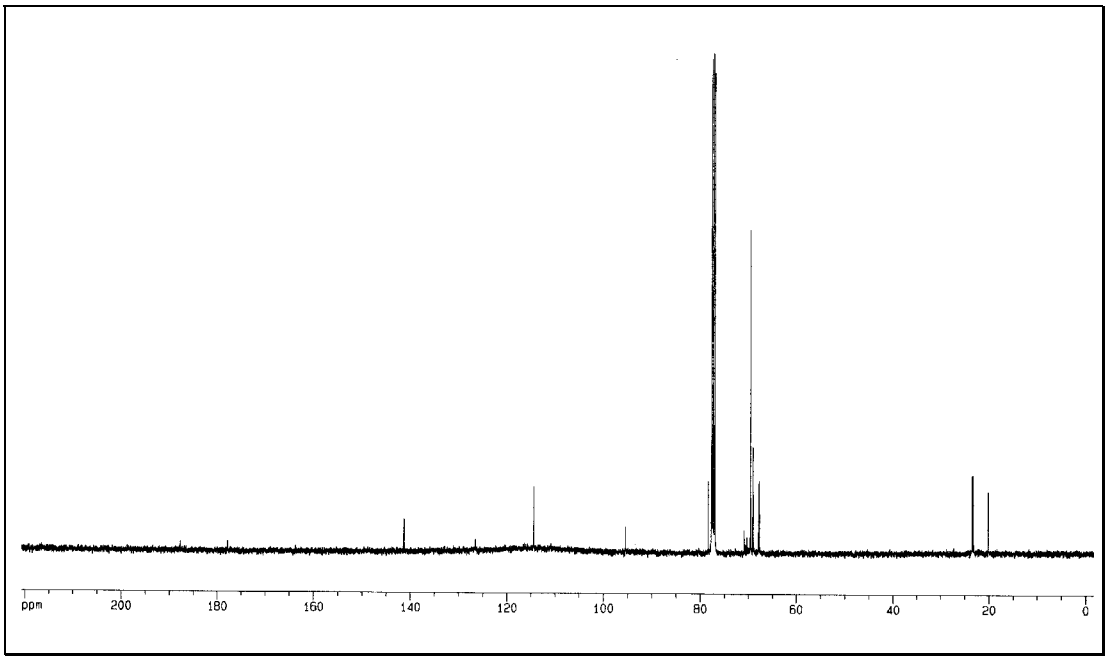

Figure A14. ^{13}C-NMR Spectrum (100 MHz) of ferrocenyl cyclobutenone **45A**

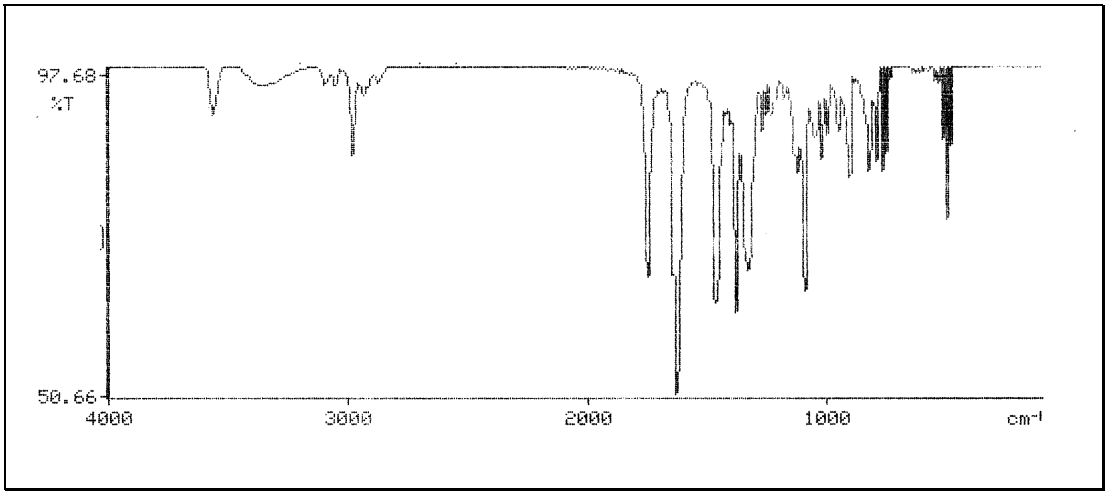

Figure A15. FT-IR Spectrum of ferrocenyl cyclobutenone **45A**

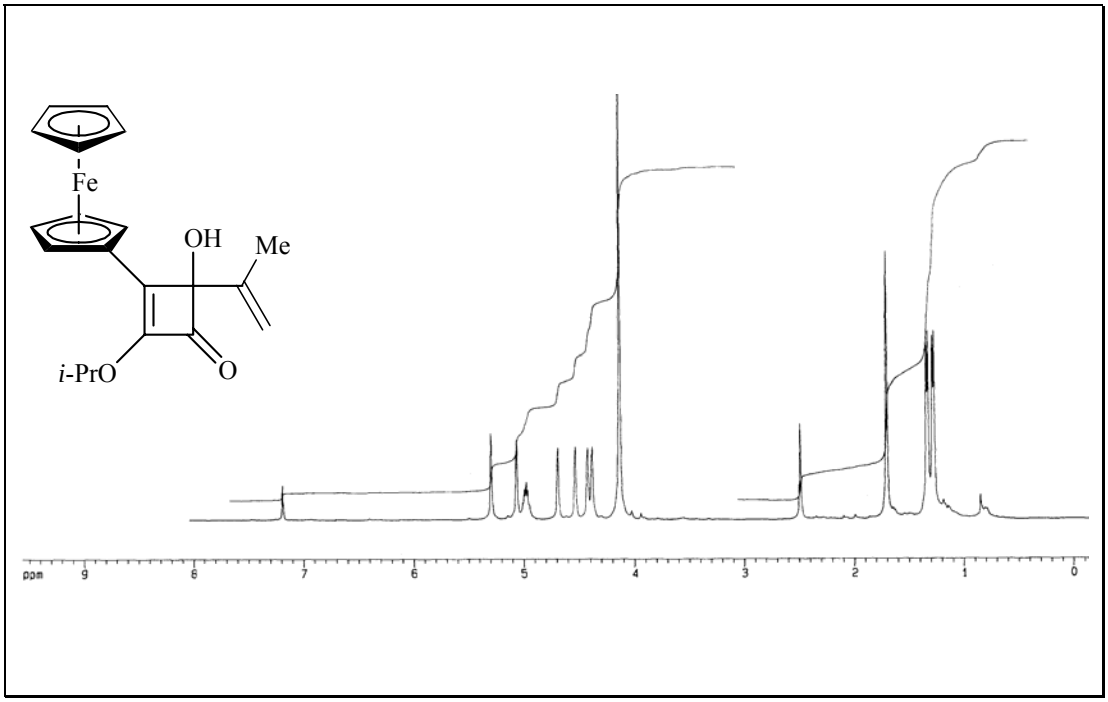

Figure A16. ^{1}H-NMR Spectrum (400 MHz) of ferrocenyl cyclobutenone **46A**

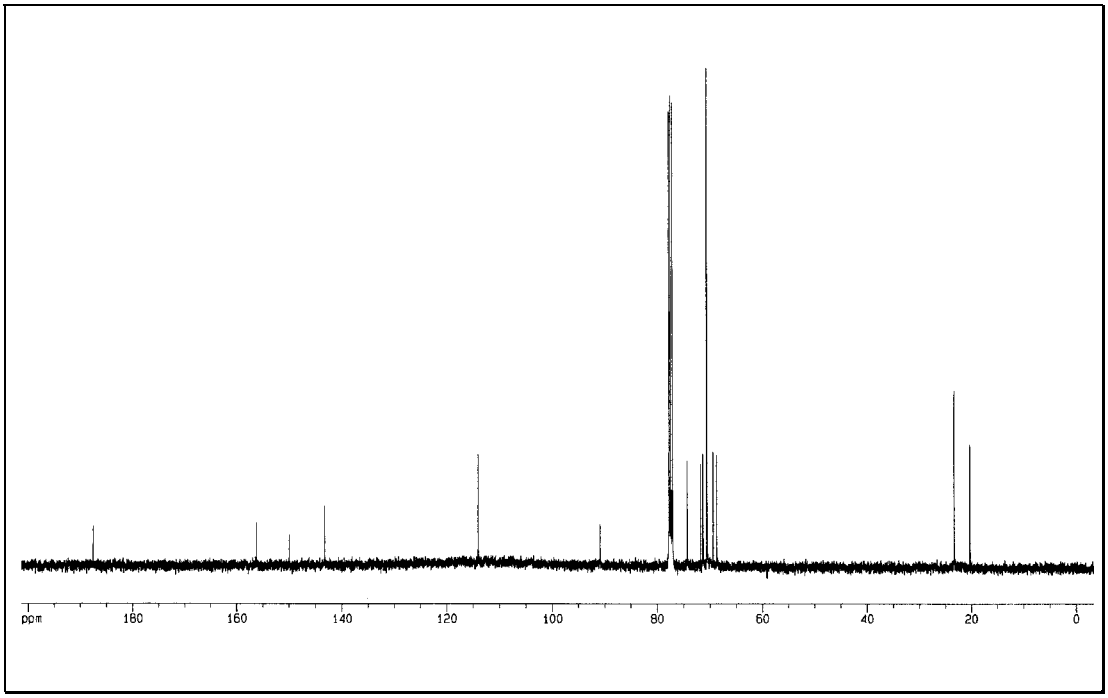

Figure A17. ^{13}C-NMR Spectrum (100 MHz) of ferrocenyl cyclobutenone **46A**

