Aromatic Organo-Diiron Chemistry: Synthesis of Polyaromatic Ethers

by

David C. Schriemer

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AROMATIC ORGANO-DIIRON CHEMISTRY: SYNTHESIS OF POLYAROMATIC ETHERS

BY

DAVID C. SCHRIEMER

A Thesis submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

For Tammy and my parents

Abstract

A new development in the chemistry of arenes activated towards S_NAr reactions by the cyclopentadienyliron ($CpFe^+$) moiety is presented in this work. A class of di-iron complexes of diphenoxybenzenes was prepared in a highly efficient and very mild fashion. Dihydroxyaromatic compounds served as dinucleophiles, allowing for the formation of di-iron complexes. This could be achieved in either a one or two step procedure. A wide variety of dinucleophiles were incorporated into this study, as well as an extensive number of $CpFe^+$-activated arenes. It is shown that these reactions are not inhibited by bulky substituents on either the dinucleophiles or activated arenes. The di-iron complexes themselves could also undergo S_NAr reactions, provided that the complexed arenes contain a Cl substituent. This allowed for the functionalization of the complexes with species that could not be introduced directly in their synthesis. The carbon nucleophiles generated from ethyl cyanoacetate and phenylsulfonylacetonitrile could be attached to the complexed ethers in this manner.

The $CpFe^+$ moieties were removed very easily by a photolytic procedure. This has allowed for the recovery of a wide range of functionalized diphenoxybenzenes. A comparative study between the technique developed herein and conventional aromatic ether synthesis is also presented. It is conclusively shown that the $CpFe^+$-mediated synthesis has advantages over all existing techniques.

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Part I

Introduction

1 Aromatic Ethers

1.1 Uses of these Compounds

Aromatic ethers are undoubtedly one of the more important classes of organic compounds, finding extensive application in both their pure form and as substituents of more complex molecules. A vast amount of research has been conducted in the area of poly(aromatic ether) synthesis, of both low and high molecular weights, with regards to their synthesis and application. These polyaromatic ethers have a number of very desirable physical properties, allowing for their use in extremely hostile environments [1, 2, 3, 4]. Polymers containing such aromatic ether units tend to be very thermally stable, a consequence of their high glass transition temperatures (T_g) [5, 6]. Other enticing features of polymers containing these units include oxidative stability, resistance to radiation damage, hydrolytic stability, creep resistance, and high degree of toughness [7]. These polymers include bis S polyether produced by Imperial Chemical Industries (figure 1), and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), produced by General Electric (figure 2). At present, polyaromatic ethers are being used as high performance synthetic lubricants [8, 9], and are being considered for use in the aerospace industry as structural resins [5]. It has been accepted that the ether linkage provides the stability and flexibility of these aromatic polymers, whereas linkages such as -SO_2- for example, contribute to the radiation damage and

water absorption they can experience [6].

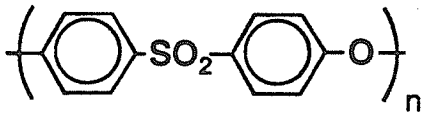


Figure 1: Bis S polyether

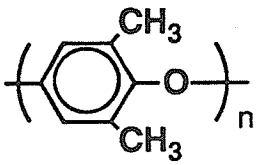


Figure 2: Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)

The above features have led to the incorporation of various aromatic ethers in a large number of polymers. For example, in the search for high strength polymers with improved processability (i.e.: higher solubility, lower degree of crystallinity), diphenoxybenzene monomeric units have been copolymerized with those monomers which, when polymerized, form fibers with high modulus and tensile strengths values. Evers et al. have investigated this approach for improving the processability of heterocyclic polymers, without eroding the exceptional properties of the polymers [10]. A range of diphenoxybenzene compounds were copolymerized with 2,6-benzobisoxazole, 2,6-benzobisthiazole and 2,6-benzobisimidazole units, producing so-called articulated polymers (see figure 3 for example). It was found that the ductility of the resulting polymers was somewhat improved, while the liquid crys-

talline nature was maintained, and only a slight drop in thermooxidative stability experienced.

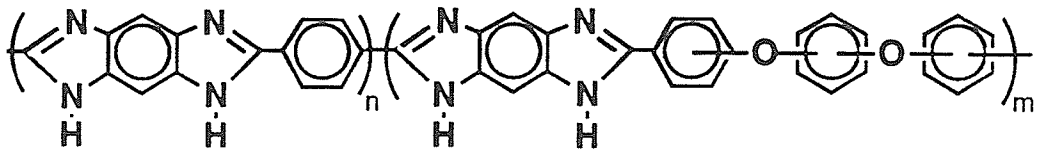


Figure 3: Articulated 2,6-benzobisimidazole polymer

Aromatic ether linkages also appear very frequently in naturally occurring macrocyclic peptides, most notably the vancomycin family of antibiotics [11, 12, 13]. This is a group of antibiotics that inhibit bacterial cell-wall biosynthesis. The aromatic ether linkages in these antibiotics serve as rigidifiers in otherwise flexible macrocyclic peptides, thereby creating hydrophobic pockets where the amino and carboxyl group binding sites reside [14]. Therefore, while these aromatic ether units play no direct role in the activity of these natural products, they are instrumental in creating the proper environment for the observed biological activity, in which the binding sites adhere to the bacterial cell walls by hydrogen bonding. Apparently, this hydrogen bonding interaction is enhanced by the hydrophobic environment the aromatic ether linkages create about the binding sites. The presence of aromatic ether linkages is by no means restricted to this class of natural products, as they are also present in a wide range of alkaloids and thyromimetics [15, 16].

1.2 Synthesis of Aromatic Ethers

Surprisingly, aromatic ethers suffer from relatively few general, preparative synthetic methods, both in the preparation of the polymers and the monomers. This is a consequence of the low reactivity of most simple aromatic species, stemming from the inherent stability of electron-delocalized systems. Therefore, the generation of more extensive aromatic systems (such as aromatic ethers) from simpler ones requires some sort of activation of the ring system. By far the most common and successful approach to aromatic ether synthesis involves the activation of the rings to nucleophilic substitution reactions (S_NAr) by the withdrawl of ring electron density. One sees a very wide assortment of polymeric materials obtained from monomers activated with electron-withdrawing substituents such as sulfonyl or carbonyl groups. The synthesis of biphenyl polyether sulfone is a good example (figure 4) [1]. Nucleophilic substitution reactions of this type leading to high molec-

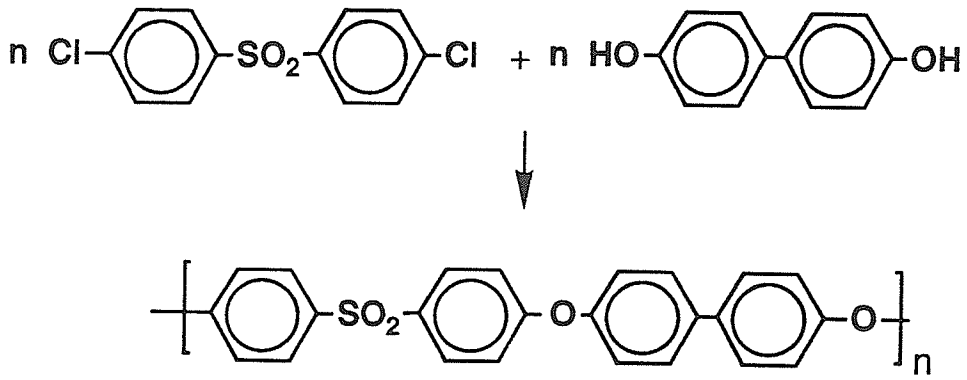


Figure 4: Synthesis of biphenyl polyether sulfone

ular weight poly(aromatic ethers) are very common [1]. The price and availability of suitably activated monomers are restrictive, and few suitable techniques exist

for their synthesis (substituent-activated S_NAr, Ullmann condensation and oxidative coupling of aryl halides) [1, 2, 3, 17]. A review of these conventional syntheses follows, focussing on the range of aromatic ethers obtainable, their benefits and drawbacks. Novel organometallic methods of arene activation to S_NAr reactions are also discussed.

1.2.1 Nucleophilic Aromatic Substitution

It is a fundamental principle of organic chemistry that aromatic rings are not susceptible to nucleophilic substitution reactions, due to their electron-rich nature [18]. However, they can be activated to allow for substitution reactions by incorporation of a suitable leaving group or by the presence of electron withdrawing groups on the ring. The N_2 leaving group can be incorporated into the arene by the preparation of the diazonium salt, which involves treatment of aniline with nitrous acid, followed by H_2O elimination [18]. Since N_2 is a good leaving group, many otherwise unreactive nucleophiles may be introduced to the ring, such as halides originating from cuprous halides. If the intent is to activate the aromatic ring such that substituents like halide, cyano, or nitro groups can be substituted, the presence of electron-withdrawing groups is required. The substitution occurs by an addition-elimination mechanism, in which a transient Meisenheimer (or σ) complex first forms, followed by loss of the leaving group [19, 20]. This can be demonstrated in the reaction between trinitrobenzene and 2,4,6-trimethylphenoxide in DMSO at room temperature (figure 5), in which nitro displacement occurs [21]. This type of nucleophilic substitution reaction has been extended to the synthesis of diphenoxybenzenes as well. Using the nitro displacement reaction patented by Heath and Wirth [22] in

which cyano groups serve as the activators, Evers and coworkers synthesized a class

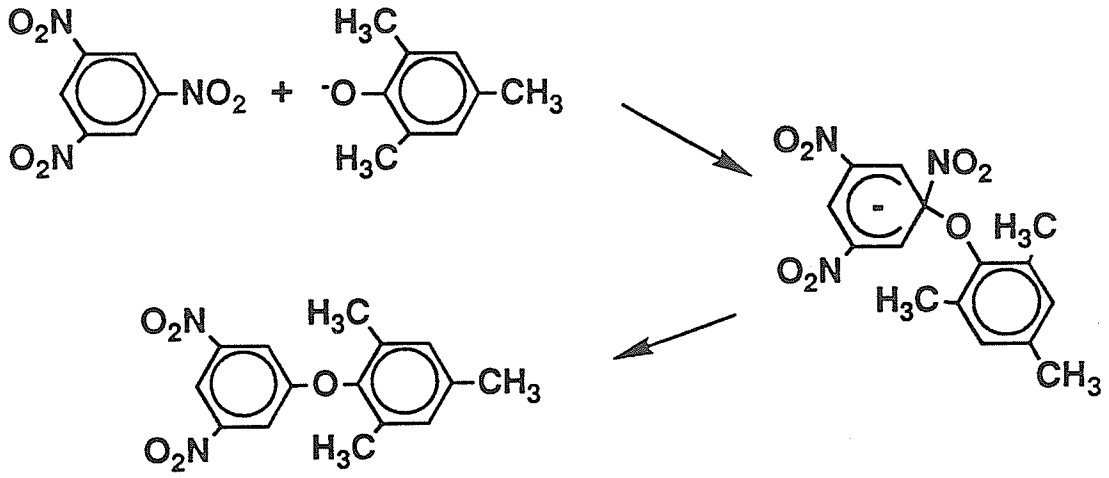


Figure 5: Aromatic nitro displacement reaction with a phenoxide nucleophile

of di(4-cyanophenoxy)benzenes from 4-nitrobenzonitrile and the appropriate dihydroxybenzene in 45-85% yields (figure 6) [10]. However, this technique is limited to

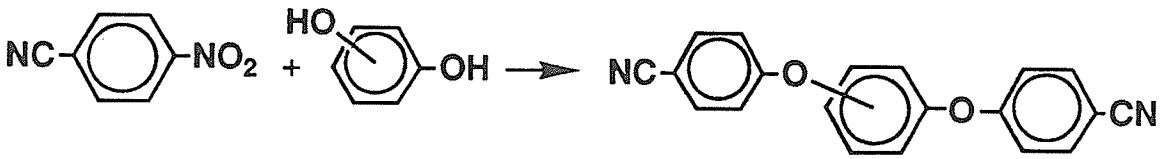


Figure 6: The nitro displacement reaction activated by CN

the synthesis of diphenoxybenzenes containing cyano groups only in the 2,2′ or 4,4′ positions. This is a restriction imposed by the need for the activating cyano group to be in the ortho or para position in the nitrobenzonitrile. In the above work,

the two cyano groups in the end product could be converted to diacids or diacid chlorides, allowing for their use as monomers in polymer synthesis.

Carbon nucleophiles tend to substitute poorly even with nitro-activated aryl halides, as electron transfer reactions between the carbanion and the aromatic nitro compound tend to dominate, rather than the desired substitution [18]. One reasonably successful example involves the substitution of the chloro substituent in 1-chloro-2,4-dinitrobenzene with the carbanion of ethyl cyanoacetate (figure 7) [19]. Of course, one is then faced with the removal of the unwanted activating nitro

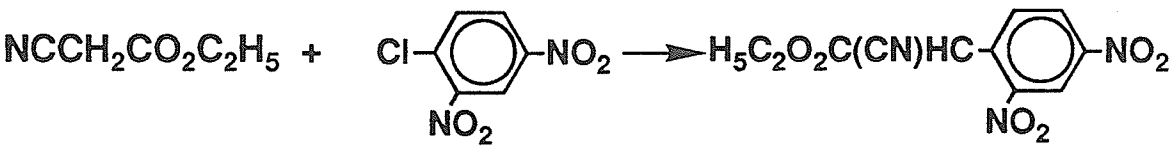


Figure 7: Introduction of a carbanion to a nitro-activated aromatic

groups, which can be difficult to impossible, depending on the nature of the other functional groups present [18].

1.2.2 Ullmann Condensation Reaction

This is the foremost method for the synthesis of both pure and functionalized aromatic ethers, but is essentially limited to the synthesis of low molecular weight aromatic ethers. Discovered by Ullmann in 1904 [23], the original method involved the heating of an aryl halide and potassium phenoxide to 200 °C, in the presence of copper powder as a catalyst, to generate phenyl ether. It has since been discovered that copper oxides and halide salts appear to be the better catalysts for this particular reaction [24]. In addition, it was found that phenol could be used

directly, provided that the base K_2CO_3 is included, or Cu_2O is used as the catalyst. In almost all cases, the order of reactivity for the aryl halides is I > Br > Cl $\gg$ F. It is interesting to note that this order of reactivity is opposite that observed in activated aryl halide systems. A study was undertaken to compare the yields of phenyl ether arising from three different aryl halides (figure 8) [25]. The yields fall from a high of 70% for iodobenzene to 10% for chlorobenzene. It is an unfortunate fact

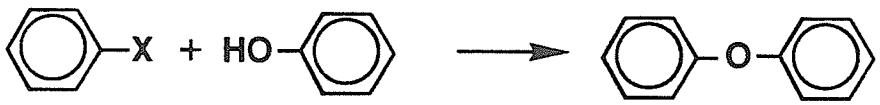


Figure 8: Synthesis of phenyl ether by the Ullmann condensation reaction

that the considerably more expensive aryl halides provide the higher yields. The choice of solvent in these reactions is a conditional one, but the most effective seems to be pyridine. Other solvents, such as collidine, N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), and alcohols have been used with varying degrees of success [8, 23]. Elevated temperatures are standard for these reactions, usually determined by the boiling point of the solvent, with the typical temperature range being 100-300 °C [8]. Reaction times do vary, however, depending on the substitution of the aryl halide, with times of 18 hours or more not uncommon. Dihydroxy aromatics can also be used, in the salt form or as the pure dihydroxy compound with a suitable base. This allows for the synthesis of a class of diphenoxy aromatics. Consider, for example, a series of diphenoxybenzenes. There are two possible

ways to synthesis these compounds: the first involves a 2:1 ratio of aryl halide to a dihydroxybenzene residue, while the second a 2:1 ratio of a phenolic residue to aryl dihalide (figure 9). It is interesting to note a number of restrictions here. The high

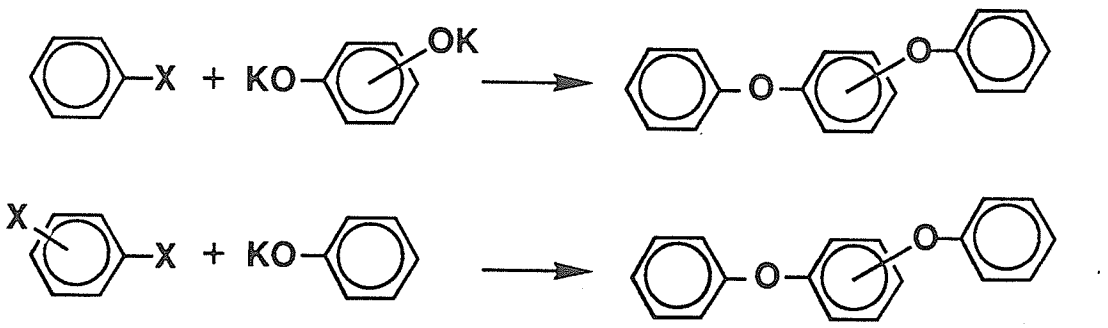


Figure 9: Two approaches to diphenoxybenzenes by the Ullmann condensation reaction

cost of diiodo- and dibromobenzenes usually favor the first synthetic route. When this route is used, alkali salts of the dihydroxybenzenes provide the better yields. In fact, this is the only way to prepare 1,3-diphenoxybenzene [9] (in a 70% yield). It is also very common, when undertaking Ullmann condensation reactions of this type, to use an excess of aryl halide. In the above synthesis of 1,3-diphenoxybenzene, a 4:1 ratio of bromobenzene to the disodium salt of resorcinol was used [9]. Electron releasing, or weakly electron withdrawing substituents on the aryl halide generally decrease the yields, especially when they happen to be methyl, methoxy or chloro groups [9, 24]. For example, 1,3-di(4-chlorophenoxy)benzene, produced in a manner similar to 1,3-diphenoxybenzene, is synthesized in only a 34% yield [9]. Electron withdrawing groups, particularly NO_2, have an enhancing effect on the yield of the expected product when they are ortho or para to the halogen. Yields have been

known to reach 80 to 90% for the o- and p- halogenated nitrobenzenes. This is confirmed by an albeit restricted study of substituents on the bromobenzene in the syntheses of 1,3-dibromobenzenes [9]. In this study, the authors have generated a Hammett plot, resulting in a value of ρ equal to 1.4.

The possibility usually exists for the sequential introduction of different aryloxy groups to an aryl dihalide. For example, in one of the few successful condensation reactions (in terms of yields) involving a chlorinated aromatic, o-dichlorobenzene was reacted with potassium phenolate first, the product of which was reacted with the potassium salt of 2-hydroxybiphenyl [26] (figure 10). Note that a different catalyst,

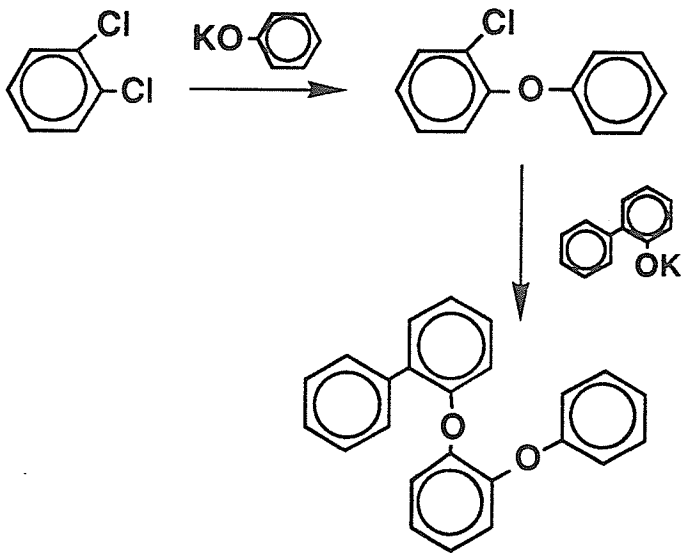


Figure 10: Synthesis of an unsymmetrical aromatic ether by the Ullmann approach

as well as reaction temperature and time is required for the second condensation reaction. An additional benefit of the condensation reaction is that in many cases, sensitive functionality on the aromatic halide do not require special protection (e.g.:

CHO, OH, and NH_2).

Substitution of the phenolic component can also affect the yield of desired product. For example, 2,6-dimethylphenol combined with bromobenzene gives next to no ether, presumably for steric reasons [27]. Even one ortho methyl group has been known to reduce yields to 25% [8]. Nitro-substituted phenols also enter into the condensation reaction with great difficulty, where the phenol is highly deactivated towards substitution when the NO_2 group is in the ortho and para positions [24].

The Ullmann condensation also suffers from a number of possible side reactions, most notably reductive dehalogenation and the coupling of phenols to form biphenols. Reductive dehalogenation occurs as a result of the phenolic group acting as a hydrogen donor [24, 27] to the haloaromatic, where it is common for the dehalogenated aromatic to be produced in equal amounts with the ether. Consider the condensation reaction between bromonaphthalene and phenol [24], where the yields of the ether and naphthalene are 38% and 36% respectively (figure 11). Biphenols resulting from the coupling reactions tend to be somewhat minor but

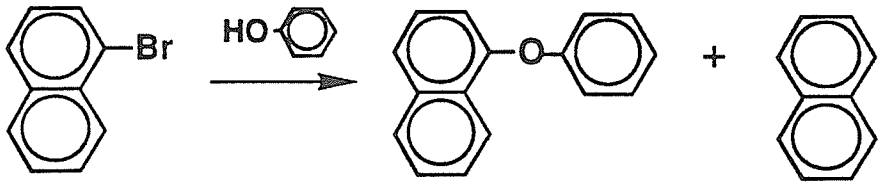


Figure 11: Dehalogenation side-reaction in the Ullmann synthesis

ever-present byproducts. In the condensation reaction between bromobenzene and 2,6-dimethylphenol mentioned above, 4,4′-dihydroxy-3,5,3′,5′-tetramethylbiphenyl is

formed in a 20% yield (figure 12) [27]. It is important to realize that those features

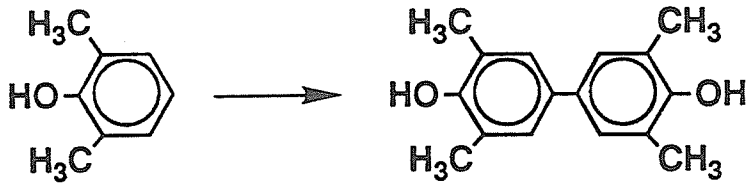


Figure 12: Coupling side-reaction in the Ullmann synthesis

favoring a high reactivity in the condensation also favor the side reactions. Therefore, the presence of a nitro or carboxyl group in the haloaromatic can sometimes suppress ether formation and make reductive dehalogenation the major process [23]. One functional group extremely sensitive to the process is the carboxyl group, where decarboxylation usually occurs under the conditions of extreme heating [23]. The mixture of products obtained from the Ullmann ether condensation usually demands considerable effort in the isolation of the desired ether (chromatographic separation).

Unfortunately, no one copper-containing catalyst is effective in all Ullmann condensation reactions leading to aromatic ethers. Cu_2O appears to be the superior reagent in terms of yield and generality, however, numerous examples are known in which this species is completely inactive. Consequently, a wide range of copper(I) halides have been used, as well as copper metal, and CuO [23]. The active form of catalyst is generally accepted to be Cu(I), and the presently accepted mechanism sees the copper acting as an additional electron-withdrawing group, through an interaction with the π electrons of the halobenzene (figure 13) [28]. In essence, this mechanism suggests that the Ullmann reaction is an aromatic nucleophilic substitution reaction. In fact, copper catalysts have been implemented in the substitution

of aromatic halogens with a variety of other nucleophiles as well, such as nitrogen, sulfur and carbon containing species. For an excellent review, see Lindley [23].

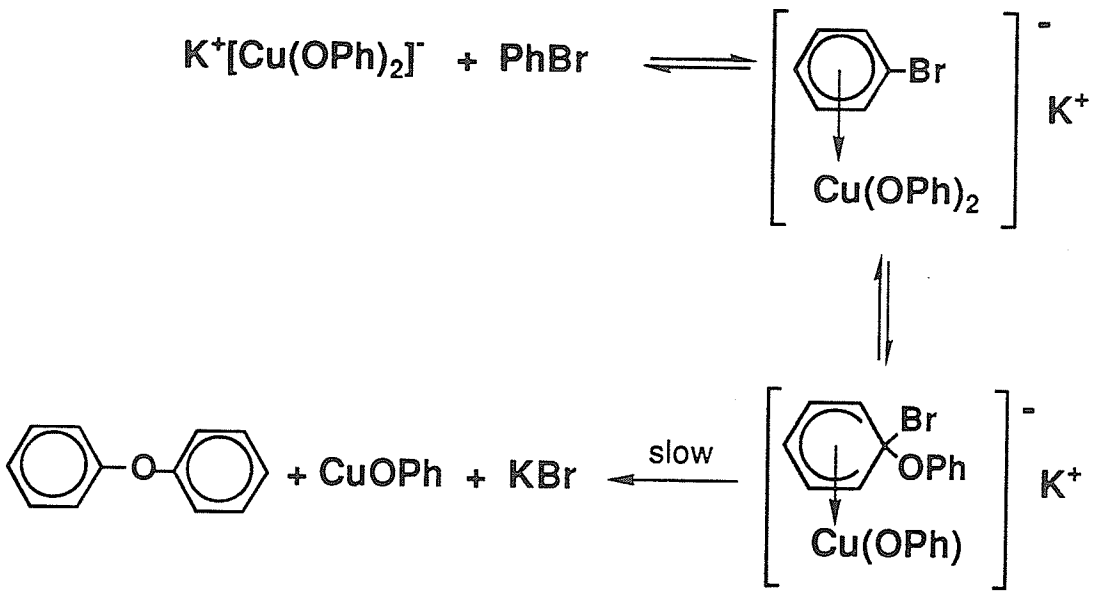


Figure 13: Proposed mechanism for the Ullmann condensation reaction

1.2.3 Coupling Reactions

Activated nucleophilic aromatic substitution and the Ullmann condensation reaction are the primary methods for aromatic ether synthesis. Recently, two types of coupling reactions have been developed which lead to the formation of more extensive aromatic ethers: the Scholl and nickel-catalyzed coupling reactions. These reactions do not produce the etheric linkage, rather they couple existing aromatic ethers by creating a direct aryl-aryl bond. The Scholl reaction involves the elimination of two aryl hydrogens, leading to the formation of the aryl-aryl bond through the action of Friedel-Crafts catalysts [2, 17, 29]. In such a manner, two 4-(1-naphthoxy)phenyl phenyl sulfones can be coupled together in nitrobenzene with anhydrous $FeCl_3$ (figure 14) [17]. The nickel-catalysed coupling reactions involve the elimination of two

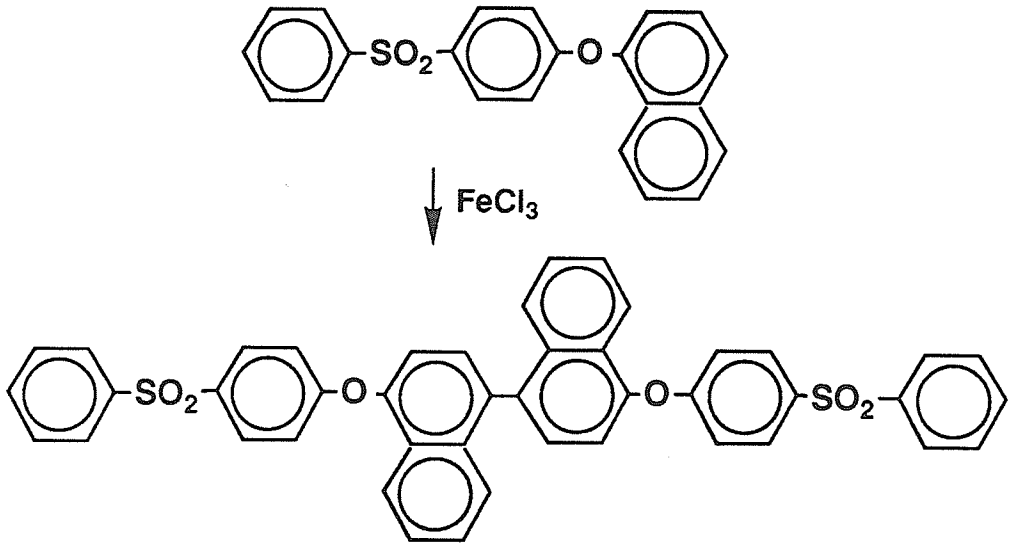


Figure 14: Coupling of 4-(1-naphthoxy)phenyl phenyl sulfones by the Scholl reaction

aryl halides, leading to the formation of an aryl-aryl bond, through the action of a catalytic amount of nickel, triphenylphosphine and an excess of zinc in a dry, dipolar aprotic solvent [1, 30]. For example, (4-chlorophenoxy)benzene can be efficiently coupled under these conditions to produce 4,4′-diphenoxybiphenyl (figure 15). Both reactions require scrupulously dry environments, and the yields are moderate to good. These coupling reactions are much more successful as polymerization techniques than the Ullmann ether condensation reactions. In fact, they were devised

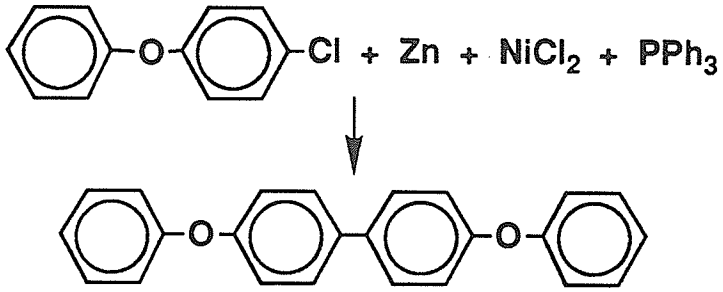


Figure 15: Nickel catalyzed coupling of (4-chlorophenoxy)benzene

by polymer chemists in order to provide alternatives to the Ullmann approach and nucleophilic substitution as methods of polymerization.

2 Organometallic Arene Activation

Alternative methods exist for the activation of aromatic compounds, allowing for nucleophilic substitution reactions with a wide variety of nucleophiles. These are organometallic in nature, and rely on the temporary complexation of a metal moiety to the π-electron system of the aromatic compound. A number of metal moieties may be successfully applied in this activating process. These include cyclopentadienyliron ($CpFe^+$), cyclopentadienylruthenium ($CpRu^+$), chromium tricarbonyl ($Cr(CO)_3$) and manganese tricarbonyl ($Mn(CO)_3{}^+$). These are capable of activating arenes to participate in extensive and varied types of reactions, however only S_NAr reactions will be considered here. As the iron system provides the basis of the present work, it will be discussed in detail. The other systems will only receive a brief introduction.

2.1 [η^6-Arene-η^5-Cyclopentadienyl]iron Complexes

With the discovery of ferrocene in the early 1950's came a great deal of research focussed on ways to apply this novel complex to synthetic problems. An important modification of ferrocene involves the replacement of one cyclopentadienyl ring with a range of functionalized arenes [31, 32, 33]. This has led to the synthesis of η^6-arene-η^5-cyclopentadienyliron cationic complexes, having a host of different properties, as can be found in two excellent reviews of aromatic organoiron chemistry (by Astruc [34], and Sutherland [35]). This introduction will only be concerned with the synthesis of these complexes and the nucleophilic substitution reactions they can undergo. The interested reader is directed to Astruc's review for a comprehensive overview of the other properties of these complexes.

2.1.1 Synthesis

The typical synthesis of η^6-arene-η^5-cyclopentadienyliron complexes proceeds by a ligand exchange process, in which the appropriate arene, when combined with ferrocene, $AlCl_3$, and Al, replaces one of the cyclopentadienyl rings (figure 16). The

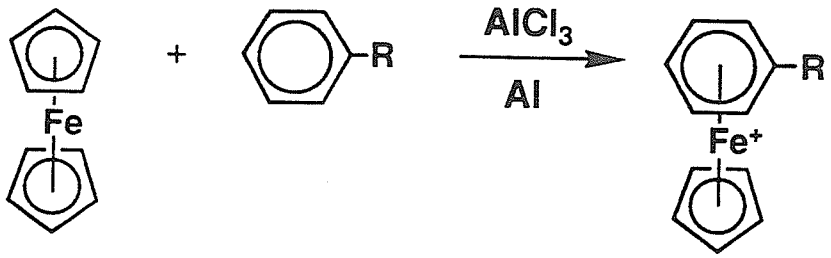


Figure 16: The ligand exchange reaction

mixture is heated, usually between 30 and 165 °C, for a duration of 4 to 24 hours [36, 37, 38, 39, 40]. Al powder is present in these reactions to prevent oxidation of the $AlCl_3$. Cationic complexes result from this reaction, which are typically isolated as their hexafluorophosphate or tetrafluoroborate salts. Yields for such reactions rarely exceed 40%, yet in certain cases 90% yields have been reported when certain amounts of H_2O or concentrated HCl are present [35]. The mechanism for this process has been studied (see [35] for leading references), and it has been concluded that the active catalyst is $HAlCl_4$, allowing the formation of the key intermediate $[(Cp)_2FeH]AlCl_4$. This intermediate then undergoes exchange with the arene of choice.

Ligand exchange cannot be carried out between ferrocene and arenes containing electron-withdrawing substituents, most likely since the the mechanism of exchange is based on an electrophilic aromatic substitution [37]. Therefore, removal of ring electron density by substituents such as keto groups prevents ligand exchange from

taking place [37]. However, exchange reactions are not limited to simple arene ligands, as a wide range of polyaromatics and heterocycles can be effectively complexed [36, 38, 39, 41]. Furthermore, polyaromatic systems can also undergo more than one ligand exchange reaction when an excess of ferrocene is used, to yield di(cyclopentadienyliron) complexes [36, 39, 40, 42, 43]. The review by Sutherland [35] states that the only way to obtain di-iron complexes is by such ligand exchange reactions. The work presented in this thesis demonstrates a new way to synthesize di-iron complexes.

2.1.2 Nucleophilic Substitution Reactions

The reactivity of [η^6-arene-η^5-cyclopentadienyl]iron complexes is high, allowing for a great deal of diverse chemistry to be carried out. The reactivity of the iron center and cyclopentadienyl ring contribute to this diversity, but this thesis will only be concerned with the activation of the complexed arene towards nucleophilic substitution reactions.

It has been stated that the $CpFe^+$ moiety is roughly the equivalent to two nitro groups in terms of activation of an arene towards nucleophilic substitution [34]. The efficiency of this withdrawing group has allowed for the substitution of chlorine and nitro substituents on the arene of [η^6-arene-η^5-cyclopentadienyl]iron complexes, in which the substitution of the nitro group is almost as efficient as that of the chloro substituent [44, 45]. This has led to the generation of a whole series of complexes incorporating O, N, and S containing nucleophiles, with yields ranging from 50-90%. In these reactions, the [η^6-arene-η^5-cyclopentadienyl]iron complex is combined with the appropriate nucleophile and a suitable base to activate the nucleophile (figure 17)

[44, 45, 46, 47]. These complexed chloro- and nitro-aromatics have also been reacted with an extensive number of stabilized carbanion nucleophiles, resulting in C-C bond formation [48, 49, 50, 51, 52]. The synthesis of complexes of arylated 1,3-dicarbonyl compounds by this approach is quite simple and efficient, allowing for the preparation of a range of important biologically active compounds, or their precursors. For

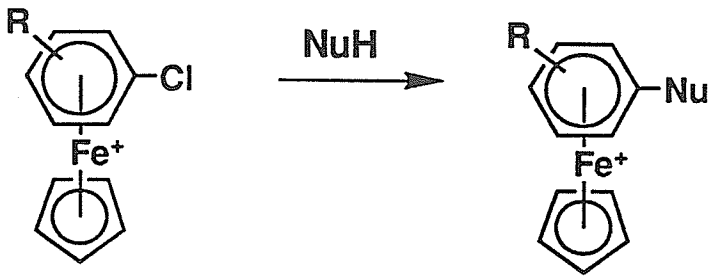


Figure 17: Cyclopentadienyliron-activated S_NAr reactions

example, precursors to 5-ethyl-5-phenylbarbituric acid (phenobarbital) and related barbiturates can be synthesized from [η^6-arene-η^5-cyclopentadienyl]iron complexes combined with diethyl methylmalonate (figure 18) [49]. An immediately apparent benefit of this synthetic approach over other methods is the ease with which additional functional groups can be included on the aryl group, before or after the C-C bond formation. A second chloro substituent on the complexed aromatic allows the introduction of a second nucleophile (the same or different). In this way, diethyl methylmalonate was arylated and further modified by nucleophilic substitution reactions after arylation (figure 19) [49].

More rigorous studies of the substitution of [η^6-dichlorobenzene-η^5-cyclopenta-

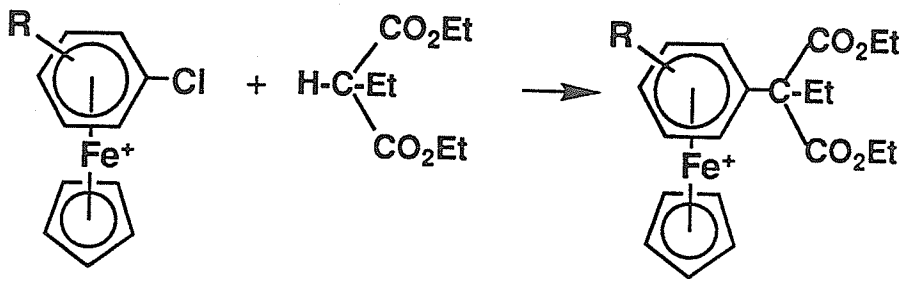


Figure 18: Introduction of carbanions to $CpFe^+$ complexes

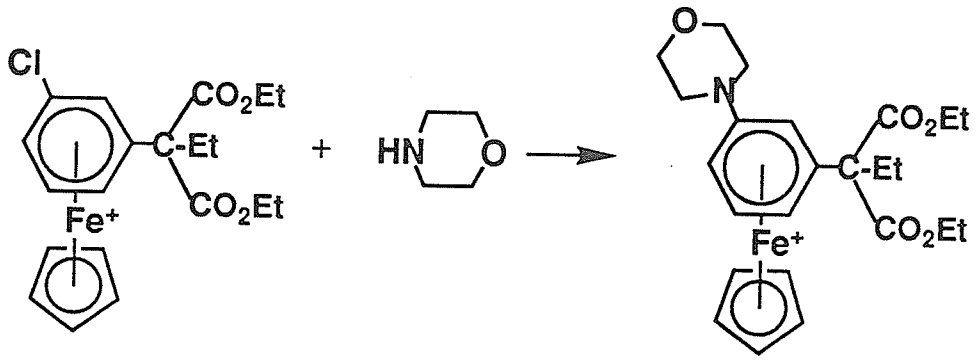


Figure 19: Multiple functionalization of $CpFe^+$ complexes by S_NAr reactions

dienyl]iron complexes have been undertaken [50, 53, 54]. In one, a number of primary amine nucleophiles were reacted in excess with these complexes, resulting in only monosubstitution [53]. Disubstitution was not possible here, due to the formation of a zwitterion-cyclohexadienyl equilibrium complex upon monosubstitution, a result of the basic reaction conditions (figure 20). The formation of the cyclohexadienyl

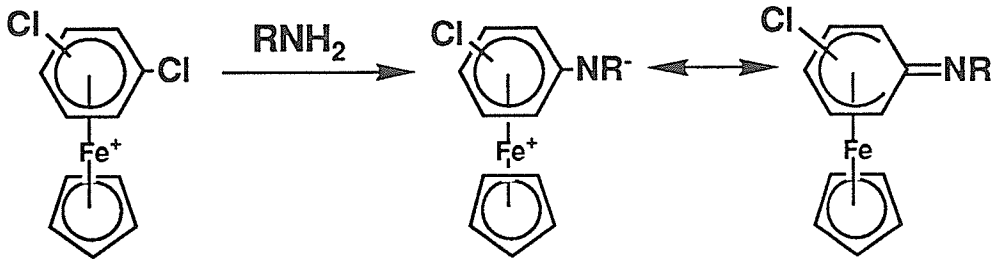


Figure 20: Deactivation of the $CpFe^+$ complexes by zwitterion formation

complex, as first observed by Helling and Hendrickson [55], effectively deactivates the complex to further substitution. Similar behavior has been observed when these complexes are reacted with carbanion nucleophiles possessing an additional acidic proton on the carbon attached to the arene [48, 50]. In the case of the amino complexes this may be overcome, and disubstitution achieved, when a certain amount of acetic acid is added to the reaction mixture [53].

It has also been found that these dichlorobenzene complexes can undergo similar reactions with O and S containing nucleophiles [12, 54, 56]. For example, an excess of phenol can be reacted with [η^6-o-dichlorobenzene-η^5-cyclopentadienyl]iron complex, resulting in disubstitution. Monosubstitution can only be achieved by a high dilution technique, in which a solution of an equimolar amount of phenol is added dropwise to a solution of the o-dichlorobenzene complex [54]. An interesting

method of heterocycle synthesis has also been achieved via arene activation with cyclopentadienyliron [36, 46, 57, 58]. The complex [η^6-o-dichlorobenzene-η^5-cyclopentadienyl]iron can be combined with a range of aromatic 1,2-dinucleophiles, such as catechol and 1,2-hydroxythiophenol for example (figure 21). The work in this

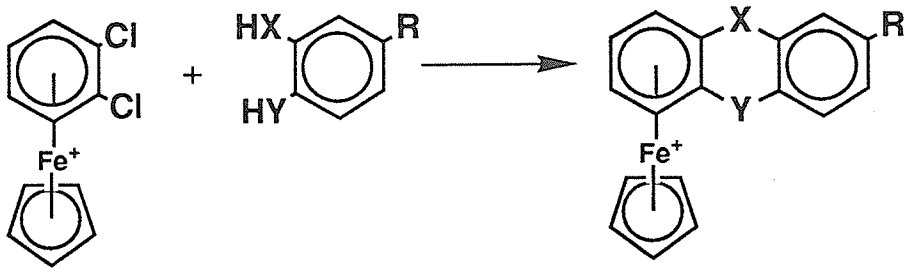


Figure 21: Heterocycle formation by $CpFe^+$-activated S_NAr reactions

area has developed to include the synthesis of heterocycles containing pyridine fragments [59], and structural studies have been undertaken to determine the relative orientation of the heterocycle to the iron moiety [60, 61, 62].

The utility of the cyclopentadienyliron moiety in organic synthesis would be diminished were it not for its ability to be removed easily and in a number of ways. Currently, the most commonly used method is photolytic demetallation, in which a solution of the cyclopentadienyliron complex is visible-light irradiated, causing the liberation of the aromatic ligand as well as the production of ferrocene and an iron(II) salt [63, 64, 65]. This is outlined in figure 22. In a somewhat limited study, Nesmeyanov has shown that the yields from this photodisproportionation are highly dependent on the solvent [66]. This study was carried out under ultraviolet light, and with only one type of counterion. Gill and Mann have conducted more rigorous studies in which solvent type and counterions were varied [67, 68, 69]. While these

studies were primarily concerned with the mechanism of disproportionation, they concluded that CH_3CN was one of the most efficient solvents. The suggestion by Nesmeyanov that the disproportionation occurred through a photoinduced electron transfer from solvent to complex was supported by this work, by the identification of a $[(\eta^5\text{-}C_5H_5)Fe(CH_3CN)_3]^+$ intermediate. Using this technique, the aromatic ligand can typically be recovered in yields of 50-100%. Another viable technique is pyrolytic sublimation, where the complex is heated between 100-200 °C under a partial vacuum (approximately 1 torr), resulting in a similar disproportionation [40, 41, 70]. Electrolytic reduction of the cationic complexes can also cause a loss of the metal moiety. This method, as well as the electrochemical behavior of this class of iron complexes has been much studied by Astruc [34] as well as Abd-El-Aziz [50].

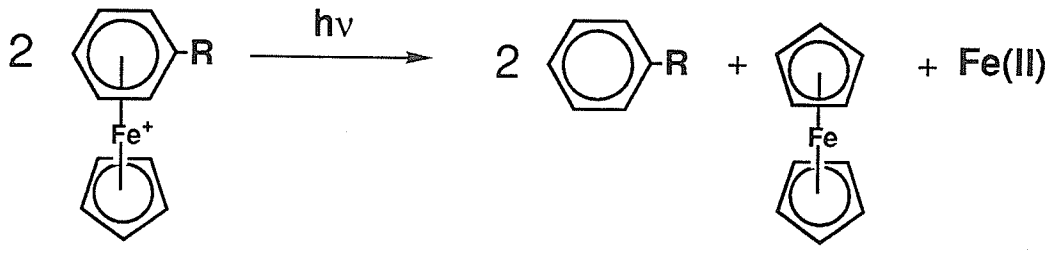


Figure 22: Liberation of the arene by photodissociation

2.1.3 NMR Studies of These Complexes

Very interesting features have been observed in the ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra of $[\eta^6$-arene-η^5-cyclopentadienyl]iron cationic complexes. Initial ^1H NMR studies have been undertaken by Nesmeyanov [71], revealing that

complexation to the $CpFe^+$ moiety results in a dramatic upfield shift of approximately 0.7 to 1 ppm for the protons of the complexed arene. In this study, a series of related complexes were investigated, and their shifts correlated with Hammett equation parameters. A more rigorous investigation of the effects that complexation has on the arenes has been conducted by Steele, Sutherland and Lee, focussing on the ^{13}C NMR spectra [72]. The large upfield shifts in the ^1H and ^{13}C spectra of the complexed arenes cannot be simply due to the positive charge that these systems possess, since related uncharged iron-arene complexes also exhibit upfield shifts. Rather, it has been proposed that the changes in the hybridization of the arene electrons due to bonding interactions with the metal d orbitals are responsible for these shifts [39, 71, 72].

2.2 Other Metal Systems

Other metal moieties exist that, when complexed to chloro-aromatics, will result in activation towards nucleophilic substitution. The more noteworthy and successful include $Cr(CO)_3$, $CpRu^+$ and $Mn(CO)_3^+$. These, along with $CpFe^+$, can be ranked according to their relative electron-withdrawing ability (figure 23) [34]. Activation

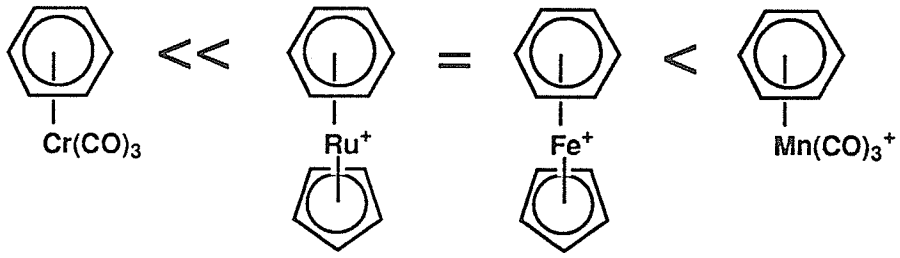


Figure 23: Relative electron-withdrawing ability of various metal moieties

by $Cr(CO)_3$ has received the most attention over the years, likely due to the wide variety of functionalized arenes to which it can be complexed [73, 74, 75, 76, 77]. However, this moiety results in relatively poor activation of nucleophilic substitution reactions, leading to the investigation of the other metal moieties. The $Mn(CO)_3^+$ group is best in terms of activation, but it is quite limited in the number of aromatics to which it can be complexed [13, 78, 79]. The above two moieties also involve toxic co-ligands, making the work-up that much more involved. The $CpRu^+$ group is very similar to $CpFe^+$ in terms of activation, and a good deal of related work has been undertaken [78, 80], however the cost of ruthenium is a prohibiting factor in its widespread usage. The usefulness of these systems in aromatic ether synthesis will be assessed against the iron system developed in the present work.

3 Focus of the Present Study

The intent of this work was to develop a new and useful method for the synthesis and functionalization of aromatic ethers via the cyclopentadienyliron moiety. It extends the investigation of [η^6-arene-η^5-cyclopentadienyl]iron complexes in a new direction. A series of *di-iron* complexes has been synthesized via newly developed double nucleophilic substitution reactions between [η^6-chloroarene-η^5-cyclopentadienyl]iron complexes and dihydroxyaromatic nucleophiles. These reactions resulted in the formation of polyaromatic ether linkages between the metal centers. An extensive series of such complexes was prepared in order to establish the generality of the technique. Functionalization of the complexed ethers was achieved by further nucleophilic substitution reactions involving carbon nucleophiles and certain di-iron complexes. These bridging ligands and modified bridging ligands were retrieved through the efficient removal of the cyclopentadienyliron moieties by photolytic demetallation. The description of the new technique for aromatic ether synthesis is followed by a comparative study with the existing techniques.

Part II

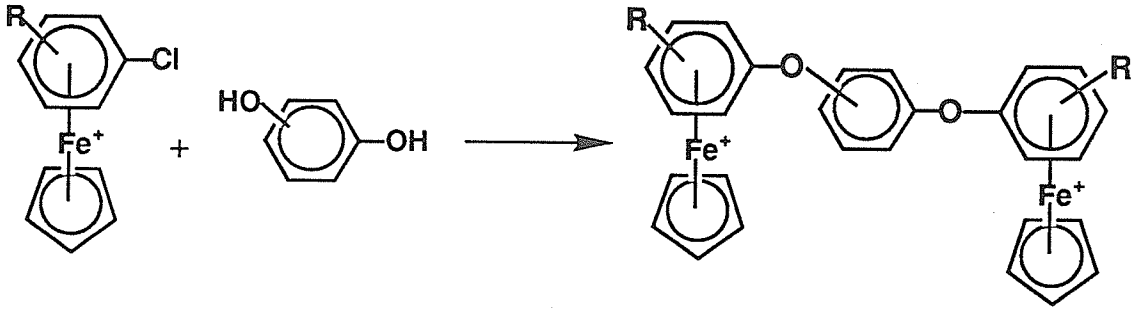
Results and Discussion

1 Synthesis of Substituted Diphenoxybenzenes

A simple one-step reaction has been developed for the synthesis of a new class of di-iron complexes, by a novel extension of previously studied aromatic nucleophilic substitution (S_NAr) reactions activated by the cyclopentadienyliron ($CpFe^+$) moiety. Previously, compounds with only one nucleophilic site have been incorporated into arenes activated by this metal moiety. This, of course, limits the method to the functionalization of mono-iron complexes only. In the present work, *dinucleophiles* were used and it is shown below that di-iron complexes could be produced directly in a one-pot double nucleophilic substitution reaction. The discovery of this reaction constitutes a significant advance in preparative organometallic chemistry, however the greatest benefit lies in the application of this reaction to the synthesis of a wide range of organic compounds. In this study, dihydroxybenzenes were incorporated as the dinucleophiles, allowing access to a large number of complexed diphenoxybenzenes, which serve as precursors to the purely organic diphenoxybenzenes.

To arrive at these complexes, the appropriate [η^6-chloroarene-η^5-cyclopentadienyl]iron complex was reacted with a dihydroxyaromatic compound under mild temperatures, in a polar aprotic solvent system such as a mixture of dimethylformamide (DMF) and tetrahydrofuran (THF). The presence of a weak base is also required, in order to activate the nucleophile by proton abstraction. The weak base K_2CO_3 was

sufficient in this respect. The resulting di-iron products, since they are di-cationic, required isolation as their hexafluorophosphate salts. A series of such di-iron complexes has been synthesized, as indicated in scheme 1.

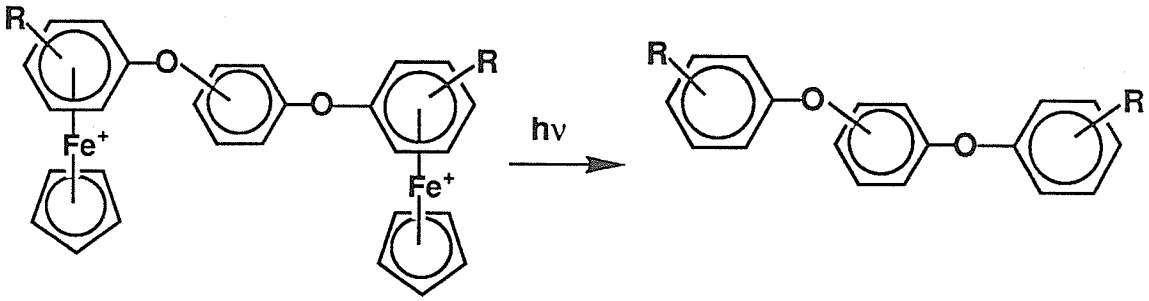


Scheme 1

R	mono-iron	di-iron		
		1,4	1,3	1,2
H	i	**2.1a**	**2.8a**	**2.15a**
o-Cl	ii	**2.2a**	**2.9a**	—
m-Cl	iii	**2.3a**	**2.10a**	**2.16a**
p-Cl	iv	**2.4a**	**2.11a**	**2.17a**
o-CH_3	v	**2.5a**	**2.12a**	**2.18a**
m-CH_3	vi	**2.6a**	**2.13a**	**2.19a**
p-CH_3	vii	**2.7a**	**2.14a**	**2.20a**

Photolytic demetallation of the di-iron complexes allows for the generation of the organic diphenoxybenzenes in high yields. These dissociation reactions take

place in the presence of a coordinating solvent such as CH_3CN or a mixture of CH_3CN and CH_2Cl_2, under intense visible light. Therefore, just as photolysis is a viable technique for the liberation of arenes in mono-iron complexes, so it is for di-iron complexes. All of the complexes presented in scheme 1 have proved to respond well to this technique, allowing for the liberation of the diphenoxybenzenes (scheme 2). The photolytic dissociation procedure benefits from the presence of a



Scheme 2

R	1,4	1,3	1,2
H	**2.1b**	**2.8b**	**2.15b**
o-Cl	**2.2b**	**2.9b**	—
m-Cl	**2.3b**	**2.10b**	**2.16b**
p-Cl	**2.4b**	**2.11b**	**2.17b**
o-CH_3	**2.5b**	**2.12b**	**2.18b**
m-CH_3	**2.6b**	**2.13b**	**2.19b**
p-CH_3	**2.7b**	**2.14b**	**2.20b**

good coordinating solvent. As was previously mentioned, CH_3CN is very efficient in this respect, as the iron can be coordinated by a σ-type interaction with the lone electron pair of the nitrogen. A CH_3CN/CH_2Cl_2 mixture was usually used in which a minimal amount of CH_3CN was present. It was found that CH_2Cl_2 did not hamper the efficiency of the photolytic process, and that using as little CH_3CN as possible contributed to the ease in workup. A description and characterization of the products presented in schemes 1 and 2, as well as certain features of the reactions producing these products are discussed below.

1.1 Reactions with 1,4-dihydroxybenzene

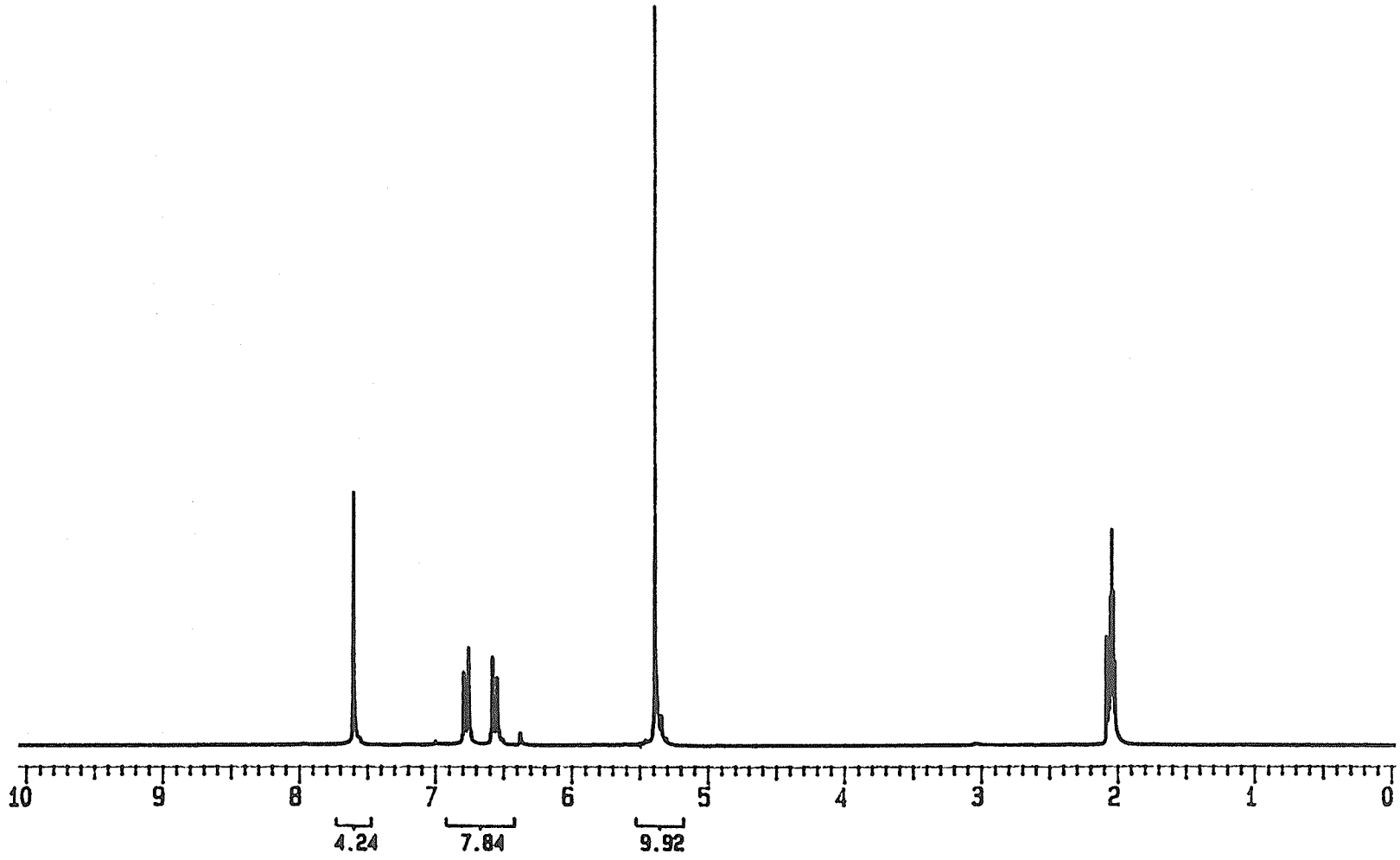
The synthesis of all complexes **2.1a-2.7a** was achieved under the same conditions. The dinucleophile 1,4-dihydroxybenzene (hydroquinone) was typically combined with the substituted [η^6-chlorobenzene-η^5-cyclopentadienyl]iron complex in a 1:2 molar ratio. Reaction times were a standard eight hours, whether the second substituent was a methyl or chloro group, in the ortho, meta or para position. This procedure involved refluxing of the reagents in a THF/DMF solvent system (4:1 ratio). An alternative method, in which the reagents were stirred at room temperature in an equivalent amount of DMF only, produced the di-iron complexes in similar yields, however a reaction time of 18 hours was usually required. The negligible solubility of these complexes in water allowed for their precipitation as yellow solids by the inclusion of a NH_4PF_6 solution. Apparently, the nature and position of the second substituent of the mono-iron complex had no effect on the reaction conditions necessary to affect double substitution. This is true for both preparative techniques investigated. ^1H and ^{13}C NMR data for these complexes can be found in tables 1

and 2, while their yields and analytical data are listed in table 3. NMR spectra for 1,4-di([η^6-4-chlorophenoxy-η^5-cyclopentadienyl]iron)benzene dihexafluorophosphate (**2.4a**) is presented in figure 24 and figure 25. The symmetry of this complex on the NMR time-scale is readily apparent. In the ^{1}H spectrum, one singlet at 5.38 ppm exists for both cyclopentadienyl rings, and one singlet at 7.59 ppm for the four protons of the uncomplexed arene ring. The 6.58-6.80 ppm region contains the resonances of the two complexed arenes, also equivalent due to symmetry, and corresponds to an AA'BB' spin system common in para-disubstituted benzenes. As the figure shows, integration of the various regions of the ^{1}H spectrum agrees with the above assignments. The ^{13}C-APT (Attached Proton Test)[1] NMR spectrum reflects the symmetry as well, revealing only one resonance for the cyclopentadienyl ring carbons (80.57 ppm) and one for the carbons of the uncomplexed arene CH's (124.43 ppm). There are two carbon resonances for the CH's of the complexed arenes, at 77.16 and 87.86 ppm. Both of these spectra demonstrate that the $CpFe^+$ moiety causes an upfield shift in the resonances of the complexed arenes, caused by the electron withdrawing action of $CpFe^+$ [43, 72]. This effect is also evident in the locations of the resonances for the quaternary carbons in the ^{13}C-APT spectrum. The resonance for the uncomplexed arene can be found at 151.96 ppm, while those for the complexed arenes are at 134.03 ppm (C-O) and 105.06 ppm (C-Cl).

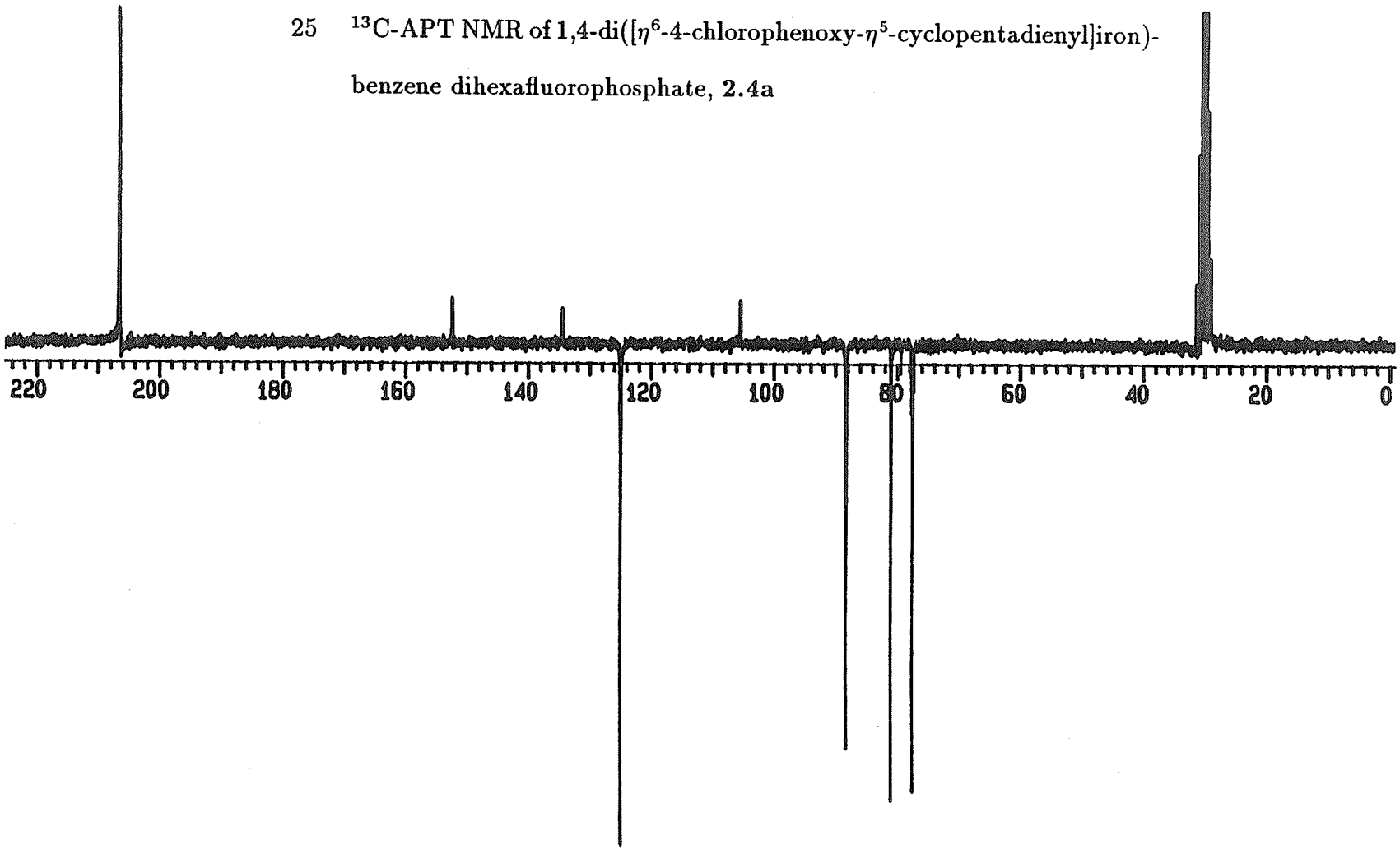
Demetallation was achieved through irradiation of CH_3CN/CH_2Cl_2 solutions of the complexes, under the photolytic conditions more fully outlined in the experimental section, producing the purely organic diphenoxybenzenes **2.1b–2.7b**. All di-iron complexes were subject to the same conditions, with the exception of the

[1]This variation in recording ^{13}C spectra is discussed more fully in section 4.2.

24 ^{1}H NMR of 1,4-di([η^6-4-chlorophenoxy-η^5-cyclopentadienyl]iron)benzene dihexafluorophosphate, **2.4a**

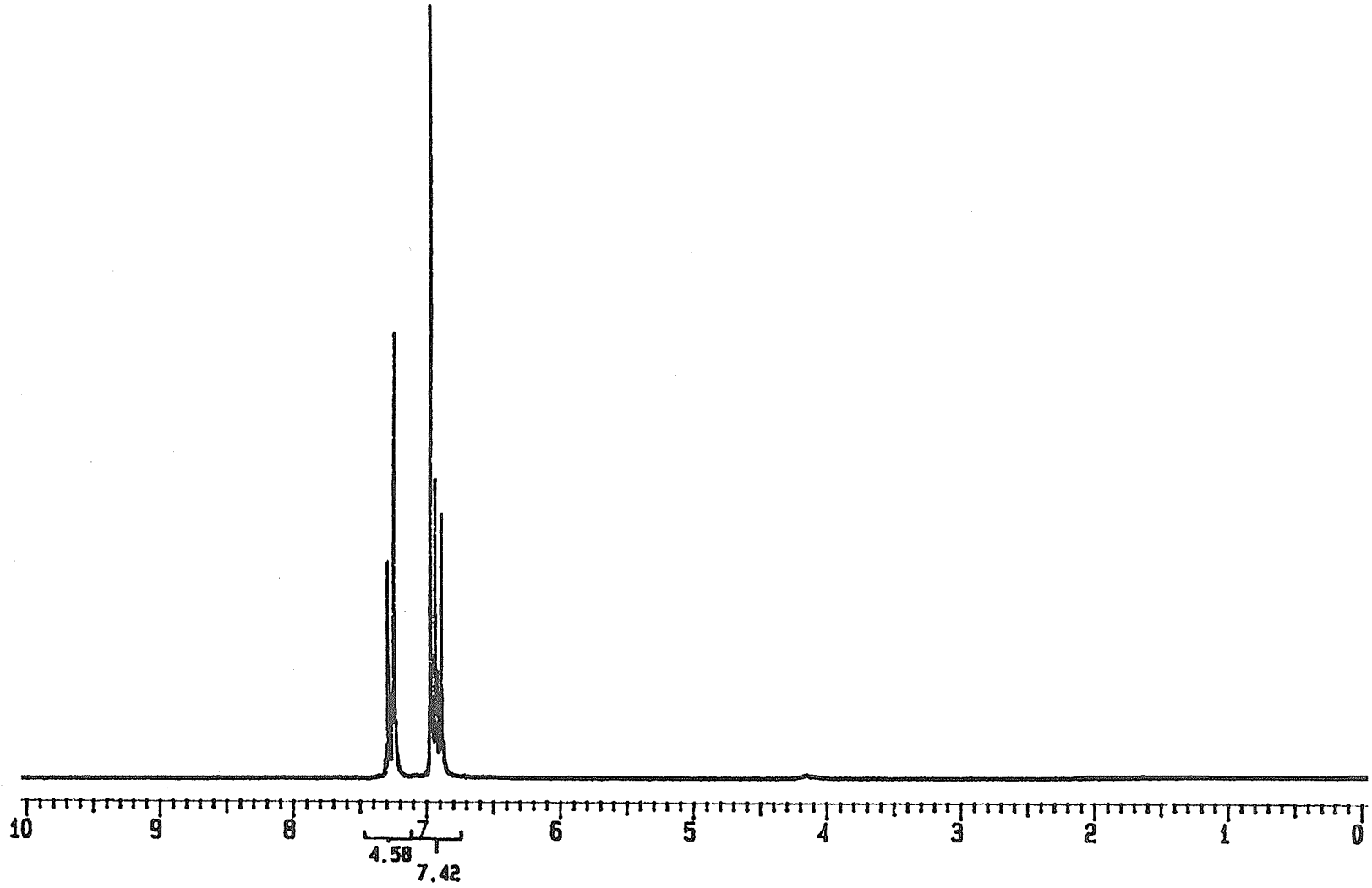


25 ^{13}C-APT NMR of 1,4-di([η^6-4-chlorophenoxy-η^5-cyclopentadienyl]iron)-benzene dihexafluorophosphate, **2.4a**

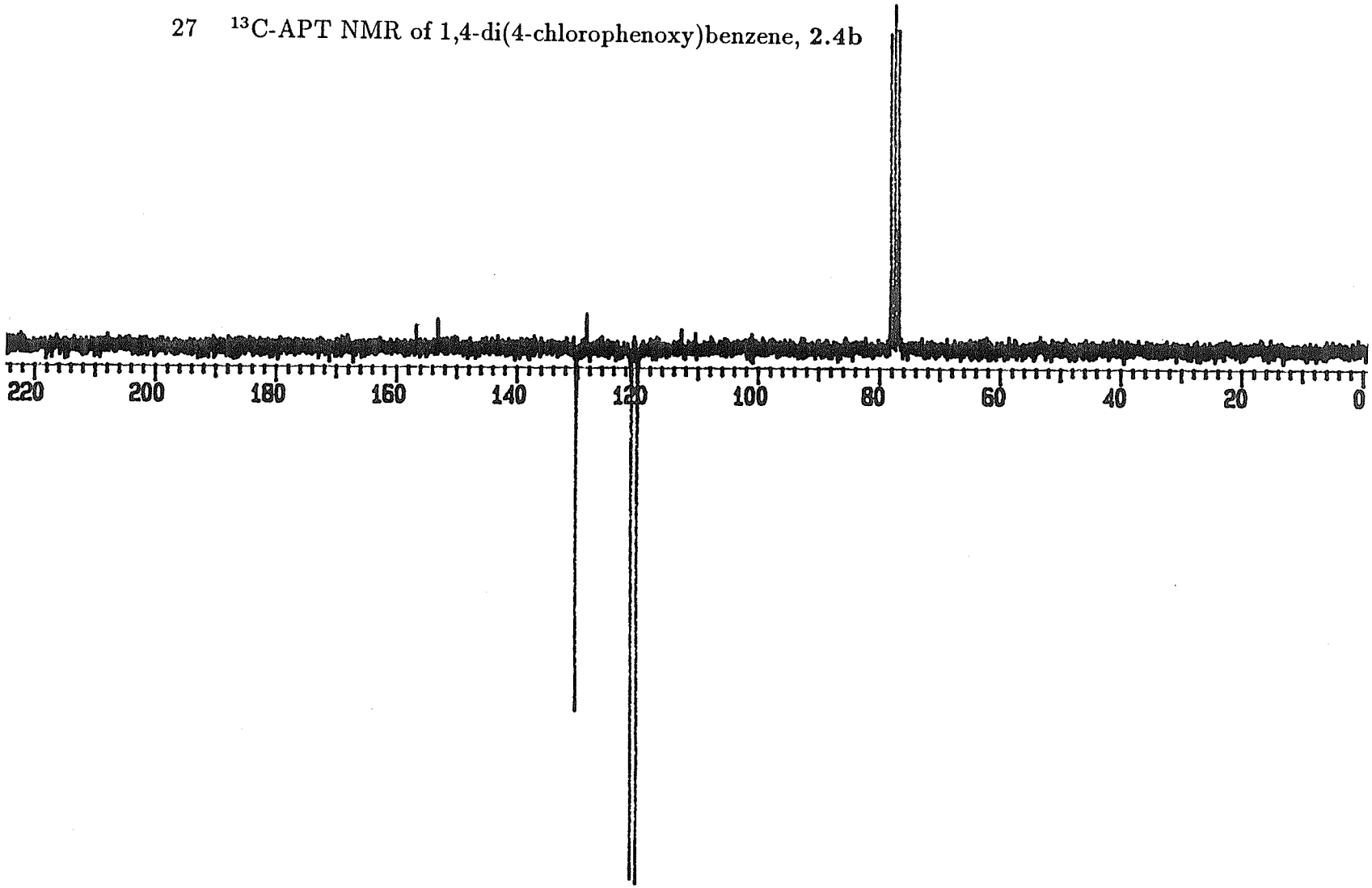


solvent ratio. The ^{1}H and ^{13}C-APT NMR data have been recorded in tables 4 and 5. Mass spectra were also taken, and the data can be found with the ^{1}H NMR summaries. Uncorrected melting points were measured for those compounds which could be isolated as solids, and have been included with the ^{13}C-APT NMR data. Yields were also high for this final step, ranging between 76–93%, and can be found in table 6, along with the elemental analysis data. The spread in the yields could be related to the variation in the solvent combination used, however no clear trend was noted. The spectra for 1,4-di(4-chlorophenoxy)benzene (**2.4b**), obtained from the photolysis of **2.4a**, are shown in figure 26 and figure 27. Apart from the obvious disappearance of the resonance for the cyclopentadienyl rings, the ^{1}H spectrum reveals a large downfield shift in the proton resonances of the liberated arenes (6.89-7.29 ppm). It can still be described as an AA'BB' spin system, however. Interestingly, the singlet arising from the protons of the central arene is also substantially affected, shifting approximately 0.6 ppm upfield to 6.97 ppm. This can be explained by the modification of the inductive effect for the phenoxy substitutent. When complexed to the strongly withdrawing $CpFe^{+}$, the phenoxy group becomes a much better electron-withdrawing group, causing the indicated shift in the resonance. Similar effects can be noted in the ^{13}C-APT spectrum. The carbon resonance for the cyclopentadienyl rings has disappeared, and the two carbon resonances for the CH's of the liberated arenes have shifted to dramatically higher frequencies (to 120.04 and 130.22 ppm). The carbon resonance for the CH's of the central arene have shifted upfield only slightly to 121.00 ppm. whereas the quaternary carbon of the central arene has shifted *downfield* to 156.78 ppm, relative to its position in the complex. The quaternaries of the liberated arenes have also shifted downfield to 153.12 (C-O)

26 ^{1}H NMR of 1,4-di(4-chlorophenoxy)benzene, 2.4b



27 ^{13}C-APT NMR of 1,4-di(4-chlorophenoxy)benzene, **2.4b**



and 128.61 (C-Cl). The melting point for this white solid was found to be 94-5 °C. The mass spectrum reveals an intense molecular ion peak (M^+) at an m/z of 330, and the presence of 2 Cl's is confirmed by the characteristic M+2 and M+4 peaks. It was found that all compounds **2.1b–2.7b** produced a very intense molecular ion peak, indicating their stability.

Table 1: ^{1}H NMR data for complexes **2.1a–2.7a**

δ (referenced to acetone-d_6)			
Complex	*Complexed aromatics*	*Cp's*	*Others*
2.1a	6.31(bs,2H) 6.45(bs,8H)	5.26(s,10H)	7.59(s,4H)(Ar)
2.2a	6.33(t,2H,*J* 6.2) 6.45(d,2H,*J* 5.6) 6.50(t,2H,*J* 6.0) 7.00(d,2H,*J* 6.0)	5.33, 5.35 (2s,10H)	7.72, 7.73 (2s,4H)(Ar)
2.3a	6.42(d,2H,*J* 6.6) 6.55(2H,*J* 6.4) 6.70(d,2H,*J* 6.2)	5.35, 5.36 (2s,10H)	7.62(s,4H)(Ar)
2.4a	6.56(d,4H,*J* 7.0) 6.78(d,4H,*J* 7.0)	5.38(s,10H)	7.59(s,4H)(Ar)
2.5a	6.22-6.25(m,6H) 6.54-6.57(m,2H)	5.19, 5.21 (2s,10H)	2.67(s,6H)(CH_3); 7.58(s,4H)(Ar)
2.6a	6.20-6.23(m,2H) 6.30-6.36(m,4H) 6.48(s,2H)	5.20(s,10H)	2.39(s,6H)(CH_3); 7.53(s,4H)(Ar)
2.7a	6.32-6.44(m,8H)	5.22(s,10H)	2.51(s,6H)(CH_3); 7.55(s,4H)(Ar)

Table 2: ^{13}C NMR data for complexes **2.1a–2.7a**

δ (referenced to acetone-d_6)			
Complex	*Complexed aromatics*	*Cp's*	*Others*
2.1a	77.79, 85.93, 87.93, 134.73*	78.21	124.47, 151.91*(Ar)
2.2a	77.32, 77.39, 85.89, 86.89, 89.15, 97.90*, 131.69*	80.27, 80.32	124.39, 152.16* 152.23*(Ar)
2.3a	76.61, 79.10, 86.45, 86.94, 107.21*, 134.22*	80.47	124.25, 151.98*(Ar)
2.4a	77.16, 87.86, 105.06*, 134.03*	80.57	124.43, 151.96*(Ar)
2.5a	76.80, 85.23, 86.17, 89.73, 93.75*, 132.88*	78.34	16.31(CH_3); 124.13, 152.16*(Ar)
2.6a	76.01, 79.02, 79.06, 86.24, 86.83, 103.97*, 132.98*	78.42	20.33(CH_3); 123.98, 151.96*(Ar)
2.7a	77.09, 87.92, 101.63*, 133.61*	78.60	19.94(CH_3); 124.21, 152.01*(Ar)

* denotes quaternary carbon atoms

Table 3: Yields and elemental composition data for complexes **2.1a–2.7a**

		elemental composition found(calculated), %	
Complex	*% yield*	*C*	*H*
2.1a	95	42.43(42.35)	3.13(3.05)
2.2a	90	39.04(38.97)	2.60(2.57)
2.3a	90	38.88(38.97)	2.47(2.57)
2.4a	88	38.91(38.97)	2.57(2.57)
2.5a	89	43.70(43.83)	3.35(3.43)
2.6a	88	43.89(43.83)	3.50(3.43)
2.7a	85	44.01(43.83)	3.35(3.43)

Table 4: ^{1}H NMR and MS data for compounds **2.1b–2.7b**

δ (referenced to chloroform-d)			
Compound	*Aromatics*	*Others*	M^+,*m/z (rel.ab.)*
2.1b	6.98(s,4H), 6.99-7.35(m,10H)	—	262 (100)
2.2b	6.95(s,6H), 7.05(t,2H,J 8.0), 7.17(t,2H,J 8.0), 7.44(d,2H,J 8.0)	—	330 (100) 332 (64) 334 (11)
2.3b	7.01(s,4H), 6.84-7.28(m,8H)	—	330 (100), 332 (64) 334 (11)
2.4b	6.97(s,4H), 6.89-6.93(m,4H), 7.24-7.29(m,4H)	—	330 (100) 332 (66) 334 (11)
2.5b	6.87(s,4H), 6.94-7.24(m,8H)	2.26(s,6H)(CH_3)	290 (100)
2.6b	6.76-6.90(m,6H), 6.97(s,4H), 7.15-7.24(m,2H)	2.32(s,6H)(CH_3)	290 (100)
2.7b	6.88-6.92(m,4H), 6.95(s,4H), 7.10-7.15(m,4H)	2.32(s,6H)(CH_3)	290 (100)

Table 5: ^{13}C NMR and melting point data for compounds **2.1b–2.7b**

δ (referenced to chloroform-*d*)			
Compound	*Aromatics*	*Others*	*M.P.(°C)*
2.1b	118.30, 120.44, 122.99, 129.72, 152.72*, 157.78*	—	87
2.2b	119.54, 120.05, 124.42, 125.40*, 127.89, 130.78, 152.54*, 152.93*	—	88-90 (white)
2.3b	116.33, 118.45, 120.93, 123.19, 130.52, 135.09*, 152.34*, 158.52*	—	59
2.4b	120.04, 121.00, 130.22, 128.61*, 153.12*, 156.78*	—	94-95 (white)
2.5b	118.67, 118.99, 123.51, 127.03, 131.38, 129.41*, 152.85*, 155.27*	16.16(CH_3)	oil (yellowish)
2.6b	115.29, 119.00, 120.32, 123.79, 129.40, 139.90*, 152.71*, 157.73*	21.38(CH_3)	oil (yellowish)
2.7b	118.43, 119.90, 130.18, 132.55*, 152.98*, 155.42*	20.63(CH_3)	93 (white)

* denotes quaternary carbon atoms

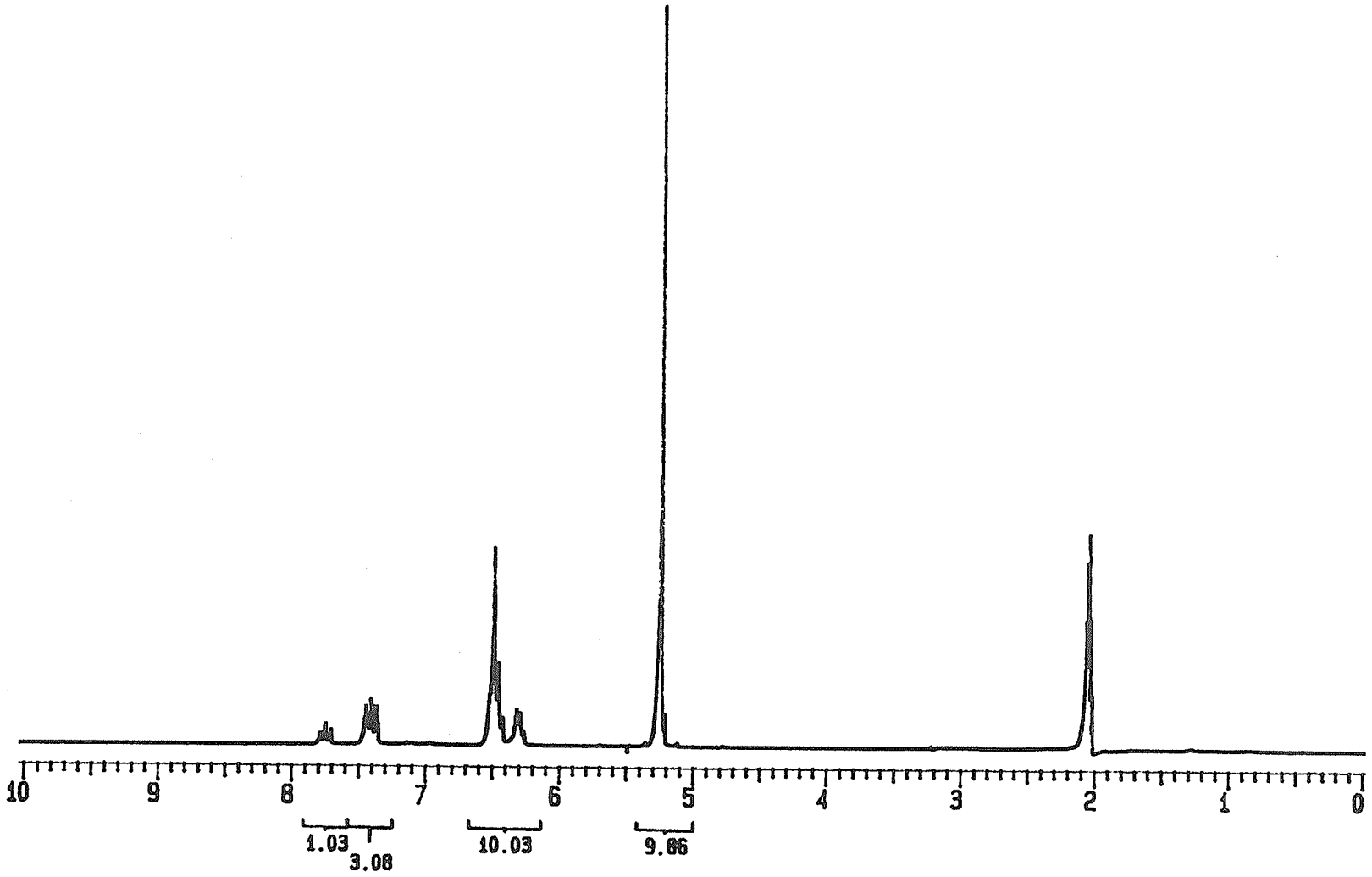
Table 6: Yields and elemental composition data for compounds **2.1b–2.7b**

		elemental composition found(calculated), %	
Compound	*% yield*	*C*	*H*
2.1b	82	82.52(82.42)	4.46(5.38)
2.2b	84	65.21(65.28)	3.61(3.65)
2.3b	93	65.40(65.28)	3.66(3.65)
2.4b	76	65.38(65.28)	3.69(3.65)
2.5b	85	82.58(82.73)	6.25(6.25)
2.6b	80	82.89(82.73)	6.20(6.25)
2.7b	78	82.81(82.73)	6.16(6.25)