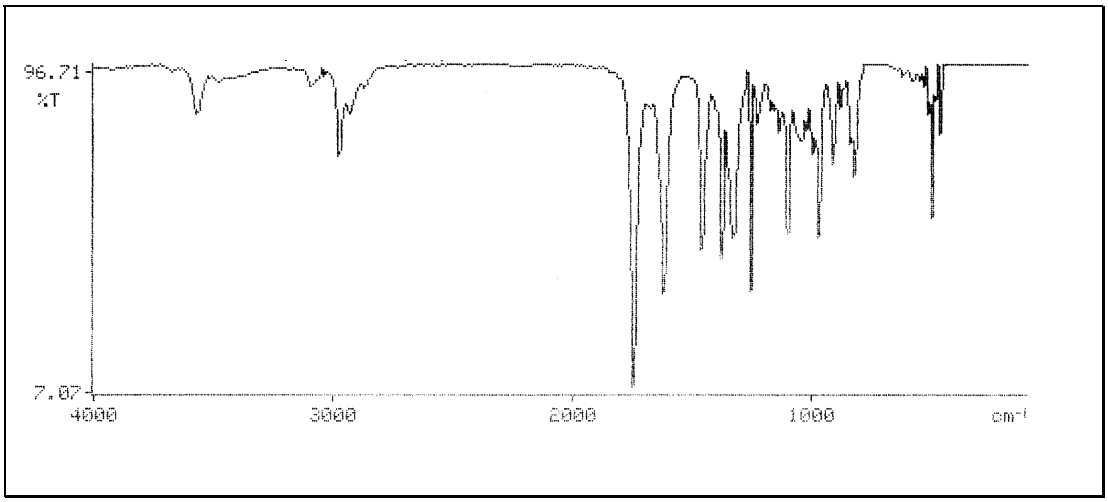

Figure A18. FT-IR Spectrum of ferrocenyl cyclobutenone **46A**

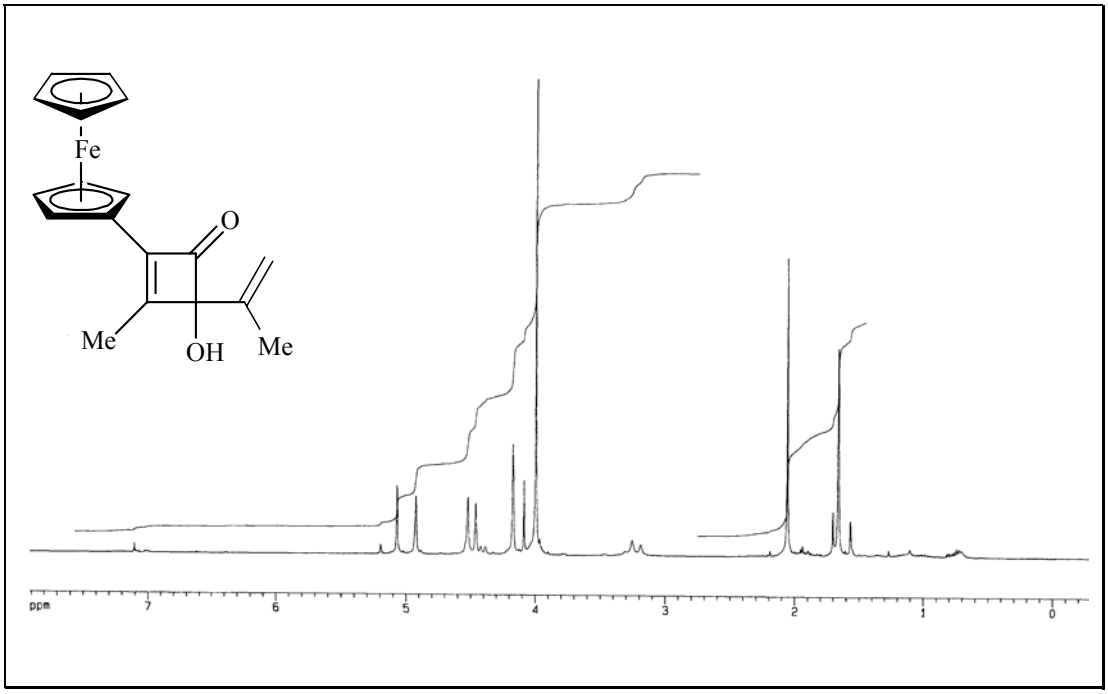

Figure A19. ^{1}H-NMR Spectrum (400 MHz) of ferrocenyl cyclobutenone **45B**

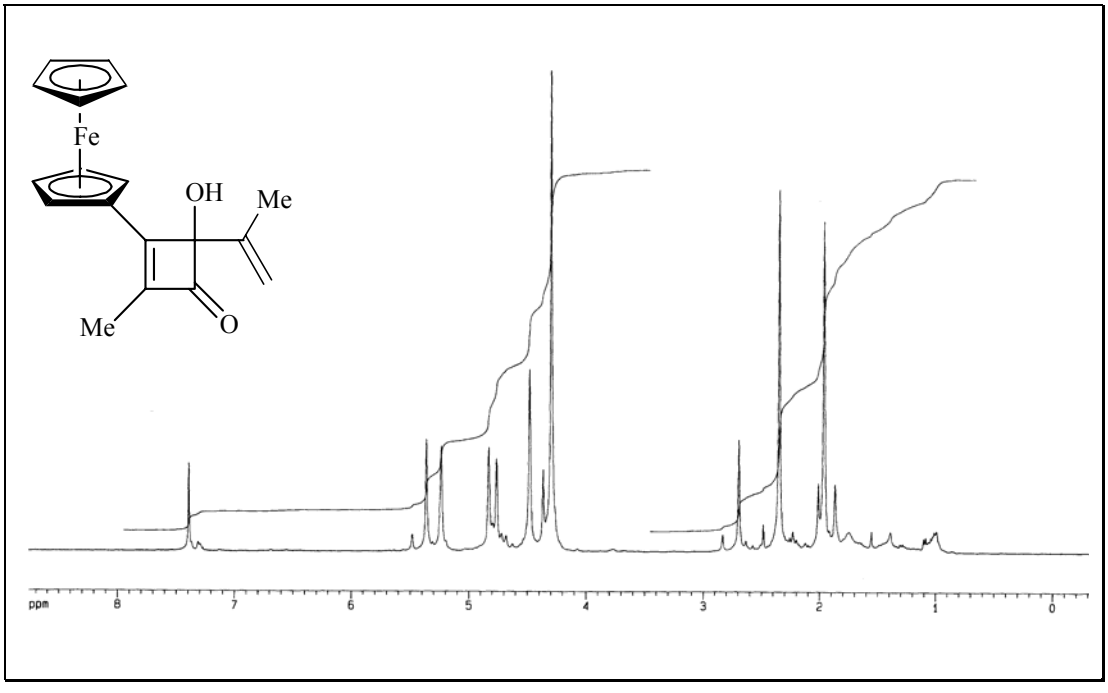

Figure A20. ^{1}H-NMR Spectrum (400 MHz) of ferrocenyl cyclobutenone **46B**

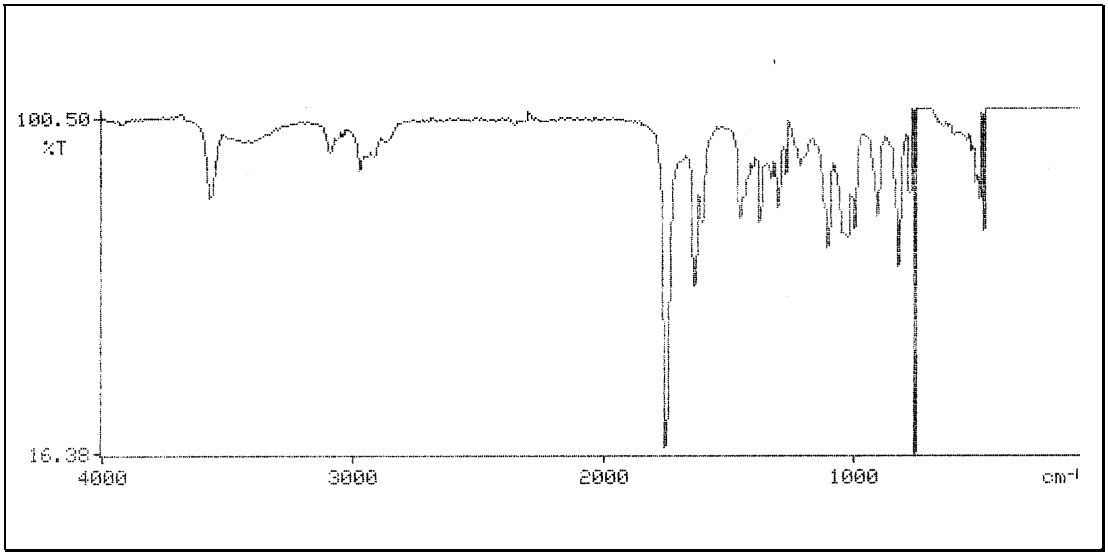

Figure A21. FT-IR Spectrum of ferrocenyl cyclobutenone **46B**

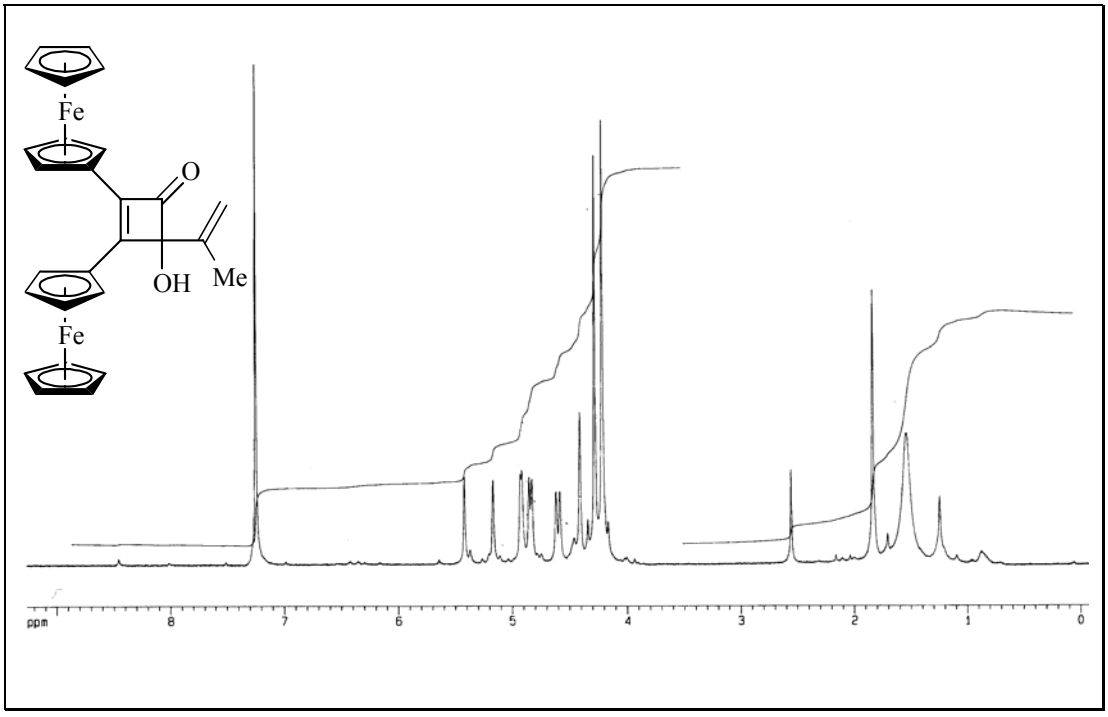

Figure A22. ^{1}H-NMR Spectrum (400 MHz) of ferrocenyl cyclobutenone **45C**

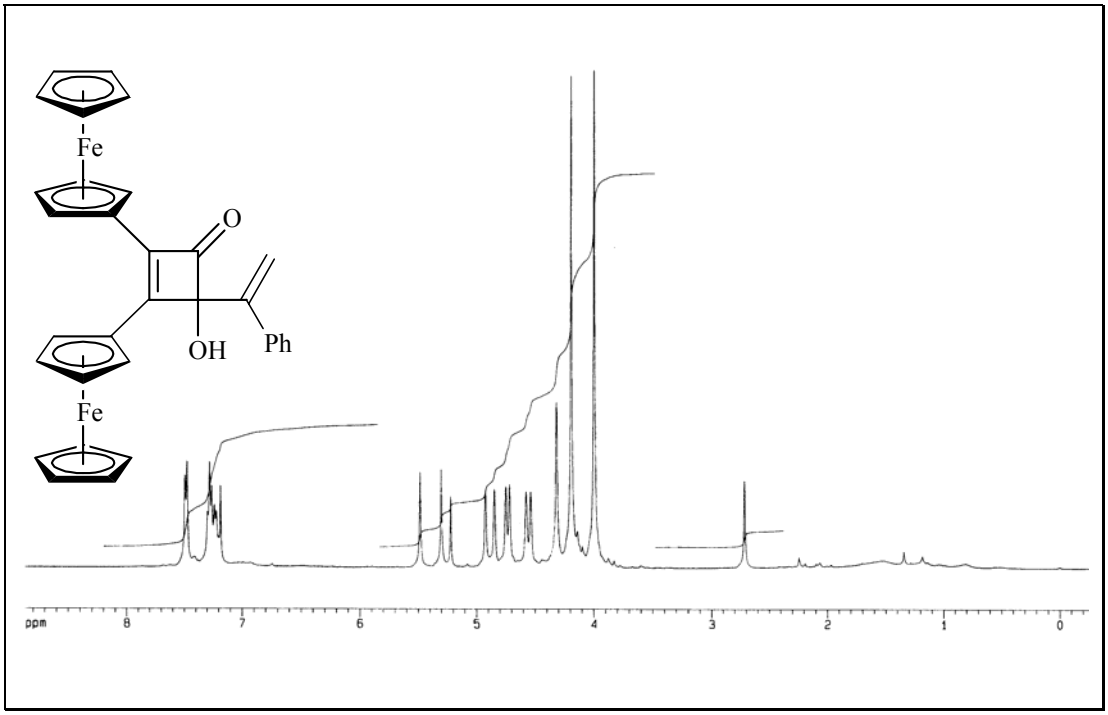

Figure A23. ^{1}H-NMR Spectrum (400 MHz) of ferrocenyl cyclobutenone **45E**

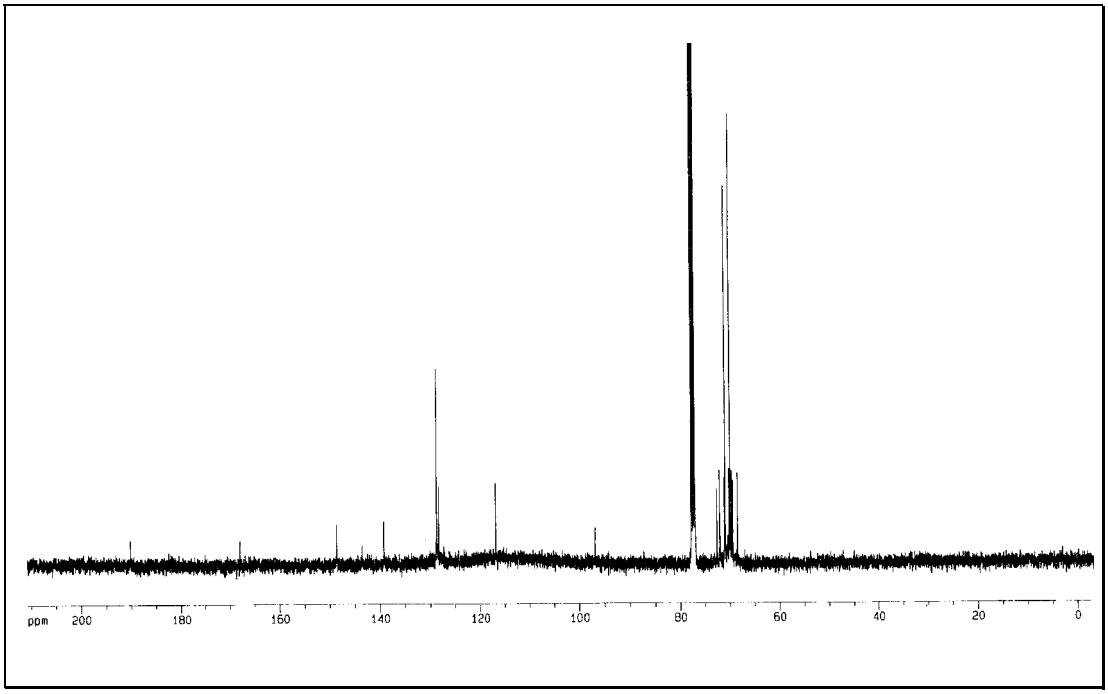

Figure A24. ^{13}C-NMR Spectrum (100 MHz) of ferrocenyl cyclobutenone **45E**

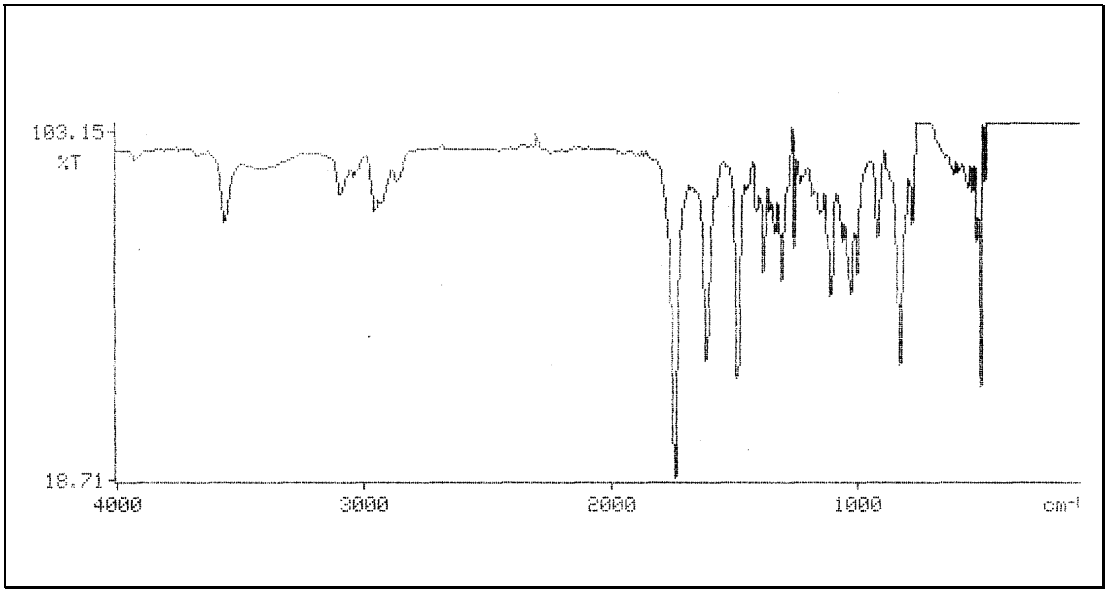

Figure A25. FT-IR Spectrum of ferrocenyl cyclobutenone **45E**

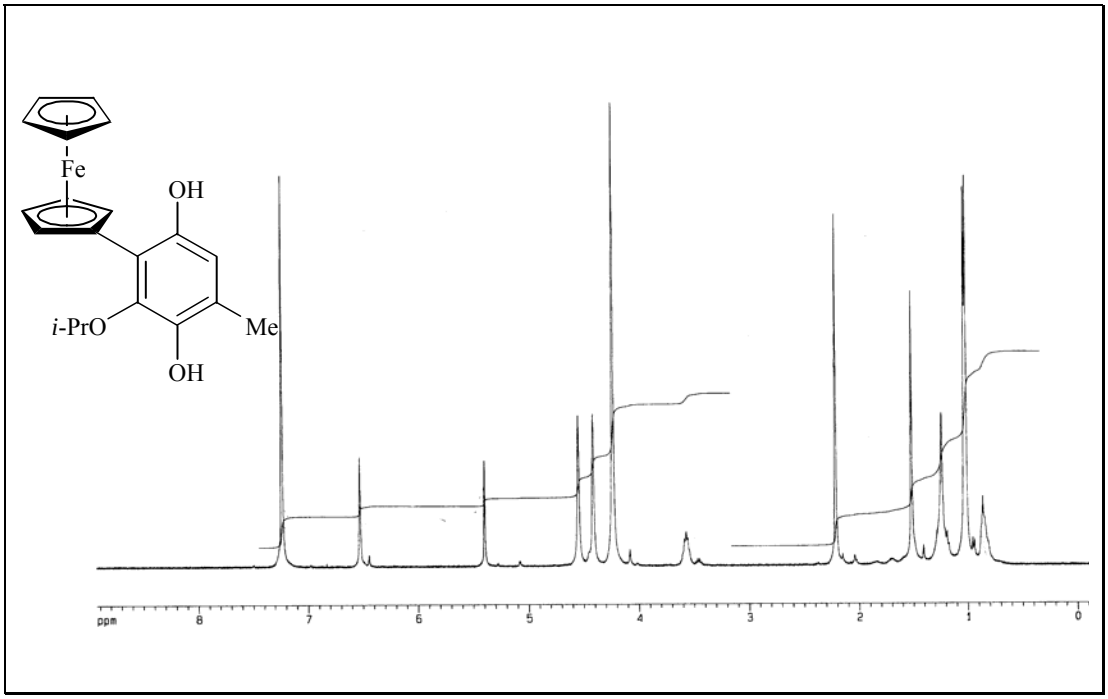

Figure A26. ^{1}H-NMR Spectrum (400 MHz) of hydroquinone **59A**