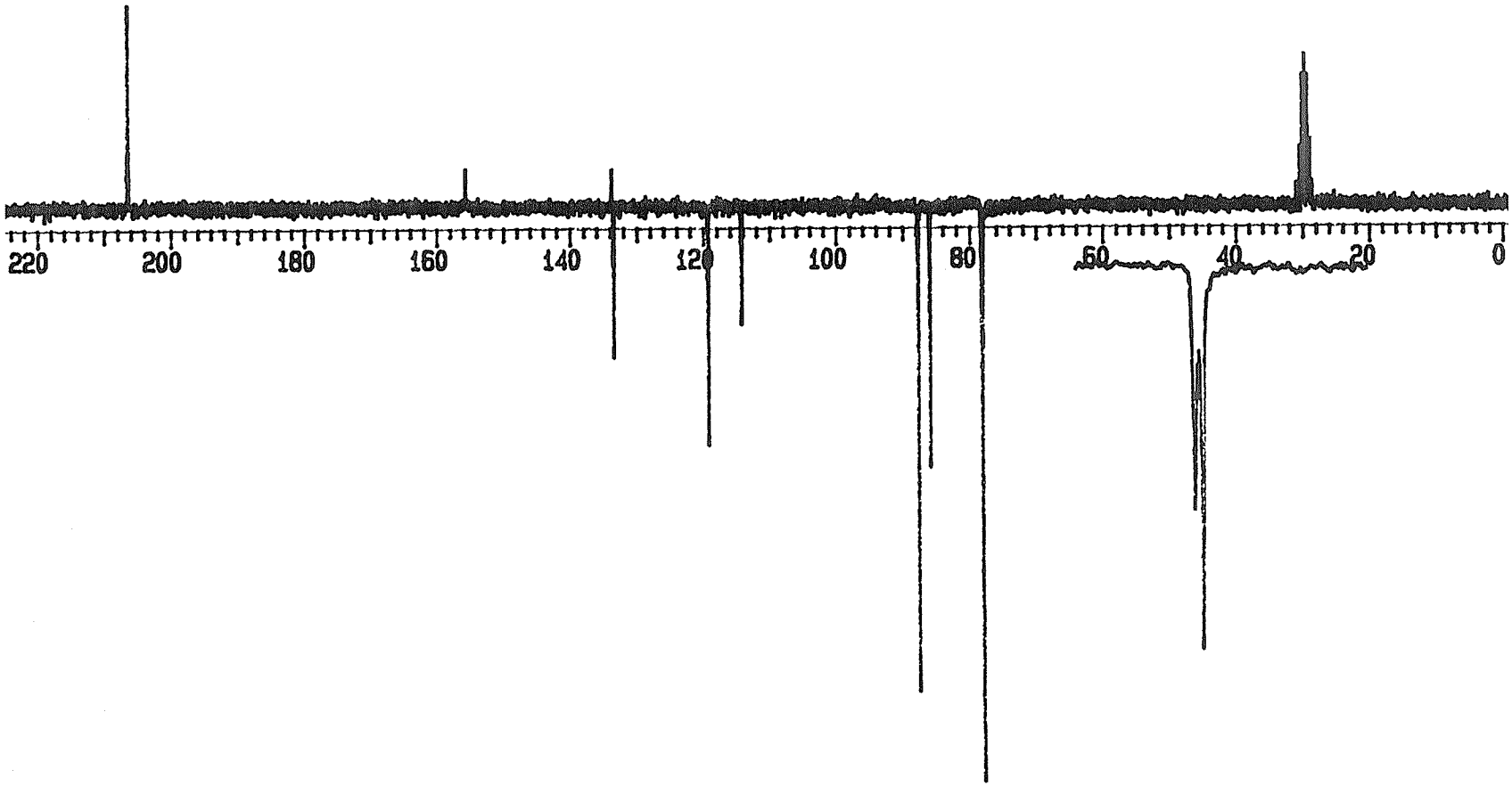
1.2 Reactions with 1,3-dihydroxybenzene

The synthesis of the complexes of the substituted 1,3-diphenoxybenzene isomers **2.8a-2.14a** proceeded in a fashion similar to that of the 1,4-diphenoxybenzene complexes. Reaction conditions were identical and the yields obtained were also high. The alternative procedure involving DMF as the only solvent and a reaction time of 16 hours proved to be a successful technique as well, and usually resulted in slightly higher yields (85-95%). The ^{1}H and ^{13}C-APT NMR data for this series of complexes have been summarized in tables 7 and 8. The yields can be found in table 9, along with the elemental analysis data. The ^{1}H and ^{13}C-APT NMR spectra for 1,3-di([η^6-phenoxy-η^5-cyclopentadienyl]iron)benzene (**2.8a**) are presented in figure 28 and figure 29. In the ^{1}H spectrum of this complex, the singlet corresponding to the cyclopentadienyl rings can be found at 5.24 ppm, while the complexed arenes display a triplet at 6.29 ppm (J=5.6 Hz, two protons) and a multiplet in the 6.26-6.55 ppm range (eight protons). The uncomplexed arene exhibits two distinct regions. A multiplet integrating as three protons can be found in the 7.35-7.45 ppm range, while a triplet integrating as one proton is situated at 7.74 ppm (J=8.0 Hz). Interestingly, complexation of the $CpFe^{+}$ moiety to the arene results in a decrease in aromatic coupling constants in addition to the upfield shift in resonance. This is in keeping with the reduction in the "aromaticity" of the ring complexed to the $CpFe^{+}$ moiety, and has been noted in a previous study [72]. The ^{13}C-APT spectrum is very typical of these complexes, with the resonance for the cyclopentadienyl carbons situated at 78.09 ppm. Three distinct resonances exist for the carbons in the CH's of the complexed arene: 78.22, 85.95 and 87.71 ppm. There are also three resonances arising from the CH's of the uncomplexed arene: at 114.26, 119.28 and 133.51 ppm. The

28 ^{1}H NMR of 1,3-di([η^{6}-phenoxy-η^{5}-cyclopentadienyl]iron)benzene, 2.8



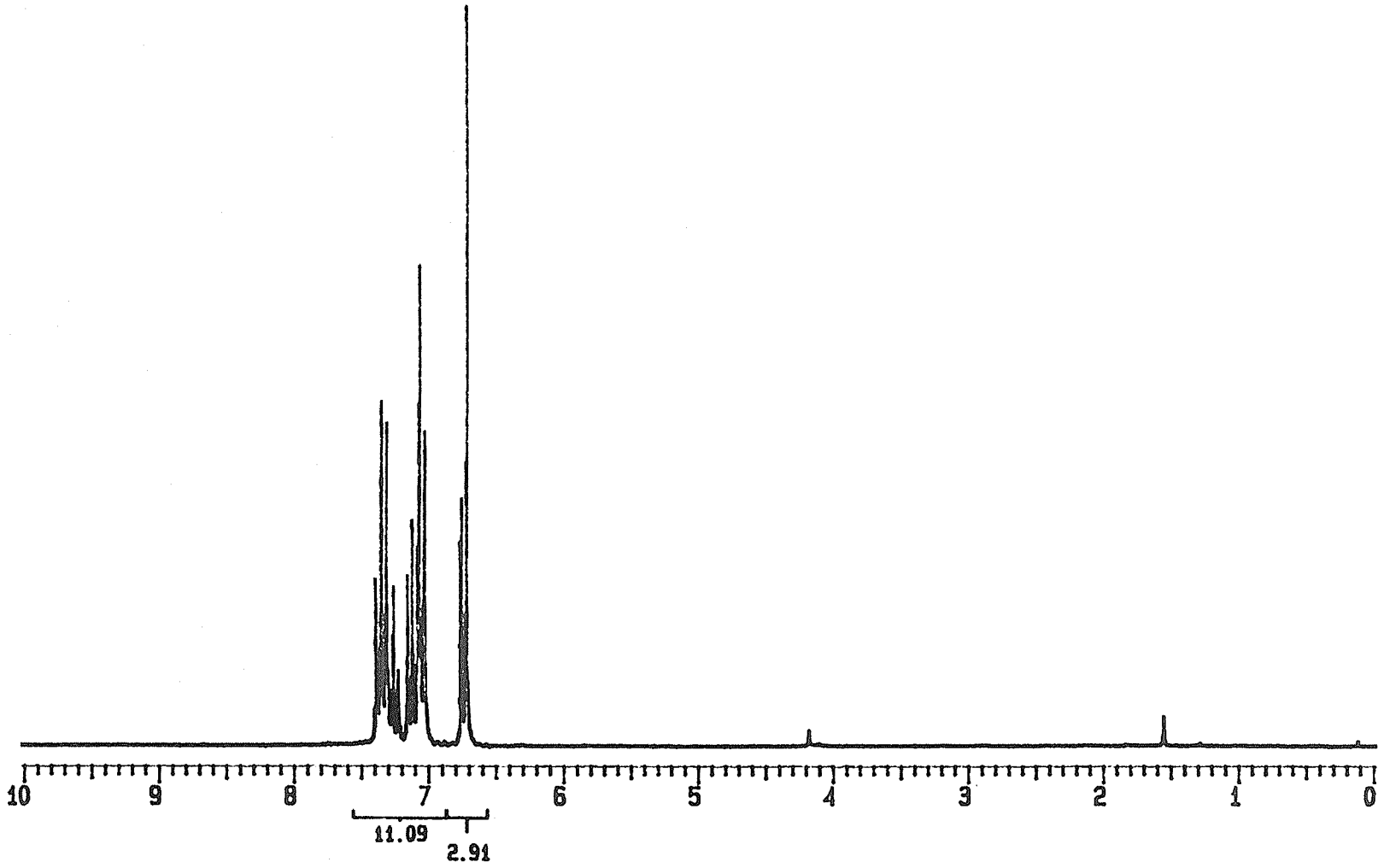
29 ^{13}C-APT NMR of 1,3-di([η^6-phenoxy-η^5-cyclopentadienyl]iron)benzene, **2.8**



quaternaries are situated further downfield at 133.79 ppm (complexed arene) and 155.69 ppm (uncomplexed arene). The demetallation reactions undertaken on these substituted 1,3-diphenoxybenzene complexes were no different than those performed on the substituted 1,4-diphenoxybenzene complexes. The liberated aromatic ethers (compounds **2.8b–2.14b**) were fully characterized by ^{1}H, ^{13}C-APT NMR and mass spectrometry (tables 10 and 11), as well as elemental analysis (table 12). This latter table also records the yields, which were between 76 and 94%.

All of these compounds were isolated as oils, with the exception of 1,3-diphenoxybenzene (**2.8b**), which was obtained as a solid with a melting point of 39 °C (see table 11). Compound **2.8b** was obtained by the photolysis of complex **2.8a**. The ^{1}H and ^{13}C-APT NMR spectra have been reproduced in figures 30 and 31, respectively. The ^{1}H spectrum reveals a very complex aromatic region between 6.72 and 7.39 ppm and is highly second order, however the ^{13}C-APT spectrum is easily analysed. The three carbon resonances arising from the CH's of the central arene can be found at 109.30, 113.11 and 130.31 ppm, with the quaternary at 158.65 ppm. The remaining resonances, at 119.12, 123.55 and 129.74 ppm with the quaternary at 156.65 ppm are due to the outer arene rings. The mass spectrum reveals an intense molecular ion peak (M^{+}) at an m/z of 262. In all compounds of this series, the molecular ion peak is the most intense peak, with an exception arising in compound **2.9b**.

30 ^{1}H NMR of 1,3-diphenoxybenzene, 2.8b



31 ^{13}C-APT NMR of 1,3-diphenoxybenzene, 2.8b

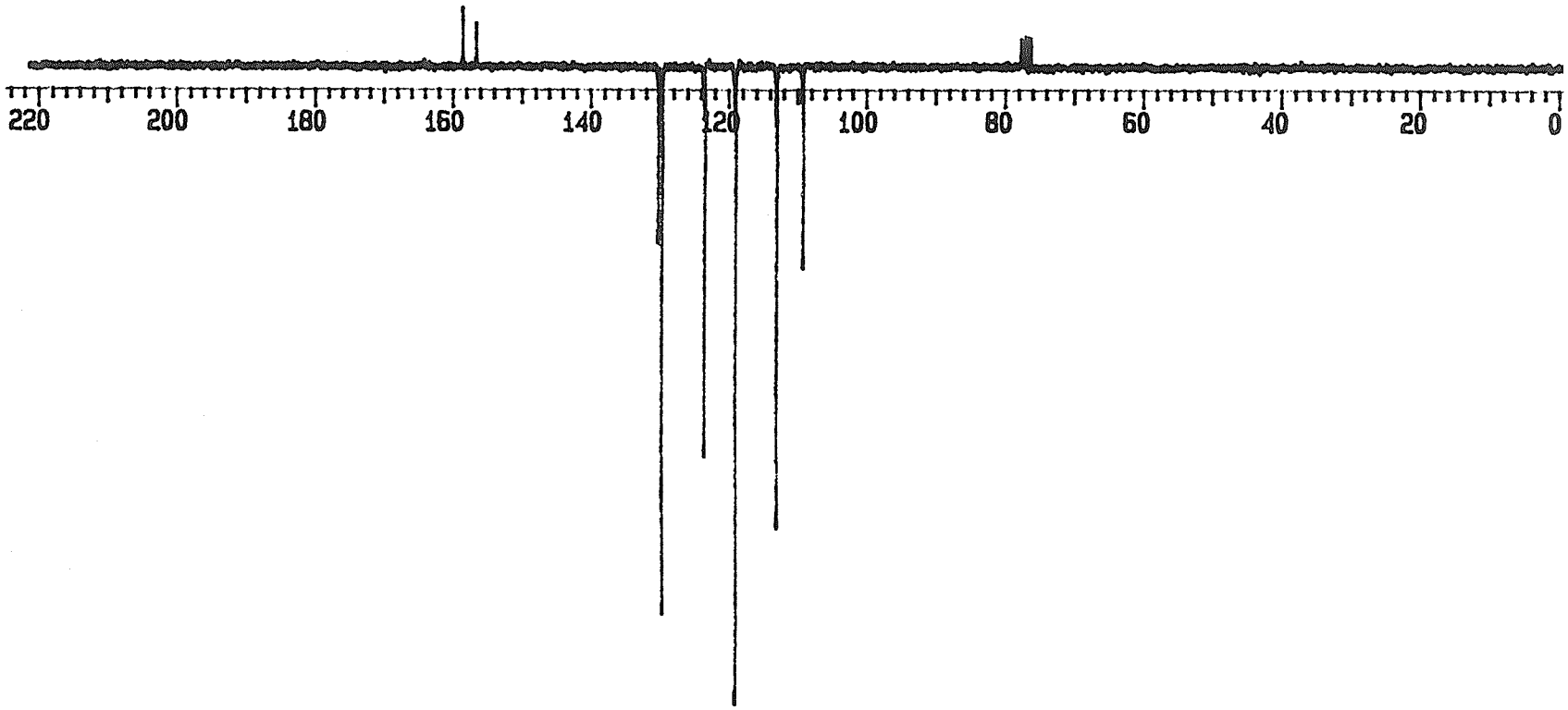


Table 7: ^{1}H NMR data for complexes **2.8a–2.14a**

δ (referenced to acetone-d_6)			
Complex	*Complexed aromatics*	*Cp's*	*Others*
2.8a	6.29(t,2H,*J* 5.6), 6.42-6.49(m,8H)	5.24(s,10H)	7.35-7.45(m,3H), 7.74(t,1H)(Ar)
2.9a*	6.38-6.43(m,4H), 6.62(t,2H,*J* 5.9), 6.98(d,2H,*J* 6.2)	5.31, 5.33 (2s,10H)	7.46(d,*J* 8.3), 7.49(d,*J* 8.3)(2H); 7.57(m,1H); 7.78(t,*J* 8.3), 7.80(t,*J* 8.3)(Ar)(1H)
2.10a	6.50-6.74(m,6H)	5.37, 5.38 (2s,10H)	7.38-7.73(m,4H)(Ar)
2.11a	6.61(d,4H,*J* 5.4), 6.79(d,4H,*J* 5.4)	5.37(s,10H)	7.38-7.44(m,3H), 7.76(t,1H,*J* 8.2)(Ar)
2.12a	6.21(t,2H,*J* 5.2), 6.27(d,2H,*J* 5.4), 6.34(t,2H,*J* 5.9), 6.54(d,2H,*J* 5.6)	5.17, 5.19 (2s,10H)	2.62(s,6H)(CH_3); 7.28-7.37(m,3H), 7.65-7.76(m,1H)(Ar)
2.13a	6.22(d,2H,*J* 5.2), 6.33-6.42(m,4H), 6.52(s,2H)	5.19(s,10H)	2.57(s,6H)(CH_3); 7.30-7.38(m,3H), 7.70(t,1H,*J* 8.3)(Ar)
2.14a	6.35-6.47(m,8H)	5.21(s,10H)	2.49(s,6H)(CH_3); 7.33-7.39(m,3H), 7.72(t,1H,*J* 8.3)(Ar)

* Data obtained from a 500 MHz spectrometer

Table 8: ^{13}C NMR data for complexes **2.8a–2.14a**

δ (referenced to acetone-d_6)			
Complex	*Complexed aromatics*	*Cp's*	*Others*
2.8a	78.22, 85.95, 87.71, 133.79*	78.09	114.26, 118.28, 133.51, 155.69*(Ar)
2.9a	78.39, 78.66, 86.20, 86.92, 86.96, 89.16, 98.57*, 130.54*, 130.66*	80.38, 80.41	113.51, 113.57, 119.06, 119.29, 133.82, 133.90, 155.98*, 156.09*(Ar)
2.10a	76.98, 77.04, 79.15, 86.30, 86.65, 106.88*, 133.17*	80.21	113.73, 119.13, 133.47, 155.40*(Ar)
2.11a	77.64, 87.74, 105.07*, 133.17*	80.50	114.17, 119.50, 133.75, 155.59*(Ar)
2.12a	77.88, 78.14, 85.58, 86.28, 89.71, 94.46*, 131.87*	78.48	16.25(CH_3); 113.46, 118.49, 118.69, 133.45, 133.50, 156.51*(Ar)
2.13a	76.69, 76.74, 79.45, 86.49, 86.96, 103.99*, 133.42*	78.52	20.34(CH_3); 114.00, 114.03, 119.07, 133.48, 156.00*(Ar)
2.14a	77.68, 87.91, 101.89*, 132.87*	78.64	19.89(CH_3); 114.16, 119.19, 133.54, 156.03*(Ar)

* denotes quaternary carbon atoms

Table 9: Yields and elemental composition data for complexes **2.8a–2.20a**

		elemental composition found(calculated), %	
Complex	*% yield*	*C*	*H*
2.8a	95	42.51(42.35)	2.98(3.05)
2.9a	94	39.10(38.97)	2.67(2.57)
2.10a	85	38.85(38.97)	2.69(2.57)
2.11a	92	38.95(38.97)	2.62(2.57)
2.12a	87	43.95(43.82)	3.38(3.43)
2.13a	90	44.02(43.83)	3.32(3.43)
2.14a	88	43.97(43.83)	3.49(3.43)
2.15a	79	42.47(42.35)	3.15(3.05)
2.16a	83	39.07(38.97)	2.64(2.57)
2.17a	83	39.02(38.97)	2.53(2.57)
2.18a	82	43.90(43.83)	3.48(3.43)
2.19a	86	43.98(43.83)	3.41(3.43)
2.20a	85	43.83(43.83)	3.39(3.43)

Table 10: ^{1}H NMR and MS data for compounds **2.8b–2.14b**

δ (referenced to chloroform-*d*)			
Compound	*Aromatics*	*Others*	M^+,*m/z (rel.ab.)*
2.8b	6.72-6.77(m,3H), 7.03-7.39(m,11H)	—	262 (100)
2.9b	6.58-6.99(m,3H), 7.02-7.44(m,9H)	—	330 (23.6) 332 (15.4) 334 (1.4)
2.10b	6.70(t,1H,*J* 2.2), 6.79(dd,2H,*J* 2.4,8.2), 6.92(ddd,2H,*J* 1,2.2,8.2), 7.03(t,2H,*J* 2.2), 7.10(ddd,2H,*J* 1,2.0,8.2), 7.25(d,1H,*J* 8.2), 7.30(dd,2H,*J* 1.8,8.2)	—	330 (100) 332 (64) 334 (10)
2.11b	6.64(t,1H,*J* 2.2), 6.70(dd,2H,*J* 2.2,8.2), 6.92-6.97(m,4H), 7.22-7.31(m,5H)	—	330 (100) 332 (64) 334 (11)
2.12b	6.56-6.6.59(m,3H), 6.96-7.28(m,9H)	2.27(s,6H)(CH_3)	290 (100)
2.13b	6.69-6.95(m,9H), 7.18-7.7.30(m,3H)	2.34(s,6H)(CH_3)	290 (100)
2.14b	6.62-6.66(m,3H), 6.89-6.93(m,4H), 7.10-7.7.19(m,5H)	2.32(s,6H)(CH_3)	290 (100)

Table 11: ^{13}C NMR and melting point data for compounds **2.8b–2.14b**

δ (referenced to chloroform-*d*)			
Compound	*Aromatics*	*Others*	*M.P.(°C)*
2.8b	109.30, 113.11, 119.12, 123.55, 129.74, 130.31, 156.65*, 158.63*	—	39 (white)
2.9b	107.61, 112.25, 121.25, 125.08, 126.06*, 127.98, 130.41, 130.82, 151.89*, 158.31*	—	oil (yellowish)
2.10b	110.15, 114.24, 117.07, 119.25, 123.74, 130.57, 130.76, 135.13*, 157.59*, 157.88*	—	oil (yellowish)
2.11b	109.32, 113.44, 120.38, 129.81, 128.76*, 130.61, 155.25*, 158.39*	—	oil (yellowish)
2.12b	106.61, 110.81, 119.96, 124.22, 127.13, 131.44, 130.03*, 130.14, 154.04*, 159.25*	16.12(CH_3)	oil (yellowish)
2.13b	109.25, 113.00, 116.12, 119.78, 124.34, 129.43, 130.21, 139.92*, 156.62*, 158.68*	21.35(CH_3)	oil (yellowish)
2.14b	108.45, 112.27, 119.29, 130.15, 130.24, 133.19*, 154.21*, 159.13*	20.70(CH_3)	oil (yellowish)

* denotes quaternary carbon atoms

Table 12: Yields and elemental composition data for compounds **2.8b–2.20b**

		elemental composition found(calculated), %	
Compound	*% yield*	*C*	*H*
2.8b	94	82.49(82.42)	5.39(5.38)
2.9b	82	65.40(65.28)	3.68(3.65)
2.10b	87	65.25(65.28)	6.62(3.65)
2.11b	76	65.34(65.28)	3.60(3.65)
2.12b	69	82.79(82.73)	6.29(6.25)
2.13b	91	82.71(82.73)	6.27(6.25)
2.14b	88	82.88(82.73)	6.31(6.25)
2.15b	95	82.34(82.42)	5.31(5.38)
2.16b	87	65.35(65.28)	3.71(3.65)
2.17b	98	65.25(65.28)	3.70(3.65)
2.18b	90	82.88(82.73)	6.31(6.25)
2.19b	85	82.62(82.73)	6.28(6.25)
2.20b	96	82.61(82.73)	6.33(6.25)

1.3 Reactions with 1,2-dihydroxybenzene

The preparation of the 1,2-([η^6-aryloxy-η^5-cyclopentadienyl]iron)benzene dihexafluorophosphate complexes could not be achieved in high yields from a refluxing THF/DMF solution. At best, yields of 50% could be obtained with this procedure. Attempts to improve the yield by increasing the reaction time (to 16 hours for example) resulted in an increasing amount of decomposition. Ferrocene was identified as one of the decomposition products, suggesting that a process similar to photolytic demetallation could be induced by excessive heating.[2] Consequently, the more polar solvent DMF was used alone, and the mixture stirred at room temperature for approximately 20 hours. The procedure is outlined more extensively in the experimental section dealing with these complexes. Using this approach, the yields increased to 76-86% for the complexes **2.15a–2.20a**. This technique was developed specifically for improving the yields of these complexes, whereupon it was found that it applied to the synthesis of the other complexed diphenoxybenzenes as well. It is clear that the nature of the solvent contributes significantly to the activity of the chloroarene-cyclopentadienyliron complexes towards nucleophilic substitution reactions. However, it is not simply a matter of polarity since dimethylsulfoxide (DMSO), a solvent with a polarity similar to DMF, is an extremely poor solvent for these reactions. With this solvent, decomposition occurs even when stirred at room temperature. This is also true of CH_3CN. Both DMSO and CH_3CN appear to be good metal cation coordinating solvents, thereby increasing the likelihood of

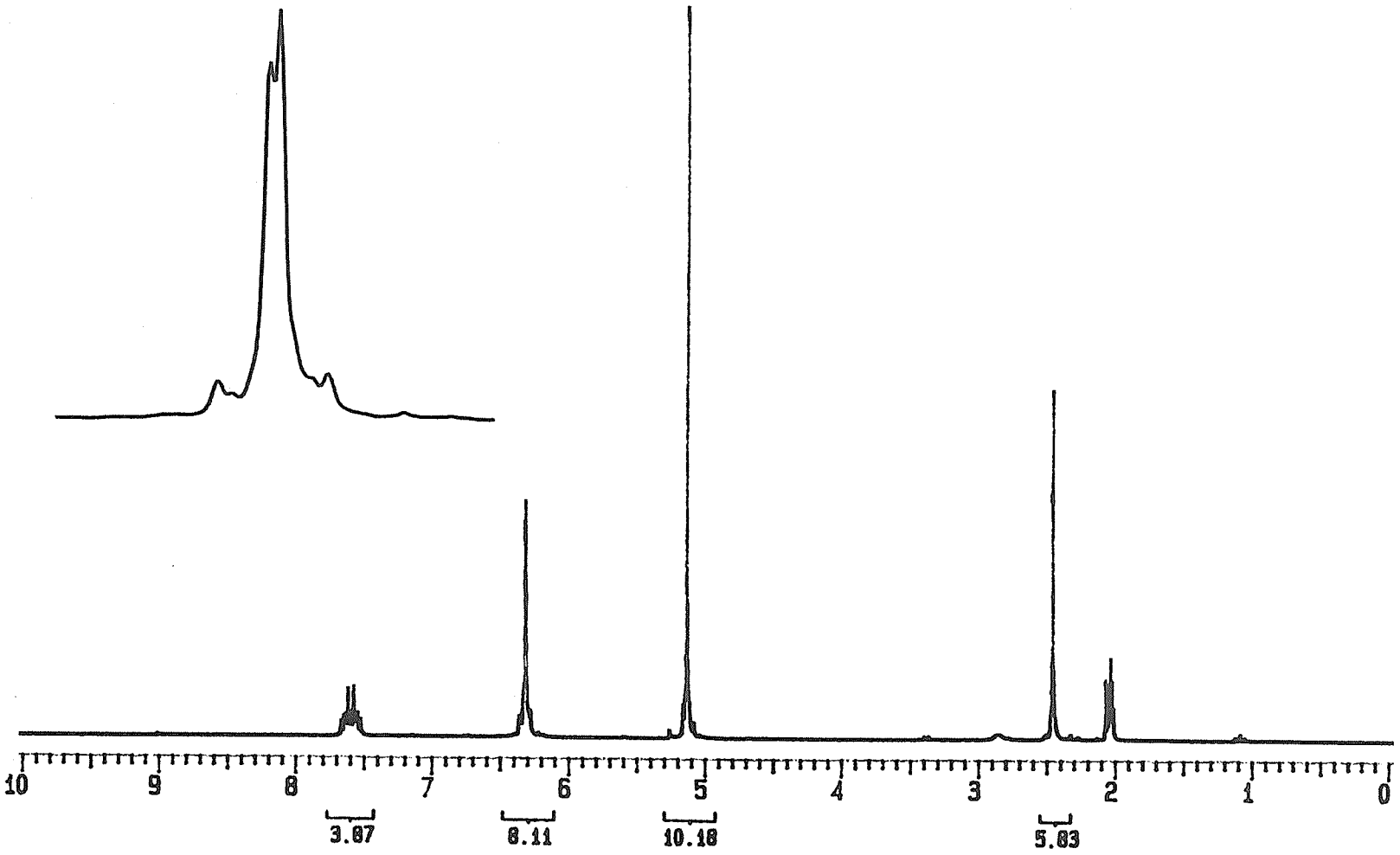
[2]In fact, thermolysis is one of the possible techniques for the liberation of arenes from the $CpFe^+$ moiety, although conditions are somewhat different than those of the above reactions.

a demetallation side reaction in the course of the synthetic procedure. DMF has proven to be the best solvent, both in terms of activity and low coordinating ability.

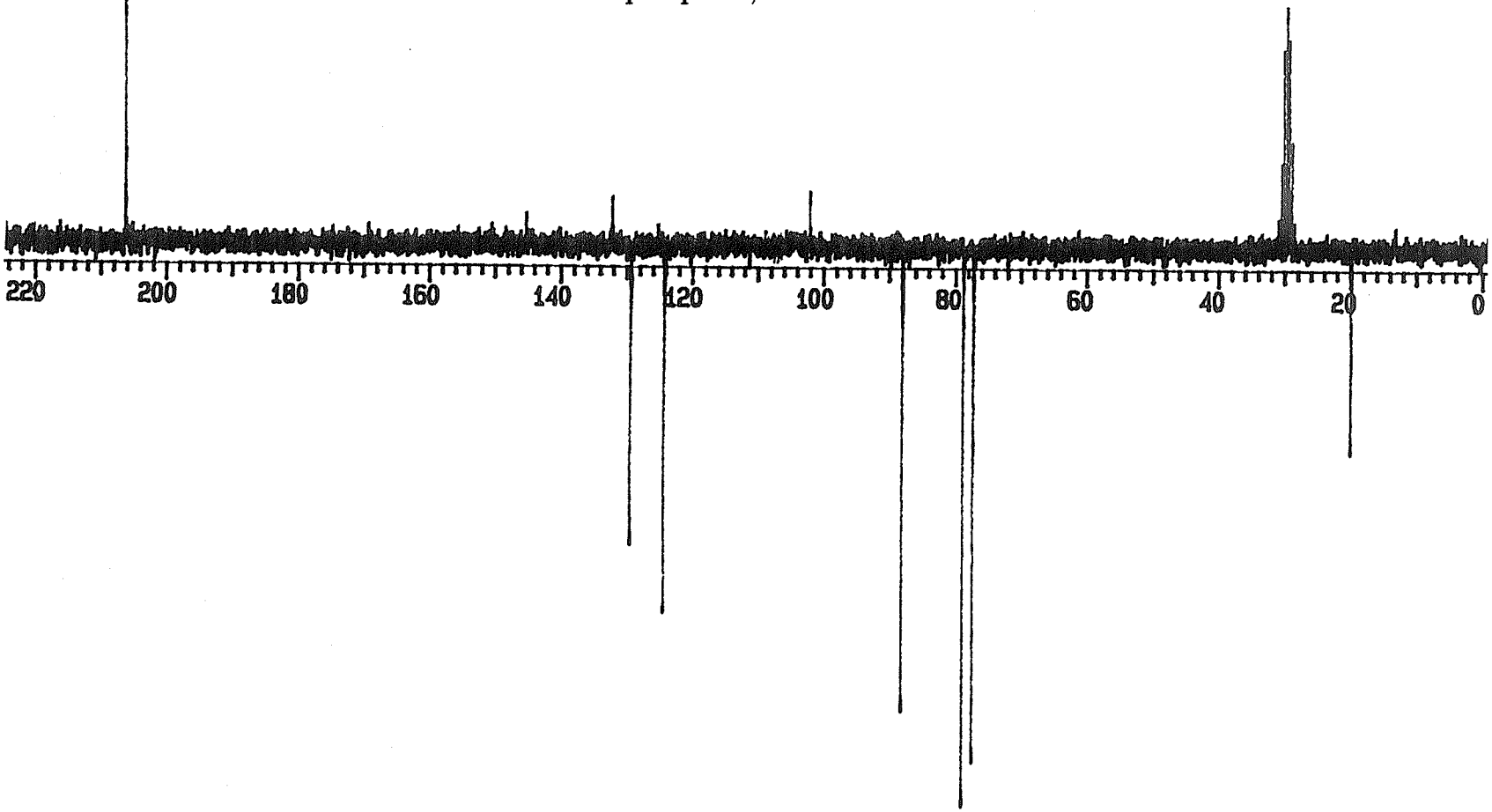
The ^{1}H and ^{13}C-APT NMR data for these complexes has been summarized in tables 13 and 14, respectively. The yields and elemental analysis data are contained in table 9. Figures 32 and 33 display the NMR spectra for 1,2-([η^6-4-methylphenoxy-η^5-cyclopentadienyl]iron)benzene dihexafluorophosphate (**2.20a**) and confirm its structure. The ^{1}H spectrum reveals the three typical regions: cyclopentadienyl, complexed arene and uncomplexed arene. The cyclopentadienyl rings produce a sharp singlet at 5.14 ppm. The protons of the complexed arene form an AA'BB' spin system, the resonances of which fall in the 6.27-6.37 ppm range (see expansion). The protons of the uncomplexed arene also form an AA'BB' spin system, displaying resonances in the 7.52-7.67 ppm range (see expansion also). In addition, the singlet for the two methyl groups can be found at 2.46 ppm. The ^{13}C-APT NMR spectrum shows the expected carbon resonances for the cyclopentadienyl rings (78.68 ppm), the CH's of the complexed aromatics (77.12, 87.86 ppm) and uncomplexed aromatics (124.10, 129.24 ppm). The three quaternary resonances can also be found at 102.14 ppm (complexed C-CH_3), 132.25 ppm (complexed C-O) and 145.45 ppm (uncomplexed C-O). The carbon resonance for the methyl groups is situated at 19.81 ppm. Photolytic reactions proceeded as usual for these complexes, allowing for the liberation of aromatic ethers **2.15b–2.20b**. Again, yields were very high (>85%), and are recorded in table 12. Analytical data for these compounds have been summarized in table 15 (^{1}H, mass spectrometry) and 16 (^{13}C, melting point). Elemental analysis data can be found with the yields in table 12.

The NMR spectra for 1,2-di(4-methylphenoxy)benzene (compound **2.20b**) are

32 ^{1}H NMR of 1,2-([η^6-4-methylphenoxy-η^5-cyclopentadienyl]iron)benzene dihexafluorophosphate, **2.20a**



33 ^{13}C-APT NMR of 1,2-([η^6-4-methylphenoxy-η^5-cyclopentadienyl]iron)-benzene dihexafluorophosphate, **2.20a**



presented in figures 35 and 36. The ^{1}H spectrum reveals the second-order nature of the aromatic region (6.78-7.10 ppm), consisting of two multiplets integrating as four and eight protons. The proton resonance for the equivalent methyl groups can be found at 2.30 ppm, a slight upfield shift from its position in the ^{1}H spectrum of the corresponding complex **2.20a**. The ^{13}C-APT spectrum displays four carbon resonances for the aromatic CH's: 120.86 and 124.17 ppm (central arene); 117.83 and 129.93 ppm (outer arenes). The three aromatic quaternaries are at 132.32 ppm (C-CH_3), 148.11 ppm (C-O, central arene) and 155.14 (C-O, outer arenes), whereas the carbon resonance for the methyl groups is upfield at 20.63 ppm. This compound was isolated as a white solid with a melting point of 68 °C. The mass spectrum indicates that the molecular ion peak is the base peak, with the first significant fragment (m/z = 183) resulting from the loss of -$OC_6H_4CH_3$.

Scheme 1 and 2 indicate the absence of one particular 1,2-diphenoxybenzene isomer. It was not possible to prepare 1,2-di([η^6-2-chlorophenoxy-η^5-cyclopentadienyl]iron)benzene dihexafluorophosphate using the synthetic techniques developed. Application of the technique resulted in a mixture of products, identified by ^{1}H and ^{13}C-APT NMR as starting complex, [η^6-dibenzodioxin-η^5-cyclopentadienyl]iron hexafluorophosphate and [2-chloro-(2-hydroxyphenoxy)-η^6-benzene-η^5-cyclopentadienyl]iron hexafluorophosphate (figure 34). The complex of the heterocycle has been synthesized previously by Sutherland and co-workers from equimolar amounts of catechol and [η^6-dibenzodioxin-η^5-cyclopentadienyl]iron hexafluorophosphate in a THF solution, in a 78% yield [36, 57]. Isolation of the heterocycle from the above reaction mixture indicated a 72% conversion of catechol into the heterocycle, the NMR spectra of which are in agreement with the literature data [57].