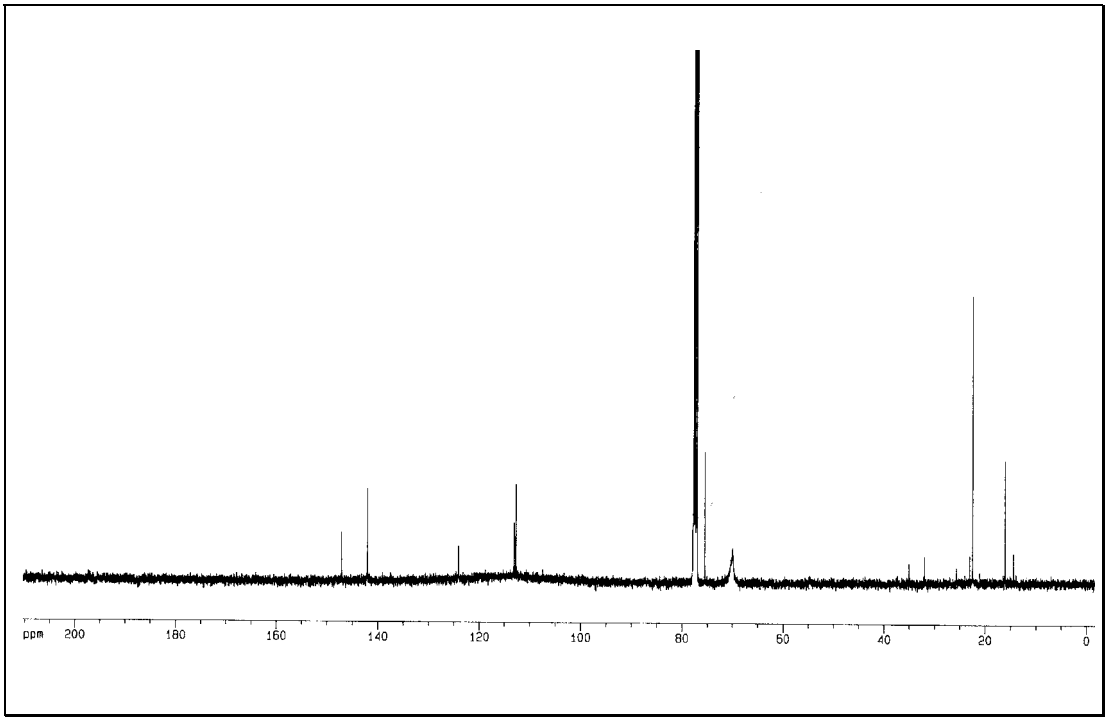

Figure A27. ^{13}C-NMR Spectrum (100 MHz) of hydroquinone **59A**

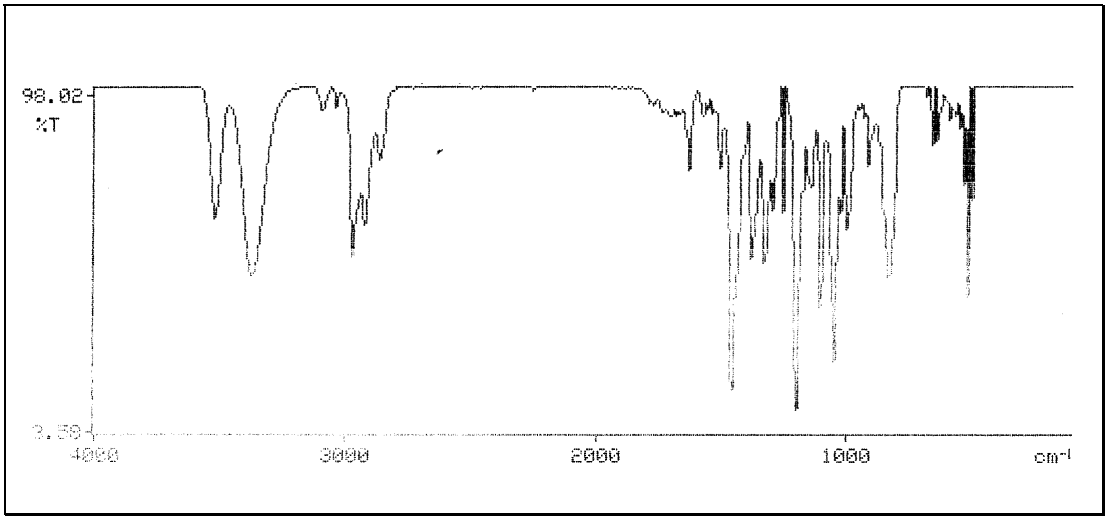

Figure A28. FT-IR Spectrum of hydroquinone **59A**

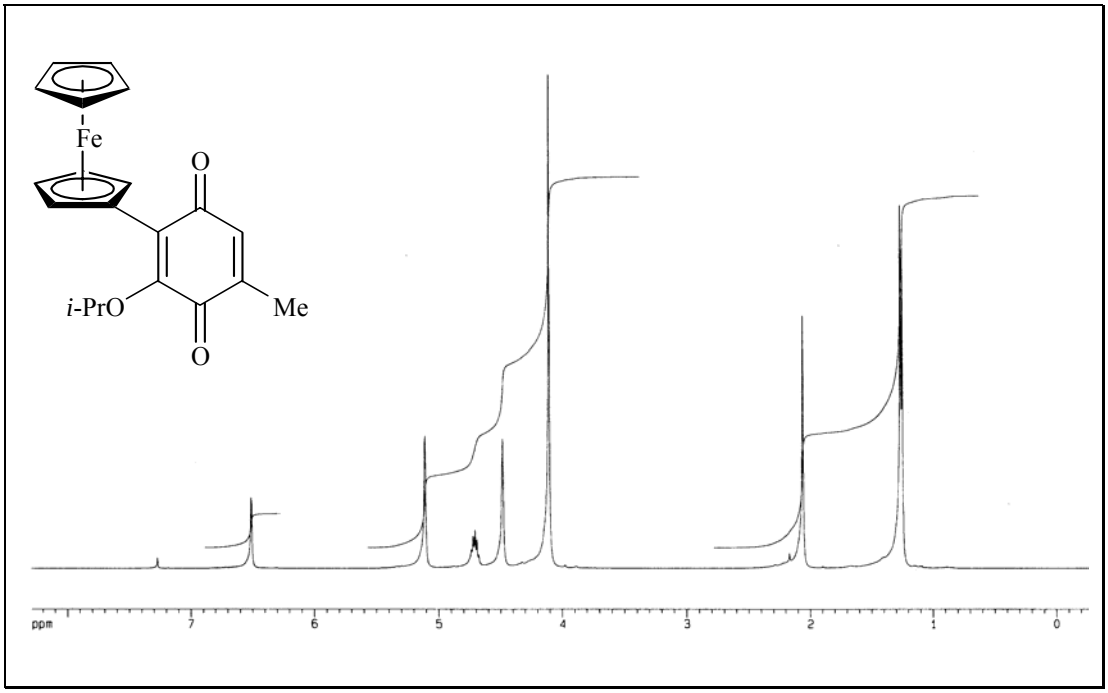

Figure A29. ^{1}H-NMR Spectrum (400 MHz) of ferrocenyl quinone **60A**

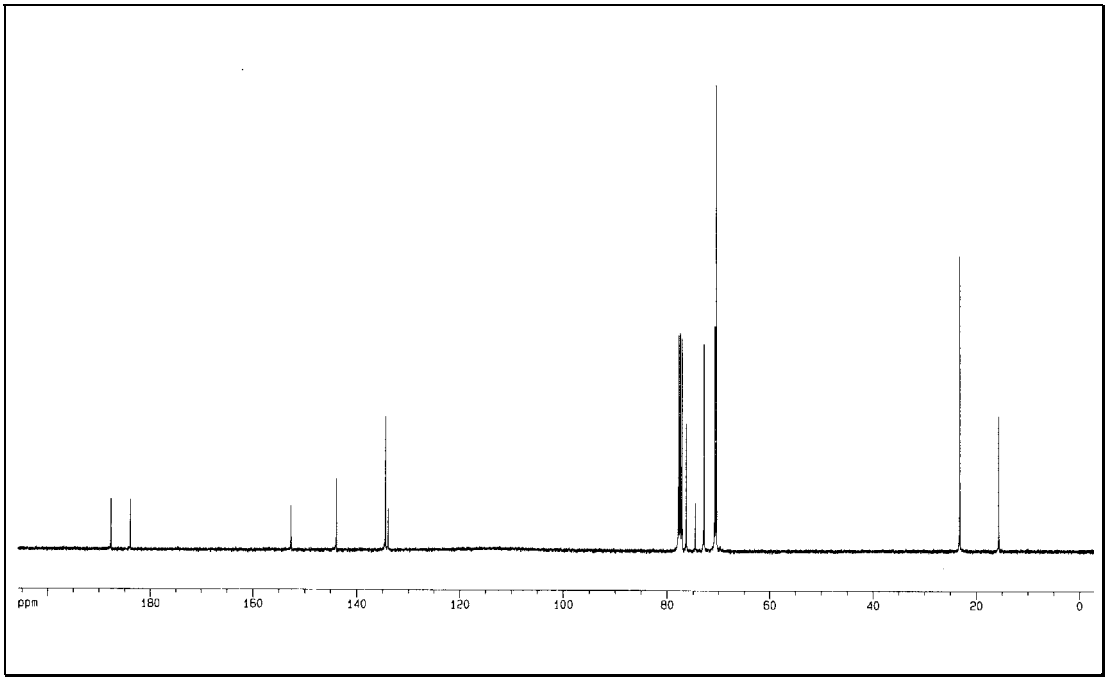

Figure A30. ^{13}C-NMR Spectrum (100 MHz) of ferrocenyl quinone **60A**

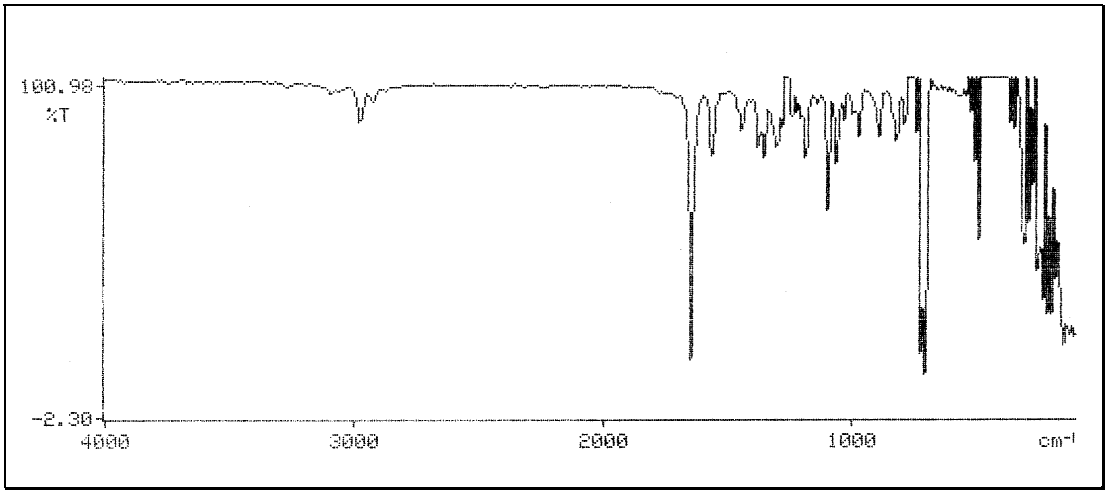