Upon monosubstitution of the dichlorobenzene complex by an OH of catechol, the second nucleophilic OH lies in very close proximity to the second substitution site, thereby favoring an intramolecular substitution over the inclusion of a second iron complex. The formation of the heterocycle is obviously the favored reaction, since

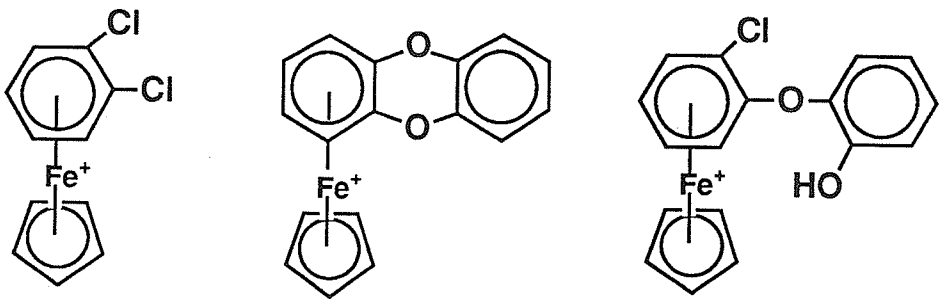
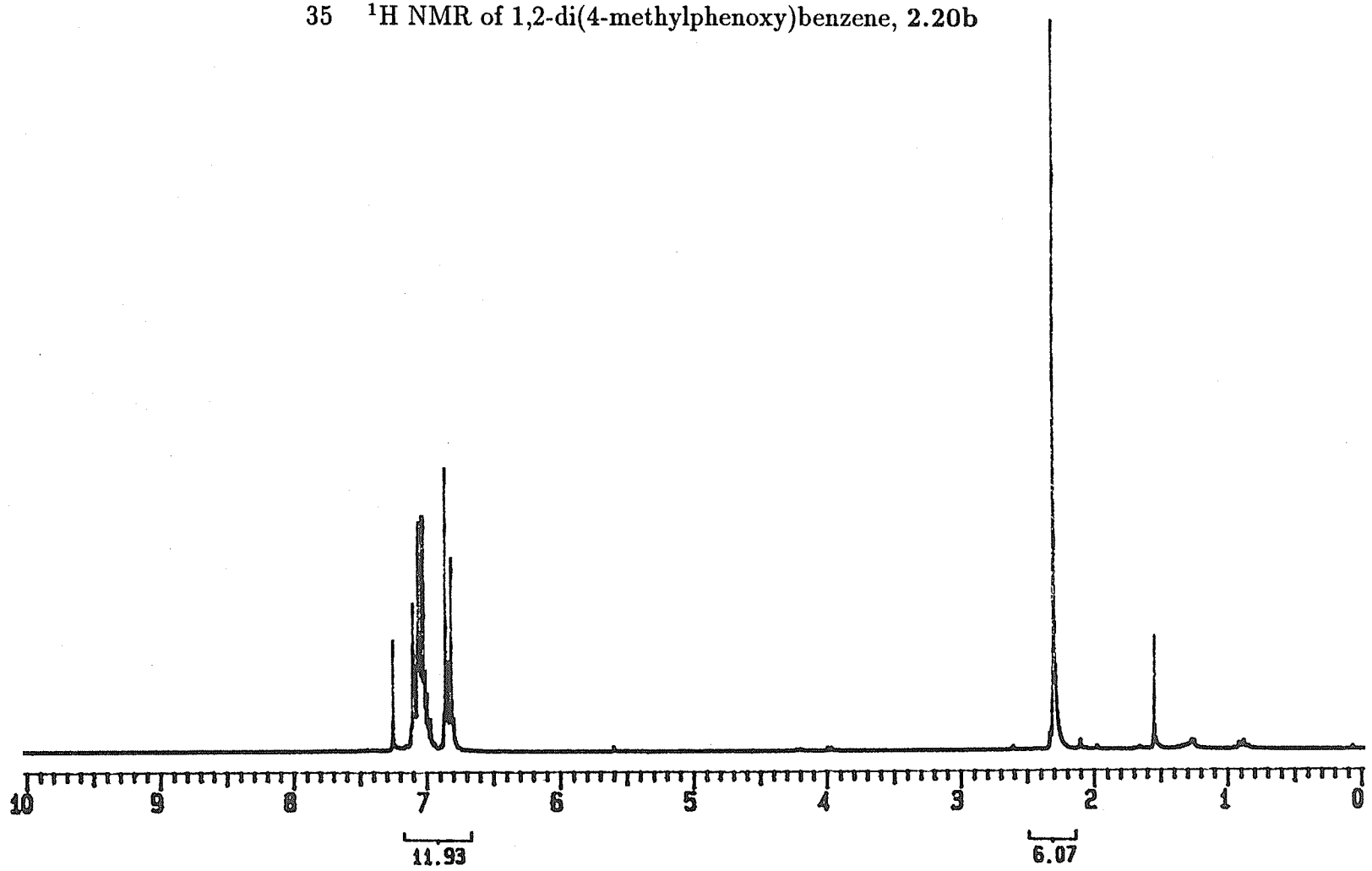


Figure 34: Products arising from the attempted synthesis of 1,2-di([η^6-2-chlorophenoxy-η^5-cyclopentadienyl]iron)benzene dihexafluorophosphate

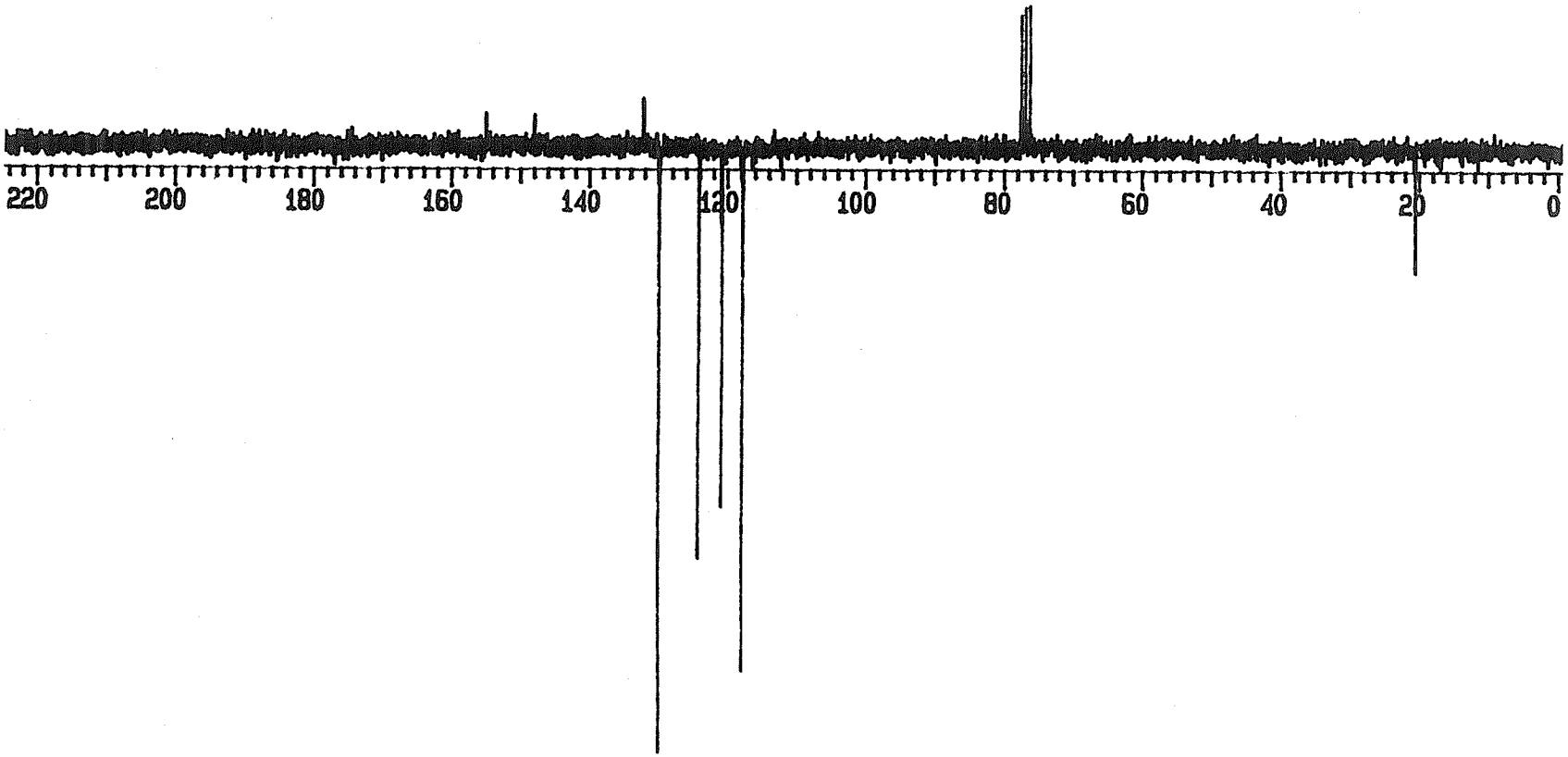
the amount of product obtained seems quite insensitive to the amount of starting complex present.[3]

[3]Yields are similar when either a 1:1 ratio or 1:2 ratio is used.

35 ^{1}H NMR of 1,2-di(4-methylphenoxy)benzene, **2.20b**



36 ^{13}C-APT NMR of 1,2-di(4-methylphenoxy)benzene, **2.20b**



1.4 Isomeric Complex Formation

It should be noted that none of the examples of di-iron complexes presented in section 1.1–1.3 contain ortho or meta substituents on the complexed arenes. It turns out that the complexes containing such substituents are a mixture of two diastereomers, and NMR in theory can resolve these isomers. Figure 37, for example, displays these two possible isomers for the class of di([η^6-2-methylphenoxy-η^5-cyclopentadienyl]iron)benzene dihexafluorophosphate complexes. The bridging ligands created in the reactions involving ortho and meta substituted starting complexes are *prochiral* molecules, when considered apart from their $CpFe^+$'s [81, 82]. When complexed to the $CpFe^+$ moieties, the whole molecule becomes chiral. Although there are no asymmetrically substituted atoms, these complexes can still be said to be chiral. Molecules of this type are considered to possess a *chiral plane*, coplanar with the complexed aromatic rings [83]. More specifically, two structurally identical chiral groups arise in the di-iron complex. The existence of these two structurally identical chiral groups, and the symmetry of the complex, requires that only two isomers be distinct (after all, the identical sites could be arranged asymmetrically) [83]. These can be designated as (R,R) for the one diastereomer and (R,S) for the other (properly referred as the meso form).

The diastereomeric relationship of the two complexes in figure 37 makes it possible for NMR to distinguish between them [84]. In practice, the ^1H and ^{13}C-APT spectra of these complexes resolve the diastereomers to varying degrees. The degree of resolution was generally insufficient to ascertain the relative abundancies of the diastereomers, however it was possible to do so for 1,2-di([η^6-2-methylphenoxy-η^5-cyclopentadienyl]iron)benzene dihexafluorophosphate (complex **2.18a**). The NMR

spectra for this complex are presented in figure 38 and 39. The two diastereomers produce quite distinct ^{1}H and ^{13}C-APT NMR spectra. In the ^{1}H spectrum, the re-

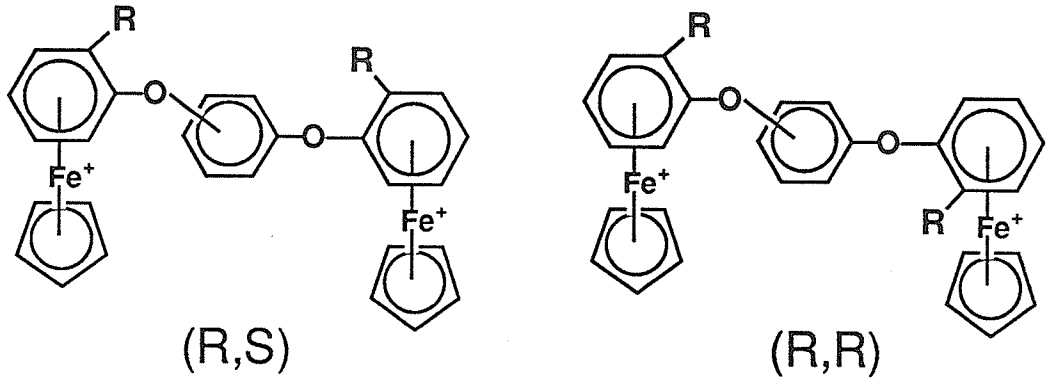
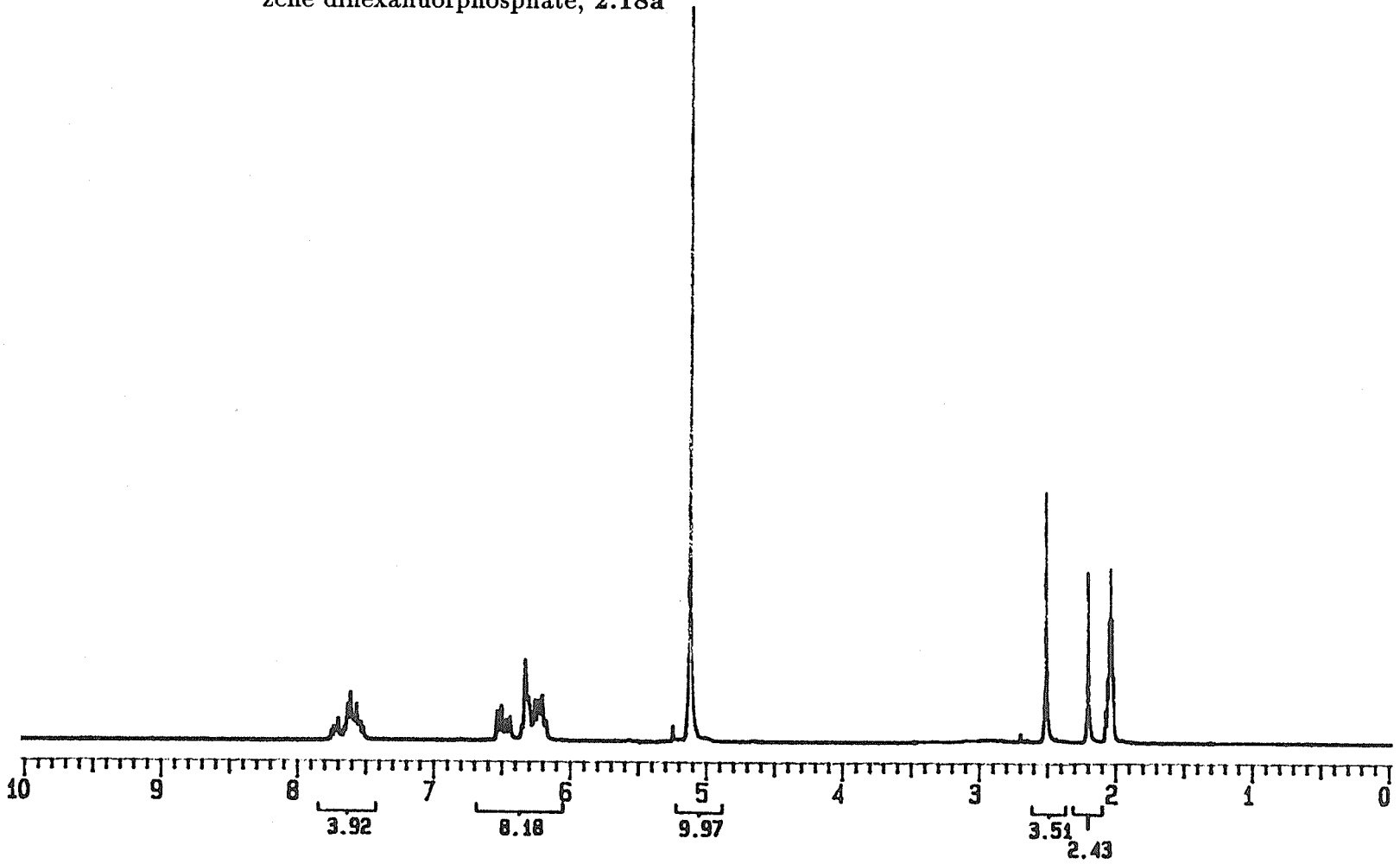


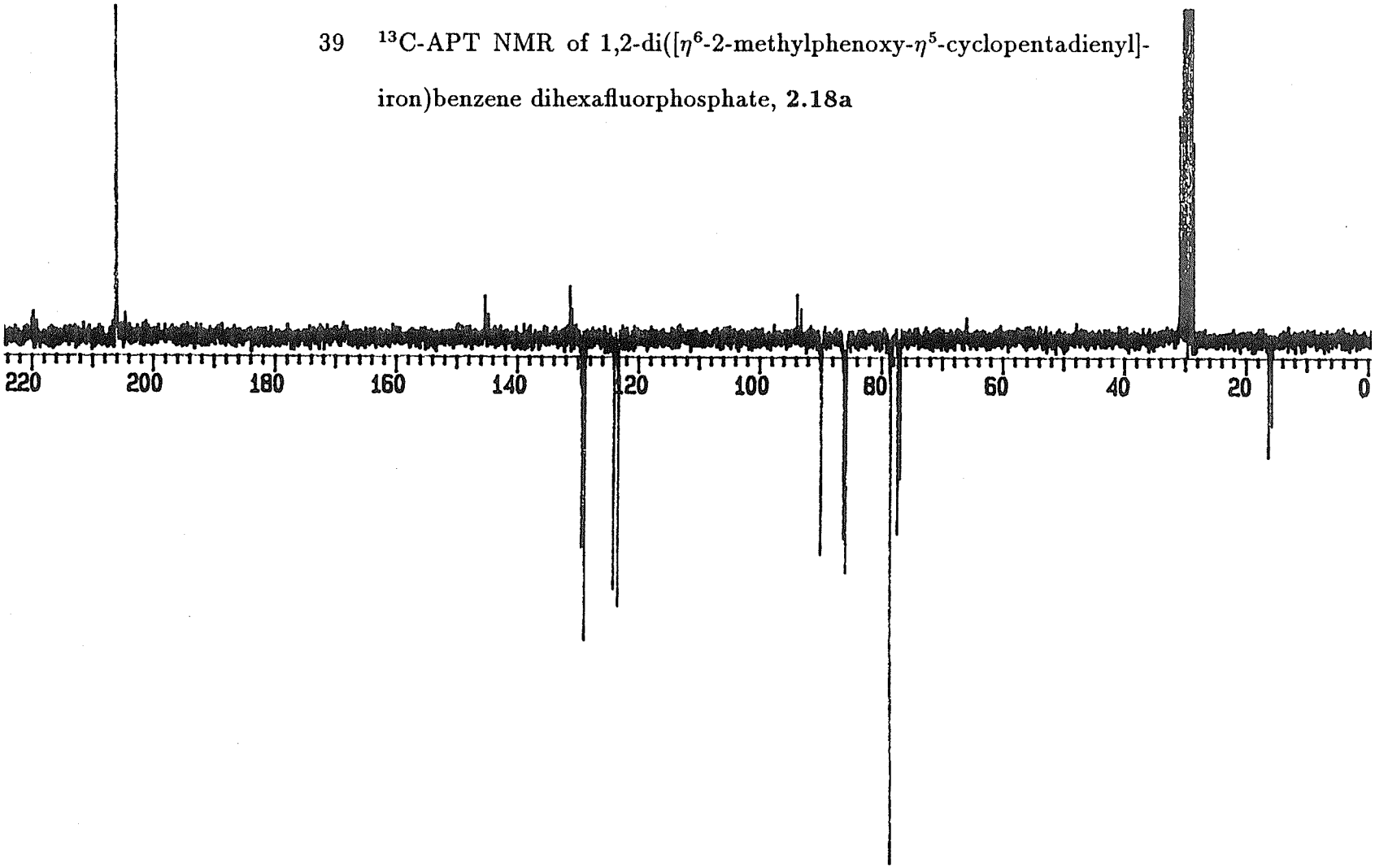
Figure 37: The two diastereomers of ortho substituted di-iron complexes

gion of the uncomplexed arene resonances at 7.50-7.75 ppm is quite complex, more so than can be expected from one pure AA'BB' spin system (compare with the spectrum of complex **2.20a**). This is equally true of the region of complexed arene resonances at 6.20-6.52 ppm. The cyclopentadienyl proton resonance also shows splitting into two signals, although there is incomplete resolution. There are, however, two very well separated methyl resonances at 2.21 and 2.52 ppm. Assigning each peak to a different isomer allows for a determination of the relative abundance of these isomers. Integration gives an approximate 2.4:3.4 ratio. The ^{13}C-APT spectrum very clearly confirms the presence of two isomers. Four resonances in the uncomplexed aromatic CH region can be found, instead of two. There are eight resonances for complexed aromatic CH region, rather than four. There are also two sets of three aromatic quaternary carbons, and two methyl carbon resonances. The cyclopentadienyl carbon resonance at 78.54 ppm shows splitting but two peaks

38 ^{1}H NMR of 1,2-di([η^6-2-methylphenoxy-η^5-cyclopentadienyl]iron)benzene dihexafluorphosphate, **2.18a**



39 ^{13}C-APT NMR of 1,2-di([η^6-2-methylphenoxy-η^5-cyclopentadienyl]-iron)benzene dihexafluorphosphate, **2.18a**



cannot be completely resolved. This is not surprising given that the cyclopentadienyl rings are more remote from the chiral plane. The spectra of the liberated 1,2-di(2-methylphenoxy)benzene (compound **2.18b**) reveal isomeric purity, as all resonances can be rationalized as arising from one compound. This is in keeping with the suggested prochiral nature of these bridging ligands, and serves as further proof that complexation produces the isomers indicated in the NMR spectra.

Table 13: ^{1}H NMR data for complexes **2.15a–2.20a**

δ (referenced to acetone-d_6)			
Complex	*Complexed aromatics*	*Cp's*	*Others*
2.15a	6.32(t,2H,*J* 5.6), 6.40-6.48(m,8H)	5.22(s,10H)	7.58-7.74(m,4H)(Ar)
2.16a	6.44(d,2H,*J* 6.4), 6.59(t,2H,*J* 6.4), 6.69(d,2H,*J* 6.2), 6.94(s,2H)	5.33(s,10H)	7.62-7.74(m,8H)(Ar)
2.17a	6.52(d,4H,*J* 6.6), 6.79(d,4H,*J* 6.8)	5.33(s,10H)	7.55-7.70(m,4H)(Ar)
2.18a	6.20-6.35(m,6H), 6.47(d,1H,*J* 6.4), 6.52(d,1H,*J* 6.4)	5.13(s,10H)	2.21(s)(CH_3), 2.52(s)(CH_3)(6H); 7.50-7.75(m,4H)(Ar)
2.19a	6.22(d,2H,*J* 5.8), 6.31(t,2H,*J* 6.0), 6.36(d,2H,*J* 6.2), 6.41(s,2H)	5.15(s,10H)	2.54(s,6H)(CH_3); 7.53-7.70(m,4H)(Ar)
2.20a	6.27-6.37(m,8H)	5.14(s,10H)	2.46(s,6H)(CH_3); 7.52-7.67(m,4H)(Ar)

Table 14: ^{13}C NMR data for complexes **2.15a–2.20a**

δ (referenced to acetone-d_6)			
Complex	*Complexed aromatics*	*Cp's*	*Others*
2.15a	78.00, 86.40, 87.94, 133.32*	78.35	124.21, 129.39, 145.30*(Ar)
2.16a	76.60, 76.68, 78.82, 86.79, 86.97, 107.04*, 133.02*	80.55	124.18, 129.68 144.88*
2.17a	77.32, 87.90, 105.39*, 132.57*	80.70	124.25, 129.74, 145.00*(Ar)
2.18a	77.00, 77.45, 85.79, 85.85, 86.16, 86.24, 89.86, 89.91, 93.24*, 93.89*, 131.07*, 131.41*	78.54	16.35(CH_3); 15.85(CH_3); 123.36, 124.08, 128.87, 129.40, 144.89*, 145.44*(Ar)
2.19a	76.07, 76.10, 78.78, 78.88, 86.73, 86.97, 104.04*, 133.12*, 133.15*	78.63	20.35(CH_3); 124.26, 124.31, 129.31, 145.37*(Ar)
2.20a	77.12, 87.86, 102.14*, 132.25*	78.68	19.81(CH_3); 124.10, 145.45*(Ar)

* denotes quaternary carbon atoms

Table 15: ^{1}H NMR and MS data for compounds **2.15b–2.20b**

δ (referenced to chloroform-d)			
Compound	*Aromatics*	*Others*	M^+,*m/z (rel.ab.)*
2.15b	6.90-7.33(m,14H)	—	262 (100)
2.16b	6.71-7.21(m,12H)	—	330 (100) 332 (65) 334 (11)
2.17b	6.76-6.80(m,4H), 7.08-7.23(m,8H)	—	330 (100) 332 (68) 334 (12)
2.18b	6.75-6.79(m,2H), 6.92-7.17(m,10H)	2.07(s,6H)(CH_3)	290 (100)
2.19b	6.71-6.87(m,6H), 7.06-7.16(m,6H)	2.29(s,6H)(CH_3)	290 (100)
2.20b	6.78-6.86(m,4H), 6.96-7.10(m,8H)	2.30(s,6H)(CH_3)	290 (100)

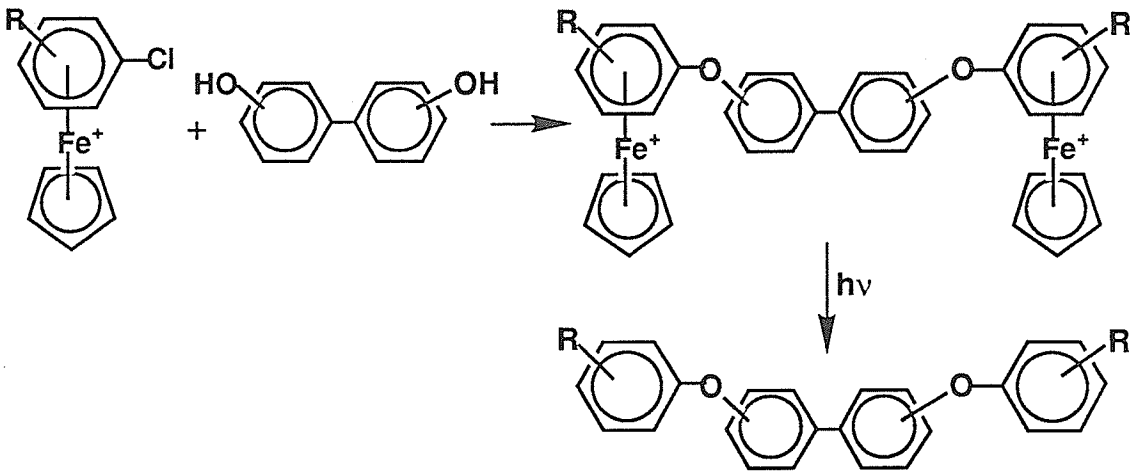
Table 16: ^{13}C NMR and melting point data for compounds **2.15b–2.20b**

δ (referenced to chloroform-d)			
Compound	*Aromatics*	*Others*	*M.P.(°C)*
2.15b	117.60, 121.60, 122.79, 124.70, 129.46, 147.73*, 157.45*	—	89-90 (white)
2.16b	115.42, 117.51, 122.33, 122.96, 125.65, 130.23, 134.85*, 146.93*, 158.12*	—	oil (yellowish)
2.17b	118.53, 121.91, 125.34, 127.82*, 129.48, 147.23*, 155.98*	—	oil (yellowish)
2.18b	117.12, 120.36, 123.02, 123.99, 126.75, 128.61*, 131.07, 147.50*, 155.21*	15.80(CH_3)	oil (yellowish)
2.19b	114.63, 118.34, 121.47, 123.57, 124.47, 129.12, 139.54*, 147.80*, 157.42*	21.46(CH_3)	oil (yellowish)
2.20b	117.83, 120.86, 124.17, 129.95, 132.32*, 148.11*, 155.14*	20.63(CH_3)	68 (white)

* denotes quaternary carbon atoms

2 Synthesis of Substituted Diphenoxybiphenyls

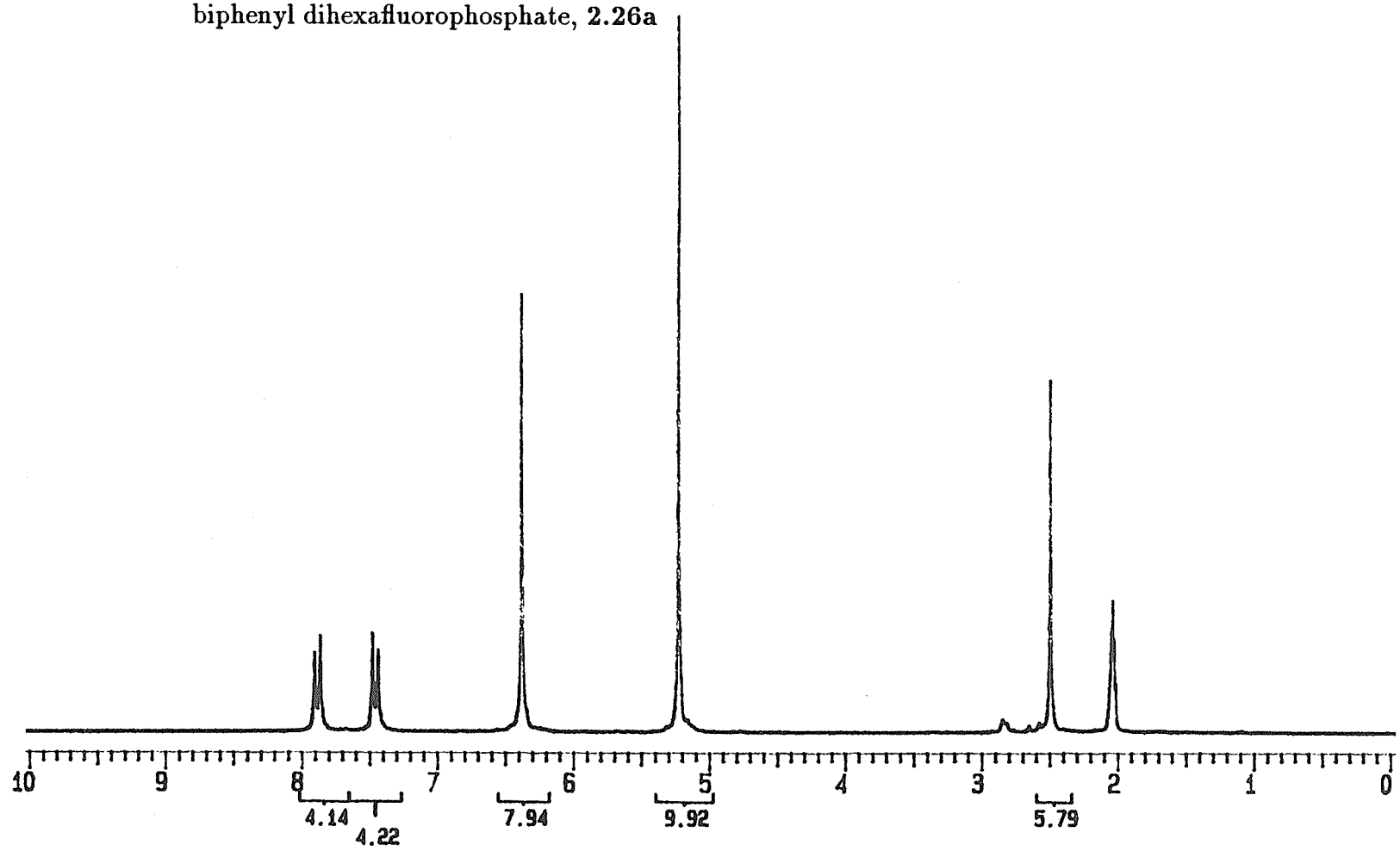
Dihydroxybiphenols can easily be incorporated into the synthetic procedure as well, allowing for a range of di([η^6-aryloxy-η^5-cyclopentadienyl]iron)biphenyl dihexafluorophosphate complexes to be prepared (**2.21a-2.26a**). These were photolysed in the normal fashion to liberate the diaryloxybiphenyls (compounds **2.21b–2.26b**). Scheme 3 presents the approach, including the photolytic step yielding the diaryloxybiphenyls. This easy route to these compounds constitutes a significant advancement in the synthesis of aromatic ether monomers for polymerization. This is discussed more fully in section 5.3. The analytical data for the complexes have been collated in table 17 (^{1}H NMR), table 18 (^{13}C-APT NMR) and table 19 (yields and elemental composition). The NMR spectra for 4,4′-di([η^6-(4-methylphenoxy)-η^5-cyclopentadienyliron)biphenyl dihexafluorophosphate (complex **2.26a**) can be found in figure 40 and 41. The characteristic cyclopentadienyl resonance in the ^{1}H spectrum is situated at 5.23 ppm. An interesting feature of this spectrum is the simplicity of the resonances for the complexed aromatic CH's. An AA′BB′ spin system usually produces a fairly complicated resonance pattern, however, an apparent singlet at 6.38 ppm arises from the AA′BB′ spin system of this complex. The AA′BB′ spin system of the two equivalent uncomplexed arenes produces a more common spitting pattern in the range of 7.43-7.91 ppm. The protons of the two equivalent methyl groups induce a resonance at 2.50 ppm. The ^{13}C-APT NMR data support the suggested structure. The carbon resonance of the cyclopentadienyl rings can be found at 78.50 ppm. The presence of the complexed aromatics is confirmed by the two aromatic CH carbon resonances at 77.26 and 87.82 ppm. Two intense carbon



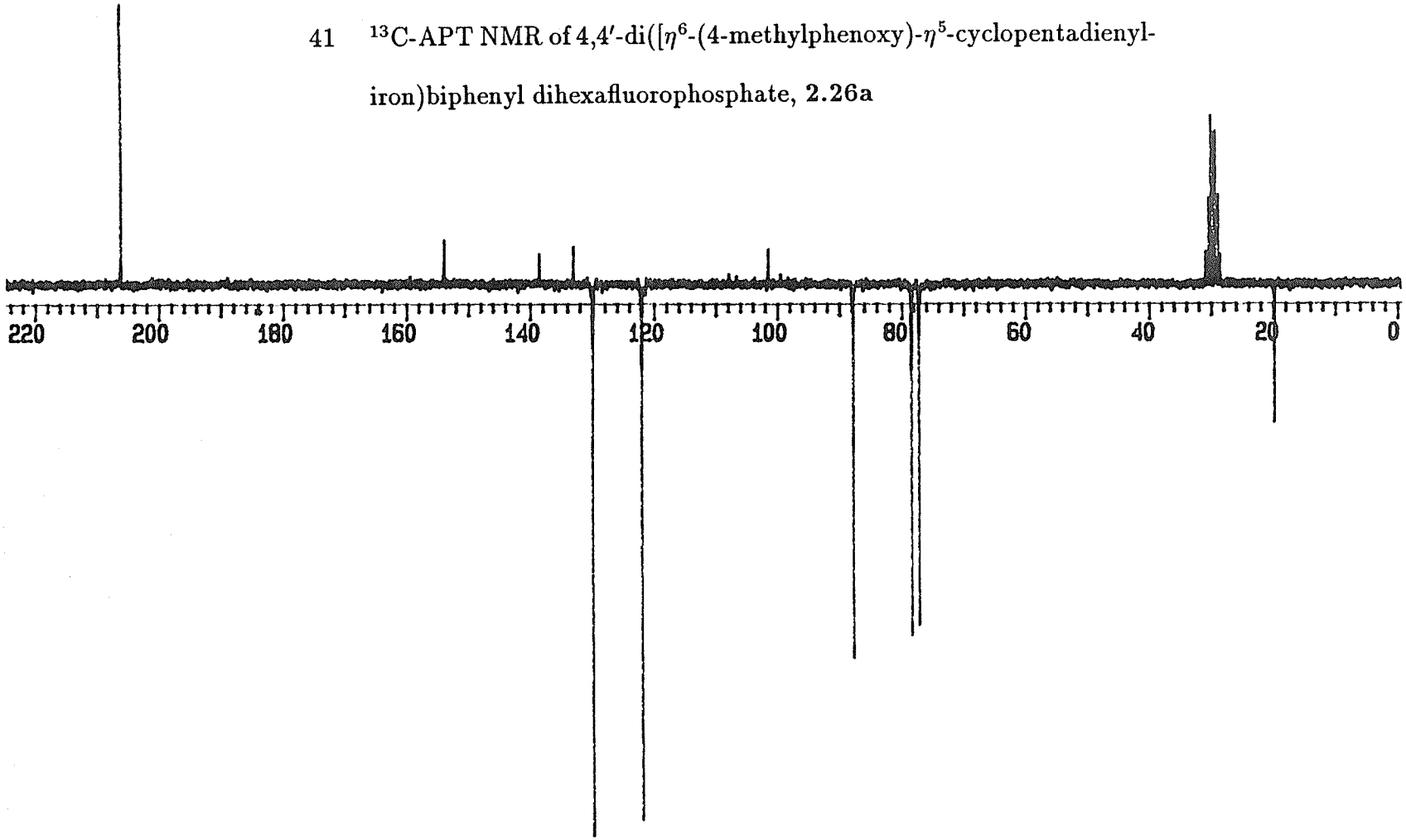
Scheme 3

R	biphenol	complex	compound
H	4,4′	**2.21a**	**2.21b**
H	2,2′	**2.22a**	**2.22b**
o-Cl	4,4′	**2.23a**	**2.23b**
m-Cl	4,4′	**2.24a**	**2.24b**
p-Cl	4,4′	**2.25a**	**2.25b**
p-CH_3	4,4′	**2.26a**	**2.26b**

40 ^{1}H NMR of 4,4′-di([η^6-(4-methylphenoxy)-η^5-cyclopentadienyliron)-biphenyl dihexafluorophosphate, **2.26a**



41 ^{13}C-APT NMR of 4,4′-di([η^6-(4-methylphenoxy)-η^5-cyclopentadienyl-iron)biphenyl dihexafluorophosphate, **2.26a**

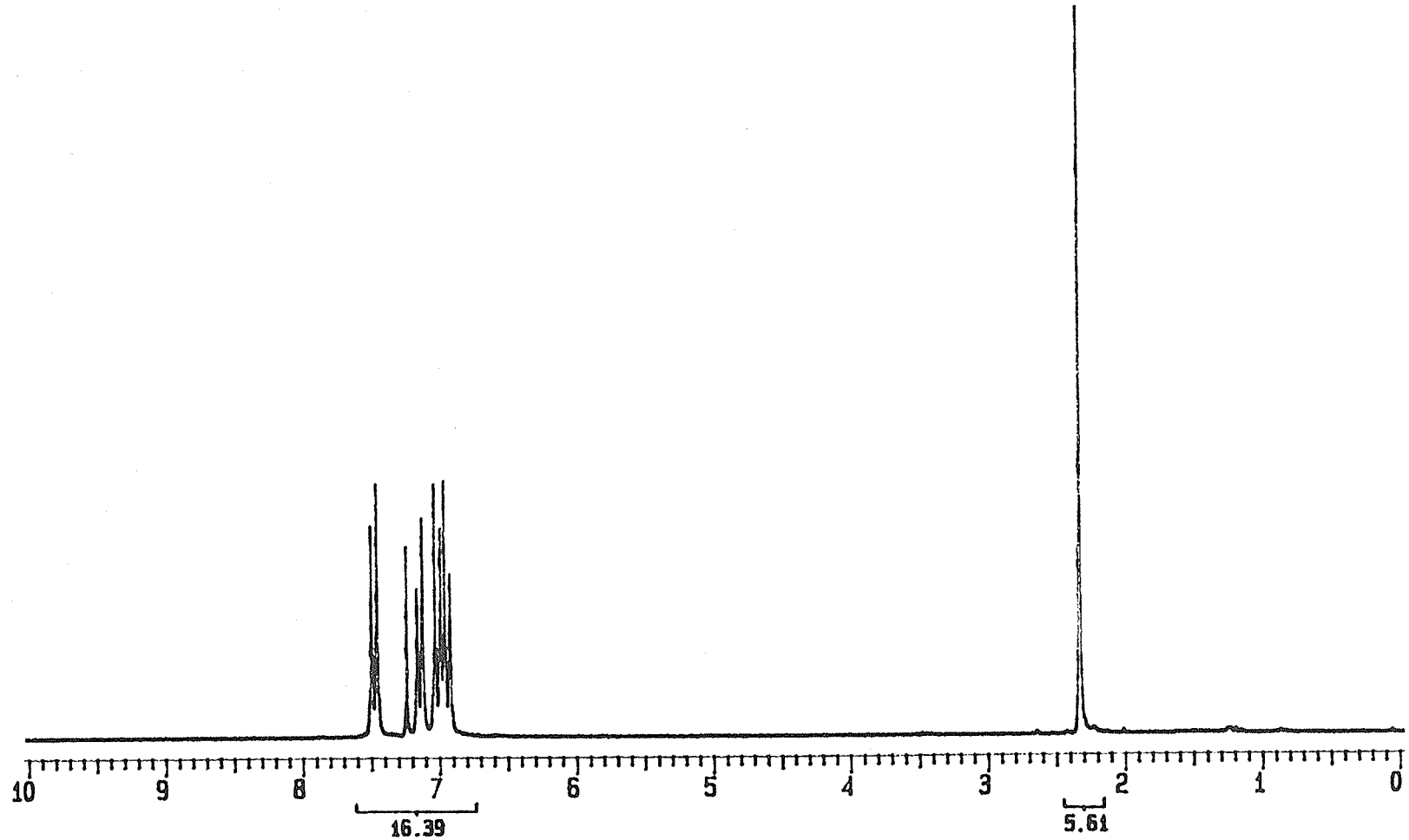


resonances for the uncomplexed aromatic CH's occur at 122.04 and 129.98 ppm. The four aromatic quaternary carbon resonances arise as expected. The two for the complexed aromatics occur at 101.60 ppm (C-CH_3) and 133.15 ppm (C-O), while those for the uncomplexed aromatic can be found at 138.62 ppm (C-C) and 154.05 ppm (C-O). The carbon resonance for the methyl group is situated at 19.81 ppm.

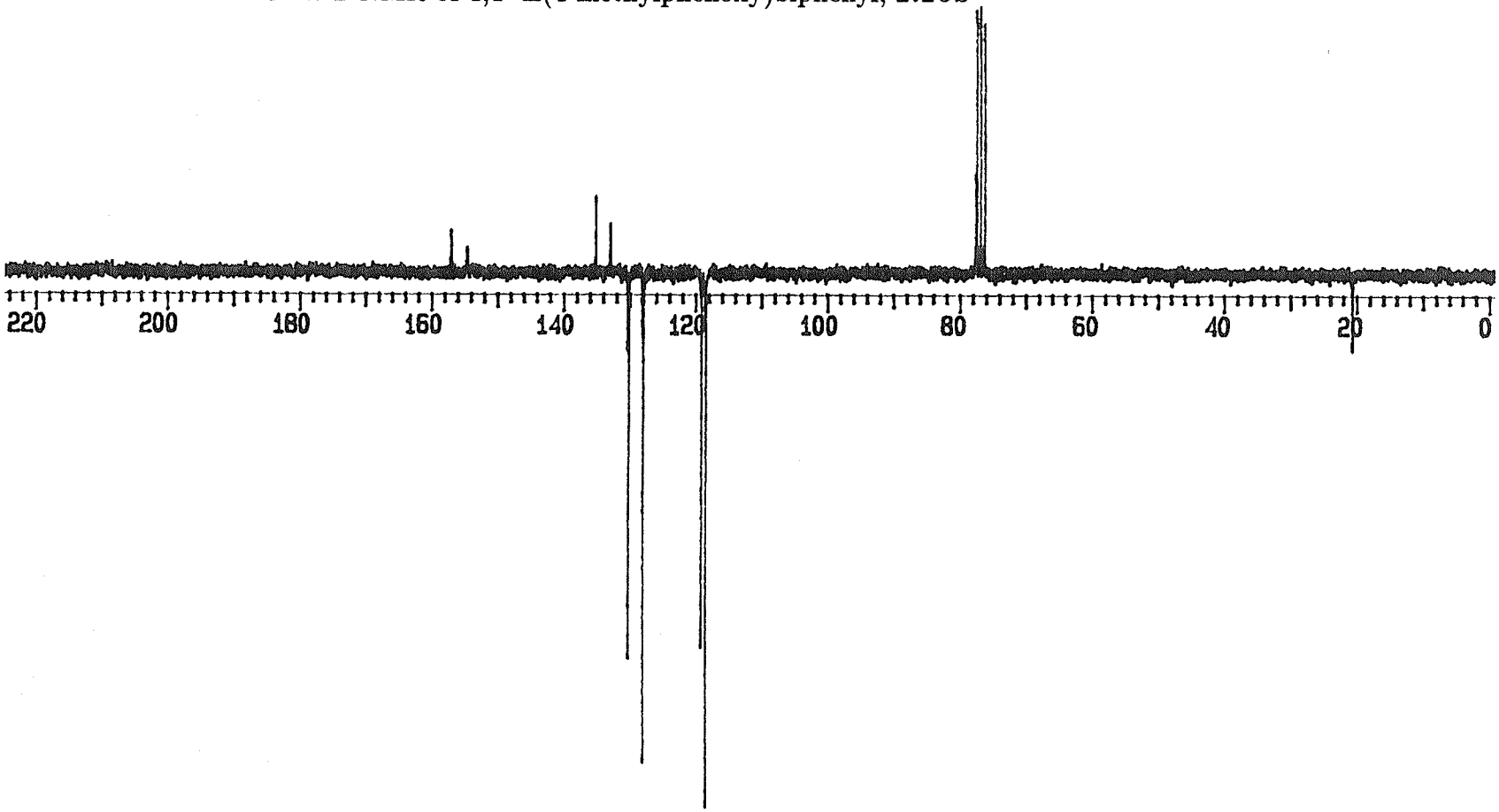
No problems were encountered when the photolytic demetallation procedure was applied to these complexes. All diaryloxybiphenyl compounds **2.21b–2.26b** could be isolated in high yield as white powders by column chromatography. Analytical data can be found in table 20 (^{1}H NMR, mass spectrometry) and table 21 (^{13}C-APT NMR, melting point). Yields and elemental analysis data for these compounds have been recorded in table 22. All these compounds gave rise to a base peak corresponding to the molecular ion in the mass spectral studies.