Figure A31. FT-IR Spectrum of ferrocenyl quinone **60A**

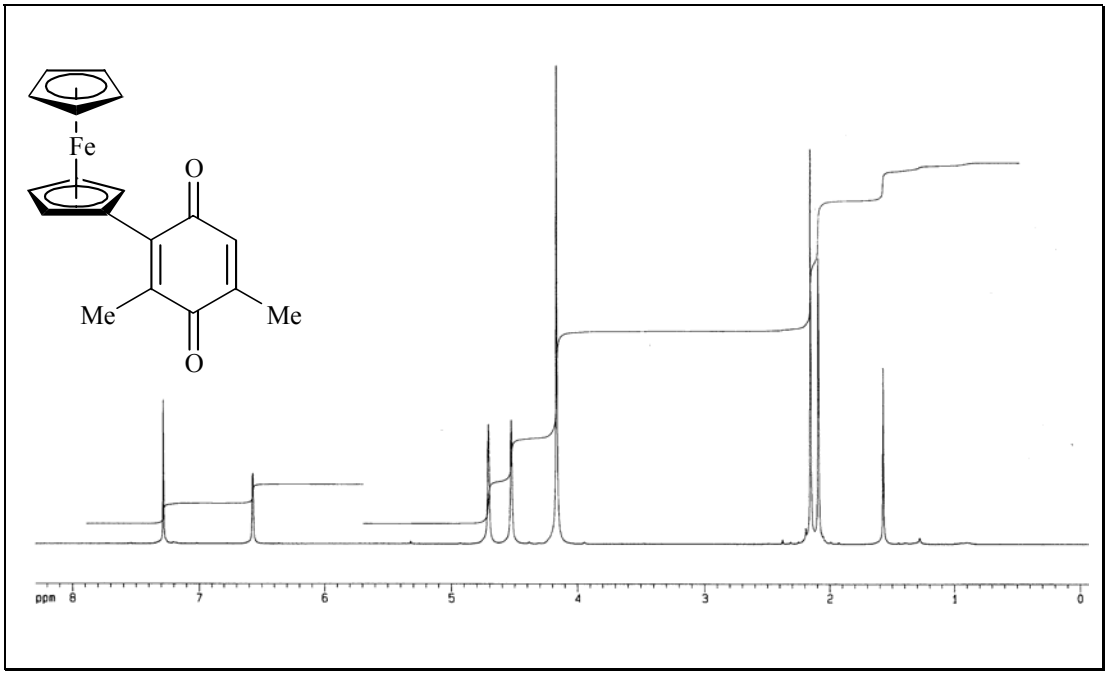

Figure A32. ^{1}H-NMR Spectrum (400 MHz) of ferrocenyl quinone **60B**

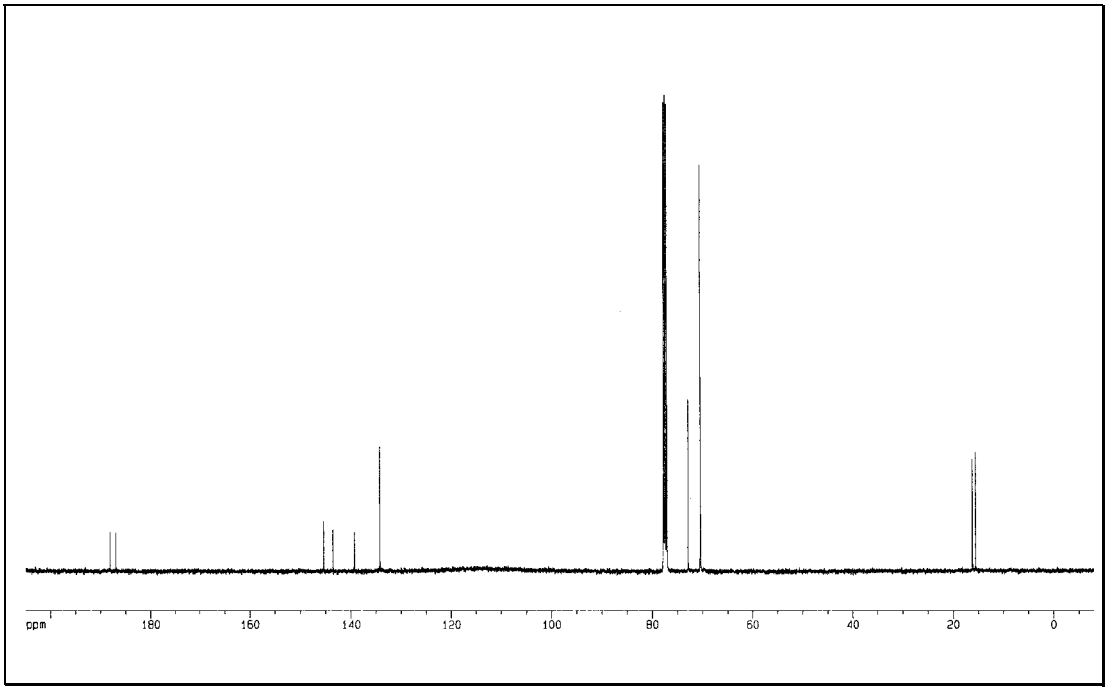

Figure A33. ^{13}C-NMR Spectrum (100 MHz) of ferrocenyl quinone **60B**

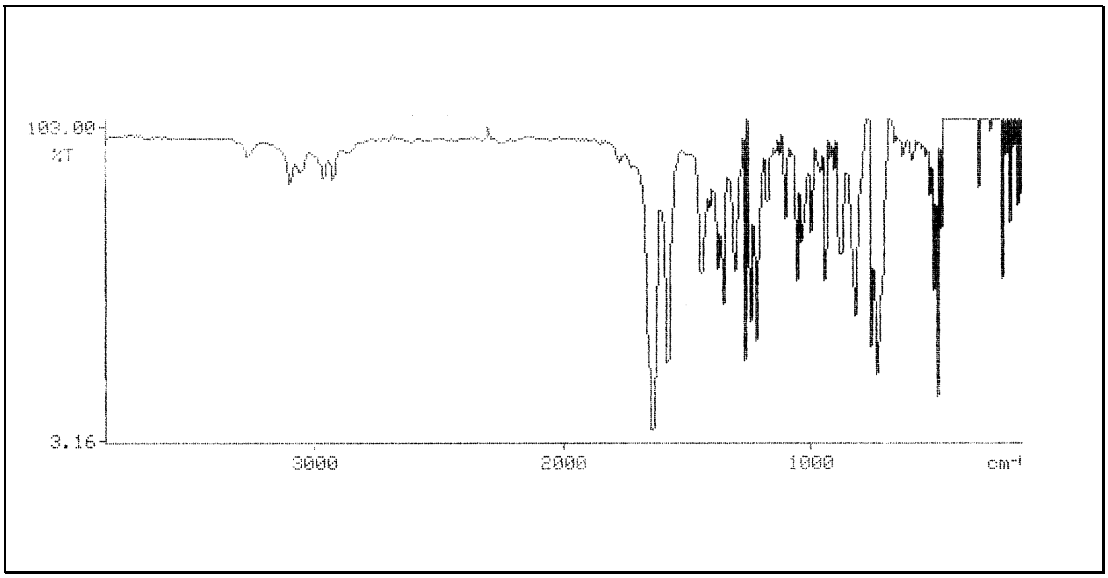

Figure A34. FT-IR Spectrum of ferrocenyl quinone **60B**

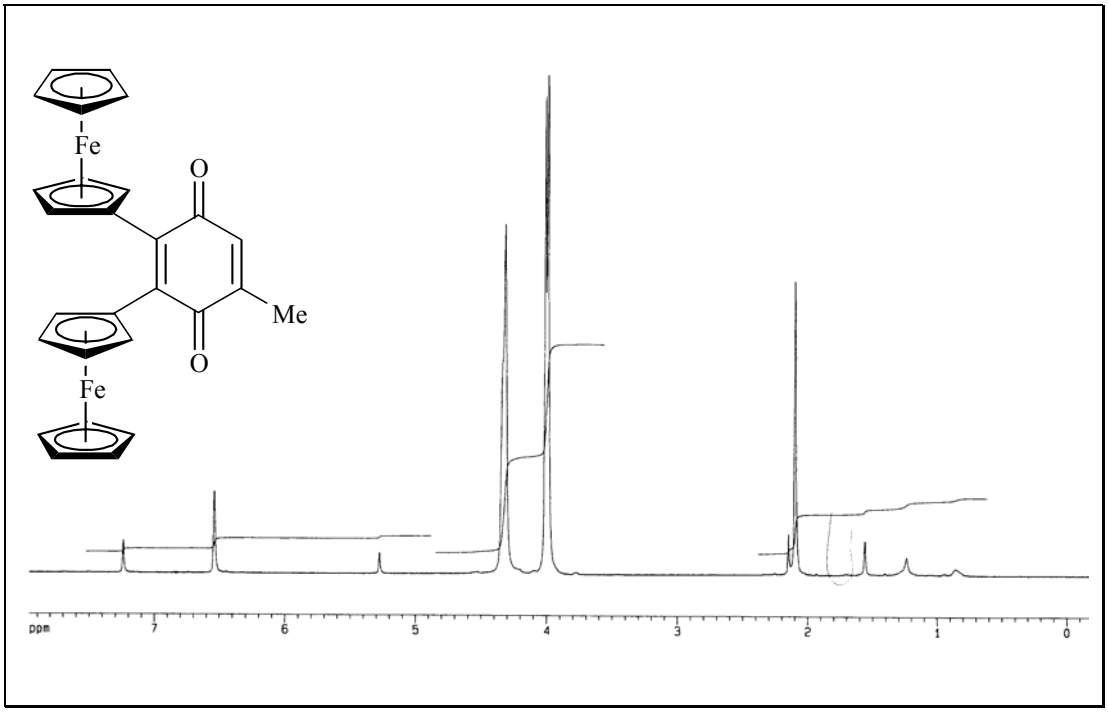

Figure A35. ^{1}H-NMR Spectrum (400 MHz) of ferrocenyl quinone **60C**