The NMR spectra of 4,4′-di(4-methylphenoxy)biphenyl (compound **2.70**), liberated from complex **2.26a**, are presented in figure 42 and 43. The ^{1}H spectrum of this compound is also quite simple, in spite of the two AA′BB′ spin systems it contains. The resonances in the aromatic region (6.92-7.50 ppm) appear very much as that which would arise from two overlapping A_2B_2 spin systems. It is for this reason that these (and similar) resonances are recorded as doublets in the ^{1}H NMR tables. The accompanying coupling constants were determined simply by the peak separations. These values serve as approximations in the absence of a more rigorous spectral analysis. The resonance for the two equivalent methyl groups appears at 2.33 ppm. In the ^{13}C-APT NMR, two carbon resonances for the CH's of the biphenyl unit exist at 118.53 and 128.05 ppm. The remaining two resonances in this region (119.18 and 130.27 ppm) arise from the carbons in the CH's of the outer arene rings.

42 ^{1}H NMR of 4,4′-di(4-methylphenoxy)biphenyl, **2.26b**



43 ^{13}C-APT NMR of 4,4′-di(4-methylphenoxy)biphenyl, **2.26b**



The four resonances observed for the aromatic quaternary carbons agree with the indicated structure. The biphenyl unit gives rise to two resonances at 133.10 ppm ($C\text{-}CH_3$) and 154.64 (C-O). The outer arene rings also produce two resonances, at 135.30 ppm (C-C) and 157.14 ppm (C-O). The resonance for the carbons of the equivalent methyl groups occur further upfield at 20.72 ppm.

Table 17: ^{1}H NMR data for complexes **2.21a–2.26a**

δ (referenced to acetone-d_6)			
Complex	*Complexed aromatics*	*Cp's*	*Others*
2.21a	6.32(t,2H,*J* 6.2), 6.46-6.55(m,6H)	5.28(s,10H)	7.55(d,4H,*J* 8.8), 7.91(m,4H,*J* 8.8)(Ar)
2.22a	6.19-6.27(m,2H), 6.30-6.42(m,8H)	5.00(s,10H)	7.35-7.68(m,8H)(Ar)
2.23a	6.39-6.52(m,6H), 6.96-7.02(m,2H)	5.36(s,10H)	7.56(d,4H,*J* 8.8), 7.93(m,4H,*J* 8.8)(Ar)
2.24a	6.46(d,2H,*J* 5.8), 6.58-6.72(m,4H) 6.91(s,2H)	5.39(s,10H)	7.54(d,4H,*J* 8.4), 7.92(d,4H,*J* 8.4)(Ar)
2.25a	6.57(d,4H,*J* 7.0), 6.85(d,4H,*J* 7.0)	5.41(s,10H)	7.49(d,4H,*J* 8.6), 7.90(d,4H,*J* 8.6)(Ar)
2.26a	6.38(s,8H)	5.23(s,10H)	2.50(s,6H)(CH_3); 7.46(d,4H,*J* 8.8), 7.88(d,4H,*J* 8.8)(Ar)

Table 18: ^{13}C NMR data for complexes **2.21a–2.26a**

δ (referenced to acetone-d_6)			
Complex	*Complexed aromatics*	*Cp's*	*Others*
2.21a	78.11, 85.96, 87.90, 134.32*	78.17	122.21, 130.09, 138.83*, 154.00*(Ar)
2.22a	78.77, 86.11, 87.82, 133.59*	78.19	121.28, 127.48, 130.49*, 131.80, 133.34, 152.65*(Ar)
2.23a	77.97, 85.90, 86.81, 89.16, 98.48*, 130.18*	80.27	121.72, 130.18, 138.88*, 154.20*(Ar)
2.24a	77.04, 79.23, 86.47, 87.13, 107.18*, 134.10*	80.52	122.17, 130.19, 138.95*, 153.87*(Ar)
2.25a	76.45, 86.83, 103.74*, 132.01*	79.43	121.32, 129.16, 137.31*, 152.74*(Ar)
2.26a	77.26, 87.82, 101.60*, 133.15*	78.50	19.81(CH_3); 122.04, 129.98, 138.62*, 154.05*(Ar)

* denotes quaternary carbon atoms

Table 19: Yields and elemental composition data for complexes **2.21a–2.30a**

		elemental composition found(calculated), %	
Complex	*% yield*	*C*	*H*
2.21a	88	46.80(46.93)	3.12(3.24)
2.22a	88	46.99(46.93)	3.31(3.24)
2.23a	74	43.61(43.49)	2.83(2.79)
2.24a	86	43.39(43.49)	2.82(2.79)
2.25a	91	43.33(43.49)	2.85(2.79)
2.26a	96	48.28(48.14)	3.62(3.59)
2.27a	81	43.26(43.10)	3.32(3.24)
2.28a	95	43.21(43.10)	3.29(3.24)
2.29a	90	47.16(46.93)	3.12(3.24)
2.30a	86	47.99(47.82)	3.92(3.80)

Table 20: ^{1}H NMR and MS data for compounds **2.21b–2.26b**

δ (referenced to chloroform-d)			
Compound	*Aromatics*	*Others*	M^+,*m/z (rel.ab.)*
2.21b	7.02-7.10(m,10H), 7.24-7.38(m,4H), 7.49-7.53(m,4H)	—	338 (100)
2.22b	6.81-7.43(m,18H)	—	338 (100)
2.23b	6.99-7.29(m,10H), 7.46-7.56(m,6H)	—	406 (69) 408 (44) 410 (9)
2.24b	6.88-7.56(m,16H)	—	406 (100) 408 (68) 410 (13)
2.25b	6.94-7.05(m,8H), 7.23-7.31(m,4H), 7.48-7.55(m,4H)	—	406 (100) 408 (68) 410 (12)
2.26b	6.92-7.17(m,12H), 7.46-7.51(m,4H)	2.33(s,6H)(CH_3)	366 (100)

Table 21: ^{13}C NMR and melting point data for compounds **2.21b–2.26b**

δ (referenced to chloroform-*d*)			
Compound	*Aromatics*	*Others*	*M.P.(°C)*
2.21b	118.96, 119.07, 123.35, 128.15, 129.77, 135.63*, 156.62*, 157.14*	—	149-150 (white)
2.22b	118.69, 118.78, 122.66, 123.04, 129.22, 129.37, 129.70*, 131.96, 154.66*, 157.42*	—	90-91 (white)
2.23b	118.05, 120.95, 124.80, 125.91*, 127.94, 128.15, 130.78, 135.60*, 152.30*, 156.32*	—	114-115 (white)
2.24b	116.78, 118.87, 119.64, 123.33, 128.39, 130.52, 135.08*, 136.23*, 155.78*, 158.20*	—	67-68 (white)
2.25b	119.14, 120.12, 128.29, 128.30*,#, 129.76, 135.89*, 155.81*, 156.31*	—	179 (white)
2.26b	118.53, 119.18, 128.05, 130.27, 133.10*, 135.30*, 154.64*, 157.14*	20.72(CH_3)	172-173 (white)

#: Obtained by a modification of the APT pulse sequence. See section II.4.2
* denotes quaternary carbon atoms

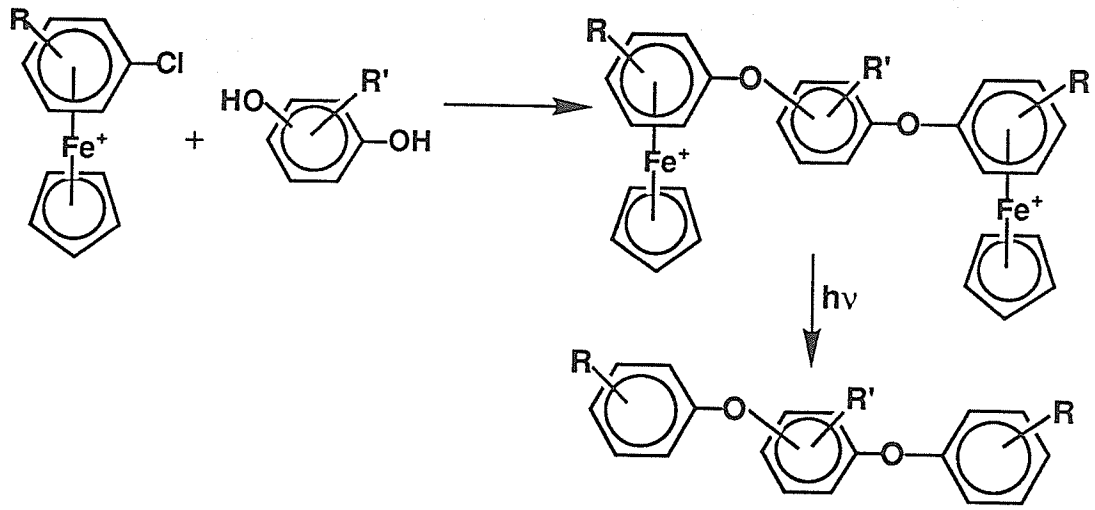
Table 22: Yields and elemental composition data for compounds **2.21b–2.26b**

		elemental composition found(calculated), %	
Compound	*% yield*	*C*	*H*
2.21b	96	85.29(85.18)	5.40(5.36)
2.22b	97	85.10(85.18)	5.38(5.36)
2.23b	85	70.89(70.78)	3.91(3.96)
2.24b	96	70.91(70.78)	4.01(3.96)
2.25b	65	70.68(70.78)	3.94(3.96)
2.26b	93	85.37(85.22)	5.98(6.05)

3 Incorporation of Substituted Nucleophiles

The complexes presented to this point have all been prepared from simple, unsubstituted dihydroxyaromatics. An extensive number of substituted dihydroxyaromatic compounds exist, allowing the extension of the synthetic technique to more complex aromatic ethers. This has also provided an opportunity to investigate how sterically crowded nucleophiles and starting complexes might affect the success of these reactions. Scheme 4 demonstrates a number of complexes and their corresponding compounds prepared with this intent. Spectral data for these complexes can be found in table 23 (^{1}H NMR) and table 24 (^{13}C-APT NMR), while yields and elemental analysis data are summarized in table 19.

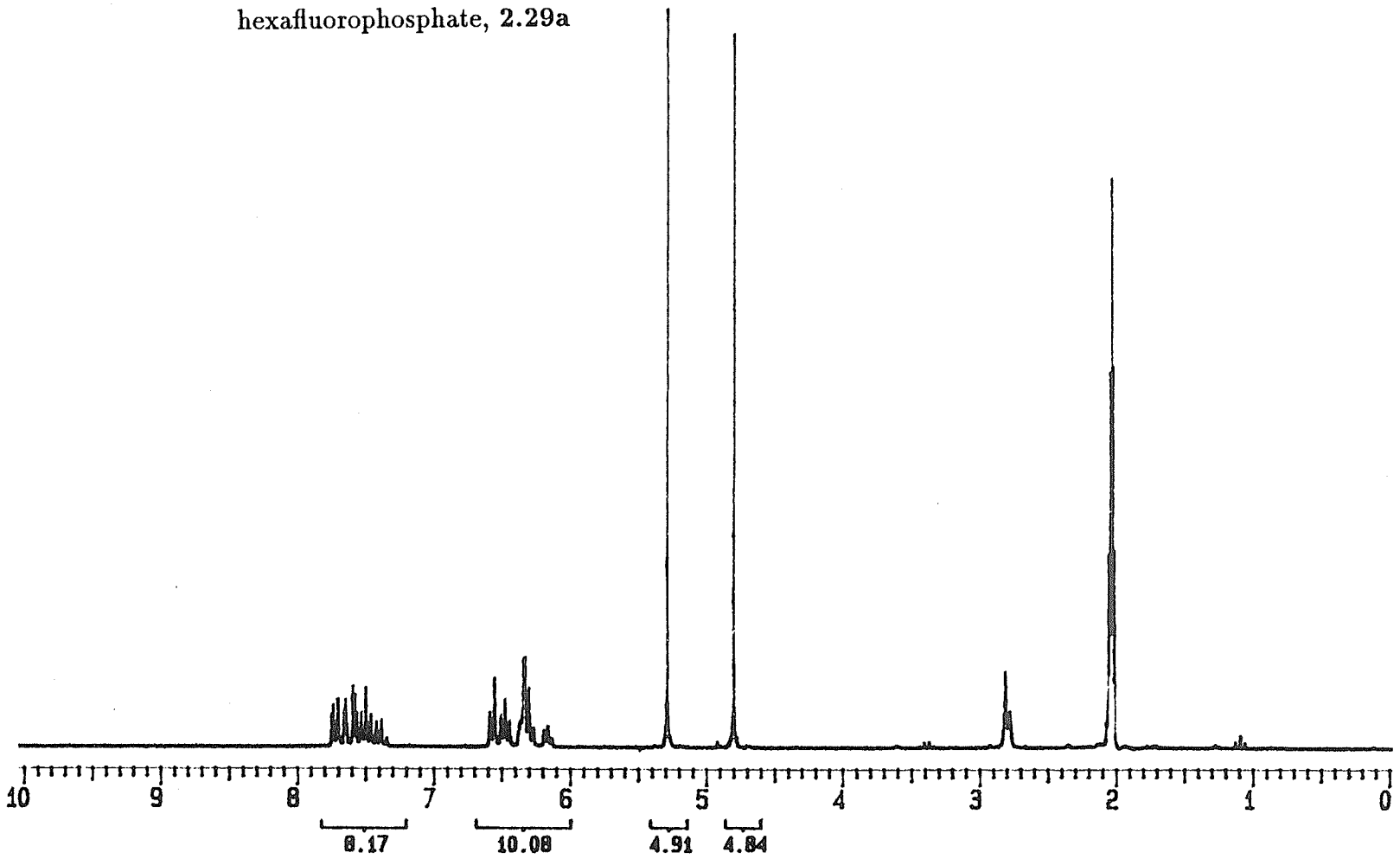
The synthesis of 1,4-di([η^6-phenoxy-η^5-cyclopentadienyl]iron)-2-methylbenzene dihexafluorophosphate (**2.28a**) presented no problems. The reaction proceeded in the same fashion as complexes **2.1a**–**2.7a**. This would be expected, since the previous complexes also contain CH_3 substituents, although on the complex arenes. The complex 2,5-di([η^6-phenoxy-η^5-cyclopentadienyl]iron)biphenyl dihexafluorophosphate (**2.29a**) could also be synthesized, by refluxing a solution of phenylhydroquinone and the appropriate mono-iron complex **i** in THF/DMF. However, this synthesis required a reaction time of only *five* hours, implying that the phenyl substituent does not sterically hinder the formation of this complex, or adversely affect the reaction time. This is not surprising given that 2,2′-di([η^6-phenoxy-η^5-cyclopentadienyl]iron)biphenyl dihexafluorophosphate (**2.29a**) was also easily prepared, however this is the shortest reaction time for all complexes prepared in this study. The NMR spectra for complex **2.29a** are presented in figure 44 and 45. The ^{1}H



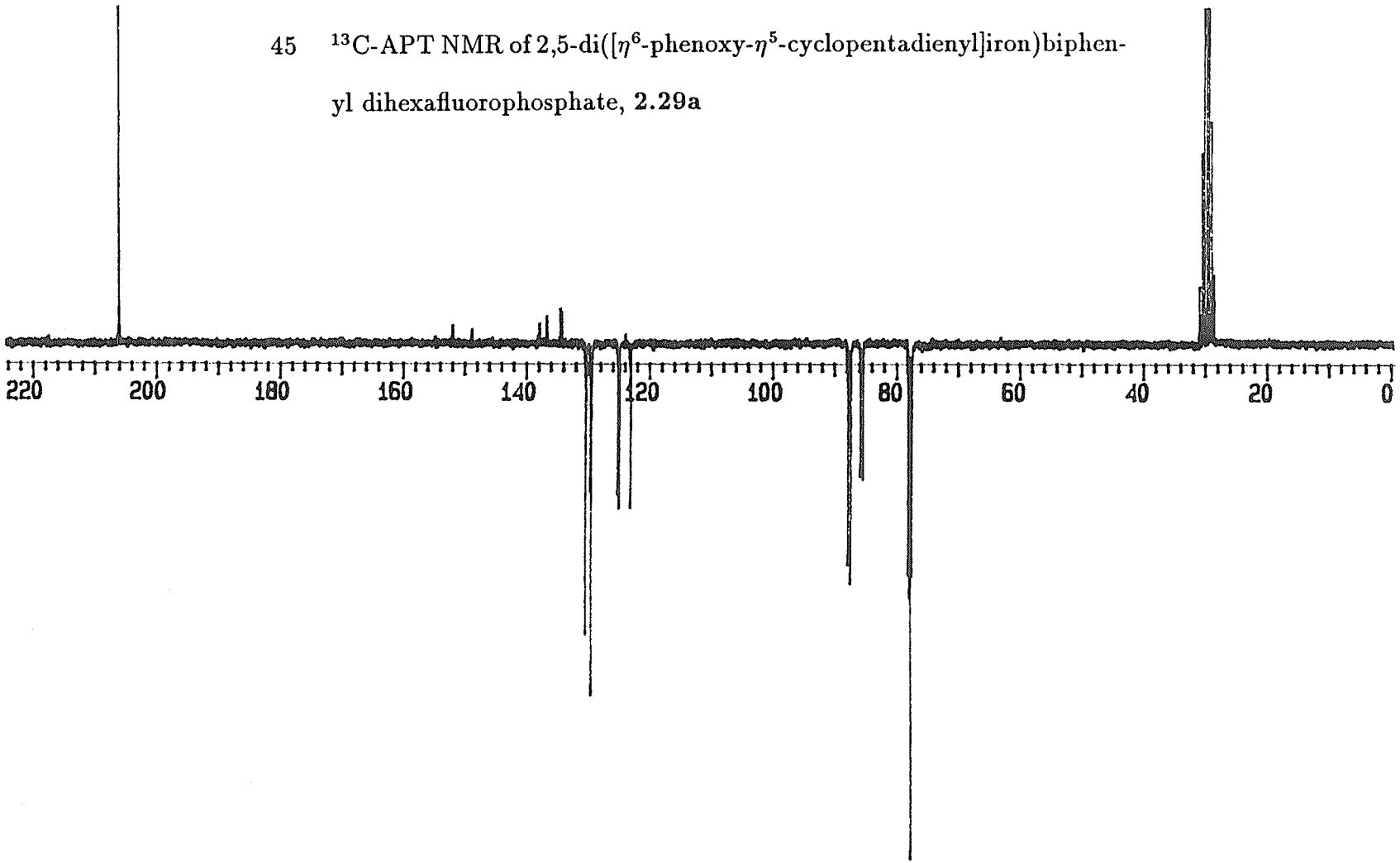
Scheme 4

R	R′	dihydroxybenzene	complex	compound
H	CH_3	1,4-	**2.27a**	**2.27b**
H	2-CH_3	1,3-	**2.28a**	**2.28b**
H	Ph	1,4-	**2.29a**	**2.29b**
2,6-(CH_3)	Ph	1,4-	**2.30a**	**2.30b**

44 ^{1}H NMR of 2,5-di([η^6-phenoxy-η^5-cyclopentadienyl]iron)biphenyl dihexafluorophosphate, **2.29a**



45 ^{13}C-APT NMR of 2,5-di([η^6-phenoxy-η^5-cyclopentadienyl]iron)biphenyl dihexafluorophosphate, **2.29a**



spectrum is quite different from all those presented above in that two widely spaced resonances due to the protons of the non-equivalent cyclopentadienyl rings appear. They occur at 4.81 and 5.29 ppm. The former resonance represents the largest upfield shift of all the complexes prepared in this study. Both the complexed aromatic region (6.12-6.59 ppm) and uncomplexed aromatic region (7.35-7.75 ppm) show a high degree of complexity, as expected given the lowered symmetry of this complex. The ^{13}C-APT NMR spectrum shows two closely related sets of three resonances for the carbons of the CH's in the two complexed aromatics (in the 77.58-87.84 ppm range). In this spectrum, however, the two non-equivalent cyclopentadienyl rings give rise to coincidental resonances at 77.87 ppm. Six resonances for the carbons in the CH's of the uncomplexed aromatics can be found as expected, in the 123.14-130.41 ppm range. The requisite number of aromatic quaternary carbon resonances (six) are present between 134.35 and 152.08 ppm. A more detailed assignment can be found in table 24.

The related complex **2.30a** required a much longer time for its synthesis (24 hours), and in fact could not be achieved with the THF/DMF system. The length of this reaction is likely due to some steric inhibition provided by the interference of the methyl groups with the phenyl substituent of phenylhydroquinone. It might prove possible to selectively substitute with the 4-OH of phenylhydroquinone based on this steric effect. In the course of developing a successful reaction procedure for **2.30a**, it was found that shorter reaction times or different reaction solvents resulted in a mixture of products, but with 2-hydroxy-5-([η^6-(2,6-dimethylphenoxy)-η^5-cyclopentadienyl]iron)biphenyl hexafluorophosphate present in the main (figure 46). No further investigations into the synthesis of this complex were made, however. Pho-

tolysis of this and all complexes **2.27a–2.30a** resulted in compounds **2.27b–2.30b** which were isolated as off-white needle-like solids, with the exception of **2.28a**, recovered as a yellowish oil. All yields were very high (77-90%). The ^{1}H NMR

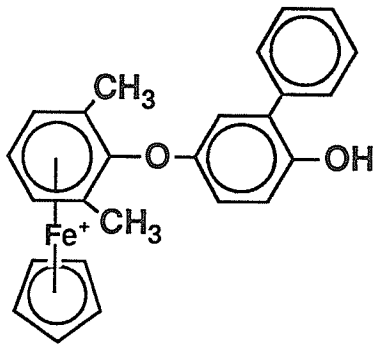
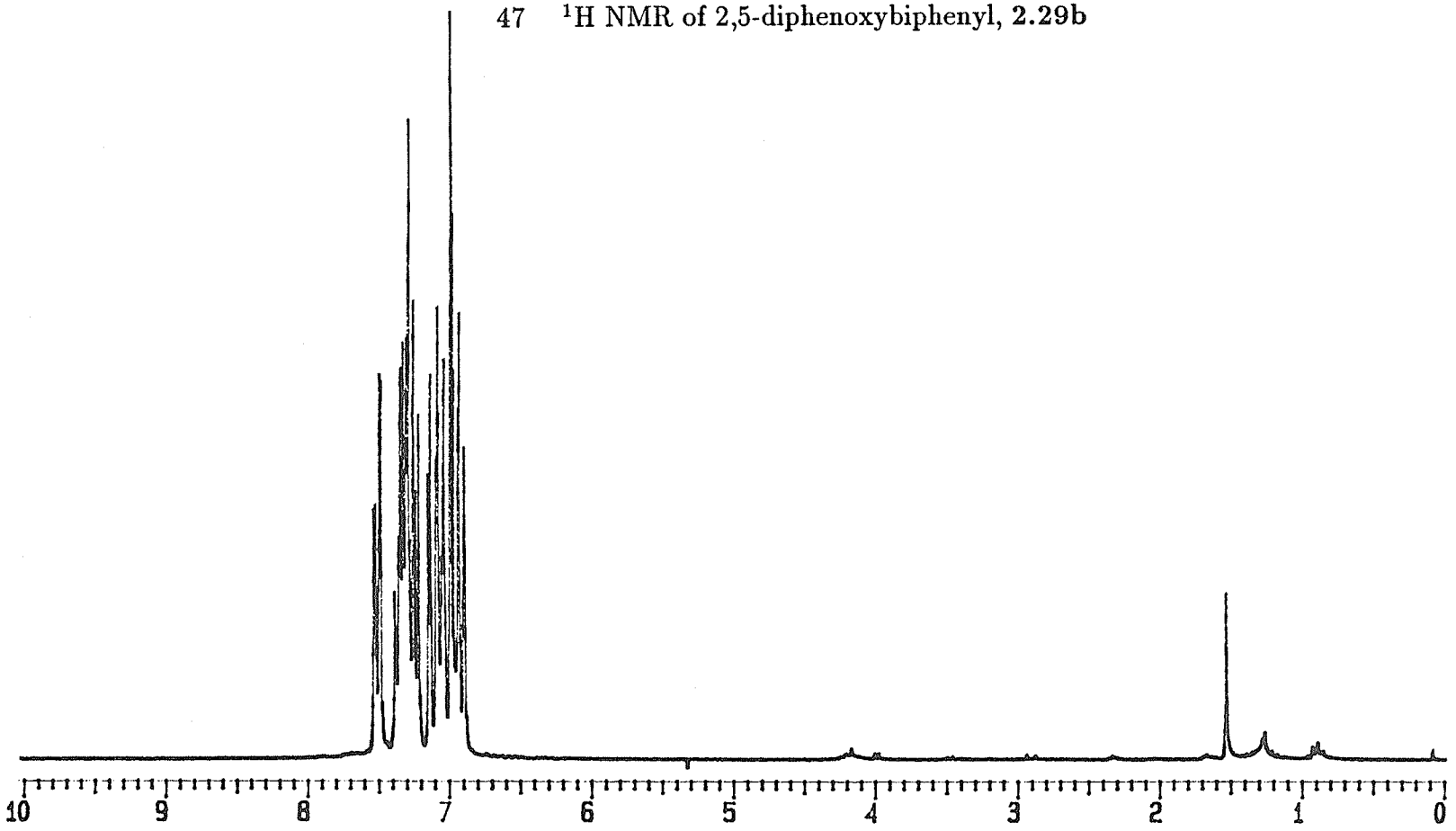


Figure 46: 2-hydroxy-5-([η^6-(2,6-dimethylphenoxy)-η^5-cyclopentadienyl]-iron)biphenyl hexafluorophosphate

data can be found in table 25 along with mass spectrometry data. ^{13}C-APT NMR data and melting points have been collected in table 26. Elemental analysis data and yields can be found in table 27. For completeness, the NMR spectra of 2,5-diphenoxybiphenyl (compound **2.29b**) can be found in figure 47 and 48.

The aromatic region of the ^{1}H NMR spectrum is very complex, as one would expect for a molecule of this nature. ^{13}C-APT NMR provides a more readily interpretable spectrum, containing 12 distinct resonances for the carbons of the aromatic CH's and six aromatic quaternary carbon resonances, as expected for this molecule. A more detailed assignment of these resonances can be found in table 26.

47 ^{1}H NMR of 2,5-diphenoxybiphenyl, **2.29b**



48 ^{13}C-APT NMR of 2,5-diphenoxybiphenyl, **2.29b**

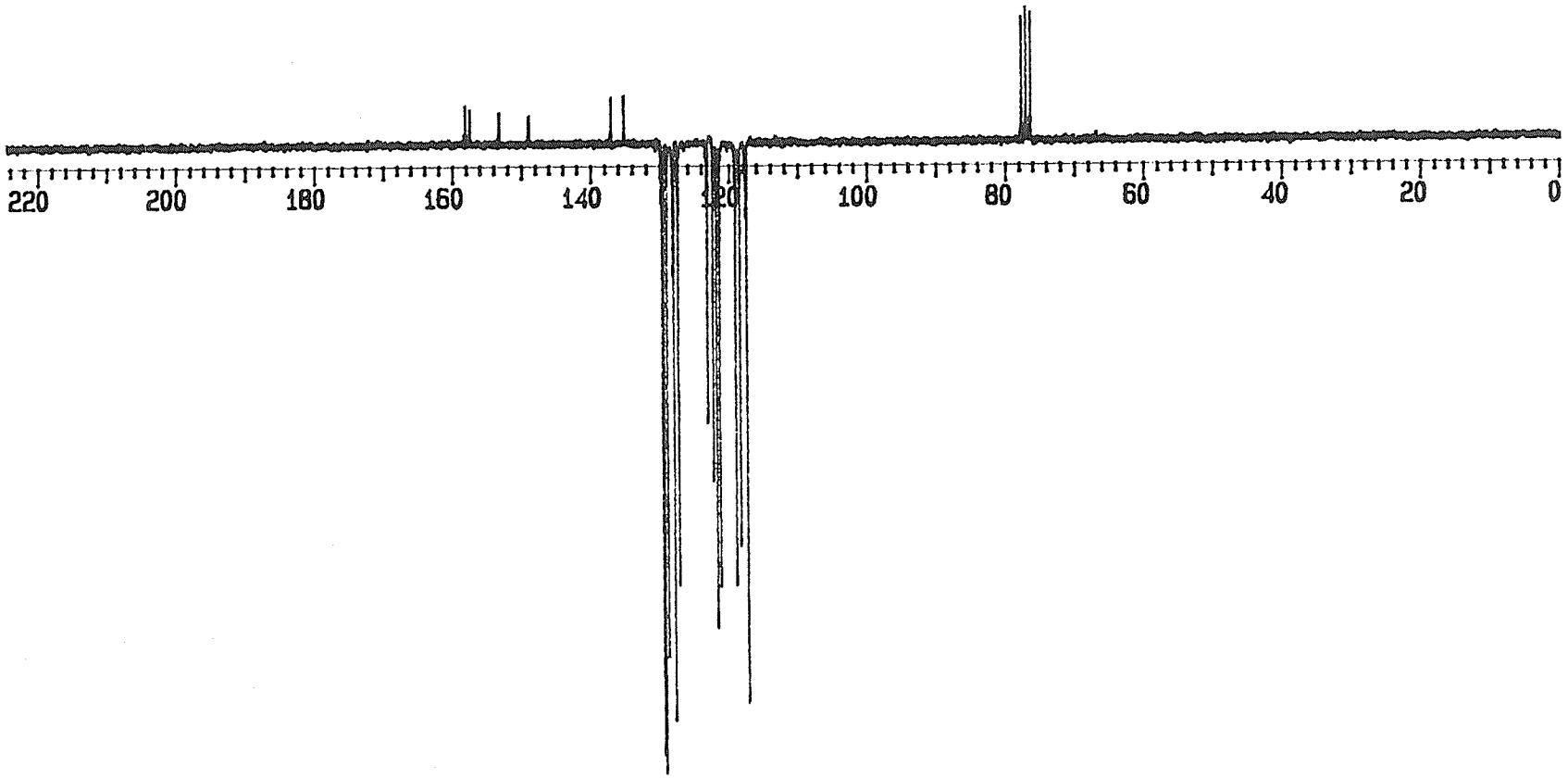


Table 23: ^{1}H NMR data for complexes **2.27a–2.30a**

δ (referenced to acetone-d_6)			
Complex	*Complexed aromatics*	*Cp's*	*Others*
2.27a	6.27-6.34(m,2H), 6.43-6.49(m,8H)	5.24(s,5H), 5.26(s,5H)	2.28(s,3H)(CH_3); 7.35-7.54(m,3H)(Ar)
2.28a	6.30-6.40(m,2H), 6.40-6.52(m,8H)	5.28(s,10H)	2.19(s,3H)(CH_3); 7.34(d,2H,*J* 8.4), 7.55(t,1H,*J* 8.4)(Ar)
2.29a	6.12-6.59(m,10H)	4.81(s,5H), 5.29(s,5H)	7.35-7.75(m,8H)(Ar)
2.30a	6.19(t,1H,*J* 6.4), 6.25(t,1H,*J* 6.4), 6.41(d,2H,*J* 6.2), 6.47(d,2H,*J* 6.2)	4.97(s,5H), 5.20(s,5H)	6.76(d,1H,*J* 9.0), 6.90(dd,1H,*J* 9.0,3.0), 7.18(d,1H,*J* 3.0), 7.42-7.63(m,3H), 7.74-7.82(m,2H)(Ar)

Table 24: ^{13}C NMR data for complexes **2.27a–2.30a**

δ (referenced to acetone-d_6)			
Complex	*Complexed aromatics*	*Cp's*	*Others*
2.27a	77.45, 77.65, 85.77, 87.79, 87.87, 134.61*, 134.70*	78.11	16.87(CH_3); 121.50, 123.90, 125.47, 134.16*, 150.09*, 151.66*(Ar)
2.28a	78.01, 85.88, 87.82, 134.05*	78.15	9.99(CH_3); 119.19, 129.92, 123.79*, 154.08*(Ar)
2.29a	77.58, 78.15, 85.49, 85.85, 87.42, 87.84, 134.35*, 134.59*	77.87	123.14, 124.98, 125.17, 129.46, 129.62, 130.41, 136.73*, 138.01*, 148.92*, 152.08*
2.30a	86.38, 86.50, 88.79, 99.00*, 99.47*, 126.65*, 126.85*	79.19, 79.38	16.75(CH_3); 116.24, 116.44, 118.42, 129.09, 129.27, 130.50, 133.67*, 137.06*, 150.10*, 153.78*

* denotes quaternary carbon atoms

Table 25: ^{1}H NMR and MS data for compounds **2.27b–2.30b**

δ (referenced to chloroform-*d*)			
Compound	*Aromatics*	*Others*	*M^+,m/z (rel.ab.)*
2.27b	6.84-7.34(m,13H)	2.19(s,3H)(CH_3)	276 (100)
2.28b	6.69-7.35(m,13H)	2.14(s,3H)(CH_3)	276 (100)
2.29b	6.90-6.53(m,18H)	—	338 (100)
2.30b	6.28(d,1H,*J* 9), 6.43(dd,1H,*J* 3.2,9), 6.85(d,1H,*J* 3), 6.96-7.08(m,6H), 7.31-7.47(m,3H), 7.61-7.70(m,2H)	2.10(s,6H)(CH_3), 2.17(s,6H)(CH_3)	394 (100)

Table 26: ^{13}C NMR and melting point data for compounds **2.27b–2.30b**

δ (referenced to chloroform-*d*)			
Compound	*Aromatics*	*Others*	*M.P.(°C)*
2.27b	116.71, 117.65, 118.40, 121.35, 121.86, 122.15, 122.96, 129.64, 129.70, 131.88*, 149.85*, 153.12*, 157.71*, 158.25*	16.33(CH_3)	52 (white)
2.28b	115.09, 117.55, 122.41*, 122.63, 126.79, 129.69, 155.86*, 157.70*	9.37(CH_3)	oil (yellowish)
2.29b	117.54, 118.48, 119.14, 121.42, 121.89, 122.38, 123.15, 127.46, 128.14, 129.03, 129.56, 129.77, 135.21*, 137.08*, 148.91*, 153.22*, 157.51*, 158.18*	—	91 (white)
2.30b	113.69, 113.94, 117.03, 124.72, 124.89, 127.10, 127.96, 128.92, 128.95, 129.51, 130.87*, 131.31*, 131.45*, 138.03*, 148.95*, 151.47*, 151.70*, 152.20*	16.48(CH_3)	119-120 (white)

* denotes quaternary carbon atoms

Table 27: Yields and elemental composition data for compounds **2.27b–2.30b** and **2.34b–2.36b**

		elemental composition found(calculated), %	
Compound	*% yield*	*C*	*H*
2.27b	77	82.68(82.58)	5.89(5.84)
2.28b	90	82.56(82.58)	5.89(5.84)
2.29b	91	85.09(85.18)	5.29(5.36)
2.30b	90	85.17(85.25)	6.65(6.64)
2.34b	83	72.99(72.85)	4.48(4.42)
2.35b	82	73.58(73.43)	4.79(4.86)
2.36b	93	81.09(80.99)	5.58(5.52)

4 Stepwise Preparation and Functionalization of Aromatic Ethers

If the goal were to simply prepare the above isomeric materials, a related technique might be used, which involves the use of only one dichlorobenzene complex and hydroxyaromatic nucleophiles (figure 49) [16, 54, 78]. An extensive number of hy-

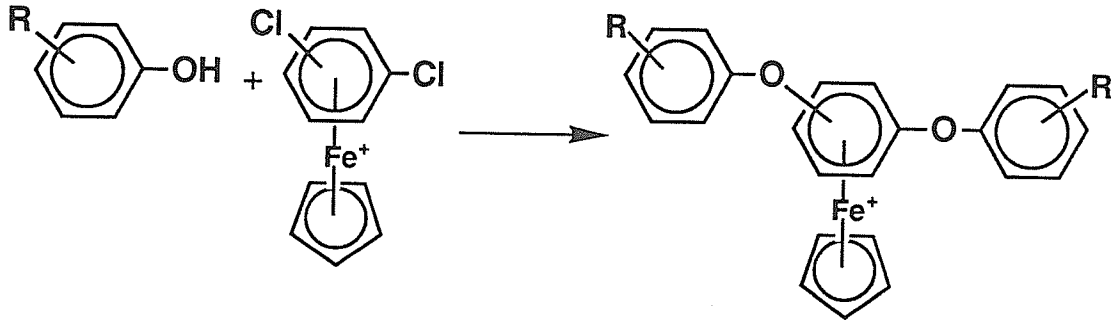


Figure 49: Mono-iron route to substituted diphenoxybenzenes

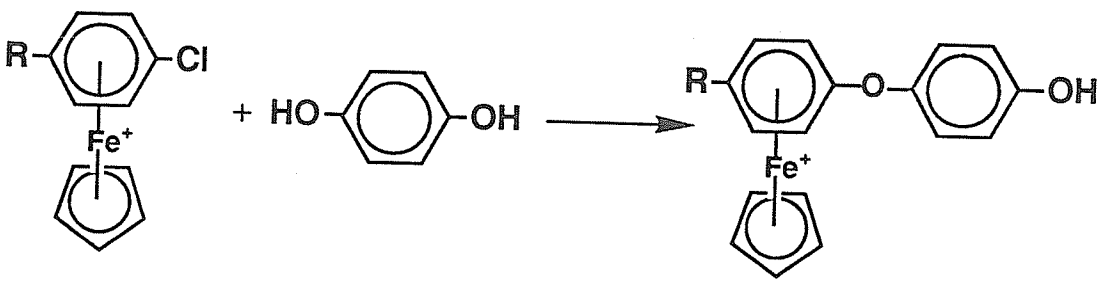
droxyaromatic compounds do exist, allowing for its wide application. Unfortunately, a limited number of arenes can be incorporated into the complexed arene ring, due to the severity of the ligand exchange reaction conditions. The system developed in the current work not only provides an alternative approach to aromatic ethers, but it also allows for the synthesis of triaryl diethers with more extensive functionality on the central arene. In this sense, these two methods of triaryl diether synthesis are complementary. However, there are a number of benefits provided by the currently

developed system. *Monosubstitution* reactions can be carried out with *dinucleophiles* leaving one nucleophilic site free for further reactions. This allows for the stepwise synthesis of di-iron complexes, as well as more extensive multi-iron systems (section 4.1). The mono-iron route could be implemented in a stepwise fashion, but cannot be used to generate multi-iron species. Furthermore, the mono-iron ether complexes in scheme 5 do not allow for further $CpFe^+$-activated nucleophilic substitution reactions. The di-iron complexes described herein can be built up with additional carbon, nitrogen and oxygen nucleophiles, provided chloro groups are present on the complexed arene rings (complex **2.4a** for example). This is an important advantage, if aromatic ethers are to be built into larger molecules such as vancomycin. Section 4.2 explores this advantage with selected carbon nucleophiles.

4.1 Mono-iron Complexes as Nucleophiles

The synthetic procedure could be modified to allow for a single substitution reaction between [η^6-chloroarene-η^5-cyclopentadienyl]iron complexes and dihydroxyarene compounds. Two of these mono-iron complexes have been prepared, as shown in scheme 6. To achieve these products required an 8:1 ratio of nucleophile to mono-iron complex (see experimental section). When the reaction was attempted with lower ratios, the corresponding di-iron complexes **2.1a** and **2.7a** were formed as side products. In fact, when a 1:1 ratio was used these di-iron complexes became the main products. ^{1}H and ^{13}C-APT NMR data for these complexes have been recorded, and may be found in table 28 and 29. Yields, elemental analysis and infra-red spectroscopy data are contained in table 30. The NMR spectra for [(4-hydroxyphenoxy-η^6-toluene)-η^5-cyclopentadienyl]iron hexafluorophosphate (complex **2.32a**) are

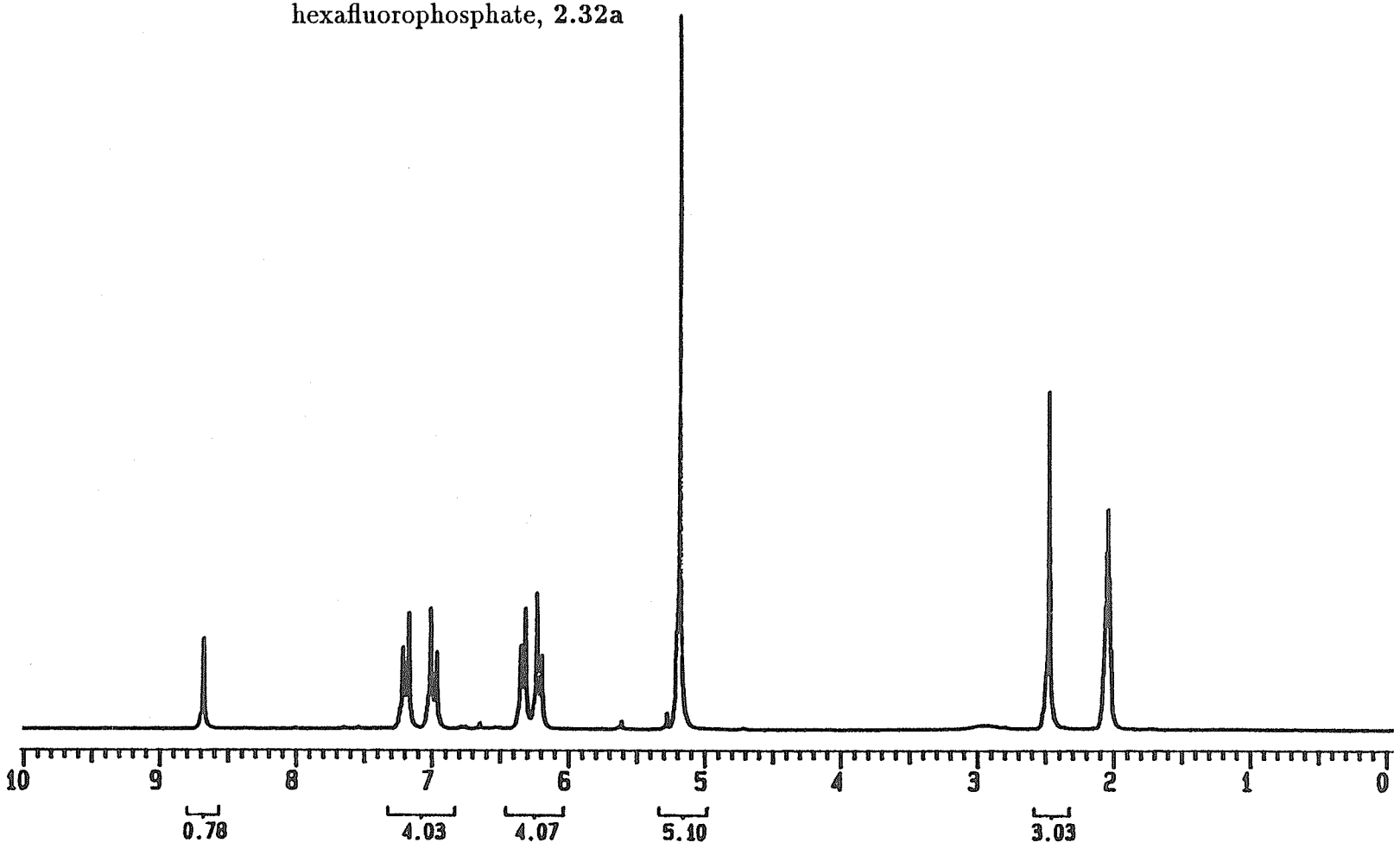
presented in figure 50 and figure 51.