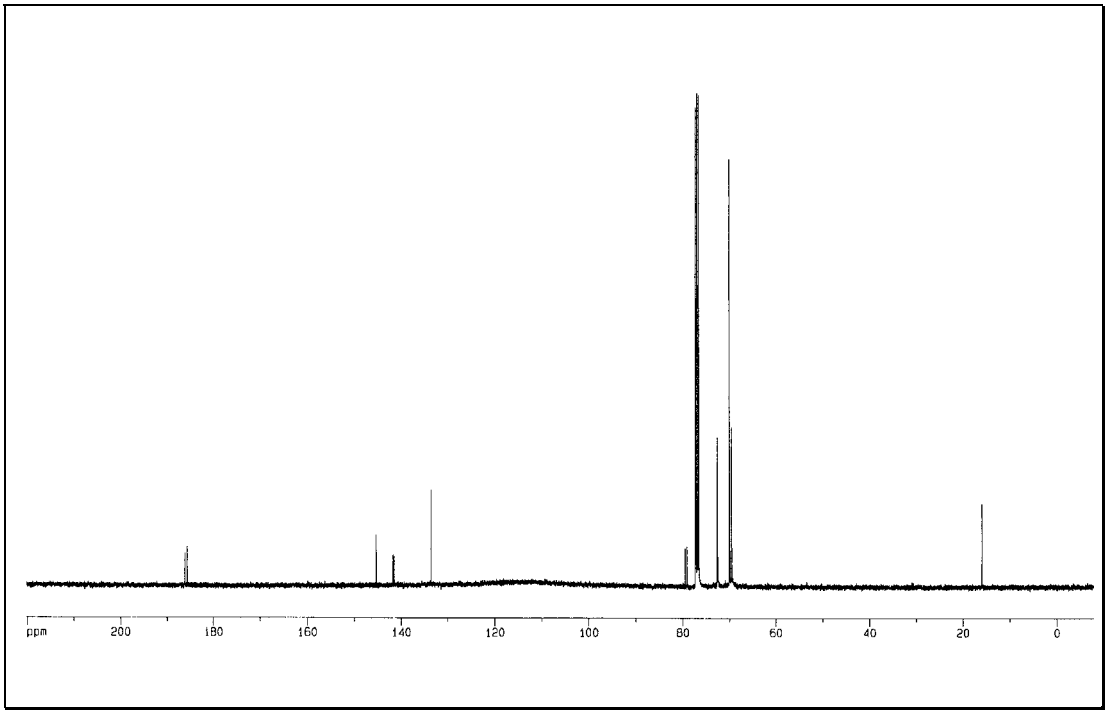

Figure A36. ^{13}C-NMR Spectrum (100 MHz) of ferrocenyl quinone **60C**

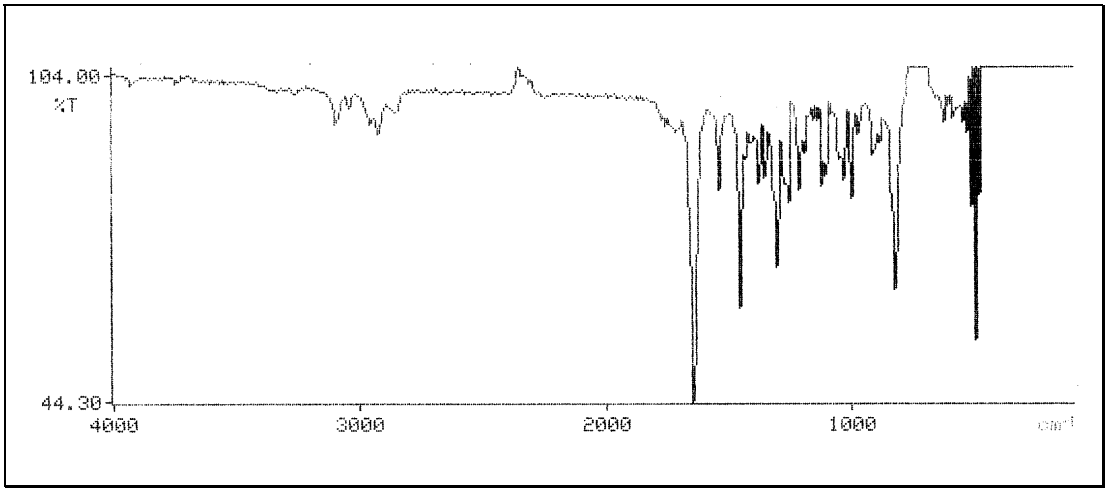

Figure A37. FT-IR Spectrum of ferrocenyl quinone **60C**

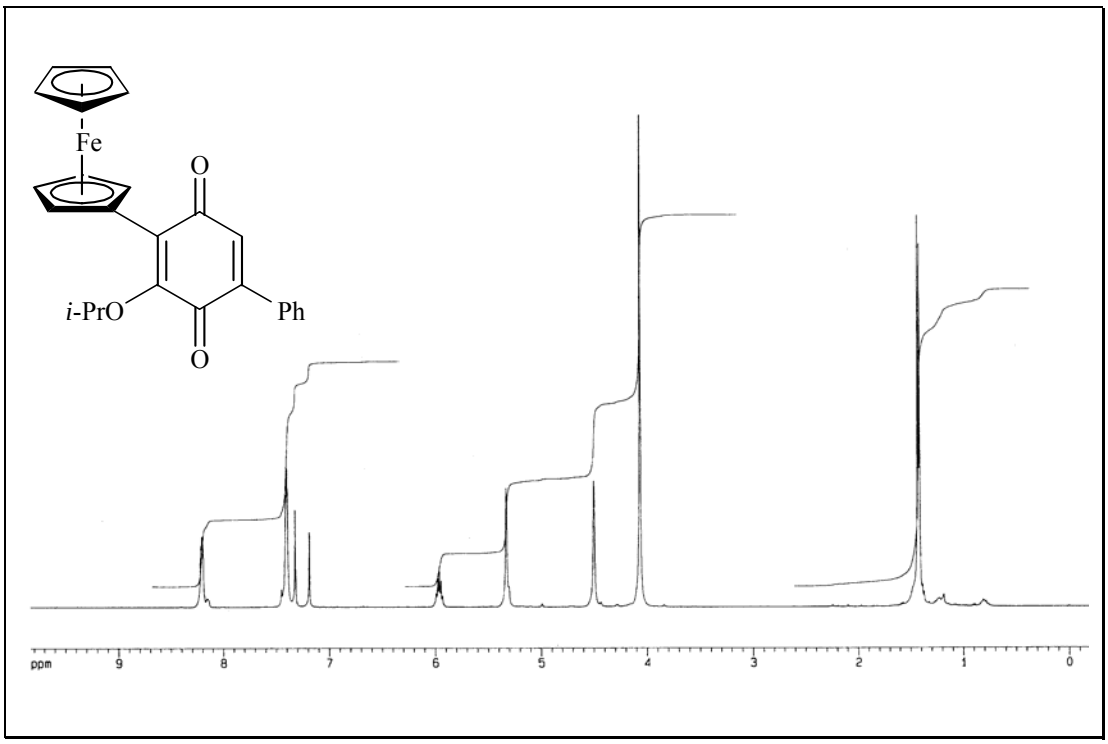

Figure A38. ^{1}H-NMR Spectrum (400 MHz) of ferrocenyl quinone **60D**

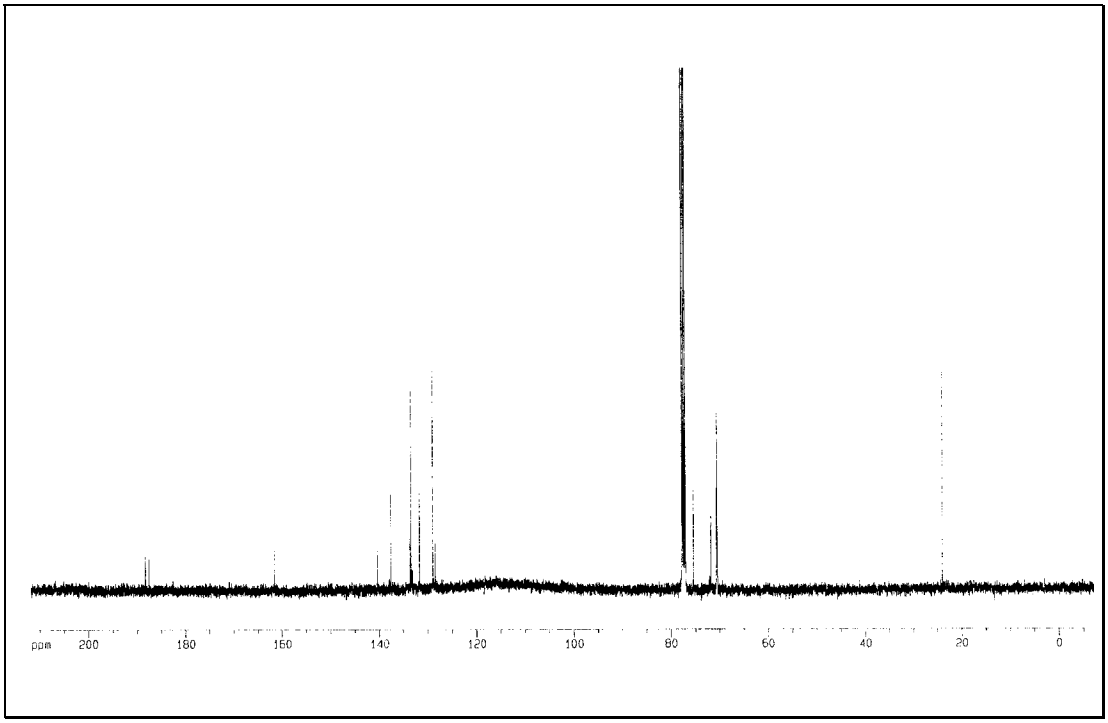

Figure A39. ^{13}C-NMR Spectrum (100 MHz) of ferrocenyl quinone **60D**