R = H (2.31)
R = CH_3 (2.32)

Scheme 6

50 ^{1}H NMR of[(4-hydroxyphenoxy-η^6-toluene)-η^5-cyclopentadienyl]iron hexafluorophosphate, **2.32a**



51 ^{13}C-APT NMR of [(4-hydroxyphenoxy-η^6-toluene)-η^5-cyclopentadienyl]-iron hexafluorophosphate, **2.32a**

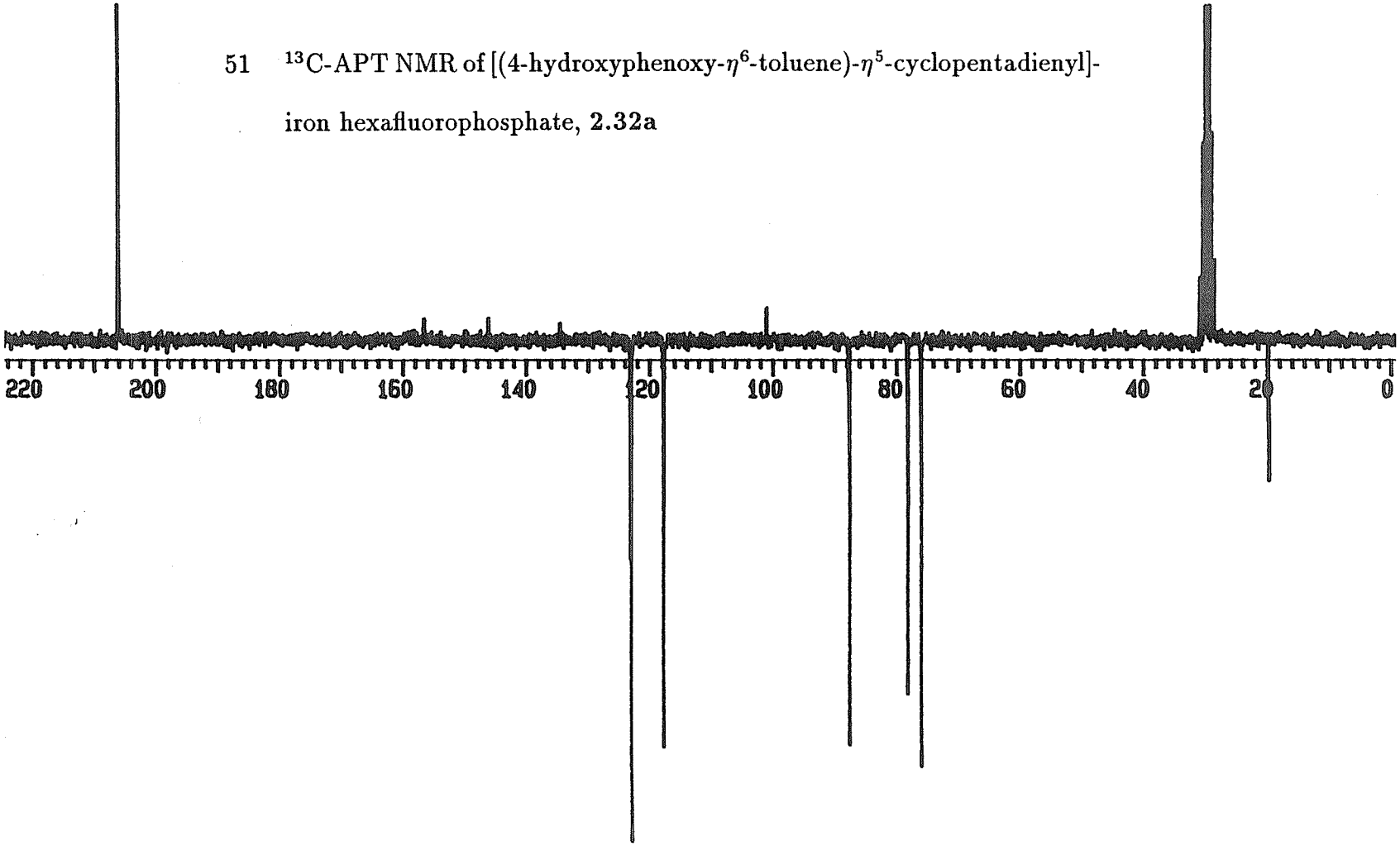


Table 28: ^{1}H NMR data for complexes **2.31–2.36a**

δ (referenced to acetone-d_6)			
Complex	*Complexed aromatics*	*Cp's*	*Others*
2.31	6.27-6.48(m,5H)	5.23(s,5H)	7.00(d,2H,*J* 9.0), 7.22(d,2H,*J* 8.8)(Ar); 8.71(s,1H,OH)
2.32	6.21(d,2H,*J* 6.8), 6.33(d,2H,*J* 6.8)	5.18(s,5H)	2.47(s,3H)(CH_3); 6.98(d,2H,*J* 8.8), 7.19(d,2H,*J* 9.0)(Ar); 8.67(s,1H,OH)
2.33	6.10(s,4H)	5.14(s,5H)	6.90(d,4H,*J* 8.4), 7.12(d,4H,*J* 8.4)(Ar); 9.88(s,2H,OH)
2.34a	6.53(d,2H,*J* 7.0), 6.25-6.35(m,1H), 6.42-6.44(m,4H), 6.74(m,2H,*J* 6.8)	5.24(s,5H), 5.36(s,5H)	7.58(s,4H)(Ar)
2.35a	6.31-6.41(m,4H), 6.56(d,2H,*J* 7.0), 6.77(d,2H,*J* 7.0)	5.21(s,5H), 5.38(s,5H)	2.51(s,3H)(CH_3); 7.57(s,4H)(Ar)
2.36a	6.30-6.41(m,12H)	5.22(s,5H), 5.34(s,10H)	2.52(s,3H)(CH_3); 7.58(s,8H)(Ar)

Table 29: ^{13}C NMR data for complexes **2.31–2.36a**

δ (referenced to acetone-d_6)			
Complex	*Complexed aromatics*	*Cp's*	*Others*
2.31	76.79, 85.35, 87.59, 135.51*	77.77	117.75, 123.09, 145.99*, 156.70*(Ar)
2.32	76.04, 87.65, 101.06*, 134.55*	78.23	19.77(CH_3); 117.74, 123.06, 146.19*, 156.68*(Ar)
2.33	73.58, 131.23*	77.46	116.88, 122.08, 144.84*, 155.78*(Ar)
2.34a	77.01, 77.56, 85.80, 87.76, 104.94*, 134.01*, 134.57*	78.08, 80.49	124.30, 124.50, 151.66*, 151.92*(Ar)
2.35a	76.90, 77.06, 87.79, 101.56*, 104.99*, 133.51*, 134.03*	78.51, 80.50	19.86(CH_3); 124.25, 124.36, 151.61*, 152.17*(Ar)
2.36a	75.45, 76.74, 87.80, 101.54*, 132.24*, 133.67*	78.51, 78.96	19.92(CH_3); 124.33, 124.43, 151.92*, 152.08*(Ar)

* denotes quaternary carbon atoms

Table 30: Yields, IR and elemental composition data for complexes **2.31–2.36a**

			elemental composition found(calculated), %	
Complex	*% yield*	*IR(cm^{-1})*	*C*	*H*
2.31	53	3535(OH)	45.01(45.16)	3.24(3.34)
2.32	74	3550(OH)	46.26(46.38)	3.59(3.68)
2.33	51	3530(OH)	49.51(49.31)	3.60(3.42)
2.34a	92	—	40.70(40.59)	2.66(2.80)
2.35a	86	—	41.49(41.34)	3.08(2.99)
2.36a	96	—	44.54(44.37)	3.15(3.25)

The ^{1}H NMR spectrum for this complex reveals the expected singlet for the cyclopentadienyl protons at 5.18 ppm, and the resonances for the complexed arene (6.19-6.34 ppm). The methyl resonance can be found at 2.47 ppm. The presence of the hydroxyphenoxy substituent is confirmed by the aromatic resonances in the 6.96-7.21 ppm range and the characteristic hydroxyl proton resonance at 8.67 ppm. The proposed identity of this complex is further supported by the ^{13}C-APT NMR spectrum, which reveals the expected cyclopentadienyl resonance and four complexed aromatic resonances (two CH's and two quaternaries), the methyl resonance as well as four uncomplexed aromatic resonances (two CH's and two quaternaries). A strong absorption in the infra-red spectrum at 3550 cm^{-1}, indicative of a hydroxyl stretch, lends additional confirmation of the proposed structure. It should be noted that [(1-chloro-4(hydroxyphenoxy)-η^6-benzene)-η^5-cyclopenta-

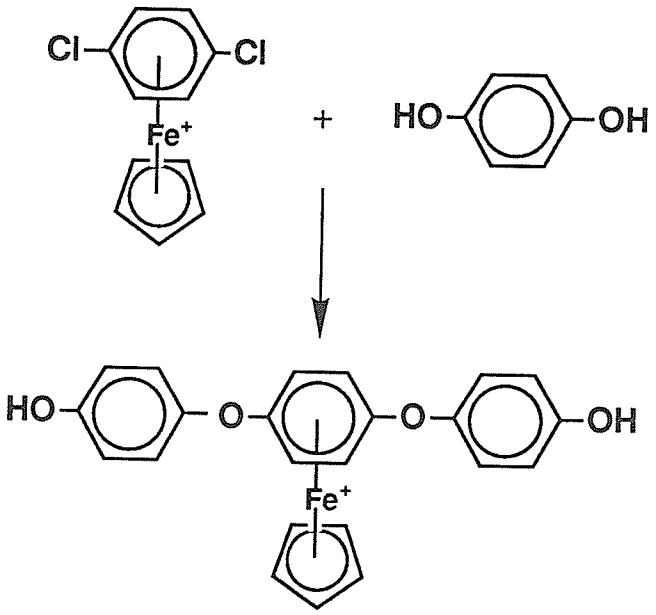
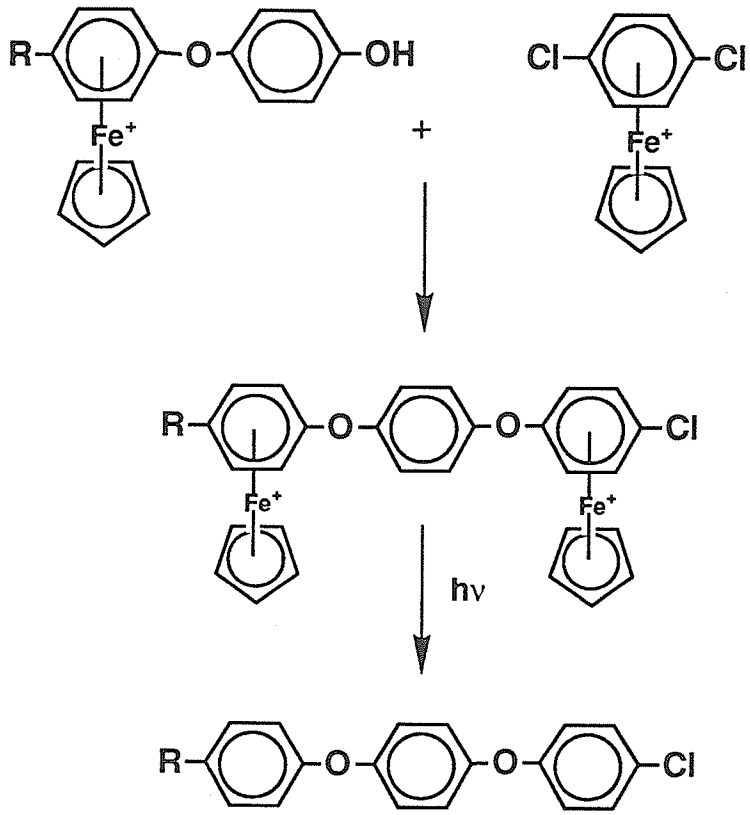


Figure 52: Disubstitution of iv with an excess of hydroquinone

dienyl]iron hexafluorophosphate and related complexes cannot be prepared with the above procedure, for both chloro groups of the required [η^6-dichlorobenzene-η^5-cyclopentadienyl]iron starting complex would be substituted when an excess of nucleophile is used. For example, when a five-fold excess of hydroquinone was reacted with [η^6-1,4-dichlorobenzene-η^5-cyclopentadienyl]iron hexafluorophosphate, the disubstituted complex [1,4-di(4-hydroxyphenoxy)-η^6-benzene-η^5-cyclopentadienyl]iron hexafluorophosphate (**2.33a**) was formed (figure 52). Analytical data for this complex are contained in table 28 (^{1}H) and table 29 (^{13}C-APT NMR), as well as table 30 (yield, elemental analysis and infra-red spectroscopy).

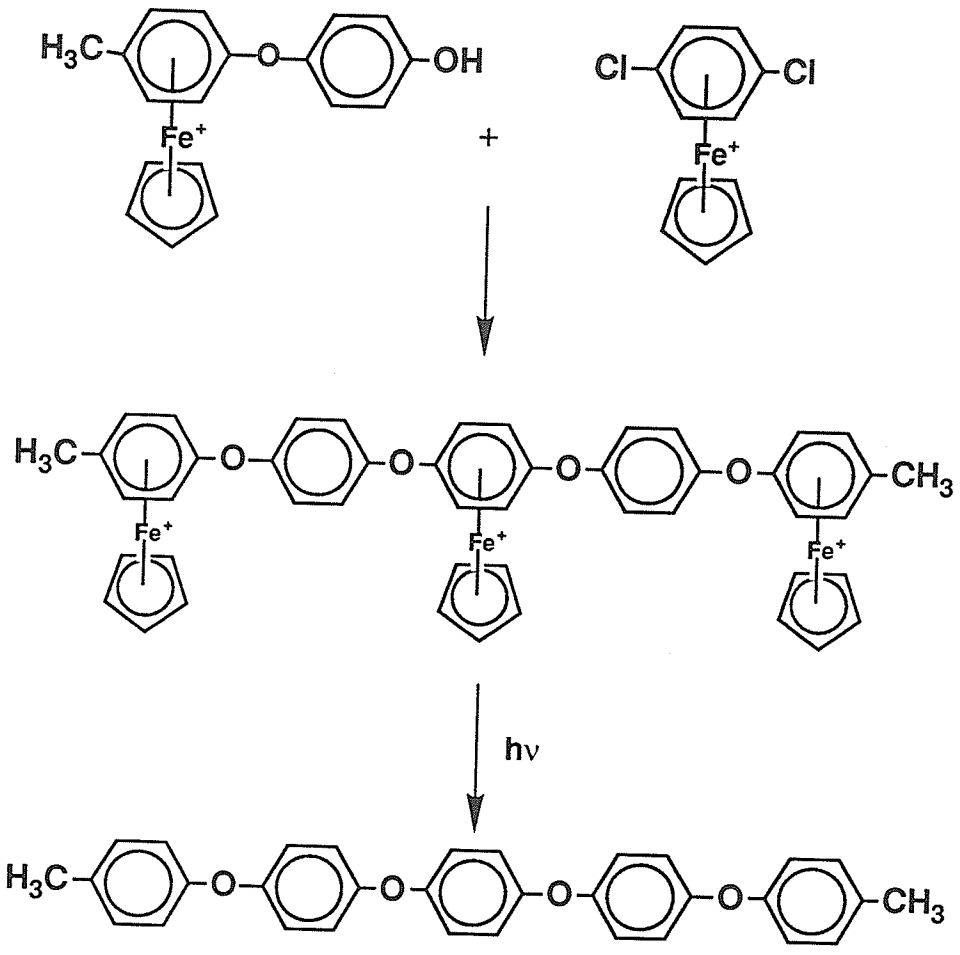
Due to the presence of the hydroxyl group, these mono-iron cationic complexes themselves could be used as nucleophiles with additional [η^6-chloroarene-η^5-cyclopentadienyl]iron complexes. This was investigated in two separate types of reactions, the first leading to the di-iron complexes **2.34a** and **2.35a** (scheme 7), the second to the tri-iron complex **2.36a** (scheme 8). Such reactions were carried out in the normal fashion, using DMF as the solvent, and K_2CO_3 as the base (see experimental). No variations to the standard conditions were required. The photolytic procedure was applied as usual, liberating the aromatic ethers **2.34b**–**2.36b** of scheme 7 and 8. NMR data for the complexes can be found in table 28 (^{1}H) and table 29 (^{13}C-APT), while the yields and elemental analysis data may be found in table 30. Data for the corresponding compounds are contained in table table 31 (^{1}H NMR, mass spectrometry), table 32 (^{13}C-APT NMR, melting point) and table 27 (yields, elemental analysis).

These few examples are sufficient to demonstrate the ability of this synthetic methodology to generate a wide variety of unsymmetrical aromatic ethers. They



R = H (2.34a, 2.34b)
R = CH_3 (2.35a, 2.35b)

Scheme 7



(2.36a, 2.36b)

Scheme 8

also demonstrate the possibility of preparing higher molecular weight poly(aromatic ethers), beyond that obtained from the tri-iron complex.

Table 31: ^{1}H NMR and MS data for compounds **2.34b–2.36b**

δ (referenced to chloroform-*d*)			
Compound	*Aromatics*	*Others*	M^+,*m/z (rel.ab.)*
2.34b	6.99(s,4H), 6.90-7.13(m,5H), 7.25-7.37(m,4H)	—	296 (100) 298 (33)
2.35b	6.99(s,4H), 6.91-7.01(m,4H), 7.14-7.18(m,2H), 7.26-7.34(m,2H)	2.35(s,3H)(CH_3)	310 (100) 312 (35)
2.36b	6.95(s,8H), 6.96(s,4H), 6.86-6.91(m,4H), 7.09-7.14(m,4H)	2.31(s,6H)(CH_3)	474 (1.6)

Table 32: ^{13}C NMR and melting point data for compounds **2.34b–2.36b**

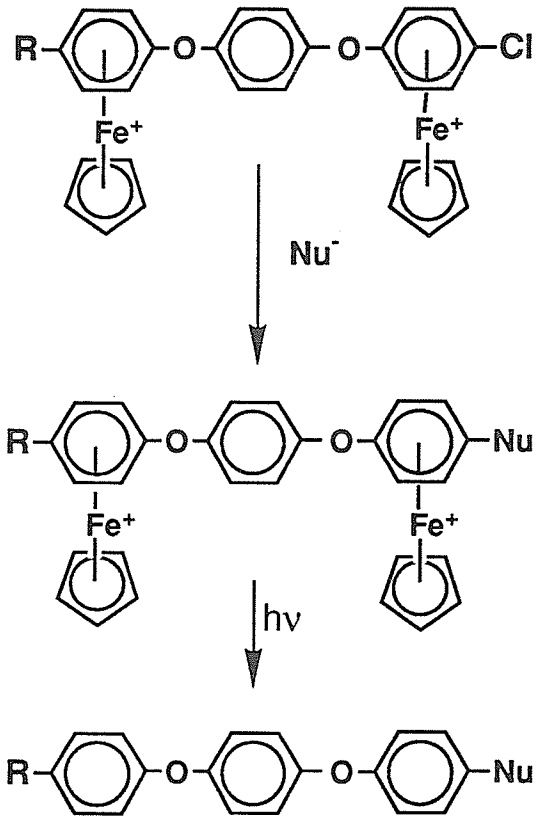
δ (referenced to chloroform-*d*)			
Compound	*Aromatics*	*Others*	*M.P.(°C)*
2.34b	118.41, 119.42, 120.43, 120.51, 123.15, 127.95*, 129.69, 129.76, 152.22*, 153.09*, 156.47*, 157.59*	—	63-64 (white)
2.35b	118.66, 119.29, 119.84, 120.52, 127.83*, 129.65, 130.26, 132.84*, 151.81*, 153.74*, 155.06*, 156.58*	20.68(CH_3)	122 (white)
2.36b	118.47, 119.80, 119.92, 130.21, 132.65*, 152.94*, 153.11*, 155.30*	20.67(CH_3)	170-171 (white)

* denotes quaternary carbon atoms

4.2 Substitution Reactions between Di-iron Complexes and Carbanions

The introduction of soft carbon nucleophiles into the aromatic ring of [η^6-chloroarene-η^5-cyclopentadienyl]iron cations is a relatively recent development in aromatic organoiron chemistry. Initial work has focussed on substitution reactions between these complexes and the anions of 1,3-dicarbonyl compounds such as dialkyl malonates and ethyl acetoacetate, among others [44, 48, 51, 54]. Recognition of the ease with which phenyl substituents could be introduced into the carbon skeletons of molecules sparked further research by a number of groups [49, 52, 56, 65, 78]. These researchers have shown that this technique of arylation is very promising in the synthesis of precursors to a host of biologically important compounds, such as 5-ethyl-5-phenylbarbituric acid (a drug targeting the central nervous system), Ibuprofen (a common analgesic), the vancomycin group of antibiotics and SK+F L-94901 (a selective thyromimetic). The present work continues the development of this methodology, by incorporating carbon nucleophiles into the chlorinated di-iron complexes discussed above. Scheme 9 demonstrates that the mono-chloro complexes **2.34a** and **2.35a** could undergo S_NAr reactions with either phenylsulfonylacetonitrile or ethyl cyanoacetate, in a DMF solution with an excess of K_2CO_3. This resulted in the synthesis of 1-([η^6-aryloxy-η^5-cyclopentadienyl]iron)-4-(ethyl{[η^6-(4-phenoxy)-η^5-cyclopentadienyl]iron}cyanoacetate)benzene dihexafluorophosphate complexes **2.37a** and **2.38a**, and the 1-([η^6-aryloxy-η^5-cyclopentadienyl]iron)-4-({[η^6-(4-phenoxy)-η^5-cyclopentadienyl]iron}phenylsulphonylacetonitrile)benzene dihexafluorophosphate complexes **2.39a** and **2.40a**. These products were achieved in a very high yield

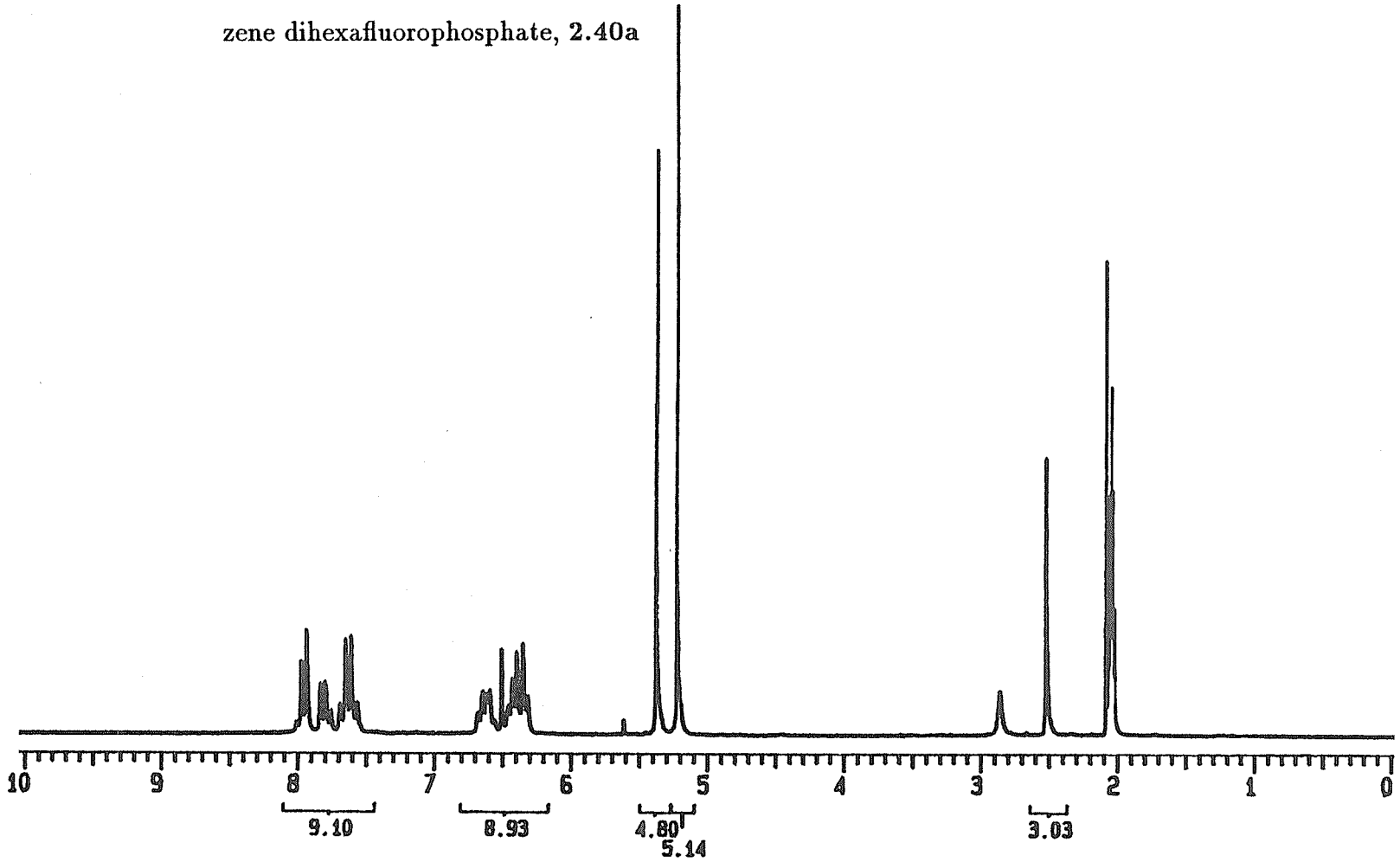
(78-97%). The conditions for their synthesis were similar to those reported by Abd-El-Aziz for the preparation of [η^6-(ethyl tolylcyanoacetate)-η^5-cyclopentadienyl]iron cations [52], although no heating was required and a shorter time could be used (five hours). Analytical information for these complexes can be found in table 33 (^{1}H NMR), table 34 (^{13}C-APT NMR) and table 35 (elemental analysis, infra-red spectroscopy and yields). The presence of the additional CN, CO_2 and SO_2 functional groups did not prohibit the use of photolysis as a means of liberating the functionalized triaryl diethers. Yields for the resulting 1-(aryloxy)-4-(ethyl [4-phenoxy]-cyanoacetate)benzene compounds **2.37b** and **2.38b**, as well as the 1-(aryloxy)-4-([4-phenoxy]phenylsulfonylacetonitrile)benzene compounds **2.39b** and **2.40b** were good, ranging between 67-88%. These compounds were thoroughly characterized by ^{1}H NMR and mass spectrometry (table 36), ^{13}C-APT NMR and melting point (table 37) as well as elemental analysis and infra-red spectroscopy (table 38, with yields). The NMR for complex **2.40a** and the corresponding compound **2.40b** are displayed in figures 53 and 54, and figures 55 and 56, respectively. The ^{1}H NMR spectrum of the complex reveals two cyclopentadienyl peaks, as expected due to the asymmetry of the molecule. The region containing the resonances of the two complexed aromatics overlaps the resonance of the methine group, although for this complex it could be distinguished at 6.50 ppm. The methyl group of the complexed aromatic appears upfield at 2.52 ppm, unchanged from its position in complex **2.35a**. The aromatic region contains the resonances of both uncomplexed rings. Four resonances for the other complexed aromatic appear in the ^{13}C-APT NMR spectrum of **2.40a**, as the inset in figure 53 shows, where two might be expected. A possible explanation concerns the orientation of the phenylsulfonylacetonitrile substituent.



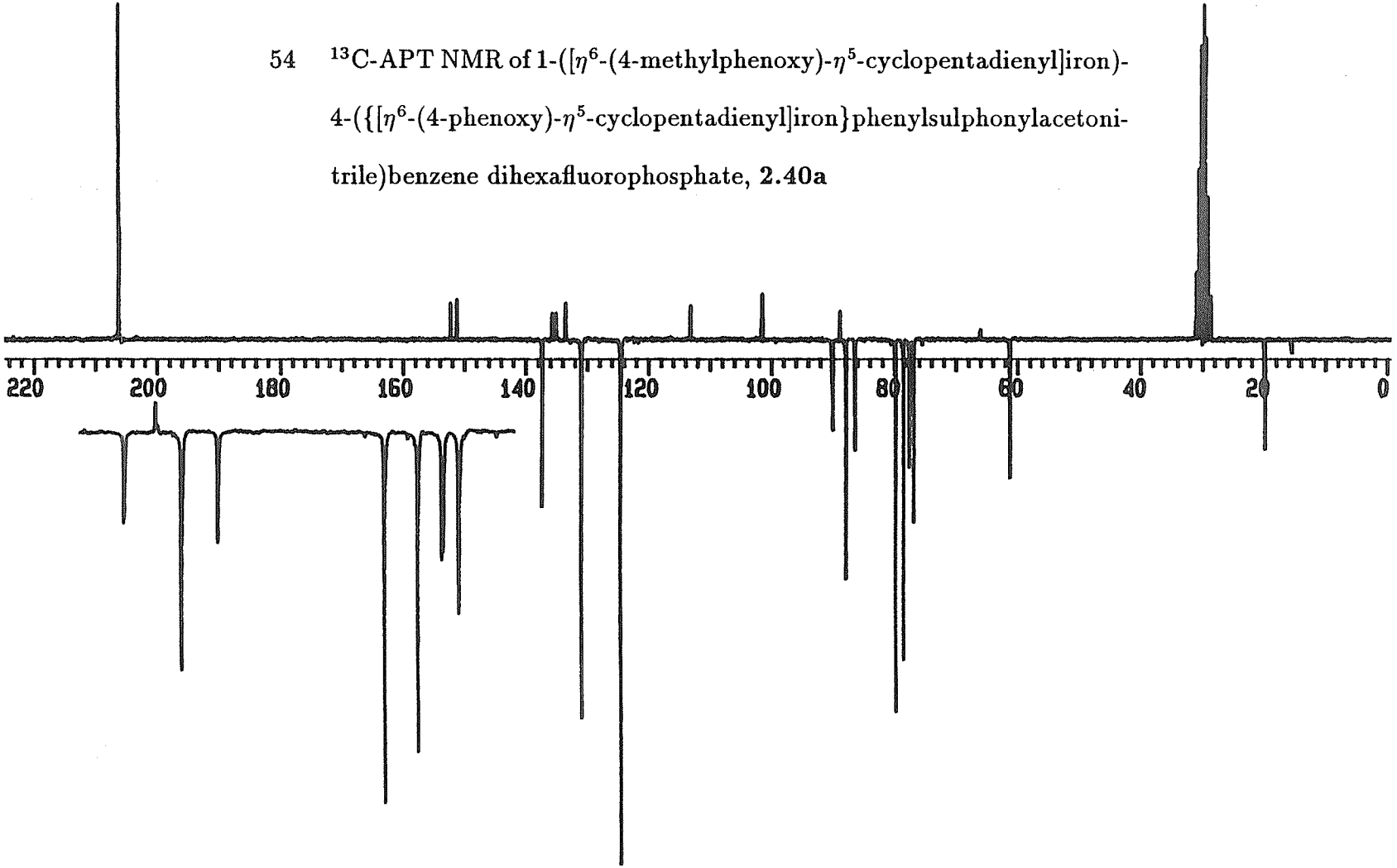
Scheme 9

R	Nu	complex	compound
H	$CH(CN)CO_2C_2H_5$	**2.37a**	**2.37b**
CH_3	$CH(CN)CO_2C_2H_5$	**2.38a**	**2.38b**
H	$CH(CN)SO_2Ph$	**2.39a**	**2.39b**
CH_3	$CH(CN)SO_2Ph$	**2.40a**	**2.40b**

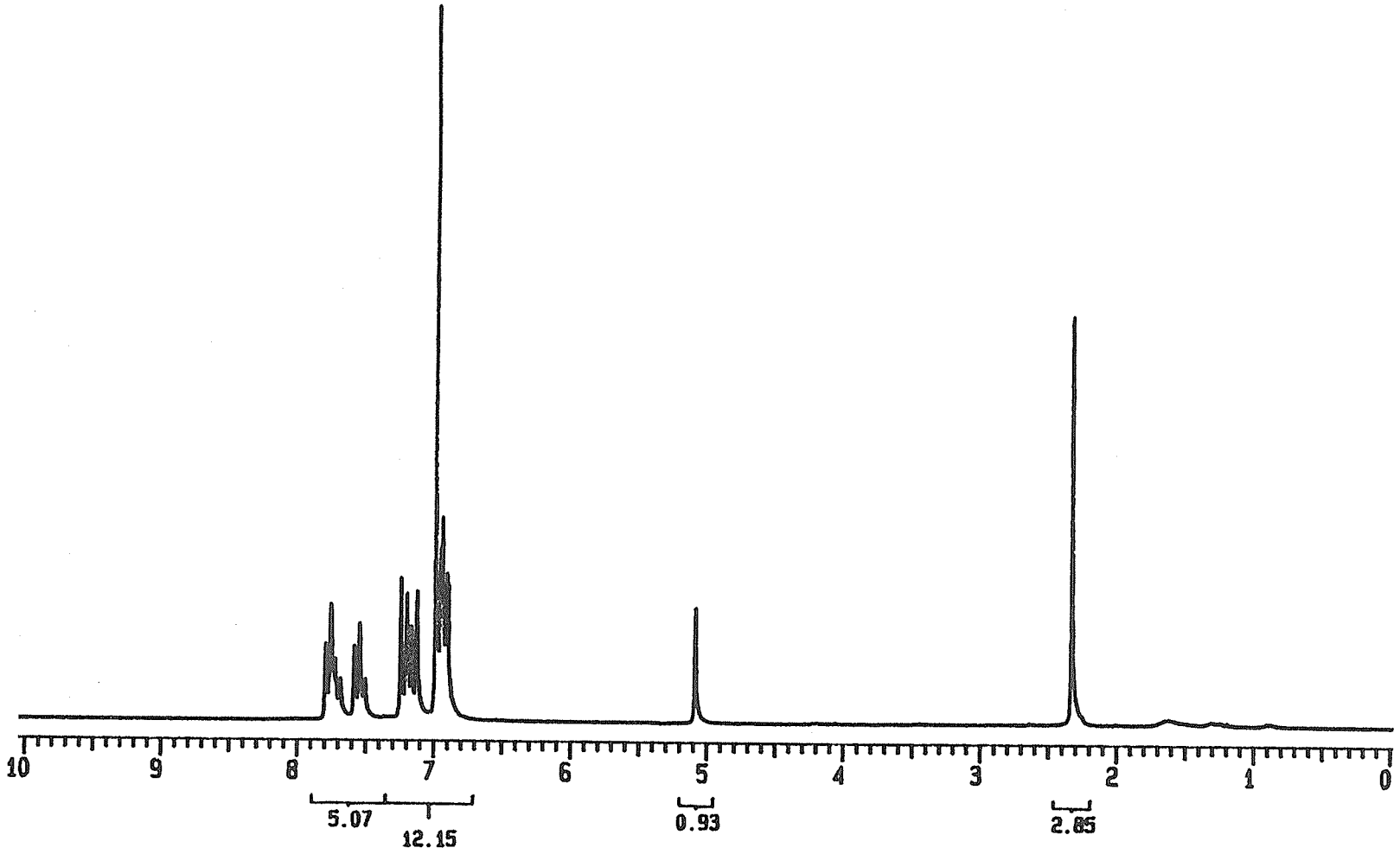
53 ^{1}H NMR of 1-([η^6-(4-methylphenoxy)-η^5-cyclopentadienyl]iron)-4-({[η^6-(4-phenoxy)-η^5-cyclopentadienyl]iron}phenylsulphonylacetonitrile)benzene dihexafluorophosphate, **2.40a**



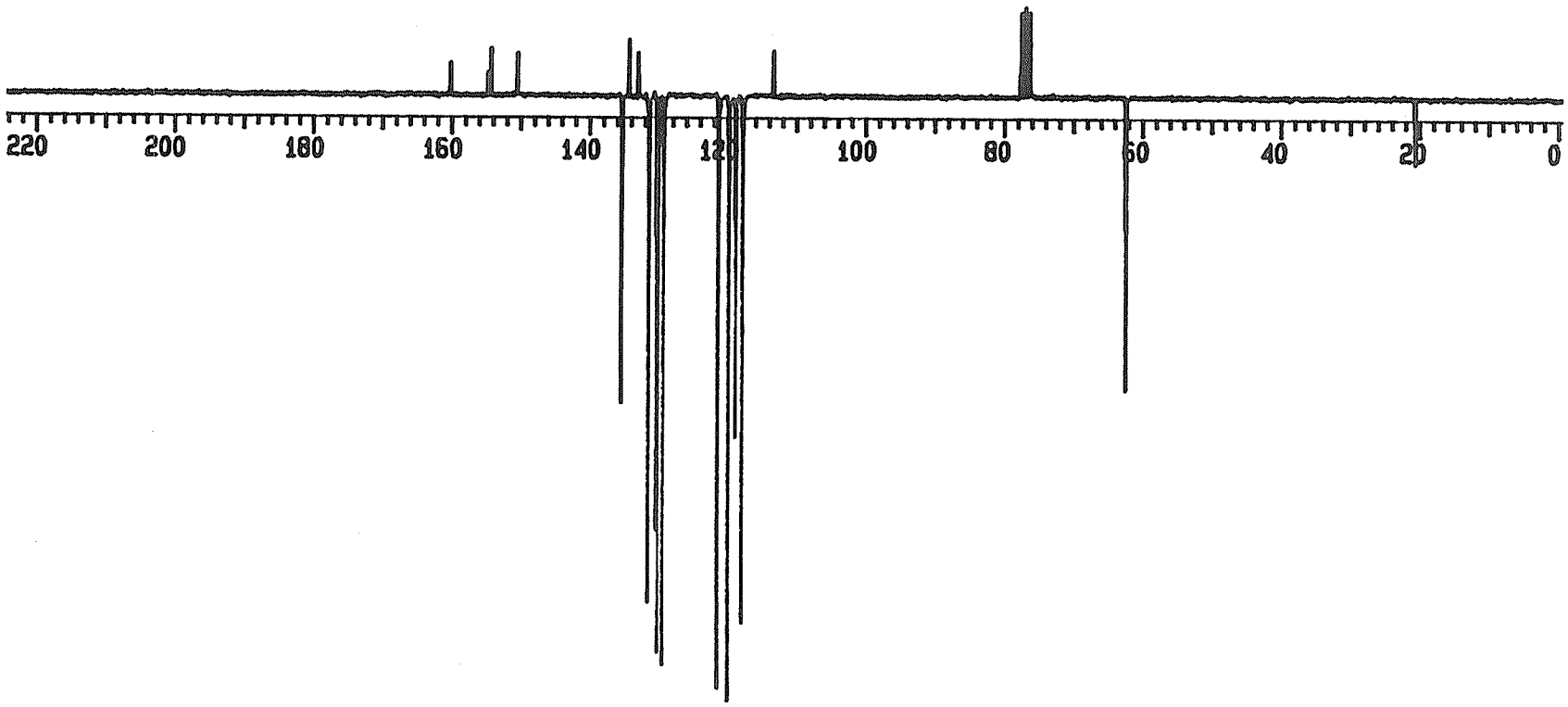
54 ^{13}C-APT NMR of 1-([η^6-(4-methylphenoxy)-η^5-cyclopentadienyl]iron)-4-({[η^6-(4-phenoxy)-η^5-cyclopentadienyl]iron}phenylsulphonylacetonitrile)benzene dihexafluorophosphate, **2.40a**



55 ^{1}H NMR of 1-(4-methylphenoxy)-4-([4-phenoxy]phenylsulfonylaceto-nitrile)benz ene, **2.40b**



56 ^{13}C-APT NMR of 1-(4-methylphenoxy)-4-([4-phenoxy]phenylsulfonylacetonitrile)benz ene, **2.40b**



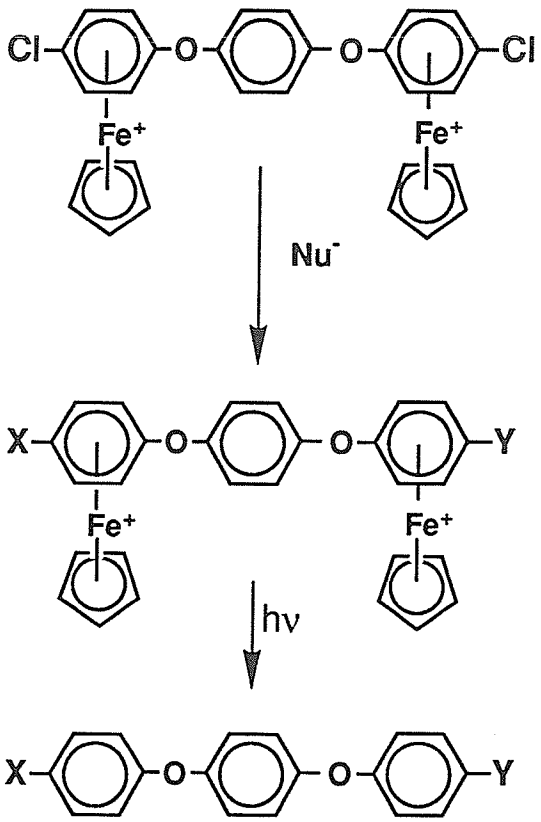
Two specific conformations could exist, where each conformation gives rise to a distinct set of resonances. It might also be possible that the asymmetry of the substituent allows for the distinction between the CH's of the complexed arenes. The assignment of the remaining resonances can be found in table 34. The proposed identity of this complex receives further support from the infra-red spectrum, in which absorptions due to the CN and SO_2 groups can be distinguished.