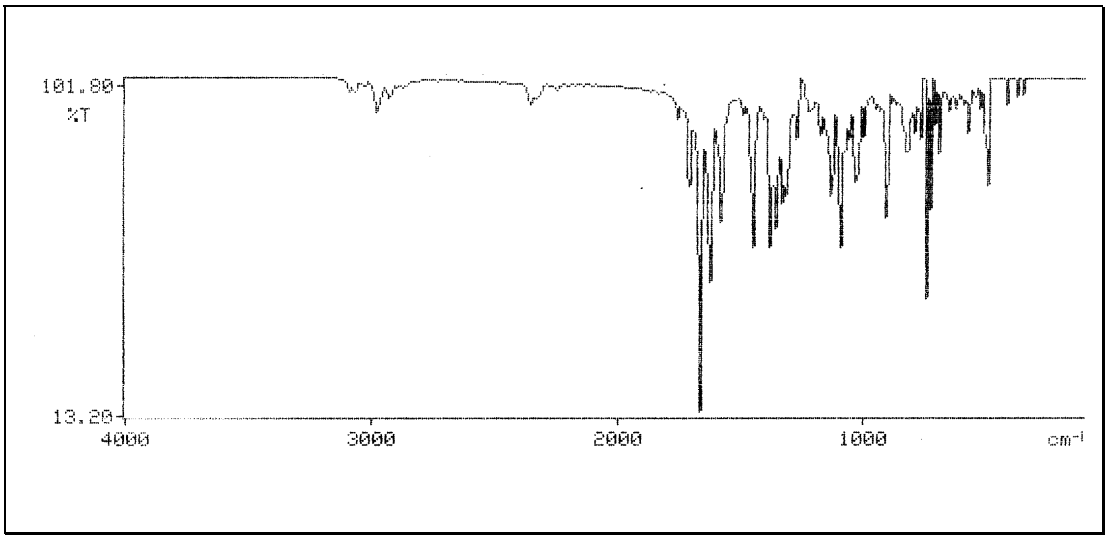

Figure A40. FT-IR Spectrum of ferrocenyl quinone **60D**

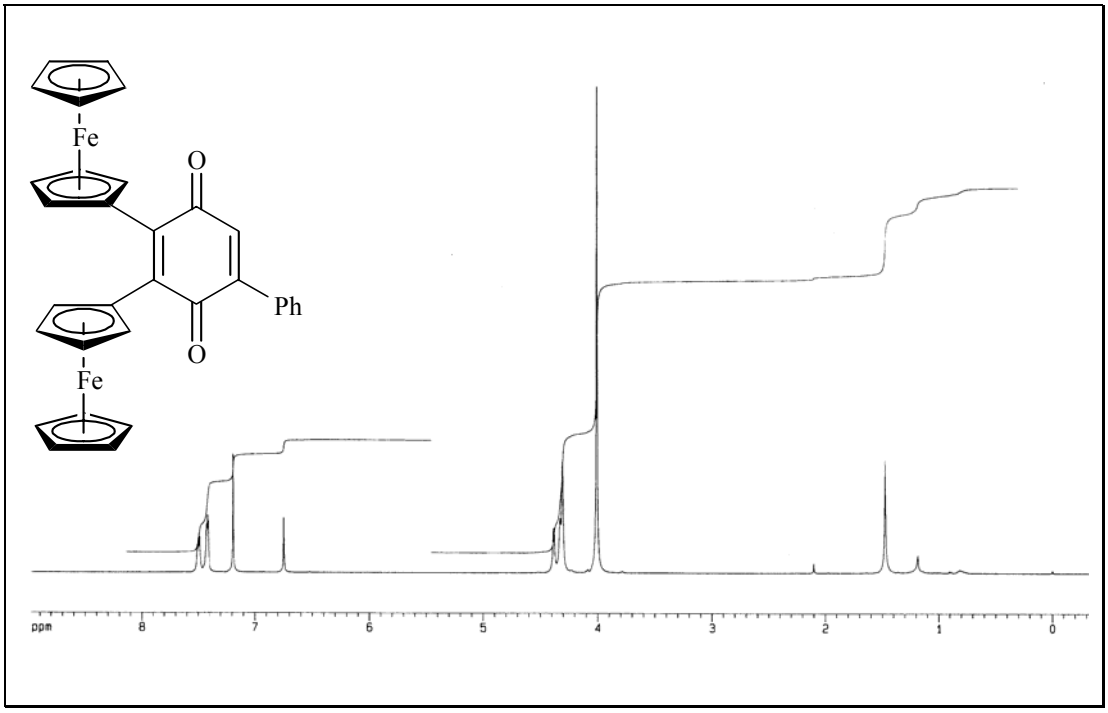

Figure A41. ^{1}H-NMR Spectrum (400 MHz) of ferrocenyl quinone **60E**

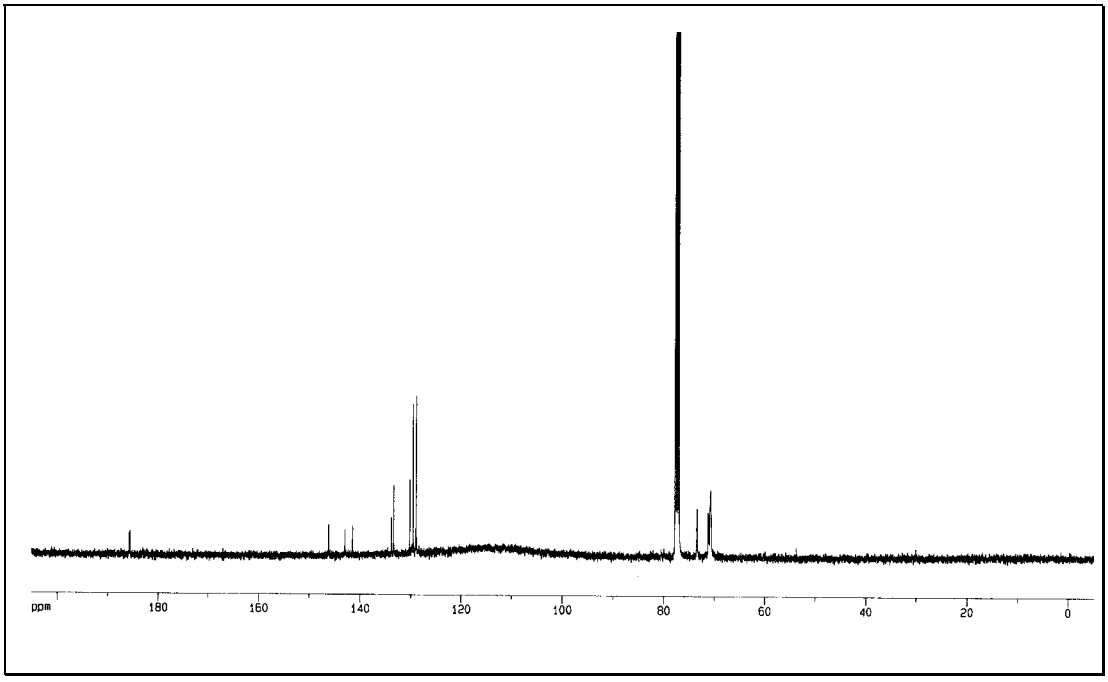

Figure A42. ^{13}C-NMR Spectrum (100 MHz) of ferrocenyl quinone **60E**

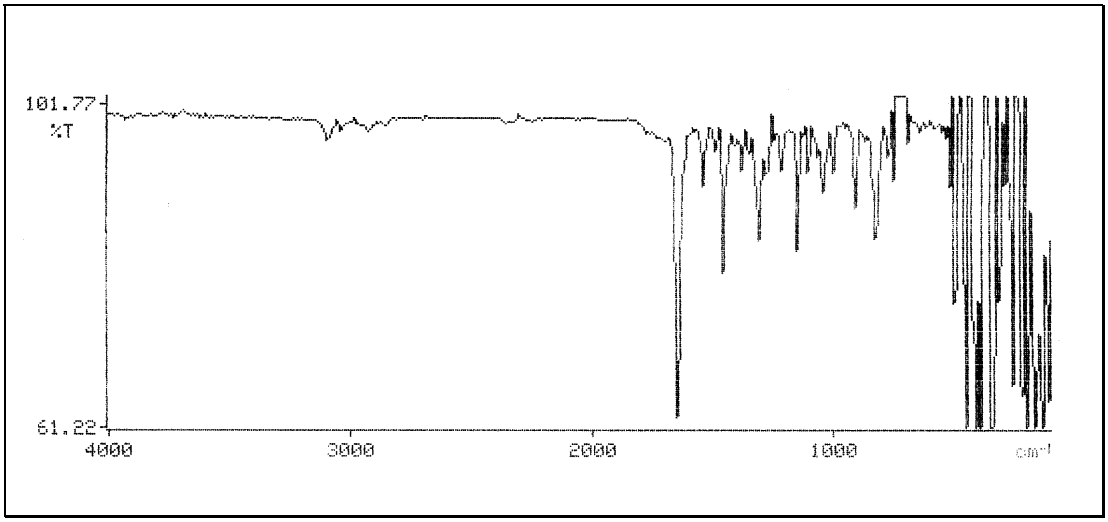

Figure A43. FT-IR Spectrum of ferrocenyl quinone **60E**

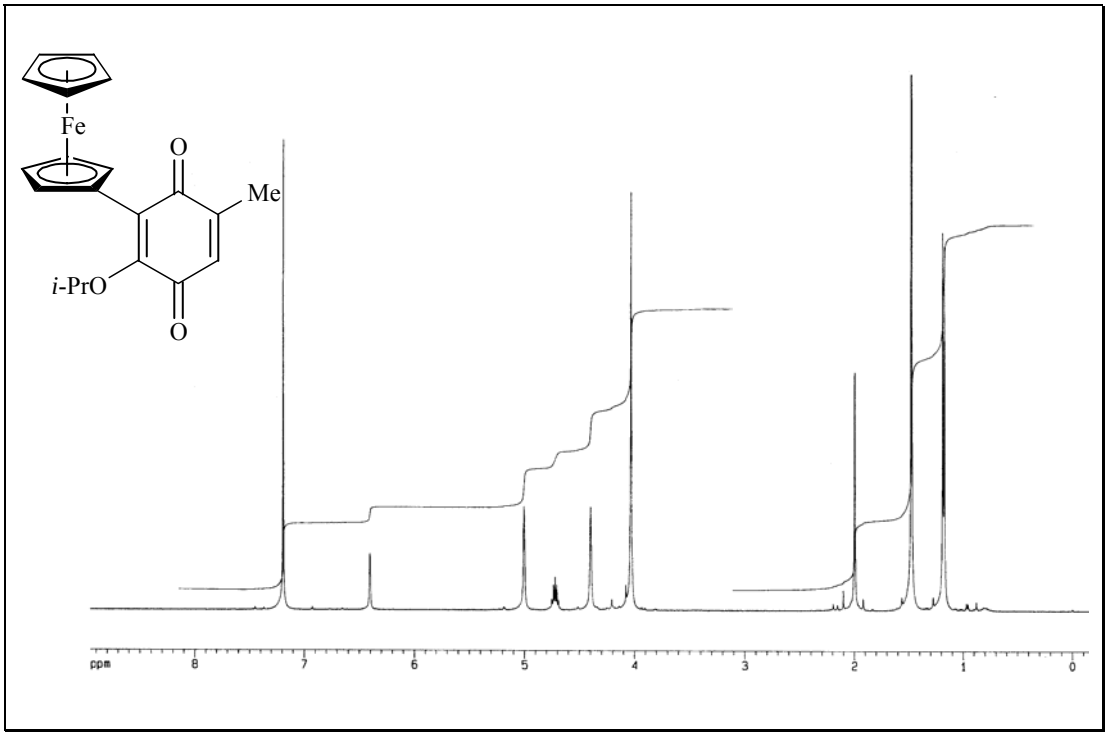

Figure A44. ^{1}H-NMR Spectrum (400 MHz) of ferrocenyl quinone **62A**

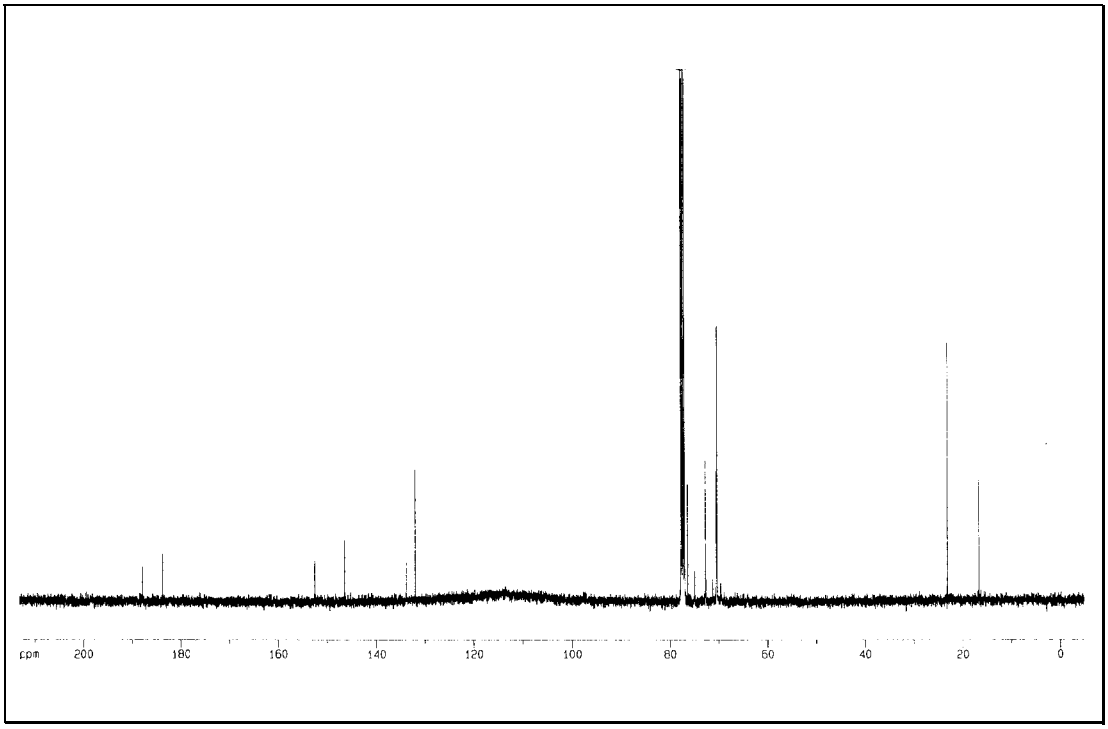

Figure A45. ^{13}C-NMR Spectrum (100 MHz) of ferrocenyl quinone **62A**

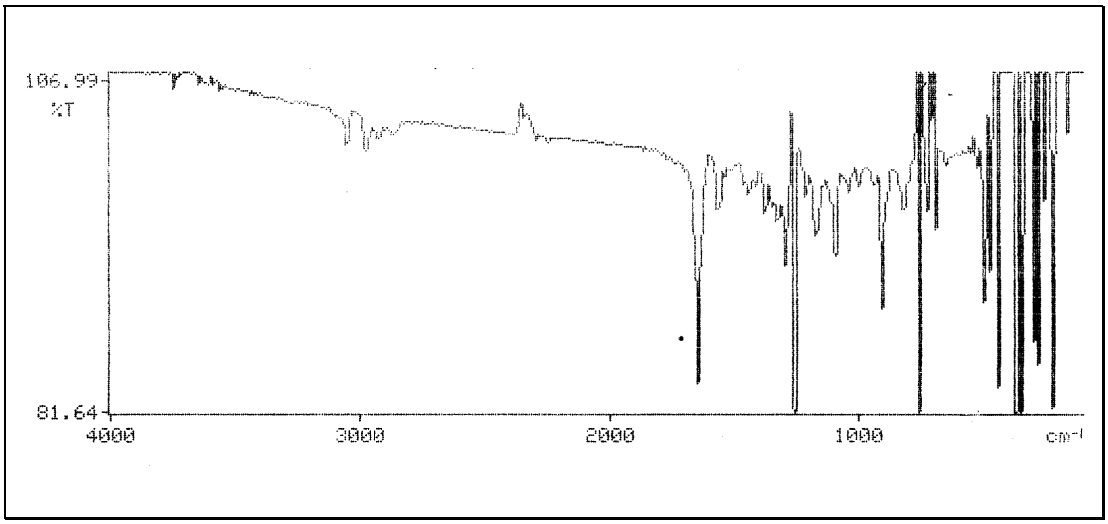

Figure A46. FT-IR Spectrum of ferrocenyl quinone **62A**

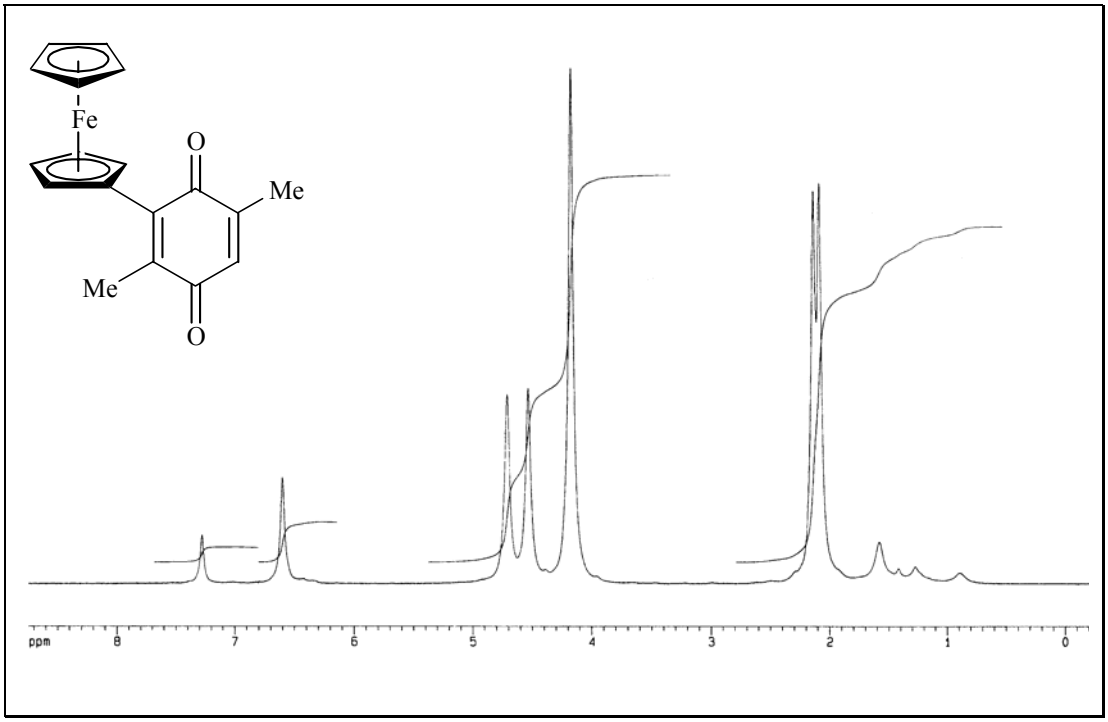

Figure A47. ^{1}H-NMR Spectrum (400 MHz) of ferrocenyl quinone **62B**

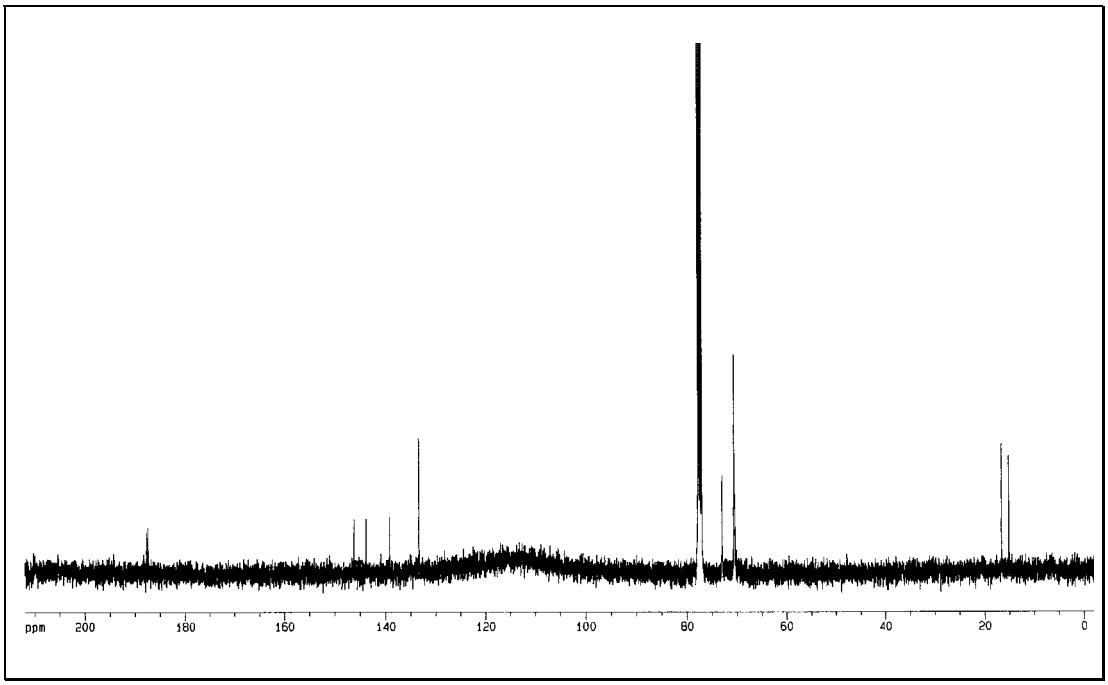

Figure A48. ^{13}C-NMR Spectrum (100 MHz) of ferrocenyl quinone **62B**