The NMR spectra for the compound are in full agreement with its assigned structure. The ^1H spectrum shows the expected downfield shifts in the liberated aromatic resonances, but also shows that the CH resonance has shifted significantly upfield. Interestingly, only two resonances exist for the arene attached to the phenylsulfonylacetonitrile group in the ^{13}C-APT spectrum of this compound. While this substituent is still asymmetric, the same resonance pattern as observed in complex **2.40a** is not observed here. It would seem that the $CpFe^+$ moiety is instrumental in causing the observed behavior in the ^{13}C-APT spectrum of the complex, and is not a phenomenon attributable to the phenylsulfonylacetonitrile group alone. Studies are in progress to determine the possibility of interactions between the $CpFe^+$ moiety and this substituent.

Careful scrutiny of the routine ^{13}C-APT NMR spectrum of the compound reveals that the resonance for one aromatic quaternary (C-CH) appears missing. This resonance was obscured by an aromatic CH resonance, but could be obtained by a variation of the APT pulse sequence. This is a double spin echo technique, in which the delay time between pulses can be adjusted to change the amplitude of the signals [85]. A delay of 7.00×10^{-3} seconds allows one to distinguish between those carbons with an odd or even number of directly attached protons. All the ^{13}C-

APT NMR spectra recorded above have employed this delay time. A delay time of 3.15 x 10^{-3} seconds was necessary to observe the missing resonance. This resulted in a spectrum in which all the aromatic CH resonances were suppressed, revealing the resonance for the C-CH quaternary at 118.81 ppm. The mass spectrum of this compound indicates a molecular ion peak at an m/z of 455, which agrees with its molecular weight. The base peak occurs at an m/z of 314, which corresponds to the loss of the SO_2Ph unit.

The synthetic procedure has also been extended by double substitution to allow for difunctionalization of di([η^6-(4-chlorophenoxy)-η^5-cyclopentadienyl]iron)benzene dications, leading to both symmetrical and unsymmetrical complexes and compounds (scheme 10). In this study, complex **2.4a** was reacted with ethyl cyanoacetate in a 1:2 ratio, resulting in the synthesis of 1,4-di(ethyl {[η^6-(4-phenoxy)-η^5-cyclopentadienyl]iron}cyanoacetate)benzene dihexafluorophosphate, complex **2.41a**. In a similar fashion, **2.4** could be reacted with phenylsulfonylacetonitrile in a 1:2 ratio, producing the 1,4-di({[η^6-(4-phenoxy)-η^5-cyclopentadienyl]iron}phenylsulfonylacetonitrile)benzene dihexafluorophosphate complex (**2.42**). However if the latter reaction was carried out for any longer than three hours, excessive decomposition occurred, resulting in a very low yield. A yield of 50% was the maximum that could be achieved from a room-temperature DMF reaction mixture. It has also been found that, provided soft nucleophiles are used, di-iron complexes such as **2.4a** can be mono-substituted. Ethyl cyanoacetate was reacted with **2.4a** under standard conditions in a 1:1 ratio, allowing for the synthesis and isolation of the 1-([η^6-(4-chlorophenoxy)-η^5-cyclopentadienyl]iron)-4-(ethyl{[η^6-(4-phenoxy)-η^5-cyclopentadienyl]iron}cyanoacetate)benzene dihexafluorophosphate



Scheme 10

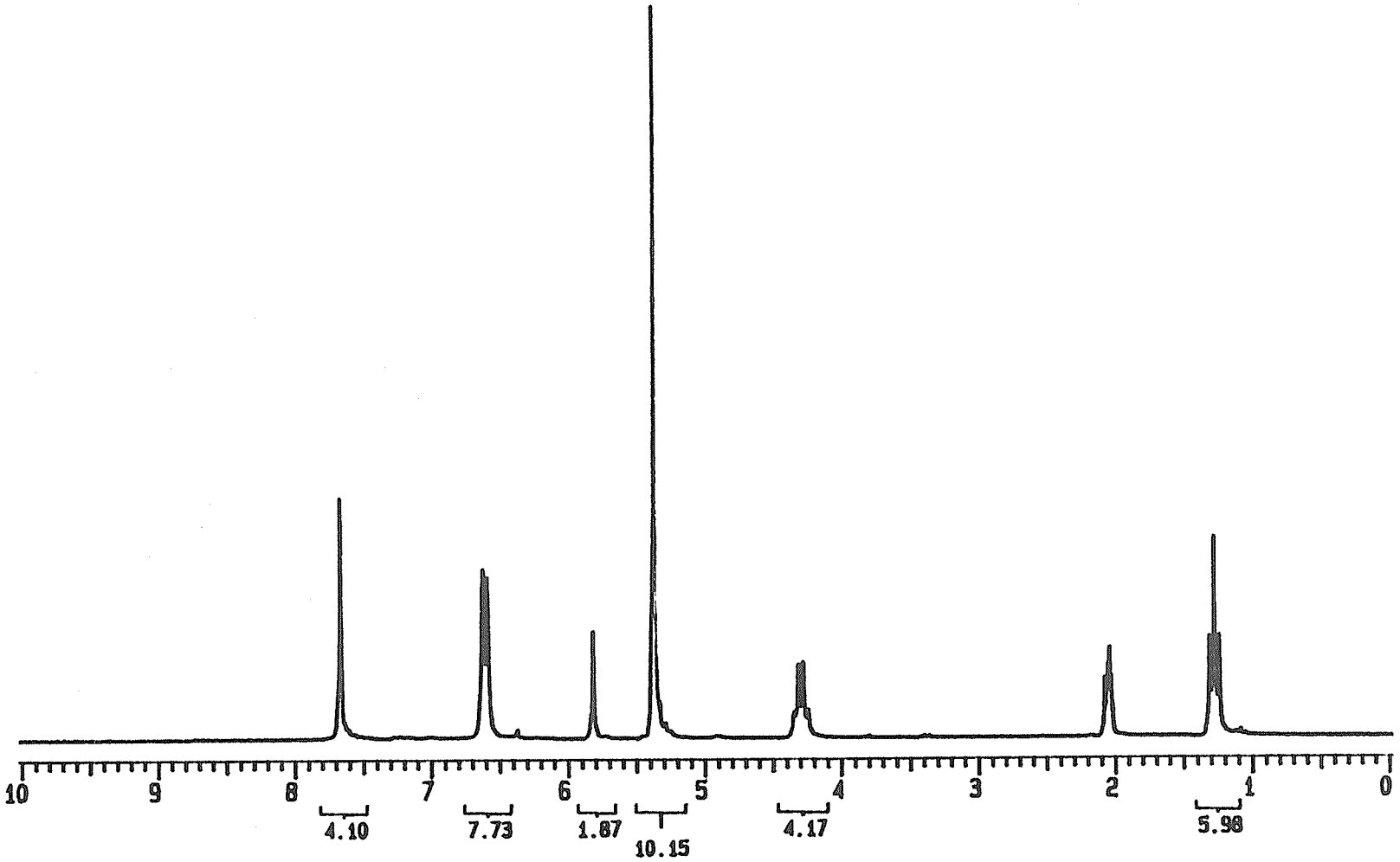
X	Y	complex	compound
$CH(CN)CO_2C_2H_5$	$CH(CN)CO_2C_2H_5$	**2.41a**	**2.41b**
$CH(CN)SO_2Ph$	$CH(CN)SO_2Ph$	**2.42**	—
$CH(CN)CO_2C_2H_5$	Cl	**2.43a**	**2.43b**
$CH(CN)CO_2C_2H_5$	$CH(CN)SO_2Ph$	**2.44**	—

complex (**2.43a**). Related studies on the reactivity of complexes such as **2.4a** carried out by our research group have suggested that harder nucleophiles such as phenylsulfonylacetonitrile and hydroxyaromatics cannot undergo such a reaction cleanly under these conditions. A co-product resulting from double substitution usually appears in substantial amounts. This is not surprising, as one would expect little difference in reactivity between the chloro group of the mono-substituted di-iron complex and the chloro groups of the unsubstituted complex **2.4a**. The relative isolation of the two reactive sites in these complexes would seem to indicate this. Ethyl cyanoacetate appears to be a poor enough nucleophile such that only the chloro groups of the unsubstituted di-iron complex are replaced. However, carrying out this reaction at elevated temperatures (50 °C) results in a reaction mixture containing mono- and di-substitution products, as well as unreacted di-iron complex.

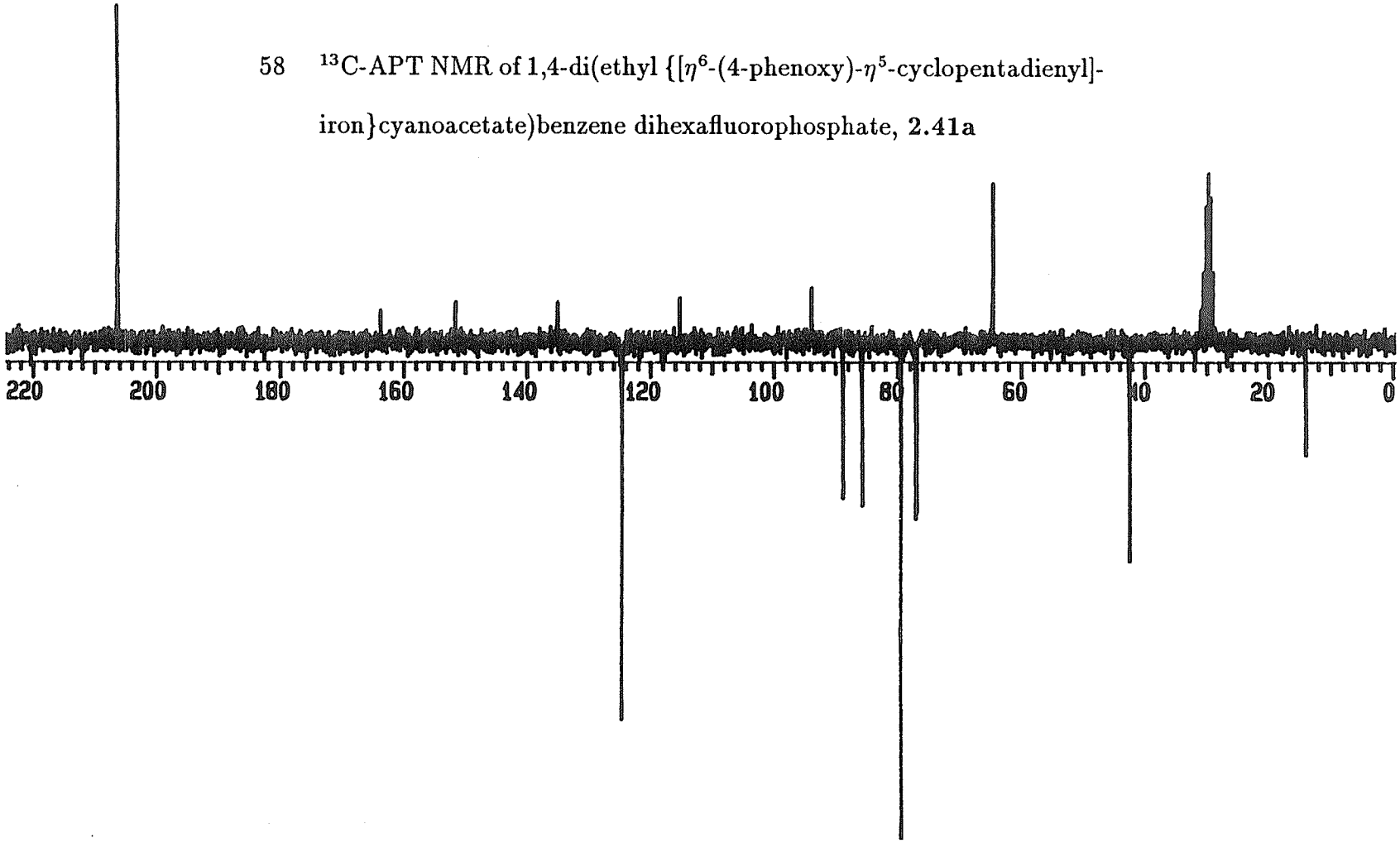
All complexes **2.41a–2.44** were well characterized by the standard techniques. ^{1}H NMR data have been tabulated in table 39, and the ^{13}C-APT NMR in table 40. Elemental analysis and infra-red spectroscopy data (as well as yields) can be found in table 35. Figure 57 and 58 present the NMR spectra collected for complex **2.41a**.

The ^{1}H NMR spectrum of this complex reveals a high degree of symmetry, as expected. One resonance exists for the cyclopentadienyl rings, at 5.36 ppm. The resonances arising from the AA′BB′ spin system of the complexed aromatics are very simple, appearing as a doublet (6.59-6.62 ppm), whereas all the equivalent protons of the uncomplexed aromatic give rise to a singlet at 7.66 ppm. The methine proton resonance can be clearly seen at 5.82 ppm. The resonances arising from the methyl group can be found at 1.27 ppm (triplet), while the methylene resonance appears at 4.29 ppm (quartet). The coupling constant between the protons of these groups is

57 ^{1}H NMR of 1,4-di(ethyl {[η^6-(4-phenoxy)-η^5-cyclopentadienyl]iron}-cyanoacetate)benzene dihexafluorophosphate, **2.41a**



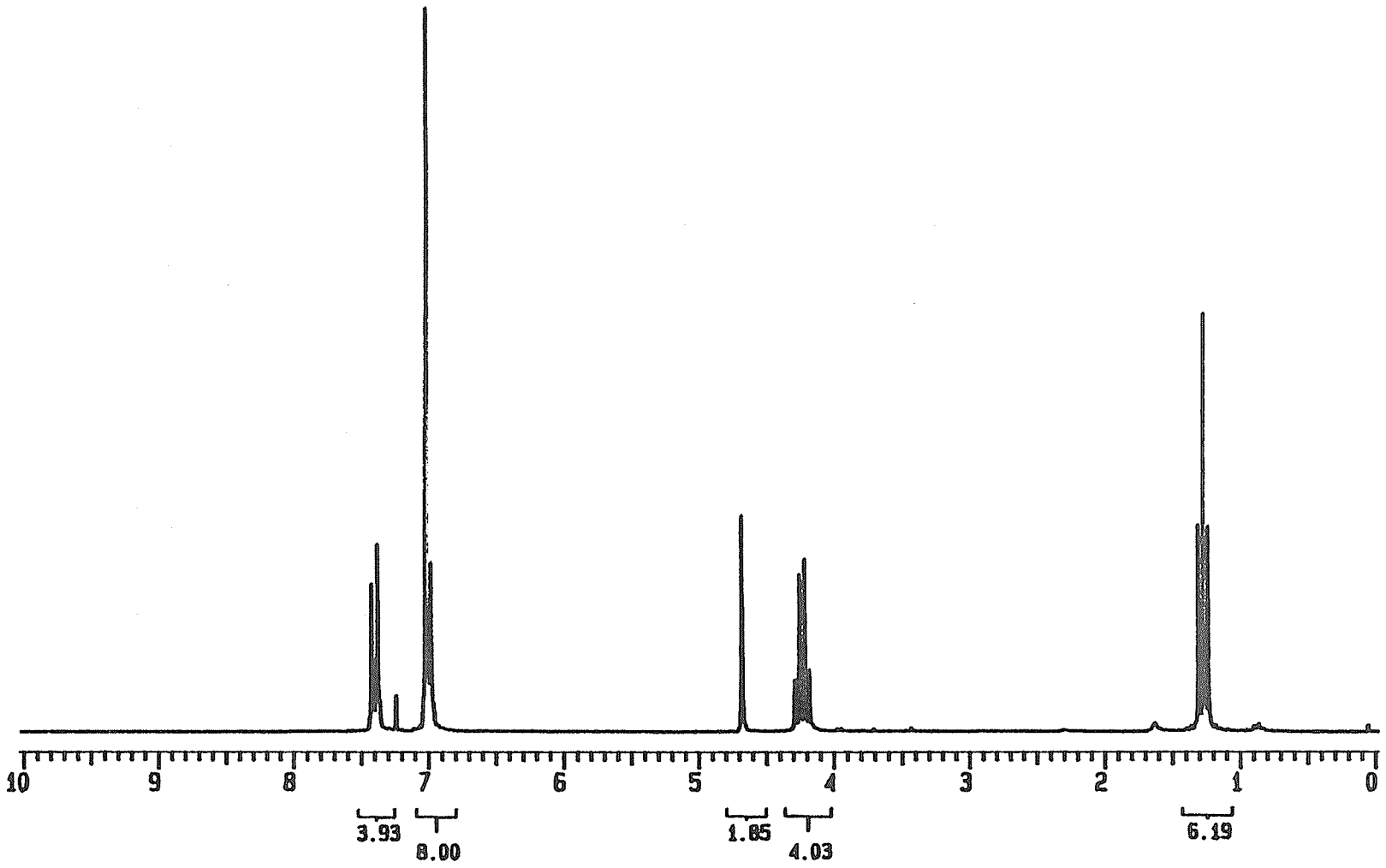
58 ^{13}C-APT NMR of 1,4-di(ethyl {[η^6-(4-phenoxy)-η^5-cyclopentadienyl]-iron}cyanoacetate)benzene dihexafluorophosphate, **2.41a**



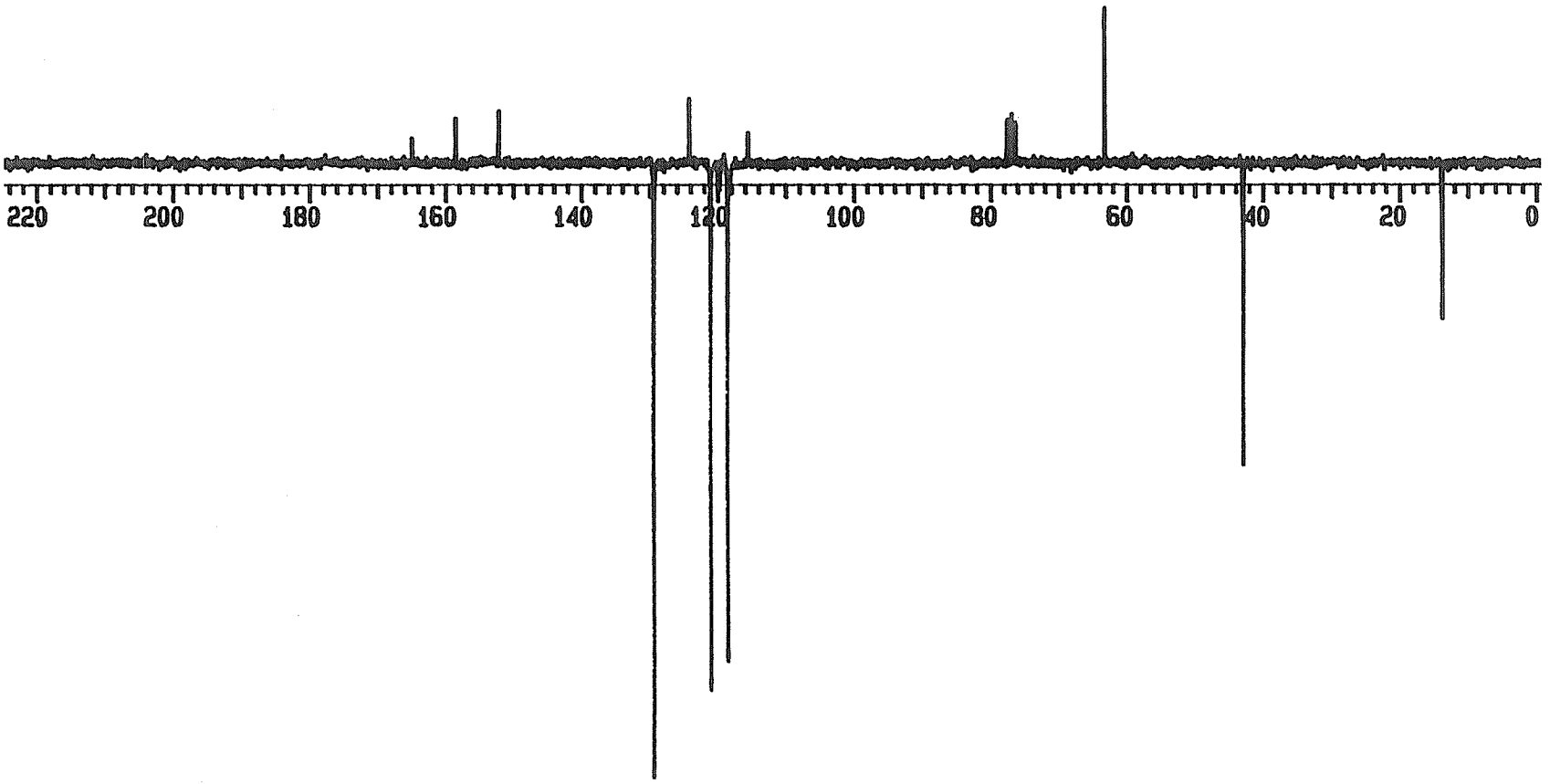
7.0 Hz, as is typical. In the ^{13}C-APT spectrum, four distinguishable resonances for the carbons of the complexed aromatics exist, where one might expect only two from symmetry considerations only. The previous arguments for the rationalization of the ^{13}C-APT spectrum of **2.40a** would seem to hold here as well. The two resonances at 85.72 and 88.80 ppm arise from the two carbons β to the chiral carbon. The effect of the substituent is minimized with distance, as the two γ carbon atom resonances are nearly isochronous (76.98 and 77.10 ppm). A single resonance exists for the carbons of the remote uncomplexed aromatic. The remaining resonances, including those of the ethyl cyanoacetate fragment are recorded in table 40. The infra-red spectrum reveals absorptions indicative of the carbonyl group (1750 cm^{-1}) and cyano group (2165 cm^{-1}).

Interestingly, when complexes **2.41a–2.44** were photolyzed and the liberated arenes isolated by column chromatography, only **2.41a** and **2.43a** yielded products corresponding to the expected functionalized ethers 1,4-di(ethyl 4-[phenoxy]-cyanoacetate)benzene (**2.41b**) and 1-(4-chlorophenoxy)-4-(ethyl [4-phenoxy]cyano-acetate)benzene (**2.43b**). Analytical data for these compounds have been summarized in table 36 (^{1}H NMR, mass spectrometry), table 41 (^{13}C-APT NMR) and table 38 (elemental analysis, infra-red spectroscopy, yields). The compounds 1,4-di([4-phenoxy]phenylsulfonylacetonitrile)benzene and 1-(ethyl [4-phenoxy]cyanoacetate)-4-([4-phenoxy]phenylsulfonylacetonitrile)benzene have not been isolated at this point. The NMR spectra for compound **2.41b** are recorded in figure 59 and 60. The most notable difference between the ^{1}H NMR spectrum of this compound and its corresponding complex, aside from the downfield shift of the resonances for the liberated aromatics is the large upfield shift for the methine resonance (by 1.15 ppm). The

59 ^{1}H NMR of 1,4-di(ethyl 4-[phenoxy]cyanoacetate)benzene, **2.41b**



60 ^{13}C-APT NMR of 1,4-di(ethyl 4-[phenoxy]cyanoacetate)benzene, **2.41b**



resonances for the methyl and methylene groups are essentially unaffected by demetallation. Curiously, the position of the carbon signal for the methine group in the ^{13}C-APT NMR spectrum for this compound remains unchanged at 42.92 ppm. Also noteworthy is the simplification of the resonances for the liberated aromatics. Only two signals exist, at 118.52 and 121.05 ppm. The remaining signals are recorded in table 41.

Table 33: ^{1}H NMR data for complexes **2.37a–2.40a**

δ (referenced to acetone-d_6)			
Complex	*Complexed aromatics*	*Cp's*	*Others*
2.37a	6.27-6.50(m,5H), 6.59-6.63(m,4H)	5.26(s,5H), 5.38(s,5H)	1.28(t,3H,J 7.0)(CH_3); 4.30(q,2H,J 7.0)(CH_2); 5.83(s,1H)(CH); 7.55-7.70(m,4H)(Ar)
2.38a	6.30-6.45(m,4H), 6.55-6.70(m,4H)	5.21(s,5H), 5.37(s,5H)	1.28(t,3H,J 7.0)(CH_3); 2.51(s,3H)(CH_3); 4.30(q,2H,J 7.0)(CH_2); 5.82(s,1H)(CH); 7.53-7.66(m,4H)(Ar)
2.39a	6.25-6.70(m,10H)	5.25(s,5H), 5.36(s,5H)	(CH)#; 7.58-7.70(m,4H)(Ar); 7.72-8.10(m,5H,SO_2Ph)
2.40a	6.30-6.70(m,9H)	5.21(s,5H), 5.36(s,5H)	2.52(s,3H)(CH_3); (CH)# 7.58-7.72(m,4H)(Ar); 7.73-8.05(m,5H,SO_2Ph)

The indicated resonance is obscured by the resonances due to the complexed aromatics.

Table 34: ^{13}C NMR data for complexes **2.37a–2.40a**

δ (referenced to acetone-d_6)			
Complex	*Complexed aromatics*	*Cp's*	*Others*
2.37a	77.07, 77.19, 77.59, 85.81, 87.79, 88.87, 93.95*, 135.14*, 134.62*	78.10, 79.56	14.06(CH_3); 42.50(CH); 64.72(CH_2); 115.37*(CN); 124.57, 124.53, 151.50*, 151.98*(Ar) 163.88(CO)
2.38a	76.85, 77.02, 77.17, 85.72, 87.74, 88.83, 93.90*, 101.48*, 133.51*, 135.11*	78.48, 79.52	14.03(CH_3); 19.84(CH_3); 42.47(CH); 64.68(CH_2); 115.33(CN); 124.36, 124.42, 151.36*, 152.15*(Ar); 163.85(CO)
2.39a	77.46, 77.56, 85.78, 86.30, 87.74, 88.81*, 89.00, 134.56*, 135.00*	78.06, 79.82	61.17(CH); 113.11(CN); 124.61, 124.68, 151.34*, 152.03*(Ar); 130.81, 130.90, 135.71*, 137.28(SO_2Ph)
2.40a	76.93, 77.53, 77.59, 86.38, 87.80, 88.84*, 90.06, 101.54*, 135.09*, 135.76*	78.53, 79.84	19.88(CH_3); 61.19(CH); 113.16(CN); 124.45, 151.30*, 152.29*(Ar); 130.85, 130.92, 137.29, 135.76*(SO_2Ph)

* denotes quaternary carbon atoms

Table 35: Yields, IR and elemental composition data for complexes **2.37a–2.44**

			elemental composition found(calculated), %		
Complex	*% yield*	*IR(cm^{-1})*	*C*	*H*	*N*
2.37a	93	1750(CO) 2260(CN)	43.61(43.79)	3.23(3.23)	1.49(1.55)
2.38a	78	1753(CO) 2260(CN)	44.64(44.43)	3.47(3.40)	1.50(1.52)
2.39a	97	1160, 1345(SO_2) 2160(CN)	44.53(44.43)	2.85(3.00)	1.53(1.44)
2.40a	91	1165, 1350(SO_2)	45.16(45.01)	3.10(3.17)	1.49(1.42)
2.41a	93	1750(CO) 2165(CN)	44.84(44.91)	3.34(3.37)	2.40(2.43)
2.42	50	1160, 1340(SO_2) 2310(CN)	45.71(45.86)	2.92(2.97)	2.40(2.43)
2.43a	91	1160, 1340(SO_2) 1758(CO) 2180(CN)	42.26(42.18)	3.09(3.00)	1.56(1.49)
2.44	92	1165, 1340(SO_2) 1755(CO) 2170(CN)	45.23(45.41)	3.11(3.16)	2.60(2.58)

Table 36: ^{1}H NMR and MS data for compounds **2.37b–2.41b, 2.43b**

δ (referenced to chloroform-*d*)			
Compound	*Aromatics*	*Others*	M^+,*m/z (rel.ab.)*
2.37b	7.00(s,4H), 6.97-7.12(m,5H), 7.29-7.41(m,4H)	1.28(t,3H,*J* 7.0)(CH_3); 4.24(q,2H,*J* 7.0)(CH_2); 6.97(s,1H)(CH)	373 (24.2)
2.38b	6.88-7.40(m,12H)	1.28(t,3H,*J* 7.0)(CH_3); 2.32(s,3H)(CH_3); 4.24(q,2H,*J* 7.0)(CH_2); 4.66(s,1H)(CH)	387 (6.6)
2.39b	6.94-7.80(m,18H)	5.08(s,1H)(CH)	441 (4.0)
2.40b	6.89-6.95(m,4H), 6.98(s,4H), 7.12-7.24(m,4H); 7.54-7.79(m,5H)(SO_2Ph)	2.33(s,3H)(CH_3); 5.08(s,1H)(CH)	455 (5.5)
2.41b	7.02(s,4H), 6.98-7.00(m,4H), 7.38-7.42(m,4H)	1.27(t,3H,*J* 7.0)(CH_3); 4.23(q,2H,*J* 7.0)(CH_2); 4.68(s,2H)(CH)	484 (9.4)
2.43b	6.90-7.41(m,12H)	1.28(t,3H,*J* 7.0)(CH_3); 4.24(q,2H, *J* 7.0)(CH_2); 4.67(s,1H)(CH)	407 (100) 409 (35)

Table 37: ^{13}C NMR and melting point data for compounds **2.37b–2.40b**

δ (referenced to chloroform-*d*)			
Compound	*Aromatics*	*Others*	*M.P.(°C)*
2.37b	118.31, 118.44, 120.35, 121.05, 123.17, 123.96*, 129.36, 129.73, 151.44*, 153.39*, 157.40*, 158.82*	13.86(CH_3); 42.92(CH); 63.26(CH_2); 115.65(CN); 164.98(CO)	oil (yellowish)
2.38b	118.24, 118.72, 119.78, 121.07, 123.87*, 129.35, 130.25, 132.90*, 151.08*, 154.08*, 154.91*, 158.96*	13.88(CH_3); 20.66(CH_3); 42.96(CH); 63.29(CH_2); 115.67(CN); 165.02(CO)	oil (yellowish)
2.39b	117.84, 118.57, 118.87*, 120.36, 121.31, 123.32, 129.24, 129.79, 130.06, 131.36, 134.42*, 135.27, 150.95*, 153.76*, 157.22*, 160.14*	62.37(CH); 113.41(CN)	170-171 (off-white)
2.40b	117.75, 118.81*,#, 118.82, 119.76, 121.27, 129.23, 130.05, 130.28, 131.33, 133.03*, 134.24*, 135.25, 150.57*, 154.39*, 154.79*, 160.22*	20.66(CH_3); 62.37(CH); 113.43(CN)	153-154 (off-white)

Obtained by a variation of APT pulse sequence. See section II.4.2
* denotes quaternary carbon atoms

Table 38: Yields, IR and elemental composition data for compounds **2.37b–2.41b, 2.43b**

			elemental composition found(calculated), %		
Compound	*% yield*	*IR(cm^{-1})*	*C*	*H*	*N*
2.37b	71	1750(CO) 2245(CN)	73.85(73.98)	5.10(5.13)	3.77(3.75)
2.38b	74	1750(CO) 2250(CN)	74.52(74.40)	5.44(5.46)	3.67(3.62)
2.39b	67	1155, 1335(SO_2)	70.67(70.73)	4.35(4.34)	3.21(3.17)
2.40b	88	1155, 1340(SO_2)	71.30(71.19)	4.61(4.65)	3.11(3.07)
2.41b	75	1750(CN) 2250(CO)	69.44(69.41)	5.02(4.99)	5.74(5.78)
2.43b	73	1750(CO) 2250(CN)	67.81(67.73)	4.47(4.45)	3.48(3.43)

Table 39: ^{1}H NMR data for complexes **2.41a–2.44**

δ (referenced to acetone-d_6)			
Complex	*Complexed aromatics*	*Cp's*	*Others*
2.41a	6.59-6.62(m,8H)	5.36(s,10H)	1.27(t,3H,*J* 7.0)(CH_3); 4.30(q,2H,*J* 7.0)(CH_2); 5.82(s,1H)(CH); 7.66(s,4H)(Ar)
2.42	6.40-6.80(m,10H)	5.37(s,10H)	(CH)#; 7.72(s,4H)(Ar); 7.58-7.07(m,10H,SO_2Ph)
2.43a	6.50-6.79(m,8H)	5.37(s,10H)	1.28(t,3H,*J* 7.0)(CH_3); 4.30(q,2H,*J* 7.0)(CH_2); 5.83(s,1H)(CH); 7.55-7.70(m,4H)(Ar)
2.44	6.39-6.69(m,9H)	5.37,5.38 (2s,10H)	1.28(t,3H,*J* 7.0)(CH_3); 4.30(q,2H,*J* 7.0)(CH_2); (CH)# 5.84(s,1H)(CH) 7.67-7.72(m,4H)(Ar); 7.75-8.05(m,5H,SO_2Ph)

The indicated resonance is obscured by the resonances due to the complexed aromatics.

Table 40: ^{13}C NMR data for complexes **2.41a–2.44**

δ (referenced to acetone-d_6)			
Complex	*Complexed aromatics*	*Cp's*	*Others*
2.41a	76.98, 77.10, 85.72, 88.80, 93.90*, 135.08*	79.49	14.00(CH_3); 42.44(CH); 64.65(CH_2); 115.35(CN); 124.60, 151.65*(Ar); 163.85(CO)
2.42	75.50, 77.52, 78.94, 86.30, 88.72*, 134.89*	79.78	61.11(CH); 113.04(CN); 124.66, 151.55(Ar); 130.75, 130.86, 137.24, 135.59*(SO_2Ph)
2.43a	76.93, 76.97, 85.67, 87.69, 88.78, 93.87*, 104.88*, 133.94*, 135.05*	79.48, 80.44	14.00(CH_3); 42.43(CH); 64.65(CH_2); 115.30(CN); 124.36, 124.39, 124.57, 151.63*, 151.79*(Ar), 163.82(CO)
2.44	77.06, 77.08, 77.50, 77.55, 85.77, 86.33, 88.82*,#, 88.85, 90.02, 93.95*, 135.01*, 135.07*	79.55, 79.84	61.17(CH); 113.11(CN) 14.04(CH_3); 42.47(CH); 64.69(CH_2); 115.31(CN); 124.47, 151.57*, 151.68*(Ar); 130.81, 130.90, 137.27, 135.68(SO_2Ph)

Obtained by a modification of the APT pulse sequence.
* denotes quaternary carbon atoms

Table 41: ^{13}C NMR and melting point data for compounds **2.41b**, **2.42b**

δ (referenced to chloroform-*d*)			
Compound	*Aromatics*	*Others*	*M.P.(°C)*
2.41b	118.52, 121.05, 124.21*, 129.42, 153.23*, 158.54*	13.85(CH_3); 42.92(CH); 63.29(CH_2); 115.63(CN); 164.95(CO)	oil (yellowish)
2.43b	118.46, 119.63, 120.09, 120.46, 124.15*, 129.44, 129.73, 151.88*, 152.26*, 152.97*, 156.14*, 158.68*	13.90(CH_3); 42.97(CH); 63.34(CH_2); 115.46(CN); 164.99(CO)	oil (yellowish)

* denotes quaternary carbon atoms

5 Comparison with Conventional Aromatic Ether Synthesis

The technique developed in the present work appears to be the mildest and most flexible synthetic route to aromatic ethers. In order to demonstrate the advantages of the technique over others currently used, it was necessary to prepare an extensive number of di-iron complexes and their corresponding ethers. With the exception of 1,2-di(2-chlorophenoxy)b923Xen, all the isomers of diphenoxybenzenes containing chloro or methyl groups can be synthesized. The system easily allows for the incorporation of other dihydroxyaromatics, as has been shown with the various biphenols and substituted dihydroxybenzenes. The reactions are not sterically hindered by incorporating bulky substituents on either the mono-iron complex or the dinucleophile. Even the yields are unaffected. This technique is by no means restricted to the preparation of diphenoxybenzenes either. It holds much promise for the synthesis of low and high molecular weight poly(aromatic ethers). Initial studies on the reactivity of the chlorinated di-iron complexes towards carbon nucleophiles reveals that the complexed ethers can be built into more complex molecular systems, thereby demonstrating the usefulness of this procedure in the preparation of precursors to larger systems. The ease with which the cyclopentadienyliron moiety can be removed, even in the presence of sensitive functional groups, is an additional attribute of the process. Comparisons between this iron-mediated approach and the methods outlined in the introduction will now be made.

5.1 Ullmann Condensation Reaction

The technique developed in the present work has been demonstrated to produce triaryl diether compounds from [η^6-chloroarene-η^5-cyclopentadienyl]iron cationic complexes in very high yields. While the Ullmann reaction is widely used in the synthesis of aromatic ethers, a primary limitation is lower yields, often even in the presence of additional activating groups such as NO_2. It is not uncommon to find yields for phenyl ethers and diphenoxybenzenes with simple substituents such as Cl, CH_3, OH and NO_2 in the 5-60% range. The present method represents a distinct advantage in this regard. It could be argued that relatively low efficiency of the ferrocene conversion into η^6-chloroarene-η^5-cyclopentadienyliron cationic complexes ($\approx$ 40%) reduces the appeal of the method outlined in this work. However, current synthetic methods for these complexes have never really been optimized for yields, and possibility for improvement exists. In addition, unreacted ferrocene and chloroarene in the initial ligand reaction could be reclaimed easily enough and incorporated into further reactions.

The double nucleophilic substitution process benefits from the use of chloroarene compounds, whereas the Ullmann synthesis usually requires the much more expensive, and less available, bromo- or iodoarenes. In addition, the nucleophiles can be incorporated without any modification. In the Ullmann method, it is often necessary to prepare the sodium or potassium salt of the hydroxyaromatic prior to reaction. This is especially true for reactions involving 1,3-dihydroxybenzenes, in which the direct employment of resorcinol yields essentially no 1,3-diphenoxybenzene. An excess of base can completely inhibit a reaction by destroying the catalyst, therefore no residual base used in the synthesis of the alkali salt can be present [9]. Further-

more, oxygen must be rigorously excluded from the reaction in order for product to be obtained [8]. The Ullmann synthesis tends to be more sensitive to small amounts of impurities such as water and molecular oxygen, and also requires elevated temperatures. Reaction times are comparable, but elevated temperatures are always required in the Ullmann condensation reaction, sometimes reaching 300 °C.

Therefore, while both procedures do not involve complicated procedures, the double nucleophilic substitution method requires less harsh conditions. The often-present side reactions of the copper-catalysed condensation (reductive dehalogenation, aryl-aryl coupling), as well as the fairly large excesses of aryl halides commonly used, makes for a potentially complicated isolation process. Photolysis of the di-iron complexes produced in the present work produces ferrocene and iron salt in addition to the liberated arene, which suggests that the isolation of the desired product in this process is also problematic. However, the salt is easily removed by filtration, and a number of techniques for the removal of ferrocene exist. Ferrocene could be easily removed by sublimation, in addition to the chromatographic technique applied in this work. Another alternative involves the inclusion of concentrated H_2SO_4 in the mixture of products. This results in the oxidation of ferrocene to the ferrocenium cation, a water-soluble species. The liberated arene could then be extracted with the appropriate organic solvent [64].

The greatest limitation for the double nucleophilic approach is the relatively low number of chloroarenes that can be complexed to the cyclopentadienyliron moiety. Arenes containing electron withdrawing groups such as CO or SO_2 cannot undergo ligand exchange with a cyclopentadienyl ring of ferrocene. This restriction is partially alleviated by the ability of the di-iron complexes to undergo further nucleo-

philic substitution reactions with nucleophiles containing these groups, as has been shown above with the chlorinated di-iron complexes. Even the di-iron complexes containing methyl groups (such as **2.7a**) could be synthetic precursors to a variety of functionalized aromatic complexes. For example, it is known that [η^6-toluene-η^5-cyclopentadienyl]iron complexes can be oxidized, resulting in the corresponding complex of the benzoic acid [34]. Reactions of this nature could easily be extended to the di-iron complexes.

5.2 Substituent-Activated Nucleophilic Substitution

Simply activating aryl halides to nucleophilic substitution reactions of this type by the presence of NO_2 or SO_2 groups does not seem a practical approach, as it would entail the subsequent removal of these substituents if their presence were undesired. The reactivity of the complexed chloroarenes incorporated in this study is roughly equivalent to that of 1-chloro-2,4-dinitrobenzene. So, if similar reactions and conditions were sought, one would be faced with the removal of four NO_2's. A more promising approach is the nucleophilic aromatic nitro displacement reaction. This reaction needs to be activated as well, by either an additional NO_2, CN, or even imides and esters [86]. Only the cyano group demonstrates an activating effect in any way similar to that achieved with the cyclopentadienyliron moiety. In this method, the phenolic compounds must be treated with a strong base to generate the more reactive phenoxide ions, for substitution reactions will not occur otherwise. Most importantly, the activating groups must be in either the ortho or para position to the NO_2 group, or activation will not occur. This is the primary limitation of an otherwise versatile technique. In our technique, all isomers of the target compounds

could be prepared equally well (save one).

The nitro displacement reaction is better than the Ullmann condensation in terms of yields and lack of complicating side reactions. It does require the removal of the activating group, but at the same time it opens up another level of reactivity as the CN, for example, can be transformed into different functional groups. One research group hydrolyzed the cyano groups to carboxylic acids, and used the resulting diacid as a monomer for polymer synthesis [10].

5.3 Coupling Reactions

Coupling reactions serve only to produce more extensive aromatic ethers from existing chlorinated aromatic ethers. These are usually high yield routes to aromatic ethers with biphenyl units, and while the catalytic system can be somewhat complex, reaction conditions are not extreme. These coupling methods were developed with the goal of increasing the number of monomers accessible for polymerization. That is, basing the polymerization process on the formation of an aryl-aryl bond through the loss of two chloro groups provides a wider pool of monomers to choose from when compared to polymerization by activated aromatic nucleophilic substitution (see figure 4, introduction). However, these coupling methods still rely on the substitution techniques for the synthesis of the necessary chlorinated aromatic ethers and are, by association, subject to all their limitations as well. Considering these factors leads one to the conclusion that our technique is very complimentary, as it increases the variety of chlorinated aromatic ethers available.

6 A Comparison with Other Metal Systems

The cyclopentadienyliron moiety is not the only group capable of activating chloroaromatics for the synthesis of aromatic ether related to those described herein. Cyclopentadienylruthenium ($CpRu^+$) has also demonstrated success, as has manganese tricarbonyl ($Mn(CO)_3^+$) and chromium tricarbonyl ($Cr(CO)_3$) . None of these possess all the favorable features of cyclopentadienyliron however, as is shown below.

6.1 Ruthenium

As has been mentioned previously, the $CpRu^+$ and $CpFe^+$ moieties are roughly equivalent in their electron withdrawing ability, therefore it is not surprising that a limited amount of related research has been carried out. A communication appeared in 1985 on the synthesis of poly(aromatic ethers) via activated nucleophilic aromatic substitution using the [η^6-p-dichlorobenzene-η^5-cyclopentadienyl]ruthenium complex [80]. It was shown that a di-ruthenium complex could be synthesized in a one step reaction from the above ruthenium complex and the disodium salt of dihydroxybenzophenone (figure 61). A DMF solution of these reagents was heated to 70 °C for one hour to produce the desired product in an unrecorded yield. The same reagents were combined in a 1:1 molar ratio in DMSO, and heated for 1.5 hours at 85-90 °C, creating a poly(ether-ether-ketone) (PEEK) with pendant $CpRu^+$ units. Thermolysis of this organometallic polymer resulted in the removal of the $CpRu^+$ moieties and the free PEEK with an unreported molecular weight. However, it was stated that the starting ruthenium complex underwent a 75% conversion to the

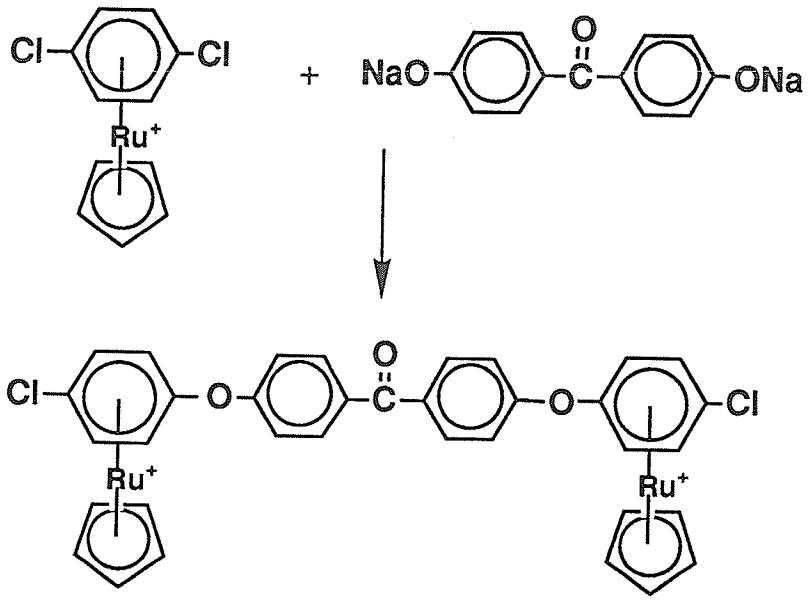


Figure 61: Synthesis of a related di-ruthenium complex

PEEK. No follow-up study has since appeared.

Subsequent work has been directed towards the disubstitution of [η^6-dichlorobenzene-η^5-cyclopentadienyl]ruthenium complexes with phenoxide ions, rather than continuing with the double nucleophilic substitution approach. Pearson and coworkers have been active in this particular area. An extensive study has been published in which the $CpFe^+$ and $CpRu^+$ complexes of m-dichlorobenzene have been reacted with various phenoxides [78]. The results indicate little difference between the two approaches to triaryl diethers, and that both allow for sequential substitution of the chloro groups. The [η^6-chloroarene-η^5-cyclopentadienyl]iron complexes are easier to prepare than their ruthenium analogues, however the ruthenium system is in some sense catalytic. Efficient demetallation techniques can allow for $[CpRu(CH_3CN)_3]PF_6$ to be reclaimed and incorporated into another ligand ex-

change step. Nevertheless, a sufficient amount of ruthenium is lost in this ligand exchange step to make the iron system much more economical, since ruthenium compounds are very expensive. Based on these cost considerations, activation by the cyclopentadienyliron moiety would seem to be the favored technique. Nevertheless, cyclopentadienylruthenium can complex a wider variety of functionalized arenes due to the softer ligand exchange conditions, implying that the ruthenium system could serve as a alternative technique in those situations where the iron system fails.

6.2 Chromium

The most studied metal system with respect to activating chloroarenes towards nucleophilic substitution has seldom been applied to aryloxy nucleophiles, oddly enough. Compounds of similar or lower nucleophilicity have been used and investigated for years [73, 76, 87], but only two very recent publications consider aryloxy nucleophiles in any depth [16, 77]. The study conducted by Voyle [16] demonstrated that when η^6-1,4-dichlorobenzenechromium tricarbonyl is reacted with five equivalents of sodium phenoxide in DMSO at room temperature, only the monosubstitution product results. The very recent work by Percec [77] investigates the reactivity of this chromium complex more closely. Upon reaction of this chromium complex with 2-5 equivalents of phenoxide (in DMSO or benzene) a mixture of chromium products and demetallated products often resulted, as shown in figure 62. While Voyle demonstrated the reaction could work at room temperature in DMSO, Percec elected to use temperatures in the 80-110 °C range. Under these conditions, only the latter two products resulted. Substitution and then complete demetallation occurred. Only when benzene was used as a solvent and a selective cation seques-

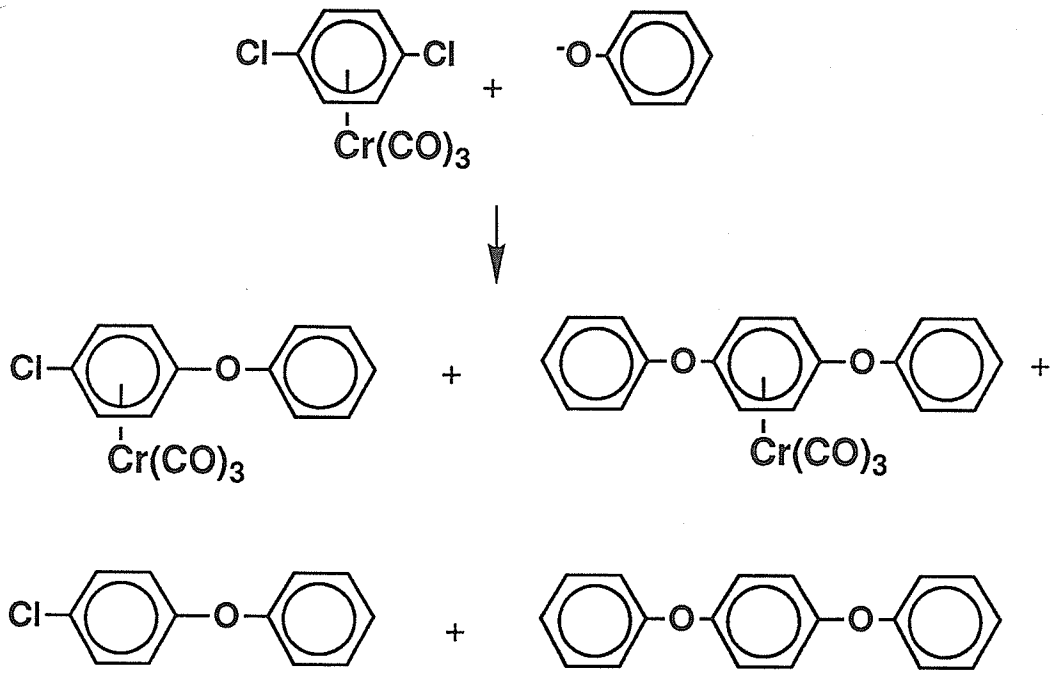


Figure 62: Attempted synthesis of 1,4-diphenoxybenzene from 1,4-dichlorobenzene activated by $Cr(CO)_3$

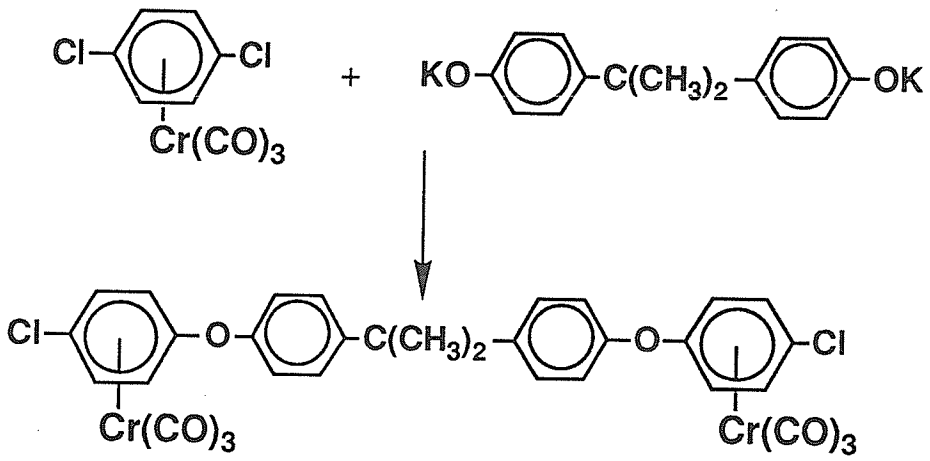


Figure 63: Synthesis of a related di-chromium complex

tering agent such as 18-crown-6 ether added could the monosubstitution product be isolated pure and in high yield. Presumably the crown ether further enhances the nucleophilicity of phenoxide ion through the trapping of the counter-ion. Even when the isolated 1-chloro-4-phenoxy[η^6-benzene]chromium tricarbonyl itself was combined with excess phenoxide under the most favorable conditions only a mixture of the last three products ever resulted. Clearly, the mono-chromium route to compounds of the type synthesized in the current work is not a viable alternative. Percec was successful in preparing a dichromium complex by one-step double nucleophilic substitution from the chromium complex and the potassium salt of 4,4′-isopropylidenediphenol, using the crown-ether assisted technique (figure 63). A yield of 73% was recorded for the di-chromium complex. Demetallation was carried out by oxidation with I_2, producing the aromatic ether in a 79% yield. It should be noted that equimolar amounts of the crown-ether were necessary to obtain reasonable yields. No further reactions were attempted. The iron system developed

herein is superior if for no other reason than its greater simplicity. Nothing beyond a common weak base is required to activate the hydroxyaromatic compounds. Furthermore, the necessity of activating the nucleophiles in the chromium technique is an indication of the lower reactivity of this system. Finally, while a greater number of arenes can be complexed by the ligand exchange reaction with $Cr(CO)_6$, the toxicity and cost of this material make the technique unappealing.

6.3 Manganese

It was shown a number of years ago that chloroarene-$Mn(CO)_3$ cations can react with phenoxide nucleophiles to give the corresponding complexes of the diaryl ethers [88]. Demetallation occurs easily by thermolysis in a good coordinating solvent such as CH_3CN. The yields for this preparation of diaryl ethers are good: the substitution reaction results in a 70-80% yield of the diaryl ether complex, while thermolysis produces the free arene in a 75-85% yield. Pearson and coworkers have analysed this activating system very closely in their attempts to tailor a multi-step synthesis of vancomycin [13, 78, 79]. They stress that an important requirement for any system which prepares functionalized diphenoxybenzenes is the ability to selectively arylate polyhydric phenols. The manganese system is capable of doing so, as is demonstrated in figure 64 [79]. These reactions were undertaken in a CH_3CN solution, with potassium fluoride (KF) serving as the base. A reaction time of 24 hours was sufficient to complete the reaction and cleave the $Mn(CO)_3^+$ group as well. In synthesis of complexes **2.31**, **2.32**, **2.34a** and **2.35a**, it has been shown that the iron system is also capable of allowing for sequential substitution.

The preparation of the necessary chloroarene manganese tricarbonyl also pro-

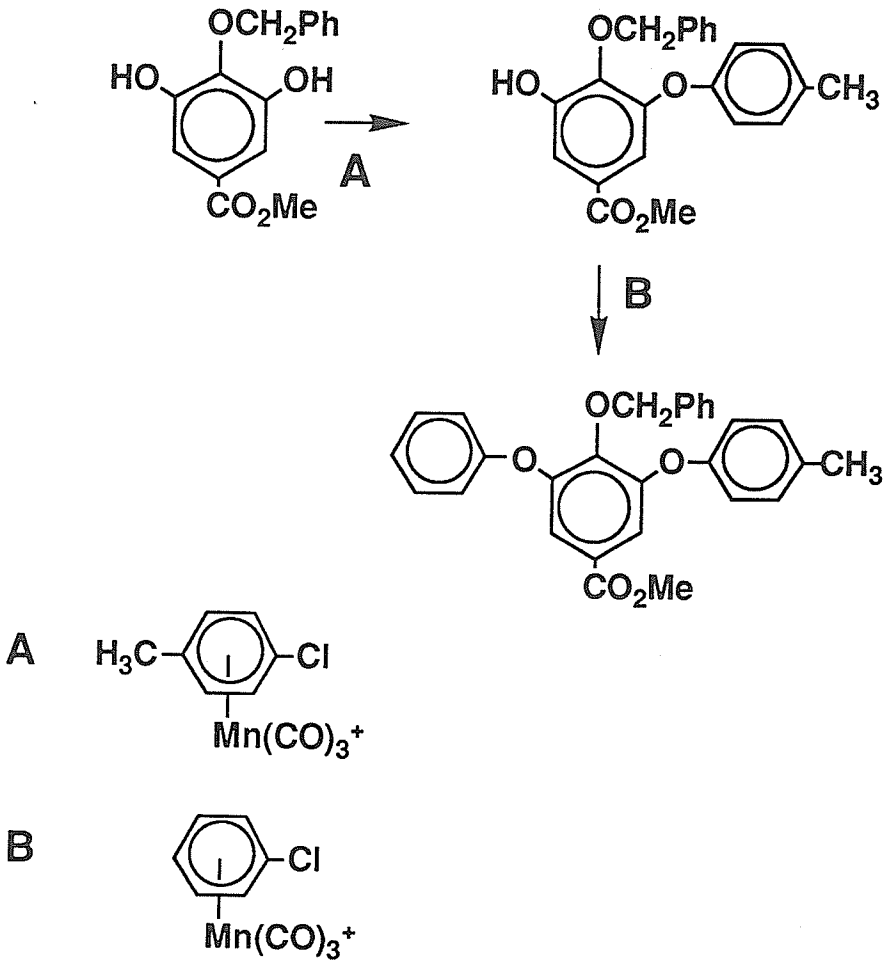


Figure 64: Stepwise synthesis of a diphenoxybenzene derivative via chloroarenes activated by $Mn(CO)_3$

ceeds through a Lewis acid-catalyzed ligand exchange reaction, in which the starting complex is $(CO)_5MnBr$ [82]. The toxicity and cost of this complex again makes this system somewhat undesireable, particularly in light of the cheaper, more benign iron system. The greatest disadvantage of the manganese system lies in the current inability to complex dichlorobenzenes. Therefore, while the system can be used in double substitution reactions, the resulting di-manganese complexes of the diphenoxybenzenes cannot undergo further nucleophilic substitution reactions. This constitutes a distinct disadvantage of this system when compared to the di-iron system developed in this work.

Part III

Experimental

1 Reagents and Instrumentation

The synthetic procedures implemented and developed did not require chemicals of a purity in excess of that commercially available. The ferrocene used in the ligand exchange reactions (described in section I.2.1.1) was purchased from the Aldrich Chem. Co., whereas the various chlorinated aromatics were obtained from Mallinkrodt or Fisher Scientific Company. The anhydrous $AlCl_3$ and Al powder also used in these reactions were purchased from Mallinkrodt. The nucleophilic substitution reactions used nucleophiles purchased from Aldrich Chem. Co., with the exception of resorcinol (Fisher Scientific) and catechol (Matheson, Collman and Bell). Potassium carbonate (K_2CO_3), used as the base in these reactions, was obtained from BDH. Two solvents were typically employed in this study, namely dimethylformamide (DMF) and tetrahydrofuran (THF). The anhydrous DMF (Aldrich) did not require distillation, whereas THF (Mallinkrodt) was distilled over Na metal and benzophenone in an N_2 atmosphere, just prior to use. All other solvents used in the work-up procedures for the complexes and the photolysis experiments were of reagent grade. The counter-ion for the cationic complexes prepared and described herein was provided by ammonium hexafluorophosphate (Aldrich).

Liquid chromatographic separations were carried out in order to retrieve the desired compound from the other degradation products resulting from the photolytic

process (see section III.4 for a description of the photolytic technique). Silica gel (60-200 mesh, Mallinkrodt) served as the column packing material, and was prepared from a hexane slurry. Hexane, chloroform and diethyl ether (reagent grade) served as the eluants.

Product identification and characterization for the organometallic species was achieved with high resolution ^{1}H and ^{13}C nuclear magnetic resonance (NMR) experiments on a Gemini-200 instrument (Varian) at the University of Winnipeg. This spectrometer operates at 200 MHz for ^{1}H and at 125 MHz for ^{13}C. Supplementary data was obtained from infra-red spectra, recorded on a Perkin-Elmer 781 series infra-red spectrophotometer. The organic compounds resulting from the photolysis of the organometallic complexes were also characterized by the NMR and infra-red experiments. In addition, mass spectral data was collected from a Hewlett-Packard series 5970 mass selective detector, with a Hewlett-Packard series 5890 gas chromatograph serving as the injection system, also at the University of Winnipeg. However, a number of compounds required analysis at the University of Manitoba by direct-injection electron impact mass spectrometry, due to the limitations of the equipment at the University of Winnipeg. Melting points were also also obtained, where possible. These were recorded with a Gallenkamp melting point apparatus (model 889339), and were not corrected for thermometer inaccuracies. All elemental analyses of the compounds as well as their organometallic precursors were carried out at the University of Saskatchewan.

2 Ligand Exchange Reactions

The ligand exchange reactions of this study followed accepted procedure. The following provides an illustration of a typical experiment. In the synthesis of [η^6-p-dichlorobenzene-η^5-cyclopentadienyl]iron hexafluorophosphate (complex **iv**), ferrocene (27.9 g, 150 mmol) was combined with p-dichlorobenzene (45.0 g, 315 mmol) in a 500 ml round bottom flask. Also included were $AlCl_3$ (40.0 g, 300 mmol), Al powder (4.1 g, 150 mmol) and 120 ml of decalin. The resulting slurry was heated to 135°C under an N_2 atmosphere for five hours, turning a progressively darker green. Upon cooling, the dark green mixture was carefully poured into 400 ml of ice water, to deactivate the excess $AlCl_3$. This mixture was then filtered through sand to remove the Al powder, whereupon the filtrate was washed with petroleum ether (3 $\times$ 50 ml) and then diethyl ether (1 $\times$ 50 ml) to remove the unreacted ferrocene and the excess dichlorobenzene. NH_4PF_6 (12.2 g, 74.8 mmol) was slowly added to the aqueous phase, with stirring, causing the precipitation of a light green solid. The crude precipitate was collected by filtration, and redissolved in CH_2Cl_2. To increase the amount of product recovered, the filtrate from this step was extracted once with CH_2Cl_2 (100 ml). The two CH_2Cl_2 solutions were combined and then dried over $MgSO_4$. After another filtration step to remove the drying agent, the solution was concentrated by evaporation under reduced pressure, and the product precipitated as a fine light green powder. The final product was collected by filtration and washed with small amounts of diethyl ether. The product was vacuum dried and then stored in a dessicator. Characterization of the product by ^1H and ^{13}C NMR was found to agree with the analytical data cited in the literature [35, 72].

3 Nucleophilic Substitution Reactions

3.1 One-Step Synthesis of Di-iron Complexes

The general procedure for the synthesis of these complexes involved the combination of a mono-iron complex with the difunctional nucleophile, an excess of K_2CO_3 and the appropriate solvent. All reactions were carried out under an N_2 atmosphere. The reaction conditions varied somewhat, as is described below. A standard work-up procedure was followed for all di-iron complexes synthesized, in which the reaction mixture was first filtered through a sintered glass crucible into a 10% (v/v) HCl solution, causing a granular yellow precipitate. Excess K_2CO_3 and an off-white salt remained as solid residue in the crucible. The reaction flask and crucible were washed with acetone, and these washings were added to the filtrate. This typically caused dissolution of the precipitate. The filtrate was then concentrated by evaporation of volatiles under reduced pressure, whereupon the product was precipitated as a yellow powder by inclusion of an aqueous solution of NH_4PF_6. The product was then filtered off and washed with several portions of cold water. After drying for a time over vacuum, the product was washed twice with small amounts of diethyl ether, producing a fine yellow solid after further drying. The product did not usually require additional purification beyond this point. A more detailed description of the synthetic procedure for a representative of each class of diphenoxybenzene complexes may be found below.

1,4-di([η^6-4-chlorophenoxy-η^5-cyclopentadienyl]iron)benzene dihexafluorophosphate (complex 2.4a)

Complex **iv** (1.65 g, 4.01 mmol) was combined with hydroquinone (0.220 g, 2.00 mmol) in a 50 ml round bottom flask which contained K_2CO_3 (0.694 g, 5.02 mmol), 15 ml of THF/DMF (4:1 ratio) and a magnetic stir bar. The flask was fitted with a water-cooled condensor column, and the flask contents were refluxed ($\approx$ 65 °C) under an N_2 atmosphere, with stirring, for seven hours. The solution at this point was a yellow-brown color, and a white precipitate was noted. The workup proceeded as described above. The product was recovered in an 88% yield (1.52 g, 1.76 mmol). The analytical data for this complex can be found summarized in tables 1 and 2. This procedure is typical of those reactions in which hydroquinone served as the difunctional nucleophile. A variation of this procedure uses DMF as the only solvent (10 ml). No heating was required, however the reaction time had to be increased to 12 hours. Yields with this technique are comparable to that in which THF/DMF was used.

1,3-di([η^6-3-methylphenoxy-η^5-cyclopentadienyl]iron)benzene dihexafluorophosphate (complex 2.13a)

Complex **vi** (0.800 g, 2.04 mmol) was combined with resorcinol (0.112 g, 1.02 mmol), K_2CO_3 (0.539 g, 3.90 mmol) and 15 ml of THF/DMF (4:1 ratio) in a 50 ml round bottom flask. The experimental conditions and work-up procedure were identical to those for the synthesis of the 1,4-di([η^6-3-aryloxy-η^5-cyclopentadienyl]iron)benzene complexes (complexes **2.1a–2.7a**). The product was recovered from the yellow-brown solution in a 90 % yield (0.755 g, 0.918 mmol). Analytical data are recorded in

tables 7 and 8. This procedure was followed in the synthesis of all di-iron complexes in which resorcinol served as the difunctional nucleophile. The alternative technique used in the synthesis of 1,4-di([η^6-3-aryloxy-η^5-cyclopentadienyl]iron)benzenes was also successful in the synthesis of these complexes. The reaction time had to be increased to approximately 18 hours, however slightly higher yields resulted (an additional 5–15%).

1,2-di([η^6-4-chlorophenoxy-η^5-cyclopentadienyl]iron)benzene dihexafluorophosphate (complex 2.17a)

A slight excess of monoiron complex **iv** (0.905 g, 2.19 mmol) was combined with catechol (0.110 g, 1.00 mmol), along with K_2CO_3 (0.427 g, 3.09 mmol) and 10 ml of DMF in a 50 ml round bottom flask. The mixture was stirred under an N_2 atmosphere for 20 hours, during which time the solution turned a dark green-brown. The usual work-up procedure was followed, resulting in an 83% yield (0.714 g, 0.827 mmol) of the di-iron complex calculated from the conversion of the catechol. This procedure was applied to the synthesis of all 1,2-di([η^6-aryloxy-η^5-cyclopentadienyl]iron) benzene complexes. Application of the technique involving THF/DMF as the solvent combination resulted in relatively low yields and decomposition, as discussed in section II.1.3. It should be noted that, with the exception of this complex, these complexes could only be recovered in an approximate 60% yield by precipitation from the DMF solution. Typically, an additional 20% could be recovered from the filtrate of the above step by an extraction technique. The filtrate was extracted with two 100 ml portions of CH_2Cl_2, and the resulting CH_2Cl_2 solution washed repeatedly with water to remove the extracted DMF. The washed CH_2Cl_2

solution was then dried over $MgSO_4$, filtered and concentrated by evaporation of the solvent under reduced pressure. Diethyl ether was then included to precipitate the di-iron product.

Attempted synthesis of 1,2-di([η^6-2-chlorophenoxy-η^5-cyclopentadienyl]-iron)benzene dihexafluorophosphate

Complex **ii** (0.857 g, 2.08 mmol) was combined with catechol (0.108 g, 0.981 mmol) in a 50 ml round bottom flask, together with an excess of K_2CO_3 (0.563 g, 4.07 mmol) and 10 ml of DMF. The mixture was stirred under an N_2 atmosphere for 18 hours, the standard technique for reactions involving catechol. The resulting green-brown solution was filtered through a crucible into a 10% (v/v) HCl solution, as were the acetone washings, resulting in a golden colored filtrate. This aqueous solution was extracted with CH_2Cl_2 (2 $\times$ 100 ml), whereupon the combined CH_2Cl_2 extracts were washed repeatedly with water (25 ml) to remove the DMF. After drying over $MgSO_4$, the CH_2Cl_2 solution was filtered, and the solvent removed by evaporation under reduced pressure. The resulting dark yellow oil was then placed under vacuum for further drying. ^1H and ^{13}C spectra were obtained, revealing a mixture of products. The results of this experiment are discussed thoroughly in section II.1.3.

4,4′-di([η^6-4-methylphenoxy-η^5-cyclopentadienyl]iron)biphenyl dihexafluorophosphate(complex 2.26a)

Complex **vii** (0.845 g, 2.15 mmol) and 4,4′-biphenol (0.195 g, 1.05 mmol) were added to a 50 ml round bottom flask, together with an excess of K_2CO_3 (0.430 g, 3.11 mmol) and 10 ml of DMF. The mixture was stirred magnetically under an

N_2 atmosphere for 18 hours. The general workup procedure for di-iron complexes was followed, resulting in the recovery of a pale yellow-green powder in a 96% yield (0.904 g, 1.01 mmol). The analytical data for this complex can be found summarized in tables 17 and 18.

3.2 Stepwise Synthesis of Di- and Tri-iron Complexes

3.2.1 Mono-iron Complexes Generated by Nucleophilic Substitution

[4-(4-hydroxyphenoxy)-η^6-toluene-η^5-cyclopentadienyl]iron hexafluorophosphate, (complex 2.32a)

Complex **vii** (1.57 g, 4.01 mmol) was added to a 100 ml round bottom flask containing an excess of hydroquinone (3.53 g, 32.1 mmol), K_2CO_3 (0.860 g, 6.22 mmol) and 20 ml of THF/DMF (4:1 ratio). The flask was fitted with a condensor column and the solution stirred magnetically. This mixture was refluxed ($\approx$ 65 °C) under an N_2 atmosphere for eight hours. The contents of the flask were then added to a 250 ml separatory funnel, to which was also added 150 ml CH_2Cl_2 and 20 ml of 10% (v/v) HCl solution. The organic phase was extracted after vigorous shaking, and washed repeatedly with dilute solutions of NH_4PF_6 to remove the THF and DMF. This CH_2Cl_2 solution was then dried over $MgSO_4$, filtered, and the solvent removed by evaporation under reduced pressure until a tacky solid was obtained. This solid was then washed with diethyl ether to remove most of the excess hydroquinone, whereupon the crude mono-iron product was twice precipitated from CH_2Cl_2/diethyl ether. The product was recovered as a dark yellow solid in a 78% yield (1.48 g, 3.17 mmol). The ^1H and ^{13}C NMR spectra were recorded, and can be

found summarized in tables 28 and 29.

3.2.2 Synthesis of Unsymmetrical Di-iron Complexes

1-([η^6-4-methylphenoxy-η^5-cyclopentadienyl]iron)-4-([η^6-4-chlorophenoxy-η^5-cyclopentadienyl]iron)benzene dihexafluorobenzene (2.35a)

Complex **2.32a**(1.46 g, 3.13 mmol) was added to a slight excess of complex **iv** (1.45 g, 3.50 mmol), and combined with an excess of K_2CO_3 (0.563 g, 4.07 mmol) and 20 ml of THF/DMF (4:1 ratio) in a 100 ml round bottom flask. The flask was fitted with a condensor column and the mixture was gently refluxed for six hours under N_2, with stirring. The product was recovered as a yellow solid via the standard work-up technique, then further purified by precipitation from acetone/diethyl ether. The resulting fluffy yellow material was recovered in an 86% yield (2.27 g, 2.69 mmol). Spectral data for this complex have been recorded in tables 28 and 29.

3.2.3 Synthesis of a Tri-iron Complex

1,4-bis[4-([η^6-4-methylphenoxy-η^5-cyclopentadienyl]iron)phenoxy][η^6-benzene-η^5-cyclopentadienyl]iron trihexafluorophosphate, (complex 2.36a)

A slight excess of complex **2.32a** (0.604 g, 1.30 mmol) was combined with complex **iv** (0.949 g, 1.10 mmol) as well as K_2CO_3 (0.274 g, 1.98 mmol) and 10 ml THF/DMF (7:3 ratio) in a 50 ml round bottom flask. The mixture was refluxed ($\approx$ 65 °C) under an N_2 atmosphere, with stirring, for six hours. A yellow-brown precipitate was noted during the course of the reaction. At the end of this reaction, the precipitate was dissolved by addition of acetone, whereupon the regular work-up procedure was followed. The resulting light yellow solid was identified as the desired product by

^{1}H and ^{13}C NMR, and the data can be found in tables 28 and 29. A yield of 96% was obtained (1.34g, 1.06 mmol).

3.3 Functionalization of Di-iron Complexes

The work-up procedure developed to isolate the previously mentioned di-iron complexes was also applicable to the isolation of the functionalized di-iron complexes. Two different carbanion nucleophiles were used in the preparation of a series of these complexes, and representative synthetic methodology is presented below.

3.3.1 Reactions with ethyl cyanoacetate

1-([η^6-phenoxy-η^5-cyclopentadienyl]iron)-4-(ethyl{[η^6-4-phenoxy-η^5-cyclopentadienyl]iron}cyanoacetate)benzene dihexafluorophosphate (complex 2.37a)

Complex **2.34a** (0.862 g, 1.04 mmol) was dissolved in 10 ml of DMF in a 50 ml round bottom flask, to which was added K_2CO_3 (0.189 g, 1.67 mmol) and a slight excess of ethyl cyanoacetate (0.189 g, 1.67 mmol). The solution was stirred magnetically at room temperature, under an N_2 atmosphere, turning a deep cherry-red color within 15 minutes. The solution was stirred under these conditions for five hours before work-up. The product was recovered as a light yellow-orange powder in a 93% yield (0.879 g, 0.971 mmol). The spectral data can be found summarized in tables 33 and 34.

1-([η^6-4-chlorophenoxy-η^5-cyclopentadienyl]iron)-4-(ethyl{[η^6-4-phenoxy-η^5-cyclopentadienyl]iron}cyanoacetate)benzene dihexafluorophosphate

(complex 2.43a)

Complex **2.4a** (0.964 g, 1.12 mmol) was added to a 50 ml flask containing an equimolar amount of ethyl cyanoacetate (0.126 g, 1.11 mmol), K_2CO_3 (0.278 g, 2.01 mmol), and 10 ml of DMF. The solution was heated to 50 °C and stirred magnetically under an N_2 atmosphere, turning a deep cherry-red color within 15 minutes. The solution was then stirred for an additional 9 hours before work-up. The product was recovered as a light yellow-orange powder in a 91% yield (0.955 g, 1.02 mmol). The spectral data can be found summarized in tables 39 and 40.

3.3.2 Reactions with phenylsulfonylacetonitrile

1-([η^6-4-methylphenoxy-η^5-cyclopentadienyl]iron)-4-({[η^6-4-phenoxy-η^5-cyclopentadienyl]iron}phenylsulfonylacetonitrile)benzene dihexafluorophosphate (complex 2.40a)

Complex **2.35a** (0.878 g, 1.04 mmol) was combined with phenylsulfonylacetonitrile (0.227 g, 1.25 mmol), K_2CO_3 (0.350 g, 2.53 mmol) and 10 ml of DMF in a 50 ml round bottom flask. The mixture was magnetically stirred under an N_2 atmosphere for four hours. The product was recovered in the typical fashion as a yellow solid in a 91% yield (0.928 g, 0.940 mmol). Spectral data for this complex can be found in tables 33 and 34.

1,4-di({[η^6-4-phenoxy-η^5-cyclopentadienyl]iron}phenylsulfonylacetonitrile)benzene dihexafluorophosphate (complex 2.42)

Complex **2.4a** (0.652 g, 0.755 mmol) and phenylsulfonylacetonitrile (0.309 g, 1.71 mmol) were added to a 50 ml round bottom flask containing K_2CO_3 (0.296 g, 2.14

mmol) and 10 ml DMF. The mixture was magnetically stirred under an N_2 atmosphere for only three hours. At this point, the solution had turned an opaque orange, from an initial dark red color. The product was isolated in the usual manner as a light yellow solid, in a 50% yield (0.435 g, 0.378 mmol). Analytical data for this complex have been presented in tables 35 and 39, as well as table 40.

1-(ethyl {[η^6-4-phenoxy-η^5-cyclopentadienyl]iron}cyanoacetate)-4-({[η^6-4-phenoxy-η^5-cyclopentadienyl]iron}phenylsulfonylacetonitrile)benzene dihexafluorophosphate (complex 2.44)

Complex **2.43a** (0.505 g, 0.537 mmol) was combined with phenylsulfonylacetonitrile (0.100 g, 0.552 mmol), K_2CO_3 (0.217 g, 1.57 mmol) and 10 ml of DMF in a 50 ml round bottom flask. The solution turned red immediately upon mixing, and was stirred magnetically under an N_2 atmosphere for four hours, at room temperature. The routine workup procedure for di-iron complexes was followed, resulting in the isolation of a yellow powder, identified as the above complex, in a 92% yield (0.539 g, 0.497 mmol). Analytical data are contained in table 35, table 39 and table 40.

4 Liberation of the Aromatic Ethers

The bridging ligands were recovered in a two step process which has been outlined below.

4.1 Photolytic Demetallation Reactions

Approximately 0.5 mmol of a di-iron complex was added to a 50 ml Pyrex photolysis tube, and typically dissolved in 40 ml of a CH_2Cl_2/CH_3CN solvent mixture. CH_3CN

was used to allow for a greater dissolution of the complex, and for its high photoactivity (see introduction). The solution was then flushed with N_2 for 30 minutes to an hour, and subsequently irradiated under the Xenon lamp for two to four hours. This process usually resulted in the darkening of the previously yellow-gold solution, and the formation of a granular brown precipitate.

4.2 Isolation of the Aromatic Ethers

The photolyzed solution was concentrated to 1-2 ml by evaporation of solvent under reduced pressure. This concentrate, which included the precipitate, was then introduced to a short column of silica gel ($\approx$ 5 cm) prepared from a hexane slurry, whereupon the desired organic compound and ferrocene were simultaneously eluted with approximately 100 ml of $CHCl_3$. All the solvent was then removed by evaporation under reduced pressure, and the resulting yellow material further dried under vacuum for a minimum of one day. The material was then weighed, and a ^1H NMR spectrum taken to confirm the presence of only the aromatic ether and ferrocene. A percent conversion of the di-iron complex into the aromatic ether was then determined, based on the 1:1 ratio of aromatic ether to ferrocene resulting from the photolytic process (see introduction).

The ferrocene/aromatic ether mixture was then added as a concentrated hexane solution to a longer column of silica gel prepared with hexane (10-15 cm). Ferrocene was eluted as a yellow band with hexane, and collected in typically two fractions (50 ml each). The aromatic ether was then eluted by hexane/$CHCl_3$, with typically two fractions (50 ml each) being collected. The solvent was then removed from the latter fractions by evaporation under reduced pressure, and a percent recovery of

aromatic ether determined after the material from these fractions was dried under vacuum for one day. This technique allowed for the recovery of the aromatic ethers in amounts equivalent to that determined after the first chromatographic purification. The products obtained ranged from oils to solids. The results and discussion section can be referred to for the description and characterization of these compounds.

Part IV

Summary and Future Work

The above work demonstrates the development of a new and potentially useful technique in the synthesis of aromatic ethers via double nucleophilic substitution reactions, with arenes activated by the cyclopentadienyliron moiety. An extensive number of isomeric diphenoxybenzenes have been prepared from catechol, resorcinol and hydroquinone dinucleophiles with simple chlorinated arenes complexed to $CpFe^+$. With the exception of one isomer, all could be prepared with equal success, using one of two related techniques. It was found that di-iron complexes prepared from the more crowded nucleophiles (like catechol and phenylhydroquinone for example) required longer reaction times and could only be synthesized in high yield from a pure DMF solution of the appropriate starting materials.

The technique was applied very successfully to a large number of dihydroxy nucleophiles, including various biphenols and fuctionalized hydroquinones. The resulting di-iron complexes were open to further reactivity by nucleophilic substitution, allowing for the introduction of different carbon nucleophiles. A modification of the synthetic procedure allowed for sequential substitution reactions. In the first step, only one of the nucleophilic sites of the dinucleophile is involved in a substitution reaction, leaving the second open to further substitution in a second step. In this fashion, two different mono-iron complexes could be incorporated into a diphenoxybenzene complex. This stepwise approach also allowed for the preparation of a tri-iron complex. The application of a very simple photolytic procedure re-

sulted in the liberation of aromatic ethers in high yield. This is true even for the multifunctional ethers prepared in this study.

The simplicity and flexibility of the overall synthetic route in the synthesis of aromatic ethers has been shown, and it is felt that it possesses certain advantages over all of the existing techniques for the synthesis of this class of compounds. Even though the Ullmann condensation reaction is usually a one-step method, the possibility of complicating side reactions and poor yields reduces its appeal as a general preparative method. Substituent activated S_NAr reactions are very useful, but only in those cases where the presence of the activating groups is desired. Furthermore, the activating substituents are only effective in the ortho and para positions of the arene to be substituted. The development of the catalysed coupling reactions is only an indirect technique for the synthesis of aromatic ethers. It has been shown that the $CpFe^+$-activated technique benefits from mild reaction conditions and the ability to produce all isomers of simple diphenoxybenzenes. The one exception could be prepared by the mono-iron route, if necessary. The same system that was developed for the preparation of aromatic ethers also allowed for the incoporation of carbon nucleophiles, demonstrating that the aromatic ethers prepared in this way could be introduced into more complex molecular structures. This is a very definite advantage over the conventional techniques. It is also felt that this system is better than the alternative metal-activating approaches. Although little work has been done in the area of aromatic ether synthesis using these other metals, it is clear that the $CpFe^+$-activated technique is both cheaper and easier to use.

The content of this thesis represents the development and initial application of a di-iron system produced by double nucleophilic substitution. The intent has

been to demonstrate its utility in organic synthesis. Only dioxygen nucleophiles were used, but it is reasonable to assume that other dinucleophiles could be incorporated as well. Currently, analogous systems are being developed for dinitrogen and disulfur nucleophiles. The preparation of the tri-iron complex described above reveals the possibility for direct polymer synthesis by this technique. The results of the limited ruthenium study seem to encourage further effort in this area. Perhaps the most direct application of the diphenoxybenzenes prepared with the $CpFe^{+}$-activated method is in the area of polymer synthesis. The chlorinated aromatic ethers prepared herein supplement the Scholl coupling technique very well, and should provide for the synthesis of a more extensive number of poly(aromatic ethers).

From a more fundamental organometallic point of view, the reactivity of the di-iron system beyond nucleophilic substitution has yet to be probed. These include nucleophilic addition, oxidation of substituents and many other reactions possible with the mono-iron systems.

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